Lewis Base Catalyzed Aldol Additions of Chiral Trichlorosilyl Enolates and Silyl Enol Ethers

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SUPPORTING INFORMATION

Table of Contents	Page
General Experimental	S1
Literature Preparations	S3
Experimental Procedures	S3
Preparation of TMS Enol Ethers	S3
Aldol Addition of Trichlorosilyl Enolates	S23
Aldol Addition of Trimethylsilyl Enol Ethers	S57
References	S120
¹ H NMR Spectra of Trichlorosilyl Enolates	S121

General Experimental

All reactions were performed in oven (140 °C) and/or flame-dried glassware under an atmosphere of dry argon, unless otherwise stated. All reaction temperatures correspond to internal temperatures measured by Teflon-coated thermocouples unless otherwise noted. Solvents for extraction and chromatography were technical grade and distilled from the indicated drying agents: dichloromethane (CH₂Cl₂), pentane, hexane: CaCl₂; ethyl acetate (EtOAc): K₂CO₃; acetone and methanol (MeOH) were reagent grade. *n*-Butyllithium was titrated according to the method of Gilman.¹ “Brine” refers to a saturated aqueous solution of NaCl.

¹H, ¹³C and ³¹P NMR spectra were recorded at 400 MHz ¹H, 100 MHz ¹³C, 162 MHz ³¹P or 500 MHz ¹H, 125 MHz ¹³⁷C, 202 MHz ³¹P in deuterochloroform unless otherwise stated. Data are reported in the following order: chemical shift in ppm (δ); multiplicities are indicated (br (broadened), s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet)); coupling constants,

J, are reported in hertz (Hz); integration is provided; and assignment is indicated. ^1H and ^{13}C NMR assignments are corroborated by 2D experiments (HETCOR and COSY). Spectra are available on request from denmark@scs.uiuc.edu.

Low resolution electron impact (EI) spectra were performed at 70 eV, chemical ionization (CI) spectra were obtained using methane as the carrier gas. Data are reported in the form of *m/z* (intensity relative to base peak = 100). Infrared spectra (IR) are reported in cm^{-1} with indicated intensities: s (strong, 67 – 100% absorption), m (medium, 34 – 66%), w (weak, 0 – 33%). Optical rotation data was obtained on a digital polarimeter and are reported as follows: concentration (*c* = g/100 mL), and solvent Analytical supercritical fluid chromatography (SFC) was performed using a built in photometric detector (λ = 220, 258 nm). Analytical columns used were Daicel Chiralpak AD and AS, Chiralcel OJ and OD and Regis (*R,R*)-Welk-01. Retention times (*t_R*) and peak areas for SFC were obtained from reporting integrators.

Analytical thin-layer chromatography was performed on Merck silica gel plates with F-254 indicator. Visualization was accomplished by UV light, iodine, potassium permanganate solution (KMnO_4), phosphomolibdic acid stain (PMA), *p*-anisaldehyde stain or dinitrophenylhydrazine (DNP) solution. Column chromatography was performed by the method of Still² with 32-63 mm silica gel (Merck). Bulb-to-bulb distillations were performed on a Kugelrohr and boiling points (bp) correspond to uncorrected, air bath temperatures. Melting points (mp) were determined in sealed capillary tubes and are corrected.

Literature Preparations

The following compounds were prepared by literature methods: The enolization using LiTMP followed the procedure described by Collum *et al.*³ The deprotection of TBS group followed the procedure described by Prakash *et al.*⁴ Diol **73** has been characterized by Albizati *et al.*⁵ The enolization using DBU to synthesize (*Z*)-enol ethers followed the procedure described by Yamaguchi, *et. al.*⁶ *tert*-Butyltritylamine (TBTA) was prepared according to the procedure described by Corey, *et. al.*⁷

Experimental Procedures

(3*S*)-4-(*tert*-Butyldimethylsilanyloxy)-3-methyl-2-trimethylsilanyloxy-but-1-ene (**8**)

n-Butyllithium (1.54 M in hexane, 11.1 mL, 7.18 mmol, 1.4 equiv) was added dropwise to a solution of diisopropylamine (1.67 mL, 11.9 mmol, 1.5 equiv) in 30 mL of tetrahydrofuran at 0 °C. The reaction mixture was stirred at 0 °C for 10 min then was cooled to −78 °C. To the reaction mixture was added trimethylchlorosilane (1.51 mL, 11.9 mmol, 1.5 equiv) and the ketone **7** (1.71 g, 7.90 mmol) and the reaction mixture was stirred for 30 min. The reaction mixture was gradually warmed up to 0 °C and was quenched with 40 mL of cold deionized water. The layers were separated and the aqueous layer was extracted twice with pentane. The combined extracts were washed with 50 mL of saturated aqueous copper sulfate, 25 mL of water and 50 mL of brine. The organic extracts were dried over sodium sulfate and were concentrated to give 2.32 g of crude oil. After distillation using a Vigreux column, the enolate **8** (1.94 g, 6.72 mmol, 85%) was obtained as colorless oil.

Data for **8**:

bp: 64 °C at 1.0 mmHg

¹H NMR: (500 MHz, CDCl₃)
 4.05 (d, *J* = 0.7, 1H, HC(1)); 4.04 (d, *J* = 0.7, 1 H, HC(1)); 3.70-3.37 (ABX, 2 H, H₂C(4)); 2.25 (sext, *J* = 6.6, 1 H, HC(3)); 1.01 (d, *J* = 6.8, 3 H, H₃C(5)); 0.89 (s, 9 H, H₃C(9)); 0.20 (s, 9 H, H₃C(6)); 0.04 (s, 6 H, H₃C(7))

¹³C NMR: (125 MHz, CDCl₃)
 160.8 (C(2)); 89.4 (C(1)); 66.0 (C(4)); 43.1 (C(3)); 25.9 (C(9)); 18.3 (C(8)); 15.0 (C(5)); 0.1 (C(6)); -5.4 (C(7))

IR: (neat)
 3112 (w); 2958 (s); 2930 (s); 2898 (m); 2859 (m); 1657 (w); 1626 (m); 1471 (m); 1254 (s); 1088 (s); 1010 (s); 845 (s),

MS: (FI)291 (11); 290 (26); 289 (M^+); 273 (12); 231 (61); 145 (10); 115 (16); 73 (39)Opt. rot.: -1.32 (CHCl_3 , $c=2.5$)Analysis: Calc for $\text{C}_{14}\text{H}_{32}\text{O}_2\text{Si}_2$ (288.57)

Calc. C 58.27%; H 11.18%

Found: C 58.05%; H 11.02%

(3S)-4-(tert-Butyldimethylsilanyloxy)-3-methyl-2-trichlorosilanyloxy-but-1-ene (9)

Silicon tetrachloride (1.74 mL, 15.1 mmol, 2 equiv) was added to a solution of palladium(II) acetate (85 mg, 0.38 mmol, 0.05 equiv) in 7.57 mL of methylene chloride. Trimethylsilyl enol ether **8** (2.18 g, 7.57 mmol) was added to the reaction mixture using a cannula, and the reaction mixture was stirred at rt for 1 h. Trichlorosilyl enolate **9** (1.88 g, 5.37 mmol, 71%) was obtained by fractional distillation of the reaction mixture as a clear liquid.

Data for **9**:bp: 70-72 °C at 0.1 mmHg ^1H NMR: (400 MHz)

4.58 (d, $J = 2.4$, 1 H, HC(2)); 4.45 (d, $J = 2.4$, 1 H, HC(2)); 3.68-3.46 (ABX, 2 H, $\text{H}_2\text{C}(4)$); 2.39 (sext, $J = 6.6$, 1 H, HC(3)); 1.07 (d, $J = 6.8$, 3 H, $\text{H}_3\text{C}(5)$); 0.89 (s, 9 H, $\text{H}_3\text{C}(8)$); 0.04 (s, 6 H, $\text{H}_3\text{C}(6)$)

(4S)-4-(tert-Butyldimethylsilyloxy)-2-trimethylsilyloxy-1-pentene (11)

n-Butyllithium (1.54 M in hexane, 4.20 mL, 6.47 mmol, 1.4 equiv) was added dropwise to a solution of diisopropylamine (0.971 mL, 6.93 mmol, 1.5 equiv) in 15 mL of tetrahydrofuran at 0 °C. The reaction mixture was stirred at 0 °C for 10 min then was cooled to –78 °C. To the reaction mixture was added trimethylchlorosilane (0.879 mL, 6.93 mmol, 1.5 equiv) and the ketone **10** (1.00 g, 4.62 mmol) and the reaction mixture was stirred for 30 min. The reaction mixture was gradually warmed up to 0 °C and was quenched with 20 mL of cold deionized water. The layers were separated and the aqueous layer was extracted twice with pentane. The combined extracts were washed with 20 mL of saturated aqueous copper sulfate, 15 mL of water and 20 mL of brine. The organic extracts were dried over sodium sulfate and were concentrated to give 1.61 g of crude oil. After distillation using a Kugelrohr apparatus, enol ether **11** (1.18 g, 4.09 mmol, 89%) was obtained as colorless oil.

Data for **11:**

bp: 75 °C ABT at 0.5 mmHg

¹H NMR: (500 MHz, CDCl₃)
 4.04 (d, *J* = 7.6, 2 H, H₂C(1)); 4.04 (sext, *J* = 6.5, 1 H, HC(4)); 2.26-2.01 (ABX, 2 H, H₂C(3)); 1.15 (d, *J* = 6.1, 3 H, H₃C(5)); 0.88 (s, 9 H, H₃C(9)); 0.20 (s, 9 H, H₃C(6)); 0.05 (d, *J* = 1.9, 6 H, H₃C(7))

¹³C NMR: (126 MHz, CDCl₃)
 156.7 (C(2)); 91.8 (C(1)); 66.4 (C(4)); 47.5 (C(3)); 25.9 (C(9)); 23.4 (C(8)); 18.2 (C(5)); 0.1 (C(6)); -4.7, -4.8 (C(7))

IR: (neat)
 2959 (s); 2930 (m); 2898 (m); 2858 (m); 1660 (m); 1637 (m); 1464 (m); 1377 (m); 1304 (m); 1254 (s); 1211 (m); 1128 (m); 1087 (m); 1014 (m)

MS: (FI)289 (61, M⁺); 273 (8); 254 (4); 231 (100); 199 (1); 185 (3); 159 (41); 131 (3); 115 (6); 73 (40)Opt. Rot.: $[\alpha]_D^{24} + 6.81$ (CHCl₃, c=3.5)Analysis: Calc for C₁₄H₃₂O₂Si₂ (288.57)

Calcd: C, 58.27%; H, 11.18%

Found: C, 58.15%; H, 11.41%

(4S)-4-Triisopropylsilyloxy-2-trimethylsilyloxy-1-pentene (36)

n-Butyllithium (1.54 M in hexane, 2.29 mL, 3.53 mmol, 1.4 equiv) was added dropwise to a solution of diisopropylamine (0.53 mL, 3.78 mmol, 1.5 equiv) in 10 mL of tetrahydrofuran at 0 °C. The reaction mixture was stirred at 0 °C for 10 min then was cooled to −78 °C. To the reaction mixture was added trimethylchlorosilane (0.48 mL, 3.78 mmol, 1.5 equiv) and the ketone **48** (651 mg, 2.52 mmol) and the reaction mixture was stirred for 30 min. The reaction mixture was gradually warmed up to 0 °C and was quenched with 20 mL of cold deionized water. The layers were separated and the aqueous layer was extracted twice with pentane. The combined extracts were washed with 20 mL of saturated aqueous copper sulfate, 15 mL of water and 20 mL of brine. The organic extracts were dried over sodium sulfate and were concentrated to give 1.61 g of crude oil. After distillation using a Kugelrohr apparatus, the enol ether **36** (688 mg, 2.08 mmol, 83%) was obtained as colorless oil.

Data for 36:bp: 125 °C ABT at 1.0 mmHg¹H NMR: (500 MHz, CDCl₃)4.12 (sextd, *J* = 6.5, 1.5, 1 H, HC(4)); 4.04 (d, *J* = 11.7, 2 H, H₂C(1)); 2.38-2.02 (ABX, 2 H, H₂C(3)); 1.18 (d, *J* = 6.1, 3 H, H₃C(5)); 1.06 – 1.01 (m, 21 H, H₃C(8)),

HC(7)); 0.19 (d, $J = 1.9$, 6 H, H₃C(6))

¹³C NMR: (126 MHz, CDCl₃)

156.9 (C(2)); 91.6 (C(1)); 66.5 (C(4)); 47.8 (C(3)); 23.2 (C(5)); 18.1 (C(8)); 12.3 (C(7)); -0.0 (C(6))

IR: (neat)

2962 (s); 2945 (s); 2885 (m); 2868 (s); 1659 (w); 1624 (w); 1464 (w); 1378 (w); 1303 (m); 1254 (m); 1211 (w); 1126 (m); 1090 (m); 1014 (s)

MS: (FI)

332 (21); 331 (65, M⁺); 289 (11); 288 (25); 287 (100); 201 (60); 73 (25)

Opt. Rot.: $[\alpha]_D^{24} + 11.5$ (CHCl₃, c=0.95)

Analysis: C₁₇H₃₈O₂Si₂ (288.57)

Calcd: C, 61.75%; H, 11.58%

Found: C, 61.79%; H, 11.80%

(4S)- 4-(tert-Butyldimethylsilyloxy)-2-trichlorosilyloxy-1-pentene (12)

Silicon tetrachloride (0.46 mL, 4.02 mmol, 2.0 equiv) was added to a solution of palladium(II) acetate (22.6 mg, 0.10 mmol, 0.05 equiv) in 2.00 mL of methylene chloride. Trimethylsilyl enol ether **11** (580 mg, 2.01 mmol) was added to the reaction mixture using a cannula, and the reaction mixture was stirred at rt for 30 min. Trichlorosilyl enolate **12** (526 mg, 1.50 mmol, 75%) was obtained by Kugelrohr distillation of the reaction mixture as clear liquid.

Data for **12:**

bp: 125 °C ABT at 1 mmHg

¹H NMR: (400 MHz, CDCl₃)

4.59 (d, $J = 1.9$, 1 H, H₂C(1)); 4.46 (d, $J = 2.0$, 1 H, H₂C(1)); 4.04 (sext, $J = 6.2$, 1 H, HC(4)); 2.35-2.16 (ABX, 2 H, H₂C(3)); 1.18 (d, $J = 5.8$, 3 H, H₃C(5)); 0.88 (s,

9 H, H₃C(8); 0.06 (d, $J = 3.6$, 6 H, H₃C(6))

(4S)-(2Z)-3-Trimethylsilyloxy-4-*tert*-butyldimethylsilyloxy-pent-2-ene ((Z)-14)

Trimethylsilyl trifluoromethanesulfonate (TMSOTf) (240 μ L, 1.32 mmol, 1.2.0 equiv) was dissolved in benzene (2 mL) at room temperature. Triethylamine (210 μ L, 1.65 mmol, 1.5 equiv) was carefully added via syringe and the entire solution was cooled in an ice bath. Silyloxy ketone **13** (232 mg, 1.1 mmol) was then added dropwise via syringe. The reaction was allowed to warm to room temperature and monitored by TLC. After 3 h, the biphasic mixture was quickly poured in to cold water (10 mL, 0 °C) with rapid stirring. The layers were separated and the aqueous phase was extracted with pentane (3 $\times$ 5 mL). The combined organic extracts were then washed with brine (5 mL), dried over Na₂SO₄, filtered and concentrated to give a crude oil. The residue was distilled under reduced pressure to afford 288 mg (96%) of **14** as a clear, colorless oil, suitable for use in subsequent reactions. To obtain an analytically pure sample, **14** was sacrificially purified by chromatography (SiO₂, pentane/CH₂Cl₂, 6/1). The residue was again distilled under reduced pressure to afford 159 mg (53%) of analytically pure **14**.

Data for **14**:

bp: 110 °C (0.1 mmHg, ABT)

¹H NMR: (CDCl₃, 500 MHz)

4.84 (qd, $J = 6.6, 0.6$, 1 H, HC(4)); 4.08 (q, $J = 6.2$, 1 H, HC(2)); 1.54 (dd, $J = 6.6, 0.9$, 3 H, H₃C(5)); 1.25 (d, $J = 6.2$, 3 H, H₃C(1)); 0.92 (s, 9 H, H₃C(9)); 0.23 (s, 9 H, H₃C(6)); 0.08, (d, $J = 4.1$, 6 H, H₃C(7))

¹³C NMR: (CDCl₃, 125 MHz)

153.5 (C(3)); 101.5 (C(2)); 70.5 (C(4)); 25.9 (C(5)); 22.6 (C(9)); 18.3 (C(8)); 10.5 (C(1)); 0.7 (C(6)); -4.7 (C(7)); -5.0 (C(7))

MS: (FI)

289 (M⁺+1, 27), 288 (M⁺, 100), 231 (4), 120 (2)

IR: (neat)

2958 (s), 2931 (s), 2858 (m), 1257 (s), 1119 (m), 1078 (m), 1049 (m), 837 (s), 777 (m)

Opt. Rot.: $[\alpha]_D^{23} -4.1^\circ$ ($c = 2.00$, CHCl_3)

Analysis: $\text{C}_{14}\text{H}_{32}\text{O}_2\text{Si}_2$ (288.58)

Calculated: C, 58.27; H, 11.18%

Found: C, 58.11; H, 11.31%

(S)-(Z)-Trichloro[(1-((1-((dimethyl)-(1,1-dimethylethyl)silyl)oxy)ethyl)propenyl)-oxy]-silane ((Z)-23)

Mercuric acetate (32 mg, 0.1 mmol, 0.01 equiv) was suspended in CH_2Cl_2 (10 mL) at room temperature. Silicon tetrachloride (2.3 mL, 20 mmol, 2.0 equiv) was then carefully added via syringe and the cloudy mixture was allowed to stir for several minutes. TMS enol ether **14** (2.7 g, 10 mmol) was then added dropwise via syringe. The reaction was allowed to stir at room temperature and could be monitored by careful removal of 10 μL aliquots for ^1H NMR analysis. After 18 h, the mercury salts were allowed to settle and the supernatant was carefully transferred to a dry 35 mL round bottom flask via cannula. The volatile components were removed at 100 mmHg and the residual oil was purified by distillation to afford 2.3 g (65%) of **23** as a 15/1 mixture of *Z/E* isomers by ^1H NMR.

Data for (Z)-23:

bp: 150 $^\circ\text{C}$ (0.1 mmHg, ABT)

^1H NMR: (CDCl_3 , 500 MHz)

5.04 (q, $J = 7.0$ 1 H, HC(2), *Z*); 4.95 (q, $J = 7.0$, 1 H, HC(2), *E*); 4.21 (q, $J = 6.8$, 1 H, HC(1'), *Z*); 4.18 (q, $J = 6.8$, 1 H, HC(1'), *E*); 1.60 (d, $J = 7.0$, 3 H, $\text{H}_3\text{C}(3)$); 1.31 (d, $J = 6.8$, 3 H, $\text{H}_3\text{C}(2')$); 0.93 (s, 9 H, $\text{H}_3\text{C}(3'')$); 0.07, (d, $J = 4.1$, 6 H, $\text{H}_3\text{C}(1'')$)

¹³C NMR: (CDCl₃, 125 MHz)

150.9 (C(1)); 108.3 (C(2)); 69.5 (C(1')); 25.8 (C(3'')); 22.2 (C(2'')); 18.6 (C(2''));
10.5 (C(3)); 0.7 (C(1''')); -4.7 (C(1'')); -5.0 (C(1''))

(-)-(S)-(E)-Trimethyl[(1-((1-((dimethyl)-(1,1-dimethylethyl)silyl)oxy)ethyl)-propenyl)oxy]
silane ((E)-**14**)

TMSCl (2.7 mL, 21.2 mmol, 2 equiv) was added via syringe to a solution containing LiTMP (13.8 mmol, 1.3 equiv) in THF (25 mL) at -78 °C. Ketone **13** (2.3 g, 10.6 mmol, 1 equiv) was then added dropwise over several minutes maintaining a temperature below -65 °C. Upon complete addition, the reaction was allowed to warm to room temperature and quenched with H₂O (25 mL). The reaction mixture was then washed with aqueous CuSO₄ (3 × 15 mL), H₂O (1 × 15 mL) and brine (1 × 15 mL). The organic phase was dried over Na₂SO₄, filtered and concentrated in vacuo. Purification by column chromatography (SiO₂, 20/1 pentane/CH₂Cl₂) and distillation afforded 650 mg (22%) of (E)-**14** as a clear, colorless oil.

Data for (E)-**14**:

bp: 110 °C (0.1 mmHg, ABT)

¹H NMR: (CDCl₃, 500 MHz)

5.01 (qd, *J* = 7.0, 0.6, 1 H, HC(2)); 4.08 (q, *J* = 6.2, 1 H, HC(1')); 1.54 (dd, *J* = 6.6, 0.9, 3 H, H₃C(3)); 1.25 (d, *J* = 7.0, 3 H, H₃C(2')); 0.92 (s, 9 H, H₃C(3'')); 0.23 (s, 9 H, H₃C(1''')); 0.08, (d, *J* = 4.1, 6 H, H₃C(1''))

¹³C NMR: (CDCl₃, 125 MHz)

153.5 (C(1)); 101.5 (C(2)); 70.5 (C(1')); 25.9 (C(3'')); 22.6 (C(2'')); 18.3 (C(2''));
10.5 (C(3)); 0.7 (C(1''')); -4.7 (C(1'')); -5.0 (C(1''))

MS: (FI)

288 (M⁺, 100), 231 (4), 120 (2)

IR: (neat)

2958 (s), 2931 (s), 2858 (m), 1257 (s), 1119 (m), 1078 (m), 1049 (m), 837 (s), 777

(m)

Opt. Rot.: $[\alpha]_{\text{D}}^{23} -4.8^{\circ}$ ($c = 2.00$, CHCl_3)Analysis: $\text{C}_{14}\text{H}_{32}\text{O}_2\text{Si}_2$ (288.58)

Calculated: C, 58.27; H, 11.18%

Found: C, 58.15; H, 11.25%

**(S)-(Z)-Trichloro[(1-((1-((dimethyl)-(1,1-dimethylethyl)silyl)oxy)ethyl)-propenyl)oxy]silane
(E)-23**

TMS enol ether (*E*)-**14** (225 mg, 1 mmol, 1 equiv) was added to a 10 mL, 2 neck flask containing Et₂O (3 mL) cooled to 0 °C in an ice water bath. To this was added MeLi (0.88 mL, 1.2 mmol, 1.2 equiv) slowly via syringe. Upon complete addition, the reaction mixture was allowed to stir at rt for 6 h. The contents of the reaction flask were then transferred dropwise via cannula to a solution containing SiCl₄ (1.1 mL, 10 mmol, 10 equiv) in Et₂O (3 mL) at -78 °C. The cryobath was removed and upon warming, the presence of a white precipitate was observed. The contents of the reaction were transferred via cannula to a clean flask, concentrated carefully in vacuo to afford 238 mg (68%) of (*E*)-**23** as a colorless oil.

Data for (*E*)-23:¹H NMR: (CDCl₃, 500 MHz)

5.14 (q, $J = 7.0$ 1 H, HC(2), *Z*); 4.95 (q, $J = 7.0$, 1 H, HC(2), *E*); 4.21 (q, $J = 6.8$, 1 H, HC(1'), *Z*); 4.18 (q, $J = 6.8$, 1 H, HC(1'), *E*); 1.60 (d, $J = 7.0$, 3 H, H₃C(3)); 1.31 (d, $J = 6.8$, 3 H, H₃C(2'')); 0.93 (s, 9 H, H₃C(3'')); 0.07, (d, $J = 4.1$, 6 H, H₃C(1''))

(2Z,4S)- 5-(tert-Butyldimethylsilyloxy)-4-methyl-3-trimethylsilyloxy-2-pentene ((Z)-17)

In a 50-mL two-neck flask was placed a solution of trimethylsilyl triflate (TMSOTf, 0.93 mL, 5.17 mmol, 1.2 equiv) in benzene (15 mL) at 0 °C. To the solution were added sequentially triethylamine (0.88 mL, 6.45 mmol, 1.5 equiv) and **15** (990 mg, 4.30 mmol). The reaction mixture was allowed to warm up to rt and stirred for 5 h. The reaction mixture was cooled using an ice bath and was quenched with cold water (15 mL). The biphasic mixture was extracted with pentane (2 x 20 mL), and the combined extracts were washed sequentially with saturated CuSO₄ aq. (2 x 15 mL), water (10 mL) and brine (10 mL). The solution was dried over sodium sulfate and concentrated to yield 1.42 g of crude oil. The crude oil was chromatographed (hexane/CH₂Cl₂, 8/1) to afford 100 mg (0.33 mmol, 8%) of (*E*)-**17** and 688 mg (2.27 mmol, 53%) of (*Z*)-**17** both as clear colorless oil. The analytically pure (*Z*)-**17** was obtained by further distillation using the Kugelrohr apparatus (125 °C ABT at 1.0 mmHg).

Data for (*Z*)-**17**:

bp: 170 °C (ABT) at 15 mmHg

¹H NMR: (500 MHz, CDCl₃)

4.53 (qd, *J* = 6.9, 0.8, 1 H, HC(2)); 3.75-3.30 (ABX, 2 H, H₂C(5)); 2.20 (sext, *J* = 6.1, 1 H, HC(4)); 1.50 (dd, *J* = 6.8, 0.9, 3 H, H₃C(3)); 1.02 (d, *J* = 6.8, 3 H, H₃C(6)); 0.88 (s, 9 H, H₃C(10)); 0.20 (s, 9 H, TMS); 0.03 (s, 6 H, H₃C(8))

¹³C NMR: (126 MHz, CDCl₃)

152.9 (C(3)); 101.6 (C(2)); 66.4 (C(5)); 43.1 (C(4)); 25.9 (C(10)); 18.3 (C(9)); 15.3 (C(7)); 10.9 (C(1)); 0.7 (C(6)); -5.4 (C(8))

IR: (neat)

2958 (s); 2931 (s); 2860 (m); 1675 (m); 1472 (m); 1389 (w); 1319 (w); 1254 (s); 1191 (m); 1087 (s)

MS: (FI)
 305 (2); 304 (12); 303 (31); 302.(100, M⁺); 245 (2); 199 (2)

Opt. Rot.: $[\alpha]_D^{24} +1.50^\circ$ (CHCl₃, c=1.0)

TLC: *R_f* 0.25 (hexane/CH₂Cl₂, 5/1) [silica gel, KMnO₄]

Analysis: C₁₅H₃₄O₂Si₂ (302.60)

Calcd: C, 59.54%; H, 11.33%

Found: C, 59.27%; H, 11.52%

(2*E*,4*S*)- 5-(*tert*-Butyldimethylsilyloxy)-4-methyl-3-trimethylsilyloxy-2-pentene ((*E*)-17)

In a 100-mL two-neck flask was placed a solution of *tert*-butyl-tritylamine (TBTA, 2.05 g, 6.51 mmol, 1.5 equiv) in THF (30 mL) at 0 °C. To the solution was added dropwise *n*-BuLi (3.95 mL, 6.08 mmol, 1.4 equiv, 1.54 M in hexane). The solution was stirred at 0 °C for 10 min then cooled to –72 °C using an acetone/dry ice bath. To the solution was added sequentially TMSCl (0.83 mL, 6.51 mmol, 1.5 equiv) and **15** (1.00 g, 4.34 mmol). The reaction mixture was stirred for 30 min at –72 °C, then gradually warmed up to 0°C over 1 h. The reaction mixture was poured into cold deionized water (15 mL). The layers were separated and the aqueous layer was extracted using pentane (2 x 25 mL). The combined organic extracts were washed with saturated CuSO₄ aq. (2 x 10 mL), water (10 mL) and brine (10 mL), dried over sodium sulfate and concentrated. The crude oil was purified by distillation using Kugelrohr (175 °C ABT at 15 mmHg) followed by column chromatography (silica gel, hexane/CH₂Cl₂, 5/1, 40 mm) to afford 727 mg (2.40 mmol, 55%) of (*E*)-**17** as a clear oil and 68 mg (0.22 mmol, 5%, 1/1 *Z/E* mixture) of **17** as colorless oil.

Data for (*E*)-17:

bp: 150 °C (ABT) at 1.0 mmHg

¹H NMR: (500 MHz, CDCl₃)

4.58 (q, $J = 6.8$, 1 H, HC(2)); 3.60-3.38 (ABX, 2 H, H₂C(5)); 2.73 (sext, $J = 7.1$, 1 H, HC(4)); 1.55 (d, $J = 6.8$, 3 H, H₃C(3)); 0.93 (d, $J = 6.9$, 3 H, H₃C(6)); 0.88 (s, 9 H); 0.20 (s, 9 H, TMS); 0.03 (s, 6 H)

¹³C NMR: (126 MHz, CDCl₃)

153.0 (C(3)); 100.3 (C(2)); 65.8 (C(5)); 36.7 (C(4)); 25.9 (C(10)); 18.3 (C(9)); 14.1 (C(7)); 11.5 (C(1)); 0.4 (C(6)); -5.4, -5.4 (C(8))

IR: (neat)

2958 (m); 2932 (m); 2898 (m); 2860 (m); 1667 (m); 1472 (m); 1388 (w); 1363 (w); 1253 (s); 1223 (s); 1105 (s); 1048 (m)

MS: (FI)

304 (10); 303 (30); 302 (100, M⁺); 199 (2); 199 (2)

Opt. Rot.: $[\alpha]_D^{24} -8.99^\circ$ (CHCl₃, c=0.67)

TLC: R_f 0.38 (hexane/CH₂Cl₂, 5/1) [silica gel, KMnO₄]

Analysis: C₁₅H₃₄O₂Si₂ (302.60)

Calcd: C, 59.54%; H, 11.33%

Found: C, 59.54%; H, 11.63%

(2Z,4S)- 5-(Triisopropylsilyloxy)-4-methyl-3-trimethylsilyloxy-2-pentene ((Z)-18)

In a 100-mL round-bottom flask was placed a solution of TMSCl (3.25 mL, 25.6 mmol, 1.2 equiv) in dichloromethane (40 mL) at rt. To the solution were added DBU (3.84 mL, 25.6 mmol, 1.2 equiv) and **15** (5.80 g, 21.3 mmol). The flask was fitted to a reflux condenser and the reaction mixture was refluxed for 4 h. The reaction mixture was cooled using an ice bath and quenched with cold NaHCO₃ aq. (40 mL). The product was extracted in pentane (2 x 50 mL),

and the combined extracts were washed with brine (40 mL). The organic extracts were dried over sodium sulfate and concentrated to yield 5.50 g of crude oil. The crude oil was chromatographed (silica gel, pentane/CH₂Cl₂, 5/1, 50 mm), and 5.03 g of (Z)-**18** (14.6 mmol, 69%) as clear colorless oil. Analytically pure sample of (Z)-**18** was obtained by distillation using the Kugelrohr apparatus.

Data for (Z)-**18**:

bp: 125 °C (ABT) at 0.05 mmHg

¹H NMR: (500 MHz, CDCl₃)

4.55 (q, *J* = 6.7, 1 H, HC(2)); 3.85-3.38 (ABX, 2 H, H₂C(5)); 2.23 (sext, *J* = 6.3, 1 H, HC(4)); 1.51 (d, *J* = 6.6, 3 H, H₃C(3)); 1.10 – 1.03 (m, 24 H, H₃C(7), H₃C(8), HC(8)); 0.19 (s, 9 H, TMS);

¹³C NMR: (126 MHz, CDCl₃)

153.2 (C(3)); 101.9 (C(2)); 67.0 (C(5)); 43.6 (C(4)); 18.2 (C(9)); 15.6 (C(7)); 12.2 (C(8)); 11.1 (C(1)); 0.9 (C(6));

IR: (neat)

2958 (s); 2931 (s); 2860 (m); 1675 (m); 1472 (m); 1389 (w); 1319 (w); 1254 (s); 1191 (m); 1087 (s)\

MS: (FI)

347 (2); 346 (12); 345 (31); 344 (100, M⁺);

Opt. Rot.: [α]_D²⁴ +4.18° (CHCl₃, c=2.5)

TLC: *R_f* 0.33 (pentane/CH₂Cl₂, 5/1) [silica gel, KMnO₄]

Analysis: Calc for C₁₈H₄₀O₂Si₂ (344.68)

Calcd: C, 62.72%; H, 11.70%

Found: C, 62.63%; H, 11.61%

General Procedure I: MeLi Mediated Transsilylation of 17: (2Z,4S)- 5-(tert-Butyldimethylsilyloxy)-4-methyl-3-trichlorosilyloxy-2-pentene ((Z)-24)

In a 25-mL two-neck flask was placed a solution of (Z)-17 (908 mg, 3.00 mmol) in ether (6 mL) at 0 °C. To the solution was slowly added MeLi (3.00 mL, 4.50 mmol, 1.5 equiv, 1.5 M in ether). The reaction mixture was stirred for 4.5 h at rt, then cooled to -70 °C using an dry ice/isopropanol bath. The reaction mixture was transferred dropwise using a cannula to a 100-mL two-neck flask containing a cold (-70 °C) solution of silicon tetrachloride (3.45 mL, 30.0 mmol, 10 equiv) in ether (6 mL). The reaction mixture was stirred at -70 °C for 1 h and gradually warmed to rt. The precipitate settled at the bottom of the flask, and the supernatant was transferred to a 35-mL round-bottom flask. The volatiles were removed under vacuum (0.5 mmHg) and the residue was distilled using a Kugelrohr apparatus (150 °C ABT at 1.0 mmHg), to afford 901 mg (2.48 mmol, 83%) of (Z)-24 as a clear colorless oil.

Data for (Z)-24:

bp: 150 °C (ABT) at 1.0 mmHg

¹H NMR: (CDCl₃, 500 MHz)

4.53 (qd, *J* = 6.8, 0.5, 1 H, HC(2)); 3.69-3.43 (ABX, 2 H, H₂C(5)); 2.40 (sext, *J* = 6.3, 1 H, HC(4)); 1.60 (dd, *J* = 7.1, 0.7, 3 H, H₃C(1)); 1.07 (d, *J* = 7.1, 3 H, H₃C(6)); 0.88 (s, 9 H, H₃C(9)); 0.03 (s, 6 H, H₃C(7))

¹³C NMR: (CDCl₃, 126 MHz)

150.8 (C(3)); 106.4 (C(2)); 65.3 (C(5)); 42.1 (C(4)); 25.8 (C(9)); 18.2 (C(8)); 14.9 (C(7)); 11.0 (C(1)); -5.5, -5.4 (C(7));

150.8 (C(3)); 106.7 (C(2)); 65.0 (C(5)); 36.4 (C(4)); 25.8 (C(9)); 18.2 (C(8)); 13.6 (C(1)); 11.4 (C(6)); -5.5, -5.5 (C(7));

Following General Procedure I using (Z)-**18** (6.51 g, 18.9 mmol), MeLi (18.9 mL, 28.4

mmol, 1.5 M in ether) and SiCl_4 (21.7 mL, 189 mmol) in 50 mL of THF, 6.14 g (12.7 mmol, 67%) of (Z)-**25** was obtained as a clear colorless oil.

