Palladium-Catalyzed Addition of Silyl-Element Bonds to Bicyclopropylidene – A New Access to Bicyclopropyl and Functionally Substituted Cyclopropylidenepropane Derivatives

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Supporting Information

1,1'-Bis(trimethylsilyl)bicyclopropyl (**3a**): A solution of 548 mg (3.74 mmol) of hexamethyldisilane (**2a**), 300 mg (3.74 mmol) of bicyclopropylidene (**1**), 174 mg (1.24 mmol) of 1,1,3,3-tetramethylbutyl isocyanide and 17 mg (0.08 mmol) of $Pd(OAc)_2$ in 1 mL of toluene was heated under argon in a screw-capped Pyrex bottle at 60 °C for 4 d. After addition of 10 mL of diethyl ether the reaction mixture was washed with 10 mL of saturated $NaHCO_3$ solution and with water (2×10 mL). The organic layer was dried over $MgSO_4$, and the solvents were removed under reduced pressure. Chromatography on silica gel with pentane afforded 652 mg (77%) of **3a** ($R_f = 0.86$) as a colorless liquid (b.p. 247 °C). – IR (film): $\nu = 3067$ cm^{-1} (C–H), 2952 (C–H), 2898 (C–H), 1447, 1260 (Si–CH_3), 1211, 1054, 1021, 977, 946, 899, 867. – ^{1}H NMR (250 MHz, $CDCl_3$): $\delta = -0.05$ [s, 18 H, Si(CH_3)$_3$], 0.34–0.39 (m, 8 H, *c*Pr-H). – ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): $\delta = -0.77$ [+, 6 C, Si(*C*H$_3$)], 9.13 (C_{quat}, 2 C, *c*Pr-C_{quat}), 9.73 (–, 4 C, *c*Pr-*C*H$_2$). – MS (EI, 70 eV), *m/z* (%): 226 (6) [M^+], 181 (8), 172 (10), 155 (12), 138 (8), 123 (17), 110 (8), 73 (100) [$Si(CH_3)_3^+$]. – Anal. calcd for $C_{12}H_{26}Si_2$ (226.5): C, 63.63; H, 11.57. Found: C, 63.49; H, 11.52.

1-(Trimethylsilyl)-1-(triphenylsilyl)bicyclopropyl (**3b**): A solution of 1.24 g (3.74 mmol) of 1,1,1-trimethyl-2,2,2-triphenyldisilane (**2b**), 300 mg (3.74 mmol) of bicyclopropylidene (**1**), 174 mg (1.24 mmol) of 1,1,3,3-tetramethylbutyl isocyanide and 17 mg (0.08 mmol) of $Pd(OAc)_2$ in 2 mL of toluene was heated under argon in a screw-capped Pyrex bottle at 70 °C for 4 days. The reaction mixture was diluted with 10 mL of diethyl ether, washed with 20 mL

of a saturated $NaHCO_3$ solution and with water (2 × 10 mL). The organic layer was dried over $MgSO_4$, and the solvents were removed under reduced pressure. The residue was recrystallized from ethanol to yield 1.34 g (87%) of **3b** as a colorless solid (m.p. 128 °C). – IR (film): ν = 3131 cm^{-1} (C–H), 3042 (C–H), 3014 (C–H), 2987 (C–H), 2950 (C–H), 2897 (C–H), 1482, 1451, 1427 (Si–C_6H_5), 1248 (Si–CH_3), 1210, 1184, 1105, 1059, 1035, 1026, 948, 901, 865, 831. – ^{1}H NMR (250 MHz, $CDCl_3$): δ = –0.21 [s, 9 H, Si(CH_3)$_3$], 0.46 (m_c, 2 H, *c*Pr-H), 0.60 (m_c, 2 H, *c*Pr-H), 0.76 (m_c, 2 H, *c*Pr-H), 0.78 (m_c, 2 H, *c*Pr-H), 7.20–7.41 (m, 9 H, Ph-H), 7.53–7.62 (m, 6 H, Ph-H). – ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): δ = –0.96 [+, 3 C, Si(*C*H_3)$_3$], 7.37 (C_{quat}, *c*Pr-C_{quat}), 9.59 (C_{quat}, *c*Pr-C_{quat}), 10.85 (–, 2 C, *c*Pr-*C*H_2), 12.57 (–, 2 C, *c*Pr-*C*H_2), 127.47 (+, 6 C, Ph-C), 129.20 (+, 3 C, Ph-C), 135.43 (C_{quat}, 3 C, Ph-C), 136.75 (+, 6 C, Ph-C). – MS (EI, 70 eV), *m/z* (%): 412 (2) [M^+], 358 (5), 334 (8), 259 (100) [Si(C_6H_5)$_3^+$], 197 (5), 181 (6), 138 (4), 73 (4) [Si(CH_3)$_3^+$]. – Anal. calcd for $C_{27}H_{32}Si_2$ (412.71): C, 78.57; H, 7.82. Found: C, 78.56; H, 7.64.

