Chiral Silanes via Asymmetric Hydrosilylation with Catalytic CuH

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Supporting Information

General. Reactions were performed in oven-dried glassware under an argon atmosphere containing a Teflon coated stir bar and dry septum. THF and toluene were freshly distilled from Na/benzophenone ketyl prior to use. All commercially available reagents were distilled either from CaH₂ or molecular sieves under an inert atmosphere before use. (*R,S*)-PPF-P(*t*-Bu)₂ was generously supplied by Solvias. (*R*)-(-)-DTBM-SEGPPOS was generously provided by Takasago International Corp. GC analyses were carried out using an HP-5 capillary column (0.25 μ x 30 m; cross-linked 5% PHME siloxane) and a time program beginning with 5 min at 50 °C followed by 20 °C/min ramp to 280 °C, then 20 min at this temp. Column chromatography was performed using Davisil Grade 633 Type 60A silica gel. TLC analyses were performed on commercial Kieselgel 60 F254 silica gel plates. NMR spectra were obtained on Varian Inova systems using CDCl₃ as solvent, with proton and carbon resonances at 400 MHz and 100 MHz, respectively. FTIR spectra were obtained on an ATI Mattson Infinity series spectrometer neat on NaCl plates or KBR pellets and are reported in cm⁻¹. Mass spectral data were acquired on a VF Autospec or an analytical VG-70-250 HF instrument.

Representative Procedure for the catalytic asymmetric CuH hydrosilylation of β -silyl enoates.

(*S*)-Ethyl 3-(dimethylphenylsilyl)butanoate (Table 1, entry 1a); Method A. To a 50 mL round bottomed flask, flame dried and purged with argon, was added CuCl (1.5 mg, 0.015 mmol), (*R,S*)-PPF-P(*t*-Bu)₂ (2.7 mg, 0.005 mmol), and NaO-*t*-Bu (1.4 mg, 0.015 mmol). Toluene (1 mL) was added and the solution was stirred at 0 °C for 30 min, followed by addition of *t*-BuOH (52 μ L, 0.55 mmol). The solution was cooled to -30 °C before addition of PMHS (65 μ L, 1.0 mmol) and was further stirred at -30 °C for 10 min. Enolate (124 mg, 0.50 mmol) was added *via* syringe. The mixture was stirred at -30 °C until complete by TLC (9 h; ether/hexanes = 1/9). The reaction was quenched with sat. aq. NaHCO₃ and diluted with ether. The aqueous layer was extracted with ether and the organic layer was washed with brine, dried over anhydrous MgSO₄, filtered, and concentrated by rotary evaporation. The residue was purified by flash chromatography (ether/hexanes = 1/10) to afford the title product (120 mg, 96%) as a clear oil. The de was determined by ¹H NMR of the corresponding imide derivative to be 95%. R_f = 0.36 (ether/hexanes = 1/9); IR (neat): 3070, 2956, 1734, 1428, 1368, 1208 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 0.29 (s, 6H), 0.98 (d, *J* = 7.4 Hz, 3H), 1.24 (t, *J* = 7.1 Hz, 3H), 1.45 (m, 1H), 2.05 (dd, *J* = 15.2, 11.4 Hz, 1H), 2.38 (dd, *J* = 15.2, 4.0 Hz, 1H), 4.09 (q, *J* = 7.1 Hz, 2H), 7.33-7.40 (m, 3H), 7.47-7.54 (m, 2H); ¹³C NMR (100 MHz, CDCl₃) δ -5.14, -4.84, 14.44, 14.63, 16.66, 37.04, 60.37, 127.96, 129.26, 134.11, 137.49, 174.14; EIMS *m/z* (%): 250(5.4)[M⁺], 235(23), 205(16), 145(27), 135(100); HREIMS calcd for C₁₄H₂₂O₂Si: 250.1389; found 250.1390[M⁺].

(Table 1, entry 1b) Method B. To a 50 mL round bottomed flask, flame dried and purged with argon, was added (Ph₃P)CuH (4.9 mg, 0.015 mmol) and (*R*)-DTBM-SEGPPOS (5.9 mg, 0.005 mmol). Toluene (1 mL) was added and the solution cooled to -30 °C. Enolate (124 mg, 0.50 mmol) was introduced *via* syringe followed by PMHS (65 μ L, 1.0 mmol) and *t*-BuOH (52 μ L, 0.55 mmol). The mixture was stirred at -30 °C until complete by TLC (7.5 h; ether/hexanes = 1/9). The reaction was quenched with sat. aq. NaHCO₃ and diluted with ether. The aqueous layer was extracted with ether and the combined organic layers was washed with brine, dried over anhydrous MgSO₄, filtered, and concentrated by rotary evaporation. The residue was purified by flash chromatography (ether/hexanes = 1/15) to afford the (*S*)-product (121 mg, 97%) as a clear oil. The de was determined by ¹H NMR of the corresponding imide derivative to be 24%. Spectroscopic data matched those from experiments above.

