Supporting Information

Acid-Catalyzed Cyclization of Vinylsilanes Bearing an Amino Group. Stereoselective Synthesis of Pyrrolidines.

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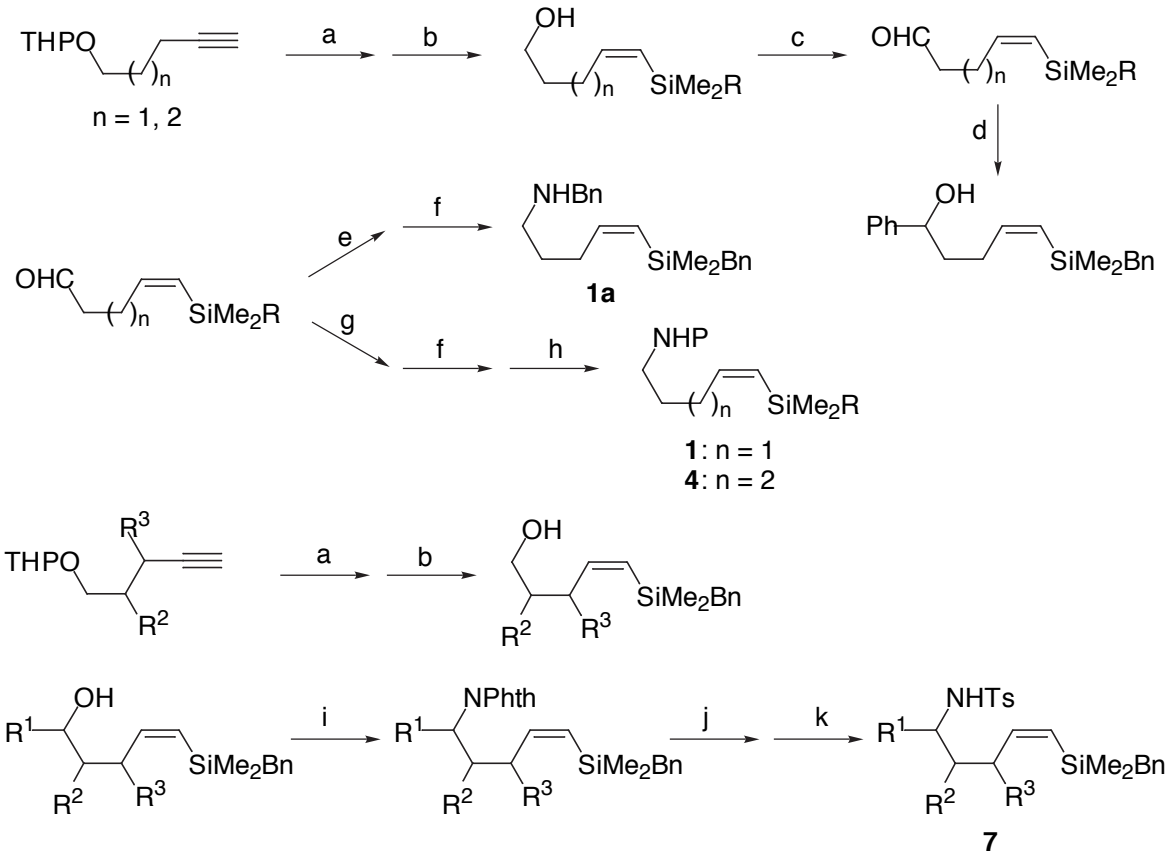
General Method. Unless otherwise noted, all reactions and distillations of solvents and reagents were carried out under N_2. Solvents were dried by distillation from sodium metal/benzophenone ketyl (THF, Et_2O), $CaCl_2$-$NaHCO_3$ ($CHCl_3$), and CaH_2 (CH_2Cl_2). $TiCl_4$ was simply distilled and stored as a $CHCl_3$ solution (1.0 M). All other commercially obtained reagents were used as received. High performance liquid chromatography was carried out with Shimadzu LC-6A and LC-10A (Shimadzu Shim-pack CLC-SiL 0.15 m x 6.0 ϕ, rate of flow 1.0 mL/min) using hexane-ethyl acetate as an eluent. Bath temperature was employed as boiling point in distillation using Kugelrohr apparatus. ^1H NMR spectra at 270 MHz and ^{13}C NMR spectra at 67.7 MHz were determined on a JEOL JNM-EX270 instrument with tetramethylsilane (^1H, δ 0.00 ppm) or chloroform (^1H, δ 7.26 ppm; ^{13}C, δ 77.00 ppm) as an internal standard. Infrared spectra were measured with a Shimadzu IR-460 spectrophotometer. Mass spectra were measured (by EI method) on a Shimadzu QP5000 or a JEOL JMS-GCMATE (HRMS) instrument. Microanalyses were performed by the Analysis Center of University of Tsukuba.

Synthesis of Vinylsilane Bearing an Amino Group. Vinylsilanes **1**, **4**, and **7** were prepared from THP ethers of 4-pentyn-1-ols and 5-hexyn-1-ol as shown in Scheme 7. The procedures for the syntheses of **1d** and **7a** are described as representative examples.

Synthesis of 1d. BuLi (1.62 M in hexane, 136 mL, 220 mmol) was dropwise added to a solution of 1-(2-tetrahydropyranyloxy)-4-pentyne (33.9 g, 202 mmol) in THF (200 mL) at -78 °C over 20 min.

Scheme 7



(a) BuLi, THF, then RMe_2SiCl, (b) DIBALH, Et_2O-hexane, (c) DMSO, $(COCl)_2$, Et_3N, (d) PhMgBr, Et_2O, (e) $BnNH_2$, MS4A, (f) LAH, Et_2O, *i*-Pr_2O (g) NH_2OH•HCl, Na_2CO_3, H_2O, (h) P-X, Et_3N, CH_2Cl_2; P-X: Ac_2O (**1b**), CF_3CO_2Et (**1c**), TsCl (**1d**, **1h**, and **4**), MsCl (**1e**), Tf_2O (**1f**), $(Boc)_2O$ (**1g**), (i) DEAD, phthalimide, PPh_3, THF, (j) H_2NNH_2•H_2O, EtOH, (k) TsCl, Et_3N, CH_2Cl_2

After 30 min, benzylchlorodimethylsilane (40.7 g, 220 mmol) was dropwise added to the reaction mixture over 10 min. After being stirred for another 30 min at -78 °C and 2 h at rt, the resultant mixture was poured into water (100 mL). After removal of the organic layer, the aqueous layer was extracted with AcOEt (30 mL). The combined organic layer was washed with sat. NaCl aq. (100 mL), dried over Na_2SO_4, and evaporated. Distillation of the crude product gave 5-benzyldimethylsilyl-1-(2-tetrahydropyranyloxy)-4-pentyne (61.8 g, 195 mmol) in 97% yield.

To a solution of 5-benzyldimethylsilyl-1-(2-tetrahydropyranyloxy)-4-pentyne (15.9 g, 50.3 mmol) in Et_2O (100 mL) at 0 °C was dropwise added DIBALH (0.95 M in hexane, 79 mL, 75 mmol).[1] The mixture was gradually warmed to rt and stirred for 40 h. To the reaction mixture was carefully added 20% potassium sodium tartrate aq. (20 mL), then 2 M NaOH aq. (50 mL). The mixture was stirred for 30 min. After removal of the organic layer, the aqueous layer was extracted with Et_2O (50 mL). The combined organic layer was washed with sat. NaCl aq. (50 mL), dried over Na_2SO_4, and evaporated. Methanol (100 mL) and TsOH•H_2O (200 mg) was added to the residue. After being

stirred for 2 h at rt, the reaction mixture was treated with Et_3N (2 mL) and evaporated. The crude product was purified by silica-gel column chromatography eluting with hexane-AcOEt (5: 1) to give (*Z*)-5-benzyldimethylsilyl-4-penten-1-ol (7.67 g, 32.7 mmol) in 65% yield.

DMSO (3.40 mL, 48.0 mmol)-CH_2Cl_2 (10 mL) was added to a solution of $(COCl)_2$ (2.10 mL, 24.1 mmol) in CH_2Cl_2 (40 mL) over 5 min at -78 °C.[2] After 10 min, (*Z*)-5-benzyldimethylsilyl-4-penten-1-ol (4.69 g, 20.0 mmol)-CH_2Cl_2 (20 mL) was added to the mixture over 5 min. After 15 min, the reaction mixture was treated with Et_3N (14.0 mL, 100 mmol) for 10 min, warmed to rt, quenched with water (25 mL), and extracted with CH_2Cl_2 (2 x 30 mL). The extract was dried over Na_2SO_4 and evaporated. Purification of the crude product by silica-gel column chromatography (hexane-AcOEt, 7:1) gave (*Z*)-5-benzyldimethylsilyl-4-pentenal (4.28 g, 18.4 mmol) in 92% yield.

