Preparation of Functionalized Dialkylzincs via a Boron−Zinc Exchange. Reactivity and Catalytic Asymmetric Addition to Aldehydes

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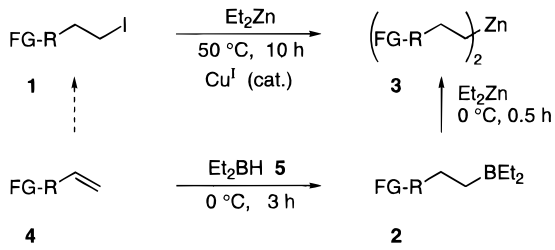
The hydroboration of olefins with Et_2BH provides diethyl(alkyl)boranes **2** which readily undergo a boron−zinc exchange with Et_2Zn providing a range of polyfunctional primary, secondary, and benzylic diorganozincs. The resulting diorganozincs **3** have been reacted with various electrophiles (allylic halides, acid chlorides, alkylidenemalonates, ethyl propiolate, nitroolefins) in the presence of CuCN·2LiCl with excellent yields. With secondary dialkylzincs prepared from diastereomerically pure diethyl(alkyl)boranes, the boron−zinc exchange occurs with loss of stereochemistry. The asymmetric addition of **3** to aldehydes in the presence of the chiral catalyst **55** furnishes optically active polyfunctional secondary alcohols (50 to over 96% ee).

Introduction

Organozinc halides (RZnX) are useful synthetic intermediates, and their chemistry has been actively investigated in the recent years.[1] They tolerate a broad range of functionalities and react in the presence of a copper salt like CuCN·2LiCl[2] with various electrophiles in excellent yields. They are readily prepared by the direct insertion of zinc dust into primary or secondary alkyl iodides.[1,3] For the less reactive alkyl, alkenyl, or aryl *bromides*, the insertion is best performed using Rieke-zinc.[4] Diorganozincs (R_2Zn) compared to organozinc halides (RZnX) are less readily available. However, they display a higher reactivity toward many electrophiles and are well suited for applications in asymmetric synthesis.[5] We have previously reported that functionalized diorganozincs can be prepared by an iodine−zinc exchange reaction.[1,5a] This method requires heating of the primary alkyl iodide **1** with Et_2Zn at 50 °C for several hours.[6] In strong contrast, we found that primary diethyl(alkyl)-boranes **2** react within minutes at 0 °C with Et_2Zn providing polyfunctional dialkylzincs **3** in over 90% yield (Scheme 1).[7] The organoboranes **2** are readily obtained by hydroboration of olefins of type **4** with Et_2BH (**5**).[8]

The first literature report of a boron−zinc exchange was the reaction of dimethylzinc with triethylborane to produce diethylzinc.[9] The reaction has also been used successfully for the preparation of benzylic and allylic diorganozincs.[10] Alkenyl zinc reagents prepared by this method have been used for the enantioselective preparation of allylic alcohols.[11] An elegant asymmetric synthesis of (−)-muscone has been reported using an intramolecular version of this reaction.[12] Our synthetic approach allows the preparation of functionalized dialkylzincs starting from olefins avoiding the use of expensive alkyl iodides as intermediates. Herein we wish to report the scope and limitations of the boron−zinc exchange reaction using diethyl(alkyl)boranes and Et_2Zn and demonstrate the utility of these reagents for the catalytic asymmetric addition to aldehydes.

Scheme 1



Results and Discussion

The hydroboration of terminal olefins is conveniently performed with Et_2BH (**5**), a hydroborating agent which is readily prepared by mixing BH_3·Me_2S and Et_3B in the ratio 1:2.[13] Diethylborane (**5**) containing ca. 0.3 equiv of Me_2S is stable for several months at 4 °C without decomposition. The hydroboration of olefins **4** with Et_2-

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(4) (a) Rieke, R. D. *Science* **1989**, *246*, 1260. (b) Zhu, L.; Wehmeyer, R. M.; Rieke, R. D. *J. Org. Chem.* **1991**, *56*, 1445.

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(12) (a) Oppolzer, W.; Radinov, R. N. *J. Am. Chem. Soc.* **1993**, *115*, 1593. (b) Oppolzer, W.; Radinov, R. N.; de Brabander, J. *Tetrahedron Lett.* **1995**, *36*, 2607.

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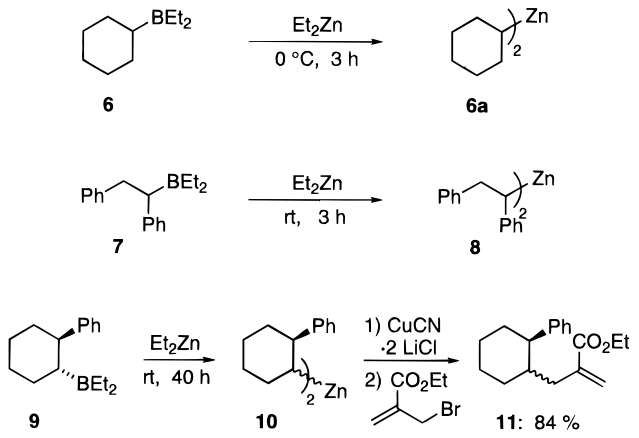
Scheme 2

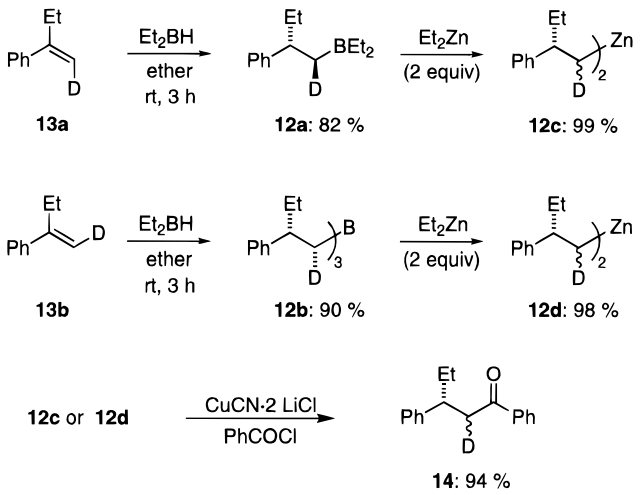


BH (**5**) displays regioselectivity comparable to disiamylborane or thexylborane[14] and is complete within a few minutes at rt affording diethyl(alkyl)boranes **2** in 80−95% yield (Scheme 1). The reaction of the organoboranes **2** with Et_2Zn (2 equiv) at 0 °C proceeds well in hexane, ether, dibutyl ether, or in the absence of a solvent. It is complete within 0.5 h with all primary diethyl(alkyl)-boranes **2** but requires longer reaction times with secondary diethyl(alkyl)boranes. Et_2Zn is especially well suited for performing the boron−zinc exchange because of the high reactivity and high energy of its carbon−zinc bond. The reaction of diethyl(octyl)borane with Et_2Zn (2 equiv) produces at 0 °C within 3 min ca. 80% of ethyl(octyl)zinc as shown by iodolysis experiments. By pumping off the formed Et_3B the equilibrium is further shifted to the right affording the desired dioctylzinc in high yield (>95%).

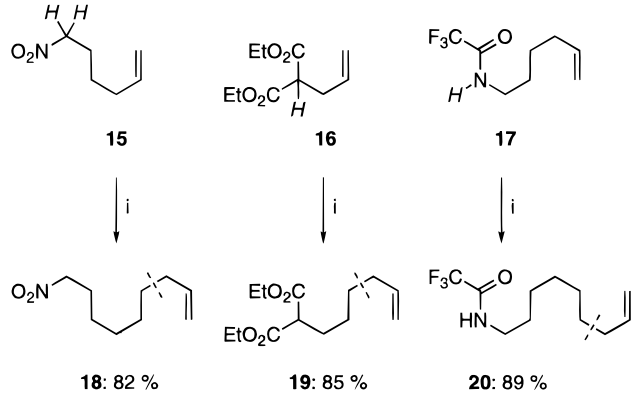
In the case of cyclohexyldiethylborane (**6**), the boron−zinc exchange is complete after 3 h at 0 °C affording dicyclohexylzinc (**6a**) in over 90% yield. Also diethyl(1,2-diphenylethyl)borane (**7**) is quantitatively converted to the corresponding zinc reagent **8** within 3 h at rt. In contrast secondary diethyl(alkyl)boranes bearing bulky substituents in the α-position like the organoborane **9** react at slower rates with Et_2Zn furnishing the corresponding dialkylzinc only after 40 h reaction time at rt. This reaction requires a large excess of Et_2Zn (6 equiv; Scheme 2).

The resulting zinc reagent **10** is obtained as a 3:1 mixture of diastereoisomers as indicated by the stereochemistry of the allylated product **11**. In order to determine if the loss of stereochemistry is due to the drastic reaction conditions required for the preparation of **10** or is an intrinsic characteristic of the boron−zinc exchange, we have submitted the primary boranes **12a** and **12b** to the reaction with Et_2Zn (Scheme 3). The diethyl(alkyl)boranes **12a** and **12b** were prepared by the diastereoselective hydroboration of the deuterated styrenes **13a** and **13b**. The treatment of **12a** and **12b** with Et_2Zn provides the zinc reagents **12c** and **12d** (0 °C, 0.5 h) which ^1H and ^2D NMR spectra clearly indicate the formation of a 1:1 mixture of diastereoisomeric organometallics. This result was confirmed by the trapping of the zinc reagents with benzoyl chloride after transmetalation with CuCN·2LiCl providing the ketone **14** in 94% yield. The incorporation of deuterium was close to 100%, but a 1:1 mixture of diastereoisomers was obtained as

Scheme 3



Scheme 4



Reagents and conditions: (i) Et_2BH, ether; then Et_2Zn, 0 °C, 10 min; then allyl bromide (excess), CuCN cat.

indicated by NMR spectroscopy. Thus, under the reaction conditions used, the boron−zinc exchange reaction occurs with *loss of stereochemistry*.[15]

The reaction tolerates a range of functional groups like an ester, nitrile, boronic ester, halide (Cl, Br, or I), acrylate, phthalimide and functionalities bearing a relatively acidic proton like a nitroalkane, alkylmalonate, or trifluoroacetamide. Thus, the olefins **15**−**17** each bearing an acidic proton[16] undergo, after hydroboration, a smooth boron−zinc exchange reaction. In the presence of a catalytic amount of CuCN and an excess of allylating agent, the intermediate zinc reagents are allylated leading to the products **18**−**20** in high overall yields, showing that diorganozincs bearing an acidic proton at the α-position of a malonate or nitro group or bearing a trifluoroacetamide function are viable intermediates (Scheme 4).

The boron−zinc exchange is considerably faster than the iodine−zinc exchange reaction. Thus the diethyl(iodoalkyl)borane **2a** prepared from 6-iodo-1-hexene can either undergo an iodine−zinc or a boron−zinc exchange. Only the latter exchange reaction provides the zinc reagent **3a**. The expected products **21**−**23** are obtained after transmetalation with CuCN·2LiCl and respective

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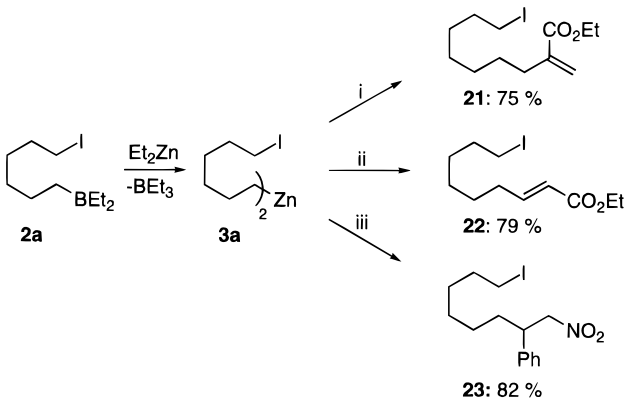
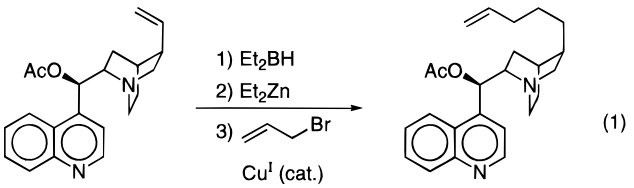
Scheme 5



Reagents and conditions: (i) CuCN·2 LiCl (1 equiv), then ethyl α-(bromomethyl)acrylate (0.8 equiv), 0 °C, 0.5 h; (ii) CuCN·2 LiCl (1 equiv), ethyl propiolate (0.9 equiv), -60 °C, 3 h; (iii) CuCN·2 LiCl (1 equiv), nitrostyrene (0.9 equiv), -30 °C, 24 h.

reaction with ethyl α-(bromomethyl)acrylate,[17] ethyl propiolate, and nitrostyrene[18] (Scheme 5).

Polyfunctional dialkylzincs derived from alkaloids can also be prepared and give access to various derivatives of biologically active molecules having therefore a potential pharmaceutical interest. The hydroboration of (−)-cinchonidine acetate (**24**) with diethylborane (**5**) furnishes in quantitative yield the corresponding organoborane which smoothly undergoes a boron−zinc exchange by treatment with Et_2Zn in CH_2Cl_2 producing after evaporation of the solvent and the excess of Et_2Zn the expected diorganozinc reagent as an orange foam. It was quantitatively allylated with an excess of allyl bromide in the presence of CuCN·2LiCl (10 mol %) leading to the product **25** (eq 1).



(1)

24 **25**: 95 %

Besides allylic halides (entries 1, 11 of Table 1), a variety of electrophiles like an alkylidenemalonate (entries 4, 8, 13), acid chlorides (entries 5, 6, 9, 10), 3-iodo-2-cyclohexenone (entries 2, 3), and nitrostyrene (entries 7, 12) react with dialkylzincs prepared via the boron−zinc exchange and subsequent transmetalation with CuCN·2LiCl providing the polyfunctional products **26**−**38**.[1] A remarkable chemoselectivity is observed in these reactions and many polyfunctional molecules become available with this reaction sequence. Especially impressive is the behavior of the unsaturated organoborane **39** obtained by the selective hydroboration of the dienic ester **40**. After a boron−zinc exchange, the diorganozinc **41** bearing a sensitive acrylate functionality is obtained (Scheme 6).

After transmetalation with CuCN·2LiCl, a copper reagent is formed. It shows no tendency to polymerize under our reaction conditions. After the addition of electrophiles like ethyl α-(bromomethyl)acrylate or diethyl benzylidenemalonate the desired coupling products **42** and **43** are obtained respectively in 77% and 71% overall yield. A chiral olefin like (−)-β-pinene (**44**) is readily converted into chiral dimyrtanylzinc (**45**) via the intermediate diethyl(myrtanyl)borane (**46**). In the presence of CuCN·2LiCl, it reacts with benzoyl chloride or ethyl α-(bromomethyl)acrylate furnishing the chiral adducts **47** and **48** in 85 and 82% overall yield (Scheme 7).

Besides primary dialkylzincs, secondary alkyl and benzylic diorganozincs can be prepared and reacted with electrophiles in the presence of a copper(I) catalyst. Steric hindrance slows down the boron−zinc exchange reaction and limits the application of this reaction to sterically noncrowded secondary alkylboranes. However, a number of secondary dialkylzincs have been prepared and reacted with electrophiles to provide products **49**−**54** (Table 2). As mentioned above, secondary diorganozincs are prepared from the corresponding boranes with loss of stereochemistry, resulting in the formation of diastereomeric mixtures of products after transmetalation and quenching with an electrophile.

The boron−zinc exchange provides an efficient entry to diorganozincs. The enantioselective addition of these organometallics to aldehydes will be examined next. The addition of diethylzinc to aldehydes in the presence of a chiral catalyst has been intensively investigated over the last 10 years.[19] We have already shown that higher dialkylzincs, as well as functionalized diorganozincs prepared via an iodine−zinc exchange,[5] can be added with high enantioselectivity to aldehydes in the presence of (1*R*,2*R*)-1,2-bis(trifluoromethanesulfonamido)cyclohexane[20] (**55**) as catalyst and Ti(O*i*-Pr)$_4$ as cocatalyst.[21] The use of olefins as starting materials for asymmetric catalysis is of special interest since it constitutes a high value adding process and has considerable synthetic potential. Olefins are usually cheap and environmentally friendly substrates, so these transformations are also of industrial relevance (Scheme 8).

