Supporting Information

Iridium-Catalyzed Diborylation of Benzylic C-H Bonds Directed by a Hydrosilyl Group: Synthesis of 1,1-Benzyl diboronate Esters

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1. General experimental details

All borylation reactions were conducted under an atmosphere of argon in an Innovative Technologies glovebox. 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. [[Ir(COD)OMe]$_2$] was obtained from Johnson-Matthey and stored at -35 °C in the glovebox. 4,4’-Di-tert-butyl-2,2’-bipyridine (dtbpy) was purchased from Sigma-Aldrich and used as received. All reagents were purchased from commercial sources and used without further purification. Column chromatography was performed on Silicyle Sila-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 (CDCl$_3$ = 7.26 ppm for $^1$H 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. General procedure of the preparation of starting materials

To a 50 mL round bottom flask containing a stirbar was added the 2-bromomethylbenzene derivative (5.00 mmol). The flask was sealed with a septum, and dry THF (15.0 mL) was added under N$_2$. The reaction mixture was cooled to -78 °C, at which time a solution of $n$-BuLi (4.69 mL, 7.50 mmol, 1.60 M in hexane) was added. The reaction was stirred for 30
minutes at -78 °C, and chlorodimethylsilane (710 mg, 7.50 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 (15.0 mL) and extracted with Et₂O (15.0 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 give 2-methylphenyl dimethylsilane derivatives (1).

(o-Tolyl)dimethylsilane (1a): The reaction was performed according to the general procedure of the preparation of starting materials with 2-bromotoluene (856 mg, 5.00 mmol). The crude mixture was purified by column chromatography on silica gel (hexanes) to give compound 1a as a colorless oil (677 mg, 90%); ¹H NMR (400 MHz, CDCl₃) δ 7.57 – 7.54 (m, 1H), 7.39 – 7.35 (m, 1H), 7.28 – 7.23 (m, 2H), 4.64 – 4.61 (m, 1H), 2.54 (s, 3H), 0.44 – 0.43 (m, 6H); ¹³C NMR (101 MHz, CDCl₃) δ 143.72, 136.15, 134.61, 129.56, 129.47, 125.08, 22.39, -3.52; HRMS (EI) calc’d for C₉H₁₄Si (M⁺) 150.0865, found 150.0869.

(o-Tolyl)diphenylsilane (1b): The reaction was performed according to the general procedure of the preparation of starting materials, except that chlorodiphenylsilane (1.20 g, 5.48 mmol) was used in place of chlorodimethylsilane, with 2-bromotoluene (856 mg, 5.00 mmol). The crude mixture was purified by column chromatography on silica gel (hexanes) to give compound 1b as a colorless oil (1.09 g, 79%); ¹H NMR (400 MHz, CDCl₃) δ 7.62 – 7.57 (m, 4H), 7.50 – 7.39 (m, 8H), 7.28 – 7.26 (d, J = 7.6 Hz, 1H), 7.23 – 7.19 (t, J = 7.3 Me SiMe₂H

![Chemical structure](image)

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Hz, 1H), 5.65 (s, 1H), 2.42 (s, 3H); $^{13}$C NMR (101 MHz, CDCl$_3$) δ $^{13}$C NMR (101 MHz, CDCl$_3$) δ 144.78, 136.97, 135.88, 133.30, 132.20, 129.74, 129.70, 128.10, 125.15, 22.81; HRMS (EI) calc’d for C$_{19}$H$_{18}$Si (M$^+$) 274.1178, found 274.1184.

(o-Tolyl)methylphenylsilane (1c): The reaction was performed according to the general procedure of the preparation of starting materials, except that chloromethylphenylsilane (862 mg, 5.50 mmol) was used in place of chlorodimethylsilane, with 2-bromotoluene (856 mg, 5.00 mmol). The crude mixture was purified by column chromatography on silica gel (hexanes) to give compound 1c as a colorless oil (882 mg, 83%); $^1$H NMR (500 MHz, CDCl$_3$) δ 7.59 – 7.57 (m, 2H), 7.55 – 7.53 (dd, $J$ = 7.3, 1.6 Hz, 1H), 7.43 – 7.36 (m, 4H), 7.26 – 7.23 (m, 2H), 5.10 (m, 1H), 2.43 (s, 3H), 0.70 – 0.69 (d, $J$ = 3.9 Hz, 3H); $^{13}$C NMR (126 MHz, CDCl$_3$) δ 144.68, 136.17, 135.99, 135.22, 134.42, 130.40, 130.03, 129.83, 128.42, 125.55, 23.06, -4.37; HRMS (EI) calc’d for C$_{14}$H$_{16}$Si (M$^+$) 212.1021, found 212.1025.

(2,5-Dimethylphenyl)dimethylsilane (1d): The reaction was performed according to the general procedure of the preparation of starting materials with 2-bromo-1,4-dimethylbenzene (926 mg, 5.00 mmol). The crude mixture was purified by column chromatography on silica gel (hexanes) to give compound 1d as a colorless oil (780 mg, 95%); $^1$H NMR (400 MHz, CDCl$_3$) δ 7.39 (s, 1H), 7.21 – 7.16 (m, 2H), 4.65 – 4.61 (m, 1H), 2.52 (s, 3H), 2.42 (s, 3H), 0.47 – 0.46 (d, $J$ = 3.8 Hz, 6H); $^{13}$C NMR (101 MHz,
CDCl$_3$ $\delta$ 140.51, 135.90, 135.33, 134.22, 130.46, 129.46, 21.84, 21.05, 1.47; HRMS (EI) calc’d for C$_{10}$H$_{16}$Si (M$^+$) 164.1021, found 164.1026.

(2-Methyl-5-(trifluoromethyl)phenyl)dimethylsilane (1e): The reaction was performed according to the general procedure of the preparation of starting materials with 2-bromo-1-methyl-4-(trifluoromethyl)benzene (1.20 g, 5.02 mmol). The crude mixture was purified by column chromatography on silica gel (hexanes) to give compound 1e as a colorless oil (887 mg, 81%); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.74 (s, 1H), 7.58 – 7.56 (d, $J = 8.0$ Hz, 1H), 7.32 – 7.30 (d, $J = 8.0$ Hz, 1H), 4.63 – 4.59 (m, 1H), 2.56 (s, 3H), 0.45 – 0.44 (d, $J = 3.8$ Hz, 6H); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 147.76, 137.36, 131.02 (q, $J_{C-F} = 3.6$ Hz), 129.58, 126.19 (q, $J_{C-F} = 3.6$ Hz), 127.4 (q, $J_{C-F} = 32.3$ Hz), 124.58 (q, $J_{C-F} = 271$ Hz), 22.33, -3.84; $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ -61.47; HRMS (EI) calc’d for C$_{10}$H$_{12}$F$_3$Si ([M–H]$^+$) 217.0660, found 217.0664.

(5-Fluoro-2-methylphenyl)dimethylsilane (1f): The reaction was performed according to the general procedure of the preparation of starting materials with 2-bromo-4-fluoro-1-methylbenzene (945 mg, 5.00 mmol). The crude mixture was purified by column chromatography on silica gel (hexanes) to give compound 1f as a colorless oil (588 mg, 70%); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.18 – 7.12 (m, 2H), 6.99 – 6.94 (td, $J = 8.5$, 2.8 Hz, 1H), 4.55 – 4.51 (m, 1H), 2.44 (s, 3H), 0.39 – 0.38 (d, $J = 3.8$ Hz, 6H); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 160.78 (d, $J_{C-F} = 245$ Hz), 138.93 (d, $J_{C-F} = 3.4$ Hz), 138.62 (d, $J_{C-F} = 3.7$ Hz), 130.88 (d, $J_{C-F} = 6.6$ Hz), 120.66 (d, $J_{C-F} = 18.9$ Hz), 116.00 (d, $J_{C-F} = 20.8$ Hz), 20.8 Hz),

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21.37, -3.86; $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ -118.12; HRMS (EI) calc’d for C$_9$H$_{13}$FSi (M$^+$) 168.0771, found 168.0775.

![Chemical Structure](image)

**(5-Chloro-2-methylphenyl)dimethylsilane (1g):** The reaction was performed according to the general procedure of the preparation of starting materials, except that tert-BuLi (5.88 mL, 10.0 mmol, 1.70 M in pentane) was used in place of $n$-BuLi, with 2-bromo-4-chloro-1-methylbenzene (1.03 g, 5.01 mmol). The crude mixture was purified by column chromatography on silica gel (hexanes) to give compound 1g as a colorless oil (730 mg, 79%); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.41 (s, 1H), 7.26 – 7.24 (m, 1H), 7.11 – 7.09 (d, $J = 8.1$ Hz, 1H), 4.54 – 4.50 (m, 1H), 2.43 (s, 3H), 0.38 – 0.37 (d, $J = 3.8$ Hz, 6H); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 141.77, 138.64, 134.04, 131.18, 130.88, 129.23, 21.62, -3.83; HRMS (EI) calc’d for C$_9$H$_{13}$ClSi (M$^+$) 184.0475, found 184.0475.

![Chemical Structure](image)

**$N$-(3-(Dimethylsilyl)-4-methylphenyl)-$N$-methylpivalamide (1h):**

To a 100 mL round bottom flask containing a stirbar was added 3-bromo-4-methylaniline (930 mg, 5.00 mmol), DMAP (6.10 mg, 0.05 mmol), pyridine (1.01 g, 10.0 mmol) and dry CH$_2$Cl$_2$ (20.0 mL). The flask was sealed with a septum and cooled to 0 °C. To this mixture, pivaloyl chloride (724 mg, 6.00 mmol) was slowly added by syringe. The reaction mixture was warmed to room temperature and stirred for 3 h. The resulting mixture was quenched with a 1M HCl solution (10.0 mL) and extracted with CH$_2$Cl$_2$ (15.0 mL x 3). The combined organic layers were washed with brine, dried over Na$_2$SO$_4$, filtered, and concentrated under reduced pressure to give $N$-(3-bromo-4-methylphenyl)pivalamide A,
which was used without purification for the next step; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.80 – 7.79 (d, $J = 2.1$ Hz, 1H), 7.36 – 7.33 (m, 2H), 7.16 – 7.14 (d, $J = 8.2$ Hz, 1H), 2.34 (s, 3H), 1.30 (s, 9H).

To a 50 mL round bottom flask containing a stirbar was added the above obtained $N$-(3-bromo-4-methylphenyl)pivalamide (A, ca. 5.00 mmol) and dry DMF (15.0 mL). The flask was cooled to 0 °C, and sodium hydride (300 mg, 7.50 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 (1.42 g, 10.0 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$_4$Cl solution (10.0 mL) and extracted with EtOAc (15.0 mL x 3). The combined organic layers were washed with brine, dried over Na$_2$SO$_4$, filtered, and concentrated under reduced pressure to give $N$-(3-bromo-4-methylphenyl)-$N$-methylpivalamide (B), which was used without purification for the next step; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.42 – 7.41 (d, $J = 2.2$ Hz, 1H), 7.27 – 7.25 (d, $J = 8.0$ Hz, 1H), 7.09 – 7.07 (dd, $J = 8.0$, 2.2 Hz, 1H), 3.19 (s, 3H), 2.43 (s, 3H), 1.07 (s, 9H).

To a 50 mL round bottom flask containing a stirbar was added the above obtained $N$-(3-bromo-4-methylphenyl)-$N$-methylpivalamide (B, cat. 4.50 mmol). The flask was sealed with a septum, and dry THF (10.0 mL) was added under N$_2$. The reaction mixture was cooled to $-78$ °C, at which time a solution of $n$-BuLi (4.22 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$_4$Cl solution (15.0 mL), and extracted with Et$_2$O (15.0 mL x 3). The combined organic layers were washed with brine, dried over Na$_2$SO$_4$, filtered, and concentrated under reduced pressure. The crude mixture was purified
by column chromatography on silica gel (hexanes:EtOAc, 85:15) to give compound 1h as a light yellow oil (1.05 g, 80% over 3 steps). $^1$H NMR (400 MHz, CDCl$_3$) δ 7.24 – 7.22 (d, J = 2.4 Hz, 1H), 7.15 – 7.13 (m, 1H), 7.09 – 7.07 (dd, J = 8.0, 2.4 Hz, 1H), 4.50 (m, 1H), 3.16 (s, 3H), 2.43 (s, 3H), 0.99 (s, 9H), 0.32 – 0.31 (d, J = 3.8 Hz, 6H); $^{13}$C NMR (101 MHz, CDCl$_3$) δ 178.12, 143.16, 142.23, 137.45, 134.50, 130.23, 129.44, 41.32, 40.67, 29.45, 29.27, 26.33, 21.86, -3.80; HRMS (EI) calc’d for C$_{15}$H$_{25}$NOSi (M$^+$) 263.1705, found 263.1710.

