

*Supporting Information - Part A*

**Functionalization of Tetraorganosilanes and Permethyloligosilanes at a Methyl Group on Silicon via Iridium-Catalyzed C(sp<sup>3</sup>)–H Borylation**

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## 1. General

All iridium- and palladium-catalyzed reactions were performed in glove box or using Schlenk technique under an atmosphere of nitrogen with magnetic stirring. Conversion of a boryl group into a hydroxyl group was carried out under air. Other reactions including preparation of starting organosilanes were carried out under an atmosphere of nitrogen. Column chromatography was performed with Ultra Pure Silica Gel (SILICYCLE, pH 7.0, 40-63  $\mu$ m, 60  $\text{\AA}$ ). Gel Permeation Chromatography (GPC) was performed by Japan Analytical Industry LC-908 with series-connected JAIGEL-1H ( $\phi$  20 mm x 600 mm) and JAIGEL-2H ( $\phi$  20 mm x 600 mm). Gas chromatography (GC) was performed by Shimadzu GC-2010 with Agilent J&W GC Column DB-1 ( $\phi$  0.32 mm x 15 m).  $^1\text{H}$  NMR spectra were recorded on a Varian 400-MR (399.89 MHz) spectrometer.  $^{13}\text{C}$  NMR spectra were recorded on a Varian 400-MR (100.55 MHz) spectrometers.  $^{11}\text{B}$  NMR spectra were recorded on a Varian 400-MR (128.30 MHz) spectrometer.  $^{29}\text{Si}$  NMR spectra were recorded on a Varian 400-MR (79.45 MHz) spectrometer.  $^1\text{H}$  NMR data were reported as follows: chemical shifts in ppm downfield from tetramethylsilane, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, and br = broad), coupling constant ( $J$ ), and integration.  $^{13}\text{C}$ ,  $^{11}\text{B}$ ,  $^{29}\text{Si}$  NMR data were reported in ppm downfield from tetramethylsilane ( $^{13}\text{C}$ ,  $^{29}\text{Si}$ ) and  $\text{BF}_3\bullet\text{OEt}_2$  ( $^{11}\text{B}$ ), respectively. High resolution mass spectra were recorded on JEOL JMS-MS700 (EI) or Thermo Scientific Exactive (ESI, APCI) spectrometers. Infrared spectra were recorded on a Shimadzu FTIR-8400 spectrometer.

## 2. Materials

*Solvents and reagents:* Cyclooctane, *n*-octane, and 2,2,4,4-tetramethylpentane were distilled over calcium hydride and degassed. Tetrahydrofuran (THF) was dried and degassed by The Ultimate Solvent System (GlassContour).  $\text{H}_2\text{O}_2$  (30% solution in  $\text{H}_2\text{O}$ ) (Wako), 4-bromotoluene (Wako), 2-bromotoluene (Wako),  $\text{CsOH}\bullet\text{H}_2\text{O}$  (nacalai), and  $\text{Ba}(\text{OH})_2\bullet8\text{H}_2\text{O}$  (nacalai) were used as received from commercial sources. Bis(pinacolato)diboron (**2**) was purchased from ChemICHIBA and was purified by

recrystallization before use. Pinacolborane was synthesized by the reported method.<sup>1</sup>

*Catalysts and ligands:*  $[\text{Ir}(\text{OMe})(\text{cod})]_2$ <sup>2</sup> and  $\text{PdCl}_2(\text{dppf})\bullet\text{CH}_2\text{Cl}_2$ <sup>3</sup> were synthesized by the method reported previously. 4,4'-Di-*tert*-butyldipyridine (dtbpy, Aldrich), 1,10-phenanthroline (phen, Aldrich), 4,7-dimethyl-1,10-phenanthroline (4,7-Me<sub>2</sub>phen, TCI), 2,9-dimethyl-1,10-phenanthroline (2,9-Me<sub>2</sub>phen, Aldrich), and 3,4,7,8-tetramethyl-1,10-phenanthroline (Me<sub>4</sub>phen, TCI) were used as received from commercial sources.

*Organosilicon compounds:* Tetramethylsilane (**1b**, TCI) and 1,4-bis(trimethylsilyl)benzene (**1g**, Aldrich) were purchased and used as received. Hexamethyldisilane (**1h**, TCI), phenyltrimethylsilane (**1k**, TCI), and tetraethylsilane (**1m**, TCI) were received from commercial sources and distilled prior to use. Octamethyltrisilane (**1i**)<sup>4</sup> and dodecamethylcyclohexasilane (**1j**)<sup>5</sup> were prepared by a coupling of chlorosilanes in the presence of lithium according to the procedure reported.

#### Trimethyl(octyl)silane (**1a**)



In a 200 mL three neck flask, a solution of *n*-octylmagnesium bromide was prepared from 1-bromooctane (3.9 g, 20 mmol) with magnesium turnings (0.49 g, 20 mmol) in THF (20 mL). The solution was cooled to 0 °C by ice-water bath. Trimethylsilyl chloride (2.4 g, 22 mmol) was then added to the solution slowly. The cooling bath was removed, and the reaction mixture was refluxed for 6 h. Excess amount of aqueous ammonium chloride solution was added, and the resulting mixture was stirred at room temperature for 30 min. The organic layer was collected, and the aqueous layer was extracted with hexane (20 mL x 3). The combined organic portions were washed with water (10 mL x 3), washed with brine (10 mL x 1), and

(1) Tucker, C. E.; Davidson, J.; Knochel, P. *J. Org. Chem.* **1992**, *57*, 3484.

(2) Usón, R.; Oro, L. A.; Cabeza, J. A. *Inorg. Synth.* **1985**, *23*, 126.

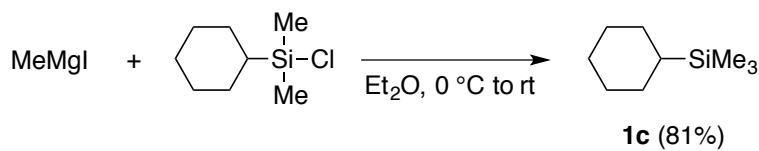
(3) Butler, I. R.; Cullen, W. R.; Kim, T.-J.; Rettig, S. J.; Trotter, J. *Organometallics* **1985**, *4*, 972.

(4) Gilman, H.; Harrell, R. L. *J. Organomet. Chem.* **1966**, *5*, 201.

(5) Gilman, H.; Tomasi, R. A. *J. Org. Chem.* **1963**, *28*, 1651.

dried over anhydrous magnesium sulfate. After removal of the volatiles by a rotary evaporator, the crude product was distilled under reduced pressure (70.0-71.0 °C/13 mmHg) to afford **1a** (2.9 g, 15 mmol, 77%) as a colorless oil. **1a**<sup>6</sup>: <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 1.23-1.34 (m, 12H), 0.88 (t, *J* = 6.8 Hz, 3H), 0.45-0.51 (m, 2H), -0.03 (s, 9H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 33.7, 32.0, 29.4, 29.3, 23.9, 22.7, 16.7, 14.1, -1.6.

