Lewis Base Activation of Lewis Acids. 2.
Addition of Silyl Ketene Acetals to Aldehydes

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SUPPORTING INFORMATION

General Experimental

All reactions were performed in oven-dried (140 °C) or flame-dried glassware under an atmosphere of dry N₂. The following reaction solvents were distilled from the indicated drying agents: dichloromethane (P₂O₅), benzene (Fisher ACS grade), hexanes (Fisher ACS grade), tetrahydrofuran (Na, benzophenone) and diethyl ether (Na, benzophenone). Solvents for chromatography and filtration were technical grade and distilled from the indicated drying agents: hexane (CaCl₂), ethyl acetate (K₂CO₃), dichloromethane (CaCl₂). Column chromatography was performed using EM Science 230-400-mesh silica gel. Benzaldehyde (**2a**), 1-naphthaldehyde (**2b**), p-tolualdehyde (**2d**), p-anisaldehyde (**2e**), p-trifluoromethylbenzaldehyde (**2f**), *trans*-cinnamaldehyde (**2g**), *trans*-methyl-*trans*-cinnamaldehyde (**2h**), furfural (**2i**), cyclohexanecarboxaldehyde (**2j**) and hydrocinnamaldehyde (**2k**) were freshly distilled before use. 2-Naphthaldehyde (**2c**) (Aldrich) was sublimed prior to use. 1-(*tert*-Butyldimethylsilyloxy)-1-methoxyethene (**1**) (Aldrich) was stored over 3 Å molecular sieves. Silicon tetrachloride (Aldrich) was heated at reflux for 24 h and then distilled prior to use. HMPA was distilled and then stored over 3 Å molecular sieves prior to use. *tert*-Butyl dimethylsilyl chloride (TBSCl, Aldrich) and 3,5-dinitrobenzoyl chloride (Aldrich) were used without further purification. Methyl propanoate, ethyl propanoate and *tert*-butyl propanoate (Aldrich) were stored over 3 Å molecular sieves. Propanoic acid phenyl ester (TCI America) was stored over 3 Å molecular sieves. Diisopropyl amine, pyridine and hexamethyldisilazane were freshly distilled from CaH₂ prior to use. Tetrabutylammonium iodide was recrystallized from

toluene and dried under vacuum prior to use. All reaction temperatures correspond to internal temperatures measured by Teflon-coated thermocouples unless otherwise noted.

^1H NMR, ^{13}C NMR, ^{19}F NMR, and low temperature spectra were recorded on a Varian Unity 400 (400 MHz, ^1H ; 100 MHz, ^{13}C , 376 MHz ^{19}F), Unity 500 (500 MHz, ^1H ; 126 MHz, ^{13}C , 202 MHz) spectrometers. Spectra were referenced to residual chloroform (7.26 ppm, ^1H , 77.23 ppm, ^{13}C), ^{19}F spectra were referenced externally to C_6F_6 . Chemical shifts are reported in ppm, multiplicities are indicated by s (singlet), d (doublet), t (triplet), q (quartet), p (pentet) h (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. EI mass spectra were performed on a 70-VSE spectrometer. FAB mass spectra were performed on a Finnigan-MATCH-5 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. Kugelrohr distillations were performed on a Büchi GKR-50 Kugelrohr and temperatures reported are air bath temperatures. Analytical thin-layer chromatography was performed on Merck silica gel plates with QF-254 indicator. Visualization was accomplished with UV(254), potassium permanganate (KMnO_4) and phosphomolybdic Acid (PMA).

Optical rotation data was obtained on a JASCO DIP-360 digital polarimeter and are reported as follows: concentration ($c = \text{g}/100 \text{ mL}$), and solvent. Analytical supercritical fluid chromatography (SFC) was performed on a Berger Instruments packed-column SFC with built-in photometric detector (220 nm) using Daicel Chiralpak OD, AD, AS columns and a Regis Whelk-O1 column. Analytical capillary gas chromatography (GC) was performed on a Hewlett Packard 5890 Series II fitted with a flame ionization detector (H_2 carrier gas, 16 mL/min) equipped with an Astec (Chiraldex) GTA 30m x 0.25mm x 0.125 μm column. The injector temperature was 225 $^\circ\text{C}$, the detector temperature was 300 $^\circ\text{C}$ Retention times (t_R) and peak ratios were determined with a Hewlett Packard 3396 Series II integrator.

Literature Preparations.

(*R,R*)-*N,N'*-Bis[4,5-dihydro-3,5-dimethyl-4-(3*H*-dinaphtho[2,1-*d*:1',2'-*f*][1,3,2]-2-oxo-diazaphosphepino)]-*N,N'*-dimethyl-1,5-pentanediamine ((*R,R*)-**3**)¹, 3-phenyl-2-propynal (**2l**)² and (*E*)-(1-ethoxy-propenyloxy)-*tert*-butyldimethylsilane (**5b**)³ were prepared by literature methods.

Experimental Procedures.

Representative Procedure 1. Addition of acetate-derived Silyl Ketene Acetals to Aromatic Aldehydes.

Preparation of Methyl (*R*)-3-Hydroxy-3-phenylpropanoate ((*R*)-**4a**)

A flame-dried, 20-mL, 2-neck flask containing a solution of 84 mg (0.1 mmol, 0.05 equiv) of bisphosphoramidate (*R,R*)-**3** in CH₂Cl₂ (10 mL) was cooled to -78 °C under nitrogen and then 200 μ L (2.0 mmol, 1.0 equiv) of benzaldehyde was added in one portion. To the resulting solution 252 μ L (2.2 mmol, 1.1 equiv) of SiCl₄ was added and the reaction mixture was allowed to stir at -78 °C for 5 min. Then 523 μ L (2.4 mmol, 1.2 equiv) of 1-(*tert*-butyldimethylsilyloxy)-1-methoxyethene (**1**) was added dropwise (over 5 min) to the reaction mixture. The resulting mixture was allowed to stir at -78 °C (bath temperature) for 15 min whereupon the cold reaction mixture was poured into a rapidly stirring solution of 1/1 sat. aq. KF/1.0 M KH₂PO₄ solution (50 mL). This biphasic mixture was stirred vigorously for 2 h after which the aqueous layer was washed with CH₂Cl₂ (3 x 50 mL). The combined organic extracts were dried over Na₂SO₄, filtered and the filtrate was concentrated *in vacuo*. The residue was purified by column chromatography (hexanes/EtOAc, 2/1). The product-containing fractions were combined and the solvent was removed *in vacuo* to yield 348 mg (97%) of (*R*)-**4a** as a colorless oil.⁴

Data for (R)-4a:¹H NMR: (400 MHz, CDCl₃)7.40-7.34 (m, 4 H, 2 x HC(5), 2 x HC(6)), 7.31-7.27 (m, 1 H, HC(7)), 5.16 (dt, *J* = 8.8, 3.4, 1 H, HC(3)), 3.73 (s, 3 H, HC(8)), 3.23 (bs, 1 H, HO), 2.75 (dd, *J* = 16.5, 8.8, 1 H, HHC(2)), 2.73 (dd, *J* = 16.4, 6.8, 1 H, HHC(2))¹³C NMR: (100 MHz, CDCl₃)

173.03 (C(1)), 142.63 (C(4)), 128.78 (C(6)), 128.05 (C(7)), 125.84 (C(5)), 70.50 (C(3)), 52.13 (C(8)), 43.31 (C(2))

IR: (neat)

3456 (s), 3031 (m), 3005 (w), 2953 (m), 1735 (s), 1494 (w), 1438 (s), 1403 (s), 1360(m), 1269 (m), 1200 (m), 1164 (m), 1060 (m), 1036 (m), 1025 (m), 988 (w), 762 (m), 701 (m)

Opt. Rot.: [α]_D²⁴ +17.7 (c = 2.05, EtOH) [Lit²: [α]_D²⁴ (R) +12.4 (c = 2.66, EtOH)]SFC: *t_R* (R)-4a, 3.81 (96.3%); *t_R* (S)-4a, 4.23 min (3.7%) (Chiralpak AD, 200 bar, 40 °C, 3.5% CH₃OH in CO₂, 2.7 mL/min, 220 nm)**Preparation of Methyl (R)-3-Hydroxy-3-(1-naphthyl)propanoate ((R)-4b)**

Following General Procedure 1, 271 μL (2.0 mmol, 1.0 equiv) of 1-naphthaldehyde was combined with 84 mg (0.1 mmol, 0.05 equiv) of bisphosphoramidate (*R,R*)-3, 252 μL (2.2 mmol, 1.1 equiv) of SiCl₄, and 523 μL (2.4 mmol, 1.2 equiv) of 1-(*tert*-butyldimethylsilyloxy)-1-methoxyethene (**1**) to yield, after purification by column chromatography (hexanes/EtOAc, 2/1), 457 mg (98%) of (R)-4b as a colorless solid. An analytical sample was obtained by recrystallization from Et₂O to afford colorless crystals.

Data for 4b:

mp: 76-77 °C (Et₂O)

¹H NMR: (400 MHz, CDCl₃)

8.05 (d, *J* = 8.3, 1 H, HC(12)), 7.89 (d, *J* = 7.5, 1 H, HC(9)), 7.80 (d, *J* = 8.1, 1 H, HC(7)), 7.71 (d, *J* = 7.0, 1 H, HC(5)), 7.51 (m, 3 H, HC(6), HC(10), HC(11)), 5.93 (m, 1 H, HC(3)), 3.78 (s, 3 H, HC(14)), 3.35 (bs, 1 H, HO), 2.91 (dd, *J* = 16.3, 5.3, 1 H, HHC(2)), 2.90 (dd, *J* = 16.3, 6.0, 1 H, HHC(2))

¹³C NMR: (100 MHz, CDCl₃)

173.31 (C(1)), 138.12 (C(4)), 133.94 (C(8)), 130.10 (C(13)), 129.22 (C(9)), 128.52 (C(7)), 126.51 (C(11)), 125.83 (C(10)), 125.72 (C(6)), 123.11 (C(5)), 122.92 (C(12)), 67.50 (C(3)), 52.23 (C(14)), 42.70 (C(2))

IR: (neat)

3459 (s), 3051 (s), 3007 (w), 2951 (m), 1731 (s), 1597 (w), 1511 (m), 1437 (s), 1356 (m), 1279 (m), 1206 (m), 1173 (s), 1083 (m), 1042 (s), 1001 (w), 906 (w), 861 (w), 803 (s), 780 (s), 737 (w), 695 (w)

MS: (EI, 70 eV)

230 (M⁺, 31), 157 (100), 129 (80)

Opt. Rot.: [α]_D²⁴ +21.00 (c = 2.12, EtOH)

TLC: *R_f* 0.35 (hexanes/EtOAc, 2/1) [UV(254)/PMA]

SFC: *t_R* (*S*)-**4b**, 5.17 (9.8%); *t_R* (*R*)-**4b**, 5.91 min (90.2%) (Chiralpak OD, 200 bar, 40 °C, 9.0% CH₃OH in CO₂, 3.0 mL/min, 220 nm)

Analysis: C₁₄H₁₄O₃ (230.26)

Calcd: C, 73.03; H, 6.13%

Found: C, 72.93; H, 6.16%

Preparation of Methyl (*R*)-3-Hydroxy-3-(2-naphthyl)propanoate ((*R*)-4c)

Following General Procedure 1, 312.3 mg (2.0 mmol, 1.0 equiv) of 2-naphthaldehyde was combined with 84 mg (0.1 mmol, 0.05 equiv) of bisphosphoramidate (*R,R*)-**3**, 252 μ L (2.2 mmol, 1.1 equiv) of SiCl_4 , and 523 μ L (2.4 mmol, 1.2 equiv) of 1-(*tert*-butyldimethylsilyloxy)-1-methoxyethene (**1**) to yield, after purification by column chromatography (hexanes/EtOAc, 2/1), 455 mg (98%) of (*R*)-**4c** as a wax-like, white solid. After Kugelrohr distillation an analytically pure, colorless oil was isolated which solidified upon standing.