Data for (Z)-**25**:

bp: 115 °C at 1.0 mmHg

^1H NMR: (500 MHz, CDCl_3)

4.85 (qd, $J = 6.9, 0.5$, 1 H, HC(2)); 3.80-3.51 (ABX, 2 H, $\text{H}_2\text{C}(5)$); 2.43 (sext, $J = 5.8$, 1 H, HC(4)); 1.60 (dd, $J = 6.9, 0.9$, 3 H, $\text{H}_3\text{C}(3)$); 1.10 (d, $J = 6.9$, 3 H, $\text{H}_3\text{C}(6)$); 1.10 – 1.00 (m, 21 H, $\text{H}_3\text{C}(8)$, HC(7));

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

164.8 (C(3)); 106.6 (C(2)); 65.9 (C(5)); 42.6 (C(4)); 18.2 (C(9)); 15.1 (C(7)); 12.2 (C(8)); 11.3 (C(1));

(2Z,5S)- 5-tert-Butyldimethylsilyloxy-3-trimethylsilyloxy-2-hexene ((Z)-21**)**

In a 50 mL three-neck flask equipped with a stopper and a reflux condenser, DBU (1.30 mL, 8.68 mmol, 2 equiv) was dissolved in 20 mL of CH_2Cl_2 . To this solution were added TMSCl (1.10 mL, 8.68 mmol, 2 equiv) and **19** (1.00 g, 4.34 mmol). The reaction mixture was heated to reflux for 4 h. The reaction mixture was cooled to rt and quenched with cold sat. aq. NaHCO_3 (20 mL) solution. The product was extracted with hexane (2 x 25 mL) and washed with brine (25 mL). The extracts were dried over sodium sulfate and concentrated. The crude oil was chromatographed (silica gel, 5/1 hexane/ CH_2Cl_2 , 40 mm) and distilled using the Kugelrohr apparatus to give 820 mg (2.71 mmol, 62%) of (Z)-**21** as clear colorless oil.

Data for (Z)-**21**:

bp: 125 °C (0.5 mmHg)

¹H NMR: (500 MHz, CDCl₃)

4.54 (q, *J* = 6.6, 1 H, HC(2)); 3.99 (sext, *J* = 6.2, 1 H, HC(4)); 2.21-1.97 (ABX, 2 H, H₂C(4)); 1.48 (d, *J* = 6.7, 3 H, H₃C(1)); 1.13 (d, *J* = 6.0, 3 H, H₃C(6)); 0.87 (s, 9 H, H₃C(10)); 0.18 (s, 9 H, H₃C(7)); 0.03 (d, *J* = 6.2, 6 H, H₃C(8))

¹³C NMR: (126 MHz, CDCl₃)

148.5 (C(3)); 104.7 (C(2)); 66.4 (C(5)); 47.5 (C(4)); 25.8 (C(10)); 23.5 (C(9)); 18.1 (C(6)); 10.8 (C(1)); 0.6 (C(7)); -4.7, -4.9 (C(8))

IR: (neat)

2958 (s); 2929 (m); 2899 (m); 2858 (m); 1680 (m); 1473 (m); 1377 (m); 1323 (m); 1254 (s); 1194 (m); 1128 (m); 1093 (m); 1070 (m); 1030 (m)

MS: (FI)

302 (100, M⁺)

Opt. Rot.: [α]_D²⁴ + 4.61 (CHCl₃, c=0.97)

TLC: *R*_f 0.20 (hexane/CH₂Cl₂, 5/1) [silica gel, KMnO₄]

Analysis: C₁₅H₃₄O₂Si₂ (302.60)

Calcd: C, 59.54%; H, 11.33%

Found: C, 59.67%; H, 11.61%

(2Z,5S)- 5-Triisopropylsilyloxy-3-trimethylsilyloxy-2-hexene ((Z)-22)

In a 50 mL three-neck flask equipped with a stopper and a reflux condenser, DBU (0.89 mL, 6.06 mmol, 1.5 equiv) was dissolved in 15 mL of CH₂Cl₂. To this solution were added TMSCl (0.77 mL, 6.06 mmol, 1.5 equiv) and **20** (1.10 g, 4.04 mmol). The reaction mixture was heated to reflux for 4 h. The reaction mixture was cooled to rt and quenched with 20 mL of cold sat. aq. NaHCO₃ solution. The product was extracted in 50 mL of hexane and washed with 25 mL of brine. The extract was dried over sodium sulfate and concentrated. The crude product

was chromatographed (silica gel, hexane/CH₂Cl₂, 8/1.40 mm) and distilled using the Kugelrohr apparatus to afford 800 mg (2.32 mmol, 57%) of (Z)-**22** as clear colorless oil.

Data for (Z)-**22**:

bp: 125 °C (0.05 mmHg)

¹H NMR: (400 MHz, CDCl₃)

4.55 (q, *J* = 6.8, 1 H, HC(2)); 4.10 (sextd, *J* = 5.6, 2.7, 1 H, HC(5)); 2.33-1.97 (ABX, 2 H, H₂C(4)); 1.48 (d, *J* = 6.8, 3 H, H₃C(1)); 1.17 (d, *J* = 5.9, 3 H, H₃C(6)); 1.16 – 1.05 (m, 21 H, H₃C(9), HC(8)); 0.18 (s, 9 H, H₃C(7))

¹³C NMR: (126 MHz, CDCl₃)

148.7 (C(3)); 104.7 (C(2)); 66.7 (C(5)); 47.8 (C(4)); 23.6 (C(6)); 18.1 (C(9)); 12.4 (C(8)); 10.9 (C(1)); 0.6 (C(7))

IR: (neat)

2961 (s); 2944 (s); 2895 (m); 2867 (s); 1678 (m); 1464 (m); 1377 (m); 1323 (m); 1253 (s); 1193 (m); 1128 (m); 1096 (m); 1069 (m); 1028 (m); 1004 (m)

MS: (FI)

346 (12); 345 (33); 344 (100, M⁺); 263 (3)

Opt. Rot.: [α]_D²⁴ + 6.57 (CHCl₃, c=0.48)

TLC: *R*_f 0.25 (hexane/CH₂Cl₂, 8/1) [silica gel, KMnO₄]

Analysis: C₁₈H₄₀O₂Si₂ (344.68)

Calcd: C, 62.72%; H, 11.70%

Found: C, 62.53%; H, 12.00%

(2E,5S)- 5-Triisopropylsilyloxy-3-trimethylsilyloxy-2-hexene ((E)-22**)**

In a 25 mL two-neck flask equipped with a stopper and a septum, TBTA (946 mg, 3.00 mmol, 1.5 equiv) was dissolved in 10 mL of THF at 0 °C. To this solution was added *n*-BuLi

(1.82 mL, 2.80 mmol, 1.4 equiv, 1.54 M in hexane) dropwise, and the solution was stirred for 10 min. The solution was cooled to -78 °C, then TMSCl (0.381 mL, 3.00 mmol, 1.5 equiv) and **20** (0.55 g, 2.00 mmol) were added. The reaction mixture was stirred for 30 min and gradually warmed to 0 °C over 2 h. The reaction mixture was quenched with 10 mL of cold sat. aq. NaHCO₃ solution. The product was extracted in 50 mL of pentane and washed with 25 mL of brine. The extract was dried over sodium sulfate and concentrated. The residue was redissolved in pentane (60 mL) and cooled to -15 °C to crystallize TBTA. The recovered TBTA was removed by filtration and the filtrate was condensed under reduced pressure. The crude product was chromatographed (silica gel, hexane/CH₂Cl₂, 8/1, 30 mm) and distilled using the Kugelrohr apparatus to give 475 mg (1.38 mmol, 69%) of (*E*)-**22** as clear colorless oil.

Data for (*E*)-**22**:

bp: 125 °C (0.05 mmHg)

¹H NMR: (400 MHz, CDCl₃)

4.67 (q, *J* = 6.8, 1 H, HC(2)); 4.14 (m, 1 H, HC(5)); 2.32-2.23 (ABX, 2 H, H₂C(4)); 1.55 (dd, *J* = 6.8, 0.5, 3 H, H₃C(1)); 1.16 (d, *J* = 6.1, 3 H, H₃C(6)); 1.07 (s, 21 H, H₃C(9), HC(8)); 0.15 (s, 9 H, H₃C(7))

¹³C NMR: (126 MHz, CDCl₃)

149.6 (C(3)); 102.6 (C(2)); 67.0 (C(5)); 42.0 (C(4)); 23.2 (C(6)); 18.1 (C(9)); 12.4 (C(8)); 12.1 (C(1)); 0.2 (C(7))

IR: (neat)

2962 (m); 2945 (m); 2895 (m); 2868 (m); 1670 (w); 1464 (m); 1379 (w); 1254 (m); 1198 (m); 1124 (m); 1107 (m); 1088 (m); 1005 (m)

MS: (FI)

347 (2); 346 (11); 345 (30); 344 (100, M⁺); 344 (2); 264 (2); 264 (3); 264 (5); 263 (3)

Opt. Rot.: [α]_D²⁴ + 6.64 (CHCl₃, c=0.39)

TLC: *R*_f 0.26 (hexane/CH₂Cl₂, 8/1) [silica gel, KMnO₄]

Analysis: C₁₈H₄₀O₂Si₂ (344.68)

Calcd: C, 62.72%; H 11.70%

Found: C, 62.38%; H, 11.94%

((2Z,5S)- 5-*tert*-Butyldimethylsilyloxy-3-trichlorosilyloxy-2-hexene ((Z)-26)

Following the General Procedure I using (Z)-**21** (972 mg, 3.21 mmol), MeLi (3.30 mL, 4.82 mmol, 1.5 equiv, 1.5 M in ether) and silicon tetrachloride (3.68 mL, 32.1 mmol, 10 equiv), 764 mg (2.10 mmol, 65%) of (Z)-**26** was obtained as a clear colorless oil.

Data for (Z)-**26**:

bp: 150 °C (ABT) at 1.0 mmHg

¹H NMR: (CDCl₃, 500 MHz)

4.83 (q, *J* = 6.9, 1 H, HC(2)); 4.03 (sext, *J* = 7.3, 1 H, HC(5)); 2.33-2.18 (ABX, 2 H, H₂C(4)); 1.58 (d, *J* = 6.8, 3 H, H₃C(1)); 1.15 (d, *J* = 6.2, 3 H, H₃C(6)); 0.87 (s, 9 H, H₃C(9)); 0.03 (d, *J* = 10.5, 6 H, H₃C(7))

((2Z,5S)- 5-Triisopropylsilyloxy-3-trichlorosilyloxy-2-hexene ((Z)-27)

Following the General Procedure I using (Z)-**22** (1.60 g, 4.64 mmol), MeLi (4.64 mL, 6.96 mmol, 1.5 M in ether) and SiCl₄ (5.32 mL, 46.4 mmol) in 10 mL of hexane, 1.13 g (2.78 mmol, 60%) of (Z)-**27** was obtained as a clear colorless oil.

Data for (Z)-**27**:

bp: 175 °C at 1.0 mmHg

$^1\text{H NMR}$: (500 MHz, CDCl_3)

4.84 (q, $J = 6.8$, 1 H, HC(2)); 4.16 (sext, $J = 7.1$, 1 H, HC(5)); 2.47-2.17 (ABX, 2 H, $\text{H}_2\text{C}(4)$); 1.59 (dt, $J = 6.8$, 1.0, 3 H, $\text{H}_3\text{C}(3)$); 1.20 (d, $J = 5.9$, 3 H, $\text{H}_3\text{C}(6)$); 1.13 – 1.01 (m, 21 H, $\text{H}_3\text{C}(8)$, HC(7));

(2*E*,5*S*)- 5-Triisopropylsilyloxy-3-trichlorosilyloxy-2-hexene ((*E*)-27)

Following General Procedure I using (*E*)-**22** (678 mg, 1.97 mmol), MeLi (1.57 mL, 2.36 mmol, 1.5 M in ether) and SiCl_4 (2.26 mL, 19.7 mmol) in 5 mL of ether, 180 mg (0.44 mmol, 23%) of (*E*)-**27** was obtained as a clear colorless oil.

Data for (*E*)-27:

bp: 150 °C at 0.5 mmHg

$^1\text{H NMR}$: (500 MHz, CDCl_3)

5.17 (q, $J = 7.1$, 1 H, HC(2)); 4.17 (m, 1 H, HC(5)); 2.56-2.31 (ABX, 2 H, $\text{H}_2\text{C}(4)$); 1.62 (d, $J = 7.1$, 3 H, $\text{H}_3\text{C}(3)$); 1.20 (d, $J = 6.1$, 3 H, $\text{H}_3\text{C}(6)$); 1.09 – 1.02 (m, 21 H, $\text{H}_3\text{C}(8)$, HC(7));

General Procedure II: Aldol Addition of Isolated Trichlorosilyl Enolates: (2*S*,5*R*)-1-*tert*-Butyldimethylsilyloxy-2-methyl-5-hydroxy-5-phenyl-3-pentanone (*syn*-28a)

Trichlorosilyl enolate **9** (140 mg, 0.40 mmol, 1.2 equiv) was added to a solution of (*R,R*)-

1 (12.2 mg, 0.033 mmol, 0.10 equiv) in 0.66 mL of CH₂Cl₂. The reaction mixture was cooled using an acetone/CO₂ bath, and PhCHO (34 μ L, 0.33 mmol, 1 equiv) was added using a syringe. The reaction was monitored by taking an aliquot from the reaction mixture and analyzing on TLC (hexane/EtOAc, 5/1). After one hour of stirring (or when the aldehyde spot disappeared), the reaction mixture was quenched by pouring into a vigorously stirring 5 mL of cold sat. aq. NaHCO₃ solution. The resulted slurry was stirred for 15 min and filtered through Celite. The layers were separated, and the aqueous layer was extracted with 10 mL of CH₂Cl₂. The organic phases were combined, washed with 2 mL of brine and dried over sodium sulfate. After filtration, the filtrate was concentrated. The crude product was purified by column chromatography (silica gel, hexane/EtOAc, 5/1), and 78 mg (0.24 mmol, 73%) of **28a** was obtained as a clear viscous oil.

Data for **28a**:

¹H NMR: (500 MHz, CDCl₃)

syn-**28a**

7.37-7.26 (m, 5 H, aromatic); 5.17 (dt, *J* = 8.5, 3.2, 1 H, HC(5)); 3.75-3.65 (ABX, 2 H, H₂C(1)); 3.50 (d, *J* = 2.9, 1 H, HO); 2.98- 2.84 (ABX, 2 H, H₂C(4)); 2.78 (sext, *J* = 7.1, 1 H, HC(2)); 1.03 (d, *J* = 7.1, 3 H, H₃C(6)); 0.87 (s, 9H, C(9)); 0.04 (d, *J* = 1.7, 6 H, C(7))

anti-**28a**

7.37-7.26 (m, 5 H, aromatic); 5.14 (dt, *J* = 9.3, 3.0, 1 H, HC(5)); 3.77-3.65 (ABX, 2 H, H₂C(1)); 3.54 (d, *J* = 3.0, 1 H, HO); 2.98- 2.84 (ABX, 2 H, H₂C(4)); 2.79 (sext, *J* = 7.1, 1 H, HC(2)); 1.04 (d, *J* = 7.1, 3 H, H₃C(6)); 0.88 (s, 9H, C(9)); 0.04 (d, *J* = 1.7, 6 H)

TLC: *syn*-**28a** R_f 0.10 (hexane/ether, 4/1, anisaldehyde reagent)

anti-**28a** R_f 0.15 (hexane/ether, 4/1, anisaldehyde reagent)

SFC: (OD column, 175 bar, 2.5 mL/min, 1.7% MeOH)

t_R *syn*-**28a** 5.414 min (91.3%); *t_R* *anti*-**28a** 5.989 min (8.7%)

General Procedure III: Aldol Addition of in-situ-generated Trichlorosilyl Enolates: (1*S*,4*R*)-5-*tert*-Butyldimethylsilyloxy-4-methyl-1-hydroxy-1-phenyl-3-pentanone (*syn*-28a**)**

To a suspension of mercury(II) acetate (3.2 mg, 0.01 mmol, 0.01 equiv) in 1 mL of methylene chloride was added silicon tetrachloride (0.23 mL, 2.0 mmol, 2.0 equiv) and the trimethylsilyl enol ether **8** (288 mg, 1.00 mmol). The reaction mixture was stirred at rt for 30 min. The excess silicon tetrachloride and the solvent were removed under vacuum. To the residue was added solution of the chiral phosphoramidate (*R,R*)-**1** (36.9 mg, 0.10 mmol, 0.10 equiv) in 2 mL of methylene chloride via a cannula. The reaction mixture was cooled to $-78\text{ }^{\circ}\text{C}$ before the addition of benzaldehyde (102 μL , 1.00 mmol, 1 equiv). The reaction mixture was stirred at $-78\text{ }^{\circ}\text{C}$ for 2.5 h, and then was quenched by pouring into a vigorously stirring 5 mL of cold saturated aqueous sodium bicarbonate. The resulting slurry was stirred for 1 h and was filtered through Celite. The layers were separated and the aqueous layer was extracted with 20 mL of methylene chloride. The combined organic extracts were washed with 5 mL of brine, dried over sodium sulfate and concentrated. The crude product was chromatographed (silica gel, hexane/ether, 5/1) to give **28a** (268 mg, 0.83 mmol, 83%) as viscous colorless oil.

Data for *syn*-**28a**:

^1H NMR: (500 MHz, CDCl_3)

7.23 – 7.47 (m, 5H, aromatic); 5.17 (dt, $J = 8.8, 3.2$, 1H, HC(1)); 3.65 – 3.76 (ABX, 2H, C(5) H_2); 3.49 (d, $J = 2.9$, 1H, OH); 2.86 – 2.96 (ABX, 2H, C(2) H_2); 2.78 (m, 1H, C(4) H); 1.03 (d, $J = 6.9$, 3H, C(6) H_3); 0.87 (s, 9H, (C(9) H_3) $_3$); 0.04 (d, $J = 2$, 6H, C(7) H_3)

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

214.7 (C(3)); 142.9, 128.5, 127.5, 125.6 (aromatic); 69.7 (C(1)); 65.6 (C(5)); 51.4 (C(2)); 49.0 (C(4)); 25.8 (C(9)); 18.2 (C(8)); 12.6 (C(6)); -5.6 (C(7))

IR: (neat)
3467 (m, br); 3064 (w); 3031 (w); 2954 (s); 2931 (s); 2885 (m); 2858 (m); 1708 (m); 1463 (m); 1388 (m); 1256 (m); 1100 (s); 838 (s)

MS: (FI)
322 (2, M⁺); 267 (6); 266 (22); 266 (2); 265 (100); 247 (7); 159 (8); 106 (3); 95 (2)

Opt. rot.: + 69.1 (CHCl₃, c=1.0)

TLC: *R_f* = 0.19 (hexane/EtOAc, 5/1, SiO₂)

SFC: (Chiralpak OD column, 150 bar, 3.0 mL/min, 1.4% MeOH)
t_R (2*S*, 5*R*)-*syn*-**28a** 4.74 min (95%); (2*S*, 5*S*)-*anti*-**28a** 5.21 min (5%)

Analysis: Calc for C₁₈H₃₀O₃Si (322.51)
Calc. C 67.03%; H 9.38%
Found: C 66.94%; H 9.42%

(1*S*,4*S*)-5-*tert*-Butyldimethylsilyloxy-4-methyl-1-hydroxy-1-phenyl-3-pentanone (*anti*-28a**)**

Following General Procedure III using **8** (288 mg, 1.00 mmol), SiCl₄ (0.23 mL, 2.00 mmol), Hg(OAc)₂ (3.2 mg, 0.01 mmol), benzaldehyde (102 μL, 1.00 mmol), (*S,S*)-**1** (37 mg, 0.10 mmol) in 2 mL of CH₂Cl₂, 121 mg (0.38 mmol, 75%) of *anti*-**28a** was obtained as colorless viscous oil after column chromatography (silica gel, hexane/EtOAc, 5/1).

Data for *anti*-28a**:**

¹H NMR: (500 MHz, CDCl₃)
7.27 – 7.38 (m, 5H, aromatic); 5.14 (dt, *J* = 9.6, 2.8, 1H, HC(1)); 3.67 – 3.77 (ABX, 2H, H₂C(5)); 3.50 (d, *J* = 3.0, 1H, OH); 2.84 – 2.97 (ABX, 2H, COC(2)H₂);

2.78 (m, 1H, COC(4)*H*); 1.05 (d, $J = 7.1$, 3H, CHC(10)*H*₃); 0.88 (s, 9H, (C(13)*H*₃)₃CSi); 0.05 (d, $J = 2$, 6H, SiC(11)*H*₃)

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

214.7 (C(3)); 142.9 (C(6)), 128.5 (C(8)), 127.5 (C(9)), 125.6 (C(7)); 70.0 (C(1));
65.4 (C(5)); 51.1 (C(2)); 48.2 (C(4)); 25.8 (C(13)); 18.2 (C(12)); 12.6 (C(10)); -
5.6 (C(11))

IR: (neat)

3467 (m, br); 3064 (w); 3032 (w); 2955 (s); 2931 (s); 2885 (m); 2859 (m); 1708 (s); 1463 (m); 1388 (m); 1256 (m); 1100 (s)

MS: (FI)

322 (2, M^+); 267 (6); 266 (21); 265 (100); 247 (16); 159 (7); 106 (3); 95 (2)

Opt. rot.: - 20.4 (CHCl₃, c=0.5)

TLC: $R_f = 0.17$ (hexane/EtOAc, 5/1, SiO₂) [*p*-anisaldehyde]

SFC: (Chiralpak OD column, 150 bar, 3.0 mL/min, 1.4% MeOH)

t_R (2*S*, 5*R*)-*syn*-**28a** 4.81 min (12%); (2*S*, 5*S*)-*anti*-**28a** 5.16 min (88%)

Analysis: Calc for C₁₈H₃₀O₃Si (322.51)

Calc. C 67.03%; H 9.38%

Found: C 66.81%; H 9.20%

(2*S*,5*R*)-1-*tert*-Butyldimethylsilyloxy-2-methyl-5-hydroxy-5-(1-naphthyl)-3-pentanone (syn-28b)

Following General Procedure III using **8** (288 mg, 1.00 mmol), SiCl₄ (0.23 mL, 2.00 mmol), Hg(OAc)₂ (3.2 mg, 0.01 mmol), naphthaldehyde (156 mg, 1.00 mmol), (*R,R*)-**1** (37 mg, 0.10 mmol) in 2 mL of CH₂Cl₂, 316 mg (0.85 mmol, 85%) of *syn*-**28b** was obtained as colorless

viscous oil after column chromatography (silica gel, hexane/EtOAc, 5/1).

Data for *syn*-**28b**:

¹H NMR: (500 MHz, CDCl₃)
7.47 – 8.02 (7H, aromatic); 5.97 (dt, *J* = 9.5, 2.5, 1H, (C(1)HOH); 3.68 - 3.80 (ABX, 2H, TBSOC(5)H₂); 3.58 (d, *J* = 2.9, 1H, OH); 2.98 – 3.13 (ABX, 2H, COC(2)H₂); 2.79 (m, 1H, COC(4)H); 1.06 (d, *J* = 7.1, 3H, CHC(16)H₃); 0.86 (s, 9H, (C(19)H₃)₃CSi); 0.04 (d, *J* = 3.9, 6H, SiC(17)H₃)

¹³C NMR: (125 MHz, CDCl₃)
214.5 (C(3)); 138.4 (C(6)), 133.7 (C(12)), 129.9 (C(7)), 129.0 (C(11)); 127.9 (C(13)); 126.2 (C(9)); 125.6 (C(10)); 125.5 (C(14)); 123.0 (C(15)); 122.8 (C(8)); 66.6 (C(1)); 65.5 (C(5)); 50.5 (C(2)); 49.2 (C(4)); 25.8 (C(19)); 18.2 (C(18)); 12.6 (C(16)); -5.6 (C(17))

IR: (neat)
3424 (m, br); 3053 (w); 2954 (s); 2931 (s); 2858 (m); 1708 (s); 1463 (m); 1389 (m); 1361 (m); 1257 (m); 1094 (s); 1030 (m)

MS: (FI)
373 (34); 372 (100, M⁺); 315 (20); 267 (13); 267 (13); 267 (15); 267 (15); 240 (12); 159 (37); 156 (58)

Opt. rot.: + 95.6 (CHCl₃, c=1.0)

TLC: *R_f* = 0.18 (hexane/EtOAc, 5/1, SiO₂) [*p*-anisaldehyde]

SFC: (Chiralpak OD column, 150 bar, 3.0 mL/min, 12.5% MeOH):
t_R (2*S*, 5*S*)-*anti*-**28b** 3.23 min (6%); (2*S*, 5*R*)-*syn*-**28b** 4.12 min (94%),

Analysis: Calc for C₂₂H₃₂O₃Si (372.57)
Calc. C 70.92%; H 8.66%
Found: C 70.74%; H 8.60%

(2*S*,5*S*)-1-*tert*-Butyldimethylsilyloxy-2-methyl-5-hydroxy-5-(1-naphthyl)-3-pentanone (*anti*-28b**)**

Following General Procedure III using **8** (288 mg, 1.00 mmol), SiCl₄ (0.23 mL, 2.00 mmol), Hg(OAc)₂ (3.2 mg, 0.01 mmol), naphthaldehyde (156 mg, 1.00 mmol), (*S,S*)-**1** (37 mg, 0.10 mmol) in 2 mL of CH₂Cl₂, 308 mg (0.85 mmol, 85%) of *anti*-**28b** was obtained as colorless viscous oil after column chromatography (silica gel, hexane/EtOAc, 5/1).

Data for *anti*-28b**:**

¹H NMR: (500 MHz, CDCl₃)

7.47 – 8.02 (7H, aromatic); 5.98 (m, *J* = 9.5, 1H, *CHOH*); 3.69 – 3.79 (ABX, 2H, TBSOCH₂); 3.68 (d, *J* = 2.8, 1H, OH); 3.01 – 3.09 (ABX, 2H, COCH₂); 2.82 (m, 1H, COCH); 1.07 (d, *J* = 7.1, 3H, CHCH₃); 0.88 (s, 9H, (CH₃)₃CSi); 0.05 (d, *J* = 3.9, 6H, SiCH₃)

¹³C NMR: (125 MHz, CDCl₃)

214.5 (C(3)); 138.4 (C(6)), 133.8 (C(12)), 129.9 (C(7)), 129.0 (C(11)); 128.0 (C(13)); 126.1 (C(9)); 125.6 (C(10)); 125.5 (C(14)); 123.0 (C(15)); 122.8 (C(8)); 66.9 (C(1)); 65.5 (C(5)); 50.2 (C(2)); 49.3 (C(4)); 25.8 (C(19)); 18.2 (C(18)); 12.7 (C(16)); -5.6 (C(17))

IR: (neat)

3479 (m, br); 3053 (w); 2954 (s); 2930 (s); 2885 (m); 2858 (m); 1706 (s); 1463 (m); 1390 (m); 1361 (m); 1256 (m); 1098 (s)

MS: (FI)

373 (29); 372 (100, M⁺); 315 (12); 267 (13); 267 (13); 267 (11); 159 (32); 156 (44)

Opt. rot.: -63.5 (CHCl₃, c=1.0)

TLC: $R_f = 0.19$ (hexane/EtOAc, 5/1, SiO₂) [*p*-anisaldehyde]

SFC: (Chiralpak OD column, 150 bar, 3.0 mL/min, 12.5% MeOH):

t_R (2*S*, 5*S*)-*anti*-**28b** 3.15 min (89%); (2*S*, 5*R*)-*syn*-**28b** 4.11 min (11%)

Analysis: Calc for C₂₂H₃₂O₃Si (372.57)

Calc. C 70.92%; H 8.66%

Found: C 70.63%; H 8.58%

(2*S*,5*R*,6*E*)-1-*tert*-Butyldimethylsilyloxy-2-methyl-5-hydroxy-7-phenyl-6-hepten-3-one (*syn*-28c**)**

Following General Procedure III using **8** (288 mg, 1.00 mmol), SiCl₄ (0.23 mL, 2.00 mmol), Hg(OAc)₂ (3.2 mg, 0.01 mmol), cinnamaldehyde (132 mg, 1.00 mmol), (*R,R*)-**1** (37 mg, 0.10 mmol) in 2 mL of CH₂Cl₂, 281 mg (0.81 mmol, 81%) of *syn*-**28c** was obtained as colorless viscous oil after column chromatography (silica gel, hexane/EtOAc, 5/1).

Data for *syn*-**28c**:

¹H NMR: (500 MHz, CDCl₃)

7.37 (d, $J = 8.6$, 1H, aromatic); 7.37 (d, $J = 5.6$, 1H, aromatic); 7.30 (t, $J = 7.7$, 2H, aromatic); 7.23 (t, $J = 7.2$, 1H, aromatic); 6.65 (d, $J = 16.2$, 1H, CH); 6.21 (dd, $J = 16.0, 6.0$, 1H, CH); 4.77 (m, 1H, CHOH); 3.66 - 3.77 (ABX, 2H, TBSOCH₂); 3.31 (d, $J = 3.4$, 1H, OH); 2.75 - 2.90 (ABX, 2H, COCH₂); 2.82 (m, 1H, COCH); 1.06 (d, $J = 7.1$, 3H, CHCH₃); 0.88 (s, 9H, (CH₃)₃CSi); 0.05 (d, $J = 5.7$, 6H, SiCH₃)

¹³C NMR: (125 MHz, CDCl₃)

214.4 (C(3)); 136.6 (C(8)), 130.2 (C(11)), 130.0 (C(7)), 128.5 (C(10)); 127.6 (C(6)); 126.4 (C(9)); 68.2 (C(1)); 65.5 (C(5)); 49.3 (C(2)); 49.0 (C(4)); 25.8 (C(14)); 18.1 (C(13)); 12.6 (C(15)); -5.6, -5.6 (C(12))

IR: (neat)

3438 (m, br); 3027 (w); 2954 (s); 2930 (s); 2858 (m); 1708 (s); 1470 (m); 1388 (m); 1256 (m); 1099 (s)

MS: (FI)

349 (29); 348 (100, M^+); 291 (8); 216 (6); 159 (32); 132 (42)

Opt. rot.: +32.2 (CHCl_3 , $c=1.0$)

TLC: $R_f = 0.12$ (hexane/EtOAc, 5/1, SiO_2) [*p*-anisaldehyde]

SFC: (Chiralpak OD column, 150 bar, 3.0 mL/min, 7.5% MeOH):

t_R (2*S*, 5*R*)-*syn*-**28c** 2.74 min (89%); (2*S*, 5*S*)-*anti*-**28c** 3.26 min (11%)

Analysis: Calc for $\text{C}_{20}\text{H}_{32}\text{O}_3\text{Si}$ (348.55)

Calc. C 68.92%; H 9.38%

Found: C 68.59%; H 9.02%

(2*S*,5*S*,6*E*)-1-*tert*-Butyldimethylsilyloxy-2-methyl-5-hydroxy-7-phenyl-6-hepten-3-one (*anti*-28c**)**

Following General Procedure III using **8** (288 mg, 1.00 mmol), SiCl_4 (0.23 mL, 2.00 mmol), $\text{Hg}(\text{OAc})_2$ (3.2 mg, 0.01 mmol), cinnamaldehyde (132 mg, 1.00 mmol), (*S,S*)-**1** (37 mg, 0.10 mmol) in 2 mL of CH_2Cl_2 , 286 mg (0.83 mmol, 83%) of *anti*-**28c** was obtained as colorless viscous oil after column chromatography (silica gel, hexane/EtOAc, 5/1).

Data for *anti*-28c**:**

$^1\text{H NMR}$: (500 MHz, CDCl_3)

7.37 (d, $J = 8.6$, 1.0, 1H, aromatic); 7.37 (d, $J = 7.7$, 1.0, 1H, aromatic); 7.31 (t, $J = 7.7$, 2H, aromatic); 7.23 (t, $J = 7.2$, 1H, aromatic); 6.67 (dd, $J = 16.1$, 1.4, 1H, *CH*); 6.22 (dd, $J = 15.9$, 6.0, 1H, *CH*); 4.75 (m, 1H, *CHOH*); 3.67 - 3.78 (ABX, 2H, TBSOCH_2); 3.34 (d, $J = 3.4$, 1H, *OH*); 2.77 - 2.92 (ABX, 2H, COCH_2); 2.84

(m, 1H, COCH); 1.07 (d, $J = 7.1$, 3H, CHCH₃); 0.88 (s, 9H, (CH₃)₃CSi); 0.05 (d, $J = 3.7$, 6H, SiCH₃)

¹³C NMR: (125 MHz, CDCl₃)
214.3 (C(3)); 136.7 (C(8)), 130.3 (C(11)), 130.2 (C(7)), 128.5 (C(10)); 127.5 (C(6)); 126.5 (C(9)); 68.6 (C(1)); 65.4 (C(5)); 49.3 (C(2)); 48.9 (C(4)); 25.8 (C(14)); 18.2 (C(13)); 12.7 (C(15)); -5.6 (C(12))

IR: (neat)
3446 (m, br); 3027 (w); 2954 (s); 2930 (s); 2858 (m); 1708 (s); 1470 (m); 1388 (m); 1256 (m); 1101 (s)

MS: (FI)
348 (1, M⁺); 331 (4); 291 (6); 273 (9); 217 (3); 201 (7); 159 (100); 133 (35); 115 (37); 103 (20); 89 (10); 75 (56)

Opt. rot.: +6.36 (CHCl₃, c=1.0)

TLC: $R_f = 0.15$ (hexane/EtOAc, 5/1, SiO₂) [*p*-anisaldehyde]

SFC: (Chiralpak OD column, 150 bar, 3.0 mL/min, 7.5% MeOH):
 t_R (2*S*, 5*R*)-*syn*-**28c** 2.55 min (19%); (2*S*, 5*S*)-*anti*-**28c** 2.96 min (81%)

Analysis: Calc for C₂₀H₃₂O₃Si (348.55)
Calc. C 68.92%; H 9.38%
Found: C 68.56%; H 9.14%

(2*S*,5*R*,6*E*)-1-*tert*-Butyldimethylsilyloxy-2,6-dimethyl-5-hydroxy-7-phenyl-6-hepten-3-one
(*syn*-**28d**)

Following General Procedure III using **8** (288 mg, 1.00 mmol), SiCl₄ (0.23 mL, 2.00

mmol), Hg(OAc)₂ (3.2 mg, 0.01 mmol), α -methylcinnamaldehyde (146 mg, 1.00 mmol), (*R,R*)-**1** (37 mg, 0.10 mmol) in 2 mL of CH₂Cl₂, 303 mg (0.84 mmol, 84%) of *syn*-**28d** was obtained as colorless viscous oil after column chromatography (silica gel, hexane/EtOAc, 5/1).

