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Catalytic Enantioselective Isomerization of Silacyclopentene Oxides. New Strategy for Stereocontrolled Assembly of Acyclic Polyols

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General

Methanol (HPLC grade), benzene (ACS grade), toluene (HPLC grade), ethyl acetate (ACS grade), hexane (ACS grade and HPLC grade), acetonitrile (HPLC grade), chloroform (HPLC grade) were purchased from Fisher Scientific and used without further purification. DMSO (anhydrous grade), DMF (anhydrous grade) were purchased from ACROS. Dichloromethane, diethyl ether were purified by passing over activated alumina. Tetrahydrofuran was purified by distillation from sodium-benzophenone, or by passing over activated alumina. Commercially available reagents were used without further purification. Reactions were monitored by thin layer chromatography (TLC) using Whatman precoated silica gel plates. Flash column chromatography was performed over EM Science Laboratories silica gel (230-400 mesh). ^{1}H NMR and ^{13}C NMR spectra were recorded on Bruker DMX-500 spectrometers using residual solvent peaks as an internal standard. Infrared spectra (IR) were recorded with Nicolet FTIR spectrometer and are reported in reciprocal centimeter (cm^{-1}). Optical rotations were measured with Perkin-Elmer Model 141 polarimeter, using the sodium D line. Mass Spectra were recorded with Agilent 1100 LCMS; APCI, POS, SCAN, 70, with methanol or dichloromethane as the eluting solvent.

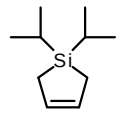
General Procedure A: Representative Preparation of 1,1-Diphenylsilacyclopent-3-ene (1a).[1] A solution of dichlorodiphenylsilane (3.54 g, 14 mmol) in dry toluene was added dropwise to a stirred suspension of magnesium-butadiene (18 mmol) in THF (20 mL). Stirring was then continued for 4 h at 0 °C and for 14 h at room temperature. The reaction was quenched by saturated NH_4Cl solution (100 mL), extracted with diethyl ether (2×50 mL), dried over $MgSO_4$, filtered, and concentrated *in vacuo*. The crude product was purified by flash chromatography on silica gel (elution with pure hexane) to give the title compound (2.76 g, 84%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.83 (s, 4H), 6.01 (s, 2H), 7.33-7.41 (m, 6H), 7.54-7.57 (m, 4H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 16.8, 127.9, 129.5, 131.0, 134.7, 135.8; IR ($CHCl_3$) 3070, 3012, 1602, 1480, 1428, 1114, 943, 904, 814 cm^{-1}. ^{1}H NMR and ^{13}C NMR spectra were in agreement with those reported previously.[2]

1a

1-Methyl-1-naphthylsilacyclopent-3-ene (1b). The title compound was prepared according to General Procedure A. ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.53 (s, 3H), 1.62 (d, 2H, J=17.0 Hz), 1.84 (d, 2H, J=17.2 Hz), 6.03(s, 2H), 7.43-7.50 (m, 3H), 7.77 (d, 1H, J=6.0 Hz), 7.85-7.90 (m, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ -1.9, 18.1, 125.1, 125.5, 125.9, 128.0, 129.1, 130.1, 131.1, 133.3, 133.8, 136.0, 136.9; IR ($CHCl_3$) 3055, 3007, 2881, 1602, 1500, 1393, 1316, 1248, 1195, 1146, 1100, 1020, 981, 943, 904, 843, 822, 779, 796, 720 cm^{-1}.

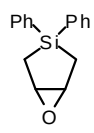
1b

1,1-Diisopropylsilacyclopent-3-ene (1c). The title compound was prepared according to General Procedure A (63% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.94-1.03 (m, 14H), 1.22 (br s, 4H), 5.84 (br s, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 10.8, 11.5, 18.0, 131.4; IR ($CHCl_3$) 3107, 2938, 2888, 1610, 1460, 1099, 993, 944, 881, 793, 717, 670, 634 cm^{-1}; MS(CI) calcd for $C_{10}H_{20}Si$ 168.4 (M^+), found 165.9.



1c

General Procedure B. Representative Preparation of 1,1-Diphenyl-6-oxa-1-silabicyclo [3,1,0] hexane (2a). mCPBA (0.53 g, 3 mmol) was added portion wise to a solution of silane **1a** (0.24 g, 1.0 mmol) in CH_2Cl_2 (7 mL). The reaction mixture was stirred at room temperature until TLC indicated disappearance of starting material.

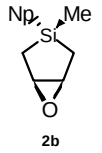


2a

[1] Richter, W. *Synthesis* **1982,** 1102.
[2] Mignani, S; Damour, D. *Syn. Comm.* **1995,** *25*, 3855-3861.

