Stereoselective Preparation of Polyfunctional Cyclopentane Derivatives by Radical Nickel- or Palladium-Catalyzed Carbozincations

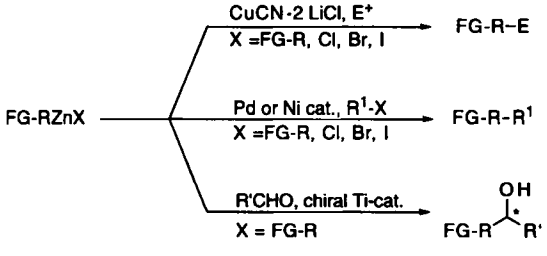
Heinz Stadtmüller, Andrea Vaupel, Charles E. Tucker, Thomas Stüdemann, and Paul Knochel*

Abstract: The reaction of 5-hexenyl iodides with diethylzinc (2 equiv) and catalytic amounts of a Pd^{II} or Ni^{II} complex like $PdCl_2(dppf)$, $PdCl_2(MeCN)_2$, or $Ni(acac)_2$ results in an efficient ring closure (THF, RT, 2–12 h) affording cyclopentylmethylzinc iodides, which, after transmetalation with CuCN·2 LiCl, can be further functionalized by treatment with a range of electrophiles like allylic halides, acyl chlorides, enones, nitroolefins, ethyl propynoate, and alkynyl halides to yield polyfunctional cyclopentane derivatives. The ring closures occur via radical intermediates, and the stereochemistry of the products can be explained according to the rules for radical cyclizations developed by Beckwith. The preparation of several di- and trisubstituted cyclopentanes has been achieved with high stereoselectivity. Tandem ring closures can be performed to construct bicyclic or tricyclic ring systems. Cyclizations of iodo-ethylenic and acetylenic esters and ketones can be accomplished, although the high reactivity of acetylenic ketones leads to unexpected cyclization products. The synthetic utility of this method has been demonstrated by an enantioselective synthesis of (+)-methyl epijasmonate and (−)-methyl cucurbate.

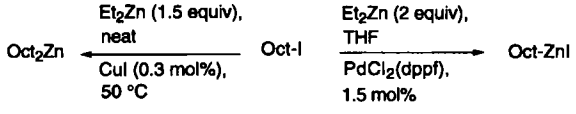
Keywords
asymmetric cyclization · catalysis · cyclopentane · natural products · palladium complexes

Introduction

Diorganozincs and organozinc halides are useful organometallic intermediates, since they tolerate a variety of functionalities.[1] In consequence, they have a low intrinsic reactivity; this explains why few synthetic applications of these organometallics have been reported in the past. However, in the last 15 years, it has been shown that organozincs can be readily transmetalated to reactive copper–zinc reagents[1, 2] or undergo efficient palladium-catalyzed cross-coupling reactions[3] or titanium-catalyzed asymmetric additions.[4, 5] These reactions have considerably enhanced the synthetic scope of organozincs in organic synthesis (Scheme 1).[1] Diorganozincs, which are of special importance for asymmetric catalysis,[4, 5] can be prepared by iodine–zinc exchange,[1] by boron–zinc exchange,[1, 6] or by a nickel-catalyzed hydrozincation.[7] In the course of the study of the iodine–zinc exchange reaction, we noticed that this reaction could be catalyzed by the addition of transition-metal compounds such as copper(I)[1] or manganese(II)[8] salts. Moreover, we observed that palladium (or nickel) catalysis was very efficient but, in contrast to copper catalysis, afforded not the expected dialkylzinc species but an alkylzinc iodide (Scheme 2).[9]



Scheme 1. Some examples of the synthetic scope of organozincs in organic synthesis.



Scheme 2.

This puzzling result led us to start a range of mechanistic experiments. In particular, for the determination of the nature of the reactive intermediate, a well-known "radical clock", 5-hexenyl iodide (**1a**),[10] was used as a substrate. The treatment of this alkenyl iodide with Et_2Zn in the presence of $PdCl_2(dppf)$ (dichloro(1,1′-bis(diphenylphosphino)ferrocenepalladium(II)) afforded the cyclized cyclopentylmethylzinc iodide (**2**), which could be trapped in the presence of CuCN·2 LiCl with ethyl (α-bromomethyl)acrylate,[11] leading to the allylated product **3** in 80% yield (Scheme 3).[9] Attempts to cyclize **1a** with diethylzinc in the absence of a palladium catalyst or by zinc metal insertion proved unsatisfactory, furnishing mixtures of cyclized and uncyclized products.[12, 13] In this paper we shall describe

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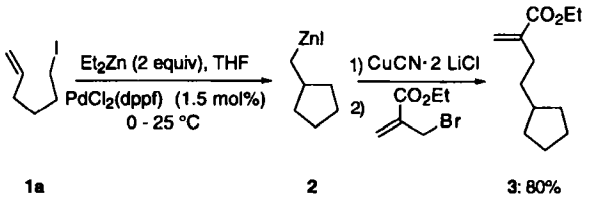
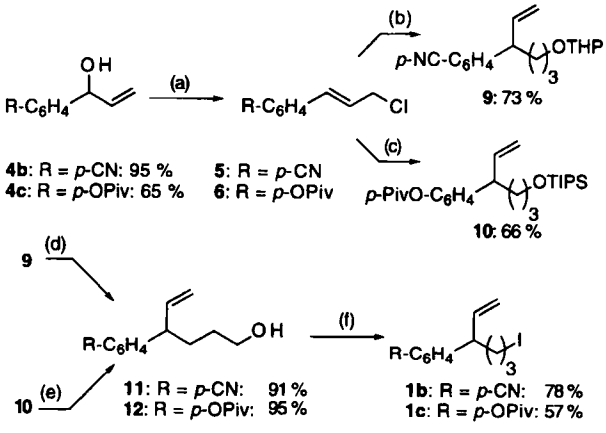


Scheme 3.

the scope of this reaction for the stereoselective preparation of cyclopentane derivatives and describe an enantioselective synthesis[14] of two major components of jasmine oil thus performed.[15]

Results and Discussion

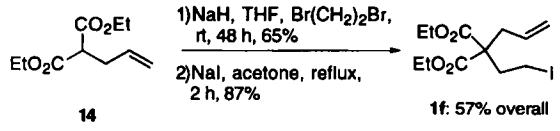
The 4-substituted 5-hexenyl iodides of type **1** required as the cyclization precursors were prepared by standard methods. Thus, the alcohols **4b–c** obtained by the addition of vinylmagnesium bromide to the corresponding aldehydes (THF, −40 °C, 3 h) were converted to the corresponding allylic chlorides **5** and **6** by treatment with thionyl chloride (−10 °C to RT, 3 h, 67–83%). These allylic chlorides undergo a clean S_N2' substitution (>95:5)[2, 16] with the zinc–copper reagents **7** and **8**[2] if the reaction is performed in a mixture of THF and *N,N*-dimethylpropyleneurea (DMPU)[17] (3.5:1) at −35 °C for 20 h, furnishing the allylated products **9** and **10** in 73% and 66% yield, respectively (Scheme 4). After the deprotection of **9** and **10** with



Scheme 4. Conditions: a) $SOCl_2$ (1.2 equiv), CH_2Cl_2, −10 °C to RT, 3 h (67–83% yield), b) $THPO(CH_2)_3Cu(CN)ZnI$ (**7**), THF/DMPU, −35 °C; c) $TIPSO(CH_2)_3Cu(CN)ZnI$ (**8**), THF/DMPU, −35 °C; d) TosOH, EtOH, RT, 8 h; e) Bu_4NF, THF, RT, 0.5 h; f) MeI·1DCC (**13**), THF, RT, 48 h.

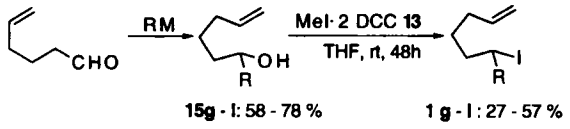
p-TosOH in ethanol (RT, 8 h, 91%) and Bu_4NF in THF (RT, 0.5 h, 95%), respectively, the resulting alcohols **11** and **12** were converted to the corresponding alkyl iodides **1b** and **1c** with *N*-methyl-*N,N'*-dicyclohexylcarbodiimidium iodide (MeI·2DCC) **13**[18] (THF, RT, 48 h, 78–57% yield; Scheme 4).

The nonfunctionalized alkyl iodide 3-phenyl-6-iodo-1-hexene (**1d**) and the 2-alkyl-substituted hexenyl iodide 2-butyl-6-iodo-1-hexene (**1e**) were prepared in the same way (see experimental section). The ester-substituted alkyl iodide **1f** is conveniently obtained from diethyl 2-propenylmalonate **14**[19] by reaction with 1,2-dibromoethane (NaH, RT, 48 h; 65% yield) followed by a Finkelstein reaction (sodium iodide, acetone, reflux, 2 h; 87% yield; Scheme 5).



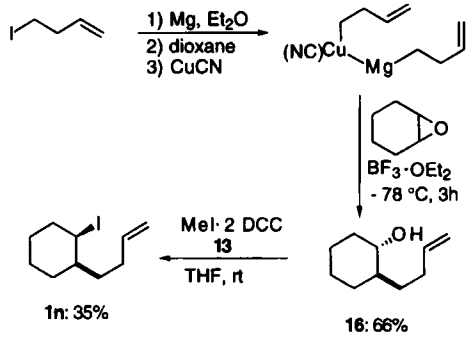
Scheme 5.

Secondary alkyl iodides **1g–i** were also used as substrates. The corresponding alcohols **15g–i** were all prepared by the addition of an organometallic reagent RM (M = ZnX, MgX, Li) to 5-hexenal[20] (Scheme 6). The preparation of polyfunc-



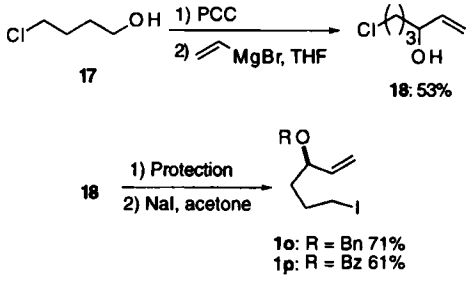
Scheme 6. For **15g**: M = Li, R = Me; **15h,i**: M = MgX, R = *c*-Hex, Et; **15j–l**: M = $ZnCu(CN)XBF_3 \cdot Et_2O$, R = $(CH_2)_4OAc$, $(CH_2)_3CN$, CH_2OPiv.

tional secondary iodides like **1j–l** was performed by the addition of zinc–copper reagents in the presence of $BF_3 \cdot OEt_2$[21] at low temperature (−30 to −20 °C, ca. 20 h) leading to intermediate alcohols of type **15j–l**. The opening of cyclohexene oxide with di(3-butenyl)magnesium and copper cyanide in THF in the presence of $BF_3 \cdot OEt_2$[22] (−78 °C, 3 h) provides the *trans*-substituted cyclohexanol **16**, which is converted in moderate yields to **1n** with MeI·2DCC (**13**) (Scheme 7). The preparation of



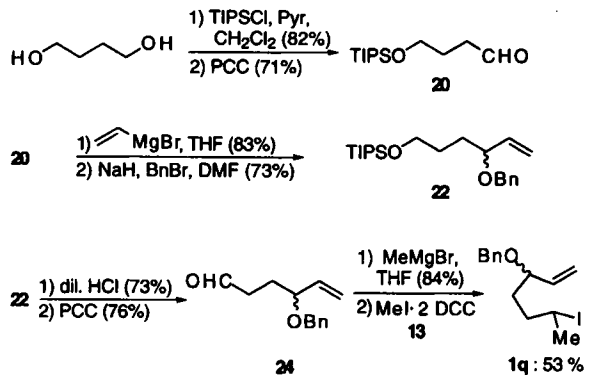
Scheme 7.

3-substituted 6-iodo-1-hexenes can be achieved by the oxidation of 4-chlorobutanol (**17**) with pyridinium chlorochromate (PCC) and subsequent addition of vinylmagnesium bromide (−40 °C, 3 h) to give the allylic alcohol **18**.[13b] The desired iodides **1o** and **1p** were obtained after benzylation (benzyl 2,2,2-trichloroacetimidate, RT, 73% yield)[23] or benzoylation (BzCl, Pyr, CH_2Cl_2, RT, 2 h; 82% yield), respectively, and subsequent chloride–iodide exchange (NaI, acetone, reflux) in satisfactory overall yield (61–71%; (Scheme 8). The secondary alkyl iodide



Scheme 8.

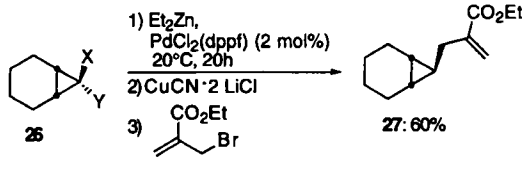
1q is prepared in a similar way starting from 1,4-butanediol. Its monoprotection with TIPSCl (TIPS = triisopropylsiloxy; 1.1 equiv, pyr, CH_2Cl_2, RT, 12 h) provides 4-triisopropylsiloxybutanol (**19**) (82% yield), which was oxidized to the aldehyde **20** by a PCC oxidation (71%). Addition of vinylmagnesium bromide to **20** gives the allylic alcohol **21** in 83% yield (0 °C, 2 h). Benzylation of **21** (NaH, BnBr, DMF) gives the benzyl ether **22** (73% yield). Desilylation of **22** with diluted HCl in ethanol (reflux, 0.5 h, 73%) leads to the alcohol **23**, which was oxidized with PCC to yield the unsaturated aldehyde **24** (76%). The addition of methylmagnesium bromide to **24** provided the secondary alcohol **25** (ether, −40 °C, 3 h, 84% yield), which was converted to the unsaturated iodide **1q** (1:1 mixture of diastereomers) with MeI·2DCC (**13**) in 53% yield (Scheme 9).



Scheme 9.

All these unsaturated alkyl iodides undergo ring closure in the presence of a palladium(II) catalyst. Dichloro(1,1'-bis(diphenylphosphino)ferrocenepalladium(II) ($PdCl_2$(dppf))[24] was found to be an excellent catalyst; however, other palladium(II) complexes such as $PdCl_2(CH_3CN)_2$ or $PdCl_2(PhCN)_2$ are equally well-suited for the cyclization reactions. The presence of a phosphine ligand, such as PPh_3, inhibits or considerably slows down the ring closures. Interestingly, nickel complexes like $Ni(acac)_2$ are highly active and permit the use of less reactive substituted 5-hexenyl *bromides* as substrates with good success.[25] Attempts to use 5-hexenyl triflates or tosylates as cyclization precursors were not successful; this suggests a radical mechanism for the ring closure, an idea supported by several experiments. Thus, the treatment of either *exo*- or *endo*-7-iodobicyclo[2.1.0]heptane[26] **26** with diethylzinc (ca. 2 equiv, 5 mol% $PdCl_2$(dppf)) in THF provides the *exo*-substituted bicyclic adduct **27** after allylation in 60% yield in a stereoconvergent manner (Scheme 10).

This stereoconvergence supports a radical mechanism for the palladium insertion reaction.[27] We propose that a primary or secondary alkyl halide like **28** reacts with the Pd^0 or Ni^0 complex (M = Ni or Pd, Scheme 11), forming the radical **29** and a

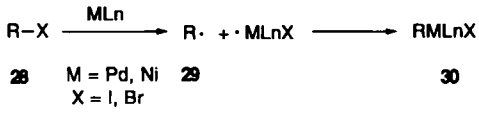


exo-**26**: X = I; Y = H
endo-**26**: X = H; Y = I

exo - **27** : *endo* - **27** = 96 : 4

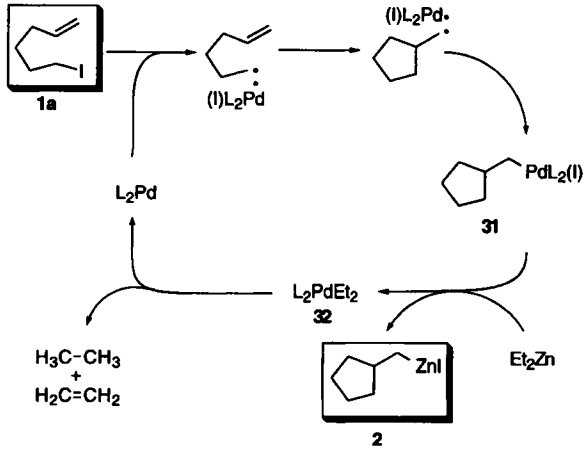
Scheme 10.

Ni^I or Pd^I complex. The carbon-centered radical **29** can rearrange (cyclize) or isomerize before its reaction with the metal moiety to give the oxidative addition product **30** (Scheme 11). In



Scheme 11.

sharp contrast to most radical cyclizations, which after ring closure provide a highly reactive radical that must be quenched immediately by an appropriate reagent, our method leads to an organopalladium species of type **31**, which can be transmetalated to give the organozinc iodide **2** as a storable organometallic intermediate (Scheme 12). In the course of this transmetalation



Scheme 12.

a diethylpalladium complex **32** is produced. This complex rapidly undergoes a β-hydride elimination, resulting in ethylene and ethane.[28] After transmetalation with CuCN·2LiCl,[1, 2a] the cyclized organozinc derivative reacts with various electrophiles, as shown in the cyclization of the 3-substituted alkyl iodide **1d** (Scheme 13). The *trans*-stereochemistry of the resulting cyclopentylmethylzinc derivative **33** can readily be rationalized by means of Beckwith's model for radical cyclizations.[29] Thus, the reaction of **33** with CuCN·2LiCl followed by 3-iodocyclohexenone[30] (−10 °C, 12 h) furnishes the 3-substituted enone **34** in 80% yield; iodolysis of **33** gives the *trans*-alkyl iodide **35**; the benzoylation of the copper derivative of **33** gives the ketone **36** (0 °C, 12 h, 76% yield); the copper-catalyzed (5 mol% CuCN) allylation of **33** with ethyl α-(bromomethyl)acrylate[11] (−20 °C, 0.5 h) furnishes the product **37** in 73% yield; and the copper derivative of **33** undergoes a smooth carbocupration with ethyl propynoate (−50 °C, 12 h) to furnish the (*E*)-acrylate **38** (>95% *E*; 64% yield). Unlike most main-group organometallic cyclizations,[31] functional groups such as an ester or a nitrile can be present in the cyclization substrates and a range of polyfunctional cyclopentane derivatives (**39**–**51**) can be prepared in satisfactory yields.

The cyclization of *gem*-disubstituted olefins like **1e** (see entry 3 of Table 1) also proceeds well, resulting in the construction of quaternary carbon centers. After transmetalation with CuCN·2LiCl, the cyclized zinc–copper derivative was added to

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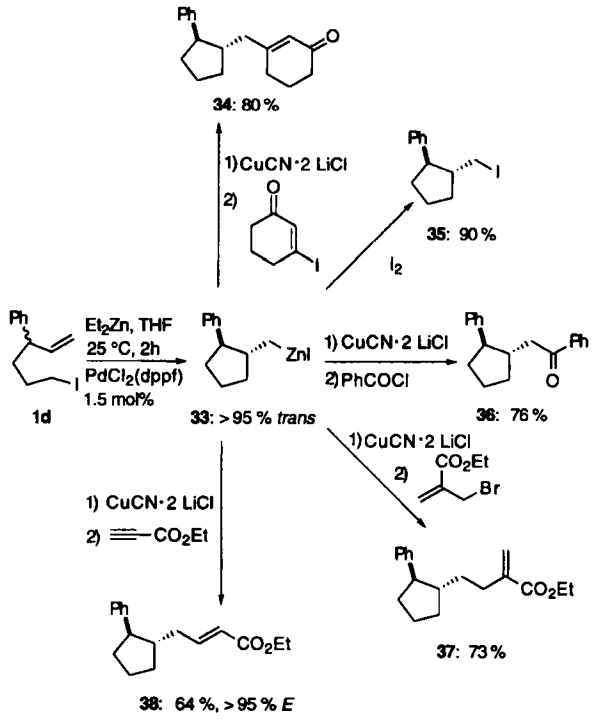
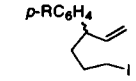
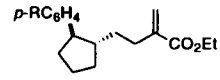
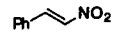
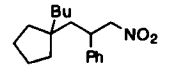
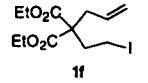
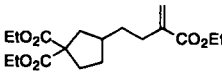
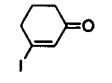
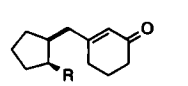
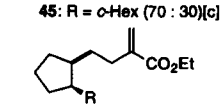
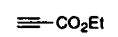
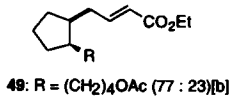
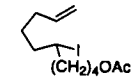
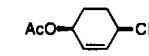
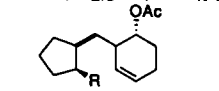


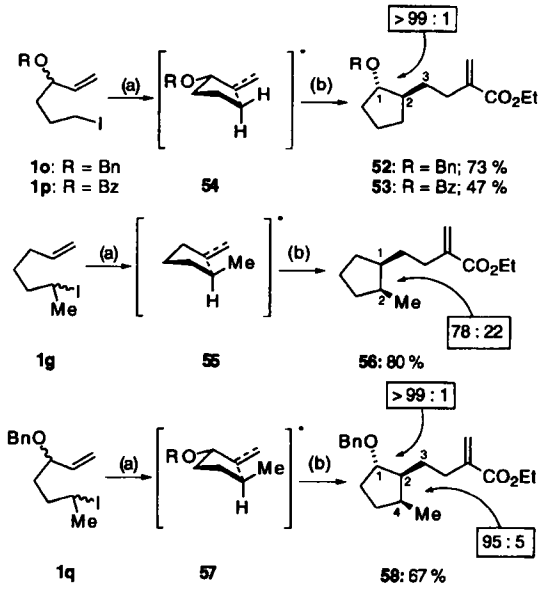
Scheme 13. The reactions of the organozinc derivative 33 obtained from the cyclization of **1d** with Et_2Zn in the presence of Pd. The stereochemistry of 33 was verified by ^1H NMR NOESY.

nitrostyrene, furnishing the nitro derivative **41** in 81% yield. Secondary alkyl iodides were found to be more reactive and to undergo a smooth cyclization.[32–34] As predicted,[29] *cis*-cyclopentylmethylzinc derivatives are formed preferentially (Table 1). The stereoselectivities are in the range of 80:20, which is comparable to related radical cyclizations.[29] However, the presence of an additional substituent on position 3 considerably enhances the *cis*-stereoselectivity. Thus, whereas the 3-substituted primary alkyl iodides **1o–p** undergo a very clean ring closure to the *trans*-cyclopentane **52–53** (*trans*:*cis* > 99:1) via the transition state **54** (Scheme 14), the secondary alkyl iodide **1g** produces the *cis*-cyclopentane derivative **56** with moderate *cis*-selectivity (*cis*:*trans* 78:22) via the conformation **55** (Scheme 14). The presence of the two substituents on positions 3 and 6 has a synergistic effect on the stereoselectivity of the ring closure. The benzyloxy substituent favors the pseudoequatorial position of all substituents and results in the most stable conformation **57**. The cyclopentane **58** is obtained with very high stereoselectivity (*cis*:*trans* = 95:5 between C1 and C2 and *cis*:*trans* ≥ 1:99 between C2 and C3). The stereoconvergence of this reaction is further evidence for the radical mechanism. Three possible reaction pathways are depicted in Scheme 15. Pathway A is the radical ring closure described above. The other two involve either a carbopalladation[35] (pathway B) or a carbozincation (pathway C) as the key step for the cyclization. The carbopalladation route seems unlikely, since it would not explain the stereoconvergence of the cyclization shown in Schemes 10 and 14. A carbozincation[13, 34] can also be excluded, since the alkyl iodide **11** (Scheme 16) undergoes a smooth cyclization and after allylation gives the expected product **59** in 87% yield. A zinc organometallic as intermediate would have led to the formation of the diene **60**, since organozinc derivatives bearing an oxygen substituent in the β-position are unstable and undergo elimination reactions. On the other hand, it is well known that carbon-

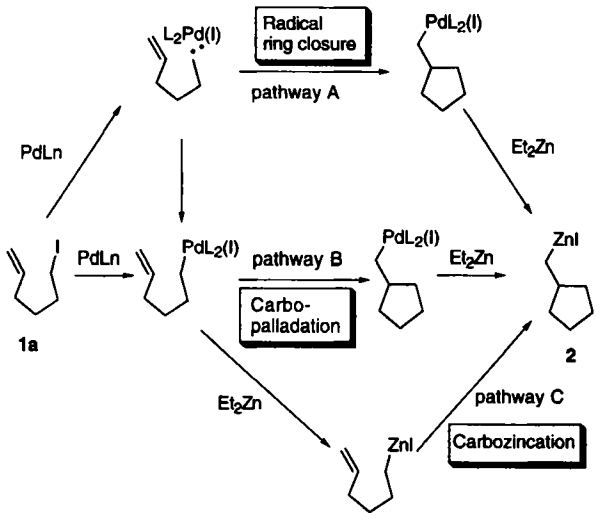
Table 1. Polyfunctional cyclopentane derivatives **39–51** obtained by the palladium-catalyzed radical cyclization of alkyl iodides **1b–k** and subsequent trapping with an electrophile.

