Enantioselective Reduction of α,β-Unsaturated Acylsilanes by Chiral Lithium Amides

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Supporting Information

Experimental Section

General: IR spectra were recorded on a Perkin-Elmer FT1640 spectrometer. ^{1}H NMR spectra were taken on Varian UnityPlus 500 (500 MHz) in $CDCl_3$ with reference to $CHCl_3$ (δ 7.26). ^{13}C NMR spectra were measured with Varian UnityPlus 500 (125 MHz) in $CDCl_3$ with reference to the $CDCl_3$ triplet (δ 77.2). Resonance patterns were described as s = singlet, d = doublet, t = triplet, m = multiplet, and br = broad. Low-and high-resolution mass spectra (EI-MS) were obtained with a JEOL JMS-D-300 spectrometer combined with a JEOL JMA-2000 data processing system. For chromatography, the following adsorbents were used: Fuji-Davison silica gel BW-200 (150-325 mesh) for column chromatography; Merck precoated silica gel 60 F-254 plates for analytical thin-layer chromatography. All moisture sensitive reactions were performed under a positive pressure of nitrogen. Anhydrous $MgSO_4$ was used for drying all organic solvent extracts in workup, and the removal of the solvents was performed with a rotary evaporator. Dry solvents and reagents were obtained by using standard procedures. Melting points (uncorrected) were determined by using a Yanagimoto micro-melting point apparatus. Elemental combustion analysis was performed at the Microanalysis Laboratory of this University.

(*E*)-*tert*-Butyldimethylsilyl 2-(Methyldiphenylsilyl)ethenyl Ketone (6h) This compound was prepared according to the procedure for 2-trimethylsilyl derivative by Reich.[1] yellow oil, R_f = 0.30 (hexane-AcOEt = 20 : 1). IR (film) 1600 cm^{-1}. ^{1}H NMR δ 0.24 (6H, s, $SiMe_2$), 0.70 (3H, s, SiMe), 0.93 (9H, s, *t*-Bu), 6.76 (1H, d, *J* = 19.0 Hz), 7.14 (1H, d, *J* = 19.0), 7.34-7.52 (10H, m, Ar). ^{13}C NMR δ -5.8 ($SiMe_2$), -4.0 (SiMe), 16.9 (CMe_3), 26.8 (*t*-Bu), 128.1, 129.8, 134.9, 134.9, 135.0, 140.5 and 150.0 (Ar), 236.5 (C=O). Anal. calcd for $C_{22}H_{30}OSi_2$: C, 72.07; H, 8.25, found: C, 71.72; H, 8.42.

(*E*)-*tert*-Butyldimethylsilyl 2-(Triphenylsilyl)ethenyl Ketone (6i) This compound was prepared according to the procedure for 2-trimethylsilyl derivative. yellow needles, R_f = 0.26 (hexane-AcOEt = 30 : 1). IR (KBr) 1595 cm^{-1}. ^{1}H NMR δ 0.23 (6H, s, $SiMe_2$), 0.92 (9H, s, *t*-Bu), 6.78 (1H, d, *J* = 19.0 Hz), 6.28 (1H, d, *J* = 19.0), 7.37-7.53 (15H, m, Ar). ^{13}C NMR δ -5.8 ($SiMe_2$), 16.9 (*C*Me_3), 26.8 (*t*-Bu), 128.3, 130.2, 133.1 and 136.1 (Ar), 138.4 (C-3), 151.1 (C-2), 236.5 (C=O). MS, *m/e*, 428 (M^+), 259 (base peak). Anal. calcd for $C_{27}H_{32}OSi_2$: C, 75.64; H, 7.52, found: C, 75.40; H, 7.45.

1. Reich, H. J.; Kelly, M. J.; Olson, R. E.; Holtan, R. C. *Tetrahedron* **1983**, *39*, 949-960.

***tert*-Butyldimethylsilyl Ethenyl Ketone (6j)** This compound was prepared according to the procedure for trimethylsilyl derivative. colorless oil, IR (film) 1600 cm^{-1}. ^1H NMR δ 0.24 (6H, s, $SiMe_2$), 0.93 (9H, s, *t*-Bu), 5.77 (1H, dd, *J* = 10.8, 1.3 Hz, H-3a), 6.03 (1H, dd, *J* = 17.7, 1.3 Hz, H-3b), 6.57 (1H, dd, *J* = 17.7, 10.8 Hz, H-2). ^{13}C NMR δ -5.9 ($SiMe_2$), 16.8 (CMe_3), 26.7 (*t*-Bu), 126.8 (C-3), 141.7 (C-2), 237.3 (C=O). HRMS calcd for $C_9H_{19}OSi$ (M^++1) 171.1205 found 171.1204.