Table 1, entry 1c. According to method A, the following amounts were used: CuCl (0.99 mg, 0.01 mmol), (*R,S*)-PPF-P(*t*-Bu)₂ (0.54 mg, 0.001 mmol), NaO-*t*-Bu (0.96 mg, 0.01 mmol), toluene (1.43 mL), PMHS (130 μ L, 2.0 mmol), enolate **Z-1** (R = Me, R' = OEt, neat, 248 mg, 1.0 mmol), and *t*-BuOH (104 μ L, 1.1 mmol). The (*S*)-product ester (225 mg, 90%) was isolated as a clear oil after a reaction time of

36 h at -20°C . The de was determined by ^1H NMR of the corresponding imide derivative to be 92%. Spectroscopic data matched those from experiments above.

(*S*)-Ethyl 3-(dimethylphenylsilyl)-3-(phenyl)propanoate (Table 1, entry 2a). According to method A, the following amounts were used: CuCl (1.5 mg, 0.015 mmol), (*R,S*)-PPF-P(*t*-Bu)₂ (2.7 mg, 0.005 mmol), NaO-*t*-Bu (1.4 mg, 0.015 mmol), toluene (1.43 mL), PMHS (65 μL , 1.0 mmol), enoate (155 mg, 0.50 mmol), and *t*-BuOH (52 μL , 0.55 mmol). The product ester (139 mg, 89%) was isolated as a clear oil after a reaction time of 15 h at -30°C . The de was determined by ^1H NMR of the corresponding imide derivative to be 91%; R_f = 0.22 (ether/hexanes = 1/10), IR (neat): 3069, 2958, 1733, 1600, 1428, 1250, 1164, 1114 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 0.22 (s, 3H), 0.26 (s, 3H), 1.04 (t, J = 7.1 Hz, 3H), 2.63 (dd, J = 15.6, 4.6 Hz, 1H), 2.75 (dd, J = 15.6, 11.3 Hz, 1H), 2.85 (dd, J = 11.3, 4.6 Hz, 1H), 3.92 (m, 2H), 6.95 (d, J = 7.8 Hz, 2H), 7.09 (t, J = 7.8 Hz, 1H), 7.20 (t, J = 7.8 Hz, 2H), 7.32-7.43 (m, 5H); ^{13}C NMR (100 MHz, CDCl_3) δ -5.36, -3.98, 14.12, 32.42, 35.02, 60.29, 125.03, 127.70, 127.84, 128.12, 129.41, 134.24, 136.57, 141.83, 173.02; EIMS m/z (%): 313(5)[M^+], 312(20), 137(13), 136(13), 135(100), 105(10), 104(21), 43(10); HREIMS calcd for $\text{C}_{19}\text{H}_{24}\text{O}_2\text{Si}$: 312.1546; found 312.1545[M^+].

Table 1, entry 2b. According to method B, the following amounts were used: (Ph_3P)CuH (2.7 mg, 0.0083 mmol), (*R*)-DTBM-SEGPPOS (0.98 mg, 0.00083 mmol), toluene (1.19 mL), enoate (259 mg, 0.83 mmol), PMHS (108 μL , 1.67 mmol), and *t*-BuOH (87 μL , 0.92 mmol). The (*S*)-product ester (236 mg, 90%) was isolated as a clear oil after a reaction time of 48 h at -20°C . The de was determined by ^1H NMR of the corresponding imide derivative to be 20%. Spectroscopic data matched those from experiments above.

(*S*)-Octyl 3-(dimethylphenylsilyl)butanoate (Table 1, entry 3a). According to method A, the following amounts were used: CuCl (1.5 mg, 0.015 mmol), (*R,S*)-PPF-P(*t*-Bu)₂ (2.7 mg, 0.005 mmol), NaO-*t*-Bu (1.4 mg, 0.015 mmol), toluene (1 mL), PMHS (65 μL , 1.0 mmol), enoate (166 mg, 0.5 mmol), and *t*-BuOH (52 μL , 0.55 mmol). The product ester (159 mg, 95%) was isolated as a clear oil after a reaction time of 9.5 h at -30°C . The de was determined by ^1H NMR of the corresponding imide derivative to be 92%; R_f = 0.31 (ether/hexanes = 1/19); IR (neat): 3070, 2955, 2929, 1734, 1428, 1250, 1208 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 0.29 (s, 6H), 0.89 (t, J = 6.9 Hz, 3H), 0.98 (d, J = 7.4 Hz, 3H), 1.20-1.38 (m, 10H), 1.45 (m, 1H), 1.59 (m, 2H), 2.05 (dd, J = 15.2, 11.3 Hz, 1H), 2.38 (dd, J = 15.2, 4.0 Hz, 1H), 4.02 (t, J = 6.8 Hz, 2H), 7.33-7.40 (m, 3H), 7.48-7.54 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ -5.33, -5.04, 14.06, 14.45, 16.47, 22.60, 25.90, 28.60, 29.14, 29.16, 31.74, 36.84, 64.43, 127.75, 129.05, 133.90, 137.30, 174.05; EIMS m/z (%): 334(2.9)[M^+], 319(14), 207(95), 145(98), 135(100); HREIMS calcd for $\text{C}_{20}\text{H}_{34}\text{O}_2\text{Si}$: 334.2328; found 334.2335[M^+].

