

Supporting Information

Iridium-Catalyzed Borylation of Secondary Benzylic C-H Bond Directed by Hydrosilane

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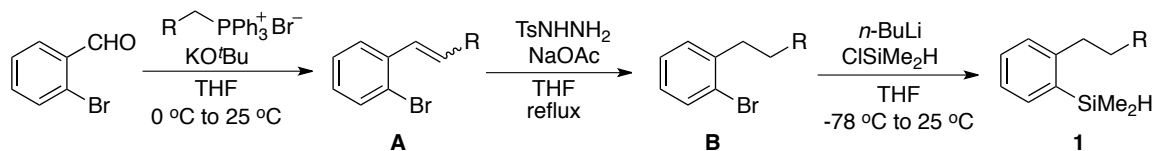
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1. General experimental details

All borylation reactions were conducted under an atmosphere of argon in an Innovative Technologies glovebox. All other reactions were conducted under a nitrogen atmosphere unless otherwise noted. The THF used for the borylation reactions was degassed by purging with argon for 45 min and then dried with a solvent purification system comprising a 1 m column containing activated alumina. $[\text{Ir}(\text{COD})\text{OMe}]_2$ was obtained from Johnson-Matthey and stored at $-35\text{ }^{\circ}\text{C}$ in the glovebox. 3,4,7,8-Tetramethylphenanthroline (Me_4phen) was purchased from Sigma-Aldrich and used as received. All reagents were purchased from commercial sources and used without further purification. 2-Bromobenzyl bromide is commercially available; other 2-bromobenzyl bromide derivatives were synthesized by published procedures.¹ Flash column chromatography was performed on Silicycle Siala-P silica gel. Borylation products were visualized on TLC plates by staining with potassium permanganate (KMnO_4). GC-MS data were obtained on an Agilent 6890-N GC system containing an Alltech EC-1 capillary column and an Agilent 5973 mass selective detector. NMR spectra were acquired on 400 MHz and 500 MHz Bruker instruments at the University of California, Berkeley NMR facility. Chemical shifts are reported in ppm relative to a residual solvent peak ($\text{CDCl}_3 = 7.26\text{ ppm}$ for ^1H and 77.16 ppm for ^{13}C). The resonances for the carbon atoms attached to boron were not observed due to the boron quadrupole. Mass spectrometric analyses were performed at the University of California, Berkeley Mass Spec Center.

2. Procedures for the preparation of starting materials

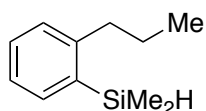
(1) Procedure for the preparation of 1a, 1b, 1d, 1e, 1j, 1l, and 1t



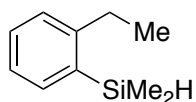
To a 100 mL round bottom flask containing a stirbar was added alkyl phosphonium bromide (6 mmol) and potassium *tert*-butoxide (6 mmol). The flask was sealed with a septum, and dry THF (25 mL) was added at 0 °C under N₂. The mixture was stirred for 30 min at room temperature at which time a solution of 2-bromobenzaldehyde (5 mmol) in THF (5 mL) was added dropwise by syringe. After 16 h, the reaction was quenched with a saturated NH₄Cl solution (15 mL) and extracted with Et₂O (15 mL x 3). The combined organic layers were washed with brine, dried over Na₂SO₄, filtered, and concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel to provide alkene (**A**) with a mixture of E and Z isomers.

To a 100 mL round bottom flask containing a stirbar was added the above obtained alkene, *p*-tosylhydrazide (5 equiv), sodium acetate trihydrate (5 equiv), and dry THF (0.3 M).² The flask was fitted with reflux condenser and heated at 80 °C for 12 h and then cooled to room temperature. The mixture was concentrated under reduced pressure to a volume of ca. 5 mL. Hexane (15 mL) was added to the reaction mixture, leading to precipitation of a solid. The solid was removed by filtration through SiO₂ and washed with hexane (15 mL x 3), followed by Et₂O (10 mL). The filtrate was concentrated under reduced pressure to give compound **B**, which was used without further purification.

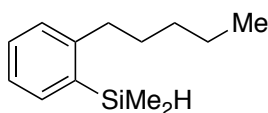
To a 50 mL round bottom flask containing a stirbar was added the above obtained 1-bromo-2-alkylbenzene (B). The flask was sealed with a septum, and dry THF (0.5 M) was added under N₂. The reaction mixture was cooled to -78 °C, at which time a solution of *n*-BuLi (1.5 equiv, 1.6 M in hexane) or *tert*-BuLi (1.5 equiv, 1.7 M in pentane) was slowly added. The reaction was stirred for 30 minutes at -78 °C, and chlorodimethylsilane (1.5 equiv) was added in one portion at the same temperature. The reaction mixture was slowly warmed to room temperature and stirred for 24 h. The reaction was quenched with a saturated NH₄Cl solution (15 mL) and extracted with Et₂O (15 mL x 3). The combined organic layers were washed with brine, dried over Na₂SO₄, filtered, and concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel to provide 2-alkylphenyl dimethylsilane derivatives (**1**).



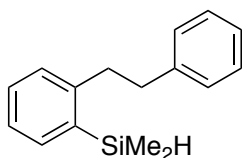
2-Propylphenyl dimethylsilane (1a): Following the general procedure, **1a** was isolated by flash column chromatography (hexane) as a pale liquid (68% in 3 steps, 606 mg); ¹H NMR (400 MHz, CDCl₃) δ 7.52 – 7.50 (m, 1H), 7.37 – 7.33 (m, 1H), 7.24 – 7.19 (m, 2H), 4.61 – 4.57 (m, 1H), 2.76 – 2.72 (m, 2H), 1.70 – 1.56 (m, 2H), 1.05 – 0.96 (t, *J* = 7.3 Hz, 3H), 0.39 – 0.38 (d, *J* = 3.8 Hz, 6H); ¹³C NMR (101 MHz, CDCl₃) δ 148.58, 135.76, 134.67, 129.42, 128.42, 125.12, 38.22, 25.48, 14.16, -2.94; HRMS (EI) calc'd for C₁₁H₁₈Si (M⁺) 178.1178, found 178.1176.



2-Ethylphenyl dimethylsilane (1b): Following the general procedure, **1b** was isolated by flash column chromatography (hexane) as a pale liquid (70% in 3 steps, 575 mg); ^1H NMR (400 MHz, CDCl_3) δ 7.52 – 7.50 (dd, $J = 7.3, 1.4$ Hz, 1H), 7.39 – 7.35 (m, 1H), 7.27 – 7.19 (m, 2H), 4.61 – 4.57 (m, 1H), 2.83 – 2.78 (q, $J = 7.5$ Hz, 2H), 1.30 – 1.26 (t, $J = 7.5$ Hz, 3H), 0.50 – 0.49 (d, $J = 3.8$ Hz, 5H); ^{13}C NMR (101 MHz, CDCl_3) δ 150.06, 135.50, 134.65, 129.65, 127.75, 125.11, 28.93, 16.29, -3.02; HRMS (EI) calc'd for $\text{C}_{10}\text{H}_{16}\text{Si}$ (M^+) 164.1021, found 164.1023.

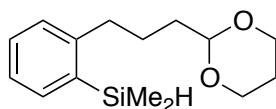


2-Pentylphenyl dimethylsilane (1d): Following the general procedure, **1d** was isolated by flash column chromatography (hexane) as a pale liquid (61% in 3 steps, 629 mg); ^1H NMR (400 MHz, CDCl_3) δ 7.56 – 7.54 (dd, $J = 7.2, 1.5$ Hz, 1H), 7.40 – 7.37 (td, $J = 7.5, 1.5$ Hz, 1H), 7.28 – 7.24 (m, 2H), 4.66 – 4.63 (m, 1H), 2.81 – 2.78 (m, 2H), 2.30 – 2.34 (m, 2H), 1.70 – 1.66 (m, 2H), 1.46 – 1.43 (m, 2H), 1.00 – 0.97 (t, $J = 7.2$ Hz, 3H), 0.44 – 0.43 (d, $J = 4.0$ Hz, 6H); ^{13}C NMR (101 MHz, CDCl_3) δ 148.91, 135.74, 134.74, 129.53, 128.47, 125.16, 36.25, 32.23, 32.05, 22.68, 14.15, -2.86; HRMS (EI) calc'd for $\text{C}_{13}\text{H}_{22}\text{Si}$ (M^+) 206.1491, found 206.1491.

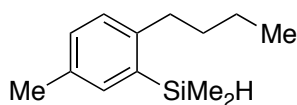


2-Phenylethylphenyl dimethylsilane (1e): Following the general procedure, **1e** was isolated by flash column chromatography (hexane) as a pale liquid (60% in 3 steps, 721 mg); ^1H NMR (400 MHz, CDCl_3) δ 7.59 – 7.57 (dd, $J = 7.4, 1.7$ Hz, 1H), 7.43 – 7.38 (m,

3H), 7.33 – 7.27 (m, 5H), 4.73 – 4.71 (m, 1H), 3.14 – 3.09 (m, 2H), 3.01 – 2.96 (m, 2H), 0.45 – 0.44 (d, $J = 3.7$, 6H); ^{13}C NMR (101 MHz, CDCl_3) δ 147.67, 141.97, 135.89, 134.82, 129.65, 128.70, 128.47, 128.43, 126.03, 125.54, 38.82, 38.33, -2.90; HRMS (EI) calc'd for $\text{C}_{16}\text{H}_{20}\text{Si}$ (M^+) 240.1334, found 240.1338.

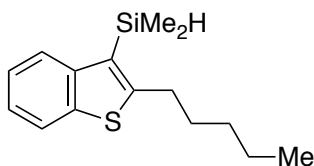


(2-(3-(1,3-Dioxan-2-yl)propyl)phenyl)dimethylsilane (1j): Following the general procedure, **1j** was isolated by flash column chromatography (hexanes:EtOAc, 100:0 to 95:5) as a pale liquid (50% in 3 steps, 661 mg); ^1H NMR (500 MHz, CDCl_3) δ 7.51 – 7.49 (dd, $J = 7.3$, 1.6 Hz, 1H), 7.36 – 7.33 (td, $J = 7.5$, 1.5 Hz, 1H), 7.25 – 7.20 (m, 2H), 4.61 – 4.57 (m, 2H), 4.16 – 4.12 (m, 2H), 3.82 – 3.76 (td, $J = 12.4$, 2.3 Hz, 2H), 2.81 – 2.78 (t, $J = 7.4$ Hz, 2H), 2.16 – 2.07 (qt, $J = 12.7$, 5.0 Hz, 1H), 1.76 – 1.76 (m, 4H), 1.38 – 1.35 (ddd, $J = 13.5$, 2.3, 1.4 Hz, 1H), 0.40 – 0.39 (d, $J = 3.9$ Hz, 6H); ^{13}C NMR (101 MHz, CDCl_3) δ 148.22, 135.76, 134.70, 129.55, 128.50, 125.27, 102.24, 66.92, 35.79, 35.08, 26.69, 25.87, -2.92; HRMS (EI) calc'd for $\text{C}_{15}\text{H}_{23}\text{O}_2\text{Si}$ ($[\text{M}-\text{H}]^+$) 263.1467, found 263.1468.



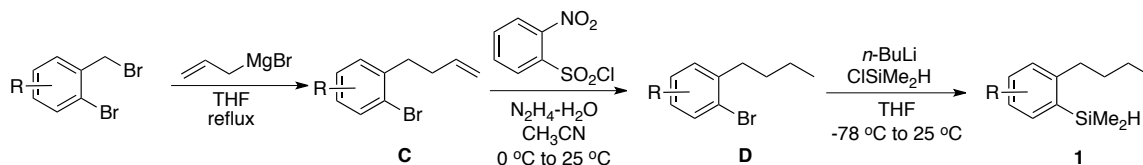
(2-Butyl-5-methylphenyl)dimethylsilane (1l): Following the general procedure, except that 2-bromo-4-methylbenzaldehyde was used in place of 2-bromobenzaldehyde, in the Wittig reaction, **1l** was isolated by flash column chromatography (hexane) as a pale liquid (70% in 3 steps, 722 mg); ^1H NMR (400 MHz, CDCl_3) δ 7.36 – 7.33 (m, 1H), 7.20 – 7.14 (dd, $J = 8.8$, 5.3 Hz, 2H), 4.63 – 4.59 (m, 1H), 2.77 – 2.73 (dd, $J = 9.1$, 7.0 Hz, 2H), 2.37

(s, 3H), 1.65 - 1.58 (m, 2H), 1.50 - 1.46 (m, 2H), 1.02 - 0.98 (t, $J = 7.3$ Hz, 3H), 0.41 - 0.40 (d, $J = 3.8$ Hz, 6H); ^{13}C NMR (101 MHz, CDCl_3) δ 145.75, 135.51, 135.37, 134.25, 130.25, 128.44, 35.39, 34.73, 22.83, 21.05, 14.06, -2.87; HRMS (EI) calc'd for $\text{C}_{13}\text{H}_{22}\text{Si}$ (M^+) 206.1491, found 206.1492.



(2-Pentylbenzothiophen-3-yl)dimethylsilane (1t): Following the general procedure, except that 3-bromobenzothiophene-2-carboxaldehyde was used in place of 2-bromobenzaldehyde, in the Wittig reaction, **1t** was isolated by flash column chromatography (hexanes:EtOAc, 100:0 to 95:5) as a yellowish liquid (54% in 3 steps, 708 mg); ^1H NMR (400 MHz, CDCl_3) δ 7.91 – 7.88 (m, 2H), 7.41 – 7.37 (dd, $J = 8.2, 7.0$ Hz, 1H), 7.34 – 7.30 (dd, $J = 8.2, 7.0$ Hz, 1H), 4.85 – 4.81 (m, 1H), 3.13 – 3.09 (t, $J = 7.8$ Hz, 2H), 1.85 – 1.77 (m, 2H), 1.48 – 1.43 (m, 4H), 1.00 – 0.97 (t, $J = 7.0$ Hz, 3H), 0.53 – 0.52 (d, $J = 3.9$ Hz, 6H); ^{13}C NMR (101 MHz, CDCl_3) δ 155.57, 144.91, 140.13, 127.91, 123.82, 123.60, 123.22, 122.02, 32.53, 31.51, 31.38, 22.55, 14.05, -2.87; HRMS (EI) calc'd for $\text{C}_{15}\text{H}_{22}\text{SSi}$ (M^+) 262.1212, found 262.1218.