[2-(Pentamethyldisilanyloxy)ethyl]bicyclopropylidene (**5**): 1.35 g (8.1 mmol) of chloropentamethyldisilane was added to a solution of 1.00 g (8.1 mmol) of (2-hydroxyethyl)-bicyclopropylidene (**4**), 1.22 g (12.1 mmol) of triethylamine and 20 mg (0.16 mmol) of 4-dimethylaminopyridine in 20 mL of tetrahydrofuran. The mixture was stirred for 24 h at 25 °C, then washed with 20 mL of a saturated NaCl solution, and the aqueous layer was extracted with diethyl ether (2 × 25 mL). The organic layer was dried over $MgSO_4$, and the solvents were removed under reduced pressure. Chromatography on silica gel with pentane afforded 1.81 g (88%) of **5** (R_f = 0.30) as a colorless oil. – IR (film): ν = 3052 cm^{-1} (C–H), 2951 (C–H), 2894 (C–H), 2859 (C–H), 1469, 1382, 1246 (Si–CH_3), 1092, 1020, 960, 933, 834. – ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.08 [s, 9 H, Si(CH_3)$_3$], 0.20 [s, 6 H, Si(CH_3)$_2$], 0.84–0.91 (m, 1 H, *c*Pr-H), 1.17 (bs, 4 H, *c*Pr-H), 1.28–1.38 (m, 1 H, *c*Pr-H), 1.47–1.58 (m, 2 H, 1'-H), 1.63–1.73 (m, 1 H, *c*Pr-H), 3.69 (t, ^3J = 6.6 Hz, 2 H, 2'-H). – ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): δ = –1.99 [+, 3 C, Si(*C*H_3)$_3$], –0.76 [+, 2 C, Si(*C*H_3)$_2$], 2.76 (–, *c*Pr-*C*H_2), 2.93 (–, *c*Pr-*C*H_2), 9.57 (–, *c*Pr-*C*H_2), 12.82 (+, C-2), 36.61 (–, C-1'), 63.70 (–, C-2'), 109. 92 (C_{quat}, *c*Pr-C_{quat}), 115.44 (C_{quat}, *c*Pr-C_{quat}). – MS (CI, NH_3), *m/z* (%): 272 (25) [M + NH_4^+], 255 (100) [M + H^+]. – Anal. calcd for $C_{13}H_{26}OSi_2$ (254.52): C, 61.35; H, 10.30. Found: C, 61.08; H, 9.97.