Cycloheptenecarbonyl(dimethyl)phenylsilane (6m) To a mixture of cycloheptanone (15.0 g, 0.134 mol) and Me_3SiCN (17.3g, 23.2 mL, 0.174 mol) in benzene (50 mL) was added zinc iodide (1.00 g, 3.13 mmol). After the reaction mixture was stirred at room temperature for 1 h, $POCl_3$ (60.0 g, 0.991 mol) and pyridine (200 mL) were added, and then the mixture was refluxed for 5 h. The cooled dark solution was poured into ice-10% hydrochloric acid (900 mL), and extracted with ether (800 mL x 3). The combined organic phases were washed with saturated brine (800 mL), dried, and concentrated. The residual oil was subjected to column chromatography (silica gel, 400g; elution with hexane-AcOEt = 20:1) to give 1-cyano-1-cycloheptene (12.9 g, 79 %) as a colorless oil.

To a cooled (0 °C) solution of 1-cyano-1-cycloheptene (10 g, 85.2 mmol) in Et_2O (200 mL) was added dropwise diisobutylaluminium hydride (0.94 M hexane solution, 100 mL, 94 mmol) over 20 min. After the reaction mixture was stirred for 1 h, the reaction was quenched by addition of MeOH (100 mL) followed by stirring at room temperature for 1 h. The mixture was filtered through a plug of Celite, and the filtrate was concentrated *in vacuo*. The residual oil was diluted with THF (300 mL), and then oxalic acid (10 % aqueous solution, 300 mL) was added at 0 °C. After stirring at room temperature for 20 min, the mixture was poured into H_2O (600 mL), and extracted with ether (600 mL x 3). The combined organic phases were washed with saturated brine (400 mL), dried, and concentrated. The residual oil was subjected to column chromatography (silica gel, 500g; elution with hexane-AcOEt = 20:1) to give 1-cycloheptenecarboxaldehyde (6.8 g, 64 %, as a colorless oil).

To a cooled (-80°C) solution of $PhMe_2SiLi$[2] (0.37 M in THF, 164 mL, 60.7 mmol) in Et_2O (300 mL) was added dropwise 1-cycloheptenecarboxaldehyde (6.8 g, 54.8 mmol). The solution was allowed to warm to 0 °C over 2 h, and then quenched by saturated aqueous NH_4Cl solution (300 mL). The mixture was diluted with water (200 mL), and then extracted with Et_2O (500 mL x 3). The combined organic phases were washed with saturated brine (500 mL), dried, and concentrated. The residual oil was subjected to column chromatography (silica gel, 400g; elution with hexane-AcOEt = 20:1) to give cycloheptenyl(dimethylphenylsilyl)methanol (12.6 g, 88 % as an yellow oil). R_f = 0.17 (hexane-AcOEt = 30 : 1). IR (film) 3455 cm^{-1}. ^1H NMR δ 0.35 and 0.37 (each 3H, s, $SiMe_2$), 1.33-1.48 (4H, m, H-4 and H-6), 1.67-1.75 (2H, m, H-5), 1.90-1.99 (2H, m, H-7), 2.06-2.21 (2H, m, H-3), 4.02 (1H, s, C*H*OH), 5.63 (1H, t, *J* = 6.6 Hz, H-2), 7.35-7.42 (3H, m, Ar-H), 7.58-7.64 (2H, m, Ar). ^{13}C NMR δ -5.0 and -4.5 ($SiMe_2$), 27.0 (C-4), 27.5 (C-6), 28.5 (C-3), 31.5 (C-7), 32.8 (C-5), 72.3 (CHOH), 123.7 (C-2), 127.9, 129.4, 134.3 and 137.2 (Ar), 146.6 (C-1). HRMS calcd for $C_{16}H_{24}OSi$ 260.1596 found 260.1604.