Entry	Iodide	Electrophile	Product	Yield (%)
1	 1b: R = CN		 39: R = CN	83 [a]
2	1c: R = OPiv		40: R = OPiv	62
3	 1e		 41	81
4	 1f		 42	73
5	 1g: R = Me		 43: R = Me (78 : 22)[b]	62
6	1h: R = Et		44: R = Et (75 : 25)[b]	81
7	1i: R = *c*-Hex		45: R = *c*-Hex (70 : 30)[c]	65
8	1h: R = Et		 46: R = Et (75 : 25)[b]	87
9	1j: R = $(CH_2)_4OAc$		47: R = $(CH_2)_4OAc$ (77 : 23)[b]	75
10	1k: R = $(CH_2)_3CN$		48: R = $(CH_2)_3CN$ (81 : 19)[b]	88
11	1j: R = $(CH_2)_4OAc$		 49: R = $(CH_2)_4OAc$ (77 : 23)[b]	57
12	1k: R = $(CH_2)_3CN$		50: R = $(CH_2)_3CN$ (81 : 19)[b]	71
13	 1j		 51: R = $(CH_2)_4OAc$ (77 : 23)[b,c]	52

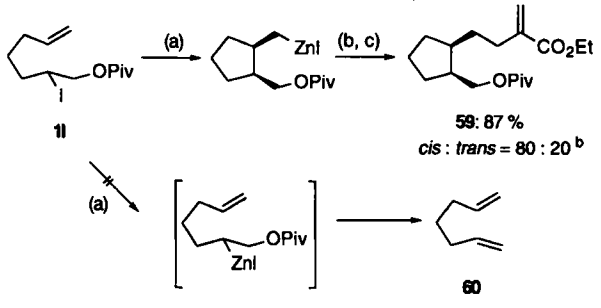
[a] All yields refer to analytically pure products. [b] *cis*:*trans* ratio; the stereochemistry was determined by ^1H NMR NOESY. [c] Mixture of diastereomers.



Scheme 14. Conditions: a) Et_2Zn (2 equiv), $PdCl_2(dppf)$ (2.5 mol%), RT, 2 h; b) CuCN·2 LiCl, $BrCH_2C(CH_2)CO_2Et$, −78 °C to RT. Stereochemistry was verified by ^1H NMR NOESY.



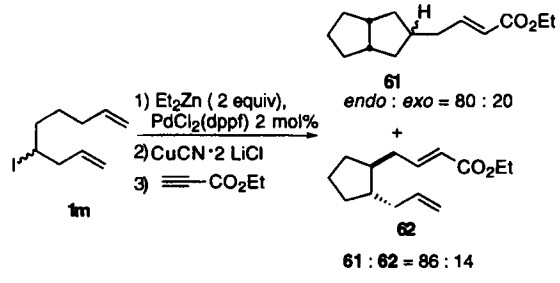
Scheme 15. Three suggested reaction pathways for the cyclization of primary alkyl iodides.



Scheme 16. Conditions: a) Et_2Zn (2 equiv), $PdCl_2(dppf)$ cat, −78 °C to RT, 2 h; b) CuCN·2LiCl; c) $BrCH_2C(CH_2)CO_2Et$. Stereochemistry was verified by ^1H NMR NOESY.

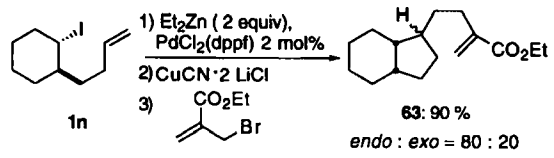
centered radicals bearing a β-oxygen substituent do not eliminate.[36]

Tandem reactions can be performed if unsaturated alkyl iodides like **1m–n** are used as substrates. Thus the reaction of **1m** under the standard cyclization conditions led to the bicyclic unsaturated ester **61** with a *cis*-ring junction and to the *trans*-cyclopentane derivative **62** (**61**:**62** = 86:14). The *exo*:*endo* ratio of **61** is 57:43; this indicates a moderate stereoselectivity in the second ring closure (Scheme 17). A better *endo* selectivity is



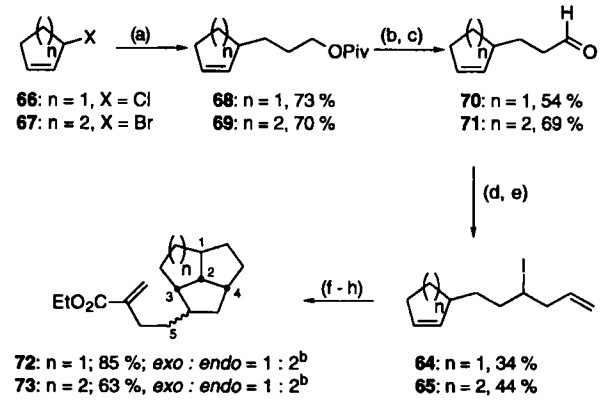
Scheme 17.

obtained in the ring closure of **1n**; in this case the *exo*:*endo* ratio is 20:80 and the allylated product **63** is isolated in 90% yield (Scheme 18).



Scheme 18.

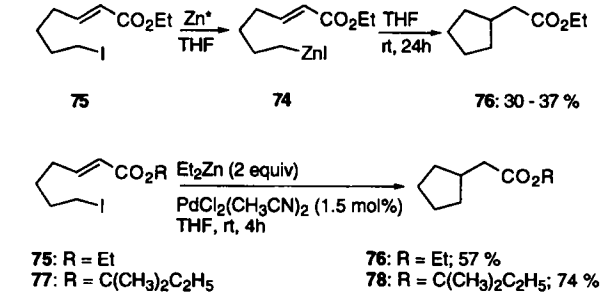
Multiple cyclizations permitting the construction of three rings are also possible. The cyclization precursors **64** and **65** are prepared from 3-chlorocyclopentene (**66**) and 3-bromocyclohexene (**67**) via the intermediates **68**–**71** as shown in Scheme 19



Scheme 19. Multiple cyclization with complete stereocontrol of the chiral centers at the ring junctions.

(see experimental section). The cyclizations proceed smoothly in both cases, leading to the tricyclic systems **72** (85%) and **73** (63%) with complete stereocontrol of the four chiral centers at the ring junctions. The remaining chiral center is obtained as an *exo*:*endo* mixture (1:2).

Attempts were made to extend these cyclization reactions to alkenyl and alkynyl esters. Lippard and Danheiser observed that the zinc reagent **74** derived from (*E*)-ethyl 7-iodo-2-heptenoate (**75**) gives the cyclized ester **76**, although in moderate yields (30–37%) and only after 24 h reaction time (Scheme 20).[37] Under our reaction conditions, the iodoenoate



Scheme 20.

75 underwent a ring closure to give the ester **76** in 57% yield after 4 h at RT (Scheme 20). A further improvement was achieved by use of the corresponding *t*-amyl ester[38] **77**, which is less prone to Claisen condensation reactions. In this case, the palladium-catalyzed ring closure (RT, 1 h) furnished the ester **78** in 74% yield. Interestingly, in the presence of $Ni(acac)_2$ as cata-

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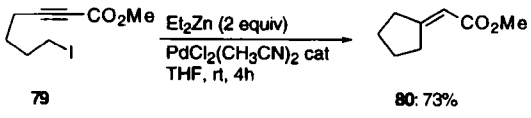
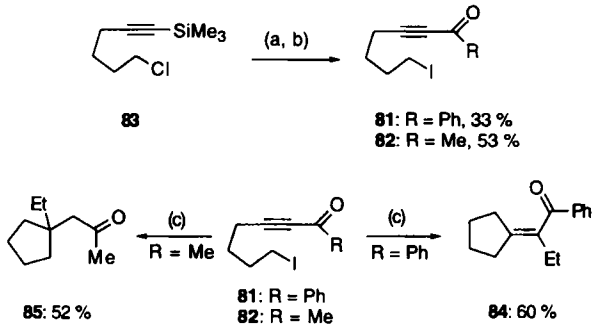
lyst and under appropriate reaction conditions (temperature, solvent) cross-coupling reactions were observed.[39]

The cyclization of acetylenic esters and ketones was also possible, but other reaction pathways were also observed (Scheme 21). For example, methyl 7-iodo-2-heptynoate[37] (**79**)



Scheme 21.

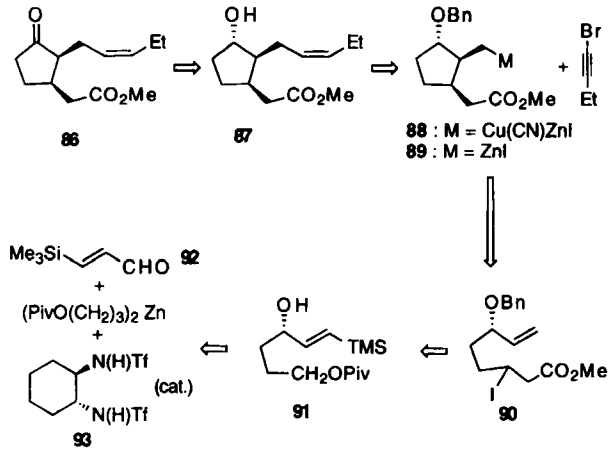
underwent a clean cyclization ($PdCl_2(CH_3CN)_2$ 1.5 mol%; THF, RT, 4 h) to furnish the *exo*-alkylidene ester **80** in 73% yield. The corresponding cyclization procedure involving the preparation of the zinc intermediate from **79** required a reaction time of 5 days and yielded 66% of the product.[37] Interestingly, the behavior of acetylenic ketones is more complex. The ketones **81** and **82** were readily prepared from 6-chloro-1-trimethylsilylhexyne (**83**)[40] by a Friedel–Crafts acylation[41] followed by a Finkelstein reaction (Scheme 22). The phenyl ketone **81** under-



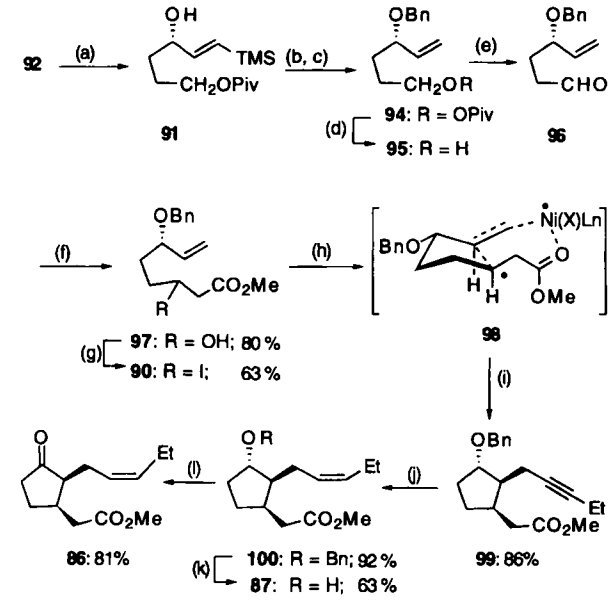
Scheme 22. Conditions: a) RCOCl, $AlCl_3$, CS_2, 2 8 C; b) NaI, acetone; c) Et_2Zn (2 equiv), $PdCl_2(CH_3CN)_2$ (1.5 mol%), THF, RT, 4 h.

went carbopalladation at the triple bond prior to reductive elimination to give the five-membered ring **84** (60% yield). In the absence of the phenyl substituent, this reductive elimination seems to be less efficient. Thus, in the case of the acetylenic methyl ketone **82**, the expected cyclization occurs, but is followed by Michael addition of an ethyl group, affording the ester **85** in 52% yield after workup (Scheme 22).

Finally, in order to demonstrate the synthetic utility of these cyclizations and to show that high levels of stereoselectivity can be obtained, two essential components of jasmine oil,[42] (+)-methyl epijasmonate (**86**) and (−)-methyl cucurbate (**87**) were synthesized.[14] The retrosynthetic analysis (Scheme 23) involves the cross-coupling of the zinc–copper reagent **88** with 1-bromobutyne.[43] The corresponding zinc reagent **89** is obtained by the nickel-catalyzed ring closure of the unsaturated iodoester **90**, which can be obtained from the chiral allylic alcohol **91**. This alcohol is obtained by the catalytic asymmetric addition[4] of bis(3-pivaloxypropyl)zinc to 3-trimethylsilylacrolein (**92**)[44] with (1*R*,2*R*)-1,2-bis(trifluoromethanesulfonamido)cyclohexane (**93**) as catalyst.[4] As expected, the addition of bis(3-pivaloxypropyl)zinc to **92** in the presence of $Ti(OiPr)_4$ (2.0 equiv) as cocatalyst and **93** (8 mol%) as catalyst gave the allylic alcohol **91** in 81% yield and 90% *ee* (toluene, −15 °C, 12 h, Scheme 24). The benzylation of **91** (NaH, BnBr, RT, 12 h, 87% yield) and desilylation (57%, HI in water, 0 °C,



Scheme 23. Retrosynthetic analysis of (+)-methyl epijasmonate (**86**) and (−)-methyl cucurbate (**87**).



Scheme 24. Conditions: a) $Zn((CH_2)_3OPiv)_2$ (2 equiv), **93** (8 mol%), toluene, −10 C, 12 h; b) NaH, BnBr, DMF, 0 C; c) 57% HI, 0 C, 10 min; d) $LiAlH_4$, ether, 0 C, 1 h; e) Dess–Martin reagent, CH_2Cl_2, RT, 1 h; f) $CH_2C(OMe)OLi$, ether, −78 C, 0.5 h; g) MeI·2DCC (**13**), THF, RT, 4 h; h) Et_2Zn (2 equiv), $Ni(acac)_2$ (2.5 mol%), THF, RT, 4 h; i) CuCN·2LiCl, BrC≡CEt, −55 C, 48 h; j) H_2 (1 atm), $Pd(BaSO_4)$ cat. pyridine; k) BCl_3 (3 equiv), CH_2Cl_2, −78 C to 10 C; l) Dess–Martin reagent, CH_2Cl_2, RT, 1 h.

10 min, 71% yield)[45] afforded the protected allylic alcohol **94**. The pivaloxy group was removed with $LiAlH_4$ (2 equiv, ether, 0 °C, 1 h; 90% yield), leading to the corresponding alcohol **95** in 90% yield. Its oxidation to the aldehyde **96** was best performed by the Dess–Martin periodinane method[46] (RT, 1 h, 81%). The addition of the lithium enolate of methyl acetate to **96** (ether, −78 °C, 0.5 h, 80% yield) gave the expected aldol product **97**, which was converted to the corresponding secondary alkyl iodide **90** as a mixture of two diastereomers by treatment with MeI·2DCC[18] (**13**, 3 equiv, THF, 30 °C, 5 h, 63%) as shown in Scheme 24.

The reaction of **90** with Et_2Zn (2.1 equiv, THF, RT, 4 h) and $Ni(acac)_2$ (2.5 mol%) provided the desired cyclopentylmethylzinc intermediate **89** with an excellent stereoselectivity, demonstrated by the >99:1 *trans*:*cis* ratio between C1 and C2 and the 95:5 *cis*:*trans* ratio between C2 and C3 of the product **99** obtained after transmetalation with CuCN·2LiCl[1, 2] followed by

cross-coupling with 1-bromo-1-butyne[43] (1.5 equiv, −55 °C, 48 h, 86% yield). The observed stereoselectivity can be explained by a transition state like **98** for the radical cyclization (Scheme 24). Lindlar reduction[47] of the functionalized alkyne **99** with H_2 (1 atm), $Pd/BaSO_4$ (cat, pyridine, 92%) yielded the *cis*-olefin **100** (96% *cis*), which was debenzylated with BCl_3[48] (3 equiv, CH_2Cl_2, −78 °C to −10 °C, 61% yield) giving (−)-methyl cucurbate (**87**) in approx. 10% overall yield and 90% *ee* starting from 3-trimethylsilylacrolein (**92**). Product **87** was oxidized cleanly with the Dess–Martin procedure[46] to give (+)-methyl epijasmonate (**86**, 95% *cis*, 90% *ee*, 81% yield, 8% overall starting from **92**).

Conclusion

In this paper we have described a new radical cyclization that permits the preparation of di- and trisubstituted cyclopentylmethylzinc iodides with excellent stereoselectivity. In contrast to most radical cyclizations, which afford a highly reactive radical after ring closure, this procedure affords an organozinc species that can react with a wide range of electrophiles. We have shown that tandem reactions leading to bicyclic or tricyclic compounds can be readily accomplished. Finally the synthetic utility of this methodology has been demonstrated in a new enantioselective preparation of (+)-methyl epijasmonate.

Experimental Procedure

General considerations: Unless otherwise indicated, all reactions were carried out under argon. Solvents (THF, ether, toluene) were dried and freshly distilled over sodium/benzophenone. *N*-Methylpyrrolidinone (NMP) and dichloromethane were freshly distilled over CaH_2. Reactions were monitored by gas–liquid-phase chromatography (GC) or thin-layer chromatography (TLC) analysis of hydrolyzed aliquots.

Starting materials: The following starting materials were prepared according to literature procedures: ethyl α-(bromomethyl)acrylate [11], 5-hexenal [19], *N*-methyl-*N*,*N*′-dicyclohexylcarbodiimidium iodide (MeI·2DCC) [18], $PdCl_2$(dppf) [23], 7-iodobicyclo[2.1.0]heptane [25], 3-iodo-2-cyclohexen-1-one [30], 6-iodo-1-hexene [9], 3-iodopropyl pivalate [44], 3-chlorocyclopentene [49].

Preparation of the cyclization precursors: **1b–q** were prepared as follows.

1-(4-Cyanophenyl)-2-propen-1-ol (4b): 4-Cyanobenzaldehyde (3.93 g, 30.0 mmol, 1 equiv) was dissolved in THF (100 mL), and the solution was cooled to −40 °C. Vinylmagnesium bromide (20.6 mL of a 1.6 M solution in THF, 33.0 mmol, 1.1 equiv) was added. After the mixture had been stirred for 3 h at this temperature, the reaction was quenched with a saturated aqueous NH_4Cl solution (50 mL). In order to dissolve the precipitated magnesium salts, 10% aqueous HCl (20 mL) was added. The aqueous layer was extracted with ether (3 × 80 mL), the combined organic layer was washed with brine (50 mL) and dried ($MgSO_4$), and the solvent was evaporated. The crude residue was purified by flash chromatography (ether/hexanes 1:4), affording the alcohol **4b** (4.54 g, 28.5 mmol, 95% yield) as a clear oil. IR (neat): $\tilde{\nu}$ = 3410 (s), 3082 (w), 2976 (m), 2876 (m), 2228 (s), 1638 (s), 1602 (m), 926 (s) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ = 7.60–7.55 (m, 2H), 7.46–7.41 (m, 2H), 5.97–5.86 (m, 1H), 5.35–5.28 (m, 1H), 5.22–5.17 (m, 2H), 2.47 (brs, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 147.8, 139.3, 132.3, 126.9, 118.8, 116.6, 111.3, 74.7; MS (EI): *m*/*z* = 160 ([*M* + 1], 5), 159 ([*M*$^+$], 54), 158 ([*M* − 1], 84), 130 (78), 117 (55), 104 (49), 71 (40); $C_{10}H_9NO$ (159.1): calcd C 75.45, H 5.70, N 8.80; found C 75.65, H 5.58, N 8.72.

3-Chloro-1-(4-cyanophenyl)-1-propene (5): The allylic alcohol **4b** (4.54 g, 28.5 mmol, 1 equiv) was dissolved in CH_2Cl_2 (30 mL) and cooled to −20 °C. Thionyl chloride (4.07 g, 2.5 mL, 34 mmol, 1.2 equiv) was added and the cooling bath was removed. Evolution of HCl was observed. After being stirred for 3 h at RT, the solution was quenched with a saturated aqueous $NaHCO_3$ solution (50 mL). The aqueous layer was extracted with CH_2Cl_2 (3 × 50 mL), washed with brine (80 mL), and dried ($MgSO_4$), and the solvent was evaporated. The crude residue was purified by flash chromatography (ether/hexanes 1:4), affording **5** (3.39 g, 19.1 mmol, 67% yield) as white needles (m.p. 202 °C). IR (KBr): $\tilde{\nu}$ = 2968 (s), 2225 (m), 1650 (s), 1605 (m), 1244 (w), 978 (m) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ = 7.64–7.60 (m, 2H), 7.49–7.46 (m, 2H), 6.69 (d, ^3J(H,H) = 15.7 Hz, 1H), 6.43 (dt, ^3J(H,H) = 15.7, 6.9 Hz, 1H), 4.27 (dd, ^3J(H,H) = 6.9, 1.1 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 140.4, 132.5, 132.1, 128.8, 127.2, 118.7, 111.5, 44.5; MS (EI): *m*/*z* = 179 ([*M* + 2], 8), 178 ([*M* + 1], 3), 177 ([*M*$^+$], 22), 143 (14), 142 (100), 116 (15), 115 (19); $C_{10}H_8ClN$ (177.6): calcd C 62.55, H 5.25, N 9.12; found C 62.50, H 5.32, N 9.02.

Tetrahydro-2-[4-(4-cyanophenyl)-5-hexenyloxy]-2H-pyran (9): A three-necked flask equipped with a magnetic stirring bar, a thermometer, and a gas inlet was charged with zinc dust (3.92 g, 60.0 mmol, 3 equiv) in THF (20 mL). 1,2-Dibromoethane (0.30 mL, 3.4 mmol, 6 mol%) was added and the suspension was heated to 55 °C and then cooled back to RT. Subsequently, TMSCl (0.30 mL, 2.3 mmol, 4 mol%) was added and an exothermic reaction occurred. The reaction mixture was heated briefly to 55 °C and allowed to cool to RT twice more. Tetrahydro-2-(3-iodopropyloxy)-2H-pyran (5.16 g, 19.1 mmol, 1 equiv) was added dropwise such that the temperature remained below 35 °C. The reaction mixture was stirred for 2 h at this temperature. The excess of zinc dust was allowed to settle down overnight and the clear solution was transferred to a solution of CuCN·2LiCl (made from CuCN, 1.79 g, 19 mmol, and LiCl, 1.62 g, 38 mmol) in THF (15 mL) at −78 °C. The cooling bath was removed and the mixture was allowed to warm to 0 °C for 5 min. The zinc–copper reagent **7** was used without further purification; it was cooled to −78 °C, and 3-chloro-1-(4-cyanophenyl)-1-propene (**5**) (3.39 g, 19.1 mmol, 1 equiv) in DMPU (10 mL) was added. The temperature was slowly raised to −35 °C, and the reaction mixture was stirred for 20 h at this temperature and then quenched with saturated aqueous NH_4Cl (60 mL) and saturated aqueous NH_3 (20 mL). The aqueous layer was extracted with ether (2 × 50 mL), the combined organic layer was washed with brine (20 mL) and dried ($MgSO_4$), and the solvents were evaporated. The residual oil was purified by flash chromatography to afford the ether **9** (3.98 g, 13.9 mmol, 73% yield) as a colorless oil (ether/hexanes 1:15–1:4). IR (neat): $\tilde{\nu}$ = 2940 (s), 2862 (s), 2221 (s), 1645 (m), 1602 (s), 1026 (s), 855 (m) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ = 7.52–7.47 (m, 2H), 7.24–7.20 (m, 2H), 5.82 (ddd, ^3J(H,H) = 17.1, 10.2, 7.5 Hz, 1H), 5.03–4.94 (m, 2H), 3.82–3.61 (m, 2H), 3.45–3.22 (m, 4H), 1.75–1.39 (m, 10H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 149.9, 140.6, 132.3, 128.5, 118.9, 115.4, 110.1, 98.9, 67.1, 62.4, 49.7, 31.8, 30.7, 27.6, 25.4, 19.7; MS (EI): *m*/*z* = 184 (4), 155 (19), 142 (20), 115 (18), 85 (100), 67 (11), 57 (18); $C_{18}H_{23}NO_2$ (285.3): calcd C 75.76, H 8.12, N 4.91; found C 75.68, H 8.30, N 5.09.