(2) Procedure for the preparation of 1c, 1m, 1n, 1o, 1p, 1q, 1r, and 1s



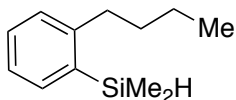
Published procedures for the synthesis of alkene from benzyl bromide³ and reduction of alkene⁴ were followed with slight modifications. To a 100 mL two-necked round bottom flask containing a stirbar was added 2-bromobenzyl bromide derivatives (5 mmol). The

flask was fitted with reflux condenser, and dry THF was added under N₂. The mixture was cooled to 0 °C, and allylmagnesium bromide (6 mmol, 1M in Et₂O) was slowly added by syringe. The solution was heated at 80 °C for 3 h and then cooled to room temperature. The resulting mixture was quenched with a saturated NH₄Cl solution (15 mL) and extracted with Et₂O (15 mL x 3). The organic layer was washed with water, dried over Na₂SO₄, filtered, and concentrated under reduced pressure to give alkene **C**, which was used without further purification.

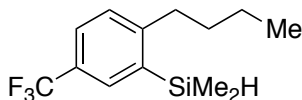
To a 50 mL round bottom flask containing a stirbar was added the above obtained alkene **C**, 2-nitrobenzenesulfonyl chloride (2 equiv) and dry CH₃CN (20 mL) under N₂. The flask was cooled to 0 °C, and hydrazine hydrate (4 equiv) was slowly added by syringe. The mixture was warmed to room temperature and stirred for 18 h. The mixture was concentrated under reduced pressure to a volume of ca. 5 mL. Hexane (15 mL) was added to the reaction mixture leading to precipitation of a solid. The solid was removed by filtration through SiO₂ and washed with hexane (15 mL x 3), followed by Et₂O (10 mL). The filtrate was concentrated under reduced pressure to give compound **D**, which was used without purification.

To a 50 mL round bottom flask containing a stirbar was added the above obtained compound **D**. The flask was sealed with a septum, and dry THF (0.5 M) was added under N₂. The reaction mixture was cooled to -78 °C, at which time a solution of *n*-BuLi (1.5 equiv, 1.6 M in hexane) or *tert*-BuLi (1.5 equiv, 1.7 M in pentane) was slowly added. The reaction was stirred for 30 minutes at -78 °C, and chlorodimethylsilane (1.5 equiv) was added at the same temperature. The reaction mixture was slowly warmed to room temperature and stirred for 24 h. The reaction was quenched with a saturated NH₄Cl solution (15 mL) and extracted with Et₂O (15 mL x 3). The combined organic layers were

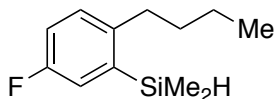
washed with brine, dried over Na₂SO₄, filtered, and concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel to provide alkylphenyl dimethylsilane derivative (**1**).



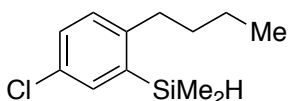
2-Butylphenyl dimethylsilane (1c): Following the general procedure, **1c** was isolated by flash column chromatography (hexane) as a pale liquid (79% in 3 steps, 760 mg); ¹H NMR (400 MHz, CDCl₃) δ 7.55 – 7.53 (dd, *J* = 7.0, 1.4 Hz, 1H), 7.41 – 7.36 (m, 1H), 7.29 – 7.23 (m, 2H), 4.66 – 4.61 (m, 1H), 2.82 – 2.78 (m, 2H), 1.71 – 1.60 (m, 2H), 1.54 – 1.45 (m, 2H), 1.04 – 1.01 (t, *J* = 7.3 Hz, 3H), 0.43 – 0.42 (d, *J* = 3.8, 6H); ¹³C NMR (101 MHz, CDCl₃) δ 148.85, 135.76, 134.73, 129.50, 128.47, 125.14, 35.93, 34.61, 22.87, 14.08, -2.88; HRMS (EI) calc'd for C₁₂H₂₀Si (M⁺) 192.1334, found 192.1339.



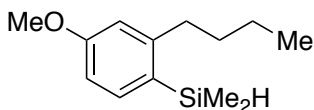
(2-Butyl-5-(trifluoromethyl)phenyl)dimethylsilane (1m): Following the general procedure, **1m** was isolated by flash column chromatography (hexane) as a pale liquid (63% in 3 steps, 820 mg); ¹H NMR (400 MHz, CDCl₃) δ 7.74 – 7.73 (d, *J* = 2.4 Hz, 1H), 7.60 – 7.54 (dd, *J* = 8.0, 2.1 Hz, 1H), 7.34 – 7.32 (d, *J* = 7.9 Hz, 1H), 4.65 - 4.60 (m, 1H), 2.83 – 2.79 (m, 2H), 1.67 – 1.60 (m, 2H), 1.51 – 1.38 (m, 2H), 1.01 - 0.98 (t, *J* = 7.3 Hz, 3H), 0.46 – 0.36 (d, *J* = 3.8, 6H); ¹³C NMR (101 MHz, CDCl₃) δ 152.78, 136.91, 131.16 (q, *J*_{C-F} = 3.7 Hz), 127.34 (q, *J*_{C-F} = 31.8 Hz), 128.55, 127.26 (q, *J*_{C-F} = 272.7 Hz), 126.13 (q, *J*_{C-F} = 3.6 Hz), 35.75, 34.22, 22.73, 13.90, -3.26.; ¹⁹F NMR (376 MHz, CDCl₃) δ -61.47; HRMS (EI) calc'd for C₁₃H₁₈F₃Si ([M-H]⁺) 259.1130, found 259.1137.



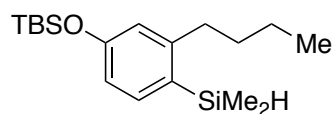
(2-Butyl-5-fluorophenyl)dimethylsilane (1n): Following the general procedure, **1n** was isolated by flash column chromatography (hexane) as a pale liquid (70% in 3 steps, 736 mg); ^1H NMR (400 MHz, CDCl_3) δ 7.18 – 7.13 (m, 2H), 7.01 – 6.96 (td, $J = 8.5, 2.8$ Hz, 1H), 4.57 – 4.53 (m, 1H), 2.72 – 2.68 (m, 2H), 1.61 – 1.54 (m, 2H), 1.46 – 1.37 (m, 2H), 0.98 – 0.94 (t, $J = 7.3$ Hz, 3H), 0.37 – 0.36 (d, $J = 3.8$ Hz, 6H); ^{13}C NMR (101 MHz, CDCl_3) δ 160.69 (d, $J_{\text{C-F}} = 245.3$ Hz), 144.19 (d, $J_{\text{C-F}} = 3.4$ Hz), 138.28 (d, $J_{\text{C-F}} = 4.0$ Hz), 129.95 (d, $J_{\text{C-F}} = 6.9$ Hz), 120.63 (d, $J_{\text{C-F}} = 18.5$ Hz), 116.01 (d, $J_{\text{C-F}} = 20.8$ Hz), 34.95, 34.63, 22.67, 13.97, -3.21; ^{19}F NMR (376 MHz, CDCl_3) δ -117.93; HRMS (EI) calc'd for $\text{C}_{12}\text{H}_{19}\text{FSi}$ (M^+) 210.1240, found 210.1244.



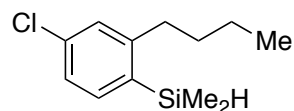
(2-Butyl-5-chlorophenyl)dimethylsilane (1o): Following the general procedure, except for the use of *tert*-BuLi in place of *n*-BuLi to introduce the hydrosilane, **1o** was isolated by flash column chromatography (hexane) as a pale liquid (78% in 3 steps, 884 mg); ^1H NMR (400 MHz, CDCl_3) δ 7.45 – 7.44 (d, $J = 2.4$ Hz, 1H), 7.32 – 7.30 (m, 1H), 7.18 – 7.16 (d, $J = 8.2$ Hz, 1H), 4.61 – 4.56 (m, 1H), 2.75 – 2.71 (m, 2H), 1.65 – 1.57 (m, 2H), 1.50 – 1.38 (m, 2H), 1.01 – 0.98 (t, $J = 7.3$ Hz, 3H), 0.41 – 0.40 (d, $J = 3.8$ Hz, 6H); ^{13}C NMR (101 MHz, CDCl_3) δ 147.01, 138.38, 134.20, 131.25, 129.98, 129.35, 35.19, 34.46, 22.73, 14.02, -3.12; HRMS (EI) calc'd for $\text{C}_{12}\text{H}_{19}\text{ClSi}$ (M^+) 226.0945, found 226.0946.



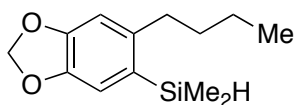
(2-Butyl-4-methoxyphenyl)dimethylsilane (1p): Following the general procedure, except for the use of *tert*-BuLi in place of *n*-BuLi to introduce the hydrosilane, **1p** was isolated by flash column chromatography (hexanes:EtOAc, 100:0 to 95:5) as a pale liquid (60% in 3 steps, 667 mg); ^1H NMR (400 MHz, CDCl_3) δ 7.36 – 7.34 (d, J = 8.1 Hz, 1H), 6.75 – 6.68 (m, 2H), 4.50 – 4.47 (m, 1H), 3.76 (s, 3H), 2.68 – 2.64 (m, 2H), 1.60 – 1.52 (m, 2H), 1.43 – 1.31 (m, 2H), 0.93 - 0.89 (t, J = 7.3 Hz, 3H), 0.30 – 0.29 (d, J = 3.8 Hz, 6H); ^{13}C NMR (101 MHz, CDCl_3) δ 160.74, 150.67, 136.09, 126.72, 114.45, 110.37, 54.90, 35.90, 34.31, 22.75, 13.96, -2.81; HRMS (EI) calc'd for $\text{C}_{13}\text{H}_{22}\text{OSi}$ (M^+) 222.1440, found 222.1444.



***tert*-Butyl(3-butyl-4-(dimethylsilyl)phenoxy)dimethylsilane (1q):** Following the general procedure, except for the use of *tert*-BuLi in place of *n*-BuLi to introduce the hydrosilane, **1q** was isolated by flash column chromatography (hexanes:EtOAc, 100:0 to 95:5) as a pale liquid (59% in 3 steps, 951 mg); ^1H NMR (400 MHz, CDCl_3) δ 7.33 – 7.31 (d, J = 7.9 Hz, 1H), 6.70 – 6.66 (m, 2H), 4.55 – 4.49 (m, 1H), 2.69 – 2.65 (m, 2H), 1.62 – 1.54 (m, 2H), 1.46 – 1.37 (m, 2H), 0.99 (s, 9H), 0.98 – 0.94 (t, J = 7.3 Hz, 3H), 0.34 – 0.33 (d, J = 3.7 Hz, 6H), 0.22 (s, 6H); ^{13}C NMR (101 MHz, CDCl_3) δ 156.89, 150.60, 135.94, 127.28, 120.21, 116.75, 35.72, 34.28, 25.66, 22.73, 18.18, 14.00, -2.78, -4.37; HRMS (EI) calc'd for $\text{C}_{18}\text{H}_{34}\text{OSi}_2$ (M^+) 322.2148, found 322.2157.

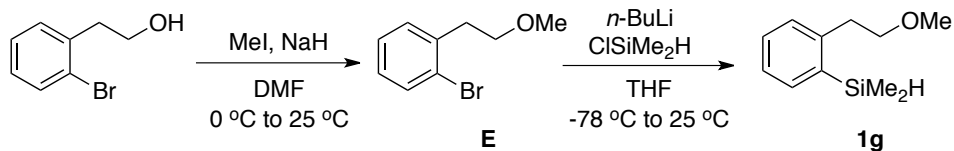


(2-Butyl-4-chlorophenyl)dimethylsilane (1r): Following the general procedure, except for the use of *tert*-BuLi in place of *n*-BuLi to introduce the hydrosilane, **1r** was isolated by flash column chromatography (hexane) as a pale liquid (70% in 3 steps, 793 mg); ^1H NMR (400 MHz, CDCl_3) δ 7.34 – 7.32 (d, J = 7.8 Hz, 1H), 7.16 – 7.09 (m, 2H), 4.51 – 4.47 (m, 1H), 2.67 – 2.63 (m, 2H), 1.58 – 1.50 (m, 2H), 1.41 – 1.32 (m, 2H), 0.92 – 0.89 (t, J = 7.3 Hz, 3H), 0.30 – 0.29 (d, J = 3.8 Hz, 6H); ^{13}C NMR (101 MHz, CDCl_3) δ 150.68, 135.92, 135.55, 134.01, 128.35, 125.19, 35.54, 34.14, 22.65, 13.91, -3.12; HRMS (EI) calc'd for $\text{C}_{12}\text{H}_{19}\text{ClSi}$ (M^+) 226.0945, found 226.0949.



(6-Butylbenzo[d][1,3]dioxol-5-yl)dimethylsilane (1s): Following the general procedure, except for the use of *tert*-BuLi in place of *n*-BuLi to introduce the hydrosilane, **1s** was isolated by flash column chromatography (hexanes:EtOAc, 100:0 to 90:10) as a pale liquid (51% in 3 steps, 602 mg); ^1H NMR (400 MHz, CDCl_3) δ 6.98 (s, 1H), 6.79 (s, 1H), 5.97 (s, 2H), 4.61 – 4.55 (m, 1H), 2.74 – 2.70 (m, 2H), 1.66 – 1.60 (m, 2H), 1.51 – 1.41 (m, 2H), 1.03 – 0.99 (t, J = 7.3 Hz, 3H), 0.40 – 0.39 (d, J = 3.8 Hz, 6H); ^{13}C NMR (101 MHz, CDCl_3) δ 148.82, 145.29, 143.49, 127.60, 113.52, 109.45, 100.62, 35.59, 34.81, 22.74, 14.07, -2.73; HRMS (EI) calc'd for $\text{C}_{13}\text{H}_{20}\text{O}_2\text{Si}$ (M^+) 236.1233, found 236.1236.

