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The First Catalytic, Diastereoselective and Enantioselective Crossed-Aldol Reactions of Aldehydes

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General Experimental

All reactions were performed in oven-dried (140 °C) or flame-dried glassware under an atmosphere of dry argon or N_2. The following reaction solvents were distilled from the indicated drying agents: dichloromethane (P_2O_5), chloroform (P_2O_5), tetrahydrofuran (sodium, benzophenone), solvents for crystallization benzene (Fisher ACS grade), hexanes (Fisher ACS grade) were used as received. Solvents for chromatography and filtration were technical grade and distilled from the indicated drying agents: hexane ($CaCl_2$); ethyl acetate (K_2CO_3); dichloromethane ($CaCl_2$); isopropanol (Fisher ACS grade) was used as received. Column chromatography was performed using EM Science 230-400-mesh silica gel. Heptanal, propanal, benzaldehyde, (*E*)-cinnamaldehyde, (*E*)-α-methyl-cinnamaldehyde, 1-naphthaldehyde, and (*E*)-2-butenal, cyclohexanecarboxaldehyde, hydrocinnamaldehyde were freshly distilled before use. 2-Naphthaldehyde (Aldrich) was used as received. Silicon tetrachloride (Aldrich) was heated at reflux for 24 h and then distilled prior to use. TMSCl was freshly distilled under nitrogen before use. Triethylamine, diisopropylethylamine and pyridine were distilled from CaH_2 before use. *tert*-Butyldimethylsilyl chloride was used as purchased from Lancaster.

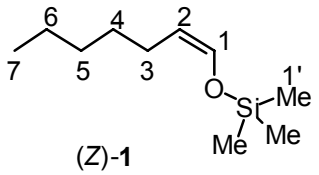
^{1}H NMR, ^{13}C NMR and ^{31}P NMR spectra were recorded on a Varian Unity 400 (400 MHz, ^{1}H; 100 MHz, ^{13}C, 162 MHz ^{31}P), Unity 500 (500 MHz, ^{1}H; 126 MHz, ^{13}C, 202 MHz ^{31}P). Spectra were referenced to residual chloroform (δ 7.26 ppm, ^{1}H; δ 77.00 ppm, ^{13}C), ^{31}P spectra were referenced externally to H_3PO_4 (0.00 ppm). Chemical shifts are reported in ppm (δ); multiplicities are indicated by s (singlet), d (doublet), t (triplet), q (quartet), quint (pentet) sext (hextet) m (multiplet) and br (broad). Coupling constants, *J*, are reported in Hertz. Mass spectroscopy was performed by the University of Illinois Mass Spectrometer Center. Electron impact (EI) spectra were performed on Finnigan-MAT CH-5 spectrometer, chemical ionization (CI) spectra were obtained on a VG 70-VSE spectrometer using methane as the carrier gas, FAB

spectra were performed on a VG ZAB-SE spectrometer. Data are reported in the form of (*m/z*). Infrared spectra (IR) were recorded on a Mattson Galaxy 5020 spectrophotometer in NaCl cells. Peaks are reported in cm^{-1} with indicated relative intensities: s (strong, 67-100%); m (medium, 34-66%); w (weak, 0-33%). Elemental analyses were performed by the University of Illinois Microanalytical Service Laboratory. Melting points (mp) were determined on a Thomas-Hoover capillary melting point apparatus in sealed tubes and are uncorrected. Bulb-to-bulb distillations were performed on a Büchi GKR-50 Kugelrohr and boiling points (bp) correspond to the uncorrected air bath temperatures (ABT). Analytical thin-layer chromatography was performed on Merck silica gel plates with QF-254 indicator. Visualization was accomplished with 2,4-dinitrophenylhydrazine or $KMnO_4$. All reaction temperatures correspond to internal temperatures measured by Teflon-coated thermocouples unless otherwise noted.

Optical rotation data was obtained on a JASCO DIP-360 digital polarimeter and are reported as follows: concentration (c = g/100 mL), and solvent. Analytical capillary gas chromatography (GC) was performed on a Hewlett Packard 5890 Series II chromatograph fitted with a flame ionization detector (H_2 carrier gas, 16 mL/min). The following column was used: HP-5, 50 m X 0.2 mm X 0.3 μm. The injector temperature was 225 °C and the detector temperature was 300 °C. Temperature programs are given as initial temperature, ramp, final temperature. Retention times (t_R) and peak areas were determined on a Hewlett Packard 3396 Series II reporting integrator. Analytical supercritical fluid chromatography (SFC) was performed on a Berger Instruments packed-column SFC with built-in photometric detector (λ = 220, 258 nm) using Daicel Chiralpak OD, AD, OJ, AS, and Regis Whelco columns.

Synthesis of Enoxysilanes.

Preparation of (*Z*)-1-Trimethylsilyloxy-1-heptene ((*Z*)-1)



(*Z*)-**1**

Freshly distilled heptanal (14 mL, 0.1 mol, 1 equiv) was added dropwise over 0.5 h to a cold (0 °C) solution of TMSOTf (18.1 mL, 0.1 mol, 1 equiv) and Et_3N (28 mL, 0.2 mol, 2 equiv) in dry Et_2O (300 mL). After the addition, the reaction mixture was allowed to stir at room temperature for 24 h and the ether layer was separated and washed with $NaHCO_3$ solution. The organic layer was dried over $MgSO_4$, filtered and concentrated to give a crude oil. Column

chromatography (SiO_2, pentane/Et_3N, 99.5/0.5) followed by distillation gave 2.1g (11%) of the (*Z*)-**1** as a clear, colorless liquid.

Data for (*Z*)-1-Trimethylsilyloxy-1-heptene:

bp: 70 °C (7 mmHg)

^{1}H NMR: (500 MHz, $CDCl_3$)
6.14 (dt, *J* = 6, 1.5, 1 H, HC(1)), 4.49 (dt, *J* = 6, 7.3, 1 H, HC(2)), 2.06 (dq, *J* = 1.5, 7.3, 2 H, H_2C(3)), 1.35-1.26 (m, 6 H, H_2C(4), H_2C(5), H_2C(6)), 0.88 (t, 3 H, *J* = 7.1, H_3C(1)), 0.17 (s, 9 H, 3 x H_3C(1'))

^{13}C NMR: (126 MHz, $CDCl_3$)
137.59 (C(1)), 111.78 (C(2)), 31.48 (C(3)), 29.37 (C(4)), 23.51 (C(5)), 22.50 (C(6)), 14.06 (C(7)), -0.59 (C(1'))

IR: (neat)
3030 (w), 2958 (s), 2927 (s), 2873 (m), 2858 (s), 1657 (s), 1458 (w), 1402 (w), 1255 (s), 1134 (m), 1088 (s)

MS: (EI, 70 eV)
186 (M^+, 15), 171 (M^+-Me, 21), 143 (15), 129 (M^+-*n*-Bu, 84), 73 (Me_3Si, 100)

HRMS: calcd for $C_{10}H_{22}OSi$: 186.143994; found: 186.144305

Preparation of (*E*)-1-Trimethylsilyloxy-1-heptene ((*E*)-1)

Butylmagnesium chloride (2 M in THF, 39 mL, solution, 78 mmol, 2.2 equiv) was added to a cold (-50 °C) suspension of a freshly prepared Cu(I)Br Me_2S complex (7.9 g, 38.5 mmol, 1.1 equiv) in THF (110 mL). After the addition, the reaction mixture was allowed to stir at -50 °C for 2 h and then was cooled to -88 → -92 °C. Trimethylsilyl chloride (12.7 ml, 100 mmol, 2.85 equiv), Et_3N (15.5 ml, 110 mmol, 3.1 equiv) and a solution of acrolein (2.4 mL, 35 mmol, 1 equiv) in THF (8 mL) were then added in succession. The reaction mixture was allowed to stir for 1 h and was slowly warmed up to -20 °C (total 2 h). The reaction mixture was again cooled (-50 °C), whereupon pentane (150 mL) and water (50 mL) were added. The reaction mixture turned to a thick mass and was allowed to warm to 0 °C, then was filtered through Celite and washed with pentane. The pentane layer was separated and the aqueous layer was extracted with pentane. The combined organic layers were washed with water, sat. aq. $NaHCO_3$ solution and brine, then were dried over $MgSO_4$ and concentrated. The resulting oil was distilled to give 2.65 g (41%) of (*E*)-**1** as clear, colorless oil. The *E*/*Z* ratio was found to be 25/1 by ^{1}H NMR analysis.

Data for (*E*)-1-Trimethylsilyloxy-1-heptene:

bp: 68 °C (4 mmHg)

^{1}H NMR: (500 MHz, $CDCl_3$)
6.18 (dt, *J* = 12, 1.3, 1 H, HC(1)), 4.99 (dt, *J* = 12, 7.5, 1 H, HC(2)), 1.87 (dq, *J* = 1.3, 7.5, 2 H, H_2C(3)), 1.34-1.22 (m, 6 H, H_2C(4), H_2C(5), H_2C(6)), 0.88 (t, *J* = 7.1, 3 H, H_3C(7)), 0.18 (s, 9 H, 3 x H_3C(1'))

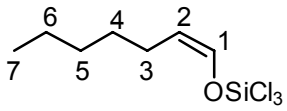
^{13}C NMR: (126 MHz, $CDCl_3$)
139.23 (C(1)), 112.16 (C(2)), 31.20 (C(3)), 30.08 (C(4)), 27.28 (C(5)), 22.46 (C(6)), 14.05 (C(7)), -0.51 (C(1'))

IR: (neat)
3035 (w), 2958 (s), 2925 (s), 2873 (m), 2856 (s), 1664 (s), 1460 (m), 1253 (s), 1165 (s), 922 (s)

MS: (EI, 70 eV)
186 (M^+, 20), 171 (M^+-Me, 26), 143 (17), 129 (M^+-*n*-Bu, 98), 124 (20), 73 (Me_3Si, 100)

HRMS: calcd for $C_{10}H_{22}OSi$: 186.143994; found: 186.144504

Preparation of (*Z*)-1-Trichlorosilyloxy-1-heptene ((*Z*)-2)



(*Z*)-**2**

A solution of the silyl ether (*Z*)-**1** (1.78 g, 9.55 mmol, 1 equiv) in Et_2O (5 mL) was added to cold (0 °C) methyllithium (1.4 M in Et_2O, solution, 10 mL, 14 mmol, 1.4 equiv) under argon atmosphere. After 0.5 h at 0 °C, the reaction mixture was allowed to reach room temperature and then was stirred for 2 h. The resulting lithium enolate solution was slowly added via cannula to a cold (-90 °C) solution of $SiCl_4$ (11 mL, 95 mmol, 10 equiv) in Et_2O (10 mL). The reaction mixture was slowly warmed to room temperature (total 3 h). Solvent and volatile materials were removed under vacuum (up to 5 mmHg). The residual liquid was distilled to give 1.25 g (53%) of (*Z*)-**2** as a clear, colorless oil.

Data for (*Z*)-1-Trichlorosilyloxy-1-heptene:

bp: 60 °C (2 mmHg)

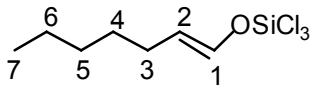
^{1}H NMR: (400 MHz, $CDCl_3$)
6.26 (dt, *J* = 5.6, 1.7, 1 H, HC(1)), 4.89 (dt, *J* = 5.6, 7.3, 1 H, HC(2)), 2.12 (dq, *J* = 1.7, 7.6, 2 H, $H_2C(3)$), 1.40-1.26 (m, 6 H, $H_2C(4)$, $H_2C(5)$, $H_2C(6)$), 0.89 (t, *J* = 7.1, $H_3C(1)$)

^{13}C NMR: (101 MHz, $CDCl_3$)
134.01 (C(1)), 117.09 (C(2)), 31.35 (C(3)), 28.76 (C(4)), 23.77 (C(5)), 22.45 (C(6)), 14.04 (C(7))

MS: (EI, 70 eV)
252 ($C_7H_{13}{}^{37}Cl_3OSi$, M^+, 2), 250 ($C_7H_{13}{}^{37}Cl_2{}^{35}ClOSi$, M^+, 9), 248 ($C_7H_{13}{}^{37}Cl^{35}Cl_2OSi$, M^+, 23), 246 ($C_7H_{13}{}^{35}Cl_3OSi$, M^+, 21), 195 (M^+-*n*-Bu, 7), 193 (M^+-*n*-Bu, 40), 191 (M^+-*n*-Bu, 100), 189 (M^+-*n*-Bu, 93)

HRMS: calcd for $C_7H_{13}Cl_3OSi$: 245.980127; found: 245.979544

Preparation of (*E*)-1-Trichlorosilyloxy-1-heptene ((*E*)-2)



(*E*)-**2**

A solution of the silyl ether (*E*)-**1** (2.32 g, 12.44 mmol, 1 equiv) in Et_2O (7 mL) was added to cold (0 °C) methyllithium (1.4 M in Et_2O, solution, 11.6 mL, 16.2 mmol, 1.3 equiv) under argon atmosphere. After 0.5 h at 0 °C, the reaction mixture was allowed to reach room temperature and was stirred for 2 h. The resulting lithium enolate solution was slowly added via cannula to a cold (-90 °C) solution of $SiCl_4$ (13 mL, 112 mmol, 10 equiv) in Et_2O (10 mL). The reaction mixture was slowly warmed to room temperature (total 3 h). Solvent and volatile materials were removed under vacuum (up to 5 mmHg). The residual liquid was distilled to give 2.2 g (71%) of (*E*)-**2** as a clear, colorless oil.

Data for (*E*)-1-Trichlorosilyloxy-1-heptene:

bp: 67 °C (2.5 mmHg)

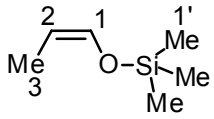
^{1}H NMR: (500 MHz, $CDCl_3$)
6.24 (dt, *J* = 12, 1.5, 1 H, HC(1)), 5.39 (dt, *J* = 12, 7.5, 1 H, HC(2)), 1.95 (dq, *J* = 1.5, 7.5, 2 H, $H_2C(3)$), 1.39-1.24 (m, 6 H, $H_2C(4)$, $H_2C(5)$, $H_2C(6)$), 0.89 (t, *J* = 7.3, $H_3C(1)$)

^{13}C NMR: (126 MHz, $CDCl_3$)
135.41 (C(1)), 118.04 (C(2)), 31.13 (C(3)), 29.18 (C(4)), 26.84 (C(5)), 22.39 (C(6)), 14.00 (C(7))

MS: (EI, 70 eV)
252 ($C_7H_{13}{}^{37}Cl_3OSi$, M^+, 2), 250 ($C_7H_{13}{}^{37}Cl_2{}^{35}ClOSi$, M^+, 5), 248 ($C_7H_{13}{}^{37}Cl{}^{35}Cl_2OSi$, M^+, 7), 246 ($C_7H_{13}{}^{35}Cl_3OSi$, M^+, 4), 192 ($C_3H_3{}^{37}Cl_2{}^{35}ClOSi$, ($M^+$-(H+Bu)), 6), 190 ($C_3H_3{}^{37}Cl{}^{35}Cl_2OSi$, ($M^+$-(H+Bu)), 14), 188 ($C_3H_3{}^{35}Cl_3OSi$, ($M^+$-(H+Bu)), 13), 97 (11), 96 (26), 95 (10), 70 (100), 57 (50)

HRMS: calcd for $C_7H_{13}OSiCl_3$: 245.980127; found: 245.980674

Preparation of (*Z*)-1-Trimethylsilyloxy-1-propene ((*Z*)-3)



(*Z*)-**3**

Freshly distilled propanal (58 mL, 0.8 mol, 1 equiv) and TMSCl (100 mL, 0.8 mol, 1 equiv) were added simultaneously over 15 min to a stirred mixture of Et_3N (115 mL, 0.8 mol, 1 equiv) and DMF (600 mL) at room temperature. The reaction mixture was warmed to 100 °C and stirred at that temperature for 7 h. The reaction mixture was cooled to room temperature then was filtered and washed with pentane. The pentane layer was separated and the DMF layer was extracted (2 X 300 mL) of pentane. The combined pentane extracts were washed with water and $CuSO_4$ solution then were dried over K_2CO_3 and concentrated. ^{1}H NMR analysis showed a *Z*/*E* ratio of 71/29. The residual liquid was fractionally distilled. The fraction (54 g) which boils between 98-101 °C and the fraction which boils between 102-105 °C (19 g; *Z*/*E*, 1/1) were collected separately. Column chromatography (SiO_2, pentane/Et_2O, 99.5/0.5) of 41 g of the low boiling fraction followed by distillation gave 18.2 g (44% recovery) of (*Z*)-**3** as a clear, colorless liquid.

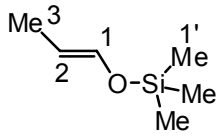
Data for (*Z*)-1-Trimethylsilyloxy-1-propene:

bp: 100 °C (760 mmHg)

^{1}H NMR: (500 MHz, $CDCl_3$)
6.16 (dq, *J* = 6, 1.7, 1 H, HC(1)), 4.55 (dq, *J* = 6, 6.9, 1 H, HC(2)), 1.57 (dd, *J* = 6.9, 1.7, 3 H, H_3C(1)), 0.18 (s, 9 H, 3 x H_3C(1'))

^{13}C NMR: (126 MHz, $CDCl_3$)
138.55 (C(1)), 105.63 (C(2)), 8.96 (C(3)), -0.57 (C(1'))
IR: (neat)
3041 (m), 2961 (s), 2921 (m), 2866 (w), 1663 (s), 1405 (s), 1260 (s), 1128 (s), 1066 (s)
MS: (EI, 70 eV)
130 (M^+, 24), 115 (M-Me, 65) 85 (51), 75 (27), 73 (Me_3Si, 91), 59 (100)
HRMS: calcd for $C_6H_{14}OSi$: 130.081394; found: 130.081414
GC: t_R 5.52 min (HP-5; 60 ° 2 min, 5 °/min, 100 °C)

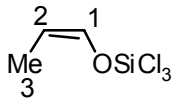
Preparation of (*E*)-1-Trimethylsilyloxy-1-propene ((*E*)-3



(*E*)-**3**

Diphenylketene (24 g, 124 mmol, 1.3 equiv) was slowly added to a cold (-10 °C) enolate **3** (*Z*/*E*, 1/1) (26.8 g, contains 7.5% HMDS, 186 mmol, 2 equiv). After the addition, the orange solution was stirred at 0 °C for 23 h. The volatile materials were removed between 1.5-3 mmHg and collected in a cold (-78 °C) trap. The collected liquid was distilled to give 13.4 g (99% recovery) of enolate (*E*)-**3**. The product is contaminated with about 8.5% of HMDS.
Data for (*E*)-1-Trimethylsilyloxy-1-propene:
bp: 103 °C (760 mmHg)
^{1}H NMR: (500 MHz, $CDCl_3$)
6.19 (dq, *J* = 12, 1.7, 1 H, HC(1)), 4.99 (dq, *J* = 12, 6.7, 1 H, HC(2)), 1.52 (dd, *J* = 1.7, 6.8, 3 H, H_3C(1)), 0.17 (s, 9 H, 3 x H_3C(1'))
^{13}C NMR: (126 MHz, $CDCl_3$)
139.81 (C(1)), 106.12 (C(2)), 12.21 (C(3)), -0.51 (C(1'))
IR: (neat)
3036 (m), 2960 (s), 2926 (m), 2893 (m), 2863 (m), 1668 (s), 1457 (w), 1441 (w), 1255 (s), 1172 (s), 1108 (m), 1057 (s), 927 (s)
MS: (EI, 70 eV)
130 (M^+, 55), 115 (M^+-Me, 100), 85 (32), 73 (Me_3Si, 59)
HRMS: calcd for $C_6H_{14}OSi$: 130.081394; found: 130.081196
GC: t_R 5.99 min (HP-5; 60 °, 2 min, 5 °/min, 100 °C)

Preparation of (*Z*)-1-Trichlorosilyloxy-1-propene ((*Z*)-4)



(*Z*)-**4**

The silyl enol ether (*Z*)-**3** (4 g, HMDS content 6.5%, 28.5 mmol, 1 equiv) was added to cold (0 °C) methyllithium (1.5 M in Et_2O, solution, 19 mL, 28.5 mmol, 1 equiv) under argon atmosphere. After 0.5 h at 0 °C, the reaction mixture was allowed to reach room temperature and was stirred for 2 h. The solvent and volatile materials were removed under vacuum (0.2 mmHg) for 1 h. The solid was dissolved in Et_2O (15 mL) and the resulting lithium enolate solution was slowly added via cannula to a cold (-78 °C) solution of $SiCl_4$ (33 mL, 285 mmol, 10 equiv) in Et_2O (15 mL). The reaction mixture was slowly warmed to room temperature (total 3 h) and stirred at room temperature for 6 h. Solvent and volatile materials were removed under vacuum (up to 150 mmHg) and the residual liquid was removed at 10 mmHg and collected in a cold (-78 °C) trap. The condensed liquid was distilled to give 1.62 g (30%) of (*Z*)-**4** as a clear, colorless oil. ^{1}H NMR analysis shows the *Z*/*E* ratio is 98/2 and HMDS content is 2%.