4-(4-Cyanophenyl)-5-hexen-1-ol (11): The THP ether **9** (3.98 g, 13.9 mmol, 1 equiv) was dissolved in EtOH (30 mL), and pyridinium *p*-toluenesulfonate (3.00 g, 11.9 mmol, 0.9 equiv) was added. After stirring the mixture for 8 h, the solvent was evaporated. Ether (100 mL) was added to the residue and the organic layer was successively washed with an aqueous HCl solution (10%, 100 mL), an aqueous 1 M NaOH solution (50 mL), and brine (50 mL) and then dried ($MgSO_4$), and the solvent was evaporated. The crude residue was purified by flash chromatography (ether/hexanes 1:4–1:1), affording the alcohol **11** (2.55 g, 12.6 mmol, 91% yield) as a clear oil. IR (neat): $\tilde{\nu}$ = 3388 (s), 2933 (s), 2221 (s), 1645 (m), 1602 (s), 1175 (m) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ = 7.56–7.52 (m, 2H), 7.27–7.22 (m, 2H), 5.84 (ddd, ^3J(H,H) = 17.1, 10.3, 7.5 Hz, 1H), 5.07–4.98 (m, 2H), 3.59 (t, ^3J(H,H) = 6.4 Hz, 2H), 3.32–3.24 (m, 1H), 1.80–1.70 (m, 2H), 1.58–1.35 (m, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 149.9, 140.6, 132.4, 128.5, 119.0, 115.6, 110.2, 62.6, 49.7, 31.4, 30.6; MS (EI): *m*/*z* = 202 ([*M* + 1], 2), 201 ([*M*$^+$], 14), 168 (27), 155 (100), 142 (40), 129 (47), 115 (55), 89 (20); $C_{13}H_{15}NO$ (201.2): calcd C 77.58, H 7.51, N 6.96; found C 77.41, H 7.65, N 7.10.

3-(4-Cyanophenyl)-6-iodo-1-hexene (1b): The alcohol **11** (2.55 g, 12.6 mmol) was dissolved in THF (100 mL), MeI·2DCC (8.77 g, 15.8 mmol, 1.25 equiv) was added, and the reaction mixture was stirred for 40 h at 35 °C. The solvent was evaporated and hexanes (100 mL) added to the residue. The organic layer was washed with a 4:1 mixture of methanol/water (3 × 50 mL). The combined organic layer was washed with saturated aqueous $Na_2S_2O_3$ (30 mL) and dried ($MgSO_4$), and the solvent was evaporated. The crude residue was filtered through a short plug of silica gel (ether/hexanes 1:4). The solvent was evaporated and the residue purified by flash chromatography (ether/hexanes 1:10–1:6), affording the iodide **1b** (3.06 g, 9.83 mmol, 78% yield) as a colorless oil. IR (neat): $\tilde{\nu}$ = 2935 (m), 2229 (s), 1638 (w), 1607 (s), 1503 (m), 922 (m), 837 (m) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ = 7.61–7.57 (m, 2H), 7.30–7.27 (m, 2H), 5.88 (ddd, ^3J(H,H) = 17.1, 10.2, 7.6 Hz, 1H), 5.12–5.03 (m, 2H), 3.36–3.29 (m, 1H), 3.16 (t, ^3J(H,H) = 6.4 Hz, 2H), 1.87–1.22 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 149.4, 140.1, 132.4, 128.4, 118.9, 115.9, 110.4, 49.0, 35.8, 31.2, 6.3; MS (EI): *m*/*z* = 312 ([*M* + 1], 1), 311 ([*M*$^+$], 10), 184 (9), 142 (100), 116 (29), 54 (11); $C_{13}H_{14}NI$ (311.1): calcd C 50.18, H 4.53, N 4.50; found C 50.20, H 4.76, N 4.70.

1-(4-Pivaloxyphenyl)-2-propen-1-ol (4c): Pyridine (8.70 g, 8.90 mL, 110 mmol, 1.1 equiv) and pivaloyl chloride (13.3 g, 13.6 mL, 110 mmol, 1.1 equiv) were dissolved in CH_2Cl_2 (80 mL) and cooled to 0 °C. 4-Hydroxybenzaldehyde (12.2 g, 100 mmol, 1 equiv) in CH_2Cl_2 (80 mL) was slowly added. The reaction mixture was warmed to RT and was stirred for 12 h. The organic layer was successively washed with an aqueous HCl solution (10%, 100 mL), an aqueous NaOH solution (1 M, 50 mL) and brine (100 mL), and dried ($MgSO_4$). The solvent was evaporated and the crude product was recrystallized (ether/hexanes 1:1), affording 4-pivaloxybenzaldehyde (12.6 g, 61.0 mmol, 61% yield) as white crystals (m.p. 27 °C). IR (KBr): 2983 (s), 1752 (s), 1688 (s), 1603 (s), 1290 (s), 1109 (s), 903 (m) cm^{-1}; ^1H NMR

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(300 MHz, $CDCl_3$): δ = 9.94 (s, 1H), 7.90–7.85 (m, 2H), 7.23–7.18 (m, 2H), 1.34 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 190.9, 176.4, 156.0, 133.9, 131.2, 122.4, 39.3, 27.1; MS (EI): m/z = 206 ([M^+], 1), 138 (51), 122 (11), 121 (26), 85 (44), 57 (100); $C_{12}H_{14}O_3$ (206.2): calcd C 69.89, H 6.84; found C 69.92, H 6.63.

This 4-pivaloxybenzaldehyde (12.4 g, 60.0 mmol) was then used in the same procedure described above for the preparation of **4b** along with vinylmagnesium bromide (45.0 mL of a 1.6 M solution, 72.0 mmol, 1.3 equiv). The usual workup gave a viscous oil, which was purified by flash chromatography (ether/hexanes 1:2), affording **4c** (8.67 g, 39.0 mmol, 65% yield) as a clear oil. IR (neat): $\tilde{\nu}$ = 3475 (s), 2975 (m), 2875 (w), 1750 (s), 1507 (s), 1480 (s), 1200 (s), 1117 (s), 928 (m) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ = 7.39–7.35 (m, 2H), 7.07–7.02 (m, 2H), 6.08–5.97 (m, 1H), 5.37–5.32 (m, 1H), 5.22–5.19 (m, 2H), 1.57 (br s, 1H), 1.36 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 177.1, 150.6, 140.1, 139.9, 127.4, 121.5, 115.3, 74.8, 39.1, 27.1; MS (EI): m/z = 235 ([M + 1], 1), 234 ([M^+], 8), 150 (48), 149 (37), 121 (24), 107 (23), 95 (22), 85 (26), 57 (100); $C_{14}H_{18}O_3$ (234.2): calcd C 71.77, H 7.74; found C 71.64, H 7.72.

3-Chloro-1-(4-pivaloxyphenyl)-1-propene (6): The procedure described above for the preparation of the allylic chloride **5** was used. The alcohol **4c** (8.05 g, 36.0 mmol, 1 equiv) was treated with thionyl chloride (4.8 g, 2.9 mL, 40 mmol, 1.1 equiv). The usual workup gave a viscous oil, which was purified by flash chromatography (ether/hexanes 1:2), affording the allylic chloride **6** (7.19 g, 29.8 mmol, 83% yield) as white crystals (m.p. 95 °C). IR (KBr): $\tilde{\nu}$ = 2977 (s), 1748 (s), 1507 (s), 1482 (m), 1267 (s), 1200 (s), 1167 (s), 1121 (s), 970 (s) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ = 7.39–7.35 (m, 2H), 7.04–6.99 (m, 2H), 6.62 (d, ^3J(H,H) = 15.7 Hz, 1H), 6.26 (dt, ^3J(H,H) = 15.6, 7.2 Hz, 1H), 4.22 (dd, ^3J(H,H) = 7.1, 1.1 Hz, 2H), 1.35 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 176.9, 151.1, 133.5, 133.2, 127.6, 125.0, 121.6, 45.3, 39.1, 27.1; MS (EI): m/z = 254 ([M + 1], 2), 252 ([M − 1], 8), 168 (14), 133 (52), 85 (22), 57 (100); $C_{14}H_{17}ClO_2$ (252.7): calcd C 66.53, H 6.78; found C 66.68, H 6.79.

4-(4-Pivaloxyphenyl)-1-triisopropylsiloxy-5-hexene (10): The procedure described above for the preparation of **9** was used. 3-Iodo-1-triisopropylsiloxypropane (6.86 g, 20.0 mmol, 1 equiv) was converted to the zinc–copper reagent **8** and was treated with the allylic chloride **6** (4.81 g, 20.0 mmol, 1 equiv). The residual oil was purified by flash chromatography (ether/hexanes 1:10–1:4), affording the product **10** (5.71 g, 13.2 mmol, 66% yield) as a colorless oil. IR (neat): $\tilde{\nu}$ = 2944 (s), 2867 (s), 1756 (s), 1507 (m), 1202 (s), 1167 (s), 1119 (s), 883 (m) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ = 7.17–7.13 (m, 2H), 6.98–6.93 (m, 2H), 5.94–5.83 (m, 1H), 5.02–4.95 (m, 2H), 3.64 (t, ^3J(H,H) = 6.3 Hz, 2H), 3.25–3.20 (m, 1H), 1.78–1.72 (m, 2H), 1.54–1.45 (m, 2H), 1.32 (s, 9H), 1.03–0.98 (m, 21H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 177.0, 149.3, 142.1, 141.6, 128.4, 121.2, 114.0, 63.1, 48.9, 38.9, 31.5, 30.8, 27.1, 18.0, 11.9; MS (FD): m/z = 434 ([M + 1], 6), 433 ([M^+], 18), 432 ([M − 1], 12), 390 (23), 389 (63); $C_{26}H_{44}O_3Si$ (423.7): calcd C 72.17, H 10.25; found C 72.36, H 10.05.

4-(4-Pivaloxyphenyl)-5-hexen-1-ol (12): The TIPS ether **10** (4.33 g, 10.0 mmol) was treated with NBu_4F (11.0 mL of a 1 M solution in THF, 11.0 mmol) at 0 °C for 0.5 h. The solution was further stirred for 0.5 h at RT, and saturated aqueous NH_4Cl (50 mL) was added. The aqueous phase was extracted with ether (3 × 50 mL), the combined organic layer was dried ($MgSO_4$), and the solvent was evaporated. The crude residue was purified by flash chromatography (ether/hexanes 1:10–1:2), affording the alcohol **12** (2.63 g, 9.50 mmol, 95% yield) as a clear oil. IR (neat): $\tilde{\nu}$ = 3309 (m), 3097 (m), 2975 (s), 2875 (s), 1752 (s), 1507 (s), 1202 (s), 1167 (s), 1121 (s) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ = 7.13–7.10 (m, 2H), 6.94–6.90 (m, 2H), 5.91–5.80 (m, 1H), 5.00–4.93 (m, 2H), 3.53 (t, ^3J(H,H) = 6.4 Hz, 2H), 3.22–3.15 (m, 1H), 1.75–1.62 (m, 3H), 1.52–1.33 (m, 2H), 1.28 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 177.1, 149.3, 141.8, 141.3, 128.3, 121.3, 114.2, 62.6, 48.9, 38.9, 31.4, 30.6, 27.0; MS (EI): m/z = 277 ([M + 1], 1), 276 ([M^+], 5), 232 (14), 149 (21), 150 (51), 133 (76), 85 (15), 57 (100); $C_{17}H_{24}O_3$ (276.37): calcd C 73.88, H 8.75; found C 73.90, H 8.51.

3-(4-Pivaloxyphenyl)-6-iodo-1-hexene (1c): The procedure described above for the preparation of **1b** was followed; the alcohol **12** (2.63 g, 9.50 mmol) was used. After flash-chromatographic purification (ether/hexanes 1:20–1:10), the iodide **1c** (2.09 g, 5.42 mmol, 57% yield) was obtained as a colorless oil. IR (neat): $\tilde{\nu}$ = 2975 (m), 1752 (s), 1506 (s), 1479 (w), 1279 (m), 1204 (s), 1167 (s), 1119 (s) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ = 7.15–7.11 (m, 2H), 6.98–6.93 (m, 2H), 5.92–5.80 (m, 1H), 5.02–4.95 (m, 2H), 3.26–3.19 (m, 1H), 3.12 (t, ^3J(H,H) = 6.3 Hz, 2H), 1.79–1.63 (m, 4H), 1.30 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 176.9, 149.5, 141.4, 140.9, 128.3, 121.4, 114.6, 48.2, 39.0, 36.1, 31.3, 27.1, 6.6; MS (EI): m/z = 387 ([M + 1], 2), 386 ([M^+], 18), 302 (15), 134 (10), 133 (100), 85 (27), 57 (86); $C_{17}H_{23}IO_2$ (386.2): calcd C 52.86, H 6.00; found C 52.64, H 5.76.

6-Iodo-3-phenyl-1-hexene (1d): The procedure described above for the preparation of **8** was followed; 3-iodopropyl acetate (22.8 g, 100 mmol) was used. The resulting zinc–copper reagent was treated with cinnamyl chloride (14.5 mL, 95 mmol) as described above. After the usual workup the crude product was deprotected by dissolution of the reaction mixture in MeOH (100 mL) and addition of a solution of K_2CO_3 (41.5 g, 300 mmol) in MeOH (500 mL). After 2 h of stirring at RT, the reaction mixture was worked up, and after evaporation of the solvents the residue was distilled (0.1 mm Hg), affording 4-phenyl-5-hexen-1-ol as a clear oil (11.1 g, 63 mmol, 63% yield). IR (neat): $\tilde{\nu}$ = 3550 (b), 3090 (w), 3030 (w), 2950 (s), 920 (m) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ = 7.35–7.16 (m, 5H), 6.03–5.89 (m, 1H), 5.09–5.00 (m, 2H), 3.63 (t, ^3J(H,H) = 6.4 Hz, 2H), 3.26 (q, ^3J(H,H) = 7.5 Hz, 1H), 1.89–1.70 (m, 2H), 1.67–1.40 (m, 2H), 1.25 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 144.1, 142.0, 128.4, 127.5, 126.4, 126.2, 114.1, 62.8, 49.6, 31.4, 30.7; MS (EI, 70 eV): m/z = 176 (1), 117 (100), 91 (20); $C_{12}H_{16}O$ (176.2): calcd C 81.89, H 9.16; found C 81.33, H 9.21.

This 4-phenyl-5-hexen-1-ol (19.6 g, 111.5 mmol) was used in the procedure described for the preparation of **1b** together with MeI·2DCC (69.5 g, 125 mmol, 1.1 equiv). After flash-chromatographic purification (ether/hexanes 1:10), **1d** (26.15 g, 91.4 mmol, 82% yield) was isolated as a colorless oil. IR (neat): $\tilde{\nu}$ = 3090 (w), 3030 (w), 2950 (s), 920 (m) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ = 7.34–7.15 (m, 5H), 6.02–5.88 (m, 1H), 5.10–5.01 (m, 2H), 3.32–3.21 (m, 1H), 3.15 (t, ^3J(H,H) = 6.4 Hz, 2H), 1.89–1.65 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 143.7, 141.6, 128.6, 127.5, 126.4, 126.0, 114.5, 49.2, 48.9, 36.1, 32.5, 31.4, 6.8; MS (EI): m/z = 287 (1), 286 (8), 117 (100), 91 (23); $C_{12}H_{15}I$ (286.1): calcd C 50.40, H 5.29; found C 50.43, H 5.25.

2-Butyl-6-iodo-1-hexene (1e): Zinc powder (100 g, 170 mmol) was suspended in THF (10 mL) in a 250 mL three-necked flask equipped with an argon inlet, a thermometer, and a rubber septum. The zinc dust was activated by adding 1,2-dibromoethane (0.26 g, 1.4 mmol) and TMSCl (0.05 g, 0.5 mmol) and was heated under reflux for 5 min. After cooling to 35 °C, a solution of 3-iodopropyl acetate [44] (12.7 g, 56 mmol) in THF (11 mL) was added dropwise over 5 min. The reaction mixture was stirred for 0.5 h and then the excess of zinc powder was allowed to settle. The supernatant solution was transferred to a solution of CuCN (6.0 g, 50 mmol) and dry LiCl (4.7 g, 110 mmol) in THF (55 mL) at −50 °C. The reaction mixture was warmed up to 0 °C and cooled again to −78 °C. The copper–zinc reagent was treated with 2-bromomethyl-1-hexene (8.2 g, 47 mmol); the mixture was warmed up to RT and stirred for a further 1.5 h. The excess of the organometallic reagent was quenched with saturated aqueous NH_4Cl (50 mL) at −20 °C. After the usual workup the crude product was purified by chromatography (hexane:ether 10:1) giving 5-butyl-5-hexenyl acetate (8.9 g, 45 mmol, 96%) as a colorless oil.

A solution of this product (9.5 g, 48 mmol) in EtOH (100 mL) was treated with KOH (3.0 g, 97 mmol). The solution was stirred for 1 h at RT. The solvent was distilled off and ether (100 mL) was added. The organic phase was washed successively with 10% aqueous HCl and aqueous NH_4Cl (50 mL) and was dried ($MgSO_4$). The solvents were evaporated, and the residue was purified by chromatography (hexanes:ether 4:1), affording the alcohol (6.7 g, 43 mmol, 89%) as a colorless oil.

To a solution of this alcohol (1.56 g, 10 mmol) in THF (10 mL), 2DCC·MeI (7.0 g, 20 mmol) was added. The reaction mixture was stirred for 16 h at 35 °C and the solvent was evaporated. The residue was extracted with hexanes (100 mL) and then washed with aqueous methanol (20 mL MeOH in 80 mL H_2O). The organic layer was dried ($MgSO_4$) and the solvents were evaporated. The crude product was purified by chromatography (hexanes) giving the iodide **1e** (2.4 g, 9.1 mmol, 91%) as a colorless oil. IR (neat): $\tilde{\nu}$ = 2930 (s), 1640 (m), 1450 (m), 1385 (m), 1265 (m), 1210 (m), 990 (s), 890 (m), 830 (m) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ = 4.65 (m, 2H), 3.14 (t, ^3J(H,H) = 7.0 Hz, 2H), 1.99–1.91 (m, 4H), 1.78–1.71 (m, 2H), 1.52–1.45 (m, 2H), 1.37–1.21 (m, 4H), 0.85 (t, ^3J(H,H) = 7.0 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 149.1, 109.1, 35.5, 34.8, 33.1, 29.9, 28.5, 22.4, 13.9, 6.8; MS (EI): m/z = 224 (7), 97 (20), 55 (100), 41 (26); $C_{10}H_{19}I$ (266.1): calcd C 45.13, H 7.19; found C 45.44, H 7.30.

Diethyl 2-allyl-2-(2-iodoethyl)malonate (1f): Diethyl allylmalonate (16.0 g, 15.8 mL, 89.0 mmol, 1.1 equiv) was added to a suspension of NaH (2.64 g of a 80% suspension in oil, 88.0 mmol, 1.1 equiv) at 0 °C. After stirring for 0.5 h at this temperature, 1,2-dibromoethane (15.0 g, 6.90 mL, 80.0 mmol, 1 equiv) was added and the cooling bath was removed. After stirring for 48 h at RT, the reaction mixture was quenched with saturated aqueous NH_4Cl (50 mL). The aqueous phase was extracted with ether (3 × 100 mL), the combined organic layer was dried ($MgSO_4$), and the solvent was evaporated. The residue was distilled to furnish diethyl 2-allyl-2-bromoethyl malonate (16.0 g, 52.0 mmol, 65% yield) as a clear liquid (b.p. 130 °C, 0.1 mm Hg). IR (neat): $\tilde{\nu}$ = 3075 (w), 2983 (s), 1730 (s), 1638 (w), 1368 (m), 926 (m), 855 (m) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ = 5.65–5.51 (m, 1H), 5.10–5.01 (m, 4H), 4.14 (q, ^3J(H,H) = 7.1 Hz, 6H), 3.32–3.26 (m, 2H), 2.59 (d, ^3J(H,H) = 7.4 Hz, 2H), 2.40–2.34 (m, 2H), 1.19 (t, ^3J(H,H) = 7.1 Hz, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 170.1, 131.7, 119.5, 61.4, 57.4, 37.7, 36.2, 26.9, 13.9; MS (EI): m/z = 234 (58), 232 (61), 200 (98), 199 (100), 153 (81), 108 (61), 81 (85), 79 (63), 67 (53); $C_{12}H_{19}BrO_4$ (307.1): calcd C 46.92, H 6.23; found C 47.06, H 6.27.

This diethyl 2-allyl-2-bromoethylmalonate (16.0 g, 52.0 mmol) was treated with sodium iodide (15.3 g, 52 mmol, 1 equiv) in acetone (80 mL). The reaction mixture was refluxed for 1 h and cooled to RT, and the salts were filtered. A further amount of sodium iodide (23.9 g, 79.9 mmol, 1.5 equiv) was added. After refluxing for 2 h the solvent was evaporated, ether (30 mL) was added and the organic layer was washed with saturated aqueous $Na_2S_2O_3$ (30 mL). The aqueous phase was extracted with ether (3 × 100 mL), the combined organic layer was dried, and the solvent was evaporated. The crude residue was purified by flash chromatography (ether/hexanes 1:10–1:4), affording the iodide **1f** (16.0 g, 45.2 mmol, 87% yield) as a clear liquid.

IR (neat): $\tilde{\nu}$ = 3075 (w), 2976 (s), 1730 (s), 1638 (w), 1367 (m), 919 (m), 855 (m) cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.68–5.54 (m, 1H), 5.20–5.08 (m, 2H), 4.18 (q, ^3J(H,H) = 7.1 Hz, 4H), 3.10–3.04 (m, 2H), 2.61 (d, ^3J(H,H) = 7.4 Hz, 2H), 2.48–2.42 (m, 2H), 1.23 (t, ^3J(H,H) = 7.1 Hz, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 170.0, 131.8, 119.5, 61.5, 59.0, 37.8, 37.4, 14.0, −2.5; MS (EI): m/z = 263 (24), 227 (100), 200 (34), 171 (22), 153 (32), 125 (39), 109 (52), 81 (58); $C_{12}H_{19}IO_4$ (354.1): calcd C 40.69, H 5.41; found C 40.94, H 5.51.

6-Iodo-1-heptene (1g): The procedure described above for the preparation of **1b** was repeated with 6-hepten-2-ol (**15g**) [50] (4.40 g, 30 mmol) and MeI·2DCC (21 g, 38 mmol, 1.25 equiv). After the usual workup the residue was purified by flash chromatography (ether/hexanes 1:10), giving the unsaturated iodide **1g** (4.0 g, 18 mmol, 60% yield) as a colorless oil. IR (neat): $\tilde{\nu}$ = 2925 (vs), 1641 (m), 1447 (s) cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.71 (ddt, ^3J(H,H) = 17.1, 10.3, 6.6 Hz, 1H), 4.91 (d, ^3J(H,H) = 17.1 Hz, 1H), 4.89 (d, ^3J(H,H) = 10.1 Hz, 1H), 4.10 (m, 1H), 2.00 (m, 2H), 1.81 (d, ^3J(H,H) = 6.8 Hz, 3H), 1.78 (m, 1H), 1.52 (m, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 138.1, 114.9, 42.5, 32.8, 29.7, 29.0, 28.9; MS (EI): m/z = 224 ([M^+], 1.3), 97 (52), 55 (100); $C_7H_{13}I$ (224.0): calcd C 37.67, H 5.87; found C 37.50, H 5.79.

7-Octen-3-ol (15h): The procedure described above for the preparation of **4b** was repeated with 5-hexenal and ethylmagnesium bromide (20 mL of 1.0 M solution, 20 mmol, 1 equiv). The crude residue was purified by flash chromatography (ether/hexanes 1:10–1:4), affording the alcohol **15h** (1.72 g, 13.4 mmol, 67% yield) as a colorless oil. IR (neat): $\tilde{\nu}$ = 3403 (m), 2940 (s), 1638 (m), 1453 (m) cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$): δ = 5.83–5.65 (m, 1H), 5.01–4.83 (m, 2H), 2.03–1.87 (m, 2H), 1.59–1.20 (m, 8H), 0.88 (t, ^3J(H,H) = 7.4 Hz, 3H); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 139.2, 115.0, 75.0, 38.0, 34.7, 31.4, 23.2, 8.2; MS (EI): m/z = 128 ([M^+], 46), 127 ([$M^+ - 1$], 100); $C_8H_{16}O$ (128.2): calcd C 74.94, H 12.58; found C 74.75, H 12.70.

6-Iodo-1-octene (1h): The procedure described above for the preparation of **1b** was performed with **15h** (1.67 g, 13.0 mmol, 1 equiv) and MeI·2DCC (9.1 g, 16.3 mmol, 1.25 equiv). Flash-chromatographic purification (hexanes) gave the pure alkyl iodide **1h** (1.64 g, 6.89 mmol, 53% yield) as a colorless oil. IR (neat): $\tilde{\nu}$ = 2961 (s), 2932 (s), 1638 (m), 1453 (m) cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.80–5.64 (m, 1H), 4.99–4.87 (m, 2H), 4.06–3.98 (m, 1H), 2.10–1.98 (m, 2H), 1.88–1.38 (m, 6H), 0.96 (t, ^3J(H,H) = 7.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 138.2, 114.9, 41.8, 39.6, 33.7, 32.9, 28.8, 14.1; MS (EI): m/z = 113 (1), 111 (25), 69 (100), 55 (63); $C_8H_{15}I$ (238.1): calcd C 40.36, H 6.34; found C 40.55, 6.46.

