Stereoselective Preparation and Reactions of Configurationally Defined Dialkylzinc Compounds

Andreas Boudier, Christophe Darcel, Felix Flachsmann, Laurent Micouin, Martin Oestreich, and Paul Knochel*[a]

Abstract: The reaction of cyclic and open-chain diastereomerically pure *secondary* organoboranes with diisopropylzinc allows the preparation of *secondary* dialkylzinc reagents with good to excellent retention of configuration as shown by deuterolysis and Cu^I- and Pd^0-mediated reactions with electrophiles. The importance of a high boron–zinc exchange rate to obtain high diastereoselectivity has been shown. Improvement of the configurational stability and stereomeric purity of the zinc intermediates has been obtained by using mono-isopinocampheylborane ((−)-$IpcBH_2$) providing optically active dialkylzinc compounds (up to 96% *ee*) with enhanced diastereoselectivities.

Keywords: boron–zinc exchange • organozinc compounds • stereoselective synthesis • zinc

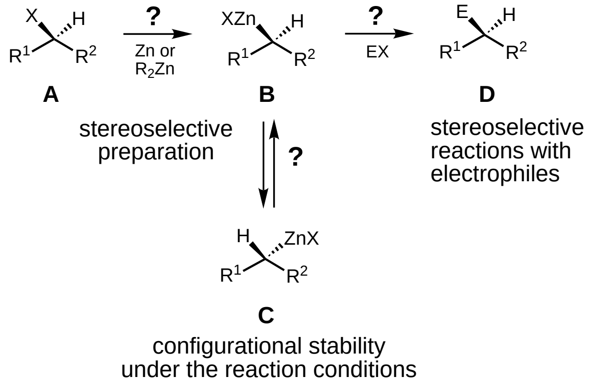
Introduction

Organometallic species bearing a chiral carbon center attached to the metal center are important chiral intermediates, since after reaction with an organic electrophile, a variety of chiral organic products is obtained. The preparation of chiral organolithiums bearing a heteroatom in the α-position to the carbon–lithium bond has been an active research field and led to configurationally stable organometallic compounds which proved to be of a great utility in organic synthesis.[1]

Unfortunately, the absence of a heteroatom at the α-position led to configurationally unstable organolithium compounds. It is anticipated that organometallic compounds bearing a more covalent carbon–metal bond should be configurationally more stable.[2] Recently, we have reported that several cyclic *secondary* organozinc derivatives are configurationally stable and that the reaction with electrophiles takes place under high retention of configuration.[3, 4a] Herein, we report our results on the preparation and reactions of configurationally defined cyclic and acyclic diorganozinc compounds.[4a, 4b] Furthermore we present our studies on the preparation of enantiomerically enriched diorganozinc compounds (up to 97%*ee*) and their Cu^I- or Pd^0-mediated reactions with electrophiles.

Results and Discussion

We envisioned a general method for the preparation of *secondary* organozinc compounds and the study of their configurational stability. Three main problems exist in such an approach. First, the conversion of the starting material **A** to the chiral zinc reagent **B** should be stereoselective (Scheme 1). Second, under the reaction conditions used (solvent, temperature, additives), the zinc intermediate **B** should be configurationally stable and not interconvert to the epimeric organometallic **C**. Finally, the organozinc species **B** should react stereoselectively with a broad range of electrophiles to products **D**.



Scheme 1. Configurational stability of organozinc compounds.

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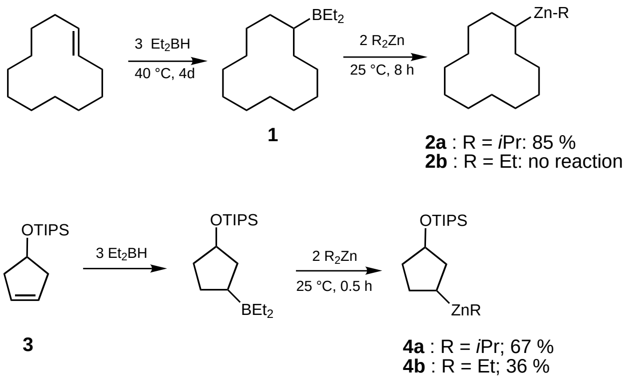
A synthetically useful process only results, if all these conditions are fulfilled. Below we will report such a successful reaction sequence based on a stereoselective boron–zinc exchange. The oxidative addition of an alkyl iodide to metallic zinc, which proceeds via radical intermediates, can be used in some cases for the stereoselective preparation of zinc organometallics, but is far from being general.[3a] We have found that the boron–zinc exchange reaction gives better results.[5] This reaction allows the efficient conversion of *primary* alkyldiethylboranes to the corresponding dialkylzinc compounds by treatment with diethylzinc. In the case of *secondary* alkyldiethylboranes, we have found that the use of diethylzinc leads in several cases to a slow and equilibrated reaction, however by using the *secondary* diorganozinc $i\mathrm{Pr_2Zn}$ for performing the exchange, a faster reaction is observed (Scheme 2).[6]

$$\mathrm{R\text{-}BEt_2} + \mathrm{Et_2Zn} \underset{\longleftarrow}{\overset{\text{slow}}{\rightleftharpoons}} \mathrm{RZnEt} + \mathrm{Et_3B}$$

$$\mathrm{R\text{-}BEt_2} + i\mathrm{Pr_2Zn} \overset{\text{fast}}{\rightleftharpoons} \mathrm{RZn}i\text{-}\mathrm{Pr} + \mathrm{Et_2B}i\mathrm{Pr}$$

Scheme 2. The boron–zinc exchange of secondary alkyldiethylboranes.

Thus, diethylborylcyclododecane (**1**), prepared by the reaction of $\mathrm{Et_2BH}$ with cyclododecene (40 °C, 4 d),[7] does not react at all with $\mathrm{Et_2Zn}$, but smoothly reacts with $i\mathrm{Pr_2Zn}$ (2 equiv, ca. 5 M in $\mathrm{Et_2O}$, 25 °C, 8 h) providing the desired mixed isopropylcyclododecylzinc compound **2a** in about 85 % yield (as determined by iodolysis experiments) (Scheme 3).

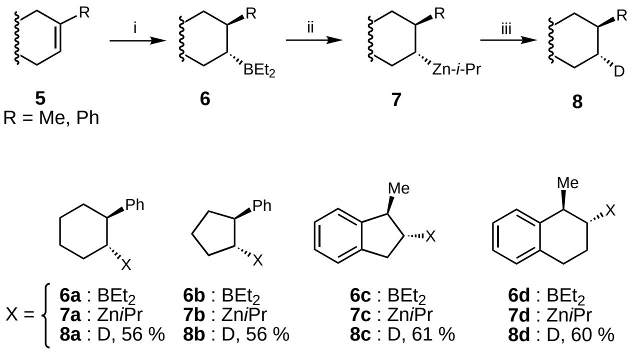


Scheme 3. Relative ratio of the boron–zinc exchange with $\mathrm{Et_2Zn}$ and $i\mathrm{Pr_2Zn}$.

Abstract in German: *Durch die Reaktion zyklischer und offenkettiger diastereomerenreiner sekundärer Organoborane mit Diisopropylzink gelangt man zu sekundären Dialkylzinkverbindungen mit guter bis hervorragender Retention der Konfiguration. Dies wird anhand von Deuterolyseexperimenten und* $\mathit{Cu^I}$*- und* $\mathit{Pd^0}$*-vermittelten Reaktionen mit Elektrophilen bewiesen. Die Notwendigkeit eines schnellen Bor-Zinkaustauschs zur Erlangung hoher Diastereoselektivitäten wird dargelegt. Des weiteren konnte, durch die Verwendung von (−)-*$\mathit{IpcBH_2}$ *als chiralem Hydroborierungsreagens, sowohl ein Zugang zu optisch angereicherten Dialkylzinkverbindungen gefunden (bis zu 96 %ee), als auch die Diastereoselektivitäten verbessert werden.*

Similarly, the hydroboration product of the silylated cyclopentenol **3** reacts to give the corresponding zinc reagent **4** in 36 % yield using $\mathrm{Et_2Zn}$ (25 °C, 0.5 h), whereas 67 % conversion is obtained with $i\mathrm{Pr_2Zn}$.

The hydroboration of various trisubstituted cyclopentene or cyclohexene derivatives **5** with $\mathrm{Et_2BH}$ provides the *trans*-organoboranes **6** ($\mathrm{Et_2BH}$, 3 equiv, 40 °C, 4 d, Scheme 4).[5] Subsequently we found that a shorter reaction time at a higher temperature (50 °C, 18 h) is usually sufficient to complete the hydroboration of trisubstituted olefins.



Scheme 4. Preparation and deuterolysis of configurationally defined zinc reagents. i) $\mathrm{Et_2BH}$, 40 °C, 4 d; ii) $i\mathrm{Pr_2Zn}$, −10 to 25 °C; iii) $\mathrm{D_2O}$, THF, −78 °C.

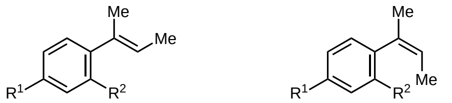
The treatment of the compounds **6** with $i\mathrm{Pr_2Zn}$ (ca. 5 M in $\mathrm{Et_2O}$) provides mixed isopropylcycloalkylzinc intermediates of type **7** which by treatment with $\mathrm{D_2O}$ in THF generate the *trans*-monodeuterated products **8a–d** with good to excellent *trans*:*cis* ratios (Table 1). The use of $i\mathrm{Pr_2Zn}$ allows for the first time the generation of stereochemically well defined *secondary* diorganozinc compounds.[8]

Table 1. Influence of the B–Zn exchange conditions on the stereoselectivity of **8**.

Entry	5	8	*T* [°C][a]	*t* [h][b]	*trans*:*cis*[c]	Yield [%][d]
1	**a**	**a**	25	7	100:0	56
2	**b**	**b**	25	7	87:13	54
3	**b**	**b**	−10	10	98:2	56
4	**c**	**c**	25	10	99:1	61
5	**d**	**d**	−10	10	97:3	60

[a] Temperature required for the boron–zinc exchange reaction. [b] Time required for the boron–zinc exchange reaction. [c] The *trans:cis* ratio was determined by ^{2}H NMR spectroscopy. [d] Overall yield of analytically pure products based on olefin **5**.

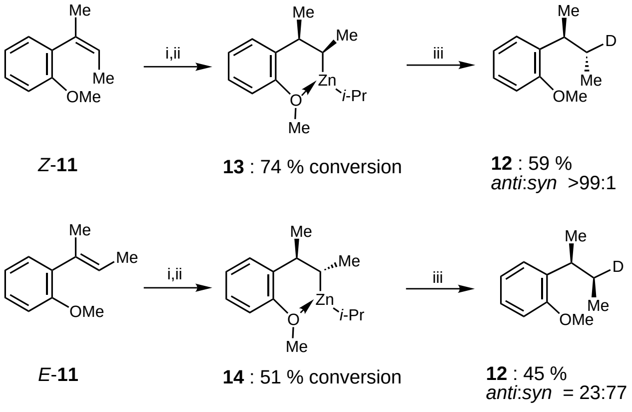
The *trans*:*cis* ratio of the deuterated products was determined by using ^{2}H NMR spectroscopy. The performance of the deuterolysis at −78 °C is essential for the diastereoselectivity of the quenching reaction. Thus, quenching of the dialkylzinc compound **7c** with a solution of $\mathrm{D_2O}$ in THF at −78 °C furnishes the deuterated product with a *trans*:*cis* ratio of 99:1, whereas deuterolysis at 0 °C yields a *trans*:*cis* ratio of 94:6. On the other side, phenylcyclohexene (**5a**) gives via this sequence pure *trans*-2-deuterio-1-phenylcyclohexane (**8a**) by operating at 25 °C. It was observed that in some cases better results are obtained by performing the boron–zinc exchange at $-10\,^{\circ}C$ (Table 1). Thus, with phenylcyclopentene (**5b**), a *trans*:*cis* ratio of 87:13 is obtained for the deuterated product **8b**, if the boron–zinc exchange is performed at 25 °C, while a *trans*:*cis* ratio of 98:2 is obtained by performing the reaction at $-10\,^{\circ}C$. Similar results are obtained for **5d**. However, in the case of **5c**, an excellent selectivity could be obtained by performing the boron–zinc exchange at 25 °C. The reasons for the better stereoselectivity of the boron–zinc exchange at 0 °C or $-10\,^{\circ}C$ compared to room temperature are not completely clear. The partial epimerization observed by carrying out the reaction at 25 °C may be due to radical side reactions induced by Et_3B. A practical problem arises when the boron–zinc exchange is slow. In these cases, this reaction has to be performed at 25 °C which unfortunately may lead to substantial epimerization. The formation of the zinc reagents **7** during the boron–zinc exchange was monitored by quenching reaction aliquots with an aqueous 3 M NaOH solution and subsequent oxidation with aqueous 30 % H_2O_2. With this procedure, the zinc reagent is protonated affording the corresponding hydrocarbon while the residual organoborane is oxidized to the corresponding alcohol. The ratio between this hydrocarbon and the alcohol can be easily determined by GC analysis and provides the conversion of the reaction with good accuracy. Typical conversions of most reactions were in the range between 60 % and 80 %. To prove the stereoselectivity of the boron–zinc exchange reaction, we have hydroborated the open-chain *E*- and *Z*-olefins **9**–**11** and performed the boron–zinc exchange reaction followed by deuterolysis (Scheme 5).[4b]



E-**9** : $R^1 = R^2 = H$
E-**10** : R^1 = MeO; R^2 = H
E-**11** : R^1 = H; R^2 = MeO
Z-**9** : $R^1 = R^2 = H$
Z-**10** : R^1 = MeO; R^2 = H
Z-**11** : R^1 = H; R^2 = MeO

Scheme 5. Acyclic olefins used for the B–Zn exchange reaction.

Unfortunately, for the olefins **9** and **10** no separation of the deuterium signals in ^2H NMR spectroscopy could be obtained. However, in the case of the alkenes *E*- and *Z*-**11**, a 2H NMR determination was possible showing that *Z*-**11** undergoes the deuterolysis with > 99 % *anti*-diastereoselectivity if the boron–zinc exchange is performed at 0 °C furnishing the *anti*-product (*anti*-**12**) (Scheme 6). By using the *E*-isomeric alkene (*E*-**11**), the *syn*-diasteromer (*syn*-**12**) is produced as the major product with a selectivity of *syn*:*anti* of 77:23. In contrast, by performing the boron–zinc exchange at 25 °C, lower stereoselectivities were obtained, respectively a *syn*:*anti* ratio of 22:78 starting with *Z*-**11** and a *syn*:*anti* ratio of 73:27 starting with *E*-**11**. Interestingly, the presence of an *ortho*-methoxy substituent significantly accelerates the boron–zinc exchange reaction. In fact, 68 % conversion was observed for *E*-**11** after 1.5 h at 25 °C.

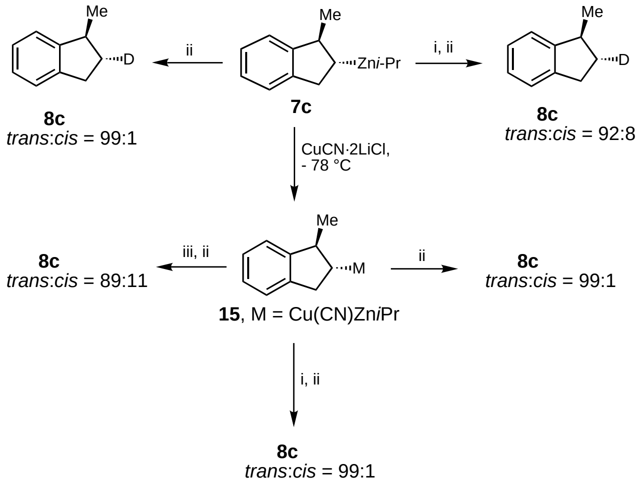


Scheme 6. Diastereoselective deuterolysis of chiral secondary dialkylzinc compounds(only the major diastereomer is represented). i) Et_2BH (3 equiv), 25 °C, 14.5 h; ii) iPr_2Zn (2 equiv), 0 °C, 3 h; iii) D_2O, THF, $-78\,^{\circ}C$.

For the *para*-substituted *E*-**10** and the unsubstituted analogue *E*-**9**, corresponding conversions are only 36 % and 40 %, respectively, after 1.5 h reaction time. This acceleration may be due to a precomplexation of iPr_2Zn to the methoxy group leading to the chelate-stabilized zinc reagents **13** and **14**. This behavior is quite general and the presence of an ether function in close proximity to the carbon–boron bond accelerates dramatically the rate of the exchange reaction. The above results illustrate the stereoselectivity of the boron–zinc exchange reaction for open-chain *secondary* dialkylzinc compounds. Interestingly, the deuterolysis of *secondary* zinc reagents such as *trans*-isopropyl-(2-phenylcyclopentyl)zinc (**7b**), which was stored for one week at 5 °C, proceeded with the same *trans*:*cis* selectivity of 98:2 showing that stock solutions of these zinc reagents may be prepared and stored at low temperature.

