Use of Pentamethyldisiloxane in the Palladium–Catalyzed Cyclization/Hydrosilylation of Functionalized Dienes

Tao Pei and Ross A. Widenhoefer*

Duke University

P. M. Gross Chemical Laboratory

Durham, NC 27708–0346

Supporting Information

Experimental procedures and analytical and spectroscopic data for new compounds (12 pages).

Experimental

General Methods. All reactions were performed under an atmosphere of nitrogen employing standard Schlenk techniques. NMR were obtained on a Varian spectrometer operating at 400 MHz for ^{1}H and 100 MHz for ^{13}C in $CDCl_3$ unless otherwise noted. IR spectra were obtained on a Bomen MB-100 FT IR spectrometer. Gas chromatography was performed on a Hewlett-Packard 5890 gas chromatograph equipped with a 25 m polydimethylsiloxane capillary column. Flash chromatography was performed employing 200-400 mesh silica gel (EM) eluting with mixtures of hexane and ethyl acetate. Elemental analyses were performed by E+R Microanalytical Laboratories (Parsippany, NJ). CH_2Cl_2 and 1,2-dichloroethane (DCE) were distilled from CaH_2 under nitrogen. Dimethyl diallylmalonate (Lancaster) and pentamethyldisiloxane (Gelest) were used as received. The syntheses of the remaining dienes have been reported.

***trans*-1,1-Dicarbomethoxy-3-(1,1,2,2,2-pentamethyldisiloxyl)methyl-4-methylcyclopentane (3).** Dimethyl diallylmalonate (1.06 g, 5.0 mmol) and pentamethyldisiloxane (2.15 g, 15.0 mmol) were added sequentially to a solution of (phen)PdMeCl (84 mg, 0.25 mmol) and $NaBAr_4$ (259 mg, 0.25 mmol) in DCE (50 mL) at 0 °C and the resulting pale yellow solution was stirred for 10 min to form a dark brown solution. Solvent and excess silane were evaporated under vacuum and the brown residue was dissolved in hexane/EtOAc (24:1) and filtered through a plug of silica gel to give *trans*-1,1-dicarbomethoxy-4-methyl-3-[(pentamethyldisiloxy)methyl] cyclopentane (**3**) (1.76 g, 98%) as a pale yellow oil which was 95% pure and subjected to oxidation without further purification. ^{1}H NMR: δ 3.70 (s, 6 H), 2.58 (dd, *J*= 6.2, 13.4 Hz, 1 H), 2.49 (dd, *J* = 6.2, 13.4 Hz, 1 H), 1.68 (m, 2 H), 1.45 (m, 2 H), 0.95 (d, *J* = 6.0 Hz, 3 H), 0.87 (dd, *J* = 2.4, 14.8 Hz, 1 H), 0.31 (dd, *J* = 10.8, 14.8 Hz, 1 H), 0.08 (s, 6 H), 0.06 (s, 9 H). $^{13}C\{^{1}H\}$ NMR: δ 173.8, 58.5, 52.9, 43.7, 43.2, 43.0, 42.5, 22.2, 17.5, 2.3, 1.5. HRMS(EI) calcd (found) for $C_{15}H_{29}O_5Si_2$ ($M^+–CH_3$): 345.1554 (345.1555).

The remaining silylated carbocycles were synthesized by procedures analogous to that employed in the synthesis of **3**.

***trans*-1,1-Dicarbomethoxy-3-hydroxymethyl-4-methylcyclopentane (4).** A suspension of diene **3** (0.63 g, 1.75 mmol), KF (0.81 g, 14.0 mmol), and peracetic acid (32% wt in acetic acid, 5.0 mL, 21.0 mmol) in DMF (14 mL) was stirred at room temperature for 48 h. Water (20 mL) was added and the resulting suspension was extracted with ethyl acetate. The combined organic extracts were washed with 10 % Na_2SO_3 and saturated $NaHCO_3$, dried (Na_2SO_4), concentrated under vacuum, and chromatographed to give **4** (0.37 g, 92%) as a colorless oil. ^{1}H NMR: δ 3.71 (s, 6 H), 3.69 (dd, *J* = 4.0, 10.8 Hz, 1 H), 3.52 (dd, *J* = 6.4, 10.8 Hz, 1 H), 2.48 (m, 2 H), 2.08 (dd, *J* = 9.0, 13.8 Hz, 1 H), 1.80 (m, 2 H), 1.78 (m, 1 H), 1.74 (s, 1 H), 1.02 (d, *J* = 5.6 Hz, 3 H). ^{13}C{^{1}H} NMR: δ 173.6, 173.3, 64.5, 58.8, 52.9, 49.0, 43.0, 37.8, 36.2, 18.6. IR (neat, cm^{-1}): 3412, 2954, 2873, 1723, 1436, 1379, 1253, 1206, 1116, 1017, 959, 948, 896, 705. Anal. calcd (found) for $C_{11}H_{18}O_5$: C, 57.38 (57.02); H, 7.88 (8.06).

The remaining alcohols were synthesized by procedures analogous to that employed in the synthes1s of **4**.