Data for (*R*)-4c:

bp: 145°C (1.8×10^{-4} mmHg, ABT)

^1H NMR: (400 MHz, CDCl_3)

7.83 (m, 4 H, H(Ar)), 7.48 (m, 3 H, H(Ar)), 5.31 (m, 1 H, HC(3)), 3.74 (s, 3 H, HC(14)), 3.34 (m, 1 H, HO), 2.84 (dd, $J = 16.4, 6.0$, 1 H, $\text{HHC}(2)$), 2.83 (dd, $J = 16.4, 2.0$, 1 H, $\text{HHC}(2)$)

^{13}C NMR: (100 MHz, CDCl_3)

173.06 (C(1)), 140.03 (C(4)), 133.48 (C(12)), 133.24 (C(7)), 128.65 (C(8)), 128.25 (C(11)), 127.90 (C(5)), 126.47 (C(6)), 126.24 (C(13)), 124.68 (C(10)), 123.89 (C(9)), 70.63 (C(3)), 52.16 (C(14)), 43.28 (C(2))

IR: (neat)

3442 (s), 3055 (s), 3022 (m), 2952 (m), 1732 (s), 1601 (w), 1509 (m), 1437 (s), 1404 (w), 1358 (m), 1274 (s), 1203 (m), 1169 (m), 1067 (m), 1034 (m), 897 (w), 821 (s), 748 (s), 692 (w)

MS: (EI, 70 eV)

230 (M^+ 41), 157 (100), 129 (120)

Opt. Rot.: $[\alpha]_{\text{D}}^{24} +15.66$ ($c = 2.11$, EtOH)

TLC: R_f 0.30 (hexanes/EtOAc, 2/1) [UV(254)/PMA]

SFC: t_R (*R*)-**4c**, 4.72 (96.8%); t_R (*S*)-**4c**, 5.26 min (3.2%) (Chiralpak AD, 150 bar, 40 °C, 10.0% CH₃OH in CO₂, 3.0 mL/min, 220 nm)

Analysis: C₁₄H₁₄O₃ (230.26)

Calcd: C, 73.03; H, 6.13%

Found: C, 72.82; H, 6.02%

Preparation of Methyl (*R*)-3-Hydroxy-3-(4-methylphenyl)propanoate ((*R*)-**4d**)

Following General Procedure 1, 236 μ L (2.0 mmol, 1.0 equiv) of anisaldehyde was combined with 84 mg (0.1 mmol, 0.05 equiv) of bisphosphoramidate (*R,R*)-**3**, 252 μ L (2.2 mmol, 1.1 equiv) of SiCl₄, and 523 μ L (2.4 mmol, 1.2 equiv) of 1-(*tert*-butyldimethylsilyloxy)-1-methoxyethene (**1**) to yield, after purification by column chromatography (hexanes/EtOAc, 2/1), 378 mg (97%) of (*R*)-**4d** as a clear oil. After Kugelrohr distillation an analytically pure, colorless oil was collected.

Data for (*R*)-**4d**:

bp: 105 °C (1.4 x 10⁻⁴ mmHg, ABT)

¹H NMR: (400 MHz, CDCl₃)

7.28 (d, J = 8.1, 2 H, HC(5)), 7.18 (d, J = 8.1, 2 H, HC(6)), 5.12 (dt, J = 9.0, 3.6, 1 H, HC(3)), 3.75 (s, 3 H, HC(9)), 3.13, (d, J = 3.4, 1 H, HO), 2.76 (dd, J = 16.4, 7.8, 1 H, HHC(2)), 2.74 (dd, J = 16.4, 5.3, 1 H, HHC(2)), 1.60 (s, 3 H, HC(8))

¹³C NMR: (100 MHz, CDCl₃)

173.08 (C(1)), 139.69 (C(4)), 137.80 (C(7)), 129.46 (C(6)), 125.80 (C(5)), 70.39 (C(3)), 52.13 (C(9)), 43.32 (C(2)), 21.34 (C(8))

IR: (neat)

3450 (s), 3023 (w), 2952 (m), 2922 (m), 1737 (s), 1515 (m), 1438 (m), 1357 (w), 1267 (w), 1198 (m), 1162 (m), 1067 (w), 1035 (m), 1019 (w), 989 (w), 818 (m)

MS: (EI, 70 eV)
 194 (M^+ , 22) 179 (10), 122 (10), 121 (100), 105 (10)

Opt. Rot.: $[\alpha]_D^{24} +16.51$ ($c = 2.21$, EtOH)

TLC: R_f 0.33 (hexanes/EtOAc, 2/1) [UV(254)/PMA]

SFC: t_R (*R*)-**4d**, 3.97 (97.2%); t_R (*S*)-**4d**, 4.37 min (2.8%) (Chiralpak AD, 150 bar, 40 °C, 4.0% CH₃OH in CO₂, 3.0 mL/min, 220 nm)

Analysis: C₁₁H₁₄O₃ (194.23)

Calcd:	C, 68.02;	H, 7.27%
Found:	C, 67.83;	H, 7.32%

Preparation of Methyl (*R*)-3-Hydroxy-3-(4-methoxyphenyl)propanoate ((*R*)-**4e**)

Following General Procedure 1, 243 μ L (2.0 mmol, 1.0 equiv) of anisaldehyde was combined with 84 mg (0.1 mmol, 0.05 equiv) of bisphosphoramidate (*R,R*)-**3**, 252 μ L (2.2 mmol, 1.1 equiv) of SiCl₄, and 523 μ L (2.4 mmol, 1.2 equiv) of 1-(*tert*-butyldimethylsilyloxy)-1-methoxyethene (**1**) to yield, after purification by column chromatography (hexanes/EtOAc, 2/1), 410 mg (97%) of (*R*)-**4e** as a white solid. After recrystallization from benzene/hexanes, analytically pure, colorless needles were isolated.

Data for (*R*)-**4e**:

mp: 67-68 °C (benzene/hexanes)

¹H NMR: (400 MHz, CDCl₃)
 7.30 (m, 2 H, HC(5)), 6.89 (m, 2 H, HC(6)), 5.09 (dt, $J = 9.0, 3.7$, 1 H, HC(3)), 3.80 (s, 3 H, HC(8)), 3.72 (s, 3 H, HC(9)), 3.10 (d, $J = 3.4$, 1 H, OH), 2.73 (dd, $J = 16.4, 8.7$, 1 H, HHC(2)), 2.72 (dd, $J = 16.4, 6.6$, 1 H, HHC(2))

¹³C NMR: (100 MHz, CDCl₃)

172.74 (C(1)), 159.11 (C(7)), 134.50 (C(4)), 126.84 (C(5)), 113.81 (C(6)), 69.84 (C(3)), 55.18 (C(8)), 51.79 (C(9)), 43.00 (C(2))

IR: (neat)

3439 (s), 3001 (w), 2953 (m), 2837 (m), 1735 (s), 1612 (m), 1586 (w), 1514 (s), 1438 (m), 1358 (w), 1302 (m), 1248 (s), 1201 (m), 1174 (m), 1111 (w), 1032 (s), 833 (m).

MS: (EI, 70 eV)

210 (M⁺, 10), 161 (10), 138 (10), 137 (100)

Opt. Rot.: [α]_D²⁴ +14.4 (c = 2.05, EtOH)

TLC: R_f 0.20 (hexanes/EtOAc, 2/1) [UV(254)/PMA]

SFC: t_R (*R*)-**4e**, 3.95 (98.7%); t_R (*S*)-**4e**, 4.45 min (1.3%) (Chiralpak AD, 150 bar, 40 °C, 6.0% CH₃OH in CO₂, 3.0 mL/min, 220 nm)

Analysis: C₁₁H₁₄O₄ (210.23)

Calcd: C, 62.85; H, 6.71%

Found: C, 62.83; H, 6.75%

Preparation of Methyl (*R*)-3-Hydroxy-3-(4-trifluoromethylphenyl)propanoate ((*R*)-**4f**)

Following General Procedure 1, 273 μL (2.0 mmol, 1.0 equiv) of 4-trifluoromethylbenzaldehyde was combined with 84 mg (0.1 mmol, 0.05 equiv) of bisphosphoramidate (*R,R*)-**3**, 252 μL (2.2 mmol, 1.1 equiv) of SiCl₄, and 523 μL (2.4 mmol, 1.2 equiv) of 1-(*tert*-butyldimethylsilyloxy)-1-methoxyethene (**1**) to yield, after purification by column chromatography (hexanes/EtOAc, 2/1), 484 mg (97%) of (*R*)-**4f** as a white solid. Recrystallization from hexane afforded analytically pure, colorless needles.