Data for *syn*-**28d**:

¹H NMR: (500 MHz, CDCl₃)

7.33 (t, *J* = 7.7, 2H, aromatic); 7.27 (d, *J* = 5.4, 2H, aromatic); 7.21 (t, *J* = 7.4, 1H, aromatic); 6.58 (s, 1H, CH); 4.64 (dt, *J* = 9.5, 2.6 1H, CHOH); 3.67 - 3.77 (ABX, 2H, TBSOCH₂); 3.27 (d, *J* = 3.0, 1H, OH); 2.77 – 2.89 (m, 3H, COCH₂, COCH); 1.88 (s, 3H, CH₃); 1.06 (d, *J* = 7.1, 3H, CHCH₃); 0.88 (s, 9H, (CH₃)₃CSi); 0.06 (d, *J* = 5.1, 6H, SiCH₃)

¹³C NMR: (125 MHz, CDCl₃)

214.9 (C(3)); 138.4 (C(6)); 137.5 (C(8)); 128.9 (C(10)); 128.0 (C(9)) 126.4 (C(11)), 125.5 (C(7)); 72.7 (C(5)); 65.6 (C(1)) 49.0 (C(2)); 48.2 (C(4)); 25.7 (C(14)); 18.1 (C(13)); 14.0 (C(16)); 13.0 (C(15)); -5.6, -5.7 (C(12))

IR: (neat)

3446 (m, br); 3056(w); 3025 (w); 2954 (s); 2931 (s); 2885 (m); 2859 (m); 1708 (s); 1463 (m); 1388 (m); 1257 (m); 1100 (s); 1007 (m)

MS: (FI)

364 (8); 364.0 (32); 362 (100, M⁺); 362 (3); 327 (3); 305 (6); 257 (3); 216 (3); 160 (3); 159 (29); 153 (4); 147 (5); 146 (39)

Opt. rot.: +36.3 (CHCl₃, c=1.0)

TLC: *R_f* = 0.17 (hexane/EtOAc, 5/1, SiO₂) [*p*-anisaldehyde]

SFC: (Chiralpak OD column, 150 bar, 3.0 mL/min, 7.5% MeOH):

t_R (2*S*, 5*R*)-*syn*-**28d** 2.76 min (91%); (2*S*, 5*S*)-*anti*-**28d** 3.03 min (9%)

Analysis: Calc for C₂₁H₃₄O₃Si (362.58)

Calc. C 69.56%; H 9.45%

Found: C 69.53%; H 9.45%

(2*S*,5*S*,6*E*)-1-*tert*-Butyldimethylsilyloxy-2,6-dimethyl-5-hydroxy-7-phenyl-6-hepten-3-one
(*anti*-28d)

Following General Procedure III using **8** (288 mg, 1.00 mmol), SiCl₄ (0.23 mL, 2.00 mmol), Hg(OAc)₂ (3.2 mg, 0.01 mmol), α -methylcinnamaldehyde (146 mg, 1.00 mmol), (*S,S*)-**1** (37 mg, 0.10 mmol) in 2 mL of CH₂Cl₂, 285 mg (0.80 mmol, 80%) of *anti*-**28d** was obtained as colorless viscous oil after column chromatography (silica gel, hexane/EtOAc, 5/1).

Data for *anti*-28d:

¹H NMR: (500 MHz, CDCl₃)

7.33 (t, *J* = 7.6, 2H, aromatic); 7.27 (d, *J* = 6.6, 2H, aromatic); 7.21 (t, *J* = 7.2, 1H, aromatic); 6.58 (s, 1H, CH); 4.62 (dt, *J* = 9.0, 2.8 1H, CHOH); 3.68 - 3.78 (ABX, 2H, TBSOCH₂); 3.30 (d, *J* = 2.9, 1H, OH); 2.78 – 2.88 (m, 3H, COCH₂, COCH); 1.88 (d, *J* = 1.3, 3H, CH₃); 1.08 (d, *J* = 7.1, 3H, CHCH₃); 0.89 (s, 9H, (CH₃)₃CSi); 0.06 (d, *J* = 5.1, 6H, SiCH₃)

¹³C NMR: (125 MHz, CDCl₃)

214.9 (C(3)); 138.4 (C(6)); 137.5 (C(8)); 128.9 (C(10)); 128.0 (C(9)) 126.4 (C(11)), 125.6 (C(7)); 73.1 (C(5)); 65.5 (C(1)) 49.3 (C(2)); 47.8 (C(4)); 25.8 (C(14)); 18.2 (C(13)); 13.9 (C(16)); 12.7 (C(15)); -5.6 (C(12))

IR: (neat)

3468 (m, br); 3057(w); 3025 (w); 2955 (s); 2931 (s); 2885 (m); 2856 (m); 1707 (s); 1463 (m); 1388 (m); 1361 (m); 1256 (m); 1099 (s); 1007 (m)

MS: (FI)

364 (7); 364 (29); 362 (100, M⁺); 327 (2); 305 (5); 160 (2); 159 (20); 153 (3); 147 (3); 146 (26)

Opt. rot.: +6.55 (CHCl₃, c=1.0)

TLC: R_f = 0.19 (hexane/EtOAc, 5/1, SiO₂) [*p*-anisaldehyde]

SFC: (Chiralpak OD column, 150 bar, 3.0 mL/min, 7.5% MeOH):

t_R (2*S*, 5*R*)-*syn*-**28d** 2.65 min (13%); (2*S*, 5*S*)-*anti*-**28d** 2.91 min (87%)

Analysis: Calc for C₂₁H₃₄O₃Si (362.58)

Calc. C 69.56%; H 9.45%

Found: C 69.52%; H 9.49%

(2*S*,5*R*,6*E*)-1-*tert*-Butyldimethylsilyloxy-2-methyl-5-hydroxy-6-octen-3-one (*syn*-28e**)**

Following General Procedure III using **8** (288 mg, 1.00 mmol), SiCl₄ (0.23 mL, 2.00 mmol), Hg(OAc)₂ (3.2 mg, 0.01 mmol), crotonaldehyde (70 mg, 1.00 mmol), (*R,R*)-**1** (37 mg, 0.10 mmol) in 2 mL of CH₂Cl₂, 244 mg (0.84 mmol, 84%) of *syn*-**28e** was obtained as colorless viscous oil after column chromatography (silica gel, hexane/EtOAc, 5/1).

Data for *syn*-**28e**:

¹H NMR: (500 MHz, CDCl₃);

5.71 (dq, J = 15.4, 6.6, 1.0, 1H, CH); 5.49 (ddq, J = 15.5, 6.6, 1.4, 1H, CH); 4.52 (m, 1H, CHOH); 3.63 - 3.74 (ABX, 2H, TBSOCH₂); 3.13 (d, J = 3.4, 1H, OH); 2.64 - 2.78 (ABX, 2H, COCH₂); 2.78 (m, 1H, COCH); 1.69 (dt, J = 6.6, 0.8, 3H, CH₃); 1.02 (d, J = 6.8, 3H, CHCH₃); 0.87 (s, 9H, (CH₃)₃CSi); 0.03 (d, J = 6.4, 6H, SiCH₃)

¹³C NMR: (125 MHz, CDCl₃)

214.8 (C(3)); 132.0 (C(6)); 126.9 (C(7)); 68.4 (C(5)); 65.6 (C(1)); 49.3 (C(2)); 49.0 (C(4)); 25.8 (C(11)); 18.2 (C(10)); 17.7 (C(8)); 12.6 (C(12)); -5.6, -5.6 (C(9))

IR: (neat)

3444 (m, br); 2956 (s); 2932 (s); 2886 (m); 2859 (m); 1708 (s); 1463 (m); 1388

(m); 1362 (w); 1257 (m); 1099 (s)

MS: (FI)286 (2, M⁺); 231 (5); 230 (18); 229 (100); 211 (3); 159 (5); 113 (2)Opt. rot.: +36.7 (CHCl₃, c=1.0)TLC: R_f = 0.12 (hexane/EtOAc, 5/1, SiO₂) [*p*-anisaldehyde]

SFC: (5-benzoyloxy-**28e**, Chiralpak OD column, 150 bar, 3.0 mL/min, 1.5% MeOH):
 t_R (2*S*, 5*R*)-*syn*-5-benzoyloxy-**28e** 4.44 min (83%); (2*S*, 5*S*)-*anti*-5-benzoyloxy-**28e** 5.26 min (17%)

Analysis: Calc for C₁₅H₂₀O₃Si (286.48)

Calc. C 62.89%; H 10.55%

Found: C 62.69%; H 10.67%

(2*S*,5*S*,6*E*)-1-*tert*-Butyldimethylsilyloxy-2-methyl-5-hydroxy-6-octen-3-one (*anti*-28e**)**

Following General Procedure III using **8** (288 mg, 1.00 mmol), SiCl₄ (0.23 mL, 2.00 mmol), Hg(OAc)₂ (3.2 mg, 0.01 mmol), crotonaldehyde (70 mg, 1.00 mmol), (*S,S*)-**1** (37 mg, 0.10 mmol) in 2 mL of CH₂Cl₂, 238 mg (0.83 mmol, 83%) of *anti*-**28e** was obtained as colorless viscous oil after column chromatography (silica gel, hexane/EtOAc, 5/1).

Data for *anti*-**28e**:¹H NMR: (500 MHz, CDCl₃);

5.69 (dq, J = 15.1, 6.6, 1.0, 1H, CH); 5.48 (ddq, J = 15.5, 6.6, 1.2, 1H, CH); 4.47 (m, 1H, CHOH); 3.61 - 3.74 (ABX, 2H, TBSOCH₂); 3.15 (d, J = 3.4, 1H, OH); 2.62 - 2.77 (m, 3H, COCH₂, COCH); 1.67 (dd, J = 6.3, 0.7, 3H, CH₃); 1.02 (dd, J = 6.9, 1.0, 3H, CHCH₃); 0.85 (d, J = 0.9, 9H, (CH₃)₃CSi); 0.02 (d, J = 3.2, 6H, SiCH₃)

¹³C NMR: (101 MHz, CDCl₃)
 219.6 (C(3)); 132.0 (C(6)); 126.8 (C(7)); 68.6 (C(5)); 65.3 (C(1)); 49.1 (C(2));
 48.9 (C(4)); 25.7 (C(11)); 18.1 (C(10)); 17.6 (C(8)) 12.6 (C(12)); -5.7 (C(9))

IR: (neat)
 3448 (m, br); 2956 (s); 2932 (s); 2886 (m); 2859 (m); 1708 (s); 1463 (m); 1388 (m); 1257 (m); 1099 (s)

MS: (FI)
 287 (4); 286 (3, M⁺); 231 (4); 230 (19); 229 (100); 159 (4); 113 (3); 113 (3); 111 (3); 110 (3); 70 (3)

Opt. rot.: +15.6 (CHCl₃, c=1.0)

TLC: *R_f* = 0.18 (pentane/ether, 3/1, SiO₂) [*p*-anisaldehyde]

SFC: (5-benzoyloxy-**28e**, Chiralpak OD column, 150 bar, 3.0 mL/min, 1.5% MeOH):
t_R (2*S*, 5*R*)-*syn*-5-benzoyloxy-**28e** 4.47 min (26%); (2*S*, 5*S*)-*anti*-5-benzoyloxy-**28e** 5.14 min (74%)

Analysis: Calc for C₁₅H₂₀O₃Si (286.48)
 Calc. C 62.89%; H 10.55%
 Found: C 62.70%; H 10.57%

(2*S*,5*R*)-1-*tert*-Butyldimethylsilyloxy-2,6-dimethyl-5-hydroxy-6-hepten-3-one (*syn*-28f**)**

Following General Procedure III using **8** (288 mg, 1.00 mmol), SiCl₄ (0.23 mL, 2.00 mmol), Hg(OAc)₂ (3.2 mg, 0.01 mmol), methacrolein (70 mg, 1.00 mmol), (*R,R*)-**1** (37 mg, 0.10 mmol) in 2 mL of CH₂Cl₂, 232 mg (0.81 mmol, 81%) of *syn*-**28f** was obtained as colorless viscous oil after column chromatography (silica gel, hexane/EtOAc, 5/1).

Data for *syn*-**28f**:

<u>¹H NMR:</u>	(500 MHz, CDCl ₃); 5.01 (s, 1H, CH ₂); 4.86 (s, 1H, CH ₂); 4.51 (d, <i>J</i> = 9.5, 1H, CHOH); 3.65 - 3.74 (ABX, 2H, TBSOCH ₂); 3.17 (d, <i>J</i> = 3.2, 1H, OH); 2.80 (m, 1H, COCH); 2.67 - 2.82 (ABX, 2H, COCH ₂); 1.75 (s, 3H, CH ₃); 1.03 (d, <i>J</i> = 6.8, 3H, CHCH ₃); 0.87 (s, 9H, (CH ₃) ₃ CSi); 0.04 (d, <i>J</i> = 5.8, 6H, SiCH ₃)
<u>¹³C NMR:</u>	(101 MHz, CDCl ₃) 214.9 (C(3)); 145.7 (C(6)); 111.0 (C(7)); 70.8 (C(5)); 65.6 (C(1)); 49.0 (C(2)); 48.1 (C(4)); 25.8 (C(10)); 18.4 (C(12)); 18.3 (C(9)) 12.6 (C(11)); -5.6, -5.7 (C(8))
<u>IR:</u>	(neat) 3467 (m, br); 3078 (m); 2955 (s); 2932 (s); 2886 (m); 2859 (m); 1709 (s); 1653 (w); 1463 (m); 1388 (m); 1362 (w); 1257 (m); 1099 (s); 1007 (m)
<u>MS:</u>	(FI) 287 (1); 286 (1, M ⁺); 231 (6); 229 (100); 211 (2); 159 (4); 111 (1); 111 (2); 110 (2); 110 (2); 110 (2); 110 (1)
<u>Opt. rot. :</u>	+76.3 (CHCl ₃ , c=0.35)
<u>TLC:</u>	<i>R_f</i> = 0.17 (hexane/EtOAc, 5/1, SiO ₂) [<i>p</i> -anisaldehyde]
<u>SFC:</u>	(5-benzoyloxy- 28f , Chiralpak OD column, 150 bar, 3.0 mL/min, 1.5% MeOH): <i>t_R</i> (2 <i>S</i> , 5 <i>S</i>)- <i>anti</i> -5-benzoyloxy- 28f 5.26 min (6%); (2 <i>S</i> , 5 <i>R</i>)- <i>syn</i> -5-benzoyloxy- 28f 4.44 min (94%)
<u>Analysis:</u>	Calc for C ₁₅ H ₂₀ O ₃ Si (286.48) Calc. C 62.89%; H 10.55% Found: C 62.81%; H 10.68%

(2*S*,5*S*)-1-*tert*-Butyldimethylsilyloxy-2,6-dimethyl-5-hydroxy-6-hepten-3-one (*anti*-28f**)**

Following General Procedure III using **8** (288 mg, 1.00 mmol), SiCl₄ (0.23 mL, 2.00 mmol), Hg(OAc)₂ (3.2 mg, 0.01 mmol), methacrolein (70 mg, 1.00 mmol), (*S,S*)-**1** (37 mg, 0.10 mmol) in 2 mL of CH₂Cl₂, 240 mg (0.84 mmol, 84%) of *anti*-**28f** was obtained as colorless viscous oil after column chromatography (silica gel, pentane/ether, 3/1).

Data for *anti*-28f:

¹H NMR: (500 MHz, CDCl₃);

5.01 (m, 1H, CH₂); 4.86 (t, *J* = 1.2, 1H, CH₂); 4.49 (m, 1H, CHOH); 3.65 - 3.76 (ABX, 2H, TBSOCH₂); 3.21 (d, *J* = 3.2, 1H, OH); 2.80 (m, 1H, COCH); 2.67 - 2.75 (ABX, 2H, COCH₂); 1.75 (s, 3H, CH₃); 1.05 (d, *J* = 6.9, 3H, CHCH₃); 0.87 (s, 9H, (CH₃)₃CSi); 0.04 (d, *J* = 3.6, 6H, SiCH₃)

¹³C NMR: (126 MHz, CDCl₃)

214.9 (C(3)); 145.7 (C(6)); 110.1 (C(7)); 71.2 (C(5)); 65.5 (C(1)); 49.2 (C(2)); 47.6 (C(4)); 25.8 (C(10)); 18.3 (C(12)); 18.2 (C(9)); 12.7 (C(11)); -5.6 (C(8))

IR: (neat)

3468 (m, br); 3078 (w); 2955 (s); 2932 (s); 2886 (m); 2859 (m); 1708 (s); 1653 (w); 1463 (m); 1389 (m); 1362 (w); 1257 (m); 1100 (s); 1007 (m)

MS: (FI)

287 (1); 286 (1, M⁺); 231 (5); 230 (17); 229 (100); 229 (1); 211 (1); 159 (2); 111 (1); 110 (1); 110 (2); 110 (2)

Opt. rot.: -10.6 (CHCl₃, c=0.35)

TLC: *R_f* = 0.24 (pentane/ether, 3/1, SiO₂) [*p*-anisaldehyde]

SFC: (5-benzoyloxy-**28f**, Chiralpak OD column, 150 bar, 3.0 mL/min, 1.5% MeOH):

t_R (2*S*, 5*S*)-*anti*-5-benzoyloxy-**28f** 5.26 min (89%); (2*S*, 5*R*)-*syn*-5-benzoyloxy-**28f**

4.44 min (11%)

Analysis: Calc for C₁₅H₂₀O₃Si (286.48)

Calc. C 62.89%; H 10.55%

Found: C 62.50%; H 10.51%

(2*S*,5*R*,6*E*)-1-*tert*-Butyldimethylsilyloxy-2,6-dimethyl-5-hydroxy-6-octen-3-one (syn-28g)

Following General Procedure III using **8** (288 mg, 1.00 mmol), SiCl₄ (0.23 mL, 2.00 mmol), Hg(OAc)₂ (3.2 mg, 0.01 mmol), tiglic aldehyde (84 mg, 1.00 mmol), (*R,R*)-**1** (37 mg, 0.10 mmol) in 2 mL of CH₂Cl₂, 235 mg (0.78 mmol, 78%) of *syn*-**28g** was obtained as colorless viscous oil after column chromatography (silica gel, hexane/EtOAc, 5/1).

Data for *syn-28g*:

¹H NMR: (500 MHz, CDCl₃);

5.53 (qt, $J = 6.5, 1.2$, 1H, CH); 4.46 (td, $J = 6.4, 1.5$, 1H, CHOH); 3.64 - 3.74 (ABX, 2H, TBSOCH₂); 3.06 (d, $J = 2.7$, 1H, OH); 2.79 (m, 1H, COCH); 2.64 - 2.76 (ABX, 2H, COCH₂); 1.63 (d, $J = 1.0$, 3H, CH₃); 1.61 (d, $J = 6.6$, 3H, CH₃); 1.03 (d, $J = 7.1$, 3H, CHCH₃); 0.87 (s, 9H, (CH₃)₃CSi); 0.03 (d, $J = 6.9$, 6H, SiCH₃)

¹³C NMR: (126 MHz, CDCl₃)

215.1 (C(3)); 136.1 (C(6)); 120.6 (C(7)); 72.6 (C(5)); 65.6 (C(1)); 49.0 (C(2));
48.1 (C(4)); 25.8 (C(11)); 18.2 (C(10)); 13.0 (C(8)) 12.6 (C(13)); 11.7 (C(12)); -
5.6, -5.6 (C(9))

IR: (neat)

3446 (m, br); 2956 (s); 2931 (s); 2886 (m); 2860 (m); 1709 (s); 1471 (m); 1387 (m); 1362 (w); 1257 (m); 1099 (s); 1008 (m)

MS: (FI)302 (5); 301 (17); 300 (75, M⁺); 245 (5); 244 (19); 243 (100); 225 (3); 159 (9); 104 (2); 84 (3)Opt. rot.: +48.6 (CHCl₃, c=1.0)TLC: *R_f* = 0.17 (hexane/EtOAc, 5/1, SiO₂) [*p*-anisaldehyde]SFC: (5-benzoyloxy-**28g**, Chiralpak OD column, 150 bar, 3.0 mL/min, 2.5% MeOH):
t_R (2*S*, 5*R*)-*syn*-5-benzoyloxy-**28g** 2.94 min (96%); (2*S*, 5*S*)-*anti*-5-benzoyloxy-**28g** 3.45 min (4%)Analysis: Calc for C₁₅H₂₀O₃Si (300.51)

Calc. C 63.95%; H 10.73%

Found: C 64.04%; H 10.86%

(2*S*,5*S*,6*E*)-1-*tert*-Butyldimethylsilyloxy-2,6-dimethyl-5-hydroxy-6-octen-3-one (*anti*-28g**)**

Following General Procedure III using **8** (288 mg, 1.00 mmol), SiCl₄ (0.23 mL, 2.00 mmol), Hg(OAc)₂ (3.2 mg, 0.01 mmol), tiglic aldehyde (84 mg, 1.00 mmol), (*S,S*)-**1** (37 mg, 0.10 mmol) in 2 mL of CH₂Cl₂, 226 mg (0.75 mmol, 75%) of *anti*-**28g** was obtained as colorless viscous oil after column chromatography (silica gel, hexane/EtOAc, 5/1).

Data for *anti*-**28g**:¹H NMR: (500 MHz, CDCl₃);5.54 (qd, *J* = 6.7, 1.0, 1H, CH); 4.44 (d, *J* = 9.8, 1H, CHOH); 3.64 - 3.76 (ABX, 2H, TBSOCH₂); 3.11 (d, *J* = 2.7, 1H, OH); 2.79 (m, 1H, COCH); 2.64 - 2.80 (ABX, 2H, COCH₂); 1.63 (d, *J* = 1.0, 3H, CH₃); 1.61 (d, *J* = 6.8, 3H, CH₃); 1.05 (d, *J* = 7.0, 3H, CHCH₃); 0.88 (s, 9H, (CH₃)₃CSi); 0.04 (d, *J* = 3.7, 6H, SiCH₃)

¹³C NMR: (126 MHz, CDCl₃)
 215.2 (C(3)); 136.2 (C(6)); 120.7 (C(7)); 73.0 (C(5)); 65.5 (C(1)); 49.2 (C(2));
 47.7 (C(4)); 25.8 (C(11)); 18.2 (C(10)); 13.0 (C(8)) 12.7 (C(13)); 11.7 (C(12)); -
 5.6 (C(9))

IR: (neat)
 3467 (m, br); 2955 (s); 2931 (s); 2886 (m); 2860 (m); 1708 (s); 1463 (m); 1387
 (m); 1362 (w); 1256 (m); 1100 (s); 1008 (m)

MS: (FI)
 314 (4); 302 (5); 301 (18); 300 (74, M⁺); 245 (5); 244 (20); 243 (100); 225 (4);
 160 (2); 159 (17); 104 (2); 84 (5)

Opt. rot.: +4.96 (CHCl₃, c=0.75)

TLC: *R_f* = 0.20 (hexane/EtOAc, 5/1, SiO₂) [*p*-anisaldehyde]

SFC: (5-benzoyloxy-**28g**, Chiralpak OD column, 150 bar, 3.0 mL/min, 2.5% MeOH):
t_R (2*S*, 5*R*)-*syn*-5-benzoyloxy-**28g** 3.03 min (18%); (2*S*, 5*S*)-*anti*-5-benzoyloxy-
28g 3.48 min (82%)

Analysis: Calc for C₁₅H₂₀O₃Si (300.51)
 Calc. C 63.95%; H 10.73%
 Found: C 63.74%; H 10.87%

(2*S*,5*R*)-1-*tert*-Butyldimethylsilyloxy-2-methyl-5-hydroxy-7-phenyl-6-heptyn-3-one (syn-28h**)**

Following the general procedure III using **8** (288 mg, 1.00 mmol), SiCl₄ (0.23 mL, 2.00 mmol), Hg(OAc)₂ (3.2 mg, 0.01 mmol), phenylpropargyl aldehyde (130 mg, 1.00 mmol), (*R,R*)-**1** (37 mg, 0.10 mmol) in 2 mL of CH₂Cl₂, 288 mg (0.83 mmol, 83%) of *syn*-**28h** was obtained as

colorless viscous oil after column chromatography (silica gel, hexane/EtOAc, 5/1).

Data for *syn*-**28h**:

¹H NMR: (500 MHz, CDCl₃)
7.28 – 7.43 (m, 5H, aromatic); 5.01 – 5.06 (m, 1H, *CHOH*); 3.67 – 3.77 (ABX, 2H, TBSOCH₂); 3.33 (d, *J* = 5.1, 1H, *OH*); 2.96 – 3.13 (ABX, 2H, COCH₂); 2.82 (m, 1H, COCH); 1.08 (d, *J* = 7.1, 3H, CHCH₃); 0.88 (s, 9H, (CH₃)₃CSi); 0.06 (d, *J* = 5.1, 6H, SiCH₃)

¹³C NMR: (126 MHz, CDCl₃)
213.2 (C(3)); 131.7 (C(9)); 128.4 (C(11)); 128.2 (C(10)); 122.4 (C(8)); 88.5 (C(6)); 84.6 (C(7)); 65.3 (C(5)); 58.8 (C(1)); 49.4 (C(2)); 49.0 (C(4)); 25.7 (C(14)); 18.1 (C(13)); 12.4 (C(15)); -5.7, -5.7 (C(12))

IR: (neat)
3419 (m, br); 3075(w); 2955 (s); 2931 (s); 2885 (m); 2859 (m); 2250 (w); 1711 (s); 1491 (m); 1471 (m); 1389 (m); 1362 (m); 1256 (m); 1102 (s); 1077 (s); 1029 (m)

MS: (FI)
347 (6); 346 (11, M⁺); 328 (3); 291 (6); 290 (23); 289 (100); 271 (9); 159 (6); 145 (10); 130 (5)

Opt. rot.: +37.6 (CHCl₃, c=2.1)

TLC: *R_f* = 0.16 (hexane/EtOAc, 5/1, SiO₂) [*p*-anisaldehyde]

SFC: (Chiralpak OD column, 150 bar, 3.0 mL/min, 7.5% MeOH):
t_R (2*S*, 5*R*)-*syn*-**28h** 3.35 min (76%); (2*S*, 5*S*)-*anti*-**28h** 3.82 min (24%)

Analysis: Calc for C₂₀H₃₀O₃Si (346.54)
Calc. C 69.32%; H 8.73%
Found: C 69.20%; H 8.77%

(2*S*,5*S*)-1-*tert*-Butyldimethylsilyloxy-2-methyl-5-hydroxy-7-phenyl-6-heptyn-3-one (*anti*-**28h**)

Following General Procedure III using **8** (288 mg, 1.00 mmol), SiCl₄ (0.23 mL, 2.00 mmol), Hg(OAc)₂ (3.2 mg, 0.01 mmol), phenylpropargyl aldehyde (130 mg, 1.00 mmol), (*S,S*)-**1** (37 mg, 0.10 mmol) in 2 mL of CH₂Cl₂, 282 mg (0.82 mmol, 82%) of *anti*-**28h** was obtained as colorless viscous oil after column chromatography (silica gel, hexane/EtOAc, 5/1).

Data for *anti*-28h**:**

¹H NMR: (500 MHz, CDCl₃)

7.28 – 7.43 (m, 5H, aromatic); 5.01 – 5.06 (m, 1H, *CHOH*); 3.67 – 3.79 (ABX, 2H, TBSOCH₂); 3.29 (d, *J* = 5.1, 1H, OH); 2.97 – 3.13 (ABX, 2H, COCH₂); 2.82 (m, 1H, COCH); 1.09 (d, *J* = 7.1, 3H, CHCH₃); 0.88 (s, 9H, (CH₃)₃CSi); 0.05 (d, *J* = 3.9, 6H, SiCH₃)

¹³C NMR: (126 MHz, CDCl₃)

213.1 (C(3)); 131.7 (C(9)); 128.4 (C(11)); 128.2 (C(10)); 122.4 (C(8)); 88.5 (C(6)); 84.6 (C(7)); 65.2 (C(5)); 59.0 (C(1)); 49.2 (C(2)); 49.0 (C(4)); 25.8 (C(14)); 18.1 (C(13)); 12.6 (C(15)); -5.7 (C(12))

IR: (net)

3427 (m, br); 3059(w); 2955 (s); 2930 (s); 2885 (m); 2858 (m); 2249 (w); 1710 (s); 1599 (w); 1491 (m); 1471 (m); 1389 (m); 1362 (m); 1256 (m); 1102 (s); 1078 (s); 1029 (m)

MS: (FI)

348 (2); 347 (7); 346 (9, M⁺); 328 (2); 291 (6); 290 (24); 289 (100); 271 (6); 159 (3); 145 (2); 145 (7); 130 (3)

Opt. rot.: +14.1 (CHCl₃, c=2.1)

TLC: $R_f = 0.14$ (hexane/EtOAc, 5/1, SiO₂) [*p*-anisaldehyde]

SFC: (Chiralpak OD column, 150 bar, 3.0 mL/min, 7.5% MeOH):

t_R (2*S*, 5*R*)-*syn*-**28h** 3.47 min (43%); (2*S*, 5*S*)-*anti*-**28h** 3.94 min (57%)

Analysis: Calc for C₂₀H₃₀O₃Si (346.54)

Calc. C 69.32%; H 8.73%

Found: C 69.13%; H 8.75%

(2*S*,5*R*)-1-*tert*-Butyldimethylsilyloxy-2-methyl-5-hydroxy-7-phenyl-3-heptanone (*syn*-28i**)**

Following the general procedure III using **8** (288 mg, 1.00 mmol), SiCl₄ (0.23 mL, 2.00 mmol), Hg(OAc)₂ (3.2 mg, 0.01 mmol), hydrocinnamaldehyde (134 mg, 1.00 mmol), (*R,R*)-**1** (37 mg, 0.10 mmol) in 2 mL of CH₂Cl₂, 120 mg (0.34 mmol, 34%) of *syn*-**28i** was obtained as colorless viscous oil after column chromatography (silica gel, hexane/EtOAc, 5/1).

Data for *syn*-**28i**:

¹H NMR: (500 MHz, CDCl₃)

7.17 – 7.30 (m, 5H, aromatic); 4.07 (m, 1H, *CHOH*); 3.62 – 3.73 (ABX, 2H, TBSOCH₂); 3.24 (dd, $J = 3.5, 0.8$, 1H, *OH*); 2.56 – 2.85 (m, 5H, COCH₂, COCH, PhCH₂); 1.65 – 1.86 (2m, 2H, CH₂); 1.02 (d, $J = 7.0$, 3H, CHCH₃); 0.86 (s, 9H, (CH₃)₃CSi); 0.03 (d, $J = 9.0$, 6H, SiCH₃)

¹³C NMR: (126 MHz, CDCl₃)

215.4 (C(3)); 141.9 (C(8)); 128.4 (C(10)); 128.3 (C(11)); 125.8 (C(9)); 66.7 (C(5)); 65.6 (C(1)); 49.3 (C(2)); 48.8 (C(4)); 38.0 (C(6)); 31.7 (C(7)); 25.7 (C(14)); 18.1 (C(13)); 12.6 (C(15)); -5.7, 5.7 (C(12))

IR: (neat)

3467 (m, br); 3063(w); 3028 (w); 2953 (s); 2930 (s); 2858 (m); 1707 (s); 1604

(w); 1496 (m); 1462 (m); 1388 (m); 1256 (m); 1094 (s)

MS: (FI)

351 (3); 350 (5, M⁺); 295 (6); 294 (22); 293 (100); 275 (6); 159 (4); 147 (7); 134 (3)

Opt. rot.: +46.3 (CHCl₃, c=1.5)

TLC: R_f = 0.14 (hexane/EtOAc, 5/1, SiO₂) [*p*-anisaldehyde]

SFC: (Chiralpak OD column, 150 bar, 3.0 mL/min, 5% MeOH):

t_R (2*S*,5*R*)-*syn*-**28i** 3.45 min (91%); (2*S*,5*S*)-*anti*-**28i** 3.87 min (9%)

Analysis: Calc for C₂₀H₃₄O₃Si (350.57)

Calc. C 68.52%; H 9.78%

Found: C 68.59%; H 9.91%

(2*S*,5*S*)-1-*tert*-Butyldimethylsilyloxy-2-methyl-5-hydroxy-7-phenyl-3-heptanone (*anti*-28i**)**

Following General Procedure III using **8** (288 mg, 1.00 mmol), SiCl₄ (0.23 mL, 2.00 mmol), Hg(OAc)₂ (3.2 mg, 0.01 mmol), hydrocinnamaldehyde (134 mg, 1.00 mmol), (*S,S*)-**1** (37 mg, 0.10 mmol) in 2 mL of CH₂Cl₂, 76 mg (0.22 mmol, 22%) of *anti*-**28i** was obtained as colorless viscous oil after column chromatography (silica gel, hexane/EtOAc, 5/1).

Data for *anti*-**28i**:

¹H NMR: (500 MHz, CDCl₃)

7.17 – 7.30 (m, 5H, aromatic); 4.03 (m, 1H, CHOH); 3.62 – 3.75 (ABX, 2H, TBSOCH₂); 3.28 (dd, J = 3.2, 0.7, 1H, OH); 2.56 – 2.85 (m, 5H, COCH₂, COCH, PhCH₂); 1.66 – 1.87 (2m, 2H, CH₂); 1.03 (d, J = 7.0, 3H, CHCH₃); 0.87 (s, 9H, (CH₃)₃CSi); 0.04 (d, J = 3.2, 6H, SiCH₃)

¹³C NMR: (126 MHz, CDCl₃)
 215.7 (C(3)); 142.2 (C(8)); 128.7 (C(10)); 128.6 (C(11)); 126.1 (C(9)); 67.3 (C(5)); 65.7 (C(1)); 49.4 (C(2)); 49.3 (C(4)); 38.4 (C(6)); 32.0 (C(7)); 26.0 (C(14)); 18.4 (C(13)); 13.0 (C(15)); -5.4 (C(12))

IR: (neat)
 3467 (m, br); 3063(w); 3027 (w); 2953 (s); 2931 (s); 2859 (m); 1706 (s); 1471 (m); 1388 (m); 1256 (m); 1096 (s)

MS: (EI)
 351 (3); 350 (5, M⁺); 295 (6); 294 (22); 293 (100); 275 (3); 159 (2); 147 (5); 134 (3)

Opt. rot.: +16.5 (CHCl₃, c=0.55)

TLC: *R_f* = 0.16 (hexane/EtOAc, 5/1, SiO₂) [*p*-anisaldehyde]

SFC: (Chiralpak OD column, 150 bar, 3.0 mL/min, 5% MeOH):
t_R (2*S*,5*R*)-**syn-28i** 3.51 min (29%); (2*S*,5*S*)-**anti-28i** 3.88 min (71%)

Analysis: Calc for C₂₀H₃₄O₃Si (350.57)
 Calc. C 68.52%; H 9.78%
 Found: C 68.64%; H 9.78%

(2*S*,5*R*)-1-*tert*-Butyldimethylsilyloxy-2-methyl-5-hydroxy-5-cyclohexyl-3-pentanone (syn-28j)

Following General Procedure III using **8** (288 mg, 1.00 mmol), SiCl₄ (0.23 mL, 2.00 mmol), Hg(OAc)₂ (3.2 mg, 0.01 mmol), cyclohexanecarboxaldehyde (112 mg, 1.00 mmol), (*R,R*)-**1** (37 mg, 0.10 mmol) in 2 mL of CH₂Cl₂, 155 mg (0.47 mmol, 47%) of **syn-28j** was obtained as colorless viscous oil after column chromatography (silica gel, hexane/EtOAc, 5/1).

