Catalytic Asymmetric Addition of Polyfunctional Dialkylzincs to β-Stannylated and β-Silylated Unsaturated Aldehydes

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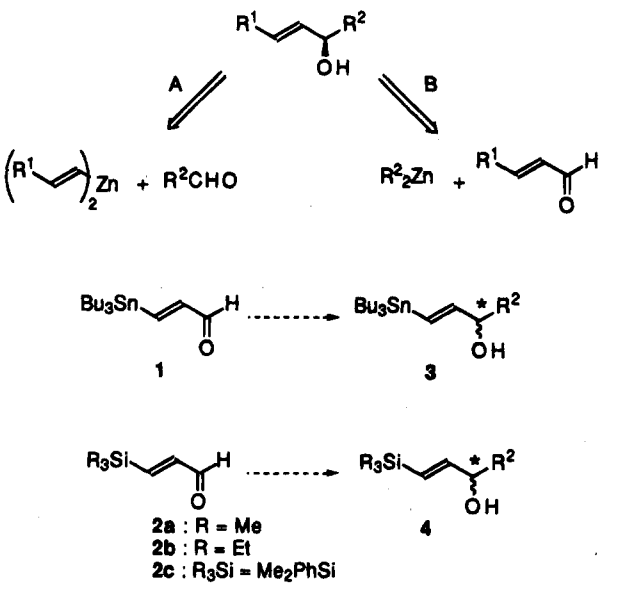
The addition of functionalized dialkylzincs to readily available β-stannylated or β-silylated unsaturated aldehydes in the presence of a catalytic amount of (1*R*,2*R*)-1,2-bis(trifluorosulfonamido)-cyclohexane (8 mol %) provides chiral allylic alcohols in good yields (60–90%) and excellent enantioselectivity (usually in the range of 85–95% ee). The synthetic utility of these allylic alcohols as chiral building blocks is demonstrated. The γ-stannylated allylic alcohols were submitted to a Stille coupling leading to polyfunctional allylic alcohols and γ-alkoxy enones. A treatment with CuCN in *N*-methylpyrrolidone at 130 °C provided chiral unsaturated γ-hydroxy nitriles. Finally, the desilylation of the γ-silylated alcohols gave chiral allylic alcohols having a terminal double bond. The catalytic asymmetric addition was found to show an important inverse temperature dependance. A mechanism for this addition is proposed.

Introduction

The enantioselective preparation of scalemic secondary alcohols by the addition of an organometallic to an aldehyde[1] constitutes the most general preparation of this important class of compounds, besides the asymmetric hydrogenation of unsymmetrical ketones.[2] Dialkylzincs have proven to be especially useful reagents for performing the asymmetric addition reaction in the presence of catalytic amounts of a chiral amino alcohol.[3] The limited availability of dialkylzincs has hampered the synthetic applications of the method, although a transmetalation of organomagnesium derivatives with zinc chloride followed by a precipitation of the resulting magnesium salts with dioxane provides an access to nonfunctional dialkylzincs.[4] Recently, we have found that a range of *functionalized* dialkylzincs can be prepared via an iodine–zinc exchange reaction.[5] This convenient preparation of dialkylzincs has greatly expanded the scope of the asymmetric addition reaction allowing the enantioselective synthesis of various polyfunctional secondary alcohols using either functionalized dialkylzincs or (and) functionalized aldehydes.[6,7] Secondary allylic alcohols can be prepared by this approach, adding either an alkenylzinc derivative to a saturated aldehyde (retrosynthetic pathway A; Scheme 1)[8] or by adding a dialkylzinc to an unsaturated aldehyde (retrosynthetic pathway B). Herein, we wish to report the enantioselective addition of functionalized dialkylzincs to β-stannylated or β-silylated unsaturated aldehydes **1** and **2a–c** leading to the scalemic polyfunctional allylic alcohols of type **3** and **4** (Scheme 1). The carbon–tin or carbon–silicon bond present in these molecules can be submitted to further useful conversions affording a range of chiral molecules which demonstrate the synthetic utility of the alcohols **3** and **4a,b** as chiral building blocks.

Scheme 1



Results

The unsaturated aldehyde (*E*)-3-(tributylstannyl)-2-propenal (**1**) was prepared in two steps from 3,3-diethoxy-1-propyne (**5**).[9] The treatment of **5** with $Bu_3Sn(Bu)Cu$-

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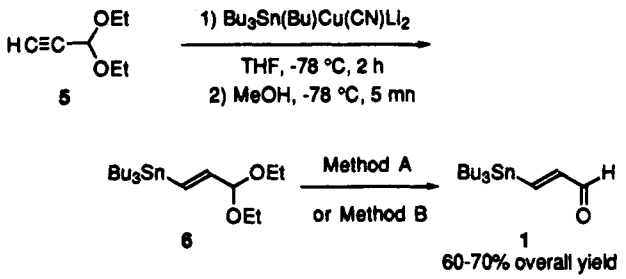
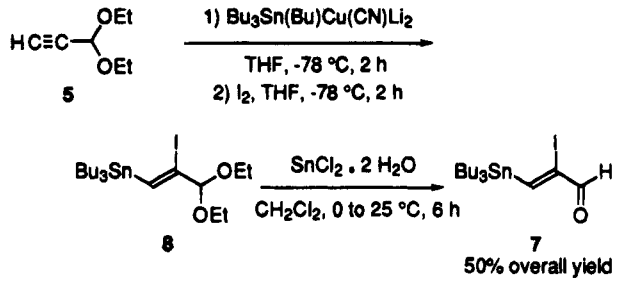
Scheme 2[a]



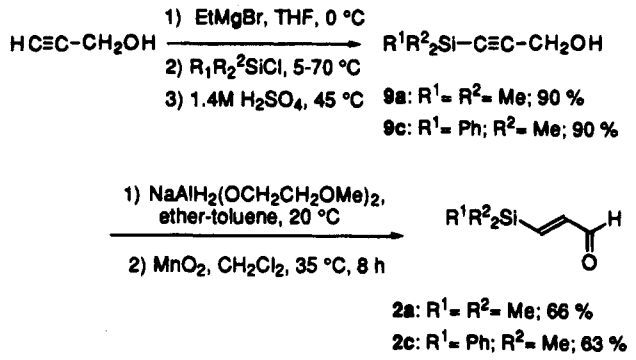
[a] Method A: acetone, H_2O, TsOH cat., 56 °C, 6 h. Method B: wet SiO_2, CH_2Cl_2, 25 °C, 15 min.

Scheme 3

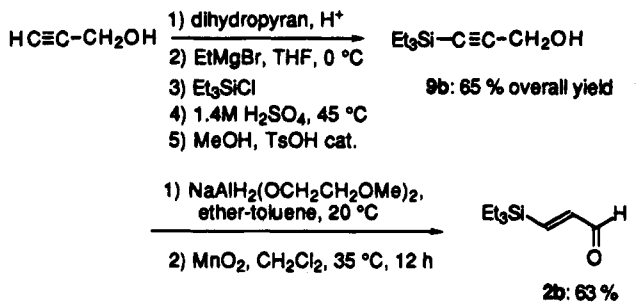


$(CN)Li_2$[10] in THF (−78 °C, 2 h) provides after a methanol quenching the crude unsaturated acetal **6** contaminated with several tributyltin derivatives.[11] The hydrolysis of the acetal **6** can be performed either in refluxing acetone–water in the presence of a catalytic amount of *p*-toluenesulfonic acid (6 h) giving an overall yield of 70% (method A)[12] or by treatment with wet silica gel in CH_2Cl_2 in the presence of a catalytic amount of oxalic acid (25 °C, 15 min; method B; Scheme 2).[13] The same approach was used to prepare (*Z*)-2-iodo-3-(tributylstannyl)-2-propenal (**7**). In this case, the intermediate unsaturated iodo acetal **8** was converted to the corresponding aldehyde using $SnCl_2{\cdot}2H_2O$[14] in CH_2Cl_2 (25 °C, 6 h, 50% overall yield; Scheme 3). The silylated aldehydes **2a–c** were prepared from propargyl alcohol.[15] The double deprotonation of propargyl alcohol with ethylmagnesium bromide, silylation, respectively, with TMSCl and $PhMe_2SiCl$,[16] and selective oxygen monodesilylation produces, according to the procedure of Denmark,[15] the propargylic alcohols **9a** and **9c** in 90% yield (Scheme 4). In the case of the preparation of **2b**, propargyl alcohol was first converted to the corresponding THP ether (78% yield) which was submitted to the same reaction sequence

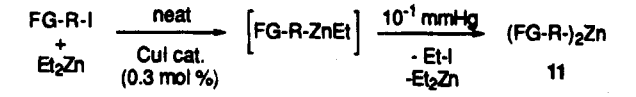
Scheme 4



Scheme 5



Scheme 6



as described precedently, leading after the removal of the THP group (MeOH, cat. TsOH) to the propargylic alcohol **9b** in 83% yield (Scheme 5). The alcohols **9a–c** were stereoselectively reduced with a toluene solution of sodium bis(2-methoxyethoxy)aluminum hydride (Red-Al) to the (*E*)-3-silylated allylic alcohols (**10a–c**; see Experimental Section) in 68–83% yield.[15] The oxidation of these alcohols with MnO_2 in CH_2Cl_2 proceeds smoothly (35 °C, 8–12 h),[17] affording almost quantitatively (93–97% yield) the desired unsaturated aldehydes **2a–c** in 41–59% overall yield (Schemes 4 and 5). The dialkylzincs necessary for the asymmetric addition were prepared from the corresponding primary alkyl iodides via an iodine–zinc exchange reaction using diethylzinc (1.5 equiv, 55 °C, 4–9 h) in the presence of a catalytic amount of copper(I) iodide (0.3 mol %).[6] The intermediate mixed (ethyl)(alkyl)zinc derivative was converted to the dialkylzinc **11** by pumping off the excess Et_2Zn and the formed EtI (Scheme 6).[5] By using (1*R*,2*R*)-1,2-bis(trifluorosulfonamido)cyclohexane[18] (**12**; 8 mol %) as a catalyst, the dialkylzincs **11** were found to add to the aldehydes **1**, **2a,b**, and **7** with an excellent enantioselectivity (Scheme 7 and Table 1). This addition is always performed in the presence of $Ti(O\text{-}i\text{-}Pr)_4$ (2 equiv) whose role is to complex the resulting zinc alcoholate (R*OZnR-FG). In the absence of $Ti(O\text{-}i\text{-}Pr)_4$, a very slow, and nonselective addition is observed. The reaction also requires the use of an excess of dialkylzinc reagent (2.5–3 equiv) and is very sensitive to the reaction temperature. In the case

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Scheme 7

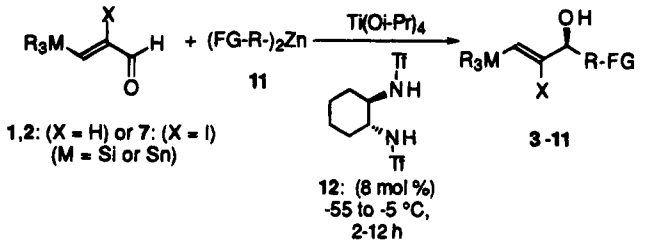

Table 1. Functionalized Allylic Alcohols 3a–h and 4a–k Obtained by the Catalytic Asymmetric Addition of a Dialkylzinc 11 to the Aldehydes 1, 2a–c, and 7 in the Presence of 12 (8 mol %)

entry	aldehyde	dialkylzinc 11 (FG-R)	product 3 or 4[a]	yield[b] (%)	ee[c] (%)	$[\alpha]_D$[d] (deg)
1	1	ethyl	**3a**	87	90–93	−0.30
2	1	C_5H_{11}	**3b**	88	92	−0.21
3	1	C_8H_{17}	**3c**	72	90	−0.23
4	1	$(CH_2)_5OAc$	**3d**	75	91	−0.15
5	1	$(CH_2)_4Cl$	**3e**	69	92–95[f]	−1.75
6	1	$(CH_2)_3OPiv$	**3f**	67	90	−1.50
7	7	ethyl	**3g**[e]	75	94	−1.10
8	7	$Bn(Tf)N(CH_2)_3$	**3h**[e]	62	82	−2.76
9	2c	ethyl	**4a**	93	94	+19.6
10	2c	$(CH_2)_3OTIPS$	**4b**	67	0	
11	2a	C_5H_{11}	**4c**	72	80	−9.73
12	2a	$(CH_2)_5OPiv$	**4d**	67	85	+5.36
13	2a	$(CH_2)_3OPiv$	**4e**	62	90	+4.67
14	2a	$(CH_2)_4Cl$	**4f**	59	70	−40.4
15	2b	$(CH_2)_3OPiv$	**4g**	71	90	+3.95
16	2b	ethyl	**4h**	92	90	+9.80
17	2b	C_5H_{11}	**4i**	81	99	+8.03
18	2b	C_8H_{17}	**4j**	76	87	+3.66
19	2b	$(CH_2)_5OAc$	**4k**	61	93	+6.61

[a] X = H unless otherwise indicated. [b] Isolated yield of analytically pure compounds (>97% pure by GC analysis). [c] The enantiomeric excesses were determined by integration of the ^1H NMR spectra of *O*-acetylmandelic esters (ref 26). [d] The optical rotations were measured in benzene. [e] X = I. [f] The reaction was also performed using procedure B (see Experimental Section).