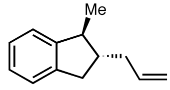
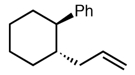
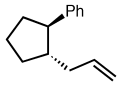
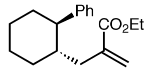
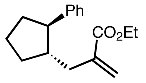
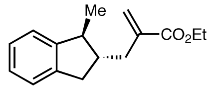
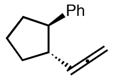
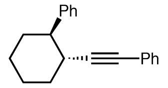
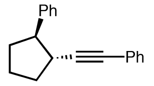
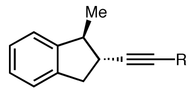
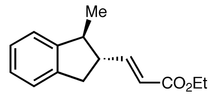
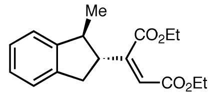
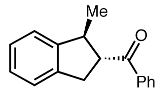
The stereoselective formation of new carbon–carbon bonds with these *secondary* zinc reagents was also investigated. Especially, the copper(I)-mediated allylation of cyclic zinc reagents **7** was studied in some detail. Although the reaction of organozinc compounds with allylic halides is slow, a rapid reaction occurs if the dialkylzinc compound is first transmetalated with the THF-soluble copper salt CuCN · 2 LiCl.[9] Therefore, we studied the influence of transmetalation reactions on the configuration of the indenylzinc reagent **7c**. First we found that the treatment of **7c** with $ZnBr_2$ (2 equiv, $-78\,^{\circ}C$, 0.5 h) leads to a significant isomerization after deuterolysis. The *trans*:*cis* ratio was 92:8 compared to 99:1 before the addition of $ZnBr_2$, showing that the addition of $ZnBr_2$ considerably reduces the configurational stability of the *secondary* alkylzinc compound **7c**. On the other hand, addition of CuCN · 2LiCl (2 equiv) leading to the zinc–copper reagent **15**, followed by deuterolysis, furnishes the deuterated indene **8c** with a *trans*:*cis* ratio of 99:1 (Scheme 7). Subsequent addition of $ZnBr_2$ (2 equiv, $-78\,^{\circ}C$, 15 min) did not lead to any epimerization and afforded after deuterolysis **8c** with an unchanged *trans*:*cis* ratio of 99:1. Finally, generation of the zinc–copper reagent **15** at $-78\,^{\circ}C$ and warming up to 0 °C over 15 min, led to substantial isomerization of the organometallic compound **15**.

With these results in hand, we performed the allylation of the zinc reagent **7c** after transmetalation with CuCN · 2 LiCl



Scheme 7. Transmetalations of secondary alkylzinc reagents. i) $ZnBr_2$, −78°C; ii) D_2O, THF, −78°C; iii) −78°C to 0°C, 15 min.

Table 2. Stereoselective reactions of the zinc reagents **7** with carbon electrophiles after transmetalation with CuCN · 2LiCl.

Entry	7	Product	16	*trans*:*cis* ratio	Yield [%][a]
1	c		**16a**	95:5	58
2	a	 **16b**	**16b**	98:2	46
3	b		**16c**	95:5	36
4	a		**16d**	96:4	35
5	b		**16e**	91:9	48
6	c		**16f**	93:7	45
7	b		**16g**	88:12	42
8	a		**16h**	91:9	44
9	b		**16i**	96:4	41
10	c		**16j**; R = Ph	93:7	42
11	c		**16k**; R = Bu	93:7	27
12	c		**16l**; R = 1-cyclohexenyl	89:11	48
13	c		**16m**	90:10	41
14	c		**16n**	89:11	31
15	c		**16o**	89:11	41

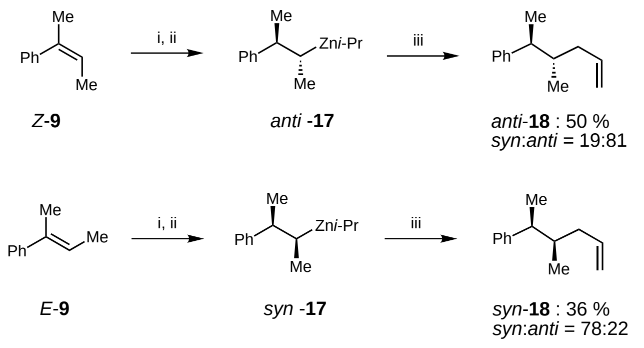
[a] Yield of analytically pure product based on the starting olefin.

(2 equiv, −78°C, 20 min) and obtained the desired *trans*-allylated product **16a** in 58% yield and a *trans*:*cis* ratio of 95:5 showing that little isomerization occurs during the allylation step (Table 2, entry 1). Attempts to improve this stereoselectivity by changing the reaction conditions (temperature, rate of addition, addition of cosolvents like *N*-methylpyrrolidinone or pyridine) failed. Furthermore, the use of allylating reagents other than allyl bromide (allyl diethylphosphate or allyl iodide) also resulted in lower *trans*:*cis* ratios (90–85:10–15).

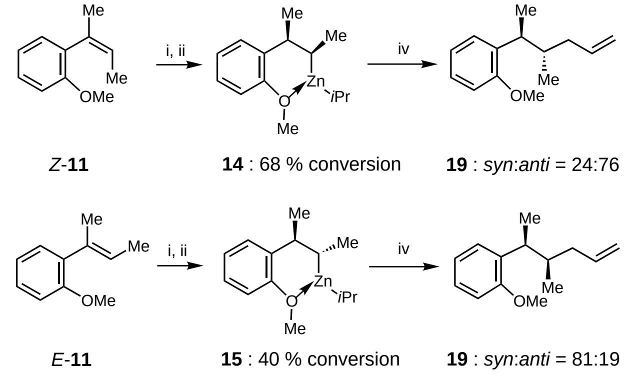
A range of other allylation reactions was performed using various allylic bromides and the cyclic organozinc reagents **7a–c** leading to diastereoselectivities better than 91:9 and up to 98:2 (Table 2, entry 2). The use of propargyl bromide furnishes the expected allene **16g** in 42% yield and a *trans*:*cis* ratio of 88:12. Cross-coupling reactions with alkynyl bromides provide the corresponding alkynes **16h–l** in 27–48% yield and up to 96:4 *trans*:*cis* ratio.[10] Addition to ethyl propiolate or dimethyl acetylenedicarboxylate furnishes the unsaturated esters **16m, n** again with diastereoselectivities of ca. 90:10 (Table 2entries 13 and 14). Finally, a palladium-catalyzed benzoylation of **7c** ($[Pd(dba)_2]$ 5 mol%, $P(o\text{-Tol})_3$ 20 mol%, 25°C, 11 h) furnishes the *trans*-phenylketone **16o** (41%, *trans*:*cis* = 89:11).

The allylation reactions were also performed on the open-chain *secondary* dialkylzinc systems. Thus, the hydroboration of both *E*-**9** and *Z*-**9** with Et_2BH, followed by the boron–zinc exchange with $i\text{Pr}_2\text{Zn}$ (3 equiv) at 25°C for 3–4 h, furnishes the expected epimeric zinc reagents *syn*-**17** and *anti*-**17** (Scheme 8) which were transmetalated with CuCN · 2LiCl at −78°C and treated with allyl bromide affording the desired allylated products, respectively *syn*- and *anti*-**18** with the ratios 78:22 and 19:81 showing also the stereoselectivity of the allylation reaction in open-chain systems.

Attempts to improve these selectivities, by lowering the reaction temperature of the boron–zinc exchange to 0°C or changing the allylation reaction conditions, failed. Furthermore, *E*- and *Z*-2-(4-methoxyphenyl)-but-2-ene (*E*-**10**, *Z*-**10**), for which the boron–zinc exchange of the intermediate borane was slow, undergo stereoconvergent allylation reactions leading to the same mixture of diastereomeric allylated products. On the other hand, *E*- and *Z*-2-(2-methoxyphenyl)-but-2-ene (*E*-**11**, *Z*-**11**) furnish intermediate organoboranes, which undergo a fast boron–zinc exchange. Thus, by performing the boron–zinc exchange at 0°C for 3 h (68% conversion) followed by transmetalation with CuCN · 2LiCl and allylation, the two diastereomeric allylated products **19** were obtained respectively with a selectivity of *syn*:*anti* of 24:76 starting from *Z*-**11** and *syn*:*anti* of 81:19 starting from *E*-**11** (Scheme 9). An *ortho*-methoxy group in alkenes **11** enhances the ratio of the boron–zinc exchange, whereas the presence of a methoxy group in *para*-position in olefins **10** lowers the rate of the boron–zinc exchange and may be



Scheme 8. Diastereoselective allylation of chiral open chain secondary zinc reagents. i) Et_2BH (3 equiv), 25 °C, 13 h; ii) $i$$Pr_2Zn$ (3 equiv), 25 °C, 4 h; iii) CuCN · 2 LiCl (2 equiv), allyl bromide (2 equiv), – 78 °C to 25 °C.



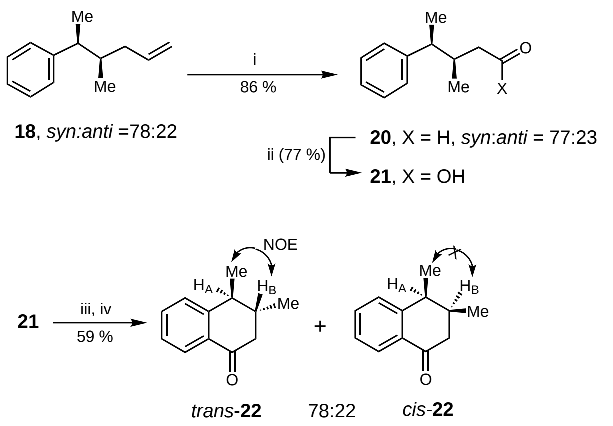
Scheme 9. i) Et_2BH (3 equiv), 25 °C, 15 h; ii) $i$$Pr_2Zn$ 3 equiv), 0 °C, 3 h; iii) $i$$Pr_2Zn$ (3 equiv), 0 °C, 3.5 h; iv) CuCN · 2 LiCl (2 equiv), allyl bromide (2 equiv), – 78 °C to 25 °C.

responsible for the stereoconvergent allylation results. To prove the deleterious influence of a polar ether function for the performance of the boron–zinc exchange, we have added *para*-methylanisole (1 equiv) to the alkene *E*-**9** (after hydroboration) which leads to a nonstereoselective boron–zinc exchange and to a 43:57 mixture of the *syn*:*anti* product **18** (compared to a *syn*:*anti* ratio of 78:22; Scheme 8).

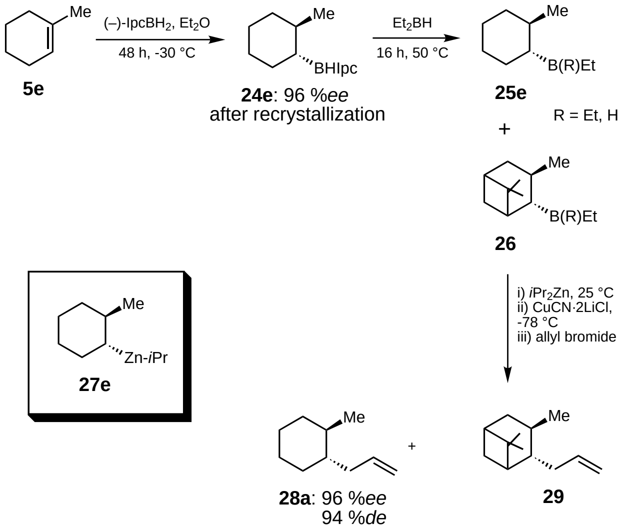
The relative configuration of the products **18** obtained after allylation was established by treating a *syn*:*anti* mixture (78:22) of **18** with O_3 (CH_2Cl_2, – 78 °C, 20 min), followed by a reductive work-up leading to the aldehyde **20** (86 % yield, Scheme 10). Further oxidation of **20** with $NaClO_2$ in the presence of 2-methylbut-2-ene and NaH_2PO_4 in *t*BuOH (25 °C, 1 h) furnishes the carboxylic acid **21** in 77 % yield.[11]

This acid was converted to the corresponding acid chloride ($SOCl_2$, neat, 60 °C, 1 h), which was cyclized under Friedel–Crafts conditions ($AlCl_3$, 1,2-dichloroethane, 25 °C, 4 h) leading to a *trans-cis* mixture (78:22) of the α-tetralone **22** in 59 % yield. Both the major *trans* isomer and the minor *cis* isomer could be unequivocally identified by NMR spectroscopy.

Having found an access to configurationally defined cyclic and acyclic diorganozinc compounds, we envisioned an asymmetric route allowing to prepare enantiomerically enriched diorganozinc compounds. Since the pioneering work of Brown, asymmetric hydroboration has become a powerful tool in organic synthesis and numerous papers have been published.[12] We therefore thought of an asymmetric hydroboration/ boron–zinc exchange sequence which should lead to enantiomerically enriched organozinc reagents. Monoisopinocampheylborane ((–)-$IpcBH_2$) (**23**) is the reagent of choice for conducting asymmetric hydroborations with trisubstituted olefins.[13] First experiments with methylcyclohexene (**5e**) revealed that the intermediate organyl-isopinocampheylborane (**24a**) did not give any boron–zinc exchange after treatment with $i$$Pr_2Zn$ (Scheme 11).



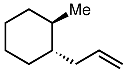
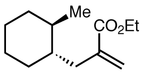
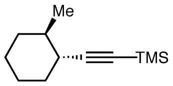
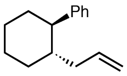
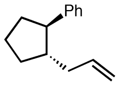
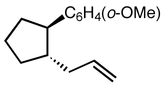
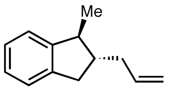
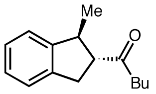
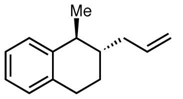
Scheme 10. i) O_3, then Me_2S; ii) $NaClO_2$, 2-methylbut-2-ene, NaH_2PO_4 in *t*BuOH, 25 °C, 1 h; iii) $SOCl_2$, 60 °C, 1 h; iv) $AlCl_3$ (1.25 equiv) in 1,2-dichloroethane, 25 °C, 4 h.



Scheme 11. Ligand redistribution on boron and further reactions.

This lack of reactivity might be due to steric hindrance around the boron atom. This problem could be circumvented by a ligand redistribution reaction on boron employing excess Et_2BH (ca. 7 M in Me_2S) to the optically active organo-isopinocampheylborane **24e**.[5] On heating **24e** for 16 h at 50 °C with excess Et_2BH as solvent (3–6 equiv), a redistribution of the ligands on boron takes place affording a mixture of ethyl- and diethylorganoboranes **25e** together with ethyl- and diethyl-isopinocampheylboranes **26**. After the excess Et_2BH had been evaporated, the residual organoboranes were treated with $i$$Pr_2Zn$ (3 equiv) to afford the enantiomerically enriched organozinc compounds **27**. Subsequent transmetalation with CuCN · 2LiCl (1 equiv) and addition of allyl bromide provided (1*S*, 2*R*)-1-(1-propen-3-yl)-2-methylcyclohexane **28a** (94 % *de*, 96 % *ee*,). Unfortunately, products derived from 1-methylcyclohexene could not be obtained in analytically pure form because of the inseparable by-product **29** derived from pinane (see Table 3, entries 1–3). In all the other cases the pinane-derived by-product could easily be separated by flash chromatography.[14]

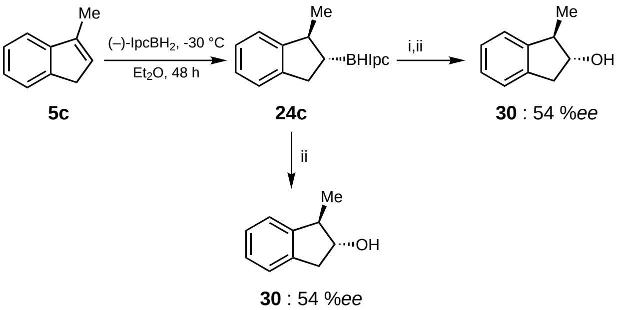
Table 3. Stereoselective reactions of the optically enriched zinc reagents **27** with carbon electrophiles after transmetalation with CuCN · 2LiCl.

Entry	27	Product	28	*trans*:*cis* ratio	*ee*[a]	Yield [%][b]
1	**e**		**28a**	98:2	94	[c]
2	**e**		**28b**	93:7	96	[c]
3	**e**		**28c**	94:6	96	[c]
4	**a**		**28d**	97:3	20	45
5	**b**		**28e**	97:3	94	47
6	**f**		**28f**	98:2	84	77
7	**c**		**28g**	97:3	66	40
8	**c**		**28h**	99:1	64	43
9	**d**		**28i**	98:2	42	40

[a] Enantiomeric ratio of the major diastereomer determined by GC analysis on a chiral *β*-cyclodextrin column. [b] Yield of analytically pure product based on the starting olefin. [c] Desired products are contaminated by pinene-derived products with electrophiles.

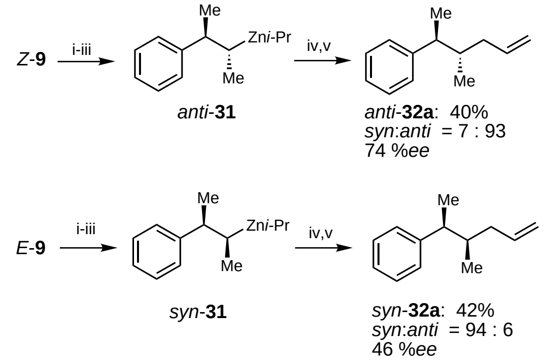
The enantiomeric ratio could be determined by GC analysis on a chiral *β*-cyclodextrin column. We have verified that the enantioselectivity of the initial asymmetric hydroboration is conserved in this redistribution process by the following experiment: methylindene **5c** was hydroborated with (−)-IpcBH$_2$ (**23**, 0.7 M in Et$_2$O, 1 equiv, −30 °C) affording the optically active organoborane **24c**. An aliquot was directly oxidized with aqueous 3 M NaOH/aqueous 30 % H$_2$O$_2$ to afford the alcohol **30**. A second aliquot was first heated with excess Et$_2$BH (50 °C, 16 h) then also oxidized to the alcohol **30**. In both cases, the enantiomeric ratio of the alcohol **30** was 77:23 showing that the enantioselectivity is conserved during this equilibration step (Scheme 12).

By employing this asymmetric one-pot sequence (asymmetric hydroboration/equilibration/ boron–zinc exchange) to the cyclic olefins **5a–f**, we obtained the chiral organozinc species **27a–f**. After transmetalation to copper, the reaction with a variety of electrophiles (allylic halides, acid chlorides, 1-bromoalkynes) afforded the products **28a–i** with excellent diastereomeric ratios (d.r. 93:7) and moderate to excellent enantioselectivities (up to 96 % *ee*) (see Table 3).[15]



Scheme 12. i) Et$_2$BH, 50 °C, 16 h; ii) aq. NaOH/H$_2$O$_2$.