(3) Procedure for the preparation of **1g**, **1h** and **1i**

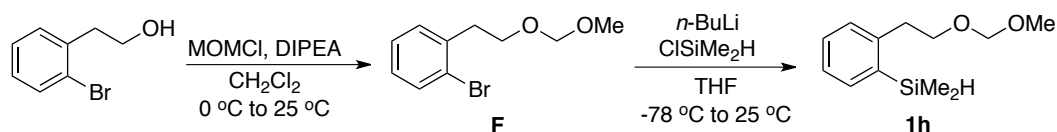


To a 50 mL round bottom flask containing a stirbar was added 2-(2-bromophenyl)ethanol (1.02 g, 5.07 mmol) and dry DMF (15 mL). The flask was cooled to 0 °C and sodium

hydride (240 mg, 6.00 mmol, 60% in mineral oil) was added in one portion. The flask was sealed with a septum and stirred for 30 min before the addition of MeI (852 mg, 6.01 mmol) by syringe at 0 °C. The reaction mixture was warmed to room temperature and stirred for 4 h. The resulting mixture was quenched with a saturated NH₄Cl solution (10 mL) and extracted with EtOAc (15 mL x 3). The combined organic layers were washed with brine, dried over Na₂SO₄, filtered, and concentrated under reduced pressure to give 1-bromo-2-(2-methoxyethyl)benzene (**E**), which was used without purification.

To a 50 mL round bottom flask containing a stirbar was added the above obtained 1-bromo-2-(2-methoxyethyl)benzene (**E**, ca. 5.00 mmol). The flask was sealed with a septum, and dry THF (10 mL) was added under N₂. The reaction mixture was cooled to –78 °C, at which time a solution of *n*-BuLi (4.68 mL, 7.50 mmol, 1.6 M in hexane) was slowly added. The reaction was stirred for 30 minutes at –78 °C, and chlorodimethylsilane (710 mg, 7.50 mmol) was added at the same temperature. The reaction mixture was slowly warmed to room temperature and stirred for 24 h. The reaction was quenched with a saturated NH₄Cl solution (15 mL), and extracted with Et₂O (15 mL x 3). The combined organic layers were washed with brine, dried over Na₂SO₄, filtered, and concentrated under reduced pressure. The crude product was purified by column chromatography (hexanes:EtOAc, 95:5) on silica gel to provide **1g** as a pale liquid (88% in 2 steps, 855 mg); ¹H NMR (400 MHz, CDCl₃) δ 7.53 – 7.51 (m, 1H), 7.37 – 7.34 (td, *J* = 7.6, 1.5 Hz, 1H), 7.27 – 7.22 (m, 2H), 4.64 – 4.60 (m, 1H), 3.64 – 3.60 (dd, *J* = 8.0, 7.1 Hz, 2H), 3.40 (s, 3H), 3.09 – 3.05 (t, *J* = 7.6 Hz, 2H), 0.40 – 0.39 (d, *J* = 3.8 Hz, 6H); ¹³C NMR (101 MHz, CDCl₃) δ 144.12, 136.46, 134.78, 129.51, 129.07, 125.75,

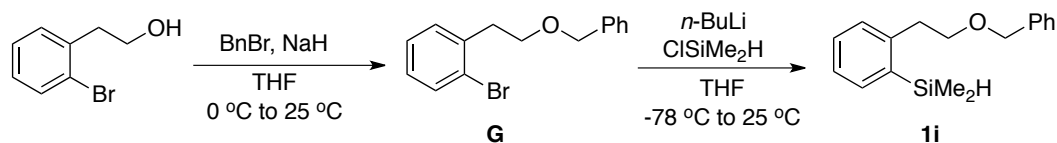
73.91, 58.66, 36.09, -3.05; HRMS (EI) calc'd for C₁₁H₁₇OSi ([M-H]⁺) 193.1049, found 193.1050.



To a 50 mL round bottom flask containing a stirbar was added 2-(2-bromophenyl)ethanol (1.02 g, 5.07 mmol) and dry CH₂Cl₂ (15 mL) under N₂. The flask was sealed with a septum, and *N,N*-diisopropylethylamine (1.42 g, 11.0 mmol) and chloromethyl methyl ether (710 mg, 7.50 mmol) were sequentially added at 0 °C. The reaction mixture was warmed to room temperature and stirred for 12 h. The resulting mixture was quenched with a saturated NH₄Cl solution (10 mL) and extracted with EtOAc (15 mL x 3). The organic layer was washed with brine, dried over Na₂SO₄, filtered, and concentrated under reduced pressure. The crude mixture was purified by column chromatography (hexanes:EtOAc, 95:5) on silica gel to provide 1-bromo-2-(2-(methoxymethoxy)ethyl)benzene (**F**, 90%, 1.10 g). ¹H NMR (500 MHz, CDCl₃) δ 7.57 – 7.55 (dd, *J* = 8.0, 1.4 Hz, 1H), 7.32 – 7.28 (m, 1H), 7.26 – 7.25 (m, 1H), 7.12 – 7.09 (td, *J* = 7.6, 1.8 Hz, 1H), 4.65 (s, 2H), 3.81 – 3.79 (t, *J* = 7.1 Hz, 2H), 3.33 (s, 3H), 3.09 – 3.07 (t, *J* = 7.1 Hz, 2H).

To a 50 mL round bottom flask containing a stirbar was added the above obtained 1-bromo-2-(2-(methoxymethoxy)ethyl)benzene (**F**, 1.10 g, 4.48 mmol). The flask was sealed with a septum, and dry THF (10 mL) was added under N₂. The reaction mixture was cooled to -78 °C, at which time a solution of *n*-BuLi (4.21 mL, 6.75 mmol, 1.6 M in hexane) was slowly added. The reaction was stirred for 30 minutes at -78 °C, and chlorodimethylsilane (640 mg, 6.76 mmol) was added in one portion at the same

temperature. The reaction mixture was slowly warmed to room temperature and stirred for 24 h. The reaction was quenched with a saturated NH_4Cl solution (15 mL) and extracted with Et_2O (15 mL x 3). The combined organic layers were washed with brine, dried over Na_2SO_4 , filtered, and concentrated under reduced pressure. The crude mixture was purified by column chromatography (hexanes: EtOAc , 90:10) on silica gel to provide compound **1h** (95%, 960 mg); ^1H NMR (400 MHz, CDCl_3) δ 7.51 – 7.49 (dd, J = 7.3, 1.5 Hz, 1H), 7.36 – 7.32 (td, J = 7.5, 1.5 Hz, 1H), 7.27 – 7.21(m, 2H), 4.65 (s, 2H), 4.64 – 4.58 (m, 1H), 3.77 – 3.74 (m, 2H), 3.34 (s, 3H), 3.09 – 3.05 (t, J = 7.5 Hz, 2H), 0.39 – 0.38 (d, J = 3.7 Hz, 6H); ^{13}C NMR (101 MHz, CDCl_3) δ 144.04, 136.50, 134.77, 129.46, 129.04, 125.75, 96.29, 68.70, 55.13, 36.16, -3.06; HRMS (EI) calc'd for $\text{C}_{12}\text{H}_{19}\text{O}_2\text{Si}$ ($[\text{M}-\text{H}]^+$) 223.1154, found 223.1155.

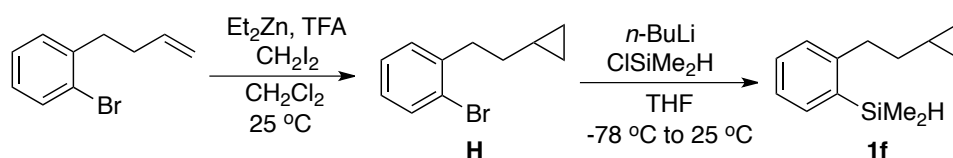


To a 50 mL round bottom flask containing a stirbar was added 2-(2-bromophenyl)ethanol (1.02 g, 5.07 mmol) and dry THF (15 mL). The flask was cooled to 0 °C, and sodium hydride (240 mg, 6.00 mmol, 60% in mineral oil) was added in one portion. The flask was sealed with a septum and stirred for 30 min before the addition of benzyl bromide (860 mg, 5.03 mmol) by syringe at 0 °C. The reaction mixture was warmed to room temperature and stirred for 4 h. The resulting mixture was quenched with a saturated NH_4Cl solution (10 mL) solution and extracted with EtOAc (15 mL x 3). The combined organic layers were washed with brine, dried over Na_2SO_4 , filtered, and concentrated under reduced pressure. The crude mixture was purified by column chromatography (hexanes: EtOAc , 90:10) on silica gel to provide 1-(2-(benzyloxy)ethyl)-2-bromobenzene

(**G**, 92%, 1.34 g). ^1H NMR (400 MHz, CDCl_3) δ 7.59 – 7.57 (dd, J = 7.9, 1.2 Hz, 1H), 7.40 – 7.26 (m, 7H), 7.15 – 7.11 (td, J = 7.6, 1.9 Hz, 1H), 4.59 (s, 2H), 3.78 – 3.75 (t, J = 7.1 Hz, 2H), 3.16 – 3.12 (t, J = 7.1 Hz, 2H)

To a 50 mL round bottom flask containing a stirbar was added the above obtained 1-(2-(benzyloxy)ethyl)-2-bromobenzene (**G**, 1.34 g, 4.60 mmol). The flask was sealed with a septum, and dry THF (10 mL) was added under N_2 . The reaction mixture was cooled to -78°C , at which time a solution of $n\text{-BuLi}$ (4.31 mL, 6.9 mmol, 1.6 M in hexane) was slowly added. The reaction was stirred for 30 minutes at -78°C , and chlorodimethylsilane (652 mg, 6.89 mmol) was added in one portion at the same temperature. The reaction mixture was slowly warmed to room temperature and stirred for 24 h. The reaction was quenched with a saturated NH_4Cl solution (15 mL), and extracted with Et_2O (15 mL x 3). The combined organic layers were washed with brine, dried over Na_2SO_4 , filtered, and concentrated under reduced pressure. The crude mixture was purified by column chromatography (hexanes: EtOAc , 90:10) on silica gel to provide compound **1i** (94%, 1.17 g) ^1H NMR (400 MHz, CDCl_3) δ 7.55 – 7.53 (dd, J = 7.1, 1.5 Hz, 1H), 7.40 – 7.36 (m, 6H), 7.31 – 7.25 (m, 2H), 4.65 – 4.61 (m, 1H), 4.60 (s, 2H), 3.75 – 3.71 (t, J = 7.6 Hz, 2H), 3.17 – 3.13 (t, J = 7.6 Hz, 2H), 0.41 – 0.40 (d, J = 3.8 Hz, 6H); ^{13}C NMR (101 MHz, CDCl_3) δ 144.22, 138.41, 136.56, 134.83, 129.52, 129.25, 128.40, 127.71, 127.60, 125.79, 73.05, 71.57, 36.36, -2.98; HRMS (EI) calc'd for $\text{C}_{17}\text{H}_{22}\text{OSi}$ ($[\text{M}-\text{H}]^+$) 269.1362, found 269.1364.

(4) Procedure for the preparation of **1f**

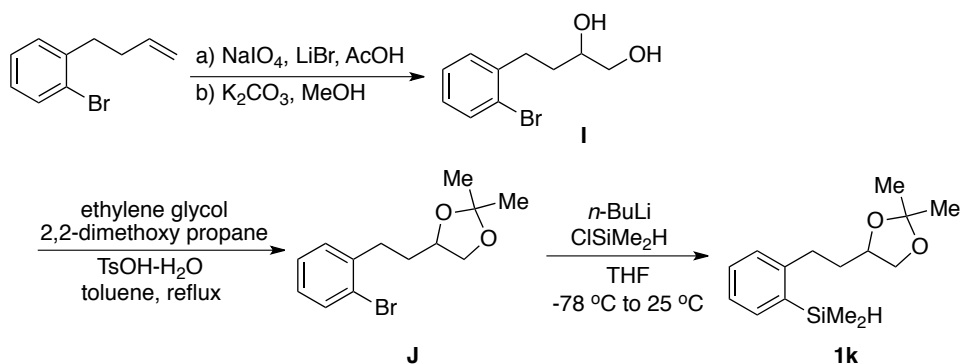


A published procedure for the synthesis of cyclopropane from alkene was followed with slight modifications.⁵ To a 250 mL round bottom flask containing a stirbar was added Et₂Zn (20.0 mmol, 1.0 M in hexanes) and dry CH₂Cl₂ (20 mL) under N₂. The solution was cooled to 0 °C, and a solution of trifluoroacetic acid (1.54 mL, 20.0 mmol) in CH₂Cl₂ (10 mL) was added dropwise into the reaction mixture by syringe. After stirring for 20 min, a solution of CH₂I₂ (1.61 mL, 20.0 mmol) in CH₂Cl₂ (10 mL) was added. After an additional 20 minutes of stirring, a solution of the alkene³ (2.11 g, 10.0 mmol) in CH₂Cl₂ (10 mL) was added, and the reaction mixture was slowly warmed to room temperature. After an additional 30 min of stirring, the reaction mixture was quenched with a 0.1 M aqueous solution of HCl (50 mL) and extracted with Et₂O (20 mL x 3). The combined organic layers were washed with brine, dried over Na₂SO₄, filtered, and concentrated under reduced pressure. The crude mixture was purified by column chromatography on silica gel (hexane) to provide 1-bromo-2-(2-cyclopropylethyl)benzene (**H**, 90%, 2.02 g). ¹H NMR (400 MHz, CDCl₃) δ 7.58 – 7.56 (m, 1H), 7.30 – 7.25 (m, 2H), 7.11 – 7.07 (ddd, *J* = 8.0, 6.1, 3.0 Hz, 1H), 2.95 – 2.90 (m, 2H), 1.64 – 1.56 (m, 2H), 0.88 – 0.79 (ddd, *J* = 12.7, 7.6, 5.2 Hz, 1H), 0.54 – 0.52 (dd, *J* = 8.1, 1.6 Hz, 2H), 0.18 – 0.14 (m, 2H).