Data for (*R*)-**4f**:

mp: 42-43 °C (hexane)

¹H NMR: (400 MHz, CDCl₃)
 7.58 (d, *J* = 8.3, 2 H, HC(5)), 7.46 (d, *J* = 8.0, 2 H, HC(6)), 5.15 (m, 1 H, HC(3)),
 3.75 (d, *J* = 3.7, 1 H, OH), 3.68 (s, 3 H, HC(9)), 2.71 (m, 2 H, HC(2))

¹³C NMR: (100 MHz, CDCl₃)
 172.72 (C(1)), 146.68 (C(4)), 130.10 (q, *J* = 32.0, C(7)), 126.13 (C(5)), 125.60
 (C(6)), 124.22 (q, *J* = 271.8, C(8)), 69.78 (C(3)), 52.14 (C(9)), 43.15 (C(2))

¹⁹F NMR: (376 MHz, CDCl₃)
 -63.1 (F₃C(8))

IR: (neat)
 3456 (s), 3005 (w), 2957 (m), 2851 (w), 1734 (s), 1621 (m), 1439 (m), 1416 (m),
 1327 (s), 1272 (w), 1164 (s), 1124 (s), 1068 (s), 1017 (m), 845 (m)

MS: (CI)
 248 (M⁺, 8), 230 (43), 223 (21), 212 (10), 184 (11), 175 (27), 168 (26), 157 (100)

Opt. Rot.: [α]_D²⁴ +13.60 (c = 2.27, EtOH)

TLC: *R_f* 0.25 (hexanes/EtOAc, 2/1) [UV(254)/PMA]

SFC: *t_R* (*R*)-**4f**, 3.75 (95.7%); *t_R* (*S*)-**4f**, 4.14 min (4.3%) (Chiralpak AS, 150 bar, 40 °C,
 7.5% CH₃OH in CO₂, 2.5 mL/min, 220 nm)

Analysis: C₁₁H₁₁F₃O₃ (248.20)
 Calcd: C, 53.23; H, 4.47%
 Found: C, 53.49; H, 4.61%

Preparation of Methyl (*R*)-3-Hydroxy-5-phenyl-4-pentenoate ((*R*)-**4g**)

Following General Procedure 1, 252 μL (2.0 mmol, 1.0 equiv) of cinnamaldehyde was combined with 84 mg (0.1 mmol, 0.05 equiv) of bisphosphoramidate (*R,R*)-**3**, 252 μL (2.2 mmol, 1.1 equiv) of SiCl₄, and 523 μL (2.4 mmol, 1.2 equiv) of 1-(*tert*-butyldimethylsilyloxy)-1-

methoxyethene (**1**) to yield, after purification by column chromatography (hexanes/EtOAc, 2/1), 393 mg (95%) of (*R*)-**4g** as a colorless oil.⁵

Data for (*R*)-**4g**:

¹H NMR: (400 MHz, CDCl₃)

7.39 (bd, *J* = 7.1, 2 H, 2 x HC(7)), 7.34 (bt, *J* = 7.1 2 H, 2 x HC(8)), 7.28 (bt, *J* = 6.1, 1 H, HC(9)), 6.67 (d, *J* = 15.9, 1 H, HC(5)), 6.24 (dd, *J* = 15.9, 6.1, 1 H, HC(4)), 4.75 (m, 1 H, HC(3)), 3.74 (s, 3 H, HC(10)), 3.23 (d, *J* = 4.6, 1 H, HO), 2.67 (dd, *J* = 16.4, 1.2, 1 H, HHC(2)), 2.66 (dd, *J* = 16.4, 3.0, 1 H, HHC(2))

¹³C NMR: (100 MHz, CDCl₃)

172.74 (C(1)), 136.50 (C(6)), 130.89 (C(5)), 130.06 (C(4)), 128.70 (C(7)), 127.95 (C(9)), 126.67 (C(8)), 68.98 (C(3)), 52.03 (C(10)), 41.50 (C(2))

IR: (neat)

3448 (s), 3058 (w), 3026 (m), 2952 (m), 1735 (s), 1494 (m), 1438 (s), 1403 (w), 1357 (m), 1283 (m), 1205 (m), 1166 (s), 1104 (m), 1030 (m), 969 (s), 751 (s), 694 (s)

Opt. Rot.: [α]_D²⁴ -17.0 (c = 2.07, EtOH)

SFC: *t_R* (*R*)-**4g**, 3.61 (96.9%); *t_R* (*S*)-**4g**, 4.24 min (3.1%) (Chiralpak OD, 150 bar, 40 °C, 7.5% CH₃OH in CO₂, 3.0 mL/min, 220 nm)

Preparation of Methyl (*R*)-3-Hydroxy-4-methyl-5-phenyl-4-pentenoate ((*R*)-4h**)**

Following General Procedure 1, 279 μL (2.0 mmol, 1.0 equiv) of -methylcinnamaldehyde was combined with 84 mg (0.1 mmol, 0.05 equiv) of bis-phosphoramidate (*R,R*)-**3**, 252 μL (2.2 mmol, 1.1 equiv) of SiCl₄, and 523 μL (2.4 mmol, 1.2 equiv) of 1-(*tert*-butyldimethylsilyloxy)-1-methoxyethene (**1**) to yield, after purification by column

chromatography (hexanes/EtOAc, 2/1), 432 mg (98%) of (*R*)-**4h** as a colorless oil. Kugelrohr distillation afforded an analytically pure, colorless oil.⁶

Data for (*R*)-**4h**:

bp: 115 °C (1.3 x 10⁻⁴ mmHg, ABT)

¹H NMR: (400 MHz, CDCl₃)

7.35 (m, 2 H, HC(7)), 7.25 (m, 3 H, HC(8), HC(9)), 6.62 (bs, 1 H, HC(5)), 4.64 (m, 1 H, HC(3)), 3.76 (s, 3 H, HC(11)), 2.94 (d, *J* = 3.4, 1 H, HO), 2.68 (m, 2 H, 2 x HC(2)), 1.90 (d, *J* = 1.5, 3 H, H₃C(10))

¹³C NMR: (100 MHz, CDCl₃)

173.23 (C(1)), 138.26 (C(4)), 137.45 (C(6)), 129.20 (C(8)), 128.35 (C(9)), 126.83 (C(7)), 126.26 (C(5)), 73.77 (C(3)), 52.18 (C(11)), 40.28 (C(2)), 14.03 (C(10))

IR: (neat)

3456 (s), 3024 (w), 2984 (w), 2952 (m), 2917 (w), 1736 (s), 1599 (m), 1492 (m), 1439 (s), 1347 (m), 1273 (s), 1169 (s), 1074 (m), 1042 (m), 990 (m), 920 (w), 870 (w), 753 (m)

MS: (CI)

220 (M⁺, 29), 202 (17), 147 (100), 129 (74), 118 (63)

Opt. Rot.: [α]_D²⁴ -13.70 (c = 2.23, EtOH)

TLC: *R_f* 0.31 (hexanes/EtOAc, 2/1) [UV(254)/PMA]

SFC: *t_R* (*R*)-**4h**, 4.34 (72.7%); *t_R* (*S*)-**4h**, 4.45 min (27.3%) (Chiralpak AD, 150 bar, 40 °C, 6.0% CH₃OH in CO₂, 3.0 mL/min, 220 nm)

Analysis: C₁₃H₁₆O₃ (220.26)

Calcd: C, 70.89; H, 7.32%

Found: C, 70.61; H, 7.33%

Preparation of Methyl (*R*)-3-Hydroxy-3-(2-furyl)propanoate ((*R*)-4i)

Following General Procedure 1, 165 μL (2.0 mmol, 1.0 equiv) of furfural was combined with 84 mg (0.1 mmol, 0.05 equiv) of bisphosphoramidate (*R,R*)-**3**, 252 μL (2.2 mmol, 1.1 equiv) of SiCl_4 , and 523 μL (2.4 mmol, 1.2 equiv) of 1-(*tert*-butyldimethylsilyloxy)-1-methoxyethene (**1**) to yield, after purification by column chromatography (hexanes/EtOAc, 2/1), 320 mg (94%) of (*R*)-**4i** as a colorless oil.

Data for (*R*)-4i:

bp: 75 $^{\circ}\text{C}$ (2.2×10^{-4} mmHg, ABT)

^1H NMR: (400 MHz, CDCl_3)

7.38 (m, 1 H, HC(7)), 6.33 (m, 1 H, HC(6)), 6.27 (m, 1 H, HC(5)), 5.12 (d, $J = 4.4$, 1 H, HC(3)), 3.73 (s, 3 H, HC(8)), 3.21 (bs, 1 H, HO), 2.90 (dd, $J = 16.4, 6.3$, 1 H, $\text{HHC}(2)$), 2.88 (dd, $J = 16.4, 5.4$, 1 H, $\text{HHC}(2)$)

^{13}C NMR: (100 MHz, CDCl_3)

172.64 (C(1)), 154.83 (C(4)), 142.56 (C(7)), 110.52 (C(6)), 106.62 (C(5)), 64.38 (C(3)), 52.28 (C(8)), 39.78 (C(2))

IR: (neat)

3460 (s), 2955 (m), 1736 (s), 1504 (w), 1439 (m), 1363 (m), 1284 (m), 1211 (m), 1164 (m), 1066 (w), 1030 (m), 1011 (m), 741 (m)

MS: (EI, 70 eV)

170 (M^+ , 18), 110 (14), 97 (100), 84 (46), 71 (13)

Opt. Rot.: $[\alpha]_{\text{D}}^{24} +22.65$ ($c = 2.15$, EtOH)

TLC: R_f 0.30 (hexanes/EtOAc, 2/1) [UV(254)/PMA]

SFC: t_R (*R*)-**4i**, 4.02 (93.4%); t_R (*S*)-**4i**, 4.55 min (6.6%) (Chiralpak AS, 150 bar, 40 $^{\circ}\text{C}$, 7.5% CH_3OH in CO_2 , 2.5 mL/min, 220 nm)

Preparation of Methyl (*R*)-3-Hydroxy-3-cyclohexylpropanoate ((*R*)-4j)

A flame-dried, 20-mL, 2-neck flask containing a solution of 168 mg (0.2 mmol, 0.1 equiv) of bisphosphoramidate (*R,R*)-**3** in CH_2Cl_2 (10 mL) was cooled to -78°C under nitrogen. Into this reaction mixture was added 242 μL (2.0 mmol, 1.0 equiv) of cyclohexanecarboxaldehyde. To the resulting mixture 252 μL (2.2 mmol, 1.1 equiv) of SiCl_4 was added and the reaction mixture was allowed to stir at -78°C for 5 min. Then 523 μL (2.4 mmol, 1.2 equiv) of 1-(*tert*-butyldimethylsilyloxy)-1-methoxyethene (**1**) was added dropwise (over 5 min) the resulting mixture was allowed to stir at -78°C (bath temperature) for 6 h. The cold reaction mixture was then poured into a rapidly stirring 1/1 sat. aq. $\text{KF}/1.0\text{ M KH}_2\text{PO}_4$ solution (50 mL). This biphasic mixture was stirred vigorously for 2 h after which the aqueous layer was washed with CH_2Cl_2 (3 x 50 mL). The combined organic extracts were dried over Na_2SO_4 , filtered and the filtrate was concentrated *in vacuo*. The residue was purified by column chromatography (hexanes/EtOAc, 2/1). The product-containing fractions were combined and the solvent was removed *in vacuo* to yield 321 mg (86%) of (*R*)-**4j** as a colorless oil.⁶ Analysis of the enantiomeric composition was performed on the trifluoroacetate derivative.