***trans*-1,1-Dicarbobenzoxy-3-(1,1,2,2,2-pentamethyldisiloxyl)methyl-4-methylcyclopentane (Table 1, entry 1, 98% pure).** ^{1}H NMR: δ 7.26 (m, 4 H), 7.22 (m, 6 H), 5.07 (s, 4 H), 2.59 (dd, *J* = 6.4, 13.6 Hz, 1 H), 2.49 (dd, *J* = 6.4, 13.4, Hz, 1 H), 1.70 (m, 2 H), 1.43 (m, 2 H), 0.92 (d, *J* = 6.0 Hz, 3 H), 0.80 (m, 1 H), 0.28 (dd, *J* = 10.4, 14.2 Hz, 1 H), 0.02 (s, 6 H), 0.01 (s, 9 H). ^{13}C{^{1}H}NMR: δ 172.9, 136.0, 128.8, 128.4, 128.3, 67.3, 58.7, 43.7, 43.1, 43.0, 42.4, 22.3, 17.5, 2.3, 1.4. HRMS(EI) calcd (found) for $C_{27}H_{37}O_5Si_2$ (M^+–CH_3): 497.2180 (497.2173).

***trans*-1,1-Dicarbobenzoxy-3-hydroxymethyl-4-methylcyclopentane (Table 1, entry 1).** ^{1}H NMR: δ 7.28 (m, 6 H), 7.22 (m, 4 H), 5.07 (s, 4 H), 3.64 (dd, *J* = 4.0, 10.8 Hz, 1 H), 3.48 (dd, *J* = 6.0, 10.8 Hz, 1 H), 2.49 (m, 2 H), 2.09 (dd, *J*

= 8.2, 13.8 Hz, 1 H), 1.80 (m, 2 H), 1.76 (m, 1 H), 1.55 (s, 1 H), 0.98 (d, *J* = 5.6 Hz, 3 H). $^{13}C\{^{1}H\}$NMR: δ 172.8, 172.5, 135.8, 128.8, 128.6, 128.4, 128.3, 67.5, 67.4, 64.7, 59.2, 49.1, 43.1, 37.7, 36.2, 18.7. IR (neat, cm^{-1}): 3425, 3089, 3064, 3032, 2953, 2872, 1954, 1836, 1729, 1497, 1454, 1376, 1258, 1174, 1144, 1112, 1003, 958. Anal. calcd (found) for $C_{23}H_{26}O_5$: C, 72.23 (71.92); H, 6.85 (7.09).

***trans*-1,1-Bis(methoxymethyl)-3-(1,1,2,2,2-pentamethyldisiloxyl)methyl-4-methylcyclopentane (Table 1, entry 2, 94% pure).** ^{1}H NMR: δ 3.33 (s, 6 H), 3.18 (m, 4 H), 1.79 (dd, *J* = 6.6, 13.0 Hz, 1 H), 1.70 (dd, *J* = 6.6, 13.0 Hz, 1 H), 1.36 (m, 2 H), 0.91 (d, *J* = 5.6 Hz, 3 H), 0.87 (dd, *J* = 10.6, 14.6 Hz, 1 H), 0.24 (dd, *J* = 6.6, 14.6 Hz, 1 H), 0.06 (s, 6 H), 0.05 (s, 9 H). $^{13}C\{^{1}H\}$ NMR: δ 78.4, 59.6, 45.6, 43.4, 42.7, 42.1, 41.6, 22.6, 18.0, 2.3, 1.8. HRMS(EI) calcd (found) for $C_{16}H_{36}O_3Si_2$ (M^+): 332.2203 (332.2213).

***trans*-1,1-Dimethoxymethyl-3-hydroxymethyl-4-methylcyclopentane (Table 1, entry 2).** ^{1}H NMR: δ 3.67 (dd, *J* = 4.0, 10.8 Hz, 1 H), 3.46 (dd, *J* = 6.4, 10.4 Hz, 1 H), 3.30 (d, *J* = 1.2 Hz, 6 H), 3.19 (d, *J* = 3.4 Hz, 4 H), 1.95 (s, 1 H), 1.75 (m, 2 H), 1.64 (m, 2 H), 1.22 (dd, *J* = 10.0, 13.2 Hz, 1 H), 1.05 (dd, *J* = 10.0, 12.6 Hz, 1 H), 1.96 (d, *J* = 6.0 Hz, 3 H). $^{13}C\{^{1}H\}$ NMR: δ 78.3, 78.1, 65.7, 59.5, 49.2, 45.8, 42.3, 36.8, 36.3, 19.0. IR (neat, cm^{-1}): 3409, 2948, 2927, 2824, 1474, 1457, 1448, 1376, 1198, 1109, 1008, 962. Anal. calcd (found) for $C_{11}H_{22}O_3$: C, 65.31 (64.89); H, 10.96 (10.68).

***trans*-1,1-Bis(benzoxymethyl)-3-(1,1,2,2,2-pentamethyldisiloxyl)methyl-4-methylcyclopentane (Table 1, entry 3, 95% pure).** ^{1}H NMR: δ 7.31 (m, 10 H), 4.52 (s, 4 H), 3.34 (d, *J*= 3.2 Hz, 4 H), 1.88 (dd, *J* = 6.6, 13.2 Hz, 1 H), 1.78 (dd, *J* = 6.6, 13.2 Hz, 1 H), 1.35 (m, 2 H), 1.01 (m, 2 H), 0.91 (d, *J* = 5.8 Hz, 3 H), 0.85 (m, 1 H), 0.21 (m, 1 H), 0.06 (s, 9 H), 0.05 (s, 6 H). $^{13}C\{^{1}H\}$ NMR: δ 139.4, 128.6, 127.7, 127.6, 75.8, 73.5, 45.8, 43.4, 42.7, 42.3, 41.7,

22.7, 18.0, 2.4, 1.7. HRMS(EI) calcd (found) for $C_{28}H_{44}O_3Si_2$ (M^+): 484.2829 (484.2830).

