Lewis Base Activation of Lewis Acids: Catalytic, Enantioselective 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. All temperatures refer to bath temperatures unless otherwise noted. Reaction solvents including dichloromethane (Fisher, HPLC Grade), diethyl ether (Fisher, BHT stabilized HPLC Grade) and tetrahydrofuran (Fisher, HPLC Grade) were dried by percolation through two columns packed with neutral alumina under a positive pressure of argon. Reaction solvents including benzene (Fisher, thiophene free ACS Grade), hexane (Fisher, OPTIMA Grade) and toluene (Fisher, ACS Grade) were dried by percolation through a column packed with neutral alumina and a column packed with Q5 reactant, a supported copper catalyst for scavenging oxygen, under a positive pressure of argon. Solvents for chromatography and filtration were: hexane (Fisher, ACS Grade), ethyl acetate (technical grade, distilled from K₂CO₃), dichloromethane (technical grade, distilled from CaCl₂). Column chromatography was performed using EM Science 230-400-mesh silica gel. Benzaldehyde (**5a**), 1-naphthaldehyde (**5b**),¹ 4-tolualdehyde (**5d**), 4-anisaldehyde (**5e**), 4-trifluoromethylbenzaldehyde (**5f**), *trans*-cinnamaldehyde (**5g**), 2-methyl-*trans*-cinnamaldehyde (**5f**), crotonaldehyde (**5m**), 2-furfuraldehyde (**5i**), thiophene-2-carboxaldehyde (**5l**), cyclohexanecarboxaldehyde (**5j**), isovaleraldehyde (**5o**), hydrocinnamaldehyde (**5k**), chlorotrimethylsilane (Aldrich), 1-(*tert*-butyldimethylsilyloxy)-1-methoxyethene (Aldrich, **1a**), methyl trimethylsilyl dimethylketene acetal (Aldrich, **3**) and 2,2,6-trimethyl-1,3-dioxin-4-one (Lancaster) were freshly distilled before use. 2-Naphthaldehyde (**5c**) (Aldrich) was sublimed prior to use. Silicon tetrachloride (Aldrich) was heated at reflux for 24 h and then distilled prior to use. Hexamethylphosphoramide

(Aldrich, HMPA) was distilled and then stored over 3Å molecular sieves prior to use. Trifluoroacetic anhydride (Aldrich), *tert*-butyl dimethylsilyl chloride (TBSCl, Gelest), 3,5-dinitrobenzoyl chloride (Aldrich), benzoyl chloride (Aldrich), ethyl 3,3-dimethyl acrylate (Aldrich), methyl tiglate (Lancaster), ethyl crotonate (Aldrich) and (*E*)-2-pentenoic acid (Lancaster) were used without further purification. *tert*-Butyl acetate, methyl propanoate (Aldrich), ethyl propanoate, *tert*-butyl propanoate, ethyl butyrate (Aldrich), propionic acid phenyl ester (TCI America), ethyl isovalerate (Fluka), ethyl isocaproate (Fluka) and 1,3-dimethyl-3,4,5,6-tetrahydro-2(1H)-pyrimidinone (Aldrich, DMPU) were stored over 3Å molecular sieves. Diisopropylamine, diisopropylethylamine (DIPEA), triethylamine, pyridine and hexamethyldisilazane were freshly distilled from CaH₂ prior to use. Tetrabutylammonium iodide (Aldrich) was recrystallized from toluene and dried under vacuum prior to use.

¹H NMR, ¹³C NMR, ¹⁹F NMR, ³¹P NMR, ²⁹Si NMR and all low temperature spectra were recorded on a Varian Unity 400 (400 MHz, ¹H; 100 MHz, ¹³C, 376 MHz, ¹⁹F; 376.288 ³¹P), Unity 500 (500 MHz, ¹H; 126 MHz, ¹³C, 202 MHz) and Unity 600 (99.443 MHz, ²⁹Si) spectrometers. Spectra were referenced to residual chloroform (7.26 ppm, ¹H, 77.23 ppm, ¹³C) and ¹⁹F spectra were referenced externally to C₆F₆. 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 and CI 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 corrected. Kugelrohr distillations were performed on a Büchi GKR-50 Kugelrohr and temperatures reported are air bath temperatures (ABT). Analytical thin-layer chromatography was performed on Merck silica gel plates with QF-254 indicator. Visualization was accomplished with UV(254), potassium permanganate (KMnO₄), *p*-anialdehyde and phosphomolybdic acid (PMA) staining solutions.

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 (CSP-SFC) was performed on a Berger Instruments packed-column SFC with built-in photometric detector (220 nm) using Daicel Chiralpak OD, OJ, OB, AD and AS columns as well as 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) and equipped with an Astec (Chiraldex) GTA 30m x 0.25mm x 0.125 μm column. The injector temperature was 225 °C, the detector temperature was 300 °C Retention times (t_R) and peak ratios were determined with a Hewlett Packard 3396 Series II integrator. Ozonolyses were performed with a Welsbach Model T-816 Ozonator set at 55 W / 90 V with a 1 slpm flow rate.

Literature Preparations.

(*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*)-**6**),² 3-phenyl-2-propynal (**5n**),³ (*E*)-(1-ethoxy-propenyloxy)-*tert*-butyldimethylsilane (**2b**),⁴ 6-(*tert*-butyldimethylsiloxy)hexanal (**5p**),⁵ 6-(benzyloxy)hexanal (**5q**)⁶ and 6-(benzoyloxy)hexanal (**5r**)⁷ were prepared by literature methods.

Experimental Procedures.

General Procedure 1. Enolization of Alkanoates to form Silyl Ketene Acetals.

Preparation of (*E*)-[(1-Methoxy)propenyloxy]-*tert*-butyldimethylsilane (**2a**)

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) was added slowly over 5 min. The resulting solution was stirred for an additional 30 min at –78 °C in a dry ice/isopropanol bath. 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%, *E/Z* 82/18) of **2a** as a colorless oil. The NMR spectral data matched that previously reported in the literature.⁸

Data for (*E*)-**2a**:

bp: 100 °C (1 mmHg, ABT)

¹H NMR: (500 MHz, CDCl₃)

3.65 (q, *J* = 6.6, 1 H, HC(2)), 3.54 (s, 3 H, H₃C(4)), 1.49 (d, *J* = 6.6, 3 H, H₃C(3)), 0.94 (s, 9 H, H₃C(7)), 0.18 (s, 6 H, H₃C(5))

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

Preparation of (*E*)-[(1-Isopropoxy)propenyloxy]*tert*-butyldimethylsilane (2c**)**

Following General Procedure 1, 1.54 mL of diisopropylamine (11 mmol, 1.1 equiv) was combined with 6.70 mL of *n*-BuLi (1.64 M in hexane, 11 mmol, 1.1 equiv), 1.16 g of isopropyl propanoate (10 mmol, 1.0 equiv.), 1.65 g of TBSCl (11 mmol, 1.1 equiv) and 2.1 mL of HMPA (12 mmol, 1.2 equiv) to yield, after Kugelrohr distillation, 1.67 g (73 %, *E/Z* 71/29) of **2c** as a colorless oil. NMR spectral data matched that previously reported in the literature.⁹

Data for (*E*)-**2c**:

bp: 100 °C (0.5 mmHg, ABT)

^1H NMR: (500 MHz, CDCl_3)
 4.33 (septet, $J=6.6$, 1 H, HC(4)), 3.79 (q, $J=6.6$, 1 H, HC(2)), 1.45 (d, $J=6.6$,
 $\text{H}_3\text{C}(3)$), 1.18 (d, $J=6.3$, 6 H, $\text{H}_3\text{C}(5)$), 0.92 (s, 9 H, $\text{H}_3\text{C}(8)$), 0.0 (s, 6 H, $\text{H}_3\text{C}(6)$)

^{13}C NMR: (125 MHz, CDCl_3)
 152.18 (C(1)), 82.01 (C(2)), 68.83 (C(4)), 25.60 (C(3)), 21.96 (C(5)), 18.08
 (C(8)), 9.79 (C(7)), -5.04 (C(6))

IR: (neat)

2975 (s), 2959 (s), 2931 (s), 2841 (s), 1682 (s), 1464 (m), 1372 (m), 1362 (m),
1340 (m), 1304 (m), 1254 (s), 1208 (s), 1110 (s), 1041 (m)

MS: (EI, 70 ev)

230 (M^+ , 3), 187 (3), 173 (3), 131 (51), 117 (6), 75 (100)

Preparation of (*E*)-[(1-Phenoxy)propenyloxy]-*tert*-butyldimethylsilane (2d**)**

Following General Procedure 1, 3.08 mL of diisopropylamine (22 mmol, 1.1 equiv) was combined with 14.0 mL of *n*-BuLi (1.55 M in hexane, 22 mmol, 1.1 equiv), 2.86 mL of propanoic acid phenyl ester (20 mmol, 1.0 equiv), 3.3 g of TBSCl (22 mmol, 1.1 equiv) and 8 mL of HMPA (44 mmol, 2.2 equiv) to yield, after Kugelrohr distillation, 2.64 g (50%, *E/Z* 94/6) of **2d** as a colorless oil.

Data for (*E*)-2d:

bp: 125 °C (1 mmHg, ABT)

¹H NMR: (399 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)

HRMS: calcd for $C_{15}H_{24}O_2Si$: 264.154501, found: 264.154559

Preparation of (*E*)-[(1-*tert*-Butyloxy)propenyloxy]*tert*-butyldimethylsilane (2e**)**

Following General Procedure 1, 6.2 mL of diisopropylamine (44 mmol, 1.1 equiv) was combined with 28 mL of *n*-BuLi (1.58 M in hexane, 44 mmol, 1.1 equiv), 6.0 mL of *tert*-butyl propanoate (40 mmol, 1.0 equiv), 6.6 g of TBSCl (44 mmol, 1.1 equiv) and 16 mL of HMPA (88 mmol, 2.2 equiv) to yield, after short path distillation, 6.8 g (70%, *E/Z* 95/5) of **2e** as a colorless oil.

Data for (*E*)-2e**:**

bp: 70°C (1 mmHg, ABT)

¹H NMR: (399 MHz, CDCl₃)

3.93 (q, *J* = 6.6, 1 H, HC(2)), 1.48 (d, *J* = 6.6, 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 (M^{+1} , 15), 244 (10), 190 (13), 189 (76), 188 (60), 187 (20), 173 (30), 132

(14), 131 (100), 130 (11), 115 (11), 75 (90), 73 (45), 57 (55)

Anal: C₁₃H₂₈O₂Si (244.19)

Calcd: C, 63.87; H, 11.55%

Found: C, 63.91; H, 11.58%

Preparation of (Z)-[(1-*tert*-Butoxy)propenyloxy]-*tert*-butyldimethylsilane (2e)

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) was added slowly over 5 min. The resulting solution was stirred for an additional 1 h at –78 °C in a dry ice/isopropanol bath. 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%, *E/Z* 12/88) of **2e** as a colorless oil.

Data for (Z)-**2e**:bp: 70 °C (1 mmHg)¹H NMR: (499 MHz, CDCl₃)

3.98 (q, *J* = 6.0, 1 H, HC(2)), 1.50 (d, *J* = 6.6, 3 H, HC(3)), 1.28 (s, 9 H, H₃C(5)),
0.95 (s, 9 H, H₃C(8)), 0.16 (s, 6 H, H₃C(6))

^{13}C NMR: (125 MHz, CDCl_3)

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

Preparation of 1-[(*tert*-Butoxy)ethenyloxy]*tert*-butyldimethylsilane (**1b**)

Following General Procedure 1, 8.1 mL of diisopropylamine (58 mmol, 1.1 equiv) was combined with 36.1 mL of *n*-BuLi (1.6 M in hexanes, 58 mmol, 1.1 equiv), 7.1 mL of *tert*-butyl acetate (53 mmol), 8.72 g of TBSCl (58 mmol, 1.1 equiv) and 10.1 mL of HMPA (58 mmol, 1.1 equiv) to yield, after short path distillation, 9.11 g (75%) of **1b** as a colorless oil. The NMR spectral data matched that previously reported in the literature.⁹

Data for **1b**:

bp: 66 °C (5.0 mmHg, ABT)

^1H NMR: (500 MHz, CDCl_3)

3.49 (m, 1 H, HC(2)), 3.44 (m, 1 H, HC(2)), 1.38 (s, 9 H, HC(4)), 0.95 (s, 9 H, HC(7)), 0.20 (s, 6 H, HC(5))

Preparation of (*E*)-*tert*-Butyl(1-ethoxy-1-butenyloxy)dimethylsilane (10a**)**

Following General Procedure 1, 1.54 mL of diisopropylamine (11 mmol, 1.1 equiv) was combined with 7.15 mL of *n*-BuLi (1.55 M in hexane, 11 mmol, 1.1 equiv), 1.32 mL of ethyl butyrate (10 mmol), 1.65 g of TBSCl (11 mmol, 1.1 equiv) and 2.1 mL of HMPA (12 mmol, 1.2 equiv) to yield, after short path distillation, 1.46 g (64 %, *E/Z* 82/18) of **10a** as a colorless oil.

Data for (*E*)-**10a**:

bp: 62 °C (1 mmHg)

¹H NMR: (400 MHz, CDCl₃)

3.84 (q, *J* = 7.1, 2 H, H₂C(5)), 3.73 (t, *J* = 7.3, 1 H, HC(2)), 1.96 (pent, *J* = 7.6, 2 H, H₂C(3)), 1.22 (t, *J* = 7.1, 3 H, H₃C(6)), 0.93 (s, 9 H, H₃C(9)), 0.91 (t, *J* = 7.6, 3 H, H₃C(4)), 0.17 (s, 6 H, H₃C(7))

¹³C NMR: (100 MHz, CDCl₃)

152.40 (C(1)), 88.06 (C(2)), 78.32 (C(5)), 62.98 (C(3)), 25.62 (C(6)), 25.71 (C(9)), 18.05 (C(4)), 14.83 (C(8)), -5.04 (C(7))

IR: (neat)

3072 (w), 3050 (w), 2959 (m), 2932 (m), 2859 (m), 1681 (s), 1473 (w), 1428 (m), 1374 (m), 1299 (s), 1248 (s), 1115 (s), 1020 (w)

MS: (EI, 70 ev)

230 (M⁺, 9), 215 (8), 174 (13), 145 (76), 131 (6), 115 (8), 103 (44), 75 (100)

HRMS: calcd for C₁₂H₂₆O₂Si: 230.170764, found: 230.170209

Analysis: C₁₂H₂₆O₂Si (230.42)

Calcd: C, 62.55; H, 11.37%

Found: C, 62.37; H, 11.38%

Preparation of (*E*)-*tert*-Butyl(1-ethoxy-3-methyl-1-butenyloxy)dimethylsilane (10b**)**

Following General Procedure 1, 1.54 mL of diisopropylamine (11 mmol, 1.1 equiv) was combined with 7.15 mL of *n*-BuLi (1.55 M in hexane, 11 mmol, 1.1 equiv), 1.5 mL of ethyl isovalerate (10 mmol), 1.65 g of TBSCl (11 mmol, 1.1 equiv) and 2.1 mL of HMPA (12 mmol, 1.2 equiv) to yield, after short path distillation, 1.58 g (65 %, *E/Z* 78:22) of **10b** as a colorless oil.

Data for (*E*)-**10b**:

bp: 62 °C (0.5 mmHg)

¹H NMR: (400 MHz, CDCl₃)

3.84 (q, *J* = 7.1, 2 H, H₃C(5)), 3.61 (d, *J* = 9.0, 1 H, HC(2)), 2.53 (m, 1 H, HC(3)), 1.21 (t, *J* = 7.1, 3 H, H₃C(6)), 0.93 (s, 9 H, H₃C(9)), 0.90 (d, *J* = 6.5, 6 H, H₃C(4)), 0.17 (s, 6 H, H₃C(7))

¹³C NMR: (100 MHz, CDCl₃)

151.43 (C(1)), 95.15 (C(2)), 77.31 (C(5)), 62.98 (C(3)), 25.72 (C(6)), 25.63 (C(9)), 24.09 (C(4)), 14.83 (C(8)), -5.05 (C(7))

IR: (neat)

2957 (s), 2898 (m), 2862 (m), 1677 (s), 1472 (m), 1464 (m), 1390 (w), 1379 (w), 1367 (w), 1275 (m), 1254 (s), 1199 (s), 1128 (s), 1099 (m), 1063 (m)

MS: (EI, 70 ev)

244 (M⁺, 19), 229 (44), 188 (17), 143 (14), 159 (38), 103 (60), 69 (100)

HRMS: calcd for C₁₃H₂₈O₂Si: 244.186088, found: 244.185859

Preparation of (*E*)-*tert*-Butyl(1-ethoxy-4-methyl-1-penten-1-yl)dimethylsilane (10c**)**

Following General Procedure 1, 1.54 mL of diisopropylamine (11 mmol, 1.1 equiv) was combined with 7.15 mL of *n*-BuLi (1.55 M in hexane, 11 mmol, 1.1 equiv), 1.66 mL of ethyl isocaproate (10 mmol), 1.65 g of TBSCl (11 mmol, 1.1 equiv) and 2.1 mL of HMPA (12 mmol, 1.2 equiv) to yield, after short path distillation, 1.62 g (63 %, *E/Z* 84:16) of **10c** as a colorless oil.

Data for (*E*)-10c**:**

bp: 73 °C (1 mmHg)

¹H NMR: (400 MHz, CDCl₃)

3.83 (q, *J* = 7.1, 2 H, H₂C(6)), 3.71 (t, *J* = 7.3, 1 H, HC(2)), 1.86 (t, *J* = 7.1, 2 H, H₂C(3)), 1.51 (octet, *J* = 6.6, 1 H, HC(4)), 1.21 (t, *J* = 7.1, 3 H, H₃C(7)), 0.94 (s, 9 H, H₃C(10)), 0.87 (d, *J* = 6.6, 6 H, H₃C(5)), 0.18 (s, 6 H, H₃C(8))

¹³C NMR: (100 MHz, CDCl₃)

153.08 (C(1)), 85.12 (C(2)), 74.72 (C(6)), 62.87 (C(3)), 33.80 (C(4)), 29.22 (C(7)), 25.63 (C(10)), 22.28 (C(5)), 14.88 (C(9)), -4.98 (C(8))

IR: (neat)

2956 (s), 2932 (s), 2897 (m), 2862 (m), 1679 (s), 1471 (m), 1464 (m), 1367 (m), 1252 (s), 1198 (s), 1133 (m), 1096 (m)

MS: (EI, 70 ev)

258 (M⁺, 28), 215 (96), 173 (5), 129 (13), 115 (14), 103 (23), 73 (100)

HRMS: calcd for C₁₄H₃₀O₂Si: 258.201846, found: 258.201509

Analysis: C₁₄H₃₀O₂Si (258.47)

Calcd: C, 65.06; H, 11.70%

Found: C, 64.83; H, 11.82%

General Procedure 2. Enolization of Alkenoates to Silyl Dienol Ethers.**Preparation of (Z)-tert-Butyl(1-ethoxy-1,3-butadienyloxy)dimethylsilane (4a)**

To a flame-dried, 100 mL, 3-neck round-bottom flask was added 1.54 mL of diisopropylamine (11 mmol, 1.1 equiv) and 11 mL of THF. The solution was cooled to 0 °C in an ice-water bath and then 7.1 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 prior to cooling to -78 °C in a dry ice/isopropanol bath. To this solution was added 2.1 mL of HMPA (12 mmol, 1.2 equiv). The solution was stirred for 30 min at -78 °C in a dry ice/isopropanol bath and a white precipitate formed. Then, 1.24 mL of ethyl crotonate (10 mmol) was added slowly over 5 min. The resulting solution was stirred for 30 min at -78 °C prior to slow addition of 1.65 g of TBSCl (11.6 mmol, 1.2 equiv) in 6 mL of THF 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 (50 mL) and washed with cold H₂O (3 x 50 mL). The organic layer was dried over Na₂SO₄ (10 g), filtered through a pad of Celite and the filtrate was concentrated *in vacuo*. The residue was purified by short path distillation to yield 1.63 g (71 %, *Z/E* 86/14) of **4a** as a colorless oil.

Data for (Z)-4a:

bp: 70 °C (1 mmHg)

¹H NMR: (500 MHz, CDCl₃)

6.53 (dt, *J* = 17.1, 10.5, 1 H, HC(3)), 4.81 (dd, *J* = 17.5, 1.9, 1 H, HC(4)), 4.57 (dd, *J* = 10.7, 1.5, 1 H, HC(4)), 4.43 (d, *J* = 10.5, 1 H, HC(2)), 3.79 (q, *J* = 7.1, 2 H, HC(5)), 1.30 (t, *J* = 7.1, 3 H, H₃C(6)), 0.95 (s, 9 H, H₃C(9)), 0.19 (s, 6 H, H₃C(7))

NOE ^1H NMR: (500 MHz, CDCl_3)

Irradiation at 3.79 ppm (HC(5)) enhanced signal at 4.43 ppm (HC(2)) in major isomer

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

157.73 (C(1)), 132.58 (C(3)), 106.26 (C(4)), 80.52 (C(5)), 63.26 (C(2)), 25.69 (C(9)), 25.52 (C(6)), 14.35 (C(8)), -4.15 (C(7))

IR: (neat)

3085 (w), 2958 (m), 2933 (m), 2888 (m), 2859 (m), 1648 (s), 1602 (w), 1473 (w), 1425 (m), 1369 (m), 1334 (m), 1255 (m), 1214 (s), 1176 (m), 1079 (m), 1025 (m)

MS: (CI, 70 eV)

229 (M^+ , 27), 205 (26), 187 (36), 171 (36), 147 (30), 115 (52), 75 (100)

HRMS: calcd for $\text{C}_{12}\text{H}_{24}\text{O}_2\text{Si}$: 229.126413, found: 229.1249

Preparation of (Z)-tert-Butyl(1-methoxy-2-methyl-1,3-butadienyloxy)dimethylsilane (**4b**)

Following General Procedure 2, 1.54 mL of diisopropylamine (11 mmol, 1.1 equiv) was combined with 7.1 mL of *n*-BuLi (1.55 M in hexane, 11 mmol, 1.1 equiv), 2.1 mL of HMPA (12 mmol, 1.2 equiv), 1.2 mL of methyl tiglate (10 mmol) and 1.65 g of TBSCl (11.6 mmol, 1.2 equiv) to yield, after short path distillation, 1.48 g (65 %, *Z/E* 58:42) of **4b** as a colorless oil. NMR spectral data matched that previously reported in the literature.¹⁰

Data for (Z)-**4b**:

bp: 66 °C (1 mmHg)

^1H NMR: (500 MHz, CDCl_3)

6.76 (dd, $J = 17.6, 11.0$, 1 H, HC(3)), 4.85 (dd, $J = 17.6, 1.5$, 1 H, HC(4)), 4.78 (dd, $J = 10.5, 1.5$, 1 H, HC(4)), 3.58 (s, 3 H $\text{H}_3\text{C}(5)$), 1.63 (s, 3 H, $\text{H}_3\text{C}(6)$), 0.97 (s, 9 H, $\text{H}_3\text{C}(9)$), 0.18 (s, 6 H, $\text{H}_3\text{C}(7)$)

¹³C NMR: (100 MHz, CDCl₃)
 153.20 (C(1)), 134.54 (C(3)), 107.55 (C(4)), 97.43 (C(2)), 57.83 (C(5)), 25.62 (C(9)), 18.15 (C(6)), 10.65 (C(8)), -4.49 (C(7))

IR: (neat)
 3089 (w), 2958 (s), 2935 (s), 2896 (m), 2859 (s), 1658 (s), 1463 (m), 1440 (m), 1290 (s), 1255 (s), 1209 (s), 1170 (s), 1124 (s), 1043 (m)

MS: (CI, 70 eV)
 229 (M⁺, 6), 213 (4), 187 (100), 173 (12)

HRMS: calcd for C₁₂H₂₄O₂Si: 229.126413, found: 229.1264

Preparation of (Z)-tert-Butyl(1-ethoxy-3-methyl-1,3-butadienyloxy)dimethylsilane (4c)

Following General Procedure 2, 1.54 mL of diisopropylamine (11 mmol, 1.1 equiv) was combined with 7.1 mL of *n*-BuLi (1.55 M in hexane, 11 mmol, 1.1 equiv), 2.1 mL of HMPA (12 mmol, 1.2 equiv), 1.39 mL of ethyl senecioate (10 mmol) and 1.65 g of TBSCl (11.6 mmol, 1.2 equiv) to yield, after short path distillation, 1.65 g (68 %, *Z/E* >99/1) of **4c** as a colorless oil.

