Catalytic Asymmetric Rearrangement of α,α -Dialkyl- α -siloxy Aldehydes to Optically Active Acyloins Using Axially Chiral Organoaluminum Lewis Acids

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Supporting Information

I. General. Infrared (IR) Spectra were recorded on a Shimadzu FT-IR. ^1H and ^{13}C NMR spectra were measured on JEOL JNM-FX400 (400 MHz) and JEOL AL-400 (400 MHz) spectrometers. Chemical shifts of ^1H NMR spectra were reported in ppm relative to tetramethylsilane (δ 0). Chemical shifts of ^{13}C NMR spectra were reported in ppm relative to the residual solvent (chloroform, δ 77.07). Analytical high performance liquid chromatography (HPLC) was performed on a Shimadzu LC-10AT instrument equipped with a column of Daicel Chiralcel OD-H, OJ-H, Chiralpak AD-H or AS-H. Optical rotations were measured on a JASCO DIP-1000 digital polarimeter. The high-resolution mass spectra (HRMS) were measured on an BRUKER DALTONICS microTOF focus-KR spectrometer. Analytical thin layer chromatography (TLC) was performed on Merck precoated TLC plates (silica gel 60 GF₂₅₄, 0.25 mm) throughout this work. Flash column chromatography was performed on silica gel 60 (Merck 1.09386.9025, 230-400 mesh). An EYELA PSL-1400 constant temperature bath was used for low temperature asymmetric rearrangement reactions.

All air- and moisture-sensitive reactions were performed under an atmosphere of argon in flame-dried, round bottom flasks fitted with rubber septa. The manipulations for asymmetric rearrangements were carried out with standard Schlenk techniques under nitrogen. In experiments requiring dry solvent, toluene was purified by both A2 alumina and Q5 reactant using a GlassContour solvent dispensing system. Ethylene glycol dimethyl ether (DME) was dried over 4Å molecular sieves pellets. Diethyl ether and Tetrahydrofuran (THF) were purchased from Kanto Chemical Co., Ltd. as “dehydrated”. Trimethylaluminum was kindly supplied from Tosoh-Finechem Co., Ltd., Japan. Other simple chemicals were purchased and used as such.

Experimental Procedure:

II. Preparation of Substrates

2-Benzyl-3-phenyl-2-trimethylsiloxypropanal [1a (R² = Me)]

To a solution of 1,3-diphenyl-2-propanone (2.10 g, 10 mmol) and trimethylsilyl cyanide (1.33 mL, 10 mmol) in CH₂Cl₂ (30 mL) was added I₂ (253 mg, 1 mmol) at 0 °C under argon. After stirring for 30 min at 0 °C, the reaction was quenched with saturated Na₂SO₃ and extractive workup was conducted with ether. The organic extracts were then washed with brine and dried over anhydrous Na₂SO₄. After evaporation of solvents and drying under vacuum, the crude products were dissolved into CH₂Cl₂ (20 mL) under argon. A 1 M toluene solution of DIBAH (20 mL, 20 mmol) was introduced to this solution at -78 °C, and the reaction mixture was stirred for 1 h at the same temperature. Then, the mixture was quenched with 1N HCl and extracted with ether. The organic extracts were washed with brine and dried over anhydrous Na₂SO₄, and concentrated. The residual oil was purified by column chromatography on silica gel (CH₂Cl₂/hexane = 1/4 as eluant) to give the title compound (2.97 g, 9.5 mmol, 95% yield) as white solid. ¹H NMR (400 MHz, CDCl₃) δ 9.66 (1H, s, CHO), 7.21-7.28 (6H, m, Ph-H), 7.13-7.15 (4H, m, Ph-H), 3.07 (2H, d, *J* = 14.0 Hz, PhCH₂), 2.87 (2H, d, *J* = 14.0 Hz, PhCH₂), -0.16 (9H, s, SiMe₃); ¹³C NMR (100 MHz, CDCl₃) δ 202.8, 135.5, 130.6, 127.9, 126.7, 84.8, 43.8, 2.2; IR (neat) 3030, 2953, 1741, 1494, 1454, 1247, 1143, 985, 837, 750, 684, 630 cm⁻¹; HRMS (ESI-TOF) Calcd. for C₁₉H₂₄NaO₂Si ([M+Na]⁺): 335.1438, Found: 335.1450. Other substrates were synthesized by the same procedure from known ketones¹ and cyanosilanes.

2-Benzyl-3-phenyl-2-triethylsiloxypropanal [1a (R² = Et)]

¹H NMR (400 MHz, CDCl₃) δ 9.64 (1H, s, CHO), 7.21-7.27 (6H, m, Ph-H), 7.14-7.16 (4H, m, Ph-H), 3.06 (2H, d, *J* = 14.0 Hz, PhCH₂), 2.89 (2H, d, *J* = 14.0 Hz, PhCH₂), 0.82 (9H, t, *J* = 8.0 Hz, CH₃CH₂Si), 0.45 (6H, q, *J* = 8.0 Hz, CH₃CH₂Si); ¹³C NMR (100 MHz, CDCl₃) δ 203.2, 135.4, 130.6, 127.9, 126.5, 83.7, 43.6, 7.2, 6.9; IR (neat) 2953, 2910, 2873, 2362, 1739, 1494, 1454, 1238, 1141, 1091, 1002, 729, 698, 669 cm⁻¹; HRMS (ESI-TOF) Calcd. for C₂₂H₃₁O₂Si ([M+H]⁺): 355.2088, Found: 355.2087.

2-Benzyl-2-*tert*-butyldimethylsiloxy-3-phenylpropanal [1a ($R^2_3 = t$ -BuMe₂)]

¹H NMR (400 MHz, CDCl₃) δ 9.67 (1H, s, CHO), 7.21-7.27 (6H, m, Ph-H), 7.14-7.16 (4H, m, Ph-H), 3.12 (2H, d, $J = 14.0$ Hz, PhCH₂), 2.94 (2 H, d, $J = 14.0$ Hz, PhCH₂), 0.87 (9H, s, *t*-BuSi), -0.24 (6H, s, Me₂Si); ¹³C NMR (100 MHz, CDCl₃) δ 203.4, 135.5, 130.8, 128.1, 126.8, 84.3, 44.5, 26.3, 18.9, -2.7; IR (neat) 3030, 2953, 2927, 2856, 2358, 1722, 1496, 1471, 1454, 1253, 1093, 943, 835, 812, 777, 750, 732, 698, 669 cm⁻¹; HRMS (ESI-TOF) Calcd. for C₂₂H₃₀NaO₂Si ([M+Na]⁺): 377.1918, Found: 377.1920.

2-(4-Methoxybenzyl)-3-(4-methoxyphenyl)-2-triethylsiloxypropanal (1b)

¹H NMR (400 MHz, CDCl₃) δ 9.60 (1H, s, CHO), 7.06 (4H, d, $J = 6.8$ Hz, Ar-H), 6.79 (4H, d, $J = 6.8$ Hz, Ar-H), 3.78 (6H, s, MeOPh), 2.93 (2H, d, $J = 14.0$ Hz, PhCH₂), 2.82 (2 H, d, $J = 14.0$ Hz, PhCH₂), 0.85 (9H, t, $J = 8.0$ Hz, CH₃CH₂Si), 0.48 (6H, q, $J = 8.0$ Hz, CH₃CH₂Si); ¹³C NMR (100 MHz, CDCl₃) δ 203.6, 158.2, 131.4, 127.4, 113.3, 83.8, 55.1, 42.5, 7.2, 6.9; IR (neat) 2953, 2910, 2873, 1739, 1612, 1512, 1463, 1301, 1247, 1176, 1143, 1035, 829, 732 cm⁻¹; HRMS (ESI-TOF) Calcd. for C₂₄H₃₄NaO₄Si ([M+Na]⁺): 437.2119, Found: 437.2132.

2-(4-Fluorobenzyl)-3-(4-fluorophenyl)-2-triethylsiloxypropanal (1c)

¹H NMR (400 MHz, CDCl₃) δ 9.61 (1H, s, CHO), 7.08-7.25 (4H, m, Ar-H), 6.92-6.97 (4H, m, Ar-H), 2.94 (2H, d, $J = 14.0$ Hz, PhCH₂), 2.83 (2 H, d, $J = 14.0$ Hz, PhCH₂), 0.84 (9H, t, $J = 8.0$ Hz, CH₃CH₂Si), 0.48 (6H, q, $J = 8.0$ Hz, CH₃CH₂Si); ¹³C NMR (100 MHz, CDCl₃) δ 203.0, 161.7 (d, $J_{C-F} = 246$ Hz), 132.0 (d, $J_{C-F} = 7.4$ Hz), 131.0 (d, $J_{C-F} = 3.3$ Hz), 114.7 (d, $J_{C-F} = 20.6$ Hz), 83.6, 42.4, 7.1, 6.9; IR (neat) 2953, 2910, 2873, 1741, 1585, 1490, 1456, 1413, 1230, 1184, 1147, 1114, 1002, 983, 937, 840, 754, 727, 671 cm⁻¹; HRMS (ESI-TOF) Calcd. for C₂₂H₂₈F₂NaO₂Si ([M+Na]⁺): 413.1730, Found: 413.1738.

2-(4-Chlorobenzyl)-3-(4-chlorophenyl)-2-triethylsiloxypropanal (1d)

¹H NMR (400 MHz, CDCl₃) δ 9.60 (1H, s, CHO), 7.23 (4H, d, $J = 8.0$ Hz, Ar-H), 7.07 (4H, d, $J = 8.0$ Hz, Ar-H), 2.93 (2H, d, $J = 14.0$ Hz, PhCH₂), 2.83 (2 H, d, $J = 14.0$ Hz, PhCH₂), 0.85 (9H, t, $J = 8.0$ Hz, CH₃CH₂Si), 0.48 (6H, q, $J = 8.0$ Hz, CH₃CH₂Si); ¹³C NMR (100 MHz, CDCl₃) δ 203.1, 133.8, 132.8, 132.0, 128.2, 83.5, 42.6, 7.0, 6.8; IR (neat) 2954, 2910, 2875, 1741, 1490, 1409, 1240, 1143, 1089, 1016, 987, 825, 806, 727 cm⁻¹; HRMS (ESI-TOF) Calcd. for C₂₂H₂₈Cl₂NaO₂Si ([M+Na]⁺): 445.1139, Found: 445.1138.

2-(2-Naphthylmethyl)-3-(2-naphthyl)-2-triethylsiloxypentanal (1e)

^1H NMR (400 MHz, CDCl_3) δ 9.71 (1H, s, CHO), 7.74-7.82 (6H, m, Ar-H), 7.63 (2H, s, Ar-H), 7.42-7.47 (4H, m, Ph-H), 7.25-7.32 (2H, m, Ar-H), 3.19 (2H, d, $J = 14.0$ Hz, PhCH_2), 3.11 (2H, d, $J = 14.0$ Hz, PhCH_2), 0.82 (9H, t, $J = 8.0$ Hz, $\text{CH}_3\text{CH}_2\text{Si}$), 0.50 (6H, q, $J = 8.0$ Hz, $\text{CH}_3\text{CH}_2\text{Si}$); ^{13}C NMR (100 MHz, CDCl_3) δ 203.2, 133.1, 133.0, 132.2, 129.3, 128.8, 127.4, 127.3, 127.3, 125.8, 125.4, 83.9, 43.6, 7.2, 7.0; IR (neat) 3055, 2953, 2908, 2873, 2357, 2322, 1732, 1600, 1508, 1456, 1379, 1367, 1271, 1240, 1157, 1136, 1124, 1001, 956, 891, 854, 815, 732, 669 cm^{-1} ; HRMS (ESI-TOF) Calcd. for $\text{C}_{30}\text{H}_{34}\text{NaO}_2\text{Si}$ ($[\text{M}+\text{Na}]^+$): 477.2231, Found: 477.2223.