***trans*-1,1-Dibenzoxymethyl-3-hydroxymethyl-4-methylcyclopentane (Table 1, entry 3).** ^{1}H NMR: δ 7.27 (m, 10 H), 4.48 (d, *J* = 1.6 Hz, 4 H), 3.66 (dd, *J* = 4.2, 10.6 Hz, 1 H), 3.45 (dd, *J* = 6.4, 10.4 Hz, 1 H), 3.33 (s, 4 H), 1.83 (m, 2 H), 1.63 (m, 2 H), 1.46 (s, 1 H), 1.26 (dd, *J* = 10.2, 13.2 Hz, 1 H), 1.10 (dd, *J* = 10.6, 13.0 Hz, 1 H), 0.95 (d, *J* = 5.6 Hz, 3 H). ^{13}C{^{1}H}NMR: δ 139.2, 128.6, 127.7, 75.7, 75.4, 73.5, 65.9, 49.3, 46.1, 42.4, 36.9, 36.4, 19.1. IR (neat, cm^{-1}): 3403, 3086, 3062, 3028, 2922, 2862, 1949, 1870, 1803, 1718, 1601, 1471, 1495, 1452, 1361, 1271, 1095, 1027, 1009, 802, 712. Anal. calcd (found) for $C_{23}H_{30}O_3$: C, 77.93 (77.76); H, 8.53 (8.27).

***trans*-1,1-Bis(acetoxymethyl)-3-(1,1,2,2,2-pentamethyldisiloxyl)methyl-4-methylcyclopentane (Table 1, entry 4, 82% pure).** ^{1}H NMR: δ 3.92 (s, 4 H), 2.05 (s, 6 H), 1.85 (dd, *J* = 6.6, 13.4 Hz, 1 H), 1.72 (dd, *J* = 6.6, 13.4 Hz, 1 H), 1.40 (m, 2 H), 1.03 (m, 2 H), 0.93 (d, *J* = 6.0 Hz, 3 H), 0.86 (dd, *J* = 2.2, 14.6 Hz, 1 H), 0.25 (dd, *J* = 11.0, 14.6 Hz, 1 H), 0.06 (s, 6 H), 0.05 (s, 9 H). ^{13}C{^{1}H}NMR: δ 171.6, 68.7, 43.5, 43.3, 42.8, 41.7, 41.1, 22.5, 21.2, 17.8, 2.3, 1.6. HRMS(EI) calcd (found) for $C_{17}H_{33}O_5Si_2$ $(M–CH_3)^+$: 373.1867 (373.1864).

***trans*-1,1-Diacetoxymethyl-3-hydroxymethyl-4-methylcyclopentane (Table 1, entry 4).** ^{1}H NMR: δ 3.95 (s, 4 H), 3.72 (dd, *J* = 4.4, 10.8 Hz, 1 H), 3.50 (dd, *J* = 6.4, 10.8 Hz, 1 H), 2.05 (s, 6 H), 1.80 (m, 2 H), 1.70 (m, 2 H), 1.30 (dd, *J* = 10.2, 13.4 Hz, 1 H), 1.12 (dd, *J* = 10.2, 12.6 Hz, 1 H), 1.00 (d, *J* = 6.0 Hz, 3 H). ^{13}C{^{1}H}NMR: δ 171.6, 68.5, 68.1, 65,3, 49.0, 44.0, 41.8, 36.6, 36.1, 21.2, 18.9. IR (neat, cm^{-1}): 3427, 2951, 2873, 1727, 1494, 1451, 1435, 1262, 1200, 1170, 1100, 1035, 912. HRMS(CI) calcd (found) for $C_{13}H_{23}O_5$ (MH^+): 259.1545 (259.1544).

***trans*-1,1-Bis(trimethylacetoxymethyl)-3-(1,1,2,2,2-pentamethyldisiloxyl) methyl-4-methylcyclopentane (Table 1, entry 5, 90% pure).** ^{1}H NMR: δ 3.90 (s, 4 H), 1.87 (d, *J* = 6.6, 13.4 Hz, 1 H), 1.74 (dd, *J* = 6.6, 13.4 Hz, 1 H), 1.42 (m, 2 H), 1.19 (1s, 18 H), 1.09 (m, 2 H), 0.94 (d, *J* = 6.0 Hz, 3 H), 0.87 (m, 1 H), 0.26 (dd, *J* = 6.6, 14.6 Hz, 1 H), 0.06 (s, 6H), 0.05 (s, 9 H). ^{13}C{^{1}H} NMR: δ 178.8, 68.5, 44.0, 43.4, 42.7, 41.8, 41.1, 39.3, 27.5, 22.7, 17.9, 2.4, 1.5. HRMS (EI) calcd (found) for $C_{23}H_{45}O_5Si_2$ (M^+–CH_3): 457.2806 (457.2815).