2,2-Dimethyl-1-[1-(trimethylsilyl)cyclopropyl]-3-oxa-2-silabicyclo[4.1.0]heptane (**6**): A solution of 300 mg (1.18 mmol) of **5**, 30 mg (0.22 mmol) of 1,1,3,3-tetramethylbutyl isocyanide and 5 mg (0.02 mmol) of $Pd(OAc)_2$ in 1 mL of benzene was heated under argon in a screw-capped Pyrex bottle at 70 °C for 3 d. After addition of 10 mL of diethyl ether, the solution was washed with 10 mL of a saturated $NaHCO_3$ solution and with water (2 × 10 mL). The organic layer was dried over $MgSO_4$, and the solvents were removed under reduced pressure. Chromatography on silica gel eluting with diethyl ether afforded 234 mg (78%) of **6** (R_f = 0.82) as a colorless oil. – IR (film): ν = 3052 cm^{-1} (C–H), 2955 (C–H), 2920 (C–H), 2861 (C–H), 1740, 1482, 1434, 1404, 1363, 1250 (Si–CH_3), 1124, 1083, 1021, 965, 941, 904, 835. – ^{1}H NMR (250 MHz, $CDCl_3$): δ = –0.2 [s, 9 H, Si(CH_3)$_3$], 0.11 [s, 6 H, Si(CH_3)$_2$], 0.34 [m_c, 4 H, 2'(3')-H], 0.40–0.48 (m, 1 H, 7-H), 0.62–0.69 (m, 1 H, 7-H), 1.02–1.10 (m, 1 H, 6-H), 1.57–1.68 (m, 2 H, 5-H), 3.40–3.52 (m, 1 H, 4-H), 3.62–3.67 (m, 1 H, 4-H). – ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): δ = –0.91 [+, 3 C, Si(*C*H_3)$_3$], –0.17 [+, Si(*C*H_3)$_2$], 0.69 [+, Si(*C*H_3)$_2$], 8.90 (C_{quat}, C-1'), 9.25 (–, C-2'*), 10.44 (–, C-3'*), 12.40 (C_{quat}, C-1), 13.52 (–, C-7), 18.53 (+, C-6), 27.60 (–, C-5), 58.97 (–, C-4). – MS (EI, 70 eV), *m/z* (%): 254 (5) [M^+], 237 (8), 211 (13), 181 (19) [M^+ – Si$(CH_3)_3$], 165 (7), 147 (81) [$(CH_3)_3SiSi(CH_3)_2O^+$], 133 (68), 109 (15), 101 (17), 73 (100) [$Si(CH_3)_3^+$]. – Anal. calcd for $C_{13}H_{26}OSi_2$ (254.52): C, 61.35; H, 10.30. Found: C, 61.32; H, 10.63.

[2-(Pentamethyldisilyl)ethyl]bicyclopropylidene (**8**): 1.68 g (9.0 mmol) of (2-bromoethyl)-bicyclopropylidene (**7**) was slowly added to a suspension of 220 mg (9.05 mmol) of magnesium in 10 mL of tetrahydrofuran at 25 °C. The reaction mixture was stirred at 25 °C for 90 min. After addition of 1.51 g (9.05 mmol) of chloropentamethyldisilane, the reaction mixture was stirred at 25 °C for 16 h. Then 30 mL of diethyl ether was added, the reaction mixture was washed with 30 mL of a saturated $NaHCO_3$ solution, and the aqueous layer was extracted with diethyl ether (2 × 10 mL). The organic layer was dried over $MgSO_4$, and the solvents were removed under reduced pressure. Chromatography on silica gel eluting with pentane afforded 1.64 g (76%) of **8** (R_f = 0.67) as a colorless oil. – IR (film): ν = 3053 cm^{-1} (C–H), 3037 (C–H), 2983 (C–H), 2945 (C–H), 2912 (C–H), 2891 (C–H), 2847 (C–H), 1444, 1414, 1256 (Si–CH_3), 1244 (Si–CH_3), 1021, 964, 941, 872. – ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.01 [s, 6 H, Si(CH_3)$_2$], 0.05 [s, 9 H, Si(CH_3)$_3$], 0.68–0.79 (m, 2 H, 1"-H), 0.92 (t, ^3J = 6.9 Hz, 2 H, 2"-H), 1.14–1.20 (m, 4 H, *c*Pr-H), 1.23–1.48 (m, 3 H, *c*Pr-H). – ^{13}C NMR

(62.9 MHz, $CDCl_3$, plus DEPT): δ = –4.35 [+, Si(*C*H_3)$_2$], –4.32 [+, Si(*C*H_3)$_2$], –2.07 [+, 3 C, Si(*C*H_3)$_3$], 2.69 (–, *C*H_2), 2.99 (–, *C*H_2), 9.55 (–, *C*H_2), 14.43 (–, *C*H_2), 19.28 (+, C-2), 28.34 (–, *C*H_2), 109.33 (C_{quat}, C-1*), 116.29 (C_{quat}, C-1'*). – MS (EI, 70 eV), *m/z* (%): 205 (45), 189 (13), 147 (37), 131 (76) [$(CH_3)_3SiSi(CH_3)_2^+$], 117 (19), 73 (100) [$Si(CH_3)_3^+$].