5-Phenyl-2-(3-phenyl-2-propenyl)-2-triethylsiloxypentenal (1f)

^1H NMR (400 MHz, CDCl_3) δ 9.65 (1H, s, CHO), 7.20-7.34 (10H, m, Ph-H), 6.43 (2H, d, $J = 16.0$ Hz, PhCH), 6.19 (2H, dt, $J = 16.0, 7.6$ Hz, $\text{PhCH}=\text{CH}$), 2.60 (2H, dd, $J = 7.6, 1.2$ Hz, $\text{CH}=\text{CHCH}_2$), 2.58 (2H, dd, $J = 7.6, 1.2$ Hz, $\text{CH}=\text{CHCH}_2$), 0.99 (9H, t, $J = 8.0$ Hz, $\text{CH}_3\text{CH}_2\text{Si}$), 0.67 (6H, q, $J = 8.0$ Hz, $\text{CH}_3\text{CH}_2\text{Si}$); ^{13}C NMR (100 MHz, CDCl_3) δ 203.7, 137.2, 133.9, 128.5, 127.3, 126.1, 123.5, 82.6, 40.3, 7.0, 6.8; IR (neat) 3026, 2954, 2908, 2873, 1735, 1598, 1494, 1448, 1238, 1145, 1114, 1066, 1002, 966, 740, 727, 692 cm^{-1} ; HRMS (ESI-TOF) Calcd. for $\text{C}_{26}\text{H}_{34}\text{NaO}_2\text{Si}$ ($[\text{M}+\text{Na}]^+$): 429.2231, Found: 429.2228.

5-Methyl-2-(3-methyl-2-butenyl)-3-triethylsiloxypentenal (1g)

^1H NMR (400 MHz, CDCl_3) δ 9.54 (1H, s, CHO), 5.09-5.13 (2H, m, $\text{Me}_2\text{C}=\text{CH}$), 2.27-2.37 (4H, m, $\text{C}=\text{CHCH}_2$), 1.69 (3H, s, $\text{Me}_2\text{C}=\text{CH}$), 1.58 (3H, s, $\text{Me}_2\text{C}=\text{CH}$), 0.96 (9H, t, $J = 7.6$ Hz, $\text{CH}_3\text{CH}_2\text{Si}$), 0.62 (6H, q, $J = 7.6$ Hz, $\text{CH}_3\text{CH}_2\text{Si}$); ^{13}C NMR (100 MHz, CDCl_3) δ 204.3, 134.5, 117.8, 83.2, 35.0, 25.8, 17.9, 6.9, 6.7; IR (neat) 2956, 2912, 2875, 1737, 1456, 1377, 1240, 1141, 1112, 1091, 1008, 977, 727 cm^{-1} ; HRMS (ESI-TOF) Calcd. for $\text{C}_{18}\text{H}_{34}\text{NaO}_2\text{Si}$ ($[\text{M}+\text{Na}]^+$): 333.2231, Found: 333.2219.

2-Isobutyl-4-methyl-2-triethylsiloxypentanal (1h)

^1H NMR (400 MHz, CDCl_3) δ 9.57 (1H, s, CHO), 1.72-1.85 (2H, m, Me_2CHCH_2), 1.51-1.62 (4H, m, Me_2CHCH_2), 0.96 (9H, t, $J = 8.0$ Hz, $\text{CH}_3\text{CH}_2\text{Si}$), 0.90 (3H, d, $J = 6.8$ Hz, Me_2CH), 0.86 (3H, d, $J = 6.8$ Hz, Me_2CH), 0.65 (6H, q, $J = 8.0$ Hz, $\text{CH}_3\text{CH}_2\text{Si}$); ^{13}C NMR (100 MHz, CDCl_3) δ 204.0, 83.7, 46.2, 24.5, 24.0, 23.6, 7.1, 7.0; IR (neat) 2954, 2910, 2875, 1737, 1458, 1186, 1165, 1101, 1008, 977, 727 cm^{-1} ; HRMS (ESI-TOF) Calcd. for $\text{C}_{16}\text{H}_{34}\text{NaO}_2\text{Si}$ ($[\text{M}+\text{Na}]^+$): 309.2231, Found: 309.2216.

2,2-Dicyclohexyl-2-triethylsiloxyethanal (**1i**)

^1H NMR (400 MHz, CDCl_3) δ 9.58 (1H, s, CHO), 1.73-1.80 (8H, m, -CH-), 1.63-1.66 (6H, m, -CH-), 1.50-1.54 (2H, m, -CH-), 0.95-1.21 (10H, m, -CH-), 0.96 (9H, t, $J = 8.0$ Hz, $\text{CH}_3\text{CH}_2\text{Si}$), 0.68 (6H, q, $J = 8.0$ Hz, $\text{CH}_3\text{CH}_2\text{Si}$); ^{13}C NMR (100 MHz, CDCl_3) δ 206.5, 88.4, 42.4, 27.9, 26.7, 26.5, 26.4, 26.3, 7.4, 7.3; IR (neat) 2931, 2873, 2852, 1737, 1448, 1238, 1166, 1147, 1008, 734 cm^{-1} ; HRMS (ESI-TOF) Calcd. for $\text{C}_{20}\text{H}_{38}\text{NaO}_2\text{Si}$ ($[\text{M}+\text{Na}]^+$): 361.2533, Found: 361.2537.

III. General Procedure for Catalytic Asymmetric Rearrangement of α,α -Dialkyl- α -siloxy Aldehydes to Optically Active Acyloins.

To a solution of 2-hydroxy-2'-[3,5-bis(trifluoromethyl)]phenyl-3-{2-[3,5-bis(trifluoromethyl)]benzenesulfonylamino}phenyl-1,1'-binaphthyl (**4**, 46.7 mg, 0.055 mmol) in toluene (10 mL) was added a 1 M toluene solution of trimethylaluminum (50 μL , 0.050 mmol) at room temperature under nitrogen and stirred for 30 min. After being cooled to -20 $^{\circ}\text{C}$, **1a** ($\text{R}^2 = \text{Et}$) (354.5 mg, 1 mmol) was added to this solution and the stirring was maintained at -20 $^{\circ}\text{C}$ for 12 h. Then, sodium fluoride (8.4 mg, 0.20 mmol) and water (2.7 μL , 0.15 mmol) were added and the whole mixture was stirred for 30 min at room temperature. To remove precipitates, filtration through celite with EtOAc was carried out. Concentration of the filtrate and purification by column chromatography on silica gel ($\text{CH}_2\text{Cl}_2/\text{hexane} = 1/4$ as eluant) afforded **2a** ($\text{R}^2 = \text{Et}$) (342.9 mg, 0.97 mmol, 97% yield) as colorless oil.

IV. Catalytic Asymmetric Rearrangement with Chiral Organoaluminum Catalyst Prepared from Other Ligands

entry	chiral ligand	yield (%) ^a	ee (%) ^b
1	8	99	29
2	9a (R = H)	25	19
3	9b (R = Ph)	34	49
4	10a (Ar = Ph)	82	48
5	10b (Ar = 3,5-(CF ₃) ₂ -C ₆ H ₃)	91	57

^a Isolated yield.

^b Enantiomeric excess was determined by HPLC analysis using a chiral column.

V. Preparation of Chiral Ligand 9b

2-Methoxymethoxy-2'-trifluoromethanesulfoxy-1,1'-binaphthyl (**11**)

To a solution of *(S)*-binaphthol (5.73 g, 20 mmol) and $i\text{-Pr}_2\text{NEt}$ (3.48 mL, 20 mmol) in CH_2Cl_2 (100 mL) was added Ti_2O (3.36 mL, 20 mmol) at 0°C under argon, and the reaction mixture was stirred for 30 min and quenched with saturated NaHCO_3 . Extractive workup was performed with CH_2Cl_2 , and the combined extracts were washed with brine and dried over anhydrous Na_2SO_4 . After evaporation of solvents and drying under vacuum, the crude products were dissolved into THF (80 mL) under argon. To this solution was added NaH (0.96 g; 60% dispersion in mineral oil, 24 mmol) at 0°C , and the reaction mixture was maintained at the same temperature for 15 min with stirring. Chloromethyl methyl ether (1.82 mL, 24 mmol) was added dropwise to the solution at 0°C , and stirring was continued for 3 h at room temperature. The reaction was quenched with water and extractive workup was conducted with EtOAc . The organic extracts were washed with brine and dried over anhydrous Na_2SO_4 . Removal of solvents and purification of the residual oil by column chromatography on silica gel ($\text{EtOAc}/\text{hexane} = 1/10$ as eluant) gave **11** (8.97 g, 19.4 mmol, 97% yield) as white powder. ^1H NMR (400 MHz, CDCl_3) δ 8.05 (1H, d, $J = 9.2$ Hz, Ar-H), 8.02 (1H, d, $J = 9.6$ Hz, Ar-H), 7.98 (1H, d, $J = 8.4$ Hz, Ar-H), 7.89 (1H, d, $J = 8.0$ Hz, Ar-H), 7.63 (1H, d, $J = 9.2$ Hz, Ar-H), 7.57 (1H, d, $J = 8.8$ Hz, Ar-H), 7.54 (1H, m, Ar-H), 7.34-7.38 (3H, m, Ar-H), 7.25 (1H, m, Ar-H), 7.03 (1H, d, $J = 8.4$ Hz, Ar-H), 5.19 (1H, d, $J = 7.2$ Hz, ArOCH_2), 5.03 (1H, d, $J = 7.2$ Hz, ArOCH_2), 3.22 (3H, s, OCH_3).

2-Methoxymethoxy-2'-(*N,N*-dibenzyl)amino-1,1'-binaphthyl (**12**)

To a mixture of palladium acetate (436 mg, 1.94 mmol), DPE-phos (2.09 g, 3.88 mmol) and cesium carbonate (7.59 g, 23.3 mmol) was added a solution of **11** (8.97 g, 19.4 mmol) and benzylamine (2.55 mL, 23.3 mmol) in toluene under argon, and the reaction mixture was heated at 110 °C for 12 h with stirring. After cooling to room temperature, the solution was filtered off and the filtrate was washed with brine. The organic layer was dried over Na₂SO₄ and concentrated. A mixture of the crude products, benzyl bromide (2.53 mL, 21.2 mmol) and potassium carbonate (2.93 g, 21.2 mmol) in CH₃CN was stirred at 80 °C for 3 h, and then poured into water and extracted with ether. The organic extracts were washed with brine and dried over anhydrous Na₂SO₄. Removal of solvents and purification of the residual oil by column chromatography on silica gel (EtOAc/hexane = 1/10 as eluant) afforded **12** (10.4 g, 17.7 mmol, 91% yield) as yellow powder. ¹H NMR (400 MHz, CDCl₃) δ 7.95 (1H, d, *J* = 9.2 Hz, Ar-H), 7.90 (1H, d, *J* = 8.0 Hz, Ar-H), 7.83 (2H, d, *J* = 9.2 Hz, Ar-H), 7.58 (1H, d, *J* = 9.2 Hz, Ar-H), 7.02-7.38 (13H, m, Ar-H), 6.77-6.79 (4H, m, Ar-H), 5.07 (1H, d, *J* = 7.0 Hz, ArOCH₂), 4.98 (1H, d, *J* = 7.0 Hz, ArOCH₂), 4.01 (2H, d, *J* = 14.6 Hz, NCH₂Ph), 3.88 (2H, d, *J* = 14.6 Hz, NCH₂Ph), 3.09 (3H, s, OCH₃).

2-Methoxymethoxy-3-bromo-2'-(*N,N*-dibenzyl)amino-1,1'-binaphthyl (**13**)

To a solution of *n*-BuLi (17.7 mL; 1.5 M hexane solution, 26.6 mmol) in THF (30 mL) was added *N,N,N',N'*-tetramethylethylenediamine (4.01 mL, 26.6 mmol) at -78 °C under argon. The mixture was stirred for 15 min and transferred into a solution of **12** (10.4 g, 17.7 mmol) in THF (50 mL) at the same temperature. After stirring for 3 h at 0 °C, the resulting mixture was cooled to -78 °C again and 1,2-dibromo-1,1,2,2-tetrafluoroethane (3.16 mL, 26.6 mmol) was added slowly. This whole reaction mixture was stirred overnight at room temperature. The reaction was quenched with water and extractive workup was performed with ether. The ethereal extracts were washed with brine and dried over anhydrous Na₂SO₄. Removal of solvents and purification of the residual oil by column chromatography on silica gel (EtOAc/hexane = 1/10 as eluant) furnished **13** (9.36 g, 15.9 mmol, 90% yield) as yellow powder. ¹H NMR (400 MHz, CDCl₃) δ 8.19 (1H, s, Ar-H), 7.83 (2H, t, *J* = 8.4 Hz, Ar-H), 7.76 (1H, d, *J* = 8.0 Hz, Ar-H), 7.35 (2H, t, *J* = 7.2 Hz, Ar-H), 7.31 (1H, d, *J* = 7.2 Hz, Ar-H), 7.13-7.25 (10H, m, Ar-H), 6.97-7.00 (4H, m, Ar-H), 4.74 (1H, d, *J* = 5.4 Hz, ArOCH₂), 4.52 (1H, d, *J* = 5.4 Hz, ArOCH₂), 3.80 (2H, d, *J* = 14.4 Hz, NCH₂Ph), 3.78 (2H, d, *J* = 14.4 Hz, NCH₂Ph), 2.54 (3H, s, OCH₃).