Thus, a one-pot procedure allowing the conversion of olefins **4** to chiral polyfunctional alcohols **56** would be of great interest. Herein, we report our results demonstrating that this approach provides a predictable method for the asymmetric synthesis of a variety of optically active secondary alcohols.[22] A range of dialkylzincs prepared via the boron−zinc exchange reaction can be added to various aliphatic, unsaturated, or aromatic aldehydes using **55** (8 mol %) as catalyst and Ti(O*i*-Pr)$_4$ (2 equiv) as cocatalyst.[22] Various dialkylzincs have been used directly after pumping off the excess diethylzinc and triethylborane formed during their preparation. The zinc reagent was added to a solution of the preformed catalyst

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(20) (a) Galsbol, F.; Steenbol, P.; Sondergaard-Sorensen, B. *Acta Chem. Scand.* **1972**, *26*, 3605. (b) Larrow, J. F.; Jacobsen, E. N.; Gao, Y.; Hong, Y.; Nie, X.; Zepp, C. M. *J. Org. Chem.* **1994**, *59*, 1939.
(21) (a) Takahashi, H.; Kawakita, T.; Ohno, M.; Yoshioka, M.; Kobayashi, S. *Tetrahedron* **1992**, *48*, 5691. For other titanium-mediated asymmetric additions to aldehydes, see: (b) Schmidt, B.; Seebach, D. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 99. (c) Seebach, D.; Behrendt, L.; Felix, D. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 1008. (d) Schmidt, B.; Seebach, D. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 1321. (e) v. d. Bussche-Hünnefeld, J. L.; Seebach, D. *Tetrahedron* **1992**, *48*, 5719. (f) Seebach, D.; Plattner, D. A.; Beck, A. K.; Wang, Y. M.; Hunziker, D.; Petter, W. *Helv. Chim. Acta* **1992**, *75*, 2171. (g) Seebach, D.; Beck, A. K.; Schmidt, B.; Wang, Y. M. *Tetrahedron* **1994**, *50*, 4363. (h) Weber, B.; Seebach, D. *Tetrahedron* **1994**, *50*, 7473.
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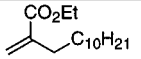
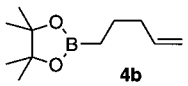
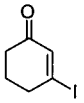
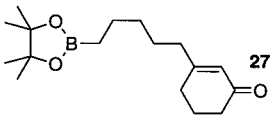
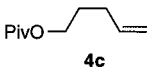
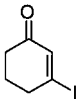
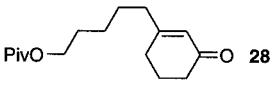
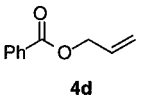
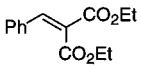
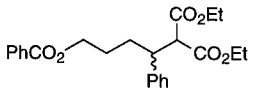
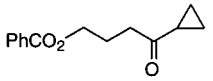
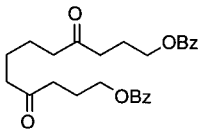
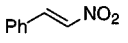
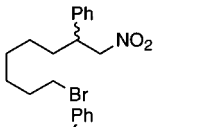
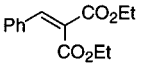
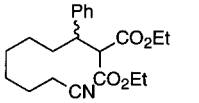
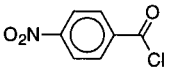
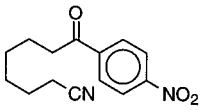
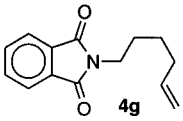
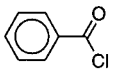
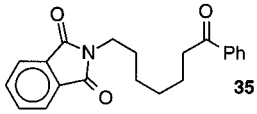
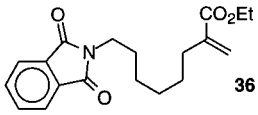
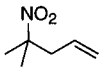
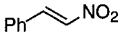
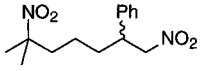
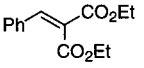
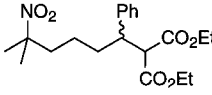
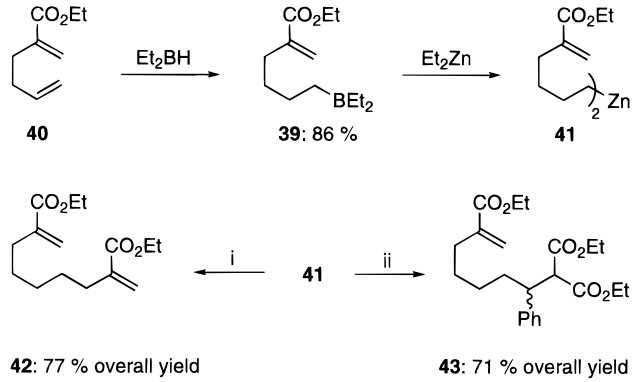
Table 1. Polyfunctional Products 26–38 Obtained from Olefins 4a–h by Successive Hydroboration, Boron–Zinc Exchange, Transmetalation with CuCN·2LiCl and Reaction with an Electrophile

	olefin **4**	yield (%)[a]	electrophile	product		yield (%)[b]
1	 **4a**	99[c]			**26**	82 (80)
2	 **4b**	95			**27**	85 (81)
3	 **4c**	81			**28**	82 (66)
4	 **4d**	81			**29**	87 (71)
5	**4d**	81			**30**	80 (64)
6	**4d**	81			**31**	65 (53)
7	 **4e**	86			**32**	84 (70)
8	 **4f**	91			**33**	81 (74)
9	**4f**	91			**34**	76 (69)
10	 **4g**	85			**35**	80 (68)
11	**4g**	85			**36**	95 (81)
12	 **4h**	80			**37**	74 (59)
13	**4h**	80			**38**	77 (62)

[a] Yield of the intermediate organoborane **2** obtained by hydroboration with Et_2BH (>95 % pure by ^1H and ^{13}C NMR analysis).
[b] Isolated yield of analytically pure product based on the electrophile. The yield in parentheses corresponds to the overall yield starting from the olefin **4**.
[c] The triorganoborane $B(C_{10}H_{21})_3$ was prepared using BH_3·SMe_2.

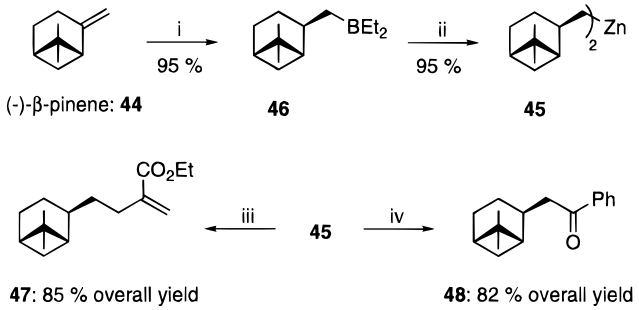
consisting of **55** and $Ti(O\textit{i}\text{-}Pr)_4$ at −60 °C followed by the addition of the aldehyde at −20 °C. The reaction mixture was generally stirred for 5–10 h at this temperature, providing the chiral alcohols **56** in 11–88% yield and with 50 to over 96% ee. Remarkably, a range of functionalities are tolerated in this reaction (Table 3). The addition of long chain dialkylzincs proceeds well although poor solubility of the dialkylzinc in toluene leads in some cases to moderate yields and enantioselectivities (entries 1–5 of Table 3). Better results are obtained by performing these reactions in ether (entry 4). The addition of dimyrtanylzinc (**45**) to aldehydes is complicated by a β-hydride transfer resulting in the reduction of the aldehyde and low yields (17%) of the addition product (**56f**). Nevertheless, the ligand-controlled diastereoselectivity of the addition is excellent (>96% de; entry 6). The more reactive *secondary* dialkylzincs like $(c\text{-}Hex)_2Zn$ (**6a**) furnish alcohols with lower enantioselectivity (entry

Scheme 6



Reagents and conditions: (i) CuCN·2 LiCl (1 equiv), ethyl-α (bromomethyl)acrylate, 0 °C, 0.5 h; (ii) CuCN·2 LiCl (1 equiv), diethyl benzylidene malonate, rt, 12 h.

Scheme 7

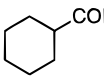
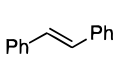
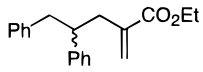
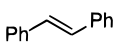
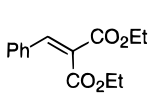
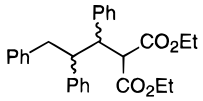
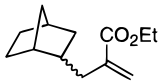
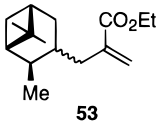
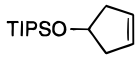
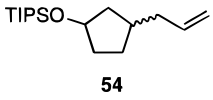


Reagents and conditions: (i) Et_2BH; (ii) Et_2Zn; (iii) CuCN·2 LiCl (1 equiv), ethyl α-(bromomethyl)acrylate (0.9 equiv), 0 °C, 0.5 h; (iv) CuCN·2 LiCl (1 equiv), PhCOCl (0.9 equiv), -30 °C, 12 h.

7). An alcohol function protected as the corresponding pivalic ester can be present in dialkylzincs without significant loss of enantiomeric excess, even if the pivaloxy group is relatively close (γ-position) to the carbon−zinc bond (entries 8−12). Interestingly, an ethyl acrylate function does not disturb the course of the asymmetric addition and highly functionalized molecules like **56m**−**o** can be prepared in 80−95% ee and satisfactory yields (69−72%). The use of silyl protecting groups is more problematic and whereas a TMS-group is not suited, the more bulky TIPS-group[23] gives better results and a TBDMS protected alcohol separated by four carbon atoms from the zinc adds highly selectively to unsaturated aldehydes (entries 16−18). Iodine or bromine substituted dialkylzincs add smoothly to aldehydes and afford the corresponding alcohols in good enantiomeric excess (60−90% ee; entries 19−23). Although, most diorganozincs can be handled without special precautions, it is recommended to use a protecting shield and a reaction temperature below 10 °C for reactions involving $(Br(CH_2)_5)_2Zn$ since an explosive decomposition of this specific reagent has been observed twice during its preparation.

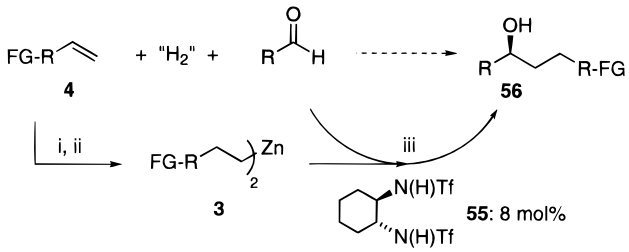
As an application of this methodology, we have performed a short synthesis of ginnol **57** ((*S*)-10-nonacosanol)[24] in three steps starting from commercially available material (61% overall yield and 92% ee). Ginnol is found in several plants and possess the interesting

Table 2. Polyfunctional Products 49−54 Obtained by the Reaction of Secondary Dialkylzincs with Electrophiles in the Presence of CuCN·2LiCl

olefin **4**	electrophile	product	yield[a]
	PhCOCl	 **49**	86
		 **50**	95[b]
		 **51**	90[b]
		 **52**	93[b]
		 **53**	84[b]
		 **54**	72[b]

[a]Isolated yield in % of analytically pure product. [b]Mixture of diastereoisomers.

Scheme 8



Reagents: (i) Et_2BH; (ii) Et_2Zn; (iii) toluene or ether, $Ti(O\textit{i}\text{-}Pr)_4$.

property (if enantiomerically enriched) of crystallizing in double layers forming small lipophilic tubes.[24] Thus, the oxidation of eicosanol (**58**) with PCC on SiO_2 (CH_2Cl_2, 0 °C to rt) provides the aldehyde **59** in 94% yield.[25] The treatment of **59** with bis(5-bromopentyl)zinc in the presence of the chiral catalyst **55** (8 mol %) and $Ti(O\textit{i}\text{-}Pr)_4$ in ether (0 °C, 10 h) affords the bromo alcohol **60** in 69% yield and 92% ee as determined by ^1H NMR analysis of the *O*-acetylmandelate using (*S*)-(+)-*O*-acetylmandelic acid for derivatization.[26] Coupling of **60** with $Bu_2Cu(CN)Li_2$[27] (5 equiv, −60 °C to 0 °C, 1 h) provides **57** in 95%

(23) Rücker, C. *Chem. Rev.* **1995**, *95*, 1009.
(24) Furhop, J.-H.; Bedurke, T.; Hahn, A.; Grund, S.; Gatzmann, J.; Riederer, M. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 350.
(25) (a) Corey, E. J.; Suggs, J. W. *Tetrahedron Lett.* **1975**, 2647. (b) Piancatelli, G.; Scettri, A.; D'Auria, M. *Synthesis* **1982**, 245.
(26) Parker, D. *J. Chem. Soc., Perkin Trans. 2* **1983**, 83.
(27) (a) Lipshutz, B. H. *Synthesis* **1987**, 325. (b) Lipshutz, B. H. *Synlett* **1990**, 119. (c) Lipshutz, B. H.; Wilhelm, R. S.; Kozlowski, J. A. *Tetrahedron* **1984**, *40*, 5005.

Table 3: Polyfunctional Secondary Alkohols 56a–w Obtained by a One-Pot Hydroboration, Boron–Zinc Exchange and Asymmetric Addition to the Aldehydes 57

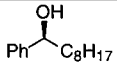
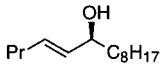
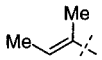
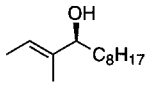
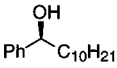
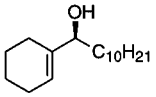
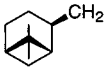
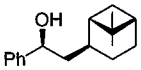
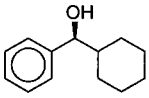
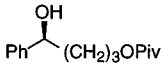
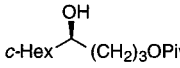
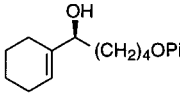
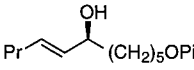
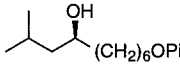
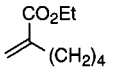
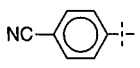
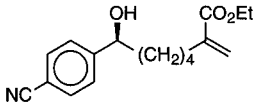
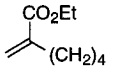
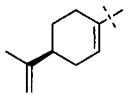
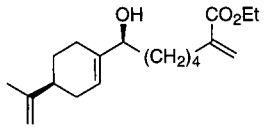
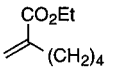
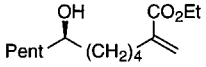
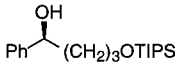
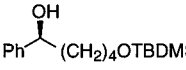
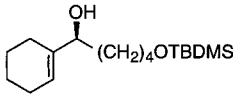
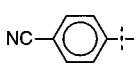
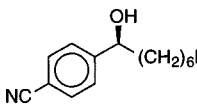
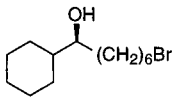
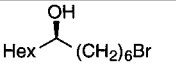
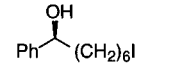
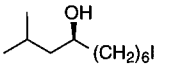
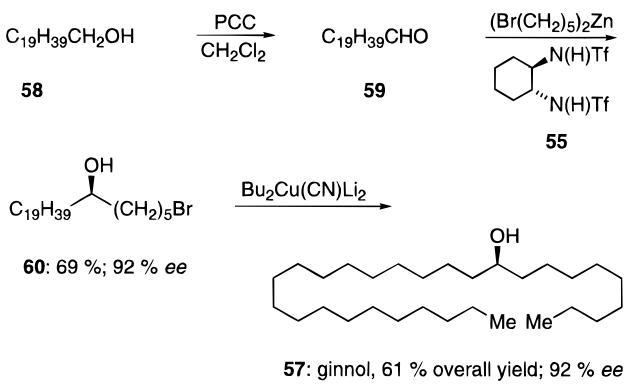
entry	FG-R in **3**	R in RCHO **57**	product **56**		yield (%)[a]	*ee* (%)[b]
1	C_8H_{17}	Ph		**56a**	87	92
2	C_8H_{17}			**56b**	75	78 (96)[c]
3	C_8H_{17}			**56c**	62	> 96
4	$C_{10}H_{21}$	Ph		**56d**	57 (88)	64 (>96)[d]
5	$C_{10}H_{21}$			**56e**	73	> 96
6		Ph		**56f**	17	> 96[e]
7	*c*-Hex	Ph		**56g**	67	80
8	PivO$(CH_2)_3$	Ph		**56h**	70	93
9	PivO$(CH_2)_3$	*c*-Hex		**56i**	22	78
10	PivO$(CH_2)_4$			**56j**	52	95
11	PivO$(CH_2)_5$			**56k**	41	95[c]
12	PivO$(CH_2)_6$	*i*-PrCH$_2$		**56l**	60	90
13				**56m**	69	80
14				**56n**	71	85[e]
15		Pent		**56o**	72	95
16	$(CH_2)_3$OTIPS	Ph		**56p**	60	50
17	$(CH_2)_4$OTBDMS	Ph		**56q**	82	92
18	$(CH_2)_4$OTBDMS			**56r**	63	94
19	$(CH_2)_6$Br			**56s**	85	88
20	$(CH_2)_6$Br	*c*-Hex		**56t**	11	60

Table 3 (Continued)

entry	FG-R in **3**	R in RCHO **57**	product **56**		yield (%)[a]	*ee* (%)[b]
21	$(CH_2)_6Br$	Hex		**56u**	77	90
22	$(CH_2)_6I$	Ph		**56v**	58	86
23	$(CH_2)_6I$	*i*-$PrCH_2$		**56w**	32	73

[a] Isolated yield of analytically pure products.
[b] Determined by preparing the corresponding *O*-acetylmandelates using (S)-(+)-*O*-acetylmandelic acid.
[c] $Ti(O\textit{t}\text{-}Bu)_4$ was used instead of $Ti(O\textit{i}\text{-}Pr)_4$.
[d] Ether was used as solvent.
[e] Diastereomeric excess.

Scheme 9



60: 69 %; 92 % *ee*

57: ginnol, 61 % overall yield; 92 % *ee*

yield (Scheme 9). Although the direct addition of dinonylzinc to **59** proceeds well, it was not possible to determine the optical purity of the resulting product **57** by standard methods due to the similarity of the alkyl substituents attached to the chiral center.

In summary, we have described a general preparation of functionalized dialkylzincs starting from olefins using a hydroboration followed by a boron−zinc exchange mediated by diethylzinc. The method can be applied to prepare primary and secondary dialkylzincs as well as benzylic zinc reagents. The synthetic utility of these organometallics after transmetalation with CuCN·2LiCl has been demonstrated. Furthermore the addition of these diorganozincs to aldehydes in the presence of the chiral catalyst **55** and $Ti(O\textit{i}\text{-}Pr)_4$ proceeds with high enantioselectivity giving a unique access to polyfunctional secondary alcohols with often excellent optical purity (50 to over 96% ee).

Experimental Section

General Considerations. Unless otherwise indicated all reactions were carried out under argon. Solvents (THF, ether, toluene) were dried and freshly distilled over sodium/benzophenone. Reactions were monitored by gas chromatography (GC) or thin-layer chromatography (TLC) analysis of hydrolyzed aliquots. For handling Et_2Zn, Et_3B and Et_2BH, a laboratory coat, leather gloves, and a helmet with a face protection shield were worn due to the pyrophoric nature of these reagents. Any contact of them with air or moisture was carefully avoided. Small amounts of Et_2Zn or volatile boranes that have been distilled from reaction mixtures were collected in a cold trap and decomposed by diluting with hexanes and dropwise addition of 2-propanol.