Data for (Z)-4c:

bp: 68 °C (1 mmHg)

¹H NMR: (400 MHz, CDCl₃)
 4.77 (d, *J* = 2.4, 1 H, HC(4)), 4.51 (d, *J* = 2.4, 1 H, HC(4)), 4.2 (s, 1 H, HC(2)), 3.78 (q, *J* = 6.8, 2 H, H₂C(5)), 1.95 (s, 3 H, H₃C(7)), 1.29 (t, *J* = 7.1, 3 H, H₃C(6)), 0.94 (s, 9 H, H₃C(10)), 0.20 (s, 6 H, H₃C(8))

¹³C NMR: (100 MHz, CDCl₃)
 156.62 (C(1)), 140.50 (C(3)), 107.02 (C(4)), 80.39 (C(4)), 63.42 (C(2)), 25.85 (C(10)), 23.96 (C(6)), 18.14 (C(7)), 14.37 (C(9)), -3.70 (C(8))

IR: (neat)

3079 (w), 2960 (m), 2931 (s), 2859 (m), 1650 (s), 1606 (w), 1473 (m), 1452 (m), 1349(m), 1375 (m), 1275 (m), 1195 (s), 1087 (s), 1031 (m)

MS: (CI, 70 eV)

243 (M^+ , 41), 201 (73), 185 (46), 147 (38), 127 (29), 103 (70), 75 (100)

HRMS: calcd for $C_{13}H_{26}O_2Si$: 243.140368, found: 243.14034

Preparation of (2E)-2-Pentenoic Acid *tert*-Butyl Ester (**30**)

A 250 mL Parr flask containing a solution of 22.7 mL of *trans*-2-pentenoic acid (0.225 mol) and 2.25 mL of conc. sulfuric acid (0.04 mol, 0.17 equiv) in 10 mL of Et₂O was cooled to –78 °C in a dry ice/isopropanol bath before condensation of ~30 mL of isobutylene (0.34 mmol, 1.5 equiv) into the solution. The flask was then placed in a sealed Parr shaker and it was shaken for 24 h. The flask was vented and the excess isobutylene was removed by sparging the solution with an N₂ stream. The solution was diluted with 50 mL of Et₂O, washed with sat. aq. NaHCO₃ solution (50 mL), brine (50 mL), dried over K₂CO₃ (10 g), filtered and the filtrate was concentrated by distillation of the remaining Et₂O at atmospheric pressure. The residue was then purified by short path distillation to yield 8.94 g (25%) of (2E)-**30** as a colorless oil. NMR spectral data matched that reported in the literature.¹¹

Data for (2E)-**30**:

bp: 72 °C (32 mmHg)

¹H NMR: (400 MHz, CDCl₃)

6.90 (dt, $J = 15.1, 6.3$, 1 H, HC(3)), 5.74 (dt, $J = 15.1, 1.7$, 1 H, HC(2)), 2.18 (dpent, $J = 1.4, 7.6$, 2 H, H₂C(4)), 1.47 (s, 9 H, H₃C(7)), 1.04 (t, $J = 7.6$, 3 H, H₃C(5))

¹³C NMR: (100 MHz, CDCl₃)

166.26 (C(1)), 149.38 (C(3)), 122.03 (C(2)), 79.95 (C(6)), 28.12 (C(4)), 25.10 (C(7)), 12.19 (C(5))

Preparation of (1Z,3Z)-[1-(*tert*-Butyloxy)-1,3-pentadienyloxy]*tert*-butyldimethylsilane (4d**)**

Following General Procedure 2, 1.54 mL of diisopropylamine (11 mmol, 1.1 equiv) was combined with 7.1 mL of *n*-BuLi (1.55 M in hexane, 11 mmol, 1.1 equiv), 2.1 mL of HMPA (12 mmol, 1.2 equiv), 1.55 g of *tert*-butyl 2-pentenoate (10 mmol) and 1.65 g of TBSCl (11.6 mmol, 1.2 equiv) to yield, after short path distillation, 1.41 g (52 %, 1Z,3Z/others isomers 89/11) of **4d** as a colorless oil.

Data for (1Z,3Z)-**4d**:

bp: 68 °C (1 mmHg)

¹H NMR: (500 MHz, CDCl₃)

6.12 (dt, *J* = 1.7, 10.7, 1 H, HC(3)), 5.14 (dq, *J* = 10.2, 6.3, 1 H, HC(4)), 4.87 (d, *J* = 10.8, 1 H, HC(2)), 1.65 (dd, *J* = 6.8, 1.5, 3 H, H₃C(5)), 1.37 (s, 9 H, H₃C(7)), 0.95 (s, 9 H, H₃C(10)), 0.17 (s, 6 H, H₃C(8))

NOE ¹H NMR: (500 MHz, CDCl₃)

Irradiation at 4.87 ppm (HC(2)) enhanced signal at 1.65 ppm (HC(5)) in major isomer

¹³C NMR: (100 MHz, CDCl₃)

153.22 (C(1)), 124.73 (C(3)), 118.08 (C(4)), 88.38 (C(6)), 79.39 (C(2)), 29.09 (C(5)), 28.50 (C(7)), 18.06 (C(10)), 13.25 (C(9)), -4.13 (C(8))

IR: (neat)

2977 (s), 2958 (s), 2931 (s), 2859 (s), 1648 (s), 1610 (s), 1473 (m), 1367 (m), 1319 (m), 1299 (m), 1253 (s), 1201 (m), 1132 (s), 1062 (m)

MS: (EI, 70 eV)

270 (M⁺, 6), 231 (5), 214 (100), 198 (42), 156 (38), 82 (98)

HRMS: calcd for C₁₅H₃₀O₂Si: 270.202029, found: 270.201509

Preparation of *tert*-Butyl-(2,2-dimethyl-6-methylene-6*H*-[1,3]dioxin-4-yloxy)dimethylsilane (13)

Following General Procedure 2, 1.54 mL of diisopropylamine (11 mmol, 1.1 equiv) was combined with 7.1 mL of *n*-BuLi (1.55 M in hexane, 11 mmol, 1.1 equiv), 2.1 mL of HMPA (12 mmol, 1.2 equiv), 1.3 mL of 2,2,6-Trimethyl-1,3-dioxin-4-one (10 mmol) and 1.65 g of TBSCl (11.6 mmol, 1.2 equiv) to yield, after short path distillation, 1.52 g (59 %) of **13** as a colorless oil.

Data for **13**:

bp: 78 °C (1 mmHg)

¹H NMR: (400 MHz, CDCl₃)

4.65 (s, 1 H, HC(2)), 4.05 (s, 1 H, HC(4)), 3.86 (s, 1 H, HC(4)), 1.54 (s, 6 H, HC(6)), 0.93 (s, 9 H, H₃C(9)), 0.20 (s, 6 H, H₃C(7))

¹³C NMR: (100 MHz, CDCl₃)

153.54 (C(1)), 151.94 (C(3)), 102.45 (C(5)), 84.67 (C(4)), 76.64 (C(2)), 25.49 (C(9)), 24.50 (C(6)), 18.01 (C(8)), -4.28 (C(7))

IR: (neat)

2996 (m), 2958 (m), 2933 (m), 2888 (w), 2861 (m), 1668 (s), 1633 (m), 1473 (w), 1386 (m), 1375 (m), 1344 (s), 1294 (m), 1261 (s), 1224 (s), 1205 (s), 1126 (m), 1031 (m)

MS: (CI, 70 eV)

257 (M⁺, 100), 215 (21), 173 (22), 143 (24), 85 (29)

HRMS: calcd for C₁₃H₂₄O₃Si: 257.157488, found: 257.157298

General Procedure 3. Addition of Acetate-derived Silyl Ketene Acetals to Aromatic Aldehydes. Preparation of (3*R*)-Methyl 3-Hydroxy-3-phenylpropanoate (7aa)

A flame-dried, 20-mL, 2-neck flask containing a solution of 84 mg (0.1 mmol, 0.05 equiv) of bis-phosphoramidate ((*R,R*)-**6**) in CH₂Cl₂ (10 mL) was cooled to -78 °C under nitrogen in a dry ice/isopropanol bath and then 200 µL (2.0 mmol) of benzaldehyde was added in one portion. To the resulting solution 252 µL (2.2 mmol, 1.1 equiv) of SiCl₄ was added and the reaction mixture was allowed to stir at -78 °C for 5 min in a dry ice/isopropanol bath. Then 523 µL (2.4 mmol, 1.2 equiv) of 1-(*tert*-butyldimethylsilyloxy)-1-methoxyethene (**1a**) was added dropwise (over 5 min) to the reaction mixture. The resulting mixture was allowed to stir at -78 °C for 15 min in a dry ice/isopropanol bath 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 silica gel 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 (3*R*)-methyl 3-hydroxy-3-phenylpropanoate (**7aa**) as a colorless oil. NMR spectral data matched that previously reported in the literature.¹²

Data for (3*R*)-7aa**:**

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)

SFC: t_R (*R*)-**7aa**, 3.81 (96.3%); t_R (*S*)-**7aa**, 4.23 min (3.7%) (Chiralpak AD, 200 psi, 40 °C, 3.5% CH₃OH in CO₂, 2.7 mL/min, 220 nm)

Opt. Rot.: $[\alpha]_D^{24} +17.7$ (c = 2.05, EtOH) [Lit¹²: $[\alpha]_D^{24}$ (*R*) +12.4 (c = 2.66, EtOH)]

Preparation of Methyl 3-Hydroxy-3-(1-naphthyl)propanoate (**7ab**)

Following General Procedure 3, 271 μ L (2.0 mmol) of 1-naphthaldehyde was combined with 84 mg (0.1 mmol, 0.05 equiv) of bis-phosphoramidate ((*R,R*)-**6**), 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 (**1a**) to yield, after purification by silica gel column chromatography (hexanes/EtOAc, 2/1), 457 mg (98%) of methyl 3-hydroxy-3-(2-naphthyl) propanoate (**7ab**) as a colorless solid. An analytical sample was obtained by recrystallization from Et₂O to afford colorless crystals.

Data for **7ab**:

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))

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

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)

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

Opt. Rot.: $[\alpha]_{\text{D}}^{24} +21.00$ (c = 2.12, EtOH)

SFC: t_R (S)-**7ab**, 5.17 (9.8%); t_R (R)-**7ab**, 5.91 min (90.2%) (Chiralpak OD, 200 psi, 40 °C, 9.0% CH_3OH in CO_2 , 3.0 mL/min, 220 nm)

Analysis: $\text{C}_{14}\text{H}_{14}\text{O}_3$ (230.26)

Calcd: C, 73.03; H, 6.13%

Found: C, 72.93; H, 6.16%

Preparation of Methyl 3-Hydroxy-3-(2-naphthyl)propanoate (**7ac**)

Following General Procedure 3, 312.3 mg (2.0 mmol) of 2-naphthaldehyde was combined with 84 mg (0.1 mmol, 0.05 equiv) of bis-phosphoramidate $((R,R)$ -**6**), 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 (**1a**) to yield, after purification by silica gel column chromatography (hexanes/EtOAc, 2/1), 455 mg (98%) of methyl 3-hydroxy-3-(2-naphthyl) propanoate (**7ac**) as a wax-like, white solid. After Kugelrohr distillation an analytically pure, colorless oil was isolated which solidified upon standing.

Data for 7ac:

bp: 145°C (1.8 x 10⁻⁴ mmHg, ABT)

¹H NMR: (400 MHz, CDCl₃)
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, HHC(2)), 2.83(dd, *J* = 16.4, 2.0, 1 H, HHC(2))

¹³C NMR: (100 MHz, CDCl₃)
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)

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

Opt. Rot.: [α]_D²⁴ +15.66 (c = 2.11, EtOH)

SFC: *t_R* (*R*)-**7ac**, 4.72 (96.8%); *t_R* (*S*)-**7ac**, 5.26 min (3.2%) (Chiralpak AD, 150 psi, 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 3-Hydroxy-3-(4-methylphenyl)propanoate (7ad)

Following General Procedure 3, 236 μL (2.0 mmol) of anisaldehyde was combined with 84 mg (0.1 mmol, 0.05 equiv) of bis-phosphoramidate ((*R,R*)-**6**), 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 (**1a**) to yield, after purification by silica gel column chromatography (hexanes/EtOAc, 2/1), 378 mg (97%) of methyl 3-hydroxy-3-(4-methylphenyl) propanoate (**7ad**) as a clear oil. After Kugelrohr distillation an analytically pure, colorless oil was collected.

Data for **7ad**:

bp: 105 $^{\circ}\text{C}$ (1.4×10^{-4} mmHg, ABT)

^1H NMR: (400 MHz, CDCl_3)

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))

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

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)

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

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

SFC: t_R (*R*)-**7ad**, 3.97 (97.2%); t_R (*S*)-**7ad**, 4.37 min (2.8%) (Chiralpak AD, 150 psi, 40 $^{\circ}\text{C}$, 4.0% CH_3OH in CO_2 , 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 3-Hydroxy-3-(4-methoxyphenyl)propanoate (**7ae**)

Following General Procedure 3, 243 μ L (2.0 mmol) of anisaldehyde was combined with 84 mg (0.1 mmol, 0.05 equiv) of bis-phosphoramidate ((*R,R*)-**6**), 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 (**1a**) to yield, after purification by silica gel column chromatography (hexanes/EtOAc, 2/1), 410 mg (97%) of methyl 3-hydroxy-3-(4-methoxyphenyl) propanoate (**7ae**) as a white solid. After recrystallization from benzene/hexanes, analytically pure, colorless needles were isolated.

Data for **7ae**:

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)

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

Opt. Rot.: $[\alpha]_D^{24} +14.4$ ($c = 2.05$, EtOH)

SFC: t_R (*R*)-**7ae**, 3.95 (98.7%); t_R (*S*)-**7ae**, 4.45 min (1.3%) (Chiralpak AD, 150 psi, 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 3-Hydroxy-3-(4-trifluoromethylphenyl)propanoate (**7af**)

Following General Procedure 3, 273 μ L (2.0 mmol) of 4-trifluoromethylbenzaldehyde was combined with 84 mg (0.1 mmol, 0.05 equiv) of bis-phosphoramidate ((*R,R*)-**6**), 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 (**1a**) to yield, after purification by silica gel column chromatography (hexanes/EtOAc, 2/1), 484 mg (97%) of methyl-3-hydroxy-3-(4-trifluoromethylphenyl)propanoate (**7af**) as a white solid. Recrystallization from hexane afforded analytically pure, colorless needles.

Data for **7af**:

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)

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

Opt. Rot.: $[\alpha]_D^{24} +13.60$ ($c = 2.27$, EtOH)

SFC: t_R (*R*)-**7af**, 3.75 (95.7%); t_R (*S*)-**7af**, 4.14 min (4.3%) (Chiralpak AS, 150 psi, 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 3-Hydroxy-5-phenyl-4-pentenoate (**7ag**)

Following General Procedure 3, 252 μ L (2.0 mmol) of cinnamaldehyde was combined with 84 mg (0.1 mmol, 0.05 equiv) of bis-phosphoramidate ((*R,R*)-**6**), 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 (**1a**) to yield, after purification by silica gel column chromatography (hexanes/EtOAc, 2/1), 393 mg (95%) of 3-hydroxy-5-phenyl-4-pentenoate (**7ag**) as a colorless oil. NMR spectral data matched that previously reported in the literature.¹³

Data for **7ag**:

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, H(C(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))

^{13}C NMR: (100 MHz, CDCl_3)
 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.: $[\alpha]_{\text{D}}^{24}$ -17.0 ($c = 2.07$, EtOH)

SFC: t_R (*R*)-**7ag**, 3.61 (96.9%); t_R (*S*)-**7ag**, 4.24 min (3.1%) (Chiralpak OD, 150 psi, 40 °C, 7.5% CH_3OH in CO_2 , 3.0 mL/min, 220 nm)

Preparation of Methyl 3-Hydroxy-4-methyl-5-phenyl-4-pentenoate (**7ah**)

Following General Procedure 3, 279 μL (2.0 mmol) of α -methylcinnamaldehyde was combined with 84 mg (0.1 mmol, 0.05 equiv) of bis-phosphoramidate ((*R,R*)-**6**), 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 (**1a**) to yield, after purification by silica gel column chromatography (hexanes/EtOAc, 2/1), 432 mg (98%) of methyl 3-hydroxy-4-methyl-5-phenyl-4-pentenoate (**7ah**) as a colorless oil. Kugelrohr distillation afforded an analytically pure, colorless oil. NMR spectral data matched that previously reported in the literature.¹⁴

Data for **7ah**:

mp: 115 °C (1.3×10^{-4} mmHg, ABT)

^1H NMR: (400 MHz, CDCl_3)
 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, $\text{H}_3\text{C}(11)$), 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, $\text{H}_3\text{C}(10)$)

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

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(6)), 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)

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

Opt. Rot.: $[\alpha]_D^{24}$ -13.70 (c = 2.23, EtOH)

SFC: t_R (*R*)-**7ah**, 4.34 (72.7%); t_R (*S*)-**7ah**, 4.45 min (27.3%) (Chiralpak AD, 150 psi, 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 3-Hydroxy-3-(2-furyl)propanoate (**7ai**)

Following General Procedure 3, 165 μ L (2.0 mmol) of 2-furfuraldehyde was combined with 84 mg (0.1 mmol, 0.05 equiv) of bis-phosphoramidate ((*R,R*)-**6**), 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 (**1a**) to yield, after purification by silica gel column chromatography (hexanes/EtOAc, 2/1), 320 mg (94%) of methyl 3-hydroxy-3-(2-furyl) propanoate (**7ai**) as a colorless oil.

Data for 7ai:bp: 75 °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, HHC(2)), 2.88 (dd, $J = 16.4$, 5.4, 1 H, 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)TLC: R_f 0.30 (hexanes/EtOAc, 2/1) [UV(254)/PMA]Opt. Rot.: $[\alpha]_D^{24} +22.65$ ($c = 2.15$, EtOH)SFC: t_R (*R*)-**7ai**, 4.02 (93.4%); t_R (*S*)-**7ai**, 4.55 min (6.6%) (Chiralpak AS, 150 psi, 40 °C, 7.5% CH_3OH in CO_2 , 2.5 mL/min, 220 nm)**Preparation of Methyl 3-Hydroxy-3-cyclohexylpropanoate (7aj)**

A flame-dried, 20-mL, 2-neck flask containing a solution of 168 mg (0.2 mmol, 0.1 equiv) of bis-phosphoramidate ((*R,R*)-**6**) in CH_2Cl_2 (10 mL) was cooled to $-78\text{ }^\circ\text{C}$ under nitrogen in a dry ice/isopropanol bath. Into this reaction mixture was added 242 μL (2.0 mmol) 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 $-78\text{ }^\circ\text{C}$ for 5 min in a dry ice/isopropanol bath. Then 523 μL (2.4 mmol, 1.2 equiv) of 1-(*tert*-butyldimethylsilyloxy)-1-

methoxyethene (**1a**) was added dropwise (over 5 min) the resulting mixture was allowed to stir at -78 °C for 6 h in a dry ice/isopropanol bath. 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 silica gel 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 methyl 3-hydroxy-3-cyclohexylpropanoate (**7aj**) as a colorless oil. NMR spectral data matched that previously reported in the literature. Analysis of the enantiomeric composition was preformed on the trifluoroacetate derivative, **31**.

Data for 7aj:

¹H NMR: (400 MHz, CDCl₃)

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, CDCl₃)

174.20 (C(1)), 72.35 (C(3)), 52.10 (C(10)), 43.23 (C(11)), 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)

GC: *t_R* (*S*)-**31**, 7.73 (5.8%); *t_R* (*R*)-**31**, 8.20 min (94.2%) (GTA, 16 psi, 100 °C isothermal)

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

Preparation of Methyl 3-Trifluoromethylacetoxy-3-cyclohexylpropanoate ((3*R*)-**31**)

To a stirred solution of 61 mg (1.1 mmol) of (3*R*)-**7aj** 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 column chromatography (hexane/EtOAc, 10/1), afforded 88 mg (95%) of methyl 3-trifluoromethylacetoxy-3-cyclohexylpropanoate ((3*R*)-**31**).