***trans*-1,1-Di(trimethyl)acetoxymethyl-3-hydroxymethyl-4-methylcyclopentane (Table 1, entry 5).** ^{1}H NMR: δ 3.93 (s, 4 H), 3.74 (dd, *J* = 3.8, 10.6 Hz, 1 H), 3.51 (dd, *J* = 6.2, 10.6 Hz, 1 H), 1.83 (m, 2 H), 1.52 (m, 2 H), 1.50 (s, 1 H), 1.32 (dd, *J* = 10.2, 13.4 Hz, 1 H), 1.19 (s, 18 H), 1.14 (m, 1 H), 1.01 (d, *J* = 6.0 Hz, 3 H). ^{13}C{^{1}H} NMR: δ 178.8, 68.3, 68.0, 65.3, 49.1, 44.4, 41.8, 39.3, 36.6, 36.1, 27.5, 18.9. IR (neat, cm^{-1}): 3444, 2957, 2870, 1730, 1480, 1397, 1364, 1283, 1152, 1028. Anal. calcd (found) for $C_{19}H_{34}O_5$: C, 66.63 (66.19); H, 10.01 (9.88).

***trans*-1,1-Dicarbomethoxy-3-(1,1,2,2,2-pentamethyldisiloxyl)methyl-4-ethylcyclopentane (Table 1, entry 6, 86% pure).** ^{1}H NMR: δ 3.71 (s, 6 H), 2.57 (dd, *J* = 6.8, 13.2 Hz, 1 H), 2.51 (dd, *J* = 7.4, 13.8 Hz, 1 H), 1.70 (dd, *J* = 11.0, 13.4 Hz, 2 H), 1.63 (m, 2 H), 1.54 (m, 1 H), 1.35 (m, 1 H), 1.04 (m, 1 H), 0.89 (t, *J* = 7.4 Hz, 3 H), 0.32 (dd, *J* = 11.0, 14.6 Hz, 1 H), 0.06 (s, 6 H), 0.05 (s, 9 H). ^{13}C{^{1}H}NMR: δ 173.8, 58.5, 52.9, 50.5, 42.9, 41.2, 39.8, 26.0, 22.6, 12.7, 2.3, 1.5. HRMS(EI) calcd (found) for $C_{17}H_{34}O_5Si_2$ (M^+): 374.1945 (374.1933).

***trans*-1,1-Dicarbomethoxy-3-hydroxymethyl-4-ethylcyclopentane (Table 1, entry 6).** ^{1}H NMR: δ 3.71 (d, *J* = 2.8 Hz, 6 H), 3.68 (dd, *J* = 4.4, 10.6 Hz, 1 H), 3.50 (dd, *J* = 6.6, 10.6 Hz, 1 H), 2.51 (dd, *J* = 7.2, 13.4 Hz, 1 H), 2.45 (dd, *J* = 8.8, 13.6 Hz, 1 H), 2.11 (dd, *J* = 8.4, 13.6 Hz, 1 H), 1.84 (m, 2 H), 1.80 (s, 1 H), 1.67 (m, 1 H), 1.57 (m, 1 H), 1.20 (m, 1 H), 0.89 (t, *J* = 7.6 Hz, 3 H). ^{13}C{^{1}H} NMR:

δ 173.5, 173.2, 64.9, 58.9, 53.0, 52.9, 47.2, 42.9, 40.4, 37.5, 27.2, 12.7. IR (neat, cm^{-1}): 3434, 2956, 2927, 2875, 1730, 1459, 1434, 1379, 1252, 1199, 1173, 1138, 1065, 1017, 939, 857, 820. Anal. calcd (found) for $C_{12}H_{20}O_5$: C, 59.00 (58.90); H, 8.25 (8.42).

***trans*-1,1-Dicarbomethoxy-3-(1,1,2,2,2-pentamethyldisiloxyl)methyl-4-*n*-pentylcyclopentane (Table 1, entry 7, 89% pure).** ^{1}H NMR: δ 3.71 (s, 6 H), 2.57 (dd, *J* = 7.2, 13.2 Hz, 1 H), 2.50 (dd, *J* = 7.2, 13.4 Hz, 1 H), 1.70 (dd, *J* = 10.8, 13.2 Hz, 2 H), 1.53 (m, 2 H), 1.39 (m, 2 H), 1.28 (m, 4 H), 0.98 (m, 2 H), 0.88 (t, *J* = 6.8 Hz, 3 H), 0.85 (m, 1 H), 0.31 (dd, *J* = 11.2, 14.4 Hz, 1 H), 0.07 (s, 6 H), 0.06 (s, 9 H). ^{13}C{^{1}H} NMR: δ 173.8, 58.6, 52.9, 49.0, 42.9, 41.6, 40.3, 33.4, 32.5, 28.2, 23.0, 22.6, 14.4, 2.3, 1.5. HRMS (EI) calcd (found) for $C_{20}H_{40}O_5Si_2$ (M^+): 416.2414 (416.2416).

