Supporting Information

**Base-free Nickel-catalyzed Hydroboration of Simple Alkene with Bis(pinacolato)diboron in Alcoholic Solvent**

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1. General Information
Unless mentioned otherwise, all manipulations were performed in an argon-filled glove box MBRAUN LAB star or using standard Schlenk techniques. NMR spectra were recorded on a Bruker AV 400 spectrometer at 400 MHz ($^1$H NMR), 100 MHz ($^{13}$C NMR). Chemical shifts were reported in ppm relative to internal TMS for $^1$H NMR data, deuterated solvent for $^{13}$C NMR data, respectively. Data are presented in the following space: chemical shift, multiplicity, coupling constant in hertz (Hz), and signal area integration in natural numbers. Melting points were measured on a RY-I apparatus and uncorrected. Optical rotations were determined using a Perkin Elmer 341 polarimeter. High-resolution mass spectra were recorded on an IonSpec FT-ICR mass spectrometer with ESI resource. All the solvents used for reactions were distilled under argon after drying over an appropriate drying agent.

2. General Procedure for Nickel-Catalyzed Hydroboration
2.1 Arylalkene Hydroboration

\[
\text{Ar}^+ + \text{B}_2\text{pin}_2 \xrightarrow{\text{Ni(cod)}_2, (2 \text{ mol})} \text{MeOH, 75°C} \xrightarrow{\text{Bu}_3\text{P} (4 \text{ mol})} \text{Ar}^+ \text{Bpin}
\]

In an argon-filled glove-box, an oven-dried sealed tube was charged with a stir bar, Ni(cod)$_2$ (5.5 mg, 0.02 mmol), $^3$Bu$_3$P (10% in toluene, 81 mg, 0.04 mmol), and bis(pinacolato) diboron (1.1 mmol). Arylalkene 1 (1.0 mmol) and MeOH (2 mL) was injected into the tube. The tube was then sealed and removed out from the glove-box. The reaction mixture was heated at 75°C for 10 h, then cooled to room temperature and concentrated in vacuo. The crude product was purified by flash column chromatography using ethyl acetate/hexane as eluent.

4,4,5,5-Tetramethyl-2-phenethyl-1,3,2-dioxaborolane (2a)$^1$
Yield: 91%. Colourless oil. $^1$H NMR (400 MHz, CDCl$_3$) δ 7.28 – 7.20 (m, 4H), 7.17 – 7.13 (m, 1H), 2.75 (t, $J = 8.0$ Hz, 2H), 1.22 (s, 12H), 1.14 (t, $J = 8.0$ Hz, 2H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 144.4, 128.2, 128.0, 29.9, 24.8.

2-(4-(Benzyloxy)phenethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2b)
Yield: 91%. White solid. $^1$H NMR (400 MHz, CDCl$_3$) δ 7.42 (d, $J = 8.0$ Hz, 2H), 7.37 (t, $J = 8.0$ Hz, 2H), 7.31 (t, $J = 8.0$ Hz, 1H), 7.13 (d, $J = 8.0$ Hz, 2H), 6.88 (d, $J = 8.0$ Hz, 2H), 5.03 (s, 2H), 2.69 (t, $J = 8.0$ Hz, 2H), 1.21 (s, 12H), 1.11 (t, $J = 8.0$ Hz, 2H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 156.8, 137.3, 136.8, 128.9, 128.5, 127.8, 127.4, 114.6, 83.0, 29.0, 24.8. HRMS (ESI): $m/z [M+H]^+$ calculated for C$_{21}$H$_{28}$BO$_3$: 339.2126; found: 339.2132.
2-(4-Methoxyphenethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2c)
Yield: 93%. Colourless oil. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.13 (d, $J$ = 8.0 Hz, 2H), 6.80 (d, $J$ = 8.0 Hz, 2H), 3.77 (s, 3H), 2.69 (t, $J$ = 8.0 Hz, 2H), 1.22 (s, 12H), 1.11 (t, $J$ = 8.0 Hz, 2H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 157.5, 136.5, 128.8, 113.5, 83.0, 55.2, 29.0, 24.8.