Data for (3*R*)-**31**:

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* (3*S*)-**31**, 7.73 (5.8%); *t_R* (3*R*)-**31**, 8.20 min (94.2%) (GTA, 16 psi, 100 °C isothermal)

Preparation of Methyl 3-Hydroxy-5-phenylpentanoate (7ak)

A flame-dried, 20-mL, 2-neck flask containing a solution of 168 mg (0.2 mmol, 0.1 equiv) of bis-phosphoramidate ((*R,R*)-**6**) in CH_2Cl_2 (10 mL) was cooled to $-78\text{ }^\circ\text{C}$ under nitrogen in a dry ice/isopropanol bath. To this reaction mixture was added 263 μL (2.0 mmol) of hydrocinnamaldehyde. To the resulting mixture was added 252 μL (2.2 mmol, 1.1 equiv) of SiCl_4 and the reaction mixture was allowed to stir at $-78\text{ }^\circ\text{C}$ for 5 min in a dry ice/isopropanol bath. Then 523 μL (2.4 mmol, 1.2 equiv) of 1-(*tert*-butyldimethylsilyloxy)-1-methoxyethene (**1a**) was added dropwise (over 5 min) to the reaction mixture. The resulting mixture was allowed to stir at $-78\text{ }^\circ\text{C}$ for 6 h in a dry ice/isopropanol bath. 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 silica gel 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 methyl 3-hydroxy-5-phenylpentanoate (**7ak**) as a colorless oil. NMR spectral data matched that previously reported in the literature.¹⁵

Data for 7ak:

^1H NMR: (400 MHz, CDCl_3)

7.28-7.18 (m, 5H, HC(7,8,9)), 4.01 (m, 1 H, HC(3)), 3.70 (s, 3 H, $\text{H}_3\text{C}(10)$), 3.10 (d, $J = 3.6$, 1 H, OH), 2.82 (m, 1 H, $\text{HHC}(5)$), 2.69 (m, 1 H, $\text{HHC}(5)$), 2.50 (dd, $J = 16.5, 3.4$, 1 H, $\text{HHC}(2)$), 2.46 (dd, $J = 16.5, 8.7$, 1 H, $\text{HHC}(2)$), 1.84 (m, 1 H, $\text{HHC}(4)$), 1.74 (m, 1 H, $\text{HHC}(4)$),

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

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)

SFC: t_R (*S*)-**7ak**, 3.46 (90.7%); t_R (*R*)-**7ak**, 4.13 min (9.3%) (Chiralpak OD, 150 psi, 40
°C, 5.0% CH₃OH in CO₂, 3.0 mL/min, 220 nm)

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

General Procedure 4. Preparation of *tert*-butyl 3-Hydroxy-3-phenylpropanoate (**7ba**)

A flame-dried, 25 mL, 2-neck flask containing a solution of 17 mg (0.02 mmol, 0.01 equiv) of bis-phosphoramidate ((*R,R*)-**6**) in CH₂Cl₂ (10 mL) was cooled to -78 °C and then 200 μ L (2.0 mmol) of benzaldehyde was added in one portion. To the resulting solution, 250 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, 552 mg (2.4 mmol, 1.2 equiv) of **1b** was added dropwise (over 1 min) to the reaction mixture. The resulting mixture was allowed to stir at -78 °C for 1 h whereupon the cold reaction mixture was poured into a rapidly stirring solution of saturated aqueous NaHCO₃ (50 mL) and the resulting mixture was stirred for 3 h at room temperature. The solution was then filtered through Celite and the filter cake was washed with CH₂Cl₂ (100 mL). The aqueous layer was washed with CH₂Cl₂ (50 mL) and the combined organics were dried over K₂CO₃ (5g) and concentrated *in vacuo* to give a colorless oil (480 mg). Crude ¹H NMR analysis indicated that a 4.4:1 mixture of the *tert*-butyl ester **7ba** and the *tert*-butyldimethylsilyl ester **8a** had formed. The residue was dissolved in CH₂Cl₂ (50 mL) poured into a stirred solution of 1/1 sat. aq. KF / 1.0 M KH₂PO₄ (50 mL) and the resulting mixture was stirred for 3 h after which it was diluted with water (100 mL) and the aqueous layer washed with CH₂Cl₂ (3 x 50 mL). The combined organic extracts were dried over K₂CO₃ (5g), filtered through Celite and concentrated *in vacuo*. The residue was purified by Kugelrohr distillation to yield 302 mg (68%) of **7ba** as a colorless oil. The NMR spectral data matched that previously reported in the literature.^{16,17}

Data for 7ba:

bp: 200 °C (0.5 mmHg, ABT)

¹H NMR: (500 MHz, CDCl₃)

7.40-7.32 (m, 4 H, HC(5,6)), 7.30-7.26 (m, 1 H, HC(7)), 5.09 (dd, $J = 8.5, 4.0$, 1 H, HC(3)), 3.48 (br s, 1 H, OH), 2.68 (dd, $J = 17.0, 8.5$, 1 H, *HHC*(2)), 2.64 (dd, $J = 17.0, 4.0$, 1 H, *HHC*(2)), 1.45 (s, 9 H, HC(9))

¹³C NMR: (125 MHz, CDCl₃)

172.18 (C(1)), 142.83 (C(4)), 128.71 (C(5)), 127.90 (C(7)), 125.95 (C(6)), 81.75 (C(8)), 70.61 (C(3)), 44.45 (C(2)), 28.27 (C(9))

IR: (thin film)

3435 (m), 2977 (m), 1718 (s)

MS: (ESI)

245 (M^{+Na} , 100), 229 (32)

HRMS: calcd for C₁₃H₁₈O₃Na: 245.1154, found 245.1152

TLC: R_f 0.3 (hexanes/EtOAc, 4/1) [UV(254)/KMnO₄]

Opt. Rot.: $[\alpha]_D^{24} +11.8$ (c = 0.85, EtOH)

SFC: t_R (3*R*)-**7ba**, 5.15 (97.9%); t_R (3*S*)-**7ba**, 5.58 (2.1%) (OD column, 125 psi, 40 °C, 2.0% CH₃OH in CO₂, 2.5 mL/min, 220 nm)

Analysis: C₁₃H₁₈O₃ (222.28)

Calcd: C, 70.24; H, 8.16%

Found: C, 70.03; H, 8.07%

Preparation of *tert*-Butyl 3-Hydroxy-3-(1-naphthyl)propanoate (**7bb**)

Following General Procedure 4, 270 μL (2.0 mmol) of 1-naphthaldehyde¹⁸ was combined with 17 mg (0.02 mmol, 0.01 equiv) of bis-phosphoramidate ((*R,R*)-**6**), 250 μL (2.2 mmol, 1.1 equiv) of SiCl_4 and 552 mg of **1b** (2.4 mmol, 1.2 equiv) to yield a clear colorless oil (480 mg). Crude ^1H NMR analysis indicated that a 6:1 mixture of the *tert*-butyl ester **7bb** and the *tert*-butyldimethylsilyl ester **8b** had formed. After additional quenching in a stirred solution of 1/1 sat. aq. KF / 1.0 M K_2HPO_4 (50 mL), this residue was purified by Kugelrohr distillation to yield 430 mg (79%) of **7bb** as a white crystalline solid. Recrystallization from hexanes afforded colorless needles. The NMR spectral data matched that previously reported in the literature.¹⁷

Data for **7bb**:

bp: 250 $^{\circ}\text{C}$ (0.5 mmHg, ABT)

mp: 79-79.5 $^{\circ}\text{C}$ (hexanes)

^1H NMR: (500 MHz, CDCl_3)

8.07 (d, $J = 8.0$, 1 H, HC(12)), 7.90-7.86 (m, 1 H, HC(9)), 7.79 (d, $J = 8.0$, 1 H, HC(7)), 7.70 (d, $J = 7.0$, 1 H, HC(5)), 7.56-7.46 (m, 3 H, HC(6,10,11)), 5.88 (dd, $J = 10.0$, 3.0, 1 H, HC(3)), 3.60 (br s, 1 H, OH), 2.85 (dd, $J = 17.0$, 3.0, 1 H, $\text{HHC}(2)$), 2.77 (dd, $J = 17.0$, 10.0, $\text{HHC}(2)$), 1.50 (s, 9 H, HC(15))

^{13}C NMR: (125 MHz, CDCl_3)

172.46 (C(1)), 138.32 (C(4)), 133.97 (C(8)), 130.27 (C(13)), 129.20 (C(9)), 128.40 (C(7)), 126.43 (C(11)), 125.78 (C(10)), 125.74 (C(6)), 123.23 (C(5)), 123.12 (C(12)), 81.88 (C(14)), 67.60 (C(3)), 43.82 (C(2)), 28.37 (C(15))

IR: (thin film)

3436 (m), 2977 (m), 1719 (s)

MS: (ESI)

295 ($\text{M}^{+\text{Na}}$, 100), 279 (30), 255 (55), 199 (25)

HRMS: calcd for $\text{C}_{17}\text{H}_{20}\text{O}_3\text{Na}$: 295.1337, found 295.1325

TLC: R_f 0.3 (Hexanes/EtOAc, 4/1) [UV(254)/KMnO₄]

Opt. Rot.: $[\alpha]_D^{24}$ +28.2 ($c = 2.2$, EtOH)

SFC: t_R (3*S*)-**7bb**, 3.4 (3.1%); t_R (3*R*)-**7bb**, 4.4 (96.9%) (OD column, 200 psi, 40 °C, 10.0% MeOH, in CO₂, 3.0 mL/min, 220 nm)

Analysis: C₁₇H₂₀O₃ (272.34)

Calcd: C, 74.97; H, 7.40%

Found: C, 74.92; H, 7.47%

Preparation of *tert*-Butyl 3-Hydroxy-4-methyl-5-phenyl-4-pentenoate (**7bh**)

Following General Procedure 4, 280 mL (2.0 mmol) α -methylcinnamaldehyde was combined with 17 mg (0.02 mmol, 0.01 equiv) of bis-phosphoramidate ((*R,R*)-**6**), 250 μ L (2.2 mmol, 1.1 equiv) of SiCl₄ and 552 mg of **1b** (2.4 mmol, 1.2 equiv) to yield a clear colorless oil (580 mg). Crude ¹H NMR analysis indicated a 2.2:1 mixture of the *tert*-butyl ester **7bh** and the *tert*-butyldimethylsilyl ester **8h** had formed. After additional quenching in a stirred solution of 1/1 sat. aq. KF / 1.0 M KH₂PO₄ (50 mL), filtration through a 1 cm pad of SiO₂ (hexanes/EtOAc, 4/1) and concentration *in vacuo* yielded 303 mg (58%) of **7bh** as a white solid. Recrystallization from hexanes afforded fine, colorless needles.

Data for **7bh**:

mp: 78-79 °C (hexanes)

¹H NMR: (400 MHz, CDCl₃)

7.34 (t, $J = 7.0$, 2 H, HC(9)), 7.28-7.18 (m, 3 H, HC(8,10)), 6.59 (s, 1 H, HC(6)), 4.59-4.51 (m, 1 H, HC(3)), 3.22 (d, $J = 3.0$, 1 H, OH), 2.58 (d, $J = 6.0$, 2 H, HC(2)), 1.88 (br s, 3 H, HC(5)), 1.47 (s, 9 H, HC(12))

¹³C NMR: (100 MHz, CDCl₃)

172.27 (C(1)), 128.45 (C(7)), 127.65 (C(4)), 129.22 (C(8)), 128.33 (C(9)), 126.73

(C(10)), 126.06 (C(6)), 81.72 (C(11)), 73.85 (C(3)), 41.40 (C(2)), 28.35 (C(12)), 14.13 (C(5))

IR: (thin film)

3435 (m), 2977 (m), 1719 (s)

MS: (ESI)

285 (M^{+Na} , 17), 189 (100)

HRMS: calcd for $C_{16}H_{22}O_3Na$: 285.1467, found 285.1452

TLC: R_f 0.3 (hexanes/EtOAc, 4/1) [UV(254)/KMnO₄]

Opt. Rot.: $[\alpha]_D^{24}$ -23.9 (c = 0.95, EtOH)

SFC: t_R (3*S*)-**7bh**, 3.4 (14.5%); t_R (3*R*)-**7bh**, 3.7 (85.5%) (AD column, 150 psi, 40 °C, 5.0% MeOH in CO₂, 3.0 mL/min, 220 nm)

Analysis: $C_{16}H_{22}O_3$ (262.30)

Calcd: C, 73.25; H, 8.45%

Found: C, 73.19; H, 8.40%

Preparation of Methyl 3-Hydroxy-5-phenylpentanoate (**7bk**)

A flame-dried, 25 mL, 2-neck flask containing a solution of 17 mg (0.02 mmol, 0.01 equiv) of bis-phosphoramide ((*R,R*)-**6**) in CH₂Cl₂ (10 mL) was cooled to -78 °C and 260 μ L (2.0 mmol) of hydrocinnamaldehyde and 70 μ L (0.4 mmol, 0.2 equiv) of DIPEA were added. To the resulting solution, 250 μ L (2.2 mmol, 1.1 equiv) of SiCl₄ was added and the reaction was allowed to stir at -78 °C for 5 min. Then, 552 mg (2.4 mmol, 1.2 equiv) of **1b** was added dropwise (over 1 min) to the reaction mixture. The resulting mixture was allowed to stir at -78 °C for 6 h whereupon the cold reaction mixture was poured into a rapidly stirring solution of saturated aqueous NaHCO₃ (50 mL) and the resulting mixture was stirred for 30 min at room temperature. The solution was then filtered through Celite and the filter cake was washed with CH₂Cl₂ (100 mL). The aqueous layer was washed with CH₂Cl₂ (50 mL) and the combined organics were dried over K₂CO₃ (5g)

and concentrated *in vacuo* to give a colorless oil (280 mg). Crude ^1H NMR analysis indicated that a 95:5 mixture of the *tert*-butyl ester **7bk** and the *tert*-butyldimethylsilyl ester **8k** had formed. However, the *tert*-butyldimethylsilyl ester **8k** was found to hydrolyse rapidly in the NaHCO_3 solution and therefore this may not be representative of the true ratio. The residue was purified by column chromatography (hexanes/EtOAc, 3/1) to yield 232 mg (46%) of **7bk** as a colorless oil.

Data for **7bk**:

^1H NMR: (500 MHz, CDCl_3)

7.31-7.27 (m, 2 H, HC(7)), 7.22-7.17 (m, 3 H, HC(8,9)), 4.00-3.94 (m, 1 H, HC(3)), 3.22 (br s, 1 H, OH), 2.82 (ddd, $J = 13.5, 10.0, 5.0$, 1 H, $\text{HHC}(5)$), 2.70 (ddd, $J = 13.5, 9.5, 6.5$, 1 H, $\text{HHC}(5)$), 2.43 (dd, $J = 17.0, 4.0$, 1 H, $\text{HHC}(2)$), 2.36 (dd, $J = 16.5, 9.0$, 1 H, $\text{HHC}(2)$), 1.87-1.79 (m, 1 H, $\text{HHC}(4)$), 1.75-1.68 (m, 1 H, $\text{HHC}(4)$), 1.46 (s, 9 H, HC(11))

^{13}C NMR: (125 MHz, CDCl_3)

172.80 (C(1)), 142.12 (C(6)), 128.71 (C(7)), 128.64 (C(8)), 126.08 (C(9)), 81.60 (C(1)), 67.71 (C(3)), 42.44 (C(2)), 38.28 (C(5)), 31.96 (C(4)), 28.31 (C(11))

IR: (thin film)

3436 (m), 2929 (m), 1718 (s)

MS: (ESI)

273 ($\text{M}^{+\text{Na}}$, 50), 157 (100), 195 (55), 177 (30)

HRMS: calcd for $\text{C}_{15}\text{H}_{22}\text{O}_3\text{Na}$: 273.1467, found 273.1465

TLC: R_f 0.5 (Hexanes/EtOAc, 3/1) [UV(254)/ KMnO_4]

Opt. Rot.: $[\alpha]_{\text{D}}^{24}$ -14.8 ($c = 0.45$, EtOH)

SFC: t_R (3*S*)-**7bk**, 3.0 (96.9%); t_R (3*R*)-**7bk**, 3.6 (3.1%) (OD column, 150 psi, 40 °C, 5.0% MeOH in CO_2 , 3.0 mL/min, 220 nm)

Analysis: $\text{C}_{15}\text{H}_{22}\text{O}_3$ (250.30)

Calcd: C, 71.97; H, 8.86%

Found: C, 71.77; H, 8.93%

General Procedure 5. Addition of propionate-derived Silyl Ketene Acetals to Aromatic Aldehydes: Preparation of *tert*-Butyl 3-Hydroxy-2-methyl-3-phenylpropanoate ((2*S*,3*R*)-9ea**)**

A flame-dried, 10-mL, 2-neck flask containing a solution of 8.4 mg (0.01 mmol, 0.01 equiv) of bis-phosphoramidate ((*R,R*)-**6**) in CH₂Cl₂ (5 mL) was cooled to -78 °C under nitrogen in a dry ice/isopropanol bath and then 102 µL (1.0 mmol) 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 in a dry ice/isopropanol bath. Then 293 mg (1.2 mmol, 1.2 equiv) of (*E*)-1-[(*tert*-butoxy)-propenyl]-*tert*-butyl-dimethylsilane (**2e**) was added dropwise (over 5 min) to the reaction mixture. The resulting mixture was allowed to stir at -78 °C for 3 h in a dry ice/isopropanol bath 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 *tert*-butyl 3-hydroxy-2-methyl-3-phenyl propanoate ((2*S*,3*R*)-**9ea**) as a colorless oil. NMR spectral data matched that previously reported in the literature.¹⁹

Data for (2*S*,3*R*)-**9ea**:

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* = 7.3, 1 H, HC(2)), 1.44 (s, 9 H, H₃C(10)), 1.01 (d, *J* = 7.3, 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)

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

SFC: *t_R* (2*S*,3*R*)-**9ea**, 2.32 (>99.9%); *t_R* (2*R*,3*S*)-**9ea**, 2.81 min (<0.1%) (Chiralpak AS,
 150 psi, 40 °C, 1.0% CH₃OH in CO₂, 3.5 mL/min, 220 nm)

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

Analysis: C₁₄H₂₀O₃ (230.26)
 Calcd: C, 71.16; H, 8.53%
 Found: C, 70.93; H, 8.46%

Preparation of *tert*-Butyl 3-Hydroxy-2-methyl-3-(1-naphthyl)propanoate (**9eb**)

Following General Procedure 5, 136 μ L (1.0 mmol) of 1-naphthaldehyde was combined with 8.4 mg (0.01 mmol, 0.01 equiv) of bis-phosphoramidate ((*R,R*)-**6**), 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*-butyl-dimethylsilane (**2e**) to yield, after Kugelrohr distillation, 280 mg (98%) of *tert*-butyl 3-hydroxy-2-methyl-3-(1-naphthyl) propanoate (**9eb**) as a colorless wax. NMR spectral data matched that previously reported in the literature.²⁰

Data for **9eb**:

bp: 210°C (0.01 mmHg, ABT)

¹H NMR: (499 MHz, CDCl₃)
8.2 (d, *J* = 8.1, 1 H, HC(11)), 7.88 (d, *J* = 7.9, 1 H, HC(14)), 7.8 (d, *J* = 8.4, 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, 5.2, 1 H, HC(3)), 3.52 (d, *J* = 5.2, 1 H, OH), 3.04 (pent, *J* = 7.3, 1 H, HC(2)), 1.44 (s, 9 H, H₃C(16)), 1.06 (d, *J* = 7.1, 3 H, H₃C(4))

¹³C NMR: (125 MHz, CDCl₃)
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: (CHCl₃)
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)

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

Opt. Rot.: [α]_D²⁴ +28.61 (c = 1.0, EtOH)

SFC: *t_R* (2*S*,3*R*)-**9eb**, 4.11 (2.8%); *t_R* (2*R*,3*S*)-**9eb**, 4.52 min (97.2%) (Chiralpak AD, 150 psi, 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 3-Hydroxy-2-methyl-3-(2-naphthyl)propanoate (**9ec**)

Following General Procedure 5, 156 mg (1.0 mmol) of 2-naphthaldehyde was combined with 8.4 mg (0.01 mmol, 0.01 equiv) of bis-phosphoramidate ((*R,R*)-**6**), 123 μ L (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*-butyl-dimethylsilane (**2e**) to yield, after Kugelrohr distillation, 271 mg (95%) of *tert*-butyl 3-hydroxy-2-methyl-3-(2-naphthyl) propanoate (**9ec**) as a colorless wax.

Data for **9ec**:

bp: 210°C (0.01 mmHg, ABT)

¹H NMR: (499 MHz, CDCl_3)

7.83 (m, 4 H, H(Ar)), 7.48 (m, 3 H, H(Ar)), 4.87 (d, $J = 8.2$, 1 H, HC(3)), 3.33 (br s, 1 H, OH), 2.82 (pent, $J = 7.2$, 1 H, HC(2)), 1.44 (s, 9 H, $\text{H}_3\text{C}(16)$), 1.04 (d, $J = 7.2$, 3 H, $\text{H}_3\text{C}(4)$)

¹³C NMR: (125 MHz, CDCl_3)

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(6)), 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)), 14.72 (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)

TLC: R_f 0.44 (hexanes/EtOAc, 8/2) [UV(254)/ KMnO_4]

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

SFC: t_R (2*S*,3*R*)-**9ec**, 3.26 (99.6%); t_R (2*R*,3*S*)-**9ec**, 3.67 min (0.4%) (Chiralpak AS, 150 psi, 40 °C, 5.0% CH_3OH in CO_2 , 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 3-Hydroxy-3-(4-methoxyphenyl)-2-methylpropanoate (9ee**)**

Following General Procedure 5, 122 μ L (1.0 mmol) of *p*-anisaldehyde was combined with 8.4 mg (0.01 mmol, 0.01 equiv.) of bis-phosphoramidate ((*R,R*)-**6**), 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*-butyl-dimethylsilane (**2e**) to yield, after Kugelrohr distillation, 233 mg (88%) of *tert*-butyl 3-hydroxy-3-(4-methoxyphenyl)-2-methyl propanoate (**9ee**) as a colorless oil.

Data for **9ee**:

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* = 8.4, 1 H, HC(3)), 2.99 (s, 1 H, OH), 2.57 (pent, *J* = 7.3, 1 H, HC(2)), 1.35 (s, 9 H, H₃C(11)), 0.88 (d, *J* = 7.3, 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)

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

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

SFC: t_R (2*S*,3*R*)-**9ee**, 2.46 (99.2%); t_R (2*R*,3*S*)-**9ee**, 3.05 min (0.8%) (Chiralpak AS, 150 psi, 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 3-Hydroxy-2-methyl-3-(4-trifluoromethylphenyl)propanoate (**9ef**)

Following General Procedure 5, 136 μL (1.0 mmol) of 4-trifluoromethylbenzaldehyde was combined with 8.4 mg (0.01 mmol, 0.01 equiv) of bis-phosphoramidate ((*R,R*)-**6**), 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*-butyl-dimethylsilane (**2e**) to yield, after Kugelrohr distillation, 284 mg (93%) of *tert*-butyl 3-hydroxy-2-methyl-3-(4-trifluoromethylphenyl) propanoate (**9ef**) as a white crystalline solid.

Data for **9ef**:

mp: 84-86 °C

¹H NMR: (399 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)), 124.34 (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))

^{19}F NMR: (376 MHz, CDCl_3)

-62.89 (t, 3 F, $\text{F}_3\text{C}(9)$)

IR: (CHCl_3)

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

MS.: (EI, 70 eV)

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

TLC: R_f 0.48 (hexanes/EtOAc, 8/2) [UV(254)/ KMnO_4]

Opt. Rot.: $[\alpha]_{\text{D}}^{24} +39.50$ ($c = 1$, EtOH)

SFC: t_R (2*S*,3*R*)-**9ef**, 2.44 (96.0%); t_R (2*R*,3*S*)-**9ef**, 3.08 min (4.0%) (Whelk-O1, 150 psi, 40 °C, 1.0% CH_3OH in CO_2 , 3.5 mL/min, 220 nm)

Analysis: $\text{C}_{15}\text{H}_{19}\text{F}_3\text{O}_3$ (304.30)

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

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

Preparation of *tert*-Butyl 3-(2-Furyl)-3-hydroxy-2-methylpropanoate (**9ei**)

Following General Procedure 5, 100 μL of 2-furaldehyde **5i** (1.0 mmol) was combined with 8.4 mg (0.01 mmol, 0.01 equiv) of bis-phosphoramidate ((*R,R*)-**6**), 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*-butyl-dimethylsilane (**2e**) to yield, after silica gel column chromatography (hexanes/EtOAc, 9/1), 217 mg (96 %) of *tert*-butyl 3-(2-furyl)-3-hydroxy-2-methyl propanoate **9ei** as a colorless oil.

Data for **9ei**:

bp: 150 °C ABT (0.01 mmHg)

¹H NMR: (400 MHz, CDCl₃)

7.37 (d, *J* = 1.7, 1 H HC(7)), 6.33 (dd, *J* = 3.2, 1.7, 1 H, HC(6)), 6.27 (d, *J* = 3.2 1 H, HC(5)), 4.72 (t, *J* = 7.1, 1 H, HC(3)), 3.27 (d, *J* = 6.6, 1 H, OH), 2.90 (pent, *J* = 7.1, 1 H, HC(2)), 1.45 (s, 9 H, H₃C(9)), 1.01 (d, *J* = 7.1, 3 H H₃C(10))

¹³C NMR: (100 MHz, CDCl₃)

174.94 (C(1)), 154.53 (C(4)), 142.13 (C(7)), 110.12 (C(6)), 107.20 (C(6)), 81.34 (C(8)), 69.89 (C(3)), 45.05 (C(2)), 27.98 (C(9)), 14.35 (C(10))

IR: (neat)

3454 (m), 2978 (s), 2937 (m), 1730 (s), 1505 (w), 1458 (m), 1368 (s), 1256 (m), 1153 (s), 1010 (m)

MS: (EI, 70 eV)

226 (M⁺, 3), 209 (5), 170 (31), 153 (35), 97 (100), 57 (25)

Opt. Rot.: +28.12 (c = 1.0, EtOH)

TLC: *R_f* 0.26 (hexanes/EtOAc, 9/1) [UV(254)/KMnO₄]

SFC: *t_R* (2*S*,3*R*)-**9ei**, 2.26 (96.9%); *t_R* (2*R*,3*S*)-**9ei**, 2.85 (3.1%) (Chiralpak AS, 125 psi, 40 °C, 0.5% CH₃OH in CO₂, 3.5 mL/min, 220 nm)

Analysis: C₁₂H₁₈O₄ (226.27)

Calcd: C, 63.70; H, 8.02%

Found: C, 63.50; H, 8.12%

Preparation of *tert*-Butyl 3-(2-Thienyl)-3-hydroxy-2-methylpropanoate (**9el**)

Following General Procedure 5, 8.4 mg of bis-phosphoramidate (*R,R*)-**6** (0.01 mmol, 0.01 equiv) was combined with 93 μL of 2-thiophene carboxaldehyde **5I** (1.0 mmol), 123 μL of SiCl₄ (1.1 mmol, 1.1 equiv) and 293 mg of **2e** (1.2 mmol, 1.2 equiv) to yield, after silica gel column

chromatography (hexanes/EtOAc, 9/1), 218 mg (90 %) of *tert*-butyl 3-(2-thiophenyl)-3-hydroxy-2-methyl propanoate **9el** as a colorless oil.