Importantly, extension of this procedure to the acyclic olefins *Z*-**9** and *E*-**9** afforded products with significantly higher diastereoselectivities than those obtained by the achiral hydroboration method presented in the first part of this paper. Thus, the reaction of *Z*-2-phenyl-2-butene (*Z*-**9**) with (−)-IpcBH$_2$ (**23**, −35 °C, 48 h), followed by the equilibration with Et$_2$BH (50 °C, 16 h) and the boron–zinc exchange (*i*Pr$_2$Zn, 25 °C, 5h), furnishes the intermediate zinc reagent *anti*-**31**, which after Cu^I-mediated allylation affords the desired product *anti*-**32** in 40 % yield with high diastereoselectivity (*syn*:*anti* 7:93) and 74 % *ee*. Respectively, starting with *E*-**9** the product *syn*-**32** is obtained in 42 % yield with a *syn*:*anti* ratio of 94:6 and 46 % *ee* (Scheme 13).

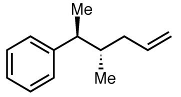
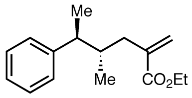
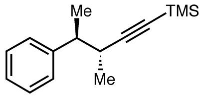
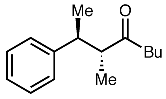
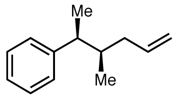
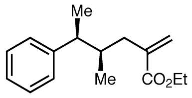
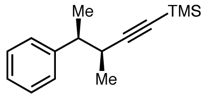
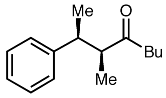


Scheme 13. i) (−)-IpcBH$_2$ (1 equiv), 48 h, −30 °C; ii) Et$_2$BH (3 equiv), 16 h, 50 °C then vacuo; iii) *i*Pr$_2$Zn (3 equiv), 5 h, 25 °C then vacuo; iv) CuCN · 2LiCl, THF, −78 °C; v) allyl bromide, −78 °C.

These diastereoselectivities are significantly higher than those obtained with the achiral hydroboration procedure (see Scheme 8). The quenching with different electrophiles is possible and provides products **32** with good to excellent retention of configuration (Table 4).[15]

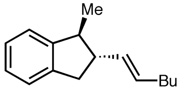
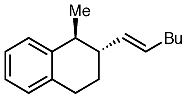
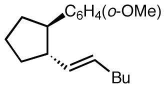
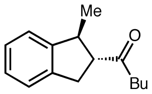
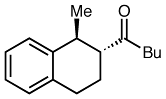
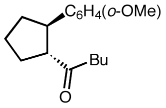
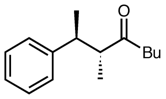
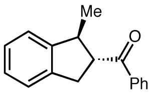
Pd^0-catalyzed reactions of the optically active diorganozinc compounds **27** and **31** have also been examined. Pd^0-catalyzed cross-couplings of **27** with *E*-1-iodo-hex-1-ene and acylations using pentanoyl and benzoyl chloride afforded products of

Table 4. Stereoselective reactions of the optically enriched zinc reagents **31** with carbon electrophiles after transmetalation with CuCN · 2 LiCl.

Entry	31	Product	32	*anti:syn* ratio	ee[a]	Yield [%][b]
1	*anti*		*anti*-**32a**	92:8	74	40
2	*anti*		*anti*-**32b**	90:10	74	38
3	*anti*		*anti*-**32c**	94:6	82	41
4	*anti*		*anti*-**32d**	97:3	56	41
5	*syn*		*syn*-**32a**	6:94	46	42
6	*syn*		*syn*-**32b**	2:98	44	35
7	*syn*		*syn*-**32c**	11:89	46	35
8	*syn*		*syn*-**32d**	5:95	56	38

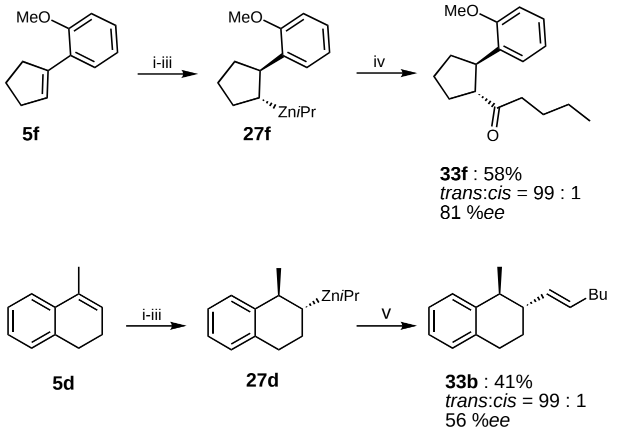
[a] Enantiomeric ratio of ther major diastereomer determined by GC analysis on a chiral β-cyclodextrin column. [b] Yield of analytically pure products based on the olefin.

Table 5. Stereoselective reactions of the optically enriched zinc reagents **27** with carbon electrophiles after transmetalation with Pd^0.

Entry	27	Product	33	*trans:cis* ratio	ee[a]	Yield [%][b]
1	**c**		**33a**	99:1	56	35
2	**d**		**33b**	99:1	52	41
3	**f**		**33c**	98:2	83	40
4	**c**		**33d**	92:8	64	39
5	**d**		**33e**	92:8	60	43
6	**f**		**33f**	99:1	81	58
7	*anti*-**31**		**33g**	90:10	88	45
8	**c**		**33h**	95:5	60	41

[a] Enantiomeric ratio of major diastereomer determined by GC analysis on a chiral β-cyclodextrin column. [b] Yield of analytically pure products based on the starting olefin.

type **33**. We were very pleased to find that cyclic diorganozinc compounds **27** gave excellent *trans:cis* ratios (d.r. 98:2) under the reaction conditions (25 °C, 16 h) of the cross-coupling, without any epimerization of the C–Zn bond (see Scheme 14 and Table 5).[16] In general, the diastereoselectivities obtained by Pd^0-catalyzed acylations were lower than those obtained with Cu^I-mediated acylations.

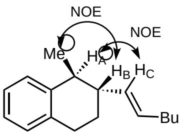


33f : 58%
trans:cis = 99 : 1
81 %*ee*

33b : 41%
trans:cis = 99 : 1
56 %*ee*

Scheme 14. i) (−)-IpcBH$_2$, 48 h, −30 °C; ii) Et$_2$BH, 16 h, 50 °C then vacuo; iii) *i*Pr$_2$Zn, 5 h, 25 °C then vacuo; iv) [Pd(dba)$_2$] (2 mol%), P(*o*-tolyl)$_3$ (4 mol%), pentanoyl chloride, dioxane , 0 °C to 25 °C, 16 h; v) [Pd(dba)$_2$] (2 mol%), P(*o*-tolyl)$_3$ (4 mol%), *E*-1-iodohexene, THF, 0 °C then 25 °C, 16 h.

The *trans* relationship of the vinylation products could be proven in the case of **33b**. For this compound, a COSY-NMR experiment showed a NOE correlation between the benzylic methyl group and H$_B$ as well as a NOE correlation between H$_A$ and the vinylic proton H$_C$ (Scheme 15).



Scheme 15. Determination of stereochemistry of **33b** by COSY-NMR spectroscopy.

Conclusion

In summary, we have shown that the boron–zinc exchange is an appropriate method for the preparation of both stereochemically defined cyclic and acyclic diorganozinc compounds. The choice of the reaction conditions and a high boron–zinc exchange rate are essential for obtaining a good stereoselectivity as shown by D$_2$O-quenching experiments. An achiral method using a hydroboration/boron–zinc exchange sequence proceeds with good stereoselectivities for cyclic substrates (d.r. 88:12) but only moderate diastereoselectivities are obtained for acyclic substrates (d.r. 76:24).

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An extension of this method to optically active diorganozinc species was found by employing a one-pot sequence of asymmetric hydroboration/equilibration/boron–zinc exchange. This asymmetric reaction sequence provides better diastereoselectivities both with cyclic (d.r.) 93:7 and upto 99:1 and acyclic (d.r.) 89:11 and upto 98:2 substrates. Furthermore, the enantioselectivity of the initial asymmetric hydroboration is conserved in this one-pot process and ranges from 44 to 96 % *ee* depending on the starting olefin.

The effectiveness of these two methods could be demonstrated by showing that a variety of products are obtained by the Cu^I- or Pd^0-mediated reactions of these configurationally stable cyclic or acyclic diorganozinc compounds. The above results represent the first general method for preparing chiral main group organometallic compounds through the stereoselective reaction with several classes of electrophiles.

Experimental Section

General considerations: Unless otherwise indicated, all reactions were carried out under argon. Solvents (THF, diethyl ether) were dried and freshly distilled over sodium/benzophenone. Reactions were monitored by liquid-gas chromatography (GC) or thin-layer chromatography (TLC) analysis of hydrolyzed aliquots. The ratios between diastereomers were determined by ^{1}H NMR spectroscopy and/or GC analysis.

Starting materials: The following starting materials were prepared according to literature procedures: ethyl α-(bromomethyl)acrylate,[17] 1-phenylcyclopent-1-ene (**5b**),[18] 1-methyl-3*H*-indene (**5c**),[19] 3,4-dihydro-1-methylnaphthalene (**5d**),[19] *E*-2-phenylbut-2-ene (*E*-**9**),[20] *Z*-2-phenylbut-2-ene (*Z*-**9**),[20] *E*-2-(2-*p*-anisyl)-but-2-ene (*E*-**10**),[21] *Z*-2-(2-*p*-anisyl)-but-2-ene (**Z-10**), [21] *E*-3-methyl-5-phenylpent-2-ene (*E*-**12**),[22] *Z*-3-methyl-5-phenylpent-2-ene (*Z*-**12**).[22]

Preparation of the starting materials

Diisopropylzinc: A 1.3 M solution of isopropylmagnesium bromide in diethyl ether was prepared from 2-bromopropane (38.8 g, 0.32 mol) and magnesium (8.5 g, 0.35 mol) and transferred by cannula to a 500 mL 2-necked flask. Zinc bromide (35.5 g, 0.16 mol) was dried (120 °C, 1 mmHg, 2 h) and dissolved in diethyl ether (150 mL, ca. 30 min). This solution was carefully added to the Grignard reagent at 0 °C and the resulting biphasic mixture was stirred vigorously overnight. After most of the diethyl ether had been distilled off at 40–50 °C (ca. 2 h), a Schlenk-tube equipped with a magnetic stirring bar was connected to the distillation apparatus and cooled with liquid nitrogen. Vacuum was applied (1 mmHg) and a mixture of diisopropylzinc and diethyl ether was distilled from the remainig salts by slowly raising the temperature from 25 °C to 100 °C (ca. 2 h). After the condensate was warmed to 25 °C, excess diethyl ether was evaporated by slowly lowering the pressure to 20 mmHg under stirring over 1 h. The diisopropylzinc thus obtained (18 mL, ca. 60 %) contained 10–15 % diethyl ether (^{1}H NMR) and was about 5 M (titration with 1 M I_2 solution in tetrahydrofuran). It should be kept under exclusion of light.

***Z*- and *E*-1-methoxy-2-(1-methyl-1-propenyl)benzene (11)**: A solution of 2-methoxyacetophenone (24.8 g, 0.16 mol) in diethyl ether (50 mL) was added at 25 °C dropwise over 30 min to the Wittig reagent prepared from triphenylethylphosphonium bromide (61.8 g, 0.17 mol) and butyllithium (1.45 M solution in hexane, 115 mL, 0.17 mol) in diethyl ether (350 mL). The resulting yellow suspension was stirred at 25 °C for 14 h. After evaporation of the solvents, the residue was taken up in hexane, successively washed with water, water/MeOH (2:1) mixture, and brine. After drying ($MgSO_4$), **11** was obtained (25 g; 90 %), which was distilled over a 1 m long spinning band column. Besides fractions of mixtures (6 g), the *Z* isomer (7 g; *Z*:*E* = 97:3) was isolated at b.p. 116–120 °C/17 mmHg and the *E* isomer (2 g; *E*:*Z* = 98:2) at b.p. 135–137 °C/17 mmHg. The two isomers were unequivocally asigned by NOESY-experiments.

Z-11: IR (film): $\tilde{\nu}$ = 2961 (s), 2935 (s), 1598 (m), 1579 (m), 1491 (s), 1460 (s), 1433 (s), 1244 (vs), 1028 (s); ^{1}H NMR ($CDCl_3$, 200 MHz): δ = 7.15–7.05 (m, 1 H), 6.90–6.71 (m, 3 H), 5.45 (qd, *J* = 3.8, 1.4 Hz, 1 H), 3.66 (s, 3 H), 1.84 (br s, 3 H), 1.31 (dt, *J* = 4.0 Hz, *J* = 1.4 Hz, 3 H); ^{13}C NMR ($CDCl_3$, 50 MHz): δ = 159.0, 137.2, 133.3, 132.4, 130.3, 124.9, 122.9, 131.3, 57.8, 26.9, 17.2; MS (EI): *m/z* (%): 162 (100) [M^+], 147 (28), 131 (22), 105 (22), 91 (45); elemental analysis calcd for $C_{11}H_{14}O$ (162.23): C 81.44, H 8.70; found: C 81.53, H 8.42.

***E*-11**: IR (film): $\tilde{\nu}$ = 2918 (s), 1596 (m), 1578 (m), 1489 (vs), 1461 (vs), 1435 (vs), 1377 (m), 1257 (vs), 1230 (vs), 1180 (m), 1030 (vs), 752 (vs); ^{1}H NMR ($CDCl_3$, 200 MHz): δ = 7.33–7.21 (m, 2 H), 7.01–6.82 (m, 2 H), 5.64 (q, *J* = 6.0 Hz, 1 H), 3.89 (s, 3 H), 2.07 (s, 3 H), 1.86 (d, *J* = 6.7 Hz, 3 H); ^{13}C NMR ($CDCl_3$, 50 MHz): δ = 156.9, 135.9, 135.3, 129.9, 127.9, 124.1, 120.8, 110.9, 55.6, 17.0, 14.2; elemental analysis calcd for $C_{11}H_{14}O$ (162.23): C 81.44, H 8.70; found: C 81.27, H 8.50.

***Z*- and *E*-1-methoxy-4-(1-methyl-1-propenyl)benzene (10)**: Following the same procedure as above, the crude product (33.0 g; 74 %) was obtained from 4-methoxyacetophenone (40.4 g). Distillation over a spinning band column afforded the *Z* isomer (6 g; *Z*:*E* = 98:2) at b.p. 102–105 °C/19 mmHg and the *E* isomer (8 g; *E*:*Z* = 97:3) at b.p. 120–122 °C/19 mmHg, besides fractions of mixtures (11 g). Spectroscopic and physical data are in accordance with those already reported.[16]

General procedure I: Deuteration of zinc reagents 7: A 25-mL two-necked-flask equipped with a rubber septum and an argon inlet was charged with the olefin (10 mmol). After degassing the olefin, diethylborane (2.94 g, 30 mmol, 3.0 equiv) was added dropwise over 10 min by syringe at 25 °C. The resulting mixture was stirred for 4 d at 40 °C. The excess diethylborane was distilled off (25 °C, 1 mmHg, 3 h). *i*Pr_2Zn (4 mL, 20 mmol, 2 equiv) was carefully added by syringe at 25 °C. For the boron–zinc exchange, the reaction mixture was stirred at 25 °C for 7 h, during which time the flask was covered with aluminum foil to exclude light. The excess *i*Pr_2Zn was distilled off (25 °C, 1 mmHg, 1 h), the flask was equipped with an internal thermometer, and the organozinc compound was diluted with dry THF (15 mL) and cooled to −78 °C. Deuterium oxide (3.0 g) was added slowly. Then the mixture was stirred at −78 °C for 15 min, warmed to 25 °C, and worked-up as usual. The crude product was purified by flash chromatography (hexanes).

***trans*-2-Deuterio-1-phenylcyclohexane (8a)**: Deuteration of 1-phenyl-1-cyclohexene (**5a**) (1.500 g, 9.5 mmol) according to general procedure I afforded **8a** as a clear oil (0.850 g, 56 % yield). For the boron–zinc exchange, the reaction mixture was stirred at 25 °C for 7 h; IR (film): $\tilde{\nu}$ = 3062 (w), 3027 (m), 2925 (vs), 2854 (vs), 2165 (w), 1602 (m), 1584 (m), 1493 (s), 1447 (s), 754 (s); ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.45–7.33 (m, 5 H), 2.69–2.61 (m, 1 H), 2.03–1.91 (m, 4 H), 1.62–1.43 (m, 5 H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 148.0, 128.2 (2C), 127.9 (2C), 126.0, 44.5, 34.4, 34.1 (t, $^1J_{C\Delta}$ = 19.6 Hz), 26.9, 26.8, 26.2; ^{2}H NMR (CD_2Cl_2, 77 MHz): δ = 1.95 (*trans*-D); MS (EI): *m/z* (%): 161 (97) [M^+], 118 (50), 117 (94), 105 (63), 104 (100), 92 (39), 91 (68); elemental analysis calcd for $C_{12}H_{15}D$ (161.26): C 89.38, H/D 10.62; found: C 89.14, H/D 10.52.

***trans*-2-Deuterio-1-phenylcyclopentane (8b)**: Deuteration of 1-phenylcyclopent-1-ene (**5b**) (1.50 g, 10.4 mmol) according to general procedure I afforded **8b** as a clear oil (0.850 g, 56 % yield) with a *trans*–*cis* ratio of 98:2. For the boron–zinc exchange, the reaction mixture was stirred at 0 °C for 10 h; IR (film): $\tilde{\nu}$ = 3062 (w), 3029 (m), 2954 (vs), 2871 (s), 1603 (m), 1492 (m), 1453 (m), 1030 (w), 756 (s); ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.40–7.25 (m, 5 H), 3.12–3.03 (m, 1 H), 2.22–2.14 (m, 1 H), 1.91–1.68 (m, 6 H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 146.3, 128.2 (2C), 127.1 (2C), 125.6, 45.9, 34.6, 34.2 (t, $^1J_{C\Delta}$ = 20.0 Hz), 25.5, 25.4; ^{2}H NMR (CD_2Cl_2, 77 MHz): δ = 2.10 (*trans*-D), 1.73 (*cis*-D); MS (EI): *m/z* (%): 147 (96) [M^+], 117 (100), 105 (78), 104 (93), 92 (40), 91(53); elemental analysis calcd for $C_{11}H_{13}D$ (147.23): C 89.74, H/D 10.26; found: C 89.40, H/D 10.48.