2-(2-(2-Methoxyphenyl)ethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2d)
Yield: 79%. Colourless oil. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.20 – 7.10 (m, 2H), 6.89 – 6.79 (m, 2H), 3.79 (s, 3H), 2.73 (t, $J$ = 8.0 Hz, 2H), 1.22 (s, 12H), 1.12 (t, $J$ = 8.0 Hz, 2H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 157.3, 132.6, 129.0, 126.6, 120.1, 109.90, 82.86, 55.0, 24.7, 24.3.

2-(3-Methoxyphenethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2e)
Yield: 76%. Colourless oil. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.17 (t, $J$ = 8.0 Hz, 1H), 6.81(d, $J$ = 8.0 Hz, 1H), 6.78(d, $J$ = 2.4 Hz, 1H), 6.70 (dd, $J$ = 8.0, 2.4 Hz, 1H), 3.78 (s, 3H), 2.72 (t, $J$ = 8.0 Hz, 2H), 1.23 (s, 12H), 1.14 (t, $J$ = 8.0 Hz, 2H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 159.5, 146.1, 129.1, 120.4, 113.6, 110.9, 83.1, 55.1, 30.0, 24.8.

4,4,5,5-Tetramethyl-2-(4-methylphenethyl)-1,3,2-dioxaborolane (2f)
Yield: 94%. Colourless oil. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.08 (q, $J$ = 8.0 Hz, 4H), 2.70 (t, $J$ = 8.0 Hz, 2H), 2.30 (s, 3H), 1.23 (s, 12H), 1.12 (t, $J$ = 8.0 Hz, 2H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 141.4, 134.8, 128.8, 127.8, 83.0, 29.5, 24.8, 21.0.

2-(4-(tert-Butyl)phenethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2g)
Yield: 80%. Colourless oil. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.28 (d, $J$ = 8.0 Hz, 2H), 7.15(d, $J$ = 8.0 Hz, 2H), 2.71 (t, $J$ = 8.0 Hz, 2H), 1.31 (s, 9H), 1.23 (s, 12H), 1.15 (t, $J$ = 8.0 Hz, 2H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 148.2, 141.3, 127.6, 125.0, 83.0, 34.3, 31.4, 29.3, 24.8.
2-(2-([1,1'-Biphenyl]-4-yl)ethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2h)\textsuperscript{5}

Yield: 86%. White solid. \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) \(\delta 7.59 – 7.57\) (m, 2H), 7.50 (d, \(J = 8.0\) Hz, 2H), 7.42 (t, \(J = 8.0\) Hz, 2H), 7.28 – 7.34 (m, 3H), 2.79 (t, \(J = 8.0\) Hz, 2H), 1.23 (s, 12H), 1.18 (t, \(J = 8.0\) Hz, 2H). \textsuperscript{13}C NMR (100 MHz, CDCl\textsubscript{3}) \(\delta 143.6, 141.2, 138.5, 128.7, 128.4, 127.0, 126.9, 83.1, 29.6, 24.8\).

2-(4-Fluorophenethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2i)\textsuperscript{1}

Yield: 86%. Colourless oil. \(\textsuperscript{1}H\) NMR (400 MHz, CDCl\textsubscript{3}) \(\delta 7.18 – 7.14\) (m, 2H), 6.95-6.91 (m, 2H), 2.71 (t, \(J = 8.0\) Hz, 2H), 1.21 (s, 12H), 1.12 (t, \(J = 8.0\) Hz, 2H). \textsuperscript{13}C NMR (100 MHz, CDCl\textsubscript{3}) \(\delta 161.0\) (d, \(J = 239\) Hz), 139.9 (d, \(J = 3.0\) Hz), 129.3 (d, \(J = 7.6\) Hz), 114.8 (d, \(J = 20.8\) Hz), 83.1, 29.1, 24.8.