(5-(1,3-Dioxolan-2-yl)-2-methylphenyl)dimethylsilane (1i): 2-(3-Bromo-4-methylphenyl)-1,3-dioxolane was prepared by following a literature procedure.$^{[1]}$ The reaction was then performed according to the general procedure of the preparation of starting materials with 2-(3-bromo-4-methylphenyl)-1,3-dioxolane (1.22 g, 5.01 mmol). The crude mixture was purified by column chromatography on silica gel (hexanes:EtOAc, 100:0 to 90:10) to give (5-(1,3-dioxolan-2-yl)-2-methylphenyl)dimethylsilane 1i as a light yellow oil (990 mg, 89%); $^1$H NMR (400 MHz, CDCl$_3$) δ 7.59 (d, J = 2.0, 1H), 7.43 – 7.40 (dd, J = 7.8, 2.0 Hz, 1H), 7.22 – 7.20 (d, J = 7.8 Hz, 1H), 5.80 (s, 1H), 4.58 – 4.54 (m 1H), 4.18 – 4.16 (m, 2H), 4.09 – 4.03 (m, 2H), 2.48 (s, 3H), 0.39 – 0.38 (d, J = 3.8 Hz, 6H); $^{13}$C NMR (101 MHz, CDCl$_3$) δ 144.85, 136.24, 134.20, 132.65, 129.43, 127.57, 103.91, 65.28, 22.15, -3.65; HRMS (EI) calc’d for C$_{12}$H$_{17}$O$_2$Si ([M–H]$^-$) 221.0998, found 221.1004.
To a 50 mL round bottom flask containing a stirbar was added (3-bromo-4-methylphenyl)methanol (1.00 g, 5.00 mmol), \(N,N\)-diisopropylethylamine (1.42 g, 11.0 mmol) and dry \(\text{CH}_2\text{Cl}_2\) (20.0 mL). The reaction mixture was cooled to 0°C and chloromethyl methyl ether (641 mg, 7.50 mmol) was slowly added by syringe at 0°C. The reaction mixture was warmed to room temperature and stirred for 12 h. The resulting mixture was quenched with a saturated \(\text{NH}_4\text{Cl}\) solution (10.0 mL) and extracted with \(\text{CH}_2\text{Cl}_2\) (15.0 mL x 3). The combined organic layers were washed with brine, dried over \(\text{Na}_2\text{SO}_4\), filtered, and concentrated under reduced pressure. The crude mixture was purified by column chromatography on silica gel (hexanes:EtOAc, 90:10) to give 2-bromo-4-((methoxymethoxy)methyl)-1-methylbenzene (D, 1.16 g, 95%).

To a 50 mL round bottom flask containing a stirbar was added the above obtained 2-bromo-4-((methoxymethoxy)methyl)-1-methylbenzene (D, 1.16 g, 4.75 mmol). The flask was sealed with a septum, and dry THF (10.0 mL) was added under \(\text{N}_2\). The reaction mixture was cooled to -78°C, at which time a solution of \(n\)-BuLi (4.45 mL, 7.13 mmol, 1.6 M in hexane) was slowly added. The reaction was stirred for 30 minutes at -78°C, and chlorodimethylsilane (674 mg, 7.13 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 \(\text{NH}_4\text{Cl}\) solution (15.0 mL), and extracted with \(\text{Et}_2\text{O}\) (15.0 mL x 3). The combined organic layers were washed with brine, dried over \(\text{Na}_2\text{SO}_4\), filtered, and concentrated under reduced pressure. The crude mixture was purified by column chromatography on silica gel (hexanes:EtOAc, 90:10) to give compound 1j as a light yellow oil (906 mg, 85%).

\(^1\text{H}\) NMR (400 MHz, \(\text{CDCl}_3\)) \(\delta\) 7.50 – 7.49 (d, \(J = 2.0\) Hz, 1H), 7.34 – 7.32 (dd, \(J = 7.7, 2.0\) Hz, 1H), 7.22 – 7.20 (d, \(J = 7.7\) Hz, 1H), 4.75 (s, 2H), 4.61 (s, 2H), 4.60 – 4.56 (m, 1H), 3.47 (s, 3H), 2.50 (s, 3H), 0.42 – 0.41 (d, \(J = 3.8\) Hz, 6H);

\(^{13}\)C NMR (101 MHz, \(\text{CDCl}_3\)) \(\delta\) 143.28, 136.33, 134.43, 134.24, 129.56, 129.38, 95.66,
69.23, 55.35, 22.06, -3.56; HRMS (EI) calc’d for \( \text{C}_{12}\text{H}_{20}\text{O}_{2}\text{Si} \) (M⁺) 224.1233, found 224.1238.

**(2,4-Dimethylphenyl)dimethylsilane (1k):** The reaction was performed according to the general procedure of the preparation of starting materials with 1-bromo-2,4-dimethylbenzene (926 mg, 5.00 mmol). The crude mixture was purified by column chromatography on silica gel (hexanes) to give compound 1k as a colorless oil (764 mg, 93%); \(^1\)H NMR (400 MHz, CDCl₃) \( \delta \) 7.43 – 7.41 (d, \( J = 7.8 \) Hz, 1H), 7.07 – 7.05 (m, 2H), 4.59 – 4.55 (m, 1H), 2.37 (s, 3H), 0.41 – 0.40 (d, \( J = 3.8 \) Hz, 6H); \(^{13}\)C NMR (101 MHz, CDCl₃) \( \delta \) 143.67, 139.42, 134.70, 132.46, 130.44, 125.82, 22.23, 21.30, -3.46; HRMS (EI) calc’d for \( \text{C}_{10}\text{H}_{16}\text{Si} \) (M⁺) 164.1021, found 164.1025.

**(4-Methoxy-2-methylphenyl)dimethylsilane (1l):** The reaction was performed according to the general procedure of the preparation of starting materials, except that tert-BuLi (5.88 mL, 10.0 mmol, 1.70 M in pentane) was used in place of \( n \)-BuLi, with 1-bromo-4-methoxy-2-methylbenzene (1.00 g, 4.97 mmol). The crude mixture was purified by column chromatography on silica gel (hexanes:EtOAc, 100:0 to 95:5) to give compound 1l as a colorless oil (798 mg, 89%); \(^1\)H NMR (400 MHz, CDCl₃) \( \delta \) 7.43 – 7.41 (d, \( J = 7.7 \) Hz, 1H), 6.78 – 6.76 (m, 2H), 4.55 – 4.52 (m, 1H), 3.83 (s, 3H), 2.47 (s, 3H), 0.38 – 0.37 (d, \( J = 3.8 \) Hz, 6H); \(^{13}\)C NMR (101 MHz, CDCl₃) \( \delta \) 160.76, 145.51, 136.02, 127.08, 115.53, 110.29, 54.95, 22.49, -3.35; HRMS (EI) calc’d for \( \text{C}_{10}\text{H}_{16}\text{OSi} \) (M⁺) 180.0970, found 180.0975.
**tert-Butyl(4-(dimethylsilyl)-3-methylphenoxy)dimethylsilane (1m):** The reaction was performed according to the general procedure of the preparation of starting materials, except that tert-BuLi (5.88 mL, 10.0 mmol, 1.70 M in pentane) was used in place of n-BuLi, with 4-bromo-3-methylphenoxy-tert-butyl dimethylsilane (1.50 g, 5.00 mmol). The crude mixture was purified by column chromatography on silica gel (hexanes:EtOAc, 100:0 to 95:5) to give compound 1m as a colorless oil (1.23 g, 88%); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.37 – 7.35 (d, $J$ = 7.8 Hz, 1H), 6.72 – 6.69 (m, 2H), 4.55 – 4.52 (m, 1H), 2.44 (s, 3H), 1.04 (s, 9H), 0.38 – 0.37 (d, $J$ = 3.8 Hz, 6H), 0.25 (s, 6H); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 156.95, 145.47, 135.90, 127.71, 121.41, 116.56, 25.71, 22.35, 18.22, -3.32, -4.32; HRMS (EI) calc’d for C$_{15}$H$_{28}$OSi$_2$ (M$^+$) 280.1679, found 280.1683.

![Structure of tert-Butyl(4-(dimethylsilyl)-3-methylphenoxy)dimethylsilane (1m)](image)

**4-(Benzylxy)-2-methylphenyl)dimethylsilane (1n):** The reaction was performed according to the general procedure of the preparation of starting materials, except that tert-BuLi (5.88 mL, 10.0 mmol, 1.70 M in pentane) was used in place of n-BuLi, with 1-bromo-4-(benzylxy)-2-methylbenzene (1.38 g, 4.98 mmol). The crude mixture was purified by column chromatography on silica gel (hexanes:EtOAc, 100:0 to 95:5) to give compound 1n as a colorless oil (1.06 g, 83%); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.50 – 7.38 (m, 6H), 6.89 – 6.84 (m, 2H), 5.11 (s, 2H), 4.57 – 4.54 (m, 1H), 2.49 (s, 3H), 0.40 – 0.39 (d, $J$ = 3.7 Hz, 6H); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 160.07, 145.60, 137.08, 136.08, 128.61, 127.96, 127.49, 116.46, 111.16, 69.70, 22.54, -3.31; HRMS (EI) calc’d for C$_{16}$H$_{20}$OSi (M$^+$) 256.1283, found 256.1283.

![Structure of 4-(Benzylxy)-2-methylphenyl)dimethylsilane (1n)](image)
(4-Chloro-2-methylphenyl)dimethylsilane (1o): The reaction was performed according to the general procedure of the preparation of starting materials, except that tert-BuLi (5.88 mL, 10.0 mmol, 1.70 M in pentane) was used in place of n-BuLi, with 1-bromo-4-chloro-2-methylbenzene (1.03 g, 5.01 mmol). The crude mixture was purified by column chromatography on silica gel (hexanes) to give compound 1o as a colorless oil (712 mg, 77%); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.41 – 7.39 (dd, $J$ = 7.4, 0.9 Hz, 1H), 7.19 – 7.17 (m, 2H), 4.53 (m, 1H), 2.46 (s, 3H), 0.38 – 0.37 (d, $J$ = 3.8 Hz, 6H); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 145.53, 135.81, 135.51, 134.42, 129.37, 125.13, 22.11, -3.69; HRMS (EI) calc’d for C$_9$H$_{13}^{35}$ClSi (M$^+$) 184.0475, found 184.0479.

![Chemical structure of 1o]

(2,3-Dimethylphenyl)dimethylsilane (1p): The reaction was performed according to the general procedure of the preparation of starting materials with 1-bromo-2,3-dimethylbenzene (926 mg, 5.00 mmol). The crude mixture was purified by column chromatography on silica gel (hexanes) to give compound 1p as a colorless oil (748 mg, 91%); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.52 – 7.40 (m, 1H), 7.35 – 7.33 (m, 1H), 7.29 – 7.25 (t, $J$ = 7.4 Hz, 1H), 4.77 – 4.73 (m, 1H), 2.54 (s, 3H), 2.44 (s, 3H), 0.54 – 0.53 (d, $J$ = 3.8 Hz, 6H); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 142.17, 136.36, 136.33, 132.37, 132.57, 131.41, 125.39, 20.54, 19.44, -3.10; HRMS (EI) calc’d for C$_{10}$H$_{16}$Si (M$^+$) 164.1021, found 164.1025.

