

Preparation and Applications of Functionalized Organozinc Compounds

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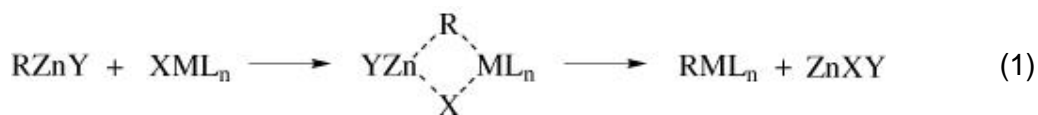
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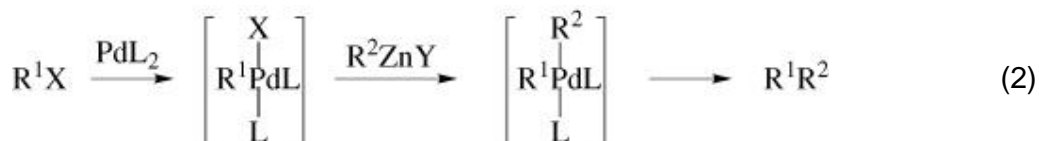
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1. Introduction

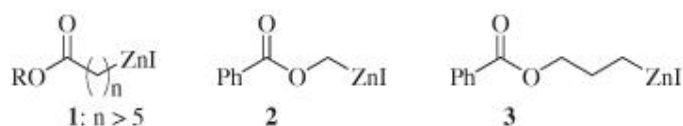
Organozinc compounds have been known for more than 150 years. (1, 2) With the exception of zinc enolates (Reformatsky reagents) (3-6) and iodomethylzinc derivatives (Simmons-Smith, (6-10) Furukawa, (11, 12) and Sawada (13) reagents), their synthetic potential has only been recently recognized. (14-19) This is certainly due to their low reactivity and to the absence of general methods of preparation. Although the carbon-zinc bond in diethylzinc has a dissociation energy of 34.5 kcal/mol, (20) it has, because of the similar electronegativities of zinc and carbon, a highly covalent character (ca. 85 %), (21) which is comparable to a carbon-tin bond. The carbon-zinc bond is therefore inert to moderately polar electrophiles such as aldehydes, ketones, esters, or nitriles. On the other hand, the presence of empty low-lying *p* orbitals at the zinc center allows transmetalations with a number of transition metal complexes (Eq. 1). This is favored for both kinetic and thermodynamic



reasons. (20) The availability of *d* orbitals at the metal center in these compounds allows for new reaction pathways with electrophilic reagents that were not available for the corresponding zinc reagents. This reactivity has been exploited for the formation of new carbon-carbon bonds and efficient cross-coupling reactions between organozinc derivatives and unsaturated organic halides, as Negishi has demonstrated using catalytic amounts of palladium(0) salts (Eq. 2). (22-28) Similar catalytic processes have been reported with copper(I) and titanium(IV) complexes, which can mediate numerous reactions of organozinc reagents with organic electrophiles. (14)



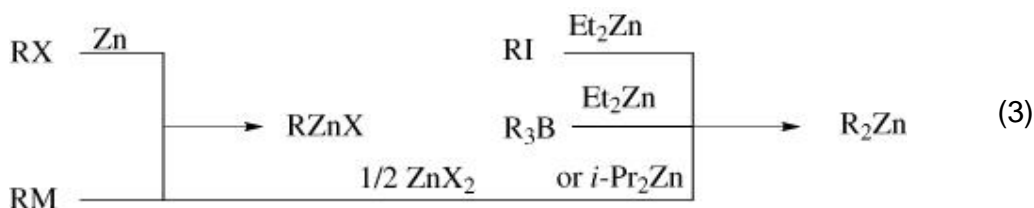
The scope and synthetic applications of zinc organometallics were greatly extended when it was found that these species can accommodate a wide range of functional groups. They are ideally suited for the construction of polyfunctional organic molecules without the use of multiple protection and deprotection steps. Although some functionalized organozinc compounds bearing ester groups such as **1**, (29) **2**, (30-34) or **3** (30-34) had been reported, it was only recently that systematic studies have shown the synthetic potential of these reagents. (14-18) This chapter



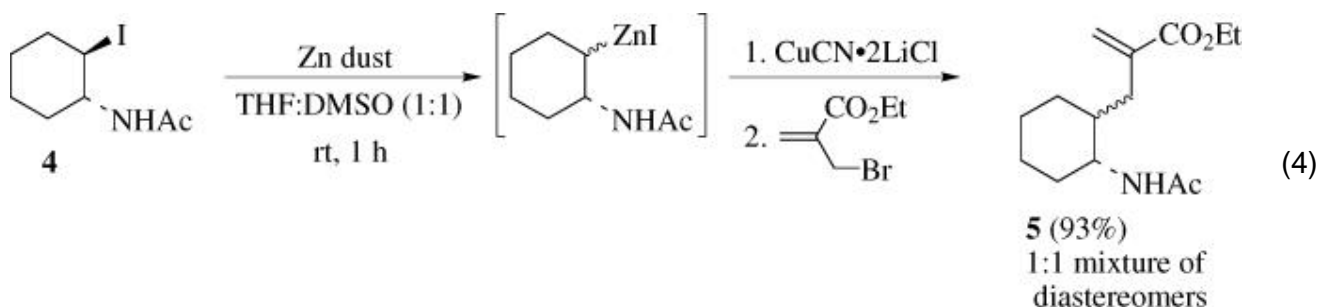
describes methods for the preparation of functionalized organozinc halides, diorganozincs, and organozincates and their reactions with electrophilic reagents in the presence of transition metal catalysts, as well as synthetic applications demonstrating their synthetic utility for natural product synthesis. Only the preparation and reactivity of zinc organometallics bearing relatively reactive functional groups are covered. Thus, the chemistry of organozinc compounds bearing an ether, acetal, ketal, trialkylsilyl, or polyfluoroalkyl group is, in general, not covered.

2. Mechanism and Stereochemistry

Several methods are available for preparing alkylzinc organometallics. Thus, alkylzinc halides are obtained either by transmetalations from other organometallics, typically organolithium or magnesium derivatives, or by the direct insertion of zinc metal into a carbon-halogen bond. Diorganozincs are prepared by transmetalations, iodine-zinc exchange reactions, or boron-zinc exchange reactions (Eq. 3).

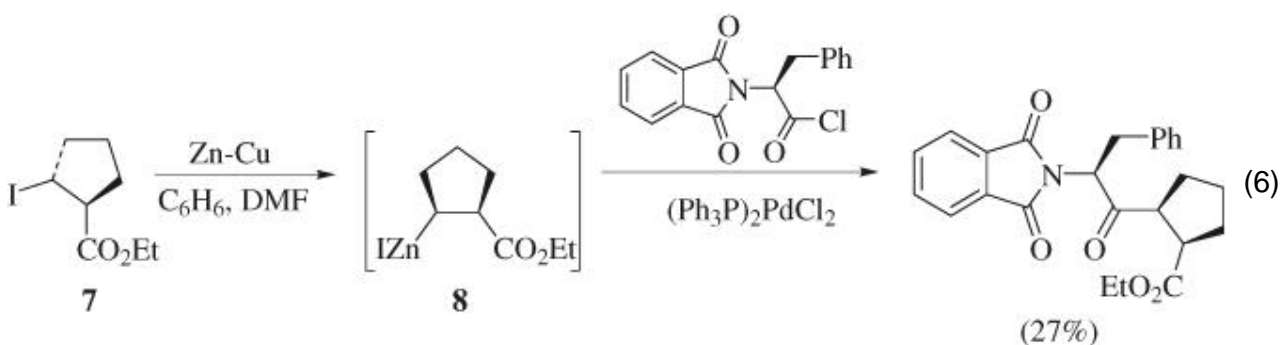
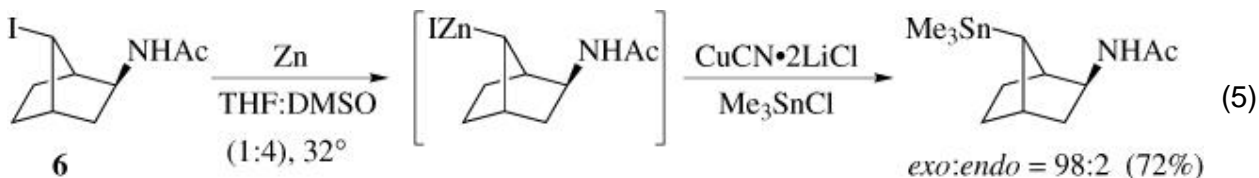


The mechanism of formation of zinc organometallics from the corresponding alkyl iodides has not been studied in detail, and only partial information is available. There is no general method for producing secondary alkylzinc halides with a well-defined configuration starting from a chiral alkyl iodide. The insertion of zinc dust into secondary alkyl iodides proceeds nonselectively, certainly via a SET mechanism to afford a mixture of stereoisomers. Thus, pure *trans*-1-acetamido-2-iodocyclohexane (**4**) affords, after zinc insertion, transmetalation with $\text{CuCN} \cdot 2\text{LiCl}$, and allylation, the allylated product **5** as a 1:1 mixture of diastereomers (Eq. 4). (35) Nevertheless, in the case of strained and sterically



hindered alkyl iodides such as **6**, zinc insertion occurs with complete retention of configuration. Interestingly, the zinc organometallic species formed is further transmetalated with $\text{CuCN} \cdot 2\text{LiCl}$ with retention of configuration and is quenched with trimethyltin chloride with retention of configuration (Eq. 5). (35)

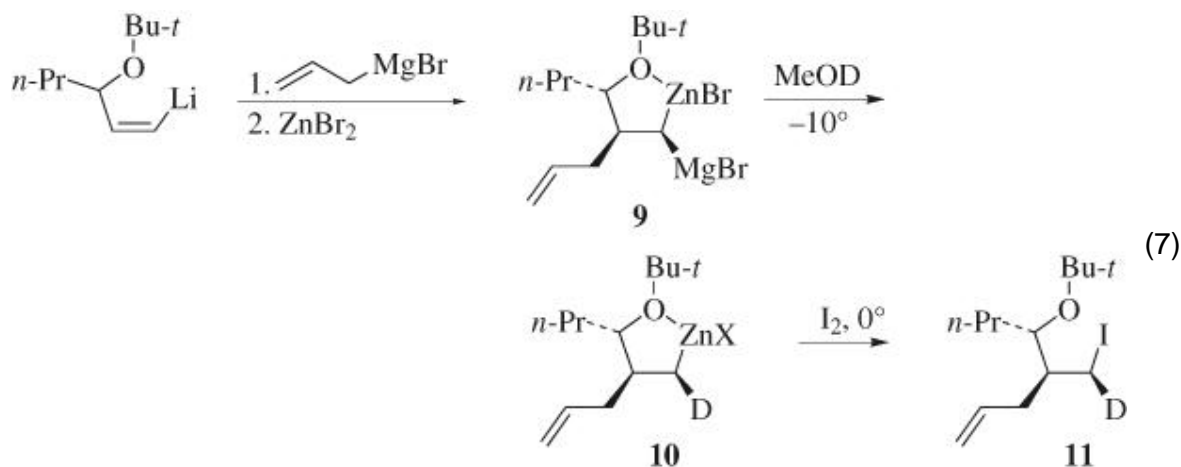
Similarly, the organozinc reagent derived from β -iodoester **7** reacts with an acid chloride in the presence of catalytic amounts of $(\text{Ph}_3\text{P})_2\text{PdCl}_2$ and provides only products derived from the *cis*-zinc reagent **8** (Eq. 6). (36-38) Although the configurational



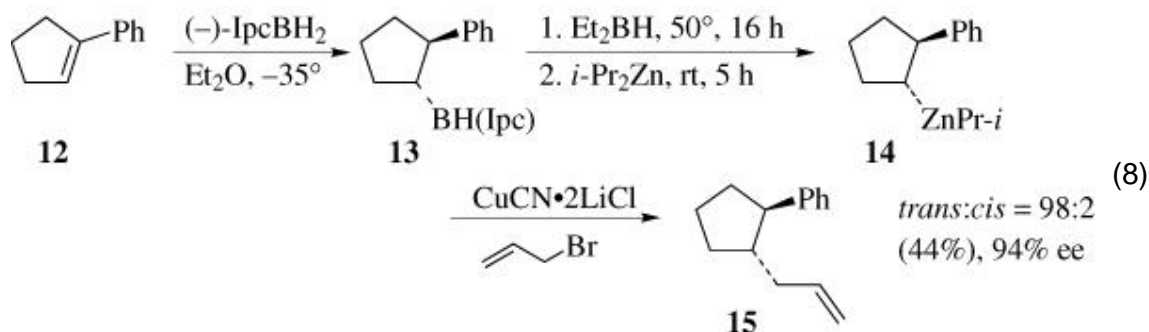
stability of acyclic organozinc derivatives has not been investigated for preparative applications, ^1H NMR studies have shown that secondary dialkylzincs such as dineohexylzinc have high configurational stability, and the activation energy for inversion has been estimated to be ~ 26 kcal/mol. (39) As shown in Eq. 5, the transmetallation of a secondary organozinc iodide with $\text{CuCN} \cdot 2\text{LiCl}$ occurs with retention of configuration. Similarly it has been shown that the transmetallation from zinc(II) to palladium(II)-species occurs with retention of configuration. (40) At present, the data available indicate that transmetallation of secondary organozinc reagents to at least organocoppers or organopalladiums occurs with retention of configuration. Tentatively, this is best explained by assuming a four-center mechanism (Eq. 1). No comprehensive study is available showing that this stereoselectivity for transmetallation is general. Interestingly, the preparation of chiral secondary organozinc derivatives via a boron-zinc exchange reaction also occurs with high retention of configuration, making this reaction the best suited for the preparation of chiral secondary dialkylzincs.

Starting from 1,1-bimetallic reagents of magnesium and zinc of type **9**, it is possible to perform a selective deuterolysis of the reactive carbon-magnesium bond followed by iodolysis of the organozinc intermediate **10** leading to the product **11** as a 60:40 mixture of stereoisomers. Starting with α -deuterated bimetallic compound **9** and performing a protonation with MeOH followed by

iodolysis furnishes the primary alkyl iodide **11** as a 34:66 mixture of diastereoisomers, showing that some open-chain primary organozinc halides can retain their configuration (Eq. 7). (41)

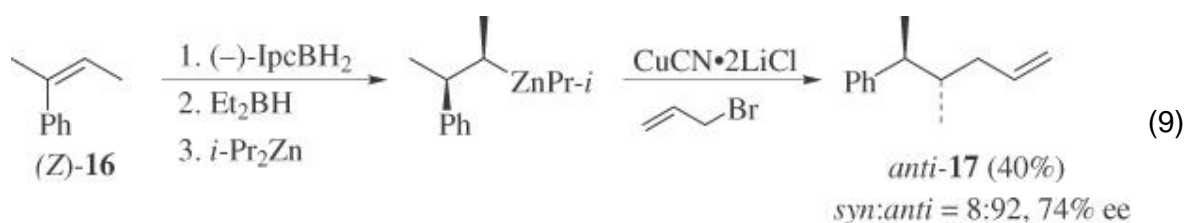


The best and most general method for preparing configurationally stable secondary diorganozincs involves a boron-zinc exchange reaction. (40, 42) Thus, the hydroboration of phenylcyclopentene **12** with monoisopinocampheylborane [(-)-lpcBH₂; 99% ee] (43) provides, after recrystallization, the chiral borane **13** with 94% ee. Treatment of **13** with diethylborane to remove the lpc group (50°, 16 hours) followed by the addition of *i*-Pr₂Zn provides the configurationally stable mixed diorganozinc reagent **14**, which in the presence of CuCN·2LiCl and allyl bromide furnishes the alkylated product **15** (Eq. 8). (44)

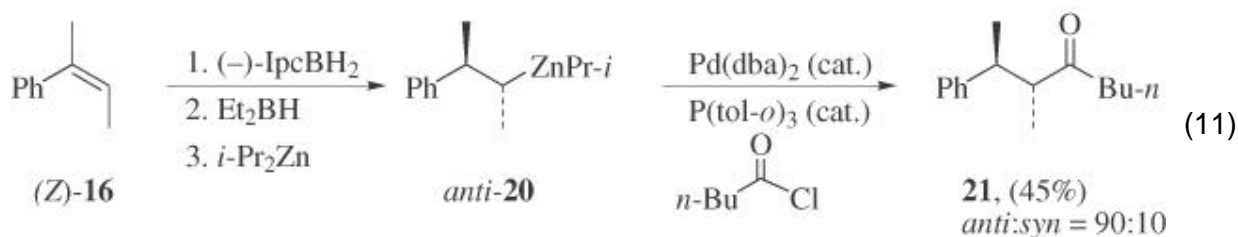
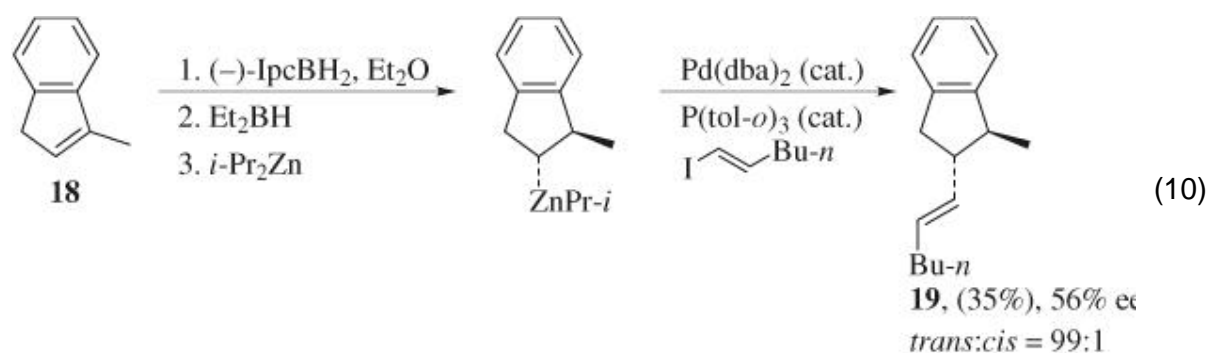


Interestingly, this reaction sequence can be extended to open-chain olefins.

The *Z*-styrene (**Z-16**) furnishes the *anti* product (*anti*-**17**) with high diastereoselectivity (*syn:anti* = 8:92) under these conditions. The enantioselectivity of the asymmetric hydroboration of these open-chain organoboranes lies between 46 and 74% ee (Eq. 9). (44) Several other electrophiles react with the intermediate zinc-copper reagents with retention of configuration. (44a)



It is also possible to perform stereoselective palladium(0)-catalyzed cross-coupling reactions. Thus, the palladium(0)-catalyzed alkenylation of 1-methylindene (**18**) via the hydroboration–boron-zinc exchange sequence provides *trans*-indane derivative **19** with 99:1 *trans:cis* selectivity (Eq. 10). Similarly, the palladium(0) catalyzed acylation of styrene **Z-16** furnishes the *anti*-ketone **21** (*anti:syn* ratio = 90:10; 88% ee) via the zinc reagent *anti*-**20** (Eq. 11).

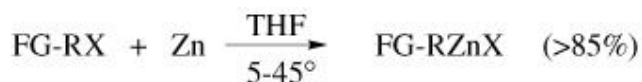


3. Scope and Limitations

3.1. Preparation Methods

3.2. Direct Insertion of Zinc Metal into Organic Halides

The insertion of zinc dust into organic halides is the most general method for preparation of functionalized organozinc halides. The reaction is sensitive to the reaction conditions (solvent, concentration, temperature), to the nature of the organic halide, and to the method of zinc activation. Whereas several solvent systems have been used in the past, (2) performing the reaction in THF as first described by Gaudemar (45) is the most convenient. Thus, the addition of a primary alkyl iodide as a 2.5–3.0 M solution in THF to zinc dust previously activated by 1,2-dibromoethane and chlorotrimethylsilane (46, 47) leads to rapid formation of the corresponding alkylzinc iodide (35–40°, 2 hours). Secondary alkyl iodides react even faster (room temperature, 1–2 hours) and provide the secondary alkylzinc iodides in high yields without the formation of elimination products. Most importantly, this modified procedure of Gaudemar (45) can be performed with a variety of polyfunctional iodides and gives unique access to polyfunctional alkylzinc halides. Functional groups such as ester, (47-74) ether, (50, 51, 66) acetate, (50-57, 59, 60, 63, 64, 68) ketone, (47-49) cyano, (47-57, 63, 65-76) halide, (47, 48, 57, 64, 67, 73) *N*, *N*-bis(trimethylsilyl)amino, (76) primary and secondary amino, (77) amide and phthalimide, (35, 78-80) trialkoxysilyl, (81) sulfoxide, (82) sulfide, (83) sulfone, (82, 83) thioester, (83) boronic ester, (61, 62, 64, 67, 84-86) enone, (54, 87-89) and phosphate (53, 90) can be present during formation of the organozinc reagent (Eq. 12). (14)



X = I, Br;

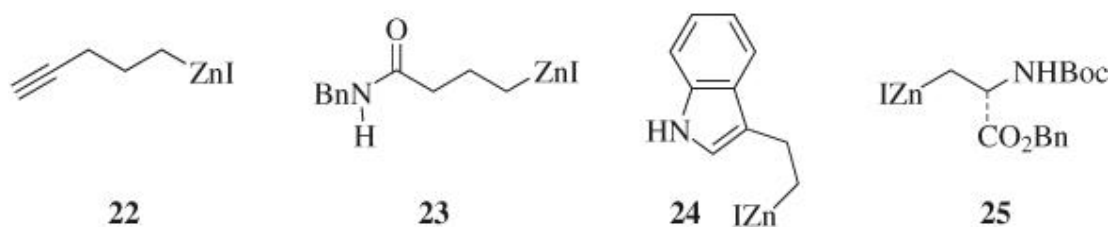
FG = CO₂R, enoate, CN, halide, (RCO)₂N, (TMS)₂N, RNH, NH₂, RCONH, (RO)₃Si, (RO)₂PO, RS, RSO, RSO₂, PhCOS

R = alkyl, aryl, benzyl, allyl

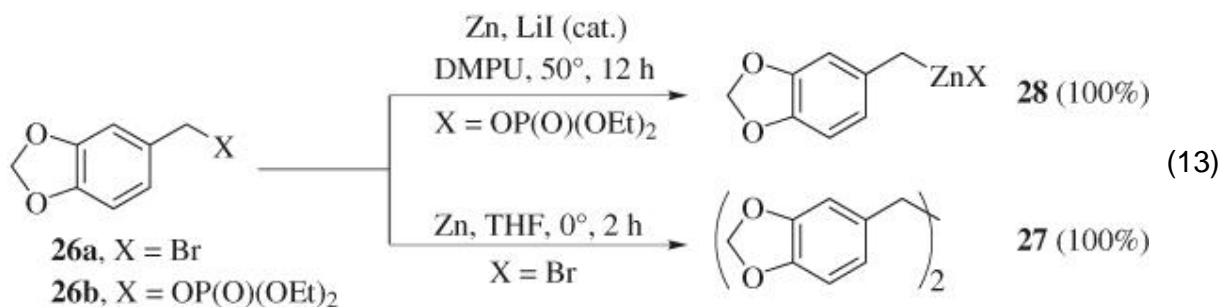
(12)

The presence of highly acidic protons of alcohols, phenols, some *N*-heterocycles (imidazole, adenine, uracil), diamines (1,2-diaminobenzene) or ethyl acetoacetate is very disadvantageous. (78) However, the preparation of primary alkylzinc iodides tolerates the presence of a wide range of primary or secondary amines. (78) Primary amines even enhance the rate of zinc

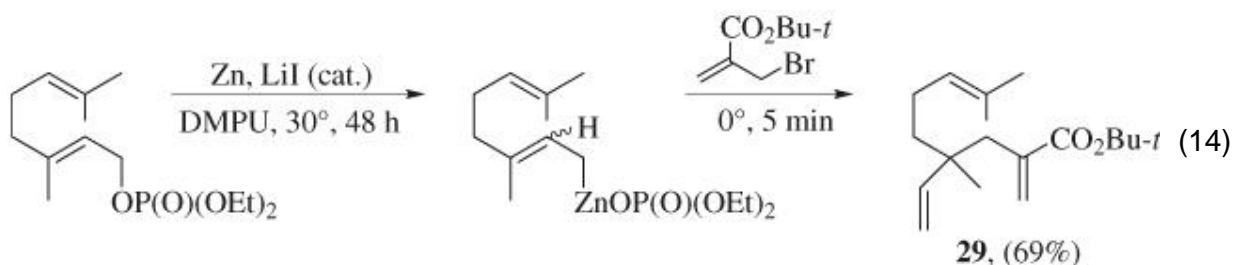
insertion into the alkyl iodide. Organozinc derivatives bearing relatively acidic protons, such as (22–25), can be prepared under standard conditions. (35, 78), (91–102) Functional groups like nitro or azide, which can readily accept an electron from the zinc surface, inhibit organozinc formation.



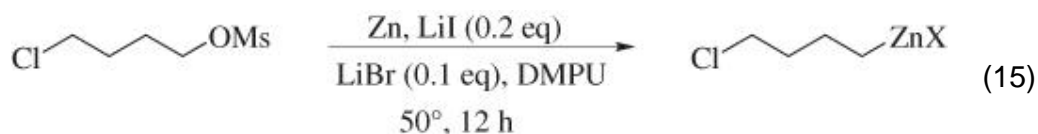
Whereas alkyl iodides in THF insert zinc dust between 20–40°, more reactive benzylic or allylic halides react with zinc powder under even milder conditions. (45) With these substrates, the formation of Wurtz-coupling products can be a problem. However, zinc insertion usually leads to smaller amounts of reductive coupling in these cases than does the corresponding insertion of magnesium or lithium. Therefore, allylzinc halides are the reagents of choice for performing nucleophilic allylation reactions. (45) The presence of electron-donating substituents in the benzylic or allylic halide enhances the Wurtz-coupling byproducts, and with benzylic bromide 26a only the homocoupling product 27 is obtained (THF, 0°). By using the corresponding phosphate 26b and performing the reaction in dimethyltetrahydropyrimidinone (DMPU) in the presence of LiI, the desired benzylic zinc reagent 28 is obtained without any self-coupling byproduct (Eq. 13). (103) Similarly, allylic phosphates are smoothly converted to the corresponding allylzinc reagents under these conditions. These reagents in the polar solvent



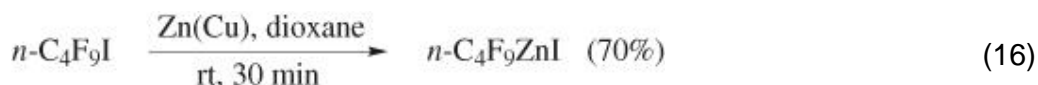
DMPU react with allylic bromides from the most substituted end of the allylic anion, leading to a branched product such as the trienic ester 29 (Eq. 14). (103)



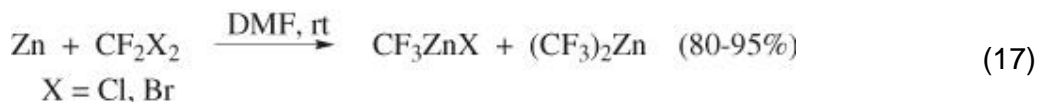
Not only primary alkyl iodides can serve as substrates for the preparation of alkylzinc derivatives, but also primary alkyl phosphates, mesylates, chlorides, bromides, and tosylates likewise react with zinc dust in dimethylacetamide (DMAC) or DMPU under mild conditions in the presence of lithium, sodium, or cesium iodides and provide access to various functionalized zinc reagents (Eq. 15). (103) The preparation of alkylzinc iodides can also be performed in



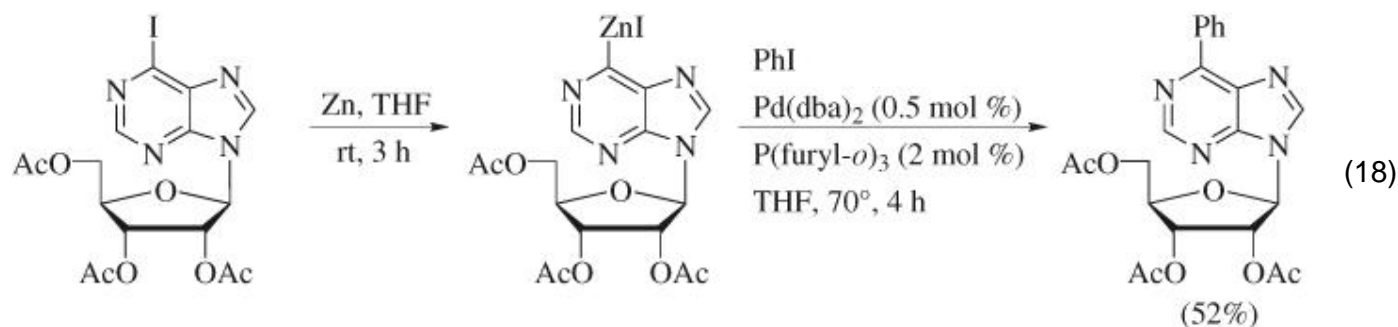
mixtures of benzene and DMAC or hexamethylphosphoramide (HMPA) using zinc-copper couple. (80, 104, 105) Polyfluorinated organozinc iodides have also been prepared by the insertion of zinc metal in THF or dioxane (Eq. 16). (106-115)



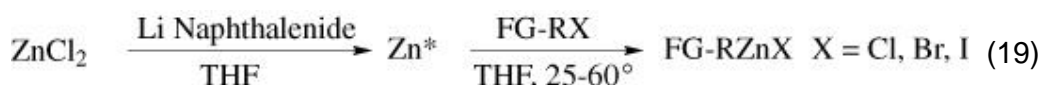
A complex reaction occurs when difluorodihalomethanes such as CF_2Cl_2 or CBr_2F_2 are subjected to zinc insertion in dimethylformamide (DMF), producing a mixture of bis(trifluoromethyl)zinc and trifluoromethylzinc halide in excellent yield (Eq. 17). (116, 117) The insertion of zinc dust into primary alkyl bromides in



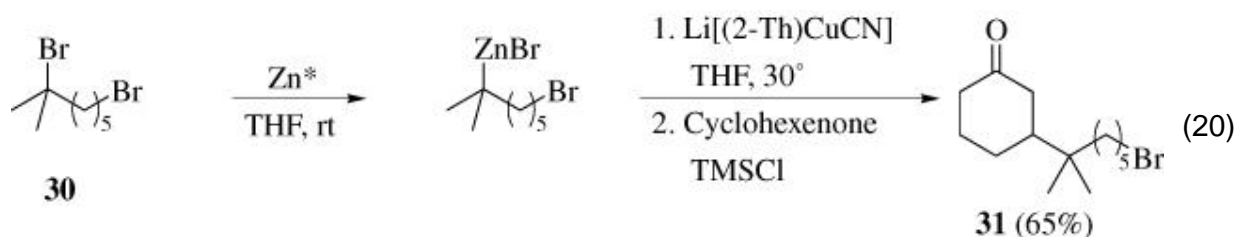
THF is possible only if activated zinc is used. (46) Iodinated nucleosides can be converted to the corresponding zinc reagents under mild conditions using either DMAC or THF as solvent depending on the solubility of the substrate. After a palladium(0) catalyzed cross-coupling reaction with an aryl iodide, arylated nucleosides are obtained in satisfactory yields (Eq. 18). (118, 119)



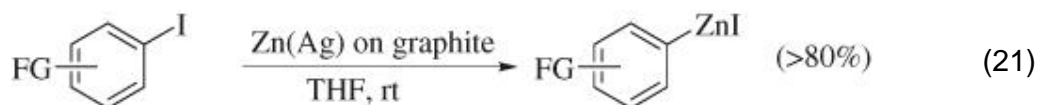
An especially active zinc powder can be generated by reducing zinc chloride with lithium naphthalenide in THF. This activated zinc reacts with alkyl bromides (THF, room temperature) in a few hours and with aromatic bromides in THF at reflux, affording alkylzinc and arylzinc bromides. This procedure tolerates the presence of various functional groups (i.e. ester, nitrile, aromatic ketone or halide) (Eq. 19). (120-127)



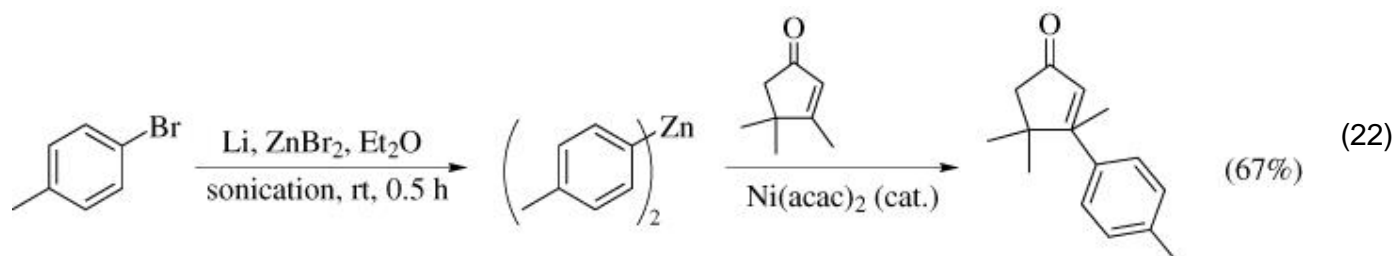
Secondary and tertiary alkyl bromides react even more readily, leading to the desired zinc reagents under mild conditions. (128-131) Thus, remarkable chemoselectivity is observed with a dibromoalkane such as **30** that bears both a primary and a tertiary alkyl bromide function. Only zinc insertion into the tertiary carbon-bromine bond is observed, which after transmetalation to an intermediate copper species and Michael addition leads to product **31** in 65% yield (Eq. 20). (132) Functionalized secondary zinc reagents are obtained from secondary bromides in this way. (131)



A related procedure based upon reaction of the graphite intercalation compound C_8K with a slurry of zinc chloride and silver acetate (10 mol %) produces a zinc-silver couple deposited on graphite which reacts with aromatic and heteroaromatic iodides at room temperature (Eq. 21). (133)



Interestingly, secondary alkyl bromides have such high reactivity that a direct insertion using moderately active zinc deposited on titanium dioxide is sufficient to provide the corresponding secondary organozinc compound. (134) In general, zinc insertion into an sp^2 C — I bond is far more difficult than into an sp^3 C-I bond and requires either the use of polar solvents (48, 135) or the use of highly activated zinc. (136-142) A potentially promising preparation of diarylzincs is the direct reaction of aryl bromides with lithium metal and zinc chloride under sonication. (143-149) The resulting diarylzincs are quite reactive and undergo Michael additions to enones in the presence of nickel(II) salts (Eq. 22). (143)

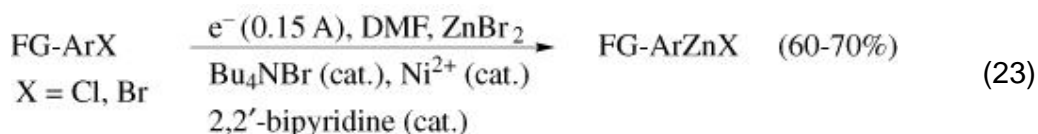


The substituents attached to the aromatic ring or to the double bond of an

alkenyl iodide greatly influence the rate of insertion of zinc. Electron-withdrawing substituents facilitate zinc insertion. Also, the presence of a heteroatom (S, N, O) at the position γ to the carbon-iodine bond has a positive effect. Thus, 3-iodo-2-cyclohexenone is converted to the corresponding zinc derivative **32** under mild conditions (THF, 25–50°, 0.5 hour; >85 % yield). (87, 88)



Similarly, 2-bromotrifluoropropene reacts with the Zn(Ag) couple in the presence of *N,N,N',N'*-tetramethylethylenediamine (TMEDA), leading to the zinc reagent **33** in 93 % yield (THF, 60°, 9 hours). (150-154) Electrochemical methods (155) using sacrificial zinc anodes in the presence of nickel 2,2'-bipyridyl provide an excellent alternative to the preparation of functionalized arylzinc halides (Eq. 23). (156-159) The method can be applied to heterocyclic compounds like 2- and 3-chloropyridine or 2- and 3-bromothiophene. (159, 160)

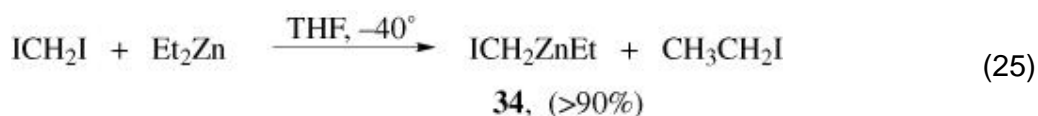
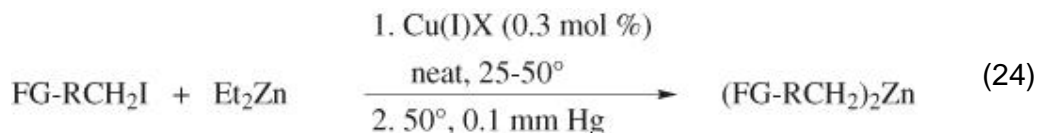


Zinc metal containing catalytic amounts of zinc formed by electroreduction of ZnX_2 (X = Br, Cl) is very reactive toward α -bromoesters and allylic or benzylic bromides. (161, 162)

3.3. Halide-Zinc Exchange

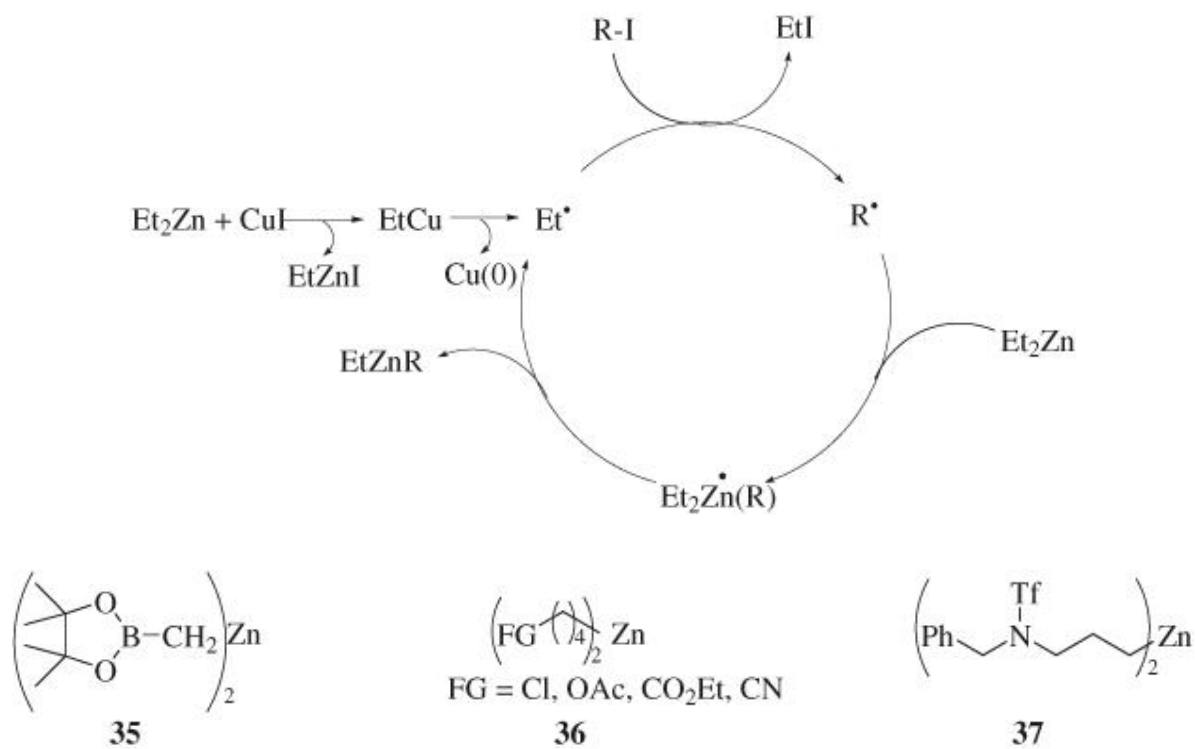
Diorganozincs are important reagents because they are more reactive than organozinc halides, and they have been used extensively in asymmetric synthesis. (14, 163) Until a few years ago, the preparation of diorganozincs had been limited to nonfunctionalized reagents since they were obtained by transmetalation of organolithiums or organomagnesium halides with zinc salts. (2) An iodine-zinc exchange reaction is a practical way for preparing

polyfunctional diorganozincs (FG-R)₂Zn (Eq. 24). Diiodomethane reacts readily with diethylzinc to provide ethyl(iodomethyl)zinc (34) and ethyl iodide via an iodine-zinc exchange reaction (Eq. 25). (11, 12) Recently, it was found that a wide range of polyfunctional primary alkyl iodides

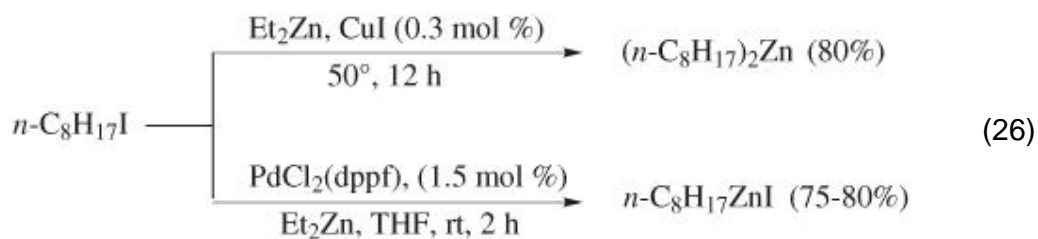


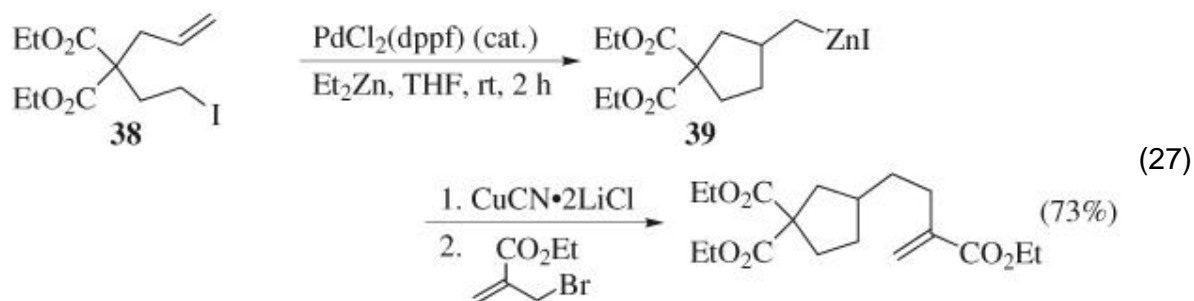
undergo this exchange if treated neat with diethylzinc in the presence of a catalytic amount of copper(I) iodide or copper(I) cyanide. (64, 164) In the absence of copper salts, the reaction requires a large excess of diethylzinc (3–5 equivalents) and longer reaction times. A possible mechanism for the catalytic effect of the copper salt is given in Scheme 1. The reaction of diethylzinc with copper(I) iodide generates ethylcopper, which decomposes at 50° to an ethyl radical and copper(0). A copper mirror is observed at the end of the reaction. The ethyl radical undergoes radical substitution with the primary alkyl iodide to provide the radical (R·), which adds to diethylzinc. A mixed alkyl(ethyl)zinc and an ethyl radical are produced after fragmentation. The ethyl radical initiates a new catalytic cycle. (164) This method provides general access to functionalized dialkylzincs such as 35–37. Because of the higher reactivity of dialkylzincs compared to alkylzinc halides, functional groups such as ketones or terminal acetylenes are not tolerated in these reagents. Besides copper(I) salts, a variety of transition metal salts catalyze the halide-zinc exchange.

Scheme 1.

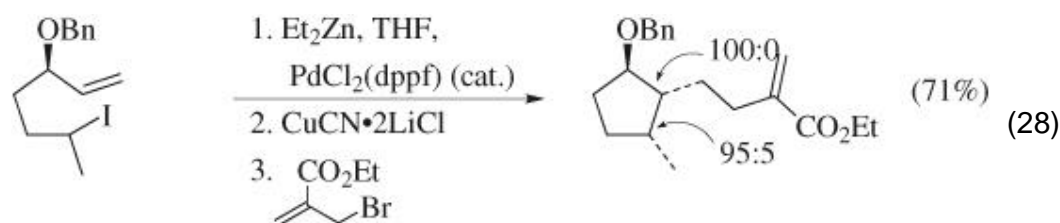


Especially interesting is the palladium(II)- or nickel(II)-catalyzed exchange reaction. In these cases, the product is not a dialkylzinc but rather an alkylzinc iodide (Eq. 26). (165–166a) The mechanism almost certainly involves radical intermediates. Treatment of the unsaturated iodide **38** with diethylzinc produces the cyclopentylmethylzinc iodide **39**, which can be subsequently trapped with an electrophile (Eq. 27). (165-167)

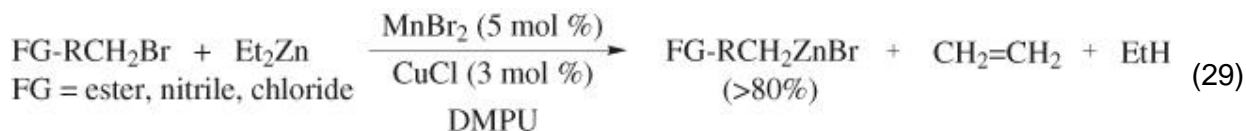




This radical cyclization leading to zinc organometallics can also be performed with secondary alkyl iodides and proceeds with high stereoselectivity with the appropriate substituents (Eq. 28). (166) The preparation of polycyclic molecules via tandem cyclization is also possible. (168) Applications of the method to the synthesis of (+)-methyl jasmonate, (169) (–)-methyl curcubate, (169) and (–)-methylenolactocin (170, 171) using a nickel-catalyzed carbocation have been reported.

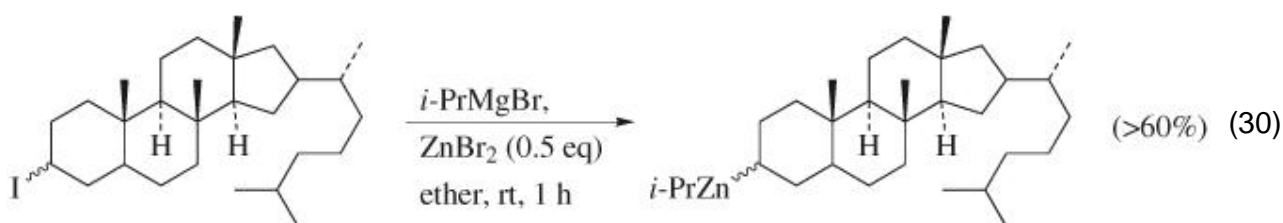


Finally, this method can be applied to the preparation of benzylic zinc reagents. (165, 172) Mixed metal catalysis using manganese(II) bromide and copper(I) chloride allows bromine-zinc exchange to occur with functionalized primary alkyl bromides in the polar solvent (173-175) DMPU under very mild conditions (room temperature, 4–10 hours; Eq. 29). (176)

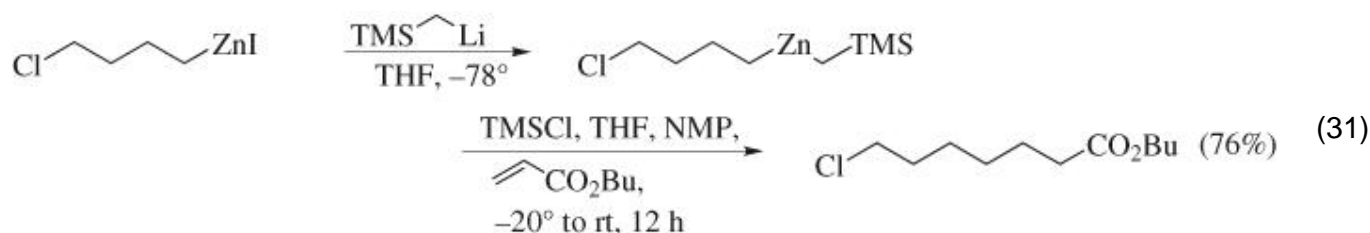


The direct insertion of zinc metal into primary alkyl bromides does not proceed

in THF and is slow in DMPU. (103) Interestingly, the iodine-zinc exchange reaction can be light-initiated. (177) A favorable equilibrium occurs in solution at room temperature with only 1 equivalent of Et_2Zn when a solution of the alkyl iodide in CH_2Cl_2 is irradiated at $>280\text{ nm}$, allowing a faster synthesis of the dialkylzinc compared to the thermal copper-catalyzed reaction. The halide-zinc exchange can be performed with $i\text{-Pr}_2\text{Zn}$. This reagent needs to be salt-free if configurationally well-defined reagents are to be prepared. (16-18) However, if the configuration of the zinc organometallics is not relevant, then the in situ generation of $i\text{-Pr}_2\text{Zn}$ from $i\text{-PrMgBr}$ and ZnBr_2 (0.5 equivalent) is a convenient method for preparing complex secondary diorganozincs (Eq. 30). (178)



Mixed diorganozincs of the type $\text{RZnCH}_2\text{SiMe}_3$ allow selective transfer of the group R. (179, 180) The Me_3SiCH_2 group is too unreactive to be transferred and plays the role of a dummy ligand. These mixed reagents avoid the waste of a precious organic group R in the reaction of diorganozincs with electrophiles (Eq. 31). (180)

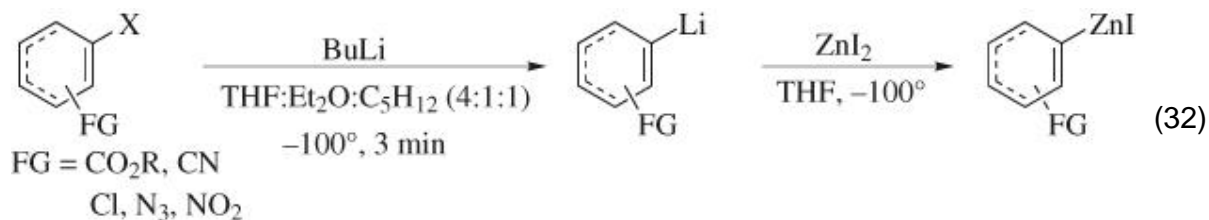


3.4. Transmetalation Reactions

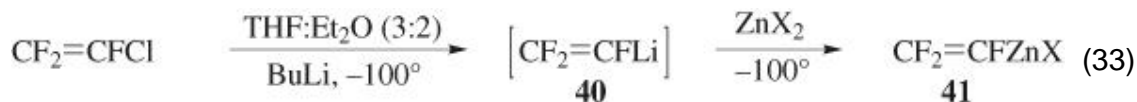
3.4.1. Lithium-Zinc Exchange

Alkylolithiums are too reactive to tolerate most functionalities. (21, 181-183) However, alkenyl- and aryllithiums are significantly less reactive than their alkyl counterparts and therefore at very low temperatures tolerate the presence of several functional groups (i.e., halide, (184-188) sulfone, (189)

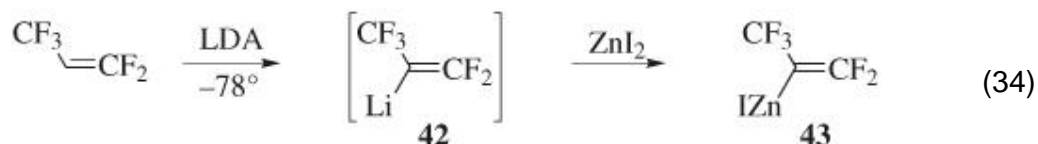
epoxide, (190) ester, (191-202) or cyano (198) groups). (203-208) The stability of these functionalized lithium derivatives can be greatly improved by performing a transmetalation with zinc salts to give the corresponding aryl- or alkenyl-zinc halide (Eq. 32). (209, 210) Whereas 1,2,2-trifluoroethyllithium (40) is a very unstable carbenoid



reagent, the addition of zinc(II) salts leads to an organozinc reagent 41, which is stable at room temperature and can be used for the formation of carbon-carbon bonds with a large number of electrophiles (Eq. 33). (154, 211-215) Similarly,



the perfluorinated 2-propenyllithium 42 can be stabilized by transmetalation with zinc iodide, leading to 43 (Eq. 34). (114, 151-153) This method allows the preparation of functionalized organozinc reagents not available by other methods.



The presence of an azide function in an alkenyl iodide such as 44 completely inhibits zinc insertion. However, treatment of 44 with butyllithium (216-220) at low temperature followed by addition of a THF solution of zinc iodide leads to the desired alkylzinc iodide 45, which can be further transmetalated with CuCN·2LiCl and added to ethyl propiolate (Eq. 35). (209)

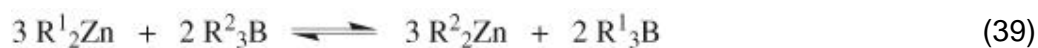
with an alkyl iodide in the presence of *p*-trifluoromethylstyrene as promoter (Eq. 38). (230) The role of the promoter is believed to lower electron density at the nickel center thereby facilitating reductive elimination to the cross-coupling product.



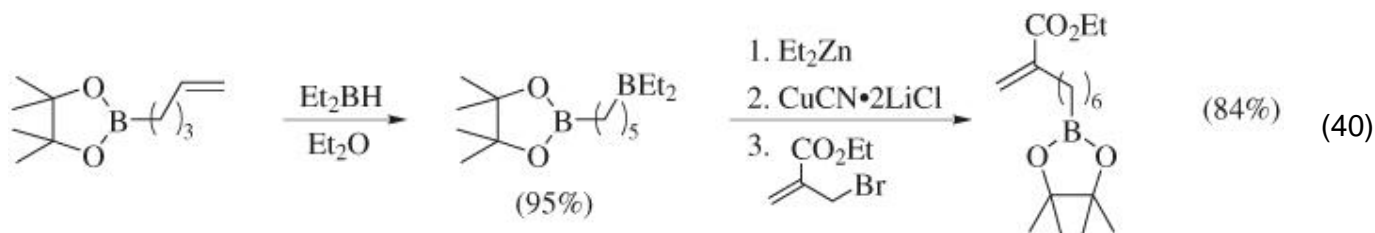
This iodine-magnesium exchange can be extended to the preparation of polyfunctional pyridylmagnesium derivatives. (230a-231) Also, some alkenyl iodides bearing a coordinating heteroatom in close proximity to the carbon-iodine bond undergo a smooth iodine-magnesium exchange leading to polyfunctional alkenylmagnesium compounds with retention of the double bond configuration. (232)

3.4.3. Boron-Zinc Exchange

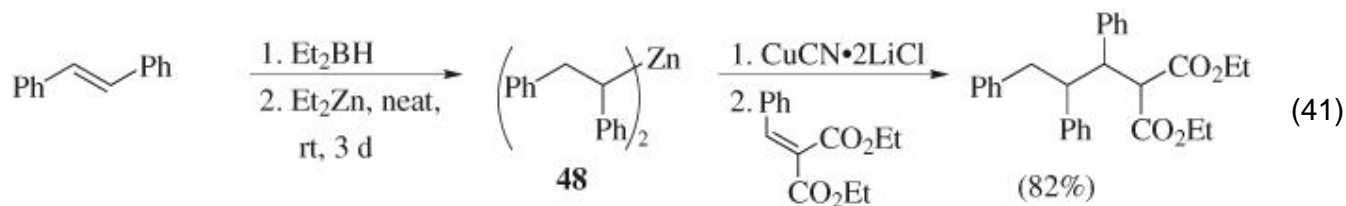
Triorganoboranes readily undergo transmetalation reactions with dialkylzincs (Eq. 39). (2) The driving force for the reaction is formation of volatile boranes such as trimethylborane ($R^1 = \text{CH}_3$). The reaction has



proven to be very useful for the preparation of allyl or benzylzinc reagents as well as chiral secondary zinc reagents. (233-235), (40), (44) The transmetalation of alkenylboranes proceeds under especially mild conditions, leading to mixed alkenyl(alkyl)zincs in almost quantitative yield. (236, 237) Interestingly, the alkenyl moiety attached to zinc is more reactive than the alkyl group and is selectively transferred to an organic electrophile. Functionalized alkenylzinc derivatives are available by this method. (238) Similarly, functionalized trialkylboranes are transmetalated to dialkylzincs (Eq. 40). (239, 240)

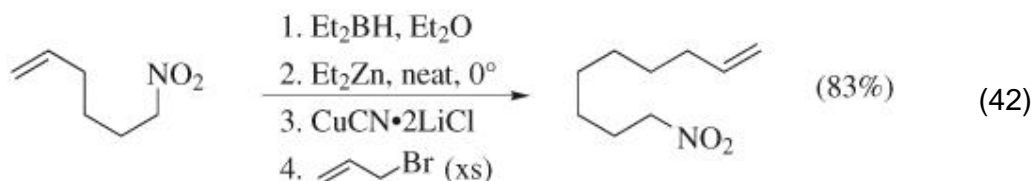


The use of diethylborane in hydroborations (241) leads to the desired boranes in excellent yields and avoids the use of a large excess of diethylzinc for transmetalation (Eq. 40). This hydroboration reagent can be conveniently prepared by mixing the borane-methyl sulfide complex and triethylborane in the appropriate stoichiometry (1:2). The regioselectivity of hydroboration is often excellent. (241) The procedure allows for the preparation of zinc organometallics not available from the corresponding organic halides. Thus, stilbene is cleanly converted to the secondary benzylic zinc reagent **48**, which after transmetalation with copper cyanide-lithium chloride complex adds smoothly to diethyl benzyldenemalonate (Eq. 41). (240) The mild conditions required for performing the boron-zinc exchange make this method one of the simplest, most general, and highest yielding syntheses of polyfunctional diorganozincs.



This procedure has great synthetic potential and is the most general and versatile method for preparation of functionalized diorganozincs. Remarkably, substrates bearing acidic hydrogens, like primary nitroalkanes or alkylidenemalonates, are readily hydroborated and undergo smooth boron-zinc exchange. After a copper catalyzed allylation, the expected allylated products are obtained in high yields (Eq. 42). (242) The boron-zinc exchange proceeds under significantly milder conditions (0° instead of 50°) for primary alkyl derivatives, and requires only a few minutes compared to the several hours that are necessary in the iodine-zinc exchange. Nevertheless,

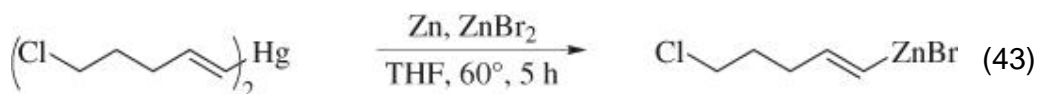
the boron-zinc exchange reaction using Et_2Zn has some drawbacks and does not proceed rapidly with hindered secondary



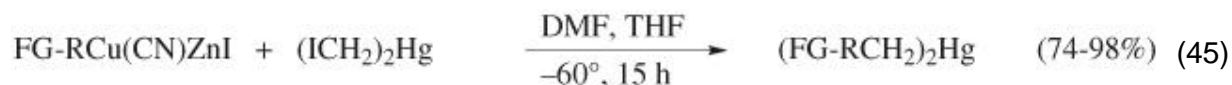
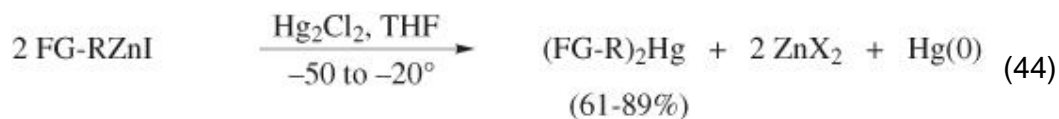
alkyldiethylboranes. Also, a 1:1 mixture of diastereomeric zinc reagents is obtained with diastereomerically pure alkylboranes. As described above, these problems can be solved by using $i\text{-Pr}_2\text{Zn}$ instead of Et_2Zn , thereby allowing the synthesis of secondary dialkylzincs. (40, 44)

3.4.4. Mercury-Zinc Exchange

Owing to the weak carbon-mercury bond, organomercurials readily undergo reductive transmetalation with zinc metal. (243) This method can be applied to functionalized organomercurials $[(\text{FG-R})_2\text{Hg}]$ leading to a range of functionalized dialkylzincs (FG = ester, nitrile, chloride). (67) The transmetalation rate can be enhanced by zinc salts. In such a case, the reaction is complete within a few hours at 60° , whereas a temperature of 110° is required in the absence of ZnX_2 . (67) Polyfunctional (*E*)-alkenylzinc halides with high stereoisomeric purity can be prepared (Eq. 43). (67) The required diorganomercurials



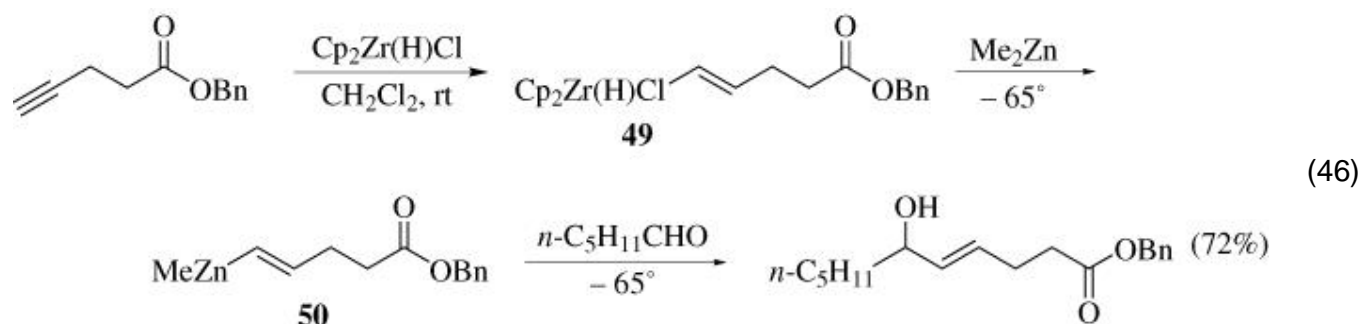
are obtained by various methods such as (1) the reaction of functionalized alkylzinc halides with mercury(I) chloride (67) (Eq. 44), (2) the substitution reaction between bis(iodomethyl)mercury and copper-zinc organometallics ($\text{FG-RCu}(\text{CN})\text{ZnI}$, Eq. 45), (67) or (3) the transmetalation of alkenylboronic esters



obtained by the hydroboration of alkynes with pinacolborane. (67, 244)
 Polyfluorinated zinc reagents can be prepared by the transmetalation of bis(trifluoromethyl)mercury with dimethylzinc in pyridine. (245, 246)

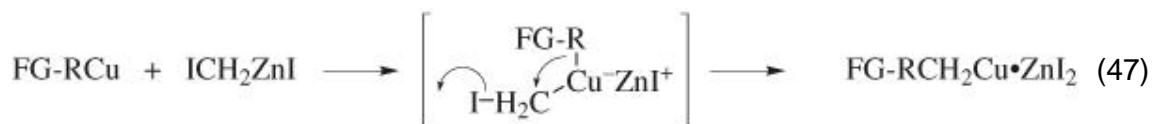
3.4.5. Zirconium-Zinc Exchange

Transition alkenyl organometallics such as alkenylzirconium **49** undergo a smooth transmetalation to the corresponding alkenylzinc compound **50** by the treatment with Me_2Zn at -65° . The reaction is complete within a few minutes and a smooth reaction with aldehydes furnishes the corresponding allylic alcohols. The starting alkenylzirconium reagents are readily prepared from alkynes by hydrozirconation with $\text{Cp}_2\text{Zr}(\text{H})\text{Cl}$ (Eq. 46). (247)

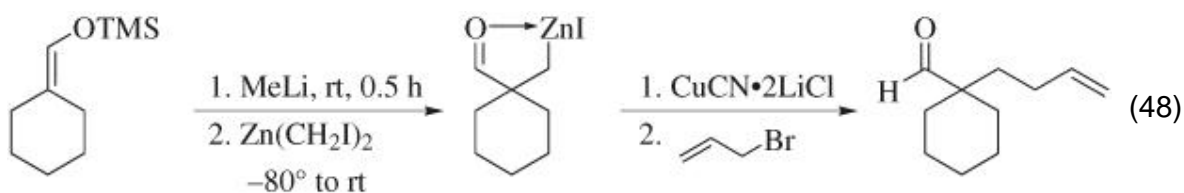


3.5. Insertion Reactions Using ICH_2ZnX

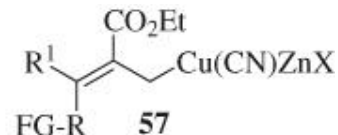
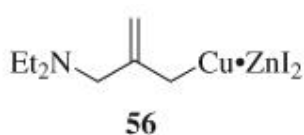
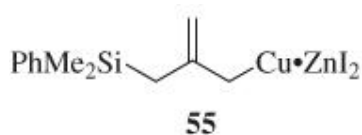
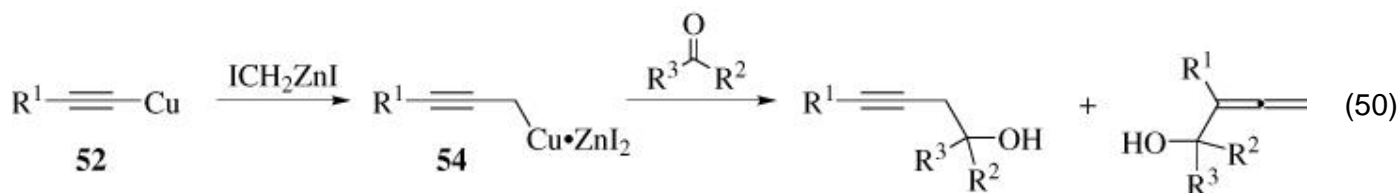
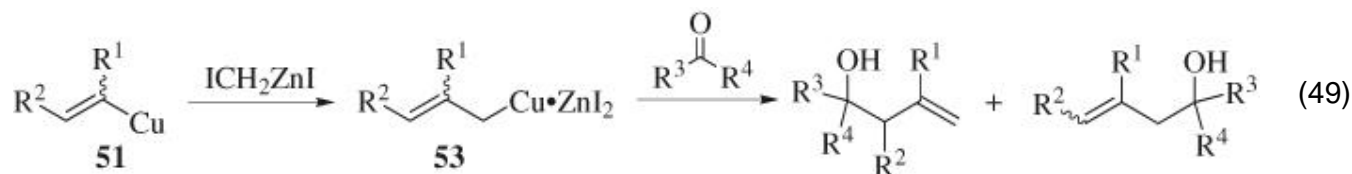
Zinc carbenoids such as (iodomethyl)zinc iodide (248, 249) have been used principally for cyclopropanation reactions. (7-12, 250-265) However, these reagents have recently been used for the homologation of organocopper derivatives to provide new zinc-copper species (Eq. 47). (266-271)

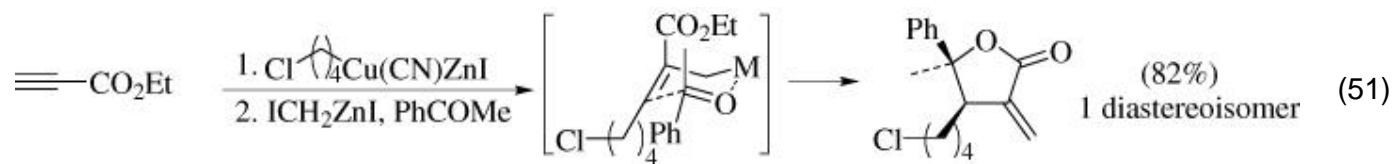


The scope of the reaction is relatively broad. Copper enolates of nitriles, ketones, or aldehydes can be used, thus providing a route to homoenolates (Eq. 48). (65, 266, 270) Especially interesting are alkenyl- and alkynylcopper reagents

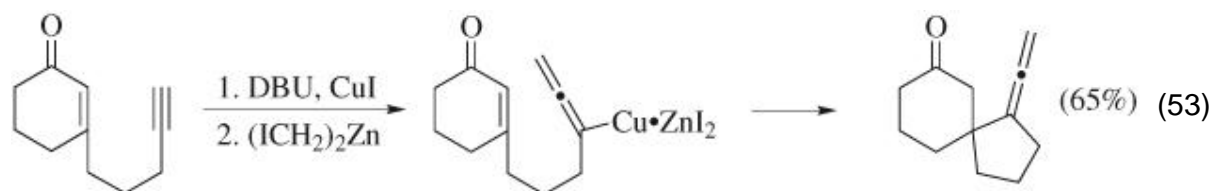
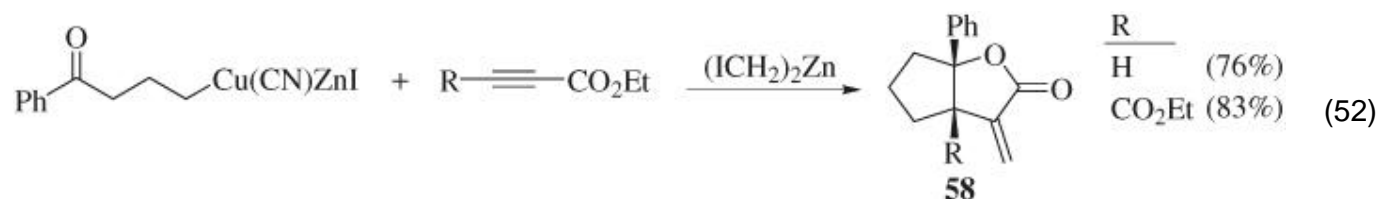


51 and **52**, which after methylene homologation afford highly reactive allylic and propargylic copper-zinc compounds **53** and **54**. By performing the reaction with iodomethylzinc iodide in the presence of a carbonyl compound, the resulting organometallics **53** and **54** are trapped by this electrophile (Eqs. 49 and 50). (266-271) Several polyfunctional allylic zinc reagents such as (**55–57**) can be generated in situ by this method. (270) The addition of functionalized copper-zinc compounds to acetylenic compounds produces functionalized alkenylcoppers, which after homologation with ICH_2ZnI lead to allylic zinc-copper compounds **57**. These are efficiently trapped with carbonyl compounds to produce α -methylene- γ -butyrolactones with excellent stereoselectivity (Eq. 51). (270, 271)

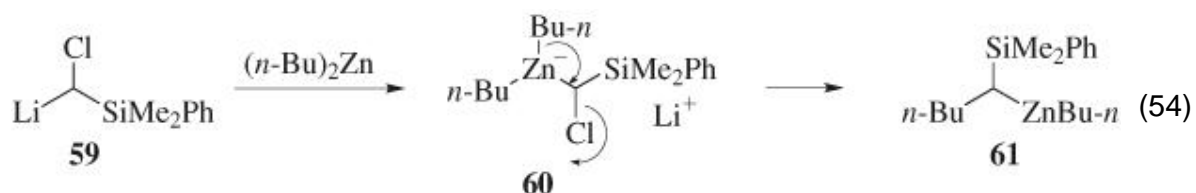




An intramolecular version of this process allows the construction of bicyclic γ -butyrolactones **58** (Eq. 52). (270, 271) Intramolecular trapping of methylene homologated alkenylcoppers provides new cyclization products (Eq. 53). (270)

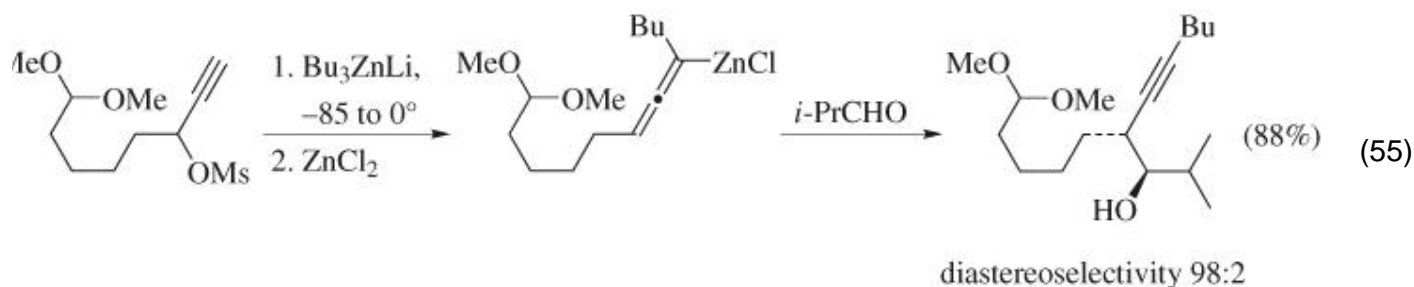


Higher homologs of ICH_2ZnX can also be used for homologation reactions. For example, the addition of lithium carbenoid **59** to dibutylzinc furnishes an intermediate zincate **60**, which after 1,2-migration gives the zinc-silicon 1,1-bimetallic compound **61** (Eq. 54). (272, 273)



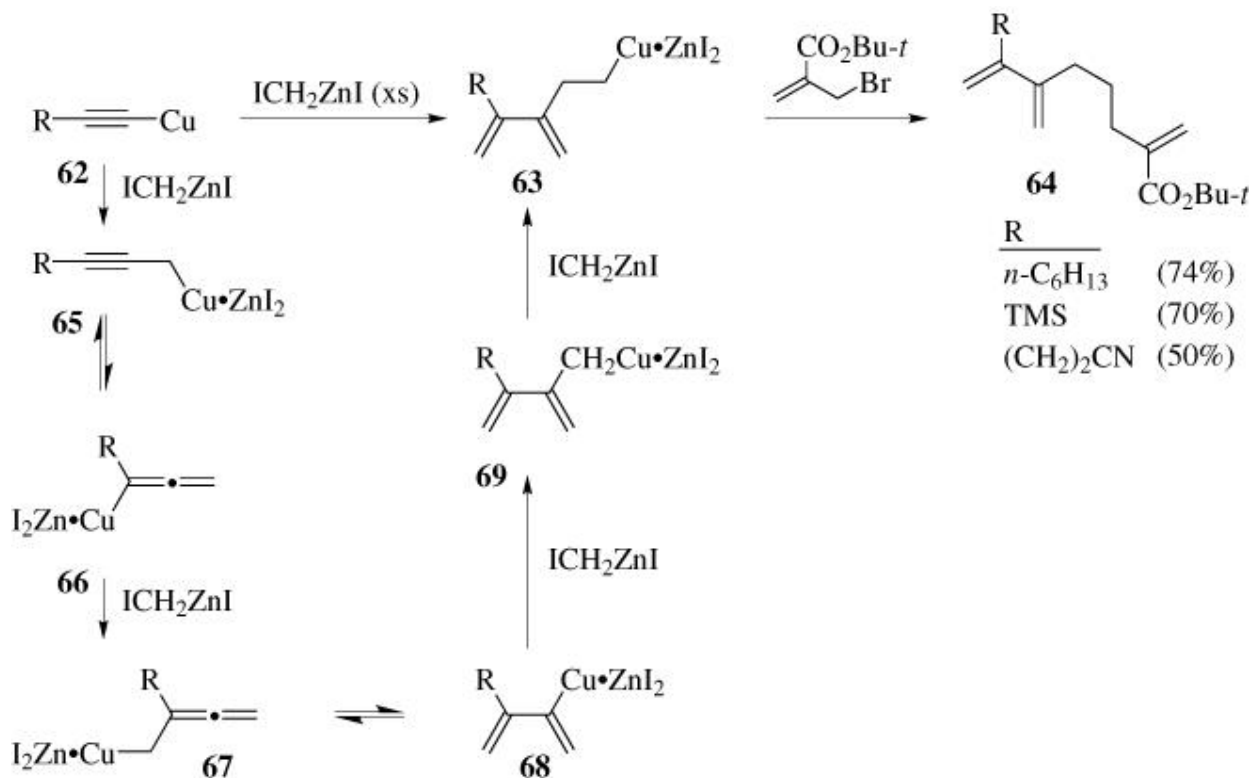
Zincates undergo the halide-zinc exchange reaction with various

1,1-dibromides to form zinc carbenoids, which undergo 1,2-migration (274-282) to give mixed dialkylzincs. (283-288) Only a few functional groups are tolerated under these reaction conditions. A related 1,2-migration delivers allenylzinc derivatives starting from propargylic mesylates. The trapping of allenylzincs with aldehydes provides homopropargylic alcohols with high diastereoselectivity (Eq. 55). (288)

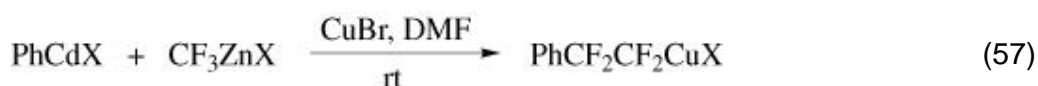
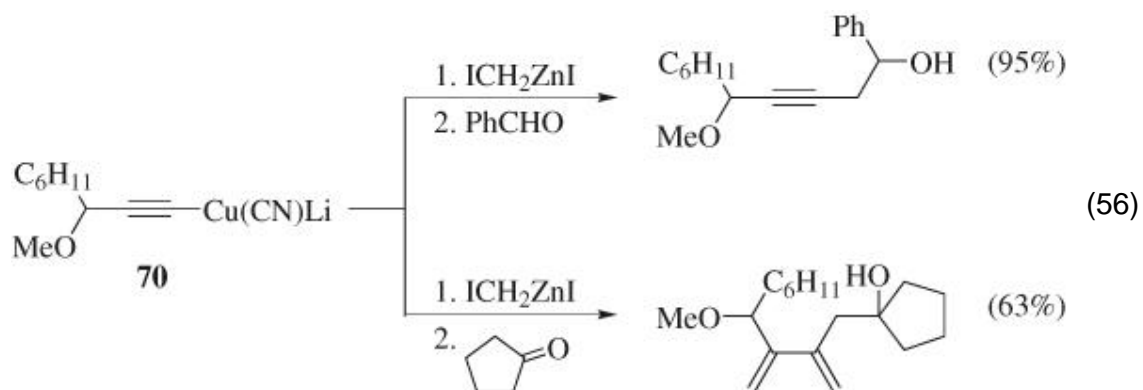


Polymethylene homologations are generally performed in the presence of an excess of ICH_2ZnX . After the first methylene homologation of an alkynylcopper, zinc-copper species are produced with reactivities different from the starting organometallics, so that very clean polymethylene homologation reactions can be achieved. Thus, treatment of an alkynylcopper **62** with an excess of (iodomethyl)zinc iodide produces the dienylcopper **63**, which can be trapped by *tert*-butyl α -(bromomethyl)acrylate to form unsaturated ester **64** (Scheme 2). (268) The first step is a methylene insertion leading to propargylzinc-copper intermediate **65**, which is in equilibrium with the allenylcopper **66**. The reaction of **66** with another equivalent of iodomethylzinc iodide produces allylcopper-zinc reagent **67** that is in equilibrium with the dienyl organometallic **68**.

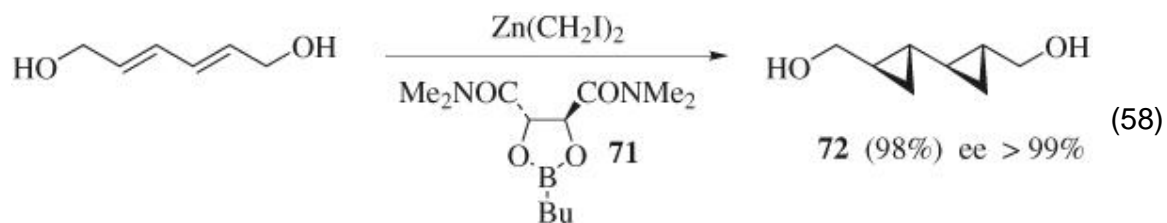
Scheme 2.



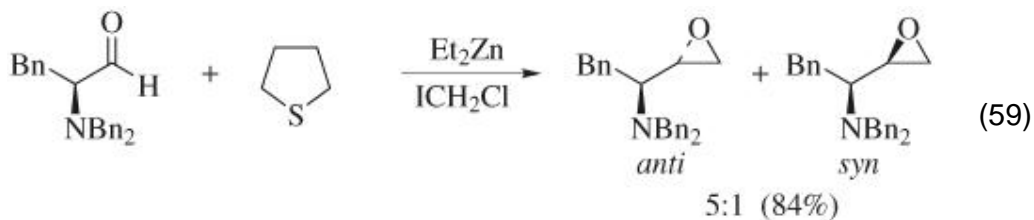
Further reaction of **68** with iodomethylzinc iodide leads to the reactive allylic reagent **69**, which readily inserts a new methylene unit to give the unsaturated alkylcopper-zinc species **63**, which, under mild reaction conditions (-80 to 0°) does not undergo further insertion reactions and can be trapped by an allylic bromide. The copper-zinc species **63** is especially unreactive. This is explained by the presence of large amounts of zinc salts, which form mixed zinc-copper clusters in which the organic moiety has a high probability of being attached to zinc. The degree of polymethylene homologation also depends on the reactivity of the electrophile added. Thus, the metallated propargylic ether **70** reacts with benzaldehyde after a single methylene homologation. However, in the presence of the less reactive cyclopentanone, three methylene homologations occur first to generate a very reactive allylzinc-copper reagent, which is subsequently trapped by the ketone (Eq. 56). (270) Polyfluorinated zinc-copper reagents can be prepared by double insertion of difluoromethylene units brought about by reaction of a phenylcadmium halide with a trifluoromethylzinc derivative in the presence of CuBr (Eq. 57). (289)



Recently, the Simmons-Smith reagent ICH_2ZnI has found renewed interest for the conversion of β -keto esters to γ -keto esters (290) or for stereoselective cyclopropanation of allylic alcohols. (291-291a) In the presence of the chiral dioxaborolane ligand **71**, chiral polycyclopropane compounds **72** have been prepared with high enantiomeric excess (Eq. 58). (292, 293) Substituted zinc carbenoids like $(\text{CH}_3\text{CHI})_2\text{Zn}$

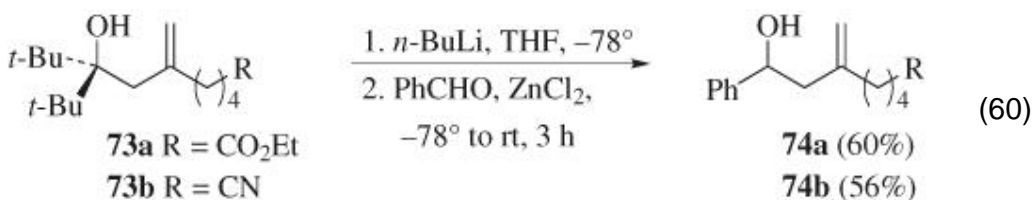


effect diastereoselective and enantioselective cyclopropanations of allylic alcohols under these reaction conditions. (294) An elegant epoxide synthesis starting from an aldehyde and using an intermediate zinc carbenoid has been reported (Eq. 59). (295)

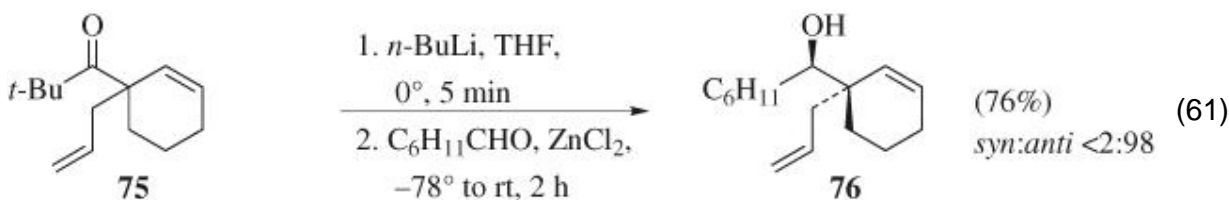


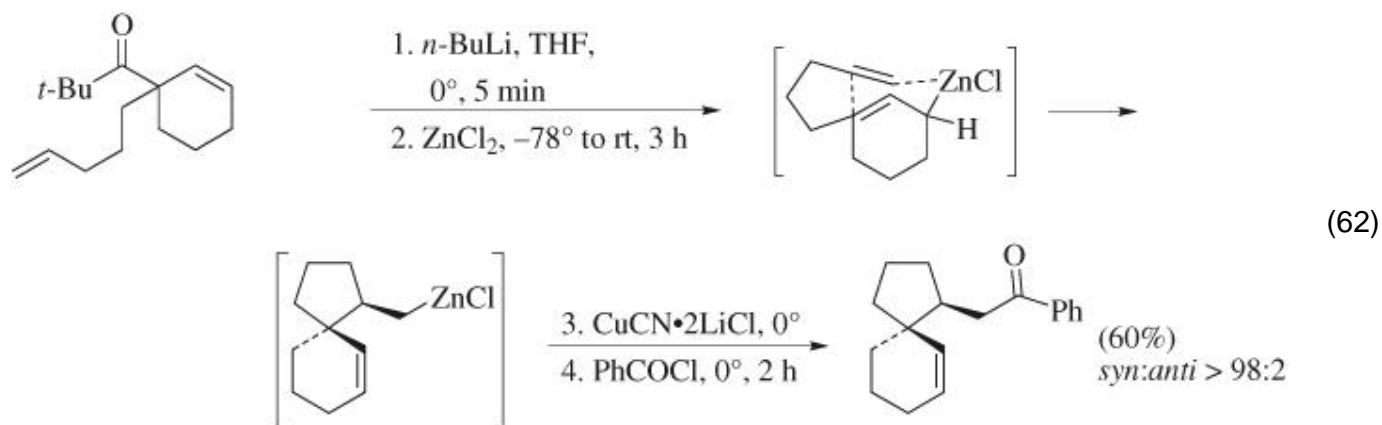
3.6. Fragmentation of Homoallylic Zinc Alcoholates

Substituted or functionalized allylic zinc reagents are difficult to prepare by direct zinc metal insertion because of extensive formation of Wurtz-homocoupling products. This problem has been solved by performing a fragmentation of zinc homoallylic alcoholates. Thus, conversion of alcohols **73a-b** to the corresponding zinc alcoholates leads to a fragmentation reaction with formation of a polyfunctional allylic zinc reagent that adds to benzaldehyde leading to the alcohols **74a-b** (Eq. 60). (296, 297) Remarkably, this reaction is highly diastereoselective.



Thus, ketone **75** is converted to an allylic zinc alcoholate by the addition of *n*-BuLi followed by zinc chloride in the presence of an aldehyde, leading to the homoallylic alcohol **76** in 76% yield as one diastereoisomer (*syn:anti* > 2:98, Eq. 61). (297, 298) The generation of highly substituted allylic zinc reagents has also been exploited in intramolecular ene reactions (Eq. 62). (299)

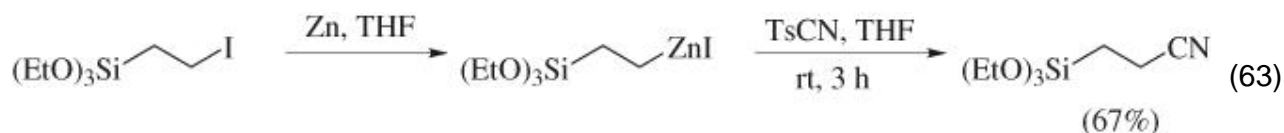




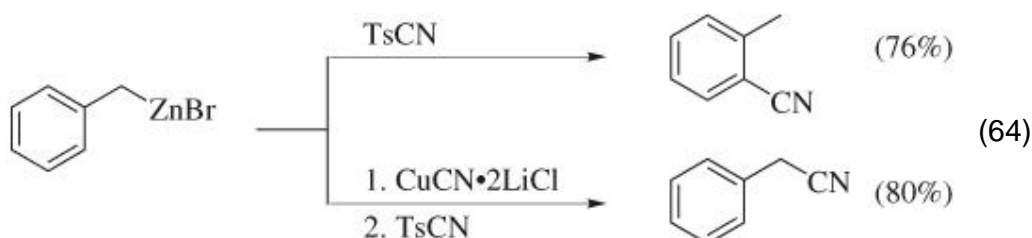
3.7. Reactivity of Functionalized Organozincs

3.8. Uncatalyzed Reactions

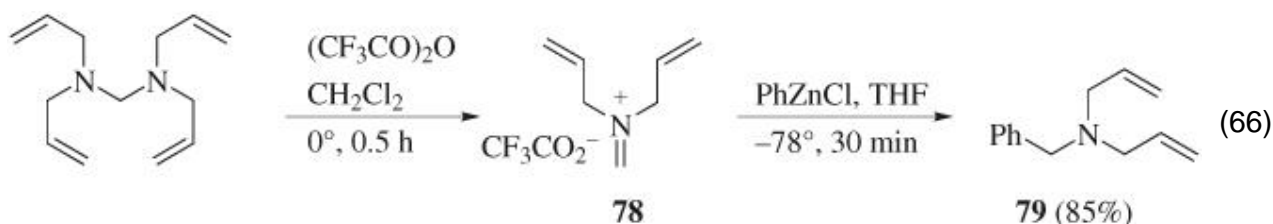
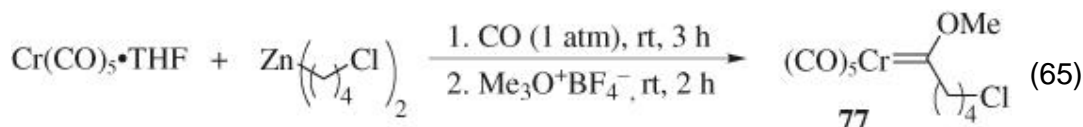
Diorganozincs and organozinc halides display only moderate reactivity toward most organic electrophiles. However, several powerful electrophilic reagents react directly with zinc organometallics. Thus, the bromination or iodination of zinc derivatives proceeds in excellent yield. (2) Direct oxidation of organozinc reagents with oxygen allows efficient access to hydroperoxides. (2) Whereas most organometallic reagents (RM) react rapidly with oxygen, the resulting metal hydroperoxides (ROOM) are often reactive enough to oxidize the starting organometallic species, leading to a mixture of metal hydroperoxide and alkoxide (ROM). The moderate reactivity of zinc organometallics (300, 301) allows the preparation of hydroperoxides with good selectivity (Table I). The use of perfluorinated solvents leads to excellent results in these reactions, owing to the exceptionally high solubility of oxygen in these media. With perfluorohexane (302) as solvent, functionalized hydroperoxides can be obtained with excellent selectivity. (303-303a) Functionalized organozincs prepared by hydrozincation, carbozincation, or by boron-zinc exchange can be oxidized directly in a selective manner to the corresponding functionalized alcohols or hydroperoxides, depending on the reaction conditions. Pseudohalogens such as tosyl cyanide also react with a range of polyfunctional aryl-, alkenyl-, alkynyl-, and alkylzinc halides to provide the corresponding nitriles (Eq. 63 and Table I). (304) An interesting regioselectivity is observed with



benzylic organometallics. Whereas the reaction of tosyl cyanide with benzylzinc bromide selectively provides 2-methylbenzonitrile (76%) via an allylic rearrangement, reaction of the corresponding copper-zinc reagent leads to benzyl cyanide (80%; Eq. 64). (304) Diorganozincs rapidly react with chromium(0) pentacarbonyl- THF complex to give an intermediate organochromium(0) salt, (305-307) which under

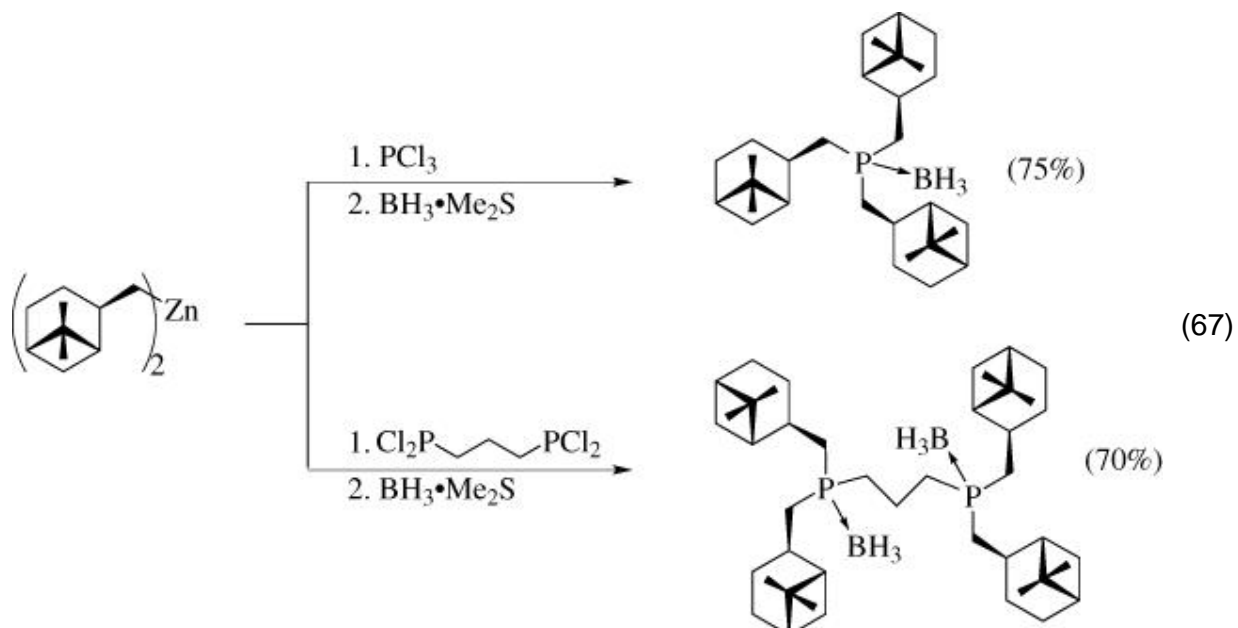


one atmosphere of carbon monoxide undergoes an insertion reaction producing an acylmetallate that can be trapped with the Meerwein reagent to furnish functionalized Fischer-carbene **77** (Eq. 65). (308) Interestingly, immonium salt **78** reacts with organozinc derivatives leading to diallylamines of type **79**, which can be readily deprotected (Eq. 66). (309)

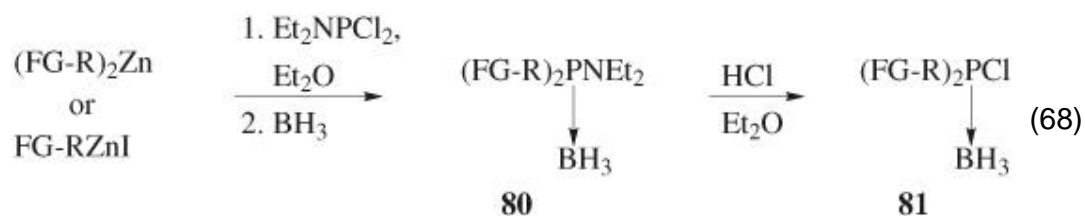


The relatively polar chlorodiorganophosphines react with organozinc halides and diorganozincs to furnish polyfunctional phosphines in high yield. (310) The preparation of chiral phosphines is possible starting from terpenes. The hydroboration of β -pinene with $\text{BH}_3 \cdot \text{Me}_2\text{S}$ gives tris(myrtanyl)borane, which after a boron-zinc exchange with Et_2Zn gives bis(myrtanyl)zinc in quantitative yield. Its reaction with chlorophosphines provides chiral phosphines of

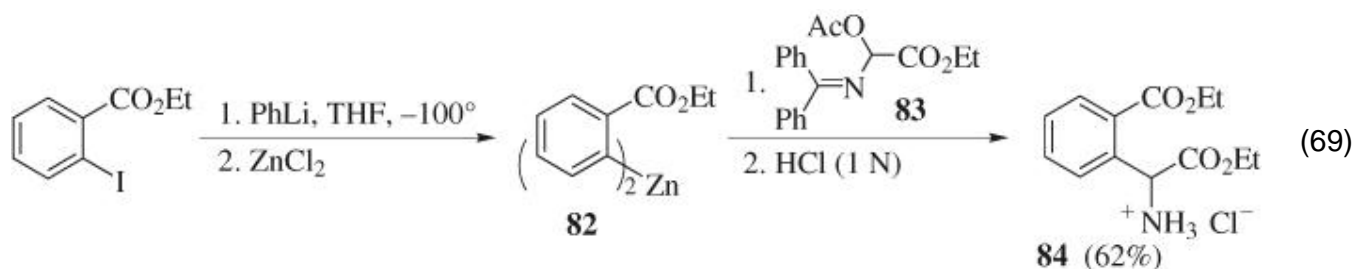
potential interest as ligands for catalytic asymmetric reactions (Eq. 67). (311)
 The preparation of



polyfunctional chlorophosphines **81** can be achieved by the reaction of Et_2NPCl_2 with organozinc compounds. After protection with BH_3 , the corresponding aminophosphine-borane complexes **80** are obtained. Treatment with HCl in ether provides the borane-protected chlorophosphine **81** (Eq. 68). (312)



The reactivity of organozinc compounds can be increased by using polar solvents. Thus, in DMF functionalized diarylzincs **82** add to the reactive Schiff base **83** leading to the amino acid derivative **84** (Eq. 69). (313) Similarly, in NMP-THF



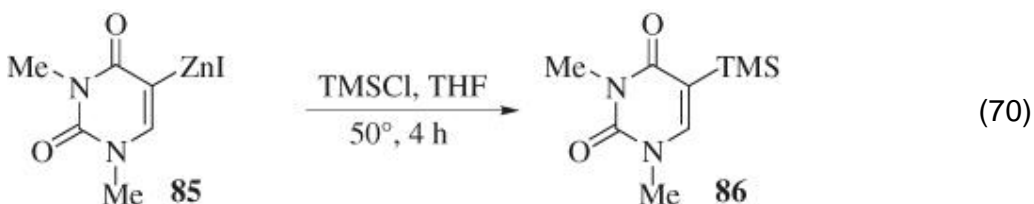
mixtures and in the presence of TMSCl, diorganozincs efficiently add to enones, unsaturated nitriles, and nitroolefins to afford the desired Michael adducts. (314-314a)

3.9. Reactions Mediated by Copper(I) Salts

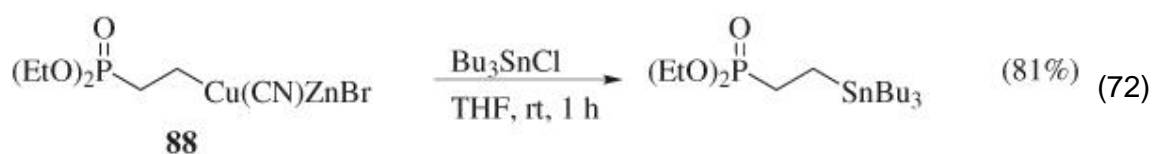
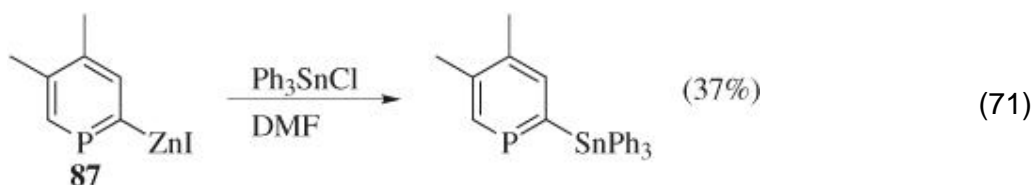
For most synthetic applications of organozincs, transmetalation to a more reactive organometallic species is required. Of special interest for synthetic applications is the transmetalation of organozinc reagents to the mixed copper-zinc reagents tentatively represented as $\text{RCu}(\text{CN})\text{ZnX}$. These reagents are obtained by treating either an organozinc halide or a diorganozinc with the THF-soluble complex of copper(I) cyanide and lithium chloride ($\text{CuCN} \cdot 2\text{LiCl}$). (47) The resulting copper species display a similar, but somewhat reduced, reactivity compared with organocopper compounds prepared from magnesium or lithium organometallics. (315-318) Only the opening of epoxides cannot be performed with copper-zinc reagents. All other reactions that lithium and magnesium cuprates normally undergo can be performed with zinc-copper organometallics. The structure of these mixed zinc-copper reagents is not known, but EXAFS spectroscopy indicates that the cyanide ligand is coordinated to the copper center. (319) They display high thermal stability and can be heated in solvents such as 1,2-dimethoxyethane or DMPU at 60–85° for several hours without appreciable decomposition. (14)

3.9.1. Substitution Reactions

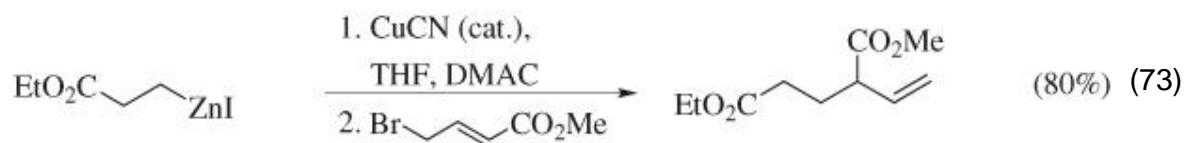
Normally, zinc- or zinc-copper organometallics do not react with organosilicon halides such as TMSCl efficiently. However under certain conditions, the reaction proceeds, as in the case of the zincated uracil derivative **85**, which gives the corresponding silylated heterocycle **86** at 50° (Eq. 70). (320) Triorganotin halides react more readily, and a stannylated phosphabenzene



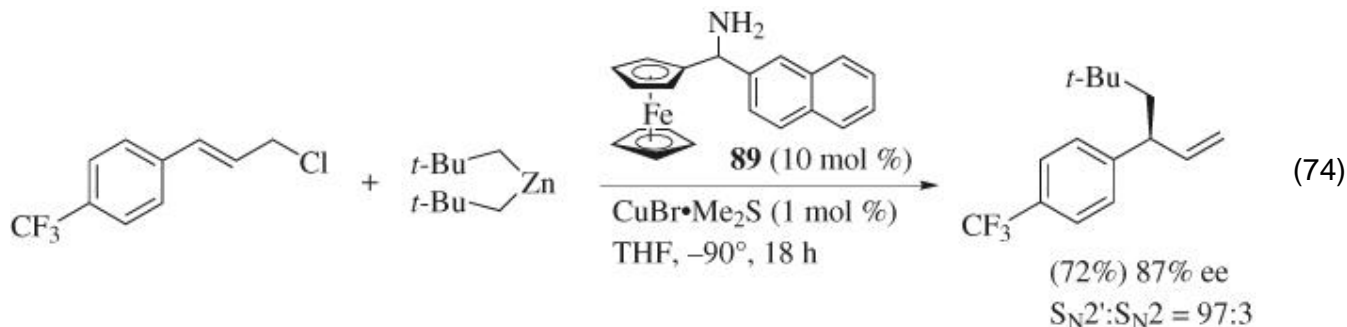
has been obtained by the direct reaction of triphenylchlorostannane with the heteroaromatic zinc derivative **87** (Eq. 71). (321) The copper-zinc reagents **88** are stannylated much more readily and afford polyfunctional stannanes in excellent yields (Eq. 72; Table II). (90)



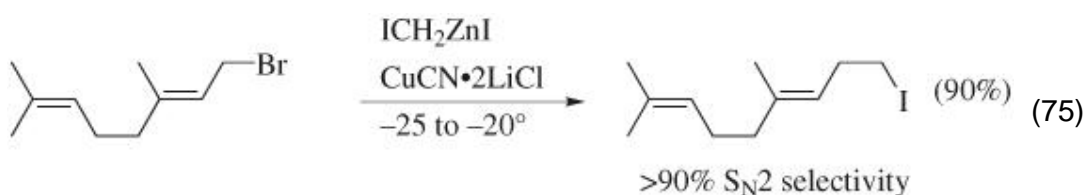
Allylation of copper-zinc organometallics with allylic chlorides, bromides, or phosphates proceeds under mild conditions and usually in excellent yield. The substitution reactions show a very high S_N2 selectivity (120, 139-141, 322-324) (Eq. 73 and Tables III-V). (141)



In the presence of chiral ferrocenylamine **89** or related amines, an enantioselective substitution reaction can be performed with an enantioselectivity up to 98% ee (Eq. 74). (325-325a) In contrast, in the presence of nickel(0) or palladium(0) complexes, the S_N2 substitution product is preferentially obtained. (75, 324)

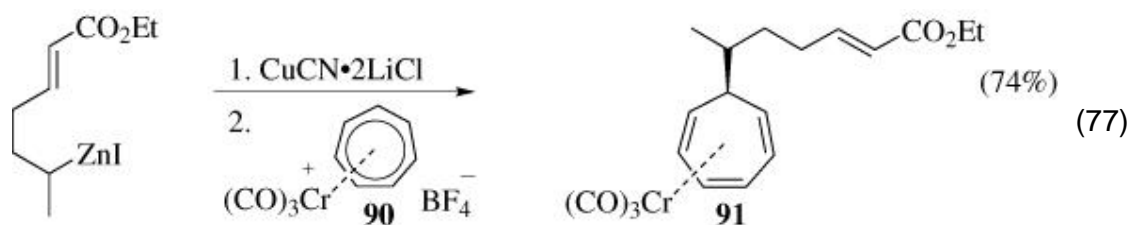
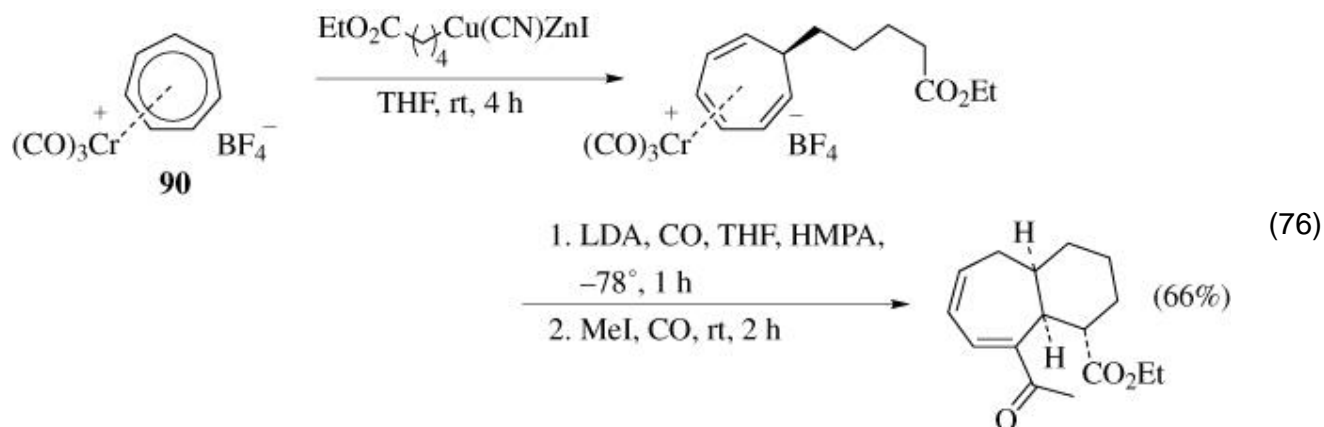


Similarly, the in situ-generated copper carbenoid iodomethylcopper reacts with geranyl bromide with high S_N2 selectivity (Eq. 75). (58) The allylation procedure can be applied to the preparation of isocarbocyclins. (324) The reaction of copper-zinc reagents with propargylic halides or tosylates provides allenes (Table VI). (94, 141)

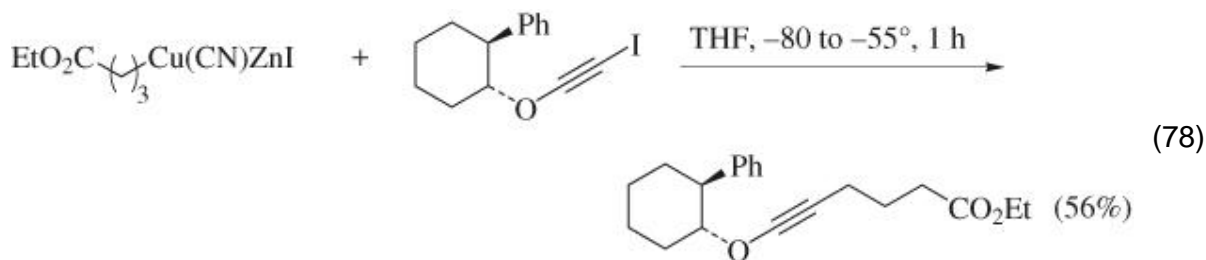


A range of cationic unsaturated metal complexes such as pentadienyliron and pentadienylmolybdenum complexes readily add functionalized zinc-copper reagents to afford the corresponding cyclohexadienyl metal complexes (Table VII). (68-73) This reaction can be used for the construction of fused bicyclic ring systems (Eq. 76). (73)

Alkylation of tropylium ion chromium carbonyl complex **90** with a functionalized alkylzinc iodide furnishes chromium complex **91**, which is a key intermediate in a cedrene synthesis (Eq. 77). (326)

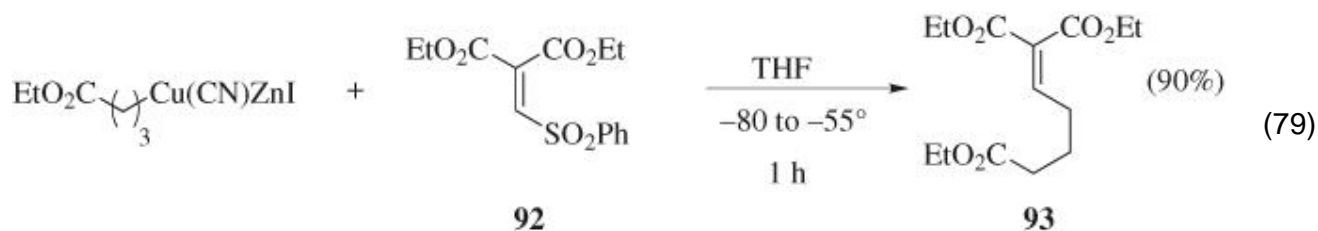


The cross-coupling reaction with unactivated alkynyl, alkenyl or alkyl iodides occurs under well-defined experimental conditions (Table VIII). Thus, the highly reactive alkynyl iodides and bromides react with copper-zinc organometallics at -60° to provide polyfunctional alkynes (**55**) (Table IX and Eq. 78). (327) Performing this coupling at higher temperatures with 1-iodoalkynes leads to the formation of

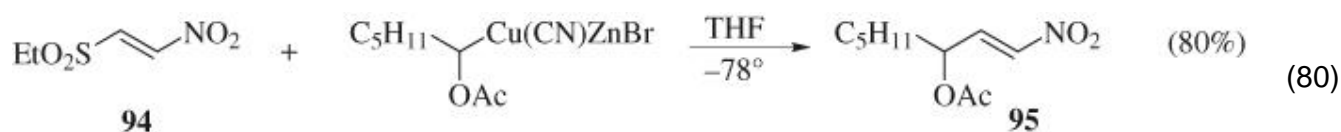


copper acetylides as byproducts (iodine-copper exchange reaction). (**55**) Cross-coupling with alkenyl iodides occurs readily if the alkenyl halide bears an electron-withdrawing substituent (such as nitro, ester, or keto) in the β position. In these cases, the substitution reaction certainly occurs via an addition-elimination mechanism. Thus, the addition of zinc-copper reagents to diethyl [(phenylsulfonyl)methylene]malonate (**92**) gives β -substituted

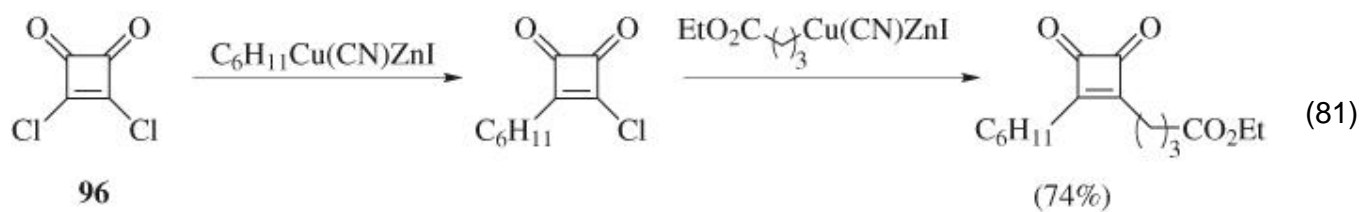
alkylidenemalonates **93** (Eq. 79). (57, 328) These products do not react with the excess zinc-copper organometallics under the mild reaction conditions used. (57, 328)



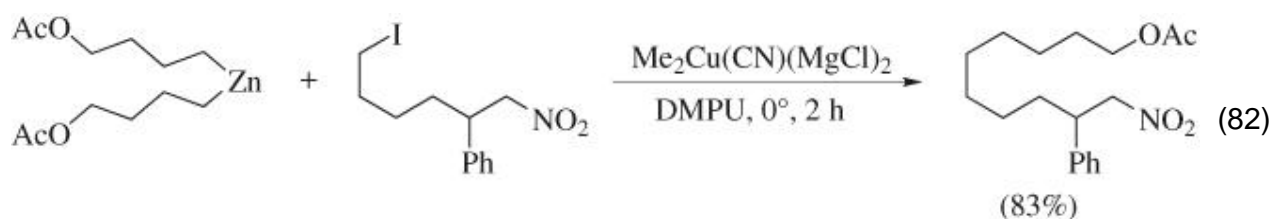
Similarly, the addition of α -alkoxyalkyl zinc-copper derivatives to (*E*)-2-(ethylsulfonyl)-1-nitroethylene (**94**) provides a simple access to *trans*- γ -acetoxynitroalkenes **95** (Eq. 80). (60) A range of other polyfunctional pure (*E*)-nitroalkenes can be prepared by this method. (63, 74) The addition of β -iodoenones proceeds particularly well and furnishes substituted enones (Table VIII). (209)



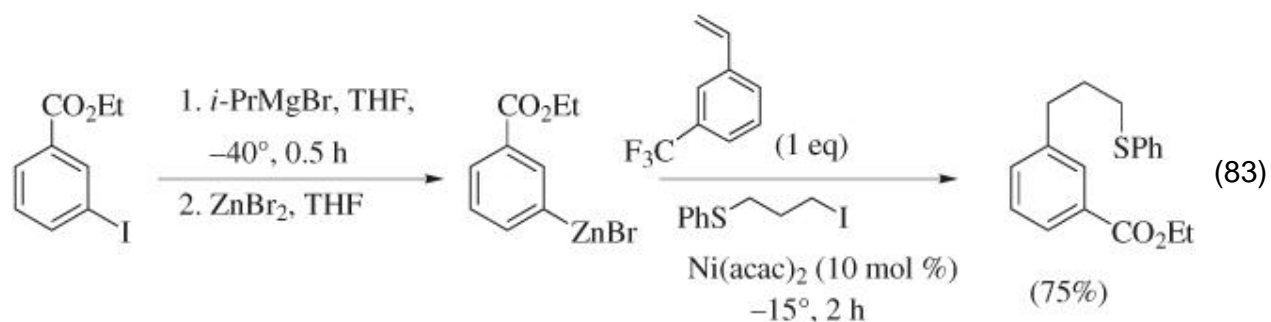
Squaric acid derivatives, which are of interest for pharmaceutical applications and for the preparation of new materials, can be obtained by a double addition-elimination of zinc-copper compounds to 3,4-dichlorocyclobutene-1,2-dione (**96**). If the first organometallic is sufficiently bulky, a selective addition of two different zinc-copper reagents can be performed (Eq. 81). (329)



The coupling reaction with unactivated alkenyl iodides requires harsh reaction conditions. (330) However, the cross-coupling reaction occurs with retention of configuration of the alkenyl moiety and allows the preparation of polyfunctional alkenes (Table X). (330) Alkylation reactions with primary alkyl halides and benzylic halides proceed well with diorganozincs treated with one equivalent of a magnesium dimethylcyanocuprate [Me₂Cu(CN)(MgCl)₂] in DMPU. The alkylation tolerates a range of functionalities (ester, cyanide, halide, nitroalkane), and transfer of the methyl group is not observed under these reaction conditions (Eq. 82). (331)

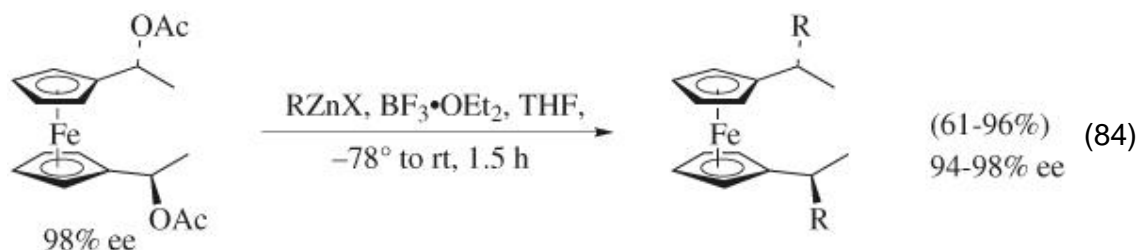


Recently, a promising nickel-catalyzed cross-coupling reaction between dialkylzincs and primary alkyl halides was reported. (332, 333) In the presence of *m*-trifluoromethylstyrene as promoter, dialkylzincs undergo a smooth cross-coupling reaction with functionalized primary alkyl iodides. (332) This cross-coupling allows the coupling of functionalized arylzincs with functionalized primary alkyl iodides, leading to polyfunctional aromatic compounds (Eq. 83). (230) The scope of the reaction appears to be broad.

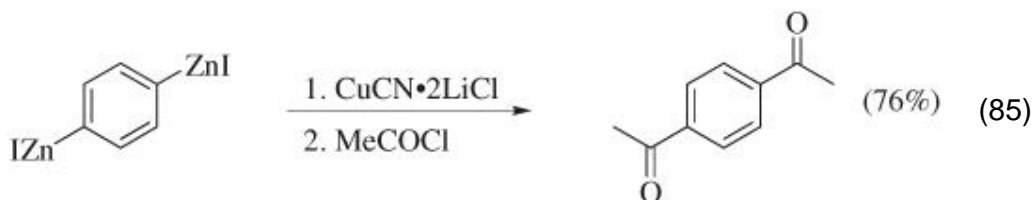


The substitution of ferrocenyl acetates with various alkylzinc halides or

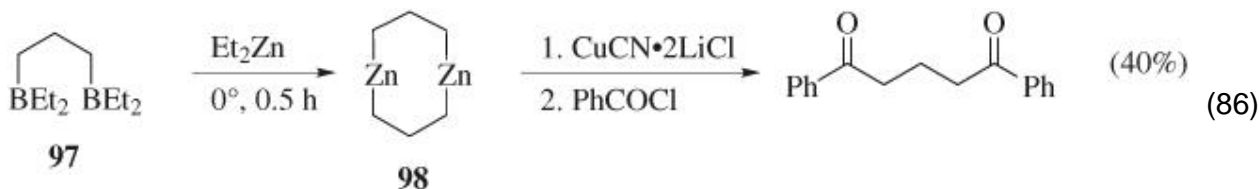
allylzinc bromides in the presence of $\text{BF}_3 \cdot \text{OEt}_2$ proceeds with high retention of configuration, furnishing polyfunctional ferrocenes in optically pure or highly enriched form. These compounds can be readily converted into useful chiral ligands for asymmetric catalysis (Eq. 84). (334-336)



The uncatalyzed reaction of acid chlorides with organozincs is sluggish and inefficient. In the presence of catalytic (10 mol %) or stoichiometric amounts of copper cyanide-lithium halide complex in THF (-20 to 0° , 6–12 hours), a clean reaction occurs to produce ketones in excellent yields (Table XI). The acylation reaction can be applied to dizinc organometallics (Eq. 85). (120)

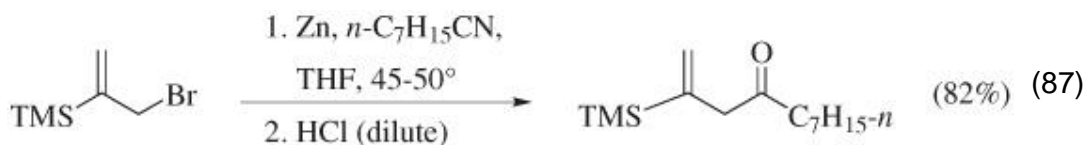


Especially interesting is the benzylation of the 1,3-dizincapropane **98** obtained by boron-zinc exchange from the 1,3-diborane **97** (Eq. 86). (337, 338)
Allylic



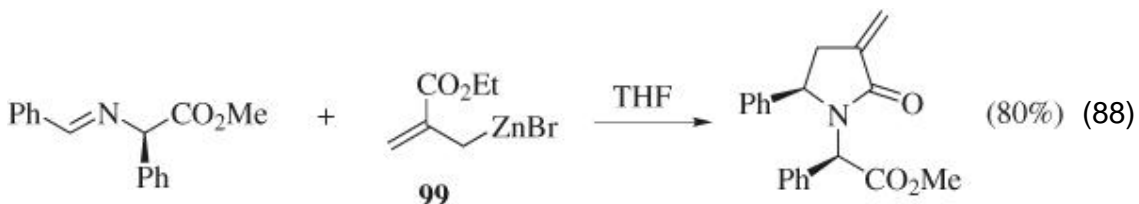
zinc reagents react readily with acid chlorides and anhydrides; however, a double addition of the allylic moiety usually occurs, (45, 339) leading to tertiary

alcohols. The double addition can be avoided by using a nitrile as the acylating agent under Barbier conditions (340-343) (Eq. 87). (341)

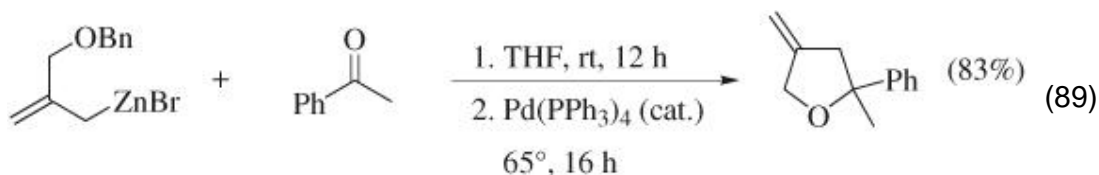


3.9.2. Addition Reactions

Allylic, and to some extent propargylic, organozinc reagents add to aldehydes and ketones (Table XII). (344, 345) Thus, 2-carbomethoxyallylzinc bromide (99), (346, 347) which is readily prepared by reaction of ethyl α -(bromomethyl)acrylate (348, 349) with zinc powder (30 mesh) in THF (17–20°, 0.5 hour), reacts with a variety of aldehydes and imines to provide a direct entry to α -methylene- γ -butyrolactones and lactams. (346) Chiral lactams can be prepared by using amino acid derived imines (350, 351) (Eq. 88). (351) Unsymmetrically substituted

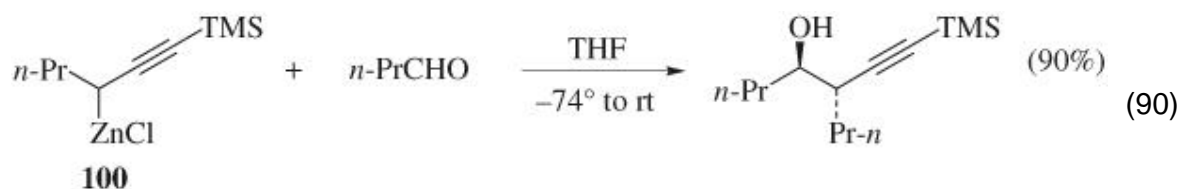


allylic zinc reagents react with carbonyl compounds at the more substituted end of the allylic system. (344, 345, 347) The use of allylic zinc reagents functionalized in position 2 allows for the preparation of various carbo- and heterocycles (352-359) (Eq. 89). (355)

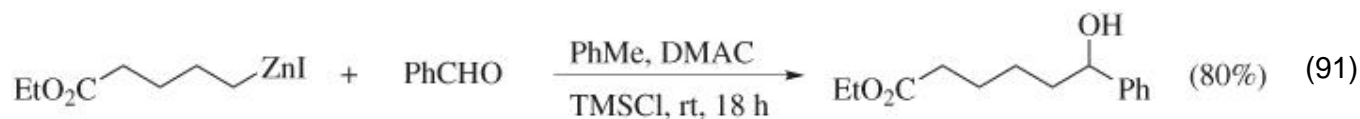


The addition of propargylic zinc derivatives to aldehydes or ketones often provides a mixture of homopropargylic and allenic alcohols. (360-364) With

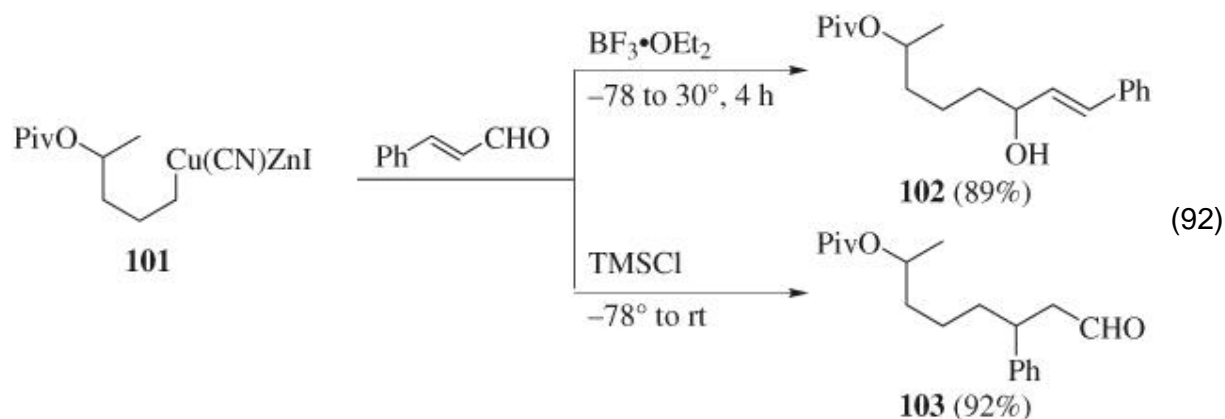
silylated propargylic zinc reagents **100**, only *anti*-homopropargylic alcohols are obtained (Eq. 90). (365) Interestingly, alkenylzinc halides seem to possess high reactivity, and a direct addition of ethenylzinc chloride to a protected α -aminoaldehyde has been reported. (366)



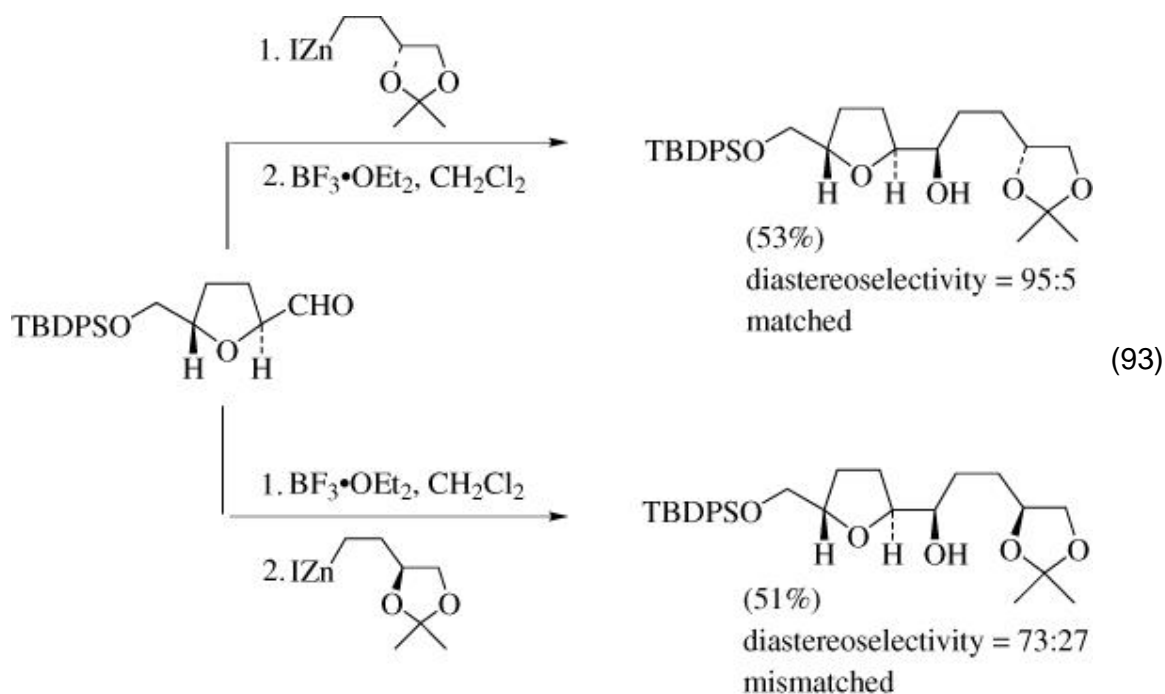
Alkylzinc derivatives do not easily add to aldehydes or ketones. (2) However, in the presence of Lewis acids like titanium alkoxides, (135, 367) TMSCl, (368) or $\text{BF}_3 \cdot \text{OEt}_2$, (54) the reaction occurs smoothly (Table XIII and Eq. 91). (368)



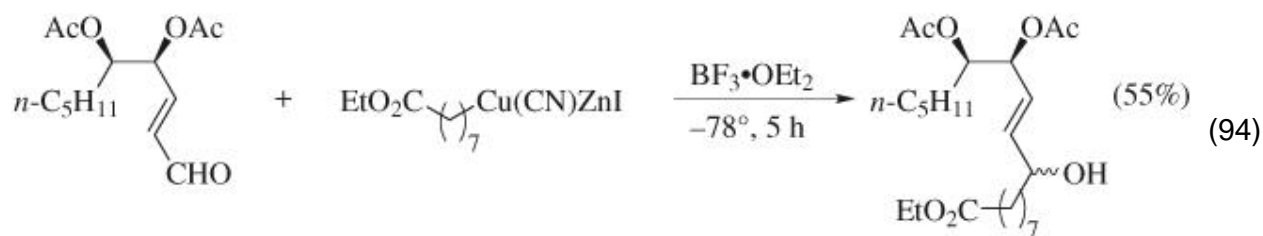
By using either TMSCl or $\text{BF}_3 \cdot \text{OEt}_2$, it is possible to direct the reaction with α , β -unsaturated aldehydes toward either the 1,4- or the 1,2-adduct. Thus the treatment of cinnamaldehyde with the functionalized zinc-copper reagent **101** in the presence of $\text{BF}_3 \cdot \text{OEt}_2$ produces only the allylic alcohol **102**. Conversely, performing the same reaction in the presence of TMSCl produces only the Michael adduct **103** (Eq. 92). (54)



Whereas unsaturated aldehydes react directly with alkylzinc halides in the presence of $\text{BF}_3 \cdot \text{OEt}_2$, the less reactive aliphatic aldehydes require transmetalation to the corresponding zinc-copper species. In a noncomplexing solvent such as CH_2Cl_2 , alkylzinc iodides react directly with polyfunctional aldehydes leading to alcohols with excellent diastereoselectivity in the “matched” case (Eq. 93). (369)

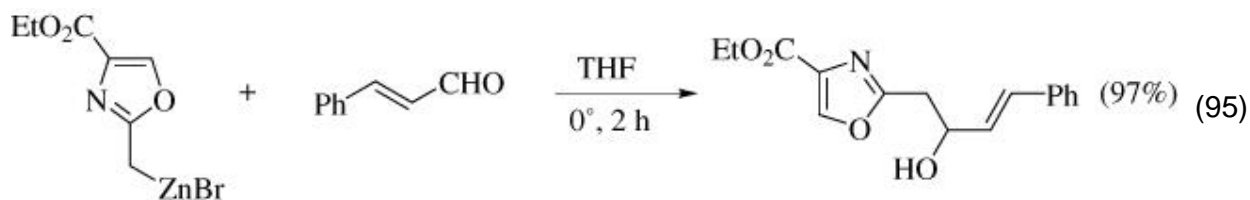


Like organotitanium reagents, (370) the addition of functionalized zinc-copper reagents to α -chiral aldehydes proceeds with good Cram selectivity. (54) Polyoxygenated metabolites of unsaturated fatty acids have been prepared by the addition of functionalized zinc-copper reagents in the presence of $\text{BF}_3 \cdot \text{OEt}_2$ (Eq. 94). (371)

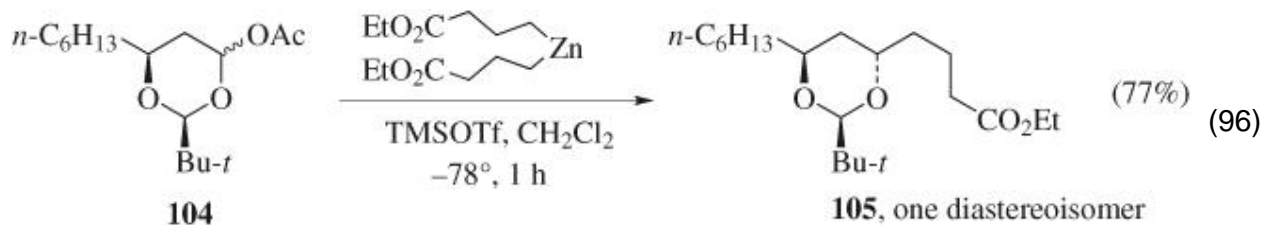


Functionalized 2-bromomethyloxazoles insert zinc under the conditions typical for benzylic halides (THF , 0°), and the resulting zinc reagents react with

aldehydes and ketones in the absence of a Lewis acid to provide a range of polyfunctional oxazoles in excellent yields (Eq. 95). (372)



Dialkylzincs undergo formal substitution with 4-acetoxy-6-alkyl-1,3-dioxanes **104** in the presence of trimethylsilyl triflate (TMSOTf), leading to the corresponding *trans*-4,6-dialkyl-1,3-dioxanes **105** with excellent diastereoselectivity (Eq. 96). (373, 374)

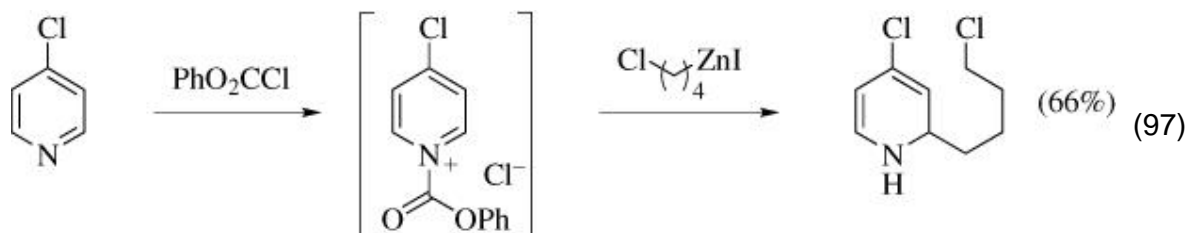


With Barbier conditions and sonication, polyfluorinated alkyl iodides can be added to chiral aryl aldehyde-chromium complexes, leading to perfluoroalkyl arylcarbinols in 30–66% ee after removal of the tricarbonylchromium moiety. (374a)

Since the direct addition of dialkylzincs to aldehydes is rather slow, use of a chiral catalyst in many cases allows the preparation of chiral secondary alcohols. This strategy has been widely developed with mostly diethylzinc or higher dialkylzincs. (163, 375, 376) An important extension in which a chiral titanium catalyst is used allows the catalytic enantioselective addition of functionalized dialkylzincs to aldehydes. This type of reaction is discussed in detail later.

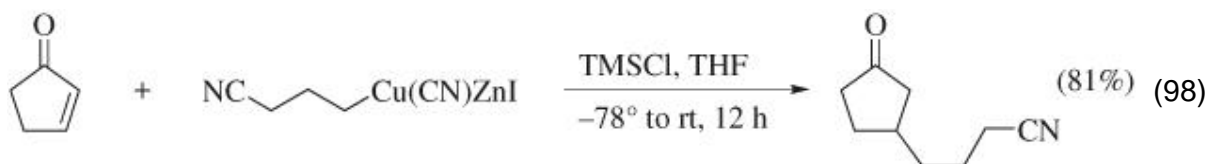
Ketones, except for some aryl ketones, do not add alkylzinc derivatives even in the presence of a Lewis acid catalyst. Similarly, nonactivated imines do not react with alkylzinc compounds. However, 1,2-diimines add dialkylzincs to give

alkylated amine derivatives. This allows the preparation of fused heterocycles. (377-379) Activated imines bearing an electron-withdrawing group at nitrogen are more reactive, and *N*-diphenylphosphinoylimines add dialkylzincs in the presence of a chiral β -amino alcohol providing, after acidic hydrolysis, chiral amines with excellent enantioselectivity (75–98% ee). (339, 380, 381) The in situ activation of imines by formation of an acyliminium salt has been used to activate pyridines and related heterocycles (382-386) (Eq. 97 (382)). Organozinc derivatives have also been added

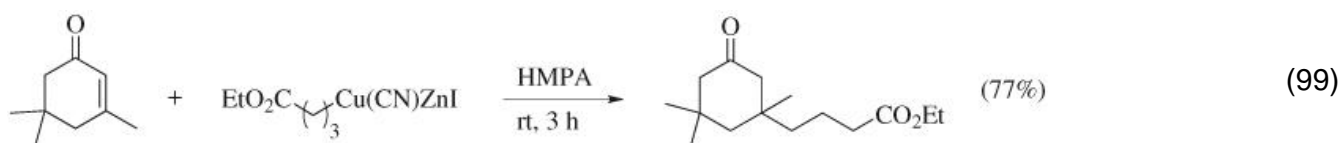


to iminium ions generated from α -aminothioethers, (387-390) cyclic γ -alkoxyenamines, (391) or α -cyanodihydropyridines. (392) Dialkylzincs add to imines in the presence of titanium tetrachloride in satisfactory yields. (393)

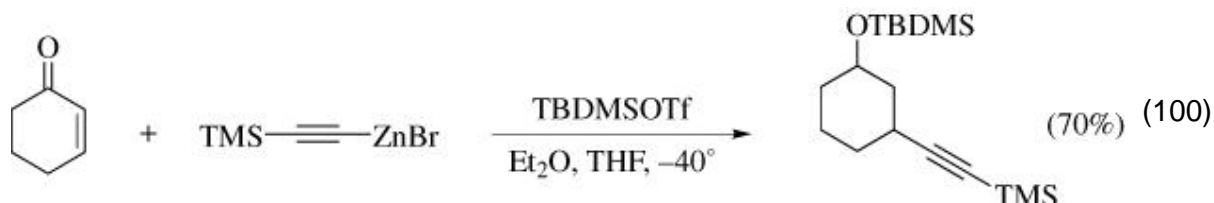
One of the most important synthetic properties of classical organocopper reagents is their ability to undergo 1,4-addition reactions with high regioselectivity. (315-320, 394, 395) In the same manner, copper-zinc organometallics prepared by the reaction of an organozinc halide or a diorganozinc with the THF-soluble complex copper cyanide-lithium chloride (47) react with β -monosubstituted enones in the presence of TMSCl (396-407) to furnish the Michael adducts in excellent yields (Eq. 98). (47) The addition to β -disubstituted enones under these conditions does not



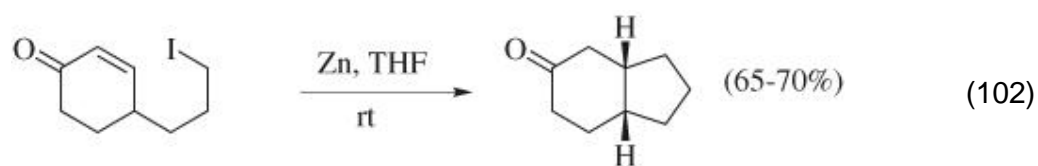
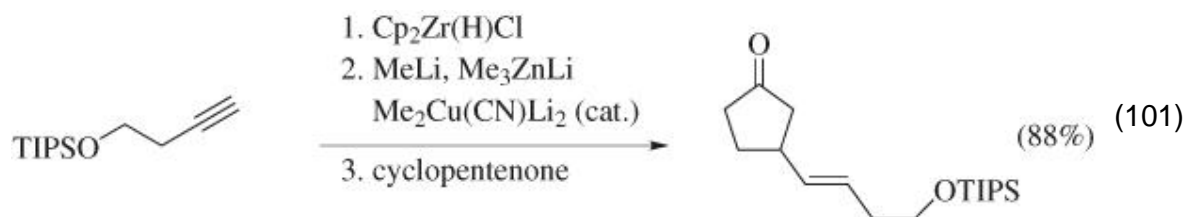
proceed well. However, by performing the reaction in HMPA, addition to β -disubstituted enones or to methyl acrylate occurs with satisfactory yields (Eq. 99). (142)



A Lewis-acid activation with $\text{BF}_3 \cdot \text{OEt}_2$ allows the addition of functionalized zinc-copper reagents to β -disubstituted enones. (52) Interestingly, trialkylsilyl triflates promote the conjugate addition of alkynylzinc compounds to α, β -unsaturated enones, affording acetylenic silyl enol esters (Eq. 100). (408) Polyfunctional

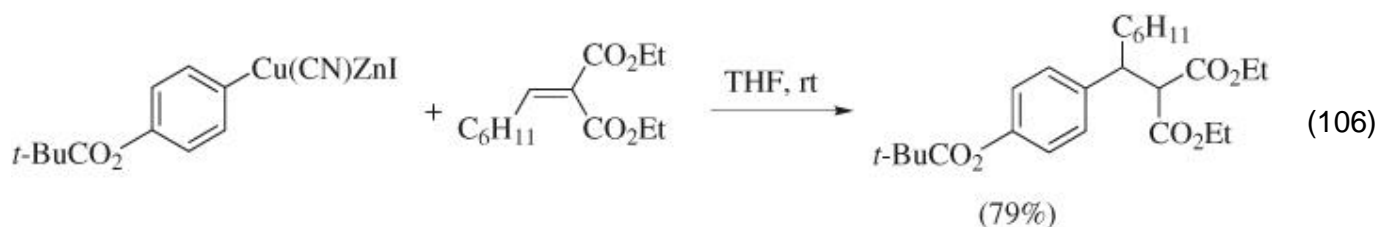


alkenylzincates can be generated in situ from alkenylzirconium derivatives and added to enones in excellent overall yields (Eq. 101). (409) Intramolecular Michael additions have also been described, (65, 270) some under Barbier conditions

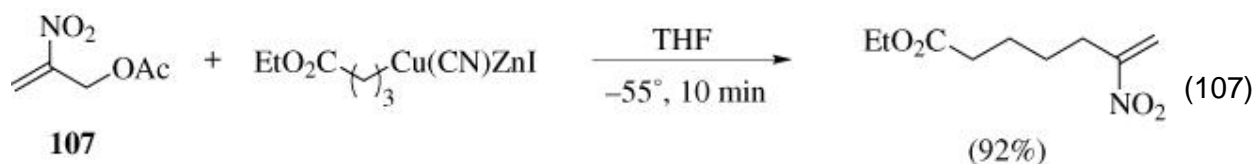


(Eq. 102). (89) Mechanistic studies of intramolecular addition reactions performed under Barbier conditions show that a small part of the cyclization product is formed through a radical mechanism, whereas the predominant reaction pathway proceeds via an organometallic intermediate. (89) Arylzinc halides generated by electrochemical reduction from the corresponding aromatic chloride or bromide using a sacrificial zinc electrode, after transmetalation with the copper bromidemethyl sulfide complex, undergo Michael additions with enones (Eq. 103). (156) The conjugate addition of functionalized zinc-copper reagents has been successfully applied to the synthesis of prostaglandins and related molecules (Eq. 104). (410-412)

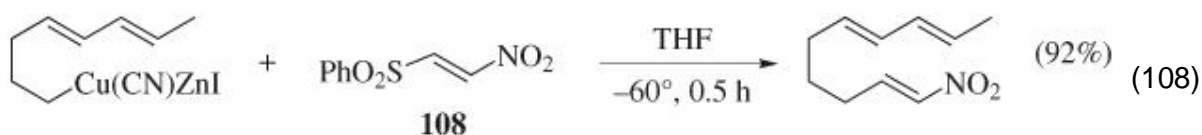
Nickel(II) salts catalyze the 1,4-addition of diorganozincs to enones. (415) However, the scope of the reaction is narrow compared to the corresponding copper(I) mediated reactions. In the presence of chiral ligands, both the nickel(II)- (416-427) and copper(I)- (428, 429) catalyzed reactions lead to optically active conjugate addition products. (416-429) The addition to α , β -unsaturated esters is difficult. However, zinc-copper organometallics readily add to alkylidenemalonates (59, 60, 210) or related doubly activated Michael acceptors (59, 60) in high yields (Eq. 106). (210)



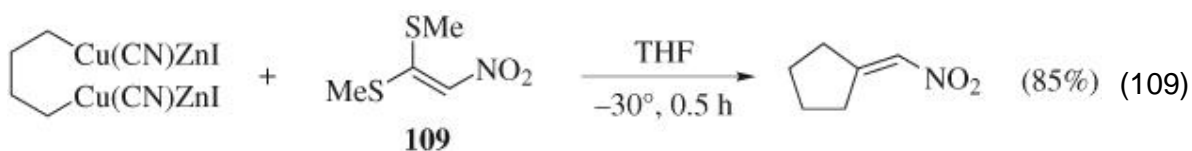
Nitroolefins undergo conjugate addition of a number of nucleophiles to give functionalized nitroalkanes, which are important intermediates and can be readily converted to amines by reduction or to carbonyl compounds by a Nef reaction. (430-434) The addition of organometallic nucleophiles to nitroolefins is less straightforward and often requires carefully chosen reaction conditions in order to avoid multiple additions of the metallic nitronate to the remaining nitroolefin. (435-437) Thus, addition of lithium or magnesium cuprates to nitrostyrene does not occur cleanly. (438-440) In contrast, copper reagents derived from functionalized organozinc halides (56, 63, 74) or diorganozincs (64) add to nitroolefins in high yields. Nitroolefins with a leaving group in the β -position, such as 1-acetoxy-2-nitro-2-propene (107), are especially reactive, and polyfunctional 2-nitroalkenes can be prepared by this method (Eq. 107). (56, 74) A similar high reactivity is observed



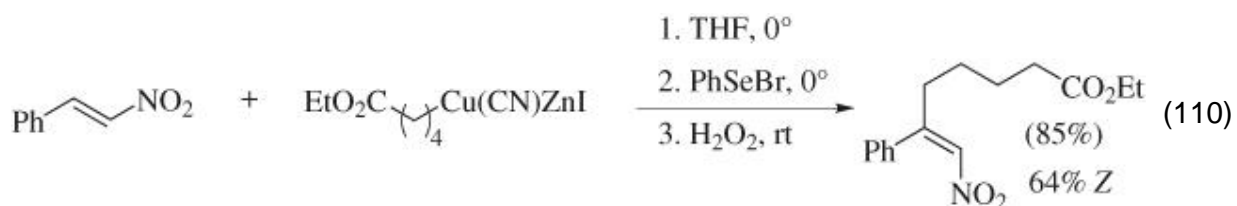
with (2-phenylsulfonyl)nitroethylene (108) and related molecules. They react with zinc-copper reagents at -60° providing pure (*E*)-nitroolefins via an addition-elimination mechanism (Eq. 108). (63, 74) The addition to



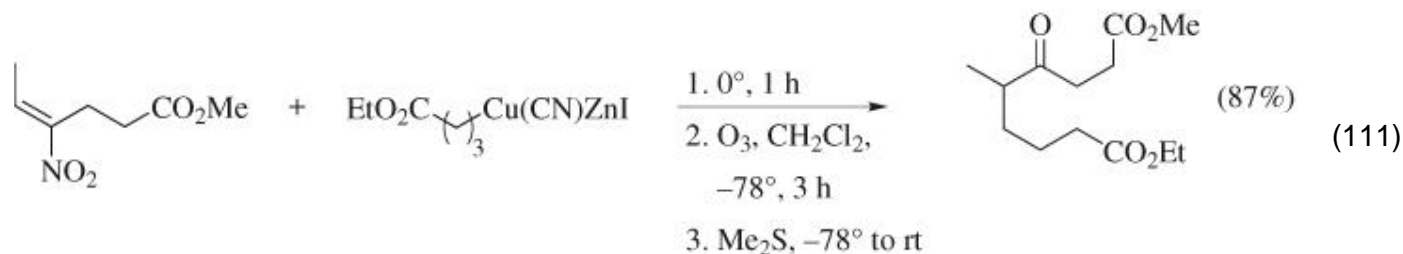
2,2-bis(methylthio)-1-nitroethylene (**109**) gives β -disubstituted nitroolefins, (**74**) which are not readily prepared by a nitroaldol reaction since the reaction of nitroalkanes with ketones is reversible. By using a dimetallic zinc-copper species, *exo*-(methylene)cycloalkanes are obtained (Eq. **109**). (**74**) An alternative preparation of



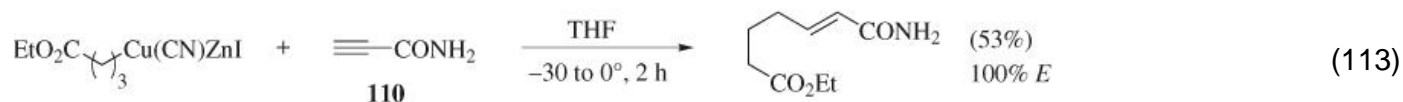
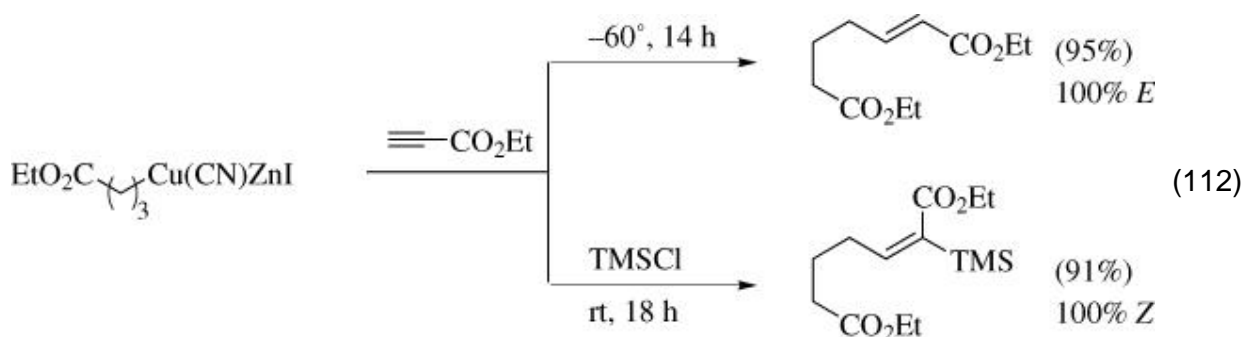
β -disubstituted nitroolefins can be performed by adding zinc-copper reagents to nitroolefins and quenching the resulting zinc nitronates with phenylselenyl bromide. The resulting nitroselenides can be oxidized with hydrogen peroxide to afford *E/Z* mixtures of β -disubstituted nitroalkenes (Table **XVI** and Eq. **110**). (**441**)



Aliphatic nitroolefins with no additional activating groups react with zinc-copper organometallics at -20° , whereas nitrostyrene derivatives or functionalized nitroolefins require several hours at 0° for complete addition. (**56**, **74**) The intermediate zinc nitronates can be directly submitted to an oxidative Nef reaction with ozone to afford polyfunctional ketones in good overall yields (Eq. **111**). (**74**)

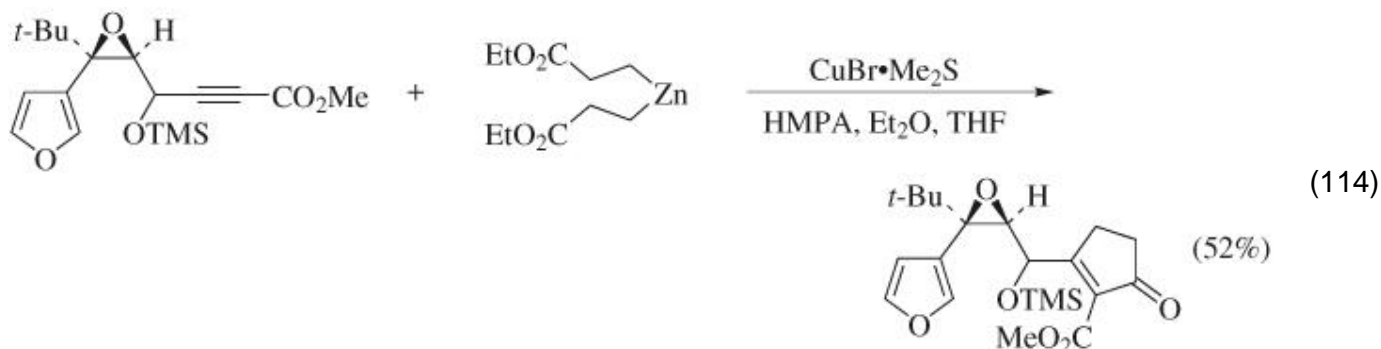


The *syn* addition of zinc-copper organometallics to acetylenic esters is an excellent method for the preparation of α , β -unsaturated esters of defined stereochemistry (Table XVII). Thus, the addition of polyfunctional zinc-copper reagents to ethyl propiolate at -60 to -50° produces the *syn* addition product after a low temperature protonation. By allowing the reaction mixture to warm up in the presence of excess TMSCl, an equilibration occurs leading to a C-silylated unsaturated ester (Eq. 112). (55) Dimethyl acetylenedicarboxylate (78, 140) and propiolamide (110) react in a similar way. The acidic hydrogens of the amido group do not interfere with the addition reaction (Eq. 113). (78)

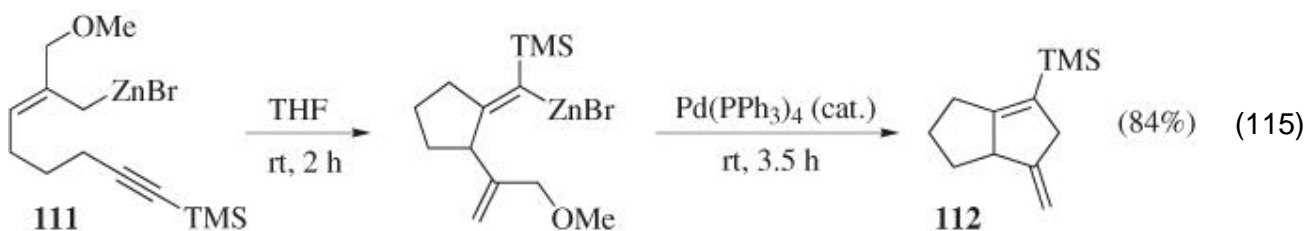


With other acetylenic esters bearing alkyl substituents in the β position, the addition occurs less readily and requires increasing the temperature to -30° or -20° , which leads to partial isomerization of the intermediate alkenyl organometallic and to a mixture of (*E*) and (*Z*)- α , β -unsaturated esters. (55) The addition of bis-(2-carboethoxyethyl)zinc to acetylenic esters in the presence

of copper(I) bromide-methyl sulfide complex and in a solvent mixture containing HMPA produces 2-carboalkoxycyclopentenone derivatives. (442-444) This efficient formal [3 + 2] cycloaddition has been used to prepare a precursor of (\pm)-bilobalide (Eq. 114). (444)



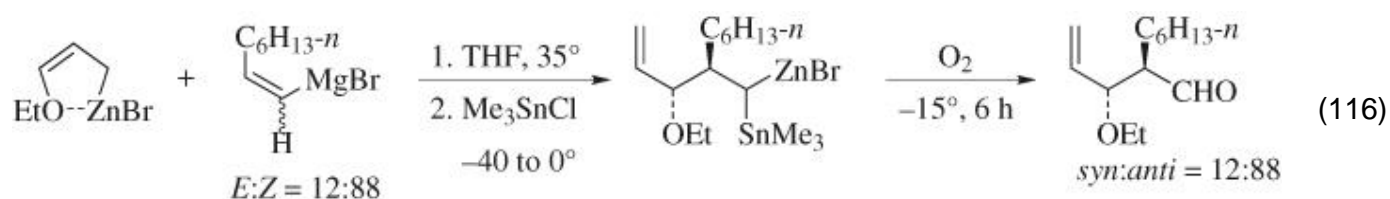
The addition of organometallics to unactivated alkynes and alkenes represents a unique method for stereospecifically preparing (*E*)- or (*Z*)-trisubstituted alkenes, (445, 446) although only a few types of zinc derivatives are reactive enough to add to alkynes. Thus, allylic zinc halides add to a range of alkynes. (445, 446) The intramolecular addition of the functionalized allylic zinc bromide **111** to a triple bond produces the bicyclic diene **112** after a palladium(0)-catalyzed allylation (Eq. 115). (447) The addition of allylic zinc halides to 1-trimethylsilylalkynes, (448, 449)



α , β -unsaturated acetals, (450) and cyclopropenes (451) has been reported. Alkylzinc derivatives do not add readily to unactivated alkenes. (445) However, dialkylzincs and alkylzinc halides can be added to terminal alkynes with moderate regioselectivity and to internal alkynes in the presence of diiodozirconocene. (452) The addition of di-*tert*-butylzinc to terminal alkenes (453-456) and phenylacetylene (454) occurs under harsh conditions.

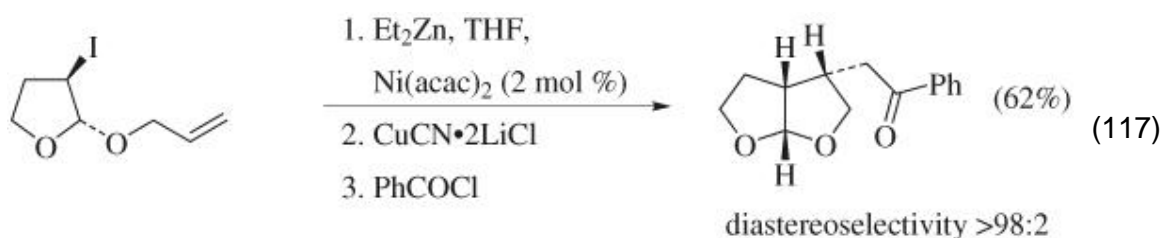
Alkynes or functionalized allylic zinc reagents have been added to alkenylmagnesium derivatives, (457-466) and this reaction has been applied to

the preparation of aldol products obtained after oxidation of the intermediate α -trialkylstannylalkylzinc halides with oxygen (Eq. 116). (467)

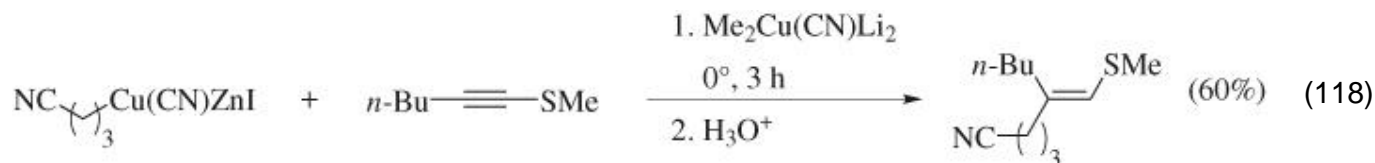


The intramolecular carbozincation of some primary and secondary unsaturated iodides has been performed by generating the zinc reagent using Rieke-zinc (5, 127-132) or diethylzinc, (64) leading to functionalized cyclopentane derivatives with modest diastereoselectivity. (468, 469) In contrast, performing the carbozincation with diethylzinc in the presence of a catalytic amount of a palladium(II) or nickel(II) (165-168) complex leads to cyclopentylmethyl derivatives with high diastereoselectivity, allowing stereochemical control of three adjacent chiral centers (Eq. 28). (166)

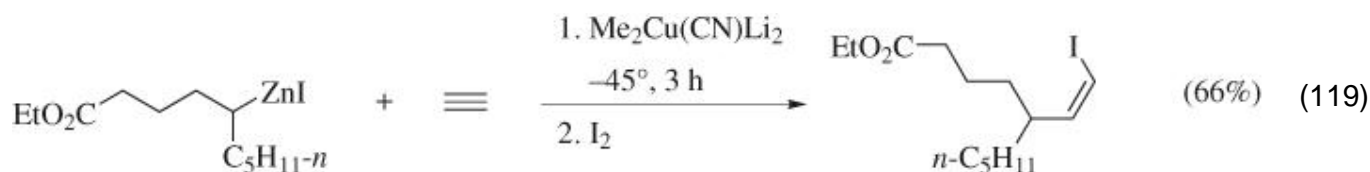
The reaction proceeds via a radical mechanism: the palladium(0) or nickel(0) complex converts the alkyl iodide to an alkyl radical which undergoes ring closure, leading to a cyclopentylmethyl radical. It is trapped by a palladium(I) or nickel(I) halide, leading to a cyclopentylmethyl palladium (or nickel)(II) halide, which undergoes transmetalation with diethylzinc to give a cyclopentylmethylzinc derivative. The reaction can be applied to a variety of substrates (Table XVIII) and provides a new highly diastereoselective preparation of fused bicyclic tetrahydrofuran derivatives (Eq. 117). (470)



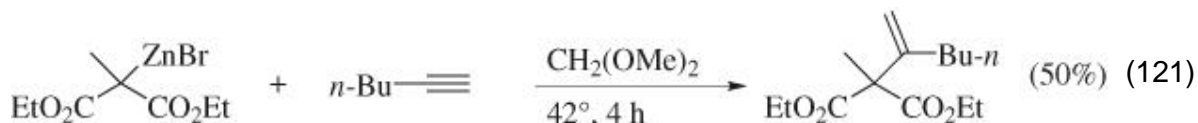
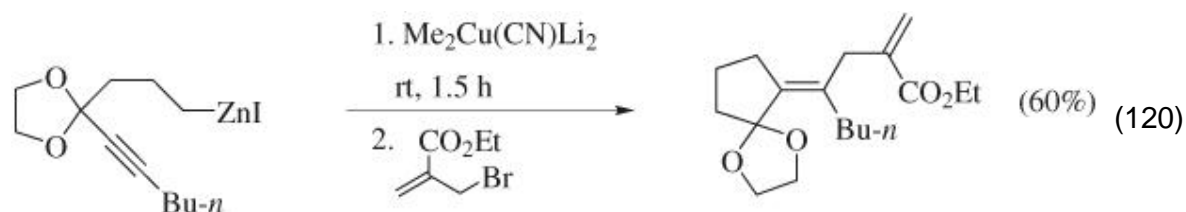
Organozinc derivatives treated with lithium dimethylcyanocuprate add to 1-alkylthioalkynes (*syn* addition), leading to tri- or tetrasubstituted olefins after trapping the intermediate alkenylcopper with an electrophile (Eq. 118). (471)



Unactivated alkynes do not add primary zinc-copper organometallics under these conditions. However, the addition of secondary zinc-copper compounds proceeds easily (Eq. 119). (471) An intramolecular carbometallation is more facile and allows



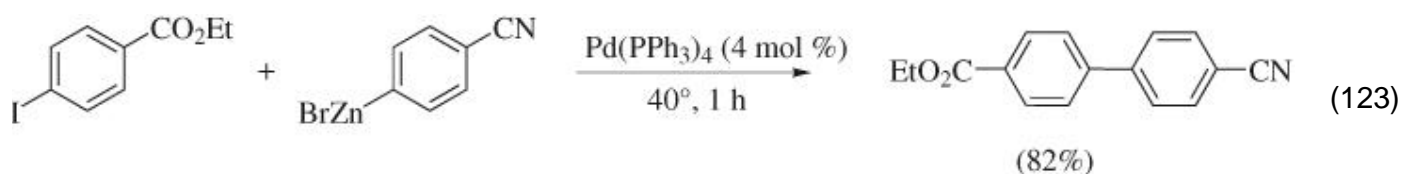
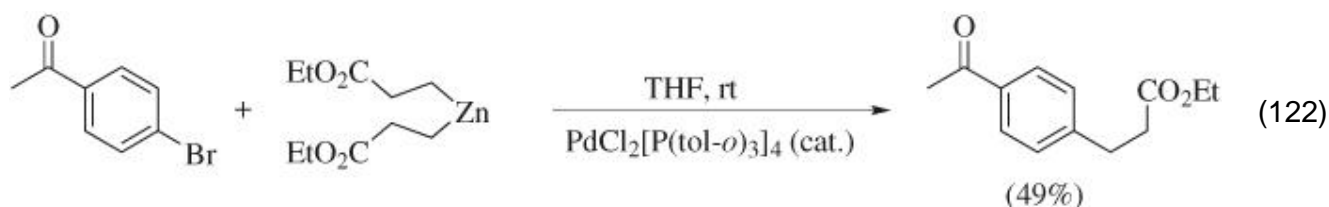
the preparation of polyfunctional *exo*-alkylidenecyclopentanones (Eq. 120). (471) Interestingly, zinc malonates and related compounds are sufficiently reactive to add to alkynes, leading to β , γ -unsaturated malonates (Eq. 121). (472)



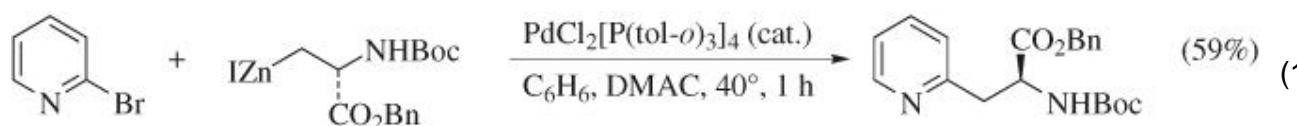
3.10. Reactions Catalyzed by palladium(0) or Nickel(0) Complexes

Organozincs undergo a variety of cross-coupling reactions with alkenyl or aryl halides in the presence of catalytic amounts of palladium(0) complexes (20-26) or nickel salts. (473, 474) These coupling reactions have found numerous applications owing to the broad functional group tolerance and the wide range of unsaturated substrates that can be used (Tables XIX and XX). These

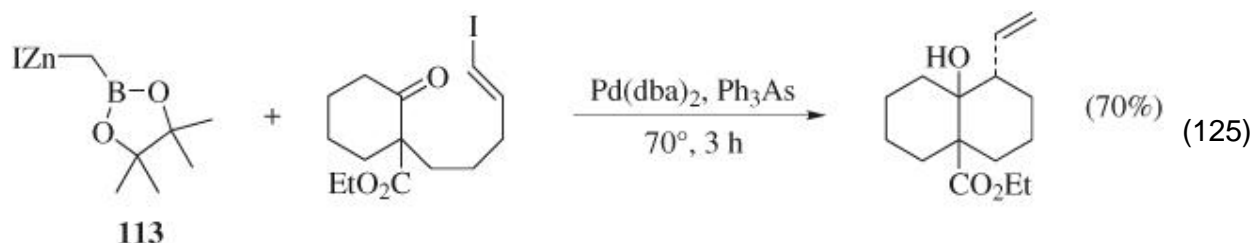
cross-coupling reactions can be performed with a range of polyfunctional organozinc halides (475-491) bearing a silylated acetylene, (477) alkenylsilane, (479) allylsilane, (488) 1-alkoxyacetylene, (480) polythiophene, (481) substituted aromatic (123, 482, 489) and heterocyclic rings, (483-487) ester, (27, 120, 159, 209, 490) nitrile, (120, 209) ketone, (138) protected ketone, (483) protected α -aminoester, (91, 92, 98, 102) stannane, (491) or boronic ester. (62, 84-86) The coupling of homoenolates with aromatic or alkenyl halides in the presence of catalytic amounts of nickel or palladium(II) complexes provides a range of γ -unsaturated esters, with bis(tris-*o*-tolylphosphine)palladium dichloride being an exceptionally efficient catalyst in these reactions (Eq. 122). (27) Various polyfunctional biphenyl derivatives can be prepared using the cross-coupling between an arylzinc halide and an aryl iodide (Eq. 123). (120) The use of alkenyl (138) or aryl (489) triflates instead of



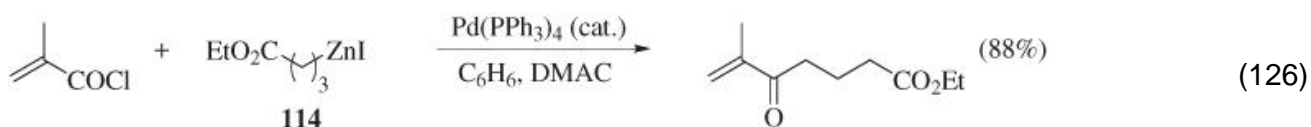
the corresponding iodides or bromides can be advantageous. New α -amino acids in optically pure form have been prepared by the palladium-catalyzed coupling of unsaturated halides and a zinc reagent derived from serine (91, 92, 98-100, 102), or glutamic acid (97, 101) (Eq. 124). (98) Starting from the corresponding alkyl iodides derived from protected glutamic and aspartic acids, β - and γ -amino acids have also been prepared by using the intermediate zinc reagents, which were coupled with aromatic iodides in the presence of a palladium catalyst. (99), (a)



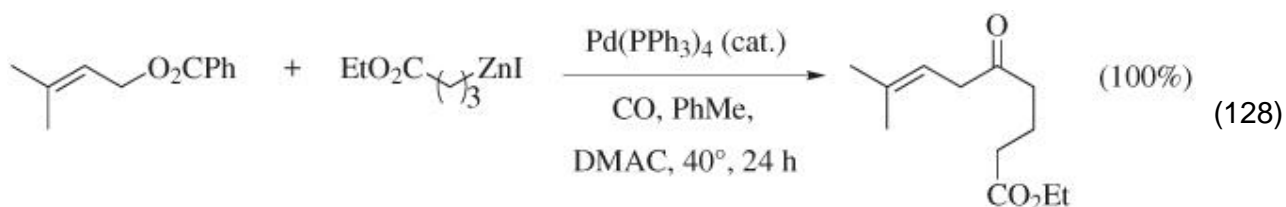
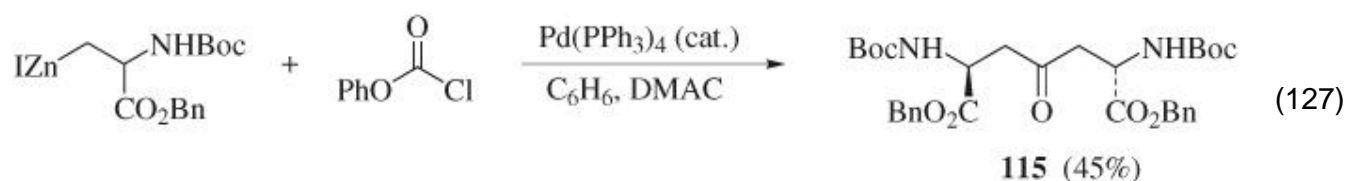
The coupling of alkynylzinc halides or fluorinated alkenylzinc halides with fluorinated alkenyl iodides allows the preparation of a range of fluorinated dienes or enynes. (150, 154, 211-215) Coupling reactions between polyfunctional alkenyl halides and (dialkylboryl)methylzinc iodide **113** provide allylic boronates, which are versatile precursors for cyclization reactions (84-86) (Eq. 125). (86) In some cases, reduction (172, 492-494) or a halide-zinc exchange (165) is observed instead of the expected coupling reaction.



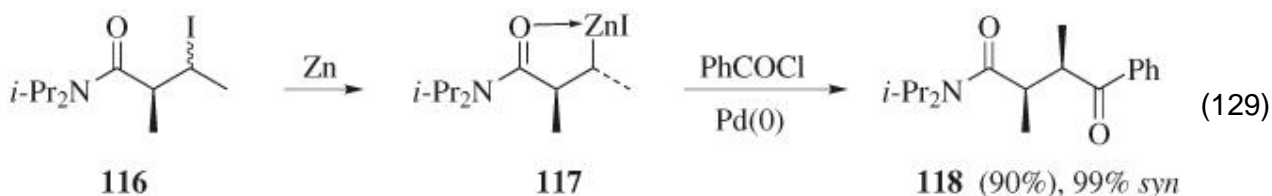
Acylation of organozincs with acid chlorides is efficiently catalyzed by palladium(0) complexes. (25, 26, 105, 120) Many functional groups are tolerated in this reaction. Thus, the coupling of 3-carbethoxypropylzinc iodide (**114**) with an unsaturated acid chloride provides a useful access to polyfunctional enones (105, 495) (Eq. 126). (495) Acylation of a serine- (91, 93, 98) or glutamic acid- (97) derived zinc species



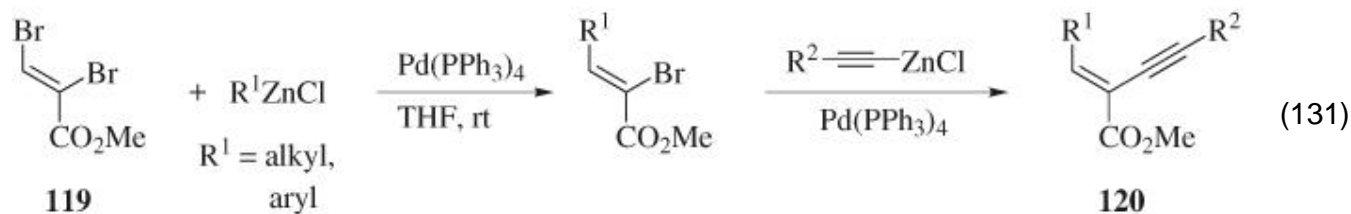
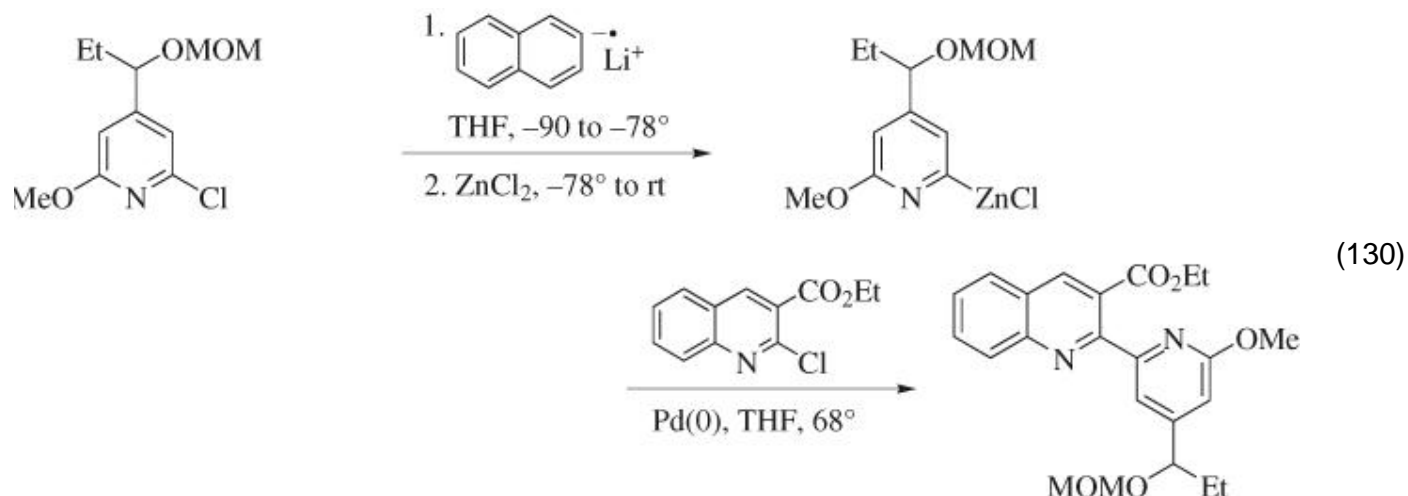
catalyzed by palladium(0) provides chiral γ -keto α -amino acid derivatives in good to excellent yield. The acylation of zinc reagents with phenyl chloroformate or the direct treatment of an organozinc reagent with carbon monoxide under sonication in the presence of catalytic bis(triphenylphosphine)palladium(0) dichloride provides products **115**, corresponding formally to the double acylation by phosgene (Eq. 127). (95) In a related reaction, organozinc halides are treated with carbon monoxide and an allylic benzoate in the presence of a catalytic amount of a palladium(0) complex to provide δ -ketoesters (Eq. 128). (496)



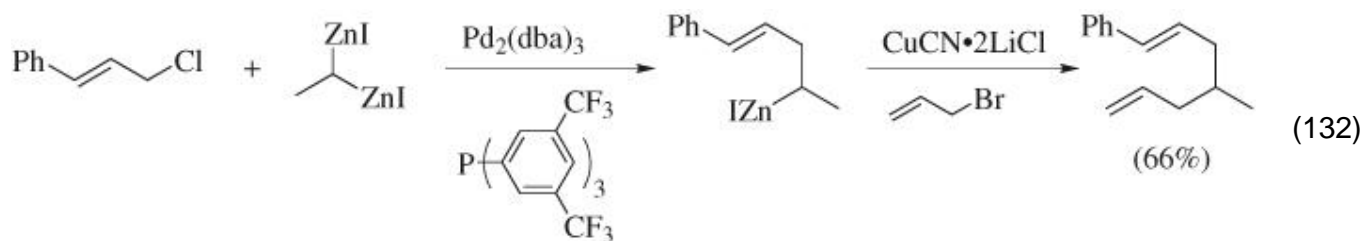
The reaction of *syn*- or *anti*-3-iodo-2-methylbutanamide **116** with zinc powder furnishes the same reagent **117**. Acylation of **117** with benzoyl chloride in the presence of a palladium(0) catalyst gives the C2-C3-*syn* product **118** (Eq. 129). (497)



Functionalized heterocyclic zinc reagents are useful building blocks that readily react in Pd-catalyzed cross couplings (Eq. 130). (498) A selective cross-coupling reaction of (*Z*)-2,3-dibromopropenoate **119** with organozinc compounds allows the preparation of highly functionalized enoates **120** (Eq. 131). (499) Alkenylzinc



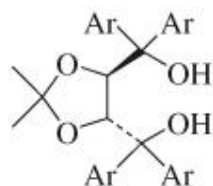
reagents obtained by a titanium(IV)-catalyzed hydrozincation undergo palladium catalyzed cross-couplings with aryl or alkenyl iodides. (500) Bis(iodozinc)ethane undergoes two sequential couplings with electrophiles with successive palladium catalysis and copper catalysis with excellent overall yields (Eq. 132). (501)



3.11. Reactions Catalyzed by Titanium(IV) Complexes

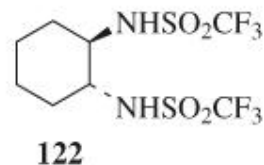
Oguni (502-504) has shown that chiral aminoalcohols catalyze the addition of diethylzinc to aldehydes. (163, 375, 376) Yoshioka and Ohno, (505-507) as well as Seebach, (508-514) have found that a chiral titanium catalyst leads to a very fast addition reaction, allowing extension of the addition reactions to other

diorganozincs (Table XXI). Thus, the transmetallation of alkylmagnesium halides with zinc chloride in ether followed by the addition of 1,4-dioxane constitutes a convenient method for preparing higher salt-free dialkylzincs. (512) A few functionalized dialkylzincs have been prepared in this way and added to aldehydes with good enantioselectivity using 2,2-dimethyl- α , α' , α -tetraaryl-1,3-dioxolane-4,5-dimethanol (TADDOL) (121) as the chiral ligand attached to titanium (Eq. 133). (512) Of special interest is

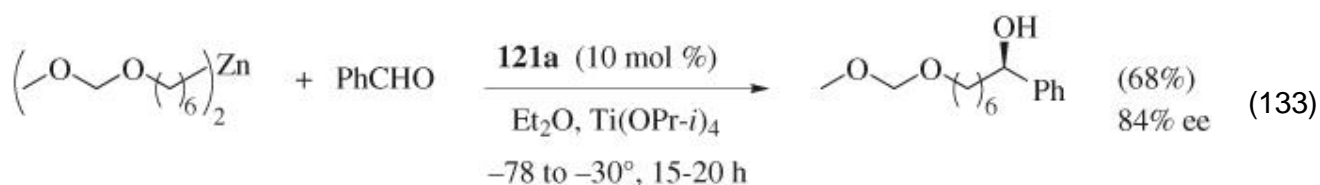


TADDOL: **121a**, Ar = Ph

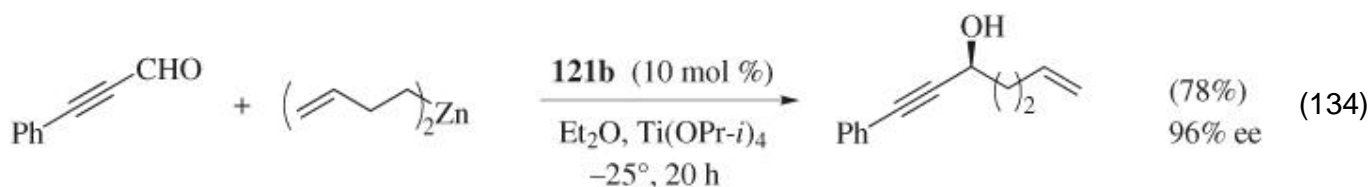
121b, Ar = 2-naphthyl



122

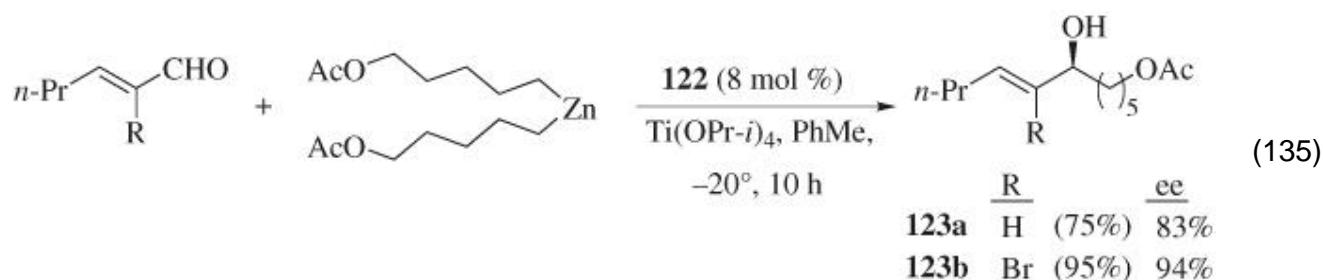


the addition of dialkylzincs to α , β -acetylenic aldehydes in the presence of TADDOL (Ar = 2-naphthyl), since it provides functionalized propargylic alcohols in high optical purity (511, 514) (Eq. 134). (514)

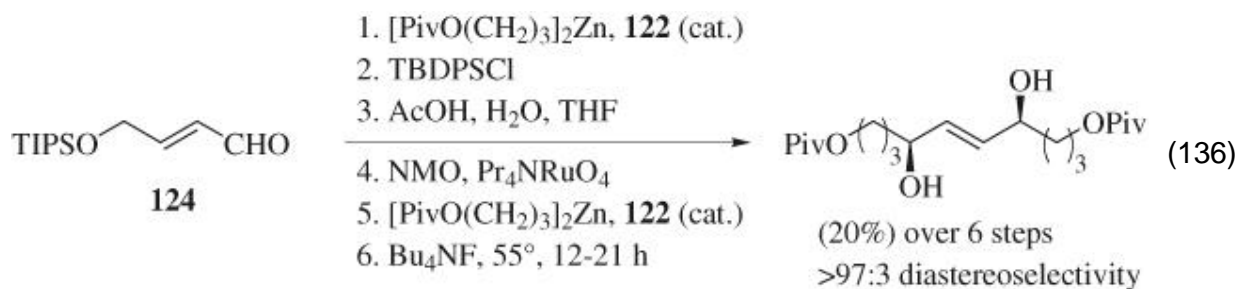


The iodine-zinc (64) and the boron-zinc exchange reactions (239, 240, 515) are general methods for preparing polyfunctional dialkylzincs. Zinc reagents obtained by both methods are suitable for performing catalytic asymmetric additions to aldehydes in the presence of *trans*-(1*R*,2*R*)-bis(trifluoromethanesulfonamido)cyclohexane (122); (505-507) (8 mol %) and titanium tetraisopropoxide (2 equivalents). The addition to aliphatic or aromatic aldehydes proceeds with good enantioselectivity. (64) Unsaturated aldehydes add under especially mild conditions. The presence of

an α substituent in the aldehyde is important for obtaining high enantioselectivities. (164) Thus, the addition of bis(5-acetoxypentyl)zinc to (*E*)-2-hexenal produces the allylic alcohol **123a** ($R = H$) with 83% ee, whereas by using (*Z*)-2-bromo-2-hexenal the alcohol **123b** is obtained with 94% ee (Eq. 135). (164) Interestingly, replacing titanium(IV) isopropoxide with a more

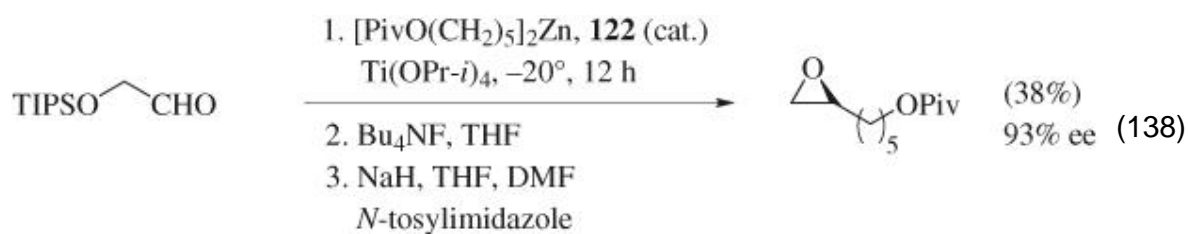
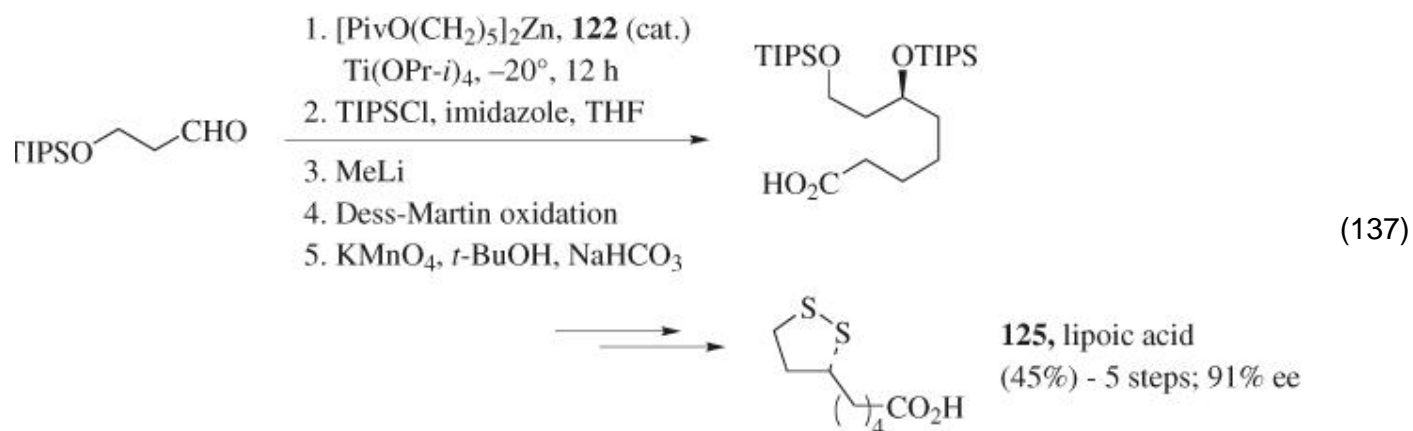


bulky titanium alkoxide such as titanium(IV) *tert*-butoxide leads to higher enantioselectivity. (516) This enantioselective preparation of allylic alcohols has been applied to the prostaglandin side chain. (517-522) The addition of a dialkylzinc to the γ -alkoxyaldehyde **124** (523) followed by simple functional group interconversions and addition of the same dialkylzinc reagent in the presence of **122** leads to C_2 -symmetrical 1,4-diols with excellent diastereoselectivity (Eq. 136). (164, 524) A similar approach has been used to prepare a C_3 -symmetrical triol. (525)

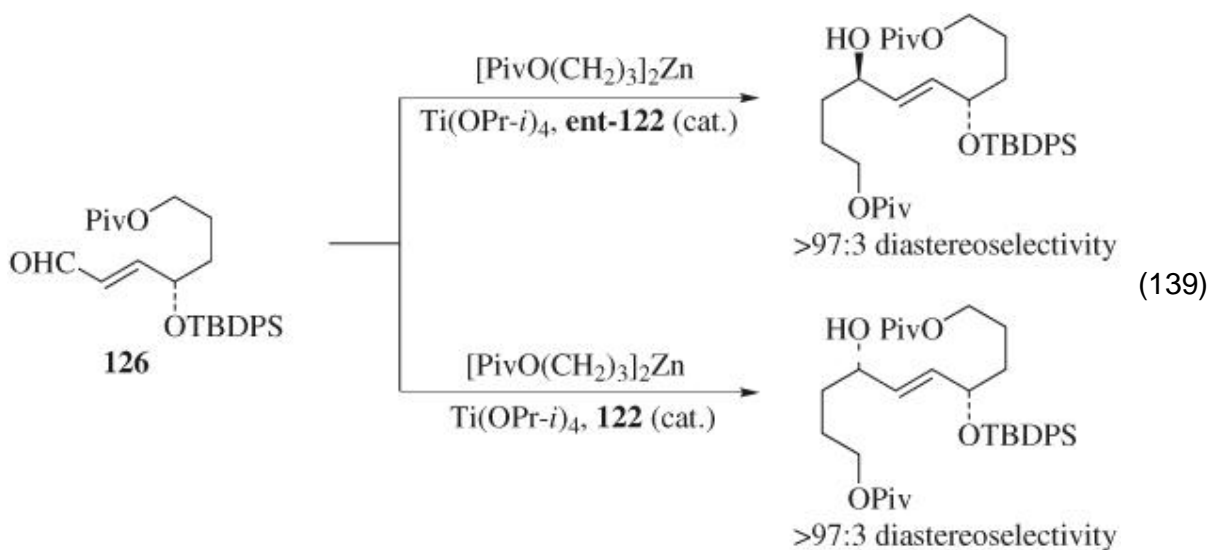


Aldol adducts can also be obtained by the catalytic enantioselective addition of functionalized dialkylzincs to 3-triisopropylsilylpropionaldehyde followed by a protection-deprotection and oxidation sequence, with an excellent stereoselectivity. (526) The method can be used to prepare lipoic acid (**125**) in 91% ee (Eq. 137). (527, 528) Further applications to the synthesis of chiral polyoxygenated molecules (527, 529, 368) and to the natural product (–)-mucocin (**530**) have been reported. Epoxides are versatile chiral building blocks, and the asymmetric synthesis of this class of compounds is of special

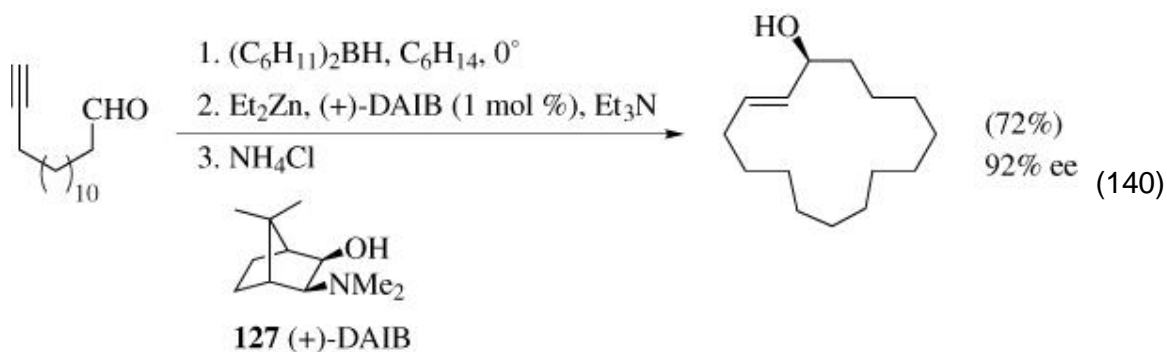
importance. (531) The addition of dialkylzincs to α -alkoxyaldehydes provides a general approach to monoprotected 1,2-diols, which can be converted to epoxides (Eq. 138). (532) The absolute configuration of



all the optically active products can be predicted knowing the configuration of the catalyst used. (524) Interestingly, the configuration on the newly formed chiral center of the alcohol does not depend on the configuration of a chiral center already present in the molecule. Thus, by treating the γ -alkoxyaldehyde **126** with bis(3-pivaloyloxypropyl)zinc in the presence of **122** (8 mol %), the C₂-symmetrical diol is obtained (diastereoselectivity > 97:3). On the other hand by performing the asymmetric addition in the presence of catalyst **122** with the opposite configuration (e.g. **ent-122**), only the *meso*-diol is produced (512, 514, 524, 532) (diastereoselectivity > 97:3; Eq. 139). (524)



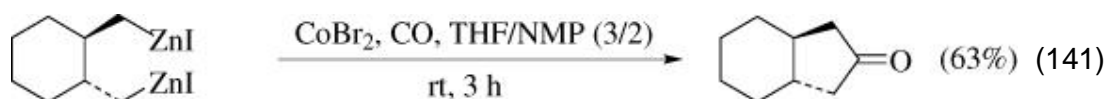
Most of the asymmetric syntheses shown are performed using dialkylzincs prepared via an iodine-zinc exchange. However, the boron-zinc exchange constitutes an outstanding method for the preparation of a range of functionalized zinc reagents. Diorganozincs prepared in this way can be added with high enantioselectivity to aldehydes. (240, 515) An elegant synthesis of (*R*)-(-)-muscone has been reported using the intramolecular enantioselective addition of an alkenylzinc to an aldehyde in the presence of chiral aminoalcohol **127** (Eq. 140). (533)



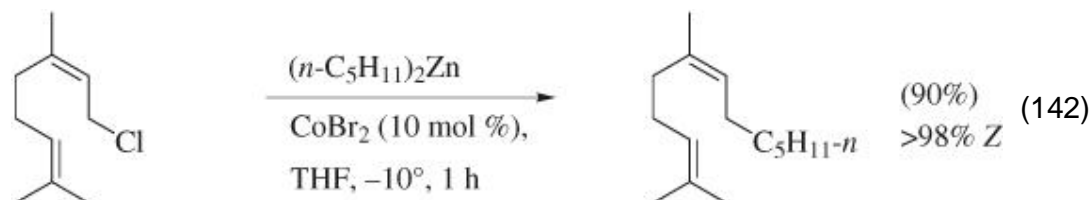
3.12. Reactions Catalyzed by Cobalt(II), Iron(III), or Manganese(II) Complexes

The reaction of transition metal salts with organolithiums or Grignard reagents often leads to sensitive transition metal organometallics that decompose readily if a β -hydrogen atom is present in the alkyl chain. Consequently, such

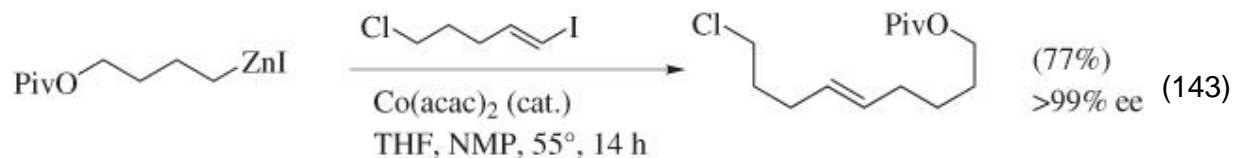
transmetallations have found only a few applications in organic synthesis. (534) Organozinc reagents are far less prone to transfer several organic groups to the transition metal and therefore lead to alkyl transition metal complexes displaying good or acceptable thermal stabilities. Thus, the reaction of cobalt(II) bromide with dialkylzincs in THF:NMP furnishes blue solutions of organocobalt intermediates that have a half-life of ca. 40 minutes at -10° . Similarly, from iron(III) chloride, a gray solution of an organoiron intermediate with a half-life of 2.5 hours at -10° is obtained. The new organocobalt(II) species undergo smooth carbonylations at room temperature to afford symmetrical ketones in satisfactory yields (Eq. 141). (535)



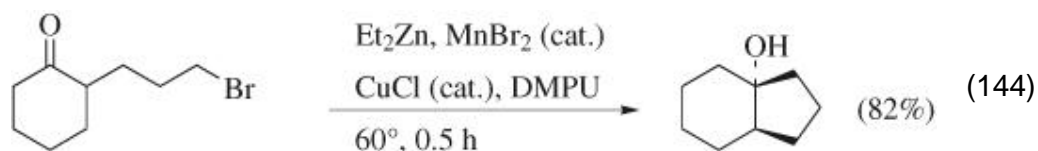
Cobalt(II) bromide also catalyzes the acylation of diorganozincs, affording unsymmetrical ketones. (536) Allylic chlorides react with zinc organometallics in the presence of cobalt(II) bromide (Eq. 142). (536)



In the presence of cobalt salts alkenyl iodides undergo a smooth cross-coupling reaction with organozinc derivatives with retention of the double bond geometry (Eq. 143). (537)

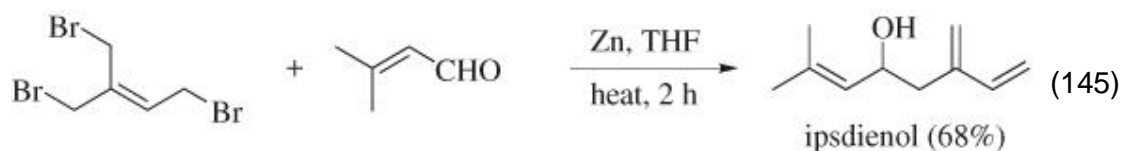


Although organozinc reagents do not undergo transmetalations with manganese(II) salts, the use of the mixed copper—manganese system formed from copper(I) chloride and manganese(II) bromide allows cyclization reactions with good to excellent stereoselectivities (Eq. 144). (538, 539)

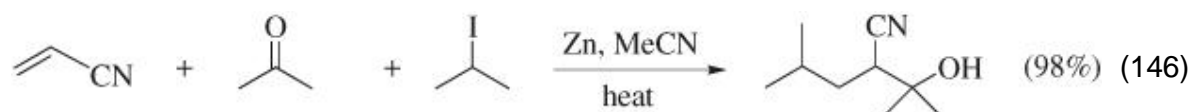


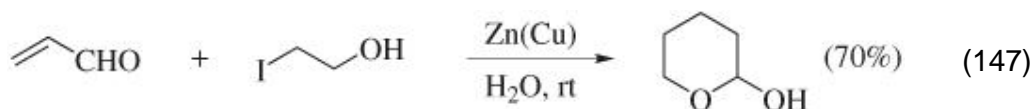
3.13. Barbier Reactions

Barbier reactions (540) are performed under conditions in which the organic halide, the organic electrophile, and zinc dust are mixed without the preformation of an organozinc species. These reactions have found increasing applications in organic synthesis. The nature of the reactive intermediate is not clear. (541) The formation of a zinc organometallic reagent is unlikely, since many of these reactions are performed in water. (148, 542-544) The formation of a free radical, which in many cases is a reasonable reactive intermediate, has not been proven in the addition of an allylic bromide to an aldehyde in the presence of zinc using aqueous ammonium chloride and THF as solvent. Interestingly, a range of unprotected hydroxyaldehydes can be used in this reaction. (148, 542, 543) Functionalized allylic halides have been used. (545) Short syntheses of ipsdienol and ipsenol have been performed using a Barbier reaction (Eq. 145). (546) The use of a Michael acceptor instead



of an aldehyde as the electrophile allows an efficient three-component reaction (147, 547-553) (Eq. 146). (547) Functionalized halides bearing a hydroxy function can be used if the reaction is performed in aqueous medium (Eq. 147). (147) A zinc-promoted Barbier-reaction between 2-bromo-3,3,3-trifluoropropene and aldehydes allows the preparation of fluorinated allylic alcohols. (553)





The zinc coupling of allyl bromides with allyl bromides and chlorotributyl-stannane or dichlorodibutylstannane allows for the preparation of allylstannanes in aqueous medium. (554) Unsymmetrical ketones can be prepared by palladium coupling between acid chlorides and alkyl iodides in the presence of a zinc-copper couple. (136) A new five-membered ring annulation of unsaturated ketones, ketonitriles, ketoximes, or keto aldehydes is mediated by zinc powder in the presence of TMSCl and 2,6-lutidine in THF. (555)

3.14. Comparison with Other Methods

The formation of new carbon-carbon bonds is a major synthetic goal in organic chemistry. Polar main-group organometallics of lithium, magnesium, and to some extent boron and aluminum, have shown their great utility for this purpose. (21) They possess high reactivity toward many organic electrophiles and often furnish high yields of products. In recent years, it has become increasingly important to control the regio- and stereochemistry of new carbon-carbon bond formation and, owing to the increasing complexity of target molecules, the chemoselectivity of reactions of organometallic reagents has become an important issue. Organomagnesium halides and organolithium compounds are often too reactive because of the polar nature of the carbon-metal bond, and display low chemo- and stereoselectivities. In contrast, transition metal organometallics of titanium, (370, 556, 557) copper, (315-320, 394) manganese, (557-562) and palladium (24, 563) are very selective reagents and have a broad range of synthetic applications. Unfortunately, although transition metal organometallics tolerate many organic functionalities, they were originally prepared from the corresponding highly reactive organolithiums or Grignard reagents, and thus very few functionalities could be present in these reactive intermediates. Consequently they were used only to transfer simple organic fragments. This limitation has been solved by using organozinc chemistry. (14) The low polarity of the carbon-zinc bond allows the preparation of organozinc compounds bearing a range of functional groups. Owing to the presence of two vacant *p* orbitals at the zinc center with the appropriate energy for interacting efficiently with the orbitals of many metal salts, a wide range of transmetalation reactions with transition metal halides can be performed. Their subsequent transmetalation with transition metal salts allows one to prepare reactive and functionalized transition metal organometallic intermediates in situ and therefore facilitates the rapid

synthesis of highly functionalized molecules. (14) Alternative methods for the preparation of the same polyfunctional compounds often require several protection-deprotection steps or several functional group interconversions. The use of highly functionalized nucleophilic organic moieties in the synthesis of complex molecules certainly constitutes one of the major advantages of organozinc chemistry.

The preparation of organozinc derivatives has been greatly improved over recent years. (2) Whereas the direct insertion of zinc into organic halides (45) allows the most general access to polyfunctional organozinc halides, (47) the preparation of functionalized diorganozincs is best performed by using an iodine-zinc (64) or boron-zinc exchange. (237, 239, 240) The latter utilizes milder conditions. (237, 240) Treatment of organozinc halides with the copper cyanide-lithium chloride complex (47) leads to copper-zinc species which are significantly less reactive than the corresponding copper derivatives prepared from lithium or magnesium organometallics, but which undergo the same reactions, usually in excellent yield. (14, 65, 120) Whereas conjugate additions to enones (47) or nitroolefins, (74) carbometallations, (471) additions to aldehydes, (54) and coupling reactions with alkyl iodides (329) are best performed with the stoichiometrically prepared zinc-copper species, other reactions such as allylations (47) or acylations (47) can be efficiently performed by using catalytic amounts of the copper cyanide-lithium chloride complex (10 mol %). The simple and general approach to polyfunctional diorganozincs is proving to be extremely useful for catalytic asymmetric additions to aldehydes in the presence of chiral catalysts 121, 122 and 127. The use of organozincs in many transition metal catalyzed reactions often gives better results than that using other main group organo-metallics. The moderate reactivity of zinc organometallics is sufficient to form the reactive transition metal intermediates but avoids the formation of various transition metalate species, which undergo side-reactions like homocouplings or fast β -hydride eliminations. Several methods are now available for preparing configurationally stable secondary alkylzinc reagents in high optical purity.

4. Experimental Conditions

The nature of zinc (dust, foil, shots) is important for the success of the formation of an organozinc halide by oxidative addition. Usually, the use of zinc dust (-325 mesh) from Aldrich or Riedel de Haen gives the best results (see list of suppliers). Procedures for activation may involve chiefly removal of inert oxide by washing several times with 5% hydrochloric acid and washing in turn with water, methanol, ether, and drying. (564) The preparation of functionalized alkylzinc halides is best performed by adding a THF solution of an alkyl iodide to zinc dust (2–3 equivalents) which has been successively activated with 1,2-dibromoethane (3–5 mol %) and TMSCl (1 mol %). (47) It is important to add the alkyl iodide as a concentrated solution (2.5–3 M) in THF in order to obtain a rapid zinc insertion. (79) Under these conditions, primary alkyl iodides undergo zinc insertion between 30 and 40°, whereas secondary alkyl iodides react more readily (15° to room temperature). Organozinc halide formation is usually complete after a few hours. The organometallic solution is diluted with THF (to a 1.5–1.0 M solution), and the excess zinc dust is allowed to settle. The clear, colorless supernatant liquid can be transferred with a syringe or cannula to a separate flask and used for further applications.

The titration of organozinc halides can be conveniently performed by GC analysis. This also constitutes the best method for following formation of the zinc species. Thus, an internal standard (dodecane or other inert alkane) is added to the alkyl iodide before the addition to the zinc slurry in THF. The ratio between the two compounds is determined by GC analysis. (79) At the end of the reaction, no more alkyl iodide should be present. A small reaction aliquot is then treated with a THF solution of iodine and the new ratio between the reformed alkyl iodide and the internal standard is determined, allowing a precise evaluation of the yield of the organozinc reagent. Determination of the volume of the organozinc solution using a separatory funnel allows calculation of the concentration of the zinc reagent. THF solutions of organozinc halides are not pyrophoric, but are rapidly decomposed by air or by humidity.

Benzylic zinc halides have to be prepared at 0° and the benzylic halide has to be added as a 1 M THF solution in order to avoid the formation of Wurtz-coupling byproducts. (50, 51, 53) If electron-rich benzylic systems have to be converted to the corresponding zinc reagents, the best method consists of preparing the corresponding phosphates, which insert zinc in DMPU without the formation of homocoupling byproducts. (103)

Whereas zinc dust gives the best results in all the above reactions, the preparation of allylic zinc reagents gives better yields if cut zinc foil (45) or granular zinc (30 mesh) (79) is used. Recently, a new fragmentation reaction

of homoallylic alcohols has allowed the preparation of highly substituted and functionalized allylic zinc reagents. (296-298) Similarly, only mediocre results are obtained if (iodomethyl)zinc iodide is prepared using zinc dust, but cut zinc foil gives excellent yields. (270) Aryl and alkenyl zinc halides cannot be prepared in THF with zinc dust; their synthesis requires the use of highly reactive zinc prepared by the reduction of zinc chloride with lithium naphthalenide. (120) This procedure even allows the use of aryl bromides as precursors. An alternative method consists of using zinc on graphite, (133) prepared by the reduction of zinc chloride with potassium-graphite in the presence of silver acetate. This second type of activated zinc is not as active as Rieke zinc and always requires the use of an aryl iodide. If the aromatic ring or alkenyl iodide bears an electron-withdrawing group, the direct insertion of zinc dust in DMAC (48) or even THF usually works very well. (88)

Since the insertion of metallic zinc into a carbon-halide bond proceeds via a radical mechanism, the configuration of an alkenyl iodide is lost. This isomerization can be avoided by performing an iodine-lithium exchange reaction at low temperature, in which the double bond geometry is retained, (-100 to -90°) followed by transmetallation to the corresponding alkenyl zinc derivative using zinc iodide. (209)

When using diethylzinc (or diisopropylzinc) for either iodine-zinc (64) or boron-zinc exchanges, (238-240) it is important to maintain strictly the absence of moisture and air, because of the high reactivity of these reagents with water and oxygen. Special care has to be taken during subsequent removal of the excess diethylzinc. Diethylzinc is a highly flammable liquid and mixtures of diethylzinc and liquid oxygen are explosive (the condensation of oxygen into a trap containing diethylzinc must be strictly avoided). However, dilution of diethylzinc with acetone, toluene, or THF (~ 1 M solution) affords a solution that does not burn spontaneously in air.

