Diastereoselective Aldol Additions of Chiral β -Hydroxy Ethyl Ketone Enolates Catalyzed by Lewis Bases

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SUPPORTING INFORMATION

General Experimental

^1H , ^{13}C and ^{31}P NMR spectra were recorded on Varian Unity-400 (400 MHz ^1H , 100 MHz ^{13}C , 162 MHz ^{31}P), Unity-500 (500 MHz ^1H , 125 MHz ^{13}C , 202 MHz ^{31}P) and Varian Unity Inova 500 (500 MHz ^1H) spectrometers in deuteriochloroform unless otherwise stated. Data are reported in the following order: chemical shift in ppm (); 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. Mass spectrometry was performed by the University of Illinois Mass Spectrometry Center. Electron impact (EI) spectra were performed on a Finnigan-MAT CH-5 spectrometer, chemical ionization (CI) spectra were obtained on a VG 70-VSE spectrometer using methane as the carrier gas, and field ionization (FI) spectra were obtained from VG 70-VSE A spectrometer. Data are reported in the form of m/z (intensity relative to base peak = 100). Infrared spectra (IR) were recorded on a Mattson Galaxy 5020 spectrophotometer. Peaks are reported in cm^{-1} with indicated intensities: s (strong, 67 – 100% absorption), m (medium, 34 – 66%), w (weak, 0 – 33%). Optical rotations were measured on a Jasco DIP-360 digital polarimeter and are reported in the standard format for []. Elemental analyses were performed by the University of Illinois Microanalytical Service Laboratory.

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 Still¹ with 32-63 mm silica gel (Merck). Bulb-to-bulb distillations were performed on a Buchi GKR-50 Kugelrohr and boiling points (bp) correspond to uncorrected, air bath temperatures. Analytical supercritical fluid chromatography (SFC) was performed on a Berger Instruments packed-column SFC with built in photometric detector. Analytical columns used were Daicel Chiralpak AD and AS, Chiralcel OJ and OD and Regis (*R,R*)-Welk-01. Melting points (mp) were determined on a Thomas-Hoover melting point apparatus and are uncorrected.

All reactions were performed in oven (140 °C) and/or flame-dried glassware under an atmosphere of dry nitrogen, unless otherwise stated. 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.² “Brine” refers to a saturated solution of NaCl.

Literature Preparations

The following compounds were prepared by literature methods: (*S*)-*N*-Methoxy-*N*-methyl-3-hydroxy-2-methylpropionamide (**9**)³, (*S*)-*N*-Methoxy-*N*-methyl-3-triisopropylsilanyloxy-2-methylpropionamide (**12**)⁴, (*S*)-*N*-Methoxy-*N*-methyl-3-(*tert*-butyldimethylsilanyloxy)-2-methylpropionamide (**11**)⁵, (*S*)-1-triisopropylsilanyloxy-2-methyl-3-pentanone (**4**)⁴

The enolisation using LiTMP followed the procedure described by Collum *et al.*⁶ The enolization using DBU to synthesize (*Z*)-enol ethers followed the procedure described by Yamaguchi, *et. al.*⁷ *tert*-Butyltritylamine (TBTA) was prepared according to the procedure described by Corey, *et. al.*⁸

Experimental Procedures

(*S*)-1-*tert*-Butyldimethylsilyloxy-2-methyl-3-pentanone (**3**)

Amide **11** (9.50 g, 36.4 mmol) was dissolved in 100 mL of Et₂O at 0 °C. To this solution was added slowly a solution of ethyl magnesium chloride (2.0 M in Et₂O, 21.0 mL, 41.9 mmol, 1.15 equiv). The reaction mixture was stirred at 0 °C for 1 h, then was gradually warmed up to rt over 11 h. The reaction mixture was quenched by slow addition of sat. aq. ammonium chloride solution (ca. 50 mL). The layers were separated and the aqueous layer was extracted twice with 100 mL of Et₂O. The extracts were combined, dried over (MgSO₄), filtered, and concentrated to give 9.68 g of an oil. The crude product was purified by chromatography (pentane/ether, 3/1, SiO₂) and distillation to afford 7.84 g of **3** (34.0 mmol, 93%) as a clear, colorless liquid.