### Cyclohexyltrimethylsilane (**1c**)

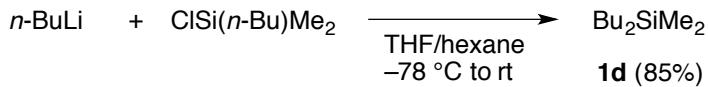


In a 200 mL three neck flask, a solution of methylmagnesium iodide was prepared from iodomethane (3.1 g, 22 mmol) with magnesium turnings (0.54 g, 22 mmol) in Et<sub>2</sub>O (25 mL). The solution was cooled to 0 °C by ice-water bath. Cyclohexyldimethylsilyl chloride (3.5 g, 20 mmol) was then added to the solution slowly. The cooling bath was removed, and the reaction mixture was allowed to warm to room temperature. After stirring at that temperature for 8 h, excess amount of aqueous ammonium chloride solution was added, and the resulting mixture was stirred at room temperature for 30 min. The organic layer was collected, and the aqueous layer was extracted with hexane (20 mL x 3). The combined organic portions were washed with water (10 mL x 3), washed with brine (10 mL x 1), and dried over anhydrous magnesium sulfate. After removal of the volatiles by a rotary evaporator, the crude product was distilled under reduced pressure (48.5-49.0 °C/9 mmHg) to afford **1c** (2.5 g, 16 mmol, 81%) as a colorless oil. **1c**<sup>7</sup>: <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 1.62-1.76 (m, 5H), 0.98-1.28 (m, 5H), 0.53 (tt, *J* = 12.8, 3.2 Hz, 1H), -0.07 (s, 9H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 28.1, 27.4, 27.0, 26.2, -3.6.

(6) Yus, M.; Herrera, R. P.; Guijarro, A. *Chem. Eur. J.* **2002**, 8, 2574.

(7) Daniel, R. G.; Paquette, L. A. *J. Org. Chem.* **1981**, 46, 2901.

### Dibutyldimethylsilane (**1d**)



Butyldimethylsilyl chloride (6.0 g, 40 mmol) and THF (40 mL) were charged in a 300 mL three neck flask. The solution was cooled to  $-78\text{ }^\circ\text{C}$  by dryice-acetone bath. A hexane solution of *n*-butyllithium (nacalai, 1.6 M, 28 mL, 44 mmol) was then added to the solution slowly. After stirring for 30 min, the cooling bath was removed, and the reaction mixture was allowed to warm to room temperature. After stirring at that temperature for 2 h, excess amount of aqueous ammonium chloride solution was added, and the resulting mixture was stirred at room temperature for 30 min. The organic layer was collected, and the aqueous layer was extracted with  $\text{Et}_2\text{O}$  (40 mL x 3). The combined organic portions were washed with water (20 mL x 3), washed with brine (20 mL x 1), and dried over anhydrous magnesium sulfate. After removal of the volatiles by a rotary evaporator, the crude product was distilled under reduced pressure (90.0-91.5  $^\circ\text{C}$ /30 mmHg) to afford **1d** (5.9 g, 34 mmol, 85%) as a colorless oil. **1d**<sup>8</sup>:  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  1.22-1.37 (m, 8H), 0.88 (t,  $J = 6.8\text{ Hz}$ , 6H), 0.45-0.51 (m, 4H), -0.06 (s, 6H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  26.7, 26.2, 15.0, 13.8, -3.4.

### Tributylmethylsilane (**1e**)



Trichloro(methyl)silane (2.4 g, 16 mmol) and THF (20 mL) were charged in a 200 mL three neck flask. The solution was cooled to  $-78\text{ }^\circ\text{C}$  by dryice-acetone bath. A hexane solution of *n*-butyllithium (nacalai, 1.6 M, 40 mL, 64 mmol) was then added to the solution slowly. After stirring for 15 min, the cooling bath was removed, and the reaction mixture was allowed to warm to room temperature. After stirring at that temperature for 2 h, excess amount of aqueous ammonium chloride solution was added, and the resulting mixture was stirred at room temperature for 30 min. The organic layer was collected, and the aqueous

(8) Jones, P. R.; Cheng, A. H.-B.; Albanesi, T. E. *Organometallics* **1984**, 3, 78.

layer was extracted with hexane (20 mL x 3). The combined organic portions were washed with water (10 mL x 3), washed with brine (10 mL x 1), and dried over anhydrous magnesium sulfate. After removal of the volatiles by a rotary evaporator, the crude product was distilled under reduced pressure (77.0-77.5 °C/3 mmHg) to afford **1e** (2.4 g, 11 mmol, 69%) as a colorless oil. **1e**<sup>9</sup>: <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 1.20-1.37 (m, 12H), 0.88 (t, *J* = 6.8 Hz, 9H), 0.45-0.51 (m, 6H), -0.08 (s, 3H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 26.8, 26.2, 13.8, 13.6, -5.2.

### Bis(trimethylsilyl)methane (**1f**)

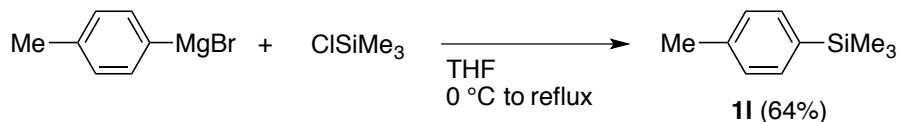


In a 300 mL three neck flask, a solution of (trimethylsilyl)methylmagnesium chloride was prepared from (chloromethyl)trimethylsilane (6.8 g, 55 mmol) with magnesium turnings (1.3 g, 55 mmol) in THF (55 mL). The solution was cooled to 0 °C by ice-water bath. Trimethylsilyl chloride (5.4 g, 50 mmol) was then added to the solution slowly. The cooling bath was removed, and the reaction mixture was allowed to warm to room temperature. After stirring at that temperature for 4 h, excess amount of aqueous ammonium chloride solution was added, and the resulting mixture was stirred at room temperature for 30 min. The organic layer was collected, and the aqueous layer was extracted with Et<sub>2</sub>O (50 mL x 3). The combined organic portions were washed with water (20 mL x 3), washed with brine (20 mL x 1), and dried over anhydrous magnesium sulfate. After removal of the volatiles by a rotary evaporator, the crude product was distilled under reduced pressure (78.0-79.5 °C/100 mmHg) to afford **1f** (4.3 g, 27 mmol, 53%) as a colorless oil. **1f**<sup>10</sup>: <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 0.02 (s, 18H), -0.27 (s, 2H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 4.3, 1.3.

(9) Boudin, A.; Cerveau, G.; Chuit, C.; Corriu, R. J. P.; Reye, C. *Bull. Chem. Soc. Jpn.* **1988**, 61, 101.

(10) Schmidbaur, H. *Chem. Ber.* **1964**, 97, 270.