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2. Fleming, I.; Henning, R.; Parker, D. C.; Plaut, H. E.; Sanderson, P. E. J. *J. Chem. Soc. Perkin 1*, **1995**, 317-337.

A solution of cycloheptenyl(dimethylphenylsilyl)methanol (6.0 g, 23.0 mmol) in CH_2Cl_2 (9 mL) was added at -60 °C over 10 min to a solution of chloro(dimethyl)sulfonium chloride, which was prepared by dropwise addition of solution of DMSO (3.6 g, 3.27 mL, 46.1 mmol) in CH_2Cl_2 (6 mL) to a cooled (-70 °C) solution of oxalyl chloride (3.2 g, 2.2 mL, 25.2 mmol) in CH_2Cl_2 (9 mL) over 5 min, followed by stirring at -60 to -70 °C for 30 min. After stirring at ca. -65 °C for 30 min, triethylamine (11.6 g, 16 mL, 1.15 mmol) was added. The solution was allowed to warm to room temperature over 30 min. The mixture was diluted with water (100 mL), and extracted with CH_2Cl_2 (75 mL x 2). The combined organic phases were washed with saturated brine (75 mL), dried, and concentrated. The residual oil was subjected to column chromatography (silica gel, 550g; elution with hexane-AcOEt = 30:1) to give cycloheptenecarbonyl(dimethyl)phenylsilane (5.8 g, 98 %) as an yellow oil, which solidified on keeping in a refrigerator. Yellow prisms, mp 62-64 °C (hexane). R_f = 0.33 (hexane-AcOEt = 30 : 1). IR (KBr) 1575 cm^{-1}. ^1H NMR δ 0.52 (6H, s, $SiMe_2$), 1.38-1.43 (2H, m, H-6), 1.46-1.51 (2H, m, H-4), 1.79-1.76 (2H, m, H-5), 2.25-2.30 (2H, m, H-3), 2.36-2.40 (2H, H-7), 6.92 (1H, t, *J* = 6.4 Hz, H-2), 7.34-7.54 (3H, m, Ar-H), 7.50-7.54 (2H, m, Ar). ^{13}C NMR δ -2.2 ($SiMe_2$), 23.9 (C-7), 25.9 (C-6), 26.1 (C-4), 29.4 (C-3), 32.0 (C-5), 127.9, 129.3, 133.7 and 136.9 (Ar), 151.8 (C-2), 152.0 (C-1), 232.6 (C=O). Anal. calcd for $C_{16}H_{22}OSi$: C, 74.36; H, 8.58, found: C, 74.27; H, 8.65.

General Procedure for LDA reduction To a cooled (-80 °C) solution of β-*t*-butylacryloylsilane **6e** (96 mg, 0.424 mmol) in THF (4.2 mL) was added dropwise a solution of lithium diisopropylamide (LDA), prepared from diisopropylamine (77.2 μL, 55.8 mg, 0.551 mmol) and *n*-BuLi (1.46 M in hexane, 378 μL, 0.551 mmol) in THF (0.8 mL). After the solution was stirred at -80 °C for 30 min, a solution of acetic acid (33 mg, 0.55 mmol) in THF (2 mL) was added rapidly in one portion. The reaction mixture was poured into half saturated aqueous NH_4Cl solution, and extracted with Et_2O (30 mL x 3). The combined organic phases were washed with saturated brine (30 mL), dried, and concentrated. The residual oil was subjected to column chromatography (silica gel, 10 g; elution with hexane-AcOEt = 30:1) to give corresponding alcohol **7e** (90.0 mg, 93%).

7a (X = Me) colorless oil, R_f = 0.22 (hexane-AcOEt = 30 : 1). IR (film) 3450 cm^{-1}. ^1H NMR δ -0.06 and 0.01 (each 3H, s, $SiMe_2$), 0.94 (9H, s, *t*-Bu), 1.71 (3H, dt, *J* = 6.4, 1.5 Hz, H-4), 4.05 (1H, ddq, *J* = 7.1, 1.5, 1.5 Hz, H-1), 5.50 (1H, dqd, *J* = 15.3, 6.4, 1.5 Hz, H-3), 5.65 (1H, ddq, *J* = 15.3, 7.1, 1.5 Hz, H-2). ^{13}C NMR δ -8.7 and-7.5 ($SiMe_2$), 17.1 (CMe_3), 18.1 and 27.1 (*t*-Bu), 67.1 (C-1), 122.5 (C-3), 133.4 (C-2). HRMS calcd for $C_{10}H_{22}OSi$ 186.1440 found 186.1424.