Data for (*Z*)-1-Trichlorosilyloxy-1-propene:

bp: 56 °C (120 mmHg)

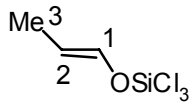
^{1}H NMR: (500 MHz, $CDCl_3$)
6.27 (dq, *J* = 5.9, 1.7, 1 H, HC(1)), 4.95 (dq, *J* = 5.9, 1 H, HC(2)), 1.65 (dd, *J* = 1.7, 5.9, 3 H, H_3C(3))

^{13}C NMR: (126 MHz, $CDCl_3$)
135.00 (C(1)), 111.34 (C(2)), 9.26 (C(3))

MS: (EI, 70 eV)
192 (C_3H_5 ^{37}Cl $^{35}Cl_2OSi$, M^+, 3), 191 (C_3H_4 ^{37}Cl $^{35}Cl_2OSi$, M^+-H, 3), 190 (C_3H_5 $^{35}Cl_3OSi$, M^+, 5), 189 (C_3H_4 $^{35}Cl_3OSi$, M^+-H, 3), 58 (100)

HRMS: calcd for C_3H_4OSiCl (M-H): 188.909701; found: 188.910097

Preparation of (*E*)-1-Trichlorosilyloxy-1-propene ((*E*)-4)



(*E*)-**4**

The silyl ether (*E*)-**3** (4.3 g, HMDS content 8.5%, 29.6 mmol, 1 equiv) was added to cold (0 °C) methyllithium (1.5 M in Et_2O, solution, 20 mL, 30 mmol, 1 equiv) under argon atmosphere. After 0.5 h at 0 °C, the reaction mixture was allowed to reach room temperature and was stirred for 2 h. The solvent and volatile materials were removed under vacuum (0.2 mmHg) for 1 h. The solid was suspended in Et_2O (15 mL) and then was cooled to -78 °C. A cold (-78 °C) solution of $SiCl_4$ (33 mL, 285 mmol, 10 equiv) in Et_2O (15 mL) was rapidly added via cannula to the enolate suspension and the reaction mixture was slowly warmed to room temperature (total 3 h). After 6 h, solvent and volatile materials were removed under vacuum (up to 150 mmHg) and the residual liquid was removed at 10 mmHg and collected in a cold (-78 °C) trap. The condensed liquid was distilled to give 1.95 g (34%) of (*E*)-**4** as a clear, colorless oil. ^{1}H NMR analysis shows the *E*/*Z* ratio is >99/1 and HMDS content is 0.5%.

Data for (*E*)-1-Trichlorosilyloxy-1-propene:

bp: 62 °C (120 mmHg)

^{1}H NMR: (500 MHz, $CDCl_3$)
6.25 (dq, *J* = 12, 1.7, 1 H, HC(1)), 5.40 (dq, *J* = 12, 7.1, 1 H, HC(2)), 1.60 (dd, *J* = 7.1, 1.7, 3 H, H_3C(1))

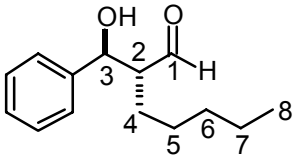
^{13}C NMR: (126 MHz, $CDCl_3$)
135.95 (C(1)), 112.46 (C(2)), 11.91 (C(3))

MS: (EI, 70 eV)
196 (C_3H_5 $^{37}Cl_3OSi$, M^+, 5), 195 (C_3H_4 $^{37}Cl_3OSi$, M^+-H, 2), 194 (C_3H_5 $^{37}Cl_2$ $^{35}ClOSi$, M^+, 8), 193 (C_3H_4 $^{37}Cl_2$ $^{35}ClOSi$, M^+-H, 11), 192 (C_3H_5 ^{37}Cl $^{35}Cl_2OSi$, M^+, 22), 191 (C_3H_4 ^{37}Cl $^{35}Cl_2OSi$, M^+-H, 29), 190 (C_3H_5 $^{35}Cl_3OSi$, M^+, 44), 189 (C_3H_4 $^{35}Cl_3OSi$, M^+-H, 28), 156 (14), 155 (25), 154 (16), 153 (22), 152 (11)

HRMS: calcd for $C_3H_4OSiCl_3$ (M-H): 188.909701; found: 188.910195

Establishment of Quenching Conditions.

(α*S*,β*S*)-β-Hydroxy-α-pentylbenzenepropanal (*syn*-(7a))



syn-**7a**

Trichlorosilyl enolate (*Z*)-**2** (124 mg, 0.5 mmol, 1 equiv) was added to a cold (-78 °C) solution of the phosphoramide (*S,S*)-**5** (18.5 mg, 0.05 mmol, 0.1 equiv) in CH_2Cl_2 (0.5 mL) and the mixture was allowed to stir for 10 min. Freshly distilled benzaldehyde (0.051 mL, 0.5 mmol, 1 equiv) was then added. After 5 h at -78 °C, a mixture of THF/Et_3N/H_2O, 9/0.5/0.5 (5 mL) was added and the mixture was warmed to room temperature (total 1 h), then was poured into cold $NaHCO_3$ solution and was stirred for 1 h. The reaction mixture was filtered through Celite and washed with pentane/Et_2O, 1/1. The organic layer was separated and the aqueous layer was extracted once with pentane/Et_2O, 1/1. The combined extracts were dried over $MgSO_4$ and were concentrated. Column chromatography (SiO_2, hexane/EtOAc, 85/15) provided 104 mg (94%) of *syn*-**7a**. The ^{1}H NMR spectrum showed a complex mixture of products. Bulb-to-bulb distillation gave a better sample which also oligomerized upon standing.

Data for (α*S*,β*S*)-β-Hydroxy-α-pentylbenzenepropanal (*syn*-(**7a**)):

bp: 110 °C (0.2 mmHg, ABT)

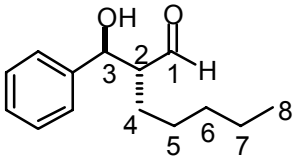
^{1}H NMR: (500 MHz, $CDCl_3$)
9.75 (d, *J* = 2.2, 1 H, HC(1)), 7.38-7.27 (m, 5 H, H-Aryl), 5.12 (d, *J* = 4.7, 1 H, HC(3)), 2.69-2.64 (m, 1 H, HC(2)), 2.26 (s, broad, 1 H, OH), 1.77-1.69 (m, 1 H, 1/2 H_2C(4)), 1.58-1.51 (m, 1 H, 1/2 H_2C(4)), 1.36-1.29 (m, 1 H, 1/2 H_2C(5)), 1.25-1.14 (m, 5 H, 1/2 H_2C(5), H_2C(6), H_2C(7)), 0.83 (t, *J* = 7.1, 3 H, H_3C(8))

(1*S*,2*S*)-3,3-Dimethoxy-2-pentyl-1-phenyl-1-propanol ((*syn*)-8a)

Trichlorosilyl enolate (*Z*)-**2** (124 mg, 0.5 mmol, 1 equiv) was added to a cold (-78 °C) solution of the phosphoramide (*S,S*)-**5** (18.5 mg, 0.05 mmol, 0.1 equiv) in CH_2Cl_2 (0.5 mL) and the mixture was allowed to stir for 10 min. Freshly distilled benzaldehyde (0.051 mL 0.5 mmol, 1 equiv) was then added. After 5 h, MeOH (5 mL) was added and the mixture was stirred for 45 min at -78 °C. The cold bath was removed and reaction mixture was allowed to warm to room temperature (total time 0.5 h), then was poured into cold $NaHCO_3$ solution and was stirred for 4 h. The reaction mixture was filtered through Celite and was washed with Et_2O. The organic

layer was separated and the aqueous layer was extracted once with Et_2O. The combined extracts were dried over $MgSO_4$ and were concentrated. Column chromatography (SiO_2, hexane/EtOAc, 85/15) of the residue gave 118 mg (89%) of *syn*-**8a** as a clear, colorless, thick liquid (syn/anti, >99/1).

(α*R*,β*S*)-β-Hydroxy-α-pentylbenzenepropanal ((*anti*)-7a)



anti-**7a**

Trichlorosilyl enolate (*E*)-**2** (124 mg, 0.5 mmol, 1 equiv) was added to a cold (-78 °C) solution of the phosphoramide (*S,S*)-**5** (18.5 mg, 0.05 mmol, 0.1 equiv) in CH_2Cl_2 (0.5 mL) and the mixture was allowed to stir for 10 min. Freshly distilled benzaldehyde (0.051 mL, 0.5 mmol, 1 equiv) was then added. After 5 h at -78 °C, a mixture of THF/Et_3N/H_2O, 9/0.5/0.5 (5 mL) was added and the mixture was warmed to room temperature (total 1 h), then was poured into cold $NaHCO_3$ solution and was stirred for 1 h. The reaction mixture was filtered through Celite and washed well with pentane/Et_2O, 1/1. The organic layer was separated and the aqueous layer was extracted once with pentane/Et_2O, 1/1. The combined extract was dried over $MgSO_4$ and was concentrated. Column chromatography (SiO_2, hexane/EtOAc, 85/15) provided 106 mg (96%) of *anti*-**6a**. The ^1H NMR spectrum showed a complex mixture of products. Bulb-to-bulb distillation gave a better sample which also oligomerized upon standing.

Data for (α*R*,β*S*)-β-Hydroxy-α-pentylbenzenepropanal ((*anti*)-**7a**):

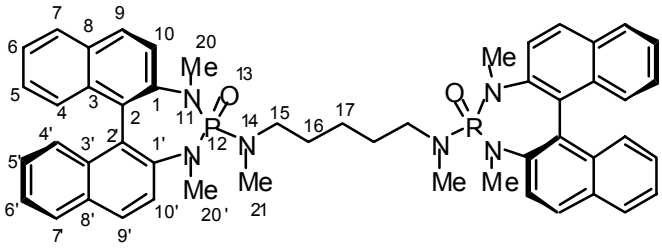
bp: 110 °C (0.2 mmHg, ABT)

^1H NMR: (500 MHz, $CDCl_3$)
9.79 (d, *J* = 2.9, 1 H, HC(1)), 7.40-7.30 (m, 5 H, H-Aryl), 4.89 (dd, *J* = 3.4, 8.3, 1 H, HC(3)), 2.68 (tt, *J* = 3.5, 8.3, 1 H, HC(2)), 2.44 (d, *J* = 3.4, 1 H, OH), 1.58-1.48 (m, 1 H, 1/2 $H_2C(4)$), 1.34-1.07 (m, 7 H, 1/2 $H_2C(4)$, $H_2C(5)$, $H_2C(6)$, $H_2C(7)$), 0.82 (t, *J* = 7.1, 3 H, $H_3C(8)$)

(1*S*,2*R*)-3,3-Dimethoxy-2-pentyl-1-phenyl-1-propanol ((*anti*)-8a)

Trichlorosilyl enolate (*E*)-**2** (124 mg, 0.5 mmol, 1 equiv) was added to a cold (-78 °C) solution of the phosphoramide (*S,S*)-**5** (18.5 mg, 0.05 mmol, 0.1 equiv) in CH_2Cl_2 (0.5 mL) and the mixture was allowed to stir for 10 min. Freshly distilled benzaldehyde (0.051 mL 0.5 mmol, 1 equiv) was then added. After 5 h, MeOH (5 mL) was added and the mixture was stirred for 45 min at -78 °C. The cold bath was removed and reaction mixture was allowed to warm to room temperature (total time 0.5 h), then was poured into cold $NaHCO_3$ solution and was stirred for 4 h. The reaction mixture was filtered through Celite and was washed with Et_2O. The organic layer was separated and the aqueous layer was extracted once with Et_2O. The combined extracts were dried over $MgSO_4$ and were concentrated. Column chromatography (SiO_2, hexane/EtOAc, 85/15) of the residue gave 119.5 mg (90%) of *anti*-**8a** as a clear, colorless, thick liquid (anti/syn, 49/1).

(*R,R*)-*N,N*'-Bis[4,5-dihydro-3,5-dimethyl-4-(3H-dinaphtho[2,1-d:1',2'-f][1,3,2]-2-oxo-diazaphosphepino)]-*N,N*'-dimethyl-1,5-pentanediamine ((*R,R*)-6a)



(*R,R*)-**6a**

A flame-dried, 250-mL, 2-neck flask containing a solution of 3.00 g of (*R*)-*N,N*'-dimethylbinapthyldiamine (9.6 mmol 2.2 equiv) in THF (5 mL) was cooled to -78 °C and then 12.8 mL of a solution of *n*-butyllithium (1.55 M in hexanes, 19.2 mmol, 4.4 equiv) was added dropwise under argon. The resultant, orange solution was allowed to warm to -20 °C over 20 min then was cooled back down to -78 °C, prior to the slow (dropwise) addition of 790 μL of PCl_3 (9.1 mmol, 2.0 equiv). The reaction mixture was allowed to slowly warm to room temperature and was stirred for 12 h. The reaction mixture was then cooled back down to -78 °C, whereupon 577 mg of *N,N*'-dimethyl-1,5-pentanediamine (4.3 mmol) and 926 mg of triethylamine (1.3 mL, 9.6 mmol, 2.2 equiv) were added, and the reaction mixture was slowly warmed to room temperature and was stirred for 12 h. The reaction mixture was then cooled back down to -20 °C and a solution of 2.48 g of *m*-CPBA (14.4 mmol, 3.3 equiv) in THF (10 mL) was added dropwise. The reaction mixture was then allowed to stir at room temperature for 12 h, after which sat. aq. $NaHCO_3$ solution (50 mL) was added. The resulting biphasic mixture

was washed with CH_2Cl_2 (3 X 75 mL), and the combined extracts were dried over Na_2SO_4, filtered, and concentrated *in vacuo*. Purification of the residue by silica gel chromatography (CH_2Cl_2/*i*-PrOH, 19/1 → 9/1) afforded 2.64 g (72%) of (*R,R*)-**6a**. Analytically pure material was obtained by crystallization from benzene. The resulting crystals were dried by heating in a Kugelrohr oven for 3 h at 150 °C at 0.1 mmHg.

Analytical Data for (*R,R*)-**6a**

mp: 216-218 °C (benzene)

^{1}H NMR: (400 MHz, $CDCl_3$)
7.97 (d, *J* = 9.0, 2 H, 2 x HC(4)), 7.94 (d, *J* = 9.0, 2 H, 2 x HC(4')), 7.89 (d, *J* = 8.1, 2 H, 2 x HC(7)), 7.87 (d, *J* = 8.1, 2 H, 2 x HC(7')), 7.72 (d, *J* = 8.8, 2 H, 2 x HC(10)), 7.62 (d, *J* = 8.8, 2 H, 2 x HC(10')), 7.40 (ddd, *J* = 8.1, 6.2, 1.5, 2 H, 2 x HC(6)), 7.36 (ddd, *J* = 8.1, 7.5, 0.7, 2 H, 2 x HC(5)), 7.24 (d, *J* = 7.3, 2 H, 2 x HC(9)), 7.21 (ddd, *J* = 7.5, 6.2, 1.0, 2 H, 2 x HC(6')), 7.13 (ddd, *J* = 7.9, 6.7, 1.3, 2 H, 2 x HC(5')), 7.05 (d, *J* = 8.6, 2 H, 2 x HC(9')), 3.20 (m, 2 H, 2 x HC(15)), 3.06 (d, *J* = 9.0, 6 H, 2 x H_3CN(20)), 3.04 (d, *J* = 10.3, 6 H, 2 x H_3CN(20')) 3.05-2.90 (m, 2 H, 2 x HC(15)), 2.28 (bd, 6 H, *J* = 8.0, 6 H, 2 x H_3C(21), 1.65-1.59 (m, 4 H, 2 x H_2C(16)), 1.30-1.20 (m, 2 H, H_2C(17))

^{13}C NMR: (126 MHz, $CDCl_3$)
143.4 (C(2)), 141.7 (C(2')), 132.7 (C(3)), 132.5 (C(3')), 131.2 (C(8)), 131.0 (C(8')), 129.6 (C(4)), 129.0 (C(4')), 128.3 (C(1)), 128.0 (C(10)), 127.94 (10')), 127.9 (C(9)), 127.4 (C(9')), 127.3 (d, *J* = 1.9, C(1')), 126.1 (C(7)), 126.0 (C(7')), 125.1 (C(6)), 124.8 (C(6')), 123.0 (C(5)), 122.7 (C(5')), 49.6 (d, *J* = 2.4, C(15)), 35.7 (d, *J* = 5.4 C(21)), 35.0 (d, *J* = 4.8, C(20')), 34.2 (d, *J* = 3.5, C(20)), 28.5 (d, *J* = 1.8, C(16)), 23.9 (C(17)

^{31}P NMR: (202 MHz, $CDCl_3$)
27.86

IR: (neat)
3052 (m), 2933 (m), 2877 (m), 2817 (w), 1617 (m), 1592 (m), 1506 (m), 1467 (m), 1429 (w), 1332 (s), 1280 (s), 1224 (s), 1174 (m), 1147 (m), 1091 (s), 1025 (m), 1000 (m), 937 (s)

MS: (FAB M+1)
843 (M^+ + 1, 100), 357 (37), 307 (20), 281 (45), 154 (58), 136 (38)

TLC: R_f 0.4 (EtOAc/EtOH, 4/1) [$KMnO_4$]

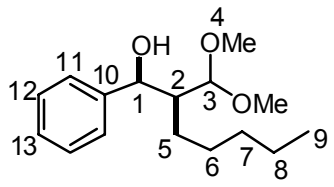
Opt. Rot.: $[\alpha]_D^{24}$ -390 ° (*c* = 1.07, MeOH)

Anal: $C_{51}H_{52}N_6P_2O_2$ (842.96)

Calcd.: C, 72.67;	H, 6.22;	N, 9.97;	P, 7.35
Found: C, 72.52;	H, 6.16;	N, 9.93;	P, 7.06

Aldol Addition Reactions.

Preparation of (1*S*,2*S*)-3,3-Dimethoxy-2-pentyl-1-phenyl-1-propanol ((*syn*)-8a)



syn-**8a**

Trichlorosilyl enolate (*Z*)-**2** (496 mg, 2 mmol, 1 equiv) was added to a cold (-78 °C) solution of the bisphosphoramide (*R*,*R*)-**6a** (84 mg, 0.1 mmol, 0.05 equiv) in $CHCl_3/CH_2Cl_2$, 4/1 (8 mL) and the mixture was stirred for 10 min. Freshly distilled benzaldehyde (0.205 mL, 2 mmol, 1 equiv) was then added. After 6 h at -78 °C, MeOH (32 mL) was added and the mixture was stirred at that temperature for 45 min. The cold bath was removed and reaction mixture was allowed to warm to room temperature (total time 0.5 h), then was poured into cold sat. aq. $NaHCO_3$ solution and was stirred for 4 h. The reaction mixture was filtered through Celite and was washed with pentane/Et_2O, 1/1. The organic layer was separated and the aqueous layer was extracted once with pentane/Et_2O, 1/1. The combined extracts were dried over $MgSO_4$ and were concentrated. Column chromatography (SiO_2, hexane/EtOAc, 85/15) followed by bulb-to-bulb distillation gave 491 mg (92%) of *syn*-**8a** as a clear, colorless, thick liquid.