Table 2. Temperature Dependence of the Enantioselectivity in the Addition of Bis(3-pivaloxypropyl)zinc to the Unsaturated Aldehydes 2a and 2b Leading, Respectively, to 4e and 4g

entry	aldehyde	T[a] (°C)	yield[b] (%)	ee[c] (%)
1	**2a**	−40	62	80
2	**2a**	−30	65	85
3	**2a**	−15	72	90
4	**2a**	−5	68	85
5	**2b**	−30	65	83
6	**2b**	−15	67	85
7	**2b**	−5	71	90

[a] Bath temperature. [b] Isolated yield of analytically pure product. [c] The enantiomeric excesses were determined by integration of the ^1H NMR spectra of *O*-acetylmandelic esters (ref 26).

of the β-stannylated aldehyde (**1**) the reaction is best performed between −55 and −40 °C, and an important temperature effect has been observed for the β-silylated aldehydes **2a** and **2b** (Table 2). Thus, the addition of bis(3-pivaloxypropyl)zinc to **2a** produces the allylic alcohol **4e** with an enantiomeric excess of 80%, if the bath temperature is held between −60 and −40 °C, whereas by increasing the temperature to −15 °C, the enantioselectivity raises to 90% ee. A further temperature increase to −5 °C furnishes again a lower ee value (85% ee; compare entries 1–4 of Table 2). Similarly, the same temperature dependance is observed for the unsaturated aldehyde **2b** for which the optimal temperature seems to be higher (−5 °C, see entries 4–7 of Table 2). This *inverse temperature effect* may be explained by assuming that some ligand exchanges at the chiral titanium complex are too slow at lower temperature, resulting in a catalyst poisoning and leading to lower ee values. The addition reaction also seems to be sensitive to the steric hindrance of the unsaturated aldehyde since the aldehyde **2c** bearing in the β-position a bulky phenyldimethylsilyl group reacts well only with the most reactive dialkylzinc (diethylzinc; 94% ee; entry 9 of Table 1). With the less reactive zinc reagent, bis[[(triisopropylsilyl)oxy]propyl]zinc, no enantioselectivity is obtained (entry 10 of Table 1). The triethylsilyl group present in the aldehyde **2b** displays a lower steric hindrance and permits the preparation of the allylic alcohols **4g–k** in higher enantioselectivity than the less bulky β-(trimethylsilyl)-substituted aldehyde **2a** (see Table 1, entries 15–19). As shown in Table 1, a range of functionalized dialkylzincs bearing either an ester group (entries 4, 6, 12, 13, 15, and 19), a chloride (entries 5 and 14), or a protected amino function (entry 8) can be used. Promising results were expected from the α-iodo-β-stannylated aldehyde **7**, since it was observed that the introduction of a substituent at the α-position of an α,β-unsaturated aldehyde had a beneficial effect on the enantioselectivity.[6a] The α-substituent favors the more reactive and sterically more demanding *s-cis* conformation of the aldehyde.[6a] As predicted, the aldehyde **7** adds diethylzinc in satisfactory yield and with an excellent enantioselectivity. Functionalized zinc reagents such as $(Bn(Tf)N(CH_2)_3)_2Zn$ add with a satisfactory enantioselectivity (82% ee); however, the unstability of the product **3h** allows the isolation of only 62% of this allylic alcohol (entries 7 and 8). The stannylated alcohols **3a–f** can be used as chiral building blocks and have been further converted to valuable products. Thus, the iodination of **3b** (I_2 (1 equiv), 25 °C, 5 min)[19] provides (*E*)-1-iodo-1-octen-3-ol (**13b**) (98% yield) which has been used to prepare the side chain of various prostaglandins.[3b,20] By using the Stille reaction,[21] a new carbon–carbon bond can be formed with a range of functionalized electrophiles leading to polyfunctional unsaturated alcohols **14–18** in an optically enriched form (Scheme 8). By using bis(dibenzylideneacetone)palladium [$Pd(dba)_2$] (4 mol %)[22] and tri-*o*-furylphosphane (TFP; 8/16 mol %),[23] these coupling reactions proceed under mild conditions and with satisfactory yields. Interestingly, the palladium-catalyzed acylation of the protected stannylated allylic alcohols **19** allows a facile preparation of a range of γ-alkoxy-α,β-unsaturated ketones of type **20**. Although an acetate is a satisfactory

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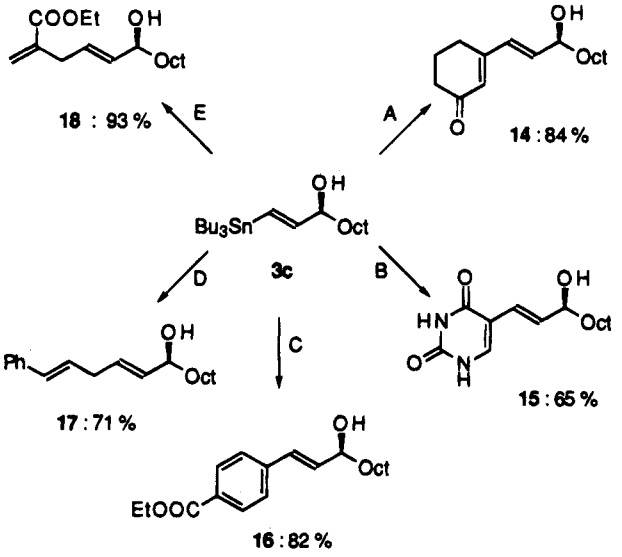
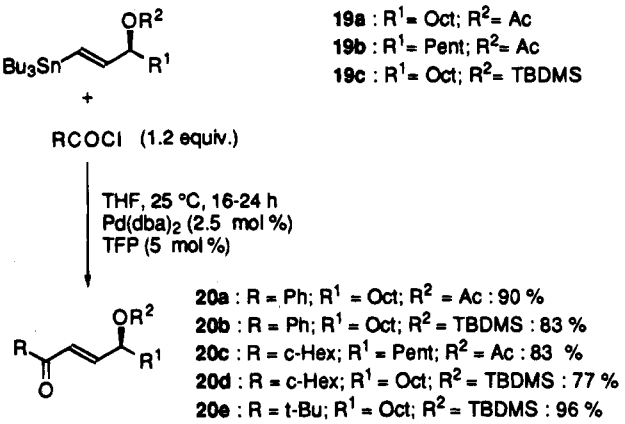
Scheme 8[a]



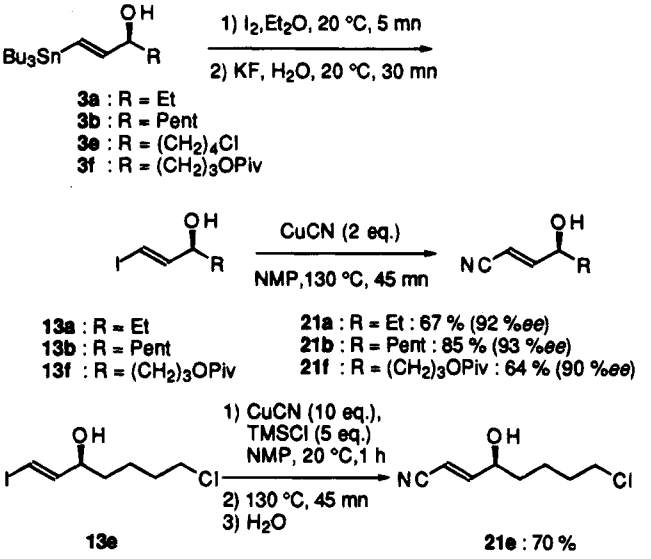
[a] Key: (A) 3-iodo-2-cyclohexen-1-one (1.2 equiv), $Pd(dba)_2$ (4 mol %); TFP (8 mol %), THF, 25 °C, 2 d; 84%; (B) 5-iodouracil (1.0 equiv), $Pd(dba)_2$ (4 mol %); TFP (8 mol %), NMP, 40 °C, 2 d; 65%; (C) *p*-carbethoxyiodobenzene (1.2 equiv), $Pd(dba)_2$ (4 mol %); TFP (8 mol %), THF, 25 °C, 2 d; 82%; (D) cinnamyl chloride (1.0 equiv), $Pd(dba)_2$ (4 mol %), TFP (16 mol %), THF, 40 °C, 2 d, 71%; (E) ethyl 2-(bromomethyl)acrylate (1.2 equiv), $Pd(dba)_2$ (4 mol %), TFP (16 mol %), THF, 40 °C, 1 d, 93%.

Scheme 9

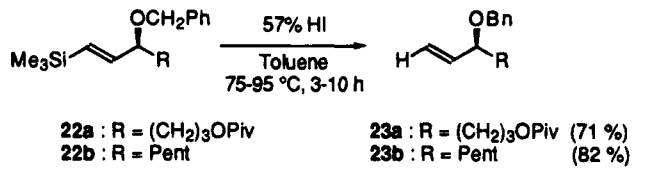


protecting group, the acylation of **19b** with cyclohexanecarbonyl chloride affords the desired enone **20c** as a 9:1 *E*/*Z* mixture. The use of a *tert*-butyldimethylsilyl protecting group allows the acylation of the allylic alcohol **19c** with no isomerization of the double bond (**20d**: *E*/*Z* > 99:1; Scheme 9). It has been shown that such γ-alkoxy enones undergo substitution reactions or Michael additions with various nucleophiles with excellent diastereoselectivity.[24] Similarly, polyfunctional allylic alcohols **3a,b**, **3e**, and **3f** can be converted to chiral γ-hydroxy α,β-unsaturated nitriles **21a,b**, **21e**, and **21f** via the intermediate alkenyl iodides **13a,b**, **13e**, and **13f** (Scheme 10). The cyanation reaction is performed with copper(I) cyanide (2 equiv) in *N*-methylpyrrolidone (NMP) (130 °C, 45 min)[25] in 54–85% overall yield. The conservation of

Scheme 10



Scheme 11



the optical activity of the nitriles **21** was verified in each case by preparing a mandelic ester derivative (see Experimental Section).[26] In the case of **13e**, the above reaction conditions lead to a side product, presumed to be the tetrahydropyran derived from internal substitution of the chloride by the hydroxy group; this was totally avoided by *in situ* protection of the alcohol **13e** as a TMS ether and by using an excess of copper cyanide (Scheme 10). The direct addition of a dialkylzinc to acrolein in the presence the chiral catalyst **12** does not proceed well and affords a mixture of 1,2- and 1,4-addition products. The corresponding allylic alcohols can be cleanly prepared by adding divinylzinc to an aldehyde; however, this procedure requires the preparation of divinylzinc which is a somewhat unstable zinc reagent.[27] Another preparation of such chiral allylic alcohols bearing a terminal double bond can be realized by performing a desilylation of the alcohols **4a–h**. Thus, the treatment of the benzyl ethers **22a,b**, prepared, respectively, from **4e** (83%) and **4c** (81%), with a 57% toluene solution of HI (75–95 °C, 3–10 h)[28] produces the desired desilylated allylic ethers **23a,b** respectively in 82% and 71% yield (Scheme 11).

Discussion

The catalytic asymmetric addition described herein allows the synthesis of highly functionalized allylic alcohols. We propose the catalytic cycle described in Scheme 12 for explaining the observed enantioselectivity. The trifluoromethanesulfonyl groups of the catalyst **12** are responsible for the conformation of the two isopropoxy ligands which induces the position of the complexed aldehyde. The complexation of the dialkylzinc organometallic to the two isopropoxy ligands prior to the

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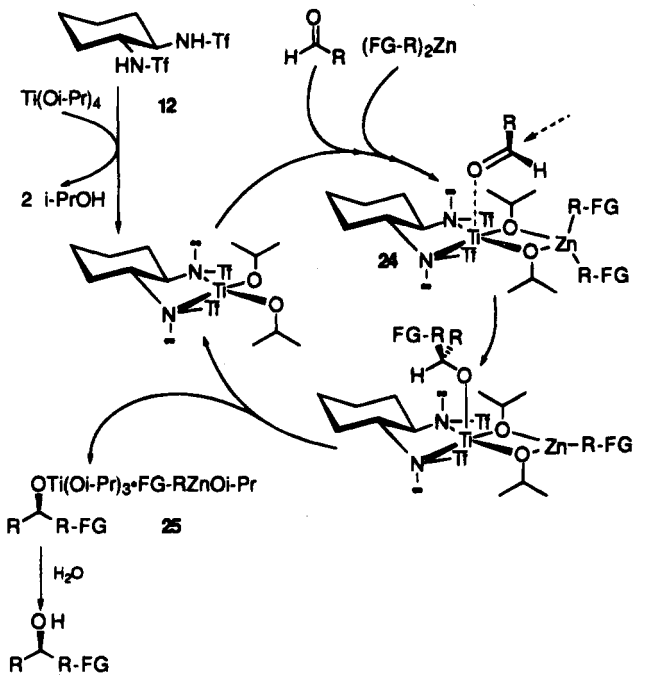
Scheme 12



transfer of the alkyl group to the carbonyl group should also be favored and will lead to the highly ordered bimetallic complex **24**.[29] The role of titanium tetraisopropoxide is to remove the zinc alkoxide from the titanium center by forming the mixed complex R^1-OZnR-Ti(O-*i*-Pr)$_4$ **25**. The inverse temperature dependance of the enantioselectivity can be explained by assuming that with bulky and (or) complexing R groups the removal of $RZnOR^1$ from the chiral titanium center may be slow at low temperature, so that the less acidic and achiral titanium center of Ti(O-*i*-Pr)$_4$ will compete under these conditions and will also catalyze the carbonyl addition reaction leading to low enantioselectivities. In summary, this catalytic enantioselective addition to β-silylated or β-stannylated unsaturated aldehydes provides a convenient access to various polyfunctional allylic alcohols whose synthetic utility as useful chiral building blocks has been demonstrated.

Experimental Section

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

Starting Materials. 3,3-Diethoxy-1-propyne (**5**),[9] chlorodimethylphenylsilane,[16] dipentylzinc,[30] (1*R*,2*R*)-1,2-bis[(trifluoromethyl)sulfonamido]cyclohexane,[18,31] bis(dibenzylideneacetone)palladium,[22] and tri-*o*-furylphosphane (TFP)[23] were obtained according to the literature. The starting alkyl iodides necessary for the preparation of the corresponding dialkylzincs were prepared by standard methods (4-iodobutyl acetate,[32] 5-iodopentyl acetate[32]). 3-Iodopropyl pivalate was obtained from 3-chloropropanol in two steps: (i) esterification with pivaloyl chloride (1.5 equiv), pyridine (3.0 equiv), 0 °C, 1 h, and (ii) NaI (3 equiv), acetone, reflux, 24 h.[6a]

***N*-Benzyl-*N*-[(trifluoromethyl)sulfonyl]-3-iodopropylamine** was prepared in three steps starting from commercially available 3-chloropropylamine hydrochloride: 3-Chloropropylamine hydrochloride (1.72 g, 55 mmol) was dissolved in CH_2Cl_2 (70 mL) and triethylamine (22 mL, 150 mmol) was added. The reaction mixture was cooled to −60 °C, trifluoromethanesulfonic anhydride (10.9 mL, 65 mmol) in CH_2Cl_2 (45 mL) was slowly added, and then the mixture was warmed to 0 °C within 1 h and diluted with water (150 mL) and 1 N HCl (150 mL). The organic phase was separated, and the aqueous phase was extracted with CH_2Cl_2 (2 × 100 mL). The combined organic layer was dried over $MgSO_4$, and the solvents were evaporated affording crude *N*-[(trifluoromethyl)sulfonyl]-3-chloropropylamine which was dissolved in acetone (50 mL). Benzyl bromide (7 mL, 59 mmol) and K_2CO_3 (21.8 g, 158 mmol) were successively added, and the reaction mixture was stirred for 1 h at rt. After the usual workup, the crude *N*-benzyl-*N*-[(trifluoromethyl)sulfonyl]-3-chloropropylamine was again dissolved in acetone containing NaI (9.7 g, 65 mmol), the heterogeneous mixture was refluxed for 2 days and cooled to rt, and hexane (200 mL) was added. The resulting thick precipitate was filtered, and the crude iodo amine obtained after evaporation of the solvents was purified by flash chromatography (solvent hexane:ether 10:1 (to 4:1)) affording pure (*N*-benzyl-*N*-[(trifluoromethyl)sulfonyl]-3-iodopropylamine (11.4 g, 28 mmol, 51% overall yield). IR (neat): 1445 (w), 1379 (m), 1319 (m). ^{1}H NMR ($CDCl_3$, 200 MHz): δ 7.60 (s, 5H), 4.70 (brs, 2H), 3.56 (t, 2H, J = 11 Hz), 3.15 (t, 2H, 7 Hz), 2.09 (m, 2H). ^{13}C-NMR ($CDCl_3$, 50 MHz): δ 134.0, 129.0, 128.7, 128.5, 120.0 (q, CF_3, J = 323 Hz), 52.9, 49.2, 31.6. MS (EI): 407 (M^+, 1), 280 (13), 92 (15), 91 (100). Anal. Calcd for $C_{11}H_{13}F_3INO_2S$: C, 32.45; H, 3.22; N, 3.44. Found: C, 32.62; H, 3.22; N, 3.64.