Data for *syn*-**28j**:¹H NMR: (500 MHz, CDCl₃)

3.83 (m, 1H, *CHOH*); 3.64 - 3.76 (ABX, 2H, *TBSOCH*₂); 3.12 (d, *J* = 3.4, 1H, *OH*); 2.82 (m, 1H, *COCH*); 2.54 – 2.77 (ABX, 2H, *COCH*₂); 1.66 – 1.89 (5H, *CH*_{eq}); 1.00 – 1.38 (6H, *CH*_{ax}); 1.03 (d, *J* = 7.1, 3H, *CHCH*₃); 0.88 (s, 9H, (*CH*₃)₃CSi); 0.05 (d, *J* = 5.6, 6H, Si*CH*₃)

¹³C NMR: (126 MHz, CDCl₃)

215.7 (C(3)); 71.3 (C(5)); 65.6 (C(1)); 48.9 (C(2)); 46.6 (C(4)); 42.9 (C(6)); 28.7, 28.3 (C(7)); 26.4 (C(9)); 26.2, 26.0 (C(8)) 25.7 (C(12)); 18.1 (C(11)); 12.7 (C(13)); -5.7 (C(10))

IR: (neat)

3481 (m, br); 2929 (s); 2857 (m); 1707 (m); 1463 (m); 1388 (m); 1256 (m); 1099 (s)

MS: (FI)

329 (0, M⁺); 273 (6); 272 (21); 271 (100); 253 (2); 159 (2)

Opt. rot.: +49.1 (CHCl₃, c=0.4)TLC: *R_f* = 0.27 (hexane/EtOAc, 5/1, SiO₂) [*p*-anisaldehyde]SFC: (5-benzoyloxy-**28j**, Chiralpak OD column, 150 bar, 3.0 mL/min, 2% MeOH):

t_R (2*S*,5*R*)-*syn*-5-benzoyloxy-**28j** 4.59 min (94%); (2*S*, 5*S*)-*anti*-5-benzoyloxy-**28j** 5.52 min (6%)

Analysis: Calc for C₁₈H₃₆O₃Si (328.56)

Calc. C 65.80%; H 11.04%

Found: C 65.92%; H 11.26%

(2*S*,5*S*)-1-*tert*-Butyldimethylsilyloxy-2-methyl-5-hydroxy-5-cyclohexyl-3-pentanone (*anti*-**28j**)

Following General Procedure III using **8** (288 mg, 1.00 mmol), SiCl₄ (0.23 mL, 2.00 mmol), Hg(OAc)₂ (3.2 mg, 0.01 mmol), cyclohexanecarboxaldehyde (112 mg, 1.00 mmol), (*S,S*)-**1** (37 mg, 0.10 mmol) in 2 mL of CH₂Cl₂, 102 mg (0.31 mmol, 31%) of *anti*-**28j** was obtained as colorless viscous oil after column chromatography (silica gel, hexane/EtOAc, 5/1).

Data for *anti*-**28j**:

¹H NMR: (500 MHz, CDCl₃)

3.81 (m, 1H, *CHOH*); 3.64 - 3.78 (ABX, 2H, TBSOCH₂); 3.15 (d, *J* = 3.5, 1H, *OH*); 2.81 (m, 1H, *COCH*); 2.54 - 2.73 (ABX, 2H, *COCH*₂); 1.66 - 1.89 (5H, *CH*_{eq}); 0.97 - 1.42 (6H, *CH*_{ax}); 1.05 (d, *J* = 7.0, 3H, *CHCH*₃); 0.89 (s, 9H, (CH₃)₃CSi); 0.06 (d, *J* = 2.7, 6H, SiCH₃)

¹³C NMR: (126 MHz, CDCl₃)

215.9 (C(3)); 71.8 (C(5)); 65.5 (C(1)); 49.2 (C(2)); 46.1 (C(4)); 43.0 (C(6)); 28.8, 28.2 (C(7)); 26.4 (C(9)); 26.2, 26.1 (C(8)) 25.8 (C(12)); 18.1 (C(11)); 12.8 (C(13)); -5.6, -5.7 (C(10))

IR: (neat)

3502 (m, br); 2929 (s); 2857 (m); 1706 (m); 1463 (m); 1388 (m); 1256 (m); 1100 (s)

MS: (FI)

329 (0, M⁺); 273 (6); 272 (21); 271 (100); 253 (2); 159 (1)

Opt. rot.: -5.39° (CHCl₃, c=0.3)

TLC: *R*_f = 0.32 (hexane/EtOAc, 5/1, SiO₂) [*p*-anisaldehyde]

SFC: (5-benzoyloxy-**28j**, Chiralpak OD column, 150 bar, 3.0 mL/min, 2% MeOH):

t_R (2*S*, 5*R*)-*syn*-5-benzoyloxy-**28j** 4.41 min (20%); (2*S*, 5*S*)-*anti*-5-benzoyloxy-**28j** 5.17 min (80%)

Analysis: Calc for C₁₈H₃₆O₃Si (328.56)
 Calc. C 65.80%; H 11.04%
 Found: C 65.80%; H 11.19%

(2*S*,5*R*)-1-*tert*-Butyldimethylsilyloxy-2,6,6-trimethyl-5-hydroxy-3-heptanone (*syn*-28k**)**

Following General Procedure III using **8** (288 mg, 1.00 mmol), SiCl₄ (0.23 mL, 2.00 mmol), Hg(OAc)₂ (3.2 mg, 0.01 mmol), pivaldehyde (86 mg, 1.00 mmol), (*R,R*)-**1** (37 mg, 0.10 mmol) in 2 mL of CH₂Cl₂, 220 mg (0.73 mmol, 73%) of *syn*-**28k** was obtained as colorless viscous oil after column chromatography (silica gel, pentane/ether, 3/1).

Data for *syn*-28k**:**

¹H NMR: (500 MHz, benzene-*d*₆)
 3.84 (dt, *J* = 10.5, 2.2, 1H, CHOH); 3.41 - 3.64 (ABX, 2H, TBSOCH₂); 3.17 (d, *J* = 2.9, 1H, OH); 2.37 - 2.59 (ABX, 2H, COCH₂); 2.48 (m, 1H, COCH); 0.95 (s, 9H, C(CH₃)₃); 0.91 (s, 9H, (CH₃)₃CSi); 0.82 (d, *J* = 6.8, 3H, CHCH₃); -0.01 (d, *J* = 1.9, 6H, SiCH₃)

¹³C NMR: (126 MHz, CDCl₃)
 215.9 (C(3)); 74.4 (C(5)); 65.7 (C(1)); 48.9 (C(2)); 44.7 (C(4)); 34.0 (C(6)); 25.7 (C(7)); 25.6 (C(10)); 18.1 (C(9)); 12.7 (C(11)); -5.7 (C(8))

IR: (neat)
 3525 (m, br); 2957 (s); 2934 (s); 2861 (m); 1707 (m); 1471 (m); 1388 (m); 1364 (m); 1256 (m); 1087 (s); 1007 (m)

MS: (FI)
303 (1, M⁺); 247 (6); 246 (18); 245 (100); 159 (1)

Opt. rot.: +45.0 (CHCl₃, c=0.25)

TLC: R_f = 0.24 (pentane/ether, 3/1, SiO₂) [*p*-anisaldehyde]

Analysis: Calc for C₁₆H₃₄O₃Si (302.52)
Calc. C 63.52%; H 11.33%
Found: C 63.41%; H 11.44%

(2*S*,5*S*)-1-*tert*-Butyldimethylsilyloxy-2,6,6-trimethyl-5-hydroxy-3-heptanone (*anti*-28k)

Following General Procedure III using **8** (288 mg, 1.00 mmol), SiCl₄ (0.23 mL, 2.00 mmol), Hg(OAc)₂ (3.2 mg, 0.01 mmol), pivaldehyde (86 mg, 1.00 mmol), (*S,S*)-**1** (37 mg, 0.10 mmol) in 2 mL of CH₂Cl₂, 236 mg (0.78 mmol, 78%) of *anti*-**28k** was obtained as colorless viscous oil after column chromatography (silica gel, pentane/ether, 3/1).

Data for *anti*-28k:

¹H NMR: (500 MHz, benzene-*d*₆)
3.77 (dt, *J* = 9.2, 3.2, 1H, *CHOH*); 3.44 - 3.64 (ABX, 2H, TBSOCH₂); 3.24 (d, *J* = 3.0, 1H, *OH*); 2.37 - 2.59 (m, 3H, COCH₂, COCH); 0.94 (s, 9H, C(CH₂)₃); 0.93 (s, 9H, (CH₃)₃CSi); 0.85 (d, *J* = 6.8, 3H, CHCH₃); 0.01 (s, 6H, SiCH₃)

¹³C NMR: (126 MHz, CDCl₃)
216.4 (C(3)); 75.2 (C(5)); 65.9 (C(1)); 49.5 (C(2)); 44.5 (C(4)); 34.4 (C(6)); 26.0 (C(7)); 25.9 (C(10)); 18.4 (C(9)); 13.0 (C(11)); 5.4, -5.4 (C(8))

IR: (neat)
3524 (m, br); 2957 (s); 2934 (s); 2861 (m); 1706 (m); 1471 (m); 1388 (m); 1364 (m); 1257 (m); 1103 (s); 1007 (m)

MS: (FI)303.3 (0.1, M⁺); 247 (5); 246 (18); 245 (100); 227 (2); 159 (3)**Opt. rot.:** -12.9 (CHCl₃, c=0.65)**TLC:** *R_f* = 0.30 (pentane/ether, 3/1, SiO₂) [*p*-anisaldehyde]**Analysis:** Calc for C₁₆H₃₄O₃Si (302.52)

Calc. C 63.52%; H 11.33%

Found: C 63.27%; H 11.43%

General Procedure IV: (1*R*,5*S*)-5-*tert*-Butyldimethylsilyloxy-1-hydroxy-1-phenyl-3-hexanone (*anti*-35a**)**

To a suspension of mercury(II) acetate (3.2 mg, 0.01 mmol, 0.01 equiv) in 1 mL of methylene chloride was added silicon tetrachloride (0.23 mL, 2.0 mmol, 2.0 equiv) and the trimethylsilyl enol ether **11** (289 mg, 1.00 mmol). The reaction mixture was stirred at rt for 30 min. The excess silicon tetrachloride and the solvent were removed under vacuum. To the residue was added solution of the chiral phosphoramidate (*R,R*)-**1** (36.9 mg, 0.10 mmol, 0.10 equiv) in 2 mL of methylene chloride via a cannula. The reaction mixture was cooled to -78 °C before the addition of benzaldehyde (102 μ L, 1.00 mmol, 1 equiv). The reaction mixture was stirred at -78 °C for 4 h, and then was quenched by pouring into a vigorously stirring 5 mL of cold saturated aqueous sodium bicarbonate. The resulting slurry was stirred for 3 h and was filtered through Celite. The layers were separated and the aqueous layer was extracted with 20 mL of methylene chloride. The combined organic extracts were washed with 5 mL of brine, dried over sodium sulfate and concentrated. The crude product was chromatographed (silica gel, pentane/ether, 3/1) to give **35a** (198 mg, 0.61 mmol, 61%) as viscous colorless oil.

Data for anti-35a:¹H NMR: (500 MHz, CDCl₃)

7.35 – 7.34 (m, 4 H, HC(8), HC(9)); 7.29 – 7.26 (m, 1 H, HC(10)); 5.15 (dt, *J* = 8.6, 3.5, 1H, HC(1)); 4.32 (sext, *J* = 6.1, 1 H, HC(5)); 3.36 (d, *J* = 3.2, 1 H, OH); 2.92 – 2.82 (ABX, 2H, H₂C(2)); 2.67 – 2.41 (ABX, 2H, H₂C(4)); 1.17 (d, *J* = 6.2, 3H, H₃C(6)); 0.86 (s, 9H, H₃C(13)); 0.05 (d, *J* = 12.4, 6H, H₃C(11))

¹³C NMR: (125 MHz, CDCl₃)

210.6 (C(3)); 142.7 (C(7)); 128.5 (C(9)); 127.6 (C(10)); 125.6 (C(8)); 69.6 (C(5)); 65.6 (C(1)); 53.3 (C(4)); 52.9 (C(2)); 25.7 (C(13)); 24.0 (C(6)); 17.9 (C(12)); -4.5, -5.0 (C(11))

IR: (neat)

3438 (m, br); 3064 (w); 3032 (w); 2956 (s); 2929 (s); 2895 (m); 2850 (m); 1711 (s); 1495 (w); 1462 (m); 1377 (m); 1255 (m); 1134 (m); 1090 (m); 1066 (s); 1041 (m); 1007 (m)

MS: (FI)

323 (5, M⁺); 265 (100); 159 (3); 106 (3)

Opt. Rot.: [α]_D²⁴ + 47.1° (EtOH, c=0.64)TLC: *R*_f = 0.10 (pentane/ether, 3/1) [silicagel, *p*-anisaldehyde]SFC: *t*_R = 4.695 min (OD, 150 bar, 3 mL/min, 2% MeOH)Analysis: C₁₈H₃₀O₃Si (322.51)

Calcd: C, 67.03%; H, 9.38%

Found: C, 66.94%; H, 9.52%

(1*S*,5*S*)-5-*tert*-Butyldimethylsilyloxy-1-hydroxy-1-phenyl-3-hexanone (*syn*-35a)

Following General Procedure IV using **11** (289 mg, 1.00 mmol), SiCl₄ (0.23 mL, 2.00 mmol), Hg(OAc)₂ (3.2 mg, 0.01 mmol), benzaldehyde (102 μL, 1.00 mmol), (*S,S*)-**1** (37 mg,

0.10 mmol) in 2 mL of CH₂Cl₂, 188 mg (0.58 mmol, 58%) of *syn*-**35a** was obtained as colorless viscous oil after column chromatography (silica gel, pentane/ether, 3/1).

Data for *syn*-**35a**:

¹H NMR: (500 MHz, CDCl₃)

7.36 – 7.34 (m, 4 H, HC(8), HC(9)); 7.29 – 7.26 (m, 1 H, HC(10)); 5.16 – 5.13 (m, 1H, HC(1)); 4.32 (sext, *J* = 6.1, 1 H, HC(5)); 3.38 (d, *J* = 3.2, 1 H, OH); 2.88 – 2.85 (ABX, 2H, H₂C(2)); 2.68 – 2.43 (ABX, 2H, H₂C(4)); 1.17 (d, *J* = 6.1, 3H, H₃C(6)); 0.86 (s, 9H, H₃C(13)); 0.06 (d, *J* = 10.3, 6H, H₃C(11))

¹³C NMR: (126 MHz, CDCl₃)

210.5 (C(3)); 142.7 (C(7)); 128.5 (C(9)); 127.6 (C(10)); 125.6 (C(8)); 69.8 (C(5)); 65.5 (C(1)); 53.0 (C(4)); 52.8 (C(2)); 25.8 (C(13)); 24.0 (C(6)); 18.0 (C(12)); -4.6, -5.0 (C(11))

IR: (neat)

3441 (m, br); 3064 (w); 3032 (w); 2956 (s); 2930 (s); 2895 (m); 2858 (m); 1710 (m); 1495 (w); 1462 (m); 1376 (m); 1253 (m); 1132 (m); 1090 (m); 1068 (m); 1032 (m); 1007 (m)

MS: (FI)

323 (5, M⁺); 265 (100); 159 (3); 106 (3)

Opt. Rot.: [α]_D²⁴ + 1.61 (EtOH, c=0.95)

TLC: *R*_f = 0.11 (pentane/ether, 3/1) [silicagel, *p*-anisaldehyde]

SFC: *t*_R = 4.984 min (OD, 150 bar, 3 mL/min, 2% MeOH)

Analysis: C₁₈H₃₀O₃Si (322.51)

Calcd: C, 67.03%; H, 9.38%

Found: C, 67.00%; H, 9.57%

(1*R*,5*S*)-5-Triisopropylsilyloxy-1-hydroxy-1-phenyl-3-hexanone (*anti*-37a)

Following General Procedure IV using **36** (331 mg, 1.00 mmol), SiCl₄ (0.23 mL, 2.00 mmol), Hg(OAc)₂ (3.2 mg, 0.01 mmol), benzaldehyde (102 μ L, 1.00 mmol), (*R,R*)-**1** (37 mg, 0.10 mmol) in 2 mL of CH₂Cl₂, 325 mg (0.89 mmol, 89%) of *anti*-**37a** was obtained as colorless viscous oil after column chromatography (silica gel, pentane/ether, 3/1).

Data for *anti*-37a:

¹H NMR: (500 MHz, CDCl₃)

7.37 (m, 4 H, HC(8), HC(9)); 7.30 (m, 1 H, HC(10)); 5.17 (dt, *J* = 9.0, 3.1, 1H, HC(1)); 4.47 (sext, *J* = 6.1, 1 H, HC(5)); 3.35 (d, *J* = 3.2, 1 H, OH); 2.96 – 2.85 (ABX, 2H, H₂C(2)); 2.73 – 2.52 (ABX, 2H, H₂C(4)); 1.24 (d, *J* = 6.1, 3H, H₃C(6)); 1.07 (s, 21H, H₃C(12), HC(11))

¹³C NMR: (126 MHz, CDCl₃)

210.3 (C(3)); 142.7 (C(7)); 128.5 (C(9)); 127.6 (C(10)); 125.6 (C(8)); 69.7 (C(1)); 65.4 (C(5)); 53.3 (C(4)); 52.8 (C(2)); 24.1 (C(6)); 18.1 (C(12)); 12.4 (C(11))

IR: (neat)

3441 (m, br); 2961 (s); 2944 (s); 2893 (s); 2867 (s); 1710 (s); 1463 (m); 1375 (m); 1130 (s); 1092 (s); 1066 (s); 1040 (m); 1013 (s)

MS: (FI)

365 (2, M⁺); 321 (100); 215 (7); 144 (2); 106 (3)

Opt. Rot.: [α]_D²⁴ + 11.5 (EtOH, c=0.43)

TLC: *R*_f = 0.15 (pentane/ether, 3/1) [silica gel, *p*-anisaldehyde]

SFC: *t*_R = 3.745 min (OD, 150 bar, 3 mL/min, 5% MeOH)

Analysis: C₂₁H₃₆O₃Si (364.59)

Calcd: C, 69.18%; H, 9.95%

Found: C, 69.04%; H, 10.05%

(1*S*,5*S*)-5-Triisopropylsilyloxy-1-hydroxy-1-phenyl-3-hexanone (*syn*-37a)

Following General Procedure IV using **36** (331 mg, 1.00 mmol), SiCl₄ (0.23 mL, 2.00 mmol), Hg(OAc)₂ (3.2 mg, 0.01 mmol), benzaldehyde (102 μ L, 1.00 mmol), (*S,S*)-**1** (37 mg, 0.10 mmol) in 2 mL of CH₂Cl₂, 315 mg (0.86 mmol, 86%) of ***syn*-37a** was obtained as colorless viscous oil after column chromatography (silica gel, pentane/ether, 3/1).

Data for *syn*-37a:

¹H NMR: (500 MHz, CDCl₃)

7.37 (m, 4 H, HC(8), HC(9)); 7.30 (m, 1 H, HC(10)); 5.17 (m, 1H, HC(1)); 4.45 (sext, *J* = 6.1, 1 H, HC(5)); 3.35 (d, *J* = 2.9, 1 H, HO); 2.96 – 2.85 (ABX, 2H, H₂C(2)); 2.73 – 2.59 (ABX, 2H, H₂C(4)); 1.24 (d, *J* = 6.1, 3H, H₃C(6)); 1.07 (s, 21 H, H₃C(13), HC(11))

¹³C NMR: (126 MHz, CDCl₃)

210.2 (C(3)); 142.8 (C(7)); 128.5 (C(9)); 127.6 (C(10)); 125.6 (C(8)); 69.7 (C(1)); 65.3 (C(5)); 53.4 (C(4)); 52.5 (C(2)); 24.0 (C(6)); 18.0 (C(12)); 12.3 (C(11))

IR: (neat)

3438 (m, br); 2961 (s); 2944 (s); 2893 (s); 2867 (s); 1710 (s); 1463 (m); 1375 (m); 1130 (m); 1092 (m); 1066 (m); 1038 (m); 1014 (m)

MS: (FI)

365 (2, M⁺); 321 (100); 215 (6)

Opt. Rot.: [α]_D²⁴ - 5.84 (EtOH, c=1.07)

TLC: *R*_f = 0.14 (pentane/ether, 3/1) [silica gel, *p*-anisaldehyde]

SFC: *t*_R = 4.163 min (OD, 150 bar, 3 mL/min, 5% MeOH)

Analysis: C₂₁H₃₆O₃Si (364.59)

Calcd: C, 69.18%; H, 9.95%

Found: C, 69.03%; H, 10.20%

General Procedure V: Aldol Addition of Trimethylsilyl Enol Ethers: (1*R*,4*S*)-5-*tert*-Butyldimethylsilyloxy-4-methyl-1-hydroxy-1-phenyl-3-pentanone (*syn*-28a**)**

In a 10 mL Schlenk flask was placed (*R,R*)-**2** (42 mg, 0.05 mmol, 0.05 equiv) in dichloromethane (1 mL). To the solution was added benzaldehyde (0.102 mL, 1.00 mmol), and the solution was cooled to $-78\text{ }^\circ\text{C}$ (bath temperature) using a dry ice/acetone bath. To the solution was added silicon tetrachloride (0.172 mL, 1.50 mmol, 1.5 equiv), and the solution was stirred for 5 min. To the solution was added dropwise **8** (346 mg, 1.20 mmol, 1.2 equiv), and the reaction mixture was stirred at $-78\text{ }^\circ\text{C}$ (bath temperature) for 4 h. The reaction mixture was quenched by pouring into a vigorously stirring cold ($0\text{ }^\circ\text{C}$) saturated aqueous NaHCO_3 solution (15 mL), and the resulting emulsion was stirred for at least 2 h. The emulsion was filtered through a pad of Celite, and the filtrate was transferred into a 60-mL separatory funnel. The biphasic mixture was extracted with dichloromethane (2 x 20 mL), and the combined extracts were washed with brine (10 mL). The solution was dried over Na_2SO_4 and concentrated under reduced pressure. The resulting crude oil was chromatographed (silica gel, pentane/ether, 3/1, 30 mm) to afford 294 mg (0.91 mmol, 91%) of **28a** as a clear colorless oil.

Data for *syn*-28a**:**

^1H NMR: (500 MHz, CDCl_3)

7.23 – 7.47 (m, 5H, aromatic); 5.17 (dt, $J = 8.8, 3.2$, 1H, HC(1)); 3.65 – 3.76 (ABX, 2H, C(5) H_2); 3.49 (d, $J = 2.9$, 1H, OH); 2.86 – 2.96 (ABX, 2H, C(2) H_2); 2.78 (m, 1H, C(4) H); 1.03 (d, $J = 6.9$, 3H, C(6) H_3); 0.87 (s, 9H, (C(9) H_3) $_3$); 0.04 (d, $J = 2$, 6H, C(7) H_3)

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

214.7 (C(3)); 142.9, 128.5, 127.5, 125.6 (aromatic); 69.7 (C(1)); 65.6 (C(5)); 51.4 (C(2)); 49.0 (C(4)); 25.8 (C(9)); 18.2 (C(8)); 12.6 (C(6)); -5.6 (C(7))

TLC: $R_f = 0.19$ (hexane/EtOAc, 5/1, SiO_2)

SFC: (Chiralpak OD column, 125 bar, 3.0 mL/min, 2.0% MeOH)

t_R (1*R*, 4*S*)-*syn*-**28a** 4.797 min (95.9%); (1*S*, 4*S*)-*anti*-**28a** 5.271 min (4.1%)

(1*S*,4*R*)-5-*tert*-Butyldimethylsilyloxy-4-methyl-1-hydroxy-1-phenyl-3-pentanone (*anti*-28a**)**

Following General Procedure V using **8** (346 mg, 1.00 mmol), SiCl₄ (0.172 mL, 2.00 mmol), benzaldehyde (102 μ L, 1.00 mmol), (*S,S*)-**2** (42 mg, 0.05 mmol) in 1 mL of CH₂Cl₂, 304 mg (0.94 mmol, 94%) of *anti*-**28a** was obtained as colorless viscous oil after column chromatography (silica gel, pentane/ether, 3/1, 30 mm).

Data for *anti*-28a**:**

¹H NMR: (500 MHz, CDCl₃)

7.27 – 7.38 (m, 5H, aromatic); 5.14 (dt, J = 9.6, 2.8, 1H, HC(1)); 3.67 – 3.77 (ABX, 2H, H₂C(5)); 3.50 (d, J = 3.0, 1H, OH); 2.84 – 2.97 (ABX, 2H, COC(2)H₂); 2.78 (m, 1H, COC(4)H); 1.05 (d, J = 7.1, 3H, CHC(10)H₃); 0.88 (s, 9H, (C(13)H₃)₃CSi); 0.05 (d, J = 2, 6H, SiC(11)H₃))

¹³C NMR: (125 MHz, CDCl₃)

14.7 (C(3)); 142.9 (C(6)), 128.5 (C(8)), 127.5 (C(9)), 125.6 (C(7)); 70.0 (C(1)); 65.4 (C(5)); 51.1 (C(2)); 48.2 (C(4)); 25.8 (C(13)); 18.2 (C(12)); 12.6 (C(10)); -5.6 (C(11))

TLC: R_f = 0.17 (hexane/EtOAc, 5/1, SiO₂)

SFC: (Chiralpak OD column, 125 bar, 3.0 mL/min, 2.0% MeOH)

t_R *syn*-**28a** 4.790 min (2.0%); t_R *anti*-**28a** 5.203 min (98.0%)

(2*S*,5*R*,6*E*)-1-*tert*-Butyldimethylsilyloxy-2-methyl-5-hydroxy-7-phenyl-6-hepten-3-one (*syn*-28c**)**

Following General Procedure V using **8** (346 mg, 1.00 mmol), SiCl₄ (0.172 mL, 2.00 mmol), cinnamaldehyde (126 μ L, 1.00 mmol), (*R,R*)-**2** (42 mg, 0.05 mmol) in 1 mL of CH₂Cl₂, 295 mg (0.85 mmol, 85%) of *syn*-**28c** was obtained as pale yellow viscous oil after column chromatography (silica gel, pentane/ether, 2/1, 30 mm).

Data for *syn*-28c**:**

¹H NMR: (500 MHz, CDCl₃)

7.37 (d, *J* = 8.6, 1H, aromatic); 7.37 (d, *J* = 5.6, 1H, aromatic); 7.30 (t, *J* = 7.7, 2H, aromatic); 7.23 (t, *J* = 7.2, 1H, aromatic); 6.65 (d, *J* = 16.2, 1H, *CH*); 6.21 (dd, *J* = 16.0, 6.0, 1H, *CH*); 4.77 (m, 1H, *CHOH*); 3.66 - 3.77 (ABX, 2H, TBSOCH₂); 3.31 (d, *J* = 3.4, 1H, *OH*); 2.75 - 2.90 (ABX, 2H, COCH₂); 2.82 (m, 1H, COCH); 1.06 (d, *J* = 7.1, 3H, CHCH₃); 0.88 (s, 9H, (CH₃)₃CSi); 0.05 (d, *J* = 5.7, 6H, SiCH₃)

¹³C NMR: (125 MHz, CDCl₃)

214.4 (C(3)); 136.6 (C(8)), 130.2 (C(11)), 130.0 (C(7)), 128.5 (C(10)); 127.6 (C(6)); 126.4 (C(9)); 68.2 (C(1)); 65.5 (C(5)); 49.3 (C(2)); 49.0 (C(4)); 26.0 (C(14)); 18.1 (C(13)); 12.6 (C(15)); -5.6, -5.6 (C(12))

TLC: *R_f* = 0.12 (hexane/EtOAc, 5/1, SiO₂)

SFC: (Chiralpak OD column, 125 bar, 3.0 mL/min, 7.5% MeOH)

t_R *syn*-**28c** 3.236 min (97.0%); *t_R* *anti*-**28c** 3.886 min (3.0%)

(2*S*,5*S*,6*E*)-1-*tert*-Butyldimethylsilyloxy-2-methyl-5-hydroxy-7-phenyl-6-hepten-3-one (syn-28c**)**

Following General Procedure V using **8** (346 mg, 1.00 mmol), SiCl₄ (0.172 mL, 2.00 mmol), cinnamaldehyde (126 μ L, 1.00 mmol), (*S,S*)-**2** (42 mg, 0.05 mmol) in 1 mL of CH₂Cl₂, 291 mg (0.83 mmol, 83%) of *anti*-**28c** was obtained as pale yellow viscous oil after column chromatography (silica gel, pentane/ether, 2/1, 30 mm).

Data for *anti*-28c**:**

¹H NMR: (500 MHz, CDCl₃)

7.37 (d, *J* = 8.6, 1.0, 1H, aromatic); 7.37 (d, *J* = 7.7, 1.0, 1H, aromatic); 7.31 (t, *J* = 7.7, 2H, aromatic); 7.23 (t, *J* = 7.2, 1H, aromatic); 6.67 (dd, *J* = 16.1, 1.4, 1H, CH); 6.22 (dd, *J* = 15.9, 6.0, 1H, CH); 4.75 (m, 1H, CHOH); 3.67 - 3.78 (ABX, 2H, TBSOCH₂); 3.34 (d, *J* = 3.4, 1H, OH); 2.77 - 2.92 (ABX, 2H, COCH₂); 2.84 (m, 1H, COCH); 1.07 (d, *J* = 7.1, 3H, CHCH₃); 0.88 (s, 9H, (CH₃)₃CSi); 0.05 (d, *J* = 3.7, 6H, SiCH₃)

¹³C NMR: (125 MHz, CDCl₃)

214.3 (C(3)); 136.7 (C(8)), 130.3 (C(11)), 130.2 (C(7)), 128.5 (C(10)); 127.5 (C(6)); 126.5 (C(9)); 68.6 (C(1)); 65.4 (C(5)); 49.3 (C(2)); 48.9 (C(4)); 25.8 (C(14)); 18.2 (C(13)); 12.7 (C(15)); -5.6 (C(12))

TLC: *R_f* = 0.15 (hexane/EtOAc, 5/1, SiO₂)

SFC: (Chiralpak OD column, 125 bar, 3.0 mL/min, 7.5% MeOH)

t_R *syn*-**28c** 3.218 min (2.8%); *t_R* *anti*-**28c** 3.854 min (97.2%)

(2*S*,5*R*)-1-*tert*-Butyldimethylsilyloxy-2-methyl-5-hydroxy-5-(1-naphthyl)-3-pentanone (syn-28b)

Following General Procedure V using **8** (346 mg, 1.00 mmol), SiCl_4 (0.172 mL, 2.00 mmol), 1-naphthaldehyde (132 μL , 1.00 mmol), (*R,R*)-**2** (42 mg, 0.05 mmol) in 1 mL of CH_2Cl_2 , 316 mg (0.85 mmol, 85%) of *syn*-**28b** was obtained as pale yellow viscous oil after column chromatography (silica gel, pentane/ether, 3/1, 30 mm).

Data for *syn*-**28b**:

^1H NMR: (500 MHz, CDCl_3)

7.47 – 8.02 (7H, aromatic); 5.97 (dt, $J = 9.5, 2.5$, 1H, (C(1)HOH); 3.68 – 3.80 (ABX, 2H, TBSOC(5) H_2); 3.58 (d, $J = 2.9$, 1H, OH); 2.98 – 3.13 (ABX, 2H, COC(2) H_2); 2.79 (m, 1H, COC(4) H); 1.06 (d, $J = 7.1$, 3H, CHC(16) H_3); 0.86 (s, 9H, (C(19) H_3) $_3\text{CSi}$); 0.04 (d, $J = 3.9$, 6H, SiC(17) H_3)

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

214.5 (C(3)); 138.4 (C(6)), 133.7 (C(12)), 129.9 (C(7)), 129.0 (C(11)); 127.9 (C(13)); 126.2 (C(9)); 125.6 (C(10)); 125.5 (C(14)); 123.0 (C(15)); 122.8 (C(8)); 66.6 (C(1)); 65.5 (C(5)); 50.5 (C(2)); 49.2 (C(4)); 25.8 (C(19)); 18.2 (C(18)); 12.6 (C(16)); -5.6 (C(17))

TLC: $R_f = 0.18$ (hexane/EtOAc, 5/1, SiO_2)

SFC: (Chiralpak OD column, 125 bar, 3.0 mL/min, 12.5% MeOH)

t_R *anti*-**28b** 3.037 min (5.0%); t_R *syn*-**28b** 3.786 min (95.0%)

(2*S*,5*S*)-1-*tert*-Butyldimethylsilyloxy-2-methyl-5-hydroxy-5-(1-naphthyl)-3-pentanone (*anti*-28b**)**

Following General Procedure V using **8** (346 mg, 1.00 mmol), SiCl_4 (0.172 mL, 2.00 mmol), 1-naphthaldehyde (132 μL , 1.00 mmol), (*S,S*)-**2** (42 mg, 0.05 mmol) in 1 mL of CH_2Cl_2 , 308 mg (0.83 mmol, 83%) of *anti*-**28b** was obtained as pale yellow viscous oil after column chromatography (silica gel, pentane/ether, 3/1, 30 mm).

Data for *anti*-**28b**:

^1H NMR: (500 MHz, CDCl_3)

7.47 – 8.02 (7H, aromatic); 5.98 (m, $J = 9.5$, 1H, CHOH); 3.69 – 3.79 (ABX, 2H, TBSOCH_2); 3.68 (d, $J = 2.8$, 1H, OH); 3.01 – 3.09 (ABX, 2H, COCH_2); 2.82 (m, 1H, COCH); 1.07 (d, $J = 7.1$, 3H, CHCH_3); 0.88 (s, 9H, $(\text{CH}_3)_3\text{CSi}$); 0.05 (d, $J = 3.9$, 6H, SiCH_3)

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

214.5 (C(3)); 138.4 (C(6)), 133.8 (C(12)), 129.9 (C(7)), 129.0 (C(11)); 128.0 (C(13)); 126.1 (C(9)); 125.6 (C(10)); 125.5 (C(14)); 123.0 (C(15)); 122.8 (C(8)); 66.9 (C(1)); 65.5 (C(5)); 50.2 (C(2)); 49.3 (C(4)); 25.8 (C(19)); 18.2 (C(18)); 12.7 (C(16)); -5.6 (C(17))

TLC: $R_f = 0.19$ (hexane/EtOAc, 5/1, SiO_2)

SFC: (Chiralpak OD column, 125 bar, 3.0 mL/min, 12.5% MeOH)

t_R *anti*-**28b** 2.947 min (92.4%); t_R *syn*-**28b** 3.729 min (2.2%)

(2*S*,5*R*)-1-*tert*-Butyldimethylsilyloxy-2-methyl-5-hydroxy-7-phenyl-6-heptyn-3-one (*syn*-28h**)**

Following General Procedure V using **8** (346 mg, 1.00 mmol), SiCl₄ (0.172 mL, 2.00 mmol), phenylpropargyl aldehyde (122 μ L, 1.00 mmol), (*R,R*)-**2** (42 mg, 0.05 mmol) in 1 mL of CH₂Cl₂, 255 mg (0.74 mmol, 74%) of *syn*-**28h** was obtained as pale yellow viscous oil after column chromatography (silica gel, pentane/ether, 3/1, 30 mm).