List of suppliers :

Sigma-Aldrich Chemical Co. Ltd.

USA : PO Box 355, Milwaukee, WI 53201. Tel. 0414-2733850

UK : The Old Brickyard, New Road, Gillingham, Dorset SP8 4JL. Tel. 0800-717181.

Germany : Sigma-Aldrich Chemie GmbH, Grünwalder Weg 30, D-82091 Deisenhofen. Tel. 0800-5155 000.

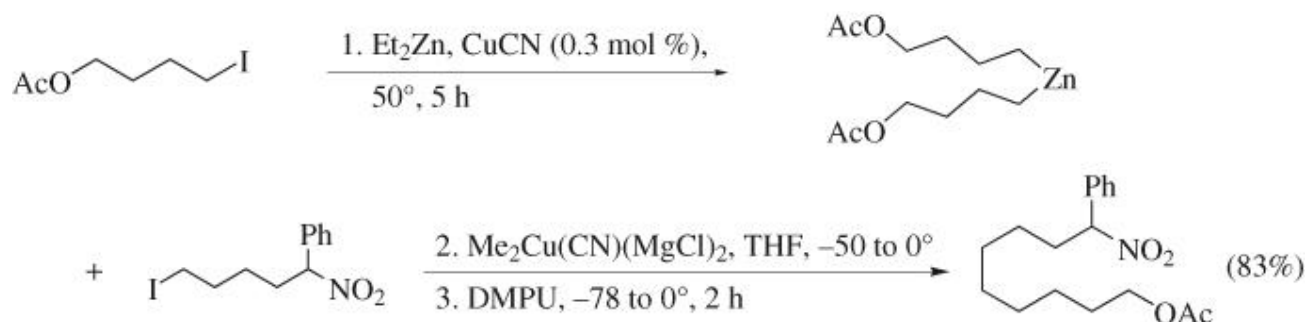
France : L'Isle D'abeau Chesnes, BP 701, 38297 Saint-Quentin Fallavier Cedex. Tel. 0800 211408.

Japan : Sigma-Aldrich Japan K. K., 1-1-7 Higashi Nihonbashi, Chuo-Ku Tokyo 103-0012. Tel. 81—5821-3111.

Riedel de Haen.

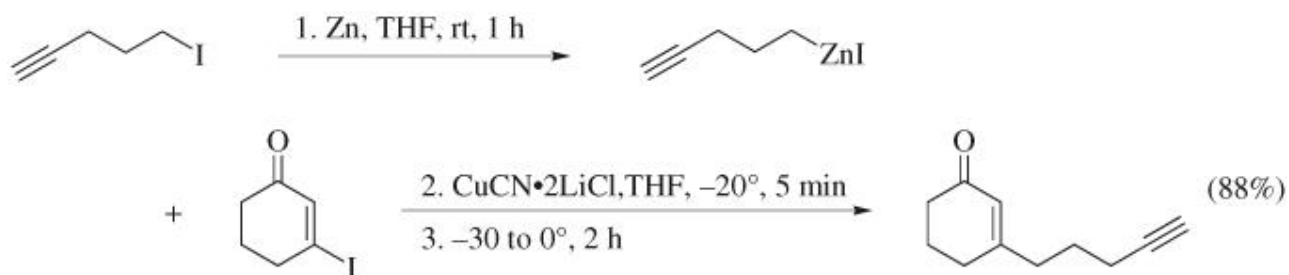
Germany : Wunstorfer Strasse 40, Postfach, D-30926 Seelze. Tel.
05137-9990.

5. Experimental Procedures



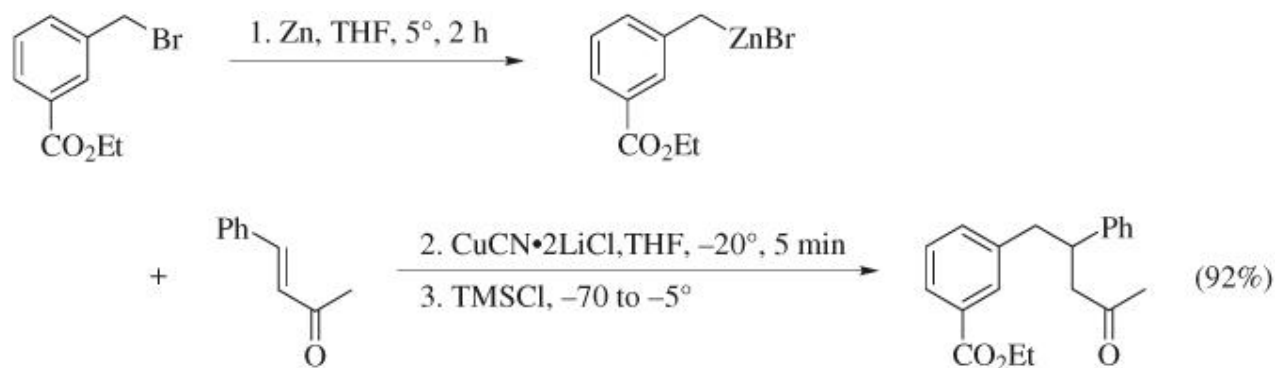
5.1.1. 10-Nitro-9-phenyldeacyl Acetate (Coupling of a Copper-Zinc Reagent with a Primary Alkyl Iodide) (331)

To 4-iodobutyl acetate (2.42 g, 10 mmol) and copper(I) cyanide (5 mg) was added diethylzinc (2.0 mL, 20 mmol), and the reaction mixture was stirred at 50° for 5 hours. The excess diethylzinc and newly formed ethyl iodide were removed under vacuum (0.1 mm Hg, 50° , 1.5 hours), and THF (5 mL) was added with stirring. The suspension was allowed to settle, and the supernatant liquid was transferred to a THF solution of $\text{Me}_2\text{Cu}(\text{CN})(\text{MgCl}_2)$ (5 mmol, 1 M solution) at -50° . The resulting solution was warmed to 0° and then cooled to -78° , and DMPU (5 mL) was added, followed by 6-iodo-1-nitro-2-phenylhexane (1.0 g, 3 mmol). The reaction mixture was allowed to warm to 0° , stirred for 2 hours, poured into a saturated aqueous ammonium chloride solution (50 mL) and extracted with ether (3×20 L). The combined organic phases were washed with brine, dried over magnesium sulfate, and filtered. The crude residue was purified by flash chromatography (ether:hexanes 1:4) yielding the desired product as a clear oil (0.80 g, 83 % yield). IR (neat): 1735, 1551, 1241 cm^{-1} ; ^1H NMR (CDCl_3) δ : 7.33-7.11 (m, 5 H), 4.50 (dd, $J = 7.1, 4.5$ Hz, 2 H), 3.99 (t, $J = 6.7$ Hz, 2 H), 3.47-3.33 (m, 1 H), 1.98 (s, 3 H), 1.68-1.49 (m, 4 H), 1.31-1.10 (m, 10 H). Anal. Calcd. for $\text{C}_{18}\text{H}_{27}\text{O}_4$: C, 67.26; H, 8.47. N, 4.36. Found: C, 67.05; H, 8.67; N, 4.09.



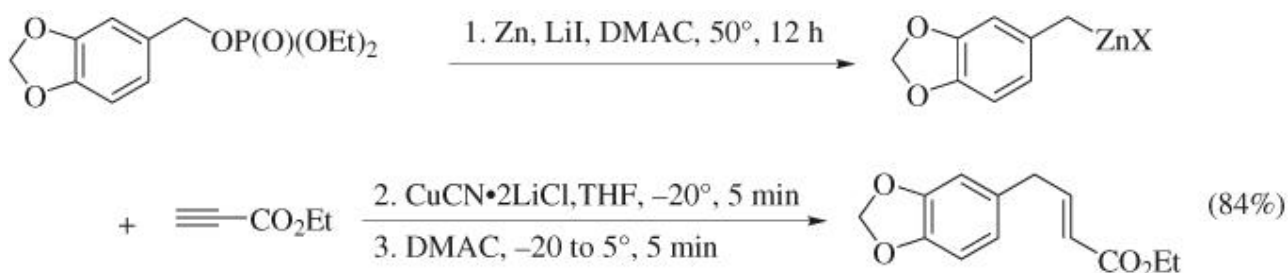
5.1.2. 3-(4-Pentynyl)-2-cyclohexenone (Coupling of a Zinc-Copper Reagent with an Activated Alkenyl Iodide) (78)

To a suspension of zinc dust (325 mesh, 3.27 g, 50 mmol) in THF (4 mL) activated as described above with 1,2-dibromoethane and TMSCl was added a THF solution (8 mL) of 4-pentynyl iodide (4.46 g, 23 mmol). The temperature was maintained below 40° during the addition. The reaction was complete after 0.5–1 hour of stirring at room temperature as indicated by GLC analysis of hydrolyzed reaction aliquots. After the addition of THF (10 mL), the excess zinc was allowed to settle, affording a colorless solution of 4-pentynylzinc iodide. One-half of this solution was transferred via syringe to a THF solution (10 mL) of copper(I) cyanide (900 mg, 10 mmol) and lithium chloride (840 mg, 20 mmol) at –20°. A dark red solution of the copper-zinc reagent formed immediately. The reaction mixture was cooled to –60° after 5 minutes, and 3-iodo-2-cyclohexenone (1.55 g, 7 mmol) was added. The reaction mixture was stirred one hour at –30°, slowly warmed to 0° (1–2 hours), and worked up by pouring into a saturated aqueous ammonium chloride solution (50 mL) and extracting with ether (3 × 30 mL). The combined organic phases were washed with brine (2 × 20 mL), dried over magnesium sulfate, filtered, and concentrated. The crude residue was purified by flash chromatography (dichloromethane:ether:hexane = 10:1:80) affording the desired product (1.0 g, 88% yield). IR (neat): 2115, 1672, 1623 cm⁻¹; ¹H NMR (CDCl₃) δ : 5.87 (s, 1 H), 2.35-2.17 (m, 8 H), 2.01-1.89 (m, 3 H), 1.76-1.66 (m, 2 H). Exact mass calcd. for C₁₁H₁₄O : 162.1045, obsd. 162.1031.



5.1.3. Ethyl 3-(4-Oxo-2-phenylpentyl)benzoate (Preparation of a Benzylic Zinc Reagent from a Benzylic Bromide and Conjugate Addition of the Corresponding Zinc-Copper Reagent to an Enone) (51)

To a suspension of zinc dust (325 mesh, 0.67 g, 10.5 mmol) in dry THF was added dropwise at 5° (ice bath) a THF (7 mL) solution of 3-(carbethoxy)benzyl bromide (1.69 g, 7 mmol; one drop each 5–10 seconds). The reaction mixture was stirred at 5° for two hours. The reaction mixture was allowed to stand for two hours in order to let the excess zinc settle. The supernatant solution of benzylic zinc reagent was transferred via syringe at -20° to a THF solution (5 mL) of copper cyanide (0.63 g, 7 mmol) and lithium chloride (0.60 g, 14 mmol). After being stirred 5 minutes, the reaction mixture was cooled to -70°, and a solution of *trans*-4-phenyl-3-buten-2-one (0.88 g, 6 mmol) and TMSCl (1.9 mL, 15 mmol) in THF (3 mL) was added over 5 minutes. The reaction mixture was allowed to warm slowly to -5°, poured into an aqueous saturated solution of ammonium chloride (10 mL), and was stirred for 10 minutes. The mixture was diluted with ether (50 mL), the aqueous phase was further extracted with ether (2 × 20 mL), and the combined organic phases were washed with an aqueous saturated ammonium chloride solution (2 × 20 mL), brine (20 mL), and dried over magnesium sulfate. The crude residue obtained after evaporation of the solvents was purified by flash chromatography (ether:hexane = 1:4), affording the desired product as a clear oil (1.71 g, 92% yield). IR (neat): 1719 cm⁻¹; ¹H NMR (CDCl₃) δ : 7.87 (m, 2 H), 7.26-7.06 (m, 7 H), 4.33 (q, 2 H, *J* = 7.1 Hz), 3.46 (quint, 1 H, *J* = 8 Hz), 2.97-2.75 (m, 4 H), 2.01 (s, 3 H), 1.37 (t, 3 H, *J* = 7.1 Hz). Exact mass calcd. for C₂₀H₂₃O₃: 311.1647, obsd. 311.1654.



5.1.4. Ethyl (E)-4-[3,4-(Methylenedioxy)phenyl]but-2-enoate (Preparation of a Benzylic Zinc Reagent from a Benzylic Phosphate and Addition of the Corresponding Zinc-Copper Reagent to ethyl Propiolate) (103)

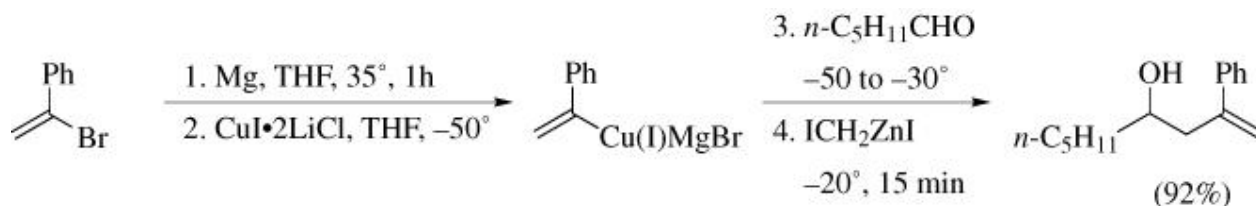
Diethyl 3,4-(methylenedioxy)benzyl phosphate (1.44, g, 5 mmol) and lithium iodide (0.13 g, 1 mmol) were added to a zinc dust suspension (300 mesh, 0.98 g, 15 mmol) in DMAC (4 mL) previously activated with 1,2-dibromoethane (4 mol%) and TMSCl (1 mol%). After 12 hours of stirring at 50°, formation of the zinc reagent was complete as shown by GLC analysis of hydrolyzed reaction aliquots. The reaction mixture was diluted with THF (5 mL) and was allowed to stand for 2 hours in order to let the excess zinc settle. The supernatant solution of benzylic zinc reagent was transferred via syringe at -20° to a THF solution (5 mL) of copper cyanide (0.45 g, 5 mmol) and lithium chloride (0.43 g 10 mmol). After stirring for 5 minutes, ethyl propiolate (0.39 g, 4 mmol) was added and the reaction mixture was warmed to 0°, stirred for 5 minutes, and poured into a saturated aqueous solution of ammonium chloride (50 mL). After successive extractions with ether (3 × 50 mL), the combined organic layers were washed with brine (2 × 20 mL), and dried over magnesium sulfate. The crude residue obtained after evaporation was purified by flash chromatography (hexane:ether 19:1), affording the pure (*E*)-ester (790 mg, 84% yield, >98% pure by GLC analysis). IR (neat): 1715, 1654 cm⁻¹; ¹H NMR (CDCl₃) δ : 7.04 (dt, 1 H, *J* = 16.4, 6.5 Hz), 6.75 (d, 1 H, *J* = 7.7 Hz), 6.63 (m, 2 H), 5.94 (s, 2 H), 5.78 (dt, 1 H, *J* = 15.5, 1.6 Hz), 4.17 (q, 2 H, *J* = 7.1 Hz), 3.42 (dd, 2 H, *J* = 6.7, 1.6 Hz), 1.27 (t, 3 H, *J* = 7.1 Hz). Exact mass calcd. for C₁₃H₁₄O₄: 234.0892; obsd. 234.0887.



5.1.5. Iodomethylzinc Iodide (Methylene Homologation Reagent) (270)

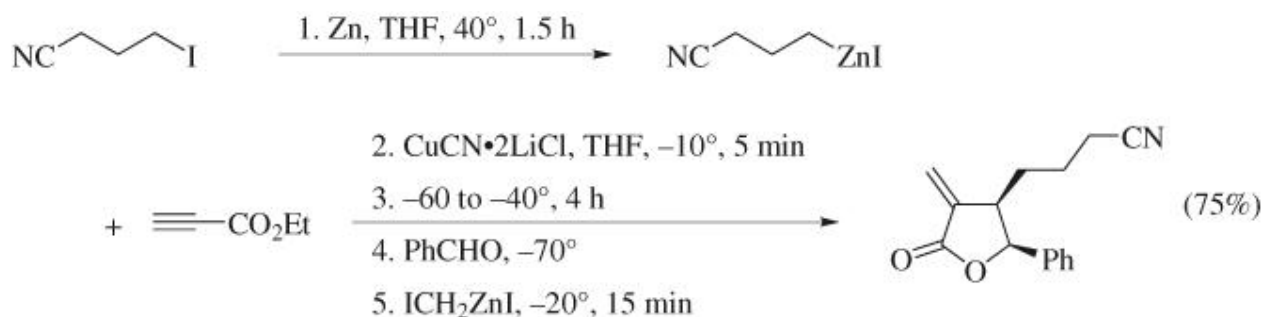
To a suspension of cut zinc foil (ca. 1 × 3 × 0.5 mm) in THF (4 mL) was added 1,2-dibromoethane (200 mg, 1 mmol), and the reaction mixture was heated to

reflux for one minute. The mixture was cooled to room temperature, TMSCl (0.1 mL, 0.8 mmol) was added, and the activated zinc was stirred for 5 minutes. A THF solution (15 mL) of diiodomethane (13.4 g, 50 mmol) was added via an addition funnel at room temperature within 15 minutes. After 4 hours at this temperature, the reagent was ready to use. A yield of ~85% by GLC analysis of an iodolyzed reaction aliquot and a concentration of ~1.4 M was determined.



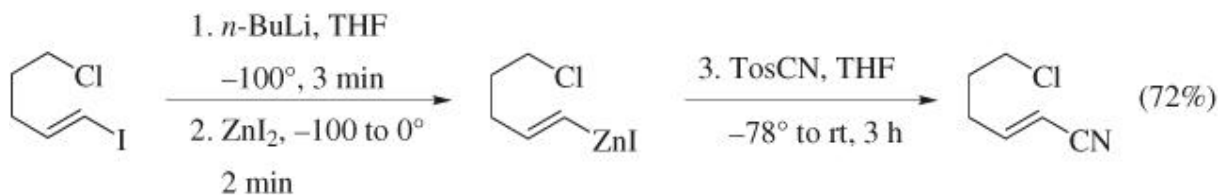
5.1.6. 2-Phenyl-1-nonen-4-ol (Methylene Homologation of an Alkenylcopper with (Iodomethyl)zinc Iodide and Trapping with an Aldehyde) (270)

To a solution of copper(I) iodide (1.15 g, 6 mmol) and lithium iodide (1.33 g, 10 mmol) in THF (25 mL) was added a THF solution of 1-phenylvinylmagnesium bromide (11 mL, 6 mmol) at -50° . The reaction mixture was warmed to room temperature, leading to an orange suspension, which was cooled to -50° . A solution of hexanal (400 mg, 4 mmol) in THF (2 mL) was added, and the reaction mixture was warmed to -30° . A solution of (iodomethyl)zinc iodide (10 mmol) prepared as described above was added, and the reaction mixture was warmed to -20° , stirred for 15 minutes at this temperature, poured into a saturated aqueous solution of ammonium chloride (100 mL), and extracted with ether (3×50 mL). The combined organic phases were washed with water (2×30 mL), brine (2×20 mL), dried over magnesium sulfate, and concentrated. The crude residue was purified by flash chromatography (hexanes:ether 19:1), affording the pure allylic alcohol (825 mg, 3.70 mmol, 92% yield). IR (neat): 3410 cm^{-1} . $^1\text{H NMR}$ (CDCl₃) δ : 7.4–7.25 (m, 5 H), 5.4 (s, 1 H), 5.15 (s, 1 H), 3.7–3.6 (m, 1 H), 2.8 (dd, 1 H, $J = 14.2, 3.8$ Hz), 2.5 (dd, 1 H, $J = 14.2, 9$ Hz), 1.65 (s, 1 H), 1.5–1.4 (m, 2 H), 1.3–1.2 (m, 5 H), 0.9–0.8 (m, 3 H). Exact. mass calcd. for C₁₅H₂₂O: 218.1670, obsd. 218.1674.



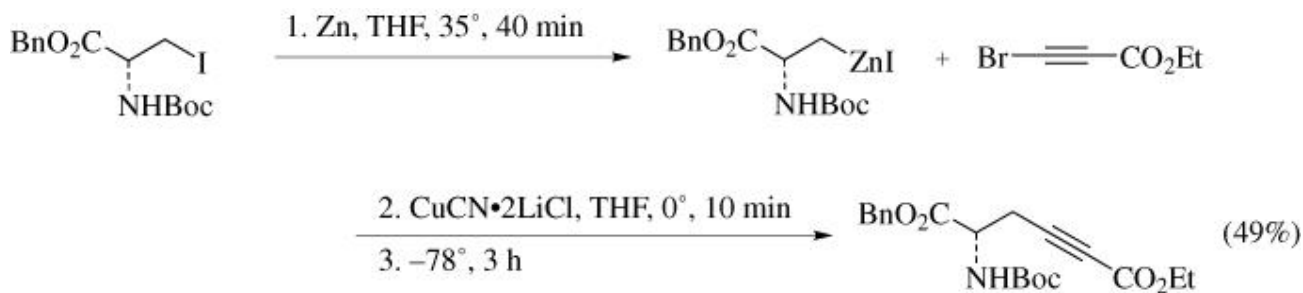
5.1.7. 4-(3-Cyanopropyl)-4,5-dihydro-3-methylene-5-phenyl-2-(3H)-furan (One-Pot Preparation of an α -Methylene- γ -butyrolactone Using Methylene Homologation of an Alkenylcopper Bearing an ester Function) (270)

To a suspension of zinc dust (325 mesh, 1.3 g, 20 mmol) pretreated with 1,2-dibromoethane (0.3 g, 1.5 mmol) and TMSCl (0.1 mL) was added 4-iodobutyronitrile (1.38 g, 7.1 mmol) in THF (4 mL). An exothermic reaction occurred, and the mixture was stirred 1.5 hours at 40°. THF (4 mL) was added, and the reaction mixture was allowed to stand for 2 hours. The supernatant solution was added via syringe to a solution of copper(I) cyanide (635 mg, 7.1 mmol) and lithium chloride (600 mg, 14 mmol) in THF (8 mL) at -10°. After 5 minutes, the reaction mixture was cooled to -60°, and ethyl propiolate (588 mg, 6 mmol) was added. After 4 hours of stirring between -60 and -40°, a solution of benzaldehyde (530 mg, 6 mmol) in THF (2 mL) was added, followed by a freshly prepared solution of (iodomethyl)zinc iodide (ca. 16 mmol) in THF (10 mL). The reaction mixture was warmed to 0°, stirred for 30 minutes at this temperature, poured into a saturated aqueous ammonium chloride solution (100 mL), and extracted with ether (3 \times 50 mL). The combined organic phases were washed with brine (2 \times 20 mL), dried over magnesium sulfate, and concentrated. The residue was purified by flash chromatography (hexane:ethyl acetate 7:3), affording the lactone as a clear oil (*cis* : *trans* mixture (90:10); 900 mg, 75% yield). IR (neat): 1750, 1662 cm^{-1} . ^1H NMR (CDCl_3) δ : 7.43-7.1 (m, 5 H), 6.38 (d, 1 H, J = 2.3 Hz), 5.67 (d, 1 H, J = 2.1 Hz), 5.58 (d, 1 H, J = 7.2 Hz), 3.35-3.32 (m, 1 H), 2.41-2.3 (m, 1 H), 2.15 (t, 2 H, J = 6.8 Hz), 1.75-1.5 (m, 1 H), 1.5-1.2 (m, 2 H), 1.2-1.05 (m, 1 H). Exact mass calcd for $\text{C}_{15}\text{H}_{15}\text{O}_2\text{N}$: 241.1102, obsd. 241.1085.



5.1.8. (*E*)-6-Chloro-2-hexenenitrile (Preparation of an Alkenylzinc Iodide via an Iodine-Lithium Exchange Followed by Transmetalation with Zinc Iodide and Cyanation) (304)

A three-necked flask was charged with (*E*)-5-chloro-1-iodo-1-pentene (1.38 g, 6.0 mmol) in THF (5 mL) and cooled to -100° (liquid nitrogen/ether bath), and *n*-butyllithium (6.3 mmol, 1.6 M in hexane) was added over four minutes. The resulting colorless solution was stirred for three minutes at -100° , and a THF solution (5 mL) of zinc iodide (1.91 g, 6.0 mmol) was added. The mixture was warmed to 0° for two minutes and cooled back to -78° . *p*-Toluenesulfonyl cyanide (0.90 g, 5 mmol) in THF (5 mL) was added, and the reaction mixture was warmed to room temperature and stirred for three hours. The reaction mixture was poured into a saturated aqueous solution of ammonium chloride (10 mL) and extracted with ether (3 × 30 mL), washed with saturated aqueous ammonium chloride (2 × 20 mL), brine (20 mL), and dried over magnesium sulfate. The crude residue obtained after evaporation of the solvents was purified by flash chromatography (hexane:ether 10:1), affording the pure (*E*)- α , β -unsaturated nitrile (466 mg, 72% yield) as a clear oil. IR (film): 2230, 1630 cm^{-1} ; ^1H NMR (CDCl₃) δ : 6.64 (dt, $J = 8.2, 16.4$ Hz, 1 H), 5.35 (d, $J = 16.3$ Hz, 1 H), 3.48 (t, $J = 6.4$ Hz, 2 H), 2.39–2.31 (m, 2 H), 1.91–1.82 (m, 2 H); Anal. Calcd. for C₆H₈ClN: C, 55.61; H, 6.22; N, 10.80. Found: C, 55.73; H, 6.19; N, 10.52.

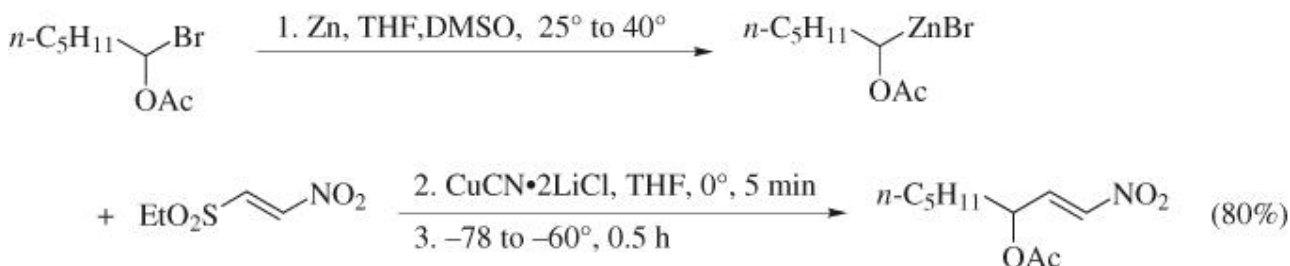


5.1.9. Benzyl

2(S)-[(*tert*-Butoxycarbonyl)amino]-5-carbethoxy-4-pentynoate (Coupling of a Zinc-Copper Reagent with a 1-Bromoalkyne) (100)

A suspension of zinc (300 mg, 4.5 mmol) in dry THF (0.34 mL) and 1,2-dibromoethane (19.4 μ L, 0.225 mmol) was heated under nitrogen to 60° for 3 minutes. After cooling the mixture to 35°, TMSCl (6 μ L, 0.046 mmol) was added, and the mixture was stirred vigorously for 0.5 hour (alternatively, the reaction mixture was placed in an ultrasonic bath and sonicated for 0.5 hour). The reaction mixture was warmed to 35° and benzyl

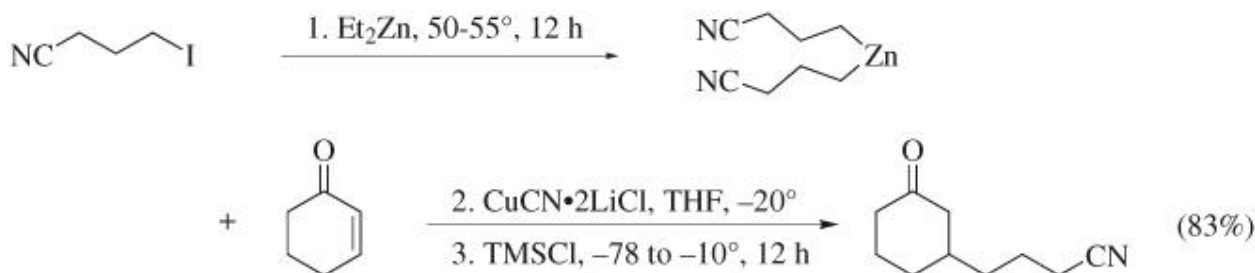
2(*R*)-[(*tert*-butoxycarbonyl)amino]-3-iodopropionate (400 mg, 0.99 mmol) in THF (1.5 mL) was slowly added, and the mixture was stirred for 15–40 minutes until no starting material remained (as judged by TLC). The solution of zinc reagent was cooled to –10°, and a solution prepared from copper cyanide (67 mg, 0.75 mmol) and lithium chloride (64 mg, 1.5 mmol) in THF (1.5 mL) was added. The mixture was stirred at 0° for 10 minutes and then cooled to –78°, and ethyl bromopropiolate (177 mg, 1.0 mmol) in THF (2 mL) was added. After 3 hours at this temperature, the reaction mixture was diluted with ethyl acetate (50 mL) and washed with aqueous hydrochloric acid (20 mL; 0.1 M) and water (30 \times 20 mL), followed by drying over sodium sulfate. Concentration under reduced pressure gave a crude product, which was purified by flash chromatography over silica gel (hexanes-ethyl acetate gradient) to afford the pure product (138 mg, 0.37 mmol, 49% yield); $[\alpha]_D^{25} + 11.1^\circ$ (*c* 1.06, dichloromethane); IR (film) 2241, 1743 cm^{-1} ; $^1\text{H NMR}$ (CCl_4) δ 7.35 (s, 5 H), 5.39 (bd, 1 H), 5.23 (d, 1 H, *J* = 12.1 Hz), 5.21 (d, 1 H, *J* = 12.1 Hz), 4.56 (m, 1 H), 4.20 (q, 2 H, *J* = 7.1 Hz), 2.90 (d, 2 H, *J* = 5.0 Hz), 1.44 (s, 9 H), 1.30 (t, 3 H, *J* = 7.1 Hz).



5.1.10. (*E*)-3-Acetoxy-1-nitro-1-octene (Preparation of an α -Acyloxyalkylzinc Bromide and Conjugate Addition-Elimination of the Corresponding Zinc-Copper Compound to 2-(Ethylsulfonyl)nitroethylene) (74)

To a suspension of zinc dust (0.98 g, 15 mmol) previously activated with 1,2-dibromoethane (0.1 mL) and TMSCl (0.05 mL) in a mixture of THF (3.5 mL)

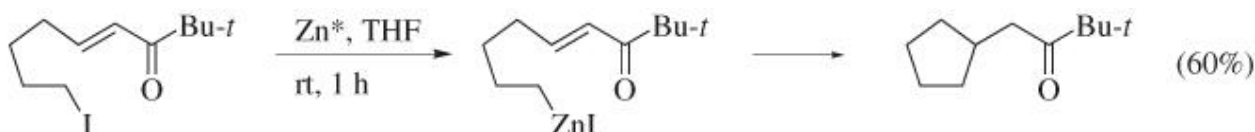
and DMSO (1 mL) was slowly added 1-bromohexyl acetate (1.12 g, 5 mmol) at room temperature. The addition was exothermic and the temperature reached 40°. GLC analysis of a hydrolyzed reaction aliquot showed complete formation of the zinc reagent. THF (5 mL) was added and the mixture was allowed to stand while excess zinc settled. The resulting clear solution was slowly added to a solution of copper(I) cyanide (0.4 g, 4.5 mmol) and lithium chloride (0.38 g, 9 mmol) in THF (2 mL) at -40°, and warmed to 0° for 5 minutes. It was then cooled to -78°, and 2-(ethylsulfonyl)nitroethylene (0.58 g, 3.5 mmol) in THF (5 mL) was slowly added. The reaction mixture was stirred at -60° for 30 minutes, poured into a saturated aqueous solution of ammonium chloride (50 mL) and extracted with ether (3 × 25 mL). The combined organic layers were washed with brine (2 × 20 mL), dried over magnesium sulfate, filtered, and concentrated. The residual oil was purified by flash chromatography (hexane:ether 97:3) to afford the pure (*E*)-nitroolefin (0.52 g, 80% yield). IR (neat): 1658, 1513, 1354 cm⁻¹. ¹H NMR (CDCl₃) δ : 7.15 (dd, 1 H, *J* = 5.0, 13.3 Hz), 7.04 (d, 1 H, *J* = 13.4 Hz), 5.50 (m, 1 H), 2.11 (s, 3 H), 1.72 (m, 2 H), 1.30 (m, 6 H), 0.88 (t, 3 H, *J* = 6.7 Hz). Exact mass calcd. for C₁₀H₁₇NO₄NH₄⁺ 233.1501, obsd. 233.1497.



5.1.11. 3-(3-Cyanopropyl)cyclohexanone (Preparation of a Dialkylzinc from a Functionalized Alkyl Iodide via an Iodine-Zinc Exchange and Conjugate Addition to an Enone) (64)

A Schlenk flask equipped with a septum cap and an argon outlet was charged with 4-iodobutyronitrile (1.20 g, 6 mmol) and diethylzinc (3.0 mL, 30 mmol). The reaction mixture was warmed to 50–55° and stirred for 12 hours at this temperature. GLC analysis of a hydrolyzed aliquot indicated completion of the reaction. The ethyl iodide formed and excess diethylzinc were removed under vacuum (50°, 2 hours; ~0.1 mm Hg). The resulting oily bis(3-cyanopropyl)zinc was dissolved in THF (3 mL) and added to a THF solution (6 mL) of copper(I) cyanide (270 mg, 3 mmol) and lithium chloride (255 mg, 6 mmol, dried 2 hours at 150° under 0.1 mm Hg) at -20°. The resulting light green solution was cooled to -78°, and TMSCl (0.8 g, 7 mmol) and 2-cyclohexenone (335 mg, 3.5 mmol) were successively added. The mixture was slowly warmed to -10°

overnight, poured into saturated aqueous ammonium chloride (25 mL), stirred for 5 minutes at room temperature, and extracted with ether (3 × 25 mL). The combined organic phases were washed with brine (2 × 10 mL), dried over magnesium sulfate, and concentrated. The crude residue was purified by flash chromatography (30% ethyl acetate in hexane) affording the pure product as a colorless oil (483 mg, 83% yield). IR (neat): 2245, 1708 cm^{-1} ; $^1\text{H NMR}$ (CDCl_3) δ 2.48–2.22 (m, 5 H), 2.12–1.98 (m, 2 H), 1.96–1.88 (m, 1 H), 1.86–1.75 (m, 1 H), 1.74–1.6 (m, 3 H), 1.59–1.29 (m, 3 H). Exact mass calcd. for $\text{C}_{10}\text{H}_{15}\text{NO}$: 165.1153, obsd. 165.1140.

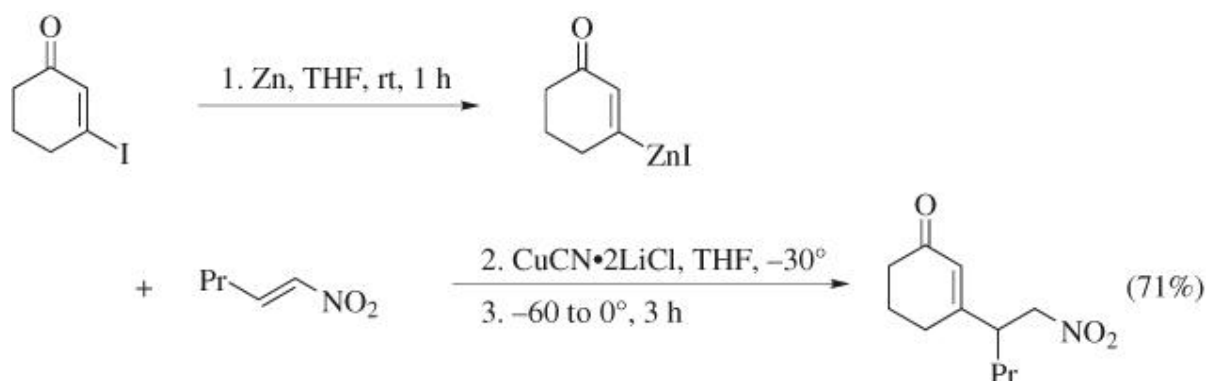


5.1.12. 1-Cyclopentyl-3,3-dimethyl-2-butanone (Intramolecular Conjugate Addition) (89)

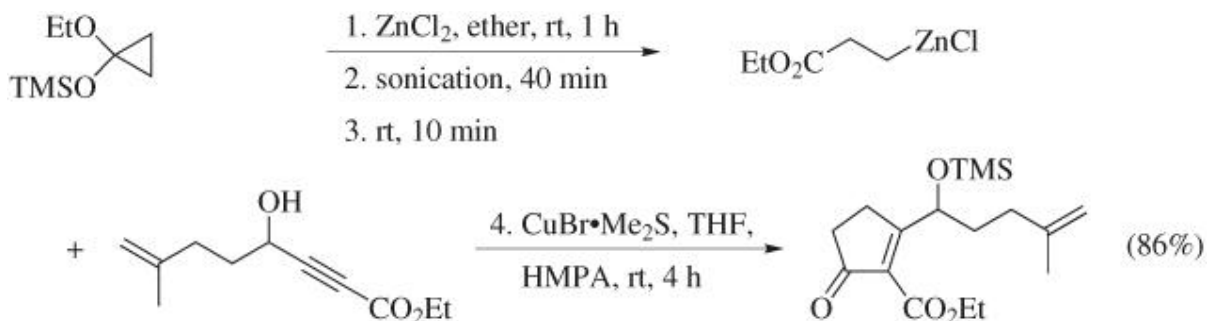
A 50-mL, three-necked, round-bottomed flask equipped with an argon inlet, 10 mL pressure-equalizing addition funnel, and rubber septum was charged with lithium (32 mg, 4.61 mmol), naphthalene (615 mg, 4.80 mmol) and THF (3 mL). After 2.5 hours, a solution of zinc chloride (327 mg, 2.40 mmol) in THF (5 mL) was added over 15 minutes to the blue-green solution of lithium naphthalenide. A dark gray suspension of active zinc metal formed immediately. To this mixture was added a solution of (*E*)-2,2-dimethyl-9-iodo-4-nonen-3-one (294 mg, 1.0 mmol) in THF (4 mL). After one hour, the reaction mixture was quenched with an aqueous 1 N HCl solution (10 mL) and diluted with diethyl ether (10 mL). The aqueous layer was separated and washed with diethyl ether (3 × 20 mL), and the combined organic layers were washed with aqueous saturated sodium sulfite (20 mL), brine (20 mL), dried over magnesium sulfate, filtered, and concentrated. Column chromatography on silica gel (elution with 0–50 % dichloromethane-hexane) provided the desired product as a colorless oil (101 mg, 60% yield). IR (film): 1704 cm^{-1} ; $^1\text{H NMR}$ (CDCl_3) δ : 2.48 (d, $J = 7$ Hz, 2 H), 2.32–2.16 (m, 1 H), 1.85–1.74 (m, 2 H), 1.63–1.46 (m, 4 H), 1.09 (s, 9 H), 1.07–0.94 (m, 2 H).

5.1.13. 3-(1-Propyl-2-nitroethyl)-2-cyclohexen-1-one (Zinc Insertion into an Activated Iodoalkene and Conjugate Addition of the Corresponding Zinc-Copper Reagent to a Nitroolefin) (88)

To zinc dust was added a solution of 1,2-dibromethane (200 mg, 1 mmol) in THF (3 mL). The zinc suspension was heated to ebullition with a heat gun, allowed to cool, and heated again. This process

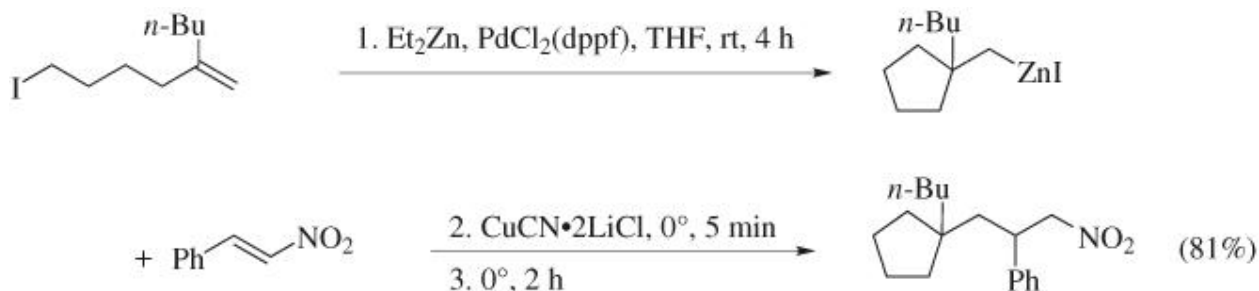


was repeated three times. TMSCl (0.15 mL, ~1.2 mmol) was added and after 10 minutes of stirring, a solution of 3-iodo-2-cyclohexen-1-one (2.22 g, 10 mmol) in THF (3 mL) was added dropwise over 15–20 minutes. During the addition, the reaction temperature reached 55°. The reaction mixture was stirred 1 hour at room temperature, THF (8 mL) was added, and the mixture was allowed to stand for 1–2 hours, leading to a colorless solution of the zinc reagent. GLC analysis of an aliquot indicated complete conversion of the alkenyl iodide to the zinc organometallic as well as formation of less than 8% of dimer. The solution of zinc reagent was transferred via cannula or syringe to a THF solution (10 mL) of copper(I) cyanide (900 mg, 10 mmol) and lithium chloride (850 mg, 20 mmol) at -30°. After 5 minutes of stirring, the reaction mixture was cooled to -60°, and 1-nitro-1-pentene (804 mg, 7 mmol) was added, and the mixture was allowed to warm to 0° within 3 hours. The mixture was cooled to -70° and a solution of acetic acid (1 mL) in THF (3 mL) was slowly added. The mixture was poured into a saturated aqueous ammonium chloride solution (50 mL) and extracted with ether (3 × 30 mL). The combined organic phases were washed with brine (2 × 25 mL), dried over magnesium sulfate, filtered, and concentrated. Flash chromatographic purification of the residue using ethyl acetate:hexane (1:5) as solvent afforded the desired product (1.13 g, 71% yield) as a colorless oil. IR (neat) 1706, 1668 cm⁻¹; ¹H NMR (CDCl₃) δ 5.87 (s, 1 H), 4.43 (d, 2 H, *J* = 6.7 Hz), 3.04 (quintet, 1 H, *J* = 6.9 Hz), 2.37 (t, 2 H, *J* = 6.4 Hz), 2.28 (t, 2 H, *J* = 6.2 Hz), 2.00 (quintet, 2 H, *J* = 6.0 Hz), 1.48 (m, 2 H), 1.28 (m, 2 H), 0.91 (t, 3 H, *J* = 7.1 Hz). Exact mass calcd. for C₁₁H₁₇NO₃: 211.1208, obsd. 211.1207.



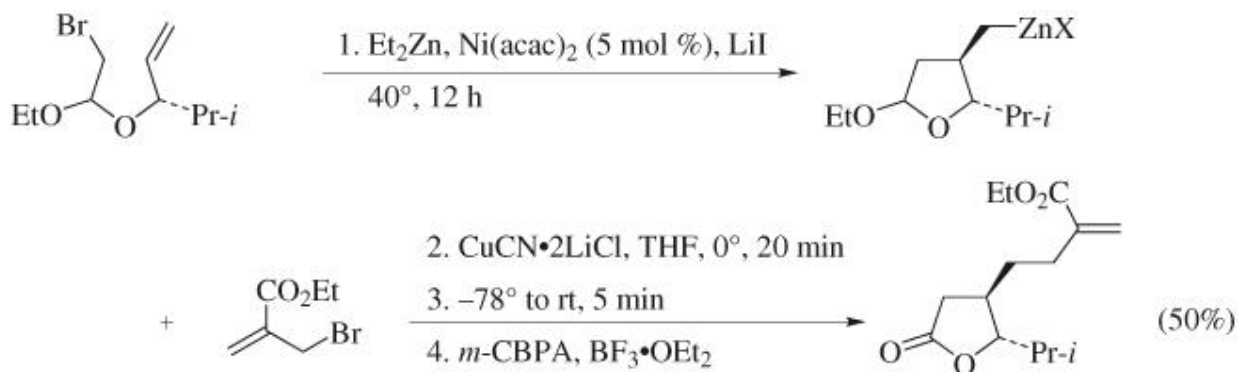
5.1.14. 2-Carbethoxy-3-(1-trimethylsilyloxy-4-methyl-4-penten-1-yl)-2-cyclopenten-1-one (Addition of a Zinc Homoenoate to an Acetylenic ester: A Formal [3 + 2] Cycloaddition) (443)

To a solution of [(1-ethoxycyclopropyl)oxy]trimethylsilane (4.8 mL, 24 mmol) in diethyl ether (18 mL) was added a diethyl ether solution of zinc chloride (18 mL, 18 mmol) at room temperature. The mixture was sonicated for 40 minutes and was stirred at room temperature for an additional 10 minutes. The heterogeneous mixture was cooled to 0° , and copper(I) bromide-dimethyl sulfide complex (308 mg, 1.5 mmol) and ethyl 4-hydroxy-7-methyl-8-ynoate (980 mg, 5 mmol) in THF (18 mL) and hexamethylphosphoramide (HMPA, 4.2 mL, 24 mmol) were successively added. The mixture was stirred for 5 minutes at 0° , and then for 4 hours at room temperature. The reaction mixture was quenched with saturated aqueous ammonium chloride solution (25 mL), and the organic layer was washed with half-saturated ammonium hydroxide solution until no blue color appeared in the wash. The resulting organic layer was washed with water (2×25 mL) and brine (20 mL), dried over magnesium sulfate, and concentrated. The crude residue was purified by chromatography (10% ethyl acetate-hexanes) to give the trimethylsilyl-protected hydroxycyclopentenone (1.27 g, 86% yield). ^1H NMR (CDCl_3) δ 5.14 (dd, $J = 9.5, 5.7$ Hz, 1 H), 4.68 (bd, $J = 13.3$ Hz, 2 H), 4.27 (q, $J = 7.6$ Hz, 2 H), 2.72 (dt, $J = 20.8, 5.7$ Hz, 2 H), 2.43 (t, $J = 5.7$ Hz, 2 H), 2.2–1.56 (m, 4 H), 1.68 (bs, 3 H), 1.31 (t, $J = 7.6$ Hz, 3 H), 0.08 (s, 9 H).



**5.1.15. 1-Butyl-1-(3-nitro-2-phenylpropyl)cyclopentane
(Palladium-Catalyzed Diethylzinc-Mediated Cyclization of a 5-Hexenyl
Iodide Followed by Trapping the Cyclized Zinc-Copper Reagent with a
Nitroolefin) (165)**

A THF solution (5 mL) of dichloro-[1,1'-bis(diphenylphosphino)ferrocene]palladium(II) [$\text{PdCl}_2(\text{dppf})$] (70 mg, 2 mol %) in THF (5 mL) was cooled to -78° . 5-Butyl-1-iodo-5-hexene (1.33 g, 5 mmol) and diethylzinc (1.0 mL, 1.23 g, 10 mmol) were added. The mixture was warmed to room temperature and stirred for 4 hours. The solvent and excess diethylzinc were evaporated (0.1 mm Hg, room temperature, 1 hour). After addition of THF (5 mL) and cooling to -40° , a solution of copper(I) cyanide (450 mg, 5 mmol) and lithium chloride (430 mg, 10 mmol) in THF (5 mL) was added and the reaction mixture was warmed to 0° (5 minutes) and cooled back to -78° . β -Nitrostyrene (1.12 g, 7.5 mmol) in THF (3 mL) was added and the reaction mixture was slowly warmed to 0° and stirred for 2 hours. The reaction mixture was poured into a solution of saturated aqueous ammonium chloride (50 mL) and extracted with ether (3×30 mL). The combined organic phases were washed with brine (2×20 mL), dried over magnesium sulfate, and concentrated. The crude residue was purified by flash chromatography (ether:hexanes 1:9) to yield the desired product as a clear oil (1.16 g, 81% yield). IR (neat) $1555, 1385 \text{ cm}^{-1}$. $^1\text{H NMR}$ (CDCl_3) δ : 7.39–7.20 (m, 5 H), 4.73 (d, 2 H, $J = 9.7$ Hz), 4.66–4.51 (m, 2 H), 3.48 (q, 1 H, $J = 7.6$ Hz), 2.00–1.93 (m, 4 H), 1.77–1.69 (m, 2 H), 1.47–1.17 (m, 8 H), 0.92 (t, 3 H, $J = 6.0$ Hz). Anal. Calcd. for $\text{C}_{18}\text{H}_{27}\text{NO}_2$: C, 74.70; H, 9.40; N, 4.84. Found: C, 74.86; H, 9.65; N, 4.70.

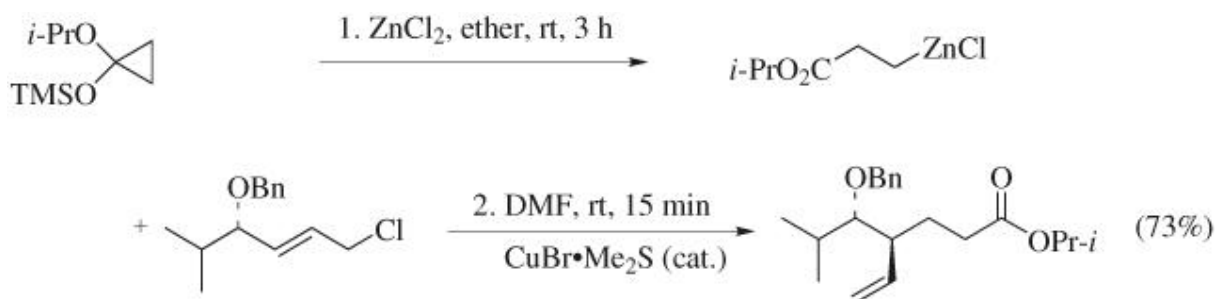


5.1.16. *trans*-4,5-Dihydro-4-(3-carbethoxy-3-butenyl)-5-isopropyl-2-(3H)-furanone (Nickel(II)-Catalyzed Diethylzinc-Mediated Cyclization of an Allylic Iodoacetal Followed by Trapping the Cyclized Zinc-Copper Reagent with an Allylic Bromide) (470)

To a suspension of nickel(II) bis(acetylacetonate) (60 mg, 0.25 mmol), lithium iodide (160 mg, 1.25 mmol), and 1-bromo-2-ethoxy-4-isopropyl-3-oxa-5-hexene (1.25 g, 5.0 mmol) in THF (5 mL) was added diethylzinc (1.0 mL, 10 mmol). The reaction mixture was warmed to room temperature within an hour, leading to a black solution. The cyclization reaction was completed by heating the mixture at 40° for 12 hours. A THF solution (15 mL) of copper(I) cyanide (1.33 g, 15 mmol) and lithium chloride (1.26 g, 30 mmol) was added at -60° . The reaction mixture was stirred for 20 minutes at 0° , ethyl (2-bromomethyl)acrylate (2.95 g, 15 mmol) was added at -78° , and the reaction mixture was warmed to room temperature. After 5 minutes it was poured into a saturated aqueous ammonium chloride solution (50 mL) and extracted with ether (3×100 mL). The combined organic phases were washed with brine (2×20 mL), dried over magnesium sulfate, and concentrated to afford the crude THF derivative, which was converted directly to the lactone in the following way.

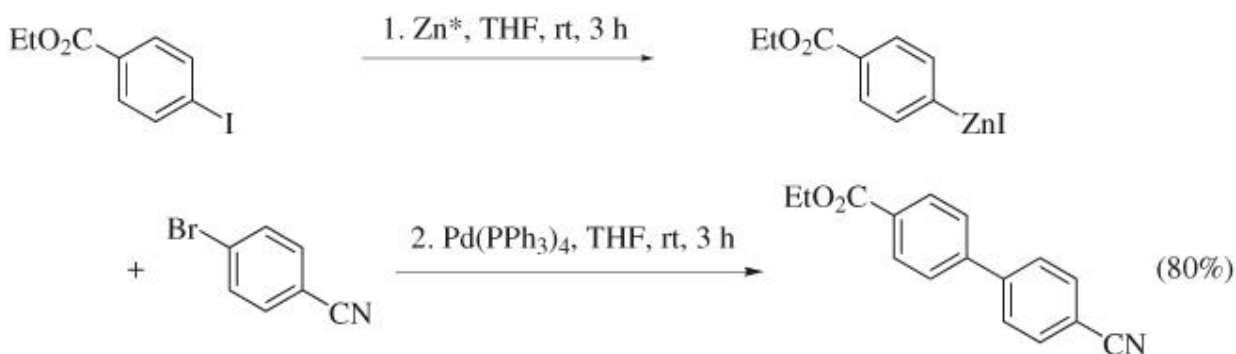
A solution of *m*-chloroperbenzoic acid (1.64 g, 9.6 mmol, purity 50%) in dichloromethane (10 mL) was dried with magnesium sulfate (~2 g). To this filtered solution were added successively at room temperature boron trifluoride etherate (0.2 mL, 1.58 mmol) and the previously obtained crude oil dissolved in dichloromethane (2–3 mL). After one hour of stirring, the mixture was diluted with ether (30 mL) and washed successively with a saturated aqueous solution of sodium thiosulfate (2×20 mL), a saturated aqueous solution of potassium carbonate (10 mL), and brine (2×20 mL). The organic layer was dried over magnesium sulfate, filtered, and concentrated. The crude product was purified by chromatography (hexanes:ether 4:1) to afford the *trans*- γ -butyrolactone (0.63 g, 50% overall yield). IR (neat) 1790, 1750 cm^{-1} . $^1\text{H NMR}$ (CDCl_3) δ 6.10

(s, 1 H), 5.48 (s, 1 H), 4.13 (q, 2 H, $J = 7.1$ Hz), 3.89 (dd, 1 H, $J = 5.4$ Hz), 2.62 (dd, 1 H, $J = 19.8, 11.2$ Hz), 2.20 (m, 4 H), 1.76 (m, 1 H), 1.6 (m, 1 H), 1.47 (m, 1 H), 1.24 (t, 3 H, $J = 1.7$ Hz), 0.90 (t, 6 H, $J = 7.5$ Hz). Anal. Calcd. for $C_{14}H_{22}O_4$: C, 66.40; H, 8.66. Found: C, 66.16; H, 8.92.



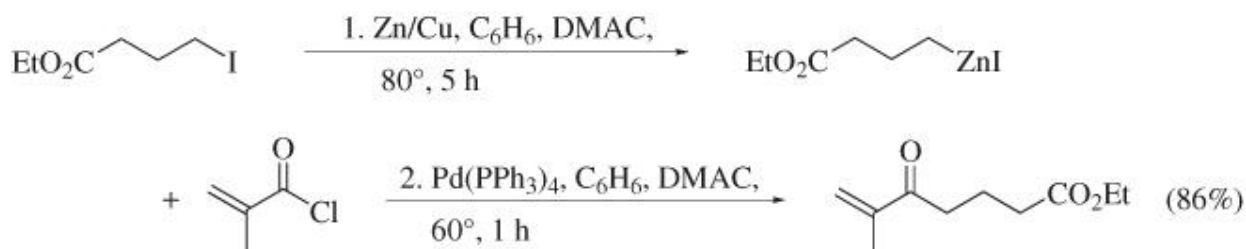
5.1.17. Isopropyl (4*R,5*S**)-5-(Benzyloxy)-4-ethenyl-6-methylheptanoate (*S_N2'*-Allylation of a Zinc Homoenate Prepared from a Cyclopropylacetal) (323)**

To freshly fused zinc chloride (40.9 mg, 0.3 mmol) was added 1-isopropoxy-1-(trimethylsilyloxy)cyclopropane (119 mg, 0.6 mmol) in ether (3 mL). After 3 hours at room temperature, copper(I) bromide-dimethyl sulfide complex (5 μ mol, 1 mg) and 4-benzyloxy-5-methyl-2-hexenyl chloride (47.7 mg, 0.20 mmol) in DMF (2 mL) were added. The reaction was stirred for 15 hours at room temperature, and potassium fluoride (100 mg) in water (20 μ L) was added. After stirring for one hour, the mixture was filtered through a short column of silica gel with ether to give the desired ester as an oil (48.2 mg, 73 % yield). IR (neat) 1735 cm^{-1} ; 1H NMR ($CDCl_3$) δ 7.49–7.20 (m, 5 H), 5.76 (ddd, $J = 10.1, 10.1, 17.1$ Hz, 1 H), 5.17–4.91 (m, 3 H), 4.60 (s, 2 H), 3.01 (dd, $J = 2.5, 6.3$ Hz, 1 H), 2.41–2.06 (m, 3 H), 1.94–1.66 (m, 3 H), 1.23 (d, $J = 6.3$ Hz, 6 H), 1.00 (d, $J = 6.3$ Hz, 3 H), 0.90 (d, $J = 6.3$ Hz, 3 H). Anal. Calcd. for $C_{20}H_{30}O_3$: C, 75.43; H, 9.50. Found: C, 75.51; H, 9.56.



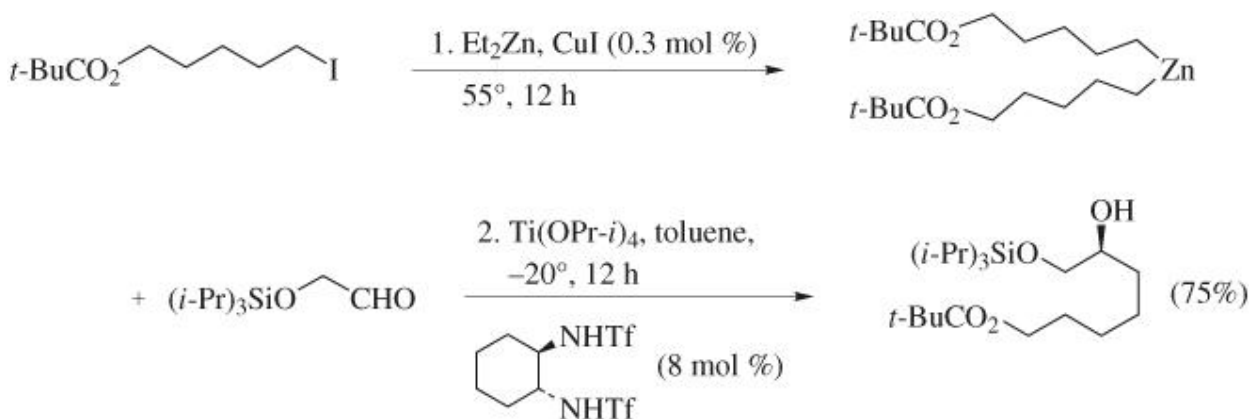
5.1.18. Ethyl 4-(4-Cyanophenyl)benzoate (Palladium-Catalyzed Cross-Coupling with an Arylzinc Iodide Prepared Using Rieke Zinc) (120)

Two 50-mL two-necked flasks, A and B, were equipped with rubber septa, condensers trapped with argon inlets, and magnetic stir bars. Flask A was charged with freshly cut lithium (213 mg, 30.6 mmol) and naphthalene (3.99 g, 31.2 mmol). Flask B was charged with anhydrous zinc chloride (2.09 g, 15.4 mmol). Both of these operations were performed in a argon atmosphere drybox. The flasks were then transferred to the manifold system and the argon inlet fitted. Freshly distilled THF (15 mL) was added to both flasks. The lithium was consumed in about 2 hours, leading to a dark green solution. The zinc chloride solution was transferred dropwise to flask A over 15 minutes. (The active zinc was typically used at this point, but it could be washed with fresh solvent if naphthalene presents a problem with product isolation.) ethyl 4-iodobenzoate (1.93 g, 7.0 mmol) was added to the active zinc (~15.4 mmol) at room temperature. The reaction mixture was stirred for 3 hours, then the solution was allowed to stand while excess zinc settled from the dark brown organozinc iodide solution. The supernatant solution was then ready for further transformations. Thus (4-carbethoxyphenyl)zinc iodide (2.16 mmol in THF (~10 mL) was transferred via cannula to a THF solution of Pd(PPh₃)₄ (127 mg, 0.11 mmol) and 4-bromobenzonitrile (400 mg, 2.19 mmol) at room temperature. After 3 hours of stirring, the reaction mixture was poured into a saturated aqueous ammonium chloride solution (10 mL) and extracted with diethyl ether (3 × 10 mL). The combined organic layers were dried over calcium chloride. The resultant crude product was purified by flash chromatography on silica gel using a gradient elution (hexanes to remove naphthalene first, then hexanes-ethyl acetate) to give pure ethyl 4-(4-cyanophenyl)benzoate (433 mg, 1.73 mmol, 80 % yield) as a crystalline solid, mp 114–115°. IR (CCl₄) 2231, 1722, 1608 cm⁻¹; ¹H NMR (CDCl₃) δ 8.21 – 7.60 (m, 8 H), 4.42 (q, *J* = 7.1 Hz, 2 H), 1.42 (t, *J* = 7.1 Hz, 3 H); Anal. Calcd. for C₁₆H₁₃NO₂: C, 76.48; H, 5.21; N, 5.57. Found: C, 76.25; H, 5.17; N, 5.31.



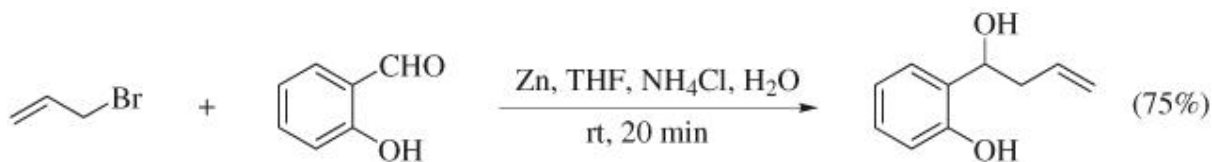
5.1.19. Ethyl 5-Oxo-6-methyl-6-heptenoate (palladium(0)-Catalyzed Acylation of an Alkylzinc Iodide Prepared in DMAC and Benzene) (496)

To a 300-mL four-necked flask flushed with nitrogen and containing a zinc-copper couple (5.6 g, 85.5 mmol) in dry benzene (20 mL) were added ethyl 4-iodobutyrate (13.8 g, 57 mmol) in DMAC (9 mL) and benzene (70 mL) within 3 minutes at room temperature. The mixture was stirred for one hour at room temperature and was then heated at gentle reflux in an oil bath for 4.5 hours. After the reaction mixture was cooled to 60°, a solution of Pd(PPh₃)₄ (0.58 g, 0.5 mmol) in benzene (15 mL) was added over one minute. A solution of methacryloyl chloride (5.23 g, 50 mmol) in benzene (10 mL) was added over 5 minutes and stirring was continued for one hour. The reaction mixture was filtered through a Celite pad, and the filtrate was washed successively with aqueous 1 N ammonium chloride (50 mL), aqueous saturated sodium hydrogen carbonate (10 mL), and saturated aqueous sodium chloride (50 mL). The aqueous phases were extracted with diethyl ether (100 mL). The combined organic extracts were dried over magnesium sulfate and the solvents were removed to yield a deep brown oil. This product was purified by chromatography on silica gel using a hexane-diethyl ether gradient followed by a Kugelrohr distillation in the presence of hydroquinone (10 mg) to give the pure product as a colorless liquid (8.0–8.1 g, 87–88%), bp 185° (20 mm). IR (film) 1730, 1680 cm⁻¹; ¹H NMR (CDCl₃) δ 5.96 (s, 1 H), 5.77 (brs, 1 H), 4.13 (q, 2 H, *J* = 7.1 Hz), 2.76 (t, 2 H, *J* = 7.1 Hz), 2.35 (t, 2 H, *J* = 6.8 Hz), 1.75–2.11 (m, 5 H), 1.25 (t, 3 H, *J* = 7.1 Hz).



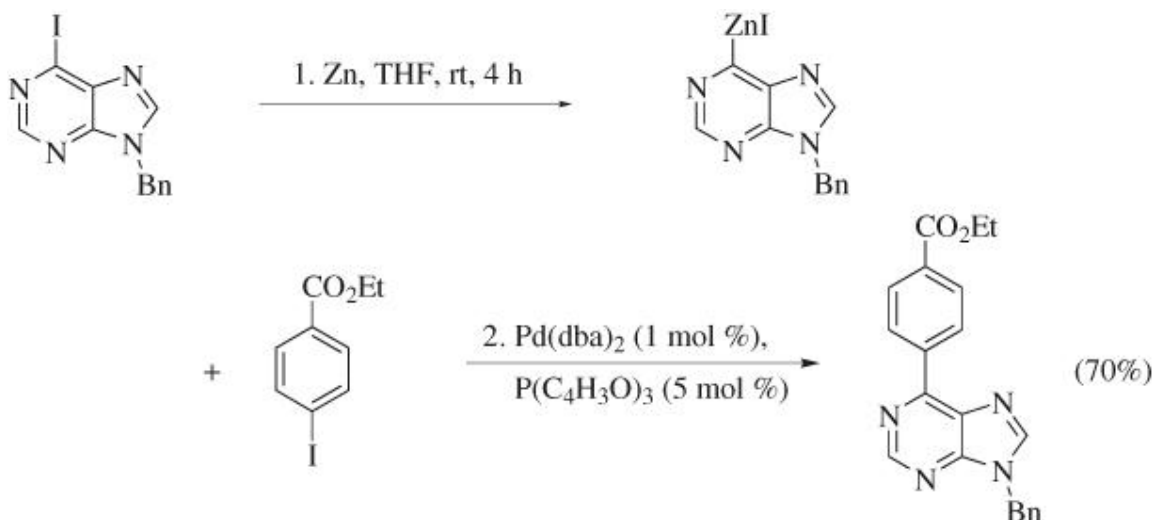
5.1.20. (6*S*)-(+)-6-Hydroxy-7-triisopropylsilyloxyheptyl Pivalate (Enantioselective Addition of a Functionalized Dialkylzinc to an α -Alkoxyaldehyde Affording a Protected 1,2-Diol) (532)

To 5-iodopentyl pivalate (7.40 g, 24 mmol), were added copper(I) iodide (ca. 14 mg, 0.3 mmol %) and diethylzinc (3.6 mL, 36 mmol). The reaction mixture was warmed to 55° and stirred for 12 hours. The flask was connected to a vacuum (0.1 mm Hg), and the resulting ethyl iodide and excess diethylzinc were distilled (ca. 4 hours). The resulting dialkylzinc was dissolved in toluene (8 mL). A second flask charged with (1*R*, 2*R*)-1,2-bis(trifluoromethanesulfonamido)cyclohexane (121 mg, 0.3 mmol) and Ti(OPr-*i*)₄ (2.4 mL, 8 mmol) in toluene (2 mL) was heated to 50° for 0.5 hour and then cooled to -40°. The toluene solution of the zinc reagent was added, followed by 2-triisopropylsilyloxyethanal (0.86 g, 4 mmol). The reaction mixture was warmed to -20°, was stirred at this temperature overnight, and then poured into a saturated aqueous ammonium chloride solution (50 mL) and extracted with ether (3 × 40 mL). The combined organic phases were washed with brine (2 × 20 mL), dried over magnesium sulfate, and concentrated. The residue was purified by flash chromatography (hexane:ether 4:1) affording the desired alcohol as a clear oil (1.17 g, 75% yield, 93% ee); [α]_D²⁵ = +0.64° (c 4.71, benzene). IR (neat) 1635 cm⁻¹. ¹H NMR (CDCl₃) δ 4.04 (t, *J* = 6.6 Hz, 2 H), 3.72–3.65 (m, 2 H), 3.50–3.44 (m, 1 H), 2.56 (bs, 1 H), 1.68–1.61 (m, 3 H), 1.48–1.37 (m, 6 H), 1.18 (s, 9 H), 1.14–1.02 (m, 21 H). Anal. Calcd. for C₂₁H₄₄O₄Si C, 64.91; H, 11.41. Found: C, 64.95; H, 11.60.



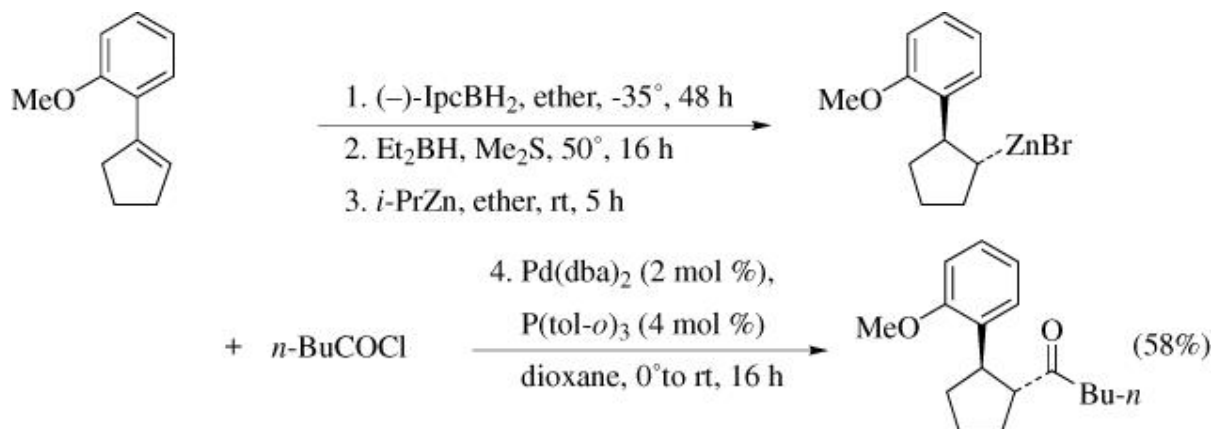
5.1.21. 1-(2-Hydroxy)phenyl-3-buten-1-ol (Barbier Reaction Performed in Aqueous Medium) (148)

A mixture of 2-hydroxybenzaldehyde (244 mg, 2 mmol), allyl bromide (492 mg, 4 mmol), zinc powder (260 mg, 4 mmol) in THF (1 mL), and saturated aqueous ammonium chloride (3 mL) was stirred at room temperature. An exothermic reaction proceeded, and the reaction was complete within 20 minutes. The reaction mixture was extracted with ether (3 × 25 mL), and the combined organic phases were washed with brine (10 mL), dried over magnesium sulfate, and purified by flash chromatography (hexane-ether). The product was the pure benzylic alcohol (330 mg, 75% yield). IR (neat) 3350, 1640 cm⁻¹; ¹H NMR (CDCl₃) δ 8.0 (brs, 1 H), 7.3–6.7 (m, 4 H), 6.1–5.6 (m, 1 H), 5.3–5.0 (m, 2 H), 4.8 (t, 1 H), 2.6 (t, 2 H).



5.1.22. *N*-Benzyl-6-(4-carbethoxyphenyl)purine (Palladium-Catalyzed Cross-Coupling Reaction of a Heteroaromatic Zinc Compound with a Functionalized Aryl Iodide) (118)

To a suspension of zinc dust (0.85 g, 13 mmol) in THF pretreated with 1,2-dibromoethane (0.15 g, 0.8 mmol) and TMSCl (0.1 g, 0.92 mmol) was added a solution of *N*-benzyl-6-iodopurine (0.75 g, 2.2 mmol) in THF (3 mL). The suspension was stirred for 4 hours at room temperature. Meanwhile, a two-necked flask equipped with an argon inlet was charged with palladium bis(dibenzylideneacetone) (15 mg, 0.026 mmol, 10 mol %), tri(2-furyl)phosphine (28 mg, 0.12 mmol, 5 mol %) and THF (2 mL). The solution was stirred until the red color disappeared (~ 10 minutes), indicating formation of the catalyst. A solution of ethyl 4-iodobenzoate (0.95 g, 3.4 mmol) in THF (2 mL) was added to the catalyst, followed by the red solution of the zinc compound. The reaction mixture was heated to 70° and stirred for 5 hours. The mixture was cooled to room temperature, quenched with a saturated aqueous ammonium chloride solution, and extracted with dichloromethane. The combined organic extracts were washed with brine, dried over magnesium sulfate, and concentrated at reduced pressure to give a solid. The crude residue was purified by chromatography (hexane/ether 5/1 to 1/1) to afford the desired product (0.54 g, 70 %). IR (neat) 2972, 1708, 1584, 1561, 1294, 1107, 775, 726 cm⁻¹. ¹H NMR (CDCl₃) δ 8.90 (s, 1 H), 8.70 (d, *J* = 8.2 Hz, 2 H), 8.01 (d, *J* = 8.4 Hz, 2 H), 7.94 (s, 1 H), 7.18 (s, 5 H), 5.40 (s, 2 H), 4.22 (q, *J* = 7.2 Hz, 2 H), 1.24 (t, *J* = 7.2 Hz, 3 H). Anal. Calcd for C₁₂H₂₅Br : C, 70.38; H, 5.06; N, 15.63; Found: C, 70.18; H, 5.13; N, 15.70.



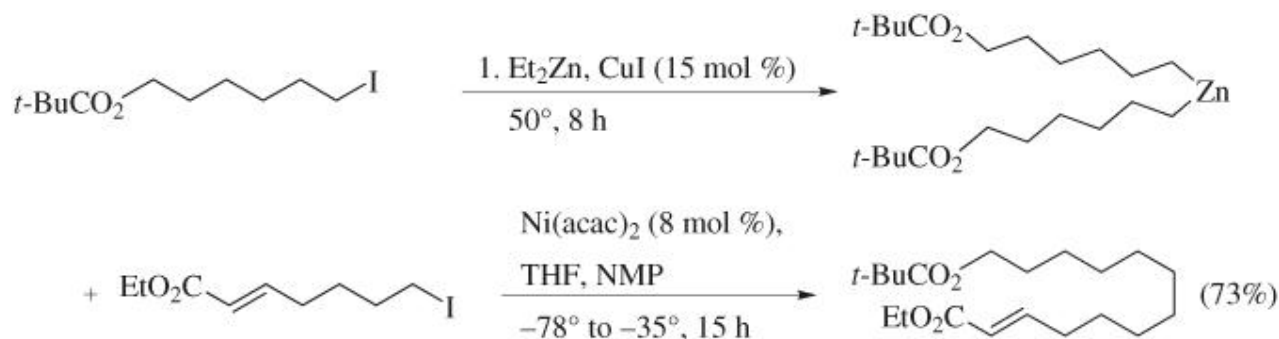
5.1.23. (1*S*,2*R*)-1-(*o*-Methoxyphenyl)-2-(1-oxopentyl)cyclopentane (Palladium-Catalyzed Stereoselective Acylation of a Chiral Secondary Diorganozinc) (40)

A Schlenk flask was charged with (-)-monoisopinocampheylborane (3.1 mL, 2.5 mmol, 0.8 M) in ether, cooled to -35°, and 1-(*o*-methoxyphenyl)cyclopentene (435 mg, 2.5 mmol) in ether (1 mL) was added. The reaction mixture was stirred at -35° for 48 hours, and the solvents were then carefully evaporated under reduced pressure. Diethylborane (2.1 mL of a 7.3 M solution in dimethyl sulfide, 15 mmol) was added, and the resulting solution was stirred at 50° for 16 hours. The solvents were evaporated under reduced pressure (25°, 2 hours). Diisopropylzinc (2.5 mL of a 0.3 M solution in ether, 7.5 mmol) was added over 10 minutes, and the reaction mixture was stirred at 25° for 5 hours. The volatiles were evaporated under reduced pressure (0 to 25°, 30 minutes), and the resulting gray residue was dissolved in dioxane (5 mL). The mixture was filtered under inert gas and cooled to 0°. A previously prepared mixture of palladium bis(dibenzylidene)acetone (20 mg, 2 mol %), tri(*o*-tolyl)phosphine (30 mg, 4 mol %), and pentanoyl chloride (905 mg, 7.5 mmol) in dioxane (3 mL) was added. The reaction mixture was allowed to warm slowly to 25°. After 12 hours the reaction mixture was quenched with an aqueous ammonia solution and stirred for 15 minutes. Then aqueous 2 M hydrochloric acid was added and the mixture was extracted with ether. After drying over magnesium sulfate and evaporating the solvents, the crude residue was purified by chromatography (hexane:ether, 49:1), affording 375 mg of pure product (58% yield based on the starting alkene). The *syn:anti* ratio (dr = 1:99) and the enantioselectivity (er = 90.5:9.5) were determined by capillary GLC analysis on a chiral cyclodextrin column (CP-Chirasil-Dex CB-Chrompack). IR (neat) 2956, 2870, 1708, 1492, 1463, 1243, 1030, 753 cm⁻¹. ¹H NMR (CDCl₃) δ 7.12-7.06 (m, 4 H), 3.70 (s, 3 H), 3.53-3.44 (q, *J* = 8.0 Hz, 1 H), 3.04-2.95 (q, *J* = 8.0 Hz, 1 H), 2.22-2.16 (td, *J* = 7.5, 3.5 Hz, 2 H), 2.04-1.64 (m, 6 H), 1.42-1.33 (quint,

$J = 7.5$ Hz, 2 H), 1.19-1.05 (sext, $J = 7.5$ Hz, 2 H). Exact mass calcd. for $C_{17}H_{24}O_2$: 260.1776, obsd. 260.1774.

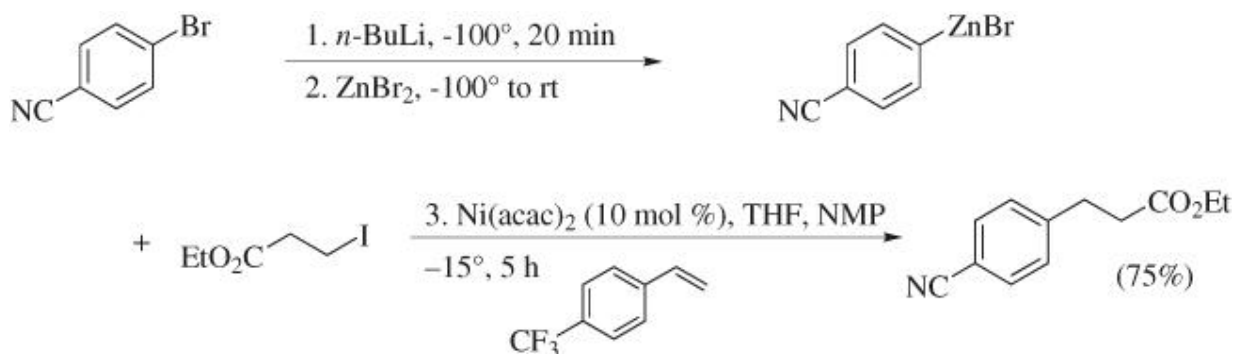
5.1.24. Ethyl (E)-13-Pivaloxy-2-tridecenoate (Nickel(II)-Catalyzed Cross-Coupling of a Functionalized Dialkylzinc with a Functionalized Alkyl Iodide) (333)

A two-necked flask equipped with an argon inlet was charged with 6-iodohexyl pivalate (3.75 g, 12 mmol), copper(I) iodide (4 mg, 0.02 mmol), and diethylzinc (1.3 mL, 13 mmol). The reaction mixture was heated at 50° and



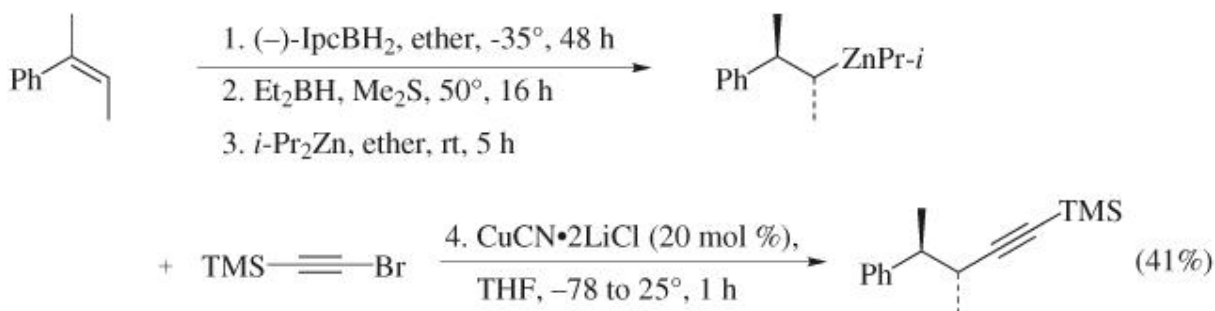
stirred for 8 hours. The ethyl iodide formed and excess diethylzinc were removed under vacuum (50°, 2 hours, ~0.1 mm Hg). The resulting oily bis(6-pivaloxyhexyl)zinc was dissolved in THF (4 mL) at room temperature. Meanwhile a three-necked flask equipped with an argon inlet was charged with nickel(II) bis(acetylacetonate) (116 mg, 0.45 mmol, 8 mol%), NMP (1.5 mL), and THF (2.5 mL).

(E)-Ethyl 7-iodo-2-heptenoate (1.69 g, 6 mmol) was added to the catalyst solution at -78°. The solution of bis(6-pivaloxyhexyl)zinc was slowly added at -78°. The resulting mixture was allowed to warm to -35° and stirred for 15 hours. The reaction was carefully quenched with a saturated aqueous ammonium chloride solution and was extracted with ether. The combined organic layers were washed with brine, dried over magnesium sulfate, and evaporated under vacuum. The crude residue was purified by flash chromatography (hexane:ether = 19:1 to 5:9) to afford the desired product (1.49 g, 73 %). IR (neat) 2935, 1730, 1465, 1160 cm^{-1} ; ¹H NMR (CDCl₃) δ 6.93-6.83 (m, 1 H), 5.73 (d, $J = 15.7$ Hz, 1 H), 4.09 (q; $J = 7.1$ Hz, 2 H), 3.96 (t, $J = 6.6$ Hz, 2 H), 2.11 (t, $J = 7.1$ Hz, 2 H), 1.56-1.49 (m, 2 H), 1.39-1.35 (m, 2 H), 1.28-1.17 (m, 15 H), 1.11 (s, 9 H). Anal. Calcd. for C₂₀H₃₆NO₄: C, 70.54; H, 10.65. Found: C, 70.48; H, 10.61.



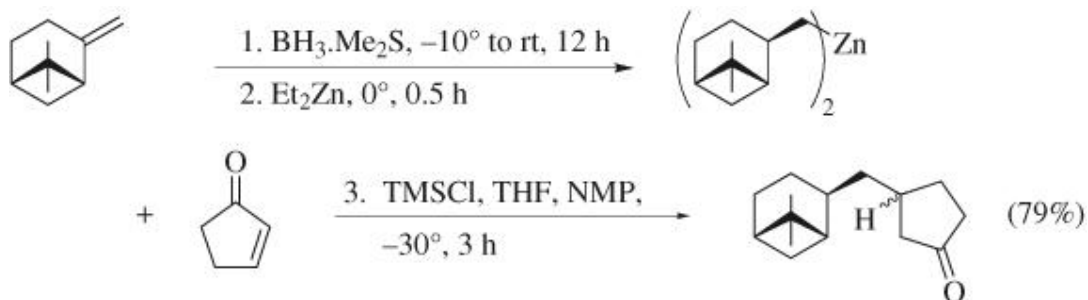
5.1.25. Ethyl [3-(*p*-Cyanophenyl)propionate [Nickel(II)-Catalyzed Cross-Coupling of a Polyfunctional Arylzinc Derivative with a Primary Alkyl Iodide] (230)

A three-necked flask equipped with a thermometer, a gas inlet, and an addition funnel was charged with 4-bromobenzonitrile (2.27 g, 12.5 mmol) in THF (20 mL). The reaction mixture was cooled to -100° , and *n*-butyllithium (8.7 mL, 12.9 mmol, 1.6 M in hexane) was added over 5 minutes. A precipitate formed immediately and the reaction mixture was stirred for 20 minutes at this temperature. A THF solution of zinc bromide (6.25 mL, 2.81 g, 12.5 mmol) was slowly added and the mixture was allowed to warm to room temperature and was concentrated by evaporation of the solvents under vacuum. The resulting ~ 1.2 M solution was transferred at -78° to a two-necked flask equipped with an argon inlet and a septum and containing ethyl 3-iodopropionate (1.14 g, 5 mmol), 4-trifluoromethylstyrene (0.75 mL, 5 mmol, 1 equivalent), nickel(II) bis(acetylacetonate) (128 mg, 0.5 mmol, 10 mol %) in THF (1.7 mL), and NMP (0.8 mL). The reaction mixture was allowed to warm to -15° and stirred for 5 hours. The reaction mixture was quenched with a saturated aqueous ammonium chloride solution and extracted with ether. The combined organics were dried over magnesium sulfate and evaporated under vacuum. The crude residue was purified by flash chromatography (hexane-ether) to afford the desired product (0.762 g, 75% yield) as a colorless oil. IR (neat) 3061, 3026, 2980, 2936, 2228, 1733, 1513, 1246, 1175, 1034 cm^{-1} . ^1H NMR (CDCl_3) δ 7.58 (d, $J = 8.3$ Hz, 2 H), 7.32 (d, $J = 8.3$ Hz, 2 H), 4.12 (q, $J = 7.1$ Hz, 2 H), 3.01 (t, $J = 7.5$ Hz, 2 H), 2.64 (t, $J = 7.5$ Hz, 2 H), 1.22 (t, $J = 7.1$ Hz, 3 H). Anal. Calcd. for $\text{C}_{12}\text{H}_{13}\text{NO}_2$: C, 70.92; N, 6.89; H, 6.45. Found: C, 70.75; N, 7.08; H, 6.57.



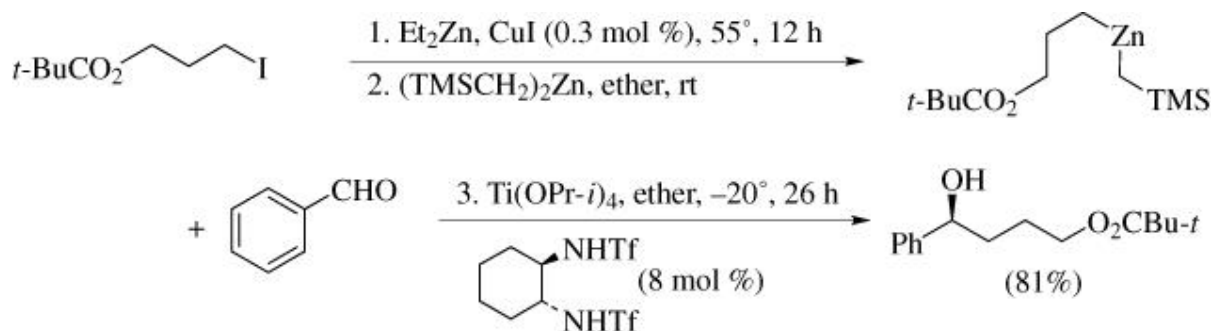
**5.1.26. (3*R*,4*R*)-3-Methyl-4-phenyl-1-trimethylsilylpentyne
 [copper(I)-Catalyzed Stereoselective Alkynylation of a Chiral Secondary
 Diorganozinc] (44)**

A one-necked Schlenk flask was charged with (-)-monoisopinocampheylborane (4.3 mL, 3 mmol, 0.7 M in ether), cooled to -35°, and (*Z*)-2-phenyl-2-butene (396 mg, 3 mmol) in ether (1 mL) was added. The reaction mixture was stirred at -35° for 48 hours, and the solvents were carefully evaporated under reduced pressure. Diethylborane (2.5 mL of a 7.3 M solution in dimethyl sulfide, 18 mmol) was added, and the resulting solution was stirred at 50° for 16 hours. The solvents were evaporated under reduced pressure (room temperature, 2 hours). Diisopropylzinc (1.8 mL of a 5 M solution in ether, 9 mmol) was added over 10 minutes, and the reaction mixture was stirred for 5 hours at room temperature. The volatiles were evaporated under reduced pressure (0 to 25°, 30 minutes), and the resulting gray residue was dissolved in THF (5 mL). A 1 M THF solution of copper(I) cyanide (215 mg, 2.4 mmol) and lithium chloride (204 mg, 4.8 mmol) was added at -78°. The reaction mixture was stirred at -78° for 10 minutes, and 2-bromo-1-trimethylsilylacetylene (1.59 g, 9 mmol) was added. The reaction mixture was stirred 1 hour at -78°, and the cooling bath was removed, allowing the reaction to rise to room temperature. The reaction mixture was quenched with a saturated aqueous ammonium chloride solution and extracted with ether. After drying over magnesium sulfate and evaporating the solvents, the crude residue was purified by chromatography (silica, hexane), affording 283 mg of pure (3*R*,4*R*)-3-methyl-4-phenyl-1-trimethylsilylpentyne (41 % yield based on the starting alkene). The *syn:anti* ratio and the enantioselectivity were determined by capillary GLC analysis on a chiral β-cyclodextrin column (CP-Chirasil-Dex CB, Chrompax). IR (neat) 2166, 1454, 1249, 842, 760 cm⁻¹. ¹H NMR (CDCl₃) δ 7.19-7.05 (m, 5 H), 2.61-2.45 (m, 2 H), 1.28 (d, *J* = 6.5 Hz, 3 H), 0.0 (s, 9 H). Anal. Calcd. for C₁₅H₂₂Si : C, 78.19; H, 9.62, Found: C, 77.81; H, 9.58.



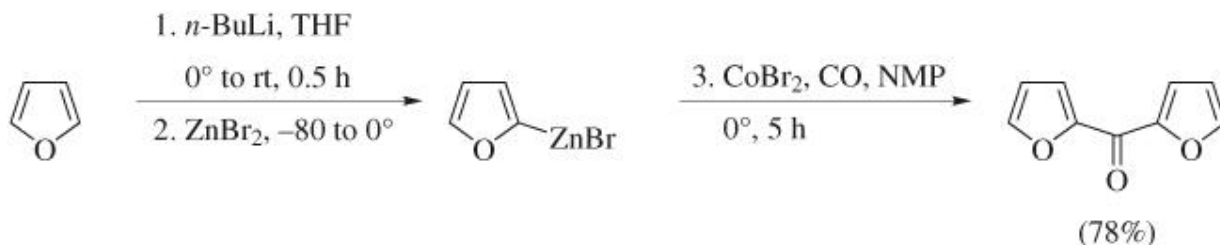
5.1.27. 3-Myrtanilylcyclopentanone (Conjugate Addition of Dimyrtanylzinc to an Enone in *N*-Methylpyrrolidinone) (314)

A two-necked flask equipped with an argon inlet was charged with (1*S*)-(-)- β -pinene (13.6 g, 100 mmol) and cooled to -10° . Borane-methyl sulfide complex (2.28 g, 30 mmol) was added to form a thick precipitate (10 minutes), which was dissolved in ether (15 mL). The resulting solution was stirred at 0° for 2 hours, and warmed to room temperature for a further 8 hours. The solvent and excess (1*S*)-(-)- β -pinene were removed under reduced pressure (0.1 mm Hg, room temperature, 1 hour) to give tri(*cis*-myrtanylborane) (12.5 g, 99%). The resulting white solid was dissolved in hexane (12 mL) before cooling to 0° . Diethylzinc (6 mL, 60 mmol) was added, and the resulting mixture was stirred at 0° for 30 minutes. The solvent and the excess diethylzinc were removed under reduced pressure (0.1 mm Hg, room temperature, 1 hour). The reaction with diethylzinc was repeated a second time before heating at 40° for 4 hours under reduced pressure (0.1 mm Hg) to ensure removal of all excess diethylzinc. The resulting oily dimyrtanylzinc was allowed to cool to room temperature. Meanwhile a three-necked flask equipped with an argon inlet was charged with 2-cyclopenten-1-one (0.41 g, 5 mmol), THF (2 mL) and *N*-methylpyrrolidinone (3 mL). This solution was cooled to -30° , and TMSCl (0.54 g, 5 mmol) and dimyrtanylzinc (1.7 g, 5 mmol) were added. The resulting mixture was stirred at -30° for 3 hours, diluted with THF (30 mL), and poured into aqueous 10 % hydrochloric acid (10 mL). The mixture was stirred for 15 minutes and extracted with ether. The combined organics were washed with brine, dried over magnesium sulfate, and concentrated under reduced pressure. The crude residue was purified by flash chromatography (hexane:ether, 19:1) to afford the desired product (0.87 g, 79% of a 1:1 mixture of diastereomers); IR (neat) 2907, 1744, 1468, 1404, 1159 cm^{-1} . ^1H NMR (CDCl_3) δ 2.28-1.74 (m, 12 H), 1.49-1.32 (m, 4 H), 1.11 (s, 5 H), 0.94 (s, 3 H). Anal. Calcd. for $\text{C}_{15}\text{H}_{24}\text{O}$: C, 81.76; H, 10.97, Found: C, 81.92; H, 10.94.



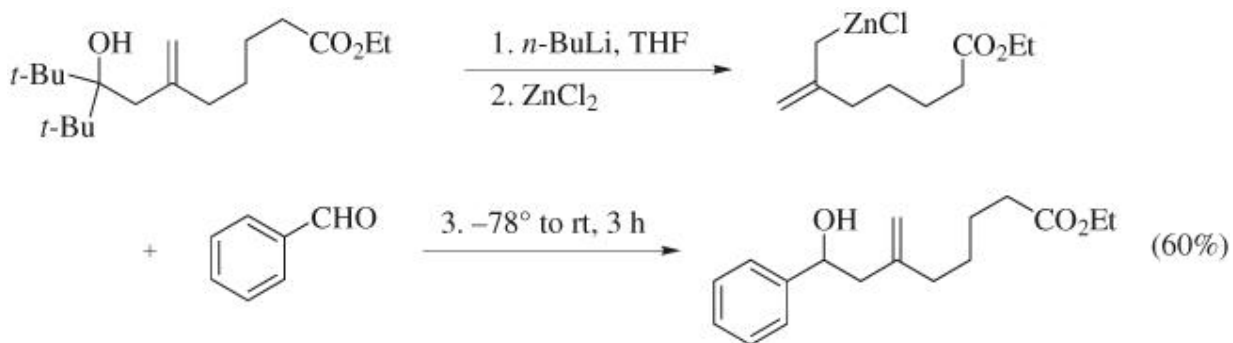
5.1.28. (S)-4-Hydroxy-4-phenylbutyl Pivalate (Enantioselective Addition of a Mixed Diorganozinc to Benzaldehyde) (565)

To 3-iodopropyl pivalate (1.49 g, 5.5 mmol) and copper(I) iodide (57 mg, 0.3 mmol) was added diethylzinc (3.6 mL, 36 mmol). The reaction mixture was warmed to 55° and stirred for 12 hours. The flask was connected to vacuum (0.1 mm Hg), and ethyl iodide and excess diethylzinc were distilled off (50° , 4 hours). The resulting oily bis(3-pivaloyloxypropyl)zinc was dissolved in ether at room temperature (1.5 mL), and bis(trimethylsilyl)zinc (0.57 g, 2.4 mmol) was added. Meanwhile a three-necked flask was charged under argon with (1*R*,2*R*)-1,2-bis(trifluoromethanesulfonamido)cyclohexane (61 mg, 0.18 mmol), $\text{Ti}(\text{OPr-}i)_4$ (0.36 mL, 1.2 mmol) and ether (3 mL). This catalyst solution was cooled to -20° , and the (3-pivaloyloxypropyl)(trimethylsilylmethyl)zinc solution was slowly added. After 10 minutes, benzaldehyde (0.21 g, 2 mmol) was added, and the reaction mixture was stirred at -20° for 26 hours. The reaction mixture was quenched with a saturated aqueous ammonium chloride solution and extracted with ether. The combined organics were washed with brine and dried over magnesium sulfate. The solvents were evaporated under reduced pressure and the crude residue was purified by chromatography (hexane:ether, 4:1) to afford the product (81% yield; 96% ee). The enantiomeric excess was determined by chiral HPLC analysis: Chiracel OD, heptane:2-propanol, 90:10; flow 0.6 mL/min; 12.6 minutes (major isomer) and 15.3 minutes (minor isomer). $[\alpha]_D^{25} = -20.3^\circ$ (c 2.87, benzene). IR (neat) 3540, 2970, 2930, 1720, 1480 cm^{-1} . $^1\text{H NMR}$ (CDCl_3) δ 7.36-7.28 (m, 5 H), 4.72-4.70 (m, 1 H), 4.10-4.06 (t, $J = 6.0$ Hz, 2 H), 1.86-1.31 (m, 5 H), 1.20 (s, 3 H).



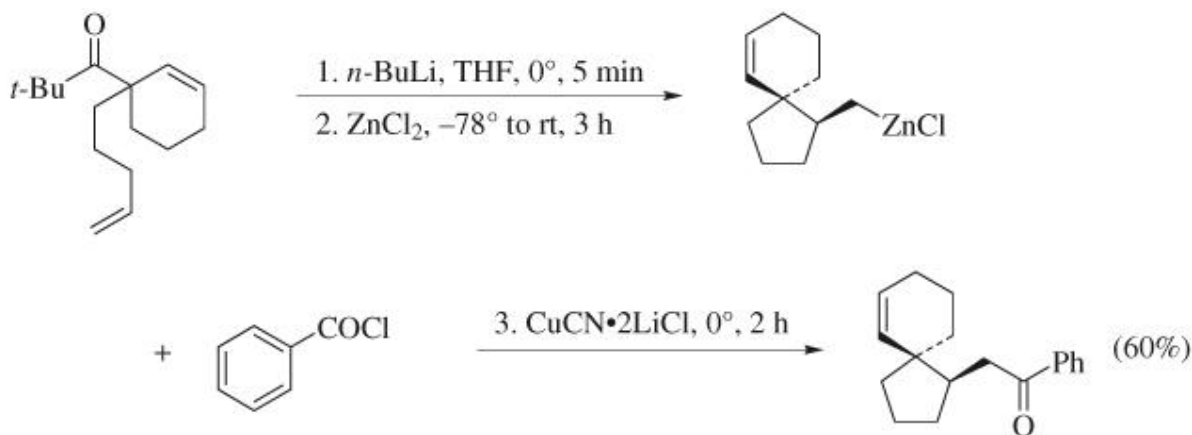
5.1.29. Bis(2-Furyl) Ketone [Cobalt(II)-Mediated Carbonylation of 2-Furylzinc Bromide] (536)

A three-necked flask was charged with furan (1.7 g, 25 mmol) and THF (10 mL) and was cooled to 0°. A solution of *n*-butyllithium (12.5 mL, 20 mmol, 1.6 M in hexane) was added dropwise over 5 minutes. The solution was stirred for 30 minutes at room temperature. A solution of zinc bromide (4.5 g, 20 mmol) in ether (15 mL) was added at -80°. The reaction mixture was allowed to warm to 0°. Meanwhile a second three-necked flask was charged with cobalt(II) bromide (4.38 g, 20 mmol), THF (5 mL), and NMP (15 mL). The solution was cooled to 0° and carbon monoxide was bubbled through using a pipette. The solution of 2-furylzinc bromide was added dropwise at 0°. The reaction mixture was stirred at this temperature for 3 hours. The carbon monoxide stream was stopped, and stirring was continued for an additional 2 hours. The mixture was poured into hexane (200 mL) and stirred for 2 hours to decompose the intermediate cobalt-carbonyl complexes. The reaction was quenched with a saturated aqueous ammonium chloride solution, and extracted with ether. The combined organics were washed with brine, dried over magnesium sulfate, and the solvents were evaporated under reduced pressure. The crude residue was purified by flash chromatography (hexane:ether = 19:1) to afford 1.26 g of the desired product (78% yield); IR (neat) 1632, 1572, 1468, 1396, 1312, 1032, 839 cm⁻¹. ¹H NMR (CDCl₃) δ 7.53 (s, 2 H), 7.35 (d, *J* = 4.0 Hz, 2 H), 6.41 (m, 2 H). Anal. Calcd. for C₉H₆O₃: C, 66.66; H, 3.72; Found: C, 66.53; H, 3.75.



5.1.30. Ethyl (8-Hydroxy-8-phenyl-6-methylene)octanoate (Addition of a Masked Functionalized Allylzinc Reagent to Benzaldehyde) (296)

A two-necked flask equipped with an argon inlet was charged with ethyl (8-*tert*-butyl-9,9-dimethyl-8-hydroxy-6-methylene)decanoate (0.26 g, 0.83 mmol) and THF (4 mL). The solution was cooled to -78° and *n*-butyllithium (9.52 mL, 0.79 mmol, 1.5 M hexane) was added slowly. After 15 minutes a solution of zinc chloride (110 mg, 0.79 mmol) in THF (2 mL) was added followed by benzaldehyde (84 mg, 0.79 mmol). The mixture was stirred for 1 hour at -78° and slowly warmed to room temperature over 3 hours. The reaction was quenched with a saturated aqueous ammonium chloride solution and the mixture was extracted with ether. The combined organics were washed successively with water and brine, dried over magnesium sulfate, and evaporated under reduced pressure. The crude residue was purified by flash chromatography (pentane:ether, 80:20 to 60:40) to afford 130 mg of a colorless oil (60 % yield). $^1\text{H NMR}$ (CDCl_3) δ 7.30-7.18 (m, 5 H), 4.83 (m, 2 H), 4.70 (dd, $J = 5.2$ Hz, 8.3 Hz, 1 H). 4.20 (q, $J = 7.1$ Hz, 2 H), 2.34 (m, 2 H), 2.21 (t, $J = 7.5$ Hz, 2 H), 2.18 (s, 1 H), 2.00 (t, $J = 7.5$ Hz, 2 H), 1.60-1.36 (m, 4 H), 1.19 (t, $J = 7.1$ Hz, 3 H). Anal. Calcd. for $\text{C}_{17}\text{H}_{24}\text{O}_3$: C, 73.88; H, 8.75; Found: C, 73.66; H, 8.71.



5.1.31. 1-(Phenylcarbonylmethyl)spiro[4,5]dec-6-ene (Zinc-Ene Cyclization from a Masked Cyclic Allylzinc Reagent) (299)

A two-necked flask equipped with an argon inlet was charged with 3-(4-pentenyl)-3-(2,2-dimethylpropionyl)cyclohexene (0.24 g, 1.02 mmol) and THF (4 mL). The solution was cooled to 0° , and a solution of *n*-butyllithium (0.68 mL, 1.025 mmol, 1.5 M in hexane) was added. After 5 minutes the orange mixture was cooled to -78° , and a THF (2 mL) solution of zinc(II) chloride (0.14 g, 1.02 mmol) was added. The reaction mixture was slowly

warmed to room temperature over 3 hours. A THF (2 mL) solution of copper(I) cyanide (90 mg, 1.02 mmol) and lithium chloride (90 mg, 2.04 mmol) was added at 0°. After stirring the resulting yellow mixture for 5 minutes, benzoyl chloride (0.15 g, 1.08 mmol) was added. The reaction mixture was stirred for 2 hours at 0° and quenched with a saturated aqueous ammonium chloride solution. The mixture was diluted with ether and the white precipitate was removed by filtration. The aqueous layer was extracted with ether. The combined organics were washed with brine, dried over magnesium sulfate, and concentrated under reduced pressure. The crude residue was purified by flash chromatography (pentane:ether, 98:2) to afford a colorless oil. The pure product was obtained by crystallization from pentane (0.2 g, 60% yield). IR (neat) 2930, 1677, 1446, 981, 784, 684, 569 cm⁻¹. ¹H NMR (CDCl₃) δ 7.87 (d, *J* = 7.0 Hz, 2 H), 7.47-7.19 (m, 3 H), 5.63 (dt, *J* = 10.2, 3.6 Hz, 1 H), 5.49 (d, *J* = 10.2 Hz, 1 H), 2.97 (dd, *J* = 16.2, 3.3 Hz, 1 H), 2.66 (dd, *J* = 16.2, 10.4 Hz, 1 H), 2.12-2.02 (m, 1 H), 1.96-1.30 (m, 13 H). Anal. Calcd. for C₁₈H₂₂O : C, 84.99; H, 8.72; Found: C, 84.75; H, 8.63.

6. Tabular Survey

The tables include examples of functionalized organozincs reactivity collected during the last 20 years up to the end of December, 1999.

Yields are given in parentheses in the product column of the tables.

In all tables except Table XVIII, the first column has a header that represents a zinc reagent. The structures in this column contain a bond with a wavy line drawn through it. This symbol denotes the point of attachment of the zinc reagent that is indicated in the column header. There are four headers for the zinc reagent (FG = functional group):

FG-RZnX (Tables I, XIX, XX)

FG-RCu(CN)ZnX (Tables II-VII, IX, XI, and XV)

FG-RML_n (Tables VIII, X, XII-XIV, XVII)

(FG-R)₂Zn (Table XXI)

Abbreviations:

C₄H₃S 2-thienyl

C₁₀H₇-1 1-naphthyl

Bn benzyl

Boc *tert*-butoxycarbonyl

Bz benzoyl

DMAC *N,N*-dimethylacetamide

DME 1,2-dimethoxyethane

DMF *N,N*-dimethylformamide

DMPU *N,N*¢-dimethylpropyleneurea

HMPA hexamethylphosphortriamide

LDA lithium diisopropylamide

Ms mesyl

NMP *N*-methylpyrrolidinone

Nf perfluorobutyl (nonaflate)

Piv pivaloyl

TBDMS *tert*-butyldimethylsilyl

TBDPS *tert*-butyldiphenylsilyl

THP tetrahydropyranyl

TIPS triisopropylsilyl

TMEDA *N,N,N',N'*-tetramethylethylenediamine
TMS trimethylsilyl
TMSCl trimethylsilyl chloride
Tol tolyl
Ts tosyl

Table I. Hydroperoxides and Nitriles from Functionalized Zinc-Copper Reagents

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Table II. Functionalized Stannanes from Functionalized Zinc-Copper Reagents

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Table III. Reactions of Aliphatic Zinc-Copper Reagents with Allylic Halides

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Table IV. Reactions of Benzylic Zinc-Copper Reagents with Allylic Halides

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Table V. Reactions of Alkenyl or Aromatic Zinc-Copper Reagents with Allylic Halides

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Table VI. Reactions of Propargylic Halides/Tosylates with Organozinc-Copper Reagents

[View PDF](#)

Table VII. Reactions of Cationic Metal Complexes with Organozinc-Copper Reagents

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Table VIII. Reactions of Alkenyl/Aromatic Halides and Sulfones with Zinc-Copper Reagents

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Table IX. Reactions of Zinc-Copper Organometallics with 1-Haloalkynes

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Table X. Coupling Reactions Between Functionalized Zinc Reagents and Alkyl Halides

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Table XI. Additions of Zinc-Copper Reagents to Acid Chlorides and Anhydrides

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Table XII. 1,2-Additions of Organometallic Reagents to Carbonyl and Related Compounds

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Table XIII. 1,2-Additions of Zinc/Copper Reagents to Carbonyl and Related Compounds

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Table XIV. 1,4-Additions of Zinc/Copper Reagents to Enones and Related Compounds

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Table XV. $\text{BF}_3 \cdot \text{OEt}_2$ Mediated 1,4-Additions of Zinc Cuprates to Enones

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Table XVI. Additions of Zinc-Copper Reagents to Nitroolefins

[View PDF](#)

Table XVII. Carbometallations of Alkynes with Dialkylzinc or Zinc-Copper Reagents

[View PDF](#)

Table XVIII. Intramolecular Carbozincation of Functionalized Alkenes or Alkynes

[View PDF](#)

Table XIX. Cross Coupling of Zinc Reagents with Aryl/Vinyl Halides and Sulfonates

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Table XX. Palladium-Catalyzed Acylation of Functionalized Zinc Reagents

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Table XXI. Enantioselective Additions of Functionalized Diorganozinc Reagents to Aldehydes

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TABLE I. HYDROPEROXIDES AND NITRILES FROM FUNCTIONALIZED ZINC-COPPER REAGENTS^a

FG-RZnX (FG-R)	Conditions	Product(s) and Yield(s) (%)	Refs.
<i>A. Reactions of Functionalized Zinc-Copper Reagents with Oxygen</i>			
C ₆ 	O ₂ , C ₆ F ₆ , THF, -60°, 1 h	(61)	303
C ₉ 	O ₂ , C ₆ F ₆ , THF, -60°, 1 h	(58)	303
C ₁₅ 	O ₂ , C ₆ F ₆ , THF, -60°, 1 h	(62)	303
<i>B. Reactions of Functionalized Zinc-Copper Reagents with Tosyl Cyanide</i>			
C ₅ 	TsCN, THF, 0 to 25°, 3 h	(81)	304
	TsCN, THF, 0 to 25°, 4 h	(72)	304
C ₆ 	TsCN, THF, 0 to 25°, 3 h	(81)	304
C ₇ 	TsCN, THF, 0 to 25°, 1 h	(83)	304
C ₈ 	TsCN, THF, 0 to 25°, 3 h	(67)	304
	TsCN, THF, 0 to 25°, 3 h	(69)	304
	TsCN, THF, 0 to 25°, 3 h	(69)	304
	TsCN, THF, 0 to 25°, 3 h	(67)	304
C ₁₀ 	TsCN, THF, 0 to 25°, 3 h	(75)	304
C ₁₁ 	TsCN, THF, 0 to 25°, 3 h	(70)	304
C ₁₅ 	TsCN, THF, 0 to 25°, 3 h	(76)	304
	TsCN, THF, C ₆ H ₁₄ , -85°, 15 h	(73) E:Z = 1:2.1	566 ^b

^a Unless otherwise indicated, the organozinc reagents were prepared by insertion of zinc metal into an organic halide.

^b The organozinc reagent was prepared by a transmetallation reaction.

TABLE II. FUNCTIONALIZED STANNANES FROM FUNCTIONALIZED ZINC-COPPER REAGENTS^a

FG-RCu(CN)ZnX (FG-R)	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₁ 	Me ₃ SnCl, THF, 0°, 1 h	(63)	35
C ₅ 	Me ₃ SnCl, THF, Me ₂ S, -30 to 0°, 3 h	(99) <i>E:Z</i> = 0:100	87
C ₆ 	Me ₃ SnCl, THF, Me ₂ S, -78 to 0°, 1 h	(93)	88, 87
	Me ₃ SnCl, THF, 25°, 12 h	(56)	567 ^b
	Bu ₃ SnCl, THF, -40 to 25°, 0.5 h	Bu ₃ Sn-OPiv (93)	58
	Bu ₃ SnCl, THF, -78 to -30°, 1 h	Bu ₃ Sn-P(O)(OEt) ₂ (81)	90
C ₇ 	Bu ₃ SnCl, THF, 5°, 1 h	(84)	51
	Ph ₃ SnCl, THF	Ph ₃ Sn- (37)	321
-CH(Pr)CH ₂ P(O)(OMe) ₂	Me ₃ SnCl, THF, -78 to -30°, 4 h	Me ₃ SnCH(Pr)CH ₂ P(O)(OMe) ₂ (67)	90
	Me ₃ SnCl, THF, -25 to 25°, 0.5 h	(87)	61
C ₈ 	Bu ₃ SnCl, THF, 5°, 2 h	Bu ₃ Sn- (86)	51
	Bu ₃ SnCl, THF, -70 to -20°, 8 h	Bu ₃ Sn-S-C(=O)Ph (64)	83
C ₉ 	Me ₃ SnCl, THF, 0°, 1 h	Me ₃ Sn- (67)	35
	Me ₃ SnCl, THF, Me ₂ S, -70 to 0°, 1 h	(69)	88
	Me ₃ SnCl, THF, -20 to 25°, 0.5 h	Me ₃ Sn-S-C(=O)Ph (90)	82, 83
	Me ₃ SnCl, THF, DMSO, 0°, 1 h	(64) 85:15	35
	Me ₃ SnCl, THF, DMSO, 0°, 1 h	I + II 2:98 (72)	35
C ₁₀ 	Me ₃ SnCl, C ₆ H ₆ , THF, 25°, 2 h	Me ₃ Sn-S-C(=O)Ph (65)	138

TABLE II. FUNCTIONALIZED STANNANES FROM FUNCTIONALIZED ZINC-COPPER REAGENTS (Continued)^a

	FG-RCu(CN)ZnX (FG-R)	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₁₁		Bu ₃ SnCl, THF, -70 to 25°, 2 h	(88)	51
C ₁₂		Me ₃ SnCl, THF, DMSO, 0°, 1 h	(76) dr = 1:1	35
C ₁₄		Me ₃ SnCl, THF, -78 to 25°, 2 h	(89) E : Z = 82:18	62
C ₁₇		Me ₃ SnCl, THF, 0°, 1 h	(82)	35
C ₁₈		Me ₃ SnCl, THF, -78 to 25°, 1 h	(74)	66
C ₁₈		Me ₃ SnCl, THF, -78 to 25°, 1 h	(65)	66

^a Unless otherwise indicated, the organozinc reagents were prepared by insertion of zinc metal into an organic halide. Transmetalation to the corresponding copper compound was not required.

^b The organozinc reagent was prepared by halide-zinc exchange.

TABLE III. REACTIONS OF ALIPHATIC ZINC-COPPER REAGENTS WITH ALLYLIC HALIDES^a

	FG-RCu(CN)ZnX (FG-R)	Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₁			THF, -15 to 25°, 12 h	(96)	58
			THF, -15 to 25°, 12 h	(89)	58
			THF, -15 to 25°, 12 h	(90)	58
			THF, -15 to 25°, 12 h	(79)	58
			THF, -15 to 25°, 12 h	(95)	58
			THF, -15 to 25°, 12 h	(90)	58
C ₃			THF, 0°, 2.5 h	(83)	75
			THF, 0°, 2.5 h	(84)	75
			THF, -40 to 0°	(84)	266 ^b
			THF, 0°, 2.5 h	(92)	75
				(90)	

TABLE III. REACTIONS OF ALIPHATIC ZINC-COPPER REAGENTS WITH ALLYLIC HALIDES (Continued)^a

FG-RCu(CN)ZnX (PG-R)	Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
		THF, 0°, 2.5 h	 (95)	75
		THF, -60 to 0°, 1 h	 (91)	119
		1. BF ₃ •OEt ₂ , Ultrasound 2. CH ₂ Cl ₂ , 25°, 10 min	 (63), α:β = 9:1	568
C ₄		THF, -25 to 0°, 3 h	 I + (85) I:II = 97:3	47
		THF, -25 to 0°, 3 h	 I + (88) I:II = 96:4	47
		THF, 25°, 14 h	 I + (88) I:II = 87:13	53
		THF, 25°, 15 h	 (85) <i>E</i> : <i>Z</i> = 8:92	53
		1. BF ₃ •OEt ₂ , ultrasound 2. CH ₂ Cl ₂ , 25°, 10 min	 (63), α:β = 5:1	568
		(—)	 (68)	176 ^c
		THF, -40 to 0°	 (69)	266 ^b
		THF, -60 to 0°, 1 h	 (68)	119
		THF, -30 to 25°, 24 h	 (82)	35
		THF, -30 to 25°, 12 h	 (79)	35
		THF, -40 to 0°, 1.5 h	 (82)	35
		THF, -78°, 4 h	 (98)	569
		THF, -78°, 4 h	 (82)	569

TABLE III. REACTIONS OF ALIPHATIC ZINC-COPPER REAGENTS WITH ALLYLIC HALIDES (Continued)^a

FG-RCu(CN)ZnX (FG-R)	Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.																				
		THF, -78°, 4 h	(40) + (40)	569																				
		THF, -78 to 25°, 12 h	(91)	570																				
		THF, -78 to 25°, 12 h	(35)	570																				
C ₅ 		THF, -78 to 25°	(86)	78																				
		THF, DMAC, 60°, 3 h	(89)	141																				
		THF, DMAC, 60°, 1 h	(82)	141																				
		THF, DMAC, 60°, 1 h	I + II	141																				
			<table border="1"> <thead> <tr> <th>R¹</th> <th>R²</th> <th>I + II</th> <th>I:II</th> </tr> </thead> <tbody> <tr> <td>Me</td> <td>OTs</td> <td>(50)</td> <td>72:28</td> </tr> <tr> <td>Ph</td> <td>OTs</td> <td>(80)</td> <td>87:13</td> </tr> <tr> <td>Ph</td> <td>Cl</td> <td>(99)</td> <td>87:13</td> </tr> <tr> <td>Ph</td> <td>Br</td> <td>(93)</td> <td>88:12</td> </tr> </tbody> </table>	R ¹	R ²	I + II	I:II	Me	OTs	(50)	72:28	Ph	OTs	(80)	87:13	Ph	Cl	(99)	87:13	Ph	Br	(93)	88:12	
R ¹	R ²	I + II	I:II																					
Me	OTs	(50)	72:28																					
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Ph	Cl	(99)	87:13																					
Ph	Br	(93)	88:12																					
		THF, DMAC, 60°, 1 h	(80)	141																				
		THF, DMAC, 60°, 1 h	(89)	141																				
		DMF, Et ₂ O, 25°, 16 h	(59)	140 ^d																				
		CuCl, 25°		571																				
	X		<table border="1"> <thead> <tr> <th>S_N2' : S_N2</th> <th></th> </tr> </thead> <tbody> <tr> <td>97:3</td> <td>(68)</td> </tr> <tr> <td>96:4</td> <td>(91)</td> </tr> <tr> <td>98:2</td> <td>(90)</td> </tr> <tr> <td>99:1</td> <td>(95)</td> </tr> </tbody> </table>	S _N 2' : S _N 2		97:3	(68)	96:4	(91)	98:2	(90)	99:1	(95)											
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97:3	(68)																							
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99:1	(95)																							

TABLE III. REACTIONS OF ALIPHATIC ZINC-COPPER REAGENTS WITH ALLYLIC HALIDES (Continued)^d

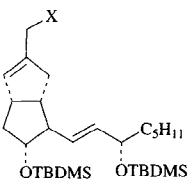
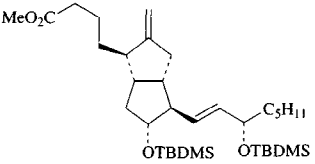
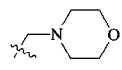
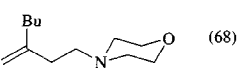
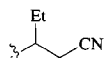
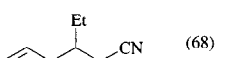
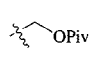
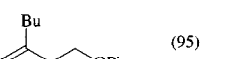
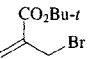
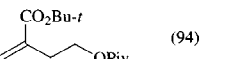
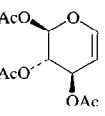
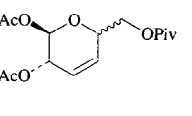
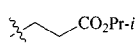

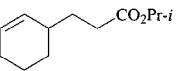
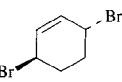
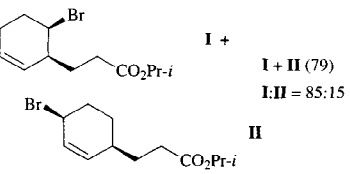
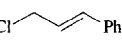
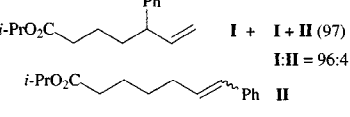
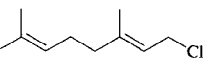
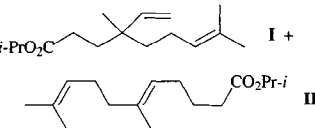
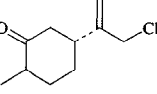
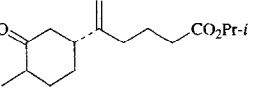
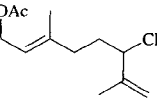
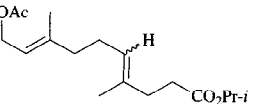
FG-RCu(CN)/ZnX (FG-R)	Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
	 X OP(S)(OEt) ₂ OP(O)(OEt) ₂ OP(O)(OMe) ₂ OP(O)(OEt) ₂	CuCl, 25°	 S _N 2' : S _N 2 88:12 (84) 87:13 (86) 86:14 (96) 84:16 (95)	571
502		THF, -40 to 0°, 12 h	 (68)	266 ^b
C ₆		THF, -78 to 0°	 (68)	180 ^c
		THF, -40 to 25°, 0.5 h	 (95)	58
		THF, -40 to 25°, 0.5 h	 (94)	58
		1. BF ₃ •OEt ₂ , ultrasound 2. CH ₂ Cl ₂ , 25°, 10 min	 (29), α:β = 4:1	568
		DMF, Et ₂ O, 25°, 1 h	 (93)	140 ^d
		DMF, Et ₂ O, 25°, 1 h	 I + II (79) I:II = 85:15	140 ^d
		DMF, Et ₂ O, 25°, 1 h	 I + II (97) I:II = 96:4	140 ^d
503		DMF, Et ₂ O, 25°, 1 h	 I + II (81), I:II = 88:12	140 ^d
		DMF, Et ₂ O, 25°, 1 h	 (87)	140 ^d
		DMF, Et ₂ O, 25°, 1 h	 (72)	140 ^d

TABLE III. REACTIONS OF ALIPHATIC ZINC-COPPER REAGENTS WITH ALLYLIC HALIDES (Continued)^a

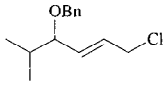
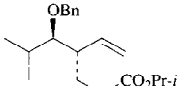
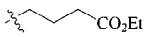
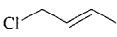
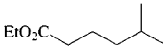
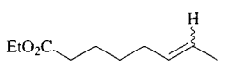
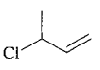
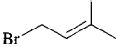
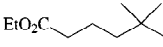
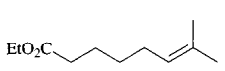
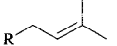
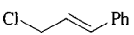

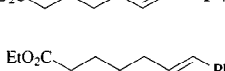
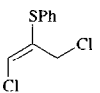
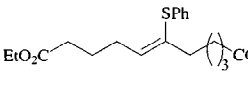
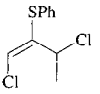
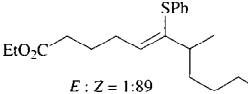
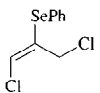
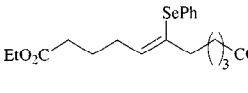
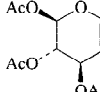
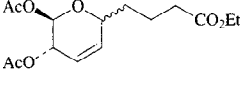
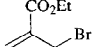
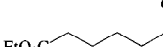
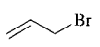
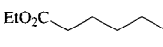
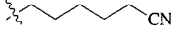

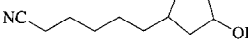
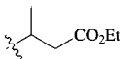
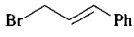
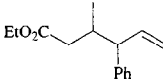
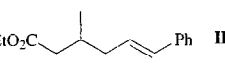
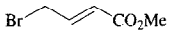
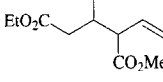
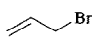
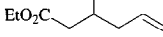
FG-RCu(CN)ZnX (FG-R)	Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
		CuBr•SMe ₂ , THF, -70 to 25°, 1 h	 (73)	323 ^d
		THF, 0°, 0.5 h	 I +  I + II (83) I:II = 96:4	368
		THF, 0°, 0.5 h	II (87)	120
		THF, 0°, 1 h	 I +  I + II (88) I:II = 98:2	120
		THF, DMAC, 60°, 1 h	I + II R I + II I:II Br (91) 83:17 TsO (95) 73:27	141
		THF, 0°, 1 h	 I +  I + II (86) I:II = 93:7	120
		THF, 25°, 18 h	 (88) E:Z = 21:79	53
		THF, 25°, 12 h	 (89) E:Z = 1:89	53
		THF, 25°, 7 h	 (89) E:Z = 20:80	53
		1. BF ₃ •OEt ₂ , ultrasound 2. CH ₂ Cl ₂ , 25°, 10 min	 (87) α:β = 5:1	568
		THF, -40 to 0°	 (71)	176 ^c , 567 ^c
		(→)	 (74)	176 ^c
		THF, -78°, 4 h	 (78)	569
		THF, DMAC, 25°, 12 h	 I +  I + II (85) I:II = 86:14	141
		THF, DMAC, 25°, 12 h	 (79)	141
		THF, -78 to 0°	 (77)	178 ^c

TABLE III. REACTIONS OF ALIPHATIC ZINC-COPPER REAGENTS WITH ALLYLIC HALIDES (Continued)^a

FG-RCu(CN)ZnX (FG-R)	Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
		THF, -78 to 0°, 0.5 h	 (95)	59, 60
		THF, 0°, 0.5 h	 I + II (94) I:II = 98:2	120
		THF, -40 to 0°, 12 h	 (76)	266 ^b
		THF, -80 to 25°, 2 h	 (82)	240 ^c , 242 ^c
		THF, -78 to 25°, 4 h	 (92)	90
		THF, -78 to 25°, 4 h	 (79)	90
		THF, -78 to 0°, 6 h	 (90) E : Z = 8:92	53
		THF, -78 to 0°, 2 h	 (56)	338 ^c
		THF, -60 to 0°, 1 h	 (71)	119
		THF, -78 to 0°, 1 h	 (86) cis:trans = 14:86	76
C₇ 		THF, 0°, 0.5 h	 I + II (91) I:II = 97:3	120
		THF, 0°, 0.5 h	 I + II (87) I:II = 3:97	120
		THF, 0°, 0.5 h	 I + II (87) I:II = 98:2	120
		THF, -78 to -10°, 12 h	 (88)	64
		THF, -78 to -10°, 1 h	 (90)	61

TABLE III. REACTIONS OF ALIPHATIC ZINC-COPPER REAGENTS WITH ALLYLIC HALIDES (Continued)^a

FG-RCu(CN)ZnX (FG-R)	Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
		THF, -78 to 0°, 1 h	 (76)	567 ^c
		THF, -78 to 25°, 3 h	 (66)	567 ^c
		THF, -78 to 0°, 1 h	 (95) <i>cis:trans</i> = 18:82	76
C₈ 		THF, -78 to 0°, 0.5 h	 (87)	82, 83
		THF, -78 to 25°, 14 h	 (80) <i>E:Z</i> = 70:30	53
		THF, 25°, 15 h	 (76) <i>E:Z</i> = 70:30	53
		THF, -78 to 0°, 6 h	 (70)	35
		THF, -30 to 25°, 6 h	 (74)	35
		THF, -78 to 0°, 0.5 h	 (90)	83
		THF, -78 to 0°, 1 h	 R Bu (75) CO ₂ Et (95) CO ₂ Bu- <i>t</i> (89) SO ₂ Bu- <i>t</i> (70)	83
		THF, -78 to 25°, 2 h	 (58)	572
C₉ 		THF, -78 to 0°, 0.5 h	 (75)	83
		THF, -78 to 0°, X h	 R ¹ R ² X (h) SPH CO ₂ Bu- <i>t</i> 0.5 (87) S(O)Ph CO ₂ Et 1 (76) SO ₂ Ph CO ₂ Et 0.5 (88)	82, 83 82, 83 83
		THF, -40 to 0°, 1 h	 (64)	266 ^b
		THF, -60 to 0°, 2 h	 (50)	270 ^b
		THF, -78 to 0°, 0.5 h	 (95)	59, 60

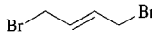
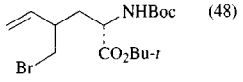

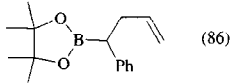

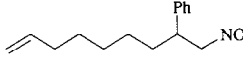

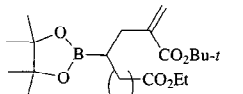

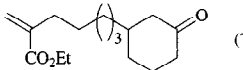

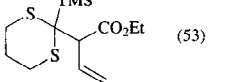

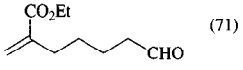

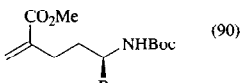

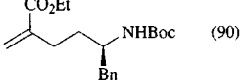

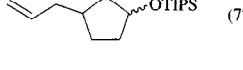

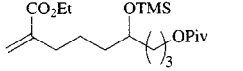

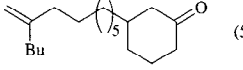

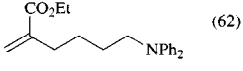

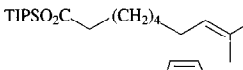

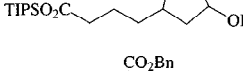

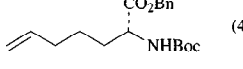

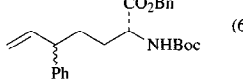

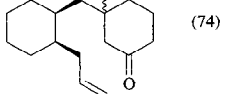

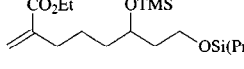
TABLE III. REACTIONS OF ALIPHATIC ZINC-COPPER REAGENTS WITH ALLYLIC HALIDES (Continued)^d

FG-RCu(CN)ZnX (FG-R)	Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
		THF, DMSO, C ₆ H ₁₄ , 0°, 0.5 h	 I + II (68) I:II = 97:3	35
		THF, DMSO, C ₆ H ₁₄ , 0°, 0.5 h	I + II (71) I:II = 70:30	35
		THF, -60 to 0°, 2 h	(70)	270 ^b
		THF, -60 to 0°, 12 h	(87)	35
		THF, -60 to 0°, 1 h	(57)	119
		THF, -60 to 0°, 0.5 h	(74)	119
		THF, -40 to 25°	(70)	119
		THF, -78 to 25°, 3 h	(83)	573 ^c
		THF, -78 to 25°, 3 h	(70)	573 ^c
C ₁₀ 		THF, -70 to -20°, 1 h	(95)	78
		THF, -80 to 25°, 2 h	(85)	240, 242
		THF, -78 to 25°, 2 h	(45)	572
		THF, -78 to 25°	(65) <i>syn:anti</i> = 19:81	42
		DMF, -55 to 0°	(82)	574
		THF, -60 to 0°, 1 h	(80)	67 ^e

TABLE III. REACTIONS OF ALIPHATIC ZINC-COPPER REAGENTS WITH ALLYLIC HALIDES (Continued)^a

FG-RCu(CN)ZnX (FG-R)	Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.	
C ₁₁			THF, -78 to 0°, 1 h	(74)	567 ^c
			THF, -60 to 0°, 12 h	(73)	567 ^c
			THF, 25°, 24 h	(70)	138
			THF, -78 to 0°, 0.5 h	(86)	59, 60
			THF, -78 to 0°, 0.5 h	(69)	59, 60
			THF	(83)	62
			THF, -78 to 25°, 0.5 h	(62)	66
			THF, -78 to 25°, 0.5 h	(68)	66
			THF, DMPU, -40 to 0°, 12 h	(75)	266 ^b
			THF, -78 to 25°	(47)	42
		THF, -78 to 25°	(47)	42	
C ₁₂			DMF, -55 to 0°	(87)	574
			THF, -78 to 0°, 0.5 h	(92)	82, 83
			THF, -78 to 0°, 0.5 h	(67)	66
			THF, -60 to 0°, 2 h	(74)	270 ^b
			THF, -25 to 0°, 3 h	I (65)	94
			THF, -25 to 0°, 3 h	I (56)	94
			THF, -25 to 0°, 3 h	(48)	94
		THF, -25 to 0°, 3 h	(55)	94	

TABLE III. REACTIONS OF ALIPHATIC ZINC-COPPER REAGENTS WITH ALLYLIC HALIDES (Continued)^a

FG-RCu(CN)ZnX (FG R)	Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
		THF, -25 to 0°, 3 h	 (48)	94
C ₁₃		(-)	 (86)	575
		THF, -78 to 25°, 0.5 h	 (64)	66
		THF, 0°, 0.5 h	 (83)	61
		THF, -78 to 25°, 0.5 h	 (70)	66
		THF, -78 to 25°, 12 h	 (53)	570 ^c
		THF, -78 to 25°, 3 h	 (71)	573 ^c
C ₁₄		THF, -25 to 0°, 3 h	 (90)	94
		THF, -30 to 25°, 6 h	 (90)	35
		THF, 0°, 1 h	 (72)	240 ^c , 242 ^c
		1. THF, 0°, 0.5 h 2. NH ₄ Cl	 (67)	576 ^c
C ₁₅		THF, -78 to 25°, 0.5 h	 (59)	66
		THF, -78 to 0°	 (62)	567 ^c
		THF, -78°, 4 h	 (87)	569
		THF, -78°, 4 h	 (80)	569
C ₁₆		THF, -30°, 3 h	 (42)	97
		THF, -30°, 3 h	 (62)	97
C ₁₇		THF, -78 to 25°, 0.5 h	 (74)	66
		1. THF, 0°, 0.5 h 2. NH ₄ Cl	 (62)	576 ^c

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TABLE III. REACTIONS OF ALIPHATIC ZINC-COPPER REAGENTS WITH ALLYLIC HALIDES (Continued)^a

	FG-RCu(CN)ZnX (FG-R)	Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
			THF, -90 to 25°, 1 h	(61) dr >97	577 ^e
C ₁₈			(-)	(77)	575
C ₁₉			THF, -78 to 0°, 1 h	(62)	567 ^c
C ₂₅			THF, -78 to 25°, 0.5 h	(75)	66
C ₂₇			THF, -78 to 0°	(58)	180 ^c

^a Unless otherwise indicated, the organozinc reagents were prepared by insertion of zinc metal into an organic halide.

^b The organozinc reagent was prepared by an insertion reaction using ICH₂ZnI.

^c The organozinc reagent was prepared by halide-zinc exchange.

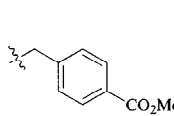
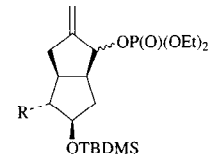
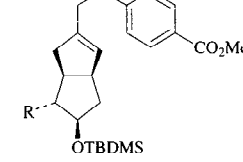
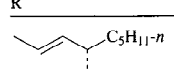
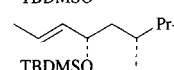
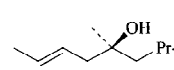
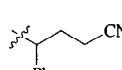
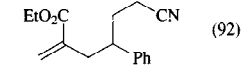
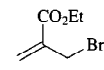
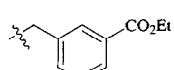
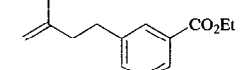
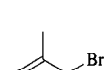
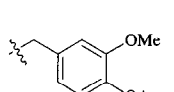
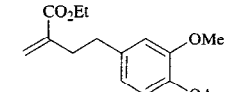
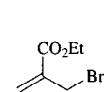
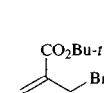
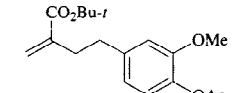
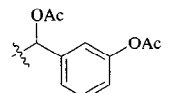
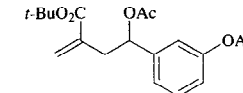
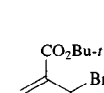
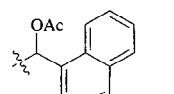
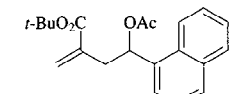
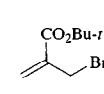
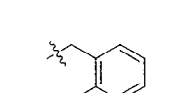
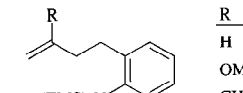
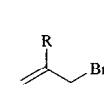
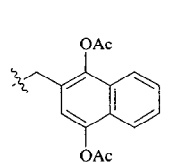
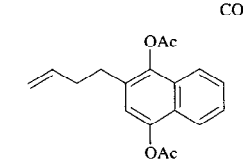
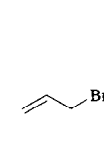
^d The organozinc reagent was prepared by ultrasonic irradiation of an ether solution of (ethoxycyclopropyloxy)trimethylsilane and zinc chloride.

^e The organozinc reagent was prepared by a transmetalation reaction.

TABLE IV. REACTIONS OF BENZYLIC ORGANOZINC-COPPER REAGENTS WITH ALLYLIC HALIDES^a

	FG-RCu(CN)ZnX (FG-R)	Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₅			THF, -40 to 0°, 12 h	 X O (74) S (96)	266 ^b
C ₇			THF, -20°, 1 h	(95)	51
			THF, -20°, 12 h	(86)	103
			THF, -78 to -20°, 12 h	(95)	50
C ₈			THF, -78 to 0°	(97)	51
C ₉			THF, -40 to 0°, 12 h	(93)	266 ^b
			THF, -78 to 20°, 0.5 h	(91)	59, 60

TABLE IV. REACTIONS OF BENZYLIC ORGANOZINC-COPPER REAGENTS WITH ALLYLIC HALIDES (Continued)^a

FG-RCu(CN)ZnX (FG-R)	Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
		THF, -78 to -20°	 (92)	578
	R			
	 TBDMSO		(92)	
	 TBDMSO		(88)	
	 Pr-n		(88)	
C ₁₀		THF, DMSO, -78 to 0°	 (92)	51, 76
				
		THF, -70 to 0°, 2 h	 (87)	51
				
		THF, -20°, 12 h	 (82)	103
				
		THF, -70 to -20°, 12 h	 (98)	50
C ₁₁		THF, -15°, 2 h	 (89)	59, 60
				
C ₁₃		THF, -10°, 2 h	 (71)	59, 60
				
		THF, -78 to 0°, 1 h	 (86)	77
				
			R	
			H (81)	
			OMOM (81)	
			CH ₂ OPh (93)	
			CO ₂ Bu-t (84)	
C ₁₅		THF, -78 to 0°, 3 h	 (82)	51
				

^a Unless otherwise indicated, the organozinc reagents were prepared by insertion of zinc metal into an organic halide.^b The organozinc reagent was prepared by an insertion reaction using ICH₂ZnI.

TABLE V. REACTIONS OF ALKENYL OR AROMATIC ZINC-COPPER REAGENTS WITH ALLYLIC HALIDES^a

	FG-RCu(CN)ZnX (FG-R)	Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₄			THF, -60 to 0°, 1 h		579 ^b
			THF, -60 to 0°, 1 h		579 ^b
C ₅			THF, -78 to 0°, 1 h		209 ^b
C ₆			THF, DMF, -78 to 0°, 1 h		48
			THF, -60 to 0°, 1 h		579 ^b
					(88)
			THF, -78 to 0°, 1 h		209 ^b
			THF, -60 to 0°, 1 h		87, 88
			THF, -60 to 0°, 2 h		567
C ₇			THF, DMF, -78 to 0°, 1 h		48
			THF, DMF, -78 to 0°, 1 h		48
C ₈			THF, TMEDA		156 ^c
					(41)
			THF, DMF, 30°		578
					(92)
					(88)
					(88)
			THF, -60 to 0°		579 ^b
C ₉			THF, DMF, 78 to 0°, 1 h		48

TABLE V. REACTIONS OF ALKENYL OR AROMATIC ZINC-COPPER REAGENTS WITH ALLYLIC HALIDES (Continued)^a

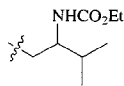
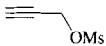
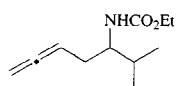

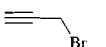

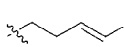
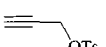
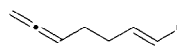
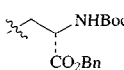
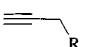
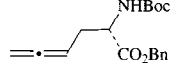
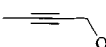
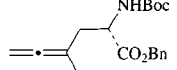
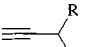
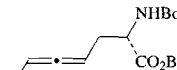
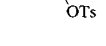
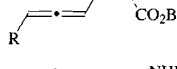
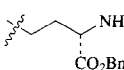
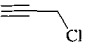
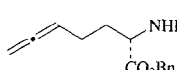
FG-RCu(CN)ZnX (FG-R)	Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.									
		THF, -78 to 0°, 1 h	(71)	87, 88									
		THF, 0°, 0.5 h		I (93) 120									
		THF, 0°, 0.5 h	+ I (86), 80:20	120									
C ₁₁ 		1. THF, -78 to 0°, 0.5 h 2. H ₂ O ₂ , NaOAc	(59)	62									
C ₁₂ 		1. THF, -78 to 0°, 0.5 h 2. H ₂ O ₂ , NaOAc	(69)	62									
C ₁₃ 		THF, X, 78 to 0°, 1 h	<table border="1" style="display: inline-table; vertical-align: middle;"> <tr> <td>R</td> <td>X</td> <td></td> </tr> <tr> <td>Ph</td> <td>DMAC</td> <td>(83)</td> </tr> <tr> <td>C₆H₁₁</td> <td>DMF</td> <td>(72)</td> </tr> </table>	R	X		Ph	DMAC	(83)	C ₆ H ₁₁	DMF	(72)	48
R	X												
Ph	DMAC	(83)											
C ₆ H ₁₁	DMF	(72)											

^a Unless otherwise indicated, the organozinc reagents were prepared by insertion of zinc metal into an organic halide.^b The organozinc reagent was prepared by a transmetalation reaction.^c The organozinc reagent was prepared by Nakamura's method (ref. 140).

TABLE VI. REACTIONS OF PROPARGYLIC HALIDES/TOSYLATES WITH ORGANOZINC-COPPER REAGENTS^a

	FG-RCu(CN)ZnX (FG-R)	Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₄			THF, 0 to 25°, 1.5 h	 (84)	122
			THF, 0°, 1 h	 (67)	35
C ₆			THF, -78 to 25°, 1 h	 (95)	122
			THF, -78 to 25°, 1 h	 (92)	122
C ₇			THF, -78 to 25°, 1 h	 (97)	122
C ₈			THF, 0 to 25°, 1.5 h	 (93)	122
			THF, 0 to 25°, 1.5 h	 (93)	122

TABLE VI. REACTIONS OF PROPARGYLIC HALIDES/TOSYLATES WITH ORGANOZINC-COPPER REAGENTS (Continued)^a

FG-RCu(CN)ZnX (FG-R)	Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
		THF, 0°, 1 h	 (84)	35
C ₉ 		THF, -60 to -10°, 12 h	 (68)	567 ^b
C ₁₃ 		THF, -78 to -30°, 7 h	 (68)	573 ^c
C ₁₅ 		THF, 0°, 3 h	 (55)	94
		THF, 0°, 3 h	 (68)	100
		THF, 0°, 3 h	 (81)	100
		THF, 0°, 3 h	 (51)	100
C ₁₆ 		THF, -30°, 3 h	 (36)	97, 580

^a Unless otherwise indicated, the organozinc reagents were prepared by insertion of zinc metal into an organic halide.^b The organozinc reagent was prepared by a transmetallation reaction.^c The organozinc reagent was prepared by Nakamura's method (ref. 140).

TABLE VII. REACTIONS OF CATIONIC METAL COMPLEXES WITH ORGANOZINC-COPPER REAGENTS (Continued)^a

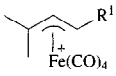
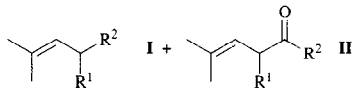







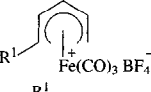
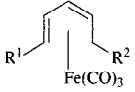


FG-RCu(CN)ZnX (FG-R)	Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
<i>B. Cationic Iron Complexes</i>				
				
$\frac{R^2}{\text{---}}$	$\frac{R^1}{\text{---}}$		$\frac{I+II}{\text{---}} \quad \frac{I:II}{\text{---}}$	
	H	THF, 0°, 3 h	(45) 100:0	69
	H	THF, 0°, 3 h	(65) 100:0	69
	H	THF, 0°, 3 h	(57) 100:0	69
	H	THF, 0°, 3 h	(68) 100:0	69
	Me	THF, -10°, 3 h	(56) 1:1.8	69
	Me	THF, 0°, 3 h	(51) 1.2:1	69
	Me	THF, -10°, 3 h	(58) 1:2.9	69
				
$\frac{R^2}{\text{---}}$	$\frac{R^1}{\text{---}}$		(84)	68
	H	THF, 5 to 23°, 2 h	(84)	68
	H	THF, 5 to 23°, 2 h	(90)	68

TABLE VII. REACTIONS OF CATIONIC METAL COMPLEXES WITH ORGANOZINC-COPPER REAGENTS (Continued)^a

FG-RCu(CN)ZnX (FG-R)	Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
<i>B. Cationic Iron Complexes</i>				
<u>R²</u>	<u>R¹</u>		<u>I + II</u> <u>I:II</u>	
	H	THF, 0°, 3 h	(45) 100:0	69
	H	THF, 0°, 3 h	(65) 100:0	69
	H	THF, 0°, 3 h	(57) 100:0	69
	H	THF, 0°, 3 h	(68) 100:0	69
	Me	THF, -10°, 3 h	(56) 1:1.8	69
	Me	THF, 0°, 3 h	(51) 1.2:1	69
	Me	THF, -10°, 3 h	(58) 1:2.9	69
<u>R²</u>	<u>R¹</u>			
	H	THF, 5 to 23°, 2 h	(84)	68
	H	THF, 5 to 23°, 2 h	(90)	68
	H	(—)	(69)	581
	H	THF, 5 to 23°, 2 h	(95)	72
	H	THF, 5 to 23°, 2 h	(97)	68
	H	(—)	(88)	581
	Me	THF, 5 to 23°, 2 h	(75)	68
	Me	THF, 5 to 23°, 2 h	(82)	72
	Me	THF, 5 to 23°, 2 h	(82)	72
<u>R</u>				
		THF, 5 to 23°, 2 h	(99)	72
		THF, 5 to 23°, 2 h	(83)	72
		THF, MeCN, -20°, 16 h	(59)	96
		THF, MeCN, -20°, 16 h	(57)	96

TABLE VII. REACTIONS OF CATIONIC METAL COMPLEXES WITH ORGANOZINC-COPPER REAGENTS (Continued)^a

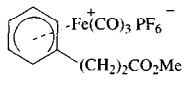
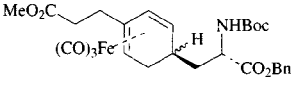
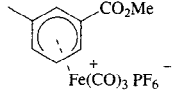
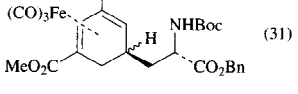
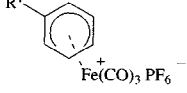
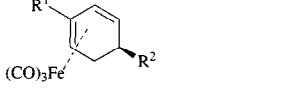
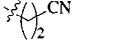
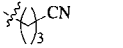
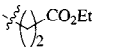
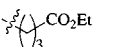
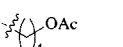
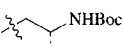
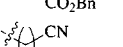
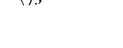
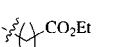
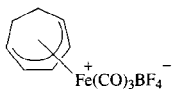
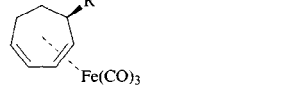
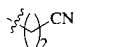
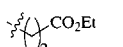
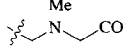

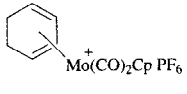
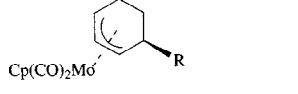
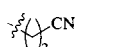
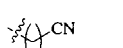
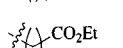
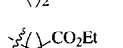
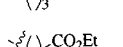
FG-RCu(CN)ZnX (FG-R)	Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
		THF, MeCN, -20°, 16 h	 (52)	96
		THF, MeCN, -20°, 16 h	 (31)	96
R^2				
	H	THF, 5 to 23°, 2 h	(78)	68
	H	THF, 5 to 23°, 2 h	(75)	68
	H	THF, 5 to 23°, 2 h	(83)	72
	H	THF, 5 to 23°, 2 h	(83)	68
	H	THF, 5 to 23°, 2 h	(60)	68
	H	THF, MeCN, -20°, 16 h	(68)	96
	OMe	THF, 25°, 2 h	(70)	72
	OMe	THF, 5 to 25°, 2 h	(76)	68
	OMe	THF, MeCN, -20°, 16 h	(57)	96
R				
		THF, 25°, 2 h	(50)	71
		THF, 25°, 2 h	(65)	71
		THF, 25°, 2 h	(93)	71
		THF, 25°, 2 h	(93)	71
<i>C. Cationic Molybdenum Complexes</i>				
R				
		THF, 0°, 5 h	(41)	70
		THF, 0°, 5 h	(58)	70
		THF, 0°, 5 h	(33)	70
		THF, 0°, 5 h	(90)	70
		THF, 0°, 5 h	(90)	70

TABLE VII. REACTIONS OF CATIONIC METAL COMPLEXES WITH ORGANOZINC-COPPER REAGENTS (*Continued*)^a

FG-RCu(CN)ZnX (FG-R)	Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.	
		THF, 0°, 5 h	(51)	70	
		THF, 0°, 5 h	(57)	70	
<i>D. Cationic Manganese Complexes</i>					
R					
		Et ₂ O, -5°, 2 h	(50)	582	
		Et ₂ O, -5°, 2 h	(69)	582	
		Et ₂ O, -5°, 2 h	(63)	582	
		Et ₂ O, -5°, 2 h	(58)	582	
		Et ₂ O, -5°, 2 h	(69)	582	
		Et ₂ O, -5°, 2 h	(67)	582	

^a The organozinc reagents were generated by direct insertion of zinc metal into organic halides.

TABLE VIII. REACTIONS OF ALKENYL/AROMATIC HALIDES AND SULFONES WITH ZINC-COPPER REAGENTS^a


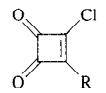
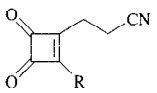
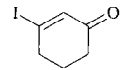
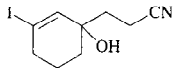
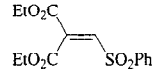
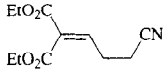
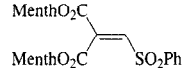
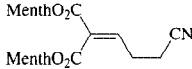
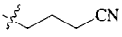
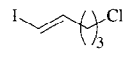
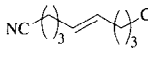
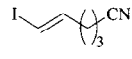
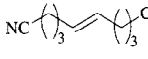
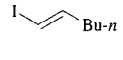
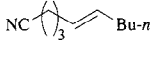
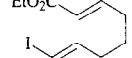
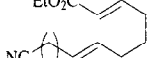
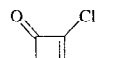
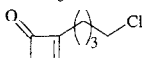
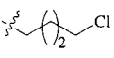
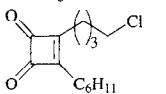
FG-RML _n (FG-R)	Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.												
<i>A. Reactions with organozinc cuprates (ML_n = Cu(CN)ZnX)</i>																
C ₃ 		THF, -78 to 0°, X h	 <table border="1" style="display: inline-table; vertical-align: middle;"> <tr> <td>R</td> <td>X</td> <td></td> </tr> <tr> <td>(CH₂)₂CN</td> <td>2</td> <td>(83)</td> </tr> <tr> <td>Bu-<i>t</i></td> <td>1</td> <td>(77)</td> </tr> <tr> <td>C₆H₁₁</td> <td>1</td> <td>(65)</td> </tr> </table>	R	X		(CH ₂) ₂ CN	2	(83)	Bu- <i>t</i>	1	(77)	C ₆ H ₁₁	1	(65)	329
	R	X														
	(CH ₂) ₂ CN	2	(83)													
	Bu- <i>t</i>	1	(77)													
C ₆ H ₁₁	1	(65)														
	THF, -30°, 2 h	 (89)	52													
	THF, -78 to -30°, 2 h	 (83)	57, 328													
	THF, -30°, 2 h	 (67)	328													
C ₄ 		NMP, 60°, 12 h	 (77)	330												
		NMP, 60°, 12 h	 (82)	330												
		NMP, 60°, 12 h	 (72)	330												
		NMP, 60°, 12 h	 (65)	330												
		NMP, 60°, 12 h	 (65)	330												
	THF, -78 to 0°, 1 h	 (57)	329													

TABLE VIII. REACTIONS OF ALKENYL/AROMATIC HALIDES AND SULFONES WITH ZINC-COPPER REAGENTS (Continued)^a

FG-RML _n (FG-R)	Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
		THF, -30°, 2 h	 (84)	52, 64 ^b
C ₅		THF, -78 to -30°, 2 h	 (84)	57, 328
		THF, -60 to -30°, 1 h	 (88)	78
		THF, -30°, 3 h	 (79)	52
		THF, -30°, 2 h	 (88)	57, 328
		DMF, 25°, 12 h	 Z (95) E (79)	583
		DMF, 25°, 12 h	 Z (70) E (89)	583
		DMF, 25°, 12 h		583
C ₆		DMA, 25°, 24 h ultrasound	 (60)	584
		THF, -78 to 0°, 1 h	 (79)	329
		THF, -78 to -20°, 2 h	 (70)	209 ^c
		THF, -15 to 5°, 12 h	 (97)	58, 60
		THF, -30 to 5°, 14 h	 (97)	60
		THF, -78 to -60°, 2 h	 (74)	60
		THF, -78 to 10°, 48 h	 (40)	338 ^c
		THF, -78 to 0°, X h	 R X (CH ₂) ₃ CO ₂ Et 2 (83) Bu- <i>t</i> 1 (77) C ₆ H ₁₁ 1 (65)	329
		THF, -30°, 2 h	 R Et (90) Pr- <i>i</i> (82) C ₆ H ₁₁ (74)	57, 328

TABLE VIII. REACTIONS OF ALKENYL/AROMATIC HALIDES AND SULFONES WITH ZINC-COPPER REAGENTS (Continued)^a

FG-RML _n (FG R)	Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
		THF, -30°, 2 h	(87)	328
		THF, -30°, 2 h	(74)	328
C ₇		THF, -78 to -30°, 4 h	(86)	90
		THF, -78 to -30°, 2 h	(46)	48
		NMP, 60°, 12 h	(76)	330
		THF, DMF, -78 to 0°, 1 h	(85)	51
		THF, -78 to 0°, 2 h	(89)	329
		THF, -78 to 0°, 2 h	(67)	329
		THF, -10°, 12 h	(86)	103
C ₈		THF, -78 to -30°, 4 h	(95)	90
		THF, -78 to -30°, 12 h	(84)	50, 51
		THF, -30°, 2 h	(40)	57
		THF, -78°, 0.5 h	(80)	60
		NMP, 60°, 12 h	(70)	330
		THF, -30°, 2 h	(88)	57
		THF, -30 to 25°, 6 h	(75)	35
C ₉		THF, -78 to -30°, 23 h	(93)	83
		THF, -78 to -30°, 5 h	(76)	573 ^c

TABLE VIII. REACTIONS OF ALKENYL/AROMATIC HALIDES AND SULFONES WITH ZINC-COPPER REAGENTS (*Continued*)^a

FG-RML _n (FG-R)	Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
		THF, -30 to 5°, 16 h	(70)	87, 88
		THF, 42°, 8 h	(72)	60
		THF, -78 to -20°, 2 h	(89)	76
		NMP, 60°, 12 h	(87)	330
		NMP, 60°, 12 h	(77)	330
		NMP, 60°, 12 h	(50)	330
		THF, -78 to 25°, 12 h	(86)	82, 83
		THF, -78 to -25°, 12 h	(85)	82, 83
C ₁₀		THF, -30°, 2 h	(74)	57
		THF, -78 to 0°, 2 h	(72)	329
		THF, -78 to 25°, 12 h	(88)	82, 83
		THF, -78 to -20°, 12 h	(97)	77
		THF, -78 to 25°, 15 h	(64)	66
		THF, -78 to -20°, 7 h	(81)	573 ^c
		THF, -78 to -30°, 12 h	(85)	103
C ₁₁		THF, -30°, 10 h	(82)	242 ^c
		THF, -78 to -60°, 2 h	(74)	60

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TABLE IX. REACTIONS OF ZINC-COPPER ORGANOMETALLICS WITH 1-HALOALKYNES^a

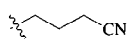
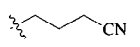
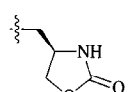
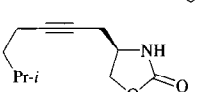
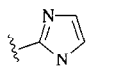
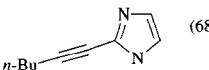
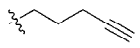
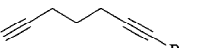
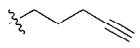
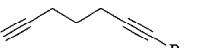
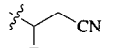
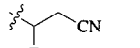

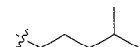
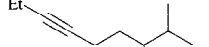
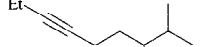
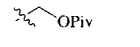

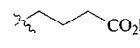
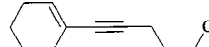
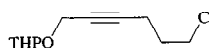

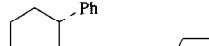
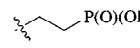
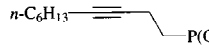
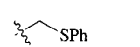
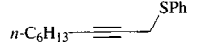
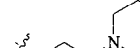


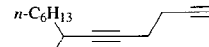
	FG-RCu(CN)ZnX (FG-R)	Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.		
540	C ₄		Br-C≡C-C ₆ H _{13-n}	THF, -78 to -55°, 18 h	NC-CH ₂ -CH ₂ -CH ₂ -C≡C-C ₆ H _{13-n} (81)	55	
			Br-C≡C-Cyclohexyl	THF, -78 to -55°, 18 h	NC-CH ₂ -CH ₂ -CH ₂ -C≡C-Cyclohexyl (79)	55	
		I-C≡C-CH ₂ -CH ₂ -Pr- <i>i</i>	THF, -30 to 0°, 6 h	 (96)	35		
		Br-C≡C-Cyclohexyl	THF, -78 to -55°, 18 h	Cl-CH ₂ -CH ₂ -CH ₂ -C≡C-Cyclohexyl (81)	55		
		I-C≡C-Bu- <i>n</i>	THF, -60 to -45°, 48 h	 (68)	119		
		C ₅		I-C≡C-Bu- <i>n</i>	THF, -60 to -30°, 1 h	 (60)	78
			I-C≡C-Bu- <i>n</i>	THF, -55°, 48 h	 (81)	87, 88	
	541	C ₆		Br-C≡C-Ph	THF, -78 to 0°	Ph-C≡C-CH ₂ -CH ₂ -CN (65)	178 ^b
				I-C≡C-Bu- <i>n</i>	THF, -60°, 24 h	 (92)	87, 88
			Br-C≡C-Et	THF, -60°, 2 d	 (68)	567 ^b	
I-C≡C-C ₆ H _{13-n}			THF, -30°, 3 h	 (76)	59, 60		
		Br-C≡C-C ₆ H _{13-n}	THF, -50°, 8 h	 (72)	58, 60		
			Br-C≡C-R	THF, -78 to -55°, 18 h	R-C≡C-CH ₂ -CH ₂ -CO ₂ Et	R (73) Ph (76) C ₆ H _{13-n} (76)	55
Br-C≡C-Cyclohexyl			THF, -78 to -55°, 18 h	 (74)	55		
Br-C≡C-CH ₂ -OTHP		THF, -78 to -40°, 2.5 h	 (74)	586			
		I-C≡C-O-Cyclohexyl-Ph	THF, -84 to -55°, 40 min	 (56)	327 ^c		
			Br-C≡C-C ₆ H _{13-n}	THF, -78 to -30°, 3 h	 (89)	90	
C ₇			Br-C≡C-C ₆ H _{13-n}	THF, -70 to -60°, 15 h	 (70)	82, 83	
		Br-C≡C-C ₆ H _{13-n}	THF, -60°, 4 d	 (64)	567 ^b		
C ₈		I-C≡C-C ₆ H _{13-n}	THF, -78 to -55°, 40 min	 (56)	327 ^c		

TABLE IX. REACTIONS OF ZINC-COPPER ORGANOMETALLICS WITH 1-HALOALKYNES (Continued)^a

FG-RCu(CN)ZnX (FG-R)	Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
		THF, -78 to -55°, 40 min	 (61)	327 ^c
C ₉		THF, -60°	 (77)	67
		THF, -78 to 0°, 6 h	 (86)	60
C ₁₀		THF, -53°, 2 d	 (71)	567 ^b
		THF, -78 to -55°, 18 h	 (86)	55
		THF, -78 to -20°, 4 h	 (66)	209 ^c
C ₁₁		THF, -78 to -55°, 18 h	 (75)	55
		1. THF, -30°, 17 h 2. H ₂ O ₂ , NaOAc	 (87)	62
C ₁₂		1. THF, -30°, 17 h 2. H ₂ O ₂ , NaOAc	 (86)	62
C ₁₅		THF, -78°, 3 h	 (49)	100
C ₁₇		THF, -90 to 25°, 1 h	 (53) dr >97 (40) dr >97	577 ^c

^a Unless otherwise indicated, the organozinc reagents were prepared by insertion of zinc metal into an organic halide.^b The organozinc reagent was prepared by halide-zinc exchange.^c The organozinc reagent was prepared by a transmetalation reaction.

TABLE X. COUPLING REACTIONS BETWEEN FUNCTIONALIZED ZINC REAGENTS AND ALKYL HALIDES^a

FG-RML _n (FG-R)	Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
<i>A. Reactions with Organozinc Cuprates [ML_n = Cu(MgCl)•Me₂Zn]</i>				
C ₆		THF, DMPU, -78 to 0°, 2 h		(83) 331
		THF, DMPU, -78 to 0°, 2 h		(87) 331
		THF, DMPU, -78 to 0°, 2 h		(71) 331
	<i>n</i> -C ₈ H ₁₇ I	THF, DMPU, -78 to 0°, 2 h		(72) 331
C ₇		THF, DMPU, -78 to 0°, 2 h		(93) 331
		THF, DMPU, -78 to 0°, 2 h		(81) 331
		THF, DMPU, -78 to 0°, 2 h		(74) 331
	<i>n</i> -C ₈ H ₁₇ I	THF, DMPU, -78 to 0°, 2 h		(80) 331
C ₁₁		THF, DMPU, -78 to 0°, 2 h		(77) 331
<i>B. Nickel-Catalyzed Reactions with Organozincs</i>				
C ₆		Ni(acac) ₂ , <i>p</i> -CF ₃ styrene, THF, NMP, -15°		(71) 230 ^b
C ₇		Ni(acac) ₂ , <i>p</i> -CF ₃ styrene, THF, NMP, -35°		(76) 332
		Ni(acac) ₂ , <i>p</i> -CF ₃ styrene, THF, NMP, -35°		(68) 332
		Ni(acac) ₂ , <i>p</i> -CF ₃ styrene, THF, NMP, -35°		(70) 332
		Ni(acac) ₂ , <i>p</i> -CF ₃ styrene, THF, NMP, -35°		(70) 332
		Ni(acac) ₂ , <i>p</i> -CF ₃ styrene, THF, NMP, -35°		(68) 332
		Ni(acac) ₂ , <i>p</i> -CF ₃ styrene, THF, NMP, -35°		(78) 333
		Ni(acac) ₂ , <i>p</i> -CF ₃ styrene, THF, NMP, -15°		(75) 230 ^b
		Ni(acac) ₂ , <i>p</i> -CF ₃ styrene, THF, NMP, -15°		(80) 230
		Ni(acac) ₂ , <i>p</i> -CF ₃ styrene, THF, NMP, -15°		(71) 230 ^b
C ₉		Ni(acac) ₂ , <i>p</i> -CF ₃ styrene, THF, NMP, -35°		(67) 332

TABLE X. COUPLING REACTIONS BETWEEN FUNCTIONALIZED ZINC REAGENTS AND ALKYL HALIDES (Continued)^a

FG-RML _n (FG-R)	Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
		Ni(acac) ₂ , <i>p</i> -CF ₃ styrene, THF, NMP, -15°	(72)	230 ^b
		Ni(acac) ₂ , <i>p</i> -CF ₃ styrene, THF, NMP, -15°	(75)	230 ^b
		Ni(acac) ₂ , <i>p</i> -CF ₃ styrene, THF, NMP, -15°	(72)	230 ^b

^a Unless otherwise indicated, the organozinc reagents were prepared by insertion of zinc metal into an organic halide.^b The organozinc reagent was prepared by a transmetalation reaction.

TABLE XI. ADDITION OF ZINC-COPPER REAGENTS TO ACID CHLORIDES AND ANHYDRIDES^a

	FG-RCu(CN)ZnX (FG-R)	Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₃			THF, 0°, 2 h	 R -(CH ₂) ₃ Cl (77) Ph (83) C ₆ H ₁₁ (79)	75
C ₄			THF, -20 to 0°, 3 h	(93)	47
			THF, 0°, 10 h	(71)	35
			THF, 0°, 10 h	(51)	35
C ₅			THF, -30 to 0°, 4 h	(68)	78
			THF, -45 to 25°, 4 h	(67)	78
			THF, -78 to -14°, 8 h	(93)	60
			THF, 25°, 4 h	(75)	192, 587, 131
			THF, HMPA, 0°, 6 h	(76)	140 ^b

TABLE XI. ADDITION OF ZINC-COPPER REAGENTS TO ACID CHLORIDES AND ANHYDRIDES (Continued)^a

FG-RCu(CN)ZnX (FG-R)	Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.												
		THF, HMPA, 0°, 6 h	(89)	140 ^b												
C ₆		THF, -78 to 0°	(68)	178 ^c												
-C ₆ F ₅		THF, -20 to 0°, 10 h	(89)	133												
		THF, -25°	(76)	120												
		THF, -25°	(90)	120												
		THF, -78 to -5°, 2 d	(61)	567 ^c												
		THF, -20°, 2 h	(75)	209 ^d												
		THF, 0°, 2 h	(67)	76												
		THF, 0°, 2 h	(81)	58-60												
		THF, -20°, 8 h	(82)	58-60												
		THF, -10°, 3 h	(42)	58, 60												
		THF, 0°, 5 h	(90)	58, 60												
		THF, -10 to 0°, 2 h	(81)	58, 60												
		THF, -10°, 8 h	(66)	58, 60												
		THF, -25°	(91)	120												
		DME, -25 to 0°, 3 h	(95)	120, 47												
		THF, -25°	(85)	120												
		THF, 0°, X h	<table border="1" style="display: inline-table; vertical-align: middle;"> <thead> <tr> <th>R</th> <th>X</th> <th></th> </tr> </thead> <tbody> <tr> <td>C₅H_{11-n}</td> <td>5</td> <td>(84)</td> </tr> <tr> <td>Ph</td> <td>2</td> <td>(96)</td> </tr> <tr> <td>C₆H₁₁</td> <td>5</td> <td>(86)</td> </tr> </tbody> </table>	R	X		C ₅ H _{11-n}	5	(84)	Ph	2	(96)	C ₆ H ₁₁	5	(86)	90
R	X															
C ₅ H _{11-n}	5	(84)														
Ph	2	(96)														
C ₆ H ₁₁	5	(86)														

TABLE XI. ADDITION OF ZINC-COPPER REAGENTS TO ACID CHLORIDES AND ANHYDRIDES (Continued)^a

FG-RCu(CN)ZnX (FG-R)	Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
		THF, -78 to -10°, 6 h		338 ^d
C ₇ 		THF, -20 to 0°, 10 h		133
		THF, -25°		120
		THF, -25° DMAC, 0°, 1 h	 	120 48
		THF, 25°, 1 h		588
		THF, -78 to -20°, 7 h		573 ^d
	(CF ₃ CO) ₂ O	(—)	 	156 ^e
		THF, -25°		120
		THF, -20 to 0°, 10 h		133, 209, 120
		THF, -70 to -20°, 12 h		50
		THF, 0°, 2 h	 <i>cis:trans</i> = 1:4	76
		THF, -25°		152
		THF, -10°, 12 h		240 ^d , 242 ^d
		THF, -10°, 12 h		64
C ₈ 		THF, -78 to 25°, 8 h		83

TABLE XI. ADDITION OF ZINC-COPPER REAGENTS TO ACID CHLORIDES AND ANHYDRIDES (Continued)^a

FG-RCu(CN)ZnX (FG-R)	Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.																		
	<i>n</i> -BuCOCl	THF, -25°	 (80)	120																		
	(CF ₃ CO) ₂ O	(—)	 (52)	156 ^c																		
		THF, -30°	 (80)	515																		
	C ₆ H ₁₁ COCl	THF, -70 to -20°, 8 h	 (93)	50, 51																		
	ClCOCOCI	(—)	 (77)	65																		
-SiMe ₂ Ph	RCOCl	THF, -20 to 25°, 12 h	 <table border="0"> <tr><td>R</td><td></td></tr> <tr><td><i>c</i>-C₃H₅</td><td>(85)</td></tr> <tr><td><i>c</i>-C₄H₇</td><td>(60)</td></tr> <tr><td><i>c</i>-C₆H₁₁</td><td>(70)</td></tr> <tr><td><i>n</i>-C₁₁H₂₃</td><td>(90)</td></tr> <tr><td>C₄H₉S</td><td>(81)</td></tr> <tr><td>C₄H₉O</td><td>(98)</td></tr> <tr><td>MeO₂CCH₂</td><td>(96)</td></tr> <tr><td>Cl(CH₂)₃</td><td>(70)</td></tr> </table>	R		<i>c</i> -C ₃ H ₅	(85)	<i>c</i> -C ₄ H ₇	(60)	<i>c</i> -C ₆ H ₁₁	(70)	<i>n</i> -C ₁₁ H ₂₃	(90)	C ₄ H ₉ S	(81)	C ₄ H ₉ O	(98)	MeO ₂ CCH ₂	(96)	Cl(CH ₂) ₃	(70)	589 ^d
R																						
<i>c</i> -C ₃ H ₅	(85)																					
<i>c</i> -C ₄ H ₇	(60)																					
<i>c</i> -C ₆ H ₁₁	(70)																					
<i>n</i> -C ₁₁ H ₂₃	(90)																					
C ₄ H ₉ S	(81)																					
C ₄ H ₉ O	(98)																					
MeO ₂ CCH ₂	(96)																					
Cl(CH ₂) ₃	(70)																					
			 <table border="0"> <tr><td>R¹</td><td></td></tr> <tr><td>4-Me</td><td>(90)</td></tr> <tr><td>2,4,6-Me₃</td><td>(71)</td></tr> <tr><td>4-F</td><td>(95)</td></tr> <tr><td>4-CN</td><td>(80)</td></tr> <tr><td>2-OAc</td><td>(52)</td></tr> </table>	R ¹		4-Me	(90)	2,4,6-Me ₃	(71)	4-F	(95)	4-CN	(80)	2-OAc	(52)							
R ¹																						
4-Me	(90)																					
2,4,6-Me ₃	(71)																					
4-F	(95)																					
4-CN	(80)																					
2-OAc	(52)																					
		THF, -20 to 25°, 12 h	 (53)	589 ^d																		
		THF, -20 to 25°, 12 h	 (65)	589 ^d																		
	PhCOCl	THF, 0°, 2 h	 (82)	76																		
	PhCOCl	THF, -78 to -10°, 15 h	 (79)	82, 83																		
	RCOCl	THF, -25°	 <table border="0"> <tr><td>R</td><td></td></tr> <tr><td><i>n</i>-Bu</td><td>(94)</td></tr> <tr><td>Ph</td><td>(92)</td></tr> </table>	R		<i>n</i> -Bu	(94)	Ph	(92)	120												
R																						
<i>n</i> -Bu	(94)																					
Ph	(92)																					

552

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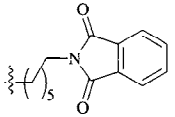

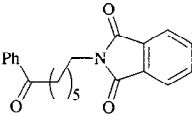
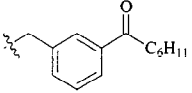

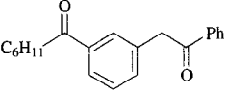
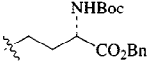

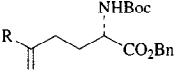
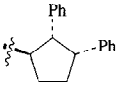

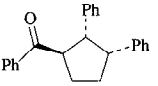
TABLE XI. ADDITION OF ZINC-COPPER REAGENTS TO ACID CHLORIDES AND ANHYDRIDES (Continued)^a

FG-RCu(CN)ZnX (FG-R)	Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
		THF, -25°	(83)	120, 48
		THF, -20 to 0°, 10 h	(68)	133
		THF, -25°	(83)	120
			(88)	120
		THF, -45 to 25°	(60)	131
		THF, -40 to 25°, 4 h	(60)	131
		THF, -70 to -20°, 12 h	(87)	82, 83
		THF, -78 to -5°, 24 h	(65)	567 ^c
		THF, 25°, 1 h	(70)	588 ^d
	$\frac{R}{Ph}$		(70)	
	<i>p</i> -MeOC ₆ H ₄		(65)	
	<i>p</i> -O ₂ NC ₆ H ₄		(80)	
	<i>n</i> -Pr		(67)	
	<i>i</i> -Pr		(67)	
	<i>t</i> -Bu		(64)	
		THF, 25°, 1 h	(58)	588 ^d
		THF, -78 to 25°, 3 h	(75)	573 ^d
		THF, -78 to 25°, 3 h	(74)	573 ^d
		THF, -60 to -20°, 8 h	(83)	51
		THF, -78 to -10°, 12 h	(93)	82, 83
		THF, -10°, 10 h	(80)	240 ^d , 242 ^d

TABLE XI. ADDITION OF ZINC-COPPER REAGENTS TO ACID CHLORIDES AND ANHYDRIDES (Continued)^d

FG-RCu(CN)ZnX (FG-R)	Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
		THF, 0°, 10 h	(80)	47
		THF, -20°, 4 h	(85)	240 ^d , 242 ^d
		THF, -25 to 0°, 3 h	(93)	47
		THF, -45 to 25°	(54)	131
C ₁₁ 		THF, 0 to 25°, 1 h	(82)	146
		THF, 0 to 5°, 12 h	(74)	79
C ₁₂ 		THF, 0°, 2 h	(68)	76
		1. THF, -20°, 14 h 2. H ₂ O	(75)	77
		1. THF, -20°, 14 h 2. H ₂ O	(73)	77
		1. THF, -20°, 14 h 2. H ₂ O	(53)	77
		1. THF, -20°, 14 h 2. H ₂ O	(80)	77
		1. THF, -20°, 14 h 2. H ₂ O	(78)	77
		1. THF, -20°, 14 h 2. H ₂ O	(94)	77
		1. THF, -20°, 14 h 2. H ₂ O	(76)	77
C ₁₃ 		1. THF, 0°, 2 h 2. H ⁺	(74)	61
		THF, 0 to 25°, 1 h	(85)	146
		THF, -78 to -20°, 7 h	(73) (72)	573 ^d

TABLE XI. ADDITION OF ZINC-COPPER REAGENTS TO ACID CHLORIDES AND ANHYDRIDES (Continued)^d

FG-RCu(CN)ZnX (FG-R)	Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.												
C ₁₄ 		THF, -10°, 10 h	 (80)	240 ^d , 242 ^d												
		THF, -60 to -20°, 12 h	 (90)	50, 51												
C ₁₆ 		THF, -30°	 <table border="0" style="display: inline-table; vertical-align: middle;"> <tr><td>R</td><td>_____</td></tr> <tr><td>Me</td><td>(52)</td></tr> <tr><td>2-C₄H₉O</td><td>(40)</td></tr> <tr><td>C₅H_{11-n}</td><td>(44)</td></tr> <tr><td>Ph</td><td>(46)</td></tr> <tr><td>C₆H₁₁</td><td>(55)</td></tr> </table>	R	_____	Me	(52)	2-C ₄ H ₉ O	(40)	C ₅ H _{11-n}	(44)	Ph	(46)	C ₆ H ₁₁	(55)	97
R	_____															
Me	(52)															
2-C ₄ H ₉ O	(40)															
C ₅ H _{11-n}	(44)															
Ph	(46)															
C ₆ H ₁₁	(55)															
C ₁₇ 		THF, -90 to 25°	 (49), dr >97	577 ^d												

^a Unless otherwise indicated, the organozinc reagents were prepared by insertion of zinc metal into an organic halide.^b The organozinc reagent was prepared by ultrasonic irradiation of an ether solution of (ethoxycyclopropyloxy)trimethylsilane and zinc chloride.^c The organozinc reagent was prepared by halide-zinc exchange.^d The organozinc reagent was prepared by a transmetallation reaction.^e The organozinc reagent was prepared by Nakamura's method (ref. 140).

TABLE XII. 1,2-ADDITIONS OF ORGANOMETALLIC REAGENTS TO CARBONYL AND RELATED COMPOUNDS^a

FG-RML _n (FG-R)	Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
<i>A. Reactions of Allylic/Allenic Organozinc Halides (ML_n = ZnX)</i>				
C ₃ 	CH ₃ CHO	THF	 (78)	590
		THF	 (64)	590
		THF	 (61)	590
		THF	 (73)	590
	RCHO	THF	 <div style="display: flex; align-items: center;"> <div style="margin-right: 10px;"> $\frac{R}{o\text{-ClC}_6\text{H}_4}$ (52) $\frac{R}{p\text{-ClC}_6\text{H}_4}$ (65) $\frac{R}{\text{Ph}}$ (80) $\frac{R}{p\text{-MeC}_6\text{H}_4}$ (67) $\frac{R}{p\text{-MeOC}_6\text{H}_4}$ (62) </div> </div>	590
		THF	 <div style="display: flex; align-items: center;"> <div style="margin-right: 10px;"> $\frac{R}{\text{Me}}$ (62) $\frac{R}{\text{Ph}}$ (68) </div> </div>	590

TABLE XII. 1,2-ADDITIONS OF ORGANOMETALLIC REAGENTS TO CARBONYL AND RELATED COMPOUNDS (Continued)^a

FG-RML _n (FG-R)	Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₄ 	MeCHO	THF, -78°	(85)	591
		THF, -78°	(97)	591
		THF, -78°	I + II I + II (95), I:II = 1:3	591
		THF, -78°	(93)	591
C ₅ 		THF, 20–30°	(70)	350
C ₆ 	PhCHO	THF, 25°	(88)	347
		THF, reflux 1 h	(75)	347
		THF, reflux 1 h	(82)	347
		THF, 20–30°	(78) (75) (85)	351
		THF, reflux 1 h	(91)	347
		Et ₂ O, 25°, 1 h	(65) 3:1 mixture of diastereomers	592 ^b
		Et ₂ O, 25°, 1 h	(90)	592 ^b

TABLE XII. 1,2-ADDITIONS OF ORGANOMETALLIC REAGENTS TO CARBONYL AND RELATED COMPOUNDS (Continued)^a

FG-RML _n (FG-R)	Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.	
C ₇		Et ₂ O, 25°, 1 h	 (76) <i>syn:anti</i> = 1:1	592 ^b	
		BF ₃ •OEt ₂ , Et ₂ O, -15°, 10 min	 (66)	592 ^b	
		PhCHO	Pd(PPh ₃) ₄ , THF, reflux, 18 h	 (78) <i>cis:trans</i> = 78:22	356
		PhCHO	Pd(PPh ₃) ₄ , THF, reflux, 18 h	 (100) <i>cis:trans</i> = 66:34	356
C ₈		PhCHO	THF, 25°	 (87)	347
		RCHO	THF, -78 to 25°, 1 h	 R Me Ph (20) (37)	593 ^b
		CH ₃ CHO	THF, -78 to 25°, 1 h	 (64)	593 ^b
C ₉		Ph-CHO	(—)	 R Me Ph (77) (85)	351
		PhCHO	THF, -78 to 25°, 4 h	 (60)	296 ^c
		PhCHO	THF, reflux	 (33)	347
		PhCHO	THF, reflux	 (89)	347
C ₁₀		RCHO	THF, -78 to 25°, 4 h	 R Ph (77) <i>syn:anti</i> = 5:95 C ₆ H ₁₁ (76) <i>syn:anti</i> > 2:98	299 ^c
		PhCHO	THF, -78 to 25°, 4 h	 (67) <i>syn:anti</i> = 90:10	299 ^c
C ₁₀		RCHO	THF, DMAC, 25°, X h	 I + II R X I+II I:II Ph 2 (95) 4:1 C ₆ H ₁₁ 12 (78) 9:1	103

TABLE XII. 1,2-ADDITIONS OF ORGANOMETALLIC REAGENTS TO CARBONYL AND RELATED COMPOUNDS (Continued)^a

FG-RML _n (FG-R)	Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.															
		1. THF, 0°, 50 min 2. DMF, Bu ₄ NF		594															
C ₁₃		THF, -78 to 25°, 4 h		296 ^c															
	PhCHO	Pd(PPh ₃) ₄ , THF, reflux, 18 h		356															
	RCHO	Pd(PPh ₃) ₄ , THF, reflux, 18 h	<table border="1"> <thead> <tr> <th>R</th> <th>cis:trans</th> <th></th> </tr> </thead> <tbody> <tr> <td>Ph</td> <td>90:10</td> <td>(98)</td> </tr> <tr> <td>4-MeOC₆H₄</td> <td>77:23</td> <td>(73)</td> </tr> <tr> <td>4-MeO₂CC₆H₄</td> <td>86:14</td> <td>(14)</td> </tr> <tr> <td>4-n-BuO₂CC₆H₄</td> <td>86:14</td> <td>(64)</td> </tr> </tbody> </table>	R	cis:trans		Ph	90:10	(98)	4-MeOC ₆ H ₄	77:23	(73)	4-MeO ₂ CC ₆ H ₄	86:14	(14)	4-n-BuO ₂ CC ₆ H ₄	86:14	(64)	
R	cis:trans																		
Ph	90:10	(98)																	
4-MeOC ₆ H ₄	77:23	(73)																	
4-MeO ₂ CC ₆ H ₄	86:14	(14)																	
4-n-BuO ₂ CC ₆ H ₄	86:14	(64)																	
	Ph-CH=CH-NMe	Pd(PPh ₃) ₄ , THF, reflux, 18 h	 <table border="1"> <thead> <tr> <th>Product</th> <th>Yield (%)</th> <th>cis:trans</th> </tr> </thead> <tbody> <tr> <td>I (29)</td> <td>12</td> <td>88</td> </tr> <tr> <td>II (16)</td> <td>1</td> <td>1</td> </tr> <tr> <td>III (27)</td> <td>—</td> <td>—</td> </tr> </tbody> </table>	Product	Yield (%)	cis:trans	I (29)	12	88	II (16)	1	1	III (27)	—	—	356			
Product	Yield (%)	cis:trans																	
I (29)	12	88																	
II (16)	1	1																	
III (27)	—	—																	
C ₁₄		THF, -85°		288 ^d															
	PhCHO	THF, -85°		288 ^d															
	<i>i</i> -PrCHO	THF, -85°, 1 h		595 ^d															
		THF, -85°, 1 h		595 ^d															
C ₁₇		Pd(PPh ₃) ₄ , THF, reflux 18 h		356															
		Pd(PPh ₃) ₄ , THF, reflux 18 h		356															
	MeO ₂ C-C ₆ H ₄ -CHO	Pd(PPh ₃) ₄ , THF, reflux 18 h		356															
	MeO ₂ C-C ₆ H ₄ -CHO	Pd(PPh ₃) ₄ , THF, reflux 18 h		356															
	<i>B. Reactions of Allylic/Allenic/Propargylic Organozinc Cuprates (ML_n = Cu(CN)Zn)</i>																		
C ₆		THF, 25°		347															
C ₈		THF, -50 to -20°, 15 min		267 ^c															
		THF, -50 to -20°, 15 min		267 ^c															
C ₉		THF, -60 to 0°, 2 h		268 ^c															
C ₁₀		THF, -60 to 0°, 5 h		271 ^c															
		THF, -60 to 0°, 2 h		268 ^c															
		THF, -60 to 0°, 5 h		271 ^c															

TABLE XII. 1,2-ADDITIONS OF ORGANOMETALLIC REAGENTS TO CARBONYL AND RELATED COMPOUNDS (Continued)^a

FG-RML _n (FG-R)	Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
	PhCHO	THF, -50 to -20°, 15 min	(96)	267 ^e
	C ₆ H ₁₁ CHO	THF, -60 to 0°, 5 h	I + II (76), I:II = 4:1	271 ^e
C ₁₁ 		1. THF, 0°, 12 h 2. Pd(PPh ₃) ₄ , reflux	(92)	355
		1. THF, 0°, 12 h 2. Pd(PPh ₃) ₄ , reflux	(53)	355
		1. THF, 0°, 12 h 2. Pd(PPh ₃) ₄ , reflux	(96)	355
	PhCHO	1. THF, 0°, 12 h 2. Pd(PPh ₃) ₄ , reflux	(82)	355
	PhCOMe	1. THF, 0°, 12 h 2. Pd(PPh ₃) ₄ , reflux	(83)	355
		1. THF, 0°, 12 h 2. Pd(PPh ₃) ₄ , reflux	(58)	355
		1. THF, 0°, 12 h 2. Pd(PPh ₃) ₄ , reflux	(78)	355
C ₁₂ 		THF, -60 to 0°, 2 h	(70)	268 ^e
		THF, -50 to -20°, 15 min	(71)	267 ^e
		THF, -60 to 0°, 5 h	(68)	271 ^e
	PhCHO	THF, -60 to 0°, 5 h	I + II (85), I:II = 95:5	271 ^e
C ₁₃ 	PhCHO	THF, -60 to 0°, 5 h	I + II (78), I:II = 92:8	271 ^e
	C ₆ H ₁₁ CHO	THF, -60 to 0°, 5 h	I + II (93), I:II = 95:5	271 ^e

TABLE XII. 1,2-ADDITIONS OF ORGANOMETALLIC REAGENTS TO CARBONYL AND RELATED COMPOUNDS (Continued)^a

FG-RML _n (FG-R)	Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.																				
C ₁₄ 	PhCHO	THF, -60 to 0°, 5 h	 I + II (76) I:II = 95:5	271 ^e																				
C ₁₅ 	BnCHO	THF, -60 to 0°, 5 h	 I + II (86), I:II = 85:15	271 ^e																				
C ₁₆ 	PhCHO	THF, -60 to 0°, 5 h	 I + II <table border="1"> <thead> <tr> <th>R¹</th> <th>R²</th> <th>I + II</th> <th>I:II</th> </tr> </thead> <tbody> <tr> <td>Ph</td> <td><i>n</i>-Bu</td> <td>(85)</td> <td>98:2</td> </tr> <tr> <td><i>n</i>-Bu</td> <td>Ph</td> <td>(78)</td> <td>60:40</td> </tr> <tr> <td>C₆H₁₁</td> <td><i>n</i>-Bu</td> <td>(67)</td> <td>98:2</td> </tr> <tr> <td><i>n</i>-Bu</td> <td>C₆H₁₁</td> <td>(60)</td> <td>75:25</td> </tr> </tbody> </table>	R ¹	R ²	I + II	I:II	Ph	<i>n</i> -Bu	(85)	98:2	<i>n</i> -Bu	Ph	(78)	60:40	C ₆ H ₁₁	<i>n</i> -Bu	(67)	98:2	<i>n</i> -Bu	C ₆ H ₁₁	(60)	75:25	271 ^e
R ¹	R ²	I + II	I:II																					
Ph	<i>n</i> -Bu	(85)	98:2																					
<i>n</i> -Bu	Ph	(78)	60:40																					
C ₆ H ₁₁	<i>n</i> -Bu	(67)	98:2																					
<i>n</i> -Bu	C ₆ H ₁₁	(60)	75:25																					
		THF, -60 to 0°, 2 h	 (58)	268 ^e																				
C ₂₂ 		1. ZnI ₂ , THF, -10° 2. THF, -78°	 I (64) + II (22)	269 ^e																				
		THF, -78°	 (29)	269 ^e																				
		ZnI ₂ , THF, -10°	 (32)	269 ^e																				
C ₂₃ 	PhCHO	THF, -78°	 I (46) + II (23)	269 ^e																				

^a Unless otherwise indicated, the organozinc reagents were prepared by insertion of zinc metal into an organic halide.^b The organozinc reagent was prepared by a transmetalation reaction.^c The organozinc reagent was prepared by an electrochemical reaction.^d The organozinc reagent was prepared by halide-zinc exchange.^e The organozinc reagent was prepared by an insertion reaction using ICH₂ZnI.

TABLE XIII. 1,2-ADDITIONS OF ZINC/COPPER REAGENTS TO CARBONYL AND RELATED COMPOUNDS^a

FG-RML _n (FG-R)	Substrate	Additive	Conditions	Product(s) and Yield(s) (%)	Refs.
<i>A. Reactions of Organozinc Compounds (ML_n = ZnX)</i>					
C ₂		—	THF, -30 to 0°, 1.5 h		366 ^b
		—	THF, -30 to 0°, 1.5 h		366 ^b
C ₄		—	THF, -30 to 0°, 1.5 h		366 ^b
570		—	THF, -30 to 0°, 1.5 h		366 ^b
		—	THF, -30 to 0°, 1.5 h		366 ^b
		—	THF, -30 to 0°, 1.5 h		366 ^b
		—	THF, -30 to 0°, 1.5 h		366 ^b
		—	THF, -30 to 0°, 1.5 h		366 ^b
		—	THF, -30 to 0°, 1.5 h		366 ^b
		—	THF, -30 to 0°, 1.5 h		366 ^b
		—	THF, -30 to 0°, 1.5 h		366 ^b
		—	THF, -30 to 0°, 1.5 h		366 ^b
		—	THF, -30 to 0°, 1.5 h		366 ^b
		—	THF, -30 to 0°, 1.5 h		366 ^b
		—	THF, -30 to 0°, 1.5 h		366 ^b
		—	THF, -30 to 0°, 1.5 h		366 ^b
		—	THF, -30 to 0°, 1.5 h		366 ^b
		—	THF, -30 to 0°, 1.5 h		366 ^b
		—	THF, -30 to 0°, 1.5 h		366 ^b
		—	THF, -30 to 0°, 1.5 h		366 ^b
		—	THF, -30 to 0°, 1.5 h		366 ^b
		—	THF, -30 to 0°, 1.5 h		366 ^b
		—	THF, -30 to 0°, 1.5 h		366 ^b
		—	THF, -30 to 0°, 1.5 h		366 ^b
		—	THF, -30 to 0°, 1.5 h		366 ^b
		—	THF, -30 to 0°, 1.5 h		366 ^b
		—	THF, -30 to 0°, 1.5 h		366 ^b
		—	THF, -30 to 0°, 1.5 h		366 ^b
		—	THF, -30 to 0°, 1.5 h		366 ^b
		—	THF, -30 to 0°, 1.5 h		366 ^b
		—	THF, -30 to 0°, 1.5 h		366 ^b
		—	THF, -30 to 0°, 1.5 h		366 ^b
		—	THF, -30 to 0°, 1.5 h		366 ^b
		—	THF, -30 to 0°, 1.5 h		366 ^b
		—	THF, -30 to 0°, 1.5 h		366 ^b
		—	THF, -30 to 0°, 1.5 h		366 ^b
		—	THF, -30 to 0°, 1.5 h		366 ^b
		—	THF, -30 to 0°, 1.5 h		366 ^b
		—	THF, -30 to 0°, 1.5 h		366 ^b
		—	THF, -30 to 0°, 1.5 h		366 ^b
		—	THF, -30 to 0°, 1.5 h		366 ^b
		—	THF, -30 to 0°, 1.5 h		366 ^b
		—	THF, -30 to 0°, 1.5 h		366 ^b
		—	THF, -30 to 0°, 1.5 h		366 ^b
		—	THF, -30 to 0°, 1.5 h		366 ^b
		—	THF, -30 to 0°, 1.5 h		366 ^b
		—	THF, -30 to 0°, 1.5 h		366 ^b
		—	THF, -30 to 0°, 1.5 h		366 ^b
		—	THF, -30 to 0°, 1.5 h		366 ^b
		—	THF, -30 to 0°, 1.5 h		366 ^b
		—	THF, -30 to 0°, 1.5 h		366 ^b
		—	THF, -30 to 0°, 1.5 h		366 ^b
		—	THF, -30 to 0°, 1.5 h		366 ^b
		—	THF, -30 to 0°, 1.5 h		366 ^b
		—	THF, -30 to 0°, 1.5 h		366 ^b
		—	THF, -30 to 0°, 1.5 h		366 ^b
		—	THF, -30 to 0°, 1.5 h		366 ^b
		—	THF, -30 to 0°, 1.5 h		366 ^b
		—	THF, -30 to 0°, 1.5 h		366 ^b
		—	THF, -30 to 0°, 1.5 h		366 ^b
		—	THF, -30 to 0°, 1.5 h		366 ^b
		—	THF, -30 to 0°, 1.5 h		366 ^b
		—	THF, -30 to 0°, 1.5 h		366 ^b
		—	THF, -30 to 0°, 1.5 h		366 ^b
		—	THF, -30 to 0°, 1.5 h		366 ^b
		—	THF, -30 to 0°, 1.5 h		366 ^b
		—	THF, -30 to 0°, 1.5 h		366 ^b
		—	THF, -30 to 0°, 1.5 h		366 ^b
		—	THF, -30 to 0°, 1.5 h		366 ^b
		—	THF, -30 to 0°, 1.5 h		366 ^b
		—	THF, -30 to 0°, 1.5 h		366 ^b
		—	THF, -30 to 0°, 1.5 h		366 ^b
		—	THF, -30 to 0°, 1.5 h		366 ^b
		—	THF, -30 to 0°, 1.5 h		366 ^b
		—	THF, -30 to 0°, 1.5 h		366 ^b
		—	THF, -30 to 0°, 1.5 h		366 ^b
		—	THF, -30 to 0°, 1.5 h		366 ^b
		—	THF, -30 to 0°, 1.5 h		366 ^b
		—	THF, -30 to 0°, 1.5 h		366 ^b
		—	THF, -30 to 0°, 1.5 h		366 ^b
		—	THF, -30 to 0°, 1.5 h		366 ^b
		—	THF, -30 to 0°, 1.5 h		366 ^b
		—	THF, -30 to 0°, 1.5 h		366 ^b
		—	THF, -30 to 0°, 1.5 h		366 ^b
		—	THF, -30 to 0°, 1.5 h		366 ^b
		—	THF, -30 to 0°, 1.5 h		366 ^b
		—	THF, -30 to 0°, 1.5 h		

TABLE XIII. 1,2-ADDITIONS OF ZINC/COPPER REAGENTS TO CARBONYL AND RELATED COMPOUNDS (Continued)^a

FG-RML _n (FG-R)	Substrate	Additive	Conditions	Product(s) and Yield(s) (%)	Refs.
		TMSOTf	CH ₂ Cl ₂ , -78°, 1 h		(77) 373 ^c
		TMSOTf	CH ₂ Cl ₂ , -78°, 1 h		(60) 373 ^c
		—	THF, -40°, 3 h		(73) 596
	PhCHO	—	THF, -78°, 1 h		(68) 597 ^c
C ₇		—	THF, 0°, 2 h		(52) 372
		—	THF, 0°, 2 h		(90) 372
		—	THF, 0°, 2 h		(62) 372
		—	THF, 0°, 2 h		(40) 372
		—	THF, 0°, 2 h		(49) 372
	<i>n</i> -C ₅ H ₁₁ CHO	—	THF, 0°, 2 h		(92) 372
		—	THF, 0°, 2 h		(39) 372
	PhCHO	—	THF, 0°, 2 h		(96) 372
		—	THF, 0°, 2 h		(47) 372
		—	THF, 0°, 2 h		(97) 372
		—	THF, 0°, 2 h		(93) 372
		—	THF, 0°, 2 h		(62) 372

TABLE XIII. 1,2-ADDITIONS OF ZINC/COPPER REAGENTS TO CARBONYL AND RELATED COMPOUNDS (Continued)^a

FG-RML _n (FG-R)	Substrate	Additive	Conditions	Product(s) and Yield(s) (%)	Refs.
		BF ₃ •OEt ₂	CH ₂ Cl ₂ , -30 to 0°, 3 h	I (50) + II (3)	369, 598
		BF ₃ •OEt ₂	CH ₂ Cl ₂ , -30 to 0°, 3 h	I (37) + II (14)	369, 598
		BF ₃ •OEt ₂	CH ₂ Cl ₂ , -30 to 0°, 3 h	(36) + (15)	369, 598
		BF ₃ •OEt ₂	CH ₂ Cl ₂ , -30 to 0°, 3 h	(71) + (21)	369, 598
	PhCHO	BF ₃ •OEt ₂	CH ₂ Cl ₂ , -30 to 0°, 3 h	(73) + (23)	369, 598
	TBDPSO-CHO	BF ₃ •OEt ₂	CH ₂ Cl ₂ , -30 to 0°, 3 h	(49) + (9)	369, 598
		—	1. C ₆ H ₆ , 25°, 0.5 h 2. H ⁺	(64)	391
	RCHO	BF ₃ •OEt ₂	CH ₂ Cl ₂ , -30 to 0°, 3 h	I + II	369, 598
				R	
				Et	(41) (15)
				<i>n</i> -Pr	(52) (24)
				<i>i</i> -Pr	(43) (13)

TABLE XIII. 1,2-ADDITIONS OF ZINC/COPPER REAGENTS TO CARBONYL AND RELATED COMPOUNDS (Continued)^d

FG-RML _n (FG-R)	Substrate	Additive	Conditions	Product(s) and Yield(s) (%)	Refs.
576		TMSCl	MeCN		599 ^d
		TMSCl	MeCN		599 ^d
C ₁₀		—	THF, -78°, 1 h		597 ^c
		—	1. THF, 80° 2. H ⁺		600
C ₁₁		TMSI	MeCN, 25°, 2 h		601
C ₁₂		—	THF, C ₆ H ₁₄ , -85°, 15 h		566 ^b
		—	CH ₂ Cl ₂ , 0°, 1.5 h		247 ^b
C ₁₅		—	THF, C ₆ H ₁₄ , -85°, 15 h		566 ^b
C ₂₂		—	THF, C ₆ H ₁₄ , -85°, 15 h		566 ^b
C ₂			—		486 ^b
			—		486 ^b
B. Reactions of Organozinc Cuprates [ML _n = Cu(CN)ZnI]					
C ₂		—	DMF, 25°, ultrasound		374a

TABLE XIII. 1,2-ADDITIONS OF ZINC/COPPER REAGENTS TO CARBONYL AND RELATED COMPOUNDS (Continued)^d


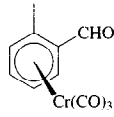
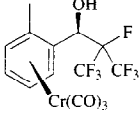
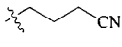
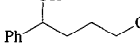
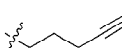
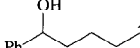
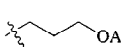
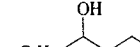
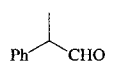
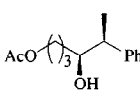
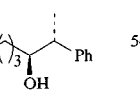
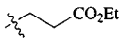
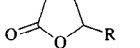

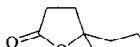
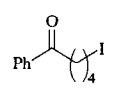
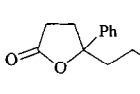
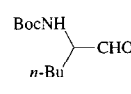
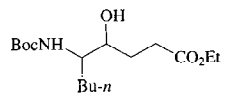
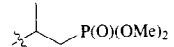
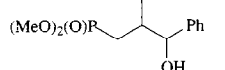
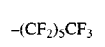
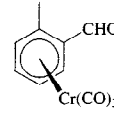
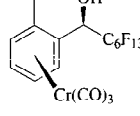
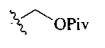
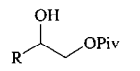
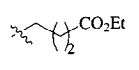
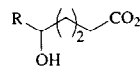
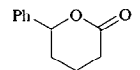
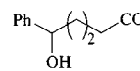
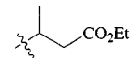
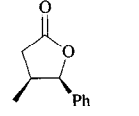
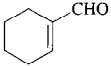
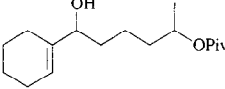
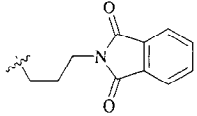
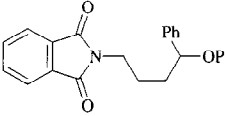
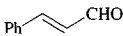
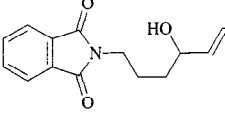
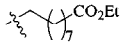
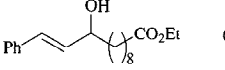
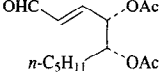
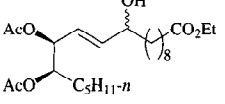
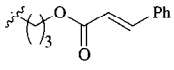
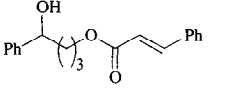
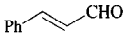
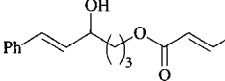

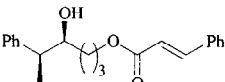
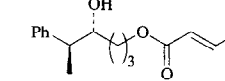
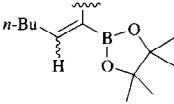
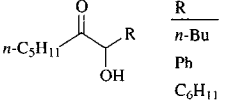

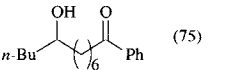
FG-RML _n (FG-R)	Substrate	Additive	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₃ 		—	DMF, 25°, ultrasound	 (100)	374a
C ₄ 	PhCHO	BF ₃ •OEt ₂	THF, -78 to -30°, 16 h	 (85)	54
C ₅ 	PhCHO	BF ₃ •OEt ₂	THF, -60 to 0°, 17 h	 (75)	78
	<i>n</i> -C ₆ H ₁₃ CHO	BF ₃ •OEt ₂	THF, -78 to -30°, 16 h	 (91)	54
	PhCHO	BF ₃ •OEt ₂	THF, -78 to 25°, 1 h	 I +  II I + II (77), I:II = 83:17	54
	RCHO	TiCl(OPr- <i>i</i>) ₃	DMAC, C ₆ H ₆ , 0°, 2 h	 R R <i>n</i> -Bu (100) Ph (95)	135 135, 368
		TiCl(OPr- <i>i</i>) ₃	DMAC, C ₆ H ₆ , 0 to 20°, 16 h	 Bu- <i>t</i> (88)	135
		TiCl(OPr- <i>i</i>) ₃	DMAC, C ₆ H ₆ , 0°, 2 h	 Ph (95)	135
		—	THF, -78 to 25°, 1 h	 (32)	367
	PhCHO	BF ₃ •OEt ₂	THF, -78 to 15°, 12 h	 (81)	90
C ₆ 		—	DMF, 25°, ultrasound	 (80)	374a
	RCHO	BF ₃ •OEt ₂	THF, -30 to -20°, 12 h	 R R <i>n</i> -C ₆ H ₁₃ (73) Ph (89)	58, 60
	RCHO	TMSCl	DMAC, PhMe, 25°, X h	 R R X <i>t</i> -Bu 72 (40) <i>p</i> -FC ₆ H ₄ 18 (88) <i>o</i> -MeOC ₆ H ₄ 3 (97) PhCH=CH 4.5 (68)	368
	PhCHO	BF ₃ •OEt ₂	THF, -78 to -30°, 16 h	 (72)	54
	PhCHO	TiCl(OPr- <i>i</i>) ₃	DMAC, C ₆ H ₆ , 0°, 8 h	 (80)	135
	PhCHO	TiCl(OPr- <i>i</i>) ₃	DMAC, C ₆ H ₆ , 0°, 8 h	 (94)	135

TABLE XIII. 1,2-ADDITIONS OF ZINC/COPPER REAGENTS TO CARBONYL AND RELATED COMPOUNDS (Continued)^d

FG-RML _n (FG-R)	Substrate	Additive	Conditions	Product(s) and Yield(s) (%)	Refs.	
		TiCl(OPr- <i>i</i>) ₃	DMAC, C ₆ H ₆ , 0°, 8 h	 I + II (95), I:II = 83:17	135	
		TMSCl	DMAC, PhMe, 25°, 6 h	(70)	368	
		BF ₃ •OEt ₂	THF, -78 to -15°, 12 h		R n-C ₆ H ₁₃ (88) Ph (96)	90
C ₇		BF ₃ •OEt ₂	THF, -78 to -30°, 12 h		(93)	50, 51
		BF ₃ •OEt ₂	THF, 0°, 36 h	(71)		82, 83
		TMSCl	DMAC, PhMe, 60°, 6 h		R n-C ₅ H ₁₁ (22) Ph (80)	368
		BF ₃ •OEt ₂	1. THF, -78 to 25°, 14 h 2. H ₂ O ₂		(93)	76
C ₈		BF ₃ •OEt ₂	THF, -78 to -30°, 45 min		(94)	65, 64
		TiCl(OPr- <i>i</i>) ₃	DMAC, C ₆ H ₆ , 0°, 8 h		(95)	135
C ₉		TMSOTf	CH ₂ Cl ₂ , 78°, 1 h		(36)	373, 376
		—	C ₆ H ₁₄ , 0°, 12 h		(68)	236 ^b
C ₁₀		TiCl(OPr- <i>i</i>) ₃	DMAC, C ₆ H ₆ , 0°, 2 h		(76)	135
		BF ₃ •OEt ₂	THF, -70 to -20°, 12 h		(97)	51
		BF ₃ •OEt ₂	THF, -70 to -30°, 4 h		(85)	50, 51
		BF ₃ •OEt ₂	THF, -70 to -20°, 15 h		(64)	66
		BF ₃ •OEt ₂	THF, -70 to -30°, 16 h		(80)	54
		BF ₃ •OEt ₂	THF, -70 to -30°, 16 h		(77)	54

TABLE XIII. 1,2-ADDITIONS OF ZINC/COPPER REAGENTS TO CARBONYL AND RELATED COMPOUNDS (Continued)^a

FG-RML _n (FG-R)	Substrate	Additive	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₁₁		BF ₃ •OEt ₂	THF, -70 to -30°, 16 h	 (84)	54
		BF ₃ •OEt ₂	THF, -70 to -30°, 16 h	 (89)	54
		BF ₃ •OEt ₂	THF, -60 to 0°, 15 h	 (50)	79
C ₁₂		BF ₃ •OEt ₂	THF, -30°, 12 h	 (80)	371
		BF ₃ •OEt ₂	THF, -78°, 5 h	 (55) dr = 1:1	371
		BF ₃ •OEt ₂	THF, -70 to -30°, 16 h	 (93)	54
		BF ₃ •OEt ₂	THF, -70 to -30°, 16 h	 (79)	54
C ₁₃		BF ₃ •OEt ₂	THF, -70 to -30°, 16 h	 I +  II I + II (73), I:II = 85:15	54
		BF ₃ •OEt ₂	1. THF, -15°, 15 h 2. H ₂ O ₂ , NaOAc	 R n-C ₅ H ₁₁ n-Bu (74) Ph (76) C ₆ H ₁₁ (87)	62
		TiCl(OPr- <i>i</i>) ₃	DMAC, C ₆ H ₆ , 0°, 2 h	 (75)	135

^a Unless otherwise indicated, the organozinc reagents were prepared by insertion of zinc metal into an organic halide.^b The organozinc reagent was prepared by a transmetalation reaction.^c The organozinc reagent was prepared by halide-zinc exchange.^d The organozinc reagent was prepared by Nakamura's method (ref. 140).