***trans*-1,1-Dicarbomethoxy-3-hydroxymethyl-4-*n*-pentylcyclopentane (Table 1, entry 7).** ^{1}H NMR: δ 3.65 (s, 6 H), 3.62 (dd, *J* = 4.4, 10.8 Hz, 1 H), 3.43 (dd, *J* = 6.8, 10.8 Hz, 1 H), 2.46 (dd, *J* = 7.0, 13.0 Hz, 1 H), 2.41 (dd, *J* = 8.2, 13.8 Hz, 1 H), 2.31 (s, 1 H), 2.03 (dd, *J* = 8.8, 13.6 Hz, 1 H), 1.77 (m, 2H), 1.65 (m, 1 H), 1.47 (m, 1 H), 1.21 (m, 6 H), 1.13 (m, 1 H), 0.81 (t, *J* = 6.8 Hz, 3 H). ^{13}C{^{1}H}NMR: δ 173.5, 173.3, 64.8, 59.0, 52.9, 47.6, 41.3, 40.8, 37.6, 34.5, 32.3, 28.1, 22.8, 14.2. IR (neat, cm^{-1}): 3439, 2953, 2925, 2856, 1734, 1457, 1436, 1377, 1255, 1199, 1171, 1125, 1048, 948, 858, 799. Anal. calcd (found) for $C_{15}H_{26}O_5$: C, 62.91 (62.73); H, 9.15 (9.02).

***trans*-1,1-Dicarbomethoxy-3-(1,1,2,2,2-pentamethyldisiloxyl)methyl-4-benzylcyclopentane (Table 1, entry 8, 81% pure).** ^{1}H NMR: δ 7.23 (m, 2 H), 7.13 (m, 3 H), 3.67 (s, 3 H), 3.63 (s, 3 H), 2.92 (dd, *J* = 3.8, 13.4 Hz, 1 H), 2.57 (dd, *J* = 6.8, 13.2 Hz, 1 H), 2.26 (m, 2 H), 1.79 (m, 2 H), 1.74 (m, 2 H), 0.89 (m, 1 H), 0.38 (dd, *J* = 11.0, 14.6 Hz, 1 H), 0.06 (s, 9 H), 0.05 (s, 6 H). ^{13}C{^{1}H}NMR: δ 173.7, 141.3, 129.2, 128.6, 126.2, 58.4, 52.9, 50.5, 42.7,

41.4, 39.9, 39.8, 22.7, 2.3, 1.6. HRMS (EI) calcd (found) for $C_{22}H_{36}O_5Si_2$ (M^+): 436.2101 (436.2105).

***trans*-1,1-Dicarbomethoxy-3-hydroxymethyl-4-benzylcyclopentane (Table 1, entry 8).** ^{1}H NMR: δ 7.24 (m, 2 H), 7.14 (m, 3 H), 3.68 (s, 3 H), 3.65 (s, 3 H), 3.56 (dd, *J* = 4.4, 10.8 Hz, 1 H), 3.42 (dd, *J* = 6.2, 10.8 Hz, 1 H), 2.81 (dd, *J* = 5.6, 13.6 Hz, 1 H), 2.51 (dd, *J* = 8.6, 13.4 Hz, 1 H), 2.45 (dd, *J* = 8.6, 13.8 Hz, 1 H), 2.32 (dd, *J* = 7.2, 13.2 Hz, 1 H), 2.12 (dd, *J* = 8.4, 14.0 Hz, 2 H), 1.95 (dd, *J* = 10.0, 13.2 Hz, 2 H), 1.66 (s, 1 H). ^{13}C{^{1}H} NMR: δ 173.4, 173.2, 140.9, 129.1, 128.7, 126.4, 64.8, 58.9, 53.1, 47.2, 42.8, 40.9, 40.7, 37.6. IR (neat, cm^{-1}): 3427, 3026, 2951, 1949, 1886, 1727, 1634, 1494, 1451, 1435, 1262, 1200, 1170, 1100, 1035, 912. Anal. calcd (found) for $C_{17}H_{22}O_5$: C, 66.65 (66.41); H, 7.24 (7.26).

***trans*-1,1-Dicarbomethoxy-3-(1,1,2,2,2-pentamethyldisiloxyl)methyl-4-phenoxyethylcyclopentane (Table 1, entry 9, 99% pure).** ^{1}H NMR: δ 7.24 (m, 2 H), 6.86 (m, 3 H), 3.93 (m, 2 H), 3.68 (d, *J* = 2.6 Hz, 6 H), 2.56 (m, 2 H), 2.10 (m, 1 H), 1.83 (dd, *J* = 10.0, 13.6 Hz, 1 H), 1.73 (dd, *J* = 11.0, 13.0 Hz, 1 H), 1.60 (m, 2 H), 1.51 (m, 1 H), 0.88 (dd, *J* = 2.2, 14.6 Hz, 1 H), 0.36 (dd, *J* = 10.6, 14.6 Hz, 1 H), 0.04 (s, 6 H), 0.03 (s, 9 H). ^{13}C{^{1}H}NMR: δ 173.6, 159.3, 129.8, 120.9, 114.8, 67.2, 58.8, 53.0, 46.0, 42.6, 41.8, 40.1, 33.1, 22.5, 2.3, 1.6. HRMS (EI) calcd (found) for $C_{23}H_{38}O_6Si_2$ (M^+): 466.2207 (466.2215).