Data for **3**:

bp: 64 °C (0.5 mmHg)

¹H NMR: (500 MHz, CDCl₃)

3.74-3.58 (ABX, 2 H, H₂C(1)); 2.78 (sext, *J* = 6.1, 1 H, HC(2)); 2.52 (ABX, 2 H, H₂C(4)); 1.03 (t, *J* = 7.1, 3 H, H₃C(5)); 1.02 (d, *J* = 7.1, 3 H, H₃C(9)); 0.86 (s, 9 H, H₃C(8)); 0.03 (d, *J* = 7.1, 6 H, H₃C(6))

¹³C NMR: (126 MHz, CDCl₃)

214.70 (C(3)); 65.93 (C(1)); 48.49 (C(2)); 36.17 (C(4)); 25.99 (C(8)); 18.37 (C(7)); 13.28 (C(9)); 7.65 (C(5)); -5.38, -5.40 (C(6))

IR: (neat)

2956 (s); 2932 (s); 2886 (m); 2859 (m); 1718 (s); 1463 (m); 1388 (w); 1361 (w); 1257 (m); 1092 (s)

MS: (FI)

231.1 (1); 230.1 (1, M⁺); 175.1 (4); 174.1 (14); 173.1 (100); 122.1 (1)

Opt. Rot.: $[\alpha]_{\text{D}}^{24} +43.70$ ($c=1.0$, CHCl_3)

TLC: R_f 0.28 (hexane/EtOAc, 10/1) [silica gel, KMnO_4]

R_f 0.53 (pentane/ether, 3/1) [silica gel, KMnO_4]

Analysis: $\text{C}_{12}\text{H}_{26}\text{O}_2\text{Si}$ (230.42)

Calcd: C, 62.55; H, 11.37%

Found: C, 62.29; H, 11.52%

(2Z,4S)-5-(tert-Butyldimethylsilyloxy)-4-methyl-3-trimethylsilyloxy-2-pentene ((Z)-13)

(Using triethylamine/TMSOTf)

Trimethylsilyl triflate (TMSOTf, 0.93 mL, 5.17 mmol, 1.2 equiv) was dissolved in 15 mL of benzene at 0 °C. To the solution was added triethylamine (0.88 mL, 6.45 mmol, 1.5 equiv) and **3** (990 mg, 4.30 mmol). The reaction mixture was allowed to warm to rt and was stirred for 5 h. The reaction mixture was cooled using an ice bath and 15 mL of cold water was added. The product was extracted with 45 mL of pentane, and the pentane extracts were washed with sat. aq. CuSO_4 solution, 10 mL of water, and 10 mL of brine. The organic layer was dried (Na_2SO_4), filtered, and concentrated to yield 1.42 g of an oil. The crude product was purified by chromatography (hexane/ CH_2Cl_2 , 8/1, SiO_2) to afford 100 mg of (*E*)-**13** (0.33 mmol, 8%) and 688 mg of (*Z*)-**13** (2.27 mmol, 53%) both as clear, colorless oils. Ether (*Z*)-**13** was further purified by Kugelrohr distillation.

Data for (*Z*)-13:

bp: 170 °C (15 mmHg, ABT)

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)

152.85 (C(3)); 101.64 (C(2)); 66.40 (C(5)); 43.06 (C(4)); 25.90 (C(10)); 18.30 (C(9)); 15.26 (C(7)); 10.91 (C(1)); 0.70 (C(6)); -5.40 (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)

305.1 (2); 304.1 (12); 303.1 (31); 302.1 (100, M⁺); 245.0 (2); 198.8 (2)

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

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*)-13)

(Using TBTA/TMSCl)