Derivatization of the secondary alcohols **56** with (*S*)-*O*-acetylmandelic acid was performed according to Parker's method.[26] Completion of the esterification was monitored by GC or TLC analysis. The precipitate formed was removed by filtration and the solvents were evaporated. The crude residue was directly analyzed by ^1H NMR spectroscopy.

Starting Materials. Pyridinium chlorochromate (PCC), copper cyanide, (−)-*β*-pinene, ethyl propiolate, nitrostyrene, (−)-cinchonidine, diethyl benzylidenemalonate, benzoyl chloride, allyl bromide, titanium tetraisopropoxide, and diethyl allylmalonate (**16**) were purchased and directly used or in some cases after distillation. Lithium chloride was dried 1 h at 140 °C under vacuum (0.1 mmHg). Ethyl α-(bromomethyl)acrylate,[17] 3-iodo-2-cyclohexen-1-one,[28] (1*R*,2*R*)-1,2-bis(trifluoromethanesulfonamido)cyclohexane **25**,[20] triisopropylsilyl chloride,[29] titanium tetra-*tert*-butoxide,[30] (*Z*)- and (*E*)-2-deuterio-1-ethyl-1-phenylethylene **13a** and **13b**,[31] pinacol 4-pentenylboronate (**4b**),[32] 6-nitro-1-hexene (**15**),[33] 3-pivaloxy-1-propene,[34] 4-pivaloxy-1-butene,[34] 5-pivaloxy-1-pentene (**4c**),[34] 6-pivaloxy-1-hexene,[34] allyl benzoate (**4d**),[35] 5-bromo-1-pentene,[36] 6-bromo-1-hexene (**4e**),[36] 6-cyano-1-hexene (**4f**),[37] *N*-(5-hexenyl)phthalimide (**4g**),[38] 4-methyl-4-nitro-1-pentene (**4h**),[39] 4-triisopropylsiloxycyclopentene,[40] 3-(triisopropylsiloxy)-1-propene,[40] 4-(*tert*-butyldimethylsiloxy)-1-butene,[40] 6-iodo-1-hexene,[41] and (−)-cinchonidine acetate (**24**)[42] were prepared according to literature procedures.

Preparation of Diethylborane (5). A solution of diethylborane (**5**) was prepared by mixing triethylborane (30.3 g,

(28) Piers, E.; Nagakura, I. *Synth. Commun.* **1975**, *5*, 193.
(29) (a) Cunico, R. F.; Bedell, L. *J. Org. Chem.* **1980**, *45*, 4797. (b) Cunico, R. F.; Dexheimer, E. M. *Synth. React. Inorg. Met.-Org. Chem.* **1974**, *4*, 23. (c) Colvin, E. W. *Silicon Reagents in Organic Synthesis*; Academic Press: London, 1988; p 120.
(30) (a) Bradley, D. C.; Thomas, I. M. *J. Chem. Soc.* **1959**, 3404. (b) Rust, J. B.; Takimoto, H. H.; Denault, G. C. *J. Org. Chem.* **1960**, *25*, 2040. (c) Nowotny, S.; Vettel, S.; Knochel, P. *Tetrahedron Lett.* **1994**, *35*, 4539.
(31) (a) Achyutha Rao, S.; Knochel, P. *J. Am. Chem. Soc.* **1991**, *113*, 5735. (b) Chou, S.-S. P.; Kuo, H.-L.; Wang, C.-Y.; Tsai, C.-Y.; Sun, C.-M. *J. Org. Chem.* **1989**, *54*, 868. (c) Shibata, K.; Aida, T.; Inoue, S. *Tetrahedron Lett.* **1992**, *33*, 1077.
(32) Tucker, C. E.; Davidson, J.; Knochel, P. *J. Org. Chem.* **1992**, *57*, 3482.
(33) Andersen, S. H.; Das, N. B.; Joergensen, R. D.; Kjeldsen, G.; Knudsen, J. S.; Subhash, S. C.; Torssell, K. B. G. *Acta Chem. Scand. Ser. B* **1982**, *36*, 1.
(34) (a) Gaylord, N. G.; Eirich, F. R. *J. Am. Chem. Soc.* **1952**, *74*, 334. (b) Zamarlik, M. H. *C. R. Acad. Sci. (C)* **1970**, *271*, 1138.
(35) Deming, T. J.; Novak, B. M. *J. Am. Chem. Soc.* **1993**, *115*, 9101.
(36) Antczak, K.; Kingston, J. F.; Alward, S. J.; Fallis, A. G. *Can. J. Chem.* **1984**, *62*, 829.
(37) Lipshutz, B. H.; Parker, D. A.; Nguyen, S. L.; McCarthy, K. E.; Barton, J. C.; Whitney, S. E.; Kotsuni, H. *Tetrahedron* **1986**, *42*, 2873.
(38) Barlin, G. B.; Ireland, S. J.; Jiravinyu, C.; Nguyen, T. M. T.; Kotecka, B.; Rieckmann, K. H. *Aust. J. Chem.* **1993**, *46*, 1695.
(39) (a) Aleksandrowicz, P.; Piotrowska, H.; Sas, W. *Tetrahedron* **1982**, *38*, 1321. (b) Ono, N.; Zinsmeister, K.; Kaji, A. *Bull. Chem. Soc. Jpn.* **1985**, *58*, 1069.
(40) (a) Pirrung, M. C.; Webster, N. J. G. *J. Org. Chem.* **1987**, *52*, 3603. (b) Corey, E. J.; Venkateswarlu, A. *J. Am. Chem. Soc.* **1972**, *94*, 6190.
(41) Ashby, M. T.; Enemark, J. M.; Lichtenberger, D. L. *Inorg. Chem.* **1988**, *27*, 191.
(42) Pettit, G. R.; Gupta, S. K. *J. Chem. Soc., C* **1986**, 1208.

310 mmol) and borane−dimethyl sulfide complex (11.4 g, 150 mmol) at 0 °C. The reaction mixture was ready to use after 5 min of stirring. Diethylborane prepared under these conditions contains ca. 0.3 equiv of dimethyl sulfide and is stable at 4 °C (refrigerator) for several months.

Cyclohexyldiethylborane (6). The hydroboration was performed by mixing cyclohexene (4.52 g, 55 mmol) and diethylborane freshly prepared as described above (8.70 g, 50 mmol). After 2 h of stirring at rt, the solvent was carefully distilled off (760 mmHg, rt to 60 °C) affording a crude product (**6**) which was used directly (6.69 g, 88% yield). Distillation of this crude reaction mixture led to extensive disproportionation affording mixtures of **6** (bp 39 °C/0.2 mmHg), dicyclohexylethylborane, and tricyclohexylborane. This behavior is typical for all secondary organoboranes prepared.

Diethyl(1,2-diphenylethyl)borane (7). A mixture of stilbene (2.82 g, 15.6 mmol) and diethylborane (2.86 g, 15.6 mmol) was stirred at rt for 5 h. The solvent was evaporated (0.1 mmHg, rt, 3 h) affording crude **7** (3.10 g, 79% yield) which was directly used for the next step. The crude ^{1}H NMR and ^{13}C NMR spectra of **7** clearly show that also bis- and tris(1,2-diphenylethyl)borane derivatives have been formed (ca. 50%). ^{1}H NMR (200 MHz, $CDCl_3$): δ 7.60−6.90 (m, 10H), 3.30 (m, 1H), 3.05 (m, 2H), 1.45 (m, 4H), 0.95 (m, 6H). ^{13}C NMR (50 MHz, $CDCl_3$): δ 141.5, 141.3, 141.2, 140.4, 128.7, 128.6, 128.5, 128.4, 128.3, 128.2, 128.1, 127.9, 46.6 (br), 36.8, 17.3 (br), 8.5, 8.1.

Diethyl(*trans*-2-phenylcyclohexyl)borane (9). A mixture of 1-phenylcyclohexene (7.91 g, 50 mmol) and diethylborane (6.73 g, 50 mmol) was stirred at 50 °C for 3 days affording the organoborane **9** (9.30 g, 96% yield) which was directly used without further purification for the next step. The ^{1}H NMR and ^{13}C NMR spectra of **9** show that a bis(diorgano)ethylborane has also been formed. ^{1}H NMR ($CDCl_3$, 200 MHz): δ 7.30 (m, 5H), 2.95−2.55 (m, 1H), 2.15−1.80 (m, 4H), 1.70−0.90 (m, 14H), 0.60−0.35 (m, 1H). ^{13}C NMR (50 MHz, $CDCl_3$): δ 148.9, 148.6, 148.4, 128.2, 127.3, 127.0, 125.6, 125.4, 46.3, 46.2, 46.1, 41.2 (br), 37.3, 36.6, 36.5, 27.4, 27.3, 27.2, 26.9, 26.8, 26.4, 26.1, 25.0, 18.5 (br), 17.8 (br), 17.3 (br), 8.5, 8.0.

Ethyl 2-[(*trans*-2-Phenylcyclohexyl)methyl]acrylate (11). Preparation according to the typical procedure A (see below) using the organoborane **9** (1.93 g, 10.0 mmol) and ethyl α-(bromomethyl)acrylate[17] (1.74 g, 9.0 mmol). Reaction conditions: rt, 40 h (B/Zn-exchange) and −20 °C, 1 h (reaction with electrophile). Yield of **11**: 2.06 g, 84% (3:1 mixture of diastereoisomers). IR (neat): 2920 (s), 1715 (s), 1445 (s), 1030 (s), 755 (s), 700 (s) cm^{-1}. ^{1}H NMR ($CDCl_3$, 200 MHz): δ 7.12 (m, 5H), 5.97 (m, 1H), 5.24 (m, 0.75H), 5.19 (s, 0.25H), 4.03 (sext, J = 7.2Hz, 2H), 2.30−2.20 (m, 2H), 1.90−1.55 (m, 6H), 1.45−1.10 (m, 3H), 1.15 (t, J = 7.2 Hz, 2.25H), 1.07 (t, J = 7.2 Hz, 0.75H), 0.82 (q, J = 10.5 Hz, 1H). ^{13}C NMR (50 MHz, $CDCl_3$): δ 167.1, 146.0, 145.1, 140.1, 139.4, 128.2, 127.9, 127.6, 125.9, 125.7, 125.6, 125.4, 60.3, 51.4, 46.0, 40.8, 38.9, 37.4, 36.2, 31.7, 28.5, 28.1, 26.8, 26.3, 26.2, 25.2, 20.2, 14.1, 14.0. MS (EI): 273 (4), 158 (38), 114 (28), 104 (26), 91 (100). Anal. Calcd for $C_{18}H_{24}O$: C, 79.37; H, 8.88. Found: C, 79.08; H, 8.90.

(1*R,2*S**)-(1-Deuterio-2-phenylbutyl)diethylborane (12a).** A mixture of the styrene derivative **13a** (0.89 g, 6.7 mmol) and diethylborane (0.98 g, 6.7 mmol) was stirred at rt for 3 h affording the borane derivative **12a** (1.12 g, 82% yield). The crude **12a** was used directly for the next step (boron−zinc exchange). ^{1}H NMR ($CDCl_3$, 200 MHz): δ 7.33 (m, 5H), 3.04 (quin, J = 7.2 Hz, 1H), 1.80−1.50 (m, 3H), 1.40−1.25 (m, 2H), 1.10−0.80 (m, 10H). ^{2}D NMR ($CDCl_3$, 77 MHz): 1.77 (m, 1D). ^{13}C NMR (50 MHz, $CDCl_3$): δ 148.0 (t, J = 6.8 Hz), 128.1, 127.3, 125.5, 43.9 (d, J = 4.0 Hz), 34.2 (br), 33.1, 20.0 (br), 11.5 (d, J = 3.0 Hz), 8.2.

Tris((1*R,2*R**)-(1-deuterio-2-phenylbutyl))borane (12b).** A mixture of the styrene derivative **13b** (1.10 g, 8.2 mmol) and diethylborane (1.21 g, 8.2 mmol) was stirred at rt for 3 h affording after removing of all volatiles in high vacuum the borane derivative **12b** (1.02 g, 90% yield). The crude **12b** was used directly for the next step (boron−zinc-exchange). ^{1}H NMR ($CDCl_3$, 200 MHz): δ 7.03 (m, 15H), 2.74 (quin, J = 7.2 Hz, 3H), 1.55−0.85 (m, 9H), 0.80−0.80 (m, 9H). ^{2}D NMR ($CDCl_3$, 77 MHz): 1.52 (m). ^{13}C NMR ($CDCl_3$, 50 MHz): δ 147.7 (t, J = 6.5 Hz), 128.1, 127.3, 125.6, 44.0, 35.9 (br), 33.0, 12.3.

Bis(1-deuterio-2-phenylbutyl)zinc (12c and 12d). Preparation according to the typical procedure A (see below) using either the organoborane **12a** (0.97 g, 4.78 mmol) or **12b** (1.00 g, 2.42 mmol) and diethylzinc (1.18 g, 9.55 mmol and 1.49 g, 12.1 mmol) yielding **12c** (0.79 g, 99%) and **12d** (1.18 g, 98%) as a 1:1 mixture of diastereoisomers. The ^{1}H and ^{13}C NMR spectra of both **12c** and **12d** are identical. ^{1}H NMR ($CDCl_3$, 200 MHz): δ 7.64 (m, 4H), 7.47 (m, 6H), 3.01 (q, J = 6.8 Hz, 2H), 1.87 (m, 4H), 1.14 (t, J = 7.2 Hz, 6H), 0.80 (d, J = 8.0 Hz, 1H), 0.70 (d, J = 10.0 Hz, 1H). ^{2}D NMR ($CDCl_3$, 77 MHz): δ 0.80 (s, 1D), 0.70 (s, 1D). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 151.2, 128.6, 128.5, 125.5, 45.5, 34.0, 26.0 (t, J = 18.6 Hz), 12.8.

(1-Deuterio-2-phenylbutyl)phenyl Ketone (14a and 14b). Preparation according to the typical procedure A (see below) using the organozinc **12c** or **12d** (0.66 g, 2.0 mmol) and benzoyl chloride (0.56 g, 4.0 mmol). Reaction conditions: −20 °C, 10 h. Yield of **14a** and **14b** (1:1 mixture of diastereoisomers): 0.90 g, 94%. IR (neat): 1680 (vs), 1450 (s), 1275 (m), 755 (s), 700 (s), 685 (s), 555 (m) cm^{-1}. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.93 (d, J = 9.0 Hz, 2H), 7.55 (t, J = 7.4 Hz, 1H), 7.45 (t, J = 7.5 Hz, 2H), 7.36−7,20 (m, 5H), 3.30 (m, 2H), 1.84 (m, 1H), 1.69 (m, 1H), 0.86 (t, J = 7.4 Hz, 3H). ^{2}D NMR ($CDCl_3$, 77 MHz): 3.40−3.20 (m, 1D). ^{13}C NMR (50 MHz, $CDCl_3$): δ 199.1, 144.5, 137.1, 132.8, 128.4, 128.3, 128.1, 127.5, 126.2, 45.1 (t, J = 19.1 Hz), 42.9, 29.1 (d, J = 2.5 Hz), 12.0. MS (EI): 239 (14), 210 (44), 118 (100), 105 (99), 77 (100). Anal. Calcd for $C_{17}H_{17}DO$: C, 85.31; H, 7.16. Found: C, 85.25; H, 7.36.

Typical Procedure A for the Boron−Zinc Exchange and Copper(I)-Mediated Reaction with an Electrophile: Preparation of Diethyl 6-Carbethoxy-1-phenyl-6-heptenylmalonate (43) (Scheme VI). Ethyl 3-butenylacrylate (**40**) (1.85 g, 12.0 mmol) was cooled to 0 °C, and Et_2BH (12.0 mmol, 1 equiv; prepared from BH_3·Me_2S (3.80 g, 50 mmol), BEt_3 (9.80 g, 100 mmol), and Et_2O (14.8 g)) was slowly added via syringe. After 3 h at rt, the solvents were removed under vacuum (0.1 mmHg, 0 °C, 0.5 h) affording the expected diethyl(alkyl)borane (2.30 g, 86% yield) having ca. 95% purity as shown by ^{1}H and ^{13}C NMR analysis. The organoborane (1.01 g, 4.5 mmol) was transferred to a 50 mL Schlenk-flask and cooled to 0 °C, and Et_2Zn (9.0 mmol, 0.92 mL, 2 equiv) was added. After 0.5 h at 0 °C, the excess of Et_2Zn and formed Et_3B were pumped off (0.1 mmHg, 0 °C, 3 h). The resulting oil was diluted with THF (3 mL) and cooled to −80 °C, and a THF solution (4.5 mL) of CuCN·2LiCl (prepared from CuCN (0.40 g, 4.5 mmol) and LiCl (0.38 g, 9.0 mmol)) was added. The reaction mixture was warmed to 0 °C and immediately cooled back to −80 °C. Diethyl benzylidenemalonate (1.00 g, 4.05 mmol, 0.9 equiv) was added, and the reaction mixture was allowed to warm to rt. After 2 h, the conversion was complete as shown by GC analysis of a reaction aliquot. The reaction mixture was quenched with a saturated aqueous NH_4Cl solution (50 mL) and diluted with ether (100 mL). The aqueous phase was extracted with ether (2 × 50 mL). The combined organic phase was dried ($MgSO_4$), evaporating of the solvents afforded a crude oil which was purified by chromatography (hexanes/ether 9:1), and pure **43** (1.36 g, 82%; overall yield: 71%, based on the olefin **40**) was obtained.