Trimethyl(4-methylphenyl)silane (**1l**)

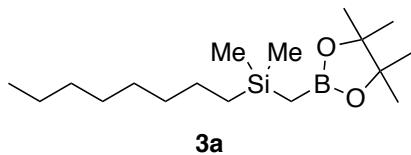


In a 200 mL three neck flask, a solution of p-tolylmagnesium bromide was prepared from 4-bromotoluene (3.4 g, 20 mmol) with magnesium turnings (0.49 g, 20 mmol) in THF (20 mL). The solution was cooled to 0 °C by ice-water bath. Trimethylsilyl chloride (2.4 g, 22 mmol) was then added to the solution slowly. The cooling bath was removed, and the reaction mixture was refluxed for 3 h. Excess amount of aqueous ammonium chloride solution was added, and the resulting mixture was stirred at room temperature for 30 min. The organic layer was collected, and the aqueous layer was extracted with hexane (20 mL x 3). The combined organic portions were washed with water (10 mL x 3), washed with brine (10 mL x 1), and dried over anhydrous magnesium sulfate. After removal of the volatiles by a rotary evaporator, the crude product was distilled under reduced pressure (89.0-90.5 °C/18 mmHg) to afford **1l** (2.1 g, 13 mmol, 64%) as a colorless oil. **1l**<sup>11</sup>: <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.43 (d, *J* = 8.0 Hz, 2H), 7.19 (d, *J* = 8.0 Hz, 2H), 2.36 (s, 3H), 0.26 (s, 9H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 138.6, 136.8, 133.4, 128.6, 21.4, -1.1.

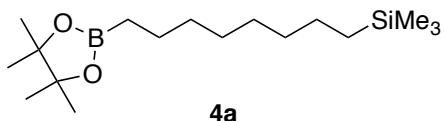
### 3. Screening of Reaction Conditions in C–H Borylation of **3a** (Table 1)

*General Procedure:* In a glove box, a glass tube having PTFE stopcock (J. Young), equipped with a magnetic stirring bar, was charged with [Ir(OMe)(cod)]<sub>2</sub> (5.0 mg, 0.0075 mmol), a ligand (0.015 mmol), bis(pinacolato)diboron (**2**) (38 mg, 0.15 mmol), cyclooctane (0.3 mL), and trimethyl(octyl)silane (**1a**) (112 mg, 0.60 mmol). The tube was sealed by the stopcock and was taken out from the glove box. The mixture was heated at 110-135 °C with stirring. After 12 h, the mixture was cooled to room temperature and tridecane (30 mg, 0.15 mmol, internal standard) was added. The resulting mixture was analyzed by GC to determine the yield of the borylated products and the ratio of **3a:4a**.

(11) Ball, L. T.; Green, M.; Lloyd-Jones, G. C.; Russell, C. A. *Org. Lett.* **2010**, *12*, 4724.



**Dimethyl[(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl](octyl)silane (3a, entry 2):** According to the general procedure, the reaction was carried out using  $[\text{Ir}(\text{OMe})(\text{cod})]_2$  (9.9 mg, 0.015 mmol),  $\text{Me}_4\text{phen}$  (0.030 mmol), **1a** (224 mg, 1.2 mmol), and **2** (76 mg, 0.30 mmol) in cyclooctane (0.6 mL). The title compound **3a** was obtained as a mixture of **4a** (73 mg, 78%, **3a**:**4a** = 95:5) after column chromatography on silica gel (eluent: hexane:Et<sub>2</sub>O = 20:1). **3a** and **4a** could be separated by GPC (eluent:  $\text{CHCl}_3$ ). **3a**:  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  1.22-1.33 (m, 12H), 1.23 (s, 12H), 0.88 (t,  $J$  = 6.8 Hz, 3H), 0.48-0.55 (m, 2H), 0.08 (s, 2H), 0.02 (s, 6H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  82.7, 33.6, 32.0, 29.32, 29.28, 24.9, 23.8, 22.7, 17.1, 14.1, -0.6 (C–B, broad), -1.4.  $^{11}\text{B}$  NMR (128 MHz,  $\text{CDCl}_3$ )  $\delta$  33.5. HRMS (APCI, negative)  $m/z$  calcd for  $\text{C}_{17}\text{H}_{36}\text{BO}_2\text{Si}^-$  [M – H]<sup>-</sup>: 311.2583, found: 311.2585.

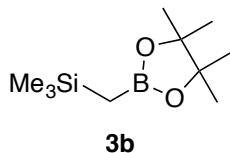


**Trimethyl[8-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)octyl]silane (4a):**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  1.35-1.44 (m, 12H), 1.20-1.32 (m, 10H), 1.24 (s, 12H), 0.76 (t,  $J$  = 8.0 Hz, 2H), 0.42-0.50 (m, 2H), -0.04 (s, 9H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  82.8, 33.6, 32.5, 29.36, 29.31, 24.8, 24.0, 23.9, 16.7, 11.2 (C–B, broad), -1.6.  $^{11}\text{B}$  NMR (128 MHz,  $\text{CDCl}_3$ )  $\delta$  33.7. HRMS (ESI, positive)  $m/z$  calcd for  $\text{C}_{17}\text{H}_{38}\text{BO}_2\text{Si}^+$  [M + H]<sup>+</sup>: 313.2729, found: 313.2733.

#### 4. Synthesis of (Borylmethyl)silanes via Iridium-Catalyzed C–H Borylation (Table 2)

*General Procedure:* In a glove box, a glass tube having PTFE stopcock (J. Young), equipped with a magnetic stirring bar, was charged with  $[\text{Ir}(\text{OMe})(\text{cod})]_2$  (9.9 mg, 0.015 mmol),  $\text{Me}_4\text{phen}$  (7.1 mg, 0.030 mmol), **2** (76 mg, 0.30 mmol), cyclooctane (0.6 mL), and **1** (1.2 mmol). The tube was sealed by the stopcock and was taken out from the glove box. The mixture was heated at 135 °C for 12 h with stirring.

After cooling to room temperature, the volatiles in the reaction mixture were removed under reduced pressure. The residue was purified by column chromatography on silica gel to afford a borylated product.

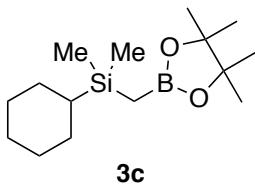


**Trimethyl[(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl]silane (3b, entry 1):** According to the general procedure, the reaction was carried out at 100 °C using **1b** (265 mg, 3.0 mmol, 10 equiv) with **2** (76 mg, 0.30 mmol). The title compound **3b** (53 mg, 82%) was obtained as a colorless oil after column chromatography on silica gel (eluent: hexane:Et<sub>2</sub>O = 20:1). The reaction was accompanied by formation of double borylated **5** (4%), which could be separated by the chromatography. **3b**<sup>12</sup>: <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 1.23 (s, 12H), 0.10 (s, 2H), 0.05 (s, 9H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 82.7, 24.9, 0.9 (C–B, broad), 0.4. The <sup>11</sup>B NMR (128 MHz, CDCl<sub>3</sub>) δ 33.6. HRMS (ESI, positive) *m/z* calcd for C<sub>10</sub>H<sub>24</sub>BO<sub>2</sub>Si<sup>+</sup> [M + H]<sup>+</sup>: 215.1633, found: 215.1630.