Data for (*R*)-4j:

¹H NMR: (400 MHz, CDCl_3)

3.78 (m, 1 H, HC(3)), 3.71 (s, 3 H, HC(10)), 2.81 (d, $J = 4.1$, 1 H, HO), 2.52 (dd, $J = 16.1$, 2.7, 1 H, *HHC*(2)), 2.43 (dd, $J = 16.1$, 9.4, 1 H, *HHC*(2)), 1.86 (bd, 1 H, C(9)), 1.80-1.72 (m, 2 H, 2 x HC(8)), 1.66 (m, 2 H, 2 x HC(5)) 1.42-1.32 (m, 1 H, HC(4)), 1.30 - 0.95 (m, 5 H, 2 x HC(7), HC(9), 2 x HC(6))

¹³C NMR: (100 MHz, CDCl_3)

174.20 (C(1)), 72.35 (C(3)), 52.10 (C(10)), 43.23 (C(4)), 38.56 (C(2)), 28.98 (C(7)), 28.43 (C(5)), 26.60 (C(6)), 26.34 (C(8)), 26.23 (C(9))

IR: (neat)

3462 (s), 2926 (s), 2853 (s), 1737 (s), 1439 (s), 1407 (w), 1366 (w), 1311 (w),
1281 (w), 1192 (w), 1168 (m), 992 (m), 892 (m), 843 (w)

Opt. Rot.: $[\alpha]_D^{24} + 17.5$ (c = 2.84, EtOH)

GC: t_R (*S*)-**8**, 7.73 (5.8%); t_R (*R*)-**8**, 8.20 min (94.2%) (GTA, 16 psi, 100 °C isothermal)

Preparation of Methyl (*R*)-3-Hydroxy-5-phenylpentanoate ((*S*)-**4k**)

A flame-dried, 20-mL, 2-neck flask containing a solution of 168 mg (0.2 mmol, 0.1 equiv) of bisphosphoramidate (*R,R*)-**3** in CH₂Cl₂ (10 mL) was cooled to -78 °C under nitrogen. To this reaction mixture was added 263 μL (2.0 mmol, 1.0 equiv) of hydrocinnamaldehyde. To the resulting mixture was added 252 μL (2.2 mmol, 1.1 equiv) of SiCl₄ and the reaction mixture was allowed to stir at -78 °C for 5 min. Then 523 μL (2.4 mmol, 1.2 equiv) of 1-(*tert*-butyldimethylsilyloxy)-1-methoxyethene (**1**) was added dropwise (over 5 min) to the reaction mixture. The resulting mixture was allowed to stir at -78 °C (bath temperature) for 6 h. The cold reaction mixture was then poured into a rapidly stirring 1/1 sat. aq. KF/1.0 M KH₂PO₄ solution (50 mL). This biphasic mixture was stirred vigorously for 2 h after which the aqueous layer was washed with CH₂Cl₂ (3 x 50 mL). The combined organic extracts were dried over Na₂SO₄, filtered and the filtrate was concentrated *in vacuo*. The residue was purified by column chromatography (hexanes/EtOAc, 2/1). The product-containing fractions were combined and the solvent was removed *in vacuo* to yield 300 mg (72%) of (*S*)-**4k** as a colorless oil.⁷

Data for (S)-4k:¹H NMR: (400 MHz, CDCl₃)

7.28-7.18 (m, 5 H, HC(7,8,9)), 4.01 (m, 1 H, HC(3)), 3.70 (s, 3 H, H₃C(10)), 3.10 (d, *J* = 3.6, 1 H, OH), 2.82 (m, 1 H, HHC(5)), 2.69 (m, 1 H, HHC(5)), 2.50 (dd, *J* = 16.5, 3.4, 1 H, HHC(2)), 2.46 (dd, *J* = 16.5, 8.7, 1 H, HHC(2)), 1.84 (m, 1 H, HHC(4)), 1.74 (m, 1 H, HHC(4))

¹³C NMR: (100 MHz, CDCl₃)

173.31 (C(1)), 141.61 (C(6)), 128.38 (C(7)), 128.35 (C(8)), 125.83 (C(9)), 67.12 (C(3)), 51.72 (C(10)), 41.07 (C(5)), 38.05 (C(2)), 31.69 (C(4))

IR: (neat)

3450 (w), 2951 (s), 2929 (s), 2862 (w), 1737 (s), 1603 (w), 1496 (m), 1454 (s), 1439 (s), 1409 (m), 1359 (m), 1303 (s), 1254 (s), 1198 (s), 1177 (s), 1158 (s), 1082 (s), 1060 (s), 1045 (s), 1031 (m), 1002 (m)

Opt. Rot.: [α]_D²⁴ +17.5 (c = 2.84, EtOH)

SFC: *t_R* (S)-4k, 3.46 (90.7%); *t_R* (R)-4k, 4.13 min (9.3%) (Chiralpak OD, 150 bar, 40 °C, 5.0% CH₃OH in CO₂, 3.0 mL/min, 220 nm)

(E)-[(1-Methoxy)-propenyloxy]-*tert*-butyldimethylsilane ((E)-5a)

To a flame-dried, 100-mL, 3-neck round-bottom flask was added 1.54 mL of diisopropylamine (11 mmol, 1.1 equiv) and 14 mL of THF. The solution was cooled to 0 °C in a ice-water bath and then 9.2 mL of *n*-BuLi (1.2 M in hexane, 11 mmol, 1.1 equiv) was added slowly over five min. The resulting solution was stirred for 30 min at 0 °C prior to cooling to -78 °C in a dry ice/isopropanol bath. Then 0.96 mL of methyl propanoate (10 mmol, 1.0 equiv) was added slowly over five min. The resulting solution was stirred for an additional 30 min at

-78 °C. Then a solution of 1.65 g of TBSCl (11 mmol, 1.1 equiv) and 4 mL of HMPA (22 mmol, 2.2 equiv) in 4 mL of THF was added slowly via cannula. The dry ice/isopropanol bath was then removed and the solution allowed to stir for 1 h at room temperature. The yellow solution was diluted with cold pentane (50 mL) and was washed with cold water (3 x 75 mL). The organic layer was dried over Na₂SO₄ (10 g), and filtered through Celite and the filtrate was concentrated *in vacuo*. The residue was purified by Kugelrohr distillation to yield 0.852 g (42%, 82/18 *E/Z*) of **5a** as a colorless oil.⁸

Data for (*E*)-**5a**:

bp: 100 °C (1 mmHg, ABT)

¹H NMR: (500 MHz, CDCl₃)

3.65 (q, *J* = 6.59, 1 H, HC(2)), 3.54 (s, 3 H, H₃C(4)), 1.49 (d, *J* = 6.59, 3 H, H₃C(3)), 0.941 (s, 9 H, H₃C(7)), 0.175 (s, 6 H, H₃C(5))

¹³C NMR: (100 MHz, CDCl₃)

154.32 (C(1)), 78.83 (C(2)), 55.06 (C(4)), 25.86 (C(3)), 18.37 (C(7)), 9.67 (C(6)), -4.77 (C(5))

IR: (neat)

2597 (s), 2932 (s), 2860 (s), 1686 (s), 1472 (m), 1254 (s), 1221 (s), 1177 (m), 1110 (m)

MS: (EI, 70 eV)

203 (M⁺, 31), 189 (43), 163 (12), 147 (43), 131 (28), 115 (15), 89 (38), 73 (100)

(*E*)-[(1-Phenoxy)propenyloxy]-*tert*-butyldimethylsilane ((*E*)-5c**)**

To a flame-dried, 250-mL, 3-neck round-bottom flask was added 3.08 mL of diisopropylamine (22 mmol, 1.1 equiv) and 28 mL of THF. The solution was cooled to 0 °C under nitrogen in an ice-water bath and then 14 mL of *n*-BuLi (1.55 M in hexane, 22 mmol, 1.1

equiv) was added slowly over 5 min. The resulting solution was stirred for 30 min at 0 °C prior to cooling to -78 °C in a dry ice/isopropanol bath. Then 2.86 mL of propanoic acid phenyl ester (20 mmol, 1.0 equiv) was added slowly over 5 min. The resulting solution was stirred for an additional 30 min at -78 °C. Then a solution of 3.3 g of TBSCl (22 mmol, 1.1 equiv) and 8 mL of HMPA (44 mmol, 2.2 equiv) in 8 mL of THF was added slowly via cannula. The dry ice/isopropanol bath was then removed and the solution was allowed to stir for 1 h at room temperature. The yellow solution was diluted with cold pentane (100 mL) and washed with cold water (3 x 75 mL). The organic layer was dried over Na₂SO₄ (25 g), filtered through Celite and the filtrate was concentrated *in vacuo*. The residue was purified by Kugelrohr distillation to yield 2.64 g (50%, 94/6 *E/Z*) of **5c** as a colorless oil.

Data for (*E*)-**5c**:

bp: 125 °C (1 mmHg, ABT)

¹H NMR: (400 MHz, CDCl₃)

7.26 (m, 2 H, HC(5)), 7.0 (m, 3 H, HC(6,7)), 4.26 (q, *J* = 6.56, 1 H, HC(2)), 1.52 (d, *J* = 6.64, 3 H, H₃C(3)), 0.819 (s, 9 H, H₃C(10)), 0.09 (s, 6 H, H₃C(8))

¹³C NMR: (100 MHz, CDCl₃)

155.57 (C(4)), 150.18 (C(1)), 129.5 (C(6)), 122.03 (C(7)), 116.13 (C(5)), 86.57 (C(2)), 25.36 (C(3)), 17.91 (C(10)), 9.72 (C(9)), -5.04 (C(8))

IR: (neat)

2957 (s), 2931 (s), 2887 (m), 2860 (s), 1695 (s), 1596 (s), 1491 (s), 1472 (s), 1297 (m)

MS: (EI, 70 eV)

264 (M⁺, 17), 207 (24), 193 (28), 171 (29), 151 (26), 137 (18), 115 (21), 105 (10), 73 (100)

(E)-[(1-*tert*-Butoxy)propenyloxy]-*tert*-butyldimethylsilane ((E)-5d)

To a flame-dried, 250-mL, 3-neck round-bottom flask was added 6.2 mL of diisopropylamine (44 mmol, 1.1 equiv) and 56 mL of THF. The solution was cooled to 0 °C under nitrogen in an ice-water bath and then 28 mL of *n*-BuLi (1.58 M in hexane, 44 mmol, 1.1 equiv) was added slowly over 5 min. The resulting solution was stirred for 30 min at 0 °C prior to cooling to -78 °C in a dry ice/isopropanol bath. Then 6.0 mL of *tert*-butyl propanoate (40 mmol, 1.0 equiv) was added slowly over 5 min. The resulting solution was stirred for an additional 30 min at -78 °C. Then a solution of 6.6 g of TBSCl (44 mmol, 1.1 equiv) and 16 mL of HMPA (88 mmol, 2.2 equiv) in 8 mL of THF was added slowly via cannula. The dry ice/isopropanol bath was then removed and the solution allowed to stir for 1 h at room temperature. The yellow solution was diluted with cold pentane (100 mL) and washed with cold water (3 x 75 mL). The organic layer was dried over Na₂SO₄ (50 g), filtered through Celite and the filtrate was concentrated *in vacuo*. The residue was purified by short path distillation to yield 6.8 g (70%, 95/5 *E/Z*) of **5d** as a colorless oil.