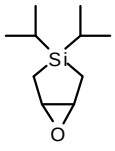
Diethyl ether (75 mL) was added. The solution was washed with $NaHCO_3$ (2×30 mL), water (30 mL), dried over $MgSO_4$, filtered, and concentrated *in vacuo*. The crude product was purified by flash chromatography on silica gel (elution with ether:hexane=1:4) to give the title compound (0.25 g, 98%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.45 (d, 2H, J=15.0 Hz), 1.74 (d, 2H, J=16.0 Hz), 3.6 (s, 2H), 7.29-7.43 (m, 6H), 7.49-7.54 (m, 4H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 15.1, 57.9, 127.7, 128.0, 129.4, 129.5, 134.8, 135.2, 135.3; IR ($CHCl_3$) 3009, 1428, 1179, 1114, 931, 920, 809, 720, 698 cm^{-1}; MS(CI) calcd for $C_{16}H_{16}OSi$ 252.4 (M^+), found 252.1.

1-Methyl-1-naphthyl-6-oxa-1-silabicyclo [3,1,0] hexane (2b). The title compound was prepared according to General Procedure B (56% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.48 (s, 3H), 1.45 (d, 2H, J=15.0 Hz), 1.63 (d, 2H, J=16.0 Hz), 3.61 (s, 2H), 7.42 (dd, 1H, J=8.0, 7.0 Hz), 7.50 (dquintet, 2H, J=7.0, 2.0 Hz), 7.65 (dd, 1H, J=7.0, 1.0 Hz), 7.79-7.81 (m, 1H), 7.88 (br d, 2H, J=7.0 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ 0.46, 15.9, 58.4, 125.1, 125.6, 126.0, 127.8, 129.2, 130.1, 133.3, 133.5, 136.0, 136.3; IR ($CHCl_3$) 2992, 1506, 1179, 931, 909, 832, 812, 798, 783, 730 cm^{-1}; MS(CI) calcd for $C_{15}H_{16}OSi$ 240.4 (M^+), found 240.1.



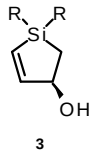
2b

1,1-Diisopropyl-6-oxa-1-silabicyclo [3,1,0] hexane (2c). The title compound was prepared according to General Procedure B (62% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.84 (dd, 2H, J=16.2, 1.7 Hz), 0.89-0.97 (m, 14H), 1.11 (d, 2H, J=16.2 Hz), 3.84 (br s, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 10.0, 11.2, 11.5, 18.1, 18.4, 58.1; IR ($CHCl_3$) 2938, 2864, 1460, 1177, 993, 963, 923, 881, 906, 784, 708 cm^{-1}; MS(CI) calcd for $C_{10}H_{20}OSi$ 184.4 (M^+), found 185.1 (M+1)



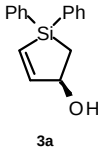
2c

General Procedure C. Preparation of Silacyclopent-4-en-3-ol (3) (Stoichiometric Isomerization Procedure). n-BuLi (1.5 equiv) was added dropwise to a solution of chiral amine (1.5 equiv) in THF at 0 °C. The resulting yellowish solution was stirred at 0 °C for 20 min, and DBU (1.5 equiv) was added with THF. After 10 min, the solution was cooled to –78 °C, then a solution of epoxide **2** (1 mmol) in THF was added via cannula. The reaction mixture was stirred for 24 h allowing to slowly warm from –78 °C to 0 °C. The reaction was quenched with 10% solution of citric acid (20 mL), extracted with ether (3×20 mL). Combined organic layers were washed with water (20 mL), dried over $MgSO_4$, filtered, and concentrated *in vacuo*. The crude product was purified by flash chromatography on silica gel to give alcohol **3**.



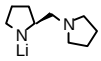
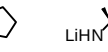
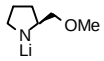
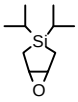
3

1,1-Diphenyl silacyclopent-4-en-3-ol (3a). The title compound was prepared according to General Procedure C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.12 (dd, 1H, J=15.0, 5.4 Hz), 1.70 (br s, 1H), 1.91 (dd, 1H, J=15.0, 7.5 Hz), 4.98-5.00 (m, 1H), 6.38 (dd, 1H, J=10.0, 1.6 Hz), 7.04 (dd, 1H, J=10.0, 2.0 Hz), 7.34-7.42 (m, 6H), 7.48-7.56 (m, 4H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 21.6, 76.0, 128.0, 128.01, 129.73, 129.78, 130.0, 134.5, 134.86, 134.89, 135.0, 157.6; IR ($CHCl_3$) 3319, 1428, 1146, 1115, 1017, 998, 907, 866, 809 cm^{-1}; MS(CI) calcd for $C_{16}H_{16}OSi$ 252.4 (M^+), found 252.1.