***N*-(5-Hexenyl)trifluoroacetamide (17).** To a suspension of oil-free NaH (6.00 g, 250 mmol, 2 equiv) in DMF (50 mL) was slowly added trifluoroacetamide (25.4 g, 225 mmol, 1.8 equiv) in DMF (15 mL) leading to a vigorous evolution of H_2. After 0.5 h of stirring, the reaction mixture was treated with 6-bromo-1-hexene (20.4 g, 125 mmol, 1 equiv) and the reaction mixture was heated to 80 °C for 10 h. The resulting precipitate was filtered, the solvent was evaporated under reduced pressure, and the residue was purified by distillation (bp 52−55 °C, 0.2 mmHg) affording the amide **17** as a colorless oil (12.2 g, 50% yield). IR (neat): 3310 (vs), 2940 (s), 1705 (vs), 1185 (vs), 914 (s) cm^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$): δ 7.10 (s, 1H), 5.70 (m, 1H), 4.90 (m, 2H), 3.27 (q, J = 6.7 Hz, 2H), 2.01 (q, J = 6.9 Hz, 2H), 1.53 (m, 2H), 1.35 (m, 2H). ^{13}C NMR (50 MHz,

$CDCl_3$): δ 157.7 (q, J = 37 Hz), 138.2, 116.1 (q, J = 288 Hz), 115.2, 40.1, 33.3, 28.4, 26.0. MS (EI): 195 (1), 126 (38), 82 (100), 67 (54), 54 (36), 41 (18). Anal. Calcd for $C_8H_{12}F_3NO$: C, 49.23; H, 6.20; N, 7.18. Found: C, 48.94; H, 6.18; N, 7.19.

Analytical Data of Products 18−23 Prepared According to the Typical Procedure A. 9-Nitro-1-nonene (18). Overall yield (1.07 g, 82%) based on 6-nitro-1-hexene (0.98 g, 7.6 mmol) and allyl bromide (6 g, 50 mmol). Reaction conditions: 0 °C, 1 h. Purification by flash chromatography (hexanes/ether = 9:1). IR (neat): 3080 (s), 2930 (vs), 1640 (s), 1555 (vs), 910 (m) cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$): δ 5.72 (m, 1H), 4.89 (m, 2H), 4.30 (t, J = 7.1 Hz, 2H), 1.95 (m, 4H), 1.27 (m, 8H). ^{13}C NMR (50 MHz, $CDCl_3$): δ (138.7, 114.1, 75.5, 33.5, 28.5, 27.2, 26.0. MS (EI): 81 (29), 69 (30), 55 (100), 41 (67). Anal. Calcd for $C_9H_{17}NO_2$: C; 63.13; H, 10.01; N, 8.18. Found: C, 63.28; H, 9.93; N, 8.29.

Diethyl 5-Hexenylmalonate (19).[43] Overall yield (1.09 g, 85%) based on diethyl allylmalonate (1.05 g, 5.26 mmol) and allyl bromide (6 g, 50 mmol). Reaction conditions: 0 °C, 1 h. Purification by flash chromatography (hexanes/ether = 9:1). IR (neat): 3080 (w), 2980 (m), 2935 (m), 1750 (vs), 1735 (vs), 1150 (s), 910 (m) cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$): δ 5.70 (m, 1H), 4.89 (m, 2H), 4.12 (q, J = 7.1 Hz, 4H), 3.24 (t, J = 7.5 Hz, 1H), 1.98 (q, J = 7.0 Hz, 2H), 1.82 (q, J = 7.4 Hz, 2H), 1.28 (m, 4H), 1.19 (t, J = 7.1 Hz, 6H). ^{13}C NMR (50 MHz, $CDCl_3$): δ 169.7, 138.7, 114.8, 61.4, 52.2, 33.6, 28.8, 28.7, 26.9, 14.3. MS (EI): 196 (11), 173 (41), 160 (57), 80 (100), 55 (44).

***N*-(8-Nonenyl)trifluoroacetamide (20).** Overall yield (1.13 g, 94%) based on **17** (1.04 g, 5.32 mmol) and allyl bromide (6 g, 50 mmol). Reaction conditions: 0 °C, 1 h. Purification by flash chromatography (hexanes/ether = 9:1). IR (neat): 3305 (s), 2940 (vs), 1705 (vs), 1561 (s), 1185 (vs), 910 (m) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 7.10 (s, 1H), 5.71 (m, 1H), 4.88 (m, 2H), 3.25 (q, J = 6.8 Hz, 2H), 1.96 (q, J = 6.9 Hz, 2H), 1.50 (quint, J = 7.0 Hz, 2H), 1.24 (s, 8H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 157.3 (q, J = 37 Hz), 138.7, 115.8 (q, J = 288 Hz), 114.0, 39.8, 33.5, 28.8, 28.7, 28.6, 28.5, 26.4. MS (EI): 124 (56), 96 (19), 82 (51), 69 (43), 55 (100), 41 (48). Anal. Calcd for $C_{11}H_{18}F_3NO$: C, 55.69; H, 7.65; N, 5.90. Found: C, 55.47; H, 7.66; N, 6.00.

Ethyl (7-Iodoheptyl)acrylate (21). Overall yield (1.09 g, 75%) based on 6-iodo-1-hexene (1.31 g, 6.25 mmol) and ethyl α-(bromomethyl)acrylate[17] (0.87 g, 4.50 mmol). Reaction conditions: −20 °C, 1 h. Purification by flash chromatography (hexanes/ether = 19:1). IR (neat): 2930 (s), 2860 (m), 1720 (s), 1190 (m) cm^{-1}. ^1H NMR ($CDCl_3$, 200 MHz): δ 6.01 (s, 1H), 5.49 (s, 1H), 4.18 (q, J = 7.1 Hz, 2H), 3.16 (t, J = 7.3 Hz, 2H), 2.27 (t, J = 7.7 Hz, 2H), 1.79 (quin, J = 7.3 Hz, 2H), 1.45−1.25 (m, 8H), 1.27 (t, J = 8.1 Hz, 3H). ^{13}C NMR (50 MHz, $CDCl_3$): δ 166.5, 140.2, 123.5, 59.8, 32.7, 31.1, 29.7, 28.2, 27.6, 13.5, 6.5. MS (EI): 324 (1), 197 (21), 123 (100), 81 (61), 67 (45), 55 (65). Anal. Calcd for $C_{12}H_{21}IO_2$: C, 44.46; H, 6.53. Found: C, 44.51; H, 6.45.

***(E)*-Ethyl 9-Iodo-2-nonenoate (22).** Overall yield (1.39 g, 79%) based on 6-iodo-1-hexene (1.47 g, 7 mmol) and ethyl propiolate (0.56 g, 5.7 mmol). Reaction conditions: −50 °C to −40 °C, 10 h. Purification by flash chromatography (hexanes/ether = 9:1). IR (neat): 2930 (s), 1720 (s), 1660 (m), 1200 (s), 1040 (m) cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$): δ 6.89 (m, 1H), 5.76 (d, J = 15.6 Hz, 1H), 4.13 (q, J = 7.1 Hz, 2H), 3.13 (t, J = 6.9 Hz, 2H), 2.15 (q, J = 7.1 Hz, 2H), 1.76 (quint, J = 6.7 Hz, 2H), 1.32 (m, 6H), 1.23 (t, J = 6.2 Hz, 3H). ^{13}C NMR (50 MHz, $CDCl_3$): δ 165.1, 147.4, 120.0, 58.6, 31.8, 30.5, 28.7, 26.5, 26.3, 12.8, 5.6; MS (EI): 310 (10), 265 (23), 109 (100), 95 (22), 67 (25), 55 (30). Anal. Calcd for $C_{11}H_{19}IO_2$: C, 42.60; H, 6.17. Found: C, 42.86; H, 6.10.

8-Iodo-1-nitro-2-phenyloctane (23). Overall yield (1.69 g, 4.7 mmol, 82% yield) based on 6-iodo-1-hexene (1.47 g, 7 mmol) and nitrostyrene (0.85 g, 5.7 mmol). Reaction conditions: −40 °C, 1 h; −10 °C, 8 h. Purification by flash chromatography (hexanes/ether = 9:1). IR (neat): 2930 (s), 1550 (s), 1380 (m), 1200 (w), 700 (m) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 7.37 (m, 5H), 4.65 (d, J = 8.0 Hz, 2H), 3.55 (quint, J = 7.6 Hz, 1H), 3.24 (t, J = 6.0 Hz, 2H), 1.80 (m, 4H), 1.39 (m, 6H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 139.5, 128.9, 127.6, 127.5, 80.9, 44.3, 33.3, 32.8, 30.2, 28.2, 26.7, 7.5. MS (EI): 361 (1), 314 (8), 118 (100), 104 (30), 91 (93), 55 (20). Anal. Calcd for $C_{14}H_{20}INO_2$: C, 46.88; H, 5.58; N, 3.88. Found: C, 46.35; H, 5.57; N, 3.93.

Preparation of (−)-Cinchonidine Acetate (24).[42] (−)-Cinchonidine (5.89 g, 20 mmol, 1 equiv) and Et_3N (3.04 g, 30 mmol, 1.5 equiv) in CH_2Cl_2 (150 mL) were cooled to 0 °C. Acetyl chloride (2.09 g, 27 mmol, 1.3 equiv) in CH_2Cl_2 (10 mL) was added within 3 h to give a clear yellow solution. After 8 h at rt, the reaction mixture was worked up as usual affording after evaporation of the solvent a pure material which was directly used for the next step (5.99 g, 89% yield). ^1H NMR (200 MHz, $CDCl_3$): δ 8.78 (d, J = 4.6 Hz, 1H), 8.14 (d, J = 9.3 Hz, 1H), 8.03 (d, J = 9.3 Hz, 1H), 7.58 (t, J = 8.3 Hz, 1H), 7.46 (t, J = 8.4 Hz, 1H), 7.31 (d, J = 4.5 Hz, 1H), 6.43 (d, J = 7.5 Hz, 1H), 5.71 (m, 1H), 4.89 (m, 2H), 4.26 (m, 1H), 2.90 (m, 2H), 2.49 (m, 2H), 2.15 (m, 1H), 1.97 (s, 3H), 1.85−1.30 (m, 5H). ^{13}C NMR (50 MHz, $CDCl_3$): δ 169.7, 149.7, 148.4, 145.1, 141.5, 130.2, 128.9, 126.5, 125.8, 123.2, 118.5, 114.2, 73.8, 59.4, 56.4, 42.1, 49.4, 27.5, 27.3, 24.3, 20.8.

Allylation of the Cinchonidine Acetate (24) via the Hydroboration/Boron−Zinc Exchange Sequence. Preparation of the Allylated Cinchonidine 25. Diethylborane (4 mmol) prepared by mixing borane−dimethyl sulfide complex (Fluka; 101 mg, 1.33 mmol, 1 equiv) and triethylborane (Aldrich, 261 mg, 2.66 mmol, 2 equiv) at rt was added at 0 °C to a solution of **24** (1.35 g, 4 mmol) in ether (8 mL) and was stirred at 40 °C for 12 h giving a white suspension. All the solvents were pumped off at 40 °C, 0.2 mmHg during 6 h yielding a diethylborane adduct as a white powder (1.63 g, 4 mmol). Diethylzinc (8 mmol, ca. 0.8 mL, 2 equiv) was added at rt to a suspension of the intermediate diethylborane derivative (1.63 g, 4 mmol, 1 equiv) in CH_2Cl_2 (5 mL). After 10 min of stirring, the white suspension turned into a clear orange solution. The solvent, the excess diethylzinc, and the formed triethylborane were removed under vacuum at rt (0.2 mmHg, 2 h). The entire procedure (5 mL CH_2Cl_2, 1 mL Et_2Zn, then pumping off) was repeated to insure complete conversion to the diorganozinc compound. Traces of remaining Et_2Zn were removed by evaporating twice with toluene (5 mL) and finally with CH_2Cl_2 (5 mL) at 40 °C (0.2 mmHg, 6 h) giving an orange foam of the intermediate zinc reagent. A suspension of copper(I) cyanide (36 mg, 0.4 mmol, 0.1 equiv), lithium chloride (34 mg, 0.8 mmol, 0.2 equiv), allyl bromide (4.84 g, 40 mmol, 10 equiv), and THF (1 mL) was added at −80 °C to a solution of the diorganozinc compound (2 mmol, 0.5 equiv) in THF (8 mL). The cooling bath was removed, and the reaction mixture was allowed to slowly warm to rt. After the usual workup the solvents were evaporated and the remaining volatile compounds were removed at 50 °C (0.2 mmHg, 3 h). The crude product was purified by flash chromatography (ether/THF = 4:1) yielding the desired product **25** as a yellow foam (1.44 g, 95%). IR (neat): (2925 (s), 1745 (s), 1230 (s), 1025 (s), 760 (s) cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$): δ 8.80 (d, J = 4.6 Hz, 1H), 16 (d, J = 9.2 Hz, 1H), 8.04 (d, J = 9.4 Hz, 1H), 7.61 (t, J = 8.3 Hz, 1H), 7.49 (t, J = 8.3 Hz, 1H), 7.31 (d, J = 4.5 Hz, 1H), 5.67 (m, 1H), 4.85 (m, 2H), 3.29 (m, 1H), 2.93 (m, 2H), 2.52 (m, 1H), 2.19 (m, 1H), 2.01 (s, 3H), 1.15−1.95 (m, 13H). ^{13}C NMR (50 MHz, $CDCl_3$): δ 169.4, 149.5, 148.2, 145.0, 138.2, 130.0, 128.7, 126.4, 125.6, 123.0, 118.3, 114.1, 73.6, 59.0, 58.0, 42.0, 34.9, 33.9, 33.4, 27.9, 26.4, 25.2, 23.7, 20.6. MS (EI): 378 (13), 319 (43), 168 (100), 159 (18), 84 (22). Anal. Calcd for $C_{24}H_{30}N_2O_2$: C, 76.16; H, 7.99; N, 7.40. Found: C, 75.80; H, 8.18; N, 7.41.

Products 26−38 of Table 1 Prepared According to the Typical Procedure A. Ethyl 2-undecylacrylate (26). Overall yield based on 1-decene: 1.02 g, 80% using 1-decene (0.70 g, 5.0 mmol) and ethyl α-(bromomethyl)acrylate[17] (0.87 g, 4.5 mmol). Purification of **26** by flash chromatography (hexanes/ether = 19:1). IR (neat): 2930 (vs), 2860 (vs), 1720 (vs), 1465 (s), 1180 (s) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 6.04 (s, 1H), 5.42 (s, 1H), 4.13 (q, J = 7.2 Hz, 2H), 2.22 (t, J = 7.5 Hz, 2H), 1.40 (t, J = 7.3 Hz, 2H), (m, 19H), 0.80 (t, J = 6.6 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 167.2, 141.0, 123.8, 60.3, 32.5, 31.7,

(43) Salomon, R. G.; Coughlin, D. J.; Ghosh, S.; Zagorski, M. G. *J. Am. Chem. Soc.* **1982**, *104*, 998.

29.5, 29.4, 29.3, 29.2, 29.0, 28.3, 22.5, 14.0, 13.9. MS (EI): 254 (18), 209 (22), 141 (14), 115 (100), 102 (93). Anal. Calcd for $C_{16}H_{30}O_2$: C, 75.54; H, 11.89. Found: C, 75.52; H, 12.04.

Pinacol 5-(3-Oxocyclohexenyl)boronate (27). Overall yield (1.31 g, 81%) based on pinacol 4-pentylboronate (**4b**) (1.22 g, 6.2 mmol) and 3-iodo-2-cyclohexen-1-one[28] (1.23 g, 5.5 mmol). Reaction conditions: −30 °C, 10 h. Purification by flash chromatography (hexanes/ether = 2:1). IR (neat): 2940 (s), 1660 (s), 1630 (m), 1370 (s), 1140 (s), 960 (m) cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$): δ 5.71 (s, 1H), 2.23−2.07 (m, 6H), 1.83 (quin, J = 6.4 Hz, 2H), 1.45−1.09 (m, 6H), 1.09 (s, 12H), 0.65 (t, J = 7.0 Hz, 2H). ^{13}C NMR (50 MHz, $CDCl_3$): δ 199.7, 166.7, 125.6, 82.9, 38.0, 37.4, 31.9, 29.7, 26.7, 24.9, 23.8, 22.8, 11.0 (br). MS (EI): 292 (5), 234 (8), 193 (35), 179 (21), 123 (45), 110 (34), 82 (58), 55 (30), 40 (100). Calcd for $C_{17}H_{29}BO_3$: C, 69.87; H, 10.00. Found: C, 69.61; H, 10.16.

3-(5-Pivaloxypentyl)-2-cyclohexen-1-one (28). Overall yield (1.31 g, 66%) based on 4-pentenyl pivalate (**4c**) (1.16 g, 6.8 mmol) and 3-iodo-2-cyclohexen-1-one[28] (1.23 g, 5.53 mmol). Reaction conditions: −30 °C, 10 h. Purification by flash chromatography (hexanes/ether = 9:1). IR (neat): 2940 (s), 1720 (s), 1670 (s), 1480 (m), 1290 (s), 1160 (s) cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$): δ 5.80 (s, 1H), 3.98 (t, J = 6.5 Hz, 2H), 2.32−2.12 (m, 6H), 1.91 (quin, J = 7.0 Hz, 2H), 1.66−1.27 (m, 6H), 1.12 (s, 9H). ^{13}C NMR (50 MHz, $CDCl_3$): δ 198.8, 177.5, 165.2, 124.7, 63.0, 37.7, 36.9, 36.3, 28.6, 27.4, 26.2, 25.5, 24.6, 21.7. MS (EI): 266 (7), 181 (15), 123 (38), 110 (20), 82 (28), 69 (18), 57 (100), 41 (47). Anal. Calcd for $C_{16}H_{26}O_3$: C, 72.14; H, 9.84. Found: C, 71.97; H, 9.90.