2-(3-Fluorophenethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2j)\textsuperscript{4}

Yield: 87%. Colourless oil. \(\textsuperscript{1}H\) NMR (400 MHz, CDCl\textsubscript{3}) \(\delta 7.23 – 7.18\) (m, 1H), 6.98 (d, \(J = 8.0\) Hz, 1H), 6.94 – 6.91 (m, 1H), 6.86 – 6.82 (m, 1H), 2.74 (t, \(J = 8.0\) Hz, 2H), 1.22 (s, 12H), 1.13 (t, \(J = 8.0\) Hz, 2H). \textsuperscript{13}C NMR (100 MHz, CDCl\textsubscript{3}) \(\delta 162.8\) (d, \(J = 237\) Hz), 147.0 (d, \(J = 7.1\) Hz), 129.5 (d, \(J = 8.3\) Hz), 123.6 (d, \(J = 2.6\) Hz), 114.8 (d, \(J = 20.6\) Hz), 112.3 (d, \(J = 20.9\) Hz), 83.2, 29.7, 24.8.

4,4,5,5-Tetramethyl-2-(4-trifluoromethyl)phenethyl)-1,3,2-dioxaborolane (2k)\textsuperscript{4}

Yield: 49%. Colourless oil. \(\textsuperscript{1}H\) NMR (400 MHz, CDCl\textsubscript{3}) \(\delta 7.51\) (d, \(J = 8.0\) Hz, 2H), 7.32 (d, \(J = 8.0\) Hz, 2H), 2.80 (t, \(J = 8.0\) Hz, 2H), 1.22 (s, 12H), 1.15 (t, \(J = 8.0\) Hz, 2H). \textsuperscript{13}C NMR (100 MHz, CDCl\textsubscript{3}) \(\delta 148.5, 128.3, 127.6\) (q, \(J = 30.0\) Hz), 124.0 (q, \(J = 271\) Hz), 83.2, 29.8, 24.8.

2-(2-(Benzo[d][1,3]dioxol-5-yl)ethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2l)
Yield: 91%. Colourless oil. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 6.78 – 6.62 (m, 3H), 5.89 (s, 2H), 2.66 (t, $J$ = 8.0 Hz, 2H), 1.22 (s, 12H), 1.09 (t, $J$ = 8.0 Hz, 2H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 147.3, 145.3, 138.3, 120.5, 108.6, 107.9, 100.6, 83.1, 29.7, 24.8. HRMS (ESI): $m/z$ [M+H]$^+$ calculated for C$_{15}$H$_{22}$BO$_4$: 277.1606; found: 277.1611.

2-(2,5-Dimethylphenethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2m)

Yield: 89%. Colourless oil. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.01 (d, $J$ = 8.0 Hz, 2H), 6.94 – 6.87 (m, 1H), 2.69 (t, $J$ = 8.0 Hz, 2H), 2.29 (s, 3H), 2.28 (s, 3H), 1.25 (s, 12H), 1.10 (t, $J$ = 8.0 Hz, 2H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 142.3, 135.1, 132.5, 129.8, 129.0, 126.2, 83.0, 27.2, 24.8, 21.0, 18.7.

4,4,5,5-Tetramethyl-2-(2,4,6-trimethylphenethyl)-1,3,2-dioxaborolane (2n)

Yield: 67%. Colourless oil. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.01 (d, $J$ = 8.0 Hz, 2H), 6.94 – 6.87 (m, 1H), 2.69 (t, $J$ = 8.0 Hz, 2H), 2.29 (s, 3H), 2.28 (s, 3H), 1.25 (s, 12H), 1.10 (t, $J$ = 8.0 Hz, 2H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 142.3, 135.1, 132.5, 129.8, 129.0, 126.2, 83.0, 27.2, 24.8, 21.0, 18.7.

2-(3,4,5-Trimethoxyphenethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2o)

Yield: 84%. White solid. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 6.44 (s, 2H), 3.83 (s, 6H), 3.80 (s, 3H), 2.69 (t, $J$ = 8.0 Hz, 2H), 1.22 (s, 12H), 1.13 (t, $J$ = 8.0 Hz, 2H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 152.9, 140.2, 135.7, 104.7, 83.1, 60.8, 55.9, 30.3, 24.8.