2-Methoxymethoxy-3-phenyl-2'-(*N,N*-dibenzyl)amino-1,1'-binaphthyl (**14**)

A mixture of **13** (9.36 g, 15.9 mmol), phenylboronic acid (2.32 g, 19.0 mmol), barium

hydroxide octahydrate (5.99 g, 19.0 mmol), palladium acetate (426.5 mg, 1.9 mmol) and triphenylphosphine (1.99 g, 7.6 mmol) in DME (84 mL) and H₂O (14 mL) was refluxed for 10 h with stirring under argon. After cooling to room temperature, the solution was filtered off and the filtrate was washed with brine. The organic layer was dried over anhydrous Na₂SO₄. Removal of solvents and purification of the residual oil by column chromatography on silica gel (EtOAc/hexane = 1/15 as eluant) afforded **14** (7.79 g, 13.3 mmol, 84% yield) as yellow powder. ¹H NMR (400 MHz, CDCl₃) δ 7.92 (1H, s, Ar-H), 7.88 (1H, d, *J* = 8.4 Hz, Ar-H), 7.84 (1H, d, *J* = 8.8 Hz, Ar-H), 7.80 (1H, d, *J* = 8.0 Hz, Ar-H), 7.63-7.65 (2H, m, Ar-H), 7.30-7.45 (6H, m, Ar-H), 7.08-7.25 (9H, m, Ar-H), 7.03-7.04 (5H, m, Ar-H), 4.21 (1H, d, *J* = 5.6 Hz, ArOCH₂), 4.15 (1H, d, *J* = 5.6 Hz, ArOCH₂), 4.14 (2H, d, *J* = 14.6 Hz, NCH₂Ph), 2.11 (2H, d, *J* = 14.6 Hz, NCH₂Ph), 2.54 (3H, s, OCH₃).

Chiral Ligand **9b**

A mixture of **14** (7.79 g, 13.3 mmol) and palladium-activated carbon (1.4 g; Pd 10%, 1.3 mmol) in EtOH (40 mL) and CHCl₃ (10 mL) was stirred for 5 h at room temperature under H₂ (1 atm). The mixture was filtered off, and the filtrate was concentrated and dried under vacuum. To a solution of the crude products (5.81 g, 9.4 mmol) and *i*-Pr₂N-Et (3.28 mL, 18.8 mmol) in CH₂Cl₂ (30 mL) was added Tf₂O (1.58 mL, 9.4 mmol) at -78 °C under argon, and the reaction mixture was stirred there for 2 h and quenched with saturated NaHCO₃. Extractive workup was performed with CH₂Cl₂, and the combined extracts were washed with brine and dried over anhydrous Na₂SO₄. After evaporation of solvents and drying under vacuum, the crude products were dissolved into 1,4-dioxane (30 mL) and *conc.* HCl (2-4 mL) was added at room temperature. Then, the mixture was stirred for 5 h at 70 °C. After cooling to room temperature, the solution was poured into water and extracted with ether. The ethereal extracts were washed with brine and dried over anhydrous Na₂SO₄. Removal of solvents and purification of the residual oil by column chromatography on silica gel (EtOAc/hexane = 1/5 as eluant) gave **9b** (5.17 g, 10.5 mmol, 79% yield). [α]_D²⁵ -20.7° (*c* 1.00, CHCl₃); ¹H NMR (400 MHz, CDCl₃) δ 8.04 (1H, d, *J* = 9.6 Hz, Ar-H), 7.99 (1H, s, Ar-H), 7.95 (1H, d, *J* = 8.4 Hz, Ar-H), 7.92 (2H, t, *J* = 8.2 Hz, Ar-H), 7.63-7.65 (2H, m, Ar-H), 7.26-7.53 (8H, m, Ar-H), 6.97 (1H, d, *J* = 8.4 Hz, Ar-H), 6.67 (1H, br, NH), 5.30 (1H, br, OH); ¹³C NMR (100 MHz, CDCl₃) δ 148.8, 136.2, 132.6, 132.5, 131.9, 131.7, 131.4, 130.5, 130.3, 129.2, 129.1, 129.0, 128.5, 128.2, 128.2, 127.6, 127.5, 126.3, 125.8, 124.5, 123.6, 123.3, 119.9, 119.3 (q, *J*_{C-F} = 324 Hz), 112.7; IR (neat) 3523, 3321, 3059, 2358, 1705, 1423, 1220, 1197, 1139, 995, 752, 704, 603 cm⁻¹; HRMS (ESI-TOF) Calcd. for C₂₇H₁₇F₃NO₃S ([M-H]⁻): 492.0886, Found: 492.0895.

VI. Representative Procedure for the Synthesis of Chiral Ligand 4 and 10:

Chiral Ligand 10b

2-Hydroxy-2'-[3,5-bis(trifluoromethyl)]phenyl-1,1'-binaphthyl (**15**)

To a solution of (*S*)-binaphthol (5.73 g, 20 mmol) and *i*-Pr₂NEt (3.48 mL, 20 mmol) in CH₂Cl₂ (100 mL) was added Tf₂O (3.36 mL, 20 mmol) at 0 °C under argon, and the reaction mixture was stirred for 30 min and quenched with saturated NaHCO₃. Extractive workup was performed with CH₂Cl₂, and the combined extracts were washed with brine and dried over anhydrous Na₂SO₄. After evaporation of solvents and drying under vacuum, the crude product was dissolved into benzene (40 mL) under argon. To this solution was added a 1 M ether solution of MeMgI (20 mL, 20 mmol) at 0 °C, and the reaction solution was maintained at the same temperature for 15 min with stirring. The successive addition of NiCl₂(dppe) (0.53 g, 1 mmol) and a 1 M ether solution of 3,5-bis(trifluoromethyl)phenyl magnesium bromide was performed at room temperature, and stirring was continued for 1 h at room temperature. The reaction was quenched with saturated NH₄Cl carefully and extractive workup was conducted with ether. The organic extracts were washed with brine and dried over anhydrous Na₂SO₄. Removal of solvents and purification of the residual oil by column chromatography on silica gel (Et₂O/hexane = 1/10 then EtOAc/hexane = 1/10 as eluants) afforded **15** (5.70 g, 11.8 mmol, 59% yield) as yellow powder. ¹H NMR (400 MHz, CDCl₃) δ 8.14 (1H, d, *J* = 8.8 Hz, Ar-H), 8.02 (1H, d, *J* = 8.4 Hz, Ar-H), 7.78 (1H, d, *J* = 9.2 Hz, Ar-H), 7.76 (1H,

d, $J = 9.2$ Hz, Ar-H), 7.69 (1H, d, $J = 8.8$ Hz, Ar-H), 7.38-7.59 (6H, m, Ar-H), 7.19-7.28 (2H, m, Ar-H), 7.13 (1H, d, $J = 8.8$ Hz, Ar-H), 6.97 (1H, d, $J = 8.4$ Hz, Ar-H), 4.74 (1H, s, HO); ^{13}C NMR (100 MHz, CDCl_3) δ 151.0, 142.6, 138.1, 133.5, 132.8, 130.6 (q, $J_{\text{C-F}} = 33.8$ Hz), 130.4, 129.9, 129.7, 128.7, 128.2, 128.1, 127.6, 127.1, 127.1, 126.9, 126.2, 124.1, 123.4, 122.9 (q, $J_{\text{C-F}} = 274$ Hz), 120.5, 120.4, 120.4, 116.9, 116.4; HRMS (ESI-TOF) Calcd. for $\text{C}_{28}\text{H}_{15}\text{F}_6\text{O}$ ($[\text{M-H}]^-$): 481.1021, Found: 481.1035.

2-Methoxymethoxy-2'-[3,5-bis(trifluoromethyl)]phenyl-1,1'-binaphthyl (16)

To a solution of **15** (5.70 g, 11.8 mmol) in THF (30 mL) was added NaH (5.7 g; 60% dispersion in mineral oil, 14.1 mmol) at 0 °C carefully, and the mixture was stirred for 15 min. Chloromethyl methyl ether (1.07 mL, 14.1 mmol) was added dropwise to the mixture at 0 °C, and the whole reaction mixture was then stirred for 1 h at room temperature. The mixture was quenched with water and extracted with ether. The organic extracts were washed with brine and dried over anhydrous Na_2SO_4 . Removal of solvents and purification of the residual oil by short column chromatography on silica gel (EtOAc/hexane = 1/10 as eluant) gave **16** (6.22 g, 11.8 mmol, quant) as white powder. ^1H NMR (400 MHz, CDCl_3) δ 8.07 (1H, d, $J = 8.8$ Hz, Ar-H), 7.98 (1H, d, $J = 8.0$ Hz, Ar-H), 7.83 (1H, d, $J = 9.2$ Hz, Ar-H), 7.76 (1H, d, $J = 8.0$ Hz, Ar-H), 7.64 (1H, d, $J = 8.4$ Hz, Ar-H), 7.59 (2H, s, Ar-H), 7.49-7.51 (2H, m, Ar-H), 7.43 (1H, d, $J = 9.2$ Hz, Ar-H), 7.19-7.33 (4H, m, Ar-H), 7.00 (1H, d, $J = 8.0$ Hz, Ar-H), 4.98 (1H, d, $J = 6.8$ Hz, OCH_2O), 4.92 (1H, d, $J = 6.8$ Hz, OCH_2O), 3.12 (3H, s, OCH_3); ^{13}C NMR (100 MHz, CDCl_3) δ 152.8, 143.7, 136.7, 133.7, 133.2, 132.9, 130.3 (q, $J_{\text{C-F}} = 33.0$ Hz), 130.0, 129.2, 128.9, 128.8, 128.4, 127.9, 126.7, 126.7, 126.6, 126.3, 124.7, 123.9, 123.0 (q, $J_{\text{C-F}} = 274$ Hz), 121.2, 120.0, 119.9, 119.9, 115.4, 94.6, 55.7; HRMS (ESI-TOF) Calcd. for $\text{C}_{30}\text{H}_{20}\text{F}_6\text{NaO}_2$ ($[\text{M}+\text{Na}]^+$): 549.1259, Found: 549.1277.

2-Methoxymethoxy-2'-[3,5-bis(trifluoromethyl)]phenyl-3-(2-amino)phenyl-1,1'-binaphthyl (17)

To a solution of *N,N,N',N'*-tetramethylethylenediamine (2.67 mL, 17.7 mmol) in THF (30 mL) was added a 1.5 M hexane solution of *n*-BuLi (11.8 mL, 17.7 mmol) at -78 °C under argon, and the mixture was stirred for 30 min. A solution of **16** (6.22 g, 11.8 mmol) in THF (10 mL) was added to this mixture at -78 °C and the resulting mixture was kept at -78 °C for 30 min and at 0 °C for 5 h with stirring. The reaction mixture was cooled to -78 °C again and transferred into a solution of triisopropyl borate (4.08 mL, 17.7 mmol) in THF (10 mL). After stirring for 1 h at -78 °C, the solution was stirred overnight at room temperature. 1N HCl was added and the mixture was stirred vigorously for another 1 h. Then extractive workup was performed with ether, and the ethereal extracts were washed with brine and dried over anhydrous Na_2SO_4 . After