Data for (1*S*,2*S*)-3,3-Dimethoxy-2-pentyl-1-phenyl-1-propanol:

bp: 125-130 °C (0.2 mmHg, ABT)

^{1}H NMR: (400 MHz, $CDCl_3$)

7.35-7.30 (m, 4 H, H-Aryl), 7.25-7.20 (m, 1 H, H-Aryl), 5.16 (t, *J* = 3.4, 1 H, HC(1)), 4.28 (d, *J* = 4.4, 1 H, HC(3)), 3.57 (d, *J* = 3.4, 1 H, HO), 3.49 (s, 3 H, H_3C(4)), 3.43 (s, 3 H, H_3C(4)), 1.96-1.91 (m, 1 H, HC(2)), 1.46-1.36 (m, 1 H, HC(5)), 1.33-1.05 (m, 7 H, HC(5), H_2C(6), H_2C(7), H_2C(8)), 0.81 (t, *J* = 7.1, 3 H, H_3C(9))

^{13}C NMR: (101 MHz, $CDCl_3$)
142.84 (C(10)), 127.91 (C(11)), 126.61 (C(13)), 125.86 (C(12)), 107.99 (C(3)), 71.80 (C(1)), 56.55 (C(4)), 54.69 (C(4)), 47.63 (C(2)), 31.92 (C(5)), 27.61 (C(6)), 23.34 (C(7)), 22.40 (C(8)), 13.97 (C(9))

IR: (neat)
3480 (br), 3087 (w), 3062 (w), 3027 (m), 2954 (s), 2931 (s), 2871 (s), 2859 (s), 2832 (s), 1604 (w), 1494 (m), 1452 (s), 1413 (m), 1379 (m), 1332 (w), 1246 (w), 1195 (s), 1139 (s), 1110 (s), 1068 (s), 1056 (s), 974 (m), 918 (w)

MS: (FI)
266 (M^+, 5), 234 (M^+-MeOH, 100), 128 ($C_6H_{12}CH(OMe)$, 47), 106 (45), 86 (41), 84 (61), 75 ($CH(OMe)_2$, 20)

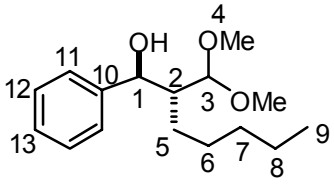
Opt. Rot.: $[\alpha]_D^{24}$ -28.6 (c = 1.04, MeOH)

TLC: R_f 0.33 (hexane/EtOAc, 4/1) [DNP]

SFC: t_R (1*S*,2*S*)-**8a**, 4.91 min (94.7%); t_R (1*R*,2*R*)-**8a**, 5.91 min (5.3%) (Column: OD, MeOH 5%, pressure 125, flow 2.3 mL/min)

Analysis: $C_{16}H_{26}O_3$ (266.37)
Calculated: C: 72.14; H: 9.84%
Found: C: 72.21; H: 10.09%

Preparation of (1*S*,2*R*)-3,3-Dimethoxy-2-pentyl-1-phenyl-1-propanol ((*anti*)-8a)



anti-**8a**

Trichlorosilyl enolate (*E*)-**2** (496 mg, 2 mmol, 1 equiv) was added to a cold (-78 °C) solution of the bisphosphoramide (*R*,*R*)-**6a** (84 mg, 0.1 mmol, 0.05 equiv) in $CHCl_3/CH_2Cl_2$, 4/1 (8 mL) and the mixture was stirred for 10 min. Freshly distilled benzaldehyde (0.205 mL, 2 mmol, 1 equiv) was then added. After 6 h at -78 °C, MeOH (32 mL) was added and the mixture was stirred at that temperature for 45 min. The cold bath was removed and reaction mixture was allowed to warm to room temperature (total time 0.5 h), then was poured into cold sat. aq. $NaHCO_3$ solution and was stirred for 4 h. The reaction mixture was filtered through Celite and was washed well with pentane/Et_2O, 1/1. The organic layer was separated and the aqueous layer was extracted once with pentane/Et_2O, 1/1. The combined extracts were dried over $MgSO_4$ and

were concentrated. Column chromatography (SiO_2, hexane/EtOAc, 85/15) followed by bulb-to-bulb distillation gave 489 mg (91%) of *anti*-**8a** as a clear colorless thick liquid.

Data for (1*S*,2*R*)-3,3-Dimethoxy-2-pentyl-1-phenyl-1-propanol:

bp: 125-130 °C (0.2 mmHg, ABT)

^{1}H NMR: (400 MHz, $CDCl_3$)
7.34-7.31 (m, 4 H, H-Aryl), 7.28-7.23 (m, 1 H, H-Aryl), 4.79 (dd, *J* = 4.2, 7.1, 1 H, HC(1)), 4.27 (d, *J* = 3.9, 1 H, HC(3)), 4.11 (d, *J* = 4.2, 1 H, OH), 3.42 (s, 3 H, H_3C(4)), 3.40 (s, 3 H, H_3C(4)), 2.02-1.96 (m, 1 H, HC(2)), 1.35-1.09 (m, 8 H, H_2C(5), H_2C(6), H_2C(7), H_2C(8)), 0.81 (t, *J* = 6.8, 3 H, H_3C(9))

^{13}C NMR: (101 MHz, $CDCl_3$)
143.39 (C(10)), 128.17 (C(11)), 127.18 (C(13)), 126.46 (C(12)), 107.66 (C(3)), 74.12 (C(1)), 56.38 (C(4)), 54.96 (C(4)), 47.12 (C(2)), 31.96 (C(5)), 26.79 (C(6)), 25.57 (C(7)), 22.38 (C(8)), 13.97 (C(9))

IR: (neat)
3468 (br), 3085 (w), 3063 (m), 3029 (m), 2954 (s), 2931 (s), 2871 (s), 2860 (s), 1603 (w), 1493 (m), 1454 (s), 1414 (m), 1377 (s), 1337 (s), 1336 (m), 1202 (s), 1111 (s), 1069 (s), 972 (s), 916 (w)

MS: (FI)
266 (M^+, 31), 234 (M^+-MeOH, 14), 128 ($C_6H_{12}CH(OMe)$, 100), 106 (26), 75 ($CH(OMe)_2$, 25)

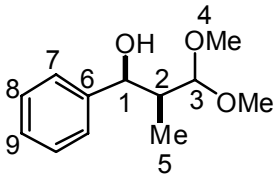
Opt. Rot.: $[\alpha]_D^{24}$ -18.7 (*c* = 1.084, MeOH)

TLC: R_f 0.31 (hexane/EtOAc, 4/1) [DNP]

SFC: t_R (1*S*,2*R*)-**8a**, 6.06 min (91.0%); t_R (1*R*,2*S*)-**8a**, 6.85 min (9.0%) (Column: OD, MeOH 2.5%, pressure 150, flow 3 mL/min)

Analysis: $C_{16}H_{26}O_3$ (266.37)
Calculated: C: 72.14; H: 9.84%
Found: C: 72.30; H: 10.19%

Preparation of (1*S*,2*S*)-3,3-Dimethoxy-2-methyl-1-phenyl-1-propanol ((*syn*)-9a)



syn-**9a**

Trichlorosilyl enolate (*Z*)-**4** (302 mg, >95% purity, 1.5 mmol, 1 equiv) was added to a cold (-78 °C) solution of the bisphosphoramide (*R*,*R*)-**6a** (63.2 mg, 0.075 mmol, 0.05 equiv) in $CHCl_3/CH_2Cl_2$, 4/1 (6 mL) and the mixture was stirred for 10 min. Freshly distilled benzaldehyde (0.153 mL, 1.5 mmol, 1 equiv) was then added. After 6 h at -78 °C, MeOH (24 mL) was added and the mixture was stirred at that temperature for 45 min. The cold bath was removed and reaction mixture was allowed to warm to room temperature (total time about 0.5 h), then was poured into cold sat. aq. $NaHCO_3$ solution and was stirred for 3 h. The reaction mixture was diluted with CH_2Cl_2, then was filtered through Celite and was washed with CH_2Cl_2. The organic layer was separated and the aqueous layer was extracted once with CH_2Cl_2. The combined extracts were dried over $MgSO_4$ and were concentrated. Column chromatography (SiO_2, pentane/Et_2O, 1/1) followed by bulb-to-bulb distillation gave 301 mg (95%) of *syn*-**9a** as a clear, colorless, thick liquid.

Data for (1*S*,2*S*)-3,3-Dimethoxy-2-methyl-1-pheny-l-propanol:

bp: 120-125 °C (0.2 mmHg, ABT)

^{1}H NMR: (500 MHz, $CDCl_3$)
7.36-7.31 (m, 4 H, H-Aryl), 2.26-2.22 (m, 1 H, H-Aryl), 5.04 (t, J = 3, 1 H, HC(1)), 4.25 (d, J = 5.1, 1 H, HC(3)), 3.47 (s, 3 H, H_3C(4)), 3.42 (s, 3 H, H_3C(4)), 3.18 (d, J = 3.6, 1 H, OH), 2.12-2.05 (m, 1 H, HC(2)), 0.85 (d, J = 7.3, 3 H, H_3C(5))

^{13}C NMR: (126 MHz, $CDCl_3$)
142.90 (C(6)), 128.01 (C(7)), 126.85 (C(9)), 125.92 (C(8)), 108.38 (C(3)), 73.07 (C(1)), 55.91 (C(4)), 54.33 (C(4)), 42.53 (C(2)), 8.11 (C(5))

IR: (neat)
3457 (broad), 3085 (w), 3062 (w), 3027 (w), 2981 (s), 2939 (s), 2833 (s), 1604 (w), 1494 (m), 1452 (s), 1141 (w), 1382 (m), 1328 (w), 1267 (w), 1243 (w), 1195 (s), 1145 (s), 1107 (s), 1085 (s), 1068 (s), 1051 (s), 995 (s), 976 (s), 943 (s), 918 (w)

MS: (FI)
210 (M^+, 60), 178 (M^+-MeOH, 65), 135 (18), 106 (33), 72 ($CH_3CHCHOMe$, 100)

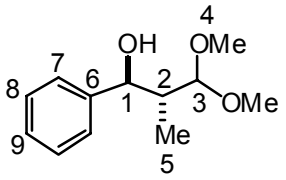
Opt. Rot.: $[\alpha]_D^{24}$ -18.50 (*c* = 1.07, MeOH)

TLC: R_f 0.39 (hexane/EtOAc, 3/1) [DNP]

SFC: t_R (1*R*,2*R*)-**9a**, 4.89 min (9.3%); t_R (1*S*,2*S*)-**9a**, 5.28 min (90.7%) (Column: OJ, MeOH 2%, pressure 125, flow 2 mL/min)

Analysis: $C_{12}H_{18}O_3$ (210.26)
Calculated: C: 68.55; H: 8.63%
Found: C: 68.57; H: 8.78%

Preparation of (1*S*,2*R*)-3,3-Dimethoxy-2-methyl-1-phenyl-1-propanol ((*anti*)-9a)



anti-**9a**

Trichlorosilyl enolate (*E*)-**4** (302 mg, >95% purity, 1.5 mmol, 1 equiv) was added to a cold (-78 °C) solution of the bisphosphoramide (*R*,*R*)-**6a** (63.2 mg, 0.075 mmol, 0.05 equiv) in $CHCl_3/CH_2Cl_2$, 4/1 (6 mL) and the mixture was allowed to stir for 10 min. Freshly distilled benzaldehyde (0.153 mL, 1.5 mmol, 1 equiv) was then added. After 6 h at -78 °C, MeOH (24 mL) was added and the mixture was stirred at that temperature for 45 min. The cold bath was removed and reaction mixture was allowed to warm to room temperature (total time about 0.5 h), then was poured into cold sat. aq. $NaHCO_3$ solution and was stirred for 3 h. The reaction mixture was diluted with CH_2Cl_2, then was filtered through Celite and was washed with CH_2Cl_2. The organic layer was separated and the aqueous layer was extracted once with CH_2Cl_2. The combined extracts were dried over $MgSO_4$ and were concentrated. Column chromatography (SiO_2, pentane/Et_2O, 1/1) followed by bulb-to-bulb distillation gave 305 mg (97%) of *anti*-**9a** as a clear, colorless, thick liquid.

Data for (1*S*,2*R*)-3,3-Dimethoxy-2-methyl-1-phenyl-1-propanol:

bp: 120-125 °C (0.2 mmHg, ABT)

^{1}H NMR: (500 MHz, $CDCl_3$)
7.36-7.31 (m, 4 H, H-Aryl), 7.30-7.25 (m, 1 H, H-Aryl), 4.58 (dd, *J* = 2.1, 8.4, 1 H, HC(1)), 4.34 (d, *J* = 5.6, 1 H, HC(3)), 4.01 (d, *J* = 2.1, 1 H, OH), 3.48 (s, 3 H, H_3C(4)), 3.41 (s, 3 H, H_3C(4)), 2.18-2.11 (m, 1 H, HC(2)), 0.68 (d, *J* = 7.1, 3 H, H_3C(5))

^{13}C NMR: (126 MHz, $CDCl_3$)
142.86 (C(6)), 128.24 (C(7)), 127.53 (C(9)), 126.96 (C(8)), 108.45 (C(3)), 76.38 (C(1)), 55.82 (C(4)), 53.52 (C(4)), 42.37 (C(2)), 11.92 (C(5))

IR: (neat)
3451 (broad), 3085 (w), 3062 (w), 3030 (m), 2975 (s), 2937 (s), 2914 (s), 2833 (s), 1602 (w), 1492 (w), 1457 (s), 1413 (w), 1382 (s), 1315 (w), 1272 (w), 1236 (w), 1203 (s), 1145 (s), 1101 (s), 1070 (s), 975 (m), 947 (s), 920 (m)

MS: (FI)
210 (M^+, 55), 178 (M^+-MeOH, 9), 135 (11), 106 (28), 72 ($CH_3CHCHOMe$, 100)

Opt. Rot.: $[\alpha]_D^{24}$ -16.20 (*c* = 1.06, MeOH)

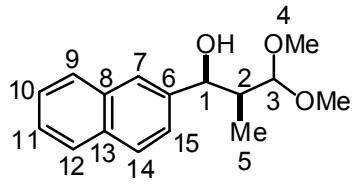
TLC: R_f 0.39 (hexane/EtOAc, 3/1) [DNP]

SFC: t_R (1*R*,2*S*)-**9a**, 4.23 min (20.7%); t_R (1*S*,2*R*)-**9a**, 4.49 min (79.3%) (Column: AD, MeOH 4%, pressure 125, flow 2 mL/min)

Analysis: $C_{12}H_{18}O_3$ (210.26)

Calculated:	C: 68.55;	H: 8.63%
Found:	C: 68.38;	H: 8.74%

Preparation of (1*S*,2*S*)-3,3-Dimethoxy-2-methyl-1-(2-naphthyl)-1-propanol ((*syn*)-9b)



syn-**9b**

Trichlorosilyl enolate (*Z*)-**4** (252 mg, >95% purity, 1.25 mmol, 1 equiv) was added to a cold (-78 °C) solution of the bisphosphoramide (*R*,*R*)-**6a** (52.7 mg, 0.062 mmol, 0.05 equiv) and 2-naphthaldehyde (195 mg, 1.25 mmol, 1 equiv) in $CHCl_3/CH_2Cl_2$, 4/1 (5 mL). After 6 h at -78 °C, MeOH (20 mL) was added and the mixture was stirred at that temperature for 45 min. The

cold bath was removed and reaction mixture was allowed to warm to room temperature (total time about 0.5 h), then was poured into cold sat. aq. $NaHCO_3$ solution and was stirred for 3 h. The reaction mixture was diluted with CH_2Cl_2, then was filtered through Celite and was washed with CH_2Cl_2. The organic layer was separated and the aqueous layer was extracted once with CH_2Cl_2. The combined extracts were dried over $MgSO_4$ and were concentrated. Column chromatography (SiO_2, pentane/Et_2O, 1/1) provided 325 mg (99%) of *syn*-**9b** which solidified on standing. Crystallization from hexane gave 215 mg (66%) enantiomerically pure material as judged by SFC analysis.

Data for (1*S*,2*S*)-3,3-Dimethoxy-2-methyl-1-(2-naphthyl)-1-propanol:

mp: 100-101 °C (hexane)

^{1}H NMR: (500 MHz, $CDCl_3$)
7.85-7.80 (m, 4 H, H-Aryl), 7.49-7.40 (m, 3 H, H-Aryl), 5.23 (t, J = 2.8, 1 H, HC(1)), 4.31 (d, J = 4.9, 1 H, HC(3)), 3.51 (s, 3 H, H_3C(4)), 3.45 (s, 3 H, H_3C(4)), 3.31 (broad, 1 H, OH), 2.22-2.16 (m, 1 H, HC(2)), 0.88 (d, J = 7.1, 3 H, H_3C(5))

^{13}C NMR: (126 MHz, $CDCl_3$)
140.40 (C(6)), 133.20 (C(8)), 132.60 (C(13)), 127.94 (C(7)), 127.64 (C(9)), 127.59 (C(12)), 125.98 (C(14)), 125.54 (C(15)), 124.54 (C(10)), 124.30 (C(11)), 108.59 (C(3)), 73.07 (C(1)), 56.12 (C(4)), 54.57 (C(4)), 42.54 (C(2)), 8.08 (C(5))

IR: ($CHCl_3$)
3610 (w), 3509 (broad), 3060 (w), 3010 (s), 2981 (m), 2937 (m), 2195 (m), 2885 (w), 2834 (m), 1633 (w), 1602 (w), 1508 (w), 1457 (m), 1415 (w), 1383 (w), 1363 (m), 1270 (w), 1238 (w), 1211 (m), 1190 (w), 1143 (m), 1222 (m), 1105 (s), 1085 (s), 1064 (s), 993 (w), 980 (w), 949 (m), 912 (w)

MS: (EI, 70 eV)
260 (M^+, 23), 228 (M-MeOH, 13), 196 (12), 171 (11), 168 (11), 157 (31), 156 (M^+-CH_3-CH_2-$CH(OMe)_2$, 64), 155 (49), 129 (33), 128 (38), 127 (53), 126 (11), 75 ($CH(OMe)_2$, 51), 72 (MeCHCHOMe, 100)

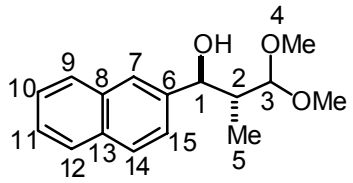
Opt. Rot.: $[\alpha]_D^{24}$ -23.20 (c = 1.08, MeOH)

TLC: R_f 0.32 (hexane/EtOAc, 3/1) [DNP]

SFC: t_R (1*R*,2*R*)-**9b**, 5.35 min (6.8%); t_R (1*S*,2*S*) **9b**, 5.95 min (93.2%) [product after chromatography] (Column: OJ, MeOH 6%, pressure 150, flow 3 mL/min)

Analysis: $C_{16}H_{20}O_3$ (260.33)
Calculated: C: 73.82; H: 7.74%
Found: C: 73.84; H: 7.70%

Preparation of (1*S*,2*R*)-3,3-Dimethoxy-2-methyl-1-(2-naphthyl)-1-propanol ((*anti*)-9b)



anti-**9b**

Trichlorosilyl enolate (*E*)-**4** (252 mg, >95% purity, 1.25 mmol, 1 equiv) was added to a cold (-78 °C) solution of the bisphosphoramide (*R*,*R*)-**6a** (52.7 mg, 0.062 mmol, 0.05 equiv) and 2-naphthaldehyde (195 mg, 1.25 mmol, 1 equiv) in $CHCl_3/CH_2Cl_2$, 4/1 (5 mL). After 6 h at -78 °C, MeOH (20 mL) was added and the mixture was stirred at that temperature for 45 min. The cold bath was removed and reaction mixture was allowed to warm to room temperature (total time about 0.5 h), then was poured into cold sat. aq. $NaHCO_3$ solution and was stirred for 3 h. The reaction mixture was diluted with CH_2Cl_2, then was filtered through Celite and was washed with CH_2Cl_2. The organic layer was separated and the aqueous layer was extracted once with CH_2Cl_2. The combined extracts were dried over $MgSO_4$ and were concentrated. Column chromatography (SiO_2, pentane/Et_2O, 1/1) provided 325 mg (99%) of *anti*-**9b** as a thick gum.