To a solution of *tert*-butyltritylamine (2.05 g, 6.51 mmol, 1.5 equiv) in 30 mL of THF at 0 °C was added dropwise a solution of *n*-BuLi (1.54 M in hexane, 3.95 mL, 6.08 mmol, 1.4 equiv). The solution was stirred at 0 °C for 10 min then was cooled to -78 °C and TMSCl (0.83 mL, 6.51 mmol, 1.5 equiv) was added. A solution of ketone **3** in 5 mL of THF (1.00 g, 4.34

mmol) was added to the reaction mixture via a cannula. The reaction mixture was stirred for 30 min, then was gradually warmed to 0 °C and was poured into 15 mL of cold, deionized water. The layers were separated and the aqueous layer was extracted with 50 mL of pentane. The combined organic layers were washed with 20 mL of sat. aq. CuSO₄ solution, 10 mL of water, and 10 mL of brine, then were dried (Na₂SO₄), filtered, and concentrated. The crude product was purified by Kugelrohr distillation (175 °C ABT at 15 mmHg) and column chromatography (hexane/CH₂Cl₂, 5/1, SiO₂) to afford 727 mg of (*E*)-**13** (2.40 mmol, 55%) as a clear, colorless oil and 68 mg of **13** (0.22 mmol, 5%, 1/1, *Z/E* mixture) as colorless oil.

Data for (*E*)-**13**:

bp: 150 °C (1.0 mmHg, ABT)

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)

153.03 (C(3)); 100.27 (C(2)); 65.76 (C(5)); 36.69 (C(4)); 25.90 (C(10)); 18.29 (C(9)); 14.07 (C(7)); 11.45 (C(1)); 0.39 (C(6)); -5.38, -5.41 (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)

304.1 (10); 303.1 (30); 302.1 (100, M⁺); 199.0 (2); 198.6 (2)

Opt. Rot.: [α]_D²⁴ -8.99 (c=0.67, CHCl₃)

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)-14)

Trimethylsilyl chloride (TMSCl, 3.25 mL, 25.6 mmol, 1.2 equiv) was dissolved in 40 mL of CH₂Cl₂ at rt. To the solution was added DBU (3.84 mL, 25.6 mmol, 1.2 equiv) and **4** (5.80 g, 21.3 mmol). The reaction mixture was heated to reflux for 4 h. The reaction mixture was cooled using an ice bath and 40 mL of cold, sat. aq. NaHCO₃ solution was added. The product was extracted with 100 mL of pentane, and the pentane extracts were washed with 40 mL of brine. The organic layer was dried (Na₂SO₄), filtered, and concentrated to afford 5.50 g of an oil. The crude product was purified by chromatography (pentane/CH₂Cl₂, 5/1, SiO₂) to afford 5.03 g of (*Z*)-**14** (14.6 mmol, 69%) as clear, colorless oil. Silyl ether (*Z*)-**14** was subsequently purified by Kugelrohr distillation.

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

bp: 125 °C (0.05 mmHg, ABT)

 ^1H NMR: (500 MHz, CDCl_3)

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);

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

153.19 (C(3)); 101.86 (C(2)); 66.97 (C(5)); 43.58 (C(4)); 18.22 (C(9)); 15.55 (C(7)); 12.18 (C(8)); 11.14 (C(1)); 0.92 (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)

347.4 (2); 346.4 (12); 345.4 (31); 344.4 (100, M⁺);

Opt. Rot.: $[\alpha]_D^{24} +4.18$ (c=2.5, CHCl₃)

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 transilylation of 13: (2Z,4S)- 5-(*tert*-Butyl-dimethylsilyloxy)-4-methyl-3-trichlorosilyloxy-2-pentene ((Z)-5)

Silyl enol ether (Z)-**13** (908 mg, 3.00 mmol) was dissolved in 6 mL of Et₂O at 0 °C. To the solution was slowly added a solution of MeLi (1.5 M in Et₂O, 3.00 mL, 4.50 mmol, 1.5 equiv). The reaction mixture was stirred for 4.5 h at rt, then was cooled to −78 °C. The reaction mixture was transferred via cannula to a cold solution of silicon tetrachloride (3.45 mL, 30.0 mmol, 10 equiv) in 6 mL of Et₂O. The reaction mixture was stirred at −78 °C for 1 h and was gradually allowed to warm to rt. The precipitate was allowed to settle to the bottom of the flask, and the supernatant was transferred to another flask and was concentrated in vacuo. The product was purified by Kugelrohr distillation to afford 901 mg (2.48 mmol, 83%) of (Z)-**5** as a clear, colorless oil.