Data for (E)-5d:

bp: 70°C (1 mmHg, ABT)

¹H NMR: (399 MHz, CDCl₃)

3.93 (q, *J* = 6.59, 1 H, HC(2)), 1.48 (d, *J* = 6.59, 3 H, H₃C(3)), 1.32 (s, 9 H, H₃C(5)), 0.92 (s, 9 H, H₃C(8)), 0.15 (s, 6 H, H₃C(6))

¹³C NMR: (100 MHz, CDCl₃)

152.21 (C(1)), 86.04 (C(2)), 78.32 (C(4)), 29.09 (C(3)), 25.74 (C(5)), 17.99 (C(8)), 10.89 (C(7)), -4.81 (C(6))

IR: (neat)

2997 (s), 2960 (s), 2932 (s), 2861 (s), 1678 (s), 1256 (s), 1207 (s), 1152 (s), 1110 (m), 861 (s), 839 (s), 781 (m)

MS: (EI, 70 eV)

245 (15), 244 (10), 190 (13), 189 (76), 188 (60), 187 (20), 173 (30), 132 (15), 131 (100), 130 (11), 115 (11), 75 (90), 73 (45), 57 (56)

Analysis: C₁₃H₂₇O₂Si (244.19)

Calcd: C, 63.87; H, 11.55%

Found: C, 63.91; H, 11.58%

(Z)-[(1-*tert*-Butoxy)-propenyloxy]-*tert*-butyldimethylsilane ((Z)-5d)

To a flame-dried, 250-mL, 3-neck round-bottom flask was added 2.46 mL of hexamethyldisilazane (11 mmol, 1.0 equiv) and 18 mL of THF. The solution was cooled to 0 °C under nitrogen in an ice-water bath and then 7.15 mL of *n*-BuLi (1.55 M in hexane, 11 mmol, 1.1 equiv) was added slowly over 5 min. The resulting solution was stirred for 30 min at 0 °C prior to cooling to -78 °C in a dry ice/isopropanol bath. To this solution was added 12 mL of HMPA (88 mmol, 2.2 equiv). Then 1.65 mL of *tert*-butyl propanoate (11 mmol, 1.0 equiv) was added slowly over 5 min. The resulting solution was stirred for an additional 1 h at -78 °C. Then a solution of 1.8 g of TBSCl (12 mmol, 1.1 equiv) in 8 mL of THF was added slowly via cannula. The dry ice/isopropanol bath was then removed and the solution allowed to stir for 1 h at room temperature. The yellow solution was diluted with cold pentane (100 mL) and washed with cold water (3 x 75 mL). The organic layer was dried over Na₂SO₄ (10 g), filtered through Celite and the filtrate was concentrated *in vacuo*. The residue was purified by short path distillation to yield 1.72 g (64%, 12/88 *E/Z*) of **5d** as a colorless oil.

Data for (Z)-**5d**:

bp: 70 °C (1 mmHg, ABT)

¹H NMR: (500 MHz, CDCl₃)

3.98 (q, $J = 6.0$, 1 H, HC(2)), 1.50 (d, $J = 6.64$, 3 H, HC(3)), 1.28 (s, 9 H, H₃C(5)), 0.948 (s, 9 H, H₃C(8)), 0.158 (s, 6 H, H₃C(6))

¹³C NMR: (125 MHz, CDCl₃)

151.63 (C(1)), 87.02 (C(2)), 78.22 (C(4)), 29.10 (C(3)), 28.48 (C(5)), 17.99 (C(8)), 10.70 (C(7)), -4.21 (C(6))

IR: (neat)

2978 (s), 2959 (s), 2931 (s), 2860 (s), 1680 (s), 1473 (m), 1389 (m), 1366 (m), 1306 (s), 1254 (s), 1209 (m), 1146 (s), 1104 (m), 1049 (s)

MS: (EI, 70 eV)

244 (1.00, M⁺), 188 (28), 173 (7), 157 (4), 147 (7), 131 (56), 115 (16), 75 (100), 57 (75)

General Procedure 2. Addition of Propionate-derived Silyl Ketene Acetals to Aromatic Aldehydes.

Preparation of *tert*-Butyl (2*S*,3*R*)-3-Hydroxy-2-Methyl-3-Phenylpropanate ((2*S*,3*R*)-6da)

A flame-dried, 10-mL, 2-neck flask containing a solution of 8.4 mg (0.01 mmol, 0.01 equiv) of bisphosphoramidate (*R,R*)-**3** in CH₂Cl₂ (5 mL) was cooled to -78 °C under nitrogen and then 102 μL (1.0 mmol, 1.0 equiv) of benzaldehyde was added. To the resulting solution was added 123 μL (1.1 mmol, 1.1 equiv) of SiCl₄ and the reaction mixture was allowed to stir at -78 °C for 5 min. Then 293 mg (1.2 mmol, 1.2 equiv) of (*E*)-1-[(*tert*-butoxy)propenyl]-*tert*-butyldimethylsilane ((*E*)-**5d**) was added dropwise (over 5 min) to the reaction mixture. The resulting mixture was allowed to stir at -78 °C (bath temperature) for 3 h whereupon the cold reaction mixture was poured into a rapidly stirring 1/1 sat. aq. KF/1.0 M KH₂PO₄ solution (20 mL). This biphasic mixture was stirred vigorously for 1 h before filtration through Celite. The aqueous layer was washed with CH₂Cl₂ (3 x 50 mL). The combined organic extracts were

washed with brine (50 mL), dried over Na₂SO₄ (2g), filtered and the filtrate was concentrated *in vacuo*. The residue was purified by Kugelrohr distillation to yield 217 mg (93%) of (2*S*,3*R*)-**6da** as a colorless oil.

Data for (2*S*,3*R*)-**6da**:

bp: 150 °C (0.01 mmHg, ABT)

¹H NMR: (499 MHz, CDCl₃)

7.40-7.20 (m, 5 H, HC(6,7,8)), 4.70 (dd, *J* = 7.9, 4.9, 1 H, HC(3)), 3.19 (d, *J* = 4.9, 1 H, OH), 2.70 (pent, *J* = 7.29, 1 H, HC(2)), 1.44 (s, 9 H, H₃C(10)), 1.01 (d, *J* = 7.29, 3 H, H₃C(4))

¹³C NMR: (125 MHz, CDCl₃)

175.3 (C(1)), 141.8 (C(5)), 128.3 (C(7)), 127.8 (C(8)), 126.3 (C(6)), 81.2 (C(9)), 76.3 (C(3)), 47.68 (C(2)), 27.9 (C(10)), 14.6 (C(4))

IR: (neat)

3455 (w), 2978 (s), 2936 (m), 1727 (s), 1456 (m), 1368 (s), 1253 (m), 1154 (s), 1021 (m), 701 (m)

MS: (FAB)

237 (M⁺, 6), 181 (11), 163 (25), 155 (43), 135 (50), 119 (100)

Opt. Rot.: [α]_D²⁴ +36.70 (c = 1.0, EtOH)

TLC: *R_f* 0.35 (hexanes/EtOAc, 8/2) [UV(254)/KMnO₄]

SFC: *t_R* (2*S*,3*R*)-**6da**, 2.32 (>99.9%); *t_R* (2*R*,3*S*)-**6da**, 2.81 min (<0.1%) (Chiralpak AS, 150 bar, 40 °C, 1.0% CH₃OH in CO₂, 3.5 mL/min, 220 nm)

Analysis: C₁₄H₂₀O₃ (230.26)

Calcd: C, 71.16; H, 8.53%

Found: C, 70.93; H, 8.46%

Preparation of *tert*-Butyl (2*S*,3*R*)-3-Hydroxy-2-methyl-3-(1-naphthalenyl)propanoate ((2*S*,3*R*)-6db)

Following General Procedure 2, 136 μL (1.0 mmol, 1.0 equiv.) of 1-naphthaldehyde was combined with 8.4 mg (0.01 mmol, 0.01 equiv) of bisphosphoramidate (*R,R*)-**3**, 123 μL (1.1 mmol, 1.1 equiv) of SiCl_4 , and 293 mg (1.2 mmol, 1.2 equiv) of (*E*)-1-[(*tert*-butoxy)-propenyl]-*tert*-butyldimethylsilane ((*E*)-**5d**) to yield, after Kugelrohr distillation, 280 mg (98%) of (2*S*,3*R*)-**6db** as a colorless wax.