Data for **9el**:

bp: 150 °C ABT (0.01 mmHg)²¹

¹H NMR: (400 MHz, CDCl₃)

7.27 (m, 1 H, HC(7)), 6.97 (m, 2 H, HC(5,6)), 4.95 (dd, *J* = 7.1, 5.8, 1 H HC(3)), 3.44 (d, *J* = 5.8, 1 H, OH), 2.77 (pent, *J* = 7.1, 1 H, HC(2)), 1.44 (s, 9 H, H₃C(9)), 1.12 (s, *J* = 7.3, 3 H, H₃C(10))

¹³C NMR: (100 MHz, CDCl₃)

174.98 (C(1)), 126.50 (C(4)), 125.00 (C(7)), 124.90 (C(6)), 124.60 (C(5)), 81.46 (C(3)), 72.33 (C(8)), 47.88 (C(2)), 27.98 (C(9)), 14.69 (C(10))

IR: (neat)

3463 (m), 2978 (m), 2936 (m), 1727 (s), 1458 (m), 1368 (s), 1255 (m), 1154 (s), 1035 (m)

MS: (EI, 70 eV)

242 (M⁺, 1), 225 (1), 186 (20), 169 (18), 113 (100), 74 (11), 57 (46)

Opt. Rot.: +14.34 (c = 1.0, EtOH)

TLC: *R_f* 0.30 (hexanes/EtOAc, 9/1) [UV(254)/KMnO₄]

SFC: *t_R* (2*S*,3*R*)-**9el**, 2.21 (94.3%); *t_R* (2*R*,3*S*)-**9el**, 2.54 (5.7%) (Chiralpak AS, 125 psi, 40 °C, 1.5% CH₃OH in CO₂, 3.5 mL/min, 220 nm)

Analysis: C₁₂H₁₈O₃S (242.34)

Calcd: C, 59.47; H, 7.49%

Found: C, 59.72; H, 7.68%

Preparation of *tert*-Butyl 3-Hydroxy-2-methyl-5-phenyl-4-pentenoate (9eg**)**

Following General Procedure 5, 141 μL (1.0 mmol) of cinnamaldehyde was combined with 8.4 mg (0.01 mmol, 0.01 equiv) of bis-phosphoramidate ((*R,R*)-**6**), 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*-butyl-dimethylsilane (**2e**) to yield, after Kugelrohr distillation, 256 mg (98%) of *tert*-butyl 3-hydroxy-2-methyl-5-phenyl-pent-4-enoate (**9eg**) as a white crystalline solid.

Data for **9eg:**

mp: 80-82 $^{\circ}\text{C}$

bp: 200 $^{\circ}\text{C}$ (0.01 mmHg, ABT)

^1H NMR: (399 MHz, CDCl_3)

7.15 (m, 5 H, HC(8,9,10)), 6.64 (d, $J = 15.9$, 1 H, HC(5)), 6.19 (dd, $J = 15.9$, 6.6, 1 H, HC(4)), 4.33 (t, $J = 6.6$, 1 H, HC(3)), 2.55 (pent, $J = 7.1$, 1 H, HC(2)), 1.46 (s, 9 H, $\text{H}_3\text{C}(12)$), 1.20 (d, $J = 7.3$, 3 H, $\text{H}_3\text{C}(6)$)

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

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)

263 (M^{+1} , 3), 245 (20), 206 (37), 189 (99), 143 (25), 133 (9100), 105 (16), 57 (86)

TLC: R_f 0.36 (hexanes/EtOAc, 8/2) [UV(254)/ KMnO_4]

Opt. Rot.: $[\alpha]_{\text{D}}^{24}$ -17.48 ($c = 1$, EtOH)

SFC: t_R (2*S*,3*S*)-**9eg**, 3.31 (>99.0%); t_R (2*R*,3*R*)-**9eg**, 4.13 min (<1.0%) (Chiralpak AS, 150 psi, 40 $^{\circ}\text{C}$, 1.0% CH_3OH in CO_2 , 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 3-Hydroxy-2,4-dimethyl-5-phenyl-4-pentenoate (9eh**)**

Following General Procedure 5, 140 μ L (1.0 mmol) of α -methylcinnamaldehyde was combined with 8.4 mg (0.01 mmol, 0.01 equiv) of bis-phosphoramidate ((*R,R*)-**6**), 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*-butyl-dimethylsilane (**2e**) to yield, after Kugelrohr distillation, 248 mg (90%) of *tert*-butyl 3-hydroxy-2,4-dimethyl-5-phenyl-pent-4-enoate (**9eh**) as a colorless wax.

Data for **9eh**:

bp: 225 °C (0.01 mmHg, ABT)

¹H NMR: (399 MHz, CDCl₃)

7.25 (m, 5 H, HC(9,10,11)), 6.53 (s, 1 H, HC(5)), 4.20 (d, *J* = 7.8, 1 H, HC(3)), 3.00 (s, 1 H, OH), 2.67 (pent, *J* = 7.8, 1 H, HC(2)), 1.87 (s, 3 H, H₃C(7)), 1.47 (s, 9 H, H₃C(13)), 1.13 (d, *J* = 7.3, 3 H, H₃C(6))

¹³C NMR: (100 MHz, CDCl₃)

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: (CHCl₃)

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)

TLC: R_f 0.39 (hexanes/EtOAc, 8/2) [UV(254)/KMnO₄]
Opt. Rot.: $[\alpha]_D^{24}$ -66.28 ($c = 1.0$, EtOH)
SFC: t_R (2*S*,3*R*)-**9eh**, 3.63 (96.1%); t_R (2*R*,3*S*)-**9eh**, 4.13 min (3.9%) (Chiralpak AS, 150 psi, 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 3-Hydroxy-2-methyl-4-hexenoate (**9em**)

A flame-dried, 25 mL, 2-neck flask containing a solution of 8.4 mg of bis-phosphoramidate (*R,R*)-**6** (0.01 mmol, 0.01 equiv) and 82 μL of crotonaldehyde **5m** (1.0 mmol) in CH₂Cl₂ (5 mL) was cooled to -78°C under nitrogen. To the resulting solution was added 123 μL of SiCl₄ (1.1 mmol, 1.1 equiv). Then 293 mg of **2e** (1.2 mmol, 1.2 equiv) was added dropwise over 5 min to the reaction mixture. The solution was allowed to stir at -78°C (bath temperature) for 3 h whereupon a solution 464 μL of triethylamine (3.3 mmol, 3.3 equiv) in MeOH (2 mL) was added by cannula. The resulting solution was allowed to warm to room temperature and stirred for 1 h prior to pouring into a rapidly stirring, sat. sodium bicarbonate solution (20 mL). This mixture was stirred vigorously for 1 h before filtration through Celite. The aqueous layer was washed with CH₂Cl₂ (3 x 25 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 silica gel column chromatography (hexanes/EtOAc, 9/1) to yield 109 mg (55 %) of **9em** as a colorless oil. Enantiomeric composition was determined on the benzoate derivative **32**.

Data for **9em**:¹H NMR: (400 MHz, CDCl₃)

5.72 (ddq, $J = 15.4, 0.9, 6.6$, 1 H, HC(5)), 5.45 (ddq, $J = 15.4, 7.4, 1.7$, 1 H, HC(4)), 4.08 (t, $J = 7.1$, 1 H, HC(3)), 2.7 (bs, 1 H, OH), 2.41 (pent, $J = 7.1$, 1 H, HC(2)), 1.70 (dd, $J = 6.6, 1.2$, 3 H, H₃C(6)), 1.45 (s, 9 H, H₃C(8)), 1.11 (d, $J = 7.3$, 3 H, H₃C(9))

¹³C NMR: (100 MHz, CDCl₃)

175.13 (C(1)), 131.29 (C(5)), 128.54 (C(4)), 80.98 (C(7)), 74.73 (C(3)), 46.19 (C(2)), 28.07 (C(8)), 17.71 (C(6)), 14.13 (C(9))

IR: (neat)

3448 (m), 2977 (s), 2937 (m), 2883 (w), 1727 (s), 1457 (m), 1369 (s), 1225 (m), 1159 (s), 1031 (m)

MS: (EI, 70 eV)

201 (M⁺, 7), 183 (5), 145 (22), 127 (100), 109 (5), 71 (12)

Opt. Rot.: $[\alpha]_{\text{D}}^{24}$ -17.17 (c = 1.0, EtOH)TLC: R_f 0.25 (hexanes/EtOAc, 9/1) [KMnO₄]SFC: t_R (2*S*,3*S*)-**32**, 6.57 (98.2%); t_R (2*R*,3*R*)-**32**, 7.50 (1.8%) (Chiralpak AD, 125 psi, 40 °C, 1.0% CH₃OH in CO₂, 2.0 mL/min, 220 nm)Analysis: C₁₁H₂₀O₃ (200.14)

Calcd: C, 65.97; H, 10.07%

Found: C, 65.79; H, 10.18%

Preparation of *tert*-Butyl 3-Benzoyloxy-2-methyl-4-hexenoate (32**)**

To a stirred solution of 39 mg of *tert*-butyl 3-hydroxy-2-methyl-4-hexenoate **9em** (0.2 mmol) in pyridine (1.0 mL) and 1 mL of THF was added 30 μ L of benzoyl chloride (0.2 mmol, 1 equiv) at 0 °C under nitrogen. After the addition was completed, the solution was allowed to stir at room temperature for 24 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 column chromatography (hexanes/EtOAc, 9/1), afforded 40 mg (67%) of **32** as a colorless oil.

Data for **32:**

¹H NMR: (400 MHz, CDCl₃)
 8.03 (m, 2 H, HC(12)), 7.53 (m, 1 H, HC(14)), 7.41 (m, 2 H, HC(13)), 5.92 (ddq, $J = 15.2, 0.7, 6.6$, 1 H, HC(5)), 5.56 (t, $J = 8.4$, 1 H, HC(3)), 5.43 (ddq, $J = 8.1, 15.2, 1.7$, 1 H, HC(4)), 2.76 (pent, $J = 7.1$, 1 H, HC(2)), 1.71 (dd, $J = 6.4, 1.3$, 3 H, H₃C(6)), 1.35 (s, 9 H, H₃C(8)), 1.15 (d, $J = 7.1$, 3 H, H₃C(9))

¹³C NMR: (100 MHz, CDCl₃)
 172.29 (C(1)), 165.29 (C(10)), 132.84 (C(14)), 132.06 (C(5)), 130.42 (C(10)), 129.60 (C(12)), 128.27 (C(13)), 126.64 (C(4)), 80.59 (C(7)), 76.74 (C(3)), 45.26 (C(2)), 27.88 (C(8)), 17.78 (C(6)), 13.19 (C(9))

TLC: R_f 0.44 (hexanes/EtOAc, 9/1) [UV(254)/KMnO₄]

SFC: t_R (2*S*,3*S*)-**32**, 6.57 (98.2%); t_R (2*R*,3*R*)-**32**, 7.50 (1.8%) (Chiralpak AD, 125 psi, 40 °C, 1.0% CH₃OH in CO₂, 2.0 mL/min, 220 nm)

Preparation of *tert*-Butyl 3-Hydroxy-2-ethyl-5-phenyl-4-pentynoate (9en**)**

Following General Procedure 5, 122 μ L (1.0 mmol) of 3-phenyl-2-propynal was combined with 8.4 mg (0.01 mmol, 0.01 equiv) of bis-phosphoramidate ((*R,R*)-**6**), 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*-butyl-dimethylsilane (**2e**) to yield, after Kugelrohr distillation, 240 mg (92%) of *tert*-butyl 3-hydroxy-2-methyl-5-phenyl-pent-4-ynoate ((2*S*,3*R*)-**9en**) as a white crystalline solid.

Data for **9en:**

bp: 210 °C (0.01 mmHg, ABT)

mp: 68-70 °C

¹H NMR: (499 MHz, CDCl₃)

7.42 (m, 2 H, HC(8)), 7.30 (m, 3 H, HC(9,10)), 4.67 (t, *J* = 7.1, 1 H, HC(3)), 3.09 (d, *J* = 7.1, 1 H, OH), 2.73 (pent, *J* = 7.1, 1 H, HC(2)), 1.48 (s, 9 H, H₃C(12)), 1.32 (d, *J* = 7.3, 3 H, H₃C(6))

¹³C NMR: (125 MHz, CDCl₃)

174.10 (C(1)), 131.71 (C(9)), 128.48 (C(10)), 128.27 (C(8)), 122.45 (C(7)), 87.96 (C(5)), 85.54 (C(4)), 81.46 (C(11)), 64.85 (C(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)

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

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

SFC: *t_R* (2*S*,3*R*)-**9en**, 4.78 (84.5%); *t_R* (2*R*,3*S*)-**9en**, 5.71 min (15.5%) (Chiralpak AS, 150 psi, 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 3-Hydroxy-2-methyl-5-phenylpentanoate (**9bk**)

A flame-dried, 10-mL, 2-neck round bottom flask containing a solution of 42.1 mg (0.05 mmol, 0.05 equiv) of bis-phosphoramidate ((*R,R*)-**6**) 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) 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*-butyl-dimethylsilane (**2b**) 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 silica gel column chromatography (hexanes/EtOAc, 9/1), to yield 167 mg (71%) of ethyl 3-hydroxy-2-methyl-5-phenylpropanoate (**9bk**) as a colorless oil.

Data for **9bk**:

¹H NMR: (399 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(3)), 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))

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

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)

SFC: t_R (2*S*,3*S*)-**9bk**, 4.34 (94.9%); t_R (2*R*,3*R*)-**9bk**, 5.04 min (5.2%) (Chiralpak OD, 150 psi, 40 °C, 2.0% CH_3OH in CO_2 , 3.5 mL/min, 220 nm)

MS: (EI, 70 eV)

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

TLC: R_f 0.1 (hexanes/EtOAc, 9/1) [UV(254)/ KMnO_4]

Opt. Rot.: $[\alpha]_{\text{D}}^{24}$ -14.87 ($c = 1.0$, EtOH)

Analysis: $\text{C}_{14}\text{H}_{20}\text{O}_3$ (236.31)

Calcd: C, 71.16; H, 8.53%

Found: C, 70.95; H, 8.52%

Preparation of Ethyl 3-Cyclohexyl-3-hydroxy-2-methylpropanoate (**9bj**)

A flame-dried, 10-mL, 2-neck round bottom flask containing a solution of 84.2 mg (0.1 mmol, 0.1 equiv) of bis-phosphoramidate ((*R,R*)-**6**) and 37 mg (0.1 mmol, 0.1 equiv) of tetrabutylammonium iodide in CH_2Cl_2 (1.25 mL) was cooled to -40 °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) of cyclohexanecarboxaldehyde 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*-butyl-dimethylsilane (**2b**) was added dropwise (over 5 min) to the reaction mixture. The resulting mixture was allowed to

stir at -40 °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 silica gel column chromatography (hexanes/EtOAc, 9/1), to yield 86 mg (40%) of ethyl 3-cyclohexyl-3-hydroxy-2-methyl propanoate (**9bj**) as a colorless oil. Enantiomeric composition was determined on the 3,5-dinitrobenzoate derivative **33**.

Data for **9bj**:

¹H NMR: (399 MHz, CDCl₃)

4.17 (m, 2 H, HC(11)), 3.35 (q, *J* = 6.6, 1 H, HC(3)), 2.65 (pent, *J* = 5.9, 1 H, HC(2)), 2.57 (d, *J* = 7.8, 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* = 7.1, 3 H, H₃C(12)), 1.22 (d, *J* = 7.08, 3 H, H₃C(10)), 1.2-1.0 (m, 3 H, HC(4,7))

¹³C NMR: (100 MHz, CDCl₃)

176.57 (C(1)), 77.79 (C(11)), 60.52 (C(3)), 41.79 (C(2)), 41.19 (C(4)), 29.91 (C(7)), 27.13 (C(5)), 26.36 (C(6)), 26.32 (C(8)), 26.04 (C(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)

SFC: *t_R* (2*S*,3*S*)-**33**, 8.30 (67.8%); *t_R* (2*R*,3*R*)-**33**, 9.16 min (32.8%) (Chiralpak OD, 150 psi, 40 °C, 3.0% CH₃OH in CO₂, 3.0 mL/min, 220 nm)

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)

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

Opt. Rot.: [α]_D²⁴ +5.26 (c = 1.0, EtOH)

Analysis: C₁₂H₂₂O₃ (214.16)

Calcd: C, 67.26; H, 10.35%

Found: C, 67.03; H, 10.55%

Preparation of Ethyl 3-Cyclohexyl-3-(3,5-dinitrobenzoyloxy)-2-methylpropanoate (33)

To a stirred solution of 134 mg (0.627 mmol) of (2*S*,3*S*)-**9bj** 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 ethyl 3-cyclohexyl-3-(3,5-dinitrobenzoyloxy)-2-methyl propanoate (**33**).

Data for 33:

¹H NMR: (499 MHz, CDCl₃)

9.22 (s, 1 H, HC(13)), 9.14 (s, 2 H, HC(12)), 5.29 (t, *J* = 6.10 Hz, HC(3)), 4.12 (q, *J* = 7.08 Hz, 2 H, HC(15)), 3.01 (pent, *J* = 6.38 Hz, 1 H, HC(2)), 1.83-1.65 (m, 8 H, HC(5,6,8,9)), 1.27 (t, *J* = 7.08 Hz, 3 H, H₃C(16)), 1.22 (d, *J* = 7.0 Hz, 3 H, H₃C(14)), 1.2-0.9 (m, 2 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)), 26.30 (C(6)), 26.22 (C(8)), 26.02 (C(9)), 14.43 (C(17)), 14.33 (C(15))

SFC: *t_R* (2*S*,3*S*)-**33**, 8.30 (67.8%); *t_R* (2*R*,3*R*)-**33**, 9.16 min (32.8%) (Chiralpak OD, 150 psi, 40 °C, 3.0% CH₃OH in CO₂, 3.0 mL/min, 220 nm)

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

Preparation of Ethyl 3-Hydroxy-2,5-dimethylhexanoate (9bo)

A flame-dried, 25 mL, 2-neck flask containing a solution of 42 mg of bis-phosphoramidate (*R,R*)-**6** (0.05 mmol, 0.05 equiv), 8 μ L of *i*-Pr₂EtN (0.05 mmol, 0.05 equiv) and 107 μ L of isovaleraldehyde **5o** (1.0 mmol) in CH₂Cl₂ (5 mL) was cooled to -78 °C under nitrogen. To the resulting solution was added 123 μ L of SiCl₄ (1.1 mmol, 1.1 equiv). Then 260 mg of **2b** (1.2 mmol, 1.2 equiv) was added dropwise over 5 min to the reaction mixture. The solution 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 25 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 silica gel column chromatography (hexanes/EtOAc, 9/1) to yield 142 mg (76 %) of **9bo** as a colorless oil. Enantiomeric analysis was determined on the benzoate derivative **34**.

Data for **9bo**:

¹H NMR: (400 MHz, CDCl₃)

4.17 (m, 2 H, H₂C(7)), 3.72 (ddd, *J* = 9.6, 6.0, 3.0, 1 H, HC(3)), 2.46 (pent, *J* = 6.9, 1 H, HC(2)), 1.85 (m, 1 H, HC(5)), 1.39 (ddd, *J* = 14.1, 10.1, 4.5, 1 H, HC(4)), 1.27 (t, *J* = 7.1, 3 H, H₃C(8)), 1.25 (m, 1 H, HC(4)), 1.21 (d, *J* = 7.1, 3 H, H₃C(9)), 0.93 (d, *J* = 7.1, 3 H, H₃C(6)), 0.91 (d, *J* = 7.1, 3 H, H₃C(6))

¹³C NMR: (100 MHz, CDCl₃)

176.14 (C(1)), 71.49 (C(3)), 60.51 (C(7)), 45.64 (C(2)), 44.03 (C(5)), 24.45 (C(4)), 23.63 (C(8)), 21.62 (C(9)), 14.33 (C(6)), 14.17 (C(6))

IR: (neat)

3475 (m), 2956 (s), 2871 (m), 1722 (s), 1467 (m), 1371 (m), 1257 (m), 1186 (s), 1130 (m), 1034 (m)

MS: (EI, 70 eV)

189 (M^{+1} , 8), 171 (7), 143 (6), 131 (61), 102 (100), 85 (31), 74 (52), 57 (15)

Opt. Rot.: $[\alpha]_D^{24}$ -12.90 (c = 1.0, EtOH)

TLC: R_f 0.29 (hexanes/EtOAc, 9/1) [$KMnO_4$]

SFC: t_R (2*S*,3*S*)-**34**, 4.62 (89.7%); t_R (2*R*,3*R*)-**34**, 5.09 (10.3%) (Chiralpak OD, 125 psi, 40 °C, 1.0% CH₃OH in CO₂, 2.0 mL/min, 220 nm)

Analysis: C₁₀H₂₀O₃ (188.14)

Calcd: C, 63.80; H, 10.71%

Found: C, 63.60; H, 10.88%

Preparation of Ethyl 3-Benzoyloxy-2,5-dimethylhexanoate (**34**)

To a stirred solution of 51 mg of ethyl 3-hydroxy-2-methyl-4-hexanoate **9bo** (0.31 mmol) in pyridine (1.0 mL) and 1 mL of THF was added 37 μ L of benzoyl chloride (0.31 mmol, 1 equiv) at 0 °C under nitrogen. After the addition was completed, the solution was allowed to stir at room temperature for 24 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 column chromatography (hexanes/EtOAc, 9/1), afforded 52 mg (62%) of **34** as a colorless oil.