1-Cyclohexyl-6-hexen-1-ol (15i): The procedure described above for the preparation of **4b** was used. 5-Hexenal (1.96 g, 20.0 mmol, 1 equiv) was treated with cyclohexylmagnesium bromide (26 mL of a 0.85 M solution, 22.1 mmol, 1.1 equiv). The crude residue was purified by flash chromatography (ether/hexanes 1:15–1:6), affording the alcohol **15i** (2.84 g, 15.6 mmol, 78% yield) as a colorless oil. IR (neat): $\tilde{\nu}$ = 3360 (m), 2926 (s), 2855 (s), 1638 (w) cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$): δ = 5.78–5.52 (m, 1H), 4.93–4.75 (m, 2H), 3.26–3.15 (m, 1H), 2.01–1.81 (m, 2H), 1.79–0.78 (m, 18H); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 139.1, 114.8, 76.3, 44.0, 34.2, 33.9, 29.6, 28.2, 26.9, 26.8, 26.6, 25.6; MS (EI): m/z = 182 ([M^+], 1), 139 (13), 113 (13), 95 (82), 81 (100); $C_{12}H_{22}O$ (182.3): calcd C 79.06, H 12.16; found C 79.02, H 12.19.

6-Cyclohexyl-6-iodo-1-hexene (1i): The procedure described above for the preparation of **1b** was followed. The alcohol **15i** (2.74 g, 15.0 mmol, 1.0 equiv) was treated with MeI·2DCC (10.4 g, 18.8 mmol, 1.3 equiv). Flash-chromatographic purification (hexanes) gave the unsaturated iodide **1i** (2.10 g, 7.20 mmol, 48% yield) as a colorless oil. IR (neat): $\tilde{\nu}$ = 2926 (s), 2848 (s), 1638 (l), 1446 (m) cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.88–5.72 (m, 1H), 5.08–4.92 (m, 2H), 4.18–4.06 (m, 1H), 2.18–1.62 (m, 12H), 1.58–1.02 (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 138.2, 114.8, 49.8, 44.9, 37.1, 32.8, 32.7, 31.2, 29.1, 26.2, 26.0, 25.9; MS (EI): m/z = 223 (7), 165 (7), 59 (5), 58 (20), 39 (100); $C_{12}H_{21}I$ (292.2): calcd C 49.33, H 7.24; found C 49.40, H 7.23.

5-Hydroxy-9-decenylacetate (15j): 4-Iodobutyl acetate (9.64 g, 40.0 mmol) was converted to the corresponding copper–zinc reagent, following the procedure described for the preparation of **9**. The copper–zinc reagent dissolved in THF (60 mL) was cooled to −78 °C and BF_3·Et_2O (9.90 mL, 80 mmol, 2 equiv) and 5-hexenal (3.90 g, 40.0 mmol) were added dropwise. The reaction mixture was allowed to warm to −20 °C and was stirred for 12 h. After the usual workup and evaporation of the solvents, the residual oil obtained was purified by flash chromatography (ether/hexanes 1:1), affording the alcohol **15j** (4.70 g, 26.5 mmol, 64% yield) as a colorless oil. IR (neat): $\tilde{\nu}$ = 3470 (br), 2910 (s), 1710 (vs), 1625 (w) cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.79–5.63 (m, 1H), 4.86 (d, ^3J(H,H) = 20.5 Hz, 1H), 4.79 (d, ^3J(H,H) = 11.2 Hz, 1H), 4.00 (t, ^3J(H,H) = 6.6 Hz, 2H), 3.43–3.41 (m, 1H), 2.67 (s, 1H), 1.91 (s, 3H), 1.50–1.47 (m, 4H), 1.37–1.30 (m, 8H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 171.1, 138.5, 114.5, 71.1, 64.3, 36.8, 36.7, 33.5, 28.5, 24.7, 21.9, 20.8; MS (EI): m/z = 111 (18), 85 (100), 56 (93); $C_{12}H_{22}O_3$ (214.3): calcd C 67.26, H 10.35; found C 67.24, H 10.53.

5-Iodo-9-decenyl acetate (1j): The procedure described above for the preparation of **1b** was repeated with **15j** (1.90 g, 10.0 mmol) and MeI·2DCC (6.9 g, 12.5 mmol, 1.25 equiv). After flash-chromatographic purification (ether/hexanes 1:9) the alkyl iodide **1j** (2.20 g, 7.10 mmol, 71% yield) was isolated as a colorless oil. IR (neat): $\tilde{\nu}$ = 2920 (s), 1752 (vs), 1250 (vs) cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.72 (m, 1H), 4.95 (d, ^3J(H,H) = 18.7 Hz, 1H), 4.92 (d, ^3J(H,H) = 10.2 Hz, 1H), 4.08–4.04 (m, 3H), 2.04–2.02 (m, 3H), 1.99 (s, 3H), 1.80–1.77 (m, 2H), 1.53–1.46 (m, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 170.9, 138.2, 115.0, 64.1, 40.2, 39.8, 39.0, 32.8, 28.7, 27.8, 26.0, 21.0; MS (EI): m/z = 155 (2), 137 (30), 95 (100); $C_{12}H_{22}IO_2$ (198.3): calcd C 44.58, H 6.54; found C 44.46, H 6.66.

1-Cyano-8-nonen-4-ol (15k): The procedure described above for the preparation of **15j** was followed; 4-iodobutyronitrile (7.76 g, 40.0 mmol) was used. After the usual workup, the residual oil was purified by flash chromatography (ether/hexanes 1:1), affording the alcohol **15k** (4.10 g, 25.0 mmol, 62% yield) as a colorless oil. IR (neat): $\tilde{\nu}$ = 3446 (vs), 2934 (vs), 2247 (m), 1458 (s), 1427 (s) cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.67–5.61 (m, 1H), 4.81 (d, ^3J(H,H) = 19.4 Hz, 1H), 4.76 (d, ^3J(H,H) = 11.0 Hz, 1H), 3.39 (m, 1H), 3.28 (s, 1H), 2.20 (t, ^3J(H,H) = 7.1 Hz, 2H), 1.88–1.87 (m, 2H), 1.66–1.64 (m, 2H), 1.60–1.58 (m, 2H), 1.40–1.34 (m, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 138.4, 119.7, 114.5, 70.3, 36.9, 35.8, 33.4, 24.6, 21.6, 16.9; MS (EI): m/z = 98 (21), 81 (65), 54 (100); $C_{10}H_{17}NO$ (167.2): calcd C 71.81, H 10.25, N 8.37; found C 71.62, H 10.50, N 8.44.

5-Iodo-9-decenenitrile (1k): The procedure described above for the preparation of **1b** was repeated with the alcohol **15k** (4.10 g, 25.0 mmol) and MeI·2DCC (17.25 g, 31.3 mmol, 1.25 equiv). After flash-chromatographic purification (ether/hexanes 1:4), the iodide **1k** (4.00 g, 15.0 mmol, 60% yield) was isolated as a colorless oil. IR (neat): $\tilde{\nu}$ = 2920 (vs), 2250 (m), 1630 (s) cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.69 (ddt, ^3J(H,H) = 17.1, 10.2, 6.7 Hz, 1H), 4.90 (d, ^3J(H,H) = 17.0 Hz, 1H), 4.86 (d, ^3J(H,H) = 10.0 Hz, 1H), 4.02–3.93 (m, 1H), 2.27 (t, ^3J(H,H) = 6.6 Hz, 2H), 2.02–2.00 (m, 1H), 1.99–1.97 (m, 2H), 1.88–1.86 (m, 3H), 1.67–1.62 (m, 2H), 1.51–1.44 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 138.1, 119.3, 115.2, 39.9, 37.0, 33.1, 28.7, 25.6, 16.5; MS (EI): m/z = 148 (58), 147 (10), 41 (100); $C_{10}H_{16}IN$ (277.1): calcd C 43.48, H 5.83, N 5.07; found C 43.84, H 6.02, N 5.12.

2-Hydroxy-6-heptenyl pivalate (15l): The zinc–copper compound IZnCu(CN)$CH_2OCOtC_4H_9$ was prepared from iodomethyl pivalate [44] (4.84 g, 20.0 mmol, 1 equiv) at 12 °C. The solution of the zinc–copper organometallic compound in THF (25 mL) was treated with 5-hexenal (1.96 g, 20.0 mmol, 1 equiv) and then BF_3·OEt_2 (5.68 g, 40.0 mmol, 2 equiv) at −78 °C. The solution was warmed to −10 °C and was stirred at this temperature overnight. After the usual workup, the crude residue was purified by flash chromatography (ethyl acetate/hexanes 1:1), affording the alcohol **15l** (2.47 g, 11.5 mmol, 58% yield) as a colorless oil. IR (neat): $\tilde{\nu}$ = 3474 (m), 2976 (m), 1716 (s), 1637 (m), 1161 (s) cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.82–5.74 (m, 1H), 5.00–4.86 (m, 2H), 4.06–4.00 (m, 1H), 3.96–3.86 (m, 1H), 3.82–3.70 (m, 1H), 2.32–2.28 (m, 1H), 2.04–1.98 (m, 2H), 1.50–1.38 (m, 4H), 1.16 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 178.6, 138.3, 114.7, 69.8, 68.4, 38.8, 33.4, 32.7, 72.1, 24.5; MS (EI): m/z = 196 (1), 145 (1), 116 (12), 103 (6), 101 (29); $C_{12}H_{18}O_3$ (210.2): calcd C 67.26, H 10.35; found C 67.20, H 10.60.

2-Iodo-6-heptenyl pivalate (1l): The procedure described above for the preparation of **1b** was repeated with **15l** (2.43 g, 15.0 mmol, 1 equiv) and MeI·2DCC (7.83 g, 14.1 mmol, 1.25 equiv). Flash-chromatographic purification (hexanes) gave the alkyl iodide **1l** (1.69 g, 5.21 mmol, 46% yield) as a colorless oil. IR (neat): $\tilde{\nu}$ = 2976 (m), 1730 (s), 1638 (m), 1148 (s) cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.78–5.62 (m, 1H), 5.00–4.86 (m, 2H), 4.30–4.06 (m, 3H), 2.06–1.98 (m, 2H), 1.78–1.54 (m, 3H), 1.48–1.34 (m, 1H), 1.14 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 177.6, 137.8, 115.1, 68.8, 38.8, 35.7, 32.7, 30.6, 28.2, 27.1; MS (EI): m/z = 197 (13), 111 (16), 69 (54), 57 (100); $C_{12}H_{21}IO_2$ (320.1): calcd C 44.46, H 6.53; found C 44.50, H 6.61.

1,8-Nonadien-4-ol (15m): The procedure described above for the preparation of **4b** was repeated with 5-hexenal (1.96 g, 20.0 mmol, 1 equiv) and allylmagnesium bromide (20 mL of a 1.0 M solution in ether, 20.0 mmol, 1 equiv). The crude residue was purified by flash chromatography (ether/hexanes 1:15–1:6), affording the alcohol **15m** (1.94 g, 13.8 mmol, 69% yield) as a colorless oil. IR (neat): $\tilde{\nu}$ = 3445 (m), 3075 (m), 2933 (s), 1638 (s), 991 (s) cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$): δ = 5.82–5.61 (m, 2H), 5.12–4.85 (m, 5H), 2.19–2.11 (m, 4H), 2.03–1.96 (m, 1H), 1.43–1.27 (m, 4H); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 137.6, 132.7, 117.7, 113.7, 72.4, 42.7, 37.6, 33.1, 21.7; MS (EI): m/z = 140 ([M^+], 6), 139 ([$M^+ - 1$], 100); $C_9H_{16}O$ (140.1): calcd C 77.15, H 11.51; found C 77.41, H 11.21.

4-Iodo-1,8-nonadiene (1m): The procedure described above for the preparation of **1b** was repeated with the alcohol **15m** (1.88 g, 13.4 mmol, 1 equiv) and MeI·2DCC (9.29 g, 16.8 mmol, 1.25 equiv). Flash-chromatographic purification (hexanes) gave the alkyl iodide **1m** (1.98 g, 7.92 mmol, 59% yield) as a colorless oil. IR (neat): $\tilde{\nu}$ = 2930 (vs), 1650 (s), 1430 (s), 990 (s), 920 (vs) cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.80–5.69 (m, 2H), 5.11–4.89 (m, 4H), 4.04–4.03 (m, 1H), 2.61–2.55 (m, 2H), 2.05–2.00 (m, 2H), 1.80–1.60 (m, 3H), 1.46–1.38 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 138.2, 136.4, 117.7, 115.1, 44.9, 39.3, 36.8, 32.9, 28.8; MS (EI): m/z = 123 (13), 81 (89), 67 (61), 41 (100); $C_9H_{15}I$ (250.1): calcd C 44.22, H 6.05; found C 43.39, H 6.17.

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2-(3-Butenyl)cyclohexan-1-ol (16): To a suspension of magnesium turnings (3.65 g, 150 mmol) in ether (20 mL), a solution of 1-iodo-3-butene (10.0 g, 55 mmol) in ether (30 mL) was added over 0.5 h, while the temperature was maintained below 35 °C. After completion of the addition, the reaction mixture was stirred for 0.5 h. The solution was decanted to remove the excess magnesium, and 1,4-dioxane (2.29 g, 25 mmol) was added. After stirring for 15 min, the precipitate was allowed to settle. The supernatant solution was transferred to a suspension of CuCN (2.23 g, 25 mmol) in THF (50 mL) at −78 °C and was stirred for 1 h at this temperature. Then $BF_3 \cdot OEt_2$ (3.54 g, 25 mmol) was added and stirring was continued for 5 min, followed by the addition of cyclohexene oxide (2.45 g, 25 mmol) at −78 °C. The reaction mixture was warmed up to −18 °C and was stirred for 3 h. It was quenched with saturated aqueous NH_4Cl and worked up as usual. The crude product was purified by chromatography (hexanes/ether 4:1) giving the alcohol **16** (2.58 g, 17 mmol, 68%) as a colorless oil (as a 1:1 mixture of diastereomers). IR (neat): $\tilde{\nu}$ = 3360 (br), 2915 (s), 1640 (m), 1445 (m), 1645 (m), 990 (m), 970 (m), 915 (s) 750 (m) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ = 5.78–5.69 (m, 2H), 4.97–4.83 (m, 4H), 3.79 (s, 1H), 3.15–3.11 (m, 1H), 2.09–1.11 (m, 26H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 139.0, 138.9, 14.1, 113.9, 74.3, 69.0, 44.4, 40.5, 35.5, 32.9, 31.3, 31.0, 30.8, 30.7, 29.9, 26.3, 25.3, 24.9, 24.7, 20.3; MS (EI): *m/z* = 154 ([*M*$^+$], 5), 136 (14), 121 (20), 111 (100), 98 (46), 94 (37), 81 (67), 57 (70), 41 (42); $C_{10}H_{18}O$ (154.2): calcd C 77.87, H 11.76; found C 77.92, H 11.92.

***trans*-2-(3-Butenyl)-1-iodocyclohexane (1n)**: To a solution of triphenylphosphine (2.67 g, 14 mmol) in dichloromethane (14 mL) iodine (3.56 g, 14 mmol) was added at 0 °C. After stirring at RT for 10 min, imidazole (0.95 g, 14 mmol) was added and stirring was continued for an additional 20 min, after which the alcohol **16** (1.08 g, 7.0 mmol) was added. After stirring for 2 h at RT the resulting suspension was filtered over a plug of silica gel and washed with hexanes (2 × 50 mL). The solvents were evaporated and the residue was purified by chromatography (hexanes), affording the alkyl iodide **1n** (1.63 g, 6.2 mmol, 89%) as a colorless oil. IR (neat): $\tilde{\nu}$ = 2920 (s), 1640 (m), 1445 (s), 1255 (m), 1166 (m), 995 (m), 910 (s) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ = 5.85–5.72, (m, 1H), 5.05–4.92 (m, 2H), 4.70 (m, 2H), 2.18–1.97 (m, 4H), 1.75–1.70 (m, 3H), 1.60–1.40 (m, 2H), 1.36–1.26 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 138.3, 114.6, 47.6, 41.5, 37.2, 36.6, 30.1, 28.8, 25.7, 22.7; MS (EI): *m/z* = 136 (44), 95 (95), 81 (100), 67 (48), 55 (63), 47 (45); $C_{10}H_{17}I$ (264.1): calcd C 45.47, H 6.49; found C 45.69, H. 6.71.

3-Benzyloxy-6-iodo-1-hexene (1o): 6-Chloro-1-hexen-3-ol (**18**) [13b] (2.60 g, 19.3 mmol) and benzyl 2,2,2-trichloroacetimidate (6.34 g, 4.68 mL, 25.1 mmol, 1.3 equiv) were dissolved in cyclohexane/dichloromethane 2:1 (39 mL) and triflic acid (0.43 g, 0.25 mL, 2.85 mmol, 0.15 equiv) was added. An exothermic reaction is observed. The reaction mixture was stirred for 3 h, filtered, and quenched with $NaHCO_3$ solution (30 mL). The aqueous phase was extracted with ether (2 × 50 mL), the combined organic layer was dried ($MgSO_4$), and the solvent was evaporated. The crude residue was purified by flash chromatography (ether/hexanes 1:20–1:10) to afford the desired benzyl ether (3.17 g, 14.1 mmol, 73% yield). IR (neat): $\tilde{\nu}$ = 2954 (m), 2855 (s), 1766 (m), 1638 (w), 1446 (s), 1069 (s), 926 (s), 734 (s), 699 (s) cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$): δ = 7.32–7.16 (m, 5H), 5.77–5.58 (m, 1H), 5.20–5.11 (m, 2H), 4.52 (d, ^3J(H,H) = 11.9 Hz, 1H), 4.26 (d, ^3J(H,H) = 11.9 Hz, 1H), 3.75–3.65 (m, 1H), 3.47–3.40 (m, 2H), 1.94–1.52 (m, 4H); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 138.8, 128.6, 128.0, 127.8, 117.8, 79.9, 70.4, 45.3, 33.1, 28.9; MS (EI): *m/z* = 225 ([*M* + 1], 0.5), 210 (1), 147 (14), 92 (12), 91 (100), 65 (6); $C_{13}H_{17}ClO$ (224.7): calcd C 69.48, H 7.62; found C 69.21, H 7.56.

The procedure described above for the preparation of **1f** was repeated with 3-benzyloxy-6-chloro-1-hexene (3.14 g, 14.0 mmol) in acetone (30 mL) and sodium iodide (5.24 g, 35.0 mmol, 2.5 equiv). The usual workup gave a viscous oil, which was purified by flash chromatography (ether/hexanes 1:50–1:20), affording the alkyl iodide **1o** (3.59 g, 11.3 mmol, 83% yield) as a colorless oil. IR (neat): $\tilde{\nu}$ = 2926 (s), 2855 (s), 1638 (w), 1069 (s), 926 (m), 734 (s), 692 (s) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ = 7.40–7.31 (m, 5H), 5.79 (ddd, ^3J(H,H) = 16.8, 10.7, 7.7 Hz, 1H), 5.31–5.24 (m, 2H), 4.64 (d, ^3J(H,H) = 11.9 Hz, 1H), 4.39 (d, ^3J(H,H) = 11.9 Hz, 1H), 3.84–3.76 (m, 1H), 3.21 (t, ^3J(H,H) = 6.9 Hz, 2H), 2.00–1.60 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 138.5, 128.3, 127.6, 127.4, 117.3, 79.2, 70.0, 36.3, 29.4, 6.6; MS (EI): *m/z* = 316 ([*M*$^+$], 0.04), 224 (1), 189 (3), 147 (21), 92 (21), 91 (100), 65 (12); $C_{13}H_{17}IO$ (316.1): calcd C 49.38, H 5.42; found C 49.35, H 5.63.

3-Benzoyloxy-6-iodo-1-hexene (1p): To a solution of pyridine (1.74 g, 1.78 mL, 22.0 mmol, 1.1 equiv) and benzoyl chloride (3.09 g, 2.55 mL, 22.0 mmol, 1.1 equiv) in CH_2Cl_2 (15 mL) was added the alcohol **18** (2.69 g, 20.0 mmol, 1 equiv) at 0 °C. The cooling bath was removed and the reaction mixture was stirred for 12 h at RT and quenched with saturated aqueous NH_4Cl (50 mL). The aqueous layer was extracted with CH_2Cl_2 (3 × 30 mL), the combined organic layer was dried ($MgSO_4$) and the solvent was evaporated. The crude residue was purified by flash chromatography (ether/hexanes 1:4), affording 3-benzoyloxy-6-chloro-1-hexene (3.92 g, 16.4 mmol, 82% yield). IR (neat): $\tilde{\nu}$ = 3068 (w), 2954 (m), 1716 (s), 1645 (w), 1602 (w), 1446 (m), 1268 (s), 1111 (s), 713 (s) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ = 8.08–8.05 (m, 2H), 7.59–7.53 (m, 1H), 7.47–7.42 (m, 2H), 5.96–5.84 (m, 1H), 5.58–5.52 (m, 1H), 5.38–5.32 (m, 1H), 5.25–5.21 (m, 1H), 3.58 (t, ^3J(H,H) = 5.9 Hz, 2H), 1.98–1.84 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 165.6, 135.9, 132.7, 130.2, 129.4, 128.3, 116.9, 74.2, 44.5, 31.5, 28.1; MS (FD): *m/z* = 240 ([*M* + 2], 21), 239 ([*M* + 1], 10), 238 ([*M*$^+$], 100), 223 (1), 203 (1), 105 (3); $C_{13}H_{15}O_2Cl$ (238.7): calcd C 65.41, H 6.33; found C 65.21, H 6.46.

The procedure for the preparation of **1f** was used with 3-benzoyloxy-6-chloro-1-hexene (3.70 g, 15.5 mmol, 1 equiv) in acetone (30 mL) and sodium iodide (5.81 g, 38.8 mmol, 2.5 equiv). The usual workup gave an oil, which was purified by flash chromatography (ether/hexanes 1:10–1:4) to afford the alkyl iodide **1p** (4.45 g, 13.5 mmol, 87% yield) as a colorless oil. IR (neat): $\tilde{\nu}$ = 2954 (w), 1721 (s), 1648 (w), 1451 (m), 1272 (s), 1111 (s), 712 (s) cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$): δ = 8.09–8.02 (m, 2H), 7.60–7.39 (m, 3H), 5.88 (ddd, ^3J(H,H) = 17.3, 10.5, 6.2 Hz, 1H), 5.56–5.47 (m, 1H), 5.33 (ddd, ^3J(H,H) = 17.3, 1.3, 1.2 Hz, 1H), 5.22 (ddd, ^3J(H,H) = 10.5, 1.3, 1.2 Hz, 1H), 3.21 (t, ^3J(H,H) = 6.5 Hz, 2H), 1.96–1.82 (m, 4H); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 165.6, 135.9, 133.0, 130.2, 129.5, 128.3, 117.1, 74.0, 35.0, 28.9, 6.1; MS (EI): *m/z* = 203 (6), 123 (3), 105 (100), 81 (23), 77 (19), 54 (11), 51 (6), 41 (7); $C_{13}H_{15}IO_2$ (330.1): calcd C 47.29, H 4.58; found C 47.36, H 4.64.

4-Triisopropylsiloxybutan-1-ol (19): To a solution of pyridine (8.70 g, 8.90 mL, 110 mmol, 1.0 equiv) and TIPSCl (21.2 g, 23.3 mL, 110 mmol, 1.0 equiv) in CH_2Cl_2 (100 mL) was added 1,4-butanediol (39.6 g, 39.1 mL, 440 mmol, 4 equiv) at 0 °C. The reaction mixture was stirred for 12 h at RT and was quenched with saturated aqueous NH_4Cl (100 mL). The organic layer was washed successively with saturated aqueous $NaHCO_3$ (100 mL) and brine (50 mL), dried ($MgSO_4$) and concentrated in vacuo. The residue was distilled (78 °C, 0.1 mm Hg) to furnish the alcohol **19** (22.3 g, 90.5 mmol, 82% yield) as a colorless liquid. IR (neat): $\tilde{\nu}$ = 3346 (m), 2940 (s), 2862 (s), 1460 (m), 1104 (s) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ = 3.69–3.65 (m, 2H), 3.62–3.53 (m, 2H), 2.87 (brs, 1H), 1.65–1.54 (m, 4H), 1.09–0.93 (m, 3H), 0.99 (d, ^3J(H,H) = 4.2 Hz, 18H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 63.5, 62.6, 30.1, 29.9, 17.9, 12.1; MS (FI): *m/z* = 247 ([*M* + 1], 5), 245 ([*M* − 1], 1), 205 (6), 204 (16), 203 (100); $C_{13}H_{30}O_2Si$ (246.4): calcd C 63.35, H 12.27; found C 63.21, H 12.37.