TABLE XIV. 1,4-ADDITIONS OF ZINC/COPPER REAGENTS TO ENONES AND RELATED COMPOUNDS^d

FG-RML _n (FG-R)	Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.																					
<i>A. Reactions with Dialkylzinc and Alkylzinc Halide Reagents</i>																									
C ₄		TMSCl, THF, -78 to -10°, 12 h	NC-CH ₂ -CH ₂ -CH ₂ -Cyclohexenone (83)	64 ^b																					
		TMSBr, THF, NMP, -30 to 25°, 12 h		<table border="0"> <tr> <td></td> <td>R¹</td> <td>R²</td> <td></td> </tr> <tr> <td></td> <td>H</td> <td>Me</td> <td>(74)</td> </tr> <tr> <td></td> <td>Me</td> <td>Et</td> <td>(71)</td> </tr> <tr> <td></td> <td>H</td> <td>OBn</td> <td>(76)</td> </tr> </table>		R ¹	R ²			H	Me	(74)		Me	Et	(71)		H	OBn	(76)	180, 602				
	R ¹	R ²																							
	H	Me	(74)																						
	Me	Et	(71)																						
	H	OBn	(76)																						
		TMSBr, THF, NMP, -30 to 25°, 12 h		<table border="0"> <tr> <td></td> <td>X</td> <td></td> </tr> <tr> <td></td> <td>S</td> <td>(58)</td> </tr> <tr> <td></td> <td>O</td> <td>(73)</td> </tr> </table>		X			S	(58)		O	(73)	180 ^c											
	X																								
	S	(58)																							
	O	(73)																							
		A. TMSBr, THF, NMP, -30 to 25°, 12 h B. THF, NMP, -60 to -30°, 3 h		<table border="0"> <tr> <td></td> <td>R¹</td> <td>R²</td> <td>Cond.</td> </tr> <tr> <td></td> <td>H</td> <td>Me</td> <td>A (55)</td> </tr> <tr> <td></td> <td>Me</td> <td>Et</td> <td>A (95)</td> </tr> <tr> <td></td> <td>Me</td> <td>Me</td> <td>B (95)</td> </tr> <tr> <td></td> <td>H</td> <td>Me</td> <td>B (92)</td> </tr> </table>		R ¹	R ²	Cond.		H	Me	A (55)		Me	Et	A (95)		Me	Me	B (95)		H	Me	B (92)	180 ^c 180 ^c 602 ^c 602 ^c
	R ¹	R ²	Cond.																						
	H	Me	A (55)																						
	Me	Et	A (95)																						
	Me	Me	B (95)																						
	H	Me	B (92)																						
C ₅		TMSCl, Et ₂ O, HMPA, 0 to 25°, 3 h		(75) E : Z = 24:76 140 ^d																					
		TMSCl, Et ₂ O, HMPA, 0 to 25°, 3 h		(75) 140 ^d																					
		TMSCl, Et ₂ O, HMPA, 0 to 25°, 3 h		(73) 140 ^d																					
		TMSCl, Et ₂ O, HMPA, 0 to 25°, 3 h		(76) 140 ^d																					
		TMSCl, Et ₂ O, HMPA, 0 to 25°, 3 h		(92) 140 ^d																					
		TMSCl, Et ₂ O, HMPA, 0 to 25°, 3 h		(78) cis:trans = 28:72 140 ^d																					
		TMSCl, Et ₂ O, HMPA, 0 to 25°, 3 h		(91) 140 ^d																					
		TMSBr, THF, NMP, -30 to 25°, 12 h		(54) 180 ^c																					
		TMSBr, THF, NMP, -30 to 25°, 12 h		(58) 180																					
C ₆		TMSCl, Et ₂ O, HMPA, 25°		I + II <table border="0"> <tr> <td>R</td> <td>I+II</td> </tr> <tr> <td>SnMe₃</td> <td>(93)</td> </tr> <tr> <td>Ac</td> <td>(88)</td> </tr> <tr> <td>MOM</td> <td>(95)</td> </tr> </table> I:II = 1:1 140 ^d	R	I+II	SnMe ₃	(93)	Ac	(88)	MOM	(95)													
R	I+II																								
SnMe ₃	(93)																								
Ac	(88)																								
MOM	(95)																								

TABLE XIV. 1,4-ADDITIONS OF ZINC/COPPER REAGENTS TO ENONES AND RELATED COMPOUNDS (Continued)^a

FG-RML _n (FG-R)	Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.																				
		TMSCl, Et ₂ O, HMPA, 0 to 25°, 3 h	(93)	140 ^d																				
	TMSBr, THF, NMP, -30 to 25°, 12 h	(49)	180, 179																					
		TMSBr, THF, NMP, -30 to 25°, 12 h		<table border="1"> <tr> <td>R¹</td> <td>R²</td> <td>R³</td> <td></td> </tr> <tr> <td>H</td> <td>H</td> <td>Me</td> <td>(85) 180, 602</td> </tr> <tr> <td>H</td> <td><i>n</i>-Bu</td> <td>H</td> <td>(68) 180, 602</td> </tr> <tr> <td>H</td> <td>H</td> <td>OBn</td> <td>(86) 180</td> </tr> <tr> <td>Me</td> <td>Me</td> <td>H</td> <td>(51) 180, 602</td> </tr> </table>	R ¹	R ²	R ³		H	H	Me	(85) 180, 602	H	<i>n</i> -Bu	H	(68) 180, 602	H	H	OBn	(86) 180	Me	Me	H	(51) 180, 602
R ¹	R ²	R ³																						
H	H	Me	(85) 180, 602																					
H	<i>n</i> -Bu	H	(68) 180, 602																					
H	H	OBn	(86) 180																					
Me	Me	H	(51) 180, 602																					
		Ni(acac) ₂ , Et ₂ O, -15°, 10 min	(80)	603 ^c																				
	NMP, -30°	(74)	314 ^c																					
		NMP, -30°	(82)	314 ^c																				
		NMP, -30°	(84)	314 ^c																				
		TMSBr, THF, NMP, -30 to 25°, 12 h		<table border="1"> <tr> <td>X</td> <td></td> </tr> <tr> <td>O</td> <td>(84)</td> </tr> <tr> <td>S</td> <td>(59)</td> </tr> </table>	X		O	(84)	S	(59)	180 ^c , 179 ^c 180 ^c													
X																								
O	(84)																							
S	(59)																							
		NMP, -30°	(72)	314 ^c																				
		TMSBr, THF, NMP, -30 to 25°, 12 h	(78)	180 ^c																				
		TMSBr, THF, NMP, -30 to 25°, 12 h	(68)	180																				
		1. THF, 0 to 25° 2. H ₂ O 3. NaH, Pd(PPh ₃) ₄	(63)	358																				
		1. THF, 0 to 25° 2. H ₂ O 3. NaH, Pd(PPh ₃) ₄		<table border="1"> <tr> <td>R</td> <td></td> </tr> <tr> <td>CN</td> <td>(31)</td> </tr> <tr> <td>CO₂Et</td> <td>(78)</td> </tr> </table>	R		CN	(31)	CO ₂ Et	(78)	358													
R																								
CN	(31)																							
CO ₂ Et	(78)																							
		1. THF, 0 to 25° 2. H ₂ O 3. NaH, Pd(PPh ₃) ₄		<table border="1"> <tr> <td>R¹</td> <td>R²</td> <td></td> </tr> <tr> <td>CO₂Et</td> <td>CO₂Et</td> <td>(51)</td> </tr> <tr> <td>CN</td> <td>CO₂Et</td> <td>(51)</td> </tr> <tr> <td>CN</td> <td>CN</td> <td>(29)</td> </tr> </table>	R ¹	R ²		CO ₂ Et	CO ₂ Et	(51)	CN	CO ₂ Et	(51)	CN	CN	(29)	358							
R ¹	R ²																							
CO ₂ Et	CO ₂ Et	(51)																						
CN	CO ₂ Et	(51)																						
CN	CN	(29)																						
		1. THF, 0 to 25° 2. H ₂ O 3. NaH, Pd(PPh ₃) ₄	(83)	358																				
		1. THF, 0 to 25° 2. H ₂ O 3. NaH, Pd(PPh ₃) ₄	(75)	358																				

TABLE XIV. 1,4-ADDITIONS OF ZINC/COPPER REAGENTS TO ENONES AND RELATED COMPOUNDS (Continued)^a

FG-RML _n (FG-R)	Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
		1. THF, 0 to 25° 2. H ₂ O 3. NaH, Pd(PPh ₃) ₄		358
		TMSBr, THF, NMP, -30 to 25°, 12 h	 $\frac{n}{0}$ (60) $\frac{n}{1}$ (70)	180 ^b , 179 ^b 180 ^b
<i>B. Reactions of Organozinc Cuprates [ML_n = Cu(CN)ZnI]</i>				
C ₃ 		TMSCl, THF, -78 to 25°		75
		TMSCl, THF, -78 to 25°		75
C ₄ 		TMSCl, THF, -78 to 25°		75, 266
		TMSCl, dioxane, HMPA, 0°, 16 h		142
		TMSCl, THF, Et ₂ O, -78 to 25°, 15 h		47
		TMSCl, THF, Et ₂ O, -78 to 25°, 15 h		47
		TMSCl, dioxane, HMPA, 27°, 4 h		142
		TMSCl, dioxane, HMPA, 7°, 19 h		142
		TMSCl, THF, Et ₂ O, -78 to 25°, 15 h		47
		TMSCl, dioxane, HMPA, 7°, 10 h		142
		TMSCl, dioxane, HMPA, 7°, 5 h		142
		DMPU		176 ^b
		TMSCl, THF, -70 to 20°, 8 h		78 ^a
		THF, Et ₂ O, C ₅ H ₁₂ , -30 to 25°, 5 h	 $\frac{R}{\text{Ph}}$ (80) $\frac{R}{\text{C}_6\text{H}_{13}}$ (71)	210 ^c 210 ^c , 604 ^c
		THF, Me ₂ S, 25°, 6 h		604 ^c

TABLE XIV. 1,4-ADDITIONS OF ZINC/COPPER REAGENTS TO ENONES AND RELATED COMPOUNDS (Continued)^a

FG-RML _n (FG-R)	Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₆		TMSCl, dioxane, HMPA, 0°, 40 h	(54)	142
		THF, Et ₂ O, C ₅ H ₁₂ , -30 to 25°, 5 h	(82)	210 ^c , 604 ^c
		1. THF, -78°, 1 h 2. <i>n</i> -Bu ₄ NF, THF, 0°, 3 h	(64)	567 ^b
		TMSCl, THF, -78 to 25°, 12 h	(84), dr = 67:33	76
		TMSCl, THF, -78 to 25°, 12 h	(83), dr = 76:24	76
		BF ₃ ·OEt ₂ , THF, 38 to 25°, 45 h	(59)	60
		1. TMSCl, THF 2. HCl (1 N)	(83)	412
		THF, 25°, 8 h	(89) mixture of diastereomers	60
		THF, -78 to 25°, 10 h	(86) mixture of diastereomers	60, 59
		TMSCl, dioxane, HMPA, 27°, 5 h	(73)	142
		TMSCl, dioxane, HMPA, 27°, 1.5 h	(94)	47, 142, 120
		TMSCl, dioxane, HMPA, 27°, 23 h	(77)	142
		TMSCl, dioxane, HMPA, 27°, 3 h	(77)	142
		TMSCl, dioxane, HMPA, 7°, 1.5 h	(94)	142
		DMPU	(68)	176 ^b
		TMSCl, dioxane, HMPA, 7°, 1.5 h	(78)	142

TABLE XIV. 1,4-ADDITIONS OF ZINC/COPPER REAGENTS TO ENONES AND RELATED COMPOUNDS (Continued)

FG-RML _n (FG-R)	Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
		THF, 25°, 2 h	 (77)	240 ^c
		TMSCl, THF, -78 to 25°, 12 h	 (71)	90
		TMSCl, THF, -78 to 25°, 12 h	 (88)	90
C ₇		TMSCl, DMF, 30 to 40°	 (52)	156 ^c
		TMSCl, DMAC, DMF	 (61)	48
		TMSCl, DMF, 30 to 40°	 (35)	156 ^c
		THF, -30 to 25°, 5 h	 R Ph (90) C ₆ H ₁₁ (92)	210 ^c
		1. THF, DMF, -55°, 15 min 2. <i>o</i> -chloroanil, PhMe	 R ¹ R ² Br H (44) F H (60) H H (50) Me H (46) CO ₂ Me H (45) CO ₂ Me Me (43)	383 ^c
		1. THF, -78°, 2 h 2. O ₂	 R H (43) CN (66) Me (61) CO ₂ Me (39)	384 385 385 385
		TMSCl, THF, -70 to 25°, 12 h	 (93)	50, 51
		1. THF, -78°, 2 h 2. O ₂	 (56)	384
		TMSCl, DMF, 30 to 40°	 (54)	156 ^c
		TMSCl, THF, -78 to 25°	 (95)	410

TABLE XIV. 1,4-ADDITIONS OF ZINC/COPPER REAGENTS TO ENONES AND RELATED COMPOUNDS (Continued)^a

FG-RML _n (FG-R)	Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
		TMSCl, THF, -78 to 25°		410
		TMSCl, THF, -78 to 25°		76
		TMSCl, THF, -78 to 25°		76
		TMSCl, THF, -78 to 25°		410
		TMSCl, THF, -78 to 25°		410
		THF, -78 to 25°		410
		TMSCl, THF		411
		TMSCl, THF, -78 to 25°		410
		1. TMSCl, THF, -78 to 25°, 40 h 2. H2O2, NaOAc		61
		THF, -78 to 0°, 2 d		567 ^b
		TMSCl, DMF, 30 to 40°		156 ^c

TABLE XIV. 1,4-ADDITIONS OF ZINC/COPPER REAGENTS TO ENONES AND RELATED COMPOUNDS (Continued)^a

FG-RML _n (FG-R)	Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
		1. THF, DMF, -55°, 15 min 2. <i>o</i> -chloroanil, PhMe	 R H (57) 383 ^c , 386 ^c F (38) 383 ^c CN (29) 383 ^c Mc (46) 383 ^c	
			 R H (50) 383 ^c , 386 ^c OMe (41) 383 ^c	
				(40) 384 ^c
				(74) mixture of diastereomers 65, 66
	1. 2.	1. TMSCl, THF, -78 to -25°, 15 h 2. -78 to 25°, 0.5 h		(76) 142
				(84) 82, 83
		TMSCl, THF, -78 to 25°, 12 h		(81) 83
				(81) 83
		TMSCl, THF, -70 to -10°, 15 h		(82) 240 ^c
				(82) 240 ^c
		THF, 25°, 2 h		(71) 409 ^c
				(71) 409 ^c
		THF, -78°, 1 h		(78) 82, 83
				(78) 82, 83
		THF, Et ₂ O, C ₅ H ₁₂ , -30 to 25°, 5 h		(76) 210 ^c , 604 ^c
				(76) 210 ^c , 604 ^c
		TMSCl, THF, Et ₂ O, -78 to 25°		(94) 47
				(92) 54
		TMSCl, THF, -78 to 25°, 12 h		(92) 54
				(92) 54
		THF, -30 to 25°, 5 h		(85) 210 ^c
				(79) 210 ^c
		TMSCl, THF, -78 to 25°, 12 h		(86) mixture of diastereomers 76
				(86) mixture of diastereomers 76

TABLE XIV. 1,4-ADDITIONS OF ZINC/COPPER REAGENTS TO ENONES AND RELATED COMPOUNDS (Continued)^a

	FG-RML _n (FG-R)	Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₁₂			THF, -78°, 1 h	 (78)	409 ^c
			1. TMSCl, THF, 78 to 25°, 12 h 2. H ₂ O ₂ , NaOAc	 (76)	62
			THF, -78°, 1 h	 (86)	409 ^c
C ₁₃			TMSCl, dioxane, HMPA, 0°, 6 h	 (70)	142
			TMSCl, dioxane, HMPA, 0°, 15 h	 (71)	142
			1. TMSCl, THF, 78 to 25°, 12 h 2. H ₂ O ₂ , NaOAc	 (73)	62
			THF, -78°, 1 h	 (88)	409 ^c
			THF, -78°, 1 h	 I + II (81), <i>cis:trans</i> = 1:8	409 ^c
			TMSCl, THF	 (74)	61
			TMSCl, THF	 (57)	61
			THF, 25°, 10 h	 (86)	61
			THF, 25°, 10 h	 (95)	61

TABLE XIV. 1,4-ADDITIONS OF ZINC/COPPER REAGENTS TO ENONES AND RELATED COMPOUNDS (Continued)^a

FG-RML _n (FG-R)	Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₁₄		THF, -78 to -30°, 4 h	(75)	573 ^c
C ₁₅		TMSCl, THF, -70 to 25°, 12 h	(95)	408
		TMSCl, C ₆ H ₆ , HMPA, -20 to 25°, 14 h	$\frac{R}{H}$ (66) $\frac{R}{Me}$ (38)	491
<i>C. Copper-Catalyzed Reactions with Dialkylzinc Reagents [ML_n = Cu(CN)ZnR]</i>				
C ₄		1. TMSCl, THF, -78° 2. <i>n</i> -Bu ₄ NF	$\frac{R^1}{H} \frac{R^2}{i-Pr}$ (89) ^f $\frac{R^1}{Me} \frac{R^2}{H}$ (83)	605 ^b
C ₆		1. TMSCl, THF, -78° 2. <i>n</i> -Bu ₄ NF	(85) 10:1 mixture of diastereomers	605 ^b
C ₇		1. TMSCl, THF, -78° 2. <i>n</i> -Bu ₄ NF	(81) 7:1 mixture of diastereomers	605 ^b
		1. TMSCl, THF, -78° 2. <i>n</i> -Bu ₄ NF	(72)	605 ^b
		1. TMSCl, THF, -78° 2. <i>n</i> -Bu ₄ NF	(83) 7:1 mixture of diastereomers	605 ^b
C ₈		1. TMSCl, THF, -78° 2. <i>n</i> -Bu ₄ NF	(90)	605 ^b
		1. TMSCl, THF, -78° 2. <i>n</i> -Bu ₄ NF	(77)	605 ^b
C ₁₀		1. TMSCl, THF, -78° 2. <i>n</i> -Bu ₄ NF	(85)	605 ^b
C ₁₆		1. TMSCl, THF, -78° 2. <i>n</i> -Bu ₄ NF	(74)	605 ^b

^a Unless otherwise indicated, the organozinc reagents were prepared by insertion of zinc metal into an organic halide.^b The organozinc reagent was prepared by halide-zinc exchange.^c The organozinc reagent was prepared by a transmetalation reaction.^d The organozinc reagent was prepared by ultrasonic irradiation of an ether solution of (ethoxycyclopropyloxy)trimethylsilane and zinc chloride.^e The organozinc reagent was prepared by Nakamura's method (ref. 140).^f The *anti:syn* ratio was 9:1.

TABLE XV. BF₃•OEt₂ MEDIATED 1,4-ADDITIONS OF ZINC CUPRATES TO ENONES^a

	FG-RCu(CN)ZnI (FG-R)	Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₄			BF ₃ •OEt ₂ , THF, -78 to -30°	 (88)	52
			BF ₃ •OEt ₂ , THF, -30 to 0°, 5 h	 (81)	52
			BF ₃ •OEt ₂ , THF, -30 to 0°, 5 h	 (94) mixture of diastereomers	52
C ₅			BF ₃ •OEt ₂ , THF, -78 to -30°	 (87)	52
			BF ₃ •OEt ₂ , TMSCl, THF, -30 to 25°, 13 h	 (53)	131
C ₆			BF ₃ •OEt ₂ , THF, -30°, 3 d	 (71)	58
			BF ₃ •OEt ₂ , Et ₂ O, -15°, 10 min	 (34)	603 ^b
			BF ₃ •OEt ₂ , THF, -78 to -30°	 (88)	52
			BF ₃ •OEt ₂ , TMSCl, THF, -78 to 0°, 5 h	 (74)	120
			BF ₃ •OEt ₂ , THF, -30 to 0°, 16 h	 (94)	52
			BF ₃ •OEt ₂ , TMSCl, THF, -78 to 0°, 5 h	 (77)	120
C ₉			BF ₃ •OEt ₂ , TMSCl, THF, -78 to 0°, 5 h	 (68)	120
C ₁₀			BF ₃ •OEt ₂ , THF, -30 to 0°, 16 h	 (88)	52
			BF ₃ •OEt ₂ , THF, -30 to 0°, 16 h	 (86)	52
C ₁₂			BF ₃ •OEt ₂ , THF, -30 to 0°, 16 h	 (88)	52
			BF ₃ •OEt ₂ , THF, -30 to 0°, 16 h	 (98)	52
			BF ₃ •OEt ₂ , THF, -78 to -30°	 (84) mixture of diastereomers	52

^a Unless otherwise indicated, the organozinc reagents were prepared by insertion of zinc metal into an organic halide. ^b The reagent was prepared by halide-zinc exchange.

TABLE XVI. ADDITIONS OF ZINC-COPPER REAGENTS TO NITROOLEFINS^a

FG-RML _n (FG-R)	Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.	
<i>A. Reactions with Diorganozinc Reagents: FG-RML_n = (FG-R)₂Zn</i>					
C ₄		Et-CH=CH-NO ₂	THF, NMP, -60 to -30°, 3 h	(64)	602, 180
C ₇		R-CH=CH-NO ₂	THF, NMP, -30°, 3 h	(84) (85)	314 ^b
<i>B. Reactions with Zinc-Copper Reagents: FG-RML_n = (FG-R)Cu(CN)ZnX</i>					
C ₄		<i>n</i> -Pr-CH=CH-NO ₂	THF, -78 to 0°, 4 h	(94)	56, 74
		<i>n</i> -Pr-CH=C(CH ₃)-NO ₂	1. THF, -78 to 0°, 4 h 2. NH ₄ Cl, H ₂ O	(76)	56, 74
			1. THF, -78 to 0°, 4 h 2. NH ₄ Cl, H ₂ O	(74)	74
		Ph-CH=CH-NO ₂	THF, 0°, 12 h	(84)	56, 74
		<i>n</i> -Pr-CH=CH-NO ₂	THF, -78 to 0°, 4 h	(90)	56, 74
C ₅		<i>n</i> -Pr-CH=CH-NO ₂	THF, -78 to 0°, 4 h	(81)	56, 74
		Ph-CH=CH-NO ₂	THF, -20°	(91)	90
		Ph-CH=CH-NO ₂	THF, -78 to 0°, 1 h	(78)	78
		R-CH=CH-NO ₂	THF, Me ₂ S,	(86) (85) (88)	605 ^c
		R	0°, 8 h	(86)	
		Ph	10°, 5 h	(85)	
		C ₅ H _{11-n}	8 h	(88)	
		<i>Pr-i</i>			
C ₆		Ph-CH=CH-NO ₂	THF, DMSO, -78 to 0°, 12 h	(72)	59, 60
			THF, -55°, 10 min	(92)	56, 74
		<i>n</i> -Pr-CH=CH-NO ₂	THF, -78 to 0°, 4 h	(94)	56, 74
		<i>n</i> -Pr-CH=C(CH ₃)-NO ₂	1. THF, -78 to 0°, 4 h 2. NH ₄ Cl, H ₂ O	(82)	56, 74
		<i>n</i> -Pr-CH=C(CH ₃)(Et)-NO ₂	1. THF, -78 to 0°, 4 h 2. O ₃ , Me ₂ S	(85)	74

TABLE XVI. ADDITIONS OF ZINC-COPPER REAGENTS TO NITROOLEFINS (Continued)^a

FG-RML _n (FG-R)	Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
		1. THF, -78 to 0°, 4 h 2. O ₃ , Me ₂ S	 (87)	74
		THF, 0°, 12 h	 (90)	56, 74, 78
		THF, 0°	 (72)	56, 74
		THF, 0°, 12 h	 (84)	240 ^b
		THF, 0°, 12 h	 (74)	240 ^b
		THF, 0°	 (80)	90
		1. THF, -78 to 0°, 4 h 2. O ₃ , Me ₂ S	 (70)	90
		1. THF, -78 to 0°, 4 h 2. O ₃ , Me ₂ S	 (78)	74
		THF, -20°	 (81)	90
		THF, -78 to 0°, 12 h	 (51)	338 ^b
C ₇		THF, -78 to 0°, 4 h	 (75)	56, 74
		THF, 5°, 12 h	 (85)	103
		1. THF, 0° 2. PhSeBr, 0° 3. H ₂ O ₂ , THF, 25°	 (85) E : Z = 36:64	441
		THF	 (82)	64 ^c
		THF, -78 to 0°, 5 h	 (84)	606 ^b
		THF, -78 to 25°, 48 h	 (62)	606 ^b
C ₈		1. THF, -78 to -10°, 2 h 2. H ₂ O	 (74)	66

TABLE XVI. ADDITIONS OF ZINC-COPPER REAGENTS TO NITROOLEFINS (Continued)^a

FG-RML _n (FG-R)	Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
		THF, -55°, 10 min	(88)	56, 74
		THF, -78 to 0°, 4 h	(76)	56, 74
		1. THF, 0°, 4 h 2. NH ₄ Cl, H ₂ O	(71)	56, 74
C ₉		1. THF, -78 to 0°, 4 h 2. O ₃ , Me ₂ S	(75)	74
C ₉		THF, -78 to 0°, 1 h	(83)	83
C ₁₀		THF, 0°, 10 h	(68) mixture of diastereomers	60
C ₁₀		THF, 0°, 12 h	(77)	56, 74
C ₁₂		1. THF, 0°, 1 h 2. H ₂ O ₂ , NaOAc 3. DBU, CH ₂ Cl ₂	(69)	62

^a Unless otherwise indicated, the organozinc reagents were prepared by insertion of zinc metal into an organic halide.

^b The organozinc reagent was prepared by halide-zinc exchange.

^c The organozinc reagent was prepared by a transmetalation reaction.

TABLE XVII. CARBOMETALLATIONS OF ALKYNES WITH DIALKYLZINC OR ZINC-COPPER REAGENTS^a

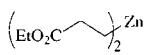
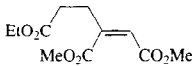
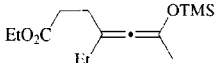
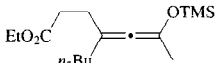
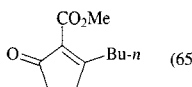
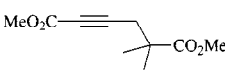
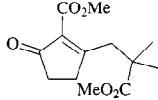
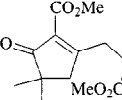

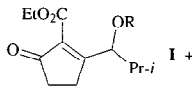
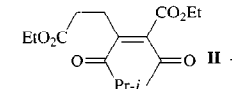
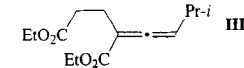
FG-RML _n (FG-R)	Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.												
<i>A. Copper-Catalyzed Carbometallations of Alkynes with Dialkylzinc Reagents: FG-RML_n = (FG-R)₂Zn</i>																
C ₅ 	MeO ₂ C—C≡C—CO ₂ Me	TMSCl, Et ₂ O, HMPA, 0 to 35°, 4 h	 (63) <i>E</i> : <i>Z</i> = 2:98	140 ^b , 442 ^b , 443 ^b												
	Et—C≡C—COMe	TMSCl, Et ₂ O, HMPA, 0 to 35°, 4 h	 (73)	140 ^b												
	<i>n</i> -Bu—C≡C—COMe	TMSCl, Et ₂ O, HMPA, 25°, 2 h	 (73)	442 ^b												
	<i>n</i> -Bu—C≡C—CO ₂ Me	TMSCl, Et ₂ O, HMPA, 25°, 2 h	 (65)	442 ^b , 443 ^b												
		TMSCl, Et ₂ O, HMPA, 25°, 2 h	 (11) +  (54)	443 ^b												
		TMSCl, Et ₂ O, HMPA, 25°, 2 h	 I +													
	R Ac MOM TMS		 II + <table border="1" style="display: inline-table; vertical-align: middle;"> <thead> <tr> <th>I</th> <th>II</th> <th>III</th> </tr> </thead> <tbody> <tr> <td>(49)</td> <td>(35)</td> <td>(5)</td> </tr> <tr> <td>(72)</td> <td>(—)</td> <td>(—)</td> </tr> <tr> <td>(70)</td> <td>(—)</td> <td>(—)</td> </tr> </tbody> </table>	I	II	III	(49)	(35)	(5)	(72)	(—)	(—)	(70)	(—)	(—)	442 ^b , 443 ^b 442 ^b 443 ^b
I	II	III														
(49)	(35)	(5)														
(72)	(—)	(—)														
(70)	(—)	(—)														
			 III													

TABLE XVII. CARBOMETALLATIONS OF ALKYNES WITH DIALKYLZINC OR ZINC-COPPER REAGENTS (Continued)^a

FG-RML _n (FG-R)	Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
		TMSCl, Et ₂ O, HMPA, 0°, 2 h	 (80)	443 ^b
		TMSCl, Et ₂ O, HMPA, 0°, 2 h	 (40)	443 ^b
		TMSCl, Et ₂ O, HMPA, 0°, 2 h	 (65)	442 ^b
		TMSCl, Et ₂ O, HMPA, 0°, 2 h	 (50) Ac (78) MOM (70) TMS (70)	442 ^b 443 ^b 443 ^b
		TMSCl, Et ₂ O, HMPA, 0°, 4 h	 (86)	443 ^b
		TMSCl, Et ₂ O, HMPA, 0°, 4 h	 (85)	443 ^b
		TMSCl, Et ₂ O, HMPA, 0°, 4 h	 (69) H (67) Me (67)	443 ^b
		TMSCl, Et ₂ O, HMPA, 0°, 2 h	 (65)	442 ^b 443 ^b
		TMSCl, Et ₂ O, HMPA, 0°, 4 h	 (54)	443 ^b
		TMSCl, Et ₂ O, HMPA, 0°, 4 h	 (80)	443 ^b
		TMSCl, Et ₂ O, HMPA, 25°, 2 h	 (52)	444 ^b
		TMSCl, Et ₂ O, HMPA, 0°, 4 h	 (85)	443 ^b

TABLE XVII. CARBOMETALLATIONS OF ALKYNES WITH DIALKYLZINC OR ZINC-COPPER REAGENTS (Continued)^a

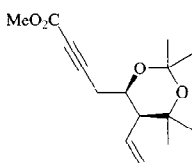
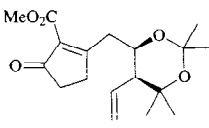
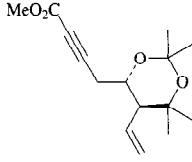
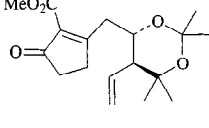
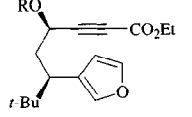
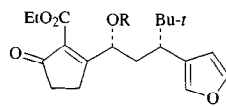
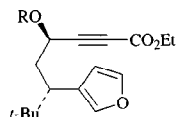
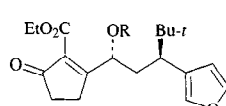
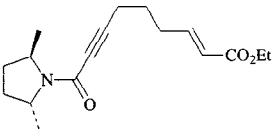
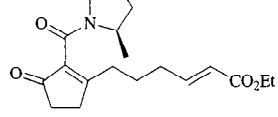
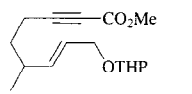
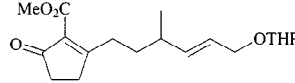
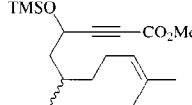
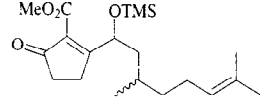
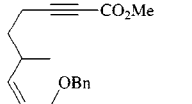
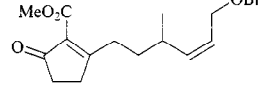
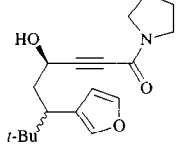
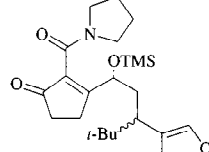
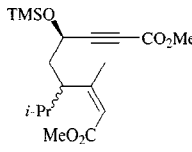
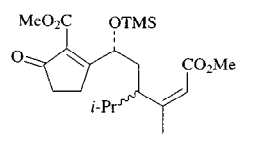
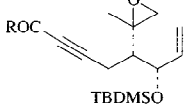
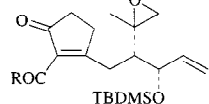
FG-RML _n (FG-R)	Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
		TMSCl, Et ₂ O, HMPA, 25°, 2 h	 (72)	443 ^b
		TMSCl, Et ₂ O, HMPA, 25°, 2 h	 (60)	443 ^b
		TMSCl, Et ₂ O, HMPA, 0°, 4 h	 (83) R H (83) TMS (83) MOM (65)	442 ^b
		TMSCl, Et ₂ O, HMPA, 0°, 4 h	 (82) R TMS (82) MOM (65)	442 ^b
		TMSCl, Et ₂ O, HMPA, 0°, 4 h	 (89)	443 ^b
		TMSCl, Et ₂ O, HMPA, 0°, 4 h	 (51)	443 ^b
		TMSCl, Et ₂ O, HMPA, 0°, 4 h	 (70)	443 ^b
		TMSCl, Et ₂ O, HMPA, 0°, 4 h	 (55)	443 ^b
		TMSCl, Et ₂ O, HMPA, 0°, 4 h	 (86)	443 ^b
		TMSCl, Et ₂ O, HMPA, 0°, 4 h	 (66)	443 ^b
		TMSCl, Et ₂ O, HMPA, 0°, 4 h	 (38) R OMe (38) NMe ₂ (71)	443 ^b

TABLE XVII. CARBOMETALLATIONS OF ALKYNES WITH DIALKYLZINC OR ZINC-COPPER REAGENTS (Continued)^a

FG-RML _n (FG-R)	Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.																												
		TMSCl, Et ₂ O, HMPA, 0°, 4 h		443 ^b																												
		TMSCl, Et ₂ O, HMPA, 0°, 4 h		443 ^b																												
		TMSCl, Et ₂ O, HMPA, 25°	 <table border="1"> <thead> <tr> <th>R¹</th> <th>R²</th> <th>I</th> <th>II</th> </tr> </thead> <tbody> <tr> <td>MOM</td> <td>(CH₂)₃CH=CH₂</td> <td>(71)</td> <td>(23)</td> </tr> <tr> <td>MOM</td> <td>C₅H_{11-n}</td> <td>(68)</td> <td>(—)</td> </tr> <tr> <td>MOM</td> <td>(CH₂)₂CH=CH₂</td> <td>(63)</td> <td>(—)</td> </tr> <tr> <td>MOM</td> <td>Pr-<i>i</i></td> <td>(35)</td> <td>(—)</td> </tr> <tr> <td>MOM</td> <td>CH₂Bn</td> <td>(60)</td> <td>(—)</td> </tr> <tr> <td>TBDMS</td> <td>(CH₂)₃C(CH₃)=CH₂</td> <td>(65)</td> <td>(—)</td> </tr> </tbody> </table>	R ¹	R ²	I	II	MOM	(CH ₂) ₃ CH=CH ₂	(71)	(23)	MOM	C ₅ H _{11-n}	(68)	(—)	MOM	(CH ₂) ₂ CH=CH ₂	(63)	(—)	MOM	Pr- <i>i</i>	(35)	(—)	MOM	CH ₂ Bn	(60)	(—)	TBDMS	(CH ₂) ₃ C(CH ₃)=CH ₂	(65)	(—)	607
R ¹	R ²	I	II																													
MOM	(CH ₂) ₃ CH=CH ₂	(71)	(23)																													
MOM	C ₅ H _{11-n}	(68)	(—)																													
MOM	(CH ₂) ₂ CH=CH ₂	(63)	(—)																													
MOM	Pr- <i>i</i>	(35)	(—)																													
MOM	CH ₂ Bn	(60)	(—)																													
TBDMS	(CH ₂) ₃ C(CH ₃)=CH ₂	(65)	(—)																													
<i>B. Carbometallations of Alkynes with Zinc-Copper Reagents FG-RML_n = FG-RCu(CN)ZnI</i>																																
C ₄			<p>THF, -78 to 23°, 17 h</p> <p>TMSCl, THF, -78 to 23°, 17 h</p> <p>THF, 25°</p> <p>THF, -78 to 23°, 17 h</p>	<p>NC- (83) <i>E</i> : <i>Z</i> = 97:3</p> <p>NC- (84) <i>E</i> : <i>Z</i> > 99:1</p> <p>NC- (60)</p> <p>NC- (82)</p>	55 55 471 ^c 55																											
		EtO ₂ C-≡-CO ₂ Et	THF, -78 to 0°, 6 h	(87) <i>E</i> : <i>Z</i> > 95:5	35																											
			<p>TMSCl, THF, -78 to 23°, 17 h</p> <p>THF, 25°</p>	<p>Cl- (85) <i>E</i> : <i>Z</i> > 99:1</p> <p>Cl- (66)</p>	55 471 ^c																											
C ₅			THF, Et ₂ O, C ₅ H ₁₂ , -78 to -20°, 2 h	<p>R- (70)</p> <p><i>E</i> : <i>Z</i> > 99:1</p> <p> (81)</p>	209 ^c , 604 ^c																											
C ₆			<p>THF, DMSO, 25°, 4 h</p> <p>THF, DMSO, -30°, 1 h</p>	<p><i>i</i>-Pr- (91) <i>E</i> : <i>Z</i> > 96:4</p> <p><i>i</i>-Pr- (93) <i>E</i> : <i>Z</i> > 97:3</p>	59, 60 59, 60																											

TABLE XVII. CARBOMETALLATIONS OF ALKYNES WITH DIALKYLZINC OR ZINC-COPPER REAGENTS (Continued)^a

FG-RML _n (FG-R)	Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
	≡	1. THF, -40°, 1 h 2. I ₂	(26) <i>E</i> : <i>Z</i> = 1:99	471 ^c
	≡-CONH ₂	THF, -30 to 0°, 19 h	(53)	78
	≡-CO ₂ Et	THF, -20°, 12 h	(99)	55, 103
	≡-CO ₂ Et	TMSCl, THF, -78 to 23°, 12 h	(91)	55
	<i>n</i> -Bu-≡-SMe	THF, 25°	(92)	471 ^c
	<i>n</i> -Bu-≡-SMe	1. THF, 25° 2. I ₂	(91)	471 ^c
	<i>n</i> -Bu-≡-SMe	1. THF, 25° 2.	(70)	471 ^c
	Ph-≡-CO ₂ Et	THF, 20°, 12 h	(92)	471 ^c
	≡-CO ₂ Et	THF, -78 to -30°, 12 h	(70)	240 ^c
	≡-CO ₂ Et	THF, -78 to 25°, 3 h	(85)	90
	MeO ₂ C-≡-CO ₂ Me	THF, -78 to -20°, 3 h	(91)	90
	≡-CO ₂ Et	THF, -78°, 14 h	(53)	338 ^c
C ₇ 	≡-CO ₂ Et	THF, -30 to 0°, 17 h	(53)	55
C ₈ 	≡-CO ₂ Et	THF, DMAC, -20°, 12 h	(84)	103
	≡-CO ₂ Me	TMSCl, THF, -78 to 23°, 17 h	(76), I:II = 17:83	55
	≡-CO ₂ Et	THF, -60 to -50°, 2 h	(95)	83
	EtO ₂ C-≡-CO ₂ Et	THF, -78 to -50°, 1 h	(87)	83
	EtO ₂ C-≡-CO ₂ Et	THF, -30 to 25°, 4 h	(68) <i>E</i> : <i>Z</i> > 95:5	35
C ₉ 	≡-CO ₂ Et	THF, -78 to -30°, 12 h	(34)	35
	≡-CO ₂ Et	THF, -78 to -30°, 12 h	(69)	573 ^c

TABLE XVII. CARBOMETALLATIONS OF ALKYNES WITH DIALKYLZINC OR ZINC-COPPER REAGENTS (Continued)^a

FG-RML _n (FG-R)	Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
	$\equiv\text{CO}_2\text{Et}$	THF, DMSO, -78 to 25°, 12 h	(69) <i>E</i> : <i>Z</i> > 95:5	60
	$\equiv\text{CO}_2\text{Et}$	THF, DMSO, -60 to 25°, 2 h	(92)	78
	$\equiv\text{CO}_2\text{Me}$	TMSCl, THF, -78 to 23°, 17 h	I + I + II (76) I : II = 12:88	55
	$n\text{-C}_6\text{H}_{13}\text{-}\equiv\text{CO}_2\text{Me}$	THF, 22°, 3 h	(77)	55
	$n\text{-C}_6\text{H}_{13}\text{-}\equiv\text{CO}_2\text{Me}$	TMSCl, THF, 22°, 18 h	I + I + II (73) I : II = 22:78	55
	$\equiv\text{CO}_2\text{Et}$	THF, Et ₂ O, C ₃ H ₁₂ , -78 to -20°, 2 h	68	209 ^c , 604 ^c
		1. THF, CH ₂ Cl ₂ , 25°, 5 h 2. NH ₄ Cl	(32) <i>E</i> : <i>Z</i> = 1:0.66	608
		1. Cp ₂ TiCl ₂ , THF, DMF, 58°, 15 h 2. H ₂ O	(55)	609
	$\text{RO}_2\text{C}\text{-}\equiv\text{-CO}_2\text{R}$	THF, -60°, 2 h	$\frac{\text{R}}{\text{Me}}$ (71) $\frac{\text{R}}{\text{Et}}$ (71)	78 35
	$\equiv\text{CO}_2\text{Et}$	THF, -50 to -40°, 3 h	(72)	62
		1. THF, CH ₂ Cl ₂ , 25°, 5 h 2. NH ₄ Cl	(27) <i>E</i> : <i>Z</i> = 1:6.8	608
	—	1. THF, 25° 2.	(60)	471 ^c
	$\equiv\text{CO}_2\text{Et}$	1. THF, -80 to -40°, 3 h 2. H ₂ O ₂ , NaOAc	(91)	62

TABLE XVII. CARBOMETALLATIONS OF ALKYNES WITH DIALKYLZINC OR ZINC-COPPER REAGENTS (Continued)^a

FG-RML _n (F-G-R)	Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
	\equiv	1. THF, -40°, 1 h 2. I ₂		471 ^c
	<i>n</i> -Bu— \equiv —SMe	THF, 25°		471 ^c
	\equiv	1. THF, 25° 2. TMSCl		471 ^c
C ₁₃ 	MeO ₂ C— \equiv —CO ₂ Me	THF, -10°, 2 h		60
C ₁₄ 	\equiv —CO ₂ Et	THF, -78 to -30°, 18 h		77
C ₁₄ 	EtO ₂ C— \equiv —CO ₂ Et	THF, 0°, 4 h		35
C ₁₄ 	\equiv —CO ₂ Et	THF, DMSO, -78 to -30°, 3 h		51
C ₁₇ 	\equiv —CO ₂ Et	THF, -78 to -10°, 12 h		567 ^d

^a Unless otherwise indicated, the organozinc reagents were prepared by insertion of zinc metal into an organic halide.^b The organozinc reagent was prepared by ultrasonic irradiation of an ether solution of (ethoxycyclopropoxy)trimethylsilane and zinc chloride.^c The organozinc reagent was prepared by a transmetalation reaction.^d The organozinc reagent was prepared by an insertion reaction using ICH₂ZnI.

TABLE XVIII. INTRAMOLECULAR CARBOZINCATION OF FUNCTIONALIZED ALKENES OR ALKYNES

	Alkene/ Alkyne	Cyclization Conditions	Electrophile	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
C ₆		Zn, DMF	I ₂	(—)	(80)	468
		PdCl ₂ (dppf) (2%) Et ₂ Zn, THF, -78 to 25°, 2 h		CuCN•2LiCl, -78 to 25°, 1 h	(80)	165, 167
		Ni(acac) ₂ , THF, NMP, Cl(CH ₂) ₄ Zn, -78 to -40°, 20 h	(—)	(—)	(68)	610
C ₇		PdCl ₂ (dppf) (2%) Et ₂ Zn, THF, -78 to 25°, 4 h		CuCN•2LiCl, -78 to 0°, 12 h	(62) <i>cis:trans</i> = 78:22	167
		Ni(acac) ₂ (2%), THF, Et ₂ Zn, -78 to 25°, 2 h		CuCN•2LiCl, 0°, 12 h	(83)	171
		Ni(acac) ₂ (2%), THF, Et ₂ Zn, -78 to 25°, 2 h	PhCOCl	CuCN•2LiCl, 0°, 12 h	(64)	470, 171
		Ni(acac) ₂ (2%), THF, Et ₂ Zn, -78 to 0°, 2 h		CuCN•2LiCl, -78 to 0°, 12 h	(63) dr = 15:85	171
C ₈		PdCl ₂ (dppf) (2%) Et ₂ Zn, THF, -78 to 25°, 4 h		CuCN•2LiCl, -78 to -10°, 12 h	(81) <i>cis:trans</i> = 75:25	167
		PdCl ₂ (dppf) (2%) Et ₂ Zn, THF, -78 to 25°, 2 h		CuCN•2LiCl, -78 to 25°, 1 h	(85) <i>cis:trans</i> = 75:25	167
		Zn, rt, 5 d	H ₂ O	—	(66)	79
		PdCl ₂ (MeCN) ₂ Et ₂ Zn, THF, 25°, 4 h	H ₂ O	—	(73)	167
		1. LDA, Et ₂ O, -40 to 0° 2. ZnBr ₂ , Et ₂ O, -40°		CuCN•2LiCl, -40 to 25°, 12 h	(55)	226, 222
		Zn, rt, 50 min	H ₂ O	—	(56)	89
		Rieke zinc, Et ₂ O rt, 3 h	H ₂ O	—	I (52) + II (38)	468
		Et ₂ Zn, Et ₂ O, CuCN•2LiCl, 25°	H ₂ O	—	I (51) + II (41)	468
	Rieke zinc, Et ₂ O 20°, 3 h	I ₂	—	I (41) + II (29)	468	
	Et ₂ Zn, Et ₂ O, CuCN•2LiCl, 25°	I ₂	—	I (50) + II (40)	468	

TABLE XVIII. INTRAMOLECULAR CARBOZINCATION OF FUNCTIONALIZED ALKENES OR ALKYNES (Continued)

Alkene/ Alkyne	Cyclization Conditions	Electrophile	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
	Et ₂ Zn, Et ₂ O, CuCN•2LiCl, 25°		—	 (39) + (33)	468
	MnBr ₂ , CuCl, Et ₂ Zn, DMPU, 60°, 12 h		CuCN•2LiCl, THF, DMPU, -30 to -10°, 1 h	 I (71)	611
	Ni(acac) ₂ (2%), THF, Et ₂ Zn, 0°, 0.5 h		CuCN•2LiCl, THF, -78 to 25°, 1 h	I (66)	171
	PdCl ₂ (dppf), Et ₂ Zn, THF, -78 to 0°		CuCN•2LiCl, THF, -78 to 0°, 12 h	I (66)	171
	Ni(acac) ₂ (2%), THF, Et ₂ Zn, 0°, 0.5 h		CuCN•2LiCl, THF, -78 to 25°, 1 h	 (62) <i>cis:trans</i> = 15:85	171, 470
	Zn, THF, 25°, 1 h	H ₂ O	—	 (70)	89
	Zn, THF, 25°, 1 h	MeI	MeLi, -78 to 25°, 2.5 h	 (49) + (9)	89
	Zn, THF, 25°, 1 h	MeCHO	1. MeLi, -78 to 25°, 3 h 2. TsOH (cat.), C ₆ H ₆ , 25°, 12 h	 (38)	89
	MnBr ₂ , CuCl, Et ₂ Zn, DMPU, 60°, 12 h	H ₂ O	—	 (82)	612
	PdCl ₂ (dppf) (2%), Et ₂ Zn, THF, rt, 5 h		CuCN•2LiCl, THF, -70 to -10°, 2 h	 (12) + (70) dr = 78:22	166, 167
	Zn, THF, TMSCl, rt, 24 h	H ₂ O	—	 (37)	89
	PdCl ₂ (MeCN) ₂ Et ₂ Zn, THF, rt, 4 h	H ₂ O	—	 (57)	167
	Ni(acac) ₂ (2%), THF, Et ₂ Zn, 0°, 0.5 h		CuCN•2LiCl, THF, -60 to -30°	 (61) <i>cis:trans</i> = 15:85	470, 171
	Ni(acac) ₂ (2%), THF, Et ₂ Zn, 0°, 0.5 h		CuCN•2LiCl, THF, -60 to -30°	 (70) <i>cis:trans</i> = 15:85	470, 171

TABLE XVIII. INTRAMOLECULAR CARBOZINCATION OF FUNCTIONALIZED ALKENES OR ALKYNES (Continued)

Alkene/ Alkyne	Cyclization Conditions	Electrophile	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
	Zn, THF, 25°, 24 h	H ₂ O	—	(74)	89
	Zn, THF, TMSCl, 25°, 48 h	H ₂ O	—	(51)	89
	PdCl ₂ (dppf) (2%) Et ₂ Zn, THF, -78 to 25°, 5 h	Ph-CH=CH-NO ₂	CuCN•2LiCl, THF, -78 to 0°	(78)	165, 167
	Ni(acac) ₂ (2%), THF, Et ₂ Zn, 40°, 0.5 h		CuCN•2LiCl, 0 to 25°, 6 h	(61)	171, 470
	Ni(acac) ₂ (2%), THF, Et ₂ Zn, 40°, 0.5 h		1. CuCN•2LiCl, 0 to 25°, 6 h 2. MCPBA, BF ₃ •OEt ₂	(53)	171, 470
	Ni(acac) ₂ (2%), THF, Et ₂ Zn, 40°, 0.5 h		1. CuCN•2LiCl, 0 to 25°, 6 h 2. MCPBA, BF ₃ •OEt ₂	(50)	171, 470
	Ni(acac) ₂ , LiI, THF, Et ₂ Zn, -78 to -40°, 12 h		CuCN•2LiCl, -78 to 25°, 12 h	(61)	171, 470
	PdCl ₂ (dppf) (2%) Et ₂ Zn, THF, 25°, 5 h	≡-CO ₂ Et	CuCN•2LiCl, THF, -78 to -10°	(88) <i>cis:trans</i> = 81:19	167
	PdCl ₂ (dppf) (2%) Et ₂ Zn, THF, 25°, 5 h		CuCN•2LiCl, THF, -78 to 0°	(71) <i>cis:trans</i> = 81:19	167
	MnBr ₂ , CuCl, Et ₂ Zn, DMPU, 60°	H ₂ O	—	(95)	611
	Ni(acac) ₂ (2%), THF, Et ₂ Zn, -78 to 0°, 2 h		CuCN•2LiCl, -78 to 0°, 1.5 h	(67)	171
	Zn, THF, 25°, 1 h	H ₂ O	—	(63)	89
	Rieke zinc, Et ₂ O, 20°, 1-3 h	H ₂ O	—	(49) + (36)	468

TABLE XVIII. INTRAMOLECULAR CARBOZINCATION OF FUNCTIONALIZED ALKENES OR ALKYNES (Continued)

Alkene/ Alkyne	Cyclization Conditions	Electrophile	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
	—		THF, 0°	 (78)	227
	PdCl ₂ (dppf) (2%) Et ₂ Zn, THF, 25°, 5 h		CuCN•2LiCl, THF, -78 to 0°	 (85) <i>exo:endo</i> = 1:2	165, 167, 131
	Rieke zinc, Et ₂ O, 20°, 1-3 h	H ₂ O	—	 (48) + (39)	468
	Rieke zinc, Et ₂ O, 20°, 1-3 h	I ₂	—	 (40) + (33)	468
	Rieke zinc, Et ₂ O, 20°, 1-3 h	MeCOCl	CuCN•2LiCl, THF	 (33) + (33)	468
	Ni(acac) ₂ (2%), THF, Et ₂ Zn, -78 to -40°, 12 h		CuCN•2LiCl, THF, -78 to 25°, 1 h	 (66)	171
	Ni(acac) ₂ , LiI, THF, Et ₂ Zn, -78 to -40°, 2.5 h	O ₂	—	 (63)	612
	MnBr ₂ , CuCl, Et ₂ Zn, DMPU, 60°, 7 h	I ₂	—	 (80)	611
	MnBr ₂ , CuCl, Et ₂ Zn, DMPU, 60°, 7 h		CuCN•2LiCl, THF, DMPU, -30 to -10°	 (73)	611
	PdCl ₂ (dppf) (2%) Et ₂ Zn, THF, -78 to 25°, 5 h	I ₂	—	 (90)	165, 167
	PdCl ₂ (dppf) (2%) Et ₂ Zn, THF, -78 to 25°, 5 h		CuCN•2LiCl, -78 to -10°, 2 h	 (64)	165, 167
	PdCl ₂ (dppf) (2%) Et ₂ Zn, THF, -78 to 25°, 5 h		CuCN•2LiCl, -78 to 0°, 8 h	 (80)	165, 167
	PdCl ₂ (dppf) (2%) Et ₂ Zn, THF, -78 to 25°, 5 h		CuCN•2LiCl, 25°, 0.5 h	 (73)	165, 167
	PdCl ₂ (dppf) (2%) Et ₂ Zn, THF, -78 to 25°, 5 h	PhCOCl	CuCN•2LiCl, -78 to 25°, 2 h	 (76)	165, 167

TABLE XVIII. INTRAMOLECULAR CARBOZINCATION OF FUNCTIONALIZED ALKENES OR ALKYNES (Continued)

Alkene/ Alkyne	Cyclization Conditions	Electrophile	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
	PdCl ₂ (dppf) (2%) Et ₂ Zn, THF, 25°, 5 h		CuCN•2LiCl, THF, -78 to 0°	 (63) <i>exo:endo</i> = 1:2	165, 167
	PdCl ₂ (dppf) (2%) Et ₂ Zn, THF, -78 to 25°, 5 h		CuCN•2LiCl, -78 to -10°, 2 h	 (80) <i>dr</i> = 78:22	166, 167
	PdCl ₂ (dppf) (2%) Et ₂ Zn, THF, -78 to 25°, 5 h		CuCN•2LiCl, 0°, 2 h	 (87) <i>dr</i> = 78:22	166, 167
	PdCl ₂ (dppf) (2%) Et ₂ Zn, THF, -78 to 25°, 5 h		CuCN•2LiCl, 0°, 2 h	 (75) <i>dr</i> = 77:23	166
	PdCl ₂ (dppf) (2%) Et ₂ Zn, THF, -78 to 25°, 5 h		CuCN•2LiCl, 0°, 2 h	 (67) <i>dr</i> = 77:23	167
	PdCl ₂ (dppf) (2%) Et ₂ Zn, THF, -78 to 25°, 5 h		CuCN•2LiCl, 0°, 2 h	 (52) <i>dr</i> = 77:23	166
	PdCl ₂ (2%) (dppf) Et ₂ Zn, THF, 25°, 5 h		CuCN•2LiCl, THF, -78 to 0°	 (73)	165, 167
	MnBr ₂ , CuCl, Et ₂ Zn, DMPU, 60°, 7 h	H ₃ O ⁺	—	 (71)	611
	MnBr ₂ , CuCl, Et ₂ Zn, DMPU, 60°, 7 h	I ₂	—	 (75)	611
	PdCl ₂ (dppf) (2%) Et ₂ Zn, THF, -78 to 25°, 5 h		CuCN•2LiCl, 0°, 2 h	 (83)	165, 167
	PdCl ₂ (dppf) (2%) Et ₂ Zn, THF, -78 to 25°, 5 h		CuCN•2LiCl, 0°, 2 h	 R <i>dr</i> Bz >99:1 (41) Bn >99:1 (67)	166
	Ni(acac) ₂ (2%), THF, Et ₂ Zn, 40°, 0.5 h		CuCN•2LiCl, -30°, 6 h	 (60) <i>dr</i> > 99:1	171, 470
	Ni(acac) ₂ (2%), THF, Et ₂ Zn, 40°, 0.5 h		1. CuCN•2LiCl, -30°, 6 h 2. MCPBA, BF ₃ •OEt ₂	 (56) <i>dr</i> > 99:1	171, 470
	Ni(acac) ₂ (2%), THF, Et ₂ Zn, -78 to 40°, 12 h		CuCN•2LiCl, -78 to 25°, 1 h	 (61) <i>dr</i> > 99:1	171, 470
	Ni(acac) ₂ (2%), THF, Et ₂ Zn, -78 to 40°, 12 h		CuCN•2LiCl, -78 to 10°, 12 h	 (60) <i>dr</i> > 99:1	171, 470

TABLE XVIII. INTRAMOLECULAR CARBOZINCATION OF FUNCTIONALIZED ALKENES OR ALKYNES (Continued)

Alkene/ Alkyne	Cyclization Conditions	Electrophile	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
	Ni(acac) ₂ (2%), THF, Et ₂ Zn, -78 to 40°, 12 h		CuCN•2LiCl, -78 to 0°, 1 h	 (64) dr > 99:1	171
	Ni(acac) ₂ (2%), THF, Et ₂ Zn, -78 to 40°, 12 h		CuCN•2LiCl, -78 to 0°, 12 h	 (61) dr > 99:1	171
	Ni(acac) ₂ (2%), THF, Et ₂ Zn, 0°, 0.5 h		CuCN•2LiCl, -30°, 6 h	 (61) dr > 99:1	171
	MnBr ₂ , CuCl, Et ₂ Zn, DMPU, 60°	H ₂ O	—	 (72)	612
	MnBr ₂ , CuCl, Et ₂ Zn, DMPU, 60°	H ₂ O	—	 (73)	171
	PdCl ₂ (dppf) (2%) Et ₂ Zn, THF, -78 to 25°, 5 h		CuCN•2LiCl, 0°, 2 h	 (71) dr = 95:5	166, 167
	Ni(acac) ₂ (2%), THF, Et ₂ Zn, -78 to 0°, 2 h		CuCN•2LiCl, -78 to 25°, 2 h	 (75) dr = 96:4	171
	MnBr ₂ , CuCl, Et ₂ Zn, DMPU, 60°, 12 h		CuCN•2LiCl, THF, DMPU, -30 to -10°	 (63)	611
	MnBr ₂ , CuCl, Et ₂ Zn, DMPU, 60°, 12 h		PdCl ₂ (dppf), 60°, 4 h	 (61)	611
	Ni(acac) ₂ (2%), THF, Et ₂ Zn, -78 to 0°, 2 h		CuCN•2LiCl, -78 to 0°, 1 h	 (65) dr = 96:4	171
	Pd(PPh ₃) ₄ , Et ₂ Zn, Et ₂ O, 35°, 1.5 h	X	—	 C ₆ F ₅ -N-CH ₂ -CH ₂ -R X R NH ₄ Cl H (88)	613
	Pd(PPh ₃) ₄ , Et ₂ Zn, Et ₂ O, 35°, 1.5 h	TsCN	1. CuCN•2LiCl, Et ₂ O, -78°, 1 h 2. -30°, 16 h	 (73)	613
	Ni(acac) ₂ (2%), THF, Et ₂ Zn, 0°, 0.5 h		CuCN•2LiCl, -30°, 6 h	 (69) dr > 99:1	171, 470
	Ni(acac) ₂ (2%), THF, Et ₂ Zn, 40°, 0.5 h		1. CuCN•2LiCl, -30°, 6 h 2. MCPBA, BF ₃ •OEt ₂	 (45) dr > 99:1	171, 470
	Ni(acac) ₂ (2%), THF, Et ₂ Zn, -78 to 0°, 2 h	PhCHO	BF ₃ •OEt ₂ , -78 to -20°, 12 h	 (60) dr > 99:1	171

TABLE XVIII. INTRAMOLECULAR CARBOZINCATION OF FUNCTIONALIZED ALKENES OR ALKYNES (Continued)

Alkene/ Alkyne	Cyclization Conditions	Electrophile	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
	1. LDA, Et ₂ O, -40 to 0° 2. ZnBr ₂ , -40°		CuCN·2LiCl, THF, -40 to 25°, 12 h	 (65)	225
	Ni(acac) ₂ (2%), THF, Et ₂ Zn, 0°, 0.5 h	AcOD	—	 (73) <i>exo:endo</i> >96:4 100% D incorporation	171, 470
	Ni(acac) ₂ (2%), THF, Et ₂ Zn, 25°, 4 h		CuCN·2LiCl, -55°, 48 h	 (86)	167, 614
	Ni(acac) ₂ , LiI, THF, Et ₂ Zn, -78 to -10°, 1.5 h	O ₂	THF, -10°, 12 h	 (59) <i>cis:trans</i> = 17:83	612
	1. <i>n</i> -BuLi, THF, 0°, 5 min 2. ZnCl ₂ , -78 to 25°, 3 h	PhCOCl	CuCN·2LiCl, THF, 0°, 2 h	 (60) <i>syn:anti</i> >98:2	299
	1. <i>n</i> -BuLi, THF, 0°, 5 min 2. ZnCl ₂ , -78 to 25°, 3 h		CuCN·2LiCl, THF, -78 to 25°, 2 h	 (60) <i>syn:anti</i> >98:2	299
	Pd(PPh ₃) ₄ , Et ₂ Zn, Et ₂ O, 35°, 1.5 h	X	—	 $\begin{matrix} X & R \\ NH_4Cl & H \end{matrix}$ (44) $\begin{matrix} X & R \\ I_2 & I \end{matrix}$ (51)	613
	Pd(PPh ₃) ₄ , Et ₂ Zn, Et ₂ O, 35°, 1.5 h	X	—	 $\begin{matrix} X & R \\ NH_4Cl & H \end{matrix}$ (45) $\begin{matrix} X & R \\ I_2 & I \end{matrix}$ (43)	613
	Pd(PPh ₃) ₄ , Et ₂ Zn, Et ₂ O, 35°, 1.5 h	NH ₄ Cl	—	 (83)	613
	PdCl ₂ (dppf) (2%) Et ₂ Zn, THF, -78 to 25°, 5 h		CuCN·2LiCl, 0°, 2 h	 (62) <i>dr</i> = 98:2	165, 167
	Ni(acac) ₂ (2%), THF, Et ₂ Zn, 40°, 0.5 h	O ₂	1. TMS, THF, -5° 2. Jones oxidation 0°, 15 min	 (50) <i>dr</i> > 99:1	461, 615
	1. <i>s</i> -BuLi, Et ₂ O, -78° 2. ZnBr ₂ , -40°, 5 min		Pd(PPh ₃) ₄ , THF, 30°, 45 min	 (61)	614
	1. <i>s</i> -BuLi, Et ₂ O, -78° 2. ZnBr ₂ , -40°, 5 min		Pd(PPh ₃) ₄ , THF	 (68)	616

TABLE XVIII. INTRAMOLECULAR CARBOZINCATION OF FUNCTIONALIZED ALKENES OR ALKYNES (Continued)

	Alkene/ Alkyne	Cyclization Conditions	Electrophile	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
636		1. <i>s</i> -BuLi, Et ₂ O, -78° 2. ZnBr ₂ , -40°, 5 min		CuCN·2LiCl, THF		(74) 617
		1. <i>s</i> -BuLi, Et ₂ O, -78° 2. ZnBr ₂ , -40°, 5 min		Pd(PPh ₃) ₄ , THF		(50) 617
C22		Pd(PPh ₃) ₄ , Et ₂ Zn, Et ₂ O, 35°, 1.5 h	X	—		$\frac{X}{NH_4Cl}$ $\frac{R}{H}$ (79) I ₂ I (62) 613
		Pd(PPh ₃) ₄ , Et ₂ Zn, Et ₂ O, 35°, 1.5 h	TsCN	1. CuCN·2LiCl, Et ₂ O, -78°, 1 h 2. -30°, 16 h		(58) 613
C23		1. <i>s</i> -BuLi, Et ₂ O, -78° 2. ZnBr ₂ , -40°, 5 min		—		(70) <i>cis:trans</i> = 85:15 222
C28		Pd(PPh ₃) ₄ , Et ₂ Zn, Et ₂ O, 35°, 1.5 h	NH ₄ Cl	—		(79) 613
C31		Pd(PPh ₃) ₄ , Et ₂ Zn, Et ₂ O, 35°, 1.5 h	NH ₄ Cl	—		(87) 613
		Pd(PPh ₃) ₄ , Et ₂ Zn, Et ₂ O, 35°, 1.5 h	I ₂	—		(81) 613

TABLE XIX. CROSS COUPLING OF ZINC REAGENTS WITH ARYL/VINYL HALIDES AND SULFONATES^a

	FG-RZnX (FG-R)	Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.										
C ₂			Pd(PPh ₃) ₄ , THF		618 ^b										
		R													
		4-OMe	22°, 1 h	(95)											
		4-F	22°, 1 h	(94)											
		4-NO ₂	0°, 3 h	(93)											
		4-CO ₂ Me	22°, 1 h	(92)											
		2-OMe	22°, 2 h	(77)											
2,5-Me ₂	22°, 24 h	(92)													
		2,4,6-Me ₃	DMF, 60°, 18 h	(74)											
839			Pd(PPh ₃) ₄ , DMF, 60°, 6 h		619										
		R													
		4-OMe		(93)											
		2-CF ₃		(83)											
		3-NO ₂		(96)											
		2-Me		(81)											
		3-Me		(93)											
4-Me		(77)													
		4-I			619										
C ₃			Co(acac) ₃ , THF, NMP, 55°, 12 h		(50) 537										
			Pd(dba) ₂ , (2-C ₆ H ₄ O) ₃ P, THF, 25°, X h		<table border="1"> <tr> <td>R</td> <td>X</td> <td></td> </tr> <tr> <td>C₆F₉</td> <td>5</td> <td>(94)</td> </tr> <tr> <td>CF₃</td> <td>12</td> <td>(—)</td> </tr> </table>	R	X		C ₆ F ₉	5	(94)	CF ₃	12	(—)	620
		R	X												
C ₆ F ₉	5	(94)													
CF ₃	12	(—)													
	Pd(PPh ₃) ₂ Cl ₂ , THF, <i>n</i> -BuLi, 65°, X h		<table border="1"> <tr> <td>R</td> <td>X</td> <td></td> </tr> <tr> <td>OMe</td> <td>1</td> <td>(64)</td> </tr> <tr> <td>NO₂</td> <td>2</td> <td>(56)</td> </tr> </table>	R	X		OMe	1	(64)	NO ₂	2	(56)	621 ^b		
R	X														
OMe	1	(64)													
NO ₂	2	(56)													
639			Pd(PPh ₃) ₂ Cl ₂ , THF, 65°, 1 h		(54) 622 ^b										
			Pd(PPh ₃) ₂ Cl ₂ , THF, <i>n</i> -BuLi, 65°, 14 h		(52) 622 ^b										
			Pd(PPh ₃) ₂ Cl ₂ , THF, <i>n</i> -BuLi, 65°, 1 h		(83) 621 ^b										
C ₄			Pd(PPh ₃) ₂ Cl ₂ , THF, C ₆ H ₁₄ , 25°, 4 h		<table border="1"> <tr> <td>R</td> <td></td> </tr> <tr> <td>H</td> <td>(65)</td> </tr> <tr> <td>Cl</td> <td>(65)</td> </tr> <tr> <td>Me</td> <td>(63)</td> </tr> </table>	R		H	(65)	Cl	(65)	Me	(63)	480 ^b	
R															
H	(65)														
Cl	(65)														
Me	(63)														

TABLE XIX. CROSS COUPLING OF ZINC REAGENTS WITH ARYL/VINYL HALIDES AND SULFONATES (Continued)^d

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FG-RZnX (FG-R)	Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
		Co(acac) ₃ , THF, NMP, 55°, 12 h	Ph-CH=CH-CH ₂ CH ₂ CH ₂ CH ₂ CN (75)	537
		PdCl ₂ (dppf), THF, DMPU, -30 to 65°, 12 h	(72)	176
		Ni/C, PPh ₃ , THF, 55°	(80)	623
		PdCl ₂ (PPh ₃) ₂ , C ₆ H ₆ , DMAC, 50°, 1 h	(95)	490
		PdCl ₂ (PPh ₃) ₂ , C ₆ H ₆ , DMAC, 50°, 1 h	(77)	490
		PdCl ₂ (PPh ₃) ₂ , C ₆ H ₆ , DMAC, 50°, 1 h	(28)	490
		PdCl ₂ (PPh ₃) ₂ , C ₆ H ₆ , DMAC, 50°, 1 h	(76)	490
		Pd(PPh ₃) ₄ , THF, 25°, 10 min	$\frac{X}{O}$ (80) S (50)	624 ^b
		Pd(PPh ₃) ₄ , DMF, 60°, 2 h	(81)	160 ^b
		Pd(PPh ₃) ₄ , DMF, 60°, 2 h	(47)	160 ^b
		Ni(BF ₄) ₂ bpy ₃ , DMF, 25°, 1 h	(50)	625 ^c
		Pd(PPh ₃) ₄ , DMF, 60°, 2 h	(40)	160 ^b
		Pd(PPh ₃) ₄ , THF, 65°, 5 h	(83)	626
		Pd(PPh ₃) ₄ , THF, 65°, 14 h	(74)	626
		Pd(dba) ₂ , (2-C ₄ H ₉ O) ₃ P THF, 25°, 24 h	(70)	627

640

641

TABLE XIX. CROSS COUPLING OF ZINC REAGENTS WITH ARYL/VINYL HALIDES AND SULFONATES (Continued)^a

FG-RZnX (FG-R)	Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
		Pd(dba) ₂ , (2-C ₄ H ₇ O) ₃ P THF, 25°, 72 h		627
		Pd(PPh ₃) ₄ , THF, 25°		628 ^b
		Pd(PPh ₃) ₄ , THF, 25°		628 ^b
C ₅ 		Pd(dba) ₂ , (2-C ₄ H ₇ O) ₃ P THF, 25°, 5 h		622 ^b
		Pd(PPh ₃) ₂ Cl ₂ , THF, C ₆ H ₁₄ , 25°, 4 h		480 ^b
		Pd(dba) ₂ , PPh ₃ , THF, 25°, 5 h		88
		Pd(dba) ₂ , PPh ₃ , THF, 25°, 24 h		88
		Pd(dba) ₂ , PPh ₃ , THF, 25°, 26 h		88
		Pd(dba) ₂ , PPh ₃ , THF, 25°, 24 h		88
		Pd(PPh ₃) ₂ Cl ₂ , DMAC, C ₆ H ₆ , 70°, 12 h		490
		Pd(PPh ₃) ₂ Cl ₂ , DMAC, C ₆ H ₆ , 25°, 0.5 h		490
		Pd[P(Tol- <i>o</i>) ₃] ₂ Cl ₂ , THF, 60°, 1 h		137
		Pd[P(Tol- <i>o</i>) ₃] ₂ Cl ₂ , THF, 60°, 1 h		137, 140 ^d
		Pd[P(Tol- <i>o</i>) ₃] ₂ Cl ₂ , THF, 25°		140 ^d , 27
		Pd(PPh ₃) ₂ Cl ₂ , DMAC, C ₆ H ₆ , 60°, 16 h		490
		Pd(PPh ₃) ₂ Cl ₂ , DMAC, C ₆ H ₆ , 25°, 2 h		490

TABLE XIX. CROSS COUPLING OF ZINC REAGENTS WITH ARYL/VINYL HALIDES AND SULFONATES (Continued)^a

FG-RZnX (FG-R)	Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
		Pd(PPh ₃) ₂ Cl ₂ , DMAC, C ₆ H ₆ , 50°, 14 h	(20)	490
		Pd(PPh ₃) ₂ Cl ₂ , DMAC, C ₆ H ₆ , 25°, 0.5 h	(47)	490
		Pd(PPh ₃) ₂ Cl ₂ , THF, 60°, 1 h	(90)	137
		Pd(PPh ₃) ₂ Cl ₂ , THF, 60°, 1 h	(95)	137
		Pd[P(Tol- <i>o</i>) ₃] ₂ Cl ₂ , THF, 60°, 1 h	(96)	137
		Pd[P(Tol- <i>o</i>) ₃] ₂ Cl ₂ , THF, 25°	(87)	140 ^d
		Pd[P(Tol- <i>o</i>) ₃] ₂ Cl ₂ , THF, 25°	(85)	140
		Pd[P(Tol- <i>o</i>) ₃] ₂ Cl ₂ , THF, 25°	(49)	27, 140 ^d
		Pd[P(Tol- <i>o</i>) ₃] ₂ Cl ₂ , THF, 25°	(73)	27, 140 ^d
		Pd(PPh ₃) ₄ , THF, 60°, 0.5 h	(74)	140
		Pd[P(Tol- <i>o</i>) ₃] ₂ Cl ₂ , THF, 25°	(79)	140 ^d
		Pd[P(Tol- <i>o</i>) ₃] ₂ Cl ₂ , THF, 25°	(79)	140 ^d
		Pd[P(Tol- <i>o</i>) ₃] ₂ Cl ₂ , THF, 25°	(85)	140 ^d
		Pd(PPh ₃) ₄ , THF, 0 to 20°	(42)	470
		Ni/C, PPh ₃ , THF, 55°	(84)	623
		Pd(MeCN) ₂ Cl ₂ , DMF, Et ₂ O, 25°, 12 h	(81)	629 ^c
		Pd(MeCN) ₂ Cl ₂ , DMF, Et ₂ O, 25°, 12 h	(88)	629 ^c

TABLE XIX. CROSS COUPLING OF ZINC REAGENTS WITH ARYL/VINYL HALIDES AND SULFONATES (Continued)^d

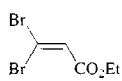
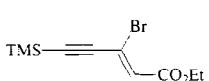
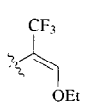
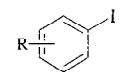
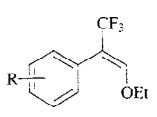
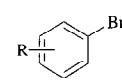
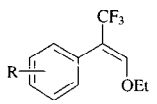
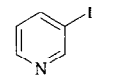
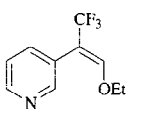
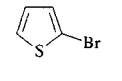
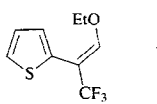
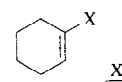
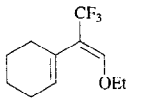
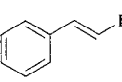
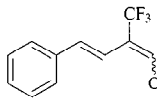
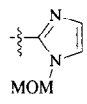
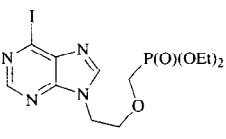
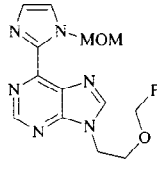

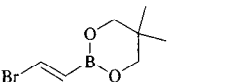
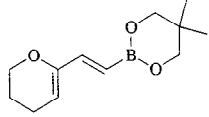

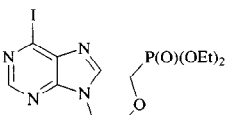
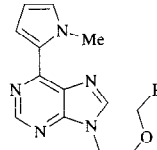

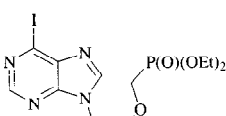
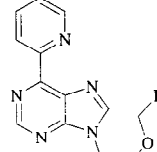
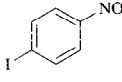
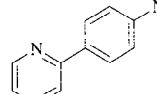
FG-RZnX (FG-R)	Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.												
		Pd(OAc) ₂ , AsPh ₃ , THF, 20°, 4 h	 (91)	476 ^e												
		Pd(PPh ₃) ₄ , THF, 50°, X h	 <table border="1" data-bbox="1197 447 1371 562"> <thead> <tr> <th>R</th> <th>X</th> <th>Yield (%)</th> </tr> </thead> <tbody> <tr> <td>H</td> <td></td> <td>6 (95)</td> </tr> <tr> <td>4-Br</td> <td></td> <td>7 (94)</td> </tr> <tr> <td>4-NO₂</td> <td></td> <td>7 (94)</td> </tr> </tbody> </table>	R	X	Yield (%)	H		6 (95)	4-Br		7 (94)	4-NO ₂		7 (94)	630
	R	X	Yield (%)													
H		6 (95)														
4-Br		7 (94)														
4-NO ₂		7 (94)														
	Pd(PPh ₃) ₄ , THF, 70°, X h	 <table border="1" data-bbox="1197 574 1371 677"> <thead> <tr> <th>R</th> <th>X</th> <th>Yield (%)</th> </tr> </thead> <tbody> <tr> <td>H</td> <td></td> <td>8 (90)</td> </tr> <tr> <td>2-CHO</td> <td></td> <td>12 (72)</td> </tr> <tr> <td>4-NO₂</td> <td></td> <td>8 (92)</td> </tr> </tbody> </table>	R	X	Yield (%)	H		8 (90)	2-CHO		12 (72)	4-NO ₂		8 (92)	630	
R	X	Yield (%)														
H		8 (90)														
2-CHO		12 (72)														
4-NO ₂		8 (92)														
		Pd(PPh ₃) ₄ , THF, 70°, 6 h	 (91)	630												
		Pd(PPh ₃) ₄ , THF, 70°, 7 h	 (85)	630												
		Pd(PPh ₃) ₄ , THF	 <table border="1" data-bbox="1197 918 1371 1021"> <thead> <tr> <th>X</th> <th>Yield (%)</th> </tr> </thead> <tbody> <tr> <td>Br</td> <td>70°, 7 h (90)</td> </tr> <tr> <td>I</td> <td>50°, 7 h (93)</td> </tr> <tr> <td>OTf</td> <td>50°, 7 h (86)</td> </tr> </tbody> </table>	X	Yield (%)	Br	70°, 7 h (90)	I	50°, 7 h (93)	OTf	50°, 7 h (86)	630				
X	Yield (%)															
Br	70°, 7 h (90)															
I	50°, 7 h (93)															
OTf	50°, 7 h (86)															
		Pd(PPh ₃) ₄ , THF, 70°, 7 h	 (91) Z:E = 1:1	630												
		Pd(PPh ₃) ₄ , THF, 65°, 14 h	 (73)	626												
		Pd(PPh ₃) ₄ , THF, 25°	 (66)	628 ^b												
		Pd(PPh ₃) ₄ , THF, 65°, 14 h	 (60)	626												
		Pd(PPh ₃) ₄ , THF, 65°, 6 h	 (84)	626												
		Pd(dba) ₂ , (2-C ₄ H ₉ O) ₃ P THF, 25°, 14 h	 (84)	627												

TABLE XIX. CROSS COUPLING OF ZINC REAGENTS WITH ARYL/VINYL HALIDES AND SULFONATES (Continued)^d


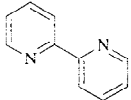
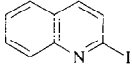
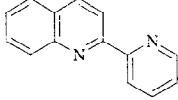
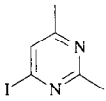
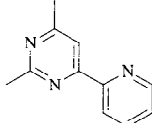
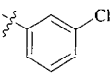
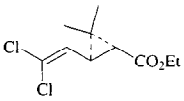
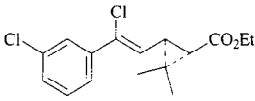
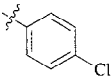
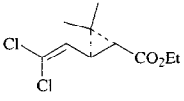
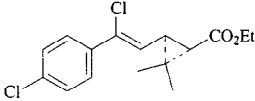
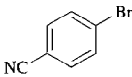
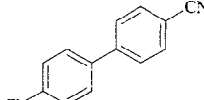
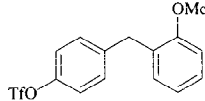
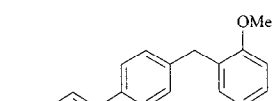
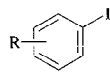
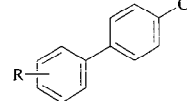

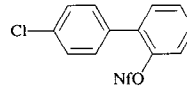
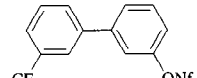
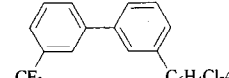
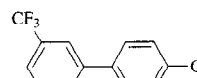
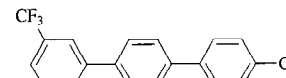
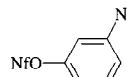
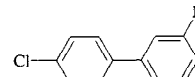
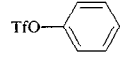
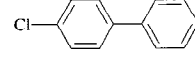
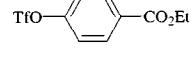
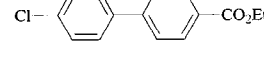
FG-RZnX (FG-R)	Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.															
		Pd(PPh ₃) ₄ , THF, 25°, 48 h	 (81)	631															
		Pd(PPh ₃) ₄ , THF, 25°, 45 h	 (73)	631															
		Pd(PPh ₃) ₄ , THF, 65°, 14 h	 (84)	631															
		Pd(dppb)Cl ₂ , THF, 25°, 8 h	 (81)	632 ^e															
		Pd(dppb)Cl ₂ , THF, 25°, 8 h	 (81)	632 ^e															
		Pd(PPh ₃) ₂ Cl ₂ , DMF, 25°, 2 h	 (59)	159															
		Pd(dba) ₂ , dppf, THF, C ₆ H ₁₄ , 60°, 12-48 h	 (93)	633															
		Pd(dba) ₂ , (2-C ₃ H ₃ O) ₃ P THF, 25°, X h	 <table border="1" data-bbox="1225 1317 1390 1439"> <thead> <tr> <th>X</th> <th>R</th> <th></th> </tr> </thead> <tbody> <tr> <td>6</td> <td>4-CO₂Et</td> <td>(88)</td> </tr> <tr> <td>—</td> <td>4-NO₂</td> <td>(71)</td> </tr> <tr> <td>—</td> <td>4-OAc</td> <td>(71)</td> </tr> <tr> <td>1.5</td> <td>2-CO₂Me</td> <td>(79)</td> </tr> </tbody> </table> (88) ^b	X	R		6	4-CO ₂ Et	(88)	—	4-NO ₂	(71)	—	4-OAc	(71)	1.5	2-CO ₂ Me	(79)	634 ^b
X	R																		
6	4-CO ₂ Et	(88)																	
—	4-NO ₂	(71)																	
—	4-OAc	(71)																	
1.5	2-CO ₂ Me	(79)																	
		Pd(dba) ₂ , (2-C ₃ H ₃ O) ₃ P THF, 25°, 5 h	 (88)	620															
		Pd(dba) ₂ , dppf, THF, 60°, 3 h	 (96)	620															
		Pd(dba) ₂ , dppf, THF, 60°, 1.5 h	 (90)	620															
		Pd(dba) ₂ , dppf, THF, 60°, 1.5 h	 (84)	635															
		Pd(dba) ₂ , (2-C ₃ H ₃ O) ₃ P THF, 25°, 0.5-2 h	 (86)	635															
		Pd(dba) ₂ , dppf, THF, 60°, 0.5 h	 (83)	634 ^b															

TABLE XIX. CROSS COUPLING OF ZINC REAGENTS WITH ARYL/VINYL HALIDES AND SULFONATES (Continued)^a

FG-RZnX (FG-R)	Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
		Pd(PPh ₃) ₄ , THF, 25°, 3 h	(80)	636 ^b
		Pd(dba) ₂ , dppf, THF, 65°, 28 h	(77)	637 ^b
		Pd(dba) ₂ , dppf, THF, 65°, 5 h	(91)	637 ^b
		Pd(dba) ₂ , dppf, THF, 65°, 25 h	(57)	637 ^b
		Pd(PPh ₃) ₄ , THF, 20°	(84)	499 ^b
		Pd(dppf)Cl ₂ , THF, 25°, 8 h	(89) (72)	632 ^c
		Pd(dba) ₂ , dppf, THF, 25°, 2 h	(85)	627, 133
		Pd(dba) ₂ , dppf, THF, 70°, 12 h	(70) (68) (62)	627
		Pd(dba) ₂ , dppf, THF, 70°, 12 h	(83)	627
		Pd(PPh ₃) ₄ , PPh ₃ , THF, 25°, 8 h	(71)	27, 88
		Pd(PPh ₃) ₄ , PPh ₃ , THF, rt, 24 h	(97)	87, 88
		Pd(PPh ₃) ₄ , PPh ₃ , THF, rt, 1 h	(73)	88
		Pd[P(Tol-o)] ₂ Cl ₂ , THF, rt	(76)	140 ^d
		Pd[P(Tol-o)] ₂ Cl ₂ , THF, rt	(90)	140 ^d
		Pd[P(Tol-o)] ₂ Cl ₂ , THF, rt	(55)	140 ^d
		Pd[P(Tol-o)] ₂ Cl ₂ , THF, rt	(76)	140 ^d

TABLE XIX. CROSS COUPLING OF ZINC REAGENTS WITH ARYL/VINYL HALIDES AND SULFONATES (Continued)^d

FG-RZnX (FG-R)	Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
		Pd[P(Tol-o) ₃] ₂ Cl ₂ , THF, 25°	(76)	27, 140 ^d
		Pd(PPh ₃) ₂ Cl ₂ , C ₆ H ₆ , DMAC, Cond.	$\frac{X}{Cl}$ 80°, 24 h (14) 490 $\frac{X}{Br}$ 25°, 0.5 h (89)	
		Pd(PPh ₃) ₂ Cl ₂ , C ₆ H ₆ , DMAC, 25°, 1 h	$\frac{X}{Br}$ (43) $\frac{X}{I}$ (44)	490
		Pd[P(Tol-o) ₃] ₂ Cl ₂ , THF, 60°, 0.5 h	(78)	137
		Pd(PPh ₃) ₄ , THF, 25°, 3 h	(90)	120, 176
		Pd(dppf)Cl ₂ , THF, DMPU, -30 to 65°, 12 h	(73)	176
		Pd[P(Tol-o) ₃] ₂ Cl ₂ , THF, 60°, 0.5 h	(90)	137
		Pd(PPh ₃) ₂ Cl ₂ , C ₆ H ₆ , DMAC, T°, 2 h	$\frac{X}{Br}$ 60 (28) $\frac{X}{I}$ 70 (33)	490
		Pd(PPh ₃) ₂ Cl ₂ , C ₆ H ₆ , DMAC, Cond.	$\frac{X}{Cl}$ 80°, 24 h (30) 490 $\frac{X}{I}$ 25°, 2 h (91)	
		Pd(PPh ₃) ₂ Cl ₂ , C ₆ H ₆ , DMAC, 25°, 2 h.	$\frac{X}{Cl}$ (65) $\frac{X}{I}$ (90)	490
		Pd(PPh ₃) ₄ , THF, 60°, 4 h	I + II (83) I:II = 9:1	137
		Pd(PPh ₃) ₄ , THF, 60°, 4 h	(89)	137
		Pd(PPh ₃) ₄ , THF, 60°, 4 h	(71)	137
		Pd(PPh ₃) ₄ , THF, 25°, 3 h	(93)	120, 176
	Pd(PPh ₃) ₄ , THF, 60°, 4 h	$\frac{R}{2-MeO}$ (95) 137 $\frac{R}{4-MeO}$ (75)		
	Pd(PPh ₃) ₂ Cl ₂ , DMAC, C ₆ H ₆ , rt, 0.5 h	(78)	490	
	Pd(PPh ₃) ₄ , THF, 70°, 2 h	(75)	137	

TABLE XIX. CROSS COUPLING OF ZINC REAGENTS WITH ARYL/VINYL HALIDES AND SULFONATES (Continued)^a

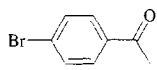
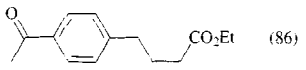
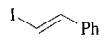
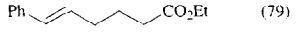
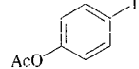
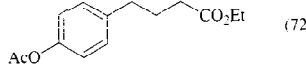
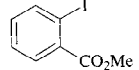
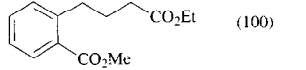
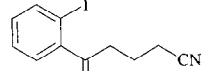
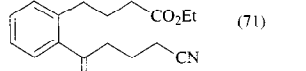
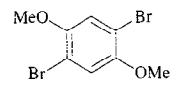
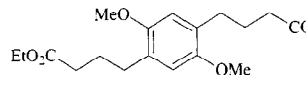
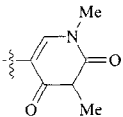
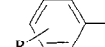
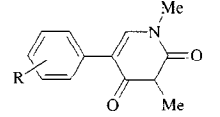
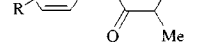
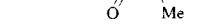
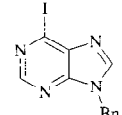
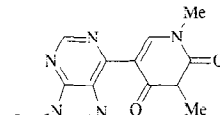


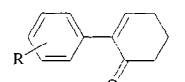

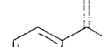
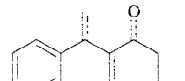
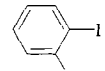
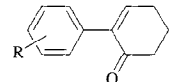
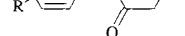

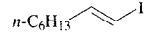
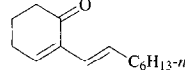
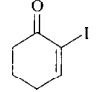
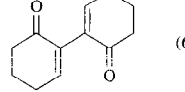
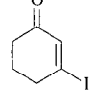
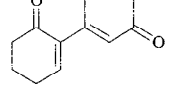
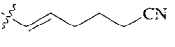
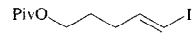
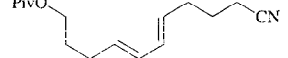
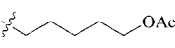
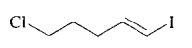
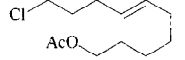
FG-RZnX (FG-R)	Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
		Pd(PPh ₃) ₄ , THF, 25°, 3 h	 (86)	120
		Pd(PPh ₃) ₄ , THF, 70°, 2 h	 (79)	137
		Pd(dppf)Cl ₂ , THF, DMPU, -30 to 65°, 12 h	 (72)	176
		Pd[P(Tol- <i>o</i>) ₃] ₂ Cl ₂ , THF, 60°, 0.5 h	 (100)	137
		Pd(dppf)Cl ₂ , THF, DMPU, -30 to 65°, 12 h	 (71)	176
		Pd(PPh ₃) ₄ , THF, 55°, 12 h	 (41)	638
		Pd(dba) ₂ , dppf, THF, 25°, 0.5 h	 (78)  (83)  (80)	627
		Pd(dba) ₂ , dppf, THF, 25°, 0.5 h	 (79)	627
		Pd(PPh ₃) ₄ , THF, 60°	 (94)  (62)	639 ^b
		Pd(PPh ₃) ₄ , THF, 60°, 20 h	 (62)	639 ^b
		Pd(dba) ₂ , (2-C ₄ H ₉ O) ₃ P, THF, 25°, 16 h	 (85)  (88)  (78)	630
		Pd(dba) ₂ , (2-C ₄ H ₉ O) ₃ P, THF, 25°, 1 h	 (80)	49 ^b
		Pd(dba) ₂ , dppf, THF, 25°, 0.5 h	 (60)	49 ^b
		Pd(dba) ₂ , (2-C ₄ H ₉ O) ₃ P, THF, 25°, 4 h	 (71)	49 ^b
		Pd(dba) ₂ , PPh ₃ , THF, 25°	 (81)	634 ^b
		Co(acac) ₂ , THF, NMP, 55°, 12 h	 (77)	537

TABLE XIX. CROSS COUPLING OF ZINC REAGENTS WITH ARYL/VINYLS HALIDES AND SULFONATES (Continued)^a

FG-RZnX (FG-R)	Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
		Pd(dba) ₂ , PPh ₃ THF, 25°		634 ^b
	R 4-OAc	6 h	(90)	
	2-CO ₂ Me	—	(80)	
	3-CO ₂ Et	16 h	(93)	
	4-CO ₂ Et	—	(87)	
		Pd(dba) ₂ , PPh ₃ THF, 25°	(69)	634 ^b
		Pd(dba) ₂ , PPh ₃ THF, 25°	(89)	634 ^b
		Pd(dba) ₂ , PPh ₃ THF, 25°	(81)	634 ^b
		Pd(dba) ₂ , dppf, THF, C ₆ H ₁₄ , 65°, 12-48 h	(90)	633
		Pd(PPh ₃) ₄ , THF, 55°, 12 h	(53)	638 ^b
		Pd(PPh ₃) ₄ , THF, 25°, 3 h	(95)	120
		Pd(dba) ₂ , dppf, THF, 60°, 0.5 h	(74)	634 ^b
		Pd(dba) ₂ , dppf, THF, 60°	(74)	635
		Pd(dba) ₂ , dppf, THF, 60°, 5 h	(94)	620
		Pd(dba) ₂ , dppf, THF, 60°, 12 h	(89)	620
		Pd(dba) ₂ , (2-C ₄ H ₉ O) ₃ P THF, 25°, 0.5-2 h	(72)	635
		Pd(PPh ₃) ₄ , THF, 25°, 3 h	(93)	120
		Pd(PPh ₃) ₄ , THF, 25°, 3 h	(82)	120
		Ni(acac) ₂ , PPh ₃ , 25°, 2 h	(68)	489 ^b

TABLE XIX. CROSS COUPLING OF ZINC REAGENTS WITH ARYL/VINYL HALIDES AND SULFONATES (Continued)^a

FG-RZnX (FG-R)	Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
		1. Pd(PPh ₃) ₄ , THF, rt, 2 h 2. HCl		483
		1. Pd(PPh ₃) ₄ , THF, rt, 2 h 2. HCl		483
		1. Pd(PPh ₃) ₄ , THF, rt, 2 h 2. HCl		483
		Pd(OAc) ₂ , AsPh ₃ , THF, rt, 3 h		476 ^b
		Pd(OAc) ₂ , AsPh ₃ , THF, rt, 5.5 h		476 ^b
		Pd(OAc) ₂ , AsPh ₃ , THF, rt, 3 h		636 ^b
		Pd(PPh ₃) ₄ , THF, 55°, 12 h		638 ^b
		Pd(dba) ₂ , dppf, THF, DMF, 65°, 15 h		637 ^b
		Pd(dba) ₂ , dppf, THF, C ₆ H ₁₄ , 65°, 12-48 h		633
		Pd(dba) ₂ , dppf, THF, C ₆ H ₁₄ , 65°, 12-48 h		633
		Pd(dba) ₂ , dppf, THF, C ₆ H ₁₄ , 65°, 12-48 h		633
		Pd(dba) ₂ , dppf, THF, C ₆ H ₁₄ , 65°, 12-48 h		633
		Pd(dba) ₂ , (2-C ₄ H ₉ O) ₃ P THF, 25°		633
				633
		Pd(PPh ₃) ₄ , THF, 25°, 44 h		631
		Pd(PPh ₃) ₂ Cl ₂ , THF, 65°, 12 h		640 ^b

TABLE XIX. CROSS COUPLING OF ZINC REAGENTS WITH ARYL/VINYL HALIDES AND SULFONATES (Continued)^a

FG-RZnX (FG-R)	Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
				(52) 640 ^b
		Pd(MeCN) ₂ Cl ₂ , DMF, Et ₂ O, 25°, 12 h		(71) 640 ^b
		Pd(PPh ₃) ₄ , THF, 25°		(88) 641 ^b
		Pd(dppf)Cl ₂ , THF, 25°		(81) 641 ^b
		Pd(dppf)Cl ₂ , THF, 25°		(84) 641 ^b
		Pd(dppf)Cl ₂ , THF, 25°		(87) 641 ^b
		Pd(dppf)Cl ₂ , THF, 25°		(64) 641 ^b
		Pd(dppf)Cl ₂ , THF, 25°		(21) 641 ^b
		Pd(dppf)Cl ₂ , THF, 25°		(19) 641 ^b
		Pd(dppf)Cl ₂ , THF, 25°		$\frac{X}{CH}$ (31) N (31) 641 ^b
		Pd(dppf)Cl ₂ , THF, 25°		(40) 641 ^b
		Pd(PPh ₃) ₄ , THF, 65°, 6 h		(31) 639 ^b
		Pd(PPh ₃) ₄ , THF, 65°, 24 h		(48) 639 ^b
	PhI	Pd(PPh ₃) ₄ , THF, 50°, 10 h		(83) 477 ^r

TABLE XIX. CROSS COUPLING OF ZINC REAGENTS WITH ARYL/VINYL HALIDES AND SULFONATES (Continued)^a

FG-RZnX (FG-R)	Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
		Pd(PPh ₃) ₂ Cl ₂ , THF, 50°, 5 h	 R Br (69) H (91) CN (67) CHO (78) COMe (86) CO ₂ Me (90) CH ₂ SMe (93)	84
		Pd(dba) ₂ , AsPh ₃ , THF, 50°, 3 h	 (61)	85
		Pd(dba) ₂ , AsPh ₃ , THF, 50°, 3 h	 <i>n</i> -Bu (55)	85
		Pd(PPh ₃) ₄ , THF, 50°, 3 h	 R Ph (68) PhS (54)	85
		Pd(PPh ₃) ₄ , THF, 50°, 3 h	 (54)	85
		Pd(PPh ₃) ₂ Cl ₂ , THF, 50°, 5 h	 R CO ₂ Me (76) OMOM (80)	84
		Pd(OAc) ₂ , PPh ₃ , THF, C ₆ H ₆ , 70°, 3 h	 (47)	86
		Pd(OAc) ₂ , PPh ₃ , THF, C ₆ H ₆ , 70°, 3 h	 (50)	86
		Pd(OAc) ₂ , PPh ₃ , THF, C ₆ H ₆ , 70°, 3 h	 (78)	86, 85
		Pd(OAc) ₂ , PPh ₃ , THF, C ₆ H ₆ , 70°, 3 h	 (71)	86
		Pd(OAc) ₂ , PPh ₃ , THF, C ₆ H ₆ , 70°, 3 h	 (71)	86
		Pd(OAc) ₂ , PPh ₃ , THF, C ₆ H ₆ , 70°, 3 h	 (80)	86
		Pd(dba) ₂ , PPh ₃ , THF, 40°, 12 h	 <i>n</i> -Bu (86)	62
	Pd(OAc) ₂ , PPh ₃ , THF, C ₆ H ₆ , 70°, 3 h	 (64)	86	

TABLE XIX. CROSS COUPLING OF ZINC REAGENTS WITH ARYL/VINYL HALIDES AND SULFONATES (Continued)^a

FG-RZnX (FG-R)	Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
		Pd(PPh ₃) ₂ Cl ₂ , DMF, 25°, 2 h	(48)	159 ^c
		Pd(PPh ₃) ₂ Cl ₂ , DMF, 25°, 2 h	(84)	159 ^c
		Ni(BF ₄) ₂ bpy ₃ , DMF, 25°, 1 h	(40)	625
		Pd(PPh ₃) ₄ , THF, 25°, 40 h	(—)	484
		Ni(acac) ₂ , <i>i</i> -PrMgCl, THF, 25°, 12 h	(68)	489 ^b
		Ni(acac) ₂ , <i>i</i> -PrMgCl, THF, 25°, 12 h	(57)	489 ^b
		Ni(acac) ₂ , <i>i</i> -PrMgCl, THF, 25°, 12 h	(60) (29)	489 ^b
		Pd ₂ (dba) ₃ , PPh ₃ , THF, reflux 4.5 h	(53)	482
		Pd(PPh ₃) ₂ Cl ₂ , DMF, 25°, 2 h	(84) (83)	159
		Pd(dba) ₂ , dppf, THF, 60°, 20 h	(93)	620
		Pd(dba) ₂ , dppf, THF, 60°, 20 h	(87)	620
		Pd(dba) ₂ , dppf, THF, 60°, 36 h	(89)	620

TABLE XIX. CROSS COUPLING OF ZINC REAGENTS WITH ARYL/VINYL HALIDES AND SULFONATES (Continued)^d

FG-RZnX (FG-R)	Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
		Pd(dba) ₂ , (2-C ₄ H ₉ O) ₃ P, THF, 25°, 2-18 h	 R 4-CO ₂ Et (92) 4-NO ₂ (80) 2-OMe (84)	630
		Pd(dba) ₂ , (2-C ₄ H ₉ O) ₃ P, THF, 2-18 h	 R (93) (90) (88) (82)	49 ^b
		Pd(dba) ₂ , (2-C ₄ H ₉ O) ₃ P, THF, 2-18 h	 R (79) (85) (85) (74)	49 ^b
		Co(acac) ₂ , THF, NMP, 55°, 12 h	(77)	537
		Ni(acac) ₂ , MeMgBr, PPh ₃ , THF, 25°	(92)	489 ^b
		Pd(PPh ₃) ₄ , THF, 55°, 12 h	(65)	638 ^b
		Pd(PPh ₃) ₄ , THF, 55°, 12 h	(93)	638 ^b
		Ni(BF ₄) ₂ bpy ₃ , DMF, 25°, 1 h	(60)	625 ^c
		Pd(dba) ₂ , dppf, THF, 65°, 22 h	(85)	637 ^b
		Pd(PPh ₃) ₂ Cl ₂ , DMF, Et ₂ O, 25°, 12 h	(69)	629 ^c
		Pd(dba) ₂ , (2-C ₄ H ₉ O) ₃ P, THF, 65°, 2 h	 R H (47) CN (60)	572

TABLE XIX. CROSS COUPLING OF ZINC REAGENTS WITH ARYL/VINYL HALIDES AND SULFONATES (Continued)^a


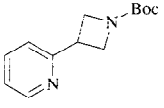

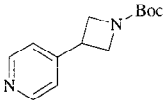

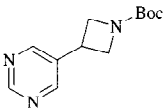
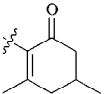
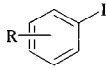
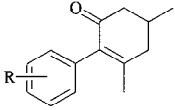
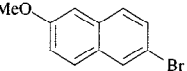
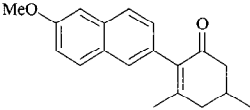
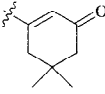
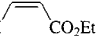
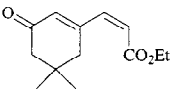
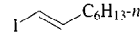
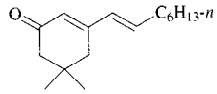
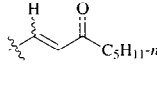
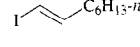
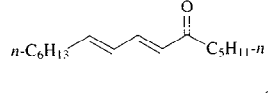
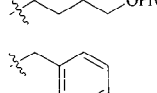
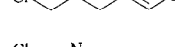
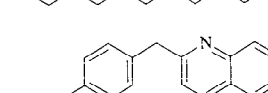
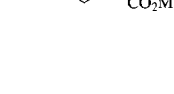
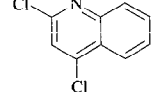
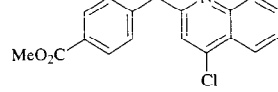
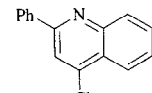
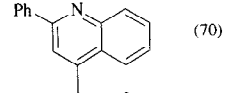
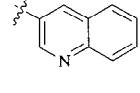

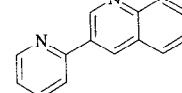
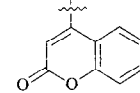
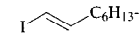
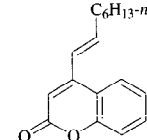
FG-RZnX (FG-R)	Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
		Pd(dba) ₂ , (2-C ₄ H ₉ O) ₃ P, THF, 65°, 2 h	 (63)	572
		Pd(dba) ₂ , (2-C ₄ H ₉ O) ₃ P, THF, 25°	 (55)	572
		Pd(dba) ₂ , (2-C ₄ H ₉ O) ₃ P, THF, 65°, 2 h	 (46)	572
	 R 4-Cl 3-F	Pd(PPh ₃) ₄ , THF 65°, 8 h 20 to 65°, 85 h	 (88) (70)	639 ^b
		Pd(PPh ₃) ₄ , THF, 65°, 22 h	 (84)	639 ^b
		Pd(PPh ₃) ₂ Cl ₂ , DMF, 25°, 24 h	 (93)	88
		Pd(PPh ₃) ₂ Cl ₂ , DMF, 25°, 1.5 h	 (82)	88
		Pd(PPh ₃) ₂ Cl ₂ , DMF, 25°, 4 h	 (55)	88
		Co(acac) ₂ , THF, 55°, 12 h	 (65)	537
		Pd(PPh ₃) ₄ , THF, 25°, 16 h	 (80)	642
		Pd(PPh ₃) ₄ , THF, 25°, 16 h	 (70)	642
		Pd(PPh ₃) ₄ , THF, 25°, 67 h	 (60)	631
		Pd(PPh ₃) ₂ Cl ₂ , DMF, 25°, 5 h	 (71)	88

TABLE XIX. CROSS COUPLING OF ZINC REAGENTS WITH ARYL/VINYL HALIDES AND SULFONATES (Continued)^a

FG-RZnX (FG-R)	Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
		Pd(dba) ₂ , (2-C ₄ H ₅ O) ₃ P, THF, 25°, 4 h	(61)	627
		Pd(PPh ₃) ₄ , THF, 25°, 3 h	(82)	120
		Pd(dba) ₂ , PPh ₃ , THF, 25°, 12 h	(81)	133
		Pd(PPh ₃) ₄ , THF, 25°, 3 h	(80)	120
		Pd(PPh ₃) ₄ , THF, 25°, 3 h	(94)	120
		Pd(PPh ₃) ₄ , THF, reflux 4 h	(80) (81)	643
		Pd(dba) ₂ , (2-C ₄ H ₅ O) ₃ P, THF, 25°, 4 h	(72)	627
		Pd(dba) ₂ , (2-C ₄ H ₅ O) ₃ P, THF, 45°, 24 h	(73)	627
		Pd(dba) ₂ , (2-C ₄ H ₅ O) ₃ P, THF, 25°, 3 h	(55)	627
		Pd(dba) ₂ , (2-C ₄ H ₅ O) ₃ P, THF, 45°, 24 h	(71)	627
		Pd(dba) ₂ , (2-C ₄ H ₅ O) ₃ P, THF, 60°, 2 h	(86)	627
		Pd(PPh ₃) ₂ Cl ₂ , <i>n</i> -BuLi, THF, 65°, 1 h	(67)	621 ^b
		Pd(PPh ₃) ₂ Cl ₂ , <i>n</i> -BuLi, THF, 65°, 1 h	(84)	621 ^b
		Pd(PPh ₃) ₂ Cl ₂ , <i>n</i> -BuLi, THF, 65°, 1 h	(67)	621 ^b

TABLE XIX. CROSS COUPLING OF ZINC REAGENTS WITH ARYL/VINYL HALIDES AND SULFONATES (Continued)^a

FG-RZnX (FG-R)	Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
		Pd ₂ (dba) ₃ , (<i>o</i> -Tol) ₃ P, DMF, 50°	(69)	644
		Pd ₂ (dba) ₃ , (<i>o</i> -Tol) ₃ P		644
	R			
	H	DMF, 50°	(64)	
	2-F	DMF, 50°	(40)	
	2-NO ₂	DMF, 50°	(28)	
	4-F	DMF, 50°	(58)	
	2-OMe	DMF, 50°	(57)	
	4-NO ₂	THF, 50°	(62)	
672	C ₁₀			
		Pd[P(Tol- <i>o</i>) ₃] ₂ Cl ₂ , HMPA, 40°, 1 h	(99)	138
		Pd[P(Tol- <i>o</i>) ₃] ₂ Cl ₂ , HMPA, 40°, 1 h	(77)	138
		Pd[P(Tol- <i>o</i>) ₃] ₂ Cl ₂ , HMPA, 40°, 1 h	(67)	138
		1. Pd(PPh ₃) ₄ , THF, 22° 2. HCl (2 M)	(80)	483
		1. Pd(PPh ₃) ₄ , THF, 22° 2. HCl (2 M)	(76)	483
		1. Pd(PPh ₃) ₄ , THF, 22° 2. HCl (2 M)	(78)	483
		Pd(dba) ₂ , (<i>o</i> -Tol) ₃ P, THF, 0 to 25°, 12 h	(35), 56% ee <i>trans:cis</i> = 99:1	40
		Pd ₂ (dba) ₃ , (<i>o</i> -Tol) ₃ P, DMF, 25°, 3 h		99
	R			
	H		(73)	
	4-Me		(73)	
	2-OMe		(56)	
	4-OMe		(68)	
	2-NH ₂		(33)	
	2-Br		(58)	
	2-F		(46)	
	4-F		(65)	
	2-NO ₂		(20)	
	3-NO ₂		(47)	
	4-NO ₂		(89)	
673				
		Pd ₂ (dba) ₃ , (<i>o</i> -Tol) ₃ P, DMF, 25°, 3 h	(61)	99

TABLE XIX. CROSS COUPLING OF ZINC REAGENTS WITH ARYL/VINYL HALIDES AND SULFONATES (Continued)^a

FG-RZnX (FG-R)	Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
		Pd ₂ (dba) ₃ , (2-C ₄ H ₃ O) ₃ P, THF, DMA, 80°, 2 h		572
		PdCl ₂ (MeCN) ₂ , DMF, Et ₂ O, 25°, 12 h		629 ^e
		Pd(PPh ₃) ₄ , THF, DMF, 85°, 2 h		645 ^b
	R		(78)	
	2-F		(91)	
	2-OMe		(66)	
	4-OH		(88)	
	2-NH ₂		(80)	
	2-NO ₂		(83)	
	2-CHO		(83)	
		Pd(PPh ₃) ₄ , THF, DMF, 85°, 2 h		645 ^b
		Pd(PPh ₃) ₄ , THF, DMF, 85°, 2 h		645 ^b
		Pd(PPh ₃) ₄ , THF, DMF, 85°, 2 h		645 ^b
		Pd(dba) ₂ , (2-C ₄ H ₃ O) ₃ P, THF, 25°		620
	R		(86)	
	4-OAc	12 h	(83)	
	3-CO ₂ Et	0.5 h	(83)	
		1. Pd(dba) ₂ , PPh ₃ , THF, 55°, 10 h 2. HCl		646
		Pd(dba) ₂ , (2-C ₄ H ₃ O) ₃ P, THF, 65°, 2.5 h		627
		Pd(dba) ₂ , PPh ₃ , THF, 25°, 12 h		133
		Pd(PPh ₃) ₄ , THF, 25°, 3 h		120
	R		(95)	
	H		(93)	
	Me		(93)	
		Pd(dba) ₂ , PPh ₃ , THF, 25°, 12 h		133
		Ni(acac) ₂ , <i>i</i> -PrMgCl, THF, 25°, 12 h		489 ^b

TABLE XIX. CROSS COUPLING OF ZINC REAGENTS WITH ARYL/VINYL HALIDES AND SULFONATES (Continued)^a

FG-RZnX (FG-R)	Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
		Pd(dba) ₂ , (<i>o</i> -Tol) ₃ P, THF, 0 to 25°, 12 h	 (41), 52% ee <i>trans:cis</i> = 99:1	40
		Pd ₂ (dba) ₃ , (<i>o</i> -Tol) ₃ P, DMF, 25°, 3 h	 (68) (68) (69) (68) (56) (34) (80)	99
		Pd(PPh ₃) ₂ Cl ₂ , THF, Dibal-H, 25°, 2 h	 (68)	647 ^b
		Pd(PPh ₃) ₄ , THF, 65°	 (81)	498 ^b
		Ni/C, PPh ₃ , THF, 55°	 (66)	623 ^b
		Pd(PPh ₃) ₄ , Et ₂ O, C ₆ H ₁₄ , 35°	 (75) (66) (48) (70) (54)	643 ^b
		Pd(PPh ₃) ₄ , Et ₂ O, C ₆ H ₁₄ , 35°	 (31)	643 ^b
		Pd(PPh ₃) ₄ , Et ₂ O, C ₆ H ₁₄ , 35°	 (78)	643 ^b
		Pd(PPh ₃) ₄ , Et ₂ O, C ₆ H ₁₄ , 35°	 (54)	643 ^b

TABLE XIX. CROSS COUPLING OF ZINC REAGENTS WITH ARYL/VINYL HALIDES AND SULFONATES (Continued)^d

FG-RZnX (FG-R)	Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
		Pd(PPh ₃) ₄ , Et ₂ O, C ₆ H ₁₄ , 35°	(72)	643 ^b
C ₁₂		Pd(PPh ₃) ₄ , Et ₂ O, C ₆ H ₁₄ , 35°	$\frac{X}{Cl}$ (71)	643 ^b
			(52)	
		Ni(acac) ₂ , <i>i</i> -PrMgCl, THF, 25°, 12 h	(65)	489 ^b
		Pd(dba) ₂ , PPh ₃ , THF, 20 to 35°, 12 h		62
		Pd(dba) ₂ , (<i>o</i> -Tol) ₃ P, THF, 0 to 25°, 12 h	 (40), 83% ee <i>trans:cis</i> = 98:2	40
		Pd(dba) ₂ , (2-C ₄ H ₅ O) ₃ P, THF, 25°, 1 h	$\frac{R}{CF_3}$ (70)	49 ^b
			$\frac{R}{CO_2Et}$ (81)	
		Pd(dba) ₂ , (2-C ₄ H ₅ O) ₃ P, THF, 25°, 1 h	(73)	49 ^b
			Pd(dba) ₂ , (2-C ₄ H ₅ O) ₃ P, THF, 60°, 4 h	$\frac{R}{H}$ (80)
$\frac{R}{2-CF_3}$ (74)				
$\frac{R}{4-CO_2Et}$ (70)				
C ₁₃		Pd ₂ (dba) ₃ , (<i>o</i> -Tol) ₃ P, THF, 50°, 1 h	$\frac{R}{F}$ (65)	101
			$\frac{R}{Br}$ (42)	
		Pd ₂ (dba) ₃ , (<i>o</i> -Tol) ₃ P, THF, 50°, 1 h	(26)	101
			Pd ₂ (dba) ₃ , (<i>o</i> -Tol) ₃ P, THF, 50°, 1 h	$\frac{R}{NO_2}$ (54)
$\frac{R}{H}$ (61)				
		Pd ₂ (dba) ₃ , (<i>o</i> -Tol) ₃ P, THF, 50°, 1 h	(41)	101

TABLE XIX. CROSS COUPLING OF ZINC REAGENTS WITH ARYL/VINYL HALIDES AND SULFONATES (Continued)^a

FG-RZnX (FG-R)	Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
		Pd ₂ (dba) ₃ , (<i>o</i> -Tol) ₃ P, THF, 50°, 1 h	 (53)	101
		Pd(PPh ₃) ₄ , THF, 50°, 1 h	 R NO ₂ (76) COEt (85) OMe (78)	643 ^b
		Pd[P(Tol- <i>o</i>) ₃] ₂ Cl ₂ , HMPA, 40°, 1 h	 (74)	138
		Ni(acac) ₂ , <i>i</i> -PrMgCl, THF, 25°, 12 h	 X Br (94) TfO (89)	489 ^b
		Ni(acac) ₂ , <i>i</i> -PrMgCl, THF, 25°, 12 h	 (40)	489 ^b
		Pd(PPh ₃) ₄ , THF, reflux 4 h	 R H (80) 3-NO ₂ (85) 2-OMe (40) 4-OMe (52)	643 ^b
		Pd(dba) ₂ , PPh ₃ , THF, 25°, 24 h	 (40)	88
		Pd(PPh ₃) ₄ , THF, 25°, 16 h	 (52)	642
		Pd(PPh ₃) ₂ Cl ₂ , THF, 65°, 4 h	 (78)	648 ^b
		Pd(PPh ₃) ₂ Cl ₂ , THF, 65°, 4 h	 (94)	648 ^b
		Pd(PPh ₃) ₂ Cl ₂ , THF, 65°, 4 h	 R OMe (80) OH (40)	648 ^b
		Pd(PPh ₃) ₂ Cl ₂ , THF, 65°, 4 h	 R 3-CO ₂ Me (80) 4-CO ₂ Me (95) 5-CO ₂ Me (83)	648 ^b
		Pd(PPh ₃) ₂ Cl ₂ , THF, 65°, 4 h	 (95)	648 ^b

TABLE XIX. CROSS COUPLING OF ZINC REAGENTS WITH ARYL/VINYL HALIDES AND SULFONATES (Continued)^a

FG-RZnX (FG-R)	Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
		Pd(PPh ₃) ₂ Cl ₂ , THF, 65°, 4 h	 (95)	648 ^b
		Pd(PPh ₃) ₂ Cl ₂ , THF, 65°, 4 h	 (88)	648 ^b
		Pd(PPh ₃) ₂ Cl ₂ , THF, 65°, 4 h	 R OMe (77) OH (63)	648 ^b
		Pd(PPh ₃) ₂ Cl ₂ , THF, 65°, 4 h	 R 3-CO ₂ Me (90) 4-CO ₂ Me (95) 5-CO ₂ Me (97)	648 ^b
		Pd(PPh ₃) ₂ Cl ₂ , THF, 65°, 4 h	 (80)	648 ^b
		1. Pd(PPh ₃) ₂ Cl ₂ , THF, DIBAL-H, 65°, 4 h 2. TsOH, EtOH, 2.5 h	 H (91)	648 ^b
		Pd(PPh ₃) ₂ Cl ₂ , THF, 65°, 4 h	 (50)	648 ^b
		Pd(PPh ₃) ₂ Cl ₂ , THF, 65°, 4 h	 (45)	648 ^b
		Pd(PPh ₃) ₂ Cl ₂ , THF, 65°, 4 h	 (55)	648 ^b
C ₁₅ 		Pd(PPh ₃) ₂ Cl ₂ , THF, DMAC, 5 h	 R OH (33) OTBDMS (54) OMe (74) OP(O)(OEt) ₂ (86)	649 649 649 650
		Pd(OAc) ₂ , (<i>o</i> -Tol) ₃ P, C ₆ H ₆ , 2 h	 (50-55)	651
		Pd[P(Tol- <i>o</i>) ₃] ₂ Cl ₂ , THF, DMA, 25 to 50°	 (83)	652
		Pd[P(Tol- <i>o</i>) ₃] ₂ Cl ₂ , THF, DMA, 25 to 50°	 (78)	652

TABLE XIX. CROSS COUPLING OF ZINC REAGENTS WITH ARYL/VINYL HALIDES AND SULFONATES (Continued)^a

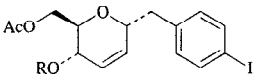
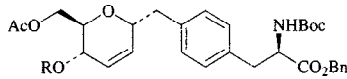
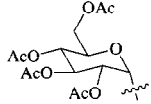
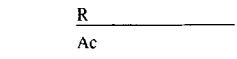
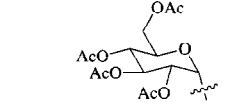
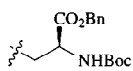
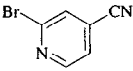
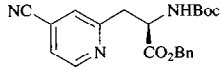
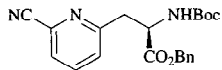
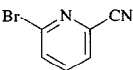
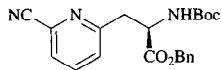
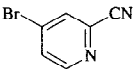
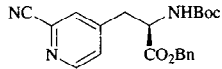
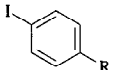
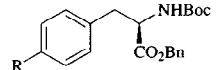
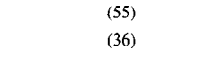
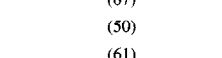
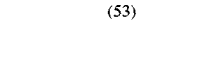
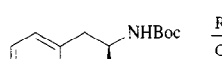
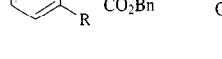
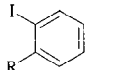
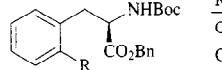

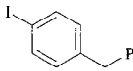
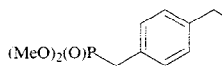
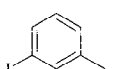
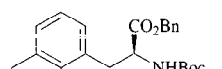
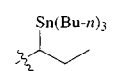
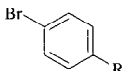
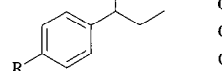
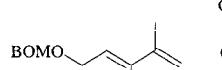
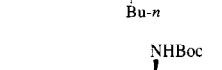
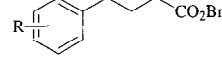
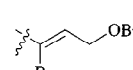
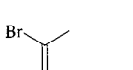
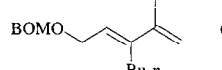
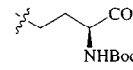
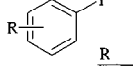
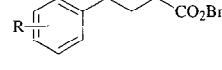
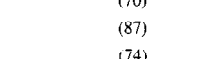
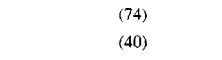
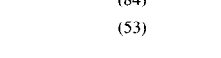



FG-RZnX (FG-R)	Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
		Pd[P(Tol- <i>o</i>) ₃] ₂ Cl ₂ , THF, DMA, 25 to 50°	 (82)  (55)	652
	 R Ac			
				
		Pd(PPh ₃) ₂ Cl ₂ , THF, 20°, 16 h	 (48)  (65)	100
		Pd(PPh ₃) ₂ Cl ₂ , THF, 20°, 16 h	 (65)	100
		Pd(PPh ₃) ₂ Cl ₂ , THF, 20°, 16 h	 (47)	100
	 R H F Br Me NO ₂ OAc	Pd[P(Tol- <i>o</i>) ₃] ₂ Cl ₂ , THF, DMAC, 50°, 1 h	 (55)  (36)  (67)  (50)  (61)  (53)	92, 98
	 R	Pd[P(Tol- <i>o</i>) ₃] ₂ Cl ₂ , THF, DMAC, 50°, 1 h	 (40)  (12)	92, 98
	 P(O)(OMe) ₂	Pd[P(Tol- <i>o</i>) ₃] ₂ Cl ₂ , THF, 50°, 2 h	 (36)	i02
		Pd[P(Tol- <i>o</i>) ₃] ₂ Cl ₂ , THF, DMAC, 50°, 1 h	 (64)	92, 98
	 R	Pd(PPh ₃) ₂ Cl ₂ , HMPA, C ₆ H ₆ , 25°, 0.5 h	 (86)  (70)  (92)  (87)	491
		Pd(PPh ₃) ₂ Cl ₂ , THF, 25°, 21 h	 (52)	653 ^b
	 R H 4-Me 4-OMe 2-OMe 2-NO ₂ 4-NO ₂ 2-NH ₂	Pd ₂ (dba) ₃ , (<i>o</i> -Tol) ₃ P, DMF, 25°, 3 h	 (70)  (87)  (74)  (74)  (40)  (84)  (53)	644

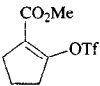
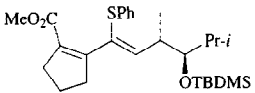
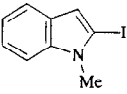
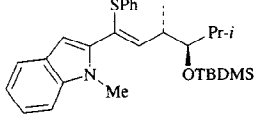
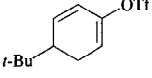
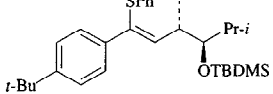
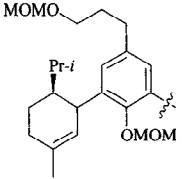
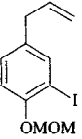
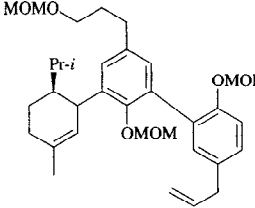
TABLE XIX. CROSS COUPLING OF ZINC REAGENTS WITH ARYL/VINYL HALIDES AND SULFONATES (Continued)^d

FG-RZnX (FG-R)	Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
		Pd ₂ (dba) ₃ , (o-Tol) ₃ P, DMF, 25°, 3 h	 (88)	644
	PhI	Pd(PPh ₃) ₄ , THF, 25°, 18 h	 (41)	483
	PhI	Pd(dba) ₂ , (2-C ₄ H ₃ O) ₃ P, THF, 65°, 4 h	 (52)	627
		Pd(dba) ₂ , (2-C ₄ H ₃ O) ₃ P, THF, 0 to 25°, 10 min	 (58)	627
		Pd ₂ (dba) ₃ , (2-C ₄ H ₃ O) ₃ P, DMF, 25°, 3 h	 (77)	644
		Pd ₂ (dba) ₃ , (2-C ₄ H ₃ O) ₃ P, DMF, 25°, 3 h	 (77) (84) (42) (62) (10) (75)	644
	R			
	H		(77)	
	4-Me		(84)	
	2-OMe		(42)	
	4-OMe		(62)	
	2-NO ₂		(10)	
	4-NO ₂		(75)	
		Pd(PPh ₃) ₄ , THF, reflux 18 h	 (44)	483
	PhI	Pd(PPh ₃) ₄ , THF, reflux 18 h	 (44)	483
		Pd ₂ (dba) ₃ , PPh ₃ , THF, reflux 4.5 h	 (75)	482
		Pd ₂ (dba) ₃ , PPh ₃ , THF, reflux 4.5 h	 (45)	482

TABLE XIX. CROSS COUPLING OF ZINC REAGENTS WITH ARYL/VINYL HALIDES AND SULFONATES (Continued)^a

FG-RZnX (FG-R)	Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.	
		Pd(dba) ₂ , (2-C ₄ H ₉ O) ₃ P, THF, 25°, 1.5 h	(96)	620	
		Pd(dba) ₂ , (2-C ₄ H ₉ O) ₃ P, THF, 25°, 1 h	$\frac{R}{\text{CO}_2\text{Et}}$ (62) $\frac{R}{\text{CF}_3}$ (68) $\frac{R}{\text{NO}_2}$ (77)	627	
		Pd(dba) ₂ , (2-C ₄ H ₉ O) ₃ P, THF, 25°, 4 h	$\frac{R}{\text{H}}$ (72) 4-Cl (70) 3-CO ₂ Et (76)	49	
C ₁₉			Pd(dba) ₂ , (2-C ₄ H ₉ O) ₃ P, THF, 25°, 12 h	(89) (81) (80) (89) (86) (62) (66) (76) (80) (95)	654
		Pd(dba) ₂ , (2-C ₄ H ₉ O) ₃ P, THF, 25°, 12 h	(75)	654	
C ₂₀			Pd(PPh ₃) ₄ , THF, 25°, 3 h	$\frac{X}{\text{O}}$ (64) S (55)	655 ^b
		Pd(PPh ₃) ₄ , THF, 60°, 6 h	(75)	655 ^b	
		Pd(PPh ₃) ₄ , THF, 25°, 3 h	(54)	655 ^b	
		Pd(PPh ₃) ₄ , THF, 60°, 6 h	(73)	655 ^b	
		Pd(dba) ₂ , AsPh ₃ , THF, 25°, 5 min	(61)	655 ^b	
		Pd(PPh ₃) ₄ , THF, 25°, 3 h	(47)	655 ^b	
		Pd(PPh ₃) ₄ , THF, 60°, 6 h	(85)	655 ^b	

TABLE XIX. CROSS COUPLING OF ZINC REAGENTS WITH ARYL/VINYL HALIDES AND SULFONATES (Continued)^a

FG-RZnX (FG-R)	Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
		Pd(dba) ₂ , AsPh ₃ , THF, 25°, 5 min	 (76)	655 ^b
		Pd(PPh ₃) ₄ , THF, 25°, 3 h	 (55)	655 ^b
		Pd(PPh ₃) ₄ , THF, 60°, 6 h	 (81)	655 ^b
		Pd(PPh ₃) ₂ Cl ₂ , THF, Dibal-H, 25°, 16 h	 (37)	647 ^b

^a Unless otherwise indicated, the organozinc reagents were prepared by insertion of zinc metal into an organic halide.

^b The organozinc reagent was prepared by a transmetallation reaction.

^c The organozinc reagent was prepared by Nakamura's method (ref. 140).

^d The organozinc reagent was prepared by ultrasonic irradiation of an ether solution of (ethoxycyclopropyloxy)trimethylsilane and zinc chloride.

^e The organozinc reagent was prepared by halide-zinc exchange.

TABLE XX. PALLADIUM-CATALYZED ACYLATION OF FUNCTIONALIZED ZINC REAGENTS*

FG-RZnX (FG-R)	Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
		Pd(PPh ₃) ₄ , HMPA, C ₆ H ₆ , 40°, 2 h	$\frac{R}{Ph}$ (53) $n-C_7H_{15}$ (62)	138
		Pd(PPh ₃) ₄ , HMPA, C ₆ H ₆ , 40°, 2 h	(85)	138
		Pd(PPh ₃) ₄ , THF, reflux 4 h	(84)	105
		Pd(PPh ₃) ₄ , THF, reflux 4 h	(90)	105
		Pd(PPh ₃) ₄ , THF, reflux 4 h	(100)	105
		Pd(PPh ₃) ₄ , THF, 25°, 4 h	(100)	105, 140 ^b , 408
		Pd(PPh ₃) ₄ , HMPA, C ₆ H ₆ , 60°, 4 h	$\frac{R}{2-OMe}$ (81) $\frac{R}{4-OMe}$ (94)	105
		Pd(PPh ₃) ₄ , HMPA, C ₆ H ₆ , 60°, 4 h	(100)	105

TABLE XX. PALLADIUM-CATALYZED ACYLATION OF FUNCTIONALIZED ZINC REAGENTS (Continued)^d

FG-RZnX (FG-R)	Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
		Pd(PPh ₃) ₄ , HMPA, C ₆ H ₆ , 60°, 4 h	(92)	105
		Pd(PPh ₃) ₄ , HMPA, 60°, 4 h	(83)	140 ^b
		Pd(PPh ₃) ₄ , HMPA, CO, THF, 25°, 60 h	(24)	496
		Pd(PPh ₃) ₄ , HMPA, CO, THF, 25°, 90 h	(24)	496
	PhCOCl	Pd(PPh ₃) ₂ Cl ₂ , THF, 25°, 4 h	(93)	140
		Pd(PPh ₃) ₂ Cl ₂ , DMF, C ₆ H ₆ , 35°, 40 min	(62)	36
		Pd(PPh ₃) ₂ Cl ₂ , DMF, C ₆ H ₆ , 35°, 40 min	(57)	36
		Pd(PPh ₃) ₂ Cl ₂ , DMF, C ₆ H ₆ , 35°, 40 min	(47)	36
		Pd(PPh ₃) ₂ Cl ₂ , DMF, C ₆ H ₆ , 35°, 40 min	(61)	36
		Pd(PPh ₃) ₄ , HMPA, THF, 25°, 4 h	(81)	140 ^b
	<i>t</i> -BuCOCl	Pd(PPh ₃) ₄ , HMPA, THF, 25°, 4 h	(50)	140 ^b
	PhCOCl	Pd(PPh ₃) ₄ , THF, 25°, 6 h	(95)	25
		Pd(PPh ₃) ₄ , DMAC, C ₆ H ₆ , 25°, 1 h	(88)	496
		Pd(PPh ₃) ₄ , DMAC, C ₆ H ₆ , 60°, 4 h	(90)	105
	<i>n</i> -C ₇ H ₁₅ COCl	Pd(PPh ₃) ₄ , DMAC, C ₆ H ₆ , 60°, 4 h	(94)	105
		Pd(PPh ₃) ₄ , HMPA, CO, THF, 25°, 4 h	(78)	496
		Pd(PPh ₃) ₄ , DMAC, C ₆ H ₆ , 60°, 4 h	(89)	105

TABLE XX. PALLADIUM-CATALYZED ACYLATION OF FUNCTIONALIZED ZINC REAGENTS (Continued)^a

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FG-RZnX (FG-R)	Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
		Pd(PPh ₃) ₄ , HMPA, CO, PhMe, 25°, 24 h	(37)	496
		Pd(PPh ₃) ₄ , HMPA, CO, PhMe, 25°, 24 h	(60)	496
		Pd(PPh ₃) ₄ , HMPA, CO, PhMe, 25°, 17 h	(64)	496
		Pd(PPh ₃) ₄ , THF, CO, DMAC, 40°, 24 h	(60)	496
		Pd(PPh ₃) ₄ , HMPA, CO, PhMe, 25°, 24 h	(85)	496
		Pd(PPh ₃) ₄ , DMAC, C ₆ H ₆ , 60°, 4 h	(72)	105
		Pd(PPh ₃) ₄ , THF, CO, DMAC, 25°, 20 h	(74)	496
C ₇		Pd(PPh ₃) ₄ , DMAC, C ₆ H ₆ , 40°, 2 h	(74)	138
		—	(63)	656
C ₈		PhCOCl	(72)	88
		Pd(PPh ₃) ₂ Cl ₂ , DMF, C ₆ H ₆ , 35°, 40 min	I (23) + II (33)	36
		Pd(PPh ₃) ₂ Cl ₂ , DMF, C ₆ H ₆ , 35°, 40 min	I (13) + II (22)	36
		Pd(PPh ₃) ₄ , Et ₂ O, 0 to 25°, 12 h	(97) (93)	657 ^c
		Pd(PPh ₃) ₄ , Et ₂ O, 0 to 25°, 12 h	(75)	657 ^c
C ₁₀		Pd(dba) ₂ , (2-C ₄ H ₉ O) ₃ P, THF, 25°	(38)	336

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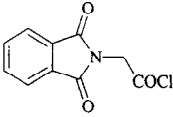
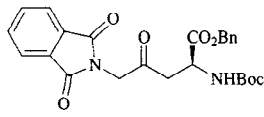
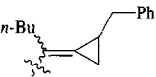
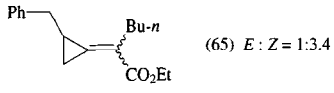
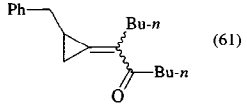
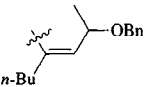
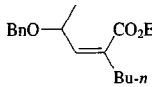
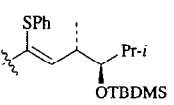
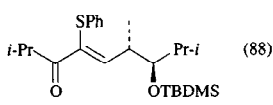
TABLE XX. PALLADIUM-CATALYZED ACYLATION OF FUNCTIONALIZED ZINC REAGENTS (Continued)^a

FG-RZnX (FG-R)	Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
	RCOCl	Pd(PPh ₃) ₄ , HMPA, C ₆ H ₆ , 40°, 2 h	 R ————— Ph (90) C ₇ H ₁₅ -n (80)	138
	RCOCl	Pd ₂ (dba) ₃ , (<i>o</i> -Tol) ₃ P, dioxane, 0 to 25°, 12 h	 R ————— Ph (41) 60 Bu- <i>n</i> (39) 64 95:5 92:8	40
	<i>n</i> -BuCOCl	Pd ₂ (dba) ₃ , (<i>o</i> -Tol) ₃ P, dioxane, 0 to 25°, 12 h	 (45), 88% ee <i>anti:syn</i> = 90:10	40
	PhCOCl	Pd(PPh ₃) ₄ , THF, 25°, 64 h	 (56)	631
	MeCOCl	Pd(PPh ₃) ₄ , THF, 25°, 64 h	 (85)	645
	RCOCl	Pd(PPh ₃) ₄ , THF, 20°, 2 h	 R ————— <i>i</i> -Bu (77) Ph (69) CH ₂ =CH (90)	645 ^d
C ₁₁				
	RCOCl	Pd(PPh ₃) ₄ , HMPA, C ₆ H ₆ , 40°, 2 h	 R ————— Et (77) Ph (76)	138
	<i>n</i> -BuCOCl	Pd ₂ (dba) ₃ , (<i>o</i> -Tol) ₃ P, dioxane, 0 to 25°, 12 h	 (43), 60% ee <i>anti:syn</i> = 92:8	631 ^d
	RCOCl	Pd[P(<i>o</i> -Tol) ₃] ₄ , dioxane, 25°	 <i>i</i> -Pr ₂ N ————— (89) (70) (55) (30)	601
	R ————— Ph 4-MeC ₆ H ₄ 4-MeOC ₆ H ₄ 2-MeOC ₆ H ₄	15 h 13.5 h 1 h 19 h		
	RCOCl	Pd(PPh ₃) ₄ , Et ₂ O, 0 to 25°, 4 h	 R ————— Ph (92) <i>c</i> -C ₃ H ₉ (86)	657 ^c
		Pd(PPh ₃) ₄ , Et ₂ O, 0 to 25°	 (83)	657 ^c
	RCOCl	Pd(PPh ₃) ₄ , Et ₂ O, THF, 0 to 70°, 16 h	 R ————— Ph (69) <i>c</i> -C ₃ H ₉ (55)	657 ^c

TABLE XX. PALLADIUM-CATALYZED ACYLATION OF FUNCTIONALIZED ZINC REAGENTS (Continued)^a

FG-RZnX (FG-R)	Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₁₂			 (57)	657 ^c
		Pd(PPh ₃) ₄ , Et ₂ O, THF, 0 to 70°	 (85)	138
C ₁₃			 (58), 81% ee <i>anti:syn</i> = 99:1	40 ^d
		Pd(PPh ₃) ₄ , Et ₂ O, THF, 0 to 25°, 12 h	 R Ph (95) <i>c</i> -C ₅ H ₉ (94)	657 ^c
		Pd(PPh ₃) ₄ , Et ₂ O, 0 to 25°	 (76)	657 ^c
C ₁₄			 (91)	138
		Pd(PPh ₃) ₄	 (64)	286 ^e
		Pd(PPh ₃) ₄ , THF, 25°, 16 h	 (64)	566 ^e
C ₁₅			 R CO ₂ Bn NHBOC (39)	98
		C ₆ H ₆ , 25°, 0.5 h	(80)	98
		25°, 0.5 h	(10)	95
		30°, 1 h	(64)	98
		25°, 0.5 h	(34)	95
		20°, 2 h	(34)	95
		Pd(PPh ₃) ₂ Cl ₂	 (83)	658
		Pd(PPh ₃) ₂ Cl ₂ , THF, 50°, 2 h	 (83)	98
		Pd(PPh ₃) ₄ , THF, 50°, 2 h	 (10)	95
		Pd(PPh ₃) ₂ Cl ₂ , DMAC, C ₆ H ₆ , 25°	 R CO ₂ Bn NHBOC (90)	98
		0.5 h	(76)	98
		0.5 h	(84)	98
		0.5 h	(70)	98
		0.5 h	(45)	95
		1 h	(41)	98
		0.5 h	(43)	98
		0.5 h	(72)	98
		0.5 h	(63)	98
		0.5 h		98
		0.5 h		98

TABLE XX. PALLADIUM-CATALYZED ACYLATION OF FUNCTIONALIZED ZINC REAGENTS (Continued)^a

FG-RZnX (FG-R)	Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
		Pd(PPh ₃) ₂ Cl ₂ , DMAC, C ₆ H ₆ , 25°, 0.5 h	 (53)	98
	ClCO ₂ Et	Pd(PPh ₃) ₂ Cl ₂ , THF, C ₆ H ₁₄ , -20 to 25°	 (65) <i>E</i> : <i>Z</i> = 1:3.4	566 ^d
	<i>n</i> -BuCOCl	Pd(PPh ₃) ₂ Cl ₂ , THF, C ₆ H ₁₄ , -20 to 25°	 (61)	566 ^d
C ₁₆ 	ClCO ₂ Et	Pd(PPh ₃) ₂ Cl ₂ , THF, 25°	 (56)	653 ^c
C ₂₀ 	<i>i</i> -PrCOCl	Pd ₂ (dba) ₃ , AsPh ₃ , THF, 25°, 5 min	 (88)	655 ^d

^a Unless otherwise indicated, the organozinc reagents were prepared by insertion of zinc metal into an organic halide.^b The organozinc reagent was prepared by ultrasonic irradiation of an ether solution of (ethoxycyclopropyloxy)trimethylsilane and zinc chloride.^c The organozinc reagent was prepared by halide-zinc exchange.^d The organozinc reagent was prepared by a transmetalation reaction.^e The organozinc reagent was prepared by an electrochemical reaction.

TABLE XXI. ENANTIOSELECTIVE ADDITIONS OF FUNCTIONALIZED DIORGANOZINC REAGENTS TO ALDEHYDES^a

(FG-R) ₂ Zn (FG-R)	Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.												
C ₄ 	<i>A. Reactions of Organozincs</i>															
		122^b (8 mol%), PhMe, Ti(O <i>i</i> Bu) ₄ , 0°, 6 h		(68) 95% ee	164											
		122^b (8 mol%), PhMe, Ti(OPr- <i>i</i>) ₄														
			<table border="1"> <thead> <tr> <th>Yld</th> <th>% ee</th> </tr> </thead> <tbody> <tr> <td>(59)</td> <td>70</td> </tr> <tr> <td>(76)</td> <td>96</td> </tr> <tr> <td>(69)</td> <td>95</td> </tr> <tr> <td>(71)</td> <td>80</td> </tr> <tr> <td>(71)</td> <td>80</td> </tr> </tbody> </table>	Yld	% ee	(59)	70	(76)	96	(69)	95	(71)	80	(71)	80	
	Yld	% ee														
	(59)	70														
	(76)	96														
	(69)	95														
	(71)	80														
	(71)	80														
TMS	-55°, 3 h			522												
CH ₂ OTIPS	-78 to -15°, 6 h			524												
Sn(Bu- <i>n</i>) ₃	-60°, 2 h			517												
Ph	-45 to -20°, 16 h			565												
Pr- <i>n</i>	-45 to -25°, 16 h			659												
EtCHO	122^b (8 mol%), PhMe, Ti(OPr- <i>i</i>) ₄ , -20°		(86) 94% ee	660												
PhCHO	122^b (8 mol%), PhMe, Ti(OPr- <i>i</i>) ₄ , -60 to -20°, 2 h		(95) 93% ee	64												
	122^b (8 mol%), PhMe, Ti(OPr- <i>i</i>) ₄ , -60 to -20°, 2 h		(95) 97% ee													
	122^b (8 mol%), PhMe, Ti(OPr- <i>i</i>) ₄ , -75 to -20°, 6 h		(68) dr = 97:3	369, 524												

TABLE XXI. ENANTIOSELECTIVE ADDITIONS OF FUNCTIONALIZED DIORGANOZINC REAGENTS TO ALDEHYDES (Continued)^a

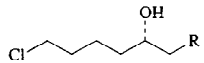
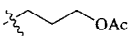
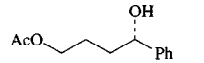
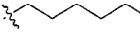
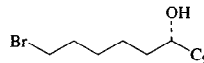
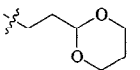
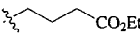
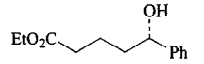
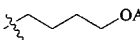
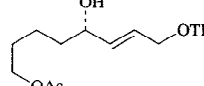
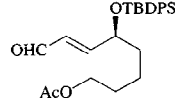
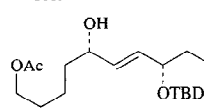
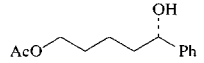
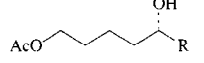
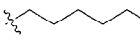
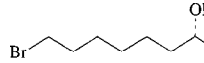
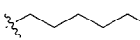
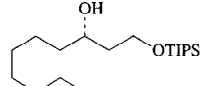
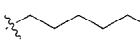
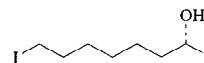
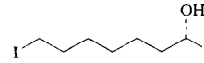
(FG-R) ₂ Zn (FG-R)	Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.	
C ₅	OHC-CH ₂ -R	122 ^b (8 mol%), PhMe, Ti(OPr- <i>i</i>) ₄			
	R		Yld % ee		
	OTIPS	-20°, 12 h	(70) 85	532	
	CH ₂ SiMe ₂ Ph	-20°, 12 h	(70) 96	526	
	CH ₂ Sn(Bu- <i>n</i>) ₃ (CH ₂) ₂ OTIPS	-35°, 16 h 0°, 6 h	(79) 95 (58) 96	517 524	
	PhCHO	122 ^b (8 mol%), PhMe, Ti(OPr- <i>i</i>) ₄ , -60 to -20°, 2 h	 (75) 86% ee	64	
	<i>n</i> -C ₉ H ₁₉ CHO	122 ^b (8 mol%), Et ₂ O, Ti(OPr- <i>i</i>) ₄ , -20°, 10 h	 (69) 92% ee	515	
C ₆		PhCHO	121a ^c (10 mol%), Et ₂ O, Ti(OPr- <i>i</i>) ₄ , -78 to -30°, 20 h	(10) 84% ee	512 ^d
		PhCHO	122 ^b (8 mol%), PhMe, Ti(OPr- <i>i</i>) ₄ , -60 to -20°, 2 h	 (75) 60% ee	64
		OHC-CH=CH-OTIPS	122 ^b (8 mol%), PhMe, Ti(OPr- <i>i</i>) ₄ , -78 to -15°, 6 h	 (60) 87% ee	524
			122 ^b (8 mol%), PhMe, Ti(OPr- <i>i</i>) ₄ , -75 to -15°, 6 h	 (69) dr = 94:6	524
	PhCHO	122 ^b (8 mol%), PhMe, Ti(OPr- <i>i</i>) ₄ , -60 to -20°, 2 h	 (72) 92% ee	64	
OHC-CH ₂ -R	122 ^b (8 mol%), PhMe, Ti(OPr- <i>i</i>) ₄				
R		Yld % ee			
OTIPS	-20°, 12 h	(89) 85	532		
OTBDPS	-20°, 12 h	(62) 86	532		
CH ₂ OTIPS	-20°, 12 h	(62) 99	526 ^d		
CH ₂ Sn(Bu- <i>n</i>) ₃	-20°, 12 h	(85) 93	517		
(CH ₂) ₂ OTIPS	-78 to -15°, 6 h	(65) 89	524		
	RCHO	122 ^b (8 mol%), PhMe, Ti(OPr- <i>i</i>) ₄ , -20°, 12 h			
R		Yld % ee			
<i>n</i> -C ₅ H ₁₁		(77) 90	515		
<i>n</i> -C ₆ H ₁₃		(70) 90	242 ^d		
C ₆ H ₁₁		(11) 60	242 ^d		
4-NCC ₆ H ₄		(85) 88	242 ^d		
	TIPSO-CH ₂ -CHO	122 ^b (8 mol%), PhMe, Ti(OPr- <i>i</i>) ₄ , -20°, 12 h	 (59) 66% ee	526 ^d	
	PhCHO	122 ^b (8 mol%), PhMe, Ti(OPr- <i>i</i>) ₄ , -20°, 5 h	 (58) 86% ee	515, 242 ^d	
<i>i</i> -BuCHO	122 ^b (8 mol%), PhMe, Ti(OPr- <i>i</i>) ₄ , -20° 12 h	 (32) 73% ee	242 ^d		

TABLE XXI. ENANTIOSELECTIVE ADDITIONS OF FUNCTIONALIZED DIORGANOZINC REAGENTS TO ALDEHYDES (Continued)^a

(FG-R) ₂ Zn (FG-R)	Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.													
C ₇ 		122^b (8 mol%), PhMe, Ti(OPr- <i>i</i>) ₄ , -60 to -20°, 10 h	(77) 80% ee	164													
		122^b (8 mol%), PhMe, Ti(OPr- <i>i</i>) ₄ , -60 to -20°, 10 h	(95) 94% ee	164													
		122^b (8 mol%), PhMe, Ti(OPr- <i>i</i>) ₄ , -60 to -20°, 10 h	(68) 68% ee	164													
		122^b (8 mol%), PhMe, Ti(OPr- <i>i</i>) ₄ , -60 to -20°, 10 h		<table border="1"> <thead> <tr> <th>R</th> <th>Yld</th> <th>%ee</th> </tr> </thead> <tbody> <tr> <td>H</td> <td>(70)</td> <td>98</td> </tr> <tr> <td>CO₂Et</td> <td>(78)</td> <td>80</td> </tr> </tbody> </table>	R	Yld	%ee	H	(70)	98	CO ₂ Et	(78)	80	64 164			
	R	Yld	%ee														
	H	(70)	98														
	CO ₂ Et	(78)	80														
	RCHO	122^b (8 mol%), PhMe, Ti(OPr- <i>i</i>) ₄ , -60 to -20°, 2 h		<table border="1"> <thead> <tr> <th>R</th> <th>Yld</th> <th>%ee</th> </tr> </thead> <tbody> <tr> <td>C₆H₁₁</td> <td>(83)</td> <td>97</td> </tr> <tr> <td><i>n</i>-C₅H₁₁</td> <td>(62)</td> <td>97</td> </tr> <tr> <td>Ph</td> <td>(79)</td> <td>93</td> </tr> </tbody> </table>	R	Yld	%ee	C ₆ H ₁₁	(83)	97	<i>n</i> -C ₅ H ₁₁	(62)	97	Ph	(79)	93	64 64 64, 660 ^d
	R	Yld	%ee														
	C ₆ H ₁₁	(83)	97														
<i>n</i> -C ₅ H ₁₁	(62)	97															
Ph	(79)	93															
	122^b (8 mol%), PhMe, Ti(OPr- <i>i</i>) ₄		<table border="1"> <thead> <tr> <th>R</th> <th>Yld</th> <th>%ee</th> </tr> </thead> <tbody> <tr> <td>SiEt₃</td> <td>-30°, 12 h</td> <td>(61) 93</td> </tr> <tr> <td>Sn(Bu-<i>n</i>)₃</td> <td>-35°, 16 h</td> <td>(75) 91</td> </tr> <tr> <td>Pr-<i>n</i></td> <td>-60 to -20°, 10 h</td> <td>(75) 83</td> </tr> </tbody> </table>	R	Yld	%ee	SiEt ₃	-30°, 12 h	(61) 93	Sn(Bu- <i>n</i>) ₃	-35°, 16 h	(75) 91	Pr- <i>n</i>	-60 to -20°, 10 h	(75) 83	522 517 164	
R	Yld	%ee															
SiEt ₃	-30°, 12 h	(61) 93															
Sn(Bu- <i>n</i>) ₃	-35°, 16 h	(75) 91															
Pr- <i>n</i>	-60 to -20°, 10 h	(75) 83															
	122^b (8 mol%), PhMe, Ti(OPr- <i>i</i>) ₄		<table border="1"> <thead> <tr> <th>R</th> <th>Yld</th> <th>%ee</th> </tr> </thead> <tbody> <tr> <td>SiMe₂Ph</td> <td>-20°, 12 h</td> <td>(70) 96</td> </tr> <tr> <td>OTIPS</td> <td>-20°, 12 h</td> <td>(71) 91</td> </tr> <tr> <td>Sn(Bu-<i>n</i>)₃</td> <td>-35°, 16 h</td> <td>(81) 92</td> </tr> </tbody> </table>	R	Yld	%ee	SiMe ₂ Ph	-20°, 12 h	(70) 96	OTIPS	-20°, 12 h	(71) 91	Sn(Bu- <i>n</i>) ₃	-35°, 16 h	(81) 92	526 526 517	
R	Yld	%ee															
SiMe ₂ Ph	-20°, 12 h	(70) 96															
OTIPS	-20°, 12 h	(71) 91															
Sn(Bu- <i>n</i>) ₃	-35°, 16 h	(81) 92															
	122^b (8 mol%), PhMe, Ti(OPr- <i>i</i>) ₄ , -35 to -20°, 14 h	(56) 94% ee	661 ^d														
C ₈ 		122^b (8 mol%), PhMe, Ti(OPr- <i>i</i>) ₄		<table border="1"> <thead> <tr> <th>R</th> <th>Yld</th> <th>%ee</th> </tr> </thead> <tbody> <tr> <td>Me</td> <td>-30°</td> <td>(63) 95</td> </tr> <tr> <td>Pr-<i>n</i></td> <td>-60 to -20°, 10 h</td> <td>(68) 95</td> </tr> <tr> <td>Ph</td> <td>-30°</td> <td>(73) 90</td> </tr> </tbody> </table>	R	Yld	%ee	Me	-30°	(63) 95	Pr- <i>n</i>	-60 to -20°, 10 h	(68) 95	Ph	-30°	(73) 90	164, 662 662 662
	R	Yld	%ee														
	Me	-30°	(63) 95														
	Pr- <i>n</i>	-60 to -20°, 10 h	(68) 95														
	Ph	-30°	(73) 90														
	RCHO	122^b (8 mol%), PhMe, Ti(OPr- <i>i</i>) ₄		<table border="1"> <thead> <tr> <th>R</th> <th>Yld</th> <th>%ee</th> </tr> </thead> <tbody> <tr> <td>Et</td> <td>-20°</td> <td>(81) 96</td> </tr> <tr> <td>C₆H₁₁</td> <td>-20°, 12 h</td> <td>(22) 78</td> </tr> <tr> <td>Ph</td> <td>-60 to -20°, 2 h</td> <td>(90) 93</td> </tr> </tbody> </table>	R	Yld	%ee	Et	-20°	(81) 96	C ₆ H ₁₁	-20°, 12 h	(22) 78	Ph	-60 to -20°, 2 h	(90) 93	660 ^d 242 ^d 515, 64
	R	Yld	%ee														
	Et	-20°	(81) 96														
	C ₆ H ₁₁	-20°, 12 h	(22) 78														
	Ph	-60 to -20°, 2 h	(90) 93														
	122^b (8 mol%), PhMe, Ti(OPr- <i>i</i>) ₄ , -20°, 12 h		<table border="1"> <thead> <tr> <th>R</th> <th>Yld</th> <th>%ee</th> </tr> </thead> <tbody> <tr> <td>OTBDPS</td> <td>(47)</td> <td>92</td> </tr> <tr> <td>OTIPS</td> <td>(74)</td> <td>90</td> </tr> <tr> <td>CH₂OTIPS</td> <td>(55)</td> <td>40</td> </tr> </tbody> </table>	R	Yld	%ee	OTBDPS	(47)	92	OTIPS	(74)	90	CH ₂ OTIPS	(55)	40	532 532 526	
R	Yld	%ee															
OTBDPS	(47)	92															
OTIPS	(74)	90															
CH ₂ OTIPS	(55)	40															

TABLE XXI. ENANTIOSELECTIVE ADDITIONS OF FUNCTIONALIZED DIORGANOZINC REAGENTS TO ALDEHYDES (Continued)^a

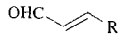
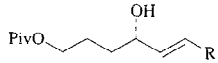
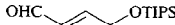
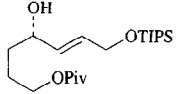
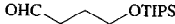
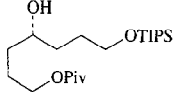
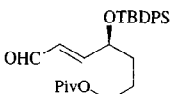
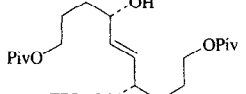

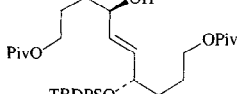
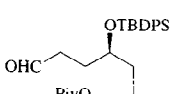
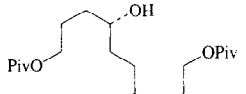
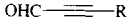
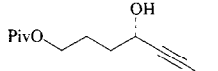
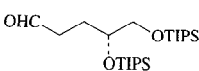
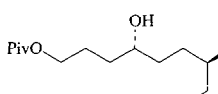
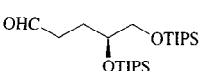
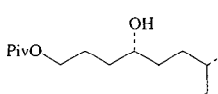
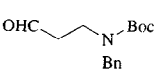
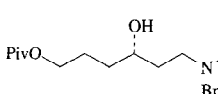
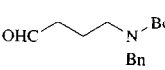
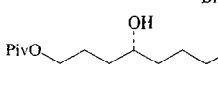
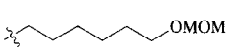
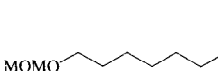
(FG-R) ₂ Zn (FG-R)	Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.	
 R Me Pr- <i>n</i> Ph SiMe ₃ SiEt ₃ Sn(Bu- <i>n</i>) ₃	 PivO	122^b (8 mol%), PhMe, Ti(OR ¹) ₄	Yld %ee (74) 92 (49) 93 (91) 90 (62) 90 (71) 90 (67) 90	565 ^d 516 565 ^d 522 522 517	
		 OTIPS	122^b (8 mol%), PhMe, Ti(OPr- <i>i</i>) ₄ , -75 to -20°, 6 h	 (63) 97% ee	524
		 OTIPS	122^b (8 mol%), PhMe, Ti(OPr- <i>i</i>) ₄ , -75 to -20°, 6 h	 (62) 96% ee	524
		 OTBDPS PivO	122^b (8 mol%), PhMe, Ti(OPr- <i>i</i>) ₄ , -75 to -15°, 12 h	 (73) dr >97:3	524
		 OTBDPS PivO	ent-122^b (8 mol%), PhMe, Ti(OPr- <i>i</i>) ₄ , -75 to -15°, 12 h	 (64) dr >97:3	524
		 OTBDPS PivO	122^b (8 mol%), PhMe, Ti(OPr- <i>i</i>) ₄ , -75 to -15°, 12 h	 (61) dr = 96:4	524
 R Bu- <i>n</i> Ph TIPS CH ₂ OTBDPS	 PivO	122^b (15 mol%), PhMe, Ti(OPr- <i>i</i>) ₄ , Ti(OBu- <i>t</i>) ₄ , -35 to -25°	Yld %ee (83) 90 (85) 88 (71) 92 (76) 94	662	
		 OTIPS	122^b (8 mol%), PhMe, Ti(OPr- <i>i</i>) ₄ , -40 to -25°	 (71) 369, 598 <i>syn:anti</i> > 98:2	
		 OTIPS	ent-122^b (8 mol%), PhMe, Ti(OPr- <i>i</i>) ₄ , -40 to -25°	 (61) 369, 598 <i>syn:anti</i> > 2:98	
		 Boc Bn	122^b (8 mol%), Et ₂ O, Ti(OPr- <i>i</i>) ₄ , -20°	 (90) 95% ee	663 ^d
 Boc Bn	122^b (8 mol%), Et ₂ O, Ti(OPr- <i>i</i>) ₄ , -20°	 (66) 79% ee	663 ^d		
 MOM	PhCHO	121a^c (10 mol%), Et ₂ O, Ti(OPr- <i>i</i>) ₄ , -78 to -30°, 20 h	 (68) 84% ee	512 ^d	

TABLE XXI. ENANTIOSELECTIVE ADDITIONS OF FUNCTIONALIZED DIORGANOZINC REAGENTS TO ALDEHYDES (Continued)^d

(FG-R) ₂ Zn (FG-R)	Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.	
C ₉ 	RCHO	122^b (8 mol%), PhMe, Ti(OPr- <i>i</i>) ₄ , -20°			
	<u>R</u>		<u>Yld</u> <u>%ee</u>		
	<i>n</i> -C ₅ H ₁₁	10 h	(72) 95	515, 242 ^d	
	Ph	—	(81) 93	660 ^d	
	4-NCC ₆ H ₄	12 h	(69) 80	515, 242 ^d	
		122^b (8 mol%), PhMe, Ti(OPr- <i>i</i>) ₄ , -20°, 12 h		(71)	242 ^d
			<i>syn:anti</i> = 93:7		
		RCHO	122^b (8 mol%), PhMe, Ti(OPr- <i>i</i>) ₄ , -20°		
	<u>R</u>		<u>Yld</u> <u>%ee</u>		
	Et	—	(81) 97	660 ^d	
Ph	12 h	(82) 89	664 ^d		
	RCHO	122^b (8 mol%), Et ₂ O, Ti(OPr- <i>i</i>) ₄ , -30°		662	
<u>R</u>		<u>Yld</u> <u>%ee</u>			
Me		(85) 92			
Pr- <i>n</i>		(88) 96			
Ph		(78) 84			
	RCHO	122^b (8 mol%), PhMe, Ti(OPr- <i>i</i>) ₄ , -20°, 12 h		(45) 93% ee	532
	RCHO	122^b (8 mol%), PhMe, Ti(OPr- <i>i</i>) ₄ , -20°, 12 h		(52) 95% ee	242 ^d
	RCHO	122^b (8 mol%), PhMe, Ti(OPr- <i>i</i>) ₄			
<u>R</u>		<u>Yld</u> <u>%ee</u>			
Me	-45 to -25°, 16 h	(76) 94	565 ^d		
Pr- <i>n</i>	-45 to -25°, 16 h	(82) 95	659, 516		
Bu- <i>t</i>	-45 to -25°, 16 h	(61) 97	565 ^d		
Ph	-45 to -20°, 16 h	(93) 90	565 ^d		
CH ₂ OTIPS	-75 to -15°, 6 h	(58) 95	524		
	RCHO	122^b (15 mol%), PhMe, Ti(OPr- <i>i</i>) ₄ , Ti(OBu- <i>t</i>) ₄ , -35 to -25°			662
<u>R</u>		<u>Yld</u> <u>%ee</u>			
Bu- <i>n</i>		(73) 82			
TIPS		(86) 86			
	RCHO	122^b (8 mol%), PhMe, Ti(OPr- <i>i</i>) ₄ , -75 to -15°, 6 h		(69) 95% ee	524, 576
	RCHO	122^b (8 mol%), PhMe, Ti(OPr- <i>i</i>) ₄ , -20°		(87) 95% ee	660 ^d

TABLE XXI. ENANTIOSELECTIVE ADDITIONS OF FUNCTIONALIZED DIORGANOZINC REAGENTS TO ALDEHYDES (Continued)^d

(FG-R) ₂ Zn (FG-R)	Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.								
		122^b (8 mol%), Et ₂ O, Ti(OPr- <i>i</i>) ₄ , -20°	 (81) 31% ee	663 ^d								
		122^b (8 mol%), Et ₂ O, Ti(OPr- <i>i</i>) ₄ , -20°	 (87) 96% ee	663 ^d								
		122^b (8 mol%), Et ₂ O, Ti(OPr- <i>i</i>) ₄ , -20°	 (85) 87% ee	663 ^d								
		122^b (8 mol%), Et ₂ O, Ti(OPr- <i>i</i>) ₄ , -20°	 (47) <i>syn:anti</i> = 16:84	663 ^d								
		<i>ent</i> - 122^b (8 mol%), Et ₂ O, Ti(OPr- <i>i</i>) ₄ , -20°	 (36) <i>syn:anti</i> = 85:15	663 ^d								
		122^b (8 mol%), PhMe, Ti(OPr- <i>i</i>) ₄ , -35 to -20°, 14 h	 (61) 95% ee	661 ^d								
		122^b (8 mol%), Et ₂ O, Ti(OPr- <i>i</i>) ₄ , -20°	 (46) 85% ee	661 ^d								
		122^b (8 mol%), Et ₂ O, Ti(OPr- <i>i</i>) ₄ , -20°	 (61) 91% ee	661 ^d								
C ₁₀		122^b (5 mol%), PhMe, Ti(OPr- <i>i</i>) ₄ , -45 to -25°, 16 h	 (69) 83% ee	659 ^d								
		122^b (8 mol%), Et ₂ O, Ti(OBu- <i>t</i>) ₄ , -20°, 12 h	 (41) <i>syn:anti</i> = 94:6 >95% ee	515, 242 ^d								
		122^b (8 mol%), Et ₂ O, Ti(OPr- <i>i</i>) ₄ , -30°	 <table border="1"> <thead> <tr> <th>Yld</th> <th>%ee</th> </tr> </thead> <tbody> <tr> <td>(76)</td> <td>84</td> </tr> <tr> <td>(72)</td> <td>86</td> </tr> </tbody> </table>	Yld	%ee	(76)	84	(72)	86	662		
Yld	%ee											
(76)	84											
(72)	86											
		122^b (8 mol%), PhMe, Ti(OPr- <i>i</i>) ₄ , -40 to -25°	 (59) <i>syn:anti</i> = 94:6	369, 598								
		<i>ent</i> - 122^b (8 mol%), PhMe, Ti(OPr- <i>i</i>) ₄ , -40 to -25°	 (61) <i>syn:anti</i> = 5:95	369, 598								
		122^b (5 mol%), PhMe, Ti(OPr- <i>i</i>) ₄	 <table border="1"> <thead> <tr> <th>Yld</th> <th>%ee</th> </tr> </thead> <tbody> <tr> <td>(54)</td> <td>97</td> </tr> <tr> <td>(91)</td> <td>93</td> </tr> <tr> <td>(67)</td> <td>85</td> </tr> </tbody> </table>	Yld	%ee	(54)	97	(91)	93	(67)	85	565 ^d 565 ^d 522
Yld	%ee											
(54)	97											
(91)	93											
(67)	85											
		-45 to -25°, 16 h -20°, 16 h -40°, 12 h										

TABLE XXI. ENANTIOSELECTIVE ADDITIONS OF FUNCTIONALIZED DIORGANOZINC REAGENTS TO ALDEHYDES (Continued)^a

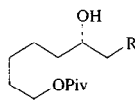
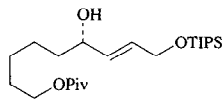
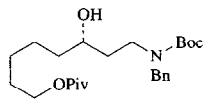
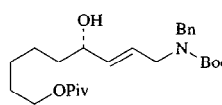
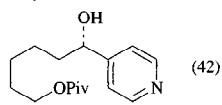
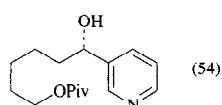
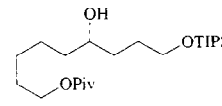
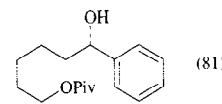
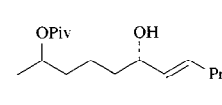
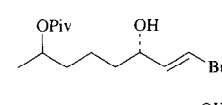
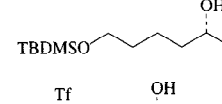
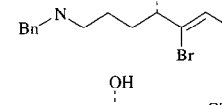
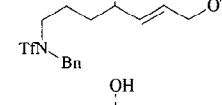
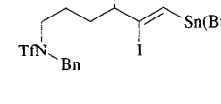
(FG-R) ₂ Zn (FG-R)	Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
	OHC-CH ₂ -R	122^b (8 mol%), PhMe, Ti(OPr- <i>i</i>) ₄ , -20°, 12 h		
	R		Yld %ee	
	Bn		(79) 82	660 ^d
	OTIPS		(75) 93	532
	CH ₂ OTIPS		(72) 91	526
	OTBDPS		(39) 70	532
	OHC-CH=CH-OTIPS	122^b (5 mol%), PhMe, Ti(OPr- <i>i</i>) ₄ , -60 to -20°, 10 h	 (90) 92% ee	164
	OHC-CH ₂ -N(Bn)-Boc	122^b (8 mol%), Et ₂ O, Ti(OPr- <i>i</i>) ₄ , -20°	 (90) 97% ee	663 ^d
	OHC-CH=CH-N(Bn)-Boc	122^b (8 mol%), Et ₂ O, Ti(OPr- <i>i</i>) ₄ , -20°	 (75) 90% ee	663 ^d
	OHC-C ₆ H ₄ -N ⁺ (BEt ₃) ⁻	122^b (8 mol%), Et ₂ O, Ti(OPr- <i>i</i>) ₄ , -20°	 (42) 88% ee	661 ^d
	OHC-C ₅ H ₄ -N ⁺ (BEt ₃) ⁻	122^b (8 mol%), Et ₂ O, Ti(OPr- <i>i</i>) ₄ , -20°	 (54) 93% ee	661 ^d
	OHC-CH ₂ -CH ₂ -CH ₂ -OTIPS	122^b (8 mol%), PhMe, Ti(OPr- <i>i</i>) ₄ , -55 to -15°, 6 h	 (43) 96% ee	524
	PhCHO	122^b (8 mol%), PhMe, Ti(OPr- <i>i</i>) ₄ , -20°, 12 h	 (81) 95% ee	664 ^d
	OHC-CH=CH-Pr- <i>n</i>	122^b (5 mol%), PhMe, Ti(OPr- <i>i</i>) ₄ , -45°, 20 h	 (82) 94% ee	565 ^d
	OHC-CH=CH-Bu- <i>t</i>	122^b (5 mol%), PhMe, Ti(OPr- <i>i</i>) ₄ , -45 to -25°, 16 h	 (82) 94% ee	565 ^d
	PhCHO	122^b (8 mol%), PhMe, Ti(OPr- <i>i</i>) ₄ , -20°, 12 h	 (82) 92% ee	515
C ₁₁	OHC-CH=CH-Pr- <i>n</i>	122^b (8 mol%), PhMe, Ti(OPr- <i>i</i>) ₄ , -20°, 12 h	 (56) 86% ee	164
	OHC-CH=CH-OTIPS	122^b (8 mol%), PhMe, Ti(OPr- <i>i</i>) ₄ , -75 to -15°, 6 h	 (48) 73% ee	524
	OHC-CH=CH-Sn(Bu- <i>n</i>) ₃	122^b (8 mol%), PhMe, Ti(OPr- <i>i</i>) ₄ , -60 to -20°, 10 h	 (62) 82% ee	164

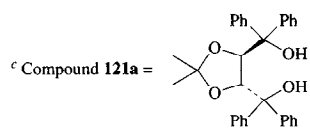
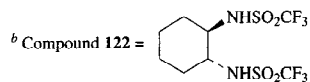
TABLE XXI. ENANTIOSELECTIVE ADDITION OF FUNCTIONALIZED DIORGANOZINC REAGENTS TO ALDEHYDES (Continued)^d

	(FG-R) ₂ Zn (FG-R)	Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₁₂			122^b (8 mol%), PhMe, Ti(OBu- <i>t</i>) ₄ , -20°, 12 h	 (60) 90% ee	242 ^d
		PhCHO	122^b (8 mol%), PhMe, Ti(OPr- <i>i</i>) ₄ , -20°, 12 h	 (60) 50% ee	515
C ₁₃			122^b (8 mol%), PhMe, Ti(OPr- <i>i</i>) ₄ , -40°, 12 h	 (67) 93% ee	522
		RCHO <u>R</u> <i>i</i> -Bu <i>n</i> -C ₃ H ₇ Ph	122^b (8 mol%), Et ₂ O, Ti(OPr- <i>i</i>) ₄ , -20°, 12 h	 Yld %ee (60) 92 (66) 91 (77) 96	573 ^d
C ₁₅			122^b (8 mol%), Et ₂ O, Ti(OPr- <i>i</i>) ₄ , -20°, 12 h	 (55) 85% ee	573 ^d
			122^b (8 mol%), Et ₂ O, Ti(OPr- <i>i</i>) ₄ , -20°, 12 h	 (45) 96% ee	573 ^d
			122^b (8 mol%), PhMe, Ti(OBu- <i>t</i>) ₄ , -70 to -15°, 6 h	 (48) 81% ee	524
			122^b (5 mol%), PhMe, Ti(OPr- <i>i</i>) ₄ , -45 to -25°, 16 h	 (82) 92% ee	565 ^d
			122^b (5 mol%), PhMe, Ti(OPr- <i>i</i>) ₄ , -45 to -25°, 16 h	 (80) 93% ee	565 ^d
C ₁₇		—	127 (1 mol%), C ₆ H ₁₅ , 0°, 4 h	 (75) 92% ee	238
C ₁₈		—	ent-127 (1 mol%), C ₆ H ₁₅ , 0°	 (52) 79% ee	533 ^d
		—	ent-127 (1 mol%), C ₆ H ₁₅ , 0°, 2.5 h	 (60) <i>syn:anti</i> = 91:9	533 ^d
		—	127 (1 mol%), C ₆ H ₁₅ , 0°, 2.5 h	 (40) <i>syn:anti</i> = 15:85	533 ^d

TABLE XXI. ENANTIOSELECTIVE ADDITION OF FUNCTIONALIZED DIORGANOZINC REAGENTS TO ALDEHYDES (Continued)^a

	(FG-R) ₂ Zn (FG-R)	Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
<i>B. Reactions with Mixed Diorganozincs</i>					
C ₈		PhCHO	PhMe, -30°, 12 h, (10 mol%)	 (66) 99% ee	582 ^d
C ₁₃		PhCHO	PhMe, -30°, 12 h, (10 mol%)	 (67) 92% ee	582 ^d

^a Unless otherwise indicated, the organozinc reagents were prepared by halide-zinc exchange.



^d The organozinc reagent was prepared by a transmetallation reaction.

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References

1. Frankland, E. Liebigs Ann. Chem. 1849, **71**, 171, 213.
2. Nützel, K. In Methoden der Organischen Chemie, Metallorganische Verbindungen Be, Mg, Ca, Sr, Ba, Zn, Cd, Volume **13/2a**, Thieme: Stuttgart, 1973, p. 552.
3. Reformatsky Chem Ber. 1887, **20**, 1210; 1895, 28, 2842.
4. Fürstner, A. Synthesis 1989, 571.
5. Fürstner, A. Angew. Chem., Int. Ed. Engl. 1993, **32**, 164.
6. Shriner, R. L. Org. React. 1942, **1**, 1.
7. Simmons, H. E.; Smith, R. D. J. Am. Chem. Soc. 1985, **80**, 5323.
8. Simmons, H. E.; Smith, R. D. J. Am. Chem. Soc. 1959, **81**, 4256.
9. Blanchard, E. P.; Simmons, H. E. J. Am. Chem. Soc. 1964, **86**, 1337, 1347.
10. Simmons, H. E.; Cairns, T. L.; Vladuchick, A.; Hoiness, C. M. Org. React. 1972, **20**, 1.
11. Furukawa, J.; Kawabata, N.; Nishimura, J. Tetrahedron Lett. 1966, 3353.
12. Furukawa, J.; Kawabata, N. Adv. Organomet. Chem. 1974, **12**, 83.
13. Sawada, S.; Inouye, Y. Bull Chem. Soc. Jpn. 1969, **42**, 2669.
14. Knochel, P.; Singer, R. D. Chem. Rev. 1993, **93**, 2117.
15. Knochel, P. Synlett 1995, 393.
16. Knochel, P.; Vettel, S.; Eisenberg, C. Applied Organomet. Chem. 1995, **9**, 175.
17. Knochel, P.; Langer, F.; Rottländer, M.; Stüdemann, T. Chem. Ber. 1997, **130**, 387.
18. Knochel, P.; Almena, J.; Jones, P. Tetrahedron 1998, **54**, 8275.
19. Knochel, P.; Jones, P. *Organozinc Reagents. A Practical Approach*, Oxford University Press, 1999.
20. Skinner, H. A. Adv. Organometal. Chem. 1964, **2**, 49.
21. Negishi, E. Organometallics in Organic Synthesis, Volume **1**, Wiley: New York, 1980.
22. Negishi, E.; Valente, L. F.; Kobayashi, M. J. Am. Chem. Soc. 1980, **102**, 3298.
- 22a. Erdik, E. Tetrahedron 1992, **48**, 9577.
23. Kobayashi, M.; Negishi, E. J. Org. Chem. 1980, **45**, 5223.
24. Negishi, E. Acc. Chem. Res. 1982, **15**, 340.
25. Negishi, E.; Bagheri, V.; Chatterjee, S.; Luo, F.-T.; Miller, J. A.; Stoll, A. T. Tetrahedron Lett. 1983, **24**, 5181.

26. Grey, R. A. *J. Org. Chem.* 1984, **49**, 2288.
27. Nakamura, E.; Kuwajima, I. *Tetrahedron Lett.* 1986, **27**, 83.
28. Sato, T.; Naruse, K.; Enokiya, M.; Fujisawa, T. *Chem. Lett.* 1981, 1135.
29. Hunsdiecker, H.; Erlbach, H.; Vogt, E., German Patent 722467, 1942; *Chem. Abstr.* 1943, **37**, 5080.
30. Wittig, G.; Jautelat, M. *Liebigs Ann. Chem.* 1967, **702**, 24.
31. Wittig, G.; Schwarzenbach, K. *Angew. Chem.* 1959, **71**, 652.
32. Wittig, G.; Schwarzenbach, K. *Liebigs Ann. Chem.* 1961, **650**, 1.
33. Wittig, G.; Wingler, F. *Liebigs Ann. Chem.* 1962, **656**, 18.
34. Wittig, G.; Wingler, F. *Chem. Ber.* 1964, **97**, 2139, 2146.
35. Rajagopal, D.; Eckhardt, M.; Furlong, M.; Knoess, H. P.; Berger, S.; Knochel, P. *Tetrahedron* 1994, **50**, 2415.
36. Sakurai, M.; Hata, T.; Yabe, Y. *Tetrahedron Lett.* 1993, **34**, 5939.
37. Sakami, S.; Houkawa, T.; Asaoka, M.; Takei, H. *J. Chem. Soc., Perkin Trans. 1*, 1995, 285.
38. Houkawa, T.; Ueda, T.; Sakami, S.; Takei, H. *Tetrahedron Lett.* 1996, **37**, 1045.
39. Witanowski, M.; Roberts, J. D. *J. Am. Chem. Soc.* 1966, **88**, 737.
40. Boudier, A.; Knochel, P. *Tetrahedron Lett.* 1999, **40**, 687.
41. Wang, F.; Labaudinière, L.; Marek, I.; Normant, J.-F. *Synlett* 1995, 723.
42. Darcel, C.; Flachsmann, F.; Knochel, P. *Chem. Commun.* 1998, 205.
43. Brown, H. C.; Mandal, A. K.; Yoon, N. M.; Singaram, B.; Schwier, J. R.; Jadhav, P. K. *J. Org. Chem.* 1982, **47**, 5069.
44. Boudier, A.; Flachsmann, F.; Knochel, P. *Synlett* 1998, 1438.
- 44a. Hupe, E.; Knochel, P. *Org. Lett.* 2001, **3**, 127.
45. Gaudemar, M. *Bull. Soc. Chim. Fr.* 1962, 974.
46. Erdik, E. *Tetrahedron* 1987, **43**, 2203.
47. Knochel, P.; Yeh, M. C. P.; Berk, S. C.; Talbert, J. *J. Org. Chem.* 1988, **53**, 2390.
48. Majid, T. N.; Knochel, P. *Tetrahedron Lett.* 1990, **31**, 4413.
49. Prasad, A. S. B.; Knochel, P. *Tetrahedron* 1997, **53**, 16711.
50. Berk, S. C.; Knochel, P.; Yeh, M. C. P. *J. Org. Chem.* 1988, **53**, 5798.
51. Berk, S. C.; Yeh, M. C. P.; Jeong, N.; Knochel, P. *Organometallics* 1990, **9**, 3053.
52. Yeh, M. C. P.; Knochel, P.; Butler, W. M.; Berk, S. C. *Tetrahedron Lett.* 1988, **29**, 6693.
53. Chen, H. G.; Gage, J. L.; Barrett, S. D.; Knochel, P. *Tetrahedron Lett.* 1990, **31**, 1829.

54. Yeh, M. C. P.; Knochel, P.; Santa, L. E. *Tetrahedron Lett.* 1988, **29**, 3887.
55. Yeh, M. C. P.; Knochel, P. *Tetrahedron Lett.* 1989, **30**, 4799.
56. Retherford, C.; Yeh, M. C. P.; Schipor, I.; Chen, H. G.; Knochel, P. J. *Org. Chem.* 1989, **54**, 5200.
57. Tucker, C. E.; AchyuthaRao, S.; Knochel, P. J. *Org. Chem.* 1990, **55**, 5446.
58. Knochel, P.; Chou, T.-S.; Chen, H. G.; Yeh, M. C. P.; Rozema, M. J. J. *Org. Chem.* 1989, **54**, 5202.
59. Chou, T.-S.; Knochel, P. J. *Org. Chem.* 1990, **55**, 4791.
60. Knochel, P.; Chou, T.-S.; Jubert, C.; Rajagopal, D. J. *Org. Chem.* 1993, **58**, 588
61. Knochel, P. J. *Am. Chem. Soc.* 1990, **112**, 7431.
62. Waas, J. R.; AchyuthaRao, S.; Knochel, P. *Tetrahedron Lett.* 1992, **33**, 3717.
63. Retherford, C.; Knochel, P. *Tetrahedron Lett.* 1991, **32**, 441.
64. Rozema, M. J.; AchyuthaRao, S.; Knochel, P. J. *Org. Chem.* 1992, **57**, 1956.
65. Knochel, P.; Rozema, M. J.; Tucker, C. E.; Retherford, C.; Furlong, M.; AchyuthaRao, S. *Pure Appl. Chem.* 1992, **64**, 361.
66. AchyuthaRao, S.; Knochel, P. J. *Org. Chem.* 1991, **56**, 4591.
67. Rozema, M. J.; Rajagopal, D.; Tucker, C. E.; Knochel, P. J. *Organomet. Chem.* 1992, **438**, 11.
68. Yeh, M. C. P.; Sun, M.-L.; Lin, S.-K. *Tetrahedron Lett.* 1991, **32**, 113.
69. Yeh, M. C. P.; Tau, S.-J. *J. Chem. Soc., Chem. Commun.* 1992, 13.
70. Yeh, M. C. P.; Tsou, C.-J.; Chuang, C.-N.; Lin, H.-C. *J. Chem. Soc., Chem. Commun.* 1992, 890.
71. Blankenfeldt, W.; Liao, J.-W.; Lo, L.-C.; Yeh, M. C. P. *Tetrahedron Lett.* 1996, **37**, 7361.
72. Yeh, M. C. P.; Shen, B.-A.; Fu, H.-W.; Tau, S. I.; Chuang, L. W. *J. Am. Chem. Soc.* 1993, **115**, 5941.
73. Yeh, M.C.P.; Chuang, C.-N. *J. Chem. Soc., Chem. Commun.* 1994, 703.
74. Jubert, C.; Knochel, P. J. *Org. Chem.* 1992, **57**, 5431.
75. Yeh, M. C. P.; Knochel, P. *Tetrahedron Lett.* 1988, **29**, 2395.
76. Majid, T. N.; Yeh, M. C. P.; Knochel, P. *Tetrahedron Lett.* 1989, **30**, 5069.
77. Chen, H. G.; Hoehstetter, C.; Knochel, P. *Tetrahedron Lett.* 1989, **30**, 4795.
78. Knoess, H. P.; Furlong, M. T.; Rozema, M. J.; Knochel, P. J. *Org. Chem.*

- 1991, **56**, 5974.
79. Yeh, M. C. P.; Chen, H. G.; Knochel, P. *Org. Synth.* 1991, **70**, 195.
80. Tamaru, Y. In *New Trends in Organometallic Chemistry*, Sakurai, H., Ed., Tohoku University, Sendai, Japan, 1990, 304.
81. Knochel, P.; Yeh, M. C. P. 1988, unpublished results.
82. AchyuthaRao, S.; Tucker, C. E.; Knochel, P. *Tetrahedron Lett.* 1990, **31**, 7575.
83. AchyuthaRao, S.; Chou, T.-S.; Schipor, I.; Knochel, P. *Tetrahedron*, 1992, **48**, 2025.
84. Kanai, G.; Miyaura, N.; Suzuki, A. *Chem. Lett.* 1993, 845.
85. Watanabe, T.; Miyaura, N.; Suzuki, A. *J. Organomet. Chem.* 1993, **444**, C1.
86. Watanabe, T.; Sakai, M.; Miyaura, N.; Suzuki, A. *J. Chem. Soc., Chem. Commun.* 1994, 467.
87. JanakiramRao, C.; Knochel, P. *J. Org. Chem.* 1991, **56**, 4593.
88. Knochel, P.; JanakiramRao, C. *Tetrahedron* 1993, **49**, 29.
89. Bronk, B. S.; Lippard, S. J.; Danheiser, R. L. *Organometallics* 1993, **12**, 3340.
90. Retherford, C.; Chou, T.-S.; Schelkun, R. M.; Knochel, P. *Tetrahedron Lett.* 1990, **31**, 1833.
91. Jackson, R. F. W.; James, K.; Wythes, M. J.; Wood, A. *J. Chem. Soc., Chem. Commun.* 1989, 644.
92. Jackson, R. F. W.; Wythes, M. J.; Wood, A. *Tetrahedron Lett.* 1989, **30**, 5941.
93. Jackson, R. F. W.; Wood, A.; Wythes, M. J. *Synlett* 1990, 735.
94. Dunn, M. J.; Jackson, R. F. W. *J. Chem. Soc., Chem. Commun.* 1992, 319.
95. Jackson, R. F. W.; Wishart, N.; Wythes, M. J. *J. Chem. Soc., Chem. Commun.* 1992, 1587.
96. Dunn, M. J.; Jackson, R. F. W.; Stephenson, G. R. *Synlett* 1992, 905.
97. Jackson, R. F. W.; Wishart, N.; Wythes, M. J. *Synlett* 1993, 219.
98. Jackson, R. F. W.; Wishart, N.; Wood, A.; James, K.; Wythes, M. J. *J. Org. Chem.* 1992, **57**, 3397.
99. Dexter, C. S.; Jackson, R. F. W. *J. Chem. Soc., Chem. Commun.* 1998, 75.
- 99a. Dunn, M.; Jackson, R.F.W.; Pietruszka, J.; Turner, D. *J. Org. Chem.* 1995, **60**, 2210.
100. Dunn, M. J.; Jackson, R. F. W.; Pietruszka, J.; Wishart, N.; Ellis, D.; Wythes, M. J. *Synlett* 1993, 499.

101. Fraser, J.L.; Jackson, R.F.W.; Porter, B. *Synlett* 1994, 379.
102. Dow, R.L.; Bechler, B.M. *Synlett* 1994, 293.
103. Jubert, C.; Knochel, P. *J. Org. Chem.* 1992, **57**, 5425.
104. Tamaru, Y.; Ochiai, H.; Yoshida, Z. *Tetrahedron Lett.* 1984, **25**, 3861.
105. Tamaru, Y.; Ochiai, H.; Nakamura, T.; Tusbaki, K.; Yoshida, Z. *Tetrahedron Lett.* 1985, **26**, 5559.
106. Haszeldine, R. N.; Walaschewski, E. G. *J. Chem. Soc.* 1953, 3607.
107. Miller, W. T.; Bergmann, E.; Fainberg, A. H. *J. Am. Chem. Soc.* 1957, **79**, 4159.
108. Chambers, R. D.; Musgrave, W. K. R.; Savory, J. J. *J. Chem. Soc.* 1962, 1993.
109. Kumai, S.; Munekata, S.; Yamabe, M. *Asahi Garasu Kenkyu Hokoku* 1981, **31**, 91; *Chem. Abstr.* 1982, **97**, 23253b.
110. Blancou, H.; Commeyras, A. *J. Fluorine Chem.* 1982, **20**, 255.
111. Benefice, S.; Blancou, H.; Commeyras, A. *J. Fluorine Chem.* 1983, **23**, 47.
112. Benefice-Malouet, S.; Blancou, H.; Commeyras, A. *J. Fluorine Chem.* 1985, **30**, 171.
113. Burton, D. J. *Tetrahedron* 1992, **48**, 189.
114. Burton, D.J.; Yang, Z.-Y.; Morken, P.A. *Tetrahedron* 1994, **50**, 2993.
115. Blancou, H.; Moreau, P.; Commeyras, A. *Tetrahedron* 1977, **33**, 2061.
116. Burton, D. J.; Wiemers, D. M. *J. Am. Chem. Soc.* 1985, **107**, 5014.
117. Wiemers, D. M.; Burton, D. J. *J. Am. Chem. Soc.* 1986, **108**, 832.
118. Stevenson, T.; Prasad, B. A. S.; Citineni, J. R.; Knochel, P. *Tetrahedron Lett.* 1996, **37**, 8375.
119. Prasad, B. A. S.; Stevenson, T.; Citineni, J. R.; Nyzam, V.; Knochel, P. *Tetrahedron.* 1997, **53**, 7237.
120. Zhu, L.; Wehmeyer, R. M.; Rieke, R. D. *J. Org. Chem.* 1991, **56**, 1445.
121. Rieke, R. D.; Kim, S.-H.; Wu, X. *J. Org. Chem.* 1997, **62**, 6921.
122. Zhu, L.; Rieke, R. D. *Tetrahedron Lett.* 1991, **32**, 2865.
123. Rieke, R. D.; Soll, M. S.; Xiong, H. *J. Am. Chem. Soc.* 1995, **117**, 5429.
124. Rieke, R. D.; Uhm, S. J.; Hudnall, P. M. *J. Chem. Soc., Chem. Commun.* 1973, 269.
125. Rieke, R. D.; Li, P. T.-J.; Burns, T. P.; Uhm, S. T. *J. Org. Chem.* 1981, **46**, 4323.
126. Rieke, R. D.; Uhm, S. J. *Synthesis* 1975, 452.
127. Rieke, R. D. *Science* 1989, **246**, 1260.
128. Hanson, M. V.; Brown, J. D.; Rieke, R. D. *Tetrahedron Lett.* 1994, **35**, 7205.

129. Hanson, M. V.; Rieke, R. D. *Synth. Comm.* 1995, **25**, 101.
130. Hanson, M. V.; Rieke, R. D. *J. Am. Chem. Soc.* 1995, **117**, 10775.
131. Rieke, R. D.; Hanson, M. V.; Brown, J. D. *J. Org. Chem.* 1996, **61**, 2726.
132. Guijarro, A.; Rieke, R. D. *Angew. Chem., Int. Ed. Engl.* 1998, **37**, 1679.
133. Fürstner, A.; Singer, R.; Knochel, P. *Tetrahedron Lett.*, 1994, **35**, 1047.
134. Stadtmüller, H.; Greve, B.; Lennick, Chair, A.; Knochel, P. *Synthesis* 1995, 69.
135. Ochiai, H.; Nishihara, T.; Tamaru, Y.; Yoshida, Z. *J. Org. Chem.* 1988, **53**, 1343.
136. Tamaru, Y.; Ochiai, H.; Sanda, F.; Yoshida, Z. *Tetrahedron Lett.* 1985, **26**, 5529.
137. Tamaru, Y.; Ochiai, H.; Nakamura, T.; Yoshida, Z. *Tetrahedron Lett.* 1986, **27**, 955.
138. Tamaru, Y.; Ochiai, H.; Nakamura, T.; Yoshida, Z. *Angew. Chem.* 1987, **99**, 1193.
139. Nakamura, E.; Sekiya, K.; Kuwajima, I. *Tetrahedron Lett.* 1987, **28**, 337.
140. Nakamura, E.; Aoki, S.; Sekiya, K.; Oshino, H.; Kuwajima, I. *J. Am. Chem. Soc.* 1987, **109**, 8056.
141. Ochiai, H.; Tamura, Y.; Tsubaki, K.; Yoshida, Z. *J. Org. Chem.* 1987, **52**, 4418.
142. Tamaru, Y.; Tanigawa, H.; Yamamoto, T.; Yoshida, Z. *Angew. Chem., Int. Ed. Engl.* 1989, **28**, 351.
143. Einhorn, C.; Einhorn, J.; Luche, J.-L. *Synthesis* 1990, 787.
144. Petrier, C.; de Souza Barbosa, J. C.; Dupuy, C.; Luche, J.-L. *J. Org. Chem.* 1985, **50**, 5761.
145. de Souza Barbosa, J. C.; Petrier, C.; Luche, J.-L. *Tetrahedron Lett.* 1985, **26**, 829.
146. Corey, E. J.; Link, J. O.; Shao, Y. *Tetrahedron Lett.* 1992, **33**, 3435.
147. Petrier, C.; Dupuy, C.; Luche, J. L. *Tetrahedron Lett.* 1986, **27**, 3149.
148. Einhorn, C.; Luche, J.-L. *J. Organomet. Chem.* 1987, **322**, 177.
149. Luche, J.-L.; Einhorn, C.; Einhorn, J.; Sinisterra-Gago, J. V. *Tetrahedron Lett.* 1990, **31**, 4125.
150. Jiang, B.; Xu, Y. *J. Org. Chem.* 1991, **56**, 7336.
151. Morken, P. A.; Lu, H.; Nakamura, A.; Burton, D. J. *Tetrahedron Lett.* 1991, **32**, 4271.
152. Hansen, S. W.; Spawn, T. D.; Burton, D. J. *J. Fluorine Chem.* 1987, **35**, 415.
153. Morken, P. A.; Burton, D. J. *J. Org. Chem.* 1993, **58**, 1167.
154. Gillet, J. P.; Sauvetre, R.; Normant, J. F. *Synthesis* 1986, 538.

155. Habeeb, J. J.; Osman, A.; Tuck, D. G. *J. Organomet. Chem.* 1980, **185**, 117.
156. Sibille, S.; Ratovelomanana, V.; Périchon, J. *J. Chem. Soc., Chem. Commun.* 1992, 283.
157. Chaussard, J.; Folest, J.-C.; Nédélec, J.-Y.; Périchon, J.; Sibille, S.; Troupel, M. *Synthesis* 1990, 369.
158. Durandetti, M.; Devaud, M.; Périchon, J. *New J. Chem.* 1996, **20**, 659.
159. Sibille, S.; Ratovelomanana, V.; Nédélec, J.-Y.; Périchon, J. *Synlett* 1993, 425.
160. Gosmini, C.; Nédélec, J. Y.; Périchon, J. *Tetrahedron Lett.* 1997, **38**, 1941.
161. Zylber, N.; Zylber, J.; Rollin, Y.; Dunach, E.; Périchon, J. *J. Organomet. Chem.* 1993, **444**, 1.
162. Rollin, Y.; Derien, S.; Dunach, E.; Gébéhenne, C.; Périchon, J. *Tetrahedron*, 1993, **49**, 7723.
163. Soai, K.; Niwa, S. *Chem. Rev.* 1992, **92**, 833.
164. Rozema, M. J.; Eisenberg, C.; Lütjens, H.; Ostwald, R.; Belyk, K.; Knochel, P. *Tetrahedron Lett.* 1993, **34**, 3115.
165. Stadtmüller, H.; Lentz, R.; Tucker, C. E.; Stüdemann, T.; Dörner, W.; Knochel, P. *J. Am. Chem. Soc.* 1993, **115**, 7027.
166. Stadtmüller, H.; Tucker, C. E.; Vaupel, A.; Knochel, P. *Tetrahedron Lett.* 1993, **34**, 7911.
- 166a Vettel, S.; Vaupel, A.; Knochel, P. *J. Org. Chem.* 1996, **61**, 7473.
167. Stadtmüller, H.; Vaupel, A.; Tucker, C. E.; Stüdemann, T.; Knochel, P. *Chem. Eur. J.* 1996, **2**, 1204.
168. Knochel, P. unpublished results, Marburg, 1992–1993.
169. Stadtmüller, H.; Knochel, P. *Synlett* 1995, 463.
170. Vaupel, A.; Knochel, P. *Tetrahedron Lett.* 1995, **36**, 231.
171. Vaupel, A.; Knochel, P. *J. Org. Chem.* 1996, **61**, 5743.
172. Agrios, K. A.; Srebnik, M. *J. Org. Chem.* 1993, **58**, 6908.
173. Mukhopadhyay, T.; Seebach, D. *Helv. Chim. Acta* 1982, **65**, 385.
174. Seebach, D.; Beck, A. K.; Mukhopadhyay, T.; Thomas, E. *Helv. Chim. Acta* 1982, **65**, 1101.
175. Bengtsson, M.; Liljefors, T. *Synthesis* 1988, 250.
176. Klement, I.; Chau, K.; Cahiez, G.; Knochel, P. *Tetrahedron Lett.* 1994, **35**, 1177.
177. Charette, A. B.; Beauchemin, A.; Marcoux, J.-F. *J. Am. Chem. Soc.* 1998, **20**, 5114.

178. Micouin, L.; Knochel, P. *Synlett* 1997, 327.
179. Berger, S.; Langer, F.; Lutz, C.; Knochel, P.; Mobley, T. A.; Reddy, C. K. *Angew. Chem., Int. Ed. Engl.* 1997, **36**, 1496.
180. Jones, P.; Reddy, C. K.; Knochel, P. *Tetrahedron* 1998, **54**, 1471.
181. Wakefield, B. J. In *Organolithium Methods*, Academic: London, 1988.
182. Stowell, J. C. In *Carbanions in Organic Synthesis*, Wiley: New York, 1979.
183. Brandsma, L.; Verkruijsse, H. In *Preparative Polar Organometallic Chemistry, Volume 1*; Springer-Verlag: Berlin, 1987.
184. Piers, E.; Karunaratne, V. *Can. J. Chem.* 1984, **62**, 629.
185. Piers, E.; Karunaratne, V. *J. Chem. Soc., Chem. Commun.* 1983, 935.
186. Piers, E.; Karunaratne, V. *J. Chem. Soc., Chem. Commun.* 1984, 959.
187. Piers, E.; Karunaratne, V. *J. Org. Chem.* 1983, **48**, 1774.
188. Piers, E.; Yeung, B. W. A. *J. Org. Chem.* 1984, **49**, 4567.
189. Najera, C.; Yus, M. *J. Org. Chem.* 1988, **53**, 4708.
190. Peterson, P. E.; Nelson, D. J.; Risener, R. *J. Org. Chem.* 1986, **51**, 2381.
191. Herrmann, J. L.; Berger, M. H.; Schlessinger, R. H. *J. Am. Chem. Soc.* 1979, **101**, 1544.
192. Midland, M. M.; Tramontano, A.; Cable, J. R. *J. Org. Chem.* 1980, **45**, 28.
193. Parham, W. E.; Jones, L. D.; Sayed, Y. *J. Org. Chem.* 1975, **40**, 2394.
194. Parham, W. E.; Jones, L. D. *J. Org. Chem.* 1976, **41**, 1187.
195. Parham, W. E.; Jones, L. D. *J. Org. Chem.* 1976, **41**, 2704.
196. Parham, W. E.; Piccirilli, R. M. *J. Org. Chem.* 1977, **42**, 257.
197. Parham, W. E.; Boykin, D. W. *J. Org. Chem.* 1977, **42**, 260.
198. Parham, W. E.; Bradsher, C. K. *Acc. Chem. Res.* 1982, **15**, 300.
199. Bolitt, V.; Mioskowski, C.; Reddy, S. P.; Falck, J. R. *Synthesis* 1988, 388.
200. Köbrich, G.; Buck, P. *Chem. Ber.* 1970, **103**, 1412.
201. Buck, P.; Köbrich, G. *Chem. Ber.* 1970, **103**, 1420.
202. Cameron, J. F.; Fréchet, J. M. J. *J. Am. Chem. Soc.* 1991, **113**, 4303.
203. Caine, D.; Frobese, A. S. *Tetrahedron Lett.* 1978, 5167.
204. Negishi, E.; Boardman, L. D.; Tour, J. M.; Sawada, H.; Rand, C. L. *J. Am. Chem. Soc.* 1983, **105**, 6344.
205. Sengupta, S.; Snieckus, V. *J. Org. Chem.* 1990, **55**, 5680.
206. Duhamel, L.; Duhamel, P.; Enders, D.; Karl, W.; Leger, F.; Poirier, J. M.; Raabe, G. *Synthesis* 1991, 649.

207. Cooke, M. P. *J. Org. Chem.* 1984, **49**, 1144.
208. Cooke, M. P.; Widener, R. K. *J. Org. Chem.* 1987, **52**, 1381.
209. Tucker, C. E.; Majid, T. N.; Knochel, P. J. *Am. Chem. Soc.* 1992, **114**, 3983.
210. Cahiez, G.; Venegas, P.; Tucker, C. E.; Majid, T. N.; Knochel, P. J. *Chem. Soc., Chem. Commun.* 1992, 1406.
211. Gillet, J.-P.; Sauvêtre, R.; Normant, J.-F. *Tetrahedron Lett.* 1985, **26**, 3999.
212. Tellier, F.; Sauvêtre, R.; Normant, J.-F. *J. Organomet. Chem.* 1986, **303**, 309.
213. Tellier, F.; Sauvêtre, R.; Normant, J.-F. *J. Organomet. Chem.* 1987, **328**, 1.
214. Tellier, F.; Sauvêtre, R.; Normant, J.-F.; Dromzee, Y.; Jeannin, Y. J. *Organomet. Chem.* 1987, **331**, 281.
215. Martinet, P.; Sauvêtre, R.; Normant, J. F. *J. Organomet. Chem.* 1989, **367**, 1.
216. Bailey, W. F.; Patricia, J. J. *J. Organomet. Chem.* 1988, **352**, 1.
217. Bailey, W. F.; Punzalan, E. R. *J. Org. Chem.* 1990, **55**, 5404.
218. Negishi, E.; Swanson, D. R.; Rousset, C. J. *J. Org. Chem.* 1990, **55**, 5406.
219. Seebach, D.; Neumann, H. *Chem. Ber.* 1974, **107**, 847.
220. Cahiez, G.; Bernard, D.; Normant, J. F. *Synthesis* 1976, 245.
221. Superchi, S.; Sotomayor, N.; Miao, G.; Joseph, B.; Snieckus, V. *Tetrahedron Lett.* 1996, **37**, 6057.
222. Lorthiois, E.; Marek, I.; Normant, J. F. *Tetrahedron Lett.* 1997, **38**, 89.
223. Karoyan, P.; Chassaing, G. *Tetrahedron Lett.* 1997, **38**, 85.
224. Karoyan, P.; Triolo, A.; Nannicini, R.; Gianotti, D.; Altamura, M.; Chassaing, G.; Perotta, E., *Tetrahedron Lett.* 1999, **40**, 71.
225. Lorthiois, E.; Marek, I.; Normant, J. F. *J. Org. Chem.* 1998, **63**, 566.
226. Lorthiois, E.; Marek, I.; Normant, J. F. *J. Org. Chem.* 1998, **63**, 2442.
227. Kubota, K.; Nakamura, E. *Angew. Chem. Int., Ed. Engl.* 1997, **36**, 2491.
228. Nakamura, E.; Sakata, G.; Kubota, K. *Tetrahedron Lett.* 1998, **39**, 2157.
229. Boymond, L.; Rottländer, M.; Cahiez, G.; Knochel, P. *Angew. Chem., Int. Ed. Engl.* 1998, **37**, 1701.
230. Giovannini, R.; Knochel, P. J. *Am. Chem. Soc.* 1998, **120**, 11186.
- 230a Rottländer, M.; Boymond, L.; Bérillon, L.; Leprêtre, A.; Varchi, G.; Avolio, S.; Laaziri, H.; Quéguiner, G.; Ricci, A.; Cahiez, G.; Knochel, P. *Chem. Eur. J.* 2000, **6**, 767.
231. Bérillon, L.; Leprêtre, A.; Turck, A.; Plé, N.; Quéguiner, G.; Cahiez, G.;

- Knochel, P. Synlett 1998, 1359.
232. Rottländer, M.; Boymond, L.; Cahiez, G.; Knochel, P. J. Org. Chem. 1999, **64**, 1080.
233. Thiele, K.-H.; Zdunneck, P. J. Organomet. Chem. 1965, **4**, 10.
234. Zakharin, L. I.; Okhlobystin, O. Y., Z. Obshch. Chim. 1960, **30**, 2134; Engl. trans., p. 2109, Chem. Abstr. 1961, **55**, 9319a.
235. Thiele, K.-H.; Engelhardt, G.; Köhler, J.; Arnstedt, M. J. Organomet. Chem. 1967, **9**, 385.
236. Srebnik, M. Tetrahedron Lett. 1991, **32**, 2449.
237. Opolzer, W.; Radinov, R. N. Helv. Chim. Acta 1992, **75**, 170.
238. Opolzer, W.; Radinov, R. N. J. Am. Chem. Soc. 1993, **115**, 1593.
239. Langer, F.; Waas, J.; Knochel, P. Tetrahedron Lett. 1993, **34**, 5261.
240. Langer, F.; Devasagayaraj, A.; Chavant, P.-Y.; Knochel, P. Synlett 1994, 410.
241. Köster, R.; Griasnow, G.; Larbig, W.; Binger, P. Liebigs Ann. Chem. 1964, **672**, 1.
242. Langer, F.; Schwink, L.; Devasagayaraj, A.; Chavant, P.-Y.; Knochel, P. J. Org. Chem. 1996, **61**, 8229.
243. Frankland, E.; Duppa, D. F. Liebigs Ann. Chem. 1864, **130**, 117.
244. Tucker, C. E.; Davidson, J.; Knochel, P. J. Org. Chem. 1992, **57**, 3482
245. Liu, E. K. S. Inorg. Chem. 1980, **19**, 266.
246. Liu, E. K. S.; Asprey, L. B. J. Organomet. Chem. 1979, **169**, 249.
247. Wipf, P.; Xu, W. Tetrahedron Lett. 1994, **35**, 5197.
248. Seyferth, D.; Dertouzos, H.; Todd, L. J. J. Organomet. Chem. 1965, **4**, 18.
249. Seyferth, D.; Andrews, S. B. J. Organomet. Chem. 1971, **30**, 151.
250. Staroscik, J. A.; Rickborn, B. J. Org. Chem. 1972, **37**, 738.
251. Kawabata, N.; Nakagawa, T.; Nakao, T.; Yamashita, S. J. Org. Chem. 1977, **42**, 3031.
252. Johnson, C. R.; Barbachyn, M. R. J. Am. Chem. Soc. 1982, **104**, 4290.
253. Fabisch, B.; Mitchell, T. N. J. Organomet. Chem. 1984, **269**, 219.
254. Bartnik, R.; Mloston, G. Synthesis 1983, 924.
255. Arai, I.; Mori, A.; Yamamoto, H. J. Am. Chem. Soc. 1985, **107**, 8254.
256. Mash, E.; Nelson, K. A. J. Am. Chem. Soc. 1985, **107**, 8256.
257. Mori, A.; Arai, I.; Yamamoto, H. Tetrahedron 1986, **42**, 6447.
258. Sugimura, T.; Futagawa, T.; Tai, A. Tetrahedron Lett. 1988, **29**, 5775.
259. Sugimura, T.; Futagawa, T.; Yoshikawa, M.; Tai, A. Tetrahedron Lett. 1989, **30**, 3807.

260. Mash, E. A.; Nelson, K. A.; Van Deusen, S.; Hemperly, S. B. *Org. Synth.* 1989, **68**, 92.
261. Mash, E. A.; Torok, D. S. *J. Org. Chem.* 1989, **54**, 250.
262. Mash, E. A.; Hemperly, S. B.; Nelson, K. A.; Heidt, P. C.; Van Deusen, S. *J. Org. Chem.* 1990, **55**, 2045.
263. Newman-Evans, R. H.; Simon, R. J.; Carpenter, B. K. *J. Org. Chem.* 1990, **55**, 695.
264. Friedrich, E. C.; Lewis, E. J. *J. Org. Chem.* 1990, **55**, 2491.
265. Imai, T.; Mineta, H.; Nishida, S. *J. Org. Chem.* 1990, **55**, 4986.
266. Knochel, P.; Jeong, N.; Rozema, M. J.; Yeh, M. C. *P. J. Am. Chem. Soc.* 1989, **111**, 6474.
267. Knochel, P.; AchyuthaRao, S. *J. Am. Chem. Soc.* 1990, **112**, 6146.
268. Rozema, M. J.; Knochel, P. *Tetrahedron Lett.* 1991, **32**, 1855.
269. Burns, M. R.; Coward, J. K. *J. Org. Chem.* 1993, **58**, 528.
270. Sidduri, A.; Rozema, M. J.; Knochel, P. *J. Org. Chem.* 1993, **58**, 2694.
271. AchyuthaRao, S.; Knochel, P. *J. Am. Chem. Soc.* 1992, **114**, 7579.
272. Negishi, E.; Akiyoshi, K. *J. Am. Chem. Soc.* 1988, **110**, 646.
273. Negishi, E.; Akiyoshi, K.; O'Connor, B.; Takagi, K.; Wu, G. *J. Am. Chem. Soc.* 1989, **111**, 3089.
274. Miller, J. A. *J. Org. Chem.* 1989, **54**, 998.
275. Kocienski, P.; Wadmann, S.; Cooper, K., J. *Am. Chem. Soc.* 1989, **111**, 2363.
276. Mortimore, M.; Kocienski, P. *Tetrahedron Lett.* 1988, **27**, 3357.
277. Ramig, K.; Bhupathy, M.; Cohen, T. *J. Org. Chem.* 1989, **54**, 4404.
278. Charreau, P.; Julia, M.; Verpeaux, J.-N. *J. Organomet. Chem.* 1989, **379**, 201.
279. Michnick, T. J.; Matteson, D. S. *Synlett* 1991, 631.
280. Nguyen, T.; Negishi, E. *Tetrahedron Lett.* 1991, **32**, 5903.
281. Villiéras, J.; Reliquet, A.; Normant, J. F. *J. Organomet. Chem.* 1978, **144**, 1, 263.
282. Villiéras, J.; Reliquet, A.; Normant, J. F. *Synthesis* 1978, 27.
283. Harada, T.; Hattori, K.; Katsuhira, T.; Oku, A. *Tetrahedron Lett.* 1989, **30**, 6035, 6039.
284. Harada, T.; Katsuhira, T.; Hattori, K.; Oku, A. *J. Org. Chem.* 1993, **58**, 2958.
285. Harada, T.; Hara, D.; Hattori, K.; Oku, A. *Tetrahedron Lett.* 1988, **29**, 3821.
286. Harada, T.; Kotani, Y.; Katsuhira, T.; Oku, A. *Tetrahedron Lett.* 1991, **32**, 1573.