***trans*-2-Deuterio-1-methyl-2,3-dihydro-*1H*-indene (8c)**: Deuteration of 1-methyl-3*H*-ind-1-ene (**5c**) (1.00 g, 7.68 mmol) according to general procedure I afforded **8c** as a clear oil (0.620 g, 61 % yield) with a *trans*–*cis* ratio of 99:1. For the boron–zinc exchange, the reaction mixture was stirred at 25 °C for 5 h; IR (film): $\tilde{\nu}$ = 3070 (m), 3022 (m), 2958 (vs), 2869 (s), 2850 (s), 2196 (w),1492 (m), 1478 (m), 1461 (s), 1374 (m), 1324 (w), 1297 (w), 757 (vs); ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.36–7.25 (m, 4 H), 3.37–3.27 (m, 1 H), 3.09–3.00 (m, 2 H), 1.81–1.77 (m, 1 H), 1.48 (d, *J* = 6.8 Hz, 3 H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 147.7, 143.8, 126.1, 128.08, 124.3, 123.1, 39.5, 34.4 (t, $^1J_{C\Delta}$ = 20.0 Hz), 31.5, 19.9; ^{2}H NMR (CD_2Cl_2, 77 MHz): δ = 2.38 (*trans*-D), 1.66 (*cis*-D); MS (EI): *m/z* (%): 133 (96) [M^+], 118 (100), 117 (12), 116 (16), 85 (15), 84 (27), 49 (21); elemental analysis (%) calcd for $C_{10}H_{11}D$ (133.21): C 90.17, H/D 9.83; found: C 89.95, H/D 9.94.

***trans*-2-Deuterio-1-methyl-1,2,3,4-tetrahydronaphthalene (8d)**: Deuteration of 3,4-dihydro-1-methylnaphthalene (**5d**) (1.50 g, 10.4 mmol) according to general procedure I afforded **8d** as a clear oil (0.900 g, 59% yield) with a *trans–cis* ratio of 97:3. For the boron–zinc exchange, the reaction mixture was stirred at 0°C for 10 h; IR (film): $\tilde{\nu} = 3062$ (w), 3018 (w), 2960 (m), 2929 (m), 2871 (m), 1490 (m), 1447 (m), 754 (s), 726 (m); ^{1}H NMR ($CDCl_3$, 300 MHz): $\delta = 7.29$–7.21 (m, 4H), 3.11–3.02 (m, 1H), 2.99–2.87 (m, 2H), 2.12–2.02 (m, 2H), 1.74–1.69 (m, 1H), 1.58 (d, $J = 7.1$ Hz, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz): $\delta = 142.1$, 136.8, 129.0, 128.0, 125.6, 125.4, 32.4, 31.2 (t, $^1J_{C\Delta} = 19.4$ Hz) 29.9, 22.9, 20.1; ^{2}H NMR (CD_2Cl_2, 77 MHz): $\delta = 2.06$ (*trans*-D), 1.67 (*cis*-D); MS (EI): *m/z* (%): 147 (3) [M^+], 133 (10), 132 (100), 131 (29), 118 (17), 117 (13), 92 (11), 91 (96); elemental analysis (%) calcd for $C_{11}H_{13}D$ (147.23): C 89.74, H/D 10.26; found: C 89.50, H/D 9.95.

anti*-2-(2-Methoxybenzene)-3-deuteriobutane (*anti*-12)**: Deuteration of *cis*-2-(*o*-anisyl)-but-2-ene (Z*-11**) (0.20 g, 1.23 mmol) according to general procedure I afforded ***anti*-12** as a clear oil (0.120 g, 59% yield) with a *syn–anti* ratio of < 1: > 99. After 3.25 h at 0°C, the boron–zinc conversion was 74%; IR (film): $\tilde{\nu} = 3065$ (w), 3030 (w), 2962 (s), 2932 (m), 2874 (m), 2835 (m), 1600 (s), 1585 (w), 1491 (s), 1462 (s), 1439 (m), 1240 (vs), 1174 (w), 1096 (w), 1051 (w), 1032 (m), 751 (s); ^{1}H NMR ($CDCl_3$, 200 MHz): $\delta = 7.10$–7.03 (m, 2H), 6,90–6,70 (m, 2H), 3.63 (s, 3H), 3.03 (sext, $J = 7.0$ Hz, 1H), 1.68–1.34 (m, 1H), 1.11 (d, $J = 7.0$ Hz, 3H), 0.76 (t, $J = 6.9$ Hz, 3H); 13C NMR ($CDCl_3$, 50 MHz): $\delta = 157.1$, 135.9, 126.7, 126.4, 120.5, 110.4, 55.3, 33.5, 29.8, 20.4, 12.1; ^{2}H NMR ($CHCl_3$, $CDCl_3$, 77 MHz): $\delta = 1.62$; MS (EI): *m/z* (%): 165 (6) [M^+], 164 (18) [$M^+ - 1$], 136 (14), 135 (100), 105 (16); elemental analysis (%) calcd for $C_{11}H_{15}DO$ (165.25): C 79.96, H/D 10.36; found: C 80.22, H/D 9.96.

syn*-2-(2-Methoxybenzene)-3-deuteriobutane (*syn*-12)**: Deuteration of *trans*-2-(*o*-anisyl)-but-2-ene (E*-11**) (0.15 g, 0.9 mmol) according to general procedure I afforded ***syn*-12** as a clear oil (0.067 g, 45% yield) with a *syn–anti* ratio of 77:23. After 3.25 h at 0°C, the boron–zinc conversion was 51%; IR (film): $\tilde{\nu} = 3065$ (w), 3030 (w), 2962 (s), 2932 (m), 2874 (m), 2835 (m), 1600 (s), 1585 (w), 1491 (s), 1462 (s), 1439 (m), 1240 (vs), 1174 (w), 1096 (w), 1051 (w), 1032 (m), 751 (s); ^{1}H NMR ($CDCl_3$, 200 MHz): $\delta = 7.10$–7.03 (m, 2H), 6,87–6,78 (m, 2H), 3.72 (s, 3H), 3.03 (sext, $J = 7.0$ Hz, 1H), 1.68–1.34 (m, 1H), 1.11 (d, $J = 7.0$ Hz, 3H), 0.76 (t, $J = 6.9$ Hz, 3H); ^{13}C NMR ($CDCl_3$, 50 MHz): $\delta = 157.1$, 135.9, 126.7, 126.4, 120.5, 110.4, 55.3, 33.5, 29.8, 20.4, 12.1; ^{2}H NMR ($CHCl_3$, $CDCl_3$, 77 MHz): $\delta = 1.70$; MS (EI): *m/z* (%): 165 (10) [M^+], 164 (15) [$M^+ - 1$], 136 (12), 135 (100), 105 (24), 91 (14), 77 (10); elemental analysis (%) calcd for $C_{11}H_{15}DO$ (165.240): C 79.96; H, D 10.36, found: C 80.22; H, D 9.96.

General procedure II: Cu^I-catalyzed reactions of zinc reagents 7 with electrophiles: A 25-mL two-necked-flask equipped with a rubber septum and an argon inlet was charged with the olefin (10 mmol). After degassing the olefin, diethylborane (prepared from triethylborane and borane–methyl sulfide complex (2.94 g, 30 mmol, 3.0 equiv) was added dropwise over 10 min by syringe at 25°C. The resulting mixture was stirred for 4 d at 40°C. Excess diethylborane was distilled off (25°C, 1 mmHg, 3 h). *i*Pr_2Zn (4 mL, 20 mmol, 2.0 equiv) was carefully added via syringe at 25°C. The reaction mixture was stirred at the indicated temperature with exclusion of light. Meanwhile a mixture of CuCN (20 mmol, 2.0 equiv) and LiCl (40 mmol, 4 equiv) was dried in vacuo (130°C, 3 h). The copper and lithium salts were dissolved in dry THF (20 mL) and cooled to −78°C. Then the excess of *i*Pr_2Zn was distilled off (25°C, 1 h) covering the flask with aluminium foil to exclude light. The flask was equipped with an internal thermometer and the organozinc compound was diluted with dry THF (40 mL) and cooled to −78°C. The previously prepared $CuCN \cdot 2LiCl$ solution was added. The reaction mixture was stirred at −78°C for 20 min and the electrophile (20 mmol, 2.0 equiv) in dry THF (10 mL) was added dropwise over 20 min keeping the temperature below −70°C. The reaction mixture was stirred at −70°C for 20 min, warmed up to 25°C and worked-up as usual. The crude product was purified by flash-chromatography (hexanes).

***trans*-2-Allyl-1-methyl-2,3-dihydro-*1H*-indene (16a)**: Reaction of 1-methyl-3*H*-ind-1-ene (**5c**) and 3-bromoprop-1-ene according to general procedure II afforded **16a** as a clear oil (0.999 g, 58% yield) with a *trans:cis* ratio of 95:5; IR (film): $\tilde{\nu} = 3076$ (s), 3045 (m), 3022 (s), 2958 (vs), 2902 (vs), 2869 (vs), 2840 (vs), 1642 (s), 1478 (vs), 1461 (s), 996 (s), 911 (vs), 770 (vs), 743 (vs); ^{1}H NMR ($CDCl_3$, 300 MHz): $\delta = 7.23$–7.15 (m, 4H), 6.00–5.86 (m, 1H), 5.17–5.06 (m, 2H), 3.08 (dd, $J = 15.8$ Hz, $J = 7.8$ Hz, 1H), 2.96–2.84 (m, 1H), 2.63 (dd, $J = 15.8$ Hz, $J = 8.8$ Hz, 1H), 2.54–2.45 (m, 1H), 2.17–2.28 (m, 1H), 2.14–2.01 (m, 1H), 1.36 (d, $J = 6.8$ Hz, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz): *trans* product: $\delta = 148.2$, 142.6, 137.5, 126.2 (2C), 124.4, 123.2, 115.5, 48.4, 44.74, 38.4, 37.7, 18.5; *cis* product: 149.2, 142.3, 138.0, 126.2 (2C), 124.4, 123.5, 115.3, 43.0, 41.7, 36.5, 34.4, 15.2; MS (EI): *m/z* (%): 172 (2) [M^+], 143 (17), 131 (23), 130 (100), 129 (25), 115 (22), 91 (16); elemental analysis (%) calcd for $C_{13}H_{16}$ (172.27): C 90.64, H 9.36; found: C 90.39, H 9.64.

***trans*-1-Allyl-2-phenylcyclohexane (16b)**: Reaction of with 1-phenylcyclohex-1-ene (**5a**) and 3-bromoprop-1-ene according to general procedure II afforded **16b** as a clear oil (0.921 g, 46% yield) with a *trans–cis* ratio of 98:2. For the boron–zinc exchange, the reaction mixture was stirred at 25°C for 7 h; IR (film): $\tilde{\nu} = 3076$ (m), 3064 (m), 3027 (s), 2925 (vs), 2854 (vs), 1640 (m), 1493 (s), 1447 (s), 996 (m), 909 (s), 756 (vs), 700 (vs); ^{1}H NMR ($CDCl_3$, 300 MHz): $\delta = 7.31$–7.26 (m, 2H), 7.20–7.15 (m, 3H), 5.72–5.60 (m, 1H), 4.93–4.82 (m, 2H), 2.26–2.18 (m, 1H), 2.00–1.91 (m, 2H), 1.85–1.78 (m, 3H), 1.69-1.58 (m, 2H), 1.53-1.27 (m, 3H), 1.11–0.93 (m, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz): $\delta = 146.5$, 137.2, 128.3, 128.3, 127.6 (2C), 125.9, 115.5, 50.4, 43.2, 38.7, 36.1, 32.0, 26.9, 26.5; MS (EI): *m/z* (%): 200 (6) [M^+], 159 (18), 158 (72), 117 (25), 104 (34), 91 (100), 81 (22); elemental analysis (%) calcd for $C_{15}H_{20}$ (200.32) : C 89.94, H 10.06; found: C 89.72, H 9.99.

***trans*-1-Allyl-2-phenylcyclopentane (16c)**: reaction of 1-phenylcyclopent-1-ene (**5b**) and 3-bromoprop-1-ene according to general procedure II afforded **16c** as a clear oil (0.671 g, 36% yield) with a *trans–cis* ratio of 95:5. For the boron–zinc exchange, the reaction mixture was stirred at 0°C for 10 h; IR (film): $\tilde{\nu} = 3029$ (w), 2954 (s), 2873 (s), 1640 (w), 1493 (m), 1453 (m), 994 (m), 911 (s), 756 (s), 700 (vs); ^{1}H NMR ($CDCl_3$, 300 MHz): $\delta = 7.39$–7.20 (m, 5H), 5.88–5.74 (m, 1H), 5.07–4.96 (m, 2H), 2.67–2.61 (m, 1H), 2.31–2.20 (m, 1H), 2.18–1.76 (m, 5H), 1.47–1.41 (m, 2H), 0.97–0.87 (m, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz): $\delta = 145.5$, 137.8, 128.3 (2C), 127.6 (2C), 125.9, 115.1, 52.3, 47.7, 28.3, 35.5, 31.8, 24.1; MS (EI): *m/z* (%): 186 (2) [M^+], 145 (23), 144 (100), 143 (15), 104 (50), 91 (79); elemental analysis (%) calcd for $C_{14}H_{18}$ (186.29): C 90.26, H 9.74, found: C 90.17, H 9.78.

***trans*-Ethyl-2-[2′-phenylcyclohexylmethyl]acrylate (16d)**: Reaction of 1-phenylcyclohex-1-ene (**5a**) and ethyl 2-(bromomethyl)acrylate according to general procedure II afforded **16d** as a clear oil (0.953 g, 35% yield) with a *trans–cis* ratio of 96:4. For the boron–zinc exchange, the reaction mixture was stirred at 25°C for 7 h; IR (film): $\tilde{\nu} = 2910$ (w), 2840 (s), 1717 (vs), 1610 (m), 1590 (m), 1480 (s), 1430 (s), 1325 (m), 1300 (s), 1250 (vs), 1030 (s), 745 (s); ^{1}H NMR ($CDCl_3$, 200 MHz): $\delta = 7.21$–7.09 (m, 5H), 6.00 (s, 1H), 5.25 (s, 1H), 4.08 (q, $J = 7.1$ Hz, 2H), 2.21 (d, $J = 11.6$ Hz, 2H), 1.18 (d, $J = 7.1$ Hz, 3H), 2.06–0.70 (m, 10H); ^{13}C NMR ($CDCl_3$, 75 MHz): $\delta = 167.3$, 146.1, 139.4, 128.2, 127.7, 125.9, 125.8, 60.3, 51.4, 40.8, 37.4, 36.2, 31.8, 27.0, 26.2, 14.1; MS (EI): *m/z* (%): 272 (15) [M^+], 159 (24), 158 (39), 117 (20), 115 (14), 114 (25), 92 (10), 91 (100), 86 (19), 80 (15); HRMS calcd for $C_{18}H_{24}O_2$: 272.1763, found 272.1776

***trans*-Ethyl-2-[2′-phenylcyclopentylmethyl]acrylate (16e)**: Reaction of 1-phenylcyclopent-1-ene (**5b**) and ethyl 2-(bromomethyl)-acrylate according to general procedure II afforded **16e** as a clear oil (1.240 g, 48% yield) with a *trans–cis* ratio of 91:9. For the boron–zinc exchange, the reaction mixture was stirred at 0°C for 10 h; IR (film): $\tilde{\nu} = 3062$ (w), 3029 (m), 2956 (vs), 2871 (s), 1717 (vs), 1630 (m), 1493 (m), 1453 (s), 1368 (s), 1331 (m), 1302 (s), 1179 (vs), 1123 (s), 1030 (s), 756 (s), 700 (vs); ^{1}H NMR ($CDCl_3$, 300 MHz): $\delta = 7.27$–7.11 (m, 5H), 6.03 (m, 1H), 5.41 (m, 1H), 4.11–4.05 (q, $J = 7.2$ Hz, 2H), 2.57–2.42 (m, 2H), 2.13–2.03 (m, 3H), 1.92–1.88 (m, 1H), 1.74–1.63 (m, 3H), 1.27–1.23 (m, 1H), 1.18 (t, $J = 7.4$ Hz, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz): $\delta = 167.3$, 145.0, 140.3, 128.3 (2C), 127.8 (2C), 125.9, 125.0, 60.4, 52.8, 46.2, 36.7, 35.6, 31.9, 23.8, 14.1; MS (EI): *m/z* (%): 258 (31) [M^+], 212 (19), 145 (73), 144 (100), 143 (21), 117 (29), 115 (26), 114 (45), 104 (80), 91 (98), 86 (41), 67 (18); elemental analysis (%) calcd for $C_{17}H_{22}O_2$ (258.36): C 79.03, H 8.58; found: C 78.96, H 8.69.

***trans*-Ethyl-2-[1′-methyl-2′,3′-dihydro-*1H*-2-indenylmethyl)] acrylate (16f)**: Reaction of 1-methyl-3*H*-ind-1-ene (**5c**) and ethyl 2-(bromomethyl)acrylate according to general procedure II afforded **16f** as a clear oil (1.100 g, 45% yield) with a *trans–cis* ratio of 93:7. After 9 h at room temperature, the boron–zinc conversion was 72%; IR (film): $\tilde{\nu} = 3070$ (w), 3020 (w), 2957 (m), 2931 (m), 2870 (m), 1717 (vs), 1630 (s), 1476 (m), 1459 (m), 1369 (m), 1323 (m), 1300 (m), 1258 (m), 1180 (vs); ^{1}H NMR ($CDCl_3$, 300 MHz): $\delta = 7.20$-7.05 (m, 4H), 6.18 (d, $J = 1.3$ Hz, 1H), 5.56 (d, $J = 1.1$ Hz, 1H), 4.28–4.14 (m, 2H), 3.10–2.05 (m, 6H), 1.40–1.20 (m, 6H); ^{13}C NMR ($CDCl_3$, 75 MHz): $\delta = 167.3$, 148.0, 142.4, 140.1, 128.9, 126.3, 125.5, 124.3, 123.3, 47.5, 45.1, 37.8, 36.8, 18.5, 14.3; MS (EI): m/z (%): 245 (5) [M^++H], 244 (30) [M^+], 215 (16), 143 (13), 131 (93), 130 (100), 129 (24), 128 (16), 116 (12), 115 (33), 114 (23), 91 (20), 86 (33); HRMS calcd for $C_{16}H_{20}O_2$: 244.1463, found 244.1464.