4-Triisopropylsiloxybutanal (20): To a suspension of PCC (19.4 g, 89.8 mmol, 1.1 equiv) and Celite (30 g) in CH_2Cl_2 (120 mL) was added the alcohol **19** (20.1 g, 81.6 mmol, 1 equiv) at 0 °C. The reaction mixture was stirred overnight at RT and filtered over a short plug of silica gel. The solvent was evaporated and the crude residue was purified by flash chromatography (ether/hexanes 1:50–1:10), resulting in the aldehyde **20** (14.2 g, 57.9 mmol, 71% yield) as a clear oil. IR (neat): $\tilde{\nu}$ = 2869 (s), 1709 (s), 1461 (m), 1104 (s), 877 (m) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ = 9.74 (t, ^3J(H,H) = 1.7 Hz, 1H), 3.67 (t, ^3J(H,H) = 5.9 Hz, 2H), 2.47 (dt, ^3J(H,H) = 7.1, 1.7 Hz, 2H), 1.85–1.76 (m, 2H), 1.07–0.92 (m, 3H), 0.98 (d, ^3J(H,H) = 3.7 Hz, 18H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 202.5, 62.3, 40.7, 25.6, 17.9, 11.9; MS (FI): *m/z* = 245 ([*M* + 1], 0.3), 217 (4), 203 (5), 202 (17), 201 (100), 187 (2); $C_{13}H_{28}O_2Si$ (244.4): calcd C 63.87, H 11.54; found C 63.72, H 11.55.

6-Triisopropylsiloxy-1-hexen-3-ol (21): The procedure described above for the preparation of **4b** was repeated with the aldehyde **20** (13.9 g, 56.9 mmol) and vinylmagnesium bromide (39.0 mL of a 1.6 M solution in THF, 62.4 mmol, 1.1 equiv). The usual workup gave a viscous oil, which was purified by flash chromatography (ether/hexanes 1:20–1:4), affording the allylic alcohol **21** (12.9 g, 47.2 mmol, 83% yield) as a clear oil. IR (neat): $\tilde{\nu}$ = 3381 (m), 2940 (s), 2862 (s), 1460 (w), 1104 (m) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ = 5.81 (ddd, ^3J(H,H) = 17.2, 10.4, 5.9 Hz, 1H), 5.20–5.13 (m, 1H), 5.04–4.98 (m, 1H), 4.12–4.02 (m, 1H), 3.69–3.63 (m, 2H), 2.72 (brs, 1H), 1.65–1.53 (m, 4H), 1.07–0.94 (m, 3H), 0.99 (d, ^3J(H,H) = 4.2 Hz, 18H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 141.3, 114.2, 72.7, 63.6, 34.4, 28.9, 18.0, 12.0; MS (EI): *m/z* = 131 (11), 119 (11), 103 (10), 82 (8), 81 (100), 75 (14); $C_{15}H_{32}O_2Si$ (272.5): calcd C 66.11, H 11.83; found C 65.76, H 11.77.

4-Benzyloxy-1-triisopropylsilyloxy-5-hexene (22): To a solution of the alcohol **21** (12.7 g, 46.6 mmol, 1 equiv) and benzyl bromide (8.76 g, 6.10 mL, 51.3 mmol, 1.1 equiv) in DMF (70 mL) was added NaH (3.0 g of a 80% suspension in oil, 51.3 mmol, 1.1 equiv) at −20 °C. The reaction mixture was slowly warmed to RT and then quenched with saturated aqueous NH_4Cl (150 mL). The aqueous layer was extracted with ether (3 × 100 mL), the combined organic layer was dried ($MgSO_4$), and the solvent was evaporated. The crude residue was purified by flash chromatography (ether/hexanes 1:50–1:10), affording the protected alcohol **22** as a colorless oil. IR (neat): $\tilde{\nu}$ = 2940 (s), 2862 (s), 1716 (m), 1460 (m), 1270 (w), 1097 (s), 884 (m) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ = 7.39–7.29 (m, 5H), 5.81 (ddd, ^3J(H,H) = 18.8, 11.0, 7.8 Hz, 1H), 5.30–5.23 (m, 2H), 4.65 (d, ^3J(H,H) = 11.9 Hz, 1H), 4.41 (d, ^3J(H,H) = 11.9 Hz, 1H), 3.84–3.78 (m, 1H), 3.74–3.71 (m, 2H), 1.79–1.60 (m, 4H), 1.18–1.03 (m, 3H), 1.11 (d, ^3J(H,H) = 3.1 Hz, 18H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 139.1, 138.8, 128.2, 127.6, 127.2, 116.8, 80.3, 69.9, 63.1, 31.7, 28.7, 17.9, 11.9; MS (FD): *m/z* = 362 ([*M*$^+$], 1), 361 ([*M* − 1], 1), 319 (3), 255 (1), 157 (1), 105 (1); $C_{22}H_{38}O_2Si$ (362.6): calcd C 72.87; H 10.56; found C 72.86, H 10.64.

4-Benzyloxy-5-hexen-1-ol (23): The protected alcohol **22** (12.1 g, 33.4 mmol) was dissolved in ethanol and an aqueous 0.01 N HCl solution (50 mL) was added. The reaction mixture was heated under reflux for 0.5 h and ethanol was evaporated. The aqueous layer was extracted with ether (3 × 100 mL), the combined organic layer was dried ($MgSO_4$), and the solvent was evaporated. The crude residue was purified by flash chromatography (hexanes, then ether/hexanes 1:4), affording the deprotected alcohol **23** (6.27 g, 30.4 mmol, 91% yield) as a colorless oil. IR (neat):

$\tilde{\nu}$ = 3395 (s), 2940 (s), 2869 (m), 1716 (s), 1446 (w), 1268 (s), 1062 (s) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ = 7.33–7.23 (m, 5H), 5.74 (ddd, $^3J(H,H)$ = 16.7, 10.9, 7.8 Hz, 1H), 5.24–5.18 (m, 2H), 4.59 (d, $^3J(H,H)$ = 11.8 Hz, 1H), 4.34 (d, $^3J(H,H)$ = 11.8 Hz, 1H), 3.79–3.73 (m, 1H), 3.60–3.55 (m, 2H), 2.21 (brs, 1H), 1.72–58 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 138.7, 138.4, 128.3, 127.8, 127.5, 117.3, 80.4, 70.2, 62.7, 32.2, 28.7; MS (FD): *m/z* = 208 ([*M* + 2], 2), 207 ([*M* + 1], 63), 206 ([*M*$^+$], 1), 147 (8), 107 (8), 91 (26); $C_{13}H_{18}O_2$ (206.2): calcd C 75.69, H 8.74; found C 75.45, H 8.88.

4-Benzyloxy-5-hexenal (24): The procedure described above for the preparation of **20** was repeated with the alcohol **23** (6.03 g, 29.2 mmol) and PCC (6.94 g, 32.1 mmol, 1.1 equiv). The usual workup gave a viscous oil, which was purified by flash chromatography (ether/hexanes 1:50–1:4), affording the aldehyde **24** (4.53 g, 22.1 mmol, 76% yield) as a colorless oil. IR (neat): $\tilde{\nu}$ = 3033 (w), 2931 (m), 2863 (m), 1723 (s), 1455 (m), 1071 (s), 698 (s) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ = 9.71 (t, $^3J(H,H)$ = 1.6 Hz, 1H), 7.34–7.24 (m, 5H), 5.72 (ddd, $^3J(H,H)$ = 16.4, 11.2, 7.5 Hz, 1H), 5.26–5.20 (m, 2H), 4.55 (d, $^3J(H,H)$ = 11.8 Hz, 1H), 4.30 (d, $^3J(H,H)$ = 11.8 Hz, 1H), 3.80–3.73 (m, 1H), 2.52–2.43 (m, 2H), 1.98–1.79 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 202.2, 138.5, 138.3, 128.5, 127.9, 127.7, 117.9, 79.4, 70.3, 40.1, 28.2; MS (FD): *m/z* = 205 ([*M* + 1], 1), 153 (1), 122 (1), 107 (1), 91 (16); $C_{13}H_{16}O_2$ (204.2): calcd C 76.44, H 7.95; found C 76.45, H 7.89.

5-Benzyloxy-6-hepten-2-ol (25): The procedure described above for the preparation of **4b** was repeated with the aldehyde **24** (4.42 g, 21.6 mmol) and methylmagnesium bromide (23.8 mL of a 1 M solution in THF, 23.8 mmol, 1.1 equiv). The usual workup gave a viscous oil, which was purified by flash chromatography (ether/hexanes 1:20–1:4), affording the alcohol **25** (4.02 g, 18.3 mmol, 84% yield) as a colorless oil. IR (neat): $\tilde{\nu}$ = 3395 (s), 3025 (m), 2961 (s), 1638 (w), 1453 (s), 1062 (s) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ = 7.30–7.21 (m, 5H), 5.75–5.64 (m, 1H), 5.23–5.15 (m, 2H), 4.56 (d, $^3J(H,H)$ = 11.8 Hz, 1H), 4.55 (d, $^3J(H,H)$ = 11.8 Hz, 1H), 4.31 (d, $^3J(H,H)$ = 11.8 Hz, 1H), 3.74–3.67 (m, 2H), 2.20 (brs, 1H), 2.15 (brs, 1H), 1.68–1.44 (m, 4H), 1.17–1.10 (m, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 138.8, 138.6, 138.5, 128.5, 127.9, 127.6, 117.4, 117.3, 80.7, 80.6, 70.3, 70.2, 68.0, 67.9, 35.3, 35.2, 32.0, 31.9, 23.6; MS (FD): *m/z* = 222 ([*M* + 2], 10), 221 ([*M* + 1], 100), 203 (2), 113 (7), 91 (70); $C_{14}H_{20}O_2$ (220.3): calcd C 76.33, H 9.15; found C 76.51, H 9.25.

3-Benzyloxy-6-iodo-1-heptene (1q): The procedure described above for the preparation of **1b** was repeated with the alcohol **25** (3.98 g, 18.1 mmol) and MeI·2DCC (12.5 g, 22.6 mmol, 1.25 equiv). Workup gave an oil, which was purified by flash chromatography (hexanes to ether/hexanes 1:10) to give the alkyl iodide **1q** (3.16 g, 9.57 mmol, 53% yield) as a colorless oil. IR (neat): $\tilde{\nu}$ = 3029 (m), 2970 (s), 1495 (m), 1454 (s), 1160 (s), 1063 (m), 695 (s) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ = 7.31–7.21 (m, 5H), 5.75–5.65 (m, 1H), 5.23–5.16 (m, 2H), 4.56 (d, $^3J(H,H)$ = 11.9 Hz, 1H), 4.31 (d, $^3J(H,H)$ = 11.9 Hz, 1H), 4.30 (d, $^3J(H,H)$ = 11.9 Hz, 1H), 4.17–4.03 (m, 1H), 3.75–3.68 (m, 1H), 1.90–1.58 (m, 4H), 1.88 (d, $^3J(H,H)$ = 6.7 Hz, 3H), 1.86 (d, $^3J(H,H)$ = 6.7 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 138.5, 128.2, 127.6, 127.4, 117.4, 117.3, 79.6, 79.1, 70.0, 69.9, 38.7, 38.2, 35.6, 35.3, 30.1, 29.9, 28.9, 28.8; MS (EI): *m/z* = 208 (1), 147 (5), 95 (19), 91 (100), 65 (9), 55 (5); $C_{14}H_{19}IO$ (330.2): calcd C 50.92, H 5.80; found C 50.72, H 5.62.

Typical procedure for the cyclization of 6-iodo-1-hexene derivatives: preparation of ethyl 2-(2-cyclopentylethyl)acetate (3): A three-necked flask equipped with a magnetic stirring bar, a thermometer, and a gas inlet was charged with $PdCl_2$(dppf) (0.07 g, 2.0 mol%) in THF (5 mL) and was cooled to −78 °C. The alkyl iodide (**1a**) (1.05 g, 5.0 mmol) and Et_2Zn (1.0 mL, 1.23 g, 10.0 mmol, 2 equiv) were added. The reaction mixture was warmed to RT and stirred for 4 h. The solvent and excess Et_2Zn were removed in vacuo (0.1 mm Hg, 40 °C, 2 h). After addition of THF (5 mL) and cooling to −40 °C, CuCN·2LiCl (CuCN, 0.45 g, 5.0 mmol; LiCl, 0.42 g, 10 mmol) in THF (5 mL) was added. The reaction mixture was warmed to 0 °C (5 min) and cooled back to −78 °C. Ethyl α-(bromomethyl)acrylate (0.97 g, 5.0 mmol, 1 equiv) was added and the reaction mixture was slowly warmed to RT and was stirred for 2 h. After the usual workup the crude residue was purified by flash chromatography (ether/hexanes 1:19), affording the cyclized product **3** as a clear oil (0.78 g, 80% yield). IR (neat): $\tilde{\nu}$ = 2948 (s), 2866 (m), 1733 (s), 1631 (m) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ = 6.10 (s, 1H), 5.50 (s, 1H), 4.20 (q, $^3J(H,H)$ = 7.1 Hz, 2H), 2.27–2.19 (m, 2H), 1.75–1.64 (m, 2H), 1.56–1.35 (m, 6H), 1.23 (t, $^3J(H,H)$ = 7.2 Hz, 3H), 1.07–0.97 (m, 2H), 0.82–0.75 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 167.2, 141.7, 123.5, 60.3, 39.8, 35.1, 32.6, 31.1, 25.2, 14.1; MS (EI): *m/z* = 196 (9), 150 (20), 115 (100), 102 (25), 86 (36), 67 (42), 55 (41), 41 (41). HR-MS ($C_{12}H_{20}O_2$): calcd 196.1463, found 196.1461.

7-(3-Carbethoxy-3-butenyl)bicyclo[2.1.0]heptane (27): The procedure described above for the preparation of **3** was repeated with 7-iodobicyclo[2.1.0]heptane (**26**) [26] (*endo* or *exo* isomer, 1.00 g, 4.5 mmol) and Et_2Zn (1.5 mL, 5 mmol, 3.3 equiv). After 20 h the conversion to the corresponding zinc compound was complete. Transmetalation to the zinc–copper compound and the reaction with ethyl α-(bromomethyl)acrylate were performed as described above. Flash-chromatographic purification (ether/hexanes 1:10–1:4) afforded the allylated product **27** (0.56 g, 2.7 mmol, 60%; *endo*:*exo* ratio = 96:4) as a colorless oil. IR (neat): $\tilde{\nu}$ = 2986 (m), 2928 (s), 2853 (m), 1719 (s), 1251 (m), 1174 (m), 1161 (m) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ = 6.10 (dt, $^3J(H,H)$ = 1.67, 1.13 Hz, 1H), 5.60 (dt, $^3J(H,H)$ = 1.71, 1.41 Hz, 1H), 4.18 (q, $^3J(H,H)$ = 7.15 Hz, 2H), 2.26 (t, $^3J(H,H)$ = 7.65 Hz, 1H), 2.17 (td, $^3J(H,H)$ = 1.24, 6.76 Hz, 1H), 1.90–1.78 (m, 2H), 1.66–1.53 (m, 2H), 1.28 (t, $^3J(H,H)$ = 6.82 Hz, 3H), 1.24–1.06 (m, 4H), 0.90 (t, $^3J(H,H)$ = 7.36 Hz, 1H), 0.77–0.66 (m, 1H), 0.63 (t, $^3J(H,H)$ = 4.91 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 167.50, 140.99, 123.67, 60.39, 36.13, 23.62, 21.90, 21.52, 14.14, 13.54; MS (EI): *m/z* = 208 ([*M*$^+$], 3), 162 (10), 135 (44), 134 (35), 133 (13), 99 (10), 95 (100), 67 (57), 41 (51); $C_{13}H_{20}O_2$ (208.3): calcd C 74.96, H 9.68; found C 74.82, H 9.82.

***trans*-3-(2-Phenylcyclopentylmethyl)-2-cyclohexen-1-one (34)**: The procedure described above for the preparation of **3** was repeated with the alkyl iodide **1d** (1.43 g, 5.0 mmol) and 3-iodo-2-cyclohexen-1-one (1.11 g, 5.0 mmol, 1 equiv) as the electrophile. Yield: 1.02 g (4.0 mmol, 80%); −10 °C, 12 h. Purified by flash chromatography (ether/hexanes 1:9). IR (neat): $\tilde{\nu}$ = 3030 (w), 2950 (m), 2850 (w), 1680 (m), 1630 (s), 1600 (w) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ = 7.24–7.18 (m, 2H), 7.13–7.08 (m, 3H), 5.77 (s, 1H), 2.47 (m, 1H), 2.24–1.87 (m, 9H), 1.84–1.49 (m, 5H), 1.38–1.12 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 199.7, 165.6, 144.8, 128.4, 127.6, 126.5, 126.1, 53.1, 45.7, 43.5, 37.2, 35.6, 32.5, 29.5, 24.0, 22.5; MS (EI): *m/z* = 254 (2), 144 (100), 110 (17), 91 (24); $C_{18}H_{22}O$ (254.3): calcd C 85.12, H 8.73; found C 85.02, H 8.53.

***trans*-(1-Iodomethyl)-2-phenylcyclopentane (35)**: The procedure described above for the preparation of **3** was repeated with the alkyl iodide **1d** (1.43 g, 5.0 mmol). Iodine (1.27 g, 5.0 mmol) was added at −78 °C to the zinc reagent (−78 °C, 30 min). The crude residue was purified by flash chromatography (hexanes), affording **35** (1.29 g, 4.5 mmol, 90% yield) as a colorless oil. IR (neat): $\tilde{\nu}$ = 3026 (m), 2954 (s), 2907 (m), 1492 (m), 1452 (m), 1182 (m), 754 (m) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ = 7.38–7.18 (m, 5H), 3.26 (dd, $^3J(H,H)$ = 9.7, 3.5 Hz, 1H), 3.02 (dd, $^3J(H,H)$ = 7.4, 2.2 Hz, 1H), 2.63–2.53 (m, 1H), 2.19–1.64 (m, 6H), 1.55–1.38 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 143.6, 128.5, 127.3, 126.3, 52.3, 49.6, 35.5, 33.2, 23.3, 13.2; MS (EI): *m/z* = 286 (7), 159 (42), 117 (21), 91 (100); $C_{12}H_{15}I$ (286.1): calcd C 50.40, H 5.29; found C 50.30, H 5.26.

***trans*-1-(2-Oxo-2-phenylethyl)-2-phenylcyclopentane (36)**: The procedure described above for the preparation of **3** was repeated with the alkyl iodide **1d** (1.43 g, 5.0 mmol) and benzoyl chloride (0.70 g, 5.0 mmol, 1 equiv) as the electrophile (−10 °C, 12 h). The crude residue was purified by flash chromatography (ether/hexanes 1:10), affording **36** (1.00 g, 3.8 mmol, 76% yield) as a white solid (m.p. 65 °C). IR (neat): $\tilde{\nu}$ = 2900 (s), 1690 (m) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ = 7.82–7.78 (m, 2H), 7.54–7.48 (m, 1H), 7.42–7.18 (m, 7H), 3.45 (dd, $^3J(H,H)$ = 16.1, 3.3 Hz, 1H), 2.79 (dd, $^3J(H,H)$ = 16.1, 10.1 Hz, 1H), 2.64 (q, $^3J(H,H)$ = 10.4 Hz, 1H), 2.54–2.40 (m, 1H), 2.24–2.07 (m, 2H), 1.92–1.68 (m, 1H), 1.44–1.26 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 200.2, 144.2, 137.1, 132.8, 128.5, 128.0, 127.7, 126.3, 52.9, 44.2, 43.0, 34.9, 32.4, 23.8; MS (EI): *m/z* = 264 (11), 144 (100), 105 (44), 77 (40), 28 (23); $C_{19}H_{20}O$ (264.3): calcd C 86.32, H 7.63; found C 86.21, H 7.60.

***trans*-1-(3-Carbethoxy-3-butenyl)-2-phenylcyclopentane (37)**: The procedure described above for the preparation of **3** was repeated with the alkyl iodide **1d** (1.43 g, 5.0 mmol). Ethyl (α-bromomethyl)acrylate (0.98 g, 5.0 mmol, 1.0 equiv) was used as the electrophile (−78 °C to RT, 1 h). The crude residue was purified by flash chromatography (ether/hexanes 1:10), affording **37** (0.99 g, 3.7 mmol, 73% yield) as a colorless oil. IR (neat): $\tilde{\nu}$ = 2940 (s), 2870 (m), 1720 (s), 1640 (m) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ = 7.30–7.19 (m, 5H), 6.03 (s, 1H), 2.20–2.00 (m, 3H), 1.94–1.53 (m, 5H), 1.37–1.26 (m, 2H), 1.23 (t, $^3J(H,H)$ = 7.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 167.3, 145.6, 141.2, 128.5, 127.9, 126.1, 123.9, 60.5, 53.1, 47.7, 35.7, 33.2, 32.2, 30.8, 24.2, 14.2; MS (EI): *m/z* = 272 (12), 158 (29), 117 (32), 104 (100), 91 (63); $C_{18}H_{24}O_2$ (272.3): calcd C 79.48, H 8.89; found C 79.77, H 8.81.

***trans*-1-8(*E*)-3-Carbethoxy-2-propenyl)-2-phenylcyclopentane (38)**: The procedure described above for the preparation of **3** was repeated with the alkyl iodide **1d** (1.43 g, 5.0 mmol) and ethyl propynoate (0.49 g, 5.0 mmol, 1 equiv) as the electrophile (−50 °C, 12 h). The crude residue was purified by flash chromatography (ether/hexanes 1:10), affording **38** (0.83 g, 3.2 mmol, 64% yield) as a colorless oil. IR (neat): $\tilde{\nu}$ = 3060 (w), 3040 (w), 2989 (s), 1725 (s), 1660 (m), 1050 (m), 980 (m), 750 (m) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ = 7.30–7.12 (m, 5H), 6.83 (dt, $^3J(H,H)$ = 15.6, 7.1 Hz, 1H), 6.71 (d, $^3J(H,H)$ = 15.6 Hz, 1H), 4.11 (q, $^3J(H,H)$ = 7.1 Hz, 2H), 2.55–2.46 (m, 1H), 2.32–2.24 (m, 1H), 2.09–1.92 (m, 4H), 1.80–1.60 (m, 3H), 1.37–1.28 (m, 1H), 1.22 (t, $^3J(H,H)$ = 7.1 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 166.7, 148.2, 144.8, 128.5, 127.6, 126.2, 122.1, 60.2, 52.7, 47.3, 36.6, 35.3, 31.9, 24.0, 14.3; $C_{17}H_{22}O_2$ (258.3): calcd C 79.14, H 8.59; found C 79.24, H 8.57.

***trans*-1-(3-Carbethoxy-3-butenyl)-2-(4-cyanophenyl)cyclopentane (39)**: The procedure described above for the preparation of **3** was repeated with the alkyl iodide **1b** (1.56 g, 5.0 mmol); ethyl (α-bromomethyl)acrylate (0.98 g, 5.0 mmol, 1.0 equiv) was used as the electrophile (−78 °C to RT, 1 h). The crude residue was purified by flash chromatography (ether/hexanes 1:4), affording **39** (1.23 g, 4.2 mmol, 83% yield) as a colorless oil. IR (neat): $\tilde{\nu}$ = 2962 (s), 1757 (vs), 1721 (vs), 1142 (vs), 796 (m) cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$): δ = 7.22–6.92 (m, 4H), 6.05–6.03 (m, 1H), 5.38–5.36 (m, 1H), 4.14 (q, $^3J(H,H)$ = 7.1 Hz, 2H), 2.58–2.49 (m, 1H), 2.41–1.97 (m,

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5H), 1.96–1.54 (m, 7H), 1.34 (s, 9H), 1.23 (t, ^3J(H,H) = 7.1 Hz, 3H); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 177.1, 167.2, 149.2, 142.8, 141.0, 128.3, 124.0, 121.1, 60.4, 52.5, 47.8, 39.0, 35.8, 33.1, 32.1, 30.7, 27.1, 24.0, 14.1; MS (EI): m/z = 372 (1), 174 (22), 133 (23), 107 (27), 57 (100); $C_{23}H_{32}O_4$ (372.5): calcd C 74.16, H 8.66; found C 74.02, H 8.61.

***trans*-1-(3-Carbethoxy-3-butenyl)-2-(4-pivaloxyphenyl)cyclopentane (40)**: The procedure described above for the preparation of **3** was repeated with the alkyl iodide **1c** (1.93 g, 5.0 mmol); ethyl (α-bromomethyl)acrylate (0.98 g, 5.0 mmol, 1 equiv) was used as the electrophile (− 78 °C to RT, 1 h). The crude residue was purified by flash chromatography (ether/hexanes 1:10–1:4), affording **40** (1.14 g, 3.1 mmol, 61% yield) as a colorless oil. IR (neat): $\tilde{\nu}$ = 2953 (s), 2223 (m), 1717 (vs), 1612 (m), 832 (m) cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.56–7.24 (m, 4H), 6.03–5.99 (m, 1H), 5.40–5.37 (m, 1H), 4.10 (d, ^3J(H,H) = 7.1 Hz, 1H), 2.60–2.51 (m, 1H), 2.17–2.09 (m, 1H), 2.08–1.99 (m, 3H), 1.96–1.79 (m, 4H), 1.70–1.62 (m, 2H), 1.20 (t, ^3J(H,H) = 7.1 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 151.5, 140.8, 132.1, 128.2, 124.1, 119.0, 109.7, 60.4, 53.0, 47.8, 35.5, 33.1, 32.1, 30.6, 24.1, 14.0; MS (EI): m/z = 297 (47), 183 (49), 129 (95), 72 (97), 115 (100); $C_{19}H_{23}O_2N$ (297.3): calcd C 76.74, H 7.79, N 4.71; found C 76.84, H 7.91, N 4.76.