Data for *syn*-28h**:**

¹H NMR: (500 MHz, CDCl₃)

7.28 – 7.43 (m, 5H, aromatic); 5.01 – 5.06 (m, 1H, *CHOH*); 3.67 – 3.77 (ABX, 2H, TBSOCH₂); 3.33 (d, *J* = 5.1, 1H, *OH*); 2.96 – 3.13 (ABX, 2H, COCH₂); 2.82 (m, 1H, COCH); 1.08 (d, *J* = 7.1, 3H, CHCH₃); 0.88 (s, 9H, (CH₃)₃CSi); 0.06 (d, *J* = 5.1, 6H, SiCH₃)

¹³C NMR: (125 MHz, CDCl₃)

213.2 (C(3)); 131.7 (C(9)); 128.4 (C(11)); 128.2 (C(10)); 122.4 (C(8)); 88.5 (C(6)); 84.6 (C(7)); 65.3 (C(5)); 58.8 (C(1)); 49.4 (C(2)); 49.0 (C(4)); 25.7 (C(14)); 18.1 (C(13)); 12.4 (C(15)); -5.7, -5.7 (C(12))

TLC: *R_f* = 0.16 (hexane/EtOAc, 5/1, SiO₂)

SFC: (Chiralpak OD column, 125 bar, 3.0 mL/min, 7.5% MeOH)

t_R *syn*-**28h** 3.130 min (39.6%); *t_R* *anti*-**28h** 3.494 min (60.4%)

(2*S*,5*S*)-1-*tert*-Butyldimethylsilyloxy-2-methyl-5-hydroxy-7-phenyl-6-heptyn-3-one (*anti*-28h**)**

Following General Procedure V using **8** (346 mg, 1.00 mmol), SiCl₄ (0.172 mL, 2.00 mmol), phenylpropargyl aldehyde (122 μL, 1.00 mmol), (*S,S*)-**2** (42 mg, 0.05 mmol) in 1 mL of CH₂Cl₂, 248 mg (0.72 mmol, 72%) of *anti*-**28h** was obtained as pale yellow viscous oil after column chromatography (silica gel, pentane/ether, 3/1, 30 mm).

Data for *anti*-**28h**:

¹H NMR: (500 MHz, CDCl₃)

7.28 – 7.43 (m, 5H, aromatic); 5.01 – 5.06 (m, 1H, *CHOH*); 3.67 – 3.79 (ABX, 2H, TBSOCH₂); 3.29 (d, *J* = 5.1, 1H, *OH*); 2.97 – 3.13 (ABX, 2H, COCH₂); 2.82 (m, 1H, COCH); 1.09 (d, *J* = 7.1, 3H, CHCH₃); 0.88 (s, 9H, (CH₃)₃CSi); 0.05 (d, *J* = 3.9, 6H, SiCH₃)

¹³C NMR: (125 MHz, CDCl₃)

213.1 (C(3)); 131.7 (C(9)); 128.4 (C(11)); 128.2 (C(10)); 122.4 (C(8)); 88.5 (C(6)); 84.6 (C(7)); 65.2 (C(5)); 59.0 (C(1)); 49.2 (C(2)); 49.0 (C(4)); 25.8 (C(14)); 18.1 (C(13)); 12.6 (C(15)); -5.7 (C(12))

TLC: *R_f* = 0.14 (hexane/EtOAc, 5/1, SiO₂)

SFC: (Chiralpak OD column, 125 bar, 3.0 mL/min, 7.5% MeOH)

t_R *syn*-**28h** 3.097 min (19.9%); *t_R* *anti*-**28h** 3.493 min (80.1%)

(1*R*,5*S*)-5-*tert*-Butyldimethylsilyloxy-1-hydroxy-1-phenyl-3-hexanone (*anti*-35a)

Following General Procedure V using **11** (346 mg, 1.00 mmol), SiCl_4 (0.172 mL, 2.00 mmol), benzaldehyde (102 μL , 1.00 mmol), (*R,R*)-**2** (42 mg, 0.05 mmol) and diisopropylethylamine (0.034 mL, 0.20 mmol, 0.2 equiv) in 2 mL of CH_2Cl_2 , 298 mg (0.92 mmol, 92%) of *anti*-**35a** was obtained as clear colorless oil after column chromatography (silica gel, pentane/ether, 3/1, 30 mm).

Data for *anti*-35a:

^1H NMR: (500 MHz, CDCl_3)

7.35 – 7.34 (m, 4 H, HC(8), HC(9)); 7.29 – 7.26 (m, 1 H, HC(10)); 5.15 (dt, $J = 8.6, 3.5$, 1H, HC(1)); 4.32 (sext, $J = 6.1$, 1 H, HC(5)); 3.36 (d, $J = 3.2$, 1 H, OH); 2.92 – 2.82 (ABX, 2H, $\text{H}_2\text{C}(2)$); 2.67 – 2.41 (ABX, 2H, $\text{H}_2\text{C}(4)$); 1.17 (d, $J = 6.2$, 3H, $\text{H}_3\text{C}(6)$); 0.86 (s, 9H, $\text{H}_3\text{C}(13)$); 0.05 (d, $J = 12.4$, 6H, $\text{H}_3\text{C}(11)$)

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

210.6 (C(3)); 142.7 (C(7)); 128.5 (C(9)); 127.6 (C(10)); 125.6 (C(8)); 69.6 (C(5)); 65.6 (C(1)); 53.3 (C(4)); 52.9 (C(2)); 25.7 (C(13)); 24.0 (C(6)); 17.9 (C(12)); -4.5, -5.0 (C(11))

TLC: $R_f = 0.16$ (pentane/ether, 3/1, SiO_2)

SFC: (Chiralpak OD column, 125 bar, 3.0 mL/min, 3.0 % MeOH)

t_R *anti*-**35a** 5.243 min (97.3%); t_R *syn*-**35a** 5.614 min (2.7%)

(1*S*,5*S*)-5-*tert*-Butyldimethylsilyloxy-1-hydroxy-1-phenyl-3-hexanone (*syn*-35a)

Following General Procedure V using **11** (346 mg, 1.00 mmol), SiCl_4 (0.172 mL, 2.00 mmol), benzaldehyde (102 μL , 1.00 mmol), (*S,S*)-**2** (42 mg, 0.05 mmol) and diisopropylethylamine (0.034 mL, 0.20 mmol, 0.2 equiv) in 2 mL of CH_2Cl_2 , 302 mg (0.94 mmol, 94%) of *syn*-**35a** was obtained as clear colorless oil after column chromatography (silica gel, pentane/ether, 3/1, 30 mm).

Data for *syn*-35a:

^1H NMR: (500 MHz, CDCl_3)

7.36 – 7.34 (m, 4 H, HC(8), HC(9)); 7.29 – 7.26 (m, 1 H, HC(10)); 5.16 – 5.13 (m, 1H, HC(1)); 4.32 (sext, $J = 6.1$, 1 H, HC(5)); 3.38 (d, $J = 3.2$, 1 H, OH); 2.88 – 2.85 (ABX, 2H, $\text{H}_2\text{C}(2)$); 2.68 – 2.43 (ABX, 2H, $\text{H}_2\text{C}(4)$); 1.17 (d, $J = 6.1$, 3H, $\text{H}_3\text{C}(6)$); 0.86 (s, 9H, $\text{H}_3\text{C}(13)$); 0.06 (d, $J = 10.3$, 6H, $\text{H}_3\text{C}(11)$)

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

210.5 (C(3)); 142.7 (C(7)); 128.5 (C(9)); 127.6 (C(10)); 125.6 (C(8)); 69.8 (C(5)); 65.5 (C(1)); 53.0 (C(4)); 52.8 (C(2)); 25.8 (C(13)); 24.0 (C(6)); 17.9 (C(12)); -4.6, -5.0 (C(11))

TLC: $R_f = 0.19$ (pentane/ether, 3/1, SiO_2)

SFC: (Chiralpak OD column, 125 bar, 3.0 mL/min, 3.0% MeOH)

t_R *anti*-**35a** 5.276 min (2.7%); t_R *syn*-**35a** 5.577 min (97.3%)

(2*S*,6*R*)-2-(*tert*-Butyldimethylsilanyloxy)-6-hydroxy-8-phenyl-oct-7-en-4-one (*anti*-35c**)**

Following General Procedure V using **11** (346 mg, 1.00 mmol), SiCl₄ (0.172 mL, 2.00 mmol), cinnamaldehyde (126 μL, 1.00 mmol), (*R,R*)-**2** (42 mg, 0.05 mmol) and diisopropylethylamine (0.034 mL, 0.20 mmol, 0.2 equiv) in 2 mL of CH₂Cl₂, 309 mg (0.88 mmol, 88%) of *anti*-**35c** was obtained as pale yellow viscous oil after column chromatography (silica gel, pentane/ether, 2/1, 30 mm).

Data for *anti*-**35c**:

¹H NMR: (500 MHz, CDCl₃)

7.36 – 7.26 (m, 5 H, 2 x HC(7), 2 x HC(8), HC(9)); 4.78 (dd, *J* = 8.0, 4.8, 1 H, HC(1)); 3.78 (ABX, 2 H, 2 x HC(5)); 3.09 (d, *J* = 4.6, 1 H, HO); 3.05 (pent, *J* = 7.6, 1 H, HC(2)); 2.89 (sextd, *J* = 5.1, 1.2, 1 H, HC(4)); 1.04 (m, 21 H, 3 x HC(12), 18 x HC(13)); 0.97 (d, *J* = 7.1, 3 H, 3 x HC(10)); 0.93 (d, *J* = 7.1, 3 H, 3 x HC(11))

¹³C NMR: (126 MHz, CDCl₃)

217.9 (C(3)); 142.3 (C(6)); 128.3 (2 x C(7)); 127.7 (C(9)); 126.5 (2 x C(8)); 76.5 (C(1)); 65.5 (C(5)); 53.1 (C(2)); 49.1 (C(4)); 17.9, 17.9 (6 x C(13)); 13.8 (C(10)); 12.8 (C(11)); 11.8 (3 x C(12))

IR: (neat)

3452 (br, m); 3064 (w); 3032 (w); 2943 (s); 2893 (m); 2868 (s); 1711 (m); 1495 (w); 1462 (m); 1383 (m); 1248 (m); 1101 (m); 1066 (m); 1011 (m)

MS: (FI)

379 (3, M⁺); 337 (7); 336 (25); 335 (100); 272 (4); 229 (4); 58 (7)

Opt. Rot.: [α]_D²⁴ +29.4° (EtOH, c=0.7)

TLC: *R_f* 0.21 (silica gel, pentane/ether, 2/1)

SFC: (Chiralpak OD column, 125 bar, 3.0 mL/min, 5.0% MeOH)

t_R *syn*-**35c** 7.515 min (3.2%); *t_R* *anti*-**35c** 8.085 min (96.8%)

Analysis: C₂₂H₃₈O₃Si (348.55)
 Calcd: C, 68.92%; H, 9.25%
 Found: C, 69.08%; H, 9.05%

(2*S*,6*S*)- 2-(*tert*-Butyldimethylsilanyloxy)-6-hydroxy-8-phenyl-oct-7-en-4-one (*syn*-35c**)**

Following General Procedure V using **11** (346 mg, 1.00 mmol), SiCl₄ (0.172 mL, 2.00 mmol), cinnamaldehyde (126 μL, 1.00 mmol), (*S,S*)-**2** (42 mg, 0.05 mmol) and diisopropylethylamine (0.034 mL, 0.20 mmol, 0.2 equiv) in 2 mL of CH₂Cl₂, 326 mg (0.93 mmol, 93%) of *syn*-**35c** was obtained as pale yellow viscous oil after column chromatography (silica gel, pentane/ether, 2/1, 30 mm).

Data for *syn*-35c**:**

¹H NMR: (500 MHz, CDCl₃)
 7.37 (d, *J* = 7.0, 2 H, 2 x HC(10)); 7.31 (t, *J* = 7.8, 2 H, 2 x HC(11)); 7.26 (t, *J* = 7.3, 1 H, HC(7), HC(12)); 6.63 (d, *J* = 16.1, 1 H, HC(8)); 6.19 (dd, *J* = 16.1, 6.1, 1 H, HC(7)); 4.75 (m, 1 H, HC(6)); 4.32 (sext, *J* = 6.1, 1 H, HC(2)); 3.17 (d, *J* = 3.7, 1 H, HO); 2.77 (ABX, *J*_{AB} = 17.6, 2 H, 2 x HC(5)); 2.58 (ABX, *J*_{AB} = 15.2, 2 H, 2 x HC(3)); 1.18 (d, *J* = 6.1, 3 H, 3 x HC(1)); 0.86 (s, 9 H, 9 x HC(15)); 0.07 (s, 3 H, 3 x HC(13)); 0.05 (s, 3 H, 3 x HC(13'))

¹³C NMR: (126 MHz, CDCl₃)
 210.6 (C(4)); 136.5 (C(9)); 130.2 (C(12)); 130.2 (C(8)); 128.5 (2 x C(11)); 127.6 (C(7)); 126.4 (2 x C(10)); 68.3 (C(6)); 65.3 (C(2)); 53.0 (C(3)); 50.6 (C(5)); 25.7 (3 x C(15)); 23.9 (C(1)); 17.8 (C(14)); -4.6, -5.0 (2 x C(13))

IR: (neat)
 3432 (br, m); 3087 (w); 3061 (w); 3028 (w); 2956 (s); 2930 (s); 2895 (m); 2857 (s); 1710 (s); 1638 (w); 1599 (w); 1496 (w); 1472 (m); 1463 (m); 1449 (m); 1376

(m); 1361 (m); 1256 (s); 1203 (w); 1130 (m); 1083 (m); 1029 (m); 1004 (m)

MS: (FI)

348 (100, M^+); 331 (7); 291 (44); 244 (9); 216 (5); 159 (11); 146 (18); 132 (16); 115 (5)

Opt. Rot.: $[\alpha]_D^{24} +18.9$ (EtOH, $c=1.58$)

TLC: R_f 0.23 (silica gel, pentane/ether, 2/1)

SFC: (Chiralpak OD column, 125 bar, 3.0 mL/min, 5.0% MeOH)

t_R *syn*-**35c** 7.413 min (99.1%); t_R *anti*-**35c** 8.069 min (0.9%)

Analysis: $C_{22}H_{38}O_3Si$ (348.55)

Calcd: C, 68.92%; H, 9.25%

Found: C, 68.73%; H, 9.19%

(1*R*,5*S*)- 5-(*tert*-Butyldimethylsilyloxy)-1-hydroxy-1-naphthalen-1-yl-hexan-3-one (*anti*-35b**)**

Following General Procedure V using **11** (346 mg, 1.00 mmol), $SiCl_4$ (0.172 mL, 2.00 mmol), 1-naphthaldehyde (136 μ L, 1.00 mmol), (*R,R*)-**2** (42 mg, 0.05 mmol) and diisopropylethylamine (0.034 mL, 0.20 mmol, 0.2 equiv) in 2 mL of CH_2Cl_2 , 276 mg (0.74 mmol, 74%) of *anti*-**35b** was obtained as pale yellow viscous oil after column chromatography (silica gel, pentane/ether, 4/1, 30 mm).

Data for *anti*-35b**:**

1H NMR: (500 MHz, $CDCl_3$)

8.01 (dd, $J = 7.1, 2.5$, 1 H, HC(9)); 7.88 (dd, $J = 6.8, 2.7$, 1 H, HC(12)); 7.79 (d, $J = 8.3$, 1 H, HC(14)); 7.68 (d, $J = 7.1$, 1 H, HC(16)); 7.52 – 7.47 (m, 3 H, HC(10), HC(11), HC(15)); 5.96 (td, $J = 6.1, 3.2$, 1 H, HC(1)); 4.37 (sextd, $J = 4.9, 1.4$, 1 H, HC(5)); 3.45 (d, $J = 3.2$, 1 H, OH); 3.01 (d, $J = 6.1$, 2 H, 2 x HC(2)); 2.58 (ABX, $J_{AB} = 15.1$, 2 H, 2 x HC(4)); 1.18 (d, $J = 6.1$, 3 H, HC(6)); 0.86 (s, 9 H, 9 x HC(19)); 0.08 (s, 3 H, 3 x HC(17)); 0.07 (s, 3 H, 3 x HC(17'))

¹³C NMR: (126 MHz, CDCl₃)
 210.2 (C(3)); 138.2 (C(7)); 133.7 (C(13)); 129.8 (C(8)); 128.9 (C(12)); 128.0 (C(14)); 126.1 (C(10)); 125.5 (C(11)); 125.5 (C(15)); 123.0 (C(16)); 122.8 (C(9)); 66.5 (C(1)); 65.4 (C(5)); 52.9 (C(4)); 52.2 (C(2)); 25.8 (3 x C(19)); 23.9 (C(6)); 17.9 (C(18)); -4.5 (C(17)); -4.9 (C(17'))

IR: (neat)
 3440 (br, m); 3052 (m); 2956 (s); 2929 (s); 2896(m); 2856 (s); 1713 (s); 1598 (w); 1511 (m); 1472 (m); 1463 (m); 1445 (w); 1375 (s); 1361 (m); 1255 (s); 1213 (w); 1188 (w); 1159 (m); 1138(m); 1092 (s); 1047 (m); 1019 (m);

MS: (FI)
 372 (15, M⁺); 348 (100); 331 (7); 315 (5); 303 (2); 291 (38); 268 (6); 243 (10); 216 (4); 177 (2); 159 (4); 146 (19); 115 (4); 89 (5)

Opt. Rot.: [α]_D²⁴ +84.2 (EtOH, c=1.6)

TLC: *R_f* 0.19 (silica gel, pentane/ether, 4/1)

SFC: (Chiralpak OD column, 125 bar, 3.0 mL/min, 15.0% MeOH)
t_R *syn*-**35b** 2.937 min (4.5%); *t_R* *anti*-**35b** 3.294 min (95.5%)

Analysis: C₂₂H₃₂O₃Si (372.57)
 Calcd: C, 70.92%; H, 8.66%
 Found: C, 70.71%; H, 8.67%

(1*S*,5*S*)- 5-(*tert*-Butyldimethylsilyloxy)-1-hydroxy-1-naphthalen-1-yl-hexan-3-one (*syn*-35b**)**

Following General Procedure V using **11** (346 mg, 1.00 mmol), SiCl₄ (0.172 mL, 2.00 mmol), 1-naphthaldehyde (136 μ L, 1.00 mmol), (*S,S*)-**2** (42 mg, 0.05 mmol) and diisopropylethylamine (0.034 mL, 0.20 mmol, 0.2 equiv) in 2 mL of CH₂Cl₂, 294 mg (0.79 mmol, 79%) of *syn*-**35b** was obtained as pale yellow viscous oil after column chromatography

(silica gel, pentane/ether, 2/1, 30 mm).

Data for *syn*-**35b**:

¹H NMR: (500 MHz, CDCl₃)

8.01 (d, *J* = 8.0, 1 H, HC(9)); 7.88 (d, *J* = 8.3, 1 H, HC(12)); 7.79 (d, *J* = 8.3, 1 H, HC(14)); 7.69 (d, *J* = 7.3, 1 H, HC(16)); 7.53 – 7.47 (m, 3 H, HC(10), HC(11), HC(15)); 5.93 (dd, *J* = 9.2, 2.9, 1 H, HC(1)); 4.35 (sext, *J* = 6.0, 1 H, HC(5)); 3.51 (d, *J* = 2.7, 1 H, OH); 3.02 (ABX, *J*_{AB} = 18.1, 2 H, 2 x HC(2)); 2.59 (ABX, *J*_{AB} = 14.9, 2 H, 2 x HC(4)); 1.19 (d, *J* = 6.1, 3 H, HC(6)); 0.85 (s, 9 H, 9 x HC(19)); 0.07 (s, 3 H, 3 x HC(17)); 0.05 (s, 3 H, 3 x HC(17'))

¹³C NMR: (126 MHz, CDCl₃)

210.5 (C(3)); 138.2 (C(7)); 133.7 (C(13)); 129.8 (C(8)); 128.9 (C(12)); 127.9 (C(14)); 126.1 (C(10)); 125.5 (C(11)); 125.4 (C(15)); 123.0 (C(16)); 122.8 (C(9)); 66.6 (C(1)); 65.5 (C(5)); 53.0 (C(4)); 52.1 (C(2)); 25.7 (3 x C(19)); 24.0 (C(6)); 17.9 (C(18)); -4.5 (C(17)); -5.0 (C(17'))

IR: (neat)

3468 (br, m); 2930 (s); 2857 (s); 1708 (s); 1472 (m); 1376 (m); 1257 (m); 1129 (m); 1095 (m)

MS: (FI)

372 (100, M⁺); 348 (3); 315 (7); 267 (9); 156 (7)

Opt. Rot.: [α]_D²⁴ -8.9 (EtOH, c=1.25)

TLC: *R*_f 0.39 (silica gel, pentane/ether, 2/1)

SFC: (Chiralpak OD column, 125 bar, 3.0 mL/min, 15.0% MeOH)

*t*_R *syn*-**35b** 2.856 min (98.4%); *t*_R *anti*-**35b** 3.279 min (1.6%)

Analysis: C₂₂H₃₂O₃Si (372.57)

Calcd: C, 70.92%; H, 8.66%

Found: C, 70.52%; H, 8.68%

(2*S*,6*R*)-2-(*tert*-Butyldimethylsilanyloxy)-6-hydroxy-8-phenyl-oct-7-yn-4-one (*anti*-35h)

Following General Procedure V using **11** (346 mg, 1.00 mmol), SiCl₄ (0.172 mL, 2.00 mmol), phenylpropargyl aldehyde (122 μ L, 1.00 mmol), (*R,R*)-**2** (42 mg, 0.05 mmol) and diisopropylethylamine (0.034 mL, 0.20 mmol, 0.2 equiv) in 2 mL of CH₂Cl₂, 258 mg (0.74 mmol, 74%) of *anti*-**35h** was obtained as pale yellow viscous oil after column chromatography (silica gel, pentane/ether, 3/1, 30 mm).

Data for *anti*-35h:

¹H NMR: (500 MHz, CDCl₃)

7.43 – 7.28 (m, 5 H, 2 x HC(10), 2 x HC(11), HC(12)); 5.01 (m, 1 H, HC(6)); 4.33 (m, 1 H, HC(2)); 3.22 (d, *J* = 5.1, 1 H, HO); 3.00 (ABX, *J*_{AB} = 18.0, 2 H, 2 x HC(5)); 2.56 (ABX, *J*_{AB} = 14.8, 2 H, 2 x HC(3)); 1.18 (d, *J* = 6.2, 3 H, 3 x HC(1)); 0.87 (s, 9 H, 9 x HC(15)); 0.07 (s, 3 H, 3 x HC(13)); 0.04 (s, 3 H, 3 x HC(13'))

¹³C NMR: (126 MHz, CDCl₃)

209.3 (C(4)); 131.7 (2 x C(10)); 128.5 (C(12)); 128.2 (2 x C(11)); 122.4 (C(9)); 88.3 (C(7)); 84.7 (C(8)); 65.5 (C(2)); 58.7 (C(6)); 52.9 (C(3)); 51.0 (C(5)); 25.8 (3 x C(15)); 24.0 (C(1)); 17.9 (C(14)); -4.5, -5.0 (2 x C(13))

IR: (neat)

3390 (br, m); 3064 (w); 2955 (s); 2930 (s); 2886 (m); 2857 (s); 2187 (w); 1713 (s); 1652 (s); 1599 (m); 1491 (w); 1472 (m); 1463 (m); 1452 (m); 1444 (m); 1407 (m); 1362 (m); 1315 (w); 1255 (s); 1177 (w); 1072 (m); 1030 (m); 1008 (m)

MS: (FI)

347 (32, M⁺); 329 (5); 289 (100); 159 (3)

Opt. Rot.: [α]_D²⁴ +14.5 (EtOH, c=1.72)

TLC: *R*_f 0.15 (silica gel, pentane/ether, 3/1)

SFC: (Chiralpak OD column, 125 bar, 3.0 mL/min, 5.0% MeOH)
 t_R *syn*-**35h** 9.683 min (44.3%); t_R *anti*-**35h** 10.472 min (55.7%)

Analysis: C₂₀H₃₀O₃Si (346.54)
 Calcd: C, 69.32%; H, 8.73%
 Found: C, 69.00%; H, 8.89%

(2*S*,6*S*)-2-(*tert*-Butyldimethylsilanyloxy)-6-hydroxy-8-phenyl-oct-7-yn-4-one (*syn*-35h**)**

Following General Procedure V using **11** (346 mg, 1.00 mmol), SiCl₄ (0.172 mL, 2.00 mmol), phenylpropargyl aldehyde (122 μ L, 1.00 mmol), (*S,S*)-**2** (42 mg, 0.05 mmol) and diisopropylethylamine (0.034 mL, 0.20 mmol, 0.2 equiv) in 2 mL of CH₂Cl₂, 258 mg (0.74 mmol, 74%) of *syn*-**35h** was obtained as pale yellow viscous oil after column chromatography (silica gel, pentane/ether, 3/1, 30 mm).

Data for *syn*-35h**:**

¹H NMR: (500 MHz, CDCl₃)
 7.42 – 7.26 (m, 5 H, 2 x HC(10), 2 x HC(11), HC(12)); 5.01 (m, 1 H, HC(6));
 4.31 (m, 1 H, HC(2)); 3.33 (d, $J = 5.1$, 1 H, HO); 3.00 (ABX, $J_{AB} = 14.7$, 2 H, 2 x HC(5));
 2.60 (ABX, $J_{AB} = 15.2$, 2 H, 2 x HC(3)); 1.17 (d, $J = 6.2$, 3 H, 3 x HC(1)); 0.86 (s, 9 H, 9 x HC(15)); 0.06 (s, 3 H, 3 x HC(13)); 0.05 (s, 3 H, 3 x HC(13'))

¹³C NMR: (126 MHz, CDCl₃)
 208.8 (C(4)); 131.7 (2 x C(10)); 128.4 (C(12)); 128.2 (2 x C(11)); 122.4 (C(9));
 88.4 (C(7)); 84.7 (C(8)); 65.2 (C(2)); 58.7 (C(6)); 52.8 (C(3)); 51.0 (C(5)); 25.7 (3 x C(15)); 23.8 (C(1)); 17.8 (C(14)); -4.6, -5.1 (2 x C(13))

IR: (neat)
 3391 (br, m); 3064 (w); 2956 (s); 2930 (s); 2886 (m); 2857 (s); 2197 (w); 1713 (s); 1652 (s); 1599 (m); 1491 (w); 1472 (m); 1463 (m); 1452 (m); 1407 (m); 1255

(s); 1072 (m)

MS: (FI)347 (15, M^+); 289 (100); 271 (4); 159 (4)Opt. Rot.: $[\alpha]_D^{24} +20.5$ (EtOH, $c=1.48$)TLC: R_f 0.12 (silica gel, pentane/ether, 3/1)SFC: (Chiralpak OD column, 125 bar, 3.0 mL/min, 5.0% MeOH) t_R *syn*-**35h** 9.887 min (46.2%); t_R *anti*-**35h** 10.671 min (53.8%)Analysis: $C_{20}H_{30}O_3Si$ (346.54)

Calcd: C, 69.32%; H, 8.73%

Found: C, 68.93%; H, 8.38%

(1*R*,4*S*)-1,5-Dihydroxy-4-methyl-1-phenyl-pentan-3-one (31)

In a 25-mL round-bottom flask were placed *syn*-**28a** (83 mg, 0.26 mmol), pyridinium *p*-toluenesulfonate (20 mg, 0.08 mmol, 0.33 equiv) in ethanol (2 mL). The reaction mixture was heated to 55 °C (bath temperature) and stirred for 22 h. The reaction mixture was cooled to rt, and the volatiles were removed under reduced pressure. The residue was triturated with ether (10 mL), and the solution was transferred into a 60-mL separatory funnel. The solution was washed sequentially with brine (3 mL) and with water (3 mL), dried over Na_2SO_4 and concentrated under reduced pressure. The crude white solid was chromatographed (silica gel, hexanes/EtOAc, 2/1, 10 mm) to afford 43 mg (0.21 mmol, 80%) of **31** as white needles. The physical properties of the product matched with the literature.⁸ The crystal suitable for X-ray was obtained by recrystallization from acetone/hexane (1/1) by slow evaporation at rt.

Data for 31:mp: 88 – 92 °C (acetone/hexanes) 1H NMR: (500 MHz, $CDCl_3$)7.37 – 7.25 (m, 5 H, aromatic); 5.21 (dt, $J = 9.7, 3.0$, 1 H, HC(1)); 3.75 (ABX, J_{ax}

= 5.7, $J_{\text{bx}} = 4.3$, $J_{\text{ab}} = 7.1$, 2H, $\text{H}_2\text{C}(5)$); 3.19 (d, $J = 3.2$, 1 H, OH); 2.92 (ABX, J_{ax} = 9.5, $J_{\text{bx}} = 2.7$, $J_{\text{ab}} = 17.4$, 2H, $\text{H}_2\text{C}(2)$); 2.81 (sext, $J = 6.2$, 1 H, $\text{HC}(4)$); 2.06 (t, $J = 6.2$, 1 H, OH); 1.12 (d, $J = 7.3$, 3 H, $\text{H}_3\text{C}(6)$)

(1*R*, 5*S*)-1,5-Dihydroxy-1-phenyl-hexan-3-one (38)

In a 25-mL round-bottom flask were placed *anti*-**35a** (242 mg, 0.75 mmol), pyridinium *p*-toluenesulfonate (188 mg, 0.75 mmol, 1.0 equiv) in ethanol (7.5 mL). The reaction mixture was heated to 55 °C (bath temperature) and stirred for 24 h. The reaction mixture was cooled to rt, and the volatiles were removed under reduced pressure. The residue was triturated with ether (30 mL), and the solution was transferred into a 60-mL separatory funnel. The solution was washed sequentially with brine (10 mL) and with water (10 mL), dried over Na_2SO_4 and concentrated under reduced pressure. The crude white solid was chromatographed (silica gel, pentane/ether, 2/1, 20 mm) to afford 94 mg (0.45 mmol, 60%) of **38** as white needles. The crystal suitable for X-ray was obtained by recrystallization from acetone/hexane (1/1) by slow evaporation at rt.

Data for **38**:

mp: 58-59 °C (acetone/hexane)

^1H NMR: (500 MHz, CDCl_3)

7.38 – 7.27 (m, 5 H, 2 x $\text{HC}(8)$, 2 x $\text{HC}(9)$, $\text{HC}(10)$); 5.18 (dt, $J = 9.5$, 3, 1 H, $\text{HC}(6)$); 4.26 (m, 1 H, $\text{HC}(2)$); 3.15 (d, $J = 3.2$, 1 H, HO); 2.85 (ABX, $J_{\text{AB}} = 17.1$, 2 H, 2 x $\text{HC}(5)$); 2.93 (d, $J = 3.3$, 1 H, HO); 2.60 (d, $J = 5.8$, 2 H, 2 x $\text{HC}(3)$); 1.20 (d, $J = 6.3$, 3 H, 3 x $\text{HC}(1)$)

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

211.7 (C(4)); 142.7 (C(7)); 128.6 (2 x C(9)); 127.8 (C(10)); 125.6 (2 x C(8)); 70.0 (C(6)); 63.9 (C(2)); 52.0 (C(3)); 51.6 (C(5)); 22.5 (C(1))

IR: (neat)
 3393 (br, s); 3063 (w); 3031 (w); 2971 (s); 2928 (m); 1707 (s); 1655 (m); 1606 (m); 1577 (w); 1495 (m); 1452 (m); 1376 (m); 1204 (m); 1115 (m); 1049 (m)

MS: (FI)
 208 (100, M⁺); 190 (4)

Opt. Rot.: $[\alpha]_D^{24}$ -11.8 (EtOH, c=0.06)

TLC: R_f 0.06 (silica gel, pentane/ether, 2/1)

Analysis: C₁₂H₁₆O₃Si (208.25)
 Calcd: C, 69.21%; H, 7.74%
 Found: C, 69.13%; H, 7.77%

General Procedure VI: Aldol Addition of 23: (+)-(2*S*,4*R*,5*S*)-5-Hydroxy-4-methyl-5-phenyl-2-(((dimethyl)-(1,1-dimethylethyl)silyl)oxy)-3-pentanone (41a)⁹

Silyl enol ether (Z)-14 (273 mg, 1.0 mmol) was added quickly to a stirred suspension of silicon tetrachloride (230 μL , 2.0 mmol, 2.0 equiv) and mercuric acetate (3.2 mg, 0.01 mmol, 0.01 equiv) in CH₂Cl₂ (1.0 mL) at room temperature. After addition, the mixture was stirred at room temperature for 18 h, then the volatile components were removed under reduced pressure (0.1 mmHg) to give a cloudy oil. A solution of (R,R)-1 (18 mg, 0.05 mmol, 0.05 equiv) in CH₂Cl₂ (2.0 mL) was then added via cannula and the mixture was cooled to -78 °C. Benzaldehyde (102 μL , 1.0 mmol) was then added dropwise via syringe and the reaction mixture was allowed to stir at -78 °C for 10 h. The reaction mixture was then poured into a rapidly stirring sat. aq. NaHCO₃ solution (30 mL) submerged in an ice bath and was allowed to stir at room temperature for 6 h. The heterogeneous mixture was then filtered through Celite, the organic phase was separated and the aqueous phase was extracted with CH₂Cl₂ (3 $\times$ 15 mL). The organic extracts were combined, dried over Na₂SO₄, filtered and concentrated to give a crude oil.

Purification by column chromatography (silica gel, pentane/Et₂O, 6/1) afforded 284 mg (88%) of **41a**¹⁰ as a clear, colorless oil. The diastereomeric ratio was determined to be (*syn,syn*)-**41a**/minor isomers, 95/5 by SFC analysis.

Data for **41a**:

¹H NMR: (CDCl₃, 500 MHz)

7.38-7.20 (m, 5 H, 2 × H(C2''), 2 × HC(3''), HC(4'')); 5.06 (dd, *J* = 5.0, 2.8, 1 H, HC(5), *syn,syn*); 5.01 (dd, *J* = 5.0, 2.8, 1 H, HC(5), *anti,syn*); 4.77 (dd, *J* = 8.5, 4.2, 1 H, HC(5), *anti-relative*); 4.73 (dd, *J* = 8.5, 4.2, 1 H, HC(5), *anti-relative*); 4.19 (q, *J* = 6.9, 1 H, HC(2)); 3.37 (dq, *J* = 7.2, 5.0, 1 H, HC(4)); 3.25, (d, *J* = 2.8, 1 H, OH); 1.27 (d, *J* = 6.9, 3 H, H₃C(1)); 1.05 (d, *J* = 7.2, 3 H, H₃C(1')); 0.90 (s, 9 H, H₃C(3''')); 0.08 (s, 3 H, H₃C(1''')); 0.06 (s, 3 H, H₃C(1'''))

¹³C NMR: (CDCl₃, 125 MHz)

218.7 (C(3)); 141.7 (C(1'')); 128.2 (C(3'')); 127.2 (C(4'')); 126.0 (C(2'')); 74.6 (C(2)); 72.8 (C(5)); 46.9 (C(4)); 25.7 (C(3''')); 21.1 (C(1)); 18.0 (C(8)); 10.4 (C(1')); -4.7 (C(1''')); -5.0 (C(1'''))

TLC: *R*_f 0.15 (pentane/Et₂O, 6/1, anisaldehyde)

SFC: *t*_R (2*S*,4*R*,5*S*)-**41a**, 5.1 min (Daicel Chiralpak AD, 5% MeOH in CO₂, 150 bar, 40 °C, 3.0 mL min⁻¹)

(+)-(2*S*,4*R*,5*R*)-5-Hydroxy-4-methyl-5-(1-naphthyl)-2-(((dimethyl)-(1,1-dimethylethyl)silyl)oxy]-3-pentanone (41b**)**

Following General Procedure VI: from silyl enol ether (*Z*)-**14** (273 mg, 1.0 mmol), silicon tetrachloride (230 μL, 2.0 mmol, 2.0 equiv) and mercuric acetate (3.2 mg, 0.01 mmol,

0.01 equiv) in CH₂Cl₂ (1.0 mL) followed by (*R,R*)-**1** (18 mg, 0.05 mmol, 0.05 equiv) in CH₂Cl₂ (2.0 mL) and 1-naphthaldehyde (135 μL, 1.0 mmol) was obtained after chromatography (silica gel, pentane/Et₂O, 6/1), 270 mg (72%) of **41b** as a clear, colorless oil. The diastereomeric ratio was determined to be (*syn,syn*)-**41b**/ minor isomers, 98/1/1 by SFC analysis.