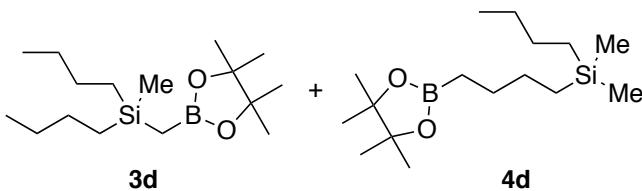


**Dimethylbis[(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl]silane (5, entry 2):** The title compound **5** (50 mg, 49%) was obtained as a colorless plate crystal from **3b** (257 mg, 1.2 mmol) with **2** (76 mg, 0.30 mmol) after column chromatography on silica gel (eluent: hexane:Et<sub>2</sub>O = 20:1 to recover **3b**, and then hexane:Et<sub>2</sub>O = 5:1 to obtain **5**). Unreacted **3b** (216 mg, 1.01 mmol, 96% based on theoretical amount of remaining **3b**) was recovered. **5**: <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 1.23 (s, 24H), 0.15 (s, 4H), 0.11 (s, 6H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 82.7, 24.9, 1.4 (C–B, broad), 0.5. <sup>11</sup>B NMR (128 MHz, CDCl<sub>3</sub>) δ 33.2. HRMS (APCI, positive) *m/z* calcd for C<sub>16</sub>H<sub>35</sub>B<sub>2</sub>O<sub>4</sub>Si<sup>+</sup> [M + H]<sup>+</sup>: 341.2485, found: 341.2478.

(12) Matteson, D. S.; Majumdar, D. *Organometallics* **1983**, 2, 230.

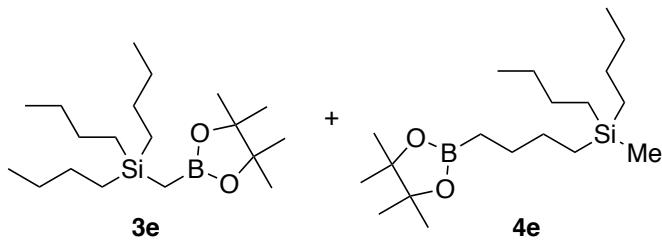


**Cyclohexyldimethyl[(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl]silane (3c, entry 3):** The title compound **3c** (60 mg, 71%) was obtained as a colorless oil from **1c** (188 mg, 1.2 mmol) with **2** (76 mg, 0.30 mmol) after column chromatography on silica gel (eluent: hexane:Et<sub>2</sub>O = 20:1). **3c:** <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 1.61-1.78 (m, 5H), 1.12-1.26 (m, 3H), 1.23 (s, 12H), 0.90-1.12 (m, 2H), 0.55 (tt, *J* = 12.8, 3.2 Hz, 1H), 0.04 (s, 2H), 0.02 (s, 6H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 82.7, 28.1, 27.2, 27.0, 26.6, 24.9, -3.4. The boron-bound carbon was not detected due to quadrupolar relaxation. <sup>11</sup>B NMR (128 MHz, CDCl<sub>3</sub>) δ 33.7. HRMS (APCI, positive) *m/z* calcd for C<sub>15</sub>H<sub>32</sub>BO<sub>2</sub>Si<sup>+</sup> [M + H]<sup>+</sup>: 283.2259, found: 283.2254.

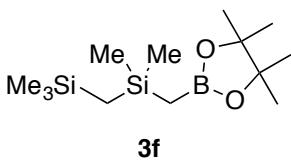


**Dibutylmethyl[(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl]silane (3d) and Butyldimethyl[4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butyl]silane (4d) (entry 4):** A mixture of **3d** and **4d** (72:28, 52 mg, 58%) was obtained from **1d** (207 mg, 1.2 mmol) with **2** (76 mg, 0.30 mmol) after column chromatography on silica gel (eluent: hexane:Et<sub>2</sub>O = 20:1). **3d** and **4d** could be separated by GPC (eluent: CHCl<sub>3</sub>). **3d:** <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 1.22-1.37 (m, 8H), 1.23 (s, 12H), 0.88 (t, *J* = 7.2 Hz, 6H), 0.50-0.56 (m, 4H), 0.06 (s, 2H), 0.00 (s, 3H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 82.6, 26.7, 26.0, 25.0, 15.3, 13.8, -2.2 (C-B, broad), -3.3. <sup>11</sup>B NMR (128 MHz, CDCl<sub>3</sub>) δ 33.6. HRMS (ESI, positive) *m/z* calcd for C<sub>16</sub>H<sub>36</sub>BO<sub>2</sub>Si<sup>+</sup> [M + H]<sup>+</sup>: 299.2573, found: 299.2575. **4d:** <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 1.38-1.47 (m, 2H), 1.20-1.33 (m, 6H), 1.24 (s, 12H), 0.87 (t, *J* = 7.2 Hz, 3H), 0.77 (t, *J* = 7.6 Hz, 2H), 0.44-0.50 (m, 4H), -0.07 (s, 6H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 82.8, 28.0, 26.64, 26.60, 26.1, 24.8, 15.1, 15.0, 13.8, 10.8 (C-B, broad), -3.4. <sup>11</sup>B NMR (128 MHz, CDCl<sub>3</sub>) δ 34.0. HRMS (ESI, positive) *m/z* calcd

for  $C_{16}H_{39}NBO_2Si^+ [M + NH_4]^+$ : 316.2841, found: 316.2839.

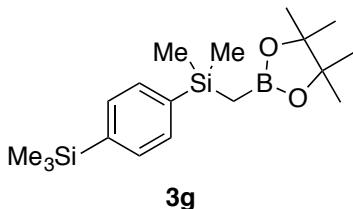


**Tributyl[(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl]silane (3e) and dibutylmethyl[4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butyl]silane (4e) (entry 5):** A mixture of **3e** and **4e** (29:71, 52 mg, 51%) was obtained from **1e** (257 mg, 1.2 mmol) with **2** (76 mg, 0.30 mmol) after column chromatography on silica gel (hexane:Et<sub>2</sub>O = 20:1). The borylated products **3e** and **4e** could be separated by GPC (eluent: CHCl<sub>3</sub>). **3e**: <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  1.23-1.35 (m, 12H), 1.23 (s, 12H), 0.88 (t, *J* = 6.8 Hz, 9H), 0.51-0.55 (m, 6H), 0.04 (s, 2H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  82.6, 26.8, 26.0, 25.0, 13.9, 13.8, -3.8 (C-B, broad). <sup>11</sup>B NMR (128 MHz, CDCl<sub>3</sub>)  $\delta$  33.3. HRMS (APCI) *m/z* calcd for C<sub>19</sub>H<sub>42</sub>BO<sub>2</sub>Si<sup>+</sup> [M + H]<sup>+</sup>: 341.3042, found: 341.3036. **4e**: <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  1.42 (quintet, *J* = 7.2 Hz, 2H), 1.18-1.34 (m, 10H), 1.24 (s, 12H), 0.87 (t, *J* = 7.2 Hz, 6H), 0.77 (t, *J* = 7.8 Hz, 2H), 0.45-0.50 (m, 6H), -0.10 (s, 3H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  82.8, 28.2, 26.8, 26.6, 26.2, 24.8, 13.8, 13.7, 13.6, 10.9 (C-B, broad), -5.2. <sup>11</sup>B NMR (128 MHz, CDCl<sub>3</sub>)  $\delta$  33.5. HRMS (APCI, positive) *m/z* calcd for C<sub>19</sub>H<sub>42</sub>BO<sub>2</sub>Si<sup>+</sup> [M + H]<sup>+</sup>: 341.3042, found: 341.3039.