Data for (1*S*,2*R*)-3,3-Dimethoxy-2-methyl-1-(2-naphthyl)-1-propanol:

^{1}H NMR: (500 MHz, $CDCl_3$)
7.85-7.82 (m, 3 H, H-Aryl), 7.77 (s, 1 H, HC(7)), 7.51-7.44 (m, 3 H, H-Aryl), 4.76 (dd, *J* = 2, 8.3, 1 H, HC(1)), 4.38 (d, *J* = 5.6, 1 H, HC(3)), 4.16 (d, *J* = 2.1, 1 H, OH), 3.50 (s, 3 H, H_3C(4)), 3.44 (s, 3 H, H_3C(4)), 2.30-2.22 (m, 1 H, HC(2)), 0.71 (d, *J* = 7.1, 3 H, H_3C(5))

^{13}C NMR: (125 MHz, $CDCl_3$, APT)
140.27 (C(6)), 133.19 (C(8)), 133.05 (C(13)), 128.11 (C(7)), 127.95 (C(9)), 127.64 (C(12)), 126.03 (C(14)), 125.97 (C(15)), 125.72 (C(10)), 124.79 (C(11)), 108.53 (C(3)), 76.52 (C(1)), 55.91 (C(4)), 53.60 (C(4)), 42.28 (C(2)), 12.02 (C(5))

IR: (neat)
3450 (broad), 3055 (m), 2973 (s), 2937 (s), 2912 (s), 2833 (s), 1633 (w), 1602 (m), 1508 (m), 1460 (s), 1413 (m), 1382 (s), 1365 (s), 1311 (m), 1270 (m), 1243 (m), 1207 (s), 1190 (s), 1143 (s), 1099 (s), 1068 (s), 975 (m), 944 (s), 900 (m)

MS: (EI, 70 eV)
260 (M^+, 7), 228 (M^+-MeOH, 11), 168 (11), 156 (M^+-$CH_3CH_2CH(OMe)_2$, 39), 129 (42), 128 (31), 127 (33), 75 ($CH(OMe)_2$, 66), 72 ($CH_3CHCHOMe$, 100)

Opt. Rot.: $[\alpha]_D^{24}$ -12.50 (*c* = 1.04, MeOH)

TLC: R_f 0.28 (hexane/EtOAc, 3/1) [DNP]

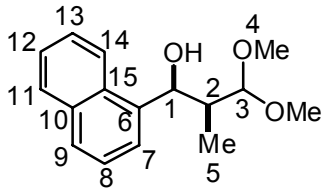
SFC: t_R (1*S*,2*R*)-**9b**, 5.41 min (76.5%); t_R (1*R*,2*S*)-**9b**, 6.53 min (23.5%) (Column: OJ, MeOH 6%, pressure 150, flow 3 mL/min)

Analysis: $C_{16}H_{20}O_3$ (260.33)

Calculated: C: 73.82; H: 7.74%

Found: C: 73.81; H: 7.96%

Preparation of (1*S*,2*S*)-3,3-Dimethoxy-2-methyl-1-(1-naphthyl)-1-propanol ((*syn*)-9c)



syn-**9c**

Trichlorosilyl enolate (*Z*)-**4** (252 mg, >95% purity, 1.25 mmol, 1 equiv) was added to a cold (-78 °C) solution of the bisphosphoramide (*R*,*R*)-**6a** (52.7 mg, 0.062 mmol, 0.05 equiv) in $CHCl_3/CH_2Cl_2$, 4/1 (5 mL) and the mixture was stirred for 10 min. Freshly distilled 1-naphthaldehyde (195 mg, 1.25 mmol, 1 equiv) was then added. After 6 h at -78 °C, MeOH (20 mL) was added and the mixture was stirred at that temperature for 45 min. The cold bath was removed and reaction mixture was allowed to warm to room temperature (total time about 40 min), then was poured into cold sat. aq. $NaHCO_3$ solution and was stirred for 4 h. The reaction mixture was diluted with CH_2Cl_2, then was filtered through Celite and was washed with CH_2Cl_2. The organic layer was separated and the aqueous layer was extracted once with CH_2Cl_2. The combined extracts were dried over $MgSO_4$ and were concentrated. Column chromatography (SiO_2, pentane/Et_2O, 1/1) followed by bulb-to-bulb distillation provided 314 mg (97%) of *syn*-**9c** as a thick gum.

Data for (1*S*,2*S*)-3,3-Dimethoxy-2-methyl-1-(1-naphthyl)-1propanol:

bp: 150 °C (0.2 mmHg, ABT)

^{1}H NMR: (400 MHz, $CDCl_3$)

8.00 (d, *J* = 8.3, 1 H, HC(7)), 7.87 (dd, *J* = 1.7, 8.7, 1 H, HC(11)), 7.76 (d, *J* = 8.3, 1 H, HC(9)), 7.75 (d, *J* = 7.1, 1 H, HC(14)), 7.53-7.45 (m, 3 H, HC(8), HC(12), HC(13)), 6.02 (s, broad, 1 H, HC(1)), 4.44 (d, *J* = 4.2, 1 H, HC(3)), 3.58 (s, 3 H, H_3C(4)), 3.52 (s, 3 H, H_3C(4)), 3.02 (d, *J* = 2, 1 H, OH), 2.24 (ddq, *J* = 1.7, 4.2, 7.1, 1 H, HC(2)), 0.84 (d, *J* = 7.1, 3 H, H_3C(5))

^{13}C NMR: (100 MHz, $CDCl_3$)
138.41 (C(6)), 133.60 (C(10)), 129.85 (C(15)), 128.88 (C(11)), 127.28 (C(9)), 125.81 (C(14)), 125.27 (C(12)), 125.18 (C(13)), 123.53 (C(8)), 122.73 (C(7)), 109.75 (C(3)), 68.40 (C(1)), 57.08 (C(4)), 55.18 (C(4)), 41.31 (C(2)), 7.78 (C(5))

IR: (neat)
3456 (broad), 3051 (m), 2979 (s), 2937 (s), 2833 (s), 2680 (w), 1596 (m), 1510 (m), 1457 (s), 1421 (m), 1379 (s), 1336 (m), 1297 (w), 1255 (w), 1205 (s), 1190 (s), 1166 (s), 1145 (s), 1105 (s), 1086 (s), 1062 (s), 1018 (w), 989 (s), 968 (s), 941 (s), 918 (m)

MS: (EI, 70 eV)
260 (M^+, 9), 228 (M^+-MeOH, 8), 196 (7), 157 (M^+-$CH_3CH_2CH(OMe)_2$, 36), 156 (M^+-$CH_3CHCH(OMe)_2$, 45), 155 (25), 129 (44), 128 (53), 127 ($C_{10}H_7$, 35), 75 ($CH(OMe)_2$, 46), 72 ($CH_3CHCHOMe$, 100)

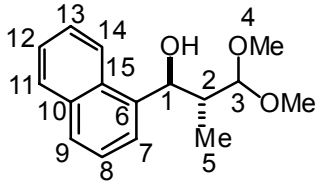
Opt. Rot.: $[\alpha]_D^{24}$ -30.8 (*c* = 1.02, MeOH)

TLC: R_f 0.37 (hexane/EtOAc, 3/1) [DNP]

SFC: t_R (1*R*,2*R*)-**9c**, 5.41 min (22.8%); t_R (1*S*,2*S*)-**9c**, 5.92 min (77.2%) (Column: OJ, MeOH 2.5%, pressure 150, flow 3 mL/min)

Analysis: $C_{16}H_{20}O_3$ (260.33)
Calculated: C: 73.82; H: 7.74%
Found: C: 73.86; H: 7.70%

Preparation of (1*S*,2*R*)-3,3-Dimethoxy-2-methyl-1-(1-naphthyl)-1-propanol ((*anti*)-9c)



anti-**9c**

Trichlorosilyl enolate (*E*)-**4** (252 mg, >95% purity, 1.25 mmol, 1 equiv) was added to a cold (-78 °C) solution of the bisphosphoramide (*R*,*R*)-**6a** (52.7 mg, 0.062 mmol, 0.05 equiv) in $CHCl_3/CH_2Cl_2$, 4/1 (5 mL) and the mixture was stirred for 10 min. Freshly distilled 1-naphthaldehyde (195 mg, 1.25 mmol, 1 equiv) was then added. After 6 h at -78 °C, MeOH (20 mL) was added and the mixture was stirred at that temperature for 45 min. The cold bath was removed and reaction mixture was allowed to warm to room temperature (total time about 40 min), then was poured into cold sat. aq. $NaHCO_3$ solution and was stirred for 4 h. The reaction

mixture was diluted with CH_2Cl_2, then was filtered through Celite and was washed with CH_2Cl_2. The organic layer was separated and the aqueous layer was extracted once with CH_2Cl_2. The combined extracts were dried over $MgSO_4$ and were concentrated. Column chromatography (SiO_2, pentane/Et_2O, 1/1) followed by bulb-to-bulb distillation provided 317 mg (97%) of *anti*-**9c** as a thick gum.

Data for (1*S*,2*R*)-3,3-Dimethoxy-2-methyl-1-(1-naphthyl)-1-propanol:

bp: 150 °C (0.2 mmHg, ABT)

^{1}H NMR: (500 MHz, $CDCl_3$)
8.28 (d, *J* = 8.3, 1 H, HC(7)), 7.87 (dd, *J* = 1.7, 8.7, 1 H, HC(11)), 7.79 (d, *J* = 8.1, 1 H, HC(9)), 7.59 (d, *J* = 6.8, 1 H, HC(14)), 7.52-7.46 (m, 3 H, HC(8), HC(12), HC(13)), 5.37 (dd, *J* = 2.4, 8.3, 1 H, HC(1)), 4.42 (d, *J* = 4.9, 1 H, HC(3)), 4.20 (d, *J* = 2.7, 1 H, OH), 3.48 (s, 3 H, H_3C(4)), 3.47 (s, 3 H, H_3C(4)), 2.51 (ddq, *J* = 8.3, 4.9, 7.1, 1 H, HC(2)), 0.70 (d, *J* = 7.1, 3 H, H_3C(5))

^{13}C NMR: (126 MHz, $CDCl_3$)
138.60 (C(6)), 133.92 (C(10)), 131.22 (C(15)), 128.82 (C(11)), 128.08 (C(9)), 125.73 (C(14)), 125.36 (C(12)), 125.31 (C(13)), 125.01 (C(8)), 123.91 (C(7)), 108.76 (C(3)), 73.78 (C(1)), 56.22 (C(4)), 54.01 (C(4)), 42.26 (C(2)), 12.18 (C(5))

IR: (neat)
3460 (broad), 3049 (m), 2975 (s), 2937 (s), 2832 (s), 2680 (w), 1596 (w), 1512 (m), 1460 (s), 1419 (w), 1381 (s), 1357 (m), 1311 (w), 1261 (w), 1226 (w), 1207 (m), 1190 (m), 1166 (m), 1143 (s), 1101 (s), 1068 (s), 997 (m), 977 (m), 947 (s), 921 (m), 863 (w), 802 (s), 781 (s), 736 (w), 676 (w)

MS: (EI, 70 eV)
260 (M^+, 6), 228 (M^+-MeOH, 3.17), 157 (M^+-$CH_3CH(OMe)_2$, 26), 156 (M^+-$CH_3CH_2CH(OMe)_2$, 11), 129 (65), 128 (76), 127 ($C_{10}H_7$, 59), 126 (17), 102 (11), 77 (10), 75 ($CH(OMe)_2$, 100), 72 ($CH_3CHCHOMe$, 86), 71 (38), 57 (28)

Opt. Rot.: $[\alpha]_D^{24}$ -24.1 (*c* = 1.25, MeOH)

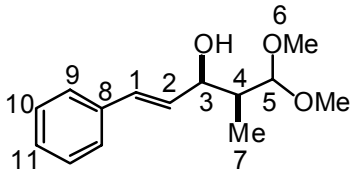
TLC: R_f 0.33 (hexane/EtOAc, 3/1) [DNP]

SFC: t_R (1*S*,2*R*)-**9c**, 5.15 min (84.8%); t_R (1*R*,2*S*)-**9c**, 6.83 min (15.2%) (Column: OJ, MeOH 2.5%, pressure 150, flow 3 mL/min)

Analysis: $C_{16}H_{20}O_3$ (260.33)

Calculated:	C: 73.82;	H: 7.74%
Found:	C: 73.90;	H: 7.77%

Preparation of (*E*)-(3*R*,4*S*)-5,5-Dimethoxy-4-methyl-1-phenyl-1-penten-3-ol ((*syn*)-9d)



syn-**9d**

Trichlorosilyl enolate (*Z*)-**4** (252 mg, >95% purity, 1.25 mmol, 1 equiv) was added to a cold (-78 °C) solution of the bisphosphoramide (*R*,*R*)-**6a** (52.7 mg, 0.062 mmol, 0.05 equiv) in $CHCl_3/CH_2Cl_2$, 4/1 (5 mL) and the mixture was stirred for 10 min. Freshly distilled cinnamaldehyde (0.158 mL, 1.25 mmol, 1 equiv) was then added. After 6 h at -78 °C, MeOH (20 mL) was added and the mixture was stirred at that temperature for 45 min. The cold bath was removed and reaction mixture was allowed to warm to room temperature (total time about 35 min), then was poured into cold sat. aq. $NaHCO_3$ solution and was stirred for 4 h. The reaction mixture was diluted with CH_2Cl_2, then was filtered through Celite and was washed with CH_2Cl_2. The organic layer was separated and the aqueous layer was extracted once with CH_2Cl_2. The combined extracts were dried over $MgSO_4$ and were concentrated. Column chromatography (SiO_2, pentane/Et_2O, 1/1) followed by bulb-to-bulb distillation provided 255 mg (86%) of *syn*-**9d** as a thick liquid.

Data for (*E*)-(3*R*,4*S*)-5,5-Dimethoxy-4-methyl-1-phenyl-1-penten-3-ol:

bp: 150°C (0.2 mmHg, ABT)

^{1}H NMR : (500 MHz, $CDCl_3$)
7.40-7.38 (m, 2 H, H-Aryl), 7.33-7.30 (m, 2 H, H-Aryl,), 7.23 (tt, *J* = 1.2, 7.3, 1 H, HC(11)), 6.64 (dd, *J* = 1.2, 15.9, 1 H, HC(1)), 6.23 (dd, *J* = 5.6, 15.9, 1 H, HC(2)), 4.50 (tt, *J* = 2.2, 5.4, HC(3)), 4.32 (d, *J* = 6.3, HC(5)), 3.45 (s, 3 H, H_3C(6)), 3.39 (s, 3 H, H_3C(6)), 3.12 (d, *J* = 5.4, 1 H, OH), 2.09 (d quint, *J* = 2.7, 7.1, 1 H, HC(4)), 0.99 (d, *J* = 7.1, 3 H, H_3C(7))

^{13}C NMR: (126 MHz, $CDCl_3$)
137.02 (C(8)), 130.19 (C(2)), 130.06 (C(1), 128.55 (C(9)), 127.42 (C(11)), 126.39 (C(10)), 108.01 (C(5)), 72.66 (C(3)), 55.70 (C(6)), 53.39 (C(6)), 40.94 ((C(4)), 9.75 (C(7))

IR: (neat)
3457 (broad), 3100 (w), 3081 (w), 3058 (w), 3025 (w), 2979 (s), 2937 (s), 2913 (s), 2831 (m), 1652 (w), 1598 (w), 1577 (w), 1497 (w), 1450 (m), 1409 (w), 1382 (w), 1365 (w), 1334 (w), 1263 (w), 1203 (w),1189 (w), 1143 (m), 1106 (s), 1085 (s), 1068 (s), 968 (s), 943

MS: (FI)
237 (M^++H, 17), 236 (M^+, 100).

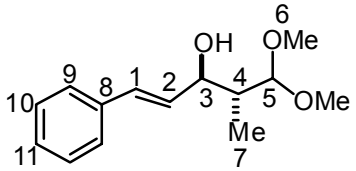
Opt. Rot.: $[\alpha]_D^{24}$ +1.4 (*c* = 1.08, MeOH)

TLC: R_f 0.29 (hexane/EtOAc; 3/1) [DNP]

SFC: t_R(3*S*,4*R*)-**9d**, 4.38 min (29.5%); t_R(3*R*,4*S*)-**9d** 5.69 min (70.5%) (Column: OD, MeOH 4%, pressure150, flow 3 mL/min)

Analysis: $C_{14}H_{20}O_3$ (236.31)
Calculated: C: 71.16; H: 8.53%
Found: C: 71.08; H: 8.57%

Preparation of (*E*) (3*R*,4*R*)-5,5-Dimethoxy-4-methyl-1-phenyl-1-penten-3-ol ((*anti*)-9d)



anti-**9d**

Trichlorosilyl enolate (*E*)-**4** (252 mg, >95% purity, 1.25 mmol, 1 equiv) was added to a cold (-78 °C) solution of the bisphosphoramide (*R*,*R*)-**6a** (52.7 mg, 0.062 mmol, 0.05 equiv) in $CHCl_3/CH_2Cl_2$, 4/1 (5 mL) and the mixture was stirred for 10 min. Freshly distilled cinnamaldehyde (0.158 mL, 1.25 mmol, 1 equiv) was then added. After 6 h at -78 °C, MeOH (20 mL) was added and the mixture was stirred at that temperature for 45 min. The cold bath was removed and reaction mixture was allowed to warm to room temperature (total time about 35 min), then was poured into cold sat. aq. $NaHCO_3$ solution and was stirred for 4 h. The reaction mixture was diluted with CH_2Cl_2, then was filtered through Celite and was washed with CH_2Cl_2. The organic layer was separated and the aqueous layer was extracted once with CH_2Cl_2. The combined extracts were dried over $MgSO_4$ and were concentrated. Column chromatography (SiO_2, pentane/Et_2O, 1/1) followed by bulb-to-bulb distillation provided 259 mg (88%) of *anti*-**9d** as a thick liquid.

Data for (*E*)-(3*R*,4*R*)-5,5-Dimethoxy-4-methyl-1-phenyl-1-penten-3-ol:

bp: 150°C (0.2 mmHg, ABT)

^{1}H NMR : (500 MHz, $CDCl_3$)
7.40-7.38 (m, 2 H, H-Aryl), 7.33-7.29 (m, 2 H, H-Aryl,), 7.23 (tt, *J* = 1.7, 8.4, 1 H, HC(11)), 6.60 (d, *J* = 15.9, 1 H, HC(1)), 6.18 (dd, *J* = 7.3, 15.9, 1 H, HC(2)), 4.34 (d, *J* = 5.6, HC(5)), 4.25 (dt, *J* = 1.7, 7.3, HC(3)), 3.65 (d, *J* = 2.4, 1 H, OH), 3.44 (s, 3 H, H_3C(6)), 3.39 (s, 3 H, H_3C(6)), 2.03 (sext, *J* = 7.1,1 H, HC(4)), 0.92 (d, *J* = 7.1, 3 H, H_3C(7))

^{13}C NMR: (126 MHz, $CDCl_3$)
136.77 (C(8)), 131.29 (C(2)), 130.39 (C(1)), 128.41 (C(9)), 127.43 (C(11)), 126.38 (C(10)), 107.96 (C(5)), 74.28 (C(3)), 55.37 (C(6)), 53.50 (C(6)), 41.23 ((C(4)), 11.26 (C(7))

IR: (neat)
3434 (broad), 3100 (w), 3081 (w), 3058 (w), 3025 (w), 2971 (s), 2937 (s), 2912 (s), 2832 (m), 1654 (w), 1598 (w), 1577 (w), 1494 (w), 1450 (m), 1407 (w), 1382 (w), 1363 (w), 1311 (w), 1205 (w), 1189 (w), 1145 (m), 1108 (s), 1093 (s), 1066 (s), 976 (s), 944 (m)

MS: (FI)
237 (M^++H, 16), 236 (M^+, 100)

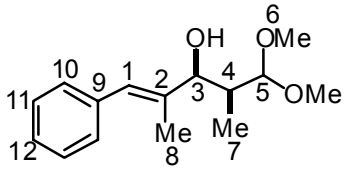
Opt. Rot.: $[\alpha]_D^{24}$ -11.3 (*c* = 0.75, MeOH)

TLC: R_f 0.30 (hexane/EtOAc, 3/1) [DNP]

SFC: t_R(3*R*,4*R*)-**9d**, 4.58 min (63%); t_R(3*S*,4*S*)-**9d**, 5.43 min (37%) (Column: OD, MeOH 4%, pressure 150, flow 3 mL/min)

Analysis: $C_{14}H_{20}O_3$ (236.31)
Calculated: C: 71.16; H: 8.53%
Found: C: 71.04; H: 8.53%

Preparation of (*E*)-(3*S*,4*S*)-5,5-Dimethoxy-2,4-dimethyl-1-phenyl-1-penten-3-ol ((*syn*)-9e)



syn-**9e**

Trichlorosilyl enolate (*Z*)-**4** (252 mg, >95% purity, 1.25 mmol, 1 equiv) was added to a cold (-78 °C) solution of the bisphosphoramide (*R*,*R*)-**6a** (52.7 mg, 0.062 mmol, 0.05 equiv) in $CHCl_3/CH_2Cl_2$, 4/1 (5 mL) and the mixture was stirred for 10 min. Freshly distilled (*E*)-α–methylcinnamaldehyde (0.175 mL, 1.25 mmol, 1 equiv) was then added. After 6 h at -78 °C, MeOH (20 mL) was added and the mixture was stirred at that temperature for 45 min. The cold bath was removed and reaction mixture was allowed to warm to room temperature (total time about 40 min), then was poured into cold sat. aq. $NaHCO_3$ solution and was stirred for 4 h. The reaction mixture was diluted with CH_2Cl_2, then was filtered through Celite and was washed with CH_2Cl_2. The organic layer was separated and the aqueous layer was extracted once with CH_2Cl_2. The combined extracts were dried over $MgSO_4$ and were concentrated. Column chromatography (SiO_2, pentane/Et_2O, 1/1) followed by bulb-to-bulb distillation provided 284 mg (91%) of *syn*-**9e** as a thick liquid.