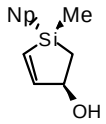
3a

Table 1. Base-Mediated Rearrangement (ee, %)

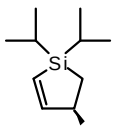
epoxides \ amides	 **4**	 **5**	 **6**	 **7**
 **2a**	95	79	81	39
 **2b**	95	90	56	88
 **2c**	93	84	81	50

* Enantiomeric excess was determined by ^{1}H NMR (500 MHz) analysis of the corresponding Mosher esters.

1-Methyl-1-naphthylsilacyclopent-4-en-3-ol (3b). The title compound was prepared according to General Procedure C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.61 (s, 3H), 0.99 (dd, 1H, J=14.8, 5.6 Hz), 1.75 (br s, 1H), 1.94 (dd, 1H, J=14.8, 7.6 Hz), 4.85-4.90 (m, 1H), 6.47 (dd, 1H, J=10.0, 1.0 Hz), 6.92 (dd, 1H, J=10.0, 2.0 Hz), 7.42 (dd, 1H, J=8.0, 6.0 Hz), 7.50 (dquintet, 2H, J=7.0, 1.0 Hz), 7.66 (dd, 1H, J=7.0, 1.0 Hz), 7.83-7.88 (m, 1H), 7.98 (br d, 1H, J=8.0 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ 0.2, 22.4, 76.2, 125.1, 125.6, 126.0, 127.8, 129.1, 130.2, 131.8, 133.3, 133.7, 135.7, 136.6, 156.2; IR ($CHCl_3$) 3317, 1500, 1316, 1248, 1146, 1010, 972, 905, 870, 826, 795, 778 cm^{-1}; MS(CI) calcd for $C_{15}H_{16}OSi$ 240.4 (M^+), found 239.1(M-1).

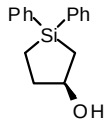

3b

1,1-Diisopropylsilacyclopent-4-en-3-ol (3c). The title compound was prepared according to General Procedure C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.53 (dd, 1H, J=14.8, 5.6 Hz), 0.90-1.04 (m, 14H), 1.34 (dd, 1H, J=14.8, 7.8 Hz), 1.61 (br s, 1H), 4.72-4.77 (m, 1H), 5.97 (dd, 1H, J=10.0, 1.0 Hz), 6.80 (dd, 1H, J=10.0, 2.0 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ 11.1, 16.3, 18.1, 18.2, 18.24, 18.3, 76.1, 129.1, 156.3; IR ($CHCl_3$) 3307, 2952, 2940, 2890, 2863, 1563, 1456, 1316, 1141, 1018, 881, 801cm^{-1}; MS(CI) calcd for $C_{10}H_{20}OSi$ 184.4 (M^+), found 185.1 (M+1).


3c

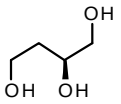
Preparation of 1,1-Diphenylsilacyclopent-4-en-3-ol (3a). (Catalytic Isomerization Procedure) n-BuLi (0.4 mL, 1 mmol, 2.5 M in hexane) was added dropwise to a solution of amine **4** (9 mg, 0.05 mmol, 10 mol%) and DIPA (140 μL, 1 mmol) in THF/DBU(4 mL/0.46 mL) at 0 °C. The resulting yellowish solution was stirred at 0 °C for 30 min, then cooled to –78 °C. A solution of epoxide **2a** (126 mg, 0.50 mmol) in THF (2.5 mL) was added via cannula. The reaction mixture was stirred for 36 h allowing to slowly warm from –78 °C to 0 °C. The reaction was quenched with 10% solution of citric acid (20 mL), extracted with ether (3×20 mL). Combined organic phase was washed with water (20 mL), dried over $MgSO_4$, filtered, and concentrated *in vacuo*. The crude product was purified by flash chromatography on silica gel (elution with EtOAc:hexane=1:3) to give the title compound (98 mg, 78%). Enantiomeric excess was determined to be 93% by ^{1}H NMR (500 MHz) analysis of the corresponding Mosher ester.