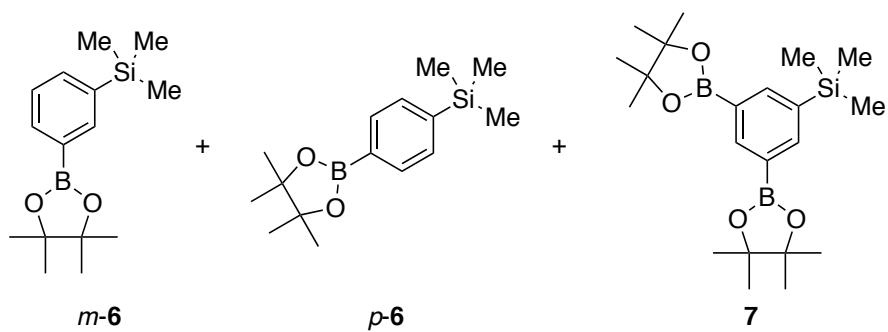
**Dimethyl(trimethylsilylmethyl)[(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl]silane (3f, entry 6):** The title compound **3f** (62 mg, 72%) was obtained as a colorless oil from **1f** (192 mg, 1.2 mmol) with **2** (76 mg, 0.30 mmol) after column chromatography on silica gel (eluent: hexane:Et<sub>2</sub>O = 20:1). **3f**: <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  1.24 (s, 12H), 0.11 (s, 2H), 0.08 (s, 6H), 0.02 (s, 9H), -0.21 (s, 2H). <sup>13</sup>C NMR

(101 MHz,  $\text{CDCl}_3$ )  $\delta$  82.7, 25.0, 4.8, 1.4, 1.3. The boron-bound carbon was not detected due to quadrupolar relaxation.  $^{11}\text{B}$  NMR (128 MHz,  $\text{CDCl}_3$ )  $\delta$  33.5. HRMS (APCI, positive)  $m/z$  calcd for  $\text{C}_{13}\text{H}_{32}\text{BO}_2\text{Si}_2^+ [\text{M} + \text{H}]^+$ : 287.2032, found: 287.2024.



**Dimethyl(4-trimethylsilylphenyl)[(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl]silane (3g)**

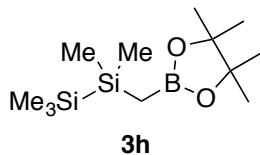
**entry 7:** The title compound **3g** (60 mg, 57%) was obtained as a colorless oil from **1g** (267 mg, 1.2 mmol) with **2** (76 mg, 0.30 mmol) after column chromatography on silica gel (eluent: hexane:Et<sub>2</sub>O = 20:1). The reaction accompanied with formation of **6** (29%, *o*:*m*:*p* = 0:62:38) and **7** (4%) (see below), which could be separated from **3g** by column chromatography. **3g:** <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.48-7.56 (m, 4H), 1.19 (s, 12 H), 0.36 (s, 2H), 0.33 (s, 6H), 0.26 (s, 9H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  140.9, 140.7, 132.7, 132.5, 82.8, 24.9, -1.0, -1.2. The boron-bound carbon was not detected due to quadrupolar relaxation. <sup>11</sup>B NMR (128 MHz, CDCl<sub>3</sub>)  $\delta$  33.3. HRMS (ESI, positive) *m/z* calcd for C<sub>18</sub>H<sub>37</sub>NBO<sub>2</sub>Si<sub>2</sub><sup>+</sup> [M + NH<sub>4</sub>]<sup>+</sup>: 366.2450, found: 366.2449.



**Trimethyl[3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl]silane (*m-6*)<sup>13</sup>:** Authentic sample of

(13) Tajuddin, H.; Harrison, P.; Bitterlich, B.; Collings, J. C.; Sim, N.; Batsanov, A. S.; Cheung, M. S.; Kawamorita, S.; Maxwell, A. C.; Shukla, L.; Morris, J.; Lin, Z.; Marder, T. B.; Steel, P. G. *Chem. Sci.* **2012**, *3*, 3505.

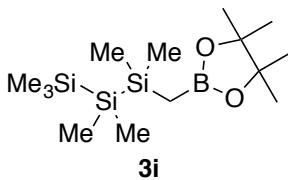
the title compound **m-6** was synthesized by borylation of phenyltrimethylsilane (**1k**) (see section 5). **m-6**: <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.96 (dt, *J* = 1.6, 0.8 Hz, 1H), 7.80 (dt, *J* = 7.2, 1.6 Hz, 1H), 7.62 (dt, *J* = 7.2, 1.6 Hz, 1H), 7.36 (dt, *J* = 7.2, 0.8 Hz, 1H), 1.35 (s, 12H), 0.28 (s, 9H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 139.6, 139.5, 136.3, 135.3, 127.0, 83.7, 24.9, -1.1. The boron-bound carbon was not detected due to quadrupolar relaxation. <sup>11</sup>B NMR (128 MHz, CDCl<sub>3</sub>) δ 30.5. HRMS (APCI, positive) *m/z* calcd for C<sub>15</sub>H<sub>26</sub>BO<sub>2</sub>Si<sup>+</sup> [M + H]<sup>+</sup>: 277.1790, found: 277.1783. **Trimethyl[4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl]silane (p-6)**<sup>13,14</sup>: Authentic sample of the title compound **p-6** was synthesized by borylation of phenyltrimethylsilane (**1k**) (see section 5). **p-6**<sup>14</sup>: <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.77-7.80 (m, 2H), 7.51-7.55 (m, 2H), 1.34 (s, 12H), 0.27 (s, 9H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 144.2, 133.8, 132.6, 83.7, 24.8, -1.3. The boron-bound carbon was not detected due to quadrupolar relaxation. <sup>11</sup>B NMR (128 MHz, CDCl<sub>3</sub>) δ 30.3. HRMS (APCI, positive) *m/z* calcd for C<sub>15</sub>H<sub>26</sub>BO<sub>2</sub>Si<sup>+</sup> [M + H]<sup>+</sup>: 277.1790, found: 277.1782. **Trimethyl[3,5-di(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl]silane (7)**<sup>13</sup>: Authentic sample of the title compound **7** was synthesized by borylation of phenyltrimethylsilane (**1k**) (see section 5). **7**: <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.27 (t, *J* = 1.6 Hz, 1H), 8.05 (d, *J* = 1.6 Hz, 2H), 1.34 (s, 24H), 0.29 (s, 9H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 142.6, 141.9, 138.5, 83.7, 24.9, -1.0. The boron-bound carbon was not detected due to quadrupolar relaxation. <sup>11</sup>B NMR (128 MHz, CDCl<sub>3</sub>) δ 30.1. HRMS (APCI, positive) *m/z* calcd for C<sub>21</sub>H<sub>37</sub>B<sub>2</sub>O<sub>4</sub>Si<sup>+</sup> [M + H]<sup>+</sup>: 403.2642, found: 403.2637.