Under air, Na_2CO_3 aq. (489 mg in water (2.5 mL), 4.61 mmol) was dropwise added to a mixture of (*Z*)-5-benzyldimethylsilyl-4-pentenal (2.14 g, 9.20 mmol), NH_2OH•HCl (799 mg, 11.5 mmol), and water (2.5 mL) at rt.[3] After being stirred for 1 h, the mixture was extracted with Et_2O (2 x 15 mL). The combined organic layer was washed with water (25 mL), dried over Na_2SO_4, and evaporated. Purification of the crude product by silica-gel column chromatography (hexane-AcOEt, 5:1) gave (4*Z*)-5-benzyldimethylsilyl-4-pentenal oxime (2.26 g, 9.13 mmol) in 99% yield.

A solution of (4*Z*)-5-benzyldimethylsilyl-4-pentenal oxime (2.26 g, 9.13 mmol) in Et_2O (25 mL)-*i*-Pr_2O (75 mL) was added to a suspension of LAH (1.14 g, 30.1 mmol) in Et_2O (15 mL)-*i*-Pr_2O (50 mL) at 0°C over 30 min.[3] The mixture was warmed to 55 °C and stirred for 24 h. The resultant mixture was cooled to rt, treated with 20% potassium sodium tartrate aq. (10 mL), and acidified (pH < 2) with 1 M HCl aq. After removal of the aqueous layer, the organic layer was extracted with 1 M HCl aq. (50 mL). The combined aqueous layer was alkalized (pH > 12) with 2 M NaOH and extracted with Et_2O (2 x 30 mL). The extract was dried over Na_2SO_4 and evaporated. The crude product ((*Z*)-5-benzyldimethylsilyl-4-penten-1-amine, 1.80 g, 7.69 mmol, 84%) was almost pure and directly used for the following transformation.

TsCl (772 mg, 4.05 mmol) was added to a solution of (*Z*)-5-benzyldimethylsilyl-4-penten-1-amine (886 mg, 3.80 mmol) and Et_3N (1.1 mL, 7.9 mmol) in CH_2Cl_2 (7 mL) at 0°C. After 1 h, the mixture was poured into sat. $NaHCO_3$ aq. (25 mL). After removal of the organic layer, the aqueous layer was extracted with CH_2Cl_2 (15 mL). The combined organic layer was dried over Na_2SO_4 and evaporated. Purification of the crude product by silica-gel column chromatography (hexane-AcOEt, 5:1) gave *N*-((*Z*)-5-benzyldimethylsilyl-4-pentenyl)*p*-toluenesulfonamide (**1d**, 1.42 g, 3.66 mmol) in 96% yield. **1d**: IR (neat) 3280, 2955, 1599, 1327, 1160, 832 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.07 (s, 6H), 1.45 (tt, *J* = 7.6, 7.3 Hz, 2H), 1.94 (td, *J* = 7.6, 7.3 Hz, 2H), 2.11 (s, 2H), 2.42 (s, 3H), 2.88 (td, *J* = 7.3, 5.9 Hz, 2H), 4.21 (t, *J* = 5.9 Hz, 1H), 5.46 (d, *J* = 14.2 Hz, 1H), 6.20 (dt, *J* = 14.2, 7.3 Hz, 1H), 6.96-7.08 (m, 3H), 7.15-7.22 (m, 2H), 7.30 (d, *J* = 8.1 Hz, 2H), 7.73 (d, *J* = 8.1 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ -1.80 (CH_3 x 2), 21.37 (CH_3), 26.47 (CH_2), 29.27 (CH_2), 30.50 (CH_2), 42.72 (CH_2), 123.85 (CH), 126.95 (CH x 2), 127.82 (CH), 127.98 (CH x 2), 128.07 (CH x 2), 129.56 (CH x 2), 136.77 (C), 139.82 (C), 143.18 (C), 148.21 (CH); MS *m/z* (rel intensity) 372 (M^+ - CH_3, 0.7), 296 (100), 149 (30), 91 (92).

Synthesis of 7a. According to the above-mentioned procedure, (*Z*)-5-benzyldimethylsilyl-4-pentenal was prepared from 1-(2-tetrahydropyranyloxy)-4-pentyne. A solution of the aldehyde (3.32 g, 14.3 mmol) in Et_2O (15 mL) was added to PhMgBr (1.13 M in Et_2O, 14.0 mL, 15.8 mmol) at 0 °C over 5 min. After 30 min, the reaction mixture was quenched with iced 1 M HCl aq. (50 mL). After removal of the organic layer, the aqueous layer was extracted with Et_2O (20 mL). The combined organic layer was washed with sat. $NaHCO_3$ aq. (50 mL), dried over Na_2SO_4, and evaporated. Purification of the crude product by silica-gel column chromatography (hexane-AcOEt, 7:1) gave (*Z*)-5-benzyldimethylsilyl-1-phenyl-4-penten-1-ol (4.21 g, 13.6 mmol) in 95% yield.

Diethyl azodicarboxylate (DEAD, 1.94 g, 11.1 mmol) was added to a mixture of (*Z*)-5-benzyldimethylsilyl-1-phenyl-4-penten-1-ol (3.13 g, 10.1 mmol), THF (20 mL), phthalimide (1.62 g, 11.0 mmol), and PPh_3 (2.89 g, 11.0 mmol) at rt over 40 min.[4] After being stirred for 57 h, the reaction mixture was evaporated, rinsed with Et_2O-hexane (1:1, 20 mL), and filtered. After evaporation of the filtrate, the crude product was purified by silica-gel column chromatography (hexane-AcOEt, 5:1) to give *N*-((*Z*)-5-benzyldimethylsilyl-1-phenyl-4-pentenyl)phthalimide (2.59 g, 5.89 mmol) in 58% yield.

Under air, hydrazine monohydrate (326 mg, 6.51 mmol) was added to a solution of *N*-((*Z*)-5-benzyldimethylsilyl-1-phenyl-4-pentenyl)phthalimide (2.59 g, 5.89 mmol) in EtOH (20 mL) at rt.[4] After 12 h, the reaction mixture was diluted with 2 M NaOH aq. (50 mL) and evaporated for removal of EtOH. The concentrated aqueous mixture was extracted with Et_2O (2 x 20 mL). The extract was washed with 2 M NaOH aq. (50 mL), dried over Na_2SO_4, and evaporated. The crude product (1.23 g) was diluted with CH_2Cl_2 (15 mL) under N_2. Et_3N (1.15 mL, 8.25 mmol) and TsCl (834 mg, 4.37 mmol) was added to the solution at 0 °C. The mixture was warmed to rt, stirred for 24 h, and poured into sat. $NaHCO_3$ aq. (50 mL). After removal of the organic layer, the aqueous layer was extracted with CH_2Cl_2 (20 mL). The combined organic layer was dried over Na_2SO_4 and evaporated. Purification of the crude product by silica-gel column chromatography (hexane-AcOEt, 5:1) gave *N*-((*Z*)-5-benzyldimethylsilyl-1-phenyl-4-pentenyl)*p*-toluenesulfonamide (**7a**, 1.63 g, 3.52 mmol) in 60% yield. **7a**: ^{1}H NMR ($CDCl_3$) δ -0.07 (s, 6H), 1.56-1.92 (m, 4H), 2.01 (s, 2H), 2.34 (s, 3H), 4.22 (dt, *J* = 7.4, 7.0 Hz, 1H), 4.97 (d, *J* = 7.4 Hz, 1H), 5.41 (d, *J* = 14.0 Hz, 1H), 6.19 (dt, *J* = 14.0, 6.9 Hz, 1H), 6.91-7.01 (m, 4H), 7.05-7.22 (m, 8H), 7.53 (d, *J* = 8.3 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ -2.01 (CH_3), -1.97 (CH_3), 21.35 (CH_3), 26.45 (CH_2), 30.03 (CH_2), 37.32 (CH_2), 58.06 (CH), 123.88 (CH), 126.49 (CH x 2), 126.94 (CH x 2), 127.30 (CH), 127.89 (CH), 128.01 (CH x 2), 128.14 (CH x 2), 128.36 (CH x 2), 129.22 (CH x 2), 137.63 (C), 139.91 (C), 140.40 (C), 142.84 (C), 147.91 (CH); MS *m/z* (rel intensity) 372 (M^+ - $C_6H_5CH_2$, 16), 228 (33), 149 (36), 91 (100). Anal. Calcd for $C_{27}H_{33}NO_2SSi$: C, 69.94; H, 7.17; N, 3.02. Found: C, 69.91; H, 7.34; N, 2.95.