![Chemical structure of 1p]

(3-Chloro-2-methylphenyl)dimethylsilane (1q): The reaction was performed according to the general procedure of the preparation of starting materials, except that tert-BuLi (5.88 mL, 10.0 mmol, 1.70 M in pentane) was used in place of n-BuLi, with 1-bromo-3-chloro-
2-methylbenzene (1.03 g, 5.01 mmol). The crude mixture was purified by column chromatography on silica gel (hexanes) to give compound 1q as a colorless oil (767 mg, 83%); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.41 – 7.37 (t, $J = 7.4$ Hz, 2H), 7.16 – 7.12 (t, $J = 7.6$ Hz, 1H), 4.57 (m, 1H), 2.52 (s, 3H), 0.40 – 0.39 (d, $J = 3.7$ Hz, 6H); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 140.86, 138.90, 134.91, 132.89, 130.36, 126.51, 19.71, -3.46; HRMS (EI) calc’d for C$_9$H$_{13}$ClSi (M$^+$) 184.0475, found 184.0471.

(2,4,5-Trimethylphenyl)dimethylsilane (1r): The reaction was performed according to the general procedure of the preparation of starting materials with 1-bromo-2,4,5-trimethylbenzene (996 mg, 5.00 mmol). The crude mixture was purified by column chromatography on silica gel (hexanes) to give compound 1r as a colorless oil (856 mg, 96%); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.33 (s, 1H), 7.07 (s, 1H), 4.63 – 4.59 (m, 1H), 2.50 (s, 3H), 2.34 (s, 6H), 0.46 – 0.45 (d, $J = 3.8$ Hz, 6H); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 141.09, 138.01, 136.03, 132.99, 132.91, 131.07, 21.71, 19.63, 19.17, -3.38. HRMS (EI) calc’d for C$_{11}$H$_{18}$Si (M$^+$) 178.1178, found 178.1178.

(2-Methylnaphthalen-1-yl)dimethylsilane (1s): The reaction was performed according to the general procedure of the preparation of starting materials with 1-bromo-2-methylnaphthalene (1.10 g, 4.97 mmol). The crude mixture was purified by column chromatography on silica gel (hexanes) to give compound 1s a colorless oil (887 mg, 89%); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.27 – 8.25 (d, $J = 8.0$ Hz, 1H), 7.84 – 7.82 (d, $J = 8.0$ Hz, 1H), 7.80 – 7.78 (d, $J = 8.0$ Hz, 1H), 7.52 – 7.50 (m, 1H), 7.48 – 7.42 (m, 1H), 7.33 – 7.31 (d, $J = 8.0$ Hz, 1H), 5.12 – 5.08 (m, 1H), 2.71 (s, 3H), 0.57 – 0.56 (d, $J = 4.1$ Hz,


3. General procedure for the diborylation of benzylic C-H bonds

In a nitrogen-filled glovebox, the (2-methylphenyl)dimethylsilane derivative 1 (0.500 mmol) and B$_2$pin$_2$ (1.00 mmol) were added to a 4-mL vial with a stir bar. To this vial, freshly prepared stock solutions of [Ir(COD)OMe]$_2$ (2.50 µmol, 0.500 mol %) in THF (1.00 mL), and 4,4’-di-tert-butyl-2,2’-bipyridine (5.00 µmol, 1.00 mol %) in THF (1.00 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 50 °C and stirred for the indicated period of time. The reaction progress was monitored by GC analysis. 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 give pure 1,1-benzyl diboronate ester products 3.

1,1-Benzyldiboronate ester 3a: The reaction was performed according to the general procedure for the diborylation of benzylic C-H bonds with 1a (75.2 mg, 0.500 mmol), B$_2$pin$_2$ (254 mg, 1.00 mmol), [Ir(COD)OMe]$_2$ (2.50 µmol, 0.500 mol %) in THF (1.00 mL), and 4,4’-di-tert-butyl-2,2’-bipyridine (5.00 µmol, 1.00 mol %) in THF (1.00 mL) at 50 °C for 4 h. The crude mixture was purified by column chromatography on silica gel (hexanes:EtOAc, 100:0 to 95:5) to give compound 3a as a white solid (175 mg, 87%); $^1$H NMR (400 MHz, CDCl$_3$) δ 7.49 – 7.47 (dd, J = 8.1, 1.3 Hz, 1H), 7.46 – 7.44 (dd, J = 7.3, 1.5 Hz, 1H), 7.35 – 7.31 (td, J = 7.6, 1.6 Hz, 1H), 7.15 – 7.13 (td, J = 7.3, 1.2 Hz, 1H), 4.59 – 4.55 (dt, J = 7.5, 3.8 Hz, 1H), 2.60 (s, 1H), 1.27 (s, 12H), 1.25 (s, 12H), 0.38 – 0.37
(d, J = 3.7 Hz, 6H); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 145.61, 135.35, 134.28, 129.38, 129.05, 123.64, 83.34, 24.65, 24.60, -3.19; $^{11}$B NMR (128 MHz, CDCl$_3$) $\delta$ 30.80; HRMS (EI) calc’d for C$_{21}$H$_{36}$$^{11}$B$_2$O$_4$Si (M$^+$) 402.2569, found 402.2578.

1,1-Benzyldiboronate ester 3b: The reaction was performed according to the general procedure for the diboration of benzylic C-H bonds with 1b (137 mg, 0.500 mmol), B$_2$pin$_2$ (254 mg, 1.00 mmol), and [Ir(COD)OMe]$_2$ (2.50 µmol, 0.500 mol %) in THF (1.00 mL), and 4,4’-di-tert-butyl-2,2’-bipyridine (5.00 µmol, 1.00 mol %) in THF (1.00 mL) at 50 °C for 4 h. The crude mixture was purified by column chromatography on silica gel (hexanes:EtOAc, 100:0 to 95:5) to give compound 3b as a white solid (203 mg, 77%); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.63 – 7.56 (m, 5H), 7.46 – 7.35 (m, 8H), 7.16 – 7.12 (dd, J = 7.9, 6.7 Hz, 1H), 5.69 (s, 1H), 2.72 (s, 1H), 1.21 (s, 24H); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 147.06, 136.84, 136.11, 133.90, 131.21, 130.10, 129.81, 129.43, 127.93, 123.80, 83.35, 24.70, 24.62; $^{11}$B NMR (128 MHz, CDCl$_3$) $\delta$ 31.30; HRMS (EI) calc’d for C$_{31}$H$_{40}$$^{11}$B$_2$O$_4$Si (M$^+$) 526.2882, found 526.2891.

1,1-Benzyldiboronate ester 3c: The reaction was performed according to the general procedure for the diboration of benzylic C-H bonds with 1c (106 mg, 0.500 mmol), B$_2$pin$_2$ (254 mg, 1.00 mmol), and [Ir(COD)OMe]$_2$ (2.50 µmol, 0.500 mol %) in THF (1.00 mL), and 4,4’-di-tert-butyl-2,2’-bipyridine (5.00 µmol, 1.00 mol %) in THF (1.00 mL) at 50 °C for 4 h. The crude mixture was purified by column chromatography on silica gel
(hexanes:EtOAc, 100:0 to 95:5) to give compound 3c as a white solid (197 mg, 85%); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.57 – 7.54 (dd, $J = 6.9$, 2.8 Hz, 2H), 7.49 – 7.47 (d, $J = 7.9$ Hz, 1H), 7.43 – 7.42 (d, $J = 7.4$ Hz, 1H), 7.36 – 7.32 (m, 4H), 7.14 – 7.10 (t, $J = 7.3$ Hz, 1H), 5.09 – 5.06 (m, 1H), 2.60 (s, 1H), 1.20 (s, 12H), 1.18 (s, 12H), 0.65 – 0.64 (d, $J = 3.8$ Hz, 3H); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 146.32, 136.00, 135.62, 134.98, 133.10, 129.81, 129.46, 129.02, 127.77, 123.73, 83.32, 24.63, 24.61, 24.57, -4.34; $^{11}$B NMR (128 MHz, CDCl$_3$) $\delta$ 31.80; HRMS (EI) calc’d for C$_{26}$H$_{38}$B$_2$O$_4$Si (M$^+$) 464.2725, found 464.2734.

1,1-Benzyl diboronate ester 3d: The reaction was performed according to the general procedure for the diborylation of benzylic C-H bonds with 1d (82.2 mg, 0.500 mmol), B$_2$pin$_2$ (254 mg, 1.00 mmol), and [Ir(COD)OMe]$_2$ (2.50 µmol, 0.500 mol %) in THF (1.00 mL), and 4,4'-di-tert-butyl-2,2'-bipyridine (5.00 µmol, 1.00 mol %) in THF (1.00 mL) at 50 $^\circ$C for 2 h. The crude mixture was purified by column chromatography on silica gel (hexanes:EtOAc, 100:0 to 95:5) to give compound 3d as a white solid (200 mg, 96%); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.40 – 7.38 (d, $J = 7.9$ Hz, 1H), 7.27 (s, 1H), 7.18 – 7.16 (dd, $J$ = 8.0, 2.1 Hz, 1H), 4.59 – 4.54 (m, 1H), 2.59 (s, 1H), 2.35 (s, 3H), 1.29 (s, 12H), 1.27 (s, 12H), 0.40 – 0.39 (d, $J = 3.8$ Hz, 6H); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 142.42, 135.15, 132.53, 130.05, 129.34, 83.35, 24.72, 24.70, 21.11, -3.04; $^{11}$B NMR (128 MHz, CDCl$_3$) $\delta$ 32.62; HRMS (EI) calc’d for C$_{22}$H$_{38}$B$_2$O$_4$Si (M$^+$) 416.2725, found 416.2734.

Scale up Reaction of 1d:

The reaction was performed according to the general procedure for the diborylation of benzylic C-H bonds with 1d (822 mg, 5.00 mmol), B$_2$pin$_2$ (2.54 g, 10.0 mmol), and [Ir(COD)OMe]$_2$ (2.50 µmol, 0.500 mol %) in THF (10.0 mL), and 4,4'-di-tert-butyl-2,2'-...
bipyridine (5.00 µmol, 1.00 mol %) in THF (100 mL) at 50 °C for 12 h. The crude mixture was purified by column chromatography on silica gel (hexanes:EtOAc, 100:0 to 95:5) to give compound 3d as a white solid (1.93 g, 93%), which gave spectral data identical to that obtained previously.

1,1-Benzyldiboronate ester 3e: The reaction was performed according to the general procedure for the diborylation of benzylic C-H bonds with 1e (109 mg, 0.500 mmol), B₂pin₂ (254 mg, 1.00 mmol), and [Ir(COD)OMe]₂ (2.50 µmol, 0.500 mol %) in THF (1.00 mL), and 4,4’-di-tert-butyl-2,2’-bipyridine (5.00 µmol, 1.00 mol %) in THF (1.00 mL) at 50 °C for 12 h. The crude mixture was purified by column chromatography on silica gel (hexanes:EtOAc, 100:0 to 95:5) to give compound 3e as a white solid (219 mg, 93%); ¹H NMR (400 MHz, CDCl₃) δ 7.62 (s, 1H), 7.55 – 7.50 (m, 2H), 4.56 – 4.52 (m, 1H), 2.64 (s, 1H), 1.24 (s, 12H), 1.26 (s, 12H), 0.38 – 0.37 (d, J = 3.8 Hz, 6H); ¹³C NMR (101 MHz, CDCl₃) δ 150.17, 136.25, 130.89 (q, J₁C–F = 3.6 Hz), 129.60, 125.79 (q, J₁C–F = 3.6 Hz), 125.69 (q, J₁C–F = 24.2 Hz), 124.92 (q, J₁C–F = 272 Hz), 83.68, 24.65, 24.62, -3.41; ¹⁹F NMR (376 MHz, CDCl₃) δ -61.15; ¹¹B NMR δ 32.4. HRMS (EI) calc’d for C₂₂H₃₄B₂F₃O₄Si ([M–H]⁻) 469.2365, found 469.2374.