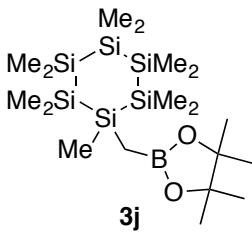
**1,1,1,2,2-Pentamethyl-2-[(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl]disilane (3h, entry 8):** The title compound **3h** (40 mg, 49%) was obtained as a colorless oil from **1h** (176 mg, 1.2 mmol) with **2**

(14) Tsoi, Y.-T.; Zhou, Z.; Yu, W.-Y. *Org. Lett.* **2011**, *13*, 5370.

(76 mg, 0.30 mmol) after column chromatography on silica gel (eluent: hexane:Et<sub>2</sub>O = 20:1). **3h**: <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  1.24 (s, 12H), 0.11 (s, 2H), 0.09 (s, 6H), 0.05 (s, 9H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  82.7, 25.0, -2.3, -2.4. The boron-bound carbon was not detected due to quadrupolar relaxation. <sup>11</sup>B NMR (128 MHz, CDCl<sub>3</sub>)  $\delta$  34.1. HRMS (APCI, negative) *m/z* calcd for C<sub>12</sub>H<sub>28</sub>BO<sub>2</sub>Si<sub>2</sub><sup>-</sup> [M - H]<sup>-</sup>: 271.1726, found: 271.1725.



**1,1,1,2,2,3,3-Heptamethyl-3-[(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl]trisilane (3i, entry 9):** The title compound **3i** (52 mg, 52%) was obtained as a colorless oil from **1i** (245 mg, 1.2 mmol) with **2** (76 mg, 0.30 mmol) after column chromatography on silica gel (eluent: hexane:Et<sub>2</sub>O = 20:1). **3i**: <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  1.24 (s, 12H), 0.139 (s, 2H), 0.136 (s, 6H), 0.08 (s, 9H), 0.07 (s, 6H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  82.8, 25.0, -1.4, -1.5, -7.0. The boron-bound carbon was not detected due to quadrupolar relaxation. <sup>11</sup>B NMR (128 MHz, CDCl<sub>3</sub>)  $\delta$  33.2. HRMS (ESI, positive) *m/z* calcd for C<sub>14</sub>H<sub>36</sub>BO<sub>2</sub>Si<sub>3</sub><sup>+</sup> [M + H]<sup>+</sup>: 331.2111, found: 331.2097.



**1,1,2,2,3,3,4,4,5,5,6-Undecamethyl-6-[(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl]cyclohexasilane (3j, entry 10):** The title compound **3j** (46 mg, 32%) was obtained as a pale yellow oil from **1j** (419 mg, 1.2 mmol) with **2** (76 mg, 0.30 mmol) after column chromatography on silica gel (eluent: hexane:Et<sub>2</sub>O = 20:1). Unreacted **1j** (363 mg, 1.04 mmol, 94% based on theoretical amount of remaining **1j**) was recovered. **3j**: <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  1.23 (s, 12H), 0.190 (s, 3H), 0.185 (s,

2H), 0.16 (s, 12H), 0.14 (s, 6H), 0.13 (s, 3H), 0.121 (s, 3H), 0.115 (s, 6H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  82.8, 25.0, -5.4, -5.7, -5.8, -6.0, -6.2, -6.40, -6.44. The boron-bound carbon was not detected due to quadrupolar relaxation.  $^{11}\text{B}$  NMR (128 MHz,  $\text{CDCl}_3$ )  $\delta$  33.3. HRMS (APCI, positive)  $m/z$  calcd for  $\text{C}_{18}\text{H}_{48}\text{BO}_2\text{Si}_6^+ [\text{M} + \text{H}]^+$ : 475.2357, found: 475.2349.

## 5. Ir/Me<sub>4</sub>phen-Catalyzed C–H Borylation of Phenyltrimethylsilane (1k) (ref. 15)

According to the general procedure described in section 4, **1k** (180 mg, 1.2 mmol) was reacted with **2** (76 mg, 0.30 mmol) in cyclooctane (0.6 mL) at 135 °C. The mono-borylated product **6** (122% based on **2**, *o:m:p* = 0:65:35) and the double-borylated product **7** (6% based on **2**) were obtained, respectively, after column chromatography on silica gel (eluent: hexane:Et<sub>2</sub>O = 20:1 to 5:1.). The *meta*- and *para*-isomers of **6** could be separated by GPC (eluent: CHCl<sub>3</sub>). Compound characterization data of *m*-**6**, *p*-**6**, and **7** are shown in section 4.

## 6. Reaction of 8, 10, 11, and 1m under the Iridium-Catalyzed C–H Borylation Conditions (eqs 1-4)

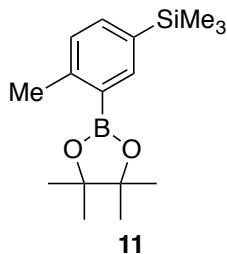
*Reaction of n-octane (8) (eq 1):* According to the general procedure described in section 4, **8** (137 mg, 1.2 mmol) was reacted with **2** (76 mg, 0.30 mmol) in cyclooctane (0.6 mL) at 135 °C. GC analysis after 12 h indicated formation of 4,4,5,5-tetramethyl-2-octyl-1,3,2-dioxaborolane (**9**)<sup>15</sup> in 17% yield (internal standard: tridecane).

*Reaction of 2,2,4,4-tetramethylpentane (10) (eq 2):* According to the general procedure described in section 4, **10** (154 mg, 1.2 mmol) was reacted with **2** (76 mg, 0.30 mmol) in cyclooctane (0.6 mL) at 135 °C. GC,  $^1\text{H}$  NMR, and  $^{11}\text{B}$  NMR analyses after 12 h indicated no formation of borylated products.

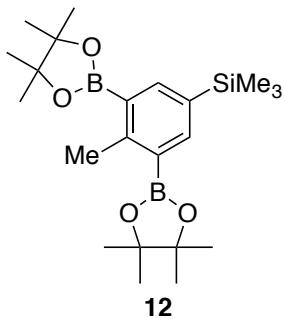
*Reaction of trimethyl(p-tolyl)silane (11) (eq 3):* According to the general procedure described in section 4, **11** (197 mg, 1.2 mmol) was reacted with **2** (76 mg, 0.30 mmol) in cyclooctane (0.6 mL) at 135 °C. Borylbenzene **11** (71 mg, 81%) and a mixture of **12**, **13**, and **3l** [34 mg, **12:13:3l** = 5:61:34, a calculated yields of **12** (2%), **13** (23%), and **3l** (13%)] were obtained, respectively, after column

(15) Liskey, C. W.; Hartwig, J. F. *J. Am. Chem. Soc.* **2012**, *134*, 12422.

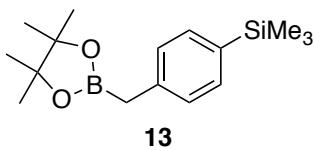
chromatography on silica gel (eluent: hexane:Et<sub>2</sub>O = 20:1). Diborylbenzene **12** and benzylboronate **13** could be isolated by GPC (eluent: CHCl<sub>3</sub>) from a mixture of **12**, **13**, and **3I**. (Borylmethyl)silane **3I** was difficult to obtain as a single compound, thus characterization of **3I** was achieved using a mixture with **13**.