(*E*)-3-(Tributylstannyl)-2-propenal (1). (a) (*Z*)-1,1-Diethoxy-3-(tributylstannyl)-2-propene (6). A three-necked, 250-mL flask equipped with an argon inlet, a stirring bar, a low-temperature thermometer, and a septum cap was charged with copper(I) cyanide (4.31 g, 48.2 mmol) and THF (130 mL). The suspension was cooled to −78 °C, and BuLi (63.2 mL, 96.4 mmol; 1.53 N solution in hexane) was slowly added.[10] The reaction mixture was warmed to −50 °C resulting in a clear yellow solution. It was cooled back to −78 °C, and Bu_3SnH (30.9 mL, 96.4 mmol) was added.[10] A gas evolution was observed. After 10 min of stirring, 1,1-diethoxy-2-propyne (**5**)[9] (5.16 g, 40.2 mmol) was added, and after 2 h at −78 °C, methanol (5 mL) was added, producing a deep red solution.[11] The reaction mixture was allowed to warm to 0 °C, and a saturated aqueous NH_4Cl solution (50 mL) was added. After an ethereal extraction and the usual workup the crude acetal **6** contaminated with Bu_4Sn was directly used for the preparation of **1**.

(b) Deprotection of 6. Method A.[12] The above described acetal **6** (ca. 31 g) was dissolved in acetone (300 mL) containing water (3 mL) and a catalytic amount of *p*-TsOH (ca. 50 mg) and was heated to reflux for 6 h. The solvents were evaporated, and the residue was purified by flash chromatography (hexane–ether 96.5:3.5) affording pure (*E*)-3-(tributylstannyl)-2-propenal (**1**) as a light yellow oil (9.70 g, 70%).

Method B.[13] (Preparation starting with 80.4 mmol of **5**). An aqueous solution of 10% oxalic acid was added to a slurry of silica gel (G60, 190 g) in CH_2Cl_2 (250 mL), followed by the crude acetal **6** (ca. 62 g). After 15 min at rt, solid $NaHCO_3$ (6.3 g, 75 mmol) was added. The reaction mixture was filtered, and the silica gel was washed with CH_2Cl_2 (2 × 200 mL). The organic layer was dried ($MgSO_4$), and the residue obtained after evaporation of the solvents was purified by flash chromatography (hexane–ether 98:2) affording pure **1** (23.2 g, 71% yield). IR (neat): 2945 (s), 2917 (s), 2844 (s), 2695 (m), 1682 (s), 1456 (s). ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 9.39 (d, 1H, J = 7.7 Hz), 7.82 (d, 1H, J = 19.1 Hz), 6.61 (dd, 1H, J = 19.1, 7.7 Hz), 1.55–1.45 (m, 6H), 1.36–1.24 (m, 6H), 1.00–0.94 (m, 6H), 0.88 (t, 9H, J = 7.2 Hz). ^{13}C-NMR ($CDCl_3$, 75 MHz): δ 193.5, 163.1, 147.5, 28.8, 27.1, 13.5, 9.7. MS (EI): 289 (100), 287 (67), 285 (36), 233 (70), 231 (52), 177 (69), 175 (85), 173 (36),

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121 (23). Anal. Calcd for $C_{15}H_{30}OSn$: C, 52.20; H, 8.76. Found: C, 52.42; H, 8.83.

(Z)-2-Iodo-3-(tributylstannyl)-2-propenal (7). (a) (Z)-1,1-Diethoxy-2-iodo-3-(tributylstannyl)-2-propene (8). The same procedure as described above for the preparation of **6** was used. The intermediate alkenylcopper reagent obtained from CuCN (4.31 g, 48.2 mmol), BuLi (58.8 mL, 96.4 mmol of a 1.64 N solution in hexane), Bu_3SnH (25.5 mL, 96.4 mmol), and 1,1-diethoxy-2-propyne (**5**) (4.50 g, 35 mmol) was treated at −78 °C with iodine (17.8 g, 70 mmol) in THF (10 mL). After 2 h at −60 °C, the reaction mixture was quenched with a saturated aqueous NH_4Cl solution. After the usual workup procedure, the crude acetal **8** contaminated with Bu_4Sn was obtained and used directly for the preparation of **7**.

(b) (Z)-2-Iodo-3-(tributylstannyl)-2-propenal (7). The above-prepared crude acetal **8** was dissolved in CH_2Cl_2 (400 mL) and was slowly added to a solution of $SnCl_2{\cdot}2H_2O$[14] (6.70 g, 30 mmol) in CH_2Cl_2 (300 mL). After the reaction mixture was stirred for 6 h at rt, it was filtered and the solvents were evaporated. The crude product was purified by flash chromatography (hexane−ether 98.5:1.5) affording pure **7** as a light yellow oil (8.24 g, 50% overall yield). IR (neat): 2960 (s), 2919 (s), 2872 (s), 1737 (m), 1458 (s). ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 8.87 (s, 1H), 8.31 (s, 1H), 1.54−1.46 (m, 6H), 1.33−1.20 (m, 6H), 1.14−1.08 (m, 6H), 0.85 (t, 9H, J = 7.2 Hz). ^{13}C-NMR ($CDCl_3$, 75 MHz): δ 187.1, 173.3, 125.3, 29.0, 27.3, 13.7, 11.0. MS (FD): 472 (M+1, 12), 450 (12), 289 (4), 162 (12), 161 (12). Anal. Calcd for $C_{15}H_{29}OISn$: C, 38.25; H, 6.20. Found: C, 38.10; H, 6.42.

(E)-3-(Trimethylsilyl)-2-propenal (2a). (*E*)-3-(Trimethylsilyl)-2-propen-1-ol[15] (15.63 g, 120 mmol) was dissolved in dry CH_2Cl_2 (100 mL). MnO_2 (70 g, 0.8 mol, 6.7 equiv) was added, and after 0.5 h the reaction mixture was heated to reflux. After 5 h, a second portion of MnO_2 (21 g, 0.24 mol, 2 equiv) was added and the reaction mixture was stirred for 8 h at rt. Silica gel (40 g) was added, and the heterogeneous mixture was filtered over a short silica gel column and washed further with CH_2Cl_2. After evaporation of the solvent, the pure aldehyde was isolated (14.62 g, 95% yield). IR (neat): 2960 (m), 1696 (s), 1618 (w). ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 9.39 (d, 1H, J = 7.6 Hz), 7.14 (d, 1H, J = 18.7 Hz), 6.42 (dd, 1H, J = 7.6, 18.7 Hz), 0.11 (s, 9H). ^{13}C-NMR ($CDCl_3$, 75 MHz): δ 194.8, 158.8, 144.1, −2.0. MS (FI) : 129(100), 127 (19), 113 (33). Anal. Calcd for $C_6H_{12}OSi$: C, 56.19; H, 9.43. Found: C, 56.07; H, 9.24.

3-(Triethylsilyl)propyn-1-ol (9b). A three-neck flask equipped with an argon inlet, a thermometer, and a septum cap was charged with EtMgBr (0.1 mol) in THF (50 mL), and tetrahydropyranyl propargyl ether[33] (14.0 g, 0.1 mol) was added below 10 °C. After the mixture was stirred for 10 h, Et_3SiCl (15 g, 0.1 mol) was added and the reaction mixture was heated to reflux for 20 h. After the mixture was cooled to rt, 1 M HCl solution (100 mL) was added, and the reaction mixture was stirred for 0.5 h. After the usual workup[27] and evaporation of the solvents, the crude product was dissolved in methanol (100 mL) and *p*-TsOH (2.5 g, ca. 13 mmol) was added. The reaction mixture was stirred for 8 h, and the solvent was evaporated. The crude residue was dissolved in ether (200 mL), washed successively with saturated aqueous $NaHCO_3$ solution (50 mL) and saturated aqueous NaCl solution (2 × 50 mL), and dried ($MgSO_4$), the solvent was removed, and the residue was distilled (bp 72−75 °C/0.5 mmHg) affording the pure alcohol **9b** (14.13 g, 83%). IR (neat): 3174 (m), 2876 (m), 2172 (w). ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 4.21 (s, 2H), 2.47 (s, 1H), 0.92 (t, 9H, J = 7.8 Hz), 0.54 (q, 6H, J = 7.8 Hz). ^{13}C-NMR ($CDCl_3$, 75.5 MHz): δ 104.9, 87.6, 51.3, 7.2, 4.1. MS (FI): 171 (19), 170 (100), 153 (3). Anal. Calcd for $C_9H_{18}OSi$: C, 63.48; H, 10.65. Found: C, 63.41; H, 10.53.

3-(Dimethylphenylsilyl)-2-propyn-1-ol (9c). This alcohol was prepared as **2a** using propargyl alcohol (11.6 mL, 0.2 mol) in THF (10 mL), EtMgBr (0.4 mol), and a mixture of dimethylphenylchlorosilane and dimethylphenylbromosilane (0.2 mol)[16] leading to **9c** (34.27 g, 90% yield) as a colorless oil. IR (neat): 3301 (m), 2961 (m), 2178 (m). ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 7.61−7.31 (m, 5H), 4.25 (d, 2H, J = 6.0 Hz), 1.91 (m, 1H), 0.40 (s, 6H). ^{13}C-NMR ($CDCl_3$, 75.5 MHz): δ 136.7, 133.8, 129.7, 128.1, 105.7, 88.9, 51.8, −0.9. MS (FI): 191 (13), 190 (100). Anal. Calcd for $C_{11}H_{14}OSi$: C, 69.42; H, 7.41. Found: C, 69.52; H, 7.45.

The Red-Al reductions of **9a−c** leading to **10a−c** were performed according to the procedure of Denmark.[15]

(E)-3-(Triethylsilyl)-2-propen-1-ol (10b). IR (neat): 3307 (m), 2956 (s), 1625 (w). ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 6.17 (dt, 1H, J = 18.8, 4.4 Hz), 5.82 (dt, 1H, J = 18.8, 1.8 Hz), 4.14 (m, 1H), 2.40 (s, 1H), 0.92 (t, 9H, J = 7.9 Hz), 0.56 (q, 6H, J = 7.9 Hz). ^{13}C-NMR ($CDCl_3$, 75.5 MHz): δ 146.2, 125.6, 65.5, 7.2, 3.4. MS (FD): 106 (0.6), 58 (17). Anal. Calcd for $C_9H_{20}OSi$: C, 62.73: H, 11.70. Found: C, 62.42; H, 11.60.

(E)-3-(Dimethylphenylsilyl)-2-propen-1-ol (10c). IR (neat): 3253 (s), 2954 (s), 1617 (w), 1254 (m). ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 7.51−7.30 (m, 5H), 6.20 (dt, 1H, J = 18.8, 4.1 Hz), 5.99 (dt, 1H, J = 18.8, 1.6 Hz), 4.15 (m, 2H), 1.70 (s, 1H), 0.32 (s, 6H). ^{13}C-NMR ($CDCl_3$, 75.5 MHz): δ 149.6, 141.1, 136.6, 131.7, 130.9, 130.5, 68.0, −0.5. MS (FI): 192 (100), 115 (13), 75 (13). Anal. Calcd for $C_{11}H_{16}OSi$: C, 68.69; H, 8.38. Found: C, 68.42; H, 8.40.

(E)-3-(Triethylsilyl)-2-propenal (2b). Prepared as **2a** using 3-(triethylsilyl)-2-propen-1-ol (**10b**) (9.3 g, 54 mmol) and MnO_2 (ca. 40 g, 0.47 mol). Yield: 8.92 g, 97%. IR (neat): 2956 (s), 1698 (s), 1615 (m). ^{1}H-NMR (300 MHz, $CDCl_3$): δ 9.38 (d, 1H, J = 7.6 Hz), 7.10 (dd, 1H, J = 18.8 Hz), 6.47 (dd, 1H, J = 18.8, 7.5 Hz), 0.90 (t, 9H, J = 7.5 Hz), 0.60 (q, 6H, J = 7.6 Hz). ^{13}C-NMR ($CDCl_3$, 75.5 MHz): δ 194.4, 155.9, 145.3, 7.0, 2.8. MS (FI): 170 (61), 157 (100), 152 (90). Anal. Calcd for $C_9H_{18}OSi$: C, 63.47, H, 10.64. Found: C, 63.50; H, 10.36.

(E)-(Dimethylphenylsilyl)-2-propenal (2c). Prepared as **2a** using 3-(dimethylphenylsilyl)-2-propen-1-ol (23.5 g, 0.12 mol) and MnO_2 (91 g, 1.04 mol). Yield: 21.24 g, 93%. IR (neat): 2960 (s), 1694 (s), 1590 (w), 1086 (s). ^{1}H-NMR ($CDCl_3$, 200 MHz): δ 9.42 (d, 1H, J = 7.9 Hz), 7.38−7.21 (m, 5H), 7.11 (d, 1H, J = 17.7 Hz), 6.38 (dd, 1H, J = 17.9, 7.6 Hz), 0.30 (s, 6H). ^{13}C-NMR ($CDCl_3$, 50 MHz): δ 194.5, 156.4, 145.1, 135.7, 133.8, 129.8, 128.1, −3.4. MS (FI): 141 (8), 140 (100), 143 (2). Anal. Calcd for $C_{11}H_{14}OSi$: C, 68.69; H, 7.41. Found: C, 68.66; H, 7.52.