1,1-Benzyldiboronate ester 3f: The reaction was performed according to the general procedure for the diborylation of benzylic C-H bonds with 1f (84.1 mg, 0.500 mmol), B₂pin₂ (254 mg, 1.00 mmol), and [Ir(COD)OMe]₂ (2.50 µmol, 0.500 mol %) in THF (1.00 mL), and 4,4’-di-tert-butyl-2,2’-bipyridine (5.00 µmol, 1.00 mol %) in THF (1.00 mL) at
50 °C for 12 h. The crude mixture was purified by column chromatography on silica gel (hexanes:EtOAc, 100:0 to 95:5) to give compound 3f as a white solid (162 mg, 77%); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.42 – 7.39 (dd, \(J = 8.6, 5.3\) Hz, 1H), 7.09 – 7.06 (dd, \(J = 9.1, 2.9\) Hz, 1H), 7.00 – 6.95 (td, \(J = 8.6, 2.9\) Hz, 1H), 4.53 – 4.49 (m, 1H), 2.53 (s, 1H), 1.24 (s, 12H), 1.22 (s, 12H), 0.35 – 0.34 (d, \(J = 3.7\) Hz, 6H); \(^13\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 160.01 (d, \(J_{C-F} = 244\) Hz), 140.90 (d, \(J_{C-F} = 3.0\) Hz), 137.63 (d, \(J_{C-F} = 3.3\) Hz), 130.84 (d, \(J_{C-F} = 6.4\) Hz), 120.20 (d, \(J_{C-F} = 18.4\) Hz), 115.80 (d, \(J_{C-F} = 20.8\) Hz), 83.43, 24.63, 24.58, -3.44; \(^{11}\)B NMR \(\delta\) 32.5; HRMS (EI) calc’d for \(C_{21}H_{35}\(^{11}\)B\(_2\)\(^{35}\)ClO\(_4\)Si (M\(^+\)) 420.2475, found 420.2484.

**1,1-Benzylidiboronate ester 3g:** The reaction was performed according to the general procedure for the diborylation of benzylic C-H bonds with 1g (92.4 mg, 0.500 mmol), B\(_2\)pin\(_2\) (254 mg, 1.00 mmol), and [Ir(COD)OMe]\(_2\) (2.50 µmol, 0.500 mol %) in THF (1.00 mL), and 4,4’-di-tert-butyl-2,2’-bipyridine (5.00 µmol, 1.00 mol %) in THF (1.00 mL) at 50 °C for 12 h. The crude mixture was purified by column chromatography on silica gel (hexanes:EtOAc, 100:0 to 95:5) to give compound 3g as a white solid (190 mg, 87%); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.42 – 7.40 (dd, \(J = 8.4, 1.8\) Hz, 1H), 7.37 – 7.35 (t, \(J = 2.2\) Hz, 1H), 7.30 – 7.26 (m, 1H), 4.55 – 4.52 (m, 1H), 2.56 (s, 1H), 1.27 (s, 12H), 1.25 (s, 12H), 0.38 – 0.37 (d, \(J = 3.7\) Hz, 6H); \(^13\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 144.03, 137.91, 133.81, 131.00, 129.82, 129.05, 83.55, 24.68, 24.62, -3.37; \(^{11}\)B NMR (128 MHz, CDCl\(_3\)) \(\delta\) 31.69; HRMS (EI) calc’d for \(C_{23}H_{35}\(^{11}\)B\(_2\)\(^{35}\)ClO\(_4\)Si (M\(^+\)) 436.2179, found 436.2180.
1,1-Benzyl diboronate ester 3h: The reaction was performed according to the general procedure for the diborylation of benzylic C-H bonds with 1h (132 mg, 0.500 mmol), B$_2$pin$_2$ (254 mg, 1.00 mmol), and [Ir(COD)OMe]$_2$ (2.50 µmol, 0.500 mol %) in THF (1.00 mL), and 4,4'-di-tert-butyl-2,2'-bipyridine (5.00 µmol, 1.00 mol %) in THF (1.00 mL) at 50 °C for 4 h. The crude mixture was purified by column chromatography on silica gel (hexanes:EtOAc, 100:0 to 85:15) to give compound 3h as a white solid (245 mg, 95%); $^1$H NMR (400 MHz, CDCl$_3$) δ 7.49 – 7.47 (d, $J$ = 8.2 Hz, 1H), 7.20 – 7.10 (d, $J$ = 2.5 Hz, 1H), 7.13 – 7.10 (dd, $J$ = 8.2, 2.5 Hz, 1H), 4.58 – 4.52 (m, 1H), 3.24 (s, 3H), 2.62 (s, 1H), 1.29 (s, 3H), 1.25 (s, 12H), 1.22 (s, 12H), 1.01 (s, 9H), 0.35 – 0.34 (d, $J$ = 3.7 Hz, 6H); $^{13}$C NMR (101 MHz, CDCl$_3$) δ 178.39, 145.57, 140.66, 136.57, 134.12, 130.12, 129.15, 83.49, 41.12, 40.73, 29.48, 25.04, 24.71, 24.51, -3.32; $^{11}$B NMR (128 MHz, CDCl$_3$) δ 32.57; HRMS (EI) calc’d for C$_{27}$H$_{47}$B$_2$NO$_5$Si (M$^+$) 515.3410, found 515.3421.

1,1-Benzyl diboronate ester 3i: The reaction was performed according to the general procedure for the diborylation of benzylic C-H bonds with 1i (111 mg, 0.500 mmol), B$_2$pin$_2$ (254 mg, 1.00 mmol), and [Ir(COD)OMe]$_2$ (2.50 µmol, 0.500 mol %) in THF (1.00 mL), and 4,4'-di-tert-butyl-2,2'-bipyridine (5.00 µmol, 1.00 mol %) in THF (1.00 mL) at 50 °C for 6 h. The crude mixture was purified by column chromatography on silica gel (hexanes:EtOAc, 100:0 to 85:15) to give compound 3i as a white solid (171 mg, 72%); $^1$H NMR (500 MHz, CDCl$_3$) δ 7.50 (s, 1H), 7.48 – 7.46 (d, $J$ = 10.0 Hz, 1H), 7.42 – 7.40 (d, $J$ = 10.0 Hz, 1H), 5.76 (s, 1H), 4.55 – 4.52 (m, 1H), 4.18 – 4.13 (m, 2H), 4.07 – 4.02 (m, 2H), 2.58 (s, 1H), 1.23 (s, 12H), 1.21 (s, 12H), 0.36 – 0.35 (d, $J$ = 3.7 Hz, 6H); $^{13}$C NMR (126 MHz, CDCl$_3$) δ 147.06, 135.39, 132.55, 132.32, 129.56, 127.28, 104.37, 83.50, 83.39,
1,1-Benzyl diboronate ester 3j: The reaction was performed according to the general procedure for the diborylation of benzylic C-H bonds with 1j (112 mg, 0.500 mmol), B₂pin₂ (254 mg, 1.00 mmol), and [Ir(COD)OMe]₂ (2.50 µmol, 0.500 mol %) in THF (1.00 mL), and 4,4'-di-tert-butyl-2,2'-bipyridine (5.00 µmol, 1.00 mol %) in THF (1.00 mL) at 50 °C for 6 h. The crude mixture was purified by column chromatography on silica gel (hexanes:EtOAc, 100:0 to 90:10) to give compound 3j as a white solid (205 mg, 86%); ¹H NMR (400 MHz, CDCl₃) δ 7.33 – 7.31 (d, J = 7.5 Hz, 1H), 7.26 (s, 1H), 6.95 – 6.93 (d, J = 7.4 Hz, 1H), 4.55 – 4.52 (m, 1H), 2.55 (s, 1H), 2.35 (s, 3H), 1.26 (s, 12H), 1.24 (s, 12H), 0.35 – 0.34 (d, J = 3.8 Hz, 6H); ¹³C NMR (101 MHz, CDCl₃) δ 145.39, 135.49, 134.40, 132.44, 129.57, 129.26, 95.80, 83.39, 69.71, 55.28, 24.68, 24.65, -3.16; ¹¹B NMR δ 32.8; HRMS (EI) calc’d for C₂₄H₃₉¹¹B₂O₆Si (M⁺) 476.2937, found 476.2943.

1,1-Benzyl diboronate ester 3k: The reaction was performed according to the general procedure for the diborylation of benzylic C-H bonds with 1k (82.2 mg, 0.500 mmol), B₂pin₂ (254 mg, 1.00 mmol), and [Ir(COD)OMe]₂ (2.50 µmol, 0.500 mol %) in THF (1.00 mL), and 4,4'-di-tert-butyl-2,2'-bipyridine (5.00 µmol, 1.00 mol %) in THF (1.00 mL) at 50 °C for 6 h. The crude mixture was purified by column chromatography on silica gel (hexanes:EtOAc, 100:0 to 95:5) to give compound 3k as a white solid (175 mg, 84%); ¹H NMR (400 MHz, CDCl₃) δ 7.33 – 7.31 (d, J = 7.5 Hz, 1H), 7.26 (s, 1H), 6.95 – 6.93 (d, J = 7.4 Hz, 1H), 4.55 – 4.52 (m, 1H), 2.55 (s, 1H), 2.35 (s, 3H), 1.26 (s, 12H), 1.24 (s, 12H), 0.35 – 0.34 (d, J = 3.8 Hz, 6H); ¹³C NMR (101 MHz, CDCl₃) δ 145.39, 135.49, 134.40, 132.44, 129.57, 129.26, 95.80, 83.39, 69.71, 55.28, 24.68, 24.65, -3.16; ¹¹B NMR δ 32.8; HRMS (EI) calc’d for C₂₄H₄₂¹¹B₂O₆Si (M⁺) 476.2937, found 476.2943.
7.4 Hz, 1H), 4.55 – 4.52 (m, 1H), 2.55 (s, 1H), 2.35 (s, 3H), 1.26 (s, 12H), 1.24 (s, 12H), 0.35 – 0.34 (d, J = 3.8 Hz, 6H); ¹³C NMR (101 MHz, CDCl₃) δ 145.51, 138.61, 134.36, 132.02, 130.18, 124.75, 83.30, 24.72, 24.58, 21.58, -3.00; ¹¹B NMR δ 31.61; HRMS (EI) calc’d for C_{22}H_{37}^{11}B_{2}O_{4}Si ([M–H]⁻) 416.2647, found 416.2656.

**1,1-Benzyl diboronate ester 3l:** The reaction was performed according to the general procedure for the diborylation of benzylic C-H bonds with 1l (90.2 mg, 0.500 mmol), B₂pin₂ (254 mg, 1.00 mmol), and [Ir(COD)OMe]₂ (2.50 µmol, 0.500 mol %) in THF (1.00 mL), and 4,4′-di-tert-butyl-2,2′-bipyridine (5.00 µmol, 1.00 mol %) in THF (1.00 mL) at 50 °C for 6 h. The crude mixture was purified by column chromatography on silica gel (hexanes:EtOAc, 100:0 to 90:10) to give compound 3l as a white solid (190 mg, 88%); ¹H NMR (400 MHz, CDCl₃) δ 7.38 – 7.36 (d, J = 8.2 Hz, 1H), 7.12 – 7.1 (d, J = 2.5 Hz, 1H), 6.73 – 6.70 (dd, J = 8.2, 2.5 Hz, 1H), 4.57 – 4.53 (m, 1H), 3.85 (s, 3H), 2.60 (s, 1H), 1.28 (s, 12H), 1.27 (s, 12H), 0.37 – 0.36 (d, J = 3.8 Hz, 6H); ¹³C NMR (101 MHz, CDCl₃) δ 160.40, 147.55, 135.57, 126.74, 115.62, 109.43, 83.40, 54.89, 24.73, 24.69, -2.91; ¹¹B NMR (128 MHz, CDCl₃) δ 32.21; HRMS (EI) calc’d for C_{22}H_{38}^{11}B_{2}O_{5}Si (M⁻) 432.2675, found 432.2683.

**1,1-Benzyl diboronate ester 3m:** The reaction was performed according to the general procedure for the diborylation of benzylic C-H bonds with 1m (140 mg, 0.500 mmol), B₂pin₂ (254 mg, 1.00 mmol), and [Ir(COD)OMe]₂ (2.50 µmol, 0.500 mol %) in THF (1.00 mL), and 4,4′-di-tert-butyl-2,2′-bipyridine (5.00 µmol, 1.00 mol %) in THF (1.00 mL) at
50 °C for 6 h. The crude mixture was purified by column chromatography on silica gel (hexanes:EtOAc, 100:0 to 90:10) to give compound 3m as a white solid (234 mg, 88%); \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) \(\delta\) 7.31 – 7.29 (d, \(J = 8.0\) Hz, 1H), 7.09 – 7.08 (d, \(J = 2.4\) Hz, 1H), 6.67 – 6.4 (dd, \(J = 8.0, 2.4\) Hz, 1H), 4.56 – 4.52 (m, 1H), 2.60 (s, 1H), 1.29 (s, 12H), 1.26 (s, 12H), 1.07 (s, 9H), 0.38 – 0.37 (d, \(J = 3.7\) Hz, 6H), 0.25 (s, 6H); \textsuperscript{13}C NMR (101 MHz, CDCl\textsubscript{3}) \(\delta\) 156.56, 147.23, 135.45, 126.77, 121.24, 115.84, 83.35, 25.89, 24.79, 24.64, 18.30, -2.96, -4.30; \textsuperscript{11}B NMR (128 MHz, CDCl\textsubscript{3}) \(\delta\) 32.30; HRMS (EI) calc’d for C\textsubscript{27}H\textsubscript{50}\textsuperscript{11}B\textsubscript{2}O\textsubscript{5}Si\textsubscript{2} (M\textsuperscript{+}) 532.3383, found 532.3371.