Data for 41b:

¹H NMR: (CDCl₃, 500 MHz)

7.90-7.44 (m, 7 H, HC(2''), HC(3''), HC(4''), HC(6''), HC(7''), HC(8''), HC(9'')); 5.88 (br s, 1 H, HC(5)); 4.27 (q, *J* = 6.9, 1 H, HC(2)); 3.70 (d, *J* = 1.9, 1 H, OH); 3.59, (dq, *J* = 7.3, 2.8, 1 H, HC(4)); 1.35 (d, *J* = 6.9, 3 H, H₃C(1)); 1.05 (d, *J* = 7.3, 3 H, H₃C(1')); 0.86 (s, 9 H, H₃C(3''')); 0.10 (d, *J* = 1.9, 6 H, H₃C(1'''))

¹³C NMR: (CDCl₃, 125 MHz)

219.5 (C(3)); 136.5 (C(1'')); 133.7 (C(5'')); 129.7 (C(10'')); 129.1 (CAr); 127.7 (CAr); 126.0 (CAr); 125.4 (CAr); 125.3 (CAr); 124.4 (CAr); 122.6 (CAr); 74.8 (C(2)); 69.4 (C(5)); 45.2 (C(4)); 25.7 (C(3''')); 21.4 (C(1)); 18.1 (C(2''')); 10.2 (C(1')); -4.8 (C(1''')); -5.0 (C(1'''))

MS: (FI)

372 (M⁺, 100), 315 (6), 267 (12), 216 (5), 156 (16)

IR: (neat)

3502 (br), 2931 (m), 2958 (m), 1699 (m), 1255 (m), 1128 (m), 837 (s), 777 (s)

TLC: *R_f* 0.19 (pentane/Et₂O, 6/1, anisaldehyde)

Opt. Rot.: [α]_D²³ +53.1° (*c* = 1.00, CHCl₃)

SFC: *t_R* (2*S*,4*R*,5*R*)-**41b**, 2.8 min (Daicel Chiralpak AS, 4% MeOH in CO₂, 150 bar, 40 °C, 3.0 mL min⁻¹)

Analysis: C₂₂H₃₂O₃Si (372.58)

Calculated: C, 70.92; H, 8.66%

Found: C, 70.78; H, 8.42%

(–)-(2*S*,4*R*,5*S*)-(*E*)-5-Hydroxy-4-methyl-7-phenyl-2-[(*tert*-butyldimethylsilyloxy)]-6-hepten-3-one (**41c**)

Following General Procedure VI: from silyl enol ether (*Z*)-**14** (273 mg, 1.0 mmol), silicon tetrachloride (230 μ L, 2.0 mmol, 2.0 equiv) and mercuric acetate (3.2 mg, 0.01 mmol, 0.01 equiv) in CH_2Cl_2 (1.0 mL) followed by (*R,R*)-**1** (18 mg, 0.05 mmol, 0.05 equiv) in CH_2Cl_2 (2.0 mL) and (*E*)-cinnamaldehyde (130 μ L, 1.0 mmol) was obtained after chromatography (silica gel, pentane/ Et_2O , 6/1), 283 mg (81%) of **41c** as a clear, colorless oil. The diastereomeric ratio was determined to be (*syn,syn*)-**41c**/minor isomers, 93/5/2 by SFC analysis.

Data for 41c:

$^1\text{H NMR}$: (CDCl_3 , 500 MHz)

7.40–7.22 (m, 5 H, $2 \times \text{H}(\text{C}2'')$, $2 \times \text{HC}(3'')$, $\text{HC}(4'')$); 6.66 (dd, $J = 15.9$, 1.5, 1 H, $\text{HC}(7)$); 6.14 (dd, $J = 16.1$, 5.9, 1 H, $\text{HC}(6)$); 4.61 (m, 1 H, $\text{HC}(5)$); 4.25 (q, $J = 6.9$, 1 H, $\text{HC}(2)$); 3.31 (dq, $J = 7.1$, 3.4, 1 H, $\text{HC}(4)$); 3.02 (d, $J = 2.8$, 1 H, OH); 1.35 (d, $J = 6.9$, 3 H, $\text{H}_3\text{C}(1)$); 1.19 (d, $J = 7.1$, 3 H, $\text{H}_3\text{C}(1')$); 0.93 (s, 9 H, $\text{H}_3\text{C}(3''')$); 0.10 (d, $J = 1.5$, 6 H, $\text{H}_3\text{C}(1''')$)

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

218.2 ($\text{C}(3)$); 136.7 ($\text{C}(1'')$); 131.0 ($\text{C}(3'')$); 129.0 ($\text{C}(4'')$); 128.6 ($\text{C}(6)$); 127.6 ($\text{C}(7)$); 126.5 ($\text{C}(4'')$); 74.6 ($\text{C}(2)$); 71.9 ($\text{C}(5)$); 45.1 ($\text{C}(4)$); 25.7 ($\text{C}(3''')$); 21.2 ($\text{C}(1)$); 18.0 ($\text{C}(8)$); 10.8 ($\text{C}(1')$); -4.6 ($\text{C}(1''')$); -5.0 ($\text{C}(1''')$)

MS: (FI)

348 (M^+ , 100), 291 (12), 244 (5), 216 (6), 159 (13), 132 (19)

IR: (neat)

3467 (br), 2931 (s), 2858 (m), 1712 (m), 1462 (m), 1365 (m), 1255 (m), 1124 (m), 835 (s), 779 (s)

TLC: R_f 0.13 (pentane/ Et_2O , 6/1, anisaldehyde)

Opt. Rot.: $[\alpha]_D^{23} -17.8^\circ$ ($c = 1.00$, CHCl_3)

SFC: t_R (2*S*,4*R*,5*S*)-**41c**, 5.7 min (Daicel Chiralpak AD, 1% MeOH in CO_2 , 150 bar, 40 $^\circ\text{C}$, 3.0 mL min $^{-1}$)

Analysis: $\text{C}_{20}\text{H}_{32}\text{O}_3\text{Si}$ (348.56)

Calculated: C, 68.92; H, 9.25%

Found: C, 68.75; H, 9.20%

(-)-(2*S*,4*R*,5*S*)-(*E*)-5-Hydroxy-4-methyl-2-(((dimethyl)-(1,1-dimethylethyl)silyl)oxy)-6-octen-3-one (*syn, syn*-**41e**)

Following General Procedure VI: from silyl enol ether (*Z*)-**14** (273 mg, 1.0 mmol), silicon tetrachloride (230 μL , 2.0 mmol, 2.0 equiv) and mercuric acetate (3.2 mg, 0.01 mmol, 0.01 equiv) in CH_2Cl_2 (1.0 mL) followed by (*R,R*)-**4** (18 mg, 0.05 mmol, 0.05 equiv) in CH_2Cl_2 (2.0 mL) and (*E*)-crotonaldehyde (83 μL , 1.0 mmol) was obtained after chromatography (silica gel, pentane/ Et_2O , 6/1), 244 mg (85%) of **47** as a clear, colorless oil. The diastereomeric ratio was determined to be (*syn, syn*)-**47**/minor isomers, 93/4/3 by SFC analysis.

Data for 47:

$^1\text{H NMR}$: (CDCl_3 , 500 MHz)

5.71 (dq, $J = 15.2, 6.4$, 1 H, HC(7)); 5.44 (ddd, $J = 15.4, 6.4, 1.7$, 1 H, HC(6)); 4.33 (br s, 1 H, HC(5)); 4.22 (q, $J = 7.1$, 1 H, HC(2)); 3.19 (dq, $J = 7.1, 3.9$, 1 H, HC(4)); 2.73, (d, $J = 2.8$, 1 H, OH); 1.71 (d, $J = 6.4$, 3 H, $\text{H}_3\text{C}(8)$); 1.33 (d, $J = 6.9$, 3 H, $\text{H}_3\text{C}(1)$); 1.14 (d, $J = 7.1$, 3 H, $\text{H}_3\text{C}(1')$); 0.92 (s, 9 H, $\text{H}_3\text{C}(3''')$); 0.09 (s, 6 H, $\text{H}_3\text{C}(1''')$)

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

218.0 (C(3)); 130.6 (C(6)); 127.8 (C(7)); 74.6 (C(2)); 72.2 (C(5)); 45.1 (C(4)); 25.7 (C(3''')); 21.3 (C(1)); 18.1 (C(8)); 17.8 (C(2''')); 11.1 (C(1')); -4.7 (C(1''')); -

5.0 (C(1'''))

MS: (FI)286 (M⁺, 11), 229 (100), 159 (4), 110 (2)IR: (neat)

3460 (br), 2956 (m), 2933 (m), 2858 (m), 1712 (m), 1461 (m), 1255 (m), 1120 (m), 966 (m), 935 (m), 835 (s), 777 (m)

TLC: *R_f* 0.13 (pentane/Et₂O, 6/1, anisaldehyde)Opt. Rot.: [α]_D²³ -3.7° (*c* = 2.00, CHCl₃)SFC: *t_R* (2*S*,4*R*,5*S*)-**47**, 2.0 min (Daicel Chiralpak AD, 5% MeOH in CO₂, 150 bar, 40 °C, 2.0 mL min⁻¹)Analysis: C₁₅H₃₀O₃Si (286.49)

Calculated: C, 62.89; H, 10.56%

Found: C, 62.64; H, 10.71%

(-)-(2*S*,4*R*,5*R*)-5-Hydroxy-4-methyl-7-phenyl-2-(((dimethyl)-(1,1-dimethylethyl)silyl)oxy]-6-heptyn-3-one (41h**)**

Following General Procedure VI: from silyl enol ether (*Z*)-**14** (273 mg, 1.0 mmol), silicon tetrachloride (230 μ L, 2.0 mmol, 2.0 equiv) and mercuric acetate (3.2 mg, 0.01 mmol, 0.01 equiv) in CH₂Cl₂ (1.0 mL) followed by (*R,R*)-**1** (18 mg, 0.05 mmol, 0.05 equiv) in CH₂Cl₂ (2.0 mL) and 3-phenyl propynal (122 μ L, 1.0 mmol) was obtained after chromatography (silica gel, pentane/Et₂O, 4/1), 274 mg (79%) of **41h** as a clear, colorless oil. The diastereomeric ratio was determined to be (*syn,syn*)-**41h**/minor isomers, 95/3/2 by SFC analysis.

Data for **41h**:¹H NMR: (CDCl₃, 500 MHz)7.46-7.26 (m, 5 H, 2 $\times$ H(C2''), 2 $\times$ HC(3''), HC(4'')); 4.92 (t, *J* = 4.5, 1 H, HC(5));

4.31 (q, $J = 6.9$, 1 H, HC(2)); 3.41 (dq, $J = 6.9, 4.1$, 1 H, HC(4)); 3.01, (d, $J = 4.7$, 1 H, OH); 1.41 (d, $J = 6.6$, 3 H, H₃C(1)); 1.41 (d, $J = 6.9$, 3 H, H₃C(1'')); 0.96 (s, 9 H, H₃C(3''')); 0.14 (s, 3 H, H₃C(1''')); 0.13 (s, 3 H, H₃C(1'''))

¹³C NMR: (CDCl₃, 125 MHz)

216.4 (C(3)); 131.8 (CAr); 128.5 (CAr); 128. (CAr); 122.5 (C(1'')); 87.8 (C(6)); 85.3 (C(7)); 74.5 (C(2)); 63.5 (C(5)); 46.8 (C(4)); 25.7 (C(3''')); 21.2 (C(1)); 18.0 (C(8)); 18.0 (C(2''')); 11.6 (C(1')); -4.6 (C(1''')); -5.1 (C(1'''))

MS: (FI)

346 (M⁺, 1), 289 (100), 216 (1), 187 (2), 159 (7), 145 (5), 130 (2)

IR: (neat)

3440 (br), 2954 (s), 2931 (s), 2858 (m), 1714 (m), 1462 (m), 1365 (m), 1255 (m), 1126 (m), 935 (m), 835 (s), 779 (s), 758 (s), 692 (m)

TLC: R_f 0.24 (pentane/Et₂O, 4/1, anisaldehyde)

Opt. Rot.: $[\alpha]_D^{23} -1.2^\circ$ ($c = 2.00$, CHCl₃)

SFC: t_R (2*S*,4*R*,5*S*)-**41h**, 5.7 min (Daicel Chiralpak AD, 2% MeOH in CO₂, 150 bar, 40 °C, 3.0 mL min⁻¹)

Analysis: C₂₀H₃₀O₃Si (346.54)

Calculated: C, 69.32; H, 8.73%

Found: C, 69.17; H, 8.96%

(-)-(2*S*,4*R*,5*R*)-5-Hydroxy-4-methyl-5-(2-naphthyl)-2-(((dimethyl)-(1,1-dimethylethyl)silyl)oxy)-3-pentanone (41l**)**

Following General Procedure VI: from silyl enol ether (**Z**)-**14** (273 mg, 1.0 mmol), silicon tetrachloride (230 μL , 2.0 mmol, 2.0 equiv) and mercuric acetate (3.2 mg, 0.01 mmol, 0.01 equiv) in CH₂Cl₂ (1.0 mL) followed by (*R,R*)-**1** (18 mg, 0.05 mmol, 0.05 equiv) in CH₂Cl₂

(2.0 mL) and 2-naphthaldehyde (156 mg, 1.0 mmol) was obtained after chromatography (silica gel, pentane/Et₂O, 4/1), 265 mg (71%) of **411** as a clear, colorless oil. The diastereomeric ratio was determined to be (*syn,syn*)-**411**/ minor isomers, 94/3/3 by SFC analysis.

Data for **411**:

¹H NMR: (CDCl₃, 500 MHz)

7.86-7.36 (m, 7 H, HC(1''), HC(3''), HC(4''), HC(6''), HC(7''), HC(8''), HC(9'')); 5.23 (br s, 1 H, HC(5)); 4.21 (q, *J* = 6.9, 1 H, HC(2)); 3.51 (dq, *J* = 7.1, 3.2, 1 H, HC(4)); 3.46 (d, *J* = 1.9, 1 H, OH); 1.32 (d, *J* = 6.9, 3 H, H₃C(1)); 1.09 (d, *J* = 7.1, 3 H, H₃C(1')); 0.93 (s, 9 H, H₃C(3''')); 0.11 (s, 3 H, H₃C(1''')); 0.09 (s, 3 H, H₃C(1'''))

¹³C NMR: (CDCl₃, 125 MHz)

219.1 (C(3)); 139.0 (C(2'')); 133.2 (C(10'')); 132.7 (C(5'')); 128.1 (CAr); 127.9 (CAr); 127.6 (CAr); 126.1 (CAr); 125.8 (CAr); 124.9 (CAr); 123.9 (CAr); 74.6 (C(2)); 72.77 (C(5)); 46.58 (C(4)); 25.68 (C(3''')); 21.15 (C(1)); 18.01 (C(2''')); 10.21 (C(1'')); -4.70 (C(1''')); -5.01 (C(1'''))

MS: (FI)

372 (M⁺, 100), 315 (8), 267 (15), 216 (4), 156 (10)

IR: (neat)

3487 (br), 2954 (m), 2931 (m), 2858 (m), 1711 (m), 1462 (m), 1363 (m), 1255 (m), 1124 (m), 935 (m), 835 (s), 779 (m), 735 (m)

TLC: *R_f* 0.26 (pentane/Et₂O, 4/1, anisaldehyde)

Opt. Rot.: [α]_D²³ -1.7° (*c* = 2.00, CHCl₃)

SFC: *t_R* (2*S*,4*R*,5*R*)-**411**, 2.5 min (Daicel Chiralpak AS, 4% MeOH in CO₂, 150 bar, 40 °C, 3.0 mL min⁻¹)

Analysis: C₂₂H₃₂O₃Si (372.58)

Calculated: C, 70.92; H, 8.66%

Found: C, 70.62; H, 8.78%

(–)-(2*S*,4*R*,5*R*)-5-Hydroxy-4-methyl-5-(1-furyl)-2-(((dimethyl)-(1,1-dimethylethyl)silyl)oxy)-3-pentanone (41n)

Following General Procedure II: from silyl enol ether (*Z*)-**14** (273 mg, 1.0 mmol), silicon tetrachloride (230 μ L, 2.0 mmol, 2.0 equiv) and mercuric acetate (3.2 mg, 0.01 mmol, 0.01 equiv) in CH₂Cl₂ (1.0 mL) followed by (*R,R*)-**1** (18 mg, 0.05 mmol, 0.05 equiv) in CH₂Cl₂ (2.0 mL) and 2-furaldehyde (83 μ L, 1.0 mmol) was obtained after chromatography (silica gel, pentane/Et₂O, 6/1), 257 mg (82%) of **41n** as a clear, colorless oil. The diastereomeric ratio was determined to be (*syn,syn*)-**41n**/minor isomers, 94/6 by SFC analysis.

Data for 41n:

¹H NMR: (CDCl₃, 500 MHz)

7.34 (d, *J* = 1.7, 1 H, HC(4'')); 6.33 (dd, *J* = 3.2, 1.7, 1 H, HC(3'')); 6.27 (d, *J* = 3.2, 1 H, HC(2'')); 5.03 (t, *J* = 4.1, 1 H, HC(5)); 4.20 (q, *J* = 7.1, 1 H, HC(2)); 3.58 (dq, *J* = 7.1, 4.1, 1 H, HC(4)); 2.95, (d, *J* = 3.6, 1 H, OH); 1.31 (d, *J* = 6.6, 3 H, H₃C(1)); 1.18 (d, *J* = 7.2, 3 H, H₃C(1')); 0.95 (s, 9 H, H₃C(3''')); 0.12 (s, 3 H, H₃C(1''')); 0.11 (s, 3 H, H₃C(1'''))

¹³C NMR: (CDCl₃, 125 MHz)

217.6 (C(3)); 154.4 (C(1'')); 141.7 (C(4'')); 110.3 (C(3'')); 106.6 (C(2'')); 74.4 (C(2)); 68.3 (C(5)); 44.7 (C(4)); 25.7 (C(3''')); 21.0 (C(1)); 18.0 (C(2'')); 11.3 (C(1')); -4.7 (C(1''')); -5.1 (C(1'''))

MS: (FI)

312 (M⁺, 44), 255 (100), 209 (8), 159 (16), 96 (6)

IR: (neat)

3467 (br), 2956 (m), 2933 (m), 2858 (m), 1714 (m), 1255 (m), 1126 (m), 1006 (m), 931 (m), 835 (s), 779 (m)

TLC: *R_f* 0.13 (pentane/Et₂O, 6/1, anisaldehyde)

Opt. Rot.: $[\alpha]_D^{23} -1.2^\circ$ ($c = 2.00$, CHCl_3)

SFC: t_R (2*S*,4*R*,5*R*)-**41n**, 4.0 min (Daicel Chiralpak AD, 1.5% MeOH in CO_2 , 150 bar, 40 °C, 2.5 mL min⁻¹)

Analysis: $\text{C}_{16}\text{H}_{28}\text{O}_3\text{Si}$ (312.48)

Calculated: C, 61.50; H, 9.03%

Found: C, 61.30; H, 9.04%

General Procedure VII: Aldol Addition of (Z)-24 and 25: (1*R*, 2*R*, 4*S*)-5-tert-Butyldimethylsilyloxy-2,4-dimethyl-1-hydroxy-1-phenyl-3-pentanone (*syn, syn*-45a)

In a 10-mL Schlenk flask was placed a solution of (*R,R*)-**1** (37 mg, 0.10 mmol, 0.10 equiv) in CH_2Cl_2 (1 mL). To the solution was added (Z)-**24** (364 mg, 1.00 mmol) and the solution was cooled to -70°C using an acetone/ CO_2 bath. To the solution was added dropwise PhCHO (102 μL , 1.00 mmol, 1 equiv) and the reaction mixture was stirred for 6 h at -70°C . The reaction mixture was quenched by pouring into a vigorously stirring cold saturated NaHCO_3 aq (5 mL). The resulting slurry was stirred for 1 h and filtered through Celite. The layers were separated, and the aqueous layer was extracted with CH_2Cl_2 (2 x 10 mL). The combined organic extrates were washed with brine (5 mL), dried over sodium sulfate and concentrated under reduced pressure. The crude product was purified by column chromatography (silica gel, pentane/ether, 3/1, 30 mm) to afford 241 mg (0.72 mmol, 72%) of **45a** as a clear viscous oil.

Data for (*syn, syn*)-45a:

^1H NMR: (500 MHz, CDCl_3)

7.34-7.32 (m, 4 H, HC(7), HC(8)); 7.25 (m, 1 H, HC(9)); 5.22 (t, $J = 2.4$, 1 H, HC(1)); 3.75-3.60 (ABX, 2 H, $\text{H}_2\text{C}(5)$); 3.45 (d, $J = 2.4$, 1 H, HO); 3.02 (sext, $J = 5.4$, 1 H, HC(4)); 2.97 (qd, $J = 7.1, 2.7$, 1 H, HC(2)); 1.02 (d, $J = 6.8$, 3 H, $\text{H}_3\text{C}(11)$); 1.01 (d, $J = 7.3$, 3 H, $\text{H}_3\text{C}(10)$); 0.89 (s, 9H, $\text{H}_3\text{C}(14)$); 0.06 (d, $J = 3.2$,

6 H, H₃C(12))¹³C NMR: (126 MHz, CDCl₃)

219.2 (C(3)); 141.7 (C(6)); 128.1 (C(8)); 127.1 (C(9)); 125.8 (C(7)); 71.9 (C(5)); 66.3 (C(1)); 52.8 (C(2)); 47.3 (C(4)); 25.9 (C(14)); 18.3 (C(13)); 13.2 (C(11)); 8.8 (C(10)); -5.6 (C(12))

IR: (neat)

3469 (br, w); 2954 (m); 2931 (m); 2858 (m); 1702 (m); 1462 (m); 1389 (w); 1255 (m); 1097 (m)

MS: (FI)336 (M⁺, 40); 279 (100); 265 (24); 230 (12); 173 (6); 159 (3); 106 (8)Opt. Rot.: [α]_D²⁴ -9.16 (EtOH, c=2.0)TLC: *R_f* 0.33 (pentane/ether, 3/1) [silica gel, p-anisaldehyde]SFC: *t_R* = 1.834 min (AD, 150 bar, 3 mL/min, 5% MeOH)Analysis: C₁₉H₃₂O₃Si (336.54)

Calcd: C, 67.81%; H, 9.58%

Found: C, 67.74%; H, 9.69%

(1*S*, 2*S*, 4*S*)-5-*tert*-Butyldimethylsilyloxy-2,4-dimethyl-1-hydroxy-1-phenyl-3-pentanone
(*syn,anti*-45a)

Following General Procedure VII using (*Z*)-**24** (364 mg, 1.00 mmol), PhCHO (102 μ L, 1.00 mmol) and (*S,S*)- **1** (37 mg, 0.10 mmol) in 1 mL of CH₂Cl₂, 241 mg (0.72 mmol, 72%) of **45a** was obtained as a clear viscous oil after column chromatography (silica gel, pentane/ether, 3/1).

Data for (syn,anti)-45a:¹H NMR: (500 MHz, CDCl₃)

7.34 (d, $J = 4.2$, 4 H, HC(7), HC(8)); 7.25 (m, 1H, HC(9)); 5.05 (t, $J = 3.2$, 1 H, HC(1)); 3.81-3.53 (ABX, 2 H, H₂C(5)); 3.23 (d, $J = 2.2$, 1 H, HO); 2.95 (qd, $J = 6.9$, 2.9, 1H, HC(2)); 2.89 (sext, $J = 5.4$, 1 H, HC(4)); 1.04 (d, $J = 7.1$, 3 H, H₃C(11)); 0.89 (d, $J = 6.6$, 3 H, H₃C(10)); 0.87 (s, 9H, H₃C(14)); 0.03 (d, $J = 6.4$, 6 H, H₃C(12))

¹³C NMR: (126 MHz, CDCl₃)

218.1 (C(3)); 142.1 (C(6)); 128.2 (C(8)); 127.3 (C(9)); 126.1 (C(7)); 73.5 (C(5)); 65.3 (C(1)); 52.8 (C(2)); 48.0 (C(4)); 25.8 (C(14)); 18.2 (C(13)); 12.9 (C(11)); 9.9 (C(10)); -5.6 (C(12))

IR: (neat)

3442 (br, m); 3064 (w); 3032 (w); 2956 (s); 2932 (s); 2859 (s); 1706 (s); 1462 (m); 1388 (m); 1361 (m); 1257 (s); 1099 (s); 1001 (s)

MS: (FI)

336 (M⁺, 58); 279 (100); 230 (13); 173 (5); 106 (6)

Opt. Rot.: $[\alpha]_{\text{D}}^{24} + 49.34$ (EtOH, c=3.8)TLC: R_f 0.33 (pentane/ether, 3/1) [silica gel, *p*-anisaldehyde]SFC: $t_R = 2.278$ min (AD, 150 bar, 3 mL/min, 5% MeOH)Analysis: C₁₉H₃₂O₃Si (336.54)

Calcd: C, 67.81%; H, 9.58%

Found: C, 67.74%; H, 9.73%

(1*R*, 2*R*, 4*S*)-5-Triisopropylsilyloxy-2,4-dimethyl-1-hydroxy-1-phenyl-3-pentanone (*syn, syn*-46a)

Following General Procedure VII using (*Z*)-**25** (479 mg, 1.00 mmol), PhCHO (102 μL , 1.00 mmol) and (*R,R*)-**1** (37 mg, 0.10 mmol) in 1 mL of CH_2Cl_2 for 8 h, 319 mg (0.84 mmol, 84%) of **46a** was obtained as a clear viscous oil after column chromatography (silica gel, pentane/ether, 5/1).

Data for (*syn, syn*)-46a:

^1H NMR: (500 MHz, CDCl_3)

7.35-7.31 (m, 4 H, HC(7), HC(8)); 7.25 (m, 1 H, HC(9)); 5.23 (t, $J = 2.5$, 1 H, HC(1)); 3.85-3.67 (ABX, 2 H, $\text{H}_2\text{C}(5)$); 3.47 (d, $J = 2.2$, 1 H, HO); 3.01 (sext, $J = 5.4$, 1 H, HC(4)); 2.98 (qd, $J = 7.3, 2.7$, 1 H, HC(2)); 1.14 – 1.02 (m, 27 H, $\text{H}_3\text{C}(11)$, $\text{H}_3\text{C}(10)$, $\text{H}_3\text{C}(13)$, HC(12))

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

219.8 (C(3)); 141.9 (C(6)); 128.4 (C(8)); 127.3 (C(9)); 126.1 (C(7)); 72.1 (C(5)); 67.0 (C(1)); 53.1 (C(4)); 47.8 (C(2)); 18.2 (C(13)); 13.5 (C(11)); 12.0 (C(12)); 9.1 (C(10))

IR: (neat)

3467 (br, m); 2942 (s); 2891 (s); 2868 (s); 1703 (s); 1462 (s); 1385 (m); 1101 (s); 1070 (m); 997 (s)

MS: (FI)

379 (M^+ , 6); 337 (7); 336 (26); 335 (100)

Opt. Rot.: $[\alpha]_{\text{D}}^{24} -10.84^\circ$ (EtOH, $c=1.01$)

TLC: R_f 0.23 (pentane/ether, 5/1) [silica gel, *p*-anisaldehyde]

SFC: $t_R = 2.220$ min (AD, 150 bar, 3 mL/min, 5% MeOH)

Analysis: C₂₂H₃₈O₃Si (378.62)

Calcd: C, 69.79%; H, 10.12%

Found: C, 69.53%; H, 10.24%

(1*S*, 2*S*, 4*S*)-1-Triisopropylsilyloxy-2,4-dimethyl-5-hydroxy-5-phenyl-3-pentanone (*syn,anti*-46a**)**

Following General Procedure VII using (Z)-**25** (479 mg, 1.00 mmol), PhCHO (102 μ L, 1.00 mmol) and (S,S)-**1** (37 mg, 0.10 mmol) in 1 mL of CH₂Cl₂ for 8 h, 310 mg (0.82 mmol, 82%) of **46a** was obtained as a clear viscous oil after column chromatography (silica gel, pentane/ether, 5/1).

Data for (*syn,anti*)-**46a**:

mp: 22 °C (Hexane)

¹H NMR: (500 MHz, CDCl₃)

7.34-7.25 (m, 5 H, HC(7), HC(8), HC(9)); 5.06 (dd, *J* = 3.9, 2.4, 1 H, HC(1)); 3.91-3.61 (ABX, 2 H, H₂C(5)); 3.18 (d, *J* = 2.2, 1 H, HO); 2.99 (qd, *J* = 7.1, 4.1, 1 H, HC(2)); 2.89 (sext, *J* = 5.1, 1 H, HC(4)); 1.08 (d, *J* = 7.1, 3 H, H₃C(11)); 1.09 – 1.02 (m, 21 H, H₃C(13), HC(12)); 0.91 (d, *J* = 7.1, 3 H, H₃C(10))

¹³C NMR: (126 MHz, CDCl₃)

218.3 (C(3)); 141.9 (C(6)); 128.2 (C(8)); 127.3 (C(9)); 126.0 (C(7)); 73.4 (C(5)); 65.6 (C(1)); 52.9 (C(4)); 48.3 (C(2)); 17.9 (C(13)); 13.2 (C(11)); 11.9 (C(12)); 9.6 (C(10))

IR: (neat)

3367 (br, m); 2943 (s); 2866 (s); 1707 (s); 1462 (s); 1285 (m); 1265 (m); 1248 (w); 1132 (m); 1097 (s); 1065 (s); 1003 (s)

MS: (FI)379 (M^+ , 5); 337 (7); 336 (25); 335 (100); 272 (10); 229 (14); 157 (5); 157 (7); 157 (7); 127 (7); 157 (6); 156 (7); 106 (6)**Opt. Rot.:** $[\alpha]_D^{24} + 92.03$ (EtOH, $c=0.59$)**TLC:** R_f 0.18 (pentane/ether, 5/1) [silica gel, *p*-anisaldehyde]**SFC:** $t_R = 2.900$ min (AD, 150 bar, 3 mL/min, 5% MeOH)**Analysis:** $C_{22}H_{38}O_3Si$ (378.62)

Calcd: C, 69.79%; H, 10.12%

Found: C, 69.67%; H, 9.95%

(1*R*, 2*R*, 4*S*)-5-Triisopropylsilyloxy-2,4-dimethyl-1-hydroxy-1-(1-naphthyl)-3-pentanone
(*syn, syn*-46b)

Following General Procedure VII using (*Z*)-**25** (472 mg, 1.00 mmol), 1-naphthaldehyde (136 μL , 1.00 mmol), (*R,R*)-**1** (37 mg, 0.10 mmol) and TBAI (73.9 mg, 0.20 mmol) in 1 mL of CH_2Cl_2 for 8 h, 313 mg (0.71 mmol, 71%) of **46b** was obtained as a clear viscous oil after column chromatography (silica gel, pentane/ether, 5/1). Analytically pure material was obtained by recrystallization from pentane.

Data for (*syn, syn*)-46b:**mp:** 50-52 $^{\circ}\text{C}$ (pentane) **^1H NMR:** (500 MHz, CDCl_3)

7.89 – 7.88 (m, 2 H, HC(8), HC(11)); 7.77 (d, $J = 10$, 1 H, HC(13)); 7.76 (d, $J = 10$, 1 H, HC(15)); 7.51 (t, $J = 7.4$, 1 H, HC(9)); 7.55-7.42 (m, 2 H, HC(14), HC(10)); 6.03 (br s, 1 H, HC(1)); 3.95-3.72 (ABX, 2 H, $\text{H}_2\text{C}(5)$); 3.66 (d, $J = 2.4$, 1 H, HO); 3.21 (q, $J = 7.1, 2.5$, 1 H, HC(2)); 3.10 (sext, $J = 6.8, 1.7$, 1 H,

HC(4)); 1.13 – 1.00 (m, 27 H, H₃C(13), H₃C(16), HC(18), H₃C(19))

¹³C NMR: (126 MHz, CDCl₃)

219.5 (C(3)); 136.8 (C(6)); 134.0 (C(12)); 129.9 (C(7)); 129.5 (C(11)); 128.0 (C(13)); 126.2 (C(10)); 125.7 (C(9)); 125.6 (C(14)); 124.8 (C(15)); 122.6 (C(8)); 68.7 (C(1)); 66.7 (C(5)); 51.1 (C(4)); 48.2 (C(2)); 18.3 (C(19)); 14.1 (C(17)); 12.2 (C(18)); 9.6 (C(16))

IR: (CH₂Cl₂)

3469 (br, m); 3052 (w); 2943 (s); 2867 (s); 1704 (m); 1598 (w); 1511 (w); 1462 (m); 1383 (w); 1253 (w); 1101 (m); 1068 (m)

MS: (FI)

429 (14); 428 (M⁺, 37); 385 (12); 336 (25); 272 (14); 230 (17); 229 (100); 156 (69)

Opt. Rot.: $[\alpha]_D^{24} + 2.1$ (EtOH, c=0.48)

TLC: *R_f* 0.30 (pentane/ether, 4/1) [silica gel, short UV]

SFC: *t_R* = 5.555 min (OD, 150 bar, 3 mL/min, 15% MeOH)

Analysis: C₂₆H₄₀O₃Si (428.68)

Calcd: C, 72.85%; H, 9.41%

Found: C, 72.52%; H, 9.40%

(1*S*, 2*S*, 4*S*)-5-Triisopropylsilyloxy-2,4-dimethyl-1-hydroxy-1-(1-naphthyl)-3-pentanone
(*syn,anti*-46b)

Following General Procedure VII using (*Z*)-**25** (501 mg, 1.00 mmol, 19% bisenoxyasilane), 1-naphthaldehyde (136 μ L, 1.00 mmol), (*S,S*)-**1** (37 mg, 0.10 mmol) and TBAI (73.9 mg, 0.20 mmol) in 1 mL of CH₂Cl₂ for 8 h, 335 mg (0.78 mmol, 78%) of **46b** was obtained

as a clear viscous oil after column chromatography (silica gel, pentane/ether, 5/1).