1-Butyl-1-(3-nitro-2-phenylpropyl)cyclopentane (41): The procedure described for the preparation of **3** was repeated with the alkyl iodide **1e** (1.33 g, 5.0 mmol) and *trans*-ω-nitrostyrene (0.75 g, 5.0 mmol, 1 equiv); − 60 °C, 12 h. The crude residue was purified by flash chromatography (ether/hexanes 1:9), affording **41** (1.17 g, 4.1 mmol, 81% yield) as a colorless oil. IR (neat): $\tilde{\nu}$ = 2959 (s), 1555 (s), 1385 (m), 885 (m), 765 (m), 710 (s) cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.39–7.20 (m, 5H), 4.73 (d, ^3J(H,H) = 9.7 Hz, 2H), 4.66–4.51 (m, 2H), 3.48 (q, ^3J(H,H) = 7.6 Hz, 1H), 2.00–1.93 (m, 4H), 1.77–1.69 (m, 2H), 1.47–1.17 (m, 8H), 0.92 (t, ^3J(H,H) = 6.0 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 149.7, 139.5, 128.9, 127.5, 110.7, 81.0, 44.3, 35.7, 32.9, 30.0, 27.4, 26.6, 22.5, 14.0; MS (EI): m/z = 289 (1), 243 (3), 138 (22), 124 (100), 77 (84); $C_{18}H_{27}NO_2$ (289.4): calcd C 74.70, H 9.40, N 4.48; found C 74.86, H 9.65, N 4.70.

3-(3-Carbethoxy-3-butenyl)-1,1-dicarbethoxycyclopentane (42): The procedure described above for the preparation of **3** was repeated with the alkyl iodide **1f**; ethyl (α-bromomethyl)acrylate (0.98 g, 5.0 mmol, 1 equiv) was used as the electrophile (− 78 °C to RT, 1 h). The crude residue was purified by flash chromatography (ether/hexanes 1:10–1:2), affording **42** (1.14 g, 3.8 mmol, 75% yield). IR (neat): $\tilde{\nu}$ = 2981 (s), 1748 (vs), 1723 (vs), 1635 (m) cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.06–6.05 (m, 1H), 5.45–5.44 (m, 1H), 4.11 (q, ^3J(H,H) = 7.1 Hz, 4H), 4.09 (q, ^3J(H,H) = 7.1 Hz, 2H), 2.45–2.36 (m, 1H), 2.28–2.19 (m, 4H), 2.13–2.02 (m, 1H), 1.96–1.78 (m, 2H), 1.71–1.62 (m, 1H), 1.50–1.41 (m, 2H), 1.28–1.16 (m, 9H); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 172.9, 176.5, 141.1, 124.5, 61.5, 60.8, 60.3, 40.8, 39.6, 34.3, 34.0, 32.2, 31.1, 14.4, 14.3; MS (EI): m/z = 229 (3), 155 (33), 113 (71), 95 (85), 83 (56), 67 (36); $C_{18}H_{28}O_6$ (340.4): calcd C 63.51, H 8.29; found C 63.31, H 8.24.

***cis*-3-(2-Methylcyclopentylmethyl)-2-cyclohexene-1-one (43)**: The procedure described above for the preparation of **3** was repeated with the alkyl iodide **1g** (1.40 g, 6.25 mmol) and 3-iodo-2-cyclohexene-1-one (1.20 g, 5.5 mmol, 0.9 equiv) as the electrophile (− 78 °C to 0 °C, 12 h). The crude residue was purified by flash chromatography (ether/hexanes 1:4), affording **43** (0.65 g, 3.4 mmol, 62% yield) as a colorless oil. IR (neat): $\tilde{\nu}$ = 2940 (s), 1710 (vs), 1623 (m) cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.81 (s, 1H), 2.31–2.26 (m, 6H), 1.97–1.89 (m, 4H), 1.62–1.44 (m, 4H), 1.25–1.22 (m, 2H), 0.77 (d, ^3J(H,H) = 6.6 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 199.6, 166.3, 126.3, 40.5, 38.9, 37.2, 36.1, 33.1, 29.7, 29.5, 22.7, 22.3, 14.9; MS (EI): m/z = 192 (2), 110 (100), 82 (71), 28 (55); $C_{13}H_{20}O$ (192.3): calcd C 81.25, H 10.41; found C 81.31, H 10.24.

***cis*-3-(2-Ethylcyclopentylmethyl)-2-cyclohexene-1-one (44)**: The procedure described above for the preparation of **3** was repeated with the alkyl iodide **1h** (1.19 g, 5.0 mmol) and 3-iodo-2-cyclohexene-1-one (1.11 g, 5.0 mmol, 1 equiv) as the electrophile (− 10 °C, 12 h). The crude residue was purified by flash chromatography (ether/hexanes 1:9), affording **44** (0.84 g, 4.1 mmol, 81% yield). IR (neat): $\tilde{\nu}$ = 2952 (s), 2870 (s), 1666 (s), 1620 (m), 1251 (m), 886 (m) cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.80 (s, 1H), 2.14–1.96 (m, 5H), 1.95–1.82 (m, 3H), 1.80–1.38 (m, 6H), 1.35–1.15 (m, 3H), 1.14–1.03 (m, 1H), 0.83 (t, ^3J(H,H) = 7.3 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 199.9, 166.7, 126.7, 126.5, 47.9, 44.9, 44.2, 43.3, 39.7, 38.1, 37.5, 32.7, 32.4, 31.6, 30.2, 29.9, 29.7, 27.7, 25.1, 23.7, 22.9, 22.7, 22.4, 31.1, 12.8; MS (EI): m/z = 206 (1), 110 (100), 97 (44), 82 (58), 55 (79); $C_{14}H_{22}O$ (206.3): calcd C 81.50, H 10.75 ; found C 81.15, H 11.01.

3-(2-Cyclohexylcyclopentylmethyl)-2-cyclohexene-1-one (45): The procedure described above for the preparation of **3** was repeated with the alkyl iodide **1i** (1.46 g, 5.0 mmol) and 3-iodo-2-cyclohexene-1-one (1.11 g, 5.0 mmol, 1 equiv) as the electrophile (− 10 °C, 12 h). The crude residue was purified by flash chromatography (ether/hexanes 1:9), affording the product **45** (0.84 g, 3.1 mmol, 61% yield) as a colorless oil. IR (neat): $\tilde{\nu}$ = 2947 (s), 1716 (vs), 1623 (m), 1175 (vs) cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.06 (s, 1H), 5.46 (s, 1H), 4.15 (q, ^3J(H,H) = 7.2 Hz, 2H), 2.23 (m, 2H), 1.96 (m, 1H), 1.70–1.60 (m, 3H), 1.15–1.41 (m, 2H), 1.31–1.18 (m, 3H), 1.24 (t, J = 7.1 Hz, 3H), 0.73 (d, ^3J(H,H) = 7.0 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 167.3, 141.5, 123.9, 60.4, 42.9, 35.8, 33.5, 31.6, 29.6, 29.5, 22.4, 14.6, 14.1; MS (EI): m/z = 210 (6), 115 (46), 95 (37), 55 (100), 29 (45); $C_{14}H_{22}O$ (206.3): calcd C 82.38, H 11.52; found C 82.50, H 11.44.

***cis*-1-(3-Carbethoxy-3-butenyl)-2-ethylcyclopentane (46)**: The procedure described above for the preparation of **3** was repeated with the alkyl iodide **1h** (1.19 g, 5.0 mmol) and ethyl (α-bromomethyl)acrylate (0.98 g, 5.0 mmol, 1.0 equiv) as the electrophile (− 78 °C to RT, 1 h). The crude residue was purified by flash chromatography (ether/hexanes 1:4), affording **46** (0.98 g, 4.4 mmol, 87% yield). IR (neat): $\tilde{\nu}$ = 2952 (s), 1715 (s), 1629 (m), 1173 (s), 1029 (m) cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.09 (s, 1H), 5.50 (s, 1H), 4.18 (q, ^3J(H,H) = 7.2 Hz, 2H), 2.41–2.12 (m, 2H), 1.88–1.42 (m, 7H), 1.40–1.15 (m, 7H), 1.15–0.99 (m, 1H), 0.88–0.83 (m, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 167.4, 141.6, 124.0, 123.9, 60.5, 47.7, 45.3, 44.5, 42.2, 34.2, 32.3, 31.9, 31.0, 30.9, 30.3, 29.9, 28.3, 27.8, 23.9, 22.5, 22.0, 14.2, 13.0, 12.8; MS (EI): m/z = 224 (7), 115 (47), 81 (52), 69 (61), 28 (100); $C_{14}H_{24}O_2$ (224.3): calcd C 74.95, H 10.78 ; found C 74.71, H 11.0.

***cis*-1-(3-Carbethoxy-3-butenyl)-2-(4-acetoxybutyl)cyclopentane (47)**: The procedure described above for the preparation of **3** was repeated with the alkyl iodide **1j** (1.62 g, 5.0 mmol); ethyl (α-bromomethyl)acrylate (0.98 g, 5.0 mmol, 1.0 equiv) was used as the electrophile (− 78 °C to RT, 1 h). The crude residue was purified by flash chromatography (ether/hexanes 1:9–1:4), affording **47** (1.16 g, 3.8 mmol, 75% yield) as a colorless oil. IR (neat): $\tilde{\nu}$ = 2933 (s), 1716 (vs), 1651 (w), 1247 (s) cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.15 (s, 1H), 5.55 (s, 1H), 4.22 (q, ^3J(H,H) = 7.1 Hz, 2H), 4.08 (t, ^3J(H,H) = 6.7 Hz, 2H); 2.28–2.24 (m, 1H), 2.23–2.15 (m, 1H), 2.08 (s, 3H), 1.85–1.82 (m, 2H), 1.70–1.53 (m, 8H), 1.41–1.14 (m, 6H), 1.34 (t, ^3J(H,H) = 7.1 Hz, 3H); ^{1}H NMR NOESY (500 MHz, $CDCl_3$): irradiation by the resonance frequency of H1 leads to an increase of the intensity of H2 (see Scheme 14); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 171.1, 167.2, 141.5, 124.1, 64.7, 60.6, 45.7, 42.4, 42.3, 32.1, 31.0, 30.2, 28.9, 28.5, 24.9, 22.5, 21.0, 14.3; MS (EI): m/z = 309 (7), 149 (16), 95 (47), 55 (48), 43 (87), 28 (100); $C_{18}H_{30}O_4$ (310.4): calcd C 69.67, H 9.67; found C 69.43, H 9.91.

***cis*-1-(3-Carbethoxy-3-butenyl)-2-(1-cyanopropyl)cylopentane (48)**: The procedure described above for the preparation of **3** was repeated with the alkyl iodide **1k** (1.40 g, 5.0 mmol) and ethyl (α-bromomethyl)acrylate (0.82 g, 4.14 mmol, 0.8 equiv) as the electrophile. Reaction conditions − 78 °C to − 20 °C, 12 h. The crude residue was purified by flash chromatography (ether/hexanes: 1:8–1:1), affording **48** (0.96 g, 3.31 mmol, 88% yield) as a colorless oil. IR (neat): $\tilde{\nu}$ = 2920 (s), 2250 (w), 1720 (vs), 1650 (s) cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.12 (s, 1H), 5.52 (s, 1H), 4.19 (q, J = 7.2 Hz, 2H), 2.35–2.30 (m, 5H), 1.82 (m, 2H), 1.79–1.49 (m, 10H), 1.31 (t, ^3J(H,H) = 6.4 Hz, 3H), 1.29–1.27 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 167.3, 141.3, 124.3, 119.8, 60.6, 42.2, 41.8, 32.1, 30.1, 30.1, 28.7, 28.6, 24.5, 22.5, 17.5, 14.3; MS (EI): m/z = 234 (4), 150 (27), 115 (54), 41 (100); $C_{16}H_{25}NO_2$ (263.3): calcd C 72.97, H 9.56, N 5.32; found C 72.90, H 9.59, N 5.31.

***cis*-1-((*E*)-3-Carbethoxy-2-propenyl)-2-(4-acetoxybutyl)cyclopentane (49)**: The procedure described above for the preparation of **3** was repeated with the alkyl iodide **1j** (1.80 g, 6.0 mmol). Ethyl propynoate (0.54 g, 5.50 mmol, 0.9 equiv) was used as the electrophile (− 78 °C to − 20 °C, 12 h). The crude residue was purified by flash chromatography (ether/hexanes 1:9–1:4), affording **49** (0.85 g, 3.1 mmol, 57% yield) as a colorless oil. IR (neat): $\tilde{\nu}$ = 2940 (s), 1723 (vs), 1652 (m), 1239 (vs) cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.91 (dt, ^3J(H,H) = 15.53, 7.7 Hz, 1H), 5.78 (d, ^3J(H,H) = 15.6 Hz, 1H), 4.17 (q, ^3J(H,H) = 7.2 Hz, 2H), 4.05 (t, ^3J(H,H) = 6.7 Hz, 2H), 2.23–2.20 (m, 1H), 1.95 (s, 3H), 1.92–1.89 (m, 3H), 1.58–1.53 (m, 8H), 1.33–1.31 (m, 4H), 1.32 (t, ^3J(H,H) = 6.70, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 171.0, 167.5, 149.2, 1121.8, 64.6, 60.2, 42.6, 71.4, 32.4, 32.1, 30.2, 30.1, 29.5, 29.0, 25.0, 22.4, 14.3; MS (EI): m/z = 250 (2), 81 (18), 43 (10), 28 (100); $C_{17}H_{28}O_4$ (296.4): calcd C 68.92, H 9.46; found C 68.84, H 9.20.

***cis*-1-((*E*)-3-Carbethoxy-2-propenyl)-2-(1-cyanopropyl)cyclopentane (50)**: The procedure described above for the preparation of **3** was repeated with the alkyl iodide **1k** (1.40 g, 5.0 mmol). Ethyl propynoate (0.49 g, 5.0 mmol, 1 equiv) was used as the electrophile (− 78 °C to − 20 °C, 12 h). The crude residue was purified by flash chromatography (ether/hexanes 1:8–1:1), affording **50** (0.90 g, 3.6 mmol, 71% yield) as a colorless oil. IR (neat): $\tilde{\nu}$ = 2900 (s), 2240 (w), 1700 (vs), 1635 (s) cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.86 (dt, ^3J(H,H) = 15.6, 7.6 Hz, 1H), 5.75 (d, ^3J(H,H) = 15.6 Hz, 1H), 4.12 (q, ^3J(H,H) = 7.2 Hz, 2H), 2.31–2.29 (m, 3H), 2.28–2.27 (m, 1H), 2.19–1.94 (m, 4H), 1.64–1.54 (m, 6H), 1.26 (t, ^3J(H,H) = 7.1 Hz, 3H), 1.24–1.22 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 166.5, 148.5, 122.0, 119, 60.1, 41.9, 41.2, 32.2, 30.1, 29.8, 28.9, 24.4, 22.2, 17.4, 14.2; MS (EI): m/z = 205 (3), 114 (100), 86 (61); $C_{15}H_{23}NO_2$ (249.3): calcd C 71.71, H 9.16, N 5.57; found C 71.69, H 9.12, N 5.55.

1-Acetoxy-2-[2-(4-acetoxybutyl)cyclopentylmethyl]-3-cyclohexene (51): The procedure described above for the preparation of **3** was repeated with the alkyl iodide **1j** (1.77 g, 5.5 mmol). *cis*-1-Chloro-4-acetoxy-2-cyclohexene (0.90 g, 5.2 mmol, 0.94 equiv) was used as the electrophile (− 78 °C to RT, 3 d). The crude residue was purified by flash chromatography (ether/hexanes 1:9–1:4), affording **51** (0.91 g, 2.7 mmol, 52% yield) as a colorless oil. IR (neat): $\tilde{\nu}$ = 2933 (m), 1730 (s), 1438 (m), 1232 (s) cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.62–5.58 (m, 2H), 4.78–4.69

(m, 1H), 3.98 (t, ^3J(H,H) = 6.7 Hz, 2H), 2.18–2.03 (m, 1H), 1.98 (s, 3H), 1.80–1.78 (m, 1H), 1.61–1.49 (m, 8H), 1.33–1.18 (m, 8H), 1.10–1.07 (m, 2H), ^{13}C NMR (75 MHz, $CDCl_3$): δ = 171.2, 170.8, 129.2, 126.2, 74.5, 73.8, 64.7, 42.8, 41.9, 40.0, 38.9, 33.7, 30.0, 29.0, 28.4, 26.0, 25.5, 24.8, 22.8, 21.0; MS (EI): *m/z* = 181 (7), 94 (79), 67 (42), 43 (100); $C_{20}H_{32}O_4$ (336.4): calcd C 71.43, H 9.52; found C 71.39, H 9.43.

***trans*-1-Benzyloxy-2-(3-carbethoxy-3-butenyl)cyclopentane (52)**: The procedure described above for the preparation of **3** was repeated with the alkyl iodide **1o** (1.58 g, 5.0 mmol) and ethyl (α-bromomethyl)acrylate (0.98 g, 5.0 mmol, 1.0 equiv) as the electrophile (−78 °C to RT, 1 h). The crude residue was purified by flash chromatography (ether/hexanes 1:20–1:4), affording **52** (1.10 g, 3.7 mmol, 73% yield) as a colorless oil. IR (neat): $\tilde{\nu}$ = 3066 (w), 2952 (s), 2362 (m), 1721 (s), 1648 (w), 1451 (m), 1272 (s), 1111 (s), 712 (s) cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.35–7.25 (m, 5H), 6.13–6.12 (m, 1H), 5.51–5.50 (m, 1H), 4.52 (d, ^3J(H,H) = 11.9 Hz, 1H), 4.44 (d, ^3J(H,H) = 11.9 Hz, 1H), 4.20 (q, ^3J(H,H) = 7.1 Hz, 2H), 3.61–3.57 (m, 1H), 2.40–2.27 (m, 2H), 1.97–1.91 (m, 2H), 1.86–1.79 (m, 1H), 1.75–1.57 (m, 4H), 1.40–1.34 (m, 1H), 1.29 (t, ^3J(H,H) = 7.1 Hz, 3H), 1.21–1.15 (m, 1H); ^{1}H NMR NOESY (500 MHz, $CDCl_3$): irradiation by the resonance frequency of H1 leads to an increase of intensity of H3 (see Scheme 14); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 167.6, 141.3, 139.2, 128.6, 127.9, 127.6, 124.5, 86.3, 71.4, 60.8, 45.6, 33.4, 31.6, 30.8, 30.4, 22.8, 14.5; MS (FD): *m/z* = 302 ([*M*$^+$], 12), 301 ([*M* − 1], 100), 217 (2), 189 (24), 91 (1); $C_{19}H_{26}O_3$ (302.4): calcd C 75.46, H 8.67; found C 75.33, H 8.71.

***trans*-1-Benzoyloxy-2-(3-carbethoxy-3-butenyl)cyclopentane (53)**: The procedure described above for the preparation of **3** was repeated with the alkyl iodide **1p** (1.65 g, 5.0 mmol); ethyl (α-bromomethyl)acrylate (0.98 g, 5.0 mmol, 1.0 equiv) was used as the electrophile (−78 °C to RT, 1 h). The crude residue was purified by flash chromatography (ether/hexanes 1:10–1:4), affording **53** (0.74 g, 2.4 mmol, 47% yield) as a colorless oil. IR (neat): $\tilde{\nu}$ = 2958 (m), 2873 (w), 1717 (s), 1630 (w), 1453 (m), 1275 (s), 1115 (s), 714 (s) cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$): δ = 7.97–7.92 (m, 2H), 7.48–7.32 (m, 3H), 6.03–6.02 (m, 1H), 5.42–5.41 (m, 1H), 5.38–5.36 (m, 1H), 4.07 (q, ^3J(H,H) = 7.2 Hz, 2H), 2.29–2.40 (m, 2H), 2.02–1.41 (m, 9H), 1.17 (t, ^3J(H,H) = 7.2 Hz, 3H); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 168.9, 167.9, 142.6, 134.5, 132.6, 131.2, 130.1, 126.3, 80.0, 62.3, 46.1, 34.5, 32.6, 31.6, 30.1, 23.8, 15.9; MS (EI): *m/z* = 316 ([*M*$^+$], 0.5), 194 (14), 120 (19), 105 (100), 81 (28), 77 (33), 67 (7); $C_{19}H_{24}O_4$ (316.3): calcd C 72.13, H 7.65; found C 72.30, H 8.11.

***cis*-1-(3-Carbethoxy-3-butenyl)-2-methylcyclopentane (56)**: The procedure described above for the preparation of **3** was repeated with the alkyl iodide **1g** (1.11 g, 5.0 mmol) and ethyl (α-bromomethyl)acrylate (0.98 g, 5.0 mmol, 1.0 equiv) as the electrophile (−78 °C to RT, 1 h). The crude residue was purified by flash chromatography (ether/hexanes 1:9), affording **56** (0.85 g, 4.0 mmol, 80% yield) as a colorless oil. IR (neat): $\tilde{\nu}$ = 2947 (s), 1716 (vs), 1623 (m), 1175 (vs) cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.06 (s, 1H), 5.46 (s, 1H), 4.15 (q, ^3J(H,H) = 7.2 Hz, 2H), 2.23–2.20 (m, 2H), 1.96 (m, 1H), 1.70–1.60 (m, 3H), 1.15–1.41 (m, 2H), 1.31–1.18 (m, 3H), 1.24 (t, ^3J(H,H) = 7.1 Hz, 3H), 0.73 (d, ^3J(H,H) = 7.0 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 167.3, 141.5, 123.9, 60.4, 42.9, 35.8, 33.5, 31.6, 29.6, 29.5, 2.4, 14.6, 14.1; MS (EI): *m/z* = 210 (6), 115 (46), 95 (37), 55 (100), 29 (45); $C_{13}H_{22}O_2$ (210.3): calcd C 74.24, H 10.54; found C 74.10, H 10.71.

(1,2 *trans*-2,3 *cis*)-1-Benzyloxy-2-(3-carbethoxy-3-butenyl)-3-methylcyclopentane (58): The procedure described above for the preparation of **3** was repeated with the alkyl iodide **1q** (1.65 g, 5.0 mmol) and ethyl (α-bromomethyl)acrylate (0.98 g, 5.0 mmol, 1.0 equiv) as the electrophile (−78 °C to RT, 1 h). The crude residue was purified by flash chromatography (ether/hexanes 1:10–1:4), affording **58** (1.06 g, 3.4 mmol, 67% yield) as a colorless oil. IR (neat): $\tilde{\nu}$ = 2954 (s), 1717 (s), 1630 (m), 1179 (s) cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.33–7.25 (m, 5H), 6.14–6.13 (m, 1H), 5.53–5.52 (m, 1H), 4.53 (d, ^3J(H,H) = 11.8 Hz, 1H), 4.43 (d, ^3J(H,H) = 11.8 Hz, 1H), 4.20 (q, ^3J(H,H) = 7.1 Hz, 2H), 3.72–3.69 (m, 1H), 2.36–2.33 (m, 2H), 2.27–2.21 (m, 1H), 2.06–1.98 (m, 1H), 1.94–1.87 (m, 2H), 1.68–1.61 (m, 1H), 1.57–1.43 (m, 2H), 1.31–1.28 (m, 1H), 1.29 (t, ^3J(H,H) = 7.1 Hz, 3H), 0.86 (d, ^3J(H,H) = 7.2 Hz, 3H); ^{1}H NMR NOESY (500 MHz, $CDCl_3$): irradiation by the resonance frequency of H1 leads to an increase of the intensity of H3, whereas irradiation by the resonance frequency of H2 leads to an increase of the intensity of H4 (see Scheme 14); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 167.6, 141.5, 139.2, 128.5, 127.9, 127.6, 124.6, 85.2, 71.6, 60.8, 49.0, 34.5, 31.2, 31.0, 30.0, 27.5, 15.5, 14.5; MS (EI): *m/z* = 316 ([*M*$^+$], 1), 210 (18), 179 (14), 132 (10), 91 (100); $C_{20}H_{28}O_3$ (316.4): calcd C 75.91, H 8.92; found C 76.05, H 8.73.