evaporation of solvents, the crude products were dried under vacuum. A mixture of the crude products, *o*-bromoaniline (2.43 g, 14.1 mmol), potassium carbonate (1.95 g, 14.1 mmol), palladium acetate (264.9 mg, 1.18 mmol) and triphenylphosphine (1.24 g, 4.72 mmol) in dried DME (45 mL) was refluxed for 10 h with stirring under argon. After cooling to room temperature, the solution was filtered off and the filtrate was washed with brine. The Organic layer was dried over anhydrous Na₂SO₄. Removal of solvents and purification of the residual oil by column chromatography on silica gel (EtOAc/hexane = 1/15 as eluant) afforded **17** (5.81 g, 9.4 mmol, 80% yield) as a mixture of two conformational isomers (2.4:1). These conformers were interconvertible at room temperature. ¹H NMR (400 MHz, CDCl₃, major conformer) δ 8.07 (1H, d, *J* = 8.4 Hz, Ar-H), 7.98 (1H, d, *J* = 8.4 Hz, Ar-H), 7.87 (1H, d, *J* = 8.4 Hz, Ar-H), 7.80 (1H, s, Ar-H), 7.08-7.65 (12H, m, Ar-H), 6.79 (1H, t, *J* = 7.2 Hz, Ar-H), 6.60 (1H, d, *J* = 8.0 Hz, Ar-H), 4.17 (2H, s, OCH₂O), 2.85 (2H, br, NH₂), 2.18 (3H, s, OCH₃). [minor (detectable peaks)] δ 8.07 (1H, d, *J* = 8.4 Hz, Ar-H), 7.98 (1H, d, *J* = 8.4 Hz, Ar-H), 7.75-7.83 (2H, m, Ar-H), 7.08-7.65 (12H, m, Ar-H), 6.79 (1H, t, *J* = 7.2 Hz, Ar-H), 6.66 (1H, d, 6.4 Hz, Ar-H), 4.34 (1H, d, 6.0 Hz, OCH₂O), 4.23 (1H, d, 6.0 Hz, OCH₂O), 3.83 (2H, br, NH₂), 2.23 (3H, s, OCH₃); ¹³C NMR (100 MHz, CDCl₃, major conformer) δ 150.0, 144.2, 144.1, 137.4, 133.8, 133.3, 133.1, 132.2, 131.5, 131.0, 130.6, 130.5 (q, *J*_{C-F} = 33.8 Hz), 129.0, 128.7, 128.2, 127.9, 127.3, 127.0, 126.8, 126.6, 126.4, 125.5, 125.3, 124.6, 123.6, 122.9 (q, *J*_{C-F} = 274 Hz), 120.1, 120.1, 120.1, 118.2, 115.5, 98.4, 55.5. [minor (detectable peaks)] δ 151.2, 143.8, 143.6, 133.1, 133.0, 132.6, 131.2, 129.2, 128.6, 128.5, 127.8, 127.4, 126.7, 126.3, 125.4, 125.1, 123.0 (q, *J*_{C-F} = 274 Hz), 119.9, 118.3, 115.7, 98.2, 65.8; HRMS (ESI-TOF) Calcd. for C₃₆H₂₆F₆NO₂ ([M+H]⁺): 618.1862, Found: 618.1856.

Chiral Ligand 10b

To a solution of **17** (5.81 g, 9.4 mmol) and *i*-Pr₂NEt (3.28 mL, 18.8 mmol) in CH₂Cl₂ (30 mL) was added Tf₂O (1.58 mL, 9.4 mmol) at -78 °C under argon, and the reaction mixture was stirred for 2 h and quenched with saturated NaHCO₃. Extractive workup was performed with CH₂Cl₂, and the combined extracts were washed with brine and dried over anhydrous Na₂SO₄. After evaporation of solvents and drying under vacuum, the crude products were dissolved into 1,4-dioxane (30 mL) and *conc.* HCl (2-4 mL) was added at room temperature. Then, the mixture was stirred for 5 h at 70 °C. After cooling to room temperature, the solution was poured into water and extracted with ether. The ethereal extracts were washed with brine and dried over anhydrous Na₂SO₄. Removal of solvents and purification of the residual oil by column chromatography on silica gel (EtOAc/hexane = 1/5 as eluant) furnished **10b** (5.37 g, 7.6 mmol, 81% yield).

Two conformational isomers were detectable at $-40\text{ }^{\circ}\text{C}$ (^1H NMR for aromatic and phenol protons, see below).

$[\alpha]_{\text{D}}^{26} -46.4^{\circ}$ (c 1.01, CHCl_3); ^1H NMR (400 MHz, CDCl_3) δ 8.22 (1H, d, $J = 7.6$ Hz, Ar-H), 8.08 (1H, d, $J = 8.0$ Hz, Ar-H), 7.87 (1H, s, Ar-H), 7.82 (1H, d, $J = 7.6$ Hz, Ar-H), 7.75 (1H, d, $J = 8.8$ Hz, Ar-H), 7.23-7.65 (9H, m, Ar-H), 5.35 (1H, br, OH); ^{13}C NMR (100 MHz, CDCl_3) δ 147.2, 142.3, 138.3, 134.6, 133.6, 132.8, 132.6, 132.5, 132.3, 132.1, 131.5, 130.7 (q, $J_{\text{C-F}} = 33.8$ Hz), 130.6, 129.1, 128.9, 128.6, 128.5, 128.4, 128.3, 127.6, 127.5, 127.1, 126.4, 126.1, 125.5, 125.1, 124.5 (q, $J_{\text{C-F}} = 307$ Hz), 124.1, 124.0, 122.8 (q, $J_{\text{C-F}} = 274$ Hz), 120.5, 117.8; IR (neat) 3502, 3296, 3062, 2926, 1411, 1386, 1354, 1278, 1230, 1195, 1182, 1136, 896, 823, 752, 603 cm^{-1} ; HRMS (ESI-TOF) Calcd. for $\text{C}_{35}\text{H}_{19}\text{F}_9\text{NO}_3\text{S}$ ($[\text{M}-\text{H}]^-$): 704.0947, Found: 704.0951.

Chiral Ligand 10a (synthesized by the same procedure)

$[\alpha]_{\text{D}}^{26} -78.6^{\circ}$ (c 1.05, CHCl_3); ^1H NMR (400 MHz, CDCl_3) δ 8.14 (1H, d, $J = 8.8$ Hz, Ar-H), 8.02 (1H, d, $J = 8.0$ Hz, Ar-H), 7.81-7.84 (2H, m, Ar-H), 7.72 (1H, d, 8.4 Hz), 7.26-7.59 (9H, m, Ar-H), 7.03-7.25 (6H, m, Ar-H), 5.23 (1H, br, OH); ^{13}C NMR (100 MHz, CDCl_3) δ 146.8, 141.8, 140.3, 135.0, 133.9, 133.2, 132.9, 132.3, 131.8, 130.0, 129.0, 128.8, 128.6, 128.5, 128.4, 128.3, 128.0, 127.7, 127.3, 127.3, 126.8, 126.6, 126.0, 125.7, 125.1, 124.4, 119.5 (q, $J_{\text{C-F}} = 324$ Hz), 119.1 (three signals for aromatic carbons were not identified due to the overlap of the peaks); IR (neat) 3502, 3282, 3057, 2927, 1732, 1494, 1411, 1355, 1230, 1195, 1141, 1028, 952, 825, 765, 750, 700, 603 cm^{-1} ; HRMS (ESI-TOF) Calcd. for $\text{C}_{33}\text{H}_{21}\text{F}_3\text{NO}_3\text{S}$ ($[\text{M}-\text{H}]^-$): 568.1188, Found: 568.1191.

Chiral Ligand (*S,S*)-4

To a solution of **17** (1.23 g, 2.0 mmol) in THF (6 mL) was added a 1.5 M hexane solution of *n*-BuLi (2.67 mL, 4.0 mmol) slowly at $-78\text{ }^{\circ}\text{C}$, and the mixture was stirred for 30 min. 3,5-Bis(trifluoromethyl)benzenesulfonyl chloride (937.8 mg, 3.0 mmol) was added to this mixture, and the stirring was maintained for 30 min at $-78\text{ }^{\circ}\text{C}$ and 3 h at room temperature. The reaction was quenched with saturated NH₄Cl and extractive workup was conducted with ether. The organic extracts were washed with brine and dried over anhydrous Na₂SO₄. After evaporation of solvents and drying under vacuum, the crude products were dissolved into 1,4-dioxane (10 mL) and *conc.* HCl (1-2 mL) was added at room temperature. Then, the mixture was stirred for 5 h at $70\text{ }^{\circ}\text{C}$. After cooling to room temperature, the solution was poured into water and extracted with ether. The ethereal extracts were washed with brine and dried over anhydrous Na₂SO₄. Removal of solvents and purification of the residual oil by column chromatography on silica gel (EtOAc/hexane = 1/10 as eluant) afforded stereochemically pure (*S,S*)-**4** (1.00 g, 1.16 mmol, 58% yield). Diastereomeric (*S,S*)-**4** and (*S,R*)-**4** were not interconvertible, and these were separable by column chromatography on silica gel (crude product: dr = 8:1). $[\alpha]_{\text{D}}^{24} +32.2^{\circ}$ (*c* 1.04, CH₃OH); ¹H NMR (400 MHz, CDCl₃) δ 8.22 (1H, d, *J* = 4.8 Hz, Ar-H), 8.10–8.13 (1H, m, Ar-H), 7.70–7.74 (7H, m, Ar-H), 7.53 (1H, t, *J* = 7.8 Hz, Ar-H), 7.40–7.45 (7H, m, Ar-H), 7.17–7.27 (2H, m, Ar-H), 6.96 (1H, s, Ar-H), 6.88 (1H, d, *J* = 7.6 Hz, Ar-H), 5.16 (1H, br, OH); ¹³C NMR (100 MHz, CDCl₃) δ 146.8, 142.3, 141.4, 138.4, 134.2, 133.6, 132.4, 132.3, 132.1 (q, *J*_{C-F} = 34.6 Hz), 131.2, 131.0, 130.5 (q, *J*_{C-F} = 33.3 Hz), 130.4, 129.4, 128.6, 128.4, 128.2, 128.1, 127.7, 127.5, 127.4, 127.1, 126.3, 125.9, 125.7, 124.9, 124.7, 124.1, 122.8 (q, *J*_{C-F} = 273 Hz), 121.9 (q, *J*_{C-F} = 290 Hz), 120.4, 120.4, 120.3, 117.6 (two signals for aromatic carbons were not identified due to the overlap of the peaks); IR (neat) 3298, 2970, 2931, 2873, 1695, 1384, 1355, 1276, 1166, 1130, 1111, 1091, 1043, 1024, 923, 900, 844, 819, 748, 705, 698, 636 cm⁻¹; HRMS (ESI-TOF) Calcd. for C₄₂H₂₂F₁₂NO₃S ([M-H]⁻): 848.1123, Found: 848.1128.

VII. X-ray Structure of Chiral Ligand (S,S)-4

(S,S)-4 was recrystallized from hexane.

The single crystal of **4** was mounted on a CryoLoop (Hampton Research Co. Ltd.). Data of X-ray diffraction were collected by a Rigaku RAXIS-RAPID Imaging Plate two-dimensional area detector using graphite-monochromated MoK α radiation ($\lambda = 0.71075$ Å) to a maximum 2θ value of 55.0° . Crystallographic calculation was performed using CrystalStructure software package of the Rigaku Corporation and Molecular Structure Corporation. The crystal structure was solved by the direct method and refined by the full-matrix least squares using SIR-2002. All non-hydrogen atoms were refined anisotropically and hydrogen atoms were refined using the riding model. The crystallographic data are summarized in the following table.

Experimental Details

empirical formula	C ₄₂ H ₂₃ F ₁₂ NO ₃ S
formula weight	849.69
crystal system	monoclinic
space group	P2 ₁ (#4)
<i>a</i> , Å	16.029 (4)
<i>b</i> , Å	13.029 (3)
<i>c</i> , Å	17.866 (6)
<i>V</i> , Å ³	3630.1 (16)
<i>Z</i>	4
<i>D</i> _{calc} , g/cm ³	1.555
<i>T</i> , °C	−150.0
μ (MoK α), cm ^{−1}	1.942
no. of reflns meased	16618
no. of reflns obsd	15200
no. of variable	1122
<i>R</i> <i>I</i>	0.0506
<i>R</i> <i>w</i>	0.1341
Goodness of fit	1.326
Max shift/error in final cycle	0.004

(a) ORTEP

(b) Cylinder (F, S: Yellow, O: Red, N: Blue)

VIII. Characterization of Products

1,4-Diphenyl-3-triethylsiloxy-2-butanone [2a (R² = Et)]

 $[\alpha]_{\text{D}}^{21} -58.7^{\circ}$ (*c* 1.07, CHCl₃, 86% ee); ¹H NMR (400 MHz, CDCl₃) δ 7.21-7.31 (6H, m, Ph-H), 7.16-7.18 (2H, m, Ph-H), 7.05-7.07 (2H, m, Ph-H), 4.36 (1H, dd, *J* = 7.6, 4.4 Hz, SiOCH), 3.77 (1H, d, *J* = 17.2 Hz, PhCH₂CO), 3.66, (1H, d, *J* = 17.2 Hz, PhCH₂CO), 2.93 (1H, dd, *J* = 13.6, 4.4 Hz, CHCH₂Ph), 2.83 (1H, dd, *J* = 13.6, 7.6 Hz, CHCH₂Ph), 0.86 (9H, t, *J* = 8.0 Hz, CH₃CH₂Si), 0.41-0.52 (6H, m, CH₃CH₂Si); ¹³C NMR (100 MHz, CDCl₃) δ 209.8, 136.6, 133.6, 129.6, 129.5, 128.1, 128.0, 126.5, 126.4, 79.4, 44.8, 41.5, 6.7, 4.6; IR (neat) 3030, 2953, 2910, 2322, 1718, 1496, 1454, 1417, 1238, 1095, 1004, 943, 773, 727, 696, 667 cm⁻¹; HRMS (ESI-TOF) Calcd. for C₂₂H₃₁O₂Si ([M+H]⁺): 355.2088, Found: 355.2090; HPLC condition: DAICEL Chiralcel OJ-H, hexane/*i*-PrOH = 99:1, flow rate = 0.5 mL/min, λ = 223 nm, retention time: 16.6 min (*R*), 18.6 min (*S*). Absolute configuration was established by comparison of optical rotation with known literature value² after desilylation as described below.