1,1-Diphenylsilacyclopentan-3-ol (8). A solution of alcohol **3a** (50 mg, 0.20 mmol) and PtO_2 (4.5 mg, 0.02 mmol) in MeOH (1 mL) was stirred under H_2 (1 atm) for 16 h at room temperature. The reaction mixture was filtered through Celite, washed with MeOH, dried over $MgSO_4$, filtered, and concentrated *in vacuo*. The crude product was purified by flash chromatography on silica gel (elution with EtOAc:hexane=1:3) to give the title compound (45mg, 90%). $[\alpha]^{26}_D$ = -3.4°, (c=1.41 in $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.12 (dt, 1H, J=15.1, 7.8 Hz), 1.22 (dd, 1H, J=14.8, 6.7 Hz), 1.34 (dt, 1H, J=15.1, 7.2 Hz), 1.54 (dd, 1H, J=14.8, 5.2 Hz), 1.58 (br s, 1H), 1.84-1.91 (m, 1H), 1.99-2.06 (m, 1H), 4.42-4.47 (m, 1H), 7.34-7.41 (m, 6H), 7.52-7.55 (m, 2H), 7.57-7.60 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 8.6, 22.9, 35.6, 74.3, 127.9, 128.0, 129.4, 134.6, 134.8, 136.0, 136.1; IR ($CHCl_3$) 3319, 3063, 2911, 1427, 1112, 1023, 993, 977, 808, 795, 731, 721, 696, 65, 645 cm^{-1}; MS(CI) calcd for $C_{16}H_{18}OSi$ 254.4 (M^+), found 254.0.



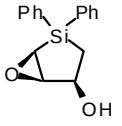
8

General Procedure D. Representative Preparation of (S)-(-)-1,2,4-Butanetriol (9).[3] To a cooled (0 °C) solution of KH (105 mg, 0.788 mmol, 30% dispersion in mineral oil, washed with 3×2 mL of hexanes) in DMF (0.6 mL) was added t-BuOOH (70%, 105 μL, 0.758 mmol) dropwise. After 10 min, a solution of alcohol **8** (40 mg, 0.157 mmol) in DMF (1 mL) was added. The mixture was stirred at room until TLC indicated disappearance of starting material. The mixture was treated with $Na_2S_2O_3$ (0.2 g) stirred for 30 min, and filtered (washed with MeOH). After removal of DMF by bulb-to-bulb distillation (50-60 °C, 0.5 mmHg), the crude product was purified by flash chromatography on silica gel (elution with EtOAc:MeOH=4:1) to give the title compound (13 mg, 78%). $[\alpha]^{26}_D$ = -22°, (c=1.0 in MeOH); ^{1}H NMR (500 MHz, CD_3OD) δ 1.55-1.63 (m, 1H), 1.69-1.75 (m, 1H), 3.44 (dd, 1H, J=11.0, 6.0 Hz), 3.49 (dd, 1H, J=11.0, 5.0 Hz), 3.68-3.71 (m, 2H), 3.72-3.77 (m, 1H); ^{13}C NMR (125 MHz, CD_3OD) δ 37.1, 60.0, 67.5, 70.8; IR (neat) 3299, 2938, 2880, 1417, 1049, 980, 955, 903, 870 cm^{-1}; MS(CI) calcd for $C_4H_{10}O_3$ 106.1 (M^+), found 105.1(M-1).



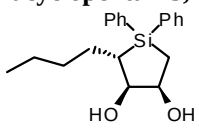
9

2,2-Diphenyl-6-oxa-2-silabicyclo [3,1,0] hexan-4-ol (10). mCPBA (0.80 g, 3.25 mmol) was added portionwise to a solution of alcohol **3a** (328 mg, 1.30 mmol) in CH_2Cl_2 (12 mL). The reaction mixture was stirred at room temperature until TLC indicated disappearance of starting material. CH_2Cl_2 (60 mL) was added. The solution was washed with 5% solution of Na_2SO_3 (20 mL), half-saturated solution of $NaHCO_3$ (20 mL), brine (20 mL), dried over $MgSO_4$, filtered, and concentrated *in vacuo*. The crude product was purified by flash chromatography on silica gel (elution with EtOAc:hexane=1:1) to give the title compound (335 mg, 96%). $[\alpha]^{27}_D$ = -39°, (c=0.51 in $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.96 (dd, 1H, J=14.5, 4.7 Hz), 1.64 (dd, 1H, J=14.5, 8.0 Hz), 1.81 (d, 1H, J=8.3 Hz), 2.93 (d, 1H, J=4.0 Hz), 3.76 (dd, 1H, J=4.0, 1.3 Hz), 4.55 (q, 1H, J=8.3 Hz), 7.36-7.48 (m, 6H), 7.51-7.55 (m, 2H), 7.65-7.68 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 14.9, 47.6, 59.8, 72.8, 128.1, 128.4, 130.4, 130.5, 131.87, 131.92, 134.8, 135.2; IR ($CHCl_3$) 3352, 3003, 1428, 1150, 1116, 1027, 998, 961, 848, 800, 729, 696 cm^{-1}; MS(CI) calcd for $C_{16}H_{18}O_2Si$ 268.4 (M^+), found 268.0.