Data for (*E*)-(3*S*,4*S*)-5,5-Dimethoxyl-2,4-dimethyl-1-phenyl-1-penten-3-ol:

bp: 150 °C (0.2 mmHg, ABT)

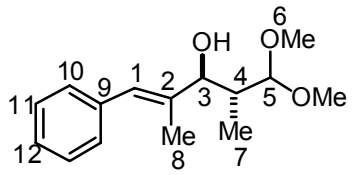
^{1}H NMR: (500 MHz, $CDCl_3$)
7.35-7.28 (m, 4 H, H-Aryl), 7.22-7.19 (m, 1 H, H-Aryl), 6.62 (s, broad, 1 H, HC(1)), 4.43 (dd, broad, 1 H, HC(3)), 4.35 (d, J = 4.9, 1 H, HC(5)), 3.47 (s, 3 H, H_3C(6)), 3.44 (s, 3 H, H_3C(6)), 2.74 (d, J = 2.9, 1 H, OH), 2.07 (ddq, J = 2.7, 5.1, 7.1, 1 H, HC(4)), 1.82 (d, J = 0.7, 3 H, HC(8)), 0.93 (d, J = 7.1, 3 H, H_3C(7))

^{13}C NMR: (126 MHz, $CDCl_3$)
138.09 (C(9)), 138.05 (C(2)), 129.00 (C(10)), 128.05 (C(11)), 126.15 (C(12)), 124.74 (C(1)), 108.67 (C(5)), 74.97 (C(3)), 55.96 (C(6)), 54.84 (C(6)), 38.55 (C(4)), 15.63 (C(8)), 7.69 (C(7))

IR: (neat)
3457 (broad), 3080 (w), 3055 (w), 3022 (w), 2977 (s), 2937 (s), 2831 (s), 1654 (w), 1599 (w), 1575 (w), 1492 (m), 1446 (m), 1378 (m), 1332 (w), 1270 (w), 1247 (w), 1205 (w), 1189 (m), 1147 (m), 1106 (s), 1085 (s), 1066 (s), 1059 (m), 977 (m), 943 (m), 922 (m)

MS: (FI)
251 ($M+1^+$, 15), 250 (M^+, 100), 73 (14)
Opt. Rot.: $[\alpha]_D^{24}$ -33.2 (*c* = 1.03, MeOH)
TLC: R_f 0.31 (hexane/EtOAc, 3/1) [DNP]
SFC: t_R (3*R*,4*R*)-**9e**, 4.13 min (16.0%); t_R (3*S*,4*S*)-**9e**, 5.09 min (84.0%) (Column: OD, MeOH 4%, pressure 150, flow 3 mL/min)
Analysis: $C_{15}H_{22}O_3$ (250.34)
Calculated: C: 71.97; H: 8.86%
Found: C: 72.01; H: 9.07%

Preparation of (*E*)-(3*S*,4*R*)-5,5-Dimethoxy-2,4-dimethyl-1-phenyl-1-pentene-3-ol ((*anti*)-9e)



anti-**9e**

Trichlorosilyl enolate (*E*)-**4** (252 mg, >95% purity, 1.25 mmol, 1 equiv) was added to a cold (-78 °C) solution of the bisphosphoramide (*R*,*R*)-**6a** (52.7 mg, 0.062 mmol, 0.05 equiv) in $CHCl_3/CH_2Cl_2$, 4/1 (5 mL) and the mixture was stirred for 10 min. Freshly distilled (*E*)-α-methylcinnamaldehyde (0.175 mL, 1.25 mmol, 1 equiv) was then added. After 6 h at -78 °C, MeOH (20 mL) was added and the mixture was stirred at that temperature for 45 min. The cold bath was removed and reaction mixture was allowed to warm to room temperature (total time about 40 min), then was poured into cold sat. aq. $NaHCO_3$ solution and was stirred for 4 h. The reaction mixture was diluted with CH_2Cl_2, then was filtered through Celite and was washed with CH_2Cl_2. The organic layer was separated and the aqueous layer was extracted once with CH_2Cl_2. The combined extracts were dried over $MgSO_4$ and were concentrated. Column chromatography (SiO_2, pentane/Et_2O, 1/1) followed by bulb-to-bulb distillation provided 291 mg (93%) of *anti*-**9e** as a thick liquid.

Data for (*E*)-(3*S*,4*R*)-5,5-Dimethoxy-2,4-dimethyl-1-phenyl-1-pentene-3-ol:

bp: 150 °C (0.2 mmHg, ABT)

^{1}H NMR: (500 MHz, $CDCl_3$)
7.34-7.27 (m, 4 H, H-Aryl), 7.23-7.20 (m, 1 H, H-Aryl), 6.48 (s, broad, 1 H, HC(1)), 4.39 (d, *J* = 5.6, 1 H, HC(5)), 4.08 (dd, *J* = 1.5, 8.8, 1 H, HC(3)), 3.88 (d, 1 H, *J* = 1.9, 1 H, OH), 3.49 (s, 3 H, H_3C(6)), 3.42 (s, 3 H, H_3C(5)), 2.09 (ddq, *J* = 5.6, 8.8, 7.1, 1 H, HC(4)), 1.87 (d, *J* = 1.5, 3 H, H_3C(8)), 0.84 (d, *J* = 7.1, 3 H, H_3C(7))

^{13}C NMR: (126 MHz, $CDCl_3$)
138.24 (C(9)), 137.58 (C(2)), 129.01 (C(10)), 128.07 (C(12)), 128.05 (C(11)), 126.42 (C(1)), 108.94 (C(5)), 80.44 (C(3)), 56.04 (C(6)), 53.50 (C(6)), 38.71 (C(4)), 12.59 (C(8)), 12.05 (C(8))

IR: (neat)
3467 (broad), 3082 (w), 3055 (w), 3024 (w), 2974 (s), 2937 (s), 2918 (s), 2833 (m), 2677 (w), 1652 (w), 1599 (w), 1575 (w), 1492 (w), 1448 (m), 1410 (w), 1382 (m), 1359 (w), 1309 (w), 1294 (w), 1209 (w), 1187 (m), 1143 (m), 1099 (s), 1068 (s), 1014 (m), 975 (m), 952 (m), 920 (m)

MS: (FI)
251 ($M+1^+$, 16), 250 (M^+, 100)

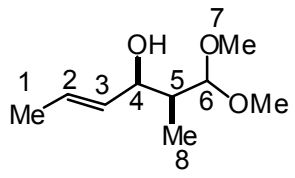
Opt. Rot.: $[\alpha]_D^{24}$ 84.2 (*c* = 1.04, MeOH)

TLC: R_f 0.32 (hexane/EtOAc, 3/1) [DNP]

SFC: t_R (3*S*,4*R*)-**9e**, 2.28 min (94.4%); t_R (3*R*,4*S*)-**9e**, 2.78 min (5.6%) (Column: OJ, MeOH 4%, pressure 150, flow 3 mL/min)

Analysis: $C_{15}H_{22}O_3$ (250.34)
Calculated: C: 71.97; H: 8.86%
Found: C: 71.97; H: 8.91%

Preparation of (*E*)-(4*R*,5*S*)-6,6-Dimethoxy-5-methyl-2-hexen-4-ol ((*syn*)-9f)



syn-**9f**

Trichlorosilyl enolate (*Z*)-**4** (302 mg, >95% purity, 1.5 mmol, 1 equiv) was added to a cold (-78 °C) solution of the bisphosphoramide (*R*,*R*)-**6a** (63.7 mg, 0.075 mmol, 0.05 equiv) in

$CHCl_3/CH_2Cl_2$, 4/1 (6 mL) and the mixture was stirred for 10 min. Freshly distilled (*E*)-2-butenal (0.125 mL, 1.5 mmol, 1 equiv) was then added. After 6 h at -78 °C, MeOH (20 mL) was added and the mixture was stirred at that temperature for 45 min. The cold bath was removed and reaction mixture was allowed to warm to room temperature (total time about 35 min), then was poured into cold sat. aq. $NaHCO_3$ solution and was stirred for 4 h. The reaction mixture was diluted with CH_2Cl_2, then was filtered through Celite and was washed with CH_2Cl_2. The organic layer was separated and the aqueous layer was extracted once with CH_2Cl_2. The combined extracts were dried over $MgSO_4$ and were concentrated. Column chromatography (SiO_2, pentane/Et_2O, 1/1) followed by bulb-to-bulb distillation provided 223 mg (85%) of *syn*-**9f** as a colorless mobile liquid. The enantiomeric ratio was determined by SFC analysis of the derived benzoate (see below).

Data for (*E*)-(4*R*,5*S*)-6,6-Dimethoxy-5-methyl-2-hexen-4-ol:

bp: 100°C (1 mmHg, ABT)

^{1}H NMR: (500 MHz, $CDCl_3$)
5.68 (ddq, *J* = 1.2, 15.1, 6.3, 1 H, HC(2)), 5.47 (ddq, *J* = 6.4, 15.1, 1.5, 1 H, HC(3)), 4.26 (d, *J* = 6.6, 1 H, HC(6)), 4.22-4.17 (m, 1 H, HC(4)), 3.41 (s, 3 H, H_3C(7)), 3.35 (s, 3 H, H_3C(7)), 2.90 (d, *J* = 5.6, 1 H, OH), 1.95 (dquint, *J* = 2.7, 7.1, 1 H, HC(5)), 1.71 (dt, *J* = 6.4, 1.5, 3 H, H_3C(1)), 0.90 (d, *J* = 7.1, 3 H, H_3C(8))

^{13}C NMR: (126 MHz, $CDCl_3$)
131.12 (C(3)), 126.82 (C(2)), 107.79 (C(6)), 72.98 (C(4)), 55.42 (C(7)), 53.04 (C(7)), 40.59 (C(5)), 17.76 (C(1)), 9.72 (C(8))

IR: (neat)
3465 (br), 2979 (s), 2939 (s), 2918 (s), 2858 (m), 2833 (s), 2732 (w), 1672 (w), 1452 (s), 1380 (s), 1326 (w), 1240 (w), 1205 (m), 1191 (m), 1145 (s), 1109 (s), 1068 (s), 1051 (s), 968 (s), 943 (s)

MS: (FI)
174 (M^+, 5), 143 (M^+-OMe, 9), 142 (M^+-MeOH, 100), 75 ($CH(OMe)_2$, 34), 72 (38), 70 (13)

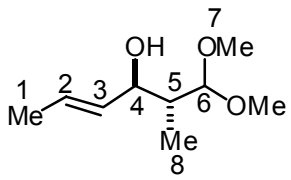
Opt. Rot.: not recorded because the product is nearly racemic

TLC: R_f 0.30 (hexane/EtOAc, 3/1) [DNP]

Analysis: $C_9H_{18}O_3$ (174.24)

Calculated:	C: 62.04;	H: 10.41%
Found:	C: 61.88;	H: 10.57%

Preparation of (*E*)-(4*R*,5*R*)-6,6-Dimethoxy-5-methyl-2-hexen-4-ol ((*anti*)-9f)



anti-**9f**

Trichlorosilyl enolate (*E*)-**4** (302 mg, >95% purity, 1.5 mmol, 1 equiv) was added to a cold (-78 °C) solution of the bisphosphoramide (*R*,*R*)-**6a** (63.7 mg, 0.075 mmol, 0.05 equiv) in $CHCl_3/CH_2Cl_2$, 4/1 (6 mL) and the mixture was stirred for 10 min. Freshly distilled (*E*)-2-butenal (0.125 mL, 1.5 mmol, 1 equiv) was then added. After 6 h at -78 °C, MeOH (20 mL) was added and the mixture was stirred at that temperature for 45 min. The cold bath was removed and reaction mixture was allowed to warm to room temperature (total time about 35 min), then was poured into cold sat. aq. $NaHCO_3$ solution and was stirred for 4 h. The reaction mixture was diluted with CH_2Cl_2, then was filtered through Celite and was washed with CH_2Cl_2. The organic layer was separated and the aqueous layer was extracted once with CH_2Cl_2. The combined extracts were dried over $MgSO_4$ and were concentrated. Column chromatography (SiO_2, pentane/Et_2O, 1/1) followed by bulb-to-bulb distillation provided 237 mg (91%) of *anti*-**9f** as a colorless, mobile liquid. The enantiomeric ratio was determined by SFC analysis of the derived benzoate (see below).

Data for (*E*)-(4*R*,5*R*)-6,6-Dimethoxy-5-methyl-2-hexen-4-ol:

bp: 100 °C (1 mmHg, ABT)

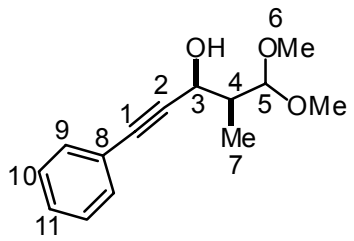
^{1}H NMR: (500 MHz, $CDCl_3$)
5.67 (ddq, *J* = 0.5, 15.1, 6.6, 1 H, HC(2)), 5.47 (ddq, *J* = 7.8, 15.1, 1.5, 1 H, HC(3)), 4.28 (d, *J* = 6.1, 1 H, HC(6)), 3.97 (dt, *J* = 1.5, 7.8, 1 H, HC(4)), 3.42 (s, 3 H, H_3C(7)), 3.37 (d, *J* = 1.5, 1 H, OH), 3.36 (s, 3 H, H_3C(7)), 1.88 (sext, *J* = 7.1, 1 H, HC(5)), 1.70 (dd, *J* = 6.6, 1.5, 3 H, H_3C(1)), 0.83 (d, *J* = 7.1, 3 H, H_3C(8))

^{13}C NMR: (126 MHz, $CDCl_3$)
132.03 (C(3)), 128.21 (C(2)), 108.28 (C(6)), 74.74 (C(4)), 55.44 (C(7)), 53.17 (C(7)), 40.83 (C(5)), 17.69 (C(1)), 11.59 (C(8))

IR: (neat)
3436 (broad), 2973 (s), 2939 (s), 2918 (s), 2856 (w), 2833 (m), 2734 (w), 1672 (w), 1452 (s), 1380 (m), 1315 (w), 1205 (m), 1190 (m), 1145 (m), 1107 (s), 1074 (s), 1014 (s), 970 (s), 945 (s)

MS: (FI)
174 (M^+, 14), 143 (M^+-OMe, 5), 142 (M^+-MeOH, 48), 75 ($CH(OMe)_2$, 33), 72 (100), 70 (38)
Opt. Rot.: $[\alpha]_D^{24}$ -10.8 (*c* = 1.20, MeOH)
TLC: R_f 0.28 (hexane/EtOAc, 3/1) [DNP]
Analysis: $C_9H_{18}O_3$ (174.24)
Calculated: C: 62.04; H: 10.41%
Found: C: 61.84; H: 10.72%

Preparation of (3*S*,4*S*)-5,5-Dimethoxy-4-methyl-1-phenyl-1-pentyn-3-ol ((*syn*)-9g)



syn-**9g**

Trichlorosilyl enolate (*Z*)-**4** (252 mg, >95% purity, 1.25 mmol, 1 equiv) was added to a cold (-78 °C) solution of the bisphosphoramide (*R*,*R*)-**6a** (52.7 mg, 0.062 mmol, 0.05 equiv) in $CHCl_3/CH_2Cl_2$, 4/1 (5 mL) and the mixture was stirred for 10 min. Freshly distilled phenylpropynal (163 mg, 1.25 mmol, 1 equiv) was then added. After 6 h at -78 °C, MeOH (20 mL) was added and the mixture was stirred at that temperature for 45 min. The cold bath was removed and reaction mixture was allowed to warm to room temperature (total time about 40 min), then was poured into cold sat. aq. $NaHCO_3$ solution and was stirred for 4 h. The reaction mixture was diluted with CH_2Cl_2, then was filtered through Celite and was washed with CH_2Cl_2. The organic layer was separated and the aqueous layer was extracted once with CH_2Cl_2. The combined extracts were dried over $MgSO_4$ and were concentrated. Column chromatography (SiO_2, pentane/Et_2O, 1/1) followed by bulb-to-bulb distillation provided 290 mg (99%) of *syn*-**9g** as a thick liquid.

Data for (3*S*,4*S*)-5,5-Dimethoxy-4-methyl-1-phenyl-1-pentyn-3-ol:

bp: 150 °C (0.2 mmHg, ABT)

^{1}H NMR: (500 MHz, $CDCl_3$)
7.45-7.41 (m, 2 H, H-Aryl), 7.32-7.28 (m, 3 H, H-Aryl), 4.61 (dd, *J* = 2.9, 8.8, 1 H, HC(3)), 4.57 (d, *J* = 8.1, 1 H, HC(5)), 3.75 (d, *J* = 9, 1 H, OH), 3.49 (s, 3 H, H_3C(6)), 3.37 (s, 3 H, H_3C(6)), 2.22 (d, quintet, *J* = 2.9, 7.1, 1 H, HC(4)), 1.08 (d, *J* = 7.1, 3 H, H_3C(7))

^{13}C NMR: (126 MHz, $CDCl_3$)
131.67 (C(9)), 128.34 (C(11)), 128.27 (C(10)), 122.71 (C(8)), 107.41 (C(5)), 88.12 (C(2)), 85.49 (C(1)), 65.16 (C(3)), 55.55 (C(6)), 52.05 (C(6)), 40.74 (C(4)), 12.02 (C(7))

IR: (neat)
3440 (broad), 3080 (w), 3057 (w), 3033 (w), 2975 (s), 2937 (s), 2832 (s), 2667 (w), 2225 (w), 1598 (m), 1574 (w), 1490 (s), 1457 (m), 1444 (m), 1385 (m), 1363 (w), 1253 (w), 1205 (m), 1192 (m), 1147 (m), 1110 (s), 1085 (s), 1068 (s), 1051 (s), 987 (m), 952 (m), 941 (m), 916 (w)

MS: (EI, 70 eV)
234 (M^+, 33), 203 (M^+-OMe, 88), 187 (16), 171 (48), 143 (27), 142 (18), 141 (15), 131 (M^+-$CH_3CHCH(OMe)_2$, 61), 130 (M^+-$CH_3CH_2CH(OMe)_2$, 26), 129 (29), 128 (13), 115 (20), 103 (26), 102 (31), 75 ($(MeO)_2CH$, 100), 73 (28), 72 (45), 71 (15), 57 (14)

Opt. Rot.: $[\alpha]_D^{24}$ 1.40 (*c* = 1.23, MeOH)

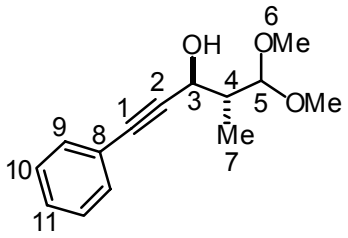
TLC: R_f 0.37 (hexane/EtOAc, 3/1) [DNP]

SFC: t_R (3*S*,4*S*)-**9g**, 3.01 min (53.5%); t_R (3*R*,4*R*)-**9g**, 4.52 min (46.5%) (Column: OD, MeOH 3.5%, pressure 150, flow 3 mL/min)

Analysis: $C_{14}H_{18}O_3$ (234.30)

Calculated:	C: 71.77;	H: 7.74%
Found:	C: 71.64;	H: 7.49%

Preparation of (3*S*,4*R*)-5,5-Dimethoxy-4-methyl-1-phenyl-1-pentyn-3-ol ((*anti*)-9g)



anti-**9g**

Trichlorosilyl enolate (*E*)-**4** (252 mg, >95% purity, 1.25 mmol, 1 equiv) was added to a cold (-78 °C) solution of the bisphosphoramide (*R*,*R*)-**6a** (52.7 mg, 0.062 mmol, 0.05 equiv) in $CHCl_3/CH_2Cl_2$, 4/1 (5 mL) and the mixture was stirred for 10 min. Freshly distilled phenylpropynal (163 mg, 1.25 mmol, 1 equiv) was then added. After 6 h at -78 °C, MeOH (20 mL) was added and the mixture was stirred at that temperature for 45 min. The cold bath was removed and reaction mixture was allowed to warm to room temperature (total time about 40 min), then was poured into cold sat. aq. $NaHCO_3$ solution and was stirred for 4 h. The reaction mixture was diluted with CH_2Cl_2, then was filtered through Celite and was washed with CH_2Cl_2. The organic layer was separated and the aqueous layer was extracted once with CH_2Cl_2. The combined extracts were dried over $MgSO_4$ and were concentrated. Column chromatography (SiO_2, pentane/Et_2O, 1/1) followed by bulb-to-bulb distillation provided 287 mg (98%) of *anti*-**9g** as a thick liquid.