To a solution of **2a** (R² = Et) (177.3 mg, 0.5 mmol) in THF (2 mL) was added a 1 M THF solution of TBAF (500 μL, 0.5 mmol) at 0 °C. After stirring for 30 min, the mixture was poured into water and extracted with EtOAc. The organic extracts were washed with brine and dried over anhydrous Na₂SO₄. Removal of solvents and purification of the residual oil by short column chromatography on silica gel (EtOAc/hexane = 1/10 as eluant) afforded 1,4-diphenyl-3-hydroxy-2-butanone² (120.2 mg, 0.5 mmol, quant).

1,4-Diphenyl-3-trimethylsiloxy-2-butanone [2a (R² = Me)]

 $[\alpha]_{\text{D}}^{24} -57.3^{\circ}$ (*c* 0.96, CHCl₃, 77% ee); ¹H NMR (400 MHz, CDCl₃) δ 7.22-7.32 (6H, m, Ph-H), 7.16-7.20 (2H, m, Ph-H), 7.11-7.13 (2H, m, Ph-H), 4.28 (1H, dd, *J* = 8.6, 4.0 Hz, SiOCH), 3.79 (1H, d, *J* = 16.8 Hz, PhCH₂CO), 3.74, (1H, d, *J* = 16.8 Hz, PhCH₂CO), 2.95 (1H, dd, *J* = 13.6, 4.0 Hz, CHCH₂Ph), 2.76 (1H, dd, *J* = 13.6, 8.6 Hz, CHCH₂Ph), -0.10 (9H, s, Me₃Si); ¹³C NMR (100 MHz, CDCl₃) δ 210.1, 137.3, 134.1, 130.0, 129.9, 128.6, 128.4, 127.0, 126.8, 79.8, 45.1, 41.6, 0.0; IR (neat) 2954, 1720, 1496, 1454, 1251, 1097, 945, 902, 840, 748, 698 cm⁻¹; HRMS (ESI-TOF) Calcd. for C₁₉H₂₄NaO₂Si ([M+Na]⁺): 335.1449, Found: 335.1435; HPLC condition: DAICEL Chiralpak AD-H, hexane/*i*-PrOH = 99:1, flow rate = 0.5 mL/min, λ = 223 nm, retention time: 9.7 min (*S*), 11.1 min (*R*).

$[\alpha]_D^{24} -41.2^\circ$ (c 1.01, CHCl_3 , 80% ee); ^1H NMR (400 MHz, CDCl_3) δ 7.21-7.33 (6H, m, Ph-H), 7.17-7.19 (2H, m, Ph-H), 7.07-7.09 (2H, m, Ph-H), 4.32 (1H, dd, $J = 8.0, 4.0$ Hz, SiOCH), 3.79 (1H, d, $J = 17.2$ Hz, PhCH_2CO), 3.72 (1H, d, $J = 17.2$ Hz, PhCH_2CO), 2.95 (1H, dd, $J = 13.6, 4.0$ Hz, CHCH_2Ph), 2.76 (1H, dd, $J = 13.6, 8.0$ Hz, CHCH_2Ph), 0.88 (9H, s, $t\text{-BuSi}$), -0.07 (3H, s, MeSi), -0.25 (3H, s, MeSi); ^{13}C NMR (100 MHz, CDCl_3) δ 210.3, 136.8, 133.8, 129.9, 129.7, 128.3, 128.2, 126.7, 126.6, 79.7, 44.6, 41.4, 25.7, 18.0, $-5.2, -5.5$; IR (neat) 3030, 2953, 2927, 2856, 1722, 1496, 1454, 1253, 1093, 943, 835, 812, 777, 752, 698 cm^{-1} ; HRMS (ESI-TOF) Calcd. for $\text{C}_{22}\text{H}_{30}\text{NaO}_2\text{Si}$ ($[\text{M}+\text{Na}]^+$): 377.1918, Found: 377.1915; HPLC condition: DAICEL Chiralcel OJ-H, hexane/*i*-PrOH = 99:1, flow rate = 0.5 mL/min, $\lambda = 223$ nm, retention time: 14.3 min (*R*), 18.2 min (*S*).

$[\alpha]_D^{29} -197.9^\circ$ (c 1.51, CHCl_3 , 85% ee); ^1H NMR (400 MHz, CDCl_3) δ 7.08 (2H, d, $J = 8.4$ Hz, Ph-H), 6.97 (2H, d, $J = 8.4$ Hz, Ph-H), 6.79-6.84 (4H, m, Ph-H), 4.32 (1H, dd, $J = 7.2, 4.8$ Hz, SiOCH), 3.79 (3H, s, MeOPh), 3.78 (3H, s, MeOPh), 3.69 (1H, d, $J = 17.2$ Hz, PhCH_2CO), 3.58 (1H, d, $J = 17.2$ Hz, PhCH_2CO), 2.87 (1H, dd, $J = 13.6, 4.8$ Hz, CHCH_2Ph), 2.79 (1H, dd, $J = 13.6, 7.2$ Hz, CHCH_2Ph), 0.88 (9H, t, $J = 8.0$ Hz, $\text{CH}_3\text{CH}_2\text{Si}$), 0.44-0.56 (6H, m, $\text{CH}_3\text{CH}_2\text{Si}$); ^{13}C NMR (100 MHz, CDCl_3) δ 210.3, 158.2, 130.5, 130.5, 128.6, 125.6, 113.6, 113.4, 79.4, 55.1, 55.0, 43.9, 40.7, 6.7, 4.6; IR (neat) 2953, 2910, 2875, 2835, 1718, 1612, 1583, 1510, 1463, 1440, 1300, 1246, 1176, 1109, 1089, 1035, 1004, 945, 819, 802, 765, 740, 729, 678 cm^{-1} ; HRMS (ESI-TOF) Calcd. for $\text{C}_{30}\text{H}_{34}\text{NaO}_2\text{Si}$ ($[\text{M}+\text{Na}]^+$): 437.2118, Found: 437.2115; HPLC condition: DAICEL Chiralcel OD-H, hexane/*i*-PrOH = 99:1, flow rate = 0.5 mL/min, $\lambda = 223$ nm, retention time: 28.5 min (major), 36.9 min (minor).

$[\alpha]_D^{29} -66.4^\circ$ (c 1.11, CHCl_3 , 90% ee); ^1H NMR (400 MHz, CDCl_3) δ 7.10-7.14 (2H, m, Ph-H), 6.94-7.01 (6H, m, Ph-H), 4.33 (1H, dd, $J = 7.2, 4.6$ Hz, SiOCH), 3.73 (1H, d, $J = 17.2$ Hz, PhCH_2CO), 3.61 (1H, d, $J = 17.2$ Hz, PhCH_2CO), 2.88 (1H, dd, $J = 14.0, 4.6$ Hz, CHCH_2Ph), 2.83 (1H, dd, $J = 14.0, 7.2$ Hz, CHCH_2Ph), 0.89 (9H, t, $J = 8.0$ Hz, $\text{CH}_3\text{CH}_2\text{Si}$), 0.45-0.55 (6H, m, $\text{CH}_3\text{CH}_2\text{Si}$); ^{13}C NMR (100 MHz, CDCl_3) δ 209.9, 161.7 (d, $J_{\text{C-F}} = 246$ Hz), 161.6 (d, $J_{\text{C-F}} = 246$ Hz), 132.2 (d, $J_{\text{C-F}} = 3.3$ Hz), 131.2 (d, $J_{\text{C-F}} = 8.3$ Hz), 131.0 (d, $J_{\text{C-F}} = 8.2$ Hz), 129.2 (d, $J_{\text{C-F}} = 3.3$ Hz), 115.1 (d, $J_{\text{C-F}} = 21.4$ Hz), 114.9 (d, $J_{\text{C-F}} = 20.6$ Hz), 79.3, 43.8,

40.7, 6.7, 4.6; IR (neat) 2954, 2912, 2877, 1720, 1602, 1508, 1458, 1415, 1340, 1220, 1157, 1099, 1087, 1004, 974, 945, 823, 804, 769, 740, 729, 678 cm⁻¹; HRMS (ESI-TOF) Calcd. for C₂₂H₂₉F₂O₂Si ([M+H]⁺): 391.1899, Found: 391.1897; HPLC condition: DAICEL Chiralpak AD-H, hexane/*i*-PrOH = 99:1, flow rate = 0.5 mL/min, λ = 223 nm, retention time: 14.4 min (major), 16.1 min (minor).

1,4-Bis(4-chlorophenyl)-3-triethylsiloxy-2-butanone (2d)

[α]_D²⁶ -67.9° (*c* 1.03, CHCl₃, 86% ee); ¹H NMR (400 MHz, CDCl₃) δ 7.22-7.25 (4H, m, Ph-H), 7.08 (2H, d, *J* = 8.8 Hz, Ph-H), 6.94 (2H, d, *J* = 8.0 Hz, Ph-H), 4.34 (1H, dd, *J* = 6.8, 4.8 Hz, SiOCH), 3.71 (1H, d, *J* = 17.2 Hz, PhCH₂CO), 3.61 (1H, d, *J* = 17.2 Hz, PhCH₂CO), 2.88 (1H, dd, *J* = 13.6, 4.8 Hz, CHCH₂Ph), 2.83 (1H, dd, *J* = 13.6, 6.8 Hz, CHCH₂Ph), 0.90 (9H, t, *J* = 8.0 Hz, CH₃CH₂Si), 0.46-0.57 (6H, m, CH₃CH₂Si); ¹³C NMR (100 MHz, CDCl₃) δ 209.5, 134.9, 132.6, 132.5, 131.9, 131.0, 128.3, 128.2, 79.1, 44.0, 40.9, 6.8, 4.7; IR (neat) 2954, 2910, 2875, 1720, 1490, 1458, 1408, 1338, 1240, 1089, 1016, 974, 947, 910, 842, 792, 767, 729, 677 cm⁻¹; HRMS (ESI-TOF) Calcd. for C₂₂H₂₉Cl₂O₂Si ([M+H]⁺): 423.1308, Found: 423.1299; HPLC condition: DAICEL Chiralpak AD-H, hexane/*i*-PrOH = 99:1, flow rate = 0.5 mL/min, λ = 223 nm, retention time: 22.1 min (major), 23.8 min (minor).

1,4-Di(2-naphthyl)-3-triethylsiloxy-2-butanone (2e)

[α]_D²³ -81.0° (*c* 1.16, CHCl₃, 85% ee); ¹H NMR (400 MHz, CDCl₃) δ 7.62-7.80 (5H, m, Ar-H), 7.57 (1H, s, Ar-H), 7.40-7.46 (4H, m, Ar-H), 7.36 (1H, dd, *J* = 8.4, 1.6 Hz, Ar-H), 7.34 (1H, s, Ar-H), 7.12 (1H, dd, *J* = 8.4, 1.6 Hz, Ar-H), 4.52 (1H, dd, *J* = 6.8, 5.0 Hz, SiOCH), 3.87 (1H, d, *J* = 16.8 Hz, ArCH₂CO), 3.79 (1H, d, *J* = 16.8 Hz, ArCH₂CO), 3.12 (1H, dd, *J* = 13.6, 5.0 Hz, CHCH₂Ar), 3.07 (1H, dd, *J* = 13.6, 6.8 Hz, CHCH₂Ar), 0.89 (9H, t, *J* = 8.0 Hz, CH₃CH₂Si), 0.48-0.55 (6H, m, CH₃CH₂Si); ¹³C NMR (100 MHz, CDCl₃) δ 210.2, 134.0, 133.2, 133.2, 132.2, 132.1, 131.1, 128.4, 128.2, 128.0, 127.8, 127.7, 127.6, 127.4, 127.4, 127.4, 125.8, 125.7, 125.4, 125.3, 79.4, 45.2, 41.8, 6.8, 4.7; IR (neat) 3053, 2953, 2908, 2875, 2357, 2313, 1718, 1508, 1456, 1417, 1338, 1238, 1093, 1016, 962, 854, 808, 742 cm⁻¹; HRMS (ESI-TOF) Calcd. for C₃₀H₃₄NaO₂Si ([M+Na]⁺): 477.2231, Found: 477.2223; HPLC condition: DAICEL Chiralpak AS-H, hexane/*i*-PrOH = 99:1, flow rate = 0.3 mL/min, λ = 223 nm, retention time: 23.7 min (major), 27.1 min (minor).