Data for (Z)-5:

bp: 150 °C (1.0 mmHg, ABT)

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))

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

150.80 (C(3)); 106.42 (C(2)); 65.31 (C(5)); 42.11 (C(4)); 25.83 (C(9)); 18.22 (C(8)); 14.85 (C(7)); 11.04 (C(1)); -5.46, -5.44 (C(7))

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

Following General Procedure I from (*E*)-**13** (705 mg, 2.33 mmol), MeLi (1.5 M in Et₂O, 2.33 mL, 3.49 mmol, 1.5 equiv) and SiCl₄ (2.67 mL, 23.3 mmol, 10 equiv) in 7 mL of ether, was obtained 705 mg (1.94 mmol, 83%) of (*E*)-**5** as a clear, colorless oil.

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

bp: 150 °C (1.0 mmHg, ABT)

^1H NMR: (CDCl_3 , 500 MHz)

5.10 (q, $J = 7.1$, 1 H, HC(2)); 3.60-3.43 (ABX, 2 H, H₂C(5)); 2.83 (sext, $J = 6.8$, 1 H, HC(4)); 1.61 (d, $J = 6.8$, 3 H, H₃C(1)); 0.99 (d, $J = 6.8$, 3 H, H₃C(6)); 0.88 (s, 9 H, H₃C(9)); 0.03 (d, $J = 2.6$, 6 H, H₃C(7))

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

150.78 (C(3)); 106.67 (C(2)); 65.00 (C(5)); 36.40 (C(4)); 25.84 (C(9)); 18.22 (C(8)); 13.63 (C(1)); 11.43 (C(6)); -5.47, -5.49 (C(7))

(2Z,4S)- 5-(Triisopropylsilyloxy)-4-methyl-3-trichlorosilyloxy-2-pentene ((Z)-6)

Following General Procedure I from (Z)-**14** (6.51 g, 18.9 mmol), MeLi (1.5 M in Et₂O, 18.9 mL, 28.4 mmol, 1.5 equiv) and SiCl₄ (21.7 mL, 189 mmol, 10 equiv) in 50 mL of THF, was obtained 6.14 g (12.7 mmol, 67%) of (Z)-**6** as a clear, colorless oil.

Data for (Z)-6:

bp: 115 °C (1.0 mmHg, ABT)

¹H NMR: (500 MHz, CDCl₃)

4.85 (qd, *J* = 6.9, 0.5, 1 H, HC(2)); 3.80-3.51 (ABX, 2 H, H₂C(5)); 2.43 (sext, *J* = 5.8, 1 H, HC(4)); 1.60 (dd, *J* = 6.9, 0.9, 3 H, H₃C(3)); 1.10 (d, *J* = 6.9, 3 H, H₃C(6)); 1.10 – 1.00 (m, 21 H, H₃C(8), HC(7))

¹³C NMR: (126 MHz, CDCl₃)

164.77 (C(3)); 106.62 (C(2)); 65.92 (C(5)); 42.59 (C(4)); 18.17 (C(9)); 15.13 (C(7)); 12.17 (C(8)); 11.26 (C(1))

General Procedure II: Aldol Addition of (Z)-5: (1R,2R,4S)-5-tert-Butyldimethylsilyloxy-2,4-dimethyl-1-hydroxy-1-phenyl-3-pentanone (*syn, syn*-16a)

Trichlorosilyl enol ether (Z)-**5** (364 mg, 1.00 mmol) was added to a solution of (*R,R*)-**1a** (37 mg, 0.10 mmol, 0.10 equiv) in 1.00 mL of CH₂Cl₂. The reaction mixture was cooled to -78

°C using an acetone/CO₂ bath, and PhCHO (102 μ L, 1.00 mmol, 1 equiv) was added by syringe. After stirring for 6 h, the reaction mixture was quenched by pouring into a vigorously stirred solution of cold, sat. aq. NaHCO₃ solution. The resulting slurry was stirred for 1 h and was 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 were dried (Na₂SO₄), filtered, and concentrated. The crude product was purified by column chromatography (pentane/ether, 3/1, SiO₂) to afford 241 mg (0.72 mmol, 72%) of **16a** as a clear, viscous oil.