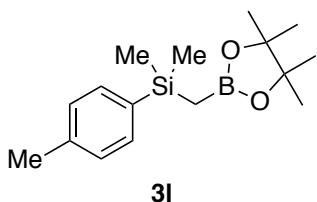
**Trimethyl[4-methyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl]silane (11):** <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.90 (d, *J* = 1.6 Hz, 1H), 7.48 (dd, *J* = 7.6, 1.6 Hz, 1H), 7.16 (d, *J* = 7.6 Hz, 1H), 2.53 (s, 3H), 1.34 (s, 12H), 0.26 (s, 9H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  145.5, 140.8, 135.9, 135.8, 129.2, 83.3, 24.9, 22.3, -1.0. The boron-bound carbon was not detected due to quadrupolar relaxation. <sup>11</sup>B NMR (128 MHz, CDCl<sub>3</sub>)  $\delta$  31.1. HRMS (APCI, positive) *m/z* calcd for C<sub>16</sub>H<sub>28</sub>BO<sub>2</sub>Si<sup>+</sup> [M + H]<sup>+</sup>: 291.1946, found: 291.1942.



**Trimethyl[4-methyl-3,5-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl]silane (12):** <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.91 (s, 2H), 2.72 (s, 3H), 1.34 (s, 24H), 0.26 (s, 9H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  151.8, 143.0, 134.4, 83.3, 24.9, 21.7, -0.9. The boron-bound carbon was not detected due to quadrupolar relaxation. <sup>11</sup>B NMR (128 MHz, CDCl<sub>3</sub>)  $\delta$  30.7. HRMS (APCI, positive) *m/z* calcd for C<sub>22</sub>H<sub>39</sub>B<sub>2</sub>O<sub>4</sub>Si<sup>+</sup> [M + H]<sup>+</sup>: 417.2798, found: 417.2794.

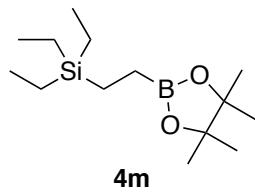


**1-Trimethylsilyl-4-[(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl]benzene (13):**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.38-7.42 (m, 2H), 7.14-7.20 (m, 2H), 2.29 (s, 2H), 1.24 (s, 12H), 0.24 (s, 9H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  139.3, 136.0, 133.4, 128.5, 83.4, 24.8, -1.0. The boron-bound carbon was not detected due to quadrupolar relaxation.  $^{11}\text{B}$  NMR (128 MHz,  $\text{CDCl}_3$ )  $\delta$  32.7. HRMS (APCI, positive)  $m/z$  calcd for  $\text{C}_{16}\text{H}_{27}\text{BO}_2\text{SiNa}^+ [\text{M} + \text{Na}]^+$ : 313.1766, found: 313.1761.



**Dimethyl[(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl](4-methylphenyl)silane (3l):**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.45 (d,  $J = 8.0$  Hz, 2H), 7.16 (d,  $J = 8.0$  Hz, 2H), 2.34, (s, 3H), 1.20 (s, 12H), 0.35 (s, 2H), 0.31 (s, 6H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  138.6, 136.6, 133.5, 128.5, 82.8, 24.9, 21.4, -0.8. The boron-bound carbon was not detected due to quadrupolar relaxation.  $^{11}\text{B}$  NMR (128 MHz,  $\text{CDCl}_3$ )  $\delta$  33.4. HRMS (APCI, positive)  $m/z$  calcd for  $\text{C}_{16}\text{H}_{27}\text{BO}_2\text{SiNa}^+ [\text{M} + \text{Na}]^+$ : 313.1766, found: 313.1760.

*Reaction of tetraethylsilane (1m) (eq 4):* According to the general procedure described in section 4, **1m** (173 mg, 1.2 mmol) was reacted with **2** (76 mg, 0.30 mmol) in cyclooctane (0.6 mL) at 135 °C. The borylated product **4m** (42 mg, 52%) was obtained as a colorless oil after column chromatography on silica gel (eluent: hexane:Et<sub>2</sub>O = 20:1).

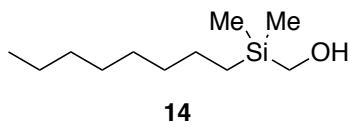


**Triethyl[2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl]silane (4m):**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  1.25 (s, 12H), 0.92 (t,  $J = 8.0$  Hz, 9H), 0.68-0.76 (m, 2H), 0.54-0.59 (m, 2H), 0.50 (q,  $J = 8.0$  Hz, 6H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  82.9, 24.8, 7.5, 3.9, 2.9. The boron-bound carbon was not

detected due to quadrupolar relaxation.  $^{11}\text{B}$  NMR (128 MHz,  $\text{CDCl}_3$ )  $\delta$  34.0. HRMS (APCI, positive)  $m/z$  calcd for  $\text{C}_{14}\text{H}_{30}\text{BO}_2\text{Si}^+ [\text{M} - \text{H}]^+$ : 269.2114, found: 269.2118.

## 7. Conversion of (Borylmethyl)silanes **3a** and **3j** (Scheme 1)

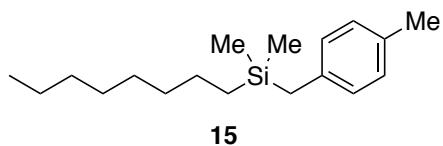
*Conversion of the C–B bond of **3a** to the C–O bond to give (hydroxymethyl)silane **14** (Scheme 1a, top):* This reaction was carried out under air. A 30 mL round-bottom flask, equipped with a magnetic stirring bar, was charged with **3a** (312 mg, 1.0 mmol) and THF (2 mL). 5N NaOH aq. (0.80 mL, 4.0 mmol) and 30%  $\text{H}_2\text{O}_2$  aq. (0.40 mL, 4.0 mmol) were then added to the flask in this order. The resulting mixture was stirred at room temperature for 4 h. After cooling to 0 °C, a saturated aqueous solution of  $\text{Na}_2\text{S}_2\text{O}_3$  (10 mL) was added slowly. The organic materials were extracted with  $\text{Et}_2\text{O}$  (10 mL x 3), and the combined organic layer was washed with water (1 mL x 3), washed with brine (1 mL x 1), and dried over anhydrous sodium sulfate. After removal of the volatiles under reduced pressure, the crude product was distilled by Kugelrohr (70 °C/0.3 mmHg) to afford **14** (200 mg, 99%) as a colorless oil.



**(Hydroxymethyl)dimethyl(octyl)silane (14):**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  3.41 (s, 2H), 1.22-1.35 (m, 12H), 0.93 (s, 1H), 0.88 (t,  $J = 6.8$  Hz, 3H), 0.56-0.60 (m, 2H), 0.04 (s, 6H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  55.6, 33.6, 31.9, 29.31, 29.26, 23.7, 22.7, 14.1, 13.5, -5.1.  $^{29}\text{Si}$  NMR (79 MHz,  $\text{CDCl}_3$ )  $\delta$  0.4. HRMS (APCI, positive)  $m/z$  calcd for  $\text{C}_{11}\text{H}_{27}\text{OSi}^+ [\text{M} + \text{H}]^+$ : 203.1826, found: 203.1824. IR (neat) 3319  $\text{cm}^{-1}$  ( $\nu_{\text{OH}}$ ).