***trans*-1-[2-(1, 2-Propadienyl)cyclopentyl]benzene (16g)**: Reaction of 1-phenylcyclopent-1-ene (**5b**) and 3-bromopropyne (80% in toluene) according to general procedure II afforded **16g** as a clear oil (0.774 g, 42% yield) with a *trans*–*cis* ratio of 88:12. For the boron–zinc exchange, the reaction mixture was stirred at 0°C for 10 h; IR (film): $\tilde{\nu} = 3062$ (m), 3029 (m), 2956 (vs), 2871 (s), 1957 (s), 1603 (m), 1493 (m), 1453 (s), 843 (s), 754 (s), 700 (vs); ^{1}H NMR ($CDCl_3$, 300 MHz): $\delta = 7.39$–7.26 (m, 5H), 5.20 (q, $J = 6.6$ Hz, 1H), 4.78–4.61 (m, 2H), 2.88–2.79 (m, 1H), 2.67–2.56 (m, 1H), 2.27–2.08 (m, 2H), 1.94–1.82 (m, 3H), 1.76–1.63 (m, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz): *trans* product: $\delta = 207.9$, 144.5, 128.2 (2C), 127.4 (2C), 125.9, 93.1, 75.5, 52.6, 46.54, 34.90, 32.58, 23.9; *cis* product: $\delta = 141.2$, 128.7 (2C), 127.2 (2C), 127.1, 91.4, 74.9, 49.5, 43.3, 30.5, 29.1, 23.0; MS (EI): m/z (%): 184 (33) [M^+], 169 (77), 156 (37), 155 (84), 141 (100), 117 (75), 115 (45), 103 (22), 91 (74), 77 (37), 65 (20), 39 (19); elemental analysis (%) calcd for $C_{14}H_{16}$ (184.28): C 91.25, H 8.75, found: C 91.41, H 8.56.

***trans*-1-Phenyl-2-(2-phenyl-ethynyl)cyclohexane (16h)**: Reaction of 1-phenylcyclohex-1-ene (**5a**) and 1-bromo-2-phenylacetylene according to general procedure II afforded **16h** as a clear oil (1.146 g, 44% yield) with a *trans*–*cis* ratio of 91:9. For the boron–zinc exchange, the reaction mixture was stirred at 25°C for 7 h; IR (film): $\tilde{\nu} = 3040$ (w), 3020 (w), 2940 (s), 2880 (m), 1620 (w), 1510 (s), 1450 (m), 780 (vs), 690 (s); ^{1}H NMR.($CDCl_3$, 300 MHz): $\delta = 7.42$–7.17 (m, 10H), 2.68–2.55 (m, 1H), 2.26–1.96 (m, 1H), 1.87–1.23 (m, 8H); ^{13}C NMR ($CDCl_3$, 75 MHz): *trans* product: $\delta = 145.4$, 131,4, 128.1, 127.9, 127.6, 127.3, 126.2, 124.0, 93.3, 81.7, 50.2, 37.0, 34.1, 33.6, 26.6, 26.3; *cis* product: $\delta = 145.0$, 131.4, 128.1, 128.0, 127.8, 127.6, 127.3, 128.2, 91.0, 84.3, 46.9, 36.1, 32.5, 27.2, 26.6, 21.5; MS (EI): m/z (%): 261 (21) [M^++H], 260 (100) [M^+], 218 (28), 217 (64), 169 (24), 141 (39), 128 (54), 115 (39), 91 (61); HRMS cacld for $C_{20}H_{20}$: 260.156490, found: 260.15649.

***trans*-1-Phenyl-2-(2-phenyl-ethynyl)cyclopentane (16i)**: Reaction of 1-phenylcyclopent-1-ene (**5b**) and 1-bromo-2-phenylacetylene according to general procedure II afforded **16i** as a clear oil (1.01 g, 41% yield) with a *trans*–*cis* ratio of 96:4. For the boron–zinc exchange, the reaction mixture was stirred at 0°C for 10 h; IR (film): $\tilde{\nu} = 3062$ (w), 3029 (m), 2960 (s), 2873 (m), 1600 (w), 1492 (s), 1453 (m), 756 (vs), 693 (vs); ^{1}H NMR ($CDCl_3$, 300 MHz): $\delta = 7.46$–7.39 (m, 5H), 7.33–7.28 (m, 5H), 3.35–3.17 (m, 1H), 2.98–2.89 (m, 1H), 2.41–2.27 (m, 2H), 2.14–1.86 (m, 4H); ^{13}C NMR ($CDCl_3$, 75 MHz): $\delta = 143.7$, 131.5, 128.3, 128.1, 127.4, 127.2, 126.3, 124.1, 93.0, 81.5, 53.2, 39.5, 33.8, 33.7, 24.2; MS (EI): m/z (%): 247 (19) [M^++H], 246 (100) [M^+], 245 (22), 218 (39), 217 (64), 205 (17), 155 (26), 129 (21), 128 (59), 115 (35), 91 (26); elemental analysis (%) calcd for $C_{19}H_{18}$ (246.35): C 92.64, H 7.36; found: C 92.35, H 7.39.

***trans*-1-Methyl-2-(2′-phenyl-1′-ethynyl)-2,3-dihydro-*1H*-indene (16j)**: Reaction of 1-methyl-3*H*-ind-1-ene (**5c**) and 1-bromo-2-phenylacetylene according to general procedure II afforded **16j** as a clear oil (0.976 g, 42% yield) with a *trans*–*cis* ratio of 93:7. For the boron–zinc exchange, the reaction mixture was stirred at 0°C for 10 h; IR (film): $\tilde{\nu} = 3022$ (m), 2960 (s), 2927 (m), 2869 (m), 2225 (w), 1598 (m), 1488 (s), 1478 (s), 1461 (s), 1443 (s), 791 (m), 754 (vs), 691 (vs); ^{1}H NMR ($CDCl_3$, 300 MHz): $\delta = 7.62$–7.59 (m, 2H), 7.56–7.52 (m, 2H), 7.43–7.24 (m, 5H), 3.39–3.30 (m, 2H), 3.19–3.11 (m, 1H), 3.01–2.92 (m, 1H), 1.56 (d, $J = 6.8$ Hz, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz): $\delta = 146.4$, 141.5, 132.4 (2C), 131.6, 129.11, 128.5, 128.1 (2C), 126.6, 124.1, 122.9, 91.9, 81.6, 46.7, 40.2, 38.8, 17.6; MS (EI): m/z (%): 232 (56) [M^+], 231 (23), 218 (19), 217 (97), 216 (21), 215 (37), 130 (32), 115 (32); HRMS calcd. for $C_{18}H_{16}$: 232.1251, found: 232.1209.

***trans*-2-(1′-Hexenyl)-1-methyl-2,3-dihydro-*1H*-indene (16k)**: Reaction of 1-methyl-3*H*-ind-1-ene (**5c**) and 1-bromohexyne according to general procedure II afforded **16k** as a clear oil (0.573 g, 27% yield) with a *trans*–*cis* ratio of 93:7. After 6.5 h at room temperature, the boron–zinc conversion was 48%; IR (film): $\tilde{\nu} = 3069$ (m), 3023 (m), 2956 (vs), 2932 (vs), 2871 (s), 2213 (w), 1608 (w), 1460 (m), 746 (m); ^{1}H NMR ($CDCl_3$, 300 MHz): $\delta = 7.65$–7.00 (m, 4H), 3.25–2.00 (m, 6H), 1.60–1.30 (m, 4H), 1.32 (d, $J = 6.6$ Hz, 3H), 0.90–0.80 (m, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz): $\delta = 146.7$, 141.8, 126.4, 124.1, 122.9, 81.9, 81.2, 46.8, 39.8, 39.2, 31.2, 21.9, 18.5, 17.4, 13.7; MS (EI): m/z (%): 213 (10) [M^++H], 212 (51) [M^+], 170 (51), 169 (22), 165 (10), 156 (23), 155 (100), 154 (19), 153 (16), 152 (18), 143 (38), 142 (35), 141 (83), 130 (55), 129 (53), 128 (21), 117 (13), 115 (26), 91 (16), 55 (12); HRMS calcd for $C_{16}H_{20}$: 212.1565, found: 212.1565.

***trans*-2-(2′-Cyclohexyl-1′-ethynyl)-1-methyl-2,3-dihydro-*1H*-indene (16l)**: Reaction of 1-methyl-3*H*-ind-1-ene (**5c**) and 2-bromo-1-(1-cyclohexenyl)-acetylene according to general procedure II afforded **16l** as a yellow oil (1.144 g, 48% yield) with a *trans*–*cis* ratio of 89:11. After 4.5 h at room temperature, the boron–zinc conversion was 73%; IR (film): $\tilde{\nu} = 3069$ (w), 3022 (w), 2931 (vs), 2867 (m), 2210 (w), 1674 (m), 1588 (w), 1476 (m), 1459 (m), 744 (s); ^{1}H NMR ($CDCl_3$, 300 MHz): $\delta = 7.25$–7.00 (m, 4H), 6.07 (sext, $J = 2.0$ Hz, 1H), 3.10–2.65 (m, 4H), 2.10–1.95 (m, 4H), 1.75–1.45 (m, 4H), 1.41 (d, $J = 6.8$ Hz, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz): $\delta = 146.6$, 141.7, 133.7, 126.5, 124.1, 122.9, 120.98, 88.9, 83.2, 46.8, 40.2, 39.17, 29.7, 25.6, 22.4, 21.6, 17.5; MS (EI): m/z (%): 237 (18) [M^++H], 236 (100) [M^+], 221 (50), 207 (14), 193 (33), 180 (13), 179 (37), 178 (23), 165 (22), 155 (17), 142 (13), 141 (16), 135 (28), 131 (14), 130 (99), 129 (29), 128 (20), 117 (10), 115 (25), 105 (23), 91 (33), 71 (22), 57 (27), 43 (22), 28 (47); HRMS calcd. for $C_{18}H_{20}$: 236.1565, found: 236.1566.

***trans*-Ethyl-(*E*)-3-[1′-methyl-2′,3′-dihydro-*1H*-2′-indenyl]-2-propenoate (16m)**: Reaction of 1-methyl-3*H*-ind-1-ene (**5c**) and ethyl propiolate according to general procedure II afforded **16m** as a clear oil (0.944 g, 41% yield) with a *trans*–*cis* ratio of 90:10. After 5 h at room temperature, the boron–zinc conversion was 80%; IR (film): $\tilde{\nu} = 3069$ (w), 3020 (w), 2960 (m), 2933 (m), 2901 (m), 2871 (m), 2842 (m), 1718 (vs), 1652 (s), 1585 (w), 1475 (m), 1460 (m), 1369 (m), 1301 (m), 1280 (s), 1225 (m), 1182 (s), 1153 (s), 1110 (m), 1066 (m), 1037 (m), 985 (m), 746 (s); ^{1}H NMR ($CDCl_3$, 200 MHz): $\delta = 7.60$–6.95 (m, 5H), 5.59 (dd, $J = 15.5$ Hz, $J = 0.7$ Hz, 1H), 4.14 (q, $J = 7.1$ Hz, 2H), 3.50–2.50 (m, 4H), 1.30–1.10 (m, 6H); ^{13}C NMR ($CDCl_3$, 50 MHz): $\delta = 167.1$, 151.1, 147.2, 141.1, 127.0, 124.6, 123.6, 122.1, 60.7, 52.8, 45.1, 38.1, 17.6, 14.7; MS (EI): m/z (%): 231 (4) [M^++H], 230 (31) [M^+], 185 (18), 169 (16), 157 (18), 156 (16), 155 (13), 142 (17), 141 (26), 131 (14), 130 (100), 129 (21), 128 (14), 117 (21), 115 (28), 55 (30); HRMS calcd for $C_{15}H_{18}O_2$: 230.1307, found: 230.1311.

***trans*-Dimethyl-(*Z*)–2-[1′-methyl-2′,3′-dihydro-*1H*-2′-indenyl]-2-butenedioate (16n)**: Reaction of 1-methyl-3*H*-ind-1-ene (**5c**) and dimethyl acetylenedicarboxylate according to general procedure II afforded **16n** as a clear oil (0.937 g, 31% yield) with a *trans*–*cis* ratio of 89:11. After 5 h at room temperature, the boron–zinc conversion was 73%; IR (film): $\tilde{\nu} = 3069$ (m), 3021 (m), 2955 (s), 2929 (m), 2869 (m), 1725 (vs), 1636 (s), 1586 (w), 1477 (s), 1458 (s), 1377 (s), 1271 (s), 1205 (vs); ^{1}H NMR ($CDCl_3$, 200 MHz): $\delta = 7.20$–7.00 (m, 4H), 6.72 (s, 1H), 3.90 (m, 1H), 3,68 (s, 3H), 3.67 (s, 3H), 3.60–2.80 (m, 3H), 1.20 (d, $J = 11.8$ Hz, 3H); ^{13}C NMR ($CDCl_3$, 50 MHz): $\delta = 166.1$, 165.0, 147.4, 146.0, 141.1, 127.1, 125.4, 125.3, 123.2, 122.1, 51.2, 50.8, 46.2, 43.1, 36.1, 17.0. MS (EI): m/z (%): 275 (2) [M^++H], 274 (8) [M^+], 243 (27), 242 (100), 215 (13), 214 (66), 199 (11), 183 (15), 182 (13), 155 (38), 154 (86), 153 (15), 141 (11), 130 (23), 129 (11), 128 (14), 117 (18), 115 (26), 91 (10); elemental analysis (%) calcd for $C_{16}H_{28}O_4$ (302.36): C 70.06, H 6.61, found: C 70.18, H 6.65

***trans*-1-Methyl-2,3-dihydro-*1H*-2-indenyl-phenylmethanone (16o)**: Reaction of 1-methyl-3*H*-ind-1-ene (**5c**) (0.255 g, 2.0 mmol), diethylborane (0.80 mL, 6.00 mmol, 3.0 equiv), *i*Pr_2Zn (0.78 mL, 3.9 mmol, 2.0 equiv). After 6 h at room temperature, the boron–zinc conversion was 61%. The zinc reagent was then dissolved in dry THF (3 mL) and a solution of [Pd(dba)$_2$] (0.056 g, 0.1 mmol, 5 mol%) and P(*o*-Tol)$_3$ (0.119 g, 0.4 mmol, 20 mol%) in dry THF (2 mL) was added. The mixture was stirred for 5 min and a solution of benzoyl chloride (517 mg, 3.9 mmol, 2 equiv) in THF (2 mL) was added dropwise. The mixture was stirred at room temperature for 11 h and worked up as usual. Flash chromatography purification (hexanes/ether 98:2) afforded the compound **16o** as a clear oil (0.189 g, 41% yield) with a *trans*–*cis* ratio of 89:11; IR (film): $\tilde{\nu} = 3066$ (m), 3024 (m), 2960 (s), 2929 (m), 2870 (m), 1719 (m), 1680 (vs), 1597 (m), 1581 (m), 1478 (m), 1449 (s), 1362 (m), 1271 (s), 1253 (s), 1233 (s), 1219 (s); ^{1}H NMR ($CDCl_3$, 200 MHz): $\delta = 8.35$–7.00 (m, 9H), 4.00–2.80 (m, 4H), 1.27 (d, $J = 6.6$ Hz, 3H); ^{13}C NMR ($CDCl_3$, 50 MHz): 2 diastereoisomers $\delta = 201.8$, 146.6, 140.7, 136.9, 133.0, 133.8, 129.6, 129.5, 128.7, 128.6, 128.5, 128.4, 128.3, 128.1, 127.9, 126.7, 126.6, 124.7, 124.1, 123.4, 123.2, 55.5, 55.4, 43.1, 42.1, 31.9, 26.6, 19.24, 17.33; MS (EI): m/z (%): 237 (16) [M^++H], 236 (100) [M^+], 222 (13), 221 (83), 131 (20), 130 (73), 115 (11), 107 (43), 105 (81), 91 (20), 77 (58), 28 (15); HRMS calcd. for $C_{17}H_{16}O$: 236.1201, found: 236.1201.

***syn*-1-(1,2-Dimethyl-4-pentenyl)benzene (*syn*-18)**: Reaction of *E*-2-phenylbut-2-ene (*E*-**9**) (0.250 g, 1.9 mmol) and 3-bromoprop-1-ene (0.458 g, 3.8 mmol, 2.0 equiv) according to general procedure II afforded *syn*-**18** as a clear oil (0.118 g, 36% yield) with a *syn*–*anti* ratio of 78:22. After 4 h at room temperature, the boron–zinc conversion was 40%; IR (film): $\tilde{\nu}$ = 3077 (m), 3064 (m), 3029 (m), 2967 (vs), 2928 (s), 2877 (s), 1639 (m), 1603 (w), 1494 (m), 1453 (s), 1377 (m), 1080 (m), 994 (m), 910 (s), 770 (m), 761 (m), 701 (s); ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.40–7.10 (m, 5H), 5.85–5.65 (m, 1H), 5.10–4.90 (m, 2H), 2.61 (quint, J = 7.0 Hz, 1H), 2.20–1.80 (m, 3H), 1.29 (d, J = 7.0 Hz, 3H, *anti* isomer), 1.24 (d, J = 7.0 Hz, 3H, *syn* isomer), 0.91 (d, J = 6.5 Hz, 3H, *syn* isomer), 0.76 (d, J = 6.8 Hz, 3H, *anti* isomer); ^{13}C NMR ($CDCl_3$, 75 MHz): δ = *syn* isomer: 147.0, 137.7, 128.2, 127. 7, 127. 1, 125.8, 115.7, 44.5, 39.5, 39.2, 19.0, 16.1; *anti* isomer: 146.2, 137.5, 128.1, 127.9, 127.1, 125.8, 115.8, 44.7, 39.2, 38.5, 21.8, 17.23; MS (EI): *m/z* (%): 175 (1) [M^++H], 174 (8) [M^+], 133 (14), 132 (45), 106 (38), 105 (100), 104 (11), 91 (42), 79 (15), 77 (20), 69 (11), 41 (15); elemental analysis (%) calcd for $C_{13}H_{18}$: C 89.59, H 10.41, found: C 89.08, H 10.72.