Data for (syn,syn)-**16a**:

¹H NMR: (500 MHz, CDCl₃)

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, H₂C(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, H₃C(11)); 1.01 (d, *J* = 7.3, 3 H, H₃C(10)); 0.89 (s, 9H, H₃C(14)); 0.06 (d, *J* = 3.2, 6 H, H₃C(12))

¹³C NMR: (126 MHz, CDCl₃)

219.19 (C(3)); 141.65 (C(6)); 128.14 (C(8)); 127.06 (C(9)); 125.83 (C(7)); 71.86 (C(5)); 66.27 (C(1)); 52.79 (C(2)); 47.31 (C(4)); 25.85 (C(14)); 18.25 (C(13)); 13.17 (C(11)); 8.83 (C(10)); -5.57 (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)

336.2 (M⁺, 40); 279.1 (100); 265.1 (24); 230.2 (12); 173.1 (6); 159.1 (3); 106.1 (8)

Opt. Rot.: [α]_D²⁴ -9.16 (c=2.0, EtOH)

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*-16a)

Following General Procedure II from (*Z*)-**5** (364 mg, 1.00 mmol), PhCHO (102 μ L, 1.00 mmol, 1.0 equiv) and (*S,S*)-**1a** (37 mg, 0.10 mmol, 0.1 equiv) in 1 mL of CH₂Cl₂, was obtained 241 mg (0.72 mmol, 72%) of **16a** as a clear, colorless, viscous oil after column chromatography (pentane/ether, 3/1, SiO₂).

Data for (*syn,anti*)-**16a**:

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)

218.07 (C(3)); 142.06 (C(6)); 128.19 (C(8)); 127.31 (C(9)); 126.05 (C(7)); 73.51 (C(5)); 65.29 (C(1)); 52.76 (C(2)); 48.03 (C(4)); 25.79 (C(14)); 18.19 (C(13)); 12.92 (C(11)); 9.89 (C(10)); -5.64 (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)336.2 (M^+ , 58); 279.1 (100); 230.2 (13); 173.1 (5); 106.1 (6)Opt. Rot.: $[\alpha]_D^{24} + 49.34$ (c=3.8, EtOH)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: $C_{19}H_{32}O_3Si$ (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-17a)

Following General Procedure II from (*Z*)-**6** (479 mg, 1.00 mmol), PhCHO (102 μ L, 1.00 mmol, 1.0 equiv) and (*R,R*)-**1a** (37 mg, 0.10 mmol, 0.1 equiv) in 1 mL of CH_2Cl_2 for 8 h, was obtained 319 mg (0.84 mmol, 84%) of **17a** as a clear, colorless, viscous oil after column chromatography (pentane/ether, 5/1, SiO_2).

Data for (syn,syn)-17a: ^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))

¹³C NMR: (126 MHz, CDCl₃)
 219.76 (C(3)); 141.86 (C(6)); 128.38 (C(8)); 127.29 (C(9)); 126.06 (C(7)); 72.08 (C(5)); 66.96 (C(1)); 53.10 (C(4)); 47.72 (C(2)); 18.18 (C(13)); 13.54 (C(11)); 12.04 (C(12)); 9.05 (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)
 379.4 (M⁺, 6); 337.3 (7); 336.3 (26); 335.3 (100)

Opt. Rot.: [α]_D²⁴ -10.84 (c=1.01, EtOH)

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*-17a**)**

Following General Procedure II from (*Z*)-**6** (479 mg, 1.00 mmol), PhCHO (102 μL, 1.00 mmol, 1.0 equiv) and (*S,S*)-**1a** (37 mg, 0.10 mmol, 0.1 equiv) in 1 mL of CH₂Cl₂ for 8 h, was obtained 310 mg (0.82 mmol, 82%) of **17a** as a clear, colorless, viscous oil after column chromatography (pentane/ether, 5/1, SiO₂).