287. Harada, T.; Katsuhira, T.; Oku, A. J. Org. Chem. 1992, **57**, 5805.
288. Katsuhira, T.; Harada, T.; Maejima, K.; Osada, A.; Oku, A. J. Org. Chem. 1993, **58**, 6166.
289. Yang, Z.-Y.; Wiemers, D. M.; Burton, D. J. J. Am. Chem. Soc. 1992, **114**, 4402.
290. Brogan, J. B.; Zercher, C. K. J. Org. Chem. 1997, **62**, 6444.
291. Charette, A. B.; Juteau, H. J. Am. Chem. Soc. 1994, **116**, 2651.
- 291a Charette, A. B.; Lebel, H. J. Org. Chem. 1995, **60**, 2966.
- .
292. Charette, A. B.; Lebel, H. J. Am. Chem. Soc. 1996, **118**, 10327.
293. Barrett, A. G. M.; Kasdorf, K. J. Am. Chem. Soc. 1996, **118**, 11030.
294. Charette, A. B.; Lemay, J. Angew. Chem., Int. Ed. Engl. 1997, **36**, 1090.
295. Aggarwal, V. K.; Amjad, A.; Coogan, M. P. J. Org. Chem. 1997, **62**, 8628.
296. Jones, P.; Millot, N.; Knochel, P. Chem. Commun. 1998, 2405.
297. Jones, P.; Knochel, P. J. Org. Chem. 1999, **64**, 186.
298. Jones, P.; Knochel, P. Chem. Commun. 1998, 2407.
299. Millot, N.; Knochel, P. Tetrahedron Lett. 1999, **40**, 7779.
300. Sosnovsky, G.; Brown, J.H. Chem. Rev. 1966, **66**, 529.
301. Walling, C.; Buckler, S.A. J. Am. Chem. Soc. 1955, **77**, 6032.
302. Riess, J.G.; Le Blanc, M. Angew. Chem. 1978, **90**, 654.
303. Klement, I.; Knochel, P. Synlett 1995, 1113.
- 303a Klement, I.; Lütjens, H.; Knochel, P. Tetrahedron 1997, **53**, 9135.
- .
304. Klement, I.; Lennick, K.; Tucker, C.E.; Knochel, P. Tetrahedron Lett. 1993, **34**, 4623.
305. Casey, C.P.; Polichnowski, S.W. J. Am. Chem. Soc. 1978, **100**, 7565.
306. Maher, J.M.; Beatty, R.P.; Cooper, N.J. Organometallics 1985, **4**, 1354.
307. Lee, I.; Cooper, N.J. J. Am. Chem. Soc. 1993, **115**, 4389.
308. Stadtmüller, H.; Knochel, P. Organometallics 1995, **14**, 3163.
309. Millot, N.; Piazza, C.; Avolio, S.; Knochel, P. Synthesis 2000, 941.
310. Langer, F.; Knochel, P. Tetrahedron Lett. 1995, **36**, 4591.
311. Langer, F.; Püntener, K.; Stürmer, R.; Knochel, P. Tetrahedron : Asymmetry 1997, **8**, 715.
312. Longeau, A.; Langer, F.; Knochel, P. Tetrahedron Lett. 1996, **37**, 2209.
313. Lamaty, F.; Lazaro, R.; Martinez, J. Tetrahedron Lett. 1997, **38**, 1447.
314. Reddy, C.K.; Devasagayaraj, A.; Knochel, P. Tetrahedron Lett. 1996, **37**, 4495.

- 314a Kitamura, M.; Miki, T.; Nakano, K.; Noyori, R. *Tetrahedron Lett.* 1996, **37**, 5141.
315. Posner, G. *Org. React.* 1972, **19**, 1.
316. Lipshutz, B.H. *Synthesis* 1987, 325.
317. Lipshutz, B.H.; Sengupta, S. *Org. React.* 1992, **41**, 135.
318. Posner, G. *Org. React.* 1975, **22**, 253.
319. Stemmler, T. L.; Penner-Hahn, J.E.; Knochel, P. *J. Am. Chem. Soc.* 1993, **115**, 348.
320. Janakiram Rao, C.; Knochel, P. unpublished results, Ann Arbor 1991.
321. Teunissen, H.T.; Bickelhaupt, F. *Tetrahedron Lett.* 1992, **33**, 3537.
322. Nakamura, E.; Sekiya, K.; Arai, M. Aoki, S. *J. Am. Chem. Soc.* 1989, **111**, 3091.
323. Arai, M.; Kawasuji, T.; Nakamura, E. *J. Org. Chem.* 1993, **58**, 5121.
324. Sekiya, K.; Nakamura, E. *Tetrahedron Lett.* 1988, **29**, 5155.
325. Dübner, F.; Knochel, P. *Angew. Chem., Int. Ed. Engl.* 1999, **38**, 379.
- 325a Dübner, F.; Knochel, P. *Tetrahedron Lett.* 2000, **41**, 9233.
326. Rigby, J.H.; Kirova-Snover, M. *Tetrahedron Lett.* 1997, **38**, 8153.
327. Sörensen, H.; Greene, A.E. *Tetrahedron Lett.* 1990, **31**, 7597.
328. Tucker, C.E.; Knochel, P. *Synthesis* 1993, 530.
329. Sidduri, A.; Budries, N.; Laine, R.M.; Knochel, P. *Tetrahedron Lett.* 1992, **33**, 7515.
330. Marquais, S.; Cahiez, G.; Knochel, P. *Synlett* 1994, 849.
331. Tucker, C.E.; Knochel, P. *J. Org. Chem.* 1993, **58**, 4781.
332. Giovannini, R.; Stüdemann, T.; Dussin, G.; Knochel, P. *Angew. Chem., Int. Ed. Engl.* 1998, **78**, 2387.
333. Devasagayaraj, A.; Stüdemann, T.; Knochel, P. *Angew. Chem., Int. Ed. Engl.* 1995, **34**, 2723.
334. Almena, P.J.J.; Ireland, T.; Knochel, P. *Tetrahedron Lett.* 1997, **38**, 5961.
335. Almena, P.J.J.; Börner, A.; Knochel, P. *Tetrahedron Lett.* 1998, **39**, 8073.
336. Lotz, M.; Ireland, T.; Almena, P.J.J.; Knochel, P. *Tetrahedron : Asymmetry* 1999, **10**, 1839.
337. Eick, H.; Knochel, P. *Angew. Chem., Int. Ed. Engl.* 1996, **35**, 218.
338. Prasad, A. S. B.; Eick, H.; Knochel, P. *J. Organomet. Chem.* 1998, **562**, 133.
339. Soai, K.; Suzuki, T.; Shono, T. *J. Chem. Soc., Chem. Commun.* 1994, 317.

340. El Alami, N.; Belaud, C.; Villieras, J. J. *Organomet. Chem.* 1987, **319**, 303.
341. Knochel, P.; Normant, J.-F. *Tetrahedron Lett.* 1984, **25**, 4383.
342. Rousseau, G.; Conia, J.M. *Tetrahedron Lett.* 1981, **22**, 649.
343. Rousseau, G.; Drouin, J. *Tetrahedron* 1983, **39**, 2307.
344. Miginiac, L. In *The Chemistry. of the Metal-Carbon Bond*, Hartley, F.R.; Patai, S.; Eds., Wiley, New York, 1985, Vol. **3**, p. 99.
345. Knochel, P. In *Comprehensive Organic Synthesis*, Trost, B.M.; Fleming, I.; Schreiber, S.L.; Eds., Pergamon, Oxford 1991, vol. **1**, p. 211.
346. Alami, N.E.; Belaud, C.; Villieras, J. *Tetrahedron Lett.* 1987, **28**, 59.
347. El Alami, N.; Belaud, C.; Villieras, J. J. *Organomet. Chem.* 1988, **348**, 1.
348. Villieras, J.; Rambaud, M. *Synthesis* 1982, 924.
349. Villieras, J.; Villieras, M. *Janssen Chimica Acta* 1993, **11** (3), 3.
350. Dembélé, Y.A.; Belaud, C.; Hitchcock, P.; Villieras, J. *Tetrahedron: Asymmetry* 1992, **3**, 351.
351. Dembélé, Y.A.; Belaud, C.; Villieras, J. *Tetrahedron : Asymmetry* 1992, **3**, 511.
352. Knochel, P.; Normant, J.-F. *J. Organomet. Chem.* 1986, **309**, 1.
353. van der Louw, J.; van der Baan, J.L.; Bickelhaupt, F.; Klumpp, G.W. *Tetrahedron Lett.* 1987, **28**, 2889.
354. van der Louw, J.; van der Baan, J.L.; Stieltjes, H.; Bickelhaupt, F.; Klumpp, G.W. *Tetrahedron Lett.* 1987, **28**, 5929.
355. van der Louw., J.; van der Baan, J.L.; Stichter, H.; Out, G.J.J.; Bickelhaupt, F.; Klumpp, G.W. *Tetrahedron Lett.* 1988, **29**, 3579.
356. van der Louw, J.; van der Baan, J.L.; Stichter, H.; Out, G.J.J.; de Kanter, F.J.J.; Bickelhaupt, F.; Klumpp, G.W. *Tetrahedron* 1992, **48**, 9877.
357. van der Louw, J.; van der Baan, J.L.; Out, G.J.J.; de Kanter, F.J.J.; Bickelhaupt, F.; Klumpp, G.W. *Tetrahedron* 1992, **48**, 9901.
358. van der Heide, T.A.; van der Baan, J.L.; Bickelhaupt, F.; Klumpp, G.W. *Tetrahedron Lett.* 1992, **33**, 475.
359. Molander, G.A.; Shubert, D.C. *J. Am. Chem. Soc.* 1986, **108**, 4683.
360. Moreau, J.L. In *The Chemistry of Ketenes, Allenes and Related Compounds* Patai, S.; Ed.; Wiley, New York, 1980, p. 363.
361. Moreau, J.L.; Gaudemar, M. *Bull. Soc. Chim. Fr.* 1970, **2171**, 2175.
362. Moreau, J.L. *Bull. Soc. Chim. Fr.* 1975, 1248.
363. Suzuki, M.; Morita, Y.; Noyori, R. *J. Org. Chem.* 1990, **55**, 441.
364. Yamamoto, H. In *Comprehensive Organic Synthesis*, Trost, B.M.; Fleming, I.; Schreiber, S.L.; Eds., Pergamon, Oxford 1991, vol. **2**, p. 81.
365. Zweifel, G.; Hahn, G. *J. Org. Chem.* 1984, **49**, 4565.

366. Thompson, W.J.; Tucker, T.J.; Schwering, J.E.; Barnes, J.L. *Tetrahedron Lett.* 1990, **31**, 6819.
367. DeCamp, A.E.; Kawaguchi, A.T.; Volante, R.P.; Shinkai, I. *Tetrahedron Lett.* 1991, **32**, 1867.
368. Tamaru, Y.; Nakamura, T.; Sakaguchi, M.; Ochiai, H.; Yoshida, Z. J. *Chem. Soc., Chem. Commun.* 1988, 610.
369. Berninger, J.; Koert, U.; Eisenberg-Höhl, C.; Knochel, P. *Chem. Ber.* 1995, **128**, 1021.
370. Reetz, M.T. In *Organotitanium Reagents in Organic Synthesis*, Springer, Berlin 1986.
371. Quinton, P.; Le Gall, T. *Tetrahedron Lett.* 1991, **32**, 4909.
372. Gangloff, A.R.; Akermark, B.; Helquist, P. *J. Org. Chem.* 1992, **57**, 4797.
373. Powell, N.A.; Rychnovsky, S.D. *J. Org. Chem.* 1999, **64**, 2026.
374. Rychnovsky, S.D.; Powell, N.A. *J. Org. Chem.* 1997, **62**, 6460.
- 374a Solladié-Cavallo, A.; Farkhani, D.; Fritz, S.; Lazrak, T.; Suffert, J. *Tetrahedron Lett.* 1984, **25**, 4117.
375. Evans, D. A. *Science* 1988, **240**, 420.
376. Noyori, R.; Kitamura, M. *Angew. Chem., Int. Ed. Engl.* 1991, **30**, 49.
377. Wissing, E.; Havenith, R. W. A.; Boersma, J.; van Koten, G. *Tetrahedron Lett.* 1992, **33**, 7933.
378. van der Steen, F.H.; Kleijn, H.; Jastrebski, J.T.B.H.; van Koten, G. J. *Org. Chem.* 1991, **56**, 5147.
379. van Maanen, H.L.; Jastrebski, J. T. B. H.; Verweij, J.; Kieboom, A. P. G.; Spek, A. L.; van Koten, G. *Tetrahedron: Asymmetry* 1993, **4**, 1441.
380. Soai, K.; Hatanaka, T.; Miyazawa, T. *J. Chem. Soc., Chem. Commun.* 1992, 1097.
381. Katritzky, A.R.; Harris, P.A. *Tetrahedron: Asymmetry* 1992, **3**, 437.
382. Comins, D.L.; O'Connor, S. *Tetrahedron Lett.* 1987, **28**, 1843.
383. Shiao, M.-J.; Liu, K.-H.; Lin, L.-G. *Synlett* 1992, 655.
384. Chia, W.-L.; Shiao, M.-J. *Tetrahedron Lett.* 1991, **32**, 2033.
385. Shing, T.-L.; Chia, W.-L.; Shiao, M.-J.; Chau, T.-Y. *Synthesis* 1991, 849.
386. Shiao, M.-J.; Chia, W.-L.; Shing, T.-L.; Chow, T. J. *J. Chem. Research (S)* 1992, 247.
387. Agami, C.; Couty, F.; Daran, J.-C.; Prince, B.; Puchot, C. *Tetrahedron Lett.* 1990, **31**, 2889.
388. Agami, C.; Couty, F.; Poursoulis, M.; Vaissermann, J. *Tetrahedron* 1992, **48**, 431.
389. Andrés, C.; Gonzales, A.; Pedrosa, R.; Perez-Encabo, A.; Garcia-Granda, S.; Salvado, M.A.; Gomez-Beltran, F. *Tetrahedron Lett.*

- 1992, **33**, 4743.
390. Eguchi, M.; Zeng, Q.; Korda, A.; Ojima, I. *Tetrahedron Lett.* 1993, **34**, 915.
391. Comins, D.L.; Foley, M.A. *Tetrahedron Lett.* 1988, **29**, 6711.
392. Bettiol, J.-L.; Sundberg, R.J. *J. Org. Chem.* 1993, **58**, 814.
393. Yamada, J.; Sato, H.; Yamamoto, Y. *Tetrahedron Lett.* 1989, **30**, 5611.
394. Stemmler, T. L.; Barnhart, T. M.; Penner-Hahn, J.E.; Tucker, C. E.; Knochel, P.; Böhme, M.; Frenking, G. *J. Am. Chem. Soc.* 1995, **117**, 12489.
395. Cahiez, G.; Marquais, S.; Alami, M. *Org. Synth.* 1993, **72**, 135.
396. Chuit, C.; Foulon, J.P.; Normant, J.-F. *Tetrahedron* 1981, **37**, 1385.
397. Bourgain-Commerçon, M.; Foulon, J.P.; Normant, J.-F. *J. Organomet. Chem.* 1982, **228**, 321.
398. Corey, E.J.; Boaz, N.W. *Tetrahedron Lett.* 1985, **26**, **6015**, 6019.
399. Alexakis, A.; Berlan, J.; Besace, Y. *Tetrahedron Lett.* 1986, **27**, 1047.
400. Horiguchi, Y.; Matsuzawa, S.; Nakamura, E.; Kuwajima, I. *Tetrahedron Lett.* 1986, **27**, 4025.
401. Nakamura, E.; Matsuzawa, S.; Horiguchi, Y.; Kuwajima, I. *Tetrahedron Lett.* 1986, **27**, 4029.
402. Bergdahl, M.; Lindstedt, E.-L.; Nilsson, M.; Olsson, T. *Tetrahedron* 1988, **44**, 2055.
403. Bergdahl, M.; Lindstedt, E.-L.; Nilsson, M.; Olsson, T. *Tetrahedron* 1989, **45**, 535.
404. Bergdahl, M.; Lindstedt, E.-L.; Olsson, T. *J. Organomet. Chem.* 1989, **365**, C11.
405. Bergdahl, M.; Nilsson, M.; Olsson, T. *J. Organomet. Chem.* 1990, **391**, C19.
406. Bergdahl, M.; Eriksson, M.; Nilsson, M.; Olsson, T. *J. Org. Chem.* 1993, **58**, 7238.
407. Chuit, C.; Foulon, J.P.; Normant, J.-F. *Tetrahedron* 1980, **36**, 2305.
408. Kiwe, S.; Lee, J.M. *Tetrahedron Lett.* 1990, **31**, 7627.
409. Lipshutz, B.H.; Wood, M.R. *J. Am. Chem. Soc.* 1993, **115**, 12625.
410. Tsujiyama, H.; Ono, N.; Yoshino, T.; Okamoto, S.; Sato, F. *Tetrahedron Lett.* 1990, **31**, 4481.
411. Yoshino, T.; Okamoto, S.; Sato, F. *J. Org. Chem.* 1991, **56**, 3205.
412. Miyaji, K.; Ohara, Y.; Miyauchi, Y.; Tsuruda, T.; Arai, K. *Tetrahedron Lett.* 1993, **34**, 5597.
413. Feringa, B.L.; Pineschi, M.; Arnold, L.A.; Imbos, R.; de Vries, A.H.M. *Angew. Chem.*, 1997, **109**, 2733.

414. Naasz, R.; Arnold, L.A.; Pineschi, M.; Keller, E.; Feringa, B.L. *J. Am. Chem. Soc.*, 1999, **121**, 1104.
415. Greene, A.E.; Lansard, J.P.; Lucche, J.-L.; Petrier, C. *J. Org. Chem.* 1984, **49**, 931.
416. Soai, K.; Hayasaka, T.; Ugajin, S.; Yokoyama, S. *Chem. Lett.* 1988, 1571.
417. Jansen, J.F.G.A.; Feringa, B.L. *Tetrahedron: Asymmetry*, 1992, **3**, 581.
418. Jansen, J.F.G.A.; Feringa, B.L. *J. Org. Chem.* 1990, **55**, 4168.
419. Bolm, C.; Ewald, M. *Tetrahedron Lett.* 1990, **31**, 5011.
420. Bolm, C. *Tetrahedron: Asymmetry* 1991, **2**, 701.
421. Uemura, M.; Miyake, R.; Nakayama, K.; Hayashi, Y. *Tetrahedron: Asymmetry*, 1992, **3**, 713.
422. Soai, K.; Yokoyama, S.; Hayasaka, T.; Ebihara, K. *J. Org. Chem.* 1988, **53**, 4149.
423. Soai, K.; Okudo, M.; Okamoto, M. *Tetrahedron Lett.* 1991, **32**, 95.
424. Jansen, J.F.G.A.; Feringa, B.L. *J. Chem. Soc., Chem. Commun.* 1989, 741.
425. Bolm, C.; Felder, M.; Müller, J. *Synlett.* 1992, 439.
426. de Vries, A.H.M.; Jansen, J.F.G.A.; Feringa, B.L. *Tetrahedron* 1994, **50**, 4479.
427. Asami, M.; Usui, K.; Higuchi, S.; Inoue, S. *Chem. Lett.* 1994, 297.
428. Villacorta, G.M.; Rao, C.P.; Lippard, S.J. *J. Am. Chem. Soc.* 1988, **110**, 3175.
429. Ahn, K.-H.; Klassen, R.B.; Lippard, S.J. *Organometallics* 1990, **9**, 3178.
430. Seebach, D.; Colvin, E.W.; Lehr, F.; Weller, T. *Chimia* 1979, **33**, 1.
431. Yoshikoshi, A.; Miyashita, M. *Acc. Chem. Res.* 1985, **18**, 284.
432. Barrett, A.G.M.; Graboski, G.G. *Chem. Rev.* 1986, **86**, 751.
433. Rosini, G.; Ballini, R. *Synthesis* 1988, 833.
434. Tamura, R.; Kamimura, A.; Ono, N. *Synthesis* 1991, 423.
435. Knochel, P.; Seebach, D. *Tetrahedron Lett.* 1981, **2**, 3223.
436. Knochel, P.; Seebach, D. *Tetrahedron Lett.* 1982, **23**, 3897.
437. Seebach, D.; Knochel, P. *Helv. Chim. Acta* 1984, **67**, 261.
438. Bowlus, S.B. *Tetrahedron Lett.* 1975, 3591.
439. Hansson, A.-T.; Nilsson, M. *Tetrahedron* 1982, **38**, 389.
440. Stiver, S.; Yates, P. *J. Chem. Soc., Chem. Commun.* 1983, 50.
441. Denmark, S.E.; Marcin, L.R. *J. Org. Chem.* 1993, **58**, 3850.
442. Crimmins, M.T.; Nantermet, P.G. *J. Org. Chem.* 1990, **55**, 4235.
443. Crimmins, M.T.; Nantermet, P.G.; Trotter, B.W.; Vallin, I.M.; Watson,

- P.S.; McKerlie, L.A.; Reinhold, T.L.; Cheung, A.W.-H.; Steton, K.A.; Dedopoulou, D.; Gray, J.L. *J. Org. Chem.* 1993, **58**, 1038.
444. Crimmins, M.T.; Jung, D.K.; Gray, J.L. *J. Am. Chem. Soc.* 1993, **115**, 3146.
445. Knochel, P. "Carbometallation of Alkenes and Alkynes", in *Comprehensive Organic Chemistry*, Vol. **4**, Trost, B.M., Ed., Pergamon Press 1991, p. 865.
446. Normant, J.-F.; Alexakis, A. *Synthesis* 1981, 841.
447. van der Louw, J.; Komen, C.M.D.; Knol, A.; de Kanter, F.J.J.; van der Baan, J.L.; Bickelhaupt, F.; Klumpp, G.W. *Tetrahedron Lett.* 1989, **30**, 4453.
448. Negishi, E.; Miller, J.A. *J. Am. Chem. Soc.* 1983, **105**, 6761.
449. Molander, G.A. *J. Org. Chem.* 1983, **48**, 5409.
450. Yanagisawa, A.; Habaue, S.; Yamamoto, H. *J. Am. Chem. Soc.* 1989, **111**, 366.
451. Kubota, K.; Nakamura, M.; Isaka, M.; Nakamura, E. *J. Am. Chem. Soc.* 1993, **115**, 5867.
452. Negishi, E.; Van Horn, D.E.; Yoshida, T.; Rand, C.L. *Organometallics* 1983, **2**, 563.
453. Lehmkuhl, H.; Olbrysch, O. *Liebigs Ann. Chem.* 1975, 1162.
454. Lehmkuhl, H.; Döring, I.; Nehl, H. *J. Organomet. Chem.* 1981, **221**, 123.
455. Lehmkuhl, H.; Nehl, H. *J. Org. Chem.* 1981, **221**, 131.
456. Auger, J.; Courtois, G.; Miginiac, L. *J. Organomet. Chem.* 1977, **133**, 285.
457. Gaudemar, M. *C.R. Hebd. Seances Acad. Sci., Ser. C* 1971, **273**, 1669.
458. Frangin, Y.; Gaudemar, M. *C.R. Hebd. Seances Acad. Sci., Ser. C* 1974, **278**, 885.
459. Bellasoued, M.; Frangin, Y.; Gaudemar, M. *Synthesis* 1977, 205.
460. Knochel, P.; Normant, J.-F. *Tetrahedron Lett.* 1986, **27**, 1039.
- 460a Knochel, P.; Normant, J.-F. *Tetrahedron Lett.* 1986, **27**, 1043.
- .
- 460b Knochel, P.; Normant, J.-F. *Tetrahedron Lett.* 1986, **27**, 4427.
- .
- 460c. Knochel, P.; Normant, J.-F. *Tetrahedron Lett.* 1986, **27**, 5727.
461. Beruben, D.; Marek, I.; Labaudinière, L.; Normant, J.-F. *Tetrahedron Lett.* 1993, **34**, 2303.
462. Normant, J.-F.; Quirion, J.-C. *Tetrahedron Lett.* 1989, **30**, 3959.
463. Marek, I.; Lefrançois, J.-M.; Normant, J.-F. *Synlett* 1992, 633.

464. Marek, I.; Lefrançois, J.-M.; Normant, J.-F. *Tetrahedron Lett.* 1992, **33**, 1747.
465. Marek, I.; Lefrançois, J.-M.; Normant, J.-F. *Tetrahedron Lett.* 1991, **32**, 5969.
466. Marek, I.; Normant, J.-F. *Tetrahedron Lett.* 1991, **32**, 5973.
467. Knochel, P.; Xiao, C.; Yeh, M.C.P. *Tetrahedron Lett.* 1988, **29**, 6697.
468. Meyer, C.; Marek, I.; Courtemanche, G.; Normant, J.-F. *Synlett.* 1993, 266.
469. Meyer, C.; Marek, I.; Courtemanche, G.; Normant, J.-F. *Tetrahedron Lett.* 1993, **34**, 6053.
470. Vaupel, A.; Knochel, P. *Tetrahedron Lett.* 1994, **35**, 8349.
471. Rao, S.A.; Knochel, P. *J. Am. Chem. Soc.* 1991, **113**, 5735.
472. Bertrand, M.T.; Courtois, G.; Miginiac, L. *Tetrahedron Lett.* 1974, 1945.
473. Tamao, K.; Sumitani, K.; Kumada, M. *J. Am. Chem. Soc.* 1972, **94**, 4374.
474. Corriu, R.J.P.; Masse, J.P. *J. Chem. Soc., Chem. Commun.* 1972, 144.
475. Negishi, E.; King, A.O.; Okukado, N. *J. Org. Chem.* 1977, **42**, 1821.
476. Rossi, R.; Bellina, F.; Carpita, A.; Gori, R. *Synlett* 1995, 344.
477. Negishi, E.; Matsushita, H.; Kobayashi, M.; Rand, C.L. *Tetrahedron Lett.* 1983, **24**, 3823.
478. Millar, J.G. *Tetrahedron Lett.* 1989, **30**, 4913.
479. Hyuga, S.; Yamashina, N.; Hara, S.; Suzuki, A. *Chem. Lett.* 1988, 809.
480. Löffler, A.; Himbert, G. *Synthesis* 1992, 495.
481. Mignani, G.; Leising, F.; Meyrueix, R.; Samson, H. *Tetrahedron Lett.* 1990, **31**, 4743.
482. Borner, R.C.; Jackson, R.F.W. *J. Chem. Soc., Chem. Commun.* 1994, 845.
483. Sakamoto, T.; Kondo, Y.; Takazawa, N.; Yamanaka, H. *Tetrahedron Lett.* 1993, **34**, 5955.
484. Sakamoto, T.; Kondo, Y.; Murata, N.; Yamanaka, H. *Tetrahedron Lett.* 1992, **33**, 5373.
485. Sakamoto, T.; Kondo, Y.; Takazawa, N.; Yamanaka, H. *Heterocycles* 1993, **36**, 941.
486. Trauner, D.; Schwartz, J.B.; Danishefsky, S.J. *Angew. Chem., Int. Ed. Engl.* 1999, **38**, 3543.
487. Bell, A.S.; Roberts, D.A.; Ruddock, K.S. *Synthesis* 1987, 843.
488. Minato, A.; Suzuki, K.; Tamao, K.; Kumada, M. *Tetrahedron Lett.* 1984, **25**, 2583.
489. Quesnelle, C.A.; FAMILONI, O.B.; Snieckus, V. *Synlett* 1994, 349.

490. Sakamoto, T.; Nishimura, S.; Kondo, Y.; Yamanaka, H. *Synthesis* 1988, 485.
491. Sato, T.; Kawase, A.; Hirose, T. *Synlett* 1992, 891.
492. Yuan, K.; Scott, W.J. *Tetrahedron Lett.* 1989, **30**, 4779.
493. Yuan, K.; Scott, W.J. *J. Org. Chem.* 1990, **55**, 6188.
494. Park, K.; Yuan, K.; Scott, W.J. *J. Org. Chem.* 1993, **58**, 4866.
495. Tamaru, Y.; Ochiai, H.; Nakamura, T.; Yoshida, Z. *Org. Synth.* 1988, **67**, 98.
496. Tamaru, Y.; Yasui, K.; Takanabe, H.; Tanaka, S.; Fugami, K. *Angew. Chem.* 1992, **104**, 662.
497. Asaoka, M.; Tamaka, M.; Houkawa, T.; Ueda, T.; Sakami, S.; Takei, H. *Tetrahedron* 1998, **54**, 471.
498. Murata, N.; Sugihara, T.; Kondo, Y.; Sakamoto, T. *Synlett* 1997, 298.
499. Rossi, R.; Bellina, F.; Bechini, C.; Mannina, L.; Vergamini, P. *Tetrahedron* 1998, **54**, 135.
500. Gao, Y.; Harada, K.; Hata, T.; Urabe, H.; Sato, F. *J. Org. Chem.* 1995, **60**, 290.
501. Utimoto, K.; Toda, N.; Mizuno, T.; Kobata, M.; Matsubara, S. *Angew. Chem., Int. Ed. Engl.* 1997, **36**, 2804.
502. Oguni, N.; Omi, T.; Yamamoto, Y.; Nakamura, A. *Chem. Lett.* 1983, 841.
503. Oguni, N.; Omi, T. *Tetrahedron Lett.* 1984, **25**, 2823.
504. Oguni, N.; Matsuda, Y.; Kaneko, T. *J. Am. Chem. Soc.* 1988, **110**, 7877.
505. Yoshioka, M.; Kawakita, T.; Ohno, M. *Tetrahedron Lett.* 1989, **30**, 1657.
506. Takahashi, H.; Kawakita, T.; Yoshioka, M.; Kobayashi, S.; Ohno, M. *Tetrahedron Lett.* 1989, **30**, 7095.
507. Takahashi, H.; Kawakita, T.; Ohno, M.; Yoshioka, M.; Kobayashi, S. *Tetrahedron* 1992, **48**, 5691.
508. Beck, A.K.; Bastani, B.; Plattner, D.A.; Petter, W.; Seebach, D.; Braunschweiger, H.; Gysi, P.; LaVecchia, L. *Chimia* 1991, **45**, 238.
509. Schmidt, B.; Seebach, D. *Angew. Chem., Int. Ed. Engl.* 1991, **30**, 99.
510. Seebach, D.; Behrendt, L.; Felix, D. *Angew. Chem., Int. Ed. Engl.* 1991, **30**, 1008.
511. Schmidt, B.; Seebach, D. *Angew. Chem., Int. Ed. Engl.* 1991, **30**, 1321.
512. von dem Bussche-Hünnefeld, J.L.; Seebach, D. *Tetrahedron* 1992, **48**, 5719.
513. Seebach, D.; Plattner, D.A.; Beck, A.K.; Wang, Y.M.; Hunziker, D.; Petter, W. *Helv. Chim. Acta* 1992, **75**, 2171.
514. Seebach, D.; Beck, A.K.; Schmidt, B.; Wang, Y.M. *Tetrahedron* 1994, **50**, 4364.

515. Schwink, L.; Knochel, P. *Chem. Eur. J.* 1998, **4**, 950.
516. Nowotny, S.; Vettel, S.; Knochel, P. *Tetrahedron Lett.* 1994, **35**, 4539.
517. Brieden, W.; Ostwald, R.; Knochel, P. *Angew. Chem., Int. Ed. Engl.* 1993, **32**, 582.
518. Noyori, R.; Suzuki, M. *Angew. Chem., Int. Ed. Engl.* 1984, **23**, 847.
519. Suzuki, M.; Yanagisawa, A.; Noyori, R. *J. Am. Chem. Soc.* 1990, **107**, 3348.
520. Morita, Y.; Suzuki, M.; Noyori, R. *J. Org. Chem.* 1989, **54**, 1785.
521. Noyori, R.; Suga, S.; Kawai, K.; Okada, S.; Kitamura, M. *Pure Appl. Chem.* 1988, **60**, 1597.
522. Ostwald, R.; Chavant, P.-Y.; Stadtmüller, H.; Knochel, P. *J. Org. Chem.* 1994, **59**, 4143.
523. Roush, W.R.; Koyama, K. *Tetrahedron Lett.* 1992, **33**, 6227.
524. Vettel, S.; Knochel, P. *Tetrahedron Lett.* 1994, **35**, 5849.
525. Lütjens, H.; Knochel, P. *Tetrahedron: Asymmetry* 1994, **5**, 1161.
526. Knochel, P.; Brieden, W.; Rozema, M.J.; Eisenberg, C. *Tetrahedron Lett.* 1993, **34**, 5881.
527. Eisenberg, C. Ph. D. Thesis, Marburg, 1994.
528. Gopalan, A.S.; Jacobs, H.K. *J. Chem. Soc., Perkin Trans 1*, 1990, 1897.
529. Fürstner, A.; Müller, T. *J. Org. Chem.* 1998, **63**, 424.
530. Bäurle, S.; Hoppen, S.; Koert, U. *Angew. Chem.* 1999, **111**, 1341.
531. Zhang, W.; Loebach, J.L.; Wilson, S.R.; Jacobsen, E.N. *J. Am. Chem. Soc.* 1990, **112**, 2801.
532. Eisenberg, C.; Knochel, P. *J. Org. Chem.* 1994, **59**, 3760.
533. Oppolzer, W.; Radinov, R.N.; de Bradander, J. *Tetrahedron Lett.* 1995, **36**, 2607.
534. Yamamoto, T.; Yamamoto, A.; Ikeda, S. *J. Am. Chem. Soc.* 1971, **93**, 3350.
535. Devasagayaraj, A.; Knochel, P. *Tetrahedron Lett.* 1995, **36**, 8411.
536. Reddy, C.K.; Knochel, P. *Angew. Chem., Int. Ed. Engl.* 1996, **35**, 1700.
537. Avedissian, H.; Berillon, L.; Cahiez, G.; Knochel, P. *Tetrahedron Lett.* 1998, **39**, 6163.
538. Cahiez, G.; Knochel, P. *Tetrahedron Lett.* 1996, **37**, 5865.
539. Ouali, M.; Cahiez, G.; Knochel, P. *Synlett.* 1998, 143.
540. Blomberg, C.; Hartog, F.A. *Synthesis* 1977, 18.
541. Moyano, A.; Pericas, M.A.; Riera, A.; Luche, J.-L. *Tetrahedron Lett.* 1990, **31**, 7619.
542. Pétrier, C.; Luche, J.-L. *J. Org. Chem.* 1985, **50**, 910.
543. Pétrier, C.; Einhorn, J.; Luche, J.-L. *Tetrahedron Lett.* 1985, **26**, 1449.

544. Wilson, S.R.; Guazzaroni, M.E. *J. Org. Chem.* 1989, **54**, 3087.
545. Chan, T.-H.; Li, C.-J. *Organometallics* 1990, **9**, 2649.
546. Tokuda, M.; Mimura, N.; Yoshioka, K.; Karasawa, T.; Fujita, H.; Suginome, H. *Synthesis* 1993, 1086.
547. Shono, T.; Nishiguchi, I.; Sasaki, M. *J. Am. Chem. Soc.* 1978, **100**, 4314.
548. Shono, T.; Hamaguchi, H.; Nishiguchi, I.; Sasaki, M.; Miyamoto, T.; Miyamoto, M.; Fujita, S. *Chem. Lett.* 1981, 1217.
549. Giese, B.; Damm, W.; Roth, M.; Zehnder, M. *Synlett* 1992, 441.
550. Blanchard, P.; El Kortbi, M.S.; Fourrey, J.-L.; Robert-Gero, M. *Tetrahedron Lett.* 1992, **33**, 3319.
551. Pérez-Sestelo, J.; Mascarenas, J.L.; Castedo, L.; Mourino, A. *Tetrahedron Lett.* 1994, **35**, 275.
552. Sarandeses, L.A.; Mourino, A.; Luche, J.-L. *J. Chem. Soc., Chem. Commun.* 1992, 799.
553. Hong, F.; Tang, X.; Hu, C. *J. Chem. Soc., Chem. Commun.* 1994, 289.
554. Carofiglio, T.; Marton, D.; Tagliavini, G. *Organometallics* 1992, **111**, 2961.
555. Corey, E.J.; Pyne, S.G. *Tetrahedron Lett.* 1983, **24**, 2821.
556. Reetz, M.T. *Topics Curr. Chem.* 1982, **106**, 1.
- 556a Cahiez, G. *Actual. Chim.* 1984, (Sept), 24.
- .
557. Weidmann, B.; Seebach, D. *Angew. Chem., Int. Ed. Engl.* 1983, **22**, 31.
- 577a Cahiez, G.; Laboue, B. *Tetrahedron Lett.* 1989, **30**, 3545.
- .
558. Cahiez, G.; Laboue, B. *Tetrahedron Lett.* 1989, **30**, 7369.
559. Cahiez, G.; Alami, M. *Tetrahedron* 1989, **45**, 4163.
560. Cahiez, G.; Chavant, P.-Y.; Metais, E. *Tetrahedron Lett.* 1992, **33**, 5245.
561. Cahiez, G.; Figadère, B.; Clery, P. *Tetrahedron Lett.* 1994, **35**, 3065.
562. Cahiez, G.; Chau, K.; Clery, P. *Tetrahedron Lett.* 1994, **35**, 3069.
563. Heck, R.F. *Palladium Reagents in Organic Synthesis*. Academic Press, London, New York, 1985.
564. Fieser, L.F.; Fieser, M. *Reagents for Organic Synthesis*, Wiley: New York, 1967, vol. **1**, 1276.
565. Vettel, S.; Lutz, C.; Knochel, P. *Synlett* 1996, 731.
566. Harada, T.; Wada, H.; Oku, A. *J. Org. Chem.* 1995, **60**, 5370.
567. Prasad, A. S.; Knochel, P. *Tetrahedron* 1997, **53**, 16711.
568. Thorn, S. N.; Gallagher, T. *Synlett* 1996, 185.
569. Lipshutz, B.H.; Woo, K.; Buzard, D.J.; Tirado, R. *Synlett* 1997, 477.

570. Cerè, V.; De Angelis, S.; Pollicino, S.; Ricci, A.; Kishan Reddy, Ch.; Knochel, P.; Cahiez, G. *Synthesis* 1997, 1174.
571. Tanaka, T.; Bannai, K.; Hazato, A.; Koga, M.; Kurozumi, S.; Kato, Y. *Tetrahedron* 1991, **47**, 1861.
572. Billotte, S. *Synlett* 1998, 379.
573. Devasagayaraj, A.; Schwink, L.; Knochel, P. *J. Org. Chem.* 1995, **60**, 3311.
574. Dexter, C.S.; Jackson, R.F.W.; *J. Org. Chem.* 1999, **64**, 7579.
575. Matsubara, S.; Otake, Y.; Hashimoto, Y.; Utimoto, K. *Chem. Lett.* 1999, 747.
576. Vettel, S.; Vaupel, A.; Knochel, P. *Tetrahedron Lett.* 1995, **36**, 1023.
577. Lhermitte, F.; Knochel, P. *Angew. Chem., Int. Ed. Engl.* 1998, **37**, 2460.
578. Koga, M.; Fujii, T.; Tanaka, T. *Tetrahedron* 1995, **51**, 5529.
579. Stüdemann, T.; Gupta, V.; Engman, L.; Knochel, P. *Tetrahedron Lett.* 1997, **38**, 1005.
580. Jackson, R.F.W.; Fraser, J.L.; Wishart, N.; Porter, B.; Wythes, M.J. *J. Chem. Soc., Perkin Trans. 1* 1998, **12**, 1903.
581. Lai, M.-L.; Chang, S.-C.; Hwu, C.-C.; Yeh, M.-C.-P. *Tetrahedron Lett.* 1996, **37**, 6149.
582. Yun, Y.K.; McDaniel, K.F. *Tetrahedron Lett.* 1995, **36**, 4931.
583. Yokomatsu, T.; Abe, H.; Yamagishi, T.; Suemune, K.; Shibuya, S. *J. Org. Chem.* 1999, **64**, 8413.
584. Yokomatsu, T.; Murano, T.; Suemune, K.; Shibuya, S. *Tetrahedron* 1997, **53**, 815.
585. Lipshutz, B.H.; Vivian, R.W. *Tetrahedron Lett.* 1999, **40**, 2871.
586. Belyk, K.; Rozema, M.J.; Knochel, P. *J. Org. Chem.* 1992, **57**, 4070.
587. Hanson, M.V.; Brown, J.D.; Rieke, R.D. *Tetrahedron Lett.* 1994, **35**, 7205.
588. Harn, N.K.; Gramer, C.J.; Anderson, B.A. *Tetrahedron Lett.* 1995, **36**, 9453.
589. Bonini, B.F.; Comes-Franchini, M.; Mazzanti, G.; Passamonti, U.; Ricci, A.; Zani, P. *Synthesis* 1995, 92.
590. Mallaiiah, K.; Satyanarayana, J.; Ila, H.; Junjappa, H. *Tetrahedron Lett.* 1993, **34**, 3145.
591. Chou, T.-S; Tseng, H.J. *Tetrahedron Lett.* 1995, **36**, 7105.
592. Eshelby, J.J.; Crowley, P.C.; Parsons, P.J. *Synlett* 1993, 277.
593. Semmelhack, M.F.; Fewkes, E.J. *Tetrahedron Lett.* 1987, **28**, 1497.
594. Yanagisawa, A.; Habaue, S.; Yamamoto, H. *Tetrahedron* 1992, **48**, 1969.

595. Harada, T.; Osada, A.; Oku, A. *Tetrahedron Lett.* 1995, **36**, 723.
596. Jehanno, E.; Vaultier, M. *Tetrahedron Lett.* 1995, **36**, 7105.
597. Kondo, Y.; Takazawa, N.; Yamazaki, C.; Sakamoto, T. *J. Org. Chem.* 1994, **59**, 4717.
598. Koert, U.; Wagner, H.; Pidun, U. *Chem. Ber.* 1994, **127**, 1447.
599. Gosmini, C.; Rollin, Y.; Gébéhenne, C.; Lojou, E.; Ratovelomanana, V.; Périchon, J. *Tetrahedron Lett.* 1994, **35**, 5637.
600. Jain, S.; Jain, R.; Singh, J.; Anand, N. *Tetrahedron Lett.* 1994, **35**, 2951.
601. Harkawa, T.; Ueda, T.; Sakami, S.; Asaoka, M.; Takei, H. *Tetrahedron Lett.* 1996, **37**, 1045.
602. Jones, P.; Knochel, P. *J. Chem. Soc., Perkin Trans. 1* 1997, 3117.
603. Eshelby, J.J.; Crowley, P.C.; Parsons, P.J. *Synlett* 1993, 279.
604. Klement, I.; Rottländer, M.; Tucker, C.E.; Majid, T.N.; Knochel, P.; Venegas, P.; Cahiez, G. *Tetrahedron* 1996, **52**, 7201.
605. Lipshutz, B.H.; Wood, M.R.; Tirado, R. *J. Am. Chem. Soc.* 1995, **117**, 6126.
606. Streckowski, L.; Gulevich, Y.; Van Haken, K.; Wilson, D.W. *Tetrahedron Lett.* 1995, **36**, 225.
607. Crimmins, M.T.; Huang, S.; Guise, L.E.; Lacy, D.B. *Tetrahedron Lett.* 1995, **36**, 7061.
608. Reisser, M.; Maas, G. *Synthesis* 1998, 1129.
609. Crandall, J.K.; Ayers, T.A. *Organometallics* 1992, **11**, 473.
610. Stüdemann, T.; Ibrahim-Ouali, M.; Knochel, P. *Tetrahedron* 1998, **54**, 1299.
611. Riguet, E.; Klement, I.; Reddy, C. K.; Cahiez, G.; Knochel, P. *Tetrahedron Lett.* 1996, **37**, 5865.
612. Klement, I.; Lütjens, H.; Knochel, P. *Tetrahedron Lett.* 1995, **36**, 3161.
613. Oppolzer, W.; Schröder, F. *Tetrahedron Lett.* 1994, **35**, 7939.
614. Meyer, C.; Marek, I.; Courtemanche, G.; Normant, J.F. *J. Org. Chem.* 1995, **60**, 863.
615. Vaupel, A.; Knochel, P. *Tetrahedron Lett.* 1995, **36**, 231.
616. Meyer, C.; Marek, I.; Normant, J.F. *Tetrahedron Lett.* 1996, **37**, 857.
617. Lorthiois, E.; Marek, C.; Normant, J.F. *Tetrahedron Lett.* 1995, **36**, 1263.
618. Negishi, E.-I.; Kotora, M.; Xu, C. *J. Org. Chem.* 1997, **62**, 8957.
619. Nguyen, B.V.; Burton, D.J. *J. Org. Chem.* 1998, **63**, 1714.
620. Rottländer, M.; Knochel, P. *J. Org. Chem.* 1998, **63**, 203.
621. Anderson, B.A.; Harn, N.K. *Synthesis* 1996, 583.
622. Anderson, B.A.; Becke, L.M.; Booher, R.N.; Flaugh, M.E.; Harn, N.K.; Kress, T.J.; Varie, D.L.; Wepsiec, J.P. *J. Org. Chem.* 1997, **62**, 8634.

623. Lipshutz, B.H.; Blomgren, P.A. *J. Am. Chem. Soc.* 1999, **121**, 5819.
624. Vicart, N.; Castet-Caillabet, D.; Ramionderc, Y.; Plé, G.; Duhamel, L. *Synlett*, 1998, 411.
625. Gosmini, C.; Lasry, S.; Nédélec, J.Y.; Périchon, J. *Tetrahedron* 1998, **54**, 1289.
626. Hocek, M.; Masojdkova, M.; Holy, A., *Collect. Czech. Chem. Comm.* 1997, **62**, 138.
627. Prasad, A.S.B.; Stevenson, T.M.; Citineni, J.R.; Nyzam, V.; Knochel, P. *Tetrahedron* 1997, **53**, 7237.
628. Mazal, C.; Vaultier, M. *Tetrahedron Lett.* 1994, **35**, 3089.
629. Ababri, M.; Parrain, J.C.; Cintrat, J.C.; Duchêne, A. *Synthesis* 1996, 82.
630. Shi, G-Q.; Huang, X.H.; Hong, F. *J. Org. Chem.* 1996, **61**, 3200.
631. Sakamoto, T.; Kondo, Y.; Murata, N.; Yamanaka, H. *Tetrahedron* 1993, **49**, 9713.
632. Minato, A. *J. Org. Chem.* 1991, **56**, 4052.
633. Röttlander, M.; Knochel, P. *Tetrahedron Lett.* 1997, **38**, 1749.
634. Klement, I.; Röttlander, M.; Tucker, C.E.; Majid, T.N.; Knochel, P. *Tetrahedron* 1996, **52**, 7201.
635. Röttlander, M.; Palmer, N.; Knochel, P. *Synlett*, 1996, 573.
636. Amadji, M.; Cahard, D.; Moriggi, J-D.; Toupet, L.; Plaquevent, J.C. *Tetrahedron : Asymmetry* 1998, **9**, 1657.
637. Bellina, F.; Ciucci, D.; Rossi, R.; Vergamini, P. *Tetrahedron* 1999, **55**, 2103.
638. Palmgren, A.; Thorarensen, A.; Bäckvall, J.E. *J. Org. Chem.* 1998, **63**, 3764.
639. Rossi, R.; Bellina, F.; Ciucci, D. *J. Organomet. Chem.* 1997, **542**, 113.
640. Vaillancourt, L.; Simard, M.; Wuest, J.D. *J. Org. Chem.* 1998, **63**, 9746.
641. Superchi, S.; Sotomayor, N.; Miao, G.; Joseph, B.; Snieckus, V., *Tetrahedron Lett.* 1996, **37**, 6057.
642. Shioto, T.; Yamamori, T., *J. Org. Chem.* 1999, **64**, 453.
643. Koch, K.; Chambers, R.J.; Biggers, M.S. *Synlett* 1994, 347.
644. Jackson, R.F.W.; Moore, R.J.; Dexter, C.S., *J. Org. Chem.* 1998, **62**, 7875.
645. Kristensen, J.; Begtrup, M.; Veds, P. *Synthesis* 1998, 1604.
646. Stüdemann, T.; Knochel, P. *Angew. Chem., Int. Ed. Engl.* 1997, **36**, 93.
647. Agharahimi, M.R.; Lebel, N.A. *J. Org. Chem.* 1995, **60**, 1856.
648. Amat, M.; Hadida, S.; Pshenichnyi, G.; Bosch, J. *J. Org. Chem.* 1997, **61**, 3158.
649. Ye, B.; Burk, Jr., T.R. *J. Org. Chem.* 1995, **60**, 2640.

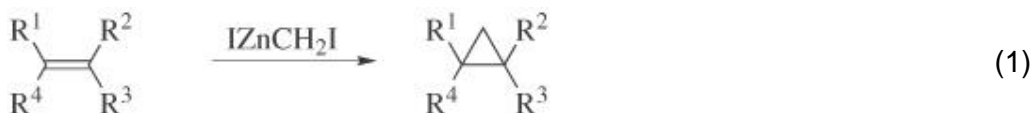
650. Ye, B.; Otaka, A.; Burk, Jr., T.R. *Synlett* 1996, 459.
651. Malan, C.; Morin, C. *Synlett*. 1996, 167.
652. Pearce, A.J.; Ramaya, S.; Thorn, S.N.; Bloomberg, G.B.; Walter, D.S., Gallagher, T. *J. Org. Chem.* 1999, **64**, 5435.
653. Harada, T.; Katsuhira, T.; Hara, D.; Kotani, Y.; Maejima, K.; Kaji, R.; Oku, A. *J. Org. Chem.* 1993, **58**, 4897.
654. Bérillon, L.; Wagner, R.; Knochel, P. *J. Org. Chem.* 1998, **63**, 9117.
655. Pimm, A.; Kocienski, P.; Street, S.D.A. *Synlett* 1992, 886.
656. Agnel, G.; Owezarczyk, Z.; Negishi, E.I. *Tetrahedron Lett.* 1992, **33**, 1543.
657. Evans, P.A.; Nelson, J.D.; Stanley, A.L. *J. Org. Chem.* 1995, **60**, 2298.
658. Jackson, F.W.; Graham, L.J.; Rettie, A.B. *Tetrahedron Lett.* 1994, **35**, 4417.
659. Vettel, S.; Lutz, C.; Diefenbach, A.; Haderlein, G.; Hammerschmidt, S.; Kühling, K.; Mofid, M.R.; Zimmermann, T.; Knochel, P. *Tetrahedron : Asymmetry* 1997, **8**, 779.
660. Lutz, C.; Knochel, P. *J. Org. Chem.* 1997, **62**, 7895.
661. Lutz, C.; Graf, C.-D.; Knochel, P. *Tetrahedron* 1998, **54**, 10317.
662. Lütjens, H.; Nowotny, S.; Knochel, P. *Tetrahedron : Asymmetry* 1995, **6**, 2675.
663. Lutz, C.; Knochel, P. *Tetrahedron* 1998, **54**, 6385.
664. Lutz, C.; Jones, P.; Knochel, P. *Synthesis* 1999, **2**, 312.

Simmons-Smith Cyclopropanation Reaction

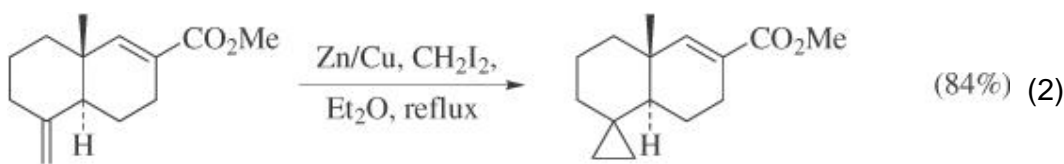
André B. Charette, Université de Montréal, Montréal, Québec, Canada
André Beauchemin, Université de Montréal, Montréal, Québec, Canada

1. Introduction

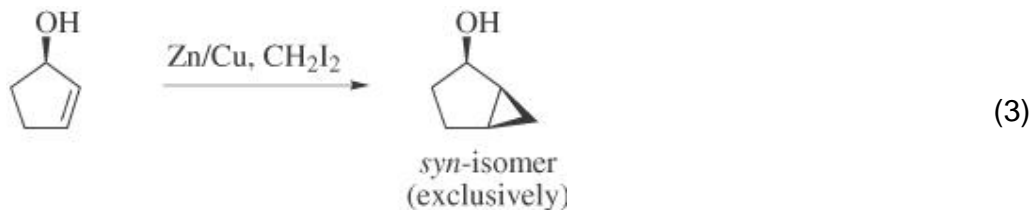
Almost 30 years after Emschwiller prepared IZnCH_2I , (1) Simmons and Smith discovered that the reagent formed by mixing a zinc-copper couple with CH_2I_2 in ether (2, 3) could be used for the stereospecific conversion of alkenes to cyclopropanes (Eq. 1). Nowadays, the Simmons-Smith cyclopropanation reaction is



one of the most widely used reactions in the organic chemist's arsenal for the conversion of olefins into cyclopropanes. (4) This popularity is mainly due to the stereospecificity of the reaction with respect to the double bond geometry and its compatibility with a wide range of functional groups. The chemoselectivity of the reaction toward some olefins is excellent and very few side reactions are observed with functionalized substrates. The metal carbenoid is electrophilic in nature and electron-rich alkenes usually react much faster than electron-poor alkenes (Eq. 2). (5, 6)



Furthermore, the ability to use proximal hydroxy or ether groups to dictate the stereochemical outcome of the C — C bond forming process was recognized early on, (7) and this unique property has been successfully exploited on numerous occasions (Eq. 3). (8) It has been recognized that halomethylmetal reagents are powerful synthetic tools for the stereoselective addition of a methylene unit to chiral



acyclic allylic alcohols and allylic ethers. (9) In addition, the use of halomethylzinc reagents in the presence of chiral additives is one of the few ways to cyclopropanate allylic alcohols efficiently and with good enantiocontrol. (10)

Carbenoids can be divided into the following two classes: (1) those of general structure MCH_2X and (2) those corresponding to $\text{M} = \text{CH}_2$. This review is focussed exclusively on the first class in which $\text{M} = \text{Zn}$, Sm , or Al . Although other metal carbenoids of type MCH_2X , such as those derived from Cu , (11) Cd , (12) Hg , (13) and In , (14) have been reported to be effective reagents for the cyclopropanation of some olefins, they have been used only sporadically, and this review does not highlight these reactions. This chapter covers cyclopropanation reactions involving haloalkylzinc, aluminum, and samarium reagents published since the comprehensive chapter in *Organic Reactions* by Simmons that surveyed the literature up to 1973. (15)

2. Mechanism

2.1. Solid-State and Solution Studies of Haloalkylmetal Reagents

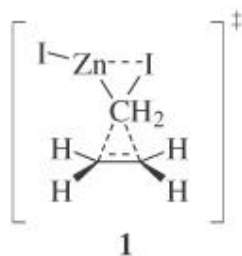
The mechanistic features of the Simmons-Smith cyclopropanation reaction have been discussed extensively in early reviews on the topic. (4, 15) It has been clearly established that the Simmons-Smith cyclopropanation reaction involving iodomethylzinc iodide and an alkene proceeds in a concerted fashion with retention of configuration with regard to the olefinic double bond. Since then, the main advances that have been accomplished are in the structural elucidation of the simplest zinc reagents. Indeed, the solid-state structures of the halomethyl-zinc reagents have remained speculative until very recently when the first X-ray crystal structure of one of these reagents was reported. (16, 17) A complex between $\text{Zn}(\text{CH}_2\text{I})_2$ and a chiral diether provided monomeric crystals suitable for X-ray diffraction analysis. This complex was also fully characterized in solution by ^1H and ^{13}C NMR, the characteristic resonances being those for ZnCH_2I at ~ 1.4 ppm (^1H) and -20 ppm (^{13}C). The structures of the complexes between benzo-18-crown-6 as the coordinating ether and both IZnCH_2I and $\text{Zn}(\text{CH}_2\text{I})_2$ are also known. (18)

The exact nature of the structural features of these reagents in solution has given rise to many postulates. Among those, the possible Schlenk equilibrium between IZnCH_2I and $\text{Zn}(\text{CH}_2\text{I})_2/\text{ZnI}_2$ has been widely accepted by the scientific community to explain the stereochemical outcome of some cyclopropanation reactions but little has actually been unequivocally established. In-depth spectroscopic studies have recently shown that the equilibrium between these species lies heavily on the side of IZnCH_2I . (19, 20) This observation is in agreement with what has been reported for organozinc iodides (RZnI) (21-23) but is in sharp contrast with what has been reported for BrZnCH_2Br . (24)

Using similar spectroscopic studies, the solution structure of the Furukawa reagent (EtZnCH_2I) has been established. (19) This reagent is in equilibrium with Et_2Zn and $\text{Zn}(\text{CH}_2\text{I})_2$ and it eventually rearranges to PrZnI . Since the rate of this self-destructive pathway can be competitive with the cyclopropanation reaction of some unreactive alkenes, it may be advantageous in some cases to add additional CH_2I_2 to generate IZnCH_2I from PrZnI .

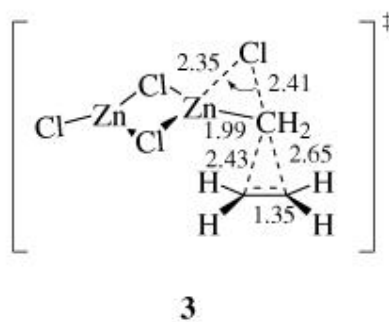
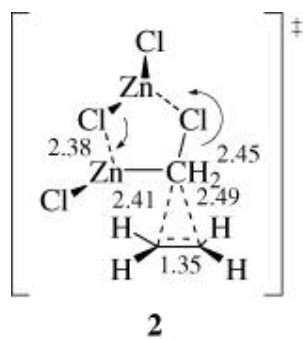
2.2. Theoretical Studies

It has been postulated based on experimental observations that the cyclopropanation reaction of simple alkenes occurs via the "butterfly type" transition state (1). (3) Several theoretical studies at various computational levels have been performed



and they are in agreement with this postulate. The first theoretical investigations were carried out using ab initio gradient techniques and the 3–21G basis set for the reaction between LiCH₂F and ethylene, and a butterfly type transition structure similar to **(1)** lies at a minimum. **(25)** Two additional studies (at the density functional theory level) of the Simmons-Smith cyclopropanation of ethylene with chloromethylzinc chloride **(26, 27)** and iodomethylzinc iodide **(28)** concluded that a three-centered transition state structure such as **(1)** is the favored reaction pathway for the production of the cyclopropane.

Recently, theoretical studies of the cyclopropanation of ethylene with chloromethylzinc chloride and of the cyclopropanation of chloromethylzinc allylic alkoxides, both in the presence of a Lewis acid (ZnCl₂), have been performed at the density functional theory level (B3LYP/631A). **(29)** Transition state **(2)**, in which a five-centered complex is involved, is kinetically favored over the related four-centered complex **(3)** by 1.3 kcal/mol. Although this explanation appears to be consistent with the observation that added Lewis acids can produce a rate acceleration in the cyclopropanation reaction of zinc alkoxides, **(30, 31)** other modes of activation cannot be ruled out at this time. There is still a need for additional and more conclusive experimental evidence on the effect of added Lewis acids in the cyclopropanation of zinc alkoxides. These studies may have a significant impact on the development of new asymmetric catalytic processes.



3. Scope and Limitations

3.1. Preparation of Haloalkylmetal Reagents

3.1.1. Zinc Carbenoids

There are three classes of reactions that can generate the reactive haloalkylzinc species: (1) the oxidative addition of zinc metal into a carbon — halogen bond, (2) the alkyl group exchange between an organozinc reagent and a dihaloalkane, and (3) the insertion of a diazoalkane into a zinc — iodide bond. The oxidative addition of an activated form of zinc metal into a C— X bond is by far the most widely used method for the cyclopropanation of simple olefins. (32) Simmons and Smith recommended the use of a zinc-copper couple for this purpose. Their original procedure (33) (heating a mixture of zinc dust and cupric oxide under a hydrogen atmosphere) has been replaced by a more convenient method (treatment of zinc powder with cupric sulfate solution), which produces a reagent of comparable reactivity. (34, 35) A later modification calls for the treatment of zinc dust with a hot solution of cupric acetate in acetic acid. (36) Alternatively, zinc dust can be activated by mixing it with cuprous chloride under nitrogen. (37, 38) These procedures have been used in >90% of the cyclopropanation reactions involving a zinc-copper couples over the last 25 years. The analogous zinc-silver couple has been found to be useful, giving in some cases higher yields of cyclopropanes and/or shorter reaction times compared to those obtained with the zinc-copper couple. (39) Commercial zinc dust devoid of lead impurities is suitable for the reagent preparation. (40)

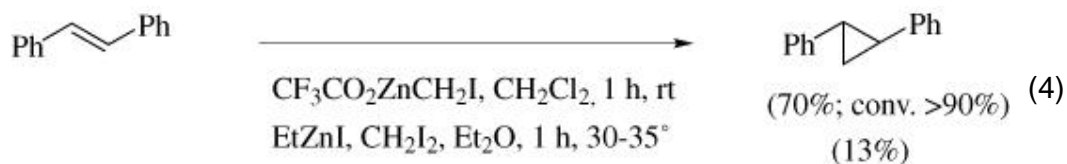
The addition of acetyl chloride to the Zn/ CuCl combination produces a reagent that can react with dibromomethane to generate bromomethylzinc bromide. (41) Commercial zinc metal of lower purity can be activated by the addition of TMSCl (40, 42) or TiCl₄, (43) by heating to 140–150° for 3 hours, (44) or by sonication. (45) Alternatively, highly reactive zinc powder suitable for reagent formation can be prepared by in situ reduction of zinc(II) salts. (46) The main advantage of these methods that involve commercial zinc metal for reagent preparation is practicality, since these reagents are more stable and easy to handle; however, none of these methods has found a wide acceptance in the literature.

Finally, one major limitation of the reactions involving the oxidative addition of an activated form of zinc metal into a C — X bond is that an ethereal solvent must necessarily be used (most commonly ether, THF or DME). Under these conditions, the electrophilic character of the reagent is lowered by the presence of a basic solvent. (9) In addition, the vast majority of stereoselective cyclopropanation reactions involving zinc reagents use other methods to generate the zinc carbenoid to avoid the presence of complexing solvents (vide infra). In conclusion, the methods outlined above for generating the

active zinc reagent should be used only with very reactive alkenes and when an ethereal solvent can be used. They are not compatible with most stereoselective cyclopropanation reactions involving substrate/chiral ligand-directed reactions since an ethereal solvent generally decreases the level of stereocontrol. Although there are numerous methods for activating zinc metal, the activation procedures using CuSO_4 , (34) $\text{Cu}(\text{OAc})_2$, (36) or CuCl (37) are still used in >90% of all the examples.

A superb and practical method for generating iodomethylzinc species quantitatively and reproducibly was reported by Furukawa and coworkers. (47, 48) These workers found that a similar reactive species could be prepared by using Et_2Zn to form presumably EtZnCH_2I (Furukawa's reagent). This alkyl exchange reaction to generate the reagent generally proceeds smoothly in a variety of solvents, but it is thought that traces of molecular oxygen are necessary to initiate carbenoid formation. (49, 50) However, for most applications, the adventitious oxygen present as an impurity is sufficient to initiate the process. Since diethylzinc is readily available neat or as a solution in several solvents, the cyclopropanation reaction can be carried out in a wide range of noncomplexing solvents such as dichloromethane, 1,2-dichloroethane, benzene, and toluene. The reactivity profile of $\text{Zn}(\text{CH}_2\text{X})_2$ ($\text{X} = \text{I}, \text{Cl}$), prepared from 1 equivalent of Et_2Zn and two equivalents of XCH_2I ($\text{X} = \text{I}, \text{Cl}$), indicates that these reagents are sometimes more effective than those derived from zinc metal, especially in stereoselective transformations. (51) Bis(chloromethyl)zinc in 1,2-dichloroethane is often the best reagent to use with less reactive alkenes. Another good and underused method for preparing IZnCH_2I involves the alkyl exchange reaction between EtZnI (prepared from Zn metal and EtI) and CH_2I_2 , especially if the reagent has to be prepared on a large scale and if Et_2Zn is not a viable option. (52)

It has been reported that the reagent derived from a 1:1:1 mixture of trifluoroacetic acid, diethylzinc, and diiodomethane is effective for the cyclopropanation of simple alkenes (Eq. 4). (53) In some cases, such as in the cyclopropanation of (*E*)-stilbene, this reagent is far superior to that derived from the zinc-copper couple or diethylzinc and diiodomethane. (52, 54) Alternatively, this reagent can be prepared by mixing trifluoroacetic acid and bis(iodomethyl)zinc, but this procedure is not recommended on large scale because of the exothermicity of reagent formation and the relatively rapid decomposition of bis(iodomethyl)zinc into iodomethylzinc iodide at temperatures above -20° in the absence of a complexing solvent.



Finally, shortly after the Simmons and Smith seminal publication, Wittig (55, 56) reported that treatment of zinc iodide with either one or two equivalents of diazomethane was an alternative method for preparing IZnCH_2I or the analogous bis(iodomethyl)zinc reagent $[\text{Zn}(\text{CH}_2\text{I})_2]$. However, this method for the preparation of the reagent has not been widely used in the last 30 years. A brief comparison of the various approaches to zinc carbenoids is shown in Table A.

**Table A. Methods for the Preparation of Cyclopropanating Reagents
“ ZnCH_2X ”**

Reactants (best solvents)	Comments
Zn/activator, CH_2X_2 (Et_2O , THF, DME, etc)	Oldest and still most widely used. No significant advantage over other methods other than the stability and availability of precursors. Traditional method of activation used in >90% of cyclopropanations involving zinc metal. Reaction conditions lead to a much less reactive but more stable reagent.
Et_2Zn , CH_2X_2 (CH_2Cl_2 , $\text{ClCH}_2\text{CH}_2\text{Cl}$)	Best reagents for stereoselective reactions and oxygen-directed cyclopropanations. When $\text{X} = \text{Cl}$, very reactive reagent that usually produces higher yields with less reactive alkenes. Stoichiometry may be an important factor in stereoselective reactions; 1:1 stoichiometry is the best combination for acid-sensitive substrates (minimizes formation of ZnI_2).
EtZnI (prepared in Et_2O), CH_2X_2 ,	Especially good if the reaction has to be done on large scale and the use of Et_2Zn

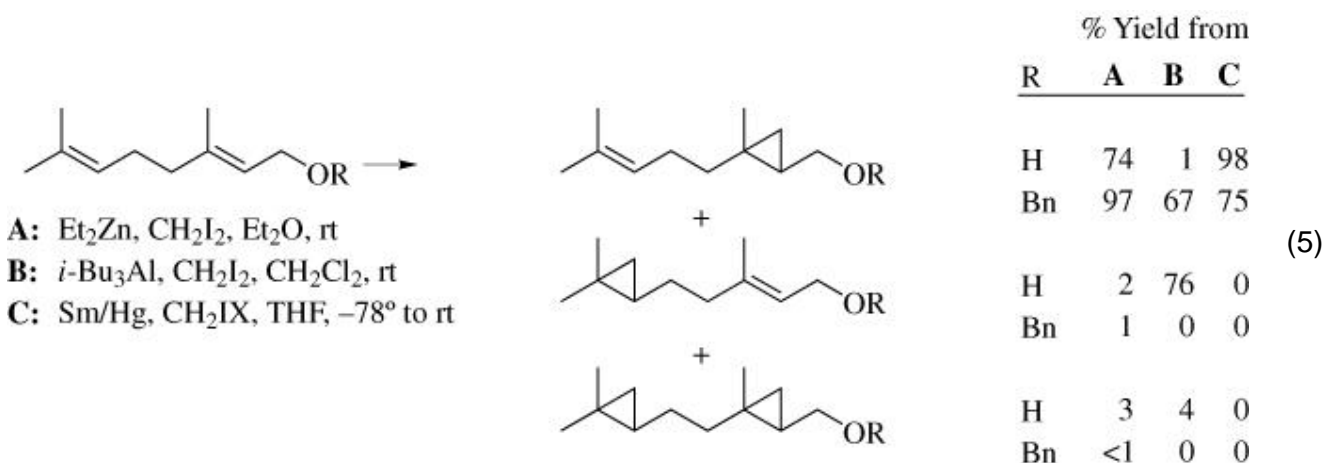
(CH ₂ Cl ₂ , ClCH ₂ CH ₂ Cl)	is to be avoided.
CF ₃ CO ₂ H / Et ₂ Zn / CH ₂ I ₂ (CH ₂ Cl ₂)	Very good reagent for the cyclopropanation of less reactive alkenes (such as styrene or halosubstituted alkenes). Very high reactivity, but slightly acidic conditions may lead to some decomposition with acid-sensitive substrates.
ZnX ₂ , CH ₂ N ₂ (Et ₂ O)	Rarely used

3.1.2. Nature of the Solvent

The solvent used in zinc-mediated cyclopropanation reactions plays an important role in these reactions, owing to the electrophilic nature of the zinc carbenoid and the Lewis acidity of the reagent. Dichloromethane and 1,2-dichloroethane are the solvents of choice since they are non-basic, unreactive toward the zinc reagents, and polar enough to solubilize the substrates. When basic solvents are used, the rate of cyclopropanation usually decreases as the basicity of the solvent increases. (9)

3.1.3. Aluminum and Samarium Carbenoids

Carbenoids of aluminum and samarium that display interesting properties compared with those of the zinc reagents have been reported. Iodo- or chloromethylsamarium iodide in THF (57, 58) is a superb reagent for the chemoselective cyclopropanation of allylic alcohols in the presence of other alkenes. With this reagent, the cyclopropanation of an isolated olefin is not observed. Conversely, dialkyl(iodomethyl)aluminum (59-61) displays outstanding chemoselectivity for the cyclopropanation of olefins in the presence of allylic alcohols. Each reagent is compared in the cyclopropanation of geraniol (Eq. 5).



(5)

The high chemoselectivity favoring cyclopropanation at the terminal double bond obtained with the aluminum reagent is possible only when the reaction is run in the presence of an allylic alcohol. For example, treatment of the benzyl ether of geraniol with aluminum or zinc reagents results in cyclopropanation at the allylic ether position. (62) A similar reaction with the samarium carbenoid (X = I) requires a large excess of the reagent to produce a good yield of the desired product (Eq. 5).

Although several trialkylaluminum reagents have been used as the starting materials for the aluminum carbenoid, *i*-Bu₃Al and Et₃Al are usually used. Samarium carbenoid reactions typically require a large excess of reagent in order to achieve high conversions, and samarium metal or SmI₂ (62a) with CH₂IX have been used to form the reactive species. When samarium metal is used, HgCl₂ must be added as an activator, otherwise the reaction is sluggish and often fails to initiate. Alternatively, TMSCl can also activate samarium, and has shown in many examples a beneficial effect on the yields and stereoselectivity of the reactions when compared to HgCl₂. (63)

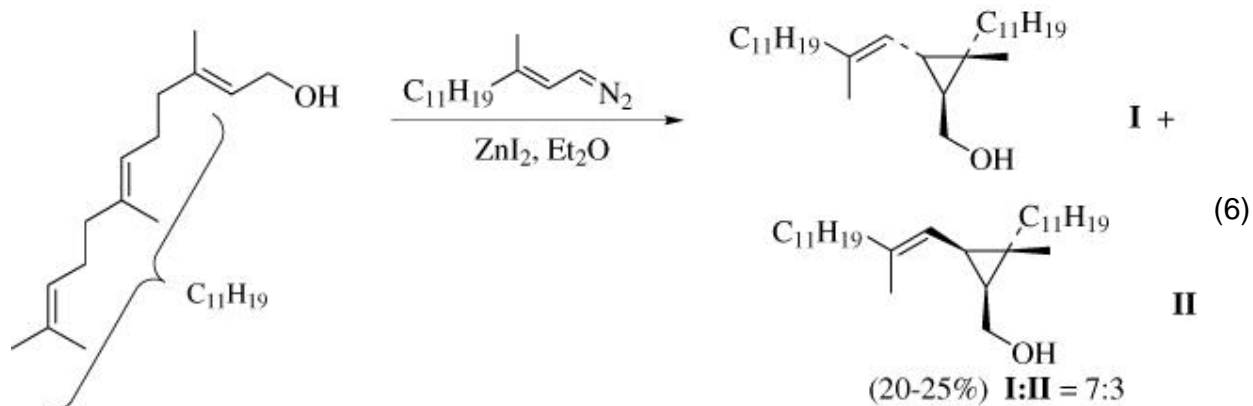
3.1.4. Substituted Carbenoids

More complex zinc carbenoids can be prepared by reacting diethylzinc or zinc metal with more substituted dihaloalkanes. The reactions are generally more effective with iodo-substituted alkanes. These more highly substituted reagents are effective at generating 1,2,3-substituted cyclopropanes. The substituted reagents that have been used to generate highly substituted cyclopropane derivatives are shown in Table B.

Table B. Preparation of Substituted Carbenoids

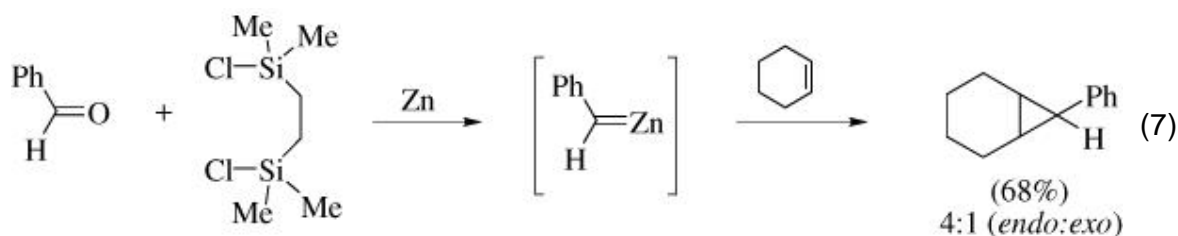
Substituted Dihalide	Metal Reagent	Carbene Unit	Reference
MeCHI ₂	Zn/Cu	MeCH	(64)
	EtZnI		(65)
	Zn/Ag		(66)
	Et ₂ Zn		(67)
	Sm		(57)
	Me ₃ Al		(59)
	<i>i</i> -Bu ₃ Al		(59)
MeCHBr ₂	Zn/Cu	MeCH	(68)
TIPSOCH ₂ CH ₂ CHI ₂	Et ₂ Zn	TIPSOCH ₂ CH ₂ CH	(69)
Me ₂ CBr ₂	Zn	Me ₂ C	(70)
Me ₂ Cl ₂	Et ₂ Zn		(71)
PhCHCl ₂	Zn	PhCH	(70)
PhCHBr ₂	Zn		(70)
PhCHI ₂	Et ₂ Zn		(67)
CHI ₃	Et ₂ Zn	CHI	(72)
CHBr ₃	Et ₂ Zn	CHBr	(73)
CHCl ₃	Zn	CHCl	(70)
CHBrCl ₂	Zn	CHCl	(70)
CHBr ₂ Cl	Zn	CHCl	(70)
CHF ₂	Et ₂ Zn	CHF	(72)
CF ₂ Br ₂	Zn	CF ₂	(74)

In general, the reagent formation is more effective if a diiodo precursor is used, but in some cases dibromides and activated dichlorides have also been successfully converted into suitable reagents. Functionalized zinc carbenoids have been prepared from diiodoalkanes and diethylzinc and used in stereoselective transformations, but their use is limited by the availability of the diiodoalkane. (69) Alternatively, reaction of a diazoalkane with ZnI₂ (vide supra) can offer a valuable alternative to access complex zinc carbenoids (Eq. 6). (75)



3.1.5. In Situ Formation of the Carbenoid

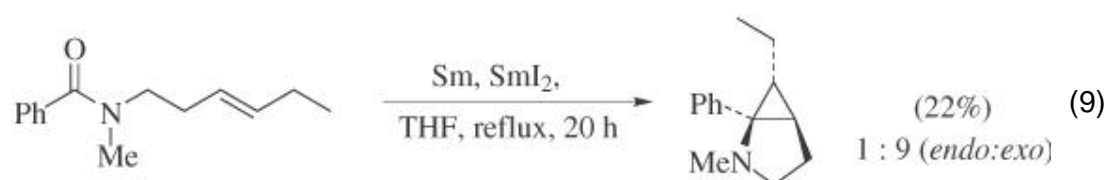
Functionalized zinc carbenoids can be prepared from carbonyl compounds by an indirect strategy. (76) The direct deoxygenation of a carbonyl compound to an organozinc carbenoid can be induced by reaction with zinc and TMSCl in a sequence which parallels the mechanism of the Clemmensen reduction. Therefore, the aldehyde or ketone is treated with TMSCl or 1,2-bis(chlorodimethylsilyl)ethane, the olefin, and zinc amalgam to produce a good *endo:exo* ratio for the cyclopropanation product. For example, treatment of cyclohexene with the carbenoid derived from benzaldehyde proceeds satisfactorily (Eq. 7).



In addition, although the yields and selectivities are modest, this method is quite effective for the production of alkoxy-substituted cyclopropane derivatives. Indeed, when trimethyl orthoformate is used as the carbenoid precursor under similar reaction conditions, a 64% yield of the desired methoxycyclopropane is obtained (Eq. 8). (77)



In a similar fashion, amino-substituted cyclopropanes can be generated by the intramolecular cyclopropanation of an alkene by conversion of a benzamide to a samarium carbenoid. However, this reaction is limited to the intramolecular version, and the yields are modest (Eq. 9). (78)



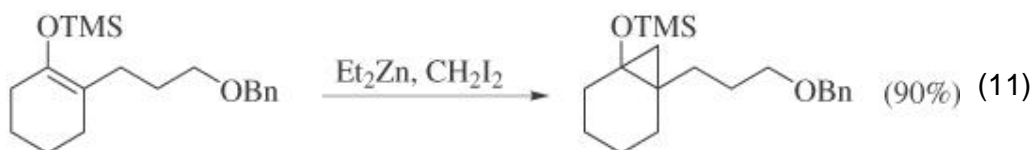
The next sections highlight the synthetic scope of reactions involving these reagents with a strong focus on stereocontrol.

3.2. Achiral Alkenes

The cyclopropanation of simple alkenes has been used for a number of years to test and compare the efficiency of new reagents. For example, cyclohexene has been treated with a variety of reagents to generate bicyclo[4.1.0]heptane to compare the efficiency of the conversions (Table A). The best reagent to cyclopropanate unfunctionalized alkenes is $\text{Zn}(\text{CH}_2\text{Cl})_2$ in 1,2-dichloroethane. (51) It appears that $\text{TFA}/\text{Et}_2\text{Zn}/\text{CH}_2\text{I}_2$ and $\text{R}_3\text{Al}/\text{CH}_2\text{I}_2$ are also quite effective reagents, but these reactions are not well documented at this time.

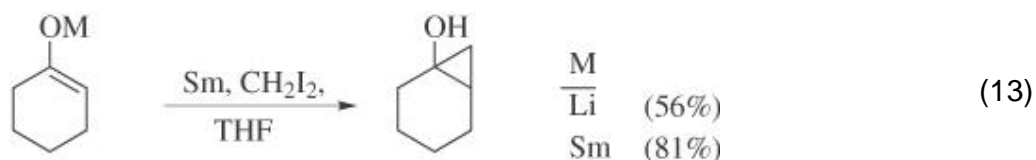
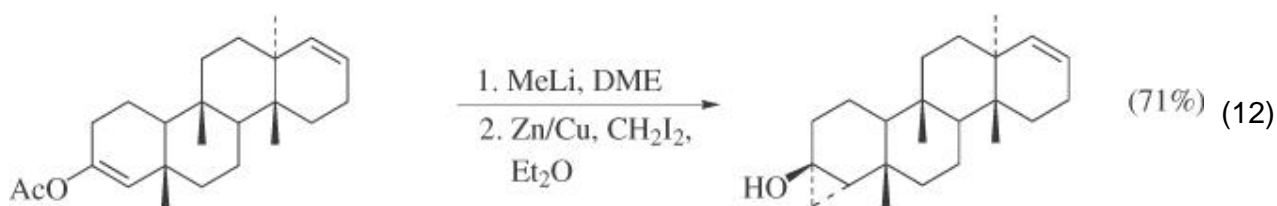
The cyclopropanation of enol ethers is usually quite facile (48) (Eqs. 10–11). (79, 80) Trimethylsilyloxy-substituted olefins are by far the most widely used in this category



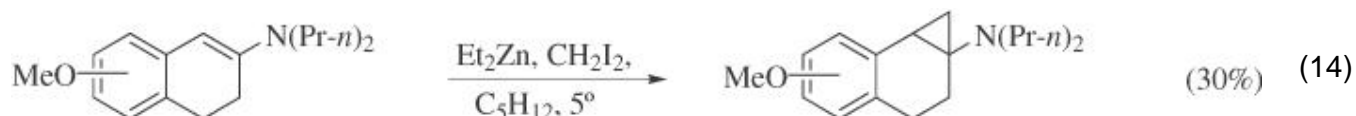


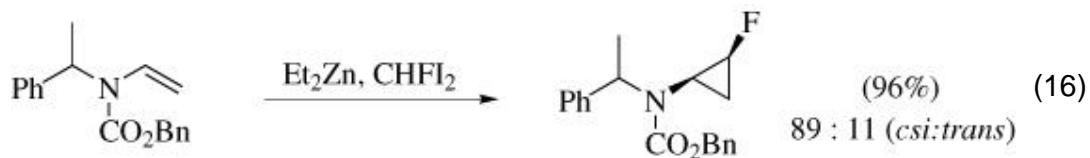
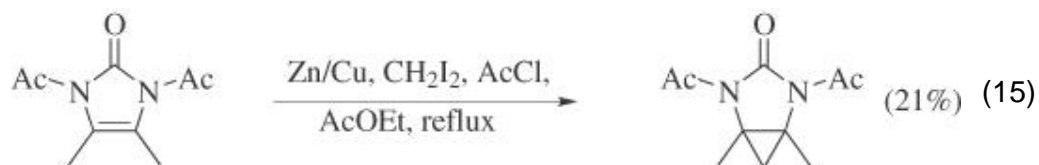
since the starting material is readily available by enolization of the corresponding ketone. (81-84) Problems resulting from the Lewis acid sensitivity of the products are sometimes observed, (79) but in general these electron-rich olefins react rapidly with the zinc reagents, especially those prepared from Et_2Zn in noncoordinating solvents.

On the other hand, even if enol esters have rarely been used directly under Simmons-Smith conditions, they can be valuable precursors for cyclopropanols by allowing generation, then in situ cyclopropanation of the parent metalloenolate (85) (Eq. 12). (86) Metalloenolates can also be converted to the corresponding hydroxycyclopropanes by the use of samarium reagents (Eq. 13). (87, 88)

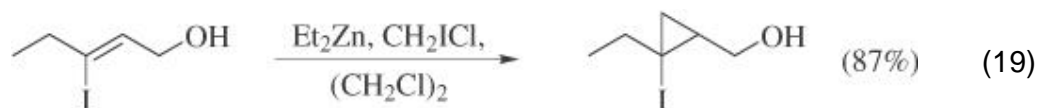
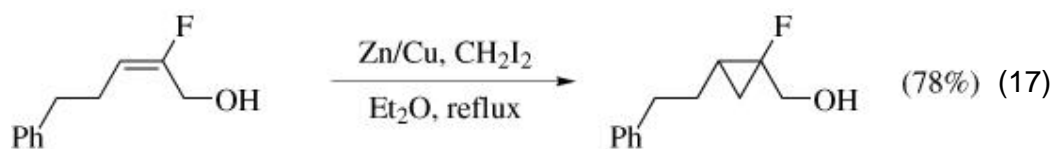


The cyclopropanation of *N*-substituted alkenes is much more problematic since *N*-alkylation can become an important competing pathway. Conversely, introducing an electron-withdrawing protecting group on nitrogen decreases the nucleophilicity of the alkene, and lower yields are observed unless highly electrophilic reagents are used (Eqs. 14–16). (89-91)





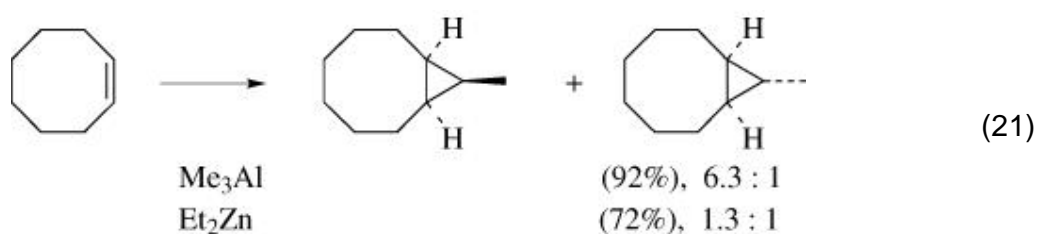
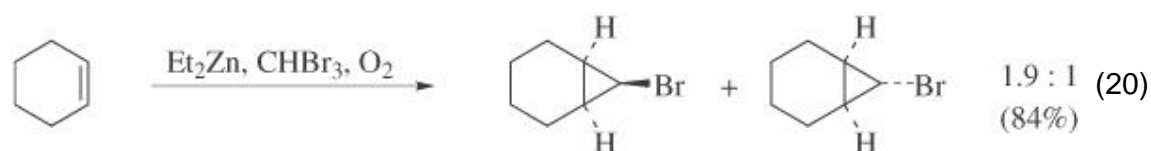
The cyclopropanation of vinyl halides is also quite effective, and fluoro-, (92) bromo- (93) and iodo-substituted (94) cyclopropanes can be prepared using zinc carbenoids (Eqs. 17–19). For vinyl iodides and bromides, bis(chloromethyl)zinc in 1,2-dichloroethane is a superior reagent. (51)



The cyclopropanation of vinylorganometallic and heteroatom-substituted

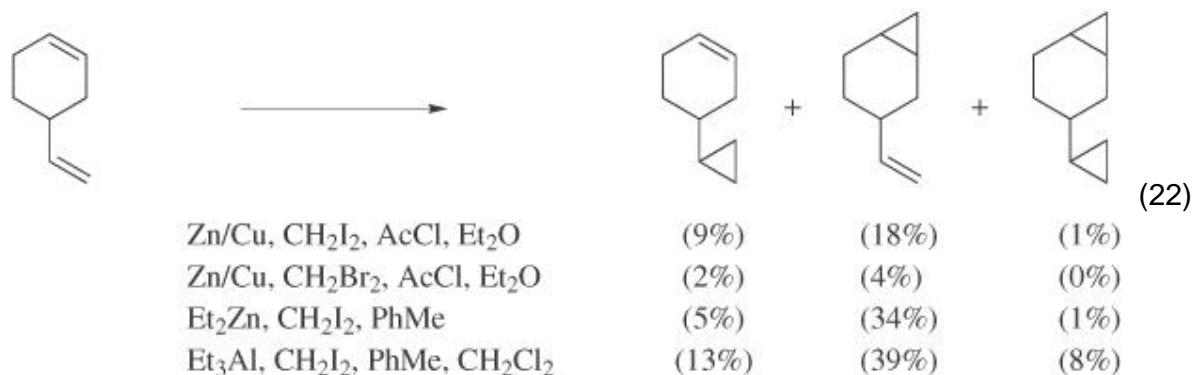
vinyl compounds is also quite efficient with the zinc, samarium, and aluminum reagents. For example, vinylboronates, (95) -alanes, (96) -zincs, (97) -stannanes, (98) -phosphonates, (99) -germanes, (100) and silanes (101, 102) are readily converted into cyclopropane derivatives.

When halo- (103) or alkyl-substituted reagents are used, the *endo:exo* selectivity is usually poor (<2.5:1) (Eqs. 20–21). (59, 71) Sometimes, higher diastereoselectivities are observed with the aluminum reagent or with other more sterically demanding zinc reagents (Eq. 21).

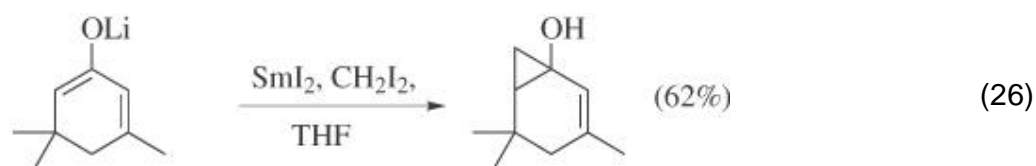
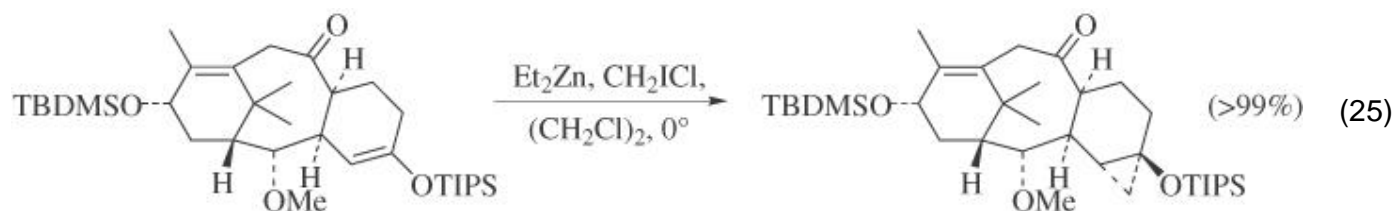
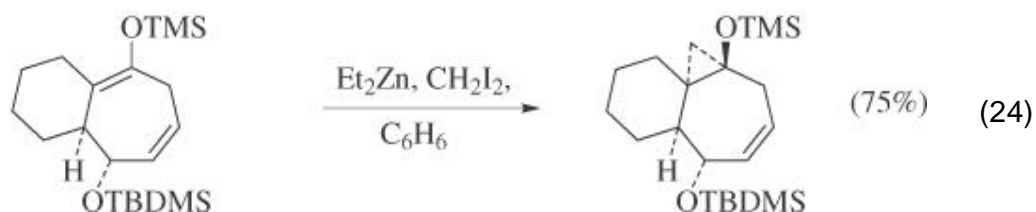
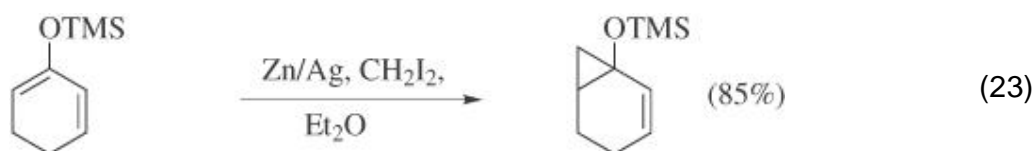


3.3. Polyenes

When a polyene is treated with a haloalkylzinc reagent, very little chemoselectivity is observed when there is no basic group to direct the reaction (Eq. 22). (104) The relative rates for the cyclopropanation of various alkenes have been measured

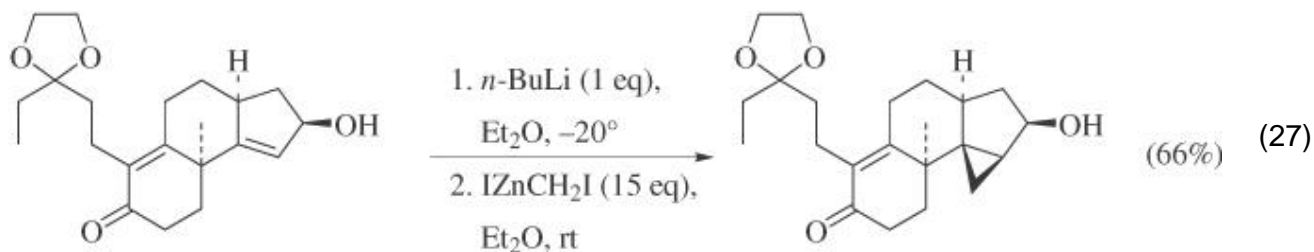


and the influential factors have been highlighted. A combination of steric and electronic effects has been invoked to explain the chemoselectivity using iodomethylzinc iodide, but little is known regarding other reagents. (105, 106) Because of the electrophilic nature of the reagents, highly substituted double bonds generally react faster than less substituted ones. Neither of the reagents (aluminum and zinc) is superior to the other. However, a highly chemoselective cyclopropanation is observed when one double bond is significantly more nucleophilic than the others. For example, excellent chemoselectivity is observed when one of the double bonds is an enol ether (Eqs. 23–25) (107-109) or a lithium enolate (Eq. 26). (110)



Allylic alcohols or isolated olefins can be cyclopropanated with high

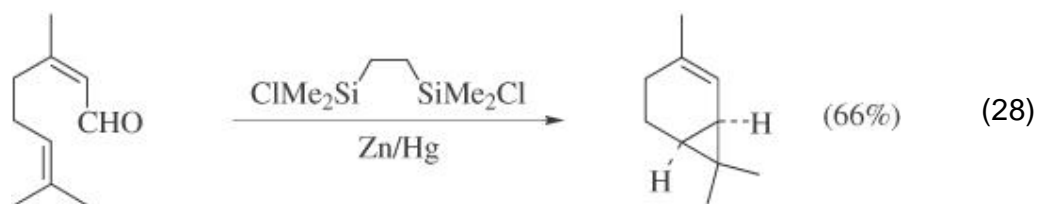
chemoselectivity in the presence of the other with the appropriate choice of reagents and reaction conditions (Eq. 5). This reaction has been applied to more complex systems, and the chemoselectivity is usually excellent (Eq. 27). (111) It is important to



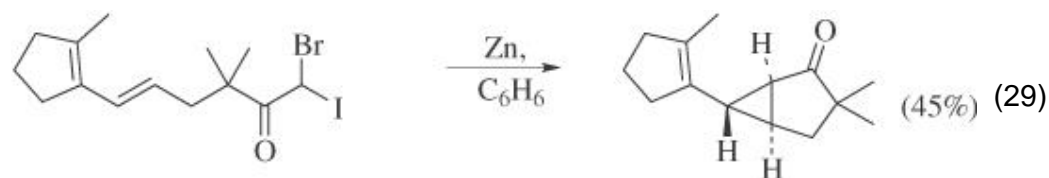
point out that the presence of a basic group at the allylic position is mandatory to observe any reaction with the samarium reagent. More work is needed to determine the ability of the samarium and aluminum reagents to participate in directed cyclopropanation reactions.

3.4. Intramolecular Cyclopropanation

Examples of intramolecular cyclopropanation of alkenes using zinc, aluminum or samarium carbenoids are rare. The most widely found involve preparation of the carbenoid from the corresponding carbonyl derivative (Eq. 28). (112)

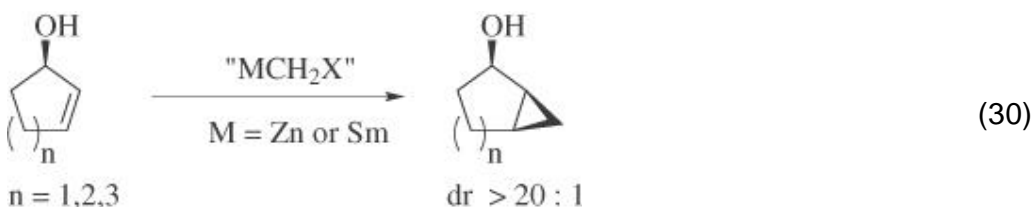


Alternatively, a bromiodoalkene produces the corresponding bicyclic system upon treatment with zinc dust in benzene (Eq. 29). (113) This is one of the few known examples of an intramolecular cyclopropanation reaction involving a dihaloalkene.

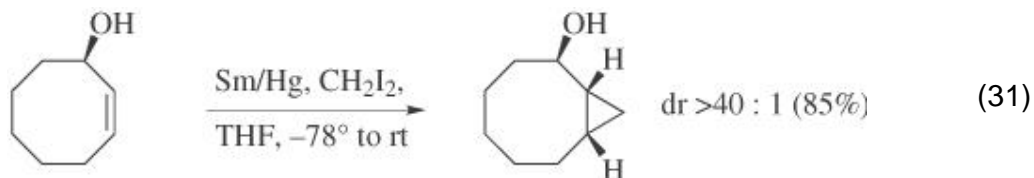


3.5. Cyclic Chiral Alkenes

Cyclic alkenes that bear basic functional groups which can give rise to precoordination to the electrophilic zinc reagent are readily converted into cyclopropanes. For example, it was observed early on that proximal hydroxy groups could direct the delivery of the methylene group. (7) Subsequent, simple cycloalkenols have served as model substrates for kinetic studies. Transition state models have recently been proposed for these directed processes. (8) The cyclopropanation of five-, six-, and seven-membered ring 1-cycloalken-3-ols generally produces high *syn:anti* ratios with both zinc and samarium reagents (Eq. 30). (57, 114)



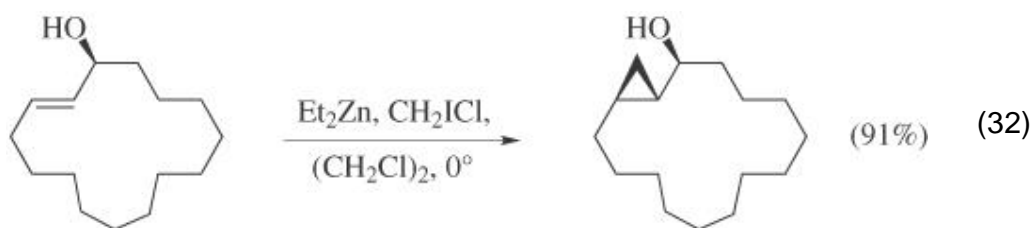
A reversal of selectivity is observed with the analogous eight- or nine-membered rings (Eq. 31). (58, 115) This can be explained by simple conformational analysis of the ground state structures. 2-Cycloocten-1-ol prefers to adopt a chair-boat



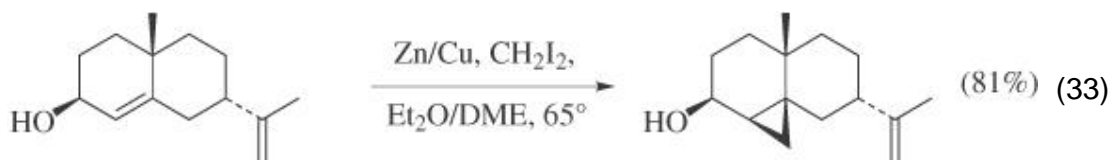
conformation in which the bulky hydroxy group has the equatorial orientation. This reversal of stereochemical outcome is also observed in the directed epoxidation of 2-cycloocten-1-ol. (116)

One example of cyclopropanation of a macrocyclic alkenol indicates that outstanding levels of diastereoselectivity can also be obtained with this class of substrates. This reaction has been used in an elegant synthesis of (*R*)-muscone (Eq. 32). (117) This complete diastereocontrol is best explained

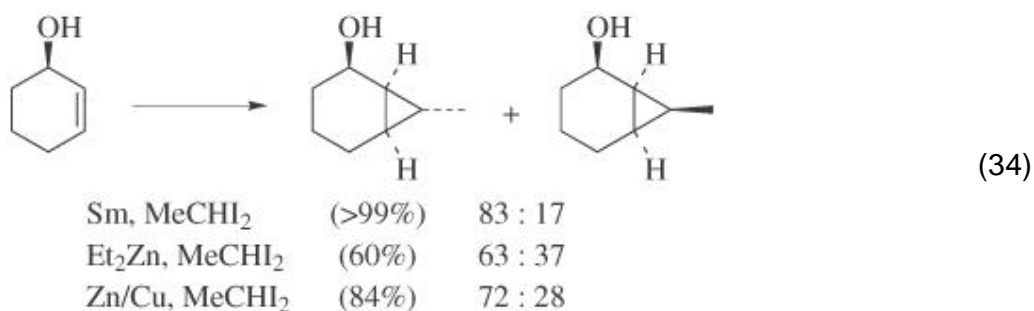
by the minimization of the A (1, 3) strain and is similar to that proposed for stereoselection in similar reactions of acyclic chiral allylic alcohols (vide infra).



Additional examples of stereocontrol in the cyclopropanation of functionalized cycloalkenol derivatives are presented in Tables VII and IX. This collection highlights the compatibility of a variety of functional groups under the cyclopropanation conditions, especially when an alcohol or a basic group is present to direct the reaction. Furthermore, the reaction usually proceeds quite well even when delivery occurs on the more sterically hindered face of the double bond (Eq. 33). (118)

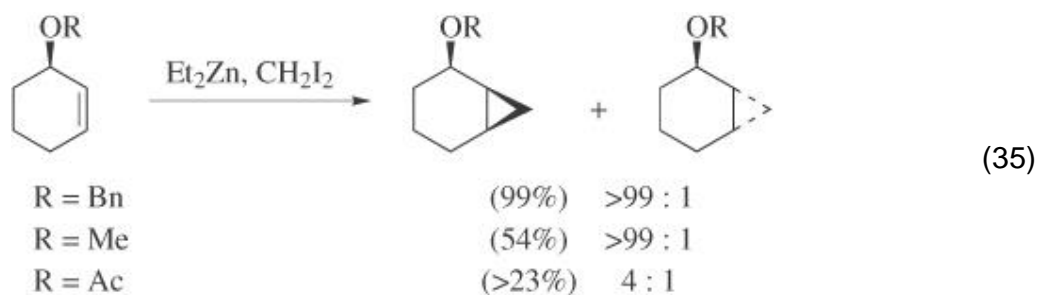


Strong directing effects are also observed when more highly substituted reagents are used. However, although the *exo:endo* selectivity is modest, the samarium reagent is slightly superior (Eq. 34). (57, 119, 120)

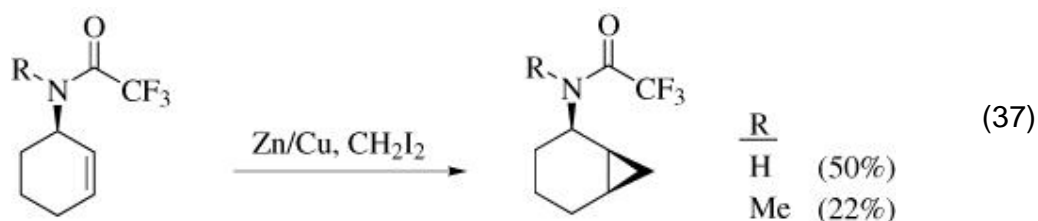
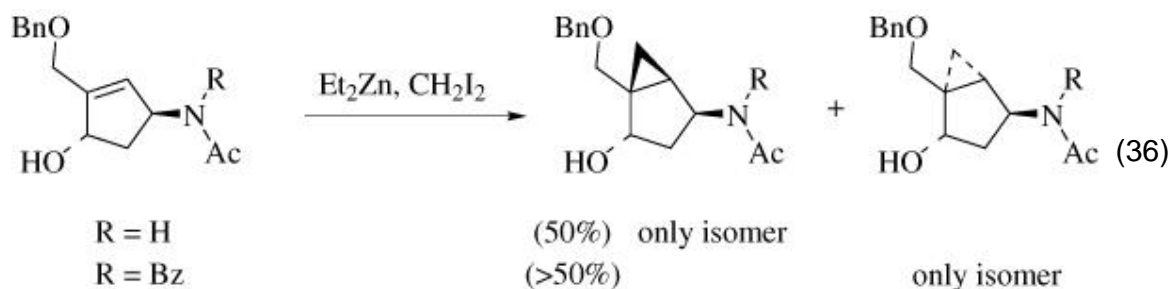


Even though the hydroxy group has been used extensively as a directing group for the cyclopropanation of alkenes, other basic groups are also

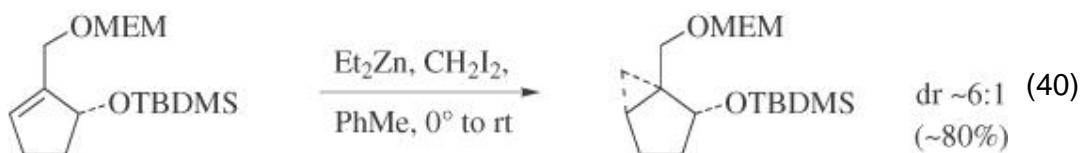
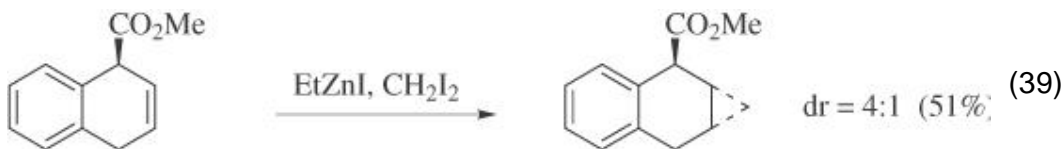
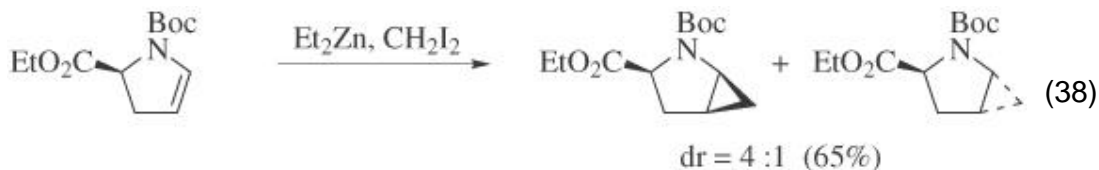
effective with zinc reagents (Table VII). Benzyl ethers, (51) methyl ethers, (114) and acetates (121) are able to direct the zinc reagent to various degrees (Eq. 35). An interesting example



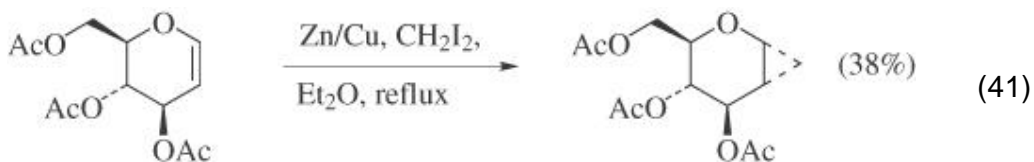
involves competition between an acetamide and a hydroxy group (Eq. 36), (122) in which the acetamide is a better directing group than the zinc alkoxide, but the selectivity is reversed upon benzoylation of the amide. Similarly, trifluoroacetamides are also able to direct the cyclopropanation reaction (Eq. 37). (123)



Esters can also be good directing groups, producing modest *syn* selectivities, but the sense of induction seems to be substrate- or reagent-dependent (Eqs. 38–39). (124, 125) In some cases, TBDMS ethers appear to direct the reaction (Eq. 40), (126)



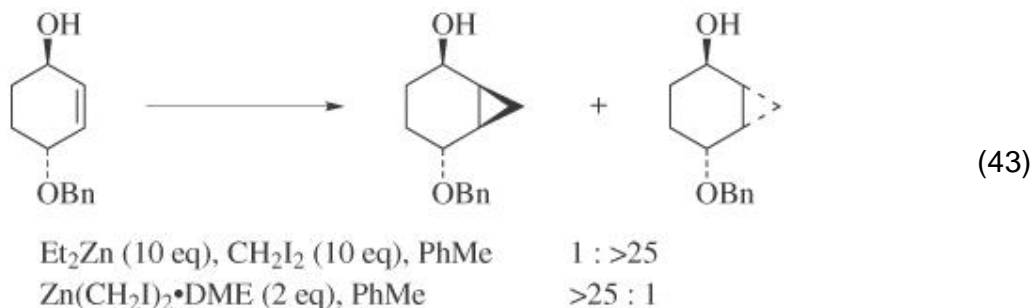
but in other cases the double bond does not react, probably because of steric hindrance by the protecting group. (127) When acetate groups are used (Eqs. 35, 41 and 42), (121, 128, 128a) reports indicate that their directing ability is highly substrate-



solvent- and/or reagent-dependent. Allylic acetates appear to lose their directing ability when a slightly complexing solvent (diethyl ether) is used. It appears that use of the Furukawa reagent in a noncomplexing solvent ensures good *syn* selectivity. The synthesis of cyclopropanated sugars, involving a directed cyclopropanation of glucal derivatives, is a good example of a substrate for which the directing ability of various groups has been cleverly used to control the cyclopropanation reaction.

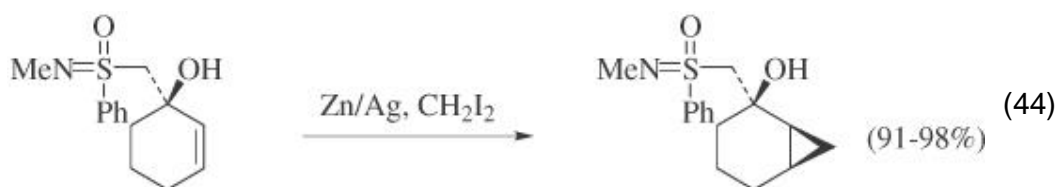
There are no systematic studies on the relative directing ability of oxygenated

groups with various reagents and reaction conditions. However, the results of cyclopropanation of monoprotected *trans*-2-cyclohexene-1,4-diol as a function of reaction conditions and reagents are quite surprising (Eq. 43). (9) The directing

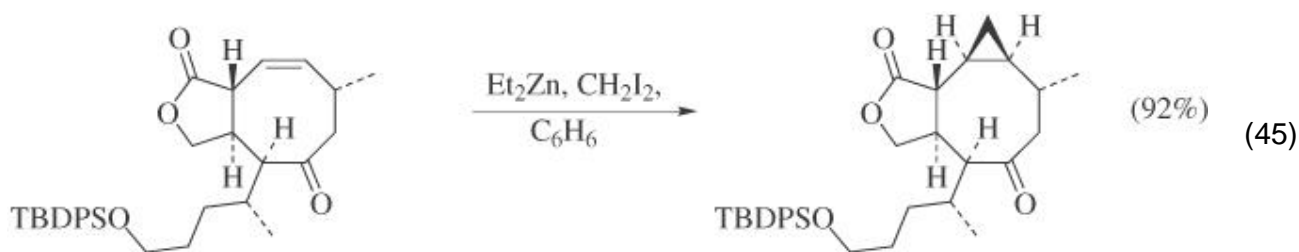


ability of oxygenated groups is highly dependent upon the reaction conditions. For example, a benzyl ether is a superior directing group when the reaction is run at high concentrations with excess EtZnCH₂I in a noncoordinating solvent. Conversely, the directing ability of the zinc alkoxide takes over if only one equivalent of the reagent is used.

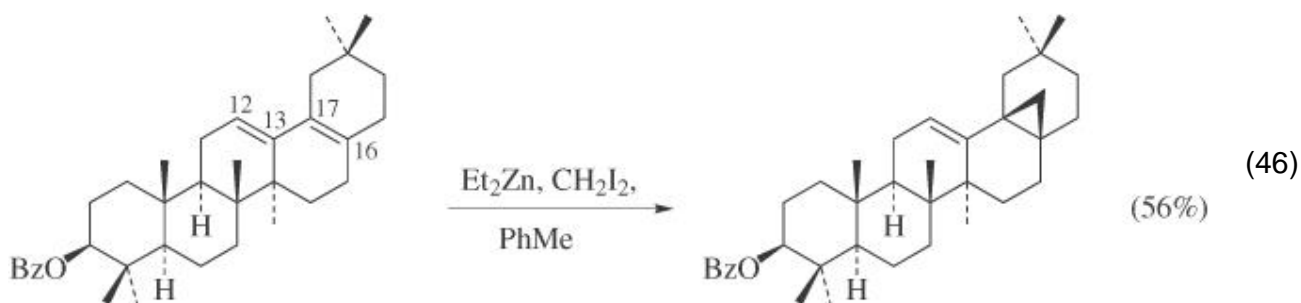
In the synthesis of enantiomerically pure cyclopropyl ketones, the directing effect of β-hydroxysulfoximines derived from cyclic enones leads to the cyclopropane *syn* to the hydroxy group (Eq. 44). (129) Basic cleavage of the sulfoximine generates the cyclopropyl ketone. This is one of the first examples in which two relatively basic functionalities (hydroxy and sulfoximino) compete for the group-assisted methylene delivery.



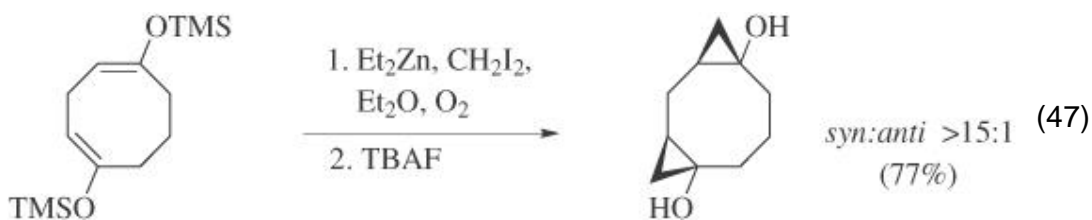
In the absence of a directing group, the cyclopropanation of cyclic olefins is generally controlled by steric effects. The level of stereochemical induction is usually high, and the sense can be predicted on the basis of the prevailing ground state conformation of the starting olefin. For example, stereoselective cyclopropanation is directed to the more accessible β face to produce a key intermediate in the synthesis of (+)-acetoxycrenulide (Eq. 45). (130)



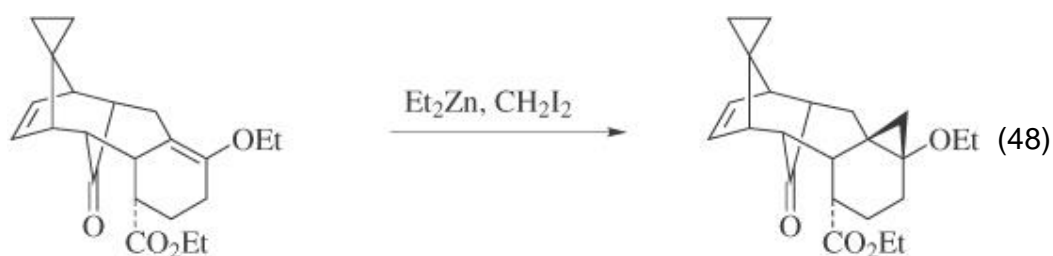
The stereo- and regioselective cyclopropanation of a diene is a key step in introducing a hydroxymethyl group at C(17) in the total synthesis of β -amyrin. (131) The resulting vinylcyclopropyl unit was opened under free radical conditions to yield the C(17) hydroxymethyl substituent. The selective cyclopropanation of the 16,17-double bond is striking since in an analogous reaction, the dibromocarbene adds exclusively to the 12,13-double bond (Eq. 46).



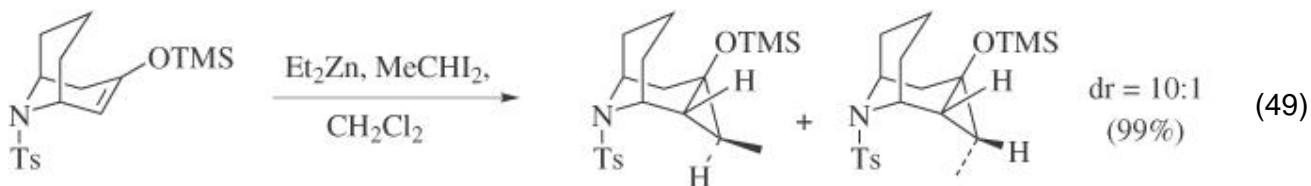
Cyclopropanation of unsaturated medium ring size compounds and macrolides can be quite diastereoselective. For example, a cyclic bis(trimethylsilyl)enol ether can be efficiently cyclopropanated with excellent stereocontrol using Furukawa's reagent (Eq. 47). (130) The cyclopropanation produces the *syn*-dicyclopropane in a high diastereomeric ratio (>15:1).



Steric factors can and sometimes do override the directing effect of functional groups. For example, cyclopropanation of the cyclic enol ether leads to only one isomer in which the cyclopropanation occurs *anti* to the ester and to the ketone (Eq. 48). (133)



In the course of the enantioselective synthesis of (–)-pinidine, a highly diastereoselective cyclopropanation reaction of a silyl enol ether with the reagent derived from 1,1-diiodoethane and diethylzinc was reported (Eq. 49). (134) The level of induction in that reaction is highly dependent on the nature of the nitrogen protecting group.

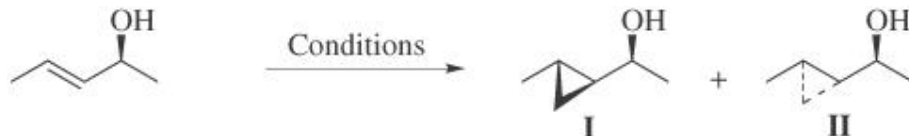


3.6. Acyclic Chiral Alkenes

3.6.1. Allylic and Homoallylic Alcohols

Despite the remarkable success in controlling the relative configuration of cyclopropanation products in cyclic systems, the stereocontrol on acyclic

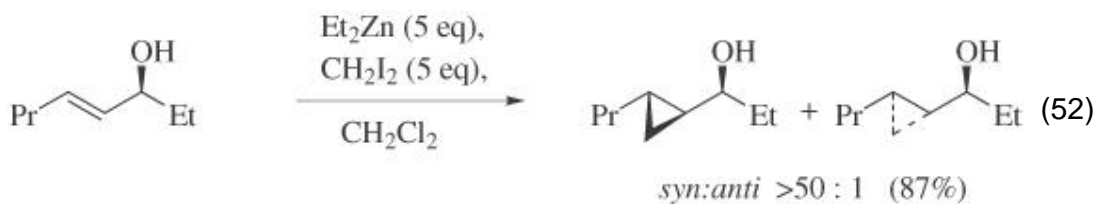
systems has been recognized only recently. The stereoselective cyclopropanation of a chiral acyclic allylic alcohol was first studied using the Simmons-Smith reagent (Zn/Cu, CH₂I₂). (135) High *syn*-selectivities (>200:1) are obtained with *Z* disubstituted double bonds (Eq. 50), but the analogous reaction on *E* disubstituted double bonds gives modest ratios (<2:1) (Eq. 51). However, the nature of the zinc carbenoid and solvent used in these reactions is extremely important for obtaining high diastereoselectivities, especially with *E* disubstituted olefins. (136, 136a) The importance of the reaction conditions and



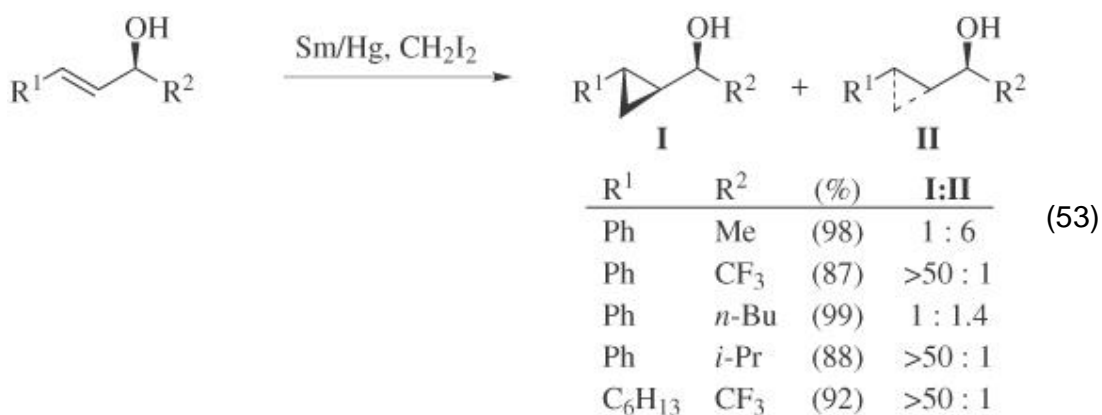
Conditions	I : II	(%)
Zn/Cu, CH ₂ I ₂ , Et ₂ O	57 : 43	(—)
Et ₂ Zn (5 eq), CH ₂ I ₂ (5 eq), CH ₂ Cl ₂	88 : 12	(>95%)
Et ₂ Zn (5 eq), CH ₂ I ₂ (5 eq), Et ₂ O	82 : 18	(50%)
Zn(CH ₂ I) ₂ (2 eq), CH ₂ Cl ₂	73 : 27	(90%)
Sm/Hg, CH ₂ I ₂ , THF	25 : 75	(75%)

(51)

the nature of the reagent are highlighted by the cyclopropanation of (*E*)-3-penten-2-ol (Eq. 51). The classical Simmons-Smith conditions (I₂ZnCH₂I from Zn/Cu, CH₂I₂) or Zn(CH₂I)₂ generally give low diastereomeric ratios. Conversely, the use of an excess (5 equivalents) of Furukawa's reagent (EtZnCH₂I prepared from a 1:1 mixture of Et₂Zn and CH₂I₂) in CH₂Cl₂ produces the highest selectivities to date with this substrate. The choice of solvent in these processes is important for optimizing the diastereoselectivities. For example, the ratio drops from 7:1 to 4.7:1 if diethyl ether is used as the solvent with Furukawa's reagent. Interestingly, the samarium-derived reagent leads to the formation of the *anti* isomer as the major product with this substrate. It is clear from the data presented in Table VIII that EtZnCH₂I is the most general reagent for access to the *syn* isomer with *E*-disubstituted olefins. Furthermore, the level of *syn* selectivity increases significantly with this reagent when the substituents are bulkier, indicating the importance of the A (1, 3) strain in these reactions (Eq. 52). (136)



The samarium reagent is also quite effective, but the selectivities are highly substrate dependent (Eq. 53). (57, 58, 137) It is clear that stereoelectronic effects play an important role since substitution of a methyl group by a trifluoromethyl group has a spectacular impact on the level of selectivity. The increase in selectivity has

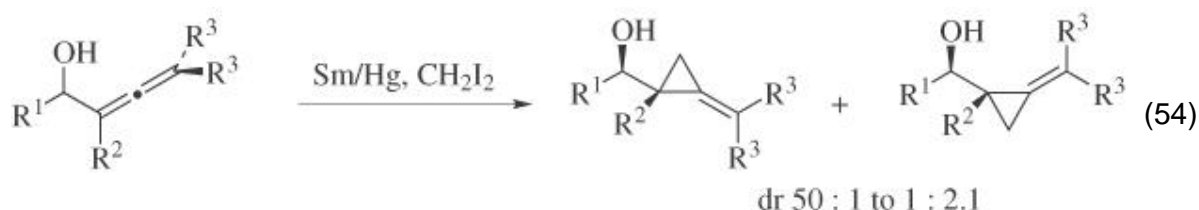


been attributed to the formation of a tighter complex between the substrate and the reagent. Alternatively, this might be due to the influence of the R² group on A (1, 2)/A (1, 3) strain and hyperconjugative effects. (138) This reaction can be extended to silyl- and stannyl-substituted alkenes. (139, 140)

In the cyclopropanation of *Z*-disubstituted and trisubstituted double bonds, uniformly high *syn* selectivities are obtained with various reagents. The stereochemical outcome of these reactions can be predicted qualitatively by assuming an oxygen group-assisted delivery of the reagent from a conformation in which the minimization of A (1, 3) strain is the predominant controlling element. (141) However, it is clear that other important factors should be taken into account in order to explain the level of induction.

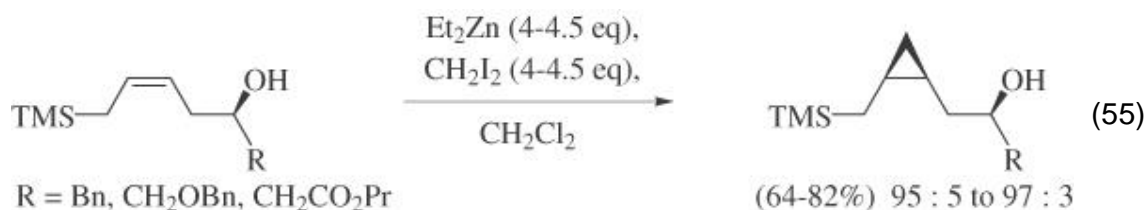
The cyclopropanation of α -allylic alcohols using Sm/CH₂I₂ provides a variety of methylene- and alkylidenecyclopropane carbinols in good yield and with high regioselectivities. (142) The *syn:anti* diastereoselectivities vary from 1:2.1 to 50:1 depending upon the substituents on the carbinol side chain and on the

substitution of the allene (Eq. 54). The “Houk outside model” (143, 144) has been used to explain



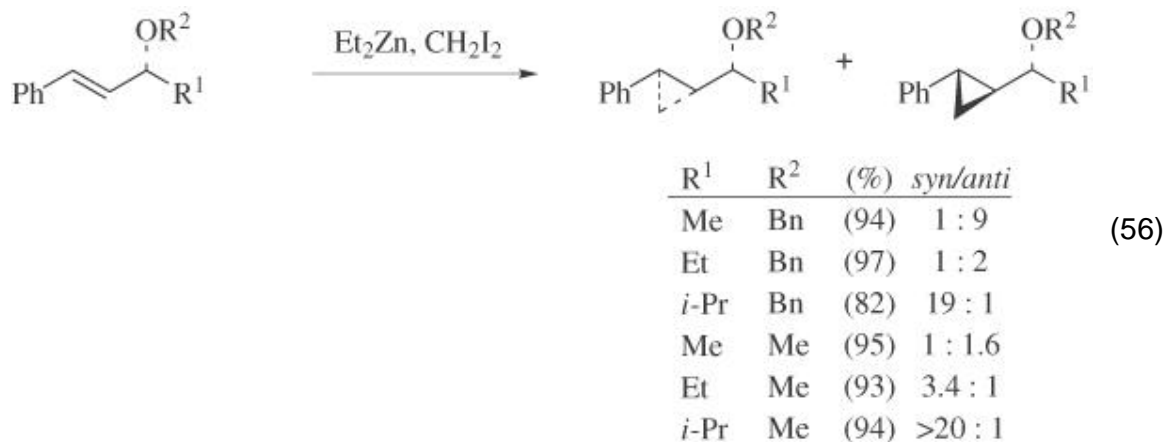
the sense and level of the diastereoselection in the samarium-carbenoid reactions. Use of the samarium reagent is essential to maximize the regioselectivity of this process and to avoid the formation of spirocyclic carbinols. Both aluminum and zinc carbenoids are known to form mixtures of methylenecyclopropanes and spirocyclic carbinols (see Table X).

The diastereoselective cyclopropanation of homoallylic alcohols has been used with moderate success. For example, the cyclopropanation of (*Z*)-5-hydroxy-2-alkenylsilanes occurs with high levels of stereochemical induction (Eq. 55). (145) This is one of the few acyclic homoallylic alcohols in which the cyclopropanation occurs with good stereocontrol.



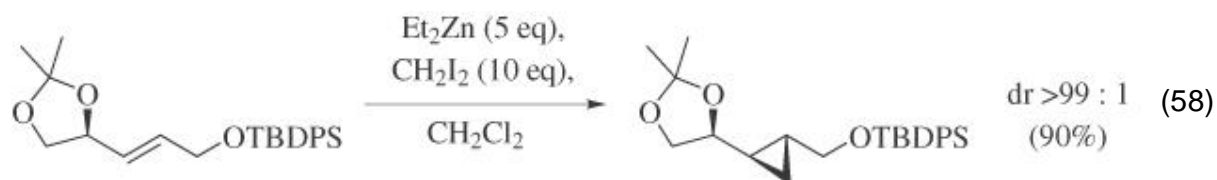
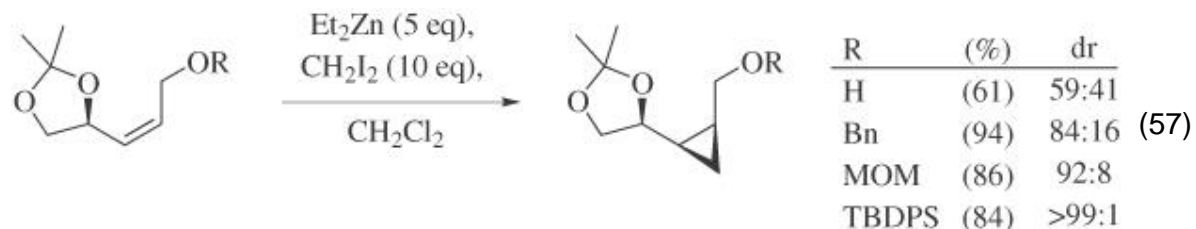
3.6.2. Allylic Ethers

The diastereoselective cyclopropanation of allylic ethers using Furukawa's reagent has been systematically investigated (Eq. 56). (136, 145a) Both the bulk of the substituents and the nature of the protecting group are key elements for obtaining high selectivities and for determining the sense of induction. Two trends have been identified. First, the sense of induction reverses from

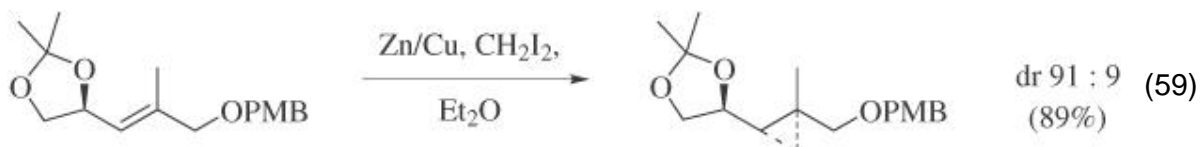


anti to *syn* as the steric bulk of the substituent on the carbinol side chain increases. This first trend, although not as important, is also seen with allylic alcohols. Secondly, increasing the steric bulk of the protecting group decreases the *syn* selectivity. These data clearly show that the involvement of simple A (1, 2)/ A (1, 3) strain arguments is not sufficient to explain the diastereoselection in these reactions, and that binding of the reagent to the ether oxygen must also be taken into consideration.

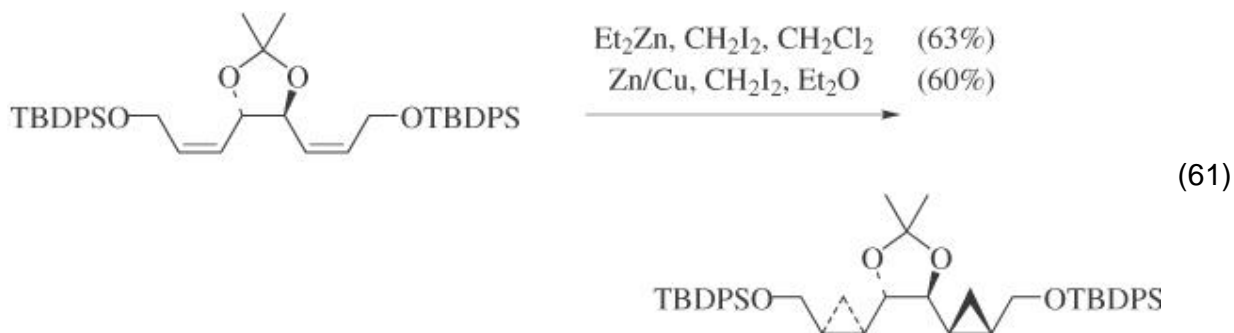
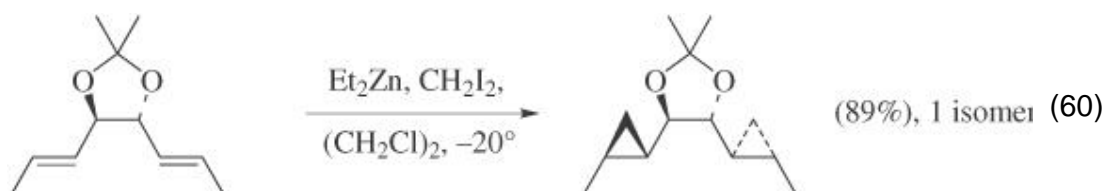
The diastereoselective cyclopropanation of (*E*)- and (*Z*)-allylic alcohols derived from 2,3-*O*-isopropylidenglyceraldehyde has been the subject of several investigations since the products are precursors to cyclopropyl carbocyclic nucleosides, which are potential chemotherapeutic agents (Eqs. 57–58). (146, 147) With both isomers, the use of a noncomplexing protecting group (TBDPS) is important for obtaining high yields and levels of stereocontrol.



A related transformation was used in the total synthesis of (+)-bicyclohumulenone. Cyclopropanation of the methallyl alcohol derivative proceeded with the opposite diastereofacial selectivity (Eq. 59). (148) The divergence of the stereochemical

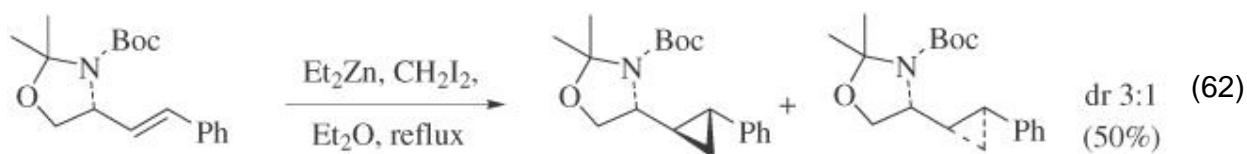


pathways may be a consequence of the difference in solvent (ether vs CH_2Cl_2), reagent (IZnCH_2I vs EtZnCH_2I), protecting group (PMB vs TBDPS), or the influence of additional A (1, 2) strain imparted by the additional methyl group. This reaction has been used quite extensively in approaches to produce bis(cyclopropane) derivatives in which the diol obtained after deprotection can be oxidatively cleaved (Eqs. 60–61). (149, 150)

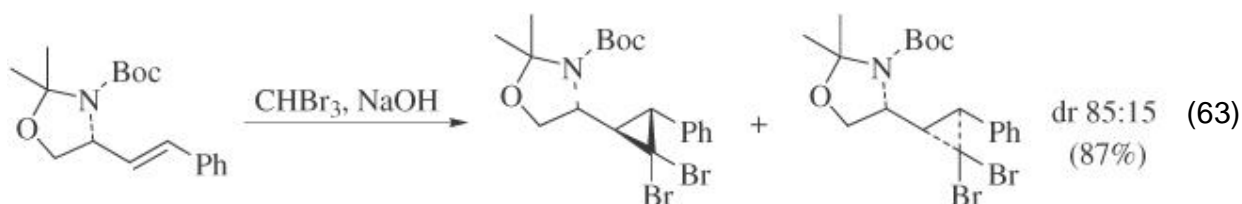


3.6.3. Allylic Amines

Cyclopropanation of a chiral protected allylic amine produces the *anti* isomer with low selectivity (Eq. 62). (151) The analogous dibromocyclopropanation of *tert*-butyl 2,2-dimethyl-4-(2-phenylvinyl)-3-oxazolidinecarboxylate

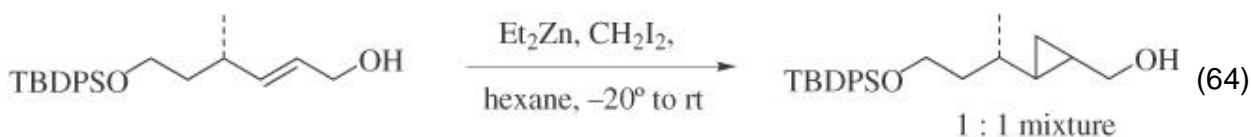


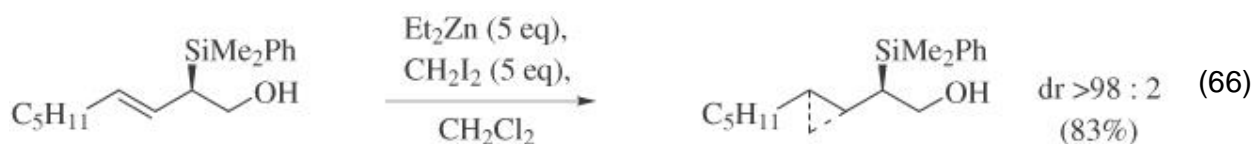
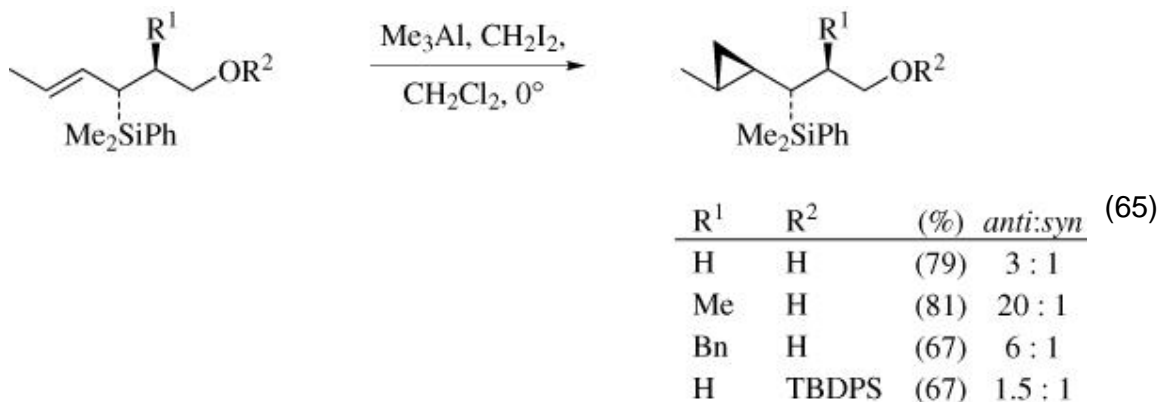
affords slightly better diastereomeric ratios of dibromocyclopropanes (Eq. 63). (151) In both cases, unassisted delivery of the carbenoid from the least hindered face of the olefin in its most stable ground state conformation can be invoked to predict the stereochemical outcome of the reaction.



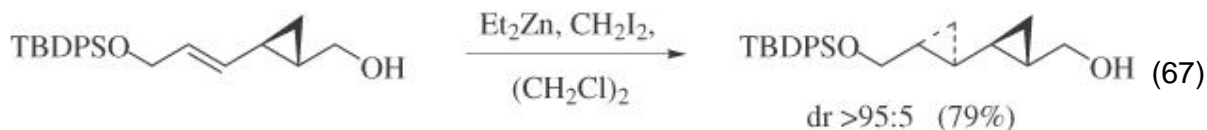
3.6.4. Acyclic Chiral Alkenes Without a Directing Group on the Stereogenic Center

The cyclopropanation reactions of chiral acyclic alkenes without a directing group on the stereogenic center at the allylic position rarely display a reasonable level of diastereoselection. However, in successful examples one of the allylic substituents is significantly larger than the others (such as a silyl group) (Eqs. 64–66). (152-154) The stereochemical outcome of these reactions is a consequence





of cyclopropanation on the conformer that minimizes A (1, 3) strain. The cyclopropanation of an *E*-vinylcyclopropane proceeds with high induction (Eq. 67). This may be due to the fact that there is a strong conformational preference minimizing A (1, 3) strain in the ground state. (155)



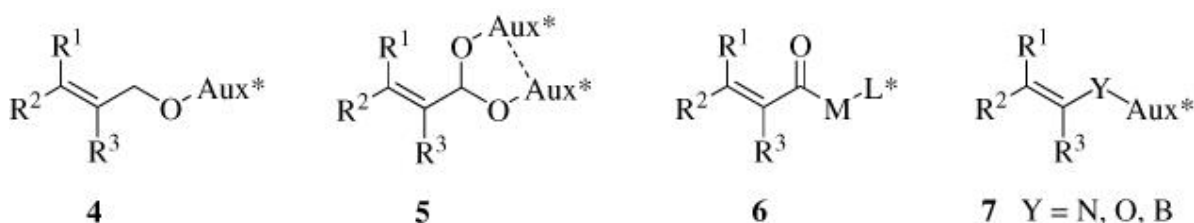
3.7. Cleavable Chiral Auxiliaries

A number of auxiliary-based approaches have been developed for the cyclopropanation of olefins, and many of them offer the advantage of producing enantiomerically pure cyclopropyl derivatives after cleavage of the auxiliary. The different chiral auxiliaries that have been developed for the reaction with various halomethylmetal reagents are encompassed into various general classes: chiral allylic ethers (4), acetals (5), α , β -unsaturated acylmetals (6), enamines, enol ethers and boronates (7).

3.7.1. Chiral Allylic Alcohols and Ethers

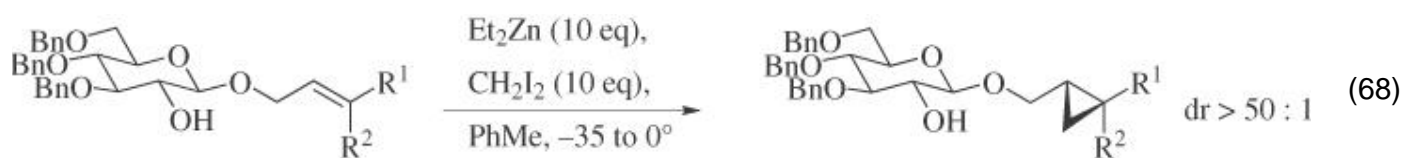
The chiral auxiliaries in each class are shown in Tables XI and XII. As discussed earlier, the β -hydroxysulfoximine moiety derived from enones can

act as a chiral auxiliary. Cyclopropanation occurs *syn* to the hydroxy group (Eq. 44). (131) Basic cleavage of the sulfoximine

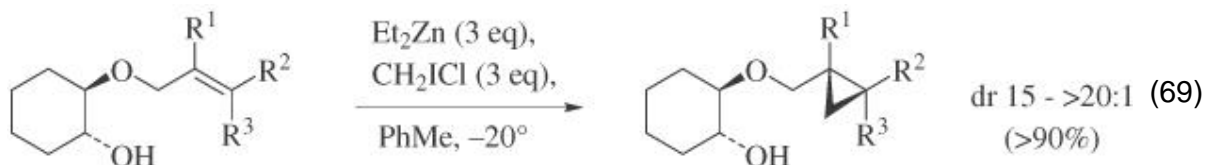


generates the enantiomerically pure cyclopropyl ketone. The drawback of this approach is that a mixture of separable diastereomers is produced by the nonstereoselective addition of enantiopure *N*-methylphenylsulfonimidoylmethyl lithium to the enone.

Alternatively, carbohydrate-derived chiral auxiliaries (156) have produced extremely high diastereoselectivities in the cyclopropanation of acyclic allylic double bonds (Eq. 68). It is believed that the glucosidic template acts as a bidentate



ligand to complex to the zinc reagent since the presence of a free hydroxy group (which will form the zinc alkoxide) is mandatory for high diastereoselection. (157, 158) This postulate has given rise to the more simple auxiliary derived from cyclohexanediol (Eq. 69). (159) Cleavage of the chiral auxiliary is then accomplished

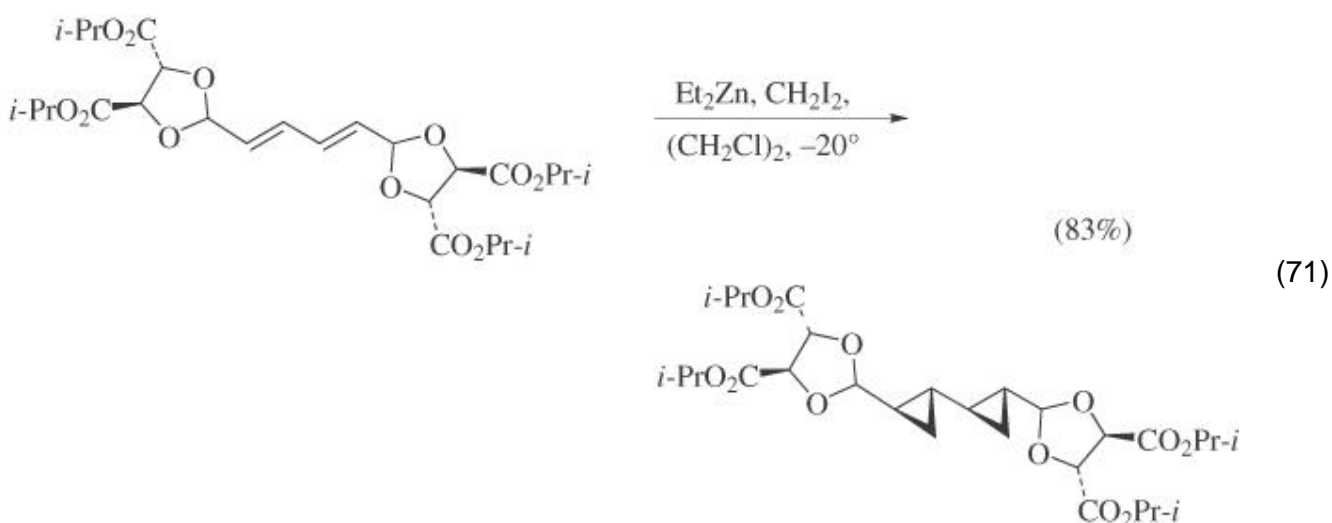
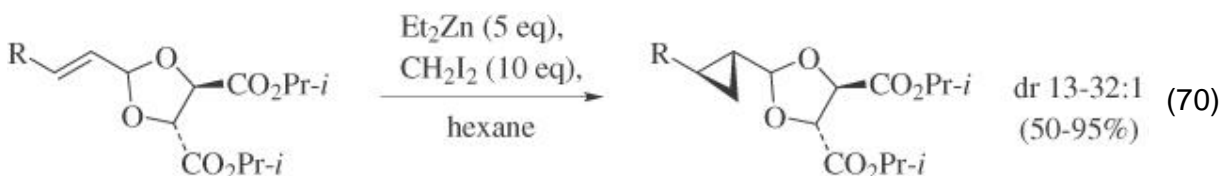


by a ring contraction reaction (glucose-derived auxiliary) (159a) or by a three-step sequence involving conversion of the alcohol into an iodide and reductive elimination of the cyclopropylmethanol moiety upon treatment with BuLi. (159) The diastereoselectivities obtained with the tri-*O*-benzylglucopyranoside are high for most substituted allylic alcohols, but sometimes a large excess of the zinc reagent is required.

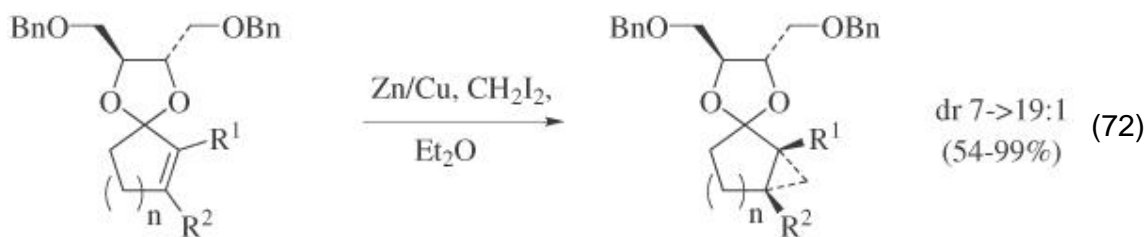
3.7.2. Chiral Acetals

A number of C₂-symmetric acetals have been developed for this reaction. The most efficient auxiliaries are based on tartaric acid or threitol derivatives.

Diisopropyl tartrate is particularly effective with *E* disubstituted and trisubstituted acyclic substrates (Eq. 70). (160, 161) This auxiliary has been applied to the synthesis of bis(cyclopropane) derivatives. The diastereoselective cyclopropanation of the diene produces the desired compound with an excellent level of stereocontrol (Eq. 71). (162)

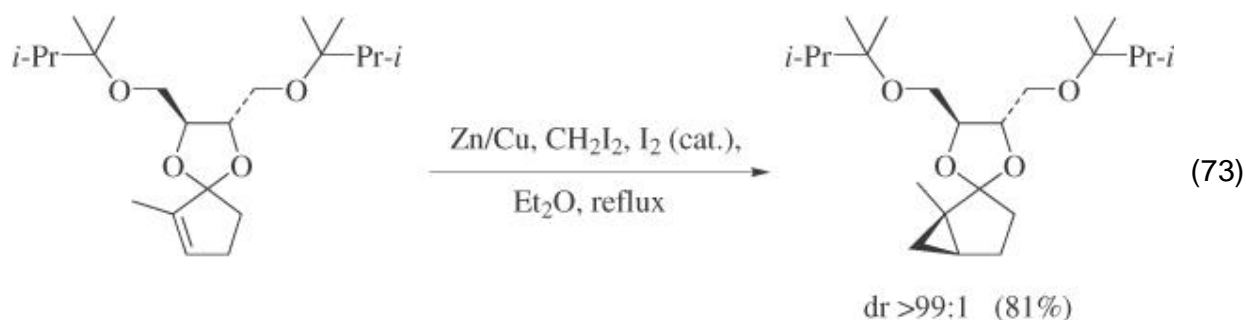


On the other hand, di-*O*-benzylthreitol undergoes efficient and diastereoselective cyclopropanation with cyclic substrates (Eq. 72). (163, 164) This auxiliary can be used effectively on 5- to 16-membered cyclic enones. (165) Both auxiliaries are readily

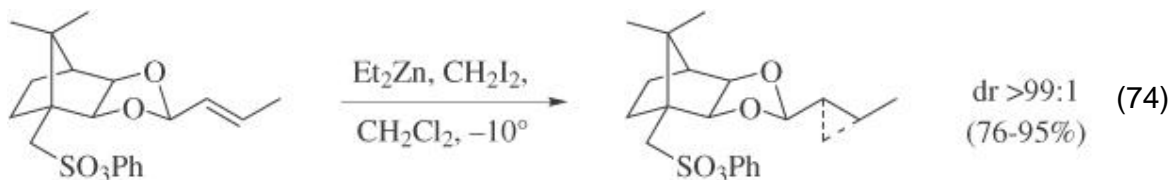


cleaved under acidic conditions to produce the corresponding cyclopropyl ketone or aldehyde. In the case of cyclic enones, studies support a mechanistic model that involves preferential coordination of the reagent to the least sterically hindered dioxolane oxygen lone pair proximal to the alkene. The auxiliary derived from dihydrobenzoin is even superior to the tartrate-derived counterpart with cyclic enones (166) but attempts to use it with acyclic systems do not produce high ratios. (167) The sense of induction is consistent with the fact that bidentate chelation by the chiral auxiliary is not favored in this case since the reaction is done in a complexing solvent (ether). Quite interestingly, the sense of induction in the dioxolane acyclic system is opposite to that found in the cyclic system. This can be accounted for by assuming that the chiral auxiliary acts as a bidentate ligand under the conditions used [$\text{Zn}(\text{CH}_2\text{I}_2)_2$, hexane]. Replacement of the benzyl ethers of the threitol auxiliary by bulkier groups that further preclude any undesirable complexation of the reagent by the ether oxygens leads to better enantioselectivities, but this method is not as practical (Eq. 73). (168)

Other chiral auxiliaries in this class include derivatives of from 1-aryl-2,2-dimethyl-1,3-propanediols (169) and D-fructose, (170) but their installation leads to

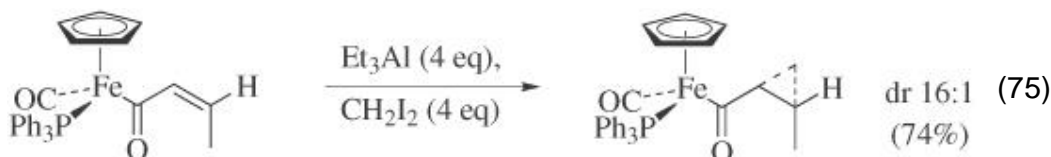


diastereomers that need to be separated, and the selectivities observed are lower than those presented above. Recently, another promising template was disclosed. Indeed, cyclopropanation of the acetal derived from phenyl 2,3-dihydroxybornane-10-sulfonate occurs with outstanding diastereocontrol (Eq. 74). (171)



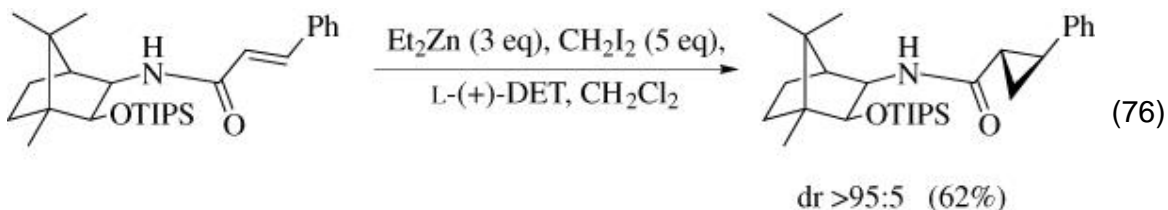
3.7.3. α , β -Unsaturated Acylmetals

The use of chiral α , β -unsaturated esters, amides, or other derivatives is not very common since the electrophilic nature of these reagents often inhibits the cyclopropanation reaction. The asymmetric synthesis of *Z*, *E* disubstituted and trisubstituted cyclopropanecarboxylic acid derivatives was achieved by a stereoselective electrophilic methylene transfer to α , β -unsaturated acyl ligands bound to an iron chiral auxiliary (Eq. 75). (172) It was



proposed that the double bond adopts a conformation approximately orthogonal to the acyl group, thus increasing its nucleophilicity. The aluminum-derived reagent is superior with this auxiliary.

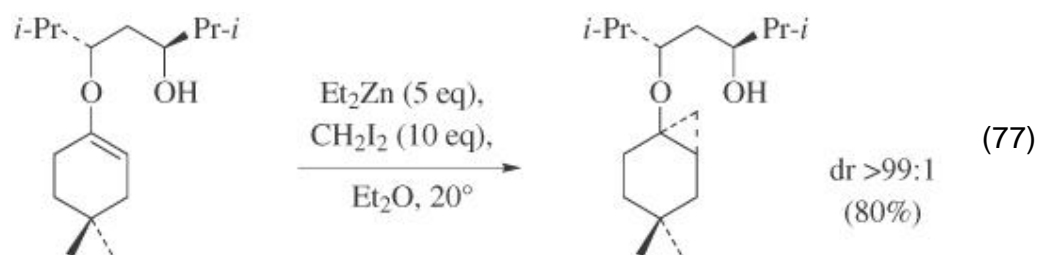
The *exo*- and *endo*-3-amino-2-hydroxybornane auxiliaries are also effective, but only when the hydroxy group is protected as a triisopropylsilyl ether (Eq. 76). (173) Furthermore, the addition of L-(+)-diethyl tartrate is necessary to increase the yield of the cyclopropane product. Unfortunately, only one example (cinnamic acid) is reported.



3.7.4. Chiral Enol Ethers, Vinylboronates, and Enamines

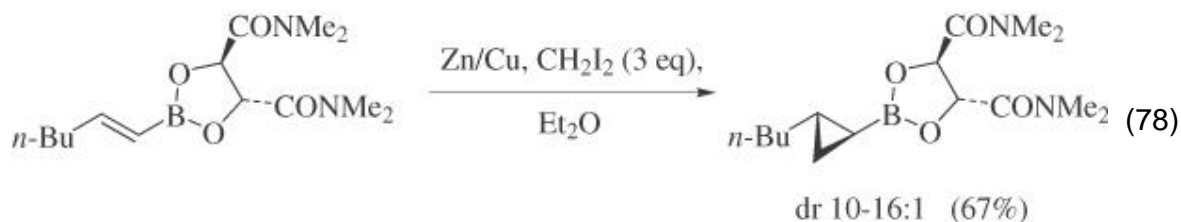
Enantiomerically enriched cyclopropyl alcohols and amines can also be prepared with the help of several chiral auxiliaries. The nucleophilic enol ethers

derived from ketones react smoothly with bis(iodomethyl)zinc to produce cyclopropyl ethers with outstanding diastereoselectivities (Eq. 77). (174) The auxiliary is introduced by treating the

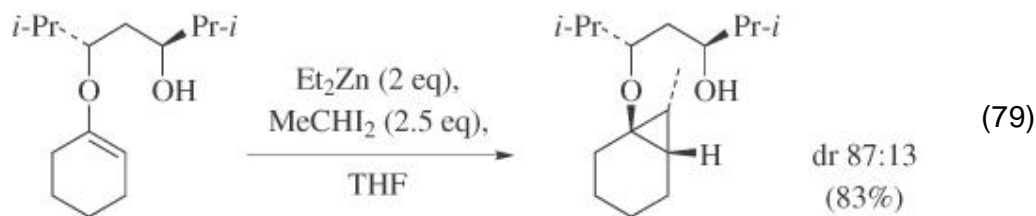


corresponding acetal with triisobutylaluminum. The destructive cleavage of the auxiliary produces cyclopropanol derivatives (1. PCC; 2. K_2CO_3). (175, 176) This reaction has been extended to both cyclic and acyclic ketones but is limited to symmetrical ketones or those that can be regioselectively enolized. (177)

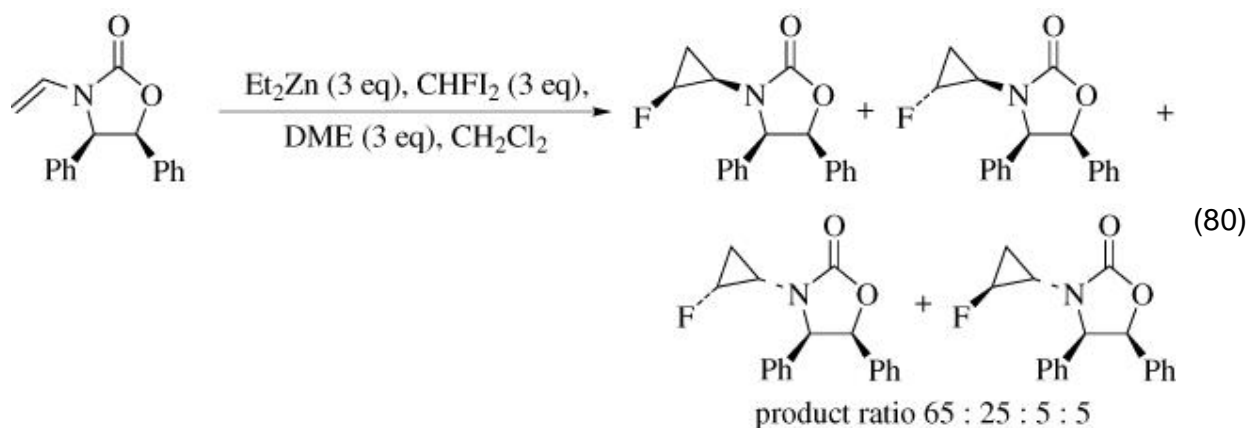
1-Alkenylboronic esters bearing the tetramethyltartramide group undergo highly diastereoselective cyclopropanation to produce 2-substituted cyclopropanols after oxidation (H_2O_2 , $KHCO_3$) (Eq. 78). (178) The reaction product can also be used for in situ Suzuki coupling to produce enantiomerically enriched disubstituted cyclopropanes. (179)



Very little work has been reported on the use of more complex diiodoalkanes as precursors for more substituted haloalkylzinc reagents. In the approach shown, the chiral auxiliary is relatively effective for producing one major diastereomer in the ethylidenation reaction (Eq. 79). (180) Conversely, the diastereoselective cyclopropanation



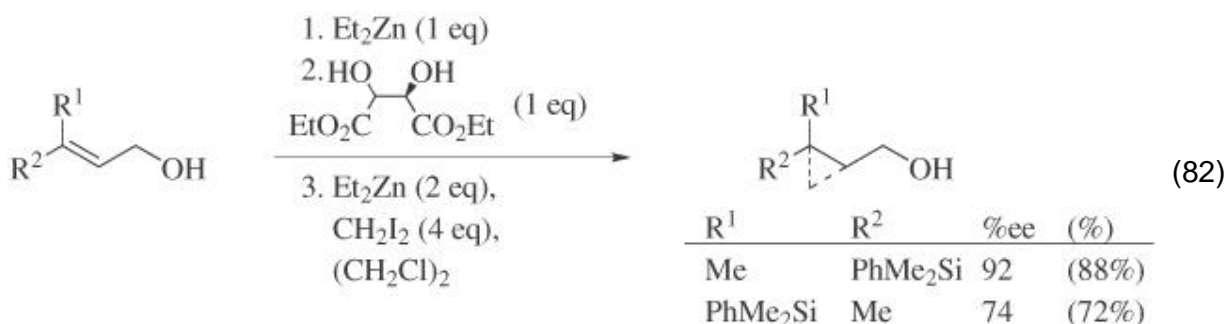
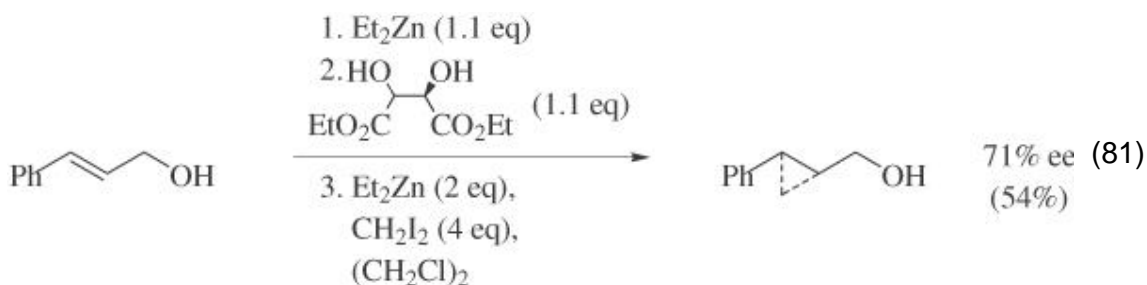
of a chiral 3-vinyl-2-oxazolidinone with a zinc monofluorocarbenoid produces the corresponding 2-fluorocyclopropylamine with modest selectivity (Eq. 80). (181)



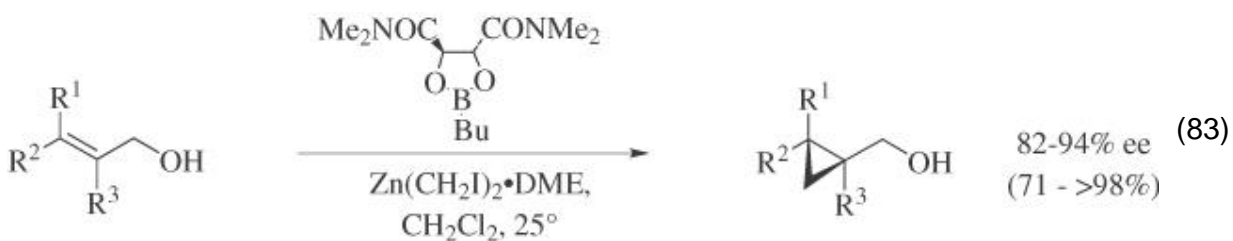
3.8. Stoichiometric Quantities of Chiral Additives

The first attempts to control absolute configuration in the cyclopropanation of substrates by adding external chiral ligands were reported in 1968. It was found that very low yields (15%) and enantiomeric excesses (3.4%) were obtained if a mixture of (–)-menthol and IZnCH_2I was added to α , β -unsaturated esters. (54, 121) Later, very low enantioselectivities were observed when L-leucine was employed as an additive in the cyclopropanation of vinyl ethers. (67) Modest enantioselectivities are observed in the enantioselective cyclopropanation of cinnamyl alcohol using a (1*R*,2*S*)-*N*-methylephedrine-modified halomethylzinc reagent. (182)

The first report on enantioselective cyclopropanation of allylic alcohols that described moderate levels of enantioselection (70-81% ee) involved the addition of a stoichiometric amount of diethyl tartrate to a mixture of the allylic alcohol, diethylzinc, and diiodomethane (Eq. 81). (183) Slightly higher selectivities were obtained in the cyclopropanation of silicon-substituted allylic alcohols (Eq. 82). (184)



One of the most effective additives currently available is a dioxaborolane (Eq. 83). This agent is readily prepared from the commercially available

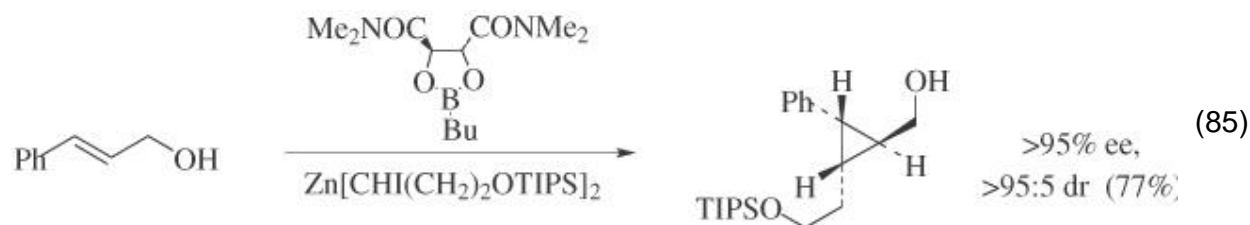
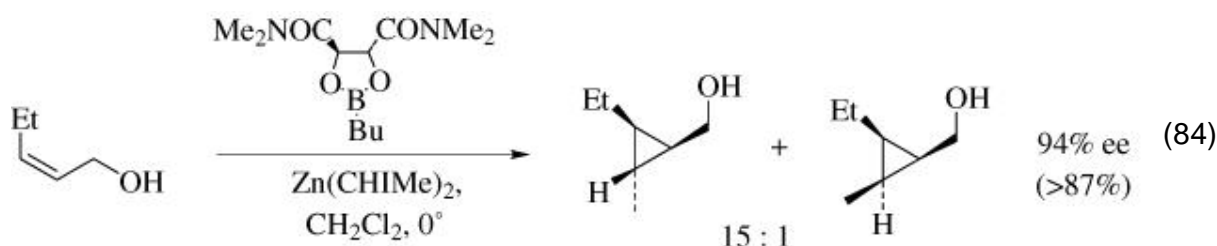


N,N,N',N'-tetramethyltartaric acid diamide and butylboronic acid and is an efficient chiral controller for the cyclopropanation reaction (Eq. 83). (185-187)

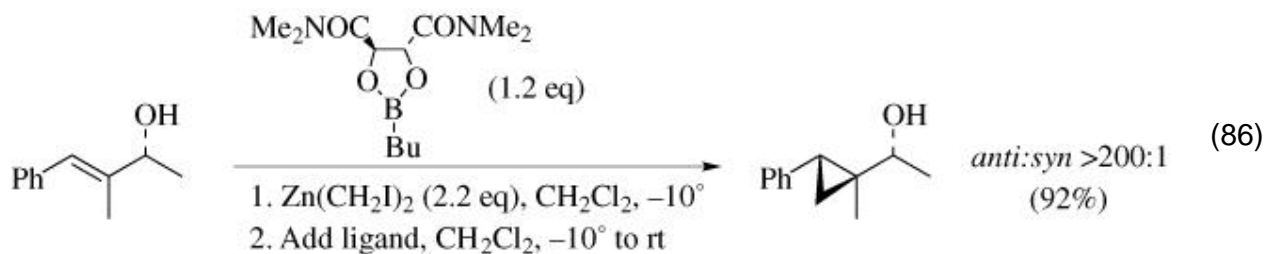
The corresponding substituted cyclopropylmethanols of a variety of allylic alcohols are produced with excellent enantioselectivities (90–93% ee) when a mixture of the alcohol and the dioxaborolane ligand is added to the preformed halomethylzinc reagent. This method has since been extended to the enantioselective cyclopropanation of 3-tributylstannyl-2-propen-1-ol, (188) 3-iodo-2-propen-1-ol and polyenes. (189)

The enantioselective cyclopropanation reaction using the dioxaborolane-derived ligand is quite general and practical. (190) Accordingly, it has been used to elaborate the chiral cyclopropane subunits of Curacin A, (191) and bidirectional strategies have been employed for the synthesis of the structurally fascinating FR-900848 (192) and U-106305 (examples found in Table XIII). (193–194)

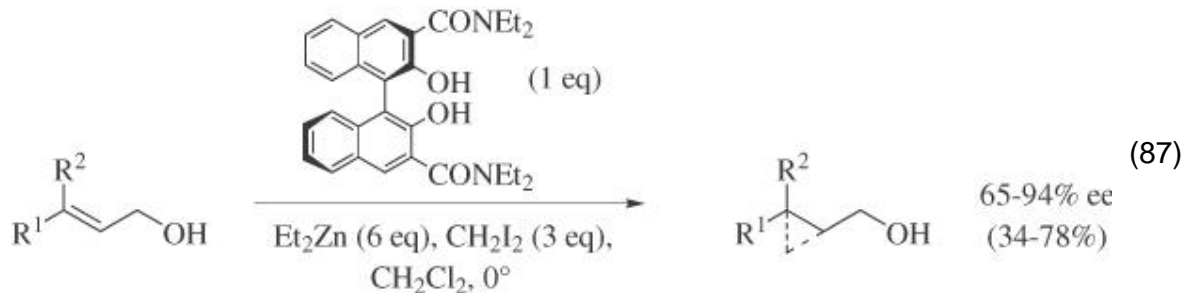
The chiral dioxaborolane can also be used to generate functionalized 1,2,3-substituted cyclopropanes by using appropriately functionalized 1,1-diodoalkanes as precursors (Eqs. 84-85). (69) However, this methodology is limited since there are very few methods for generating this class of dihaloalkanes. (193, 194)



Recently, the chiral dioxaborolane was applied to the cyclopropanation of chiral nonracemic (*E*)-allylic alcohols to provide a new access to *anti*-cyclopropylmethanol derivatives (Eq. 86). (197) This new approach is complementary to the directed cyclopropanation using EtZnCH₂I, which affords predominantly the *syn* product (for example, see Eq. 52).



Finally, *N,N,N',N'*-tetraethyl-1,1'-bi-2-naphthol-3,3 ϕ -dicarboxamide, a ligand prepared in 4 steps from binaphthol, can be used for the enantioselective cyclopropanation of allylic alcohols (Eq. 87). (198, 199) The scope of the reaction seems

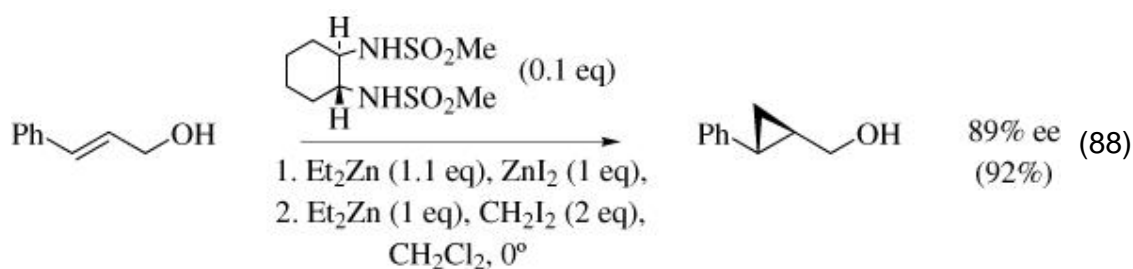


somewhat limited since only (*E*)-substituted allylic alcohols can be converted into the corresponding cyclopropanes with reasonably good yields and enantioselectivities. Furthermore, a significantly large excess of diethylzinc is also required (ee and yield drop dramatically if less than 6 equivalents of diethylzinc are used).

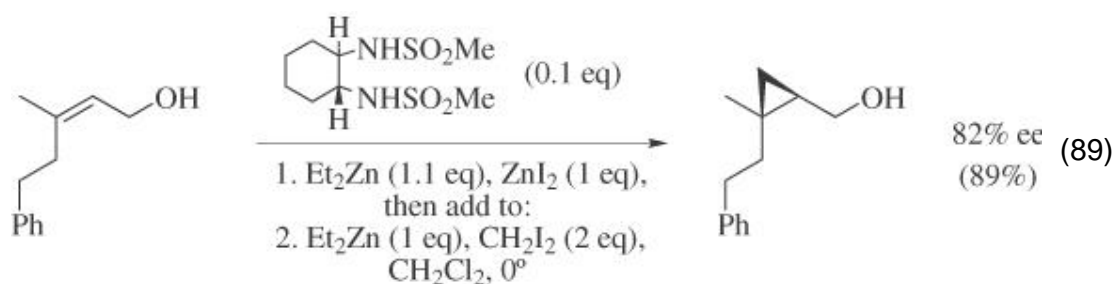
3.9. Chiral Catalysts

The notion that Lewis acids can accelerate the cyclopropanation of olefins using haloalkylmetal reagents has been contemplated for several decades. (56) Unfortunately, the electrophilic nature of the reagents precludes the use of highly basic chiral ligands that could coordinate to the metal center in a reversible fashion to produce significant rate accelerations to overcome the uncatalyzed, racemic pathway. Although the mechanism for rate acceleration by the addition of chiral catalysts is not well understood, two notable and quite effective substoichiometric systems are available for the cyclopropanation of allylic alcohols.

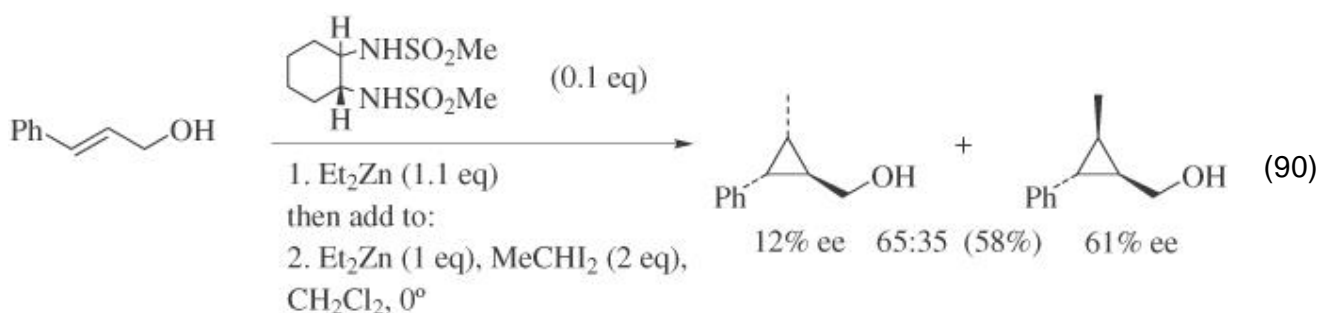
The Simmons-Smith cyclopropanation reaction is significantly accelerated by the addition of 0.1 equivalent of a C_2 -symmetric chiral disulfonamide ligand (Eq. 88). (200, 201)



Numerous disulfonamides have been tested (202) and the bis(methanesulfonamide) of *trans*-cyclohexanediamine gives consistently high enantioselectivities with *cis*- and *trans*-allylic alcohols and some trisubstituted allylic alcohols (Eq. 89, Table XIV).



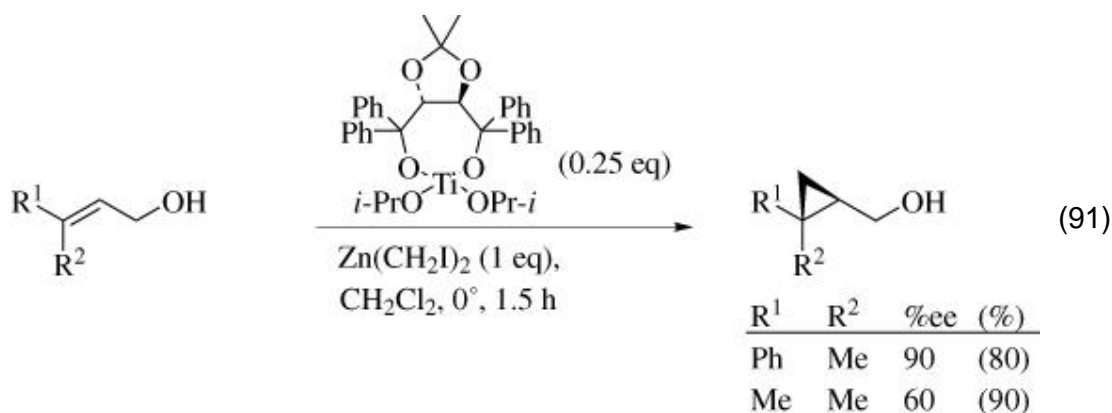
The enantioselective cyclopropanation of tetrasubstituted olefins was attempted but lower ees are generally observed. In addition, reactions involving more substituted reagents need further development (Eq. 90). (202a) This method has



also been extended to the enantioselective cyclopropanation of vinylsilanes and -stannanes. (203) Slightly lower enantioselectivities are obtained if the zinc salt is replaced by an aluminum salt; (204) the titanium analog is ineffective.

The rate and selectivity of the catalytic enantioselective cyclopropanation of cinnamyl alcohol utilizing bis(iodomethyl)zinc and the bis(sulfonamide) catalyst are greatly dependent on the order of addition of the reagents. (20, 205) The independent preformation of the ethylzinc alkoxide and bis(iodomethyl)zinc is crucial. The reaction displays autocatalytic behavior, which is shown to be due to the generation of zinc iodide. In addition, an in-depth solution study of a chiral zinc-sulfonamide complex relevant to the enantioselective cyclopropanation has been reported as well as an X-ray crystal structure of a catalytically active species. (206)

An alternative method for the Lewis acid-catalyzed cyclopropanation reaction of allylic alcohols, in which the uncatalyzed process is minimized, has been reported. (31) The addition of $\text{Zn}(\text{CH}_2\text{I})_2$ (1 equivalent) to an allylic alcohol (1 equivalent) produces the iodomethylzinc alkoxide. Methylene transfer from these less reactive species is triggered by the addition of a Lewis acid in catalytic amounts. Several achiral Lewis acids are effective in inducing the cyclopropanation. Conversely, the use of a chiral Lewis acid [derived from TADDOL (207) and $\text{Ti}(\text{OPr-}i)_4$] produces the corresponding cyclopropane derived from aryl-substituted allylic alcohols in up to 90% ee. (31) Although this system is effective with aryl-substituted allylic alcohols, the cyclopropanation of alkyl-substituted allylic alcohols still needs to be improved. The disulfonamide system is superior with some of these allylic alcohols (Eq. 91). (31)

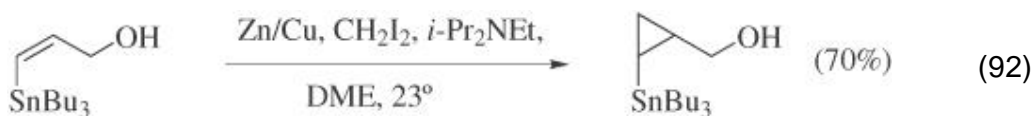


It is apparent that significant progress has been made toward the development of an efficient catalytic, asymmetric cyclopropanation using zinc-derived reagents, but there is still room for improvement. More specifically, the design of better catalysts to increase the scope of the reaction and to improve the enantioselectivities are among the top priorities in this area of research.

Furthermore, simplification of the reaction protocol would contribute greatly to making this approach an attractive alternative for synthetic chemists seeking asymmetric catalytic cyclopropanation methods.

3.10. Functional Group Compatibility and Side Reactions

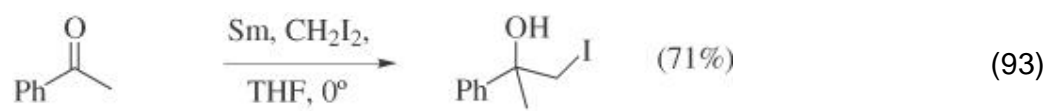
One of the principal assets of the haloalkylzinc-mediated cyclopropanation of alkenes is its compatibility with a wide range of functional groups. Tables I-XVI indicate that a large number of functional groups are compatible with these reagents (alkynes, silanes, stannanes, germanes, alcohols, ethers, sulfonate esters, aldehydes, ketones, carboxylic acids and derivatives, carbonates, carbamates, imidates, oxime ethers, boronates, phosphonates, sulfones, sulfonates, sulfonylimines, and sulfoximines). In addition, in certain cases experimental conditions can be modified to minimize byproduct formation. Among the possible side reactions of the zinc carbenoids, the reduction or protonolysis of vinylic stannane groups or C-halogen (when Zn metal is used) is most often observed. This side reaction with tin can be minimized by adding diisopropylethylamine (Eq. 92). (208)



Sometimes problems can occur with acid-sensitive substrates since ZnI_2 is formed as a byproduct. To minimize these side reactions, it is usually better to use the $\text{Et}_2\text{Zn} / \text{CH}_2\text{I}_2$ combination with excess Et_2Zn to scavenge ZnI_2 since these species will equilibrate to form the less acidic EtZnI . Alternatively, to avoid side reactions with acid-sensitive substrates, it is sometimes important to quench the reaction with pyridine to scavenge ZnI_2 and excess reagent. (39)

The methylation of heteroatoms and ylide formation are two of the most important side reactions of these zinc reagents, both deriving from their electrophilic nature. When a large excess of reagent is used for long reaction times, methylation of alcohols is almost always observed, (209) especially with bis(chloromethyl)zinc. In some cases, amines, thioethers and phosphines react readily with zinc reagents to generate ammonium salts, (210) and sulfonium (211) and phosphonium ylides. (212) Terminal alkynes generally lead to a large number of byproducts. (213)

The functional group compatibility of the analogous aluminum and samarium reagents is not well documented, but it is expected to be similar to that of the zinc reagents. However, it is known that samarium carbenoids can undergo 1,2-addition or dimerization (Eq. 93). (87, 110)

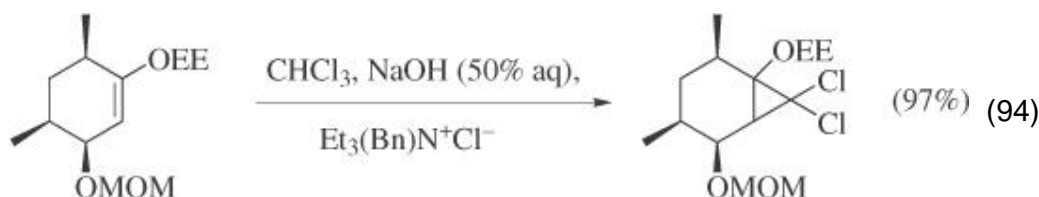


4. Comparison with Other Methods

The fascination of organic chemists for the smallest and highly strained cycloalkanes has resulted in the development of numerous methodologies for their synthesis. (214) Most of the early efforts provided access to cyclopropane derivatives in racemic forms, whereas recent synthetic strategies have focused on their enantioselective synthesis. (215-221) The most important enantioselective cyclopropanation methods are briefly described below and their scope is compared with that of the Simmons-Smith cyclopropanation.

4.1. Dihalocarbenes

Dihalocarbenes are the electrophilic reagents of choice for reaction with electron-rich alkenes to generate dihalocyclopropanes (Eq. 94). (222) These reagents are most conveniently prepared by basic treatment of a trihalomethane, by BuLi



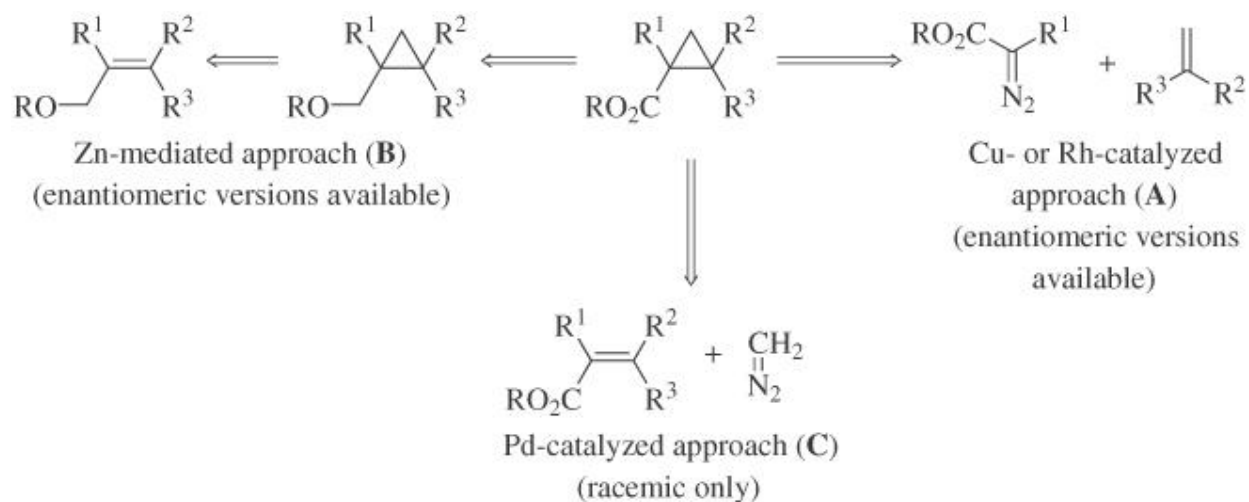
treatment of a tetrahalomethane, or by thermal decomposition of trihaloacetate derivatives. (223) In contrast, the analogous trihalomethylzinc reagents are much more difficult to prepare since the insertion of zinc into a tetrahalomethane (or the alkyl group exchange with Et_2Zn) is not a facile process. Furthermore, the trihalomethylzinc reagents usually produce very low yields of the corresponding cyclopropanes (see Table XV for specific examples). The dihalocarbenes have been used in some diastereoselective processes, and they have supplanted the related trihalomethylzinc reagents. In some examples, the diastereoselectivities observed with these reagents have been comparable to those observed with the zinc reagents (see for example Eq. 63), but they have not been widely used to generate enantiomerically enriched derivatives.

4.2. Transition-Metal-Catalyzed Diazoalkane Decomposition

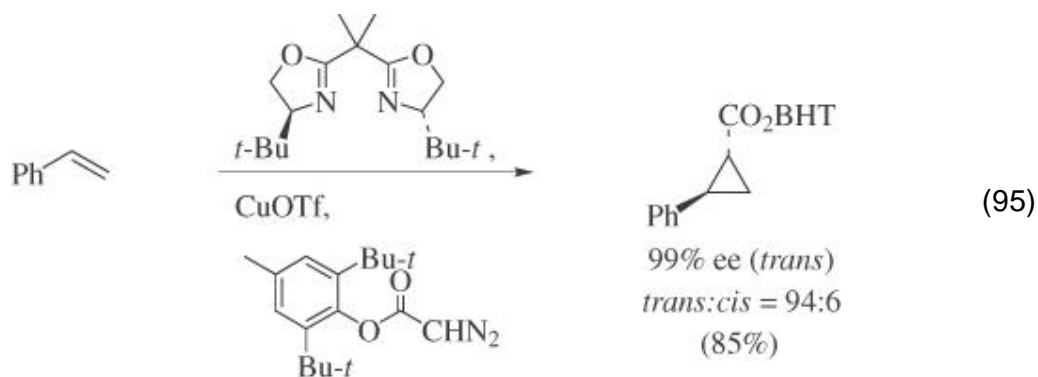
The cyclopropanation of alkenes using the transition metal-catalyzed decomposition of α -diazocarbonyl compounds, vinyl or aryldiazoesters is one of the best methods available for accessing specific classes of enantiomerically enriched cyclopropane derivatives (Figure 1, $\text{R}^1 = \text{H}, \text{PhCH} = \text{CH}, \text{Ar}$). (224–225a) Conceptually, the stereoselective carbon-carbon bond construction involved in these reactions is quite different and complementary

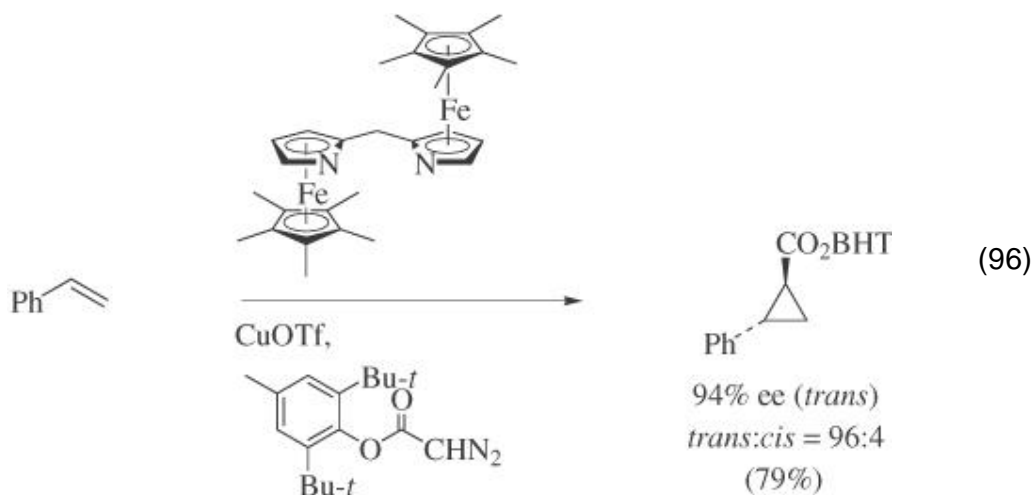
to that involving the Simmons-Smith reagents (Figure 1, path A vs B, vide infra).

Fig. 1.



Copper catalysts are among the most effective for the intermolecular cyclopropanation reactions involving unsubstituted diazoester derivatives (Fig. 1, $R^1 = H$) (Eqs. 95–96). (226-228) Conversely, chiral rhodium complexes are superior

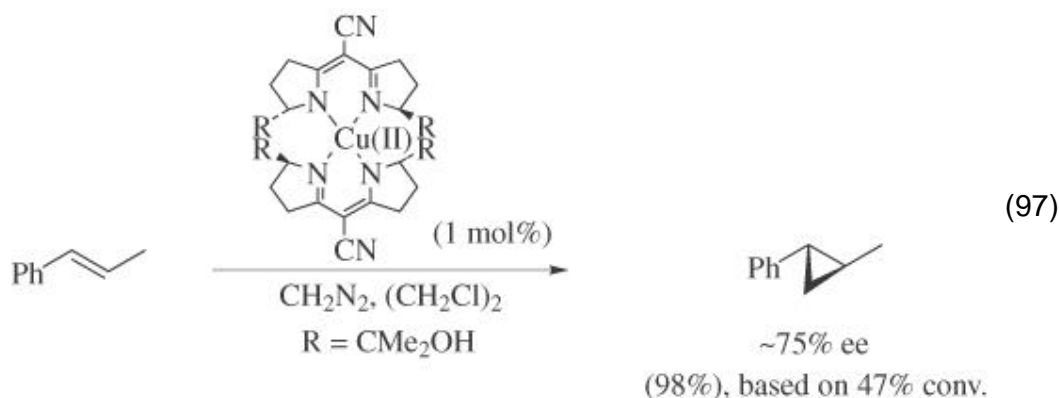




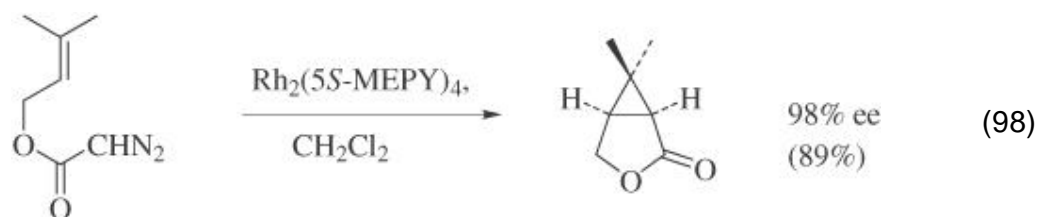
catalysts with substituted diazoesters (Fig. 1, $R^1 = \text{PhCH} = \text{CH}$ or Ar), but these carbenoids react only with mono- or 1,1-disubstituted olefins. (229) The intermolecular version of the reaction is quite practical with a certain number of terminal, monosubstituted alkenes and with other simple and readily available alkenes. The chemoselective cyclopropanation of dienes is usually more effective using the copper-catalyzed process since monosubstituted alkenes react much faster than more substituted ones. (230)

The main advantage of this reaction when compared to the Simmons-Smith reaction is that it involves a truly catalytic process (1 mol%). The main drawback of the intermolecular transition metal-catalyzed diazoester decomposition reaction is that it is usually limited to simple alkenes, since an excess (5–10 equivalents) of the olefin is often mandatory to obtain high yields. For this reason, the yields are usually reported relative to the starting diazoester reagent. Moreover, its scope is limited by the possibility of generating diastereomers in addition to enantiomers with substituted alkenes. Efficient access to simple *cis*-disubstituted cyclopropanes is not possible in the intermolecular version of this reaction, and the Simmons-Smith reaction is much superior for generating the *cis*-disubstituted cyclopropanes. For example, chiral rhodium complexes give at best ~2:1 *cis-trans* ratio, and the enantioselection is generally low (<80%), except for some examples also using a chiral diazoester. (231-233)

In addition, little success has been achieved with diazomethane as the carbenoid precursor (Figure 1, path C, *vide supra*). (234) The racemic process proceeds well with palladium acetate as the catalyst as long as an electron-deficient olefin is used. However, enantiocontrol is possible only in one system (235, 236) so far involving a copper catalyst (Eq. 97). (237) The Simmons-Smith processes are by far superior for generating stereodefined 1,2-disubstituted cyclopropanes.



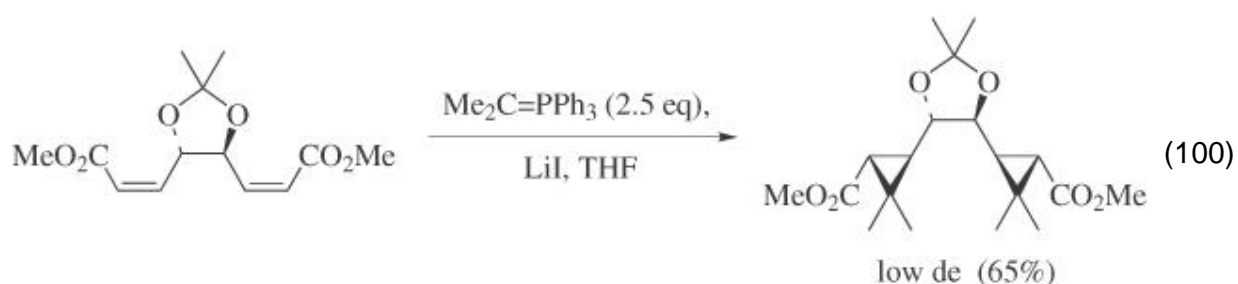
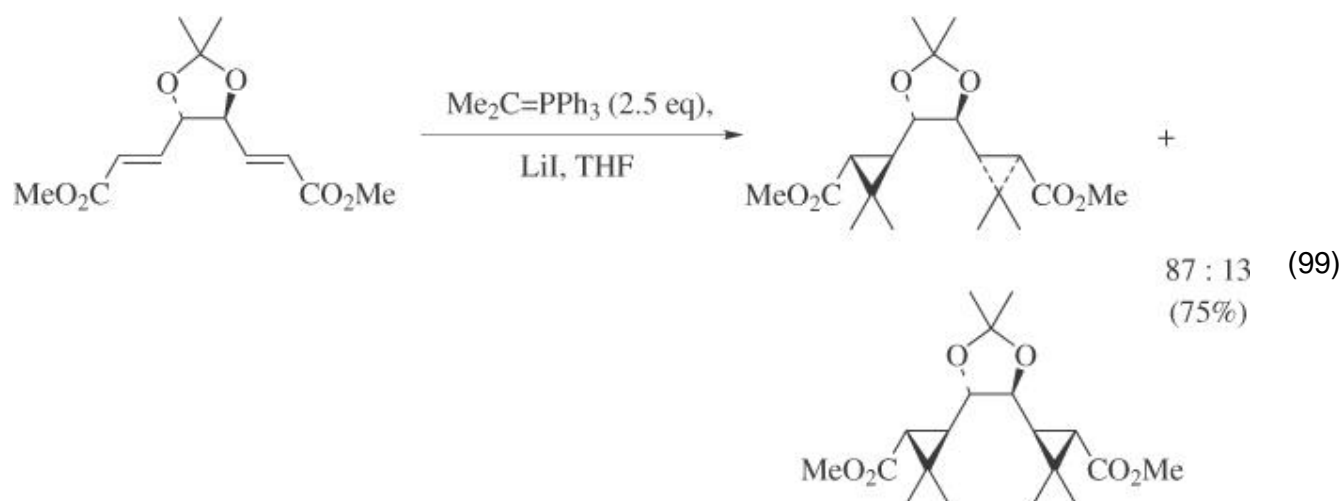
On the other hand, the intramolecular version of the reaction between diazocarbonyl derivatives and alkenes using chiral dirhodium(II) carboxylate catalysts provides a powerful access to functionalized *cis*-substituted cyclopropanes in good yields, with excellent enantio- and diastereoselectivities (Eq. 98). (238, 239) However, the need for a tethered reagent puts an inherent limitation on the structural features of the compounds that can be prepared with this reaction. The parent asymmetric intramolecular Simmons-Smith process has not been reported to



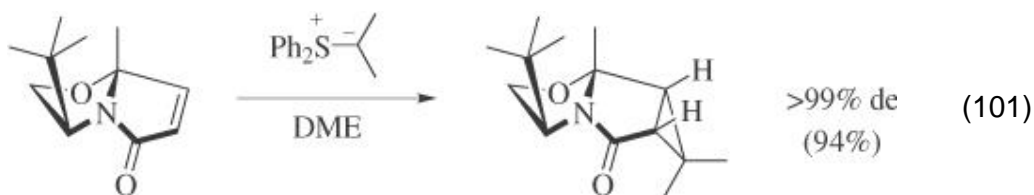
date and therefore this approach is one of the best available for generating enantioenriched 1,2,3-trisubstituted cyclopropanes.

4.3. Michael-Initiated Ring Closure

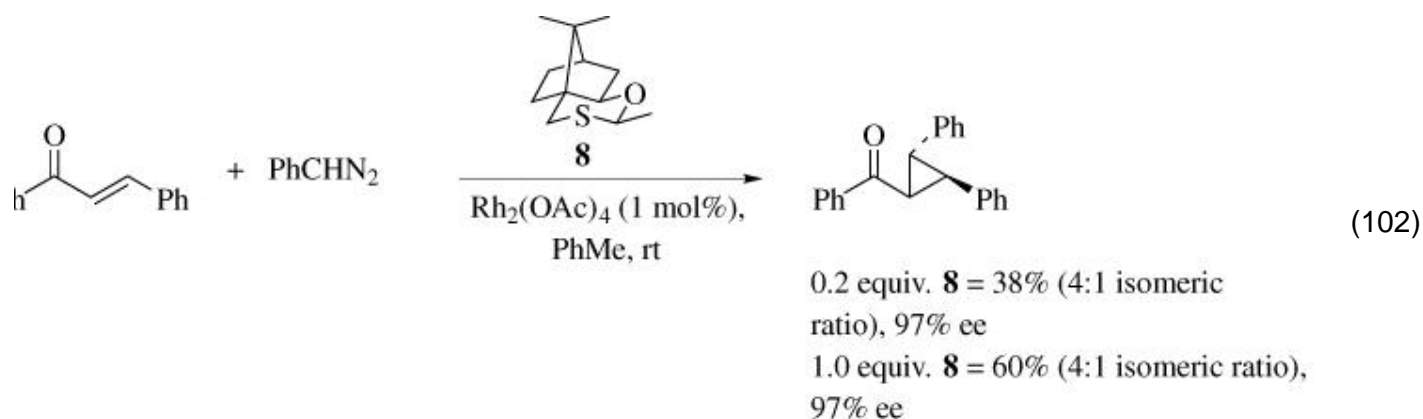
Cyclopropanations that involve conjugate addition to an electrophilic alkene to produce an enolate that subsequently undergoes an intramolecular ring closure are defined as Michael-Initiated Ring Closure (MIRC) reactions. Although there are exceptions, cyclopropanations via the MIRC reaction of acyclic olefins are usually nonstereospecific, and both (*E*)- and (*Z*)-olefins give the *trans*-cyclopropanes (Eqs. 99–100). (240, 241) For the synthesis of 1,2-disubstituted cyclopropanes, the MIRC process is not as powerful as the Simmons-Smith



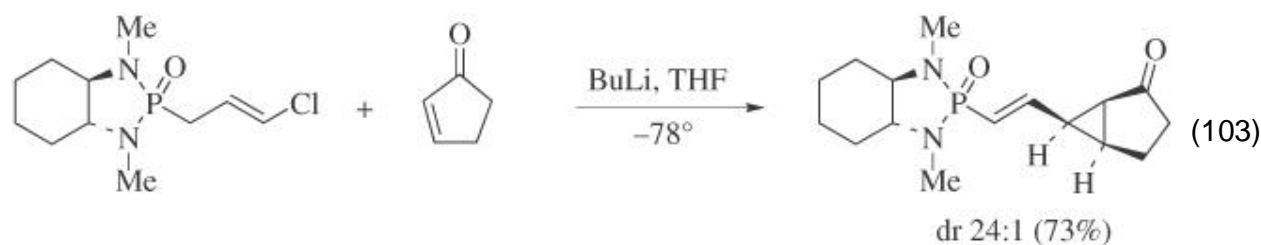
reaction. However, this reaction does provide access to stereodefined 1,2,3-trisubstituted cyclopropanes, which are otherwise difficult or impossible to synthesize using either the Simmons-Smith reaction or the transition metal-catalyzed decomposition of diazoesters. Cyclopropanations using the MIRC reaction on cyclic systems can be stereospecific, and one notable example is shown in Eq. 101. (242) Enantioselective versions involving catalytic amounts of sulfur ylides



are available but the reaction is limited to aryl-substituted cyclopropanes (Eq. 102). (243, 244)



Another powerful, auxiliary-based approach to 1,2,3-trisubstituted cyclopropanes involves the highly stereocontrolled conjugate 1,4-addition of the anion derived from a *trans*-chloroallylphosphonamide to conjugated compounds (Eq. 103). (245, 246) Subsequent intramolecular attack of the enolate upon the intermediate



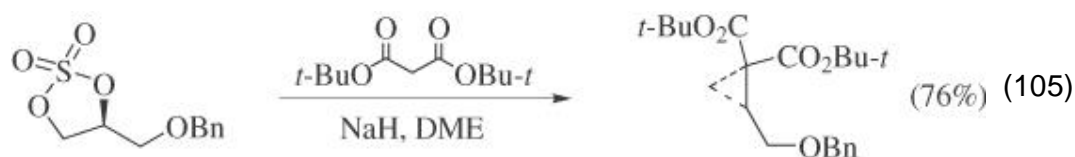
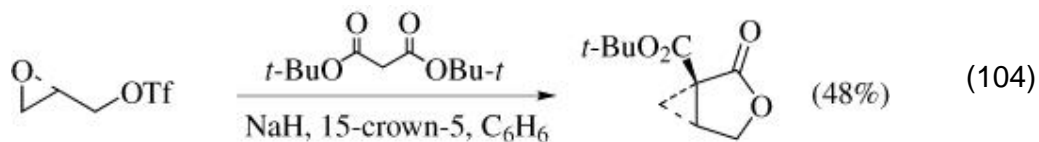
allylic chloride provides the corresponding *endo,endo*-cyclopropanes with both excellent yield and diastereoselectivity. Alternatively, *cis*-chloroallyl-phosphonamide reagents under the same conditions give the *exo,endo*-product.

In conclusion, one of the most appealing aspects of the MIRC reactions compared to those of the Simmons-Smith reaction and of diazocarbonyl cyclopropanations is that it provides access to 1,2,3-trisubstituted cyclopropanes bearing substituents with a unique configuration, and is often complementary to the other cyclopropanation methods. For the synthesis of 1,2-disubstituted cyclopropanes, the Simmons-Smith reaction is in most cases a more effective method.

4.4. Intramolecular Cyclization

The enantioselective synthesis of cyclopropane rings by intramolecular cyclization has gained much popularity since methods for the preparation of

the enantioenriched precursors have become available. Two notable examples are the generation of cyclopropanes from epoxy alcohols prepared by asymmetric epoxidation (247) (Eq. 104) (248) and their formation from diols obtained by asymmetric dihydroxylation (249) (Eq. 105). (250) These methods are appealing since they use two



efficient catalytic asymmetric processes. However, the cyclopropane product is necessarily substituted with two geminal electron-withdrawing substituents. This class of compounds cannot be directly synthesized by the Simmons-Smith reaction, and a multistep sequence is necessary to elaborate them. Since the bond construction in these two processes is quite different from that involving the Simmons-Smith reaction, both methods may be complementary depending upon the availability of the precursors.

5. Experimental Conditions

Commercial zinc dust devoid of lead impurities is suitable for reagent preparation in trials involving the Zn/Cu couple. Generally more active, it is preferred over zinc powder.

Extreme care should be taken in reactions involving the pyrophoric (neat) diethylzinc and trialkylaluminums. These organometallic reagents should be transferred with dry gas-tight syringes using standard procedures for handling air-sensitive reagents. (251-253) Immediately after use and to avoid clogging, these syringes should be rinsed by purging them several times in an Erlenmeyer flask containing an anhydrous solvent such as acetone, dichloromethane or hexane. Moreover, use of a cannula instead of a syringe is recommended for reactions involving a large amount of the pyrophoric precursor. In addition, the dihaloalkane should be added to a solution of diethylzinc/trialkylaluminum. Explosions have been reported to occur when the order of addition of the reagents is inverted (48) (addition of diethylzinc to CH_2I_2), presumably owing to peroxide formation. (254, 255) In addition, catalytic amounts of oxygen might be involved in the carbenoid formation reaction (vide supra). (49, 50) Nitrogen is recommended as the inert gas, and opening the system after addition of the dihaloalkane will ensure carbenoid formation when the amount of adventitious oxygen is not sufficient. Experimentally, removing the nitrogen line and placing a small needle through the septum for 10 seconds is usually sufficient on large scale or when rigorously anhydrous reaction vessels and deoxygenated conditions are used.

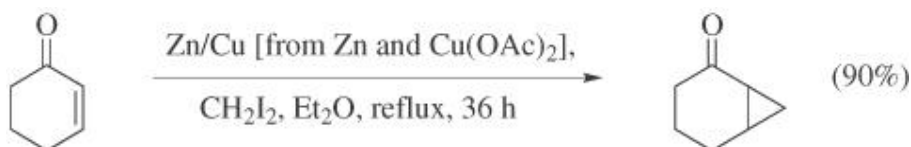
For cyclopropanation reactions with zinc carbenoids, dichloromethane and 1,2-dichloroethane are the solvents of choice since they are nonbasic, unreactive toward the zinc reagents, and polar enough to solubilize the substrates. When basic solvents are used, the rate of cyclopropanation usually decreases as the basicity of the solvent increases. However, reactions involving the Zn/Cu couple must be carried out in ethereal solvents to ensure that the oxidative addition proceeds well. In the trialkylaluminum/diiodoalkane system, ethereal solvents must be avoided since reactions carried out in these solvents lead to complete recovery of the starting olefins. Cyclopropanations with samarium carbenoids have been reported only using THF as solvent.

Typical reaction temperatures are below or at room temperature (zinc and aluminum carbenoids). Aside from reactions involving the Zn/Cu couple (which require heating in an ethereal solvent), there are numerous examples of carbenoids possessing a strong reactivity profile at 0° . Heating is not necessary and most other cyclopropanation reactions are carried out in the -10 to 20° temperature range. Samarium reagents are usually formed at -78°

and warmed to room temperature.

Since the byproduct formed under various reaction conditions is a Lewis acid, acid-sensitive substrates may require optimization of the reaction conditions. Carrying out the reaction in an ethereal solvent or addition of a Lewis base like diisopropylethylamine (*vide supra*) can allow reactions to proceed satisfactorily.