(*Z*)-*N*-Benzyl-5-benzyldimethylsilyl-4-penten-1-amine (1a): ^{1}H NMR ($CDCl_3$) δ 0.09 (s, 6H), 1.32 (br s, 1H), 1.55 (tt, *J* = 7.6, 7.3 Hz, 2H), 2.08 (tdd, *J* = 7.6, 7.3, 1.3 Hz, 2H), 2.15 (s, 2H), 2.61 (t, *J* = 7.3 Hz, 2H), 3.78 (s, 2H), 5.46 (dt, *J* = 14.2, 1.3 Hz, 1H), 6.33 (dt, *J* = 14.2, 7.3 Hz, 1H), 6.99-7.08 (m, 3H), 7.16-7.34 (m, 7H); ^{13}C NMR ($CDCl_3$) δ -1.63 (CH_3 x 2), 26.70 (CH_2), 30.03 (CH_2), 31.50

(CH_2), 49.08 (CH_2), 54.04 (CH_2), 123.95 (CH), 126.88 (CH), 127.13 (CH), 128.09 (CH x 4), 128.21 (CH x 2), 128.37 (CH x 2), 140.09 (C), 140.50 (C), 149.65 (CH).

***N*-((*Z*)-5-Benzyldimethylsilyl-4-pentenyl)acetamide (1b)**: IR (neat) 3285, 2965, 1647, 1595, 1554, 1250, 831, 697 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.10 (s, 6H), 1.51 (tt, *J* = 7.6, 7.3 Hz, 2H), 1.95 (s, 3H), 2.01 (tdd, *J* = 7.6, 7.3, 1.3 Hz, 2H), 2.15 (s, 2H), 3.18 (td, *J* = 7.3, 5.9 Hz, 2H), 5.36 (br s, 1H), 5.49 (dt, *J* = 14.2, 1.3 Hz, 1H), 6.30 (dt, *J* = 14.2, 7.3 Hz, 1H), 6.99-7.10 (m, 3H), 7.17-7.26 (m, 2H); ^{13}C NMR ($CDCl_3$) δ -1.67 (CH_3 x 2), 23.25 (CH_3), 26.63 (CH_2), 29.42 (CH_2), 30.93 (CH_2), 39.23 (CH_2), 123.95 (CH), 127.73 (CH), 128.09 (CH x 2), 128.19 (CH x 2), 139.98 (C), 148.75 (CH), 169.95 (C); MS *m/z* (rel intensity) 260 (M^+ - CH_3, 1.8), 184 (100), 149 (4.5), 110 (31), 69 (70), 43 (73).

***N*-((*Z*)-5-Benzyldimethylsilyl-4-pentenyl)trifluoroacetamide (1c)**: bp 90 °C (bath temp., 0.09 Torr). IR (neat) 3305, 2960, 1698, 1559, 1206, 1180, 833, 698 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.11 (s, 6H), 1.56 (tt, *J* = 7.6, 6.9 Hz, 2H), 2.01 (tdd, *J* = 7.6, 7.3, 1.3 Hz, 2H), 2.15 (s, 2H), 3.28 (dt, *J* = 6.9, 6.6 Hz, 2H), 5.53 (dt, *J* = 14.2, 1.3 Hz, 1H), 6.20 (br s, 1H), 6.28 (dt, *J* = 14.2, 7.3 Hz, 1H), 6.99-7.10 (m, 3H), 7.17-7.24 (m, 2H); ^{13}C NMR ($CDCl_3$) δ -1.67 (CH_3 x 2), 26.62 (CH_2), 28.68 (CH_2), 30.64 (CH_2), 36.59 (CH_2), 115.80 (C, q, J_{C-F} = 288.1 Hz), 124.01 (CH), 128.12 (CH x 2), 128.23 (CH x 2), 128.52 (CH), 139.89 (C), 147.91 (CH), 157.11 (C, q, J_{C-F} = 36.6 Hz); MS *m/z* (rel intensity) 314 (M^+ - CH_3, 0.8), 238 (100), 188 (24), 91 (25), 77 (98), 69 (60). Anal. Calcd for $C_{16}H_{22}F_3NOSi$: C, 58.33; H, 6.73; N, 4.25. Found: C, 58.14; H, 6.82; N, 4.35.

***N*-((*Z*)-5-Benzyldimethylsilyl-4-pentenyl)methanesulfonamide (1e)**: IR (neat) 3285, 2960, 1601, 1322, 1152, 832 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.12 (s, 6H), 1.57 (tt, *J* = 7.6, 7.3 Hz, 2H), 2.03 (tdd, *J* = 7.6, 7.3, 1.3 Hz, 2H), 2.15 (s, 2H), 2.93 (s, 3H), 3.06 (td, *J* = 7.3, 6.9 Hz, 2H), 4.17 (br s, 1H), 5.52 (dt, *J* = 14.2, 1.3 Hz, 1H), 6.28 (dt, *J* = 14.2, 7.3 Hz, 1H), 6.99-7.10 (m, 3H), 7.18-7.26 (m, 2H); ^{13}C NMR ($CDCl_3$) δ -1.63 (CH_3 x 2), 26.62 (CH_2), 29.99 (CH_2), 30.51 (CH_2), 40.27 (CH_3), 42.88 (CH_2), 124.01 (CH), 128.12 (CH x 2), 128.23 (CH x 2), 128.30 (CH), 139.93 (C), 148.07 (CH); MS *m/z* (rel intensity) 220 (M^+ - $C_6H_5CH_2$, 100), 152 (16), 91 (13), 75 (27), 59 (30).

***N*-((*Z*)-5-Benzyldimethylsilyl-4-pentenyl)trifluoromethanesulfonamide (1f)**: bp 110 °C (bath temp., 0.07 Torr). IR (neat) 3305, 2955, 1601, 1375, 1194, 1147, 833 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.13 (s, 6H), 1.49-1.61 (m, 2H), 1.96 (dt, *J* = 7.3, 6.9 Hz, 2H), 2.15 (s, 2H), 3.20 (t, *J* = 6.6 Hz, 2H), 4.56 (br s, 1H), 5.54 (d, *J* = 14.2 Hz, 1H), 6.25 (dt, *J* = 14.2, 7.3 Hz, 1H), 7.00-7.08 (m, 3H), 7.19-7.28 (m, 2H); ^{13}C NMR ($CDCl_3$) δ -1.69 (CH_3 x 2), 26.60 (CH_2), 29.89 (CH_2), 30.19 (CH_2), 44.06 (CH_2), 119.59 (C, q, J_{C-F} = 321.0 Hz), 123.99 (CH), 128.16 (CH x 2), 128.28 (CH x 2), 128.72 (CH), 139.98 (C), 147.51 (CH); MS *m/z* (rel intensity) 350 (M^+ - CH_3, 0.2), 296 (0.6), 274 (85), 149 (7.8), 114 (25), 91 (12), 77 (100). Anal. Calcd for $C_{15}H_{22}O_2NF_3SSi$: C, 49.29; H, 6.07; N, 3.83. Found: C, 49.23; H, 6.09; N, 3.85.

***t*-Butoxy *N*-((*Z*)-5-Benzyldimethylsilyl-4-pentenyl)carbamate (1g)**: bp 120 °C (bath temp., 0.043 Torr). IR (neat) 3355, 2970, 1695, 1507, 1249, 1171, 832 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.10 (s, 6H), 1.44 (s, 9H), 1.43-1.55 (m, 2H), 2.02 (td, *J* = 7.6, 7.3 Hz, 2H), 2.15 (s, 2H), 3.06 (q, *J* = 6.6 Hz,

2H), 4.44 (br s, 1H), 5.47 (d, *J* = 14.2 Hz, 1H), 6.30 (dt, *J* = 14.2, 7.3 Hz, 1H), 6.99-7.09 (m, 3H), 7.17-7.23 (m, 2H); ^{13}C NMR ($CDCl_3$) δ -1.67 (CH_3 x 2), 26.67 (CH_2), 28.39 (CH_3 x 3), 29.90 (CH_2), 30.84 (CH_2), 40.16 (CH_2), 79.01 (C), 123.95 (CH), 127.57 (CH), 128.07 (CH x 2), 128.19 (CH x 2), 140.00 (C), 148.91 (CH), 155.85 (C); MS *m/z* (rel intensity) 260 (M^+ - OC_4H_9, 1.1), 186 (100), 168 (22), 142 (41). Anal. Calcd for $C_{19}H_{31}NO_2Si$: C, 68.42; H, 9.37; N, 4.20. Found: C, 68.52; H, 9.44; N, 4.21.