Diethyl [4-(Benzoyloxy)-1-phenylbutyl]malonate (29). Overall yield (0.90 g, 81%) based on allyl benzoate (**4d**) (1.01 g, 6.25 mmol) and diethyl benzylidenemalonate (1.88 g, 3.50 mmol). Reaction conditions: 0 °C, 12 h. Purification by flash chromatography (hexanes/ether = 19:1). IR (neat): 1760 (s), 1730 (s), 1260 (m), 1030 (m), 700 (m) cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$): δ 7.97 (m, 2H), 7.55−7.30 (m, 3H), 7.25−7.08 (m, 5H), 4.27 (t, J = 6.4 Hz, 1H), 4.17 (q, J = 7.1 Hz, 2H), 3.57 (d, J = 11.2 Hz, 1H), 3.19 (dt, J = 11.2 Hz, J = 3.8 Hz, 1H), 1.78−1.42 (m, 4H), 1.22 (t, J = 7.1 Hz, 3H), 0.86 (t, J = 7.1 Hz, 3H), 0.65 (t, J = 7.3 Hz, 3H). ^{13}C NMR (50 MHz, $CDCl_3$): δ 169.5, 168.8, 141.6, 133.8, 130.4, 129.3, 129.2, 129.1, 127.7, 68.5, 62.4, 62.0, 59.6, 48.3, 29.6, 28.0, 26.7, 15.0, 14.6, 12.6. MS (EI): 278 (13), 204 (74), 159 (32), 131 (41), 119 (60), 91 (100). Anal. Calcd for $C_{24}H_{28}O_6$: C, 69.89; H, 6.84. Found: C, 69.58; H, 6.85.

4-Cyclopropyl-4-oxobutyl Benzoate (30). Overall yield (1.00 g, 64%) based on allyl benzoate (**4d**) (1.20 g, 7.40 mmol) and cyclopropylcarbonyl chloride (0.56 g, 5.40 mmol). Reaction conditions: −10 °C, 10 h. Purification by flash chromatography (hexanes/ether = 9:1). IR (neat): 1720 (s), 1700 (s), 1280 (s), 1120 (m), 712 (s) cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$): δ 7.98 (d, J = 7.9 Hz, 2H), 7.52−7.35 (m, 3H), 4.29 (t, J = 8.0 Hz, 2H), 2.69 (t, J = 7.0, 2H), 2.25−1.80 (m, 3H), 1.03−0.75 (m, 2H). ^{13}C NMR (50 MHz, $CDCl_3$): δ 208.7, 165.5, 132.0, 129.3, 128.6, 127.4, 63.3, 62.5, 38.7, 27.8, 27.7, 22.0, 19.5, 9.8. MS (EI): 232 (1), 110 (48), 105 (70), 69 (100), 41 (45). Anal. Calcd for $C_{14}H_{16}O_3$: C, 72.39; H, 6.94. Found: C, 72.21; H, 6.70.

1,12-Bis(benzoyloxy)-4,9-dioxododecane (31). Overall yield (0.65 g, 53%) based on allyl benzoate (**4d**) (1.22 g, 7.40 mmol) and adipoyl chloride (0.44 g, 2.40 mmol). Reaction conditions: −10 °C, 10 h. Purification by flash chromatography (hexanes/ether = 9:1). IR (neat): 2940 (m), 1710 (s), 1280 (s), 1120 (m), 710 (s) cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$): δ 7.94 (m, 4H), 7.50−7.32 (m, 6H), 4.24 (t, J = 6.3 Hz, 4H), 2.48 (t, J = 7.2 Hz, 4H), 2.35 (m, 4H), 1.97 (quint, J = 6.8 Hz, 4H), 1.47 (m, 4H). ^{13}C NMR (50 MHz, $CDCl_3$): δ 209.7, 166.7, 133.0, 130.4, 129.7, 128.6, 64.4, 42.8, 39.2, 23.4, 23.1. MS (EI): 153 (8), 105 (100), 84 (29), 77 (25), 55 (11). Anal. Calcd for $C_{26}H_{30}O_6$: C, 71.21; H, 6.90. Found: C, 71.09; H, 6.74.

8-Bromo-1-nitro-2-phenyloctane (32). Overall yield (1.27 g, 4.04 mmol, 84%) based on 6-bromo-1-hexene (**4e**) (1.01 g, 6.2 mmol) and nitrostyrene (0.72 g, 4.80 mmol). Reaction conditions: −10 °C, 10 h. Purification by flash chromatography (hexanes/ether = 19:1). IR (neat): 2930 (s), 1550 (s), 1450 (m), 1380 (s), 700 (s) cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$): δ 708 (m, 5H), 4.48 (t, J = 7.6 Hz, 2H), 3.35 (quint, J = 7.6 Hz, 1H), 3.27 (t, J = 6.7 Hz, 2H), 1.75−1.52 (m, 4H), 1.30−1.05 (m, 6H). ^{13}C NMR (50 MHz, $CDCl_3$): δ 140.3, 129.8, 128.5, 128.4, 81.8, 45.2, 34.8, 33.7, 33.4, 29.3, 28.7, 27.6. MS (EI): 268 (1), 266 (1), 118 (100), 104 (19), 91 (58). Anal. Calcd for $C_{14}H_{20}BrNO_2$: C, 53.51; H, 6.42; N, 4.46. Found: C, 53.72; H, 6.46; N, 4.55.

Diethyl (7-Cyano-1-phenylheptyl)malonate (33). Overall yield (1.76 g, 74%) based on 6-heptenenitrile (**4f**) (0.81 g, 7.40 mmol) and diethyl benzylidenemalonate (1.50 g, 6.06 mmol). Reaction conditions: rt, 10 h. Purification by flash chromatography (hexanes/ether = 4:1). IR (neat): 2930 (s), 2500 (w), 1690 (s), 1600 (s), 1530 (s) cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$): δ 7.92 (m, 4H), 2.76 (t, J = 7.1 Hz, 2H), 2.09 (t, J = 6.9 Hz, 2H), 1.40 (sept, J = 7.2 Hz, 4H), 1.90 (m, 4H). ^{13}C NMR (50 MHz, $CDCl_3$): δ 197.8, 149.4, 140.6, 128.3, 123.1, 119.1, 38.1, 27.7, 27.5, 24.4, 22.7, 16.3. MS (EI): 260 (1), 165 (78), 150 (100), 104 (33), 83 (21). Anal. Calcd for $C_{21}H_{29}NO_4$: C, 64.60; H, 6.20 N, 10.76. Found: C, 64.43; H, 6.40; N, 10.98.

***N*-(7-Oxo-7-phenylheptyl)phthalimide (35).** Overall yield (1.18 g, 3.5 mmol, 68%) based on benzoyl chloride (0.62 g, 4.4 mmol) and *N*-(5-hexenyl)phthalimide (**4g**) (1.32 g, 5.76 mmol). Reaction conditions: −10 °C, 10 h. Purification by crystallization from EtOH (100 mL) yielding a white solid (mp 150 °C). IR (neat): 2940 (s), 1705 (vs), 1674 (s), 1400 (s), 730 (s), 729 (m) cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$): δ 7.80 (m, 2H), 7.69 (m, 2H), 7.58 (m, 2H), 7.33 (m, 3H), 3.56 (t, J = 7.2 Hz, 2H), 2.84 (t, J = 7.3 Hz, 2H), 1.59 (q, J = 7.0 Hz, 4H), 1.29 (m, 4H). ^{13}C NMR (50 MHz, $CDCl_3$): δ 200.0, 168.2, 136.7, 133.7, 132.7, 131.9, 128.4, 127.8, 122.9, 38.2, 37.7, 28.9, 28.4, 26.5, 23.9. MS (EI): 335 (16), 216 (21), 160 (33), 105 (100), 77 (36). Anal. Calcd for $C_{21}H_{21}NO_3$: C, 75.20; H, 6.31; N, 4.18. Found: C, 74.99; H, 6.41; N, 4.23.

***N*-(7-Carbethoxy-7-octenyl)phthalimide (36).** Overall yield (1.47 g, 81%) based on *N*-(5-hexenyl)phthalimide (**4g**) (1.35 g, 5.88 mmol) and ethyl α-(bromomethyl)acrylate[17] (0.87 g, 4.5 mmol). Reaction conditions: −20 °C, 1 h. Purification by flash chromatography (hexanes/ether = 4:1). IR (neat): 2935 (s), 1775 (s), 1720 (s), 1395 (s), 1185 (s), 720 (s) cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$): δ 7.85 (m, 2H), 7.61 (m, 2H), 6.01 (s, 1H), 5.40 (s, 1H), 4.10 (q, J = 7.1 Hz, 2H), 3.57 (t, J = 7.1 Hz, 2H), 2.18 (t, J = 7.1 Hz, 2H), 1.57 (s, 2H), 1.24 (m, 11H). ^{13}C NMR (50 MHz, $CDCl_3$): δ 168.1, 167.0, 140.7, 133.5, 131.9, 123.9, 122.8, 60.2, 37.7, 31.5, 28.8, 28.7, 28.3, 28.0, 26.5, 14.0. MS (EI): 343 (3), 297 (17), 160 (100), 148 (20), 122 (28). Anal. Calcd for $C_{20}H_{25}NO_4$: C, 69.95; H, 7.34; N, 4.08. Found: C, 70.01; H, 7.34; N, 4.10.

1,6-Dinitro-6-methyl-2-phenylheptane (37). Overall yield (0.83 g, 59%) based on 4-methyl-4-nitro-1-pentene (**4h**) (0.72 g, 5.6 mmol) and nitrostyrene (0.56 g, 4 mmol). Reaction conditions: −40 °C, 4 h, then 0 °C, 2 h. Purification by flash chromatography (hexanes/ether = 4:1). IR (neat): 3055 (w), 3029 (w), 2951 (m), 1603 (m), 1535 (vs), 1382 (m), 771 (s), 702 (s) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 7.38−7.28 (m, 3H), 7.20−7.17 (m, 2H), 4.54 (d, J = 7.7 Hz, 2H), 3.50−3.40 (m, 1H), 1.94−1.67 (m, 4H), 1.50 (s, 6H), 1.22−1.15 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 138.8, 129.1, 128.0, 127.9, 127.5, 127.2, 87.9, 80.8, 44.0, 40.3, 32.7, 25.8, 21.5. MS (EI): 280 (M^+, 2), 233 (3), 131 (39), 117 (50), 104 (44), 91 (100), 69 (75). Anal. Calcd for $C_{14}H_{20}N_2O_4$: C, 59.98; H, 7.19; N, 9.99. Found: C, 60.16; H, 7.15; N, 10.08.

Diethyl (5-Methyl-5-nitro-1-phenylhexyl)malonate (38). Overall yield (1.16 g, 62%) based on 4-methyl-4-nitro-1-pentene (**4h**) (0.72 g, 5.6 mmol) and diethyl benzylidenemalonate (1.0 g, 4 mmol). Reaction conditions: −78 °C to −40 °C, 4 h, then 0 °C, 8 h. Purification by flash chromatography (hexanes/ethyl acetate = 4:1). IR (neat): 3064 (w), 3031 (w), 2984 (s), 1733 (vs), 1603 (w), 1538 (vs), 702 (s) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 7.22−7.08 (m, 5H), 4.16 (q, J = 7.2 Hz, 2H), 3.78 (q, J = 7.1 Hz, 2H), 3.54 (d, J = 10.8 Hz, 1H), 3.31−3.23 (m, 1H), 1.92−1.54 (m, 4H), 1.37 (d, J = 4.3, 6.0 Hz, 6H), 1.21 (t, J = 7.1 Hz, 3H), 1.04−0.92 (m, 2H), 0.55 (t, J = 7.1 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 168.2, 167.5, 140.2, 128.4, 128.3, 128.2, 127.0, 87.9, 61.4, 61.0, 58.6, 45.0, 40.2, 33.5, 25.7, 25.5, 21.4, 14.0, 13.6. MS (EI): 379 (M^+, 5), 241 (17), 189 (71), 172 (57), 117 (98), 69 (100). Anal. Calcd for $C_{20}H_{29}NO_6$: C, 63.31; H, 7.70; N, 3.96. Found: C, 63.30; H, 7.55; N, 3.68.

Ethyl 3-Butenylacrylate (40). Allylzinc bromide prepared from allyl bromide (7.2 g, 60 mmol) in THF (10 mL) and cut zinc foil (4.71 g, 72 mmol) in THF (5 mL) according to the procedure of Gaudemar[3] was added at −70 °C to a solution of CuCN·2LiCl (prepared from CuCN (5.37 g, 60 mmol) and LiCl (5.09 g, 120 mmol)) in THF (60 mL). The reaction mixture was stirred at −30 °C for 45 min and was cooled back to −78 °C. Ethyl (α-bromomethyl)acrylate (10.4 g, 54 mmol) was added, and the reaction mixture was allowed to warm to 0 °C and was worked up as usual. The residue obtained after evaporation of the solvents was purified by distillation affording the acrylate **40** as a colorless liquid (6.47 g, 42 mmol, 77% yield; bp 81−83 °C/32 mbar). IR (neat): 2980 (vs), 1720 (vs), 1635 (s), 1450 (m), 1370 (m), 1310 (m) cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$): δ 6.11 (d, J = 1.5 Hz, 1H), 5.76 (ddt, J = 17.1, 10.2, 6.5 Hz, 1H), 5.48 (q, J = 1.4 Hz, 1H), 5.03−4.90 (m, 2H), 4.16 (q, J = 7.2 Hz, 2H), 2.40−2.32 (m, 2H), 2.25−2.13 (m, 2H), 1.26 (t, J = 7.2 Hz, 3H). ^{13}C NMR (50 MHz, $CDCl_3$): δ 167.0, 140.1, 137.6, 124.6, 115.0, 60.5, 32.4, 31.2, 14.1. MS (EI): 154 (M^+, 1), 126 (19), 111 (29), 81 (100), 53 (23), 41 (67). Anal. Calcd for $C_9H_{14}O_2$: C, 70.10; H, 9.15. Found: C, 69.75; H, 9.14.

Ethyl 2-(6-Carbethoxy-6-heptenyl)acrylate (42). Prepared according to the typical procedure A in 77% overall yield (0.97 g) using ethyl α-(bromomethyl)acrylate[17] (0.78 g, 4.05 mmol) and the acrylate **40** (0.80 g, 5.2 mmol). Reaction conditions: −20 °C, 1 h. Purified by flash chromatography (hexanes/ether = 19:1). IR (neat): 2930 (m), 1720 (s), 1630 (m), 1180 (s), 1030 (m) cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$): δ 5.85 (s, 2H), 5.23 (s, 2H), 3.93 (q, J = 7.1 Hz, 4H), 2.03 (t, J = 7.2 Hz, 4H), 1.30−1.05 (m, 6H), 1.03 (t, J = 7.1 Hz, 6H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 167.0, 140.8, 123.9, 60.2, 31.5, 28.5, 28.0, 14.0. MS (EI): 268 (1), 223 (21), 194 (54), 121 (94), 81 (100), 41 (62). Anal. Calcd for $C_{15}H_{24}O_4$: C, 67.14; H, 9.01. Found: C, 66.94; H, 9.11.

Diethyl (6-Carbethoxy-1-phenyl-6-heptenyl)malonate (43). Prepared according to the typical procedure A in 83% overall yield (1.36 g) based on diethyl benzylidenemalonate (1.01 g, 4.05 mmol) and **40** (0.80 g, 5.2 mmol). Reaction conditions: 0 °C, 10 h. Purified by flash chromatography (hexanes/ether = 9:1). IR (neat): 2940 (s), 1760 (s), 1730 (s), 1030 (s), 700 (s) cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$): δ 7.14 (m, 5H), 5.99 (s, 1H), 5.33 (s, 1H), 4.16 (q, J = 7.1 Hz, 2H), 4.08 (q, J = 7.1 Hz, 2H), 3.78 (q, J = 7.1 Hz, 2H), 3.55 (d, J = 11.0 Hz, 1H), 3.30 (m, 1H), 2.10 (m, 2H), 1.60 (m, 2H), 1.21 (t, J = 7.2 Hz, 3H), 1.19 (t, J = 7.2 Hz, 3H), 1.50−1.00 (m, 4H), 0.83 (t, J = 7.1 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 168.2, 167.6, 166.9, 140.5, 128.1, 128.0, 126.6, 124.0, 61.2, 60.8, 60.2, 58.6, 45.3, 33.5, 31.3, 27.9, 26.4, 13.9, 13.8, 13.4. MS (EI): 404 (7), 244 (31), 198 (54), 131 (49), 91 (100), 41 (29). Anal. Calcd for $C_{23}H_{32}O_6$: C, 68.29; H, 7.97. Found: C, 67.99; H, 8.01.

(−)-(*1S,2S*)-6,6-Dimethyl-2-(3-carbethoxy-3-butenyl)-bicyclo[3.1.1]heptane (47). Prepared according to the typical procedure A in 85% overall yield (0.99 g) based on (−)-β-pinene (0.71 g, 5.2 mmol) and ethyl α-(bromomethyl)acrylate[17] (0.86 g, 4.5 mmol). Reaction conditions: −20 °C, 1 h. Purified by flash chromatography (hexanes/ether = 95:5). $[\alpha]^{25}_D$ = −15.7 (*c* 2.61, benzene). IR (neat): 2935 (vs), 1719 (vs), 1630 (m), 1468 (m), 1184 (s), 1159 (s) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 6.03 (s, 1H), 5.41 (s, 1H), 4.12 (q, J = 7.1 Hz, 2H), 2.26−2.16 (m, 3H), 1.91−1.76 (m, 6H), 1.50−1.37 (m, 4H), 1.22 (t, J = 7.2 Hz, 3H), 1.11 (s, 3H), 0.91 (s, 3H). ^{13}C NMR (50 MHz, $CDCl_3$): δ 167.5, 141.6, 124.2, 60.7, 46.6, 41.7, 41.3, 38.9, 36.7, 33.9, 30.6, 28.4, 26.7, 23.5, 22.6, 14.4. MS (EI): 230 (M^+, 5), 177 (20), 161 (28), 133 (38), 121 (34), 93 (40), 82 (100), 69 (89). Anal. Calcd for $C_{16}H_{26}O_2$: C, 76.75; H, 10.47. Found: C, 76.57; H, 10.28.