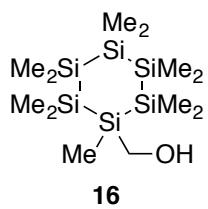
*Suzuki-Miyaura coupling of **3a** with 4-bromotoluene to give benzylic silane **15** (Scheme 1a, bottom):* In a glove box, a glass tube having PTFE stopcock (J. Young), equipped with a magnetic stirring bar, was charged with  $\text{PdCl}_2(\text{dppf})_2 \bullet \text{CH}_2\text{Cl}_2$  (16 mg, 0.020 mmol),  $\text{CsOH} \bullet \text{H}_2\text{O}$  (101 mg, 0.60 mmol), THF (1 mL), **3a** (62 mg, 0.20 mmol), 4-bromotoluene (68 mg, 0.40 mmol). The tube was sealed by the stopcock and

was taken out from the glove box. The stopcock was removed temporally under nitrogen flow. Degassed water (0.10 mL) was added to the tube and the tube was sealed by the stopcock again. The mixture was reacted at 80 °C for 24 h. After cooling to room temperature, water (10 mL) was added to the tube. The organic materials were extracted with hexane (10 mL x 3), and the combined organic layer was washed with water (1 mL x 3), washed with brine (1 mL x 1), and dried over anhydrous magnesium sulfate. After removal of the volatiles under reduced pressure, the crude product was purified by column chromatography on silica gel (eluent: hexane) to afford **15** (39 mg, 71%) as a colorless oil.



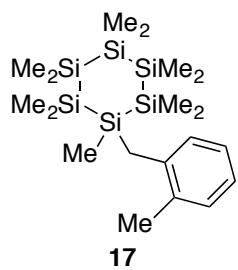
**Dimethyl(4-methylbenzyl)(octyl)silane (15):**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.02 (d,  $J$  = 8.0 Hz, 2H), 6.89 (d,  $J$  = 8.0 Hz, 2H), 2.29 (s, 3H), 2.03 (s, 2H), 1.21-1.34 (m, 12H), 0.89 (t,  $J$  = 6.8 Hz, 3H), 0.44-0.53 (m, 2H), -0.05 (s, 6H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  137.2, 133.0, 128.8, 128.0, 33.6, 31.9, 29.33, 29.27, 25.0, 23.8, 22.7, 20.9, 14.8, 14.1, -3.6.  $^{29}\text{Si}$  NMR (79 MHz,  $\text{CDCl}_3$ )  $\delta$  2.0. HRMS (EI, positive)  $m/z$  calcd for  $\text{C}_{18}\text{H}_{32}\text{Si}$  [M]: 276.2273, found: 276.2274.

*Conversion of the C–B bond of **3j** to the C–O bond to give (hydroxymethyl)silane **16** (Scheme 1b, top):* This reaction was carried out under air. A 4 mL vial, equipped with a magnetic stirring bar, was charged with **3j** (36 mg, 0.075 mmol) and THF (0.15 mL). 5N NaOH aq. (0.060 mL, 0.30 mmol) and 30%  $\text{H}_2\text{O}_2$  aq. (0.030 mL, 0.30 mmol) were then added to the vial in this order. The resulting mixture was stirred at room temperature for 8 h. After cooling to 0 °C, a saturated aqueous solution of  $\text{Na}_2\text{S}_2\text{O}_3$  (10 mL) was added slowly. The organic materials were extracted with  $\text{Et}_2\text{O}$  (10 mL x 3), and the combined organic layer was washed with water (1 mL x 3), washed with brine (1 mL x 1), and dried over anhydrous sodium sulfate. After removal of the volatiles under reduced pressure, the crude product was distilled by Kugelrohr (65 to 102 °C/0.3 mmHg) to afford **16** (21 mg, 77%) as a white solid.



**1,1,2,2,3,3,4,4,5,5,6-Undecamethyl-6-(hydroxymethyl)cyclohexasilane (16):**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  3.73 (s, 2H), 0.87 (broad s, 1H), 0.22 (s, 3H), 0.20 (s, 6H), 0.19 (s, 6H), 0.15 (s, 6H), 0.143 (s, 6H), 0.141 (s, 6H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  54.8, -5.3, -5.7, -6.0, -6.3, -6.5, -9.6.  $^{29}\text{Si}$  NMR (79 MHz,  $\text{CDCl}_3$ )  $\delta$  -40.0, -42.1, -42.3, -42.8. HRMS (ESI, negative)  $m/z$  calcd for  $\text{C}_{12}\text{H}_{35}\text{OSi}_6^-$  [M - H] $^-$ : 363.1309, found: 363.1314. IR (neat) 3325  $\text{cm}^{-1}$  ( $\nu_{\text{OH}}$ ).

*Suzuki-Miyaura coupling of **3j** with 2-bromotoluene to give **17** (Scheme 1b, bottom):* In a glove box, a glass tube having PTFE stopcock (J. Young), equipped with a magnetic stirring bar, was charged with  $\text{PdCl}_2(\text{dppf})_2 \bullet \text{CH}_2\text{Cl}_2$  (12 mg, 0.015 mmol),  $\text{Ba}(\text{OH})_2 \bullet 8\text{H}_2\text{O}$  (142 mg, 0.45 mmol), THF (0.15 mL), **3j** (71 mg, 0.15 mmol), 2-bromotoluene (77 mg, 0.45 mmol). The tube was sealed by the stopcock and was taken out from the glove box. The stopcock was removed temporally under nitrogen flow. Degassed water (0.030 mL) was added to the tube and the tube was sealed by the stopcock again. The mixture was reacted at 80 °C for 48 h. After cooling to room temperature, water (10 mL) was added to the tube. The organic materials were extracted with hexane (10 mL x 3), and the combined organic layer was washed with water (1 mL x 3), washed with brine (1 mL x 1), and dried over anhydrous magnesium sulfate. After removal of the volatiles under reduced pressure, the crude product was purified by column chromatography on silica gel (eluent: hexane) to afford **17** (32 mg, 48%) as a colorless oil. Unreacted **3j** (34 mg, 0.077 mmol, 48%) was recovered.



**1,1,2,2,3,3,4,4,5,5,6-Undecamethyl-6-(2-methylphenyl)cyclohexasilane (17):**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  6.95–7.10 (m, 4H), 2.33 (s, 2H), 2.24 (s, 3H), 0.18 (s, 6H), 0.16 (s, 6H), 0.144 (s, 3H), 0.141 (s, 3H), 0.11 (s, 6H), 0.08 (s, 3H), 0.07 (s, 6H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  139.9, 134.3, 130.1, 129.0, 125.8, 124.2, 20.4, 18.1, –4.9, –5.5, –5.6, –6.3, –6.6, –6.67, –6.69.  $^{29}\text{Si}$  NMR (79 MHz,  $\text{CDCl}_3$ )  $\delta$  –37.2, –41.2, –41.7, –42.3. HRMS (EI, positive)  $m/z$  calcd for  $\text{C}_{19}\text{H}_{42}\text{Si}_6$  [M]: 438.1902, found: 438.1911.