Data for (syn,anti)-46b:

¹H NMR: (500 MHz, CDCl₃)

7.92 (d, *J* = 8.0, 1 H, HC(8)); 7.89 (d, *J* = 7.4, 1 H, HC(11)); 7.78 (d, *J* = 8.0, 1 H, HC(13)); 7.74 (d, *J* = 7.3, 1 H, HC(15)); 7.53 - 7.47 (m, 3 H, HC(10), HC(14), C(9)); 5.90 (br d, *J* = 2.2, 1 H, HC(1)); 3.99-3.66 (ABX, 2 H, H₂C(5)); 3.57 (d, *J* = 2.2, 1 H, HO); 3.20 (qd, *J* = 7.0, 1.7, 1 H, HC(2)); 3.00 (sext, *J* = 7.1, 1.7, 1 H, HC(4)); 1.12 - 0.98 (m, 27 H, H₃C(17), H₃C(19), HC(18), H₃C(16))

¹³C NMR: (126 MHz, CDCl₃)

219.0 (C(3)); 136.7 (C(6)); 133.7 (C(12)); 129.7 (C(7)); 129.1 (C(11)); 127.8 (C(13)); 126.1 (C(10)); 125.4 (C(9)); 125.3 (C(14)); 124.4 (C(15)); 122.4 (C(8)); 69.7 (C(1)); 65.7 (C(5)); 50.1 (C(4)); 48.1 (C(2)); 17.9 (C(19)); 15.3 (C(17)); 11.9 (C(18)); 9.3 (C(16))

IR: (neat)

3470 (br, m); 3052 (w); 2943 (s); 2892 (m); 1703 (m); 1598 (w); 1511 (w); 1462 (m); 1383 (m); 1253 (w); 1102 (s); 1068 (m)

MS: (EI)

430 (13); 429 (26); 428 (M⁺, 48); 385 (58); 347 (10); 273 (13); 272 (46); 230 (13); 229 (92); 156 (100)

Opt. Rot.: [α]_D²⁴ + 47.9 (EtOH, c=0.97)

TLC: *R_f* 0.26 (pentane/ether, 5/1) [silica gel, short UV]

SFC: *t_R* = 3.44 min (OD, 150 bar, 3 mL/min, 15% MeOH)

Analysis: C₂₆H₄₀O₃Si (428.68)

Calcd: C, 72.85%; H, 9.41%

Found: C, 72.47%; H, 9.29%

(2*S*, 4*R*, 5*R*)-1-Triisopropylsilyloxy-2,4-dimethyl-5-hydroxy-7-phenyl-6-hepten-3-one
(*syn, syn*-46c)

Following General Procedure VII using (*Z*)-**25** (872 mg, 2.00 mmol), cinnamaldehyde (252 μL , 2.00 mmol), (*R,R*)-**1** (74 mg, 0.20 mmol) and TBAI (148 mg, 0.40 mmol) in 2 mL of CH_2Cl_2 for 10 h, 713 mg (1.76 mmol, 88%) of **46c** was obtained as a clear viscous oil after column chromatography (silica gel, pentane/ether, 3/1).

Data for (*syn, syn*)-46c:

^1H NMR: (500 MHz, CDCl_3)

7.38 (d, $J = 7.1$, 2 H, HC(13)); 7.31 (t, $J = 7.5$, 2 H, HC(14)); 7.24 (t, $J = 7.4$, 1 H, HC(15)); 6.64 (dd, $J = 15.8$, 0.9, 1 H, HC(7)); 6.13 (dd, $J = 15.8$, 5.6, 1 H, HC(6)); 4.75 (m, 1 H, HC(5)); 3.88-3.70 (ABX, 2 H, $\text{H}_2\text{C}(1)$); 3.30 (d, $J = 2.9$, 1 H, HO); 3.09 (sext, $J = 5.4$, 1 H, HC(2)); 2.95 (qd, $J = 7.3$, 2.7, 1 H, HC(4)); 1.17 (d, $J = 7.4$, 3 H, $\text{H}_3\text{C}(11)$); 1.11 – 1.02 (m, 24 H, $\text{H}_3\text{C}(9)$, $\text{H}_3\text{C}(10)$, HC(8))

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

219.4 (C(3)); 137.1 (C(12)); 130.9 (C(6)); 129.2 (C(7)); 128.8 (C(14)); 127.8 (C(15)); 126.6 (C(13)); 71.5 (C(1)); 67.2 (C(5)); 51.5 (C(4)); 47.6 (C(2)); 18.2 (C(9)); 13.4 (C(10)); 12.0 (C(8)); 9.6 (C(11))

IR: (neat)

3436 (br, m); 3061 (w); 3027 (w); 2943 (s); 2892 (m); 2867 (m); 1703 (m); 1600 (w); 1495(w); 1462 (m); 1384 (w); 1368 (w); 1249 (w); 1102 (m); 1069 (m)

MS: (FI)

406 (9); 405 (34); 404 (M^+ , 100); 335 (9); 272 (8); 229 (24); 132 (48)

Opt. Rot.: $[\alpha]_{\text{D}}^{24} + 20.0$ (CH_2Cl_2 , $c = 0.73$)

$[\alpha]_{\text{D}}^{24} - 47.8$ (EtOH, $c = 0.73$)

TLC: R_f 0.12 (pentane/ether, 3/1) [silica gel, short UV]

SFC: t_R = 3.348 min (OD, 150 bar, 3 mL/min, 7% MeOH)

Analysis: $C_{24}H_{40}O_3Si$ (404.66)

Calcd: C, 71.23%; H, 9.96%

Found: C, 71.27%; H, 10.08%

(2*S*, 4*S*, 5*S*)-1-Triisopropylsilyloxy-2,4-dimethyl-5-hydroxy-7-phenyl-6-hepten-3-one
(*syn,anti*-46c)

Following General Procedure VII using (*Z*)-**25** (436 mg, 1.00 mmol), cinnamaldehyde (126 μL , 1.00 mmol), (*S,S*)-**1** (37 mg, 0.10 mmol) and TBAI (73.9 mg, 0.20 mmol) in 1 mL of CH_2Cl_2 for 10 h, 303 mg (0.75 mmol, 75%) of **46c** was obtained as a clear viscous oil after column chromatography (silica gel, pentane/ether, 3/1).

Data for (*syn,anti*)-46c:

^1H NMR: (500 MHz, CDCl_3)

7.38 (d, J = 7.6, 2 H, HC(13)); 7.31 (t, J = 7.6, 2 H, HC(14)); 7.24 (t, J = 7.8, 1 H, HC(15)); 6.65 (d, J = 16.1, 1 H, HC(7)); 6.13 (dd, J = 15.8, 5.8, 1 H, HC(6)); 4.64 (br m, 1 H, HC(5)); 3.94-3.65 (ABX, 2 H, $\text{H}_2\text{C}(1)$); 3.03 (sext, J = 5.4, 1 H, HC(2)); 2.99 (d, J = 2.9, 1 H, HO); 2.92 (qd, J = 7.3, 3.6, 1 H, HC(4)); 1.18 (d, J = 6.5, 3 H, $\text{H}_3\text{C}(11)$); 1.16 – 1.04 (m, 24 H, $\text{H}_3\text{C}(9)$, $\text{H}_3\text{C}(10)$, HC(8))

^{13}C NMR: (101 MHz, CDCl_3)

218.1 (C(3)); 137.1 (C(12)); 130.9 (C(6)); 129.1 (C(7)); 128.5 (C(14)); 127.6 (C(15)); 126.4 (C(13)); 72.3 (C(1)); 65.9 (C(5)); 50.5 (C(4)); 48.1 (C(2)); 17.9 (C(9)); 15.3 (C(10)); 11.8 (C(8)); 9.9 (C(11))

IR: (neat)

3430 (br, m); 3083 (w); 3061 (w); 3027 (w); 2943 (s); 2892 (s); 2726 (w); 1706

(s); 1627 (w); 1600 (w); 1578 (w); 1495(m); 1462 (s); 1383 (m); 1368 (m); 1250 (m); 1203 (w); 1104 (s); 1068 (s)

MS: (FI)

405 (12); 404 (M^+ , 34); 287 (11); 273 (15); 269 (15); 261 (69); 245 (30); 229 (100); 217 (83); 132 (17); 106 (28)

Opt. Rot.: $[\alpha]_D^{24} + 42.1$ (CH_2Cl_2 , $c = 1.35$)

$[\alpha]_D^{24} + 109.0$ (EtOH, $c = 1.25$)

TLC: R_f 0.23 (pentane/ether, 3/1) [silica gel, short UV]

SFC: $t_R = 6.630$ min (OD, 150 bar, 3 mL/min, 7% MeOH)

Analysis: $\text{C}_{24}\text{H}_{40}\text{O}_3\text{Si}$ (404.66)

Calcd: C, 71.23%; H, 9.96%

Found: C, 71.30%; H, 9.79%

(2*S*, 4*R*, 5*R*)-1-Triisopropylsilyloxy-2,4-dimethyl-5-hydroxy-6-octen-3-one (*syn, syn*-46e**)**

Following General Procedure VII using (*Z*)-**25** (472 mg, 1.00 mmol), crotonaldehyde (83 μL , 1.00 mmol), (*R,R*)-**1** (37 mg, 0.10 mmol) and TBAI (73.9 mg, 0.20 mmol) in 1 mL of CH_2Cl_2 for 6 h, 310 mg (0.90 mmol, 90%) of **46d** was obtained as a clear viscous oil after column chromatography (silica gel, pentane/ether, 3/1).

Data for (*syn, syn*)-46e**:**

^1H NMR: (500 MHz, CDCl_3)

5.70 (dq, $J = 16.4, 6.0$, 1 H, HC(7)); 5.45 (dd, $J = 6.4, 1.5$, 1 H, HC(6)); 4.47 (m, 1 H, HC(5)); 3.86-3.67 (ABX, 2 H, $\text{H}_2\text{C}(1)$); 3.04 (sext, $J = 5.4$, 1 H, HC(2)); 3.03 (d, $J = 3.2$, 1 H, HO); 2.83 (qd, $J = 7.3, 2.9$, 1 H, HC(4)); 1.70 (dd, $J = 5.7, 1.0$, 3 H, $\text{H}_3\text{C}(8)$); 1.12 (d, $J = 7.4$, 3 H, $\text{H}_3\text{C}(11)$); 1.10 – 1.07 (m, 24 H, $\text{H}_3\text{C}(10)$),

H₃C(12), HC(9))¹³C NMR: (126 MHz, CDCl₃)

219.0 (C(3)); 130.4 (C(7)); 127.3 (C(6); 71.6 (C(1)); 66.6 (C(5)); 51.2 (C(4)); 47.5 (C(2)); 17.8 (C(10)); 17.7 (C(8)); 13.1 (C(11)); 11.7 (C(9)); 9.6 (C(12))

IR: (neat)

3514 (br, w); 2945 (m); 2868 (m); 1699 (m); 1462 (m); 1383 (w); 1247 (w); 1098 (m); 1068 (m); 1008 (m)

MS: (EI)

343 (M⁺, 5); 301 (6); 300 (25); 299 (100); 272 (6); 176 (6); 176 (9); 175 (10); 175 (8); 175 (6)Opt. Rot.: [α]_D²⁴ + 5.06 (EtOH, c = 0.23)TLC: R_f 0.25 (pentane/ether, 3/1) [silica gel, *p*-anisaldehyde]Analysis: C₁₉H₃₈O₃Si (342.59)

Calcd: C, 66.61%; H, 11.18%

Found: C, 66.34%; H, 11.16%

(2*S*, 4*S*, 5*S*)-1-Triisopropylsilyloxy-2,4-dimethyl-5-hydroxy-6-octen-3-one (*syn,anti*-46e)

Following General Procedure VII using (Z)-**25** (472 mg, 1.00 mmol), crotonaldehyde (83 μ L, 1.00 mmol), (*S,S*)-**1** (37 mg, 0.10 mmol) and TBAI (73.9 mg, 0.20 mmol) in 1 mL of CH₂Cl₂ for 6 h, 293 mg (0.85 mmol, 85%) of **46e** was obtained as a clear viscous oil after column chromatography (silica gel, pentane/ether, 3/1).

Data for (*syn,anti*)-46e:¹H NMR: (500 MHz, CDCl₃)5.72 (dq, *J* = 15.2, 6.4, 1 H, HC(7)); 5.46 (dd, *J* = 15.1, 6.6, 1 H, HC(6)); 4.36 (m,

1 H, HC(5)); 3.91-3.63 (ABX, 2 H, H₂C(1)); 2.99 (sext, $J = 7.6$, 1 H, HC(2)); 2.81 (qd, $J = 7.0, 4.0$, 1 H, HC(4)); 2.66 (d, $J = 3.2$, 1 H, HO); 1.70 (dd, $J = 7.3, 0.7$, 3 H, H₃C(8)); 1.12 (d, $J = 7.1$, 3 H, H₃C(11)); 1.11 – 1.00 (m, 24 H, H₃C(10), H₃C(12), HC(9))

¹³C NMR: (126 MHz, CDCl₃)
217.8 (C(3)); 130.9 (C(7)); 127.6 (C(6)); 72.7 (C(1)); 65.8 (C(5)); 50.8 (C(4)); 48.2 (C(2)); 17.8 (C(10)); 17.6 (C(8)); 13.1 (C(11)); 11.8 (C(9)); 9.6 (C(12))

IR: (neat)
3468 (br, w); 2944 (m); 2868 (m); 1703 (m); 1462 (m); 1383 (w); 1250 (w); 1104 (m); 1068 (m)

MS: (FI)
342 (M⁺, 1); 301 (6); 300 (23); 299 (100); 229 (15); 175 (7)

Opt. Rot.: $[\alpha]_D^{24} + 81.7$ (EtOH, $c = 0.35$)

TLC: R_f 0.25 (pentane/ether, 3/1) [silica gel, *p*-anisaldehyde]

Analysis: C₁₉H₃₈O₃Si (342.59)

Calcd: C, 66.61%; H, 11.18%

Found: C, 66.21%; H, 11.13%

(2*S*, 4*R*, 5*R*)-1-Triisopropylsilyloxy-2,4,6-trimethyl-5-hydroxy-6-octen-3-one (*syn, syn*-46g**)**

Following General Procedure VII using (*Z*)-**25** (472 mg, 1.00 mmol), tiglic aldehyde (96 μL , 1.00 mmol), (*R,R*)-**1** (37 mg, 0.10 mmol) and TBAI (73.9 mg, 0.20 mmol) in 1 mL of CH_2Cl_2 for 7 h, 303 mg (0.85 mmol, 85%) of **46g** was obtained as a clear viscous oil after column chromatography (silica gel, pentane/ether, 5/1).

Data for (*syn, syn*)-**46g**:¹H NMR: (500 MHz, CDCl₃)

5.60 (qt, *J* = 6.8, 1.5, 1 H, HC(7)); 4.42 (m, 1 H, HC(5)); 3.87-3.67 (ABX, 2 H, H₂C(1)); 3.11 (d, *J* = 2.5, 1 H, HO); 3.02 (sext, *J* = 6.8, 1 H, HC(2)); 2.88 (qd, *J* = 7.3, 2.9, 1 H, HC(4)); 1.63 (d, *J* = 6.3, 3 H, H₃C(8)); 1.56 (s, 3 H, H₃C(13)); 1.10 – 1.02 (m, 27 H, H₃C(11), H₃C(10), H₃C(12), HC(9))

¹³C NMR: (126 MHz, CDCl₃)

219.2 (C(3)); 133.7 (C(7)); 119.9 (C(6)); 73.8 (C(1)); 66.5 (C(5)); 48.6 (C(4)); 47.5 (C(2)); 17.9 (C(10)); 13.4 (C(8)); 13.3 (C(13)); 12.9 (C(11)); 11.8 (C(9)); 9.0 (C(12))

IR: (CHCl₃)

3584 (br, w); 2945 (m); 2868 (m); 1701 (w); 1461 (w); 1383 (w); 1103 (w)

MS: (FI)

357 (M⁺, 7); 311 (5); 310 (4); 231 (5); 230 (18); 229 (100)

Opt. Rot.: [α]_D²⁴ + 5.71 (EtOH, c = 0.20)TLC: *R_f* 0.20 (pentane/ether, 5/1) [silica gel, *p*-anisaldehyde]Analysis: C₂₀H₄₀O₃Si (356.62)

Calcd: C, 67.36%; H, 11.31%

Found: C, 66.99%; H, 11.28%

(2*S*, 4*S*, 5*S*)-1-Triisopropylsilyloxy-2,4,6-trimethyl-5-hydroxy-6-octen-3-one (*syn, anti*-46g**)**

Following General Procedure VII using (*Z*)-**25** (472 mg, 1.00 mmol), tiglic aldehyde (96 μ L, 1.00 mmol), (*S,S*)-**1** (37 mg, 0.10 mmol) and TBAI (73.9 mg, 0.20 mmol) in 1 mL of CH₂Cl₂ for 7 h, 286 mg (0.80 mmol, 80%) of **46g** was obtained as a clear viscous oil after column

chromatography (silica gel, pentane/ether, 5/1).

Data for (*syn,anti*)-46g:

¹H NMR: (500 MHz, CDCl₃)

5.57 (qt, $J = 6.8, 1.2$, 1 H, HC(7)); 4.36 (br s, 1 H, HC(5)); 3.89-3.63 (ABX, 2 H, H₂C(1)); 2.99 (sext, $J = 5.4$, 1 H, HC(2)); 2.92 (qd, $J = 7.1, 3.0$, 1 H, HC(4)); 2.64 (d, $J = 2.9$, 1 H, HO); 1.66 (d, $J = 6.9$, 3 H, H₃C(8)); 1.60 (s, 3 H, H₃C(13)); 1.10 (m, 27 H, H₃C(11), H₃C(10), H₃C(12), HC(9))

¹³C NMR: (126 MHz, CDCl₃)

217.9 (C(3)); 134.4 (C(6)); 120.4 (C(7)); 73.8 (C(5)); 66.0 (C(1)); 48.6 (C(4)); 48.1 (C(2)); 17.9 (C(10)); 13.4 (C(8)); 13.2 (C(13)); 12.9 (C(11)); 11.8 (C(9)); 9.5 (C(12))

IR: (neat)

3468 (br, m); 2944 (m); 2868 (m); 1703 (m); 1463 (m); 1383 (w); 1249 (w); 1102 (m); 1068 (w)

MS: (FI)

356 (M⁺, 1); 311 (5); 232 (5); 231 (6); 230 (18); 229 (100)

Opt. Rot.: $[\alpha]_{\text{D}}^{24} + 10.2$ (EtOH, $c = 0.53$)

TLC: R_f 0.20 (pentane/ether, 5/1) [silica gel, *p*-anisaldehyde]

Analysis: C₂₀H₄₀O₃Si (356.62)

Calcd: C 67.36%; H 11.31%

Found: C 66.96%; H 11.30%

General Procedure VIII: Aldol Additions of Trichlorosilyl Enolates **26 and **27**: (1*R*, 2*R*, 5*S*)-5-*tert*-Butyldimethylsilyloxy-2-methyl-1-hydroxy-1-phenyl-3-hexanone (*syn,anti*-**47a**)**

In a 10-mL Schlenk flask was placed a solution of (*R,R*)-**1** (37 mg, 0.10 mmol, 0.10 equiv) in CH₂Cl₂ (1 mL). To the solution was added (Z)-**26** (364 mg, 1.00 mmol) and the solution was cooled to –68 °C using *i*-PrOH/CO₂ bath. To the solution was added PhCHO (102 μL, 1.00 mmol, 1 equiv) and the reaction mixture was stirred for 6 h at –68 °C. The reaction mixture was quenched by pouring into a vigorously stirring cold sat. aq. NaHCO₃ solution (15 mL). The resulting slurry was stirred for 3 h and filtered through Celite. The layers were separated, and the aqueous layer was extracted with CH₂Cl₂ (2 x 15 mL). The combined extracts were washed with brine (5 mL), dried over sodium sulfate and concentrated. The crude oil was purified by column chromatography (silica gel, pentane/ether, 3/1, 30 mm) to afford 200 mg (0.59 mmol, 59%) of **47a** as a clear viscous oil.

Data for (*syn,anti*)-**47a**:

¹H NMR: (500 MHz, CDCl₃)

7.36-7.30 (m, 4 H, HC(8), HC(9)); 7.25 (m, 1 H, HC(10)); 5.15 (t, *J* = 2.9, 1 H, HC(1)); 4.32 (sext, *J* = 6.6, 1 H, HC(5)); 3.16 (d, *J* = 2.6, 1 H, HO); 2.81 (qd, *J* = 7.3, 3.1, 1 H, HC(2)); 2.72-2.43 (ABX, 2 H, H₂C(4)); 1.16 (d, *J* = 6.1, 3 H, H₃C(6)); 1.04 (d, *J* = 7.3, 3 H, H₃C(11)); 0.87 (s, 9H, H₃C(14)); 0.06 (d, *J* = 11.2, 6 H, H₃C(12))

¹³C NMR: (126 MHz, CDCl₃)

214.7 (C(3)); 141.6 (C(7)); 128.2 (C(9)); 127.2 (C(10)); 125.8 (C(8)); 72.3 (C(5)); 65.4 (C(1)); 52.5 (C(2)); 51.3 (C(4)); 25.8 (C(14)); 23.9 (C(6)); 17.9 (C(13)); 9.2 (C(11)); -4.6, -4.9 (C(12))

IR: (neat)

3458 (br, m); 3064 (w); 3032 (w); 2956 (m); 2931 (m); 2895 (m); 2858 (m); 1707 (m); 1454 (m); 1375 (m); 1255 (m); 1134 (m); 1095 (m); 1005 (m)

MS: (FI)336 (M^+ , 7); 279 (100); 230 (5); 173 (3); 107 (5)Opt. Rot.: $[\alpha]_D^{24}$ -5.55 (EtOH, c=0.63)TLC: R_f 0.20 (pentane/ether, 5/1) [silica gel, *p*-anisaldehyde]SFC: t_R = 2.441 min (OD, 150 bar, 3 mL/min, 5% MeOH)Analysis: $C_{19}H_{32}O_3Si$ (336.54)

Calcd: C, 67.81%; H, 9.58%

Found: C, 67.61%; H, 9.59%

(1*S*, 2*S*, 5*S*)-5-*tert*-Butyldimethylsilyloxy-2-methyl-1-hydroxy-1-phenyl-3-hexanone
(*syn,syn*-47a)

Following General Procedure VIII using (Z)-**26** (364 mg, 1.00 mmol), PhCHO (102 μ L, 1.00 mmol) and (S,S)-**1** (37 mg, 0.10 mmol) in 1 mL of CH_2Cl_2 , 203 mg (0.60 mmol, 60%) of **47a** was obtained as a clear viscous oil after column chromatography (silica gel, pentane/ether, 3/1). The product was further purified by recrystallization in pentane.

Data for (*syn,syn*)-47a:mp: 46 – 48 °C (pentane) ^1H NMR: (500 MHz, CDCl_3)7.35-7.31 (m, 4 H, HC(8), HC(9)); 7.27 – 7.25 (m, 1 H, HC(10)); 5.09 (t, J = 3.4, 1 H, HC(1)); 4.32 (sext, J = 6.1, 1 H, HC(5)); 3.19 (d, J = 2.5, 1 H, HO); 2.81 (qd, J = 7.3, 3.7, 1 H, HC(2)); 2.76-2.34 (ABX, 2 H, $\text{H}_2\text{C}(4)$); 1.12 (d, J = 6.1, 3 H,

H₃C(6)); 1.05 (d, $J = 7.1$, 3 H, H₃C(11)); 0.85 (s, 9H, H₃C(14)); 0.05 (d, $J = 16.8$, 6 H, H₃C(12))

¹³C NMR: (126 MHz, CDCl₃)
214.2 (C(3)); 141.7 (C(7)); 128.2 (C(9)); 127.3 (C(10)); 125.9 (C(8)); 72.8 (C(5)); 65.9 (C(1)); 53.3 (C(2)); 51.5 (C(4)); 25.7 (C(14)); 23.8 (C(6)); 17.9 (C(13)); 9.4 (C(11)); -4.7, -4.9 (C(12))

IR: (neat)
3487 (br, m); 2956 (m); 2931 (m); 2885 (m); 2858 (m); 1709 (m); 1454 (m); 1408 (w); 1375 (m); 1254 (m); 1154 (m); 1093 (m)

MS: (FI)
336 (M⁺, 8); 279 (100); 230 (7); 173 (10); 106 (7)

Opt. Rot.: $[\alpha]_D^{24} + 50.3$ (EtOH, $c=0.29$)

TLC: R_f 0.20 (pentane/ether, 5/1) [silica gel, *p*-anisaldehyde]

SFC: $t_R = 3.030$ min (OD, 150 bar, 3 mL/min, 5% MeOH)

Analysis: C₁₉H₃₂O₃Si (336.54)

Calcd: C, 67.81%; H, 9.58%

Found: C, 67.78%; H, 9.61%

(1*R*, 2*R*, 5*S*)-5-Triisopropylsilyloxy-2-methyl-1-hydroxy-1-phenyl-3-hexanone (*syn,anti*-48a)

Following General Procedure VIII using (Z)-27 (456 mg, 1.00 mmol), PhCHO (102 μ L, 1.00 mmol) and (R,R)-1 (37 mg, 0.10 mmol) in 1 mL of CH₂Cl₂ for 6 h, 317 mg (0.84 mmol, 84%) of 48a was obtained as a clear viscous oil after column chromatography (silica gel, pentane/ether, 5/1).

Data for (syn,anti)-48a:¹H NMR: (500 MHz, CDCl₃)

7.30 (d, $J = 7.6$, 2 H, HC(9)); 7.17 (t, $J = 7.3$, 2 H, HC(8)); 7.08 (t, $J = 7.2$, 1 H, HC(10)); 5.04 (t, $J = 3.2$, 1 H, HC(1)); 4.44 (sext, $J = 6.1$, 1 H, HC(5)); 2.74 (d, $J = 2.6$, 1 H, HO); 2.55 (qd, $J = 7.3, 3.9$, 1 H, HC(2)); 2.46-2.21 (ABX, 2 H, H₂C(4)); 1.11 (d, $J = 6.1$, 3 H, H₃C(6)); 1.10 – 1.02 (m, 21 H, H₃C(13), HC(12)); 0.94 (d, $J = 7.0$, 3 H, H₃C(11))

¹³C NMR: (126 MHz, CDCl₃)

214.8 (C(3)); 141.9 (C(7)); 128.5 (C(8)); 127.6 (C(10)); 126.1 (C(9)); 72.8 (C(5)); 65.4 (C(1)); 53.6 (C(2)); 52.2 (C(4)); 24.3 (C(6)); 18.3 (C(13)); 12.6 (C(12)); 9.8 (C(11))

IR: (neat)

3467 (br, m); 3064 (w); 3032 (w); 2962 (s); 2943 (s); 2893 (s); 2868 (s); 1705 (s); 1462 (s); 1375 (s); 1248 (m); 1213 (m); 1198 (m); 1128(s); 1097 (s); 1070 (m); 1012 (s)

MS: (FAB)

379 (M⁺, 13); 273 (11); 230 (18); 229 (100); 202 (10); 201 (49); 185 (15); 175 (10); 159 (12); 157 (51); 154 (11), 137 (11); 136 (13); 131 (15); 115 (24); 107 (32); 105 (11), 103 (11)

Opt. Rot.: $[\alpha]_D^{24}$ -25.9 (EtOH, c=0.24)TLC: R_f 0.17 (pentane/ether, 5/1) [silica gel, *p*-anisaldehyde]SFC: $t_R = 3.645$ min (OD, 150 bar, 3 mL/min, 5% MeOH)Analysis: C₂₂H₃₈O₃Si (378.62)

Calcd: C, 69.79%; H, 10.12%

Found: C, 69.63%; H, 10.43%

(1*S*, 2*S*, 5*S*)-1-Triisopropylsilyloxy-2-methyl-5-hydroxy-5-phenyl-3-hexanone (syn, syn-48a)

Following General Procedure VIII using (Z)-**27** (450 mg, 1.00 mmol), PhCHO (102 μL , 1.00 mmol) and (S,S)-**1** (37 mg, 0.10 mmol) in 1 mL of CH_2Cl_2 for 6 h, 327 mg (0.86 mmol, 86%) of **48a** was obtained as a clear viscous oil after column chromatography (silica gel, pentane/ether, 5/1).

Data for (syn,syn)-48a:

^1H NMR: (500 MHz, CDCl_3)

7.35 – 7.31 (m, 4 H, HC(9), HC(8)); 7.27 (m, 1 H, HC(10)); 5.09 (t, $J = 3.4$, 1 H, HC(1)); 4.40 (sext, $J = 5.9$, 1 H, HC(5)); 3.05 (d, $J = 2.7$, 1 H, HO); 2.85 (qd, $J = 7.3$, 3.9, 1 H, HC(2)); 2.87-2.48 (ABX, 2 H, $\text{H}_2\text{C}(4)$); 1.15 (d, $J = 6.1$, 3 H, $\text{H}_3\text{C}(6)$); 1.08 – 1.00 (m, 24 H, $\text{H}_3\text{C}(13)$, HC(12), $\text{H}_3\text{C}(11)$)

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

214.5 (C(3)); 141.9 (C(7)); 128.5 (C(8)); 127.6 (C(10)); 126.2 (C(9)); 73.1 (C(5)); 65.1 (C(1)); 53.4 (C(2)); 52.3 (C(4)); 24.3 (C(6)); 18.3 (C(13)); 12.6 (C(12)); 10.1 (C(11))

IR: (neat)

3461 (br, m); 2963 (s); 2943 (s); 2893 (s); 2867 (s); 1707 (s); 1461 (m); 1375 (m); 1130 (s); 1097 (m); 1013 (s)

MS: (FI)

379 (M^+ , 4); 337 (8); 336 (30); 335 (100); 272 (6); 229 (13); 157 (4); 157 (4), 157 (5); 157 (6)

Opt. Rot.: $[\alpha]_{\text{D}}^{24} + 29.1$ (EtOH, $c=0.59$)

TLC: R_f 0.17 (pentane/ether, 5/1) [silica gel, *p*-anisaldehyde]

SFC: $t_R = 4.452$ min (OD, 150 bar, 3 mL/min, 5% MeOH)

Analysis: C₂₂H₃₈O₃Si (378.62)

Calcd: C, 69.79%; H, 10.12%

Found: C, 69.54%; H, 10.32%

(1*R*, 2*R*, 5*S*)-5-Triisopropylsilyloxy-2-methyl-1-hydroxy-1-(1-naphthyl)-3-hexanone
(*syn,anti*-48b)

Following General Procedure VIII using (*Z*)-**27** (451 mg, 1.00 mmol), 1-naphthaldehyde (136 μ L, 1.00 mmol) and (*R,R*)-**1** (37 mg, 0.10 mmol) in 1 mL of CH₂Cl₂ for 8 h, 356 mg (0.83 mmol, 83%) of **48b** was obtained as a clear viscous oil after column chromatography (5/1 pentane/ether, 5/1).

Data for (*syn,anti*)-48b:

¹H NMR: (500 MHz, CDCl₃)

7.89 (d, *J* = 6.2, 1 H, HC(9)); 7.87 (d, *J* = 5.9, 1 H, HC(12)); 7.78 (d, *J* = 8.0, 1 H, HC(14)); 7.72 (d, *J* = 7.3, 1 H, HC(16)); 7.52-7.47 (m, 3 H, HC(11), HC(10), HC(15)); 5.96 (t, *J* = 2.4, 1 H, HC(1)); 4.48 (sext, *J* = 6.4, 1 H, HC(5)); 3.26 (d, *J* = 2.4, 1 H, HO); 3.03 (qd, *J* = 7.1, 4.4, 1 H, HC(2)); 2.81-2.61 (ABX, 2 H, H₂C(4)); 1.22 (d, *J* = 5.8, H₃C(6)); 1.10 – 1.04 (m, 24 H, H₃C(17), HC(18), H₃C(19))

¹³C NMR: (126 MHz, CDCl₃)

214.4 (C(3)); 136.7 (C(7)); 133.7 (C(13)); 129.6 (C(8)); 129.1 (C(12)); 127.8 (C(14)); 126.0 (C(10)); 125.4 (C(11)); 125.3 (C(15)); 124.3 (C(16)); 122.4 (C(9)); 69.1 (C(1)); 64.9 (C(5)); 51.9 (C(4)); 51.4 (C(2)); 24.1 (C(6)); 18.0 (C(19)); 12.3 (C(18)); 9.6 (C(17))

IR: (CH₂Cl₂)

3468 (br, m); 2962 (s); 2944 (s); 2892 (s); 2867 (s); 1704 (s); 1462 (s); 1374 (s); 1133 (s); 1102 (s); 1056 (m); 1029 (s); 1013 (s)

MS: (FI)

429 (M⁺, 4); 411 (7); 410 (13); 387 (7); 387 (6); 386 (28); 385 (100); 384 (4); 299 (4); 282 (4); 274 (4); 273 (15); 272 (57); 256 (4); 254 (4); 231 (4); 230 (8); 229 (58); 193 (5); 157 (8); 156 (44); 136 (5); 136 (5)

Opt. Rot.: $[\alpha]_D^{24}$ - 4.73 (EtOH, c=0.61)

TLC: *R_f* 0.09 (pentane/ether, 5/1) [silica gel, short uv]

SFC: *t_R* = 5.940 min (OD, 150 bar, 3 mL/min, 15% MeOH)

Analysis: C₂₆H₄₀O₃Si (428.68)

Calcd: C, 72.85%; H, 9.41%

Found: C, 72.68%; H, 9.49%

(1*S*, 2*S*, 5*S*)-5-Triisopropylsilyloxy-2-methyl-1-hydroxy-1-(1-naphthyl)-3-hexanone (*syn, syn*-48b**)**

Following General Procedure VIII using (Z)-**27** (451 mg, 1.00 mmol), 1-naphthaldehyde (136 μ L, 1.00 mmol) and (S,S)-**1** (37 mg, 0.10 mmol) in 1 mL of CH₂Cl₂ for 8 h, 347 mg (0.75 mmol, 75%) of **48b** was obtained as a clear viscous oil after column chromatography (silica gel, pentane/ether, 5/1).

Data for (*syn, syn*)-48b**:**

¹H NMR: (500 MHz, CDCl₃)

7.88 (d, *J* = 7.4, 1 H, HC(9)); 7.87 (d, *J* = 4.1, 1 H, HC(12)); 7.79 (d, *J* = 8.0, 1 H, HC(14)); 7.72 (d, *J* = 7.1, 1 H, HC(16)); 7.52-7.48 (m, 3 H, HC(11), HC(10),

HC(15)); 5.94 (dd, $J = 3.4, 2.5$, 1 H, HC(1)); 4.46 (sext, $J = 6.1$, 1 H, HC(5)); 3.24 (d, $J = 2.4$, 1 H, HO); 3.04 (qd, $J = 7.3, 4.4$, 1 H, HC(2)); 2.87 - 2.57 (ABX, 2 H, H₂C(4)); 1.21 (d, $J = 6.1$, H₃C(6)); 1.09 – 1.02 (m, 24 H, H₃C(17), HC(18), H₃C(19))

¹³C NMR: (126 MHz, CDCl₃)
214.3 (C(3)); 136.6 (C(7)); 133.7 (C(13)); 129.6 (C(8)); 129.1 (C(12)); 127.9 (C(14)); 126.1 (C(10)); 125.4 (C(11)); 125.3 (C(15)); 124.1 (C(16)); 122.3 (C(9)); 69.2 (C(1)); 64.9 (C(5)); 51.8 (C(4)); 51.4 (C(2)); 24.1 (C(6)); 18.0 (C(19)); 12.3 (C(18)); 9.6 (C(17))

IR: (neat)
3470 (br, m); 2963 (s); 2943 (s); 2892 (m); 2867 (s); 1704 (m); 1462 (m); 1374 (m); 1130 (m); 1104 (m); 1013 (s)

MS: (FI)
429 (M⁺, 16); 428 (10); 386 (28); 385 (95); 321 (17); 303 (11); 273 (21); 272 (58); 230 (17); 229 (97); 157 (20); 156 (100)

Opt. Rot.: $[\alpha]_D^{24} + 14.2$ (EtOH, c=0.63)

TLC: R_f 0.09 (pentane/ether, 5/1) [silica gel, short uv]

SFC: $t_R = 3.562$ min (OD, 150 bar, 3 mL/min, 15% MeOH)

Analysis: C₂₆H₄₀O₃Si (428.68)

Calcd: C, 72.85%; H, 9.41%

Found: C, 73.02%; H, 9.78%

(2*S*, 5*R*, 6*R*)-2-Triisopropylsilyloxy-5-methyl-6-hydroxy-8-phenyl-7-octen-4-one (*syn,anti*-48c**)**

Following General Procedure VIII using (Z)-**27** (451 mg, 1.00 mmol), cinnamaldehyde (126 μL , 1.00 mmol) and (R,R)-**1** (37 mg, 0.10 mmol) in 1 mL of CH_2Cl_2 for 12 h, 322 mg (0.80 mmol, 80%) of **48c** was obtained as a clear viscous oil after column chromatography (silica gel, pentane/ether, 2/1).