2,2-Dimethyl-1-[1-(trimethylsilyl)cyclopropyl]-2-silabicyclo[3.1.0]hexane (**9**): A solution of 280 mg (1.17 mmol) of **8**, 30 mg (0.22 mmol) of 1,1,3,3-tetramethylbutyl isocyanide and 5 mg (0.02 mmol) of $Pd(OAc)_2$ in 1 mL of benzene was heated under argon in a screw-capped Pyrex bottle at 70 °C for 3 d. After addition of 10 mL of diethyl ether, the solution was washed with 10 mL of a saturated $NaHCO_3$ solution and with water (2 × 10 mL). The organic layer was dried over $MgSO_4$, and the solvents were removed under reduced pressure. Chromatography on silica gel eluting with pentane afforded 207 mg (74%) of **9** (R_f = 0.75) as a colorless oil. – IR (film): ν = 3048 cm^{-1} (C–H), 3043 (C–H), 2993 (C–H), 2917 (C–H), 1502, 1253 (Si–CH_3), 1238, (Si–CH_3), 1033, 973, 881. – ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.03 [s, 9 H, Si(C*H*$_3$)$_3$], 0.08 [s, 6 H, Si(C*H*$_3$)$_2$], 0.13–0.22 (m, 6 H, *c*Pr-H), 0.78–1.03 (m, 5 H, 3-H, 4-H, 5-H). – ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): δ = –1.66 [+, 3 C, Si(*C*H_3)$_3$], –0.59 [+, 2 C, Si(*C*H_3)$_2$], 6.58 (–, *C*H_2), 6.86 (C_{quat}, C-1*), 8.77 (–, *C*H_2), 9.33 (–, *C*H_2), 11.62 (–, *C*H_2), 12.37 (C_{quat},C-1'*), 12.83 (–, *C*H_2), 21.57 (+, C-5). – MS (EI, 70 eV), *m/z* (%): 238 (5) [M^+], 223 (2) [$M^+ – CH_3$], 210 (8), 195 (11), 164 (17), 149 (12), 136 (19), 122 (21), 73 [$Si(CH_3)^+$].

***B*-[3-Cyclopropylidene-3-(dimethylphenylsilyl)propyl]pinacolborane** (**13d**): A solution of 0.80 g (3.1 mmol) of *B*-(dimethylphenylsilyl)pinacolborane (**12d**), 245 mg (3.06 mmol) of bicyclopropylidene (**1**), 143 mg (1.03 mmol) of 1,1,3,3-tetramethylbutyl isocyanide and 14 mg (0.06 mmol) of $Pd(OAc)_2$ in 2 mL of toluene was heated under argon in a screw-capped Pyrex bottle at 130 °C for 3 d. The solvent was removed under reduced pressure. Kugelrohr distillation (175 °C, 0.01 Torr) gave 584 mg (56%) of **13d** as a colorless oil. – ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.27 [s, 6 H, Si(C*H*$_3$)$_2$], 0.95–1.12 (m, 6 H, *c*Pr-H, 1'-H), 1.30 [s, 12 H, C(C*H*$_3$)$_2$], 2.28–2.34 (m, 2 H, 2'-H), 7.05–7.75 (m, 5 H, Ph-H). – ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): δ = –2.87 [+, 2 C, Si(*C*H_3)$_2$], 1.71 (–, *c*Pr-*C*H_2), 2.92 (–, *c*Pr-*C*H_2), 15.41 (–, C-1'), 24.81 [+, 4 C, C(*C*H_3)$_2$], 27.74 (–, C-2'), 82.77 [C_{quat}, 2 C, *C*$(CH_3)_2$], 127.57

(+, 2 C, Ph-C), 128.18 (C_{quat}, *c*Pr-C_{quat}^{*}), 128.58 (C_{quat}, Ph-C_{quat}^{*}), 128.99 (C_{quat}, C-3'*), 133.12 (+, Ph-C), 133.60 (+, 2 C, Ph-C).