10

General procedure E. Representative Preparation of 1,1-Diphenyl-2-butylsilacyclopentan-3,4-diol (11a).[4] To a solution of CuCN (15 mg, 0.168 mmol) in ether (1.5 mL) at –40 °C was added n-BuMgCl (0.84 mL, 1.68 mmol, 2 M in ether). The mixture was stirred for 10 min, then a solution of epoxide **10** (90 mg, 0.336 mmol) in ether (1.5 mL) was added dropwise. The reaction was stirred until TLC showed disappearance of starting material. Saturated NH_4Cl solution was added. The

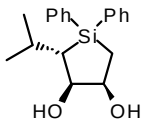


11a

[3] Smitrovich, J. H.; Woerpel, K. A. *J.Org. Chem.* **1996,** *61*, 6044-6046.
[4] Chauret, D. C.; Chong, J. M.; Ye, Q. *Tetrahedron: Asymmetry* **1999,** *10*, 3601-3614.

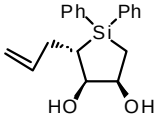
aqueous phase was extracted with ether (3×15 mL). The combined organic phase was washed with brine (20 mL), dried over $MgSO_4$, filtered, and concentrated *in vacuo*. The crude product was purified by flash chromatography on silica gel (elution with EtOAc:hexane =1:1) to give the title compound (100 mg, 91%). $[\alpha]^{29}_D$ = -5.2°, (c=0.71 in $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$); δ 0.67 (t, 3H, J=7.2 Hz), 1.02-1.34 (m, 5H), 1.36-1.46 (m, 2H), 1.52-1.56 (m, 1H), 1.64-1.69 (m, 1H), 1.95 (br s, 2H), 3.89 (dd, 1H, J=8.9, 2.6 Hz), 4.43 (q, 1H, J=3.8 Hz), 7.32-7.45 (m, 8H), 7.65-7.68 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 13.7, 17.9, 22.8, 28.2, 30.7, 32.8, 74.5, 81.6, 127.8, 128.0, 129.5, 129.6, 133.9, 135.1, 135.27, 135.31; IR ($CHCl_3$) 3363, 2916, 1427, 1212, 1111, 1043, 998, 753, 731, 697 cm^{-1}; MS(CI) calcd for $C_{20}H_{26}O_2Si$ 326.5 (M^+), found 309.1 (M-OH).

1,1-Diphenyl-2-isopropylsilacyclopentan-3,4-diol (11b). The title compound was prepared according to General Procedure E (77% yield). $[\alpha]^{24}_D$ = +6.5°, (c=0.37 in $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.75 (d, 3H, J=6.7 Hz), 1.03 (d, 3H, J=6.7 Hz), 1.40 (d, 2H, J=4.1 Hz), 1.58 (t, 1H, J=9.1 Hz), 1.76-1.84 (m, 1H), 4.09 (dd, 1H, J=9.1, 3.2 Hz), 4.44 (q, 1H, J=3.8 Hz), 7.30-7.45 (m, 8H), 7.68-7.71 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 18.1, 23.4, 24.0, 27.9, 38.2, 74.9, 80.0, 127.8, 127.9, 129.4, 129.5, 134.8, 135.1, 135.3, 135.5; IR ($CHCl_3$) 3383, 2935, 2917, 2869, 1427, 1110, 1042, 999, 759, 731, 698 cm^{-1}; MS(CI) calcd for $C_{19}H_{24}O_2Si$ 312.5 (M^+), found 311.1 (M-1).



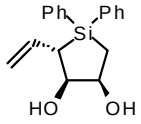
11b

1,1-Diphenyl-2-allylsilacyclopentan-3,4-diol (11c). The title compound was prepared according to General Procedure E (92% yield). $[\alpha]^{29}_D$ = +3.9°, (c=0.46 in $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.42-1.43 (m, 2H), 1.80 (q, 1H, J=8.4 Hz), 2.18 (t, 2H, J=7.7 Hz), 3.94 (dd, 1H, J=9.2, 3.0 Hz), 4.45 (q, 1H, J=3.8 Hz), 4.84-4.91 (m, 2H), 5.75-5.83 (m, 1H), 7.33-7.45 (m, 8H), 7.66-7.68 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 17.2, 30.0, 33.3, 74.1, 81.4, 115.6, 127.87, 129.90, 129.5, 129.6, 133.6, 134.8, 135.1, 135.3, 139.4 ; IR ($CHCl_3$) 3395, 3063, 2900, 1427, 1112, 1049, 998, 914, 733 cm^{-1}; MS(CI) calcd for $C_{19}H_{22}O_2Si$ 310.5 (M^+), found 309.0 (M-1).