Data for (2*S*,3*R*)-6db**:**

bp: 210°C (0.01 mmHg, ABT)

¹H NMR: (500 MHz, CDCl_3)

8.2 (d, $J = 8.1$, 1 H, HC(11)), 7.88 (d, $J = 7.9$, 1 H, HC(14)), 7.8 (d, $J = 8.35$, 1 H, HC(8)), 7.57 (d, $J = 7.5$, 1 H, HC(6)), 7.51-7.45 (m, 3 H, HC(7,12,13)), 5.48 (dd, $J = 7.5$, 5.14, 1 H, HC(3)), 3.52 (d, $J = 5.14$, 1 H, OH), 3.04 (pent, $J = 7.3$, 1 H, HC(2)), 1.44 (s, 9 H, $\text{H}_3\text{C}(16)$), 1.06 (s, 3 H, $\text{H}_3\text{C}(4)$)

¹³C NMR: (125 MHz, CDCl_3)

175.59 (C(1)), 137.44 (C(5)), 133.82 (C(9)), 130.91 (C(10)), 128.88 (C(14)), 128.39 (C(8)), 126.02 (C(12)), 125.49 (C(13)), 125.23 (C(7)), 124.51 (C(6)), 123.51 (C(11)), 81.29 (C(15)), 73.57 (C(3)), 47.05 (C(2)), 28 (C(16)), 15.29 (C(4))

IR: (CHCl_3)

3606 (w), 3474 (w), 2981 (m), 1712 (s), 1369 (s), 1154 (s), 780 (m)

MS: (EI, 70 eV)

286 (M^+ , 8), 230 (5), 213 (9), 151 (100), 129 (50), 73 (12)

Opt. Rot.: $[\alpha]_{\text{D}}^{24} +28.61$ (c = 1.0, EtOH)

TLC: R_f 0.5 (hexanes/EtOAc, 8/2) [UV(254)/KMnO₄]

SFC: t_R (2*R*,3*S*)-**6db**, 4.11 (2.8%); t_R (2*S*,3*R*)-**6db**, 4.52 min (97.2%) (Chiralpak AD, 150 bar, 40 °C, 5.0% CH₃OH in CO₂, 3.0 mL/min, 220 nm)

Analysis: C₁₈H₂₂O₃ (286.37)

Calcd: C, 75.50; H, 7.74%

Found: C, 75.57; H, 7.90%

Preparation of *tert*-Butyl (2*S*,3*R*)-3-Hydroxy-2-methyl-3-(2-naphthalenyl)propanoate ((2*S*,3*R*)-6dc**)**

Following General Procedure 2, 156 mg (1.0 mmol, 1.0 equiv.) of 2-naphthaldehyde was combined with 8.4 mg (0.01 mmol, 0.01 equiv) of bisphosphoramidate (*R,R*)-**3**, 123 μ L (1.1 mmol, 1.1 equiv) of SiCl₄, and 293 mg (1.2 mmol, 1.2 equiv) of (*E*)-1-[(*tert*-butoxy)-propenyl]-*tert*-butyldimethylsilane ((*E*)-**5d**) to yield, after Kugelrohr distillation, 271 mg (95%) of (2*S*,3*R*)-**6dc** as a colorless wax.

Data for (2*S*,3*R*)-**6dc**:

bp: 210°C (0.01 mmHg, ABT)

¹H NMR: (500 MHz, CDCl₃)

7.83 (m, 4 H, H(Ar)), 7.48 (m, 3 H, H(Ar)), 4.87 (d, J = 8.14, 1 H, HC(3)), 3.33 (br s, 1 H, OH), 2.82 (pent, J = 7.28, 1 H, HC(2)), 1.44 (s, 9 H, H₃C(16)), 1.04 (d, J = 7.28, 3 H, H₃C(4))

¹³C NMR: (125 MHz, CDCl₃)

175.3 (C(1)), 139.2 (C(5)), 133.13 (C(13)), 133.10 (C(8)), 128.2 (C(9)), 127.9 (C(12)), 127.6 (C(96)), 126.1 (C(7)), 125.9 (C(14)), 125.8 (C(11)), 124.3 (C(10)), 81.27 (C(15)), 76.5 (C(3)), 47.89 (C(2)), 27.98 (C(16)), 15.72 (C(4))

IR: (neat)

3343 (w), 2977 (s), 2935 (m), 1724 (s), 1711 (s), 1457 (s), 1368 (s), 1255 (s), 1155 (s), 1026 (s), 821 (m), 748 (m)

MS: (EI, 70 eV)

286 (M^+ , 8), 229 (10), 193 (10), 151 (100), 129 (51), 73 (12)

Opt. Rot.: $[\alpha]_D^{24} +21.37$ ($c = 1$, EtOH)

TLC: R_f 0.44 (hexanes/EtOAc, 8/2) [UV(254)/KMnO₄]

SFC: t_R (2*S*,3*R*)-**6dc**, 3.26 (99.6%); t_R (2*R*,3*S*)-**6dc**, 3.67 min (0.4%) (Chiralpak AS, 150 bar, 40 °C, 5.0% CH₃OH in CO₂, 2.5 mL/min, 220 nm)

Analysis: C₁₈H₂₂O₃ (286.37)

Calcd: C, 75.50; H, 7.74%

Found: C, 75.41; H, 7.78%

Preparation of *tert*-Butyl (2*S*,3*R*)-3-Hydroxy-3-(4-methoxyphenyl)-2-methylpropanoate ((2*S*,3*R*)-6de**)**

Following General Procedure 2, 122 μ L (1.0 mmol, 1.0 equiv) of *p*-anisaldehyde was combined with 8.4 mg (0.01 mmol, 0.01 equiv.) of bisphosphoramidate (*R,R*)-**3**, 123 μ L (1.1 mmol, 1.1 equiv) of SiCl₄, and 293 mg (1.2 mmol, 1.2 equiv) of (*E*)-1-[(*tert*-butoxy)-propenyl]-*tert*-butyldimethylsilane ((*E*)-**5d**) to yield, after Kugelrohr distillation, 233 mg (88%) of (2*S*,3*R*)-**6de** as a colorless oil.

Data for (2*S*,3*R*)-6de**:**

bp: 175°C (0.01 mmHg, ABT)

¹H NMR: (500 MHz, CDCl₃)

7.16 (m, 2 H, HC(6)), 6.77 (m, 2 H, HC(7)), 4.55 (d, $J = 8.36$, 1 H, HC(3)), 2.99 (s, 1 H, OH), 2.57 (pent, $J = 7.28$, 1 H, HC(2)), 1.35 (s, 9 H, H₃C(11)), 0.88 (d, $J = 7.28$, 3 H, H₃C(4))

¹³C NMR: (125 MHz, CDCl₃)

175.43 (C(1)), 159.2 (C(8)), 133.98 (C(5)), 127.84 (C(6)), 113.72 (C(7)), 81.08 (C(10)), 75.93 (C(3)), 55.23 (C(9)), 47.81 (C(2)), 27.99 (C(11)), 14.60 (C(4))

IR: (neat)

3459 (w), 2977 (m), 2936 (m), 1726 (s), 1612 (m), 1513 (s), 1460 (m), 1368 (s), 1251 (s), 1154 (s), 1035 (m), 833 (m)

MS.: (EI, 70 eV)

266 (M^+ , 8), 209 (3), 193 (10), 134 (100), 108 (9), 76 (7)

Opt. Rot.: $[\alpha]_D^{24} +24.59$ ($c = 1$, EtOH)

TLC: R_f 0.34 (hexanes/EtOAc, 8/2) [UV(254)/KMnO₄]

SFC: t_R (2*S*,3*R*)-**6df**, 2.46 (99.2%); t_R (2*R*,3*S*)-**6df**, 3.05 min (0.8%) (Chiralpak AS, 150 bar, 40 °C, 5.0% CH₃OH in CO₂, 2.5 mL/min, 220 nm)

Analysis: C₁₅H₂₂O₄ (266.33)

Calcd: C, 67.64; H, 8.33%

Found: C, 67.58; H, 8.44%

Preparation of *tert*-Butyl (2*S*,3*R*)-3-Hydroxy-2-methyl-3-(4-trifluoromethylphenyl)-propanoate ((2*S*,3*R*)-6df**)**

Following General Procedure 2, 136 μ L (1.0 mmol, 1.0 equiv) of 4-trifluoromethylbenzaldehyde was combined with 8.4 mg (0.01 mmol, 0.01 equiv) of bisphosphoramidate (*R,R*)-**3**, 123 μ L (1.1 mmol, 1.1 equiv) of SiCl₄, and 293 mg (1.2 mmol, 1.2 equiv) of (*E*)-1-[(*tert*-butoxy)-propenyl]-*tert*-butyldimethylsilane ((*E*)-**5d**) to yield, after Kugelrohr distillation, 284 mg (93%) of (2*S*,3*R*)-**6df** as a white crystalline solid.

Data for (2*S*,3*R*)-6df**:**

mp: 84-86 °C (hexane)

¹H NMR: (400 MHz, CDCl₃)

7.53 (m, 4 H, HC(6,7)), 4.57 (d, $J = 7.56$, 1 H, HC(3)), 3.48 (s, 1 H, OH), 2.69 (pent, $J = 7.32$, 1 H, HC(2)), 1.41 (s, 9 H, H₃C(11)), 1.06 (d, $J = 7.08$, 3 H, H₃C(4))

¹³C NMR: (100 MHz, CDCl₃)

175.24 (C(1)), 146.20 (C(5)), 130.30 (q, *J* = 32.04, C(8)), 127.17 (C(6)), 125.52 (C(7)), 14.34 (q, *J* = 271.6, C(9)), 81.63 (C(10)), 75.60 (C(3)), 47.38 (C(2)), 27.93 (C(11)), 14.63 (C(4))

¹⁹F NMR: (376 MHz, CDCl₃)

-62.89 (t, 3 F, F₃C(9))

IR: (CHCl₃)

3492 (w), 3009 (w), 2982 (9w), 2938 (w), 1707 (s), 1369 (m), 1166 (s), 1131 (s), 1068 (m), 844 (9m)

MS.: (EI, 70 eV)

305 (2), 248 (13), 229 (16), 175 (60), 130 (32), 73 (59)

Opt. Rot.: [α]_D²⁴ +39.50 (c = 1, EtOH)

TLC: *R_f* 0.48 (hexanes/EtOAc, 8/2) [UV(254)/KMnO₄]

SFC: *t_R* (2*S*,3*R*)-**6df**, 2.44 (96.0%); *t_R* (2*R*,3*S*)-**6df**, 3.08 min (4.0%) (Whelk-O1, 150 bar, 40 °C, 1.0% CH₃OH in CO₂, 3.5 mL/min, 220 nm)

Analysis: C₁₅H₁₉F₃O₃ (248.20)

Calcd: C, 59.20; H, 6.29; F, 18.73%

Found: C, 59.05; H, 6.21; F, 18.61%

Preparation of *tert*-Butyl (2*S*,3*S*)-3-Hydroxy-2-methyl-5-phenyl-4-pentenoate ((2*S*,3*S*)-**6dg**)

Following General Procedure 2, 141 μL (1.0 mmol, 1.0 equiv) of cinnamaldehyde was combined with 8.4 mg (0.01 mmol, 0.01 equiv) of bisphosphoramidate (*R,R*)-**3**, 123 μL (1.1 mmol, 1.1 equiv) of SiCl₄, and 293 mg (1.2 mmol, 1.2 equiv) of (*E*)-1-[(*tert*-butoxy)-propenyl]-*tert*-butyldimethylsilane (**5d**) to yield, after Kugelrohr distillation, 256 mg (98%) of (2*S*,3*S*)-**6dg** as a white crystalline solid.