***trans*-1,1-Dicarbomethoxy-3-hydroxymethyl-4-phenoxyethylcyclopentane (Table 1, entry 9).** ^{1}H NMR: δ 7.26 (m, 2 H), 6.86 (m, 3 H), 3.96 (m, 2 H), 3.69 (d, *J* = 1.0 Hz, 6 H), 3.67 (dd, *J* = 4.0, 10.6 Hz, 1 H), 3.54 (dd, *J* = 5.6, 10.6 Hz, 1 H), 2.55 (m, 1 H), 2.44 (dd, *J* = 8.0, 13.6 Hz, 1 H), 2.10 (dd, *J* = 8.4, 13.6 Hz, 1 H), 2.01 (m, 1 H), 1.95 (m, 2 H), 1.92 (m, 1 H), 1.78 (s, 1 H), 1.71 (m, 1 H). ^{13}C{^{1}H} NMR: δ 173.4, 173.2, 159.1, 129.8, 121.1, 114.8, 66.9, 64.8, 59.2, 53.2, 47.6, 40.9, 38.6, 37.4, 34.0. IR (neat, cm^{-1}): 3456, 3060, 3028,

2951, 2876, 2023, 1932, 1730, 1586, 1495, 1434, 1391, 1245, 1171, 1118, 1017, 950, 819. Anal. calcd (found) for $C_{18}H_{24}O_6$: C, 64.27 (63.97); H, 7.19 (7.08).

***trans*-1,1-Dicarbomethoxy-3-(1,1,2,2,2-pentamethyldisiloxyl)methyl-4-(2'-phthalamido)ethylcyclopentane (Table 1, entry 10, 99% pure).** ^{1}H NMR: δ 7.84 (m, 2 H), 7.71 (m, 2 H), 3.72 (d, *J* = 2.0 Hz, 6 H), 3.67 (m, 2 H), 2.67 (dd, *J* = 7.2, 13.2 Hz, 1 H), 2.58 (dd, *J* = 7.2, 13.2 Hz, 1 H), 1.98 (m, 1 H), 1.86 (dd, *J* = 10.0, 13.6 Hz, 1 H), 1.71 (dd, *J* = 11.0, 13.6 Hz, 1 H), 1.56 (m, 1 H), 1.42 (m, 2 H), 0.83 (dd, *J* = 2.8, 14.4 Hz, 1 H), 0.31 (dd, *J* = 11.4, 14.4 Hz, 1 H), 0.04 (s, 15 H). ^{13}C{^{1}H} NMR: δ 173.5, 168.6, 154.2, 132.5, 123.5, 58.7, 53.0, 46.6, 42.5, 41.7, 39.8, 32.4, 22.4, 2.3, 1.6. HRMS(EI) calcd (found) for $C_{25}H_{37}NO_7Si_2$ (M^+): 519.2109 (519.2107).

***trans*-1,1-Dicarbomethoxy-3hydroxymethyl-4-(2'-phthalamido)ethylcyclopentane (Table 1, entry 10).** ^{1}H NMR: δ 7.82 (m, 2 H), 7.70 (m, 2 H), 3.70 (d, *J* = 2.8 Hz, 6 H), 3.66 (m, 2 H), 3.63 (dd, *J* = 4.8, 10.8 Hz, 1 H), 3.53 (dd, *J* = 6.0, 10.8 Hz, 1 H), 2.64 (dd, *J* = 7.0, 13.6 Hz, 1 H), 2.46 (dd, *J* = 8.2, 13.6 Hz, 1 H), 2.09 (dd, *J* = 8.8, 13.6 Hz, 1 H), 1.97 (dd, *J* = 10.6, 13.6 Hz, 1 H), 1.88 (m, 2 H), 1.80 (m, 1 H), 1.58 (m, 1 H). ^{13}C{^{1}H} NMR: δ 173.5, 168.6, 154.2, 132.5, 123.5, 58.7, 53.0, 46.6, 42.5, 41.7, 39.8, 37.4, 32.4, 22.4, 2.3, 1.6. IR (neat, cm^{-1}): 3463, 3029, 2873, 1770, 1704, 1613, 1436, 1398, 1176, 1050, 866, 795, 722. Anal. calcd (found) for $C_{20}H_{23}NO_7$: C, 61.69 (61.46); H, 5.95 (5.82).

***trans*-1,1-Dicarbomethoxy-4-(1,1,2,2,2-pentamethyldisiloxyl)methyl-2,2,3-trimethylcyclopentane (Table 1, entry 11, 94% pure).** ^{1}H NMR: δ 3.71 (s, 3 H), 3.67 (s, 3 H), 2.73 (dd, *J* = 10.2, 14.2 Hz, 1 H), 1.89 (m, 1 H), 1.72 (m, 2 H), 1.68 (m, 1 H), 1.14 (s, 3 H), 0.82 (d, *J* = 6.8 Hz, 3 H), 0.77 (s, 3 H), 0.53 (dd, *J* = 11.6, 14.4 Hz, 1 H), 0.06 (s, 15 H). ^{13}C{^{1}H} NMR: δ 173.5, 172.1, 67.2, 52.4, 52.3, 51.5, 47.9, 39.8, 38.3, 24.3, 22.9, 19.3, 12.3, 2.3, 1.6. HRMS (EI) calcd (found) for $C_{18}H_{36}O_5Si_2$ (M^+): 388.2101 (388.2101).