To a 100 mL round bottom flask containing a stirbar was added the above obtained 1-bromo-2-(2-cyclopropylethyl)benzene (**H**, 2.02 g, 8.97 mmol). The flask was sealed with a septum, and dry THF (20 mL) was added under N₂. The reaction mixture was cooled to –78 °C, at which time a solution of *n*-BuLi (8.44 mL, 13.5 mmol, 1.6 M in hexane) was slowly added. The reaction was stirred for 30 minutes at –78 °C, and chlorodimethylsilane (1.28 g, 13.5 mmol) was added in one portion at the same temperature. The reaction mixture was slowly warmed to room temperature and stirred for 24 h. The reaction was quenched with a saturated NH₄Cl solution (15 mL) and

extracted with Et₂O (15 mL x 3). The combined organic layers were washed with brine, dried over Na₂SO₄, filtered, and concentrated under reduced pressure. The crude mixture was purified by column chromatography on silica gel (hexane) to provide compound **1f** (96%, 1.76 g); ¹H NMR (400 MHz, CDCl₃) δ 7.56 - 7.54 (m, 1H), 7.41 - 7.37 (m, 1H), 7.30 - 7.24 (m, 2H), 4.68 - 4.65 (m, 1H), 2.95 - 2.91 (m, 2H), 1.63 - 1.57 (m, 2H), 0.89 - 0.79 (m, 1H), 0.55 - 0.51 (m, 2H), 0.45 - 0.44 (d, *J* = 3.8 Hz, 6H), 0.18 - 0.15 (m, 2H); ¹³C NMR (101 MHz, CDCl₃) δ 148.48, 135.77, 134.70, 129.50, 128.59, 125.19, 37.57, 36.19, 11.08, 4.64, -2.86; HRMS (EI) calc'd for C₁₃H₂₀NaSi (M⁺) 204.1334, found 204.1335.

(5) Procedure for the preparation of **1k**



A published procedure for the synthesis of diol from alkene³ was followed with slight modifications.⁶ To a 50 mL round-bottom flask containing a stirbar was added alkene³ (1.06 g, 5.07 mmol), NaIO₄ (321 mg, 1.50 mmol), and LiBr (87.0 mg, 1.00 mmol). Glacial acetic acid (5 mL) was added, and the reaction mixture was heated at 95 °C for 24 h. The light yellow colored reaction mixture became purple after the completion of the reaction. The reaction was quenched with H₂O (15 mL) and extracted with EtOAc (15 mL x 3). The combined organic layers were washed with H₂O and an aqueous solution of NaHCO₃. The organic layer was dried over Na₂SO₄, and concentrated under reduced

pressure to give crude product, which was subjected to basic hydrolysis without purification. To a 100 mL round bottom flask containing a stirbar was added the above obtained crude product, K_2CO_3 (1.03 g, 7.45 mmol) and methanol (20 mL). The reaction was stirred at 25 °C for 24 h. After completion of the reaction, methanol was removed under reduced pressure, and the reaction mixture was extracted with EtOAc (15 mL x 3). The combined organic layers were dried over Na_2SO_4 , filtered, and concentrated under reduced pressure. The crude mixture was purified by column chromatography on silica gel (hexanes:EtOAc, 100:0 to 90:10) to provide diol (**I**, 56%, 686 mg). ^1H NMR (400 MHz, CDCl_3) δ 7.53 – 7.43 (d, J = 7.9 Hz, 1H), 7.27 – 7.20 (m, 2H), 7.07 – 7.03 (t, J = 7.0 Hz, 1H), 3.76 – 3.74 (d, J = 7.6 Hz, 1H), 3.69 – 3.67 (d, J = 11.0 Hz, 1H), 3.52 – 3.47 (dd, J = 11.2, 7.3 Hz, 1H), 3.06 (s, 2H), 3.95 – 2.89 (m, 1H), 2.84 – 2.78 (m, 1H), 1.75 – 1.73 (d, J = 7.9 Hz, 2H).

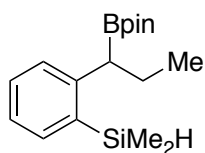
To a 50 mL round bottomed flask containing a stirbar was added the above obtained diol **I** (686 mg, 2.71 mmol), *p*-toluenesulfonic acid monohydrate (53.5 mg, 0.281 mmol), 2,2-dimethoxypropane (1 mL), and acetone (5 mL). The flask was sealed with a septum and stirred for 12 h at room temperature. The reaction was quenched with a saturated NaHCO_3 solution (15 mL) and extracted with EtOAc (15 mL x 3). The combined organic layers were dried over Na_2SO_4 , filtered, and concentrated under reduced pressure. The crude mixture was purified by column chromatography on silica gel (hexanes:EtOAc, 95:5) to provide protected diol **J** (96%, 766 mg); ^1H NMR (400 MHz, CDCl_3) δ 7.54 – 7.52 (m, 1H), 7.27 – 7.24 (m, 2H), 7.09 – 7.05 (ddd, J = 8.0, 5.5, 3.6 Hz, 1H), 4.18 – 4.13 (m, 1H), 4.08 – 4.05 (dd, J = 7.9, 6.0 Hz, 1H), 3.62 – 3.58 (dd, J = 7.9, 6.9 Hz, 1H), 2.94 – 2.86 (m, 1H), 2.80 – 2.73 (m, 1H), 1.94 – 1.83 (m, 2H), 1.45 (s, 3H), 1.38 (s, 3H).

To a 50 mL round bottom flask containing a stirbar was added the above obtained protected diol **J** (766 mg, 2.68 mmol). The flask was sealed with a septum and added dry THF (7 mL) under N₂. The reaction mixture was cooled to -78 °C, at which time a solution of *n*-BuLi (2.50 mL, 4.00 mmol, 1.6 M in hexane) was slowly added. The reaction was stirred for 30 minutes at -78 °C and chlorodimethylsilane (380 mg, 4.01 mmol) was added in one portion at the same temperature. The reaction mixture was slowly warmed to room temperature and stirred for 24 h. The reaction was quenched with a saturated NH₄Cl solution (10 mL) and extracted with Et₂O (15 mL x 3). The combined organic layers were washed with brine, dried over Na₂SO₄, filtered, and concentrated under reduced pressure. The crude mixture was purified by column chromatography on silica gel (hexanes:EtOAc, 100:0 to 95:5) to provide compound **1k** (86%, 614 mg); ¹H NMR (400 MHz, CDCl₃) δ 7.57 – 7.55 (dd, *J* = 7.2, 1.6 Hz, 1H), 7.42 – 7.38 (m, 1H), 7.30 – 7.26 (m, 2H), 4.69 – 4.66 (m, 1H), 4.28 – 4.22 (ddd, *J* = 12.8, 7.0, 5.7 Hz, 1H), 4.15 – 4.11 (dd, *J* = 7.9, 6.0 Hz, 1H), 3.67 – 3.63 (t, *J* = 7.5 Hz, 1H), 3.04 – 2.96 (ddd, *J* = 13.6, 10.9, 5.2 Hz, 1H), 2.87 – 2.80 (ddd, *J* = 13.6, 10.8, 5.9 Hz, 1H), 2.05 – 1.99 (m, 1H), 1.97 – 1.86 (m, 1H), 1.53 (s, 3H), 1.46 (s, 3H), 0.46 – 0.45 (d, *J* = 3.9 Hz, 6H); ¹³C NMR (101 MHz, CDCl₃) δ 147.51, 135.87, 134.87, 129.69, 128.59, 125.54, 108.87, 75.65, 69.35, 36.35, 32.19, 27.03, 25.78, -2.90, -2.94; HRMS (EI) calc'd for C₁₅H₂₄O₂Si (M⁺) 264.1546, found 264.1547.

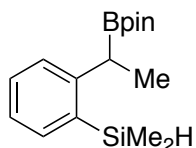
3. Procedure for the borylation of secondary benzylic C-H bond

In an N₂-filled glovebox, the 2-alkylphenyl dimethylsilane (**1**, 0.300 mmol) and B₂pin₂

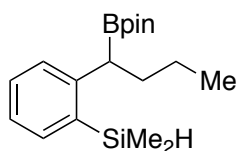
(0.300 mmol) were combined in a 4-mL vial with a stir bar. To this vial, freshly prepared stock solutions of $[\text{Ir}(\text{COD})\text{OMe}]_2$ (1.5 μmol , 0.5 mol %) in THF (0.50 mL), and a slurry of Me_4phen (3.0 μmol , 1.0 mol %) in THF (0.50 mL) were added. The vial was sealed with a Teflon-lined screw cap, and then removed from the glovebox. The vial was placed in a pre-heated aluminum block at 80 °C and stirred for the indicated period of time. The reaction progress was monitored by GC/MS or ^{11}B NMR spectroscopy. After full conversion of the reactant, the solution was filtered through a pad of Celite and concentrated under reduced pressure. The crude mixture was purified by column chromatography on silica gel to provide the pure benzylboronate ester products.



Boronate ester 2a: The reaction was performed according to the general procedure with **1a** (54.0 mg, 0.302 mmol), B_2pin_2 (76.5 mg, 0.301 mmol), $[\text{Ir}(\text{COD})\text{OMe}]_2$ (1.5 μmol , 0.5 mol %) in THF (0.50 mL), and Me_4phen (3.0 μmol , 1.0 mol %) in THF (0.5 mL) at 80 °C for 18 h. The crude mixture was purified by flash column chromatography (hexanes: Et_2O , 100:0 to 95:5) to give the boronate ester **2a** as a colorless oil (93%, 85 mg). ^1H NMR (500 MHz, CDCl_3) δ 7.51 – 7.49 (m, 1H), 7.36 – 7.34 (m, 2H), 7.19 – 7.16 (m, 1H), 4.65 – 4.62 (m, 1H), 2.57 – 2.54 (dd, J = 8.7, 6.9, 1H), 1.99 – 1.90 (m, 1H), 1.77 – 1.68 (m, 1H), 1.26 (s, 6H), 1.24 (s, 6H) 0.98 – 0.97 (t, J = 7.3 Hz, 3H), 0.43 – 0.41 (t, J = 3.6 Hz, 6H); ^{13}C NMR (126 MHz, CDCl_3) δ 149.75, 136.33, 134.76, 129.44, 127.73, 124.55, 83.18, 27.30, 24.73, 24.66, 14.01, -2.66, -2.95; ^{11}B NMR (160 MHz, CDCl_3) δ 33.60; HRMS (EI) calc'd for $\text{C}_{17}\text{H}_{29}^{11}\text{BO}_2\text{Si}$ (M^+) 304.2030, found 304.2031.

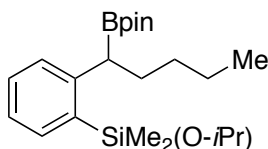


Boronate ester 2b: The reaction was performed according to the general procedure with **1b** (74.0 mg, 0.450 mmol), B₂pin₂ (76.5 mg, 0.301 mmol), [Ir(COD)OMe]₂ (1.5 μmol, 0.5 mol %) in THF (0.50 mL), and Me₄phen (3.0 μmol, 1.0 mol %) in THF (0.5 mL) at 80 °C for 18 h. The crude mixture was purified by flash column chromatography (hexanes:Et₂O, 100:0 to 95:5) to give the boronate ester **2b** as a colorless oil (73%, 64 mg). ¹H NMR (500 MHz, CDCl₃) δ 7.50 – 7.48 (dd, *J* = 7.3, 1.6 Hz, 1H), 7.38 – 7.34 (m, 1H), 7.32 – 7.28 (m, 1H), 7.19 – 7.16 (td, *J* = 7.3, 1.4 Hz, 1H), 4.62 – 4.59 (m, 1H), 2.72 – 2.68 (q, *J* = 7.4 Hz, 1H), 1.38 – 1.37 (d, *J* = 7.4 Hz, 3H), 1.26 – 1.25 (d, *J* = 8.0 Hz, 12H), 0.41 – 0.40 (d, *J* = 3.8 Hz, 6H); ¹³C NMR (126 MHz, CDCl₃) δ 151.53, 135.75, 134.75, 129.61, 127.61, 124.62, 83.27, 24.70, 24.67, 18.73, -2.84, -2.92; ¹¹B NMR (160 MHz, CDCl₃) δ 33.38; HRMS (EI) calc'd for C₁₆H₂₇¹¹BO₂Si (M⁺) 290.1873, found 290.1877.



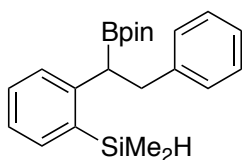
Boronate ester 2c: The reaction was performed according to the general procedure with **1c** (58.0 mg, 0.301 mmol), B₂pin₂ (76.5 mg, 0.301 mmol), [Ir(COD)OMe]₂ (1.5 μmol, 0.5 mol %) in THF (0.50 mL), and Me₄phen (3.0 μmol, 1.0 mol %) in THF (0.5 mL) at 80 °C for 18 h. The crude mixture was purified by flash column chromatography (hexanes:Et₂O, 100:0 to 95:5) to give the boronate ester **2c** as a colorless oil (80%, 76.5 mg). ¹H NMR (400 MHz, CDCl₃) δ 7.47 – 7.46 (dd, *J* = 7.2, 1.2 Hz, 1H), 7.35 – 7.31 (m, 2H), 7.16 – 7.13 (ddd, *J* = 8.1, 6.0, 2.4 Hz, 1H), 4.62 – 4.59 (m, 1H), 2.63 – 2.60 (t, *J* =

7.9 Hz, 1H), 1.91 – 1.83 (m, 1H), 1.68 – 1.60 (m, 1H), 1.39 – 1.28 (m, 2H), 1.23 (s, 6H), 1.20 (s, 6H), 0.92 – 0.89 (t, $J = 7.3$ Hz, 3H), 0.42 (dd, $J = 6.2, 3.7$ Hz, 6H); ^{13}C NMR (101 MHz, CDCl_3) δ 149.89, 136.22, 134.69, 129.42, 127.73, 124.49, 83.16, 36.40, 24.70, 24.67, 22.66, 14.43, -2.63, -2.99; ^{11}B NMR (160 MHz, CDCl_3) δ 32.61; HRMS (EI) calc'd for $\text{C}_{18}\text{H}_{31}^{11}\text{BO}_2\text{Si} (\text{M}^+)$ 318.2186, found 318.2191.