***N*-((*Z*)-5-Dimethylphenylsilyl-4-pentenyl)*p*-toluenesulfonamide (1h)**: bp 195 °C (bath temp., 0.45 Torr). IR (neat) 3280, 2955, 1602, 1426, 1327, 1160, 815, 732, 703 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.34 (s, 6H), 1.38 (tt, *J* = 7.6, 6.9 Hz, 2H), 1.96 (tdd, *J* = 7.6, 7.3, 1.0 Hz, 2H), 2.43 (s, 3H), 2.76 (td, *J* = 6.9, 6.6 Hz, 2H), 4.00 (br s, 1H), 5.67 (dd, *J* = 13.9, 1.0 Hz, 1H), 6.27 (dt, *J* = 13.9, 7.3 Hz, 1H), 7.23-7.35 (m, 5H), 7.46-7.53 (m, 2H) 7.70 (d, *J* = 8.3 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ -1.08 (CH_3 x 2), 21.48 (CH_3), 29.22 (CH_2), 30.57 (CH_2), 42.64 (CH_2), 127.03 (CH x 2), 127.84 (CH x 2), 128.28 (CH), 128.95 (CH), 129,61 (CH x 2), 133.66 (CH x 2), 136.96 (C), 139.46 (C), 143.27 (C), 148.77 (CH); MS *m/z* (rel intensity) 358 (M^+ - CH_3, 26), 281 (12), 218 (73), 149 (36), 135 (91), 91 (100).

***N*-((*Z*)-6-Benzyldimethylsilyl-5-hexenyl)*p*-toluenesulfonamide (4a)**: IR (neat) 3280, 2955, 1600, 1328, 1160, 1095, 830 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.06 (s, 6H), 1.20-1.45 (m, 4H), 1.94 (q, *J* = 7.3 Hz, 2H), 2.12 (s, 2H), 2.42 (s, 3H), 2.90 (q, *J* = 6.6 Hz, 2H), 4.29 (br s, 1H), 5.43 (d, *J* = 14.2 Hz, 1H), 6.21 (dt, *J* = 14.2, 7.3 Hz, 1H), 6.97-7.08 (m, 3H), 7.15-7.22 (m, 2H), 7.30 (d, *J* = 8.2 Hz, 2H), 7.74 (d, *J* = 8.2 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ -1.67 (CH_3 x 2), 21.46 (CH_3), 26.40 (CH_2), 26.63 (CH_2), 29.08 (CH_2), 32.89 (CH_2), 43.06 (CH_2), 123.94 (CH), 127.04 (CH x 2), 127.35 (CH), 128.05 (CH x 2), 128.16 (CH x 2), 129.65 (CH x 2), 136.93 (C), 139.96 (C), 143.29 (C), 149.16 (CH); MS *m/z* (rel intensity) 386 (M^+ - CH_3, 1.4), 310 (100), 149 (31), 91 (89).

***N*-[(*Z*)-6-dimethyl(1-phenylethyl)silyl-5-hexenyl]*p*-toluenesulfonamide (4b)**: IR (neat) 3270, 1600, 1328, 1160 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.01 (s, 3H), 0.03 (s, 3H), 1.18-1.44 (m, 7H) including 1.35 (d, *J* = 7.7 Hz), 1.88 (tdd, *J* = 7.4, 7.4, 1.2 Hz, 2H), 2.21 (q, *J* = 7.7 Hz, 1H), 2.42 (s, 3H), 2.89 (td, *J* = 6.8, 6.5 Hz, 2H), 4.38 (br t, *J* = 6.5 Hz, 1H), 5.40 (dt, *J* = 14.0, 1.2 Hz, 1H), 6.22 (dt, *J* = 14.0, 7.4 Hz, 1H), 7.01-7.10 (m, 3H), 7.18-7.32 (m, 4H), 7.72-7.76 (m, 2H); ^{13}C NMR ($CDCl_3$) δ -3.11 (CH_3), -2.86 (CH_3), 14.90 (CH_3), 21.44 (CH_3), 26.40 (CH_2), 29.06 (CH_2), 29.51 (CH), 32.81 (CH_2), 43.04 (CH_2), 124.24 (CH), 126.49 (CH), 127.03 (CH x 2), 127.12 (CH x 2), 127.85 (CH x 2), 129.63 (CH x 2), 136.93 (C), 143.25 (C), 145.46 (C), 149.38 (CH); MS *m/z* (rel intensity) 400 (M^+ - CH_3, 7.9), 310 (73), 91 (100).

***N*-((*Z*)-5-Benzyldimethylsilyl-2-phenyl-4-pentenyl)*p*-toluenesulfonamide (7b)**: IR (neat) 3275, 1600, 1330, 1150 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.04 (s, 3H), 0.05 (s, 3H), 2.08 (s, 2H), 2.18-2.28 (m, 2H), 2.42 (s, 3H), 2.59-2.71 (m, 1H), 2.95 (ddd, *J* = 12.5, 9.5, 4.2 Hz, 1H), 3.27 (ddd, *J* = 12.5, 8.6, 5.3 Hz, 1H), 4.12 (br s, 1H), 5.47 (dd, *J* = 14.3, 1.2 Hz, 1H), 6.11 (ddd, *J* = 14.3, 7.4, 6.8 Hz, 1H), 6.88-7.08 (m, 6H), 7.14-7.31 (m, 6H), 7.64 (d, *J* = 8.3 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ -1.76 (CH_3), -1.67 (CH_3), 21.49 (CH_3), 26.53 (CH_2), 37.56 (CH_2), 45.72 (CH), 47.73 (CH_2), 124.03 (CH), 127.04 (CH x 2), 127.26 (CH), 127.66 (CH x 2), 128.12 (CH x 2), 128.19 (CH x 2), 128.90 (CH x 2), 129.22

(CH), 129.67 (CH x 2), 136.82 (C), 139.84 (C), 140.72 (C), 143.38 (C), 146.18 (CH); MS *m/z* (rel intensity) 372 (M^+ - $C_6H_5CH_2$, 16), 228 (23), 91 (100).

***N*-((*Z*)-5-Benzyldimethylsilyl-3-phenyl-4-pentenyl)*p*-toluenesulfonamide (7c)**: IR (neat) 3270, 1599, 1492, 1329, 1157 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.10 (s, 3H), 0.13 (s, 3H), 1.60-1.90 (m, 2H), 2.12 (s, 2H), 2.41 (s, 3H), 2.75-2.84 (m, 2H), 3.36 (dt, *J* = 10.4, 7.4 Hz, 1H), 4.17 (br s, 1H), 5.50 (d, *J* = 14.0 Hz, 1H), 6.39 (dd, *J* = 14.0, 10.4 Hz, 1H), 6.94-7.09 (m, 5H), 7.14-7.29 (m, 7H), 7.66 (d, *J* = 8.3 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ -1.51 (CH_3), -1.42 (CH_3), 21.44 (CH_3), 26.62 (CH_2), 36.50 (CH_2), 41.40 (CH_2), 46.60 (CH), 124.03 (CH), 126.47 (CH), 127.04 (CH x 4), 127.49 (CH), 128.14 (CH x 2), 128.23 (CH x 2), 128.70 (CH x 2), 129.63 (CH x 2), 136.77 (C), 139.75 (C), 143.02 (C), 143.31 (C), 151.28 (CH); MS *m/z* (rel intensity) 448 (M^+ - CH_3, 4.3), 372 (17), 281 (5.0), 91 (100).