\textbf{1,1-Benzyl diboronate ester 3n:} The reaction was performed according to the general procedure for the diborylation of benzylic C-H bonds with 1n (128 mg, 0.500 mmol), B\textsubscript{2}pin\textsubscript{2} (254 mg, 1.00 mmol), and [Ir(COD)OMe\textsubscript{2}]\textsubscript{2} (2.50 \(\mu\)mol, 0.500 mol \%) in THF (1.00 mL), and 4,4'-di-tert-butyl-2,2'-bipyridine (5.00 \(\mu\)mol, 1.00 mol \%) in THF (1.00 mL) at 50 °C for 6 h. The crude mixture was purified by column chromatography on silica gel (hexanes:EtOAc, 100:0 to 90:10) to give compound 3n as a white solid (203 mg, 80%); \textsuperscript{1}H NMR (500 MHz, CDCl\textsubscript{3}) \(\delta\) 7.51 – 7.50 (d, \(J = 7.5\) Hz, 2H), 7.44 – 7.41 (t, \(J = 7.6\) Hz, 2H), 7.37 – 7.35 (m, 2H), 7.19 – 7.18 (d, \(J = 2.5\) Hz, 1H), 6.79 – 6.77 (dd, \(J = 8.1, 2.5\) Hz, 1H), 5.12 (s, 2H), 4.56 – 4.53 (m, 1H), 2.60 (s, 1H), 1.26 (s, 12H), 1.25 (s, 12H), 0.36 – 0.35 (d, \(J = 3.7\) Hz, 6H); \textsuperscript{13}C NMR (126 MHz, CDCl\textsubscript{3}) \(\delta\) 159.77, 147.60, 137.58, 135.58, 128.52, 127.80, 127.62, 127.06, 116.16, 110.65, 83.40, 69.64, 24.74, 24.69, -2.91; \textsuperscript{11}B NMR (160 MHz, CDCl\textsubscript{3}) \(\delta\) 32.54; HRMS (EI) calc’d for C\textsubscript{28}H\textsubscript{42}\textsuperscript{11}B\textsubscript{2}O\textsubscript{5}Si (M\textsuperscript{+}) 508.2988, found 508.2996.
1,1-Benzyl diboronate ester 3o: The reaction was performed according to the general procedure for the diborylation of benzylic C-H bonds with 1o (92.4 mg, 0.500 mmol), B$_2$pin$_2$ (254 mg, 1.00 mmol), and [Ir(COD)OMe]$_2$ (2.50 µmol, 0.500 mol %) in THF (1.00 mL), and 4,4’-di-tert-butyl-2,2’-bipyridine (5.00 µmol, 1.00 mol %) in THF (1.00 mL) at 50 °C for 12 h. The crude mixture was purified by column chromatography on silica gel (hexanes:EtOAc, 100:0 to 95:5) to give compound 3o as a white solid (175 mg, 80%); $^1$H NMR (400 MHz, CDCl$_3$) δ 7.48 – 7.47 (d, $J = 2.0$ Hz, 1H), 7.36 – 7.34 (d, $J = 8.0$ Hz, 1H), 7.12 – 7.10 (dd, $J = 7.9$, 2.0 Hz, 1H), 4.56 – 4.52 (m, 1H), 2.58 (s, 1H), 1.28 (s, 12H), 1.26 (s, 12H), 0.37 – 0.36 (d, $J = 3.8$ Hz, 6H); $^{13}$C NMR (101 MHz, CDCl$_3$) δ 147.82, 135.52, 135.22, 133.88, 129.37, 124.00, 83.61, 24.73, 24.60, -3.20; $^{11}$B NMR (160 MHz, CDCl$_3$) δ 32.43; HRMS (EI) calc’d for C$_{21}$H$_{34}$B$_2$SiClO$_4$Si ([M–H]$^+$) 435.2101, found 435.2107.

1,1-Benzyl diboronate ester 3p: The reaction was performed according to the general procedure for the diborylation of benzylic C-H bonds with 1p (82.2 mg, 0.500 mmol), B$_2$pin$_2$ (254 mg, 1.00 mmol), and [Ir(COD)OMe]$_2$ (2.50 µmol, 0.500 mol %) in THF (1.00 mL), and 4,4’-di-tert-butyl-2,2’-bipyridine (5.00 µmol, 1.00 mol %) in THF (1.00 mL) at 50 °C for 12 h. The crude mixture was purified by column chromatography on silica gel (hexanes:EtOAc, 100:0 to 95:5) to give compound 3p as a white solid (187 mg, 90%); $^1$H NMR (400 MHz, CDCl$_3$) δ 7.35 – 7.33 (dd, $J = 7.3$, 1.7 Hz, 1H), 7.22 – 7.19 (dd, $J = 7.5$, 1.6 Hz, 1H), 7.12 – 7.08 (t, $J = 7.4$ Hz, 1H), 4.59 – 4.55 (m, 1H), 2.59 (s, 1H), 2.38 (s, 3H), 1.30 (12H), 1.27 (s, 12H), 0.40 – 0.39 (d, $J = 3.6$ Hz, 6H); $^{13}$C NMR (101 MHz, CDCl$_3$) δ
144.53, 136.84, 136.13, 132.25, 131.74, 124.23, 83.29, 25.07, 24.45, 21.30, -2.62; $^{11}$B NMR (128 MHz, CDCl$_3$) $\delta$ 32.49; HRMS (EI) calc’d for C$_{22}$H$_{37}$B$_2$O$_4$Si ([M–H]$^+$) 416.2647, found 416.2658.

1,1-Benzyl diboronate ester 3q: The reaction was performed according to the general procedure for the diborylation of benzylic C-H bonds with 1a (92.4 mg, 0.500 mmol), B$_2$pin$_2$ (254 mg, 1.00 mmol), and [Ir(COD)OMe]$_2$ (2.50 µmol, 0.500 mol %) in THF (1.00 mL), and 4,4’-di-tert-butyl-2,2’-bipyridine (5.00 µmol, 1.00 mol %) in THF (1.00 mL) at 50 °C for 12 h. The crude mixture was purified by column chromatography on silica gel (hexanes:EtOAc, 100:0 to 95:5) to give compound 3q as a white solid (186 mg, 85%); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.39 – 7.36 (m, 2H), 7.12 – 7.08 (m, 1H), 4.57 – 4.50 (m, 1H), 2.61 (s, 1H), 1.29 (s, 12H), 1.27 (s, 12H), 0.39 – 0.38 (d, $J = 3.4$ Hz, 6H); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 144.57, 138.88, 134.67, 132.91, 130.47, 125.42, 83.36, 25.13, 24.34, -2.95; $^{11}$B NMR (128 MHz, CDCl$_3$) $\delta$ 32.39; HRMS (EI) calc’d for C$_{21}$H$_{34}$B$_2$ClO$_4$Si ([M–H]$^+$) 435.2101, found 435.2110.

1,1-Benzyl diboronate ester 3r: The reaction was performed according to the general procedure for the diborylation of benzylic C-H bonds with 1r (89.2 mg, 0.500 mmol), B$_2$pin$_2$ (254 mg, 1.00 mmol), and [Ir(COD)OMe]$_2$ (2.50 µmol, 0.500 mol %) in THF (1.00 mL), and 4,4’-di-tert-butyl-2,2’-bipyridine (5.00 µmol, 1.00 mol %) in THF (1.00 mL) at 50 °C for 12 h. The crude mixture was purified by column chromatography on silica gel (hexanes:EtOAc, 100:0 to 95:5) to give compound 3r as a white solid (181 mg, 84%); $^1$H
NMR (400 MHz, CDCl$_3$) δ 7.23 (s, 1H), 7.21 (s, 1H), 4.57 – 4.54 (m, 1H), 2.53 (s, 1H), 2.31 (s, 3H), 2.27 (s, 3H), 1.30 (m, 12H), 1.28 (s, 12H), 0.38 – 0.37 (d, $J = 3.8$ Hz, 6H); $^{13}$C NMR (101 MHz, CDCl$_3$) δ 142.93, 137.39, 135.88, 132.51, 131.52, 130.79, 83.32, 24.77, 24.66, 19.93, 19.31, -2.87; $^{11}$B NMR (128 MHz, CDCl$_3$) δ 32.17; HRMS (EI) calc’d for C$_{23}$H$_{40}$B$_2$O$_4$Si (M$^+$) 430.2882, found 430.2888.

1,1-Benzyl diboronate ester 3s: The reaction was performed according to the general procedure for the diborylation of benzylic C-H bonds with 1s (100 mg, 0.500 mmol), B$_2$pin$_2$ (254 mg, 1.00 mmol), and [Ir(COD)OMe]$_2$ (2.50 µmol, 0.500 mol %) in THF (1.00 mL), and 4,4’-di-tert-butyl-2,2’-bipyridine (5.00 µmol, 1.00 mol %) in THF (1.00 mL) at 80 °C for 12 h. The crude mixture was purified by column chromatography on silica gel (hexanes:EtOAc, 100:0 to 95:5) to give compound 3s as a light yellow solid (181 mg, 80%); $^1$H NMR (400 MHz, CDCl$_3$) δ 8.32 – 8.30 (d, $J = 8.5$ Hz, 1H), 7.86 – 7.81 (m, 2H), 7.59 – 7.57 (d, $J = 8.5$ Hz, 1H), 7.49 – 7.46 (m, 1H), 7.44 – 7.42 (t, $J = 7.3$ Hz, 1H), 5.11 – 5.05 (m, 1H), 2.90 (s, 1H), 1.31 (s, 12H), 1.29 (s, 12H), 0.62 – 0.61 (d, $J = 4.0$ Hz, 6H); $^{13}$C NMR (101 MHz, CDCl$_3$) δ 146.02, 137.89, 131.38, 129.59, 129.15, 128.78, 127.59, 125.11, 123.81, 83.47, 24.87, 24.55, -1.66; $^{11}$B NMR (128 MHz, CDCl$_3$) δ 31.54; HRMS (EI) calc’d for C$_{25}$H$_{38}$B$_2$O$_4$Si (M$^+$) 452.2725, found 452.2734.

4. General procedure for the conversion of a hydrosilyl group

(1) Cleavage of a hydrosilyl group

A published procedure$^{[2]}$ for the cleavage of hydrosilyl group was followed with slight modifications. To a 4 mL vial containing a stir bar was added 1,1-benzyl diboronate ester 3 (1.00 equiv), KI (1.20 equiv), TMSCl (1.20 equiv), H$_2$O (1.20 equiv), and CH$_3$CN (0.100
The reaction was sealed with a Teflon-lined cap and stirred 2 h at room temperature. The mixture was filtered through a pad of SiO$_2$ and concentrated under reduced pressure. The crude mixture was purified by column chromatography to give the desilylated 1,1-benzyldiboronate ester 4.

**Desilylated 1,1-benzyldiboronate ester 4a:** The reaction was performed according to the general procedure for the cleavage of hydrosilyl group with 3a (2.01 g, 5.00 mmol), KI (996 mg, 6.00 mmol), TMSCl (652 mg, 6.00 mmol), H$_2$O (108 mg, 6.00 mmol) and CH$_3$CN (50.0 mL). The crude mixture was purified by column chromatography on silica gel (hexanes:EtOAc, 100:0 to 95:5) to give compound 4a as a white solid (1.65 g, 96%); $^1$H NMR (500 MHz, CDCl$_3$) δ 7.30 – 7.28 (m, 2H), 7.25 – 7.22 (t, $J$ = 7.7 Hz, 2H), 7.12 – 7.08 (td, $J$ = 7.2, 1.5 Hz, 1H), 2.33 (s, 1H), 1.26 (s, 12H), 1.24 (s, 12H); $^{13}$C NMR (126 MHz, CDCl$_3$) δ 139.50, 129.15, 127.95, 124.18, 83.37, 24.71, 24.62; $^{11}$B NMR (160 MHz, CDCl$_3$) δ 32.78.