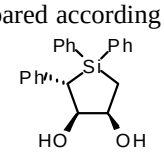
11c

1,1-Diphenyl-2-vinylsilacyclopentan-3,4-diol (11d). The title compound was prepared according to General Procedure E (87% yield). $[\alpha]^{29}_D$ = -15.5°, (c=0.28 in $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.47-1.49 (m, 2H), 2.18 (d, 1H, J=2.7 Hz), 2.39 (s, 1H), 2.63 (t, 1H, J=10.2 Hz), 4.03 (br d, 1H, J=10.7 Hz), 4.54 (q, 1H, J=3.4 Hz), 4.96 (dd, 1H, J=10.1, 1.4 Hz), 5.05 (br d, 1H, J=16.8 Hz), 5.69 (dt, 1H, J=16.9, 9.9 Hz), 7.34-7.42 (m, 6H), 7.46-7.48 (m, 2H), 7.62-7.64 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 16.8, 38.8, 73.2, 79.4, 114.8, 127.9, 128.0, 129.8, 133.1, 134.6, 135.0, 135.4, 137.2; IR ($CHCl_3$) 3374, 1625, 1427, 1211, 1111, 1046, 998, 752, 730, 697 cm^{-1}; MS(CI) calcd for $C_{18}H_{20}O_2Si$ 296.4 (M^+), found 297.0.



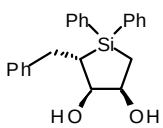
11d

1,1-Diphenyl-2-phenylsilacyclopentan-3,4-diol (11e). The title compound was prepared according to General Procedure E (92% yield). $[\alpha]^{29}_D$ = -8.1°, (c=1.47 in $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.54 (dd, 1H, J=16.0, 1.8 Hz), 1.63 (dd, 1H, J=16.0, 5.0 Hz), 3.29 (d, 1H, J=11.5 Hz), 4.42 (dd, 1H, J=11.5, 3.0 Hz),4.60-4.63 (m, 1H), 6.91 (d, 2H, J=7.2 Hz), 7.03-7.13 (m, 5H), 7.18 (t, 2H, J=7.6 Hz), 7.28-7.32 (m, 1H), 7.33-7.42 (m, 3H), 7.64-7.66 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 16.6, 40.2, 73.2, 79.4, 125.1, 127.6, 127.8, 128.0, 128.5, 129.6, 129.7, 132.5, 134.9, 135.2, 135.3, 139.2; IR ($CHCl_3$) 3357, 3052, 3019, 2889, 1598, 1489, 1427, 1211, 1109, 1048, 998, 863, 781, 752, 730, 695 cm^{-1}; MS(CI) calcd for $C_{22}H_{22}O_2Si$ 346.5 (M^+), found 347.0.



11e

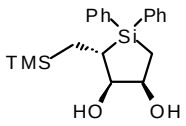
1,1-Diphenyl-2-benzylsilacyclopentan-3, 4-diol (11f). The title compound was prepared according to General Procedure E (86% yield). $[\alpha]^{25}_D$ = -10.7°, (c=2.9



11f

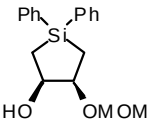
in $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$) δ 1.41 (dd, 1H, J=16.0, 5.0 Hz), 1.48 (dd, 1H, J=15.5, 3.0 Hz), 2.01 (q, 1H, J=8.5 Hz), 2.13 (br s, 2H), 2.70 (dd, 1H, J=13.5, 8.5 Hz), 2.77 (dd, 1H, J=13.5, 8.5 Hz), 4.01 (dd, 1H, J=9.5, 3.0 Hz), 4.47 (q, 1H, J=3.8 Hz), 6.91-6.93 (m, 2H), 7.13-7.19 (m, 3H), 7.27-7.44 (m, 10H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 17.3, 33.2, 35.0, 74.2, 81.4, 126.1, 127.8, 127.9, 128.5, 128.7, 129.5, 129.7, 133.8, 134.4, 135.0, 135.4, 142.2; IR ($CHCl_3$) 3372, 2976, 2873, 1495, 1427, 1217, 1111, 1045, 997, 946, 873 cm^{-1}; MS(CI) calcd for $C_{23}H_{24}O_2Si$ 360.5 (M^+), found 360.1.