7b (X = *i*-Pr) colorless oil, R_f = 0.22 (hexane-AcOEt = 28 : 1). IR (film) 3455 cm^{-1}. ^1H NMR δ -0.06 and 0.00 (each 3H, s, $SiMe_2$), 0.94 (9H, s, *t*-Bu), 0.98 and 0.99 (6H, d, *J* = 1.5 Hz), 2.31 (1H, m, H-4), 4.06 (1H, ddd, *J* = 0.9, 1.5, 6.8 Hz, H-1), 5.45 (1H, ddd, *J* = 1.5, 6.6, 15.4 Hz, H-3), 5.59 (1H, ddd, *J* = 1.1, 6.8, 15.4 Hz, H-2). ^{13}C NMR δ -8.7 and-7.5 ($SiMe_2$), 17.2 (CMe_3), 22.8 and 27.2 (*t*-Bu), 31.2 (C-4), 67.0 (C-1), 129.3 (C-2), 134.9 (C-3). HRMS calcd for $C_{12}H_{25}OSi$ 213.1675(M^+ -1) found 213.1665.

7c (X = *c*-C_6H_{11}) colorless oil, R_f = 0.32 (hexane-AcOEt = 30 : 1). IR (film) 3455 cm^{-1}. ^1H NMR δ -0.07 and -0.01 (each 3H, s, $SiMe_2$), 0.94 (9H, s, *t*-Bu), 0.95-1.28 and 1.62-1.73 (10H, m, *c*-C_6H_{11}), 1.97 (1H, m, H-4), 4.06 (1H, br d, *J* = 6.8, H-1), 5.43 (1H, ddd, *J* = 15.4, 6.6, 1.5 Hz, H-3), 5.58 (1H, ddd, *J* = 15.4, 6.8,

1.3 Hz, H-2). ^{13}C NMR δ -8.7 and-7.4 ($SiMe_2$), 17.2 (CMe_3), 27.2 (*t*-Bu), 26.4 and 33.4 (*c*-C_6H_{11}), 40.8 (C-4), 67.1 (C-1), 129.7 (C-2), 133.7 (C-3). HRMS calcd for $C_{15}H_{30}OSi$ 254.2066 found 254.2063.

7d (X = *c*-C_3H_5) colorless oil, R_f = 0.23 (hexane-AcOEt = 30 : 1).IR (film) 3455 cm^{-1}. ^{1}H NMR δ -0.06 and 0.00 (each 3H, s, $SiMe_2$), 0.33 and 0.68(each 2H, m, *c*-C_3H_5), 0.94 (9H, s, *t*-Bu), 1.38 (1H, m, H-4), 4.04 (1H, dd, *J* = 1.5, 7.2, H-1), 5.06 (1H, ddd, *J* = 1.5, 8.5, 15.3 Hz, H-3), 5.69 (1H, dd, *J* = 7.2, 15.3 Hz, H-2). ^{13}C NMR δ -8.7 and-7.5 ($SiMe_2$), 6.8 and 6.9 (*c*-C_3H_5), 13.7 (C-4), 17.2 (CMe_3), 27.2 (*t*-Bu), 67.0 (C-1), 129.9 (C-2), 131.7 (C-3). HRMS calcd for $C_{12}H_{25}OSi$ (M^+ + 1) 213.1675 found 213.1673.

7e (X = *t*-Bu) colorless oil, R_f = 0.32 (hexane-AcOEt = 30 : 1). IR (film) 3848 cm^{-1}. ^{1}H NMR δ -0.07 and -0.01 (each 3H, s, $SiMe_2$), 0.94 (9H, s, *t*-Bu), 4.07 (1H, d, *J* = 5.7 Hz, H-1), 5.50 (1H, d, *J* = 15.8 Hz, H-3), 5.54 (1H, dd, *J* = 5.7, 15.8 Hz, H-2). ^{13}C NMR δ -8.6 and-7.5 ($SiMe_2$), 17.2 (CMe_3), 27.2 and 30.0 (*t*-Bu), 33.0 (C-4), 67.1 (C-1), 127.0 (C-2), 134.9 (C-3). HRMS calcd for $C_{13}H_{27}OSi$ (M^+ - 1) 227.1831 found 227.1829.