Table 1, entry 3b. According to method B, the following amounts were used: (Ph_3P)CuH (4.9 mg, 0.015 mmol), (*R*)-DTBM-SEGPPOS (5.9 mg, 0.005 mmol), toluene (1 mL), enoate (166 mg, 0.50 mmol), PMHS (65 μL , 1.0 mmol), and *t*-BuOH (52 μL , 0.55 mmol). The (*S*)-product ester (153 mg, 92%) was isolated as a clear oil after a reaction time of 7 h at -30°C . The de was determined by ^1H NMR of the corresponding imide derivative to be 15%. Spectroscopic data matched those from experiments above.

(*R*)-Ethyl 3-(dimethylphenylsilyl)butanoate (Table 1 entry 4a). According to method A, the following amounts were used: CuCl (1.5 mg, 0.015 mmol), (*R,S*)-PPF-P(*t*-Bu)₂ (2.7 mg, 0.005 mmol), NaO-*t*-Bu (1.4 mg, 0.015 mmol), toluene (1 mL), PMHS (65 μL , 1.0 mmol), enoate (124 mg, 0.50 mmol), and *t*-BuOH (52 μL , 0.55 mmol). The product ester (123 mg, 98%) was isolated as a clear oil after a reaction time of 18 h at -78°C . The de was determined by ^1H NMR of the corresponding imide

derivative to be >95%. Spectroscopic data matched those from experiments above.

Table 1, entry 4b. According to method A, the following amounts were used: CuCl (1.5 mg, 0.015 mmol), (*S,R*)-PPF-P(*t*-Bu)₂ (2.7 mg, 0.005 mmol), NaO-*t*-Bu (1.4 mg, 0.015 mmol), toluene (1 mL), PMHS (65 μ L, 1.0 mmol), enoate (124 mg, 0.50 mmol), and *t*-BuOH (52 μ L, 0.55 mmol). The (*S*)-product ester (119 mg, 95%) was isolated as a clear oil after a reaction time of 24 h at -78°C . The de was determined by ^1H NMR of the corresponding imide derivative to be >95%. Spectroscopic data matched those from experiments above.

Table 1, entry 4c. According to method B, the following amounts were used: (Ph₃P)CuH (4.9 mg, 0.015 mmol), (*R*)-DTBM-SEPHOS (5.9 mg, 0.005 mmol), toluene (1 mL), enoate (124 mg, 0.50 mmol), PMHS (65 μ L, 1.0 mmol), and *t*-BuOH (52 μ L, 0.55 mmol). The (*R*)-product ester (122 mg, 98%) was isolated as a clear oil after a reaction time of 5 h at -30°C . The de was determined by ^1H NMR of the corresponding imide derivative to be 83%. Spectroscopic data matched those from experiments above.

(*R*)-Methyl 3-(dimethylphenylsilyl)butanoate (Table 1, entry 5). According to method A, the following amounts were used: CuCl (1.5 mg, 0.015 mmol), (*R,S*)-PPF-P(*t*-Bu)₂ (2.7 mg, 0.005 mmol), NaO-*t*-Bu (1.4 mg, 0.015 mmol), toluene (1 mL), PMHS (65 μ L, 1.0 mmol), enoate (117 mg, 0.50 mmol), and *t*-BuOH (52 μ L, 0.55 mmol). The product ester (115 mg, 97%) was isolated as a clear oil after a reaction time of 12 h at -60°C . The de was determined by ^1H NMR of the corresponding imide derivative to be >95%; R_f = 0.32 (ethyl acetate/hexanes = 1/20); IR (neat): 3071, 2953, 2876, 1738, 1428, 1251, 1211, 1153, 1111, 1005 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 0.29 (s, 6H), 0.98 (d, J = 7.4 Hz, 3H), 1.45 (m, 1H), 2.08 (dd, J = 15.2, 11.4 Hz, 1H), 2.41 (dd, J = 15.2, 4.0 Hz, 1H), 3.63 (s, 3H), 7.35-7.39 (m, 3H), 7.48-7.53 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ -5.19, -4.82, 14.70, 16.70, 36.83, 51.61, 127.98, 129.30, 134.10, 137.43, 174.61; EIMS m/z (%): 236(10)[M^+], 221(29), 159(13), 151(23), 145(12), 136(13), 135(100), 105(10), 89(12), 42(10); HREIMS calcd for $\text{C}_{13}\text{H}_{20}\text{O}_2\text{Si}$: 236.1232; found 236.1232[M^+].