***cis*-1-(3-Carbethoxy-3-butenyl)-2-(pivaloxymethyl)cyclopentane (59)**: The procedure described above for the preparation of **3** was repeated with the alkyl iodide **1l** (1.61 g, 5.0 mmol) and ethyl (α-bromomethyl)acrylate (0.98 g, 5.0 mmol, 1 equiv) as the electrophile (−78 °C to RT, 1 h). The crude residue was purified by flash chromatography (ether/hexanes 1:10–1:4), affording **59** (1.33 g, 4.4 mmol, 87% yield) as a colorless oil. IR (neat): $\tilde{\nu}$ = 2962 (s), 1724 (s), 1259 (s), 1090 (s), 1027 (s), 800 (s) cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.92–6.80 (m, 1H), 6.75 (d, ^3J(H,H) = 15.5 Hz, 1H), 4.11 (q, ^3J(H,H) = 7.1 Hz, 2H), 3.95 (d, ^3J(H,H) = 6.9 Hz, 2H), 3.21–2.19 (m, 2H), 2.10–1.91 (m, 2H), 2.10–1.91 (m, 2H), 1.79–1.43 (m, 4H), 1.41–1.22 (2H), 1.17 (t, ^3J(H,H) = 8.3 Hz, 3H), 1.13 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 177.0, 166.6, 148.4, 147.8, 122.1, 65.0, 60.3, 44.2, 41.7, 41.1, 40.7, 38.8, 37.8, 32.8, 32.2, 30.9, 29.4, 28.1, 27.3, 22.9, 14.3; MS (EI): *m/z* = 250 (2), 148 (27), 121 (24), 81 (41), 57 (93); $C_{17}H_{28}O_4$ (296.4): calcd C 68.89, H 9.52; found C 68.61, H 9.71.

3-((*E*)-3-Carbethoxy-2-propenyl)bicyclo[3.3.0]octane (61): The procedure described above for the preparation of **3** was repeated with the alkyl iodide **1m** (1.25 g, 5.0 mmol) and ethyl (α-bromomethyl)acrylate (0.98 g, 5.0 mmol, 1.0 equiv) as the electrophile (−78 °C to RT, 1 h). A 86:14 mixture of the bicyclized product **61**:monocyclized product **62** was obtained. The crude residue was purified by flash chromatography (ether/hexanes 1:10–1:4), affording **61** and **62** (0.91 g, 4.1 mmol, 82% yield). IR (neat): $\tilde{\nu}$ = 2936 (s), 1717 (s), 1654 (m), 1262 (s), 1180 (s) cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.93–6.80 (m, 1H), 5.78–5.67 (m, 1H), 4.15–4.05 (m, 2H), 2.40–2.24 (m, 2H), 2.16–2.05 (m, 2H), 2.00–1.91 (m, 2H), 1.80–1.68 (m, 2H), 1.56–1.36 (m, 4H), 1.35–1.17 (m, 4H), 1.15–1.01 (m, 1H), 0.85–0.86 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 166.8, 148.8, 148.7, 148.5, 137.7, 122.0, 121.6, 121.5, 115.3, 60.1, 45.0, 44.1, 42.9, 42.5, 41.2, 41.1, 40.0, 39.1, 37.9, 37.7, 37.6, 37.5, 34.9, 33.3, 32.0, 31.9, 27.1, 24.8, 23.7, 14.3; MS (EI): *m/z* = 222 (3), 177 (16), 114 (97), 86 (37), 67 (100); $C_{14}H_{22}O_2$ (222.3): calcd C 75.63, H 9.97; found C 75.35, H 10.02.

5-(3-Carbethoxy-3-butenyl)bicyclo[4.3.0]octane (63): The procedure described above for the preparation of **3** was repeated with the alkyl iodide **1n** (1.31 g, 5.0 mmol) and ethyl (α-bromomethyl)acrylate (0.98 g, 5.0 mmol, 1.0 equiv) as the electrophile (−78 °C to RT, 1 h). The crude residue was purified by flash chromatography (ether/hexanes 1:10–1:4), affording **63** (1.13 g, 4.5 mmol, 90% yield). IR (neat): $\tilde{\nu}$ = 2951 (s), 1722 (s), 1640 (m), 1210 (m), 880 (m) cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.04 (s, 1H), 5.43 (s, 1H), 4.18–4.08 (m, 2H), 2.34–2.18 (m, 2H), 2.04–1.91 (m, 1H), 1.90–1.55 (m, 5H), 1.54–1.11 (m, 12H), 1.10–0.97 (m, 1H), 0.96–0.75 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 167.4, 141.6, 123.9, 60.5, 45.0, 44.2, 41.9, 40.5, 39.4, 39.1, 34.9, 31.2, 31.0, 29.9, 29.8, 29.6, 28.7, 28.4, 27.2, 26.9, 25.6, 25.5, 24.4, 22.8, 22.0, 21.0, 14.2; MS (EI): *m/z* = 250 (3), 205 (8), 118 (62), 82 (45), 57 (84), 28 (100); $C_{16}H_{26}O_2$ (250.3): calcd C 76.75, H 10.47; found C 76.58, H 10.51.

3-(2-Cyclopentenyl)propyl pivalate (68): The zinc–copper reagent was prepared following the method used for **6** with 3-iodopropyl pivalate (54.0 g, 200 mmol). 3-Chlorocyclopentene (**66**, 20.7 g, 200 mmol, 1 equiv) was added at −78 °C. The reaction mixture was slowly warmed to RT and stirred for 1 h. After the usual workup the residual oil was purified by distillation, affording the product **68** (30.7 g, 146 mmol, 73% yield) as a pale yellow oil (b.p. 63–65 °C, 0.1 mm Hg). IR (neat): $\tilde{\nu}$ = 3052 (m), 2957 (s), 2854 (m), 1733 (s), 1482 (m), 1285 (s), 1156 (s) cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.78–5.74 (m, 1H), 5.71–5.67 (m, 1H), 4.08 (t, ^3J(H,H) = 6.6 Hz, 2H), 2.72–2.68 (m, 1H), 2.36–2.30 (m, 2H), 2.11–2.05 (m, 1H), 1.71–1.66 (m, 2H), 1.51–1.37 (m, 3H), 1.23 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 178.4, 134.6, 130.4, 64.4, 45.0, 38.6, 32.1, 31.8, 29.6, 27.0, 26.9; MS (FD): *m/z* = 211 ([*M* + 1], 2), 210 ([*M*$^+$], 15), 209 ([*M* − 1], 100); $C_{13}H_{22}O_2$ (210.3): calcd C 74.24, H 10.54; found C 74.58, H 10.63.

3-(2-Cyclopentenyl)propanal (70): To a solution of the alcohol **68** (13.9 g, 66.1 mmol) in THF (60 mL) was added methyllithium (85 mL of 1.6 M solution in hexane, 136 mmol, 1.0 equiv) at −78 °C. The reaction mixture was stirred for 15 min and was quenched with saturated aqueous NH_4Cl (100 mL). The suspension was warmed to RT, and ether (100 mL) and aqueous HCl (50 mL, 10% solution) were added. The aqueous phase was extracted with ether (2 × 100 mL), the combined organic layer was dried ($MgSO_4$), and the solvents were evaporated. The crude residue was oxidized as previously described (see preparation of **20**). After flash-chromatographic purification (ether/hexanes 1:20) the aldehyde **70** was isolated (4.34 g, 34.9 mmol, 54% yield from **66**) as a colorless oil. IR (neat): $\tilde{\nu}$ = 3054 (w), 2958 (s), 2856 (s), 2717 (m), 1729 (s), 1463 (w), 722 (w) cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 9.71 (t, ^3J(H,H) = 1.8 Hz, 1H), 5.71–5.67 (m, 1H), 5.59–5.55 (m, 1H), 2.69–2.56 (m, 1H), 2.39 (dt, ^3J(H,H) = 7.7, 1.8 Hz, 2H), 2.31–2.15 (m, 2H), 2.03–1.96 (m, 1H), 1.74–1.51 (m, 2H), 1.39–1.27 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 202.6, 133.9, 131.3, 44.8, 42.1, 31.9, 29.4, 27.9; MS (EI): *m/z* = 95 (3), 81 (9), 80 (100), 79 (27), 67 (60), 65 (6); $C_8H_{12}O$ (124.1): calcd C 77.37, H 9.74; found: C 77.15, H 9.83.

6-(2-Cyclopentenyl)-4-iodo-1-hexene (64): In the first stage, the procedure described above for the preparation of **4b** was repeated with the aldehyde **70** (3.87 g, 31.2 mmol) and allylmagnesium chloride (18.7 mL of a 1.6 M solution in THF, 37.4 mmol, 1.2 equiv). The crude alcohol (3.51 g, 21.2 mmol) was treated with MeI·2DCC (14.7 g, 26.5 mmol, 1.25 equiv) in THF (150 mL) as described above for **1b**. After flash-chromatographic purification (hexanes) the alkyl iodide **64** (2.75 g, 34% yield over two steps) was isolated as a colorless oil. IR (neat): $\tilde{\nu}$ = 3052 (m), 2925 (s), 2850 (s), 1642 (w), 1431 (w), 918 (m), 720 (m) cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.87–5.63 (m, 3H), 5.18–5.08 (m, 2H), 4.12–4.04 (m, 1H), 2.71–2.53 (m, 3H), 2.41–2.20 (m, 2H), 2.10–1.97 (m, 1H), 1.93–1.31 (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 136.3, 134.6, 134.4, 130.7, 130.6, 117.5, 44.8, 44.7, 44.6, 38.1, 37.2, 35.6, 31.9, 29.8, 29.6; MS (EI): *m/z* = 149 (14), 93 (8), 81 (14), 79 (12), 67 (100), 53 (7); $C_{11}H_{17}I$ (276.1): calcd C 47.84, H 6.20; found C 48.05, H 6.23.

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3-(2-Cyclohexyl)propyl pivalate (69): The procedure described above for the preparation of **68** was used again with 3-iodopropyl pivalate (13.5 g, 50.0 mmol, 1 equiv) and 3-bromocyclohexene [51] (7.25 g, 45.0 mmol, 0.9 equiv). After the usual workup, the pivalate **69** (7.10 g, 31.6 mmol, 70% yield) was isolated as a yellow oil. IR (neat): $\tilde{\nu}$ = 3020 (w), 2933 (s), 2860 (m), 1733 (s), 1482 (m), 1285 (s), 1156 (s) cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$): δ = 5.50–5.30 (m, 2H), 3.83 (t, ^3J(H,H) = 6.6 Hz, 2H), 1.93–1.69 (m, 3H), 1.64–1.01 (m, 8H), 0.97 (s, 9H); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 178.3, 131.4, 126.9, 64.3, 38.4, 34.5, 32.2, 28.7, 26.9, 25.8, 25.0, 21.2; MS (EI): *m/z* = 122 (40), 107 (13), 95 (15), 94 (100), 81 (64), 79 (48), 57 (85); $C_{14}H_{24}O_2$ (224.3): calcd C 74.95, H 10.78; found C 74.56, H 11.03.

3-(2-Cyclohexenyl)propanal (71): The procedure described above for the preparation of **70** was repeated with the pivalate **69** (7.00 g, 31.2 mmol). After flash-chromatographic purification (ether/hexanes 1:20) the aldehyde **71** was isolated (2.98 g, 21.5 mmol, 69% yield) as a colorless oil. IR (neat): $\tilde{\nu}$ = 3018 (m), 2927 (s), 2861 (s), 2720 (w), 1725 (s), 1451 (m), 723 (m) cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$): δ = 9.72 (t, ^3J(H,H) = 1.8 Hz, 1H), 5.93–5.69 (m, 1H), 5.50–5.43 (m, 1H), 2.41 (dt, ^3J(H,H) = 7.8, 1.8 Hz, 2H), 1.90–0.84 (m, 9H); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 203.0, 131.0, 128.2, 41.6, 34.8, 28.9, 28.4, 25.5, 21.5; MS (EI): *m/z* = 136 (5), 97 (11), 94 (100), 81 (54), 79 (73), 67 (26), 55 (18); $C_9H_{14}O$ (138.2): calcd C 78.21, H 10.21; found C 78.09, H 10.18.

6-(2-Cyclohexenyl)-4-iodo-1-hexene (65): The procedure described above for the preparation of **64** was repeated with the aldehyde **71** (1.94 g, 14.0 mmol). After flash chromatography (hexanes), the alkyl iodide **65** (1.54 g, 6.2 mmol, 44% yield) was isolated as a colorless oil. IR (neat): $\tilde{\nu}$ = 3080 (w), 3016 (m), 2927 (s), 2857 (m), 1449 (m), 1434 (m), 918 (s), 721 (m) cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$): δ = 5.96–5.50 (m, 3H), 5.20–5.10 (m, 2H), 4.20–4.08 (m, 1H), 2.75–2.57 (m, 2H), 2.20–1.22 (m, 11H); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 136.6, 131.8, 131.5, 127.7, 127.6, 117.8, 45.0, 44.9, 37.6, 37.5, 37.4, 36.2, 36.1, 34.8, 34.7, 29.4, 29.1, 25.5, 21.7, 21.6; MS (EI): *m/z* = 253 (2), 121 (9), 97 (15), 95 (14), 81 (100), 79 (23), 67 (51); $C_{12}H_{19}I$ (290.1): calcd C 49.67, H 6.60; found C 49.54, H 6.67.

2-[1-(3-Carbethoxy-3-butenyl)]tricyclo[5.2.1.0.^{4,10}]decane (72): The procedure described above for the preparation of **3** was repeated with the alkyl iodide **64** (1.38 g, 5.0 mmol) and ethyl (α-bromomethyl)acrylate (0.98 g, 5.0 mmol, 1 equiv) as the electrophile (−78 °C to RT, 1 h). The crude residue was purified by flash chromatography (ether/hexanes 1:50–1:10), affording **72** (1.12 g, 4.3 mmol, 85% yield) as a colorless oil. IR (neat): $\tilde{\nu}$ = 2941 (s), 2860 (m), 1721 (s), 1468 (w), 1304 (w), 1185 (m), 1148 (m) cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.05–6.00 (m, 1H), 5.45–5.40 (m, 1H), 4.13 (q, ^3J(H,H) = 7.2 Hz, 2H), 2.65 (m, 1H), 2.32–2.18 (m, 4H), 1.95–0.96 (m, 14H), 1.23 (t, ^3J(H,H) = 7.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 167.2, 141.5, 123.7, 123.6, 60.3, 54.4, 51.3, 47.4, 44.7, 44.4, 44.0, 43.8, 43.6, 43.5, 38.3, 36.5, 34.2, 32.3, 32.2, 32.0, 31.9, 31.6, 31.6, 31.3, 31.0, 30.8, 30.1, 24.9, 14.1; MS (EI): 263 ([*M* + 1], 9), 262 ([*M*$^+$], 43), 148 (62), 133 (20), 115 (56), 93 (52), 79 (58), 67 (100), 55 (22); $C_{17}H_{26}O_2$ (262.3): calcd C 77.81, H 9.99; found C 77.69, H 10.02.

6-[1-(3-Carbethoxy-3-butenyl)]tricyclo[6.2.1.0.^{5,11}]undecane (73): The procedure described above for the preparation of **3** was repeated with the alkyl iodide **65** (1.45 g, 5.0 mmol) and ethyl (α-bromomethyl)acrylate (0.98 g, 5.0 mmol, 1 equiv) as the electrophile (−78 °C to RT, 1 h). The crude residue was purified by flash chromatography (ether/hexanes 1:50–1:10), affording the product **73** (0.87 g, 3.2 mmol, 63% yield) as a colorless oil. IR (neat): $\tilde{\nu}$ = 2923 (s), 2860 (m), 1721 (s), 1466 (m), 1181 (s), 1150 (m), 939 (w) cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.10–6.09 (m, 1H), 5.50–5.48 (m, 1H), 4.19 (q, ^3J(H,H) = 7.1 Hz, 2H), 2.40–2.20 (m, 4H), 1.99–1.90 (m, 2H), 1.82–1.78 (m, 1H), 1.72–1.38 (m, 10H), 1.29 (t, ^3J(H,H) = 7.1 Hz, 3H), 1.25–1.15 (m, 1H), 1.06–0.92 (m, 2H), 0.84–0.76 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 167.3, 141.6, 141.5, 123.8, 123.6, 60.4, 48.2, 45.9, 44.7, 44.5, 44.6, 42.8, 42.6, 41.9, 39.0, 38.9, 37.2, 37.0, 36.2, 35.8, 33.5, 32.3, 31.6, 31.0, 30.7, 29.7, 29.0, 27.5, 25.5, 24.2, 22.7, 16.2, 14.2; MS (EI): *m/z* = 276 ([*M*$^+$], 17), 162 (76), 121 (63), 115 (89), 93 (58), 81 (92), 79 (82), 67 (82); HR-MS ($C_{18}H_{28}O_2$): calcd 276.2111, found 276.2100.

Ethyl cyclopentylacetate (76): The procedure described above for the preparation of **3** was repeated with the alkyl iodide **75** [37] (1.33 g, 5.0 mmol) and $PdCl_2(MeCN)_2$ (20 mg, 1.5 mol%) as a catalyst. After adding Et_2Zn (1.0 mL, 10 mmol, 2 equiv) the reaction mixture was allowed to warm to RT and was quenched with water. Purification by bulb-to-bulb distillation affords the product **76** (0.44 g, 2.9 mmol, 57% yield) as a clear oil (b.p. 150 °C, 0.1 mm Hg). IR (neat): $\tilde{\nu}$ = 2950 (s), 2870 (s), 1735 (s), 1450 (m), 1375 (s), 1290 (s), 1255 (s), 1185 (s), 1130 (s), 1035 (s) cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$): δ = 4.06 (q, ^3J(H,H) = 7.2 Hz, 2H), 2.24–2.15 (m, 3H), 1.88–1.72 (m, 2H), 1.56–1.50 (m, 4H), 1.18 (t, ^3J(H,H) = 7.2 Hz, 3H), 1.15–1.01 (m, 2H); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 173.6, 60.2, 40.7, 36.7, 32.6, 25.2, 14.4; MS (EI): *m/z* = 156 (4), 111 (34), 88 (100), 55 (33); $C_9H_{16}O_2$ (156.2): calcd C 69.19, H 10.32; found C 68.94, H 10.42.

(*E*)-*tert*-Amyl 7-iodo-2-heptenoate (77): The procedure described above for the preparation of **9** was used. 1-Chloro-4-iodobutane (12.4 g, 57.0 mmol) was converted to the corresponding zinc–copper reagent and was treated with *tert*-amyl propynoate (8.0 g, 57 mmol). After the usual workup, the crude product was purified by flash chromatography (ether/hexanes 1:20), affording (*E*)-*tert*-amyl 7-chloro-2-heptenoate (10.6 g, 45.6 mmol, 80% yield) as a colorless oil.

The (*E*)-*tert*-amyl 7-chloro-2-heptenoate (3.7 g, 16 mmol) thus obtained was dissolved in acetone and sodium iodide (24 g, 160 mmol) and refluxed for 12 h. After the usual workup the crude product was purified by chromatography (ether/hexanes 1:20), affording the alkyl iodide **77** (4.65 g, 14.4 mmol, 90% yield) as a colorless oil. IR (neat): $\tilde{\nu}$ = 2980 (s), 2930 (s), 1710 (s), 1650 (m), 1460 (m), 1380 (m), 1370 (m), 1350 (m), 1320 (s), 1290 (s), 1210 (s), 1150 (s), 980 (m), 850 (m) cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$): δ = 6.75 (dt, ^3J(H,H) = 6.8, 15.6 Hz, 1H), 5.68 (dt, ^3J(H,H) = 1.6, 15.6 Hz, 1H), 3.11 (t, ^3J(H,H) = 6.8 Hz, 2H), 2.13 (dq, ^3J(H,H) = 1.4, 7.2 Hz, 2H), 1.78–1.71 (m, 2H), 1.53–1.50 (m, 2H), 1.37 (s, 6H), 0.82 (t, ^3J(H,H) = 7.4 Hz, 3H); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 166.1, 147.1, 123.8, 82.9, 33.8, 33.1, 31.2, 29.2, 26.0, 8.6, 6.7; MS (EI): *m/z* = 254 ([*M*$^+$ − C_5H_{10}], 18), 237 (37), 70 (100), 55 (24); $C_{12}H_{21}O_2I$ (324.2): calcd C 44.47, H 6.53; found C 44.52, H 6.64.

***tert*-Amyl cyclopentylacetate (78)**: The procedure decribed above for the preparation of **3** was repeated with the alkyl iodide **77** (1.38 g, 4.3 mmol) and $PdCl_2(MeCN)_2$ (17 mg, 1.5 mol%) as catalyst. After adding Et_2Zn (0.86 mL, 8.6 mmol, 2 equiv), the reaction mixture was slowly (over 4 h) warmed to RT and then quenched with water. Flash-chromatographic purification (ether/hexanes 1:20) affords the acetate **78** (0.62 g, 3.3 mmol, 74% yield) as a colorless oil. IR (neat): $\tilde{\nu}$ = 2930 (s), 2870 (s), 1720 (s), 1455 (m), 1370 (m), 1285 (m), 1265 (m), 1235 (m), 1200 (m), 1130 (brs), 930 (w), 8.30 (m) cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$): δ = 2.15–2.14 (m, 3H), 1.69 (q, ^3J(H,H) = 7.4 Hz, 2H), 1.75–1.64 (m, 2H), 1.53–1.48 (m, 4H), 1.34 (s, 6H), 1.28–0.95 (m, 2H), 0.81 (t, ^3J(H,H) = 7.4 Hz, 3H); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 173.1, 82.6, 42.2, 37.0, 33.78, 32.7, 25.9, 25.3, 8.5; MS (EI): *m/z* = 111 (49), 83 (37), 71 (100), 55 (29), 43 (45); $C_{12}H_{22}O_2$ (198.3): calcd C 72.73, H 11.18; found C 72.52, H 11.26.

(*E*)-Ethyl 7-iodo-2-heptenoate (75): The procedure described above for the preparation of **9** was used. 1-Chloro-4-iodobutane (5.0 g, 23.0 mmol) was converted to the related zinc–copper reagent and treated with ethyl propynoate (2.32 mL, 23 mmol). The reaction mixture was quenched with saturated aqueous NH_4Cl. After the usual workup the crude product was purified by flash chromatography (ether/hexanes 1:20), affording (*E*)-ethyl 7-chloro-2-heptenoate (**75**) (3.96 g, 19.4 mmol, 85% yield) as a colorless oil.

A solution of compound **75** (3.8 g, 20 mmol) and sodium iodide (30 g, 200 mmol) in acetone (75 mL) was refluxed for 18 h. After the usual workup, the crude product was purified by flash chromatography (ether/hexanes 1:20), furnishing the alkyl iodide **75** (5.13 g, 18.2 mmol, 91% yield) as a colorless oil. IR (neat): $\tilde{\nu}$ = 2980 (s), 2940 (m), 1720 (s), 1655 (s), 1450 (m), 1310 (s), 1270 (s), 1190 (s), 1045 (s), 980 (s) cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$): δ = 6.86 (dt, ^3J(H,H) = 15.6, 7.0 Hz, 1H), 5.76 (dt, ^3J(H,H) = 15.6, 1.6 Hz, 1H), 4.11 (q, ^3J(H,H) = 7.2 Hz, 2H), 3.12 (t, ^3J(H,H) = 6.8 Hz, 2H), 2.16 (dq, ^3J(H,H) = 7.2, 1.4 Hz, 2H), 3.12 (t, ^3J(H,H) = 6.8 Hz, 2H), 2.16 (dq, ^3J(H,H) = 7.2, 1.4 Hz, 2H), 1.78–1.74 (m, 2H), 1.55–1.51 (m, 2H), 1.22 (t, ^3J(H,H) = 7.2 Hz, 3H); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 165.5, 147.0, 120.9, 59.2, 31.7, 29.9, 27.8, 13.2, 5.0; MS (EI): *m/z* = 282 ([*M*$^+$], 11), 237 (26), 155 (55), 127 (34), 109 (36), 81 (100), 55 (73), 41 (65); $C_9H_{15}O_2I$ (282.1): calcd C 38.31, H 5.35; found C 38.04, H 5.35.

Methyl cyclopentylideneacetate (80): The procedure described above for the preparation of compound **3** was repeated with the alkyl iodide **79** (1.33 g, 5.0 mmol) [37] and $PdCl_2(MeCN)_2$ (20 mg, 1.5 mol%) as catalyst . After adding Et_2Zn (1.0 mL, 10.0 mmol, 2 equiv), the reaction mixture was warmed to RT over 4 h and then quenched with water. Purification by flash chromatography (ether/hexanes 1:20) affords the ester **80** (0.51 g, 3.7 mmol, 73% yield) as a colorless oil. IR (neat): $\tilde{\nu}$ = 2945 (s), 2880 (s), 1710 (s), 1655 (s), 1430 (brs), 1360 (s), 1305 (s), 1260 (s), 1205 (s), 1125 (s), 1030 (s) 960 (m), 905 (m), 855 (s), 780 (m), 720 (m) cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$): δ = 5.71 (q, ^3J(H,H) = 2.5 Hz, 1H), 3.60 (s, 3H), 2.69 (t, ^3J(H,H) = 7.6 Hz, 2H), 2.35 (t, 2H, ^3J(H,H) = 7.2 Hz), 1.70–1.58 (m, 4H); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 169.7, 167.5, 111.5, 51.0, 36.2, 32.9, 26.7, 25.8; MS (EI): *m/z* = 140 ([*M*$^+$], 100), 81 (49), 74 (24), 67 (26), 53 (21); $C_8H_{12}O_2$ (140.1): calcd C 68.54, H 8.62; found C 68.70, H 8.66.