7f (X = $SiMe_3$) colorless oil, R_f = 0.39 (hexane-AcOEt = 30 : 1). IR (film) 3435 cm^{-1}. ^{1}H NMR δ -0.05 and -0.02 (each 3H, s, $SiMe_2$), 0.06 (9H, s, $SiMe_3$), 0.95 (9H, s, *t*-Bu), 4.21 (1H, dd, *J* = 2.1, 4.7 Hz, H-1), 5.67 (1H, dd, *J* = 2.1, 18.8 Hz, H-3), 6.28 (1H, dd, *J* = 4.7, 18.8 Hz, H-2). ^{13}C NMR δ -8.8 and-7.4 ($SiMe_2$), -0.9 ($SiMe_3$), 17.3 (CMe_3), 27.1 (*t*-Bu), 69.6 (C-1), 122.9 (C-3), 133.4 (C-2). HRMS calcd for $C_{12}H_{28}OSi_2$ 244.1679 found 244.1654.

7g (X = $SiMe_2Ph$) colorless oil, R_f = 0.31 (hexane-AcOEt = 30 : 1). IR (film) 3430 cm^{-1}. ^{1}H NMR δ -0.05 and -0.01 (each 3H, s, Me of $SiMe_2Bu^t$), 0.34 (6H, s, Me of $SiMe_2Ph$), 0.95 (9H, s, *t*-Bu), 4.26 (1H, br, H-1), 5.82 (1H, dd, *J* = 2.1, 18.8 Hz, H-3), 6.35 (1H, dd, *J* = 4.5, 18.8 Hz, H-2), 7.26-7.53 (5H, m, Ar-H). ^{13}C NMR δ -8.8 and-7.3 (Me of $SiMe_2Bu^t$), -2.2 (Me of $SiMe_2Ph$), 17.3 (CMe_3), 27.1 (*t*-Bu), 69.6 (C-1), 120.4 (C-3), 127.9, 129.1 and 134.7 (Ar), 150.7 (C-2). HRMS calcd for $C_{17}H_{30}OSi_2$ 306.1835 found 306.1859.

7h (X = $SiMePh_2$) colorless oil, R_f = 0.13 (hexane-AcOEt = 35 : 1). IR (film) 3455 cm^{-1}. ^{1}H NMR δ -0.05 and 0.02 (each 3H, s, $SiMe_2$), 0.64 (3H, s, SiMe), 0.95 (9H, s, *t*-Bu), 4.31 (1H, dd, *J* = 2.2, 4.3 Hz, H-1), 6.03 (1H, dd, *J* = 2.2, 18.8 Hz, H-3), 6.38 (1H, dd, *J* = 4.3, 18.8 Hz, H-2) 7.34-7.55 (10H, m, Ar-H). ^{13}C NMR δ -8.8 ($SiMe_2$), -3.3 (SiMe), 17.2 (CMe_3), 27.1 and 27.2 (*t*-Bu), 69.7 (C-1), 118.1 (C-3), 128.0, 129.4, 134.9 and 135.0 (Ar), 153.1 (C-2). HRMS calcd for $C_{22}H_{32}OSi_2$ 368.1992 found 368.1965.

7i (X = $SiPh_3$) colorless oil, R_f = 0.29 (hexane-AcOEt = 15 : 1). IR (film) 3490cm^{-1}. ^{1}H NMR δ -0.10and 0.01 (each 3H, s, $SiMe_2$), 0.92 (9H, s, *t*-Bu), 4.34 (1H, br, H-1), 6.26 (1H, dd, *J* = 2.1, 18.7Hz, H-3), 6.38 (1H, dd, *J* = 3.8, 18.7 Hz, H-2) 7.34-7.65 (15H, m, Ar-H). ^{13}C NMR δ -12.4 ($SiMe_2$), 13.7 (CMe_3), 23.6 (*t*-Bu), 66.3 (C-1), 112.5 (C-3), 124.5, 126.1, 131.6 and 132.6 (Ar), 151.7 (C-2). HRMS calcd for $C_{27}H_{34}OSi_2$ 430.2148 found 430.2156.