6. Experimental Procedures



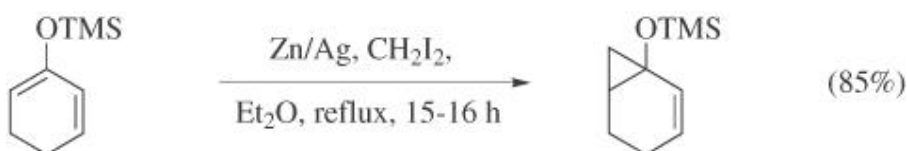
6.1.1. Bicyclo[4.1.0]heptan-2-one [Cyclopropanation of a Cyclic Alkene Using the Zinc/Copper Couple prepared from Cu(OAc)₂] (256)

6.1.1.1. Preparation of the Zn/Cu couple

In a 250-mL Erlenmeyer flask equipped with a stirbar, cupric acetate monohydrate (0.16 g, 0.8 mmol) was dissolved upon heating in 5 mL of glacial acetic acid. Zinc powder (2.8 g, 42.8 mmol) was added to this stirred solution, and after 30 to 60 seconds, the green coloration disappeared and metallic red copper deposited on the zinc. The stirring was stopped and the supernatant liquid was decanted and replaced with 5 mL of glacial acetic acid. The suspension was stirred once again and the supernatant liquid was once again decanted and then replaced with 10 mL of ether. The couple was washed in the same fashion 3 times with 10-mL ether portions. Finally, the couple was covered with 20 mL of ether.

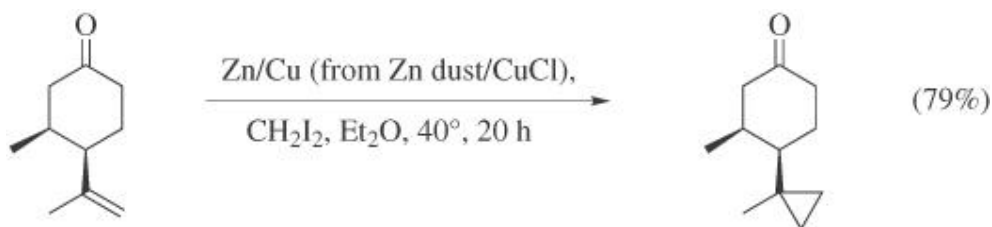
6.1.1.2. Cyclopropanation Reaction

The Erlenmeyer flask was fitted with a condenser, an addition funnel and a CaCl₂ trap. A few drops of CH₂I₂ were added and a slightly exothermic reaction occurred. Then, the mixture of cyclohexen-2-one (0.96 g, 0.01 mol) and CH₂I₂ (7.5 g, 28 mmol) was added dropwise, inducing a gentle reflux for 30 minutes to 1 hour. The mixture was stirred and heated to reflux over 36 hours. A white solid deposited after a few hours, and larger amounts formed with time. After cooling the flask to room temperature, distilled water (2 mL) was added dropwise and the mixture was stirred one hour. After centrifugation, the ether phase was decanted and this solution was washed with 10% aqueous HCl, then 3 times with distilled water. The solution was dried over Na₂SO₄, filtered and concentrated to afford 1.0 g (90%) of bicyclo[4.1.0]heptan-2-one as a colorless liquid: bp₁₅ 91°; ¹H NMR δ 1.80 (m, 7 H), 1.14 (s, 1 H), 1.01 (m, 2 H).



6.1.2. 1-Trimethylsilyloxybicyclo[4.1.0]hept-2-ene (Cyclopropanation of a Cyclic Silyl Enol Ether Using the Zinc/Silver Couple) (107)

In a 250-mL, two-necked flask equipped with a condenser and magnetic stirring bar containing boiling glacial acetic acid (100 mL) was added silver acetate (100 mg). Upon dissolution of the silver acetate, zinc powder (20 g) was added all at once to the stirring hot solution. After 30 seconds the liquid was carefully decanted and the zinc-silver couple was washed with five 100-mL portions of anhydrous ether. Ether (100 mL) was added, followed by 2-trimethylsilyloxycyclohexa-1,3-diene (16.8 g, 0.10 mol) and the flask was fitted with an addition funnel containing CH_2I_2 (40.2 g, 0.15 mol) and a CaCl_2 trap. The suspension was stirred moderately and CH_2I_2 was added dropwise. The reaction induced a gentle reflux that increased upon CH_2I_2 addition. After complete addition, the mixture was heated to reflux for 15–16 hours. The flask was then cooled to 0° and a solution of dry pyridine (23.8 g, 0.3 mol) in ether (50 mL) was added dropwise via the addition funnel. Upon addition of pyridine, a precipitate was formed. After complete addition, the precipitate was filtered off and was washed with ether. The combined filtrate and washes were concentrated in vacuo. The crude product was dissolved in pentane and filtered. Upon solvent concentration, the residue was purified by distillation to afford 15.5 g, 85% of 1-trimethylsilyloxybicyclo[4.1.0]hept-2-ene: $\text{bp}_{0.03}$ $40\text{--}43^\circ$; IR (film) 3080, 3040, 2960, 1640, 1450, 1255, 1220, 1010, 845, 760 cm^{-1} ; ^1H NMR (CCl_4) δ 6.14–6.00 (br s, 1 H), 5.45–5.10 (m, 1 H), 2.00–1.10 (m, 4 H), 1.00–0.55 (m, 3 H), 0.12 (s, 9 H); LRMS calcd: M 183, found: M^+ 182 (75%) and m/z (%): 167 (100), 154 (50), 151 (52), 93 (97), 75 (95).

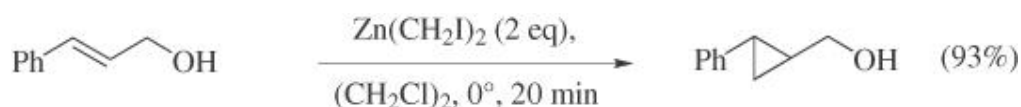


6.1.3. (3S,4R)-(-)-3-Methyl-4-(1-methylcyclopropyl)cyclohexanone (Cyclopropanation of an Acyclic Alkene Using the Zinc/Copper Couple Prepared from CuCl) (257)

A mixture of zinc dust (2.57 mmol, 0.167 g) and cuprous chloride (2.57 mmol, 0.254 g) in anhydrous ether (1 mL) was heated at reflux for 30 minutes with stirring under nitrogen. CH_2I_2 (1.28 mmol, 0.103 μL) was added, and the mixture was heated at 40° until bubbles appeared and the solution turned dark. (3S,4R)-(-)-3-Methyl-4-isopropenylcyclohexanone (0.99 mmol, 0.150 g) and

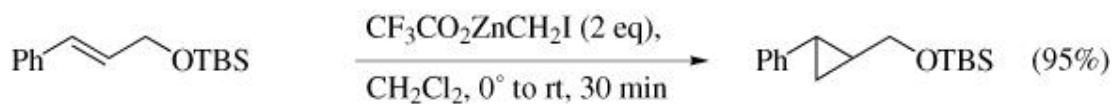
CH₂I₂ (0.500 mL) were added and the mixture was kept at 40° with stirring for 20 hours. The solution was diluted with ether and filtered through Celite, washed with 5% aqueous HCl, water, and brine, dried over anhydrous Na₂SO₄ silver-nitrate-impregnated silica gel (eluting with 5% ethyl acetate-hexane) to give

(3*S*,4*R*)-(-)-3-methyl-4-(1-methylcyclopropyl)cyclohexanone (0.130 g, 79%): [α]_D²⁰ -19.3° (c 0.71); IR (neat) 3100, 1720, 1180 cm⁻¹; ¹H NMR δ 1.05 (s, 3 H), 1.00 (d, *J* = 8 Hz, 3 H), 0.45 (m, 2 H), 0.28 (m, 2 H); LRMS *m/z* 166 (1, M⁺), 138 (45), 111 (75), 96 (56), 82 (53), 67 (47), 55 (100); HRMS calcd for C₁₁H₁₈O : 166.13576, found: 166.13543.



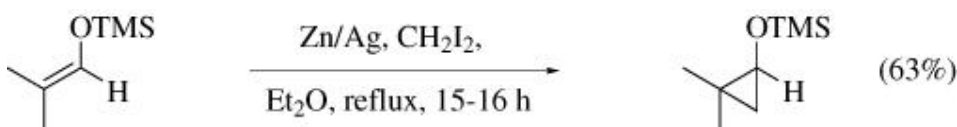
6.1.4. (1*R*,2*R*)-2-Phenylcyclopropanemethanol [Cyclopropanation of an Acyclic Alkene Using bis(Chloromethylzinc)] (51)

In a 25-mL, two-neck flask, a solution of Et₂Zn (410 μL, 4.00 mmol, 2.00 equiv.) in 1,2-dichloroethane (7 mL) was cooled to 0°, and CH₂I₂ (585 μL, 8.03 mmol, 4.0 equiv.) was added via syringe. The solution was stirred for 5 minutes at 0°, and a solution of cinnamyl alcohol (268 mg, 2.00 mmol) in 1,2-dichloroethane (3 mL) was added slowly via syringe. The reaction mixture was stirred for 20 minutes at 0° and then was quenched carefully with saturated aqueous NH₄Cl solution (20 mL). The mixture was allowed to warm to room temperature, stirred vigorously for 10 minutes, and extracted with *tert*-butyl methyl ether (3 × 20 mL). The extracts were washed with water (1 × 20 mL) and brine (1 × 20 mL), combined, dried (K₂CO₃), filtered through a pad of silica gel, and concentrated at aspirator pressure. The crude product was purified by silica gel chromatography (hexane/EtOAc, 6/1) and bulb-to-bulb distillation to afford 275 mg (93%) of the title cyclopropane as a clear, colorless oil: bp 145–150° (2 Torr); ¹H NMR (300 MHz) δ 7.15 (m, 5 H), 3.60 (dd, *J* = 2.33 and 6.71 Hz, 2 H), 1.81 (m, 1 H), 1.78 (br s, 1 H), 1.43 (m, 1 H), 0.94 (m, 2 H); ¹³C NMR (75.5 MHz) 142.37, 128.30, 125.74, 125.58, 66.48, 25.25, 21.24, 13.83; TLC *R*_f 0.10 (hexane/EtOAc, 4/1); GC T_r 8.60 min (170 °C isothermal, HP 50-m HP-5 capillary column). Anal. Calcd for C₁₀H₁₂O : 81.04; H, 8.16. Found: C, 80.99; H, 8.18.



6.1.5. (1,1-Dimethylethyl)dimethyl([(1R,2R)-2-phenylcyclopropyl]methoxy)silane (Cyclopropanation of an Acyclic Alkene Using the TFA-Accelerated Reaction Protocol) (53)

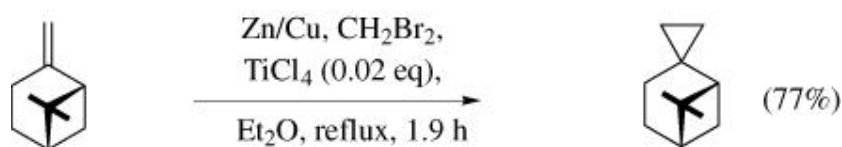
To freshly distilled CH_2Cl_2 (20 mL) was added Et_2Zn (1.0 M in hexanes) (20 mL, 20 mmol) under N_2 (it is best to use an inlet adapter for the nitrogen line since needles often become clogged). The solution was cooled in an ice bath and a solution of trifluoroacetic acid (1.54 mL, 20 mmol) in CH_2Cl_2 (10 mL) was then dripped very slowly into the reaction mixture via syringe. Upon stirring for 20 minutes, a solution of CH_2I_2 (1.61 mL, 20 mmol) in CH_2Cl_2 (10 mL) was added. After an additional 20 minutes stirring, a solution of (*E*)-cinnamyl alcohol TBS ether (2.60 g, 10 mmol) in CH_2Cl_2 (10 mL) was added and the ice bath was removed. After an additional 30 minutes stirring, the reaction mixture was quenched with 0.1 N HCl (50 mL) (or saturated aqueous NH_4Cl) and hexanes (25 mL) and the layers were separated. The aqueous layer was extracted with hexanes. The combined organic layers were washed with saturated aqueous NaHCO_3 , water, and brine, then dried over Na_2SO_4 , filtered, concentrated, and purified by column chromatography (hexanes/ether, 50/1) to yield the cyclopropane product (2.61 g, 95%): IR (film) 2955, 2933, 2892, 2857, 1605 cm^{-1} ; ^1H NMR δ 7.26 (m, 2 H), 7.15 (m, 1 H), 7.08 (m, 2 H), 3.72 (dd, $J = 10.8, 5.7$ Hz, 1 H), 3.61 (dd, $J = 10.8, 6.0$ Hz, 1 H), 1.83 (dt, $J = 8.5, 4.8$ Hz, 1 H), 1.37 (m, 1 H), 0.94 (m, 2 H), 0.93 (s, 9H), 0.09 (s, 6 H); ^{13}C NMR δ 143.3, 128.4, 126.1, 125.5, 66.0, 26.2, 25.4, 20.9, 18.6, 13.7, -5.0. Anal. Calcd for $\text{C}_{12}\text{H}_{26}\text{OSi}$: C, 73.22; H, 9.98. Found: C, 73.19; H, 9.71.



6.1.6. 1-Trimethylsilyloxy-2,2-dimethylcyclopropane (Cyclopropanation of an Acyclic Silyl Enol Ether Using the Zinc/Silver Couple) (107)

In a 250-mL, two-necked flask equipped with a condenser and magnetic stirring bar containing boiling glacial acetic acid (100 mL) was added silver acetate (100 mg). Upon dissolution of silver acetate, zinc powder (20 g) was added all at once to the stirring hot solution. After 30 seconds the liquid was carefully decanted and the zinc-silver couple was washed with five 100-mL portions of anhydrous ether. Then, ether (100 mL) was added, followed by 1-trimethylsilyloxy-2-methylpropene (0.10 mol) and the flask was fitted with an addition funnel containing CH_2I_2 (40.2 g, 0.15 mol) and a CaCl_2 trap. The

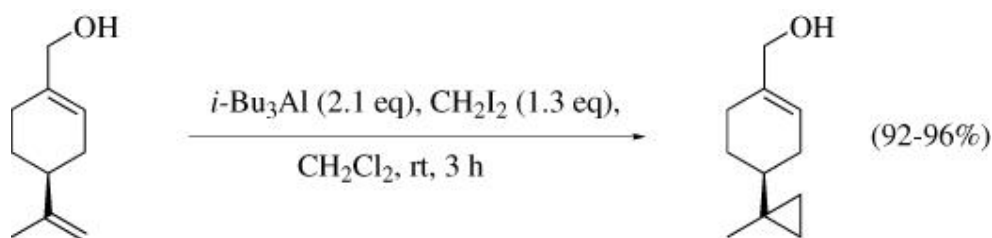
suspension was moderately stirred and CH_2I_2 was added dropwise. The reaction induced a gentle reflux that increased upon CH_2I_2 addition. After complete addition, the mixture was heated to reflux for 15–16 hours. The flask was then cooled to 0° and a solution of dry pyridine (23.8 g, 0.3 mol) in diethyl ether (50 mL) was added dropwise via the addition funnel. Upon addition of pyridine, a precipitate was formed. After complete addition, the precipitate was filtered off and was washed with ether. The combined filtrate and washes were concentrated in vacuo. The crude product was dissolved in pentane and filtered. Upon solvent concentration, the residue was purified by distillation to afford 63% of 1-trimethylsiloxy-2,2-dimethylcyclopropane: bp₁₂ 25–27°; IR (film) 3080, 2960, 1450, 1255, 1180, 1030, 850, 755 cm^{-1} ; ^1H NMR (CCl_4) δ 2.95 (dd, 1 H), 1.05 (s, 3 H), 0.95 (s, 3 H), 0.49–0.10 (m, 3 H), 0.12 (s, 9 H); LRMS calcd: M 158, found: M^+ 158 (5%) and m/z (%): 143 (82), 75 (65), 73 (100).



**6.1.7. 6,6-Dimethylspiro(bicyclo[3.1.1]heptane-2,1'-cyclopropane)
(Cyclopropanation of a Cyclic Alkene Under TiCl_4 -Promoted Conditions)
(43)**

A 500-mL, three-necked, round-bottom flask was fitted with a double condenser system (Allihn on bottom, Friedrich on top), a mechanical stirrer, and a pressure-equalizing dropping funnel containing ether for use in maintaining solvent volume during the course of the reaction. A gas collection apparatus or gas bubbler was attached to the Friedrich condenser to measure the amount of ethylene evolved and/or to monitor the course of the reaction. Zinc dust (52.3 g, 0.80 mol), copper(I) chloride (7.92 g, 0.80 mol), ether (125 mL), dibromomethane (104 g, 0.60 mol), and β -pinene (27.2 g, 0.20 mol) were added in the order listed. After stirring was commenced, titanium(IV) chloride (2.28 g, 0.012 mol) was added by syringe (*Caution!* Use of more than 2 mol % of titanium(IV) chloride based on starting dihaloalkane has resulted in unmanageable reactions), and the reaction mixture was heated at 45 – 50° with an oil bath. The oil bath was lowered if the reaction became too vigorous, and the ether volume was replenished through the addition funnel when necessary. Upon completion of the reaction, as indicated by a slowing or stopping of gas evolution, the contents of the reaction flask were transferred to another vessel, cooled in ice, and treated while stirring with saturated aqueous NH_4Cl (ca. 25 mL per 0.1 mol of starting zinc dust). Initial addition must be done carefully to avoid foaming the contents out of the vessel. The solids were removed by

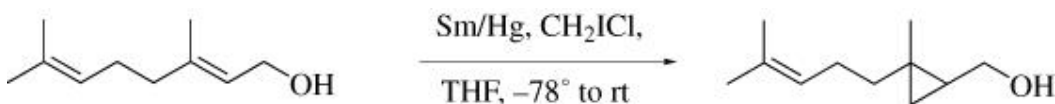
vacuum filtration (*Caution!* Potential fire hazard if air is drawn through the zinc residue. The residue should be thoroughly wet with water before disposal) and washed twice with *n*-pentane. The aqueous layer of the filtrate was separated and washed twice with *n*-pentane, and the combined organic layers were washed three times with 10% NaOH and once with saturated aqueous NaCl solution and dried over anhydrous Na₂SO₄. The solvents were removed on a steam bath through a Vigreux column or a rotary vacuum evaporator, and the remaining oil was distilled, giving 23.0 g (77%) of 97% pure 6,6-dimethylspiro[bicyclo[3.1.1]heptane-2,1'-cyclopropane], bp 78–92° (25 Torr), $n_D^{23} = 1.4765$ [lit. (257a) bp 71–73° (18 Torr), $n_D^{25} = 1.4765$]. The distillation pot residue weighed 7.2 g. For pure 6,6-dimethylspiro[bicyclo[3.1.1]heptane-2,1'-cyclopropane]: ¹H NMR (CDCl₃) δ 2.2 (m, 1 H), 2.1–1.7 (m, 4 H), 1.6 (d, *J* = 9.7 Hz, 1 H), 1.25 (m, 1 H), 1.2 (s, 3 H), 1.1 (m, 1 H), 1.0 (s, 3 H), 0.45 (m, 1 H), 0.35 (m, 1 H), 0.15 (m, 2 H); ¹³C NMR (CDCl₃) δ 51.2, 40.9, 40.7, 27.2, 26.7, 26.6, 24.2, 21.8, 19.6, 16.3, 11.8.



6.1.8. (S)-4-(1-Methylcyclopropyl)-1-cyclohexene-1-methanol (Chemoselective Cyclopropanation of a Polyene Using an Aluminum Carbenoid) (258)

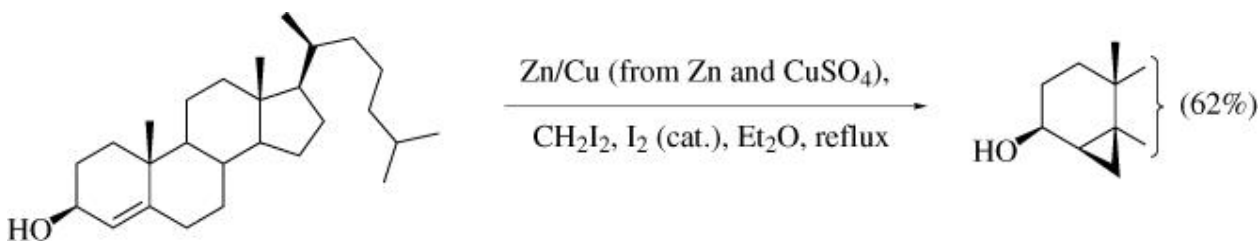
A dry, 1-L, three-necked, round-bottomed flask was equipped with a gas inlet, a 50-mL pressure-equalizing dropping funnel, rubber septum, and a Teflon-coated magnetic stirring bar. The flask was flushed with argon, after which (S)-(-)-perillyl alcohol (10.65 g, 0.07 mol) followed by CH₂Cl₂ (350 mL) were injected through the septum into the flask. The solution was stirred and *i*-Bu₃Al (37.3 mL, 0.147 mol) was added from the dropping funnel over a period of 20 minutes at room temperature. The mixture was stirred at room temperature for 20 minutes and then CH₂I₂ (7.3 mL, 0.091 mol) was added dropwise with a syringe over a 10-minute period. The mixture was stirred at room temperature for 4 hours and poured into 400 mL of ice-cold 8% aqueous NaOH. The organic layer was separated, and the aqueous layer was extracted twice with 100-mL portions of CH₂Cl₂. The combined extracts were dried over anhydrous Na₂SO₄ and concentrated with a rotary evaporator at ca. 20 mm. The residual oil was distilled under reduced pressure to give 10.64–11.13 g (92–96%) of (S)-4-(1-methylcyclopropyl)-1-cyclohexene-1-methanol as a

colorless liquid: bp 132–134° (24 mm Hg); IR (film): 3330, 2960–2830, 1460–1423, 1390, 1010, 1000 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 5.69 (br s, 1 H), 3.99 (br t, 2 H), 2.16-1.91 (m, 4 H), 1.83-1.77 (m, 1 H), 1.47-1.36 (m, 1 H), 1.30-1.24 (m, 1 H), 0.93 (s, 3 H), 0.92-0.80 (m, 1 H), 0.26-0.22 (m, 4 H).



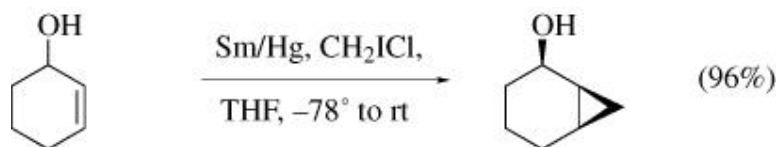
6.1.9. (1*S,2*S**)-2-Methyl-2-(4-methyl-3-pentenyl)cyclopropanemethanol (Chemoselective Cyclopropanation of a Polyene Using a Samarium Carbenoid) (58)**

To a dry 25-mL round-bottom flask equipped with a stirbar was added samarium metal (2.1 mmol, 0.316 g). The flask was simultaneously flushed with argon and flamed dry. To the cooled flask was added 5 mL of THF, followed by a solution of mercury(II) chloride (0.2 mmol, 0.054 g) in 5 mL of THF. This was allowed to stir for 10 minutes followed by addition of geraniol (0.5 mmol). The flask was cooled to -78° , and CH_2I_2 (2.0 mmol) was added dropwise. The mixture was allowed to warm to room temperature and stirred for an additional 1–2 hours. The reaction was followed by TLC and GC. The reaction was quenched with saturated K_2CO_3 and extracted with ethyl ether. The ether layer was washed with brine three times, dried over K_2CO_3 , filtered and concentrated in vacuo to yield the crude material. Flash chromatography or Kugelrohr distillation yielded the pure cyclopropyl carbinol. This general procedure was followed to yield 97% (0.082 g, 0.487 mmol) of (1*S**,2*S**)-2-methyl-2-(4-methyl-3-pentenyl)cyclopropanemethanol as a clear colorless oil after Kugelrohr distillation ($55\text{--}65^\circ$ at 0.1 mm Hg). The isolated product was 94% pure as indicated by GLC analysis: IR (neat) 3415, 2930, 1450, 1385, 1034 cm^{-1} ; ^1H NMR (CDCl_3) δ 5.11-5.08 (m, 1 H), 3.73-3.64 (dd, $J = 11.4, 6.5$ Hz, 1 H), 3.51-3.41 (dd, $J = 11.4, 8.5$ Hz, 1 H), 2.06-0.85 (m, 6 H), 1.64 (s, 3 H), 1.58 (s, 3 H), 1.06 (s, 3 H), 0.51-0.44 (m, 1 H), 0.12-0.07 (m, 1 H); ^{13}C NMR (CDCl_3) δ 131.37, 124.68, 63.96, 41.12, 26.30, 25.74, 25.54, 19.97, 17.73, 17.68, 17.11.



6.1.10. (3 β , 4 α , 5S)-3',4-Dihydrocyclopropa[4,5]cholestan-3-ol (Directed Cyclopropanation of a Chiral Cyclic Allylic Alcohol Involving a Zinc Carbenoid) (259)

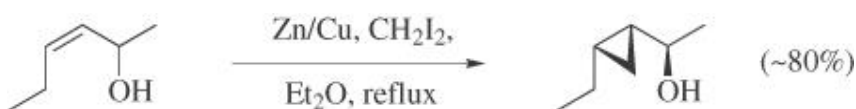
To a magnetically stirred mixture of zinc-copper couple (0.687 g, 10.5 mmol), (15) dry ether (12 mL), and a small crystal of iodine, there was added CH₂I₂ (2.34 g, 8.75 mmol). The mixture was warmed with an infrared lamp until the reaction started, and then allowed to react for 30 minutes in a water bath at 35°. A solution of 3 β -hydroxy- Δ^4 -cholestene (0.967 g, 2.5 mmol) in dry ether (7 mL) was added over a period of 20 minutes, and the mixture was stirred for 1 additional hour at 40°. The ice-cooled mixture was diluted with a saturated solution of NH₄Cl, the supernatant layer was decanted from the precipitate, and the precipitate was washed twice with ether. The combined ethereal extracts were washed with saturated NaCl solution and dried over anhydrous Na₂SO₄, and the solvent was removed under reduced pressure. The residue was purified immediately on 50 g of alumina (activity III). Hexane was used as first solvent to remove CH₂I₂ and a dimer. Benzene eluted 0.622 g (62 %) of crystalline (3 β , 4 α , 5S)-3',4-dihydrocyclopropa[4,5]cholestan-3-ol, which was recrystallized from acetone to give fine white needles: mp 94–95° (a second crop of crystalline material formed as a white powder, mp 81.0–81.5°); [α]_D – 10° (c 0.92); IR 3600, 3400 cm⁻¹; ¹H NMR δ 0.02 (q, *J* = 4.5 and 4.0 Hz). Anal. Calcd for C₂₈H₄₈O : C, 83.93; H, 12.08. Found: C, 84.03; H, 12.02.



6.1.11. cis-Bicyclo[4.1.0]heptan-2-ol (Directed Cyclopropanation of a Cyclic Allylic Alcohol Involving a Samarium Carbenoid) (58)

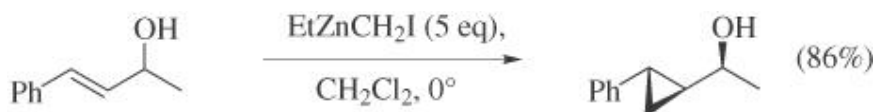
To a dry 25-mL round-bottom flask equipped with a stirbar was added samarium metal (4.2 mmol, 0.632 g). The flask was simultaneously flushed with argon and flamed dry. To the cooled flask was added THF (5 mL), followed by a solution of mercuric chloride (0.4 mmol, 0.108 g) in THF (5 mL). This was allowed to stir for 10 minutes followed by addition of cyclohex-2-en-1-ol (1 mmol). The flask was cooled to -78°, and CH₂I₂ (4.0 mmol) was added dropwise. The mixture was allowed to warm to room temperature and stirred for an additional 1–2 hours. The reaction was followed by TLC and GC. The reaction was quenched with saturated K₂CO₃ and

extracted with ethyl ether. The ether layer was washed with brine three times, dried over K_2CO_3 , filtered and concentrated in vacuo to yield the crude material. Flash chromatography or Kugelrohr distillation yielded the pure cyclopropyl carbinol. This general procedure was followed to yield 96% (0.107 g, 0.955 mmol) of *cis*-bicyclo[4.1.0]heptan-2-ol as a clear, colorless oil, isolated by silica gel chromatography eluting with 2:1 hexanes-EtOAc. The isolated product was 99 % pure as indicated by GLC analysis: IR (neat) 3400, 3050, 2950, 2850, 1050, 1000 cm^{-1} ; 1H NMR ($CDCl_3$) δ 4.26-4.04 (m, 1 H), 1.87-1.74 (m, 1 H), 1.65-1.53 (m, 2 H), 1.40-0.84 (m, 6 H), 0.59-0.48 (m, 1 H), 0.30-0.22 (m, 1 H); ^{13}C NMR ($CDCl_3$) δ 67.26, 29.83, 22.86, 20.78, 17.69, 12.76, 7.28; HRMS calcd for $C_7H_{12}O$ 112.0888, found 112.0874.



6.1.12. [1 α (R^*),2 α]-2-Ethyl- α -methylcyclopropanemethanol (Directed Cyclopropanation of a Z-Disubstituted Acyclic Allylic Alcohol) (135)

The Zn/Cu couple was prepared according to Shank and Schechter (34) and the yields of the desired cyclopropyl carbinols were around 80%. In a three-necked flask were introduced anhydrous ether (150 mL), the Zn/Cu couple (0.5 mol) and the allylic alcohol (0.2 mol). A few milliliters of CH_2I_2 was added and the flask was gently heated until the reaction started. The remaining amount of CH_2I_2 (0.5 mol) was then added dropwise. After a few hours at reflux, the reaction was quenched with a saturated aqueous NH_4Cl solution and the solid portion was filtered. The ether layer was separated and the aqueous layer was extracted with diethyl ether. The combined organic extracts were washed with a saturated aqueous K_2CO_3 solution, dried and the desired product was isolated after distillation. [1 α (R^*),2 α]-2-Ethyl- α -methyl-cyclopropanemethanol: bp 72°; 1H NMR (CCl_4) δ 3,28 (m, 1 H), 1.22 (d, 3 H), 1.2-0.2 (m, 9 H). Anal. Calcd for $C_7H_{14}O$: C, 73.68, H, 12.28. Found: C, 73.50, H, 12.14.

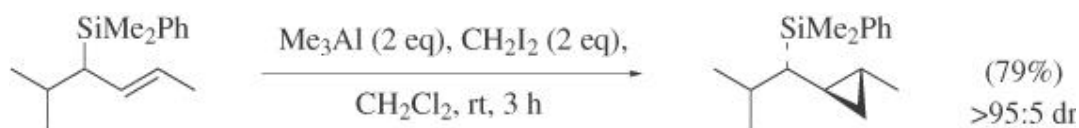


6.1.13. (α R,1R,2R)- α -Methyl-2-phenylcyclopropanemethanol (Directed Cyclopropanation of an E Disubstituted Acyclic Allylic Alcohol) (136)

To a solution of (*E*)-4-phenyl-3-buten-2-ol (296 mg, 2.0 mmol) in anhydrous CH₂Cl₂ (20 mL) at -10° was added dropwise diethylzinc (1.0 mL, 10 mmol) followed by CH₂I₂ (810 μL, 10 mmol). The bath was allowed to warm to room temperature over 3 hours and the mixture was stirred for an additional hour, after which time TLC analysis showed complete consumption of the starting material. A saturated aqueous NH₄Cl solution (10 mL) was added and the mixture was diluted with ether (80 mL) and 10% aqueous HCl (10 mL). The layers were separated and the organic layer was then successively washed with saturated aqueous Na₂SO₃ (20 mL), saturated aqueous NaHCO₃ (20 mL), and saturated aqueous NaCl (20 mL). The organic layer was dried over MgSO₄ and concentrated under reduced pressure. The diastereomeric excess was determined by GC analysis of the acetate-derived from *trans*-1-(1-hydroxyethyl)-2-phenylcyclopropane as follows: A solution of 10 mg of crude alcohol in 2 mL of pyridine and 1 mL of acetic anhydride was stirred for 30 minutes. This solution was injected directly into the GC (0.5 μL). Conditions: Column: DB-1701, 0.25 mm × 30 m. Pressure: 25 psi. Isotherm: 140°. *t*_R (minor) 10.2 min, *t*_R (major) 11.3 min. Diastereomeric ratio (*syn:anti*): 7:1 (75% de). Alternatively, silica gel chromatography of the crude alcohol using 15% ethyl acetate/hexane as the eluent produced 40 mg (12%) of the *anti* isomer followed by 280 mg (86%) of the more polar *syn* isomer.

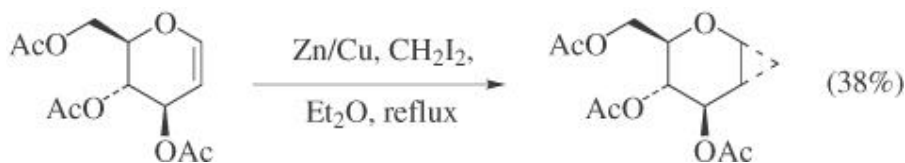
(α *R*,1*R*,2*R*)- α -Methyl-2-phenylcyclopropanemethanol: ¹H NMR (300 MHz, CDCl₃) δ 7.30-7.06 (m, 5 H), 3.39 (dq, *J* = 8 and 6 Hz, 1 H), 1.85-1.79 (m, 1 H), 1.67 (br s, 1 H), 1.36 (d, *J* = 6 Hz, 3 H), 1.33-1.24 (m, 1 H), 1.05-0.93 (m, 2 H); ¹³C NMR (100 MHz, CDCl₃) δ 142.6, 128.4, 126.0, 125.6, 71.3, 30.7, 22.8, 20.7, 13.9.

(α *R*,1*S*,2*S*)- α -Methyl-2-phenylcyclopropanemethanol: ¹H NMR (300 MHz, CDCl₃) δ 7.30-7.08 (m, 5 H), 3.40 (dq, *J* = 8 and 6 Hz, 1 H), 1.95-1.89 (m, 1 H), 1.68 (s, 1 H), 1.34 (d, *J* = 6 Hz, 3 H), 1.34-1.25 (m, 1 H), 0.98-0.90 (m, 2 H); ¹³C NMR (100 MHz, CDCl₃) δ 142.6, 128.2, 125.7, 125.5, 71.7, 30.7, 22.3, 21.2, 13.2.



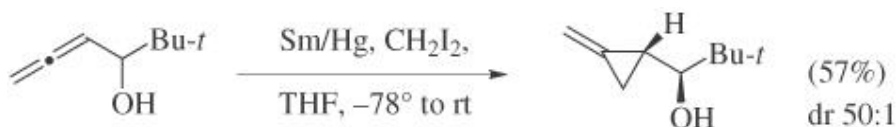
6.1.14. (1*R*,2*R*)-2-[(1'*S*)-1-Dimethyl(phenyl)silyl-2-methylpropyl]-1-methyl cyclopropane (Diastereoselective Cyclopropanation of an Acyclic Chiral Alkene) (259a)

Trimethylaluminum (2 M in hexane, 0.37 mL) was added to (1-isopropylbut-2-enyl) dimethylphenylsilane (0.37 mmol) and CH₂I₂ (200 mg, 0.74 mmol) in dry CH₂Cl₂ (1 mL) under nitrogen at room temperature and the mixture was stirred for 3 hours. CH₂Cl₂ (10 mL) and water (0.5 mL) were added to the mixture, after which the organic layer was separated, washed with brine (5 mL), dried (MgSO₄) and evaporated under reduced pressure. The residue was chromatographed (SiO₂, hexane) to give a 79% yield of (1*R*,2*R*)-2-[(1'*S*)-1-dimethyl(phenyl)silyl-2-methylpropyl]-1-methylcyclopropane. *R*_f (hexane) 0.45; IR (film) 1261, 1123 cm⁻¹; ¹H NMR (CDCl₃) δ 7.6-7.3 (m, 5 H), 1.92 (dseptet, *J* = 3.2 and 6.9 Hz, 1 H), 1.1-0.0 (m, 5 H); 0.96 (d, *J* = 6.7 Hz, 6 H), 0.89 (d, *J* = 6.9 Hz, 3 H), 0.36 (s, 3H), 0.35 (s, 3 H); LRMS calcd: (M – Pr) 203, found 203 (6%) and *m/z* (%): 135 (100), 110 (23); HRMS calcd for C₁₆H₂₆Si 203.1260, found 203.1256.



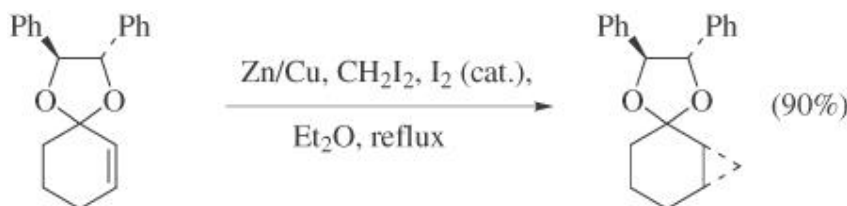
6.1.15. 3,4,6-Tri-O-acetyl-1,2-dideoxy-1,2-C-methylene- α -D-glucopyranoside (Diastereoselective Cyclopropanation of a Cyclic Chiral Enol Ether) (128)

Zn-Cu couple prepared from 2.6 g Zn by the method of Le Goff (36) was placed in dry ether (50 mL) in a three-necked flask. CH₂I₂ (3.2 mL) was added and the mixture was gently heated until small bubbles were generated from the couple. The mixture was refluxed for 30 minutes. A solution of the glucal (1.0 g) in dry ether (50 mL) was added dropwise over a 30-minute period. Heating was continued and the reaction was monitored by TLC. After 8.5 hours, TLC showed absence of the starting material. The solution was then cooled, and saturated NH₄Cl (30 mL) was added to precipitate inorganic salts. The mixture was filtered and the 2-layer filtrate was separated. The aqueous layer was extracted twice with ether (50 mL). The combined ether solutions were washed with saturated K₂CO₃ (50 mL) and saturated NaCl (50 mL), dried and evaporated to a syrup. Column chromatography of the syrup on silica gel using 1:3 chloroform-ether gave a fraction which yielded needle-like crystals; yield 38%, m.p. 65–70°; [α]_D²⁵ + 66.6° (c 1.1, CHCl₃); IR (KBr) 3012, 1724, 1429, 1362, 1227, 1106, 1042, 1015 cm⁻¹; ¹H NMR (CDCl₃) δ 2.1 (acetyl), 1.28 (cyclopropane).



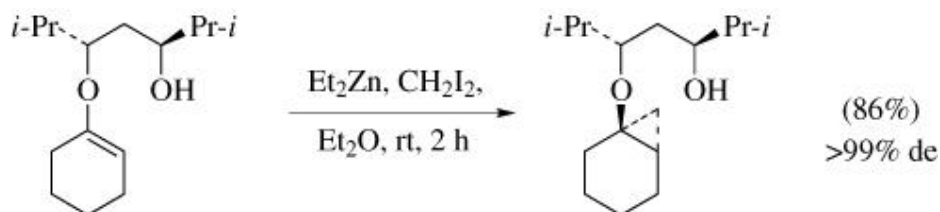
6.1.16. (*R*^{*},*S*^{*})- α -(1,1-Dimethylethyl)-2-methylenecyclopropanemethanol (Diastereoselective Cyclopropanation of an Allenic Alcohol) (142)

To a dry, round-bottomed flask equipped with a stirbar and capped with a rubber septum was added samarium metal (0.601 g, 4.0 mmol). The flask was flame dried while flushing with nitrogen. After the flask was allowed to cool to room temperature, mercuric chloride (10 mol% based on samarium) was added quickly, followed by THF (2 mL). The gray suspension was stirred for 10 minutes. The α -allenic alcohol (50 mg, 0.40 mmol) was dissolved in THF (2 mL) and transferred via cannula to the flask. The flask was cooled to -78° , and CH_2I_2 was added dropwise. The mixture was allowed to warm to room temperature over 2 hours and stirred for an additional 2–4 hours. The viscous dark blue reaction mixture was quenched with saturated aqueous K_2CO_3 solution and extracted three times with Et_2O . The organic layers were washed three times with brine, dried over anhydrous Na_2SO_4 , and filtered. After concentration of the crude product [31.8 mg (57%) of a colorless oil, a 50:1 mixture of two diastereomers as determined by GC analysis] purification was effected by flash chromatography on silica gel (elution with 20:1 pentane: ether). The solvent was carefully removed by distillation and Kugelrohr distillation to yield the pure major diastereomer. (*R*^{*},*S*^{*})- α -(1,1-Dimethylethyl)-2-methylenecyclopropanemethanol: $R_f = 0.55$ on silica gel (hexanes:diethyl ether, 1:1); IR (neat) 3416 (br, m), 3072 (w), 3051 (w), 2959 (s), 2910 (m), 2868 (m), 1483 (m), 1363 (m), 1124 (m), 1047 (m), 1005 (s), 885 (s) cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 5.40 (m, 1 H), 5.35 (m, 1 H), 2.72 (dd, $J = 8.9, 3.6$ Hz, 1 H), 1.65 (m, 1H), 1.49 (d, $J = 3.6$ Hz, 1 H), 1.25 (m, 2 H), 0.97 (s, 9 H); ^{13}C NMR (100 MHz, CDCl_3) δ 133.95, 104.32, 82.04, 35.28, 26.04, 19.27, 6.96; HRMS calcd for $\text{C}_9\text{H}_{15}\text{O}$ ($\text{M}-\text{H}$)⁺ 139.1123, found 139.1124.



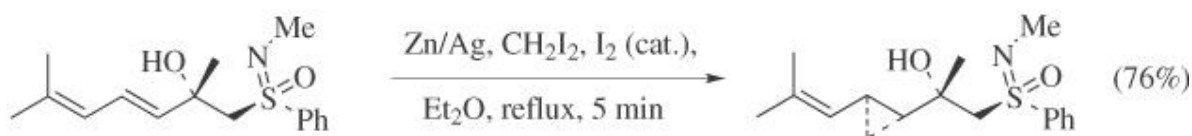
6.1.17. [4'S-[2' α (1R*,6S*),4' **α ,5' β] -4',5'-Diphenylspiro[bicyclo[4.1.0]heptane-2,2 ϕ -[1,3]dioxolane] (Diastereoselective Cyclopropanation of a Cyclic Chiral Allylic Acetal as Chiral Auxiliary) (260)**

A well-stirred suspension of freshly prepared Zn/Cu couple (~2.5 g) in ether (~5 mL) under argon was brought to reflux, and a small crystal of iodine and CH_2I_2 (1.51 mL, 18.8 mmol) were added. After 30 minutes at reflux the ene ketal (1.10 g, 3.77 mmol) was added as a solution in diethyl ether. Progress of the reaction was monitored by TLC and ^1H NMR spectroscopy. When the reaction was complete, the mixture was cooled to 0° and quenched with saturated aqueous Na_2CO_3 solution (12 equiv). After the mixture was stirred at room temperature for 30 minutes, the gray-black Zn/Cu couple was removed by filtration and washed well with diethyl ether. The combined organic extracts were washed with saturated aqueous NH_4Cl , saturated aqueous NaHCO_3 , and saturated aqueous NaCl , dried over MgSO_4 , filtered and concentrated in vacuo to afford the crude product. Column chromatography on silica gel 60 afforded a white solid as a diastereomerically pure product. Yield: 0.936 g, 3.05 mmol, 90%. Recrystallization from a minimal amount of anhydrous diethyl ether afforded colorless crystals: mp $141\text{--}142^\circ$; $[\alpha]_D^{25} - 75.0^\circ$ (c 0.42, CHCl_3); IR (CDCl_3) 3663, 3066, 3032, 3011, 3009, 2942, 2863, 2355, 1948, 1877, 1807, 1602, 1495, 1454, 1389, 1363, 1186, 1137, 1109, 1095, 1077, 1055, 1041, 1026, 1002, 978, 959, 922, 896, 869, 827, 700, 666, 649, 622 cm^{-1} ; ^1H NMR (CDCl_3) δ 7.35-7.14 (m, 10 H), 4.86 (dd, 2 H), 1.98-1.71 (m, 2 H), 1.71-1.55 (m, 2 H), 1.55-1.34 (m, 3 H), 1.34-1.18 (m, 1 H), 0.87-0.72 (m, 1 H), 0.35 (q, 1 H); ^{13}C NMR (CDCl_3) δ 137.0, 136.8, 128.3, 128.2, 128.1, 128.0, 126.8, 126.7, 110.3, 85.3, 85.2, 32.7, 22.3, 20.1, 20.0, 12.5, 9.8. Anal. Calcd for $\text{C}_{21}\text{H}_{22}\text{O}_2$: C, 82.33; H, 7.23. Found: C, 82.17; H, 7.35.

**6.1.18. [1 α (3R*,5R*),6** **α] -5-(Bicyclo[4.1.0]hept-1-yloxy)-2,6-dimethyl-3-heptanol (Diastereoselective Cyclopropanation of a Cyclic Chiral Enol Ether as Chiral Auxiliary) (176)**

To a solution of the chiral enol ether (333 mg, 1.39 mmol) in dry Et_2O (10.3 mL) was added diethylzinc (10.3 mL, 1 M in hexane) at 24° and stirred for a minute.

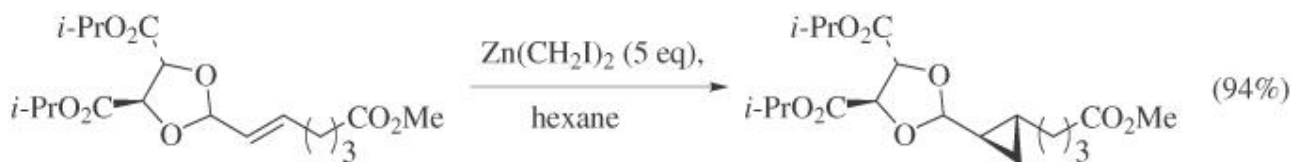
To this mixture CH_2I_2 (1.2 mL, 14.9 mmol) was added dropwise for 10 minutes, and then allowed to stand for 2 hours at the same temperature. The reaction mixture was poured into aqueous NH_4Cl , extracted twice with ether, dried over MgSO_4 , and purified by MPLC on silica gel (elution with 6% ethyl acetate in hexane) to give 304.4 mg of a colorless oil (86%, >99.5% de): IR (neat) 3500 cm^{-1} ; $^1\text{H NMR}$ (CDCl_3) δ 3.61-3.55 (m, 2 H), 3.10 (br s, 1 H), 2.12 (dt, $J = 13.2$ and 5.4 Hz, 1 H), 2.07-1.95 (m, 3 H), 1.67-1.36 (m, 5 H), 1.31-1.15 (m, 4 H), 1.05 (m, 1H), 0.93 (d, $J = 6.8$ Hz, 3 H), 0.89 (d, $J = 6.8$ Hz, 3 H), 0.87 (d, $J = 6.8$ Hz, 3 H), 0.82 (d, $J = 6.8$ Hz, 3 H), 0.26 (dd, $J = 6.4$ and 5.4 Hz, 1 H); $^{13}\text{C NMR}$ (CDCl_3) δ 80.29, 73.43, 60.46, 34.06, 33.05, 30.22, 30.10, 24.46, 21.88, 21.51, 19.78, 18.55, 17.87, 17.78, 17.56. Anal. Calcd for $\text{C}_{16}\text{H}_{30}\text{O}_2$: C, 75.54; H, 11.89. Found: C, 75.26; H, 11.92.



**6.1.19. [1S-(1 α [S*(R*)],2 β)]- α -Methyl-
 α -[(N-Methyl-S-phenylsulfonimidoyl)
Methyl]-2-(2-Methyl-1-propenyl)cyclopropanemethanol
(Diastereoselective Cyclopropanation of an Acyclic Chiral Allylic Alcohol
as Chiral Auxiliary) (261)**

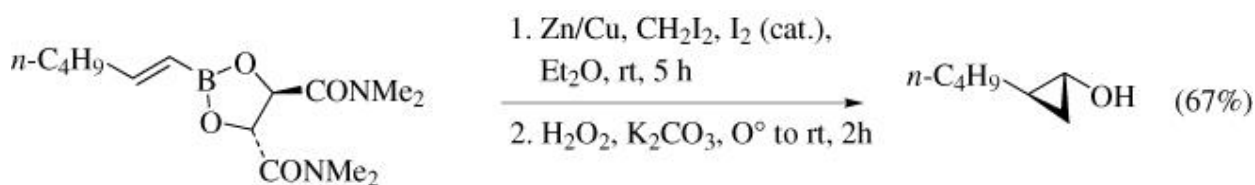
A 100-mL three-necked flask equipped with a heating mantle and magnetic stirring bar was charged with glacial acetic acid (50 mL) and silver acetate (50 mg); the suspension was brought to boiling. The heating mantle was turned off and 10-mesh granular zinc (5.583 g, 85.4 mmol) was added all at once to the stirred hot solution. After 30 seconds the liquid was carefully decanted and the zinc-silver couple was washed with five 50-mL portions of anhydrous diethyl ether. Et_2O (40 mL) was then poured onto the couple, a condenser and addition funnel were fitted to the flask, and the atmosphere was replaced with argon. A small crystal of iodine was added to the stirred ethereal suspension and the mixture was brought to reflux. CH_2I_2 (3.4 mL, 42.7 mmol) was then added dropwise via the addition funnel. After the addition was complete the suspension was refluxed a further 15 minutes and then stirred at room temperature for 1 hour. The diene (1.253 g, 4.3 mmol) in diethyl ether (10 mL) was then added and the mixture was gently refluxed. The reaction progress was monitored by TLC (2/1, hexane/ethyl acetate). After 5 minutes the starting material was consumed and the reaction mixture was filtered through glass wool into ice-cold saturated ammonium chloride (100 mL). After vigorous shaking the layers were separated and the aqueous layer was

extracted twice with 50-mL portions of ether. The combined organic extracts were washed successively with saturated aqueous NH_4Cl and saturated NaHCO_3 , then dried over MgSO_4 , filtered, and concentrated. The crude yellow gum (15:1 ratio of desired product to three minor products) was purified by medium-pressure liquid chromatography over silica gel (15/1, hexane/ethyl acetate as eluent) to provide the desired monocyclopropane as a white, crystalline solid (76%): mp 62–63°; $[\alpha]_D^{25} - 67.7^\circ$ (c 1.27, CHCl_3); IR (CHCl_3) 3240 (br), 3080 (w), 3040 (w), 3010 (s), 2935 (s), 1607 (w), 1590 (w), 1452 (s), 1380 (m), 1250 (s), 1156 (s) cm^{-1} ; $^1\text{H NMR}$ (CDCl_3) δ 8.1–7.8 (m, 2 H), 7.8–7.5 (m, 3 H), 6.63 (br s, 1 H), 4.58 (d, $J = 8.5$ Hz, 1 H), 3.25 (q, $J = 14$ Hz, 2 H), 2.65 (s, 3 H), 1.75 (s, 3 H), 1.70 (s, 6 H), 1.17–1.10 (m, 4 H); $^{13}\text{C NMR}$ (CDCl_3) δ 138.92, 133.14, 130.60, 129.63, 128.91, 127.35, 70.04, 64.78, 31.84, 28.72, 27.03, 25.47, 18.13, 13.06, 9.82. Anal. Calcd for $\text{C}_{17}\text{H}_{25}\text{NO}_2\text{S}$: C, 66.41; H, 8.20. Found: C, 66.26; H, 7.99.



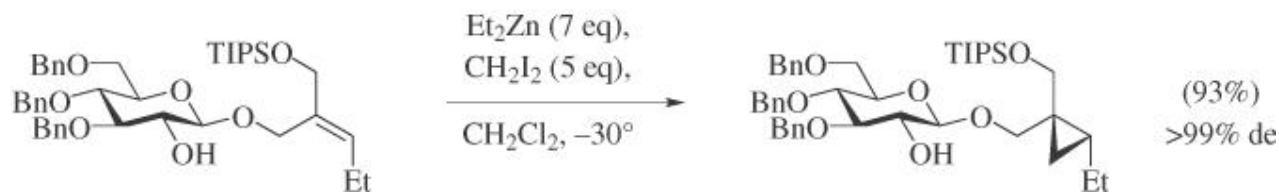
6.1.20. [4*R*-[2 α (1*R,2*R**),4 α ,5 β]]-Bis(1-methylethyl)ester, 2-[2-(4-Methoxy-4-oxobutyl)cyclopropyl]-1,3-dioxolane-4,5-dicarboxylic Acid (Diastereoselective Cyclopropanation of an Acyclic Chiral Allylic Acetal as Chiral Auxiliary) (161)**

To a solution of the acetal (0.744 g, 2 mmol) in 20 mL of dry hexane was added diethylzinc (10 mmol, 5 mL of 2.0 M hexane solution) at -20° . CH_2I_2 (1.62 mL, 20 mmol) was added dropwise to the resulting stirred solution and the mixture was vigorously stirred at -20° for 4 hours and at 0° for 4 hours. The reaction mixture was poured into cold aqueous NH_4Cl and the product was extracted with ether repeatedly. The ether layers were washed with $\text{Na}_2\text{S}_2\text{O}_3$ and water. The combined ether layers were dried over Na_2SO_4 and concentrated in vacuo. Purification by chromatography on silica gel (hexane/ethyl acetate, 3/1) afforded the pure cyclopropane as a colorless oil (0.726 g, 94% yield): IR (neat) 3000, 2950, 1750, 1735, 1375, 1220, 1105, 905 cm^{-1} ; $^1\text{H NMR}$ (CCl_4) 4.75 (d, $J = 5.8$ Hz, 1 H), 3.57 (s, 3 H), 1.28 (d, $J = 6.2$ Hz, 12 H), 0.17–1.17 (m, 4 H). Anal. Calcd for $\text{C}_{19}\text{H}_{30}\text{O}_8$: C, 59.05; H, 7.83. Found: C, 59.07; H, 7.81.



6.1.21. (1*R*,2*R*)-(-)-2-*n*-Butyl-1-cyclopropanol (Diastereoselective Cyclopropanation of an Acyclic Chiral Vinyl Boronate as Chiral Auxiliary) (178)

In a 100-mL flask under an argon atmosphere, Zn/Cu couple (12 g, from Zn and CuSO₄), (34) a small amount of I₂, CH₂I₂ (4.9 mL, 60.8 mmol), and ether (40 mL) were charged, and the mixture was refluxed for 30 minutes with magnetic stirring. To it was added at room temperature a solution of the boronate ester [20 mmol, freshly prepared from the boronic acid and (+)-*N,N,N*φ,*N*φ-tetramethyltartramide] in ether (12 mL), and a slightly exothermic reaction took place. An additional 8 mL of ether was used to wash the container. Stirring was continued for 5 hours at room temperature, then water (20 mL) was added with ice cooling, and the mixture was stirred at room temperature overnight. The excess metal was filtered off and washed with THF, and the filtrate washed with saturated aqueous NH₄Cl (3 × 20 mL). The aqueous phase was extracted with ether (3 × 20 mL), the extract combined with the organic phase, and the mixture was washed with saturated aqueous NaCl (3 × 20 mL) and dried over a small amount of MgSO₄ for a short time. Filtration of the desiccant and evaporation of the solvent gave ca. 3.4 g of slightly wet white solid that contained no olefinic protons by ¹H NMR. The crude boronic acid was dissolved in THF (70 mL) and oxidized by successive addition of 2 M KHCO₃ (20 mL) and 30% H₂O₂ (6.0 mL) with ice cooling followed by 2 hours of stirring at room temperature. Ether (70 mL) was added, and the mixture was washed with saturated aqueous NaCl (3 × 20 mL). The aqueous phase was extracted with ether (3 × 20 mL), and the extract combined with the organic phase and dried over Na₂SO₄. After filtration of the solid and evaporation of the solvent, 2.73 g of a colorless oil, from which the cyclopropanol was isolated by chromatography on silica gel (Merck Kieselgel 60 of 230–400 mesh, 130 g), 10–20% EtOAc/hexane and purified by distillation: bp (bath temperature) 80–85° (4 Torr); 1.53 g (67%); [α]_D²³ – 56.3° (c 0.678, EtOH); 94% ee (by capillary GC analysis for its MTPA ester); IR (neat) 3300, 3075, 2955, 2925, 2855, 1460, 1380, 1200, 1150 cm⁻¹; ¹H NMR (100 MHz, CDCl₃) δ 3.18 (ddd, *J* = 6.2, 2.6 and 2.4 Hz, 1 H), 2.0 (s, 1 H), 1.6–0.4 (m, 11 H), 0.4–0.1 (m, 1 H). Anal. Calcd for C₇H₁₄O : C, 73.63; H, 12.36. Found: C, 73.30; H, 12.39.



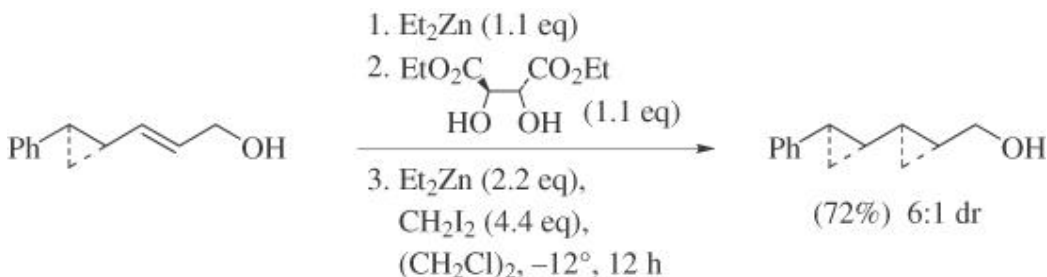
6.1.22. (2'*R*,3'*R*)-2'-[(Triisopropylsilyl)oxy]-2',3'-methanopentyl-3,4,6-tri-*O*-benzyl- β -*D*-glucopyranose (Diastereoselective Cyclopropanation of an Acyclic Chiral Ether as Chiral Auxiliary) (261a)

To a solution of the glucopyranoside (8.25 g, 11.7 mmol) in CH_2Cl_2 (120 mL) cooled to -30° was added in one portion diethylzinc (8.4 mL, 81.9 mmol). After 10 minutes of stirring, CH_2I_2 (4.7 mL, 58.5 mmol) was added to the solution over a period of one minute. When TLC analysis (15% EtOAc/hexane) no longer showed any starting material (10 hours), the cloudy solution was slowly poured in a stirred mixture of ether (200 mL) and saturated aqueous NH_4Cl (50 mL) at 0° . To this solution was added a minimum amount of 10% aqueous HCl to dissolve the white precipitate. The layers were separated, and the aqueous layer was extracted with ether (2×50 mL). The combined organic layers were washed with 0.05 M aqueous Na_2SO_3 (50 mL), saturated aqueous NaHCO_3 (50 mL), and saturated aqueous NaCl (50 mL). The organic layer was dried over MgSO_4 and concentrated under reduced pressure. The crude product of the reaction was analyzed by HPLC to obtain a diastereomeric ratio of $>100:1$ [4 μm silica gel NOVA-PAK, 8 mm \times 20 cm; 8% EtOAc/hexane; flow rate 1 mL/minute, T_r (major) 15.7 minutes, T_r (minor) 20.4 minutes]. The residue was purified by chromatography on silica gel (6% EtOAc/hexane) to produce

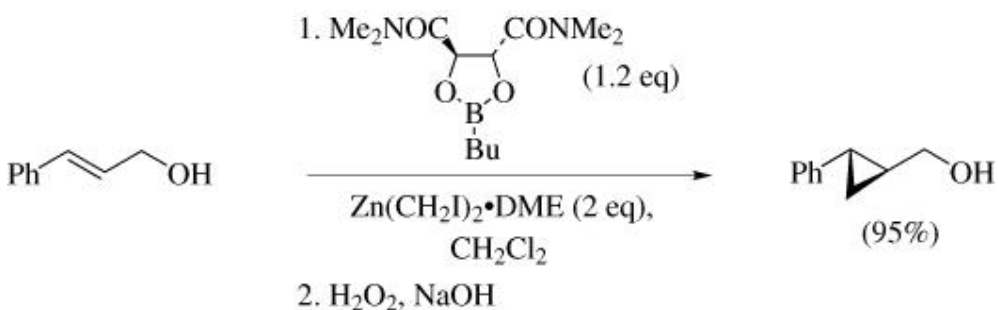
(2'*R*,3'*R*)-2'-[(triisopropylsilyl)oxy]-2',3'-methanopentyl-3,4,6-tri-*O*-benzyl- β -*D*-glucopyranose (7.8 g, 93%) as a viscous colorless oil. After chromatography, the HPLC and ^1H NMR analyses indicated the presence of only one diastereomer: R_f 0.3 (10% EtOAc/hexane); $[\alpha]_D - 11.7^\circ$ (c 2.0, CHCl_3); IR (neat) 3460 (br), 3020, 2940, 2860, 1490, 1450, 1360, 1100 (v. br), 875, 780, 740, 690 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.44-7.21 (m, 15 H), 5.02 (d, $J = 11$ Hz, 1 H), 4.89 (d, $J = 11$ Hz, 1 H), 4.86 (d, $J = 11$ Hz, 1 H), 4.65 (d, $J = 12$ Hz, 1 H), 4.60 (d, $J = 11$ Hz, 1 H), 4.58 (d, $J = 12$ Hz, 1 H), 4.36 (d, $J = 7$ Hz, 1 H), 3.95 (d, $J = 11$ Hz, 1 H), 3.82-3.72 (m, 4 H), 3.66-3.59 (m, 3 H), 3.50 (d, $J = 10$ Hz, 1 H), 3.52-3.49 (m, 1 H), 2.53 (s, 1 H), 1.53-1.36 (m, 2 H), 1.17-1.05 (m, 21 H), 1.02 (t, $J = 7$ Hz, 3 H), 0.81-0.76 (m, 1 H), 0.71 (dd, $J = 9$ and 5 Hz, 1 H), 0.23 (t, $J = 5$ Hz, 1 H); ^{13}C NMR (75 MHz, CDCl_3) 138.7, 138.2, 138.1, 128.2, 128.2, 128.2, 127.8, 127.8, 127.6, 127.5, 127.4, 127.4, 102.5, 84.4, 77.5, 75.2, 74.9, 74.9, 74.8, 73.4, 69.6, 68.9, 67.4, 26.4, 22.8, 22.0, 17.9, 14.7, 14.2, 11.9.

**6.1.23. (1*R*,3*S*,4*S*,6*R*)-1-Hydroxymethyl-6-phenylbicyclopropane
(Enantioselective Cyclopropanation of an Acyclic Alkene Using a Chiral
Tartrate as a Stoichiometric Additive) (261b)**

Et₂Zn in hexanes (1.0 M; 0.48 mL, 0.48 mmol) was added dropwise with stirring to the allylic alcohol (75 mg, 0.43 mmol) in 1,2-dichloroethane



(3 mL) at 0°. After 0.5 hour, L-(+)-diethyl tartrate (99 mg, 0.48 mmol) in 1,2-dichloroethane (1 mL) was added and the reaction mixture was stirred for 1 hour, cooled to -12° and Et₂Zn (0.89 mL, 0.89 mmol) was added. After 1 hour, CH₂I₂ (0.46 g, 0.15 mL, 1.75 mmol) was added and the resulting solution was stirred at -12° for 12 hours, quenched with saturated aqueous NH₄Cl (5 mL), and extracted with Et₂O (2 × 15 mL). The organic phase was washed with 10% NH₄Cl (15 mL), H₂O (2 × 15 mL), and brine (2 × 15 mL), dried and filtered. Rotary evaporation and chromatography (hexanes:EtOAc 4:1) gave (1*R*,3*S*,4*S*,6*R*)-1-hydroxymethyl-6-phenylbicyclopropane admixed with (1*S*,3*R*,4*S*,6*R*)-1-hydroxymethyl-6-phenylbicyclopropane (6:1, 58 mg, 72%) as a colorless oil: *R*_f 0.20 (hexanes:EtOAc 4:1); IR (film) 3360, 2871, 1605, 1499, 1021, 745, 697 cm⁻¹; ¹H NMR (270 MHz, CDCl₃) δ 7.27-7.00 (m, 5 H), 3.49-3.42 (m, 2 H), 1.74 (br s, 1 H), 1.68-1.62 (m, 1 H), 1.16-1.08 (m, 1 H), 0.98-0.73 (m, 4 H), 0.47-0.36 (m, 2 H); ¹³C NMR (75.1 MHz, CDCl₃) 143.8, 128.3, 125.6, 125.4, 66.8, 24.4, 22.2, 20.0, 18.6, 14.0, 8.0; LRMS (CI, NH₃) *m/z* 206 (M + NH₄)⁺, 188 (M⁺), 171, 77. Anal. Calcd for C₁₃H₁₆O : C, 82.94; H, 8.57. Found: C, 83.13; H, 8.74.

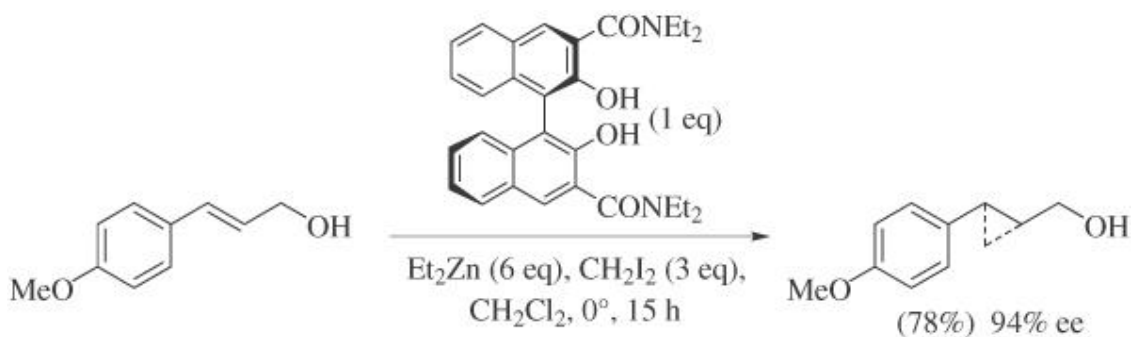


6.1.24. (+)-(1*S*,2*S*)-2-Phenylcyclopropanemethanol (Enantioselective Cyclopropanation of an Acyclic Alkene Using a Chiral Dioxaborolane as a Stoichiometric Additive) (187)

To a solution of dry DME (1.60 mL, 14.0 mmol) in anhydrous CH₂Cl₂ (45 mL) cooled at -10° (internal temperature) was added diethylzinc (1.50 mL, 14.9 mmol). Then, to this stirred solution was added CH₂I₂ (2.40 mL, 29.8 mmol) over 15–20 minutes while maintaining the internal temperature between -8 and -12°. After completion of the addition, the resulting clear solution was stirred for an additional 10 minutes at -10°. A solution of the dioxaborolane ligand (2.41 g, 8.94 mmol) in anhydrous CH₂Cl₂ (10 mL) was then added via cannula under argon over 5–6 minutes, followed immediately by a solution of cinnamyl alcohol (1.00 g, 7.45 mmol) in anhydrous CH₂Cl₂ (10 mL) added via cannula under argon over 5–6 minutes while maintaining the internal temperature under -5° at all times. The cooling bath was removed, and the reaction mixture was allowed to warm to room temperature and was stirred for 8 hours at that temperature. Then, the reaction was quenched with saturated aqueous NH₄Cl solution (10 mL) and 10% aqueous HCl solution (10 mL). The mixture was then diluted with ether (60 mL) and transferred into a separatory funnel. The reaction flask was rinsed with ether (15 mL) and 10% aqueous HCl solution, and both solutions were transferred into the separatory funnel. The two layers were separated, and the aqueous layer was extracted with ether (20 mL). The combined organic layers were transferred into an Erlenmeyer flask, and a solution containing 60 mL of 2 N aqueous NaOH and 10 mL of 30% aqueous H₂O₂ was added in one portion. The resulting biphasic solution was stirred vigorously for 5 minutes. The two layers were then separated, and the organic layer was successively washed with 10% aqueous HCl (50 mL), saturated aqueous Na₂SO₃ solution (50 mL), saturated aqueous NaHCO₃ solution (50 mL), and brine (50 mL), dried over MgSO₄, filtered, and concentrated under reduced pressure. The crude product was left under vacuum (0.2 mm Hg) overnight (12–16 hours) to remove the *n*-butanol produced in this oxidative workup (this last step is not necessary if the product is purified by flash chromatography). The product was purified by Kugelrohr distillation (90°, 0.8 mm Hg) to afford

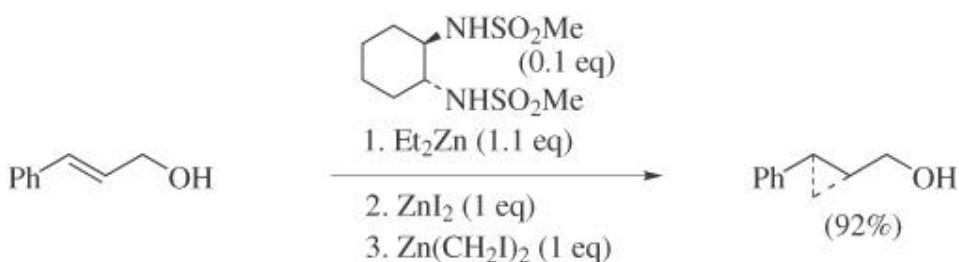
(+)-(1*S*,2*S*)-2-phenylcyclopropanemethanol (1.05 g, 95%) as a colorless oil: bp 90° (0.8 mm Hg); *R*_f 0.31 (30% EtOAc/hexanes); [α]_D + 82° (c 1.74 EtOH) [lit. (227) [α]_D - 92° (c 1.23, EtOH) for the enantiomer]; ¹H NMR (400 MHz, CDCl₃) δ 7.30-7.25 (m, 2 H), 7.20-7.15 (m, 1 H), 7.10-7.07 (m, 2 H), 3.67-3.59 (m, 2 H), 1.86-1.82 (m, 1 H), 1.75 (br s, 1 H), 1.51-1.43 (m, 1 H), 1.01-0.92 (m, 2 H); ¹³C NMR (100 MHz, CDCl₃) 142.5, 128.3, 125.8, 125.6, 66.3, 25.2, 21.2, 13.8. Anal. Calcd for C₁₀H₁₂O : C, 81.04; H, 8.16. Found: C, 81.15; H, 8.30.

The enantiomeric excess (94% ee) was determined by GC analysis of the trifluoroacetate ester derived from (1*S*,2*S*)-2-phenyl-1-cyclopropanemethanol: Column: Cyclodex G-TA, 0.32 mm × 30 m. Pressure 25 psi. Isotherm: 110°. *t*_R (minor) 11.5 minutes, *t*_R (major) 12.0 minutes.



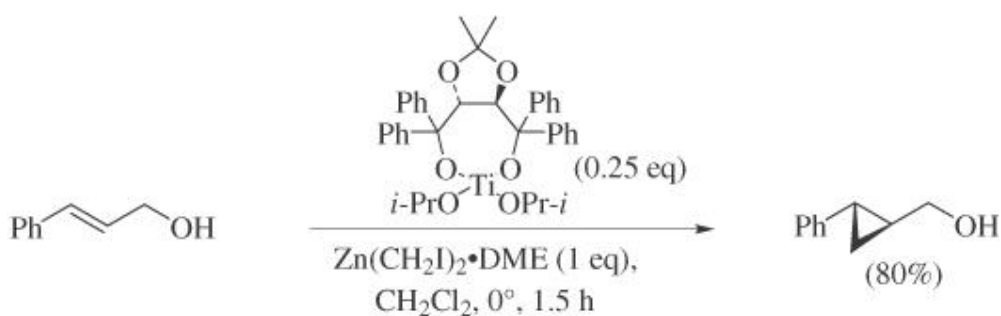
**6.1.25. (-)-(1*R*,2*R*)-2-(4-Methoxyphenyl)cyclopropanemethanol
(Enantioselective Cyclopropanation of an Acyclic Alkene Using a Chiral Binol as a Stoichiometric Additive) (199)**

To a solution of (*R*)-*N,N,N',N'*-tetraethyl-BINOL-3,3'-dicarboxamide (48 mg, 0.1 mmol) and (*E*)-3-(4-methoxyphenyl)-2-propen-1-ol (16 mg, 0.1 mmol) in anhydrous CH_2Cl_2 (1 mL) were added diethylzinc (1.0 M solution in hexane, 0.6 mL) and CH_2I_2 (0.024 mL, 0.3 mmol) at 0° under a nitrogen atmosphere and the mixture was stirred for 15 hours at the same temperature. The mixture was allowed to warm to room temperature and the reaction was quenched with 2 M NaOH solution. After extraction three times with ether, the combined organic layers were successively washed with 2 M aqueous NaOH and brine, dried over anhydrous MgSO_4 , and concentrated under reduced pressure. The residue was purified by TLC on silica gel (developed with diisopropyl ether) to give (-)-(1*R*,2*R*)-2-(4-methoxyphenyl)cyclopropanemethanol (13.9 mg, 78%) as a colorless oil. The enantiomeric excess was determined to be 94% ee by HPLC analysis using a Daicel Chiralcel OD column (hexane:*i*-PrOH=15:1). $[\alpha]_D^{23} - 63.5^\circ$ (*c* 1.05 EtOH); IR (KBr) 3318, 1518, 1461, 1255, 1178, 1032, 818 cm^{-1} ; $^1\text{H NMR}$ (CDCl_3) δ 7.01 (d, *J* = 8.9 Hz, 2 H), 6.81 (d, *J* = 8.9 Hz, 2 H), 3.78 (s, 3 H), 3.61 (m, 2 H), 1.79 (m, 1H), 1.58 (br s, 1 H), 1.40 (m, 1 H), 0.89 (m, 2 H). Anal. Calcd for $\text{C}_{11}\text{H}_{14}\text{O}_2$: C, 74.13; H, 7.92. Found: C, 74.17; H, 7.78. The chiral additive was recovered in 87% yield without loss of optical purity by acidification of the aqueous layer and extraction with chloroform.



6.1.26. (-)-(1*R*,2*R*)-2-Phenylcyclopropanemethanol (Enantioselective Cyclopropanation of an Acyclic Alkene Using a Chiral Disulfonamide as Catalyst) (201)

To a flame-dried, 15-mL, two-necked, round-bottom flask (flask A) equipped with a stir bar, septum, and argon inlet were added cinnamyl alcohol (134 mg, 1.00 mmol) and the promoter (27 mg, 0.1 mmol, 0.1 equiv.). The flask was evacuated and filled with argon (3x), and then CH₂Cl₂ (3 mL) was added. The solution was cooled under argon to 0°, and diethylzinc (113 μL, 1.10 mmol, 1.10 equiv.) was added. The solution was stirred at 0° for 10 minutes. To a flame-dried, 25-mL, two-necked, round-bottom flask (flask B) equipped with a stir bar, septum, and argon inlet were added iodine (508 mg, 2.00 mmol, 2.00 equiv) and CH₂Cl₂ (10 mL). The suspension was cooled under argon to 0°, and diethylzinc (103 μL, 1.00 mmol, 1.00 equiv.) was added. A thick white precipitate immediately formed. The slurry was stirred at 0° for 10 minutes. To a flame-dried, 100 mL, two-necked, round-bottom flask (flask C) equipped with a stir bar, septum, and argon inlet were added diiodomethane (161 μL, 2.00 mmol, 2.00 equiv.) and CH₂Cl₂ (24 mL). The solution was cooled to 0°, and diethylzinc (103 μL, 1.00 mmol, 1.00 equiv.) was added with subsequent stirring for 5 minutes (white precipitate formed after ~2 minutes). The contents of flask A were added via cannula over ~30 seconds to flask B. The resulting thick white slurry was stirred at 0° for 2 minutes and was transferred in like manner to flask C. The mixture was again a thick white slurry and was maintained at 0°, and the reaction progress was monitored periodically as follows. An aliquot (5–10 drops) was removed via cannula into a precooled (0°) solution of CH₂Cl₂ (0.5 mL) containing TMEDA (5 drops) After washing with 2 N HCl (0.5 mL), this solution was passed through a small plug of Florisil (~0.125 in.), followed by EtOAc (0.5 mL). This solution was then assayed by GC (HP-U2, isothermal 180°, *t_R* 5.9 min). The reaction was quenched after 45 minutes with 2 N NaOH (13 mL). The organic layer was removed, the aqueous layer was extracted with CH₂Cl₂ (2 × 20 mL), and the combined organic layers were dried (MgSO₄) and concentrated in vacuo. The product was then purified by silica gel column chromatography (hexane/EtOAc, 3/1) followed by bulb-to-bulb distillation to yield 136 mg (92%) of the desired product as a clear, colorless oil: bp 60° (0.01 Torr); IR 3336 (s); ¹H NMR (400 MHz) δ 7.30-7.24 (m, 2 H), 7.20-7.14 (m, 1 H), 7.10-7.06 (m, 2 H), 3.61 (ddd, *J* = 6.8, 11.2, 18.1 Hz, 2 H), 1.83 (td, *J_t* = 4.6 Hz, *J_d* = 9.3 Hz, 1 H), 1.82 (t, *J* = 4.5 Hz, 1 H), 1.46 (m, 1 H), 0.96 (m, 2H); ¹³C NMR (100 MHz) 142.38, 128.30, 125.74, 125.60, 66.52, 25.26, 21.24, 13.84; MS (EI) 148 (M⁺, 18); GC *t_R* 8.4 min (U2, isothermal 180 °C); HPLC *t_R* (1*R*,2*R*) 22.7 min (94.9%); *t_R* (1*S*,2*S*) 29.3 min (5.1%) (89% ee) (Daicel OJ, hexane/*i*-PrOH, 98/2, 1.0 mL/min); *R_f* 0.20 (hexane/EtOAc, 3/1). Anal. Calcd. for C₁₀H₁₂O (148.21): C, 81.04; H, 8.16. Found: C, 80.74; H, 8.26.



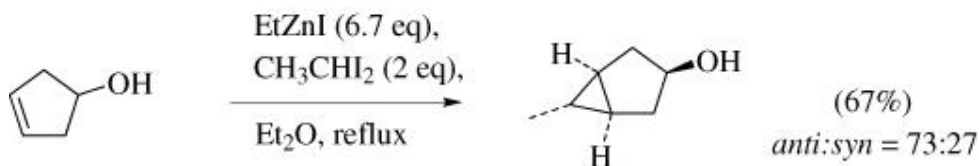
6.1.27. (+)-(1*S*,2*S*)-2-Phenylcyclopropanemethanol (Enantioselective Cyclopropanation of an Acyclic Alkene Using a Chiral Lewis Acid as Catalyst) (31)

6.1.27.1. Preparation of the catalyst

To a mixture of (4*R*,5*R*)-2,2-dimethyl- α, α' , α' -tetraphenyl-1,3-dioxolane-4,5-dimethanol (207) (TADDOL) (140 mg, 0.29 mmol) and 4 Å molecular sieves (1 g) in CH₂Cl₂ (5 mL) was added Ti(OPr-*i*)₄ (74 μ L, 0.25 mmol). After 1.5 hours of stirring at room temperature, the solvent was removed under reduced pressure and the residue was left under high vacuum for 2 hours.

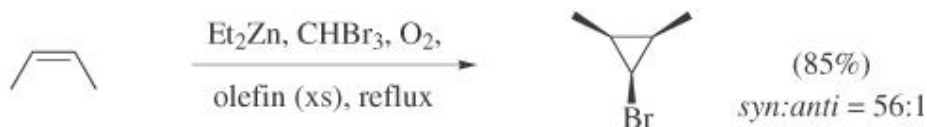
6.1.27.2. Cyclopropanation reaction

To a solution of CH₂I₂ (160 μ L, 2 mmol) in CH₂Cl₂ (5 mL) at 0° was added dropwise Et₂Zn (100 μ L, 1 mmol). The resulting solution was stirred at 0° for 15 minutes and a white precipitate was formed. The mixture was cooled to -40° and a solution of the catalyst in CH₂Cl₂ (5 mL) was added immediately followed by a solution of cinnamyl alcohol (140 mg, 1.04 mmol) in CH₂Cl₂ (5 mL). After 90 minutes of stirring at 0°, the resulting solution was cooled to -40° and poured into 30 mL of saturated aqueous NH₄Cl. The layers were separated and the aqueous layer was extracted three times with EtOAc. The combined organic layers were washed with saturated aqueous NH₄Cl, saturated aqueous NaCl, dried over MgSO₄ and concentrated under reduced pressure. The residue was purified by flash chromatography (20% EtOAc/hexanes) to afford the desired product (120 mg, 80%). The enantiomeric ratio was determined to be 90% ee by GC analysis of the trifluoroacetate derivative on a chiral stationary phase: Cyclodex GT-A column, 0.32 mm \times 30 m [25 psi, 110°, *t*_R 11.5 min (minor), 12.0 min (major)]. [α]_D + 84° (c 1.3, EtOH); lit. [α]_D + 86° (c 1.9, EtOH). (227)



6.1.28. 6-Methyl-endo-bicyclo[3.1.0]hexan-3-ol (Directed Cyclopropanation of a Cyclic Allylic Alcohol Using an Alkyl-Substituted Zinc Carbenoid) (66)

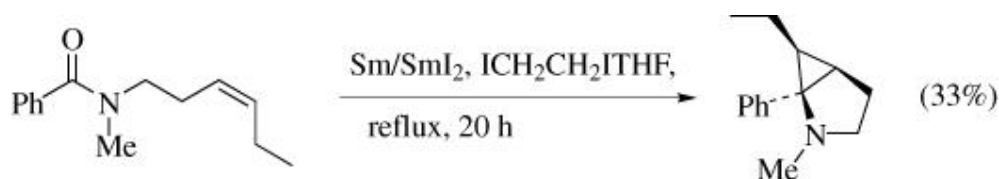
3-Cyclopenten-1-ol (0.03 mol) was added to ethylzinc iodide (0.2 mol) in ether (50 mL). The mixture was heated to reflux, ethylidene iodide (0.06 mol) was added and the reaction was continued for 12 hours. The reaction mixture was then worked up by dilution with ether followed by dropwise addition of saturated aqueous NH_4Cl (about 100 mL). The resulting aqueous layer was separated and washed with three 50-mL portions of ether. The combined ethereal layers were washed with four 50-mL portions of saturated aqueous Na_2CO_3 and four 25-mL portions of saturated aqueous NaCl , dried over a K_2CO_3 – MgSO_4 mixture, and distilled. The *anti/syn*-6-Methyl-endo-bicyclo[3.1.0]hexan-3-ol product mixture boiled at 80–83° (15 mm) and yielded 67% (*anti:syn* = 73:27) of the desired products. Anal. Calcd for $\text{C}_7\text{H}_{12}\text{O}$: C, 74.95; H, 10.80. Found: C, 74.81; H, 10.77. Individual samples of the pure *anti-endo* and *syn-endo* isomers were separated by GLC on a 2-m 20% Carbowax 20M on 60/80-mesh nonacid-washed Chromosorb W column. For *anti*-6-Methyl-endo-bicyclo[3.1.0]hexan-3-ol: $^1\text{H NMR}$ (CCl_4) δ 4.5 (m, 1 H), 3.2 (s, 1 H), 1.0 (br s, 3 H), 2.0–0.8 (m, 7 H). For *syn*-6-Methyl-endo-bicyclo[3.1.0]hexan-3-ol: $^1\text{H NMR}$ (CCl_4) δ 4.8 (m, 1 H), 3.3 (s, 1 H), 1.2 (d, $J = 7$ Hz, 3 H), 2.4–0.7 (m, 7 H).



6.1.29. *syn*-(2*S*,3*R*)-1-Bromo-2,3-dimethylcyclopropane (Directed Cyclopropanation of an Acyclic Alkene Using a Bromine-Substituted Zinc Carbenoid) (103)

The reaction was carried out in a pressure bottle of 100 mL inner volume equipped with a pressure-equilibrating dropping funnel of 50 mL volume. Into

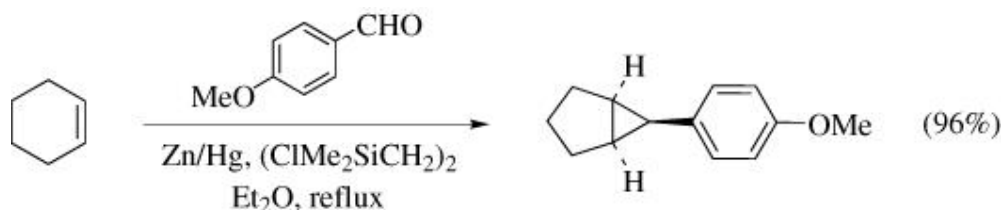
the bottle, 15 g of *cis*-but-2-ene was distilled, into which diethylzinc (2 mL, 20 mmol) was dissolved. The bottle was cooled in an ice-water bath, and bromoform (2.6 mL, 30 mmol) was added from the dropping funnel to the solution. Another pressure bottle of 140 mL volume containing oxygen at ca. 1.5 kg/cm² was connected to the reaction bottle through a needle valve and the reaction mixture was stirred for 2 hours. After the usual workup, distillation gave a 2.7-g portion boiling at 124–125° which was composed of (2*S*,3*R*)-1-bromo-2,3-dimethylcyclopropane at a purity of ca. 90% contaminated with several unidentified impurities. Some decomposition was observed during distillation. Pure (2*S*,3*R*)-1-bromo-2,3-dimethylcyclopropane was obtained by preparative GLC: ¹H NMR δ 3.25-3.05 (m, 1 H), 1.10-0.95 (m, 8 H). Anal. calcd for C₅H₉Br : C, 40.29; H, 6.09. Found: C, 40.38; H, 6.22. Detailed GLC analysis showed the presence of only trace amounts of *anti*-(2*S*,3*S*)-1-bromo-2,3-dimethylcyclopropane (~1.5%) in the reaction mixture.



6.1.30. 1-Phenyl-2-Methyl-6-endo-ethyl-2-azabicyclo[3.1.0]hexane (Intramolecular Cyclopropanation via an *in situ* Generated Samarium Carbenoid) (78)

Samarium powder (1.2–1.25 mmol), freshly distilled THF (5.5 mL), and 1,2-diiodoethane (0.55 mmol) in a 10-mL two-necked flask equipped with a condenser were placed under argon atmosphere. Heating the mixture at 67° for 1 hour with magnetic stirring provided a samarium metal/samarium iodide mixed reagent (Sm/SmI₂). To the mixture was added the alkene (1 mmol), and the resulting solution was stirred at 67° for 20 hours. After the reaction was complete, saturated NaHCO₃ (40 mL) was added to the reaction mixture and the products were extracted with Et₂O (3 × 20 mL). The combined extracts were dried (MgSO₄) and the solvent was evaporated. Purification by column chromatography on silica gel using hexane/ether (4/1) as an eluent (*R*_f = 0.6) provided 62 mg (0.31 mmol, 31%) of 1-phenyl-2-Methyl-6-endo-ethyl-2-azabicyclo[3.1.0]hexane as a pale yellow oil: IR (NaCl) 3023, 2960, 2870, 2842, 2788, 1601, 1579, 1493, 1446, 1303, 1279, 1208, 1134, 1065, 890, 756, 698 cm⁻¹; ¹H NMR (270 MHz, CDCl₃) δ 7.51-7.16 (m, 5 H), 3.48 (ddd, *J* = 9.27, 9.27, 2.44 Hz, 1 H), 1.84-1.61 (m, 2 H), 2.65 (q-like, 1 H), 2.42 (s, 3 H), 2.42-2.30 (m, 1 H), 2.02 (ddd, *J* = 7.32, 3.41,

2.44 Hz, 1 H), 1.51 (dd, $J = 8.78, 8.79$ Hz, 1 H), 1.41 (m, 1 H), 1.14 (t, $J = 7.33$ Hz, 3 H); ^{13}C NMR (68 MHz, CDCl_3) δ 143.53, 128.22, 128.04, 126.06, 57.41, 56.59, 37.33, 32.72, 30.49, 24.94, 18.98, 15.36; LRMS (EI), m/z 201 (M^+ , 13); HRMS calcd for $\text{C}_{14}\text{H}_{19}\text{N}$ 201.1518, found 201.1530.



6.1.31. 7-(4-Methoxyphenyl)bicyclo[4.1.0]heptane (Intermolecular Cyclopropanation via an *in situ*-Generated Zinc Carbenoid) (260)

6.1.31.1. Preparation of the zinc amalgam

Zinc powder (10 g, 0.153 mol) was added to a vigorously stirred solution of mercury(II) chloride (2.0 g, 7.2 mmol) and hydrochloric acid (0.5 mL, 10 M) in water (30 mL). The mixture was stirred for 10 minutes, the zinc filtered off then washed with water (75 mL), acetone (75 mL), ethanol (75 mL) and ether (75 mL). The amalgam was sieved, vacuum dried overnight and stored under argon atmosphere.

6.1.31.2. Cyclopropanation reaction

A solution of distilled *p*-methoxybenzaldehyde (0.229 mL, 1.88 mmol) in dry ether (1.8 mL) was added slowly via a motorized syringe pump over 36 hours to a vigorously stirred mixture of flame dried zinc amalgam (1.26 g, 18.8 mmol), dry ether (2 mL), cyclohexene (0.406 mL, 3.76 mmol), and 1,2-bis(chlorodimethylsilyl)ethane (2.20 mL of a 1.28 M solution in ether, 2.82 mmol) under argon at reflux. The cooled mixture was filtered through Celite and the separated zinc washed with ether (50 mL). The ethereal solution was washed with saturated aqueous sodium bicarbonate solution (2×40 mL), dried over MgSO_4 and concentrated in vacuo. The crude residue was chromatographed [silica, light petroleum (b.p. 30–40°)] twice to give the cyclopropane (0.364 g, 96%) (inseparable mixture of diastereoisomers. 15:1 *endo:exo* by NMR and GC) as a colorless oil. IR (NaCl, neat) 2999, 2930, 2860, 1608, 1573, 1507, 1242, 1033 cm^{-1} ; ^1H NMR (270 MHz, CDCl_3) δ (*endo*) 7.20 (2 H, dd, $J = 8.8$ and 2.9 Hz), 6.87 (2 H, dd, $J = 8.8$ and 2.9 Hz), 3.78 (3 H, s), 1.92–0.63 (11 H, m); m/z 202 (100%, M^+).

7. Tabular Survey

An effort has been made to tabulate all reported examples of Simmons-Smith cyclopropanation reactions (and variants) from 1973 until September 1999. Papers based on lectures given at a symposium or unpublished examples used in review articles are not included in this review; nor are articles written in languages other than French, German or English. No attempts were made to cover the patent literature.

All tables are based on the carbon count of the alkene. Protecting groups and chiral auxiliaries are not included in the carbon count. A ketal is counted as the corresponding precursor (ketone or aldehyde) and if an allylic alcohol is linked to an auxiliary, only the ether side containing the double bond is included in the count. When two compounds have the same carbon count, the compounds are ordered by increasing hydrogen number. For a given substrate, entries are ordered following increasing substitution on the carbenoid used.

Isolated yields of the combined cyclopropanes are included in parentheses and a dash indicates that no yield was reported. Where an enantiomeric (diastereomeric) excess or ratio is reported, it relates to the major product of a reaction. When polyenes are cyclopropanated, the ratio *mono:bis* refers to the selectivity toward formation of the monocyclopropanated adduct. The *syn:anti* ratio is put in brackets when the assignment of the asymmetric ratio was not made. Also, optimization trials for a given reaction protocol are not included. When a significant improvement in a specific reaction was developed, these results are tabulated as separate entries. Some examples are included in more than one table in order to facilitate the research of some substrates. Failure to cyclopropanate given substrates or miscellaneous reactions involving carbenoids are not included in the tabular survey.

The following abbreviations have been used in the tables:

5S-MEPY Methyl 2-pyrrolidine-5S-carboxylate

15-C-5 15-crown-5

Ac acetyl

AIBN azobis(isobutyronitrile)

BHT 2,6-di-*tert*-butyl-4-methylphenol

Bn benzyl

Boc *tert*-butyloxycarbonyl

Bz benzoyl

cat catalytic

conc	concentration
Cx	cyclohexyl
Dec	decomposition
DEE	1,2-diethoxyethane
DET	diethyl tartrate
DMCx	1,2-dimethoxycyclohexane
DME	1,2-dimethoxyethane
EE	1-ethoxyethyl
hex	hexane
MEM	2-methoxyethoxymethyl
MOM	methoxymethyl
Ms	methanesulfonyl
MS	molecular sieves
na	not appropriate
nd	not determined
Np	neopentyl
PMB	<i>p</i> -methoxybenzyl
PMP	<i>p</i> -methoxyphenyl
PS	polymer support
Red-Al	sodium bis(2-methoxyethoxy)aluminum hydride
TBDMS	<i>tert</i> -butyldimethylsilyl
TBDPS	<i>tert</i> -butyldiphenylsilyl
TFA	trifluoroacetic acid
THP	tetrahydropyranyl
TIPS	triisopropylsilyl
TMS	trimethylsilyl
Tr	trityl
Ts	<i>p</i> -toluenesulfonyl
xs	excess

Table I. Cyclopropanation of Cyclic, Achiral Alkenes

[View PDF](#)

Table II. Cyclopropanation of Cyclic, Achiral O- and N-Substituted Alkenes

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Table III. Cyclopropanation of Acyclic, Achiral Alkenes

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Table IV. Cyclopropanation of Acyclic, Achiral O- and N-Substituted Alkenes

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Table V. Cyclopropanation of *exo*-Methylene Containing Compounds

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Table VI. Cyclopropanation of Polyenes

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Table VII. Cyclopropanation of Cyclic, Chiral Alkenes

[View PDF](#)

Table VIII. Cyclopropanation of Acyclic, Chiral Alkenes

[View PDF](#)

Table IX. Cyclopropanation of Chiral O- and N-Substituted Alkenes

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Table X. Cyclopropanation of Allenes

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Table XI. Cyclopropanation of Cyclic Alkenes Containing a Cleavable Chiral Auxiliary

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Table XII. Cyclopropanation of Acyclic Alkenes Containing a Cleavable Chiral Auxiliary

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Table XIII. Cyclopropanation with Stoichiometric Chiral Additives

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Table XIV. Cyclopropanation with Chiral Catalysts

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Table XV. Cyclopropanation of Alkenes Using a Substituted Dihalide

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Table XVI. Cyclopropanation of Alkenes Using in situ Formation of the Carbenoid

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TABLE I. CYCLOPROPANATION OF CYCLIC, ACHIRAL ALKENES













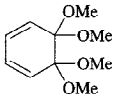
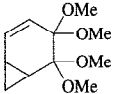
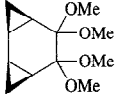
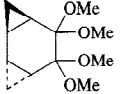



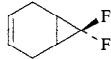








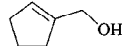
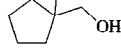


Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.										
C ₄ 	Zn/Cu, CH ₂ I ₂	 (—)	263										
C ₅ 	Et ₂ Zn, CH ₂ I ₂ , pentane	 I (—) +  II (—)	264										
	Zn, CF ₂ Br ₂ , I ₂ (cat.), THF, rt	 (21)	74										
	Et ₂ Zn, MeCHI ₂	 (40) <i>syn:anti</i> = 1.6/1	71										
	Et ₂ Zn, Me ₂ Cl ₂	 (45)	71										
	Zn/Cu, CH ₂ I ₂	 (—)	265										
C ₆ 	Zn/Ag, CH ₂ I ₂ , Et ₂ O	 I (20) +  II (2) +  III (70)	266										
		Zn/Ag, CH ₂ I ₂ (xs), Et ₂ O, reflux	 (85)	107, 267									
	Zn, CF ₂ Br ₂ , I ₂ (cat.), THF, rt	 (7)	74										
	Zn/Cu, CH ₂ I ₂	 (—)	268										
	Zn anode, 2e ⁻ , CH ₂ X ₂ , conditions, CH ₂ Cl ₂ /DMF (9:1)		<table border="1"> <thead> <tr> <th>Conditions</th> <th>X</th> <th>(%)</th> </tr> </thead> <tbody> <tr> <td>ZnBr₂ present initially</td> <td>Br</td> <td>(trace)</td> </tr> <tr> <td>ZnBr₂ absent initially</td> <td>I</td> <td>(20)</td> </tr> </tbody> </table>	Conditions	X	(%)	ZnBr ₂ present initially	Br	(trace)	ZnBr ₂ absent initially	I	(20)	70
Conditions	X	(%)											
ZnBr ₂ present initially	Br	(trace)											
ZnBr ₂ absent initially	I	(20)											
	Zn/Cu, CH ₂ I ₂	 (—)	263										
	Et ₂ Zn, CH ₂ I ₂	 (86)	71										
	Zn/Cu, CH ₂ I ₂	 (—)	269										
	Zn/Cu, CH ₂ Br ₂ , Et ₂ O, 45°, sonication	 (60)	270										
	Zn*, CH ₂ Br ₂ , solvent, reflux	<table border="1"> <thead> <tr> <th>Solvent</th> <th>(%)</th> </tr> </thead> <tbody> <tr> <td>diglyme</td> <td>(24)</td> </tr> <tr> <td>dioxane</td> <td>(18)</td> </tr> <tr> <td>THF</td> <td>(5)</td> </tr> <tr> <td>hexane</td> <td>(<1)</td> </tr> </tbody> </table>	Solvent	(%)	diglyme	(24)	dioxane	(18)	THF	(5)	hexane	(<1)	271
Solvent	(%)												
diglyme	(24)												
dioxane	(18)												
THF	(5)												
hexane	(<1)												

TABLE I. CYCLOPROPANATION OF CYCLIC, ACHIRAL ALKENES (Continued)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
CH ₂ Br ₂ , conditions	"	Conditions (%)	272
		Zn/Cu, Et ₂ O, reflux (64)	
		Zn, THF (53)	
Zn/Cu, CH ₂ Br ₂ , AcCl (0.02 eq), Et ₂ O	" (61)		41
Zn*, CH ₂ Br ₂ , Et ₂ O, reflux	" (94)		46
Zn/Cu, CH ₂ X ₂ , promoter, Et ₂ O	"	Promoter X (%)	43
		TiCl ₄ Br (58)	
		ultrasound Br (60)	
		TiCl ₄ I (69)	
Et ₂ Zn (x eq), CH ₂ ICl (y eq), C ₆ H ₆ , temp	"	x y Temp Reacted CH ₂ ICl % (%)	50
		0.8 1 35° 82 (62)	
		1 1 35° 96 (65)	
		1.5 1 35° 92 (60)	
		1 1.5 40° 58 (61)	
Et ₂ Zn (1 eq), CH ₂ ICl (1.5 eq), olefin (0.05 eq), 35°	"	Olefin (%) Reacted CH ₂ ICl (%)	273
		— (67) 65	
		2-heptene (65) 65	
		1-heptene (64) 67	
		isoprene (45) 55	
		<i>trans</i> -stilbene (34) 39	
		1,4-diphenyl-1,3-butadiene (25) 31	
		styrene (22) 31	
		α -methylstyrene (16) 21	
		1,1-diphenylethylene (12) 15	
1-phenyl-1,3-butadiene (8) 12			
Et ₂ Zn (x eq), CH ₂ X ₂ (y eq), dry air (10 mL/min), C ₆ H ₆	"	x CH ₂ X ₂ y (%)	50
		1.3 CH ₂ I ₂ 1.5 (91)	
		1.2 CH ₂ I ₂ 1.2 (35)	
		0.6 CH ₂ I ₂ 1.2 (93)	
		0.8 CH ₂ I ₂ 1.2 (92)	
		1 CH ₂ ICl 1.2 (91)	
		1 CH ₂ ICl 1.5 (99)	
		1 CH ₂ Br ₂ 1.6 (4)	
1 CH ₂ BrCl 1.5 (0)			
Zn, MX _n , CH ₂ X ₂ , Et ₂ O, reflux	"	MX _n X Zn:MX _n (%)	38
		CuCl I 10:1 (75)	
		CuSO ₄ I 10:1 (67)	
		CuI I 10:1 (67)	
		Cu(OAc) ₂ I 10:1 (49)	
		Cu(acac) ₂ I 10:1 (2)	
		CuCN I 10:1 (0)	
		Cu(OAc) ₂ I 65:1 (31)	
		AgCl I 10:1 (53)	
		AgOAc I 10:1 (54)	
AgOAc I 310:1 (75)			
AgCl Br 10:1 (38)			
Zn:CuCl (ratio), CH ₂ X ₂ , Et ₂ O, reflux	"	ratio Zn:CuCl X (%)	38
		10:1 I (75)	
		20:1 I (82)	
		50:1 I (90)	
		10:1 Br (53)	
		20:1 Br (29)	
		50:1 Br (3)	

TABLE I. CYCLOPROPANATION OF CYCLIC, ACHIRAL ALKENES (Continued)


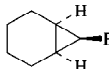
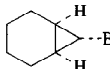

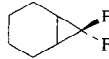

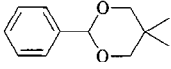
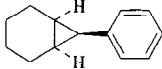
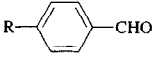
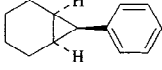
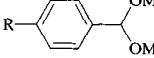
Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.																																												
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Zn*, CH ₂ I ₂ , DME/Et ₂ O	" (82)		44																																												
Zn*, MeCHBr ₂ , Et ₂ O, reflux		(24) 1:1	46																																												
Zn/Cu, MeCHI ₂ , Et ₂ O	" (5) 55:45		66																																												
Et ₂ Zn, MeCHI ₂ , cyclohexane	" (62) <i>syn:anti</i> = 1.6:1		71																																												
Et ₂ Zn (0.8 eq), CHBr ₃ (1 eq), dry air (10 mL/min), olefin (xs), 0-10°	 I +  II (84)	<i>I:II</i> = 1.9:1	73, 103																																												
Et ₂ Zn (x eq), CHBr ₃ (1 eq), dry air (y mL/min), solvent, 50°	<table border="1"> <thead> <tr> <th>x</th> <th>y</th> <th>Solvent</th> <th>(%)</th> <th><i>I:II</i></th> </tr> </thead> <tbody> <tr> <td>1</td> <td>0</td> <td>olefin</td> <td>(9)</td> <td>2.6:1</td> </tr> <tr> <td>1</td> <td>10</td> <td>olefin</td> <td>(52)</td> <td>1.3:1</td> </tr> <tr> <td>1</td> <td>10</td> <td>olefin</td> <td>(59)</td> <td>1.6:1</td> </tr> <tr> <td>0.28</td> <td>10</td> <td>hexane</td> <td>(18)</td> <td>1.8:1</td> </tr> <tr> <td>0.52</td> <td>10</td> <td>hexane</td> <td>(30)</td> <td>1.6:1</td> </tr> <tr> <td>0.74</td> <td>10</td> <td>hexane</td> <td>(36)</td> <td>1.6:1</td> </tr> <tr> <td>1</td> <td>10</td> <td>hexane</td> <td>(39)</td> <td>1.4:1</td> </tr> <tr> <td>1.4</td> <td>10</td> <td>hexane</td> <td>(32)</td> <td>1.1:1</td> </tr> </tbody> </table>	x	y	Solvent	(%)	<i>I:II</i>	1	0	olefin	(9)	2.6:1	1	10	olefin	(52)	1.3:1	1	10	olefin	(59)	1.6:1	0.28	10	hexane	(18)	1.8:1	0.52	10	hexane	(30)	1.6:1	0.74	10	hexane	(36)	1.6:1	1	10	hexane	(39)	1.4:1	1.4	10	hexane	(32)	1.1:1	103
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Et ₂ Zn, Me ₂ Cl ₂	 (59)		71																																												
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TABLE I. CYCLOPROPANATION OF CYCLIC, ACHIRAL ALKENES (Continued)

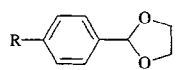
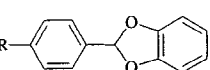

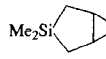
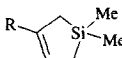
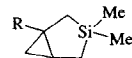

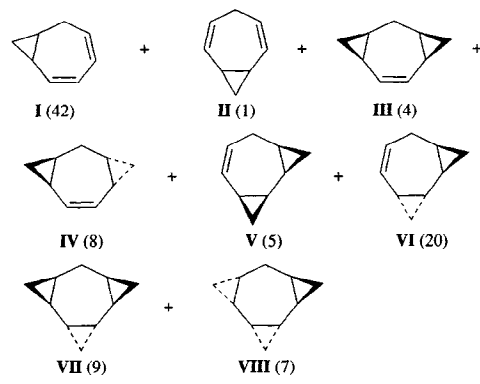


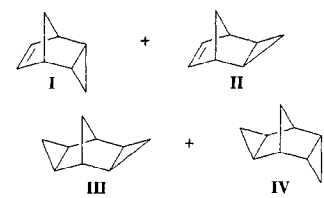

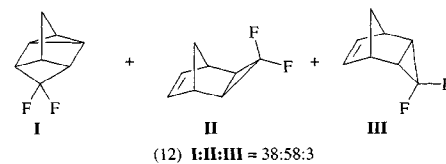

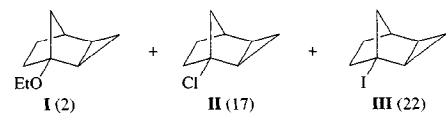
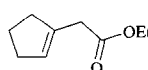
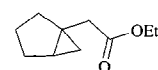
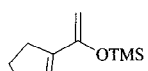
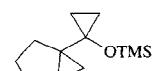
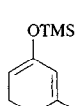
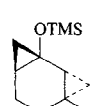
Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.												
	Zn/Hg, TMSCl, ZnCl ₂ , Et ₂ O, reflux	<table border="1"> <thead> <tr> <th>R</th> <th>(%)</th> <th>endo:exo</th> </tr> </thead> <tbody> <tr> <td>Me</td> <td>(38)</td> <td>6.1:1</td> </tr> <tr> <td>H</td> <td>(51)</td> <td>3.3:1</td> </tr> <tr> <td>Cl</td> <td>(30)</td> <td>2.9:1</td> </tr> </tbody> </table>	R	(%)	endo:exo	Me	(38)	6.1:1	H	(51)	3.3:1	Cl	(30)	2.9:1	276
R	(%)	endo:exo													
Me	(38)	6.1:1													
H	(51)	3.3:1													
Cl	(30)	2.9:1													
	Zn/Hg, TMSCl, ZnCl ₂ , Et ₂ O, reflux	<table border="1"> <thead> <tr> <th>R</th> <th>(%)</th> <th>endo:exo</th> </tr> </thead> <tbody> <tr> <td>H</td> <td>(20)</td> <td>4:1</td> </tr> <tr> <td>OMe</td> <td>(20)</td> <td>5:1</td> </tr> </tbody> </table>	R	(%)	endo:exo	H	(20)	4:1	OMe	(20)	5:1	276			
R	(%)	endo:exo													
H	(20)	4:1													
OMe	(20)	5:1													
	Zn/Cu, CH ₂ I ₂ , Et ₂ O, reflux	 (—)	277												
C ₆₋₇ 	Zn/Cu, CH ₂ I ₂	 <table border="1"> <thead> <tr> <th>R</th> <th>(%)</th> </tr> </thead> <tbody> <tr> <td>H</td> <td>(—)</td> </tr> <tr> <td>Me</td> <td>(—)</td> </tr> </tbody> </table>	R	(%)	H	(—)	Me	(—)	278						
R	(%)														
H	(—)														
Me	(—)														
C ₇ 	Zn/Cu, CH ₂ I ₂ , Et ₂ O	 <p> I (42) II (1) III (4) + IV (8) V (5) VI (20) + VII (9) VIII (7) </p>	279												
	Zn/Cu, CH ₂ I ₂ , Et ₂ O, reflux	I (12-14)	280												
	Zn/Cu, CH ₂ I ₂ , Et ₂ O	 <p> I II + (—) III IV + I:II:III:IV = — </p>	281												
	Zn, CF ₃ Br ₂ , I ₂ (cat.), THF, rt	 <p> I II III (12) I:II:III = 38:58:3 </p>	74												
	Zn/Cu, CH ₂ I ₂ , Et ₂ O, reflux	 <p> I (2) II (17) III (22) </p>	282												
	Zn/Ag, CH ₂ I ₂ , Et ₂ O, reflux	 (—)	283												
	Zn/Ag, CH ₂ I ₂ (xs), Et ₂ O, reflux	 (75)	107, 267												
	Zn/Ag, CH ₂ I ₂ (xs), Et ₂ O, reflux	 (80)	107, 267												

TABLE I. CYCLOPROPANATION OF CYCLIC, ACHIRAL ALKENES (Continued)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.								
	Zn*, CH ₂ I ₂ , DME/Et ₂ O	(67)	44								
	Zn/Cu, CH ₂ I ₂	(—)	268								
	Zn/Cu, CH ₂ I ₂	(—)	268								
	Zn/Ag, CH ₂ I ₂	(95)	284								
	Et ₂ Zn, CH ₂ I ₂	(61)	71								
	Zn/Cu, MeCH ₂ I, Et ₂ O	(13) 55:45	66								
	Zn/Cu, CH ₂ I ₂	(—)	285								
	Et ₂ Zn, MeCH ₂ I, cyclohexane	(71) <i>syn:anti</i> = 1.4:1	71								
	Zn/Cu, CH ₂ I ₂ , Et ₂ O, reflux	(50)	277								
C ₇₋₁₀	Et ₂ Zn, CH ₂ I ₂	<table border="1" style="display: inline-table; vertical-align: middle;"> <thead> <tr> <th>R</th> <th>(%)</th> </tr> </thead> <tbody> <tr> <td>Me</td> <td>(42)</td> </tr> <tr> <td><i>n</i>-Bu</td> <td>(42)</td> </tr> </tbody> </table>	R	(%)	Me	(42)	<i>n</i> -Bu	(42)	286		
R	(%)										
Me	(42)										
<i>n</i> -Bu	(42)										
C ₇₋₁₂	Et ₂ Zn, CH ₂ I ₂	" <table border="1" style="display: inline-table; vertical-align: middle;"> <thead> <tr> <th>R</th> <th>(%)</th> </tr> </thead> <tbody> <tr> <td>Me</td> <td>(—)</td> </tr> <tr> <td>Bu</td> <td>(—)</td> </tr> <tr> <td>Ph</td> <td>(—)</td> </tr> </tbody> </table>	R	(%)	Me	(—)	Bu	(—)	Ph	(—)	287
R	(%)										
Me	(—)										
Bu	(—)										
Ph	(—)										
C ₈	Zn/Ag, CH ₂ I ₂ , Et ₂ O, reflux	<table border="1" style="display: inline-table; vertical-align: middle;"> <thead> <tr> <th>X</th> <th>(%)</th> </tr> </thead> <tbody> <tr> <td>O</td> <td>(25)</td> </tr> <tr> <td>NCO₂Me</td> <td>(37)</td> </tr> <tr> <td>CH₂</td> <td>(70)</td> </tr> </tbody> </table>	X	(%)	O	(25)	NCO ₂ Me	(37)	CH ₂	(70)	288
X	(%)										
O	(25)										
NCO ₂ Me	(37)										
CH ₂	(70)										
	EtZnI, CH ₂ I ₂ , Et ₂ O, reflux	(—) I:II = 55:45	289								
	EtZnI, CH ₂ I ₂ , Et ₂ O, reflux	(23) + (28)	289								
	Zn/Cu, CH ₂ I ₂ , I ₂ (cat.), Et ₂ O, reflux	(82)	290								
	Zn/Ag, CH ₂ I ₂ , Et ₂ O, reflux	(45)	291								

TABLE I. CYCLOPROPANATION OF CYCLIC, ACHIRAL ALKENES (Continued)



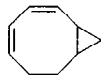
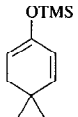
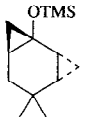

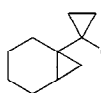

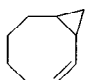


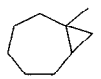

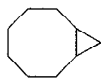
Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.																																																
 +  6 : 4	Et ₂ Zn, CH ₂ I ₂ , 50°	 (36) + other products	292																																																
	Zn/Ag, CH ₂ I ₂ (xs), Et ₂ O, reflux	 (78)	107, 267																																																
	Zn/Ag, CH ₂ I ₂ (xs), Et ₂ O, reflux	 (85)	107, 267																																																
	Zn/Cu, CH ₂ I ₂	 (—)	293																																																
	Zn anode, 2e ⁻ , CH ₂ Br ₂ , ZnBr ₂ present initially, CH ₂ Cl ₂ /DMF (9:1)	 (66)	70																																																
	Et ₂ Zn, CH ₂ I ₂ , cyclohexane	 (86)	71																																																
	Zn/Cu, CH ₂ Br ₂ , Et ₂ O, 45°, sonication	 (72)	270																																																
	Zn/Cu, CH ₂ Br ₂ , AcCl (0.02 eq), Et ₂ O	" (88)	41																																																
	Zn/Cu, CH ₂ X ₂ , promoter, Et ₂ O	<table border="1"> <thead> <tr> <th>Promoter</th> <th>X</th> <th>(%)</th> </tr> </thead> <tbody> <tr> <td>TiCl₄</td> <td>Br</td> <td>(73)</td> </tr> <tr> <td>ultrasound</td> <td>Br</td> <td>(72)</td> </tr> <tr> <td>TiCl₄</td> <td>I</td> <td>(90)</td> </tr> </tbody> </table>	Promoter	X	(%)	TiCl ₄	Br	(73)	ultrasound	Br	(72)	TiCl ₄	I	(90)	43																																				
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	Zn anode, 2e ⁻ , CH ₂ X ₂ , no ZnBr ₂ present initially, CH ₂ Cl ₂ /DMF (9:1)	<table border="1"> <thead> <tr> <th>X</th> <th>(%)</th> </tr> </thead> <tbody> <tr> <td>Br</td> <td>(64)</td> </tr> <tr> <td>I</td> <td>(75)</td> </tr> </tbody> </table>	X	(%)	Br	(64)	I	(75)	70																																										
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	Et ₂ Zn (1.3 eq), CH ₂ IX (1.5 eq), dry air (10 mL/min), C ₆ H ₆ , 50°	<table border="1"> <thead> <tr> <th>X</th> <th>(%)</th> </tr> </thead> <tbody> <tr> <td>I</td> <td>(98)</td> </tr> <tr> <td>Cl</td> <td>(99)</td> </tr> </tbody> </table>	X	(%)	I	(98)	Cl	(99)	50																																										
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I	(98)																																																		
Cl	(99)																																																		
	R ₃ Al (1.2 eq), CH ₂ I ₂ (1.2 eq), solvent, rt	<table border="1"> <thead> <tr> <th>R</th> <th>Solvent</th> <th>(%)</th> </tr> </thead> <tbody> <tr> <td>Me</td> <td>CH₂Cl₂</td> <td>(82)</td> </tr> <tr> <td>Me</td> <td>hexane</td> <td>(75)</td> </tr> <tr> <td>Et</td> <td>CH₂Cl₂</td> <td>(75)</td> </tr> </tbody> </table>	R	Solvent	(%)	Me	CH ₂ Cl ₂	(82)	Me	hexane	(75)	Et	CH ₂ Cl ₂	(75)	59																																				
R	Solvent	(%)																																																	
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Me	hexane	(75)																																																	
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	Zn, CH ₂ I ₂ , additive, Et ₂ O, 40°, 8 h	<table border="1"> <thead> <tr> <th>Source of zinc</th> <th>Pb (mol % of zinc)</th> <th>Additive</th> <th>(%)</th> </tr> </thead> <tbody> <tr> <td>Aldrich Chemical</td> <td>0</td> <td>—</td> <td>(96)</td> </tr> <tr> <td>E. Merck</td> <td>0</td> <td>—</td> <td>(96)</td> </tr> <tr> <td>Rare Metallic</td> <td>0</td> <td>—</td> <td>(89)</td> </tr> <tr> <td>Wako Pure Chemical</td> <td>0.04</td> <td>—</td> <td>(7)</td> </tr> <tr> <td>Nacalai Tesque</td> <td>0.06</td> <td>—</td> <td>(2)</td> </tr> <tr> <td>Kanto Chemical</td> <td>0.07</td> <td>—</td> <td>(1)</td> </tr> <tr> <td>F. Merck</td> <td>0</td> <td>Pb</td> <td>(20)</td> </tr> <tr> <td>E. Merck</td> <td>0</td> <td>Pb, TMSCl</td> <td>(97)</td> </tr> <tr> <td>E. Merck</td> <td>0</td> <td>Pb, Et₂AlCl</td> <td>(2)</td> </tr> <tr> <td>Wako Pure Chemical</td> <td>0.04</td> <td>Me₃SiCl</td> <td>(92)</td> </tr> <tr> <td>Wako Pure Chemical</td> <td>0.04</td> <td>Et₂AlCl</td> <td>(1)</td> </tr> </tbody> </table>	Source of zinc	Pb (mol % of zinc)	Additive	(%)	Aldrich Chemical	0	—	(96)	E. Merck	0	—	(96)	Rare Metallic	0	—	(89)	Wako Pure Chemical	0.04	—	(7)	Nacalai Tesque	0.06	—	(2)	Kanto Chemical	0.07	—	(1)	F. Merck	0	Pb	(20)	E. Merck	0	Pb, TMSCl	(97)	E. Merck	0	Pb, Et ₂ AlCl	(2)	Wako Pure Chemical	0.04	Me ₃ SiCl	(92)	Wako Pure Chemical	0.04	Et ₂ AlCl	(1)	40
Source of zinc	Pb (mol % of zinc)	Additive	(%)																																																
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TABLE I. CYCLOPROPANATION OF CYCLIC, ACHIRAL ALKENES (Continued)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.												
	Me ₃ Al (3 eq), MeCHCl ₂ (3 eq), CH ₂ Cl ₂ , rt	(92) <i>syn:anti</i> = 6.3:1	59												
	Et ₂ Zn, MeCHCl ₂ , cyclohexane	" (72) <i>syn:anti</i> = 1.3:1	71												
	Et ₂ Zn (x eq), CHBr ₃ (1 eq), dry air (10 mL/min), olefin (xs), temp	<table border="1"> <thead> <tr> <th>x</th> <th>Temp</th> <th>(%)</th> <th><i>syn:anti</i></th> </tr> </thead> <tbody> <tr> <td>0.65</td> <td>0-10°</td> <td>(75)</td> <td>7.1:1</td> </tr> <tr> <td>1</td> <td>50°</td> <td>(63)</td> <td>6.4:1</td> </tr> </tbody> </table>	x	Temp	(%)	<i>syn:anti</i>	0.65	0-10°	(75)	7.1:1	1	50°	(63)	6.4:1	73, 103 103
x	Temp	(%)	<i>syn:anti</i>												
0.65	0-10°	(75)	7.1:1												
1	50°	(63)	6.4:1												
	Et ₂ Zn (0.67 eq), CDBr ₃ (1 eq), dry air (10 mL/min), olefin (xs), 0-10°	(79) <i>syn:anti</i> = 6.9:1	103												
	Zn anode, 2e ⁻ , R ¹ R ² CX ₂ , ZnBr ₂ present initially, CH ₂ Cl ₂ /DMF (9:1)	<table border="1"> <thead> <tr> <th>R¹R²CX₂</th> <th>(%)</th> </tr> </thead> <tbody> <tr> <td>Me₂CBr₂</td> <td>(46)</td> </tr> <tr> <td>PhCHCl₂</td> <td>(20)</td> </tr> <tr> <td>PhCHBr₂</td> <td>(27)</td> </tr> </tbody> </table>	R ¹ R ² CX ₂	(%)	Me ₂ CBr ₂	(46)	PhCHCl ₂	(20)	PhCHBr ₂	(27)	70				
R ¹ R ² CX ₂	(%)														
Me ₂ CBr ₂	(46)														
PhCHCl ₂	(20)														
PhCHBr ₂	(27)														
	Et ₂ Zn, ClI ₂ I ₂	(—)	283												
	Zn/Cu, CH ₂ I ₂ , Et ₂ O, reflux	(20)	277												
C ₈₋₁₃	Zn/Cu, CH ₂ I ₂	<table border="1"> <thead> <tr> <th>R</th> <th>(%)</th> </tr> </thead> <tbody> <tr> <td>Me</td> <td>(—)</td> </tr> <tr> <td>Ph</td> <td>(—)</td> </tr> </tbody> </table>	R	(%)	Me	(—)	Ph	(—)	286						
R	(%)														
Me	(—)														
Ph	(—)														
C ₉	Zn/Cu, CH ₂ I ₂ , Et ₂ O, reflux	(—)	294												
	Zn/Cu, CH ₂ Br ₂ , AcCl (0.02 eq), Et ₂ O	(33)	41												
	Et ₂ Zn (1 eq), CH ₂ ICl (1.5 eq), dry air (10 mL/min), C ₆ H ₆ , 50°	" (77)	50												
	Zn/Cu, CH ₂ I ₂ , Et ₂ O, reflux	" (82)	294												
	Zn/Cu, CH ₂ I ₂ , I ₂ (cat.), Et ₂ O, reflux	(8) + (38)	295												
	Zn/Cu, CH ₂ I ₂ , I ₂ (cat.), Et ₂ O, reflux	I (35) + II (11)	295												
	Zn/Cu, CH ₂ I ₂	I (35) (major product)	296												

TABLE I. CYCLOPROPANATION OF CYCLIC, ACHIRAL ALKENES (Continued)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.												
	Et ₂ Zn, CH ₂ I ₂	 I (10) + II (53) + III (22)	297												
	Zn source, CH ₂ I ₂	<table border="1"> <thead> <tr> <th>Zn source</th> <th>I (%)</th> <th>II (%)</th> <th>III (%)</th> </tr> </thead> <tbody> <tr> <td>Zn/Ag</td> <td>(22)</td> <td>(35)</td> <td>(<1)</td> </tr> <tr> <td>Et₂Zn</td> <td>(14)</td> <td>(55)</td> <td>(16)</td> </tr> </tbody> </table>	Zn source	I (%)	II (%)	III (%)	Zn/Ag	(22)	(35)	(<1)	Et ₂ Zn	(14)	(55)	(16)	298
Zn source	I (%)	II (%)	III (%)												
Zn/Ag	(22)	(35)	(<1)												
Et ₂ Zn	(14)	(55)	(16)												
	Zn/Cu, CH ₂ I ₂ , I ₂ (cat.), Et ₂ O, reflux	 (68)	299												
	Zn/Cu, CH ₂ I ₂ , I ₂ (cat.), Et ₂ O, reflux	 (—)	299												
	Zn/Cu, CH ₂ I ₂ , 45°	 (-50)	300												
	Zn/Ag, CH ₂ I ₂ , Et ₂ O, reflux	" (70)	300												
	Zn/Ag, CH ₂ I ₂	 CO ₂ Et (54-62)	301, 302												
	EtZnI, CH ₂ I ₂ , Et ₂ O, reflux	 OTMS (47)	303												
	Zn/Ag, CH ₂ I ₂ (xs), Et ₂ O, reflux	 OTMS (68)	107, 267												
	Zn/Cu, CH ₂ I ₂ , Et ₂ O, reflux	 CO ₂ Et (—)	304												
	Zn/Cu, CH ₂ I ₂	 (—)	293												
 I + II I:II = 3:2	Zn/Cu, CH ₂ I ₂	 III + IV (30) III:IV = 2:3	305												
	Et ₂ Zn, CH ₂ I ₂ , cyclohexane	 (85)	71												
	Zn/Cu, CH ₂ I ₂ , I ₂ (cat.), Et ₂ O, reflux	 Fe(CO) ₃ (23)	306, 307												
	Zn/Cu, CD ₂ I ₂ , I ₂ (cat.), Et ₂ O, reflux	 D-Fe(CO) ₃ (—)	306, 307												

TABLE I. CYCLOPROPANATION OF CYCLIC, ACHIRAL ALKENES (Continued)

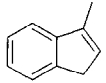
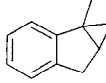
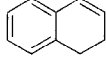
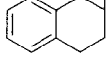
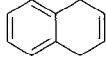
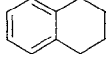

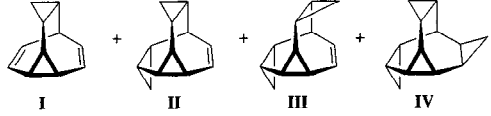

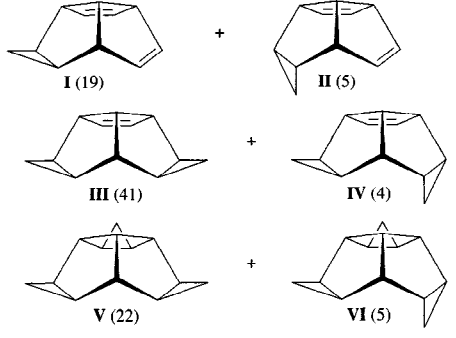
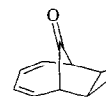
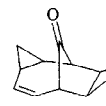
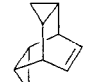
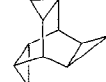
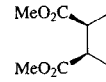
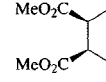
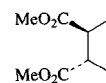
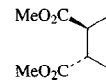
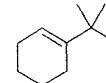
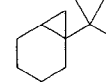
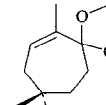
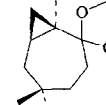
Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.															
	Zn/Cu, CH ₂ I ₂ , I ₂ (cat.), Et ₂ O	 (74)	308															
	Zn/Cu, CH ₂ I ₂ , Et ₂ O, reflux	 (47)	294															
	Zn/Cu, CH ₂ I ₂ , I ₂ (cat.), Et ₂ O, reflux	 (47)	309															
	Zn source, CH ₂ I ₂	 I + II + III + IV	298															
		<table border="1"> <thead> <tr> <th>Zn source</th> <th>I (%)</th> <th>II (%)</th> <th>III (%)</th> <th>IV (%)</th> </tr> </thead> <tbody> <tr> <td>Zn/Ag</td> <td>(4)</td> <td>(7)</td> <td>(11)</td> <td>(21)</td> </tr> <tr> <td>Et₂Zn</td> <td>(0)</td> <td>(3)</td> <td>(18)</td> <td>(59)</td> </tr> </tbody> </table>	Zn source	I (%)	II (%)	III (%)	IV (%)	Zn/Ag	(4)	(7)	(11)	(21)	Et ₂ Zn	(0)	(3)	(18)	(59)	
Zn source	I (%)	II (%)	III (%)	IV (%)														
Zn/Ag	(4)	(7)	(11)	(21)														
Et ₂ Zn	(0)	(3)	(18)	(59)														
	Zn/Ag, CH ₂ I ₂ , Et ₂ O	 I (19) + II (5) III (41) + IV (4) V (22) + VI (5)	310															
	Zn/Cu, CH ₂ I ₂	 (small amount)	295															
	Et ₂ Zn, CH ₂ I ₂	 (69)	297															
	Zn/Ag, CH ₂ I ₂ , Et ₂ O	" (67)	298															
	Et ₂ Zn (3.2 eq), CH ₂ I ₂ (5.2 eq), Et ₂ O	" (69)	298															
	Zn/Cu, CH ₂ I ₂	 (—)	311															
	Zn/Cu, CH ₂ I ₂	 (—)	311															
	Zn/Cu, CH ₂ I ₂ , Et ₂ O, reflux	 (—)	304															
	EtZnI, CH ₂ I ₂ , Et ₂ O, reflux	 (92)	312															

TABLE I. CYCLOPROPANATION OF CYCLIC, ACHIRAL ALKENES (Continued)

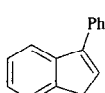
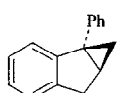
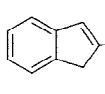
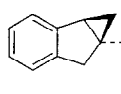
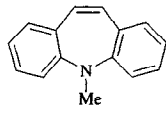
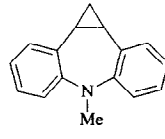
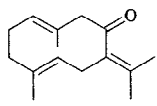
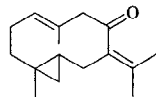
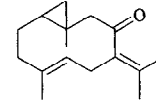
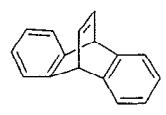
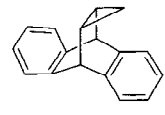
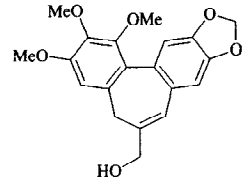
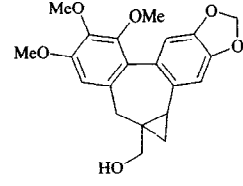
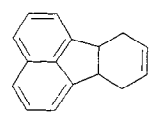
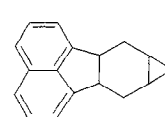
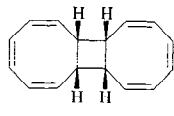
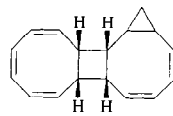
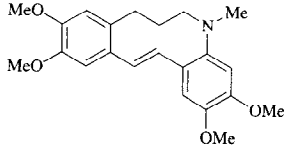
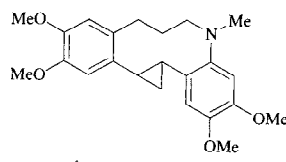
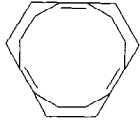
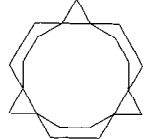
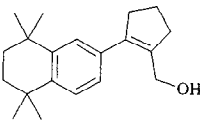
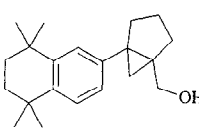
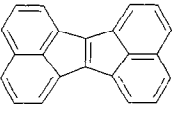
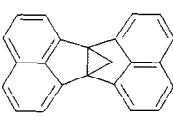
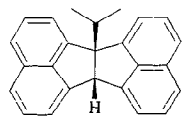
Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
	Zn/Cu, CH ₂ I ₂ , Et ₂ O, reflux	(55)	313
	Et ₂ Zn (2 eq), CH ₂ ICl (4 eq), solvent, 0°, 15 min	Solvent (%)	51
		(CH ₂ Cl) ₂ (94)	
		Et ₂ O (<1)	
		PhMe (75)	
		C ₆ H ₆ (83)	
		C ₆ H ₁₄ (7)	
	Et ₂ Zn (2 eq), CH ₂ IX (4 eq), (CH ₂ Cl) ₂ , 0°, 15 min	X (%)	51
		Cl (85)	
		I (—)	
	Zn/Cu, CH ₂ I ₂ , I ₂ (cat.), Et ₂ O, reflux	(>99)	314
C ₁₁ 	Zn/Cu, CH ₂ I ₂ , I ₂ (cat.), Et ₂ O, reflux	(42)	306, 307
	Zn/Cu, CH ₂ I ₂	(—)	315
C ₁₁ 	Zn/Cu, CD ₂ I ₂ , I ₂ (cat.), Et ₂ O, reflux	(—)	306, 307
	Zn, CF ₂ Br ₂ , I ₂ (cat.), THF, rt	(84)	74
	Zn/Ag, CH ₂ I ₂	(32) + (15) +	316
		(13)	
	Zn/Cu, CH ₂ I ₂ , Et ₂ O, reflux	(—)	304
	Zn/Cu, CH ₂ I ₂	(—)	317
C ₁₂ 	Zn/Cu, CH ₂ I ₂	(—)	318

TABLE I. CYCLOPROPANATION OF CYCLIC, ACHIRAL ALKENES (Continued)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.						
	Et ₂ Zn, CH ₂ I ₂ , Et ₂ O/C ₆ H ₆ , reflux	I (7) + II (30) + III (6) + IV (3)	319						
	Zn/Cu, CH ₂ I ₂	I (<1) + II (23) + IV (5) + V (5)	320						
	Zn/Cu, CH ₂ I ₂	I (<1) + II (41)	320						
	Zn/Cu, CH ₂ I ₂ , I ₂ (cat.), Et ₂ O, reflux	(68)	321						
	Zn/Cu, CH ₂ I ₂ , Et ₂ O, reflux; repeated once	" (76)	322						
	1. Et ₂ Zn (2 eq), CH ₂ Cl ₂ 2. TFA 3. CH ₂ I ₂ , add olefin	" (78)	53						
	Zn/Cu, CH ₂ I ₂ , Et ₂ O, reflux	<table border="1" style="display: inline-table; vertical-align: middle;"> <tr><td>R</td><td>(%)</td></tr> <tr><td>H</td><td>(53)</td></tr> <tr><td>Me</td><td>(21)</td></tr> </table>	R	(%)	H	(53)	Me	(21)	323
R	(%)								
H	(53)								
Me	(21)								
	Et ₂ Zn (1 eq), CH ₂ I ₂ (2.3 eq), C ₆ H ₆	(81)	324						
	Zn/Cu, CH ₂ I ₂ , Et ₂ O, reflux	(30)	323						
	Zn/Cu, CH ₂ I ₂ , Et ₂ O, reflux	(—)	304						
C ₁₂₋₁₃ 	Zn/Cu, CH ₂ I ₂ , I ₂ (cat.), Et ₂ O, reflux	<table border="1" style="display: inline-table; vertical-align: middle;"> <tr><td>Ar</td><td>(%)</td></tr> <tr><td>4-MeC₆H₄</td><td>(30)</td></tr> <tr><td>3-ClC₆H₄</td><td>(48)</td></tr> </table>	Ar	(%)	4-MeC ₆ H ₄	(30)	3-ClC ₆ H ₄	(48)	325
Ar	(%)								
4-MeC ₆ H ₄	(30)								
3-ClC ₆ H ₄	(48)								
C ₁₃ 	Zn/Cu, CH ₂ I ₂	(—)	326						
	Zn/Cu, CH ₂ I ₂ , I ₂ (cat.), Et ₂ O, reflux	(19) Co(η ⁵ -C ₅ H ₅)	306, 307						
C ₁₄ 	Et ₂ Zn, CH ₂ ICl	(>46) OTMS Ph	327						

TABLE I. CYCLOPROPANATION OF CYCLIC, ACHIRAL ALKENES (Continued)

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Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₁₅ 	Zn/Cu, CH ₂ I ₂ , Et ₂ O, reflux	 (37)	328
	Zn/Cu, CH ₂ I ₂ , Et ₂ O, reflux	 (28)	328
	Zn/Cu, CH ₂ IX, dioxane, reflux	 X (%) Cl (39) I (55)	329
	Zn/Cu, CH ₂ I ₂ , Et ₂ O	 I +  II (—) I:II = 7:3	330
C ₁₆ 	Zn/Cu, CH ₂ I ₂	 (~70)	331
	Zn/Cu, CH ₂ I ₂ , Et ₂ O	 (74)	331a
	Zn/Cu, CH ₂ I ₂	 (40-50)	333
	Zn/Cu, CH ₂ I ₂ , Et ₂ O, reflux	 (7)	334
C ₁₈ 	Et ₂ Zn, CH ₂ I ₂ , dioxane, 80°	 (19)	335
	Et ₂ Zn (38 eq), CH ₂ I ₂ (30 eq), C ₆ H ₆ , 60°	 (91)	336
C ₂₀ 	Et ₂ Zn, CH ₂ ICl, (CH ₂ Cl) ₂ , 0°	 (64)	337
C ₂₂ 	Et ₂ Zn, CH ₂ ICl, (CH ₂ Cl) ₂ , rt	 I (51) +  II (21)	338

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TABLE I. CYCLOPROPANATION OF CYCLIC, ACHIRAL ALKENES (Continued)

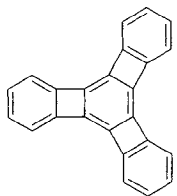
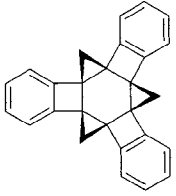
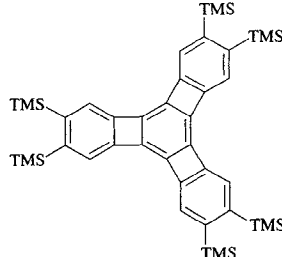
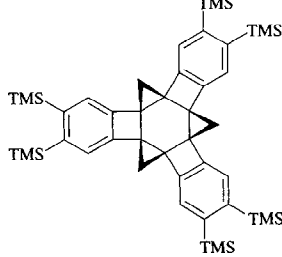
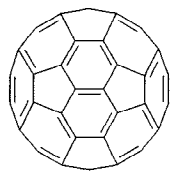
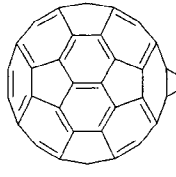
Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
<p>C₂₄</p> 	<p>Et₂Zn, CH₂I₂, PhMe, 60°</p>	 <p>(97)</p>	339
<p>C₄₂</p> 	<p>Et₂Zn, CH₂I₂, PhMe, 60°</p>	 <p>(78)</p>	339
<p>C₆₀</p> 	<p>Zn/Cu, CH₂I₂</p>	 <p>(—)</p>	340

TABLE II. CYCLOPROPANATION OF CYCLIC, ACHIRAL *O*- AND *N*-SUBSTITUTED ALKENES





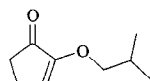
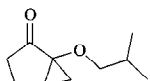
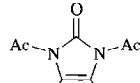
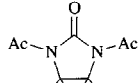
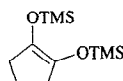
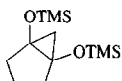


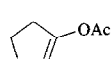
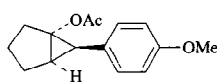
	Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.						
C ₄		Zn/Ag, CH ₂ I ₂	 (—)	341						
		Et ₂ Zn, CH ₂ I ₂ , Et ₂ O	 (59)	342						
C ₅		Zn/Cu, CH ₂ I ₂ , Et ₂ O	 (55)	343						
		Zn/Cu, CH ₂ I ₂ , AcCl, AcOEt, reflux	 (21)	90						
		Zn source, CH ₂ I ₂ , Et ₂ O	 <table border="1" style="display: inline-table; vertical-align: middle;"> <thead> <tr> <th>Zn source</th> <th>(%)</th> </tr> </thead> <tbody> <tr> <td>Zn/Ag</td> <td>(60)</td> </tr> <tr> <td>Zn/Cu</td> <td>(—)</td> </tr> </tbody> </table>	Zn source	(%)	Zn/Ag	(60)	Zn/Cu	(—)	344, 345
Zn source	(%)									
Zn/Ag	(60)									
Zn/Cu	(—)									
		Zn/Cu, CH ₂ I ₂	 <table border="1" style="display: inline-table; vertical-align: middle;"> <thead> <tr> <th>R</th> <th>(%)</th> </tr> </thead> <tbody> <tr> <td>Me</td> <td>(14)</td> </tr> <tr> <td>TMSO(CH₂)₂</td> <td>(75)</td> </tr> </tbody> </table>	R	(%)	Me	(14)	TMSO(CH ₂) ₂	(75)	346
R	(%)									
Me	(14)									
TMSO(CH ₂) ₂	(75)									
		MeO-C ₆ H ₄ -CHO Zn, (CMe ₂ SiCH ₂) ₂ , Et ₂ O, reflux	 (53) <i>endo:exo</i> = 1:1	76						

TABLE II. CYCLOPROPANATION OF CYCLIC, ACHIRAL *O*- AND *N*-SUBSTITUTED ALKENES (Continued)











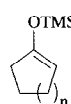



Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.																																				
	Zn/Cu, CH ₂ I ₂ , Et ₂ O, reflux	 (76)	83																																				
	Et ₂ Zn (1.5 eq), CH ₂ I ₂ (1.5 eq), Et ₂ O	" (—)	347																																				
	1. Zn/Cu, CH ₂ I ₂ , Et ₂ O, reflux; 2. MeCOCl, reflux	 (70)	348																																				
	Zn/Cu, MeCH ₂ , Et ₂ O, reflux	 I +  II (70) I:II = 2.9:1	332																																				
	Zn/Cu, CH ₂ I ₂ , Et ₂ O, reflux	 I +  II	79																																				
		<table border="1"> <thead> <tr> <th>R</th> <th>Conc (M)</th> <th>(%)</th> <th>I:II</th> </tr> </thead> <tbody> <tr> <td>Me</td> <td>0.45</td> <td>(73)</td> <td>99:1</td> </tr> <tr> <td>Me</td> <td>1.25</td> <td>(60)</td> <td>87:13</td> </tr> <tr> <td>Me</td> <td>2.0</td> <td>(62)</td> <td>29:71</td> </tr> <tr> <td>Et</td> <td>0.45</td> <td>(69)</td> <td>86:14</td> </tr> <tr> <td>Et</td> <td>1.25</td> <td>(87)</td> <td>46:54</td> </tr> <tr> <td>Et</td> <td>2.0</td> <td>(63)</td> <td>4:96</td> </tr> <tr> <td>TMS</td> <td>0.45</td> <td>(76)</td> <td>97:3</td> </tr> <tr> <td>TMS</td> <td>1.25</td> <td>(71)</td> <td>0:100</td> </tr> </tbody> </table>	R	Conc (M)	(%)	I:II	Me	0.45	(73)	99:1	Me	1.25	(60)	87:13	Me	2.0	(62)	29:71	Et	0.45	(69)	86:14	Et	1.25	(87)	46:54	Et	2.0	(63)	4:96	TMS	0.45	(76)	97:3	TMS	1.25	(71)	0:100	
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TMS	0.45	(76)	97:3																																				
TMS	1.25	(71)	0:100																																				
	Zn/Cu, CH ₂ Br ₂ , Et ₂ O, 45°, sonication	 (41)	270																																				
	Zn/Cu, CH ₂ Br ₂ , AcCl (0.02 eq), Et ₂ O	" (45)	41																																				
	Zn anode, 2e ⁻ , CH ₂ Br ₂ , ZnBr ₂ present initially, CH ₂ Cl ₂ /DMF (9:1)	" (54)	70																																				
	Zn/Cu, CH ₂ X ₂ , promoter, Et ₂ O	<table border="1"> <thead> <tr> <th>Promoter</th> <th>X</th> <th>(%)</th> </tr> </thead> <tbody> <tr> <td>TiCl₄</td> <td>Br</td> <td>(17)</td> </tr> <tr> <td>ultrasound</td> <td>Br</td> <td>(41)</td> </tr> <tr> <td>TiCl₄</td> <td>I</td> <td>(<2)</td> </tr> </tbody> </table>	Promoter	X	(%)	TiCl ₄	Br	(17)	ultrasound	Br	(41)	TiCl ₄	I	(<2)	43																								
Promoter	X	(%)																																					
TiCl ₄	Br	(17)																																					
ultrasound	Br	(41)																																					
TiCl ₄	I	(<2)																																					
C ₅₋₇ 	Et ₂ Zn (1.2 eq), CH ₂ I ₂ (0.8 eq), solvent, 20°	 <table border="1"> <thead> <tr> <th>n</th> <th>Solvent</th> <th>(%)</th> </tr> </thead> <tbody> <tr> <td>1</td> <td><i>n</i>-pentane</td> <td>(81)</td> </tr> <tr> <td>1</td> <td>Et₂O</td> <td>(70)</td> </tr> <tr> <td>2</td> <td><i>n</i>-pentane</td> <td>(82)</td> </tr> <tr> <td>2</td> <td>Et₂O</td> <td>(78)</td> </tr> <tr> <td>3</td> <td><i>n</i>-pentane</td> <td>(75)</td> </tr> <tr> <td>3</td> <td>Et₂O</td> <td>(79)</td> </tr> </tbody> </table>	n	Solvent	(%)	1	<i>n</i> -pentane	(81)	1	Et ₂ O	(70)	2	<i>n</i> -pentane	(82)	2	Et ₂ O	(78)	3	<i>n</i> -pentane	(75)	3	Et ₂ O	(79)	349															
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C ₅₋₈	Zn/Ag, CH ₂ I ₂	<table border="1"> <thead> <tr> <th>n</th> <th>(%)</th> </tr> </thead> <tbody> <tr> <td>1</td> <td>(65)</td> </tr> <tr> <td>2</td> <td>(67)</td> </tr> <tr> <td>3</td> <td>(76)</td> </tr> <tr> <td>4</td> <td>(84)</td> </tr> </tbody> </table>	n	(%)	1	(65)	2	(67)	3	(76)	4	(84)	81, 107																										
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C ₆ 	Zn/Ag, CH ₂ I ₂ , Et ₂ O, reflux	 (85)	107, 350																																				

TABLE II. CYCLOPROPANATION OF CYCLIC, ACHIRAL *O*- AND *N*-SUBSTITUTED ALKENES (Continued)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.									
	Zn/Ag, CH ₂ I ₂ (xs), Et ₂ O, reflux	 (85)	107, 267									
	Zn/Ag, CH ₂ I ₂ , Et ₂ O, reflux	 (70)	344									
	Et ₂ Zn (1.5 eq), CH ₂ I ₂ (1.5 eq), Et ₂ O	" (—)	347, 351									
	Zn source, MeCHl ₂ , solvent, reflux	 <table border="1" style="display: inline-table; vertical-align: middle;"> <thead> <tr> <th>Zn source</th> <th>Solvent</th> <th>(%)</th> </tr> </thead> <tbody> <tr> <td>Zn/Cu</td> <td>Et₂O</td> <td>(76)</td> </tr> <tr> <td>Et₂Zn</td> <td>C₆H₆</td> <td>(79)</td> </tr> </tbody> </table>	Zn source	Solvent	(%)	Zn/Cu	Et ₂ O	(76)	Et ₂ Zn	C ₆ H ₆	(79)	352
Zn source	Solvent	(%)										
Zn/Cu	Et ₂ O	(76)										
Et ₂ Zn	C ₆ H ₆	(79)										
	Zn/Cu, CH ₂ Br ₂ , AcCl (0.02 eq), Et ₂ O	 (22)	41									
	Zn/Cu, CH ₂ I ₂	 <table border="1" style="display: inline-table; vertical-align: middle;"> <thead> <tr> <th>R</th> <th>(%)</th> </tr> </thead> <tbody> <tr> <td>Me</td> <td>(64)</td> </tr> <tr> <td>TMSO(CH₂)₂</td> <td>(81)</td> </tr> </tbody> </table>	R	(%)	Me	(64)	TMSO(CH ₂) ₂	(81)	346			
R	(%)											
Me	(64)											
TMSO(CH ₂) ₂	(81)											
	1. Zn/Cu, CH ₂ I ₂ , Et ₂ O, reflux; 2. MeCOCl, reflux	 (56)	348									
	Zn/Cu, CH ₂ Br ₂ , AcCl (0.02 eq), Et ₂ O	 (60)	41									
	Zn/Cu, CH ₂ I ₂ , Et ₂ O, reflux	" (>99)	82									
	Zn/Ag, CH ₂ I ₂	" (—)	353									
	Et ₂ Zn (1.25 eq), CH ₂ I ₂ (1.25 eq), dry air, cyclohexane	" (57)	354									
	Et ₂ Zn (1.5 eq), CH ₂ I ₂ (1.5 eq), Et ₂ O	" (77-83)	347									
	Zn/Cu, CH ₂ I ₂ , Et ₂ O, reflux	 I (18) + II (37)	355									
	1. Zn/Cu, CH ₂ I ₂ , Et ₂ O, reflux; 2. MeCOCl, reflux	 (65)	348									
	Et ₂ Zn (2 eq), MeCHl ₂ (2.5 eq), hexane	 I + II (63) I:II = 29:71	180									
	Zn/Cu, MeCHl ₂ , Et ₂ O, reflux	" (65) I:II = 24:76	332									

TABLE II. CYCLOPROPANATION OF CYCLIC, ACHIRAL *O*- AND *N*-SUBSTITUTED ALKENES (Continued)







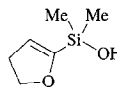
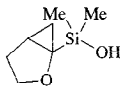








Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.																																																																				
	Zn/Cu, CH ₂ I ₂ , Et ₂ O (conc), reflux	 + 	<table border="1"> <thead> <tr> <th>R</th> <th>Conc (M)</th> <th>(%)</th> <th>I:II</th> </tr> </thead> <tbody> <tr> <td>Me</td> <td>0.45</td> <td>(72)</td> <td>98:2</td> </tr> <tr> <td>Me</td> <td>1.25</td> <td>(59)</td> <td>83:17</td> </tr> <tr> <td>Me</td> <td>2.0</td> <td>(66)</td> <td>2:98</td> </tr> <tr> <td>Et</td> <td>0.45</td> <td>(66)</td> <td>86:14</td> </tr> <tr> <td>Et</td> <td>1.25</td> <td>(87)</td> <td>44:56</td> </tr> <tr> <td>Et</td> <td>2.0</td> <td>(79)</td> <td>2:98</td> </tr> <tr> <td>TMS</td> <td>0.45</td> <td>(71)</td> <td>92:8</td> </tr> <tr> <td>TMS</td> <td>1.25</td> <td>(68)</td> <td>0:100</td> </tr> </tbody> </table>	R	Conc (M)	(%)	I:II	Me	0.45	(72)	98:2	Me	1.25	(59)	83:17	Me	2.0	(66)	2:98	Et	0.45	(66)	86:14	Et	1.25	(87)	44:56	Et	2.0	(79)	2:98	TMS	0.45	(71)	92:8	TMS	1.25	(68)	0:100	79, 356, 79, 356, 79, 356, 79, 356, 79, 356																															
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	SmI ₂ , CH ₂ I ₂ , THF	" (56)	88, 110																																																																				
	Et ₂ Zn (2 eq), CH ₂ I ₂ (3 eq), Et ₂ O, rt	 (63)	357																																																																				
C ₆₋₁₆ 	Et ₂ Zn, CH ₂ I ₂		<table border="1"> <thead> <tr> <th>n</th> <th>R</th> <th>(%)</th> <th></th> </tr> </thead> <tbody> <tr> <td>1</td> <td><i>n</i>-Bu</td> <td>(75)</td> <td>80</td> </tr> <tr> <td>1</td> <td>CH₂=CH(CH₂)₂</td> <td>(75)</td> <td>80</td> </tr> <tr> <td>1</td> <td>Cl(CH₂)₄</td> <td>(65)</td> <td>80</td> </tr> <tr> <td>1</td> <td><i>n</i>-C₆H₁₃</td> <td>(90)</td> <td>80</td> </tr> <tr> <td>1</td> <td>BnO(CH₂)₃</td> <td>(79)</td> <td>80</td> </tr> <tr> <td>1</td> <td>BnO(CH₂)₄</td> <td>(77)</td> <td>80</td> </tr> <tr> <td>1</td> <td>BnO(CH₂)₅</td> <td>(83)</td> <td>80</td> </tr> <tr> <td>2</td> <td>H</td> <td>(—)</td> <td>358</td> </tr> <tr> <td>2</td> <td>Me</td> <td>(—)</td> <td>358</td> </tr> <tr> <td>2</td> <td>Et</td> <td>(—)</td> <td>358</td> </tr> <tr> <td>2</td> <td><i>n</i>-Bu</td> <td>(—)</td> <td>358</td> </tr> <tr> <td>2</td> <td><i>n</i>-C₆H₁₃</td> <td>(—)</td> <td>80, 358</td> </tr> <tr> <td>2</td> <td><i>n</i>-C₁₀H₂₁</td> <td>(87)</td> <td>80</td> </tr> <tr> <td>2</td> <td>BnO(CH₂)₃</td> <td>(90)</td> <td>80</td> </tr> <tr> <td>2</td> <td>BnO(CH₂)₄</td> <td>(80)</td> <td>80</td> </tr> <tr> <td>3</td> <td><i>n</i>-C₆H₁₃</td> <td>(90)</td> <td>80</td> </tr> </tbody> </table>	n	R	(%)		1	<i>n</i> -Bu	(75)	80	1	CH ₂ =CH(CH ₂) ₂	(75)	80	1	Cl(CH ₂) ₄	(65)	80	1	<i>n</i> -C ₆ H ₁₃	(90)	80	1	BnO(CH ₂) ₃	(79)	80	1	BnO(CH ₂) ₄	(77)	80	1	BnO(CH ₂) ₅	(83)	80	2	H	(—)	358	2	Me	(—)	358	2	Et	(—)	358	2	<i>n</i> -Bu	(—)	358	2	<i>n</i> -C ₆ H ₁₃	(—)	80, 358	2	<i>n</i> -C ₁₀ H ₂₁	(87)	80	2	BnO(CH ₂) ₃	(90)	80	2	BnO(CH ₂) ₄	(80)	80	3	<i>n</i> -C ₆ H ₁₃	(90)	80
n	R	(%)																																																																					
1	<i>n</i> -Bu	(75)	80																																																																				
1	CH ₂ =CH(CH ₂) ₂	(75)	80																																																																				
1	Cl(CH ₂) ₄	(65)	80																																																																				
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2	H	(—)	358																																																																				
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2	<i>n</i> -C ₁₀ H ₂₁	(87)	80																																																																				
2	BnO(CH ₂) ₃	(90)	80																																																																				
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3	<i>n</i> -C ₆ H ₁₃	(90)	80																																																																				
C ₇ 	Zn/Ag, CH ₂ I ₂ , Et ₂ O, reflux	 (—)	107, 350																																																																				
	Zn/Ag, CH ₂ I ₂ (xs), Et ₂ O, reflux	 (90)	107, 267																																																																				
	Zn/Ag, CH ₂ I ₂ , Et ₂ O, reflux	 (64)	359																																																																				

TABLE II. CYCLOPROPANATION OF CYCLIC, ACHIRAL *O*- AND *N*-SUBSTITUTED ALKENES (Continued)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.												
	Et ₂ Zn, CH ₂ I ₂ , Et ₂ O	(82)	360												
	Zn/Cu, CH ₂ I ₂ , Et ₂ O, reflux	(78)	83												
	Zn/Ag, CH ₂ I ₂	" (74)	81												
	Zn/Cu, CH ₂ I ₂ , Et ₂ O (conc), reflux	<table border="1"> <thead> <tr> <th>Conc (M)</th> <th>(%)</th> </tr> </thead> <tbody> <tr> <td>2.0</td> <td>(70)</td> </tr> <tr> <td>1.25</td> <td>(78)</td> </tr> <tr> <td>0.45</td> <td>(73)</td> </tr> </tbody> </table>	Conc (M)	(%)	2.0	(70)	1.25	(78)	0.45	(73)	79, 79, 356, 79				
Conc (M)	(%)														
2.0	(70)														
1.25	(78)														
0.45	(73)														
	Et ₂ Zn (1.5 eq), CH ₂ I ₂ (1.5 eq), Et ₂ O	" (—)	347												
I + II	Zn/Ag, CH ₂ I ₂	III (—) + II (—)	81												
	SmI ₂ , CH ₂ I ₂ , THF	(62)	88												
	Zn/Cu, CH ₂ I ₂	<table border="1"> <thead> <tr> <th>R</th> <th>(%)</th> </tr> </thead> <tbody> <tr> <td>Me</td> <td>(78)</td> </tr> <tr> <td>TMSO(CH₂)₂</td> <td>(80)</td> </tr> </tbody> </table>	R	(%)	Me	(78)	TMSO(CH ₂) ₂	(80)	346						
R	(%)														
Me	(78)														
TMSO(CH ₂) ₂	(80)														
	Zn/Cu, CH ₂ I ₂ , Et ₂ O, reflux	(77)	83												
	Et ₂ Zn (1.25 eq), CH ₂ ICl (1.25 eq), dry air, cyclohexane	" (73)	354												
	Et ₂ Zn (1.5 eq), CH ₂ I ₂ (1.5 eq), Et ₂ O	" (—)	347												
	Zn/Cu, MeCHI ₂ , Et ₂ O, reflux	I + II (88) I:II = 3.1:1	332												
	SmI ₂ , CH ₂ I ₂ , THF	(58)	88												
	Zn/Cu, CH ₂ I ₂ , Et ₂ O, reflux	<table border="1"> <thead> <tr> <th>n</th> <th>(%)</th> </tr> </thead> <tbody> <tr> <td>2</td> <td>(75)</td> </tr> <tr> <td>3</td> <td>(72)</td> </tr> <tr> <td>4</td> <td>(70)</td> </tr> <tr> <td>5</td> <td>(70)</td> </tr> <tr> <td>6</td> <td>(65)</td> </tr> </tbody> </table>	n	(%)	2	(75)	3	(72)	4	(70)	5	(70)	6	(65)	361
n	(%)														
2	(75)														
3	(72)														
4	(70)														
5	(70)														
6	(65)														

TABLE II. CYCLOPROPANATION OF CYCLIC, ACHIRAL O- AND N-SUBSTITUTED ALKENES (Continued)


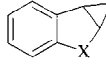
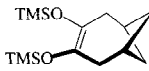
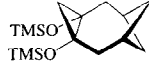
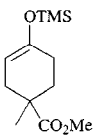
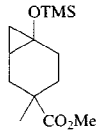
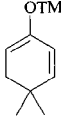
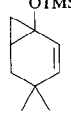

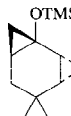
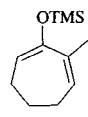
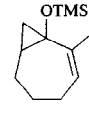
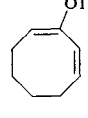
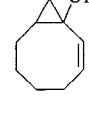
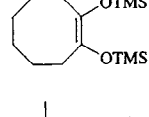
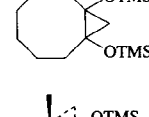
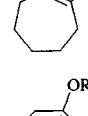
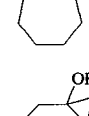
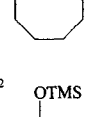
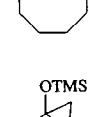
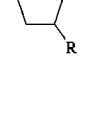
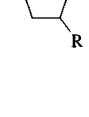
Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.														
C ₈ 	Zn/Ag, CH ₂ I ₂ , Et ₂ O, reflux	 <table border="1"> <tr><td>X</td><td>(%)</td></tr> <tr><td>O</td><td>(25)</td></tr> <tr><td>NCO₂Me</td><td>(37)</td></tr> <tr><td>CH₂</td><td>(70)</td></tr> </table>	X	(%)	O	(25)	NCO ₂ Me	(37)	CH ₂	(70)	288						
X	(%)																
O	(25)																
NCO ₂ Me	(37)																
CH ₂	(70)																
	Et ₂ Zn (5 eq), CH ₂ I ₂ (5.8 eq), Et ₂ O, 35°	 (>55)	362														
	Zn/Ag, CH ₂ I ₂ , Et ₂ O, rt	 (87)	363														
	Zn/Ag, CH ₂ I ₂ , Et ₂ O, reflux	 (88)	107, 350														
	Zn/Ag, CH ₂ I ₂ (xs), Et ₂ O, reflux	 (78)	107, 350														
	Et ₂ Zn, CH ₂ I ₂ , Et ₂ O	 (78)	360														
	Et ₂ Zn, CH ₂ I ₂ , Et ₂ O	 (55)	360														
	Et ₂ Zn (1.5 eq), CH ₂ I ₂ (1.5 eq), Et ₂ O	 (—)	347, 351														
	Zn/Cu, CH ₂ I ₂ , Et ₂ O	 (77)	364														
	Zn/Cu, CH ₂ I ₂	 <table border="1"> <tr><td>R</td><td>(%)</td></tr> <tr><td>Me</td><td>(60)</td></tr> <tr><td>TMSO(CH₂)₂</td><td>(78)</td></tr> </table>	R	(%)	Me	(60)	TMSO(CH ₂) ₂	(78)	346								
R	(%)																
Me	(60)																
TMSO(CH ₂) ₂	(78)																
C ₈₋₁₂ 	Et ₂ Zn, CH ₂ I ₂ , Et ₂ O	 <table border="1"> <tr><td>R</td><td>(%)</td></tr> <tr><td><i>n</i>-Bu</td><td>(93)</td></tr> <tr><td><i>t</i>-Bu</td><td>(74)</td></tr> <tr><td>CH₂=CHCH₂</td><td>(78)</td></tr> <tr><td>CH₂=CH(CH₂)₂</td><td>(92)</td></tr> <tr><td>Ph</td><td>(80)</td></tr> <tr><td>Bn</td><td>(87)</td></tr> </table>	R	(%)	<i>n</i> -Bu	(93)	<i>t</i> -Bu	(74)	CH ₂ =CHCH ₂	(78)	CH ₂ =CH(CH ₂) ₂	(92)	Ph	(80)	Bn	(87)	365
R	(%)																
<i>n</i> -Bu	(93)																
<i>t</i> -Bu	(74)																
CH ₂ =CHCH ₂	(78)																
CH ₂ =CH(CH ₂) ₂	(92)																
Ph	(80)																
Bn	(87)																

TABLE II. CYCLOPROPANATION OF CYCLIC, ACHIRAL *O*- AND *N*-SUBSTITUTED ALKENES (Continued)

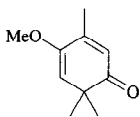
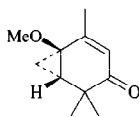
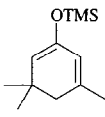
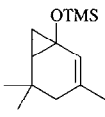

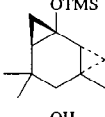
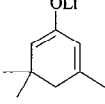
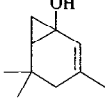
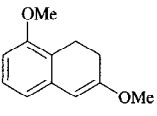
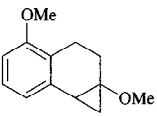
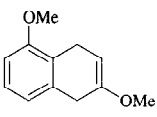
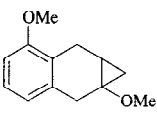
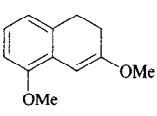
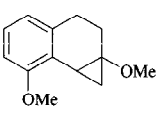
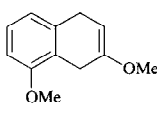
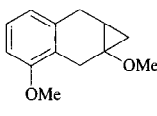
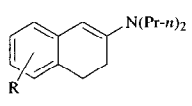
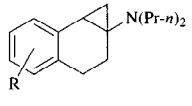
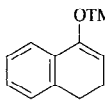
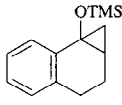

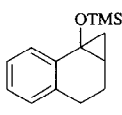
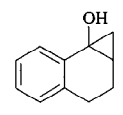
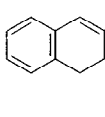
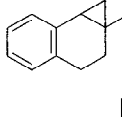
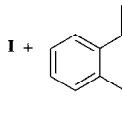
Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
	Zn/Cu, CH ₂ I ₂ , I ₂ (cat.), Et ₂ O, reflux	 (86)	366
	Zn/Ag, CH ₂ I ₂ , Et ₂ O, reflux	 (80)	107, 350
	Zn/Ag, CH ₂ I ₂ (xs), Et ₂ O, reflux	 (68)	107, 350
	SmI ₂ , CH ₂ I ₂ , THF	 (62)	88, 110
	Zn/Cu, CH ₂ I ₂ , Et ₂ O	 (30)	367
	Et ₂ Zn, CH ₂ I ₂ , C ₆ H ₆	 (94)	368
	Et ₂ Zn, CH ₂ I ₂ , C ₆ H ₆	 (74)	368
	Et ₂ Zn, CH ₂ I ₂ , C ₆ H ₆	 (67)	368
	Et ₂ Zn (1.1 eq), CH ₂ I ₂ (1.5 eq), C ₅ H ₁₂ , 5°	 N(Pr- <i>n</i>) ₂	R (%) 5-OMe (>30) 7-OMe (>26) 8-OMe (>36) 89
	Et ₂ Zn (1.25 eq), CH ₂ ICl (1.25 eq), dry air, cyclohexane	 (60)	354
	Zn/Cu, CH ₂ I ₂ , Et ₂ O (conc), reflux	"	Conc (M) (%) 2.0 (63) 1.25 (58) 0.45 (65) 79 79, 83 79
	Zn/Cu, CH ₂ I ₂ , Et ₂ O, reflux	 I +  II (78) I:II = 2.9:1	84
	Et ₂ Zn (1.5 eq), CH ₂ I ₂ (1.5 eq), Et ₂ O	 I (—)	347
	Zn/Cu, CH ₂ I ₂ , Et ₂ O (conc), reflux	I +  II	Conc (M) (%) I:II 2.0 (56) 52:48 1.25 (66) 82:18 0.45 (64) 99:1 79 79, 83

TABLE II. CYCLOPROPANATION OF CYCLIC, ACHIRAL *O*- AND *N*-SUBSTITUTED ALKENES (Continued)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
	1. Et ₂ Zn (2 eq), CH ₂ Cl ₂ 2. TFA 3. CH ₂ I ₂ , add olefin	 (50)	53
	SmI ₂ , CH ₂ I ₂ , THF	 (57)	88, 110
	Zn/Ag, CH ₂ I ₂ , Et ₂ O, reflux	 (—)	350
	Zn/Cu, CH ₂ I ₂ , Et ₂ O	 (91)	364
C ₁₀₋₁₂ 	Et ₂ Zn (1.5 eq), CH ₂ I ₂ (1.5 eq), Et ₂ O	 n (%) 5 (—) 7 (—)	351
C ₁₁ 	Et ₂ Zn (3 eq), CH ₂ I ₂ (3 eq), Et ₂ O/PhMe, reflux	 (40)	369
C ₁₁₋₁₇ 	Et ₂ Zn, CH ₂ I ₂ , Et ₂ O	 R (%) H (>72) Ph (>48)	360
C ₁₂ 	Zn/Cu, CH ₂ I ₂ , I ₂ (cat.), Et ₂ O, reflux	 (30)	370
	Et ₂ Zn (1.5 eq), CH ₂ I ₂ (1.5 eq), Et ₂ O	 (—)	347
	SmI ₂ , CH ₂ I ₂ , THF	 (46)	88, 110
	Et ₂ Zn, CH ₂ I ₂ , Et ₂ O, 0°	 (58) <i>cis:trans</i> = >99:1	371
C ₁₂₋₁₃ 	EtZnI, CH ₂ I ₂ , Et ₂ O, reflux	 n (%) 7 (75) 8 (81)	372
C ₁₃ 	Et ₂ Zn, CH ₂ I ₂ , Et ₂ O	 (88)	360

TABLE II. CYCLOPROPANATION OF CYCLIC, ACHIRAL *O*- AND *N*-SUBSTITUTED ALKENES (Continued)

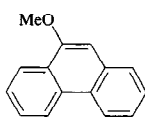
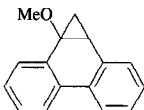
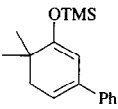
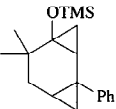
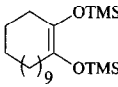
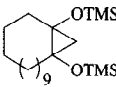
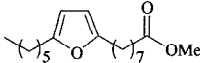
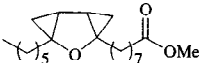
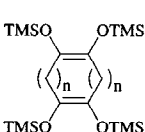
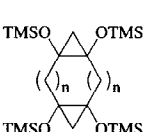
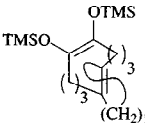
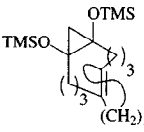
Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.										
C_{14} 	Et ₂ Zn (9 eq), CH ₂ I ₂ (9 eq), PhMe, 60°	 (75)	373										
	Et ₂ Zn, CH ₂ I ₂	 (>46)	327										
	Et ₂ Zn (2 eq), CH ₂ I ₂ (2 eq), C ₆ H ₆ , rt	 (81)	374										
C_{18} 	Zn/Cu, CH ₂ I ₂ , ultrasound, DME, 85-95°	 (57)	375										
C_{18-28} 	Et ₂ Zn (5 eq), CH ₂ I ₂ (6 eq), C ₆ H ₆ , rt	 <table border="1" style="display: inline-table; vertical-align: middle;"> <thead> <tr> <th>n</th> <th>(%)</th> </tr> </thead> <tbody> <tr> <td>7</td> <td>(>33)</td> </tr> <tr> <td>8</td> <td>(>47)</td> </tr> <tr> <td>10</td> <td>(>43)</td> </tr> <tr> <td>12</td> <td>(>35)</td> </tr> </tbody> </table>	n	(%)	7	(>33)	8	(>47)	10	(>43)	12	(>35)	376
n	(%)												
7	(>33)												
8	(>47)												
10	(>43)												
12	(>35)												
C_{20} 	Et ₂ Zn (2 eq), CH ₂ I ₂ (2 eq), PhMe, 80°	 (>35)	377										

TABLE III. CYCLOPROPANATION OF ACYCLIC, ACHIRAL ALKENES



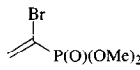
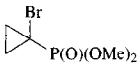
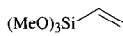
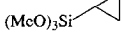




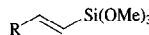
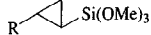


	Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.																
C ₂		Zn/Cu, CH ₂ I ₂	 (—)	378																
		Zn/Cu, CH ₂ I ₂	 (—)	99																
		Zn/Cu, CH ₂ I ₂	 (77-78)	379																
		Zn/Cu, CD ₂ I ₂ , Et ₂ O, 60°	 (5)	380, 381																
		Zn/Cu, CD ₂ I ₂	 (—)	378																
C ₂₋₃		Zn/Cu, CH ₂ I ₂	 <table border="1" data-bbox="1102 1143 1258 1304"> <thead> <tr> <th>R</th> <th>(%)</th> </tr> </thead> <tbody> <tr> <td>H</td> <td>(—)</td> </tr> <tr> <td>Cl</td> <td>(—)</td> </tr> <tr> <td>Br</td> <td>(—)</td> </tr> <tr> <td>Me</td> <td>(—)</td> </tr> <tr> <td>Si(OMe)₃</td> <td>(—)</td> </tr> </tbody> </table>	R	(%)	H	(—)	Cl	(—)	Br	(—)	Me	(—)	Si(OMe) ₃	(—)	382				
R	(%)																			
H	(—)																			
Cl	(—)																			
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Si(OMe) ₃	(—)																			
C ₂₋₅		Zn/Cu, CH ₂ I ₂	 <table border="1" data-bbox="928 1366 1137 1577"> <thead> <tr> <th>R</th> <th>(%)</th> </tr> </thead> <tbody> <tr> <td>SiMe₃</td> <td>(65)</td> </tr> <tr> <td>SiMe₂OMe</td> <td>(40)</td> </tr> <tr> <td>SiMe(OMe)₂</td> <td>(30)</td> </tr> <tr> <td>Si(OMe)₃</td> <td>(35)</td> </tr> <tr> <td>SiMe₂OTMS</td> <td>(70)</td> </tr> <tr> <td>SiMe(OTMS)₂</td> <td>(65)</td> </tr> <tr> <td>Si(OTMS)₃</td> <td>(40)</td> </tr> </tbody> </table>	R	(%)	SiMe ₃	(65)	SiMe ₂ OMe	(40)	SiMe(OMe) ₂	(30)	Si(OMe) ₃	(35)	SiMe ₂ OTMS	(70)	SiMe(OTMS) ₂	(65)	Si(OTMS) ₃	(40)	383
R	(%)																			
SiMe ₃	(65)																			
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SiMe(OTMS) ₂	(65)																			
Si(OTMS) ₃	(40)																			

TABLE III. CYCLOPROPANATION OF ACYCLIC, ACHIRAL ALKENES (Continued)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.																																								
$C_{2,9}$ 	Et ₂ Zn, CH ₂ I ₂ , PhMe, 50°		95																																								
		<table border="1"> <thead> <tr> <th>R¹</th> <th>R²</th> <th>R³</th> <th>(%)</th> </tr> </thead> <tbody> <tr> <td>H</td> <td>H</td> <td>H</td> <td>(66)</td> </tr> <tr> <td>Bu</td> <td>H</td> <td>H</td> <td>(83)</td> </tr> <tr> <td>H</td> <td>Bu</td> <td>H</td> <td>(68)</td> </tr> <tr> <td>Cl(CH₂)₃</td> <td>H</td> <td>H</td> <td>(75)</td> </tr> <tr> <td>H</td> <td>H</td> <td>Me</td> <td>(69)</td> </tr> <tr> <td>CO₂Me</td> <td>H</td> <td>H</td> <td>(62)</td> </tr> <tr> <td>PhSCH₂</td> <td>H</td> <td>H</td> <td>(60)</td> </tr> <tr> <td>TMS</td> <td>H</td> <td>H</td> <td>(71)</td> </tr> <tr> <td>Me</td> <td>Me</td> <td>H</td> <td>(65)</td> </tr> </tbody> </table>	R ¹	R ²	R ³	(%)	H	H	H	(66)	Bu	H	H	(83)	H	Bu	H	(68)	Cl(CH ₂) ₃	H	H	(75)	H	H	Me	(69)	CO ₂ Me	H	H	(62)	PhSCH ₂	H	H	(60)	TMS	H	H	(71)	Me	Me	H	(65)	
		R ¹	R ²	R ³	(%)																																						
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Me	Me	H	(65)																																								
C_3 	Zn anode, 2e-, CH ₂ Br ₂ , ZnBr ₂ present initially, CH ₂ Cl ₂ /DMF (9:1)		(15) 70																																								
			Zn/Cu, CH ₂ I ₂		(-) 384																																						
	1. Et ₂ Zn (2 eq), CH ₂ Cl ₂ 2. TFA 3. CH ₂ I ₂ , add olefin		(88) 53																																								
	Zn anode, 2e-, CH ₂ Br ₂ , ZnBr ₂ present initially, CH ₂ Cl ₂ /DMF (9:1)	" (50)	70																																								
	Zn/Cu, CH ₂ I ₂		(80) 379																																								
	Zn/Cu, CH ₂ I ₂ , Et ₂ O, sonication		(30) 385																																								
	Zn/Cu, CH ₂ I ₂ , sonication		(81) 386, 387, 388																																								
	Zn/Cu, CH ₂ I ₂	" (40)	388																																								
	Zn anode, 2e-, CH ₂ Br ₂ , ZnBr ₂ absent initially, CH ₂ Cl ₂ /DMF (9:1)		(42) 70																																								
	Zn*, CH ₂ I ₂ , DME/Et ₂ O	" (67)	44																																								
	Zinc source, MeCHI ₂ , Et ₂ O, reflux		I + II <table border="1"> <thead> <tr> <th>Zinc source</th> <th>(%)</th> <th>I:II</th> </tr> </thead> <tbody> <tr> <td>Zn/Cu</td> <td>(52)</td> <td>74:26</td> </tr> <tr> <td>Et₂Zn</td> <td>(23)</td> <td>84:16</td> </tr> </tbody> </table>	Zinc source	(%)	I:II	Zn/Cu	(52)	74:26	Et ₂ Zn	(23)	84:16																															
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	Zn/Cu, CH ₂ I ₂		(77-78) 379																																								
	Zn/Cu, CH ₂ I ₂		(12) 389																																								
	Zn/Ag, CH ₂ I ₂ (xs), Et ₂ O, reflux		(84) 107, 267																																								
	Zn/Cu, CH ₂ I ₂		(-) 390																																								

TABLE III. CYCLOPROPANATION OF ACYCLIC, ACHIRAL ALKENES (Continued)

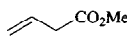
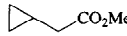
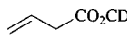
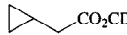
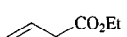
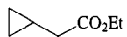


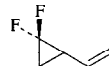
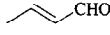


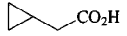
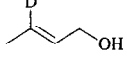
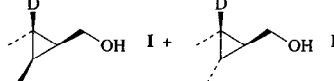
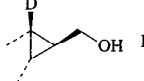
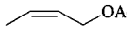

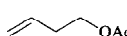
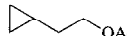
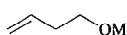

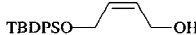
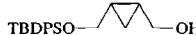
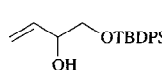
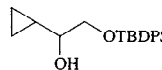
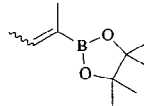
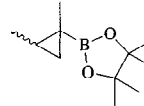


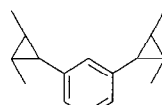








Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
	Zn/Cu, CH ₂ I ₂ , Et ₂ O	 (78)	209
	Zn/Cu, CH ₂ I ₂ , Et ₂ O	 (—)	209
	Zn/Cu, CH ₂ I ₂	 (31)	391
	Et ₂ Zn, CH ₂ I ₂	 (—)	392
	Zn, CF ₂ Br ₂ , I ₂ (cat.), THF, rt	 (17)	74
	Zn/Ag, CH ₂ I ₂	 (—)	393
	Zn/Ag, CH ₂ I ₂	" (56)	394
	Zn/Cu, CH ₂ I ₂ , Et ₂ O	 (12)	209
	Et ₂ Zn, MeCHI ₂ , Et ₂ O	 I +  II (74) I:II = 1:2	395
	Zn/Cu, CH ₂ I ₂	 (66)	396
	Zn/Cu, CH ₂ I ₂ , Et ₂ O	 (62)	209
	Zn/Cu, CH ₂ I ₂ , Et ₂ O	 (97)	209
	Et ₂ Zn (1 eq), CH ₂ I ₂ (2 eq), -78 to -20°; TiCl ₄ (0.15 eq)	 (85)	31
	Zn/Cu, CH ₂ I ₂ , DME	 (51)	397
	Et ₂ Zn, CH ₂ I ₂ , PhMe, 50°	 (63)	95
	EtZnI, CH ₂ I ₂	 (—)	398
	N ₂ HC-C ₆ H ₄ -CHN ₂	 (43)	399
	ZnBr ₂ , Et ₂ O	 (84)	73, 103
	CHBr ₃ /Et ₂ Zn (3:2), dry air (10 mL/min)	 (4)	74
	Zn, CF ₂ Br ₂ , I ₂ (cat.), THF, rt	 (4)	74
	EtZnI, CH ₂ I ₂	 (—)	398
	CHBr ₃ /Et ₂ Zn (3:2), dry air (10 mL/min)	 (85)	73, 103
	Et ₂ Zn, CHI ₃ , olefin (xs), 0 to 20°	 (63) <i>syn:anti</i> = 69:31	274
	Zn, CF ₂ Br ₂ , I ₂ (cat.), THF, rt	 (7)	74

TABLE III. CYCLOPROPANATION OF ACYCLIC, ACHIRAL ALKENES (Continued)



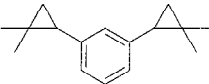


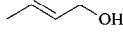
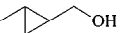
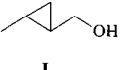
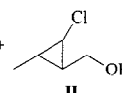
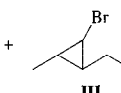
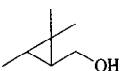

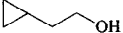

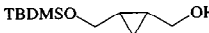
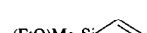

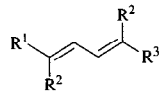
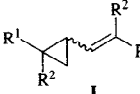
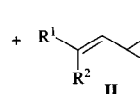
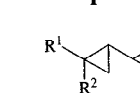
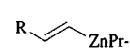
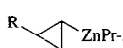
Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.																																				
	N_2HC -  - CHN_2 $\text{ZnBr}_2, \text{Et}_2\text{O}$	 (62)	399																																				
	$\text{CHBr}_3/\text{Et}_2\text{Zn}$ (3:2), dry air (10 mL/min)	 (85)	73, 103																																				
	$\text{Et}_2\text{Zn}, \text{CHI}_3$, excess olefin, 0 to 20°	 (55)	274																																				
	$\text{Zn}/\text{Cu}, \text{CH}_2\text{Br}_2$, AcCl (0.02 eq), Et_2O	 (58)	41																																				
	$\text{Zn}/\text{Cu}, \text{CH}_2\text{Br}_2$, $\text{Et}_2\text{O}, 45^\circ$, sonication	" (57)	270																																				
	$\text{Zn}/\text{Cu}, \text{CH}_2\text{X}_2$, promoter, Et_2O	<table border="1" data-bbox="923 716 1183 831"> <thead> <tr> <th>Promoter</th> <th>X</th> <th>(%)</th> </tr> </thead> <tbody> <tr> <td>TiCl_4</td> <td>Br</td> <td>(36)</td> </tr> <tr> <td>ultrasound</td> <td>Br</td> <td>(57)</td> </tr> <tr> <td>TiCl_4</td> <td>I</td> <td>(42)</td> </tr> </tbody> </table>	Promoter	X	(%)	TiCl_4	Br	(36)	ultrasound	Br	(57)	TiCl_4	I	(42)	43																								
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	Zn anode, 2e-, CH_2X_2 , conditions, $\text{CH}_2\text{Cl}_2/\text{DMF}$ (9:1)	<table border="1" data-bbox="923 854 1270 991"> <thead> <tr> <th>Conditions</th> <th>CH_2X_2</th> <th>(%)</th> </tr> </thead> <tbody> <tr> <td>no ZnBr_2 present initially</td> <td>CH_2Br_2</td> <td>(56)</td> </tr> <tr> <td>ZnBr_2 present initially</td> <td>CH_2Br_2</td> <td>(52)</td> </tr> <tr> <td>ZnBr_2 present initially</td> <td>CH_2BrCl</td> <td>(54)</td> </tr> <tr> <td>no ZnBr_2 present initially</td> <td>CH_2I_2</td> <td>(47)</td> </tr> </tbody> </table>	Conditions	CH_2X_2	(%)	no ZnBr_2 present initially	CH_2Br_2	(56)	ZnBr_2 present initially	CH_2Br_2	(52)	ZnBr_2 present initially	CH_2BrCl	(54)	no ZnBr_2 present initially	CH_2I_2	(47)	70																					
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	$\text{Et}_2\text{Zn}, \text{CH}_2\text{I}_2$, hexane	 (84)	400																																				
	$\text{Zn}/\text{Cu}, \text{CH}_2\text{I}_2$	 (77-78)	379																																				
C_{4-8} 	$\text{Zn}/\text{Cu}, \text{CH}_2\text{I}_2, \text{Et}_2\text{O}$	 I +  II +  III	401																																				
		<table border="1" data-bbox="923 1754 1357 1914"> <thead> <tr> <th>R^1</th> <th>R^2</th> <th>R^3</th> <th>I (%)</th> <th>II (%)</th> <th>III (%)</th> </tr> </thead> <tbody> <tr> <td>H</td> <td>H</td> <td>H</td> <td>(12)</td> <td>(—)</td> <td>(2)</td> </tr> <tr> <td>Me</td> <td>Me</td> <td>Me</td> <td>(11)</td> <td>(—)</td> <td>(9)</td> </tr> <tr> <td>Me</td> <td>H</td> <td>CO_2Me</td> <td>(6)</td> <td>(1)</td> <td>(—)</td> </tr> <tr> <td>CO_2Me</td> <td>H</td> <td>CO_2Me</td> <td>(4)</td> <td>(—)</td> <td>(—)</td> </tr> <tr> <td>Me</td> <td>H</td> <td>CH_2OH</td> <td>(—)</td> <td>(18)</td> <td>(—)</td> </tr> </tbody> </table>	R^1	R^2	R^3	I (%)	II (%)	III (%)	H	H	H	(12)	(—)	(2)	Me	Me	Me	(11)	(—)	(9)	Me	H	CO_2Me	(6)	(1)	(—)	CO_2Me	H	CO_2Me	(4)	(—)	(—)	Me	H	CH_2OH	(—)	(18)	(—)	
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C_{4-12} 	$\text{Et}_2\text{Zn}, \text{CH}_2\text{I}_2$, $\text{Et}_2\text{O}, 0^\circ$ to π	 ZnPr-i <table border="1" data-bbox="1062 1937 1270 2052"> <thead> <tr> <th>R</th> <th>(%)</th> </tr> </thead> <tbody> <tr> <td>$n\text{-C}_{10}\text{H}_{21}$</td> <td>(>69)</td> </tr> <tr> <td>$\text{BnO}(\text{CH}_2)_2$</td> <td>(>63)</td> </tr> <tr> <td>$\text{EtO}_2\text{C}(\text{CH}_2)_8$</td> <td>(>65)</td> </tr> </tbody> </table>	R	(%)	$n\text{-C}_{10}\text{H}_{21}$	(>69)	$\text{BnO}(\text{CH}_2)_2$	(>63)	$\text{EtO}_2\text{C}(\text{CH}_2)_8$	(>65)	97																												
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TABLE III. CYCLOPROPANATION OF ACYCLIC, ACHIRAL ALKENES (Continued)

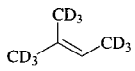
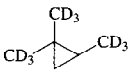
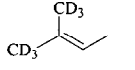
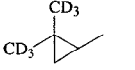
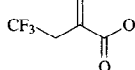
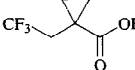
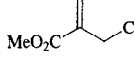
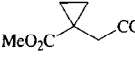
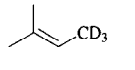
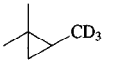
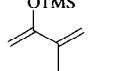
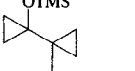
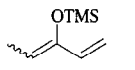
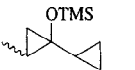
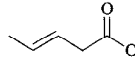
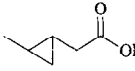
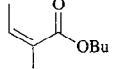
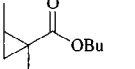
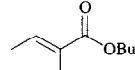
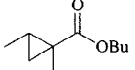
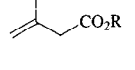
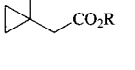
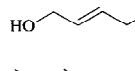
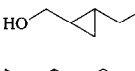
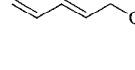

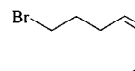
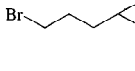
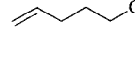
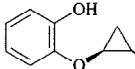
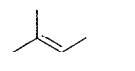
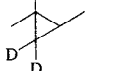
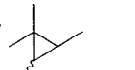
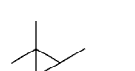
Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.						
	Zn/Cu, CH ₂ I ₂ , PhMe	 (—)	402						
	Zn/Cu, CH ₂ I ₂ , PhMe	 (—)	402						
	Zn/Ag, CH ₂ I ₂ , Et ₂ O, heat, sonication	 (25)	403						
	Zn/Ag, CH ₂ I ₂ , Et ₂ O	 (72)	404						
	Zn/Cu, CH ₂ I ₂ , PhMe	 (—)	402						
	Zn/Ag, CH ₂ I ₂ (xs), Et ₂ O, reflux	 (87)	107, 267						
 <i>E:Z</i> = 17:83	Zn/Ag, CH ₂ I ₂ (xs), Et ₂ O, reflux	 (85)	107, 267						
	Zn/Cu, CH ₂ I ₂ , I ₂ (cat.), Et ₂ O, reflux	 (69)	405						
	Zn/Cu, CH ₂ I ₂ , I ₂ (cat.), Et ₂ O, reflux	 (—)	406						
	Zn/Cu, CH ₂ I ₂ , I ₂ (cat.), Et ₂ O, reflux	 (—)	406						
	Zn/Cu, CH ₂ I ₂ , Et ₂ O, reflux	 <table border="1" data-bbox="1076 1315 1206 1384"> <tr> <td>R</td> <td>(%)</td> </tr> <tr> <td>Me</td> <td>(74)</td> </tr> <tr> <td>Et</td> <td>(—)</td> </tr> </table>	R	(%)	Me	(74)	Et	(—)	407 304
R	(%)								
Me	(74)								
Et	(—)								
	Zn/Cu, CH ₂ I ₂ , I ₂ (cat.), Et ₂ O, reflux	 (—)	408						
	Et ₂ Zn (6 eq), CH ₂ I ₂ (6 eq), (CH ₂ Cl) ₂ , -10° to rt	 (87)	409						
	Zn/Cu, CH ₂ I ₂ , Et ₂ O, reflux	 (77)	410						
	Zn/Hg, TMSCl, Et ₂ O, reflux	 (15) <i>cis:trans</i> = 2:1	77						
	Zn/Cu, CD ₂ I ₂	 (—)	411						
	Et ₂ Zn (0.67 eq), CHBr ₃ (1 eq), dry air (10 mL/min), olefin (xs), 0-10°	 (61)	103						
	Zn, CF ₂ Br ₂ , I ₂ (cat.), THF, rt	 (72)	74						

TABLE III. CYCLOPROPANATION OF ACYCLIC, ACHIRAL ALKENES (Continued)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
	Et ₂ Zn (1 eq), CH ₂ I ₂ (2 eq), -78 to -20°, TiCl ₄ (0.15 eq)	 (94)	31
	Et ₂ Zn (1 eq), CH ₂ I ₂ (2 eq), -78 to -20°, TiCl ₄ (0.15 eq)	 (90)	31
	Zn anode, 2e-, Me ₂ CBr ₂ , ZnBr ₂ present initially, CH ₂ Cl ₂ /DMF (9:1)	 (53)	70
	Et ₂ Zn (1.5 eq), CH ₂ I ₂ (3 eq), Et ₂ O, rt	 (68)	357
	Zn/Cu, CH ₂ I ₂ , Et ₂ O, 50°	 (33)	100
	Zn/Cu, CH ₂ I ₂	 (60-84)	379, 412, 413
C ₅₋₈ 	Et ₂ Zn (2 eq), CH ₂ Cl (4 eq), (CH ₂ Cl) ₂ , 0°	 R (%) H (87) HC≡CCH ₂ (51) Pr (83) CH ₂ Cl (73) TBDMSO(CH ₂) ₂ (82)	94
	Et ₂ Zn (2 eq), CH ₂ Cl (4 eq), (CH ₂ Cl) ₂ , 0°	 R (%) H (76) HC≡CCH ₂ (36)	94
C ₅₋₁₀ 	Zn/Cu, CH ₂ I ₂ , Et ₂ O	 R (%) Me (—) Et (—) <i>i</i> -Pr (—) Cx (—)	414
C ₆ 	Zn/Ag, CH ₂ I ₂ , Et ₂ O	 (55)	404
	Zn/Cu, CH ₂ I ₂ , I ₂ (cat.), Et ₂ O, reflux; repeated twice	 (67)	415
	Zn/Cu, CH ₂ I ₂ , Et ₂ O, reflux	" (54)	416, 417
	Zn/Cu, CH ₂ I ₂ , Et ₂ O, reflux	 (75)	304
	Sm (4 eq), CH ₂ I ₂ , THF, -78° to rt	 (91) mono:bis = >100:1	418
	Zn (xs), CH ₂ I ₂ (1.2 eq), Et ₂ O, 35°	" (51)	419
	Zn/Cu, CH ₂ I ₂ , Et ₂ O, reflux	" (74)	420
	Et ₂ Zn (3 eq), CH ₂ I ₂ (3 eq), C ₆ H ₆ , rt	 (63)	421
	Et ₂ Zn (1.5 eq), CH ₂ I ₂ (2.5 eq), (CH ₂ Cl) ₂ , 0°	 (96)	422
	Zn/Cu, CH ₂ Br ₂ , promoter, Et ₂ O	 Promoter (%) TiCl ₄ (49) ultrasound (30)	43

TABLE III. CYCLOPROPANATION OF ACYCLIC, ACHIRAL ALKENES (Continued)

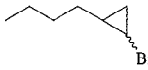
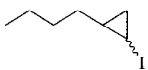
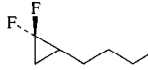












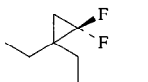


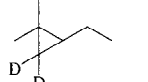


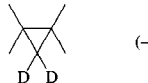
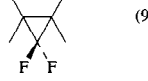






Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.													
	Zn/Cu, CH ₂ Br ₂ , Et ₂ O, 45°, sonication	" (30)	270													
	Et ₂ Zn (x eq), CHBr ₃ (y eq), dry air (10 mL/min), olefin (xs), temp	 Br	<table border="1"> <thead> <tr> <th>x/y</th> <th>Temp</th> <th>(%)</th> <th>syn:anti</th> </tr> </thead> <tbody> <tr> <td>0.65</td> <td>0-10°</td> <td>(68)</td> <td>2.5:1</td> </tr> <tr> <td>1</td> <td>50°</td> <td>(42)</td> <td>2.4:1</td> </tr> </tbody> </table>	x/y	Temp	(%)	syn:anti	0.65	0-10°	(68)	2.5:1	1	50°	(42)	2.4:1	73, 103, 103
x/y	Temp	(%)	syn:anti													
0.65	0-10°	(68)	2.5:1													
1	50°	(42)	2.4:1													
	Et ₂ Zn, CHI ₃ , olefin (xs), 50°	 I	(34) <i>syn:anti</i> = 67:33	274												
	Zn, CF ₂ Br ₂ , I ₂ (cat.), THF, rt	 F F	(6)	74												
	Zn/Cu, CH ₂ I ₂	 t-Bu	(—)	423												
	Zn/Cu, CH ₂ I ₂	 Et	(—)	424, 425												
	Zn/Cu, CH ₂ I ₂	 Et Et	(—)	424, 425												
	Zn/Cu, CH ₂ I ₂		(—)	426												
	Zn/Cu, CH ₂ I ₂	 i-Pr	(—)	423												
	Zn/Cu, CH ₂ I ₂	 Et	(—)	423												
	Zn, CF ₂ Br ₂ , I ₂ (cat.), THF, rt	 F F	(40)	74												
	Zn/Cu, CH ₂ I ₂		(—)	411												
	Zn/Cu, CD ₂ I ₂	 D D	(—)	411												
	CH ₂ Br ₂ , conditions		<table border="1"> <thead> <tr> <th>Conditions</th> <th>(%)</th> </tr> </thead> <tbody> <tr> <td>Zn/Cu, Et₂O, reflux</td> <td>(61)</td> </tr> <tr> <td>Zn, THF</td> <td>(41)</td> </tr> </tbody> </table>	Conditions	(%)	Zn/Cu, Et ₂ O, reflux	(61)	Zn, THF	(41)	24						
Conditions	(%)															
Zn/Cu, Et ₂ O, reflux	(61)															
Zn, THF	(41)															
	Zn/Ag, CH ₂ I ₂	" (—)	427													
	Zn/Cu, CD ₂ I ₂	 D D	(—)	411												
	Zn, CF ₂ Br ₂ , I ₂ (cat.), THF, rt	 F F	(96)	74												
	Et ₂ Zn (1 eq), CH ₂ I ₂ (2 eq), TiCl ₄ (0.15 eq), CH ₂ Cl ₂ , -78 to -20°	 n-Pr	(85)	31												
	Et ₂ Zn (3 eq), CH ₂ I ₂ (12 eq), C ₆ H ₆ , rt	" (81)	428													
	Et ₂ Zn (3 eq), CH ₂ I ₂ (12 eq), C ₆ H ₆ , rt	 OH	(74)	428												
	Et ₂ Zn, CH ₂ I ₂ , Et ₂ O, reflux	 OH	(78)	429												

TABLE III. CYCLOPROPANATION OF ACYCLIC, ACHIRAL ALKENES (Continued)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.																		
	Et ₂ Zn (3 eq), CH ₂ I ₂ (3 eq), CH ₂ Cl ₂ , -20° to rt	" (81)	409																		
	Zn/Cu, CH ₂ I ₂	(62)	379																		
	Zn/Cu, CH ₂ I ₂	(55)	430																		
	EtZnI, CH ₂ I ₂ , Et ₂ O	(99)	101																		
	EtZnI, CH ₂ I ₂	" (>72)	431																		
C ₆₋₁₁ 	Et ₂ Zn, CH ₂ I ₂ , (CH ₂ Cl) ₂ , -20°	I + II	155																		
		<table border="1"> <thead> <tr> <th>R</th> <th>(%)</th> <th>I:II</th> </tr> </thead> <tbody> <tr> <td>Me</td> <td>(68)</td> <td>5:1</td> </tr> <tr> <td>TBDPSOCH₂</td> <td>(72)</td> <td>>95:5</td> </tr> <tr> <td><i>i</i>-Pr</td> <td>(72)</td> <td>6:1</td> </tr> <tr> <td>Ph</td> <td>(80)</td> <td>5:1</td> </tr> <tr> <td>C₆H₁₁</td> <td>(78)</td> <td>7:1</td> </tr> </tbody> </table>	R	(%)	I:II	Me	(68)	5:1	TBDPSOCH ₂	(72)	>95:5	<i>i</i> -Pr	(72)	6:1	Ph	(80)	5:1	C ₆ H ₁₁	(78)	7:1	
R	(%)	I:II																			
Me	(68)	5:1																			
TBDPSOCH ₂	(72)	>95:5																			
<i>i</i> -Pr	(72)	6:1																			
Ph	(80)	5:1																			
C ₆ H ₁₁	(78)	7:1																			
C ₇ 	Zn/Cu, CH ₂ I ₂ , Et ₂ O, reflux	(—)	304																		
	Zn/Cu, CH ₂ I ₂ , Et ₂ O, reflux	(40-80)	408, 432, 433																		
	Zn/Cu, CH ₂ I ₂ , I ₂ (cat.), Et ₂ O, reflux	(73)	434																		
	Zn/Cu, CH ₂ I ₂ , I ₂ (cat.), Et ₂ O, reflux; repeated once	(43)	435																		
	Et ₂ Zn (x eq), CH ₂ I ₂ (y eq), dry air (10 mL/min), C ₆ H ₆ , 50°		<table border="1"> <thead> <tr> <th>x</th> <th>X</th> <th>y</th> <th>(%)</th> </tr> </thead> <tbody> <tr> <td>1</td> <td>I</td> <td>1.5</td> <td>(66)</td> </tr> <tr> <td>2</td> <td>I</td> <td>2</td> <td>(94)</td> </tr> <tr> <td>1</td> <td>Cl</td> <td>1.5</td> <td>(79)</td> </tr> </tbody> </table>	x	X	y	(%)	1	I	1.5	(66)	2	I	2	(94)	1	Cl	1.5	(79)	50	
x	X	y	(%)																		
1	I	1.5	(66)																		
2	I	2	(94)																		
1	Cl	1.5	(79)																		
	Et ₂ Zn (1 eq), CH ₂ I ₂ (1.5 eq), dry air (10 mL/min), C ₆ H ₆ , 50°, 1 h		<table border="1"> <thead> <tr> <th>X</th> <th>(%)</th> </tr> </thead> <tbody> <tr> <td>I</td> <td>(90)</td> </tr> <tr> <td>Cl</td> <td>(94)</td> </tr> </tbody> </table>	X	(%)	I	(90)	Cl	(94)	50											
X	(%)																				
I	(90)																				
Cl	(94)																				
	Zn/Cu, CH ₂ I ₂ , I ₂ (cat.), Et ₂ O, reflux	(3)	436																		
	Et ₂ Zn, CH ₂ I ₂	(72)	437																		
	Zn/Cu, CH ₂ I ₂	(86)	379																		
	EtZnI, CH ₂ I ₂	(95)	438																		
	Zn/Cu, CH ₂ I ₂ , Et ₂ O, reflux	I (75) + II (14)	438																		
C ₇₋₈ 	Zn/Cu, CH ₂ I ₂ , I ₂ (cat.), Et ₂ O, reflux		<table border="1"> <thead> <tr> <th>R¹</th> <th>R²</th> <th>(%)</th> </tr> </thead> <tbody> <tr> <td>Me</td> <td>Et</td> <td>(—)</td> </tr> <tr> <td>Et</td> <td>Me</td> <td>(—)</td> </tr> <tr> <td><i>i</i>-Pr</td> <td>Me</td> <td>(—)</td> </tr> </tbody> </table>	R ¹	R ²	(%)	Me	Et	(—)	Et	Me	(—)	<i>i</i> -Pr	Me	(—)	406					
R ¹	R ²	(%)																			
Me	Et	(—)																			
Et	Me	(—)																			
<i>i</i> -Pr	Me	(—)																			

TABLE III. CYCLOPROPANATION OF ACYCLIC, ACHIRAL ALKENES (Continued)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.																																																																														
	Zn/Cu, CH ₂ I ₂	<table border="1"> <thead> <tr> <th>R¹</th> <th>R²</th> <th>n</th> <th>(%)</th> </tr> </thead> <tbody> <tr> <td>Me</td> <td>H</td> <td>1</td> <td>(—)</td> </tr> <tr> <td>H</td> <td>Me</td> <td>1</td> <td>(—)</td> </tr> <tr> <td>Me</td> <td>Me</td> <td>1</td> <td>(—)</td> </tr> <tr> <td>Me</td> <td>H</td> <td>2</td> <td>(—)</td> </tr> <tr> <td>H</td> <td>Me</td> <td>2</td> <td>(—)</td> </tr> <tr> <td>Me</td> <td>Me</td> <td>2</td> <td>(—)</td> </tr> </tbody> </table>	R ¹	R ²	n	(%)	Me	H	1	(—)	H	Me	1	(—)	Me	Me	1	(—)	Me	H	2	(—)	H	Me	2	(—)	Me	Me	2	(—)	439																																																		
R ¹	R ²	n	(%)																																																																														
Me	H	1	(—)																																																																														
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Me	Me	2	(—)																																																																														
	Zn/Cu, CH ₂ I ₂		440																																																																														
	Et ₂ Zn, CH ₂ I _X	<table border="1"> <thead> <tr> <th>R</th> <th>(%)</th> </tr> </thead> <tbody> <tr> <td>F</td> <td>(—)</td> </tr> <tr> <td>Cl</td> <td>(—)</td> </tr> </tbody> </table>	R	(%)	F	(—)	Cl	(—)	441																																																																								
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Cl	(—)																																																																																
	Et ₂ Zn, CH ₂ I ₂		442																																																																														
	Et ₂ Zn, CH ₂ I ₂ , PhMe, 65°		443																																																																														
	CH ₂ X ₂ , conditions	<table border="1"> <thead> <tr> <th>Conditions</th> <th>X</th> <th>(%)</th> </tr> </thead> <tbody> <tr> <td>Zn/Cu, Et₂O, reflux</td> <td>Br</td> <td>(46)</td> </tr> <tr> <td>Zn, THF</td> <td>I</td> <td>(43)</td> </tr> </tbody> </table>	Conditions	X	(%)	Zn/Cu, Et ₂ O, reflux	Br	(46)	Zn, THF	I	(43)	24																																																																					
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	Zn anode, 2e ⁻ , CH ₂ X ₂ , conditions, CH ₂ Cl ₂ /DMF (9:1)	<table border="1"> <thead> <tr> <th>Conditions</th> <th>X</th> <th>(%)</th> </tr> </thead> <tbody> <tr> <td>ZnBr₂ present initially</td> <td>Br</td> <td>(26)</td> </tr> <tr> <td>no ZnBr₂ present initially</td> <td>I</td> <td>(33)</td> </tr> </tbody> </table>	Conditions	X	(%)	ZnBr ₂ present initially	Br	(26)	no ZnBr ₂ present initially	I	(33)	70																																																																					
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	1. Et ₂ Zn (2 eq), CH ₂ Cl ₂ 2. TFA 3. CH ₂ I ₂ , add olefin		53																																																																														
	Et ₂ Zn (x eq), CH ₂ I _X (y eq), catalyst, C ₆ H ₆	<table border="1"> <thead> <tr> <th>x</th> <th>X</th> <th>y</th> <th>Catalyst</th> <th>(%)</th> <th>Reacted CH₂I_X (%)</th> </tr> </thead> <tbody> <tr> <td>1</td> <td>Cl</td> <td>1.5</td> <td>—</td> <td>(0)</td> <td>0</td> </tr> <tr> <td>1</td> <td>Cl</td> <td>1.2</td> <td>—</td> <td>(4)</td> <td>11</td> </tr> <tr> <td>1</td> <td>I</td> <td>1.2</td> <td>—</td> <td>(0)</td> <td>3</td> </tr> <tr> <td>1</td> <td>I</td> <td>1.5</td> <td>O₂ (10 mL/min)</td> <td>(70)</td> <td>100</td> </tr> <tr> <td>0</td> <td>I</td> <td>1.2</td> <td>AIBN (0.5 eq)</td> <td>(0)</td> <td>2</td> </tr> <tr> <td>1</td> <td>I</td> <td>1.2</td> <td>AIBN (0.1 eq)</td> <td>(0)</td> <td>15</td> </tr> <tr> <td>1</td> <td>I</td> <td>1.2</td> <td>AIBN (0.1 eq)</td> <td>(90)</td> <td>49</td> </tr> <tr> <td>1</td> <td>I</td> <td>1.2</td> <td>AIBN (0.5 eq)</td> <td>(22)</td> <td>74</td> </tr> <tr> <td>1</td> <td>I</td> <td>1.2</td> <td>AIBN (0.9 eq)</td> <td>(24)</td> <td>87</td> </tr> <tr> <td>1</td> <td>I</td> <td>1.9</td> <td>AIBN (0.5 eq)</td> <td>(46)</td> <td>64</td> </tr> <tr> <td>0</td> <td>I</td> <td>1.2</td> <td>UV light</td> <td>(0)</td> <td>5</td> </tr> <tr> <td>1</td> <td>I</td> <td>1.2</td> <td>UV light</td> <td>(73)</td> <td>100</td> </tr> </tbody> </table>	x	X	y	Catalyst	(%)	Reacted CH ₂ I _X (%)	1	Cl	1.5	—	(0)	0	1	Cl	1.2	—	(4)	11	1	I	1.2	—	(0)	3	1	I	1.5	O ₂ (10 mL/min)	(70)	100	0	I	1.2	AIBN (0.5 eq)	(0)	2	1	I	1.2	AIBN (0.1 eq)	(0)	15	1	I	1.2	AIBN (0.1 eq)	(90)	49	1	I	1.2	AIBN (0.5 eq)	(22)	74	1	I	1.2	AIBN (0.9 eq)	(24)	87	1	I	1.9	AIBN (0.5 eq)	(46)	64	0	I	1.2	UV light	(0)	5	1	I	1.2	UV light	(73)	100	50
x	X	y	Catalyst	(%)	Reacted CH ₂ I _X (%)																																																																												
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	Et ₂ Zn (x eq), CH ₂ I _X (y eq), dry air or O ₂ (10 mL/min), C ₆ H ₆ , 50°	<table border="1"> <thead> <tr> <th>x</th> <th>X</th> <th>y</th> <th>(%)</th> </tr> </thead> <tbody> <tr> <td>1.8</td> <td>I</td> <td>2</td> <td>(79)</td> </tr> <tr> <td>1</td> <td>I</td> <td>1.2</td> <td>(58-62)</td> </tr> <tr> <td>1</td> <td>I</td> <td>1.2</td> <td>(57)</td> </tr> <tr> <td>1</td> <td>Cl</td> <td>1.2</td> <td>(63)</td> </tr> <tr> <td>1</td> <td>Cl</td> <td>1.5</td> <td>(65-70)</td> </tr> </tbody> </table>	x	X	y	(%)	1.8	I	2	(79)	1	I	1.2	(58-62)	1	I	1.2	(57)	1	Cl	1.2	(63)	1	Cl	1.5	(65-70)	50																																																						
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	Et ₂ Zn (1 eq), CHBr ₃ (1 eq), dry air (10 mL/min), olefin (xs), 50°		73, 103																																																																														
	Et ₂ Zn, CHI ₃ , olefin (xs), 50°		(44) <i>syn:anti</i> = — 274																																																																														
	Zn, CF ₂ Br ₂ , I ₂ (cat.), THF, rt		(15) 74																																																																														