***anti*-1-(1,2-Dimethyl-4-pentenyl)benzene (*anti*-18)**: Reaction of *Z*-2-phenylbut-2-ene (*Z*-**9**) (0.240 g, 1.8 mmol) and 3-bromoprop-1-ene (0.980 g, 8.0 mmol, 4.4 equiv) according to general procedure II afforded *anti*-**18** as a clear oil (0.160 g, 50% yield) with a *syn*–*anti* ratio of 19:81. After 3.5 h at room temperature, the boron–zinc conversion was 67%; IR (film): $\tilde{\nu}$ = 3074 (s), 3017 (s), 2967 (vs), 2918 (vs), 2875 (vs), 1644 (s), 1588 (m), 1488 (s), 1452 (vs), 1374 (s), 990 (m), 905 (vs), 770 (m), 748 (m), 699 (vs), ^{1}H NMR (300 MHz, $CDCl_3$): 7.35–7.30 (m, 2H), 7.24–7.10 (m, 3H), 5.89–5.78(m, 1H), 5.12–5.04 (m, 2H), 2.65 (quint, ^3J = 7.1, 1H), 2.34–2.29 (m, 1H), 1.98–1.76 (m, 2H), 1.32 (d, ^3J = 7.1, 3H), 0.80 (d, ^3J = 6.7, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 146.32(s), 137.61(d), 128.28(d), 128.18(d), 128.01(d), 127.78(d), 125.96(d), 115.96(t), 44.78(d), 39.37(d), 38.65(t), 19.11(q), 17.36(q); MS (EI): *m/z* (%): 174 (2) [M^+], 132 (16), 105 (100), 91 (16); HRMS calcd. for $C_{13}H_{18}$: 174.1408, found: 174.1409.

***syn*-1-(1, 2-Dimethyl-4-pentenyl)-2-methoxybenzene (*syn*-19)**: Reaction of *E*-2-phenylbut-2-ene (*E*-**11**) (0.280 g, 1.7 mmol) and 3-bromoprop-1-ene (0.560 g, 4.6 mmol, 2.7 equiv) according to general procedure II afforded *syn*-**19** as a clear oil (0.140 g, 40% yield) with a *syn*–*anti* ratio of 81:19. After 3.5 h at room temperature, the boron–zinc conversion was 62%; IR (film): $\tilde{\nu}$ = 3074 (m), 3029 (m), 2963 (vs), 2930 (vs), 2875 (s), 2836 (s), 1639 (m), 1599 (m), 1585 (m), 1492 (s), 1461(s), 1439 (s), 1376 (m), 1354 (m), 1288 (m), 1240 (s); ^{1}H NMR ($CDCl_3$, 200 MHz): δ = 7.08–7.04 (m, 2H), 6.84–6.73 (m, 2H), 5.68 (sym. m, 1H), 4.94–4.83 (m, 2H), 3.71 (s, 3H), 3.01 (quint, J = 7.2 1H), 2.05–1.90 (m, 1H), 1.79–1.67(m, 2H), 0.92 (d, J = 7.1 Hz, 3H), 0.79 (d, J = 6.5 Hz, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 156.9, 138.0, 135.2, 127.5, 126.6, 120.4, 115.0, 110.4, 55.2, 39.6, 37.3, 36.8, 16.3, 15.8. *anti* isomer: 157.0, 138.2, 135.4, 127.6, 126.5, 120.3, 55.3, 115.2, 110.44, 39.74, 37.4, 36.3, 16.4, 15.9; MS (EI): *m/z* (%): 205 (1) [M^++H], 204 (9) [M^+], 136 (12), 135 (100), 105 (19); elemental analysis (%) calcd for $C_{14}H_{20}O$: C 82.30, H 9.87, found: C 81.89, H 10.05.

***anti*-1-(1, 2-Dimethyl-4-pentenyl)-2-methoxybenzene (*anti*-19)**: Reaction of *Z*-2-phenylbut-2-ene (*Z*-**11**) (0.350 g, 2.2 mmol) and 3-bromoprop-1-ene (0.840 g, 6.9 mmol, 3.2 equiv) according to general procedure II afforded *anti*-**19** as a clear oil (0.210 g, 47% yield) with a *syn*–*anti* ratio of 24:76. After 3 h at room temperature, the boron–zinc conversion was 79%; IR (film): $\tilde{\nu}$ = 3074 (s), 3029 (s), 2964 (s), 2930 (s), 2875 (s), 2836 (m), 1639 (s), 1599 (m), 1585 (m), 1492 (s), 1462 (m), 1439 (m), 1240 (vs); ^{1}H NMR ($CDCl_3$, 200 MHz): δ = 7.08–7.04 (m, 2H), 6.84–6.73 (m, 2H), 5.68 (sym. m, 1H), 4.94–4.83 (m, 2H), 3.71 (s, 3H), 3.01 (quint, J = 7.2 1H), 2.25–2.19 (m, 1H), 1.79–1.67(m, 2H), 1.13 (d, J = 7.2 Hz, 3H), 0.67 (d, J = 6.6 Hz, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 157.0, 137.8, 135.0, 127.7, 126.4, 120.3, 115.3, 110.4, 55.2, 38.0, 37.9, 36.8, 17.6, 17.4; *anti* isomer: 157.0, 138.2, 135.4, 127.6, 126.5, 120.3, 55.3, 115.2, 110.44, 39.74, 37.4, 36.3, 16.4, 15.9; MS (EI): *m/z* (%): 205 (1) [M^++H], 204 (9) [M^++H], 136 (7), 135 (100), 105 (19), elemental analysis (%) calcd for $C_{14}H_{20}O$: C 82.30, H 9.87, found: C 82.15, H 10.02.

***syn*-3-Methyl-4-phenylpentanal (20)**: 4-Methyl-5-phenylhex-1-ene **18** (*syn*:*anti* 78:22, 0.220 g, 1.3 mmol) was dissolved in CH_2Cl_2 (10 mL) and ozonolyzed at −78 °C for 5 min. Dimethyl sulfide (2.1 g, 34 mmol) was added and the solution warmed to 25 °C overnight. The solvents were evaporated and the residue purified by flash chromatography (hexanes/diethyl ether 95:5) to yield the aldehyde **20** (0.190 g, 86%) as a colorless oil, *syn*:*anti* ratio of 77:23. The unstable product was directly submitted to the following oxidation.

***syn*-3-Methyl-4-phenyl-pentanoic acid (21)**: The aldehyde **20** (0.180 mg, 1.0 mmol), was dissolved in *t*BuOH (20 mL), then 2-methyl-2-butene (5.1 g, 72.7 mmol) was added, followed by the solution of $NaClO_2$ (1.36 g, 15.0 mmol) and $NaH_2PO_2 \cdot H_2O$ (1.28 g, 9.3 mmol) in H_2O (25 mL). After 1 h at 25 °C, the oxidation was complete. The *t*BuOH was evaporated at reduced pressure (50 mmHg, 40 °C) and the residue extracted five times with diethyl ether. After drying and evaporation, analytically pure acid **21** (0.150 g, 77%) was isolated as a viscous oil; IR (film): $\tilde{\nu}$ = 3600–3300 (b), 3028 (m), 1708 (vs), 1494 (m), 1453 (s), 1407 (m), 702 (vs); ^{1}H NMR ($CDCl_3$, 200 MHz): δ = 9.85 (br, 1H), 7.26–7.01 (m, 5H), 2.50 (quint., J = 7.3, 1H), 2.30–1.82 (m, 3H), 1.17 (d, J = 7.0, 3H, major isomer), 1.18 (d, J = 7.0, 3H, minor isomer), 0.92 (d, J = 6.5, 3H, major isomer), 0,76 (d, J = 6.5, 3H, minor isomer); ^{13}C NMR ($CDCl_3$, 50 MHz): major isomer: δ = 178.8, 144.7, 127.3, 126.8, 125.2, 43.7, 38.9, 35.4, 17.1, 16.0; minor isomer: δ = 178.8, 143.9, 127.3, 127.2, 126.5, 43.4, 38.0, 35.2, 17.3, 16.5; MS (EI): *m/z* (%): 192 (14) [M^+], 132 (37), 105 (100), 77 (8), 28 (14); HRMS calcd. for $C_{12}H_{16}O_2$: 192.1150, found: 192.1152.

3,4-Dimethyl-1,2,3,4-tetrahydro-1-naphthalene (22): Acid **21** (0.150 g, 0.8 mmol) was heated with $SOCl_2$ (0.2 mL, 2.7 mmol, 3.5 equiv) to 60 °C for 1 h (evolution of gases ceased). The excess $SOCl_2$ was evaporated at 1 mmHg/25 °C for 20 min, then the brown residue was dissolved in 1,2-dichloroethane (1 mL). $AlCl_3$ (130 mg, 1.0 mmol, 1.2 equiv) was added at once and the mixture stirred at 25 °C for 4 h. After quenching with an ice/water mixture and acidification (1M aqueous HCl, pH 1), the product was extracted with diethyl ether. Flash chromatography purification afforded analytically pure tetralone **22** (0.080 g; 59%), *cis*:*trans* 22:78; IR (film): $\tilde{\nu}$ = 2960 (s), 2880 (s), 1683 (vs), 1601 (s), 1454 (s), 1378 (m), 1285 (s); ^{1}H NMR ($CDCl_3$, 200 MHz): *trans* isomer: δ = 7.93 (d, J = 7.8 Hz, 1H), 7.43 (m, 1H), 7.26–7.19 (m, 2H), 2.72 (quint, J = 6.3 Hz, 1H), 2.47 (br s, 1H), 2.35 (dd, J = 16.4 Hz, J = 9.2 Hz, 1H), 2.10–2.04 (m, 1H); 1.34 (d, J = 7.1 Hz, 3H), 1.02 (d, J = 6.9 Hz, 3H); *cis* isomer: δ = 7.93 (d, J = 7.8 Hz, 1H), 7.43 (m, 1H), 7.26–7.19 (m, 2H), 2.98–2.93 (m, 1H), 2.81 (dd, J = 17.0 Hz, J = 4.5 Hz, 1H), 2.49 (d, J = 1.4 Hz, 1H), 2.45–2.39 (m, 1H); 1.15 (d, J = 7.2 Hz, 3H), 0.99 (d, J = 6.5 Hz, 3H); ^{13}C NMR ($CDCl_3$, 50 MHz): *trans* isomer: δ = 198.5, 148.1, 134.2, 132.0, 128.7, 127.5, 126.9, 43.8, 40.4, 35.9, 20.7, 16.23; *cis* isomer: δ = 198.6, 150.3, 134.1, 131.6, 128.6, 127.2, 126.8, 42.6, 38.6, 33.2, 18.2, 16.1; irradiation experiments (400 MHz, $CDCl_3$): irradiation of the methyl groups at δ = 1.34 (*cis*) and δ = 1.15 (*trans*), respectively, reveals J = 5.5 Hz for the benzylic proton at 2.72 for the *trans* isomer and J = 3.8 Hz for the benzylic proton at 2.98–2.93 for the *cis* isomer; NOESY experiments ($CDCl_3$, 400 MHz): for the *trans* isomer cross-peak between homobenzylic proton at δ = 2.10–2.04 and the benzylic methyl group at δ = 1.34 which is not observed for the *cis* isomer (δ = 2.45–2.39 and 1.15); MS (EI): *m/z* (%): 174 (60) [M^+], 159 (48), 132 (100), 104 (46), 77 (14); HRMS calcd. for $C_{12}H_{14}O$: 174.1045, found :174.1044.

***trans*-1-Methyl-2,3-dihydro-*1H*-indan-2-ol (30)**: 1-methyl-3H-indene (**5c**) (1.3 g, 10 mmol) was hydroborated with (−)-IpcBH_2 (0.7M in Et_2O, 14.3 mL, 1 equiv) at −30 °C for 48 h. A white precipitate formed (indanoyl-IpcBH) from which the solvent was separated by double-ended cannula. The crystals were washed with cold Et_2O (−30 °C) to remove residual starting olefin, weighed, and dissolved in Et_2O (0 °C) in order to get a 1M solution. An aliquot (ca. 2 mmoles) was directly oxidized with aqueous 3M NaOH/30% H_2O_2 (2 mL of each) to afford alcohol **30** as a white solid after purification. A second aliquot (ca. 2 mmoles) was first heated with excess Et_2BH (50 °C, 16 h). Then after pumping off excess volatiles (25 °C, 2 h) and redissolution of the residual organylborane in Et_2O, this sample was also oxidized with aqueous NaOH/30% H_2O_2 to afford alcohol **30**. The enantiomeric ratio was determined by chiral HPLC (Daicel Chemicals, Chiracel OD, heptane:*i*PrOH 95:5, flow: 0.6 mL min^{-1}). In both cases, the enantiomeric ratio of the alcohol **30** was 77:23. IR (film): $\tilde{\nu}$ = 3336 (b), 3069 (m), 3043 (m), 2957 (s), 1, 477 (s), 1460 (s), 1068 (s), 1019 (s), 743 (s); ^{1}H NMR ($CDCl_3$, 200 MHz): δ = 7.13–7.07 (m, 4H), 4.07 (q, J = 6.3 Hz, 1H), 3.19–2.69 (m, 2H), 2.95 (quint, J = 6.7 Hz, 1H), 2.14 (bs, 1H), 1.22 (d, J = 6.9 Hz, 3H); ^{13}C NMR (50 MHz, $CDCl_3$) δ = 146.0, 140.1, 127.3, 125.1, 124.1, 81.2, 48.3, 40.9, 17.6; MS (EI): *m/z* (%): 148 (54) [M^+], 133 (26), 119 (100), 105 (33), 91 (41), 77 (14), 65 (10), 28 (3); elemental analysis (%) calcd for $C_{10}H_{12}O$: C 81.04, H 8.16, found: C 80.69, H 8.14.

General procedure III: Cu^I-catalyzed reactions of optically enriched zinc reagents 27 with electrophiles: A one-neck Schlenk flask was charged with IpcBH_2 (**23**, 4.3 mL, 3 mmol, 0.7M in diethyl ether), cooled to −35 °C and the olefin (3 mmol, 1 equiv) in diethyl ether (1 mL) was added. The reaction mixture was stirred at −35 °C for 48 h and the solvents were carefully evaporated under reduced pressure. Et_2BH (2.5 mL of a 7.3 M solution in Me_2S, 18 mmol, 6 equiv) was added and the resulting solution was stirred at 50 °C for 16 h. The solvents were evaporated under reduced pressure (room temperature, 2 h). *i*Pr_2Zn (1.8 mL of a 5 M solution in Et_2O, 9 mmol, 3 equiv) was added over a 10 min period and the reaction mixture was stirred at room temperature for 5 h. The volatiles were evaporated under reduced pressure (0 °C to 25 °C, 30 min) and the resulting gray residue was dissolved in THF (5 mL). A 1 M solution of $CuCN \cdot 2LiCl$ (3.0 mL, 3.0 mmol, 1.0 equiv) was added at −78 °C. The reaction mixture was stirred 10 min at −78 °C and the electrophile (9 mmol, 3.0 equiv) was added. The reaction mixture was stirred 1 h at −78 °C and the cooling bath was removed allowing the reaction temperature to rise to room temperature. The reaction mixture was quenched with aqueous sat. NH_4Cl and extracted with Et_2O. After drying ($MgSO_4$) and evaporating the solvents, the crude residue obtained was purified by flash chromatography (hexanes). The *syn*:*anti* ratio and enantioselectivity were determined by capillary GC analysis on a chiral β-cyclodextrin column (CP-Chirasil-Dex CB, Chrompack). A calibration was performed in each case with racemic material.

***trans*-(1*S*, 2*R*)-1-Allyl-2-phenylcyclohexane (28d)**: Reaction of 1-phenylcyclohex-1-ene (**5a**) and 3-bromoprop-1-ene according to general procedure III afforded **28d** as a clear oil (0.270 g, 45 % yield) with a *trans*:*cis* ratio of 97:3 and 20 % *ee*; IR (film): $\tilde{\nu}$ = 3074 (w), 3026 (m), 2924 (s) , 2853 (m), 1493 (m), 1447 (m), 909 (m), 755 (s); ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.30–7.14 (m, 5H), 5.72–5.59 (m, 1H), 4.90–4.80 (m, 2H), 2.20 (td, *J* = 11.0 Hz, 3.0 Hz, 1H), 1.93–1.00 (m, 11H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 146.6, 137.3, 128.5, 127.8, 126.0,115.7, 50.6, 44.8, 38.9, 36.3, 32.2, 27.1, 26.7; MS (EI): *m/z* (%): 200 (4) [M^+], 158 (49), 129 (9), 117 (22), 104 (30), 91 (100), 81 (13), 67 (10), 55 (7), 41 (12); elemental analysis (%) calcd for $C_{15}H_{20}$ (200.32): C 89.94, H 10.06; found: C 89.71, H 10.14.

***trans*-(1*S*, 2*R*)-1-Allyl-2-phenylcyclopentane (28e)**: Reaction of 1-phenylcyclopent-1-ene (**5b**) and 3-bromoprop-1-ene according to general procedure III afforded **28e** as a clear oil (0.262 g, 47 % yield) with a *trans*:*cis* ratio of 97:3 and 94 % *ee*; IR (film): $\tilde{\nu}$ = 3076 (w), 3026 (w), 2952 (s), 2908 (m), 1492 (m), 1451 (m), 993 (m), 910 (m), 755 (m), 699 (s); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.31–7.17 (m, 5H), 5.77–5.68 (m, 1H), 4.98–4.88 (m, 2H), 2.59–2.50 (q, *J* = 9.0 Hz, 1H), 2.23–1.64 (m, 8H), 1.43–1.31 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 145.5, 137.8, 128.3, 127.6, 125.9,115.0, 52.3, 47.7, 38.3, 35.4, 31.8, 24.1; MS (EI): *m/z* (%): 186 (3) [M^+], 157 (5), 144 (100), 129 (21), 117 (26), 104 (48), 91 (72), 77 (9), 67 (20), 41 (13); elemental analysis (%) calcd for $C_{14}H_{18}$ (186,.29): C 90.26, H 9.74; found: C 90.11, H 9.54.