1,1-Diphenyl-2-trimethylsilylmethylsilacyclopentan-3, 4-diol (11g). To a solution of CuCN (111 mg, 1.24 mmol) in ether (1 mL) at –78 °C was added trimethylsilylmethyl lithium (2.48 mL, 1 M in pentane). The mixture was stirred at –78 °C for 10 min, allowed to reach room temperature, cooled to -78°C after 15 min. A solution of epoxide **10** (83 mg, 0.31 mmol) in ether (1 mL) was added. The reaction mixture was stirred for 16 h allowing to warm from –78 °C to 0 °C. Saturated NH_4Cl solution was added. The aqueous phase was extracted with ether (3×15 mL). The combined organic layers were washed with brine (20 mL), dried over $MgSO_4$, filtered, and concentrated *in vacuo*. The crude product was purified by flash chromatography on silica gel (elution with EtOAc:hexane=1:1) to give the title compound (100 mg, 91%). $[\alpha]^{25}_D$ = -14.3°, (c=2.8 in $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$) δ -0.12 (s, 9H), 0.53-0.62 (m, 2H), 1.32 (dd, 1H, J=15.0, 5.0 Hz), 1.51 (dd, 1H, J=15.0, 5.5 Hz), 1.75 (q, 1H, J=7.3 Hz), 2.29 (br s, 2H), 3.84 (dd, 1H, J=7.0, 2.5 Hz), 4.45 (q, 1H, J=4.5 Hz), 7.35-7.43 (m, 6H), 7.46-7.48 (m, 2H), 7.66-7.69 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ -1.1, 14.8, 18.1, 24.6, 74.1, 83.4, 127.82, 127.86, 129.47, 129.54, 133.7, 135.1, 135.3, 135.7; IR ($CHCl_3$) 3289, 2951, 2893, 1427, 1245, 1215, 1111, 1060, 998, 847, 833, 754, 731, 696 cm^{-1}.



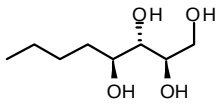
11g

1,1-Diphenyl-4-methoxymethoxysilacyclopentan-3-ol (11h). Chloromethyl-methylether (159 μL, 1.96 mmol) was added dropwise to a solution of alcohol **10** (105 mg, 0.392 mmol) and ethyldiisopropylamine (685 μL, 3.92 mmol) in CH_2Cl_2 (2 mL) at 0 °C for 12 h. Saturated $NaHCO_3$ solution was added. The aqueous phase was extracted with ether (3×10 mL). The combined organic phase was washed with brine (20 mL), dried over $MgSO_4$, filtered, and concentrated *in vacuo*. The crude product was purified by flash chromatography on silica gel (elution with ether:hexane=1:2) to give the corresponding MOM protected alcohol (99 mg, 81%). This compound (74 mg, 0.24 mmol) was treated with a suspension of $LiAlH_4$ (36 mg, 0.95 mmol) in ether (0.7 mL) at –78 °C. The mixture was stirred for 12 h allowing to warm from –78 °C to 0 °C, diluted by ether (10 mL), quenched by water, dried over $NaSO_4$, filtered, and concentrated *in vacuo*. The crude product was purified by flash chromatography on silica gel (elution with EtOAc:hexane=1:2) to give the title compound (48 mg, 65%). $[\alpha]^{25}_D$ = -48°, (c=0.33 in $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$) δ 1.32-1.51 (m, 4H), 3.37 (s, 3H), 4.12 (ddd, 1H, J=9.0, 6.5, 3.0 Hz), 4.36-4.38 (m, 1H), 4.69 (d, 1H, J=7.0 Hz), 4.78 (d, 1H, J=7.0 Hz), 7.31-7.41 (m, 6H), 7.52-7.54 (m, 2H), 7.59-7.62 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 15.0, 18.2, 55.6, 74.5, 81.5, 95.1, 127.8, 128.1, 129.5, 129.6, 134.7, 135.1, 135.4, 135.6; IR ($CHCl_3$) 3450, 2884, 1427, 1146, 1113, 1097, 1035, 1018, 997, 972, 916, 819 cm^{-1}; MS(CI) calcd for $C_{18}H_{22}O_3Si$ 314.5 (M^+), found 314.0.