TABLE III. CYCLOPROPANATION OF ACYCLIC, ACHIRAL ALKENES (Continued)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.																				
	Zn, (ClMe ₂ SiCH ₂) ₂ , Et ₂ O, reflux	(53)	76																				
	Zn, (ClMe ₂ SiCH ₂) ₂ , Et ₂ O, reflux	(44) <i>endo:exo</i> = 1:1	76																				
	Zn, (ClMe ₂ SiCH ₂) ₂ , Et ₂ O, reflux	(99) <i>cis:trans</i> = 25:1	76																				
	Zn, (ClMe ₂ SiCH ₂) ₂ , Et ₂ O, reflux	(19) <i>endo:exo</i> = 1:1	76																				
	Zn, (ClMe ₂ SiCH ₂) ₂ , Et ₂ O, reflux	(59) <i>endo:exo</i> = 11:1	76																				
	Zn, (ClMe ₂ SiCH ₂) ₂ , Et ₂ O, reflux	(55) <i>endo:exo</i> = 20:1	76																				
	Zn/Ag, CH ₂ I ₂	I (-) + II (-) + III (-) + other products	444																				
	Zn/Cu, CH ₂ I ₂ , Et ₂ O, reflux	(35)	445																				
	Et ₂ Zn, CH ₂ I ₂ , PhMe, rt	I (7-13) + II (7-45)	446																				
	Conditions	I + II + III	104																				
		<table border="1"> <thead> <tr> <th>Conditions</th> <th>I (%)</th> <th>II (%)</th> <th>III (%)</th> </tr> </thead> <tbody> <tr> <td>Zn/Cu, CH₂I₂, AcCl, Et₂O</td> <td>(9)</td> <td>(18)</td> <td>(1)</td> </tr> <tr> <td>Zn/Cu, CH₂Br₂, AcCl, Et₂O</td> <td>(2)</td> <td>(4)</td> <td>(0)</td> </tr> <tr> <td>Et₂Zn, CH₂I₂, PhMe</td> <td>(5)</td> <td>(34)</td> <td>(1)</td> </tr> <tr> <td>Et₃Al, CH₂I₂, PhMe/CH₂Cl₂</td> <td>(13)</td> <td>(39)</td> <td>(8)</td> </tr> </tbody> </table>	Conditions	I (%)	II (%)	III (%)	Zn/Cu, CH ₂ I ₂ , AcCl, Et ₂ O	(9)	(18)	(1)	Zn/Cu, CH ₂ Br ₂ , AcCl, Et ₂ O	(2)	(4)	(0)	Et ₂ Zn, CH ₂ I ₂ , PhMe	(5)	(34)	(1)	Et ₃ Al, CH ₂ I ₂ , PhMe/CH ₂ Cl ₂	(13)	(39)	(8)	
Conditions	I (%)	II (%)	III (%)																				
Zn/Cu, CH ₂ I ₂ , AcCl, Et ₂ O	(9)	(18)	(1)																				
Zn/Cu, CH ₂ Br ₂ , AcCl, Et ₂ O	(2)	(4)	(0)																				
Et ₂ Zn, CH ₂ I ₂ , PhMe	(5)	(34)	(1)																				
Et ₃ Al, CH ₂ I ₂ , PhMe/CH ₂ Cl ₂	(13)	(39)	(8)																				
	Zn/Cu, CH ₂ I ₂ , I ₂ (cat.), Et ₂ O, reflux	(77)	408																				
	Zn/Cu, CH ₂ I ₂ , I ₂ (cat.), Et ₂ O, reflux	(-)	408																				
	Et ₂ Zn (2 eq), CH ₂ ICl (4 eq), (CH ₂ Cl) ₂	(>99)	447																				

TABLE III. CYCLOPROPANATION OF ACYCLIC, ACHIRAL ALKENES (Continued)

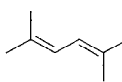
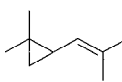
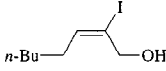
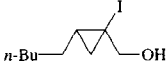
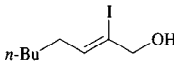
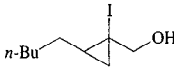
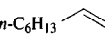
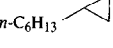
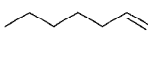
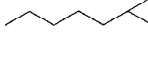
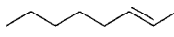
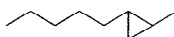
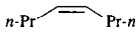


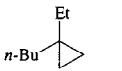
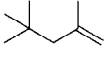
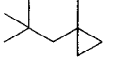
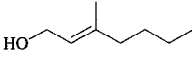
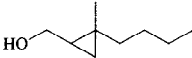
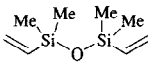
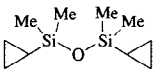
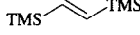

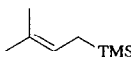
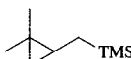
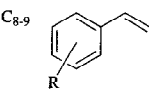
Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.												
	Zn/Cu, CH ₂ I ₂	 (87)	448												
	Et ₂ Zn (2 eq), CH ₂ ICl (4 eq), (CH ₂ Cl) ₂ , 0°	 (31)	94												
	Et ₂ Zn (2 eq), CH ₂ ICl (4 eq), (CH ₂ Cl) ₂ , 0°	 (78)	94												
	Zn/Cu, CH ₂ Br ₂ , Et ₂ O, 45°, sonication	 (28)	270												
	Zn/Cu, CH ₂ Br ₂ , AcCl (0.02 eq), Et ₂ O	" (61)	41												
	Zn anode, 2e ⁻ , CH ₂ Br ₂ , no ZnBr ₂ present initially, CH ₂ Cl ₂ /DMF (9:1)	" (66)	70												
	Zn/Cu, CH ₂ X ₂ , promoter, Et ₂ O	<table border="1" data-bbox="972 826 1232 941"> <thead> <tr> <th>Promoter</th> <th>X</th> <th>(%)</th> </tr> </thead> <tbody> <tr> <td>TiCl₄</td> <td>Br</td> <td>(50)</td> </tr> <tr> <td>ultrasound</td> <td>Br</td> <td>(28)</td> </tr> <tr> <td>TiCl₄</td> <td>I</td> <td>(56)</td> </tr> </tbody> </table>	Promoter	X	(%)	TiCl ₄	Br	(50)	ultrasound	Br	(28)	TiCl ₄	I	(56)	43
Promoter	X	(%)													
TiCl ₄	Br	(50)													
ultrasound	Br	(28)													
TiCl ₄	I	(56)													
	Et ₂ Zn (1 eq), CH ₂ IX (1.5 eq), dry air (10 mL/min), C ₆ H ₆ , 50°	<table border="1" data-bbox="972 964 1111 1044"> <thead> <tr> <th>X</th> <th>(%)</th> </tr> </thead> <tbody> <tr> <td>I</td> <td>66</td> </tr> <tr> <td>Cl</td> <td>88</td> </tr> </tbody> </table>	X	(%)	I	66	Cl	88	50						
X	(%)														
I	66														
Cl	88														
	Zn/Cu, CH ₂ I ₂	 (—)	449												
	R ₃ Al (x eq), CH ₂ I ₂ (1.2 eq), solvent, rt	<table border="1" data-bbox="972 1182 1258 1274"> <thead> <tr> <th>R</th> <th>x</th> <th>Solvent</th> <th>(%)</th> </tr> </thead> <tbody> <tr> <td>Me</td> <td>1.1</td> <td>hexane</td> <td>(75)</td> </tr> <tr> <td>Et</td> <td>1.2</td> <td>CH₂Cl₂</td> <td>(66)</td> </tr> </tbody> </table>	R	x	Solvent	(%)	Me	1.1	hexane	(75)	Et	1.2	CH ₂ Cl ₂	(66)	59
R	x	Solvent	(%)												
Me	1.1	hexane	(75)												
Et	1.2	CH ₂ Cl ₂	(66)												
	Zn/Cu, CH ₂ I ₂	 (—)	450												
	Zn/Cu, CH ₂ I ₂ , Et ₂ O, reflux	 (21)	451												
	Zn/Cu, CH ₂ I ₂	 (—)	423												
	Zn/Cu, CH ₂ I ₂	 (—)	423												
	Zn/Cu, CH ₂ I ₂ , Et ₂ O, heat	 (>40) E:Z = 76:28	452												
	Zn/Cu, CH ₂ I ₂	 (83)	379												
	Zn/Cu, CH ₂ I ₂	 (30)	379												
	Zn/Cu, CH ₂ I ₂	 (—)	453												
	Et ₂ Zn, CH ₂ I ₂	<table border="1" data-bbox="1058 1940 1215 2031"> <thead> <tr> <th>R</th> <th>(%)</th> </tr> </thead> <tbody> <tr> <td>4-OMe</td> <td>(54)</td> </tr> <tr> <td>4-Me</td> <td>(36)</td> </tr> </tbody> </table>	R	(%)	4-OMe	(54)	4-Me	(36)	454						
R	(%)														
4-OMe	(54)														
4-Me	(36)														

TABLE III. CYCLOPROPANATION OF ACYCLIC, ACHIRAL ALKENES (Continued)

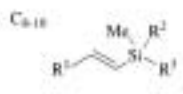
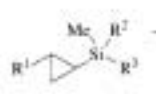
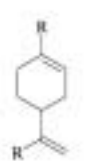
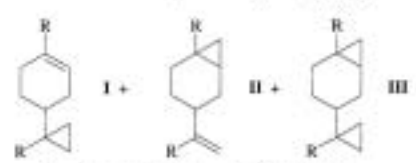
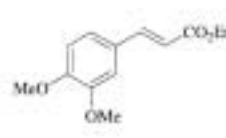
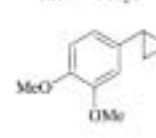
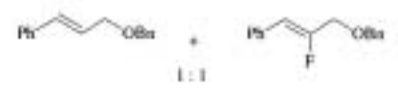
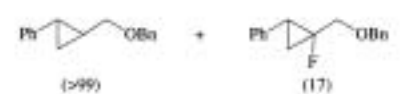
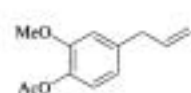
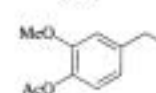
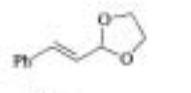
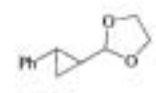
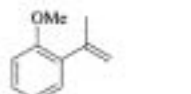
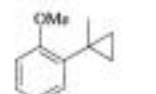
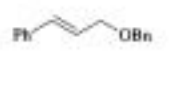
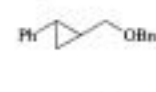

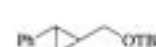
Substrate	Conditions	Product(s) and Yield(s) (%)	Ref.																																								
	ZnCu, CH ₂ I ₂ , Et ₂ O, reflux	<table border="1"> <thead> <tr> <th>R</th> <th>(%)</th> </tr> </thead> <tbody> <tr> <td>2-Me</td> <td>(45)</td> </tr> <tr> <td>4-Me</td> <td>(—)</td> </tr> <tr> <td>4-OMe</td> <td>(—)</td> </tr> <tr> <td>4-OEt</td> <td>(—)</td> </tr> </tbody> </table>	R	(%)	2-Me	(45)	4-Me	(—)	4-OMe	(—)	4-OEt	(—)	455																														
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	Et ₂ Zn (1 eq), CH ₂ I ₂ (2 eq), Et ₂ O, rt	 <table border="1"> <thead> <tr> <th>R¹</th> <th>R²</th> <th>R³</th> <th>(%)</th> </tr> </thead> <tbody> <tr> <td>Ph</td> <td>Me</td> <td>OH</td> <td>(71)</td> </tr> <tr> <td>Ph</td> <td>Me</td> <td>PhCH₂O</td> <td>(50)</td> </tr> <tr> <td>Ph</td> <td>Me</td> <td>OTMS</td> <td>(0)</td> </tr> <tr> <td>C₆H₁₁</td> <td>Me</td> <td>OH</td> <td>(100)</td> </tr> <tr> <td>C₆H₁₃</td> <td>Me</td> <td>PhCH₂O</td> <td>(81)</td> </tr> <tr> <td>C₆H₁₃</td> <td>Me</td> <td>OTMS</td> <td>(0)</td> </tr> <tr> <td>H</td> <td>Ph</td> <td>OH</td> <td>(72)</td> </tr> <tr> <td>H</td> <td>Ph</td> <td>PhCH₂O</td> <td>(trace)</td> </tr> <tr> <td>H</td> <td>Ph</td> <td>OTMS</td> <td>(0)</td> </tr> </tbody> </table>	R ¹	R ²	R ³	(%)	Ph	Me	OH	(71)	Ph	Me	PhCH ₂ O	(50)	Ph	Me	OTMS	(0)	C ₆ H ₁₁	Me	OH	(100)	C ₆ H ₁₃	Me	PhCH ₂ O	(81)	C ₆ H ₁₃	Me	OTMS	(0)	H	Ph	OH	(72)	H	Ph	PhCH ₂ O	(trace)	H	Ph	OTMS	(0)	357
R ¹	R ²	R ³	(%)																																								
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	ZnCu, CH ₂ I ₂ , Et ₂ O, reflux	 (>20)	456																																								
	ZnCu, CH ₂ I ₂ (5 eq), I ₂ (cat.), Et ₂ O, reflux, 15 h	 (>99) and (17)	92																																								
	ZnCu, CH ₂ I ₂ , I ₂ (cat.), Et ₂ O, reflux	 (42)	457																																								
	Et ₂ Zn (3 eq), CH ₂ I ₂ (6 eq), (CH ₂ Cl) ₂ , -23°, 90 min	 <table border="1"> <thead> <tr> <th>X</th> <th>(%)</th> </tr> </thead> <tbody> <tr> <td>Cl</td> <td>(100)</td> </tr> <tr> <td>I</td> <td>(85)</td> </tr> </tbody> </table>	X	(%)	Cl	(100)	I	(85)	51																																		
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	Zn/Ag, CH ₂ I ₂ , Et ₂ O, reflux	 (47)	458																																								
	Et ₂ Zn (2 eq), CH ₂ I ₂ (4 eq), (CH ₂ Cl) ₂ , 0°, 15 min	 <table border="1"> <thead> <tr> <th>X</th> <th>(%)</th> </tr> </thead> <tbody> <tr> <td>Cl</td> <td>(100)</td> </tr> <tr> <td>I</td> <td>(96)</td> </tr> </tbody> </table>	X	(%)	Cl	(100)	I	(96)	51																																		
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	RZnCH ₂ X (I) + EtZnCH ₂ X (II), CD ₂ Cl ₂ , 0°	<table border="1"> <thead> <tr> <th>R</th> <th>X</th> <th>I:II</th> <th>(%)</th> </tr> </thead> <tbody> <tr> <td>Et₂NCO(CH₂)₂</td> <td>I</td> <td>>98:2</td> <td>(0)</td> </tr> <tr> <td>EtO₂C(CH₂)₂</td> <td>I</td> <td>>97:3</td> <td>(21^a)</td> </tr> <tr> <td>EtO₂C(CH₂)₂</td> <td>Cl</td> <td>>98:2</td> <td>(42)</td> </tr> <tr> <td>BnO(CH₂)₂</td> <td>I</td> <td>72:28</td> <td>(>90)</td> </tr> <tr> <td>Me₂SiCH₂</td> <td>I</td> <td>84:16</td> <td>(>95)</td> </tr> <tr> <td>Me₂SiCH₂</td> <td>Cl</td> <td>94:6</td> <td>(>95)</td> </tr> </tbody> </table>	R	X	I:II	(%)	Et ₂ NCO(CH ₂) ₂	I	>98:2	(0)	EtO ₂ C(CH ₂) ₂	I	>97:3	(21 ^a)	EtO ₂ C(CH ₂) ₂	Cl	>98:2	(42)	BnO(CH ₂) ₂	I	72:28	(>90)	Me ₂ SiCH ₂	I	84:16	(>95)	Me ₂ SiCH ₂	Cl	94:6	(>95)	499												
R	X	I:II	(%)																																								
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	1. Et ₂ Zn (2 eq), CH ₂ Cl ₂ 2. TFA 3. CH ₂ F ₂ , add olefin	 (95)	53																																								

TABLE III. CYCLOPROPANATION OF ACYCLIC, ACHIRAL ALKENES (Continued)

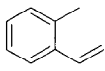
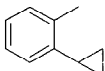
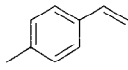
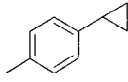



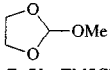

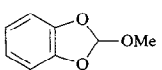
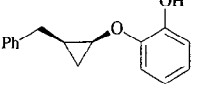






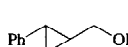
Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.										
	Zn, CH ₂ I ₂ , I ₂ (cat.), DME, reflux	 (72)	460										
	Zn/Cu, CH ₂ I ₂	 (—)	461										
Ph-CH=CH ₂	CH ₂ X ₂ , conditions	Ph- 	<table border="1"> <thead> <tr> <th>Conditions</th> <th>X</th> <th>(%)</th> </tr> </thead> <tbody> <tr> <td>Zn/Cu, Et₂O, reflux</td> <td>I</td> <td>(40)</td> </tr> <tr> <td>Zn, THF</td> <td>Br</td> <td>(35)</td> </tr> </tbody> </table>	Conditions	X	(%)	Zn/Cu, Et ₂ O, reflux	I	(40)	Zn, THF	Br	(35)	24
Conditions	X	(%)											
Zn/Cu, Et ₂ O, reflux	I	(40)											
Zn, THF	Br	(35)											
	Zn/Hg, TMSCl, HC(OR) ₃ , Et ₂ O, reflux	Ph- 	<table border="1"> <thead> <tr> <th>R</th> <th>(%)</th> <th>cis:trans</th> </tr> </thead> <tbody> <tr> <td>Me</td> <td>(64)</td> <td>2:1</td> </tr> <tr> <td>n-Pr</td> <td>(43)</td> <td>2:1</td> </tr> </tbody> </table>	R	(%)	cis:trans	Me	(64)	2:1	n-Pr	(43)	2:1	77
R	(%)	cis:trans											
Me	(64)	2:1											
n-Pr	(43)	2:1											
	Zn/Hg, TMSCl, (EtO) ₂ CH(OPh), Et ₂ O, reflux	Ph-  (67)	cis:trans = 2:1	77									
	Zn/Hg, TMSCl, Et ₂ O, reflux	Ph-  (55)	cis:trans = 3:1	77									
	Zn/Hg, TMSCl, Et ₂ O, reflux	Ph-  (23)	cis:trans = 5:2	77									
Ph-CH=CH ₂	Et ₂ Zn (5 eq), CH ₂ IX (10 eq), (CH ₂ Cl) ₂ , 23°, 1 h	Ph- 	<table border="1"> <thead> <tr> <th>X</th> <th>(%)</th> </tr> </thead> <tbody> <tr> <td>Cl</td> <td>(92)</td> </tr> <tr> <td>I</td> <td>(88)</td> </tr> </tbody> </table>	X	(%)	Cl	(92)	I	(88)	51			
X	(%)												
Cl	(92)												
I	(88)												
	Zn/Cu, CH ₂ I ₂ , I ₂ (cat.), Et ₂ O, reflux	" (41)	370										
	1. Et ₂ Zn (2 eq), CH ₂ Cl ₂ 2. TFA 3. CH ₂ I ₂ , add olefin	" (77)	53										
	Zn, CF ₂ Br ₂ , I ₂ (cat.), THF, rt	Ph-  (29)	74										
Ph-CH=CH ₂	Zn/Cu, CH ₂ I ₂	Ph-  (>75)	462										
Ph-C(CH ₃)=CH ₂	CH ₂ X ₂ , conditions	Ph- 	<table border="1"> <thead> <tr> <th>Conditions</th> <th>X</th> <th>(%)</th> </tr> </thead> <tbody> <tr> <td>Zn/Cu, Et₂O, reflux</td> <td>I</td> <td>(61)</td> </tr> <tr> <td>Zn, THF</td> <td>Br</td> <td>(35)</td> </tr> </tbody> </table>	Conditions	X	(%)	Zn/Cu, Et ₂ O, reflux	I	(61)	Zn, THF	Br	(35)	24
Conditions	X	(%)											
Zn/Cu, Et ₂ O, reflux	I	(61)											
Zn, THF	Br	(35)											
	Zn/Cu, CH ₂ I ₂	" (>75)	462										
	Zn/Hg, TMSCl, HC(OMe) ₃ , Et ₂ O, reflux	Ph-  (56)	cis:trans = 2:1	77									
	Zn, CF ₂ Br ₂ , I ₂ (cat.), THF, rt	Ph-  (71)	74										
Ph-CH=CH-CH ₂ OH	Zn anode, 2e ⁻ , CH ₂ BrCl, ZnBr ₂ present initially, CH ₂ Cl ₂ /DMF (9:1)	Ph-  (59)	70										
	Et ₂ Zn (2 eq), CH ₂ IX (4 eq), (CH ₂ Cl) ₂ , 0°, 30 min	"	<table border="1"> <thead> <tr> <th>X</th> <th>(%)</th> </tr> </thead> <tbody> <tr> <td>Cl</td> <td>(96)</td> </tr> <tr> <td>I</td> <td>(16)</td> </tr> </tbody> </table>	X	(%)	Cl	(96)	I	(16)	51			
X	(%)												
Cl	(96)												
I	(16)												
	Et ₂ Zn (2 eq), CH ₂ I ₂ (3.3 eq), hexanes, -20° to rt	" (86)	463										
	Et ₂ Zn (2 eq), CH ₂ I ₂ (3 eq), TiX ₄ (0.1 eq), PhMe/hexane, -23°, 9 h	"	<table border="1"> <thead> <tr> <th>X</th> <th>(%)</th> </tr> </thead> <tbody> <tr> <td>—</td> <td>(22)</td> </tr> <tr> <td>OPr-<i>i</i></td> <td>(35)</td> </tr> <tr> <td>Cl</td> <td>(77)</td> </tr> </tbody> </table>	X	(%)	—	(22)	OPr- <i>i</i>	(35)	Cl	(77)	30	
X	(%)												
—	(22)												
OPr- <i>i</i>	(35)												
Cl	(77)												

TABLE III. CYCLOPROPANATION OF ACYCLIC, ACHIRAL ALKENES (Continued)

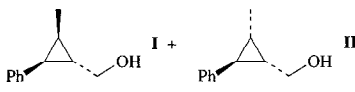
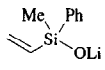
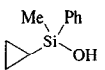
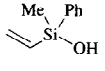
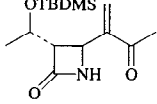
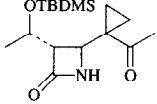
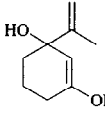
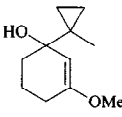
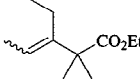
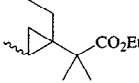
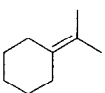
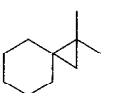
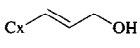

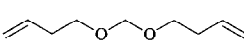
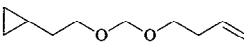
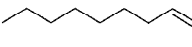
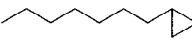
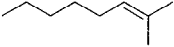
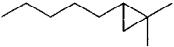
Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.																																																
	1. Et ₂ Zn (2 eq), CH ₂ Cl ₂ 2. TFA 3. CH ₂ I ₂ , add olefin	" (80)	53																																																
		<table border="1"> <thead> <tr> <th>Lewis acid</th> <th>(%) at 0°</th> <th>(%) at -20°</th> <th>(%) at -40°</th> </tr> </thead> <tbody> <tr> <td>—</td> <td>(23)</td> <td>(<5)</td> <td>(<5)</td> </tr> <tr> <td>BBr₃</td> <td>(93)</td> <td>(90)</td> <td>(60)</td> </tr> <tr> <td>B(OMe)₃</td> <td>(50)</td> <td>(10)</td> <td>(4)</td> </tr> <tr> <td>TiCl₄</td> <td>(94)</td> <td>(90)</td> <td>(60)</td> </tr> <tr> <td>Ti(OPr-<i>i</i>)₄</td> <td>(50)</td> <td>(45)</td> <td>(8)</td> </tr> <tr> <td>TiCl₂(OPr-<i>i</i>)₂</td> <td>(85)</td> <td>(80)</td> <td>(45)</td> </tr> <tr> <td>SiCl₄</td> <td>(90)</td> <td>(88)</td> <td>(58)</td> </tr> <tr> <td>SnCl₄</td> <td>(83)</td> <td>(55)</td> <td>(55)</td> </tr> <tr> <td>Et₂AlCl</td> <td>(93)</td> <td>(87)</td> <td>(70)</td> </tr> <tr> <td>Zn(OTf)₂</td> <td>(45)</td> <td>(18)</td> <td>(7)</td> </tr> <tr> <td>ZnI₂</td> <td>(50)</td> <td>(14)</td> <td>(9)</td> </tr> </tbody> </table>	Lewis acid	(%) at 0°	(%) at -20°	(%) at -40°	—	(23)	(<5)	(<5)	BBr ₃	(93)	(90)	(60)	B(OMe) ₃	(50)	(10)	(4)	TiCl ₄	(94)	(90)	(60)	Ti(OPr- <i>i</i>) ₄	(50)	(45)	(8)	TiCl ₂ (OPr- <i>i</i>) ₂	(85)	(80)	(45)	SiCl ₄	(90)	(88)	(58)	SnCl ₄	(83)	(55)	(55)	Et ₂ AlCl	(93)	(87)	(70)	Zn(OTf) ₂	(45)	(18)	(7)	ZnI ₂	(50)	(14)	(9)	31
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	Et ₂ Zn (x eq), MeCHI ₂ (y eq), CH ₂ Cl ₂ , 0°	 <table border="1"> <thead> <tr> <th>x</th> <th>y</th> <th>(%)</th> <th>I:II</th> </tr> </thead> <tbody> <tr> <td>1.5</td> <td>2.0</td> <td>(85)</td> <td>93:7</td> </tr> <tr> <td>2.2</td> <td>4.4</td> <td>(82)</td> <td>89:11</td> </tr> <tr> <td>5</td> <td>5.0</td> <td>(58)</td> <td>93:7</td> </tr> </tbody> </table>	x	y	(%)	I:II	1.5	2.0	(85)	93:7	2.2	4.4	(82)	89:11	5	5.0	(58)	93:7	69																																
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	1. Et ₂ Zn (1.1 eq) 2. ZnI ₂ 3. Zn(CHIMe) ₂ , CH ₂ Cl ₂ , 0°	" (62) I:II = 71:29	464																																																
	Et ₂ Zn (1.5 eq), CH ₂ I ₂ (3 eq), Et ₂ O, rt	 (52)	357, 465																																																
	Et ₂ Zn (1.5 eq), CH ₂ I ₂ (3 eq), Et ₂ O, rt	" (60)	357, 465																																																
	Zn/Cu, CH ₂ I ₂ , Et ₂ O	 (60-70)	466																																																
	Zn/Cu, CH ₂ I ₂ , Et ₂ O, reflux	 (81)	438																																																
	Zn/Cu, CH ₂ I ₂ , Et ₂ O, reflux	 (75)	304																																																
	Zn/Cu, CH ₂ I ₂	 (—)	467																																																
	Et ₂ Zn (3 eq), CH ₂ I ₂ (3 eq), CH ₂ Cl ₂ , -20° to rt	 (96)	468																																																
	Zn/Cu, CH ₂ I ₂ , Et ₂ O	 (35)	209																																																
	Zn/Cu, CH ₂ I ₂ , Et ₂ O, reflux	 (88)	469																																																
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TABLE III. CYCLOPROPANATION OF ACYCLIC, ACHIRAL ALKENES (Continued)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.																																																																				
	EtZnI, CH ₂ I ₂ , Et ₂ O	(92)	438																																																																				
	Zn/Cu, CH ₂ I ₂	(45)	470, 471																																																																				
	Conditions		98																																																																				
		<table border="1"> <thead> <tr> <th>R</th> <th>Conditions</th> <th>(%)</th> </tr> </thead> <tbody> <tr> <td>SnMe₃</td> <td>Zn/Cu, CH₂I₂</td> <td>(0)</td> </tr> <tr> <td>TMS</td> <td>Zn/Cu, CH₂I₂</td> <td>(0)</td> </tr> <tr> <td>SnMe₃</td> <td>Sm/Hg, CH₂I₂</td> <td>(64)</td> </tr> <tr> <td>TMS</td> <td>Sm/Hg, CH₂I₂</td> <td>(68)</td> </tr> </tbody> </table>	R	Conditions	(%)	SnMe ₃	Zn/Cu, CH ₂ I ₂	(0)	TMS	Zn/Cu, CH ₂ I ₂	(0)	SnMe ₃	Sm/Hg, CH ₂ I ₂	(64)	TMS	Sm/Hg, CH ₂ I ₂	(68)																																																						
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	Zn/Cu, CH ₂ I ₂ (x eq), I ₂ (cat.), Et ₂ O, reflux		92																																																																				
		<table border="1"> <thead> <tr> <th>R¹</th> <th>R²</th> <th>x</th> <th>(%)</th> </tr> </thead> <tbody> <tr> <td>Ph(CH₂)₂</td> <td>H</td> <td>1.2</td> <td>(0)</td> </tr> <tr> <td>Ph(CH₂)₂</td> <td>H</td> <td>5</td> <td>(77)</td> </tr> <tr> <td>Ph(CH₂)₂</td> <td>H</td> <td>5</td> <td>(78)^b</td> </tr> <tr> <td>Ph(CH₂)₂</td> <td>H</td> <td>10</td> <td>(78)</td> </tr> <tr> <td>Ph(CH₂)₂</td> <td>MOM</td> <td>5</td> <td>(40)</td> </tr> <tr> <td>Ph(CH₂)₂</td> <td>MOM</td> <td>10</td> <td>(87)</td> </tr> <tr> <td>Ph(CH₂)₂</td> <td>Bn</td> <td>5</td> <td>(47)</td> </tr> <tr> <td>Ph(CH₂)₂</td> <td>Bn</td> <td>10</td> <td>(66)</td> </tr> <tr> <td>Ph</td> <td>H</td> <td>1.2</td> <td>(0)</td> </tr> <tr> <td>Ph</td> <td>H</td> <td>5</td> <td>(78)</td> </tr> <tr> <td>Ph</td> <td>MOM</td> <td>10</td> <td>(26)</td> </tr> <tr> <td>Ph</td> <td>Bn</td> <td>5</td> <td>(12)</td> </tr> <tr> <td>Ph</td> <td>Bn</td> <td>10</td> <td>(44)</td> </tr> <tr> <td>Cx</td> <td>H</td> <td>5</td> <td>(75)</td> </tr> <tr> <td>Cx</td> <td>Bn</td> <td>5</td> <td>(39)</td> </tr> <tr> <td>Cx</td> <td>Bn</td> <td>10</td> <td>(82)</td> </tr> </tbody> </table>	R ¹	R ²	x	(%)	Ph(CH ₂) ₂	H	1.2	(0)	Ph(CH ₂) ₂	H	5	(77)	Ph(CH ₂) ₂	H	5	(78) ^b	Ph(CH ₂) ₂	H	10	(78)	Ph(CH ₂) ₂	MOM	5	(40)	Ph(CH ₂) ₂	MOM	10	(87)	Ph(CH ₂) ₂	Bn	5	(47)	Ph(CH ₂) ₂	Bn	10	(66)	Ph	H	1.2	(0)	Ph	H	5	(78)	Ph	MOM	10	(26)	Ph	Bn	5	(12)	Ph	Bn	10	(44)	Cx	H	5	(75)	Cx	Bn	5	(39)	Cx	Bn	10	(82)	
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	Et ₂ Zn (x eq), CH ₂ I ₂ (2x eq), hexane, -23 then 0°	<table border="1"> <thead> <tr> <th>R¹</th> <th>R²</th> <th>x</th> <th>(%)</th> </tr> </thead> <tbody> <tr> <td>Ph(CH₂)₂</td> <td>MOM</td> <td>5</td> <td>(0)</td> </tr> <tr> <td>Ph(CH₂)₂</td> <td>Bn</td> <td>5</td> <td>(41)</td> </tr> <tr> <td>Ph(CH₂)₂</td> <td>Bn</td> <td>7.5</td> <td>(70)</td> </tr> <tr> <td>Ph</td> <td>MOM</td> <td>5</td> <td>(0)</td> </tr> <tr> <td>Ph</td> <td>Bn</td> <td>5</td> <td>(3)</td> </tr> <tr> <td>Ph</td> <td>Bn</td> <td>7.5</td> <td>(31)</td> </tr> <tr> <td>Cx</td> <td>Bn</td> <td>5</td> <td>(0)</td> </tr> <tr> <td>Cx</td> <td>Bn</td> <td>7.5</td> <td>(34)</td> </tr> </tbody> </table>	R ¹	R ²	x	(%)	Ph(CH ₂) ₂	MOM	5	(0)	Ph(CH ₂) ₂	Bn	5	(41)	Ph(CH ₂) ₂	Bn	7.5	(70)	Ph	MOM	5	(0)	Ph	Bn	5	(3)	Ph	Bn	7.5	(31)	Cx	Bn	5	(0)	Cx	Bn	7.5	(34)	92																																
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	Zn/Cu (x eq), CH ₂ I ₂ (x eq), Et ₂ O, reflux, 20 h		92																																																																				
	Et ₂ Zn, CH ₂ I ₂ , isooctane, 100°	(—)	472																																																																				
	Zn/Cu, CH ₂ I ₂	(76)	473																																																																				
	Zn/Cu, CH ₂ I ₂ , I ₂ (cat.), Et ₂ O	(—)	474																																																																				
	Zn/Cu, CH ₂ I ₂ , Et ₂ O, reflux	I (39) + II (26)	475																																																																				
	Zn/Cu, CH ₂ I ₂ , Et ₂ O, reflux	(55)	476																																																																				
	Zn/Cu, CH ₂ I ₂ , Et ₂ O, reflux	(44)	475																																																																				

TABLE III. CYCLOPROPANATION OF ACYCLIC, ACHIRAL ALKENES (Continued)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.												
	Et ₂ Zn (7 eq), CH ₂ I ₂ (7 eq), C ₆ H ₆ , reflux	(21)	476												
	Zn/Cu, CH ₂ I ₂ , I ₂ (cat.), Et ₂ O	(—)	474												
	Zn, CH ₂ I ₂ , I ₂ (cat.), DME, reflux; repeated twice	(65)	460												
	Zn/Cu, CH ₂ I ₂ , Et ₂ O	" (63)	477												
	Et ₂ Zn (2 eq), CH ₂ I ₂ (3.3 eq), hexanes, -20° to rt	(50)	463												
	Zn/Cu, CH ₂ I ₂	(67)	473												
	Sn/Hg, CH ₂ I _X (n eq), THF, -78° to rt	<table border="1"> <thead> <tr> <th>n</th> <th>X</th> <th>(%)</th> </tr> </thead> <tbody> <tr> <td>4</td> <td>Cl</td> <td>(14)</td> </tr> <tr> <td>4</td> <td>I</td> <td>(9)</td> </tr> <tr> <td>12</td> <td>I</td> <td>(53)</td> </tr> </tbody> </table>	n	X	(%)	4	Cl	(14)	4	I	(9)	12	I	(53)	58
n	X	(%)													
4	Cl	(14)													
4	I	(9)													
12	I	(53)													
	Zn/Cu, CH ₂ I ₂	(—)	478												
	Sn/Hg (xs), CH ₂ I _X , THF, -78° to rt	<table border="1"> <thead> <tr> <th>X</th> <th>(%)</th> </tr> </thead> <tbody> <tr> <td>Cl</td> <td>(21)</td> </tr> <tr> <td>I</td> <td>(—)</td> </tr> </tbody> </table>	X	(%)	Cl	(21)	I	(—)	58						
X	(%)														
Cl	(21)														
I	(—)														
	Et ₂ Zn, CH ₂ I ₂	(70)	357, 465												
	Et ₂ Zn (1.5 eq), CH ₂ I ₂ (3 eq), Et ₂ O, rt	" (70)	357, 465												
	Et ₂ Zn (1 eq), CH ₂ I ₂ (2 eq), solvent, rt, 6 h	<table border="1"> <thead> <tr> <th>Solvent</th> <th>(%)</th> </tr> </thead> <tbody> <tr> <td>CH₂Cl₂</td> <td>(73)</td> </tr> <tr> <td>Et₂O</td> <td>(71)</td> </tr> <tr> <td>hexane</td> <td>(50)</td> </tr> <tr> <td>THF</td> <td>(0)</td> </tr> <tr> <td>DMF</td> <td>(0)</td> </tr> </tbody> </table>	Solvent	(%)	CH ₂ Cl ₂	(73)	Et ₂ O	(71)	hexane	(50)	THF	(0)	DMF	(0)	357
Solvent	(%)														
CH ₂ Cl ₂	(73)														
Et ₂ O	(71)														
hexane	(50)														
THF	(0)														
DMF	(0)														
	Et ₂ Zn (1.5 eq), CH ₂ I ₂ (3 eq), Et ₂ O, rt	(78)	357, 465												
	Zn/Hg, TMSCl, HC(OEt) ₃ , Et ₂ O, reflux	(44) <i>cis:trans</i> = 2:1	77												
	Zn/Cu, CH ₂ I ₂	(—) + several other cyclopropanation products	479												
	Zn/Cu, CH ₂ I ₂ , Et ₂ O, reflux	(79)	257												

TABLE III. CYCLOPROPANATION OF ACYCLIC, ACHIRAL, ALKENES (Continued)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.																																
	Zn/Cu, CH ₂ I ₂ , Et ₂ O, reflux	 (40)	257																																
	Conditions	 I + II + III	104																																
		<table border="1"> <thead> <tr> <th>Conditions</th> <th>I (%)</th> <th>II (%)</th> <th>III (%)</th> </tr> </thead> <tbody> <tr> <td>Zn/Cu, CH₂I₂, AcCl, Et₂O</td> <td>(30)</td> <td>(8)</td> <td>(36)</td> </tr> <tr> <td>Zn/Cu, CH₂Br₂, AcCl, Et₂O</td> <td>(27)</td> <td>(9)</td> <td>(21)</td> </tr> <tr> <td>Et₂Zn, CH₂I₂, PhMe</td> <td>(19)</td> <td>(25)</td> <td>(17)</td> </tr> <tr> <td>Et₃Al, CH₂I₂, PhMe/CH₂Cl₂</td> <td>(26)</td> <td>(13)</td> <td>(12)</td> </tr> </tbody> </table>	Conditions	I (%)	II (%)	III (%)	Zn/Cu, CH ₂ I ₂ , AcCl, Et ₂ O	(30)	(8)	(36)	Zn/Cu, CH ₂ Br ₂ , AcCl, Et ₂ O	(27)	(9)	(21)	Et ₂ Zn, CH ₂ I ₂ , PhMe	(19)	(25)	(17)	Et ₃ Al, CH ₂ I ₂ , PhMe/CH ₂ Cl ₂	(26)	(13)	(12)													
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Et ₃ Al, CH ₂ I ₂ , PhMe/CH ₂ Cl ₂	(26)	(13)	(12)																																
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	Zn/Cu, CH ₂ I ₂ , AcCl (cat.), solvent		104																																
	Zn/Cu, CH ₂ I ₂	 I (69) + II (6)	480																																
	Zn/Cu, CH ₂ I ₂ , Et ₂ O, reflux	 I (26) + II (7)	481																																
	"MCH ₂ X"	 I + II + III	59																																
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	<i>i</i> -Bu ₃ Al, CH ₂ I ₂ , CH ₂ Cl ₂ , rt	I (92-96)	258																																
	<i>i</i> -Bu ₃ Al, TCHl ₂ , CHCl ₃	 T (—)	482																																
	ClMe ₂ Si(CH ₂) ₂ SiMe ₂ Cl Zn/Hg	 (66)	112																																
	ClMe ₂ Si(CH ₂) ₂ SiMe ₂ Cl Zn/Hg	" (57)	112																																

TABLE III. CYCLOPROPANATION OF ACYCLIC, ACHIRAL ALKENES (Continued)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.												
	Zn/Cu, CH ₂ I ₂ , Et ₂ O/THF, reflux	 (5-30)	483												
	Zn/Cu, CH ₂ I ₂ ; repeated once	 (—)	484												
	Zn anode, 2e ⁻ , CH ₂ Br ₂ , ZnBr ₂ present initially, CH ₂ Cl ₂ /DMF (9:1)	 (70)	70												
	Sm source (xs), CH ₂ IX, THF, -78° to rt	<table border="1"> <thead> <tr> <th>Sm source</th> <th>X</th> <th>(%)</th> </tr> </thead> <tbody> <tr> <td>Sm/Hg</td> <td>I</td> <td>(89)</td> </tr> <tr> <td>Sm/Hg</td> <td>Cl</td> <td>(97)</td> </tr> <tr> <td>SmI₂</td> <td>Cl</td> <td>(87)</td> </tr> </tbody> </table>	Sm source	X	(%)	Sm/Hg	I	(89)	Sm/Hg	Cl	(97)	SmI ₂	Cl	(87)	57, 58 58 58
Sm source	X	(%)													
Sm/Hg	I	(89)													
Sm/Hg	Cl	(97)													
SmI ₂	Cl	(87)													
	Zn*, CH ₂ I ₂ , DME/Et ₂ O	" (77)	44												
	Sm (5 eq), CH ₂ I ₂ (5 eq), TMSCl (0.2 eq), THF, -78° to rt	" (97)	63												
	"MCH ₂ X"														
		<table border="1"> <thead> <tr> <th>MCH₂X</th> <th>(% I : % II : % III)</th> </tr> </thead> <tbody> <tr> <td>Et₂Zn, CH₂I₂</td> <td>74:3:2</td> </tr> <tr> <td><i>i</i>-Bu₃Al, CH₂I₂</td> <td>1:4:76</td> </tr> <tr> <td>Sm/Hg, CH₂ICl</td> <td>98:0:0</td> </tr> </tbody> </table>	MCH ₂ X	(% I : % II : % III)	Et ₂ Zn, CH ₂ I ₂	74:3:2	<i>i</i> -Bu ₃ Al, CH ₂ I ₂	1:4:76	Sm/Hg, CH ₂ ICl	98:0:0	59 59 58				
MCH ₂ X	(% I : % II : % III)														
Et ₂ Zn, CH ₂ I ₂	74:3:2														
<i>i</i> -Bu ₃ Al, CH ₂ I ₂	1:4:76														
Sm/Hg, CH ₂ ICl	98:0:0														
	Sm source (xs), CH ₂ IX, THF, -78° to rt	<table border="1"> <thead> <tr> <th>Sm source</th> <th>X</th> <th>(%)</th> </tr> </thead> <tbody> <tr> <td>Sm/Hg</td> <td>I</td> <td>(99)</td> </tr> <tr> <td>Sm/Hg</td> <td>Cl</td> <td>(97)</td> </tr> <tr> <td>SmI₂</td> <td>Cl</td> <td>(99)</td> </tr> </tbody> </table>	Sm source	X	(%)	Sm/Hg	I	(99)	Sm/Hg	Cl	(97)	SmI ₂	Cl	(99)	57, 58 58
Sm source	X	(%)													
Sm/Hg	I	(99)													
Sm/Hg	Cl	(97)													
SmI ₂	Cl	(99)													
	Zn/Cu, CH ₂ I ₂	 (—)	450												
	Et ₂ Zn, CH ₂ I ₂	" (65)	485												
	Zn/Hg, TMSCl, HC(OMe) ₃ , Et ₂ O, reflux	 (56)	77												
	PhCHO, Zn/Hg, (ClMe ₂ SiCH ₂) ₂ , Et ₂ O, reflux	 (29)	76												
	Et ₂ Zn, CH ₂ I ₂	 (70)	485												
	Et ₂ Zn, CH ₂ I ₂ , (CH ₂ Cl) ₂	" (—)	486												
	Zn/Hg, TMSCl, HC(OMe) ₃ , Et ₂ O, reflux	 (53) <i>cis:trans</i> = 10:1	77												
	Zn/Cu, CH ₂ I ₂ , Et ₂ O, reflux	 (—)	487												

TABLE III. CYCLOPROPANATION OF ACYCLIC, ACHIRAL ALKENES (Continued)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
	Zn/Cu, CH ₂ I ₂	(—)	450
	Zn/Cu, CH ₂ I ₂	(—)	450
	Zn/Ag, CH ₂ I ₂ , Et ₂ O, reflux	(75)	488
	Zn/Cu, CH ₂ I ₂	(—)	450
	Zn/Cu, CH ₂ I ₂ , Et ₂ O	(43)	489
	Zn/Cu, CH ₂ I ₂ , Et ₂ O	(45)	489
	EtZnI, CH ₂ I ₂ , Et ₂ O	(65)	438
	EtZnI, CH ₂ I ₂ , Et ₂ O	I + II (51) I:II = ~1:1	438
	EtZnI, CH ₂ I ₂	(—)	490
	Et ₂ Zn (1.5 eq), CH ₂ I ₂ (3 eq), Et ₂ O, rt	(85)	357
	Et ₂ Zn (1.5 eq), CH ₂ I ₂ (3 eq), Et ₂ O, rt	(80)	357
	Zn/Cu, CH ₂ I ₂	(50)	471
	EtZnI, CH ₂ I ₂	n (%) 1 (—) 2 (—)	490
	Zn/Cu, CH ₂ I ₂ , Et ₂ O, reflux	(56)	491
	Zn/Cu, CH ₂ I ₂ , I ₂ (cat.), solvent, reflux	Solvent (%) Et ₂ O (68) Et ₂ O (65) ^b DME (57)	92
	Zn/Cu, CH ₂ I ₂	(—)	461
	Zn/Cu, CH ₂ I ₂ , Et ₂ O, reflux	(—)	491
	Zn/Cu, CH ₂ I ₂ , Et ₂ O, reflux	(—)	491
	Zn/Cu, CH ₂ I ₂ , I ₂ (cat.), Et ₂ O	(—)	474

TABLE III. CYCLOPROPANATION OF ACYCLIC, ACHIRAL ALKENES (Continued)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
	Zn/Cu, CH ₂ I ₂	(61)	473
	Et ₂ Zn (1 eq), CH ₂ I ₂ (2 eq), -78 to -20°, CH ₂ Cl ₂ , TiCl ₄ (0.15 eq)	(88)	31
	Et ₂ Zn (1.5 eq), CH ₂ I ₂ (2 eq), <i>i</i> -Pr ₂ O, rt	(76)	492, 493
	Et ₂ Zn (3 eq), MeCHI ₂ (3 eq), <i>i</i> -Pr ₂ O, rt	(23) <i>cis:trans</i> = 64:36	492, 493
	Et ₂ Zn (1.5 eq), CH ₂ I ₂ (2 eq), <i>i</i> -Pr ₂ O, rt	(60)	492, 493
	Et ₂ Zn (2 eq), MeCHI ₂ (2 eq), <i>i</i> -Pr ₂ O, rt	(59) <i>cis:trans</i> = 25:1	492, 493
	Zn/Cu, CH ₂ I ₂ , Et ₂ O, reflux	(11)	257
	Zn/Cu, CH ₂ I ₂ , Et ₂ O, reflux	(46)	494
	Zn/Cu, CH ₂ I ₂	(49)	495
	Zn/Cu, CH ₂ I ₂ , Et ₂ O, reflux, 1 h	(>72)	496
	EtZnI, CH ₂ I ₂ , Et ₂ O	(98)	438
	Zn/Cu, CH ₂ I ₂	(13)	497
	Zn/Cu, CH ₂ I ₂ , Et ₂ O, reflux	(36)	498
	Zn, CH ₂ I ₂ , DME, 85-90°	(—)	499
	Zn, CH ₂ I ₂ , DME, 85-90°	(—)	499
	Zn, CH ₂ I ₂ , DME, 85-90°	(—)	499
	Et ₂ Zn, CH ₂ I ₂ , Et ₂ O, 0° to rt	(>70)	97
	Zn, CH ₂ I ₂ , DME, 85-90°	(—)	499
	Zn, CD ₂ I ₂ , DME, 85-90°	(95)	499

TABLE III. CYCLOPROPANATION OF ACYCLIC, ACHIRAL ALKENES (Continued)

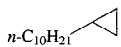

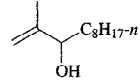
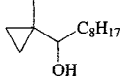
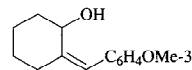
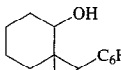
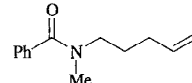
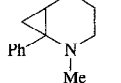
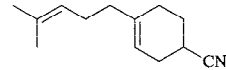
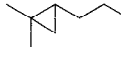
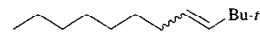

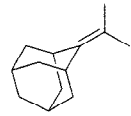
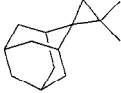
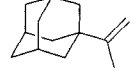
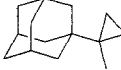
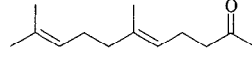
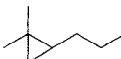
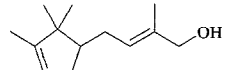


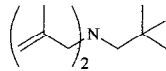
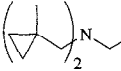
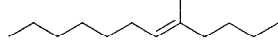
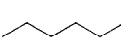
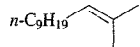
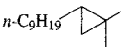
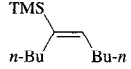
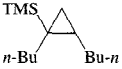
Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.																																				
$n\text{-C}_{10}\text{H}_{21}$	R_3Al (x eq), CH_2I_2 (1.2 eq), solvent, rt	 <table border="1"> <thead> <tr> <th>R</th> <th>x</th> <th>Solvent</th> <th>(%)</th> </tr> </thead> <tbody> <tr> <td>Me</td> <td>1.2</td> <td>CH_2Cl_2</td> <td>(98)</td> </tr> <tr> <td>Me</td> <td>1.2</td> <td>hexane</td> <td>(91)</td> </tr> <tr> <td>Me</td> <td>0.6</td> <td>CH_2Cl_2</td> <td>(90)</td> </tr> <tr> <td>Et</td> <td>1.2</td> <td>CH_2Cl_2</td> <td>(99)</td> </tr> <tr> <td>Et</td> <td>1.2</td> <td>C_6H_6</td> <td>(94)</td> </tr> <tr> <td>Et</td> <td>1.2</td> <td>CHCl_3</td> <td>(96)</td> </tr> <tr> <td>Et</td> <td>0.6</td> <td>hexane</td> <td>(89)</td> </tr> <tr> <td><i>i</i>-Bu</td> <td>1.2</td> <td>CH_2Cl_2</td> <td>(96)</td> </tr> </tbody> </table>	R	x	Solvent	(%)	Me	1.2	CH_2Cl_2	(98)	Me	1.2	hexane	(91)	Me	0.6	CH_2Cl_2	(90)	Et	1.2	CH_2Cl_2	(99)	Et	1.2	C_6H_6	(94)	Et	1.2	CHCl_3	(96)	Et	0.6	hexane	(89)	<i>i</i> -Bu	1.2	CH_2Cl_2	(96)	59
R	x	Solvent	(%)																																				
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Me	(94)	1.1:1																																					
<i>i</i> -Bu	(84)	0.7:1																																					
	Zn/Cu , CH_2I_2 , Et_2O , reflux	 (>22)	500																																				
C_{13} 	Zn/Cu , CH_2I_2 , Et_2O	 (98)	501																																				
	Sm/SmI_2 , THF, reflux	 (41)	78																																				
	Zn/Cu , CH_2I_2 , Et_2O , reflux	 (40)	502																																				
	Zn/Cu , CH_2I_2 , Et_2O , reflux	 (30)	469																																				
	Zn/Cu , CH_2I_2	 (70)	503																																				
	Zn/Cu , CH_2I_2 , I_2 (cat.), Et_2O	 (79)	504																																				
	Zn/Cu , CH_2I_2 , Et_2O , reflux	 (40)	505																																				
	Zn/Cu , CH_2Br_2 , Et_2O , reflux, AcBr or ultrasound	 I +  II (48) I:II = 1.3:1	506																																				
	Et_3Al , CH_2I_2 , hexane, rt	I + II (90) I:II = ~1.5:1	506																																				
	Zn/Cu , CH_2I_2 , Et_2O , reflux	 (81)	507																																				
	Zn/Cu , CH_2I_2 , Et_2O , rt	 (—) <i>E:Z</i> = 84:16	452																																				
$n\text{-C}_9\text{H}_{19}$ 	Zn/Cu , CH_2I_2	 (—)	450																																				
	Zn/Cu , CH_2I_2	 (—)	317																																				

TABLE III. CYCLOPROPANATION OF ACYCLIC, ACHIRAL ALKENES (Continued)

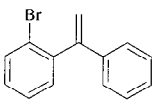
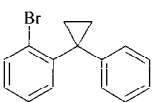
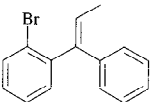


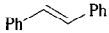
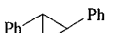

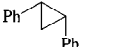
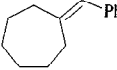
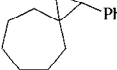
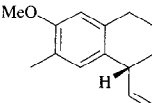
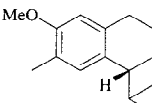
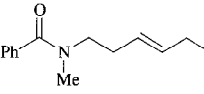
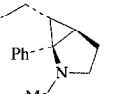
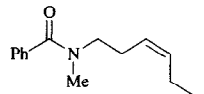
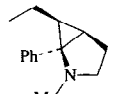
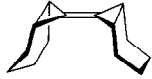

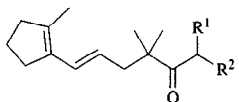
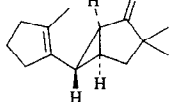
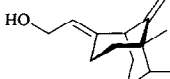

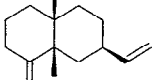
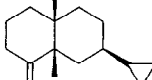
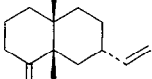
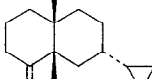
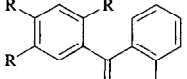
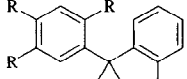
Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.												
C ₁₄ 	Zn/Cu, CH ₂ I ₂	 (38) +  (—)	508												
	Et ₂ Zn, CH ₂ I ₂	 (—)	509												
	Zn/Cu, CH ₂ I ₂ , I ₂ (cat.), Et ₂ O, reflux	 (24)	370												
	1. Et ₂ Zn (2 eq), CH ₂ Cl ₂ 2. TFA 3. CH ₂ I ₂ , add olefin	" (70)	53												
	1. Et ₂ Zn (2 eq), CH ₂ Cl ₂ 2. TFA 3. CH ₂ I ₂ , add olefin	 (72)	53												
	Zn/Cu, CH ₂ I ₂ , Et ₂ O, reflux	 (30)	510												
	Et ₂ Zn (2 eq), CH ₂ Cl ₂ (4 eq), (CH ₂ Cl) ₂	 (27)	447												
	Sm/SmI ₂ , THF, reflux	 (41) <i>endo:exo</i> = 9:1	78												
	Sm/SmI ₂ , THF, reflux	 (41) <i>endo:exo</i> = 1:8	78												
	Et ₂ Zn (2 eq), CH ₂ I ₂ (2 eq)	 (92)	511												
	Zn dust, C ₆ H ₆	 <table border="1" data-bbox="1119 1441 1328 1542"> <thead> <tr> <th>R¹</th> <th>R²</th> <th>(%)</th> </tr> </thead> <tbody> <tr> <td>Br</td> <td>Br</td> <td>(20)</td> </tr> <tr> <td>Br</td> <td>I</td> <td>(45)</td> </tr> <tr> <td>I</td> <td>I</td> <td>(20)</td> </tr> </tbody> </table>	R ¹	R ²	(%)	Br	Br	(20)	Br	I	(45)	I	I	(20)	113
R ¹	R ²	(%)													
Br	Br	(20)													
Br	I	(45)													
I	I	(20)													
	Sm/Hg, CH ₂ I ₂	 (89)	512												
	Zn/Ag, CH ₂ I ₂ , Et ₂ O, reflux, ultrasound	 (68)	513												
	Zn/Ag, CH ₂ I ₂ , Et ₂ O, reflux, ultrasound	 (63)	513												
	Zn/Cu, CH ₂ I ₂ , Et ₂ O, reflux	 <table border="1" data-bbox="1171 1924 1310 2002"> <thead> <tr> <th>R</th> <th>(%)</th> </tr> </thead> <tbody> <tr> <td>H</td> <td>(—)</td> </tr> <tr> <td>OMe</td> <td>(—)</td> </tr> </tbody> </table>	R	(%)	H	(—)	OMe	(—)	514						
R	(%)														
H	(—)														
OMe	(—)														

TABLE III. CYCLOPROPANATION OF ACYCLIC, ACHIRAL ALKENES (Continued)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.												
	Zn/Cu, CH ₂ I ₂	(—)	450												
	1. Et ₂ Zn (2 eq), CH ₂ Cl ₂ 2. TFA 3. CH ₂ I ₂ , add olefin	(99)	53												
C ₁₅ 	Zn/Cu, CH ₂ I ₂ , Et ₂ O, reflux	(78)	514a												
	Zn/Cu, CH ₂ I ₂ , Et ₂ O, reflux	(37)	515												
	Zn/Cu, CH ₂ I ₂	(15)	497												
	Zn/Ag, CH ₂ I ₂ , Et ₂ O, reflux	(52)	516												
	Zn/Cu, CH ₂ I ₂ , I ₂ (cat.), Et ₂ O	(—)	504												
	ClMe ₂ Si-CH ₂ -CH ₂ -SiMe ₂ Cl Zn/Hg	(41)	112												
	ClMe ₂ Si-CH ₂ -CH ₂ -SiMe ₂ Cl Zn/Hg	" (47)	112												
	ClMe ₂ Si-CH ₂ -CH ₂ -SiMe ₂ Cl Zn/Hg	(47)	112												
	Zn/Cu, CH ₂ I ₂ , Et ₂ O/DME, reflux	(82)	517												
	ZnI ₂ , Et ₂ O	I + II 75	75												
		<table border="1"> <thead> <tr> <th>R</th> <th>(%)</th> <th>I:II</th> </tr> </thead> <tbody> <tr> <td>C₆H₁₁</td> <td>(20-25)</td> <td>7:3</td> </tr> <tr> <td>C₁₁H₁₉</td> <td>(20-25)</td> <td>—</td> </tr> <tr> <td>C₁₆H₂₇</td> <td>(20-25)</td> <td>—</td> </tr> </tbody> </table>	R	(%)	I:II	C ₆ H ₁₁	(20-25)	7:3	C ₁₁ H ₁₉	(20-25)	—	C ₁₆ H ₂₇	(20-25)	—	
R	(%)	I:II													
C ₆ H ₁₁	(20-25)	7:3													
C ₁₁ H ₁₉	(20-25)	—													
C ₁₆ H ₂₇	(20-25)	—													
	ZnI ₂ , Et ₂ O	I + II (—) I:II = —	75												

TABLE III. CYCLOPROPANATION OF ACYCLIC, ACHIRAL ALKENES (Continued)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
	$C_{11}H_{19}$ ZnI ₂ , Et ₂ O	 I + II (-) I:II = -	75
$n-C_9H_{19}$ 	Zn/Cu, CH ₂ I ₂	$n-C_9H_{19}$ (—)	450
Bu ₃ Sn 	Et ₂ Zn, CH ₂ I ₂ , PhMe, 40°	Bu ₃ Sn (—)	518
Bu ₃ Sn 	Zn/Cu, CH ₂ I ₂ , <i>i</i> -Pr ₂ NEt, DME, 23°	Bu ₃ Sn (70)	208
	Et ₂ Zn (2 eq), CH ₂ I ₂ (2 eq), <i>i</i> -Pr ₂ O, rt	" (39)	493
	Et ₂ Zn (2 eq), MeCHI ₂ (2 eq), <i>i</i> -Pr ₂ O, rt	Bu ₃ Sn (28)	493
C ₁₆ 	EtZnI, CH ₂ I ₂ , I ₂ (cat.), THF	(46)	519
	Zn/Cu, CH ₂ I ₂ , Et ₂ O	(35)	520
	Zn/Cu, CH ₂ I ₂	(3)	521
	Zn/Cu, CH ₂ I ₂	(76)	473
	Zn/Cu, CH ₂ I ₂	(77)	522
	Zn/Cu, CH ₂ I ₂ , THF	(40)	523
	Zn/Cu, CH ₂ I ₂ , Et ₂ O, reflux	(53)	475
	Me ₃ Al, CH ₂ I ₂ , CH ₂ Cl ₂ /hexane, rt	(64)	524
	Zn/Ag, CH ₂ I ₂ , Et ₂ O, reflux	(42)	525
	Zn/Cu, CH ₂ I ₂	(—)	526
	Zn/Cu, CH ₂ I ₂	(—)	526

TABLE III. CYCLOPROPANATION OF ACYCLIC, ACHIRAL ALKENES (Continued)

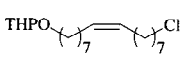
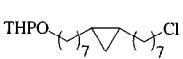
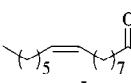
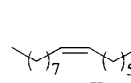
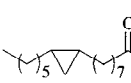

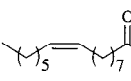

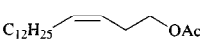

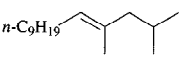
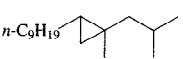
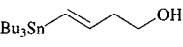
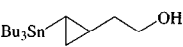
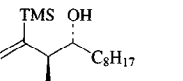
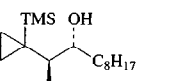
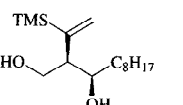
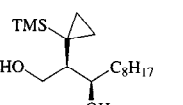
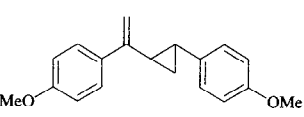
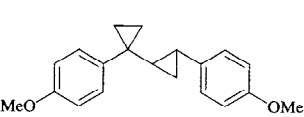
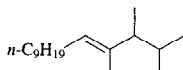
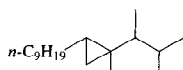
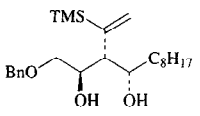
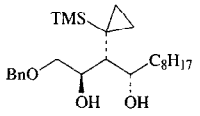
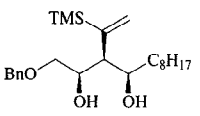
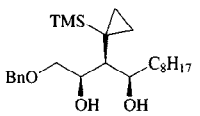
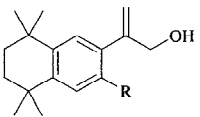
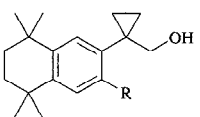
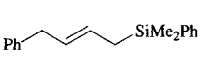
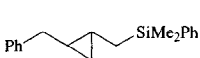
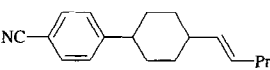
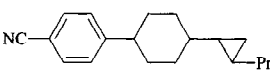
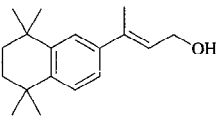
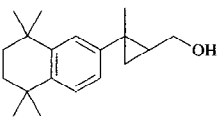
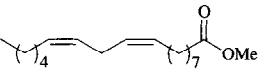
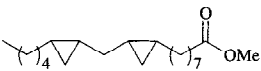
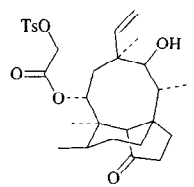
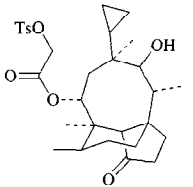
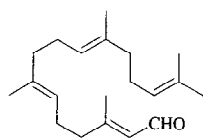
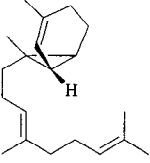
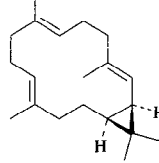
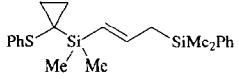
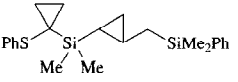
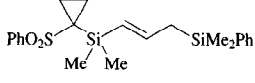
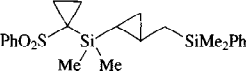
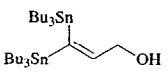
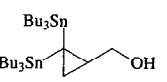
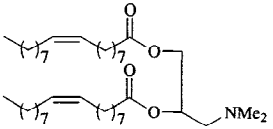
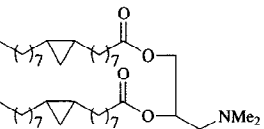
Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.						
THPO 	Et ₂ Zn, CH ₂ I ₂ , C ₆ H ₆ , O ₂	THPO  (67)	525						
 +  I:II ~ 3:1	Zn/Cu, CH ₂ I ₂	 +  (—)	527						
	Zn/Cu, CH ₂ I ₂	 (—)	528						
C ₁₂ H ₂₅ 	Zn, CH ₂ I ₂ , DME	C ₁₂ H ₂₅  (35)	529						
<i>n</i> -C ₉ H ₁₉ 	Zn/Cu, CH ₂ I ₂	<i>n</i> -C ₉ H ₁₉  (—)	450						
Bu ₃ Sn 	Et ₂ Zn, CH ₂ I ₂ , PhMe, 40°	Bu ₃ Sn  (—)	518						
	Et ₂ Zn, CH ₂ I ₂ , Et ₂ O, reflux	 (—)	530						
	Et ₂ Zn, CH ₂ I ₂ , Et ₂ O, reflux	 (—)	530						
C ₁₇ 	Zn/Ag, CH ₂ I ₂ , Et ₂ O	 (7)	531						
<i>n</i> -C ₉ H ₁₉ 	Zn/Cu, CH ₂ I ₂	<i>n</i> -C ₉ H ₁₉  (—)	450						
	Et ₂ Zn, CH ₂ I ₂ , Et ₂ O, reflux	 (—)	530						
	Et ₂ Zn, CH ₂ I ₂ , Et ₂ O, reflux	 (—)	530						
C ₁₇₋₁₈ 	Et ₂ Zn, CH ₂ I ₂ , (CH ₂ Cl) ₂ , 0°	 <table border="1" style="display: inline-table; vertical-align: middle;"> <thead> <tr> <th>R</th> <th>(%)</th> </tr> </thead> <tbody> <tr> <td>H</td> <td>(70)</td> </tr> <tr> <td>Me</td> <td>(70)</td> </tr> </tbody> </table>	R	(%)	H	(70)	Me	(70)	532
R	(%)								
H	(70)								
Me	(70)								
C ₁₈ 	Me ₃ Al, CH ₂ I ₂ , CH ₂ Cl ₂ /hexane, rt	 (90)	524						
	Zn/Cu, CH ₂ I ₂ , Et ₂ O, reflux	 (28)	533						
	Sm, CH ₂ I ₂	 (>35)	534						
	Zn/Cu, CH ₂ I ₂ , ultrasound, DME, reflux	 (97)	45						

TABLE III. CYCLOPROPANATION OF ACYCLIC, ACHIRAL ALKENES (Continued)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.								
	Zn/Cu, CH ₂ I ₂	(27)	535								
	Zn/Cu, CH ₂ I ₂ , ultrasound, DME, reflux	(91)	45								
	Zn, Red-Al, DME; CH ₂ I ₂ , ultrasound, DME, 85-90°	" (82)	536								
	Zn/Cu, CH ₂ I ₂	(—) ¹⁴ C labeled	537								
	Zn/Cu, CH ₂ I ₂	(—)	526								
	Zn/Cu, ¹⁴ CH ₂ I ₂	(—)	537								
	Zn/Cu, CH ₂ I ₂	(73)	535, 538								
	Et ₂ Zn, CH ₂ I ₂ , C ₆ H ₆	" (—)	539								
	Zn/Cu, ¹³ CH ₂ I ₂	(—)	540								
	Et ₂ Zn, CH ₂ I ₂ , C ₆ H ₆	(—)	539								
	Zn/Cu, CH ₂ I ₂	(—)	528								
	Zn/Cu, ¹³ CH ₂ I ₂	(—)	540								
	Et ₂ Zn, CH ₂ I ₂	(—)	541								
	Conditions	<table border="1" style="margin-left: 20px;"> <thead> <tr> <th>Conditions</th> <th>(%)</th> </tr> </thead> <tbody> <tr> <td>Sm/Hg, CH₂I₂, THF</td> <td>(90)</td> </tr> <tr> <td>SmI₂, CH₂Cl, THF</td> <td>(81)</td> </tr> <tr> <td>Et₂Zn, CH₂Cl, (CH₂Cl)₂</td> <td>(65)</td> </tr> </tbody> </table>	Conditions	(%)	Sm/Hg, CH ₂ I ₂ , THF	(90)	SmI ₂ , CH ₂ Cl, THF	(81)	Et ₂ Zn, CH ₂ Cl, (CH ₂ Cl) ₂	(65)	140
Conditions	(%)										
Sm/Hg, CH ₂ I ₂ , THF	(90)										
SmI ₂ , CH ₂ Cl, THF	(81)										
Et ₂ Zn, CH ₂ Cl, (CH ₂ Cl) ₂	(65)										
	Sm, CH ₂ I ₂	(>38)	534								
	Zn/Cu, CH ₂ I ₂	(—)	542								
	Et ₃ Al, CH ₂ I ₂	(98)	543								
	Zn/Cu, CH ₂ I ₂ , Et ₂ O, rt	(5)	544								

TABLE III. CYCLOPROPANATION OF ACYCLIC, ACHIRAL ALKENES (Continued)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
	Zn/Cu, CH ₂ I ₂ , I ₂ (cat.), Et ₂ O/DME	 (32)	545
	ClMe ₂ Si-CH ₂ -CH ₂ -SiMe ₂ Cl Zn/Hg	 (46) +  (30)	112
<i>n</i> -C ₁₄ H ₂₉ -CH=CH-CH ₂ CO ₂ Me	Zn/Cu, CH ₂ I ₂ , I ₂ (cat.), Et ₂ O, reflux	<i>n</i> -C ₁₄ H ₂₉ -CH ₂ -CH ₂ -CO ₂ Me (81)	408
<i>n</i> -C ₁₄ H ₂₉ -CH=CH-CH ₂ CO ₂ Me	Zn/Cu, CH ₂ I ₂ , I ₂ (cat.), Et ₂ O, reflux	<i>n</i> -C ₁₄ H ₂₉ -CH ₂ -CH ₂ -CO ₂ Me (95)	408
C ₂₁ C ₁₁ H ₂₃ -CH=CH-SiMe ₂ Ph	Me ₃ Al, CH ₂ I ₂ , CCl ₄ , 0°	C ₁₁ H ₂₃ -CH ₂ -CH ₂ -SiMe ₂ Ph (91)	102
C ₂₂ 	Me ₃ Al, CH ₂ I ₂	 (50)	546
	Et ₂ Zn, CH ₂ I ₂ , CH ₂ Cl ₂	 (>30)	546
C ₂₇ 	Sm/Hg, CH ₂ I ₂ , THF, -78° to rt	 (77)	140
C ₃₉ 	Zn/Cu, CH ₂ I ₂ , Et ₂ O, reflux	 (99)	547

^a The reaction is done in the presence of 2 equivalents of Et₂O.

^b The conditions include irradiation with ultrasound.

TABLE IV. CYCLOPROPANATION OF ACYCLIC, ACHIRAL *O*- AND *N*-SUBSTITUTED ALKENES

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.																															
C ₂ 	Et ₂ Zn, CHFI ₂ , conditions, CH ₂ Cl ₂	I + II	548																															
		<table border="1"> <thead> <tr> <th>R</th> <th>Conditions</th> <th>(%)</th> <th>I:II</th> </tr> </thead> <tbody> <tr> <td>Bn</td> <td>-40° then rt</td> <td>(<10)</td> <td>—</td> </tr> <tr> <td>Bn</td> <td>MS4Å, DME, rt</td> <td>(25)</td> <td>64:36</td> </tr> <tr> <td><i>t</i>-Bu</td> <td>MS4Å, DME, 0°</td> <td>(30)</td> <td>60:40</td> </tr> </tbody> </table>	R	Conditions	(%)	I:II	Bn	-40° then rt	(<10)	—	Bn	MS4Å, DME, rt	(25)	64:36	<i>t</i> -Bu	MS4Å, DME, 0°	(30)	60:40																
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	Et ₂ Zn (2 eq), CHFI ₂ (2 eq)	I + II	91, 548																															
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	Zn/Ag, CH ₂ I ₂ , Et ₂ O, reflux		(20)	549																														
	Et ₂ Zn (1 eq), CH ₂ Cl (x eq), dry air (y mL/min), Et ₂ O, 50°		<table border="1"> <thead> <tr> <th>x</th> <th>y</th> <th>(%)</th> </tr> </thead> <tbody> <tr> <td>1</td> <td>0</td> <td>(89)</td> </tr> <tr> <td>1.5</td> <td>10</td> <td>(94)</td> </tr> </tbody> </table>	x	y	(%)	1	0	(89)	1.5	10	(94)	50																					
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1	0	(89)																																
1.5	10	(94)																																
	Zn/Cu, CH ₂ I ₂		(—)	449																														
	1. Et ₂ Zn (2 eq), CH ₂ Cl ₂ 2. TFA 3. CH ₂ I ₂ , add olefin		(90)	53																														
	Zn/Hg, TMSCl, HC(OMe) ₃ , Et ₂ O, reflux		(46) <i>trans</i> : <i>cis</i> = 3:1	77																														
C ₂₋₄ 	Zn/Ag, CH ₂ I ₂ , Et ₂ O		<table border="1"> <thead> <tr> <th>R¹</th> <th>R²</th> <th>R³</th> <th>(%)</th> </tr> </thead> <tbody> <tr> <td>Et</td> <td>H</td> <td>H</td> <td>(18)</td> </tr> <tr> <td>Me</td> <td>Me</td> <td>Me</td> <td>(59)</td> </tr> <tr> <td>Me</td> <td>Me</td> <td>H</td> <td>(60)</td> </tr> </tbody> </table>	R ¹	R ²	R ³	(%)	Et	H	H	(18)	Me	Me	Me	(59)	Me	Me	H	(60)	550														
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C ₂₋₈ 	Et ₂ Zn, CH ₂ I ₂		<table border="1"> <thead> <tr> <th>R¹</th> <th>R²</th> <th>R³</th> <th>(%)</th> </tr> </thead> <tbody> <tr> <td>H</td> <td><i>t</i>-Bu</td> <td><i>i</i>-Pr</td> <td>(61)</td> </tr> <tr> <td>Ph</td> <td>Me</td> <td>Et</td> <td>(—)</td> </tr> </tbody> </table>	R ¹	R ²	R ³	(%)	H	<i>t</i> -Bu	<i>i</i> -Pr	(61)	Ph	Me	Et	(—)	551																		
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H	<i>t</i> -Bu	<i>i</i> -Pr	(61)																															
Ph	Me	Et	(—)																															
C ₃ 	Et ₂ Zn (1.5 eq), CH ₂ I ₂ (1.5 eq), Et ₂ O, rt		(90)	553																														
	Sm, CH ₂ I ₂ , THF, 50°		(60)	110, 552																														

TABLE IV. CYCLOPROPANATION OF ACYCLIC, ACHIRAL *O*- AND *N*-SUBSTITUTED ALKENES (Continued)






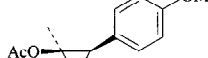


























Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.																				
	Zn/Cu, CH ₂ I ₂ , DME	 (—)	554																				
 <i>E:Z</i> = 5:95	Zn/Ag, CH ₂ I ₂	 (61)	81																				
	MeO-C ₆ H ₄ -CHO Zn, (ClMe ₂ SiCH ₂) ₂ , Et ₂ O, reflux	 (89) <i>endo:exo</i> = 2:1	76																				
C₄ 	Zn/Ag, CH ₂ I ₂ , Et ₂ O, reflux	 (75)	107, 555																				
	Zn/Ag, CH ₂ I ₂ (xs), Et ₂ O, reflux	 (84)	107, 267																				
	Zn/Ag, CH ₂ I ₂ , Et ₂ O, reflux	 (>30)	556																				
	Zn/Ag, CH ₂ I ₂ , Et ₂ O, reflux	 (>45)	556																				
 ~ 1:1 <i>E:Z</i> mixture	Zn/Cu, CH ₂ I ₂	 (42) ~ 1:1 <i>E:Z</i> mixture	557																				
	Zn/Ag, CH ₂ I ₂ , Et ₂ O, reflux	 (65)	344																				
	Et ₂ Zn (1.5 eq), CH ₂ I ₂ (1.5 eq), Et ₂ O, rt	 (70)	553																				
 <i>E:Z</i> = 57:43	Et ₂ Zn (1.25 eq), CH ₂ I ₂ (1.25 eq), dry air, cyclohexane	 (69)	354																				
	Zn/Cu, CH ₂ I ₂ , DME	 (—)	554																				
	Zn/Cu, CH ₂ I ₂ , DME	 (—)	554																				
	Zn/Ag, CH ₂ I ₂	 (63)	81																				
C_{4,8} 	Zn/Ag, CH ₂ I ₂	 <table border="1" data-bbox="1058 1733 1380 1871"> <thead> <tr> <th>R¹</th> <th>R²</th> <th>R³</th> <th>(%)</th> </tr> </thead> <tbody> <tr> <td>Me</td> <td>Me</td> <td>Me</td> <td>(—)</td> </tr> <tr> <td>Me</td> <td>Ph</td> <td>H</td> <td>(—)</td> </tr> <tr> <td>Et</td> <td>TMSOCH(Me)</td> <td>H</td> <td>(—)</td> </tr> <tr> <td>Et</td> <td>TMSOCH(Me)</td> <td>Me</td> <td>(—)</td> </tr> </tbody> </table>	R ¹	R ²	R ³	(%)	Me	Me	Me	(—)	Me	Ph	H	(—)	Et	TMSOCH(Me)	H	(—)	Et	TMSOCH(Me)	Me	(—)	341
R ¹	R ²	R ³	(%)																				
Me	Me	Me	(—)																				
Me	Ph	H	(—)																				
Et	TMSOCH(Me)	H	(—)																				
Et	TMSOCH(Me)	Me	(—)																				
C₅ 	Et ₂ Zn (1 eq), CH ₂ I ₂ (1.5 eq), Et ₂ O, 60°	 (67)	558																				

TABLE IV. CYCLOPROPANATION OF ACYCLIC, ACHIRAL *O*- AND *N*-SUBSTITUTED ALKENES (Continued)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.																
	Zn/Ag, CH ₂ I ₂ , Et ₂ O, reflux	" (75)	559, 560, 561																
	Zn/Ag, CH ₂ I ₂ , Et ₂ O, reflux	(80)	107, 555																
	Zn/Ag, CH ₂ I ₂ (xs), Et ₂ O, reflux	(87)	107, 267																
	Zn/Ag, CH ₂ I ₂ , Et ₂ O, reflux	(70)	107, 555																
	Zn/Ag, CH ₂ I ₂ (xs), Et ₂ O, reflux	(85)	107, 267																
	Zn/Ag, CH ₂ I ₂ , Et ₂ O, reflux	(>40)	556																
	Zn/Ag, CH ₂ I ₂ , Et ₂ O, reflux	(70)	344																
	Zn/Cu, CH ₂ I ₂ , Et ₂ O, reflux	(90) <i>E:Z</i> = 2:3	82																
<i>E:Z</i> = 37:63	Et ₂ Zn (1.25 eq), CH ₂ I ₂ (1.25 eq), dry air, cyclohexane	" (51)	354																
	Zn/Cu, CH ₂ I ₂ , Et ₂ O/DME, reflux	(55)	562																
	Zn/Cu, CH ₂ I ₂ , dioxane, heat	(66)	563																
<i>C</i> ₆ 	Zn/Cu, CH ₂ I ₂ , Et ₂ O, DME, reflux	(80)	564																
	Zn/Cu, CH ₂ I ₂ , Et ₂ O (conc), reflux	I + II	<table border="1"> <thead> <tr> <th>Conc (M)</th> <th>(%)</th> <th>I:II</th> </tr> </thead> <tbody> <tr> <td>10</td> <td>(80)</td> <td>15:85</td> </tr> <tr> <td>2.0</td> <td>(80)</td> <td>80:20</td> </tr> <tr> <td>1.25</td> <td>(74)</td> <td>99:1</td> </tr> <tr> <td>0.45</td> <td>(87)</td> <td>100:0</td> </tr> </tbody> </table>	Conc (M)	(%)	I:II	10	(80)	15:85	2.0	(80)	80:20	1.25	(74)	99:1	0.45	(87)	100:0	79, 565
Conc (M)	(%)	I:II																	
10	(80)	15:85																	
2.0	(80)	80:20																	
1.25	(74)	99:1																	
0.45	(87)	100:0																	
	Zn/Ag, CH ₂ I ₂ , Et ₂ O, reflux		<table border="1"> <thead> <tr> <th>R¹</th> <th>R²</th> <th>(%)</th> </tr> </thead> <tbody> <tr> <td>Et</td> <td>Et</td> <td>(70)</td> </tr> <tr> <td><i>n</i>-Pr</td> <td>Me</td> <td>(60)</td> </tr> <tr> <td><i>t</i>-Bu</td> <td>H</td> <td>(60)</td> </tr> </tbody> </table>	R ¹	R ²	(%)	Et	Et	(70)	<i>n</i> -Pr	Me	(60)	<i>t</i> -Bu	H	(60)	344			
R ¹	R ²	(%)																	
Et	Et	(70)																	
<i>n</i> -Pr	Me	(60)																	
<i>t</i> -Bu	H	(60)																	
	Zn/Cu, CH ₂ I ₂ , Et ₂ O, reflux	(80)	82																
	Zn/Cu, CH ₂ I ₂ , Et ₂ O, reflux	(57) + (10)	355																
<i>C</i> ₆₋₇ 	Et ₂ Zn, CH ₂ I ₂ , C ₆ H ₆ /cyclohexane		<table border="1"> <thead> <tr> <th>R</th> <th>(%)</th> </tr> </thead> <tbody> <tr> <td>H</td> <td>(>25)</td> </tr> <tr> <td>Me</td> <td>(73)</td> </tr> </tbody> </table>	R	(%)	H	(>25)	Me	(73)	566									
R	(%)																		
H	(>25)																		
Me	(73)																		

TABLE IV. CYCLOPROPANATION OF ACYCLIC, ACHIRAL *O*- AND *N*-SUBSTITUTED ALKENES (Continued)

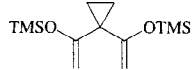
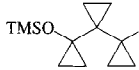
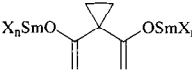

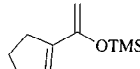
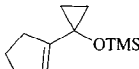
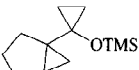
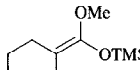
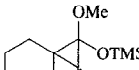
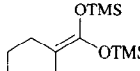
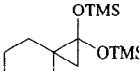
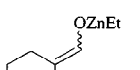
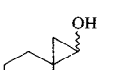
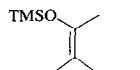
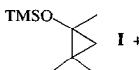
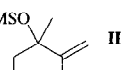
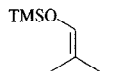
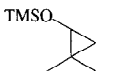
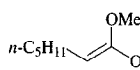
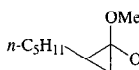
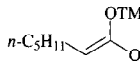
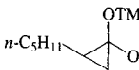


Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.																					
C ₇ 	Zn/Cu, CH ₂ I ₂ , Et ₂ O, reflux	 (70)	567																					
	Sm, CH ₂ I ₂ , THF, 50°	 (22)	110, 552																					
	Zn/Ag, CH ₂ I ₂ , Et ₂ O, reflux	 (70)	107, 555																					
	Zn/Ag, CH ₂ I ₂ (xs), Et ₂ O, reflux	 (75)	107, 267																					
	Et ₂ Zn (1.5 eq), RCHI ₂ (1.5 eq), Et ₂ O, rt	 <table border="1" style="display: inline-table; vertical-align: middle;"><thead><tr><th>R</th><th>(%)</th></tr></thead><tbody><tr><td>H</td><td>(80)</td></tr><tr><td>Me</td><td>(91)</td></tr><tr><td>Ph</td><td>(64)</td></tr></tbody></table>	R	(%)	H	(80)	Me	(91)	Ph	(64)	553													
R	(%)																							
H	(80)																							
Me	(91)																							
Ph	(64)																							
	Et ₂ Zn (2 eq), CH ₂ I ₂ (2 eq), Et ₂ O, rt	 (80)	553																					
	Et ₂ Zn, CH ₂ I ₂ , Et ₂ O	 (38)	371																					
	Zn/Cu, CH ₂ I ₂ , Et ₂ O (conc), reflux	 I +  II																						
		<table border="1" style="display: inline-table; vertical-align: middle;"><thead><tr><th>Conc (M)</th><th>(%)</th><th>I:II</th></tr></thead><tbody><tr><td>10.0</td><td>(66)</td><td>8:92</td></tr><tr><td>2.0</td><td>(77)</td><td>25:75</td></tr><tr><td>1.56</td><td>(82)</td><td>91:9</td></tr><tr><td>1.25</td><td>(80)</td><td>97:3</td></tr><tr><td>0.91</td><td>(65)</td><td>99:1</td></tr><tr><td>0.45</td><td>(78)</td><td>100:0</td></tr></tbody></table>	Conc (M)	(%)	I:II	10.0	(66)	8:92	2.0	(77)	25:75	1.56	(82)	91:9	1.25	(80)	97:3	0.91	(65)	99:1	0.45	(78)	100:0	79, 79, 565, 79, 79, 565, 79, 79, 565
Conc (M)	(%)	I:II																						
10.0	(66)	8:92																						
2.0	(77)	25:75																						
1.56	(82)	91:9																						
1.25	(80)	97:3																						
0.91	(65)	99:1																						
0.45	(78)	100:0																						
	Zn/Cu, CH ₂ I ₂ , Et ₂ O (conc), reflux	 <table border="1" style="display: inline-table; vertical-align: middle;"><thead><tr><th>Conc (M)</th><th>(%)</th></tr></thead><tbody><tr><td>2.0</td><td>(86)</td></tr><tr><td>1.25</td><td>(66)</td></tr><tr><td>0.45</td><td>(58)</td></tr></tbody></table>	Conc (M)	(%)	2.0	(86)	1.25	(66)	0.45	(58)	79, 565													
Conc (M)	(%)																							
2.0	(86)																							
1.25	(66)																							
0.45	(58)																							
	Et ₂ Zn (1.5 eq), CH ₂ I ₂ (1.5 eq), Et ₂ O, rt	 (76)	553																					
	Et ₂ Zn (2 eq), CH ₂ I ₂ (2 eq), Et ₂ O, rt	 (80)	553																					
 <i>E:Z</i> = 27:73	Zn/Ag, CH ₂ I ₂	 (81)	81																					

TABLE IV. CYCLOPROPANATION OF ACYCLIC, ACHIRAL *O*- AND *N*-SUBSTITUTED ALKENES (Continued)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_8 	Sm, CH ₂ I ₂ , THF, 0°	 R X (%) Ph Br (81) Ph I (88) 4-BrC ₆ H ₄ Br (67)	87
	Zn/Ag, CH ₂ I ₂ , Et ₂ O, reflux	(10)	344
	Et ₂ Zn (1.5 eq), RCH ₂ I (1.5 eq), Et ₂ O, rt	 R (%) H (85) Me (86)	553
	Et ₂ Zn (1.5 eq), PhCH ₂ I (1.5 eq), Et ₂ O, rt	(68)	553
	Zn/Cu, CH ₂ I ₂ , Et ₂ O, reflux	(90)	82
	Zn/Ag, CH ₂ I ₂	" (49)	107
	Et ₂ Zn (1.25 eq), CH ₂ I ₂ (1.25 eq), dry air, cyclohexane	" (88)	354
	Zn/Cu, CH ₂ I ₂ , Et ₂ O (conc), reflux	" Conc (M) (%) 2.0 (51) 1.25 (40) 0.45 (43)	79
	Zn/Cu, CH ₂ I ₂ , Et ₂ O, reflux	(67) + (10)	355
	Et ₃ Al (1.2 eq), CH ₂ I ₂ (1.2 eq), <i>n</i> -hexane, rt	(86)	59
	1. Zn/Cu, CH ₂ I ₂ , Et ₂ O, reflux; 2. MeCOCl, reflux	(48)	568
	SmI ₂ , CH ₂ I ₂ , THF	(82)	88, 110
	Sm, CH ₂ I ₂ , THF, 50°	" (71)	110, 552
	Zn/Cu, CH ₂ I ₂ , I ₂ (cat.), Et ₂ O, reflux	(39)	370
	Zn/Ag, CH ₂ I ₂ , Et ₂ O, reflux	(53)	569
	Zn/Ag, CH ₂ I ₂ , Et ₂ O, reflux	(75)	569
	Zn/Cu, CH ₂ I ₂ , I ₂ (cat.), Et ₂ O, reflux	(88)	570
	Zn/Ag, CH ₂ I ₂ , Et ₂ O, reflux	(60)	107, 555

TABLE IV. CYCLOPROPANATION OF ACYCLIC, ACHIRAL *O*- AND *N*-SUBSTITUTED ALKENES (Continued)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.																																								
	Zn/Ag, CH ₂ I ₂ (xs), Et ₂ O, reflux	(85)	107																																								
	Zn/Ag, CH ₂ I ₂ , Et ₂ O, reflux	(70)	344																																								
	SmI ₂ , CH ₂ I ₂ , THF	(52)	110																																								
	Et ₂ Zn (1.1 eq), CH ₂ I ₂ (1.4 eq), Et ₂ O, reflux	 <table border="1"> <thead> <tr> <th>R</th> <th>(%)</th> </tr> </thead> <tbody> <tr> <td>4-OMe</td> <td>(55)</td> </tr> <tr> <td>4-Me</td> <td>(80)</td> </tr> <tr> <td>2-OTMS</td> <td>(55)</td> </tr> <tr> <td>4-OTMS</td> <td>(67)</td> </tr> </tbody> </table>	R	(%)	4-OMe	(55)	4-Me	(80)	2-OTMS	(55)	4-OTMS	(67)	571																														
R	(%)																																										
4-OMe	(55)																																										
4-Me	(80)																																										
2-OTMS	(55)																																										
4-OTMS	(67)																																										
	Et ₂ Zn, CH ₂ I ₂ , Et ₂ O	 <table border="1"> <thead> <tr> <th>R¹</th> <th>R²</th> <th>M</th> <th>(%)</th> <th><i>cis:trans</i></th> </tr> </thead> <tbody> <tr> <td><i>n</i>-Bu</td> <td>Me</td> <td>Li*(<i>n</i>-Bu)₂Zn</td> <td>(61)</td> <td>67:33</td> </tr> <tr> <td><i>s</i>-Bu</td> <td>Me</td> <td>Li*(<i>s</i>-Bu)₂Zn</td> <td>(86)</td> <td>77:23</td> </tr> <tr> <td><i>n</i>-Bu</td> <td><i>n</i>-C₅H₁₁</td> <td>Li*(<i>n</i>-Bu)₂Zn</td> <td>(61)</td> <td>62:38</td> </tr> </tbody> </table>	R ¹	R ²	M	(%)	<i>cis:trans</i>	<i>n</i> -Bu	Me	Li*(<i>n</i> -Bu) ₂ Zn	(61)	67:33	<i>s</i> -Bu	Me	Li*(<i>s</i> -Bu) ₂ Zn	(86)	77:23	<i>n</i> -Bu	<i>n</i> -C ₅ H ₁₁	Li*(<i>n</i> -Bu) ₂ Zn	(61)	62:38	371																				
R ¹	R ²	M	(%)	<i>cis:trans</i>																																							
<i>n</i> -Bu	Me	Li*(<i>n</i> -Bu) ₂ Zn	(61)	67:33																																							
<i>s</i> -Bu	Me	Li*(<i>s</i> -Bu) ₂ Zn	(86)	77:23																																							
<i>n</i> -Bu	<i>n</i> -C ₅ H ₁₁	Li*(<i>n</i> -Bu) ₂ Zn	(61)	62:38																																							
	Sm, CH ₂ I ₂ , THF, 50°	(59)	110, 552																																								
	SmI ₂ , CH ₂ I ₂ , THF	(56)	88, 110																																								
	Sm, CH ₂ I ₂ , THF, 50°	(51)	110, 552																																								
	Zn/Cu, CH ₂ I ₂ , I ₂ (cat.), Et ₂ O, reflux	(>99)	570																																								
	Et ₂ Zn, CH ₂ I ₂ , Et ₂ O, rt	(80)	572																																								
	Et ₂ Zn, CH ₂ I ₂ , Et ₂ O	 <table border="1"> <thead> <tr> <th>R¹</th> <th>R²</th> <th>M</th> <th>(%)</th> <th><i>cis:trans</i></th> </tr> </thead> <tbody> <tr> <td><i>n</i>-C₈H₁₇</td> <td>Me</td> <td>ZnEt</td> <td>(82)</td> <td>93:7</td> </tr> <tr> <td><i>n</i>-C₅H₁₁</td> <td><i>n</i>-C₆H₁₃</td> <td>ZnEt</td> <td>(93)</td> <td>87:13</td> </tr> <tr> <td>Me</td> <td>Ph</td> <td>ZnEt</td> <td>(34)</td> <td>—</td> </tr> <tr> <td>CH₂=CH(CH₂)₇</td> <td><i>i</i>-Pr</td> <td>ZnEt</td> <td>(65)</td> <td>51:49</td> </tr> <tr> <td><i>n</i>-C₈H₁₇</td> <td>H</td> <td>ZnEt</td> <td>(—)</td> <td>—</td> </tr> <tr> <td><i>n</i>-C₈H₁₇</td> <td>Me</td> <td>AlMe₂</td> <td>(34)</td> <td>41:59</td> </tr> <tr> <td><i>n</i>-C₈H₁₇</td> <td>Me</td> <td>BEt₂</td> <td>(69)</td> <td>74:26</td> </tr> </tbody> </table>	R ¹	R ²	M	(%)	<i>cis:trans</i>	<i>n</i> -C ₈ H ₁₇	Me	ZnEt	(82)	93:7	<i>n</i> -C ₅ H ₁₁	<i>n</i> -C ₆ H ₁₃	ZnEt	(93)	87:13	Me	Ph	ZnEt	(34)	—	CH ₂ =CH(CH ₂) ₇	<i>i</i> -Pr	ZnEt	(65)	51:49	<i>n</i> -C ₈ H ₁₇	H	ZnEt	(—)	—	<i>n</i> -C ₈ H ₁₇	Me	AlMe ₂	(34)	41:59	<i>n</i> -C ₈ H ₁₇	Me	BEt ₂	(69)	74:26	371
R ¹	R ²	M	(%)	<i>cis:trans</i>																																							
<i>n</i> -C ₈ H ₁₇	Me	ZnEt	(82)	93:7																																							
<i>n</i> -C ₅ H ₁₁	<i>n</i> -C ₆ H ₁₃	ZnEt	(93)	87:13																																							
Me	Ph	ZnEt	(34)	—																																							
CH ₂ =CH(CH ₂) ₇	<i>i</i> -Pr	ZnEt	(65)	51:49																																							
<i>n</i> -C ₈ H ₁₇	H	ZnEt	(—)	—																																							
<i>n</i> -C ₈ H ₁₇	Me	AlMe ₂	(34)	41:59																																							
<i>n</i> -C ₈ H ₁₇	Me	BEt ₂	(69)	74:26																																							
	Sm, CH ₂ I ₂ , THF, 50°	(21)	110, 552																																								
	Zn/Cu, CH ₂ I ₂ , Et ₂ O, reflux	(26) + (7)	481																																								

TABLE IV. CYCLOPROPANATION OF ACYCLIC, ACHIRAL *O*- AND *N*-SUBSTITUTED ALKENES (Continued)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.															
	Et ₂ Zn, CH ₂ I ₂ , Et ₂ O, rt	 (73)	572															
C ₁₁ 	Et ₂ Zn, MeCHCl ₂	 I + II (—) I:II = —	573															
	Et ₂ Zn, MeCHCl ₂	 I + II (—) I:II = —	573															
C ₁₁₋₁₃ 	Et ₂ Zn, CH ₂ I ₂	 <table border="1"> <thead> <tr> <th>R¹</th> <th>R²</th> <th>(%)</th> </tr> </thead> <tbody> <tr> <td>Me</td> <td>Ph</td> <td>(50-70)</td> </tr> <tr> <td>Me</td> <td><i>n</i>-C₆H₁₃</td> <td>(50-70)</td> </tr> <tr> <td><i>i</i>-Pr</td> <td>Ph</td> <td>(50-70)</td> </tr> <tr> <td><i>i</i>-Pr</td> <td><i>n</i>-C₆H₁₃</td> <td>(50-70)</td> </tr> </tbody> </table>	R ¹	R ²	(%)	Me	Ph	(50-70)	Me	<i>n</i> -C ₆ H ₁₃	(50-70)	<i>i</i> -Pr	Ph	(50-70)	<i>i</i> -Pr	<i>n</i> -C ₆ H ₁₃	(50-70)	573
R ¹	R ²	(%)																
Me	Ph	(50-70)																
Me	<i>n</i> -C ₆ H ₁₃	(50-70)																
<i>i</i> -Pr	Ph	(50-70)																
<i>i</i> -Pr	<i>n</i> -C ₆ H ₁₃	(50-70)																
	Et ₂ Zn, CH ₂ I ₂	 <table border="1"> <thead> <tr> <th>R¹</th> <th>R²</th> <th>(%)</th> </tr> </thead> <tbody> <tr> <td>Me</td> <td>Ph</td> <td>(50-70)</td> </tr> <tr> <td>Me</td> <td><i>n</i>-C₆H₁₃</td> <td>(50-70)</td> </tr> <tr> <td><i>i</i>-Pr</td> <td>Ph</td> <td>(50-70)</td> </tr> <tr> <td><i>i</i>-Pr</td> <td><i>n</i>-C₆H₁₃</td> <td>(50-70)</td> </tr> </tbody> </table>	R ¹	R ²	(%)	Me	Ph	(50-70)	Me	<i>n</i> -C ₆ H ₁₃	(50-70)	<i>i</i> -Pr	Ph	(50-70)	<i>i</i> -Pr	<i>n</i> -C ₆ H ₁₃	(50-70)	573
R ¹	R ²	(%)																
Me	Ph	(50-70)																
Me	<i>n</i> -C ₆ H ₁₃	(50-70)																
<i>i</i> -Pr	Ph	(50-70)																
<i>i</i> -Pr	<i>n</i> -C ₆ H ₁₃	(50-70)																
C ₁₂ 	Et ₂ Zn, CH ₂ I ₂	 (63)	574															
	Et ₂ Zn (0.8 eq), CH ₂ I ₂ (1.25 eq), Et ₂ O, reflux	 (93)	575															
	Et ₂ Zn, CH ₂ I ₂ , Et ₂ O, rt	 (>72)	572															
	Et ₂ Zn, CH ₂ I ₂ , Et ₂ O	 (92) <i>cis:trans</i> = 57:43	371															
	Et ₂ Zn (1 eq), CH ₂ I ₂ (1.15 eq), THF	 (>59)	576															
	Et ₂ Zn, CH ₂ I ₂	 <table border="1"> <thead> <tr> <th>R</th> <th>(%)</th> </tr> </thead> <tbody> <tr> <td>Ph</td> <td>(50-70)</td> </tr> <tr> <td><i>n</i>-C₆H₁₃</td> <td>(50-70)</td> </tr> </tbody> </table>	R	(%)	Ph	(50-70)	<i>n</i> -C ₆ H ₁₃	(50-70)	573									
R	(%)																	
Ph	(50-70)																	
<i>n</i> -C ₆ H ₁₃	(50-70)																	
C ₁₃ 	Et ₂ Zn, CH ₂ I ₂ , Et ₂ O, rt	 (74)	572															

TABLE IV. CYCLOPROPANATION OF ACYCLIC, ACHIRAL *O*- AND *N*-SUBSTITUTED ALKENES (Continued)

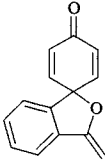
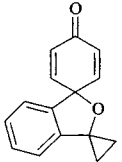
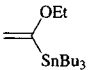
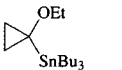
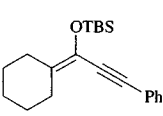
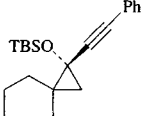
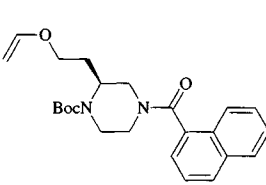
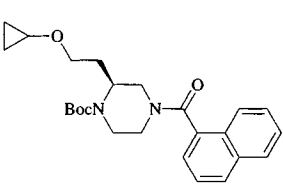
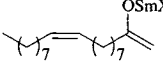
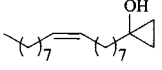
Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₁₄ 	Et ₂ Zn, CH ₂ I ₂ , Et ₂ O, reflux	 (47)	577
	Et ₂ Zn, CH ₂ I ₂ , air, PhMe, rt	 (20)	578
C ₁₅ 	Et ₂ Zn, CH ₂ I ₂	 (—)	573
C ₁₉ 	Et ₂ Zn, CH ₂ I ₂ , Et ₂ O, 30°	 (>34)	579
	Sm, CH ₂ I ₂ , THF, 50°	 (70)	110, 552

TABLE XV. CYCLOPROPANATION OF ALKENES USING A SUBSTITUTED DIHALIDE

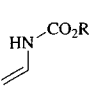
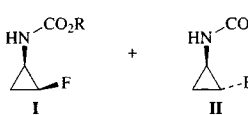
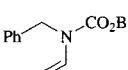
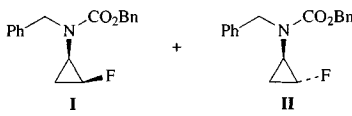
Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.																																	
C ₂ 	Et ₂ Zn, CHFI ₂ , conditions, CH ₂ Cl ₂	 <table border="1"> <thead> <tr> <th>R</th> <th>Conditions</th> <th>(%)</th> <th>I:II</th> </tr> </thead> <tbody> <tr> <td>Bn</td> <td>-40° then rt</td> <td>(<10)</td> <td>—</td> </tr> <tr> <td>Bn</td> <td>MS (4Å), DME, rt</td> <td>(25)</td> <td>64:36</td> </tr> <tr> <td><i>t</i>-Bu</td> <td>MS (4Å), DME, 0°</td> <td>(30)</td> <td>60:40</td> </tr> </tbody> </table>	R	Conditions	(%)	I:II	Bn	-40° then rt	(<10)	—	Bn	MS (4Å), DME, rt	(25)	64:36	<i>t</i> -Bu	MS (4Å), DME, 0°	(30)	60:40	548																	
R	Conditions	(%)	I:II																																	
Bn	-40° then rt	(<10)	—																																	
Bn	MS (4Å), DME, rt	(25)	64:36																																	
<i>t</i> -Bu	MS (4Å), DME, 0°	(30)	60:40																																	
	Et ₂ Zn, CHFI ₂ , conditions	 <table border="1"> <thead> <tr> <th>Conditions</th> <th>(%)</th> <th>I:II</th> </tr> </thead> <tbody> <tr> <td>hexane, -20°</td> <td>(79)</td> <td>65:35</td> </tr> <tr> <td>cyclohexane, -20°</td> <td>(63)</td> <td>65:35</td> </tr> <tr> <td>PhMe, -20°</td> <td>(64)</td> <td>65:35</td> </tr> <tr> <td>THF, -20° then rt</td> <td>(0)</td> <td>—</td> </tr> <tr> <td>Et₂O, -20°</td> <td>(73)</td> <td>63:37</td> </tr> <tr> <td>CCl₄, -20°</td> <td>(75)</td> <td>60:40</td> </tr> <tr> <td>CHCl₃, -20°</td> <td>(81)</td> <td>63:37</td> </tr> <tr> <td>CH₂Cl₂, -20°</td> <td>(79)</td> <td>69:31</td> </tr> <tr> <td>CH₂Cl₂, -40°</td> <td>(78)</td> <td>71:29</td> </tr> <tr> <td>CH₂Cl₂, -78°</td> <td>(68)</td> <td>76:24</td> </tr> </tbody> </table>	Conditions	(%)	I:II	hexane, -20°	(79)	65:35	cyclohexane, -20°	(63)	65:35	PhMe, -20°	(64)	65:35	THF, -20° then rt	(0)	—	Et ₂ O, -20°	(73)	63:37	CCl ₄ , -20°	(75)	60:40	CHCl ₃ , -20°	(81)	63:37	CH ₂ Cl ₂ , -20°	(79)	69:31	CH ₂ Cl ₂ , -40°	(78)	71:29	CH ₂ Cl ₂ , -78°	(68)	76:24	548
Conditions	(%)	I:II																																		
hexane, -20°	(79)	65:35																																		
cyclohexane, -20°	(63)	65:35																																		
PhMe, -20°	(64)	65:35																																		
THF, -20° then rt	(0)	—																																		
Et ₂ O, -20°	(73)	63:37																																		
CCl ₄ , -20°	(75)	60:40																																		
CHCl ₃ , -20°	(81)	63:37																																		
CH ₂ Cl ₂ , -20°	(79)	69:31																																		
CH ₂ Cl ₂ , -40°	(78)	71:29																																		
CH ₂ Cl ₂ , -78°	(68)	76:24																																		

TABLE V. CYCLOPROPANATION OF *exo*-METHYLENE CONTAINING COMPOUNDS (Continued)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.									
	Zn/Cu, CH ₂ I ₂	 (-)	585									
	Et ₂ Zn, CH ₂ I ₂	" (64)	71									
	Zn/Cu, MeCHI ₂ , Et ₂ O	 (31)	66									
	Zn, (ClMe ₂ SiCH ₂) ₂ , Et ₂ O, reflux	 (34)	76									
	Zn/Cu, ¹³ CH ₂ I ₂ , solvent	 <table border="1" style="display: inline-table; vertical-align: middle;"> <thead> <tr> <th>Solvent</th> <th>(%)</th> <th>syn:anti</th> </tr> </thead> <tbody> <tr> <td>pentane</td> <td>(-)</td> <td>6:1</td> </tr> <tr> <td>Et₂O</td> <td>(-)</td> <td>1:1</td> </tr> </tbody> </table>	Solvent	(%)	syn:anti	pentane	(-)	6:1	Et ₂ O	(-)	1:1	586
Solvent	(%)	syn:anti										
pentane	(-)	6:1										
Et ₂ O	(-)	1:1										
	Zn/Cu, CH ₂ I ₂ , I ₂ (cat.), Et ₂ O, reflux	 (30)	587									
	Zn/Ag, CH ₂ I ₂ , Et ₂ O	 (60)	588, 589									
	Zn/Cu, CH ₂ I ₂	 (-)	590									
	Zn/Cu, CH ₂ I ₂	 (-)	568									
	Zn/Cu, CH ₂ I ₂ , Et ₂ O, reflux	" (65)	591									
	Zn/Ag, CH ₂ I ₂ , Et ₂ O	 (46)	592									
	Zn/Cu, CH ₂ I ₂ , Et ₂ O, reflux	 (50)	593									
	Zn/Cu, CH ₂ I ₂	 (-)	585									
	Et ₂ Zn, CH ₂ I ₂ , cyclohexane	" (65)	71									
	Zn/Ag, CH ₂ I ₂ , Et ₂ O	 <table border="1" style="display: inline-table; vertical-align: middle;"> <thead> <tr> <th>R</th> <th>(%)</th> </tr> </thead> <tbody> <tr> <td>H</td> <td>(70)</td> </tr> <tr> <td>THP</td> <td>(74)</td> </tr> </tbody> </table>	R	(%)	H	(70)	THP	(74)	404			
R	(%)											
H	(70)											
THP	(74)											
	Zn/Ag, CH ₂ I ₂ , Et ₂ O	 (53)	592									
	Et ₂ Zn, CH ₂ I ₂ , Et ₂ O, reflux	" (74)	302									
	Zn/Cu, CH ₂ I ₂ , DME, ultrasound	 I + II (23) I:II = 1:2	594									
	Zn/Ag, CH ₂ I ₂ , Et ₂ O	 (78)	404									

 C₈

 C₉

TABLE V. CYCLOPROPANATION OF *exo*-METHYLENE CONTAINING COMPOUNDS (Continued)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
	Zn/Cu, CH ₂ I ₂ , Et ₂ O, reflux	I + II (95) I:II = 18:1	595
	Et ₂ Zn (1.4 eq), CH ₂ I ₂ (1.4 eq), dry air, PhMe, 55°	(30)	596
	Et ₂ Zn, CH ₂ I ₂ , Et ₂ O	(88)	597
	Et ₂ Zn (1.4 eq), CH ₂ I ₂ (1.4 eq), dry air, PhMe, 55°	(<25)	596
	Zn/Cu, CH ₂ I ₂ , Et ₂ O, reflux	(78)	598
	Zn/Ag, CH ₂ I ₂ , Et ₂ O	(63)	592
	Zn/Cu, CH ₂ I ₂ , Et ₂ O/DME	(71)	599, 600
	Et ₂ Zn (1.4 eq), CH ₂ I ₂ (1.4 eq), dry air, PhMe, 55°	(81)	596
	Zn/Ag, CH ₂ I ₂ , Et ₂ O, reflux	(99)	601
	Et ₂ Zn, CH ₂ I ₂ , Et ₂ O, rt	(12) + several other products	602
	Zn/Ag, CH ₂ I ₂ , Et ₂ O	(52)	592
	Et ₂ Zn, CH ₂ I ₂	(25-30)	603, 604
	Zn/Cu, CH ₂ I ₂ , Et ₂ O, reflux	(59)	605
	Et ₂ Zn, CH ₂ I ₂ , Et ₂ O	(87)	597
	Zn/Cu, CH ₂ I ₂ , Et ₂ O, reflux	(52)	605
	Zn/Ag, CH ₂ I ₂ , Et ₂ O, reflux	(82)	606
	Zn/Cu, CH ₂ Br ₂ , Et ₂ O, 45°, sonication	(50)	270

178

C₁₀

179

TABLE V. CYCLOPROPANATION OF *exo*-METHYLENE CONTAINING COMPOUNDS (Continued)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.												
	Zn/Cu, CH ₂ Br ₂ , AcCl (0.02 eq), Et ₂ O	" (67)	41												
	Zn/Cu, CH ₂ X ₂ , promoter, Et ₂ O	<table border="1"> <thead> <tr> <th>Promoter</th> <th>X</th> <th>(%)</th> </tr> </thead> <tbody> <tr> <td>TiCl₄</td> <td>Br</td> <td>(77)</td> </tr> <tr> <td>ultrasound</td> <td>Br</td> <td>(50)</td> </tr> <tr> <td>TiCl₄</td> <td>I</td> <td>(65)</td> </tr> </tbody> </table>	Promoter	X	(%)	TiCl ₄	Br	(77)	ultrasound	Br	(50)	TiCl ₄	I	(65)	43
Promoter	X	(%)													
TiCl ₄	Br	(77)													
ultrasound	Br	(50)													
TiCl ₄	I	(65)													
	Zn/Cu, CH ₂ I ₂ , Et ₂ O, reflux	(85)	605												
	Zn/Cu, CH ₂ I ₂ , ultrasound, DME, reflux	" (74)	45												
	R ₃ Al (1.2 eq), CH ₂ I ₂ (1.2 eq), solvent, rt	<table border="1"> <thead> <tr> <th>R</th> <th>Solvent</th> <th>(%)</th> </tr> </thead> <tbody> <tr> <td>Me</td> <td>CH₂Cl₂</td> <td>(46)</td> </tr> <tr> <td>Me</td> <td><i>n</i>-hexane</td> <td>(96)</td> </tr> <tr> <td><i>i</i>-Bu</td> <td><i>n</i>-hexane</td> <td>(73)</td> </tr> </tbody> </table>	R	Solvent	(%)	Me	CH ₂ Cl ₂	(46)	Me	<i>n</i> -hexane	(96)	<i>i</i> -Bu	<i>n</i> -hexane	(73)	59
R	Solvent	(%)													
Me	CH ₂ Cl ₂	(46)													
Me	<i>n</i> -hexane	(96)													
<i>i</i> -Bu	<i>n</i> -hexane	(73)													
	Zn/Cu, CH ₂ I ₂	(75) + (8)	480												
	Zn/Cu, CH ₂ I ₂ , Et ₂ O, reflux	(88)	595												
	Et ₂ Zn (1.4 eq), CH ₂ I ₂ (1.4 eq), dry air, PhMe, 55°	(76)	603, 604												
C ₁₁ 	Zn/Ag, CH ₂ I ₂ , Et ₂ O	(78)	404												
	Et ₂ Zn, CH ₂ I ₂ , CH ₂ Cl ₂	(69)	607												
	Zn/Cu, CH ₂ I ₂	(79)	608												
	Zn/Ag, CH ₂ I ₂ , Et ₂ O, reflux	(83)	488												
C ₁₂ 	Zn/Ag, CH ₂ I ₂ , Et ₂ O	I + II (27) I:II = 5.3:1	609												
	Et ₂ Zn (0.8 eq), CH ₂ I ₂ (1.25 eq), Et ₂ O, reflux	(93)	575												
	Et ₂ Zn (10 eq), CH ₂ I ₂ (10 eq), CH ₂ Cl ₂ , -80° to rt	(84)	611												

TABLE V. CYCLOPROPANATION OF *exo*-METHYLENE CONTAINING COMPOUNDS (Continued)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
	Zn/Ag, CH ₂ I ₂ , Et ₂ O	(63)	609
	Zn/Ag, CH ₂ I ₂	(70)	612
	Zn/Ag, CH ₂ I ₂ , Et ₂ O	(82)	609
	Zn/Ag, CH ₂ I ₂ , Et ₂ O	(82)	609
	Zn/Ag, CH ₂ I ₂ , Et ₂ O, reflux	(78)	613, 614
 (no ratio reported)	Et ₂ Zn (1.8 eq), CH ₂ I ₂ (5.5 eq), Et ₂ O	 I + II + III = (43)	615
	Et ₂ Zn (1.2 eq), CH ₂ I ₂ (1.3 eq), C ₆ H ₆	(87)	616, 617
	Zn/Cu, CH ₂ I ₂ , Et ₂ O, reflux	(50)	618
	Zn/Cu, CH ₂ I ₂ , Et ₂ O, reflux	(84)	5
	Zn/Cu, CH ₂ I ₂ , Et ₂ O, reflux	(—)	619
	Et ₂ Zn, CH ₂ I ₂ , PhMe, 60°	(94)	620
	Zn/Cu, CH ₂ I ₂	(55)	621
	Et ₂ Zn, CH ₂ I ₂ , dry air, PhMe, 50-55°	(—)	622

TABLE V. CYCLOPROPANATION OF *exo*-METHYLENE CONTAINING COMPOUNDS (Continued)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
	Zn/Ag, CH ₂ I ₂ , Et ₂ O, reflux	 (61)	623
	Zn/Cu, CH ₂ I ₂	 (—)	624
	Zn/Cu, CH ₂ I ₂ , Et ₂ O, reflux	" (—)	625
C ₁₄ 	Et ₂ Zn, CH ₂ I ₂ , Et ₂ O, reflux	 (47)	577
	Et ₂ Zn (5 eq), CH ₂ I ₂ (20 eq), CH ₂ Cl ₂	 (48)	626
	Zn/Cu, CH ₂ I ₂ , Et ₂ O/DME, 40°	 (44)	627
	Et ₂ Zn, CH ₂ I ₂	 (—)	628
	Et ₂ Zn, CH ₂ I ₂ , O ₂ (cat.), PhMe, 50°	 (74)	632
	Et ₂ Zn, CH ₂ I ₂ , PhMe	 (>70)	630
	Et ₂ Zn (1.4 eq), CH ₂ I ₂ (1.4 eq), dry air, PhMe, 60°	 (99)	631
	Et ₂ Zn, CH ₂ I ₂ , O ₂ (cat.), PhMe, 50°	 (75)	629, 632
	Et ₂ Zn, CH ₂ I ₂ , C ₆ H ₆ , 68°, O ₂	 (77)	633
	Zn/Ag, CH ₂ I ₂ , Et ₂ O, reflux	 (80)	634, 635

TABLE V. CYCLOPROPANATION OF *exo*-METHYLENE CONTAINING COMPOUNDS (Continued)

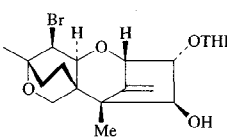
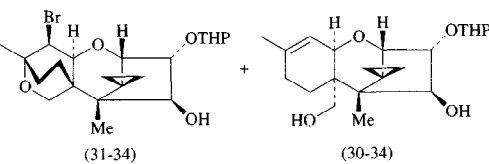
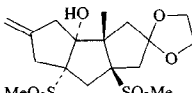
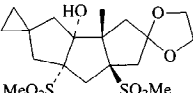
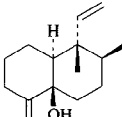
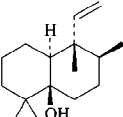
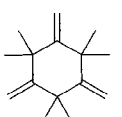
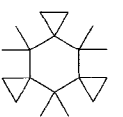
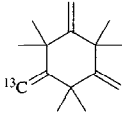
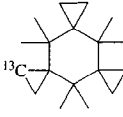
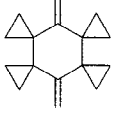
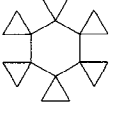
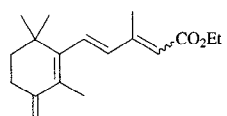
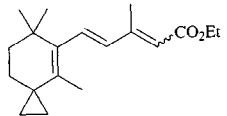
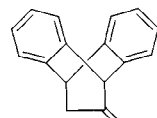
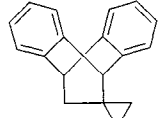
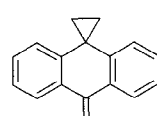
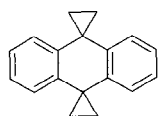
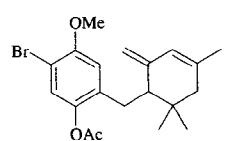
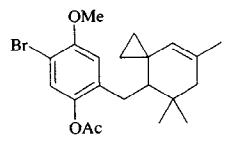
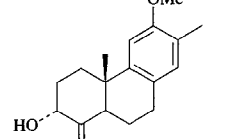
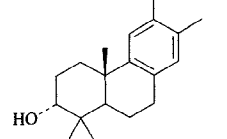
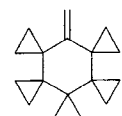
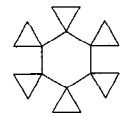
Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
<p>C₁₅</p> 	Zn/Ag, CH ₂ I ₂ , Et ₂ O, 40-50°	 (31-34) + (30-34)	636
	Et ₂ Zn, CH ₂ I ₂ , O ₂ (cat.), PhMe	 (82)	637
	Et ₂ Zn (2.4 eq), CH ₂ I ₂ (3 eq), air, C ₆ H ₆ , 0°	 (91)	638
	Zn/Ag, CH ₂ I ₂ , Et ₂ O, reflux	 (88)	488
	Zn/Ag, CH ₂ I ₂ , Et ₂ O, reflux	 (72)	488
<p>C₁₆</p> 	Et ₂ Zn, CH ₂ I ₂	 (72)	612
	Zn/Cu, CH ₂ I ₂ , I ₂ (cat.), Et ₂ O, reflux	 (67)	314
<p>C₁₇</p> 	Zn/Cu, CH ₂ I ₂ , Et ₂ O, reflux	 (45)	639
	Zn(CH ₂ I) ₂ , (CH ₂ Cl) ₂	 (37)	640
	Et ₂ Zn (5 eq), CH ₂ I ₂ (10 eq), (CH ₂ Cl) ₂ , 0°	 (96)	641
	Et ₂ Zn, CH ₂ I ₂ , PhMe	 (54)	642
	Zn/Ag, CH ₂ I ₂ , Et ₂ O	 (50-70)	643

TABLE V. CYCLOPROPANATION OF *exo*-METHYLENE CONTAINING COMPOUNDS (Continued)

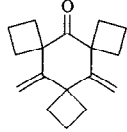
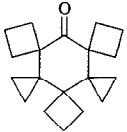
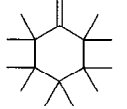
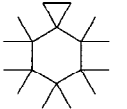
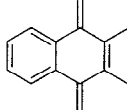
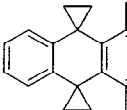
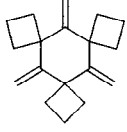
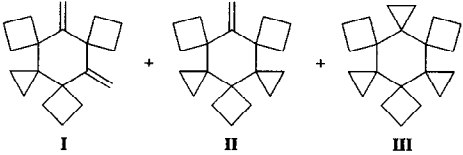
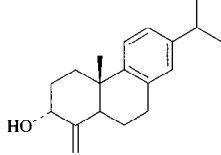
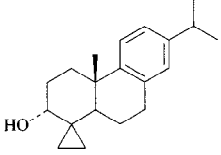
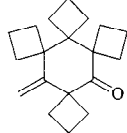
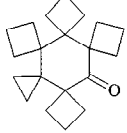
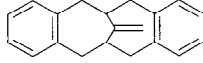

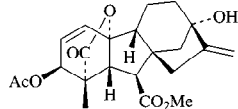
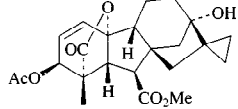
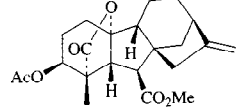
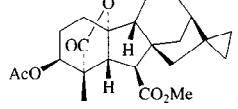
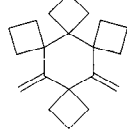
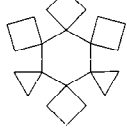
Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.								
	EtZnI, CH ₂ I ₂ , Et ₂ O	 (84)	644								
	Zn/Ag, CH ₂ I ₂ , Et ₂ O, reflux	 (87)	635								
C ₁₈ 	Zn(CH ₂ I) ₂ , (CH ₂ Cl) ₂	 (60)	640								
	"MCH ₂ X"	 I II III	645								
		<table border="1"> <thead> <tr> <th>MCH₂X</th> <th>(%I:%II:%III)</th> </tr> </thead> <tbody> <tr> <td>Zn/Ag, CH₂I₂</td> <td>0:0:100</td> </tr> <tr> <td>Zn/Ag, CH₂I₂, Et₂O</td> <td>25:21:29</td> </tr> <tr> <td>Et₂Zn, CH₂I₂, PhMe</td> <td>24:36:24</td> </tr> </tbody> </table>	MCH ₂ X	(%I:%II:%III)	Zn/Ag, CH ₂ I ₂	0:0:100	Zn/Ag, CH ₂ I ₂ , Et ₂ O	25:21:29	Et ₂ Zn, CH ₂ I ₂ , PhMe	24:36:24	
MCH ₂ X	(%I:%II:%III)										
Zn/Ag, CH ₂ I ₂	0:0:100										
Zn/Ag, CH ₂ I ₂ , Et ₂ O	25:21:29										
Et ₂ Zn, CH ₂ I ₂ , PhMe	24:36:24										
C ₁₉ 	Et ₂ Zn (10 eq), CH ₂ I ₂ (11 eq), PhMe, reflux	 (95)	646								
	EtZnI, CH ₂ I ₂ , Et ₂ O	 (71)	647								
C ₂₀ 	Zn/Cu, CH ₂ I ₂ , Et ₂ O, reflux	 (77)	648								
	Zn/Cu, CH ₂ I ₂ , Et ₂ O/DME	 (—)	649								
	Zn/Cu, CH ₂ I ₂ , Et ₂ O, reflux	 (66)	649								
	Zn/Ag, CH ₂ I ₂ , Et ₂ O	 (65)	647								

TABLE V. CYCLOPROPANATION OF *exo*-METHYLENE CONTAINING COMPOUNDS (Continued)

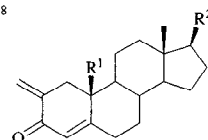
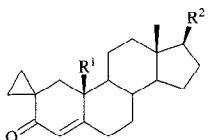
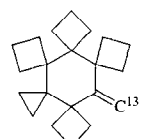
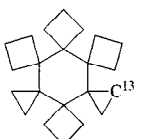
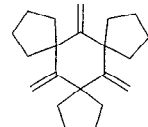
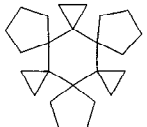
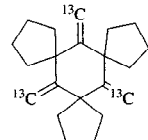
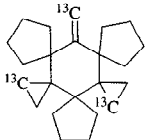
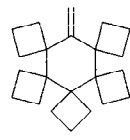
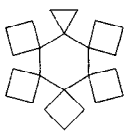

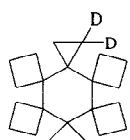
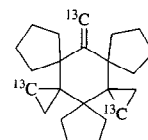
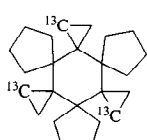
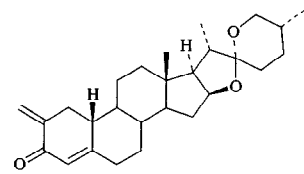
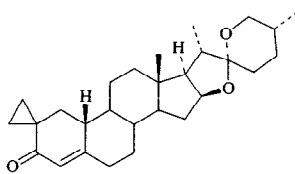
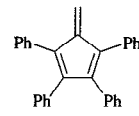
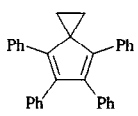
Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.																
C ₂₀₋₂₈ 	Zn/Cu, CH ₂ I ₂ , Et ₂ O, reflux		<table border="1"> <thead> <tr> <th>R¹</th> <th>R²</th> <th>(%)</th> </tr> </thead> <tbody> <tr> <td>Me</td> <td>C₈H₁₇</td> <td>(80)</td> </tr> <tr> <td>Me</td> <td>OH</td> <td>(76)</td> </tr> <tr> <td>Me</td> <td>CHO</td> <td>(90)</td> </tr> <tr> <td>Me</td> <td>O₂CCF₃</td> <td>(62)</td> </tr> </tbody> </table>	R ¹	R ²	(%)	Me	C ₈ H ₁₇	(80)	Me	OH	(76)	Me	CHO	(90)	Me	O ₂ CCF ₃	(62)	650
		R ¹	R ²	(%)															
		Me	C ₈ H ₁₇	(80)															
		Me	OH	(76)															
Me	CHO	(90)																	
Me	O ₂ CCF ₃	(62)																	
C ₂₁ 	Zn/Ag, CH ₂ I ₂ , Et ₂ O		(92)	647															
			Zn/Ag, CH ₂ I ₂ , Et ₂ O, reflux		(36)	651													
	Zn/Ag, CH ₂ I ₂ , Et ₂ O, reflux		(38)	651															
C ₂₂ 	Zn/Ag, CH ₂ I ₂ , Et ₂ O		(82)	647															
			Zn/Ag, CD ₂ I ₂ , Et ₂ O		(75)	647													
	Zn/Ag, CH ₂ I ₂ , Et ₂ O, reflux		(28)	651															
C ₂₇ 	Zn/Cu, CH ₂ I ₂ , Et ₂ O, reflux		(72)	650															
C ₃₀ 	Zn/Cu, CH ₂ I ₂ , I ₂ (cat.), Et ₂ O		(62)	652															

TABLE VI. CYCLOPROPANATION OF POLYENES






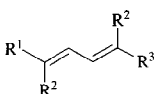
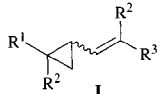
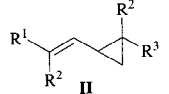
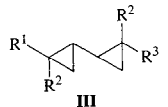






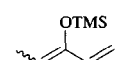


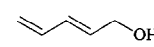

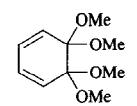
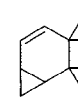

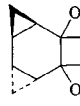
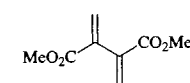
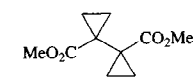
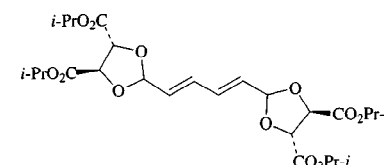
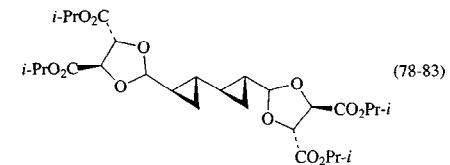
Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.																		
C ₄ 	Zn/Ag, CH ₂ I ₂ , Et ₂ O, reflux	 (75)	107, 555																		
	Zn/Ag, CH ₂ I ₂ (xs), Et ₂ O, reflux	 (84)	107, 267																		
	Et ₂ Zn, CH ₂ I ₂	 (—)	392																		
	Zn, CF ₂ Br ₂ , I ₂ (cat.), THF, rt	 (17)	74																		
C _{4.8} 	Zn/Cu, CH ₂ I ₂ , Et ₂ O	 I +  II	401																		
		 III	<table border="1"> <thead> <tr> <th>I (%)</th> <th>II (%)</th> <th>III (%)</th> </tr> </thead> <tbody> <tr> <td>(12)</td> <td>(—)</td> <td>(2)</td> </tr> <tr> <td>(11)</td> <td>(—)</td> <td>(9)</td> </tr> <tr> <td>(6)</td> <td>(1)</td> <td>(—)</td> </tr> <tr> <td>(4)</td> <td>(—)</td> <td>(—)</td> </tr> <tr> <td>(—)</td> <td>(18)</td> <td>(—)</td> </tr> </tbody> </table>	I (%)	II (%)	III (%)	(12)	(—)	(2)	(11)	(—)	(9)	(6)	(1)	(—)	(4)	(—)	(—)	(—)	(18)	(—)
	I (%)	II (%)	III (%)																		
	(12)	(—)	(2)																		
	(11)	(—)	(9)																		
(6)	(1)	(—)																			
(4)	(—)	(—)																			
(—)	(18)	(—)																			
R ¹ H	R ² H	R ³ H																			
Me	Me	Me																			
Me	H	CO ₂ Me																			
CO ₂ Me	H	CO ₂ Me																			
Me	H	CH ₂ OH																			
C ₅ 	Et ₂ Zn, CH ₂ I ₂ , pentane	 +  (—)	264																		
	Zn, CF ₂ Br ₂ , I ₂ (cat.), THF, rt	 (21)	74																		
	Zn/Ag, CH ₂ I ₂ , Et ₂ O, reflux	 (80)	107, 555																		
	Zn/Ag, CH ₂ I ₂ (xs), Et ₂ O, reflux	 (87)	107, 267																		
	 <i>E:Z</i> = 17:83	Zn/Ag, CH ₂ I ₂ , Et ₂ O, reflux	 (70)	107, 555																	
	Zn/Ag, CH ₂ I ₂ (xs), Et ₂ O, reflux	 (85)	107, 267																		
	Et ₂ Zn (6 eq), CH ₂ I ₂ (6 eq), (CH ₂ Cl) ₂ , -10° to rt	 (87)	409																		
C ₆ 	Zn/Ag, CH ₂ I ₂ , Et ₂ O	 I (20) +  II (2) +  III (70)	266																		
		Zn/Ag, CH ₂ I ₂ , Et ₂ O	 (55)	404																	
		Et ₂ Zn, CH ₂ I ₂ , (CH ₂ Cl) ₂ , -20°	 (78-83)	162, 653																	

TABLE VI. CYCLOPROPANATION OF POLYENES (Continued)








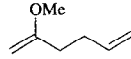

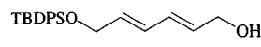
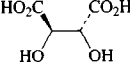
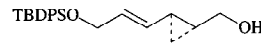
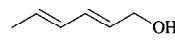

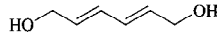
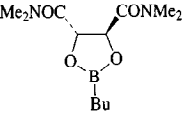

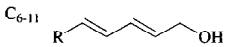

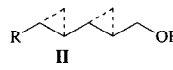




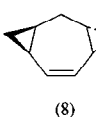

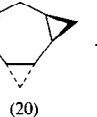
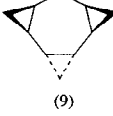
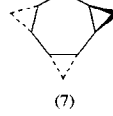
Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.																		
	Zn/Ag, CH ₂ I ₂ , Et ₂ O, reflux	 (85)	107, 350																		
	Zn/Ag, CH ₂ I ₂ (xs), Et ₂ O, reflux	 (85)	107, 267																		
	Zn/Cu, CH ₂ I ₂	 (—)	268																		
	Zn, CF ₂ Br ₂ , I ₂ (cat.), THF, rt	 (7)	74																		
	Zn/Cu, CH ₂ I ₂ , Et ₂ O/DME, reflux	 (80)	564																		
	 Et ₂ Zn, CH ₂ I ₂ , (CH ₂ Cl) ₂ , -20°	 (67)	654																		
	Sm (4 eq), CH ₂ I ₂ , THF, -78° to rt	 (91) mono:bis = >100:1	418																		
	Zn (xs), CH ₂ I ₂ , Et ₂ O, 35°	" (51)	419																		
	Zn/Cu, CH ₂ I ₂ , Et ₂ O, reflux	" (74)	420																		
	 Zn(CH ₂ I) ₂ , CH ₂ Cl ₂ , -15 to 25°	 (89)	192, 655																		
	Et ₂ Zn, CH ₂ I ₂ , (CH ₂ Cl) ₂ , -20°	 I +  II	155																		
		<table border="1"> <thead> <tr> <th>R</th> <th>(%)</th> <th>I:II</th> </tr> </thead> <tbody> <tr> <td>Me</td> <td>(68)</td> <td>5:1</td> </tr> <tr> <td>TBDPSOCH₂</td> <td>(72)</td> <td>>95:5</td> </tr> <tr> <td><i>i</i>-Pr</td> <td>(72)</td> <td>6:1</td> </tr> <tr> <td>Ph</td> <td>(80)</td> <td>5:1</td> </tr> <tr> <td>C₆H₁₁</td> <td>(78)</td> <td>7:1</td> </tr> </tbody> </table>	R	(%)	I:II	Me	(68)	5:1	TBDPSOCH ₂	(72)	>95:5	<i>i</i> -Pr	(72)	6:1	Ph	(80)	5:1	C ₆ H ₁₁	(78)	7:1	
R	(%)	I:II																			
Me	(68)	5:1																			
TBDPSOCH ₂	(72)	>95:5																			
<i>i</i> -Pr	(72)	6:1																			
Ph	(80)	5:1																			
C ₆ H ₁₁	(78)	7:1																			
	Zn/Cu, CH ₂ I ₂ , Et ₂ O	 I (42) +  (1) +  (4) +	279																		
		 (8) +  (5) +  (20) +																			
		 (9) +  (7)																			
	Zn/Cu, CH ₂ I ₂ , Et ₂ O, reflux	I (12-14)	280																		

TABLE VI. CYCLOPROPANATION OF POLYENES (Continued)



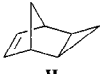



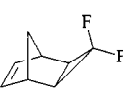
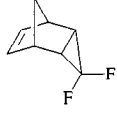
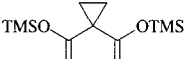

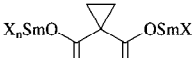
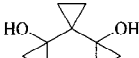
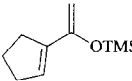
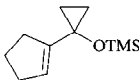
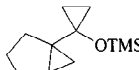



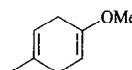
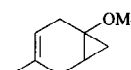



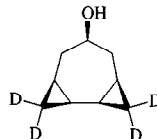
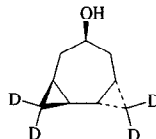
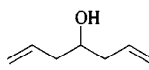
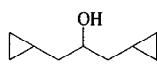
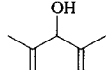
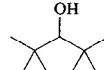



Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
	Zn/Cu, CH ₂ I ₂ , Et ₂ O	 +  (-) I:II:III:IV = --  + 	281
	Zn, CF ₂ Br ₂ , I ₂ (cat.), THF, rt	 +  +  (12) I:II:III = 38:58:3	74
	Zn/Cu, CH ₂ I ₂ , Et ₂ O, reflux	 (70)	567
	Sm, CH ₂ I ₂ , THF, 50°	 (22)	110, 552
	Zn/Ag, CH ₂ I ₂ , Et ₂ O, reflux	 (70)	107, 555
	Zn/Ag, CH ₂ I ₂ (xs), Et ₂ O, reflux	 (75)	107, 267
	Zn/Ag, CH ₂ I ₂ , Et ₂ O, reflux	 (-)	107, 350
	Zn/Ag, CH ₂ I ₂ (xs), Et ₂ O, reflux	 (90)	107, 267
	Zn/Ag, CH ₂ I ₂ , Et ₂ O, reflux	 (64)	359
	Et ₂ Zn, CH ₂ I ₂ , Et ₂ O	 (82)	360
	Zn/Ag, CD ₂ I ₂ , Et ₂ O, reflux	 (21) +  (10)	656
	Zn/Cu, CH ₂ I ₂ , I ₂ (cat.), Et ₂ O, reflux	 (73)	434
	Zn/Cu, CH ₂ I ₂ , I ₂ (cat.), Et ₂ O, reflux; repeated once	 (43)	435
	EtZnI, CH ₂ I ₂ , Et ₂ O, reflux	 +  (-) I:II = 55:45	289

TABLE VI. CYCLOPROPANATION OF POLYENES (Continued)


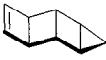
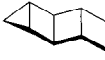
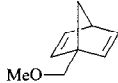
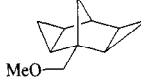
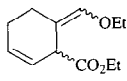
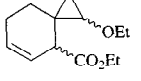


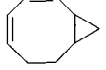
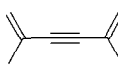


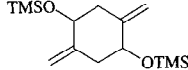
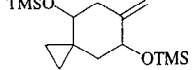
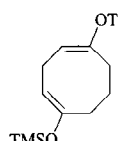
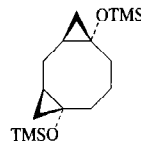
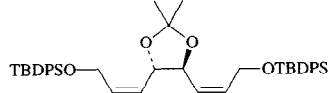
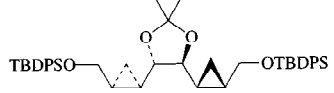
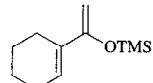
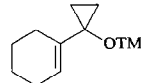
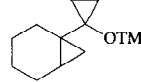
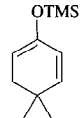
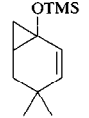
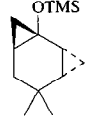
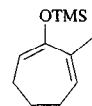
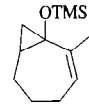
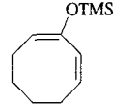
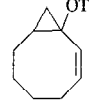
Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
	EtZnI, CH ₂ I ₂ , Et ₂ O, reflux	 (23) +  (28)	289
	Zn/Cu, CH ₂ I ₂ , I ₂ (cat.), Et ₂ O, reflux	 (82)	290
	Zn/Cu, CH ₂ I ₂ , I ₂ (cat.), Et ₂ O, reflux	 (88)	570
 +  I:II = 6 : 4	Et ₂ Zn, CH ₂ I ₂ , 50°	 (36) + other products	292
	Zn/Ag, CH ₂ I ₂	 (–) +  (–) + other products	444
	Zn/Cu, CH ₂ I ₂	 (–)	590
	Et ₂ Zn (6 eq), CH ₂ I ₂ (10 eq), Et ₂ O, O ₂	 (>77) >15:1	132
	Conditions		150, 657
		Conditions (%)	
		Et ₂ Zn, CH ₂ I ₂ , CH ₂ Cl ₂ , –25 to 0°	(75)
		Zn/Cu, CH ₂ I ₂ , Et ₂ O, 35°	(61)
	Zn/Ag, CH ₂ I ₂ , Et ₂ O, reflux	 (60)	107, 555
	Zn/Ag, CH ₂ I ₂ (xs), Et ₂ O, reflux	 (85)	107, 267
	Zn/Ag, CH ₂ I ₂ , Et ₂ O, reflux	 (88)	107, 350
	Zn/Ag, CH ₂ I ₂ (xs), Et ₂ O, reflux	 (78)	107, 267
	Et ₂ Zn, CH ₂ I ₂ , Et ₂ O	 (78)	360
	Et ₂ Zn, CH ₂ I ₂ , Et ₂ O	 (55)	360

TABLE VI. CYCLOPROPANATION OF POLYENES (Continued)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.																				
	Zn/Cu, CH ₂ I ₂	 (—)	568																				
	Zn/Cu, CH ₂ I ₂ , Et ₂ O, reflux	" (65)	591																				
	Zn anode, 2e ⁻ , CH ₂ Br ₂ , ZnBr ₂ present initially, CH ₂ Cl ₂ /DMF (9:1)	 (66)	70																				
	Zn/Cu, CH ₂ I ₂	 (—)	293																				
	Et ₂ Zn, CH ₂ I ₂ , PhMe, rt	 I (7-13) + II (7-45)	446																				
	Conditions	I + II + III	104																				
		<table border="1"> <thead> <tr> <th>Conditions</th> <th>I (%)</th> <th>II (%)</th> <th>III (%)</th> </tr> </thead> <tbody> <tr> <td>Zn/Cu, CH₂I₂, AcCl, Et₂O</td> <td>(9)</td> <td>(18)</td> <td>(1)</td> </tr> <tr> <td>Zn/Cu, CH₂Br₂, AcCl, Et₂O</td> <td>(2)</td> <td>(4)</td> <td>(0)</td> </tr> <tr> <td>Et₂Zn, CH₂I₂, PhMe</td> <td>(5)</td> <td>(34)</td> <td>(1)</td> </tr> <tr> <td>Et₃Al, CH₂I₂, PhMe/CH₂Cl₂</td> <td>(13)</td> <td>(39)</td> <td>(8)</td> </tr> </tbody> </table>	Conditions	I (%)	II (%)	III (%)	Zn/Cu, CH ₂ I ₂ , AcCl, Et ₂ O	(9)	(18)	(1)	Zn/Cu, CH ₂ Br ₂ , AcCl, Et ₂ O	(2)	(4)	(0)	Et ₂ Zn, CH ₂ I ₂ , PhMe	(5)	(34)	(1)	Et ₃ Al, CH ₂ I ₂ , PhMe/CH ₂ Cl ₂	(13)	(39)	(8)	
Conditions	I (%)	II (%)	III (%)																				
Zn/Cu, CH ₂ I ₂ , AcCl, Et ₂ O	(9)	(18)	(1)																				
Zn/Cu, CH ₂ Br ₂ , AcCl, Et ₂ O	(2)	(4)	(0)																				
Et ₂ Zn, CH ₂ I ₂ , PhMe	(5)	(34)	(1)																				
Et ₃ Al, CH ₂ I ₂ , PhMe/CH ₂ Cl ₂	(13)	(39)	(8)																				
	Zn/Ag, CH ₂ I ₂ , Et ₂ O, reflux	 (31) major	658																				
	EtZnI, CH ₂ I ₂ , Et ₂ O, reflux	 (30)	656																				
	Et ₂ Zn, CH ₂ I ₂ , (CH ₂ Cl) ₂ , -20°	 (89) only product	149																				
	Conditions	<table border="1"> <thead> <tr> <th>Conditions</th> <th>(%)</th> </tr> </thead> <tbody> <tr> <td>Et₂Zn, CH₂I₂, CH₂Cl₂, -25°</td> <td>(63)</td> </tr> <tr> <td>Zn/Cu, CH₂I₂, Et₂O, 35°</td> <td>(60)</td> </tr> </tbody> </table>	Conditions	(%)	Et ₂ Zn, CH ₂ I ₂ , CH ₂ Cl ₂ , -25°	(63)	Zn/Cu, CH ₂ I ₂ , Et ₂ O, 35°	(60)	150, 657														
Conditions	(%)																						
Et ₂ Zn, CH ₂ I ₂ , CH ₂ Cl ₂ , -25°	(63)																						
Zn/Cu, CH ₂ I ₂ , Et ₂ O, 35°	(60)																						
	Zn/Cu, CH ₂ I ₂ , Et ₂ O, reflux	 (50)	593																				
	Zn/Cu, CH ₂ I ₂	 (—)	448																				
	Zn/Cu, CH ₂ I ₂ , I ₂ (cat.), Et ₂ O, reflux	 (48)	659																				
	Zn/Cu, CH ₂ I ₂	 (83)	379																				

TABLE VI. CYCLOPROPANATION OF POLYENES (Continued)

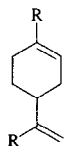
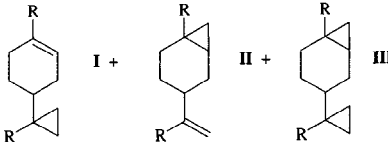
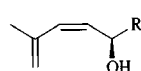

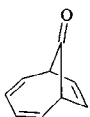
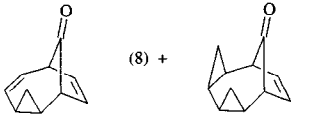
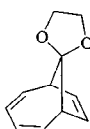
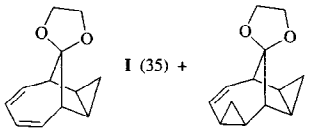

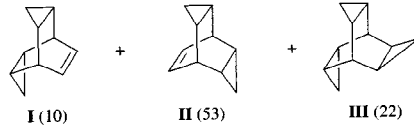
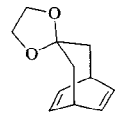
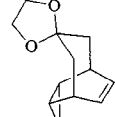
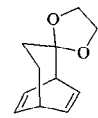
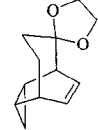
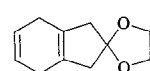
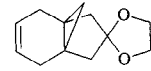
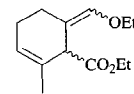
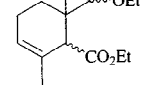
Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.																									
C ₈₋₁₀ 	Zn/Cu, CH ₂ I ₂ , AcCl (cat.), solvent	 <table border="1" data-bbox="926 546 1278 685"> <thead> <tr> <th>R</th> <th>Solvent</th> <th>I (%)</th> <th>II (%)</th> <th>III (%)</th> </tr> </thead> <tbody> <tr> <td>H</td> <td>Et₂O</td> <td>(9)</td> <td>(18)</td> <td>(1)</td> </tr> <tr> <td>Me</td> <td>Et₂O</td> <td>(26)</td> <td>(11)</td> <td>(8)</td> </tr> <tr> <td>H</td> <td><i>i</i>-Pr₂O</td> <td>(16)</td> <td>(10)</td> <td>(6)</td> </tr> <tr> <td>Me</td> <td><i>i</i>-Pr₂O</td> <td>(28)</td> <td>(6)</td> <td>(8)</td> </tr> </tbody> </table>	R	Solvent	I (%)	II (%)	III (%)	H	Et ₂ O	(9)	(18)	(1)	Me	Et ₂ O	(26)	(11)	(8)	H	<i>i</i> -Pr ₂ O	(16)	(10)	(6)	Me	<i>i</i> -Pr ₂ O	(28)	(6)	(8)	104
R	Solvent	I (%)	II (%)	III (%)																								
H	Et ₂ O	(9)	(18)	(1)																								
Me	Et ₂ O	(26)	(11)	(8)																								
H	<i>i</i> -Pr ₂ O	(16)	(10)	(6)																								
Me	<i>i</i> -Pr ₂ O	(28)	(6)	(8)																								
C ₈₋₁₂ 	Sn/Hg, CH ₂ I ₂ , THF, -50° to rt, 2 h	 <table border="1" data-bbox="1120 708 1314 801"> <thead> <tr> <th>R</th> <th>(%)</th> <th>dr</th> </tr> </thead> <tbody> <tr> <td>Et</td> <td>(71)</td> <td>>96:4</td> </tr> <tr> <td>Ph</td> <td>(81)</td> <td>>96:4</td> </tr> </tbody> </table>	R	(%)	dr	Et	(71)	>96:4	Ph	(81)	>96:4	660																
R	(%)	dr																										
Et	(71)	>96:4																										
Ph	(81)	>96:4																										
C ₉ 	Zn/Cu, CH ₂ I ₂ , I ₂ (cat.), Et ₂ O, reflux		295																									
	Zn/Cu, CH ₂ I ₂ , I ₂ (cat.), Et ₂ O, reflux		295																									
	Zn/Cu, CH ₂ I ₂	I (35) major product	296																									
	Et ₂ Zn, CH ₂ I ₂		297																									
	Zn source, CH ₂ I ₂	<table border="1" data-bbox="943 1347 1234 1429"> <thead> <tr> <th>Zn source</th> <th>I (%)</th> <th>II (%)</th> <th>III (%)</th> </tr> </thead> <tbody> <tr> <td>Zn/Ag</td> <td>(22)</td> <td>(35)</td> <td>(<1)</td> </tr> <tr> <td>Et₂Zn</td> <td>(14)</td> <td>(55)</td> <td>(16)</td> </tr> </tbody> </table>	Zn source	I (%)	II (%)	III (%)	Zn/Ag	(22)	(35)	(<1)	Et ₂ Zn	(14)	(55)	(16)	298													
Zn source	I (%)	II (%)	III (%)																									
Zn/Ag	(22)	(35)	(<1)																									
Et ₂ Zn	(14)	(55)	(16)																									
	Zn/Cu, CH ₂ I ₂ , I ₂ (cat.), Et ₂ O, reflux	 (68)	299																									
	Zn/Cu, CH ₂ I ₂ , I ₂ (cat.), Et ₂ O, reflux	 (—)	299																									
	Zn/Cu, CH ₂ I ₂ , 45°	 (~50)	300																									
	Zn/Ag, CH ₂ I ₂ , Et ₂ O, reflux	" (70)	300																									
	Zn/Cu, CH ₂ I ₂ , I ₂ (cat.), Et ₂ O, reflux	 (>99)	570																									

TABLE VI. CYCLOPROPANATION OF POLYENES (Continued)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
	Zn/Cu, CH ₂ I ₂ , I ₂ (cat.), Et ₂ O, reflux	 (86)	366
	Zn/Ag, CH ₂ I ₂ , Et ₂ O	 (53)	592
	Et ₂ Zn, CH ₂ I ₂ , Et ₂ O, reflux	" (74)	302
	Zn/Cu, CH ₂ I ₂ , DME, ultrasound	 I + II (23) I:II = 1:2	594
	Zn/Ag, CH ₂ I ₂ , Et ₂ O, reflux	 (80)	107, 350
	Zn/Ag, CH ₂ I ₂ (xs), Et ₂ O, reflux	 (68)	107, 267
	SmI ₂ , CH ₂ I ₂ , THF	 (62)	88, 110
	Zn/Cu, CH ₂ I ₂	 (-)	293
	 Zn(CH ₂ I) ₂ ·DME (2.5 eq), CH ₂ Cl ₂ , -10°	 R (%) de (%) mono:bis Bn (78) >90 8:1 TIPS (85) 90 8:1	187 187, 189
	Et ₂ Zn (2.5 eq), CH ₂ I ₂ (5 eq), CH ₂ Cl ₂ , -5° to rt	 I + II + III (66) I:II:III = -	661

TABLE VI. CYCLOPROPANATION OF POLYENES (Continued)

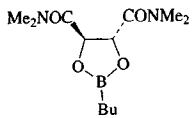

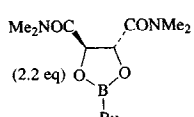
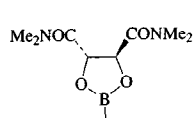
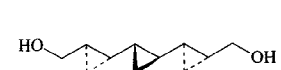


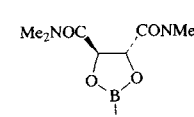

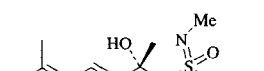
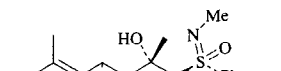
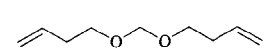
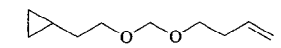
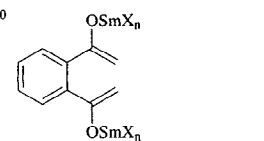
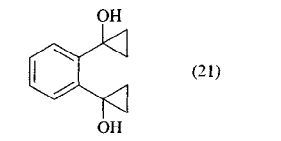
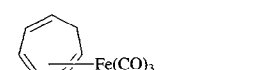
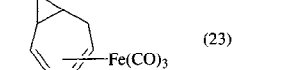


Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
	$\text{Zn}(\text{CH}_2\text{I}_2)_2$, CH_2Cl_2 , 0° to rt	 (83)	661
	$\text{Zn}(\text{CH}_2\text{I}_2)_2$ (4.4 eq), $\text{DME}/\text{CH}_2\text{Cl}_2$, 0°	" (90) 10:1 mixture of diastereomers	194
	$\text{Zn}(\text{CH}_2\text{I}_2)_2$, CH_2Cl_2 , 0° to rt	 (65)	661
	$\text{Zn}(\text{CH}_2\text{I}_2)_2 \cdot \text{DME}$, MS 4Å, CH_2Cl_2 , -40 to 25°	 (89)	193, 662
	$\text{Zn}(\text{CH}_2\text{I}_2)_2 \cdot \text{DME}$, CH_2Cl_2 , -78° to rt	 (90)	663
	Zn/Ag , CH_2I_2 , Et_2O , reflux	 (76) 15:1	261, 664
	Zn/Cu , CH_2I_2 , Et_2O	 (35)	209
	Sm , CH_2I_2 , THF, 50°	 (21)	110, 552
	Zn/Cu , CH_2I_2 , I_2 (cat.), Et_2O , reflux	 (23)	306, 307
	Zn/Cu , CD_2I_2 , I_2 (cat.), Et_2O , reflux	 (---)	306, 307

TABLE VI. CYCLOPROPANATION OF POLYENES (Continued)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.															
	Zn/Ag, CH ₂ I ₂ (3 eq), Et ₂ O	(19) + (5) + (41) + (4) + (22) + (5)	310															
	Zn source, CH ₂ I ₂	I + II + III + IV	298															
		<table border="1"> <thead> <tr> <th>Zn source</th> <th>I (%)</th> <th>II (%)</th> <th>III (%)</th> <th>IV (%)</th> </tr> </thead> <tbody> <tr> <td>Zn/Cu</td> <td>(4)</td> <td>(7)</td> <td>(11)</td> <td>(21)</td> </tr> <tr> <td>Et₂Zn</td> <td>(0)</td> <td>(3)</td> <td>(18)</td> <td>(59)</td> </tr> </tbody> </table>	Zn source	I (%)	II (%)	III (%)	IV (%)	Zn/Cu	(4)	(7)	(11)	(21)	Et ₂ Zn	(0)	(3)	(18)	(59)	
Zn source	I (%)	II (%)	III (%)	IV (%)														
Zn/Cu	(4)	(7)	(11)	(21)														
Et ₂ Zn	(0)	(3)	(18)	(59)														
	Zn/Cu, CH ₂ I ₂		295															
	Zn/Ag, CH ₂ I ₂ , Et ₂ O, rt		665															
	Et ₂ Zn, CH ₂ I ₂ , Et ₂ O, rt	(12) + several other products	602															
	Zn/Ag, CH ₂ I ₂ , DME, reflux	(-) + (-) + (-)	666															
	Zn/Ag, CH ₂ I ₂ , DME, reflux	(-) + (-) + (-)	666															
	Zn/Cu, CH ₂ I ₂	(-)	667															
	Zn/Cu, CH ₂ I ₂	(-)	667															
	Zn/Cu, CH ₂ I ₂ , Et ₂ O	(13) + (17)	668															
	Zn/Ag, CH ₂ I ₂ , Et ₂ O	(52)	592															

TABLE VI. CYCLOPROPANATION OF POLYENES (Continued)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.																				
	Zn/Cu, CH ₂ I ₂ , Et ₂ O, reflux	 I + II (95) I:II = 18:1	595																				
	Et ₂ Zn, CH ₂ I ₂ , Et ₂ O, reflux	 (87) [10:1]	669																				
	Et ₂ Zn (5 eq), CH ₂ I ₂ (10 eq), hexane, -20°(7 h); 20°(10 h)	 (61) 88% dc	160																				
	Et ₂ Zn (5 eq), CH ₂ I ₂ (10 eq), hexane, -20°(7 h); 20°(10 h)	 (50) 85% dc	160																				
	Et ₂ Zn, CH ₂ I ₂ , C ₆ H ₆	 (>22)	670																				
	Et ₂ Zn, CH ₂ I ₂ , Et ₂ O	 (84)	365																				
	Zn/Ag, CH ₂ I ₂ , Et ₂ O, reflux	 (—)	350																				
	Et ₂ Zn (5 eq), CH ₂ I ₂ (10 eq), Et ₂ O, rt	 (82) >99% dc	177																				
	Et ₂ Zn (5 eq), CH ₂ Cl (2 eq)	 (77) 97% dc	189																				
	Et ₂ Zn (5 eq), CH ₂ Cl (2 eq)	 (80) 99% dc	189																				
	Zn/Hg, TMSCl, HC(OEt) ₃ , Et ₂ O, reflux	 (44) 2:1	77																				
	Conditions	 I + II + III	104																				
		<table border="1"> <thead> <tr> <th>Conditions</th> <th>I (%)</th> <th>II (%)</th> <th>III (%)</th> </tr> </thead> <tbody> <tr> <td>Zn/Cu, CH₂I₂, AcCl, Et₂O</td> <td>(30)</td> <td>(8)</td> <td>(36)</td> </tr> <tr> <td>Zn/Cu, CH₂Br₂, AcCl, Et₂O</td> <td>(27)</td> <td>(9)</td> <td>(21)</td> </tr> <tr> <td>Et₂Zn, CH₂I₂, PhMe</td> <td>(19)</td> <td>(25)</td> <td>(17)</td> </tr> <tr> <td>Et₃Al, CH₂I₂, PhMe/CH₂Cl₂</td> <td>(26)</td> <td>(13)</td> <td>(12)</td> </tr> </tbody> </table>	Conditions	I (%)	II (%)	III (%)	Zn/Cu, CH ₂ I ₂ , AcCl, Et ₂ O	(30)	(8)	(36)	Zn/Cu, CH ₂ Br ₂ , AcCl, Et ₂ O	(27)	(9)	(21)	Et ₂ Zn, CH ₂ I ₂ , PhMe	(19)	(25)	(17)	Et ₃ Al, CH ₂ I ₂ , PhMe/CH ₂ Cl ₂	(26)	(13)	(12)	
Conditions	I (%)	II (%)	III (%)																				
Zn/Cu, CH ₂ I ₂ , AcCl, Et ₂ O	(30)	(8)	(36)																				
Zn/Cu, CH ₂ Br ₂ , AcCl, Et ₂ O	(27)	(9)	(21)																				
Et ₂ Zn, CH ₂ I ₂ , PhMe	(19)	(25)	(17)																				
Et ₃ Al, CH ₂ I ₂ , PhMe/CH ₂ Cl ₂	(26)	(13)	(12)																				

TABLE VI. CYCLOPROPANATION OF POLYENES (Continued)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.			
				Solvent	I (%)	II (%)
	Zn/Cu, CH ₂ I ₂ , AcCl (cat.), solvent	I + II + III	Et ₂ O (26) DME (26) THF (16) <i>i</i> -Pr ₂ O (25) EtOAc (14) dioxane (11) (CH ₂ Cl) ₂ (9)	(11) (9) (7) (8) (8) (5) (2)	(8) (4) (1) (2) (1) (1) (4)	104
	Zn/Cu, CH ₂ I ₂		(—) +	several other cyclopropanation products		479
	Zn/Cu, CH ₂ I ₂ , Et ₂ O, reflux		(55)			313
	"MCH ₂ X"	I + II + III				59
			MCH ₂ X	(%I:%II:%III)		
			Et ₂ Zn, CH ₂ I ₂	3:49:8		
			<i>i</i> -Bu ₃ Al, CH ₂ I ₂	79:0:0		
	<i>i</i> -Bu ₃ Al, CH ₂ I ₂ , CH ₂ Cl ₂ , rt	I (92-96)				258
	<i>i</i> -Bu ₃ Al, TCH ₂ I ₂ , CHCl ₃ , rt		(—)			482
	Me ₂ NOC, CONMe ₂ , O, B, O, Bu		(65) 65% de mono:bis = 19:1			187, 189
	Zn(CH ₂ I) ₂ •DME (3.0 eq), CH ₂ Cl ₂ , -10°					
	Me ₂ NOC, CONMe ₂ , O, B, O, Bu		(70) 65% de mono:bis = 19:1			187, 189
	Zn(CH ₂ I) ₂ •DME (2.5 eq), CH ₂ Cl ₂ , -10°					
	Zn/Cu, CH ₂ I ₂ , Et ₂ O, reflux		(26) +		(7)	481
	ClMe ₂ Si, SiMe ₂ Cl, Zn/Hg		(57)			112
	ClMe ₂ Si, SiMe ₂ Cl, Zn/Hg		(66)			112
	Zn/Ag, CH ₂ I ₂ , Et ₂ O, reflux		(83)			671

TABLE VI. CYCLOPROPANATION OF POLYENES (Continued)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.												
	Sm/Hg, CH ₂ I ₂ , THF, -78° to rt	" (58)	672												
	Zn/Cu, CH ₂ I ₂	 (75) + (8)	480												
	Et ₂ Zn (5 eq), CH ₂ ICl (2 eq), PhMe, -35 to 0°	 (>80) >94% dc	189												
	Zn anode, 2e-, CH ₂ Br ₂ , ZnBr ₂ present initially, CH ₂ Cl ₂ /DMF (9:1)	 (70)	70												
	Zn*, CH ₂ I ₂ , DME/Et ₂ O	" (77)	44												
	Sm (5 eq), CH ₂ I ₂ (5 eq), TMSCl (0.2 eq), THF, -78° to rt	" (97)	63												
	Sm source (xs), CH ₂ IX, THF, -78° to rt	<table border="1"> <thead> <tr> <th>Sm source</th> <th>X</th> <th>(%)</th> </tr> </thead> <tbody> <tr> <td>Sm/Hg</td> <td>I</td> <td>(89)</td> </tr> <tr> <td>Sm/Hg</td> <td>Cl</td> <td>(97)</td> </tr> <tr> <td>SmI₂</td> <td>Cl</td> <td>(87)</td> </tr> </tbody> </table>	Sm source	X	(%)	Sm/Hg	I	(89)	Sm/Hg	Cl	(97)	SmI ₂	Cl	(87)	57, 58 58 58
Sm source	X	(%)													
Sm/Hg	I	(89)													
Sm/Hg	Cl	(97)													
SmI ₂	Cl	(87)													
	"MCH ₂ X"	 I + II + III <table border="1"> <thead> <tr> <th>MCH₂X</th> <th>(%I:%II:%III)</th> <th></th> </tr> </thead> <tbody> <tr> <td>Et₂Zn, CH₂I₂</td> <td>74:3:2</td> <td>59</td> </tr> <tr> <td><i>i</i>-Bu₃Al, ClI₂</td> <td>1:4:76</td> <td>59</td> </tr> <tr> <td>Sm/Hg, CH₂ICl</td> <td>98:0:0</td> <td>58</td> </tr> </tbody> </table>	MCH ₂ X	(%I:%II:%III)		Et ₂ Zn, CH ₂ I ₂	74:3:2	59	<i>i</i> -Bu ₃ Al, ClI ₂	1:4:76	59	Sm/Hg, CH ₂ ICl	98:0:0	58	59 59 58
MCH ₂ X	(%I:%II:%III)														
Et ₂ Zn, CH ₂ I ₂	74:3:2	59													
<i>i</i> -Bu ₃ Al, ClI ₂	1:4:76	59													
Sm/Hg, CH ₂ ICl	98:0:0	58													
	Zn(CH ₂ I) ₂ •DME (1.6 eq), CH ₂ Cl ₂ , 0° to rt	 (87) 93% ee mono:bis = >20:1	187, 189												
	Sm source (xs), CH ₂ IX, THF, -78° to rt	<table border="1"> <thead> <tr> <th>Sm source</th> <th>X</th> <th>(%)</th> </tr> </thead> <tbody> <tr> <td>Sm/Hg</td> <td>I</td> <td>(99)</td> </tr> <tr> <td>Sm/Hg</td> <td>Cl</td> <td>(97)</td> </tr> <tr> <td>SmI₂</td> <td>Cl</td> <td>(99)</td> </tr> </tbody> </table>	Sm source	X	(%)	Sm/Hg	I	(99)	Sm/Hg	Cl	(97)	SmI ₂	Cl	(99)	57, 58 58 58
Sm source	X	(%)													
Sm/Hg	I	(99)													
Sm/Hg	Cl	(97)													
SmI ₂	Cl	(99)													
	Zn/Cu, CH ₂ I ₂ , I ₂ (cat.), Et ₂ O, reflux	 (42)	306, 307												
	Zn/Cu, CD ₂ I ₂ , I ₂ (cat.), Et ₂ O, reflux	 (-)	306, 307												
	Et ₂ Zn (3 eq), CH ₂ I ₂ (3 eq), Et ₂ O/PhMe, reflux	 (40)	369												

TABLE VI. CYCLOPROPANATION OF POLYENES (Continued)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.									
	 $\text{Zn}(\text{CH}_2\text{I})_2 \cdot \text{DME}$ (3 eq), CH_2Cl_2 , -10°	 (84) 91% ee mono:bis = >20:1	187, 189									
	Zn/Ag , CH_2I_2 , DME, 60°	 (9) + (37)	673									
	Zn/Ag , CH_2I_2	 (32) + (15) + (13)	316									
	Et_2Zn , CH_2I_2 , PhMe, heat	 (75)	108									
	Et_2Zn (1.2 eq), CH_2I_2 (1.2 eq), Et_2O	 (82)	674									
	Et_2Zn , CH_2I_2 , Et_2O	 (87)	365									
	EtZnI , CH_2I_2 , Et_2O	 (81)	438									
	Sm/Hg (xs), CH_2IX , THF, -78° to rt	 <table border="1"> <thead> <tr> <th>X</th> <th>(%)</th> <th>syn:anti</th> </tr> </thead> <tbody> <tr> <td>Cl</td> <td>(99)</td> <td>200:1</td> </tr> <tr> <td>I</td> <td>(98)</td> <td>50:1</td> </tr> </tbody> </table>	X	(%)	syn:anti	Cl	(99)	200:1	I	(98)	50:1	58
X	(%)	syn:anti										
Cl	(99)	200:1										
I	(98)	50:1										
	Sm/Hg (xs), CH_2IX , THF, -78° to rt	 <table border="1"> <thead> <tr> <th>X</th> <th>(%)</th> <th>syn:anti</th> </tr> </thead> <tbody> <tr> <td>Cl</td> <td>(98)</td> <td>200:1</td> </tr> <tr> <td>I</td> <td>(31)</td> <td>48:1</td> </tr> </tbody> </table>	X	(%)	syn:anti	Cl	(98)	200:1	I	(31)	48:1	58
X	(%)	syn:anti										
Cl	(98)	200:1										
I	(31)	48:1										
C_{11-17} 	Et_2Zn , CH_2I_2 , Et_2O	 <table border="1"> <thead> <tr> <th>R</th> <th>(%)</th> </tr> </thead> <tbody> <tr> <td>H</td> <td>(>72)</td> </tr> <tr> <td>Ph</td> <td>(>48)</td> </tr> </tbody> </table>	R	(%)	H	(>72)	Ph	(>48)	360			
R	(%)											
H	(>72)											
Ph	(>48)											
C_{12} 	Et_2Zn , CH_2I_2 , $\text{Et}_2\text{O}/\text{C}_6\text{H}_6$, reflux	 (7) + (30) + (6) + (3)	319									
	Zn/Cu , CH_2I_2	 I (<1) + II (23) + IV (5) + V (5)	320									

TABLE VI. CYCLOPROPANATION OF POLYENES (Continued)

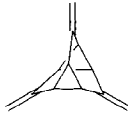


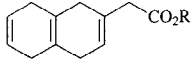
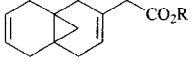
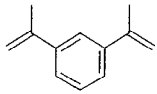
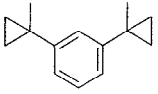
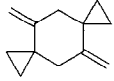

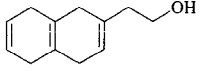
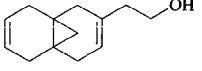

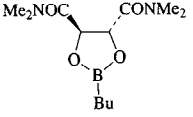

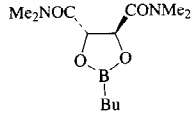
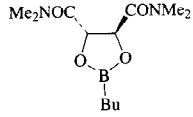

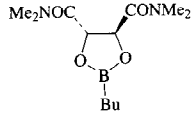
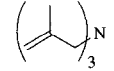
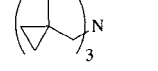
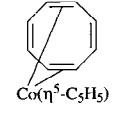
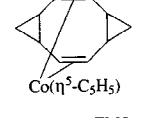
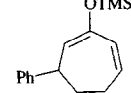
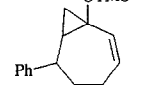
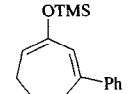
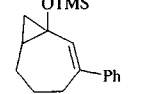
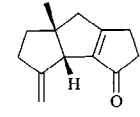
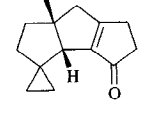
Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.						
	Zn/Ag, CH ₂ I ₂ , Et ₂ O	 I +  II (27) I:II = 5.3:1	609						
	Zn/Cu, CH ₂ I ₂ , Et ₂ O, reflux	 <table border="1" data-bbox="1145 483 1275 564"> <tr><td>R</td><td>(%)</td></tr> <tr><td>H</td><td>(53)</td></tr> <tr><td>Me</td><td>(21)</td></tr> </table>	R	(%)	H	(53)	Me	(21)	323
R	(%)								
H	(53)								
Me	(21)								
	Zn/Cu, CH ₂ I ₂	 (13)	497						
	Zn/Ag, CH ₂ I ₂	 (70)	612						
	Zn/Cu, CH ₂ I ₂ , Et ₂ O, reflux	 (30)	323						
	 Zn(CH ₂ I) ₂ , CH ₂ Cl ₂ , 0 to 25° or: Zn(CH ₂ I) ₂ , CH ₂ Cl ₂ /DME, -15 to 25°	 (100)	162, 675						
	 Zn(CH ₂ I) ₂ , CH ₂ Cl ₂ /DME, -15 to 25° or: Zn(CH ₂ I) ₂ , CH ₂ Cl ₂ , 0 to 25°	" (100)	162, 653						
	 Zn(CH ₂ I) ₂ , CH ₂ Cl ₂ /DME, -15 to 25° or: Zn(CH ₂ I) ₂ , CH ₂ Cl ₂ , 0 to 25°	 (93)	162, 192, 653, 655						
	 Zn(CH ₂ I) ₂ , CH ₂ Cl ₂ , 0 to 25°	" (94)	162, 192, 653, 675						
	Zn/Cu, CH ₂ I ₂ , Et ₂ O, reflux	 (36)	498						
	Zn/Cu, CH ₂ I ₂ , I ₂ (cat.), Et ₂ O, reflux	 (19)	306, 307						
	Et ₂ Zn, CH ₂ I ₂ , Et ₂ O	 (59)	360						
	Et ₂ Zn, CH ₂ I ₂ , Et ₂ O	 (88)	360						
	Zn/Cu, CH ₂ I ₂ , Et ₂ O, reflux	 (50)	618						

TABLE VI. CYCLOPROPANATION OF POLYENES (Continued)

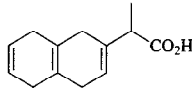
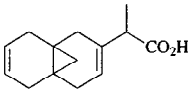
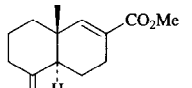
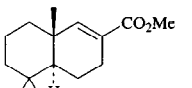
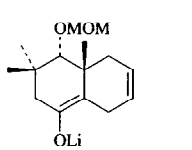
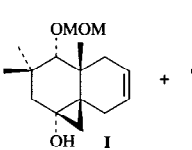
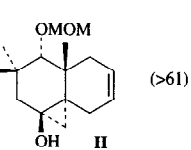
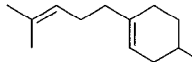
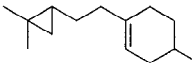
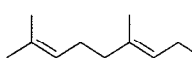
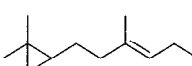
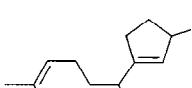
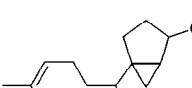
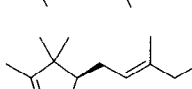
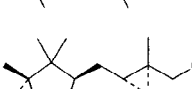
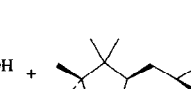


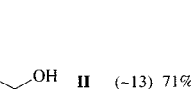
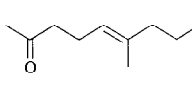
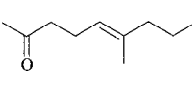
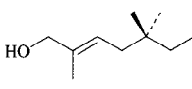
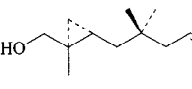
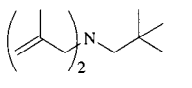
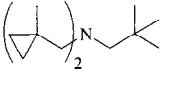
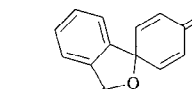
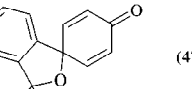
Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.																
	Zn/Cu, CH ₂ I ₂ , Et ₂ O, reflux	 (75)	323																
	Zn/Cu, CH ₂ I ₂ , Et ₂ O, reflux	 (84)	5																
	SmI ₂ , CH ₂ I ₂ , -78 to -20°	 I +  II (>61) I:II = 3:1	676																
	SmI ₂ , CH ₂ I ₂	" (→) I:II = 4.3:1																	
	Zn/Cu, CH ₂ I ₂ , Et ₂ O, reflux	 (40)	502																
	Zn/Cu, CH ₂ I ₂ , Et ₂ O, reflux	 (40)	505																
	Zn/Ag, CH ₂ I ₂ , Et ₂ O, reflux	 (70)	677																
	Zn/Cu, CH ₂ Br ₂ , Et ₂ O, reflux, AcBr or ultrasound	 I +  II (48) I:II = 1.3:1	506																
	Et ₃ Al, CH ₂ I ₂ , hexane, rt	" (90) I:II = ~1.5:1	506																
	Me ₂ NOC, CONMe ₂ , O, B, Bu Zn(CH ₂ I ₂) ₂ •DME, CH ₂ Cl ₂ , -10° to rt	 I +  II (~13) 71% de I:II = 48:43	506																
	Me ₂ NOC, CONMe ₂ , O, B, Bu Zn(CH ₂ I ₂) ₂ •DME (4.2 eq), CH ₂ Cl ₂ , 0°	 (>95) 88% ee mono:bis = >20:1	187, 189																
	Me ₂ NOC, CONMe ₂ , O, B, Bu (1.1 eq) Zn(CH ₂ I ₂) ₂ (4.2 eq), DME/CH ₂ Cl ₂ , 0°	 HO-CH ₂ -CH ₂ -CH ₂ -CH ₂ -CH ₂ -OR <table border="1" data-bbox="921 1724 1242 1827"> <thead> <tr> <th>R</th> <th>(%)</th> <th>mono:bis</th> <th>ee (%)</th> </tr> </thead> <tbody> <tr> <td>Ac</td> <td>(>95)</td> <td>>20:1</td> <td>85</td> </tr> <tr> <td>Bn</td> <td>(>95)</td> <td>>20:1</td> <td>86</td> </tr> <tr> <td>TBDPS</td> <td>(>95)</td> <td>>20:1</td> <td>87</td> </tr> </tbody> </table>	R	(%)	mono:bis	ee (%)	Ac	(>95)	>20:1	85	Bn	(>95)	>20:1	86	TBDPS	(>95)	>20:1	87	189, 678
R	(%)	mono:bis	ee (%)																
Ac	(>95)	>20:1	85																
Bn	(>95)	>20:1	86																
TBDPS	(>95)	>20:1	87																
	Zn/Cu, CH ₂ I ₂ , Et ₂ O, reflux	 (81)	507																
	Et ₂ Zn, CH ₂ I ₂ , Et ₂ O, reflux	 (47)	577																

TABLE VI. CYCLOPROPANATION OF POLYENES (Continued)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.												
	Et ₂ Zn, CH ₂ Cl ₂	 (>46)	327												
	Zn/Ag, CH ₂ I ₂ , DME, reflux		666												
	Et ₂ Zn, CH ₂ I ₂	 (-)	628												
	Zn dust, C ₆ H ₆	 <table border="1"> <thead> <tr> <th>R¹</th> <th>R²</th> <th>(%)</th> </tr> </thead> <tbody> <tr> <td>Br</td> <td>Br</td> <td>(20)</td> </tr> <tr> <td>Br</td> <td>I</td> <td>(45)</td> </tr> <tr> <td>I</td> <td>I</td> <td>(20)</td> </tr> </tbody> </table>	R ¹	R ²	(%)	Br	Br	(20)	Br	I	(45)	I	I	(20)	113
R ¹	R ²	(%)													
Br	Br	(20)													
Br	I	(45)													
I	I	(20)													
	Zn/Cu, CH ₂ I ₂	 (80) + (15)	679												
	Sm/Hg, CH ₂ I ₂	 (89)	512												
	Zn/Cu, CH ₂ I ₂ , Et ₂ O/DME, 65°	 (81)	118												
^C ₁₅	Zn/Cu, CH ₂ I ₂	 (>42)	680												
	Zn/Cu, CH ₂ I ₂	 (15)	497												
	Zn/Cu, CH ₂ I ₂ , DME, reflux	 (40)	666												
	Zn/Cu, CH ₂ I ₂ , Et ₂ O	 I (-) + II (-) I:II = 7:3	330												
	 Zn(CH ₂ I ₂) ₂ ·DME, CH ₂ Cl ₂ , -78° to rt	 (86)	663												

TABLE VI. CYCLOPROPANATION OF POLYENES (Continued)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
	 Zn(CH ₂ I) ₂ •DME, MS (4 Å), CH ₂ Cl ₂ , -40 to 25°	(83)	193, 662
	 Zn(CH ₂ I) ₂ , CH ₂ Cl ₂ , 0° to rt	(80)	661
	(2.2 eq) Zn(CH ₂ I) ₂ (4.4 eq), DME/CH ₂ Cl ₂ , 0°	" (90) + ~10% of 2 other isomers	194
	Zn/Ag, CH ₂ I ₂ , Et ₂ O, reflux	(88)	488
	Zn/Ag, CH ₂ I ₂ , Et ₂ O, reflux	(72)	488
	Zn/Cu, CH ₂ I ₂ , Et ₂ O	 I + II + III + IV (→ I:II:III:IV = 26:49:6:19)	160 330
	Et ₂ Zn (2.4 eq), CH ₂ I ₂ (3 eq), air, C ₆ H ₆ , 0°	(91)	638
	ClMe ₂ Si(CH ₂) ₂ SiMe ₂ Cl Zn/Hg	(47)	112
	ClMe ₂ Si(CH ₂) ₂ SiMe ₂ Cl Zn/Hg	(41) Starting Material E:Z ratio (%) 3:2 (41) >99:1 (47)	112
	Et ₂ Zn (5 eq), CH ₂ Cl ₂ (2 eq), PhMe, -35 to 0°	(80) (>80) >94% de	189

TABLE VI. CYCLOPROPANATION OF POLYENES (Continued)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.												
	$C_{11}H_{19}$ ZnI_2, Et_2O	 I + II (...) I:II = —	75												
	$Zn/Cu, CH_2I_2,$ $Et_2O/DME, reflux$	 (82)	517												
	R ZnI_2, Et_2O	 I + II	75												
		<table border="1"> <thead> <tr> <th>R</th> <th>(%)</th> <th>I:II</th> </tr> </thead> <tbody> <tr> <td>C_6H_{11}</td> <td>(20-25)</td> <td>7:3</td> </tr> <tr> <td>$C_{11}H_{19}$</td> <td>(20-25)</td> <td>—</td> </tr> <tr> <td>$C_{16}H_{27}$</td> <td>(20-25)</td> <td>—</td> </tr> </tbody> </table>	R	(%)	I:II	C_6H_{11}	(20-25)	7:3	$C_{11}H_{19}$	(20-25)	—	$C_{16}H_{27}$	(20-25)	—	
R	(%)	I:II													
C_6H_{11}	(20-25)	7:3													
$C_{11}H_{19}$	(20-25)	—													
$C_{16}H_{27}$	(20-25)	—													
	ZnI_2, Et_2O	 I + II (-) I:II = —	75												
	$Zn(CH_2I_2)_2 \cdot DME$ (1.6 eq), $CH_2Cl_2, 0^\circ$	 (84) 93% ee mono:bis >20:1	187, 189												
C_{16} 	$Zn/Cu, CH_2I_2$	 (3)	521												
	$Zn/Cu, CH_2I_2,$ $Et_2O, reflux$	 (7)	334												
	Et_2Zn, CH_2I_2	 (72)	612												
	$Zn/Cu, CH_2I_2, I_2$ (cat.), $Et_2O, reflux$	 (67)	314												
C_{17} 	 $Zn(CH_2I_2)_2$	 (74)	681												
	Et_2Zn (5 eq), CH_2I_2 (10 eq), $(CH_2Cl)_2, 0^\circ$	 (96)	641												

TABLE VI. CYCLOPROPANATION OF POLYENES (Continued)

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Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.								
	EtZnI, CH ₂ I ₂ , Et ₂ O, reflux	(84)	644								
C ₁₈ 	Zn(CH ₂ I) ₂ , (CH ₂ Cl) ₂	(60)	640								
	Et ₂ Zn, CH ₂ I ₂	(—)	133								
	Zn/Cu, CH ₂ I ₂ , DME	(>71)	682								
	Zn, CH ₂ I ₂ , sonication, THF ^c	" (80)	683								
	Et ₂ Zn, CH ₂ Cl, (CH ₂ Cl) ₂ , 0°	(>99)	109								
	Et ₂ Zn, CH ₂ Cl, PhMe, 0°	(66)	684								
	"MCH ₂ X"	 I II III	645								
		<table border="1"> <thead> <tr> <th>MCH₂X</th> <th>(%I:%II:%III)</th> </tr> </thead> <tbody> <tr> <td>Zn/Ag, CH₂I₂</td> <td>0:0:100</td> </tr> <tr> <td>Zn/Ag, CH₂I₂, Et₂O</td> <td>25:21:29</td> </tr> <tr> <td>Et₂Zn, CH₂I₂, PhMe</td> <td>24:36:24</td> </tr> </tbody> </table>	MCH ₂ X	(%I:%II:%III)	Zn/Ag, CH ₂ I ₂	0:0:100	Zn/Ag, CH ₂ I ₂ , Et ₂ O	25:21:29	Et ₂ Zn, CH ₂ I ₂ , PhMe	24:36:24	
MCH ₂ X	(%I:%II:%III)										
Zn/Ag, CH ₂ I ₂	0:0:100										
Zn/Ag, CH ₂ I ₂ , Et ₂ O	25:21:29										
Et ₂ Zn, CH ₂ I ₂ , PhMe	24:36:24										
	 Zn(CH ₂ I) ₂ , CH ₂ Cl ₂ /DME, -40°	(90)	192, 655								
	 Zn(CH ₂ I) ₂ , CH ₂ Cl ₂ /DME, -15 to 25°	(84)	192								

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TABLE VI. CYCLOPROPANATION OF POLYENES (Continued)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.										
	Zn/Cu, CH ₂ I ₂ , ultrasound, DME, 85-95°	(57)	375										
	Zn/Cu, CH ₂ I ₂ , ultrasound, DME, reflux	(97)	45										
	Et ₂ Zn (38 eq), CH ₂ I ₂ (30 eq), C ₆ H ₆ , 60°	(91)	336										
C ₁₈₋₂₈ 	Et ₂ Zn (5 eq), CH ₂ I ₂ (6 eq), C ₆ H ₆ , reflux, 3 h	<table border="1" style="display: inline-table; vertical-align: middle;"> <thead> <tr> <th>n</th> <th>(%)</th> </tr> </thead> <tbody> <tr> <td>7</td> <td>(>33)</td> </tr> <tr> <td>8</td> <td>(>47)</td> </tr> <tr> <td>10</td> <td>(>43)</td> </tr> <tr> <td>12</td> <td>(>35)</td> </tr> </tbody> </table>	n	(%)	7	(>33)	8	(>47)	10	(>43)	12	(>35)	376
n	(%)												
7	(>33)												
8	(>47)												
10	(>43)												
12	(>35)												
C ₁₉ 	1. <i>n</i> -BuLi (1 eq), Et ₂ O, -20° 2. IZnCH ₂ I (15 eq), Et ₂ O, rt	(66)	111										
	Zn/Cu, CH ₂ I ₂ , I ₂ (cat.), Et ₂ O, 40°	(65)	685										
	Sm, CH ₂ I ₂ , THF, 50°	(70)	110, 552										
	Zn/Ag, CH ₂ I ₂ , Et ₂ O, reflux	(85) ~1.1	81, 350										
	Zn/Ag, CH ₂ I ₂ , Et ₂ O, reflux	(—)	81, 350										
C ₂₀ 	Zn/Cu, CH ₂ I ₂ , Et ₂ O, rt	(5)	544										
	Zn/Cu, CH ₂ I ₂ , Et ₂ O/DME	(—)	649										
	Et ₂ Zn, CH ₂ I ₂	(24)	133										

TABLE VI. CYCLOPROPANATION OF POLYENES (Continued)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.										
	Zn/Ag, CH ₂ I ₂ , Et ₂ O	(65)	647										
	Zn/Ag, CH ₂ I ₂ , Et ₂ O	(57)	686										
	Zn/Ag, CH ₂ I ₂ , Et ₂ O	(87)	686										
	ClMe ₂ Si-CH ₂ -CH ₂ -SiMe ₂ Cl Zn/Hg	(46) + (30)	112										
	Et ₂ Zn (2 eq), CH ₂ I ₂ (2 eq), PhMe, 80°	(>37)	377										
	Zn/Cu, CH ₂ I ₂ , Et ₂ O, reflux	 <table border="1"> <thead> <tr> <th>R</th> <th>(%)</th> </tr> </thead> <tbody> <tr> <td>C₈H₁₇</td> <td>(80)</td> </tr> <tr> <td>OH</td> <td>(76)</td> </tr> <tr> <td>CHO</td> <td>(90)</td> </tr> <tr> <td>O₂CCF₃</td> <td>(62)</td> </tr> </tbody> </table>	R	(%)	C ₈ H ₁₇	(80)	OH	(76)	CHO	(90)	O ₂ CCF ₃	(62)	650
R	(%)												
C ₈ H ₁₇	(80)												
OH	(76)												
CHO	(90)												
O ₂ CCF ₃	(62)												
	Me ₂ NOC-CH(OH)-CONMe ₂ O-Bu Zn(CH ₂ I) ₂ •DME, MS (4 Å), CH ₂ Cl ₂ , -25° to rt	(72) + (26)	662										
	Me ₂ NOC-CH(OH)-CONMe ₂ O-Bu Zn(CH ₂ I) ₂ •DME, MS (4 Å), CH ₂ Cl ₂ , -25°	(>56)	662										
	Me ₂ NOC-CH(OH)-CONMe ₂ O-Bu Zn(CH ₂ I) ₂ •DME (3 eq), CH ₂ Cl ₂ , -10°	(81) 90% de mono:bis = 9:1	187, 189										
	Zn/Cu, CH ₂ I ₂	(70)	687										

TABLE VI. CYCLOPROPANATION OF POLYENES (Continued)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.						
	Zn/Ag, CH ₂ I ₂ , Et ₂ O, reflux	(36)	651						
	Zn/Ag, CH ₂ I ₂ , Et ₂ O, reflux	(38)	651						
	Zn/Cu, CH ₂ I ₂ , Et ₂ O, reflux	<table border="1" style="margin-left: 20px;"> <tr><td>R</td><td>(%)</td></tr> <tr><td>H</td><td>(45)</td></tr> <tr><td>Ac</td><td>(64)</td></tr> </table>	R	(%)	H	(45)	Ac	(64)	688
R	(%)								
H	(45)								
Ac	(64)								
	Zn/Cu, CH ₂ I ₂ , Et ₂ O, reflux	<table border="1" style="margin-left: 20px;"> <tr><td>R</td><td>(%)</td></tr> <tr><td>H</td><td>(42)</td></tr> <tr><td>Ac</td><td>(49)</td></tr> </table>	R	(%)	H	(42)	Ac	(49)	688
R	(%)								
H	(42)								
Ac	(49)								
	Zn/Cu, CH ₂ I ₂ , Et ₂ O/DME, reflux	(75)	689						
	Zn/Cu, CH ₂ I ₂ , Et ₂ O	(80)	86						
	 Zn(CH ₂ I ₂) ₂ ·DME, MS (4 Å), CH ₂ Cl ₂ , -25°	<table border="1" style="margin-left: 20px;"> <tr><td>R</td><td>(%)</td></tr> <tr><td>CO₂Me</td><td>(67)</td></tr> <tr><td>TBDMSOCH₂</td><td>(91)</td></tr> </table>	R	(%)	CO ₂ Me	(67)	TBDMSOCH ₂	(91)	662
R	(%)								
CO ₂ Me	(67)								
TBDMSOCH ₂	(91)								
	MeLi, DME; Zn/Cu, CH ₂ I ₂ , Et ₂ O	(71)	86						
	Zn/Pb, CH ₂ I ₂ , I ₂ (cat.), 40-45°	(34)	690						

TABLE VI. CYCLOPROPANATION OF POLYENES (Continued)

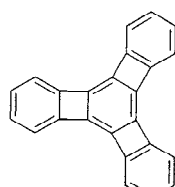
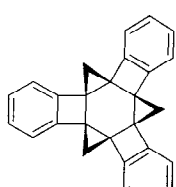
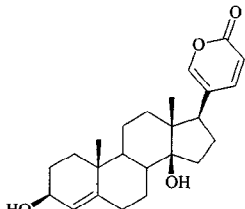
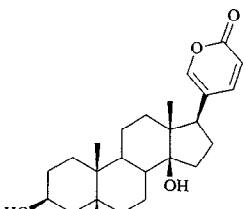
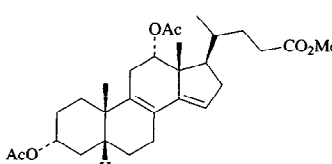
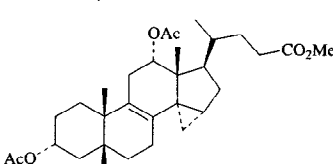
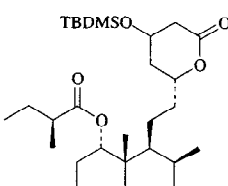
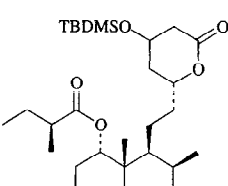
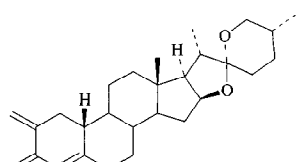
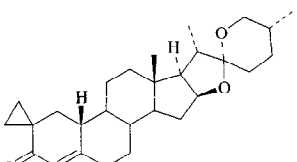
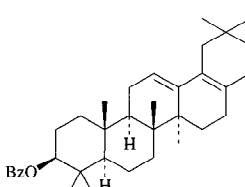
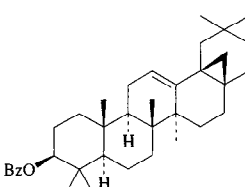
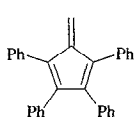
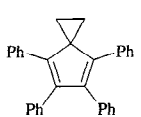
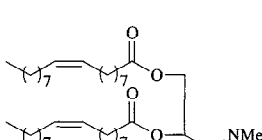
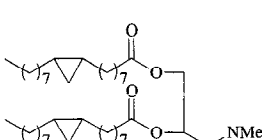
Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₂₄ 	Et ₂ Zn, CH ₂ I ₂ , PhMe, 60°	 (97)	339
	Zn/Cu, CH ₂ I ₂ , THF, 50-60°	 (63)	691
	Zn/Ag, CH ₂ I ₂ , solvent, reflux	 Solvent (%) DME (>99) THF (95) Et ₂ O (95)	692
C ₂₅ 	Zn/Cu, CH ₂ I ₂ , Et ₂ O, reflux	 (14)	693
C ₂₇ 	Zn/Cu, CH ₂ I ₂ , Et ₂ O, reflux	 (72)	650
C ₂₉ 	Et ₂ Zn, CH ₂ I ₂ , PhMe, rt, 8 h	 (56)	131
C ₃₀ 	Zn/Cu, CH ₂ I ₂ , I ₂ (cat.), Et ₂ O	 (62)	652
C ₃₉ 	Zn/Cu, CH ₂ I ₂ , Et ₂ O, reflux	 (99)	547

TABLE VI. CYCLOPROPANATION OF POLYENES (Continued)

	Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₄₂		Et ₂ Zn, CH ₂ I ₂ , PhMe, 60°	 (78)	339
C ₆₀		Zn/Cu, CH ₂ I ₂	 (—)	340
		Zn/Cu, CH ₂ I ₂	 (60)	694
	 R = <i>n</i> -Pr	Et ₂ Zn, CH ₂ I ₂ , C ₆ H ₆ , rt	 (—)	695
		Zn/Cu, CH ₂ I ₂ , Bu ₂ O, reflux	 (81)	696
		ZnI ₂ , CH ₂ N ₂ , Et ₂ O	 (—)	697

TABLE VII. CYCLOPROPANATION OF CYCLIC, CHIRAL ALKENES

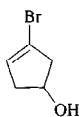
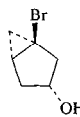
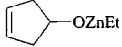
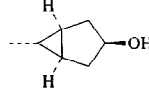

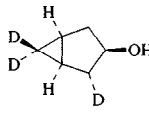



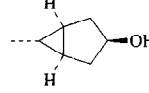
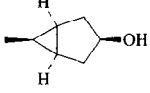
Substrate	Conditions	Product(s) and Yield(s) (%), Ratio <i>syn</i> : <i>anti</i>	Refs.																		
	Et ₂ Zn, CH ₂ I ₂ , (CH ₂ Cl) ₂ , 0°	 (69)	93																		
	Zn/Cu, MeCHBr ₂ , Et ₂ O, reflux	 (85)	68																		
	Zn/Cu, CD ₂ I ₂	 (—)	698																		
	Zn/Cu, CH ₂ Br ₂ , Et ₂ O, reflux	 (64)	699																		
	Zinc reagent, CH ₂ X ₂ , Et ₂ O, reflux	" <table border="1" data-bbox="916 1294 1274 1455"> <thead> <tr> <th>Zinc reagent</th> <th>X</th> <th>(%)</th> </tr> </thead> <tbody> <tr> <td>Zn/Cu (30 mesh)</td> <td>Br</td> <td>(75)</td> </tr> <tr> <td>Zn/Cu (30 mesh)</td> <td>I</td> <td>(81)</td> </tr> <tr> <td>Zn/Ag (30 mesh)</td> <td>I</td> <td>(82)</td> </tr> <tr> <td>Zn (dust) + CuCl</td> <td>I</td> <td>(65)</td> </tr> <tr> <td>EtZnI</td> <td>I</td> <td>(88)</td> </tr> </tbody> </table>	Zinc reagent	X	(%)	Zn/Cu (30 mesh)	Br	(75)	Zn/Cu (30 mesh)	I	(81)	Zn/Ag (30 mesh)	I	(82)	Zn (dust) + CuCl	I	(65)	EtZnI	I	(88)	66
Zinc reagent	X	(%)																			
Zn/Cu (30 mesh)	Br	(75)																			
Zn/Cu (30 mesh)	I	(81)																			
Zn/Ag (30 mesh)	I	(82)																			
Zn (dust) + CuCl	I	(65)																			
EtZnI	I	(88)																			
	Zn/Cu, MeCHBr ₂ , Et ₂ O, reflux	 I (23) +  II (7)	68																		

TABLE VII. CYCLOPROPANATION OF CYCLIC, CHIRAL ALKENES (Continued)

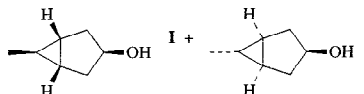
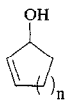
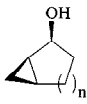
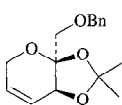
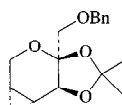
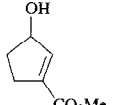
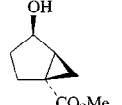
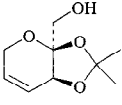
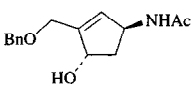
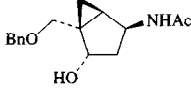
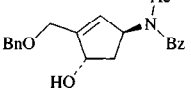
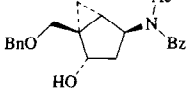
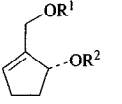
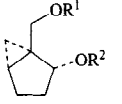
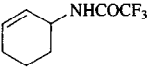
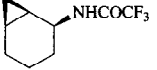
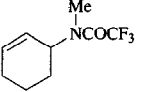
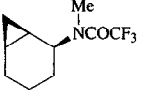
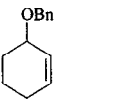
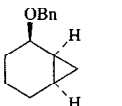
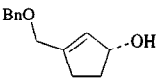
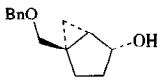
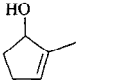
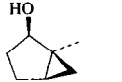
Substrate	Conditions	Product(s) and Yield(s) (%), Ratio <i>syn</i> : <i>anti</i>	Refs.																				
	Zinc reagent, MeCH ₂ , Et ₂ O, reflux	I + II <table border="1"> <thead> <tr> <th>Zinc reagent</th> <th>(%)</th> <th>I:II</th> </tr> </thead> <tbody> <tr> <td>Zn/Cu (30 mesh)</td> <td>(62)</td> <td>78:22</td> </tr> <tr> <td>Zn/Ag (30 mesh)</td> <td>(78)</td> <td>76:24</td> </tr> <tr> <td>Zn/Cu (dust)</td> <td>(71)</td> <td>76:24</td> </tr> <tr> <td>Et₂Zn</td> <td>(60)</td> <td>76:24</td> </tr> <tr> <td>EtZnI</td> <td>(67)</td> <td>73:27</td> </tr> </tbody> </table>	Zinc reagent	(%)	I:II	Zn/Cu (30 mesh)	(62)	78:22	Zn/Ag (30 mesh)	(78)	76:24	Zn/Cu (dust)	(71)	76:24	Et ₂ Zn	(60)	76:24	EtZnI	(67)	73:27	66 66 66 120 66		
Zinc reagent	(%)	I:II																					
Zn/Cu (30 mesh)	(62)	78:22																					
Zn/Ag (30 mesh)	(78)	76:24																					
Zn/Cu (dust)	(71)	76:24																					
Et ₂ Zn	(60)	76:24																					
EtZnI	(67)	73:27																					
	Zn/Cu, MeCH ₂ , Et ₂ O, reflux	 I + II (62) I:II = 78:22	700																				
C ₅₋₈ 	Zn/Cu, CH ₂ I ₂	 <table border="1"> <thead> <tr> <th>n</th> <th>(%)</th> </tr> </thead> <tbody> <tr> <td>1</td> <td>(—)</td> </tr> <tr> <td>2</td> <td>(—)</td> </tr> <tr> <td>3</td> <td>(—)</td> </tr> <tr> <td>4</td> <td>(—)</td> </tr> </tbody> </table>	n	(%)	1	(—)	2	(—)	3	(—)	4	(—)	700a										
n	(%)																						
1	(—)																						
2	(—)																						
3	(—)																						
4	(—)																						
C ₆ 	Et ₂ Zn, CH ₂ I ₂	 (5)	702																				
	Zn/Cu, CH ₂ I ₂	" (—)	702																				
	Sm/Hg, CH ₂ I ₂ , THF, -78°	 (—)	703																				
	Zn/Cu, CH ₂ I ₂	(—)	702																				
	Et ₂ Zn (10 eq), CH ₂ I ₂ (10 eq), CH ₂ Cl ₂ , 0° to rt	 (50)	122																				
	Et ₂ Zn (10 eq), CH ₂ I ₂ (10 eq), CH ₂ Cl ₂ , 0° to rt	 (<75)	122																				
	Et ₂ Zn, CH ₂ I ₂ , PhMe, 0° to rt	 <table border="1"> <thead> <tr> <th>R¹</th> <th>R²</th> <th>(%)</th> <th><i>syn:anti</i></th> </tr> </thead> <tbody> <tr> <td>H</td> <td>TBDMS</td> <td>(89)</td> <td>7.9:1</td> </tr> <tr> <td>H</td> <td>H</td> <td>(-80)</td> <td>-6:1</td> </tr> <tr> <td>MEM</td> <td>TBDMS</td> <td>(-80)</td> <td>-6:1</td> </tr> <tr> <td>MEM</td> <td>H</td> <td>(-80)</td> <td>-6:1</td> </tr> </tbody> </table>	R ¹	R ²	(%)	<i>syn:anti</i>	H	TBDMS	(89)	7.9:1	H	H	(-80)	-6:1	MEM	TBDMS	(-80)	-6:1	MEM	H	(-80)	-6:1	126
R ¹	R ²	(%)	<i>syn:anti</i>																				
H	TBDMS	(89)	7.9:1																				
H	H	(-80)	-6:1																				
MEM	TBDMS	(-80)	-6:1																				
MEM	H	(-80)	-6:1																				
	Zn/Cu, CH ₂ I ₂ , I ₂ (cat.), Et ₂ O, reflux	 (50)	123																				
	Zn/Cu, CH ₂ I ₂ , I ₂ (cat.), Et ₂ O, reflux	 (22)	123																				
	Et ₂ Zn (2 eq), CH ₂ IX (4 eq), (CH ₂ Cl) ₂	 <table border="1"> <thead> <tr> <th>X</th> <th>(%)</th> <th>de (%)</th> </tr> </thead> <tbody> <tr> <td>Cl</td> <td>(—)</td> <td>78-85</td> </tr> <tr> <td>I</td> <td>(99)</td> <td>>99.5</td> </tr> </tbody> </table>	X	(%)	de (%)	Cl	(—)	78-85	I	(99)	>99.5	51											
X	(%)	de (%)																					
Cl	(—)	78-85																					
I	(99)	>99.5																					
	Sm/Hg, CH ₂ ICl, THF, -78°	 (>99)	704, 705																				
	Zn/Cu, CH ₂ I ₂ , Et ₂ O	 (61)	706																				

TABLE VII. CYCLOPROPANATION OF CYCLIC, CHIRAL ALKENES (Continued)

Substrate	Conditions	Product(s) and Yield(s) (%), Ratio <i>syn</i> : <i>anti</i>	Refs.
	Zn/Cu, CH ₂ Br ₂ , Et ₂ O, reflux	 (29)	699
	Zn/Cu, CH ₂ I ₂ , I ₂ (cat.), Et ₂ O, reflux	 (89)	707
	Zn anode, 2e ⁻ , CH ₂ BrCl, ZnBr ₂ present initially, CH ₂ Cl ₂ /DMF (9:1)	 (75)	70
	Zn/Cu, CH ₂ Br ₂ , Et ₂ O, reflux	 (13)	708
	Et ₂ Zn (2 eq), CH ₂ IX (4 eq), (CH ₂ Cl) ₂	" X (%) de (%) Cl (93) 99 I (41-74) >99.5	51
	Sm (5 eq), CH ₂ I ₂ (5 eq), TMSCl (0.2 eq), THF, -78° to rt	" (87)	63
	Sm source, CH ₂ IX, THF, temp	" Sm source X Temp (%) <i>syn:anti</i> Sm/Hg (xs) I 0° (92) >200:1 Sm/Hg (xs) Cl -78° to rt (96) >200:1 SmI ₂ (xs) Cl -78° to rt (89) >200:1	57, 58 58 58
	EiZnI, MeCHI ₂ , Et ₂ O, reflux	 I + II (67) I:II = 70:30	708
	Zn source, MeCHI ₂ , Et ₂ O	Zinc source (%) I:II Zn/Cu (84) 72:28 Et ₂ Zn (1 eq) (79) 62:38 Et ₂ Zn (2 eq) (60) 63:37	120 119 199
	Sm, MeCHI ₂ , THF, -78° to rt	I + II (100) I:II = 5:1	57, 58
	Zn/Cu, CH ₂ I ₂ , Et ₂ O	 I + II (—) I:II = 57:43	709
	Zn/Cu, CH ₂ I ₂ , Et ₂ O	 I + II (—)	709
C ₆₋₇ 	Et ₂ Zn, CH ₂ I ₂ , dry air, (CH ₂ Cl) ₂ , 0°	 R ¹ R ² (%) H H (75-80) H Me (75-80) Me H (75-80)	710
C ₆₋₁₇ 	Et ₂ Zn, CH ₂ Cl ₂ , dry air, (CH ₂ Cl) ₂ , 0° to rt	 R (%) H (67) Me (60) Et (98) <i>n</i> -C ₄ H ₉ (88) Bn (60) <i>n</i> -C ₈ H ₁₇ (60) <i>n</i> -C ₁₁ H ₂₃ (66)	711

TABLE VII. CYCLOPROPANATION OF CYCLIC, CHIRAL ALKENES (Continued)

Substrate	Conditions	Product(s) and Yield(s) (%), Ratio <i>syn</i> : <i>anti</i>	Refs.															
C ₇ 	Zn/Cu, CH ₂ I ₂ , Et ₂ O, reflux	(2) + (17) + (22)	282															
	Zn/Cu, CH ₂ I ₂	(21)	712															
	Sm/Hg, CH ₂ I ₂ , THF, -78°	(80)	703															
	Zn/Cu, CH ₂ I ₂ , I ₂ (cat.), Et ₂ O, reflux	(28)	713															
	Zn/Ag, CD ₂ I ₂ , Et ₂ O, reflux	(21) + (10)	656															
	Zn/Cu, CH ₂ I ₂ , I ₂ (cat.), Et ₂ O, reflux	(80)	123															
	Sm/Hg, MeCHI ₂ , THF, -78°	(45)	714, 715															
	Zn/Cu, CH ₂ I ₂	(—)	449, 450															
	Zn/Cu, CH ₂ I ₂	(—)	450															
	Zn/Cu, CH ₂ Br ₂ , Et ₂ O, reflux	(27)	708															
	Sm/Hg (xs), CH ₂ I ₂ , THF, -78° to rt	(64) >30:1	58															
	SmI ₂ (xs), CH ₂ ICl, THF, -78° to rt	" (86) >30:1	58															
	Zinc source, MeCHI ₂ , Et ₂ O	I + II + III + IV																
		<table border="1"> <thead> <tr> <th>Zinc source</th> <th>(%)</th> <th>I:II:III:IV</th> </tr> </thead> <tbody> <tr> <td>Zn/Cu</td> <td>(74)</td> <td>19:2:59:20</td> </tr> <tr> <td>Et₂Zn</td> <td>(72)</td> <td>20:10:49:21</td> </tr> <tr> <td>Et₂Zn (1 eq)</td> <td>(74)</td> <td>0:49:0:51</td> </tr> <tr> <td>Et₂Zn (2 eq)</td> <td>(79)</td> <td>0:52:0:48</td> </tr> </tbody> </table>	Zinc source	(%)	I:II:III:IV	Zn/Cu	(74)	19:2:59:20	Et ₂ Zn	(72)	20:10:49:21	Et ₂ Zn (1 eq)	(74)	0:49:0:51	Et ₂ Zn (2 eq)	(79)	0:52:0:48	120, 120, 119, 119
Zinc source	(%)	I:II:III:IV																
Zn/Cu	(74)	19:2:59:20																
Et ₂ Zn	(72)	20:10:49:21																
Et ₂ Zn (1 eq)	(74)	0:49:0:51																
Et ₂ Zn (2 eq)	(79)	0:52:0:48																

TABLE VII. CYCLOPROPANATION OF CYCLIC, CHIRAL ALKENES (Continued)