(*R*)-Methyl 6-(4-methoxybenzyloxy)-3-(dimethylphenylsilyl)hexanoate (Table 1, entry 6). According to method A, the following amounts were used: CuCl (1.5 mg, 0.015 mmol), (*R,S*)-PPF-P(*t*-Bu)₂ (2.7 mg, 0.005 mmol), NaO-*t*-Bu (1.4 mg, 0.015 mmol), toluene (1 mL), PMHS (65 μ L, 1.0 mmol), enoate (199 mg, 0.50 mmol), and *t*-BuOH (52 μ L, 0.55 mmol). The product ester (166 mg, 83%) was isolated as a clear oil after a reaction time of 24 h at -30°C . The de was determined by ^1H NMR of the corresponding imide derivative to be >95%; R_f = 0.25 (ethyl acetate/hexanes = 1/10); IR (neat): 3071, 3000, 2950, 2854, 1736, 1613, 1512 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 0.30 (s, 3H), 0.31 (s, 3H), 1.26-1.68 (m, 5H), 2.25 (dd, J = 15.6, 8.1 Hz, 1H), 2.36 (dd, J = 15.6, 5.7 Hz, 1H), 3.37 (t, J = 6.3 Hz, 2H), 3.57 (s, 3H), 3.81 (s, 3H), 4.38 (s, 2H), 6.88 (d, J = 8.7 Hz, 2H), 7.24 (d, J = 8.6 Hz, 2H), 7.33-7.39 (m, 3H), 7.49-7.53 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ -4.23, -3.94, 21.8, 26.8, 29.0, 34.8, 51.6, 55.4, 70.1, 72.5, 113.8, 127.9, 129.2, 129.3, 130.8, 134.1, 137.9, 159.2, 174.8; EIMS m/z (%): 400(1)[M^+], 279(6), 221(10), 135(60), 121(100), 77(5); HRESIMS calcd for $\text{C}_{23}\text{H}_{32}\text{NaO}_4\text{Si}$: 423.1968; found 423.1975[$\text{M}^+ + \text{Na}$].

(*R*)-Methyl 3-(dimethylphenylsilyl)-3-(3,4,5-trimethoxyphenyl)propanoate (Table 1, entry 7). According to method A, the following amount were used: CuCl (1.5 mg, 0.015 mmol), (*R,S*)-PPF-P(*t*-Bu)₂ (2.7 mg, 0.005 mmol), NaO-*t*-Bu (1.4 mg, 0.015 mmol), toluene (0.5 mL), PMHS (65 μ L, 1.0 mmol), enoate (120 mg, 0.31 mmol), and *t*-BuOH (52 μ L, 0.55 mmol). The product ester (118 mg, 98%) was isolated as a clear oil after a reaction time of 24 h at 0°C ; R_f = 0.30 (ethyl acetate/hexanes =

3/7). The ee was determined on a Daicel Chiralpak OD-H HPLC column with hexane : 2-propanol = 100 : 5, flow = 5.0 mL/min. Retention times: 19.6 min [(*R*)-enantiomer], 21.4 min [(*S*)-enantiomer]; 81.6% ee; IR (neat): 2953, 1736, 1586, 1455, 1245 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 0.25 (s, 3H), 0.26 (s, 3H), 2.67-2.78 (m, 3H), 3.53 (s, 3H), 3.68 (s, 6H), 3.80 (s, 3H), 6.04 (s, 2H), 7.31-7.39 (m, 5H); ¹³C NMR (100 MHz, CDCl₃) δ -4.83, -4.20, 32.74, 34.86, 51.68, 55.98, 61.06, 104.54, 127.89, 129.56, 134.44, 135.42, 136.55, 137.55, 152.83, 173.68; EIMS *m/z*(%): 388(16)[M⁺], 387(36), 373(20), 372(46), 330(18), 194(10), 193(37), 178(12), 135(15), 134(100); HREIMS calcd for C₂₁H₂₈O₅Si: 388.1706; found 388.1711[M⁺].

(*R*)-Methyl 3-(dimethylphenylsilyl)-3-(4-chlorophenyl)propanoate (Table 1, entry 8). According to method A, the following amounts were used: CuCl (1.5 mg, 0.015 mmol), (*R,S*)-PPF-P(*t*-Bu)₂ (2.7 mg, 0.005 mmol), NaO-*t*-Bu (1.4 mg, 0.015 mmol), toluene (0.5 mL), PMHS (65 μL, 1.0 mmol), enoate (100 mg, 0.3 mmol), and *t*-BuOH (52 μL, 0.55 mmol). The product ester (82 mg, 82%) was isolated as a clear oil after a reaction time of 24 h at -30 °C. R_f = 0.40 (CH₂Cl₂/hexanes = 1/1). The ee was determined on a Daicel Chiralpak OD-H HPLC column with hexane : 2-propanol = 100 : 1, flow = 5.0 mL/min. Retention times: 20.2 min [(*R*)-enantiomer], 21.5 min [(*S*)-enantiomer]; 97.3% ee; IR (neat): 3069, 2953, 1737, 1428, 1250 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 0.23 (s, 3H), 0.25 (s, 3H), 2.61-2.85 (m, 3H), 3.49 (s, 3H), 6.86 (d, *J* = 8.0 Hz, 2H), 7.16 (d, *J* = 8.0 Hz, 2H) 7.34-7.40 (m, 5H); ¹³C NMR (100 MHz, CDCl₃) δ -5.29, -4.07, 32.08, 34.77, 51.83, 128.06, 128.44, 128.94, 129.73, 130.78, 134.33, 136.11, 140.56, 173.45; EIMS *m/z* (%): 332(11.9)[M⁺], 151(11.3), 140(11.6), 138(35.5), 136(15.7), 135(100); HREIMS calcd for C₁₈H₂₁O₂SiCl: 332.0999; found 332.0996[M⁺].