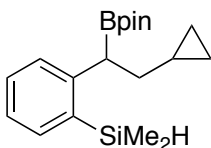


Boronate ester 2d: The reaction was performed according to the general procedure with **1d** (93.0 mg, 0.450 mmol), B_2pin_2 (76.5 mg, 0.301 mmol), $[\text{Ir}(\text{COD})\text{OMe}]_2$ (1.5 μmol , 0.5 mol %) in THF (0.50 mL), and Me_4phen (3.0 μmol , 1.0 mol %) in THF (0.5 mL) at 80 °C for 24 h. The volatile materials were removed by placing the reaction mixture directly under high vacuum for 4 h (the stir bar was temporarily removed during this operation to prevent bumping). The stir bar was replaced, and the concentrated crude mixture was then treated with $[\text{Ru}(p\text{-cymene})\text{Cl}]_2$ (0.900 mg, 1.5 μmol , 0.5 mol %) and anhydrous 2-propanol (37.0 mg, 0.615 mmol).⁷ The vial was sealed with a Teflon-lined screw cap and the resulting solution was stirred at 0 °C for 1 h (CAUTION: H_2 evolution). The reaction was filtered through a pad of Celite and concentrated under reduced pressure. The crude mixture was purified by flash column chromatography (hexanes: Et_2O , 100:0 to 95:5) to give the boronate ester **2d** as a colorless oil (70% in 2 steps, 82 mg). ^1H NMR (500 MHz, CDCl_3) δ 7.58 – 7.56 (dd, $J = 7.4, 1.5$ Hz, 1H), 7.38 – 7.36 (m, 1H), 7.34 – 7.31 (m, 1H), 7.17 – 7.14 (td, $J = 7.2, 1.4$ Hz, 1H), 4.12 – 4.04 (hept, $J = 6.0$ Hz, 1H), 2.71 – 2.67 (dd, $J = 9.8, 5.8$ Hz, 1H), 1.88 – 1.84 (m, 1H), 1.67 – 1.60 (m, 1H), 1.43 – 1.28 (m, 4H), 1.28 – 1.19 (m, 18H), 0.91 – 0.88 (t, $J = 6.9$ Hz, 3H), 0.46

(s, 3H), 0.45 (s, 3H); ^{13}C NMR (126 MHz, CDCl_3) δ 150.24, 136.70, 134.77, 129.48, 128.23, 124.26, 83.03, 65.33, 34.72, 32.04, 25.88, 25.81, 24.70, 24.67, 23.14, 14.12, 0.93, 0.70; ^{11}B NMR (160 MHz, CDCl_3) δ 32.84; HRMS (EI) calc'd for $\text{C}_{22}\text{H}_{39}^{11}\text{BO}_3\text{Si}$ (M^+) 390.2762, found 390.2764.

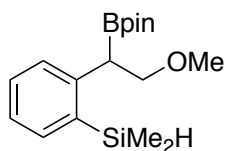


Boronate ester 2e: The reaction was performed according to the general procedure with **1e** (72.0 mg, 0.299 mmol), B_2pin_2 (76.5 mg, 0.301 mmol), $[\text{Ir}(\text{COD})\text{OMe}]_2$ (1.5 μmol , 0.5 mol %) in THF (0.50 mL), and Me_4phen (3.0 μmol , 1.0 mol %) in THF (0.5 mL) for 18 h at 80 $^\circ\text{C}$. The crude mixture was purified by flash column chromatography (hexanes: Et_2O , 100:0 to 95:5) to give the boronate ester **2e** as a colorless oil (71%, 78 mg). ^1H NMR (500 MHz, CDCl_3) δ 7.51 – 7.49 (ddd, J = 12.5, 7.6, 1.4 Hz, 2H), 7.40 – 7.36 (td, J = 7.6, 1.6 Hz, 1H), 7.27 – 7.25 (m, 4H), 7.21 – 7.17 (m, 2H), 4.68 – 4.63 (m, 1H), 3.17 – 3.12 (m, 1H), 3.03 – 2.98 (m, 2H), 1.12 (s, 12H), 0.39 – 0.38 (dd, J = 3.8, 1.9 Hz, 6H); ^{13}C NMR (126 MHz, CDCl_3) δ 148.86, 141.79, 136.46, 134.88, 129.46, 129.00, 128.17, 128.06, 125.82, 124.88, 83.29, 40.45, 24.66, 24.53, -2.63, -3.08; ^{11}B NMR (160 MHz, CDCl_3) δ 32.82; HRMS (EI) calc'd for $\text{C}_{22}\text{H}_{31}^{11}\text{BO}_2\text{Si}$ (M^+) 366.2186, found 366.2184.



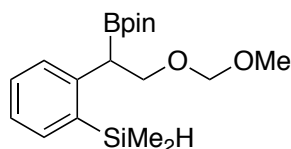
Boronate ester 2f: The reaction was performed according to the general procedure with **1f** (92.0 mg, 0.450 mmol), B_2pin_2 (76.5 mg, 0.301 mmol), $[\text{Ir}(\text{COD})\text{OMe}]_2$ (1.5 μmol , 0.5

mol %) in THF (0.50 mL), and Me₄phen (3.0 μmol, 1.0 mol %) in THF (0.5 mL) at 80 °C for 18 h. The crude mixture was purified by flash column chromatography (hexanes:Et₂O, 100:0 to 95:5) to give the boronate ester **2f** as a colorless oil (85%, 84 mg). ¹H NMR (400 MHz, CDCl₃) δ 7.48 – 7.46 (m, 1H), 7.37 – 7.29 (m, 2H), 7.18 – 7.12 (td, *J* = 7.1, 1.8 Hz, 1H), 4.68 – 4.58 (m, 1H), 2.80 – 2.72 (t, *J* = 7.8 Hz, 1H), 1.76 – 1.60 (m, 2H), 1.23 (s, 6H), 1.21 (s, 6H), 0.81 – 0.67 (m, 1H), 0.42 – 0.37 (m, 8H), 0.18 – 0.00 (m, 2H); ¹³C NMR (101 MHz, CDCl₃) δ 149.69, 136.16, 134.66, 129.31, 127.84, 124.47, 83.13, 39.34, 24.67, 24.63, 10.89, 5.18, 4.65, -2.65, -3.03; ¹¹B NMR (160 MHz, CDCl₃) δ 32.61; HRMS (EI) calc'd for C₁₉H₃₀BO₂Si ([M-H]⁺) 329.2108, found 329.2115.

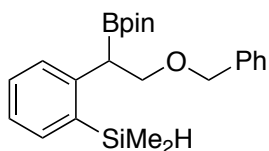


Boronate ester 2g: The reaction was performed according to the general procedure with **1g** (58.5 mg, 0.301 mmol), B₂pin₂ (76.5 mg, 0.301 mmol), [Ir(COD)OMe]₂ (1.5 μmol, 0.5 mol %) in THF (0.50 mL), and Me₄phen (3.0 μmol, 1.0 mol %) in THF (0.5 mL) at 80 °C for 18 h. The crude mixture was purified by flash column chromatography (hexanes:Et₂O, 100:0 to 90:10) to give the boronate ester **2g** as a colorless oil (95%, 91 mg). ¹H NMR (400 MHz, CDCl₃) δ 7.53 – 7.51 (dd, *J* = 7.3, 1.5 Hz, 1H), 7.47 – 7.44 (m, 1H), 7.39 – 7.35 (td, *J* = 7.6, 1.6 Hz, 1H), 7.23 – 7.19 (td, *J* = 7.3, 1.3 Hz, 1H), 4.67 – 4.63 (m, 1H), 3.81 – 3.77 (dd, *J* = 8.9, 8.0 Hz, 1H), 3.74 – 3.70 (dd, *J* = 8.9, 7.3 Hz, 1H), 3.37 (s, 3H), 3.08 – 3.05 (t, *J* = 7.6 Hz, 1H), 1.28 (s, 6H), 1.26 (s, 6H), 0.44 – 0.42 (dd, *J* = 3.7, 1.3 Hz, 6H); ¹³C NMR (101 MHz, CDCl₃) δ 146.06, 136.91, 134.90, 129.43,

128.06, 125.10, 83.43, 76.02, 58.77, 24.68, -2.77, -2.99; ^{11}B NMR (160 MHz, CDCl_3) δ 32.80; HRMS (EI) calc'd for $\text{C}_{17}\text{H}_{28}^{11}\text{BO}_3\text{Si}$ ($[\text{M}-\text{H}]^+$) 319.1901, found 319.1900.

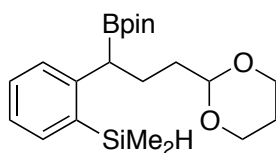


Boronate ester 2h: The reaction was performed according to the general procedure with **1h** (67.5 mg, 0.300 mmol), B_2pin_2 (76.5 mg, 0.301 mmol), $[\text{Ir}(\text{COD})\text{OMe}]_2$ (1.5 μmol , 0.5 mol %) in THF (0.50 mL), and Me_4phen (3.0 μmol , 1.0 mol %) in THF (0.5 mL) at 80 $^\circ\text{C}$ for 18 h. The crude mixture was purified by flash column chromatography (hexanes: Et_2O , 100:0 to 90:10) to give the boronate ester **2h** as a colorless oil (77%, 81 mg). ^1H NMR (400 MHz, CDCl_3) δ 7.53 – 7.51 (dd, $J = 7.4, 1.4$ Hz, 1H), 7.44 – 7.42 (dd, $J = 7.9, 1.3$ Hz, 1H), 7.38 – 7.34 (td, $J = 7.5, 1.5$ Hz, 1H), 7.23 – 7.19 (td, $J = 7.3, 1.3$ Hz, 1H), 4.69 – 4.64 (m, 2H), 4.61 – 4.60 (d, $J = 6.5$ Hz, 1H), 3.98 – 3.94 (dd, $J = 9.2, 8.0$ Hz, 1H), 3.86 – 3.82 (dd, $J = 9.2, 7.4$ Hz, 1H), 3.33 (s, 3H), 3.09 – 3.05 (t, $J = 7.7$ Hz, 1H), 1.28 (s, 6H), 1.25 (s, 6H), 0.44 – 0.42 (d, $J = 3.8$ Hz, 6H); ^{13}C NMR (101 MHz, CDCl_3) δ 145.96, 137.02, 134.94, 129.41, 128.07, 125.15, 96.35, 83.46, 70.91, 55.03, 24.73, 24.68, -2.79, -2.97; ^{11}B NMR (160 MHz, CDCl_3) δ 32.21; HRMS (EI) calc'd for $\text{C}_{18}\text{H}_{30}^{11}\text{BO}_4\text{Si}$ ($[\text{M}-\text{H}]^+$) 349.2006, found 349.2015.



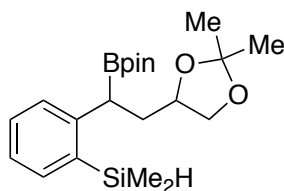
Boronate ester 2i: The reaction was performed according to the general procedure with **1i** (122 mg, 0.451 mmol), B_2pin_2 (76.5 mg, 0.301 mmol), $[\text{Ir}(\text{COD})\text{OMe}]_2$ (1.5 μmol , 0.5 mol %) in THF (0.50 mL), and Me_4phen (3.0 μmol , 1.0 mol %) in THF (0.5 mL) at 80 $^\circ\text{C}$

for 24 h. The crude mixture was purified by flash column chromatography (hexanes:Et₂O, 100:0 to 95:5) to give the boronate ester **2i** as a colorless oil (70%, 83 mg). ¹H NMR (400 MHz, CDCl₃) δ 7.50 – 7.47 (dd, *J* = 7.4, 1.5 Hz, 1H), 7.43-7.41 (m, 1H), 7.33-7.30 (m, 5H), 7.28-7.26 (m, 1H), 7.20 – 7.16 (td, *J* = 7.3, 1.2 Hz, 1H), 4.64 – 4.60 (m, 1H), 4.54 (s, 2H), 3.87 – 3.82 (t, *J* = 8.5 Hz, 1H), 3.77 – 3.73 (dd, *J* = 8.7, 6.9 Hz, 1H), 3.09 – 3.05 (t, *J* = 7.6 Hz, 1H), 1.24 (s, 6H), 1.22 (s, 6H), 0.39 – 0.38 (dd, *J* = 3.8, 1.4 Hz, 6H); ¹³C NMR (101 MHz, CDCl₃) δ 145.96, 138.77, 136.93, 134.83, 129.34, 128.20, 128.11, 127.39, 127.18, 125.05, 83.38, 73.69, 72.82, 24.66, -2.82, -3.04; ¹¹B NMR (160 MHz, CDCl₃) δ 32.75; HRMS (EI) calc'd for C₂₃H₃₂¹¹BO₃Si ([M-H]⁺) 395.2214, found 395.2218.