Data for (3*S*,4*R*)-5,5-Dimethoxy-4-methyl-1-phenyl-1-pentyn-3-ol:

bp: 150 °C (0.2 mmHg, ABT)

^{1}H NMR: (500 MHz, $CDCl_3$)
7.46-7.42 (m, 2 H, H-Aryl), 7.32-7.28 (m, 3 H, H-Aryl), 4.67 (dd, *J* = 4.6, 6.8, 1 H, HC(3)), 4.33 (d, *J* = 6.1, 1 H, HC(5)), 3.45 (s, 3 H, H_3C(6)), 3.42 (s, 3 H, H_3C(6)), 3.23 (d, *J* = 4.6, 1 H, OH), 2.21 (sext, *J* = 6.8, 1 H, HC(4)), 1.14 (d, *J* = 6.8, 3 H, H_3C(4))

^{13}C NMR: (126 MHz, $CDCl_3$)
131.70 (C(9)), 128.35 (C(11)), 128.25 (C(10)), 122.68 (C(8)), 107.33 (C(5)), 88.42 (C(1)), 85.64 (C(2)), 64.69 (C(3)), 55.52 (C(6)), 53.72 (C(6)), 41.62 (C(4)), 10.82 (C(7))

IR: (neat)
3241 (broad), 3080 (w), 3056 (w), 3033 (w), 2974 (s), 2937 (s), 2833 (s), 2684 (w), 2229 (w), 1598 (w), 1574 (w), 1491 (s), 1454 (m), 1444 (m), 1385 (m), 1362 (m), 1309 (w), 1276 (w), 1253 (w), 1205 (m), 1190 (m), 1145 (s), 1111 (s), 1070 (s), 1055 (s), 974 (m), 950 (s), 916 (w)

MS: (EI, 70 eV)
234 (M^+, 8), 203 (M^+-OMe, 95), 187 (25), 177 (10), 171 (64), 143 (39), 142 (38), 141 (31), 131 (M^+-$CH_3CHCH(OMe)_2$, 100), 130 (M^+-$CH_3CH_2CH(OMe)_2$, 38), 129 (46), 115 (24), 103 (25), 102 (33), 77 (20), 75 ($(MeO)_2CH$, 62), 73 (14), 72 (29)

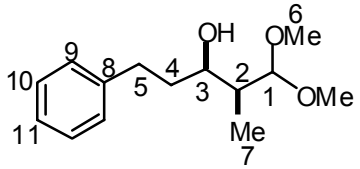
Opt. Rot.: $[\alpha]_D^{24}$ -22.1 (*c* = 1.18, MeOH)

TLC: R_f 0.30 (hexane/EtOAc, 3/1) [DNP]

SFC: t_R (3*S*,4*R*)-**9g**, 3.99 min (88.0%); t_R (3*R*,4*S*)-**9g**, 4.51 min (12.0%) (Column: OD, MeOH 4.0%, pressure 150, flow 3 mL/min)

Analysis: $C_{14}H_{18}O_3$ (234.30)
Calculated: C: 71.77; H: 7.74%
Found: C: 71.77; H: 7.77%

Preparation of (2*S*,3*R*)-1,1-Dimethoxy-2-methyl-5-phenyl-3-pentanol ((*syn*)-9h)



syn-**9h**

Trichlorosilyl enolate (*Z*)-**4** (300 mg, >95% purity, 1.5 mmol, 1 equiv) was added to a cold (-25 °C) solution of the bisphosphoramide (*R*,*R*)-**6a** (95 mg, 0.11 mmol, 0.075 equiv) in $CHCl_3$ (6 mL) and the mixture was stirred for 10 min. Freshly distilled hydrocinnamaldehyde (0.198 mL, 1.5 mmol, 1 equiv) was then added. After 20 h at -25 °C, MeOH (24 mL) was added and the mixture was allowed to warm to room temperature (total time about 1 h 20 min), then was poured into cold sat. aq. $NaHCO_3$ solution and was stirred for 3 h. The reaction mixture was diluted with CH_2Cl_2, then was filtered through Celite and was washed with CH_2Cl_2. The organic layer was separated and the aqueous layer was extracted once with CH_2Cl_2. The combined extracts were dried over $MgSO_4$ and were concentrated. Column chromatography (SiO_2, pentane/Et_2O, 1/1) followed by bulb-to-bulb distillation provided 169 mg (47%) of *syn*-**9h** as a thick liquid.

Data for (2*S*,3*R*)-1,1-Dimethoxy-2-methyl-5-phenyl-3-pentanol:

bp: 125-130 °C (0.2 mmHg, ABT)

^{1}H NMR : (500 MHz, $CDCl_3$)
7.30-7.27 (m, 2 H, H-Aryl), 7.23-7.17 (m, 3 H, H-Aryl), 4.27 (d, *J* = 5.4, HC(1)), 3.87-3.83 (m, 1 H, HC(3)), 3.42 (s, 3 H, H_3C(6)), 3.38 (s, 3 H, H_3C(6)), 2.87 (ddd, *J* = 5.1, 10.5, 13.8, 1 H, 1/2 H_2C(5)), 2.73 (d, *J* = 4.4, 1 H, OH), 2.63 (ddd, *J* = 6.3, 10.3, 13.8, 1 H, 1/2 H_2C(5)), 1.89 (ddq, *J* = 2, 5.1, 7.1, 1 H, HC(2)), 1.83-1.75 (m, 1 H, 1/2 H_2C(4)), 1.70-1.63 (m, 1 H, 1/2 H_2C(4)), 0.93 (d, *J* = 7.1, 3 H, H_3C(7))

^{13}C NMR: (126 MHz, $CDCl_3$)
142.36 (C(8)), 128.45 (C(9)), 128.35 (C(10)), 125.75 (C(11)), 108.76 (C(1)), 70.96 (C(3)), 55.75 (C(6)), 54.02 (C(6)), 40.07 (C(2)), 36.02 (C(5)), 32.76 (C(4)), 8.60 (C(7))

IR: (neat)
3469 (broad), 3085 (w), 3062 (w), 2977 (m), 2941 (s), 2861 (w), 2831 (m), 1609'4 (w), 1496 (w), 1454 (m), 1384 (w), 1322 (w), 1270 (w), 1245 (w), 1205 (w), 1190 (w), 1145 (m), 1093 (s), 1068 (s), 1051 (s), 1005 (w), 974 (w), 943 (m)

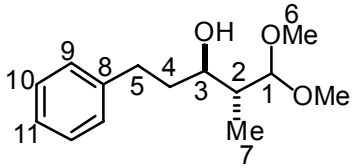
MS: (EI, 70eV)
238 (M^+, 0.010), 237 (M^+-H, 0.1), 220 (M^+-H_2O, 0.3), 206 (M^+-MeOH, 7), 174 (8), 101 (20), 91 (Bn, 40), 75 ($CH(OMe)_2$, 100), 73 (33), 72 (34)

TLC: R_f 0.29 (hexane/EtOAc, 3/1) [DNP]

SFC: t_R(2*R*,3*S*)-**9h** 3.05 min (46%), t_R(2*S*,3*R*)-**9h** 3.88 min (54%) (Column: AD; MeOH 5%, pressure 140, flow 2.5 mL/min)

Analysis: $C_{14}H_{22}O_3$ (238.33)
Calculated: C: 70.56; H: 9.30%
Found: C: 70.54; H: 9.40%

Preparation of (2*R*,3*R*)-1,1-Dimethoxy-2-methyl-5-phenyl-3-pentanol ((*anti*)-9h)



anti-**9h**

Trichlorosilyl enolate (*E*)-**4** (300 mg, >95% purity, 1.5 mmol, 1 equiv) was added to a cold (-25 °C) solution of the bisphosphoramide (*R*,*R*)-**6a** (95 mg, 0.11 mmol, 0.075 equiv) in

$CHCl_3$ (6 mL) and the mixture was stirred for 10 min. Freshly distilled hydrocinnamaldehyde (0.198 mL, 1.5 mmol, 1 equiv) was then added. After 20 h at -25 °C, MeOH (24 mL) was added and the mixture was allowed to warm to room temperature (total time about 1 h 20 min), then was poured into cold sat. aq. $NaHCO_3$ solution and was stirred for 3 h. The reaction mixture was diluted with CH_2Cl_2, then was filtered through Celite and was washed with CH_2Cl_2. The organic layer was separated and the aqueous layer was extracted once with CH_2Cl_2. The combined extracts were dried over $MgSO_4$ and were concentrated. Column chromatography (SiO_2, pentane/Et_2O, 1/1) followed by bulb-to-bulb distillation provided 284 mg (79%) of *anti*-**9h** as a thick liquid.

Data for (2*R*,3*R*)-1,1-Dimethoxy-2-methyl-5-phenyl-3-pentanol:

bp: 125°C (0.2 mmHg, ABT)

^{1}H NMR: (500 MHz, $CDCl_3$)
7.30-7.27 (m, 2 H, H-Aryl), 7.24-7.22 (m, 2 H, H-Aryl,), 7.20-7.17 (m, 1 H, H-Aryl), 4.28 (d, *J* = 5.9, HC(1)), 3.64-3.59 (m, 2 H, HC(3), OH), 3.44 (s, 3 H, H_3C(6)), 3.37 (s, 3 H, H_3C(6)), 2.87 (ddd, *J* = 5.1, 10.7, 13.6, 1 H, 1/2 H_2C(5)), 2.69 (ddd, *J* = 6.1, 10.5, 13.6, 1 H, 1/2 H_2C(5)), 1.92-1.81 (m, 2 H, HC(2), 1/2 H_2C(4)), 1.73-1.65 (m, 1 H, 1/2 H_2C(4)), 0.89 (d, *J* = 7.1, 3 H, H_3C(7))

^{13}C NMR: (126 MHz, $CDCl_3$)
142.66 (C(8)), 128.50 (C(9)), 128.32 (C(10)), 125.66 (C(11)), 108.89 (C(1)), 72.21 (C(3)), 55.69 (C(6)), 55.06 (C(6)), 40.75 (C(2)), 36.45 (C(5)), 31.57 (C(4)), 11.78 (C(7))

IR: (neat)
3479 (broad), 3085 (w), 3062 (w), 3025 (w), 2939 (s), 2833 (m), 1602 (w), 1496 (m), 1454 (m), 1384 (m), 1315 (w), 1244 (w), 1190 (m), 1145 (m), 1105(s), 1066 (s), 974 (m), 946 (s)

MS: (EI, 70eV)
238 (M^+, 0.01), 237 (M^+-H, 0.1), 220 (M^+-H_2O, 0.3), 206 (M^+-MeOH, 7), 174 (6), 101 (25); 91 (Bn, 42), 75 ($CH(OMe)_2$, 100), 73 (36); 72(36)

Opt. Rot.: $[\alpha]_D^{24}$ +25.6 (*c* = 1.16, MeOH)

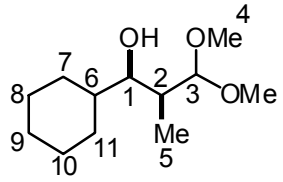
TLC: R_f 0.31 (hexane/EtOAc, 3/1) [DNP]

SFC: t_R(2*S*,3*R*)-**9h** 3.05 min (46%); t_R(2*R*,3*S*)-**9h** 3.88 min (54%) (Column: AD, MeOH 5%, pressure 140, flow 2.5 mL/min)

Analysis: $C_{14}H_{22}O_3$ (238.33)

Calculated:	C: 70.56;	H: 9.30%
Found:	C: 70.54;	H: 9.47%

Preparation of (1*R*,2*S*)-1-Cyclohexyl-3,3-dimethoxy-2-methyl-1-propanol ((*syn*)-9i)



syn-**9i**

Trichlorosilyl enolate (*Z*)-**4** (300 mg, >95% purity, 1.5 mmol, 1 equiv) was added to a cold (-25 °C) solution of the bisphosphoramide (*R*,*R*)-**6a** (95 mg, 0.11 mmol, 0.075 equiv) in $CHCl_3$ (6 mL) and the mixture was stirred for 10 min. Freshly distilled cyclohexanecarboxaldehyde (0.183 mL, 1.5 mmol, 1 equiv) was then added. After 20 h at -25 °C, MeOH (24 mL) was added and the mixture was allowed to warm to room temperature (total time about 1 h 20 min), then was poured into cold sat. aq. $NaHCO_3$ solution and was stirred for 3 h. The reaction mixture was diluted with CH_2Cl_2, then was filtered through Celite and was washed with CH_2Cl_2. The organic layer was separated and the aqueous layer was extracted once with CH_2Cl_2. The combined extracts were dried over $MgSO_4$ and were concentrated. Column chromatography (SiO_2, hexane/EtOAc, 85/15) followed by bulb-to-bulb distillation provided 136 mg (42%) of *syn*-**9i** as a thick liquid. The enantiomeric ratio was determined by SFC analysis of the derived benzoate (see below).

Data for (1*R*,2*S*)-1-Cyclohexyl-3,3-dimethoxy-2-methyl-1-propanol:

bp: 100 °C (0.2 mmHg, ABT)

^{1}H NMR : (500 MHz, $CDCl_3$)
4.27 (d, *J* = 5.1, HC(3)), 3.51 (ddd, *J* = 1.7, 2.9, 4.6, 1 H, HC(1)), 3.41 (s, 3 H, H_3C(4)), 3.39 (s, 3 H, H_3C(4)), 2.47 (d, *J* = 2.9, 1 H, OH), 2.12-2.05 (m, 1 H, HC(6)), 1.95 (ddq, *J* = 1.7, 5.1, 7.1, 1 H, HC(2)), 1.79-1.69 (m, 2 H, 1/2 H_2C(7), 1/2 H_2C(11)), 1.68-1.62 (m, 1 H, 1/2 H_2C(8)), 1.61-1.55 (m, 1 H, 1/2 H_2C(9)), 1.41-1.32 (m, 1 H, 1/2 H_2C(9)), 1.28-1.09 (m, 3 H, 1/2 H_2C(7), H_2C(10)), 0.98-0.82 (m, 2 H, 1/2 H_2C(11), H_2C(8)) 0.90 (d, *J* = 7.1, 3 H, H_3C(5))

^{13}C NMR: (126 MHz, $CDCl_3$)
109.28 (C(3)), 74.88 (C(1)), 55.59 (C(4)), 54.84 (C(4)), 40.34 (C(2)), 36.56 (C(6)), 29.98 (C(7)), 28.83 (C(11)), 26.39 (C(8)), 26.04 (C(10)), 25.87 (C(9)), 7.01 (C(5))

IR: (neat)
3479 (br), 2925 (s), 2852 (s), 1450 (s), 1413 (w), 1383 (m), 1317 (w), 1265 (w), 1207 (m), 1190 (w), 1190 (m), 1155 (m), 1111 (s), 1099 (s), 1074 (s), 983 (s), 956 (m), 941 (s)

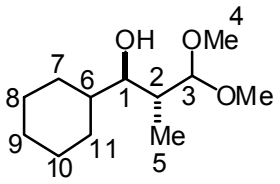
MS: (EI, 70eV)
215 (M^+-H, 0.03), 185 (M^+-OMe, 0.14), 101 (18), 95 (11), 75 ($CH(OMe)_2$, 100), 73 (32), 72 (47)

Opt. Rot.: $[\alpha]_D^{24}$ +3.9 (*c* = 1.03, MeOH)

TLC: R_f 0.33 (hexane/EtOAc, 3/1) [DNP]

Analysis: $C_{12}H_{24}O_3$ (216.32)
Calculated: C: 66.63; H: 11.18%
Found: C: 66.38; H: 11.23%

Preparation of (1*R*,2*R*)-1-Cyclohexyl-3,3-dimethoxy-2-methyl-1-propanol ((*anti*)-9i)



anti-**9i**

Trichlorosilyl enolate (*E*)-**4** (300 mg, >95% purity, 1.5 mmol, 1 equiv) was added to a cold (-25 °C) solution of the bisphosphoramide (*R*,*R*)-**6a** (95 mg, 0.11 mmol, 0.075 equiv) in $CHCl_3$ (6 mL) and the mixture was stirred for 10 min. Freshly distilled cyclohexanecarboxaldehyde (0.183 mL, 1.5 mmol, 1 equiv) was then added. After 20 h at -25 °C, MeOH (24 mL) was added and the mixture was allowed to warm to room temperature (total time about 1h 20 min), then was poured into cold sat. aq. $NaHCO_3$ solution and was stirred for 3 h. The reaction mixture was diluted with CH_2Cl_2, then was filtered through Celite and was washed with CH_2Cl_2. The organic layer was separated and the aqueous layer was extracted once with CH_2Cl_2. The combined extracts were dried over $MgSO_4$ and were concentrated. Column chromatography (SiO_2, hexane/EtOAc, 85/15) followed by bulb-to-bulb distillation provided 225 mg (69%) of *anti*-**9i** as a thick liquid. The enantiomeric ratio was determined by SFC analysis of the derived benzoate (see below).

Data for (1*R*, 2*R*)-1-Cyclohexyl-3,3-dimethoxy-2-methyl-1-propanol:

bp: 100 °C (0.2 mmHg, ABT)

^{1}H NMR: (500 MHz, $CDCl_3$)
4.31 (d, *J* = 5.6, HC(3)), 3.47 (d, *J* = 2.9, 1 H, OH), 3.43 (s, 3 H, H_3C(4)), 3.37 (s, 3 H, H_3C(4)), 3.33 (dt, *J* = 2.4, 8.3 1 H, HC(1)), 1.95 (sext, *J* = 6.8, 1 H, HC(2)), 1.80-1.72 (m, 2 H), 1.68-1.60 (m, 2 H), 1.56-1.48 (m, 1 H), 1.44-1.34 (m, 2 H), 1.30-1.10 (m, 4 H), 0.87 (d, *J* = 6.8, 3 H, H_3C(5))

^{13}C NMR: (126 MHz, $CDCl_3$)
109.13 (C(3)), 76.79 (C(1)), 55.86 (C(4)), 53.27 (C(4)), 40.15 (C(2)), 37.70 (C(6)), 30.39 (C(7)), 26.77 (C(11)), 26.53 (C(8)), 26.28 (C(10)), 25.10 (C(9)), 11.56 (C(5))

IR: (neat)
3513 (br), 2927 (s), 2852 (s), 1450 (m), 1413 (w), 1382 (w), 1315 (w), 1263 (w), 1209 (w), 1189 (w), 1147 (m), 1111 (s), 1109 (s), 1072 (s), 987 (m), 974 (m), 945 (m)

MS: (FI)
217 (M^++H, 4), 184 (M^+-MeOH, 11), 141 (M^+-$CH(OMe)_2$, 28), 133 (21), 112 (14), 83 (19), 75 ($CH(OMe)_2$, 100), 72 (42)

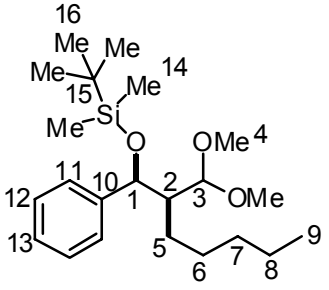
Opt. Rot.: $[\alpha]_D^{24}$ +0.5 (*c* = 1.12, MeOH)

TLC: R_f 0.33 (hexane/EtOAc, 3/1) [DNP]

Analysis: $C_{12}H_{24}O_3$ (216.32)

Calculated:	C: 66.63;	H: 11.18%
Found:	C: 66.40;	H: 11.27%

Preparation of (1*S*,2*S*)-1-*tert*-Butyldimethylsilyloxy-3,3-dimethoxy-2-pentyl-1-phenylpropane ((*syn*)-10a)



syn-**10a**

tert-Butyldimethylsilyl chloride (225 mg, 1.45 mmol, 1.5 equiv) was added to a solution of *syn*-**8a** (250 mg, 0.938 mmol, 1 equiv) and imidazole (204 mg, 3 mmol, 3 equiv) in dry DMF (1.5 mL). The reaction mixture was stirred at room temperature for 14 h. The mixture was diluted with water, then was stirred for 1 h and was extracted with hexane. The extracts were dried over $MgSO_4$, then were filtered and concentrated. Bulb-to-bulb distillation gave 353 mg (99%) of the silyl ether *syn*-**10a** as a clear, colorless, thick liquid.