Data for (syn,anti)-**48c**:

^1H NMR: (500 MHz, CDCl_3)

7.37 (d, $J = 7.3$, 2 H, HC(13)); 7.31 (t, $J = 7.6$, 2 H, HC(14)); 7.24 (t, $J = 7.1$, 1 H, HC(15)); 6.64 (d, $J = 15.9$, 1 H, HC(8)); 6.14 (dd, $J = 15.8$, 5.9, 1 H, HC(7)); 4.67 (m, 1 H, HC(6)); 4.45 (sext, $J = 6.1$, 1 H, HC(2)); 2.88 (d, $J = 3.2$, 1 H, HO); 2.82-2.59 (ABX, 2 H, $\text{H}_2\text{C}(3)$); 2.76 (qd, $J = 7.3$, 3.4, 1 H, HC(5)); 1.22 (d, $J = 6.1$, 3 H, $\text{H}_3\text{C}(1)$); 1.17 (d, $J = 7.1$, 3 H, $\text{H}_3\text{C}(11)$); 1.05 (m, 21 H, HC(9), $\text{H}_3\text{C}(10)$)

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

219.3 (C(4)); 136.6 (C(12)); 131.1 (C(7)); 128.9 (C(8)); 128.6 (C(14)); 127.7 (C(15)); 126.5 (C(13)); 71.8 (C(6)); 65.3 (C(2)); 52.0 (C(3)); 51.5 (C(5)); 24.2 (C(1)); 18.1 (C(10)); 12.4 (C(9)); 10.0 (C(11))

IR: (neat)

3442 (br, m); 2963 (s); 2943 (s); 2892 (s); 2867 (s); 1705 (s); 1462 (m); 1374 (m); 1126 (s); 1013 (s)

MS: (FI)

404 (M^+ , 9); 361 (7); 321 (2); 272 (13); 229 (100); 132 (86)

Opt. Rot.: $[\alpha]_{\text{D}}^{24}$ - 20.5 (EtOH, $c = 0.33$)

TLC: R_f 0.21 (pentane/ether, 2/1) [silica gel, short uv]

SFC: t_R = 2.348 min (OD, 150 bar, 3 mL/min, 15% MeOH)

Analysis: $C_{24}H_{40}O_3Si$ (404.66)

Calcd: C, 71.23%; H, 9.96%

Found: C, 71.20%; H, 10.21%

(2*S*, 5*S*, 6*S*)-2-Triisopropylsilyloxy-5-methyl-6-hydroxy-8-phenyl-7-octen-4-one (*syn, syn*-48c**)**

Following General Procedure VIII using (Z)-**27** (451 mg, 1.00 mmol), cinnamaldehyde (126 μL , 1.00 mmol) and (S,S)-**1** (37 mg, 0.10 mmol) in 1 mL of CH_2Cl_2 for 12 h, 304 mg (0.75 mmol, 75%) of **48c** was obtained as a clear viscous oil after column chromatography (silica gel, pentane/ether, 2/1).

Data for (*syn, syn*)-**48c**:

^1H NMR: (500 MHz, CDCl_3)

7.37 (d, J = 7.1, 2 H, HC(13)); 7.31 (t, J = 7.8, 2 H, HC(14)); 7.24 (t, J = 7.4, 1 H, HC(15)); 6.64 (dd, J = 15.9, 1.2, 1 H, HC(8)); 6.15 (dd, J = 15.8, 5.8, 1 H, HC(7)); 4.66 (m, 1 H, HC(6)); 4.45 (sext, J = 5.6, 1 H, HC(2)); 2.85 (d, J = 3.2, 1 H, HO); 2.78 (m, 1 H, HC(5)); 2.80-2.62 (ABX, 2 H, $\text{H}_2\text{C}(3)$); 1.22 (d, J = 6.1, 3 H, $\text{H}_3\text{C}(1)$); 1.18 (d, J = 7.3, 3 H, $\text{H}_3\text{C}(11)$); 1.08 – 1.03 (m, 21 H, HC(9), $\text{H}_3\text{C}(10)$)

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

214.0 (C(4)); 136.6 (C(12)); 131.1 (C(7)); 129.0 (C(8)); 128.6 (C(14)); 127.7 (C(15)); 126.5 (C(13)); 72.0 (C(6)); 65.1 (C(2)); 52.0 (C(3)); 51.4 (C(5)); 24.1 (C(1)); 18.1 (C(10)); 12.4 (C(9)); 10.2 (C(11))

IR: (neat)

3436 (br, m); 2963 (s); 2943 (s); 2892 (m); 2867 (s); 1707 (m); 1462 (m); 1374 (m); 1130 (m); 1013 (s)

MS: (EI)

404 (M^+ , 18); 385 (8); 361 (7); 321 (9); 273 (10); 272 (21); 245 (9); 230 (19); 229 (100); 156 (8); 133 (12); 132 (74)

Opt. Rot.: $[\alpha]_D^{24} + 27.7$ (EtOH, $c = 0.50$)

TLC: R_f 0.20 (pentane/ether, 2/1) [silica gel, short uv]

SFC: $t_R = 3.231$ min (OD, 150 bar, 3 mL/min, 15% MeOH)

Analysis: $C_{24}H_{40}O_3Si$ (404.66)

Calcd: C, 71.23%; H, 9.96%

Found: C, 71.29%; H, 10.31%

(2*S*, 5*R*, 6*R*)-2-Triisopropylsilyloxy-11,12-dimethyl-6-hydroxy-8-phenyl-7-octen-4-one
(*syn,anti*-48d)

Following General Procedure VIII using (Z)-27 (436 mg, 1.00 mmol), α -methylcinnamaldehyde (140 μL , 1.00 mmol) and (R,R)-1 (37 mg, 0.10 mmol) in 1 mL of CH_2Cl_2 for 10 h, 332 mg (0.79 mmol, 79%) of **48d** was obtained as a clear viscous oil after column chromatography (silica gel, pentane/ether, 3/1).

Data for (*syn,anti*)-48d:

$^1\text{H NMR}$: (500 MHz, CDCl_3)

7.33 (t, $J = 7.8$, 2 H, HC(15)); 7.27 (d, $J = 7.3$, 2 H, HC(14)); 7.21 (t, $J = 7.0$, 1 H, HC(16)); 6.63 (br s, 1 H, HC(8)); 4.53 (m, 1 H, HC(6)); 4.47 (sext, $J = 6.3$, 1 H, HC(2)); 2.99 (d, $J = 2.7$, 1 H, HO); 2.84-2.62 (ABX, 2 H, $\text{H}_2\text{C}(3)$); 2.82 (m, 1

H, HC(5)); 1.81 (d, $J = 1.0$, 3 H, H₃C(12)); 1.22 (d, $J = 5.9$, 3 H, H₃C(1)); 1.13 (d, $J = 7.3$, 3 H, H₃C(11)); 1.07 – 1.00 (m, 21 H, HC(9), H₃C(10))

¹³C NMR: (126 MHz, CDCl₃)

214.3 (C(4)); 137.6 (C(13)); 136.3 (C(7)); 129.0 (C(15)); 128.1 (C(14)); 126.4 (C(16)); 125.9 (C(8)); 74.8 (C(6)); 65.3 (C(2)); 51.7 (C(3)); 49.2 (C(5)); 24.1 (C(1)); 18.0 (C(10)); 15.3 (C(12)); 12.4 (C(9)); 9.3 (C(11))

IR: (CHCl₃)

3487 (br, w); 2962 (m); 2945 (m); 2868 (m); 1699 (w); 1464 (w); 1377 (w); 1101 (w)

MS: (FI)

418 (M⁺, 100); 375 (25); 336 (8); 272 (22); 229 (27); 187 (4); 146 (29); 115 (2)

Opt. Rot.: $[\alpha]_D^{24} - 2.13$ (EtOH, $c = 0.63$)

TLC: R_f 0.22 (pentane/ether, 3/1) [silica gel, short uv]

SFC: $t_R = 2.03$ min (OD, 150 bar, 3 mL/min, 15% MeOH)

Analysis: C₂₅H₄₂O₃Si (418.68)

Calcd: C, 71.72%; H, 10.11%

Found: C, 71.34%; H, 10.18%

(2*S*, 5*S*, 6*S*)-2-Triisopropylsilyloxy-11,12-dimethyl-6-hydroxy-8-phenyl-7-octen-4-one
(*syn,syn*-**48d**)

Following General Procedure VIII using (Z)-**27** (436 mg, 1.00 mmol), α -methylcinnamaldehyde (140 μ L, 1.00 mmol) and (S,S)-**1** (37 mg, 0.10 mmol) in 1 mL of CH₂Cl₂ for 10 h, 344 mg (0.82 mmol, 82%) of **48d** was obtained as a clear viscous oil after column chromatography (silica gel, pentane/ether, 3/1).

Data for (syn,syn)-48d:¹H NMR: (500 MHz, CDCl₃)

7.33 (t, $J = 7.3$, 2 H, HC(15)); 7.27 (d, $J = 6.6$, 2 H, HC(14)); 7.21 (t, $J = 7.4$, 1 H, HC(16)); 6.62 (br s, 1 H, HC(8)); 4.52 (br s, 1 H, HC(6)); 4.45 (sext, $J = 5.9$, 1 H, HC(2)); 2.91 (d, $J = 2.9$, 1 H, HO); 2.86 (qd, $J = 7.3$, 3.6, 1 H, HC(5)); 2.84-2.62 (ABX, 2 H, H₂C(3)); 1.83 (d, $J = 0.7$, 3 H, H₃C(12)); 1.23 (d, $J = 6.1$, 3 H, H₃C(1)); 1.13 (d, $J = 7.3$, 3 H, H₃C(11)); 1.06 (m, 21 H, HC(9), H₃C(10))

¹³C NMR: (126 MHz, CDCl₃)

214.0 (C(4)); 137.6 (C(13)); 136.4 (C(7)); 129.0 (C(15)); 128.1 (C(14)); 126.4 (C(16)); 126.0 (C(8)); 75.0 (C(6)); 65.1 (C(2)); 51.8 (C(3)); 49.0 (C(5)); 24.1 (C(1)); 18.0 (C(10)); 15.3 (C(12)); 12.4 (C(9)); 9.4 (C(11))

IR: (neat)

3467 (br, m); 2943 (s); 2866 (s); 1705 (m); 1462 (m); 1375 (m); 1130 (m); 1097 (m); 1012 (m)

MS: (FI)

418 (M⁺, 55); 401 (3); 375. (14); 337 (4); 272 (95); 229 (100); 201 (5); 146 (99)

Opt. Rot.: $[\alpha]_{\text{D}}^{24} +15.1$ (EtOH, c = 2.2)TLC: R_f 0.22 (pentane/ether, 3/1) [silica gel, short uv]SFC: $t_R = 2.983$ min (OD, 150 bar, 3 mL/min, 15% MeOH)Analysis: C₂₅H₄₂O₃Si (418.68)

Calcd: C, 71.72%; H, 10.11%

Found: C, 71.46%; H, 10.04%

(2*S*, 5*R*, 6*R*)-2-Triisopropylsilyloxy-5-methyl-6-hydroxy-7-nonen-4-one (*syn,anti*-48e)

Following General Procedure VIII using (Z)-**27** (451 mg, 1.00 mmol), crotonaldehyde (83 μL , 1.00 mmol) and (*R,R*)-**1** (37 mg, 0.10 mmol) in 1 mL of CH_2Cl_2 for 8 h, 272 mg (0.79 mmol, 79%) of **48e** was obtained as a clear viscous oil after column chromatography (silica gel, pentane/ether, 3/1).

Data for (*syn,anti*)-48e:

^1H NMR: (500 MHz, Benzene- d_6)

5.61 (dq, $J = 15.2, 6.4, 1.2$, 1 H, HC(8)); 5.37 (ddd, $J = 15.4, 6.1, 1.5$, 1 H, HC(7)); 4.51 (sext, $J = 6.3$, 1 H, HC(2)); 4.31 (m, 1 H, HC(6)); 2.68 – 2.34 (ABX, 2 H, $\text{H}_2\text{C}(3)$); 2.36 (m, 1 H, HC(5)); 2.10 (d, $J = 3.5$, 1 H, HO); 1.53 (d, $J = 6.5$, 3 H, $\text{H}_3\text{C}(9)$); 1.17 (d, $J = 6.1$, 3 H, $\text{H}_3\text{C}(1)$); 1.15 – 1.03 (m, 21 H, $\text{H}_3\text{C}(11)$, HC(10)); 1.01 (d, $J = 7.3$, 3 H, $\text{H}_3\text{C}(12)$)

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

214.1 (C(4)); 130.5 (C(7)); 127.9 (C(8)); 72.2 (C(6)); 65.2 (C(2)); 52.1 (C(3)); 51.6 (C(5)); 24.1 (C(1)); 18.0 (C(11)); 17.7 (C(9)); 12.3 (C(10)); 10.2 (C(12))

IR: (neat)

3442 (br, m); 2963 (s); 2943 (s); 2893 (s); 2868 (s); 1710 (s); 1463 (m); 1375 (m); 1130 (s); 1102 (m); 1013 (s)

MS: (FI)

343 (M^+ , 3); 301 (7); 300 (22); 300 (4); 299 (100); 281 (4); 272 (8); 230 (6); 29.1 (36); 176 (3); 176 (4); 176 (4); 176 (5); 176 (6); 176 (6); 175 (5); 175 (5); 175 (4)

Opt. Rot.: $[\alpha]_{\text{D}}^{24}$ - 15.9 (EtOH, $c = 0.54$)

TLC: R_f 0.16 (pentane/ether, 3/1) [silica gel, *p*-anisaldehyde]

Analysis: C₁₉H₃₈O₃Si (342.59)

Calcd: C, 66.61%; H, 11.18%

Found: C, 66.37%; H, 11.36%

(2*S*, 5*S*, 6*S*)-2-Triisopropylsilyloxy-5-methyl-6-hydroxy-7-nonen-4-one (*syn, syn*-48e)

Following General Procedure VIII using (Z)-**27** (451 mg, 1.00 mmol), crotonaldehyde (83 μL , 1.00 mmol) and (S,S)-**1** (37 mg, 0.10 mmol) in 1 mL of CH₂Cl₂ for 8 h, 285 mg (0.83 mmol, 83%) of **48e** was obtained as a clear viscous oil after column chromatography (silica gel, pentane/ether, 3/1).

Data for (*syn, syn*)-48e:

¹H NMR: (500 MHz, benzene-*d*₆)

5.58 (dq, *J* = 15.4, 6.4, 1.2, 1 H, HC(8)); 5.35 (ddd, *J* = 15.4, 6.1, 1.7, 1 H, HC(7)); 4.51 (sext, *J* = 5.9, 1 H, HC(2)); 4.25 (m, 1 H, HC(6)); 2.68 – 2.34 (ABX, 2 H, H₂C(3)); 2.38 (m, 1 H, HC(5)); 2.00 (d, *J* = 3.4, 1 H, HO); 1.51 (dd, *J* = 6.4, 1.0, 3 H, H₃C(9)); 1.18 (d, *J* = 6.1, 3 H, H₃C(1)); 1.16 – 1.00 (m, 21 H, H₃C(11), HC(10)); 1.05 (d, *J* = 7.1, 3 H, H₃C(12))

¹³C NMR: (126 MHz, CDCl₃)

213.7 (C(4)); 130.6 (C(7)); 128.0 (C(8)); 72.4 (C(6)); 65.0 (C(2)); 52.2 (C(3)); 51.6 (C(5)); 24.0 (C(1)); 18.0 (C(11)); 17.7 (C(9)); 12.3 (C(11)); 10.4 (C(12))

IR: (neat)

3441 (br, m); 2963 (s); 2944 (m); 2893 (m); 2867 (s); 1710 (m); 1462 (m); 1375 (m); 1132 (m); 1109 (m); 1013 (m)

MS: (FI)

343 (2); 342 (M⁺, 3); 301 (7); 300 (22); 299 (100); 229 (37); 175 (5)

Opt. Rot.: $[\alpha]_{\text{D}}^{24} + 30.4$ (EtOH, $c = 0.54$)

TLC: R_f 0.16 (pentane/ether, 3/1) [silica gel, *p*-anisaldehyde]

Analysis: $\text{C}_{19}\text{H}_{38}\text{O}_3\text{Si}$ (342.59)

Calcd: C, 66.61%; H, 11.18%

Found: C, 66.33%; H, 11.33%

General Procedure IX: Aldol Addition of TMS Enol ether **25: (1*R*,2*S*,4*S*)-1-Hydroxy-2,4-dimethyl-1-phenyl-5-triisopropylsilanyloxypentan-3-one (*anti,anti*-**46a**)**

In a 10 mL Schlenk flask were placed (*R,R*)-**2** (84 mg, 0.10 mmol, 0.10 equiv), tetrabutylammonium iodide (74 mg, 0.20 mmol, 0.2 equiv) in dichloromethane (2 mL). To the solution were added benzaldehyde (0.152 mL, 1.50 mmol, 1.5 equiv) and diisopropylethylamine (0.035 mL, 0.20 mmol, 0.2 equiv), and the solution was cooled to -72°C (internal temperature) using a dry ice/isopropanol bath. To the solution was added silicon tetrachloride (0.172 mL, 1.50 mmol, 1.5 equiv), and the solution was stirred for 5 min. To the solution was added dropwise **25** (345 mg, 1.00 mmol), and the reaction mixture was stirred at -60°C (internal temperature) for 24 h. The reaction mixture was quenched by pouring into a vigorously stirring cold (0°C) saturated aqueous NaHCO_3 solution (15 mL), and the resulting emulsion was stirred for at least 3 h. The emulsion was filtered through a pad of Celite, and the filtrate was transferred into a 60-mL separatory funnel. The biphasic mixture was extracted with dichloromethane (2 x 20 mL), and the combined extracts were washed with brine (10 mL). The solution was dried over Na_2SO_4 and concentrated under reduced pressure. The resulting crude oil was chromatographed (silica gel, pentane/ether, 4/1, 30 mm) to afford 307 mg (0.81 mmol, 81%) of **46a** as a clear colorless oil.

Data for anti,anti-46a:¹H NMR: (500 MHz, CDCl₃)

7.36 – 7.26 (m, 5 H, 2 x HC(7), 2 x HC(8), HC(9)); 4.78 (dd, *J* = 8.0, 4.8, 1 H, HC(1)); 3.78 (ABX, 2 H, 2 x HC(5)); 3.09 (d, *J* = 4.6, 1 H, HO); 3.05 (pent, *J* = 7.6, 1 H, HC(2)); 2.89 (sextd, *J* = 5.1, 1.2, 1 H, HC(4)); 1.04 (m, 21 H, 3 x HC(12), 18 x HC(13)); 0.97 (d, *J* = 7.1, 3 H, 3 x HC(10)); 0.93 (d, *J* = 7.1, 3 H, 3 x HC(11))

¹³C NMR: (126 MHz, CDCl₃)

217.9 (C(3)); 142.3 (C(6)); 128.2 (2 x C(7)); 127.1 (C(9)); 125.5 (2 x C(8)); 76.5 (C(1)); 65.5 (C(5)); 53.1 (C(2)); 49.1 (C(4)); 17.9, 17.9 (6 x C(13)); 13.8 (C(10)); 12.8 (C(11)); 11.8 (3 x C(12))

IR: (neat)

3452 (br, m); 3064 (w); 3032 (w); 2943 (s); 2893 (m); 2868 (s); 1711 (m); 1495 (w); 1462 (m); 1383 (m); 1248 (m); 1101 (m); 1066 (m); 1011 (m)

MS: (FI)

379 (3, M⁺); 337 (7); 336 (25); 335 (100); 272 (4); 229 (4); 58 (7)

Opt. Rot.: $[\alpha]_D^{24} +109.5$ (EtOH, c = 0.68)TLC: *R_f* 0.22 (silica gel, pentane/ether, 4/1)SFC: (Chiralcel-OD, 125 bar, 3 mL/min, 5.0% MeOH)

(anti,anti)-**46a** *t_R* 4.194 min (96.5%); (anti,syn)-**46a**, *t_R* = 3.311 min (1.3%); (syn,syn)-**46a**, *t_R* = 3.712 min (1.4%); (syn,anti)-**46a**, *t_R* = 4.979 min (0.7%)

Analysis: C₂₂H₃₈O₃Si (378.62)

Calcd: C, 69.79%; H, 10.12%

Found: C, 69.86%; H, 10.31%

(1*S*,2*R*,4*S*)-1-Hydroxy-2,4-dimethyl-1-phenyl-5-triisopropylsilanyloxy-pentan-3-one
(*anti*,*syn*-46a)

Following General Procedure IX using (*Z*)-**25** (345 mg, 1.00 mmol), benzaldehyde (152 μ L, 1.50 mmol), (*S,S*)-**2** (84 mg, 0.10 mmol), SiCl_4 (0.172 mL, 1.50 mmol); tetrabutylammonium iodide (74 mg, 0.20 mmol) and diisopropylethylamine (0.035 mL, 0.20 mmol) in 2 mL of CH_2Cl_2 for 24 h, 272 mg (0.72 mmol, 72%) of **46a** was obtained as a clear viscous oil after column chromatography (silica gel, pentane/ether, 4/1).

Data for *anti*,*syn*-46a:

^1H NMR: (500 MHz, CDCl_3)

7.34 – 7.27 (m, 5 H, 2 x HC(7), 2 x HC(8), HC(9)); 4.74 (dd, $J = 8.5, 3.9$, 1 H, HC(1)); 3.91 – 3.62 (ABX, 2 H, 2 x HC(5)); 3.26 (d, $J = 3.9$, 1 H, HO); 3.11 (pent, $J = 7.2$, 1 H, HC(2)); 3.04 (sext, $J = 5.9$, 1 H, HC(4)); 1.06 (m, 21 H, 3 x HC(12), 18 x HC(13), 3 x HC(11)); 0.91 (d, $J = 7.1$, 3 H, 3 x HC(10))

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

218.5 (C(3)); 142.0 (C(6)); 128.4 (2 x C(7)); 127.8 (C(9)); 126.7 (2 x C(8)); 77.1 (C(1)); 65.9 (C(5)); 53.4 (C(2)); 49.1 (C(4)); 17.9 (6 x C(13)); 14.2 (C(10)); 13.1 (C(11)); 11.8 (3 x C(12))

IR: (neat)

3477 (br, m); 3064 (w); 3032 (w); 2943 (s); 2891 (m); 2868 (s); 1707 (m); 1462 (m); 1385 (m); 1250 (m); 1101 (m); 1068 (m); 999 (m)

MS: (FI)

379 (4); 337 (9); 336 (27); 335 (100); 272 (7); 229 (3); 58 (5)

Opt. Rot.: $[\alpha]_{\text{D}}^{24}$ -47.1 (EtOH, $c = 0.83$)

TLC: R_f 0.33 (silica gel, pentane/ether, 4/1)

SFC: (Chiralcel-OD, 125 bar, 3 mL/min, 5.0% MeOH)

(*anti,syn*)-**46a**, $t_R = 3.262$ min (82.6%); (*anti,anti*)-**46a** $t_R = 4.195$ min (14.8%);
 (*syn,anti*)-**46a**, $t_R = 4.956$ min (1.6%)

Analysis: $C_{22}H_{38}O_3Si$ (378.62)

Calcd: C, 69.79%; H, 10.12%

Found: C, 69.90%; H, 10.49%

(3*S*,1'*R*,2'*S*)- 3-Triisopropylsilanyloxybutyric acid 2-Hydroxy-1-methyl-2-phenyl-ethyl ester (49)

In a 10-mL Schlenk flask was placed *m*-CPBA (393 mg, 2.28 mmol, 4.0 equiv) in dichloromethane (3 mL). To the solution were added NaH_2PO_4 (486 mg, 3.42 mmol, 6.0 equiv) and a solution of **48a** (215 mg, 0.57 mmol) in dichloromethane (0.5 mL). The reaction mixture was stirred at rt for 48 h. The reaction mixture was diluted in dichloromethane (15 mL), poured into a 60-mL separatory funnel, and washed sequentially with saturated aqueous $NaHCO_3$ solution (10 mL) and with saturated aqueous Na_2SO_3 solution (2 x 10 mL). The solution was dried over Na_2SO_4 and concentrated under reduced pressure. The crude NMR showed ca. 60% conversion. The crude oil was chromatographed (silica gel, hexanes/ether, 4/1, 30 mm) to afford 115 mg (0.29 mmol, 51%) of **49** and 75 mg (0.20 mmol, 34%) of recovered **48a**.

Data for 49:

1H NMR: (500 MHz, $CDCl_3$)

7.39 – 7.28 (m, 5 H, 2 x HC(8), 2 x HC(9), HC(10)); 5.14 (qd, $J = 6.3, 2.5, 1$ H, HC(5)); 4.86 (t, $J = 3.6, 1$ H, HC(6)); 4.35 (sext, $J = 6.8, 1$ H, HC(3)); 2.48 (ABX, $J_{AB} = 14.9, 2$ H, 2 x HC(2)); 2.25 (d, $J = 2.9, 1$ H, OH); 1.19 (d, $J = 6.1, 3$ H, 3 x HC(11)); 1.15 (d, $J = 6.6, 3$ H, 3 x HC(4)); 1.06 (m, 21 H, 18 x HC(13), 3 x HC(12))

¹³C NMR: (126 MHz, CDCl₃)

171.1 (C(1)); 139.8 (C(7)); 128.3 (2 x C(9)); 127.8 (C(10)); 126.4 (2 x C(8)); 75.5 (C(5)); 75.4 (C(6)); 74.1 (C(3)); 45.0 (C(2)); 23.7 (C(4)); 18.0, 18.0 (6 x C(13)); 13.8 (C(11)); 12.3 (3 x C(12))

IR: (neat)

3470 (br, m); 3065 (w); 3031 (w); 2944 (s); 2893 (m); 2867 (s); 2724 (w); 1736 (s); 1604 (w); 1495 (w); 1455 (m); 1379 (m); 1300 (m); 1248 (m); 1184 (s); 1128 (m); 1099 (m); 1070 (m); 1008 (m)

MS: (FI)

395 (5, M⁺); 351 (100)

Opt. Rot.: [α]_D²⁴ +23.2 (EtOH, c = 0.12)

TLC: R_f 0.12 (silica gel, hexanes/ether, 4/1)

Analysis: C₂₂H₃₈O₄Si (394.62)

Calcd: C, 66.96%; H, 9.71%

Found: C, 67.05%; H, 9.66%

(1*S*,2*R*)-1-Phenyl-propane-1,2-diol (50)

In an NMR tube was placed **49** (50 mg, 0.13 mmol) in *d*₈-THF (0.75 mL)/*d*₄-MeOH (0.75 mL)/D₂O (0.3 mL). To the solution was added K₂CO₃ (36 mg, 0.26 mmol, 2.0 equiv), and the reaction mixture was thoroughly mixed. The reaction mixture was let stand at rt for 24 h. The reaction mixture was transferred to a 25-mL round-bottom flask, and the volatiles were removed under reduced pressure. The residue was chromatographed (silica gel, pentane/ether, 1/1) to afford 18 mg (0.12 mmol, 91%) of **50** as clear colorless oil. The physical properties of **50** were consistent with the literature.¹¹

Data for 50:

¹H NMR: (500 MHz, CDCl₃)

7.27 – 7.16 (m, 5 H, aromatic); 4.58 (d, *J* = 4.9, 1 H, HC(1)); 3.92 (qd, *J* = 6.5, 4.8, 1 H, HC(2)); 0.99 (d, *J* = 6.0, 3 H, H₃C(3))

¹³C NMR: (126 MHz, CDCl₃)

140.3 (C(4)), 128.4 (C(6)), 127.9 (C(7)), 126.6 (C(5)); 77.5 (C(1)); 71.3 (C(2)); 17.3 (C(3))

IR: (neat)

3392 (br, s); 3064 (w); 3031 (m); 2978 (s); 2932 (m); 1708 (w); 1604 (w); 1494 (m); 1453 (m); 1377 (m); 1201 (m); 1130 (m); 1079 (m)

Opt. Rot.: [α]_D²⁴ +14.7 (EtOH, c = 1.2) (Lit. for (1*S*,2*R*)-**50** [α]_D²⁴ +17.2 (EtOH, c = 4.2)).¹¹

References

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exp1 #2pul

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 cn KI dnm 200
 at 4.096 dteq
 ap 65536 dteq
 av 8000.0 dteq 1.0
 cb 4000 homo
 bs 16
 bsr 35 dteq2 DEC2 0
 pwr 7.3 dteq2
 dl 0 dteq2 1
 tof 0 dteq2 0
 nt 16 dteq2 n
 ct 16 dteq2 c
 alook not used dteq2 200
 gain not used dteq2 1.0
 flags n homo2 n
 il n
 in n PROCESSING
 dp y lb 0.30
 bs nm wrfile
 DISPLAY -250.2 En not used
 wp 3500.7 match E
 vs 460
 sc 0 wait
 wc 400 wexp
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 ffl 5142.2
 rfp 3630.5
 ch 7
 lms 1.000
 nm
 ph

SMP-XII-18

expl s2pul

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 at 4.096 dres 1.0
 up 65536 homo n
 sw 8000.0 PROCESSING
 fb 4000 lb 0.30
 bs 16 wtf file
 tpwr 55 proc ft
 pw 7.3 fn not used
 dl 0 mach f
 tof 0
 nt 16 weir
 ct 16 wexp
 alock n vbs
 gain not used vnt

FLAGS

fl n
 in n
 dp y
 hs nn

DISPLAY

sp -250.1
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 sc 0
 wc 250
 hzmm 22.00
 is 33.57
 rfl 5143.3
 rfp 3630.5
 th 7
 lns 100.000
 nm ph

10 9 8 7 6 5 4 3 2 1 ppm

exp2 s1pml

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 useria/data/hjlmio- dof 0
 z:/HNMR-786-SF-IV- da
 66.fid data
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 ACQUISITION
 stgy 439.699 deeq
 tn H1 dres 1.0
 at 4.000 homo
 n
 mp 56196
 sw 7024.9 wfile
 fb 4000 proc
 bs 4 fa not used
 bpr 63 mch
 pw 6.0
 dl 0 wait
 tof 2.0 wexp
 ne 8 wds
 ct 8 wnt
 alock n
 gain not used
 flags
 il n
 la n
 op y
 hs na
 DISPLAY
 sp -249.9
 wd 5496.5
 vs 303
 ac 0
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 hnum 13.76
 ls 535.42
 rfi 1027.1
 rfb 0
 th 7
 lms 1.000
 na ph

SAMPLE										DEC. 8 YR	
date	Dec 24 2001	dfrq	499.699	RI	20.999						
solvent	CDCl3	dn		RI	20						
file	exp	dpr	0	RI	20						
ACQUISITION											
freq	499.699	dnf	0	RI <td>20</td> <td colspan="6"></td>	20						
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at	4.000	dnf	0	RI <td>200</td> <td colspan="6"></td>	200						
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sw	7024.9	dnm	1.0	RI <td>200</td> <td colspan="6"></td>	200						
fb	4000	homo	RI <td>20</td> <td colspan="7"></td>	20							
bs	4	PROCESSING									
type	63	wtile	RI <td>20</td> <td colspan="7"></td>	20							
pw	5.0	proc	RI <td>20</td> <td colspan="7"></td>	20							
dl	0	fn	not used	RI <td>20</td> <td colspan="6"></td>	20						
tof	2.0	match	RI <td>20</td> <td colspan="7"></td>	20							
nt	16	RI <td>20</td> <td colspan="8"></td>	20								
ct	16	weir	RI <td>20</td> <td colspan="7"></td>	20							
alock	RI <td>weap</td> <td>RI <td>20</td> <td colspan="7"></td> </td>	weap	RI <td>20</td> <td colspan="7"></td>	20							
gain	not used	whs	RI <td>20</td> <td colspan="7"></td>	20							
rlms	RI <td>wnt</td> <td>RI <td>20</td> <td colspan="7"></td> </td>	wnt	RI <td>20</td> <td colspan="7"></td>	20							
il	RI	RI	20								
ln	RI	RI	20								
dp	RI	RI	20								
bs	RI	RI	20								
DISPLAY											
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wp	5496.5	RI <td>20</td> <td colspan="8"></td>	20								
vs	788	RI <td>20</td> <td colspan="8"></td>	20								
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hnm	13.74	RI <td>20</td> <td colspan="8"></td>	20								
ls	31040.66	RI <td>20</td> <td colspan="8"></td>	20								
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lms	1.000	RI <td>20</td> <td colspan="8"></td>	20								
ph	RI <td>RI <td>20</td> <td colspan="8"></td> </td>	RI <td>20</td> <td colspan="8"></td>	20

SF-VII-6

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 tof 0 werr
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 ct 16 wds
 alock n wnt
 gain not used

FLAGS

ll n
 in n
 dp y
 hs nm

DISPLAY

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 lns 1.000
 nm ph

SF-IX-25

exp2 s2pul

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/HMMR-1639-SF-IX-2-	dm	nmn	
	5.fid	dmn	c
ACQUISITION			
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tn	H1	dres	1.0
at	4.096	homo	n
np	65536	PROCESSING	
sw	8000.0	lb	0.30
fb	4000	wtfile	
bs	16	proc	ft
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pw	7.3	match	f
d1	0		
tof	0	werf	
nt	8	werp	
ct	8	vbs	
alock	n	wnt	
gain	not used		
FLAGS			
fl	n		
ln	n		
dp	y		
hs	nn		
DISPLAY			
sp	-250.1		
wp	5500.7		
vs	374		
sc	0		
wc	250		
hnmn	22.00		
is	33.57		
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rtp	3630.5		
th	7		
ins	100.000		
al	ph

10 9 8 7 6 5 4 3 2 1 ppm

SF-VIII-35

exp2 s2pul

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date Mar 8 2002 dfrq 500.075
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 /HMR-1476-SF-VIII- dm nm
 -35.fid dnm c

ACQUISITION
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 at 4.096 homo n
 np 65536 PROCESSING
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fb 4000 wfile
 bs 16 proc ft
 tpwr 55 fn not used
 pw 7.3 mach f

dl 0
 tof 0 warr
 nt 16 warr
 ct 16 vbs
 alock n wnt
 gain not used

FLAGS

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 ln n
 dp y
 hs nm

DISPLAY

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