1,8-Diphenyl-5-triethylsiloxy-1,7-octadien-4-one (2f)

[α]_D²⁷ -32.0° (*c* 1.09, CHCl₃, 83% ee); ¹H NMR (400 MHz, CDCl₃) δ 7.26-7.33 (8H, m, Ph-H), 7.18-7.22 (2H, m, Ph-H), 6.94 (2H, d, *J* = 8.0 Hz, Ph-H), 6.42 (1H, d, *J* = 16.0 Hz, PhCH), 6.40 (1H, d, *J* = 16.0 Hz, PhCH), 6.31 (1H, dt, *J* = 16.0, 6.4 Hz, PhCH=CH), 6.19 (1H, dt, *J* = 16.0, 6.4 Hz, PhCH=CH), 4.25 (1H, t, *J*

= 6.4 Hz, SiOCH), 3.51 (2H, d, J = 6.4 Hz, CHCH₂CO), 2.57 (2H, t, J = 6.4 Hz, SiOCHCH₂CH), 0.97 (9H, t, J = 8.0 Hz, CH₃CH₂Si), 0.64 (6H, q, J = 8.0 Hz, CH₃CH₂Si); ¹³C NMR (100 MHz, CDCl₃) δ 211.3, 137.1, 136.9, 133.4, 133.3, 128.4, 128.4, 127.3, 127.2, 126.1, 126.1, 124.4, 121.9, 78.4, 41.8, 38.9, 6.7, 4.7; IR (neat) 3026, 2954, 2910, 2875, 1716, 1598, 1494, 1448, 1240, 1099, 1004, 964, 831, 736, 692 cm⁻¹; HRMS (ESI-TOF) Calcd. for C₂₆H₃₄NaO₂Si ([M+Na]⁺): 429.2231, Found: 429.2229; HPLC condition: DAICEL Chiralcel OJ-H, hexane/*i*-PrOH = 99:1, flow rate = 0.5 mL/min, λ = 254 nm, retention time: 34.7 min (minor), 40.7 min (major).

2,9-Dimethyl-6-triethylsiloxy-2,8-decadien-5-one (2g)

[α]_D²⁷ -6.5° (*c* 0.98, CHCl₃, 80% ee); ¹H NMR (400 MHz, CDCl₃) δ 5.27-5.31 (1H, m, C=CH), 5.10-5.14 (1H, m, C=CH), 4.07 (1H, dd, J = 6.6, 5.8 Hz, SiOCH), 3.28 (2H, d, J = 7.2 Hz, CHCH₂CO), 2.26-2.40 (2H, m, SiCHCH₂CH), 1.74 (3H, s, Me₂C=), 1.69 (3H, s, Me₂C=), 1.60 (3H, s, Me₂C=), 1.58 (3H, s, Me₂C=), 0.95 (9H, t, J = 8.0 Hz, CH₃CH₂Si), 0.60 (6H, q, J = 8.0 Hz, CH₃CH₂Si); ¹³C NMR (100 MHz, CDCl₃) δ 211.9, 135.1, 134.5, 118.7, 115.8, 78.5, 37.1, 34.0, 25.7, 25.7, 18.0, 17.9, 6.7, 4.7; IR (neat) 2956, 2912, 2875, 1737, 1456, 1377, 1238, 1143, 1091, 1010, 839, 740, 729 cm⁻¹; HRMS (ESI-TOF) Calcd. for C₁₈H₃₄NaO₂Si ([M+Na]⁺): 333.2231, Found: 333.2224. Enantiomeric excess was determined by HPLC analysis after desilylation (see the above mentioned procedure).

HPLC condition: See also ref. 2.

2,7-Dimethyl-5-triethylsiloxy-4-octanone (2h)

[α]_D²⁷ -13.3° (*c* 1.00, CHCl₃, 74% ee); ¹H NMR (400 MHz, CDCl₃) δ 4.04 (1H, dd, J = 8.6, 5.4 Hz, SiOCH), 2.41 (2H, d, J = 7.2 Hz, CH₂CO), 2.12-2.19 (1H, m, Me₂CH), 1.67-1.74 (1H, m, Me₂CH), 1.26-1.50 (2H, m, SiOCHCH₂), 0.87-0.98 (12H, m, Me₂CH), 0.93 (9H, t, J = 8.0 Hz, CH₃CH₂Si), 0.60 (6H, q, J = 8.0 Hz, CH₃CH₂Si); ¹³C NMR (100 MHz, CDCl₃) δ 213.0, 77.4, 45.6, 43.7, 23.9, 23.4, 23.1, 22.6, 22.5, 22.0, 6.7, 4.7; IR (neat) 2956, 2937, 2912, 2875, 1714, 1467, 1367, 1240, 1095, 1004, 904, 742, 729 cm⁻¹; HRMS (ESI-TOF) Calcd. for C₁₆H₃₄NaO₂Si ([M+Na]⁺): 309.2231, Found: 309.2218. Enantiomeric excess was determined by HPLC analysis after desilylation (see the above mentioned procedure) and subsequent reprotection as 3,5-dinitrobenzoate.³

¹H NMR (400 MHz, CDCl₃) δ 9.25 (1H, s, Ph-H), 9.17 (2H, s, Ph-H), 5.36 (1H, d, *J* = 10.4, 3.2 Hz, SiOCH), 2.47 (1H, dd, *J* = 16.8, 6.8 Hz, CH₂CO), 2.35 (1H, dd, *J* = 16.8, 6.8 Hz, CH₂CO), 2.19-2.26 (1H, m, CHCH₂CO), 1.84-1.94 (2H, m, SiOCHCH₂), 1.70-1.74 (1H, m, SiOCHCH₂CH), 1.05 (3H, d, *J* = 6.8 Hz, Me₂CH), 1.02 (3H, d, *J* = 6.8 Hz, Me₂CH), 0.98 (3H, d, *J* = 6.8 Hz, Me₂CH), 0.96 (3H, d, *J* = 6.8 Hz, Me₂CH); ¹³C NMR (100 MHz, CDCl₃) δ 204.9, 162.1, 148.6, 133.2, 129.5, 122.5, 79.4, 47.3, 38.4, 25.0, 24.2, 23.2, 22.4, 22.4, 21.2; HPLC condition: DAICEL Chiralpak AS-H, hexane/*i*-PrOH = 97:3, flow rate = 0.5 mL/min, λ = 254 nm, retention time: 16.8 min (minor), 19.6 min (major).

1,2-Dicyclohexyl-2-triethylsiloxyethanone (2i)

[α]_D²⁵ −5.9° (*c* 1.10, CHCl₃, 74% ee); ¹H NMR (400 MHz, CDCl₃) δ 3.89 (1H, d, *J* = 5.2 Hz, SiOCH), 2.73-2.79 (1H, m, CHCO), 1.52-1.79 (11H, m, -CH-), 1.06-1.43 (10H, m, -CH-), 0.95 (9H, t, *J* = 8.0 Hz, CH₃CH₂Si), 0.59 (6H, q, *J* = 8.0 Hz, CH₃CH₂Si); ¹³C NMR (100 MHz, CDCl₃) δ 215.4, 82.8, 45.4, 41.7, 29.5, 29.1, 28.6, 27.7, 26.2, 26.1, 26.1, 25.8, 25.7, 25.5, 6.8, 4.8; IR (neat) 2929, 2854, 1716, 1450, 1238, 1141, 1004, 835, 740 cm^{−1}; HRMS (ESI-TOF) Calcd. for C₂₀H₃₈NaO₂Si ([M+Na]⁺): 361.2533, Found: 361.2546. Enantiomeric excess was determined in a similar manner as described for **2h**.

¹H NMR (400 MHz, CDCl₃) δ 9.25 (1H, s, Ph-H), 9.16 (2H, s, Ph-H), 5.36 (1H, d, *J* = 3.6 Hz, SiOCH), 2.56-2.61 (1H, m, CHCO), 2.04-2.12 (2H, m, -CH-), 1.49-1.86 (9H, m, -CH-), 1.16-1.43 (10H, m, -CH-); ¹³C NMR (100 MHz, CDCl₃) δ 207.8, 162.0, 148.6, 133.5, 129.4, 122.5, 83.3, 47.5, 38.7, 30.2, 29.6, 27.3, 27.2, 26.2, 25.9, 25.8, 25.7, 25.5, 25.1; HPLC condition: DAICEL Chiralpak AD-H, hexane/*i*-PrOH = 95:5, flow rate = 0.5 mL/min, λ = 254 nm, retention time: 22.8 min (minor), 35.0 min (major).

IX. Preparation of Differently α,α -Disubstituted α -Siloxy Aldehydes **5**

To a solution of benzaldehyde (1.0 mL, 10 mmol) and triethylsilyl cyanide (1.41 g, 10 mmol) in CH_2Cl_2 (30 mL) was added I_2 (253 mg, 1 mmol) at $0\text{ }^\circ\text{C}$ under argon. After stirring for 30 min at $0\text{ }^\circ\text{C}$, the reaction was quenched with saturated Na_2SO_3 and extractive workup was conducted with ether. The organic extracts were then washed with brine and dried over anhydrous Na_2SO_4 . After evaporation of solvents, the crude products were dried under vacuum. To a solution of diisopropylamine (2.1 mL, 15 mmol) in THF (15 mL) was added *n*-BuLi (10 mL; 1.5 M hexane solution, 15 mmol) at $-78\text{ }^\circ\text{C}$ under argon. This solution was kept for 15 min with stirring, then slowly transferred into a THF (15 mL) solution of crude products at $-78\text{ }^\circ\text{C}$. After stirring for 30 min, benzyl bromide (1.8 mL, 15 mmol) was added. The whole reaction mixture was stirred for 3 h at the same temperature and quenched with water. Extractive workup was performed with EtOAc and the combined extracts were washed with brine and dried over anhydrous Na_2SO_4 . After concentration, the residual oil was purified by column chromatography on silica gel (EtOAc/hexane = 1/10 as eluant) to afford **18** (2.83 g, 8.4 mmol, 84% yield) as colorless oil. ^1H NMR (400 MHz, CDCl_3) δ 7.21-7.39 (8H, m, Ph-H), 7.09-7.11 (2H, m, Ph-H), 3.24 (1H, d, $J = 13.6\text{ Hz}$, PhCH_2), 3.12 (1H, d, $J = 13.6\text{ Hz}$, PhCH_2), 0.81 (9H, t, $J = 8.0\text{ Hz}$, $\text{CH}_3\text{CH}_2\text{Si}$), 0.48-0.63 (6H, m, $\text{CH}_3\text{CH}_2\text{Si}$).

To a solution of **18** in CH_2Cl_2 (16.8 mL) was added DIBAH (16.8 mL; 1 M toluene solution, 16.8 mmol) at $-78\text{ }^\circ\text{C}$, and the reaction mixture was stirred for 1 h at the same temperature. Then, the mixture was quenched with 1N HCl and extracted with ether. The organic extracts were washed with brine and dried over anhydrous Na_2SO_4 , and concentrated. The residual oil was purified by column chromatography on silica gel (CH_2Cl_2 /hexane = 1/4 as eluant) to give **5a** (2.86 g, 8.4 mmol, quant) as colorless oil.

Other substrates (**5b**, **5c** and **5d**) were synthesized by the same procedure.

5e was synthesized from a known ketone by the procedure described in S2.