Data for (1*S*,2*S*)-1-*tert*-Butyldimethylsilyloxy-3,3-dimethyoxy-2-pentyl-1-phenylpropane:

bp: 135-140 °C (0.2 mmHg, ABT)

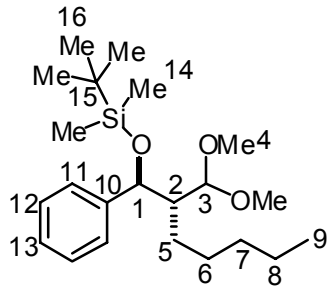
^{1}H NMR: (400 MHz, $CDCl_3$)
7.31-2.27 (m, 4 H, H-Aryl), 7.24-7.18 (m, 1 H, H-Aryl), 4.92 (d, *J* = 4.2, HC(1)), 4.15 (d, *J* = 6.6, 1 H, HC(3)), 3.33 (s, 3 H, H_3C(4)), 3.27 (s, 3 H, H_3C(4)), 1.82-1.77 (m, 1 H, HC(2)), 1.52-1.43 (m, 1 H, HC(5)), 1.40-0.96 (m, 7 H, HC(5), H_2C(6), H_2C(7), H_2C(8)), 0.92 (s, 9 H, 3 x H_3C(16)), 0.80 (t, *J* = 7.1, 3 H, H_3C(9)), 0.04 (s, 3 H, H_3C(14)), -0.24 (s, 3 H, H_3C(14))

^{13}C NMR: (101 MHz, $CDCl_3$)
144.45 (C(10)), 127.72 (C(11)), 126.64 (C(13)), 126.29 (C(12)), 105.82 (C(3)), 74.31 (C(1)), 53.69 (C(4)), 53.53 (C(4)), 48.97 (C(2)), 32.41 (C(5)), 28.52 (C(6)), 25.89 (C(16)), 24.32 (C(7)), 22.45 (C(8)), 18.13 (C(15)), 14.06 (C(9)), -4.36 (C(14)), -5.29 (C(14))

IR: (neat)
3087 (w), 3064 (w), 3029 (w), 2955 (s), 2930 (s), 2858 (s), 2831 (m), 1603 (w), 1494 (w), 1470 (m), 1463 (m), 1378 (w), 1361 (w), 1254 (s), 1194 (w), 1103 (s), 1062 (s), 1029 (w), 1006 (w), 970 (w)

MS: (FI)
380 (M^+, 15), 348 (M^+-MeOH, 31), 323 (19), 305 (50), 222 (10), 221 (M^+-$C_6H_{12}CH(OMe)_2$, 56), 195 (11), 75 ($(MeO)_2CH$, 100)
Opt. Rot.: $[\alpha]_D^{24}$ -45.1 (c = 1.01, MeOH)
TLC: R_f 0.38 (hexane/EtOAc, 24/1) [DNP]
Analysis: $C_{22}H_{40}O_3Si$ (380.64)
Calculated: C: 69.42; H: 10.59%
Found: C: 69.25; H: 10.62%

Preparation of (1*S*,2*R*)-1-*tert*-Butyldimethylsilyloxy-3,3-dimethoxy-2-pentyl-1-phenylpropane ((*anti*)-10a)



anti-**10a**

tert-Butyldimethylsilyl chloride (225 mg, 1.45 mmol, 1.5 equiv) was added to a solution of *anti*-**7a** (250 mg, 0.938 mmol, 1 equiv) and imidazole (204 mg, 3 mmol, 3 equiv) in dry DMF (1.5 mL). The reaction mixture was stirred at room temperature for 14 h. The mixture was diluted with water, then was stirred for 1 h and was extracted with hexane. The extracts were dried over $MgSO_4$, then were filtered and concentrated. Bulb-to-bulb distillation gave 351 mg (98%) of *anti*-**10a** as a clear, colorless, thick liquid.

Data for (1*S*,2*R*)-1-*tert*-Butyldimethylsilyloxy-3,3-dimethoxy-2-pentyl-1-phenylpropane:

bp: 135-140 °C (0.2 mmHg, ABT)
^{1}H NMR: (400 MHz, $CDCl_3$)
7.31-7.19 (m, 5 H, H-Aryl), 4.68 (d, J = 7.1, 1 H, HC(1)), 4.37 (d, J = 4.8, 1 H, HC(3)), 3.39 (s, 3 H, H_3C(4)), 3.34 (s, 3 H, H_3C(4)), 1.95-1.89 (m, 1 H, HC(2)), 1.32-1.24 (m, 1 H, HC(5)), 1.16-0.91 (m, 7 H, HC(5), H_2C(6), H_2C(7), H_2C(8)), 0.87 (s, 9 H, H_3C(16)), 0.76 (t, J = 6.8, 3 H, H_3C(9)), 0.02 (s, 3 H, H_3C(14)), -0.29 (s, 3 H, H_3C(14))

^{13}C NMR: (101 MHz, $CDCl_3$)
143.48 (C(10)), 127.69 (C(11)), 127.22 (C(12)), 127.01 (C(13)), 106.70 (C(3)), 75.19 (C(1)), 55.20 (C(4)), 54.30 (C(4)), 48.86 (C(2)), 32.16 (C(5)), 28.52 (C(6)), 25.84 (C(16)), 24.58 (C(7)), 22.37 (C(8)), 18.08 (C(15)), 14.02 (C(9)), -4.59 (C(14)), -5.16 (C(14))

IR: (neat)
3087 (w), 3064 (w), 3031 (w), 2955 (s), 2930 (s), 2858 (s), 2833 (s), 1603 (w), 1494 (m), 1473 (s), 1463 (s), 1455 (s), 1378 (m), 1361 (m), 1252 (s), 1201 (m), 1188 (m), 1130 (s), 1114 (s), 1065 (s), 1029 (m), 1006 (m), 972 (m), 939 (w), 912 (w)

MS: (FI)
381 ($M+1^+$, 10), 380 (M^+, 29), 348 (M^+-MeOH, 14), 323 (11), 306 (10), 305 (42), 222 (16), 221 (M^+-$C_6H_{12}CH(OCH_3)_2$, 78), 75 ($(MeO)_2CH$, 100)

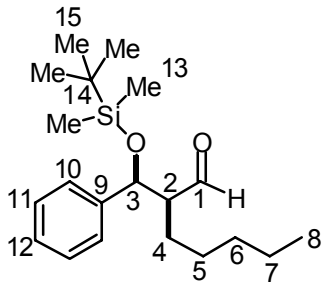
Opt. Rot.: $[\alpha]_D^{24}$ -43.1 (*c* = 1.05, MeOH)

TLC: R_f 0.43 (hexane/EtOAc, 24/1) [DNP]

Analysis: $C_{22}H_{40}O_3Si$ (380.64)

Calculated:	C: 69.42;	H: 10.59%
Found:	C: 69.17;	H: 10.65%

Preparation of (2*S*,3*S*)-3-*tert*-Butyldimethylsilyl.oxy-2-pentyl-3-phenylpropanal ((*syn*)-12a)



syn-**12a**

A solution of *syn*-**10a** (225 mg, 0.59 mmol) in CH_2Cl_2 (5 mL) was added to a slurry of SiO_2 (1.5 g) and oxalic acid (10% aqueous solution, 0.25 mL). The reaction mixture was stirred for 24 h and a pinch of solid $NaHCO_3$ was added. After 10 min, the reaction mixture was filtered and was washed with CH_2Cl_2. The filtrate was concentrated and the residue was chromatographed (SiO_2, pentane/Et_2O, 24/1) to give an oil which on bulb-to-bulb distillation provided 160 mg (81%) of *syn*-**12a** as clear, colorless, mobile liquid.

Data for (2*S*,3*S*)-3-*tert*-Butyldimethylsilyloxy-2-pentyl-3-phenylpropanal:

bp: 130 °C (0.2 mmHg, ABT)

^{1}H NMR: (500 MHz, $CDCl_3$)
9.69 (d, *J* = 2.8, 1 H, HC(1)), 7.33-7.23 (m, 5 H, H-Aryl), 5.01 (d, *J* = 5.1, 1 H, HC(3)), 2.52-2.48 (m, 1 H, HC(2)), 1.76-1.68 (m, 1 H, HC(4)), 1.50-1.43 (m, 1 H, HC(4)), 1.32-1.07 (m, 6 H, $H_2C(5)$, $H_2C(6)$, $H_2C(7)$), 0.89 (s, 9 H, 3 x $H_3C(15)$), 0.83 (t, *J* = 7.1, 3 H, $H_3C(8)$), 0.02 (s, 3 H, $H_3C(13)$), -0.19 (s, 3 H, $H_3C(13)$)

^{13}C NMR: (126 MHz, $CDCl_3$)
205.12 (C(1)), 142.23 (C(9)), 128.16 (C(10)), 127.50 (C(12)), 126.35 (C(11)), 74.60 (C(3)), 60.24 (C(2)), 31.88 (C(4)), 27.10 (C(5)), 25.72 (C(15)), 24.17 (C(6)), 22.38 (C(7)), 18.09 (C(14)), 13.94 (C(1)), -4.63 (C(13)), -5.32 (C(13))

IR: (neat)
3087 (w), 3066 (w), 3031 (w), 2956 (s), 2931 (s), 2858 (s), 2711 (w), 1726 (s), 1602 (w), 1494 (w), 1471 (m), 1463 (m), 1388 (w), 1361 (m), 1255 (s), 1087 (s), 1068 (s), 1027 (w), 1006 (w), 939 (w)

MS: (CI, 130 eV)
335 (M^++1, 13), 319 (M^+-CH_3, 16), 305 (M^+-CHO, 7), 293 (26), 277 (32), 249 (9), 221 (M^+-$C_6H_{12}CHO$, 100), 203 (17), 201 (17), 175 (13), 173 (25), 117 (13), 115 (15), 107 (12), 91 (14), 75 (21), 73 (11)

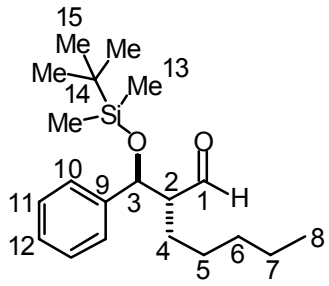
Opt. Rot.: $[\alpha]_D^{24}$ -45.5 (*c* = 1.07, $CHCl_3$)

TLC: R_f 0.44 (pentane/Et_2O, 97/3) [DNP]

Analysis: $C_{20}H_{34}O_2Si$ (334.57)

Calculated:	C: 71.80;	H: 10.24%
Found:	C: 71.73;	H: 10.45%

Preparation of (2*R*,3*S*)-3-*tert*-Butyldimethylsilyloxy-2-pentyl-3-phenylpropanal ((*anti*)-12a)



anti-**12a**

A solution of *anti*-**10a** (225 mg, 0.59 mmol) in CH_2Cl_2 (5 mL) was added to a slurry of SiO_2 (1.5 g) and oxalic acid (10% aqueous solution, 0.25 ml). The reaction mixture was stirred for 24 h and a pinch of solid $NaHCO_3$ was added. After 10 min, the reaction mixture was filtered and was washed with CH_2Cl_2. The filtrate was concentrated and the residue was chromatographed (SiO_2, pentane/Et_2O, 24/1) to give an oil which on bulb-to-bulb distillation provided 165 mg (83%) of *anti*-**12a** as clear, colorless, mobile liquid.

Data for (2*R*,3*S*)-3-*tert*-Butyldimethylsilyloxy-2-pentyl-3-phenylpropanal:

bp: 130 °C (0.2 mmHg, ABT)

^{1}H NMR: (500 MHz, $CDCl_3$)
9.71 (d, J = 3.9, 1 H, HC(1)), 7.35-7.25 (m, 5 H, H-Aryl), 4.81 (d, J = 7.5, 1 H, HC(3)), 2.57-2.52 (m, 1 H, HC(2)), 1.58-1.52 (m, 1 H, HC(4)), 1.23-1.12 (m, 7 H, HC(4), H_2C(5), H_2C(6), H_2C(7)), 0.84 (s, 9 H, H_3C(15)), 0.81 (t, J = 6.9, 3 H, H_3C(8)), 0.01 (s, 3 H, H_3C(13)), -0.28 (s, 3 H, H_3C(13))

^{13}C NMR: (126 MHz, $CDCl_3$)
204.53 (C(1)), 142.41 (C(9)), 128.30 (C(10)), 127.80 (C(12)), 126.74 (C(11)), 75.77 (C(3)), 60.42 (C(2)), 31.65 (C(4)), 26.60 (C(5)), 26.17 (C(6)), 25.63 (C(15)), 22.30 (C(7)), 18.00 (C(14)), 13.91 (C(8)), -4.56 (C(13)), -5.28 (C(13))

IR: (neat)
3087 (w), 3064 (w), 3031 (w), 2956 (s), 2931 (s), 2858 (s), 2709 (s), 1730 (s), 1602 (w), 1494 (w), 1463 (m), 1405 (w), 1388 (w), 1361 (m), 1255 (s), 1218 (w), 1083 (s), 1066 (s), 1028 (m), 1006 (m), 939 (w), 916 (w), 839 (s)

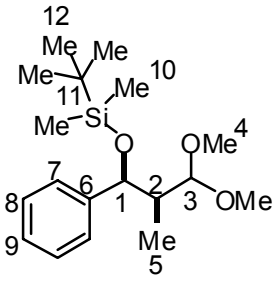
MS: (CI, CH_4 eV)
335 ($M+1^+$, 4), 319 (M^+-Me, 23), 305 (M^+-CHO, 3), 277 (M^+-Bu, 48), 221 (M^+-$C_6H_{12}CHO$, 100), 203 (29), 185 (17), 161 (23), 91 (10), 63 (22), 59 (25)

Opt. Rot.: $[\alpha]_D^{24}$ -50.2 (c = 1.03, $CHCl_3$)

TLC: R_f 0.50 (pentane/Et_2O, 97/3) [DNP]

Analysis: $C_{20}H_{34}O_2Si$ (334.57)
Calculated: C: 71.80; H: 10.24%
Found: C: 72.04; H: 10.51%

Preparation of (1*S*,2*S*)-1-*tert*-Butyldimethylsilyloxy-3,3-dimethoxy-2-methyl-1-phenylpropane ((*syn*)-11a)



syn-**11a**

tert-Butyldimethylsilyl chloride (263 mg, 1.75 mmol, 1.5 equiv) was added to a solution of *syn*-**9a** (245 mg, 1.165 mmol, 1 equiv) and imidazole (238 mg, 3.5 mmol, 3 equiv) in dry DMF (2 mL). The reaction mixture was stirred at room temperature for 24 h. The mixture was diluted with water, then was stirred for 1 h and was extracted with pentane. The extracts were dried over $MgSO_4$, then were filtered and concentrated. Column chromatography (SiO_2, pentane/Et_2O, 24/1) followed by bulb-to-bulb distillation gave 365 mg (97%) of *syn*-**11a** as a clear, colorless liquid.

Data for (1*S*,2*S*)-1-*tert*-Butyldimethylsilyloxy-3,3-dimethoxy-2-methyl-phenylpropane:

bp: 120-125 °C (0.2 mmHg, ABT)

^{1}H NMR: (500 MHz, $CDCl_3$)
7.31-7.27 (m, 4 H, H-Aryl), 7.23-7.20 (m, 1 H, H-Aryl), 4.95 (d, J = 3.4, 1 H, HC(1)), 4.18 (d, J = 7.8, 1 H, HC(3)), 3.69 (s, 3 H, H_3C(4)), 3.26 (s, 3 H, H_3C(4)), 1.88 (d, quintet, J = 3.2, 6.8, 1 H, HC(2)), 0.92 (s, 9 H, 3 x H_3C(12)), 0.83 (d, J = 6.8, 3 H, H_3C(5)), 0.04 (s, 3 H, H_3C(10)), -0.24 (s, 3 H, H_3C(10))

^{13}C NMR: (126 MHz, $CDCl_3$)
144.39 (C(6)), 127.74 (C(7)), 126.67 (C(9)), 126.33 (C(8)), 105.43 (C(3)), 73.75 (C(1)), 53.83 (C(4)), 51.93 (C(4)), 44.09 (C(2)), 25.87 (C(12)), 18.14 (C(11)), 7.58 (C(5)), -4.44 (C(10)), -5.40 (C(10))

IR: (neat)
3087 (w), 3064 (w), 3028 (w), 2954 (s), 2931 (s), 2896 (s), 2858 (s), 2831 (m), 2738 (w), 2709 (w), 1604 (w), 1494 (w), 1471 (m), 1461 (m), 1452 (m), 1406 (w), 1384 (m), 1361 (m), 1325 (w), 1253 (s), 1199 (m), 1143 (m), 1109 (s), 1072 (s), 1055 (s), 1034 (s), 1007 (w), 977 (m), 947 (m), 916 (w)

MS: (FI)
324 (M^+, 1), 292 (M^+-MeOH, 2), 267 (M^+-*t*-Bu, 6), 249 (M^+-$CH(OMe)_2$, 23), 221 (M^+-$CH_3CHCH(OMe)_2$, 9), 195 ($PhCH_2CH(Me)CH(OMe)_2$+H, 100), 75 ($CH(OMe)_2$, 59)

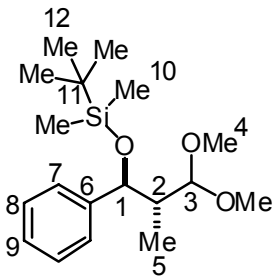
Opt. Rot.: $[\alpha]_D^{24}$ -36.1 (*c* = 1.05, MeOH)

TLC: R_f 0.36 (pentane/Et_2O, 24/1) [DNP]

Analysis: $C_{18}H_{32}O_3Si$ (324.54)

Calculated:	C: 66.62;	H: 9.94%
Found:	C: 66.50;	H: 9.98%

Preparation of (1*S*,2*R*)-1-*tert*-Butyldimethylsilyloxy-3,3-dimethoxy-2-methyl-1-phenylpropane ((*anti*)-11a)



anti-**11a**

tert-Butyldimethylsilyl chloride (263 mg, 1.75 mmol, 1.5 equiv) was added to a solution of *anti*-**9a** (245 mg, 1.165 mmol, 1 equiv) and imidazole (238 mg, 3.5 mmol, 3 equiv) in dry DMF (2 mL). The reaction mixture was stirred at room temperature for 24 h. The mixture was diluted with water, then was stirred for 1 h and was extracted with pentane. The extracts were dried over $MgSO_4$, then were filtered and concentrated. Column chromatography (SiO_2, pentane/Et_2O, 24/1) followed by bulb-to-bulb distillation gave 362 mg (96%) of *anti*-**11a** as a clear, colorless liquid.

Data for (1*S*,2*R*)-1-*tert*-Butyldimethylsilyloxy-3,3-dimethoxy-2-methyl-1-phenylpropane:

bp: 120 °C (0.2 mmHg, ABT)

^{1}H NMR: (500 MHz, $CDCl_3$)
7.30-7.26 (m, 4 H, H-Aryl), 7.24-7.21 (m, 1 H, H-Aryl), 4.64 (d, J = 7.6, 1 H, HC(1)), 4.29 (d, J = 4.9, 1 H, HC(3)), 3.40 (s, 6 H, 2 x H_3C(4)), 2.10 (d, quint, J = 5.1, 7.1, 1 H, HC(2)), 0.87 (s, 9 H, 3 x H_3C(12)), 0.66 (d, J = 7.1, 3 H, H_3C(5)), 0.02 (s, 3 H, H_3C(10)), -0.28 (s, 3 H, H_3C(10))

^{13}C NMR: (126 MHz, $CDCl_3$)
143.03 (C(6)), 127.77 (C(7)), 127.23 (C(8)), 127.11 (C(9)), 106.20 (C(3)), 75.46 (C(1)), 54.84 (C(4)), 54.58 (C(4)), 43.97 (C(2)), 25.79 (C(12)), 18.05 (C(11)), 8.51 (C(5)), -4.67 (C(10)), -5.20 (C(10))

IR: (neat)
3085 (w), 3064 (w), 3031 (w), 2954 (s), 2931 (s), 2858 (s), 2831 (m), 2773 (w), 2740 (w), 2709 (w), 1602 (w), 1492 (w), 1471 (m), 1461 (m), 1405 (w), 1379 (w), 1361 (w), 1338 (w), 1317 (w), 1251 (s), 1205 (w), 1187 (w), 1132 (s), 1072 (s), 1006 (w), 977 (w), 958 (w), 946 (w), 900 (w)

MS: (FI)
324 (M^+, 7), 292 (M^+-MeOH, 5), 267 (M^+-*t*-Bu, 36), 249 (M^+-$CH(OMe)_2$, 43), 221 (M^+-$CH_3CHCH(OMe)_2$, 30), 195 ($PhCH_2CH(Me)CH(OMe)_2$+H, 95), 75 ($CH(OMe)_2$, 100)

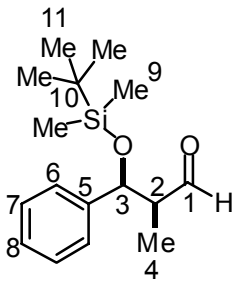
Opt. Rot.: $[\alpha]_D^{24}$ -29.8 (c = 1.02, MeOH)

TLC: R_f 0.35 (pentane/Et_2O, 24/1) [DNP]

Analysis: $C_{18}H_{32}O_3Si$ (324.54)

Calculated:	C: 66.62;	H: 9.94%
Found:	C: 66.57;	H: 9.94%

Preparation of (2*S*,3*S*)-3-*tert*-Butyldimethylsilyloxy-2-methyl-3-phenylpropanal ((*syn*)-13a)



syn-**13a**

A solution of *syn*-**11a** (265 mg, 0.816 mmol) in CH_2Cl_2 (6 mL) was added to a slurry of SiO_2 (2 g) and oxalic acid (10% aqueous solution, 0.3 ml). The reaction mixture was stirred for 26 h and a pinch of solid $NaHCO_3$ was added. After 15 min, the reaction mixture was filtered and was washed with CH_2Cl_2. The filtrate was concentrated and the residue was chromatographed (SiO_2, pentane/Et_2O, 97.5/2.5) to give an oil which on bulb-to-bulb distillation provided 161 mg (71%) of *syn*-**13a** as clear, colorless, mobile liquid.