Data for 34:

¹H NMR: (400 MHz, CDCl₃)

8.05-7.26 (m, 5 H, HC(12,13,14)), 5.47 (ddd, J = 9.2, 6.0, 3.2, 1 H, HC(3)), 4.12 (m, 2 H, H₂C(7)), 2.91 (pent, J = 5.8, 1 H, HC(2)), 1.74 (m, 2 H, HC(4,5)), 1.39

(m, 1 H, HC(4)), 1.20 (t, $J = 7.1$, 3 H, H₃C(8)), 1.19 (d, $J = 7.1$, 3 H, H₃C(9)), 0.95 (d, $J = 6.4$, 3 H, H₃C(6)), 0.93 (d, $J = 6.6$, 3 H, H₃C(6))

¹³C NMR: (100 MHz, CDCl₃)
173.40 (C(1)), 165.92 (C(10)), 137.94 (C(14)), 130.30 (C(11)), 129.65 (C(12)), 128.36 (C(13)), 73.53 (C(7)), 60.58 (C(3)), 43.71 (C(2)), 40.21 (C(5)), 24.56 (C(8)), 23.51 (C(4)), 21.82 (C(9)), 14.14 (C(6)), 12.25 (C(6))

TLC: R_f 0.52 (hexanes/EtOAc, 9/1) [UV(254)/KMnO₄]

SFC: t_R (2*S*,3*S*)-**34** 4.62 (89.7%); t_R (2*R*,3*R*)-**34**, 5.09 (10.3%) (Chiralpak OD, 125 psi, 40 °C, 1.0% CH₃OH in CO₂, 2.0 mL/min, 220 nm)

Preparation of Ethyl 3-Hydroxy-2-methylbenzenepropanoate (**11aa**)

Following General Procedure 5, 8.4 mg of bis-phosphoramidate (*R,R*)-**6** (0.01 mmol, 0.01 equiv) was combined with 102 μ L of benzaldehyde **5a** (1.0 mmol), 123 μ L of SiCl₄ (1.1 mmol, 1.1 equiv) and 276 mg of **10a** (1.2 mmol, 1.2 equiv) to yield, after silica gel column chromatography (hexanes/EtOAc, 9/1), 167 mg (75 %) of **11aa** as a colorless oil.

Data for **11aa**:

¹H NMR: (400 MHz, CDCl₃)
7.32 (m, 5 H, HC(5,6,7)), 4.80 (d, $J = 7.6$, 1 H, HC(3)), 4.16 (m, 2 H, H₂C(10)), 2.87 (s, 1 H, OH), 2.67 (m, 1 H, HC(2)), 1.58 (m, 1 H, HC(10)), 1.39 (m, 1 H, HC(10)), 1.22 (t, $J = 7.1$, 3 H, H₃C(9)), 0.87 (t, $J = 6.6$, 3 H, H₃C(11))

¹³C NMR: (100 MHz, CDCl₃)
175.26 (C(1)), 142.07 (C(4)), 128.46 (C(6)), 127.92 (C(7)), 126.39 (C(5)), 75.08 (C(3)), 60.57 (C(8)), 54.62 (C(2)), 22.27 (C(10)), 14.21 (C(9)), 11.55 (C(11))

IR: (neat)
3596 (w), 2969 (m), 1725 (s), 1456 (m), 1378 (m), 1186 (s), 1027 (m)

MS: (EI, 70 eV)
 222 (M^+ , 2), 205 (4), 193 (3), 177 (2), 116 (100), 107 (61), 77 (74)

Opt. Rot.: $[\alpha]_D^{24} +23.31$ ($c = 1.0$, EtOH)

TLC: R_f 0.16 (hexanes/EtOAc, 9/1) [UV(254)/KMnO₄]

SFC: t_R (2*S*,3*R*)-**11aa**, 2.07 (83.6%); t_R (2*R*,3*S*)-**11a**, 2.58 (16.4%) (Chiralpak AS, 150 psi, 40 °C, 3.0% CH₃OH in CO₂, 4.0 mL/min, 220 nm)

Analysis: C₁₃H₁₈O₃ (222.13)

Calcd:	C, 70.24;	H, 8.16%
Found;	C, 70.12;	H, 8.09%

Preparation of Ethyl 3-Hydroxy-2-(1-methylethyl)benzenepropanoate (**11ba**)

Following General Procedure 5, 8.4 mg of bis-phosphoramidate (*R,R*)-**6** (0.01 mmol, 0.01 equiv) was combined with 102 μ L of benzaldehyde **5a** (1.0 mmol), 123 μ L of SiCl₄ (1.1 mmol, 1.1 equiv) and 293 mg of **10b** (1.2 mmol, 1.2 equiv) to yield, after silica gel column chromatography (hexanes/EtOAc, 9/1), 193 mg (82 %) of **11ba** as a colorless oil.

Data for **11ba**:

¹H NMR: (400 MHz, CDCl₃)
 7.31 (m, 5 H, HC(5,6,7)), 4.96 (dd, $J = 7.8, 5.6$, 1 H, HC(3)), 4.03 (q, $J = 7.3$, 2 H, H₂C(8)), 3.41 (d, $J = 8.3$, 1 H, OH), 2.52 (dd, $J = 8.1, 5.6$, 1 H, HC(2)), 2.02 (octet, $J = 6.6$, 1 H, HC(10)), 1.07 (t, $J = 7.1$, 3 H, H₃C(9)), 1.06 (d, $J = 6.8$, 3 H, H₃C(11)), 0.94 (d, $J = 6.8$, 3 H, H₃C(11))

¹³C NMR: (100 MHz, CDCl₃)
 174.98 (C(1)), 142.47 (C(4)), 128.32 (C(6)), 127.47 (C(7)), 125.74 (C(5)), 72.47 (C(3)), 60.32 (C(8)), 59.28 (C(2)), 27.86 (C(9)), 20.98 (C(10)), 20.00 (C(11)), 14.07 (C(11))

IR: (neat)

3488 (m), 2964 (s), 2935 (m), 2824 (m), 1730 (s), 1465 (m), 1454 (m), 1390 (m),
1375 (s), 1287 (s), 1234 (s), 1179 (s), 1160 (s), 1060 (m), 1028 (m)

MS: (EI, 70 eV)

236 (M^+ , 3), 219 (6), 193 (6), 173 (4), 145 (6), 130 (75), 115 (100), 87 (37)

Opt. Rot.: $[\alpha]_D^{24} +19.88$ ($c = 1.0$, EtOH)

TLC: R_f 0.25 (hexanes/EtOAc, 9/1) [UV(254)/KMnO₄]

SFC: t_R (2*R*,3*S*)-**11ba**, 2.23 (14.2%); t_R (2*S*,3*R*)-**11ba**, 3.83 (85.8%) (Chiralpak OD, 125
psi, 40 °C, 1.5% CH₃OH in CO₂, 3.5 mL/min, 220 nm)

Analysis: C₁₄H₂₀O₃ (236.31)

Calcd: C, 71.16; H, 8.53%

Found: C, 71.05; H, 8.54%

Preparation of Ethyl 3-Hydroxy-2-(2-methylpropyl)benzenepropanoate (**11ca**)

Following General Procedure 5, 8.4 mg of bis-phosphoramidate (*R,R*)-**6** (0.01 mmol, 0.01 equiv) was combined with 102 μ L of benzaldehyde **5a** (1.0 mmol), 123 μ L of SiCl₄ (1.1 mmol, 1.1 equiv) and 310 mg of **10c** (1.2 mmol, 1.2 equiv) to yield, after silica gel column chromatography (hexanes/EtOAc, 9/1), 219 mg (88 %) of **11ca** as a colorless oil.

Data for **11ca**:

¹H NMR: (400 MHz, CDCl₃)

7.36 (m, 5 H, HC(5,6,7)), 4.75 (t, $J = 6.6$, 1 H, HC(3)), 4.13 (m, 2 H, H₂C(8)),
2.87 (d, $J = 5.6$, 1 H, OH), 2.84 (ddd, $J = 10.7, 7.3, 4.6$, 1 H, HC(2)), 1.65 (ddd, J
 $= 13.7, 10.7, 5.1$, 1 H, HC(10)), 1.51 (m, 1 H, HC(11)), 1.21 (t, $J = 7.1$, 3 H,
H₃C(9)), 1.08 (ddd, $J = 13.7, 9.3, 4.6$, 1 H, HC(10)), 0.84 (d, $J = 2.7$, 3 H,
H₃C(12)), 0.82 (d, $J = 2.5$, 3 H, H₃C(12))

¹³C NMR: (100 MHz, CDCl₃)
 175.55 (C(1)), 142.17 (C(4)), 128.47 (C(6)), 127.90 (C(7)), 126.32 (C(5)), 75.78 (C(3)), 60.54 (C(8)), 51.13 (C(2)), 38.69 (C(10)), 26.06 (C(11)), 23.21 (C(12)), 21.53 (C(12)), 14.15 (C(9))

IR: (neat)
 3596 (m), 3498 (w), 2960 (s), 2872 (m), 1726 (s), 1469 (m), 1454 (m), 1378 (m), 1246 (m), 1181 (s), 1017 (m)

MS: (EI, 70 eV)
 250 (M⁺, 2), 233 (2), 205 (1), 159 (3), 144 (38), 101 (100), 73 (34)

Opt. Rot.: $[\alpha]_D^{24}$ -2.51 (c = 1.0, EtOH)

TLC: *R_f* 0.25 (hexanes/EtOAc, 9/1) [UV(254)/KMnO₄]

SFC: *t_R* (2*S*,3*R*)-**11ca**, 4.59 (86.3%); *t_R* (2*R*,3*S*)-**11ca**, 7.58 (13.7%) (Chiralpak AS, 125 psi, 40 °C, 1.0% CH₃OH in CO₂, 3.5 mL/min, 220 nm)

Analysis: C₁₅H₂₂O₃ (250.33)
 Calcd: C, 71.97; H, 8.86%
 Found: C, 71.95; H, 9.06%

Preparation of (3*S*) Methyl 3-Hydroxy-2,2-dimethyl-3-phenylpropanoate ((3*S*)-**12**)

A flame-dried, 25 mL, 2-neck, round-bottom flask containing a solution of 42 mg of bis-phosphoramidate (*R,R*)-**6** (0.05 mmol, 0.05 equiv), 8 μ L of *i*-Pr₂EtN (0.05 mmol, 0.05 equiv) and 102 μ L of benzaldehyde **5a** (1.0 mmol) in CH₂Cl₂ (5 mL) was cooled to -78 °C under nitrogen. To the resulting solution was added 123 μ L of SiCl₄ (1.1 mmol, 1.1 equiv). Then 208 mg of **3** (1.2 mmol, 1.2 equiv) was added dropwise over 5 min to the reaction mixture. The solution was allowed to stir at -78 °C 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 25 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 Kugelrohr distillation, yielding 180 mg (87 %) of (3*S*)-**12** as a white, crystalline solid NMR spectral data matched that previously reported in the literature.²²

Data for (3*S*)-**12**:

mp: 62-64 °C

bp: 175 °C (0.1 mm Hg, ABT)

¹H NMR: (400 MHz, CDCl₃)

7.32-7.26 (m, 5 H, HC(5,6,7)), 4.90 (s, 1 H, HC(3)), 3.72 (s, 3 H, H₃C(8)), 3.05 (s, 1 H, OH), 1.14 (s, 3 H, H₃C(9)), 1.11 (s, 3 H, H₃C(9))

¹³C NMR: (100 MHz, CDCl₃)

178.21 (C(1)), 139.89 (C(4)), 127.77 (C(6)), 127.75 (C(5)), 127.63 (C(7)), 78.69 (C(3)), 52.11 (C(8)), 47.67 (C(2)), 23.06 (C(9)), 19.0 (C(9))

Opt. Rot.: [α]_D²⁴ +1.94 (c = 2.4, MeOH), lit. [α]_D²⁴ +5.7 (c = 2.49, MeOH) for (3*S*)-**12**²²

TLC: *R_f* 0.36 (hexanes/EtOAc, 4/1) [UV(254)/KMnO₄]

SFC: *t_R* (3*S*)-**12**, 3.69 (91.1%); *t_R* (3*R*)-**12**, 4.25 (8.9%) (Chiralpak OB, 125 psi, 40 °C, 2.0% CH₃OH in CO₂, 2.0 mL/min, 220 nm)

Preparation of Isopropyl 3-Hydroxy-2-methyl-3-phenylpropanoate (9ca)

Following General Procedure 5, 8.4 mg of bis-phosphoramidate (*R,R*)-**6** (0.01 mmol, 0.01 equiv) was combined with 102 μ L of benzaldehyde **5a** (1.0 mmol), 123 μ L of SiCl₄ (1.1 mmol, 1.1 equiv) and 276 mg of **2c** (1.2 mmol, 1.2 equiv) to yield, after Kugelrohr distillation, 177 mg (80 %) of **9ca** as a white crystalline solid. NMR spectral data matched that previously reported in the literature.⁹

Data for 9ca:mp: 45-47 °Cbp: 200 °C (0.05 mmHg, ABT)¹H NMR: (400 MHz, CDCl₃)7.36-7.26 (m, 5 H, HC(6,7,8)), 5.05 (septet, *J* = 6.3, 1 H, HC(9)), 4.73 (dd, *J* = 8.3, 4.9, 1 H, HC(3)), 3.08 (dd, *J* = 4.8, 0.9, 1 H, OH), 2.76 (pent, *J* = 7.3, 1 H, HC(2)), 1.23 (d, *J* = 6.3, 3 H, H₃C(10)), 1.20 (d, *J* = 6.3, 3 H, H₃C(10)), 1.02 (d, *J* = 7.1, 3 H, H₃C(4))¹³C NMR: (100 MHz, CDCl₃)

175.42 (C(1)), 141.66 (C(5)), 128.42 (C(7)), 127.92 (C(8)), 126.60 (C(6)), 76.27 (C(3)), 68.15 (C(9)), 47.15 (C(2)), 21.71 (C(10)), 21.67 (C(10)), 14.54 (C(4))

IR: (neat)

3475 (m), 2980 (s), 2938 (m), 1730 (s), 1455 (m), 1376 (m), 1249 (m), 1181 (s), 1108 (m), 1022 (m)

MS: (EI, 70 eV)222 (M⁺, 4), 179 (3), 163 (9), 118 (5), 116 (46), 107 (74), 74 (100)Opt. Rot.: [α]_D²⁴ +31.24 (c = 1.0, EtOH)TLC: *R_f* 0.30 (hexanes/EtOAc, 8/2) [UV(254)/KMnO₄]SFC: *t_R* (2*S*,3*R*)-**9ca**, 4.37 (91.1%); *t_R* (2*R*,3*S*)-**9ca**, 6.38 (8.9%) (Chiralpak AS, 125 psi, 40 °C, 2.0% CH₃OH in CO₂, 2.0 mL/min, 220 nm)**Preparation of Ethyl 8-(*tert*-Butyldimethylsilyl)-3-hydroxy-2-methyloctanoate (9bp)**

A flame-dried, 25 mL, 2-neck, round-bottom flask containing a solution of 42 mg of bisphosphoramidate (*R,R*)-**6** (0.05 mmol, 0.05 equiv), 8 μ L of *i*-Pr₂EtN (0.05 mmol, 0.05 equiv) and 230 mg of **5p** (1.0 mmol) in CH₂Cl₂ (5 mL) was cooled to -78 °C under nitrogen. To the resulting solution was added 123 μ L of SiCl₄ (1.1 mmol, 1.1 equiv). Then 260 mg of **2b** (1.2

mmol, 1.2 equiv) was added dropwise over 5 min to the reaction mixture. The solution was allowed to stir at -78°C for 24 h whereupon the cold reaction mixture was poured into a rapidly stirring sat. aq. NaHCO_3 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 25 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 to yield, after silica gel column chromatography (hexanes/EtOAc, 9/1), 169 mg (51 %) of **9bp** as a colorless oil. Enantiomeric analysis was determined on the 3,5-dinitrobenzoate derivative **35**.

Data for **9bp**:

^1H NMR: (400 MHz, CDCl_3)

4.16 (q, $J = 7.1$, 2 H, $\text{H}_2\text{C}(12)$), 3.61 (m, 1 H, $\text{HC}(3)$), 3.59 (t, $J = 6.4$, 2 H, $\text{H}_2\text{C}(8)$), 2.59 (d, $J = 6.8$, 1 H, OH), 2.49 (pent, $J = 6.6$, 1 H, $\text{HC}(2)$), 1.53 – 1.34 (m, 8 H, $\text{HC}(4,5,6,7)$), 1.27 (t, $J = 7.1$, 3 H, $\text{H}_3\text{C}(13)$), 1.20 (d, $J = 7.3$, 3 H, $\text{H}_3\text{C}(14)$), 0.88 (s, 9 H, $\text{H}_3\text{C}(11)$), 0.04 (s, 6 H, $\text{H}_3\text{C}(9)$)

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

176.11 (C(1)) 73.31 (C(3)), 63.16 (C(8)), 60.55 (C(12)), 45.12 (C(2)), 34.78 (C(4)), 32.77 (C(7)), 25.96 (C(6)), 25.76 (C(11)), 25.34 (C(5)), 18.36 (C(10)), 14.41 (C(13)), 14.19 (C(14)), -5.28 (C(9))

IR: (neat)

3462 (w), 2934 (s), 2852 (s), 1735 (s), 1718 (s), 1463 (m), 1388 (m), 1255 (s), 1184 (s), 1099 (s)

MS: (EI, 70 eV)

333 (M^{+1} , 2), 288 (3), 275 (15), 231 (14), 211 (11), 185 (13), 173 (13), 155 (12), 131 (42), 109 (100), 75 (89)

Opt. Rot.: $[\alpha]_{\text{D}}^{24} +5.14$ (c = 1.0, EtOH)

TLC: R_f 0.50 (hexanes/EtOAc, 8/2) [KMnO_4]

SFC: t_R (2*R*,3*R*)-**35**, 15.78 (3.3%); t_R (2*S*,3*S*)-**35**, 16.62 (96.7%) (Whelk-O1, 125 psi, 40 $^{\circ}\text{C}$, 6.0% CH_3OH in CO_2 , 3.0 mL/min, 220 nm)

Analysis: $\text{C}_{17}\text{H}_{36}\text{O}_4\text{Si}$ (332.55)

Calcd: C, 61.40; H, 10.91%

Found: C, 61.23; H, 11.12%

Preparation of Ethyl 8-(*tert*-Butyldimethylsilyl) 3-[*N*-(3,5-dinitrophenyl)carbamoyl]-2-methyloctanoate (35**)**

In a 10 mL, 1-neck, round-bottom flask fitted with a reflux condenser a solution of 120 mg of 3,5-dinitrobenzoylazide (0.51 mmol, 1.2 equiv) was heated at 120 °C for 20 minutes. A solution of ethyl 8-(*tert*-butyldimethylsilyl)-3-hydroxy-2-methyl octanoate **9bp** (0.42 mmol) in 1 mL toluene was then added and heating continued for 4 h. The solution was then cooled to room temperature, washed with 5 mL 10 % aqueous HCl, 5 mL saturated aqueous NaHCO₃ and 5 mL brine prior to drying over Na₂SO₄ (1 g), filtration and concentration *in vacuo*. Purification of the residue by silica gel column chromatography (hexanes/EtOAc, 8/2), afforded 150 mg (66%) of **35** as a white crystalline solid.

Data for **35**:

mp: 98-100 °C

¹H NMR: (400 MHz, C₆D₆)

8.14 (m, 1 H, HC(16)), 7.90 (m, 2 H, HC(14)), 6.08 (bs, 1 H, NH), 5.25 (q, *J* = 7.1, 1 H, HC(3)), 4.00 (q, *J* = 7.1, 2 H, H₂C(9)), 3.54 (t, *J* = 6.4, 2 H, H₂C(8)), 2.70 (pent, *J* = 7.1, 1 H, HC(2)), 1.62-1.40 (m, 8 H, HC(4,5,6,7)), 1.08 (d, *J* = 7.1, 3 H, H₃C(11)), 1.00 (t, *J* = 7.1, 3 H, H₃C(10)), 0.97 (s, 9 H, H₃C(19)), 0.06 (s, 6 H, H₃C(17))

¹³C NMR: (100 MHz, C₆D₆)

172.93 (C(1)), 152.31 (C(12)), 148.51 (C(15)), 140.02 (C(13)), 117.28 (C(14)), 112.33 (C(16)), 76.95 (C(3)), 63.00 (C(8)), 60.67 (C(9)), 43.61 (C(2)), 33.05 (C(4)), 31.84 (C(7)), 26.16 (C(5)), 26.09 (C(19)), 25.20 (C(6)), 18.46 (C(18)), 14.19 (C(10)), 13.19 (C(11)), -5.21 (C(17))

TLC: *R_f* 0.65 (hexanes/EtOAc, 8/2) [UV(254)/KMnO₄]

SFC: t_R (2*R*,3*R*)-**35**, 15.78 (3.3%); t_R (2*S*,3*S*)-**35**, 16.62 (96.7%) (Whelk-O1, 125 psi, 40 °C, 6.0% CH₃OH in CO₂, 3.0 mL/min, 220 nm)

Preparation of Ethyl 8-Benzyloxy-3-hydroxy-2-methyloctanoate (**9bq**)

A flame-dried, 25 mL, 2-neck, round-bottom flask containing a solution of 42 mg of bis-phosphoramidate (*R,R*)-**6** (0.05 mmol, 0.05 equiv), 8 μ L of *i*-Pr₂EtN (0.05 mmol, 0.05 equiv) and 206 mg of **5q** (1.0 mmol) in CH₂Cl₂ (5 mL) was cooled to –78 °C under nitrogen. To the resulting solution was added 123 μ L of SiCl₄ (1.1 mmol, 1.1 equiv). Then 260 mg of **2b** (1.2 mmol, 1.2 equiv) was added dropwise over 5 min to the reaction mixture. The solution was allowed to stir at –78 °C 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 25 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 to yield, after silica gel column chromatography (hexanes/EtOAc, 8/2), 215 mg (70 %) of **9bq** as a colorless oil.

Data for 9bq:

¹H NMR: (400 MHz, CDCl₃)

7.35 (m, 5 H, HC(11,12,13)), 4.49 (s, 2 H, H₂C(9)), 4.16 (q, *J* = 7.1, 2 H, H₂C(14)), 3.63 (m, 1 H, HC(3)), 3.46 (t, *J* = 6.6, 2 H, H₂C(8)), 2.59 (d, *J* = 6.8, 1 H, OH), 2.49 (pent, *J* = 7.1, 1 H, HC(2)), 1.62 (pent, *J* = 7.6, 2 H, H₂C(7)), 1.59 – 1.37 (m, 6 H, HC(4,5,6)), 1.27 (t, *J* = 7.1, 3 H, H₃C(15)), 1.20 (d, *J* = 7.1, 3 H, H₃C(16))

¹³C NMR: (100 MHz, CDCl₃)
 176.10 (C(1)), 138.61 (C(10)), 128.33 (C(12)), 127.61 (C(13)), 127.47 (C(11)),
 73.26 (C(3)), 72.87 (C(9)), 70.31 (C(8)), 60.56 (C(14)), 45.12 (C(2)), 34.70
 (C(4)), 29.68 (C(7)), 26.13 (C(6)), 25.36 (C(5)), 14.41 (C(15)), 14.19 (C(16))

IR: (neat)
 3456 (m), 2930 (s), 2938 (s), 2859 (s), 1731 (s), 1496 (m), 1455 (s), 1372 (s),
 1259 (s), 1184 (s), 1100 (s), 1028 (s)

MS: (EI, 70 eV)
 309 (M⁺, 3), 245 (1), 199 (4), 184 (13), 153 (5), 131 (8), 115 (6), 102 (25), 91
 (100), 74 (11)

Opt. Rot.: [α]_D²⁴ +19.08 (c = 1.0, EtOH)

TLC: *R_f* 0.30 (hexanes/EtOAc, 8/2) [UV(254)/KMnO₄]

SFC: *t_R* (2*R*,3*R*)-**9bq**, 5.45 (4.5%); *t_R* (2*S*,3*S*)-**9bq**, 5.92 (95.5%) (Chiralpak OJ, 125 psi,
 40 °C, 4.0% CH₃OH in CO₂, 3.0 mL/min, 220 nm)

Analysis: C₁₈H₂₈O₄ (308.41)
 Calcd: C, 70.10; H, 9.15%
 Found: C, 69.86; H, 9.38%

Preparation of Ethyl 8-Benzoyl-3-hydrox-2-methyloctanoate (**9br**)

A flame-dried, 25 mL, 2-neck, round-bottom flask containing a solution of 42 mg of bis-phosphoramidate (*R,R*)-**6** (0.05 mmol, 0.05 equiv), 8 μ L of *i*-Pr₂EtN (0.05 mmol, 0.05 equiv) and 220 mg of **5r** (1.0 mmol) in CH₂Cl₂ (5 mL) was cooled to -78 °C under nitrogen. To the resulting solution was added 123 μ L of SiCl₄ (1.1 mmol, 1.1 equiv). Then 260 mg of **2b** (1.2 mmol, 1.2 equiv) was added dropwise over 5 min to the reaction mixture. The solution 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 25 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 to yield, after silica gel column chromatography (hexanes/EtOAc, 4/1), 193 mg (60 %) of **9br** as a colorless oil. Enantiomeric analysis was determined on the 3,5-dinitrophenylcarbamate **36**.