(−)-(1*S*,2*S*)-6,6-Dimethyl-2-(2-oxo-2-phenylethyl)bicyclo-[3.1.1]heptane (48). Prepared according to the typical procedure A in 82% overall yield (0.93 g) based on (−)-β-pinene (0.71 g, 5.2 mmol) and benzoyl chloride (0.63 g, 4.5 mmol). Reaction conditions: −20 °C, 4 h. Purified by flash chromatography (hexanes/ether = 9:1) $[\alpha]^{25}_D$ = −19.0 (*c* 3.06, benzene). IR (neat): 3064 (w), 2908 (s), 1686 (vs), 1448 (m), 751 (s), 690 (s) cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$): δ 7.87−7.83 (m, 2H), 7.45−7.35 (m, 3H), 3.05−3.01 (m, 2H), 2.75−2.55 (m, 1H), 2.30−2.15 (m, 1H), 2.10−1.81 (m, 6H), 1.50−1.35 (m, 1H), 1.11 (s, 3H), 1.01 (s, 3H). ^{13}C NMR (50 MHz, $CDCl_3$): δ 199.7, 137.0, 132.5, 128.2, 127.8, 46.1, 40.9, 38.4, 36.7, 33.2, 27.8, 26.0, 23.1, 21.9. MS (EI): 242 (M^+, 5), 122 (19), 105 (100), 77 (26). Anal. Calcd for $C_{17}H_{22}O$: C, 84.25; H, 9.15. Found: C, 84.14; H, 9.14.

Analytical Data of Products 49−54 of Table 2 Prepared According to the Typical Procedure A. Cyclohexyl Phenyl Ketone (49).[44] Overall yield (1.10 g, 86%) based on cyclohexene (0.62 g, 7.5 mmol) and benzoyl chloride (0.95 g, 6.75 mmol). Reaction conditions: 0 °C, 3 h (B/Zn-exchange) and −10 °C, 10 h (reaction with electrophile). Purified by flash chromatography (hexanes/ether = 9:1). The spectral data are identical with the literature.[44]

Ethyl 2-(2,3-Diphenylpropyl)acrylate (50). Overall yield (4.24 g, 95%) based on stilbene (3.0 g, 16.5 mmol) and ethyl α-(bromomethyl)acrylate[17] (2.90 g, 15.0 mmol). Reaction conditions: rt, 3 h (B/Zn-exchange) and −20 °C, 1 h (reaction with electrophile). Purified by flash chromatography (hexanes/ether = 9:1). IR (neat): 3030 (m), 1720 (s), 1500 (m), 1450 (m), 1130 (m), 700 (s) cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$): δ 7.30−7.13 (m, 10H), 6.11 (s, 1H), 5.34 (s, 1H), 4.18 (q, J = 7.0 Hz, 2H), 3.36−2.60 (m, 5H), 1.28 (t, J = 7.1 Hz, 3H). ^{13}C NMR (50 MHz, $CDCl_3$): δ 165.3, 142.1, 138.5, 137.1, 127.4, 126.4, 126.1, 124.1, 123.7, 58.8, 45.0, 41.3, 36.6, 12.4. MS (EI): 294 (6), 203 (100), 181 (72), 157 (57), 129 (72), 114 (85), 86 (69), 55 (62). Anal. Calcd for $C_{20}H_{22}O_2$: C, 81.60; H, 7.53. Found: C, 81.57; H, 7.61.

Diethyl (1,2,3-Triphenylpropyl)malonate (51). Overall yield (5.81 g, 90%) based on diethyl benzylidenemalonate (3.72 g, 15.0 mmol) and stilbene (3.0 g, 16.5 mmol). Reaction conditions: rt, 3 h (B/Zn-exchange) and 0 °C, 24 h (reaction with electrophile). Purified by flash chromatography (hexanes/ether = 4:1). The product was isolated as a 7:3 mixture of diastereoisomers. IR (neat): 1750 (s), 1600 (m), 1500 (s), 1450 (s), 1030 (s), 700 (s) cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$): δ 7.29 (m, 15H), 4.19 (m, 2H), 3.73 (m, 4H), 3.37 (m, 1H), 3.00−2.49 (m, 2H), 1.20 (t, J = 7.1 Hz, 2.18H), 0.97 (t, J = 7.2 Hz 0.82H), 0.82 (t, J = 7.2 Hz, 0.82H), 0.68 (t, J = 7.1 Hz, 2.18H). ^{13}C NMR (50 MHz, $CDCl_3$): δ 168.6, 168.5, 167.6, 141.2, 140.2, 140.0, 139.4, 139.2, 137.0, 130.3, 130.0, 129.7, 129.2, 129.1, 128.8, 128.2, 128.1, 127.8, 127.6, 127.3, 127.2, 127.0, 126.7, 126.6, 125.9, 125.6, 61.7, 61.3, 61.1, 60.9, 56.2, 56.0, 51.7, 51.2, 49.0, 48.5, 39.7, 39.5, 14.1, 13.9, 13.7, 13.5. MS (EI): 339 (9), 250 (16), 181 (100), 131 (18), 103 (22), 84 (42). Anal. Calcd for $C_{28}H_{30}O_4$: C, 78.11; H, 7.02. Found: C, 77.96; H, 7.41.

2-(2-Carbethoxy-2-propenyl)bicyclo[2.2.1]heptane (52). Overall yield (2.03 g, 93%) based on norbornene (1.15 g, 12 mmol) and ethyl α-(bromomethyl)acrylate[17] (2.03 g, 10.5 mmol). Reaction conditions: rt, 40 h (B/Zn-exchange) and −20 °C, 1 h (reaction with electrophile). Purified by flash chromatography (hexanes/ether = 19:1). The product was isolated as a *endo*:*exo* (2:1) mixture of isomers. IR (neat): 2950 (vs), 2870 (s), 1720 (vs), 1630 (m), 1455 (m), 1175 (s) cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$): δ 6.05 (s, 1H), 5.41 (s, 1H), 4.12 (q, J = 7.1 Hz, 2H), 2.30−1.90 (m, 5H), 1.80−0.90 (m, 8H), 1.22 (t, J = 7.1 Hz, 3H). ^{13}C NMR (50 MHz, $CDCl_3$): δ 167.2, 140.5, 139.7, 124.6, 124.2, 60.2, 40.4, 40.1, 39.8, 39.7, 38.4, 37.6, 37.0, 36.5, 35.0, 34.5, 29.9, 29.7, 28.6, 22.3, 14.0. MS (EI): 208 (5), 114 (10), 95 (100), 67 (23). Anal. Calcd for $C_{13}H_{20}O_2$: C, 74.96; H, 9.68. Found: C, 74.90; H, 9.98.

3-(2-Carbethoxy-2-propenyl)-(*1S,2R*)-2,6,6-trimethylbicyclo[3.1.1]heptane (53). Overall yield (1.26 g, 84%) based on α-pinene (0.95 g, 7.0 mmol) and ethyl α-(bromomethyl)acrylate[17] (1.16 g, 6.0 mmol). Reaction conditions: rt, 40 h (B/Zn-exchange) and −20 °C, 1 h (reaction with electrophile). Purified by flash chromatography (hexanes/ether = 19:1). The product was isolated as a 3:2 mixture of diastereoisomers. IR (neat): 2900 (vs), 1720 (vs), 1630 (m), 1160 (s), 1030 (m), 940 (m) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 6.06 (s, 0.4H), 6.04 (s, 0.6H), 5.46 (s, 0.4H), 5.44 (s, 0.6H), 4.10 (m, 2H), 2.57−1.30 (m, 10H), 1.23 (t, J = 7.1 Hz, 3H), 1.10 (m, 3H), 0.94 (m, 5H), 0.86 (s, 1H). ^{13}C NMR (75 MHz,

(44) Kondo, T.; Akazome, M.; Tsuji, Y.; Watanabe, Y. *J. Org. Chem.* **1990**, *55*, 1286.

$CDCl_3$): δ 167.3, 167.2, 140.4, 139.8, 125.2, 124.4, 60.3, 49.0, 48.2, 43.5, 43.4, 41.9, 40.9, 39.3, 38.7, 36.7, 34.9, 34.7, 34.2, 34.0, 32.3, 27.9, 27.6, 23.0, 22.9, 21.3, 16.1, 14.1. MS (EI): 250 (1), 137 (73), 93 (59), 83 (100), 69 (66), 55 (68), 41 (41). Anal. Calcd for $C_{16}H_{26}O_2$: C, 76.75; H, 10.42. Found: C, 76.54; H, 10.60.

1-(Triisopropylsilyloxy)-3-allylcyclopentane (54). Overall yield (0.18 g, 2.9 mmol, 72% yield) based on 4-(triisopropylsilyl)-1-cyclopentene (0.90 g, 4.0 mmol) and allyl bromide (4.84 g, 40 mmol). Reaction conditions: 0 °C, 3 h (B/Zn-exchange) and 0 °C, 1 h (reaction with electrophile). Purification by flash chromatography (hexanes/ether = 10:1). The product was obtained as a 3:2 mixture of diastereomers. IR (neat): 2935 (s), 1465 8), 1060 (s), 885 (s), 680 (s) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 5.75 (m, 1H), 4.93 (m, 2H), 4.29 (m, 1H), 2.25−1.05 (m, 9H), 1.00 (s, 21H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 138.3, 138.1, 114.8, 74.2, 74.0, 43.0, 42.6, 42.4, 41.0, 40.5, 37.4, 36.8, 36.1, 35.9, 35.8, 30.0, 29.7, 18.0, 12.2, 12.1. MS (EI): 239 (60), 131 (87), 103 (62), 75 (100), 61 (55). Anal. Calcd for $C_{17}H_{34}OSi$: C, 72.27; H, 12.13. Found: C, 72.12; H, 12.09.

Eicosanal (59). The aldehyde **59** was prepared according to the procedure developed by Corey.[25] A suspension of PCC (0.72 g, 3.3 mmol) and Celite (2 g) in CH_2Cl_2 (5 mL) was cooled to 0 °C, and eicosanol (**58**) (0.90 g, 3.0 mmol) in CH_2Cl_2 (10 mL) was added. After 10 h of stirring at rt, the brown slurry was filtered over a short silica column which was eluted with CH_2Cl_2 (400 mL) affording after evaporation of the solvents **59** (0.84 g, 94% yield) as a colorless solid (mp 50−51 °C; lit.:[45] 77−79 °C). IR (KBr): 2920 (vs), 2740 (w), 1710 (vs), 1470 (s), 1410 (m), 715 (s), 700 (m). ^1H NMR (200 MHz, $CDCl_3$): δ 9.72 (t, J = 1.8 Hz, 1H), 2.38 (td, J = 7.3, 1.9 Hz, 2H), 1.60−1.45 (m, 2H), 1.40−1.05 (m, 32H), 0.84 (t, J = 6.5 Hz, 3H). ^{13}C NMR (50 MHz, $CDCl_3$): δ 202.7, 43.9, 31.9, 30.0 (9C), 29.6, 29.4, 29.3 (2C), 29.1, 22.7, 22.0, 14.1. MS (EI): 296 (M^+, 1), 278 (9), 96 (49), 82 (84), 68 (56), 57 (100), 43 (98). Anal. Calcd for $C_{20}H_{40}O$: C, 81.01; H, 13.60. Found: C, 81.02; H, 13.53.

(*R*)-1-Bromo-6-pentacosanol (60). Prepared according to the typical procedure B (see below). Yield (310 mg, 69%, 92% ee) based on 5-bromo-1-pentene (**4e**) (2.24 g, 15.0 mmol) (**Caution!** Bis(5-bromopentyl)zinc may decompose in an explosive manner at higher temperatures. Reaction temperatures below 10 °C and a protecting shield should be used.) and eicosanal (**59**) (300 mg, 1.01 mmol). Reaction conditions: ether, 0 °C, 12 h. Purified by chromatography (hexanes/ether 5:1) and isolated as a colorless solid (mp 63−64 °C). The enantiomeric excess was determined by integration of the ^1H NMR signals of the (*S*)-*O*-acetylmandelic ester derivative at δ 3.38 (t) and 3.22 (t) (ratio 96:4). $[\alpha]^{25}_D = +1.0$ (*c* 0.99, $CHCl_3$). IR (KBr): 3320 (m), 2930 (vs), 2860 (s), 1470 (m), 720 (w). ^1H NMR (200 MHz, $CDCl_3$): δ 3.57 (s, 1H), 3.40 (t, J = 7.3 Hz, 2H), 1.89−1.79 (m, 3H), 1.47−1.14 (m, 42H), 0.86 (t, J = 6.2 Hz, 3H). ^{13}C NMR (50 MHz, $CDCl_3$): δ 71.8, 37.6, 37.2, 33.9, 32.7, 31.9, 29.7 (13C), 29.4, 28.2, 25.6, 24.8, 22.7, 14.1. MS (EI): 430 (6), 428 (6), 297 (99), 179 (82), 97 (66), 69 (62), 57 (100). Anal. Calcd for $C_{25}H_{51}BrO$: C, 67.09; H, 11.48. Found: C, 66.97; H, 11.36.

(*S*)-10-Nonacosanol (57). To $Bu_2Cu(CN)Li_2$[27] in THF (1 mL) prepared from n-BuLi (1.4 M solution in hexanes 1.4 mL, 2 mmol) and CuCN (89 mg, 1.0 mmol) was added at −60 °C (*R*)-1-bromo-6-pentacosanol (**60**) (89 mg, 0.20 mmol) in THF (2 mL). The reaction mixture was warmed to 0 °C and stirred for 1 h. After the usual workup, the crude product was purified by chromatography (hexanes/ether/$CHCl_3$ 10:1:1) affording the desired product as a colorless solid (78 mg, 95%; mp 80−80.5 °C, lit.:[46] 81−81.5 °C). $[\alpha]^{25}_D = 0.0$ (*c* 1.05, $CHCl_3$); lit.:[46] $[\alpha]^{25}_D = 0$ (*c* 2.5, $CHCl_3$), $[\alpha]^{25}_D = 2.18$ (*c* 1.1, $CHCl_3$). IR (KBr): 3340 (m), 3240 (m), 2920 (vs), 2850 (m), 1470 (m), 720 (m). ^1H NMR (500 MHz, 318 K, $CDCl_3$): δ 3.55 (s, 1H), 1.44−1.24 (m, 53H), 0.86 (t, J = 7.0 Hz, 6H). ^{13}C NMR (125 MHz, 318 K, $CDCl_3$): δ 72.1, 37.6 (2C), 31.94, 31.91, 29.8−29.6 (16C), 29.35, 29.32, 25.7 (2C), 22.7 (2C), 14.1 (2C). MS (EI): 423 (1), 406 (18), 297 (39), 278 (2), 97 (60), 83 (100). Anal. Calcd for $C_{29}H_{60}O$: C, 82.00; H, 14.24. Found: C, 81.95; H, 14.13.

Typical Procedure B for the One-Pot Hydroboration, Boron−Zinc Exchange and Asymmetric Addition to Aldehydes. Preparation of (*R*)-Ethyl 7-Hydroxy-2-methylenedodecanoate (56o) (entry 15 of Table III). (a) Hydroboration: A 50 mL two-neck flask equipped with an argon inlet and a rubber septum was charged under argon with ethyl 3-butenylacrylate **(40)** (1.47 g, 9.1 mmol). Diethylborane (0.83 g, 9.0 mmol) was added at −10 °C over 15 min. The reaction was allowed to slowly warm to rt and was stirred for 2 h. The volatiles were evaporated under vacuum (0.3 mmHg) affording the crude hydroboration product (1.72 g).

(b) Boron−Zinc Exchange: To the organoborane prepared above was added Et_2Zn (2.0 mL, 19.5 mmol) at 0 °C. After 0.5 h, the excess diethylzinc and formed triethylborane were evaporated (0.3 mmHg, 50 °C, 4 h). The resulting dialkylzinc was diluted with toluene (4 mL) and was ready to use for the next step.

(c) Asymmetric addition: A suspension of (*1R,2R*)-1,2-bis-(trifluoromethanesulfonamido)cyclohexane (**55**) (42 mg, 0.112 mmol) and titanium(IV) isopropoxide (0.80 g, 2.81 mmol) in toluene (1 mL) was warmed to 50 °C for 0.5 h and cooled to −60 °C. The dialkylzinc prepared above was added via syringe, and the resulting yellowish-green reaction mixture was warmed to −20 °C and was stirred for 20 min at this temperature. Hexanal (140 mg, 1.40 mmol) was added and the reaction mixture was stirred at this temperature for 12 h. It was quenched with a saturated aqueous NH_4Cl solution (50 mL), and the precipitate formed was dissolved by adding aqueous HCl (10%). The aqueous phase was extracted with ether (2 × 50 mL). The combined organic phase was dried ($MgSO_4$), and evaporating of the solvents afforded a crude oil which was purified by chromatography (hexanes/ether = 3:1) leading to analytically pure **56o** (257 mg, 72% yield, 95% ee). $[\alpha]^{25}_D = +0.3$ (*c* 3.34, $CHCl_3$).