7j (X = H) colorless oil, R_f = 0.29 (hexane-AcOEt = 30 : 1). IR (film) 3390 cm^{-1}. ^{1}H NMR δ -0.04 and 0.00 (each 3H, s, $SiMe_2$), 0.96 (9H, s, *t*-Bu), 1.28 (1H, br, OH), 4.18 (1H, m, H-1), 4.99 (1H, ddd, *J* = 1.6, 3.0, 10.7 Hz, H-3a), 5.08 (1H, ddd, *J* = 1.6, 2.1, 17.0 Hz, H-3b), 6.07 (1H, ddd, *J* = 5.3, 10.7, 17.0 Hz, H-2). ^{13}C NMR δ -9.0 and -9.0 (each $SiMe_2$), 17.2 (CMe_3), 27.1 (*t*-Bu), 67.7 (C-1), 109.5 (C-3), 140.9 (C-2). HRMS calcd for $C_9H_{19}OSi$ 171.1205(M^+-1) found 171.1194.

General Procedure for Asymmetric Reduction by Chiral Lithium Amides The following procedure for **6e** is representative: To a cooled (-80°C) solution of **6e** (104 mg, 0.459 mmol) in THF (4.5 mL) was added dropwise a solution of lithium amide of **12**, prepared from **12** (159 mg, 0.549 mmol) and *n* -BuLi (1.45 M in hexane, 379 μL, 0.549 mmol) in THF (0.9 mL). After the reaction mixture was stirred at -80 °C for 30 min, the reaction was quenched by acetic acid (33 mg, 0.55mmol) in THF (2 mL). The mixture was poured into half saturated aqueous NH_4Cl solution (20 mL) and then extracted with Et_2O (30 mL x 3). The combined organic phases were washed with saturated brine (30 mL), dried, and concentrated. The residual oil was subjected to column chromatography (silica gel, 10 g; elution with hexane-AcOEt = 30:1) to give **13** (92.1 mg, 88%).

14k ($R_1 = R_2 = -(CH_2)_3-$) colorless oil, R_f = 0.21 (hexane-AcOEt = 30 : 1). IR (film) 3435 cm^{-1}. ^1H NMR δ 0.37 and 0.39 (each 3H, s, $SiMe_2$), 1.79 -2.39 (6H, m, $(CH_2)_3$), 4.28 (1H, m, H-1), 5.44 (1H, m, H-3), 7.36-7.61 (5H, m, Ph). ^{13}C NMR δ -5.2 and -5.1 (each $SiMe_2$), 23.8, 32.3, 34.0 ($(CH_2)_3$), 67.3 (C-1), 121.9 (C-3), 147.0 (C-2), 127.9, 129.5, 134.2, 147.0 (Ph). HRMS calcd for $C_{14}H_{20}OSi$ 232.1283 found 232.1283.

14l ($R_1 = R_2 = -(CH_2)_4-$) colorless oil, R_f = 0.24 (hexane-AcOEt = 30 : 1). IR (film) 3455 cm^{-1}. ^1H NMR δ 0.35 and 0.36 (each 3H, s, $SiMe_2$), 1.34 -2.05 (8H, m, $(CH_2)_4$), 3.96 (1H, br, H-1), 5.50 (1H, m, H-3), 7.36-7.60 (5H, m, Ph). ^{13}C NMR δ -5.0 and -4.8 (each $SiMe_2$), 22.9, 22.9, 25.2, 27.3 ($(CH_2)_4$), 71.0 (C-1), 119.5 (C-3), 137.2 (C-2), 127.9, 134.2, 134.3, 137.2 (Ph). HRMS calcd for $C_{15}H_{22}OSi$ 246.1440 found 246.1142.