**Desilylated 1,1-benzyldiboronate ester 4d:** The reaction was performed according to the general procedure for the cleavage of hydrosilyl group with 3d (167 mg, 0.400 mmol), KI (79.7 mg, 0.480 mmol), TMSCl (52.1 mg, 0.480 mmol), H$_2$O (8.70 mg, 0.480 mmol) and CH$_3$CN (4.00 mL). The crude mixture was purified by column chromatography on silica gel (hexanes:EtOAc, 100:0 to 95:5) to give compound 4d as a white solid (134 mg, 93%); $^1$H NMR (500 MHz, CDCl$_3$) δ 7.19 – 7.17 (dd, $J$ = 8.1, 2.4 Hz, 2H), 7.06 – 7.04 (d, $J$ = 7.5 Hz, 2H), 2.31 (s, 3H), 2.29 (s, 1H), 1.26 (s, 12H), 1.24 (s, 12H); $^{13}$C NMR (126 MHz,
CDCl$_3$ $\delta$ 136.21, 133.32, 128.97, 128.72, 83.31, 24.70, 24.63, 21.00; $^{11}$B NMR (160 MHz, CDCl$_3$) $\delta$ 32.70.

Desilylated 1,1-benzyldiboronate ester 4s: The reaction was performed according to the general procedure for the cleavage of hydrosilyl group with 3s (181 mg, 0.400 mmol), KI (79.7 mg, 0.480 mmol), TMSCl (52.1 mg, 0.480 mmol), H$_2$O (8.70 mg, 0.480 mmol) and CH$_3$CN (4.00 mL). The crude mixture was purified by column chromatography on silica gel (hexanes:EtOAc, 100:0 to 95:5) to give compound 4s as a white solid (122 mg, 77%); $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.79 – 7.76 (t, $J = 7.4$ Hz, 2H), 7.74 – 7.72 (d, $J = 8.5$ Hz, 1H), 7.70 – 7.69 (m, 1H), 7.50 – 7.48 (dd, $J = 8.4$, 1.8 Hz, 1H), 7.43 – 7.40 (ddd, $J = 8.2$, 6.8, 1.4 Hz, 1H), 7.38 – 7.35 (ddd, $J = 8.1$, 6.8, 1.4 Hz, 1H), 2.50 (s, 1H), 1.26 (s, 12H), 1.24 (s, 12H); $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 137.31, 133.81, 131.24, 128.88, 127.45, 127.34, 127.20, 126.44, 125.33, 124.33, 83.47, 24.73, 24.61; $^{11}$B NMR (160 MHz, CDCl$_3$) $\delta$ 33.02.

(2) Iodination of a hydrosilyl group

To a 4 mL vial, the boronate ester 3a (103 mg, 0.299 mmol), [Ru($\rho$-cymene)Cl]$_2$ (0.900 mg, 1.50 $\mu$mol, 0.50 mol %) and anhydrous 2-propanol (0.1 mL) were added with a stirbar. The reaction was sealed with a Teflon-lined cap and stirred at 25 °C for 4 h. The volatile materials were removed by placing the reaction mixture directly under high vacuum for 2 h. To this crude mixture, iodine monochloride (53.5 mg, 0.329 mmol) and dry CH$_2$Cl$_2$ 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 5a as a pale oil (78% in 2 steps, 110 mg).

![Chemical Structure](image)

$^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.80 – 7.79 (d, $J$ = 7.8 Hz, 1H), 7.59 – 7.57 (d, $J$ = 7.8 Hz, 1H), 7.26 – 7.25 (d, $J$ = 7.0 Hz, 1H), 6.81 – 6.78 (td, $J$ = 7.5, 1.7 Hz, 1H), 2.72 (s, 1H), 1.27 (s, 12H), 1.26 (s, 12H); $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 143.42, 139.03, 129.31, 127.99, 126.19, 103.17, 83.59, 24.86, 24.84, 24.61, 24.59. $^{11}$B NMR (128 MHz, CDCl$_3$) $\delta$ 32.71.

5. General procedure for the chemoselective Suzuki-Miyaura cross-couplings

![Chemical Reaction](image)

**Method A**: A published procedure$^{[3]}$ for the Suzuki-Miyaura cross-coupling reaction was followed with slight modifications. In a nitrogen-filled glovebox, aryl bromide (0.200 mmol), desilylated 1,1-benzyldiboronate ester 4 (1.50 equiv), base (2.00 equiv), and Pd[P(t-Bu)$_3$]$_2$ (5.00 mol %) were combined to a 4-mL vial containing a stirbar and THF (2.00 mL). 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 70 °C and stirred for 16 h. The mixture was filtered through a pad of SiO$_2$ and concentrated under reduced pressure. The crude mixture was purified by column chromatography on silica gel to give compound 6.

**Method B**: In a nitrogen-filled glovebox, aryl halide (0.200 mmol), desilylated 1,1-benzyldiboronate ester 4 (1.50 equiv), and Pd[P(t-Bu)$_3$]$_2$ (5.00 mol %) were combined to a 4-mL vial containing a stirbar and THF (2.00 mL). The reaction was sealed with a cap of septum and then removed from the glovebox. To this reaction mixture, an aqueous solution
of NaOH (3.00 equiv, 3.00 M) was added. The vial was placed in a pre-heated aluminum block at 70 °C and stirred for 16 h. The mixture was filtered through a pad of SiO₂ and concentrated under reduced pressure. The crude mixture was purified by column chromatography on silica gel to give compound 7.

**Table S1.** Evaluation of the effect of base on the chemoselective Suzuki-Miyaura cross-coupling

<table>
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<th>Entry</th>
<th>Method</th>
<th>X</th>
<th>Base (equiv)</th>
<th>Solvent</th>
<th>Temp (°C)</th>
<th>¹H NMR yield (%)</th>
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<td>A</td>
<td>Br</td>
<td>NaOH (3.0)</td>
<td>THF</td>
<td>25</td>
<td>&lt;1 27</td>
</tr>
<tr>
<td>2</td>
<td>B</td>
<td>Br</td>
<td>NaOH (3.0)</td>
<td>THF</td>
<td>70</td>
<td>&lt;1 71</td>
</tr>
<tr>
<td>3</td>
<td>B</td>
<td>I</td>
<td>NaOH (3.0)</td>
<td>THF</td>
<td>70</td>
<td>&lt;1 83(80)</td>
</tr>
<tr>
<td>4</td>
<td>A</td>
<td>Br</td>
<td>K₂CO₃ (3.0)</td>
<td>THF</td>
<td>70</td>
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</tr>
<tr>
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<td>Br</td>
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<td>THF</td>
<td>70</td>
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<tr>
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<td>16 15</td>
</tr>
<tr>
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<td>Br</td>
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<td>THF</td>
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<td>77 15</td>
</tr>
<tr>
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<td>A</td>
<td>Br</td>
<td>CsF (2.0)</td>
<td>THF</td>
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<td>88(81)        &lt;1</td>
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<tr>
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<td>A</td>
<td>Br</td>
<td>CsF (2.0)</td>
<td>THF</td>
<td>25</td>
<td>21 &lt;1</td>
</tr>
</tbody>
</table>

Method A: 4a (0.300 mmol), 4-bromotoluene (0.200 mmol), Pd[P(t-Bu)₃]₂ (5.00 mol %), base (2.0-3.0 equiv), THF (2.00 mL) at indicated temperature for 16 h. Method B: 4a (0.300 mmol), 4-iodotoluene (0.200 mmol), Pd[P(t-Bu)₃]₂ (5.00 mol %), NaOH (3.00 equiv), THF (2.00 mL) at indicated temperature for 16 h. *Isolated yield.

**Boronic acid 6a:** The reaction was performed according to the general procedure A for chemoselective Suzuki-Miyaura cross-coupling with 4a (103 mg, 0.299 mmol), 4-bromotoluene (34.2 mg, 0.200 mmol), and CsF (60.7 mg, 0.400 mmol). The crude mixture was purified by column chromatography on silica gel (hexanes:EtOAc, 100:0 to 95:5) to
give compound 6a as a white solid (50 mg, 81%); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.31 – 7.30 (m, 4H), 7.22 – 7.20 (m, 2H), 7.14 – 7.12 (m, 2H), 3.87 (s, 1H), 2.35 (s, 3H), 1.28 (s, 12H); \(^1^\)^3\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 142.40, 138.96, 135.02, 129.15, 129.04, 128.38, 128.28, 125.52, 83.70, 24.76, 24.64, 21.03; \(^1^\)^1\)B NMR (128 MHz, CDCl\(_3\)) \(\delta\) 32.25; HRMS (EI) calc’d for \(\text{C}_{20}\text{H}_{25}\text{B}_2\text{O}_2\) (M\(^{+}\)) 308.1948, found 308.1950.

**Tandem desilylation/Suzuki-Miyaura coupling of 3a**

The desilylation was performed according to the general procedure for the cleavage of hydrosilyl group with 3a (121 mg, 0.300 mmol), KI (60 mg, 0.360 mmol), TMSCl (39.1 mg, 0.360 mmol), H\(_2\)O (6.50 mg, 0.360 mmol) and CH\(_3\)CN (3.00 mL). The crude mixture was filtered through a pad of SiO\(_2\) and concentrated under reduced pressure for 2 h. The crude 4a (ca. 0.3 mmol), 4-bromotoluene (34.2 mg, 0.200 mmol), CsF (60.8 mg, 0.400 mmol), and Pd[P(t-Bu)\(_3\)]\(_2\) (5.11 mg, 0.01 mmol, 5.00 mol %) were combined in a 4-mL vial containing a stirbar and THF (2.00 mL). The reaction was sealed with a Teflon-lined cap and stirred at 70 °C for 16 h. The mixture was filtered through a pad of SiO\(_2\) and concentrated under reduced pressure. The crude mixture was purified by column chromatography on silica gel (hexanes:EtOAc, 100:0 to 95:5) to give compound 6a as a white solid (47 mg, 76% in 2 steps), which gave spectral data identical to that obtained previously.

![Boronate ester 6b](image)

**Boronate ester 6b**: The reaction was performed according to the general procedure A for chemoselective Suzuki-Miyaura cross-coupling with 4a (103 mg, 0.299 mmol), 1-bromo-4-butyylbenzene (42.6 mg, 0.200 mmol), and CsF (60.7 mg, 0.400 mmol). The crude mixture was purified by column chromatography on silica gel (hexanes:EtOAc, 100:0 to 95:5) to give compound 6b as a colorless oil (62 mg, 89%). \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\)
7.33 – 7.29 (m, 4H), 7.27 – 7.20 (m, 3H), 7.16 – 7.14 (m, 2H), 3.90 (s, 1H), 2.65 – 2.61 (t, J = 7.8 Hz, 2H), 1.68 – 1.61 (m, 2H), 1.45 – 1.39 (m, 2H), 1.30 (s, 12H), 1.01 – 0.97 (t, J = 7.3 Hz, 3H); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.33 – 7.27 (m, 4H), 7.26 – 7.22 (m, 2H), 7.22 – 7.17 (m, 1H), 6.92 – 6.82 (m, 2H), 3.85 (s, 1H), 3.82 (s, 3H), 1.28 (s, 12H); \(^1\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 157.63, 142.62, 134.05, 130.15, 128.94, 128.38, 125.50, 113.86, 83.70, 55.22, 24.64; \(^1\)B NMR (128 MHz, CDCl\(_3\)) \(\delta\) 32.21; HRMS (EI) calc’d for C\(_{20}\)H\(_{25}\)BO\(_3\) (M\(^+\)) 324.1897, found 324.1902.