Data for (2*S*,3*S*)-3-*tert*-Butyldimethylsilyloxy-2-methyl-3-phenylpropanal:

bp: 100 °C (0.2 mmHg, ABT)

^{1}H NMR: (500 MHz, $CDCl_3$)
9.77 (d, J = 1.2, 1 H, HC(1)), 7.35-7.23 (m, 5 H, H-Aryl), 5.15 (d, J = 4.2, 1 H, HC(3)), 2.59 (ddq, J = 1.2, 4.2, 6.8, 1 H, HC(2)), 1.04 (d, J = 6.8, 3 H, H_3C(4)), 0.89 (s, 9 H, 3 x H_3C(10)), 0.03 (s, 3 H, H_3C(9)), -0.17 (s, 3 H, H_3C(9))

^{13}C NMR: (126 MHz, $CDCl_3$)
204.40 (C(1)), 142.28 (C(5)), 128.14 (C(6)), 127.44 (C(8)), 126.24 (C(7)), 74.17 (C(3)), 54.74 (C(2)), 25.70 (3 x C(11)), 18.08 (C(10)), 7.93 (C(4)), -4.58 (C(9)), -5.31 (C(9))

IR: (neat)
3087 (w), 3064 (w), 3029 (w), 2956 (s), 2931 (s), 2886 (m), 2858 (s), 2823 (w), 2711 (w), 1726 (s), 1602 (w), 1587 (w), 1494 (w), 1471 (m), 1461 (m), 1454 (m), 1390 (w), 1361 (w), 1309 (w), 1209 (w), 1253 (s), 1199 (w), 1141 (m), 1105 (s), 1089 (s), 1070 (s), 1035 (s), 1006 (m), 939 (w), 914 (w)

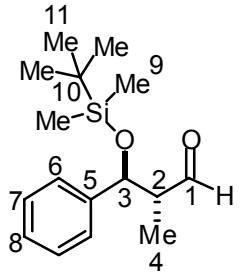
MS: (FI)
278 (M^+, 0.3), 221 (M^+-*t*-Bu, 100)

Opt. Rot.: $[\alpha]_D^{24}$ -30.3 (c = 1.03, $CHCl_3$)

TLC: R_f 0.32 (pentane/Et_2O, 24/1) [DNP]

Analysis: $C_{16}H_{26}O_2Si$ (278.47)
Calculated: C: 69.01; H: 9.41%
Found: C: 68.90; H: 9.44%

Preparation of (2*R*,3*S*)-3-*tert*-Butyldimethylsilyloxy-2-methyl-3-phenylpropanal ((*anti*)-13a)



anti-**13a**

A solution of *anti*-**11a** (265 mg, 0.816 mmol) in CH_2Cl_2 (6 mL) was added to a slurry of SiO_2 (2 g) and oxalic acid (10% aqueous solution, 0.3 ml). The reaction mixture was stirred for 26 h and a pinch of solid $NaHCO_3$ was added. After 15 min, the reaction mixture was filtered and was washed with CH_2Cl_2. The filtrate was concentrated and the residue was chromatographed (SiO_2, pentane/Et_2O, 97/3) to give an oil which on bulb-to-bulb distillation provided 169 mg (74%) of *anti*-**13a** as clear, colorless, mobile liquid.

Data for (2*R*,3*S*)-3-*tert*-Butyldimethylsilyloxy-2-methyl-3-phenylpropanal:

bp: 100 °C (0.2 mmHg, ABT)

^{1}H NMR: (500 MHz, $CDCl_3$)
9.81 (d, *J* = 2.7, 1 H, HC(1)), 7.35-7.27 (m, 5 H, H-Aryl), 4.77 (d, *J* = 7.6, 1 H, HC(3)), 2.70 (d, quint, *J* = 2.7, 7.3, 1 H, HC(2)), 0.88 (d, *J* = 7.1, 3 H, H_3C(4)), 0.85 (s, 9 H, 3 x H_3C(11)), 0.01 (s, 3 H, H_3C(9)), -0.25 (s, 3 H, H_3C(9))

^{13}C NMR: (126 MHz, $CDCl_3$)
204.60 (C(1)), 142.25 (C(5)), 128.30 (C(6)), 127.83 (C(8)), 126.68 (C(7)), 76.78 (C(3)), 54.54 (C(2)), 25.65 (3 x C(11)), 18.02 (C(10)), 11.05 (C(4)), -4.58 (C(9)), -5.29 (C(9))

IR: (neat)
3087 (w), 3064 (w), 3031 (w), 2956 (s), 2931 (s), 2886 (m), 2858 (s), 2709 (w), 1728 (s), 1602 (w), 1587 (w), 1492 (w), 1471 (m), 1456 (m), 1390 (w), 1361 (w), 1309 (w), 1255 (s), 1205 (w), 1080 (s), 1066 (s), 1006 (w), 929 (w), 914 (w)

MS: (CI)
279 (M^++H, 3), 263 (M^+-Me, 14), 221 (M^+-*t*-Bu, 100), 147 (14), 120 (18), 115 (10), 59 (13)

HRMS: calcd for $C_{16}H_{26}O_2Si$: 278.170209; found: 278.169904

Opt. Rot.: $[\alpha]_D^{24}$ -66.2 (*c* = 0.95, $CHCl_3$)

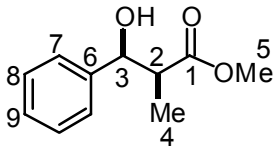
TLC: R_f 0.40 (pentane/Et_2O, 24/1) [DNP]

Analysis: $C_{16}H_{26}O_2Si$ (278.47)

Calculated:	C: 69.01;	H: 9.41%
Found:	C: 69.13;	H: 9.53%

Correlation of Absolute Configuration.

Preparation of Methyl (2*S*,3*S*)-3-Hydroxy-2-methyl-3-phenylpropanoate



A sat. aq. $KMnO_4$ solution (2 mL) was added to a stirred mixture of *syn*-**13a** (92 mg, 0.33 mmol), 5% aqueous KH_2PO_4 (1.6 mL) and *t*-BuOH (2 mL). After 5 min at room temperature, excess permanganate was destroyed by the addition of sat. aq. Na_2SO_3 solution and was made acidic by adding more KH_2PO_4. The reaction mixture was diluted with EtOAc, then was filtered through Celite. The EtOAc extract was dried over $MgSO_4$, then was filtered and evaporated. The residue was dissolved in 0.33 M HCl in MeOH (2 ml) and was left at room temperature for 1.5 h. The reaction mixture was diluted with water and was extracted with ether. The ether extract was dried over $MgSO_4$, then was filtered and evaporated. The residue was treated with ethereal diazomethane solution. After evaporation of the excess diazomethane and the solvent, the residue was chromatographed (SiO_2, pentane/Et_2O, 65/35) to give 56 mg (87%) of the propanoate.

Data for Methyl (2*S*,3*S*)-3-Hydroxy-2-methyl-3-phenylpropanoate:

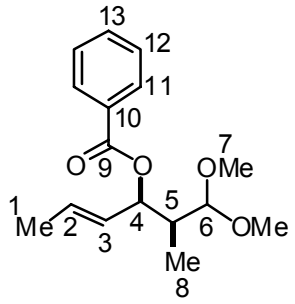
^{1}H NMR: (500 MHz, $CDCl_3$)
7.37-7.32 (m, 4 H, H-Aryl), 7.30-7.25 (m, 1 H, H-Aryl), 5.12 (t, *J* = 3.4, 1 H, HC(3)), 3.68 (s, 3 H, H_3C(5)), 2.91 (d, *J* = 3.2, 1 H, OH), 2.80 (dq, *J* = 4.2, 7.1, 1 H, HC(2)), 1.13 (d, *J* = 7.1, 3 H, H_3C(4))

^{13}C NMR: (126 MHz, $CDCl_3$)
175.26 (C(1)), 141.35 (C(6)), 128.24 (C(7)), 127.48 (C(9)), 125.92 (C(8)), 73.53 (C(3)), 51.87 (C(5)), 46.29 (C(2)), 10.63 (C(4))

IR: (neat)
3479 (br), 3087 (w), 3064 (w), 3031 (w), 2989 (w), 2950 (m), 2883 (w), 2848 (w), 1727 (s), 1604 (w), 1587 (w), 1494 (w), 1454 (s), 1436 (m), 1348 (m), 1255 (m), 1199 (s), 1172 (s), 1126 (m), 1095 (w), 1060 (m), 1035 (s), 995 (m), 900 (w)

Opt. Rot.: $[\alpha]_D$ –15.9 (*c* = 0.78, CH_2Cl_2); lit[1] $[\alpha]_D$ = –22.5 (*c* = 0.7, CH_2Cl_2)

Preparation of (*E*)-(4*R*,5*S*)-4-Benzoyloxy-6,6-dimethoxy-5-methyl-2-hexene



Freshly distilled benzoyl chloride (0.02 mL, 0.17 mmol, 3 equiv) was added to a stirred solution of *syn*-**9f**, (10 mg, 0.057 mmol, 1 equiv) and DMAP (2 mg) in pyridine (0.25 mL). After 20 h at room temperature, water (0.1 mL) was added and the mixture was stirred for 2 h. The reaction mixture was diluted with water and extracted with Et_2O. The extracts were dried over $MgSO_4$ and were concentrated. Column chromatography (SiO_2, pentane/Et_2O, 4/1) provided 15 mg (94%) of the benzoate as a thick liquid.

Data for (*E*)-(4*R*,5*S*)-4-Benzoyloxy-6,6-dimethoxy-5-methyl-2-hexene:

^{1}H NMR : (500 MHz, $CDCl_3$)
8.06-8.04 (m, 2 H, 2 X HC(11)), 7.65 (tt, *J* = 1.3, 7.6, 1 H, HC(13)), 7.46-7.43 (m, 2 H, 2 X HC(12)), 5.78 (ddq, *J* = 1.1, 15.4, 6.4, 1 H, HC(2)), 5.69-5.66 (m, 1 H, HC(4)), 5.53 (ddq, *J* = 6.6, 15.4, 1.7, 1 H, HC(3)), 4.21 (d, *J* = 7.3, 1 H, HC(6)), 3.35 (s, 3 H, H_3C(7)), 3.33 (s, 3 H, H_3C(7)), 2.06 (dquint, *J* = 3.6, 7.1, 1 H, HC(5)), 1.71 (dq, *J* = 6.6, 1, 3 H, H_3C(1)), 1.09 (d, *J* = 7.1, 3 H, H_3C(8)).

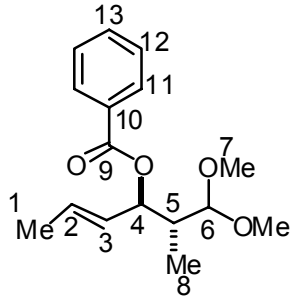
^{13}C NMR: (126 MHz, $CDCl_3$)
165.55 (C(9)), 132.85 (C(3)), 130.67 (C(10)), 129.56 (C(11)), 129.03 (C(2)), 128.37 (C(12)), 128.01 (C(13)), 105.75 (C(6)), 74.93 (C(4)), 54.72 (C(7)), 53.20 (C(7)), 40.51 (C(5)), 17.79 (C(1)), 9.12 (C(8)).

MS: (FI)
279 (M^++H, 17), 278 (M^+, 100), 247 (M^+-OMe, 4), 105 (PhCO, 6), 75 ($CH(OMe)_2$, 25).

TLC: R_f 0.32 (hexane/EtOAc, 9/1) [DNP]

SFC: t_R(4*S*,5*R*), 4.66 min (47.5%); t_R(4*R*,5*S*), 5.44 min (52.5%) (Column: Welco, MeOH 1%, pressure 150, flow 3 mL/min)

Preparation of (*E*)-(4*R*,5*R*)-4-Benzoyloxy-6,6-dimethoxy-5-methyl-2-hexene



Freshly distilled benzoyl chloride (0.02 mL, 0.17 mmol, 3 equiv) was added to a stirred solution of *anti*-**9f**, (10 mg, 0.057 mmol, 1 equiv) and DMAP (2 mg) in pyridine (0.25 mL). After 20 h at room temperature, water (0.1 mL) was added and the mixture was stirred for 2 h. The reaction mixture was diluted with water and was extracted with Et_2O. The extracts were dried over $MgSO_4$ and were concentrated. Column chromatography (SiO_2, pentane/Et_2O, 80/20) provided 15 mg (94%) of the benzoate as a thick liquid.

Data for (*E*)-(4*R*,5*R*)-4-Benzoyloxy-6,6-dimethoxy-5-methyl-2-hexene:

^{1}H NMR : (400 MHz, $CDCl_3$)
8.07-8.04 (m, 2 H, 2 X HC(11)), 7.55 (tt, *J* = 1.2, 7.6, 1 H, HC(13)), 7.46-7.42 (m, 2 H, 2 X HC(12)), 5.86 (dq, *J* =14.4, 6.4, 1 H, HC(2)), 5.58-5.48 (m, 2 H, HC(4), HC(3)), 4.21 (d, *J* = 6.8, 1 H, HC(6)), 3.38 (s, 3 H, H_3C(7)), 3.34 (s, 3 H, H_3C(7)), 2.29 (sext, *J* = 7.1, 1 H, HC(5)), 1.73 (dd, *J* = 6.4, 1, 3 H, H_3C(1)), 1.00 (d, *J* = 7.1, 3 H, H_3C(8)).

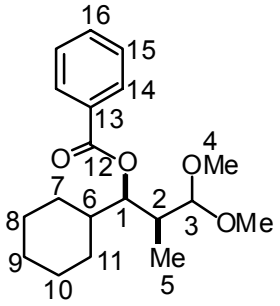
^{13}C NMR: (101 MHz, $CDCl_3$)
165.45 (C(9)), 132.78 (C(3)), 131.04 (C(2)), 130.76 (C(10)), 129.52 (C(11)), 128.32 (C(12)), 126.29 (C(13)), 105.49 (C(6)), 75.98 (C(4)), 54.10 (C(7)), 53.63 (C(7)), 39.43 (C(5)), 17.91 (C(1)), 9.51 (C(8)).

MS: (FI)
279 (M^++H, 22), 278 (M^+, 100), 247 (M^+-OMe, 8), 246 (M^+-MeOH, 15), 105 (PhCO, 7), 75 ($CH(OMe)_2$, 37)

TLC: R_f 0.32 (hexane/EtOAc; 9/1) [DNP]

SFC: t_R(4*S*,5*S*) 5.12 min (24%); t_R(4*R*,5*R*), 5.79 min (76%) (Column: Regis Whelco, MeOH 1%, pressure 150, flow 3 mL/min)

Preparation of (1*R*,2*S*)-1-Benzolyoxy-1-cyclohexyl-3,3-dimethoxy-2-methylpropane



Freshly distilled benzoyl chloride (0.02 mL, 0.17 mmol, 5.5 equiv) was added to a stirred solution of *syn*-**9i**, (10 mg, 0.031 mmol, 1 equiv) and DMAP (2 mg) in pyridine (0.25 mL). After 20 h at room temperature, water (0.1 mL) was added and the mixture was stirred for 2 h. The reaction mixture was diluted with water and was extracted with Et_2O. The extracts were dried over $MgSO_4$ and were concentrated. Column chromatography (SiO_2, pentane/Et_2O, 80/20) provided 14 mg (94%) of the benzoate as a thick liquid.

Data for (1*R*,2*S*)-1-Benzoyloxy-1-cyclohexyl-3,3-dimethoxy-2-methylpropane:

^{1}H NMR : (500 MHz, $CDCl_3$)
8.07-8.04 (m, 2 H, 2 X HC(14)), 7.56 (tt, *J* = 1.2, 7.6, 1 H, HC(16)), 7.60-7.45 (m, 2 H, 2 X HC(15)), 5.21 (dd, *J* = 2.1, 8.5, 1 H, HC(1)), 4.09 (d, *J* = 7.8, 1 H, HC(3)), 3.34 (s, 3 H, H_3C(4)), 3.28 (s, 3 H, H_3C(4)), 2.17 (dquint, *J* = 2.2, 7.1, 1 H, HC(2)), 1.80-1.60 (m, 6 H), 1.30-1.05 (m, 5 H), 1.05 (d, *J* = 7.1, 3 H, H_3C(5))

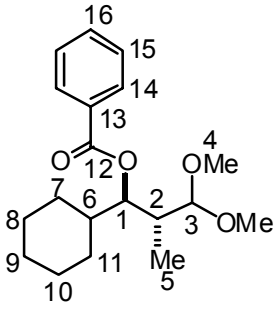
^{13}C NMR: (126 MHz, $CDCl_3$)
166.03 (C(12)), 132.76 (C(16)), 130.60 (C(13)), 129.64 (C(14)), 128.36 (C(15)), 106.18 (C(3)), 77.54 (C(1)), 54.62 (C(4)), 52.84 (C(4)), 39.51 (C(2)), 36.73 (C(6)), 29.16 (C(7), C(11)), 26.20 (C(8)), 25.95 (C(9)), 25.80 (C(10)), 8.64 (C(5))

MS: (EI, 70eV)
319 (M^+-H, 0.01), 289 (M^+-OMe, 1), 105 (PhCO, 31), 75 ($CH(OMe)_2$, 100)

TLC: R_f 0.37 (hexane/EtOAc, 9/1) [DNP]

SFC: t_R(1*S*,2*R*) 5.80 min (28%); t_R(1*R*,2*S*), 6.35 min (72%) (Column: Regis Whelco, MeOH 1%, pressure 150, flow 2.5 mL/min)

Preparation of (1*R*,2*R*)-1-Benzoyloxy-1-cyclohexyl-3,3-dimethoxy-2-methylpropane



Freshly distilled benzoyl chloride (0.02 mL, 0.17 mmol, 5.5 equiv) was added to a stirred solution of *anti*-**9i**, (10 mg, 0.031 mmol, 1 equiv) and DMAP (2 mg) in pyridine (0.25 mL). After 20 h at room temperature, water (0.1 mL) was added and the mixture was stirred for 2 h. The reaction mixture was diluted with water and was extracted with Et_2O. The extracts were dried over $MgSO_4$ and were concentrated. Column chromatography (SiO_2, pentane/Et_2O, 80/20) provided 13.6 mg (92%) of the benzoate as a thick liquid.

Data for (1*R*,2*R*)-1-Benzoyloxy-1-cyclohexyl-3,3-dimethoxy-2-methylpropane:

^{1}H NMR: (500 MHz, $CDCl_3$)
8.09-8.07 (m, 2 H, 2 X HC(14)), 7.57 (tt, *J* = 1.2, 1 H, 7.6, HC(16)), 7.48-7.45 (m, 2 H, 2 X HC(15)), 5.10 (dd, *J* = 3.7, 8.3, 1 H, HC(1)), 4.21 (d, *J* = 4.2,1 H, HC(3)), 3.36 (s, 3 H, H_3C(4)), 3.33 (s, 3 H, H_3C(4)), 2.24 (ddq, *J* = 4.2, 8.3, 7.1, 1 H, HC(2)), 1.82-1.60 (m, 6 H), 1.31-1.16 (m, 3 H), 1.13-1.01 (m, 2 H), 0.97 (d, *J* = 7.1, 3 H, H_3C(5))

^{13}C NMR: (126 MHz, $CDCl_3$)
166.16 (C(12)), 132.80 (C(16)), 130.60 (C(13)), 129.64 (C(14)), 128.41 (C(15)), 106.56 (C(3)), 78.87 (C(1)), 55.81 (C(4)), 55.28 (C(4)), 39.30 (C(2)), 37.74 (C(6)), 30.39 (C(7)), 26.32 (C(8), C(10)), 26.29 (C(9)), 26.16 (C(11)), 10.23 (C(5))

MS: (FI)
320 (M^+, 12), 289 (M^+-OMe, 11), 245 (M^+-$CH(OMe)_2$, 18), 105 (PhCO, 17), 75 ($CH(OMe)_2$, 100).

TLC: R_f 0.37 (hexane/EtOAc, 9/1) [DNP]

SFC: t_R(1*R*,2*R*), 6.12 min (59.4%); t_R(1*S*,2*S*), 7.1 min (40.6%) (Column: Welco, MeOH 1%, pressure 150, flow 2.5 mL/min)

References

(1) Yan, T.-H.; Tan, C.-W.; Lee, C.-H.; Lo, C.-H.; Huang, T.-Y. *J. Am. Chem. Soc.* **1993**, *115*, 2613.