Data for **9br**:

¹H NMR: (400 MHz, CDCl₃)

8.04 (m, 2 H, HC(11)), 7.55 (m, 1 H, HC(13)), 7.42 (m, 2 H, HC(12)), 4.32 (t, *J* = 6.6, 2 H, H₂C(8)), 4.16 (q, *J* = 7.1, 2 H, H₂C(14)), 3.65 (m, 1 H, HC(3)), 2.64 (d, *J* = 6.8, 1 H, OH), 2.50 (pent, *J* = 7.1, 1 H, HC(2)), 1.78 (pent, *J* = 6.8, 2 H, H₂C(7)), 1.66 – 1.44 (m, 6 H, HC(4,5,6)), 1.27 (t, *J* = 7.1, 3 H, H₃C(15)), 1.21 (d, *J* = 7.3, 3 H, H₃C(16))

¹³C NMR: (100 MHz, CDCl₃)

176.08 (C(1)), 166.65 (C(9)), 132.81 (C(13)), 130.42 (C(10)), 129.51 (C(11)), 128.31 (C(12)), 73.70 (C(3)), 64.94 (C(8)), 60.59 (C(14)), 45.13 (C(2)), 34.65 (C(4)), 28.71 (C(7)), 26.03 (C(6)), 25.27 (C(5)), 14.41 (C(15)), 14.19 (C(16))

IR: (neat)

3513 (m), 2979 (m), 2940 (s), 2861 (m), 1719 (s), 1602 (w), 1452 (s), 1376 (m), 1315 (m), 1276 (s), 1176 (s), 1114 (s), 1070 (s), 1026 (s)

MS: (EI, 70 eV)

322 (M⁺, 1), 258 (3), 221 (8), 192 (14), 123 (58), 105 (100), 77 (34)

Opt. Rot.: [α]_D²⁴ -2.40 (c = 1.0, EtOH)

TLC: *R_f* 0.27 (hexanes/EtOAc, 8/2) [UV(254)/KMnO₄]

SFC: *t_R* (2*R*,3*R*)-**36**, 14.07 (5.0%); *t_R* (2*S*,3*S*)-**36**, 14.75 (95.0%) (Whelk-O1, 150 psi, 40 °C, 14.0% CH₃OH in CO₂, 2.0 mL/min, 220 nm)

Analysis: C₁₈H₂₆O₅ (322.40)

Calcd: C, 67.06; H, 8.43%

Found; C, 66.77; H, 8.24%

Preparation of Ethyl 8-Benzoyl-3-[*N*-(3,5-dinitrophenyl)carbamoyl]octanoate (**36**)

In a 10 mL, 1-neck, round-bottom flask fitted with a reflux condenser a solution of 84 mg of 3,5-dinitrobenzoyl azide (0.36 mmol, 1.2 equiv) in 5 mL of toluene was heated at 120 °C for 20 minutes. A solution of **9br** (0.29 mmol) in 1 mL toluene was then added and heating continued for 4 h. The solution was then cooled to room temperature, washed with 5 mL 10 % aqueous HCl, 5 mL saturated aqueous NaHCO₃ and 5 mL brine prior to drying over Na₂SO₄ (1 g), filtration and concentration *in vacuo*. Purification of the residue by silica gel column chromatography (hexanes/EtOAc, 8/2), afforded 121 mg (78%) of **36** as a white crystalline solid.

Data for **36**:

mp: 116-118 °C

¹H NMR: (400 MHz, C₆D₆)

8.25 (m, 3 H, HC(20,21)), 8.17 (m, 2 H, HC(19)), 7.14 (m, 3 H, HC(14,16)), 6.72 (bs, 1 H, NH), 5.36 (m, 1 H, HC(3)), 4.29 (m, 2 H, H₂C(8)), 4.11 (dq, *J* = 2.7, 7.1, 2 H, H₂C(9)), 2.85 (pent, *J* = 7.1, 1 H, HC(2)), 1.67-1.29 (m, 8 H, HC(4,5,6,7)), 1.20 (d, *J* = 7.1, 3 H, H₃C(11)), 1.10 (t, *J* = 3 H, H₃C(10))

¹³C NMR: (100 MHz, C₆D₆)

173.01 (C(1)), 166.60 (C(17)), 152.45 (C(12)), 148.56 (C(15)), 140.25 (C(13)), 133.02 (C(21)), 130.82 (C(18)), 129.79 (C(19)), 128.61 (C(20)), 117.40 (C(14)), 112.35 (C(16)), 76.85 (C(3)), 64.70 (C(8)), 60.78 (C(9)), 43.61 (C(2)), 31.30 (C(4)), 28.69 (C(7)), 25.88 (C(6)), 24.74 (C(5)), 14.17 (C(10)), 13.10 (C(11))

TLC: *R_f* 0.37 (hexanes/EtOAc, 8/2) [UV(254)/KMnO₄]

SFC: *t_R* (2*R*,3*R*)-**36**, 14.07 (5.0%); *t_R* (2*S*,3*S*)-**36**, 14.75 (95.0%) (Whelk-O1, 150 psi, 40 °C, 14.0% CH₃OH in CO₂, 2.0 mL/min, 220 nm)

General Procedure 6. Addition of Silyl Dienol Ethers to Conjugated Aldehydes.**Preparation of (2*E*,5*R*) Ethyl 5-Hydroxy-5-phenyl-2-pentenoate ((2*E*,5*R*)-14aa)**

A flame-dried, 25 mL, 2-neck, round-bottom flask containing a solution of 8.4 mg of bis-phosphoramidate (*R,R*)-**6** (0.01 mmol, 0.01 equiv) and 102 μL of benzaldehyde **5a** (1.0 mmol) in CH_2Cl_2 (5 mL) was cooled to $-78\text{ }^\circ\text{C}$ under nitrogen in a dry ice/isopropanol bath. To the resulting solution was added 123 μL of SiCl_4 (1.1 mmol, 1.1 equiv). Then 272 mg of **4a** (1.2 mmol, 1.2 equiv) was added dropwise over 5 min to the reaction mixture. The solution was allowed to stir at $-78\text{ }^\circ\text{C}$ for 3 h in a dry ice/isopropanol bath 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 25 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 silica gel column chromatography (hexanes/EtOAc, 4/1) to yield 196 mg (89 %) of (2*E*,5*R*)-**14aa** as a colorless oil. NMR spectral data matched that previously reported in the literature.²³

Data for (2*E*,5*R*)-14aa:

^1H NMR: (400 MHz, CDCl_3)

7.4-7.25 (m, 5 H, HC(7,8,9)), 6.95 (dt, $J = 15.6, 7.1$, 1 H, HC(3)), 5.87 (d, $J = 15.6$, 1 H, HC(2)), 4.81 (m, 1 H, HC(5)), 4.16 (q, $J = 7.1$, 2 H, $\text{H}_2\text{C}(10)$), 2.64 (m, 2 H, $\text{H}_2\text{C}(4)$), 2.2 (bs, 1 H, OH), 1.26 (t, $J = 7.1$, 3 H, $\text{H}_3\text{C}(11)$)

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

166.29 (C(1)), 144.67 (C(3)), 142.97 (C(6)), 128.60 (C(8)), 127.89 (C(9)), 125.69 (C(7)), 124.0 (C(2)), 73.06 (C(5)), 60.29 (C(10)), 41.83 (C(4)), 14.21 (C(11))

IR: (neat)

3440 (m), 3029 (w), 2983 (m), 2939 (w), 2904 (w), 1712 (s), 1654 (s), 1494 (m), 1454 (m), 1369 (m), 1315 (s), 1278 (s), 1199 (s), 1160 (s), 1043 (s)

MS: (EI, 70 eV)

221 (M^{+1} , 3), 203 (32), 175 (3), 129 (11), 114 (100), 107 (87), 86 (37)

Opt. Rot.: $[\alpha]_D^{24} +22.86$ ($c = 1.0$, EtOH), lit. $[\alpha]_D^{24} +10.4$ ($c=1.13$, EtOH) for (5*R*)-**XX**²³

TLC: R_f 0.26 (hexanes/EtOAc, 4/1) [UV(254)/KMnO₄]

SFC: t_R (5*R*)-**14aa**, 3.25 (98.8%); t_R (5*S*)-**14aa**, 4.17 (1.2%) (Chiralpak AD, 125 psi, 40 °C, 10.0% CH₃OH in CO₂, 3.0 mL/min, 220 nm)

Analysis: C₁₃H₁₆O₃ (220.26)

Calcd: C, 70.89; H, 7.32%

Found: C, 70.64; H, 7.28%

Preparation of (2*E*,5*R*,6*E*) Ethyl 5-Hydroxy-7-phenyl-2,6-heptadienoate ((2*E*,5*R*,6*E*)-**14ag**)

Following General Procedure 6, 8.4 mg of bis-phosphoramidate (*R,R*)-**6** (0.01 mmol, 0.01 equiv) was combined with 126 μ L of cinnamaldehyde **5g** (1.0 mmol), 123 μ L of SiCl₄ (1.1 mmol, 1.1 equiv) and 272 mg of **4a** (1.2 mmol, 1.2 equiv) to yield, after silica gel column chromatography (silica gel, hexanes/EtOAc, 4/1), 207 mg (84 %) of (2*E*,5*R*,6*E*)-**14ag** as a colorless oil.

Data for (2*E*,5*R*,6*E*)-**14ag**:

¹H NMR: (400 MHz, CDCl₃)

7.4-7.2 (m, 5 H, HC(9,10,11)), 7.0 (dt, $J = 15.6, 7.3$, 1 H, HC(3)), 6.62 (d, $J = 16.1$, 1 H, HC(7)), 6.23 (dd, $J = 15.9, 6.6$, 1 H, HC(6)), 5.94 (dt, $J = 15.6, 1.5$, 1 H, HC(2)), 4.45 (q, $J = 6.1$, 1 H, HC(5)), 4.18 (q, $J = 7.1$, 2 H, H₂C(12)), 2.55 (t, $J = 7.1$, 2 H, H₂C(4)), 1.28 (t, $J = 7.08$, 3 H, H₃C(13))

¹³C NMR: (100 MHz, CDCl₃)

166.24 (C(1)), 144.17 (C(3)), 136.24 (C(8)), 131.13 (C(7)), 130.87 (C(6)), 128.61 (C(9)), 127.92 (C(11)), 126.54 (C(10)), 124.24 (C(2)), 71.53 (C(5)), 60.33 (C(12)), 40.12 (C(4)), 14.23 (C(13))

IR: (neat)

3430 (m), 3027 (w), 2983 (m), 2937 (w), 2904 (w), 1716 (s), 1654 (m), 1494 (w), 1448 (w), 1369 (m), 1317 (m), 1272 (m), 1201 (m), 1164 (m), 1041 (m)

MS: (EI, 70 eV)

245 (M^{-1} , 3), 229 (100), 183 (11), 155 (17), 133 (31), 115 (11)

Opt. Rot.: $[\alpha]_D^{24}$ -17.86 ($c = 1.0$, EtOH)

TLC: R_f 0.25 (hexanes/EtOAc, 4/1) [UV(254)/KMnO₄]

SFC: t_R (*R*)-**14ag**, 4.15 (98.3%); t_R (*S*)-**14ag**, 4.41 (1.7%) (Chiralpak AD, 125 psi, 40 °C, 10.0% CH₃OH in CO₂, 3.0 mL/min, 220 nm)

Analysis: C₁₅H₁₈O₃ (246.30)

Calcd: C, 73.15; H, 7.37%

Found: C, 72.91; H, 7.38%

General Procedure 7. Addition of Silyl Dienol Ethers to Aliphatic Aldehydes. Preparation of (*2E,5S*) Ethyl 5-Hydroxy-7-phenyl-2-heptenoate ((*2E,5S*)-14ak**)**

A flame-dried, 25 mL, 2-neck flask containing a solution of 42 mg of bis-phosphoramidate (*R,R*)-**6** (0.05 mmol, 0.05 equiv), 8 μ L of *i*-Pr₂EtN (0.05 mmol, 0.05 equiv) and 132 μ L of hydrocinnamaldehyde **5k** (1.0 mmol) in CH₂Cl₂ (5 mL) was cooled to -78 °C under nitrogen. To the resulting solution was added 123 μ L of SiCl₄ (1.1 mmol, 1.1 equiv). Then 272 mg of **4a** (1.2 mmol, 1.2 equiv) was added dropwise over 5 min to the reaction mixture. The solution was allowed to stir at -78 °C 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 25 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 silica gel

column chromatography (hexanes/EtOAc, 4/1) to yield 167 mg (68 %) of (2*E*,5*S*)-**14ak** as a colorless oil. NMR spectral data matched that previously reported in the literature.²⁴

Data for (2*E*,5*S*)-**14ak**:

¹H NMR: (500 MHz, CDCl₃)

7.3-7.18 (m, 5 H, HC(9,10,11)), 6.96 (dt, *J* = 15.6, 7.7, 1 H, HC(3)), 5.9 (dt, *J* = 15.6, 1.5, 1 H, HC(2)), 4.19 (q, *J* = 7.3, 2 H, H₂C(12)), 3.78 (m, 1 H, HC(5)), 2.80-2.69 (m, 2 H, H₂C(4)), 2.42-2.35 (m, 2 H, H₂C(7)), 1.81 (m, 2 H, H₂C(6)), 1.28 (t, *J* = 7.1, 3 H, H₃C(13))

¹³C NMR: (125 MHz, CDCl₃)

166.27 (C(1)), 144.27 (C(3)), 141.58 (C(8)), 128.49 (C(9)), 128.41 (C(10)), 125.99 (C(11)), 124.13 (C(2)), 69.79 (C(5)), 60.31 (C(12)), 40.31 (C(4)), 38.64 (C(7)), 31.92 (C(6)), 14.20 (C(13))

IR: (neat)

3442 (m), 3025 (w), 2981 (w), 2935 (m), 2863 (w), 1718 (s), 1654 (m), 1496 (m), 1454 (m), 1369 (m), 1319 (m), 1270 (s), 1211 (m), 1176 (s), 1045 (s)

MS: (EI, 70 eV)

249 (M⁺, 1), 230 (15), 203 (5), 156 (7), 135 (7), 114 (80), 91 (100)

Opt. Rot.: [α]_D²⁴ -12.77 (c = 1.0, EtOH)

TLC: *R*_f 0.21 (hexanes/EtOAc, 4/1) [UV(254)/KMnO₄]

SFC: *t*_R (*R*)-**14ak**, 7.95 (4.7%); *t*_R (*S*)-**14ak**, 8.29 (95.3%) (Chiralpak AD, 125 psi, 40 °C, 7.0% CH₃OH in CO₂, 2.0 mL/min, 220 nm)

Analysis: C₁₅H₂₀O₃ (248.32)

Calcd: C, 72.55; H, 8.12%

Found: C, 72.44; H, 8.23%

Preparation of (2*E*,5*R*) Methyl 5-Hydroxy-2-methyl-5-phenyl-2-pentenoate ((2*E*,5*R*)-14ba)

Following General Procedure 6, 8.4 mg of bis-phosphoramidate (*R,R*)-6 (0.01 mmol, 0.01 equiv) was combined with 102 μ L of benzaldehyde **5a** (1.0 mmol), 123 μ L of SiCl₄ (1.1 mmol, 1.1 equiv) and 272 mg of **4b** (1.2 mmol, 1.2 equiv) to yield, after silica gel column chromatography (hexanes/EtOAc, 4/1), 205 mg (93 %) of (2*E*,5*R*)-**14ba** as a colorless oil.

Data for (2*E*,5*R*)-14ba:

¹H NMR: (500 MHz, CDCl₃)

7.4-7.28 (m, 5 H, HC(7,8,9)), 6.83 (t, *J* = 7.5, 1 H, HC(3)), 4.83 (dd, *J* = 7.7, 5.2, 1 H, HC(5)), 3.72 (s, 3 H, H₃C(10)), 2.71-2.56 (m, 2 H, H₂C(4)), 2.0 (s, 1 H, OH), 1.79 (s, 3 H, H₃C(11))

¹³C NMR: (125 MHz, CDCl₃)

168.37 (C(1)), 143.17 (C(6)), 137.68 (C(3)), 129.95 (C(8)), 128.60 (C(9)), 127.88 (C(7)), 125.71 (C(2)), 73.46 (C(5)), 51.76 (C(10)), 38.43 (C(4)), 12.58 (C(11))

IR: (neat)

3453 (m), 3029 (w), 2950 (m), 1710 (s), 1648 (m), 1436 (s), 1278 (s), 1195 (s), 1124 (s), 1083 (s), 1051 (s)

MS: (EI, 70 eV)

221 (M⁺, 15), 203 (100), 171 (20), 143 (6), 114 (30)

Opt. Rot.: [α]_D²⁴ +2.51 (c = 1.0, EtOH)

TLC: *R_f* 0.22 (hexanes/EtOAc, 4/1) [UV(254)/KMnO₄]

SFC: *t_R* (*S*)-**14ba**, 4.17 (0.5%); *t_R* (*R*)-**14ba**, 5.33 (99.5%) (Chiralpak AD, 125 psi, 40 °C, 7.0% CH₃OH in CO₂, 3.0 mL/min, 220 nm)

Analysis: C₁₃H₁₆O₃ (220.20)

Calcd: C, 70.89; H, 7.32%

Found: C, 70.74; H, 7.31%

Preparation of (2*E*,6*E*) Methyl 5-Hydroxy-2-methyl-7-phenyl-2,6-heptadienoate ((2*E*,6*E*)-14bg**)**

Following General Procedure 6, 8.4 mg of bis-phosphoramidate (*R,R*)-**6** (0.01 mmol, 0.01 equiv) was combined with 126 μ L of cinnamaldehyde **5g** (1.0 mmol), 123 μ L of SiCl_4 (1.1 mmol, 1.1 equiv) and 272 mg of **4b** (1.2 mmol, 1.2 equiv) to yield, after silica gel column chromatography (hexanes/EtOAc, 4/1), 216 mg (88 %) of (2*E*,6*E*)-**14bg** as a colorless oil.

Data for (2*E*,6*E*)-**14bg**:

^1H NMR: (500 MHz, CDCl_3)

7.4-7.2 (m, 5 H, HC(9,10,11)), 6.85 (t, $J = 7.5$, 1 H, HC(3)), 6.63 (d, $J = 15.9$, 1 H, HC(7)), 6.24 (dd, $J = 16.1$, 6.6, 1 H, HC(6)), 4.45 (q, $J = 6.0$, 1 H, HC(5)), 3.73 (s, 3 H, $\text{H}_3\text{C}(12)$), 2.53 (m, 2 H, $\text{H}_2\text{C}(4)$), 1.88 (s, 3 H, $\text{H}_3\text{C}(13)$), 1.82 (s, 1 H OH)

^{13}C NMR: (125 MHz, CDCl_3)

168.37 (C(1)), 137.28 (C(3)), 136.36 (C(8)), 131.16 (C(7)), 130.99 (C(6)), 130.04 (C(9)), 128.63 (C(11)), 127.88 (C(10)), 126.55 (C(2)), 71.93 (C(5)), 51.29 (C(12)), 36.65 (C(4)), 12.75 (C(13))

IR: (neat)

3423 (m), 3025 (w), 2950 (m), 1710 (s), 1648 (m), 1494 (w), 1436 (m), 1282 (m), 1195 (m), 1128 (m), 1097 (m), 1081 (m), 1037 (m)

MS: (EI, 70 eV)

245 (M^+ , 4), 229 (73), 197 (17), 169 (26), 133 (100), 115 (18)

Opt. Rot.: $[\alpha]_{\text{D}}^{24} -36.88$ ($c = 1.0$, EtOH)

TLC: R_f 0.24 (hexanes/EtOAc, 4/1) [UV(254)/ KMnO_4]

SFC: t_R (*S*)-**14bg**, 3.78 (0.4%); t_R (*R*)-**14bg**, 4.62 (99.6%) (Chiralpak AD, 125 psi, 40 $^\circ\text{C}$, 10.0% CH_3OH in CO_2 , 3.0 mL/min, 220 nm)

Analysis: C₁₅H₁₈O₃ (246.30)

Calcd: C, 73.15; H, 7.37%

Found: C, 73.28; H, 7.24%

Preparation of (2*E*,5*R*) Ethyl 5-Hydroxy-3-methyl-5-phenyl-2-pentenoate ((2*E*,5*R*)-14ca**)**

Following General Procedure 6, 8.4 mg of bis-phosphoramidate (*R,R*)-**6** (0.01 mmol, 0.01 equiv) was combined with 102 μ L of benzaldehyde **5a** (1.0 mmol), 123 μ L of SiCl₄ (1.1 mmol, 1.1 equiv) and 290 mg of **4c** (1.2 mmol, 1.2 equiv) to yield, after silica gel column chromatography (hexanes/EtOAc, 4/1), 214 mg (91 %) of (*2E*,5*R*)-**14ca** as a colorless oil. NMR spectral data matched that previously reported in the literature.²⁵

Data for (2*E*,5*R*)-**14ca**:

¹H NMR: (500 MHz, CDCl₃)

7.37-7.26 (m, 5 H, HC(7,8,9)), 5.77 (s, 1 H, HC(2)), 4.90 (dd, *J* = 8.8, 4.6, 1 H, HC(5)), 4.15 (q, *J* = 7.0, 2 H, H₂C(10)), 2.57 (dd, *J* = 13.9, 8.8, 1 H, HC(4)), 2.51 (dd, *J* = 13.7, 4.4, 1 H, HC(4)), 2.22 (s, 3 H, H₃C(12)), 2.04 (s, 1 H, OH), 1.27 (t, *J* = 7.1, 3 H, H₃C(11))

NOE ¹H NMR: (500 MHz, CDCl₃)

Irradiation at 5.77 ppm (HC(2)) enhanced signal at 2.57 ppm (HC(4)) in major isomer

¹³C NMR: (125 MHz, CDCl₃)

166.44 (C(1)), 155.63 (C(3)), 143.69 (C(6)), 128.59 (C(8)), 127.85 (C(9)), 125.67 (C(7)), 118.55 (C(2)), 72.09 (C(5)), 59.64 (C(10)), 50.70 (C(4)), 18.94 (C(12)), 14.23 (C(11))

IR: (neat)

3451 (m), 3029 (w), 2981 (m), 2940 (m), 2906 (m), 1710 (s), 1648 (s), 1452 (m), 1369 (m), 1226 (s), 1151 (s), 1058 (s)

MS: (EI, 70 eV)

235 (M^{+1} , 7), 217 (100), 189 (7), 171 (15), 128 (80), 107 (37), 100 (27), 83 (30)

Opt. Rot.: $[\alpha]_D^{24} +19.61$ ($c = 1.0$, EtOH)

TLC: R_f 0.36 (hexanes/EtOAc, 4/1) [UV(254)/KMnO₄]

SFC: t_R (*R*)-**14ca**, 4.04 (96.1%); t_R (*S*)-**14ca**, 7.92 (3.9%) (Chiralpak AD, 125 psi, 40 °C, 7.5% CH₃OH in CO₂, 3.0 mL/min, 220 nm)

Analysis: C₁₄H₁₈O₃ (234.29)

Calcd: C, 71.77; H, 7.74%

Found: C, 71.65; H, 7.98%

Preparation of (2*E*,6*E*) Ethyl 5-Hydroxy-3-methyl-7-phenyl-2,6-heptadienoate ((2*E*,6*E*)-14cg**)**

Following General Procedure 6, 8.4 mg of bis-phosphoramidate (*R,R*)-**6** (0.01 mmol, 0.01 equiv) was combined with 126 μ L of cinnamaldehyde **5g** (1.0 mmol), 123 μ L of SiCl₄ (1.1 mmol, 1.1 equiv) and 290 mg of **4c** (1.2 mmol, 1.2 equiv) to yield, after silica gel column chromatography (hexanes/EtOAc, 4/1), 253 mg (97%, 2*E*/2*Z* 97/3) of (2*E*,6*E*)-**14cg** as a colorless oil.