X. General Procedure for Kinetic Resolution of α,α -Disubstituted α -Siloxy Aldehydes via Chiral Organoaluminum Catalyzed 1,2-Rearrangement

To a solution of 2-hydroxy-2'-[3,5-bis(trifluoromethyl)]phenyl-3-{2-[3,5-bis(trifluoromethyl)]benzenesulfonylamino}phenyl-1,1'-binaphthyl (**4**, 46.7 mg, 0.055 mmol) in toluene (10 mL) was added a 1 M toluene solution of trimethylaluminum (50 μL , 0.050 mmol) at room temperature under nitrogen and stirred for 30 min. After being cooled to -20°C , **5a** (354.5 mg, 1 mmol) was added to this solution and the stirring was maintained at -20°C for 12 h. Then, sodium fluoride (8.4 mg, 0.20 mmol) and water (2.7 μL , 0.15 mmol) were added and the whole mixture was stirred for 30 min at room temperature. To remove precipitates, filtration through celite with EtOAc was carried out. Concentration of the filtrate and purification by column chromatography on silica gel ($\text{CH}_2\text{Cl}_2/\text{hexane} = 1/4$ as eluant) afforded **6a** (166.9 mg, 0.49 mmol, 49% yield, The ratio of **6a**/the product through the migration of phenyl group was $>20:1$) and **5a** (173.7 mg, 0.51 mmol, 51% recovery).

XI. Characterization of **5** and **6**

2,3-Diphenyl-2-triethoxysilylpropanal (5a)
 $[\alpha]_{\text{D}}^{31} +62.1^\circ$ (c 1.02, CHCl_3 , 84% ee); ^1H NMR (400 MHz, CDCl_3) δ 9.77 (1H, s, CHO), 7.26-7.33 (5H, m, Ph-H), 7.12-7.14 (3H, m, Ph-H), 6.95-6.98 (2H, m, Ph-H), 3.32 (1H, d, $J = 14.2$ Hz, PhCH_2), 3.25 (1H, d, $J = 14.2$ Hz, PhCH_2), 0.89 (9H, t, $J = 8.0$ Hz, $\text{CH}_3\text{CH}_2\text{Si}$), 0.58 (6H, q, $J = 8.0$ Hz, $\text{CH}_3\text{CH}_2\text{Si}$); ^{13}C NMR (100 MHz, CDCl_3) δ 199.8, 139.4, 135.4, 130.7, 128.2, 127.6, 127.5, 126.3, 126.0, 85.1, 44.9, 7.0, 6.8; IR (neat) 2954, 2937, 2910, 2875, 2808, 1734, 1496, 1454, 1242, 1143, 1076, 1008, 956, 761, 729, 698 cm^{-1} ; HRMS (ESI-TOF) Calcd. for $\text{C}_{21}\text{H}_{28}\text{NaO}_2\text{Si}$ ($[\text{M}+\text{Na}]^+$): 363.1751, Found: 363.1762. Enantiomeric excess was determined by HPLC analysis after desilylation as described below.

To a solution of **5a** (68.1 mg, 0.2 mmol) in THF (2 mL) was added 1N HCl (1 mL) at room temperature. After vigorous stirring for 5 h, this mixture was treated with saturated NaHCO_3 and extractive workup was conducted with EtOAc. The combined

organics were washed with brine and dried over anhydrous Na₂SO₄. Removal of solvents and purification of the residual oil by short column chromatography gave 2,3-diphenyl-2-hydroxypropanal (45.3 mg, 0.2 mmol, quant).

¹H NMR (400 MHz, CDCl₃) δ 9.72 (1H, s, CHO), 7.55 (2H, d, *J* = 8.0 Hz, Ph-H), 7.42 (2H, t, *J* = 8.0 Hz, Ph-H), 7.34 (1H, t, *J* = 7.6 Hz, Ph-H), 7.22-7.27 (3H, m, Ph-H), 7.15 (2H, d, *J* = 7.6 Hz, Ph-H), 3.57 (1H, s, OH), 3.53 (2H, d, *J* = 14.0 Hz, PhCH₂), 3.26 (2H, d, *J* = 14.0 Hz, PhCH₂); ¹³C NMR (100 MHz, CDCl₃) δ 199.7, 138.2, 134.4, 130.4, 128.8, 128.3, 128.1, 127.1, 125.8, 81.8, 43.7; HPLC condition: DAICEL Chiralpak AD-H, hexane/*i*-PrOH = 95:5, flow rate = 0.5 mL/min, λ = 254 nm, retention time: 26.7 min (*S*), 28.9 min (*R*).

Absolute configuration was established by comparison of optical rotation with known literature value⁴ after transformation as described below.

To a solution of **5a** (68.1 mg, 0.2 mmol, 84% ee) in MeOH (2 mL) was added NaBH₄ (15.1 mg, 0.4 mmol) at 0 °C, and the reaction mixture was kept for 30 min with stirring. Then this mixture was quenched with water and extracted with EtOAc. The organic extracts were washed with brine and dried over anhydrous Na₂SO₄. After evaporation, the crude mixture was dissolved into THF (2 mL), and 1N HCl (1 mL) was added at room temperature. The whole mixture was stirred vigorously for 5 h and quenched with saturated NaHCO₃. Extractive workup was performed with EtOAc, and the combined extracts were washed with brine and dried over anhydrous Na₂SO₄. Removal of solvents and purification of the residual oil afforded 2,3-diphenylpropan-1,2-diol⁴ (43.3 mg, 0.19 mmol, 95%).

2-(4-Fluorophenyl)-3-phenyl-2-triethylsiloxypropanal (**5b**)

[α]_D³⁰ +69.2° (*c* 1.09, CHCl₃, 85% ee); ¹H NMR (400 MHz, CDCl₃) δ 9.73 (1H, s, CHO), 7.25-7.28 (2H, m, Ar-H), 7.12-7.14 (3H, m, Ar-H), 6.92-7.02 (4H, m, Ar-H), 3.28 (1H, d, *J* = 14.2 Hz, PhCH₂), 3.20 (1H, d, *J* = 14.2 Hz, PhCH₂), 0.91 (9H, t, *J* = 8.0 Hz, CH₃CH₂Si), 0.59 (6H, q, *J* = 8.0 Hz, CH₃CH₂Si); ¹³C NMR (100 MHz, CDCl₃) δ 199.5, 162.2 (d, *J*_{C-F} = 247 Hz), 135.1, 135.0, 130.6, 127.8 (d, *J*_{C-F} = 8.3 Hz), 127.6, 126.4, 115.1 (d, *J*_{C-F} = 21.4 Hz), 84.7, 44.9, 6.9, 6.8; IR (neat) 2954, 2912, 2875, 2808, 1734, 1602, 1506, 1456, 1236, 1159, 1095, 1012, 956, 833, 740, 729, 698, 669 cm⁻¹; HRMS (ESI-TOF) Calcd. for C₂₁H₂₇FNao₂Si ([M+Na]⁺): 381.1656, Found: 381.1653. Enantiomeric excess was determined by HPLC analysis after desilylation.

^1H NMR (400 MHz, CDCl_3) δ 9.64 (1H, s, CHO), 7.50-7.54 (2H, m, Ar-H), 7.22-7.26 (3H, m, Ar-H), 7.08-7.14 (4H, m, Ar-H), 3.56 (1H, s, OH), 3.49 (2H, d, $J = 14.0$ Hz, PhCH_2), 3.23 (2H, d, $J = 14.0$ Hz, PhCH_2); ^{13}C NMR (100 MHz, CDCl_3) δ 199.4, 162.5 (d, $J_{\text{C-F}} = 248$ Hz), 134.1, 133.9 (d, $J_{\text{C-F}} = 3.3$ Hz), 130.4, 128.3, 127.7 (d, $J_{\text{C-F}} = 8.2$ Hz), 127.2, 115.7 (d, $J_{\text{C-F}} = 21.4$ Hz), 81.4, 43.7; HPLC condition: DAICEL Chiralpak AD-H, hexane/*i*-PrOH = 97:3, flow rate = 0.5 mL/min, $\lambda = 233$ nm, retention time: 36.3 min (major), 54.0 min (minor).

2-(4-Methylphenyl)-3-phenyl-2-triethylsiloxypropanal (5c)

$[\alpha]_{\text{D}}^{28} +52.9^\circ$ (c 0.89, CHCl_3 , 83% ee); ^1H NMR (400 MHz, CDCl_3) δ 9.73 (1H, s, CHO), 7.11-7.26 (7H, m, Ar-H), 6.97-6.99 (2H, m, Ar-H), 3.29 (1H, d, $J = 14.4$ Hz, PhCH_2), 3.24 (1H, d, $J = 14.4$ Hz, PhCH_2), 2.32 (3H, s, Me-Ph), 0.88 (9H, t, $J = 8.0$ Hz, $\text{CH}_3\text{CH}_2\text{Si}$), 0.56 (6H, q, $J = 8.0$ Hz, $\text{CH}_3\text{CH}_2\text{Si}$); ^{13}C NMR (100 MHz, CDCl_3) δ 199.9, 137.3, 136.4, 135.6, 130.7, 129.0, 127.5, 126.2, 126.0, 85.0, 44.8, 20.9, 7.0, 6.8; IR (neat) 2954, 2916, 2875, 1732, 1454, 1242, 1151, 1112, 1010, 958, 812, 736, 729, 698 cm^{-1} ; HRMS (ESI-TOF) Calcd. for $\text{C}_{22}\text{H}_{30}\text{NaO}_2\text{Si}$ ($[\text{M}+\text{Na}]^+$): 377.1907, Found: 377.1908. Enantiomeric excess was determined by HPLC analysis after desilylation.

^1H NMR (400 MHz, CDCl_3) δ 9.68 (1H, s, CHO), 7.43 (2H, d, $J = 8.4$ Hz, Ar-H), 7.21-7.25 (5H, m, Ar-H), 7.14-7.16 (2H, m, Ar-H), 3.53 (1H, s, OH), 3.51 (2H, d, $J = 14.0$ Hz, PhCH_2), 3.24 (2H, d, $J = 14.0$ Hz, PhCH_2); ^{13}C NMR (100 MHz, CDCl_3) δ 199.6, 137.7, 135.1, 134.5, 130.3, 129.4, 128.1, 126.9, 125.7, 81.6, 43.4, 20.9; HPLC condition: DAICEL Chiralcel OJ-H, hexane/*i*-PrOH = 95:5, flow rate = 1.0 mL/min, $\lambda = 223$ nm, retention time: 18.7 min (minor), 25.3 min (major).

2,5-Diphenyl-2-triethylsiloxy-4-pentenal (5d)

$[\alpha]_{\text{D}}^{26} +56.4^\circ$ (c 0.98, CHCl_3 , 90% ee); ^1H NMR (400 MHz, CDCl_3) δ 9.61 (1H, s, CHO), 7.35-7.43 (4H, m, Ph-H), 7.16-7.30 (6H, m, Ph-H), 6.35 (1H, d, $J = 16.0$ Hz, $\text{CH}=\text{CHPh}$), 5.96 (1H, dt, $J = 16.0, 7.2$ Hz, $\text{CH}_2\text{CH}=\text{CH}$), 3.08 (1H, dd, $J = 15.2, 7.2$ Hz, $\text{CH}=\text{CHCH}_2$), 2.84 (1H, dd, $J = 15.2, 7.2$ Hz, $\text{CH}=\text{CHCH}_2$), 0.98 (9H, t, $J = 7.6$ Hz, $\text{CH}_3\text{CH}_2\text{Si}$), 0.68 (6H, q, $J = 7.6$ Hz, $\text{CH}_3\text{CH}_2\text{Si}$); ^{13}C NMR (100 MHz, CDCl_3) δ 199.7, 138.7, 137.3, 133.6, 128.5, 128.3, 127.8, 127.0, 126.1, 125.9, 123.8, 84.6, 41.1, 7.0, 6.7; IR (neat) 3026, 2954, 2910, 2875, 2802, 1734, 1494, 1458, 1240, 1139, 1074, 1014, 964, 840, 740, 729, 698 cm^{-1} ; HRMS (ESI-TOF) Calcd. for $\text{C}_{23}\text{H}_{30}\text{NaO}_2\text{Si}$ ($[\text{M}+\text{Na}]^+$): 389.1907, Found: 389.1922. Enantiomeric excess was determined by HPLC analysis after desilylation.

¹H NMR (400 MHz, CDCl₃) δ 9.65 (1H, s, CHO), 7.53 (2H, d, *J* = 8.0 Hz, Ph-H), 7.42 (2H, t, *J* = 8.0 Hz, Ph-H), 7.19-7.35 (6H, m, Ph-H), 6.53 (1H, d, *J* = 16.0 Hz, CH=CHPh), 6.08 (1H, dt, *J* = 16.0, 7.6 Hz, CH₂CH=CH), 3.75 (1H, s, OH), 3.04 (1H, dd, *J* = 14.4, 7.6 Hz, CH=CHCH₂), 2.96 (1H, dd, *J* = 14.4, 7.6 Hz, CH=CHCH₂); ¹³C NMR (100 MHz, CDCl₃) δ 199.8, 138.0, 136.6, 135.0, 128.8, 128.4, 128.1, 127.5, 126.2, 125.7, 122.2, 81.3, 40.9; HPLC condition: DAICEL Chiralcel OJ-H, hexane/*i*-PrOH = 95:5, flow rate = 1.0 mL/min, λ = 254 nm, retention time: 33.9 min (major), 40.2 min (minor).