(*R*)-Ethyl 3-(dimethylphenylsilyl)-4-(phenyl)butanoate (Table 1, entry 9). According to method A, the following amount were used: CuCl (1.5 mg, 0.015 mmol), (*R,S*)-PPF-P(*t*-Bu)₂ (2.7 mg, 0.005 mmol), NaO-*t*-Bu (1.4 mg, 0.015 mmol), toluene (0.5 mL), PMHS (65 μL, 1.0 mmol), enoate (100 mg, 0.31 mmol), and *t*-BuOH (52 μL, 0.55 mmol). The product ester (76 mg, 76%) was isolated as a clear oil after a reaction time of 24 h at 0 °C. R_f = 0.40 (ether/hexanes = 1/9). The ee was determined on a Daicel Chiralpak OD-H HPLC column with hexane : 2-propanol = 100 : 1, flow = 5.0 mL/min. Retention times: 6.2 min [(*R*)-enantiomer], 7.1 min [(*S*)-enantiomer]; 98.5% ee. IR (neat): 2955, 1731, 1245 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 0.29 (s, 3H), 0.30 (s, 3H), 1.15 (t, *J* = 6.8 Hz, 3H), 1.78-1.85 (m, 1H), 2.19-2.5 (m, 2H), 2.75 (dd, *J* = 10.4, 14Hz, 1H), 2.83 (dd, *J* = 8.8, 4.8Hz, 1H), 3.86 (q, *J* = 7.2 Hz, 2H), 7.14-7.27 (m, 5H), 7.37-7.39 (m, 3H), 7.53-7.55 (m, 2H); ¹³C NMR (100 MHz, CDCl₃) δ -4.24, -4.05, 14.31, 24.31, 34.68, 36.35, 60.40, 126.17, 128.03, 129.25, 129.35, 137.71, 141.51, 173.79 ; EIMS *m/z*(%): 249(21), 235(26), 137(24), 135(100), 129(13), 117(23), 105(13), 91(24), 75(15); HREIMS calcd for C₁₉H₂₃O₂Si: 311.1467; found 311.1477 [M⁺-CH₃].

Substrates.

General procedure for synthesis of morpholine amides from acid chlorides.¹ The acid chloride (1 equiv) was added to a flask containing CH₂Cl₂ (enough to make a 1.0 M solution of the acid chloride). The flask was cooled to 0 °C, and morpholine (3 equiv) was added slowly. The reaction was allowed to warm to rt and stirred for 30 min at which time it was diluted with EtOAc, then washed with 1 M hydrochloric acid, saturated sodium bicarbonate, and brine. The organic layer was dried over anhydrous Na₂SO₄, filtered, and concentrated in vacuo. The resulting imides were used without further purification.

General procedure for synthesis of acylsilanes from morpholine amides.¹ The morpholine amide (2 mmol) was added to a flame-dried 50 mL round-bottomed flask under dry nitrogen. To this amide, THF (3 mL) was added, and the solution was then cooled to -78 °C. Dimethylphenylsilyllithium (1.0 M

solution in THF, 3 mL) was added dropwise via syringe, and the reaction was allowed to stir for 1.5 hours, after which time it was quenched at -78°C (to prevent decomposition) by the addition of 4 mL of saturated aqueous ammonium chloride. The resulting heterogeneous mixture was allowed to warm to rt and then stirred for an additional 30 min. The reaction was then partitioned between water (5 mL) and ether (5 mL), the phases were separated, and the aqueous phase was extracted with ether (2 x 5 mL). The combined organics were washed with water (2 x 20 mL) and once with brine (20 mL), dried over anhydrous MgSO_4 , filtered, and concentrated *in vacuo*. The residue was purified by flash column chromatography using silica gel yielding pure acylsilane.

General HWE procedure for syntheses of (*E*)- β -silyl enoates from acylsilanes.¹ To a mineral oil dispersion of sodium hydride (2 mmol) was added a THF (2 mL) solution of triethylphosphonoacetate (2.0 mmol) at rt with stirring. After 30 min, acylsilane (2.0 mmol) was added dropwise and the reaction mixture was stirred overnight. The reaction mixture was quenched with DI water (5 mL) and diluted with ether (5 mL). The aqueous phase was further extracted with ether (2 x 5 mL). The combined organics were washed with NaHCO_3 (2 x 20 mL), once with brine (20 mL), and then further dried over anhydrous MgSO_4 , filtered, and concentrated *in vacuo*. The residue, which consisted of both (*E*) and (*Z*) isomers, was purified by flash column chromatography using silica gel yielding pure (*E*) enoate.