Data for (2*S*,3*S*)-**6dg**:

mp: 80-82 °C (hexane)

¹H NMR: (400 MHz, CDCl₃)

7.15 (m, 5 H, HC(8,9,10)), 6.64 (d, $J = 15.87$, 1 H, HC(5)), 6.16 (dd, $J = 15.86$, 6.59, 1 H, HC(4)), 4.33 (t, $J = 6.59$, 1 H, HC(3)), 2.55 (pent, $J = 7.08$, 1 H, HC(2)), 1.46 (s, 9 H, H₃C(12)), 1.20 (d, $J = 7.32$, 3 H, H₃C(6))

¹³C NMR: (100 MHz, CDCl₃)

174.97 (C(1)), 136.50 (C(7)), 131.73 (C(5)), 129.53 (C(4)), 128.55 (C(8)), 127.73 (C(10)), 126.50 (C(9)), 81.24 (C(11)), 74.62 (C(3)), 46.19 (C(2)), 28.05 (C(12)), 14.25 (C(6))

IR: (neat)

3521 (w), 3011 (m), 2982 (m), 2937 (m), 1718 (s), 1457 (w), 1369 (m), 1154 (s), 968 (m)

MS.: (EI, 70 eV)

262 (3), 245 (20), 206 (37), 189 (99), 143 (25), 133 (9100), 105 (16), 57 (86)

Opt. Rot.: [α]_D²⁴ -17.48 (c = 1, EtOH)

TLC: R_f 0.36 (hexanes/EtOAc, 8/2) [UV(254)/KMnO₄]

SFC: t_R (2*S*,3*S*)-**6dg**, 3.31 (>99.0%); t_R (2*R*,3*R*)-**6dg**, 4.13 min (<1.0%) (Chiralpak AS, 150 bar, 40 °C, 1.0% CH₃OH in CO₂, 3.5 mL/min, 220 nm)

Analysis: C₁₆H₂₂O₃ (262.34)

Calcd: C, 73.25; H, 8.45%

Found: C, 73.18; H, 8.45%

Preparation of *tert*-Butyl (2*S*,3*R*)-3-Hydroxy-2,4-dimethyl-5-phenyl-4-pentenoate ((2*S*,3*R*)-6dh**)**

Following General Procedure 2, 140 μL (1.0 mmol, 1.0 equiv) of -methylcinnamaldehyde was combined with 8.4 mg (0.01 mmol, 0.01 equiv) of bisphosphoramidate (*R,R*)-**3**, 123 μL (1.1 mmol, 1.1 equiv) of SiCl_4 , and 293 mg (1.2 mmol, 1.2 equiv) of (*E*)-1-[(*tert*-butoxy)-propenyl]-*tert*-butyldimethylsilane ((*E*)-**5d**) to yield, after Kugelrohr distillation, 248 mg (90%) of (2*S*,3*R*)-**6dh** as a colorless wax.

Data for (2*S*,3*R*)-**6dh**:

bp: 225 $^{\circ}\text{C}$ (0.01 mmHg, ABT)

^1H NMR: (400 MHz, CDCl_3)

7.25 (m, 5 H, HC(9,10,11)), 6.53 (s, 1 H, HC(5)), 4.20 (d, $J = 7.81$, 1 H, HC(3)), 3.00 (s, 1 H, OH), 2.67 (pent, $J = 7.81$, 1 H, HC(2)), 1.87 (s, 3 H, $\text{H}_3\text{C}(7)$), 1.47 (s, 9 H, $\text{H}_3\text{C}(13)$), 1.13 (d, $J = 7.32$, 3 H, $\text{H}_3\text{C}(6)$)

^{13}C NMR: (100 MHz, CDCl_3)

175.28 (C(1)), 137.33 (C(4)), 137.24 (C(8)), 128.98 (C(10)), 128.07 (C(11)), 127.83 (C(9)), 126.54 (C(5)), 81.22 (C(12)), 79.88 (C(3)), 43.92 (C(2)), 28.04 (C(12)), 14.67 (C(7)), 13.10 (C(6))

IR: (CHCl_3)

3454 (w), 2977 (s), 2935 (m), 1726 (s), 1454 (m), 1368 (m), 1254 (m), 1154 (s), 1009 (m), 649 (m)

MS: (EI, 70 eV)

277 (M^+ , 2), 261 (2), 220 (19), 203 (43), 157 (43), 157 (24), 147 (100), 129 (27), 91 (18), 57 (38)

Opt. Rot.: $[\alpha]_{\text{D}}^{24} -66.28$ ($c = 1.0$, EtOH)

TLC: R_f 0.39 (hexanes/EtOAc, 8/2) [UV(254)/ KMnO_4]

SFC: t_R (2*S*,3*R*)-**6dh**, 3.63 (96.1%); t_R (2*R*,3*S*)-**6dh**, 4.13 min (3.9%) (Chiralpak AS, 150 bar, 40 °C, 1.0% CH₃OH in CO₂, 3.0 mL/min, 220 nm)

Analysis: C₁₇H₂₄O₃ (276.38)

Calcd: C, 73.88; H, 8.75%

Found: C, 73.59; H, 8.63%

Preparation of *tert*-Butyl (2*S*,3*R*)-3-Hydroxy-2-methyl-5-phenyl-4-pentynoate ((2*S*,3*R*)-6dl**)**

Following General Procedure 2, 122 μ L (1.0 mmol, 1.0 equiv) of 3-phenyl-2-propynal was combined with 8.4 mg (0.01 mmol, 0.01 equiv) of bisphosphoramidate (*R,R*)-**3**, 123 μ L (1.1 mmol, 1.1 equiv) of SiCl₄, and 293 mg (1.2 mmol, 1.2 equiv) of (*E*)-1-[(*tert*-butoxy)-propenyl]-*tert*-butyldimethylsilane ((*E*)-**5d**) to yield, after Kugelrohr distillation, 240 mg (92%) of (2*S*,3*R*)-**6dl** as a white crystalline solid.

Data for (2*S*,3*R*)-6dl**:**

bp: 210 °C (0.01 mmHg, ABT)

mp: 68-70 °C (hexane)

¹H NMR: (500 MHz, CDCl₃)

7.42 (m, 2 H, HC(8)), 7.30 (m, 3 H, HC(9,10)), 4.67 (t, $J = 7.07$, 1 H, HC(3)), 3.09 (d, $J = 7.07$, 1 H, OH), 2.73 (pent, $J = 7.07$, 1 H, HC(2)), 1.48 (s, 9 H, H₃C(12)), 1.32 (d, $J = 7.29$, 3 H, H₃C(6))

¹³C NMR: (125 MHz, CDCl₃)

174.10 (C(1)), 131.71 (C(4)), 128.48 (C(10)), 128.27 (C(8)), 122.45 (C(7)), 87.96 (C(6)), 85.54 (C(7)), 81.46 (C(9,11)), 64.85 (C(9,3)), 46.95 (C(2)), 28.02 (C(12)), 13.95 (C(6))

IR: (CHCl₃)

3485 (w), 3028 (w), 3010 (m), 2982 (m), 2938 (m), 1712 (s), 1600 (w), 1490 (w),
1458 (w), 1369 (m), 1253 (m), 1155 (s), 1028 (w)

MS: (EI, 70 eV)

261 (M⁺, 23), 243 (8), 205 (44), 187 (100), 131 (39)

Opt. Rot.: [α]_D²⁴ +6.87 (c = 1.0, EtOH)

TLC: R_f 0.41 (hexanes/EtOAc, 8/2) [UV(254)/KMnO₄]

SFC: t_R (2*S*,3*R*)-**6dl**, 4.78 (84.5%); t_R (2*R*,3*S*)-**6dl**, 5.71 min (15.5%) (Chiralpak AS,
150 bar, 40 °C, 1.5% CH₃OH in CO₂, 2.5 mL/min, 220 nm)

Analysis: C₁₆H₂₀O₃ (260.33)

Calcd: C, 73.82; H, 7.74%

Found: C, 73.92; H, 7.76%

Preparation of Ethyl (2*S*,3*S*)-3-Hydroxy-2-methyl-5-phenylpentanoate ((2*S*,3*S*)-**6bk**)

A flame-dried, 10-mL, 2-neck round-bottom flask containing a solution of 42.1 mg (0.05 mmol, 0.05 equiv) of bisphosphoramidate (*R,R*)-**3** and 37 mg (0.1 mmol, 0.1 equiv) of tetrabutylammonium iodide in CH₂Cl₂ (2.5 mL) was cooled to -78 °C under nitrogen. Into this mixture was added 123 μL (1.1 mmol, 1.1 equiv) of SiCl₄. To the resulting mixture was added 132 μL (1.0 mmol, 1.0 equiv) of hydrocinnamaldehyde and it was allowed to stir at -78 °C for 5 min. Then 260 mg (1.2 mmol, 1.2 equiv) of (*E*)-[(1-ethoxy)-propenyl]-*tert*-butyldimethylsilane ((*E*)-**5b**) was added dropwise (over 5 min) to the reaction mixture. The resulting mixture was allowed to stir at -78 °C (bath temperature) for 24 h whereupon the cold reaction mixture was poured into a rapidly stirring 1/1 sat. aq. KF/1.0 M KH₂PO₄ solution (20 mL). This biphasic mixture was stirred vigorously for 1 h before filtration through Celite. The aqueous layer was washed with CH₂Cl₂ (3 x 50 mL). The combined organic extracts were washed with brine (50 mL), dried over Na₂SO₄ (2 g), filtered and the filtrate was concentrated *in vacuo*. The residue

was purified by column chromatography (hexanes/EtOAc, 9/1), to yield 167 mg (71%) of (2*S*,3*S*)-**6bk** as a colorless oil.