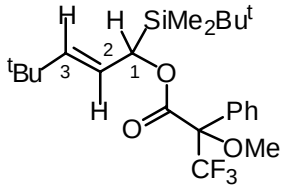
14m ($R_1 = R_2 = -(CH_2)_5-$) yellow oil, R_f = 0.17 (hexane-AcOEt = 30 : 1). IR (film) 3455 cm^{-1}. ^1H NMR δ 0.35 and 0.37 (each 3H, s, $SiMe_2$), 1.33-1.48 (4H, m, H-4,6), 1.67-1.75 (2H, m, H-5), 1.93-1.95 (2H, m, H-7), 2.06-2.21 (2H, m, H-3), 4.02 (1H, s, CHSi), 5.63 (1H, t, J = 6.6 Hz, H-2), 7.35-7.61 (5H, m, Ar-H). ^{13}C NMR δ -5.0 and -4.5 ($SiMe_2$), 27.0 (C-4), 27.5 (C-6), 28.5 (C-3), 31.5 (C-7), 32.8 (C-5), 72.3 (CHSi), 123.7 (C-2), 127.9, 129.4, 134.3 and 137.2 (Ar), 146.6 (C-1). HRMS calcd for $C_{16}H_{24}OSi$ 260.1596 found 260.1604.

Enantiomeric Purity Assays of 13, 14 and 16.[a]

	HPLC column[b]	eluent (hexane:*i*-PrOH)	flow rate (mL/min)	retention times (min) *R*	retention times (min) *S*	[ ]$_D$ ($CHCl_3$) *S*
13	OD	200 :1	0.3	17.0	14.8	-41.1 ° (c = 1.13)
14a	OD	200 :1	0.3	19.9	19.0	-36.7 ° (c = 0.65)
14b	OJ	200 :1	0.3	14.3	12.1	-38.8 ° (c = 1.90)
14c	OD	200 :1	0.3	17.2	16.1	-37.6 ° (c = 1.05)
14d	OD	200 :1	0.5	13.1	12.4	-39.1 ° (c = 1.20)
14k	-	-	-	-	-	-49.8 ° (c = 0.44)[c]
14l	OD	20 :1	0.3	16.5, 15.9[c]		-8.2 ° (c = 1.07)
14m	-	-	-	-	-	-21.2 ° (c = 1.03)[c]
16a	OD	20 : 1	1.0	12.5	7.0	-79.7 ° (c = 1.08)
16b	OD	20 : 1	1.0	8.6, 16.5[c]		-43.5 ° (c = 0.51)
16c	OD	20 : 1	1.0	15.5	12.8	+7.0 ° (c = 0.56)
16d	OD	20 : 1	1.3	8.6, 16.5[c]		-4.0 ° (c = 1.35)

[a] In the case of **16c** and **16d**, (*R*)-**12** was used. [b] OD: Daicel Chiralcel-OD ; OJ: Daicel Chiralcel-OJ. [c] The absolute configuration was not determined.

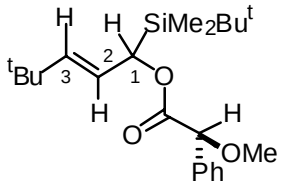
Determination of the Absolute Configuration of 13.



MTPA ester of **13**

The MTPA esters of **13** and the *O*-methylmandelates of **13** and *ent*-**13** were prepared by conventional manner.

		^{1}H chemical shift, δ (ppm) (*S*)-MTPA	^{1}H chemical shift, δ (ppm) (*R*)-MTPA	$\delta = \delta_S - \delta_R$	assigned configuration
MTPA esters of **13**	H-1	5.55	5.44	+0.11	*S*
	H-2	5.46	5.34	+0.12	
	H-3	5.68	5.57	+0.11	
	SiMe	-0.03	0.00	-0.03	
	SiMe	-0.04	-0.02	-0.02	
	t-Bu	0.86	0.89	-0.03	



(*S*)-*O*-methylmandelates of **6e** and *ent*-**13**

	^{1}H chemical shift, δ (ppm)		$\delta = \delta_{\mathbf{6e}} - \delta_{ent\text{-}\mathbf{6e}}$	assigned configuration
	15	*ent*-**15**		
H-1	5.29	5.29	0	*S*
H-2	5.17	5.35	-0.18	
H-3	4.88	5.42	-0.54	
SiMe	-0.07	-0.26	+0.19	
SiMe	-0.07	-0.26	+0.19	
t-Bu	0.77	0.72	+0.05	