General Peterson olefination procedure for syntheses of (*Z*)- β -silyl enoates from acylsilanes.¹ To a THF (3 mL) solution of 1,1,1,3,3,3-hexamethyldisilazane (194 mg, 1.2 mmol) was added a hexane solution of *n*-butyllithium (1.6 M, 0.75 mL, 1.2 mmol) at 0°C and the reaction mixture was stirred for 20 min. After cooling to -78°C , ethyl (trimethylsilyl)acetate (192 mg, 1.2 mmol) in THF (1 mL) was added, and stirring was continued for 15 min. A THF (1 mL) solution of acylsilane (1 mmol) was added, and the reaction mixture was stirred at the same temperature for 1 h. The cooling bath was removed, and the reaction mixture was allowed to warm to rt. A saturated NH_4Cl aqueous solution (10 mL) was added, and the organic materials were extracted with ether (2 x 15 mL), dried over anhydrous Na_2SO_4 , and concentrated under reduced pressure. The residue, which consisted of both (*E*) and (*Z*) isomers, was purified by flash column chromatography using silica gel yielding pure (*Z*) enoate.

Ethyl (*Z*)-3-(dimethylphenylsilyl)-2-butenate (Table 1, entry 1). Purified by SiO_2 chromatography (ether/hexanes = 1/24); R_f = 0.56 (ether/hexanes = 1/9); IR (neat): 3069, 2955, 1717, 1605, 1429, 1330, 1247, 1200, 1112, 1042 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 0.48 (s, 6H), 1.15 (t, J = 7.1 Hz, 3H), 1.96 (d, J = 1.8 Hz, 3H), 4.01 (q, J = 7.1 Hz, 2H), 6.43 (q, J = 1.8 Hz, 1H), 7.30-7.38 (m, 3H), 7.49-7.56 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ -1.88, 14.22, 26.97, 60.02, 127.68, 128.76, 132.19, 133.77, 138.86, 159.42, 166.41; EIMS m/z (%): 233(38) [$\text{M}^+ - \text{CH}_3$], 205(16), 203(12), 172(14), 171(100); HREIMS calcd for $\text{C}_{13}\text{H}_{17}\text{O}_2\text{Si}$: 233.0998; found 233.0993 [$\text{M}^+ - \text{CH}_3$].

Ethyl (*Z*)-3-(dimethylphenylsilyl)-3-phenyl-2-propenoate (Table 1, entry 2). Purified by SiO_2 chromatography (ether/hexanes = 1/15); R_f = 0.45 (ether/hexanes = 1/10); IR (neat): 3069, 2979, 1719, 1591, 1321, 1182, 1112, 1032 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 0.39 (s, 6H), 1.14 (t, J = 7.1 Hz, 3H), 4.00 (q, J = 7.1 Hz, 2H), 6.49 (s, 1H), 7.06-7.11 (m, 2H), 7.20-7.34 (m, 6H), 7.53-7.59 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ -0.50, 14.21, 60.55, 126.74, 126.89, 127.70, 128.14, 128.83, 133.87, 134.64, 138.61, 145.11, 162.27, 166.62; EIMS m/z (%): 310(0.9) [M^+], 295(89), 267(99), 233(100); HREIMS calcd for $\text{C}_{19}\text{H}_{22}\text{O}_2\text{Si}$: 310.4623; found 310.1399 [M^+].

Octyl (*Z*)-3-(dimethylphenylsilyl)-2-butenate (Table 1, entry 3). Purified by SiO_2 chromatography (ether/hexanes = 1/50); R_f = 0.52 (ether/hexanes = 1/19); IR (neat): 3069, 2928, 1717, 1604, 1331, 1246, 1197 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 0.48 (s, 6H), 0.89 (t, J = 6.9 Hz, 3H), 1.20-1.35 (m, 10H),

1.52 (m, 2H), 1.96 (d, $J = 1.7$ Hz, 3H), 3.94 (t, $J = 6.8$ Hz, 2H), 6.43 (q, $J = 1.7$ Hz, 1H), 7.29-7.37 (m, 3H), 7.49-7.56 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ -1.87, 14.25, 22.81, 26.04, 27.01, 28.74, 29.34, 29.37, 31.96, 64.37, 127.72, 128.81, 132.12, 133.85, 138.93, 159.50, 166.62; EIMS $m/z(\%)$: 317(33)[$\text{M}^+ - \text{CH}_3$], 256(20), 255(100); HREIMS calcd for $\text{C}_{19}\text{H}_{29}\text{O}_2\text{Si}$: 317.1937; found 317.1934[$\text{M}^+ - \text{CH}_3$].