**Boronate ester 6c:** The reaction was performed according to the general procedure A for chemoselective Suzuki-Miyaura cross-coupling with 4a (103 mg, 0.299 mmol), 4-bromoanisole (37.4 mg, 0.200 mmol), and CsF (60.7 mg, 0.400 mmol). The crude mixture was purified by column chromatography on silica gel (hexanes:EtOAc, 100:0 to 95:5) to give compound 6c as a white solid (50 mg, 77%); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.33 – 7.27 (m, 4H), 7.26 – 7.22 (m, 2H), 7.22 – 7.17 (m, 1H), 6.92 – 6.82 (m, 2H), 3.85 (s, 1H), 3.82 (s, 3H), 1.28 (s, 12H); \(^1\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 157.63, 142.62, 134.05, 130.15, 128.94, 128.38, 125.50, 113.86, 83.70, 55.22, 24.64; \(^1\)B NMR (128 MHz, CDCl\(_3\)) \(\delta\) 32.21; HRMS (EI) calc’d for C\(_{20}\)H\(_{25}\)BO\(_3\) (M\(^+\)) 324.1897, found 324.1902.

**Boronate ester 6d:** The reaction was performed according to the general procedure A for chemoselective Suzuki-Miyaura cross-coupling, except that 1,4-dioxane was used in place of THF as a solvent, with 4a (103 mg, 0.299 mmol), 1-bromo-4-fluorobenzene (35.0 mg, 0.200 mmol), and CsF (60.7 mg, 0.400 mmol). The crude mixture was purified by column chromatography on silica gel (hexanes:EtOAc, 100:0 to 95:5) to give compound 6d as a dark solid (41 mg, 65%); \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 7.32 – 7.16 (m, 7H), 7.01 – 6.97
Boronate ester 6e: The reaction was performed according to the general procedure A for chemoselective Suzuki-Miyaura cross-coupling with 4a (103 mg, 0.299 mmol), 3-bromotoluene (34.2 mg, 0.200 mmol), and CsF (60.7 mg, 0.400 mmol). The crude mixture was purified by column chromatography on silica gel (hexanes:EtOAc, 100:0 to 95:5) to give compound 6e as a white solid (43 mg, 70%); \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 7.30 – 7.28 (m, 4H), 7.20 – 7.19 (m, 2H), 7.13 – 7.10 (m, 2H), 7.02 – 7.00 (d, \(J = 7.4\) Hz, 1H), 3.87 (s, 1H), 2.34 (s, 3H), 1.27 (s, 12H); \(^{13}\)C NMR (126 MHz, CDCl\(_3\)) \(\delta\) 142.21, 141.90, 137.91, 129.98, 129.10, 128.38, 128.28, 126.43, 126.17, 125.56, 83.72, 24.64, 24.62, 21.54; \(^{11}\)B NMR (160 MHz, CDCl\(_3\)) \(\delta\) 33.09; HRMS (EI) calc’d for C\(_{19}\)H\(_{22}\)BFO\(_2\) (M\(^+\)) 312.1697, found 312.1693.

Boronate ester 6f: The reaction was performed according to the general procedure A for chemoselective Suzuki-Miyaura cross-coupling with 4a (103 mg, 0.299 mmol), 3-bromobenzothiophene (42.6 mg, 0.200 mmol), and CsF (60.7 mg, 0.400 mmol). The crude mixture was purified by column chromatography on silica gel (hexanes:EtOAc, 100:0 to 95:5) to give compound 6f as a white solid (39.5 mg, 56%). \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.89 – 7.87 (m, 1H), 7.75 – 7.72 (m, 1H), 7.39 (s, 1H), 7.36 – 7.30 (m, 6H), 7.22 – 7.19 (m,
1H), 4.20 (s, 1H), 1.28 (s, 6H), 1.27 (s, 6H); \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 140.51, 140.41, 139.23, 135.88, 128.70, 128.48, 125.76, 124.07, 123.70, 123.00, 122.74, 122.22, 83.93, 24.65, 24.62; \(^{11}\)B NMR (160 MHz, CDCl\(_3\)) \(\delta\) 32.57; HRMS (EI) calc’d for C\(_{21}\)H\(_{23}\)BO\(_2\)S (M\(^+\)) 350.1512, found 350.1513.

**Boronate ester 6g:** The reaction was performed according to the general procedure A for chemoselective Suzuki-Miyaura cross-coupling with 4s (118 mg, 0.299 mmol), 4-bromotoluene (34.2 mg, 0.200 mmol), and CsF (60.7 mg, 0.400 mmol). The crude mixture was purified by column chromatography on silica gel (hexanes:EtOAc, 100:0 to 95:5) to give compound 6g as a white solid (62 mg, 86%). \(^{1}\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.86 – 7.81 (m, 3H), 7.76 (m, 1H), 7.50 – 7.46 (m, 3H), 7.29 – 7.27 (d, \(J = 7.8\) Hz, 2H), 7.18 – 7.16 (d, \(J = 7.8\) Hz, 2H), 4.08 (s, 1H), 2.39 (s, 3H), 1.32 (s, 12H); \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 140.01, 138.83, 135.16, 133.80, 131.90, 129.23, 129.17, 128.18, 127.89, 127.71, 127.55, 127.02, 125.73, 125.11, 83.82, 24.71, 24.68, 21.08; \(^{11}\)B NMR (128 MHz, CDCl\(_3\)) \(\delta\) 32.73. \(^{11}\)B NMR (160 MHz, CDCl\(_3\)) \(\delta\) 32.57; HRMS (EI) calc’d for C\(_{24}\)H\(_{27}\)BO\(_2\) (M\(^+\)) 358.2104, found 358.2111.

**Boronate ester 6h:** The reaction was performed according to the general procedure A for chemoselective Suzuki-Miyaura cross-coupling with 4d (108 mg, 0.301 mmol), 1-bromobenzene (42.6 mg, 0.200 mmol), and CsF (60.7 mg, 0.400 mmol). The crude mixture was purified by column chromatography on silica gel (hexanes:EtOAc, 100:0 to 95:5) to give compound 6h as a dark oil (51 mg, 70%). \(^{1}\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 7.15
- 7.17 (m, 4H), 7.09 – 7.07 (m, 4H), 3.80 (s, 1H), 2.58 – 2.55 (t, J = 7.8 Hz, 2H), 2.31 (s, 3H), 1.61 – 1.55 (m, 2H), 1.40 – 1.34 (m, 2H), 1.25 (s, 12H), 0.94 – 0.92 (t, J = 7.3 Hz, 3H); 13C NMR (126 MHz, CDCl₃) δ 139.93, 139.40, 139.25, 134.88, 129.09, 128.96, 128.84, 128.42, 83.62, 35.24, 33.65, 24.75, 24.63, 22.46, 21.02, 14.01; 11B NMR (160 MHz, CDCl₃) δ 33.41; HRMS (EI) calc’d for C₂₄H₃₃BO₂ (M⁺) 364.2574, found 364.2582.

1-Benzyl-4-methylbenzene (7a): The reaction was performed according to the general procedure B for Suzuki-Miyaura cross-coupling with 4a (103 mg, 0.299 mmol), 4-iodotoluene (43.6 mg, 0.200 mmol), and an aqueous solution of NaOH (0.200 mL, 0.600 mmol, 3.00 M). The crude mixture was purified by column chromatography on silica gel (hexanes) to give compound 7a as a colorless oil (29 mg, 80%); ¹H NMR (400 MHz, CDCl₃) δ 7.42 – 7.32 (m, 2H), 7.30 – 7.21 (m, 3H), 7.21 – 7.11 (m, 4H), 4.01 (s, 2H), 2.39 (s, 3H); 13C NMR (101 MHz, CDCl₃) δ 141.38, 138.05, 135.47, 129.11, 128.84, 128.79, 128.39, 125.94, 41.49, 20.96.

1-Benzyl-4-butylbenzene (7b): The reaction was performed according to the general procedure B for Suzuki-Miyaura cross-coupling with 4a (103 mg, 0.299 mmol), 1-butyl-4-iodobenzene (52.0 mg, 0.200 mmol), and an aqueous solution of NaOH (0.200 mL, 0.600 mmol, 3.00 M). The crude mixture was purified by column chromatography on silica gel (hexanes) to give compound 7b as a colorless oil (39 mg, 86%); ¹H NMR (400 MHz, CDCl₃) δ 7.36 – 7.24 (m, 5H), 7.16 (s, 4H), 4.01 (s, 2H), 2.63 – 2.61 (t, J = 7.8 Hz, 2H), 1.66 – 1.62 (m, 2H), 1.44 – 1.38 (m, 2H), 1.00 – 0.96 (t, J = 7.3 Hz, 3H); 13C NMR (101
1-Benzyl-3-methoxybenzene (7c): The reaction was performed according to the general procedure B for Suzuki-Miyaura cross-coupling with 4a (103 mg, 0.299 mmol), 4-iodoanisole (46.8 mg, 0.200 mmol), and an aqueous solution of NaOH (0.200 mL, 0.600 mmol, 3.00 M). The crude mixture was purified by column chromatography on silica gel (hexanes) to give compound 7c as a colorless oil (32.5 mg, 82%); \textsuperscript{1}H NMR (400 MHz, CDCl$_3$) $\delta$ 7.29 – 7.23 (m, 2H), 7.20 – 7.15 (m, 3H), 7.11 – 7.08 (m, 2H), 6.85 – 6.81 (d, $J = 8.0$ Hz, 2H), 3.93 (s, 2H), 3.81 (s, 3H); \textsuperscript{13}C NMR (101 MHz, CDCl$_3$) $\delta$ 157.96, 141.55, 133.24, 129.84, 128.79, 128.40, 125.94, 113.86, 55.23, 41.04.

1-Benzyl-4-fluorobenzene (7d): The reaction was performed according to the general procedure B for chemoselective Suzuki-Miyaura cross-coupling with 4a (103 mg, 0.299 mmol), 1-bromo-4-fluorobenzene (44.4 mg, 0.200 mmol), and an aqueous solution of NaOH (0.200 mL, 0.600 mmol, 3.00 M). The crude mixture was purified by column chromatography on silica gel (hexanes) to give compound 7d as a colorless oil (33 mg, 88%); \textsuperscript{1}H NMR (400 MHz, CDCl$_3$) $\delta$ 7.40 – 7.30 (m, 2H), 7.30 – 7.13 (m, 5H), 7.07 – 6.95 (m, 2H), 4.00 (s, 2H); \textsuperscript{13}C NMR (101 MHz, CDCl$_3$) $\delta$ 161.41 (d, $J_{C-F} = 245.4$ Hz), 140.91, 136.75 (d, $J_{C-F} = 3.0$ Hz), 130.25 (d, $J_{C-F} = 8.1$ Hz), 128.66 (d, $J_{C-F} = 30.0$ Hz), 126.18, 115.17 (d, $J_{C-F} = 21.2$ Hz), 41.1.
1-Benzyl-3-methylbenzene (7e): The reaction was performed according to the general procedure B for chemoselective Suzuki-Miyaura cross-coupling with 4a (103 mg, 0.299 mmol), 3-iodotoluene (43.6 mg, 0.200 mmol), and an aqueous solution of NaOH (0.200 mL, 0.600 mmol, 3.00 M). The crude mixture was purified by column chromatography on silica gel (hexanes) to give compound 7e as a colorless oil (29.5 mg, 81%); 1H NMR (400 MHz, CDCl3) δ 7.29 – 7.24 (m, 2H), 7.19 – 7.17 (m, 4H), 7.16 – 6.97 (m, 3H), 3.92 (s, 2H), 2.29 (s, 3H); 13C NMR (101 MHz, CDCl3) δ 141.23, 141.00, 137.98, 129.69, 128.89, 128.40, 128.32, 126.80, 125.98, 125.96, 41.88, 21.36.

3-Benzylbenzothiophene (7f): The reaction was performed according to the general procedure B for chemoselective Suzuki-Miyaura cross-coupling with 4a (103 mg, 0.299 mmol), 3-bromobenzothiophene (42.6 mg, 0.200 mmol), and an aqueous solution of NaOH (0.200 mL, 0.600 mmol, 3.00 M). The crude mixture was purified by column chromatography on silica gel (hexanes) to give compound 7f as a colorless oil (42 mg, 93%); 1H NMR (400 MHz, CDCl3) δ 7.93 – 7.90 (m, 1H), 7.77 – 7.75 (m, 1H), 7.41 – 7.27 (m, 7H), 7.06 (s, 1H), 4.25 (s, 2H); 13C NMR (101 MHz, CDCl3) δ 140.62, 139.37, 138.85, 135.63, 128.87, 128.56, 126.37, 124.28, 123.98, 123.12, 122.89, 122.00, 35.03.