3-Cyclopropylidene-1-(tributylstannyl)-3-(trimethylsilyl)propane (**13e**): A solution of 1.36 g (3.74 mmol) of (trimethylsilyl)tributylstannane (**12e**), 300 mg (3.74 mmol) of bicyclopropylidene (**1**) and 43 mg (0.04 mmol) of $Pd(PPh_3)_4$ in 5 mL of tetrahydrofuran was heated under argon in a screw-capped Pyrex bottle at 100 °C for 4 d. The reaction mixture was poured into 10 mL of diethyl ether, and the mixture filtered through 3 g of Celite. Removal of the solvent under reduced pressure afforded a mixture of 439 mg (40%) hexabutyldistannane and 680 mg (41%) of **13e** which could not be separated. – ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.11 [s, 9 H, Si(CH_3)$_3$], 0.78–1.15 (m, 33 H, *n*-Bu-CH_3, *n*-Bu-CH_2, 2'-H, 3'-H, 1-H), 2.38 (t, ^{3}J = 6.9 Hz, 2 H, 2-H). – ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): δ = –0.70 [+, 3 C, Si(*C*H_3)$_3$], 0.77 (–, *c*Pr-*C*H_2), 2.96 (–, *c*Pr-*C*H_2), 8.70 (–, 3 C, 3 *n*-Bu-*C*H_2), 9.33 (–, C-2), 13.70 [+, 3 C, $SnBu_3$], 27.41 (–, 3 C, *n*-Bu-CH_2), 29.31 (–, 3 C, *n*-Bu-CH_2), 31.99 (–, C-1), 130.46 (C_{quat}, C-3*), 131.44 (C_{quat}, C-1'*).

3-Cyclopropylidene-3-(trimethylsilyl)-1-(trimethylstannyl)propane (**13f**): A solution of 0.886 g (3.74 mmol) of (trimethylsilyl)trimethylstannane (**12f**), 300 mg (3.74 mmol) of bicyclopropylidene (**1**) and 43 mg (0.04 mmol) of $Pd(PPh_3)_4$ in 5 mL of diethyl ether was heated under argon in a screw-capped Pyrex bottle at 50 °C for 4 d. The reaction mixture was poured into 10 mL of diethyl ether, the mixture then filtered through 3 g of Celite, and the solvent was removed under reduced pressure. Chromatography on silica gel eluting with pentane afforded 1.09 g (92%) of **13f** (R_f = 0.95) as a colorless oil. – IR (film): ν = 3046 cm^{-1} (C–H), 2974 (C–H), 2955 (C–H), 2906 (C–H), 2840 (C–H), 1444, 1404, 1315, 1247 (Si–CH_3), 1188, 1033, 995, 960, 895, 835. – ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.04 [s, 9 H, Sn(CH_3)$_3$], 0.17 [s, 9 H, Si(CH_3)$_3$], 0.90–1.12 (m, 6 H, *c*Pr-H, 1-H), 2.42 (t, ^{3}J = 7.3 Hz, 2 H, 2-H). – ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): δ = –6.07 [+, 3 C, Sn(*C*H_3)$_3$], –0.69 [+, 3 C, Si(*C*H_3)$_3$], 1.06 (–, *c*Pr-*C*H_2), 2.82 (–, *c*Pr-*C*H_2), 11.05 (–, C-1), 31.61 (–, C-2), 130.55 (C_{quat}, C-1'*), 130.76 (C_{quat}, C-3*). – MS (EI, 70 eV), *m/z* (%): 303/301/299 (57/44/20) [$M^+ - CH_3$], 275/273/271 (25/19/10), 247/245/243 (15/10/7), 165/163/161 (48/35/23) [Sn(CH_3)$_3^+$], 135 (13), 91 (8), 73 (100) [Si(CH_3)$_3^+$]. – Anal. calcd for $C_{12}H_{26}SiSn$ (317.13): C, 45.45; H, 8.26. Found: C, 45.70; H, 8.07.