Ethyl (*E*)-3-(dimethylphenylsilyl)-2-butenolate (Table 1 entry 4). Purified by SiO_2 chromatography (ether/hexanes = 1/24); $R_f = 0.43$ (ether/hexanes = 1/9); IR (neat): 3070, 2958, 1716, 1610, 1428, 1337, 1250, 1183, 1113, 1038 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 0.42 (s, 6H), 1.30 (t, $J = 7.2$ Hz, 3H), 2.19 (d, $J = 1.8$ Hz, 3H), 4.17 (q, $J = 7.2$ Hz, 2H), 6.10 (q, $J = 1.8$ Hz, 1H), 7.33-7.43 (m, 3H), 7.47-7.54 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ -3.84, 14.45, 17.62, 59.85, 127.94, 128.11, 129.60, 134.14, 136.28, 160.01, 165.76. CIMS $m/z(\%)$: 249(100)[$\text{M} + \text{H}$] $^+$, 203(32), 170(57); HRCIMS calcd for $\text{C}_{14}\text{H}_{21}\text{O}_2\text{Si}$: 249.1311; found 249.1308[$\text{M} + \text{H}$] $^+$.

Methyl (*E*)-3-(dimethylphenylsilyl)-2-butenolate (Table 1, entry 5). Purified by SiO_2 chromatography (ethyl acetate/hexanes = 1/50); $R_f = 0.36$ (ethyl acetate/hexanes = 1/20); ^1H NMR (400 MHz, CDCl_3) δ 0.41 (s, 6H), 2.18 (d, $J = 2.0$ Hz, 3H), 3.69 (s, 3H), 6.08 (q, $J = 2.0$ Hz, 1H), 7.35-7.38 (m, 3H), 7.47-7.49 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ -3.89, 17.62, 51.0, 127.43, 128.09, 129.61, 134.10, 136.14, 160.56, 166.06; HREIMS calcd for $\text{C}_{12}\text{H}_{15}\text{O}_2\text{Si}$: 219.1481; found 219.1846[$\text{M} - \text{CH}_3$] $^+$.

Methyl (*E*)-6-(4-methoxybenzyloxy)-3-(dimethylphenylsilyl)-2-hexenoate (Table 1, entry 6). Purified by SiO_2 chromatography (ethyl acetate/hexanes = 1/20); $R_f = 0.29$ (ethyl acetate/hexanes = 1/10); ^1H NMR (400 MHz, CDCl_3) δ 0.43 (s, 6H), 1.63 (m, 2H), 2.69 (t, $J = 8.0$ Hz, 2H), 3.41 (t, $J = 6.7$ Hz, 2H), 3.68 (s, 3H), 3.81 (s, 3H), 4.37 (s, 2H), 6.09 (s, 1H), 6.87 (d, $J = 8.7$ Hz, 2H), 7.23 (d, $J = 8.7$ Hz, 2H), 7.34-7.40 (m, 3H), 7.49-7.52 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ -3.21, 28.27, 29.71, 51.09, 55.34, 70.29, 72.32, 113.77, 127.96, 128.07, 129.25, 129.58, 130.88, 134.15, 136.45, 159.12, 164.72, 165.63; HREIMS calcd for $\text{C}_{23}\text{H}_{30}\text{O}_4\text{Si}$: 398.1913; found 398.1920[M] $^+$.

Methyl (*E*)-3-(3,4,5-trimethoxyphenyl)-3-(dimethylphenylsilyl)acrylate (Table 1, entry 7). Purified by SiO_2 chromatography (ethyl acetate/hexanes = 1/4); $R_f = 0.4$ (ethyl acetate/hexanes = 3/7); IR (neat): 2952, 1732, 1578, 1500, 1238, 1127 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 0.40 (s, 6H), 3.55 (s, 3H), 3.63 (s, 6H), 3.82 (s, 3H), 5.97 (s, 2H), 6.25 (s, 1H), 7.33-7.39 (m, 3H), 7.48 (d, $J = 2.0$ Hz, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ -3.59, 51.47, 55.95, 61.08, 103.44, 128.11, 128.63, 129.80, 134.46, 136.03, 136.28, 136.39, 152.77, 161.25, 165.96; EIMS $m/z(\%)$: 386(50)[M^+], 372(31), 371(73), 355(23), 310(39), 309(94), 135(100); HREIMS calcd for $\text{C}_{21}\text{H}_{26}\text{O}_5\text{Si}$: 386.1550; found 386.5554 [M] $^+$.

Methyl (*E*)-3-(4-chlorophenyl)-3-(dimethylphenylsilyl)acrylate (Table 1 entry 8). Purified by SiO_2 chromatography (CH_2Cl_2 /hexanes = 1/3); $R_f = 0.5$ (CH_2Cl_2 /hexanes = 1/1); IR (neat): 2950, 1725, 1590, 1500, 1486, 1176, 831 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 0.39 (s, 6H), 3.54 (s, 3H), 6.45 (s, 1H), 6.99 (d, $J = 2.0$ Hz, 2H), 7.24 (d, $J = 2.0$ Hz, 2H), 3.28 (dd, $J = 0.8, 2.0$ Hz, 3H), 7.50-7.53 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ -0.68, 51.62, 127.83, 128.13, 128.37, 129.04, 132.95, 133.81, 134.47, 138.10, 143.47, 161.53, 166.79; EIMS $m/z(\%)$: 314(28), 254(39), 253(19), 252(100), 134(21), 78(38); HREIMS calcd for $\text{C}_{12}\text{H}_{14}\text{ClO}_2\text{Si}$: 253.0452; found 253.0443 [M $^+ - \text{C}_6\text{H}_6$].