Preparation of (1*R*,2*R*)-1,2-Bis[(trifluoromethyl)sulfonamido]cyclohexane (12).[18,31] A three-neck flask equipped with a thermometer, a septum cap, an addition funnel, a magnetic stirring bar, and an argon outlet was charged with *trans*-(1*R*,2*R*)-cyclohexanediamine[31] (5.0 g, 43.9 mmol), CH_2Cl_2 (50 mL), and triethylamine (13.5 mL). This solution was cooled to −78 °C, and a CH_2Cl_2 (25 mL) solution of trifluoromethanesulfonic anhydride (16.2 mL, 96.6 mmol) was added dropwise over 1 h. The reaction mixture was warmed to rt, stirred for 1 h, and poured into ether (300 mL) and water (200 mL). The aqueous layer was separated and washed twice with ether (2 × 50 mL). The combined organic layer was washed with water (100 mL), dried over $MgSO_4$, and concentrated, affording a crystalline residue. Recrystallization from $CHCl_3$ and hexane furnished pure **12** (10.0 g, 60%) as a white powder (mp 148−156 °C). $[\alpha]_D$ = −6.1° (*c* = 5.78, EtOH), $[\alpha]_D$ = −43.7° (*c* = 2.06, pyridine). IR (neat): 3440 (br), 3305 (m), 2960 (s), 1460 (m), 2385 (m). ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 8.02−7.94 (m, 2H), 3.44−3.32 (m, 2H), 2.21−2.10 (m, 4H), 1.88−1.65 (m, 4H), 1.45−1.34 (m, 2H). ^{13}C-NMR ($CDCl_3$, 75.5 MHz): δ 120.9 (CF_3, J = 320 Hz), 59.7, 34.2, 25.3. MS (FD): 379 ((M + 1)$^+$, 30), 378 (100). Anal. Calcd for $C_8H_{12}N_2S_2O_4F_6$: C, 25.40; H, 3.20; N, 7.41. Found: C, 25.33; H, 3.18; N, 7.38.

Typical Procedure for the Preparation of Functionalized Dialkylzincs 11.[5] Preparation of Bis(5-acetoxypentyl)zinc. A Schlenk flask equipped with an argon inlet and a septum cap was charged with CuI (2 mg, ca. 0.01 mmol), 5-iodopentyl acetate (4.1 g, 16 mmol), and Et_2Zn (2.0 mL, 20 mmol). The reaction mixture was warmed to 50 °C and stirred for 8 h at this temperature. The Schlenk flask was connected to the vacuum (0.1 mmHg), and the excess Et_2Zn and formed EtI were collected in a trap cooled with liquid N_2. This operation required ca. 2 h at 50 °C. The resulting dialkylzinc was diluted in toluene (8 mL) and was ready to use. By

(33) Colvin, E. W. *Silicon Reagents in Organic Synthesis*; Academic Press: London, 1988; p 124.

running the reaction in the presence of an internal standard and by performing an iodolysis of a reaction aliquot, a GC yield ≥80% yield was found. In the case of the bis(4-chlorobutyl)-zinc a yield of only 60% was obtained, because this organozinc has a moderate stability under the reaction conditions. The duration of the iodine–zinc exchange was reduced to 4 h, and the removal of the byproducts *in vacuo* was performed more quickly: after 30 min at 50 °C under 0.1 mmHg, evacuation was interrupted and *n*-decane (2 mL) was added. Vacuum was applied again for 30 min at 50 °C, affording pure bis(4-chlorobutyl)zinc in 80% yield (GC analysis).

Caution: the cooled trap containing Et_2Zn and EtI should be immediately diluted with ether, THF, or hexane at the end of the reaction. The condensation of liquid oxygen on neat diethylzinc must absolutely be avoided since such mixtures are explosive.

Typical Procedure for the Asymmetric Addition of a Functionalized Dialkylzinc to 1, 2a–c, or 7. Preparation of (*S*)-(−)-7-Chloro-1-(tributylstannyl)-1-hepten-3-ol (3e). Procedure A. This procedure was used for most examples described in Table 1. A 50-mL three-neck flask equipped with an argon inlet, a thermometer, and a septum cap was charged with dry toluene (1 mL), Ti(O-*i*-Pr)$_4$ (1.2 mL, 4 mmol), and (1*R*,2*R*)-1,2-bis[(trifluoromethyl)sulfonamido]cyclohexane (63 mg, 0.16 mmol). The reaction mixture was heated to 40–45 °C for 0.5 h and then cooled to −55 °C. Bis(4-chlorobutyl)zinc (prepared from 4-chloro-1-iodobutane (3.06 g, 14 mmol, 45 °C, 4 h)) in toluene (6 mL) was added, followed after 5 min by the aldehyde **1**, **2a–c**, or **7** (2 mmol). The reaction mixture was stirred for 2–6 h at −55 °C (16–21 h at −20 °C in the case of **7**). GC analysis of a hydrolyzed reaction aliquot indicates the completion of the reaction. The reaction mixture was quenched with a 10% HCl solution and extracted with ether. The aqueous phase was extracted twice with ether, and the combined organic phase was washed successively with a saturated aqueous $NaHCO_3$ solution (2 × 100 mL) and brine (3 × 50 mL) and was dried over $MgSO_4$. After filtration and evaporation of the solvents, the residual oil was purified by flash chromatography using mixtures of hexane and ether (hexane:ether 75:25; in the case of stannyl derivatives **3**, the eluant was shaken with concd aqueous NH_4OH (1–5 mL) prior to use) leading to the pure allylic alcohol **3e** as a colorless oil (604 mg, 69% yield). The enantiomeric excess was 92–95% ee as determined by converting the allylic alcohol in the corresponding *O*-acetylmandelic ester prepared using (*S*)-(+)-*O*-acetylmandelic acid and DCC according to Parker's method (see below).[26] For most examples reported in Table 1, the alcohol was also treated with (±)-*O*-acetylmandelic acid providing a mixture of the two diastereomeric esters and allowing a facile determination of the enantiomeric excess by ^{1}H-NMR spectra analysis.

Procedure B. The catalyst was prepared as above from **12** (110 mg, 0.28 mmol) and Ti(O-*i*-Pr)$_4$ (2.18 g, 7.7 mmol) in toluene (2 mL) by heating this mixture at 50 °C for 30 min. It was cooled to −20 °C, and the toluene solution of bis(4-chlorobutyl)zinc (prepared from 4-chloro-1-iodobutane, 5.24 g, 24 mmol, in 80% yield) was added, leading to a clear yellow solution. It was stirred for 30 min at −40 °C, and the aldehyde (**1**) (1.21 g, 3.5 mmol) dissolved in toluene (2 mL) was rapidly added. Under these conditions, the reaction was rapid and a conversion >90% was observed after 15-min reaction time. After 0.5 h, the reaction mixture was quenched and workedup as usual. After flash purification of the crude residue, the alcohol **3e** was isolated as a clear oil (1.21 g, 79% yield; 95% ee).

Typical Procedure for the Preparation of the *O*-Acetylmandelic Esters of the Allylic Alcohols 3 and 4.[26] A 10-mL three-neck flask equipped with an argon inlet, a thermometer, and a septum cap was charged with (*S*)-(+)-*O*-acetylmandelic acid (97 mg, 0.5 mmol) and 4-(*N*,*N*-dimethylamino)pyridine (7.5 mg, 0.06 mmol) in CH_2Cl_2 (1 mL) and was cooled to −20 °C. A solution of the alcohol **3** or **4** (0.25 mmol) and 1,3-dicyclohexylcarbodiimide (103 mg, 0.5 mmol) in CH_2Cl_2 (0.5 mL) was added, and the reaction mixture was stirred for 2 h at −20 °C. No starting alcohol could be detected by TLC analysis. The resulting heterogeneous reaction mixture was diluted with a 1:4 mixture of ethyl acetate–hexane (10 mL) and was filtered over a short chromatography column eluted with ethyl acetate–hexane (2 × 10 mL), and the resulting solution (ca. 35 mL) was concentrated *in vacuo*. The ^{1}H-NMR spectrum of this crude oil (usually >90% pure) was used for the enantiomeric excess determination.

Analytical Data of the Alcohols 3a–h and 4a–h Described in Table 1. (*S*)-(*E*)-(−)-1-(Tributylstannyl)-1-penten-3-ol (3a). Yield: 653 mg, 87%; 90% ee. Prepared using Et_2Zn (1.2 mL, 12 mmol) and **1** (690 mg, 2 mmol). Reaction conditions: −60 °C, 2 h. Chromatography solvent: hexane–ether 90:10. $[\alpha]_D = -0.3°$ (c = 3.37, benzene). IR (neat): 3332 (br), 2959 (s), 2927 (s), 2873 (s), 2855 (s), 1464 (m). ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 6.06 (d, 1H, J = 19.1 Hz), 5.92 (dd, 1H, J = 19.1, 5.4 Hz), 3.97–3.89 (m, 1H), 1.52–1.20 (m, 15H), 0.82 (t, 9H, J = 7.1 Hz,), 0.85–0.76 (m, 9H). ^{13}C-NMR ($CDCl_3$, 75 MHz): δ 150.6, 127.7, 76.2, 29.6, 28.9, 27.0, 13.5, 9.4, 9.3. MS (FD): 330 (21), 236 (10), 163 (25), 82 (42), 39 (100). Anal. Calcd for $C_{17}H_{36}OSn$: C, 54.42; H, 9.67. Found: C, 54.47; H, 9.87.

(*S*)-(*E*)-1-(Tributylstannyl)-1-octen-3-ol (3b). Yield: 1.47 g, 88%; 92% ee. Prepared using dipentylzinc (1.66 mL, 8 mmol) and **1** (1.38 g, 4 mmol). Reaction conditions: −55 °C, 2 h. Chromatography solvent: hexane–ether 85:15. $[\alpha]_D = -0.2°$ (c = 14.42, benzene). IR (neat): 3336 (br), 2909 (s), 2873 (s), 2857 (s), 1464 (m). ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 6.06 (d, 1H, J = 19.1 Hz), 5.94 (dd, 1H, J = 19.1, 5.2 Hz), 4.03–3.96 (m, 1H), 1.48–1.18 (m, 21H), 0.83 (t, 9H, J = 7.2 Hz), 0.86–0.72 (m, 9H). ^{13}C-NMR ($CDCl_3$, 75 MHz): δ 151.3, 127.7, 75.7, 37.0, 31.9, 29.1, 27.3, 25.1, 22.7, 14.1, 13.7, 9.6. MS (FD): 418 (M + 1, 100), 417 (M^+, 11), 416 (31), 415 (24), 399 (15). Anal. Calcd for $C_{20}H_{42}OSn$: C, 57.55; H, 10.29. Found: C, 57.57; H, 10.15.

(*S*)-(*E*)-(−)-1-(Tributylstannyl)-1-undecen-3-ol (3c). Yield: 661 mg, 72%; 90% ee. Prepared using dioctylzinc (ca. 7 mmol obtained from octyl iodide (1.92 g, 8 mmol; 55 °C, 9 h)) and **1** (690 mg, 2 mmol). Reaction conditions: −55 °C, 3 h. Chromatography solvent: hexane–ether 85:15. $[\alpha]_D = -0.2°$ (c = 16.95, benzene). IR (neat): 3330 (br), 2957 (s), 2927 (s), 2873 (s), 2855 (s), 1464 (m). ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 6.09 (d, 1H, J = 19.1 Hz), 5.96 (dd, 1H, J = 19.1, 5.2 Hz), 4.06–3.99 (m, 1H), 1.50–1.21 (m, 27H), 0.92–0.77 (m, 18H). ^{13}C-NMR ($CDCl_3$, 75 MHz): δ 151.1, 127.6, 75.6, 36.9, 31.8, 29.6, 29.5, 29.2, 29.0, 27.2, 25.3, 22.6, 14.0, 13.6, 9.4. MS (FD): 460 (M + 1, 63), 459 (M^+, 63), 458 (M − 1, 100), 456 (30), 443 (28). Anal. Calcd for $C_{23}H_{48}OSn$: C, 60.14; H, 10.53. Found: C, 60.09; H, 10.65.

(*S*)-(*E*)-(−)-6-Hydroxy-8-(tributylstannyl)-7-octenyl Acetate (3d). Yield: 689 mg, 75%; 91% ee. Prepared using bis(5-acetoxypentyl)zinc (ca. 7 mmol) which was obtained from 5-iodopentyl acetate (2.05 g, 8 mmol, 55 °C, 6 h) and **1** (690 mg, 2 mmol). Reaction conditions: −55 °C, 3 h. Chromatography solvent: hexane–ether 75:25. $[\alpha]_D = -1.2°$ (c = 13.17, benzene). IR (neat): 3434 (br), 2957 (s), 2929 (s), 2873 (s), 1744 (s), 1464 (m). ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 6.11 (d, 1H, J = 19.1 Hz), 5.97 (dd, 1H, J = 19.1, 5.3 Hz), 4.04 (t, 2H, J = 6.7 Hz), 4.12–4.02 (m, 1H), 2.03 (s, 3H), 1.53–1.25 (m, 21H), 0.87 (t, 9H, J = 7.2 Hz), 0.90–0.85 (m, 6H). ^{13}C-NMR ($CDCl_3$, 75 MHz): δ 171.3, 151.0, 127.9, 75.5, 64.5, 36.8, 29.1, 28.6, 27.3, 25.9, 25.1, 21.0, 13.7, 9.5. MS (FD): 419 (40), 418 (100), 416 (22). Anal. Calcd for $C_{22}H_{44}O_3Sn$: C, 55.60; H, 9.33. Found: C, 55.43; H, 9.27.