***trans*-1-[(1*R*, 2*S*)-2′-Allylcyclopentyl]-2-methoxybenzene (28f)**: Reaction of *o*-methoxyphenyl-cyclopentene (**5f**) and 3-bromoprop-1-ene according to general procedure III afforded **28f** as a clear oil (0.500 g, 77 % yield) with a *trans*:*cis* ratio of 98:2 and 84 % *ee*; IR (film): $\tilde{\nu}$ = 2952 (s), 2870 (s), 1493 (s), 1465 (s), 1242 (s), 1033 (s), 910 (s), 752 (s); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.21–6.83 (m, 4H), 5.86–5.63 (m, 1H), 4.98–4.86 (m, 2H), 3.80 (s, 3H), 3.14–3.01 (q, *J* = 8.9 Hz, 1H), 2.29–1.19 (m, 9H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 159.8, 140.4, 135.7, 129.6, 128.7,122.8, 116.9, 112.7, 57.5, 48.3, 46.7, 40.7, 36.0, 33.9, 26.2; MS (EI): *m/z* (%): 216 (34) [M^+], 185 (5), 174 (100), 159 (11), 147 (28), 134 (28), 121 (98), 115 (15), 108 (13), 91 (77), 77 (15), 65 (12), 41 (15), 28 (17); elemental analysis (%) calcd for $C_{15}H_{20}O$ (216.32): C 83.29, H 9.32; found: C 83.17, H 9.40.

***trans*-(1*S*, 2*R*)-2-Allyl-1-methyl-2,3-dihydro-*1H*-indene (28g)**: Reaction of 1-methyl-*3H*-ind-1-ene (**5c**) and 3-bromoprop-1-ene according to general procedure III afforded **28g** as a clear oil (0.207 g, 40 % yield) with a *trans*:*cis* ratio of 97:3 and 66 % *ee*; IR (film): $\tilde{\nu}$ = 3076 (s), 3045 (m), 3022 (s), 2958 (vs), 2902 (vs), 2869 (vs), 2840 (vs), 1642 (s), 1478 (vs), 1461 (s), 996 (s), 911 (vs), 770 (vs), 743 (vs): ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.23–7.09 (m, 4H), 5.94–5.81 (m, 1H), 5.12–5.00 (m, 2H), 3.06–2.99 (m, 1H), 2.82 (quint, *J* = 7.0 Hz, 1H), 2.61–2.53 (m, 1H), 2.49–2.40 (m, 1H), 2.07–1.98 (m, 1H), 1.30 (d, 7.2 Hz, 3H), 1.10 (d, *J* = 7.2 Hz, *cis*-dia); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 148.0, 142.5, 137.4, 126.1, 126.0, 124.1, 123.0, 115.4, 48.2, 44.6, 38.3, 37.5, 18.4; MS (EI): *m/z* (%): 172 (2) [M^+], 157 (2), 143 (17), 130 (100), 115 (24), 91 (15), 77 (5), 65 (3), 51 (3), 41 (5), 28 (3); elemental analysis (%) calcd for $C_{13}H_{16}$ (172.27): C 90.70, H 9.30; found: C 90.83, H 9.52.

***trans*-1-[(1*S*, 2*R*)-1′-Methyl-2′,3′-dihydro-*1H*-indenyl]-1-pentanone (28h)**: Reaction of 1-methyl-*3H*-ind-1-ene (**5c**) and pentanoyl chloride according to general procedure III afforded **28h** as a clear oil (0.279 g, 43 % yield) with a *trans*:*cis* ratio of 99:1 and 64 % *ee*; IR (film): $\tilde{\nu}$ = 3070 (w), 3022 (w), 2959 (s), 2931 (s), 2871 (s), 1711 (s), 1477 (m), 1460 (m), 1375 (m), 745 (s); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.15–7.07 (m, 1H), 3.56–3.32 (m, 1H), 3.15–2.89 (m, 3H), 2.47 (t, *J* = 7.5 Hz, 2H), 1.55 (quint, *J* = 7.5 Hz, 3H), 1.28 (d, *J* = 6.9 Hz, 3H), 1.27 (sext, *J* = 7.5 Hz, 2H), 0.86 (t, *J* = 7.5 Hz); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 212.2, 147.0, 141.1, 127.2, 127.1,124.6, 123.6, 60.9, 42.4, 42.0, 35.6, 26.2, 22.8, 19.9, 14.3; MS (EI): *m/z* (%): 216 (14) [M^+], 201 (15), 159 (100), 131 (48), 115 (21), 91 (19), 85 (9), 57 (33), 41 (13), 29 (15); HRMS calcd. for $C_{15}H_{20}O$: 216.1514, found: 216.1517.

***trans*-(1*S*, 2*S*)-2-Allyl-1-methyl-1,2,3,4-tetrahydronaphthalene (28i)**: Reaction of 1-methyl-3,4-dihydro-1-naphthalene (**5d**) and 3-bromoprop-1-ene according to general procedure III afforded **28i** as a clear oil (0.223 g, 40 % yield) with a *trans*:*cis* ratio of 98:2 and 42 % *ee*; IR (film): $\tilde{\nu}$ = 3075 (w), 3017 (w), 2961 (m), 2928 (s), 2870 (m), 1491 (m), 1447 (m), 910 (m), 756 (s), 733 (m); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.17–7.04 (m, 4H), 5.91–5.76 (m, 1H), 5.11–4.98 (m, 2H), 2.79–2.63 (m, 3H), 2.26–2.16 (m, 1H), 2.09–1.91 (m, 2H), 1.69–1.47 (m, 2H), 1.30 (d, *J* = 7.0 Hz, 3H, *trans*-dia, 3H), 1.11. (d, *J* = 7.0 Hz, *cis*-dia, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 141.1, 137.2, 136.1, 128.9, 128.6, 125.5, 125.1, 115.7, 39.6, 37.9, 37.2, 26.7, 24.1, 23.1; MS (EI): *m/z* (%): 186 (8) [M^+], 171 (18), 157 (9), 144 (100), 129 (89), 117(45), 105 (11), 91 (35), 77 (10), 51 (5), 32 (9); elemental analysis (%) calcd for $C_{14}H_{18}$ (186.29): C 90.26, H 9.74; found: C 90.24, H 10.03.

1-[(1*S*, 2*S*)-1,2-Dimethyl-4-pentenyl]benzene (*anti*-32a): Reaction of *Z*-2-phenyl-2-butene (*Z*-**9**) and 3-bromoprop-1-ene according to general procedure III afforded *anti*-**32a** as a clear oil (0.209 g, 40 % yield) with a *anti*:*syn* ratio of 92:8 and 74 % *ee*; IR (film): $\tilde{\nu}$ = 3077 (m), 3063 (m), 2965 (s), 2928 (m), 1494 (m), 1452 (s), 910 (s), 701 (s); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.20–7.06 (m, 5H), 5.85–5.65 (m, 1H), 4.99–4.89 (m, 2H), 2.53 (quint, *J* = 7.0 Hz, 1H), 2.25–2.10 (m, 1H), 1.83–1.66 (m, 2H), 1.19 (d, *J* = 7.0 Hz, 3H, *trans*-dia), 1.15 (d, *J* = 7.0 Hz, *cis*-dia, 3H), 0.80 (d, *J* = 7 Hz, *cis*-dia, 3H) 0.66 (d, *J* = 7 Hz, *trans*-dia, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 147.0, 137.7, 128.1, 128.0, 127.9,127.7, 125.8, 115.6, 44.5, 39.5, 39.2, 17.6, 16.1; MS (EI): *m/z* (%): 174 (1) [M^+], 132 (21), 118 (4), 105 (100), 91 (24), 77 (7), 65(2), 55 (4), 41 (9), 39 (4); elemental analysis (%) calcd for $C_{13}H_{18}$ (174.28): C 89.59, H 10.41; found: C 89.97, H 10.25.

Ethyl 2-[(2*S*, 3*S*)-2-methyl-3-phenylbutyl]acrylate (*anti*-32b): Reaction of *Z*-2-phenyl-2-butene (*Z*-**9**) and ethyl 2-(bromomethyl)acrylate according to general procedure III afforded *anti*-**32b** as a clear oil (0.281 g, 38 % yield) with a *anti*:*syn* ratio of 90:10 and 74 % *ee*; IR (film): $\tilde{\nu}$ = 3084 (w), 3061 (w), 3027 (w), 2959 (s), 2928 (s), 2872 (s), 1721 (ss), 1219 (s), 1198 (s), 1159 (s), 702 (m); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.30–7.15 (m, 5H), 6.16 (s, 1H), 6.10 (s, *cis*–dia), 5.46 (s, 1H), 5.43 (s, *cis*-dia), 4.19 (q, *J* = 7.0 Hz, 2H), 2.72–2.56 (m, 2H), 1.32 (t, *J* = 7.0 Hz, 3H), 1.27 (d, *J* = 7.0 Hz, 3H), 0.83 (d, *J* = 6.5 Hz, *cis*-dia), 0.69 (d, *J* = 6 Hz, 3H, *trans*-dia); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 167.6, 146.1, 140.2, 128.3, 128.1,127.9, 126.0, 125.9, 60.7, 45.5, 45.1 (*cis*-dia), 38.3, 38.0 (*cis*-dia) , 37.2, 19.0, 17.5 (*cis*-dia), 16.9, 15.8 (*cis*-dia), 15.4 (*cis*-dia), 14.4; MS (EI): *m/z* (%): 246 (10) [M^+], 200 (3), 183 (3), 141 (32), 132 (10), 113 (37), 105 (100), 95 (18), 91 (32), 77 (10), 55 (6), 28 (4), elemental analysis (%) calcd for $C_{16}H_{22}O_2$ (246.34): C 78.01, H 9.00; found: C 77.88, H 9.22.

Trimethyl-[(3*R*, 4*S*)-3-methyl-4-phenyl-1-pentynyl]silane (*anti*-32c): Reaction of *Z*-2-phenyl-2-butene (*Z*-**9**) and 2-bromo-1-trimethylsilylacetylene according to general procedure III afforded *anti*-**32c** as a clear oil (0.283 g, 41 % yield) with a *anti*:*syn* ratio of 94:6 and 82 % *ee*; IR (film): $\tilde{\nu}$ = 2964 (s), 2166 (s), 1454 (s), 1249 (s), 842 (s), 760 (s); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.19–7.05 (m, 5H), 2.61–2.45 (m, 2H), 1.28 (d, *J* = 6.5 Hz, 3H), 0.92 (d, *J* = 6.5 Hz, 3H), 0.0 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 145.0, 128.0, 127.3, 126.1, 110.5, 85.6, 45.2, 34.0, 19.5, 19.2, 0.0; MS (EI): *m/z* (%): 230 (1) [M^+], 215 (3), 156 (9), 135 (2), 105 (100), 97 (5), 73 (14), 59 (3); elemental analysis (%) calcd for $C_{15}H_{22}Si$ (230.42): C 78.19, H 9.62; found: C 77.81, H 9.58.

(2*S*, 3*R*)-3-Methyl-2-phenyloctan-4-one (*anti*-32d): Reaction of *Z*-2-phenyl-2-butene (*Z*-**9**) and pentanoyl chloride according to general procedure III afforded *anti*-**32d** as a clear oil (0.269 g, 41 % yield) with a *anti*:*syn* ratio of 97:3 and 56 % *ee*; IR (film): $\tilde{\nu}$ = 3061 (w), 3028 (m), 2962 (s) , 2933 (s), 2874 (m), 1711 (s), 1454 (s), 1376 (m), 760 (m), 701 (s); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.32–7.15 (m, 5H), 2.92 (q, *J* = 6.7 Hz, 1H), 2.72 (q, *J* = 6.9 Hz, 1H), 2.58–2.36 (m, 2H), 1.68 (quint, *J* = 7.5 Hz, 2H), 1.34 (sext, *J* = 7.3 Hz, 2H), 1.17 (d, *J* = 6.7 Hz, 3H), 0.92 (t, *J* = 7.3 Hz, 3H), 0.82 (d, *J* = 6.9 Hz, 3H); ^{13}C NMR (75 MHz, CDCl$_3$): $\delta = 215.0$, 145.0, 128.6, 127.7, 127.5, 126.5, 53.2, 42.9, 42.7, 25.8, 22.5, 20.7, 18.4, 16.4, 14.0; MS (EI): *m/z* (%): 218 (8) [*M*$^+$], 161 (12), 133 (27), 117 (4), 105 (100), 91 (42), 85 (49), 77 (12), 57 (52), 41 (11), 29 (12); elemental analysis (%) calcd for $C_{15}H_{22}O$ (218.33): C 82.52, H 10.16; found: C 82.66, H 10.51.

1-[(1*R*, 2*R*)-1,2-Dimethyl-4-pentenyl]benzene (*syn*-32a): Reaction of *E*-2-phenyl-2-butene (*E*-**9**) and 3-bromo-prop-1-ene according to general procedure III afforded *syn*-**32a** as a clear oil (0.220 g, 42 % yield) with a *anti*:*syn* ratio of 6:94 and 46 % *ee*; IR (film) 3076 (m), 3063 (m), 2966 (s), 2928 (m), 1493 (m), 1452 (s), 908 (s), 701 (s); ^{1}H NMR (300 MHz, CDCl$_3$): $\delta = 7.40-7.10$ (m, 5H), 5.80–5.65 (m, 1H), 5.10–4.90 (m, 2H), 2.60 (quint, $J = 7.0$ Hz, 1H), 2.05 (quint, $J = 7.0$ Hz, 1H), 1.80–1.66 (m, 2H), 1.28 (d, $J = 7.0$ Hz, *trans*-dia), 1.22 (d, $J = 7.0$ Hz, 3H), 0.74 (d, $J = 7$ Hz, 3H) 0.76 (d, $J = 7$ Hz, *trans*-dia); ^{13}C NMR (75 MHz, CDCl$_3$): $\delta = 144.3$, 13.6, 126.3, 126.1, 126.0,125.7, 125.1, 123.9, 113.9, 44.7, 37.2, 36.6, 17.0, 15.3; MS (EI): *m/z* (%): 174 (1) [*M*$^+$], 132 (13), 117 (3), 105 (100), 91 (24), 77 (10), 6 (4), 55 (4), 41 (7), 39 (3); elemental analysis (%) calcd for $C_{13}H_{18}$ (174.28): C 89.59, H 10.41; found: C 89.93, H 10.33.

Ethyl 2-[(2*R*, 3*R*)-2-methyl-3-phenylbutyl]acrylate (*syn*-32b): Reaction of *E*-2-phenyl-2-butene (*E*-**9**) ethyl 2-(bromomethyl)acrylate according to general procedure III afforded *syn*-**32b** as a clear oil (0.259 g, 35 % yield) with a *anti*:*syn* ratio of 2:98 and 44 % *ee*; IR (film): $\tilde{\nu} = 3084$ (w), 3061 (w), 3027 (w), 2967 (m), 1717 (ss), 1453 (m), 1194 (m), 1175 (s), 1157 (s), 702 (s); ^{1}H NMR (300 MHz, CDCl$_3$): $\delta = 7.24-7.08$ (m, 5H), 6.07 (s, 1H), 5.35 (s, 1H), 4.10 (q, $J = 7.0$ Hz, 2H), 2.53 (quint, $J = 7.0$ Hz, 1H), 2.35–2.31 (m, 1H), 1.21 (t, $J = 7.0$ Hz, 3H), 1.17 (d, $J = 7.0$ Hz, 3H), 0.78 (d, $J = 6.0$ Hz, 3H), 0.61 (d, $J = 6$ Hz, *trans*-dia); ^{13}C NMR (75 MHz, CDCl$_3$): $\delta = 167.5$, 146.6, 140.2, 128.2, 127.8, 125.9, 125.8, 60.6, 45.1, 38.2, 38.0, 17.5, 15.8, 14.3; MS (EI): *m/z* (%): 246 (25) [*M*$^+$], 200 (7), 183 (11), 141 (57), 133 (27), 113 (56), 105 (100), 95 (34), 91 (57), 77 (35), 55 (24), 29 (25); elemental analysis (%) calcd for $C_{16}H_{22}O_2$ (246.34): C 78.01, H 9.00; found: C 77.86, H 9.25.

Trimethyl-[(3*S*, 4*R*)-3-methyl-4-phenyl-1-pentynyl]silane (*syn*-32c): Reaction of *E*-2-phenyl-2-butene (*E*-**9**) and 2-bromo-1-trimethylsilylacetylene according to general procedure III afforded *syn*-**32c** as a clear oil (0.242 g, 35% yield) with a *anti*:*syn* ratio of 11:89 and 46 % *ee*; IR (film): $\tilde{\nu} = 2962$ (s), 2166 (s), 1453 (s), 1250 (s), 842 (s), 758 (s); ^{1}H NMR (300 MHz, CDCl$_3$): $\delta = 7.19-7.07$ (m, 5H), 2.74–2.55 (m, 2H), 1.18 (d, $J = 7$ Hz, 3H), 0.93 (d, $J = 7$ Hz, 3H), 0.0 (s, 9H); ^{13}C NMR (75 MHz, CDCl$_3$): $\delta = 143.8$, 128.1, 127.7, 127.4, 162.2, 110.4, 86.0, 44.0, 33.7, 18.2, 18.1, 0.0; MS (EI): *m/z* (%): 230 (1) [*M*$^+$], 215 (4), 156 (13), 135 (2), 105 (100), 97 (4), 73 (20), 59 (3); elemental analysis (%) calcd for $C_{15}H_{22}Si$ (230.42): C 78.19, H 9.62; found: C 78.32, H 9.59.