Data for (*syn,anti*)-17a**:**

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)

218.30 (C(3)); 141.93 (C(6)); 128.23 (C(8)); 127.33 (C(9)); 126.01 (C(7)); 73.35 (C(5)); 65.64 (C(1)); 52.92 (C(4)); 48.28 (C(2)); 17.92 (C(13)); 13.17 (C(11)); 11.83 (C(12)); 9.62 (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)

379.2 (M⁺, 5); 337.2 (7); 336.2 (25); 335.2 (100); 272.1 (10); 229.1 (14); 157.4 (5); 156.9 (7); 156.7 (7); 126.6 (7); 156.5 (6); 156.3 (7); 106.0 (6)

Opt. Rot.: $[\alpha]_D^{24} + 92.03$ (c=0.59, EtOH)

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: C₂₂H₃₈O₃Si (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*-17b)

Following General Procedure II from (*Z*)-**6** (472 mg, 1.00 mmol), 1-naphthaldehyde (136 μ L, 1.00 mmol, 1.0 equiv), (*R,R*)-**1a** (37 mg, 0.10 mmol, 0.1 equiv) and tetrabutylammonium iodide (TBAI) (73.9 mg, 0.20 mmol, 0.2 equiv) in 1 mL of CH_2Cl_2 for 8 h, was obtained 313 mg (0.71 mmol, 71%) of **17b** as a clear, colorless, viscous oil after column chromatography (pentane/ether, 5/1, SiO_2). Analytically pure material was obtained by recrystallization from pentane.

Data for (*syn,syn*)-**17b**:

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, $\text{H}_3\text{C}(13)$, $\text{H}_3\text{C}(16)$, HC(18), $\text{H}_3\text{C}(19)$)

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

219.46 (C(3)); 136.77 (C(6)); 133.97 (C(12)); 129.94 (C(7)); 129.45 (C(11)); 127.97 (C(13)); 126.23 (C(10)); 125.72 (C(9)); 125.56 (C(14)); 124.79 (C(15)); 122.62 (C(8)); 68.74 (C(1)); 66.71 (C(5)); 51.11 (C(4)); 48.15 (C(2)); 18.26 (C(19)); 13.97 (C(17)); 12.19 (C(18)); 9.61 (C(16))

IR: (CH_2Cl_2)

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)429.2 (14); 428.2 (M^+ , 37); 385.2 (12); 336.2 (25); 272.1 (14); 230.0 (17); 229.1 (100); 155.9 (69)Opt. Rot.: $[\alpha]_D^{24} + 2.1$ ($c=0.48$, EtOH)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: $C_{26}H_{40}O_3Si$ (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*)-17b

Following General Procedure II from (*Z*)-**6** (501 mg, 1.00 mmol, 19% bisenoxysilane), 1-naphthaldehyde (136 μ L, 1.00 mmol, 1.0 equiv), (*S,S*)-**1a** (37 mg, 0.10 mmol, 0.1 equiv) and TBAI (73.9 mg, 0.20 mmol, 0.2 equiv) in 1 mL of CH_2Cl_2 for 8 h, was obtained 335 mg (0.78 mmol, 78%) of **17b** as a clear, colorless, viscous oil after column chromatography (pentane/ether, 5/1, SiO_2).

Data for (*syn,anti*)-17b: 1H NMR: (500 MHz, $CDCl_3$)

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, $H_2C(5)$); 3.57 (d, $J = 2.2$, 1 H, HO); 3.20 (qd, $J = 7.0, 1.7$, 1 H, HC(2)); 3.00 (sextd, $J = 7.1, 1.7$, 1 H, HC(4)); 1.12 - 0.98 (m, 27 H, $H_3C(17)$, $H_3C(19)$, HC(18), $H_3C(16)$)

Data for (syn,syn)-17c:¹H NMR: (500 MHz, CDCl₃)

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, H₂C(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, H₃C(11)); 1.11 – 1.02 (m, 24 H, H₃C(9), H₃C(10), HC(8))

¹³C NMR: (126 MHz, CDCl₃)