2-Cyclohexyl-3-phenyl-2-triethoxysiloxyprenal (5e)

[α]_D²¹ +7.6° (*c* 0.96, CHCl₃, 88% ee); ¹H NMR (400 MHz, CDCl₃) δ 9.58 (1H, s, CHO), 7.17-7.26 (3H, m, Ph-H), 7.13 (2H, d, *J* = 6.8 Hz, Ph-H), 3.09 (1H, d, *J* = 14.0 Hz, PhCH₂), 2.86 (1H, d, *J* = 14.0 Hz, PhCH₂), 1.52-1.95 (5H, m, -CH-), 1.14-1.26 (6H, m, -CH-), 0.88 (9H, t, *J* = 8.0 Hz, CH₃CH₂Si), 0.43-0.60 (6H, m, CH₃CH₂Si); ¹³C NMR (100 MHz, CDCl₃) δ 204.6, 136.0, 130.5, 127.9, 126.4, 85.6, 43.1, 40.4, 27.1, 26.5, 26.4, 26.3, 7.2, 6.9 (one signal for cyclohexyl carbon was not identified due to the overlap of the peaks); IR (neat) 2931, 2873, 2854, 2816, 1737, 1454, 1240, 1170, 1139, 1010, 964, 740, 700 cm⁻¹; HRMS (ESI-TOF) Calcd. for C₂₁H₃₄NaO₂Si ([M+Na]⁺): 369.2220, Found: 369.2218; HPLC condition: DAICEL Chiralpak AD-H, hexane/*i*-PrOH = 99:1, flow rate = 0.3 mL/min, λ = 220 nm, retention time: 14.0 min (minor), 17.0 min (major).

3-Phenyl-2-triethoxysiloxypropiophenone (6a)

[α]_D²⁷ -30.2° (*c* 1.51, CHCl₃, 86% ee); ¹H NMR (400 MHz, CDCl₃) δ 8.05-8.07 (2H, m, Ph-H), 7.56 (1H, t, *J* = 7.6 Hz, Ph-H), 7.45 (2H, t, *J* = 7.6 Hz, Ph-H), 7.21-7.29 (5H, m, Ph-H), 4.95 (1H, dd, *J* = 9.0, 4.0 Hz, SiOCH), 3.10 (1H, dd, *J* = 13.6, 4.0 Hz, PhCH₂), 3.00 (1H, dd, *J* = 13.6, 9.0 Hz, PhCH₂), 0.75 (9H, t, *J* = 8.0 Hz, CH₃CH₂Si), 0.39 (6H, q, *J* = 8.0 Hz, CH₃CH₂Si); ¹³C NMR (100 MHz, CDCl₃) δ 200.7, 137.5, 134.9, 133.0, 129.6, 129.1, 128.3, 128.1, 126.5, 78.6, 42.2, 6.4, 4.4; IR (neat) 2954, 2910, 2875, 1697, 1680, 1454, 1278, 1240, 1109, 1004, 771, 744, 731, 698 cm⁻¹; HRMS (ESI-TOF) Calcd. for C₂₁H₂₈NaO₂Si ([M+Na]⁺): 363.1751, Found: 363.1749; HPLC condition: DAICEL Chiralcel OD-H, hexane/*i*-PrOH = 99:1, flow rate = 0.3 mL/min, λ = 210 nm, retention time: 15.4 min (*S*), 16.9 min (*R*).

Absolute configuration was established by comparison of optical rotation with known literature value⁵ after desilylation.

4'-Fluoro-3-phenyl-2-triethylsiloxypropiophenone (6b)

$[\alpha]_D^{33} -23.2^\circ$ (c 1.11, CHCl_3 , 86% ee); ^1H NMR (400 MHz, CDCl_3) δ 8.10-8.14 (2H, m, Ar-H), 7.20-7.29 (5H, m, Ar-H), 7.11 (2H, t, J = 8.4 Hz, Ar-H), 4.84 (1H, dd, J = 8.4, 4.8 Hz, SiOCH), 3.09 (1H, dd, J = 13.6, 4.8 Hz, PhCH_2), 3.02 (1H, dd, J = 13.6, 8.4 Hz, PhCH_2), 0.75 (9H, t, J = 8.0 Hz, $\text{CH}_3\text{CH}_2\text{Si}$), 0.39 (6H, q, J = 8.0 Hz, $\text{CH}_3\text{CH}_2\text{Si}$); ^{13}C NMR (100 MHz, CDCl_3) δ 199.4, 165.5 (d, $J_{\text{C-F}}$ = 256 Hz), 137.2, 132.1 (d, $J_{\text{C-F}}$ = 9.0 Hz), 131.2 (d, $J_{\text{C-F}}$ = 2.5 Hz), 129.6, 128.2, 126.6, 115.4 (d, $J_{\text{C-F}}$ = 21.4 Hz), 79.4, 42.4, 6.4, 4.4; IR (neat) 2954, 2912, 2875, 1697, 1680, 1597, 1504, 1456, 1409, 1280, 1236, 1155, 1103, 1012, 981, 933, 840, 817, 777, 742, 729, 673 cm^{-1} ; HRMS (ESI-TOF) Calcd. for $\text{C}_{21}\text{H}_{27}\text{FNaO}_2\text{Si}$ ($[\text{M}+\text{Na}]^+$): 381.1656, Found: 381.1667. Enantiomeric excess was determined by HPLC analysis after desilylation.

^1H NMR (400 MHz, CDCl_3) δ 7.93-7.96 (2H, m, Ar-H), 7.16-7.27 (5H, m, Ar-H), 7.11 (2H, d, J = 7.6 Hz, Ar-H), 5.29 (1H, dt, J = 6.8, 4.4 Hz, HOCH), 3.66 (1H, d, J = 6.8 Hz, OH), 3.17 (1H, dd, J = 14.2, 4.4 Hz, PhCH_2), 2.91 (1H, dd, J = 14.2, 6.8 Hz, PhCH_2); ^{13}C NMR (100 MHz, CDCl_3) δ 199.4, 166.1 (d, $J_{\text{C-F}}$ = 257 Hz), 136.1, 131.3 (d, $J_{\text{C-F}}$ = 9.1 Hz), 130.2 (d, $J_{\text{C-F}}$ = 3.3 Hz), 129.3, 128.3, 126.8, 116.1 (d, $J_{\text{C-F}}$ = 22.3 Hz), 73.6, 41.9; HPLC condition: DAICEL Chiralpak AD-H, hexane/*i*-PrOH = 95:5, flow rate = 0.5 mL/min, λ = 254 nm, retention time: 35.7 min (minor), 39.4 min (major).

4'-Methyl-3-phenyl-2-triethylsiloxypropiophenone (6c)

$[\alpha]_D^{30} -21.8^\circ$ (c 1.03, CHCl_3 , 85% ee); ^1H NMR (400 MHz, CDCl_3) δ 7.98 (2H, d, J = 8.8 Hz, Ar-H), 7.16-7.29 (7H, m, Ar-H), 4.93 (1H, dd, J = 9.2, 4.2 Hz, SiOCH), 3.08 (1H, dd, J = 13.6, 4.2 Hz, PhCH_2), 2.98 (1H, dd, J = 13.6, 9.2 Hz, PhCH_2), 2.42 (3H, s, Me-Ph), 0.75 (9H, t, J = 8.0 Hz, $\text{CH}_3\text{CH}_2\text{Si}$), 0.39 (6H, q, J = 8.0 Hz, $\text{CH}_3\text{CH}_2\text{Si}$); ^{13}C NMR (100 MHz, CDCl_3) δ 200.3, 143.9, 137.8, 132.4, 129.7, 129.3, 129.1, 128.2, 126.5, 78.6, 42.4, 21.7, 6.5, 4.5; IR (neat) 2954, 2916, 2875, 1697, 1678, 1606, 1456, 1280, 1238, 1180, 1111, 1016, 777, 744, 698 cm^{-1} ; HRMS (ESI-TOF) Calcd. for $\text{C}_{22}\text{H}_{30}\text{NaO}_2\text{Si}$ ($[\text{M}+\text{Na}]^+$): 377.1907, Found: 377.1911; HPLC condition: DAICEL Chiralcel OJ-H, hexane/*i*-PrOH = 99:1, flow rate = 0.3 mL/min, λ = 254 nm, retention time: 14.7 min (minor), 17.1 min (major).

1,5-Diphenyl-2-triethylsiloxy-4-pentenone (6d)

$[\alpha]_D^{27} -3.7^\circ$ (c 1.08, CHCl_3 , 63% ee); ^1H NMR (400 MHz, CDCl_3) δ 8.07 (2H, d, $J = 7.2$ Hz, Ph-H), 7.56 (1H, t, $J = 7.2$ Hz, Ph-H), 7.46 (2H, t, $J = 7.2$ Hz, Ph-H), 7.18-7.32 (5H, m, Ph-H), 6.41 (1H, d, $J = 16.0$ Hz, $\text{CH}=\text{CHPh}$), 6.23 (1H, dt, $J = 16.0, 7.2$ Hz, $\text{CH}_2\text{CH}=\text{CH}$), 4.91 (1H, dd, $J = 7.6, 5.2$ Hz, SiOCH), 2.68-2.72 (2H, m, $\text{CH}=\text{CHCH}_2$), 0.90 (9H, t, $J = 8.0$ Hz, $\text{CH}_3\text{CH}_2\text{Si}$), 0.58 (6H, q, $J = 8.0$ Hz, $\text{CH}_3\text{CH}_2\text{Si}$); ^{13}C NMR (100 MHz, CDCl_3) δ 200.5, 137.2, 135.0, 133.0, 132.9, 129.0, 128.4, 128.3, 127.1, 126.0, 125.2, 77.3, 39.6, 6.6, 4.7; IR (neat) 3026, 2954, 2937, 2910, 2875, 1697, 1678, 1597, 1448, 1415, 1274, 1238, 1118, 1002, 964, 941, 923, 848, 829, 769, 742, 692 cm^{-1} ; HRMS (ESI-TOF) Calcd. for $\text{C}_{23}\text{H}_{30}\text{NaO}_2\text{Si}$ ($[\text{M}+\text{Na}]^+$): 389.1907, Found: 389.1902; HPLC condition: DAICEL Chiralcel OD-H, hexane/*i*-PrOH = 99:1, flow rate = 0.5 mL/min, $\lambda = 254$ nm, retention time: 11.0 min (major), 13.1 min (minor).

1-Cyclohexyl-3-phenyl-2-triethylsiloxypropanone (6e)

$[\alpha]_D^{22} -16.2^\circ$ (c 1.12, CHCl_3 , 77% ee); ^1H NMR (400 MHz, CDCl_3) δ 7.19-7.29 (5H, m, Ph-H), 4.30 (1H, dd, $J = 8.4, 4.0$ Hz, SiOCH), 2.96 (1H, dd, $J = 13.6, 4.0$ Hz, PhCH_2), 2.77 (1H, dd, $J = 13.6, 8.4$ Hz, PhCH_2), 2.74-2.79 (1H, m, $-(\text{CH}_2)_2\text{CHCO}$), 1.65-1.75 (5H, m, $-\text{CH}-$), 1.16-1.37 (5H, m, $-\text{CH}-$), 0.83 (9H, t, $J = 8.0$ Hz, $\text{CH}_3\text{CH}_2\text{Si}$), 0.36-0.47 (6H, m, $\text{CH}_3\text{CH}_2\text{Si}$); ^{13}C NMR (100 MHz, CDCl_3) δ 215.2, 137.5, 129.7, 128.1, 126.4, 79.4, 45.6, 41.3, 28.9, 28.0, 25.8, 25.7, 25.4, 6.6, 4.5; IR (neat) 2931, 2875, 2854, 1707, 1454, 1413, 1365, 1240, 1157, 1097, 1004, 937, 773, 740, 729, 698 cm^{-1} ; HRMS (ESI-TOF) Calcd. for $\text{C}_{21}\text{H}_{34}\text{NaO}_2\text{Si}$ ($[\text{M}+\text{Na}]^+$): 369.2220, Found: 369.2217; HPLC condition: DAICEL Chiralcel OD-H, hexane/*i*-PrOH = 99:1, flow rate = 0.3 mL/min, $\lambda = 220$ nm, retention time: 17.0 min (major), 36.6 min (minor).

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