(2*R*, 3*S*)-3-Methyl-2-phenyloctan-4-one (*syn*-32d): Reaction of *E*-2-phenyl-2-butene (*E*-**9**) and pentanoyl chloride according to general procedure III afforded *syn*-**32d** as a clear oil (0.249 g, 38 % yield) with a *anti*:*syn* ratio of 5:95 and 56 % *ee*; IR (film): $\tilde{\nu} = 3061$ (w), 3028 (m), 2962 (s) , 2933 (s), 2874 (m), 1711 (s), 1454 (s), 1376 (m), 760 (m), 701 (s); ^{1}H NMR (300 MHz, CDCl$_3$): $\delta = 7.28-7.10$ (m, 5H), 2.93 (quint, $J = 7.2$ Hz , 1H), 2.69 (quint, $J = 6.9$ Hz, 1H), 2.18–1.85 (m, 2H); ^{13}C NMR (75 MHz, CDCl$_3$): $\delta = 214.5$, 145.5, 128.4, 127.4, 126.3, 53.2, 42.3, 42.0, 25.3, 22.1, 18.0, 14.1, 13.7; MS (EI): *m/z* (%): 218 (21) [*M*$^+$], 161 (13), 133 (21), 122 (18), 114 (21), 105 (100), 91 (54), 85 (50), 72 (15), 57 (45), 41 (16), 29 (24); HRMS calcd. for $C_{15}H_{22}O$: 218.1671, found: 218.1670.

General procedure IV: Pd^0-catalyzed cross-couplings of enantiomerically enriched zinc reagents 27 with *E*-1-iodohex-1-ene: A Schlenk flask was charged with IpcBH$_2$ (**23**, 2.5 mL, 2.5 mmol, 1.0 M) in diethyl ether, cooled to −35 °C and the olefin (2.5 mmol, 1 equiv) in diethyl ether (1 mL) was added. The reaction mixture was stirred at −35 °C for 48 h and then the solvent was carefully evaporated under reduced pressure. Et$_2$BH (2.1 mL of a 7.3 M solution in Me$_2$S, 15 mmol, 6 equiv) was added and the resulting solution was stirred at 50 °C for 16 h. Excess volatiles were evaporated under reduced pressure (room temperature, 2 h). *i*Pr$_2$Zn (2.5 mL of a 3 M solution in Et$_2$O, 7.5 mmol, 3 equiv) was added over a 10 min period and the reaction mixture was stirred at room temperature for 5 h. The volatiles were evaporated under reduced pressure (0 °C to 25 °C, 30 min) and the resulting gray residue was dissolved in THF (5 mL). The mixture was filtered under inert gas and cooled to 0 °C. A previously prepared mixture of [Pd(dba)$_2$] (29 mg, 2 mol%) and P(*o*-tolyl)$_3$ (30 mg, 4 mol%) and *E*-1-iodohex-1-ene (1.575 g, 7.5 mmol, 3 equiv) in THF (3 mL) was added. The reaction mixture was allowed to warm slowly to 25 °C. After 12 h the reaction mixture was quenched with aqueous sat. NH$_4$Cl and extracted with Et$_2$O. After drying (MgSO$_4$) and evaporating the solvents, the crude residue obtained was purified by flash chromatography (hexanes). The *syn*:*anti* ratio and enantioselectivity were determined by capillary GC analysis on a chiral β-cyclodextrin column (CP-Chirasil-Dex CB, Chrompack).

***trans*-(1*S*, 2*S*)-2-((*E*)-1-Hexenyl)-1-methyl-2,3-dihydro-*1H*-indene (33a)**: Reaction of 1-methyl-3*H*-ind-1-ene (**5c**) and *trans*-1-iodohex-1-ene according to general procedure IV afforded **33a** as a clear oil (0.187 g, 35 % yield) with a *trans*:*cis* ratio of 99:1 and 56 % *ee*; IR (film): $\tilde{\nu} = 3069$ (w), 3021 (m), 2957 (s) , 2928 (s), 2872 (s), 1476 (s), 1458 (s), 760 (s), 743 (s); ^{1}H NMR (300 MHz, CDCl$_3$): $\delta = 7.23-7.10$ (m, 4H), 5.59–5.46 (m, 2H), 3.02–2.68 (m, 2H), 2.84 (quint, $J = 6.9$ Hz, 1H), 2.50–2.43 (m, 1H), 2.08–2.00 (m, 2H), 1.42–1.28 (m, 4H), 1.28 (d, $J = 6.9$ Hz), 0.91 (t, $J = 6.8$ Hz); ^{13}C NMR (75 MHz, CDCl$_3$): $\delta = 148.0$, 142.9, 132.7, 131.4, 126.3, 124.2, 123.8, 123.1, 54.5, 45.3, 38.9, 32.4, 31.9, 22.3, 17.0, 14.1; MS (EI): *m/z* (%): 214 (20) [*M*$^+$], 199 (4), 157 (22), 143 (58), 130 (100), 117 (53), 105 (5), 91 (20), 77 (5), 55 (15), 41 (18); HRMS calcd. for $C_{16}H_{22}$: 214.1721, found: 214.1717.

***trans*-(1*S*, 2*S*)-2-((*E*)-1-Hexenyl)-1-methyl-1,2,3,4-tetrahydro-naphthalene (33b)**: Reaction of 1-methyl-3*H*-ind-1-ene (**5c**) *trans*-1-iodohex-1-ene according to general procedure IV afforded **33b** as a clear oil (0.234 g, 41 % yield) with a *trans*:*cis* ratio of 99:1 and 52 % *ee*; IR (film): $\tilde{\nu} = 3061$ (m), 3017 (m), 2959 (s), 2928 (s), 2872 (m), 1491 (m), 970 (m), 908 (s), 758 (m), 734 (s); ^{1}H NMR (300 MHz, CDCl$_3$): $\delta = 7.17-6.96$ (m, 4H), 5.45–5.27 (m, 2H), 2.70 (t, $J = 6.5$ Hz, 2H), 2.56 (quint, $J = 7.0$ Hz, 1H), 2.08–1.78 (m, 4H), 1.58–1.46 (m, 1), 1.36–1.24 (m, 4H), 1.22 (d, $J = 7.0$ Hz), 0,82 (t, $J = 7.0$ Hz); ^{13}C NMR (75 MHz, CDCl$_3$): $\delta = 141.4$, 136.7, 134.5, 130.6, 128.8, 128.2, 125.8, 125.4, 45.4, 38.0, 32.4, 31.9, 28.7, 28.4, 22.3, 21.4, 14.0; MS (EI): *m/z* (%): 228 (26) [*M*$^+$], 157 (18), 143 (85), 129 (55), 118 (100), 103 (64), 91 (18), 55 (20), 41 (16), 28 (11); HRMS calcd. for $C_{17}H_{24}$: 228.1878, found: 228.1871.

***trans*-1-((1*S*, 2*S*)-2-((*E*)-1-Hexenyl)cyclopentyl-methyl)-2-methoxybenzene (33c)**: Reaction of 1-methyl-3*H*-ind-1-ene (**5c**) and *trans*-1-iodohex-1-ene according to general procedure IV afforded **33c** as a clear oil (0.258 g, 40 % yield) with a *trans*:*cis* ratio of 98:2 and 83 % *ee*; IR (film): $\tilde{\nu} = 3065$ (w), 3027 (w), 2955 (vs), 2932 (vs), 2872 (s), 1493 (s), 1242 (vs), 908 (s), 753 (m), 735 (vs); ^{1}H NMR (300 MHz, CDCl$_3$): $\delta = 7.15-6.80$ (m, 4H), 5.40–5.20 (m, 2H), 3.80 (s, 3H), 3.10 (q, $J = 9.7$ Hz, 1H), 2.67–2.52 (m, 1H), 2.20–1.48 (m, 8H), 1.40–1.10 (m, 4H), 0.85 (t, $J = 6.7$ Hz); ^{13}C NMR (75 MHz, CDCl$_3$): $\delta = 156.7$, 133.1, 133.0, 129.3, 127.3, 126.3, 120.3, 110.3, 55.2, 49.2, 45.2, 33.3, 33.0, 32.8, 32.0, 31.5, 23.7, 21.8, 13.7; MS (EI): *m/z* (%): 258 (54) [*M*$^+$], 201 (18), 187 (39), 174 (58), 160 (22), 159 (34), 147 (85), 121 (100), 91 (82), 67 (43), 41 (50), 28 (22); HRMS calcd. for $C_{18}H_{26}O$: 258.1984, found: 258.1980.

General procedure V: Pd^0-catalyzed acylations of enantiomerically enriched zinc reagents 27 with acid chlorides: A Schlenk flask was charged with IpcBH$_2$ (**23**, 3.1 mL, 2.5 mmol, 0.8 M) in diethyl ether, cooled to −35 °C and the olefin (2.5 mmol, 1 equiv) in diethyl ether (1 mL) was added. The reaction mixture was stirred at −35 °C for 48 h and then the solvent was carefully evaporated under reduced pressure. Et$_2$BH (2.1 mL of a 7.3 M solution in Me$_2$S, 15 mmol, 6 equiv) was added and the resulting solution was stirred at 50 °C for 16 h. Excess volatiles were evaporated under reduced pressure (room temperature, 2 h). *i*Pr$_2$Zn (2.5 mL of a 3 M solution in Et$_2$O, 7.5 mmol, 3 equiv) was added over a 10 min period and the reaction mixture was stirred at room temperature for 5 h. The volatiles were evaporated under reduced pressure (0 °C to 25 °C, 30 min) and the resulting gray residue was dissolved in dioxane (5 mL). The mixture was filtered under inert gas and cooled to 0 °C. A previously prepared mixture of [Pd(dba)$_2$] (29 mg, 2 mol%) and P(*o*-tolyl)$_3$ (30 mg, 4 mol%) and the acid chloride (7.5 mmol, 3 equiv) in dioxane (3 mL) was added . The reaction mixture was allowed to warm slowly to 25 °C. After 12 h the reaction mixture was quenched with aqueous 30 % NH$_3$ and stirred for 15 min. Then aqueous 2 M HCl was added and the mixture was extracted with Et$_2$O. After drying (MgSO$_4$) and evaporating the solvents, the crude residue obtained was purified by chromatography (hexanes:Et$_2$O). The *syn*:*anti* ratio and enantioselectivity were determined by capillary GC analysis on a chiral β-cyclodextrin column (CP-Chirasil-Dex CB, Chrompack).

***trans*-1-[(1*S*, 2*R*)-1′-Methyl-2′,3′-dihydro-*1H*-2′-indenyl]-1-pentanone (33d)**: Reaction of 1-methyl-3*H*-ind-1-ene (**5c**) and pentanoyl chloride according to general procedure V afforded **33d** as a clear oil (0.211 g, 39% yield) with a *trans*:*cis* ratio of 92:8 and 64 % *ee*; IR (film): $\tilde{\nu} = 3070$ (w), 3022 (w), 2959 (s), 2931 (s), 2871 (s), 1711 (s), 1477 (m), 1460 (m), 1375 (m), 745 (s); ^{1}H NMR (300 MHz, CDCl$_3$): $\delta = 7.23-7.05$ (m, 4H), 3.45 (quint, $J = 7.0$ Hz, 1H), 3.18–2.86 (m, 3H), 2.50–2.42 (td, $J = 7.0$ Hz, 2.0 Hz, 2H), 1.54 (quint, $J = 7.0$ Hz, 2H), 1.34–1.18 (m, 2H), 1.27 (d, $J = 7.0$ Hz, 3H), 0.85 (t, $J = 7.0$ Hz); ^{13}C NMR (75 MHz, CDCl$_3$): $\delta = 211.5$, 146.4, 140.6, 126.6, 126.5,124.0, 123.4, 60.3, 55.6, 41.9, 41.5, 35.0, 25.7, 22.3, 19.3, 13.9; MS (EI): m/z (%): 216 (15) [M^+], 201 (23), 159 (100), 130 (65), 115 (18), 91 (27), 85 (13), 57 (25), 43 (4), 29 (12); HRMS calcd. for $C_{15}H_{20}O$: 216.1514, found: 216.1519.

***trans*-1-[(1*S*, 2*R*)-1-Methyl-1,2,3,4-tetrahydronaphthanyl]-1-pentanone (33e)**: Reaction of 1-methyl-3,4-dihydro-1-naphthalene (**5d**) and pentanoyl chloride according to general procedure V afforded **33e** as a clear oil (0.247 g, 43% yield) with a *trans*:*cis* ratio of 92:8 and 60 % *ee*; IR (film): $\tilde{\nu} = 3061$ (w), 3018 (w), 2958 (s), 2932 (s), 2872 (m), 1710 (s), 1491 (m), 1459 (m), 1378 (m), 758 (m); ^{1}H NMR (300 MHz, CDCl$_3$): $\delta = 7.21-6.96$ (m, 4H), 3.22 (quint, $J = 7.0$ Hz, 1H), 2.78–2.64 (m, 2H), 2.58–2.32 (m, 3H), 2.00–1.62 (m, 2H), 2.53 (quint, $J = 7.5$ Hz, 2H), 1.23 (sext, $J = 7.3$ Hz,), 1.17 (d, $J = 7.0$ Hz, 3H), 0.82 (t, $J = 7.3$ Hz); ^{13}C NMR (75 MHz, CDCl$_3$): $\delta =$ 213.4, 140.5, 135.7, 128.6, 127.5, 126.1, 125.5, 55.2, 41.7, 33.5, 29.2, 25.8, 25.4, 22.4, 21.3, 13.9; MS (EI): m/z (%): 230 (29) [M^+], 215 (44), 173 (100), 145 (85), 130 (66), 91 (28), 85 (75), 57 (94), 41 (63), 28 (91); elemental analysis (%) calcd for $C_{16}H_{22}O$ (230.17): C 83.43, H 9.63; found: C 83.51, H 9.63.

***trans*-1-[(1*R*, 2*S*)-2-(2-Methoxybenzyl)cyclopentyl]-1-pentanone (33f)**: Reaction of *o*-methoxy-phenyl-cyclopent-1-ene (**5f**) and pentanoyl chloride according to general procedure V afforded **33f** as a clear oil (0.377 g, 58% yield) with a *trans*:*cis* ratio of 99:1 and 81 % *ee*; IR (film): $\tilde{\nu} = 2956$ (s), 2870 (m), 1708 (s), 1492 (s), 1463 (s), 1243 (s), 1030 (m), 753 (s); ^{1}H NMR (300 MHz, CDCl$_3$): $\delta = 7.12-7.06$ (m, 4H), 3.70 (s, 3H), 3.53–3.44 (q, $J =$ 8.0 Hz, 1H), 3.04–2.95 (q, $J = 8.0$ Hz, 1H), 2.22–2.16 (td, $J = 7.5$ Hz, 3.5 Hz, 2H), 2.04–1.64 (m, 6H), 1.42–1.33 (quint, $J = 7.5$ Hz, 2H), 1.19–1.05 (sext, $J = 7.5$ Hz, 2H), 0.71 (t, $J = 7.5$ Hz); ^{13}C NMR (75 MHz, CDCl$_3$): $\delta = 231.3$, 157.3, 132.8, 127.6, 1127.2, 120.7, 110.6, 63.4, 57.6, 55.2, 43.2, 42.1, 33.8, 30.0, 25.7, 22.4, 13.9; MS (EI): m/z (%): 260 (55) [M^+], 203 (67), 175 (72), 148 (57), 121 (100), 108 (83), 91 (52), 85 (59), 57 (68), 41 (67), 29 (59); HRMS calcd. for $C_{17}H_{24}O_2$: 260.1776, found: 260.1774.

***trans* (2*S*, 3*R*)-3-Methyl-2-phenyloctan-4-one (33g)**: Reaction of *Z*-2-phenyl-2-butene (*Z*-**9**) and pentanoyl chloride according to general procedure V afforded **33g** as a clear oil (0.245 g, 45% yield) with a *syn*:*anti* ratio of 10:90 and 88 % *ee*; IR (film): $\tilde{\nu} = 3061$ (w), 3028 (m), 2962 (s), 2933 (s), 2874 (m), 1711 (s), 1454 (s), 1376 (m), 760 (m), 701 (s); ^{1}H NMR (300 MHz, CDCl$_3$): $\delta = 7.24-7.08$ (m, 5H), 2.85 (qd, $J = 10.0$ Hz, 6.5 Hz, 1H), 2.64 (qd, $J = 10.0$ Hz, 6.9 Hz, 1H), 2.50–2.29 (m, 2H), 1.50 (quint, $J =$ 7.2 Hz, 2H), 1.25 (sext, $J = 7.2$ Hz, 2H), 1.09 (d, $J = 6.5$ Hz, 3H), 0.85 (t, $J =$ 7.2 Hz, 3H), 0.76 (t, $J = 6.9$ Hz, 3H); ^{13}C NMR (75 MHz, CDCl$_3$): $\delta = 214.6$, 144.7, 135.7, 128.2, 128.1,127.3, 126.1, 52.9, 42.6, 42.1, 25.4, 22.1, 20.4, 16.0, 13.6; MS (EI): m/z (%): 218 (16) [M^+], 161 (14), 133 (24), 114 (18), 105 (100), 91 (47), 85 (62), 72 (12), 57 (41), 41 (11), 29 (14); HRMS calcd. for $C_{15}H_{22}O$: 218.1671, found: 218.1673.

***trans*-(1*S*, 2*R*)-1-Methyl-2,3-dihydro-*1H*-2-indenyl-phenylketone (33h)**: Reaction of 1-methyl-3*H*-ind-1-ene (**5c**) and benzoyl chloride according to general procedure V afforded **33h** as a clear oil (0.242 g, 41% yield) with a *trans*:*cis* ratio of 95:5 and 60 % *ee*; IR (film): $\tilde{\nu} = 3067$ (w), 3023 (w), 2959 (w), 1680 (s), 1448 (m), 1252 (m), 1217 (m), 758 (m), 745 (m); ^{1}H NMR (300 MHz, CDCl$_3$): $\delta = 8.10-7.94$ (m, 2H), 7.62–7.34 (m, 7H), 3.89 (q, $J =$ 8.5 Hz, 1H), 3.79 (q, $J = 6.7$ Hz, 1H), 1.37 (d, $J = 6.7$ Hz, 3H); ^{13}C NMR (75 MHz, CDCl$_3$): $\delta = 201.2$, 146.7, 140.8, 137.1, 133.0,128.5, 126.8, 123.3, 55.6, 42.2, 36.7, 19.3; MS (EI): m/z (%): 236 (33) [M^+], 221 (45), 130 (65), 107 (43), 105 (92), 77 (100), 51 (17), 28 (4); elemental analysis (%) calcd for $C_{17}H_{16}O$: C 86.41, H 6.82; found: C 86.33, H 6.68.

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