Data for (2*E*,6*E*)-14cg**:**

¹H NMR: (500 MHz, CDCl₃)

7.39-7.25 (m, 5 H, HC(9,10,11)), 6.63 (d, $J = 15.8$, 1 H, HC(7)), 6.22 (dd, $J = 16.0$, 6.5, 1 H, HC(6)), 5.79 (s, 1 H, HC(2)), 4.53 (q, $J = 6.7$, 1 H, HC(5)), 4.15 (q, $J = 7.2$, 2 H, H₂C(12)), 2.45 (d, $J = 6.7$, 2 H, H₂C(4)), 2.25 (s, 3 H, H₃C(14)), 1.80 (s, 1 H, OH), 1.28 (t, $J = 7.2$, 3 H, H₃C(13))

NOE ¹H NMR: (500 MHz, CDCl₃)

Irradiation at 5.79 ppm (HC(2)) enhanced signal at 2.45 ppm (HC(4)) in major isomer

¹³C NMR: (125 MHz, CDCl₃)
 166.67 (C(1)), 155.57 (C(3)), 136.60 (C(8)). 131.37 (C(7)), 130.99 (C(6)), 128.85 (C(9)), 128.09 (C(11)), 126.77 (C(10)), 118.86 (C(2)), 70.77 (C(5)), 59.89 (C(12)), 49.01 (C(4)), 19.28 (C(14)), 14.47 (C(13))

IR: (neat)
 3440 (m), 3025 (m), 2981 (m), 2939 (w), 2906 (w), 1712 (s), 1646 (m), 1494 (w), 1448 (m), 1382 (m), 1369 (m), 1295 (m), 1224 (s), 1149 (s), 1099 (m), 1058 (m)

MS: (EI, 70 eV)
 260 (M⁺, 1), 243 (2), 213 (2), 185 (2), 157 (5), 133 (100), 115 (18), 103 (21), 91 (13), 72 (24)

Opt. Rot.: [α]_D²⁴ -9.94 (c = 1.0, EtOH)

TLC: *R_f* 0.32 (hexanes/EtOAc, 4/1) [UV(254)/KMnO₄]

SFC: *t_R* (*R*)-**14cg**, 4.10 (94.0%); *t_R* (*S*)-**14cg**, 7.35 (6.0%) (Chiralpak AD, 125 psi, 40 °C, 12.0% CH₃OH in CO₂, 3.0 mL/min, 220 nm)

Analysis: C₁₆H₂₀O₃ (260.33)
 Calcd: C, 73.82; H, 7.74%
 Found: C, 73.55; H, 7.83%

Preparation of (2*E*) Ethyl 5-Hydroxy-3-methyl-7-phenyl-2-heptenoate ((2*E*)-**14ck**)

Following General Procedure 7, 42 mg of bis-phosphoramidate (*R,R*)-**6** (0.05 mmol, 0.05 equiv) was combined with 8 μL of *i*-Pr₂EtN (0.05 mmol, 0.05 equiv), 126 μL of hydrocinnamaldehyde **5k** (1.0 mmol), 123 μL of SiCl₄ (1.1 mmol, 1.1 equiv) and 290 mg of **4c** (1.2 mmol, 1.2 equiv) to yield, after silica gel column chromatography (hexanes/EtOAc, 9/1), 190 mg (73 %) of (2*E*)-**14ck** as a colorless oil.

Data for (2E)-14ck:¹H NMR: (500 MHz, CDCl₃)

7.31-7.18 (m, 5 H, HC(9,10,11)), 5.74 (s, 1 H, HC(2)), 4.15 (q, $J = 7.2$, 2 H H₂C(12)), 3.84 (pent, $J = 6.5$, 1 H, HC(5)), 2.83 (dt, $J = 13.7$, 7.9, 1 H, HC(7)), 2.70 (dt, $J = 13.8$, 8.3, 1 H, HC(7)), 2.33 (dd, $J = 13.5$, 4.0, 1 H, HC(4)), 2.27 (dd, $J = 13.5$, 8.6, 1 H, HC(4)), 2.17 (s, 3 H, H₃C(14)), 1.79 (q, $J = 7.72$, 2 H, H₂C(6)), 1.65 (s, 1 H, OH), 1.28 (t, $J = 7.1$, 3 H, H₃C(13))

NOE ¹H NMR: (500 MHz, CDCl₃)

Irradiation at 5.74 ppm (HC(2)) enhanced signal at 2.27 ppm (HC(4)) in major isomer

¹³C NMR: (125 MHz, CDCl₃)

166.41 (C(1)), 156.06 (C(3)), 141.69 (C(8)), 128.46 (C(9)), 128.40 (C(10)), 125.95 (C(11)), 118.32 (C(2)), 68.62 (C(5)), 59.65 (C(12)), 49.04 (C(4)), 38.86 (C(7)), 31.96 (C(6)), 18.92 (C(14)), 14.23 (C(13))

IR: (neat)

3450 (m), 3025 (w), 2981 (m), 2939 (m), 2863 (m), 1712 (s), 1644 (s), 1496 (m), 1454 (m), 1369 (m), 1280 (m), 1226 (s), 1149 (s), 1068 (m)

MS: (EI, 70 eV)

263 (M⁺, 1), 244 (8), 217 (16), 171 (3), 128 (100), 117 (13), 100 (30), 91 (48), 82 (21)

Opt. Rot.: $[\alpha]_{\text{D}}^{24} -5.85$ (c = 1.0, EtOH)TLC: R_f 0.51 (hexanes/EtOAc, 4/1) [UV(254)/KMnO₄]SFC: t_R (S)-14ck, 3.52 (97.5%); t_R (R)-14ck, 4.18 (2.5%) (Chiralpak AD, 125 psi, 40 °C, 12.0% CH₃OH in CO₂, 3.0 mL/min, 220 nm)Analysis: C₁₆H₂₂O₃ (262.34)

Calcd: C, 73.25; H, 8.45%

Found: C, 73.16; H, 8.22%

Preparation of (2*E*,4*R*,5*R*) *tert*-Butyl 5-Hydroxy-4-methyl-5-phenyl-2-pentenoate ((2*E*,4*R*,5*R*)-14*da*)

Following General Procedure 6, 8.4 mg of bis-phosphoramidate (*R,R*)-**6** (0.01 mmol, 0.01 equiv) was combined with 102 μ L of benzaldehyde **5a** (1.0 mmol), 123 μ L of SiCl_4 (1.1 mmol, 1.1 equiv) and 324 mg of **4d** (1.2 mmol, 1.2 equiv) to yield, after silica gel column chromatography (hexanes/EtOAc, 4/1), 242 mg (92 %) of (2*E*,4*R*,5*R*)-**14da** as a colorless oil.

Data for (2*E*,4*R*,5*R*)-14*da*:

¹H NMR: (400 MHz, CDCl_3)

7.37-7.29 (m, 5 H, HC(7,8,9)), 6.91 (dd, $J = 15.6, 8.3$, 1 H, HC(3)), 5.84 (dd, $J = 15.9, 0.7$, 1 H, HC(2)), 4.47 (d, $J = 7.6$, 1 H, HC(5)), 2.62 (m, 1 H, HC(4)), 2.65 (s, 1 H, OH), 1.48 (s, 9 H, $\text{H}_3\text{C}(11)$), 0.89 (d, $J = 6.8$, 3 H, $\text{H}_3\text{C}(12)$)

¹³C NMR: (100 MHz, CDCl_3)

165.74 (C(1)), 149.76 (C(3)), 142.17 (C(6)), 128.45 (C(8)), 127.95 (C(9)), 126.66 (C(7)), 124.11 (C(2)), 80.27 (C(10)), 77.94 (C(5)), 44.28 (C(4)), 28.12 (C(11)), 16.17 (C(12))

IR: (neat)

3442 (m), 2977 (s), 2933 (m), 1710 (s), 1650 (m), 1454 (m), 1367 (m), 1313 (m), 1253 (m), 1157 (s), 1035 (m)

MS: (EI, 70 eV)

263 (M^+ , 29), 189 (100), 143 (37), 100(39)

Opt. Rot.: $[\alpha]_{\text{D}}^{24} +65.37$ ($c = 1.0$, EtOH)

TLC: R_f 0.45 (hexanes/EtOAc, 4/1) [UV(254)/ KMnO_4]

SFC: t_R (4*R*,5*R*)-**14da**, 6.20 (94.5%); t_R (4*S*,5*S*)-**14da**, 7.05 (5.5%) (Chiralpak AD, 125 psi, 40 $^\circ\text{C}$, 3.0% CH_3OH in CO_2 , 3.0 mL/min, 220 nm)

Analysis: C₁₆H₂₂O₃ (262.16)

Calcd: C, 73.25; H, 8.45%

Found: C, 73.18; H, 8.74%

Preparation of (2*E*,6*E*) *tert*-Butyl 5-Hydroxy-4-methyl-7-phenyl-2,6-heptadienoate ((2*E*,6*E*)-14dg**)**

Following General Procedure 6, 8.4 mg of bis-phosphoramidate (*R,R*)-**6** (0.01 mmol, 0.01 equiv) was combined with 126 μ L of cinnamaldehyde **5g** (1.0 mmol), 123 μ L of SiCl₄ (1.1 mmol, 1.1 equiv) and 324 mg of **4d** (1.2 mmol, 1.2 equiv) to yield, after silica gel column chromatography (hexanes/EtOAc, 9/1), 205 mg (71 %) of (2*E*,6*E*)-**14dg** as a colorless oil.

Data for (2*E*,6*E*)-**14dg**:

mp: 62-66 °C

¹H NMR: (400 MHz, CDCl₃)

7.39-7.23 (m, 5 H, HC(9,10,11)), 6.90 (dd, *J* = 16.1, 8.0, 1 H, HC(3)), 6.61 (d, *J* = 15.9, 1 H, HC(7)), 6.19 (dd, *J* = 15.9, 7.1, 1 H, HC(6)), 5.85 (dd, *J* = 15.6, 1.0, 1 H, HC(2)), 4.16 (t, *J* = 6.8, 1 H, HC(5)), 2.52 (m, 1 H, HC(4)), 1.78 (s, 1 H, OH), 1.48 (s, 9 H, H₃C(13)), 1.09 (d, *J* = 6.8, 3 H, H₃C(14))

¹³C NMR: (100 MHz, CDCl₃)

165.81 (C(1)), 148.75 (C(3)), 136.28 (C(8)), 132.36 (C(7)), 129.65 (C(6)), 128.58 (C(9)), 127.68 (C(11)), 126.59 (C(10)), 124.14 (C(2)), 80.33 (C(12)), 76.17 (C(5)), 42.91 (C(4)), 28.12 (C(13)), 15.66 (C(14))

IR: (CHCl₃)

3605 (w), 3027 (m), 3013 (m), 2981 (m), 1705 (s), 1651 (m), 1494 (m), 1455 (m), 1369 (m), 1301 (m), 1158 (s)

MS: (CI, 70 eV)

289 (M⁺, 1), 271 (33), 215 (100), 197 (9), 169 (10), 133 (21), 100 (3)

Opt. Rot.: $[\alpha]_{\text{D}}^{24} +5.78$ ($c = 1.0$, EtOH)

TLC: R_f 0.58 (hexanes/EtOAc, 4/1) [UV(254)/KMnO₄]

SFC: t_R (4*S*,5*R*)-**14dg**, 8.29 (8.8%); t_R (4*R*,5*S*)-**14dg**, 9.15 (91.2%) (Chiralpak OJ, 125 psi, 40 °C, 4.0% CH₃OH in CO₂, 2.0 mL/min, 220 nm)

Analysis: C₁₈H₂₄O₃ (288.38)

Calcd: C, 74.97; H, 8.39%

Found: C, 75.11; H, 8.59%

Preparation of (5*R*)-6-(2-Hydroxy-2-phenylethyl)-2,2-dimethyl-[1,3]-dioxin-4-one ((5*R*)-**15a**)

Following General Procedure 6, 8.4 mg of bis-phosphoramidate (*R,R*)-**6** (0.01 mmol, 0.01 equiv) was combined with 102 μ L of benzaldehyde **5a** (1.0 mmol), 123 μ L of SiCl₄ (1.1 mmol, 1.1 equiv) and 307 mg of **13** (1.2 mmol, 1.2 equiv) to yield, after silica gel column chromatography (hexanes/EtOAc, 6/4), 228 mg (92 %) of (5*R*)-**15a** as a white, crystalline solid. NMR spectral data matched that previously reported in the literature.²⁶

Data for (5*R*)-**15a**:

mp: 70-72 °C

¹H NMR: (400 MHz, CDCl₃)

7.4-7.28 (m, 5 H, HC(7,8,9)), 5.27 (s, 1 H, HC(2)), 4.98 (m, 1 H, HC(5)), 2.7 (dd, $J = 14.6, 8.2$, 1 H, HC(4)), 2.55 (dd, $J = 14.6, 4.8$, 1 H, HC(4)), 2.1 (d, $J = 4.0$, 1 H, OH), 1.65 (s, 3 H, H₃C(11)), 1.63 (s, 3 H, H₃C(11))

¹³C NMR: (100 MHz, CDCl₃)

168.19 (C(3)), 161.2 (C(1)), 142.65 (C(6)), 128.74 (C(8)), 128.33 (C(9)), 125.69 (C(7)), 106.66 (C(10)), 95.38 (C(2)), 71.22 (C(5)), 43.16 (C(4)), 25.39 (C(11)), 24.70 (C(11))

MS: (CI, methane, 70 eV)

249 (M^{+1} , 29), 191 (28), 173 (32), 147 (22), 131 (100), 105 (25), 85 (21)

Opt. Rot.: $[\alpha]_D^{24} +35.9$ ($c = 1.0$, CHCl_3), lit. $[\alpha]_D^{24} +35.1$ ($c = 1.0$, CHCl_3) for (5*R*)-**XX**²⁶

TLC: R_f 0.35 (hexanes/EtOAc, 6/4) [UV(254)/KMnO₄]

SFC: t_R (S)-**15a**, 3.29 (12.8%); t_R (R)-**15a**, 3.53 (87.2%) (Chiralpak AD, 125 psi, 40 °C, 10.0% CH₃OH in CO₂, 3.0 mL/min, 220 nm)

Preparation of (5*R*)-6-(2-Hydroxy-4-phenyl 3-butenyl)-2,2-dimethyl-[1,3]-dioxin-4-one ((5*R*)-15g**)**

Following General Procedure 6, 8.4 mg of bis-phosphoramidate (*R,R*)-**6** (0.01 mmol, 0.01 equiv) was combined with 126 μL of cinnamaldehyde **5g** (1.0 mmol), 123 μL of SiCl_4 (1.1 mmol, 1.1 equiv) and 290 mg of **13** (1.2 mmol, 1.2 equiv) to yield, after silica gel column chromatography (hexanes/EtOAc, 6/4), 241 mg (88 %) of (5*R*)-**15g** as a white, crystalline solid. NMR spectral data matched that previously reported in the literature.²⁶

Data for (5*R*)-15g**:**

mp: 81-82 °C

¹H NMR: (400 MHz, CDCl_3)

7.37-7.25 (m, 5 H, HC(9,10,11)), 6.63 (d, $J = 16.1$, 1 H, HC(7)), 6.21 (dd, $J = 15.8$, 6.9, 1 H, HC(6)), 5.36 (s, 1 H, HC(2)), 4.6 (q, $J = 6.9$, 1 H, HC(5)), 2.55 (m, 2 H, H₂C(4)), 1.95 (s, 1 H, OH), 1.69 (s, 3 H, H₃C(13)), 1.68 (s, 3 H, H₃C(13))

¹³C NMR: (100 MHz, CDCl_3)

168.19 (C(3)), 161.03 (C(1)), 135.96 (C(8)), 131.62 (C(7)), 130.13 (C(6)), 128.72 (C(9)), 128.17 (C(11)), 126.55 (C(10)), 106.72 (C(12)), 95.43 (C(2)), 69.83 (C(5)), 41.50 (C(4)), 25.34 (C(13)), 24.84 (C(13))

MS: (EI, 70 eV)

275 (M^{+1} , 2), 216 (45), 188 (60), 172 (23), 157 (18), 131 (44), 115 (32), 104 (100), 84 (41)

Opt. Rot.: $[\alpha]_D^{24} +14.43$ ($c = 1.0$, EtOH), $[\alpha]_D^{24} +6.79$ ($c = 1.0$, $CHCl_3$), lit $[\alpha]_D^{24} +6.2$ ($c = 1.0$, $CHCl_3$) for (5*R*)-**15g**²⁶

TLC: R_f 0.28 (hexanes/EtOAc, 6/4) [UV(254)/KMnO₄]

SFC: t_R (S)-**15g**, 6.56 (11.1%); t_R (R)-**15g**, 7.9 (88.9%) (Chiralpak AD, 125 psi, 40 °C, 8.0% CH₃OH in CO₂, 3.0 mL/min, 220 nm)

Preparation of (5*S*)-6-(2-Hydroxy-4-phenylbutyl)-2,2-dimethyl-[1,3]-dioxin-4-one ((5*S*)-**15k**)

Following General Procedure 7, 42 mg of bis-phosphoramidate (*R,R*)-**6** (0.05 mmol, 0.05 equiv) was combined with 8 μ L of *i*-Pr₂EtN (0.05 mmol, 0.05 equiv), 126 μ L of hydrocinnamaldehyde **5k** (1.0 mmol), 123 μ L of SiCl₄ (1.1 mmol, 1.1 equiv) and 272 mg of **13** (1.2 mmol, 1.2 equiv) to yield, after silica gel column chromatography (hexanes/EtOAc, 6/4), 230 mg (83 %) of (5*S*)-**15k** as a white, crystalline solid. NMR spectral data matched that previously reported in the literature.²⁶

Data for (5*S*)-**15k**:

mp: 59-60 °C

¹H NMR: (500 MHz, CDCl₃)

7.3-7.18 (m, 5 H, HC(9,10,11)), 5.31 (s, 1 H, HC(2)), 3.92 (pent, $J = 6.2$, 1 H, HC(5)), 2.81 (m, 1 H, HC(4)), 2.70 (m, 1 H, HC(4)), 2.42 (dd, $J = 14.4$, 4.3, 1 H, HC(6)), 2.36 (dd, $J = 14.6$, 8.1, 1 H, HC(6)), 1.82 (m, 2 H, H₂C(7)), 1.68 (s, 3 H, H₃C(12)), 1.66 (s, 3 H, H₃C(12))

^{13}C NMR: (125 MHz, CDCl_3)

168.95 (C(3)), 161.0 (C(1)), 141.27 (C(8)), 128.55 (C(9)), 128.37 (C(10)), 126.11 (C(11)), 106.63 (C(12)), 95.14 (C(2)), 68.32 (C(5)), 41.73 (C(4)), 38.89 (C(7)), 31.77 (C(6)), 25.16 (C(13)), 24.84 (C(13))

MS: (EI, 70 eV)

277 (M^+ , 3), 218 (28), 200 (31), 172 (7), 158 (16), 130 (24), 117 (44), 104 (22), 91 (100), 69 (26)

Opt. Rot.: $[\alpha]_{\text{D}}^{24} +10.17$ ($c = 1.0$, EtOH), $[\alpha]_{\text{D}}^{24} +3.4$ ($c = 1.0$, CHCl_3), lit. $[\alpha]_{\text{D}}^{24} +2.5$ ($c = 1.0$, CHCl_3) for (5*S*)-**15k**²⁶

TLC: R_f 0.27 (hexanes/EtOAc, 6/4) [UV(254)/ KMnO_4]

SFC: t_R (*R*)-**15k**, 4.80 (5.4%); t_R (*S*)-**15k**, 5.18 (94.6%) (Chiralpak AD, 125 psi, 40 °C, 8.0% CH_3OH in CO_2 , 3.0 mL/min, 220 nm)

General Procedure 8. Ozonolysis of an α,β -Unsaturated Ester. Preparation of (3*R*)-1-Phenyl propane-1,3-diol ((3*R*)-16**) from (2*E*,5*R*) Ethyl 5-Hydroxy-5-phenyl-2-pentenoate ((2*E*,5*R*)-**14aa**)**

A 25 mL, 1-neck, round-bottom flask containing a solution of 94 mg (2*E*,5*R*) ethyl 5-hydroxy-5-phenyl-2-pentenoate ((2*E*,5*R*)-**14aa**) (0.42 mmol) in 5 mL of pentane was cooled to $-78\text{ }^{\circ}\text{C}$ in a dry ice/isopropanol bath and a solution of ozone in oxygen was passed through it using a gas dispersion tube for 1 h. The solution was sparged with N_2 (to remove residual ozone) and then 2.89 mL of a solution of LiAlH_4 in THF (0.58 M, 1.68 mmol, 4 equiv) was added slowly at $-78\text{ }^{\circ}\text{C}$ in a dry ice/isopropanol bath. The flask was then fitted with a reflux condenser and was heated at $65\text{ }^{\circ}\text{C}$ for 1 h. The mixture was cooled to room temperature and 5 mL of sat. aq. sodium potassium tartrate solution was added and the mixture was stirred to break up the resulting precipitate. The organic layer was separated and the aqueous layer was washed with Et_2O (3 x 10 mL). The combined organic extracts were washed with brine (25 mL), dried over Na_2SO_4 (5 g), filtered and the filtrate was concentrated *in vacuo*. The residue was purified by silica gel column

chromatography (EtOAc/ hexanes, 2/1) to yield 41 mg (64%) of (3*R*)-**16** as a colorless oil. NMR spectral data matched that previously reported in the literature.²⁷

Data for (3*R*)-16**:**

¹H NMR: (400 MHz, CDCl₃)

7.36-7.25 (m, 5 H, HC(5,6,7)), 4.96 (dd, *J* = 8.5, 3.9, 1 H, HC(3)), 3.86 (t, *J* = 5.6, 2 H, H₂C(1)), 2.55 (s, 1 H, OH), 2.1-1.85 (m, 2 H, H₂C(2))

Opt. Rot.: [α]_D²⁴ +60.8 (*c* = 1.0, CHCl₃), lit. [α]_D²⁴ -63.0 (*c*=0.958, CHCl₃) for (3*S*)-**16**²⁷

TLC: *R_f* 0.28 (EtOAc/hexanes, 2/1) [p-anisaldehyde]

Preparation of (5*R*) Ethyl 5-Hydroxy-7-phenylheptanoate ((5*R*)-17**) from (2*E*,5*R*,6*E*) Ethyl 5-Hydroxy-7-phenyl-2,6-heptadienoate ((2*E*,5*R*,6*E*)-**14ag**)**

A 50 mL, 1-neck, round-bottom flask containing a suspension of 246 mg of (2*E*,5*R*,6*E*) ethyl 5-hydroxy-7-phenyl-2,6-heptadienoate ((2*E*,5*R*,6*E*)-**14ag**) (1.0 mmol) and 7.0 mg of 10% Pd-C in 25 mL of EtOAc was stirred for 3 h at 23 °C under 1 atm of H₂. After briefly evacuating the flask and venting with N₂, the suspension was then filtered through Celite and the filtrate was concentrated *in vacuo*. The residue was purified by silica gel column chromatography (hexanes/EtOAc, 4/1) to yield 206 mg (82 %) of (5*R*)-**17** as a colorless oil.