219.39 (C(3)); 137.07 (C(12)); 130.91 (C(6)); 129.19 (C(7)); 128.76 (C(14)); 127.75 (C(15)); 126.64 (C(13)); 71.48 (C(1)); 67.19 (C(5)); 51.51 (C(4)); 47.61 (C(2)); 18.15 (C(9)); 13.40 (C(10)); 12.01 (C(8)); 9.64 (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)

406.2 (9); 405.2 (34); 404.2 (M⁺, 100); 335.2 (9); 272.1 (8); 229.1 (24); 132.0 (48)

Opt. Rot.: [$\alpha \right]_D^{24} + 20.0$ (c = 0.73, CH₂Cl₂)

[$\alpha \right]_D^{24} - 47.8$ (c = 0.73, EtOH)

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: C₂₄H₄₀O₃Si (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*-17c)

Following General Procedure II from (Z)-**6** (436 mg, 1.00 mmol), cinnamaldehyde (126 μ L, 1.00 mmol, 1.0 equiv), (*S,S*)-**1a** (37 mg, 0.10 mmol, 0.1 equiv) and TBAI (73.9 mg, 0.20 mmol, 0.2 equiv) in 1 mL of CH₂Cl₂ for 10 h, was obtained 303 mg (0.75 mmol, 75%) of **17c** as a clear, colorless, viscous oil after column chromatography (pentane/ether, 3/1, SiO₂).

Data for (syn,anti)-17c:

¹H NMR: (500 MHz, CDCl₃)

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, H₂C(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, H₃C(11)); 1.16 – 1.04 (m, 24 H, H₃C(9), H₃C(10), HC(8))

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

218.13 (C(3)); 137.07 (C(12)); 130.92 (C(6)); 129.14 (C(7)); 128.54 (C(14));
127.60 (C(15)); 126.43 (C(13)); 72.33 (C(1)); 65.85 (C(5)); 50.52 (C(4)); 48.14
(C(2)); 17.94 (C(9)); 15.27 (C(10)); 11.84 (C(8)); 9.91 (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)

405.2 (12); 404.2 (M⁺, 34); 287.1 (11); 273.1 (15); 269.1 (15); 261.1 (69); 245.1 (30); 229.1 (100); 217.0 (83); 131.9 (17); 106.0 (28)

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

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

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*-17d**)**

Following General Procedure II from (*Z*)-**6** (472 mg, 1.00 mmol), crotonaldehyde (83 μL , 1.00 mmol, 1.0 equiv), (*R,R*)-**1a** (37 mg, 0.10 mmol, 0.1 equiv) and TBAI (73.9 mg, 0.20 mmol, 0.2 equiv) in 1 mL of CH_2Cl_2 for 6 h, was obtained 310 mg (0.90 mmol, 90%) of **17d** as a clear, colorless, viscous oil after column chromatography (pentane/ether, 3/1, SiO_2). The diastereomeric ratio of **17d** was determined by ^1H NMR integration of HC(5).

Data for (*syn, syn*)-**17d**:

^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, $\text{H}_3\text{C}(10)$, $\text{H}_3\text{C}(12)$, HC(9))

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

219.01 (C(3)); 130.39 (C(7)); 127.32 (C(6); 71.60 (C(1)); 66.61 (C(5)); 51.17 (C(4)); 47.47 (C(2)); 17.81 (C(10)); 17.65 (C(8)); 13.12 (C(11)); 11.72 (C(9)); 9.60 (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: (FI)

343.2 (M⁺, 5); 301.1 (6); 300.2 (25); 299.2 (100); 272.1 (6); 175.8 (6); 175.6 (9);
175.4 (10); 175.3 (8); 175.1 (6)

Opt. Rot.: $[\alpha]_{\text{D}}^{24} + 5.06$ (c = 0.23, EtOH)

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*-17d)

Following General Procedure II from (*Z*)-**6** (472 mg, 1.00 mmol), crotonaldehyde (83 μ L, 1.00 mmol, 1.0 equiv), (*S,S*)-**1a** (37 mg, 0.10 mmol, 0.1 equiv) and TBAI (73.9 mg, 0.20 mmol, 0.2 equiv) in 1 mL of CH₂Cl₂ for 6 h, was obtained 293 mg (0.85 mmol, 85%) of **17d** as a clear, colorless, viscous oil after column chromatography (pentane/ether, 3/1, SiO₂). The diastereomeric ratio was determined by ¹H NMR integration of HC(5).