***trans*-1,1-Dicarbomethoxy-4-hydroxymethyl-2,2,3-trimethylcyclopentane (Table 1, entry 11).** ^{1}H NMR: δ 3.72 (s, 3 H), 3.71 (dd, *J* = 4.2, 10.6 Hz, 1 H), 3.68 (s. 3 H), 3.62 (dd, *J* = 5.6, 10.6 Hz, 1 H), 2.61 (dd, *J* = 11.4, 15.0 Hz, 1 H), 2.06 (m, 2 H), 1.96 (s, 1 H), 1.88 (m, 1 H), 1.15 (s, 3 H), 0.89 (d, *J* = 6.8 Hz, 3 H), 0.84 (s, 3 H). ^{13}C{^{1}H}NMR: δ 173.8, 171.4, 66.8, 64.6, 52.6, 52.2, 48.6, 44.9, 43.3, 34.5, 22.4, 18.9, 12.8. IR (neat, cm^{-1}): 3424, 2955, 2878, 1729, 1454, 1433, 1391, 1369, 1263, 1175, 1055, 950, 926, 801, 766. HRMS (EI) calcd (found) for $C_{13}H_{22}O_5$ (M^+): 258.1467 (258.1465).

***trans*-1-Trifluoroacetyl-3-(1,1,2,2,2-pentamethyldisiloxyl)methyl-4-methylpyrrolidine (Table 1, entry 12, 93% pure).** ^{1}H NMR: δ 3.88 (m , 2 H), 3.11 (q, *J* = 10.8 Hz, 1 H), 3.01 (m, 1 H), 1.76 (m, 2 H), 1.05 (dd, *J* = 4.2, 6.2 Hz, 3 H), 0.90 (m, 1 H), 0.39 (m, 1 H), 0.08 (m, 15 H). ^{13}C{^{1}H}NMR: δ 116.8 (*J* = 286 Hz), 54.7, 54.1, 53.8, 53.4, 43.0, 42.8, 40.3, 40.1, 20.4, 20.2, 15.4, 15.3, 2.4, 1.5, carbonyl carbon was not observed. HRMS (EI) calcd (found) for $C_{13}H_{26}F_3NO_2Si_2$ (M^+): 341.1454 (341.1456).

***trans*-1-Trifluoroacetyl-3-hydroxymethyl-4-methylpyrrolidine (Table 1, entry 12).** ^{1}H NMR: δ 3.90 (m, 2 H), 3.78 (m, 1 H), 3.60 (m, 1 H), 3.45 (m, 1 H), 3.14 (m, 1 H), 2.21 (s, 1 H), 2.07 (m, 1 H), 1.97 (m, 1 H), 1.09 (m, 3 H). ^{13}C{^{1}H} NMR: δ 116.6 (*J* = 284.9 Hz), 62.4, 62.3, 54.6, 53.8, 50.6, 49.9, 48.6, 45.9, 35.8, 33.0, 16.7, 16.5, carbonyl carbon was not observed. IR (neat, cm^{-1}): 3427, 2951, 1727, 1494, 1451, 1435, 1262, 1200, 1170, 1100, 1035, 912. Anal. calcd (found) for $C_8H_{12}F_3NO_2$: C, 45.50 (45.22); H, 5.73 (5.63).

***trans*-5,8-Diacetoxy-6,7-dimethyl-2-(1,1,2,2,2-pentamethyldisiloxyl) methyl-3-methyl-1,2,3,4-tetrahydronaphthalene (Table 1, entry 13, 81% pure).** ^{1}H NMR: δ 2.46 (m, 1 H), 2.33 (d, *J* = 4.0 Hz, 6 H), 2.28 (m, 1 H), 2.04 (s, 6 H), 1.58 (b, 4 H), 1.01 (d, *J* = 6.8, 3 H), 0.83 (m, 1 H), 0.61 (m, 1 H), 0.07 (s, 15 H). ^{13}C{^{1}H} NMR: δ 169.8, 146.5, 145.7, 127.5, 35.0, 32.4, 31.0, 30.6, 25.0, 23.5, 21.2,

20.4, 20.2, 13.5, 2.69, 0.77. HRMS (EI) calcd (found) for $C_{25}H_{37}NO_7Si_2$ (M^+): 519.2109 (519.2107).

***trans*-5,8-Diacetoxy-6,7-dimethyl-2-hydroxymethyl-3-methyl-1,2,3,4-tetrahydronaphthalene (Table 1, entry 13).** ^{1}H NMR: δ 3.75 (b, 1 H), 3.63 (dd, *J* = 6.6, 10.6 Hz, 1 H), 2.75 (b, 2 H), 2.34 (s, 6 H), 2.04 (s, 6 H), 1.76 (b, 1 H), 1.59 (b, 1 H), 1.50 (b, 2 H), 1.06 (d, *J* = 6.8 Hz, 3 H). ^{13}C{^{1}H}NMR: δ 169.5, 169.4, 145.6, 145.3, 127.4, 65.2, 41.5, 32.4, 31.9, 29.7, 26.7, 20.9, 20.8, 19.6, 13.2. IR (neat, cm^{-1}): 3509, 2924, 2089, 1756, 1638, 1458, 1369, 1246, 1119, 1005, 962, 913, 645. Anal. calcd (found) for $C_{18}H_{24}O_5$: C, 67.48 (67.45); H, 7.55 (7.69).