Data for (5*R*)-17**:**

¹H NMR: (400 MHz, CDCl₃)

7.30-7.16 (m, 5 H, HC(9,10,11)), 4.12 (q, *J* = 7.1, 2 H, H₂C(12)), 3.61 (m, 1 H, HC(5)), 2.77 (m, 1 H, HC(7)), 2.68 (m, 1 H, HC(7)), 2.32 (dt, *J* = 1.2, 7.56, 2 H, H₂C(2)), 1.79-1.67 (m, 4 H, 2 x H₂C(4,6)), 1.50 (m, 2 H, H₂C(3)), 1.24 (t, *J* = 7.1, 3 H, H₃C(13))

¹³C NMR: (100 MHz, CDCl₃)

173.78 (C(1)), 142.01 (C(8)), 128.37 (C(9)), 128.35 (C(10)), 125.29 (C(11)), 70.65 (C(5)), 60.34 (C(12)), 39.63 (C(7)), 36.83 (C(4)), 34.05 (C(2)), 31.99 (C(6)), 20.84 (C(3)), 14.21 (C(13))

IR: (neat)

3451 (w), 2980 (w), 2866 (w), 1733 (s), 1495 (w), 1454 (m), 1373 (m), 1238 (m),
1180 (m), 1094 (m), 1031 (m)

MS: (EI, 70 eV)

251 (M^{+1} , 1), 232 (35), 204 (7), 186 (70), 117 (35), 104 (40), 91 (100), 71 (19)

Opt. Rot.: $[\alpha]_D^{24}$ -5.94 (c = 1.0, EtOH)

TLC: R_f 0.19 (hexanes/EtOAc, 4/1) [UV(254)/KMnO₄]

Analysis: C₁₅H₂₂O₃ (250.33)

Calcd: C, 71.97; H, 8.86%

Found: C, 71.91; H, 8.91%

Preparation of (5R) Ethyl 5-Hydroxy-7-phenylheptanoate (5R)-17 from (2E,5S) Ethyl 5-Hydroxy-7-phenyl-2-heptenoate (2E,5S)-14ak

A 50 mL, 1-neck, round-bottom flask containing a suspension of 50 mg of (2E,5S) ethyl 5-hydroxy-7-phenyl-2-heptenoate (2E,5S)-**14ak** (0.2 mmol) and 1.4 mg of 10% Pd-C in 5 mL of EtOAc was stirred for 3 h at 23 °C under 1 atm of H₂. After briefly evacuating the flask and venting with N₂, the suspension was then filtered through Celite and the filtrate was concentrated *in vacuo*. The residue was purified by silica gel column chromatography (silica gel, hexanes/EtOAc, 4/1) to yield 31 mg (61 %) of (5R)-**17** as a colorless oil.

Data for (5R)-17:

¹H NMR: (400 MHz, CDCl₃)

7.30-7.16 (m, 5 H, HC(9,10,11)), 4.12 (q, J = 7.1, 2 H, H₂C(12)), 3.61 (m, 1 H, HC(5)), 2.77 (m, 1 H, HC(7)), 2.68 (m, 1 H, HC(7)), 2.32 (dt, J = 1.2, 7.56, 2 H, H₂C(2)), 1.79-1.67 (m, 4 H, 2 x H₂C(4,6)), 1.50 (m, 2 H, H₂C(3)), 1.24 (t, J = 7.1, 3 H, H₃C(13))

Opt. Rot.: $[\alpha]_D^{24}$ -6.09 (c = 1.0, EtOH)

Preparation of (3*S*)-5-Phenylpentane-1,3-diol ((3*S*)-18**) from (2*E*,5*S*) Ethyl 5-Hydroxy-7-phenyl-2-heptenoate ((2*E*,5*S*)-**14ak**)**

Following General Procedure 8, a solution of 93 mg of (2*E*,5*S*) ethyl 5-hydroxy-7-phenyl-2-heptenoate (2*E*,5*S*)-**14ak** (0.37 mmol) in 5 mL of pentane was treated with a solution of ozone in oxygen followed by reduction with 2.55 mL of a solution of LiAlH₄ in THF (0.58 M, 1.48 mmol, 4 equiv) to yield, after silica gel column chromatography (EtOAc/hexanes, 2/1), 42 mg (63%) of (3*S*)-**18** as a colorless oil. NMR spectral data matched that previously reported in the literature.²⁸

Data for (3*S*)-**18**:

¹H NMR: (400 MHz, CDCl₃)

7.30-7.18 (m, 5 H, HC(7,8,9)), 3.89 (m, 2 H, H₂C(1)), 3.82 (m, 1 H, HC(3)), 2.81-2.65 (m, 2 H, H₂C(5)), 2.60 (s, 1 H, OH), 1.85-1.70 (m, 4 H, 2 x H₂C(2,4))

¹³C NMR: (100 MHz, CDCl₃)

141.88 (C(6)), 128.43 (C(7)), 128.39 (C(8)), 125.87 (C(9)), 71.53 (C(3)), 61.72 (C(1)), 39.30 (C(5)), 38.25 (C(2)), 31.84 (C(4))

Opt. Rot.: [α]_D²⁴ -10.2 (c = 1.32, EtOH), lit. [α]_D²⁴ -7.21 (c=1.52, EtOH) for (3*S*)-**18**²⁸

TLC: *R_f* 0.26 (EtOAc/hexanes, 2/1) [p-anisaldehyde]

Preparation of (3*R*)-1-Phenylpropane-1,3-diol ((3*R*)-16**) from (2*E*,5*R*) Methyl 5-Hydroxy-2-methyl-5-phenyl-2-pentenoate ((2*E*,5*R*)-**14ba**)**

Following General Procedure 8, a solution of 95 mg of (2*E*,5*R*) methyl 5-hydroxy-2-methyl-5-phenyl-2-pentenoate (2*E*,5*R*)-**14ba** (0.43 mmol) in 5 mL of pentane was treated with a solution of ozone in oxygen followed by reduction with 2.96 mL of a solution of LiAlH₄ in THF (0.58 M, 1.72 mmol, 4 equiv) to yield, after silica gel column chromatography (EtOAc/hexanes, 2/1), 47 mg (71%) of (3*R*)-**16** as a colorless oil. NMR spectral data matched that previously reported in the literature.²⁷

Data for (3*R*)-16**:**

¹H NMR: (400 MHz, CDCl₃)

7.36-7.25 (m, 5 H, HC(5,6,7)), 4.96 (dd, *J* = 8.5, 3.9, 1 H, HC(3)), 3.86 (t, *J* = 5.6, 2 H, H₂C(1)), 2.55 (s, 1 H, OH), 2.1-1.85 (m, 2 H, H₂C(2))

Opt. Rot.: [α]_D²⁴ +57.1 (*c* = 0.978, CHCl₃), lit. [α]_D²⁴ -63.0 (*c*=0.958, CHCl₃) for (3*S*)-**16**²⁷

Preparation of (4*R*)-4-(Acetyloxy)-4-phenyl-2-butanone ((4*R*)-19**) from (2*E*,5*R*) Ethyl 5-Hydroxy-3-methyl-5-phenyl-2-pentenoate ((2*E*,5*R*)-**14ca**)**

To a 25 mL, 1-neck, round-bottom flask containing a solution of 53 mg of (2*E*,5*R*) ethyl 5-hydroxy-3-methyl-5-phenyl-2-pentenoate ((2*E*,5*R*)-**14ca**) (0.23 mmol) in 0.5 mL of acetic anhydride (5.3 mmol, 23 equiv) was slowly added 0.5 mL of pyridine (6.2 mmol, 27 equiv). The solution was allowed to stir at room temperature for 90 min before the addition of 10 mL of Et₂O. The cloudy solution was then washed with 0.1 M HCl (20 mL) followed by washing with

brine (20 mL). The organic layer was then separated and dried over Na₂SO₄ (5 g), filtered and the filtrate was concentrated *in vacuo*. The residue was then transferred to a 25 mL, 1-neck flask and dissolved in a mixture of 2 mL CH₂Cl₂, 2 mL CH₃CN and 2 mL H₂O. To this solution was added 1 mg of RuCl₃·H₂O (0.0046 mmol, 0.02 equiv) and 206 mg of NaIO₄ (0.96 mmol, 4.2 equiv). The biphasic mixture was stirred at room temperature for 2 h prior to addition of 10 mL M HCl. The solution was then extracted with CH₂Cl₂ (2 x 10 mL). The combined organic layers were washed with brine (10 mL), dried over Na₂SO₄ (5 g), filtered and the filtrate was concentrated *in vacuo*. The residue was purified by silica gel column chromatography (hexanes/EtOAc, 4/1) to yield 28 mg (55%) of (4*R*)-**19** as a colorless oil. NMR spectral data matched that previously reported in the literature.²⁹

Data for (4*R*)-19**:**

¹H NMR: (400 MHz, CDCl₃)

7.34-7.29 (m, 5 H, HC(6,7,8)), 6.18 (dd, *J* = 8.5, 4.9, 1 H, HC(4)), 3.11 (dd, *J* = 16.6, 8.8, 1 H, HC(3)), 2.82 (dd, *J* = 16.6, 4.9, 1 H, HC(3)), 2.14 (s, 3 H, H₃C(1)), 2.03 (s, 3 H, H₃C(10))

¹³C NMR: (100 MHz, CDCl₃)

204.61 (C(2)), 169.77 (C(9)), 139.62 (C(5)), 128.58 (C(7)), 128.21 (C(6)), 126.39 (C(8)), 71.54 (C(4)), 49.80 (C(3)), 30.40 (C(10)), 21.03 (C(1))

Opt. Rot.: [α]_D²⁴ +60.0 (c = 0.71, CHCl₃), lit. [α]_D²⁴ +64.6 (c=0.71, CHCl₃) for (4*R*)-**19**²⁹

TLC: *R*_f 0.35 (hexanes/EtOAc, 4/1) [UV(254)/KMnO₄]

Preparation of (2*R*,3*R*)-2-Methyl-1-phenylpropane-1,3-diol ((2*R*,3*R*)-20**) from (2*E*,4*R*,5*R*) *tert*-Butyl 5-Hydroxy-4-methyl-5-phenyl-2-pentenoate ((2*E*,4*R*,5*R*)-**14da**)**

Following General Procedure 8, a solution of 95 mg of (2*E*,4*R*,5*R*) *tert*-butyl 5-hydroxy-4-methyl-5-phenyl-2-pentenoate (2*E*,4*R*,5*R*)-**14da** (0.36 mmol) in 5 mL of pentane was treated

with a solution of ozone in oxygen followed by reduction with 2.48 mL a solution of LiAlH_4 in THF (0.58 M, 1.44 mmol, 4 equiv) to yield, after silica gel column chromatography (EtOAc/hexanes, 2/1), 26 mg (44%) of (2*R*,3*R*)-**20** as a colorless oil. NMR spectral data matched that previously reported in the literature.²⁷

Data for (2*R*,3*R*)-**20**:

¹H NMR: (400 MHz, CDCl_3)

7.37-7.26 (m, 5 H, HC(5,6,7)), 4.50 (d, $J = 8.5$, 1 H, HC(3)), 3.70 (m, 2 H, $\text{H}_2\text{C}(1)$), 3.19 (s, 2 H, OH), 2.03 (m, 1 H, $\text{H}_2\text{C}(2)$), 0.67 (d, $J = 7.1$, 3 H, $\text{H}_3\text{C}(8)$)

¹³C NMR: (100 MHz, CDCl_3)

143.29 (C(4)), 128.39 (C(6)), 127.80 (C(5)), 126.66 (C(7)), 80.83 (C(3)), 67.92 (C(1)), 41.51 (C(2)), 13.75 (C(8))

Opt. Rot.: $[\alpha]_{\text{D}}^{24} +35.17$ ($c = 0.34$, CHCl_3), lit. $[\alpha]_{\text{D}}^{24} -46.8$ ($c=0.35$, CHCl_3) for (2*S*,3*S*)-**20**²⁷

TLC: R_f 0.47 (EtOAc/hexanes, 2/1) [p-anisaldehyde]

Preparation of (α-Chlorocyclohexylmethoxy)trichlorosilane (23)

Into a dry NMR tube was added 30 μL (0.25 mmol) of freshly distilled cyclohexanecarboxaldehyde **5j** and 1.0 mL of CDCl_3 at room temperature under nitrogen. To this solution was added 2.2 μL of (0.0125 mmol, 0.05 equiv) of HMPA followed by 34 μL (0.3 mmol, 1.2 equiv) of SiCl_4 . The NMR tube was vortexed for 1 min. to insure mixing. The tube was vortexed and then inserted NMR probe and the ¹H NMR spectrum was acquired at room temperature. After 24 h at room temperature, a ¹³C NMR was acquired.

Data for **23**:

¹H NMR: (500 MHz, CDCl_3)

5.78 (d, $J = 4.9$, 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))

^{13}C NMR: (126 MHz, CDCl_3)
 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))

Reaction of Crotonaldehyde with SiCl_4 in the presence of HMPA

Into an oven dried 5 mm NMR tube, 17 μL of crotonaldehyde (**5m**) (0.2 mmol) and 3 μL of HMPA (0.02 mmol, 0.1 equiv) was dissolved in 0.8 mL of CDCl_3 . The tube was cooled in a dry ice / isopropanol bath and 25 μL of SiCl_4 (0.22 mmol, 1.1 equiv) was added. The tube was vortexed and then inserted into a pre-cooled NMR probe at -70°C . The ^1H NMR spectrum was acquired at -70°C . A mixture of species was observed: 42% **5m** / 27% $\gamma\text{-Cl}$ **24** / 27% $\alpha\text{-Cl}$ **25**.

Data for **24**:

^1H NMR: (500 MHz, CDCl_3)
 6.54 (d, $J = 12.0$, 1 H, HC(1)), 5.51 (dd, $J = 12.0, 9.8$, 1 H, HC(2)), 4.54 (dq, $J = 9.6, 6.6$, 1 H, HC(3)), 1.53 (d, $J = 6.6, 3.4$, $\text{H}_3\text{C}(4)$)

Data for **25**:

^1H NMR: (500 MHz, CDCl_3)
 6.25 (d, $J = 5.6$, 1 H, HC(1)), 5.08 (dd, $J = 15.7, 5.4$, 1 H, HC(2)), 5.02 (m, 1 H, HC(3)), 1.49 (d, $J = 6.4$, 3 H, $\text{H}_3\text{C}(4)$)

Calculated Structure of the Aldehyde-Silyl cation Complex (Figure 11)

Model created using the PC version of GAMESS(US) QC package at the PM3 level.³⁰ Structure visualized using Chem3D with some hydrogens omitted for clarity.

RESULTS FROM SUCCESSFUL RHF GEOMETRY SEARCH COORDS, ORBS, GRADIENT, AND APPROX. HESSIAN COORDINATES OF SYMMETRY UNIQUE ATOMS (ANGS)				
Atom	Charge	X	Y	Z
C	6	7.08576704	-4.5424505	1.57103129
C	6	6.08218144	-4.0270331	2.34543123
C	6	7.58284018	-3.8025013	0.4749762
N	7	3.09338375	2.87554011	-0.9171932
C	6	4.38728795	3.56600712	-0.7167774
C	6	7.08350719	-2.5599204	0.19138778
C	6	1.92993776	3.7958594	-0.9008909
C	6	-7.2085942	-3.4755011	-2.1077765
C	6	6.05483553	-1.9853507	0.98920839
C	6	-6.1601344	-2.956205	-2.8182928
C	6	5.5376727	-2.7467525	2.05815336
C	6	-7.6321253	-2.8499385	-0.9136188
C	6	4.44903291	-2.2436369	2.81991553
C	6	3.89064544	-1.0383337	2.51255091
N	7	-2.3332423	2.99282974	1.34782975
C	6	4.42341075	-0.2434609	1.45625281
N	7	3.8325934	1.05664464	1.17831691
P	15	2.98423692	1.19529317	-0.369194
C	6	3.14900452	1.69617355	2.32357157

C	6	5.51289579	-0.6842203	0.71804805
C	6	6.0835264	0.11188875	-0.3844739
C	6	5.31651495	0.46432015	-1.4871189
C	6	5.92328216	1.05520637	-2.6348737
C	6	7.24848938	1.37708094	-2.6267067
C	6	8.02977845	1.16572693	-1.4572445
C	6	7.45173738	0.53917565	-0.332999
N	7	3.8915398	0.19019543	-1.4901711
C	6	3.28534912	-0.1521728	-2.7909756
C	6	8.24509409	0.37740293	0.83604997
C	6	9.54559151	0.80514202	0.8640058
C	6	10.1256877	1.41077288	-0.2729728
C	6	9.38480434	1.58773717	-1.4106807
O	8	1.43829019	0.8459831	-0.2343668
C	6	-3.5073538	3.89364582	1.34410533
C	6	-7.0111372	-1.7152737	-0.4653716
C	6	-1.0291729	3.70053866	1.37850526
C	6	-5.9293722	-1.1395062	-1.1886361
C	6	-5.4942699	-1.7855505	-2.3648527
C	6	-4.3731716	-1.2772519	-3.0754057
C	6	-3.7023782	-0.1830386	-2.614299
C	6	-4.1386783	0.48869015	-1.4353189
N	7	-3.4203128	1.66442233	-0.9709396
P	15	-2.5163114	1.43970645	0.53509634
C	6	-2.7179272	2.43939767	-2.0178926
C	6	-5.2582695	0.04797492	-0.7436125
C	6	-5.7350767	0.73251409	0.47215967
C	6	-4.9267832	0.84520687	1.59538953
C	6	-5.4548627	1.35797418	2.81693834

C	6	-6.7348392	1.82568815	2.87587216
C	6	-7.5448992	1.84770351	1.70775565
C	6	-7.047356	1.31001446	0.50198775
N	7	-3.5426296	0.4026807	1.53451516
C	6	-2.9660842	-0.1082445	2.7946377
C	6	-7.8610444	1.38839779	-0.6617041
C	6	-9.1062855	1.95555341	-0.608108
C	6	-9.6088062	2.46920802	0.60844805
C	6	-8.8452813	2.41718157	1.7437368
O	8	-1.1077169	0.78398494	0.27987444
C	6	1.77335343	4.61231188	0.38236941
C	6	0.4974222	5.43758389	0.35940293
C	6	-0.7624381	4.60701199	0.17756687
Si	14	0.16093784	-0.2901569	-0.1590629
Cl	17	1.65015594	-1.9801939	-0.6569166
C	6	-3.8744603	-4.7385572	-0.7390823
C	6	-2.9764927	-3.6869722	-0.5995046
C	6	-3.6753199	-5.9271124	-0.0442317
C	6	-2.5728252	-6.0682579	0.79672271
C	6	-1.6722593	-5.0234167	0.94444001
C	6	-1.8708786	-3.8212407	0.24794536
C	6	-0.882289	-2.7613019	0.43127183
O	8	-1.0141064	-1.6489997	-0.1172918
Cl	17	-0.332367	0.01412551	-2.3465979
H	1	7.50778321	-5.5297699	1.78662992
H	1	5.67937416	-4.5947499	3.19217981
H	1	8.37324461	-4.2365027	-0.1469472
H	1	4.55258745	3.8781661	0.32622329
H	1	4.42363112	4.46553184	-1.3481828

H	1	5.20963442	2.90316721	-1.0243493
H	1	7.47459334	-1.9909497	-0.6616107
H	1	2.05317413	4.47800962	-1.7683671
H	1	1.00095639	3.21225118	-1.096765
H	1	-7.7291413	-4.3743424	-2.4559593
H	1	-5.8208021	-3.4311596	-3.7467341
H	1	-8.4670763	-3.283	-0.3517147
H	1	4.04781548	-2.850567	3.64008225
H	1	2.99322169	-0.683301	3.05202645
H	1	2.63456527	2.61100289	1.9815884
H	1	3.9060297	1.97989419	3.06657863
H	1	2.41246464	1.02687348	2.81255911
H	1	5.30397866	1.22505132	-3.5307543
H	1	7.72453902	1.81397805	-3.5126961
H	1	3.61540486	-1.1661222	-3.0568319
H	1	3.596459	0.53593268	-3.5967975
H	1	2.18561167	-0.1655842	-2.7018778
H	1	7.79608535	-0.1030063	1.71501439
H	1	10.1504283	0.67928963	1.76873653
H	1	11.1708397	1.73620315	-0.2316536
H	1	9.82356374	2.05842189	-2.2983242
H	1	-3.6856804	4.37236442	0.36839182
H	1	-3.3592422	4.68909769	2.08851946
H	1	-4.4041629	3.32386687	1.6300928
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H	1	-1.0136067	4.29529785	2.31608622
H	1	-0.2358062	2.93070665	1.48008196
H	1	-4.0460068	-1.7865202	-3.9902654
H	1	-2.7934601	0.17692827	-3.1335076

H	1	-2.0340438	3.16841843	-1.546832
H	1	-3.4673021	2.98761173	-2.6036034
H	1	-2.1303043	1.80000029	-2.7073704
H	1	-4.817367	1.3545742	3.71605523
H	1	-7.1496912	2.20384779	3.81816037
H	1	-3.3865838	-1.1061538	2.97951041
H	1	-3.2098129	0.52479694	3.66693259
H	1	-1.8701298	-0.199569	2.70408964
H	1	-7.4736197	0.9826044	-1.6051449
H	1	-9.7264919	2.01544693	-1.5093816
H	1	-10.611732	2.90968257	0.63021091
H	1	-9.2228027	2.81612361	2.69270944
H	1	2.63885458	5.2936438	0.51565653
H	1	1.78665575	3.94558337	1.2763146
H	1	0.5566113	6.18181015	-0.4606421
H	1	0.42716934	6.02861665	1.29479141
H	1	-0.6775895	3.99348215	-0.7551649
H	1	-1.6181704	5.29299007	0.01034665
H	1	-4.7455983	-4.618108	-1.4001566
H	1	-3.1433686	-2.7556586	-1.1618859
H	1	-4.3849028	-6.7545854	-0.159032
H	1	-2.4153423	-7.0071483	1.33998442
H	1	-0.801655	-5.1390102	1.60289515
H	1	0.00262044	-2.9457676	1.07499146
Cl	17	0.50006703	-0.603103	2.12263458

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- (18) To simplify CSP-SFC analysis, the 2-naphthaldehyde had to be removed from the commercially available 1-naphthaldehyde prior to use. To do this, ethanol was added to a freshly made solution of saturated aqueous sodium bisulfite until the solution became cloudy. Water was then added until the solution was clear. The 1-naphthaldehyde was then added to this stirred solution and after 15 min, the bisulfite salt was isolated by filtration. The resulting white solid could then be recrystallized from EtOH to yield the isomerically pure, 1-naphthaldehyde bisulfite salt. The 1-naphthaldehyde could be recovered by dissolving the bisulfite salt in a small

amount of water and adding an equal volume of a saturated aqueous solution of NaHCO_3 . The resulting solution was extracted with CH_2Cl_2 , the combined organic layers were dried over K_2CO_3 and concentrated *in vacuo* to provide the isomerically pure 1-naphthaldehyde.

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