Data for (syn,anti)-17d: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)

217.83 (C(3)); 130.85 (C(7)); 127.63 (C(6)); 72.70 (C(1)); 65.82 (C(5)); 50.79 (C(4)); 48.24 (C(2)); 17.84 (C(10)); 17.62 (C(8)); 13.11 (C(11)); 11.75 (C(9)); 9.60 (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)

342.2 (M⁺, 1); 301.2 (6); 300.1 (23); 299.1 (100); 229.1 (15); 175.4 (7)

Opt. Rot.: $[\alpha]_D^{24} + 81.7$ (c = 0.35, EtOH)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*-17e**)**

Following General Procedure II from (*Z*)-**6** (472 mg, 1.00 mmol), tiglic aldehyde (96 μL , 1.00 mmol, 1.0 equiv), (*R,R*)-**1a** (37 mg, 0.10 mmol, 0.1 equiv) and TBAI (73.9 mg, 0.20 mmol, 0.2 equiv) in 1 mL of CH_2Cl_2 for 7 h, was obtained 303 mg (0.85 mmol, 85%) of **17e** as a clear, colorless, viscous oil after column chromatography (pentane/ether, 5/1, SiO_2). The diastereomeric ratio was determined by ^1H NMR integration of HC(5).

Data for (*syn, syn*)-**17e**:

^1H NMR: (500 MHz, CDCl_3)

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, $\text{H}_2\text{C}(1)$); 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, $\text{H}_3\text{C}(8)$); 1.56 (s, 3 H, $\text{H}_3\text{C}(13)$); 1.10 – 1.02 (m, 27 H, $\text{H}_3\text{C}(11)$, $\text{H}_3\text{C}(10)$, $\text{H}_3\text{C}(12)$, HC(9))

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

219.22 (C(3)); 133.69 (C(7)); 119.87 (C(6)); 73.77 (C(1)); 66.51 (C(5)); 48.61 (C(4)); 47.53 (C(2)); 17.88 (C(10)); 13.42 (C(8)); 13.27 (C(13)); 12.90 (C(11)); 11.78 (C(9)); 8.96 (C(12))

IR: (CHCl_3)

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

MS: (FI)

357.3 (M^+ , 7); 311.2 (5); 310.3 (4); 231.2 (5); 230.2 (18); 229.2 (100)

Opt. Rot.: $[\alpha]_{\text{D}}^{24} + 5.71$ ($c = 0.20$, EtOH)

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*-17e)

Following General Procedure II from (Z)-**6** (472 mg, 1.00 mmol), tiglic aldehyde (96 μ L, 1.00 mmol, 1.0 equiv), (*S,S*)-**1a** (37 mg, 0.10 mmol, 0.1 equiv) and TBAI (73.9 mg, 0.20 mmol, 0.2 equiv) in 1 mL of CH₂Cl₂ for 7 h, was obtained 286 mg (0.80 mmol, 80%) of **17e** as a clear, colorless, viscous oil after column chromatography (pentane/ether, 5/1, SiO₂). The diastereomeric ratio was determined by ¹H NMR integration of HC(5).

Data for (syn,anti)-17e:

 ^1H NMR: (500 MHz, CDCl_3)

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))

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

217.92 (C(3)); 134.37 (C(6)); 120.43 (C(7)); 73.79 (C(5)); 66.02 (C(1)); 48.61 (C(4)); 48.08 (C(2)); 17.86 (C(10)); 13.40 (C(8)); 13.15 (C(13)); 12.86 (C(11)); 11.78 (C(9)); 9.49 (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)

356.3 (M⁺, 1); 311.3 (5); 232.2(5); 231.2 (6); 230.2 (18); 229.2 (100)

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

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%

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