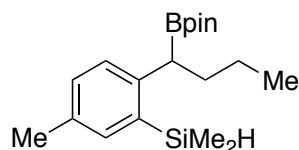


Boronate ester 2j: The reaction was performed according to the general procedure with **1j** (79.5 mg, 0.300 mmol), B₂pin₂ (76.5 mg, 0.301 mmol), [Ir(COD)OMe]₂ (1.5 μmol, 0.5 mol %) in THF (0.50 mL), and Me₄phen (3.0 μmol, 1.0 mol %) in THF (0.5 mL) at 80 °C for 24 h. The crude mixture was purified by flash column chromatography (hexanes:EtOAc, 100:0 to 95:5) to give the boronate ester **2j** as a colorless oil (74%, 87 mg). ¹H NMR (500 MHz, CDCl₃) δ 7.45 – 7.43 (m, 1H), 7.32 – 7.27 (m, 2H), 7.17 – 7.11 (m, 1H), 4.65 – 4.55 (dq, *J* = 5.3, 3.6 Hz, 1H), 4.50 – 4.44 (m, 1H), 4.13 – 4.00 (m, 2H), 3.78 – 3.66 (tt, *J* = 10.3, 2.3 Hz, 2H), 2.63 – 2.51 (t, *J* = 7.9 Hz, 1H), 2.11 – 2.00 (m, 1H), 2.00 – 1.90 (m, 1H), 1.84 – 1.73 (m, 1H), 1.71 – 1.61 (m, 1H), 1.60 – 1.51 (m, 1H), 1.35 – 1.29 (m, 1H), 1.22 (s, 6H), 1.18 (s, 6H), 0.42 – 0.35 (m, 6H); ¹³C NMR (126 MHz,

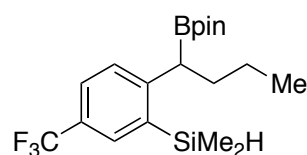
CDCl₃) δ 149.25, 136.33, 134.67, 129.48, 127.65, 124.59, 102.53, 83.21, 66.86, 34.64, 28.17, 25.83, 24.67, 24.65, -2.63, -3.07; ¹¹B NMR (160 MHz, CDCl₃) δ 33.12; HRMS (EI) calc'd for C₂₁H₃₄¹¹BO₄Si ([M-H]⁺) 389.2319, found 389.2322.



Boronate ester 2k: The reaction was performed according to the general procedure with **1k** (119 mg, 0.45 mmol), B₂pin₂ (76.5 mg, 0.301 mmol), [Ir(COD)OMe]₂ (1.5 μ mol, 0.5 mol %) in THF (0.50 mL), and Me₄phen (3.0 μ mol, 1.0 mol %) in THF (0.5 mL) at 80 °C for 36 h. The crude mixture was purified by flash column chromatography (hexanes:Et₂O, 100:0 to 90:10) to give the boronate ester **2k** as a colorless oil (63%, 74 mg). ¹H NMR (500 MHz, CDCl₃) δ 7.48 – 7.46 (ddt, *J* = 7.0, 2.2, 1.1 Hz, 1H), 7.33 – 7.32 (dt, *J* = 3.2, 1.2 Hz, 2H), 7.18 – 7.15 (ddd, *J* = 7.5, 5.3, 3.1 Hz, 1H), 4.64 – 4.59 (m, 1H), 4.13 – 4.01 (m, 1.5H), 3.82 – 3.79 (dd, *J* = 8.0, 5.8 Hz, 0.5H), 3.59 – 3.56 (t, *J* = 7.3 Hz, 0.5H), 3.39 – 3.35 (t, *J* = 7.9 Hz, 0.5H), 2.78 – 2.75 (dd, *J* = 9.0, 6.8 Hz, 0.5H), 2.72 – 2.69 (t, *J* = 7.8 Hz, 0.5H), 2.29 – 2.23 (dt, *J* = 13.6, 7.4 Hz, 0.5H), 2.10 – 2.06 (m, 0.5H), 2.02 – 1.96 (m, 0.5H), 1.91 – 1.86 (m, 0.5H), 1.42 – 1.41 (d, *J* = 3.8 Hz, 3H), 1.34 – 1.33 (d, *J* = 5.0 Hz, 3H), 1.22 – 1.19 (m, 12H), 0.42 – 0.38 (dt, *J* = 10.8, 3.8 Hz, 12H); ¹³C NMR (126 MHz, CDCl₃) δ 148.74, 148.67, 136.34, 136.22, 134.86, 134.80, 129.51, 129.42, 127.85, 127.73, 124.84, 124.82, 108.69, 108.39, 83.35, 83.33, 75.85, 75.21, 69.66, 69.51, 37.57, 37.53, 27.00, 26.99, 25.94, 25.74, 24.70, 24.67, 24.58, 24.54, 0.03, -2.63, -2.73, -3.16, -3.18; ¹¹B NMR (160 MHz, CDCl₃) δ 33.32; HRMS (EI) calc'd for C₂₀H₃₂¹¹BO₄Si ([M-CH₃]⁺) 375.2171, found 375.2172.

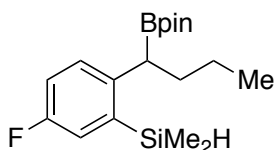


Boronate ester 2l: The reaction was performed according to the general procedure with **1l** (62.0 mg, 0.300 mmol), B₂pin₂ (76.5 mg, 0.301 mmol), [Ir(COD)OMe]₂ (1.5 μmol, 0.5 mol %) in THF (0.50 mL), and Me₄phen (3.0 μmol, 1.0 mol %) in THF (0.5 mL) at 80 °C for 18 h. The crude mixture was purified by flash column chromatography (hexanes:Et₂O, 100:0 to 95:5) to give the boronate ester **2l** as a colorless oil (81%, 80 mg). ¹H NMR (500 MHz, CDCl₃) δ 7.30 – 7.27 (d, *J* = 2.0 Hz, 1H), 7.27 – 7.23 (d, *J* = 7.9 Hz, 1H), 7.19 – 7.13 (dd, *J* = 8.0, 2.0 Hz, 1H), 4.65 – 4.57 (m, 1H), 2.63 – 2.55 (t, *J* = 7.9 Hz, 1H), 2.34 (s, 3H), 1.92 – 1.82 (m, 1H), 1.67 – 1.58 (m, 1H), 1.42 – 1.28 (m, 2H), 1.25 (s, 6H), 1.23 (s, 6H), 0.96 – 0.89 (t, *J* = 7.3 Hz, 3H), 0.41 – 0.39 (dd, *J* = 7.2, 3.7 Hz, 6H); ¹³C NMR (126 MHz, CDCl₃) δ 146.73, 135.98, 135.41, 133.49, 130.29, 127.69, 83.10, 36.57, 24.70, 24.67, 22.65, 21.10, 14.44, -2.58, -2.95; ¹¹B NMR (160 MHz, CDCl₃) δ 33.57; HRMS (EI) calc'd for C₁₉H₃₃¹¹BO₂Si (M⁺) 332.2343, found 332.2348.



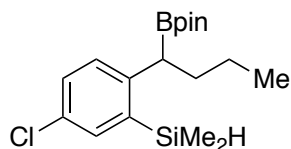
Boronate ester 2m: The reaction was performed according to the general procedure with **1m** (117 mg, 0.449 mmol), B₂pin₂ (76.5 mg, 0.301 mmol), [Ir(COD)OMe]₂ (1.5 μmol, 0.5 mol %) in THF (0.50 mL), and Me₄phen (3.0 μmol, 1.0 mol %) in THF (0.5 mL) at 80 °C for 18 h. The crude mixture was purified by flash column chromatography (hexanes:Et₂O, 100:0 to 95:5) to give the boronate ester **2m** as a colorless oil (81%, 85 mg). ¹H NMR (500 MHz, CDCl₃) δ 7.68 (s, 1H), 7.57 – 7.55 (dd, *J* = 8.1, 2.5 Hz, 1H),

7.45 – 7.43 (d, $J = 8.1$ Hz, 1H), 4.62 – 4.60 (m, 1H), 2.69 – 2.66 (t, $J = 7.7$ Hz, 1H), 1.92 – 1.86 (m, 1H), 1.68 – 1.60 (m, 1H), 1.36 – 1.21 (m, 2H), 1.25 (s, 6H), 1.21 (s, 6H), 0.92 – 0.90 (t, $J = 7.3$ Hz, 3H), 0.43 – 0.40 (dd, $J = 9.9, 3.8$ Hz, 6H); ^{13}C NMR (126 MHz, CDCl_3) δ 154.14, 137.24, 131.17 (q, $J_{\text{C-F}} = 3.0$ Hz), 127.90 (q, $J_{\text{C-F}} = 281$ Hz), 127.79, 126.21 (q, $J_{\text{C-F}} = 25$ Hz), 126.1 (q, $J_{\text{C-F}} = 3.0$ Hz), 83.42, 35.99, 24.65, 24.61, 22.54, 14.33, -2.93, -3.28; ^{11}B NMR (160 MHz, CDCl_3) δ 33.37; ^{19}F NMR (376 MHz, CDCl_3) δ -61.33; HRMS (EI) calc'd for $\text{C}_{19}\text{H}_{29}^{11}\text{BF}_3\text{O}_2\text{Si}$ ($[\text{M-H}]^+$) 385.1982, found 385.1981.

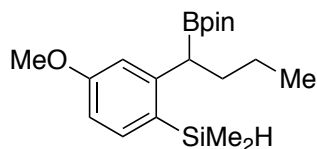


Boronate ester 2n: The reaction was performed according to the general procedure with **1n** (63.0 mg, 0.299 mmol), B_2pin_2 (76.5 mg, 0.301 mmol), $[\text{Ir}(\text{COD})\text{OMe}]_2$ (1.5 μmol , 0.5 mol %) in THF (0.50 mL), and Me_4phen (3.0 μmol , 1.0 mol %) in THF (0.5 mL) at 80 $^\circ\text{C}$ for 24 h. The crude mixture was purified by flash column chromatography (hexanes: Et_2O , 100:0 to 95:5) to give the boronate ester **2n** as a colorless oil (70%, 71 mg). ^1H NMR (400 MHz, CDCl_3) δ 7.30 – 7.26 (m, 1H), 7.12 – 7.10 (dd, $J = 9.2, 2.8$ Hz, 1H), 6.99 – 6.96 (td, $J = 8.5, 2.8$ Hz, 1H), 4.58 – 4.54 (m, 1H), 2.59 – 2.55 (t, $J = 7.8$ Hz, 1H), 1.88 – 1.78 (m, 1H), 1.60 – 1.57 (m, 1H), 1.36 – 1.28 (m, 2H), 1.21 (s, 6H), 1.19 (s, 6H), 0.91 – 0.87 (t, $J = 7.3$ Hz, 3H), 0.38 – 0.36 (dd, $J = 4.9, 3.5$ Hz, 6H); ^{13}C NMR (126 MHz, CDCl_3) δ 161.31, 159.37, 145.22 (d, $J_{\text{C-F}} = 2.0$ Hz), 138.72 (d, $J_{\text{C-F}} = 2.0$ Hz), 129.22 (d, $J_{\text{C-F}} = 5.0$ Hz), 120.57 (d, $J_{\text{C-F}} = 15.1$ Hz), 116.11 (d, $J_{\text{C-F}} = 16.1$ Hz), 83.22, 36.41, 24.66, 24.61, 22.52, 14.37, -2.91, -3.26; ^{11}B NMR (160 MHz, CDCl_3) δ 33.20; ^{19}F

NMR (376 MHz, CDCl₃) δ -117.83; HRMS (EI) calc'd for C₁₈H₃₀¹¹BFO₂Si (M⁺) 336.2092, found 336.2097.

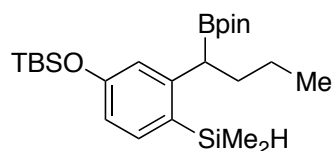


Boronate ester 2o: The reaction was performed according to the general procedure with **1o** (68.3 mg, 0.301 mmol), B₂pin₂ (76.5 mg, 0.301 mmol), [Ir(COD)OMe]₂ (1.5 μ mol, 0.5 mol %) in THF (0.50 mL), and Me₄phen (3.0 μ mol, 1.0 mol %) in THF (0.5 mL) at 80 °C for 24 h. The crude mixture was purified by flash column chromatography (hexanes:Et₂O, 100:0 to 95:5) to give the boronate ester **2o** as a colorless oil (68%, 72 mg). ¹H NMR (500 MHz, CDCl₃) δ 7.39 (d, *J* = 2.3 Hz, 1H), 7.28 (d, *J* = 2.0 Hz, 2H), 4.59 – 4.56 (m, 1H), 2.60 – 2.57 (t, *J* = 7.8 Hz, 1H), 1.89 – 1.81 (m, 1H), 1.64 – 1.60 (m, 1H), 1.37 – 1.28 (m, 2H), 1.22 (s, 6H), 1.20 (s, 6H), 0.92 – 0.89 (t, *J* = 7.4 Hz, 3H), 0.40 – 0.38 (dd, *J* = 8.0, 3.7 Hz, 6H); ¹³C NMR (126 MHz, CDCl₃) δ 148.14, 138.81, 134.13, 130.52, 129.35, 129.22, 83.29, 36.13, 24.66, 24.62, 22.51, 14.36, -2.88, -3.23; ¹¹B NMR (160 MHz, CDCl₃) δ 33.20; HRMS (EI) calc'd for C₁₈H₃₀¹¹B³⁵ClO₂Si (M⁺) 352.1797, found 352.1794.



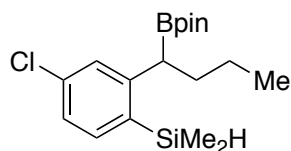
Boronate ester 2p: The reaction was performed according to the general procedure with **1p** (100 mg, 0.449 mmol), B₂pin₂ (76.5 mg, 0.301 mmol), [Ir(COD)OMe]₂ (1.5 μ mol, 0.5 mol %) in THF (0.50 mL), and Me₄phen (3.0 μ mol, 1.0 mol %) in THF (0.5 mL) at 80 °C for 24 h. The crude mixture was purified by flash column chromatography

(hexanes:Et₂O, 100:0 to 95:5) to give the boronate ester **2p** as a colorless oil (60 %, 63 mg). ¹H NMR (500 MHz, CDCl₃) δ 7.39 – 7.37 (d, *J* = 8.1 Hz, 1H), 6.93 – 6.92 (d, *J* = 2.6 Hz, 1H), 6.73 – 6.71 (dd, *J* = 8.1, 2.6 Hz, 1H), 4.59 – 4.55 (m, 1H), 3.82 (s, 3H), 2.62 – 2.59 (t, *J* = 7.7 Hz, 1H), 1.87 – 1.85 (m, 1H), 1.64 – 1.59 (m, 1H), 1.38 – 1.27 (m, 2H), 1.23 (s, 6H), 1.21 (s, 6H), 0.92 – 0.89 (t, *J* = 7.3 Hz, 3H), 0.37 – 0.35 (dd, *J* = 6.0, 3.6 Hz, 6H); ¹³C NMR (126 MHz, CDCl₃) δ 160.73, 151.84, 136.01, 127.40, 113.64, 110.17, 83.16, 54.93, 36.46, 24.73, 24.65, 22.64, 14.41, -2.46, -2.85; ¹¹B NMR (160 MHz, CDCl₃) δ 33.58; HRMS (EI) calc'd for C₁₉H₃₅¹¹BO₃Si (M⁺) 348.2292, found 348.2296.