(*S*)-(*E*)-(-)-7-Chloro-1-(tributylstannyl)-1-hepten-3-ol (3e). Yield: 604 mg, 69%; 92–95% ee. Prepared using bis(4-chlorobutyl)zinc (ca. 6 mmol) which was obtained from 4-chloro-1-iodobutane (3.06 g, 14 mmol, 45 °C, 5 h) and **1** (690 mg, 2 mmol). Reaction conditions: −55 °C, 3 h. Chromatography solvent: hexane–ether 75:25. $[\alpha]_D = -1.8°$ (c = 1.14, benzene). IR (neat): 3322 (br), 2957 (s), 2925 (s), 2873 (s), 2855 (s), 1464 (m). ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 6.09 (d, 1H, J = 19.1 Hz), 5.94 (dd, 1H, J = 19.1, 5.4 Hz), 4.06–3.98 (m, 1H), 3.48 (t, 2H, J = 6.7 Hz), 1.79–1.71 (m, 2H), 1.54–1.21 (m, 17H), 0.83 (t, 9H, J = 7.2 Hz), 0.86–0.78 (m, 6H). ^{13}C-NMR ($CDCl_3$, 75 MHz): δ 150.7, 128.1, 75.2, 44.8, 35.9, 32.4, 28.9, 27.1, 22.6, 13.6, 9.3. MS (EI): 381 (2), 210 (7), 197 (17), 195 (13), 120

(19). Anal. Calcd for $C_{19}H_{39}ClOSn$: C, 52.14; H, 8.98. Found: C, 52.06; H, 8.71.

(*S*)-(*E*)-(−)-4-Hydroxy-6-(tributylstannyl)-5-hexenyl 2,2-Dimethylpropionate (3f). Yield: 328 mg, 67%; 90% ee. Prepared using bis(3-pivaloxypropyl)zinc (ca. 2 mmol) which was obtained from 3-iodopropyl 2,2-dimethylpropionate (1.08 g, 4 mmol; 55 °C, 4 h) and **1** (345 mg, 1 mmol). Reaction conditions: −55 °C, 2 h. Chromatography solvent: hexane−ether 75:25. $[\alpha]_D = -1.5°$ ($c = 2.00$, benzene). IR (neat): 3438 (br), 2959 (s), 2929 (s), 2873 (s), 1732 (s). ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 6.10 (d, 1H, $J = 19.1$ Hz), 5.92 (dd, 1H, $J = 19.1$, 5.4 Hz), 4.03 (t, 2H, $J = 6.3$ Hz), 4.08−3.98 (m, 1H), 1.53−1.19 (m, 17H), 1.14 (s, 9H), 0.83 (t, 9H, $J = 7.2$ Hz), 0.87−0.78 (m, 6H). ^{13}C-NMR ($CDCl_3$, 75 MHz): δ 170.4, 150.5, 128.2, 74.9, 64.1, 38.6, 33.1, 28.9, 27.1, 27.1, 24.6, 13.5, 9.4. MS (FD): 490 (M +1 , 1), 489 (M^+, 5), 433 (100), 432 (64), 431 (51), 429 (20). Anal. Calcd for $C_{23}H_{46}O_3Sn$: C, 56.46; H, 9.48. Found: C, 56.68; H, 9.72.

(*S*)-(*Z*)-(−)-2-Iodo-1-(tributylstannyl)-1-penten-3-ol (3g). Yield: 353 mg, 75%; 94% ee. Prepared using diethylzinc (0.2 mL, 2 mmol) and **7** (471 mg, 1 mmol). Reaction conditions: −20 °C, 8 h. Chromatography solvent: hexane−ether 85:15. $[\alpha]_D = -1.1°$ ($c = 1.86$, benzene). IR (neat): 3390 (m), 2955 (s), 2920 (s), 1462 (s). ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 7.17 (s, 1H), 3.42−3.36 (m, 1H), 1.88−0.96 (m, 21H), 0.89−0.79 (m, 12H). ^{13}C-NMR ($CDCl_3$, 75 MHz): δ 141.8, 132.3, 83.0, 29.6, 29.1, 27.3, 13.7, 10.8, 9.5. MS (FD): 420 (30), 418 (100), 416 (11), 414 (12). Anal. Calcd for $C_{17}H_{35}IOSn$: C, 40.75; H, 7.04. Found: C, 40.53; H, 6.86.

(*S*)-(*Z*)-(−)-7-Aza-2-iodo-9-phenyl-1-(tributylstannyl)-8-[(trifluoromethyl)sulfonyl]-1-octen-3-ol (3h). Yield: 466 mg, 62%; 82% ee. Prepared using bis[[*N*-benzyl-*N*-[(trifluoromethyl)sulfonyl]-3-amino]propyl]zinc (ca. 2 mmol) which was obtained from 3-iodo-*N*-benzyl-*N*-[(trifluoromethyl)sulfonyl]-propylamine (1.69 g, 4 mmol, 55 °C, 14 h) and **7** (471 mg, 1 mmol). Reaction conditions: −20 °C, 22 h. Chromatography solvent: hexane−ether 85:15. $[\alpha]_D = -2.8°$ ($c = 1.09$, benzene). IR (neat): 3308 (m), 2970 (s), 2937 (s), 2885 (s), 2857 (s). ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 7.15 (s, 1H), 4.45 (brs, 2H), 3.45−3.39 (m, 1H), 3.30−3.02 (m, 3H), 1.51−1.19 (m, 18H), 1.01−0.96 (m, 4H), 0.84 (t, 9H, $J = 7.2$ Hz). ^{13}C-NMR ($CDCl_3$, 75 MHz): δ 142.2, 134.2, 130.9, 129.1, 128.9, 128.5, 128.4, 120.0 (q, CF_3, $J = 320$ Hz), 80.6, 51.8, 47.7, 33.0, 28.9, 27.1, 13.5, 10.6. MS (FD): 464 (0.2), 391 (2), 378 (2), 336 (0.1), 202 (1), 126 (0.6). Anal. Calcd for $C_{26}H_{43}F_3INO_3SSn$: C, 41.51; H, 5.76; N, 1.87. Found: C, 41.46; H, 5.80; N, 1.90.

(*S*)-(*E*)-(+)-1-(Dimethylphenylsilyl)-1-penten-3-ol (4a). Yield: 410 mg, 93%; 94% ee. Prepared using diethylzinc (0.51 mL, 5 mmol) and **2c** (381 mg, 2 mmol). Reaction conditions: −40 °C, 12 h. Chromatography solvent: hexane−ether 4:1. $[\alpha]_D = +19.6°$ ($c = 1.74$, benzene). IR (neat): 3379(m), 2362(s), 1621(s). ^{1}H-NMR ($CDCl_3$, 200 MHz): δ 7.56−7.31 (m, 5H), 6.15 (dd, 1H, $J = 18.8$, 4.8 Hz), 6.02 (dd, 1H, $J = 18.8$, 0.8 Hz), 3.98 (m, 1H), 1.63 (s, 1H), 1.54 (dq, 2H, $J = 0.8$, 7.2 Hz), 0.93 (t, 3H, $J = 7.3$ Hz). ^{13}C-NMR ($CDCl_3$, 50 MHz): δ 152.8, 141.2, 136.4, 131.6, 130.4, 129.7, 78.4, 32.3, 12.2, 0.0. MS (EI): 205 (5), 135 (52), 75 (100) Anal. Calcd for $C_{13}H_{20}OSi$: C, 70.85; H, 9.15. Found: C, 70.85; H, 9.20.

(*RS*)-(*E*)-1-(Dimethylphenylsilyl)-6-[(triisopropylsilyl)-oxy]-1-hexen-3-ol (4b). Yield: 505 mg, 67%; 0% ee. Prepared using bis[3-[(triisopropylsilyl)oxy]propyl]zinc (ca. 5 mmol) prepared from 1-iodo-3-[(triisopropylsilyl)oxy]propane (3.42 g, 10 mmol) and **2c** (381 mg, 2 mmol). Reaction conditions: −40 °C, 12 h. Chromatography solvent: hexane−ether 4:1. IR (neat): 3421 (m), 1621 (m), 1113 (s). ^{1}H-NMR ($CDCl_3$, 200 MHz): δ 7.45−7.25 (m, 7H), 6.09 (dd, 1H, $J = 18.8$, 4.4 Hz), 5.92 (dd, 1H, $J = 18.8$, 0.8 Hz), 4.13 (m, 1H), 3.66 (t, 2H, $J = 5.6$ Hz), 2.85 (d, 1H, $J = 3.2$ Hz), 1.60 (m, 3H), 0.99 (d, 18H, $J = 3.2$ Hz), 0.27 (s, 6H). ^{13}C-NMR ($CDCl_3$, 50 MHz): δ 153.2, 141.3, 136.4, 131.5, 130.3, 129.0, 76.6, 66.2, 37.0, 31.5, 20.5, 14.5, 0.0. MS (EI): 205 (14), 135 (58), 75 (76), 40 (100). Anal. Calcd for $C_{23}H_{42}O_2Si_2$: C, 67.92; H, 10.41. Found: C, 68.04; H, 10.53

(*S*)-(*E*)-(+)-1-(Trimethylsilyl)-1-octen-3-ol (4c). Yield: 289 mg, 72%; 80% ee. Prepared using dipentylzinc (1.04 mL, 5 mmol) and **2a** (256 mg, 2 mmol). Reaction conditions: −60 °C, 12 h. Chromatography solvent: hexane−ether 4:1. $[\alpha]_D = +9.7°$ ($c = 6.3$, benzene). IR (neat): 3352 (m), 1621(w), 866(s). ^{1}H-NMR ($CDCl_3$, 200 MHz): δ 6.03 (dd, 1H, $J = 18.8$, 5.2 Hz), 5.82 (dd, 1H, $J = 18.8$, 0.8 Hz), 4.01 (m, 1H), 1.53−1.24 (m, 9H), 0.82 (t, 3H, $J = 6.8$ Hz), 0.00 (s, 9H). ^{13}C-NMR ($CDCl_3$, 50 MHz): δ 150.1, 130.3, 76.0, 38.2, 33.1, 26.4, 23.9, 15.3, 0.0. MS (EI): 185 (3), 144 (19), 129 (24), 75 (100). Anal. Calcd for $C_{11}H_{24}OSi$: C, 65.93; H, 12.07. Found: C, 65.94; H, 12.34.

(*S*)-(*E*)-(+)-8-Pivaloxy-1-(trimethylsilyl)-1-octen-3-ol (4d). Yield: 403 mg, 67%; 85% ee. Prepared using bis(5-pivaloxypentyl)zinc (ca. 5 mmol) prepared from 1-iodo-5-pivaloxypentane (2.98 g, 10 mmol) and **2a** (256 mg, 2 mmol). Reaction conditions: −40 °C, 12 h. Chromatography solvent: hexane−ether 4:1. $[\alpha]_D = +5.4°$ ($c = 5.74$, benzene). IR (neat): 3452 (m), 1733 (s), 1621 (w), 1248 (s). ^{1}H-NMR ($CDCl_3$, 200 MHz): δ 5.97 (dd, 1H, $J = 18.7$, 5.0 Hz), 5.76 (dd, 1H, $J = 18.5$, 1.0 Hz), 3.98 (m, 3H), 1.59−1.29 (m, 9H), 1.12 (s, 9H), 0.0 (s, 9H). ^{13}C-NMR ($CDCl_3$, 50 MHz): δ 179.9, 149.9, 130.6, 75.8, 65.6, 40.0, 38.1, 29.9, 28.5, 27.2, 26.3, 0.0. MS (EI): 159 (26), 103 (62), 75 (75), 57 (100). Anal. Calcd for $C_{16}H_{32}O_3Si$: C, 63.95; H, 10.73. Found: C, 63.91; H, 10.46.

(*S*)-(*E*)-(+)-6-Pivaloxy-1-(trimethylsilyl)-1-hexen-3-ol (4e). Yield: 338 mg, 62%; 90% ee. Prepared using bis[3-(pivaloyloxy)propyl]zinc (ca. 5 mmol) prepared from 1-iodo-3-(pivaloyloxy)propane (2.70 g, 10 mmol) and **2a** (256 mg, 2 mmol). Reaction conditions: −15 °C, 12 h. Chromatography solvent: hexane−ether 4:1. $[\alpha]_D = +4.7°$ ($c = 7.18$, benzene). IR (neat): 3454 (m), 1733 (s), 1621 (w), 1248 (s). ^{1}H-NMR ($CDCl_3$, 200 MHz): δ 6.02 (dd, 1H, $J = 18.7$, 5.0 Hz), 5.83 (dd, 1H, $J = 18.7$, 1.0 Hz), 4.03 (m, 3H), 1.73−1.49 (m, 5H), 1.11 (s, 9H), 0.0 (s, 9H). ^{13}C-NMR ($CDCl_3$, 50 MHz): δ 180.0, 149.5, 131.1, 75.4, 65.6, 40.1, 34.5, 28.5, 26.0, 0.0. MS (EI): 159 (15), 113 (32), 75 (75), 57 (100). Anal. Calcd for $C_{14}H_{26}O_3Si$: C, 61.72; H, 10.36. Found: C, 61.84; H, 10.22.

(*S*)-(*E*)-(−)-7-Chloro-1-(trimethylsilyl)-1-hepten-3-ol (4f). Yield: 261 mg, 59%; 70% ee. Prepared using bis(4-chlorobutyl)zinc (ca. 5 mmol) prepared from 1-chloro-4-iodobutane (2.18 g, 10 mmol) and **2a** (256 mg, 2 mmol). Reaction conditions: −50 °C, 12 h. Chromatography solvent: hexane−ether 4:1. $[\alpha]_D = -40.4°$ ($c = 9.03$, benzene). IR (neat): 3385 (m), 1621 (w), 867 (s). ^{1}H-NMR ($CDCl_3$, 200 MHz): δ 5.97 (dd, 1H, $J = 18.6$, 5.0 Hz), 5.77 (dd, 1H, $J = 18.6$, 0.8 Hz), 4.02 (m, 1H), 3.47 (t, 2H, $J = 6.6$ Hz), 1.74−1.43 (m, 6H), 0.0 (s, 9H). ^{13}C-NMR ($CDCl_3$, 50 MHz): δ 149.6, 130.9, 75.7, 46.2, 37.3, 33.8, 24.1, 0.0. MS (EI): 185 (9), 93 (41), 75 (100). Anal. Calcd for $C_{26}H_{21}ClOSi$: C, 54.39; H, 9.59. Found: C, 54.35; H, 9.74.