Data for (2*S*,3*S*)-**6bk**:

¹H NMR: (400 MHz, CDCl₃)

7.20 (m, 5 H, HC(8,9,10)), 4.18 (q, *J* = 7.08, 2 H, HC(11)), 3.68 (m, 1 H, HC(3)), 2.89 (m, 1 H, HC(5)), 2.77 (d, *J* = 7.08, 1 H, OH), 2.67 (m, 1 H, HC(5)), 2.53 (pent, *J* = 6.34, 1 H, HC(2)), 1.80 (m, 2 H, HC(4)), 1.28 (t, *J* = 7.08, 3 H, H₃C(12)), 1.22 (d, *J* = 7.32, 3 H, H₃C(6))

¹³C NMR: (100 MHz, CDCl₃)

176.1 (C(1)), 141.94 (C(9)), 128.46 (C(10)), 128.39 (C(8)), 125.85 (C(7)), 72.63 (C(11)), 60.64 (C(3)), 45.15 (C(2)), 36.67 (C(5)), 31.91 (C(4)), 14.41 (C(12)), 14.17 (C(6))

IR: (neat)

3459 (m), 3026 (w), 2980 (s), 2940 (s), 1726 (s), 1495 (w), 1455 (s), 1376 (s), 1262 (s), 1187 (s), 1096 (s), 1043 (s)

MS: (EI, 70 eV)

237 (M⁺, 53), 219 (52), 173 (19), 144 (65), 117 (100), 91 (73)

Opt. Rot.: [α]_D²⁴ -14.87 (c = 1.0, EtOH)

TLC: *R_f* 0.1 (hexanes/EtOAc, 9/1) [UV(254)/KMnO₄]

SFC: *t_R* (2*S*,3*S*)-**6bk**, 4.34 (94.9%); *t_R* (2*R*,3*R*)-**6bk**, 5.04 min (5.2%) (Chiralpak OD, 150 bar, 40 °C, 2.0% CH₃OH in CO₂, 3.5 mL/min, 220 nm)

Analysis: C₁₄H₂₀O₃ (236.31)

Calcd: C, 71.16; H, 8.53%

Found: C, 70.95; H, 8.52%

Preparation of Ethyl (2*S*,3*S*)-3-Cyclohexyl-3-hydroxy-2-methylpropanoate ((2*S*,3*S*)-6bj**)**

A flame-dried, 10-mL, 2-neck, round-bottom flask containing a solution of 84.2 mg (0.1 mmol, 0.1 equiv) of bisphosphoramidate (*R,R*)-**3** and 37 mg (0.1 mmol, 0.1 equiv) of tetrabutylammonium iodide in CH_2Cl_2 (1.25 mL) was cooled to $-40\text{ }^\circ\text{C}$ under nitrogen. Into this mixture was added 123 μL (1.1 mmol, 1.1 equiv) of SiCl_4 . To the resulting mixture was added 121 μL (1.0 mmol, 1.0 equiv) of cyclohexane carboxaldehyde and it was allowed to stir at $-78\text{ }^\circ\text{C}$ for 5 min. Then 260 mg (1.2 mmol, 1.2 equiv) of (*E*)-[(1-ethoxy)-propenyl]-*tert*-butyldimethylsilane ((*E*)-**5b**) was added dropwise (over 5 min) to the reaction mixture. The resulting mixture was allowed to stir at $-40\text{ }^\circ\text{C}$ (bath temperature) for 24 h whereupon the cold reaction mixture was poured into a rapidly stirring 1/1 sat. aq. $\text{KF}/1.0\text{ M KH}_2\text{PO}_4$ solution (20 mL). This biphasic mixture was stirred vigorously for 1 h before filtration through Celite. The aqueous layer was washed with CH_2Cl_2 (3 x 50 mL). The combined organic extracts were washed with brine (50 mL), dried over Na_2SO_4 (2 g), filtered and the filtrate was concentrated *in vacuo*. The residue was purified by column chromatography (hexanes/EtOAc, 9/1), to yield 86 mg (40%) of (2*S*,3*S*)-**6bj** as a colorless oil.

Data for (2*S*,3*S*)-6bj**:**

¹H NMR: (400 MHz, CDCl_3)

4.17 (m, 2 H, HC(11)), 3.35 (q, $J = 6.59$, 1 H, HC(3)), 2.65 (pent, $J = 5.85$, 1 H, HC(2)), 2.57 (d, $J = 7.81$, 1 H, OH), 1.85-1.65 (m, 4 H, HC(6,8)), 1.6-1.5 (m, 4 H, HC(5,9)), 1.27 (t, $J = 7.08$, 3 H, $\text{H}_3\text{C}(12)$), 1.22 (d, $J = 7.08$, 3 H, $\text{H}_3\text{C}(10)$), 1.2-1.0 (m, 3 H, HC(4,7))

¹³C NMR: (100 MHz, CDCl_3)

176.57 (C(1)), 77.79 (C(9)), 60.52 (C(3)), 41.79 (C(2)), 41.19 (C(4)), 29.91 (C(7)), 27.13 (C(5,9)), 26.36 (C(6,8)), 26.32 (C(6,8)), 26.04 (C(5,9)), 14.91 (C(12)), 14.19 (C(10))

IR: (neat)
 3498 (w), 2979 (w), 2853 (s), 1721 (s), 1450 (m), 1376 (m), 1258 (m), 1179 (s),
 1102 (m), 1036 (m)

MS: (EI, 70 eV)
 215 (M^+ , 17), 197 (37), 169 (9), 151 (28), 131 (100), 123 (26), 102 (83), 85 (64),
 74 (51), 57 (34)

Opt. Rot.: $[\alpha]_D^{24} +5.26$ ($c = 1.0$, EtOH)

TLC: R_f 0.23 (hexanes/EtOAc, 9/1) [UV(254)/KMnO₄]

SFC: t_R (2*S*,3*S*)-**6bj**, 8.30 (67.8%); t_R (2*R*,3*R*)-**6bj**, 9.16 min (32.8%) (Chiralpak OD,
 150 bar, 40 °C, 3.0% CH₃OH in CO₂, 3.0 mL/min, 220 nm)

Analysis: C₁₂H₂₂O₃ (214.16)
 Calcd: C, 67.26; H, 10.35%
 Found: C, 67.03; H, 10.55%

Preparation of Methyl (*R*)-3-Trifluoromethylacetoxy-3-cyclohexylpropanoate ((*R*)-**8**)

To a stirred solution of 61 mg (1.1 mmol, 1.0 equiv) of (*R*)-**4j** in CH₂Cl₂ (1.0 mL) was added 0.25 mL (1.76 mmol, 1.6 equiv) of trifluoroacetic anhydride at room temperature under nitrogen. After the addition was completed, the mixture was stirred for 12 h. The reaction mixture was then concentrated *in vacuo*. Purification of the residue by silica gel chromatography (hexane/EtOAc, 10/1), afforded 88 mg (95%) of (*R*)-**8**.

Data for (*R*)-**8**:

¹H NMR: (400 MHz, CDCl₃)
 5.33 (dd, $J = 6.6, 6.1$, 1 H, HC(3)), 3.69 (s, 3 H, HC(12)), 2.69 (d, $J = 6.8$, 2 H, 2 x HC(2)), 1.81-1.64 (m, 6 H, H(Cy)), 1.28-1.00 (m, 5 H, H(Cy))

¹³C NMR: (100 MHz, CDCl₃)

170.56 (C(1)), 157.10 (q, $J = 41.9$, C(10)), 114.80 (q, $J = 286$, C(11)), 78.83 (C(3)), 52.23 (C(12)), 41.27 (C(2)), 36.18 (C(4)), 28.66 (C(7)), 27.87 (C(5)), 26.17 (C(9)), 25.93 (C(6)), 25.85 (C(8))

IR: (neat)

2934 (s), 2858 (s), 1787 (s), 1745 (s), 1451 (m), 1439 (m), 1383 (m), 1339 (m), 1285 (m), 1262 (s), 1220 (s), 992 (m), 892 (w), 837 (w), 771 (m), 732 (m)

GC: t_R (S)-**8**, 7.73 (5.8%); t_R (R)-**8**, 8.20 min (94.2%) (GTA, 16 psi, 100 °C isothermal)

Preparation of Ethyl (2*S*,3*S*)-3-Cyclohexyl-3-(3,5-dinitrobenzoyloxy)-2-methylpropanoate ((2*S*,3*S*)-9**)**

To a stirred solution of 134 mg (0.627 mmol, 1.0 equiv) of (2*S*,3*S*)-**6b**j in pyridine (1.0 mL) and 1 mL of THF was added 145 mg (0.627 mmol, 1.0 equiv) of 3,5 dinitrobenzoyl chloride at 0 °C under nitrogen. After the addition was completed, the mixture was stirred at room temperature for 5 h. The reaction mixture was then diluted with Et₂O (10 mL), washed with 0.1 M HCl (20 mL), sat. NaHCO₃ (20 mL) and brine (20 mL). The organic layer was dried over Na₂SO₄ (2 g) and filtered. The filtrate was concentrated *in vacuo*. Purification of the residue by silica gel chromatography (hexane/EtOAc, 9/1), afforded 220 mg (86%) of (2*S*,3*S*)-**9**.

Data for (2*S*,3*S*)-9:¹H NMR: (500 MHz, CDCl₃)

9.22 (s, 1 H, HC(14)), 9.14 (s, 2 H, HC(12)), 5.29 (t, $J = 6.10$, HC(3)), 4.12 (q, $J = 7.08$, 2 H, HC(16)), 3.01 (pent, $J = 6.38$, 1 H, HC(2)), 1.83-1.65 (m, 8 H, HC(5,6,8,9)), 1.27 (t, $J = 7.08$, 3 H, H₃C(17)), 1.22 (d, $J = 7.0$, 3 H, H₃C(15)), 1.2-0.9 (m, 3 H, HC(4,7))

¹³C NMR: (125 MHz, CDCl₃)

173.60 (C(1)), 162.32 (C(10)), 148.94 (C(13)), 134.21 (C(11)), 129.76 (C(12)), 122.64 (C(14)), 81.64 (C(16)), 61.11 (C(3)), 41.53 (C(2)), 39.39 (C(4)), 30.15 (C(7)), 27.44 (C(5,9)), 26.30 (C(6,8)), 26.22 (C(6,8)), 26.02 (C(5,9)), 14.43 (C(17)), 14.33 (C(15))

TLC: R_f 0.25 (hexanes/EtOAc, 9/1) [UV(254)]

SFC: t_R (2*S*,3*S*)-9, 8.30 (67.8%); t_R (2*R*,3*R*)-9, 9.16 min (32.8%) (Chiralpak OD, 150 bar, 40 °C, 3.0% CH₃OH in CO₂, 3.0 mL/min, 220 nm)

 α -Chloro(cyclohexylmethoxy)trichlorosilane (7)

Into a dry NMR tube was added 30 μ L (0.25 mmol, 1.0 equiv) of freshly distilled cyclohexanecarboxaldehyde and 1.0 mL of CDCl₃ at room temperature under nitrogen. To this solution was added 2.2 μ L of (0.0125 mmol, 0.05 equiv) of HMPA followed by 34 μ L (0.3 mmol, 1.2 equiv) of SiCl₄. The NMR tube was vortexed for 1 min to insure mixing. After 15 min the NMR tube was placed into the spectrometer at room temperature and a ¹H NMR spectrum was acquired. After 24 h at room temperature, a ¹³C NMR spectrum was acquired.

Data for 7:¹H NMR: (500 MHz, CDCl₃)

5.78 (d, $J = 4.88$, 1 H, HC(1)), 1.94-1.65 (m, 6 H, 6 x H(Cy)), 1.30-1.10 (m, 5 H, 5 x H(Cy))

¹³C NMR: (126 MHz, CDCl₃)

92.95 (C(1)), 47.05 (C(2)), 28.03 (C(3)), 27.56 (C(7)), 26.19 (C(6)), 25.73 (C(4)),
25.63 (C(5))

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