4,4,5,5-Tetramethyl-2-(2-phenylpropyl)-1,3,2-dioxaborolane (2p)

Yield: 93%. Colourless oil. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.26 – 7.24 (m, 4H), 7.16 – 7.14 (m, 1H), 3.06 – 3.00 (m, 1H), 1.27 (d, $J$ = 4.0 Hz, 3H), 1.16 (m, 14H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 149.2, 128.1, 126.6, 125.6, 82.9, 35.8, 24.9, 24.7, 24.6.
2-(2,2-Diphenylethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2q)
Yield: 83%. White solid. \(^{1}H\) NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.30 – 7.21 (m, 8H), 7.15-7.11 (m, 2H), 4.28 (t, \(J = 8.0\) Hz, 1H), 1.60 (d, \(J = 8.0\) Hz, 2H), 1.05 (s, 12H). \(^{13}C\) NMR (100 MHz, CDCl\(_3\)) \(\delta\) 146.5, 128.2, 127.6, 125.9, 83.1, 46.5, 24.5.

4,4,5,5-Tetramethyl-2-(1-phenylpropan-2-yl)-1,3,2-dioxaborolane (2r)
Yield: 85%. Colourless oil. \(^{1}H\) NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.28 – 7.11 (m, 5H), 2.80 (dd, \(J = 8.0, 13.6\) Hz, 1H), 2.54 (dd, \(J = 8.0, 13.6\) Hz, 1H), 1.42 – 1.33 (m, 1H), 1.18 (s, 6H), 1.17 (s, 6H), 0.97 (d, \(J = 8.0\) Hz, 3H). \(^{13}C\) NMR (100 MHz, CDCl\(_3\)) \(\delta\) 142.3, 128.9, 128.0, 125.6, 83.0, 39.0, 24.7, 15.3.

2-(1,2-Diphenylethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2s)
Yield: 65%. Colourless oil. \(^{1}H\) NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.29 – 7.08 (m, 10H), 3.15 (dd, \(J = 13.6, 10\) Hz, 1H), 2.96 (dd, \(J = 13.6, 6.8\) Hz, 1H), 2.68 (dd, \(J = 10, 7.2\) Hz, 1H), 1.09 (s, 6H), 1.08 (s, 6H). \(^{13}C\) NMR (100 MHz, CDCl\(_3\)) \(\delta\) 142.5, 141.6, 128.8, 128.30, 128.25, 128.0, 125.7, 125.3, 83.3, 38.8, 24.5, 24.4.

2-(Ferrocenyl) -4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2t)
Yield: 92%. Orange oil. \(^{1}H\) NMR (400 MHz, CDCl\(_3\)) \(\delta\) 4.09 (s, 5H), 4.08 – 3.99 (m, 4H), 2.43 (t, \(J = 8.0\) Hz, 2H), 1.25 (s, 3H), 1.06 (t, \(J = 8.0\) Hz, 2H). \(^{13}C\) NMR (100 MHz, CDCl\(_3\)) \(\delta\) 91.5, 82.9, 68.3, 67.6, 66.8, 24.7, 23.5. HRMS (ESI): \(m/z\) [M+H]\(^{+}\) calculated for C\(_{18}\)H\(_{26}\)BFeO\(_2\): 341.1370; found: 341.1368.

2.2 Alkylalkene Hydroboration

\[ \text{R} = \begin{array}{c} \text{B} \end{array} \text{Pin} \]