(*S*)-(*E*)-(+)-6-Pivaloxy-1-(triethylsilyl)-1-hexen-3-ol (4g). Yield: 447 mg, 71%; 90% ee. Prepared using bis[3-(pivaloyloxy)propyl]zinc (ca. 5 mmol) prepared from 1-iodo-3-(pivaloyloxy)propane (2.70 g, 2 mmol) and **2c** (341 mg, 2 mmol). Reaction conditions: - 5 °C, 12 h. Chromatography solvent: hexane−ether 4:1. $[\alpha]_D = +3.9°$ ($c = 8.86$, benzene). IR (neat): 3455 (m), 1733 (s), 1623 (w), 992 (s). ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 6.02 (dd, 1H, $J = 18.9$, 5.5 Hz), 5.75 (dd, 1H, $J = 18.9$, 1.1 Hz), 4.12−4.04 (m, 1H), 4.03 (t, 2H, $J = 6.4$ Hz), 1.93 (brs, 1H), 1.78−1.51 (m, 4H), 1.16 (s, 9H), 0.83 (t, 9H, $J = 7.9$ Hz), 0.54 (q, 6H, $J = 7.9$ Hz). ^{13}C-NMR ($CDCl_3$, 75 MHz): δ 178.6, 149.7, 125.9, 74.3, 64.2, 38.7, 33.2, 27.2, 24.6, 7.3, 4.0. MS (FD): 315 (6), 314 (1), 286 (17), 285 (100). Anal. Calcd for $C_{17}H_{34}O_3Si$: C, 64.91; H, 10.89. Found: C, 64.77; H, 10.84.

(*S*)-(*E*)-(+)-1-(Triethylsilyl)-1-penten-3-ol (4h). Yield: 369 mg, 92%; 90% ee. Prepared using Et_2Zn (0.51 mL, 5 mmol) and **2b** (341 mg, 2 mmol). Reaction conditions: −50 °C, 12 h. Chromatography solvent: hexane−ether 4:1. $[\alpha]_D = +9.8°$ ($c = 6.63$, benzene). IR (neat): 3340 (m), 1623 (w), 1017 (s). ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 5.98 (dd, 1H, $J = 18.9$, 5.5 Hz), 5.69 (dd, 1H, $J = 18.9$, 1.2 Hz), 4.00−3.90 (m, 1H), 1.92−1.82 (brs, 1H), 1.52−1.42 (m, 2H), 0.90−0.82 (m, 12H), 0.56−0.44 (m, 6H). ^{13}C-NMR ($CDCl_3$, 75 MHz): δ 149.8, 128.0, 125.3, 76.0, 29.6, 9.3, 7.1, 3.3. MS (EI): 174 (9), 102 (9), 59 (12), 58 (100). Anal. Calcd for $C_{11}H_{24}OSi$: C, 63.93; H, 12.07. Found: C, 66.03; H, 12.03.

(*S*)-(*E*)-(+)-1-(Triethylsilyl)-1-octen-3-ol (4i). Yield: 392 mg, 81%; 99% ee. Prepared using dipentylzinc (1.04 mL, 5 mmol) and **2b** (341 mg, 2 mmol). Reaction conditions: −50

°C, 12 h. Chromatography solvent: hexane–ether 10:1. $[\alpha]_D$ = +8.0° (*c* = 6.63, benzene). IR (neat): 3344 (m), 1623 (w), 1017 (s). ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 5.99 (dd, 1H, *J* = 19.0, 5.5 Hz), 5.69 (dd, 1H, *J* = 18.9, 1.2 Hz), 4.04–3.98 (m, 1H), 1.62–1.56 (m, 1H), 1.46–1.42 (m, 2H), 1.38–1.18 (m, 6H), 0.96–0.79 (m, 12H), 0.51 (q, 6H, 7.8 Hz). ^{13}C-NMR ($CDCl_3$, 75 MHz): δ 150.3, 125.3, 75.0, 37.0, 31.8, 25.0, 22.6, 14.0, 7.3, 3.5. MS (FD): 243 (31), 242 (100), 58 (15). Anal. Calcd for $C_{14}H_{30}OSi$: C, 69.35; H, 12.47. Found: C, 69.28; H, 12.56.

(*S*)-(*E*)-(+)-1-(Triethylsilyl)-1-undecen-3-ol (4j). Yield: 433 mg, 76%; 94% ee. Prepared using dioctylzinc (ca. 5 mmol) prepared from Oct-I (2.40 g, 10 mmol), and **2b** (341 mg, 2 mmol). Reaction conditions: −30 °C, 12 h. Chromatography solvent: hexane–ether 10:1. $[\alpha]_D$ = +3.7° (*c* = 1.91, benzene). ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 5.99 (dd, 1H, *J* = 18.9, 5.5 Hz), 5.69 (dd, 1H, *J* = 18.9, 1.2 Hz), 4.08–3.98 (m, 1H), 1.54 (brs, 1H), 1.50–1.40 (m, 2H), 1.38–1.16 (m, 12H), 0.92–0.78 (m, 12H), 0.56 (q, 6H, *J* = 7.5 Hz). ^{13}C-NMR ($CDCl_3$, 75 MHz): δ 150.1, 125.1, 74.8, 36.9, 31.8, 29.5, 29.4, 29.1, 25.2, 22.5, 13.9, 7.2, 3.3. MS (FD): 285 (18), 284 (41), 267 (100), 171 (20). Anal. Calcd for $C_{17}H_{36}OSi$: C, 71.76; H, 12.75. Found: C, 71.39; H, 12.65.

(*S*)-(*E*)-(+)-8-Acetoxy-1-(triethylsilyl)-1-octen-3-ol (4k). Yield: 367 mg, 61%; 93% ee. Prepared using bis(5-acetoxypentyl)zinc (ca. 5 mmol) prepared from 1-acetoxy-5-iodopentane (2.56 g, 10 mmol) and **2c** (341 mg, 2 mmol). Reaction conditions: −30 °C, 12 h. Chromatography solvent: hexane–ether 4:1. $[\alpha]_D$ = +6.6° (*c* = 7.12, benzene). IR (neat): 3444 (m), 1745 (s), 1623 (w), 1019 (s). ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 5.99 (dd, 1H, *J* = 18.9, 5.4 Hz), 5.69 (dd, 1H, *J* = 18.9, 1.2 Hz), 4.06–3.98 (m, 1H), 3.98 (t, 2H, *J* = 6.7 Hz), 1.97 (s, 3H), 1.75 (brs, 1H), 1.60–1.26 (m, 8H), 0.86 (t, 9H, *J* = 7.7 Hz), 0.49 (q, 6H, *J* = 7.8 Hz). ^{13}C-NMR ($CDCl_3$, 75 MHz): δ 171.2, 150.1, 125.4, 74.7, 64.5, 36.8, 28.6, 25.9, 25.0, 20.9, 7.3, 3.4. MS (FD): 272 (19), 271 (100). Anal. Calcd for $C_{16}H_{32}O_3Si$: C, 63.95; H, 10.73. Found: C, 64.05; H, 10.70.

Typical Procedure for the Preparation of 14–18. Preparation of (*S*)-(*E*)-(+)-3-(3′-Hydroxy-1′-undecen-1′-yl)-2-cyclohexen-1-one (14). A two-neck flask was charged with 3-iodo-2-cyclohexen-1-one (144 mg, 0.65 mmol), $Pd(dba)_2$ (12.4 mg, 0.022 mmol, 4 mol %), and TFP (10.7 mg, 0.043 mmol, 8 mol %) in THF (1 mL). The reaction mixture was stirred for a few minutes at rt leading to a yellow-green solution. (*S*)-(*E*)-(−)-3-Hydroxy-1-(tributylstannyl)-1-undecene, **3c** (250 mg, 0.54 mmol), was added, and the reaction mixture was stirred for 2 d at rt. After the usual workup, the crude residue was purified by flash chromatography (hexane–ether 6:4) affording **19a** as a colorless oil (120 mg, 84%). $[\alpha]_D$ = +24.2° (*c* = 1.3, benzene). IR (neat): 3400 (m), 2925 (s), 2850 (s), 1656 (s), 1637 (s), 1587 (w), 966 (w). ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 6.30 (d, 1H, 15.9 Hz), 6.12 (dd, 1H, *J* = 15.8, 5.9 Hz), 5.87 (s, 1H), 4.23–4.16 (m, 1H), 2.42–2.32 (m, 4H), 2.01–1.93 (m, 3H), 1.53–1.43 (m, 2H), 1.30–1.11 (m, 12H), 0.81 (brt, 3H). ^{13}C-NMR ($CDCl_3$, 75 MHz): δ 200.2, 156.6, 140.0, 130.6, 127.9, 72.3, 37.6, 37.2, 31.8, 29.5, 29.4, 29.2, 25.2, 25.1, 22.6, 22.2, 14.0. MS (EI): 264 (M^+, 2), 151 (11), 123 (100), 107 (24), 95 (11), 79 (13). Anal. Calcd for $C_{17}H_{28}O_2$: C, 77.22; H, 10.67. Found: C, 77.14; H, 10.47.

5-(3′-Hydroxy-1′-undecenyl)uracil (15). Yield: 98 mg, 65%. In this case, NMP was used instead of THF. Prepared as **14** using 5-iodouracil (129 mg, 0.54 mmol), **3c** (250 mg, 0.54 mmol), $Pd(dba)_2$ (12.4 mg, 0.022 mmol, 4 mol %), and TFP (10.7 mg, 0.043 mmol, 8 mol %) in NMP (1 mL) at 40 °C for 2 d. The solid product was recrystallized in hexane–ethyl acetate. $[\alpha]_D$ = +33.5° (*c* = 0.30, methanol). IR (KBr): 3416 (m), 3210 (w), 3068 (w), 2918 (s), 2847 (s), 1752 (s), 1673 (s), 1438 (m), 969 (m). ^{1}H-NMR (THF-d_8, 300 MHz): δ 10.09 (brs, 1H), 9.78 (brs, 1H), 7.20 (brt, 1H), 6.43 (dd, 1H, *J* = 15.8, 6.2 Hz), 6.09 (d, 1H, *J* = 15.8 Hz), 3.90–3.85 (m, 1H), 3.62 (d, 1H, *J* = 4.2 Hz), 1.34–1.19 (m, 14H), 0.78 (brt, 3H). ^{13}C-NMR (THF-d_8, 75.5 MHz): δ 163.1, 151.5, 138.3, 134.8, 121.2, 111.3, 73.0, 38.8, 32.8, 30.7, 30.6, 30.2, 26.5, 23.5, 14.4. MS (EI): 280 (2), 262 (39), 177 (71), 139 (100), 125 (51), 106 (46). Anal. Calcd for $C_{15}H_{24}N_2O_3$: C, 64.26; H, 8.63; N, 9.99. Found: C, 64.17; H, 8.51; N, 9.89.

(*S*)-(*E*)-(+)-Ethyl 4-(3′-Hydroxy-1′-undecen-1′-yl)benzoate (16). Yield: 141 mg, 82%. Prepared as **15** using *p*-carbethoxyiodobenzene (180 mg, 0.65 mmol), **3c** (250 mg, 0.54 mmol), $Pd(dba)_2$ (12.4 mg, 0.022 mmol, 4 mol %), and TFP (10.7 mg, 0.043 mmol, 8 mol %) in THF (1 mL) at rt for 2 d. Chromatography solvent hexane–ether 4:1. $[\alpha]_D$ = +4.5° (*c* = 1.1, benzene). IR (neat): 3467 (m), 2926 (s), 2855 (s), 1716 (s), 1602 (m), 1275 (s), 1111 (s), 763 (m). ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 7.93–7.90 (m, 2H), 7.37–7.34 (m, 2H), 6.55 (d, 1H, *J* = 15.9 Hz), 6.28 (dd, 1H *J* = 15.9, 6.4 Hz), 4.31 (q, 2H, *J* = 7.1 Hz), 4.27–4.24 (m, 1H), 1.72 (brs, 1H), 1.61–1.55 (m, 2H), 1.41–1.20 (m, 12H), 1.33 (t, 3H, *J* = 7.1 Hz), 0.81 (brt, 3H). ^{13}C-NMR ($CDCl_3$, 75 MHz): δ 166.5, 141.3, 135.4, 130.0, 129.4, 129.1, 126.3, 72.9, 61.0, 37.4, 31.9, 29.6, 29.6, 29.3, 25.5, 22.7, 14.4, 14.2. MS (EI): 318 (M^+, 2), 273 (18), 205 (95), 163 (63), 149 (77), 131 (72), 115 (41), 56 (100). Anal. Calcd for $C_{20}H_{30}O_3$: C, 75.43; H, 9.49. Found: C, 75.44; H, 9.37.

(*S*)-(*E*)-(+)-6-Hydroxy-1-phenyl-1,4-tetradecadiene (17). Yield: 110 mg, 71%. Prepared as **15** using cinnamyl chloride (83 mg, 0.54 mmol), **3c** (250 mg, 0.54 mmol), $Pd(dba)_2$ (12.4 mg, 0.022 mmol, 4 mol %), and TFP (21.4 mg, 0.086 mmol, 16 mol %) in THF (3 mL) at 40 °C for 2 d. Chromatography solvent hexane–ether 4:1. $[\alpha]_D$ = +16.9° (*c* = 1.5, benzene). IR (neat): 3367 (s), 2926 (s), 2855 (s), 1709 (s), 1666 (s), 1435 (m), 969 (m), 692 (m). ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 7.33–7.16 (m, 5H), 6.37 (d, 1H, *J* = 15.8 Hz), 6.17 (dt, 1H, *J* = 15.8, 6.6 Hz), 5.69 (dt, 1H, *J* = 15.4, 6.2 Hz), 5.53 (dd, 1H, *J* = 15.4, 6.8 Hz), 4.08–4.02 (m, 1H), 2.93–2.89 (m, 2H), 1.55–1.15 (m, 15H), 0.85 (brt, 3H). ^{13}C-NMR ($CDCl_3$, 75 MHz): δ 137.7, 134.6, 131.0, 129.3, 128.6, 128.3, 127.1, 126.1, 73.1, 37.5, 35.5, 32.0, 29.7, 29.7, 29.3, 25.6, 22.7, 14.2. MS (EI): 286 (M^+, 1), 284 (2), 169 (15), 155 (34), 130 (95), 107 (43), 89 (100). Anal. Calcd for $C_{20}H_{30}O$: C, 83.86; H, 10.55. Found: C, 83.69; H, 10.67.