Ethyl (*E*)-3-(dimethylphenylsilyl)-4-(phenyl)-2-butenolate (Table 1, entry 9). Purified by SiO_2 chromatography (ether/hexanes = 1/24); $R_f = 0.45$ (ether/hexanes = 1/9); IR (neat): 2958, 1716, 1599, 1172, 819 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 0.21 (s, 6H), 1.27 (t, $J = 7.2$ Hz, 3H), 4.10 (s, 2H), 4.17 (q, $J = 7.2$ Hz, 2H), 6.25 (s, 1H), 7.06 (d, $J = 7.2$ Hz, 2H), 7.14-7.20 (m, 3H), 7.33-7.41 (m, 5H); ^{13}C

NMR (100 MHz, CDCl₃) δ -2.75, 14.46, 36.97, 60.27, 126.20, 128.06, 128.35, 129.23, 129.57, 129.78, 134.29, 136.62, 138.95, 160.98, 165.87; EIMS m/z (%): 246(100), 218(39), 135(69), 115(35), 75(49); HREIMS calcd for C₁₉H₂₁O₂Si: 309.1311; found 309.1303 [M⁺-CH₃].

Determination of ee. Representative procedure for derivatization. (5*S*)-1-[(3'*S*)-3-(Dimethylphenylsilyl)butanoyl]-5-(triphenylmethoxymethyl)pyrrolidin-2-one. To a solution of ethyl (3*S*)-3-(dimethylphenylsilyl)butanoate (Table 1, entry 1; 220 mg, 0.88 mmol) in EtOH (4 mL) and H₂O (1 mL) was added NaOH (70 mg, 1.75 mmol) at rt. The mixture was stirred at rt for 14 h and then concentrated by rotary evaporation. The residue was quenched by pouring into 1 N HCl and diluted with ethyl acetate. The aqueous layer was extracted with ethyl acetate and the combined organics were washed with brine, dried over anhydrous MgSO₄, filtered, and concentrated by rotary evaporation. The residue was purified by flash chromatography (ethyl acetate/hexanes = 1/2) to afford (3*S*)-3-(dimethylphenylsilyl)butanoic acid (184 mg, 94%) as a clear oil. To a solution of (3*S*)-3-(dimethylphenylsilyl)butanoic acid (179 mg, 0.805 mmol) in CH₂Cl₂ (4 mL) was added oxalyl chloride (140 μ L, 1.61 mmol) at 0 °C. The mixture was stirred at rt for 2 h and then concentrated by rotary evaporation to afford acyl chloride. To a solution of (*S*)-5-(triphenylmethoxymethyl)pyrrolidin-2-one (288 mg, 0.81 mmol) in THF (4 mL) was added *n*-BuLi (0.60 mL, 0.97 mmol) at -78 °C. The mixture was stirred at -78 °C for 15 min. To the reaction mixture was added acyl chloride in THF (2 mL) at -78 °C and the mixture stirred at -78 °C for 2 h. The reaction was quenched by pouring into sat. aq. NH₄Cl and diluted with ethyl acetate. The aqueous layer was extracted with ethyl acetate and the combined organics were washed with brine, dried over anhydrous MgSO₄, filtered, and concentrated by rotary evaporation. The residue was purified by flash chromatography (ethyl acetate/hexanes = 1/4) to afford the title product (194 mg, 43%) as a clear oil; R_f = 0.37 (ethyl acetate/hexanes = 1/4); IR (neat): 3068, 2955, 1738, 1694, 1597, 1366, 1221, 1112, 1086 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 0.32 (s, 3H), 0.33 (s, 3H), 0.89 (d, J = 7.2 Hz, 3H), 1.51 (m, 1H), 1.88-2.10 (m, 2H), 2.45 (ddd, J = 17.8, 9.8, 1.6 Hz, 1H), 2.74 (dd, J = 16.3, 11.4 Hz, 1H), 2.89 (dd, J = 17.8, 10.6 Hz, 1H), 2.94 (dd, J = 16.3, 3.1 Hz, 1H), 3.15 (dd, J = 9.7, 2.6 Hz, 1H), 3.46 (dd, J = 9.7, 4.0 Hz, 1H), 4.43 (m, 1H), 7.16-7.27 (m, 9H), 7.29-7.37 (m, 9H), 7.50-7.56 (m, 2H); ¹³C NMR (100 MHz, CDCl₃) δ -5.01, -4.81, 14.57, 15.37, 21.30, 33.31, 39.11, 56.71, 64.17, 87.04, 127.23, 127.87, 127.97, 128.63, 129.14, 134.14, 137.78, 143.70, 173.94, 176.24; EIMS m/z (%): 561(5.5)[M⁺], 546(14), 318(18), 248(32), 244(21), 243(100); HREIMS calcd for C₃₆H₃₉NO₃Si: 561.2699; found 561.2701[M⁺].