Acid-Catalyzed Cyclization of Vinylsilanes 1, 4, and 7 (Typical Procedure). To a solution of **1d** (194 mg, 0.501 mmol) in $CHCl_3$ (2.5 mL) was added $TiCl_4$ (1.0 M solution in $CHCl_3$, 25 μL, 0.025 mmol) at rt under N_2. After being stirred for 3.3 h, the mixture was poured into sat. $NaHCO_3$ aq. (20 mL) and extracted with CH_2Cl_2 (2 x 10 mL). The extract was dried over Na_2SO_4 and evaporated. Purification of the crude product by silica-gel column chromatography (hexane-AcOEt, 10:1) gave 2-(benzyldimethylsilyl)methyl-1-*p*-toluenesulfonylpyrrolidine (**2d**, 180 mg, 0.464 mmol) in 93% yield. When TsOH•H_2O was used as a catalyst, it was charged into a reaction flask before introduction of N_2 gas, and a solution of **1d** in $CHCl_3$ was added to the flask under N_2. **2d**: IR (KBr) 2945, 1332, 1246, 1156 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.01 (s, 3H), 0.05 (s, 3H), 0.90 (dd, *J* = 14.5, 11.2 Hz, 1H), 1.33-1.54 (m, 3H), 1.57-1.82 (m, 2H), 2.13 (s, 2H), 2.43 (s, 3H), 3.21 (ddd, *J* = 10.6, 6.6, 6.6 Hz, 1H), 3.37 (ddd, *J* = 10.6, 6.6, 6.3 Hz, 1H), 3.66-3.77 (m, 1H), 6.99-7.08 (m, 3H), 7.10-7.25 (m, 2H), 7.30 (d, *J* = 8.1 Hz, 2H), 7.67 (d, *J* = 8.1 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ -2.95 (CH_3), -2.73 (CH_3), 21.40 (CH_3), 24.12 (CH_2), 24.42 (CH_2), 25.86 (CH_2), 33.62 (CH_2), 48.41 (CH_2), 58.19 (CH), 123.99 (CH), 127.31 (CH x 2), 128.09 (CH x 2), 128.12 (CH x 2), 129.51 (CH x 2), 135.06 (C), 139.66 (C), 143.04 (C); MS *m/z* (rel intensity) 372 (M^+ - CH_3, 1.7), 296 (100), 280 (2.0), 225 (1.4), 149 (10), 91 (25). Anal. Calcd for $C_{21}H_{29}NO_2SSi$: C, 65.07; H, 7.54; N, 3.61. Found: C, 64.97; H, 7.54; N, 3.67.

2-(Benzyldimethylsilyl)methyl-1-trifluoroacetylpyrrolidine (2c): IR (neat) 2955, 1687, 1599, 1491, 1453, 1238, 1202, 1139 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.02 (s, 3H), 0.07 (s, 3H), 0.66 (dd, *J* = 14.2, 11.2 Hz, 1H), 1.46 (dd, *J* = 14.2, 3.0 Hz, 1H), 1.52-1.56 (m, 1H), 1.83-2.08 (m, 3H), 2.14 (s, 2H), 3.55-3.62 (m, 2H), 4.20-4.30 (m, 1H), 6.96-7.12 (m, 3H), 7.18-7.25 (m, 2H); ^{13}C NMR ($CDCl_3$) δ -3.07 (CH_3), -2.93 (CH_3), 20.27 (CH_2), 24.42 (CH_2), 25.73 (CH_2), 31.39 (CH_2), 46.02 (CH_2), 56.80 (CH), 116.28 (C, q, J_{C-F} = 288.1 Hz), 124.03 (CH), 128.05 (CH x 2), 128.14 (CH x 2), 139.50 (C), 154.83 (C, q, J_{C-F} = 36.7 Hz); MS *m/z* (rel intensity) 314 (M^+ - CH_3, 2.9), 260 (0.7), 238 (100), 149 (5.4), 91 (13), 77 (37), 69 (61). Anal. Calcd for $C_{16}H_{22}F_3NOSi$: C, 58.33; H, 6.73; N, 4.25. Found: C, 58.33; H, 6.81; N, 4.27.

2-(Benzyldimethylsilyl)methyl-1-methanesulfonylpyrrolidine (2e): IR (neat) 2955, 1599, 1492, 1332, 1249, 1206, 1150, 833 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.02 (s, 3H), 0.05 (s, 3H), 0.87 (dd, *J* = 14.5,

11.2 Hz, 1H), 1.40 (dd, *J* = 14.5, 3.3 Hz, 1H), 1.50-1.59 (m, 1H), 1.75-2.03 (m, 3H), 2.13 (s, 2H), 2.78 (s, 3H), 3.34 (t, *J* = 6.6 Hz, 2H), 3.82 (dddd, *J* = 11.2, 8.3, 5.0, 3.3 Hz, 1H), 6.99-7.10 (m, 3H), 7.17-7.25 (m, 2H); ^{13}C NMR ($CDCl_3$) δ -2.84 (CH_3), -2.62 (CH_3), 24.15 (CH_2), 24.66 (CH_2), 25.90 (CH_2), 33.93 (CH_2), 35.98 (CH_3), 48.07 (CH_2), 58.26 (CH), 124.08 (CH), 128.12 (CH x 2), 128.18 (CH x 2), 139.64 (C); MS *m/z* (rel intensity) 296 (M^+ - CH_3, 1.5), 220 (100), 149 (5.1), 91 (8.1), 75 (20). Anal. Calcd for $C_{15}H_{25}NO_2SSi$: C, 57.84; H, 8.09; N, 4.50. Found: C, 57.79; H, 8.11; N, 4.54.

2-(Benzyldimethylsilyl)methyl-1-(trifluoromethanesulfonyl)pyrrolidine (2f): IR (neat) 2955, 1600, 1492, 1387, 1225, 1184, 835, 700 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.02 (s, 3H), 0.05 (s, 3H), 0.91 (dd, *J* = 14.2, 11.9 Hz, 1H), 1.41 (dd, *J* = 14.2, 3.3 Hz, 1H), 1.52-1.61 (m, 1H), 1.84-2.13 (m, 3H), 2.12 (s, 2H), 3.41-3.49 (m, 1H), 3.60 (ddd, *J* = 10.2, 6.6, 6.6 Hz, 1H), 4.07-4.18 (m, 1H), 6.98-7.11 (m, 3H), 7.19-7.26 (m, 2H); ^{13}C NMR ($CDCl_3$) δ -3.02 (CH_3), -2.77 (CH_3), 23.81 (CH_2), 24.61 (CH_2), 25.74 (CH_2), 33.73 (CH_2), 48.62 (CH_2), 60.35 (CH), 120.32 (C, q, $J_{C\text{-}F}$ = 324.7 Hz), 124.25 (CH), 128.08 (CH x 2), 128.28 (CH x 2), 139.22 (C); MS *m/z* (rel intensity) 350 (M^+ - CH_3, 1.0), 296 (0.3), 274 (100), 232 (0.9), 149 (11), 91 (14), 77 (58). Anal. Calcd for $C_{15}H_{22}O_2NF_3SSi$: C, 49.29; H, 6.07; N, 3.83. Found: C, 49.45; H, 6.09; N, 3.92.

2-[(Benzyldimethylsilyl)methyl]pyrrolidine (2g'). The title compound was obtained by deprotection of **2g** with 3 M HCl-MeOH (rt, 7 h). **2g'**: bp 90 °C (bath temp., 0.45 Torr). IR (neat) 3330, 2955, 1591, 1488, 1249, 836 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.007 (s, 3H), 0.011 (s, 3H), 0.71 (dd, *J* = 14.2, 8.9 Hz, 1H), 0.96 (dd, *J* = 14.2, 5.6 Hz, 1H), 1.04-1.19 (m, 1H), 1.61-1.93 (m, 4H), 2.10 (s, 2H), 2.74 (ddd, *J* = 10.7, 8.3, 7.1 Hz, 1H), 2.92-3.06 (m, 2H), 6.97-7.09 (m, 3H), 7.17-7.23 (m, 2H); ^{13}C NMR ($CDCl_3$) δ -2.93 (CH_3), -2.80 (CH_3), 22.50 (CH_2), 25.77 (CH_2), 26.04 (CH_2), 34.59 (CH_2), 46.18 (CH_2), 56.43 (CH), 123.86 (CH), 128.05 (CH x 4), 139.98 (C); MS *m/z* (rel intensity) 233 (M^+, 1.5), 218 (3.4), 142 (87), 121 (20), 91 (10), 86 (6.3), 70 (100). HRMS calcd for $C_{14}H_{23}NSi$: 233.1600, found 233.1596.