(*S*)-(*E*)-(+)-2-Carbethoxy-6-hydroxy-1,4-tetradecadiene (18). Yield: 142 mg, 93%. Prepared as **15** using ethyl 2-(bromomethyl)acrylate (125 mg, 0.65 mmol), **3c** (250 mg, 0.54 mmol), $Pd(dba)_2$ (12.4 mg, 0.022 mmol, 4 mol %), and TFP (21.4 mg, 0.086 mmol, 16 mol %) in THF (3 mL) at 40 °C for 1 d. Chromatography solvent: hexane–ether 3:2. $[\alpha]_D$ = +6.9° (*c* = 1.0, benzene). IR (neat): 3400 (m), 2922 (s), 2854 (s), 1713 (s), 1628 (w), 1138 (m). ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 6.10 (d, 1H, *J* = 1.0 Hz), 5.61 (ddt, 1H, *J* = 15.4, 6.4, 0.5 Hz), 5.48 (d, 1H, *J* = 1.0 Hz), 5.47 (dd, 1H, *J* = 15.4, 6.6 Hz), 4.13 (q, 2H, *J* = 7.1 Hz), 4.03–3.96 (m, 1H), 2.9 (d, 2H, *J* = 6.4 Hz), 1.67 (s, 1H), 1.46–1.36 (m, 2H), 1.25–1.13 (m, 14H), 1.23 (t, 3H, *J* = 7.1 Hz), 0.80 (brt, 3H). ^{13}C-NMR ($CDCl_3$, 75 MHz): δ 166.9, 139.3, 135.6, 127.7, 125.2, 72.8, 60.7, 37.3, 34.4, 31.8, 29.5, 29.5, 29.2, 25.4, 22.6, 14.2, 14.1. MS (EI): 205 (21), 169 (43), 124 (11), 123 (100), 95 (36), 84 (22), 67 (34). Anal. Calcd for $C_{17}H_{30}O_3$: C, 72.30; H, 10.71. Found: C, 72.30; H, 10.51.

Typical Procedure for the Preparation of 19a,b. Preparation of (*S*)-(*E*)-3-Acetoxy-1-(tributylstannyl)-1-undecene (19a). A three-neck flask was charged with acetic anhydride (225 mg, 25 mmol), pyridine (284 mg, 3.6 mmol), and (*N*,*N*-dimethylamino)pyridine (DMAP, 142 mg, 1.2 mmol). The alcohol **3c** (500 mg, 1.2 mmol) was slowly added, and the reaction mixture was stirred for 5 h at rt. After the usual workup, the crude residue was purified by flash chromatography (hexane–ether 85:15) affording **19a** as a colorless oil (450 mg, 87% yield). $[\alpha]_D$ = −29.9° (*c* = 1.00, benzene). IR (neat): 2957 (s), 2927 (s), 2873 (s), 2855 (s), 1744 (s). ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 6.07 (d, 1H, *J* = 19.1 Hz), 5.81 (dd, 1H, *J* = 19.1, 5.9 Hz), 5.16–5.09 (m, 1H), 2.00 (s, 3H), 1.47–1.21 (m, 26H), 0.82 (t, 9H, *J* = 7.2 Hz), 0.88–0.74 (m, 9H). ^{13}C-NMR ($CDCl_3$, 75 MHz): δ 170.4, 146.1, 130.5, 77.2, 34.3, 31.9, 29.5, 29.5, 29.3, 29.1, 27.3, 25.2, 22.7, 21.4, 14.1, 13.7, 9.6. MS (FD): 503 (13), 502 (100), 501 (3), 500 (44), 350 (16), 58 (78). Anal. Calcd for $C_{26}H_{50}O_2Sn$: C, 58.15; H, 9.76. Found: C, 58.36; H, 9.82.

(*S*)-(*E*)-(−)-3-Acetoxy-1-(tributylstannyl)-1-octene (19b). Yield: 370 mg, 81%. Prepared as **19a** using acetic anhydride (194 mg, 1.9 mmol), **3b** (370 mg, 0.89 mmol), DMAP (105 mg, 0.9 mmol), and pyridine (211 mg, 2.7 mmol). Reaction conditions: 5 h, rt. Chromatography solvent: hexane–ether 4:1. $[\alpha]_D$ = −44.8° (*c* = 1.69, benzene). IR (neat): 2957 (s), 2929 (s), 2873 (s), 2857 (s), 1744 (s). ^{1}H-NMR ($CDCl_3$, 300 MHz): δ

6.17 (d, 1H, J = 19.2Hz), 6.03 (dd, 1H, J = 19.2, 5.9 Hz), 5.25–5.18 (m, 1H), 2.09 (s, 3H), 1.62–1.26 (m, 20H), 0.91 (t, 9H, J = 7.2 Hz), 0.97–0.86 (m, 9H). ^{13}C-NMR ($CDCl_3$, 75 MHz): δ 170.4, 146.1, 130.6, 77.2, 34.2, 31.7, 29.2, 27.3, 24.8, 22.6, 21.4, 14.1, 13.8, 9.6. MS (FD): 459 (M^+, 28), 458 (100), 457 (27), 403 (17), 148 (3). Anal. Calcd for $C_{22}H_{44}O_2Sn$: C, 57.35; H, 9.65. Found: C, 57.67; H, 9.80.

Preparation of (*S*)-(*E*)-(−)-3-[(*tert*-butyldimethylsilyl)oxy]-1-(tributylstannyl)-1-undecene (19c). A 25-mL three-neck flask was charged with *tert*-butyldimethylsilyl chloride (745 mg, 5 mmol), imidazole (750 mg, 10 mmol), and DMAP (105 mg, 0.9 mmol) in DMF (3 mL). The alcohol **3c** (1.0 g, 2.18 mmol) was slowly added, and the reaction mixture was stirred at 40 °C for 4 h. The solvents were evaporated under vacuum, and the residue was purified by flash chromatography (hexane–ether 85:15) affording the silyl ether **19c** (1.19 g, 95% yield) as a colorless oil. $[\alpha]_D$ = −7.2° (c = 2.09, benzene). IR (neat): 2960 (s), 2932 (s), 2860 (s), 1462 (m). ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 5.98 (d, 1H, J = 19.1 Hz), 5.88 (dd, 1H, J = 19.0, 5.3 Hz), 4.01–3.95 (m, 1H), 1.53–1.21 (m, 26H), 0.86 (s, 9H), 0.85 (t, 9H, J = 7.2 Hz), 0.93–0.79 (m, 9H), 0.86 (s, 3H), −0.01 (s, 3H). ^{13}C-NMR ($CDCl_3$, 75 MHz): δ 152.1, 126.2, 76.8, 38.1, 31.9, 29.6, 29.6, 29.2, 29.1, 27.2, 25.9, 25.3, 22.6, 18.3, 14.0, 13.6, 9.4, −4.3, −4.8. MS (FD): 575 (33), 574 (91), 573 (58), 572 (100), 517 (14). Anal. Calcd for $C_{29}H_{62}OSiSn$: C, 60.72; H, 10.89. Found: C, 60.76; H, 10.92.

Typical Procedure for the Acylation of 19a–c. Preparation of (*S*)-(*E*)-(−)-4-Acetoxy-1-phenyl-2-dodecen-1-one (20a). A two-neck flask was charged with benzoyl chloride (65 mg, 0.46 mmol) in THF (2.5 mL), $Pd(dba)_2$ (5.5 mg, 0.0095 mmol, 2.5 mol %), and tri-*o*-furylphosphane (4.4 mg, 0.019 mmol, 5 mol %). The reaction mixture was stirred a few minutes at rt, leading to a yellow-green solution. (*S*)-(*E*)-(−)-3-Acetoxy-1-(tributylstannyl)-1-undecene (**19a**) (200 mg, 0.38 mmol) was added, and the reaction mixture was stirred for 6 h at rt. The solvent was evaporated, and the residue was purified by flash chromatography (hexane–ether 85:15) leading to the pure (*E*)-γ-acetoxy enone **20a** (108 mg, 90% yield). $[\alpha]_D$ = −8.5° (c = 0.75, benzene). IR (neat): 2983 (s), 2950 (s), 2880 (s), 1742 (s), 1605 (s). ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 7.89–7.86 (m, 2H), 7.52–7.40 (m, 3H), 6.94 (d, 1H, J = 15.5 Hz), 6.85 (dd, 1H, J = 15.5, 5.3 Hz), 5.48–5.39 (m, 1H), 2.07 (s, 3H), 1.65–1.52 (m, 2H), 2.34–1.15 (m, 10H), 0.82 (m, 5H). ^{13}C-NMR ($CDCl_3$, 75 MHz): δ 190.4, 170.3, 145.5, 133.1, 128.7, 125.6, 73.3, 34.1, 31.9, 31.7, 29.5, 29.4, 29.2, 29.0, 25.1, 22.7, 21.2, 14.2. MS (EI): 281 (18), 209 (10), 208 (20), 207 (100), 105 (37), 71 (36). Anal. Calcd for $C_{20}H_{28}O_3$: C, 75.91; H, 8.91. Found: C, 75.62; H, 9.02.

Analytical Data of 20b–e. (*S*)-(*E*)-(+)-1-Phenyl-4-[(*tert*-butyldimethylsilyl)oxy]-2-dodecen-1-one (20b). Prepared as **20a** using benzoyl chloride (93 mg, 0.66 mmol) and **19c** (250 mg, 0.44 mmol). Yield: 175 mg, 83% as a colorless oil. $[\alpha]_D$ = +8.8° (c = 2.16, benzene). IR (neat): 2994 (s), 2956 (s), 2912 (s), 1670 (s), 1625 (s). ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 7.90–7.86 (m, 2H), 7.50–7.41 (m, 3H), 7.04 (d, 1H, J = 15.4 Hz), 6.98 (dd, 1H, J = 15.2, 3.2 Hz), 4.38–4.33 (m, 1H), 1.56–1.49 (m, 2H), 1.37–1.17 (m, 12H), 0.89 (s, 9H), 0.81 (brt, 3H), 0.03 (s, 3H), 0.02 (s, 3H). ^{13}C-NMR ($CDCl_3$, 75 MHz): δ 190.6, 151.4, 138.0, 132.6, 128.5, 128.5, 123.5, 72.0, 37.4, 31.8, 29.6, 29.4, 29.2, 25.8, 24.9, 22.6, 18.2, 15.2, 14.0, −4.6, −4.9. MS (EI): 388 (M^+, 5), 332 (41), 331 (100), 275 (13), 233 (15), 105 (30). Anal. Calcd for $C_{24}H_{40}O_2Si$: C, 74.17; H, 10.37. Found: C, 74.23; H, 10.29.

(*S*)-4-Acetoxy-1-cyclohexyl-2-nonen-1-one (20c). *E*/*Z* mixture: 90:10. Prepared as **20a** using cyclohexanecarbonyl chloride (76 mg, 0.52 mg) and **19b** (200 mg, 0.43 mmol). Yield: 100 mg, 83%. IR (neat): 2960 (s), 2943 (s), 2870 (s), 1743 (s), 1630 (s). *E*-Isomer. ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 6.64 (dd, 1H, J = 15.8, 5.6 Hz), 6.20 (d, 1H, J = 15.8 Hz), 5.35–5.28 (m, 1H), 2.50–2.42 (m, 1H), 2.03 (s, 3H), 1.82–1.50 (m, 6H), 1.34–1.14 (m, 12H), 0.81 (brt, 3H). ^{13}C-NMR ($CDCl_3$, 75 MHz): δ 202.6, 170.0, 142.7, 127.7, 72.8, 49.0, 34.3, 33.8, 31.4, 28.4, 28.4, 25.8, 25.6, 24.4, 22.3, 20.9, 13.8. *Z*-Isomer. ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 6.11 (d, 1H, J = 14.6 Hz), 5.55 (dd, 1H, J = 14.6, 7.1 Hz), 5.21–5-14 (m, 1H), 2.50–2.42 (m, 1H), 1.97 (s, 3H), 1.82–1.50 (m, 6H), 1.34–1.14 (m, 12H), 0.81 (brt, 3H). ^{13}C-NMR ($CDCl_3$, 75 MHz): δ 202.6, 170.0, 132.4, 131.3, 74.2, 49.0, 34.3, 33.8, 31.4, 28.4, 28.4, 25.8, 25.6, 24.4, 22.3, 20.9, 13.8. MS (EI): 239 (13), 238 (73), 221 (40), 155 (100), 109 (42). Anal. Calcd for $C_{17}H_{28}O_3$: C, 72.82; H, 10.06. Found: C, 72.52; H, 9.89.

(*S*)-(*E*)-(+)-1-Cyclohexyl-4-[(*tert*-butyldimethylsilyl)oxy]-2-dodecen-1-one (20d). Prepared as **20a** using cyclohexanecarbonyl chloride (132 mg, 0.9 mmol) and **19c** (350 mg, 0.61 mmol). Reaction conditions: rt, 24 h. Purification by flash chromatography (hexane–ether 97:3) yielding 228 mg, 77%, of **20d** as a colorless oil. $[\alpha]_D$ = +19.1° (c = 1.15, benzene). IR (neat): 2954 (s), 2913 (s), 2852 (s), 1668 (m). ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 6.75 (dd, 1H, J = 15.6, 4.8 Hz), 6.26 (dd, 1H, J = 15.6, 1.5 Hz), 4.25–4.20 (m, 1H), 2.51–2.43 (m, 1H), 1.64–1.06 (m, 24H), 0.86 (s, 9H), 0.82 (brt, 3 H), 0.00 (s, 3H), −0.02 (s, 3H). ^{13}C-NMR ($CDCl_3$, 300 MHz): δ = 203.2, 148.5, 126.1, 71.9, 49.0, 37.4 31.7, 29.5, 29.3, 29.1, 28.6, 28.5, 25.8, 25.7, 25.6, 25.6, 24.8, 22.5, 18.1, 13.9, −4.7, −5.0. MS (EI): 394 (M^+, 3), 338 (24), 337 (100), 281 (15). Anal. Calcd for $C_{24}H_{46}O_2Si$: C, 73.03; H, 11.75. Found: C, 73.47; H, 11.69.