***trans*-(*S,S*)-1-Carbomethoxy-3-(1,1,2,2,2-pentamethyldisiloxyl) methyl-4-methyl-1-phenylcyclopentane (Table 2, entry 3, 96% pure).** ^{1}H NMR: δ 7.31-7.21 (m, 5 H), 3.61 (s, 3 H), 2.96 (dd, *J* = 5.6, 12.0 Hz, 1 H), 2.33 (m, 2 H), 1.59-1.50 (m, 3 H), [1.02 (d, *J* = 6.4 Hz), 0.98 (d, *J* = 5.2 Hz) (2.1:1), 3 H], 0.88 (m, 1 H), 0.37 (dd, *J* = 10.6, 14.6 Hz, 1 H), 0.10 (s, 6 H), 0.09 (s, 9 H). ^{13}C{^{1}H} NMR: δ 177.5, 145.3, 128.6, 126.8, 57.5, 52.7, 46.2, 44.9, 44.2, 43.2, 23.0, 19.0, 2.4, 1.5. HRMS(EI) calcd (found) for $C_{20}H_{34}O_3Si_2$ (M^+): 378.2046 (378.2050).

***trans*-(*S,S*)-1-Carbomethoxy-3-hydroxymethyl-4-methyl-1-phenylcyclopentane (Table 2, entry 3).** ^{1}H NMR: δ 7.36-7.22 (m, 5 H), 3.69 (dd, *J* = 4.8, 10.8 Hz, 1 H), [3.62 (s), 3.61 (s) (2.4:1), 3 H], 3.53 (dd, *J* = 6.2, 10.6 Hz, 1 H), 2.92 (m, 1 H), 2.85-2.71 (m, 1 H), 2.38 (m, 1 H), 2.35-2.20 (m, 1 H), 1.88-1.78 (m, 2 H), 1.08 (d, *J* = 6.4 Hz, 3 H). ^{13}C{^{1}H} NMR: δ 177.2, 144.2, 128.7, 126.9, 66.0, 57.6, 52.8, 49.5, 44.3, 40.9, 35.6, 20.7. IR (neat, cm^{-1}): 3400, 3058, 3024, 2950, 2869, 1955, 1876, 1725, 1494, 1377, 1205, 1012, 974, 909, 811, 647. Anal. calcd (found) for $C_{15}H_{20}O_3$: C, 72.55 (72.21); H, 8.12 (8.08).

***trans*-(*S,S*)-1-Carbomethoxy-3-(1,1,2,2,2-pentamethyldisiloxyl)methyl -4-methyl-1-(dimethylcarbamoyl)cyclopentane (Table 2, entry 4, 97% pure).** ^{1}H NMR: δ 3.70 (s, 3 H), 2.95 (s, 3 H), 2.79 (s, 3

H), 2.66 (dd, *J* = 6.8, 13.0 Hz, 1 H), 2.43 (dd, *J* = 6.8, 13.2 Hz, 1 H), 1.80 (dd, *J* = 11.2, 13.6 Hz, 1 H), 1.67 (dd, *J* = 10.8, 12.8 Hz, 1 H), 1.63-1.43 (m, 2 H), 0.94 (d, *J* = 6.4 Hz, 3 H), 0.86 (dd, *J* = 3.0, 14.5 Hz, 1 H), 0.34 (dd, *J* = 10.8, 14.5 Hz, 1 H), 0.08 (s, 6 H), 0.05 (s, 9 H). $^{13}C\{^{1}H\}$ NMR: δ 175.9, 172.1, 57.5, 53.0, 44.5, 43.4, 43.3, 36.9, 36.7, 22.2, 17.3, 2.3, 2.2, 1.4. HRMS(EI) calcd (found) for $C_{17}H_{35}NO_4Si_2$ (M^+): 373.2105 (373.2107).

***trans*-(*S*,*S*)-1-Carbomethoxy-3-hydroxymethyl-4-methyl-1-(dimethylcarbamoyl)cyclopentane (Table 2, entry 4).** ^{1}H NMR: δ 3.74 (dd, *J* = 4.0, 10.8 Hz, 1 H), 3.71 (s, 3 H), 3.55 (dd, *J* = 6.0, 10.8 Hz, 1 H), 2.94 (s, 3 H), 2.80 (s, 3 H), 2.53 (dd, *J* = 7.6, 13.2 Hz, 1 H), 2.42 (dd, *J* = 6.6, 13.4 Hz, 1 H), 2.02 (dd, *J* = 9.6, 13.2 Hz, 1 H), 1.97 (dd, *J* = 11.2, 13.2 Hz, 1 H), 1.81 (m, 1 H), 1.73 (m, 1 H), 1.00 (d, *J* = 6.0 Hz, 3 H). $^{13}C\{^{1}H\}$ NMR: δ 175.8, 171.7, 64.6, 57.7, 53.1, 49.4, 44.2, 39.0, 37.2, 37.0, 35.8, 18.2. IR (neat, cm^{-1}): 3431, 2924, 2871, 1733, 1646, 1636, 1628, 1458, 1436, 1389, 1260, 1215, 1137, 1057, 842. MS(CI) calcd (found) for $C_{12}H_{22}NO_4$ (MH^+): 244 (244). HRMS(EI) calcd (found) for $C_{12}H_{19}NO_3$ ($M^+–H_2O$): 225.1365 (225.1364).

References

1) Widenhoefer, R. A.; Stengone, C. N. *J. Org. Chem*. **1999**, *64*, 8681.