Substrate	Conditions	Product(s) and Yield(s) (%), Ratio <i>syn</i> : <i>anti</i>	Refs.																				
	Et ₂ Zn, CH ₂ I ₂ , CH ₂ Cl ₂ , 0°	 (66)	716, 717																				
	Zn/Cu, CH ₂ I ₂ , Et ₂ O, reflux	 (—)	R <i>syn:anti</i> Me 43:57 COMe 49:51 CN 45:55 CO ₂ Me 40:60 CO ₂ Et ^d 35:65 CO ₂ Bu- <i>t</i> 47:53 CH ₂ OH 47:53 AcOCH ₂ 43:57	718																			
	Zn/Cu, CH ₂ I ₂	 (—)	R ¹ R ² R ³ Me H H H Me H H Ph H H H Me	700a																			
	Zn/Cu, CH ₂ I ₂ , I ₂ (cat.), Et ₂ O, reflux	 (53)		719																			
	Zn/Cu, CH ₂ I ₂ , I ₂ (cat.), Et ₂ O	 (30) major		720																			
	Sm/Hg, CH ₂ I ₂	 (39)		721																			
	Zn/Cu, CH ₂ I ₂ , Et ₂ O, reflux	 (—) 20:80		718																			
	Conditions	 I + II + III		104																			
		<table border="1"> <thead> <tr> <th>Conditions</th> <th>I (%)</th> <th>II (%)</th> <th>III (%)</th> </tr> </thead> <tbody> <tr> <td>Zn/Cu, CH₂I₂, AcCl, Et₂O</td> <td>(9)</td> <td>(18)</td> <td>(1)</td> </tr> <tr> <td>Zn/Cu, CH₂Br₂, AcCl, Et₂O</td> <td>(2)</td> <td>(4)</td> <td>(0)</td> </tr> <tr> <td>Et₂Zn, CH₂I₂, PhMe</td> <td>(5)</td> <td>(34)</td> <td>(1)</td> </tr> <tr> <td>Et₃Al, CH₂I₂, PhMe/CH₂Cl₂</td> <td>(13)</td> <td>(39)</td> <td>(8)</td> </tr> </tbody> </table>	Conditions	I (%)	II (%)	III (%)	Zn/Cu, CH ₂ I ₂ , AcCl, Et ₂ O	(9)	(18)	(1)	Zn/Cu, CH ₂ Br ₂ , AcCl, Et ₂ O	(2)	(4)	(0)	Et ₂ Zn, CH ₂ I ₂ , PhMe	(5)	(34)	(1)	Et ₃ Al, CH ₂ I ₂ , PhMe/CH ₂ Cl ₂	(13)	(39)	(8)	
Conditions	I (%)	II (%)	III (%)																				
Zn/Cu, CH ₂ I ₂ , AcCl, Et ₂ O	(9)	(18)	(1)																				
Zn/Cu, CH ₂ Br ₂ , AcCl, Et ₂ O	(2)	(4)	(0)																				
Et ₂ Zn, CH ₂ I ₂ , PhMe	(5)	(34)	(1)																				
Et ₃ Al, CH ₂ I ₂ , PhMe/CH ₂ Cl ₂	(13)	(39)	(8)																				
	Et ₂ Zn, CH ₂ I ₂ , PhMe, rt	I (7-13) + II (7-45)		446																			
	Zn/Ag, CH ₂ I ₂	 (47-48)		303																			
	Et ₂ Zn, CH ₂ I ₂	" (47-48)		303																			
	EtZnI, CH ₂ I ₂ , Et ₂ O, reflux	 I + II	(>99) I:II = 7:3	303																			

TABLE VII. CYCLOPROPANATION OF CYCLIC, CHIRAL ALKENES (Continued)

Substrate	Conditions	Product(s) and Yield(s) (%), Ratio <i>syn</i> : <i>anti</i>	Refs.												
	Zn/Ag, CH ₂ I ₂ , Et ₂ O, reflux	(31) major	658												
	EtZnI, CH ₂ I ₂ , Et ₂ O, reflux	(30)	656												
	Zn/Cu, CH ₂ I ₂	(—)	722												
	Zn/Cu, CH ₂ I ₂	(—)	722												
	Zn/Cu, CH ₂ I ₂ , Et ₂ O, reflux	(52)	723												
	Zn/Cu, CH ₂ I ₂ , I ₂ (cat.), Et ₂ O, reflux	(26)	123												
	Sm/Hg (xs), CH ₂ I ₂ , THF, -78° to rt	(85) >40:1	58												
	SmI ₂ , CH ₂ I ₂ , THF, -78° to rt	" (86) >40:1	58												
	Zn/Cu, MeCHI ₂ , Et ₂ O, reflux	I + II (88) I:II = 28:72	700												
	Zinc source, MeCHI ₂ , Et ₂ O	I + II													
		<table border="1"> <thead> <tr> <th>Zinc source</th> <th>(%)</th> <th>I:II</th> </tr> </thead> <tbody> <tr> <td>Zn/Cu</td> <td>(88)</td> <td>28:72</td> </tr> <tr> <td>Et₂Zn (1 eq)</td> <td>(60)</td> <td>52:48</td> </tr> <tr> <td>Et₂Zn (2 eq)</td> <td>(76)</td> <td>29:71</td> </tr> </tbody> </table>	Zinc source	(%)	I:II	Zn/Cu	(88)	28:72	Et ₂ Zn (1 eq)	(60)	52:48	Et ₂ Zn (2 eq)	(76)	29:71	66 119 119
Zinc source	(%)	I:II													
Zn/Cu	(88)	28:72													
Et ₂ Zn (1 eq)	(60)	52:48													
Et ₂ Zn (2 eq)	(76)	29:71													
	EtZnI, MeCHI ₂ , Et ₂ O, reflux	(34)	65												
	Zn/Cu, CH ₂ I ₂	(—)	311												
	Zn/Cu, CH ₂ I ₂ , I ₂ (cat.), Et ₂ O, reflux	(69)	290												

TABLE VII. CYCLOPROPANATION OF CYCLIC, CHIRAL ALKENES (Continued)

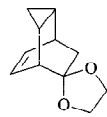
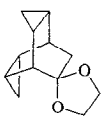


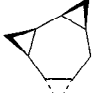
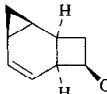
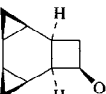
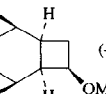
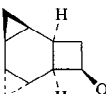
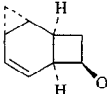
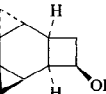
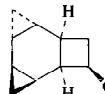
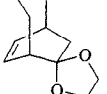
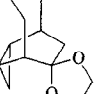
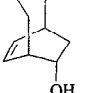
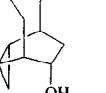
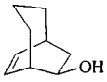
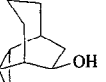
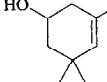
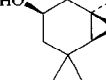
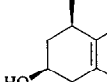
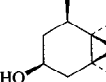
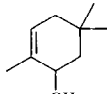
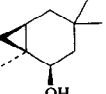
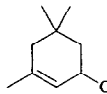
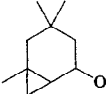
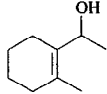
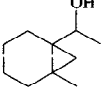
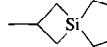
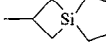
Substrate	Conditions	Product(s) and Yield(s) (%), Ratio <i>syn</i> : <i>anti</i>	Refs.
	Zn/Ag, CH ₂ I ₂ , Et ₂ O	 (60-63)	297, 298
	Zn/Ag, CH ₂ I ₂ , Et ₂ O, reflux	 I +  II (17) I:II = 35:65	303
	Zn/Cu, CH ₂ I ₂ , Et ₂ O, reflux	 (40) +  (—) +  (—)	724
	Zn/Cu, CH ₂ I ₂ , Et ₂ O, reflux	 (50-60) +  (—)	724
	Zn/Cu, CH ₂ I ₂ , I ₂ (cat.), Et ₂ O, reflux	 (92)	299
	Zn/Cu, CH ₂ I ₂ , I ₂ (cat.), Et ₂ O, reflux	 (42)	299
	Zn/Cu, CH ₂ I ₂ , I ₂ (cat.), Et ₂ O, reflux	 (6)	299
	Zn/Cu, CH ₂ I ₂	 (—)	311
	Zn/Cu, CH ₂ I ₂ , Et ₂ O, reflux	 (40)	725
	Et ₂ Zn, CH ₂ I ₂ , (CH ₂ Cl) ₂ , 0°	 (90)	726
	Zn/Ag, CH ₂ I ₂ , Et ₂ O, reflux	 (82)	727
	Zn/Ag, CH ₂ I ₂ , Et ₂ O, reflux	 (81)	728
	Zn/Ag, CH ₂ I ₂ , Et ₂ O, reflux	 (47)	729

TABLE VII. CYCLOPROPANATION OF CYCLIC, CHIRAL ALKENES (Continued)

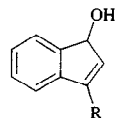
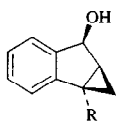
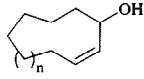
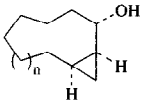
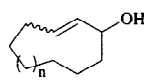
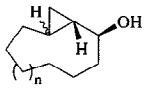
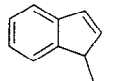
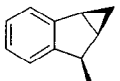
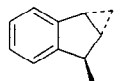
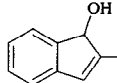
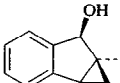
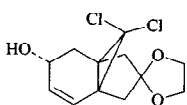
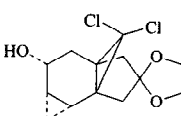
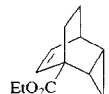
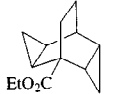

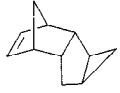
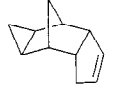
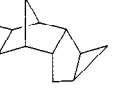

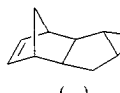
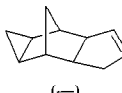
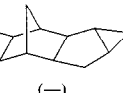
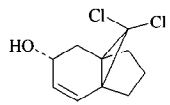
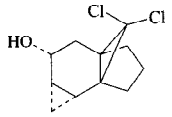
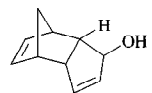
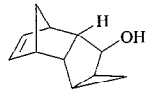
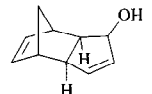
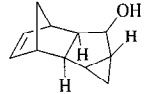
Substrate	Conditions	Product(s) and Yield(s) (%), Ratio <i>syn</i> : <i>anti</i>	Refs.																									
C ₉₋₁₀ 	Zn/Cu, CH ₂ I ₂ , Et ₂ O, reflux	 <table border="1"> <tr><td>R</td><td>(%)</td></tr> <tr><td>H</td><td>(41)</td></tr> <tr><td>Me</td><td>(58)</td></tr> </table>	R	(%)	H	(41)	Me	(58)	65																			
R	(%)																											
H	(41)																											
Me	(58)																											
	Zn/Cu, CH ₂ I ₂ , Et ₂ O, reflux	 <table border="1"> <tr><td>n</td><td>(%)</td></tr> <tr><td>1</td><td>(93)</td></tr> <tr><td>2</td><td>(63)</td></tr> </table>	n	(%)	1	(93)	2	(63)	730																			
n	(%)																											
1	(93)																											
2	(63)																											
C ₉₋₁₂  <table border="1"> <tr><td>n</td><td><i>cis:trans</i></td></tr> <tr><td>1</td><td>1:2</td></tr> <tr><td>2</td><td>5:2</td></tr> <tr><td>3</td><td><i>trans</i></td></tr> <tr><td>4</td><td><i>trans</i></td></tr> </table>	n	<i>cis:trans</i>	1	1:2	2	5:2	3	<i>trans</i>	4	<i>trans</i>	Zn/Cu, CH ₂ I ₂ , Et ₂ O, reflux	 <table border="1"> <tr><td>n</td><td><i>cis:trans</i></td><td>(%)</td></tr> <tr><td>1</td><td>1:2</td><td>(95)</td></tr> <tr><td>2</td><td>3:1</td><td>(83)</td></tr> <tr><td>3</td><td><i>trans</i></td><td>(—)</td></tr> <tr><td>4</td><td><i>trans</i></td><td>(87)</td></tr> </table>	n	<i>cis:trans</i>	(%)	1	1:2	(95)	2	3:1	(83)	3	<i>trans</i>	(—)	4	<i>trans</i>	(87)	730
n	<i>cis:trans</i>																											
1	1:2																											
2	5:2																											
3	<i>trans</i>																											
4	<i>trans</i>																											
n	<i>cis:trans</i>	(%)																										
1	1:2	(95)																										
2	3:1	(83)																										
3	<i>trans</i>	(—)																										
4	<i>trans</i>	(87)																										
C ₁₀ 	Zn/Cu, CH ₂ I ₂ , I ₂ (cat.), Et ₂ O, reflux	 (38) +  (7)	309																									
	Zn/Cu, CH ₂ I ₂ , Et ₂ O, reflux	 (60)	731																									
	Zn/Ag, CH ₂ I ₂ , Et ₂ O, reflux	 (60)	732																									
	Zn/Cu, CH ₂ I ₂ , I ₂ (cat.), Et ₂ O, reflux	 (87)	290																									
	Zn/Ag, CH ₂ I ₂ , DME, reflux	 +  + 	666																									
	Zn/Ag, CH ₂ I ₂ , DME, reflux	 +  + 	666																									
	Zn/Ag, CH ₂ I ₂ , Et ₂ O, reflux	 (72)	732																									
	Zn/Cu, CH ₂ I ₂	 (—)	667																									
	Zn/Cu, CH ₂ I ₂	 (—)	667																									

TABLE VII. CYCLOPROPANATION OF CYCLIC, CHIRAL ALKENES (Continued)

Substrate	Conditions	Product(s) and Yield(s) (%), Ratio <i>syn</i> : <i>anti</i>	Refs.																				
	Zn/Cu, CH ₂ I ₂ , I ₂ (cat.), Et ₂ O, reflux	(66)	295																				
	Zn/Cu, CH ₂ I ₂	(—)	311																				
	Zn/Cu, CH ₂ I ₂ , Et ₂ O, reflux	(90)	733																				
	Zn/Cu, CH ₂ Br ₂ , Et ₂ O, 45°, sonication	(40)	270																				
	Zn/Cu, CH ₂ Br ₂ , AcCl (0.02 eq), Et ₂ O	" (53)	41																				
	Zn/Cu, CH ₂ X ₂ , promoter, Et ₂ O	<table border="1"> <thead> <tr> <th>Promoter</th> <th>X</th> <th>(%)</th> </tr> </thead> <tbody> <tr> <td>TiCl₄</td> <td>Br</td> <td>(55)</td> </tr> <tr> <td>ultrasound</td> <td>Br</td> <td>(40)</td> </tr> <tr> <td>TiCl₄</td> <td>I</td> <td>(61)</td> </tr> </tbody> </table>	Promoter	X	(%)	TiCl ₄	Br	(55)	ultrasound	Br	(40)	TiCl ₄	I	(61)	43								
Promoter	X	(%)																					
TiCl ₄	Br	(55)																					
ultrasound	Br	(40)																					
TiCl ₄	I	(61)																					
	Zn/Cu, CH ₂ I ₂ , Et ₂ O	(53)	734																				
	Zn/Cu, CH ₂ I ₂ , ultrasound, DME, reflux	" (67)	45																				
	Zn*, CH ₂ I ₂ , DME/Et ₂ O	(54)	44																				
	Zn/Cu, CH ₂ Br ₂ , AcCl (0.02 eq), Et ₂ O	(76)	41																				
	Zn/Cu, CH ₂ Br ₂ , AcCl (0.02 eq), Et ₂ O	(76)	41																				
	R ₃ Al (x eq), CH ₂ I ₂ (1.2 eq), solvent, rt	<table border="1"> <thead> <tr> <th>R</th> <th>x</th> <th>Solvent</th> <th>(%)</th> </tr> </thead> <tbody> <tr> <td>Me</td> <td>1</td> <td>CH₂Cl₂</td> <td>(57)</td> </tr> <tr> <td>Me</td> <td>1</td> <td>hexane</td> <td>(80)</td> </tr> <tr> <td>n-Pr</td> <td>1.2</td> <td>hexane</td> <td>(78)</td> </tr> </tbody> </table>	R	x	Solvent	(%)	Me	1	CH ₂ Cl ₂	(57)	Me	1	hexane	(80)	n-Pr	1.2	hexane	(78)	59				
R	x	Solvent	(%)																				
Me	1	CH ₂ Cl ₂	(57)																				
Me	1	hexane	(80)																				
n-Pr	1.2	hexane	(78)																				
	Zn/Hg, TMSCl, HC(OMe) ₃ , Et ₂ O, reflux	(65) <i>syn:anti</i> = 5:2	77																				
	Conditions	I + II + III <table border="1"> <thead> <tr> <th>Conditions</th> <th>I (%)</th> <th>II (%)</th> <th>III (%)</th> </tr> </thead> <tbody> <tr> <td>Zn/Cu, CH₂I₂, AcCl, Et₂O</td> <td>(30)</td> <td>(8)</td> <td>(36)</td> </tr> <tr> <td>Zn/Cu, CH₂Br₂, AcCl, Et₂O</td> <td>(27)</td> <td>(9)</td> <td>(21)</td> </tr> <tr> <td>Et₂Zn, CH₂I₂, PhMe</td> <td>(19)</td> <td>(25)</td> <td>(17)</td> </tr> <tr> <td>Et₃Al, CH₂I₂, PhMe/CH₂Cl₂</td> <td>(26)</td> <td>(13)</td> <td>(12)</td> </tr> </tbody> </table>	Conditions	I (%)	II (%)	III (%)	Zn/Cu, CH ₂ I ₂ , AcCl, Et ₂ O	(30)	(8)	(36)	Zn/Cu, CH ₂ Br ₂ , AcCl, Et ₂ O	(27)	(9)	(21)	Et ₂ Zn, CH ₂ I ₂ , PhMe	(19)	(25)	(17)	Et ₃ Al, CH ₂ I ₂ , PhMe/CH ₂ Cl ₂	(26)	(13)	(12)	104
Conditions	I (%)	II (%)	III (%)																				
Zn/Cu, CH ₂ I ₂ , AcCl, Et ₂ O	(30)	(8)	(36)																				
Zn/Cu, CH ₂ Br ₂ , AcCl, Et ₂ O	(27)	(9)	(21)																				
Et ₂ Zn, CH ₂ I ₂ , PhMe	(19)	(25)	(17)																				
Et ₃ Al, CH ₂ I ₂ , PhMe/CH ₂ Cl ₂	(26)	(13)	(12)																				

TABLE VII. CYCLOPROPANATION OF CYCLIC, CHIRAL ALKENES (Continued)

Substrate	Conditions	Product(s) and Yield(s) (%), Ratio <i>syn</i> : <i>anti</i>	Product(s) and Yield(s) (%), Ratio <i>syn</i> : <i>anti</i>			Refs.
			Solvent	I (%)	II (%)	
	Zn/Cu, CH ₂ I ₂ , AcCl (cat), solvent	I + II + III	Et ₂ O (26) DME (26) THF (16) <i>i</i> -Pr ₂ O (25) EtOAc (14) dioxane (11) (CH ₂ Cl) ₂ (9)	(11) (9) (7) (8) (8) (5) (2)	(8) (4) (1) (2) (1) (1) (4)	104
	Zn/Cu, CH ₂ I ₂ , Et ₂ O, reflux		(96)			735
	Zn/Ag, CH ₂ I ₂ , Et ₂ O, reflux		(83)			671
	Sm/Hg, CH ₂ I ₂ , THF, -78° to rt	" (58)				672
	Et ₂ Zn, CH ₂ I ₂		(95)			736
	Sm/Hg, CH ₂ Cl, THF		(67)			737, 738
	Et ₂ Zn, CH ₂ I ₂ , (CH ₂ Cl) ₂ , rt		(71)			506
	Zn anode, 2e ⁻ , CH ₂ Br ₂ , ZnBr ₂ present initially, CH ₂ Cl ₂ /DMF (9:1)		(8)			70
	Zn/Cu, CH ₂ I ₂ , Et ₂ O, reflux	 I + II	(-)		I:II = ~1:1	733
	Et ₂ Zn, CH ₂ I ₂ , CH ₂ Cl ₂ , 0° to rt		(50)			739
	Et ₂ Zn, CH ₂ I ₂ , CH ₂ Cl ₂ , 0° to rt		(53)			739
^C ₁₁ 	EtZnI, CH ₂ I ₂		(51) 4:1			125
	Zn/Cu, CH ₂ I ₂ , Et ₂ O, reflux		(75)			740

TABLE VII. CYCLOPROPANATION OF CYCLIC, CHIRAL ALKENES (Continued)

Substrate	Conditions	Product(s) and Yield(s) (%), Ratio <i>syn</i> : <i>anti</i>	Refs.
	Et ₂ Zn (2 eq), CH ₂ I ₂ (2 eq), DME, reflux	(86)	741
	Zn/Ag, CH ₂ I ₂ , DME, 60°	(9) + (37)	673
	Zn/Ag, CH ₂ I ₂ , Et ₂ O, reflux	(63) + (9)	742
	Et ₂ Zn (2 eq), CH ₂ I ₂ (12 eq), C ₆ H ₆ , rt	(92)	130, 743, 744
	Et ₂ Zn, CH ₂ I ₂	(83)	745
	Et ₂ Zn (2 eq), CH ₂ I ₂ (8 eq), C ₆ H ₆	(73)	744
	Zn/Ag, CH ₂ I ₂ , Et ₂ O	(77)	671
	Zn/Cu, CH ₂ I ₂ , Et ₂ O	(96)	746
	Zn/Cu, CH ₂ I ₂ , Et ₂ O, reflux	" (76)	747
	Zn/Cu, CH ₂ I ₂ , Et ₂ O, reflux	(78)	748
	Zn/Cu, CH ₂ I ₂ , Et ₂ O, rt	(97)	749
	Zn/Cu, CH ₂ I ₂ , I ₂ (cat.), Et ₂ O, reflux	(65)	750
	Zn, CH ₂ I ₂ , DME, sonication	(68)	714, 715

TABLE VII. CYCLOPROPANATION OF CYCLIC, CHIRAL ALKENES (Continued)

Substrate	Conditions	Product(s) and Yield(s) (%), Ratio <i>syn</i> : <i>anti</i>	Refs.
	Zn, CH ₂ I ₂ , DME, sonication	(82)	715
	Zn/Cu, CH ₂ I ₂ , Et ₂ O/DME	(62)	751, 752
	Et ₂ Zn (5 eq), CH ₂ I ₂ (4 eq), PhMe, 0°	(93)	753
C ₁₂ 	Zn/Cu, CH ₂ I ₂	(50) 11:89	754
	Zn/Cu, CH ₂ I ₂ , Et ₂ O/DME	(64) + (29)	755
	Et ₂ Zn (8 eq), CH ₂ I ₂ (8 eq), CH ₂ Cl ₂ , 0° to rt	(74) >50:1	756
	Zn/Cu, CH ₂ I ₂ , I ₂ (cat.), Et ₂ O, reflux	(83)	757
	Et ₂ Zn (1.8 eq), CH ₂ I ₂ (5.5 eq), Et ₂ O	I + II + III = (43)	615
(no ratio reported)			
	Zn/Cu, CH ₂ I ₂ , Et ₂ O	(>42)	758
	Zn/Cu, CH ₂ I ₂ , Et ₂ O	(65)	355, 730
C ₁₃ 	Et ₂ Zn, CH ₂ I ₂ , Et ₂ O, reflux	(—)	759
	Et ₂ Zn, CH ₂ I ₂ , Et ₂ O, reflux	(33)	759
	Zn/Cu, CH ₂ I ₂ , I ₂ (cat.), Et ₂ O, reflux	(78)	760

TABLE VII. CYCLOPROPANATION OF CYCLIC, CHIRAL ALKENES (Continued)

Substrate	Conditions	Product(s) and Yield(s) (%), Ratio <i>syn</i> : <i>anti</i>	Refs.
	Et ₂ Zn, CH ₂ I ₂ , Et ₂ O, reflux	(—)	759
	Zn/Cu, CH ₂ I ₂ , Et ₂ O, reflux	(75)	323
	Zn/Cu, CH ₂ I ₂ , Et ₂ O, reflux	(—)	761
	Zn/Cu, CH ₂ I ₂ , Et ₂ O/DME	(78)	752, 762
	Zn/Cu, CH ₂ I ₂ , Et ₂ O/DME	(85)	752, 762
	Zn/Cu, CH ₂ Br ₂ , Et ₂ O, reflux, AcBr or ultrasound	(48) I:II = 1.3:1	506
	Et ₃ Al, CH ₂ I ₂ , hexane, rt	(90) I:II = ~1.5:1	506
	 Zn(CH ₂ I) ₂ ·DME, CH ₂ Cl ₂ , -10° to rt	I + II (~13) 71% de I:II = 48:43	506
	Zn/Ag, CH ₂ I ₂ , Et ₂ O, reflux	(70)	677
	Zn/Ag, CH ₂ I ₂ , Et ₂ O	(51)	763, 764
	Et ₂ Zn, CH ₂ I ₂ , C ₆ H ₆ , reflux	(67) I:II = 3:1	765
	Zn/Ag, CH ₂ I ₂ , DME, reflux	(—) (—) (—)	666
	Zn/Ag, CH ₂ I ₂ , Et ₂ O, reflux	(95) 7:3	766

TABLE VII. CYCLOPROPANATION OF CYCLIC, CHIRAL ALKENES (Continued)

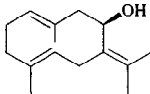
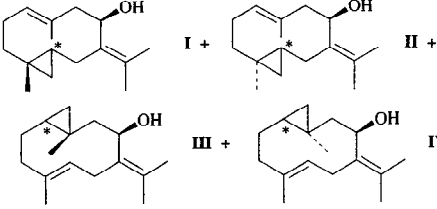
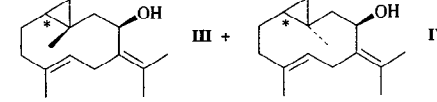
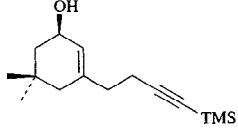
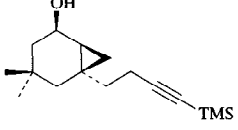
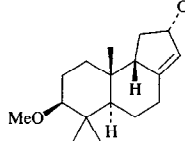
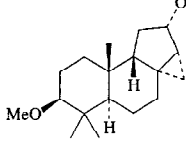
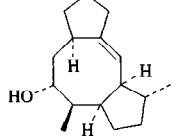
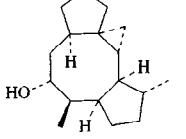
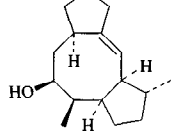
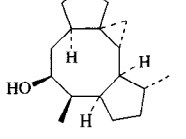
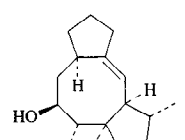
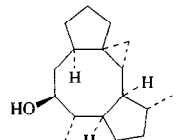
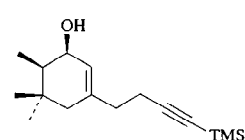
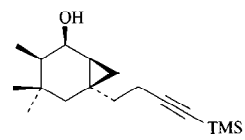
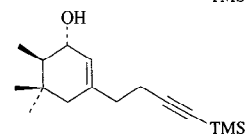
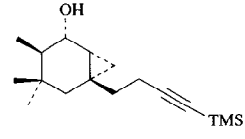
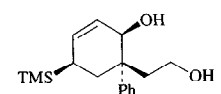
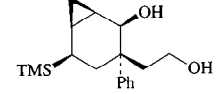
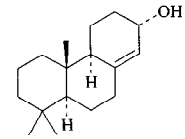
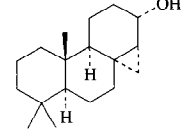
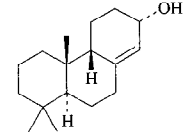
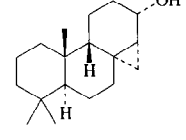
Substrate	Conditions	Product(s) and Yield(s) (%), Ratio <i>syn</i> : <i>anti</i>	Refs.
	Zn/Cu, CH ₂ I ₂ , Et ₂ O	 I + II +  III + IV (-) I:II:III:IV = 26:49:6:19	330
	Zn/Ag, CH ₂ I ₂ , Et ₂ O	 (66)	671, 770
	Et ₂ Zn, CH ₂ ICl, (CH ₂ Cl) ₂ , 0°, 2 h	 (85)	771
	Et ₂ Zn (7 eq), CH ₂ I ₂ (8 eq), C ₆ H ₆ , reflux	 (34)	772
	Et ₂ Zn (9 eq), CH ₂ I ₂ (10 eq), C ₆ H ₆ , rt	 (86)	772
	Et ₂ Zn (51 eq), CH ₂ I ₂ (56 eq), neat, rt	 (69)	772
	Zn/Ag, CH ₂ I ₂ , Et ₂ O, reflux	 (74)	671, 770
	Zn/Ag, CH ₂ I ₂ , Et ₂ O, reflux	 (84)	671, 770
	Et ₂ Zn (5 eq), CH ₂ I ₂ (4 eq), PhMe, 0°	 (93)	753
	Zn/Cu, CH ₂ I ₂ , I ₂ (cat.), Et ₂ O/THF, reflux	 (74)	366
	Sm/Hg, CH ₂ ICl, -78° to rt	 (88)	774

TABLE VII. CYCLOPROPANATION OF CYCLIC, CHIRAL ALKENES (Continued)

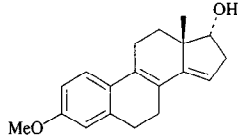
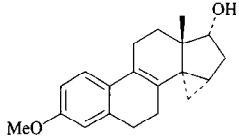
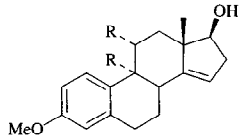
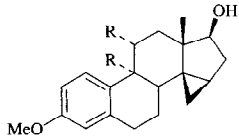
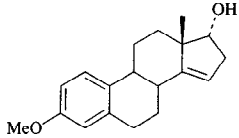
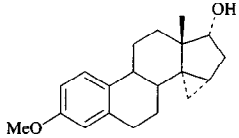
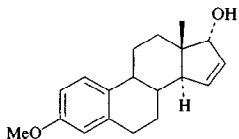
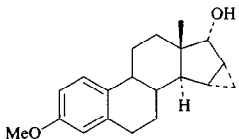
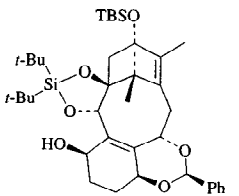
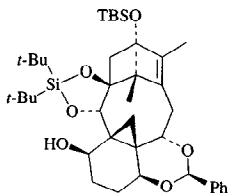
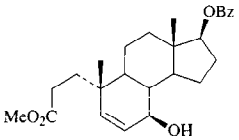
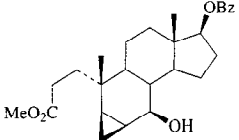
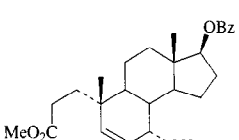
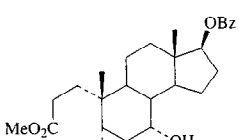
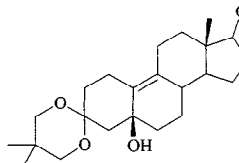
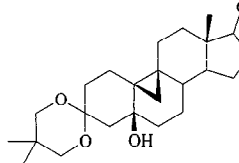
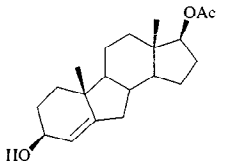
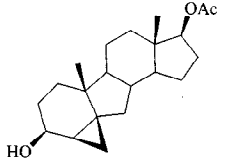
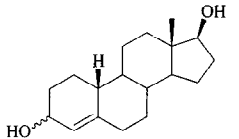
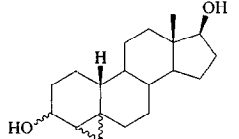
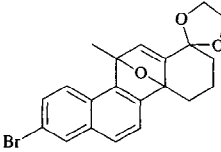
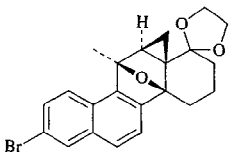
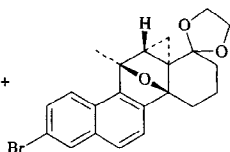
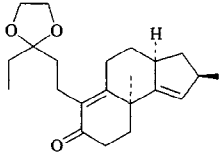
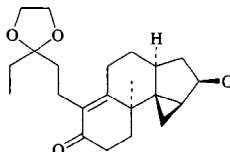
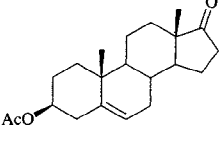
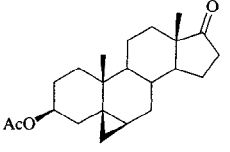
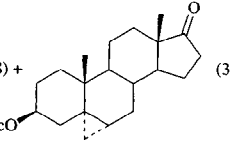
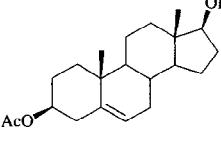
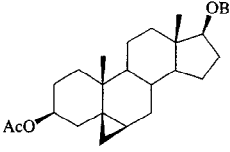
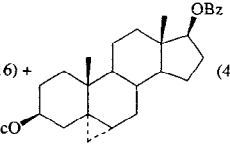
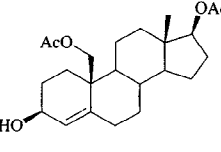
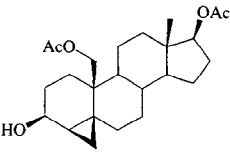
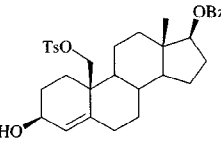
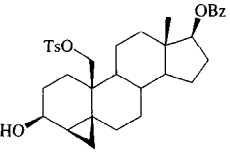
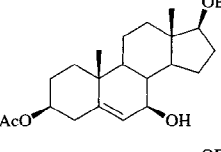
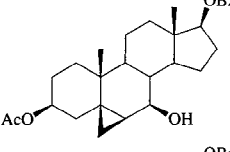
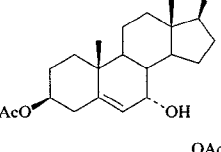
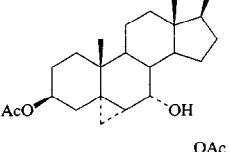
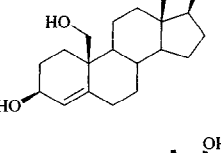
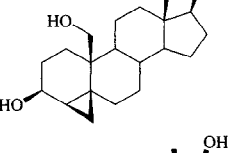
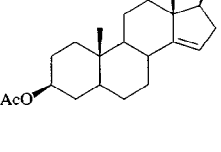
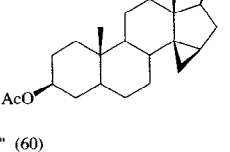
Substrate	Conditions	Product(s) and Yield(s) (%), Ratio <i>syn</i> : <i>anti</i>	Refs.
C ₁₈ 	Zn/Cu, CH ₂ I ₂ , DME	 (>71)	682
	Zn, CH ₂ I ₂ , sonication, THF	" (80)	683
	Zn/Cu, CH ₂ I ₂ , CH ₂ Cl ₂	 R (%) T (80) H (75)	775 776
	Zn/Cu, CH ₂ I ₂ , CH ₂ Cl ₂	 (73)	776
	Zn/Cu, CH ₂ I ₂ , DME/Et ₂ O, reflux	 (81)	714, 715
	Et ₂ Zn, CH ₂ Cl ₂ , PhMe, 0°	 (66)	684
	Zn/Cu, CH ₂ I ₂ , Et ₂ O, reflux	 (57)	777
	Zn/Cu, CH ₂ I ₂ , Et ₂ O, reflux	 (40)	777
	Zn/Cu, CH ₂ I ₂ , Et ₂ O	 (—)	778
	Zn/Cu, CH ₂ I ₂ , I ₂ (cat.), Et ₂ O, reflux	 (69)	773
	Zn/Cu, CH ₂ I ₂ , I ₂ (cat.), Et ₂ O, 60°	 (>14)	779

TABLE VII. CYCLOPROPANATION OF CYCLIC, CHIRAL ALKENES (Continued)

Substrate	Conditions	Product(s) and Yield(s) (%), Ratio <i>syn</i> : <i>anti</i>	Refs.
C ₁₉ 	Zn/Cu, CH ₂ I ₂ , Et ₂ O, reflux	 (37) +  (-)	780
	1. <i>n</i> -BuLi (1 eq), Et ₂ O, -20° 2. IZnCH ₂ I (15 eq), Et ₂ O, rt	 (66)	111
	Zn/Cu, CH ₂ I ₂ , Et ₂ O, 100°, autoclave	 (8) +  (3)	781
	Zn/Cu, CH ₂ I ₂ , Et ₂ O, 100°, autoclave	 (16) +  (4)	781
	Zn/Cu, CH ₂ I ₂ , I ₂ (cat.), Et ₂ O/THF, reflux	 (49)	782
	Zn/Cu, CH ₂ I ₂ , I ₂ (cat.), Et ₂ O, reflux	 (71)	783
	Zn/Cu, CH ₂ I ₂ , Et ₂ O, reflux	 (44)	784
	Zn/Cu, CH ₂ I ₂ , Et ₂ O, reflux	 (43)	784
	Zn/Cu, CH ₂ I ₂ , I ₂ (cat.), Et ₂ O/THF, reflux	 (32)	782
	Zn/Cu, CH ₂ I ₂ , DME, 50°	 (50)	776
	ZnI ₂ , CH ₂ N ₂ , Et ₂ O	" (60)	776

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TABLE VII. CYCLOPROPANATION OF CYCLIC, CHIRAL ALKENES (Continued)

Substrate	Conditions	Product(s) and Yield(s) (%), Ratio <i>syn</i> : <i>anti</i>	Refs.												
	Zn/Cu, CH ₂ I ₂ , ultrasound, DME, reflux	(75)	45												
	Zn/Cu, CH ₂ I ₂ , I ₂ (cat.), Et ₂ O, reflux	(81)	773												
	Et ₂ Zn, CH ₂ ICl, (CH ₂ Cl) ₂ , 0°	(98)	785												
	Et ₃ Al, CH ₂ I ₂ , hexane, reflux	(53)	786												
	Zn/Cu, CH ₂ I ₂	(88)	787												
	EtZnI, CH ₂ I ₂ , Et ₂ O	I + II	788												
		<table border="1"> <thead> <tr> <th>R</th> <th>(%)</th> <th>I:II</th> </tr> </thead> <tbody> <tr> <td>Me</td> <td>(-)</td> <td>85:15</td> </tr> <tr> <td>Et</td> <td>(-)</td> <td>50:50</td> </tr> <tr> <td><i>i</i>-Bu</td> <td>(70)</td> <td>15:85</td> </tr> </tbody> </table>	R	(%)	I:II	Me	(-)	85:15	Et	(-)	50:50	<i>i</i> -Bu	(70)	15:85	
R	(%)	I:II													
Me	(-)	85:15													
Et	(-)	50:50													
<i>i</i> -Bu	(70)	15:85													
	Zn/Cu, CH ₂ I ₂ , I ₂ (cat.), Et ₂ O	(63)	789												
	Zn/Cu, CH ₂ I ₂	(56)	790												
	Zn/Cu, CH ₂ I ₂	(70)	687												

TABLE VII. CYCLOPROPANATION OF CYCLIC, CHIRAL ALKENES (Continued)

Substrate	Conditions	Product(s) and Yield(s) (%), Ratio <i>syn</i> : <i>anti</i>	Refs.
	Zn/Cu, CH ₂ I ₂ , Et ₂ O, 100°	(5) + (7)	791
	Zn/Cu, CH ₂ I ₂ , Et ₂ O, reflux		688
	Zn/Cu, CH ₂ I ₂ , Et ₂ O, reflux		688
	Zn/Cu, CH ₂ I ₂ , Et ₂ O/DME, reflux		689
	Zn/Cu, CH ₂ I ₂ , Et ₂ O, reflux		688
	Zn/Cu, CH ₂ I ₂ , Et ₂ O		86
	Zn/Cu, CH ₂ I ₂ , Et ₂ O, reflux		688
	Zn/Cu, CH ₂ I ₂ , I ₂ (cat.), Et ₂ O, 60°		779
	Zn/Cu, CH ₂ I ₂ , I ₂ (cat.), Et ₂ O, reflux		166
	Zn/Cu, CH ₂ I ₂ , DME, heat		792

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TABLE VII. CYCLOPROPANATION OF CYCLIC, CHIRAL ALKENES (Continued)

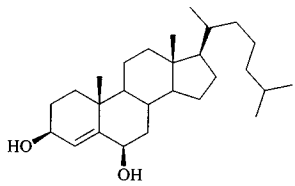
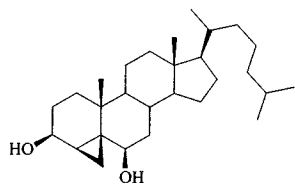
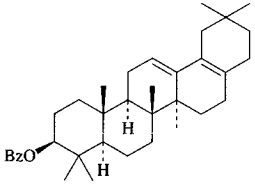
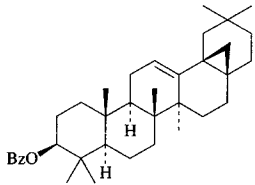
Substrate	Conditions	Product(s) and Yield(s) (%), Ratio <i>syn</i> : <i>anti</i>	Refs.
C ₂₃ 	Zn/Pb, CH ₂ I ₂ , I ₂ (cat.), 40-45°	(34)	690
C ₂₄ 	Zn/Cu, CH ₂ I ₂ , Et ₂ O/THF, 50-60°	(63)	691
	Zn/Ag, CH ₂ I ₂ , solvent, reflux	 Solvent (%) DME (>99) THF (95) Et ₂ O (95)	692
	Zn/Cu, CH ₂ I ₂ , Et ₂ O, reflux	(14)	693
	Zn/Cu, CH ₂ I ₂ , Et ₂ O, reflux	(27) 5.5:1	693
C ₂₅ 	Zn/Ag, CH ₂ I ₂ , Et ₂ O, 0°	(61)	793
C ₂₆ 	Zn/Cu, CH ₂ I ₂ , Et ₂ O, heat	(7) + (2)	794

Substrate	Conditions	Product(s) and Yield(s) (%), Ratio <i>syn</i> : <i>anti</i>	Refs.
	Zn/Cu, CH ₂ I ₂ , I ₂ (cat.), Et ₂ O, rt	 (56)	794a
	Zn/Cu, CH ₂ I ₂ , I ₂ (cat.), Et ₂ O, reflux	 (19)	794a
	Zn/Cu, CH ₂ I ₂ , Et ₂ O, heat	 (1)	794
	Zn/Cu, CH ₂ I ₂ , Et ₂ O, 100°, autoclave	 (30)	796
	Zn/Cu, CH ₂ I ₂ , Et ₂ O, 100°, autoclave	 (12)	797
	Zn/Cu, CH ₂ I ₂ , I ₂ (cat.), Et ₂ O, reflux	 (36)	798
	Zn/Cu, CH ₂ I ₂ , I ₂ (cat.), Et ₂ O, reflux	 (45)	798
	Zn/Cu, CH ₂ I ₂ , Et ₂ O, reflux	 (74)	799
	Zn/Cu, CH ₂ I ₂ , Et ₂ O, reflux	 I (R=H) (70) + II (R=Me) (30)	799

TABLE VII. CYCLOPROPANATION OF CYCLIC, CHIRAL ALKENES (Continued)

Substrate	Conditions	Product(s) and Yield(s) (%), Ratio <i>syn</i> : <i>anti</i>	Refs.
	Zn/Cu, CH ₂ I ₂ , I ₂ (cat.), Et ₂ O	 I (38) + II + II + III = (20-25) III 2	800
	Zn/Cu, CH ₂ I ₂ , Et ₂ O, reflux	 (62)	801
	Zn/Cu, CH ₂ I ₂ , Et ₂ O, reflux	 (24) + (28)	802
	Zn/Cu, CH ₂ I ₂ , Et ₂ O, reflux	 (-)	801
	Zn/Cu, CD ₂ I ₂ , Et ₂ O, reflux	 (87)	795

TABLE VII. CYCLOPROPANATION OF CYCLIC, CHIRAL ALKENES (*Continued*)

Substrate	Conditions	Product(s) and Yield(s) (%), Ratio <i>syn</i> : <i>anti</i>	Refs.
 C ₂₉	Zn/Cu, CH ₂ I ₂ , I ₂ (cat.), Et ₂ O, THF, reflux	 (36)	803
	Et ₂ Zn, CH ₂ I ₂ , PhMe, rt, 8 h	 (56)	131

^a C₆H₆ was used as solvent.

TABLE VIII. CYCLOPROPANATION OF ACYCLIC, CHIRAL ALKENES

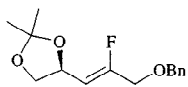
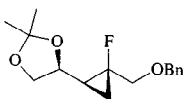


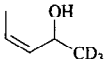

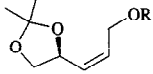
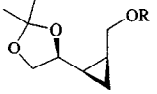
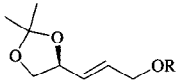
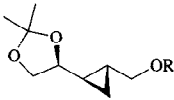
Substrate	Conditions	Product(s) and Yield(s) (%), Ratio <i>syn</i> : <i>anti</i>	Refs.																													
C_5 	Conditions, solvent		92																													
				Conditions	Solvent	(%)	de (%)																									
				Zn/Cu, CH ₂ I ₂ (5 eq)	Et ₂ O	(34)	>98																									
				Et ₂ Zn (10 eq), CH ₂ I ₂ (20 eq)	hexane	(50)	>98																									
Et ₂ Zn (2.5 eq), CH ₂ I ₂ (5 eq)	CH ₂ Cl ₂	(73)	>95																													
	Zn/Cu, CH ₂ I ₂	 (—)	804																													
	Zn/Cu, CH ₂ I ₂	 (—)	804																													
	Et ₂ Zn, CH ₂ IX		<table border="1"> <thead> <tr> <th>R</th> <th>X</th> <th>(%)</th> <th>de (%)</th> </tr> </thead> <tbody> <tr> <td>H</td> <td>Cl</td> <td>(54)</td> <td>55</td> </tr> <tr> <td>H</td> <td>I</td> <td>(61)</td> <td>17</td> </tr> <tr> <td>MOM</td> <td>I</td> <td>(86)</td> <td>84</td> </tr> <tr> <td>Bn</td> <td>I</td> <td>(94)</td> <td>68</td> </tr> <tr> <td>Bn</td> <td>I</td> <td>(73)^a</td> <td>48</td> </tr> <tr> <td>TBDPS</td> <td>Cl</td> <td>(84-95)</td> <td>>99</td> </tr> </tbody> </table>	R	X	(%)	de (%)	H	Cl	(54)	55	H	I	(61)	17	MOM	I	(86)	84	Bn	I	(94)	68	Bn	I	(73) ^a	48	TBDPS	Cl	(84-95)	>99	146, 805 147 147 147 146, 147
			R	X	(%)	de (%)																										
			H	Cl	(54)	55																										
			H	I	(61)	17																										
			MOM	I	(86)	84																										
			Bn	I	(94)	68																										
Bn	I	(73) ^a	48																													
TBDPS	Cl	(84-95)	>99																													
	Et ₂ Zn (5 eq), CH ₂ I ₂ (10 eq), CH ₂ Cl ₂ , -23 to 0°		<table border="1"> <thead> <tr> <th>R</th> <th>(%)</th> <th>de (%)</th> </tr> </thead> <tbody> <tr> <td>MOM</td> <td>(86)</td> <td>65</td> </tr> <tr> <td>Bn</td> <td>(100)</td> <td>35</td> </tr> <tr> <td>TBDPS</td> <td>(90)</td> <td>>99</td> </tr> </tbody> </table>	R	(%)	de (%)	MOM	(86)	65	Bn	(100)	35	TBDPS	(90)	>99	147																
			R	(%)	de (%)																											
			MOM	(86)	65																											
Bn	(100)	35																														
TBDPS	(90)	>99																														

TABLE VIII. CYCLOPROPANATION OF ACYCLIC, CHIRAL ALKENES (Continued)

Substrate	Conditions	Product(s) and Yield(s) (%), Ratio <i>syn</i> : <i>anti</i>	Refs.																													
	Zn/Cu, CH ₂ I ₂	(—)	804																													
	Sm, CH ₂ Cl ₂ (4 eq)	I + II (39) I:II = 3:4	806																													
	Sm, CH ₂ Cl ₂ (4 eq)	I + II (39) I:II = 2:1	806																													
	Zn/Cu, CH ₂ I ₂ , Et ₂ O, reflux	(61)	807																													
	Zn/Cu, CH ₂ I ₂ , Et ₂ O, reflux	(—)	807																													
	Zn/Cu, CH ₂ I ₂	(—)	804																													
	Zn/Cu, CD ₂ I ₂	(—)	804																													
C ₅₋₈ 	Zn/Cu, CH ₂ I ₂ , Et ₂ O, reflux		<table border="1"> <thead> <tr> <th>R¹</th> <th>R²</th> <th><i>syn:anti</i></th> </tr> </thead> <tbody> <tr> <td>Me</td> <td>H</td> <td>57:43</td> </tr> <tr> <td>Et</td> <td>H</td> <td>64:36</td> </tr> <tr> <td><i>t</i>-Bu</td> <td>H</td> <td>67:33</td> </tr> <tr> <td>H</td> <td>Me</td> <td>>99:1</td> </tr> <tr> <td>H</td> <td>Et</td> <td>>99:1</td> </tr> <tr> <td>H</td> <td><i>t</i>-Bu</td> <td>>99:1</td> </tr> </tbody> </table>	R ¹	R ²	<i>syn:anti</i>	Me	H	57:43	Et	H	64:36	<i>t</i> -Bu	H	67:33	H	Me	>99:1	H	Et	>99:1	H	<i>t</i> -Bu	>99:1	135							
R ¹	R ²	<i>syn:anti</i>																														
Me	H	57:43																														
Et	H	64:36																														
<i>t</i> -Bu	H	67:33																														
H	Me	>99:1																														
H	Et	>99:1																														
H	<i>t</i> -Bu	>99:1																														
C ₅₋₁₃ 	Et ₂ Zn (5 eq), CH ₂ I ₂ (5 eq), CH ₂ Cl ₂ , -10° to rt		<table border="1"> <thead> <tr> <th>R¹</th> <th>R²</th> <th>(%)</th> <th><i>syn:anti</i></th> </tr> </thead> <tbody> <tr> <td>Me</td> <td>Me</td> <td>(75)</td> <td>6:1</td> </tr> <tr> <td><i>n</i>-Pr</td> <td>Et</td> <td>(87)</td> <td>110:1</td> </tr> <tr> <td>Ph</td> <td>Et</td> <td>(97)</td> <td>130:1</td> </tr> <tr> <td>Ph</td> <td><i>i</i>-Pr</td> <td>(97)</td> <td>>200:1</td> </tr> <tr> <td>Ph</td> <td><i>n</i>-Bu</td> <td>(98)</td> <td>150:1</td> </tr> <tr> <td>Ph</td> <td><i>t</i>-Bu</td> <td>(84)</td> <td>>200:1</td> </tr> </tbody> </table>	R ¹	R ²	(%)	<i>syn:anti</i>	Me	Me	(75)	6:1	<i>n</i> -Pr	Et	(87)	110:1	Ph	Et	(97)	130:1	Ph	<i>i</i> -Pr	(97)	>200:1	Ph	<i>n</i> -Bu	(98)	150:1	Ph	<i>t</i> -Bu	(84)	>200:1	136
R ¹	R ²	(%)	<i>syn:anti</i>																													
Me	Me	(75)	6:1																													
<i>n</i> -Pr	Et	(87)	110:1																													
Ph	Et	(97)	130:1																													
Ph	<i>i</i> -Pr	(97)	>200:1																													
Ph	<i>n</i> -Bu	(98)	150:1																													
Ph	<i>t</i> -Bu	(84)	>200:1																													
C ₆ 	Zn/Cu, CH ₂ I ₂ , Et ₂ O, rt	(89) 81% de	148																													
	Et ₂ Zn (2 eq), CH ₂ Cl ₂ (4 eq), (CH ₂ Cl ₂) ₂ , 0°	(86)	94																													
	Zn/Cu, CH ₂ I ₂ , Et ₂ O, rt	(—) >98% de	148																													
C ₆₋₁₁ 	Zn/Cu, CH ₂ I ₂		<table border="1"> <thead> <tr> <th>R¹</th> <th>R²</th> <th>R³</th> <th>(%)</th> </tr> </thead> <tbody> <tr> <td>Ph</td> <td>H</td> <td>Me</td> <td>(—)</td> </tr> <tr> <td>Ph</td> <td>Me</td> <td>Me</td> <td>(—)</td> </tr> <tr> <td>Me</td> <td>Me</td> <td>Me</td> <td>(—)</td> </tr> </tbody> </table>	R ¹	R ²	R ³	(%)	Ph	H	Me	(—)	Ph	Me	Me	(—)	Me	Me	Me	(—)	808												
R ¹	R ²	R ³	(%)																													
Ph	H	Me	(—)																													
Ph	Me	Me	(—)																													
Me	Me	Me	(—)																													

TABLE VIII. CYCLOPROPANATION OF ACYCLIC, CHIRAL ALKENES (Continued)

Substrate	Conditions	Product(s) and Yield(s) (%), Ratio <i>syn</i> : <i>anti</i>	Refs.																				
	Conditions, CH ₂ ICl	 I + II	660, 809																				
		<table border="1"> <thead> <tr> <th>R</th> <th>Conditions</th> <th>(%)</th> <th>I:II</th> </tr> </thead> <tbody> <tr> <td>Cx</td> <td>Et₂Zn, (CH₂Cl)₂</td> <td>(80)</td> <td>20:80</td> </tr> <tr> <td>Cx</td> <td>Sm/Hg, THF</td> <td>(76)</td> <td>15:85</td> </tr> <tr> <td>PMBOCH₂</td> <td>Et₂Zn, (CH₂Cl)₂</td> <td>(81)</td> <td>70:30</td> </tr> <tr> <td>PMBOCH₂</td> <td>Sm/Hg, THF</td> <td>(90)</td> <td>35:65</td> </tr> </tbody> </table>	R	Conditions	(%)	I:II	Cx	Et ₂ Zn, (CH ₂ Cl) ₂	(80)	20:80	Cx	Sm/Hg, THF	(76)	15:85	PMBOCH ₂	Et ₂ Zn, (CH ₂ Cl) ₂	(81)	70:30	PMBOCH ₂	Sm/Hg, THF	(90)	35:65	
R	Conditions	(%)	I:II																				
Cx	Et ₂ Zn, (CH ₂ Cl) ₂	(80)	20:80																				
Cx	Sm/Hg, THF	(76)	15:85																				
PMBOCH ₂	Et ₂ Zn, (CH ₂ Cl) ₂	(81)	70:30																				
PMBOCH ₂	Sm/Hg, THF	(90)	35:65																				
C ₆₋₁₅ 	Zn/Cu, CH ₂ I ₂	 R ¹ R ² R ³ (%)	808																				
		<table border="1"> <tbody> <tr> <td>Ph</td> <td>H</td> <td>Me</td> <td>(—)</td> </tr> <tr> <td>Ph</td> <td>Me</td> <td>Me</td> <td>(—)</td> </tr> <tr> <td>Me</td> <td>Me</td> <td>Me</td> <td>(—)</td> </tr> <tr> <td>Ph</td> <td>H</td> <td>Ph</td> <td>(—)</td> </tr> </tbody> </table>	Ph	H	Me	(—)	Ph	Me	Me	(—)	Me	Me	Me	(—)	Ph	H	Ph	(—)					
Ph	H	Me	(—)																				
Ph	Me	Me	(—)																				
Me	Me	Me	(—)																				
Ph	H	Ph	(—)																				
C ₇ 	Et ₂ Zn (5 eq), CH ₂ I ₂ (10 eq), (CH ₂ Cl) ₂ , rt	 (93)	810																				
	Et ₂ Zn, CH ₂ I ₂ , CH ₂ Cl ₂ , 20°, 48 h	 (80)	811																				
	Zn/Cu, ¹³ C ₂ H ₂ I ₂ , solvent	 Solvent (%) <i>syn:anti</i> pentane (—) 6:1 Et ₂ O (—) 1:1	586																				
	Zn(CH ₂ I) ₂ , CH ₂ Cl ₂	 (—) 1.5:1	812																				
C ₇₋₉ 	Sm/Hg (xs), CH ₂ I ₂ , THF, -78° to rt	 R (%) <i>syn:anti</i> Me (67) >100:1 <i>n</i> -Pr (67) >100:1	139, 140																				
C ₇₋₁₂ 	Sm/Hg (xs), CH ₂ I ₂ , THF, -78° to rt	 R (%) <i>syn:anti</i> Me (76) 1:10 <i>n</i> -Pr (84) 1:1.3 Cx (81) 46:1	139, 140																				
C ₈ 	Conditions	 (only product) Conditions (%) Et ₂ Zn, CH ₂ I ₂ , CH ₂ Cl ₂ , -25 to 0° (75) Zn/Cu, CH ₂ I ₂ , Et ₂ O, 35° (61)	657																				
	Et ₂ Zn, CH ₂ I ₂ , Et ₂ O, 0°	 I + II (90) I:II = 1.9:1	813																				
	Et ₂ Zn (2 eq), CH ₂ I ₂ (4 eq), CH ₂ Cl ₂ , -40°	 (80)	814																				
	Zn/Cu, CH ₂ I ₂ , I ₂ (cat.), Et ₂ O, reflux	 (48)	659																				

TABLE VIII. CYCLOPROPANATION OF ACYCLIC, CHIRAL ALKENES (Continued)

Substrate	Conditions	Product(s) and Yield(s) (%), Ratio <i>syn</i> : <i>anti</i>	Refs.
	Sm/Hg (xs), CH ₂ I _X , THF, -78° to rt	 X (%) <i>syn:anti</i> Cl (67) 1:10 I (59) —	58
	Et ₂ Zn, CH ₂ I ₂ , (CH ₂ Cl) ₂ , -20°	 (89) only product	149
	Conditions	 Conditions (%) Et ₂ Zn, CH ₂ I ₂ , CH ₂ Cl ₂ , -25° (63) Zn/Cu, CH ₂ I ₂ , Et ₂ O, 35° (60) only product	150, 657
	Sm/Hg, CH ₂ I _X , THF, -78° to rt	 R X (%) <i>syn:anti</i> <i>n</i> -Bu Cl (77) >45:1 <i>n</i> -Bu I (36) 120:1 <i>t</i> -Bu Cl (80) >30:1 <i>t</i> -Bu I (99) 200:1 Ph Cl (67) 100:1 Ph I (62) 100:1	58 58 58 57, 58 58 58
	Sm/Hg, CH ₂ Cl, THF, -50° to rt, 2 h	 R (%) <i>dr</i> Et (71) >96:4 Ph (81) >96:4	660
	Sm/Hg, CH ₂ I _X , THF, -78° to rt	 R ¹ R ² X (%) <i>syn:anti</i> <i>t</i> -Bu Me I (98) 1:5.1 <i>n</i> -Bu <i>i</i> -Pr Cl (93) 5:1 <i>n</i> -Bu <i>i</i> -Pr I (74) 1.5:1 <i>t</i> -Bu <i>i</i> -Pr I (46) >200:1 Ph Me Cl (99) 1:1.3 Ph Me I (98) 1:6 Ph <i>i</i> -Pr Cl (82) 200:1 Ph <i>i</i> -Pr I (88) 200:1 Ph <i>n</i> -Bu I (99) 1:1.4 Ph <i>n</i> -Bu Cl (99) 1:1.4 Ph <i>t</i> -Bu I (76) >200:1	57, 58 58 57, 58 57, 58 58 57, 58 57, 58 57, 58 57, 58 57, 58
	Et ₂ Zn (5 eq), CH ₂ I ₂ (5 eq), CH ₂ Cl ₂ , -10° to rt	 R ¹ R ² R ³ R ⁴ R ⁵ (%) <i>syn:anti</i> H Ph H Me Me (95) 1:1.6 H Ph H Et Me (93) 3.4:1 H Ph H <i>i</i> -Pr Me (94) >20:1 H <i>n</i> -Pr H Et Bn (88) 1:2 H Ph Me Me Bn (98) 1:7 Ph(CH ₂) ₃ H H Me Bn (85) 15:1 Ph(CH ₂) ₃ H H Me Me (80) 17:1	197

TABLE VIII. CYCLOPROPANATION OF ACYCLIC, CHIRAL ALKENES (Continued)

	Substrate	Conditions	Product(s) and Yield(s) (%), Ratio <i>syn</i> : <i>anti</i>	Refs.																												
C ₉		Et ₂ Zn (2.5 eq), CH ₂ I ₂ (5 eq), CH ₂ Cl ₂	I + (66) II + III I:II:III = —	661																												
C ₉₋₁₅		Et ₂ Zn (4-4.5 eq), CH ₂ I ₂ (4-4.5 eq), CH ₂ Cl ₂ , -18 to -5°		<table border="1"> <thead> <tr> <th>R</th> <th>(%)</th> <th>GC purity (%)</th> </tr> </thead> <tbody> <tr> <td>Ph</td> <td>(82)</td> <td>97</td> </tr> <tr> <td>OBn</td> <td>(82)</td> <td>96</td> </tr> <tr> <td>CO₂Pr-<i>n</i></td> <td>(64)</td> <td>95</td> </tr> </tbody> </table>	R	(%)	GC purity (%)	Ph	(82)	97	OBn	(82)	96	CO ₂ Pr- <i>n</i>	(64)	95	145															
R	(%)	GC purity (%)																														
Ph	(82)	97																														
OBn	(82)	96																														
CO ₂ Pr- <i>n</i>	(64)	95																														
C ₁₀		Et ₂ Zn, CH ₂ I ₂ , CH ₂ Cl ₂ , rt	(—) >98:2	815																												
		Et ₂ Zn, CH ₂ I ₂ , Et ₂ O, reflux	I + II I:II = 3:1 (50)	151																												
		Et ₂ Zn (x eq), CH ₂ I ₂ (y eq), CH ₂ Cl ₂ , -10° to rt	I + II <table border="1"> <thead> <tr> <th>x</th> <th>y</th> <th>(%)</th> <th>I:II</th> </tr> </thead> <tbody> <tr> <td>2</td> <td>1</td> <td>(75)</td> <td>6.6:1</td> </tr> <tr> <td>2</td> <td>4</td> <td>(95)</td> <td>2.3:1</td> </tr> <tr> <td>5</td> <td>5</td> <td>(>95)</td> <td>7.0:1</td> </tr> <tr> <td>5</td> <td>10</td> <td>(>95)</td> <td>3.2:1</td> </tr> <tr> <td>10</td> <td>5</td> <td>(85)</td> <td>6.6:1</td> </tr> <tr> <td>2</td> <td>4</td> <td>(90)</td> <td>2.7:1</td> </tr> </tbody> </table>	x	y	(%)	I:II	2	1	(75)	6.6:1	2	4	(95)	2.3:1	5	5	(>95)	7.0:1	5	10	(>95)	3.2:1	10	5	(85)	6.6:1	2	4	(90)	2.7:1	136
x	y	(%)	I:II																													
2	1	(75)	6.6:1																													
2	4	(95)	2.3:1																													
5	5	(>95)	7.0:1																													
5	10	(>95)	3.2:1																													
10	5	(85)	6.6:1																													
2	4	(90)	2.7:1																													
		Et ₂ Zn (5 eq), CH ₂ Cl (5 eq), CH ₂ Cl ₂ , -10° to rt	I + II (80) I:II = 3.7:1	136																												
		Sm/Hg, CH ₂ I ₂		<table border="1"> <thead> <tr> <th>R</th> <th>(%)</th> <th><i>syn:anti</i></th> </tr> </thead> <tbody> <tr> <td>SnMe₃</td> <td>(26)</td> <td>>99:1</td> </tr> <tr> <td>TMS</td> <td>(40)</td> <td>>99:1</td> </tr> </tbody> </table>	R	(%)	<i>syn:anti</i>	SnMe ₃	(26)	>99:1	TMS	(40)	>99:1	98																		
R	(%)	<i>syn:anti</i>																														
SnMe ₃	(26)	>99:1																														
TMS	(40)	>99:1																														
		Sm, CH ₂ I ₂ , THF, 0°		<table border="1"> <thead> <tr> <th>R¹</th> <th>R²</th> <th>(%)</th> <th><i>syn:anti</i></th> </tr> </thead> <tbody> <tr> <td>H</td> <td>Ph</td> <td>(87)</td> <td>>99:1</td> </tr> <tr> <td>Ph</td> <td>H</td> <td>(86)</td> <td>>99:1</td> </tr> <tr> <td>H</td> <td>C₆H₁₃</td> <td>(92)</td> <td>>99:1</td> </tr> <tr> <td>C₆H₁₃</td> <td>H</td> <td>(83)</td> <td>>99:1</td> </tr> </tbody> </table>	R ¹	R ²	(%)	<i>syn:anti</i>	H	Ph	(87)	>99:1	Ph	H	(86)	>99:1	H	C ₆ H ₁₃	(92)	>99:1	C ₆ H ₁₃	H	(83)	>99:1	137							
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C ₆ H ₁₃	H	(89)	>99:1																													
C ₁₀₋₁₂		Et ₂ Zn (5 eq), CH ₂ I ₂ (5 eq), CH ₂ Cl ₂ , -10° to rt		<table border="1"> <thead> <tr> <th>R</th> <th>(%)</th> <th><i>syn:anti</i></th> </tr> </thead> <tbody> <tr> <td>Me</td> <td>(94)</td> <td>1:9</td> </tr> <tr> <td>Et</td> <td>(97)</td> <td>1:2</td> </tr> <tr> <td><i>i</i>-Pr</td> <td>(82)</td> <td>19:1</td> </tr> </tbody> </table>	R	(%)	<i>syn:anti</i>	Me	(94)	1:9	Et	(97)	1:2	<i>i</i> -Pr	(82)	19:1	136, 197															
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TABLE VIII. CYCLOPROPANATION OF ACYCLIC, CHIRAL ALKENES (Continued)

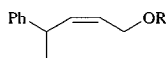
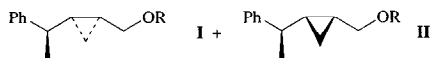
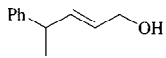

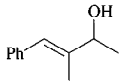
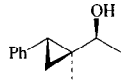
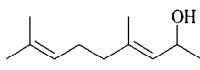
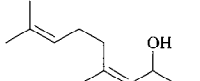
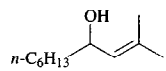
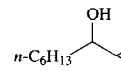
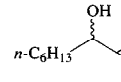
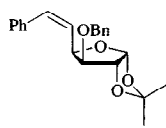
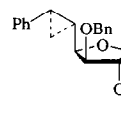
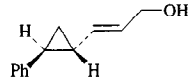
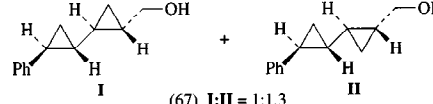
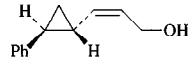
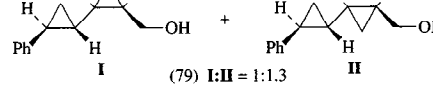
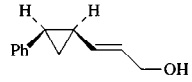
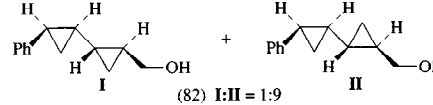
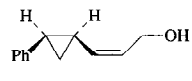
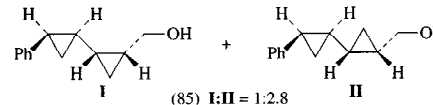
Substrate	Conditions	Product(s) and Yield(s) (%), Ratio <i>syn</i> : <i>anti</i>	Refs.																																								
C_{11} 	Conditions, CH_2IX	 I + II	660, 809																																								
		<table border="1"> <thead> <tr> <th>R</th> <th>X</th> <th>Conditions</th> <th>(%)</th> <th>I:II</th> </tr> </thead> <tbody> <tr> <td>H</td> <td>Cl</td> <td>$Et_2Zn, (CH_2Cl)_2$</td> <td>(88)</td> <td>80:20</td> </tr> <tr> <td>H</td> <td>Cl</td> <td>$Et_2Zn, PhMe$</td> <td>(94)</td> <td>85:15</td> </tr> <tr> <td>H</td> <td>I</td> <td>$Et_2Zn, (CH_2Cl)_2$</td> <td>(49)</td> <td>50:50</td> </tr> <tr> <td>H</td> <td>Cl</td> <td>Sm/Hg, THF</td> <td>(74)</td> <td>30:70</td> </tr> <tr> <td>H</td> <td>I</td> <td>Sm/Hg, THF</td> <td>(40)</td> <td>20:80</td> </tr> <tr> <td>Na</td> <td>Cl</td> <td>Et_2Zn, CH_2Cl_2</td> <td>(>99)</td> <td>80:20</td> </tr> <tr> <td>TBDMS</td> <td>Cl</td> <td>$Et_2Zn, (CH_2Cl)_2$</td> <td>(45)</td> <td>80:20</td> </tr> </tbody> </table>	R	X	Conditions	(%)	I:II	H	Cl	$Et_2Zn, (CH_2Cl)_2$	(88)	80:20	H	Cl	$Et_2Zn, PhMe$	(94)	85:15	H	I	$Et_2Zn, (CH_2Cl)_2$	(49)	50:50	H	Cl	Sm/Hg, THF	(74)	30:70	H	I	Sm/Hg, THF	(40)	20:80	Na	Cl	Et_2Zn, CH_2Cl_2	(>99)	80:20	TBDMS	Cl	$Et_2Zn, (CH_2Cl)_2$	(45)	80:20	
		R	X	Conditions	(%)	I:II																																					
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Sm/Hg, THF	(95)	50:50																																									
	Et_2Zn (5 eq), CH_2I_2 (5 eq), $CH_2Cl_2, -10^\circ$ to rt	 (95) 33:1	136																																								
	Sm/Hg (xs), CH_2IX , THF, -78° to rt	<table border="1"> <thead> <tr> <th>X</th> <th>(%)</th> <th><i>syn:anti</i></th> </tr> </thead> <tbody> <tr> <td>Cl</td> <td>(99)</td> <td>200:1</td> </tr> <tr> <td>I</td> <td>(98)</td> <td>50:1</td> </tr> </tbody> </table>	X	(%)	<i>syn:anti</i>	Cl	(99)	200:1	I	(98)	50:1	58																															
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I	(31)	48:1																																									
	Et_2Zn (2 eq), CH_2I_2 (7.5 eq), pentane	 (98)	817																																								
	$Et_2Zn, MeCH_2, Et_2O$	 (90-95) 1:2	817																																								
C_{12} 	$Zn/Cu, CH_2I_2, Et_2O$	 (48)	818																																								
			$Et_2Zn, CH_2I_2, 0^\circ$  I + II (67) I:II = 1:1.3	819, 820																																							
					$Et_2Zn, CH_2I_2, 0^\circ$  I + II (79) I:II = 1:1.3	819, 821																																					
			$Et_2Zn, CH_2I_2, 0^\circ$  I + II (82) I:II = 1:9			819, 821																																					
	$Et_2Zn, CH_2I_2, 0^\circ$  I + II (85) I:II = 1:2.8			819, 821																																							

TABLE VIII. CYCLOPROPANATION OF ACYCLIC, CHIRAL ALKENES (Continued)

Substrate	Conditions	Product(s) and Yield(s) (%), Ratio <i>syn</i> : <i>anti</i>	Refs.
	Et ₂ Zn, CH ₂ I ₂ , (CH ₂ Cl) ₂ , -20°	 (80) I:II = 1:1	155
	Et ₂ Zn, CH ₂ I ₂ , CH ₂ Cl ₂	(82) I:II ~ 1:1	822
	Zn/Cu, CH ₂ I ₂ , I ₂ (cat.), Et ₂ O, reflux, 20 h	 (39)	92
	Et ₂ Zn, CH ₂ I ₂ , CH ₂ Cl ₂ , rt	 (-) 92:8	815
C ₁₂₋₁₃ 	Et ₂ Zn (5 eq), CH ₂ I ₂ (5 eq), CH ₂ Cl ₂ , -10° to rt	 R (%) <i>syn:anti</i> Me (96) >200:1 Et (98) >200:1	136
C ₁₃ 	Et ₂ Zn, CH ₂ I ₂	 (92)	823
	Et ₂ Zn (5 eq), CH ₂ I ₂ (10 eq), CH ₂ Cl ₂ , -23 to 0°	 (91) >98	147
	Conditions, CH ₂ Cl	 I + II	660, 809
	Conditions (%) I:II		
	Et ₂ Zn, (CH ₂ Cl) ₂ (92)	85:15	
	Sm/Hg, THF (87)	40:60	
	Et ₂ Zn, CH ₂ I ₂ , air, pentane	 (55) 15:85	824
	Sm (5 eq), CH ₂ I ₂ (5 eq), TMSCl (0.2 eq), THF, -78° to rt	 (90) 1.9:1	63
C ₁₃₋₁₈ 	Me ₃ Al, CH ₂ I ₂ , CH ₂ Cl ₂ /hexane	 R (%) <i>syn:anti</i> Me (92) 42:58 <i>i</i> -Pr (79) 5:>95 Ph (95) 9:91	825, 826
	Me ₃ Al, CH ₂ I ₂ , CH ₂ Cl ₂ /hexane	 R (%) <i>syn:anti</i> Me (91) 5:>95 <i>i</i> -Pr (94) 5:>95 Ph (92) 5:>95	825, 826
C ₁₄ 	Me ₃ Al, CH ₂ I ₂ (2.8 eq), CH ₂ Cl ₂ , 0° to rt	 (-) ~1:1	153
C ₁₄₋₃₀ 	Me ₃ Al, CH ₂ I ₂ (2.8 eq), CH ₂ Cl ₂ , 0° to rt	 R ¹ R ² (%) <i>syn:anti</i> H H (86) 1:>30 Me H (74) 1:>30 Bn H (79) 1:>30 H TBDPS (-) -	153
C ₁₆ 	Zn/Cu, CH ₂ I ₂ , Et ₂ O, reflux	 (70) + (~20)	827

TABLE VIII. CYCLOPROPANATION OF ACYCLIC, CHIRAL ALKENES (Continued)

Substrate	Conditions	Product(s) and Yield(s) (%), Ratio <i>syn</i> : <i>anti</i>	Refs.																																			
	Sm/Hg (xs), CH2I2, THF, -78° to rt		140																																			
C ₁₆₋₂₅ 	Sm/Hg (xs), CH2I2, THF, -78° to rt		<table border="1"> <thead> <tr> <th>R¹</th> <th>R²</th> <th>(%)</th> <th><i>syn</i>:<i>anti</i></th> </tr> </thead> <tbody> <tr> <td>Me</td> <td>Cx</td> <td>(70)</td> <td>>50:1</td> </tr> <tr> <td>Bu</td> <td>Me</td> <td>(76)</td> <td>>50:1</td> </tr> <tr> <td>Bu</td> <td>Cx</td> <td>(75)</td> <td>>50:1</td> </tr> </tbody> </table>	R ¹	R ²	(%)	<i>syn</i> : <i>anti</i>	Me	Cx	(70)	>50:1	Bu	Me	(76)	>50:1	Bu	Cx	(75)	>50:1	140 139, 140 139, 140																		
R ¹	R ²	(%)	<i>syn</i> : <i>anti</i>																																			
Me	Cx	(70)	>50:1																																			
Bu	Me	(76)	>50:1																																			
Bu	Cx	(75)	>50:1																																			
C ₁₇ 	Me ₃ Al, CH ₂ I ₂ , CH ₂ Cl ₂ /hexane, rt		524																																			
	Zn/Cu, CH ₂ I ₂ , Et ₂ O, reflux	" (65)	524																																			
C ₁₈ 	Zn/Cu, CH ₂ I ₂		828																																			
	Zn/Cu, CH ₂ I ₂ , ultrasound, DME, 85-95°		375																																			
	Zn/Cu, CH ₂ I ₂		828																																			
	Et ₂ Zn, CH ₂ I ₂ , CH ₂ Cl ₂		829																																			
	Et ₂ Zn, CH ₂ I ₂ , CH ₂ Cl ₂		829																																			
C ₁₈₋₁₉ 	Zn source, CH ₂ I ₂ , CH ₂ Cl ₂	<table border="1"> <thead> <tr> <th>R¹</th> <th>R²</th> <th>Zn source</th> <th>(%)</th> <th>I:II</th> </tr> </thead> <tbody> <tr> <td>H</td> <td>Me</td> <td>Zn/Cu</td> <td>(62)</td> <td>4:1</td> </tr> <tr> <td>H</td> <td>Me</td> <td>Et₂Zn</td> <td>(56)</td> <td>16:1</td> </tr> <tr> <td>H</td> <td>Et</td> <td>Zn/Cu</td> <td>(58)</td> <td>4:1</td> </tr> <tr> <td>H</td> <td>Et</td> <td>Et₂Zn</td> <td>(59)</td> <td>19:1</td> </tr> <tr> <td>Me</td> <td>Me</td> <td>Zn/Cu</td> <td>(69)</td> <td>15:1</td> </tr> <tr> <td>Me</td> <td>Me</td> <td>Et₂Zn</td> <td>(82)</td> <td>19:1</td> </tr> </tbody> </table>	R ¹	R ²	Zn source	(%)	I:II	H	Me	Zn/Cu	(62)	4:1	H	Me	Et ₂ Zn	(56)	16:1	H	Et	Zn/Cu	(58)	4:1	H	Et	Et ₂ Zn	(59)	19:1	Me	Me	Zn/Cu	(69)	15:1	Me	Me	Et ₂ Zn	(82)	19:1	830
R ¹	R ²	Zn source	(%)	I:II																																		
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Me	Me	Zn/Cu	(69)	15:1																																		
Me	Me	Et ₂ Zn	(82)	19:1																																		
C ₁₈₋₂₃ 	Et ₂ Zn (2 eq), CH ₂ I ₂ (2 eq), PhMe		<table border="1"> <thead> <tr> <th>R</th> <th>(%)</th> </tr> </thead> <tbody> <tr> <td><i>n</i>-C₈H₁₁</td> <td>(91)</td> </tr> <tr> <td><i>i</i>-Pr</td> <td>(>90)</td> </tr> <tr> <td>Ph(CH₂)₂</td> <td>(>90)</td> </tr> <tr> <td>Cx</td> <td>(>90)</td> </tr> </tbody> </table>	R	(%)	<i>n</i> -C ₈ H ₁₁	(91)	<i>i</i> -Pr	(>90)	Ph(CH ₂) ₂	(>90)	Cx	(>90)	831																								
R	(%)																																					
<i>n</i> -C ₈ H ₁₁	(91)																																					
<i>i</i> -Pr	(>90)																																					
Ph(CH ₂) ₂	(>90)																																					
Cx	(>90)																																					
C ₁₉ 	Me ₃ Al, CH ₂ I ₂ , CH ₂ Cl ₂ /hexane, rt		524																																			
	Zn/Cu, CH ₂ I ₂ , Et ₂ O, reflux	" (40) 42:58	524																																			
	Zn/Cu, CH ₂ I ₂ , I ₂ (cat.), Et ₂ O, 40°		685																																			

TABLE VIII. CYCLOPROPANATION OF ACYCLIC, CHIRAL ALKENES (Continued)

Substrate	Conditions	Product(s) and Yield(s) (%), Ratio <i>syn:anti</i>	Refs.	
C ₁₉₋₂₄ 	Sm/Hg (xs), CH ₂ I ₂ , THF, -78° to rt		R (%) <i>syn:anti</i>	139, 140
		Me (85) >50:1 n-Pr (67) >50:1 Cx (80) >50:1		
C ₂₀₋₂₅ 	Sm/Hg (xs), CH ₂ I ₂ , THF, -78° to rt		R (%) <i>syn:anti</i>	140
		Me (81) >50:1 n-Pr (77) >50:1 i-Pr (89) >50:1 Cx (63) >50:1		
C ₂₃ 	Zn/Cu, CH ₂ I ₂ , Et ₂ O, reflux		(71)	524
			(74)	
C ₂₄ 	Sm (10 eq), CH ₂ I ₂ (10 eq), TMSCl (0.2 eq), THF -78° to rt		(81) >50:1	63
		Conditions	"	
		Sm/Hg, CH ₂ I ₂ , THF	(80) >50:1	140
		Zn/Cu, CH ₂ I ₂ , Et ₂ O	^b —	
		SmI ₂ , CH ₂ Cl, THF	(0) —	
		Et ₂ Zn, CH ₂ Cl, (CH ₂ Cl) ₂	(80) >50:1	
C ₂₉ 	Zn/Cu, CH ₂ I ₂ , Et ₂ O, reflux		(10)	832
C ₃₃ 	Conditions		Conditions (%) <i>syn:anti</i>	140
		Sm/Hg, CH ₂ I ₂ (71) >50:1 Et ₂ Zn, CH ₂ I ₂ (92) >50:1		

^a A Zn/Cu couple was used.^b Only the destannylated product was observed.

TABLE IX. CYCLOPROPANATION OF CHIRAL *O*- AND *N*-SUBSTITUTED ALKENES

Substrate	Conditions	Product(s) and Yield(s) (%), Ratio <i>syn</i> : <i>anti</i>	Refs.
C ₂ 	Zn/Hg, TMSCl, HC(OMe) ₃ , Et ₂ O, reflux	 (46) <i>trans</i> : <i>cis</i> = 3:1	77
C ₃ 	Zn/Hg, TMSCl, HC(OMe) ₃ , Et ₂ O, reflux	 (43) 3:1	77
C ₅ 	Et ₂ Zn, CH ₂ I ₂	 (65) I:II = 4:1	124
	Et ₂ Zn (5 eq), CH ₂ I ₂ (5 eq), PhMe, reflux	 (41) 4:1	127
C ₆ 	Et ₂ Zn, CH ₂ I ₂ , (CH ₂ Cl) ₂ , -10 to 20°	 (>45)	833
	Et ₂ Zn, CH ₂ I ₂ , PhMe, 0°	 (>32)	834
	Zn/Cu, CH ₂ I ₂ , Et ₂ O, reflux	 (38)	128
	Et ₂ Zn, CH ₂ I ₂ , Et ₂ O, rt	 (96) ~30:1	835
	Zn/Cu, CH ₂ I ₂ , AcCl, Et ₂ O, reflux	" (89)	836, 837
	Zn/Cu, CH ₂ I ₂ , AcCl, Et ₂ O, reflux	 (80)	836, 837
	Et ₂ Zn (5 eq), CH ₂ I ₂ (5 eq), Et ₂ O/hexanes	 R ¹ R ² R ³ (%) <i>syn</i> : <i>anti</i> Bn Bn Bn (92) >100:1 Me Me Me (94) ^a >100:1 TBS H H (88) ^b >100:1 CMe ₂ H (33) ^a 80:1 TBDMS TBDMS TBDMS (0) ^b —	127
	Zn/Cu, CH ₂ I ₂ , Et ₂ O, rt	 (71) + (12)	838
	Et ₂ Zn (5 eq), CH ₂ I ₂ (5 eq), PhMe	 (>85) 8.7:1	127
	Zn/Cu, CH ₂ I ₂ , AcCl, Et ₂ O, reflux	 (87)	836, 837

TABLE IX. CYCLOPROPANATION OF CHIRAL *O*- AND *N*-SUBSTITUTED ALKENES (Continued)

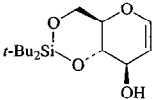
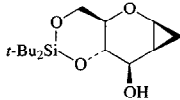
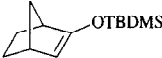

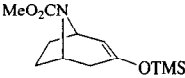
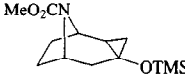
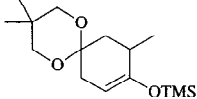
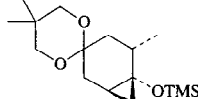




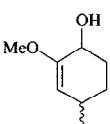
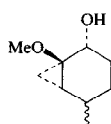
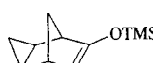
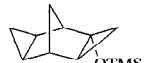
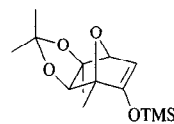
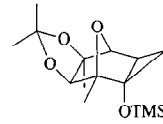
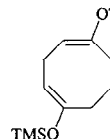
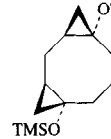
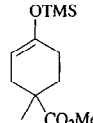
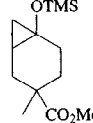
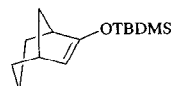

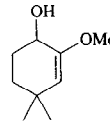
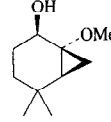
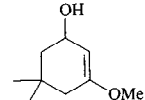
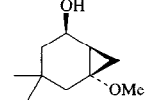
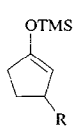
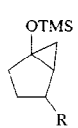
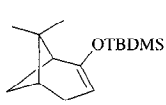
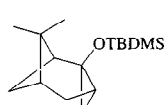
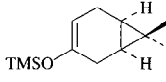
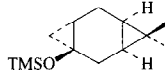
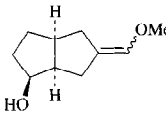
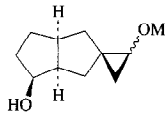
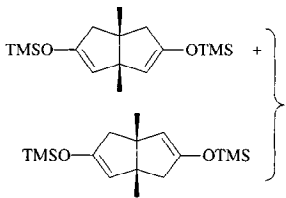
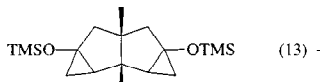
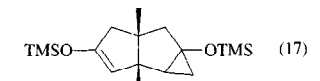
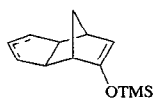
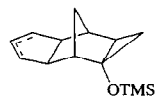
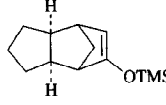
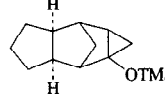
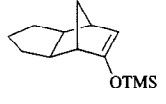
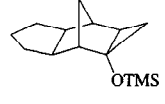
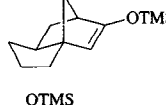
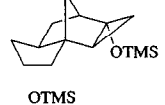
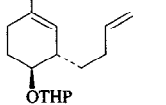
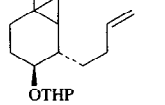
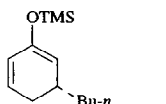
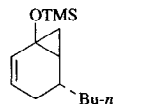
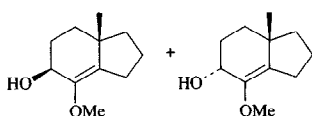
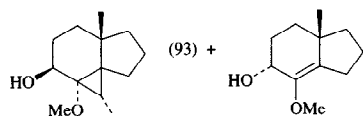
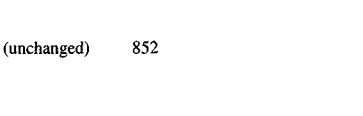
Substrate	Conditions	Product(s) and Yield(s) (%), Ratio <i>syn</i> : <i>anti</i>	Refs.
	Et ₂ Zn (3 eq), CH ₂ I ₂ (3 eq), Et ₂ O, 0°	 (96) >250:1	839
C₇ 	Zn/Ag, CH ₂ I ₂ , Et ₂ O, reflux	 (69)	840
	Et ₂ Zn, CH ₂ Cl ₂ , (CH ₂ Cl) ₂	 (99)	842
	Et ₂ Zn, CH ₂ I ₂ , PhMe, 55°	 (81) 2:1	842a
	Zn/Cu, CH ₂ I ₂ , Et ₂ O, reflux	 (64) ~1:1	83
	Zn/Ag, CH ₂ I ₂	" (74)	81
	SmI ₂ , CH ₂ I ₂ , THF, -78° to rt	 (59) 2:3	88, 110
	Et ₂ Zn, CH ₂ I ₂ , O ₂ , PhMe	 (99)	844, 845
C₈ 	Zn/Ag, CH ₂ I ₂ , Et ₂ O, reflux	 (~65)	840
	Et ₂ Zn, CH ₂ Cl ₂ , (CH ₂ Cl) ₂ , 0°	 (>81)	841
	Et ₂ Zn (6 eq), CH ₂ I ₂ (10 eq), Et ₂ O, O ₂	 (>77) >15:1	132
	Zn/Ag, CH ₂ I ₂ , Et ₂ O, reflux	 (87)	363
	Zn/Ag, CH ₂ I ₂ , Et ₂ O, reflux	 (76)	840
	Zn/Cu, CH ₂ I ₂ , I ₂ (cat.), Et ₂ O, reflux	 (~70)	846
	Zn/Cu, CH ₂ I ₂ , I ₂ (cat.), Et ₂ O, reflux	 (19)	847

TABLE IX. CYCLOPROPANATION OF CHIRAL *O*- AND *N*-SUBSTITUTED ALKENES (Continued)

Substrate	Conditions	Product(s) and Yield(s) (%), Ratio <i>syn</i> : <i>anti</i>	Refs.														
C ₈₋₁₂ 	Et ₂ Zn, CH ₂ I ₂ , Et ₂ O	 <table border="1"> <thead> <tr> <th>R</th> <th>(%)</th> </tr> </thead> <tbody> <tr> <td><i>n</i>-Bu</td> <td>(93)</td> </tr> <tr> <td><i>t</i>-Bu</td> <td>(74)</td> </tr> <tr> <td>CH₂=CHCH₂</td> <td>(78)</td> </tr> <tr> <td>CH₂=CH(CH₂)₂</td> <td>(92)</td> </tr> <tr> <td>Ph</td> <td>(80)</td> </tr> <tr> <td>Bn</td> <td>(87)</td> </tr> </tbody> </table>	R	(%)	<i>n</i> -Bu	(93)	<i>t</i> -Bu	(74)	CH ₂ =CHCH ₂	(78)	CH ₂ =CH(CH ₂) ₂	(92)	Ph	(80)	Bn	(87)	365
R	(%)																
<i>n</i> -Bu	(93)																
<i>t</i> -Bu	(74)																
CH ₂ =CHCH ₂	(78)																
CH ₂ =CH(CH ₂) ₂	(92)																
Ph	(80)																
Bn	(87)																
C ₉ 	Zn/Ag, CH ₂ I ₂ , Et ₂ O, reflux	 (~40)	840														
	Zn/Ag, CH ₂ I ₂ , Et ₂ O, reflux	 (31)	848														
	Zn/Cu, CH ₂ I ₂ , I ₂ (cat.), Et ₂ O, reflux	 (82) >98:2	849														
C ₁₀ 	Zn/Cu, CH ₂ I ₂ , Et ₂ O	 (13) +  (17)	668														
	Zn/Ag, CH ₂ I ₂ , Et ₂ O, rt	 (85)	665														
	Zn/Ag, CH ₂ I ₂ , Et ₂ O, reflux	 (—)	850														
	Zn/Ag, CH ₂ I ₂ , Et ₂ O, reflux	 (94)	665														
	Zn/Ag, CH ₂ I ₂ , Et ₂ O, reflux	 (65)	851														
	Et ₂ Zn, CH ₂ I ₂ , Et ₂ O, reflux	 (87) 10:1	669, 674														
	Et ₂ Zn, CH ₂ I ₂ , C ₆ H ₆	 (>22)	670														
	Et ₂ Zn, MeCH ₂ I, O ₂ , Et ₂ O, reflux	 (93) +  (unchanged)	852														

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TABLE IX. CYCLOPROPANATION OF CHIRAL *O*- AND *N*-SUBSTITUTED ALKENES (Continued)

Substrate	Conditions	Product(s) and Yield(s) (%), Ratio <i>syn</i> : <i>anti</i>	Refs.																				
	Et ₂ Zn, CH ₂ I ₂ , Et ₂ O	(84)	365																				
	Et ₂ Zn (2 eq), CH ₂ I ₂ (2 eq), dry air, hexane, 0° to rt	(92) 3.5:1	853																				
	Et ₂ Zn, CH ₂ I ₂ , Et ₂ O, rt	(93)	854, 855																				
	Zn/Cu, CH ₂ I ₂ , Et ₂ O, reflux	(73) 1:1	79, 83																				
	Et ₂ Zn (1.5 eq), CH ₂ I ₂ (1.3 eq), PhMe, 0°	(>91)	856																				
	Et ₂ Zn (2 eq), CHFI ₂ (2 eq), CH ₂ Cl ₂ , -40°	I + II	91, 548																				
		<table border="1"> <thead> <tr> <th>R¹</th> <th>R²</th> <th>(%)</th> <th>I:II</th> </tr> </thead> <tbody> <tr> <td>Me</td> <td>Bn</td> <td>(97)</td> <td>89:11</td> </tr> <tr> <td>Me</td> <td><i>t</i>-Bu</td> <td>(67)</td> <td>91:9</td> </tr> <tr> <td>Ph</td> <td>Bn</td> <td>(90)</td> <td>93:7</td> </tr> <tr> <td>Ph</td> <td><i>t</i>-Bu</td> <td>(87)</td> <td>93:7</td> </tr> </tbody> </table>	R ¹	R ²	(%)	I:II	Me	Bn	(97)	89:11	Me	<i>t</i> -Bu	(67)	91:9	Ph	Bn	(90)	93:7	Ph	<i>t</i> -Bu	(87)	93:7	
R ¹	R ²	(%)	I:II																				
Me	Bn	(97)	89:11																				
Me	<i>t</i> -Bu	(67)	91:9																				
Ph	Bn	(90)	93:7																				
Ph	<i>t</i> -Bu	(87)	93:7																				
	Et ₂ Zn, CH ₂ I ₂ , PhMe, heat	(75)	108																				
	Zn/Cu, CH ₂ I ₂ , Et ₂ O, reflux	(77)	857, 858																				
	Et ₂ Zn (1.2 eq), CH ₂ I ₂ (1.2 eq), Et ₂ O, reflux	(82)	674																				
	Et ₂ Zn, CH ₂ I ₂ , Et ₂ O	(87)	365																				
	Zn/Cu, CH ₂ I ₂ , Et ₂ O/DME	(59)	859																				
	Et ₂ Zn (1.3 eq), CH ₂ I ₂ (2 eq), Et ₂ O	(91) ~1:1	860																				
	Et ₂ Zn, CH ₂ I ₂ , dry air, Et ₂ O, reflux	(99)	852																				

TABLE IX. CYCLOPROPANATION OF CHIRAL *O*- AND *N*-SUBSTITUTED ALKENES (Continued)

Substrate	Conditions	Product(s) and Yield(s) (%), Ratio <i>syn</i> : <i>anti</i>	Refs.
	Zn/Ag, CH ₂ I ₂ , Et ₂ O, reflux	(65)	861
C ₁₂₋₁₉ 	Zn/Cu, CH ₂ I ₂ , Et ₂ O/DME	 R _____ (%) H (83) 3-MeOC ₆ H ₄ CH ₂ (66)	859
C ₁₃ 	Et ₂ Zn, CH ₂ I ₂ , Et ₂ O	(59)	360
	SmI ₂ , CH ₂ Cl ₂ , -78 to -20°	+ (>61) I:II = 3:1	676
	SmI ₂ , CH ₂ Cl ₂ , -78 to -20°	" (—) I:II = 4.3:1	
C ₁₄ 	Et ₂ Zn, CH ₂ I ₂ , C ₆ H ₆ , 0° to rt	(>77)	670
	Zn/Cu, CH ₂ I ₂ , I ₂ (cat.), Et ₂ O, reflux	(91)	366
C ₁₆ 	Et ₂ Zn (5 eq), CH ₂ I ₂ (10 eq), Et ₂ O, rt	(-80) ~1:1	860, 862
C ₁₇ 	Et ₂ Zn, CH ₂ I ₂ , Et ₂ O	(94)	863
C ₁₈ 	Et ₂ Zn, CH ₂ I ₂	(—)	133
	Et ₂ Zn, CH ₂ Cl ₂ , (CH ₂ Cl) ₂ , 0°	(>99)	109
	Zn/Cu, CH ₂ I ₂	(—)	864

TABLE IX. CYCLOPROPANATION OF CHIRAL *O*- AND *N*-SUBSTITUTED ALKENES (Continued)

	Substrate	Conditions	Product(s) and Yield(s) (%), Ratio <i>syn</i> : <i>anti</i>	Refs.									
C ₁₉		Zn/Ag, CH ₂ I ₂ , Et ₂ O, reflux	(—)	81, 350									
		Zn/Ag, CH ₂ I ₂ , Et ₂ O, reflux	(85) ~1:1	81, 350									
		Zn/Cu, CH ₂ I ₂ , Et ₂ O, reflux	<table border="1" style="margin-left: 20px;"> <thead> <tr> <th>R</th> <th>(%)</th> </tr> </thead> <tbody> <tr> <td>Me</td> <td>(33)</td> </tr> <tr> <td>Cl(CH₂)₂</td> <td>(45)</td> </tr> <tr> <td>Ac</td> <td>(19)</td> </tr> <tr> <td>TMS</td> <td>(—)</td> </tr> </tbody> </table>	R	(%)	Me	(33)	Cl(CH ₂) ₂	(45)	Ac	(19)	TMS	(—)
R	(%)												
Me	(33)												
Cl(CH ₂) ₂	(45)												
Ac	(19)												
TMS	(—)												
C ₂₀		Et ₂ Zn, CH ₂ I ₂	(24)	133									
		Zn/Ag, CH ₂ I ₂ , Et ₂ O	(59)	686									
		Zn/Ag, CH ₂ I ₂ , Et ₂ O	(89)	686									
C ₂₂		MeLi, DME; Zn/Cu, CH ₂ I ₂ , Et ₂ O	(71)	86									
C ₂₆		Zn/Ag, CH ₂ I ₂ , THF	(—)	866									
		LDA, THF; Zn/Ag, CH ₂ I ₂ , Et ₂ O	(67)	86									

^a 3 equiv. of Et₂Zn and CH₂I₂ were used.^b PhMe was used as solvent.

TABLE X. CYCLOPROPANATION OF ALLENES

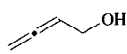
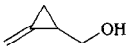
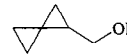




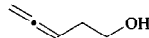
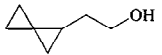
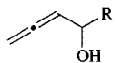
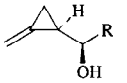
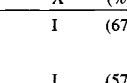
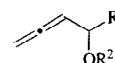
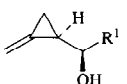
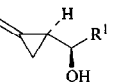
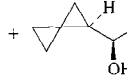
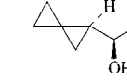
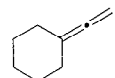
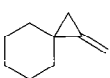
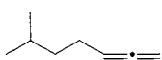
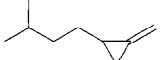
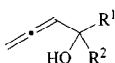
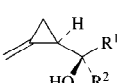
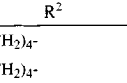
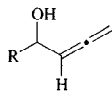
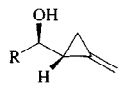
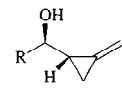
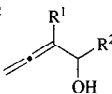
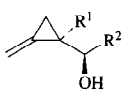
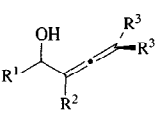
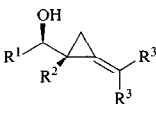
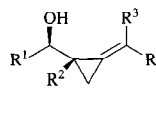
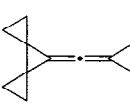
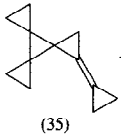
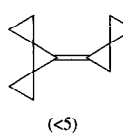
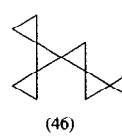
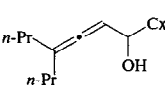
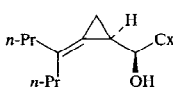
Substrate	Conditions	Product(s) and Yield(s) (%), Ratio <i>syn</i> : <i>anti</i>	Refs.																																																																																																								
C ₄ 	Zn/Cu, CH ₂ I ₂ , Et ₂ O	 (47) +  (10)	867																																																																																																								
C ₅ 	Zn/Cu, CH ₂ I ₂ , Et ₂ O, ultrasound	 I (30-40) +  II (10-15)	868																																																																																																								
	Zn/Cu, CH ₂ I ₂ , Et ₂ O	I (33) + II (13)	404																																																																																																								
	Zn/Ag, CH ₂ I ₂	 (—)	869																																																																																																								
	Me ₃ Al (3 eq), CH ₂ I ₂ (2 eq), CH ₂ Cl ₂	 (71)	581																																																																																																								
C ₇₋₁₁ 	Zn/Cu, CH ₂ I ₂ or EtZnI, CH ₂ I ₂ Sm/Hg (xs), CH ₂ IX, THF, -78° to rt	 I +  II	870																																																																																																								
		<table border="1"> <thead> <tr> <th>R</th> <th>X</th> <th>(%)</th> <th><i>syn</i>:<i>anti</i></th> </tr> </thead> <tbody> <tr> <td><i>i</i>-Pr</td> <td>I</td> <td>(67)</td> <td>4:1</td> </tr> <tr> <td><i>t</i>-Bu</td> <td>I</td> <td>(57)</td> <td>50:1</td> </tr> <tr> <td>Cx</td> <td>I</td> <td>(64)</td> <td>9.5:1</td> </tr> <tr> <td>Cx</td> <td>Cl</td> <td>(82)</td> <td>9.5:1</td> </tr> <tr> <td><i>n</i>-C₇H₁₅</td> <td>I</td> <td>(73)</td> <td>1:2.1</td> </tr> </tbody> </table>	R	X	(%)	<i>syn</i> : <i>anti</i>	<i>i</i> -Pr	I	(67)	4:1	<i>t</i> -Bu	I	(57)	50:1	Cx	I	(64)	9.5:1	Cx	Cl	(82)	9.5:1	<i>n</i> -C ₇ H ₁₅	I	(73)	1:2.1	142, 418 142, 418 142 142, 418																																																																																
R	X	(%)	<i>syn</i> : <i>anti</i>																																																																																																								
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<i>n</i> -C ₇ H ₁₅	I	(73)	1:2.1																																																																																																								
	M source, CH ₂ IX, solvent, temp	 I +  II  III +  IV	142																																																																																																								
		<table border="1"> <thead> <tr> <th>R¹</th> <th>R²</th> <th>M source (eq)</th> <th>CH₂IX (eq)</th> <th>Solvent</th> <th>Temp</th> <th>(%)</th> <th>I:III:IV</th> </tr> </thead> <tbody> <tr> <td><i>i</i>-Pr</td> <td>H</td> <td>Zn/Cu (2.1)</td> <td>CH₂I₂ (2)</td> <td>Et₂O</td> <td>reflux</td> <td>(73)</td> <td>40:10:35:15</td> </tr> <tr> <td><i>i</i>-Pr</td> <td>H</td> <td>Sm(Hg) (7)</td> <td>CH₂I₂ (7)</td> <td>THF</td> <td>-78° to rt</td> <td>(67)</td> <td>80:20:0:0</td> </tr> <tr> <td>Cx</td> <td>H</td> <td>Zn/Cu (2)</td> <td>CH₂I₂ (2)</td> <td>Et₂O</td> <td>reflux</td> <td>(40)</td> <td>83:17^a</td> </tr> <tr> <td>Cx</td> <td>H</td> <td>Zn/Cu (5)</td> <td>CH₂I₂ (3.5)</td> <td>Et₂O</td> <td>reflux</td> <td>(100)</td> <td>27:54^a</td> </tr> <tr> <td>Cx</td> <td>H</td> <td>Et₂Zn (1)</td> <td>CH₂ICl (1)</td> <td>CH₂Cl₂</td> <td>0°</td> <td>(69)</td> <td>67:3:20:10</td> </tr> <tr> <td>Cx</td> <td>H</td> <td>Et₂Zn (2.1)</td> <td>CH₂I₂ (2.1)</td> <td>PhMe</td> <td>0° to rt</td> <td>(92)</td> <td>45:55^a</td> </tr> <tr> <td>Cx</td> <td>H</td> <td>Et₃Al (1.2)</td> <td>CH₂I₂ (1.2)</td> <td>CH₂Cl₂</td> <td>0° to rt</td> <td>(<5)</td> <td>—</td> </tr> <tr> <td>Cx</td> <td>H</td> <td>Sm (10)</td> <td>CH₂ICl (10)</td> <td>THF</td> <td>-78° to rt</td> <td>(82)</td> <td>90:10:0:0</td> </tr> <tr> <td>Cx</td> <td>Li</td> <td>Et₂Zn (1)</td> <td>CH₂ICl (1)</td> <td>CH₂Cl₂</td> <td>0° to rt</td> <td>(37)</td> <td>85:trace:13:3</td> </tr> <tr> <td>Cx</td> <td>Na</td> <td>Et₂Zn (1)</td> <td>CH₂ICl (1)</td> <td>CH₂Cl₂</td> <td>0° to rt</td> <td>(83)</td> <td>91:2:4:3</td> </tr> <tr> <td>Cx</td> <td>Na</td> <td>Et₂Zn (2.4)</td> <td>CH₂ICl (2.4)</td> <td>CH₂Cl₂</td> <td>0° to rt</td> <td>(100)</td> <td>72:0:22:6</td> </tr> <tr> <td>Cx</td> <td>K</td> <td>Et₂Zn (1)</td> <td>CH₂ICl (1)</td> <td>CH₂Cl₂</td> <td>0° to rt</td> <td>(20)</td> <td>82:0:18:trace</td> </tr> </tbody> </table>	R ¹	R ²	M source (eq)	CH ₂ IX (eq)	Solvent	Temp	(%)	I:III:IV	<i>i</i> -Pr	H	Zn/Cu (2.1)	CH ₂ I ₂ (2)	Et ₂ O	reflux	(73)	40:10:35:15	<i>i</i> -Pr	H	Sm(Hg) (7)	CH ₂ I ₂ (7)	THF	-78° to rt	(67)	80:20:0:0	Cx	H	Zn/Cu (2)	CH ₂ I ₂ (2)	Et ₂ O	reflux	(40)	83:17 ^a	Cx	H	Zn/Cu (5)	CH ₂ I ₂ (3.5)	Et ₂ O	reflux	(100)	27:54 ^a	Cx	H	Et ₂ Zn (1)	CH ₂ ICl (1)	CH ₂ Cl ₂	0°	(69)	67:3:20:10	Cx	H	Et ₂ Zn (2.1)	CH ₂ I ₂ (2.1)	PhMe	0° to rt	(92)	45:55 ^a	Cx	H	Et ₃ Al (1.2)	CH ₂ I ₂ (1.2)	CH ₂ Cl ₂	0° to rt	(<5)	—	Cx	H	Sm (10)	CH ₂ ICl (10)	THF	-78° to rt	(82)	90:10:0:0	Cx	Li	Et ₂ Zn (1)	CH ₂ ICl (1)	CH ₂ Cl ₂	0° to rt	(37)	85:trace:13:3	Cx	Na	Et ₂ Zn (1)	CH ₂ ICl (1)	CH ₂ Cl ₂	0° to rt	(83)	91:2:4:3	Cx	Na	Et ₂ Zn (2.4)	CH ₂ ICl (2.4)	CH ₂ Cl ₂	0° to rt	(100)	72:0:22:6	Cx	K	Et ₂ Zn (1)	CH ₂ ICl (1)	CH ₂ Cl ₂	0° to rt	(20)	82:0:18:trace	
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<i>i</i> -Pr	H	Sm(Hg) (7)	CH ₂ I ₂ (7)	THF	-78° to rt	(67)	80:20:0:0																																																																																																				
Cx	H	Zn/Cu (2)	CH ₂ I ₂ (2)	Et ₂ O	reflux	(40)	83:17 ^a																																																																																																				
Cx	H	Zn/Cu (5)	CH ₂ I ₂ (3.5)	Et ₂ O	reflux	(100)	27:54 ^a																																																																																																				
Cx	H	Et ₂ Zn (1)	CH ₂ ICl (1)	CH ₂ Cl ₂	0°	(69)	67:3:20:10																																																																																																				
Cx	H	Et ₂ Zn (2.1)	CH ₂ I ₂ (2.1)	PhMe	0° to rt	(92)	45:55 ^a																																																																																																				
Cx	H	Et ₃ Al (1.2)	CH ₂ I ₂ (1.2)	CH ₂ Cl ₂	0° to rt	(<5)	—																																																																																																				
Cx	H	Sm (10)	CH ₂ ICl (10)	THF	-78° to rt	(82)	90:10:0:0																																																																																																				
Cx	Li	Et ₂ Zn (1)	CH ₂ ICl (1)	CH ₂ Cl ₂	0° to rt	(37)	85:trace:13:3																																																																																																				
Cx	Na	Et ₂ Zn (1)	CH ₂ ICl (1)	CH ₂ Cl ₂	0° to rt	(83)	91:2:4:3																																																																																																				
Cx	Na	Et ₂ Zn (2.4)	CH ₂ ICl (2.4)	CH ₂ Cl ₂	0° to rt	(100)	72:0:22:6																																																																																																				
Cx	K	Et ₂ Zn (1)	CH ₂ ICl (1)	CH ₂ Cl ₂	0° to rt	(20)	82:0:18:trace																																																																																																				
C ₈ 	Zn/Cu, CH ₂ I ₂ , I ₂ (cat.), Et ₂ O, reflux	 (6)	871																																																																																																								
	Zn/Cu, CH ₂ I ₂	 (low yield)	871																																																																																																								
	Sm/Hg (xs), CH ₂ IX, THF, -78° to rt	 I +  II	142																																																																																																								
		<table border="1"> <thead> <tr> <th>R¹</th> <th>R²</th> <th>X</th> <th>(%)</th> </tr> </thead> <tbody> <tr> <td>-(CH₂)₄-</td> <td></td> <td>I</td> <td>(30)</td> </tr> <tr> <td>-(CH₂)₄-</td> <td></td> <td>Cl</td> <td>(58)</td> </tr> <tr> <td><i>i</i>-Pr</td> <td>Me</td> <td>I</td> <td>(46)</td> </tr> </tbody> </table>	R ¹	R ²	X	(%)	-(CH ₂) ₄ -		I	(30)	-(CH ₂) ₄ -		Cl	(58)	<i>i</i> -Pr	Me	I	(46)	142 142 142, 418																																																																																								
R ¹	R ²	X	(%)																																																																																																								
-(CH ₂) ₄ -		I	(30)																																																																																																								
-(CH ₂) ₄ -		Cl	(58)																																																																																																								
<i>i</i> -Pr	Me	I	(46)																																																																																																								

TABLE X. CYCLOPROPANATION OF ALLENES (Continued)

Substrate	Conditions	Product(s) and Yield(s) (%), Ratio <i>syn</i> : <i>anti</i>	Refs.																																																																																																								
C_{10-11} 	Sm, CH ₂ I ₂ , additive, THF, -78° to rt	 I +  II <table border="1"> <thead> <tr> <th>R</th> <th>Additive</th> <th>(%)</th> <th>I:II</th> </tr> </thead> <tbody> <tr><td><i>n</i>-C₇H₁₅</td><td>—</td><td>(34)</td><td>2.1:1</td></tr> <tr><td><i>n</i>-C₇H₁₅</td><td>HgCl₂</td><td>(73)</td><td>1:2.1</td></tr> <tr><td><i>n</i>-C₇H₁₅</td><td>TMSCl</td><td>(82)</td><td>1:1.1</td></tr> <tr><td><i>n</i>-C₇H₁₅</td><td>TBDMSCl</td><td>(78)</td><td>1.7:1</td></tr> <tr><td><i>n</i>-C₇H₁₅</td><td>(MeO)₃SiCl</td><td>(66)</td><td>1:1.1</td></tr> <tr><td><i>n</i>-C₇H₁₅</td><td>Ti(OPr-<i>i</i>)₄</td><td>(79)</td><td>1.5:1</td></tr> <tr><td>Cx</td><td>HgCl₂</td><td>(64)</td><td>9.5:1</td></tr> <tr><td>Cx</td><td>TMSCl</td><td>(65)</td><td>17:1</td></tr> <tr><td>Cx</td><td>TBDMSCl</td><td>(60)</td><td>44:1</td></tr> <tr><td>Cx</td><td>Ti(OPr-<i>i</i>)₄</td><td>(59)</td><td>>50:1</td></tr> </tbody> </table>	R	Additive	(%)	I:II	<i>n</i> -C ₇ H ₁₅	—	(34)	2.1:1	<i>n</i> -C ₇ H ₁₅	HgCl ₂	(73)	1:2.1	<i>n</i> -C ₇ H ₁₅	TMSCl	(82)	1:1.1	<i>n</i> -C ₇ H ₁₅	TBDMSCl	(78)	1.7:1	<i>n</i> -C ₇ H ₁₅	(MeO) ₃ SiCl	(66)	1:1.1	<i>n</i> -C ₇ H ₁₅	Ti(OPr- <i>i</i>) ₄	(79)	1.5:1	Cx	HgCl ₂	(64)	9.5:1	Cx	TMSCl	(65)	17:1	Cx	TBDMSCl	(60)	44:1	Cx	Ti(OPr- <i>i</i>) ₄	(59)	>50:1	63																																																												
R	Additive	(%)	I:II																																																																																																								
<i>n</i> -C ₇ H ₁₅	—	(34)	2.1:1																																																																																																								
<i>n</i> -C ₇ H ₁₅	HgCl ₂	(73)	1:2.1																																																																																																								
<i>n</i> -C ₇ H ₁₅	TMSCl	(82)	1:1.1																																																																																																								
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<i>n</i> -C ₇ H ₁₅	Ti(OPr- <i>i</i>) ₄	(79)	1.5:1																																																																																																								
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Cx	Ti(OPr- <i>i</i>) ₄	(59)	>50:1																																																																																																								
C_{10-12} 	Sm/Hg (xs), CH ₂ I ₂ , THF, -78° to rt	 <table border="1"> <thead> <tr> <th>R¹</th> <th>R²</th> <th>(%)</th> <th><i>syn</i>:<i>anti</i></th> </tr> </thead> <tbody> <tr><td>Cx</td><td>Me</td><td>(66)</td><td>7.9:1</td></tr> <tr><td><i>n</i>-C₇H₁₅</td><td>Me</td><td>(52)</td><td>1:2.1</td></tr> <tr><td>Cx</td><td>OMe</td><td>(47)</td><td>50:1</td></tr> <tr><td><i>n</i>-C₇H₁₅</td><td>OMe</td><td>(59)</td><td>13:1</td></tr> </tbody> </table>	R ¹	R ²	(%)	<i>syn</i> : <i>anti</i>	Cx	Me	(66)	7.9:1	<i>n</i> -C ₇ H ₁₅	Me	(52)	1:2.1	Cx	OMe	(47)	50:1	<i>n</i> -C ₇ H ₁₅	OMe	(59)	13:1	142, 418 142 418 142, 418																																																																																				
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<i>n</i> -C ₇ H ₁₅	OMe	(59)	13:1																																																																																																								
C_{10-13} 	Sm (x eq), CH ₂ I ₂ (y eq), TMSCl (z eq), THF, -78° to rt	 I +  II <table border="1"> <thead> <tr> <th>R¹</th> <th>R²</th> <th>R³</th> <th>x</th> <th>y</th> <th>z</th> <th>(%)</th> <th>I:II</th> </tr> </thead> <tbody> <tr><td><i>n</i>-C₇H₁₅</td><td>H</td><td>H</td><td>10</td><td>10</td><td>8.8</td><td>(81)</td><td>1:2.2</td></tr> <tr><td><i>n</i>-C₇H₁₅</td><td>H</td><td>H</td><td>10</td><td>10</td><td>0.22</td><td>(82)</td><td>1.1:1</td></tr> <tr><td><i>n</i>-C₇H₁₅</td><td>H</td><td>H</td><td>8</td><td>8</td><td>0.4</td><td>(67)</td><td>1:1.6</td></tr> <tr><td><i>n</i>-C₇H₁₅</td><td>H</td><td>H</td><td>10</td><td>10</td><td>1.29</td><td>(62)</td><td>2.5:1</td></tr> <tr><td>Cx</td><td>H</td><td>H</td><td>10</td><td>10</td><td>0.2</td><td>(65)</td><td>17:1</td></tr> <tr><td>Cx</td><td>H</td><td>H</td><td>10</td><td>10</td><td>0.4</td><td>(65)</td><td>14.5:1</td></tr> <tr><td>Cx</td><td>H</td><td>H</td><td>10</td><td>10</td><td>0.2</td><td>(80)</td><td>7:1</td></tr> <tr><td>Cx</td><td>H</td><td>H</td><td>12</td><td>12</td><td>0.3</td><td>(44)</td><td>30:1</td></tr> <tr><td>Cx</td><td>H</td><td>H</td><td>10</td><td>10</td><td>0.2</td><td>(50)</td><td>11:1</td></tr> <tr><td>Cx</td><td>Me</td><td>H</td><td>10</td><td>10</td><td>0.28</td><td>(52)</td><td>25:1</td></tr> <tr><td><i>n</i>-C₇H₁₅</td><td>Me</td><td>H</td><td>10</td><td>10</td><td>0.24</td><td>(40)</td><td>1.2:1</td></tr> <tr><td>Cx</td><td>H</td><td><i>n</i>-Pr</td><td>10</td><td>10</td><td>0.3</td><td>(52)</td><td>4.4:1</td></tr> </tbody> </table>	R ¹	R ²	R ³	x	y	z	(%)	I:II	<i>n</i> -C ₇ H ₁₅	H	H	10	10	8.8	(81)	1:2.2	<i>n</i> -C ₇ H ₁₅	H	H	10	10	0.22	(82)	1.1:1	<i>n</i> -C ₇ H ₁₅	H	H	8	8	0.4	(67)	1:1.6	<i>n</i> -C ₇ H ₁₅	H	H	10	10	1.29	(62)	2.5:1	Cx	H	H	10	10	0.2	(65)	17:1	Cx	H	H	10	10	0.4	(65)	14.5:1	Cx	H	H	10	10	0.2	(80)	7:1	Cx	H	H	12	12	0.3	(44)	30:1	Cx	H	H	10	10	0.2	(50)	11:1	Cx	Me	H	10	10	0.28	(52)	25:1	<i>n</i> -C ₇ H ₁₅	Me	H	10	10	0.24	(40)	1.2:1	Cx	H	<i>n</i> -Pr	10	10	0.3	(52)	4.4:1	63
R ¹	R ²	R ³	x	y	z	(%)	I:II																																																																																																				
<i>n</i> -C ₇ H ₁₅	H	H	10	10	8.8	(81)	1:2.2																																																																																																				
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Cx	H	<i>n</i> -Pr	10	10	0.3	(52)	4.4:1																																																																																																				
C_{11} 	Et ₂ Zn, CH ₂ I ₂ , Et ₂ O	 (35) +  (<5) +  (46)	872																																																																																																								
C_{16} 	Sm/Hg (xs), CH ₂ I ₂ , THF, -78° to rt	 <table border="1"> <thead> <tr> <th>X</th> <th>(%)</th> <th><i>syn</i>:<i>anti</i></th> </tr> </thead> <tbody> <tr><td>Cl</td><td>(70)</td><td>1.7:1</td></tr> <tr><td>I</td><td>(43)</td><td>1.7:1</td></tr> </tbody> </table>	X	(%)	<i>syn</i> : <i>anti</i>	Cl	(70)	1.7:1	I	(43)	1.7:1	142, 418																																																																																															
X	(%)	<i>syn</i> : <i>anti</i>																																																																																																									
Cl	(70)	1.7:1																																																																																																									
I	(43)	1.7:1																																																																																																									

^a (I+II):(III+IV)

TABLE XI. CYCLOPROPANATION OF CYCLIC ALKENES CONTAINING A CLEAVABLE CHIRAL AUXILIARY

Substrate	Conditions	Product(s) and Yield(s) (%), and de (%)	Refs.																																																								
C ₂ 	Et ₂ Zn, CH ₂ I ₂ , Et ₂ O	(83) >50:1	873, 874																																																								
C ₃ 	Et ₂ Zn, CH ₂ I ₂ , Et ₂ O	(52) >50:1	873, 874																																																								
C ₅ 	Zn/Cu, CH ₂ I ₂ , I ₂ (cat.), Et ₂ O, reflux	(72) 9:1	163, 164																																																								
	Et ₂ Zn (5 eq), CH ₂ I ₂ (10 eq), Et ₂ O, 20°	(81) >99	174, 176																																																								
C ₅₋₆ 	Zn/Cu, CH ₂ I ₂ , I ₂ (cat.), Et ₂ O, reflux	<table border="1"> <thead> <tr> <th>R¹</th> <th>R²</th> <th>(%)</th> <th>dr</th> </tr> </thead> <tbody> <tr> <td>BnOCH₂</td> <td>H</td> <td>(72)</td> <td>9:1</td> </tr> <tr> <td>Ph</td> <td>H</td> <td>(66)</td> <td>13:1</td> </tr> <tr> <td>BnOCH₂</td> <td>Me</td> <td>(92)</td> <td>9:1</td> </tr> <tr> <td>MeOCH₂</td> <td>Me</td> <td>(88)</td> <td>7:1</td> </tr> <tr> <td>CO₂Pr-<i>i</i></td> <td>Me</td> <td>(36)</td> <td>3:1</td> </tr> </tbody> </table>	R ¹	R ²	(%)	dr	BnOCH ₂	H	(72)	9:1	Ph	H	(66)	13:1	BnOCH ₂	Me	(92)	9:1	MeOCH ₂	Me	(88)	7:1	CO ₂ Pr- <i>i</i>	Me	(36)	3:1	166 166, 260 166 875 166 166																																
R ¹	R ²	(%)	dr																																																								
BnOCH ₂	H	(72)	9:1																																																								
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CO ₂ Pr- <i>i</i>	Me	(36)	3:1																																																								
	Zn/Cu, CH ₂ I ₂ , I ₂ (cat.), Et ₂ O, reflux	<table border="1"> <thead> <tr> <th>R¹</th> <th>R²</th> <th>R³</th> <th>R⁴</th> <th>n</th> <th>(%)</th> <th>dc (%)</th> </tr> </thead> <tbody> <tr> <td>Me</td> <td>Me</td> <td>H</td> <td>H</td> <td>2</td> <td>(61)</td> <td>62</td> </tr> <tr> <td>Me</td> <td>Et</td> <td>H</td> <td>H</td> <td>2</td> <td>(69)</td> <td>66</td> </tr> <tr> <td>Et</td> <td>Me</td> <td>H</td> <td>H</td> <td>2</td> <td>(77)</td> <td>79</td> </tr> <tr> <td>Me</td> <td><i>i</i>-Pr</td> <td>H</td> <td>Me</td> <td>2</td> <td>(74)</td> <td>87</td> </tr> <tr> <td>Me</td> <td><i>i</i>-Pr</td> <td>H</td> <td>H</td> <td>2</td> <td>(76)</td> <td>>98</td> </tr> <tr> <td>Me</td> <td><i>i</i>-Pr</td> <td>H</td> <td>H</td> <td>3</td> <td>(90)</td> <td>>98</td> </tr> <tr> <td>Me</td> <td><i>i</i>-Pr</td> <td>Me</td> <td>H</td> <td>1</td> <td>(81)</td> <td>>98</td> </tr> </tbody> </table>	R ¹	R ²	R ³	R ⁴	n	(%)	dc (%)	Me	Me	H	H	2	(61)	62	Me	Et	H	H	2	(69)	66	Et	Me	H	H	2	(77)	79	Me	<i>i</i> -Pr	H	Me	2	(74)	87	Me	<i>i</i> -Pr	H	H	2	(76)	>98	Me	<i>i</i> -Pr	H	H	3	(90)	>98	Me	<i>i</i> -Pr	Me	H	1	(81)	>98	168
R ¹	R ²	R ³	R ⁴	n	(%)	dc (%)																																																					
Me	Me	H	H	2	(61)	62																																																					
Me	Et	H	H	2	(69)	66																																																					
Et	Me	H	H	2	(77)	79																																																					
Me	<i>i</i> -Pr	H	Me	2	(74)	87																																																					
Me	<i>i</i> -Pr	H	H	2	(76)	>98																																																					
Me	<i>i</i> -Pr	H	H	3	(90)	>98																																																					
Me	<i>i</i> -Pr	Me	H	1	(81)	>98																																																					
C ₅₋₁₆ 	Zn/Cu, CH ₂ I ₂ , I ₂ (cat.), Et ₂ O, reflux	<table border="1"> <thead> <tr> <th>n</th> <th>(%)</th> <th>dr</th> </tr> </thead> <tbody> <tr> <td>1</td> <td>(72)</td> <td>9:1</td> </tr> <tr> <td>2</td> <td>(98)</td> <td>9:1</td> </tr> <tr> <td>3</td> <td>(90)</td> <td>8:1</td> </tr> <tr> <td>4</td> <td>(80)</td> <td>>20:1</td> </tr> <tr> <td>5</td> <td>(96)</td> <td>>20:1</td> </tr> <tr> <td>12</td> <td>(70)</td> <td>>20:1</td> </tr> </tbody> </table>	n	(%)	dr	1	(72)	9:1	2	(98)	9:1	3	(90)	8:1	4	(80)	>20:1	5	(96)	>20:1	12	(70)	>20:1	165																																			
n	(%)	dr																																																									
1	(72)	9:1																																																									
2	(98)	9:1																																																									
3	(90)	8:1																																																									
4	(80)	>20:1																																																									
5	(96)	>20:1																																																									
12	(70)	>20:1																																																									
C ₆ 	Sm/Hg, CH ₂ Cl ₂ , THF	(90) 94	737, 738																																																								

TABLE XI. CYCLOPROPANATION OF CYCLIC ALKENES CONTAINING A CLEAVABLE CHIRAL AUXILIARY (Continued)

Substrate	Conditions	Product(s) and Yield(s) (%), and de (%)	Refs.																																																																																										
	Et ₂ Zn (3 eq), CH ₂ I _X (6 eq), (CH ₂ Cl) ₂	 <table border="1"> <thead> <tr> <th>X</th> <th>(%)</th> <th>de (%)</th> </tr> </thead> <tbody> <tr> <td>Cl</td> <td>(90)</td> <td>90</td> </tr> <tr> <td>I</td> <td>(—)</td> <td>86</td> </tr> </tbody> </table>	X	(%)	de (%)	Cl	(90)	90	I	(—)	86	51																																																																																	
X	(%)	de (%)																																																																																											
Cl	(90)	90																																																																																											
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	Zn/Cu, CH ₂ I ₂ , I ₂ (cat.), Et ₂ O, reflux	 <table border="1"> <thead> <tr> <th>R</th> <th>(%)</th> <th>dr</th> </tr> </thead> <tbody> <tr> <td>BnOCH₂</td> <td>(90-98)</td> <td>9:1</td> </tr> <tr> <td>MeOCH₂</td> <td>(86)</td> <td>5:1</td> </tr> <tr> <td>4-biphenylCH₂OCH₂</td> <td>(99)</td> <td>9:1</td> </tr> <tr> <td>β-naphthylCH₂OCH₂</td> <td>(76)</td> <td>9:1</td> </tr> <tr> <td>C(Me)₂OMe</td> <td>(91)</td> <td>4:1</td> </tr> <tr> <td>CO₂Me</td> <td>(37)</td> <td>3:2</td> </tr> <tr> <td>CH₂OH</td> <td>(50)</td> <td>1:2</td> </tr> <tr> <td>Me</td> <td>(86)</td> <td>9:1</td> </tr> <tr> <td>Ph(CH₂)₃</td> <td>(92)</td> <td>>9:1</td> </tr> <tr> <td>Ph</td> <td>(90)</td> <td>19:1</td> </tr> </tbody> </table>	R	(%)	dr	BnOCH ₂	(90-98)	9:1	MeOCH ₂	(86)	5:1	4-biphenylCH ₂ OCH ₂	(99)	9:1	β-naphthylCH ₂ OCH ₂	(76)	9:1	C(Me) ₂ OMe	(91)	4:1	CO ₂ Me	(37)	3:2	CH ₂ OH	(50)	1:2	Me	(86)	9:1	Ph(CH ₂) ₃	(92)	>9:1	Ph	(90)	19:1	163, 164, 166 166 166 166 166 166 166 166 166, 260																																																									
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TABLE XI. CYCLOPROPANATION OF CYCLIC ALKENES CONTAINING A CLEAVABLE CHIRAL AUXILIARY (Continued)

Substrate	Conditions	Product(s) and Yield(s) (%), and de (%)	Refs.																												
	Et ₂ Zn (5 eq), CH ₂ I ₂ (x eq), solvent	<table border="1"> <thead> <tr> <th>Solvent</th> <th>x</th> <th>(%)</th> <th>de (%)</th> </tr> </thead> <tbody> <tr> <td>Et₂O</td> <td>10</td> <td>(60)</td> <td>95</td> </tr> <tr> <td>Et₂O</td> <td>5</td> <td>(63)</td> <td>96</td> </tr> <tr> <td>THF</td> <td>10</td> <td>(15)</td> <td>90</td> </tr> <tr> <td>THF</td> <td>5</td> <td>(56)</td> <td>96</td> </tr> <tr> <td>DME</td> <td>10</td> <td>(19)</td> <td>93</td> </tr> <tr> <td>DME</td> <td>5</td> <td>(31)</td> <td>95</td> </tr> </tbody> </table>	Solvent	x	(%)	de (%)	Et ₂ O	10	(60)	95	Et ₂ O	5	(63)	96	THF	10	(15)	90	THF	5	(56)	96	DME	10	(19)	93	DME	5	(31)	95	876
Solvent	x	(%)	de (%)																												
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<p>I:II = 81:19</p>	Et ₂ Zn (5 eq), CH ₂ I ₂ (10 eq), THF	<p>(50) 94 + (14) 87</p>	877																												
	Et ₂ Zn (5 eq), CH ₂ I ₂ (10 eq), solvent, temp. 2-10 h	<table border="1"> <thead> <tr> <th>Solvent</th> <th>Temp</th> <th>(%)</th> <th>de (%)</th> </tr> </thead> <tbody> <tr> <td>hexane</td> <td>0°</td> <td>(54)</td> <td>99</td> </tr> <tr> <td>hexane</td> <td>-40 to 0°</td> <td>(75)</td> <td>99</td> </tr> <tr> <td>Et₂O</td> <td>20°</td> <td>(86)</td> <td>>99.5</td> </tr> <tr> <td>Et₂O</td> <td>0°</td> <td>(72)</td> <td>99</td> </tr> <tr> <td>Et₂O</td> <td>-40°</td> <td>(59)</td> <td>95</td> </tr> <tr> <td>THF</td> <td>20°</td> <td>(69)</td> <td>96</td> </tr> </tbody> </table>	Solvent	Temp	(%)	de (%)	hexane	0°	(54)	99	hexane	-40 to 0°	(75)	99	Et ₂ O	20°	(86)	>99.5	Et ₂ O	0°	(72)	99	Et ₂ O	-40°	(59)	95	THF	20°	(69)	96	174, 176
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	Zn/Cu, CH ₂ I ₂ , Et ₂ O, 50°	" (51) 94	174, 176																												
	Et ₂ Zn (2 eq), MeCHI ₂ (2.5 eq), solvent	<p>I + II</p>	180																												
		<p>III + IV</p> <table border="1"> <thead> <tr> <th>R</th> <th>(%)</th> <th>Solvent</th> <th>I:II:III:IV</th> </tr> </thead> <tbody> <tr> <td>H</td> <td>(32)</td> <td>hexane</td> <td>44:11:31:14</td> </tr> <tr> <td>H</td> <td>(76)</td> <td>Et₂O</td> <td>79:1:12:8</td> </tr> <tr> <td>Me</td> <td>(90)</td> <td>hexane</td> <td>80:2:18:0</td> </tr> <tr> <td>Me</td> <td>(75)</td> <td>Et₂O</td> <td>80:3:17:0</td> </tr> <tr> <td>Me</td> <td>(83)</td> <td>THF</td> <td>87:0:13:0</td> </tr> <tr> <td>Me</td> <td>(84)</td> <td>DME</td> <td>81:2:17:0</td> </tr> </tbody> </table>	R	(%)	Solvent	I:II:III:IV	H	(32)	hexane	44:11:31:14	H	(76)	Et ₂ O	79:1:12:8	Me	(90)	hexane	80:2:18:0	Me	(75)	Et ₂ O	80:3:17:0	Me	(83)	THF	87:0:13:0	Me	(84)	DME	81:2:17:0	
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C ₇	Zn/Cu, CH ₂ I ₂ , I ₂ (cat.), Et ₂ O, reflux	<p>(99) 20:1</p>	163, 164																												
	Zn/Cu, CH ₂ I ₂ , I ₂ (cat.), Et ₂ O, reflux	<table border="1"> <thead> <tr> <th>R</th> <th>(%)</th> <th>dr</th> </tr> </thead> <tbody> <tr> <td>BnOCH₂</td> <td>(90)</td> <td>8:1</td> </tr> <tr> <td>Ph</td> <td>(77)</td> <td>15:1</td> </tr> </tbody> </table>	R	(%)	dr	BnOCH ₂	(90)	8:1	Ph	(77)	15:1	163, 164, 166, 260																			
R	(%)	dr																													
BnOCH ₂	(90)	8:1																													
Ph	(77)	15:1																													
	Et ₂ Zn (10 eq), CH ₂ I ₂ (10 eq), PhMe, -35 to 0°	<p>(>97) 99</p>	157																												

TABLE XI. CYCLOPROPANATION OF CYCLIC ALKENES CONTAINING A CLEAVABLE CHIRAL AUXILIARY (Continued)

Substrate	Conditions	Product(s) and Yield(s) (%), and de (%)	Refs.
	Et ₂ Zn (5 eq), CH ₂ I ₂ (10 eq), Et ₂ O, 20°	(77) >99	174, 176
C ₈ 	Zn/Cu, CH ₂ I ₂ , I ₂ (cat.), Et ₂ O, reflux	(78) 9:1	164, 878
	Zn/Cu, CH ₂ I ₂ , I ₂ (cat.), Et ₂ O, reflux	(87)	879
	Zn/Cu, CH ₂ I ₂ , I ₂ (cat.), Et ₂ O, reflux	(54) 9:1	164
	Zn/Cu, CH ₂ I ₂ , I ₂ (cat.), Et ₂ O, reflux	(88) 14:1	163, 164
	Zn/Ag, CH ₂ I ₂ , Et ₂ O	(91-98)	129
	Zn/Ag, CH ₂ I ₂ , Et ₂ O	(77-96)	129
	Et ₂ Zn (5 eq), CH ₂ I ₂ (10 eq), Et ₂ O, 20°	(80) >99	174, 176
	Et ₂ Zn (5 eq), CH ₂ I ₂ (10 eq), Et ₂ O, 20°	(58) >99	174, 176
C ₉ 	Zn/Cu, CH ₂ I ₂ , I ₂ (cat.), Et ₂ O, reflux	(90) 7:1	164, 878
	Zn/Ag, CH ₂ I ₂ , Et ₂ O	(77-96)	129, 664

TABLE XI. CYCLOPROPANATION OF CYCLIC ALKENES CONTAINING A CLEAVABLE CHIRAL AUXILIARY (Continued)

Substrate	Conditions	Product(s) and Yield(s) (%), and de (%)	Refs.																									
	Zn/Cu, CH ₂ I ₂ , I ₂ (cat.), Et ₂ O, reflux		<table border="1"> <thead> <tr> <th>n</th> <th>(%)</th> <th>dr</th> </tr> </thead> <tbody> <tr> <td>1</td> <td>(93)</td> <td>>20:1</td> </tr> <tr> <td>2</td> <td>(84)</td> <td>13:1</td> </tr> <tr> <td>3</td> <td>(94)</td> <td>10:1</td> </tr> <tr> <td>4</td> <td>(89)</td> <td>>20:1</td> </tr> <tr> <td>5</td> <td>(88)</td> <td>10:1</td> </tr> <tr> <td>7</td> <td>(94)</td> <td>>20:1</td> </tr> <tr> <td>8</td> <td>(98)</td> <td>>20:1</td> </tr> </tbody> </table>	n	(%)	dr	1	(93)	>20:1	2	(84)	13:1	3	(94)	10:1	4	(89)	>20:1	5	(88)	10:1	7	(94)	>20:1	8	(98)	>20:1	165
		n	(%)	dr																								
		1	(93)	>20:1																								
		2	(84)	13:1																								
		3	(94)	10:1																								
		4	(89)	>20:1																								
		5	(88)	10:1																								
		7	(94)	>20:1																								
8	(98)	>20:1																										
	Et ₂ Zn (5 eq), CH ₂ I ₂ (10 eq), hexane, -20°(7 h), 20°(10 h)		(61) 88	160																								
			(50) 85	160																								
	Zn/Cu, CH ₂ I ₂ , I ₂ (cat.), Et ₂ O, reflux		(84) 8:1	880, 881																								
	Zn/Cu, CH ₂ I ₂ , I ₂ (cat.), Et ₂ O, reflux, 20 h		(80) 7:1	164, 882																								
		Zn/Cu, CH ₂ I ₂ , I ₂ (cat.), Et ₂ O, reflux	" (92) 7:1	164, 878																								
	Et ₂ Zn (5 eq), CH ₂ Cl (2 eq)		(77) 97	189																								
	Et ₂ Zn (5 eq), CH ₂ Cl (2 eq)		(80) 99	189																								
	Et ₂ Zn (5 eq), CH ₂ I ₂ (10 eq), Et ₂ O, rt		(82) >99	177																								
	Zn/Cu, CH ₂ I ₂ , I ₂ (cat.), Et ₂ O, reflux		(23) +	883																								
	Zn/Cu, CH ₂ I ₂ , I ₂ (cat.), Et ₂ O, reflux		(68)																									
	Zn/Cu, CH ₂ I ₂ , I ₂ (cat.), Et ₂ O, reflux		(30) +	883																								
	Zn/Cu, CH ₂ I ₂ , I ₂ (cat.), Et ₂ O, reflux		(35)																									
	Zn/Cu, CH ₂ I ₂ , I ₂ (cat.), Et ₂ O, reflux		(<3) +	883																								
	Zn/Cu, CH ₂ I ₂ , I ₂ (cat.), Et ₂ O, reflux		(83)																									

TABLE XI. CYCLOPROPANATION OF CYCLIC ALKENES CONTAINING A CLEAVABLE CHIRAL AUXILIARY (Continued)

Substrate	Conditions	Product(s) and Yield(s) (%), and de (%)	Refs.									
	Zn/Cu, CH ₂ I ₂ , I ₂ (cat.), Et ₂ O, reflux	 <table border="1"> <thead> <tr> <th>R</th> <th>(%)</th> <th>dr</th> </tr> </thead> <tbody> <tr> <td>OBn</td> <td>(84)</td> <td>9:1</td> </tr> <tr> <td>Ph</td> <td>(62)</td> <td>16:1</td> </tr> </tbody> </table>	R	(%)	dr	OBn	(84)	9:1	Ph	(62)	16:1	164, 878 260
R	(%)	dr										
OBn	(84)	9:1										
Ph	(62)	16:1										
C ₁₁ 	Zn/Ag, CH ₂ I ₂ , Et ₂ O	 (77-96)	129									
C ₁₂₋₁₅ 	Zn/Cu, CH ₂ I ₂ , I ₂ (cat.), Et ₂ O, reflux	 <table border="1"> <thead> <tr> <th>n</th> <th>(%)</th> <th>dr</th> </tr> </thead> <tbody> <tr> <td>8</td> <td>(—)</td> <td>—</td> </tr> <tr> <td>11</td> <td>(—)</td> <td>—</td> </tr> </tbody> </table>	n	(%)	dr	8	(—)	—	11	(—)	—	723
n	(%)	dr										
8	(—)	—										
11	(—)	—										
C ₁₃ 	Zn/Cu, CH ₂ I ₂ , I ₂ (cat.), Et ₂ O, reflux, 20 h	 (94) 8:1	882									
	Zn/Ag, CH ₂ I ₂ , Et ₂ O	 (80)	129									
	Zn/Ag, CH ₂ I ₂ , Et ₂ O	 (76)	129									
C ₁₅ 	Zn/Cu, CH ₂ I ₂ , I ₂ (cat.), Et ₂ O, reflux	 <table border="1"> <thead> <tr> <th>R</th> <th>(%)</th> <th>dr</th> </tr> </thead> <tbody> <tr> <td>Me</td> <td>(95)</td> <td>>20:1</td> </tr> <tr> <td>Bn</td> <td>(88)</td> <td>>20:1</td> </tr> </tbody> </table>	R	(%)	dr	Me	(95)	>20:1	Bn	(88)	>20:1	884
R	(%)	dr										
Me	(95)	>20:1										
Bn	(88)	>20:1										

^a Reagent was preformed

TABLE XII. CYCLOPROPANATION OF ACYCLIC ALKENES CONTAINING A CLEAVABLE CHIRAL AUXILIARY

Substrate	Conditions	Product(s) and Yield(s) (%), and de (%)	Refs.																																																				
<p>C₂</p>	<p>Et₂Zn (3 eq), CHFCl₂ (3 eq), additive, CH₂Cl₂, temp</p>	<p>I + II +</p> <p>III + IV</p> <table border="1"> <thead> <tr> <th>Additive</th> <th>Temp</th> <th>(%)</th> <th>I:II:III:IV</th> </tr> </thead> <tbody> <tr> <td>—</td> <td>rt</td> <td>(44)</td> <td>50:41:4:5</td> </tr> <tr> <td>Et₂O</td> <td>rt</td> <td>(50)</td> <td>51:36:6:7</td> </tr> <tr> <td>MS 4 Å</td> <td>rt</td> <td>(52)</td> <td>60:28:7:5</td> </tr> <tr> <td>MS 4 Å^a</td> <td>reflux</td> <td>(69)</td> <td>50:41:4:5</td> </tr> <tr> <td>Et₂O, MS 4 Å</td> <td>reflux</td> <td>(64)</td> <td>53:36:5:6</td> </tr> <tr> <td>THF, MS 4 Å</td> <td>reflux</td> <td>(73)</td> <td>56:33:5:7</td> </tr> <tr> <td>DME, MS 4 Å</td> <td>reflux</td> <td>(68)</td> <td>63:27:5:5</td> </tr> <tr> <td>DME, MS 4 Å</td> <td>reflux</td> <td>(85)</td> <td>59:28:5:8</td> </tr> <tr> <td>DME, MS 4 Å</td> <td>rt</td> <td>(76)</td> <td>65:25:5:5</td> </tr> <tr> <td>DEE, MS 4 Å</td> <td>reflux</td> <td>(88)</td> <td>59:30:5:6</td> </tr> <tr> <td>(<i>R,R</i>)-DMC_x, MS 4 Å</td> <td>reflux</td> <td>(67)</td> <td>65:25:6:4</td> </tr> <tr> <td>(<i>S,S</i>)-DMC_x, MS 4 Å</td> <td>reflux</td> <td>(67)</td> <td>65:25:6:4</td> </tr> </tbody> </table>	Additive	Temp	(%)	I:II:III:IV	—	rt	(44)	50:41:4:5	Et ₂ O	rt	(50)	51:36:6:7	MS 4 Å	rt	(52)	60:28:7:5	MS 4 Å ^a	reflux	(69)	50:41:4:5	Et ₂ O, MS 4 Å	reflux	(64)	53:36:5:6	THF, MS 4 Å	reflux	(73)	56:33:5:7	DME, MS 4 Å	reflux	(68)	63:27:5:5	DME, MS 4 Å	reflux	(85)	59:28:5:8	DME, MS 4 Å	rt	(76)	65:25:5:5	DEE, MS 4 Å	reflux	(88)	59:30:5:6	(<i>R,R</i>)-DMC _x , MS 4 Å	reflux	(67)	65:25:6:4	(<i>S,S</i>)-DMC _x , MS 4 Å	reflux	(67)	65:25:6:4	181, 885
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(<i>R,R</i>)-DMC _x , MS 4 Å	reflux	(67)	65:25:6:4																																																				
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	<p>Et₂Zn (x eq), CHFCl₂ (x eq), DME (x eq), CH₂Cl₂, MS 4 Å</p>	<p>I + II +</p> <p>III + IV</p> <table border="1"> <thead> <tr> <th>R¹</th> <th>R²</th> <th>x</th> <th>(%)</th> <th>I:II:III:IV</th> </tr> </thead> <tbody> <tr> <td>H</td> <td>H</td> <td>3</td> <td>(80)</td> <td>59:27:9:4</td> </tr> <tr> <td>Ph</td> <td>Ph</td> <td>6</td> <td>(67)</td> <td>49:26:15:9</td> </tr> </tbody> </table>	R ¹	R ²	x	(%)	I:II:III:IV	H	H	3	(80)	59:27:9:4	Ph	Ph	6	(67)	49:26:15:9	181																																					
		R ¹	R ²	x	(%)	I:II:III:IV																																																	
H	H	3	(80)	59:27:9:4																																																			
Ph	Ph	6	(67)	49:26:15:9																																																			
<p>C₃</p>	<p>Et₂Zn, CH₂I₂, ZnI₂, CH₂Cl₂, 0°</p>	<p>I + II</p> <p>(94) I:II = 36:64</p>	886																																																				
		<table border="1"> <thead> <tr> <th>R¹</th> <th>R²</th> <th>(%)</th> <th>de (%)</th> </tr> </thead> <tbody> <tr> <td>Ph</td> <td>H</td> <td>(78)</td> <td>32</td> </tr> <tr> <td>Me</td> <td>H</td> <td>(96)</td> <td>73</td> </tr> <tr> <td>Pr</td> <td>H</td> <td>(97)</td> <td>—</td> </tr> <tr> <td>Ph</td> <td>Me</td> <td>(66)</td> <td>—</td> </tr> <tr> <td>H</td> <td>H</td> <td>(73)</td> <td>—</td> </tr> </tbody> </table>	R ¹	R ²	(%)	de (%)	Ph	H	(78)	32	Me	H	(96)	73	Pr	H	(97)	—	Ph	Me	(66)	—	H	H	(73)	—	169																												
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<p>C₃₋₁₀</p>	<p>Et₂Zn (3-5 eq), CH₂I₂ (6-10 eq), PhMe</p>	<table border="1"> <thead> <tr> <th>R¹</th> <th>R²</th> <th>(%)</th> <th>de (%)</th> </tr> </thead> <tbody> <tr> <td>Ph</td> <td>H</td> <td>(97)</td> <td>21</td> </tr> <tr> <td>Me</td> <td>H</td> <td>(60)</td> <td>78</td> </tr> <tr> <td>Pr</td> <td>H</td> <td>(88)</td> <td>—</td> </tr> <tr> <td>Ph</td> <td>Me</td> <td>(70)</td> <td>—</td> </tr> </tbody> </table>	R ¹	R ²	(%)	de (%)	Ph	H	(97)	21	Me	H	(60)	78	Pr	H	(88)	—	Ph	Me	(70)	—	169																																
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TABLE XII. CYCLOPROPANATION OF ACYCLIC ALKENES CONTAINING A CLEAVABLE CHIRAL AUXILIARY (Continued)

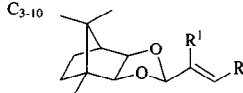
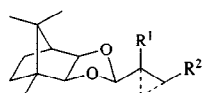
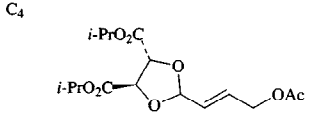
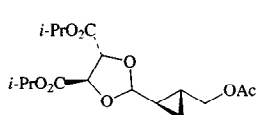
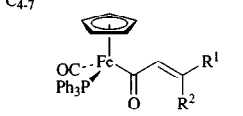
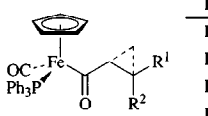
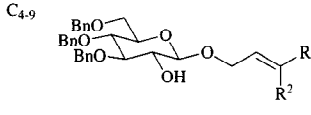
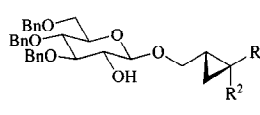
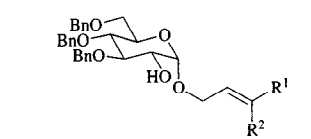
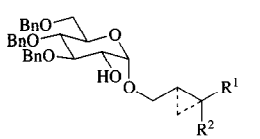
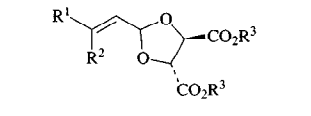
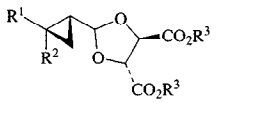
Substrate	Conditions	Product(s) and Yield(s) (%), and de (%)	Refs.																																																	
C ₃₋₁₀ 	Et ₂ Zn (5 eq), CH ₂ I ₂ (10 eq), CH ₂ Cl ₂ , -10° to rt		<table border="1"> <thead> <tr> <th>R¹</th> <th>R²</th> <th>(%)</th> <th>de (%)</th> </tr> </thead> <tbody> <tr> <td>H</td> <td>H</td> <td>(41)</td> <td>-</td> </tr> <tr> <td>H</td> <td>Me</td> <td>(72)</td> <td>62</td> </tr> <tr> <td>H</td> <td>Pr</td> <td>(84)</td> <td>70</td> </tr> <tr> <td>H</td> <td>Ph</td> <td>(74)</td> <td>66</td> </tr> <tr> <td>Me</td> <td>Ph</td> <td>(58)</td> <td>46</td> </tr> </tbody> </table>	R ¹	R ²	(%)	de (%)	H	H	(41)	-	H	Me	(72)	62	H	Pr	(84)	70	H	Ph	(74)	66	Me	Ph	(58)	46	887																								
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	Et ₂ Zn (10 eq), CH ₂ I ₂ (10 eq), <i>t</i> -BuOMe, 0°, 22 h		<table border="1"> <thead> <tr> <th>R¹</th> <th>R²</th> <th>(%)</th> <th>dr</th> </tr> </thead> <tbody> <tr> <td>Me</td> <td>H</td> <td>(93)</td> <td>16.5:1</td> </tr> <tr> <td>H</td> <td>Et</td> <td>(91)</td> <td>13.2:1</td> </tr> <tr> <td>Me</td> <td>Me</td> <td>(95)</td> <td>11.0:1</td> </tr> <tr> <td>Pr</td> <td>H</td> <td>(83)</td> <td>12.3:1</td> </tr> <tr> <td>Ph</td> <td>H</td> <td>(93)</td> <td>15.0:1</td> </tr> </tbody> </table>	R ¹	R ²	(%)	dr	Me	H	(93)	16.5:1	H	Et	(91)	13.2:1	Me	Me	(95)	11.0:1	Pr	H	(83)	12.3:1	Ph	H	(93)	15.0:1	158																								
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	Et ₂ Zn (5 eq), CH ₂ I ₂ (10 eq), hexane, conditions		<table border="1"> <thead> <tr> <th>R¹</th> <th>R²</th> <th>R³</th> <th>Conditions</th> <th>(%)</th> <th>de (%)</th> </tr> </thead> <tbody> <tr> <td>Me</td> <td>H</td> <td><i>i</i>-Pr</td> <td>-20°(1 h); 0°(4 h)</td> <td>(90)</td> <td>94</td> </tr> <tr> <td>Et</td> <td>Me</td> <td><i>i</i>-Pr</td> <td>-20°(1 h); 0°(4 h)</td> <td>(81)</td> <td>89</td> </tr> <tr> <td><i>n</i>-Pr</td> <td>H</td> <td>Et</td> <td>-20°(3 h)</td> <td>(95)</td> <td>88</td> </tr> <tr> <td><i>n</i>-Pr</td> <td>H</td> <td><i>i</i>-Pr</td> <td>-20°(1 h); 0°(5 h)</td> <td>(80)</td> <td>91</td> </tr> <tr> <td>MeO₂C(CH₂)₃</td> <td>H</td> <td><i>i</i>-Pr</td> <td>-20°(1 h); 0°(4 h)</td> <td>(99)</td> <td>90</td> </tr> <tr> <td>Ph</td> <td>H</td> <td>Et</td> <td>-20°(6 h); 0°(6 h)</td> <td>(82)</td> <td>87</td> </tr> <tr> <td>Ph</td> <td>H</td> <td><i>i</i>-Pr</td> <td>-20°(1 h); 0°(3 h)</td> <td>(92)</td> <td>91</td> </tr> </tbody> </table>	R ¹	R ²	R ³	Conditions	(%)	de (%)	Me	H	<i>i</i> -Pr	-20°(1 h); 0°(4 h)	(90)	94	Et	Me	<i>i</i> -Pr	-20°(1 h); 0°(4 h)	(81)	89	<i>n</i> -Pr	H	Et	-20°(3 h)	(95)	88	<i>n</i> -Pr	H	<i>i</i> -Pr	-20°(1 h); 0°(5 h)	(80)	91	MeO ₂ C(CH ₂) ₃	H	<i>i</i> -Pr	-20°(1 h); 0°(4 h)	(99)	90	Ph	H	Et	-20°(6 h); 0°(6 h)	(82)	87	Ph	H	<i>i</i> -Pr	-20°(1 h); 0°(3 h)	(92)	91	160, 161
			R ¹	R ²	R ³	Conditions	(%)	de (%)																																												
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TABLE XII. CYCLOPROPANATION OF ACYCLIC ALKENES CONTAINING A CLEAVABLE CHIRAL AUXILIARY (Continued)

Substrate	Conditions	Product(s) and Yield(s) (%), and de (%)	Refs.																																																												
	Et ₂ Zn (5 eq), CH ₂ I ₂ (10 eq), hexane, -20°, 2 h	<table border="1"> <thead> <tr> <th>R¹</th> <th>R²</th> <th>R³</th> <th>(%)</th> <th>de (%)</th> </tr> </thead> <tbody> <tr> <td>Me</td> <td>H</td> <td>H</td> <td>(74)</td> <td>69</td> </tr> <tr> <td><i>n</i>-Pr</td> <td>H</td> <td>H</td> <td>(95)</td> <td>71</td> </tr> <tr> <td>Ph</td> <td>H</td> <td>H</td> <td>(85)</td> <td>68</td> </tr> <tr> <td>Me</td> <td>H</td> <td>Me</td> <td>(81)</td> <td>-29</td> </tr> <tr> <td>Et</td> <td>Me</td> <td>H</td> <td>(69)</td> <td>75</td> </tr> </tbody> </table>	R ¹	R ²	R ³	(%)	de (%)	Me	H	H	(74)	69	<i>n</i> -Pr	H	H	(95)	71	Ph	H	H	(85)	68	Me	H	Me	(81)	-29	Et	Me	H	(69)	75	161																														
R ¹	R ²	R ³	(%)	de (%)																																																											
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	Et ₂ Zn, CH ₂ I ₂ , CH ₂ Cl ₂ , -10°	<table border="1"> <thead> <tr> <th>R</th> <th>(%)</th> <th>de (%)</th> </tr> </thead> <tbody> <tr> <td>Me</td> <td>(76-95)</td> <td>>99</td> </tr> <tr> <td>Pr</td> <td>(76-95)</td> <td>>99</td> </tr> <tr> <td>Ph</td> <td>(76-95)</td> <td>>99</td> </tr> </tbody> </table>	R	(%)	de (%)	Me	(76-95)	>99	Pr	(76-95)	>99	Ph	(76-95)	>99	171																																																
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Pr	(76-95)	>99																																																													
Ph	(76-95)	>99																																																													
C4-10 	Et ₂ Zn (3 eq), CH ₂ Cl (3 eq), PhMe	<table border="1"> <thead> <tr> <th>R¹</th> <th>R²</th> <th>R³</th> <th>(%)</th> <th>dr</th> </tr> </thead> <tbody> <tr> <td>H</td> <td>Me</td> <td>Me</td> <td>(98)</td> <td>23:1</td> </tr> <tr> <td>H</td> <td>Pr</td> <td>H</td> <td>(98)</td> <td>21:1</td> </tr> <tr> <td>H</td> <td>H</td> <td>Pr</td> <td>(97)</td> <td>24:1</td> </tr> <tr> <td>H</td> <td>Ph</td> <td>H</td> <td>(97)</td> <td>24:1</td> </tr> <tr> <td>Me</td> <td>Ph</td> <td>H</td> <td>(90)</td> <td>15:1</td> </tr> <tr> <td>H</td> <td>H</td> <td>TIPSOCH₂</td> <td>(95)</td> <td>>20:1</td> </tr> </tbody> </table>	R ¹	R ²	R ³	(%)	dr	H	Me	Me	(98)	23:1	H	Pr	H	(98)	21:1	H	H	Pr	(97)	24:1	H	Ph	H	(97)	24:1	Me	Ph	H	(90)	15:1	H	H	TIPSOCH ₂	(95)	>20:1	159																									
R ¹	R ²	R ³	(%)	dr																																																											
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H	H	TIPSOCH ₂	(95)	>20:1																																																											
C5 	Zn/Cu, CH ₂ I ₂ , I ₂ (cat.), Et ₂ O, reflux	(95) 1:1	163, 164																																																												
	Et ₂ Zn (5 eq), CH ₂ I ₂ (10 eq), Et ₂ O, 20°	(57) >99	174, 176																																																												
	Et ₂ Zn (10 eq), CH ₂ IX (10 eq), solvent, 0°, time	<table border="1"> <thead> <tr> <th>Solvent</th> <th>X</th> <th>Time (h)</th> <th>(%)</th> <th>dr</th> </tr> </thead> <tbody> <tr> <td>(CH₂Cl)₂</td> <td>I</td> <td>6</td> <td>(99)</td> <td>8.5:1</td> </tr> <tr> <td>CH₂Cl₂</td> <td>I</td> <td>6</td> <td>(98)</td> <td>9.2:1</td> </tr> <tr> <td>PhMe</td> <td>I</td> <td>6</td> <td>(89)</td> <td>12.1:1</td> </tr> <tr> <td>hexane</td> <td>I</td> <td>6</td> <td>(78)</td> <td>6.1:1</td> </tr> <tr> <td>Et₂O</td> <td>I</td> <td>6</td> <td>(32)</td> <td>13.9:1</td> </tr> <tr> <td>Et₂O</td> <td>I</td> <td>22</td> <td>(91)</td> <td>13.6:1</td> </tr> <tr> <td>Et₂O</td> <td>Cl</td> <td>22</td> <td>(46)</td> <td>4.4:1</td> </tr> <tr> <td>THF</td> <td>I</td> <td>22</td> <td>(6)</td> <td>13.9:1</td> </tr> <tr> <td>DME</td> <td>I</td> <td>6</td> <td>(<5)</td> <td>—</td> </tr> <tr> <td><i>t</i>-BuOMe</td> <td>I</td> <td>6</td> <td>(97)</td> <td>13.2:1</td> </tr> <tr> <td><i>t</i>-BuOMe</td> <td>Cl</td> <td>6</td> <td>(45)</td> <td>4.8:1</td> </tr> </tbody> </table>	Solvent	X	Time (h)	(%)	dr	(CH ₂ Cl) ₂	I	6	(99)	8.5:1	CH ₂ Cl ₂	I	6	(98)	9.2:1	PhMe	I	6	(89)	12.1:1	hexane	I	6	(78)	6.1:1	Et ₂ O	I	6	(32)	13.9:1	Et ₂ O	I	22	(91)	13.6:1	Et ₂ O	Cl	22	(46)	4.4:1	THF	I	22	(6)	13.9:1	DME	I	6	(<5)	—	<i>t</i> -BuOMe	I	6	(97)	13.2:1	<i>t</i> -BuOMe	Cl	6	(45)	4.8:1	158
Solvent	X	Time (h)	(%)	dr																																																											
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C5-11 	Et ₂ Zn (5 eq), CH ₂ I ₂ (10 eq), (CH ₂ Cl) ₂	<table border="1"> <thead> <tr> <th>R²</th> <th>R³</th> <th>(%)</th> <th>de (%)</th> </tr> </thead> <tbody> <tr> <td>Ph</td> <td>H</td> <td>(85)</td> <td>77</td> </tr> <tr> <td>Ph(CH₂)₂</td> <td>H</td> <td>(45)</td> <td>69</td> </tr> <tr> <td>Ph(CH₂)₂</td> <td>H</td> <td>(87)</td> <td>52</td> </tr> <tr> <td>BnOCH₂</td> <td>H</td> <td>(90)</td> <td>21</td> </tr> <tr> <td>Me</td> <td>Me</td> <td>(81)</td> <td>60</td> </tr> <tr> <td><i>n</i>-C₃H₁₁</td> <td>H</td> <td>(69)</td> <td>81</td> </tr> <tr> <td><i>n</i>-C₃H₁₁</td> <td>H</td> <td>(90)</td> <td>64</td> </tr> </tbody> </table>	R ²	R ³	(%)	de (%)	Ph	H	(85)	77	Ph(CH ₂) ₂	H	(45)	69	Ph(CH ₂) ₂	H	(87)	52	BnOCH ₂	H	(90)	21	Me	Me	(81)	60	<i>n</i> -C ₃ H ₁₁	H	(69)	81	<i>n</i> -C ₃ H ₁₁	H	(90)	64	170																												
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TABLE XII. CYCLOPROPANATION OF ACYCLIC ALKENES CONTAINING A CLEAVABLE CHIRAL AUXILIARY (Continued)

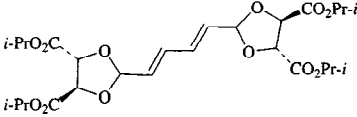
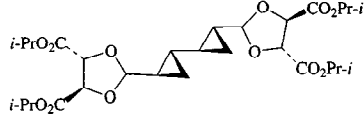
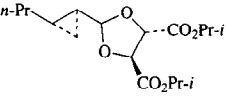
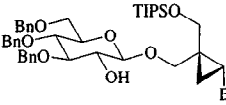
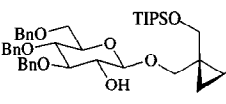
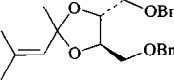
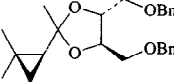
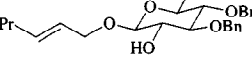
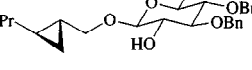
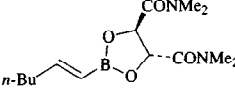
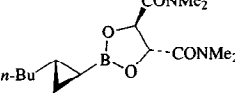
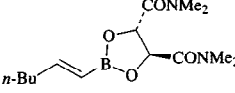
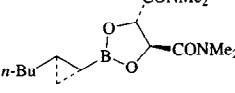
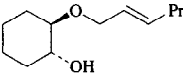
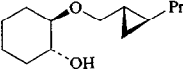
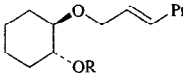
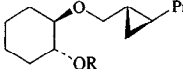
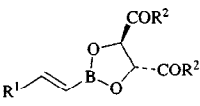
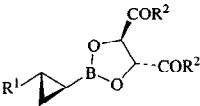
Substrate	Conditions	Product(s) and Yield(s) (%), and de (%)	Refs.																														
	Et ₂ Zn, CH ₂ I ₂ , (CH ₂ Cl) ₂ , -20°	 (78-83)	162, 653																														
	Et ₂ Zn (5 eq), CH ₂ I ₂ (10 eq), hexane, -20°, 5 h	 (94) 89	160, 161																														
	Et ₂ Zn (7 eq), CH ₂ I ₂ (5 eq), CH ₂ Cl ₂ , -30°	 (93) >99	888																														
	Et ₂ Zn (x eq), CH ₂ IX, CH ₂ Cl ₂ , temp, time	 I + II	888																														
		<table border="1"> <thead> <tr> <th>x</th> <th>CH₂IX (eq)</th> <th>Temp</th> <th>Time</th> <th>(%)</th> <th>I:II</th> </tr> </thead> <tbody> <tr> <td>7</td> <td>CH₂I₂ (5)</td> <td>-20°</td> <td>18 h</td> <td>(65)</td> <td>20:1</td> </tr> <tr> <td>7</td> <td>CH₂I₂ (5)</td> <td>0°</td> <td>2 h</td> <td>(>95)</td> <td>3:1</td> </tr> <tr> <td>7</td> <td>CH₂ICl (5)</td> <td>-20°</td> <td>40 min</td> <td>(>95)</td> <td>25:1</td> </tr> <tr> <td>4</td> <td>CH₂ICl (4)</td> <td>-60°</td> <td>18 h</td> <td>(98)</td> <td>66:1</td> </tr> </tbody> </table>	x	CH ₂ IX (eq)	Temp	Time	(%)	I:II	7	CH ₂ I ₂ (5)	-20°	18 h	(65)	20:1	7	CH ₂ I ₂ (5)	0°	2 h	(>95)	3:1	7	CH ₂ ICl (5)	-20°	40 min	(>95)	25:1	4	CH ₂ ICl (4)	-60°	18 h	(98)	66:1	
x	CH ₂ IX (eq)	Temp	Time	(%)	I:II																												
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4	CH ₂ ICl (4)	-60°	18 h	(98)	66:1																												
	Zn/Cu, CH ₂ I ₂ , I ₂ (cat.), Et ₂ O, reflux	 (58) 2:1	164, 879																														
	Et ₂ Zn (10 eq), CH ₂ I ₂ (10 eq), PhMe, -35 to 0°	 (>97) >50:1	157																														
	Zn/Cu, CH ₂ I ₂ , Et ₂ O, temp, time		<table border="1"> <thead> <tr> <th>Temp</th> <th>Time (h)</th> <th>(%)</th> <th>de (%)</th> </tr> </thead> <tbody> <tr> <td>reflux</td> <td>24</td> <td>(48)</td> <td>93</td> </tr> <tr> <td>rt</td> <td>5</td> <td>(67)</td> <td>91-94</td> </tr> </tbody> </table>	Temp	Time (h)	(%)	de (%)	reflux	24	(48)	93	rt	5	(67)	91-94																		
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rt	5	(67)	91-94																														
	Zn/Cu, CH ₂ I ₂ , Et ₂ O, reflux	 (42) 90	178																														
	Et ₂ Zn (3 eq), CH ₂ ICl (3 eq), PhMe, -20°		<table border="1"> <thead> <tr> <th>Solvent</th> <th>(%)</th> <th>dr</th> </tr> </thead> <tbody> <tr> <td>PhMe</td> <td>(97)</td> <td>21:1</td> </tr> <tr> <td>(CH₂Cl)₂</td> <td>(92)</td> <td>15:1</td> </tr> <tr> <td>CH₂Cl₂</td> <td>(90)</td> <td>15:1</td> </tr> <tr> <td>Et₂O</td> <td>(54)</td> <td>>18:1</td> </tr> <tr> <td>THF</td> <td>(<5)</td> <td>—</td> </tr> <tr> <td>DME</td> <td>(0)</td> <td>—</td> </tr> </tbody> </table>	Solvent	(%)	dr	PhMe	(97)	21:1	(CH ₂ Cl) ₂	(92)	15:1	CH ₂ Cl ₂	(90)	15:1	Et ₂ O	(54)	>18:1	THF	(<5)	—	DME	(0)	—	159								
Solvent	(%)	dr																															
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(CH ₂ Cl) ₂	(92)	15:1																															
CH ₂ Cl ₂	(90)	15:1																															
Et ₂ O	(54)	>18:1																															
THF	(<5)	—																															
DME	(0)	—																															
	Et ₂ Zn (5 eq), CH ₂ ICl (5 eq), PhMe, temp		<table border="1"> <thead> <tr> <th>R</th> <th>Temp</th> <th>(%)</th> <th>dr</th> </tr> </thead> <tbody> <tr> <td>Me</td> <td>-20° to rt</td> <td>(97)</td> <td>1.6:1</td> </tr> <tr> <td>Ac</td> <td>-20°</td> <td>(85)</td> <td>5.3:1</td> </tr> <tr> <td>Bn</td> <td>-10°</td> <td>(>95)</td> <td>1.5:1</td> </tr> <tr> <td>TBDMS</td> <td>-20°</td> <td>(>95)</td> <td>1.3:1</td> </tr> </tbody> </table>	R	Temp	(%)	dr	Me	-20° to rt	(97)	1.6:1	Ac	-20°	(85)	5.3:1	Bn	-10°	(>95)	1.5:1	TBDMS	-20°	(>95)	1.3:1	159									
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TABLE XII. CYCLOPROPANATION OF ACYCLIC ALKENES CONTAINING A CLEAVABLE CHIRAL AUXILIARY (Continued)

Substrate	Conditions	Product(s) and Yield(s) (%), and de (%)	Refs.																								
C ₆₋₁₁ 	Et ₂ Zn (2.5 eq), CH ₂ I ₂ (2.5 eq), hexane, 0°	<table border="1"> <thead> <tr> <th>R¹</th> <th>R²</th> <th>(%)</th> <th>de (%)</th> </tr> </thead> <tbody> <tr> <td>Me</td> <td>H</td> <td>(61)</td> <td>>98</td> </tr> <tr> <td>Ph</td> <td>H</td> <td>(76)</td> <td>>98</td> </tr> <tr> <td>H</td> <td>Me</td> <td>(68)</td> <td>na</td> </tr> </tbody> </table>	R ¹	R ²	(%)	de (%)	Me	H	(61)	>98	Ph	H	(76)	>98	H	Me	(68)	na	889, 890								
		R ¹	R ²	(%)	de (%)																						
		Me	H	(61)	>98																						
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	Et ₂ Zn, R ² CH ₂ , hexane, 0°	<table border="1"> <thead> <tr> <th>R¹</th> <th>R²</th> <th>(%)</th> <th>de (%)</th> </tr> </thead> <tbody> <tr> <td>H</td> <td>Me</td> <td>(76)</td> <td>79</td> </tr> <tr> <td>Me</td> <td>Me</td> <td>(80)</td> <td>68</td> </tr> <tr> <td>Me</td> <td>Ph</td> <td>(52)</td> <td>68</td> </tr> <tr> <td>Ph</td> <td>Me</td> <td>(74)</td> <td>86</td> </tr> <tr> <td>Ph</td> <td>Ph</td> <td>(62)</td> <td>85</td> </tr> </tbody> </table>	R ¹	R ²	(%)	de (%)	H	Me	(76)	79	Me	Me	(80)	68	Me	Ph	(52)	68	Ph	Me	(74)	86	Ph	Ph	(62)	85	889, 890
		R ¹	R ²	(%)	de (%)																						
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C ₇ 	Zn/Cu, CH ₂ I ₂ , I ₂ (cat.), Et ₂ O, reflux	(62) 1:1	163, 164																								
		Et ₂ Zn, CH ₂ I ₂	(65) >90	167																							
			Et ₂ Zn, CH ₂ I ₂	(60) 2:3:1	167																						
				<i>E:Z</i> = 4.5:1																							
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		<table border="1"> <thead> <tr> <th>order of addition</th> <th>(%)</th> <th>de (%)</th> </tr> </thead> <tbody> <tr> <td>CH₂I₂ + sm; Et₂Zn</td> <td>(56)</td> <td>75</td> </tr> <tr> <td>Et₂Zn + sm; CH₂I₂</td> <td>(—)</td> <td>60</td> </tr> <tr> <td>Et₂Zn + CH₂I₂; sm (20°)</td> <td>(46)</td> <td>61</td> </tr> <tr> <td>Et₂Zn + CH₂I₂; sm (-15°)</td> <td>(70)</td> <td>67</td> </tr> </tbody> </table>	order of addition	(%)	de (%)	CH ₂ I ₂ + sm; Et ₂ Zn	(56)	75	Et ₂ Zn + sm; CH ₂ I ₂	(—)	60	Et ₂ Zn + CH ₂ I ₂ ; sm (20°)	(46)	61	Et ₂ Zn + CH ₂ I ₂ ; sm (-15°)	(70)	67										
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C ₈ 	Zn/Ag, CH ₂ I ₂ , Et ₂ O, reflux	(76) 15:1	261, 664																								
		Zn/Ag, CH ₂ I ₂ , Et ₂ O	(77-96)	129																							
C ₈₋₁₁ 	Et ₂ Zn (5 eq), CH ₂ I ₂ (10 eq), (CH ₂ Cl) ₂		170																								
		<table border="1"> <thead> <tr> <th>R¹</th> <th>R²</th> <th>(%)</th> <th>de (%)</th> </tr> </thead> <tbody> <tr> <td>Bn</td> <td>Ph</td> <td>(82)</td> <td>33</td> </tr> <tr> <td>4-PhC₆H₄CH₂</td> <td>Ph(CH₂)₂</td> <td>(88)</td> <td>45</td> </tr> <tr> <td>4-PhC₆H₄CH₂</td> <td><i>n</i>-C₃H₁₁</td> <td>(84)</td> <td>54</td> </tr> </tbody> </table>	R ¹	R ²	(%)	de (%)	Bn	Ph	(82)	33	4-PhC ₆ H ₄ CH ₂	Ph(CH ₂) ₂	(88)	45	4-PhC ₆ H ₄ CH ₂	<i>n</i> -C ₃ H ₁₁	(84)	54									
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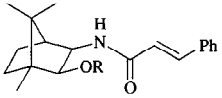
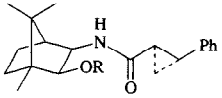
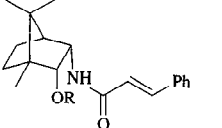
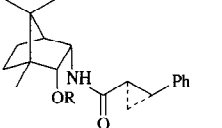
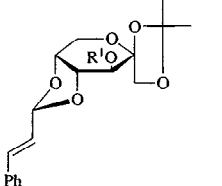
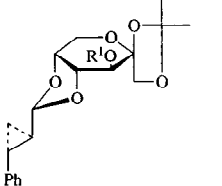
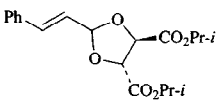
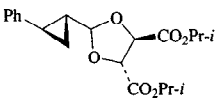
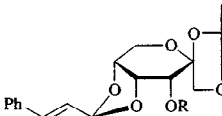
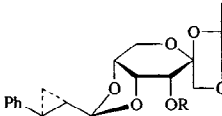
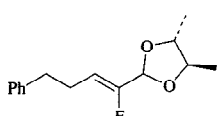
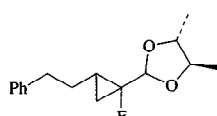
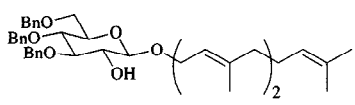

Substrate	Conditions	Product(s) and Yield(s) (%), and de (%)	Refs.																																																												
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		<table border="1"> <thead> <tr> <th>X</th> <th>(%)</th> <th>dc (%)</th> </tr> </thead> <tbody> <tr> <td>Cl</td> <td>(95)</td> <td>82</td> </tr> <tr> <td>I</td> <td>(—)</td> <td>>90</td> </tr> </tbody> </table>	X	(%)	dc (%)	Cl	(95)	82	I	(—)	>90																																																				
X	(%)	dc (%)																																																													
Cl	(95)	82																																																													
I	(—)	>90																																																													
	Et ₂ Zn (5 eq), CH ₂ I ₂ (10 eq), (CH ₂ Cl) ₂		(64) 20																																																												
		R = 4-PhC ₆ H ₄ CH ₂	170																																																												

TABLE XII. CYCLOPROPANATION OF ACYCLIC ALKENES CONTAINING A CLEAVABLE CHIRAL AUXILIARY (Continued)

Substrate	Conditions	Product(s) and Yield(s) (%), and de (%)	Refs.																																																								
<p>R = 4-PhC₆H₄CH₂</p>	Et ₂ Zn (5 eq), CH ₂ I ₂ (10 eq), (CH ₂ Cl) ₂	<p>(82) 48</p>	170																																																								
	Et ₂ Zn (5 eq), CH ₂ I ₂ (10 eq), solvent, temp		170																																																								
		<table border="1"> <thead> <tr> <th>Solvent</th> <th>Temp</th> <th>(%)</th> <th>de (%)</th> </tr> </thead> <tbody> <tr> <td>hexane</td> <td>-78 to 0°</td> <td>(0)</td> <td>—</td> </tr> <tr> <td>PhMe</td> <td>-40 to 0°</td> <td>(33)</td> <td>88</td> </tr> <tr> <td>PhMe</td> <td>-40 to 0°</td> <td>(72)</td> <td>75</td> </tr> <tr> <td>PhMe</td> <td>-78 to 0°</td> <td>(81)</td> <td>72</td> </tr> <tr> <td>PhMe^b</td> <td>-78 to -15°</td> <td>(50)</td> <td>90</td> </tr> <tr> <td>(CH₂Cl)₂</td> <td>-20 to 0°</td> <td>(61)</td> <td>82</td> </tr> <tr> <td>(CH₂Cl)₂</td> <td>-20 to 0°</td> <td>(85)</td> <td>71</td> </tr> <tr> <td>(CH₂Cl)₂^b</td> <td>-30 to -20°</td> <td>(54)</td> <td>83</td> </tr> <tr> <td>THF</td> <td>-78 to 0°</td> <td>(0)</td> <td>—</td> </tr> <tr> <td>PhMe/hex (1:2)</td> <td>0°</td> <td>(50)</td> <td>76</td> </tr> <tr> <td>(CH₂Cl)₂/hex (1:2)</td> <td>0°</td> <td>(72)</td> <td>74</td> </tr> <tr> <td>(CH₂Cl)₂^c</td> <td>0°</td> <td>(23)</td> <td>70</td> </tr> <tr> <td>THF^d</td> <td>-78 to 0°</td> <td>(0)</td> <td>—</td> </tr> </tbody> </table>	Solvent	Temp	(%)	de (%)	hexane	-78 to 0°	(0)	—	PhMe	-40 to 0°	(33)	88	PhMe	-40 to 0°	(72)	75	PhMe	-78 to 0°	(81)	72	PhMe ^b	-78 to -15°	(50)	90	(CH ₂ Cl) ₂	-20 to 0°	(61)	82	(CH ₂ Cl) ₂	-20 to 0°	(85)	71	(CH ₂ Cl) ₂ ^b	-30 to -20°	(54)	83	THF	-78 to 0°	(0)	—	PhMe/hex (1:2)	0°	(50)	76	(CH ₂ Cl) ₂ /hex (1:2)	0°	(72)	74	(CH ₂ Cl) ₂ ^c	0°	(23)	70	THF ^d	-78 to 0°	(0)	—	
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	Et ₂ Zn (10 eq), CH ₂ I ₂ (10 eq), PhMe, -35 to 0°	<p>(>97) >50:1</p>	157																																																								
	Zn/Ag, CH ₂ I ₂ , Et ₂ O	<p>(77-96)</p>	129, 664																																																								
<p>C₉₋₁₀</p>	Zn/Cu, CH ₂ I ₂ , Et ₂ O, reflux		892																																																								
		<table border="1"> <thead> <tr> <th>R</th> <th>(%)</th> <th>Optical yield (%)</th> </tr> </thead> <tbody> <tr> <td>H</td> <td>(56)</td> <td>11</td> </tr> <tr> <td>Me</td> <td>(42)</td> <td>11</td> </tr> <tr> <td>OMe</td> <td>(26)</td> <td>9</td> </tr> <tr> <td>Br</td> <td>(33)</td> <td>11</td> </tr> <tr> <td>Cl</td> <td>(52)</td> <td>10</td> </tr> </tbody> </table>	R	(%)	Optical yield (%)	H	(56)	11	Me	(42)	11	OMe	(26)	9	Br	(33)	11	Cl	(52)	10																																							
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<p>C₁₀</p>	Et ₂ Zn (5 eq), CH ₂ ICl (2 eq), PhMe, -35 to 0°	<p>(>80) >94</p>	189																																																								

TABLE XII. CYCLOPROPANATION OF ACYCLIC ALKENES CONTAINING A CLEAVABLE CHIRAL AUXILIARY (Continued)

Substrate	Conditions	Product(s) and Yield(s) (%), and dr (%)	Refs.												
C ₁₁ 	Conditions, solvent	 <table border="1"> <thead> <tr> <th>Conditions</th> <th>Solvent</th> <th>(%)</th> <th>dr</th> </tr> </thead> <tbody> <tr> <td>Zn/Cu, CH₂I₂ (5 eq)</td> <td>Et₂O</td> <td>(34)</td> <td>2.6:1</td> </tr> <tr> <td>Et₂Zn (10 eq), CH₂I₂ (20 eq)</td> <td>hexane</td> <td>(63)</td> <td>2.7:1</td> </tr> </tbody> </table>	Conditions	Solvent	(%)	dr	Zn/Cu, CH ₂ I ₂ (5 eq)	Et ₂ O	(34)	2.6:1	Et ₂ Zn (10 eq), CH ₂ I ₂ (20 eq)	hexane	(63)	2.7:1	92
Conditions	Solvent	(%)	dr												
Zn/Cu, CH ₂ I ₂ (5 eq)	Et ₂ O	(34)	2.6:1												
Et ₂ Zn (10 eq), CH ₂ I ₂ (20 eq)	hexane	(63)	2.7:1												
C ₁₅ 	Et ₂ Zn (5 eq), CH ₂ ICl (2 eq), PhMe, -35 to 0°	 (>80) >94	189												

^a Et₂O was used as solvent.^b The reagent was Et₂Zn (10 eq), CH₂I₂ (20 eq).^c CH₂ICl was used instead of CH₂I₂.^d The reaction was with Sm and CH₂I₂.

TABLE XIII. CYCLOPROPANATION WITH STOICHIOMETRIC CHIRAL ADDITIVES

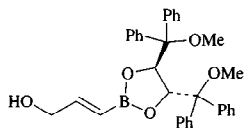
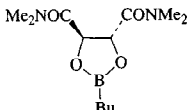
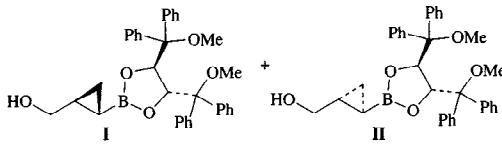
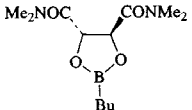
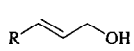
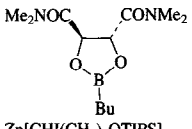
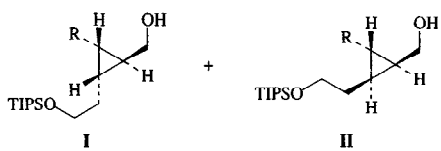
Substrate	Conditions	Product(s) and Yield(s) (%), and ee (%)	Refs.												
<p>C₃</p> 	 Et ₂ Zn, CH ₂ I ₂ , CH ₂ Cl ₂ , 0°	 (50) I:II = 60:40	886												
	 Et ₂ Zn, CH ₂ I ₂ , CH ₂ Cl ₂ , 0°	(78) I:II = 30:70	886												
<p>C₃₋₉</p> 	 Zn[CHI(CH ₂) ₂ OTIPS] ₂	 <table border="1" data-bbox="920 1435 1154 1526"> <thead> <tr> <th>R</th> <th>(%)</th> <th>I:II</th> <th>ee (%)</th> </tr> </thead> <tbody> <tr> <td>H</td> <td>(71)</td> <td>>95:5</td> <td>>95</td> </tr> <tr> <td>Ph</td> <td>(77)</td> <td>>95:5</td> <td>>95</td> </tr> </tbody> </table>	R	(%)	I:II	ee (%)	H	(71)	>95:5	>95	Ph	(77)	>95:5	>95	69
R	(%)	I:II	ee (%)												
H	(71)	>95:5	>95												
Ph	(77)	>95:5	>95												

TABLE XIII. CYCLOPROPANATION WITH STOICHIOMETRIC CHIRAL ADDITIVES

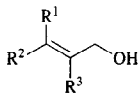
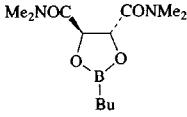

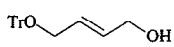
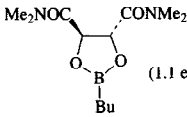

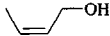
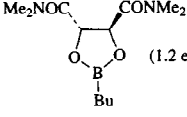
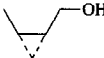
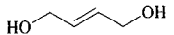
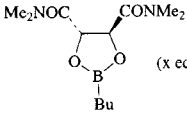

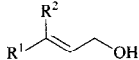
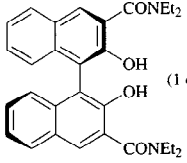
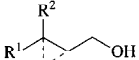
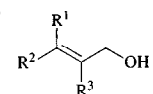
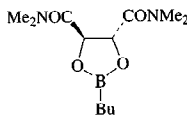
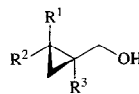
Substrate	Conditions	Product(s) and Yield(s) (%), and ee (%)	Refs.																																										
C ₃₋₁₀ 	 Et ₂ Zn (2.2 eq), MeCHCl ₂ (4.4 eq), CH ₂ Cl ₂ , 0°	 <table border="1"> <thead> <tr> <th>R¹</th> <th>R²</th> <th>R³</th> <th>(%)</th> <th>I:II</th> <th>ee (%)</th> </tr> </thead> <tbody> <tr> <td>H</td> <td>Ph</td> <td>H</td> <td>(96)</td> <td>>50:1</td> <td>98</td> </tr> <tr> <td>H</td> <td>Ph</td> <td>Me</td> <td>(83)</td> <td>14:1</td> <td>90</td> </tr> <tr> <td>BnOCH₂</td> <td>H</td> <td>H</td> <td>(80)</td> <td>>50:1</td> <td>94</td> </tr> <tr> <td>H</td> <td>H</td> <td>H</td> <td>(>84)</td> <td>20:1</td> <td>90</td> </tr> <tr> <td>Et</td> <td>H</td> <td>H</td> <td>(>87)</td> <td>15:1</td> <td>94</td> </tr> <tr> <td>H</td> <td>n-Pr</td> <td>H</td> <td>(>80)</td> <td>10:1</td> <td>93</td> </tr> </tbody> </table>	R ¹	R ²	R ³	(%)	I:II	ee (%)	H	Ph	H	(96)	>50:1	98	H	Ph	Me	(83)	14:1	90	BnOCH ₂	H	H	(80)	>50:1	94	H	H	H	(>84)	20:1	90	Et	H	H	(>87)	15:1	94	H	n-Pr	H	(>80)	10:1	93	69
R ¹	R ²	R ³	(%)	I:II	ee (%)																																								
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H	Ph	Me	(83)	14:1	90																																								
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H	n-Pr	H	(>80)	10:1	93																																								
344 C ₄ 	 Et ₂ Zn (2.5 eq), CH ₂ I ₂ (5 eq), CH ₂ Cl ₂ , -5° to rt	 (89)	661																																										
	 Zn(CH ₂ I) ₂ (2.2 eq), CH ₂ Cl ₂ , 0° to rt	 (75) >95	191, 893, 894																																										
	 Zn(CH ₂ I) ₂ ·DME, 4 Å MS, CH ₂ Cl ₂ , -40 to 25°	 (91) <table border="1"> <thead> <tr> <th>x</th> <th>ee (%)</th> </tr> </thead> <tbody> <tr> <td>1.1</td> <td>74</td> </tr> <tr> <td>2.1</td> <td>89</td> </tr> </tbody> </table>	x	ee (%)	1.1	74	2.1	89	193, 662																																				
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1.1	74																																												
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C ₄₋₁₁ 	 Et ₂ Zn (6 eq), CH ₂ I ₂ (3 eq), CH ₂ Cl ₂ , 0°, 15 h	 <table border="1"> <thead> <tr> <th>R¹</th> <th>R²</th> <th>(%)</th> <th>ee (%)</th> </tr> </thead> <tbody> <tr> <td>TBDSOCH₂</td> <td>H</td> <td>(59)</td> <td>87^a</td> </tr> <tr> <td>TrOCH₂</td> <td>H</td> <td>(64)</td> <td>88</td> </tr> <tr> <td>H</td> <td>TrOCH₂</td> <td>(34)</td> <td>65</td> </tr> <tr> <td>H</td> <td>TrOCH₂</td> <td>(76)</td> <td>16^b</td> </tr> <tr> <td>Ph</td> <td>H</td> <td>(55)</td> <td>94</td> </tr> <tr> <td>H</td> <td>Ph</td> <td>(44)</td> <td>92</td> </tr> <tr> <td>4-ClC₆H₄</td> <td>H</td> <td>(50)</td> <td>90</td> </tr> <tr> <td>4-MeOC₆H₄</td> <td>H</td> <td>(78)</td> <td>94</td> </tr> <tr> <td>Ph(CH₂)₂</td> <td>H</td> <td>(65)</td> <td>89</td> </tr> </tbody> </table>	R ¹	R ²	(%)	ee (%)	TBDSOCH ₂	H	(59)	87 ^a	TrOCH ₂	H	(64)	88	H	TrOCH ₂	(34)	65	H	TrOCH ₂	(76)	16 ^b	Ph	H	(55)	94	H	Ph	(44)	92	4-ClC ₆ H ₄	H	(50)	90	4-MeOC ₆ H ₄	H	(78)	94	Ph(CH ₂) ₂	H	(65)	89	198, 199 198, 199 198, 199 199 198, 199 199 198, 199 198, 199 198, 199		
R ¹	R ²	(%)	ee (%)																																										
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Ph(CH ₂) ₂	H	(65)	89																																										
C ₃₋₁₅ 	 Zn(CH ₂ I) ₂ ·DME, CH ₂ Cl ₂ , 25°																																												

TABLE XIII. CYCLOPROPANATION WITH STOICHIOMETRIC CHIRAL ADDITIVES

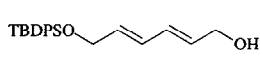
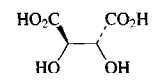
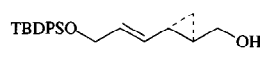
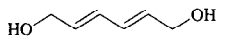
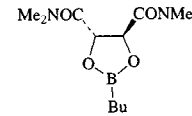

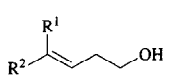
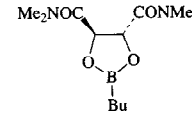
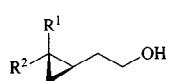
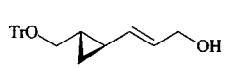
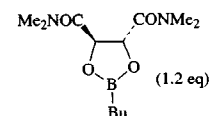

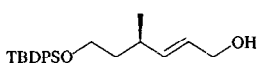
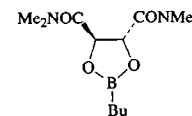
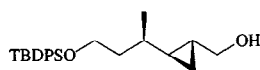
Substrate	Conditions	Product(s) and Yield(s) (%), and ee (%)				Refs.													
		R ¹	R ²	R ³	(%) ee (%)														
		H	Ph	H	(>98) ^c 93	185, 187													
		H	Ph	H	(95) 94	186, 187													
		H	3-MeOC ₆ H ₄	H	(>98) 93	187													
		H	Pr	H	(80) ^c 93	185, 187													
		H	Ph(CH ₂) ₂	H	(90) 94	187													
		H	BnOCH ₂	H	(87) 94	187													
		H	Bu ₃ Sn	H	(82) ^c -90	187													
		H	Bu ₃ Sn	H	(88) -90	187													
		H	I	H	(83) ^d 90	187													
		Bu ₃ Sn	H	H	(73) -90	187													
		I	H	H	(71) ^d 83	187													
		Et	H	H	(90) ^c 93	185, 187													
		Et	H	H	(>98) ^c -87	187													
		TBDPSOCH ₂	H	H	(80) ^c 91	185, 187													
		BnOCH ₂	H	H	(93) ^c 91	187													
		BnOCH ₂	H	H	(92) 91	186, 187													
		Me	Me	H	(85) ^c 94	185, 187													
		H	Ph	Me	(96) ^c 85	187													
		H	Ph	Me	(80) 82	187													
		H	Et	TIPSOCH ₂	(>98) 89	187													
		Me	Me	TIPSOCH ₂	(85) 88	187													
		H		-(CH ₂) ₄ -	(84) 60	187													
C ₆	 HO ₂ C  Et ₂ Zn, CH ₂ I ₂ , (CH ₂ Cl) ₂ , -20°	 (67)	654																
	 Me ₂ NOC  Zn(CH ₂ I) ₂ , CH ₂ Cl ₂ , 0° to rt	 (89)	192, 655																
C ₆₋₁₀	 Me ₂ NOC  Zn(CH ₂ I) ₂ •DME, CH ₂ Cl ₂ , -10°	 <table border="1" data-bbox="1111 1423 1336 1549"> <thead> <tr> <th>R¹</th> <th>R²</th> <th>(%)</th> <th>ee (%)</th> </tr> </thead> <tbody> <tr> <td>Et</td> <td>H</td> <td>(90)</td> <td>82</td> </tr> <tr> <td>H</td> <td>Ph</td> <td>(90)</td> <td>82</td> </tr> <tr> <td>Ph</td> <td>H</td> <td>(86)</td> <td>81</td> </tr> </tbody> </table>	R ¹	R ²	(%)	ee (%)	Et	H	(90)	82	H	Ph	(90)	82	Ph	H	(86)	81	187
R ¹	R ²	(%)	ee (%)																
Et	H	(90)	82																
H	Ph	(90)	82																
Ph	H	(86)	81																
C ₇	 Me ₂ NOC  (1.2 eq) Et ₂ Zn (2.5 eq), CH ₂ I ₂ (5 eq), CH ₂ Cl ₂ , -5° to rt	 (78)	661																
	 Me ₂ NOC  Et ₂ Zn, CH ₂ I ₂ , CH ₂ Cl ₂ , rt	 (99) >99% de	812																

TABLE XIII. CYCLOPROPANATION WITH STOICHIOMETRIC CHIRAL ADDITIVES (Continued)

Substrate	Conditions	Product(s) and Yield(s) (%), and ee (%)	Refs.																																																																																																
C7-14 	Zn(CH ₂ I) ₂ •DME (5 eq), CH ₂ Cl ₂ , -35° to reflux	<table border="1"> <thead> <tr> <th>Substrate</th> <th>(%)</th> <th>ee (%)</th> </tr> </thead> <tbody> <tr> <td>I</td> <td>(93)</td> <td>92</td> </tr> <tr> <td>II</td> <td>(49)</td> <td>96</td> </tr> <tr> <td>III</td> <td>(77)</td> <td>85</td> </tr> </tbody> </table>	Substrate	(%)	ee (%)	I	(93)	92	II	(49)	96	III	(77)	85	895																																																																																				
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C7-22 	1. Et ₂ Zn (1 eq), 0° 2. (+)-DET, 0° 3. Et ₂ Zn (3 eq), CH ₂ I ₂ (3 eq), CH ₂ Cl ₂ , temp, time	<table border="1"> <thead> <tr> <th>R¹</th> <th>R²</th> <th>Temp</th> <th>Time (h)</th> <th>(%)</th> <th>ee (%)</th> </tr> </thead> <tbody> <tr> <td>PhMe₂Si</td> <td>H</td> <td>0°</td> <td>4</td> <td>(69)</td> <td>63</td> </tr> <tr> <td>PhMe₂Si</td> <td>H</td> <td>0°</td> <td>5</td> <td>(62)</td> <td>47</td> </tr> <tr> <td>PhMe₂Si</td> <td>H</td> <td>-22°</td> <td>6</td> <td>(42)</td> <td>77</td> </tr> <tr> <td>PhMe₂Si</td> <td>Me</td> <td>0°</td> <td>21</td> <td>(78)</td> <td>78</td> </tr> <tr> <td>PhMe₂Si</td> <td>Me</td> <td>-20°</td> <td>8</td> <td>(93)</td> <td>89</td> </tr> <tr> <td>PhMe₂Si</td> <td>Me</td> <td>-30°</td> <td>5</td> <td>(88)</td> <td>92</td> </tr> <tr> <td>TMS</td> <td>Me</td> <td>-30°</td> <td>7</td> <td>(53)</td> <td>87</td> </tr> <tr> <td>Ph₃Si</td> <td>Me</td> <td>0°</td> <td>10</td> <td>(82)</td> <td>90</td> </tr> <tr> <td>PhMe₂Si</td> <td><i>n</i>-Bu</td> <td>-30°</td> <td>5</td> <td>(84)</td> <td>87</td> </tr> <tr> <td>Me</td> <td>TMS</td> <td>0°</td> <td>13</td> <td>(50)</td> <td>46</td> </tr> <tr> <td>Me</td> <td>PhMe₂Si</td> <td>0°</td> <td>5</td> <td>(83)</td> <td>62</td> </tr> <tr> <td>Me</td> <td>PhMe₂Si</td> <td>-30°</td> <td>9</td> <td>(72)</td> <td>74</td> </tr> <tr> <td>Me</td> <td>Ph₃Si</td> <td>0°</td> <td>15</td> <td>(84)</td> <td>34</td> </tr> <tr> <td>Ph</td> <td>TMS</td> <td>0°</td> <td>20</td> <td>(84)</td> <td>80</td> </tr> <tr> <td>Ph</td> <td>PhMe₂Si</td> <td>0°</td> <td>10</td> <td>(70)</td> <td>58</td> </tr> </tbody> </table>	R ¹	R ²	Temp	Time (h)	(%)	ee (%)	PhMe ₂ Si	H	0°	4	(69)	63	PhMe ₂ Si	H	0°	5	(62)	47	PhMe ₂ Si	H	-22°	6	(42)	77	PhMe ₂ Si	Me	0°	21	(78)	78	PhMe ₂ Si	Me	-20°	8	(93)	89	PhMe ₂ Si	Me	-30°	5	(88)	92	TMS	Me	-30°	7	(53)	87	Ph ₃ Si	Me	0°	10	(82)	90	PhMe ₂ Si	<i>n</i> -Bu	-30°	5	(84)	87	Me	TMS	0°	13	(50)	46	Me	PhMe ₂ Si	0°	5	(83)	62	Me	PhMe ₂ Si	-30°	9	(72)	74	Me	Ph ₃ Si	0°	15	(84)	34	Ph	TMS	0°	20	(84)	80	Ph	PhMe ₂ Si	0°	10	(70)	58	184
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TABLE XIII. CYCLOPROPANATION WITH STOICHIOMETRIC CHIRAL ADDITIVES (Continued)

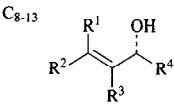
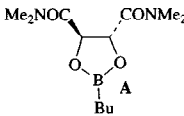
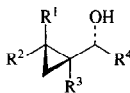
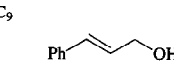
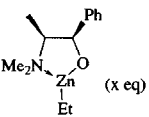
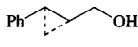
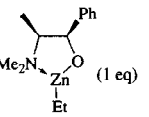
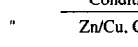
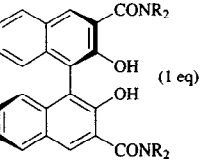
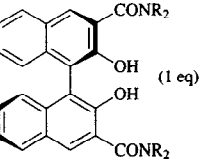
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		<table border="1"> <thead> <tr> <th>R¹</th> <th>R²</th> <th>R³</th> <th>R⁴</th> <th>A^f</th> <th>(%)^g</th> <th>syn:anti</th> </tr> </thead> <tbody> <tr> <td>H</td> <td>Ph</td> <td>H</td> <td>Me</td> <td><i>R,R</i></td> <td>(98)</td> <td><1:200</td> </tr> <tr> <td>H</td> <td>Ph</td> <td>H</td> <td>Me</td> <td><i>S,S</i></td> <td>(74)</td> <td>1:12</td> </tr> <tr> <td>H</td> <td>Ph</td> <td>Me</td> <td>Me</td> <td><i>R,R</i></td> <td>(92)</td> <td><1:200</td> </tr> <tr> <td>H</td> <td>Ph</td> <td>Me</td> <td>Me</td> <td><i>S,S</i></td> <td>(57)</td> <td>1:20</td> </tr> <tr> <td>H</td> <td>Ph</td> <td>H</td> <td>Et</td> <td><i>R,R</i></td> <td>(83)</td> <td>1:28</td> </tr> <tr> <td>H</td> <td>Ph</td> <td>H</td> <td>Et</td> <td><i>S,S</i></td> <td>(54)</td> <td>1:12</td> </tr> <tr> <td>H</td> <td><i>n</i>-Pr</td> <td>H</td> <td>Et</td> <td><i>R,R</i></td> <td>(84)</td> <td>1:32</td> </tr> <tr> <td>H</td> <td><i>n</i>-Pr</td> <td>H</td> <td>Et</td> <td><i>S,S</i></td> <td>(54)</td> <td>1:12</td> </tr> <tr> <td>H</td> <td>Ph</td> <td>H</td> <td><i>i</i>-Pr</td> <td><i>R,R</i></td> <td>(40)</td> <td>1:1.8</td> </tr> <tr> <td>H</td> <td>Ph</td> <td>H</td> <td><i>i</i>-Pr</td> <td><i>S,S</i></td> <td>(16)</td> <td>1.6:1</td> </tr> <tr> <td>Ph(CH₂)₃</td> <td>H</td> <td>H</td> <td>Me</td> <td><i>R,R</i></td> <td>(20)</td> <td>>20:1</td> </tr> <tr> <td>Ph(CH₂)₃</td> <td>H</td> <td>H</td> <td>Me</td> <td><i>S,S</i></td> <td>(30)</td> <td>>20:1</td> </tr> </tbody> </table>	R ¹	R ²	R ³	R ⁴	A ^f	(%) ^g	syn:anti	H	Ph	H	Me	<i>R,R</i>	(98)	<1:200	H	Ph	H	Me	<i>S,S</i>	(74)	1:12	H	Ph	Me	Me	<i>R,R</i>	(92)	<1:200	H	Ph	Me	Me	<i>S,S</i>	(57)	1:20	H	Ph	H	Et	<i>R,R</i>	(83)	1:28	H	Ph	H	Et	<i>S,S</i>	(54)	1:12	H	<i>n</i> -Pr	H	Et	<i>R,R</i>	(84)	1:32	H	<i>n</i> -Pr	H	Et	<i>S,S</i>	(54)	1:12	H	Ph	H	<i>i</i> -Pr	<i>R,R</i>	(40)	1:1.8	H	Ph	H	<i>i</i> -Pr	<i>S,S</i>	(16)	1.6:1	Ph(CH ₂) ₃	H	H	Me	<i>R,R</i>	(20)	>20:1	Ph(CH ₂) ₃	H	H	Me	<i>S,S</i>	(30)	>20:1	
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 <p>Conditions, solvent, rt</p>	<p>"</p>		<table border="1"> <thead> <tr> <th>Conditions</th> <th>Solvent</th> <th>(%)</th> <th>ee (%)</th> </tr> </thead> <tbody> <tr> <td>Zn/Cu, CH₂I₂</td> <td>DME</td> <td>(71)</td> <td>18</td> </tr> <tr> <td>Zn/Cu, CH₂I₂</td> <td>Et₂O</td> <td>(70)</td> <td>21</td> </tr> <tr> <td>Zn/Cu, CH₂I₂</td> <td>DME</td> <td>(68)</td> <td>24</td> </tr> <tr> <td>Zn(CH₂Cl)₂ (2 eq)</td> <td>PhMe</td> <td>(63)</td> <td>15</td> </tr> <tr> <td>Zn(CH₂Cl)₂ (2 eq)</td> <td>DME</td> <td>(54)</td> <td>19</td> </tr> </tbody> </table>	Conditions	Solvent	(%)	ee (%)	Zn/Cu, CH ₂ I ₂	DME	(71)	18	Zn/Cu, CH ₂ I ₂	Et ₂ O	(70)	21	Zn/Cu, CH ₂ I ₂	DME	(68)	24	Zn(CH ₂ Cl) ₂ (2 eq)	PhMe	(63)	15	Zn(CH ₂ Cl) ₂ (2 eq)	DME	(54)	19	182																																																																		
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TABLE XIII. CYCLOPROPANATION WITH STOICHIOMETRIC CHIRAL ADDITIVES (Continued)

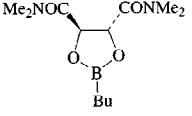

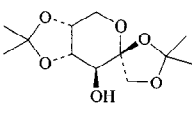

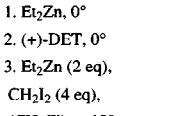

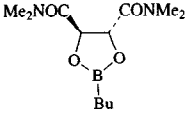

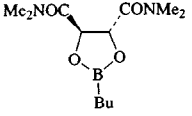
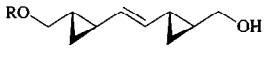
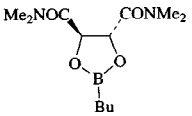

Substrate	Conditions	Product(s) and Yield(s) (%), and ee (%)	Refs.												
	1. Et ₂ Zn (1.1 eq) 2. HO-CH(CH ₂)-CH(OH)-COX XOC-CH(CH ₂)-COX	"	183												
	3. Et ₂ Zn (2 eq), CH ₂ I ₂ (4 eq), solvent, temp	X Solvent Temp (%) ee (%)													
		OEt DME 0° to rt (39) 15													
		OEt PhMe 0° to rt (55) 39													
		OEt CH ₂ Cl ₂ 0° to rt (22) 50													
		OEt CCl ₄ 0° to rt (28) 49													
		OEt (CH ₂ Cl) ₂ 0° to rt (13) 64													
		OEt (CH ₂ Cl) ₂ -12° (54) 71													
		OMe CH ₂ Cl ₂ 0° to rt (12) 64													
		OMe (CH ₂ Cl) ₂ 0° to rt (52) 23													
		OPr- <i>i</i> CH ₂ Cl ₂ 0° to rt (24) 27													
		OBu- <i>n</i> CH ₂ Cl ₂ 0° to rt (17) 58													
		1-pyrrolidinyl CH ₂ Cl ₂ 0° to rt (69) 13													
	 Zn(CH ₂ I) ₂ •DME, CH ₂ Cl ₂ , -5° to rt	 (95) 93	190												
	Zn(CH ₂ I) ₂ , Et ₂ AlCl (0.15 eq)	 (74) 51	53												
	1. Et ₂ Zn, 0° 2. (+)-DET, 0° 3. Et ₂ Zn (2 eq), CH ₂ I ₂ (4 eq), (CH ₂ Cl) ₂ , -12°	 (60) 70	183												
	 Zn(CH ₂ I) ₂ , CH ₂ Cl ₂	 (97) 89	819, 821												
	Zn(CH ₂ I) ₂ •DME (2.5 eq), CH ₂ Cl ₂ , -10°	 <table border="1" data-bbox="920 1630 1189 1721"> <thead> <tr> <th>R</th> <th>(%)</th> <th>de (%)</th> <th>mono:bis</th> </tr> </thead> <tbody> <tr> <td>Bn</td> <td>(78)</td> <td>>90</td> <td>8:1</td> </tr> <tr> <td>TIPS</td> <td>(85)</td> <td>>90</td> <td>8:1</td> </tr> </tbody> </table>	R	(%)	de (%)	mono:bis	Bn	(78)	>90	8:1	TIPS	(85)	>90	8:1	187, 187, 189
R	(%)	de (%)	mono:bis												
Bn	(78)	>90	8:1												
TIPS	(85)	>90	8:1												
	Zn(CH ₂ I) ₂ (5 eq), CH ₂ Cl ₂ , -5° to rt or: Zn(CH ₂ I) ₂ •DME, CH ₂ Cl ₂ , 0°	 (83)	661												
		(90) 91													
		" 10:1 mixture of diastereomers	194												

TABLE XIII. CYCLOPROPANATION WITH STOICHIOMETRIC CHIRAL ADDITIVES (Continued)

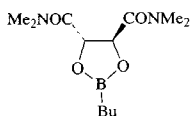


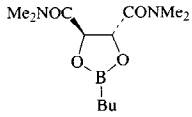

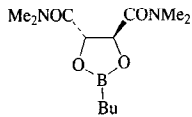

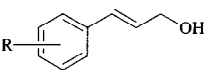
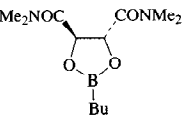
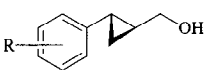
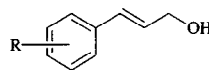
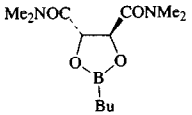
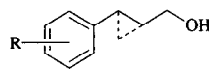
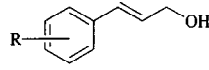
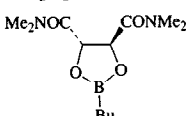
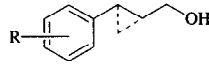
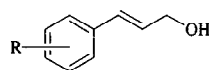
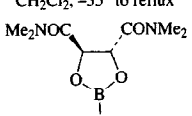
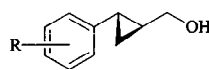
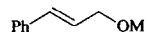
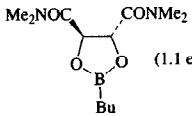

Substrate	Conditions	Product(s) and Yield(s) (%), and ee (%)	Refs.																																																								
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	$\text{Zn}(\text{CH}_2\text{I})_2$ (5.5 eq), CH_2Cl_2 , -5° to rt																																																										
	 Me_2NOC (at C2), CONMe_2 (at C5) Bu (on B)	 (90)	663																																																								
	$\text{Zn}(\text{CH}_2\text{I})_2 \cdot \text{DME}$, CH_2Cl_2 , -78° to rt																																																										
	 Me_2NOC (at C2), CONMe_2 (at C5) Bu (on B)	 (89)	193, 662																																																								
	$\text{Zn}(\text{CH}_2\text{I})_2 \cdot \text{DME}$, MS (4 Å), CH_2Cl_2 , -40 to 25°																																																										
 Mixture of R = H, 2- $\text{OC}_6\text{H}_{13-n}$, 4- NO_2	 Me_2NOC (at C2), CONMe_2 (at C5) Bu (on B)	 <table border="1" data-bbox="1137 952 1345 1067"> <thead> <tr> <th>R</th> <th>(%)</th> <th>ee (%)</th> </tr> </thead> <tbody> <tr> <td>H</td> <td>(39)</td> <td>91</td> </tr> <tr> <td>2-$\text{OC}_6\text{H}_{13-n}$</td> <td>(44)</td> <td>92</td> </tr> <tr> <td>4-NO_2</td> <td>(58)</td> <td>89</td> </tr> </tbody> </table>	R	(%)	ee (%)	H	(39)	91	2- $\text{OC}_6\text{H}_{13-n}$	(44)	92	4- NO_2	(58)	89	895																																												
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 Mixture of R = 2-OMe, 2-OPr- <i>i</i> , 4- NO_2	 Me_2NOC (at C2), CONMe_2 (at C5) Bu (on B)	 <table border="1" data-bbox="1137 1182 1345 1297"> <thead> <tr> <th>R</th> <th>(%)</th> <th>ee (%)</th> </tr> </thead> <tbody> <tr> <td>2-OMe</td> <td>(68)</td> <td>90</td> </tr> <tr> <td>2-OPr-<i>i</i></td> <td>(52)</td> <td>93</td> </tr> <tr> <td>4-NO_2</td> <td>(26)</td> <td>88</td> </tr> </tbody> </table>	R	(%)	ee (%)	2-OMe	(68)	90	2-OPr- <i>i</i>	(52)	93	4- NO_2	(26)	88	895																																												
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	$\text{Zn}(\text{CH}_2\text{I})_2 \cdot \text{DME}$ (5 eq), CH_2Cl_2 , -35° to reflux																																																										
	 Me_2NOC (at C2), CONMe_2 (at C5) Bu (on B) (1.1 eq)	 (>95)	185, 187																																																								
	$\text{Zn}(\text{CH}_2\text{I})_2$ (x eq), solvent, 25°	<table border="1" data-bbox="1067 1641 1362 2031"> <thead> <tr> <th>M</th> <th>x</th> <th>Solvent</th> <th>ee (%)</th> </tr> </thead> <tbody> <tr> <td>Li</td> <td>5</td> <td>CH_2Cl_2</td> <td>88</td> </tr> <tr> <td>Na</td> <td>5</td> <td>CH_2Cl_2</td> <td>58</td> </tr> <tr> <td>K</td> <td>5</td> <td>CH_2Cl_2</td> <td>91</td> </tr> <tr> <td>MgBr</td> <td>5</td> <td>CH_2Cl_2</td> <td>33</td> </tr> <tr> <td>ZnEt</td> <td>5</td> <td>CH_2Cl_2</td> <td>85</td> </tr> <tr> <td>H</td> <td>5</td> <td>CH_2Cl_2</td> <td>93</td> </tr> <tr> <td>H</td> <td>2.2</td> <td>CH_2Cl_2</td> <td>93</td> </tr> <tr> <td>H</td> <td>1</td> <td>CH_2Cl_2</td> <td>93^h</td> </tr> <tr> <td>H</td> <td>5</td> <td>PhMe</td> <td>93</td> </tr> <tr> <td>H</td> <td>5</td> <td>$(\text{CH}_2\text{Cl})_2$</td> <td>90</td> </tr> <tr> <td>H</td> <td>5</td> <td><i>t</i>-BuOMe</td> <td>89</td> </tr> <tr> <td>H</td> <td>5</td> <td>Et_2O</td> <td>77</td> </tr> <tr> <td>H</td> <td>5</td> <td>DME</td> <td>81</td> </tr> </tbody> </table>	M	x	Solvent	ee (%)	Li	5	CH_2Cl_2	88	Na	5	CH_2Cl_2	58	K	5	CH_2Cl_2	91	MgBr	5	CH_2Cl_2	33	ZnEt	5	CH_2Cl_2	85	H	5	CH_2Cl_2	93	H	2.2	CH_2Cl_2	93	H	1	CH_2Cl_2	93 ^h	H	5	PhMe	93	H	5	$(\text{CH}_2\text{Cl})_2$	90	H	5	<i>t</i> -BuOMe	89	H	5	Et_2O	77	H	5	DME	81	
M	x	Solvent	ee (%)																																																								
Li	5	CH_2Cl_2	88																																																								
Na	5	CH_2Cl_2	58																																																								
K	5	CH_2Cl_2	91																																																								
MgBr	5	CH_2Cl_2	33																																																								
ZnEt	5	CH_2Cl_2	85																																																								
H	5	CH_2Cl_2	93																																																								
H	2.2	CH_2Cl_2	93																																																								
H	1	CH_2Cl_2	93 ^h																																																								
H	5	PhMe	93																																																								
H	5	$(\text{CH}_2\text{Cl})_2$	90																																																								
H	5	<i>t</i> -BuOMe	89																																																								
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H	5	DME	81																																																								

TABLE XIII. CYCLOPROPANATION WITH STOICHIOMETRIC CHIRAL ADDITIVES (Continued)

Substrate	Conditions	Product(s) and Yield(s) (%), and ee (%)	Refs.									
11 	 Zn(CH ₂ I) ₂ •DME, CH ₂ Cl ₂ , -10°	 <table border="1"> <thead> <tr> <th>R</th> <th>(%)</th> <th>ee (%)</th> </tr> </thead> <tbody> <tr> <td>Ph</td> <td>(21)</td> <td>53</td> </tr> <tr> <td>Ph(CH₂)₂</td> <td>(25)</td> <td>~55</td> </tr> </tbody> </table>	R	(%)	ee (%)	Ph	(21)	53	Ph(CH ₂) ₂	(25)	~55	187
R	(%)	ee (%)										
Ph	(21)	53										
Ph(CH ₂) ₂	(25)	~55										
	 Zn(CH ₂ I) ₂ , CH ₂ Cl ₂ , -5° to rt	 (43)	661									
	 Zn(CH ₂ I) ₂ , CH ₂ Cl ₂ , -15 to 25°	 (>91)	192									
	 Zn(CH ₂ I) ₂ •DME (3 eq), CH ₂ Cl ₂ , -10°	 (65) 65% de mono:bis = 19:1	187, 189									
	 Zn(CH ₂ I) ₂ •DME (2.5 eq), CH ₂ Cl ₂ , -10°	 (70) 65% de mono:bis = 19:1	187, 189									
	 Zn(CH ₂ I) ₂ (1.5 eq), CH ₂ Cl ₂ , -5° to rt	 (70) 75% de	661									
	 Zn(CH ₂ I) ₂ •DME (1.6 eq), CH ₂ Cl ₂ , 0° to rt	 (87) 93 mono:bis = >20:1	187, 189									
1 	 Zn(CH ₂ I) ₂ •DME (3 eq), CH ₂ Cl ₂ , -10°	 (84) 91 mono:bis = >20:1	187, 189									
2 	 Zn(CH ₂ I) ₂ , CH ₂ Cl ₂	 (78) I:II = 1:6	819, 821									

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TABLE XIII. CYCLOPROPANATION WITH STOICHIOMETRIC CHIRAL ADDITIVES (Continued)

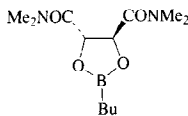
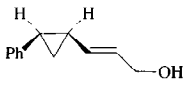
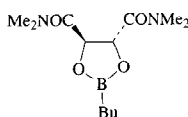
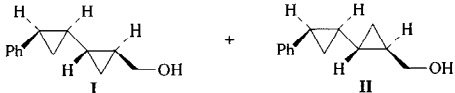
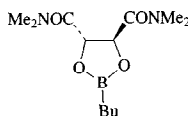
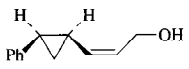
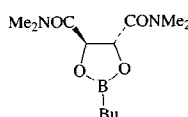
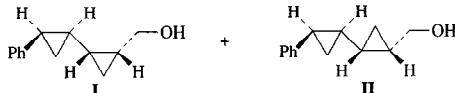
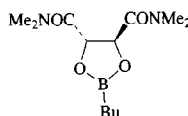
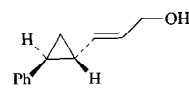
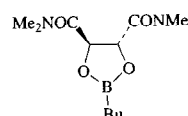
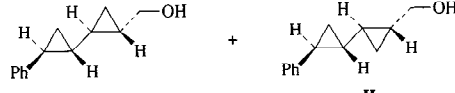
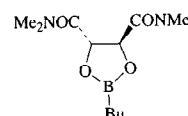
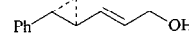
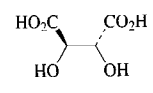
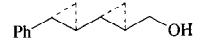
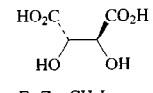
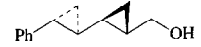
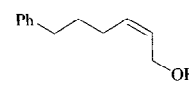
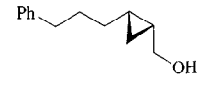
Substrate	Conditions	Product(s) and Yield(s) (%), and ee (%)	Refs.
		I + II (81) I:II = 10:1	819, 821
	Zn(CH ₂ I) ₂ , CH ₂ Cl ₂		
		 (81) I:II = 2.5:1	819, 821
	Zn(CH ₂ I) ₂ , CH ₂ Cl ₂		
		I + II (79) I:II = 1:>10	819, 821
	Zn(CH ₂ I) ₂ , CH ₂ Cl ₂		
		 (80) I:II = 1:5	819, 821
	Zn(CH ₂ I) ₂ , CH ₂ Cl ₂		
		I + II (79) I:II = 5:1	819, 821
	Zn(CH ₂ I) ₂ , CH ₂ Cl ₂		
		 (72) I:II = >10:1	819, 820
	Zn(CH ₂ I) ₂ , CH ₂ Cl ₂		
		I + II (78) I:II = 1:>10	819, 820
	Zn(CH ₂ I) ₂ , CH ₂ Cl ₂		
		 (72) 6:1	654, 822
	Et ₂ Zn, CH ₂ I ₂ , (CH ₂ Cl) ₂ , -12°		
		 (84) 6:1	654, 822
	Et ₂ Zn, CH ₂ I ₂ , (CH ₂ Cl) ₂ , -12°		
	1. Et ₂ Zn (1.1 eq), 0° 2. (+)-DET, 0° 3. Et ₂ Zn (2 eq), CH ₂ I ₂ (4 eq), (CH ₂ Cl) ₂ , -12°	 (46) 81	183

TABLE XIII. CYCLOPROPANATION WITH STOICHIOMETRIC CHIRAL ADDITIVES (Continued)


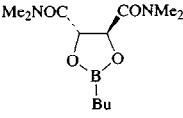


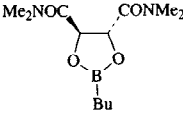

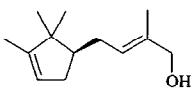
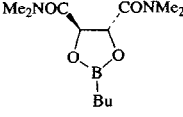
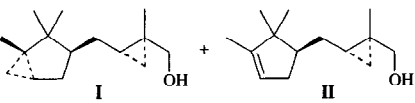
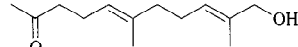
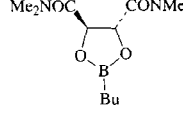
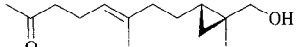
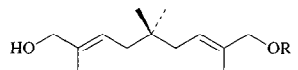
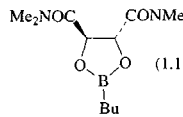
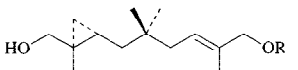

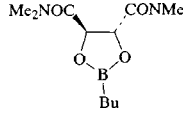

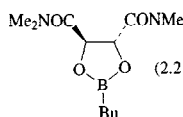
Substrate	Conditions	Product(s) and Yield(s) (%), and ee (%)	Refs.																
	 Zn(CH ₂ I) ₂ , CH ₂ Cl ₂ , 0 to 25°	 (94)	162, 192, 653, 675																
	or: Zn(CH ₂ I) ₂ , CH ₂ Cl ₂ /DME, -15 to 25°	" (93)	162, 192, 653, 655																
	 Zn(CH ₂ I) ₂ , CH ₂ Cl ₂ , 0 to 25°	 (100)	162, 675																
	or: Zn(CH ₂ I) ₂ , CH ₂ Cl ₂ /DME, -15 to 25°	" (100)	162, 653																
3 	 Zn(CH ₂ I) ₂ •DME, CH ₂ Cl ₂ , -10° to rt	 (~13) I:II = 48:43 71% de	506																
	 Zn(CH ₂ I) ₂ •DME (4.2 eq), CH ₂ Cl ₂ , 0°	 (>95) 88 mono:bis = >20:1	187, 189																
	 (1.1 eq) Zn(CH ₂ I) ₂ (4.2 eq), DME/CH ₂ Cl ₂ , 0°	 <table border="1" data-bbox="911 1492 1258 1608"> <thead> <tr> <th>R</th> <th>(%)</th> <th>mono:bis</th> <th>ee (%)</th> </tr> </thead> <tbody> <tr> <td>Ac</td> <td>(>95)</td> <td>>20:1</td> <td>85</td> </tr> <tr> <td>Bn</td> <td>(>95)</td> <td>>20:1</td> <td>86</td> </tr> <tr> <td>TBDPS</td> <td>(>95)</td> <td>>20:1</td> <td>87</td> </tr> </tbody> </table>	R	(%)	mono:bis	ee (%)	Ac	(>95)	>20:1	85	Bn	(>95)	>20:1	86	TBDPS	(>95)	>20:1	87	189, 678
R	(%)	mono:bis	ee (%)																
Ac	(>95)	>20:1	85																
Bn	(>95)	>20:1	86																
TBDPS	(>95)	>20:1	87																
15 	 Zn(CH ₂ I) ₂ (5 eq), CH ₂ Cl ₂ , -5° to rt	 (80)	661																
	 (2.2 eq) Zn(CH ₂ I) ₂ (4.4 eq), DME/CH ₂ Cl ₂ , 0°	" (90), ~10% of 2 other isomers	194																

TABLE XIII. CYCLOPROPANATION WITH STOICHIOMETRIC CHIRAL ADDITIVES (Continued)

Substrate	Conditions	Product(s) and Yield(s) (%), and ee (%)	Refs.
	 $\text{Zn}(\text{CH}_2\text{I}_2) \cdot \text{DME}$, CH_2Cl_2 , -78° to rt	(86)	663
	 $\text{Zn}(\text{CH}_2\text{I}_2) \cdot \text{DME}$, MS (4 Å), CH_2Cl_2 , -40 to 25°	(83)	193, 662
	 $\text{Zn}(\text{CH}_2\text{I}_2) \cdot \text{DME}$ (1.6 eq), CH_2Cl_2 , 0°	(84) 93 mono:bis = >20:1	187, 189
$\text{Bu}_3\text{Sn}-\text{CH}=\text{CH}-\text{CH}_2\text{OH}$	 Et_2Zn , CH_2I_2 , CH_2Cl_2	(98) 88-90	188
$\text{Bu}_3\text{Sn}-\text{CH}=\text{CH}-\text{CH}_2\text{OH}$	 Et_2Zn , CH_2I_2 , CH_2Cl_2	(98) 88-90	188
C_{17} 	 $\text{Zn}(\text{CH}_2\text{I}_2)$	(74)	681
C_{18} 	 $\text{Zn}(\text{CH}_2\text{I}_2)$, $\text{CH}_2\text{Cl}_2/\text{DME}$, -40°	(90)	192, 655
C_{18} 	 $\text{Zn}(\text{CH}_2\text{I}_2)$, $\text{CH}_2\text{Cl}_2/\text{DME}$, -15 to 25°	(84)	192
C_{21} 	 $\text{Zn}(\text{CH}_2\text{I}_2) \cdot \text{DME}$, MS (4 Å), CH_2Cl_2 , -25° to rt	(72) + (26)	662

TABLE XIII. CYCLOPROPANATION WITH STOICHIOMETRIC CHIRAL ADDITIVES (Continued)

Substrate	Conditions	Product(s) and Yield(s) (%), and ee (%)	Refs.						
	 $\text{Zn}(\text{CH}_2\text{I}_2)\cdot\text{DME}$, MS (4 Å), CH_2Cl_2 , -25°	(>56)	662						
	 $\text{Zn}(\text{CH}_2\text{I}_2)\cdot\text{DME}$ (3 eq), CH_2Cl_2 , -10°	(81) 90% de mono:bis = 9:1	187, 189						
C_{22} 	 $\text{Zn}(\text{CH}_2\text{I}_2)\cdot\text{DME}$, MS (4 Å), CH_2Cl_2 , -25°	<table border="1" style="margin-left: auto; margin-right: auto;"> <thead> <tr> <th>R</th> <th>(%)</th> </tr> </thead> <tbody> <tr> <td>CO_2Me</td> <td>(67)</td> </tr> <tr> <td>TBDMSOCH₂</td> <td>(91)</td> </tr> </tbody> </table>	R	(%)	CO_2Me	(67)	TBDMSOCH ₂	(91)	662
R	(%)								
CO_2Me	(67)								
TBDMSOCH ₂	(91)								

^a Sense of induction not determined.