(*S*)-(*E*)-(+)-1-*tert*-Butyl-4-[(*tert*-butyldimethylsilyl)oxy]-2-dodecen-1-one (20e). Prepared as **20a** using pivaloyl chloride (64 mg, 0.53 mmol) and **19c** (250 mg, 0.44 mmol). Reaction conditions: rt, 24 h. Purification by flash chromatography (hexane–ether 97:3) yielding 155 mg, 96%, of **20e** as a colorless oil. $[\alpha]_D$ = +1.4° (c = 2.2, benzene). IR (neat): 2931 (s), 2858 (s), 1694 (s), 1632 (s), 1474 (m), 1258 (m), 1082 (m), 837 (s). ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 6.85 (dd, 1H, J = 15.1, 4.3 Hz), 6.64 (dd, 1H, J = 15.1, 1.7 Hz), 4.27–4.21 (m, 1H), 1.49–1.42 (m, 2H), 1.19–1.12 (m, 12H), 1.09 (s, 9H), 0.86 (s, 9H), 0.79 (brt, 3H), 0.00 (s, 3H), −0.03 (s, 3H). ^{13}C-NMR ($CDCl_3$, 75 MHz): δ 204.3, 149.2, 122.1, 71.9, 43.0, 37.3, 31.8, 29.5, 29.4, 29.2, 26.4, 26.1, 25.8, 24.9, 22.6, 18.1, 14.0, −4.7, −4.9. MS (EI): 368 (M^+, 2), 312 (22), 311 (89), 283 (24) Anal. Calcd for $C_{22}H_{44}O_2Si$: C, 71.67; H, 12.00. Found: C, 71.99; H, 11.97.

Typical Procedure for the Iodination of the β-Stannylated Alcohols of Type 3. Preparation of (*S*)-(*E*)-(+)-1-Iodo-1-octen-3-ol (13b).[20] To a solution of the β-stannylated alcohol **3b** (417 mg, 1 mmol) in Et_2O (5 mL) was added iodine (254 mg, 1 mmol). After 5 min, potassium fluoride (0.5 g), water (0.5 mL), and a few crystals of sodium hydrogenosulfite were added until a colorless mixture was obtained. After 1 h, a precipitate of Bu_3SnF was filtered off through a Celite pad and the precipitate was further washed with ether (2 × 10 mL). The combined organic layer was dried ($MgSO_4$), the solvents were evaporated, and the crude product was purified by flash chromatography (hexane–ether 85:15) affording **13b** as a colorless oil (249 mg, 98% yield). $[\alpha]_D$ = +0.4° (c = 0.75, benzene). IR (neat): 3334 (br), 2956 (s), 2929 (s), 2859, 1466. ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 6.56 (dd, 1H, J = 14.5, 6.3 Hz), 6.33 (d, 1H, J = 14.5 Hz), 4.11–4.03 (m, 1H), 1.40–1.21 (m, 8H), 0.87 (brt, 3H). ^{13}C-NMR ($CDCl_3$, 75 MHz): δ 148.6, 76.9, 74.6, 36.5, 31.5, 24.7, 22.4, 13.9. MS (EI): 183 (100), 127 (22), 99 (25). The iodo alcohols **13 b,e,f** were prepared in a similar way but the crude product was directly used for the next step (cyanation) without purification.

Typical Procedure for the Preparation of the 4-Hydroxy-α,β-Unsaturated Nitriles 21a–d. Preparation of (*S*)-(*E*)-(+)-4-hydroxy-2-hexenenitrile (21a). The crude iodo alcohol **13a** (prepared from **3a** (375 mg, 1 mmol)) was dissolved in dry *N*-methylpyrrolidone (2 mL), and copper(I) cyanide (180 mg, 2 mmol) was added.[25] The reaction mixture was heated at 130 °C for 50 min and then allowed to cool to rt and quenched with water (5 mL). After the usual workup using ether, the crude residue obtained after evaporation of the solvent was purified by flash chromatography (hexane–ether 1:1) affording the pure hydroxy nitrile **21a** as a colorless oil (97 mg, 67%). The conversion to the corresponding mandelic ester indicated 92% ee for **21a**. $[\alpha]_D$ = +39.8° (c = 4.0, benzene). IR (neat): 3400 (s), 3020 (w), 2200 (s), 1630 (m). ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 6.69 (dd, 1H, J = 4.1, 16.2 Hz), 5.61 (dd, 1H, J = 16.2, 1.1 Hz), 4.19 (m, 1H), 1.91 (d, 1H, J = 4.7 Hz), 1.67–1.44 (m, 2H), 0.91 (t, 3H, J = 7.4 Hz). ^{13}C-NMR ($CDCl_3$, 75.5 MHz): δ 156.3, 117.2, 98.9, 72.0, 29.3, 9.2.

MS (EI): 110 (0.5), 96 (3), 82 (100). Anal. Calcd for C_6H_9NO: C, 64.84; H, 8.16; N, 12.60. Found: C, 64.58; H, 8.20; N, 12.72.

(*S*)-(*E*)-(+)-4-Hydroxy-2-nonenenitrile (21b). Yield: 173 mg, 85%. Prepared from **3b** (555 mg, 1.33 mmol). The product was purified by flash chromatography (hexane–ether 1:1). The conversion to the corresponding mandelic ester indicated 93% ee. $[\alpha]^{20}_D = +32.0°$ (chloroform, $c = 6.12$) [lit.[26a] $[\alpha]^{25}_D = +36.8°$ (chloroform, $c = 0.99$)]. IR (neat): 3440 (s), 3060 (w), 3040 (w), 2240 (m), 1635 (m). ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 6.69 (dd, 1H, $J = 4.1$, 16.2 Hz), 5.61 (dd, 1H, $J = 16.2$, 2.0 Hz), 4.25 (m, 1H), 1.73 (d, 1H, $J = 4.6$ Hz), 1.59–1.19 (m, 8H), 0.84 (t, 3H, $J = 6.7$ Hz). ^{13}C-NMR ($CDCl_3$, 75.5 MHz): δ 156.9, 117.4, 98.6, 71.0, 36.4, 31.5, 24.8, 22.5, 13.9. MS (FI): 154 (19), 153 (1), 82 (29), 71 (100). Anal. Calcd for $C_9H_{15}NO$: C, 70.55; H, 9.87; N, 9.14. Found: C, 70.40; H, 9.67; N, 9.16.

(*S*)-(*E*)-(+)-4-Hydroxy-7-pivaloxy-2-heptenenitrile (21d). Yield: 120 mg, 64%. Prepared from **3f** (410 mg, 0.84 mmol). The product was purified by flash chromatography (hexane–ether 1:1). The conversion to the corresponding mandelic ester indicates 90% ee. $[\alpha]_D = +20.9°$ ($c = 2.73$, benzene). IR (neat): 3460 (s), 3060 (w), 2230 (m), 1720 (s), 1670 (m). ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 6.70 (dd, 1H, $J = 4.0$, 16.2 Hz), 5.64 (dd, 1H, $J = 1.9$, 16.2 Hz), 4.29 (m, 1H), 4.03 (t, 2H, $J = 6.3$ Hz), 2.49 (d, 1H, $J = 4.8$ Hz), 1.76–1.44 (m, 6H), 1.13 (s, 9H). ^{13}C-NMR ($CDCl_3$, 75.5 MHz): δ 178.9, 156.5, 117.3, 99.2, 70.4, 63.9, 38.9, 32.7, 27.3, 24.5. MS (FI): 226 (12), 225 (2), 145 (2), 144 (9), 82 (25), 57 (100). Anal. Calcd for $C_{12}H_{19}NO_3$: C, 63.98; H, 8.50; N, 6.22. Found: C, 63.89; H, 8.44; N, 6.08.

Preparation of (*S*)-(*E*)-(+)-8-Chloro-4-hydroxy-2-octenenitrile (21e). The crude iodo alcohol **13e** (prepared from **3e** (386 mg, 0.88 mmol)) was dissolved in dry NMP (4 mL), copper(I) cyanide (0.90 g, 10 mmol), and TMSCl (0.64 mL, 5 mmol) were added, and the reaction mixture was stirred at rt for 1.5 h, heated at 130 °C for 50 mn,[25] and then allowed to cool to rt and quenched with water (5 mL). After filtration of the yellow precipitate and usual workup using ether, the crude residue obtained after evaporation of the solvent was purified by flash chromatography (hexane–ether 1:1) affording the pure hydroxy nitrile **21e** as a colorless oil (102 mg, 70%). The conversion to the corresponding mandelic ester indicated 94% ee. $[\alpha]_D = +22.2°$ (benzene, $c = 4.72$). IR (neat): 3500 (brs), 2910 (m), 2970 (m), 2230 (m), 1635 (s). ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 6.74 (dd, 1H, $J = 4.1$, 16.5 Hz), 5.68 (dd, 1H, $J = 2.3$, 16.5 Hz), 4,32 (m, 1H), 3.54 (t, 2H, $J = 6.5$ Hz), 1.93 (d, 1H, 4.8 Hz), 1.86–1.75 (m, 2H), 1.66–1.51(m, 4H). ^{13}C-NMR ($CDCl_3$, 75.5 MHz): δ 156.2, 117.1, 98.9, 70.6, 44.5, 35.3, 32.0, 22.3. MS (FD): 174 (85), 173 (100), 91 (52), 82 (90). Anal. Calcd for $C_8H_{12}ClNO$: C, 55.34; H, 5.53; N, 8.07. Found C; 55.30, H; 5.60, N, 8.20.

Typical Procedure for the Benzylation of the 3-Hydroxy-1-(trimethylsilyl)-1-alkenes 22a,b. Preparation of (*S*)-(−)-3-(Benzyloxy)-6-pivaloxy-1-(trimethylsilyl)-1-hexene (22a). To a solution of **4e** (2.72 g, 10 mmol) and benzyl bromide (2.22 g, 13 mmol) in DMF (20 mL) was added portionwise at −30 °C NaH (80% in oil, 0.40 g, 13 mmol). The mixture was then slowly brought to rt and stirred for 5 h. After the usual workup using ether, the crude residue obtained after evaporation of the solvents was purified by flash chromatography (hexane–ether 10:1) affording the pure **22a** as a colorless oil (3.01 g, 83%). $[\alpha]_D = -18.8°$ (benzene, $c = 2.39$). IR (neat): 2958 (s), 1729 (s), 1619 (w), 1121 (s). ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 7.29–7.12 (m, 5H), 5.83–5.76 (m, 2H), 4.52–4.20 (m, 2H), 3.98–3.91 (m, 1H), 3.75–3.68 (m, 1H), 1.74–1.43 (m, 4H), 1.13 (s, 9H), 0.00 (s, 9H). ^{13}C-NMR ($CDCl_3$, 75.5 MHz): δ 179.8, 147.3, 140.0, 134.5, 129.6, 129.0, 128.7, 83.2, 71.5, 65.5, 40.0, 32.9, 25.9, 0.0. MS (FD): 279 (100), 263 (10), 187 (12), 91 (98). Anal. Calcd for $C_{21}H_{34}O_3Si$: C, 69.56; H, 9.45. Found: C, 69.73; H, 9.36.

(*S*)-(−)-3-(Benzyloxy)-1-(trimethylsilyl)-1-octene (22b). Yield: 3.35 g, 81%. Prepared from **4c** (2.00 g, 10 mmol). The product was purified by flash chromatography (hexane–ether 10:1). $[\alpha]_D = -33.0°$ (benzene, $c = 5.95$). IR (neat): 2956 (s), 1619 (w), 1121 (s). ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 7.38–7.24 (m, 5H), 6.00–5.80 (m, 2H), 4.61–4.36 (m, 2H), 3.76–3.69 (m, 1H), 1.72–1.22 (m, 8H), 0.96–0.88 (m, 3H), 0.12 (s, 9H). ^{13}C-NMR ($CDCl_3$, 75.5 MHz): δ 146.7, 138.9, 132.5, 128.9, 127.7, 127.3, 82.5, 70.1, 35.2, 31.7, 25.0, 22.5, 14.0, −1.3. MS (FD): 290 (100), 184 (76), 179 (46). Anal. Calcd for $C_{18}H_{30}OSi$: C, 74.42; H, 10.41. Found: C, 74.63; H, 10.32.

Typical Procedure for the Preparation of the 3-(Benzyloxy)-1-alkenes 23a,b. Preparation of (*S*)-(−)-3-(Benzyloxy)-6-pivaloxy-1-hexene (23a). To a solution of the vinylsilane **22a** (1.81 g, 5 mmol) in toluene (5 mL) was added HI (57% in water, 0.33 mL, 2.5 mmol),[28] and the mixture was stirred at 50 °C for 3 h. Then, more HI was added (0.33 mL), and stirring was continued at 85 °C for 10 h. After the usual aqueous workup using ether, the crude residue obtained after evaporation of the solvents was purified by flash chromatography (hexane–ether 30:1, then 10:1) affording **23a** as a colorless oil (1.08 g, 71%). $[\alpha]_D = -13.8°$ (benzene, $c = 6.61$). IR (neat): 2961 (s), 1730 (w), 1638 (w), 1154 (s). ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 7.36–7.22 (m, 5H), 5.99 (ddd, 1H, $J = 16.9$, 10.7, 7.7 Hz), 5.28–5.20 (m, 2H), 4.62–4.32 (m, 2H), 4.10–4.01 (m, 2H), 3.81–3.72 (m, 1H), 1.79–1.51 (m, 4H), 1.19 (s, 9H). ^{13}C-NMR ($CDCl_3$, 75.5 MHz): δ 178.4, 138.6, 138.5, 128.2, 127.6, 127.3, 117.1, 79.9, 70.0, 64.1, 38.6, 31.7, 27.1, 24.5. MS (FD): 290 (2), 123 (62), 85 (51). Anal. Calcd for $C_{18}H_{26}O_3$: C, 74.44; H, 9.02. Found: C, 74.54; H, 9.30.

(*S*)-(−)-3-(Benzyloxy)-1-octene (23b). Yield: 895 mg, 82%. Prepared from **22b** (1.45 g, 5 mmol). The product was purified by flash chromatography (hexane–ether 30:1 to 10:1). $[\alpha]_D = -11.4°$ (benzene, $c = 1.5$). IR (neat): 2926 (s), 1638 (w), 1069 (s). ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 7.32–7.18 (m, 5H), 5.70 (ddd, 1H, $J = 16.9$, 10.7, 7.7 Hz), 5.22–5.14 (m, 2H), 4.59–4.29 (m, 2H), 3.72–3.65 (m, 1H), 1.74–1.18 (m, 8H), 0.88–0.80 (m, 3H). ^{13}C-NMR ($CDCl_3$, 75.5 MHz): δ 139.3, 138.9, 128.3, 127.7, 127.3, 116.8, 80.6, 70.0, 35.5, 31.7, 25.0, 22.6, 14.0. MS (FD): 217 (100), 200 (13), 123 (52). Anal. Calcd for $C_{15}H_{22}O$: C, 82.52; H, 10.15. Found: C, 82.43; H, 10.04.

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Supplementary Material Available: Copies of ^{1}H-NMR spectra of all new compounds (96 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.