Analytical Data of Compounds 56a−w of Table III Prepared According to the Typical Procedure B. (*S*)-1-Phenyl-1-nonanol (56a). Yield (495 mg, 87%, 92% ee) based on octene (1.25 g, 10.2 mmol) and benzaldehyde (275 mg, 2.60 mmol). Purified by chromatography (hexanes/ether = 10:1). The enantiomeric excess was determined by integration of the ^1H NMR signals of the (*S*)-*O*-acetylmandelic ester derivative at δ 5.96 (s) and 5.95 (s) (ratio 96:4). $[\alpha]^{25}_D = -24.2$ (*c* 6.60, $CHCl_3$); lit.:[21g] $[\alpha]^{25}_D = -25.6$ (*c* 3.12, $CHCl_3$). IR (neat): 3350 (s), 3030 (w), 2920 (vs), 2860 (s), 1450 (m), 1030 (m). ^1H NMR (200 MHz, $CDCl_3$): δ 7.33−7.24 (m, 5H), 4.66 (t, J = 6.6 Hz, 1H), 1.97 (s, 1H), 1.75−1.67 (m, 2H), 1.39−1.18 (m, 12H), 0.86 (t, J = 7.1 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 145.0, 128.4 (2C), 127.4, 125.9 (2C), 74.7, 39.1, 31.8, 29.5 (2C), 29.2, 25.8, 22.6, 14.1. MS (EI): 220 (M^+, 1), 107 (100), 77 (30), 57 (18). Anal. Calcd for $C_{15}H_{24}O$: C, 81.76; H, 10.98. Found: C, 81.68; H, 11.15.

(*S*)-(*E*)-4-Tetradecen-6-ol (56b). Yield (291 mg, 75%, > 96% ee) based on octene (2.64 g, 23.5 mmol) and hexanal (180 mg, 1.83 mmol). Reaction conditions: rt, 12 h, using $Ti(O\textit{t}\text{-}Bu)_4$.[30] Purification by chromatography (hexanes/ether = 10:1). The enantiomeric excess was determined by integration of the ^1H NMR signals at δ 5.89 (s) and 5.65 (m) of the (*S*)-*O*-acetylmandelic ester derivative (ratio: >98:<2). $[\alpha]^{25}_D = -1.6$ (*c* 5.49, $CHCl_3$). IR (neat): 3350 (s), 2930 (s), 2840 (s), 1470 (m), 1385 (w), 970 (m). ^1H NMR (200 MHz, $CDCl_3$): δ 5.61 (dt, J = 15.3, 6.4 Hz, 1H), 5.43 (ddt, J = 15.3, 6.9, 1.0 Hz, 1H), 4.01 (m, 1H), 1.99 (q, J = 7.0 Hz, 2H), 1.48−1.18 (m, 17H), 0.92−0.83 (m, 6H). ^{13}C NMR (50 MHz, $CDCl_3$): δ 133.3, 131.8, 73.2, 37.3, 34.2, 31.8, 29.5, 29.2, 25.5 (2C), 22.6, 22.3, 14.1, 13.6. MS (EI): 212 (M^+, 1), 194 (1), 99 (94), 57 (100), 43 (13). Anal. Calcd for $C_{14}H_{28}O$: C, 79.18; H, 13.29. Found: C, 79.23; H, 13.24.

(*S*)-(*E*)-3-Methyl-2-dodecen-4-ol (56c). Yield (250 mg, 62%, >96% ee) based on octene (2.22 g, 19.8 mmol) and (*E*)-2-methyl-2-butenal (170 mg, 2.02 mmol). Purification by chromatography (hexanes/ether = 10:1). The enantiomeric

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excess was determined by integration of the ^{1}H NMR signals at δ 5.23 (q) and 5.44 (q) of the (*S*)-*O*-acetylmandelic ester derivative (ratio >98:<2). $[\alpha]^{25}_D = -2.2$ (*c* 4.16, $CHCl_3$). IR (neat): 3350 (m), 2925 (vs), 2860 (s), 1470 (m), 1380 (m), 1005 (m). ^{1}H NMR (200 MHz, $CDCl_3$): δ 5.46−5.40 (m, 1H), 3.95 (t, J = 6.6 Hz, 1H), 1.59−1.46 (m, 9H), 1.25 (s, 12H), 0.86 (m, 3H). ^{13}C NMR (50 MHz, $CDCl_3$): δ 138.3, 120.7, 78.1, 34.8, 31.9, 29.6, 29.5, 29.3, 25.9, 22.6, 14.1, 13.0, 10.8. MS (EI): 198 (M^+, 2), 180 (16), 95 (44), 85 (100), 82 (33), 81 (44), 68 (55). Anal. Calcd for $C_{13}H_{26}O$: C, 78.72; H, 13.21. Found: C, 78.82; H, 13.22.

(*S*)-1-Phenyl-1-undecanol (56d). Yield (500 mg, 88%, > 96% ee) based on decene (3.19 g, 22.8 mmol) and benzaldehyde (255 mg, 240 mmol). Reaction conditions: ether, 0 °C. Purification by chromatography (hexanes/ether = 10:1). The enantiomeric excess was determined by integration of the ^{1}H NMR signals at δ 5.98 (s) and 5.96 (s) of the (*S*)-*O*-acetylmandelic ester derivative (ratio >98:<2). $[\alpha]^{25}_D = -20.1$ (*c* 6.71, $CHCl_3$). IR (neat): 3450 (s), 3065 (w), 2920 (vs), 2850 (s), 1445 (m), 1025 (m). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.37−7.28 (m, 5H), 4.68 (t, J = 6.6 Hz, 1H), 1.90 (s, 1H), 1.83−1.27 (m, 18H), 0.91 (t, J = 6.5 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 145.0, 128.3 (2C), 127.3, 125.9 (2C), 74.6, 39.1, 31.9, 29.5−29.2 (5C), 25.8, 22.6, 14.1. MS (EI): 248 (M^+, 3), 107 (100), 91 (13), 79 (37), 41 (15). Anal. Calcd for $C_{17}H_{28}O$: C, 82.20; H, 11.36. Found: C, 82.15; H, 11.38.

(*S*)-1-(1-Cyclohexenyl)-1-undecanol (56e). Yield (350 mg, 73%, >96% ee) based on decene (2.09 g, 14.9 mmol) and cyclohexenecarboxaldehyde (210 mg, 1.91 mmol). Purification by chromatography (hexanes/ether = 20:1). The enantiomeric excess was determined by integration of the ^{1}H NMR signals at δ 5.46 (m) and 5.67 (m) of the (*S*)-*O*-acetylmandelic ester derivative (ratio >98:<2). $[\alpha]^{25}_D = +1.8$ (*c* 11.9, $CHCl_3$). IR (neat): 3340 (s), 2920 (vs), 2855 (s), 1440 (m), 920 (m), 840 (w), 800 (w). ^{1}H NMR (300 MHz, $CDCl_3$): δ 5.60 (s, 1H), 3.90 (t, J = 6.7 Hz, 1H), 2.05−1.84 (m, 5H), 1.64−1.42 (m, 6H), 1.23 (s, 16H), 0.85 (t, J = 6.7 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 140.1, 122.9, 76.7, 34.8, 31.9, 29.6 (4C), 29.3, 25.8, 24.9, 23.3, 22.7 (3C), 14.0. MS (EI): 252 (M^+, 3), 234 (21), 135 (30), 121 (24), 111 (83), 107 (72), 94 (100). Anal. Calcd for $C_{17}H_{32}O$: C, 80.89; H, 12.78. Found: C, 80.64; H, 12.60.

(*S*)-[(*1S,2S*)-6,6-Dimethylbicyclo[3.1.1]hept-2-ylmethyl]-phenylmethanol (56f). Yield (70 mg, 17%, >96% *de*) as a colorless solid (mp 59−60 °C) using (−)-β-pinene (2.56 g, 18.8 mmol) and benzaldehyde (185 mg, 1.74 mmol). Purification by chromatography (hexanes/ether = 10:1). The diastereomeric excess was determined by integration of the ^{1}H NMR signals at δ 0.83 (s) and 0.94 (s) of the (*S*)-*O*-acetylmandelic ester derivative (ratio >98:<2). $[\alpha]^{25}_D = -40.5$ (*c* 2.79, $CHCl_3$). IR (neat): 3300 (s), 3050 (w), 2910 (s), 1460 (m), 1025 (m), 765 (m). ^{1}H NMR (200 MHz, $CDCl_3$): δ 7.34−7.18 (m, 5H), 4.64 (m, 1H), 2.30−2.19 (m, 2H), 1.95−0.74 (m, 10H), 1.13 (s, 3H), 0.95 (s, 3H). ^{13}C NMR (50 MHz, $CDCl_3$): δ 145.4, 128.4 (2C), 127.4, 125.8 (2C), 72.7, 47.5, 47.1, 41.3, 38.7, 37.3, 33.7, 28.1, 26.4, 23.3, 22.2. MS (EI): 244 (M^+, 3), 226 (12), 159 (22), 122 (41), 107 (100), 105 (46), 79 (75). Anal. Calcd for $C_{17}H_{24}O$: C, 83.55; H, 9.90. Found: C, 83.65; H, 9.88.

(*S*)-Cyclohexylphenylmethanol (56g). Yield (290 mg, 67%, 80% ee) as a colorless solid (mp 66 °C) using cyclohexene (1.54 g, 18.8 mmol) and benzaldehyde (240 mg, 2.26 mmol). Purified by chromatography (hexanes/ether = 10:1). $[\alpha]^{25}_D = -36.0$ (*c* 2.25, ether). The enantiomeric excess was determined by integration of the ^{1}H NMR signals at δ 5.46 (d) and 5.48 (d) of the (*S*)-*O*-acetylmandelic ester derivative (ratio 90:10). IR (KBr): 3413 (s), 3087 (w), 2917 (vs), 2849 (s), 1444 (m), 765 (m), 698 (m). ^{1}H NMR (200 MHz, $CDCl_3$): δ 7.34−7.19 (m, 5H), 4.31 (d, J = 7.1 Hz, 1H), 1.99−0.90 (m, 12H). ^{13}C NMR (50 MHz, $CDCl_3$): δ 143.6, 128.1 (2C), 127.3, 126.6 (2C), 79.3, 44.9, 29.2, 28.8, 26.4, 26.0, 25.9. MS (EI): 190 (M^+, 49), 107 (100), 79 (35), 41 (13). Anal. Calcd for $C_{13}H_{18}O$: C, 82.06; H, 9.53. Found: C, 81.92; H, 9.76.

(*S*)-1-Phenyl-4-pivaloxy-1-butanol (56h). Yield (280 mg, 70%, 93% ee) based on allyl pivalate (4.95 g, 34.8 mmol) and benzaldehyde (170 mg, 1.60 mmol). Purified by chromatography (hexanes/ether = 3:1). The enantiomeric excess was determined by integration of the ^{1}H NMR signals at δ 4.03 (t) and 3.89 (t) of the (*S*)-*O*-acetylmandelic ester derivative (ratio 96.5:3.5). $[\alpha]^{25}_D = -22.4$ (*c* 3.17, benzene). IR (neat): 3430 (m), 2960 (vs), 1710 (vs), 1290 (s), 1160 (s), 760 (m). ^{1}H NMR (200 MHz, $CDCl_3$): δ 7.34−7.26 (m, 5H), 4.70−4.65 (m, 1H), 4.08−4.02 (m, 2H), 2.10 (s, 1H), 1.88−1.60 (m, 4H), 1.17 (s, 9H). ^{13}C NMR (50 MHz, $CDCl_3$): δ 178.6, 144.5, 128.5 (2C), 127.6, 125.8 (2C), 74.0, 64.1, 38.7, 35.3, 27.2 (3C), 25.1. MS (EI): 250 (M^+, 3), 120 (53), 107 (96), 103 (91), 57 (100). HRMS. Calcd for $C_{15}H_{22}O_3$: 250.1569. Found: 250.1561.

(*S*)-1-Cyclohexyl-4-pivaloxy-1-butanol (56i). Yield (85 mg, 22%, 78% ee) based on allyl pivalate (4.95 g, 34.8 mmol) and cyclohexanecarboxaldehyde (170 mg, 1.52 mmol). Purified by chromatography (hexanes/ether = 3:1). The enantiomeric excess was determined by integration of the ^{1}H NMR signals at δ 3.99 (m) and 3.75 (m) of the (*S*)-*O*-acetylmandelic ester derivative (ratio 89:11). $[\alpha]^{25}_D = -5.0$ (*c* 2.61, $CHCl_3$). IR (neat): 3440 (m), 2925 (vs), 1730 (vs), 1290 (s), 1160 (s). ^{1}H NMR (200 MHz, $CDCl_3$): δ 4.06 (t, J = 6.0 Hz, 2H), 3.38−3.32 (m, 1H), 1.78−1.10 (m, 16H), 1.17 (s, 9H). ^{13}C NMR (50 MHz, $CDCl_3$): δ 178.6, 75.7, 64.4, 43.7, 38.7, 30.3, 29.2, 27.8, 27.2 (3C), 26.5, 26.3, 26.1, 25.2. MS (EI): 248 (1), 103 (39), 95 (28), 71 (100), 57 (53). Anal. Calcd for $C_{15}H_{28}O_3$: C, 70.27; H, 11.01. Found: C, 69.89; H, 10.70.

(*S*)-1-(1-Cyclohexenyl)-4-pivaloxy-1-pentanol (56j). Yield (272 mg, 52%, 95% ee) based on 3-butenyl pivalate (2.52 g, 16.1 mmol) and cyclohexenecarboxaldehyde (215 mg, 1.95 mmol). Purified by chromatography (hexanes/ether = 5:1). The enantiomeric excess was determined by integration of the ^{1}H NMR signals at δ 5.45 (s) and 5.67 (s) of the (*S*)-*O*-acetylmandelic ester derivative (ratio 97.5:2.5). $[\alpha]^{25}_D = +2.5$ (*c* 4.73, $CHCl_3$). IR (neat): 3420 (s), 2920 (vs), 1720 (s), 1290 (s), 1190 (s), 1030 (m). ^{1}H NMR (200 MHz, $CDCl_3$): δ 5.62 (s, 1H), 4.03 (t, J = 6.5 Hz, 2H), 3.93 (t, J = 6.6 Hz, 1H), 2.00 (s, 5H), 1.66−1.23 (m, 10H), 1.16 (s, 9H). ^{13}C NMR (50 MHz, $CDCl_3$): δ 178.6, 139.7, 123.3, 76.5, 64.2, 38.7, 34.2, 28.5, 27.2 (3C), 25.0, 23.2, 22.6 (2C), 22.2. MS (EI): 250 (1), 166 (27), 111 (53), 67 (56), 57 (100), 41 (65). Anal. Calcd for $C_{16}H_{28}O_3$: C, 71.60; H, 10.51. Found: C, 71.65; H, 10.66.

(*S*)-11-Pivaloxy-4-undecen-6-ol (56k). Yield (261 mg, 41%, 95% ee) using 4-pentenyl pivalate (2.81 g, 16.5 mmol) and (*E*)-2-hexenal (230 mg, 2.34 mmol). Reaction conditions: rt, Ti(O*t*-Bu$_4$). Purified by chromatography (hexanes/ether = 5:1). The enantiomeric excess was determined by integration of the ^{1}H NMR signals at δ 4.01 (t) and 3.91 (t) of the (*S*)-*O*-acetylmandelic ester derivative (ratio >97.5:<2.5). $[\alpha]^{25}_D = -0.2$ (*c* 4.26, $CHCl_3$). IR (neat): 3340 (m), 2940 (vs), 1730 (vs), 1485 (s), 1285 (s), 1160 (s). ^{1}H NMR (200 MHz, $CDCl_3$): δ 5.60 (dt, J = 15.4, 6.6 Hz, 1H), 5.41 (dd, J = 15.4, 7.0 Hz, 1H), 4.00 (t, J = 6.7 Hz, 3H), 1.97 (q, J = 7.0 Hz, 2H), 1.63−1.31 (m, 11H), 1.16 (s, 9H), 0.87 (t, J = 7.3 Hz, 3H). ^{13}C NMR (50 MHz, $CDCl_3$): δ 178.6, 133.1, 132.0, 73.0, 64.3, 38.7, 37.1, 34.2, 28.6, 27.2 (3C), 25.9, 25.1, 22.3, 13.6. MS (EI): 270 (M^+, 1), 252 (1), 125 (25), 103 (99), 99 (61), 85 (29), 57 (100). Anal. Calcd for $C_{16}H_{30}O_3$: C, 71.07; H, 11.18. Found: C, 71.18; H, 11.30.

(*S*)-2-Methyl-10-pivaloxy-4-decanol (56l). Yield (407 mg, 60%, 90% ee) using 5-hexenyl pivalate (3.67 g, 20.0 mmol) and 3-methylbutanal (215 mg, 2.50 mmol). Purified by chromatography (hexanes/ether = 5:1). The enantiomeric excess was determined by integration of the ^{1}H NMR signals at δ 4.00 (t) and 3.94 (t) of the (*S*)-*O*-acetylmandelic ester derivative (ratio 95:5). $[\alpha]^{25}_D = +6.1$ (*c* 2.31, $CHCl_3$). IR (neat): 3400 (m), 2920 (vs), 1725 (vs), 1370 (m), 1290 (m), 1170 (s). ^{1}H NMR (200 MHz, $CDCl_3$): δ 4.02 (t, J = 6.6 Hz, 2H), 3.64 (s, 1H), 1.74−1.15 (m, 14H), 1.16 (s, 9H), 0.89 (d, J = 6.6 Hz, 3H), 0.86 (d, J = 6.6 Hz, 3H). ^{13}C NMR (50 MHz, $CDCl_3$): δ 178.6, 69.9, 64.4, 46.9, 38.7, 37.9, 29.3, 28.5, 27.2 (3C), 25.9, 25.5, 24.6, 23.5, 22.1. MS (EI): 215 (6), 113 (20), 103 (100), 85 (37), 69 (38), 57 (84). Anal. Calcd for $C_{16}H_{32}O_3$: C, 70.54; H, 11.84. Found: C, 70.44; H, 11.73.