2-(Dimethylphenylsilyl)methyl-1-*p*-toluenesulfonylpyrrolidine (2h): ^{1}H NMR ($CDCl_3$) δ 0.33 (s, 3H), 0.35 (s, 3H), 1.11 (dd, *J* = 14.5, 11.9 Hz, 1H), 1.27-1.39 (m, 2H), 1.50-1.60 (m, 1H), 1.64-1.81 (m, 2H), 2.40 (s, 3H), 3.14 (ddd, *J* = 10.6, 6.6, 6.3 Hz, 1H), 3.36 (ddd, *J* = 10.6, 6.3, 6.3 Hz, 1H), 3.50-3.61 (m, 1H), 7.20-7.29 (m, 2H), 7.34-7.40 (m, 3H), 7.52-7.57 (m, 4H); ^{13}C NMR ($CDCl_3$) δ -2.36 (CH_3), -2.27 (CH_3), 21.46 (CH_3), 24.19 (CH_2), 25.31 (CH_2), 33.57 (CH_2), 48.74 (CH_2), 58.19 (CH), 127.43 (CH x 2), 127.86 (CH x 2), 129.03 (CH), 129.47 (CH x 2), 133.68 (CH x 2), 134.69 (C), 138.48 (C), 142.96 (C); MS *m/z* (rel intensity) 373 (M^+, 0.3), 358 (27), 296 (14), 224 (41), 135 (64), 91 (100). Anal. Calcd for $C_{20}H_{27}NO_2SSi$: C, 64.30; H, 7.28; N, 3.75. Found: C, 64.68; H, 7.45; N, 3.65.

2-(Benzyldimethylsilyl)methyl-1-*p*-toluenesulfonylpiperidine (5a): IR (neat) 2950, 1594, 1491, 1337, 1251, 1154, 1091 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.006 (s, 3H), 0.008 (s, 3H), 0.72 (dd, *J* = 14.7, 5.4 Hz, 1H), 1.00 (dd, *J* = 14.7, 10.1 Hz, 1H), 1.21-1.59 (m, 6H), 2.09 (s, 2H), 2.42 (s, 3H), 2.99 (ddd, *J* = 13.7, 12.8, 2.7 Hz, 1H), 3.71 (dd, *J* = 13.7, 3.7 Hz, 1H), 4.28-4.34 (m, 1H), 6.95-7.10 (m, 3H), 7.17-7.29 (m, 4H), 7.69 (d, *J* = 8.3 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ -3.14 (CH_3), -3.00 (CH_3), 16.19 (CH_2), 17.88 (CH_2), 21.46 (CH_3), 24.67 (CH_2), 25.75 (CH_2), 30.00 (CH_2), 40.00 (CH_2), 50.37 (CH), 123.99

(CH), 127.03 (CH x 2), 128.09 (CH x 2), 128.16 (CH x 2), 129.54 (CH x 2), 138.71 (C), 139.75 (C), 142.73 (C); MS *m/z* (rel intensity) 401 (M^+, 1.5), 386 (2.0), 310 (100), 281 (39), 207 (77), 91 (23).

2-[Dimethyl(1-phenylethyl)silyl]methyl-1-*p*-toluenesulfonylpiperidine (5b, 1:1 diastereomeric mixture): IR (neat) 2945, 1337, 1152, 1451, 1251 cm^{-1}; ^1H NMR ($CDCl_3$) δ -0.07 (s, 1.5H), -0.04 (s, 1.5H), -0.02 (s, 1.5H), 0.003 (s, 1.5H), 0.63 (dd, *J* = 14.5, 5.1 Hz, 0.5H), 0.65 (dd, *J* = 14.5, 5.1 Hz, 0.5H), 0.94 (dd, *J* = 14.5, 10.4 Hz, 1H), 1.23-1.58 (m, 9H) including 1.30 (d, *J* = 7.7 Hz) and 1.31 (d, *J* = 7.4 Hz), 2.16 (q, *J* = 7.4 Hz, 0.5H), 2.19 (q, *J* = 7.7 Hz, 0.5H), 2.42 (s, 3H), 2.89-3.03 (m, 1H), 3.67-3.74 (m, 1H), 4.23-4.28 (m, 1H), 6.96-7.11 (m, 3H), 7.18-7.29 (m, 4H), 7.64-7.71 (m, 2H); ^{13}C NMR ($CDCl_3$) δ -5.08 (CH_3 x 0.5), -4.53 (CH_3 x 0.5), -4.49 (CH_3 x 0.5), -4.44 (CH_3 x 0.5), 14.27 (CH_2 x 0.5), 14.54 (CH_2 x 0.5), 14.86 (CH_3), 17.74 (CH_2), 21.31 (CH_3), 24.58 (CH_2), 28.65 (CH), 29.78 (CH_2), 39.86 (CH_2), 50.30 (CH), 124.26 (CH), 126.86 (CH x 2), 126.92 (CH x 2), 127.89 (CH x 2), 129.43 (CH x 2), 138.62 (C), 142.61 (C), 145.19 (C x 0.5), 145.25 (C x 0.5); MS *m/z* (rel intensity) 400 (M^+ - CH_3, 0.9), 310 (100), 228 (4.4), 91 (48).

2-(Benzyldimethylsilyl)methyl-5-phenyl-1-*p*-toluenesulfonylpyrrolidine (8a, *cis*:*trans* = 62:38): ^1H NMR ($CDCl_3$) δ 0.01 (s, 1.86H), 0.04 (s, 1.14H), 0.05 (s, 1.86H), 0.10 (s, 1.14H), 0.92 (dd, *J* = 14.5, 12.5 Hz, 0.38H), 1.05 (dd, *J* = 14.5, 11.6 Hz, 0.62H), 1.35-1.58 (m, 1H), 1.62-1.87 (m, 3.24H), 2.15 (s, 1.24H), 2.16 (s, 0.76H), 2.09-2.32 (m, 0.38H), 2.35 (s, 1.14H), 2.43 (s, 1.86H), 2.39-2.52 (m, 0.38H), 3.90 (dddd, *J* = 11.6, 6.5, 6.5, 3.3 Hz, 0.62H), 4.27-4.36 (m, 0.38H), 4.77 (dd, *J* = 6.5, 5.5 Hz, 0.62H), 4.93 (dd, *J* = 8.3, 0.9 Hz, 0.38H), 6.98-7.15 (m, 6H), 7.20-7.41 (m, 6.76H), 7.67 (d, *J* = 8.3 Hz, 1.24H); ^{13}C NMR ($CDCl_3$) δ -3.00 (CH_3, major), -2.95 (CH_3, minor), -2.80 (CH_3, major), -2.66 (CH_3, minor), 21.30 (CH_3, minor), 21.42 (CH_3, major), 22.28 (CH_2, minor), 24.80 (CH_2, major), 25.77 (CH_2, major), 25.95 (CH_2, minor), 30.69 (CH_2, minor), 32.35 (CH_2, major), 33.37 (CH_2, minor), 34.23 (CH_2, major), 59.28 (CH, minor), 59.93 (CH, major), 62.97 (CH, minor), 64.15 (CH, major), 124.06 (CH), 126.20 (CH), 126.52 (CH), 126.70 (CH), 126.81 (CH), 126.90 (CH), 127.46 (CH), 127.92 (CH), 128.09 (CH), 128.16 (CH), 128.82 (CH), 129.49 (CH), 135.26 (C), 138.94 (C), 139.55 (C), 142.17 (C), 142.39 (C), 142.75 (C), 143.18 (C); MS *m/z* (rel intensity) 448 (M^+ - CH_3, 2.4), 372 (37), 228 (57), 149 (26), 91 (100).

2-(Benzyldimethylsilyl)methyl-4-phenyl-1-*p*-toluenesulfonylpyrrolidine (8b, *cis*:*trans* = 98:2): IR (neat) 1598, 1492, 1343, 1157 cm^{-1}; ^1H NMR ($CDCl_3$, only signals corresponding to the *cis* isomer are given) δ 0.02 (s, 3H), 0.06 (s, 3H), 1.04 (dd, *J* = 14.3, 11.6 Hz, 1H), 1.58 (ddd, *J* = 11.9, 11.9, 9.5 Hz, 1H), 1.77 (dd, *J* = 14.3, 3.0 Hz, 1H), 2.14 (s, 2H), 2.27 (ddd, *J* = 11.9, 6.5, 6.5 Hz, 1H), 2.46 (s, 3H), 2.50-2.64 (m, 1H), 3.31 (dd, *J* = 11.6, 11.3 Hz, 1H), 3.75-3.87 (m, 2H), 6.99-7.11 (m, 5H), 7.17-7.36 (m, 7H), 7.74 (d, *J* = 8.3 Hz, 2H); ^{13}C NMR ($CDCl_3$, only signals corresponding to the *cis* isomer are given) δ -2.78 (CH_3), -2.48 (CH_3), 21.49 (CH_3), 24.75 (CH_2), 25.99 (CH_2), 42.46 (CH_2), 43.29 (CH), 54.47 (CH_2), 59.35 (CH), 124.10 (CH), 126.88 (CH x 2), 126.99 (CH), 127.37 (CH x 2), 128.12 (CH x 2), 128.19 (CH x 2), 128.57 (CH x 2), 129.70 (CH x 2), 135.45 (C), 139.41 (C), 139.59 (C), 143.32 (C); MS *m/z* (rel intensity) 463 (M^+, 7.2), 372 (46), 228 (24), 149 (30), 91 (100).