4-Cyclopropylidene-4-(dimethylphenylsilyl)butyronitrile (13g): A solution of 2.46 g (15.3 mmol) of dimethylphenylsilyl cyanide (**12g**), 600 mg (7.48 mmol) of bicyclopropylidene (**1**), 53 mg (0.30 mmol) of $PdCl_2$ and 100 mg (1.26 mmol) of pyridine in 10 mL of toluene was heated under argon in a screw-capped Pyrex bottle at 100 °C for 14 d. The reaction mixture was diluted with 30 mL of diethyl ether, washed with 30 mL of a saturated $NaHCO_3$ solution and with water (2 × 40 mL). The organic layer was dried over Na_2SO_4, and the solvents were removed under reduced pressure. Chromatography on silica gel eluting with light petroleum/diethyl ether (4/1) afforded 1.05 g (58%) of **13g** (R_f = 0.51) as a colorless oil. – IR (film): ν = 3069 cm^{-1} (C–H), 3051 (C–H), 2958 (C–H), 2927 (C–H), 2871 (C–H), 2245 (C≡N), 1727, 1427 (Si–C_6H_5), 1249 (Si–CH_3), 1110, 976, 833. – ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.43 [s, 6 H, Si(C*H*$_3$)$_2$], 1.09 (m_c, 4 H, *c*Pr-H), 2.38 (t, ^3J = 6.7 Hz, 2 H, 3-H), 2.55 (t, ^3J = 6.9 Hz, 2 H, 2-H), 7.36–7.58 (m, 5 H, Ph-H). – ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): δ = –2.75 [+, 2 C, Si(*C*H$_3$)$_2$], 2.06 (–, *c*Pr-*C*H$_2$), 3.13 (–, *c*Pr-*C*H$_2$), 16.69 (–, C-3), 30.00 (–, C-2), 119.99 (C_{quat}, C-4*), 122.63 (C_{quat}, C-1'*), 127.81 (+, 2 C, Ph-C), 129.07 (+, Ph-C), 133.63 (+, 2 C, Ph-C), 136.57 (C_{quat}, Ph-C_{quat}*), 138.10 (C_{quat}, C-1*). – MS (CI, NH_3), *m/z* (%): 500 (1) [2 M + NH_4^+], 259 (100) [M + NH_4^+]. – Anal. calcd for $C_{15}H_{19}NSi$ (241.40): C, 74.63; H, 7.93; N, 5.80. Found: C, 74.92; H, 7.93; N, 5.77.

1-(Tributylstannyl)-1-(trimethylsilyl)bicyclopropyl (**14**): A solution of 1.36 g (3.74 mmol) of (trimethylsilyl)tributylstannane, 300 mg (3.74 mmol) of bicyclopropylidene (**1**), 174 mg (1.24 mmol) of 1,1,3,3-tetramethylbutyl isocyanide and 17 mg (0.08 mmol) of $Pd(OAc)_2$ in 2 mL of pentane was heated under argon in a screw-capped Pyrex bottle at 50 °C for 7 d. After addition of 10 mL of diethyl ether, the reaction mixture was washed with 10 mL of a saturated $NaHCO_3$ solution and with water (2 ×10 mL). The organic layer was dried over $MgSO_4$ and the solvents were removed under reduced pressure. Chromatography on silica gel eluting with pentane afforded a mixture of 0.53 g (49%) of hexabutyldistannane (**15**) and 0.76 g (45%) of **14** (R_f = 0.95) which could not be separated, as a colorless liquid. – IR (film): ν = 3061 cm^{-1} (C–H), 2956 (C–H), 2924 (C–H), 2871 (C–H), 2854 (C–H), 1464, 1419, 1376, 1340, 1257, 1247 (Si–CH_3), 1071, 1016, 972, 935, 891, 852, 834. – ^{1}H NMR (250 MHz, $CDCl_3$): δ = –0.07 [s, 9 H, Si(C*H*$_3$)$_3$], 0.32–0.42 (m, 8 H, *c*Pr-H), 0.76–0.97 (m, 15 H, *n*-Bu-H), 1.21–1.43 (m, 12 H, *n*-Bu-H). – ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): δ = –

1.40 [+, 3 C, Si(CH_3)$_3$], 8.41 (–, 2 C, *c*Pr-CH_2), 9.77 (–, 3 C, *n*-Bu-CH_2), 10.39 (–, 2 C, *c*Pr-CH_2), 11.47 (C_{quat}, *c*Pr-C_{quat}), 13.30 (C_{quat}, *c*Pr-C_{quat}), 13.68 (+, 3 C, *n*-Bu-CH_3), 27.66 (–, 3 C, *n*-Bu-CH_2), 29.24 (–, 3 C, *n*-Bu-CH_2). – MS (EI, 70 eV), *m/z* (%): 387/385/383 (100/74/44) [$M^+ - C_4H_9$], 359/357/355 (36/26/16), 291/289/287 (36/27/16), 235/233/231 (36/26/17), 121 (10), 73 (55) [$Si(CH_3)_3^+$].