In an argon-filled glove-box, an oven-dried sealed tube was charged with a stir bar, Ni(cod)\(_2\) (5.5 mg, 0.02 mmol), \text{Bu}_{3}P (10% in toluene, 81 mg, 0.04 mmol), and bis(pinacolato)diboron (1.1 mmol). Alkylalkene \(\text{3} (1.0 \text{ mmol})\) and MeOH (2 mL) was injected into the tube. The tube was then sealed and removed out from the glove-box. The reaction mixture was heated at 75\(^\circ\)C for 10 h, then cooled to room temperature and concentrated in vacuo. The crude product was purified by flash column chromatography using ethyl acetate/hexane as eluent.
2-Hexyl-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (4a)<sup>8</sup> and 2-(hexan-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (4a′)<sup>8</sup>. Combined yield of two isomers (1:1): 85%. Colourless oil. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 1.40 (s, 3H), 1.35 – 1.19 (m, 24H), 1.03 – 0.93 (m, 3H), 0.92 – 0.82 (m, 5H), 0.77 (m, 1H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 82.8, 82.7, 32.9, 32.1, 31.6, 31.2, 23.9, 22.9, 22.6, 15.5, 14.09, 14.05.

2-(3,3-Dimethylbutyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane<sup>9</sup>
Yield: 81%. Colourless oil. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 1.31 – 1.26 (m, 2H), 1.24 (s, 12H), 0.84 (s, 9H), 0.71 (m, 2H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 82.8, 37.7, 30.8, 28.8, 24.8.

2-(2,3-Dimethylbutyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane<sup>9</sup>
Yield: 43%. Colourless oil. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 1.64 – 1.57 (m, 1H), 1.51 – 1.39 (m, 1H), 1.24 (s, 12H), 0.85 – 0.80 (m, 10H), 0.62 – 0.56 (m, 1H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 82.8, 35.1, 34.2, 24.9, 24.7, 19.7, 18.6, 18.5.

4,4,5,5-Tetramethyl-2-(octan-4-yl)-1,3,2-dioxaborolane<sup>10</sup>
Yield: 58%. Colourless oil. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 1.39 – 1.33 (m, 10H), 1.23 (s, 12H), 0.98 – 0.93 (m, 1H) 0.87 – 0.90 (m, 6H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 82.7, 27.9, 27.1, 26.7, 24.7.

2-Cyclohexyl-4,4,5,5-tetramethyl-1,3,2-dioxaborolane<sup>11</sup>
Yield: 78%. Colourless oil. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 1.66 – 1.59 (m, 5H), 1.34 – 1.25 (m, 5H), 1.23 (s, 12H), 1.01 – 0.92 (m, 1H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 82.7, 27.9, 27.1, 26.7, 24.7.
exo-2-(Bicyclo[2.2.1]heptan-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane

Yield: 66%. Colourless oil. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 2.28 – 2.24 (m, 1H), 2.23 – 2.17 (m, 1H), 1.52 – 1.43 (m, 3H), 1.35 – 1.30 (m, 1H), 1.23 – 1.21 (m, 14H), 1.18 – 1.13 (m, 2H), 0.88 – 0.84 (m, 1H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 82.7, 38.7, 38.1, 36.6, 32.2, 32.1, 29.2, 24.7.

3. Mechanistic Study

In an argon-filled glove-box, an oven-dried sealed tube was charged with a stir bar, Ni(cod)$_2$ (2.8 mg, 0.01 mmol), tBu$_3$P (10% in toluene, 40.5 mg, 0.02 mmol), and bis(pinacolato)diboron (0.55 mmol), p-methylstyrene (0.5 mmol) and MeOD (1 mL) was injected into the tube. The tube was then sealed and removed out from the glove-box. The reaction mixture was heated at 75°C for 10 h, then cooled to room temperature and concentrated in vacuo. The crude product was purified by flash column chromatography using ethyl acetate/hexane as eluent.
In an argon-filled glove-box, an oven-dried sealed tube was charged with a stir bar, Ni(cod)$_2$ (2.8 mg, 0.01 mmol), t-Bu$_3$P (10% in toluene, 40.5 mg, 0.02 mmol), and bis(pinacolato)diboron (0.55 mmol). $p$-methylstyrene (0.5 mmol) and CD$_3$OD (1 mL) was injected into the tube. The tube was then sealed and removed out from the glove-box. The reaction mixture was heated at 75°C for 10 h, then cooled to room temperature and concentrated in vacuo. The crude product was purified by flash column chromatography using ethyl acetate/hexane as eluent.
References

4. NMR Spectra