***trans*-2-(Benzyldimethylsilyl)methyl-3-phenyl-1-*p*-toluenesulfonylpyrrolidine (8c)**: ^{1}H NMR ($CDCl_3$), -0.03 (s, 3H), -0.004 (s, 3H), 1.19 (dd, *J* = 14.8, 10.4 Hz, 1H), 1.43 (dd, *J* = 14.8, 2.7 Hz, 1H), 1.43-1.54 (m, 1H), 2.08 (s, 2H), 2.08-2.20 (m, 1H), 2.48 (s, 3H), 2.92 (ddd, *J* = 6.5, 6.5, 5.1 Hz, 1H), 3.39-3.56 (m, 2H), 3.88 (ddd, *J* = 10.4, 5.1, 2.7 Hz, 1H), 6.60-6.65 (m, 2H), 6.94-6.98 (m, 2H), 7.04-7.23 (m, 6H), 7.33 (d, *J* = 8.0 Hz, 2H), 7.74 (d, *J* = 8.0 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ -2.39 (CH_3), -2.35 (CH_3), 21.55 (CH_3), 24.17 (CH_2), 26.24 (CH_2), 33.05 (CH_2), 47.89 (CH_2), 52.45 (CH), 64.51 (CH), 124.03 (CH), 126.61 (CH), 126.92 (CH x 2), 127.53 (CH x 2), 128.18 (CH x 4), 128.54 (CH x 2), 129.69 (CH x 2), 135.33 (C), 139.84 (C), 142.03 (C), 143.34 (C).

Oxidative Cleavage of C–Si bond (Typical Procedure).[5] A mixture of **2d** (117 mg, 0.302 mmol), TBAF (1.0 M in THF, 1.10 mL, 1.10 mmol), methanol (1.0 mL), H_2O_2 (30% in water, 0.34 mL, 3.0 mmol), and $KHCO_3$ (62 mg, 0.62 mmol) was stirred at 40 °C for 6 h. The resultant mixture was poured into 10% $Na_2S_2O_3$ aq. (25 mL) and extracted with Et_2O (2 x 20 mL). The extract was washed with 10% $Na_2S_2O_3$ aq. (25 mL), dried over Na_2SO_4, and evaporated. Purification of the residual oil by silica-gel column chromatography (hexane-AcOEt, 1:1) gave 2-hydroxymethyl-1-*p*-toluenesulfonylpyrrolidine (**12a**, 75.3 mg, 0.295 mmol) in 98% yield. **12a**: IR (neat) 3505 (br), 1343, 1159 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.39-1.47 (m, 1H), 1.59-1.87 (m, 3H), 2.44 (s, 3H), 2.73-2.77 (m, 1H), 3.26 (ddd, *J* = 10.2, 6.9, 6.9 Hz, 1H), 3.45 (ddd, *J* = 10.2, 6.3, 5.9 Hz, 1H), 3.57-3.73 (m, 3H), 7.33 (d, *J* = 8.3 Hz, 2H), 7.73 (d, *J* = 8.3 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 21.37 (CH_3), 24.05 (CH_2), 28.61 (CH_2), 49.81 (CH_2), 61.60 (CH), 65.55 (CH_2), 127.44 (CH x 2), 129.67 (CH x 2), 133.69 (C), 143.67 (C); MS *m/z* (rel intensity) 237 (M^+ - H_2O, 0.5), 224 (66), 155 (44), 91 (100). Anal. Calcd for $C_{12}H_{17}NO_3S$: C, 56.45; H, 6.71; N, 5.49. Found: C, 56.47; H, 6.86; N, 5.34.

2-Hydroxymethyl-5-phenyl-1-*p*-toluenesulfonylpyrrolidine (12b, *cis*:*trans* = 86:14): ^{1}H NMR ($CDCl_3$) δ 1.63-2.05 (m, 3.72H), 2.23-2.39 (m, 0.14H), 2.34 (s, 0.42H), 2.41-2.57 (m, 0.14H), 2.44 (s, 2.58H), 2.71 (t, *J* = 6.5 Hz, 0.14H), 3.00 (dd, *J* = 7.1, 3.7 Hz, 0.86H), 3.68-4.06 (m, 3H), 4.78 (dd, *J* = 6.8, 5.6 Hz, 0.86H), 5.10 (dd, *J* = 8.3, 1.5 Hz, 0.14H), 6.91-7.28 (m, 0.98H), 7.30-7.42 (m, 6.30H), 7.72-7.56 (m, 1.72H); ^{13}C NMR ($CDCl_3$) δ 21.35 (CH_3), 21.49 (CH_3), 27.48 (CH_2), 28.50 (CH_2), 33.41 (CH_2), 33.71 (CH_2), 62.59 (CH), 63.49 (CH), 65.32 (CH), 65.54 (CH_2), 65.84 (CH_2), 126.11 (CH), 126.81 (CH), 126.95 (CH), 127.01 (CH), 127.17 (CH), 127.73 (CH), 128.05 (CH), 128.39 (CH), 129.00 (CH), 129.78 (CH), 134.09 (C), 137.41 (C), 141.69 (C), 142.08 (C), 142.73 (C), 143.90 (C).

2-Hydroxymethyl-4-phenyl-1-*p*-toluenesulfonylpyrrolidine (12c, *cis*:*trans* = 90:10): IR (neat) 3500 (br), 1594, 1494, 1340 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.70-1.81 (m, 0.10H), 1.89 (ddd, *J* = 12.2, 11.9, 9.2 Hz, 0.90H), 2.10-2.18 (m, 0.10H), 2.26 (ddd, *J* = 12.2, 6.9, 6.9 Hz, 0.90H), 2.45 (s, 0.30H), 2.47 (s, 2.70H), 2.50-2.71 (m, 1H) including 2.57 (dddd, *J* = 11.9, 11.6, 6.9, 6.9 Hz, 0.90H), 2.98-3.03 (m, 1H), 3.37 (dd, *J* = 11.6, 11.6 Hz, 0.90H), 3.48-3.57 (m, 0.10H), 3.69-3.95 (m, 4H), 6.99-7.10 (m, 2H), 7.17-7.40 (m, 5H), 7.72-7.82 (m, 2H); ^{13}C NMR ($CDCl_3$) for the *cis*-isomer δ 21.51 (CH_3), 36.07 (CH_2), 42.66 (CH), 55.89 (CH_2), 62.70 (CH), 65.48 (CH_2), 126.86 (CH x 2), 127.08 (CH),

127.44 (CH x 2), 128.57 (CH x 2), 129.94 (CH x 2), 134.36 (C), 138.90 (C), 143.99 (C). Anal. Calcd for $C_{18}H_{21}NO_3S$: C, 65.23; H, 6.39; N, 4.23. Found: C, 65.07; H, 6.16; N, 4.27.

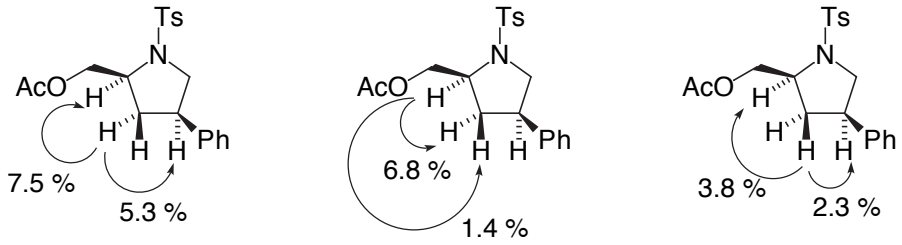
***trans*-2-Hydroxymethyl-3-phenyl-1-*p*-toluenesulfonylpyrrolidine (*trans*-12d)**: ^{1}H NMR ($CDCl_3$) δ 1.48 (dddd, *J* = 12.5, 10.4, 10.4, 7.7 Hz, 1H), 2.02 (dddd, *J* = 12.5, 6.2, 6.2, 3.0 Hz, 1H), 2.49 (s, 3H), 2.84 (dd, *J* = 7.1, 5.9 Hz, 1H), 3.18 (ddd, *J* = 10.4, 7.7, 6.2 Hz, 1H), 3.45-3.56 (m, 2H), 3.64 (ddd, *J* = 11.6, 5.9, 5.0 Hz, 1H), 3.74 (ddd, *J* = 11.6, 7.7, 3.0 Hz, 1H), 3.87 (ddd, *J* = 11.6, 7.1, 3.0 Hz, 1H), 6.74-6.81 (m, 2H), 7.11-7.20 (m, 3H), 7.38 (d, *J* = 7.7 Hz, 2H), 7.76-7.81 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 21.58 (CH_3), 32.83 (CH_2), 47.86 (CH), 50.00 (CH_2), 63.84 (CH_2), 69.08 (CH), 127.07 (CH), 127.29 (CH x 2), 127.65 (CH x 2), 128.69 (CH x 2), 129.93 (CH x 2), 134.36 (C), 140.32 (C), 144.06 (C).