1,1'-Bis(trimethylstannyl)bicyclopropyl (**16**): A solution of 1.77 g (7.48 mmol) of (trimethylsilyl)trimethylstannane, 300 mg (3.74 mmol) of bicyclopropylidene (**1**), 174 mg (1.24 mmol) of 1,1,3,3-tetramethylbutyl isocyanide and 17 mg (0.08 mmol) of $Pd(OAc)_2$ in 2 mL of pentane was heated under argon in a screw-capped Pyrex bottle at 50 °C for 4 d. After addition of 10 mL of diethyl ether, the reaction mixture was washed with 10 mL of saturated $NaHCO_3$ solution and with water (2 × 10 mL). The organic layer was dried over $MgSO_4$, and the solvents were removed under reduced pressure. Chromatography on silica gel eluting with pentane afforded 1.04 g (2.54 mmol, 68%) of **16** (R_f = 0.95) as a colorless liquid. – IR (Film): ν = 3055 cm^{-1} (C–H), 2980 (C–H), 2912 (C–H), 1646, 1425, 1265, 1187, 1118, 1016, 969, 931, 883 , 836. – ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.02 [s, 18 H, Sn(CH_3)$_3$], 1.32 (m_c, 8 H, *c*Pr-H). – ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): δ = –6.80 [+, 6 C, Sn(CH_3)$_3$], 9.02 (–, 4 C, *c*Pr-CH_2), 15.42 (C_{quat}, 2 C, *c*Pr-C_{quat}). – MS (EI, 70 eV), *m/z* (%): 395/393/391 (21/25/24) [$M^+ - CH_3$], 215/213/211 (100/69/43), 165/163/161 (97/67/43) [$Sn(CH_3)^+$], 135/133/131 (24/16/12) [$SnCH_3^+$].

1,3-Bis(trimethylsilyl)-1-cyclopropylidenepropane: A mixture of 426 mg (3.00 mmol) of methyl iodide and 73 mg (3.00 mmol) of magnesium turnings in 10 mL of diethyl ether was stirred at 25 °C for 2 h. After addition of 250 mg (1.07 mmol) of 1,3-bis(dimethylfluorosilyl)-1-cyclopropylidenepropane (**13a**), the solution was stirred under reflux for 2 h. The solution was washed with 10 mL of a saturated $NaHCO_3$ solution and with water (2 × 10 mL). The organic layer was dried over $MgSO_4$, and the solvents were removed under reduced pressure. Chromatography on silica gel eluting with pentane afforded 191 mg (79%) of 1,3-bis(trimethylsilyl)-1-cyclopropylidenepropane (R_f = 0.78) as a colorless oil. – IR (film): ν = 3047 cm^{-1} (C–H), 2954 (C–H), 2914 (C–H), 2901 (C–H), 1419, 1247 (Si–CH_3), 1132, 1039, 996, 961, 913, 834. – ^{1}H NMR (250 MHz, $CDCl_3$): δ = –0.01 [s, 9 H, Si(CH_3)$_3$], 0.11

[s, 9 H, Si(CH_3)$_3$], 0.60–0.68 (m, 2 H, 3-H), 0.91–1.09 (m, 4 H, *c*Pr-H), 2.18–2.26 (m, 2 H, 2-H). – ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): δ = –1.79 [+, 3 C, Si(*C*H_3)$_3$], –0.77 [+, 3 C, Si(*C*H_3)$_3$], 0.81 (–, *c*Pr-*C*H_2), 2.76 (–, *c*Pr-*C*H_2), 17.11 (–, C-3), 28.69 (–, C-2), 130.35 (C_{quat}, C-1'*), 130.43 (C_{quat}, C-1*). – MS (EI, 70 eV), *m/z* (%): 226 (1) [M^+], 211 (4) [M^+ – CH_3], 183 (16), 155 (47), 153 (19) [M^+ – Si$(CH_3)_3$], 138 (10), 123 (21), 109 (13), 95 (9), 73 (100) [Si$(CH_3)_3^+$], 59 (10), 45 (19). – HRMS *m/z* calcd for $C_{12}H_{26}Si_2$, 226.1576; found, 226.1573.