^a ZnI_2 (1 eq) was added.

^b $\text{Zn}(\text{CH}_2\text{I}_2)$ was used instead of $\text{Zn}(\text{CH}_2\text{I}_2)\cdot\text{DME}$.

^c $\text{Zn}(\text{CH}_2\text{I}_2)\cdot\text{DME}$ (10 eq) was used.

^d The enantiomer of the ligand was used.

^e Absolute configuration of the chiral ligand.

^f Isolated yield of the pure *anti* isomer.

^g The yield was 85%.

TABLE XIV. CYCLOPROPANATION WITH CHIRAL CATALYSTS

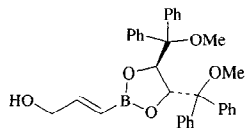
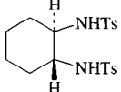
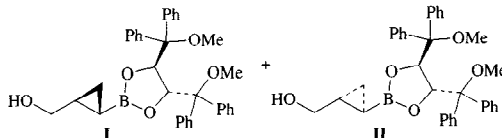
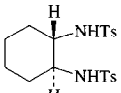
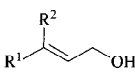
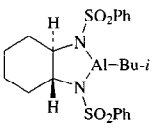
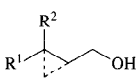
Substrate	Conditions	Product(s) and Yield(s) (%), and ee	Refs.																																								
<p>C₃</p> 	 Et ₂ Zn, CH ₂ I ₂ , ZnI ₂ , CH ₂ Cl ₂ , 0°	 (90) I:II = 20:80	886																																								
	 Et ₂ Zn, CH ₂ I ₂ , ZnI ₂ , CH ₂ Cl ₂ , 0°	(91) I:II = 60:40	886																																								
<p>C₄₋₁₁</p> 	 Et ₂ Zn (2 eq), CH ₂ I ₂ (3 eq), CH ₂ Cl ₂ /hexane, -20°, time	 <table border="1"> <thead> <tr> <th>R¹</th> <th>R²</th> <th>Time (h)</th> <th>(%)</th> <th>ee (%)</th> </tr> </thead> <tbody> <tr> <td>Ph</td> <td>H</td> <td>14</td> <td>(>99)</td> <td>76</td> </tr> <tr> <td>H</td> <td>Ph</td> <td>6</td> <td>(>99)</td> <td>73</td> </tr> <tr> <td>Ph(CH₂)₂</td> <td>H</td> <td>6</td> <td>(>99)</td> <td>78</td> </tr> <tr> <td>Ph(CH₂)₂</td> <td>H</td> <td>6</td> <td>(95)</td> <td>79</td> </tr> <tr> <td>TrOCH₂</td> <td>H</td> <td>12</td> <td>(83)</td> <td>80</td> </tr> <tr> <td>H</td> <td>TrOCH₂</td> <td>12</td> <td>(92)</td> <td>56</td> </tr> <tr> <td>H</td> <td>BnOCH₂</td> <td>26</td> <td>(91)</td> <td>26</td> </tr> </tbody> </table>	R ¹	R ²	Time (h)	(%)	ee (%)	Ph	H	14	(>99)	76	H	Ph	6	(>99)	73	Ph(CH ₂) ₂	H	6	(>99)	78	Ph(CH ₂) ₂	H	6	(95)	79	TrOCH ₂	H	12	(83)	80	H	TrOCH ₂	12	(92)	56	H	BnOCH ₂	26	(91)	26	204
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TABLE XIV. CYCLOPROPANATION WITH CHIRAL CATALYSTS (Continued)

Substrate	Conditions	Product(s) and Yield(s) (%), and ee	Refs.																																																																																
	 (0.12 eq) Et ₂ Zn (2 eq), CH ₂ I ₂ (3 eq), CH ₂ Cl ₂ /hexane, -23°, 5 h	" <table border="1"> <thead> <tr> <th>R¹</th> <th>R²</th> <th>R³</th> <th>(%)</th> <th>ee (%)</th> </tr> </thead> <tbody> <tr> <td>Ph</td> <td>H</td> <td>Ph</td> <td>(75)</td> <td>68</td> </tr> <tr> <td>Ph</td> <td>H</td> <td>2-O₂NC₆H₄</td> <td>(92)</td> <td>75</td> </tr> <tr> <td>Ph</td> <td>H</td> <td>3-O₂NC₆H₄</td> <td>(72)</td> <td>33</td> </tr> <tr> <td>Ph</td> <td>H</td> <td>4-O₂NC₆H₄</td> <td>(82)</td> <td>76</td> </tr> <tr> <td>Ph</td> <td>H</td> <td>4-CF₃C₆H₄</td> <td>(99)</td> <td>67</td> </tr> <tr> <td>Ph</td> <td>H</td> <td>3,5-(CF₃)₂C₆H₃</td> <td>(99)</td> <td>29</td> </tr> <tr> <td>H</td> <td>Ph</td> <td>2-O₂NC₆H₄</td> <td>(82)</td> <td>51</td> </tr> <tr> <td>H</td> <td>Ph</td> <td>3-O₂NC₆H₄</td> <td>(71)</td> <td>31</td> </tr> <tr> <td>H</td> <td>Ph</td> <td>4-O₂NC₆H₄</td> <td>(71)</td> <td>75</td> </tr> <tr> <td>Ph(CH₂)₂</td> <td>H</td> <td>2-O₂NC₆H₄</td> <td>(82)</td> <td>80</td> </tr> <tr> <td>Ph(CH₂)₂</td> <td>H</td> <td>4-O₂NC₆H₄</td> <td>(100)</td> <td>82</td> </tr> <tr> <td>BzOCH₂</td> <td>H</td> <td>4-O₂NC₆H₄</td> <td>(70)</td> <td>36</td> </tr> <tr> <td>TrOCH₂</td> <td>H</td> <td>4-O₂NC₆H₄</td> <td>(86)</td> <td>80</td> </tr> <tr> <td>H</td> <td>BzOCH₂</td> <td>4-O₂NC₆H₄</td> <td>(36)</td> <td>13</td> </tr> <tr> <td>H</td> <td>TrOCH₂</td> <td>4-O₂NC₆H₄</td> <td>(77)</td> <td>65</td> </tr> </tbody> </table>	R ¹	R ²	R ³	(%)	ee (%)	Ph	H	Ph	(75)	68	Ph	H	2-O ₂ NC ₆ H ₄	(92)	75	Ph	H	3-O ₂ NC ₆ H ₄	(72)	33	Ph	H	4-O ₂ NC ₆ H ₄	(82)	76	Ph	H	4-CF ₃ C ₆ H ₄	(99)	67	Ph	H	3,5-(CF ₃) ₂ C ₆ H ₃	(99)	29	H	Ph	2-O ₂ NC ₆ H ₄	(82)	51	H	Ph	3-O ₂ NC ₆ H ₄	(71)	31	H	Ph	4-O ₂ NC ₆ H ₄	(71)	75	Ph(CH ₂) ₂	H	2-O ₂ NC ₆ H ₄	(82)	80	Ph(CH ₂) ₂	H	4-O ₂ NC ₆ H ₄	(100)	82	BzOCH ₂	H	4-O ₂ NC ₆ H ₄	(70)	36	TrOCH ₂	H	4-O ₂ NC ₆ H ₄	(86)	80	H	BzOCH ₂	4-O ₂ NC ₆ H ₄	(36)	13	H	TrOCH ₂	4-O ₂ NC ₆ H ₄	(77)	65	30, 200 30, 200 30, 200 30, 200 30 30 30, 200 30, 200 30, 200 30, 200 30, 200 30, 200 30, 200 30, 200 30
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Substrate	Conditions	Product(s) and Yield(s) (%), and ee	Refs.																												
	 (0.1 eq) Et ₂ Zn (2 eq), CH ₂ I ₂ (3 eq), CH ₂ Cl ₂ , -23°	<table border="1"> <thead> <tr> <th>R¹</th> <th>R²</th> <th>(%)</th> <th>ee (%)</th> </tr> </thead> <tbody> <tr> <td>Ph</td> <td>H</td> <td>(100)</td> <td>85</td> </tr> <tr> <td>Ph(CH₂)₂</td> <td>H</td> <td>(97)</td> <td>54</td> </tr> <tr> <td>TrOCH₂</td> <td>H</td> <td>(89)</td> <td>65</td> </tr> <tr> <td>PhMe₂Si</td> <td>H</td> <td>(85)</td> <td>71</td> </tr> <tr> <td>Bu₃Sn</td> <td>H</td> <td>(93)</td> <td>60</td> </tr> <tr> <td>H</td> <td>TrOCH₂</td> <td>(88)</td> <td>39</td> </tr> </tbody> </table>	R ¹	R ²	(%)	ee (%)	Ph	H	(100)	85	Ph(CH ₂) ₂	H	(97)	54	TrOCH ₂	H	(89)	65	PhMe ₂ Si	H	(85)	71	Bu ₃ Sn	H	(93)	60	H	TrOCH ₂	(88)	39	896
R ¹	R ²	(%)	ee (%)																												
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TABLE XIV. CYCLOPROPANATION WITH CHIRAL CATALYSTS (Continued)

Substrate	Conditions	Product(s) and Yield(s) (%), and ee	Refs.												
	 Zn(CH ₂ I ₂) ₂ (1 eq), CH ₂ Cl ₂ , 0°, 1.5 h	(90) 60	31												
	 (0.12 eq) Et ₂ Zn (1 eq), CH ₂ I ₂ (3 eq), PhMe/hexane, -23°, 1.5 h	<table border="1"> <thead> <tr> <th>R</th> <th>(%)</th> <th>ee (%)</th> </tr> </thead> <tbody> <tr> <td>Me</td> <td>(99)</td> <td>-0</td> </tr> <tr> <td>Bn</td> <td>(97)</td> <td>-0</td> </tr> <tr> <td>Tr</td> <td>(<3)</td> <td>—</td> </tr> </tbody> </table>	R	(%)	ee (%)	Me	(99)	-0	Bn	(97)	-0	Tr	(<3)	—	30
R	(%)	ee (%)													
Me	(99)	-0													
Bn	(97)	-0													
Tr	(<3)	—													
	 (0.1 eq) 2,2'-Dipyridyl (0.1 eq), Et ₂ Zn (1.1 eq) 1. ZnI ₂ (1.0 eq), 2. Zn(CH ₂ I ₂) ₂ (1.0 eq)	(—) 76-84	206												
	 (0.12 eq) Et ₂ Zn (2 eq), CH ₂ I ₂ (3 eq), CH ₂ Cl ₂ , -70° to rt, 24 h	<table border="1"> <thead> <tr> <th>R</th> <th>(%)</th> <th>ee (%)</th> </tr> </thead> <tbody> <tr> <td>4-(C₂H₅)₂C₆H₄</td> <td>(70)</td> <td>65</td> </tr> <tr> <td>PS-C₆H₄</td> <td>(68)</td> <td>65</td> </tr> </tbody> </table>	R	(%)	ee (%)	4-(C ₂ H ₅) ₂ C ₆ H ₄	(70)	65	PS-C ₆ H ₄	(68)	65	897			
R	(%)	ee (%)													
4-(C ₂ H ₅) ₂ C ₆ H ₄	(70)	65													
PS-C ₆ H ₄	(68)	65													

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TABLE XIV. CYCLOPROPANATION WITH CHIRAL CATALYSTS (Continued)

Substrate	Conditions	Product(s) and Yield(s) (%), and ee	Refs.																																																																	
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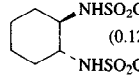
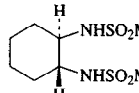
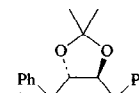

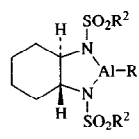

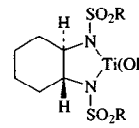
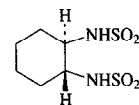

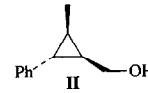
Substrate	Conditions	Product(s) and Yield(s) (%), and ee	Refs.																																													
	Et ₂ Zn (2 eq), CH ₂ I ₂ (3 eq), solvent/hexane, -23°, time	Solvent Time (h) (%) ee (%) PhMe 9 (81) 69	30																																													
		CH ₂ Cl ₂ 5.5 (92) 75																																														
		THF 8.5 (~0) —																																														
		Et ₂ O 8.5 (~0) —																																														
	1. Et ₂ Zn (1.1 eq), additive (1 eq) 2. Et ₂ Zn (1 eq), CH ₂ I ₂ (2 eq), CH ₂ Cl ₂ , 0°	Additive t _{1/2} (min) ee (%) — 8 80	20																																													
		ZnI ₂ <3 86																																														
		ZnBr ₂ <3 80																																														
		ZnCl ₂ 4 76																																														
		ZnF ₂ 10 72																																														
		Zn(OAc) ₂ 10 45																																														
		CdCl ₂ 11 83																																														
		CdI ₂ 11 75																																														
		MgI ₂ 50 23																																														
		PbI ₂ 8 72																																														
		MnI ₂ 12 32																																														
		HgI ₂ 15 39																																														
Gal ₃ Dec —																																																
	Zn(CH ₂ I ₂) ₂ (1 eq), CH ₂ Cl ₂ , 0°, 1.5 h	 (80) 90	31																																													
				204																																												
	Et ₂ Zn (2 eq), CH ₂ I ₂ (3 eq), CH ₂ Cl ₂ /hexane, -20°, time	<table border="1"> <thead> <tr> <th>R¹</th> <th>R²</th> <th>Time (h)</th> <th>(%)</th> <th>ee (%)</th> </tr> </thead> <tbody> <tr> <td>Me</td> <td>CF₃</td> <td>18</td> <td>(100)</td> <td>14</td> </tr> <tr> <td>Me</td> <td>4-O₂NC₆H₄</td> <td>3</td> <td>(100)</td> <td>70</td> </tr> <tr> <td>Et</td> <td>4-O₂NC₆H₄</td> <td>3</td> <td>(100)</td> <td>66</td> </tr> <tr> <td><i>i</i>-Bu</td> <td>4-O₂NC₆H₄</td> <td>12</td> <td>(100)</td> <td>71</td> </tr> <tr> <td><i>i</i>-Bu</td> <td>4-O₂NC₆H₄</td> <td>12</td> <td>(100)</td> <td>73</td> </tr> <tr> <td><i>i</i>-Bu</td> <td>4-CF₃C₆H₄</td> <td>18</td> <td>(100)</td> <td>66</td> </tr> <tr> <td><i>i</i>-Bu</td> <td>3,5-(CF₃)₂C₆H₃</td> <td>18</td> <td>(96)</td> <td>17</td> </tr> <tr> <td><i>i</i>-Bu</td> <td>Ph</td> <td>14</td> <td>(100)</td> <td>76</td> </tr> </tbody> </table>	R ¹	R ²	Time (h)	(%)	ee (%)	Me	CF ₃	18	(100)	14	Me	4-O ₂ NC ₆ H ₄	3	(100)	70	Et	4-O ₂ NC ₆ H ₄	3	(100)	66	<i>i</i> -Bu	4-O ₂ NC ₆ H ₄	12	(100)	71	<i>i</i> -Bu	4-O ₂ NC ₆ H ₄	12	(100)	73	<i>i</i> -Bu	4-CF ₃ C ₆ H ₄	18	(100)	66	<i>i</i> -Bu	3,5-(CF ₃) ₂ C ₆ H ₃	18	(96)	17	<i>i</i> -Bu	Ph	14	(100)	76	
		R ¹	R ²	Time (h)	(%)	ee (%)																																										
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		<i>i</i> -Bu	4-O ₂ NC ₆ H ₄	12	(100)	71																																										
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	1. Et ₂ Zn (1.1 eq) 2. ZnI ₂ , Zn(CHIME) ₂ , CH ₂ Cl ₂ , 0°	 12% ee	464																																													
		 61% ee (58) I:II = 65:35																																														

TABLE XIV. CYCLOPROPANATION WITH CHIRAL CATALYSTS (Continued)

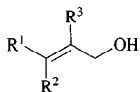
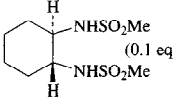
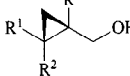
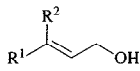
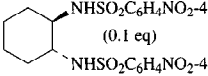
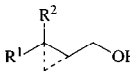
Substrate	Conditions	Product(s) and Yield(s) (%), and ee	Refs.																														
C_{9-12} 	 (0.1 eq) 1. Et ₂ Zn (1.1 eq) 2. Preformed ZnI ₂ (0.1 eq) 3. Et ₂ Zn (1 eq), CH ₂ I ₂ (2 eq), CH ₂ Cl ₂ , 0°	 <table border="1"> <thead> <tr> <th>R¹</th> <th>R²</th> <th>R³</th> <th>(%)</th> <th>ee (%)</th> </tr> </thead> <tbody> <tr> <td>Ph</td> <td>H</td> <td>H</td> <td>(92)</td> <td>89</td> </tr> <tr> <td>Ph(CH₂)₂</td> <td>H</td> <td>H</td> <td>(88)</td> <td>89</td> </tr> <tr> <td>Ph</td> <td>Me</td> <td>H</td> <td>(92)</td> <td>89</td> </tr> <tr> <td>Me</td> <td>Ph(CH₂)₂</td> <td>H</td> <td>(89)</td> <td>82</td> </tr> <tr> <td>Ph</td> <td>H</td> <td>Me</td> <td>(91)</td> <td>3</td> </tr> </tbody> </table>	R ¹	R ²	R ³	(%)	ee (%)	Ph	H	H	(92)	89	Ph(CH ₂) ₂	H	H	(88)	89	Ph	Me	H	(92)	89	Me	Ph(CH ₂) ₂	H	(89)	82	Ph	H	Me	(91)	3	201
		R ¹	R ²	R ³	(%)	ee (%)																											
Ph	H	H	(92)	89																													
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Me	Ph(CH ₂) ₂	H	(89)	82																													
Ph	H	Me	(91)	3																													
C_{11-15} 	 (0.1 eq) Et ₂ Zn (2 eq), CH ₂ I ₂ (3 eq), CH ₂ Cl ₂ /hexane, -20°	 <table border="1"> <thead> <tr> <th>R¹</th> <th>R²</th> <th>(%)</th> <th>ee (%)</th> </tr> </thead> <tbody> <tr> <td>H</td> <td>Bu₃Sn</td> <td>(75)</td> <td>66</td> </tr> <tr> <td>H</td> <td>PhMe₂Si</td> <td>(67)</td> <td>59</td> </tr> <tr> <td>PhMe₂Si</td> <td>H</td> <td>(83)</td> <td>81</td> </tr> <tr> <td>Bu₃Sn</td> <td>H</td> <td>(94)</td> <td>86</td> </tr> </tbody> </table>	R ¹	R ²	(%)	ee (%)	H	Bu ₃ Sn	(75)	66	H	PhMe ₂ Si	(67)	59	PhMe ₂ Si	H	(83)	81	Bu ₃ Sn	H	(94)	86	203										
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		PhMe ₂ Si	H	(83)	81																												
		Bu ₃ Sn	H	(94)	86																												

TABLE XV. CYCLOPROPANATION OF ALKENES USING A SUBSTITUTED DIHALIDE


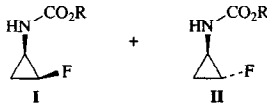
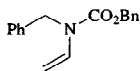
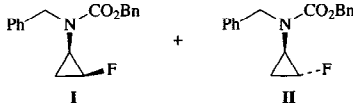
Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.																																	
C_2 	Et ₂ Zn, CHFCl ₂ , conditions, CH ₂ Cl ₂	 <table border="1"> <thead> <tr> <th>R</th> <th>Conditions</th> <th>(%)</th> <th>I:II</th> </tr> </thead> <tbody> <tr> <td>Bn</td> <td>-40° then rt</td> <td>(<10)</td> <td>—</td> </tr> <tr> <td>Bn</td> <td>MS (4Å), DME, rt</td> <td>(25)</td> <td>64:36</td> </tr> <tr> <td><i>t</i>-Bu</td> <td>MS (4Å), DME, 0°</td> <td>(30)</td> <td>60:40</td> </tr> </tbody> </table>	R	Conditions	(%)	I:II	Bn	-40° then rt	(<10)	—	Bn	MS (4Å), DME, rt	(25)	64:36	<i>t</i> -Bu	MS (4Å), DME, 0°	(30)	60:40	548																	
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TABLE XV. CYCLOPROPANATION OF ALKENES USING A SUBSTITUTED DIHALIDE (Continued)

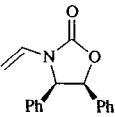
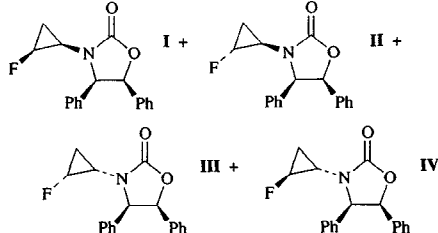
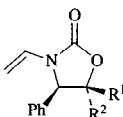
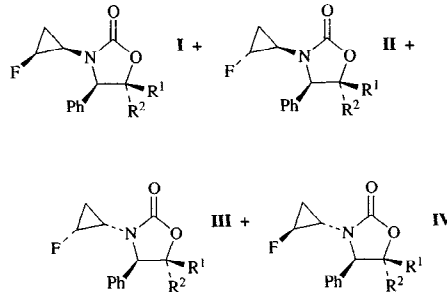
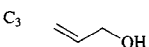
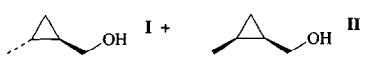
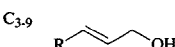
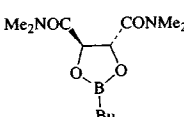
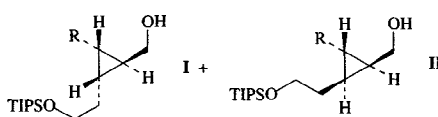
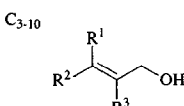
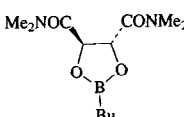
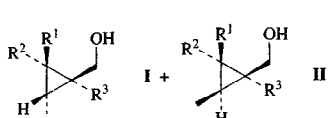
Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.																																																				
	Et ₂ Zn (3 eq), CHFI ₂ (3 eq), additive, CH ₂ Cl ₂ , temp	 <table border="1"> <thead> <tr> <th>Additive</th> <th>Temp</th> <th>(%)</th> <th>I:II:III:IV</th> </tr> </thead> <tbody> <tr> <td>—</td> <td>rt</td> <td>(44)</td> <td>50:41:4:5</td> </tr> <tr> <td>Et₂O</td> <td>rt</td> <td>(50)</td> <td>51:36:6:7</td> </tr> <tr> <td>MS (4 Å)</td> <td>rt</td> <td>(52)</td> <td>60:28:7:5</td> </tr> <tr> <td>Et₂O, MS (4 Å)^a</td> <td>reflux</td> <td>(69)</td> <td>50:41:4:5</td> </tr> <tr> <td>Et₂O, MS (4 Å)</td> <td>reflux</td> <td>(64)</td> <td>53:36:5:6</td> </tr> <tr> <td>THF, MS (4 Å)</td> <td>reflux</td> <td>(73)</td> <td>56:33:5:7</td> </tr> <tr> <td>DME, MS (4 Å)</td> <td>reflux</td> <td>(68)</td> <td>63:27:5:5</td> </tr> <tr> <td>DME, MS (4 Å)</td> <td>reflux</td> <td>(85)</td> <td>59:28:5:8</td> </tr> <tr> <td>DME, MS (4 Å)</td> <td>rt</td> <td>(76)</td> <td>65:25:5:5</td> </tr> <tr> <td>DEE, MS (4 Å)</td> <td>reflux</td> <td>(88)</td> <td>59:30:5:6</td> </tr> <tr> <td>(<i>R,R</i>)-DMC_x, MS (4 Å)</td> <td>reflux</td> <td>(67)</td> <td>65:25:6:4</td> </tr> <tr> <td>(<i>S,S</i>)-DMC_x, MS (4 Å)</td> <td>reflux</td> <td>(67)</td> <td>65:25:6:4</td> </tr> </tbody> </table>	Additive	Temp	(%)	I:II:III:IV	—	rt	(44)	50:41:4:5	Et ₂ O	rt	(50)	51:36:6:7	MS (4 Å)	rt	(52)	60:28:7:5	Et ₂ O, MS (4 Å) ^a	reflux	(69)	50:41:4:5	Et ₂ O, MS (4 Å)	reflux	(64)	53:36:5:6	THF, MS (4 Å)	reflux	(73)	56:33:5:7	DME, MS (4 Å)	reflux	(68)	63:27:5:5	DME, MS (4 Å)	reflux	(85)	59:28:5:8	DME, MS (4 Å)	rt	(76)	65:25:5:5	DEE, MS (4 Å)	reflux	(88)	59:30:5:6	(<i>R,R</i>)-DMC _x , MS (4 Å)	reflux	(67)	65:25:6:4	(<i>S,S</i>)-DMC _x , MS (4 Å)	reflux	(67)	65:25:6:4	181, 885 181 181 181, 885 181, 885 181, 885 181, 885 181, 885 181, 885 181, 885 181, 885 181, 885
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	Et ₂ Zn (x eq), CHFI ₂ (x eq), DME (x eq), CH ₂ Cl ₂ , MS (4 Å)	 <table border="1"> <thead> <tr> <th>R¹</th> <th>R²</th> <th>x</th> <th>(%)</th> <th>I:II:III:IV</th> </tr> </thead> <tbody> <tr> <td>H</td> <td>H</td> <td>3</td> <td>(80)</td> <td>59:27:9:4</td> </tr> <tr> <td>Ph</td> <td>Ph</td> <td>6</td> <td>(67)</td> <td>49:26:15:9</td> </tr> </tbody> </table>	R ¹	R ²	x	(%)	I:II:III:IV	H	H	3	(80)	59:27:9:4	Ph	Ph	6	(67)	49:26:15:9	181																																					
R ¹	R ²	x	(%)	I:II:III:IV																																																			
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	 Et ₂ Zn (2.2 eq), MeCHI ₂ (4.4 eq), CH ₂ Cl ₂ , 0°		69																																																				

TABLE XV. CYCLOPROPANATION OF ALKENES USING A SUBSTITUTED DIHALIDE (Continued)




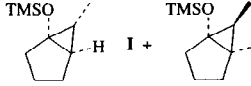


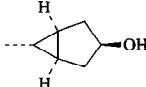





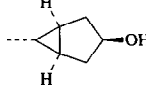
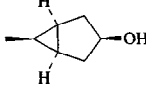
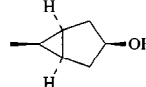
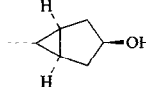



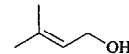
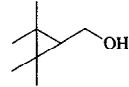


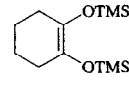
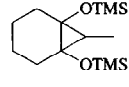
Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.																								
C ₅ 	Zn, CF ₂ Br ₂ , I ₂ (cat.), THF, rt	 (21)	74																								
	Zn/Cu, MeCHl ₂ , Et ₂ O, reflux	 I +  II (70) I:II = 2.9:1	332																								
	Zn/Cu, MeCHBr ₂ , Et ₂ O, reflux	 (85)	68																								
	Et ₂ Zn, MeCHl ₂	 (40) <i>syn:anti</i> = 1.6/1	71																								
	Et ₂ Zn, Me ₂ Cl ₂	 (45)	71																								
	Zn/Cu, MeCHBr ₂ , Et ₂ O, reflux	 I (23) +  II (7)	68																								
	Zinc reagent, MeCHl ₂ , Et ₂ O, reflux	<table border="1"> <thead> <tr> <th>I + II</th> <th>Zinc reagent (%)</th> <th>I:II</th> <th></th> </tr> </thead> <tbody> <tr> <td></td> <td>Zn/Cu (30 mesh) (62)</td> <td>78:22</td> <td>66</td> </tr> <tr> <td></td> <td>Zn/Ag (30 mesh) (78)</td> <td>76:24</td> <td>66</td> </tr> <tr> <td></td> <td>Zn/Cu (dust) (71)</td> <td>76:24</td> <td>66</td> </tr> <tr> <td></td> <td>Et₂Zn (60)</td> <td>76:24</td> <td>120</td> </tr> <tr> <td></td> <td>EtZnI (67)</td> <td>73:27</td> <td>66</td> </tr> </tbody> </table>	I + II	Zinc reagent (%)	I:II			Zn/Cu (30 mesh) (62)	78:22	66		Zn/Ag (30 mesh) (78)	76:24	66		Zn/Cu (dust) (71)	76:24	66		Et ₂ Zn (60)	76:24	120		EtZnI (67)	73:27	66	
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	EtZnI (67)	73:27	66																								
	Zn/Cu, MeCHl ₂ , Et ₂ O, reflux	 I (62) I:II = 22:78 +  II	700																								
	Et ₂ Zn (0.67 eq), CHBr ₃ (1 eq), dry air (10 mL/min), olefin (xs), 0-10°	 (61)	103																								
	Zn, CF ₂ Br ₂ , I ₂ (cat.), THF, rt	 (72)	74																								
	Zn anode, 2e ⁻ , Me ₂ CBr ₂ , ZnBr ₂ present initially, CH ₂ Cl ₂ /DMF (9:1)	 (53)	70																								
C ₆ 	Zn, CF ₂ Br ₂ , I ₂ (cat.), THF, rt	 (7)	74																								
	Zn source, MeCHl ₂ , solvent, reflux	 Zn source Solvent (%) Zn/Cu Et ₂ O (76) Et ₂ Zn C ₆ H ₆ (79)	352																								

TABLE XV. CYCLOPROPANATION OF ALKENES USING A SUBSTITUTED DIHALIDE (Continued)

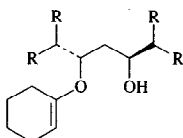
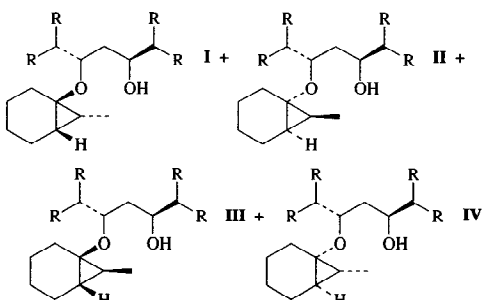

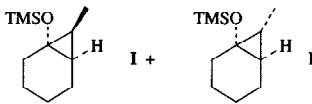

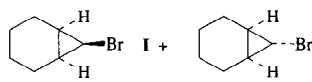
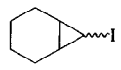
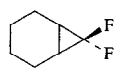
Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.																																													
	Et ₂ Zn (2 eq), MeCHCl ₂ (2.5 eq), solvent	 I + II + III + IV	180																																													
		<table border="1"> <thead> <tr> <th>R</th> <th>(%)</th> <th>Solvent</th> <th>I:II:III:IV</th> </tr> </thead> <tbody> <tr> <td>H</td> <td>(32)</td> <td>hexane</td> <td>44:11:31:14</td> </tr> <tr> <td>H</td> <td>(76)</td> <td>Et₂O</td> <td>79:1:12:8</td> </tr> <tr> <td>Me</td> <td>(90)</td> <td>hexane</td> <td>80:2:18:0</td> </tr> <tr> <td>Me</td> <td>(75)</td> <td>Et₂O</td> <td>80:3:17:0</td> </tr> <tr> <td>Me</td> <td>(83)</td> <td>THF</td> <td>87:0:13:0</td> </tr> <tr> <td>Me</td> <td>(84)</td> <td>DME</td> <td>81:2:17:0</td> </tr> </tbody> </table>	R	(%)	Solvent	I:II:III:IV	H	(32)	hexane	44:11:31:14	H	(76)	Et ₂ O	79:1:12:8	Me	(90)	hexane	80:2:18:0	Me	(75)	Et ₂ O	80:3:17:0	Me	(83)	THF	87:0:13:0	Me	(84)	DME	81:2:17:0																		
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		I:II = 29:71																																														
	Zn/Cu, MeCHCl ₂ , Et ₂ O, reflux	I + II (65) I:II = 24:76	332																																													
	Zn*, MeCHBr ₂ , Et ₂ O, reflux	(24) 1:1	46																																													
	Zn/Cu, MeCHCl ₂ , Et ₂ O	" (5) 55:45	66																																													
	Et ₂ Zn, MeCHCl ₂ , cyclohexane	" (62) <i>syn:anti</i> = 1.6:1	71																																													
	Et ₂ Zn (0.8 eq), CHBr ₃ (1 eq), dry air (10 mL/min), olefin (xs), 0-10°	 I + II (84)	73, 103																																													
		I:II = 1.9:1																																														
	Et ₂ Zn (x eq), CHBr ₃ (1 eq), dry air (y mL/min), solvent, 50°	<table border="1"> <thead> <tr> <th>x</th> <th>y</th> <th>Solvent</th> <th>(%)</th> <th>I:II</th> </tr> </thead> <tbody> <tr> <td>1</td> <td>0</td> <td>olefin</td> <td>(9)</td> <td>2.6:1</td> </tr> <tr> <td>1</td> <td>10</td> <td>olefin</td> <td>(52)</td> <td>1.3:1</td> </tr> <tr> <td>1</td> <td>10</td> <td>olefin</td> <td>(59)</td> <td>1.6:1</td> </tr> <tr> <td>0.28</td> <td>10</td> <td>hexane</td> <td>(18)</td> <td>1.8:1</td> </tr> <tr> <td>0.52</td> <td>10</td> <td>hexane</td> <td>(30)</td> <td>1.6:1</td> </tr> <tr> <td>0.74</td> <td>10</td> <td>hexane</td> <td>(36)</td> <td>1.6:1</td> </tr> <tr> <td>1</td> <td>10</td> <td>hexane</td> <td>(39)</td> <td>1.4:1</td> </tr> <tr> <td>1.4</td> <td>10</td> <td>hexane</td> <td>(32)</td> <td>1.1:1</td> </tr> </tbody> </table>	x	y	Solvent	(%)	I:II	1	0	olefin	(9)	2.6:1	1	10	olefin	(52)	1.3:1	1	10	olefin	(59)	1.6:1	0.28	10	hexane	(18)	1.8:1	0.52	10	hexane	(30)	1.6:1	0.74	10	hexane	(36)	1.6:1	1	10	hexane	(39)	1.4:1	1.4	10	hexane	(32)	1.1:1	103
x	y	Solvent	(%)	I:II																																												
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	Et ₂ Zn (x eq), CHI ₃ (y eq), olefin (xs), temp	 <table border="1"> <thead> <tr> <th>x/y</th> <th>Temp</th> <th>(%)</th> <th><i>syn:anti</i></th> </tr> </thead> <tbody> <tr> <td>0.33</td> <td>50°</td> <td>(35)</td> <td>53:47</td> </tr> <tr> <td>1</td> <td>50°</td> <td>(50)</td> <td>45:55</td> </tr> <tr> <td>1.5</td> <td>50°</td> <td>(38)</td> <td>34:66</td> </tr> <tr> <td>1</td> <td>0°</td> <td>(70)</td> <td>66:34</td> </tr> </tbody> </table>	x/y	Temp	(%)	<i>syn:anti</i>	0.33	50°	(35)	53:47	1	50°	(50)	45:55	1.5	50°	(38)	34:66	1	0°	(70)	66:34	274																									
x/y	Temp	(%)	<i>syn:anti</i>																																													
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1	0°	(70)	66:34																																													
	Zn, CF ₂ Br ₂ , I ₂ (cat.), THF, rt	 (7)	74																																													
	Zn, CF ₂ Br ₂ , solvent, additive	<table border="1"> <thead> <tr> <th>Solvent</th> <th>Additive</th> <th>(%)</th> </tr> </thead> <tbody> <tr> <td>Et₂O</td> <td>—</td> <td>(6)</td> </tr> <tr> <td>DME</td> <td>—</td> <td>(7)</td> </tr> <tr> <td>dioxane</td> <td>—</td> <td>(1)</td> </tr> <tr> <td>Et₂O</td> <td>CuCl</td> <td>(3)</td> </tr> <tr> <td>Et₂O</td> <td>HgCl₂</td> <td>(3)</td> </tr> <tr> <td>Et₂O</td> <td>1,4-(O₂N)₂C₆H₄</td> <td>(0)</td> </tr> <tr> <td>Et₂O</td> <td>hydroquinone</td> <td>(3)</td> </tr> </tbody> </table>	Solvent	Additive	(%)	Et ₂ O	—	(6)	DME	—	(7)	dioxane	—	(1)	Et ₂ O	CuCl	(3)	Et ₂ O	HgCl ₂	(3)	Et ₂ O	1,4-(O ₂ N) ₂ C ₆ H ₄	(0)	Et ₂ O	hydroquinone	(3)	275																					
Solvent	Additive	(%)																																														
Et ₂ O	—	(6)																																														
DME	—	(7)																																														
dioxane	—	(1)																																														
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TABLE XV. CYCLOPROPANATION OF ALKENES USING A SUBSTITUTED DIHALIDE (Continued)

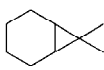
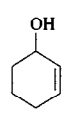
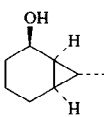
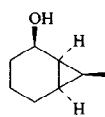
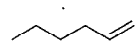
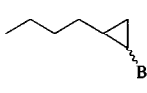
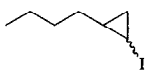
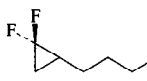
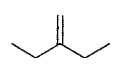
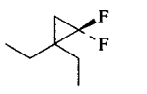

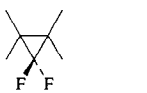
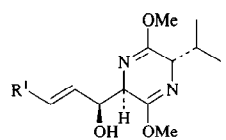
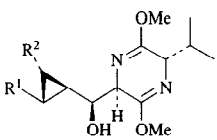


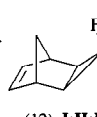
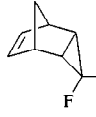
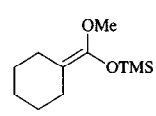
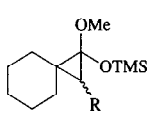
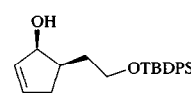
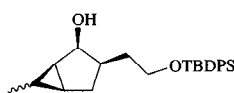

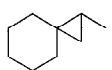

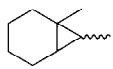
Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.																								
	Et ₂ Zn, Me ₂ Cl ₂	 (59)	71																								
	EtZnI, MeCH ₂ ₂ , Et ₂ O, reflux	 I +  II (67) I:II = 70:30	708																								
	Zn reagent, MeCH ₂ ₂ , Et ₂ O	<table border="1"> <thead> <tr> <th>I + II</th> <th>Zinc reagent</th> <th>(%)</th> <th>I:II</th> </tr> </thead> <tbody> <tr> <td></td> <td>Zn/Cu</td> <td>(84)</td> <td>72:28</td> </tr> <tr> <td></td> <td>Et₂Zn (1 eq)</td> <td>(79)</td> <td>62:38</td> </tr> <tr> <td></td> <td>Et₂Zn (2 eq)</td> <td>(60)</td> <td>63:37</td> </tr> </tbody> </table>	I + II	Zinc reagent	(%)	I:II		Zn/Cu	(84)	72:28		Et ₂ Zn (1 eq)	(79)	62:38		Et ₂ Zn (2 eq)	(60)	63:37	120 119 119								
I + II	Zinc reagent	(%)	I:II																								
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	Et ₂ Zn (2 eq)	(60)	63:37																								
	Sm, MeCH ₂ ₂ , THF, -78° to rt	I + II (100) I:II = 5:1	57, 58																								
	Et ₂ Zn (x eq), CHBr ₃ (y eq), dry air (10 mL/min), olefin (xs), temp	 $\frac{x/y}{1}$ Temp 0-10° 50° (%) (68) (42) <i>syn:anti</i> 2.5:1 2.4:1	73, 103 103																								
	Et ₂ Zn, CHI ₃ , olefin (xs), 50°	 (34) <i>syn:anti</i> = 67:33	274																								
	Zn, CF ₂ Br ₂ , I ₂ (cat.), THF, rt	 (6)	74																								
	Zn, CF ₂ Br ₂ , I ₂ (cat.), THF, rt	 (40)	74																								
	Zn, CF ₂ Br ₂ , I ₂ (cat.), THF, rt	 (96)	74																								
C ₆₋₁₁ 	Et ₂ Zn, R ² CH ₂ , hexane, 0°	 <table border="1"> <thead> <tr> <th>R¹</th> <th>R²</th> <th>(%)</th> <th>de (%)</th> </tr> </thead> <tbody> <tr> <td>H</td> <td>Me</td> <td>(76)</td> <td>79</td> </tr> <tr> <td>Me</td> <td>Me</td> <td>(80)</td> <td>68</td> </tr> <tr> <td>Me</td> <td>Ph</td> <td>(52)</td> <td>68</td> </tr> <tr> <td>Ph</td> <td>Me</td> <td>(74)</td> <td>86</td> </tr> <tr> <td>Ph</td> <td>Ph</td> <td>(62)</td> <td>85</td> </tr> </tbody> </table>	R ¹	R ²	(%)	de (%)	H	Me	(76)	79	Me	Me	(80)	68	Me	Ph	(52)	68	Ph	Me	(74)	86	Ph	Ph	(62)	85	889, 890
R ¹	R ²	(%)	de (%)																								
H	Me	(76)	79																								
Me	Me	(80)	68																								
Me	Ph	(52)	68																								
Ph	Me	(74)	86																								
Ph	Ph	(62)	85																								
C ₇ 	Zn, CF ₂ Br ₂ , I ₂ (cat.), THF, rt	 I +  II +  III (12) I:II:III = 38:58:3	74																								
	Et ₂ Zn (1.5 eq), RCH ₂ (1.5 eq), Et ₂ O, rt	 <table border="1"> <thead> <tr> <th>R</th> <th>(%)</th> </tr> </thead> <tbody> <tr> <td>Me</td> <td>(91)</td> </tr> <tr> <td>Ph</td> <td>(64)</td> </tr> </tbody> </table>	R	(%)	Me	(91)	Ph	(64)	553																		
R	(%)																										
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	Sm/Hg, MeCH ₂ ₂ , THF, -78° to rt	 (45)	714, 715																								
	Zn/Cu, MeCH ₂ ₂ , Et ₂ O	 (31)	66																								
	Zn/Cu, MeCH ₂ ₂ , Et ₂ O	 (13) 55:45	66																								

TABLE XV. CYCLOPROPANATION OF ALKENES USING A SUBSTITUTED DIHALIDE (Continued)


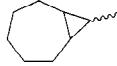
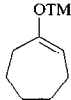
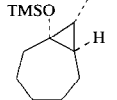
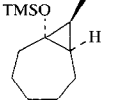
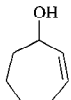
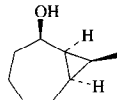
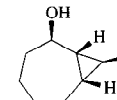
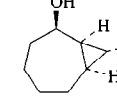
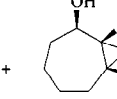
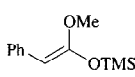
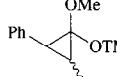
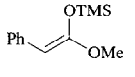
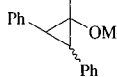





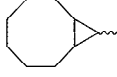
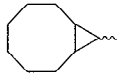
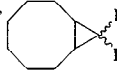
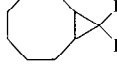
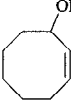
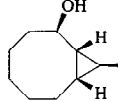
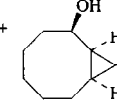
Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.															
	Et ₂ Zn, MeCHI ₂ , cyclohexane	 (71) <i>syn:anti</i> = 1.4:1	71															
	Zn/Cu, MeCHI ₂ , Et ₂ O, reflux	 I +  II (88) I:II = 3.1:1	332															
	Zinc source, MeCHI ₂ , Et ₂ O	 I +  II +  III +  IV																
		<table border="1"> <thead> <tr> <th>Zinc source</th> <th>(%)</th> <th>I:II:III:IV</th> </tr> </thead> <tbody> <tr> <td>Zn/Cu</td> <td>(74)</td> <td>19:2:59:20</td> </tr> <tr> <td>Et₂Zn</td> <td>(72)</td> <td>20:10:49:21</td> </tr> <tr> <td>Et₂Zn (1 eq)</td> <td>(74)</td> <td>0:49:0:51</td> </tr> <tr> <td>Et₂Zn (2 eq)</td> <td>(79)</td> <td>0:52:0:48</td> </tr> </tbody> </table>	Zinc source	(%)	I:II:III:IV	Zn/Cu	(74)	19:2:59:20	Et ₂ Zn	(72)	20:10:49:21	Et ₂ Zn (1 eq)	(74)	0:49:0:51	Et ₂ Zn (2 eq)	(79)	0:52:0:48	120 120 119 119
Zinc source	(%)	I:II:III:IV																
Zn/Cu	(74)	19:2:59:20																
Et ₂ Zn	(72)	20:10:49:21																
Et ₂ Zn (1 eq)	(74)	0:49:0:51																
Et ₂ Zn (2 eq)	(79)	0:52:0:48																
	Et ₂ Zn (1.5 eq), MeCHI ₂ (1.5 eq), Et ₂ O, rt	 (86)	553															
	Et ₂ Zn (1.5 eq), PhCHI ₂ (1.5 eq), Et ₂ O, rt	 (68)	553															
	Et ₂ Zn (1 eq), CHBr ₃ (1 eq), dry air (10 mL/min), olefin (xs), 50°	 (trace)	73, 103															
	Et ₂ Zn, CHI ₃ , olefin (xs), 50°	 (44) <i>syn:anti</i> = —	274															
	Zn, CF ₂ Br ₂ , I ₂ (cat.), THF, rt	 (15)	74															
	Me ₃ Al (3 eq), MeCHI ₂ (3 eq), CH ₂ Cl ₂ , rt	 (92) <i>cis:trans</i> = 6.3:1	59															
	Et ₂ Zn, MeCHI ₂ , cyclohexane	" (72) <i>syn:anti</i> = 1.3:1	71															
	Et ₂ Zn (x eq), CHBr ₃ (1 eq), dry air (10 mL/min), olefin (xs), temp	 <table border="1"> <thead> <tr> <th>x</th> <th>Temp</th> <th>(%)</th> <th><i>syn:anti</i></th> </tr> </thead> <tbody> <tr> <td>0.65</td> <td>0-10°</td> <td>(75)</td> <td>7.1:1</td> </tr> <tr> <td>1</td> <td>50°</td> <td>(63)</td> <td>6.4:1</td> </tr> </tbody> </table>	x	Temp	(%)	<i>syn:anti</i>	0.65	0-10°	(75)	7.1:1	1	50°	(63)	6.4:1	73, 103 103			
x	Temp	(%)	<i>syn:anti</i>															
0.65	0-10°	(75)	7.1:1															
1	50°	(63)	6.4:1															
	Et ₂ Zn (0.67 eq), CDBr ₃ (1 eq), dry air (10 mL/min), olefin (xs), 0-10°	 (79) <i>syn:anti</i> = 6.9:1	103															
	Zn anode, 2e ⁻ , R ¹ R ² CX ₂ , ZnBr ₂ present initially, CH ₂ Cl ₂ /DMF (9:1)	 <table border="1"> <thead> <tr> <th>R¹R²CX₂</th> <th>(%)</th> </tr> </thead> <tbody> <tr> <td>Me₂CBr₂ (46)</td> <td></td> </tr> <tr> <td>PhCHCl₂ (20)</td> <td></td> </tr> <tr> <td>PhCHBr₂ (27)</td> <td></td> </tr> </tbody> </table>	R ¹ R ² CX ₂	(%)	Me ₂ CBr ₂ (46)		PhCHCl ₂ (20)		PhCHBr ₂ (27)		70							
R ¹ R ² CX ₂	(%)																	
Me ₂ CBr ₂ (46)																		
PhCHCl ₂ (20)																		
PhCHBr ₂ (27)																		
	Zn/Cu, MeCHI ₂ , Et ₂ O, reflux	 I +  II (88) I:II = 28:72	700															

TABLE XV. CYCLOPROPANATION OF ALKENES USING A SUBSTITUTED DIHALIDE (Continued)

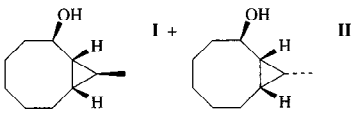
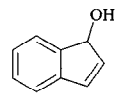
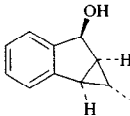
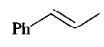
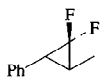

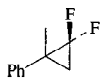
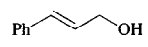
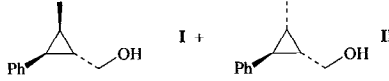
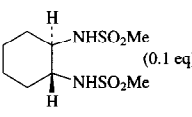
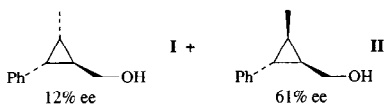
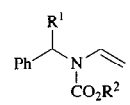
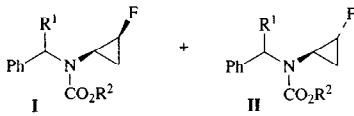
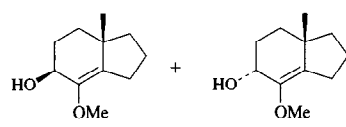
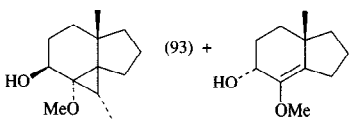
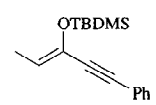
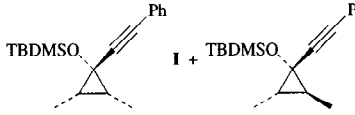
Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.																												
	Zinc source, MeCHCl ₂ , Et ₂ O	 <table border="1"> <thead> <tr> <th>Zinc source</th> <th>(%)</th> <th>I:II</th> </tr> </thead> <tbody> <tr> <td>Zn/Cu</td> <td>(88)</td> <td>28:72</td> </tr> <tr> <td>Et₂Zn (1 eq)</td> <td>(60)</td> <td>52:48</td> </tr> <tr> <td>Et₂Zn (2 eq)</td> <td>(76)</td> <td>29:71</td> </tr> </tbody> </table>	Zinc source	(%)	I:II	Zn/Cu	(88)	28:72	Et ₂ Zn (1 eq)	(60)	52:48	Et ₂ Zn (2 eq)	(76)	29:71	66 119 119																
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C ₉ 	EtZnI, MeCHCl ₂ , Et ₂ O, reflux	 (34)	65																												
	Zn, CF ₂ Br ₂ , I ₂ (cat.), THF, rt	 (29)	74																												
	Zn, CF ₂ Br ₂ , I ₂ (cat.), THF, rt	 (71)	74																												
	Et ₂ Zn (x eq), MeCHCl ₂ (y eq), CH ₂ Cl ₂ , 0°	 <table border="1"> <thead> <tr> <th>x</th> <th>y</th> <th>(%)</th> <th>I:II</th> </tr> </thead> <tbody> <tr> <td>1.5</td> <td>2.0</td> <td>(85)</td> <td>93:7</td> </tr> <tr> <td>2.2</td> <td>4.4</td> <td>(82)</td> <td>89:11</td> </tr> <tr> <td>5</td> <td>5.0</td> <td>(58)</td> <td>93:7</td> </tr> </tbody> </table>	x	y	(%)	I:II	1.5	2.0	(85)	93:7	2.2	4.4	(82)	89:11	5	5.0	(58)	93:7	69												
x	y	(%)	I:II																												
1.5	2.0	(85)	93:7																												
2.2	4.4	(82)	89:11																												
5	5.0	(58)	93:7																												
	1. Et ₂ Zn (1.1 eq) 2. ZnI ₂ 3. Zn(CHIME) ₂ , CH ₂ Cl ₂ , 0°	I + II (62) I:II = 71:29	464																												
	 (0.1 eq)	 12% ee 61% ee (58) I:II = 65:35	464																												
C ₉₋₁₅ 	Et ₂ Zn (2 eq), CHFCl ₂ (2 eq), CH ₂ Cl ₂ , -40°	 <table border="1"> <thead> <tr> <th>R¹</th> <th>R²</th> <th>(%)</th> <th>I:II</th> </tr> </thead> <tbody> <tr> <td>H</td> <td>Bn</td> <td>(68)</td> <td>76:24</td> </tr> <tr> <td>H</td> <td><i>t</i>-Bu</td> <td>(69)</td> <td>62:38</td> </tr> <tr> <td>Me</td> <td>Bn</td> <td>(97)</td> <td>89:11</td> </tr> <tr> <td>Me</td> <td><i>t</i>-Bu</td> <td>(67)</td> <td>91:9</td> </tr> <tr> <td>Ph</td> <td>Bn</td> <td>(90)</td> <td>93:7</td> </tr> <tr> <td>Ph</td> <td><i>t</i>-Bu</td> <td>(87)</td> <td>93:7</td> </tr> </tbody> </table>	R ¹	R ²	(%)	I:II	H	Bn	(68)	76:24	H	<i>t</i> -Bu	(69)	62:38	Me	Bn	(97)	89:11	Me	<i>t</i> -Bu	(67)	91:9	Ph	Bn	(90)	93:7	Ph	<i>t</i> -Bu	(87)	93:7	91, 548
R ¹	R ²	(%)	I:II																												
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Ph	Bn	(90)	93:7																												
Ph	<i>t</i> -Bu	(87)	93:7																												
C ₁₀ 	Et ₂ Zn, MeCHCl ₂ , O ₂ , Et ₂ O, rt	 (93) + (unchanged)	852																												
C ₁₁ 	Et ₂ Zn, MeCHCl ₂	 I + II (←) I:II = —	573																												

TABLE XV. CYCLOPROPANATION OF ALKENES USING A SUBSTITUTED DIHALIDE (Continued)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.												
	Et ₂ Zn, MeCHCl ₂	 I + II (—) I:II = —	573												
	Zn, CF ₃ Br ₃ , I ₂ (cat.), THF, rt	 (84)	74												
	Et ₂ Zn (3 eq), MeCHCl ₂ (3 eq), <i>i</i> -Pr ₂ O, rt	 (23) 64:36	492, 493												
	Et ₂ Zn (2 eq), MeCHCl ₂ (2 eq), <i>i</i> -Pr ₂ O, rt	 (59) 25:1	492, 493												
	Et ₂ Zn, MeCHCl ₂ , Et ₂ O	 (90-95) 1:2	817												
C ₁₂	R ₃ Al (3 eq), MeCHCl ₂ (3 eq), CH ₂ Cl ₂ , rt	 <table border="1"> <thead> <tr> <th>R</th> <th>(%)</th> <th><i>cis:trans</i></th> </tr> </thead> <tbody> <tr> <td>Me</td> <td>(94)</td> <td>1.1:1</td> </tr> <tr> <td><i>i</i>-Bu</td> <td>(84)</td> <td>0.7:1</td> </tr> </tbody> </table>	R	(%)	<i>cis:trans</i>	Me	(94)	1.1:1	<i>i</i> -Bu	(84)	0.7:1	59			
R	(%)	<i>cis:trans</i>													
Me	(94)	1.1:1													
<i>i</i> -Bu	(84)	0.7:1													
C ₁₄	Zn dust, C ₆ H ₆	 <table border="1"> <thead> <tr> <th>R¹</th> <th>R²</th> <th>(%)</th> </tr> </thead> <tbody> <tr> <td>Br</td> <td>Br</td> <td>(20)</td> </tr> <tr> <td>Br</td> <td>I</td> <td>(45)</td> </tr> <tr> <td>I</td> <td>I</td> <td>(20)</td> </tr> </tbody> </table>	R ¹	R ²	(%)	Br	Br	(20)	Br	I	(45)	I	I	(20)	113
R ¹	R ²	(%)													
Br	Br	(20)													
Br	I	(45)													
I	I	(20)													
C ₁₅	 ZnI ₂ , Et ₂ O	 I + II <table border="1"> <thead> <tr> <th>R</th> <th>(%)</th> <th>I:II</th> </tr> </thead> <tbody> <tr> <td>C₆H₁₁</td> <td>(20-25)</td> <td>7:3</td> </tr> <tr> <td>C₁₁H₁₉</td> <td>(20-25)</td> <td>—</td> </tr> <tr> <td>C₁₆H₂₇</td> <td>(20-25)</td> <td>—</td> </tr> </tbody> </table>	R	(%)	I:II	C ₆ H ₁₁	(20-25)	7:3	C ₁₁ H ₁₉	(20-25)	—	C ₁₆ H ₂₇	(20-25)	—	75
R	(%)	I:II													
C ₆ H ₁₁	(20-25)	7:3													
C ₁₁ H ₁₉	(20-25)	—													
C ₁₆ H ₂₇	(20-25)	—													
	 ZnI ₂ , Et ₂ O	 I + II (—) I:II = —	75												
	 ZnI ₂ , Et ₂ O	 I + II (—) I:II = —	75												
	Et ₂ Zn (2 eq), MeCHCl ₂ (2 eq), <i>i</i> -Pr ₂ O, rt	 (28)	493												

^a The solvent was diethyl ether.

TABLE XVI. CYCLOPROPANATION OF ALKENES USING IN SITU FORMATION OF THE CARBENOID

	Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₂		Zn/Hg, TMSCl, HC(OMe) ₃ , Et ₂ O, reflux	 (46) <i>trans:cis</i> = 3:1	77
C ₃		MeO-C ₆ H ₄ -CHO Zn/Hg, (ClMe ₂ SiCH ₂) ₂ , Et ₂ O, reflux	 (89) <i>cis:trans</i> = 2:1	76
C ₄		Zn/Hg, TMSCl, HC(OMe) ₃ , Et ₂ O, reflux	 (43) 3:1	77
063	C ₅ 	MeO-C ₆ H ₄ -CHO Zn/Hg, (ClMe ₂ SiCH ₂) ₂ , Et ₂ O, reflux	 (53) <i>endo:exo</i> = 1:1	76
		Zn/Hg, TMSCl, Et ₂ O, reflux	 (15) <i>cis:trans</i> = 2:1	77
C ₆		 Zn/Hg, TMSCl, ZnCl ₂ , Et ₂ O, reflux	 (43) <i>endo:exo</i> = 3.5:1	276
		R-C ₆ H ₄ -CHO Zn/Hg, (ClMe ₂ SiCH ₂) ₂ , Et ₂ O, reflux	 R (%) <i>endo:exo</i> Cl (46) 3:1 H (68) 4:1 Me (75) 8:1 OMe (96) 15:1	76
		R-C ₆ H ₄ -C(OMe) ₂ Zn/Hg, TMSCl, ZnCl ₂ , Et ₂ O, reflux	" R (%) <i>endo:exo</i> Me (34) 5.6:1 OMe (65) 23.5:1	276
		R-C ₆ H ₄ - Zn/Hg, TMSCl, ZnCl ₂ , Et ₂ O, reflux	" R (%) <i>endo:exo</i> Me (38) 6.1:1 H (51) 3.3:1 Cl (30) 2.9:1	276
		R-C ₆ H ₄ - Zn/Hg, TMSCl, ZnCl ₂ , Et ₂ O, reflux	" R (%) <i>endo:exo</i> H (20) 4:1 OMe (20) 5:1	276
C ₇		 Zn/Hg, (ClMe ₂ SiCH ₂) ₂ , Et ₂ O, reflux	 (34)	76
C ₈		 Zn/Hg, (ClMe ₂ SiCH ₂) ₂ , Et ₂ O, reflux	 (53)	76

TABLE XVI. CYCLOPROPANATION OF ALKENES USING IN SITU FORMATION OF THE CARBENOID (Continued)

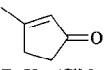

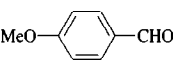
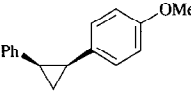
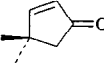
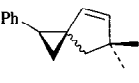
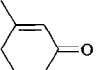
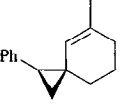
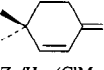
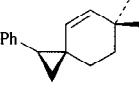






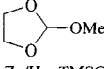
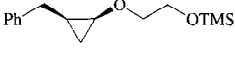
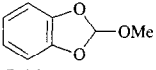
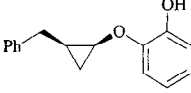
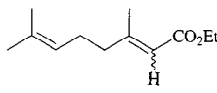
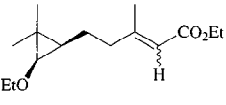
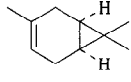
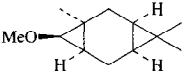
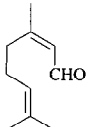
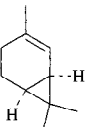
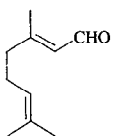
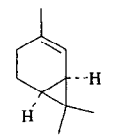
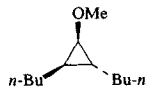
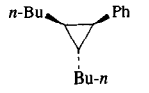
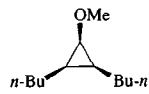
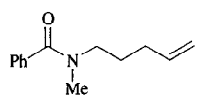
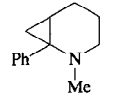
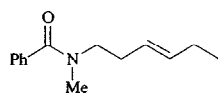
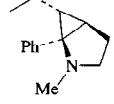
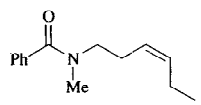
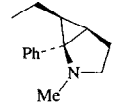
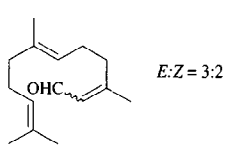
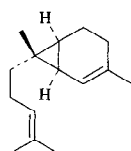
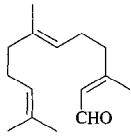
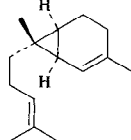
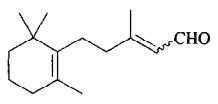
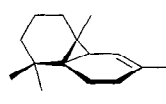
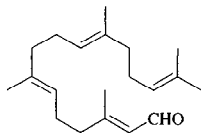
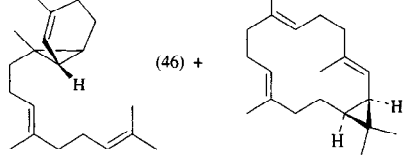
Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
	Zn/Hg, (ClMe ₂ SiCH ₂) ₂ , Et ₂ O, reflux	 (44) <i>endo:exo</i> = 1:1	76
	Zn/Hg, (ClMe ₂ SiCH ₂) ₂ , Et ₂ O, reflux	 (99) <i>endo:exo</i> = 25:1	76
	Zn/Hg, (ClMe ₂ SiCH ₂) ₂ , Et ₂ O, reflux	 (19) <i>endo:exo</i> = 1:1	76
	Zn/Hg, (ClMe ₂ SiCH ₂) ₂ , Et ₂ O, reflux	 (59) <i>endo:exo</i> = 11:1	76
	Zn/Hg, (ClMe ₂ SiCH ₂) ₂ , Et ₂ O, reflux	 (55) <i>endo:exo</i> = 20:1	76
C ₉ 	Zn/Hg, TMSCl, HC(OMe) ₃ , Et ₂ O, reflux	 (56) <i>cis:trans</i> = 2:1	77
	Zn/Hg, TMSCl, HC(OR) ₃ , Et ₂ O, reflux	 R (%) <i>cis:trans</i> Me (64) 2:1 <i>n</i> -Pr (43) 2:1	77
	Zn/Hg, TMSCl, (EtO) ₂ CH(OPh), Et ₂ O, reflux	 (67) <i>cis:trans</i> = 2:1	77
	Zn/Hg, TMSCl, Et ₂ O, reflux	 (55) <i>cis:trans</i> = 3:1	77
	Zn/Hg, TMSCl, Et ₂ O, reflux	 (23) <i>cis:trans</i> = 5:2	77
C ₁₀ 	Zn/Hg, TMSCl, HC(OEt) ₃ , Et ₂ O, reflux	 (44) 2:1	77
	Zn/Hg, TMSCl, HC(OMe) ₃ , Et ₂ O, reflux	 (65) <i>cis:trans</i> = 5:2	77
	ClMe ₂ Si(CH ₂) ₂ SiMe ₂ Cl, Zn/Hg	 (66)	112

TABLE XVI. CYCLOPROPANATION OF ALKENES USING IN SITU FORMATION OF THE CARBENOID (Continued)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
	ClMe ₂ Si-CH ₂ -CH ₂ -SiMe ₂ Cl Zn/Hg	 (57)	112
<i>n</i> -Bu-CH=CH-Bu- <i>n</i>	Zn/Hg, TMSCl, HC(OMe) ₃ , Et ₂ O, reflux	 (56)	77
<i>n</i> -Bu-CH=CH-Bu- <i>n</i>	PhCHO, Zn/Hg, (ClMe ₂ SiCH ₂) ₂ , Et ₂ O, reflux	 (29)	76
<i>n</i> -Bu-CH=CH-Bu- <i>n</i>	Zn/Hg, TMSCl, HC(OMe) ₃ , Et ₂ O, reflux	 (53) <i>cis:trans</i> = 10:1	77
C ₁₃ 	Sm/SmI ₂ , THF, reflux	 (41)	78
C ₁₄ 	Sm/SmI ₂ , THF, reflux	 (41) <i>endo:exo</i> = 9:1	78
	Sm/SmI ₂ , THF, reflux	 (41) <i>endo:exo</i> = 1:8	78
C ₁₅  <i>E:Z</i> = 3:2	ClMe ₂ Si-CH ₂ -CH ₂ -SiMe ₂ Cl Zn/Hg	 (41)	112
	ClMe ₂ Si-CH ₂ -CH ₂ -SiMe ₂ Cl Zn/Hg	 (47)	112
C ₂₀ 	ClMe ₂ Si-CH ₂ -CH ₂ -SiMe ₂ Cl Zn/Hg	 (47)	112
	ClMe ₂ Si-CH ₂ -CH ₂ -SiMe ₂ Cl Zn/Hg	 (46) + (30)	112

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References

1. Emschwiller, G. C. R. *Hebd. Seance Acad. Sci.* 1929, **188**, 1555.
2. Simmons, H. E.; Smith, R. D. *J. Am. Chem. Soc.* 1958, **80**, 5323.
3. Simmons, H. E.; Smith, R. D. *J. Am. Chem. Soc.* 1959, **81**, 4256.
4. Furukawa, J.; Kawabata, N. *Adv. Organomet. Chem.* 1974, **12**, 83.
5. Wender, P. A.; Eck, S. L. *Tetrahedron Lett.* 1982, **23**, 1871.
6. Motherwell, W. B.; Nutley, C. J. *Contemp. Org. Synth.* 1994, **1**, 219.
7. Winstein, S.; Sonnenberg, J.; de Vries, L. J. *J. Am. Chem. Soc.* 1959, **81**, 6523.
8. Hoveyda, A. H.; Evans, D. A.; Fu, G. C. *Chem. Rev.* 1993, **93**, 1307.
9. Charette, A. B.; Marcoux, J.-F. *Synlett* 1995, 1197.
10. Charette, A. B.; Lebel, H. in *Comprehensive Asymmetric Catalysis*, Jacobsen, E. N., Pfaltz, A., Yamamoto, H., Eds., Springer-Verlag, Berlin, 1999, Vol. **2**, pp. 581–603.
11. Kawabata, N.; Naka, M.; Yamashita, S. *J. Am. Chem. Soc.* 1976, **98**, 2676.
12. Furukawa, J.; Kawabata, N.; Fujita, T. *Tetrahedron* 1970, **26**, 243.
13. Seyferth, D.; Eisert, M. A.; Todd, L. J. *J. Am. Chem. Soc.* 1964, **86**, 121.
14. Maeda, T.; Tada, H.; Yasuda, K.; Okawara, R. *J. Organomet. Chem.* 1971, **27**, 13.
15. Simmons, H. E.; Cairns, T. L.; Vladuchick, S. A.; Hoiness, C. M. *Org. React.* 1973, **20**, 1.
16. Denmark, S. E.; Edwards, J. P.; Wilson, S. R. *J. Am. Chem. Soc.* 1991, **113**, 723.
17. Denmark, S. E.; Edwards, J. P.; Wilson, S. R. *J. Am. Chem. Soc.* 1992, **114**, 2592.
18. Charette, A. B.; Marcoux, J.-F.; Bélanger-Gariépy, F. *J. Am. Chem. Soc.* 1996, **118**, 6792.
19. Charette, A. B.; Marcoux, J.-F. *J. Am. Chem. Soc.* 1996, **118**, 4539.
20. Denmark, S. E.; O'Connor, S. P. *J. Org. Chem.* 1997, **62**, 3390.
21. Dessy, R. E.; Coe, G. R. *J. Org. Chem.* 1963, **28**, 3592.
22. Evans, D. F.; Wharf, I. *J. Chem. Soc. A* 1968, 783.
23. Evans, D. F.; Fazakerley, G. V. *J. Chem. Soc. A* 1971, 182.
24. Fabisch, B.; Mitchell, T. N. *J. Organomet. Chem.* 1984, **269**, 219.
25. Mareda, J.; Rondan, N. G.; Houk, K. N.; Clark, T.; Schleyer, P. v. R. *J. Am. Chem. Soc.* 1983, **105**, 6997.
26. Bernardi, F.; Bottoni, A.; Miscione, G. P. *J. Am. Chem. Soc.* 1997, **119**, 12300.

27. Hirai, A.; Nakamura, M.; Nakamura, E. *Chem. Lett.* 1998, 927.
28. Dargel, T. K.; Koch, W. J. *Chem. Soc., Perkin Trans. 2* 1996, 877.
29. Nakamura, E.; Hirai, A.; Nakamura, M. *J. Am. Chem. Soc.* 1998, **120**, 5844.
30. Takahashi, H.; Yoshioka, M.; Shibasaki, M.; Ohno, M.; Imai, N.; Kobayashi, S. *Tetrahedron* 1995, **51**, 12013.
31. Charette, A. B.; Brochu, C. J. *Am. Chem. Soc.* 1995, **117**, 11367.
32. Erdik, E. *Tetrahedron* 1987, **43**, 2203.
33. Howard, F. L. *J. Res. Nat. Bur. Stand., A* 1940, **24**, 677.
34. Shank, R. S.; Shechter, H. J. *Org. Chem.* 1959, **24**, 1825.
35. Smith, R. D.; Simmons, H. E. *Org. Synth. Coll. Vol. V*, 1973, 855.
36. LeGoff, E. J. *Org. Chem.* 1964, **29**, 2048.
37. Rawson, R. J.; Harrison, I. T. *J. Org. Chem.* 1970, **35**, 2057.
38. Schuchardt, U.; Nery, J. H. S.; Zuiani, M. A. *J. Braz. Chem. Soc.* 1991, **2**, 61.
39. Denis, J. M.; Girard, C.; Conia, J. M. *Synthesis* 1972, 549.
40. Takai, K.; Kakiuchi, T.; Utimoto, K. *J. Org. Chem.* 1994, **59**, 2671.
41. Friedrich, E. C.; Lewis, E. J. *J. Org. Chem.* 1990, **55**, 2491.
42. Picotin, G.; Miginiac, P. *J. Org. Chem.* 1987, **52**, 4796.
43. Friedrich, E. C.; Lunetta, S. E.; Lewis, E. J. *J. Org. Chem.* 1989, **54**, 2388.
44. Stenstrøm, Y. *Synth. Commun.* 1992, **22**, 2801.
45. Repic, O.; Vogt, S. *Tetrahedron Lett.* 1982, **23**, 2729.
46. Rieke, R. D.; Li, P. T.-J.; Burns, T. P.; Uhm, S. T. *J. Org. Chem.* 1981, **46**, 4323.
47. Furukawa, J.; Kawabata, N.; Nishimura, J. *Tetrahedron Lett.* 1966, 3353.
48. Furukawa, J.; Kawabata, N.; Nishimura, J. *Tetrahedron* 1968, **24**, 53.
49. Miyano, S.; Hashimoto, H. *J. Chem. Soc., Chem. Commun.* 1971, 1418.
50. Miyano, S.; Hashimoto, H. *Bull. Chem. Soc. Jpn.* 1973, **46**, 892.
51. Denmark, S. E.; Edwards, J. P. *J. Org. Chem.* 1991, **56**, 6974.
52. Sawada, S.; Inouye, Y. *Bull. Chem. Soc. Jpn.* 1969, **42**, 2669.
53. Yang, Z.; Lorenz, J. C.; Shi, Y. *Tetrahedron Lett.* 1998, **39**, 8621.
54. Sawada, S.; Oda, J.; Inouye, Y. *J. Org. Chem.* 1968, **33**, 2141.
55. Wittig, G.; Schwarzenbach, K. *Angew. Chem.* 1959, **71**, 652.
56. Wittig, G.; Wingler, F. *Chem. Ber.* 1964, **97**, 2146.
57. Molander, G. A.; Etter, J. B. *J. Org. Chem.* 1987, **52**, 3942.
58. Molander, G. A.; Haring, L. S. *J. Org. Chem.* 1989, **54**, 3525.

59. Maruoka, K.; Fukutani, Y.; Yamamoto, H. *J. Org. Chem.* 1985, **50**, 4412.
60. Miller, D. B. *Tetrahedron Lett.* 1964, 989.
61. Hoberg, H. *Liebigs Ann. Chem.* 1962, **656**, 1.
62. Charette, A. B.; Beauchemin, A. Unpublished results.
- 62a. Imamoto, A.; Takeyama, T.; Koto, H. *Tetrahedron Lett.* 1986, 3243.
63. Lautens, M.; Ren, Y. *J. Org. Chem.* 1996, **61**, 2210.
64. Simmons, H. E.; Blanchard, E. P.; Smith, R. D. *J. Am. Chem. Soc.* 1964, **86**, 1347.
65. Friedrich, E. C.; Taggart, D. B.; Saleh, M. A. *J. Org. Chem.* 1977, **42**, 1437.
66. Friedrich, E. C.; Biresaw, G. *J. Org. Chem.* 1982, **47**, 1615.
67. Furukawa, J.; Kawabata, N.; Nishimura, J. *Tetrahedron Lett.* 1968, 3495.
68. Mariano, P. S.; Bay, E.; Watson, D. G.; Rose, T.; Bracken, C. *J. Org. Chem.* 1980, **45**, 1753.
69. Charette, A. B.; Lemay, J. *Angew. Chem., Intl. Ed. Engl.* 1997, **36**, 1090.
70. Durandetti, S.; Sibille, S.; Périchon, J. *J. Org. Chem.* 1991, **56**, 3255.
71. Stahl, K.-J.; Hertzsch, W.; Musso, H. *Liebigs Ann. Chem.* 1985, 1474.
72. Nishimura, J.; Furukawa, J. *J. Chem. Soc., Chem. Commun.* 1971, 1375.
73. Miyano, S.; Matsumoto, Y.; Hashimoto, H. *J. Chem. Soc., Chem. Commun.* 1975, 364.
74. Dolbier, W. R.; Wojtowicz, H.; Burkholder, C. R. *J. Org. Chem.* 1990, **55**, 5420.
75. Altman, L. J.; Kowerski, R. C.; Laungani, D. R. *J. Am. Chem. Soc.* 1978, **100**, 6174.
76. Motherwell, W. B.; Roberts, L. R. *J. Chem. Soc., Chem. Commun.* 1992, 1582.
77. Fletcher, R. J.; Motherwell, W. B.; Popkin, M. E. *J. Chem. Soc., Chem. Commun.* 1998, 2191.
78. Ogawa, A.; Takami, N.; Sekiguchi, M.; Ryu, I.; Kambe, N.; Sonoda, N. *J. Am. Chem. Soc.* 1992, **114**, 8729.
79. Ryu, I.; Aya, T.; Otani, S.; Murai, S.; Sonoda, N. *J. Organomet. Chem.* 1987, **321**, 279.
80. Morisson, V.; Barnier, J. P.; Blanco, L. *Tetrahedron* 1998, **54**, 7749.
81. Conia, J. M.; Girard, C. *Tetrahedron Lett.* 1973, 2767.
82. Le Goaller, R.; Pierre, J.-L. *Bull. Soc. Chim. Fr.* 1973, 1531.
83. Murai, S.; Aya, T.; Sonoda, N. *J. Org. Chem.* 1973, **38**, 4354.
84. Rubottom, G. M.; Lopez, M. I. *J. Org. Chem.* 1973, **38**, 2097.

85. Whitlock, H. W.; Overman, L. E. *J. Org. Chem.* 1969, **34**, 1962.
86. Ireland, R. E.; Kowalski, C. J.; Tilley, J. W.; Walba, D. M. *J. Org. Chem.* 1975, **40**, 990.
87. Imamoto, T.; Takeyama, T.; Koto, H. *Tetrahedron Lett.* 1986, **27**, 3243.
88. Imamoto, T.; Takiyama, N. *Tetrahedron Lett.* 1987, **28**, 1307.
89. Vallgarda, J.; Arvidsson, L. E.; Svensson, B. E.; Fowler, C. J.; Hacksell, U. *Eur. J. Med. Chem.* 1993, **28**, 399.
90. Gagnon, J. L.; Zajac, W. W. *Synth. Commun.* 1996, **26**, 837.
91. Tamura, O.; Hashimoto, M.; Kobayashi, Y.; Katoh, T.; Nakatani, K.; Kamada, M.; Hayakawa, I.; Akiba, T.; Terashima, S. *Tetrahedron Lett.* 1992, **33**, 3483.
92. Morikawa, T.; Sasaki, H.; Mori, K.; Shiro, M.; Taguchi, T. *Chem. Pharm. Bull.* 1992, **40**, 3189.
93. Yong, W.; Vandewalle, M. *Synlett* 1996, 911.
94. Piers, E.; Coish, P. D. *Synthesis* 1995, 47.
95. Fontani, P.; Carboni, B.; Vaultier, M.; Maas, G. *Synthesis* 1991, 605.
96. Zweifel, G.; Clark, G. M.; Whitney, C. C. *J. Am. Chem. Soc.* 1971, **93**, 1305.
97. Yachi, K.; Shinokubo, H.; Oshima, K. *Angew. Chem., Int. Ed. Engl.* 1998, **37**, 2515.
98. Mitchell, T. N.; Kowall, B. J. *Organomet. Chem.* 1995, **490**, 239.
99. Von Dolhaine, H.; Hägele, G. *Phosphorus Sulfur* 1978, **4**, 123.
100. Shcherbinin, V. V.; Pavlov, K. V.; Shvedov, I. P.; Korneva, O. S.; Menchikov, L. G.; Nefedov, O. M. *Izv. Akad. Nauk., Ser. Khim.* 1997, **46**, 1711.
101. Wells, G. J.; Yan, T.-H.; Paquette, L. A. *J. Org. Chem.* 1984, **49**, 3604.
102. Rahman, N. A.; Fleming, I. *Synth. Commun.* 1993, **23**, 1583.
103. Miyano, S.; Hashimoto, H. *Bull. Chem. Soc. Jpn.* 1975, **48**, 3665.
104. Friedrich, E. C.; Niyati-Shirkhodae, F. *J. Org. Chem.* 1991, **56**, 2202.
105. Rickborn, B.; Chan, J. H.-H. *J. Org. Chem.* 1967, **32**, 3576.
106. Chan, J. H.-H.; Rickborn, B. *J. Am. Chem. Soc.* 1968, **90**, 6406.
107. Girard, C.; Conia, J.-M. *J. Chem. Res. (S)* 1978, 182.
108. Lee, J.; Kim, H.; Cha, J. K. *J. Am. Chem. Soc.* 1995, **117**, 9919.
109. Winkler, J. D.; Bhattacharya, S. K.; Batey, R. A. *Tetrahedron Lett.* 1996, **37**, 8069.
110. Imamoto, T.; Hatajima, T.; Takiyama, N.; Takeyama, T.; Kamiya, Y.; Yoshizawa, T. *J. Chem. Soc., Perkin Trans. 1* 1991, 3127.
111. Corey, E. J.; Virgil, S. C. *J. Am. Chem. Soc.* 1990, **112**, 6429.
112. Motherwell, W. B.; Roberts, L. R. *Tetrahedron Lett.* 1995, **36**, 1121.

113. Hudlicky, T.; Ranu, B. C.; Naqvi, S. M.; Srnak, A. J. *Org. Chem.* 1985, **50**, 123.
114. Dauben, W. G.; Berezin, G. H. *J. Am. Chem. Soc.* 1963, **85**, 468.
115. Poulter, C. D.; Friedrich, E. C.; Winstein, S. *J. Am. Chem. Soc.* 1969, **91**, 6892.
116. Cope, A. C.; Keough, A. H.; Peterson, P. E.; Simmons, H. E.; Wood, G. W. *J. Am. Chem. Soc.* 1957, **79**, 3900.
117. Oppolzer, W.; Radinov, R. N. *J. Am. Chem. Soc.* 1993, **115**, 1593.
118. Moss, R. A.; Chen, E. Y.; Banger, J.; Matsuo, M. *Tetrahedron Lett.* 1978, **19**, 4365.
119. Kawabata, N.; Nakagawa, T.; Nakao, T.; Yamashita, S. *J. Org. Chem.* 1977, **42**, 3031.
120. Friedrich, E. C.; Biresaw, G. *J. Org. Chem.* 1982, **47**, 2426.
121. Sawada, S.; Takehana, K.; Inouye, Y. *J. Org. Chem.* 1968, **33**, 1767.
122. Russ, P.; Ezzitouni, A.; Marquez, V. E. *Tetrahedron Lett.* 1997, **38**, 723.
123. Avramoff, M. *Eur. J. Med. Chem.* 1981, **16**, 199.
124. Hanessian, S.; Reinhold, U.; Saulnier, M.; Claridge, S. *Bioorg. Med. Chem. Lett.* 1998, **8**, 2123.
125. Swenton, J. S.; Burdett, K. A.; Madigan, D. M.; Johnson, T.; Rosso, P. D. *J. Am. Chem. Soc.* 1975, **97**, 3428.
126. Takano, S.; Yamane, T.; Takahashi, M.; Ogasawara, K. *Synlett* 1992, 410.
127. Hoberg, J. O.; Bozell, J. J. *Tetrahedron Lett.* 1995, **36**, 6831.
128. Albano-Garcia, E. L.; Arbolario, E. M.; Lorica, R. G. *Nat. Appl. Sci. Bull.* 1979, **31**, 61.
- 128a Kirmse, W.; Hartmann, M.; Siegfried, R.; Wroblowsky, H. J.; Zang, B.; Zellmer, V. *Chem. Ber.* 1981, **114**, 1793.
129. Johnson, C. R.; Barbachyn, M. R. *J. Am. Chem. Soc.* 1982, **104**, 4290.
130. Wang, T.-Z.; Pinard, E.; Paquette, L. A. *J. Am. Chem. Soc.* 1996, **118**, 1309.
131. Corey, E. J.; Lee, J. J. *J. Am. Chem. Soc.* 1993, **115**, 8873.
132. Schreiber, S. L.; Smith, D. B.; Schulte, G. J. *Org. Chem.* 1989, **54**, 5994.
133. Oh, J.; Cha, J. K. *Synlett* 1994, 967.
134. Momose, T.; Nishio, T.; Kirihara, M. *Tetrahedron Lett.* 1996, **37**, 4987.
135. Ratier, M.; Castaing, M.; Godet, J.-Y.; Pereyre, M. *J. Chem. Res. (S)* 1978, 179.
136. Charette, A. B.; Lebel, H. *J. Org. Chem.* 1995, **60**, 2966.
- 136a Lebel, H., Ph. D. Thesis, Université de Montréal.

137. Yamazaki, T.; Lin, J. T.; Takeda, M.; Kitazume, T. *Tetrahedron: Asymmetry* 1990, **1**, 351.
138. Professor S. E. Denmark, Univ. Illinois, personal communication.
139. Lautens, M.; Delanghe, P. H. M. *J. Org. Chem.* 1992, **57**, 798.
140. Lautens, M.; Delanghe, P. H. M. *J. Org. Chem.* 1995, **60**, 2474.
141. Hoffmann, R. W. *Chem. Rev.* 1989, **89**, 1841.
142. Lautens, M.; Delanghe, P. H. M. *J. Am. Chem. Soc.* 1994, **116**, 8526.
143. Paddon-Row, M. N.; Rondan, N. G.; Houk, K. N. *J. Am. Chem. Soc.* 1982, **104**, 7162.
144. Houk, K. N.; Rondan, N. G.; Wu, Y.-D.; Metz, J. T.; Paddon-Row, M. N. *Tetrahedron* 1984, **40**, 2257.
145. Mohr, P. *Tetrahedron Lett.* 1995, **36**, 7221.
- 145a Charette, A. B.; Lebel, H.; Gagnon, A. *Tetrahedron* 1999, **55**, 8845.
146. Zhao, Y.; Yang, T.; Lee, M.; Lee, D.; Newton, M. G.; Chu, C. K. *J. Org. Chem.* 1995, **60**, 5236.
147. Morikawa, T.; Sasaki, H.; Hanai, R.; Shibuya, A.; Taguchi, T. *J. Org. Chem.* 1994, **59**, 97.
148. Fukuyama, Y.; Hirono, M.; Kodama, M. *Chem. Lett.* 1992, 167.
149. Barrett, A. G. M.; Kasdorf, K.; Williams, D. J. *J. Chem. Soc., Chem. Commun.* 1994, 1781.
150. Onoda, T.; Shirai, R.; Koiso, Y.; Iwasaki, S. *Tetrahedron Lett.* 1996, **37**, 4397.
151. Pilar de Frutos, M.; Dolores Fernández, M.; Fernández-Alvarez, E.; Bernabé, M. *Tetrahedron Lett.* 1991, **32**, 541.
152. Iguchi, K.; Fujita, M.; Nagaoka, H.; Mitome, H.; Yamada, Y. *Tetrahedron Lett.* 1993, **34**, 6277.
153. Panek, J. S.; Garbaccio, R. M.; Jain, N. F. *Tetrahedron Lett.* 1994, **35**, 6453.
154. Landais, Y.; Parra-Rapado, L. *Tetrahedron Lett.* 1996, **37**, 1205.
155. Barrett, A. G. M.; Tustin, G. J. *J. Chem. Soc., Chem. Commun.* 1995, 355.
156. Kunz, H.; Rück, K. *Angew. Chem., Int. Ed. Engl.* 1993, **32**, 336.
157. Charette, A. B.; Côté, B.; Marcoux, J.-F. *J. Am. Chem. Soc.* 1991, **113**, 8166.
158. Charette, A. B.; Turcotte, N.; Marcoux, J.-F. *Tetrahedron Lett.* 1994, **35**, 513.
159. Charette, A. B.; Marcoux, J.-F. *Tetrahedron Lett.* 1993, **34**, 7157.
- 159a Charette, A. B.; Côté, B. *J. Org. Chem.* 1993, **58**, 933.

160. Arai, I.; Mori, A.; Yamamoto, H. *J. Am. Chem. Soc.* 1985, **107**, 8254.
161. Mori, A.; Arai, I.; Yamamoto, H.; Nakai, H.; Arai, Y. *Tetrahedron* 1986, **42**, 6447.
162. Barrett, A. G. M.; Doubleday, W. W.; Kasdorf, K.; Tustin, G. J. *J. Org. Chem.* 1996, **61**, 3280.
163. Mash, E. A.; Nelson, K. A. *J. Am. Chem. Soc.* 1985, **107**, 8256.
164. Mash, E. A.; Nelson, K. A. *Tetrahedron* 1987, **43**, 679.
165. Mash, E. A.; Math, S. K.; Arterburn, J. B. *J. Org. Chem.* 1989, **54**, 4951.
166. Mash, E. A.; Hemperly, S. B.; Nelson, K. A.; Heidt, P. C.; Van Deusen, S. *J. Org. Chem.* 1990, **55**, 2045.
167. Armstrong, R. W.; Maurer, K. W. *Tetrahedron Lett.* 1995, **36**, 357.
168. Yeh, S.-M.; Huang, L.-H.; Luh, T.-Y. *J. Org. Chem.* 1996, **61**, 3906.
169. Ebens, R.; Kellogg, R. M. *Recl. Trav. Chim. Pays-Bas* 1990, **109**, 552.
170. Kang, J.; Lim, G. J.; Yoon, S. K.; Kim, M. Y. *J. Org. Chem.* 1995, **60**, 564.
171. Kaye, P. T.; Molema, W. E. *J. Chem. Soc., Chem. Commun.* 1998, 2479.
172. Ambler, P. W.; Davies, S. G. *Tetrahedron Lett.* 1988, **29**, 6979.
173. Tanaka, K.; Uno, H.; Osuga, H.; Suzuki, H. *Tetrahedron: Asymmetry* 1994, **5**, 1175.
174. Sugimura, T.; Futagawa, T.; Yoshikawa, M.; Tai, A. *Tetrahedron Lett.* 1989, **30**, 3807.
175. Sugimura, T.; Futagawa, T.; Tai, A. *Tetrahedron Lett.* 1988, **29**, 5775.
176. Sugimura, T.; Yoshikawa, M.; Futagawa, T.; Tai, A. *Tetrahedron* 1990, **46**, 5955.
177. Sugimura, T.; Futagawa, T.; Tai, A. *Chem. Lett.* 1990, 2291.
178. Imai, T.; Mineta, H.; Nishida, S. *J. Org. Chem.* 1990, **55**, 4986.
179. Hildebrand, J. P.; Marsden, S. P. *Synlett* 1996, 893.
180. Sugimura, T.; Katagiri, T.; Tai, A. *Tetrahedron Lett.* 1992, **33**, 367.
181. Akiba, T.; Tamura, O.; Hashimoto, M.; Kobayashi, Y.; Katoh, T.; Nakatani, K.; Kamada, M.; Hayakawa, I.; Terashima, S. *Tetrahedron* 1994, **50**, 3905.
182. Denmark, S. E.; Edwards, J. P. *Synlett* 1992, 229.
183. Ukaji, Y.; Nishimura, M.; Fujisawa, T. *Chem. Lett.* 1992, 61.
184. Ukaji, Y.; Sada, K.; Inomata, K. *Chem. Lett.* 1993, 1227.
185. Charette, A. B.; Juteau, H. *J. Am. Chem. Soc.* 1994, **116**, 2651.
186. Charette, A. B.; Prescott, S.; Brochu, C. *J. Org. Chem.* 1995, **60**, 1081.
187. Charette, A. B.; Juteau, H.; Lebel, H.; Molinaro, C. *J. Am. Chem. Soc.*

- 1998, **120**, 11943.
188. Falck, J. R.; Mekonnen, B.; Yu, J.; Lai, J.-Y. *J. Am. Chem. Soc.* 1996, **118**, 6096.
189. Charette, A. B.; Juteau, H.; Lebel, H.; Deschênes, D. *Tetrahedron Lett.* 1996, **37**, 7925.
190. Charette, A. B.; Lebel, H. *Org. Synth.* 1999, **76**, 86.
191. White, J. D.; Kim, T.-S.; Nambu, M. *J. Am. Chem. Soc.* 1995, **117**, 5612.
192. Barrett, A. G. M.; Kasdorf, K. *J. Am. Chem. Soc.* 1996, **118**, 11030.
193. Barrett, A. G. M.; Hamprecht, D.; White, A. J. P.; Williams, D. J. *J. Am. Chem. Soc.* 1996, **118**, 7863.
194. Charette, A. B.; Lebel, H. *J. Am. Chem. Soc.* 1996, **118**, 10327.
195. Charreau, P.; Julia, M.; Verpeaux, J. N. *Bull. Soc. Chim. Fr.* 1990, **127**, 275.
196. Martínez, A. G.; Fernández, A. H.; Alvarez, R. M.; Barcina, J. O.; Gómez, C. G.; Subramanian, L. R. *Synthesis* 1993, 1063.
197. Charette, A. B.; Lebel, H.; Gagnon, A. *Tetrahedron* 1999, **55**, 8845.
198. Kitajima, H.; Aoki, Y.; Ito, K.; Katsuki, T. *Chem. Lett.* 1995, 1113.
199. Kitajima, H.; Ito, K.; Aoki, Y.; Katsuki, T. *Bull. Chem. Soc. Jpn.* 1997, **70**, 207.
200. Takahashi, H.; Yoshioka, M.; Ohno, M.; Kobayashi, S. *Tetrahedron Lett.* 1992, **33**, 2575.
201. Denmark, S. E.; O'Connor, S. P. *J. Org. Chem.* 1997, **62**, 584.
202. Denmark, S. E.; Christenson, B. L.; O'Connor, S. P. *Tetrahedron Lett.* 1995, **36**, 2219.
- 202a Denmark, S. E.; Christenson, B. L.; O'Connor, S. P.; Murase, N. *Pure Appl. Chem.* 1996, **68**, 23.
203. Imai, N.; Sakamoto, K.; Takahashi, H.; Kobayashi, S. *Tetrahedron Lett.* 1994, **35**, 7045.
204. Imai, N.; Takahashi, H.; Kobayashi, S. *Chem. Lett.* 1994, 177.
205. Denmark, S. E.; Christenson, B. L.; Coe, D. M.; O'Connor, S. P. *Tetrahedron Lett.* 1995, **36**, 2215.
206. Denmark, S. E.; O'Connor, S. P.; Wilson, S. R. *Angew. Chem., Int. Ed.* 1998, **37**, 1149.
207. Dahinden, R.; Beck, A. K.; Seebach, D. in *Encyclopedia of Reagents for Organic Synthesis*, Paquette, L., Ed., J. Wiley & Sons, Chichester, 1995, Vol. **3**, p. 2167–2170.
208. Corey, E. J.; Eckrich, T. M. *Tetrahedron Lett.* 1984, **25**, 2415.
209. Takakis, I. M.; Rhodes, Y. E. *J. Org. Chem.* 1978, **43**, 3496.
210. Wittig, G.; Schwarzenbach, K. *Justus Liebigs Ann. Chem.* 1962, 650. 1.

211. Kosarych, Z.; Cohen, T. *Tetrahedron Lett.* 1982, **23**, 3019.
212. Seyferth, D. *Angew. Chem.* 1960, **72**, 36.
213. Dumont, C.; Zoukal, M.; Vidal, M. *Tetrahedron Lett.* 1981, **22**, 5267.
214. Patai, S., Rappoport, Z. *The Chemistry of the cyclopropyl Group*, Wiley and Sons, New York, 1987.
215. Reissig, H.-U. in *Stereoselective Synthesis of Organic Compounds, Methods of Organic Chemistry (Houben-Weyl)*, Helmchen, G., Hoffmann, R. W., Mulzer, J., Schaumann, E., Eds., Thieme, Stuttgart, 1995, Vol. **2**, 3179.
216. Doyle, M. P. in *Catalytic Asymmetric Synthesis*, Ojima, I. Ed., VCH: Weinheim, 1993, 63.
217. Koert, U. *Nachr. Chem. Tech. Lab.* 1995, **43**, 435.
218. Reissig, H.-U. *Angew. Chem., Int. Ed. Engl.* 1996, **35**, 971.
219. Aratani, T. *Pure Appl. Chem.* 1985, **57**, 1839.
220. Salaün, J. *Chem. Rev.* 1989, **89**, 1247.
221. Lautens, M.; Klute, W.; Tam, W. *Chem. Rev.* 1996, **96**, 49.
222. Stork, G.; Nair, V. *J. Am. Chem. Soc.* 1979, **101**, 1315.
223. Nair, V. in *Comprehensive Organic Synthesis*, Trost, B. M., Fleming, I., Semmelhack, M. F., Eds., Pergamon Press, Oxford, 1991, Vol. **4**, 999.
224. Doyle, M. P.; Protopopova, M. N. *Tetrahedron* 1998, **54**, 7919.
225. Doyle, M. P.; Forbes, D. C. *Chem. Rev.* 1998, **98**, 911.
- 225a Davies, H. M. L.; Antoulinakis, E. G. *Org. React.*, 2001, **57**, 1.
226. Pfaltz, A. in *Comprehensive Asymmetric Catalysis*, Jacobsen, E. N., Pfaltz, A., Yamamoto, H., Eds., Springer-Verlag, Berlin, 1999, Vol **II**, pp. 513–538.
227. Evans, D. A.; Woerpel, K. A.; Hinman, M. M.; Faul, M. M. *J. Am. Chem. Soc.* 1991, **113**, 726.
228. Lo, M. M.-C.; Fu, G. C. *J. Am. Chem. Soc.* 1998, **120**, 10270.
229. Davies, H. M. L.; Bruzinski, P. R.; Lake, D. H.; Kong, N.; Fall, M. J. *J. Am. Chem. Soc.* 1996, **118**, 6897.
230. Fritschi, H.; Leutenegger, U.; Pfaltz, A. *Helv. Chim. Acta.* 1988, **71**, 1553.
231. Doyle, M. P.; Winchester, W. R.; Protopopova, M. N.; Müller, P.; Bernardinelli, G.; Ené, D.; Motallebi, S. *Helv. Chim. Acta* 1993, **76**, 2227.
232. Müller, P.; Baud, C.; Ené, D.; Motallebi, S.; Doyle, M. P.; Brandes, B. D.; Dyatkin, A. B.; See, M. M. *Helv. Chim. Acta* 1995, **78**, 459.
233. Ishitani, H.; Achiwa, K. *Synlett* 1997, 781.
234. Tomilov, Y. V.; Dokitchev, V. A.; Dzhemilev, U. M.; Nefedov, O. M. *Usp.*

- Khim. 1993, **62**, 847.
235. Pfaltz, A. in *Modern Synthetic Methods 1989*, Scheffold, R., Ed., Springer, Berlin, 1989, pp. 199–248.
236. Pfaltz, A. *Acc. Chem. Res.* 1993, **26**, 339.
237. Denmark, S. E.; Stavenger, R. A.; Faucher, A.-M.; Edwards, J. P. *J. Org. Chem.* 1997, **62**, 3375.
238. Lydon, K. M.; McKerverey, M. A. in *Comprehensive Asymmetric Catalysis*, Jacobsen, E. N., Pfaltz, A., Yamamoto, H., Eds., Springer-Verlag, Berlin, 1999, Vol. **II**, pp. 539–580.
239. Doyle, M. P.; Austin, R. E.; Bailey, A. S.; Dwyer, M. P.; Dyatkin, A. B.; Kalinin, A. V.; Kwan, M. M. Y.; Liras, S.; Oalman, C. J.; Pieters, R. J.; Protopopova, M. N.; Raab, C. E.; Roos, G. H. P.; Zhou, Q.-L.; Martin, S. F. *J. Am. Chem. Soc.* 1995, **117**, 5763.
240. Krief, A.; Dumont, W.; Pasau, P. *Tetrahedron Lett.* 1988, **29**, 1079.
241. Krief, A.; Dumont, W. *Tetrahedron Lett.* 1988, **29**, 1083.
242. Romo, D.; Romine, J. L.; Midura, W.; Meyers, A. I. *Tetrahedron* 1990, **46**, 4951.
243. Aggarwal, V. K.; Smith, H. W.; Jones, R. V. H.; Fieldhouse, R. J. *Chem. Soc., Chem. Commun.* 1997, 1785.
244. Li, A.-H.; Dai, L.-X.; Aggarwal, V. K. *Chem. Rev.* 1997, **97**, 2341.
245. Hanessian, S.; Andreotti, D.; Gomtsyan, A. *J. Am. Chem. Soc.* 1995, **117**, 10393.
246. Hanessian, S.; Andreotti, D.; Gomtsyan, A. *J. Am. Chem. Soc.* 1996, **118**, 2537.
247. Katsuki, T.; Martin, V. S. *Org. React.* 1996, **48**, 1.
248. Burgess, K.; Ho, K.-K. *J. Org. Chem.* 1992, **57**, 5931.
249. Kolb, H. C.; VanNieuwenhze, M. S.; Sharpless, K. B. *Chem. Rev.* 1994, **94**, 2483.
250. Burgess, K.; Ho, K.-K.; Ke, C.-Y. *J. Org. Chem.* 1993, **58**, 3767.
251. *Aldrich Technical Information Bulletin Number AL-134, Handling Air-Sensitive Reagents.*
252. Kramer, G. W.; Levy, A. B.; Midland, M. M. in Brown, H. C. *Organic Syntheses via Boranes*, John Wiley and Sons, Inc., New York, 1975.
253. Shriver, D. F. *The Manipulation of Air-Sensitive Compounds*, McGraw-Hill Book Company, New York, 1969.
254. Hock, H.; Kropf, H.; Ernst, F. *Angew. Chem.* 1959, **71**, 541.
255. Abraham, M. H. *J. Chem. Soc.* 1960, 4130.
256. Limasset, J.-C.; Amice, P.; Conia, J.-M. *Bull. Soc. Chim. Fr.* 1969, 3981.
257. Konopelski, J. P.; Sundararaman, P.; Barth, G.; Djerassi, C. *J. Am. Chem. Soc.* 1980, **102**, 2737.

- 257a Friedrich, E. C.; Domek, J. M.; Pong, R. Y. *J. Org. Chem.* 1985, **50**, 4640.
258. Maruoka, K.; Sakane, S.; Yamamoto, H. *Org. Synth.* 1989, **67**, 176.
259. Dauben, W. G.; Laug, P.; Berezin, G. H. *J. Org. Chem.* 1966, **31**, 3869.
- 259a Fleming, I.; Lawrence, N. J.; Sarkar, A. K.; Thomas, A. P. *J. Chem. Soc., Perkin Trans. 1* 1992, 3303.
260. Mash, E. A.; Torok, D. S. *J. Org. Chem.* 1989, **54**, 250.
261. Barbachyn, M. R.; Johnson, C. R.; Glick, M. D. *J. Org. Chem.* 1984, **49**, 2746.
- 261a Charette, A. B.; Côté, B. *J. Am. Chem. Soc.* 1995, **117**, 12721.
- 261b Barrett, A. G. M.; Doubleday, W. W.; Tustin, G. J. *Tetrahedron* 1996, **52**, 15325.
262. Professor W. B. Motherwell, University College London, personal communication
263. Wiberg, K. B.; Kass, S. R.; de Meijere, A.; Bishop, K. C. *J. Am. Chem. Soc.* 1985, **107**, 1003.
264. Trautmann, W.; Musso, H. *Chem. Ber.* 1981, **114**, 982.
265. Pitea, D.; Moro, G.; Favini, G. *J. Chem. Soc., Perkin Trans. 2* 1987, 313.
266. Engelhard, M.; Lüttke, W. *Chem. Ber.* 1977, **110**, 3759.
267. Girard, C.; Conia, J. M. *Tetrahedron Lett.* 1974, 3333.
268. Mil'vitskaya, E. M.; Kovner, O. Ya.; Platé, A. F.; Binebskaya, L. I. *Zh. Org. Khim.* 1977, **13**, 54.
269. Gassman, P. G.; Proehl, G. S. *J. Am. Chem. Soc.* 1980, **102**, 6862.
270. Friedrich, E. C.; Domek, J. M.; Pong, R. Y. *J. Org. Chem.* 1985, **50**, 4640.
271. Klabunde, K. J.; Murdock, T. O. *J. Org. Chem.* 1979, **44**, 3901.
272. Fabisch, B.; Mitchell, T. N. *J. Organomet. Chem.* 1984, **269**, 219.
273. Miyano, S.; Hashimoto, H. *Bull. Chem. Soc. Jpn.* 1973, **46**, 1895.
274. Miyano, S.; Hashimoto, H. *Bull. Chem. Soc. Jpn.* 1974, **47**, 1500.
275. Wu, S. H.; Liu, W. Z.; Jiang, X. K. *J. Org. Chem.* 1994, **59**, 854.
276. Motherwell, W. B.; O'Mahony, D. J. R.; Popkin, M. E. *Tetrahedron Lett.* 1998, **39**, 5285.
277. Manuel, G.; Faucher, A.; Mazerolles, P. *J. Organomet. Chem.* 1984, **264**, 127.
278. Grignon-Dubois, M.; Dunogues, J.; Calas, R. *J. Organomet. Chem.* 1979, **181**, 285.
279. Culshaw, P. N.; Dalton, M.; MacCorquodale, F.; Walton, J. C. *J. Chem. Soc., Perkin Trans. 2* 1990, 531.

280. Brookhart, M.; Dedmond, R. E.; Lewis, B. F. J. *Organomet. Chem.* 1974, **72**, 239.
281. Cheng, A. K.; Stothers, J. B. *Org. Magn. Res.* 1977, **9**, 355.
282. Freeman, P. K.; Ziebarth, T. D.; Raghavan, R. S. J. *Am. Chem. Soc.* 1975, **97**, 1875.
283. Katz, T. J.; Yang, G. X. Q. *Tetrahedron Lett.* 1991, **32**, 5895.
284. Kopecky, K. R.; Gomez, R. R. *Can. J. Chem.* 1981, **59**, 1607.
285. Prakash, G. K. S.; Fung, A. P.; Olah, G. A.; Rawdah, T. N. *Proc. Natl. Acad. Sci. USA* 1987, **84**, 5092.
286. Gassman, P. G.; Valcho, J. J.; Proehl, G. S.; Cooper, C. F. J. *Am. Chem. Soc.* 1980, **102**, 6519.
287. Gassman, P. G.; Valcho, J. J.; Proehl, G. S. J. *Am. Chem. Soc.* 1979, **101**, 231.
288. Klärner, F.-G.; Kleine, A. E.; Oebels, D.; Scheidt, F. *Tetrahedron: Asymmetry* 1993, **4**, 479.
289. Paquette, L. A.; Carmody, M. J. J. *Am. Chem. Soc.* 1976, **98**, 8175.
290. Chenier, P. J.; Christie, D. M.; Goettl, V. M. J. *Org. Chem.* 1985, **50**, 3213.
291. Kaufmann, D.; Fick, H.-H.; Schallner, O.; Spielmann, W.; Meyer, L.-U.; Göllitz, P.; de Meijere, A. *Chem. Ber.* 1983, **116**, 587.
292. Staley, S. W.; Linkowski, G. E.; Heyn, A. S. *Tetrahedron* 1975, **31**, 1131.
293. Takakis, I. M.; Agosta, W. C. J. *Am. Chem. Soc.* 1979, **101**, 2383.
294. Williams, B.; Jennings, P. W. *Inorg. Chim. Acta* 1997, **265**, 23.
295. Takakis, I. M.; Agosta, W. C. J. *Org. Chem.* 1979, **44**, 1294.
296. Takakis, I. M.; Agosta, W. C. *Tetrahedron Lett.* 1978, 2387.
297. De Meijere, A.; Schallner, O.; Weitemeyer, C. *Tetrahedron Lett.* 1973, 3483.
298. De Meijere, A.; Weitemeyer, C.; Schallner, O. *Chem. Ber.* 1977, **110**, 1504.
299. Takakis, I. M.; Agosta, W. C. J. *Org. Chem.* 1978, **43**, 1952.
300. Lipa, W. J.; Crawford, H. T.; Radlick, P. C.; Helmkamp, G. K. J. *Org. Chem.* 1978, **43**, 3813.
301. Golzke, V.; Rüdhardt, C. *Chem. Ber.* 1977, **110**, 3464.
302. de Meijere, A.; Schallner, O.; Weitemeyer, C.; Spielmann, W. *Chem. Ber.* 1979, **112**, 908.
303. Detty, M. R.; Paquette, L. A. J. *Am. Chem. Soc.* 1977, **99**, 821.
304. Bigley, D. B.; Fetter, C. L. J. *Chem. Soc., Perkin Trans. 2* 1979, 122.
305. Balenkova, E. S.; Anfilogova, S. N. *Zh. Org. Khim.* 1973, **9**, 524.
306. Reger, D. L.; Gabrielli, A. J. *Am. Chem. Soc.* 1975, **97**, 4421.

307. Reger, D. L.; Gabrielli, A. J. *Organomet. Chem.* 1980, **187**, 243.
308. Duguid, R. J.; Morrison, H. J. *Am. Chem. Soc.* 1991, **113**, 1265.
309. Perkins, M. J.; Ward, P. J. *Chem. Soc., Perkin Trans. 1* 1974, 66.
310. Bosse, D.; de Meijere, A. *Tetrahedron Lett.* 1975, 871.
311. Pizzala, L.; Bodot, H.; Fruchier, A. *Org. Magn. Res.* 1977, **9**, 260.
312. Paquette, L. A.; Ham, W. H.; Dime, D. S. *Tetrahedron Lett.* 1985, **26**, 4983.
313. Terunuma, D.; Hatta, S.; Araki, T.; Ueki, T.; Okazaki, T.; Suzuki, Y. *Bull. Chem. Soc. Jpn.* 1977, **50**, 1545.
314. Dawson, M. I.; Hobbs, P. D.; Chan, R. L.-S.; Chao, W.-R. *J. Med. Chem.* 1981, **24**, 1214.
315. Roth, H. D.; Schilling, M. L. M.; Schilling, F. C. *J. Am. Chem. Soc.* 1985, **107**, 4152.
316. Bloch, R.; Bortolussi, M. *Tetrahedron Lett.* 1976, 309.
317. Tamao, K.; Nakajima, T.; Kumada, M. *Organometallics* 1984, **3**, 1655.
318. Dodd, J. R.; Pagni, R. M.; Watson, C. R. *J. Org. Chem.* 1981, **46**, 1688.
319. Volz, W. E.; Paquette, L. A. *J. Org. Chem.* 1976, **41**, 57.
320. Kitahonoki, K.; Sakurawi, K.; Tori, K.; Ueyama, M. *Tetrahedron Lett.* 1976, 263.
321. Balsamo, A.; Battistini, C.; Crotti, P.; Macchia, B.; Macchia, F. *J. Org. Chem.* 1975, **40**, 3233.
322. Langlois, M.; Rapin, M.; Meingan, J.-P.; Vo Van, T.; Maillard, J.; Guillonnet, C.; Maloizel, C.; Nguyen, H. N.; Morin, R.; Manuel, C.; Mazmanian, C. *Eur. J. Med. Chem. Chim. Ther.* 1976, **11**, 493.
323. Nelson, P. H.; Bartsch, G. A.; Untch, K. G.; Fried, J. H. *J. Med. Chem.* 1975, **18**, 583.
324. Osawa, E.; Tahara, Y.; Togashi, A.; Iizuka, T.; Tanaka, N.; Kan, T.; Farcasiu, D.; Kent, G. J.; Engler, E. M.; Schleyer von R., P. *J. Org. Chem.* 1982, **47**, 1923.
325. Battistini, C.; Crotti, P.; Macchia, B.; Macchia, F.; DePuy, C. H. *J. Org. Chem.* 1978, **43**, 1400.
326. Meinwald, J.; Dunkerton, L. V.; Gruber, G. W. *J. Am. Chem. Soc.* 1975, **97**, 681.
327. Highton, A. J.; Majid, T. N.; Simpkins, N. S. *Synlett* 1999, 237.
328. Lamberts, J. J. M.; Laarhoven, W. H. *J. Org. Chem.* 1983, **48**, 2202.
329. Kawashima, K.; Kawano, Y. *Chem. Pharm. Bull.* 1976, **24**, 2751.
330. Peijnenburg, W. J. G. M.; Dormans, G. J. M.; Bezemer, G. J.; Buck, H. M. *Tetrahedron* 1984, **40**, 4959.
331. Cristol, S. J.; Noreen, A. L. *J. Org. Chem.* 1976, **41**, 4016.

- 331a Magnus, P.; Schultz, J.; Gallagher, T. J. *Am. Chem. Soc.* 1985, **107**, 4984.
332. Rubottom, G. M.; Beedle, E. C.; Kim, C. W.; Mott, R. C. *J. Am. Chem. Soc.* 1985, **107**, 4230.
333. Yamamoto, K.; Murata, I. *Angew. Chem., Int. Ed. Engl.* 1976, **15**, 240.
334. Hildenbrand, P.; Plinke, G.; Oth, J. F. M.; Schröder, G. *Chem. Ber.* 1978, **111**, 107.
335. Kano, S.; Yokomatsu, T.; Shibuya, S. *Chem. Pharm. Bull.* 1977, **25**, 2875.
336. McMurry, J. E.; Haley, G. J.; Matz, J. R.; Clardy, J. C.; Van Duyne, G.; Gleiter, R.; Schäfer, W.; White, D. H. *J. Am. Chem. Soc.* 1986, **108**, 2932.
337. Farmer, L. J.; Jeong, S.; Kallel, E. A.; Koch, S. S. C.; Croston, G. E.; Flatten, K. S.; Heyman, R. A.; Nadzan, A. M. *Bioorg. Med. Chem. Lett.* 1997, **7**, 2393.
338. Dyker, G.; Körning, J.; Bubenitschek, P.; Jones, P. G. *J. Chem. Res. (S)* 1997, 132.
339. Mohler, D. L.; Vollhardt, K. P. C.; Wolff, S. *Angew. Chem., Int. Ed. Engl.* 1995, **34**, 563.
340. Osterodt, J.; Vögtle, F. *J. Chem. Soc., Chem. Commun.* 1996, 547.
341. Mitani, M.; Tachizawa, O.; Takeuchi, H.; Koyama, K. *J. Org. Chem.* 1989, **54**, 5397.
342. Bredikhin, A. A.; Plemenkov, V. V. *Zh. Org. Khim.* 1976, **12**, 1001.
343. Kirmse, W.; Alberti, J. *Chem. Ber.* 1973, **106**, 236.
344. Le Goaller, R.; Pierre, J.-L. *Can. J. Chem.* 1977, **55**, 757.
345. Davis, B. R.; Rewcastle, G. W.; Woodgate, P. D. *J. Chem. Soc., Perkin Trans. 1* 1979, 2815.
346. Gassman, P. G.; Burns, S. J. *J. Org. Chem.* 1988, **53**, 5576.
347. Ito, Y.; Fujii, S.; Nakatsuka, M.; Kawamoto, F.; Saegusa, T. *Org. Synth. Coll. Vol.* **6**, 1988, 327.
348. Ryu, I.; Murai, S.; Otani, S.; Sonoda, N. *Chem. Lett.* 1976, 93.
349. Ryu, I.; Murai, S.; Sonoda, N. *Tetrahedron Lett.* 1977, 4611.
350. Girard, C.; Conia, J. M. *Tetrahedron Lett.* 1974, 3327.
351. Ito, Y.; Saegusa, T. *J. Macromol. Sci., Chem.* 1979, **A13**, 503.
352. Lewicka-Piekut, S.; Okamura, W. H. *Synth. Commun.* 1980, **10**, 415.
353. Blanco, L.; Mansouri, A. *Tetrahedron Lett.* 1988, **29**, 3239.
354. Miyano, S.; Izumi, Y.; Fujii, H.; Hashimoto, H. *Synthesis* 1977, 700.
355. Balenkova, E. S.; Karamysheva, L. A. *Zh. Org. Khim.* 1973, **9**, 2310.
356. Ryu, I.; Murai, S.; Sonoda, N. *Chem. Lett.* 1976, 1049.

357. Hirabayashi, K.; Takahisa, E.; Nishihara, Y.; Mori, A.; Hiyama, T. *Bull. Chem. Soc. Jpn.* 1998, **71**, 2409.
358. Barnier, J. P.; Blanco, L.; Rousseau, G.; Guibejampel, E.; Fresse, I. J. *Org. Chem.* 1993, **58**, 1570.
359. Schiehser, G. A.; White, J. D. *J. Org. Chem.* 1980, **45**, 1864.
360. Booker-Milburn, K. I.; Dainty, R. F. *Tetrahedron Lett.* 1998, **39**, 5097.
361. Sraga, J.; Hrnciar, P. *Acta F. R. N. Univ. Comen., Chim.* 1981, **29**, 105.
362. Paquette, L. A.; Watson, T. J.; Friedrich, D.; Bishop, R.; Bacque, E. J. *Org. Chem.* 1994, **59**, 5700.
363. Baldwin, J. E.; Broline, B. M. *J. Org. Chem.* 1982, **47**, 1385.
364. Wenkert, E.; Arrhenius, T. S.; Bookser, B.; Guo, M.; Mancini, P. J. *Org. Chem.* 1990, **55**, 1185.
365. Booker-Milburn, K. I.; Thompson, D. F. *Tetrahedron Lett.* 1993, **34**, 7291.
366. Wenkert, E.; Berges, D. A.; Golob, N. F. *J. Am. Chem. Soc.* 1978, **100**, 1263.
367. Lundkvist, J. R. M.; Arvidsson, L. E.; Hacksell, U.; Johansson, A. M. *Acta Chem. Scand. B* 1986, **40**, 508.
368. Johansson, A. M.; Mellin, C.; Hacksell, U. *J. Org. Chem.* 1986, **51**, 5252.
369. Marchand, A. P.; Rajapaksa, D.; Vidyasagar, V.; Watson, W. H.; Kashyap, R. P. *Synth. Commun.* 1996, **26**, 819.
370. Brown, R. S.; Traylor, T. G. *J. Am. Chem. Soc.* 1973, **95**, 8025.
371. Ito, S.; Shinokubo, H.; Oshima, K. *Tetrahedron Lett.* 1998, **39**, 5253.
372. Donovalova, J.; Hrnciar, P.; Sraga, J. *Chem. Zvesti* 1983, **37**, 809.
373. Dent, B. R.; Halton, B. *Aust. J. Chem.* 1987, **40**, 925.
374. Ito, Y.; Saegusa, T. *J. Org. Chem.* 1977, **42**, 2326.
375. Lie Ken Jie, M. S. F.; Lam, W. L. K. *J. Am. Oil Chem. Soc.* 1988, **65**, 118.
376. Ito, Y.; Sugaya, T.; Nakatsuka, M.; Saegusa, T. *J. Am. Chem. Soc.* 1977, **99**, 8366.
377. Marshall, J. A.; Peterson, J. C.; Lebioda, L. J. *J. Am. Chem. Soc.* 1984, **106**, 6006.
378. Keeports, D. D.; Eggers, D. F. *Spectrochim. Acta, Part. A.* 1984, **40**, 7.
379. Mironov, V. F.; Sheludyakov, V. D.; Shcherbinin, V. V.; Viktorov, E. A. *Zh. Obshh. Khim.* 1975, **45**, 1796.
380. Krongauz, V. V.; Rabinovitch, B. S. *Chem. Phys.* 1982, **67**, 201.
381. Krongauz, V. V.; Rabinovitch, B. S. *J. Chem. Phys.* 1983, **78**, 3872.
382. Pavlov, K. V.; Viktorov, N. A.; Mironov, V. F. *Izv. Akad. Nauk., Ser. Khim.* 1993, **42**, 756.

383. Schraml, J.; Grignon-Dubois, M.; Dunoguès, J.; Jancke, H.; Engelhardt, G.; Chvalovsky, V. *Coll. Czech. Chem. Commun.* 1983, **48**, 3396.
384. Shaler, T. A.; Morton, T. H. *J. Am. Chem. Soc.* 1989, **111**, 6868.
385. Moss, R. A.; Wilk, B.; Krogh-Jespersen, K.; Westbrook, J. D. *J. Am. Chem. Soc.* 1989, **111**, 6729.
386. Durig, J. R.; Little, T. S.; Zhu, X.; Dakkouri, M. *J. Mol. Struct.* 1993, **293**, 15.
387. Little, T. S.; Vaughn, C. A.; Zhu, X.; Dakkouri, M.; Durig, J. R. *J. Raman Spectrosc.* 1994, **25**, 735.
388. Dakkouri, M. *J. Mol. Struct.* 1997, **413**, 133.
389. Khusid, A. Kh.; Kryshtal, G. V.; Dombrovsky, V. A.; Kucherov, V. F.; Yanovskaya, L. A.; Kadentsev, V. I.; Chizhov, O. S. *Tetrahedron* 1977, **33**, 77.
390. Davies, A. G.; Sutcliffe, R. *J. Chem. Soc., Perkin Trans. 2* 1982, 1483.
391. Laurent, E.; Thomalla, M. *Electrochim. Acta* 1977, **22**, 531.
392. Nijveldt, D.; Vos, A. *Acta Crystallogr.* 1988, **B44**, 281.
393. Havel, J. J.; Chan, K. H. *J. Org. Chem.* 1977, **42**, 569.
394. Huhtasaari, M.; Schäfer, H. J.; Luftmann, H. *Acta Chem. Scand. B.* 1983, **37**, 537.
395. Mariano, P. S.; Bay, E. *J. Org. Chem.* 1980, **45**, 1763.
396. Bowry, V. W.; Ingold, K. U. *J. Am. Chem. Soc.* 1991, **113**, 5699.
397. Nechab, M.; Chavis, C.; Lucas, M.; Imbach, J.-L. *Synth. Commun.* 1992, **22**, 1115.
398. Dupuy, W. E.; Goldsmith, E. A.; Hudson, H. R. *J. Chem. Soc., Perkin Trans. 2* 1973, 74.
399. Goh, S. H.; Chan, K. C.; Chong, H. L. *Aust. J. Chem.* 1976, **29**, 1699.
400. Romero, A. G.; Darlington, W. H.; Piercey, M. F.; Lahti, R. A. *Bioorg. Med. Chem. Lett.* 1992, **2**, 1703.
401. Guerreiro, M. C.; Schuchardt, U. *Synth. Commun.* 1996, **26**, 1793.
402. Laderoute, K. R.; Harrison, A. G. *Org. Mass Spectrom.* 1985, **20**, 624.
403. Jacobs, R. T.; Bernstein, P. R.; Cronk, L. A.; Vacek, E. P.; Newcomb, L. F.; Aharony, D.; Buckner, C. K.; Kusner, E. J. *J. Med. Chem.* 1994, **37**, 1282.
404. Denis, J. M.; Le Perchec, P.; Conia, J. M. *Tetrahedron* 1977, **33**, 399.
405. Shono, T.; Nishiguchi, I. *Tetrahedron* 1974, **30**, 2173.
406. Monti, H.; Bertrand, M. *Tetrahedron* 1973, **29**, 2821.
407. Zimmerman, H. E.; Samuel, C. J. *J. Am. Chem. Soc.* 1975, **97**, 4025.
408. Arai, Y.; Shimoji, K.; Konno, M.; Konishi, Y.; Okuyama, S.; Iguchi, S.; Hayashi, M.; Miyamoto, T.; Toda, M. *J. Med. Chem.* 1983, **26**, 72.

409. Barrett, A. G. M.; Tam, W. J. *Org. Chem.* 1997, **62**, 4653.
410. Ostovic, D.; Kronja, O.; Borcic, S. *Croat. Chem. Acta* 1981, **54**, 203.
411. Tomilov, Y. V.; Smit, V. A.; Nefedov, O. M. *Izv. Akad. Nauk. SSSR, Ser. Khim.* 1978, 2744.
412. Grignon-Dubois, M.; Dunoguès, J.; Calas, R. *Synthesis* 1976, 737.
413. Grignon-Dubois, M.; Dunoguès, J.; Calas, R. *Tetrahedron Lett.* 1976, 1197.
414. Bloodworth, A. J.; Korkodilos, D. *Tetrahedron Lett.* 1991, **32**, 6953.
415. Delbaere, C. U. L.; Whitham, G. H. *J. Chem. Soc., Perkin Trans. 1* 1974, 879.
416. Gassman, P. G.; Bonser, S. M. *J. Am. Chem. Soc.* 1983, **105**, 667.
417. Gassman, P. G.; Bonser, S. M.; Mlinaric-Majerski, K. J. *J. Am. Chem. Soc.* 1989, **111**, 2652.
418. Lautens, M.; Delanghe, P. H. M. *J. Org. Chem.* 1993, **58**, 5037.
419. Corey, E. J.; Nagata, R. *Tetrahedron Lett.* 1987, **28**, 5391.
420. Baldwin, J. E.; Ullenius, C. J. *J. Am. Chem. Soc.* 1974, **96**, 1542.
421. Collins, P. W.; Gasielki, A. F.; Perkins, W. E.; Gullikson, G. W.; Jones, P. H.; Bauer, R. F. *J. Med. Chem.* 1989, **32**, 1001.
422. Ihara, M.; Taniguchi, T.; Tokunaga, Y.; Fukumoto, K. *Synthesis* 1995, 1405.
423. Touillaux, R.; Van Meerssche, M.; Dereppe, J. M.; Leroy, G.; Weiler, J.; Wilante, C. *Org. Magn. Res.* 1981, **16**, 71.
424. Wiberg, K. B.; Lupton, E. C.; Wasserman, D. J.; de Meijere, A.; Kass, S. R. *J. Am. Chem. Soc.* 1984, **106**, 1740.
425. Wiberg, K. B.; Kass, S. R. *J. Am. Chem. Soc.* 1985, **107**, 988.
426. Bubnov, Y. N.; Nesmeyanova, O. A.; Rudashevskaya, T. Y.; Mikhailov, B. M.; Kazanskii, B. A. *Zh. Org. Khim.* 1973, **43**, 127.
427. Law, K. Y.; de Mayo, P. J. *J. Am. Chem. Soc.* 1978, **101**, 325.
428. D'Auria, M. V.; Paloma, L. G.; Minale, L.; Riccio, R.; Zampella, A.; Debitus, C. *J. Nat. Prod.* 1993, **56**, 418.
429. Parziale, P. A.; Berson, J. A. *J. Am. Chem. Soc.* 1991, **113**, 4595.
430. Grignon-Dubois, M.; Calas, R.; Dunoguès, J. *Tetrahedron Lett.* 1981, **22**, 2883.
431. Yan, T.-H.; Paquette, L. A. *Tetrahedron Lett.* 1982, **23**, 3227.
432. Arai, Y.; Konno, M.; Shimoji, K.; Konishi, Y.; Niwa, H.; Toda, M.; Hayashi, M. *Chem. Pharm. Bull.* 1982, **30**, 379.
433. Arai, Y.; Toda, M.; Hayashi, M. *Adv. Prost. Thromb. Leuk.* 1983, **11**, 169.
434. Kerber, R. C.; Hsu, C.-M. *J. Am. Chem. Soc.* 1973, **95**, 3239.
435. Okazawa, N.; Sorensen, T. S. *Can. J. Chem.* 1978, **56**, 2355.

436. Whitesides, G. M.; Hackett, M.; Brainard, R. L.; Lavalleye, J.-P. P. M.; Sowinski, A. F.; Izumi, A. N.; Moore, S. S.; Brown, D. W.; Staudt, E. M. *Organometallics* 1985, **4**, 1819.
437. Mudryk, B.; Cohen, T. J. *Am. Chem. Soc.* 1993, **115**, 3855.
438. Paquette, L. A.; Wells, G. J.; Horn, K. A.; Yan, T.-H. *Tetrahedron* 1983, **39**, 913.
439. Lee-Ruff, E.; Khazanie, P. *Can. J. Chem.* 1975, **53**, 1708.
440. Wesener, J. R.; Moskau, D.; Günther, H. J. *Am. Chem. Soc.* 1985, **107**, 7307.
441. Dinnocenzo, J. P.; Zuilhof, H.; Lieberman, D. R.; Simpson, T. R.; McKechney, M. W. *J. Am. Chem. Soc.* 1997, **119**, 994.
442. Riley, P.; Hanzlik, R. P. *Tetrahedron Lett.* 1989, **30**, 3015.
443. Johnston, L. J.; Ingold, K. U. *J. Am. Chem. Soc.* 1986, **108**, 2343.
444. Dehmlow, S. S.; Dehmlow, E. V. *Liebigs Ann. Chem.* 1973, 1753.
445. Bee, L. K.; Beeby, J.; Everett, J. W.; Garratt, P. J. *J. Org. Chem.* 1975, **40**, 2212.
446. Ogawa, A.; Ohya, S.; Hirao, T. *Chem. Lett.* 1997, 275.
447. Tietze, L. F.; Raschke, T. *Liebigs Ann. Chem.* 1996, 1981.
448. Fahie, B. J.; Leigh, W. J. *Can. J. Chem.* 1989, **67**, 1859.
449. Cohen, T.; Herman, G.; Chapman, T. M.; Kuhn, D. J. *Am. Chem. Soc.* 1974, **96**, 5627.
450. Dias, J. R.; Djerassi, C. *Org. Mass. Spectrom.* 1973, **7**, 753.
451. Schlosser, M.; Fouquet, G. *Chem. Ber.* 1974, **107**, 1171.
452. Kitatani, K.; Hiyama, T.; Nozaki, H. *Bull. Chem. Soc. Jpn.* 1977, **50**, 1600.
453. Davies, A. G.; Hawari, J. A.-A.; Grignon-Dubois, M.; Pereyre, M. J. *Organomet. Chem.* 1983, **255**, 29.
454. Crist, D. R.; Jordan, G. J.; Moore, D. W.; Hashmall, J. A.; Borsetti, A. P.; Turujman, S. A. *J. Am. Chem. Soc.* 1983, **105**, 4136.
455. Al-Essa, R. J.; Puddephatt, R. J.; Quyser, M. A.; Tipper, C. F. H. *J. Am. Chem. Soc.* 1979, **101**, 364.
456. Gramatica, P.; Ranzi, B. M.; Manitto, P. *Bioorg. Chem.* 1981, **10**, 14.
457. Bhagat, S. D.; Mathur, R. K.; Siddhanta, N. N. *J. Chem. Eng. Data* 1982, **27**, 209.
458. Koch-Pomeranz, U.; Schmid, H.; Hansen, H.-J. *Helv. Chim. Acta* 1977, **60**, 768.
459. Charette, A. B.; Beauchemin, A.; Marcoux, J.-F. *Tetrahedron Lett.* 1999, **40**, 33.
460. Komatsu, K.; Takeuchi, K.; Abe, N.; Yasuda, K.; Okamoto, K. *J. Chem.*

- Soc., Perkin Trans. 2 1979, 262.
461. Perkins, M. J.; Peynircioglu, N. B. *Tetrahedron* 1985, **41**, 225.
462. Chum, P.-W.; Roth, J. A. *J. Catal.* 1975, **39**, 198.
463. Miller, V. P.; Fruetel, J. A.; Ortiz de Montellano, P. R. *Arch. Biochem. Biophys.* 1992, **298**, 697.
464. Denmark, S. E.; Christenson, B. L.; O'Connor, S. P.; Murase, N. *Pure Appl. Chem.* 1996, **68**, 23.
465. Hirabayashi, K.; Mori, A.; Hiyama, T. *Tetrahedron Lett.* 1997, **38**, 461.
466. Kim, C. U.; Misco, P. F.; Luh, B. Y. *Heterocycles* 1987, **26**, 1193.
467. Peters, J. A.; Van Bekkum, H. *Recl. Trav. Chim. Pays-Bas* 1973, **92**, 379.
468. Barrett, A. G. M.; Tam, W. *J. Org. Chem.* 1997, **62**, 7673.
469. Benedikt, G. M.; Cozens, R. J.; Goodall, B. L.; Rhodes, L. F.; Bell, M. N.; Kemball, A. C.; Starnes, W. H. *Macromolecules* 1997, **30**, 10.
470. Grignon-Dubois, M.; Pillot, J.-P.; Dunoguès, J.; Duffaut, N.; Calas, R.; Henner, B. *J. Organomet. Chem.* 1977, **124**, 135.
471. Grignon-Dubois, M.; Dunoguès, J. *J. Organomet. Chem.* 1986, **309**, 35.
472. Mazzocchi, P. H.; Lustig, R. S. *J. Am. Chem. Soc.* 1975, **97**, 3707.
473. Perkins, M. J.; Peynircioglu, N. B.; Smith, B. V. *J. Chem. Soc., Perkin Trans. 2* 1978, 1025.
474. Wessel, J.; Crabtree, R. H. *J. Mol. Catal. A* 1996, **113**, 13.
475. Sato, M.; Kitagawa, M.; Uchimarui, F.; Ueno, K.; Kojima, H.; Yamasaki, T. *Chem. Pharm. Bull.* 1979, **27**, 119.
476. WeidnerWells, M. A.; Oda, K.; Mazzocchi, P. H. *Tetrahedron* 1997, **53**, 3475.
477. Brown, H. C.; Cleveland, J. D. *J. Org. Chem.* 1976, **41**, 1792.
478. Trahanovsky, W. S.; Fox, N. S. *J. Am. Chem. Soc.* 1974, **96**, 7968.
479. De Smet, A.; Anteunis, M.; Tavernier, D. *Bull. Soc. Chim. Belg.* 1975, **84**, 67.
480. Molander, G. A.; McKie, J. A. *J. Org. Chem.* 1991, **56**, 4112.
481. Wenkert, E.; Rego de Sousa, J. *Synth. Commun.* 1977, **7**, 457.
482. Saljoughian, M.; Morimoto, H.; Williams, P. G.; DeMello, N. *J. Chem. Soc., Chem. Commun.* 1990, 1652.
483. Ruzo, L. O.; Casida, J. E.; Gammon, D. W. *Pesticide Biochem. Phys.* 1984, **21**, 84.
484. Vig, B.; Kad, G. L.; Ram, B. *J. Indian Chem. Soc.* 1973, 557.
485. Beruben, D.; Marek, I.; Normant, J. F.; Platzer, N. *J. Org. Chem.* 1995, **60**, 2488.
486. Beruben, D.; Marek, I.; Labaudiniere, L.; Normant, J. F. *Tetrahedron*

- Lett. 1993, **34**, 2303.
487. Batchelor, J. G.; Cushley, R. J.; Prestegard, J. H. *J. Org. Chem.* 1974, **39**, 1698.
488. Fitjer, L.; Scheuermann, H.-J.; Klages, U.; Wehle, D.; Stephenson, D. S.; Binsch, G. *Chem. Ber.* 1986, **119**, 1144.
489. Wilson, S. R.; Prodan, K. A. *Tetrahedron Lett.* 1976, 4231.
490. Paquette, L. A.; Horn, K. A.; Wells, G. J. *Tetrahedron Lett.* 1982, **23**, 259.
491. Mashima, K.; Sakai, N.; Takaya, H. *Bull. Chem. Soc. Jpn.* 1991, **64**, 2475.
492. Miura, K.; Oshima, K.; Utimoto, K. *Tetrahedron Lett.* 1989, **30**, 4413.
493. Miura, K.; Oshima, K.; Utimoto, K. *Bull. Chem. Soc. Jpn.* 1990, **63**, 1665.
494. Konopelski, J. P.; Djerassi, C. *J. Org. Chem.* 1980, **45**, 2297.
495. Grob, C. A.; Rich, R. *Helv. Chim. Acta* 1979, **62**, 2802.
496. Demin, P. M.; Pace-Asciak, C. R. *Tetrahedron Lett.* 1993, **34**, 4305.
497. Effenberger, F.; Kurtz, W. *Chem. Ber.* 1973, **106**, 511.
498. Ford, W. T. *J. Org. Chem.* 1973, **38**, 3614.
499. Duffault, J. M.; Hanoteau, P.; Parrilla, A.; Einhorn, J. *Synth. Commun.* 1996, **26**, 3257.
500. Hiyama, T.; Yamamoto, H.; Nishio, K.; Kitatani, K.; Nozaki, H. *Bull. Chem. Soc. Jpn.* 1979, **52**, 3632.
501. Ireland, R. E.; McKenzie, T. C.; Trust, R. I. *J. Org. Chem.* 1975, **40**, 1007.
502. Vig, O. P.; Trehan, I. R.; Kad, G. L.; Bedi, A. L. *Ind. J. Chem.* 1978, **16B**, 455.
503. Saba, J. A.; Fry, J. L. *J. Am. Chem. Soc.* 1983, **105**, 533.
504. Edwards, G. J.; Jones, S. R.; Mellor, J. M. *J. Chem. Soc., Perkin Trans. 2* 1977, 505.
505. Vig, O. P.; Kad, G. L.; Bedi, A. L.; Kumar, S. D. *Ind. J. Chem.* 1978, **16B**, 452.
506. Bajgrowicz, J. A.; Frank, I.; Frater, G.; Hennig, M. *Helv. Chim. Acta* 1998, **81**, 1349.
507. Quast, H.; Heuschmann, M. *Synthesis* 1978, 547.
508. Jason, M. E. *Tetrahedron Lett.* 1982, **23**, 1635.
509. Eisch, J. J.; Burlinson, N. E.; Boleslawski, M. *J. Organomet. Chem.* 1976, **111**, 137.
510. Waali, E. E.; Jones, W. M. *J. Am. Chem. Soc.* 1973, **95**, 8114.
511. Fukuda, Y.; Yamamoto, Y.; Kimura, K.; Odaira, Y. *Tetrahedron Lett.* 1979, 877.

512. Huang, H.; Forsyth, C. J. *J. Org. Chem.* 1995, **60**, 5746.
513. Vite, G. D.; Spencer, T. A. *J. Org. Chem.* 1988, **53**, 2560.
514. Walia, S.; Kulshrestha, S. K.; Mukerjee, S. K. *Tetrahedron* 1986, **42**, 4817.
- 514a Hollis, R.; Hugues, L.; Bowry, V. W.; Ingold, K. U. *J. Org. Chem.* 1992, **57**, 4284.
515. Casey, C. P.; Albin, L. D.; Burkhardt, T. J. *J. Am. Chem. Soc.* 1977, **99**, 2533.
516. Ho, K. W.; de Mayo, P. *J. Am. Chem. Soc.* 1979, **101**, 5725.
517. Kocor, M.; Sobotka, W.; Sterzycki, R.; Styczynska, B. *Rocz. Chem.* 1976, **50**, 1337.
518. Piers, E.; Jean, M.; Marrs, P. S. *Tetrahedron Lett.* 1986, **28**, 5075.
519. Witiak, D. T.; Allison, D. L.; Glaser, R.; Holliday, J. E.; Kamat, P. L.; Liebowitz, S. M.; Moeschberger, M. L.; Schaller, J. P. *J. Med. Chem.* 1983, **26**, 1679.
520. Newcomb, M.; Johnson, C. C.; Manek, M. B.; Varick, T. R. *J. Am. Chem. Soc.* 1992, **114**, 10915.
521. Beckhaus, H.-D.; Schoch, J.; Röchardt, C. *Chem. Ber.* 1976, **109**, 1369.
522. Okamoto, A.; Snow, M. S.; Arnold, D. R. *Tetrahedron* 1986, **42**, 6175.
523. Nelson, P. H.; Eugui, E.; Wang, C. C.; Allison, A. C. *J. Med. Chem.* 1990, **33**, 833.
524. Fleming, I.; Sanderson, P. E. J.; Terrett, N. K. *Synthesis* 1992, 69.
525. Gensler, W. J.; Prasad, R. S.; Chaudhuri, A. P.; Alam, I. *J. Org. Chem.* 1979, **44**, 3643.
526. Silvius, J. R.; McElhaney, R. N. *Chem. Phys. Lipids* 1979, **25**, 125.
527. Gaydou, E. M.; Ralaimanarivo, A.; Bianchini, J. P. *J. Agric. Food Chem.* 1993, **41**, 886.
528. McGarrity, J. T.; Armstrong, J. B. *Biochim. Biophys. Acta* 1981, **640**, 544.
529. Camps, F.; Hospital, S.; Rosell, G.; Delgado, A.; Guerrero, A. *Chem. Phys. Lipids* 1992, **61**, 157
530. Shimazaki, M.; Hara, H.; Suzuki, K. *Tetrahedron Lett.* 1989, **30**, 5447.
531. Donnelly, J. A.; Fox, M. J.; Hoey, J. G. *J. Chem. Soc., Perkin Trans. 1* 1979, 2629.
532. Farmer, L. J.; Zhi, L.; Jeong, S.; Kallel, E. A.; Croston, G.; Flatten, K. S.; Heyman, R. A.; Nadzan, A. M. *Bioorg. Med. Chem. Lett.* 1997, **7**, 2747.
533. Petrzilka, M.; Germann, A. *Mol. Cryst. Liq. Cryst.* 1986, **133**, 85.
534. Vuligonda, V.; Lin, Y.; Chandraratna, R. A. S. *Bioorg. Med. Chem. Lett.* 1996, **6**, 213.
535. Greter, J.; Lindstedt, S.; Steen, G. J. *Biol. Chem.* 1979, **254**, 2807.

536. Repic, O.; Lee, P. G.; Giger, U. *Org. Prep. Proc. Int.* 1984, **16**, 25.
537. Tipton, C. L.; Al-Shathir, N. M. *J. Biol. Chem.* 1974, **249**, 886.
538. Beach, D. H.; Holz, G. G.; Anekwe, G. E. *J. Parasitol.* 1979, **65**, 203.
539. Sakurada, K.; Iwase, H.; Takatori, T.; Nagao, M.; Nakajima, M.; Niiijima, H.; Matsuda, Y.; Kobayashi, M. *Biochim. Biophys. Acta, Mol. Cell Biol. Lipids* 1999, **1437**, 214.
540. Urbina, J.; Waugh, J. S. *Ann. N. Y. Acad. Sci.* 1973, **222**, 733.
541. Jiao, Y.; Yoshihara, T.; Ishikuri, S.; Uchino, H.; Ichihara, A. *Tetrahedron Lett.* 1996, **37**, 1039.
542. Sheads, R. E.; Beroza, M.; Paszek, E. C. *J. Agr. Food. Chem.* 1975, **23**, 60.
543. Dickens, J. C.; Oliver, J. E.; Mastro, V. C. *J. Chem. Ecol.* 1997, **23**, 2197.
544. Streitwieser, A.; Harmon, C. A. *Inorg. Chem.* 1973, **12**, 1102.
545. Berner, H.; Schneider, H.; Schulz, G.; Vyplel, H. *Monatsh. Chem.* 1986, **117**, 1073.
546. Angelaud, R.; Landais, Y.; Maignan, C. *Tetrahedron Lett.* 1995, **36**, 3861.
547. Moss, R. A.; Fujita, T.; Okumura, Y.; Hua, Z.; Mendelsohn, R.; Senak, L. *Langmuir* 1992, **8**, 1731.
548. Tamura, O.; Hashimoto, M.; Kobayashi, Y.; Katoh, T.; Nakatani, K.; Kamada, M.; Hayakawa, I.; Akiba, T.; Terashima, S. *Tetrahedron* 1994, **50**, 3889.
549. Wiering, P. G.; Steinberg, H. *Recl. Trav. Chim. Pays-Bas* 1986, **105**, 394.
550. Wiering, P. G.; Steinberg, H. *J. Org. Chem.* 1981, **46**, 1663.
551. Nakamura, E.; Kuwajima, I.; Oshino, H. *J. Am. Chem. Soc.* 1986, **108**, 3745.
552. Imamoto, T.; Kamiya, Y.; Hatajima, T.; Takahashi, H. *Tetrahedron Lett.* 1989, **30**, 5149.
553. Rousseau, G.; Slougui, N. *Tetrahedron Lett.* 1983, **24**, 1251.
554. Awan, I. A.; Flowers, M. C. *J. Chem. Soc., Faraday Trans. 1* 1985, **81**, 1415.
555. Girard, C.; Amice, P.; Barnier, J.-P.; Conia, J. M. *Tetrahedron Lett.* 1974, 3329.
556. Barnier, J. P.; Garnier, B.; Girard, C.; Denis, J. M.; Salaün, J.; Conia, J. M. *Tetrahedron Lett.* 1973, 1747.
557. Breitbeil, F. W.; Schranz, J. L. *J. Org. Chem.* 1979, **44**, 4649.
558. Weber, W.; de Meijere, A. *Synth. Commun.* 1986, **16**, 837.
559. Fitjer, L.; Conia, J.-M. *Angew. Chem.* 1973, **85**, 347.

560. Schmidt, A. H.; Schirmer, U.; Conia, J.-M. Chem. Ber. 1976, **109**, 2588.
561. Fitjer, L.; Conia, J.-M. Angew. Chem., Int. Ed. Engl. 1973, **12**, 332.
562. Kirmse, W.; Rode, J.; Rode, K. Chem. Ber. 1986, **119**, 3672.
563. Cunico, R. F.; Kuan, C. P. J. Org. Chem. 1985, **50**, 5410.
564. Kirmse, W.; Rode, K. Chem. Ber. 1987, **120**, 839.
565. Ryu, I.; Murai, S.; Otani, S.; Sonoda, N. Tetrahedron Lett. 1977, 1995.
566. Brown, P.; Calvert, S. H.; Chapman, P. C. A.; Cosham, S. C.; Eglinton, A. J.; Elliot, R. L.; Harris, M. A.; Hinks, J. D.; Lowther, J.; Merrikin, D. J.; Pearson, M. J.; Ponsford, R. J.; Syms, J. V. J. Chem. Soc., Perkin Trans. 1 1991, 881.
567. Zefirov, N. S.; Kozhushkov, S. I.; Kuznetsova, T. S. Zh. Org. Khim. 1988, **24**, 447.
568. Kiwus, R.; Schwarz, W.; Roxnagel, I.; Musso, H. Chem. Ber. 1987, **120**, 435.
569. Wiering, P. G.; Steinberg, H. Recl. Trav. Chim. Pays-Bas 1985, **104**, 70
570. Tokoroyama, T.; Fukuyama, Y.; Kubota, T.; Yokotani, K. J. Chem. Soc., Perkin Trans. 1 1981, 1557.
571. Van der Vecht, J. R.; Steinberg, H.; de Boer, Th. J. Recl. Trav. Chim. Pays-Bas 1976, **95**, 149.
572. Rychnovsky, S. D.; Kim, J. Tetrahedron Lett. 1991, **32**, 7219.
573. Iwasawa, N.; Matsuo, T.; Iwamoto, M.; Ikeno, T. J. Am. Chem. Soc. 1998, **120**, 3903.
574. Prakash, G. K. S.; Buchholz, H.; Reddy, V. P.; de Meijere, A.; Olah, G. A. J. Am. Chem. Soc. 1992, **114**, 1097.
575. Gilbert, J. C.; Pinto, M. J. Org. Chem. 1992, **57**, 5271.
576. Lindberg, P.; Bergman, R.; Wickberg, B. J. Chem. Soc., Perkin Trans. 1 1977, 684.
577. Biggs, T. N.; Swenton, J. S. J. Org. Chem. 1992, **57**, 5568.
578. Gadwood, R. C.; Rubino, M. R.; Nagarajan, S. C.; Michel, S. T. J. Org. Chem. 1985, **50**, 3255.
579. Williams, T. M.; Ciccarone, T. M.; MacTough, S. C.; Bock, R. L.; Conner, M. W.; Davide, J. P.; Hamilton, K.; Koblan, K. S.; Kohl, N. E.; Kral, A. M.; Mosser, S. D.; Omer, C. A.; Pompliano, D. L.; Rands, E.; Schaber, M. D.; Shah, D.; Wilson, F. R.; Gibbs, J. B.; Graham, S. L.; Hartman, G. D.; Oliff, A. I.; Smith, R. L. J. Med. Chem. 1996, **39**, 1345.
580. Hemmersbach, P.; Klessinger, M. Tetrahedron 1980, **36**, 1337.
581. Russo, J. M.; Price, W. A. J. Org. Chem. 1993, **58**, 3589.
582. Bruckmann, P.; Klessinger, M. Chem. Ber. 1974, **107**, 1108.
583. Gaudino, J. J.; Wilcox, C. S. J. Am. Chem. Soc. 1990, **112**, 4374.

584. Beckhaus, H.-D.; Rüdhardt, C.; Kozhushkov, S. I.; Belov, V. N.; Verevkin, S. P.; de Meijere, A. J. *Am. Chem. Soc.* 1995, **117**, 11854.
585. Roberts, C.; Walton, J. C. *J. Chem. Soc., Perkin Trans. 2* 1985, 841.
586. Ronald, R. C.; Ruder, S. M.; Lillie, T. S. *Tetrahedron Lett.* 1987, **28**, 131.
587. Shibata, T.; Tsuji, T.; Nishida, S. *Bull. Chem. Soc. Jpn.* 1980, **53**, 709.
588. Fitjer, L.; Conia, J.-M. *Angew. Chem.* 1973, **85**, 832.
589. Fitjer, L.; Conia, J.-M. *Angew. Chem., Int. Ed. Engl.* 1973, **12**, 761.
590. Tsuji, T.; Nishida, S. *Chem. Lett.* 1977, 631.
591. Bowry, V. W.; Luszyk, J.; Ingold, K. U. *J. Am. Chem. Soc.* 1991, **113**, 5687.
592. Asmus, P.; Klessinger, M. *Liebigs Ann. Chem.* 1975, 2169.
593. Tsuji, T.; Shibata, T.; Hienuki, Y.; Nishida, S. *J. Am. Chem. Soc.* 1978, **100**, 1806.
594. Adam, W.; Crämer, E.; Peters, E.-M.; Peters, K.; von Schnering, H. G. *Chem. Ber.* 1987, **120**, 705.
595. Gream, G. E.; Pincombe, C. F. *Aust. J. Chem.* 1974, **27**, 543.
596. Piers, E.; Karunaratne, V. *Can. J. Chem.* 1989, **67**, 160.
597. Leonard, J.; Bennett, L.; Mahmood, A. *Tetrahedron Lett.* 1999, **40**, 3965.
598. Reddy, V. P.; Olah, G. A.; Prakash, G. K. S. *J. Org. Chem.* 1993, **58**, 7622.
599. Franck-Neumann, M.; Miesch, M.; Barth, F. *Tetrahedron Lett.* 1989, **30**, 3537.
600. Franck-Neumann, M.; Miesch, M.; Barth, F. *Tetrahedron* 1993, **49**, 1409.
601. Roth, W. R.; Unger, C. *Liebigs Ann. Chem.* 1995, 1361.
602. De Meijere, A.; Wenck, H.; Kopf, J. *Tetrahedron* 1988, **44**, 2427.
603. Piers, E.; Karunaratne, V. *Can. J. Chem.* 1984, **62**, 629.
604. Piers, E.; Karunaratne, V. *Tetrahedron* 1989, **45**, 1089.
605. Ciardelli, T.; Seeliger, A.; Stewart, C. J.; Wieland, T. *Liebigs Ann. Chem.* 1981, 828.
606. Fitjer, L.; Rissom, B.; Kanschik, A.; Egert, E. *Tetrahedron* 1994, **50**, 10879.
607. Piers, E.; Marais, P. C. *Tetrahedron Lett.* 1988, **29**, 4053.
608. Hasegawa, T.; Niwa, H.; Yamada, K. *Chem. Lett.* 1985, 1385.
609. De Meijere, A.; Michelsen, K.; Gleiter, R.; Spanget-Larsen, J. *Isr. J. Chem.* 1989, **29**, 153.
610. Gais, H.-J.; Bülow, G.; Raabe, G. *J. Am. Chem. Soc.* 1993, **115**, 7215.
611. Herrmann, E.; Gais, H. J.; Rosenstock, B.; Raabe, G.; Lindner, H. J. *Eur. J. Org. Chem.* 1998, 27.

612. Proksch, E.; de Meijere, A. *Tetrahedron Lett.* 1976, 4851.
613. Oppolzer, W.; Godel, T. *J. Am. Chem. Soc.* 1978, **100**, 2583.
614. Oppolzer, W.; Godel, T. *Helv. Chim. Acta* 1984, **67**, 1154.
615. Suginome, H.; Nakayama, Y. *Tetrahedron* 1994, **50**, 7771.
616. Toyota, M.; Nishikawa, Y.; Motoki, K.; Yoshida, N.; Fukumoto, K. *Tetrahedron Lett.* 1993, **34**, 6099
617. Toyota, M.; Nishikawa, Y.; Motoki, K.; Yoshida, N.; Fukumoto, K. *Tetrahedron* 1993, **49**, 11189.
618. Mehta, G.; Murthy, A. N.; Reddy, D. S.; Reddy, A. V. *J. Am. Chem. Soc.* 1986, **108**, 3443.
619. Smith, A. B.; Wexler, B. A.; Tu, C.-Y.; Konopelski, J. P. *J. Am. Chem. Soc.* 1985, **107**, 1308.
620. Pak, H.; Canalda, I. I.; Fraser-Reid, B. *J. Org. Chem.* 1990, **55**, 3009.
621. Yamada, K.; Kyotani, Y.; Manabe, S.; Suzuki, M. *Tetrahedron* 1979, **35**, 293.
622. Trost, B. M.; Hiemstra, H. *J. Am. Chem. Soc.* 1982, **104**, 886.
623. Baker, R.; Keen, R. B. *J. Organomet. Chem.* 1985, **285**, 419.
624. Archer, M.; Casanova, J.; Zahra, J.-P.; Waegell, B. *J. Chim. Phys. Phys. Chim. Biol.* 1982, **79**, 227.
625. Casanova, J.; Waegell, B. *Bull. Soc. Chim. Fr.* 1975, 598.
626. Tori, M.; Miyake, T.; Hamaguchi, T.; Sono, M. *Tetrahedron Asymmetry* 1997, **8**, 2731.
627. Inouye, Y.; Inomata, S.; Ishihara, Y.; Kakisawa, H. *Bull. Chem. Soc. Jpn.* 1982, **55**, 208.
628. Jasperse, C. P.; Curran, D. P. *J. Am. Chem. Soc.* 1990, **112**, 5601.
629. Horton, M.; Pattenden, G. *Tetrahedron Lett.* 1983, **24**, 2125.
630. Kuo, D. L.; Money, T. *J. Chem. Soc., Chem. Commun.* 1986, 1691.
631. Kuo, D. L.; Money, T. *Can. J. Chem.* 1988, **66**, 1794.
632. Horton, M.; Pattenden, G. *J. Chem. Soc., Perkin Trans. 1* 1984, 811.
633. Raveendranath, P. C.; Newcomb, L. F.; Ray, N. C.; Clark, D. S.; Spencer, T. A. *Synth. Commun.* 1990, **20**, 2723.
634. Fitjer, L.; Scheuermann, H.-J.; Wehle, D. *Tetrahedron Lett.* 1984, **25**, 2329.
635. Wehle, D.; Scheuermann, H.-J.; Fitjer, L. *Chem. Ber.* 1986, **119**, 3127.
636. Roush, W. R.; Russo-Rodriguez, S. *J. Org. Chem.* 1987, **52**, 603.
637. Trost, B. M.; Curran, D. P. *J. Am. Chem. Soc.* 1981, **103**, 7380.
638. Piers, E.; Marais, P. C. *J. Chem. Soc., Chem. Commun.* 1989, 1222.
639. Lasne, M.-C.; Ripoll, J.-L. *Bull. Soc. Chim. Fr.* 1981, 340.
640. Rosenfeld, S.; Tingle, C. W.; Jasinski, J. P.; Whittum, J. E.;

- Woudenberg, R. C.; Van Epp, J. J. *Am. Chem. Soc.* 1994, **116**, 12049.
641. Hamann, L. G.; Farmer, L. J.; Johnson, M. G.; Bender, S. L.; Mais, D. E.; Wang, M.-W.; Crombie, D.; Goldman, M. E.; Jones, T. K. *J. Med. Chem.* 1996, **39**, 1778
642. Burnell, R. H.; Dumont, N.; Théberge, N.; Desfossés, S. *Synth. Commun.* 1992, **22**, 2571.
643. Fitjer, L. *Angew. Chem., Int. Ed. Engl.* 1976, **15**, 763.
644. Fitjer, L.; Kühn, W.; Klages, U.; Egert, E.; Clegg, W.; Schormann, N.; Sheldrick, G. M. *Chem. Ber.* 1984, **117**, 3075.
645. Fitjer, L.; Klages, U.; Kühn, W.; Stephenson, D. S.; Binsch, G.; Noltemeyer, M.; Egert, E.; Sheldrick, G. M. *Tetrahedron* 1984, **40**, 4337.
646. Burnell, R. H.; Côté, C.; Théberge, N. *J. Nat. Prod.* 1993, **56**, 1459.
647. Fitjer, L.; Giersig, M.; Wehle, D.; Dittmer, M.; Koltermann, G.-W.; Schormann, N.; Egert, E. *Tetrahedron* 1988, **44**, 393.
648. Mataka, S.; Taniguchi, M.; Mitroma, Y.; Sawada, T.; Tashiro, M. *J. Chem. Res. (S)* 1997, 48.
649. Mander, L. N.; Sherburn, M.; Camp, D.; King, R. W.; Evans, L. T.; Pharis, R. P. *Phytochemistry* 1998, **49**, 2195.
650. Desai, U. R.; Trivedi, G. K. *Liebigs Ann. Chem.* 1990, 711.
651. Wulf, K.; Klages, U.; Rissom, B.; Fitjer, L. *Tetrahedron* 1997, **53**, 6011.
652. Schröer, W.-D.; Friedrichsen, W. *Liebigs Ann. Chem.* 1978, 1648.
653. Barrett, A. G. M.; Doubleday, W. W.; Kasdorf, K.; Tustin, G. J.; White, A. J. P.; Williams, D. J. *J. Chem. Soc., Chem. Commun.* 1995, 407.
654. Barrett, A. G. M.; Doubleday, W. W.; Tustin, G. J. *Tetrahedron* 1996, **52**, 15325
655. Barrett, A. G. M.; Kasdorf, K. *J. Chem. Soc., Chem. Commun.* 1996, 325.
656. Paquette, L. A.; Detty, M. R. *J. Am. Chem. Soc.* 1977, **99**, 828.
657. Onoda, T.; Shirai, R.; Kawai, N.; Iwasaki, S. *Tetrahedron* 1996, **52**, 13327.
658. Paquette, L. A.; Detty, M. R. *J. Am. Chem. Soc.* 1977, **99**, 834.
659. Markarian, G.; Ragonnet, B.; Santelli, M.; Bertrand, M. *Bull. Soc. Chim. Fr.* 1975, 1407.
660. Cossy, J.; Blanchard, N.; Meyer, C. *Synthesis* 1999, 1063.
661. McDonald, W. S.; Verbicky, C. A.; Zercher, C. K. *J. Org. Chem.* 1997, **62**, 1215.
662. Barrett, A. G. M.; Hamprecht, D.; White, A. J. P.; Williams, D. J. *J. Am. Chem. Soc.* 1997, **119**, 8608.
663. Barrett, A. G. M.; Gross, T.; Hamprecht, D.; Ohkubo, M.; White, A. J. P.; Williams, D. J. *Synthesis* 1998, 490.

664. Johnson, C. R.; Barbachyn, M. R.; Meanwell, N. A.; Stark, C. J.; Zeller, J. R. *Phosphorus Sulfur* 1985, **24**, 531.
665. Dawson, B. A.; Ghosh, A. K.; Jurlina, J. L.; Ragauskas, A. J.; Stothers, J. B. *Can. J. Chem.* 1984, **62**, 2521.
666. Molchanov, A. P.; Kostikov, R. R.; Chernyshev, V. A. *Zh. Org. Khim.* 1991, **27**, 1648.
667. Cox, O.; Rivera, L. A. *Synth. Commun.* 1978, **8**, 261.
668. Dehmlow, E. V.; Gröning, C. *Tetrahedron* 1992, **48**, 111.
669. Iwasawa, N.; Funahashi, M.; Narasaka, K. *Chem. Lett.* 1994, 1697.
670. Asaoka, M.; Takenouchi, K.; Takei, H. *Chem. Lett.* 1988, 921.
671. Batey, R. A.; Harling, J. D.; Motherwell, W. B. *Tetrahedron* 1992, **48**, 8031.
672. Molander, G. A.; Alonso-Alija, C. *Tetrahedron* 1997, **53**, 8067.
673. Molchanov, A. P.; Kostikov, R. R. *Zh. Org. Khim.* 1993, **29**, 148.
674. Iwasawa, N.; Funahashi, M.; Hayakawa, S.; Ikeno, T.; Narasaka, K. *Bull. Chem. Soc. Jpn.* 1999, **72**, 85.
675. Barrett, A. G. M.; Doubleday, W. W.; Hamprecht, D.; Kasdorf, K.; Tustin, G. J.; White, A. J. P.; Williams, D. J. *J. Chem. Soc., Chem. Commun.* 1997, 1693.
676. Hirai, G.; Oguri, H.; Hirama, M. *Chem. Lett.* 1999, 141.
677. Corey, E. J.; Balanson, R. D. *Tetrahedron Lett.* 1973, 3153.
678. Charette, A. B.; Juteau, H. *Tetrahedron* 1997, **53**, 16277.
679. Marshall, J. A.; Ellison, R. H. *J. Am. Chem. Soc.* 1976, **98**, 4312.
680. Kotani, E.; Miyazaki, F.; Tobinaga, S. *J. Chem. Soc., Chem. Commun.* 1974, 300.
681. Jarstfer, M. B.; Blagg, B. S. J.; Rogers, D. H.; Poulter, C. D. *J. Am. Chem. Soc.* 1996, **118**, 13089.
682. Künzer, H.; Thiel, M. *Tetrahedron Lett.* 1994, **35**, 2329.
683. Siemann, H.-J.; Droescher, P.; Undeutsch, B.; Schwarz, S. *Steroids* 1995, **60**, 308.
684. Morihira, K.; Hara, R.; Kawahara, S.; Nishimori, T.; Nakamura, N.; Kusama, H.; Kuwajima, I. *J. Am. Chem. Soc.* 1998, **120**, 12980.
685. Dawson, M. I.; Vasser, M. J. *Org. Chem.* 1977, **42**, 2783.
686. Orr, J. C.; Templeton, J. F.; Majgier-Baranowska, H.; Marat, K. J. *Chem. Soc., Perkin Trans. 1* 1994, 2667.
687. Wiechert, R.; Bittler, D.; Hoyer, G.-A. *Experientia* 1974, **30**, 15.
688. Kohout, L.; Sanda, V.; Fajkos, J. *Collect. Czech. Chem. Commun.* 1982, **47**, 1503.
689. Wiechert, R.; Bittler, D.; Hoyer, G.-A. *Chem. Ber.* 1973, **106**, 888.

690. Lenz, G. R.; Schulz, J. A. *J. Org. Chem.* 1978, **43**, 2334.
691. Albrecht, H. P. *Liebigs Ann. Chem.* 1980, 886.
692. Aranda, G.; Fetizon, M.; Tayeb, N.; Guilhem, J.; Pascard, C. *Tetrahedron* 1986, **42**, 329.
693. Kuo, C. H.; Patchett, A. A.; Wendler, N. L. *J. Org. Chem.* 1983, **48**, 1991.
694. Zhou, Q.; Weber, W. P. *Polym. Bull.* 1989, **21**, 173.
695. Matsumoto, K.; Miyagawa, K.; Yamaoka, H. *Macromolecules* 1997, **30**, 2524.
696. Liao, X.; Lee, H. S. J.; Weber, W. P. *Makromol. Chem.* 1990, **191**, 2173.
697. Hummel, K.; Martl, M. G.; Chemelli, R.; Griexer, H.; Wukovnig, S.; Zekoll, H. *Makromol. Chem.* 1984, **185**, 2489.
698. Masamune, S.; Sakai, M.; Kemp-Jones, A. V.; Nakashima, T. *Can. J. Chem.* 1974, **52**, 855.
699. Friedrich, E. C.; Saleh, M. A. *J. Am. Chem. Soc.* 1973, **95**, 2617.
700. Friedrich, E. C.; Biresaw, G.; Saleh, M. A. *J. Org. Chem.* 1983, **48**, 1435.
- 700a Olah, G. A.; Prakash, G. K. S.; Rawdah, T. N. *J. Org. Chem.* 1980, **45**, 965.
701. Kropp, P. J.; Pienta, N. J.; Sawyer, J. A.; Polniaszek, R. P. *Tetrahedron* 1981, **37**, 3229.
702. Maryanoff, B. E.; Costanzo, M. J.; Nortey, S. O.; Greco, M. N.; Shank, R. P.; Schupsky, J. J.; Ortegon, M. P.; Vaught, J. L. *J. Med. Chem.* 1998, **41**, 1315.
703. Cossy, J.; Furet, N.; BouzBouz, S. *Tetrahedron* 1995, **51**, 11751.
704. Rodriguez, J. B.; Marquez, V. E.; Nicklaus, M. C.; Barchi, J. J. *Tetrahedron Lett.* 1993, **34**, 6233.
705. Rodriguez, J. B.; Marquez, V. E.; Nicklaus, M. C.; Mitsuya, H.; Barchi, J. J. *J. Med. Chem.* 1994, **37**, 3389.
706. Friedrich, E. C.; Delucca, G. *J. Org. Chem.* 1983, **48**, 4563.
707. Lightner, D. A.; Pak, C. S.; Crist, B. V.; Rodgers, S. L.; Givens, J. W. *Tetrahedron* 1985, **41**, 4321.
708. Friedrich, E. C.; Jassawalla, J. D. *C. J. Org. Chem.* 1979, **44**, 4224.
709. Steinmetz, M. G.; Chen, Q.; Zheng, Y. *J. Organomet. Chem.* 1996, **516**, 25.
710. Barnier, J. P.; Rayssac, V.; Morisson, V.; Blanco, L. *Tetrahedron Lett.* 1997, **38**, 8503.
711. Barnier, J. P.; Morisson, V.; Volle, I.; Blanco, L. *Tetrahedron: Asymmetry* 1999, **10**, 1107.
712. Kirmse, W.; Hartmann, M.; Siegfried, R.; Wroblowsky, H. J.; Zang, B.; Zellmer, V. *Chem. Ber.* 1981, **114**, 1793.

713. Fraser-Reid, B.; Holder, N. L.; Hicks, D. R.; Walker, D. L. *Can. J. Chem.* 1977, **55**, 3978.
714. Clive, D. L. J.; Daigneault, S. J. *Chem. Soc., Chem. Commun.* 1989, 332.
715. Clive, D. L. J.; Daigneault, S. J. *Org. Chem.* 1991, **56**, 3801.
716. Demaison, C.; Hourieux, C.; Roingard, P.; Agrofoglio, L. A. *Tetrahedron Lett.* 1998, **39**, 9175.
717. Agrofoglio, L. A.; Demaison, C.; Toupet, L. *Tetrahedron* 1999, **55**, 8075.
718. Tardella, P. A.; Pellacani, L. *Gazz. Chim. Ital.* 1977, **107**, 107.
719. Chenier, P. J.; Kiland, P. J.; Schmitt, G. D.; VanderWegen, P. G. *J. Org. Chem.* 1980, **45**, 5413.
720. House, H. O.; Snoble, K. A. *J. Org. Chem.* 1976, **41**, 3076.
721. Lee, P. H.; Lee, J. Y. *Tetrahedron Lett.* 1998, **39**, 7889.
722. Ronald, R. C.; Lillie, T. S. *Tetrahedron Lett.* 1986, **27**, 5787.
723. Mash, E. A.; Gregg, T. M.; Kaczynski, M. A. *J. Org. Chem.* 1996, **61**, 2743.
724. Prinzbach, H.; Hunkler, D.; Schal, H.-P.; Fritz, H. *Angew. Chem., Int. Ed. Engl.* 1980, **19**, 567.
725. Casey, C. P.; Cesa, M. C. *J. Am. Chem. Soc.* 1979, **101**, 4236.
726. Cossy, J.; BouzBouz, S.; Mouza, C. *Synlett* 1998, 621.
727. Traas, P. C.; Boelens, H.; Takken, H. J. *Recl. Trav. Chim. Pays-Bas* 1976, **95**, 57.
728. Monti, S. A.; McAninch, T. W. *Tetrahedron Lett.* 1974, 3239.
729. Terunuma, D.; Shibuya, N.; Nohira, H. *Bull. Chem. Soc. Jpn.* 1982, **55**, 2287.
730. Detert, H.; Meier, H. *Liebigs Ann. Chem.* 1997, 1557.
731. Wertheimer, V.; Glatz, A. M.; Razus, A. C. *Rev. Roum. Chim.* 1977, **22**, 11.
732. Banwell, M. G. *Aust. J. Chem.* 1988, **41**, 1037.
733. Thies, R. W.; McRitchie, D. D. *J. Org. Chem.* 1973, **38**, 112.
734. Hatem, J.; Waegell, B. *Tetrahedron* 1990, **46**, 2789.
735. El Gaied, M. M.; Bessière-Chrétien, Y. *Bull. Soc. Chim. Fr.* 1973, 1351.
736. Cossy, J.; BouzBouz, S. *Tetrahedron Lett.* 1997, **38**, 1931.
737. Kabat, M.; Kiegiel, J.; Cohen, N.; Toth, K.; Wovkulich, P. M.; Uskokovic, M. R. *Tetrahedron Lett.* 1991, **32**, 2343.
738. Kabat, M. M.; Kiegiel, J.; Cohen, N.; Toth, K.; Wovkulich, P. M.; Uskokovic, M. R. *J. Org. Chem.* 1996, **61**, 118.
739. Tori, M.; Hamaguchi, T.; Aoki, M.; Sono, M.; Asakawa, Y. *Can. J. Chem.* 1997, **75**, 634.

740. Chiche, L.; Christol, H.; Coste, J.; Plenat, F. *Can. J. Chem.* 1981, **59**, 2373.
741. Smith, III, A. B.; Wood, J. L.; Keenan, T. P.; Liverton, N.; Visnick, M. J. *Org. Chem.* 1994, **59**, 6652.
742. Banwell, M. G.; Ryan, J. H.; Winkler, D. A. *Aust. J. Chem.* 1991, **44**, 593.
743. Paquette, L. A.; Wang, T. Z.; Pinard, E. J. *Am. Chem. Soc.* 1995, **117**, 1455
744. Paquette, L. A.; Ezquerra, J.; He, W. J. *Org. Chem.* 1995, **60**, 1435.
745. Ezquerra, J.; Wei, H.; Paquette, L. A. *Tetrahedron Lett.* 1990, **31**, 6979.
746. Grieco, P. A.; Oguri, T.; Gilman, S.; DeTitta, G. T. *J. Am. Chem. Soc.* 1978, **100**, 1616.
747. Grieco, P. A.; Oguri, T.; Wang, C.-L. J.; Williams, E. J. *Org. Chem.* 1977, **42**, 4113.
748. Grieco, P. A.; Collins, J. L.; Moher, E. D.; Fleck, T. J.; Gross, R. S. J. *Am. Chem. Soc.* 1993, **115**, 6078.
749. Marshall, J. A.; Ruth, J. A. *J. Org. Chem.* 1974, **39**, 1971.
750. Moss, R. A.; Chen, E. Y. *J. Org. Chem.* 1981, **46**, 1466.
751. Ando, M.; Sayama, S.; Takase, K. *Chem. Lett.* 1981, 377.
752. Ando, M.; Sayama, S.; Takase, K. *J. Org. Chem.* 1985, **50**, 251.
753. Asaoka, M.; Kobayashi, K.; Takei, H. *Bull. Chem. Soc. Jpn.* 1994, **67**, 1141.
754. Cristol, S. J.; Ilenda, C. S. *J. Am. Chem. Soc.* 1975, **97**, 5862.
755. Kelly, D. P.; Leslie, D. R.; Smith, B. D. *J. Am. Chem. Soc.* 1984, **106**, 687.
756. Yamada, S.; Nagashima, S.; Takaoka, Y.; Torihara, S.; Tanaka, M.; Suemune, H.; Aso, M. *J. Chem. Soc., Perkin Trans. 1* 1998, 1269.
757. Smith, III, A. B.; Hartz, R. A.; Spoons, P. G.; Rainier, J. D. *Isr. J. Chem.* 1997, **37**, 69.
758. Marshall, J. A.; Conrow, R. E. *J. Am. Chem. Soc.* 1980, **102**, 4274.
759. Paquette, L. A.; Bellamy, F.; Wells, G. J.; Böhm, M. C.; Gleiter, R. *J. Am. Chem. Soc.* 1981, **103**, 7122.
760. Hunadi, R. J.; Helmkamp, G. K. *J. Org. Chem.* 1978, **43**, 1586.
761. Deyrup, J. A.; Betkouski, M. F. *J. Org. Chem.* 1975, **40**, 284.
762. Ando, M.; Sayama, S.; Takase, K. *Chem. Lett.* 1979, 191.
763. Packer, R. A.; Whitehurst, J. S. *J. Chem. Soc., Chem. Commun.* 1975, 757.
764. Packer, R. A.; Whitehurst, J. S. *J. Chem. Soc., Perkin Trans. 1* 1978, 110.
765. Feutrill, G. I.; Mirrington, R. N.; Nichols, R. J. *Aust. J. Chem.* 1973, **26**,

- 345.
766. Mandelt, K.; Fitjer, L. *Synthesis* 1998, 1523.
767. Casares, A.; Maldonado, L. A. *Synth. Commun.* 1976, **6**, 11.
768. Caine, D.; Chen, P.-C.; Frobese, A. S.; Gupton, J. T. *J. Org. Chem.* 1979, **44**, 4981.
769. Fan, W. M.; White, J. B. *J. Org. Chem.* 1993, **58**, 3557.
770. Harling, J. D.; Motherwell, W. B. *J. Chem. Soc., Chem. Commun.* 1988, 1380.
771. Raepfel, F.; Weibel, J.-M.; Heissler, D. *Tetrahedron Lett.* 1999, **40**, 6377.
772. Paquette, L. A.; Friedrich, D.; Rogers, R. D. *J. Org. Chem.* 1991, **56**, 3841.
773. Joska, J.; Fajkos, J. *Coll. Czech. Chem. Commun.* 1977, **42**, 1044.
774. Weibel, J. M.; Heissler, D. *Tetrahedron Lett.* 1994, **35**, 473.
775. Wagner, H.; Römer, J.; Kasch, H. J. *Labeled Comp. Radiopharm.* 1981, **18**, 1611.
776. Prousa, R.; Schönecker, B.; Tresselt, D.; Ponsold, K. *J. Prakt. Chem.* 1986, **328**, 55.
777. Kasal, A.; Kohout, L. *Collect. Czech. Chem. Commun.* 1982, **47**, 130.
778. Neef, G.; Cleve, G.; Ottow, E.; Seeger, A.; Wiechert, R. *J. Org. Chem.* 1987, **52**, 4143.
779. Han, M. C.; Zorumski, C. F.; Covey, D. F. *J. Med. Chem.* 1996, **39**, 4218.
780. Tochtermann, W.; Stubenrauch, G.; Reiff, K.; Schumacher, U. *Chem. Ber.* 1974, **107**, 3340.
781. Kohout, L.; Fajkos, J. *Collect. Czech. Chem. Commun.* 1973, **38**, 1415.
782. Joska, J.; Fajkos, J. *Collect. Czech. Chem. Commun.* 1982, **47**, 2423.
783. Fajkos, J.; Joska, J. *Collect. Czech. Chem. Commun.* 1989, **54**, 751.
784. Kohout, L.; Kasal, A. *Collect. Czech. Chem. Commun.* 1994, **59**, 649.
785. Piers, E.; Boulet, S. L. *Tetrahedron Lett.* 1997, **38**, 8815.
786. Lefebvre, Y.; Marshall, D. J.; Revesz, C. J. *J. Med. Chem.* 1975, **18**, 220.
787. Bittler, D.; Hofmeister, H.; Laurent, H.; Nickisch, K.; Nickolson, R.; Petzoldt, K.; Wiechert, R. *Angew. Chem.* 1982, **94**, 718.
788. Ziegler, F. E.; Wang, T.-F. *J. Am. Chem. Soc.* 1984, **106**, 718.
789. Joska, J.; Fajkos, J. *Collect. Czech. Chem. Commun.* 1981, **46**, 2751.
790. Templeton, J. F.; Kim, R.-S. *S. Steroids* 1976, **27**, 581.
791. Mironowicz, A.; Kohout, L.; Fajkos, J. *Collect. Czech. Chem. Commun.* 1974, **39**, 1780.

792. Wieland, P. *Helv. Chim. Acta* 1979, **62**, 2276.
793. Corey, E. J.; Hahl, R. W. *Tetrahedron Lett.* 1989, **30**, 3023.
794. Kohout, L.; Kasal, A. *Collect. Czech. Chem. Commun.* 1983, **48**, 2051.
- 794a Joska, J.; Fajkos, J.; Budesinsky, M. *Collect. Czech. Chem. Commun.* 1974, **39**, 1914.
795. Templeton, J. F.; Wie, C. W. *Can. J. Chem.* 1974, **52**, 517.
796. Kohout, L.; Fajkos, J. *Collect. Czech. Chem. Commun.* 1975, **40**, 3924.
797. Kohout, L.; Fajkos, J. *Collect. Czech. Chem. Commun.* 1979, **44**, 3308.
798. Joska, J.; Fajkos, J. *Collect. Czech. Chem. Commun.* 1980, **45**, 1850.
799. Kohout, L. *Collect. Czech. Chem. Commun.* 1986, **51**, 429.
800. Fajkos, J.; Joska, J. *Collect. Czech. Chem. Commun.* 1979, **44**, 251.
801. Kohout, L. *Collect. Czech. Chem. Commun.* 1981, **46**, 1828.
802. Kohout, L.; Fajkos, J. *Collect. Czech. Chem. Commun.* 1974, **39**, 1601.
803. Ishiguro, M.; Saito, H.; Ikekawa, N. *J. Chem. Soc., Perkin Trans. 1* 1980, 2507.
804. Schalley, C. A.; Schroder, D.; Schwarz, H. *J. Am. Chem. Soc.* 1994, **116**, 11089.
805. Zhao, Y.; Yang, T.-F.; Lee, M.; Chun, B. K.; Du, J.; Schinazi, R. F.; Lee, D.; Newton, M. G.; Chu, C. K. *Tetrahedron Lett.* 1994, **35**, 5405.
806. Shimamoto, K.; Ishida, M.; Shinozaki, H.; Ohfune, Y. *J. Org. Chem.* 1991, **56**, 4167.
807. Bellamy, A. J.; Campbell, E. A.; Hall, I. R. *J. Chem. Soc., Perkin Trans. 2* 1974, 1347.
808. Rocquet, F.; Sevin, A. *Bull. Soc. Chim. Fr.* 1974, 888.
809. Cossy, J.; Blanchard, N.; Meyer, C. *J. Org. Chem.* 1998, **63**, 5728.
810. Ojima, I.; Lin, S. *J. Org. Chem.* 1998, **63**, 224.
811. Zlokazov, M. V.; Veselovsky, V. V. *Mendeleev Commun.* 1999, 73.
812. Mitome, H.; Miyaoka, H.; Nakano, M.; Yamada, Y. *Tetrahedron Lett.* 1995, **36**, 8231.
813. Gurjar, M. K.; Kumar, P.; Rao, B. V. *Tetrahedron Lett.* 1996, **37**, 8617.
814. Gurjar, M. K.; Sharma, B.; Rao, B. V. *J. Carbohydr. Chem.* 1998, **17**, 1107.
815. Landais, Y.; Parra-Rapado, L. *Tetrahedron Lett.* 1996, **37**, 1209.
816. Coxon, G. D.; Knobl, S.; Roberts, E.; Baird, M. S.; Al Dulayymi, J. R.; Besra, G. S.; Brennan, P. J.; Minnikin, D. E. *Tetrahedron Lett.* 1999, **40**, 6689.
817. Wilson, S. R.; Davey, A. E.; Guazzaroni, M. E. *J. Org. Chem.* 1992, **57**, 2007.
818. Sele, A.; Baehler, B.; Tronchet, J. M. *J. Helv. Chim. Acta* 1979, **62**, 866.

819. Theberge, C. R.; Verbicky, C. A.; Zercher, C. K. *J. Org. Chem.* 1996, **61**, 8792.
820. Theberge, C. R.; Zercher, C. K. *Tetrahedron Lett.* 1994, **35**, 9181.
821. Theberge, C. R.; Zercher, C. K. *Tetrahedron Lett.* 1995, **36**, 5495.
822. Barrett, A. G. M.; Doubleday, W. W.; Tustin, G. J.; White, A. J. P.; Williams, D. J. *J. Chem. Soc., Chem. Commun.* 1994, 1783.
823. Dinnocenzo, J. P.; Conlon, D. A. *J. Am. Chem. Soc.* 1988, **110**, 2324.
824. Wilson, S. R.; Zucker, P. A. *J. Org. Chem.* 1988, **53**, 4682.
825. Fleming, I.; Sarkar, A. K.; Thomas, A. P. *J. Chem. Soc., Chem. Commun.* 1987, 157.
826. Fleming, I.; Lawrence, N. J.; Sarkar, A. K.; Thomas, A. P. *J. Chem. Soc., Perkin Trans. 1* 1992, 3303.
827. Ahmad, M. S.; Osman, S. M. *J. Am. Oil. Chem. Soc.* 1980, **57**, 363.
828. Ansari, F. H.; Osman, S. M.; Subbaram, M. R. *Indian J. Chem.* 1973, **11**, 1053.
829. Toshima, H.; Maru, K.; Jiao, Y.; Yoshihara, T.; Ichihara, A. *Tetrahedron Lett.* 1999, **40**, 935.
830. Pansare, S. V.; Jain, R. P. *Tetrahedron Lett.* 1999, **40**, 2625.
831. Itoh, T.; Emoto, S.; Kondo, M. *Tetrahedron* 1998, **54**, 5225.
832. Sheikh, Y. M.; Leclercq, J.; Djerassi, C. *J. Chem. Soc., Perkin Trans. 1* 1974, 909.
833. Gerber, P.; Vogel, P. *Tetrahedron Lett.* 1999, **40**, 3165.
834. Boyer, F.-D.; Lallemand, J.-Y. *Synlett* 1992, 969.
835. Scott, R. W.; Heathcock, C. H. *Carbohydr. Res.* 1996, **291**, 205.
836. Murali, R.; Ramana, C. V.; Nagarajan, M. *J. Chem. Soc., Chem. Commun.* 1995, 217.
837. Ramana, C. V.; Murali, R.; Nagarajan, M. *J. Org. Chem.* 1997, **62**, 7694.
838. Wilson, S. R.; Walters, M. E.; Orbaugh, B. *J. Org. Chem.* 1976, **41**, 378.
839. Hoberg, J. O. *J. Org. Chem.* 1997, **62**, 6615.
840. Ragauskas, A. J.; Stothers, J. B. *Can. J. Chem.* 1985, **63**, 2969.
841. Ainge, S. W.; Vogel, P. *Tetrahedron Lett.* 1998, **39**, 4039.
842. Newcombe, N. J.; Simpkins, N. S. *J. Chem. Soc., Chem. Commun.* 1995, 831.
- 842a Piers, E.; Friesen, R. W. *J. Org. Chem.* 1986, **51**, 3405.
843. Maurin, R.; Chorro, M.; Gilles, J. L. *Tetrahedron* 1982, **38**, 1253.
844. Gadwood, R. C.; Lett, R. M.; Wissinger, J. E. *J. Am. Chem. Soc.* 1984, **106**, 3869.
845. Gadwood, R. C.; Lett, R. M.; Wissinger, J. E. *J. Am. Chem. Soc.* 1986,

108, 6343.

846. Ceccherelli, P.; Pellicciari, R.; Golob, N. F.; Smith, R. A. J.; Wenkert, E. *Gazz. Chim. Ital.* 1973, **103**, 599.
847. Wenkert, E.; Buckwalter, B. L.; Sathe, S. S. *Synth. Commun.* 1973, **3**, 261.
848. Paquette, L. A.; Ross, R. J.; Shi, Y.-J. *J. Org. Chem.* 1990, **55**, 1589.
849. Nishida, M.; Iseki, K.; Shibasaki, M.; Ikegami, S. *Chem. Pharm. Bull.* 1990, **38**, 3230.
850. Masjedzadeh, M. R.; Dannecker-Doerig, I.; Little, R. D. *J. Org. Chem.* 1990, **55**, 2742.
851. Jurlina, J. L.; Patel, H. A.; Stothers, J. B. *Can. J. Chem.* 1984, **62**, 1159.
852. Wenkert, E.; Arrhenius, T. S. *J. Am. Chem. Soc.* 1983, **105**, 2030.
853. Davidson, B. S.; Plavcan, K. A.; Meinwald, J. *J. Org. Chem.* 1990, **55**, 3912.
854. Bertinato, P.; Sorensen, E. J.; Meng, D.; Danishefsky, S. J. *J. Org. Chem.* 1996, **61**, 8000.
855. Meng, D.; Bertinato, P.; Balog, A.; Su, D.-S.; Kamenecka, T.; Sorensen, E. J.; Danishefsky, S. J. *J. Am. Chem. Soc.* 1997, **119**, 10073.
856. Asaoka, M.; Ohkubo, T.; Itahana, H.; Kosaka, T.; Takei, H. *Tetrahedron* 1995, **51**, 3115.
857. Snowden, R. L. *Tetrahedron Lett.* 1981, **22**, 101.
858. Snowden, R. L. *Tetrahedron* 1986, **42**, 3277.
859. Ireland, R. E.; Dawson, M. I.; Kowalski, C. J.; Lipinski, C. A.; Marshall, D. R.; Tilley, J. W.; Bordner, J.; Trus, B. L. *J. Org. Chem.* 1975, **40**, 973.
860. Boeckman, Jr., R. K.; Charette, A. B.; Asberom, T.; Johnston, B. H. *J. Am. Chem. Soc.* 1991, **113**, 5337.
861. Scheller, M. E.; Frei, B.; Mathies, P.; Petter, W. *Helv. Chim. Acta* 1984, **67**, 1748.
862. Boeckman, Jr., R. K.; Charette, A. B.; Asberom, T.; Johnston, B. H. *J. Am. Chem. Soc.* 1987, **109**, 7553.
863. Fetizon, M.; Ragoussis, N. *Tetrahedron* 1978, **34**, 287.
864. Steinmeyer, A.; Neef, G.; Kirsch, G.; Schwarz, K.; Rach, P.; Haberey, M.; Thieroff-Ekerdt, R. *Steroids* 1992, **57**, 447.
865. Templeton, J. F.; Paslat, V. G.; Wie, C. W. *Can. J. Chem.* 1978, **56**, 2058.
866. Ireland, R. E.; Walba, D. M. *Tetrahedron Lett.* 1976, 1071.
867. Bottini, A.; Christensen, J. E. *Tetrahedron* 1974, **30**, 393.
868. Zefirov, N. S.; Lukin, K. A.; Politanskii, S. F.; Margulis, M. A. *Zh. Org. Khim.* 1987, **23**, 1799.

869. Fitjer, L.; Conia, J.-M. *Angew. Chem., Int. Ed. Engl.* 1973, **12**, 334.
870. Zefirov, N. S.; Kozhushkov, S. I.; Kuznetsova, T. S.; Lukin, K. A.; Kazimirchik, I. V. *Zh. Org. Khim.* 1988, **24**, 673.
871. Wolinsky, J.; Clark, G. W.; Thorstenson, P. C. *J. Org. Chem.* 1976, **41**, 745.
872. Zöllner, S.; Buchholz, H.; Boese, R.; Gleiter, R.; de Meijere, A. *Angew. Chem., Int. Ed. Engl.* 1991, **30**, 1518.
873. Seebach, D.; Stucky, G. *Angew. Chem., Int. Ed. Engl.* 1988, **100**, 1398.
874. Seebach, D.; Stucky, G.; Pfammatter, E. *Chem. Ber.* 1989, **122**, 2377.
875. Mash, E. A. *J. Org. Chem.* 1987, **52**, 4142.
876. Sugimura, T.; Yoshikawa, M.; Mizuguchi, M.; Tai, A. *Chem. Lett.* 1999, 831.
877. Sugimura, T.; Koguro, K.; Tai, A. *Tetrahedron Lett.* 1993, **34**, 509.
878. Mash, E. A.; Nelson, K. A. *Tetrahedron Lett.* 1986, **27**, 1441.
879. Mash, E. A.; Nimkar, K. S.; Baron, J. A. *Tetrahedron* 1997, **53**, 9043.
880. Mash, E. A.; Math, S. K.; Flann, C. J. *Tetrahedron Lett.* 1988, **29**, 2147.
881. Mash, E. A.; Math, S. K.; Flann, C. J. *Tetrahedron* 1989, **45**, 4945.
882. Mash, E. A.; Fryling, J. A. *J. Org. Chem.* 1987, **52**, 3000.
883. Mash, E. A.; Hemperly, S. B. *J. Org. Chem.* 1990, **55**, 2055.
884. Nelson, K. A.; Mash, E. A. *J. Org. Chem.* 1986, **51**, 2721.
885. Tamura, O.; Hashimoto, M.; Kobayashi, Y.; Katoh, T.; Nakatani, K.; Kamada, M.; Hayakawa, I.; Akiba, T.; Terashima, S. *Tetrahedron Lett.* 1992, **33**, 3487.
886. Luithle, J. E. A.; Pietruszka, J. *J. Org. Chem.* 1999, **64**, 8287.
887. Kaye, P. T.; Molema, W. E. *Synth. Commun.* 1999, **29**, 1889.
888. Charette, A. B.; Côté, B. *J. Am. Chem. Soc.* 1995, **117**, 12721.
889. Schöllkopf, U.; Tiller, T.; Bardenhagen, J. *Tetrahedron* 1988, **44**, 5293.
890. Groth, U.; Schöllkopf, U.; Tiller, T. *Liebigs Ann. Chem.* 1991, 857.
891. Pietruszka, J.; Widenmeyer, M. *Synlett* 1997, 977.
892. Cervinka, O.; Kriz, O. *Coll. Czech. Chem. Commun.* 1973, **38**, 938.
893. Nagle, D. G.; Gerald, R. S.; Yoo, H.-D.; Gerwick, W. H.; Kim, T.-S.; Nambu, M.; White, J. D. *Tetrahedron Lett.* 1995, **36**, 1189.
894. White, J. D.; Kim, T.-S.; Nambu, M. *J. Am. Chem. Soc.* 1997, **119**, 103.
895. Turnbull, M. D. *J. Chem. Soc., Perkin Trans. 1* 1997, 1241.
896. Imai, N.; Sakamoto, K.; Maeda, M.; Kouge, K.; Yoshizane, K.; Nokami, J. *Tetrahedron Lett.* 1997, **38**, 1423.
897. Halm, C.; Kurth, M. *J. Angew. Chem., Int. Ed. Engl.* 1998, **37**, 510.