2-Hydroxymethyl-1-*p*-toluenesulfonylpiperidine (12e): ^{1}H NMR ($CDCl_3$) δ 1.16-1.61 (m, 6H), 2.01 (br s, 1H), 2.42 (s, 3H), 3.09 (ddd, *J* = 14.3, 12.2, 2.7 Hz, 1H), 3.55 (dd, *J* = 11.1, 5.5 Hz, 1H), 3.76-3.85 (m, 2H), 3.87-4.03 (m, 1H), 7.29 (d, *J* = 8.3 Hz, 2H), 7.74 (d, *J* = 8.3 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 18.94 (CH_2), 21.37 (CH_3), 24.06 (CH_2), 24.57 (CH_2), 41.28 (CH_2), 54.49 (CH), 60.45 (CH_2), 126.86 (CH x 2), 129.63 (CH x 2), 138.04 (C), 143.11 (C).

Stereochemical Assignment. Alcohol **12b** derived from **8a** (*dr* = 86:14) was converted to 5-methyl-2-phenyl-1-*p*-toluenesulfonylpyrrolidine by tosylation (TsCl, Et_3N, CH_2Cl_2, 96%) and reduction (LAH, *i*-Pr_2O, 86%). The major isomer of the dehydroxylated pyrrolidine was assigned to *cis*-isomer by comparison with both isomers of 5-methyl-2-phenyl-1-(*p*-nitrobenzenesulfonyl)-pyrrolidine in ^{1}H NMR data.[6] Thus, the major isomer of **8a** was determined to have *cis*-configuration. 5-Methyl-2-phenyl-1-*p*-toluenesulfonylpyrrolidine (*cis*:*trans* = 85:15): ^{1}H NMR ($CDCl_3$) δ 1.38 (d, *J* = 6.2 Hz, 0.45H), 1.47 (d, *J* = 6.2 Hz, 2.55H), 1.43-1.77 (m, 2H), 1.83-1.94 (m, 1.70H), 2.19-2.34 (m, 0.15H), 2.34 (s, 0.45H), 2.41-2.54 (m, 0.15H), 2.42 (s, 2.55H), 3.92 (ddq, *J* = 6.5, 6.5, 6.2 Hz, 0.85H), 4.29 (dq, *J* = 6.5, 6.2 Hz, 0.15H), 4.72 (dd, *J* = 6.8, 6.2 Hz, 0.85H), 4.98 (br d, *J* = 8.0 Hz, 0.15H), 7.00-7.41 (m, 7.30H), 7.69 (d, *J* = 8.3 Hz, 1.70H); ^{13}C NMR ($CDCl_3$) for the *cis*-isomer δ 21.33 (CH_3), 22.59 (CH_3), 31.95 (CH_2), 34.22 (CH_2), 57.70 (CH), 64.78 (CH), 126.09 (CH x 2), 126.76 (CH), 127.42 (CH x 2), 128.10 (CH x 2), 129.43 (CH x 2), 134.97 (C), 142.77 (C), 143.16 (C), for the *trans*-isomer δ 21.22 (CH_3), 21.48 (CH_3), 31.20 (CH_2), 33.08 (CH_2), 57.09 (CH), 63.54 (CH), 126.34 (CH x 2), 126.63 (CH x 2), 127.87 (CH x 2), 128.21 (CH), 128.84 (CH x 2), 138.76 (C), 142.23 (C), 142.43 (C).

Alcohol **12c** derived from **8b** (*dr* = 89:11) was acetylated with Ac_2O and pyridine. The stereochemical assignment of **8b** was based on NOE experiments of the major isomer of the acetate. 2-Acetoxymethyl-4-phenyl-1-*p*-toluenesulfonylpyrrolidine (*cis*:*trans* = 89:11): ^{1}H NMR ($CDCl_3$) δ 1.73 (ddd, *J* = 12.3, 12.3, 8.9 Hz, 0.11H), 1.85 (ddd, *J* = 12.8, 11.8, 8.6 Hz, 0.89H), 2.05 (s, 2.67H), 2.09 (s, 0.33H), 2.29-2.41 (m, 1H) including 2.36 (dddd, *J* = 12.8, 7.1, 7.1, 1.2 Hz, 0.89H), 2.45 (s, 3H), 2.66 (dddd, *J* = 11.8, 11.3, 7.1, 7.1 Hz, 0.89H), 3.02 (dd, *J* = 10.7, 9.2 Hz, 0.11H), 3.31 (dd, *J* = 11.6, 11.3 Hz, 0.89H), 3.42-3.51 (m, 0.11H), 3.72-3.94 (m, 1H) including 3.90 (ddd, *J* = 11.6, 7.1, 1.2 Hz, 0.89H), 4.00-4.13 (m, 1H) including 4.05 (dddd, *J* = 8.6, 7.1, 6.2, 4.5 Hz, 0.89H), 4.20-4.33 (m,

1.11H) including 4.27 (dd, *J* = 11.0, 6.2 Hz, 0.89H), 4.38 (dd, *J* = 11.0, 4.5 Hz, 0.89H), 7.01-7.10 (m, 2H), 7.18-7.37 (m, 5H), 7.76-7.80 (m, 2H); ^{13}C NMR ($CDCl_3$) for the *cis*-isomer δ 20.83 (CH_3), 21.55 (CH_3), 36.73 (CH_2), 43.04 (CH), 55.19 (CH_2), 58.46 (CH), 66.70 (CH_2), 126.92 (CH x 2), 127.15 (CH), 127.46 (CH x 2), 128.66 (CH x 2), 129.88 (CH x 2), 135.18 (C), 139.03 (C), 143.79 (C), 170.75 (C), distinguishable signals for the *trans*-isomer δ 20.90 (CH_3), 35.37 (CH_2), 41.75 (CH), 55.08 (CH_2), 57.92 (CH), 66.15 (CH), 127.69 (CH), 129.79 (CH).



Alcohol **12d** derived from **8c** (single isomer) was converted to 2-methyl-3-phenylpyrrolidine, a known compound,[7] by tosylation (TsCl, Et_3N, CH_2Cl_2, 75%), reduction (LAH, *i*-Pr_2O, 96%), and deprotection (PhOH, HBr, H_2O, 29%). The ^{1}H NMR spectrum of the product was consistent with that of the *trans*-isomer. Therefore, the relative configuration of **8c** was proved to be *trans*. 2-Methyl-3-phenylpyrrolidine (*trans*-isomer): ^{1}H NMR ($CDCl_3$) δ 1.12 (d, *J* = 5.9 Hz, 3H), 1.43 (br s, 1H), 1.97 (dddd, *J* = 12.8, 9.2, 8.6, 6.8 Hz, 1H), 2.31 (dddd, *J* = 12.8, 8.6, 7.7, 5.6 Hz, 1H), 2.57 (ddd, *J* = 9.2, 9.2, 8.6 Hz, 1H), 3.04 (dq, *J* = 9.2, 5.9 Hz, 1H), 3.10-3.20 (m, 2H), 7.17-7.35 (m, 5H); ^{13}C NMR ($CDCl_3$) δ 19.10 (CH_3), 35.65 (CH_2), 46.16 (CH_2), 54.25 (CH), 63.00 (CH), 126.29 (CH), 127.60 (CH x 2), 128.48 (CH x 2), 143.34 (C); MS *m/z* (rel intensity) 161 (M^+, 4.1), 77 (57), 57 (100). HRMS calcd for $C_{11}H_{15}N$: 161.1206, found 161.1209.

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