(*S*)-Ethyl 7-(4-Cyanophenyl)-7-hydroxy-2-methyleneheptanoate (56m). Yield (437 mg, 69%, 80% ee) using **40** (2.16 g, 14.0 mmol) and 4-cyanobenzaldehyde (286 mg, 2.20 mmol). Purified by chromatography (hexanes/ether = 3:1). The enantiomeric excess was determined by integration of the ^{1}H NMR signals at δ 5.46 (m) and 5.38 (m) of the (*S*)-*O*-

acetylmandelic ester derivative (ratio 90:10). $[\alpha]^{25}_D = -10.5$ (*c* 3.34, $CHCl_3$). IR (neat): 3480 (s), 2940 (vs), 2230 (s), 1720 (vs), 1630 (m), 840 (m). ^{1}H NMR (200 MHz, $CDCl_3$): δ 7.57 (d, J = 8.0 Hz, 2H), 7.40 (d, J = 8.4 Hz, 2H), 6.07−6.06 (m, 1H), 5.72−5.71 (m, 1H), 4.68 (t, J = 6.0 Hz, 1H), 4.13 (q, J = 7.2 Hz, 2H), 2.70 (s, 1H), 2.23 (t, J = 7.0 Hz, 2H), 2.05−1.20 (m, 6H), 1.24 (t, J = 7.2 Hz, 3H). ^{13}C NMR (50 MHz, $CDCl_3$): δ 167.2, 150.4, 140.5, 132.1 (2C), 126.4 (2C), 124.6, 118.8, 110.8, 73.4, 60.5, 38.8, 31.6, 28.1, 25.0, 14.1. MS (EI): 269 (1), 156 (7), 120 (12), 105 (43), 91 (100), 77 (34). Anal. Calcd for $C_{17}H_{21}NO_3$: C, 71.06; H, 7.37; N, 4.87. Found: C, 71.01; H, 7.53; N, 5.18.

(*S*)-Ethyl 7-Hydroxy-7-[(*S*)-4-isopropenylcyclohexen-1-yl]heptanoate (56n). Yield (210 mg, 71%, 85% *de*) based on **40** (0.88 g, 5.70 mmol) and (*S*)-perillaldehyde (150 mg, 0.97 mmol). Purified by chromatography (hexanes/ether = 3:1). The diastereomeric excess was determined by integration of the ^{1}H NMR signals at δ 6.10−6.12 (m) and 6.07−6.09 (m) of the (*S*)-*O*-acetylmandelic ester derivative (ratio 92.5:7.5). $[\alpha]^{25}_D = -44.7$ (*c* 4.70, $CHCl_3$). IR (neat): 3400 (m), 2940 (vs), 1715 (s), 1635 (m), 1285 (s), 990 (m). ^{1}H NMR (200 MHz, $CDCl_3$): δ 6.10−6.08 (m, 1H), 5.61 (s, 1H), 5.48−5.46 (m, 1H), 4.68−4.66 (m, 2H), 4.15 (q, J = 7.2 Hz, 2H), 3.93 (t, J = 6.4 Hz, 1H), 2.30−1.41 (m, 16H), 1.69 (s, 3H), 1.25 (t, J = 7.1 Hz, 3H). ^{13}C NMR (50 MHz, $CDCl_3$): δ 167.2, 149.5, 140.8, 139.5, 124.2, 121.9, 108.5, 76.0, 60.4, 41.0, 34.7, 31.7, 30.3, 28.3, 27.3, 25.2, 23.9, 20.7, 14.1. MS (EI): 306 (M^+, 2), 288 (3), 156 (100), 149 (37), 133 (37), 105 (40), 91 (52). Anal. Calcd for $C_{19}H_{30}O_3$: C, 74.47; H, 9.87. Found: C, 74.33; H, 9.91.

(*R*)-Ethyl 7-Hydroxy-2-methylenedodecanoate (56o). Yield (257 mg, 72%, 95% ee) based on **40** (1.47 g, 9.07 mmol) and hexanal (140 mg, 1.40 mmol). Purified by chromatography (hexanes/ether = 3:1). The enantiomeric excess was determined by integration of the ^{1}H NMR signals at δ 5.48 (s) and 5.37 (s) of the (*S*)-*O*-acetylmandelic ester derivative (ratio 97.5:2.5). $[\alpha]^{25}_D = +0.3$ (*c* 3.34, $CHCl_3$). IR (neat): 3420 (m), 2930 (vs), 1720 (vs), 1630 (m), 940 (m), 820 (w). ^{1}H NMR (200 MHz, $CDCl_3$): δ 6.46 (m, 1H), 5.44 (m, 1H), 4.13 (q, J = 7.1 Hz, 2H), 3.50 (s, 1H), 2.26−2.20 (m, 2H), 1.86 (s, 1H), 1.60−1.20 (m, 14H), 1.23 (t, J = 7.2 Hz, 3H), 0.82 (t, J = 6.0 Hz, 3H). ^{13}C NMR (50 MHz, $CDCl_3$): δ 167.2, 140.8, 124.2, 71.60, 60.4, 37.3, 37.0, 32.8, 32.7, 28.4, 25.2, 25.1, 22.5, 14.0, 13.9. MS (EI): 238 (4), 185 (21), 156 (45), 139 (100), 128 (28). Anal. Calcd for $C_{15}H_{28}O_3$: C, 70.27; H, 11.01. Found: C, 69.99; H, 11.07.

(*S*)-1-Phenyl-4-(triisopropylsiloxy)-1-butanol (56p). Yield (365 mg, 60%, 50% ee) based on 3-triisopropylsiloxy-1-propene (2.54 g, 11.8 mmol) and benzaldehyde (200 mg, 1.88 mmol). Purified by chromatography (hexanes/ether = 10:1). The enantiomeric excess was determined by integration of the ^{1}H NMR signals at δ 3.65 (t) and 3.49 (t) of the (*S*)-*O*-acetylmandelic ester derivative (ratio 75:25). $[\alpha]^{25}_D = -17.0$ (*c* 3.23, $CHCl_3$). IR (neat): 3370 (m), 2945 (s), 1470 (m), 1110 (m), 885 (m), 760 (w), 700 (m). ^{1}H NMR (200 MHz, $CDCl_3$): δ 7.32−7.19 (m, 5H), 4.70−4.63 (m, 1H), 3.72 (t, J = 6.0 Hz, 2H), 3.25 (s, 1H), 1.90−1.78 (m, 2H), 1.67−1.59 (m, 2H), 1.09−0.99 (m, 21H). ^{13}C NMR (50 MHz, $CDCl_3$): δ 145.0, 128.2 (2C), 127.1, 125.8 (2C), 74.1, 63.6, 36.7, 29.3, 18.3 (6C), 11.9 (t, J = 29 Hz, 3C). MS (EI): 322 (M^+, 1), 131 (100), 91 (12), 75 (13). Anal. Calcd for $C_{19}H_{34}O_2Si$: C, 70.75; H, 10.62. Found: C, 70.54; H, 10.45.

(*S*)-5-(*tert*-Butyldimethylsiloxy)-1-phenyl-1-pentanol (56q). Yield (360 mg, 82%, 92% ee) based on 4-(*tert*-butyldimethylsiloxy)-1-butene (1.86 g, 10.0 mmol) and benzaldehyde (159 mg, 1.50 mmol). Purified by chromatography (hexanes/ether = 8:1 then 5:1). The enantiomeric excess was determined by integration of the ^{1}H NMR signals at δ 3.57 (t) and 3.42 (t) of the (*S*)-*O*-acetylmandelic ester derivative (ratio 96:4). $[\alpha]^{25}_D = -8.6$ (*c* 0.7, EtOH). IR (neat): 3360 (m), 2940 (vs), 2860 (s), 1470 (w), 1100 (s), 770 (m), 700 (m). ^{1}H NMR (200 MHz, $CDCl_3$): δ 7.32−7.18 (m, 5H), 4.58 (t, J = 5.8 Hz, 1H), 3.55 (t, J = 6.5 Hz, 2H), 2.32 (s, 1H), 1.77−1.13 (m, 6H), 0.85 (s, 9H), 0.00 (s, 6H). ^{13}C NMR (50 MHz, $CDCl_3$): δ 144.9, 128.3 (2C), 127.3, 125.8 (2C), 74.4, 63.0, 38.7, 32.5, 25.9 (3C), 22.0, 18.2, −5.4 (2C). MS (EI): 257 (1), 147 (47), 117 (23), 107 (27), 105 (45), 75 (100). Anal. Calcd for $C_{17}H_{30}O_2Si$: C, 69.33; H, 10.27. Found: C, 69.49; H, 10.08.

(*S*)-5-(*tert*-Butyldimethylsiloxy)-1-(cyclohexen-1-yl)-1-pentanol (56r). Yield (280 mg, 63%, 94% ee) based on 4-(*tert*-butyldimethylsiloxy)-1-butene (1.86 g, 10.0 mmol) and cyclohexenecarboxaldehyde (165 mg, 1.50 mmol). Purified by chromatography (hexanes/ether = 8:1). The enantiomeric excess was determined by integration of the ^{1}H NMR signals at δ 5.46 (s) and 5.67 (s) of the (*S*)-*O*-acetylmandelic ester derivative (ratio 97:3). $[\alpha]^{25}_D = 2.0$ (*c* 3.0, $CHCl_3$). IR (neat): 3340 (s), 2920 (vs), 1460 (m), 1250 (s), 1100 (s), 840 (s), 770 (m). ^{1}H NMR (200 MHz, $CDCl_3$): δ 5.60 (s, 1H), 3.91 (t, J = 6.4 Hz, 1H), 3.58 (t, J = 6.4 Hz, 2H), 2.05−1.14 (m, 15H), 0.86 (s, 9H), 0.03 (s, 6H). ^{13}C NMR (50 MHz, $CDCl_3$): δ 139.9, 123.0, 76.6, 63.1, 34.5, 32.7, 25.9 (3C), 24.9, 23.3, 22.6 (2C), 22.1, 18.3, −5.3 (2C). MS (EI): 298 (M^+, 1), 149 (60), 131 (36), 107 (39), 93 (54), 81 (93), 75 (100). Anal. Calcd for $C_{17}H_{34}O_2Si$: C, 68.40; H, 11.48. Found: C, 68.24; H, 11.50.

(*S*)-7-Bromo-1-(4-cyanophenyl)-1-heptanol (56s). Yield (503 mg, 85%, 88% ee) based on 6-bromo-1-hexene (2.61 g, 16.0 mmol) and 4-cyanobenzaldehyde (262 mg, 2.00 mmol). Purified by chromatography (hexanes/ether = 3:1). The enantiomeric excess was determined by integration of the ^{1}H NMR signals at δ 3.37 (t) and 3.32 (t) of the (*S*)-*O*-acetylmandelic ester derivative (ratio 94:6). $[\alpha]^{25}_D = -14.8$ (*c* 9.23, $CHCl_3$). IR (neat): 3430 (s), 2940 (vs), 2230 (s), 840 (m). ^{1}H NMR (200 MHz, $CDCl_3$): δ 7.57 (d, J = 8.2 Hz, 2H), 7.41 (d, J = 8.2 Hz, 2H), 4.71−4.65 (m, 1H), 3.35 (t, J = 6.7 Hz, 2H), 2.30 (s, 1H), 1.82−1.64 (m, 4H), 1.41−1.31 (m, 6H). ^{13}C NMR (50 MHz, $CDCl_3$): δ 150.2, 132.2 (2C), 126.44 (2C), 118.8, 110.9, 73.6, 38.9, 33.9, 32.5, 28.4, 27.9, 25.2. MS (EI): 297(M^+, 3), 295 (M^+, 3), 205 (7), 149 (5), 133 (16), 132 (100), 104 (15). Anal. Calcd for $C_{14}H_{18}BrNO$: C, 56.77; H, 6.12; N, 4.73. Found: C, 56.42; H, 6.18; N, 4.69.

(*S*)-7-Bromo-1-cyclohexyl-1-heptanol (56t). Yield (60 mg, 11%, 60% ee) based on 6-bromo-1-hexene (2.61 g, 16.0 mmol) and cyclohexanecarboxaldehyde (222 mg, 2.0 mmol). Purified by chromatography (hexanes/ether = 5:1). The enantiomeric excess was determined by integration of the ^{1}H NMR signals at δ 3.37 (t) and 3.30 (t) of the (*S*)-*O*-acetylmandelic ester derivative (ratio 80:20). $[\alpha]^{25}_D = -6.4$ (*c* 2.81, $CHCl_3$). IR (neat): 3350 (s), 2910 (vs), 2850 (s), 1450 (m), 1260 (m). ^{1}H NMR (200 MHz, $CDCl_3$): δ 3.38 (t, J = 6.7 Hz, 2H), 3.31 (m, 1H), 1.83−1.17 (m, 22H), ^{13}C NMR (50 MHz, $CDCl_3$): δ 76.0, 43.5, 33.9, 33.8, 32.7, 29.2, 28.8, 28.1, 27.7, 26.5, 26.3, 26.1, 25.7. MS (EI): 260 (1), 258 (1), 195 (20), 193 (15), 113 (26), 95 (100). Anal. Calcd for $C_{13}H_{25}BrO$: C, 56.32; H, 9.09. Found: C, 56.44; H, 9.13.

(*R*)-1-Bromo-7-dodecanol (56u). Yield (409 mg, 77%, 90% ee) based on 6-bromo-1-hexene (2.61 g, 16.0 mmol) and hexanal (200 mg, 2.00 mmol). Purified by chromatography (hexanes/ether = 10:1 and then 5:1). The enantiomeric excess was determined by integration of the ^{1}H NMR signals at δ 3.38 (t) and 3.32 (t) of the (*S*)-*O*-acetylmandelic ester derivative (ratio 95:5). $[\alpha]^{25}_D = -0.3$ (*c* 7.71, $CHCl_3$). IR (neat): 3350 (m), 2940 (vs), 2865 (s), 1470 (m), 1260 (m), 1020 (m), 720 (w). ^{1}H NMR (200 MHz, $CDCl_3$): δ 3.53 (s, 1H), 3.37 (t, J = 6.8 Hz, 2H), 1.86−1.79 (m, 5H), 1.39−1.27 (m, 14H), 0.86 (t, J = 6.4 Hz, 3H). ^{13}C NMR (50 MHz, $CDCl_3$): δ 71.8, 37.4, 37.2, 33.9, 32.7, 31.8, 28.8, 28.1, 25.4, 25.3, 22.6, 14.0. MS (EI): 248 (2), 246 (2), 195 (29), 193 (28), 101 (78), 95 (57), 69 (22), 55 (96), 43 (28), 41. Anal. Calcd for $C_{12}H_{25}BrO$: C, 54.34; H, 9.50. Found: C, 54.33; H, 9.43.

(*S*)-7-Iodo-1-phenyl-1-heptanol (56v). Yield (330 mg, 58%, 86% ee) based on 6-iodo-1-hexene (3.46 g, 16.5 mmol) and benzaldehyde (190 mg, 1.79 mmol). Purified by chromatography (hexanes/ether = 20:1 and then 6:1 and 1:1). The enantiomeric excess was determined by integration of the ^{1}H NMR signals at δ 3.15 (t) and 3.10 (t) of the (*S*)-*O*-acetylmandelic ester derivative (ratio 93:7). $[\alpha]^{25}_D = 14.6$ (*c* 3.22, $CHCl_3$). IR (neat): 3380 (s), 3040 (w), 2940 (vs), 2860 (s), 1495 (m), 1455 (m), 920 (m), 700 (s). ^{1}H NMR (200 MHz, $CDCl_3$): δ 7.33−7.24 (m, 5H), 4.63 (t, J = 6.1 Hz, 1H), 3.15 (t, J = 6.9 Hz, 2H), 1.97 (s, 1H), 1.85−1.62 (m, 4H), 1.42−1.18 (m, 6H). ^{13}C NMR (50 MHz, $CDCl_3$): δ 144.8, 128.4 (2C), 127.5, 125.8 (2C), 74.6, 38.9, 33.4, 30.3, 28.4, 25.6, 7.2. MS (EI): 318 (M^+, 2), 107 (100), 79 (17). Anal. Calcd for $C_{13}H_{19}IO$: C, 49.07; H, 6.02. Found: C, 49.10; H, 6.03.

(*S*)-10-Iodo-2-methyl-4-decanol (56w). Yield (180 mg, 32%, 73% ee) based on 6-iodo-1-hexene (3.46 g, 16.5 mmol) and 2-methylbutanal (160 mg, 1.85 mmol). Purified by chromatography (hexanes/ether = 20:1 and then 10:1). The enantiomeric excess was determined by integration of the ^{1}H NMR signals at δ 3.16 (t) and 3.10 (t) of the (*S*)-*O*-acetylmandelic ester derivative (ratio 86.5:13.5). $[\alpha]^{25}_D = 5.5°$ (*c* 1.46, $CHCl_3$). IR (neat): 3350 (m), 2940 (vs), 2860 (s), 1465 (m), 1370 (w). ^{1}H NMR (200 MHz, $CDCl_3$): δ 3.63 (s, 1H), 3.15 (t, J = 7.0 Hz, 2H), 1.85−1.63 (m, 3H), 1.43−1.13 (m, 11H), 0.88 (d, J = 6.7 Hz, 3H), 0.87 (d, J = 6.5 Hz, 3H). ^{13}C NMR (50 MHz, $CDCl_3$): δ 69.7, 46.7, 37.8, 33.4, 30.4, 28.5, 25.3, 24.5, 23.4, 22.0, 7.2. MS (EI): 280 (1), 241 (17), 196 (9), 155 (5), 97 (57), 87 (41), 80 (21), 69 (100), 57 (30), 43 (50). Anal. Calcd for $C_{11}H_{23}IO$: C, 44.31; H, 7.77. Found: C, 44.54; H, 8.02.

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Supporting Information Available: ^{1}H and ^{13}C NMR spectra of all new compounds (132 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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