2-Benzylthiophene (7g): The reaction was performed according to the general procedure B for chemoselective Suzuki-Miyaura cross-coupling with 4a (103 mg, 0.299 mmol), 2-bromothiophene (32.6 mg, 0.200 mmol), and an aqueous solution of NaOH (0.200 mL, 0.600 mmol, 3.00 M). The crude mixture was purified by column chromatography on silica gel (hexanes) to give compound 7g as a colorless oil (27.5 mg, 93%); 1H NMR (400 MHz, CDCl3) δ 7.86 – 7.82 (m, 1H), 7.60 – 7.57 (m, 1H), 7.41 – 7.27 (m, 7H), 7.24 (s, 1H), 4.24 (s, 2H); 13C NMR (101 MHz, CDCl3) δ 140.62, 139.37, 138.85, 135.63, 128.87, 128.56, 126.37, 124.28, 123.98, 123.12, 122.89, 122.00, 35.03.
CDCl$_3$ δ 7.31 – 7.21 (m, 5H), 7.13 – 7.11 (dd, $J$ = 1.2, 5.0 Hz, 1H), 6.92 – 6.89 (dd, $J$ = 3.2, 5.1 Hz), 6.79 – 6.77 (dd, $J$ = 1.2, 3.2 Hz, 1H); $^{13}$C NMR (101 MHz, CDCl$_3$) δ 144.01, 140.37, 125.85, 128.51, 126.79, 126.46, 125.13, 123.91, 36.01.

2-(4-Methylbenzyl)naphthalene (7h)$^5$: The reaction was performed according to the general procedure B for chemoselective Suzuki-Miyaura cross-coupling with 4s (118 mg, 0.299 mmol), 3-bromobenzo thiophene (42.6 mg, 0.200 mmol), and an aqueous solution of NaOH (0.200 mL, 0.600 mmol, 3.00 M). The crude mixture was purified by column chromatography on silica gel (hexanes) to give compound 7h as a colorless oil (42 mg, 90%); $^1$H NMR (400 MHz, CDCl$_3$) δ 7.80 – 7.75 (m, 3H), 7.64 (s, 1H), 7.46 – 7.42 (m, 2H), 7.34 – 7.32 (m, 1H), 7.13 (m, 4H), 4.12 (s, 2H), 2.33 (s, 3H); $^{13}$C NMR (101 MHz, CDCl$_3$) δ 139.06, 138.09, 135.80, 133.79, 132.23, 129.35, 129.07, 128.20, 127.79, 127.15, 126.09, 125.44, 41.85, 21.18.

6. General procedure for the synthesis of tetrasubstituted alkenylboronate esters

![Diagram of the general procedure for the synthesis of tetrasubstituted alkenylboronate esters]

A published procedure$^6$ for the synthesis of tetrasubstituted alkenylboronate ester was followed with slight modifications. To a 25 mL vial containing stir bar was added boronate ester 4a (103 mg, 0.299 mmol) and THF (0.500 mL). The reaction mixture was cooled to 0 °C, and LTMP (0.300 mmol, 0.400 M in THF) was slowly added. After 5 min, ketone (0.200 mmol) was added in one portion and stirred for 2 h at 0 °C. The reaction mixture
was filtered through a pad of SiO$_2$ and the filtrate was concentrated under reduced pressure. The crude mixture was purified by column chromatography on silica gel to give compound 8. The stereochemistry was determined by $^1$H NMR analysis based on the literature.$^{[7]}$

**Boronate ester 8a:** The reaction was performed according to the general procedure for the synthesis of tetrasubstituted alkenylboronate esters with acetophenone (24.0 mg, 0.200 mmol). The crude mixture was purified by column chromatography on silica gel (hexanes:EtOAc, 100:0 to 95:5) to give compound 8a (E/Z = 84/16) as a white solid (59.5 mg, 93%). $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.46 – 7.44 (m, 2H), 7.40 – 7.35 (m, 4H), 7.32 – 7.26 (m, 4H), 2.09 (s, 3H), 1.07 (s, 12H); $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 147.83, 145.47, 141.72, 128.78, 128.14, 128.03, 127.82, 127.18, 125.94, 83.36, 24.45, 21.51.

**Boronate ester 8b:** The reaction was performed according to the general procedure for the synthesis of tetrasubstituted alkenylboronate esters with propiophenone (26.8 mg, 0.200 mmol). The crude mixture was purified by column chromatography on silica gel (hexanes:EtOAc, 100:0 to 95:5) to give compound 8b (E/Z = 91/9) as a white solid (64 mg, 96%). $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.40 – 7.36 (m, 5H), 7.32 – 7.25 (m, 5H), 2.48 – 2.43 (q, $J$ = 7.5 Hz, 1H), 1.03 (s, 12H), 0.90 – 0.87 (t, $J$ = 7.5 Hz, 2H); $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 153.81, 143.63, 141.52, 128.46, 128.43, 128.16, 127.90, 127.04, 125.92, 83.30, 27.16, 24.39, 13.31.
Boronate ester 8c: The reaction was performed according to the general procedure for the synthesis of tetrasubstituted alkenylboronate esters with 1-acetonaphthone (34.0 mg, 0.200 mmol). The crude mixture was purified by column chromatography on silica gel (hexanes:EtOAc, 100: 0 to 95:5) to give compound 8c (E/Z = 95/5) as a white solid (67 mg, 90%). $^1$H NMR (500 MHz, CDCl$_3$) δ 8.12 – 8.10 (d, $J = 8.1$ Hz, 1H), 7.87 – 7.86 (dd, $J = 7.8$, 1.7 Hz, 1H), 7.80 – 7.79 (d, $J = 7.9$ Hz, 1H), 7.53 – 7.42 (m, 8H), 7.30 – 7.28 (m, 1H), 2.20 (s, 3H), 0.77 (s, 12H); $^{13}$C NMR (126 MHz, CDCl$_3$) δ 146.62, 143.23, 141.13, 133.67, 131.65, 128.91, 128.15, 128.01, 126.95, 126.03, 126.00, 125.81, 125.52, 125.34, 125.21, 82.92, 24.00, 22.86.

Boronate ester 8d: The reaction was performed according to the general procedure for the synthesis of tetrasubstituted alkenylboronate esters with benzophenone (36.5 mg, 0.200 mmol). The crude mixture was purified by column chromatography on silica gel (hexanes:EtOAc, 100:0 to 95:5) to give compound 8d as a white solid (74 mg, 97%). $^1$H NMR (500 MHz, CDCl$_3$) δ 7.38 – 7.37 (m, 2H), 7.33 – 7.32 (m, 3H), 7.12 – 7.11 (m, 2H), 7.11 – 7.08 (m, 6H), 7.00 – 6.98 (m, 2H), 1.16 (s, 12H); $^{13}$C NMR (126 MHz, CDCl$_3$) δ 151.42, 144.67, 141.84, 141.70, 130.95, 129.73, 129.43, 128.01, 127.97, 127.60, 127.53, 126.79, 125.87, 83.71, 24.56; $^{11}$B NMR (160 MHz, CDCl$_3$) δ 30.42.
7. General procedure for the oxidation of tetrasubstituted alkenylboronate esters

To a 25 mL vial containing a stir bar was added boronate ester 8 (0.150 mmol) and THF/EtOH (2/1, 3.00 mL). The reaction mixture was cooled to 0 °C, and an aqueous solution of NaOH (2.00 mL, 6.00 mmol, 3.00 M) and a solution of H₂O₂ (1.00 mL, 30 wt%) was added dropwise. The reaction was warmed to room temperature and stirred for 2 h. The reaction was quenched with a saturated NH₄Cl solution (5.00 mL), and the mixture was extracted with Et₂O (15.0 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 to give the desired ketone 9.

1,2-diphenylpropan-1-one (9a): The reaction was performed according to the general procedure for the oxidation of tetrasubstituted alkenylboronate esters with 8a (48.1 mg, 0.150 mmol). The crude mixture was purified by column chromatography on silica gel (hexanes:EtOAc, 100:0 to 95:5) to give compound 9a as a colorless oil (29.5 mg, 93%). ¹H NMR (400 MHz, CDCl₃) δ 7.98 – 7.96 (dt, J = 7.1, 1.4 Hz, 2H), 7.50 – 7.46 (m, 1H), 7.41 – 7.37 (m, 2H), 7.31 – 7.29 (m, 4H), 7.23 – 7.19 (m, 1H), 4.73 – 4.68 (q, J = 6.8 Hz, 1H), 1.56 – 1.54 (d, J = 6.8 Hz, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 200.30, 141.43, 136.41, 132.76, 128.95, 128.74, 128.45, 127.73, 126.86, 47.86, 19.49.
**1,2-diphenylbutan-1-one (9b)**[^8]: The reaction was performed according to the general procedure for the oxidation of tetrasubstituted alkenylboronate esters with 8b (50.1 mg, 0.150 mmol). The crude mixture was purified by column chromatography on silica gel (hexanes:EtOAc, 100:0 to 95:5) to give compound 9b as a colorless oil (33 mg, 97%). $^1$H NMR (500 MHz, CDCl$_3$) δ 8.01 – 7.99 (dd, $J = 8.4$, 1.4 Hz, 2H), 7.52 – 7.48 (m, 1H), 7.43 – 7.41 (m, 2H), 7.35 – 7.30 (m, 4H), 7.24 – 7.21 (m, 1H), 4.49 – 4.46 (t, $J = 7.3$ Hz, 1H), 2.29 – 2.18 (m, 1H), 1.94 – 1.85 (m, 1H), 0.95 – 0.92 (t, $J = 7.4$ Hz, 3H); $^{13}$C NMR (126 MHz, CDCl$_3$) δ 200.12, 139.65, 137.01, 132.81, 128.86, 128.67, 128.51, 128.28, 126.98, 55.47, 27.16, 12.35.

**8. Synthesis of (Z)-Tamoxifen**

A published procedure[^9] for the Suzuki-Miyaura cross-coupling was followed with slight modifications. To a 4 mL vial containing a stirbar was added 8b (66.9 mg, 0.20 mmol), 2-(4-iodophenoxy)-N,N-dimethylethanamine[^10] (69.8 mg, 0.240 mmol), Pd[P(t-Bu)$_3$]$_2$ (5.11 mg, 0.010 mmol, 5.00 mol %), NaOH (9.60 mg, 0.240 mmol), H$_2$O (4.32 mg, 0.240 mmol), and THF (0.20 mL). The reaction was sealed with a Teflon-lined cap and stirred at 60 °C for 24 h. After cooling the reaction mixture to room temperature, H$_2$O (3.00 mL) was added. The organic phase was separated and the aqueous phase was extracted with CHCl$_3$ (10.0 mL x 3). The combined organic layers were dried over Na$_2$SO$_4$, filtered, and concentrated under reduced pressure. The crude mixture was purified by column...
chromatography on silica gel (CHCl$_3$/MeOH/Et$_3$N, 100:10:1) to give compound 10 as a white solid (60 mg, 80%). The stereochemistry was determined by $^1$H NMR analysis. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.39 – 7.36 (t, $J$ = 7.6 Hz, 2H), 7.31 – 7.28 (m, 3H), 7.20 – 7.18 (m, 2H), 7.16 – 7.14 (m, 3H), 6.81 – 6.78 (dd, $J$ = 6.6, 2.1 Hz, 2H), 6.60 – 6.58 (d, $J$ = 7.0 Hz, 2H), 3.97 – 3.95 (t, $J$ = 5.8 Hz, 2H), 2.79 – 2.68 (t, $J$ = 5.8 Hz, 2H), 2.55 – 2.47 (q, $J$ = 7.5 Hz, 2H), 2.30 (s, 6H), 0.99 – 0.94 (m, 3H); $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 156.76, 143.83, 142.42, 141.31, 138.25, 135.54, 131.85, 129.71, 129.48, 128.10, 127.88, 126.52, 126.02, 113.38, 65.65, 58.31, 45.91, 29.03, 13.64.

9. Reference

S42
Me
SiMe₂H

Electronic Supplementary Material (ESI) for Chemical Science
This journal is © The Royal Society of Chemistry 2013
MeO-O-\text{Me}

SiMe_2H

Electronic Supplementary Material (ESI) for Chemical Science
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MeO

\text{SiMe}_2\text{H}
Me
SiMe₂H

1H NMR spectrum of the compound MeSiMe₂H.