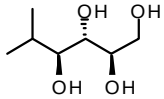
11h

(*2R, 3S, 4S*)-1,2,3,4-Octanetetraol (12a). The title compound was prepared according to General Procedure D (78% yield). $[\alpha]^{26}_D$ = -15.8°, (c=0.86 in MeOH); ^1H NMR (500 MHz, CD_3OD) δ 0.93 (t, 3H, J=7.1 Hz), 1.26-1.46 (m, 4H), 1.49-1.57 (m, 1H), 1.65-1.71 (m, 1H), 3.45 (t, 1H, J=6.5 Hz), 3.59-3.68 (m, 3H), 3.76 (dd, 1H, J=11.1, 3.4 Hz); ^{13}C NMR (125 MHz, CD_3OD) δ 14.5, 23.9, 29.0, 33.0, 64.6, 74.0, 74.4, 76.0; MS(CI) calcd for $C_8H_{18}O_4$ 178.2 (M^+), found 178.2.



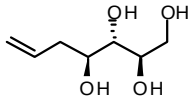
12a

(*2R, 3S, 4S*)-5-Methylhexan-1,2,3,4-tetraol (12b). The title compound was prepared according to General Procedure D (76% yield). $[\alpha]^{26}_{D}$ = -11.8°, (c=0.48 in MeOH); ^{1}H NMR (500 MHz, CD_3OD) δ 0.89 (d, 3H, J=6.8 Hz), 0.97 (d, 3H, J=7.1 Hz), 1.97-2.06 (m,1H), 3.43 (dd, 1H, J=8.4, 3.3 Hz), 3.54 (dd, 1H, J=8.4, 5.2 Hz), 3.62-3.66 (m, 1H), 3.74-3.79 (m, 2H); ^{13}C NMR (125 MHz, CD_3OD) δ 15.5, 20.4, 30.3, 64.1, 73.3, 75.3, 78.5; MS(CI) calcd for $C_7H_{16}O_4$ 164.2(M^+), found 164.0.



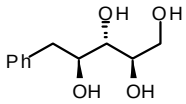
12b

(*2R, 3S, 4S*)-Hept-6-ene-1,2,3,4-tetraol (12c). The title compound was prepared according to General Procedure D (79% yield). $[\alpha]^{26}_{D}$ = -98°, (c=0.75 in MeOH); ^{1}H NMR (500 MHz, CD_3OD) δ 2.19-2.24 (m,1H), 2.43-2.47 (m, 1H), 3.48 (t, 1H, J=6.5 Hz), 3.65 (dd, 1H, J=11.0, 6.5 Hz), 3.68-3.72 (m, 2H), 3.76 (dd, 1H, J=11.0, 3.5 Hz), 5.03-5.12 (m, 2H), 5.88-5.97 (m, 1H); ^{13}C NMR (125 MHz, CD_3OD) δ 38.1, 64.6, 73.6, 74.4, 75.6, 117.2, 136.8; MS(CI) calcd for $C_7H_{14}O_4$ 162.2, found 161.1(M-1).



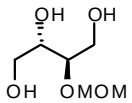
12c

(*2R, 3S, 4S*)-5-Phenyl-pentan-1,2,3,4-tetraol (12d). The title compound was prepared according to General Procedure D (70% yield). $[\alpha]^{26}_{D}$ = -31.3°, (c=0.98 in MeOH); ^{1}H NMR (500 MHz, CD_3OD) δ 2.64 (dd,1H, J=13.9, 9.6 Hz), 3.05 (dd, 1H, J=13.9, 2.7 Hz), 3.53 (t, 1H, J=6.4 Hz), 3.64 (dd, 1H, J=11.1, 6.0 Hz), 3.72-3.76 (m, 1H), 3.79 (dd, 1H, J=11.1, 3.4 Hz), 3.89 (ddd, 1H, J=9.2, 6.2, 2.8 Hz), 7.14-7.28 (m, 5H); ^{13}C NMR (125 MHz, CD_3OD) δ 39.8, 64.6, 74.4, 75.2, 75.9, 126.9, 129.1, 130.7, 140.9; MS(CI) calcd for $C_{11}H_{16}O_4$ 212.2 (M^+), found 212.3.



12d

(*2R, 3S*)-2-Methoxymethoxy-1,3,4-butanetriol (12e). The title compound was prepared according to General Procedure D (74% yield). $[\alpha]^{26}_{D}$ = -6.4°, (c=1.05 in MeOH); ^{1}H NMR (500 MHz, CD_3OD) δ 3.39 (s, 3H), 3.55-3.60 (m,2H), 3.67-3.74 (m, 3H), 3.77 (dd, 1H, J=11.9, 3.8 Hz), 4.70 (d, 1H, J=6.7 Hz), 4.75 (d, 1H, J=6.7 Hz); ^{13}C NMR (125 MHz, CD_3OD) δ 56.0, 62.6, 64.2, 72.9, 80.6, 97.7; MS(CI) calcd for $C_6H_{14}O_5$ 166.2 (M^+), found 166.2.



12e