6-Chloro-1-trimethylsilyl-1-hexyne (83) [40]: Magnesium turnings (1.58 g, 66 mmol) were suspended in THF (32 mL), and bromoethane (5 mL, 66 mmol) was added dropwise while the temperature was kept below 50 °C. After complete addition, the solution was stirred for 1 h at 50 °C. A solution of 6-chloro-1-hexyne (7.0 g, 60 mmol) in THF (3 mL) was added slowly below 10 °C. Stirring was continued for 15 h at RT. After the mixture had been cooled to 5 °C, TMSCl (8.5 mL, 66 mmol) was carefully added while the temperature was maintained beneath 20 °C. The reaction mixture was refluxed for 2 h. After the usual workup, the crude product was purified by chromatography (ether/hexanes 1:10), affording the alkyne **83** (9.8 g, 53 mmol, 88% yield) as a colorless oil. IR (neat): $\tilde{\nu}$ = 2940 (s), 2900 (s), 2170 (m), 1455 (m), 1435 (m), 1410 (m), 1245 (s), 755 (s), 695 (s) cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$): δ = 3.42 (t, ^3J(H,H) = 6.4 Hz, 2H), 2.12 (t, ^3J(H,H) = 7.0 Hz, 2H), 1.78–1.71 (m, 2H), 1.55–1.48 (m, 2H), 0.00 (s, 9H); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 106.3, 85.0, 44.3, 31.3, 25.6, 19.0, 0.0; MS (EI): *m/z* = 173 ([*M*$^+$ − CH_3], 4), 197 (14), 93 (100), 79 (28); $C_9H_{17}ClSi$ (188.7): calcd C 57.26, H 9.07; found C 57.30, H 9.24.

7-Iodo-1-phenyl-2-heptyn-1-one (81): Aluminum chloride (13 g, 98 mmol) was suspended in CS_2 (150 mL) and cooled to 0 °C. A solution of 6-chloro-1-trimethylsilyl-1-hexyne **83** (14.1 g, 74.8 mmol) and benzoyl chloride (9.6 mL, 82 mmol) in CS_2 (33 mL) was added at <8 °C. The reaction mixture was stirred at 5 °C for 1 h and was poured onto a mixture of ice (100 g) and conc. aqueous HCl (30 mL). The organic layer was separated and the aqueous phase was extracted twice with CH_2Cl_2 (100 mL). The combined organic layer was washed with brine (100 mL) and dried ($MgSO_4$). The solvent was evaporated and the crude product purified by flash chromatography (ether/hexanes 10:1), affording 7-chloro-1-phenyl-2-heptyn-1-one (6.84 g, 31 mmol, 41% yield) as a yellow oil.

The 7-Chloro-1-phenyl-2-heptyn-1-one thus obtained (6.78 g, 30.7 mmol) and sodium iodide (45 g, 300 mmol) were dissolved in acetone (100 mL). The mixture was refluxed for 18 h, the solvent was evaporated, and the organic phase extracted with ether, washed with water (100 mL), and dried ($MgSO_4$). The solvent was evaporated and the crude product was purified by chromatography (ether/hexanes 1:10), affording the alkyl iodide **81** (7.7 g, 24.8 mmol, 81% yield). IR (neat): $\tilde{\nu}$ = 3060 (m), 2930 (m), 2200 (s), 1780 (m), 1725 (m), 1650 (s), 1600 (s), 1580 (s), 1460 (s), 1320 (s), 1265 (s), 910 (m), 790 (m), 700 (s) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ = 8.10–8.06 (m, 2H), 7.53–7.53 (m, 3H), 3.17 (t, $^3J(H,H)$ = 3.5 Hz, 2H), 2.49 (t, $^3J(H,H)$ = 6.9 Hz, 2H), 2.00–1.90 (m, 2H), 1.79–1.69 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 178.0, 136.7, 134.0, 129.5, 128.7, 95.4, 80.1, 31.9, 28.5, 18.3, 5.7; MS (EI): m/z = 311 ([M^+], 1), 289 (1), 185 (38), 129 (35), 115 (38), 105 (100), 91 (18), 77 (53); $C_{13}H_{13}OI$ (312.1): calcd C 50.02, H 4.19; found C 50.01, H 4.25.

8-Iodo-3-octyn-2-one (82): The procedure described above for the preparation of **81** was repeated with acetyl chloride (2.0 mL, 30 mmol) in the presence of aluminum chloride (4.4 g, 33 mmol) and 6-chloro-1-trimethylsilyl-1-hexyne (**83**) (4.78 g, 25.4 mmol) in CS_2 (65 mL). After the usual workup, the crude product was purified by flash chromatography (ether/hexanes 1:10), affording 8-chloro-3-octyn-2-one (2.32 g, 14.7 mmol, 58% yield) as a yellow oil.

A solution of the 8-chloro-3-octyn-2-one thus obtained (2.32 g, 14.7 mmol) and sodium iodide (22 g, 150 mmol) in acetone (55 mL) was heated under reflux for 18 h. After the usual workup the crude product was purified by flash chromatography (ether/hexanes 1:10) to give the alkyl iodide **82** (3.35 g, 13.4 mmol, 91% yield) as a yellowish oil. IR (neat): $\tilde{\nu}$ = 3000 (m), 2920 (s), 2885 (m), 2205 (s), 1735 (m), 1675 (s), 1360 (s), 1330 (s), 1290 (s), 1230 (s), 1170 (m), 1020 (m), 970 (m) cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$): δ = 3.13 (t, $^3J(H,H)$ = 6.8 Hz, 2H), 2.35 (t, $^3J(H,H)$ = 7.9 Hz, 2H), 2.26 (s, 3H), 1.92–1.88 (m, 2H), 1.67–1.63 (m, 2H); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 185.1, 93.0, 82.1, 33.1, 32.5, 28.7, 18.3, 6.0; MS (EI): m/z = 235 ([$M^+ - CH_3$], 2), 143 (2), 43 (100); $C_8H_{11}OI$ (250.0): calcd C 38.42, H 4.43; found C 38.36, H 4.42.

1-Benzoyl-1-ethylmethylene cyclopentane (84): The procedure described above for the preparation of **3** was repeated with the alkyl iodide **82** (2.18 g, 7.00 mol) and $PdCl_2(MeCN)_2$ (27 mg, 1.5 mol%). After adding Et_2Zn (1.4 mL, 14.0 mmol, 2 equiv), the reaction mixture was warmed to RT over 4 h and water was added. Purification by flash chromatography (hexanes to ether/hexanes 1:10) affords the product **84** (0.89 g, 2.4 mmol, 60% yield) as a colorless oil. IR (neat): $\tilde{\nu}$ = 3080 (w), 2915 (s), 1660 (s) 1600 (m), 1580 (m), 1450 (s), 1315 (s), 1445 (s), 930 (m), 810 (m), 710 (s) cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$): δ = 7.85–7.80 (m, 2H), 7.55–7.29 (m, 3H), 2.20–2.01 (m, 4H), 1.92–1.71 (q, $^3J(H,H)$ = 7.4 Hz, 2H), 1.73–1.52 (m, 4H), 0.81 (t, $^3J(H,H)$ = 7.4 Hz, 3H); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 203.4, 141.1, 138.6, 134.9, 133.7, 131.1, 130.2, 29.8, 29.5, 29.3, 24.4, 24.1, 14.4; MS (EI): m/z = 214 ([M^+], 86), 199 (91), 171 (30), 157 (34), 105 (94), 77 (100), 67 (26), 55 (19); $C_{15}H_{18}O$ (214.3): calcd C 84.06, H 8.46; found C 84.22, H 8.43.

1-Ethyl-1-(2-oxopropyl)cyclopentane (85): The procedure described above for the preparation of **3** was repeated with the alkyl iodide **82** (1.00 g, 4.0 mmol) and $PdCl_2(MeCN)_2$ (0.020 g, 1.9 mol%). After addition of Et_2Zn (0.8 mL, 8.0 mmol, 2 equiv) the reaction mixture was warmed to RT over 4 h followed by the usual workup. Purification of the residual oil obtained after evaporation of the solvents by flash chromatography (ether/hexanes 1:10–1:5) affords the ketone **85** (0.32 g, 2.1 mmol, 52% yield) as a colorless oil. IR (neat): $\tilde{\nu}$ = 2950 (s), 2870 (s), 1725 (s), 1460 (m), 1360 (s), 1275 (s), 1125 (m), 1075 (m), 745 (m) cm $^{-1}$; ^1H NMR (200 MHz, $CDCl_3$): δ = 2.37 (s, 2H), 2.05 (s, 3H), 1.54–1.46 (m, 4H), 1.42–1.30 (m, 6H), 0.75 (t, $^3J(H,H)$ = 7.4 Hz, 3H); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 209.5, 50.9, 45.2, 37.8, 32.2, 31.0, 24.7, 9.7; MS (EI): m/z = 96 ([$M^+ - (CH_3CO)$], 76), 67 (91), 55 (34), 43 (100); $C_{10}H_{18}O$ (154.2): calcd C 77.86, H 11.76; found C 77.64, H 11.66.

Synthesis of (+)-methyl epijasmonate (86) and (−)-methyl cucurbate (87): Compounds **91**, **92**, **93**, and **94** were prepared by literature methods [44].

(*S*)-(−)-4-Benzyloxy-5-hexene-1-ol (95): The pivalate **91** (0.96 g, 3.31 mmol) was added to a suspension of $LiAlH_4$ (0.16 g, 4.3 mmol) in ether (10 mL) at 0 °C. The reaction mixture was warmed to RT, stirred for 0.5 h, and quenched with saturated aqueous NH_4Cl (10 mL) and aqueous HCl (20 mL of a 10% solution). The aqueous phase was extracted with ether (2 × 40 mL), the combined organic layer was dried ($MgSO_4$) and the solvent was evaporated. The crude residue was purified by flash chromatography (ether/hexanes 1:20–1:4), affording the alcohol **95** (0.62 g, 91% yield) as a colorless oil. $[\alpha]_D^{23}$ = − 18.64 (*c* = 2.1, benzene); IR (neat): $\tilde{\nu}$ = 3395 (s), 2940 (s), 2869 (m), 1716 (s), 1446 (w), 1268 (s), 1062 (s) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ = 7.33–7.23 (m, 5H), 5.74 (ddd, $^3J(H,H)$ = 16.7, 10.9, 7.8 Hz, 1H), 5.24–5.18 (m, 2H), 4.59 (d, $^3J(H,H)$ = 11.8 Hz, 1H), 4.34 (d, $^3J(H,H)$ = 11.8 Hz, 1H), 3.79–3.73 (m, 1H), 3.60–3.55 (m, 2H), 2.21 (brs, 1H), 1.72–1.58 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 138.7, 138.4, 128.3, 127.8, 127.5, 117.3, 80.4, 70.2, 62.7, 32.2, 28.7; MS (FD): m/z = 208 ([M + 2], 2), 207 ([M + 1], 63), 206 ([M^+], 1), 147 (8), 107 (8), 91 (26); $C_{13}H_{18}O_2$ (206.2): calcd C 75.69, H 8.74; found C 75.45, H 8.88.

(*S*)-(−)-4-Benzyloxy-5-hexenal (96): 1,1,1-Triacetoxy-1,1-dihydro-1,2-benziodoxol-3-(1*H*)one [44] (1.28 g, 3.02 mmol, 1.1 equiv) was suspended in CH_2Cl_2 (10 mL), and the alcohol **92** (0.56 g, 2.74 mmol) was added at 0 °C. This suspension was stirred for 15 min at 0 °C and 1 h at RT. After workup with a 1 M aqueous solution of NaOH (30 mL), the aqueous layer was extracted with CH_2Cl_2 (2 × 30 mL). The combined organic layer was dried ($MgSO_4$) and the solvent was evaporated. The crude residue was purified by flash chromatography (ether/hexanes 1:50–1:10), affording the aldehyde **96** (0.46 g, 2.25 mmol, 82% yield) as a colorless oil. $[\alpha]_D^{23}$ = − 31.15 (*c* = 2.7, benzene). The spectroscopic data are identical with those of the racemic aldehyde **24** (see above).

(2*RS*,5*S*)-(−)-Methyl-6-benzyloxy-2-hydroxy-7-octenoate (97): To a solution of diisopropylamine (0.42 g, 0.59 mL, 4.16 mmol, 2 equiv) in ether (8 mL) was added dropwise *n*BuLi (2.60 mL of 1.6 M solution in hexane, 4.16 mmol, 2 equiv) at − 30 °C. After stirring for 0.5 h, methyl acetate (0.31 g, 0.33 mL, 4.18 mmol, 2 equiv) was added. The solution was stirred for 1 h and the aldehyde **96** (0.42 g, 2.08 mmol, 1 equiv) dissolved in ether (2 mL) was added. The reaction mixture was stirred for 0.5 h and then quenched with saturated aqueous NH_4Cl (10 mL) and aqueous 10% HCl (10 mL). The aqueous phase was extracted with ether (2 × 30 mL). The combined organic layer was dried ($MgSO_4$) and the solvent was evaporated. The crude residue was purified by flash chromatography (ether/hexanes 1:10–1:1), affording the aldol product **97** (0.45 g, 1.62 mmol, 78% yield). $[\alpha]_D^{23}$ = − 15.07 (*c* = 2.1, benzene); IR (neat): $\tilde{\nu}$ = 3452 (s), 3025 (m), 2947 (s), 1730 (s), 1640 (w), 1496 (m), 913 (m) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ = 7.28–7.21 (m, 5H), 5.76–5.64 (m, 1H), 5.27–5.15 (m, 2H), 4.55 (d, $^3J(H,H)$ = 11.9 Hz, 1H), 4.30 (d, $^3J(H,H)$ = 11.9 Hz, 1H), 4.01–3.88 (m, 1H), 3.81–3.69 (m, 1H), 3.64 (s, 3H), 3.21 (brs, 1H), 2.49–2.31 (m, 2H), 1.70–1.48 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 173.1, 138.7, 138.6, 128.4, 127.8, 127.5, 117.3, 80.5, 80.1, 70.2, 70.1, 68.0, 67.8, 51.7, 41.4, 41.3, 32.6, 32.3, 31.6, 31.4; MS (FD): m/z = 280 ([M + 2], 2), 279 ([M + 1], 100), 277 ([M − 1], 5), 172 (20), 91 (25); $C_{16}H_{22}O_4$ (278.3): calcd C 69.04, H 7.97; found C 68.85, H 8.09.

(2*RS*,5*S*)-(−)-Methyl 6-benzyloxy-2-iodo-7-octenoate (90): To a solution of the alcohol **97** (0.50 g, 1.47 mmol, 1 equiv) in THF (10 mL), MeI·2DCC (1.53 g, 2.75 mmol, 1.88 equiv) was added. The suspension was heated to 45 °C for 3 h and 30 °C for 6 h. After flash-chromatographic purification (ether/hexanes 1:10–1:4), the alkyl iodide **90** (0.36 g, 0.93 mmol, 63% yield) was isolated as a colorless oil. $[\alpha]_D^{23}$ = − 13.31 (*c* = 2.2, benzene); IR (neat): $\tilde{\nu}$ = 2947 (m), 2855 (m), 1736 (s), 1637 (w), 1496 (w), 1431 (m), 1204 (m), 1062 (m) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ = 7.37–7.21 (m, 5H), 5.78–5.67 (m, 1H), 5.29–5.18 (m, 2H), 4.58 (d, $^3J(H,H)$ = 11.9 Hz, 1H), 4.38–4.25 (m, 2H), 3.80–3.70 (m, 1H), 3.69 (s, 3H), 3.02–2.95 (m, 2H), 1.94–1.58 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 170.9, 138.4, 138.3, 138.2, 128.2, 127.6, 127.4, 117.5, 117.4, 79.4, 79.0, 70.0, 51.8, 45.8, 45.7, 36.1, 35.7, 35.3, 35.1, 27.5, 27.4; MS (FD): m/z = 390 ([M + 2], 2), 389 ([M + 1], 69), 388 ([M^+], 78), 387 ([M − 1], 48), 261 (100), 147 (42); $C_{16}H_{21}IO_3$ (388.2): calcd C 49.50, H 5.51; found C 49.55, H 5.47.

(1*R*,2*S*,3*R*)-(+)-1-Benzyloxy-3-methylcarbomethoxy-2-(pentynyl)cyclopentane (99): The procedure described above for the preparation of **3** was repeated with the alkyl iodide **90** (332 mg, 0.86 mmol), $Ni(acac)_2$ (2 mol%) as catalyst and 1-bromo-1-butyne (171 mg, 1.28 mmol, 1.5 equiv) as the electrophile (− 55 °C, 48 h). The crude residue was purified by flash chromatography (hexanes to ethyl acetate/hexanes 1:30), affording the cyclopentane derivative **99** (231 mg, 0.74 mmol, 86% yield) as a colorless oil. $[\alpha]_D^{23}$ = + 17.69 (*c* = 1.1, benzene); IR (neat): $\tilde{\nu}$ = 3025 (w), 2940 (s), 2869 (m), 2357 (w), 1730 (s), 1432 (m), 1161 (m), 1082 (m) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ = 7.32–7.24 (m, 5H), 4.54–4.45 (m, 2H), 3.93–3.88 (m, 1H), 3.65 (s, 3H), 2.69–2.57 (m, 1H), 2.53–2.42 (m, 1H), 2.30–1.86 (m, 8H), 1.78–1.61 (m, 1H), 1.37–1.22 (m, 1H), 1.07 (t, $^3J(H,H)$ = 7.5 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 173.5, 138.9, 128.3, 127.5, 127.3, 84.4, 82.7, 77.8, 70.9, 51.4, 46.7, 36.8, 35.1, 30.1, 28.6, 17.5, 14.2, 12.4; MS (FD): m/z = 316 ([M + 2], 1), 315 ([M + 1], 9), 314 ([M^+], 12), 313 ([M − 1], 19), 123 (3), 91 (5); $C_{20}H_{26}O_3$ (314.4): calcd C 76.40, H 8.33, found C 76.21, H 8.34.

(1*R*,2*S*,3*R*)-(+)-1-Benzyloxy-3-methylcarbomethoxy-2-[(*Z*)-2-pentenyl]cyclopentane (100): Pd/$BaSO_4$ (15 mg) was suspended in pyridine (1 mL) under an atmosphere of H_2; the alkyne **99** (207 mg, 0.66 mmol) dissolved in pyridine (2 mL) was added. The reaction mixture was stirred for 1 h at RT and quenched with aqueous 10% HCl solution (10 mL). The aqueous layer was extracted with CH_2Cl_2 (3 × 30 mL) and the combined organic layer was washed with saturated aqueous $NaHCO_3$ (10 mL) and dried ($MgSO_4$), and the solvent was evaporated. The crude residue was purified by flash chromatography (ethyl acetate/hexanes 1:40), affording the hydrogenated product **100** (192 mg, 0.61 mmol, 92% yield) as

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a colorless oil. $[\alpha]_D^{23} = +12.19$ ($c = 1.2$, benzene); IR (neat): $\tilde{\nu} = 2954$ (s), 2869 (m), 1738 (s), 1645 (w), 1432 (m), 1069 (m) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): $\delta = 7.29-7.18$ (m, 5H), 5.39–5.27 (m, 2H), 4.44–4.36 (m, 2H), 3.68–3.63 (m, 1H), 3.62 (s, 3H), 2.68–2.54 (m, 1H), 2.44–2.33 (m, 1H), 2.23–1.63 (m, 8H), 1.33–1.23 (m, 1H), 1.18–1.02 (m, 1H), 0.90 (t, $^3J(H,H) = 7.5$ Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 173.5$, 138.8, 132.6, 128.1, 127.4, 127.2, 127.1, 84.1, 70.7, 51.3, 47.4, 36.8, 35.1, 29.7, 28.5, 24.7, 20.5, 14.0; MS (FD): $m/z = 317$ ([M + 1], 22), 316 ([M^+], 100), 315 ([M − 1], 2), 262 (9), 226 (15), 58 (6); $C_{20}H_{28}O_3$ (316.4): calcd C 75.91, H 8.92; found C 75.72, H 8.84.

(1*R*,2*S*,3*R*)-(−)-1-Hydroxy-3-methylcarbomethoxy-2-[(*Z*)-2-pentenyl]cyclopentane (87): To a 1.0 M solution of BCl_3 (1.7 mL, 1.7 mmol, 3.1 equiv) in CH_2Cl_2 was added the protected alcohol **100** (171 mg, 0.54 mmol, 1 equiv). The reaction mixture was slowly warmed to −10 °C, stirred for 0.5 h at this temperature and cooled back to −78 °C. Methanol (5 mL) was added, the solution was warmed to RT, and saturated aqueous $NaHCO_3$ solution (10 mL) was added. The aqueous layer was extracted with CH_2Cl_2 (3 × 20 mL), the combined organic layer was dried ($MgSO_4$), and the solvent was evaporated. The crude residue was purified by flash chromatography (ether/hexanes 1:20–1:1), affording (−)-methyl cucurbate (**87**, 77 mg, 0.34 mmol, 63% yield) as a colorless oil. $[\alpha]_D^{23} = -2.20$ ($c = 0.2$, methanol); IR (neat): $\tilde{\nu} = 3438$ (m), 2954 (s), 2869 (m), 1738 (s), 1652 (w), 1432 (m) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): $\delta = 5.42-5.24$ (m, 2H), 3.94–3.90 (m, 1H), 3.60 (s, 3H), 2.68–2.51 (m, 1H), 2.39–2.24 (m, 1H), 2.19–1.81 (m, 9H), 1.54–1.45 (m, 1H), 1.29–1.18 (m, 1H), 0.90 (t, $^3J(H,H) = 7.5$ Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 173.7$, 133.1, 127.1, 77.5, 51.5, 50.7, 36.7, 35.3, 32.6, 28.4, 25.3, 20.7, 14.2; MS (FD): $m/z = 227$ ([M + 1], 13), 226 ([M^+], 100), 208 (23), 104 (6); $C_{13}H_{22}O_3$ (226.3): calcd C 68.99, H 9.80; found C 68.94, H 9.87.

(2*S*,3*R*)-(+)-3-Methylcarbomethoxy-2-[(*Z*)-2-pentenyl]-1-cyclopentanone (86): 1,1,1-Triacetoxy-1,1-dihydro-1,2-benziodoxol-3-(1*H*)one [46] (170 mg, 0.40 mmol, 1.4 equiv) was suspended in CH_2Cl_2 (1 mL) and the alcohol **87** (67 mg, 0.296 mmol, 1 equiv) was added. The suspension was stirred for 3 h. After dilution with ether (10 mL), the reaction mixture was poured into saturated aqueous $NaHCO_3$ containing $Na_2S_2O_3$ (440 mg, 2.80 mmol, 7 equiv) and was stirred for 15 min. The aqueous layer was extracted with ether (2 × 20 mL). The combined organic layer was dried ($MgSO_4$), and the solvent was evaporated. The crude residue was purified by flash chromatography (ether/hexanes 1:10–1:4), affording (+)-methyl epijasmonate (**86**, 54 mg, 0.239 mmol, 81% yield) as a colorless oil. $[\alpha]_D^{23} = +53.21$ ($c = 0.3$, methanol); IR (neat): $\tilde{\nu} = 2954$ (s), 1736 (s), 1659 (w), 1432 (m), 1168 (s) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): $\delta = 5.43-5.20$ (m, 2H), 3.62 (s, 3H), 2.84–2.72 (m, 1H), 2.39–1.92 (m, 10H), 1.81–1.69 (m, 1H), 0.89 (t, $^3J(H,H) = 7.5$ Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 218.8$, 172.9, 133.5, 125.5, 52.7, 51.7, 35.6, 35.3, 33.7, 25.7, 23.0, 20.7, 14.1; MS (EI): $m/z = 225$ ([M + 1], 2), 224 ([M^+], 20), 151 (42), 109 (23), 95 (41), 82 (100); $C_{13}H_{20}O_3$ (224.3): calcd C 69.61, H 8.99; found C 69.73, H 9.14.

Acknowledgments: We thank the Deutsche Forschungsgemeinschaft (SFB 260) and the Fonds der Chemischen Industrie for the generous support of this research. We are grateful to BASF (Ludwigshafen, Germany), Witco (Bergkamen, Germany), Chemetall (Frankfurt) and SIPSY (Avrillé, France) for generous gifts of chemicals. We thank Dr. C. Fehr (Firmenich) for a sample of methyl epijasmonate, and W. Dörner, M. Eckhardt, R. Lentz, T. Breyhan, T. Wendrich, and B. Schmidt for the performance of some preliminary experiments.

Received: May 6, 1996 [F364]

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