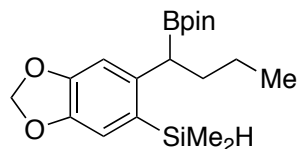


Boronate ester 2q: The reaction was performed according to the general procedure with **1q** (145 mg, 0.449 mmol), B₂pin₂ (76.5 mg, 0.301 mmol), [Ir(COD)OMe]₂ (1.5 μmol, 0.5 mol %) in THF (0.50 mL), and Me₄phen (3.0 μmol, 1.0 mol %) in THF (0.5 mL) at 80 °C for 24 h. The crude mixture was purified by flash column chromatography (hexanes:Et₂O, 100:0 to 95:5) to give the boronate ester **2q** as a colorless oil (66%, 89 mg). ¹H NMR (500 MHz, CDCl₃) δ 7.32 – 7.30 (d, *J* = 8.0 Hz, 1H), 6.87 – 6.86 (d, *J* = 2.4 Hz, 1H), 6.66 – 6.64 (dd, *J* = 8.1, 2.6 Hz, 1H), 4.56 – 4.55 (m, 1H), 2.60 – 2.57 (t, *J* = 7.8 Hz, 1H), 1.63 – 1.60 (m, 1H), 1.38 – 1.19 (m, 1H), 1.21 (s, 6H), 1.19 (s, 6H), 1.02 (s, 9H), 0.92 – 0.89 (t, 3H), 0.38 – 0.36 (dd, *J* = 5.9, 3.6 Hz, 6H), 0.24 – 0.21 (m, 6H); ¹³C NMR (126 MHz, CDCl₃) δ 156.91, 151.59, 135.85, 127.97, 119.58, 116.58, 83.11, 36.31, 25.77, 25.72, 24.80, 24.57, 22.56, 18.28, 14.41, -2.44, -2.85, -4.28, -4.32; ¹¹B NMR (160

MHz, CDCl₃) δ 33.16; HRMS (EI) calc'd for C₂₄H₄₅¹¹BO₃Si₂ (M⁺) 448.3000, found 448.3001.

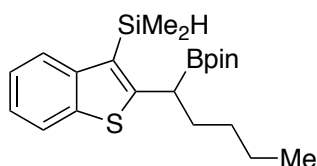


Boronate ester 2r: The reaction was performed according to the general procedure with **1r** (68.3 mg, 0.301 mmol), B₂pin₂ (76.5 mg, 0.301 mmol), [Ir(COD)OMe]₂ (1.5 μ mol, 0.5 mol %) in THF (0.50 mL), and Me₄phen (3.0 μ mol, 1.0 mol %) in THF (0.5 mL) at 80 °C for 18 h. The crude mixture was purified by flash column chromatography (hexanes:Et₂O, 100:0 to 95:5) to give the boronate ester **2r** as a colorless oil (64%, 68 mg). ¹H NMR (500 MHz, CDCl₃) δ 7.38 – 7.36 (d, *J* = 7.9 Hz, 1H), 7.33 (d, *J* = 2.1 Hz, 1H), 7.13 – 7.11 (dd, *J* = 7.9, 2.1 Hz, 1H), 4.59 – 4.56 (m, 1H), 2.61 – 2.58 (t, *J* = 7.7 Hz, 1H), 1.87 – 1.82 (m, 1H), 1.64 – 1.59 (m, 1H), 1.38 – 1.27 (m, 2H), 1.23 (s, 6H), 1.21 (s, 6H), 0.93 – 0.90 (t, *J* = 7.3 Hz, 3H), 0.38 – 0.36 (dd, *J* = 7.0, 3.7 Hz, 6H); ¹³C NMR (126 MHz, CDCl₃) δ 151.97, 135.91, 135.64, 134.54, 127.76, 124.70, 83.36, 36.07, 24.66, 24.62, 22.56, 14.35, -2.79, -3.13; ¹¹B NMR (160 MHz, CDCl₃) δ 33.06; HRMS (EI) calc'd for C₁₈H₂₉¹¹B³⁵ClO₂Si ([M-H]⁺) 351.1718, found 351.1718.



Boronate ester 2s: The reaction was performed according to the general procedure with **1s** (106 mg, 0.448 mmol), B₂pin₂ (76.5 mg, 0.301 mmol), [Ir(COD)OMe]₂ (1.5 μ mol, 0.5 mol %) in THF (0.50 mL), and Me₄phen (3.0 μ mol, 1.0 mol %) in THF (0.5 mL) at 80 °C for 24 h. The crude mixture was purified by flash column chromatography

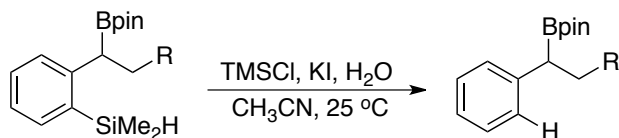
(hexanes:EtOAc, 100:0 to 90:10) to give the boronate ester **2s** as a colorless oil (50%, 54 mg). ¹H NMR (500 MHz, CDCl₃) δ 6.90 (s, 1H), 6.88 (s, 1H), 5.93 (d, *J* = 1.5 Hz, 1H), 5.92 (d, *J* = 1.5 Hz, 1H), 4.56 – 4.53 (m, 1H), 2.59 – 2.56 (t, *J* = 7.8 Hz, 1H), 1.83 – 1.79 (m, 1H), 1.60 – 1.56 (m, 1H), 1.32 – 1.29 (m, 2H), 1.23 (s, 6H), 1.21 (s, 6H), 0.91 – 0.88 (t, *J* = 7.3 Hz, 3H), 0.36 – 0.33 (dd, *J* = 7.4, 3.7 Hz, 6H); ¹³C NMR (126 MHz, CDCl₃) δ 148.80, 144.75, 144.46, 128.00, 113.45, 108.67, 100.50, 83.20, 36.51, 24.70, 24.65, 22.45, 14.41, -2.47, -2.88; ¹¹B NMR (160 MHz, CDCl₃) δ 33.34; HRMS (EI) calc'd for C₁₉H₃₁¹¹BO₄Si (M⁺) 362.2085, found 362.2091.



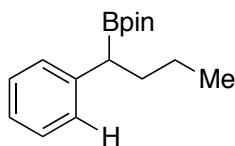
Boronate ester 2t: The reaction was performed according to the general procedure with **1t** (118 mg, 0.449 mmol), B₂pin₂ (76.5 mg, 0.301 mmol), [Ir(COD)OMe]₂ (1.5 μmol, 0.5 mol %) in THF (0.50 mL), and Me₄phen (3.0 μmol, 1.0 mol %) in THF (0.5 mL) at 80 °C for 36 h. The crude mixture was purified by flash column chromatography (hexanes:EtOAc, 100:0 to 90:10) to give the boronate ester **2t** as a colorless oil (58%, 68 mg). ¹H NMR (500 MHz, CDCl₃) δ 7.86 – 7.83 (m, 2H), 7.35 – 7.30 (ddd, *J* = 8.1, 7.1, 1.2 Hz, 1H), 7.28 – 7.23 (ddd, *J* = 8.2, 7.0, 1.2 Hz, 1H), 4.82 – 4.79 (m, 1H), 3.12 – 3.09 (dd, *J* = 9.0, 6.7 Hz, 1H), 2.00 – 1.95 (m, 1H), 1.81 – 1.75 (m, 1H), 1.40 – 1.33 (m, 4H), 1.25 (s, 6H), 1.23 (s, 6H), 0.92 – 0.87 (m, 3H), 0.50 – 0.46 (dd, *J* = 7.4, 4.0 Hz, 6H); ¹³C NMR (126 MHz, CDCl₃) δ 157.42, 144.84, 140.36, 127.38, 123.52, 123.32, 122.73, 121.95, 83.66, 33.72, 31.48, 24.68, 22.73, 14.04, -2.78, -2.83; ¹¹B NMR (160 MHz, CDCl₃) δ 32.36; HRMS (EI) calc'd for C₂₁H₃₃¹¹BSSi (M⁺) 388.2064, found 388.2068.

4. Procedure for the transformations of reaction products

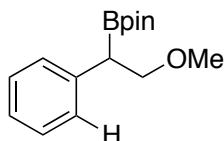
(1) Deprotection of the hydrosilane using *in situ* generated TMSI and H₂O



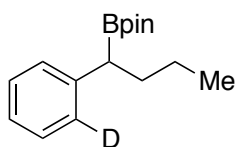
A published procedure for the deprotection of hydrosilane was followed with slight modifications.⁸ To a 4 mL vial, boronate ester **2** (0.200 mmol), KI (40.0 mg, 0.241 mmol), TMSCl (26.0 mg, 0.239 mmol), H₂O (4.30 mg, 0.239 mmol) and CH₃CN (0.4 mL) was added. The reaction was sealed with a Teflon-lined cap, and stirred 2 h at room temperature. After 2h, full conversion was observed gas chromatographic analysis. The mixture was filtered through a pad of Celite and concentrated under reduced pressure. The crude was purified by flash column chromatography to give boronate ester.



Boronate ester 3a: The general procedure was followed with **2c** (64.0 mg, 0.201 mmol) as the reagent. The crude mixture was purified by flash column chromatography (hexanes:EtOAc, 95:5) to give the boronate ester **3a** as a colorless oil (97%, 51 mg). ¹H NMR (500 MHz, CDCl₃) δ 7.30 – 7.25 (m, 2H), 7.24 – 7.22 (m, 2H), 7.17 – 7.14 (m, 1H), 2.36 – 2.23 (t, *J* = 7.9 Hz, 1H), 1.89 – 1.81 (m, 1H), 1.68 – 1.62 (m, 1H), 1.33 – 1.30 (m, 2H), 1.23 (s, 6H), 1.21 (s, 6H), 0.93 – 0.90 (t, *J* = 7.3 Hz, 3H); ¹³C NMR (126 MHz, CDCl₃) δ 143.45, 128.37, 128.22, 125.06, 83.22, 34.83, 24.64, 24.60, 22.39, 14.15; ¹¹B NMR (160 MHz, CDCl₃) δ 32.36; HRMS (EI) calc'd for C₁₆H₂₅¹¹BO₂ (M⁺) 260.1948, found 260.1950.

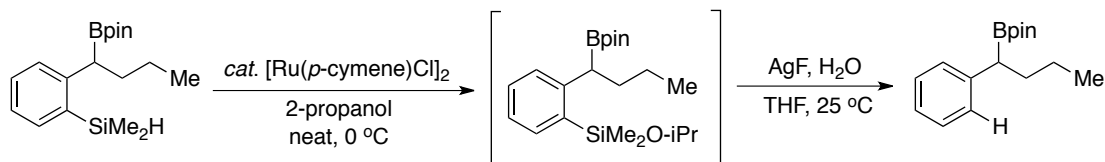


Boronate ester 3b: The general procedure was followed with **2g** (64.0 mg, 0.201 mmol) as the reagent. The crude mixture was purified by flash column chromatography (hexanes:EtOAc, 90:10) to give the boronate ester **3b** as a colorless oil (94%, 49 mg). ^1H NMR (500 MHz, CDCl_3) δ 7.31 – 7.27 (m, 4H), 7.20 – 7.17 (m, 1H), 3.79 – 3.72 (m, 2H), 3.34 (s, 3H), 2.78 – 2.75 (t, J = 7.9 Hz, 1H), 1.25 (s, 6H), 1.23 (s, 6H); ^{13}C NMR (126 MHz, CDCl_3) δ 140.10, 128.60, 128.38, 125.64, 83.50, 74.97, 58.66, 24.65, 24.59; ^{11}B NMR (160 MHz, CDCl_3) δ 32.58; HRMS (EI) calc'd for $\text{C}_{15}\text{H}_{23}^{11}\text{BO}_3$ (M^+) 262.1740, found 262.1744.



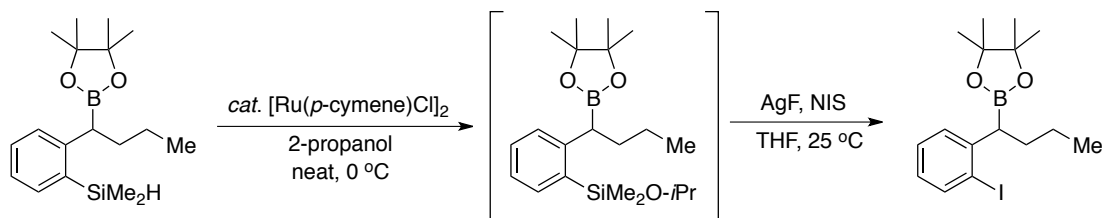
Boronate ester 3a-d: The general procedure was followed with **2c** (64.0 mg, 0.201 mmol) as the reagent, except that D_2O (4.8 mg, 0.24 mmol) was used in place of H_2O . The crude mixture was purified by flash column chromatography (hexanes:EtOAc, 95:5) to give the boronate ester **3a-d** as a colorless oil (98%, 51 mg). ^1H NMR (500 MHz, CDCl_3) δ 7.30 – 7.25 (m, 2H), 7.24 – 7.22 (m, 1H), 7.17 – 7.14 (m, 1H), 2.36 – 2.23 (t, J = 7.9 Hz, 1H), 1.89 – 1.81 (m, 1H), 1.68 – 1.62 (m, 1H), 1.33 – 1.30 (m, 2H), 1.23 (s, 6H), 1.21 (s, 6H), 0.93 - 0.90 (t, J = 7.3 Hz, 3H); ^{13}C NMR (126 MHz, CDCl_3) δ 143.45, 128.37, 128.22, 125.06, 83.22, 34.83, 24.64, 24.60, 22.39, 14.15; ^{11}B NMR (160 MHz, CDCl_3) δ 32.36.

(2) Cleavage of hydrosilane using AgF and H₂O



Published procedures for the protection of the hydrosilane⁸ and cleavage of the *O*-protected silane were followed with slight modifications.⁹ To a 4 mL vial, the boronate ester **2c** (95.5 mg, 0.300 mmol), [Ru(*p*-cymene)Cl]₂ (0.900 mg, 1.5 μmol, 0.5 mol %), and anhydrous 2-propanol (37.0 mg, 0.615 mmol) was added with a stirbar. The reaction was sealed with a Teflon-lined cap, and stirred at 0 °C for 2 h. The volatile materials were removed by placing the reaction mixture directly under high vacuum for 1 h. To this crude mixture, AgF (101 mg, 0.796 mmol), H₂O (14.4 mg, 0.800 mmol) and dry THF were sequentially added. The reaction was sealed with a Teflon-lined cap, and stirred for 12 h at room temperature. The mixture was filtered through a pad of Celite and concentrated under reduced pressure. The crude mixture was purified by flash column chromatography (hexanes:EtOAc, 95:5) to give the boronate ester **3a** as a colorless oil (65% in 2 steps, 51 mg).

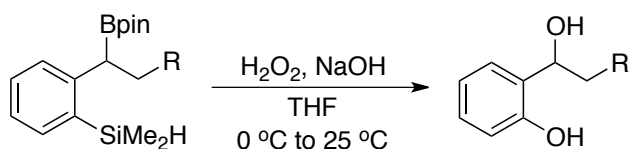
(3) Iodination of the hydrosilane



Published procedures for the protection of the hydrosilane¹ and iodination of the *O*-protected silane were followed with slight modifications.⁹ To a 4 mL vial, the boronate ester **2c** (95.5 mg, 0.300 mmol), [Ru(*p*-cymene)Cl]₂ (0.900 mg, 1.5 μmol, 0.5 mol %),

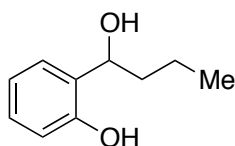
and anhydrous 2-propanol (37.0 mg, 0.615 mmol) was added with a stirbar. The reaction was sealed with a Teflon-lined cap and stirred at 0 °C for 2 h. The volatile materials were removed by placing the reaction mixture directly under high vacuum for 1 h. To this crude mixture, AgF (101 mg, 0.796 mmol), *N*-iodosuccinimide (178 mg, 0.791 mmol) and dry THF were added. The reaction was sealed with a Teflon-lined cap, and stirred for 12 h at room temperature. The mixture was filtered through a pad of Celite and concentrated under reduced pressure. The crude mixture was purified by flash column chromatography (hexanes:EtOAc, 95:5) to give boronate ester **4** as a white solid (67% in 2 steps, 78 mg). ¹H NMR (500 MHz, CDCl₃) δ 7.84 – 7.82 (m, 1H), 7.29 – 7.28 (m, 2H), 6.86 – 6.83 (ddd, *J* = 7.9, 5.9, 3.1 Hz, 1H), 2.75 – 2.72 (t, *J* = 7.7 Hz, 1H), 1.83 – 1.77 (m, 1H), 1.73 – 1.65 (m, 1H), 1.39 – 1.36 (m, 1H), 1.26 (s, 6H), 1.25 (s, 6H), 0.94 – 0.91 (t, *J* = 7.4 Hz, 3H); ¹³C NMR (126 MHz, CDCl₃) δ 146.50, 139.46, 128.58, 128.15, 126.90, 102.62, 83.41, 34.62, 24.74, 24.71, 22.16, 14.29; ¹¹B NMR (160 MHz, CDCl₃) δ 33.05; HRMS (EI) calc'd for C₁₆H₂₄¹¹BIO₂ (M⁺) 386.0914, found 386.0919.

(4) Oxidation of hydrosilyl/Bpin group.

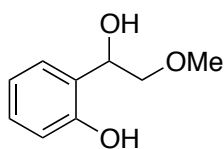


To a 25 mL vial, boronate ester **2** (0.200 mmol) and THF (1.0 mL) was added with a stirbar. The reaction mixture was cooled to 0 °C, and an aqueous solution of NaOH (2.00 mL, 6.00 mmol, 3M) and a solution of H₂O₂ (1.00 mL, 30%) was added dropwise. The reaction was slowly warmed up to room temperature. After 12 h, full conversion was observed by gas chromatographic analysis. Water (5 mL) was added, and the mixture was extracted with Et₂O (15 mL x 3). The combined organic layers were washed with brine,

dried over Na₂SO₄, filtered, and concentrated under reduced pressure. The crude mixture was purified by flash column chromatography to give the desired product.

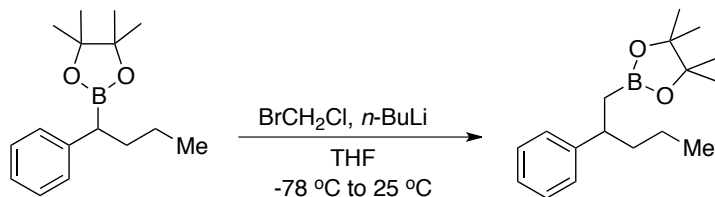


5a: The general procedure was followed with **2c** (64.0 mg, 0.201 mmol) as the reagent. The crude mixture was purified by flash column chromatography (hexanes:EtOAc, 80:20) to give compound **5a** as a colorless oil (95 %, 32 mg). ¹H NMR (500 MHz, CDCl₃) δ 8.10 (s, 1H), 7.20 – 7.17 (m, 1H), 6.96 – 6.94 (dd, *J* = 7.5, 1.7 Hz, 1H), 6.87 – 6.83 (m, 2H), 4.84 – 4.81 (t, *J* = 7.1 Hz, 1H), 2.96 (s, 1H), 1.94 – 1.86 (m, 1H), 1.82 – 1.75 (m, 1H), 1.49 – 1.46 (m, 1H), 1.37 – 1.32 (m, 1H), 0.98 – 0.95 (t, *J* = 7.4 Hz, 3H); ¹³C NMR (126 MHz, CDCl₃) δ 155.39, 128.82, 127.55, 127.24, 119.73, 117.09, 75.92, 39.25, 18.98, 13.87; HRMS (EI) calc'd for C₁₀H₁₄O₂ (M⁺) 166.0994, found 166.0998.



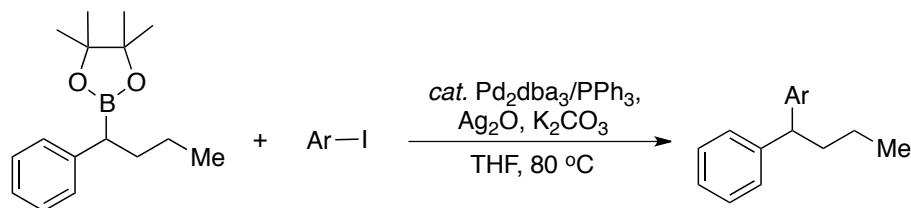
5b: The general procedure was followed with **2g** (64.0 mg, 0.201 mmol) as the reagent. The crude mixture was purified by flash column chromatography (hexanes:EtOAc, 80:20) to give compound **5b** as a colorless oil (90%, 30 mg). ¹H NMR (500 MHz, CDCl₃) δ 8.34 (s, 1H), 7.23 – 7.20 (m, 1H), 7.03 – 7.01 (dd, *J* = 7.6, 1.7 Hz, 1H), 6.91 – 6.85 (m, 2H), 5.06 – 5.03 (dd, *J* = 9.1, 3.5 Hz, 1H), 3.67 – 3.64 (m, 2H), 3.60 – 3.57 (m, 1H), 3.47 (s, 3H); ¹³C NMR (126 MHz, CDCl₃) δ 156.04, 129.44, 127.66, 122.84, 119.88, 117.48, 76.09, 74.25, 59.07; HRMS (EI) calc'd for C₉H₁₂O₃ (M⁺) 168.0786, found 168.0788.

(5) One carbon homologation of Bpin.

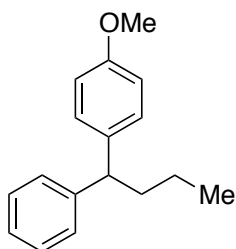


To a 10 mL round-bottom flask containing a stirbar were added benzylic boronate ester **3a** (52.5 mg, 0.201 mmol), bromochloromethane (52.0 mg, 0.401 mmol), and dry THF (2.0 mL). The flask was sealed with a septum and cooled to $-78\text{ }^{\circ}\text{C}$, at which time *n*-BuLi (0.250 mL, 0.400 mmol, 1.6 M in hexane) was slowly added. The resulting mixture was stirred for 5 min at $-78\text{ }^{\circ}\text{C}$. The reaction mixture was warmed to room temperature and stirred for an additional 2 h. The reaction was quenched with a saturated NH_4Cl solution (10 mL), and the resulting mixture was extracted with Et_2O (10 mL x 3). The combined organic layers were washed with brine, dried over Na_2SO_4 , filtered, and concentrated in *vacuo*. The residue was purified by flash column chromatography (hexanes:EtOAc, 100:0 to 95:5) to provide **6** as a colorless oil (67%, 37 mg). ^1H NMR (500 MHz, CDCl_3) δ 7.28 – 7.27 (t, $J = 7.5$ Hz, 2H), 7.22 – 7.21 (m, 2H), 7.17 – 7.14 (m, 1H), 2.89 – 2.83 (p, $J = 7.5$ Hz, 1H), 1.63 – 1.57 (m, 2H), 1.30 – 1.15 (m, 4H), 1.11 (s, 12H), 0.88 – 0.85 (t, $J = 7.3$ Hz, 3H); ^{13}C NMR (126 MHz, CDCl_3) δ 147.52, 128.02, 127.43, 125.67, 82.90, 41.87, 41.27, 24.67, 20.77, 14.15; ^{11}B NMR (160 MHz, CDCl_3) δ 33.33; HRMS (EI) calc'd for $\text{C}_{19}\text{H}_{33}^{11}\text{BO}_2$ (M^+) 332.2343, found 332.2344.

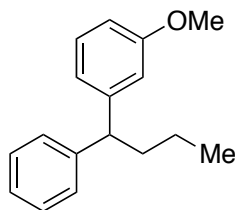
(6) Suzuki-Miyaura cross-coupling reaction of benzyl boronate ester.



A published procedure for the Suzuki-Miyaura cross-coupling reaction was followed with slight modifications.¹⁰ In a nitrogen-filled glove box, **3a** (52.5 mg, 0.201 mmol), aryl iodide (0.400 mmol), Ag₂O (70 mg, 0.302 mmol), K₂CO₃ (41.4 mg, 0.299 mmol), Pd₂(dba)₃ (9.10 mg, 0.010 mmol, 5 mol %) and PPh₃ (21.0 mg, 0.080 mmol, 40 mol %) were combined in a 25-mL vial containing a stirbar and THF (2 mL). The reaction was sealed with a Teflon-lined cap and stirred at 80 °C for 24 h. The volatile materials were evaporated under reduced pressure, and the crude boronate ester was isolated by flash column chromatography.



1-Methoxy-4-(1-phenylbutyl)benzene (7a): The general procedure was followed with 4-iodoanisole (94.0 mg, 0.401 mmol) as the reagent. The crude mixture was purified by flash column chromatography (hexanes:EtOAc, 100:0 to 90:0) to give compound **7a** as a white solid (70%, 34 mg). ¹H NMR (500 MHz, CDCl₃) δ 7.32 – 7.25 (m, 4H), 7.21 – 7.18 (m, 3H), 6.87 – 6.85 (m, 2H), 3.90 – 3.88 (t, *J* = 7.8 Hz, 1H), 3.80 (s, 3H), 2.05 – 2.01 (q, *J* = 7.8 Hz, 2H), 1.35 – 1.31 (m, 2H), 0.97 – 0.87 (t, *J* = 7.3 Hz, 3H); ¹³C NMR (126 MHz, CDCl₃) δ 157.79, 145.76, 137.51, 128.76, 128.36, 127.79, 125.91, 113.74, 55.22, 50.20, 38.12, 21.19, 14.11; HRMS (EI) calc'd for C₁₇H₂₀O (M⁺) 240.1514, found 240.1516.



1-Methoxy-3-(1-phenylbutyl)benzene (7b): The general procedure was followed with 3-iodoanisole (94.0 mg, 0.401 mmol) as the reagent. The crude mixture was purified by flash column chromatography (hexanes:EtOAc, 100:0 to 90:10) to give compound **7b** as a white solid (81%, 39 mg). ^1H NMR (500 MHz, CDCl_3) δ 7.33 – 7.28 (m, 4H), 7.25 – 7.20 (m, 2H), 6.90 – 6.88 (m, 1H), 6.85 – 6.84 (t, J = 1.9 Hz, 1H), 6.76 – 6.74 (dd, J = 8.1, 2.7 Hz, 1H), 3.94 – 3.91 (t, J = 7.8 Hz, 1H), 3.81 (s, 3H), 2.08 – 2.03 (ddd, J = 9.6, 7.6, 5.7 Hz, 2H), 1.35 – 1.31 (dd, J = 15.3, 7.5 Hz, 2H), 0.98 – 0.95 (t, J = 7.3 Hz, 3H); ^{13}C NMR (126 MHz, CDCl_3) δ 159.59, 147.03, 145.18, 129.30, 128.39, 127.85, 126.05, 120.39, 114.08, 110.82, 55.13, 51.12, 37.88, 21.20, 14.12; HRMS (EI) calc'd for $\text{C}_{17}\text{H}_{20}\text{O}$ (M^+) 240.1514, found 240.1518.

5. Reference

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