I. General Information

a. Materials

All reactions were carried out in oven-dried Schlenk tubes under an argon or nitrogen atmosphere (purity \( \geq 99.999\% \)). Palladium(II) acetate was purchased from Strem Chemicals Inc. as an tan powder and dissolved in 1,4-dioxane for further
application (1.1 mg/ml). The following chemicals were purchased as received: Tetrabutylammonium hydroxide (50 wt% in water), Trifluoromethanesulfonic anhydride (Energy Chemical), Dibromomethane, PPh$_3$, bis(pinacolato) diboron (Alfa-Aesar). Other substituted phenols were purchased from Aldrich or TCI America. All other reagents and solvents mentioned in this text were purchased from commercial sources and used without purification.

**b. Analytical Methods**

$^1$H and $^{13}$C spectra were recorded either on Bruker Avance 400 or Varian Mercury 400 spectrometer at ambient temperature in CDCl$_3$ unless otherwise noted; Data for $^1$H-NMR are reported as follows: chemical shift (δ ppm), multiplicity, integration, and coupling constant (Hz). Data for $^{13}$C-NMR are reported in terms of chemical shift (δ ppm), multiplicity, and coupling constant (Hz). Gas chromatographic (GC) analysis was acquired on a Shimadzu GC-2014 Series GC System equipped with a flame-ionization detector. GC-MS analysis was performed either on Thermo Scientific AS 3000 Series GC-MS System or Agilent 6890N gas chromatograph coupled to an Agilent 5973 inert mass selective detector. HRMS analysis was performed on Finnigan LCQ advantage Max Series MS System. Elementary Analysis was carried out on Elementar Vario EL III elemental analyzer.

**II. Preparation of Substrates**

**a. Preparation of Aryl Triflates**

Aryl Triflates were prepared according to literature procedure.$^{[1]}$

A flame-dried flask was successively charged with phenol (1.00 g, 10.6 mmol, 1.00 equiv), CH$_2$Cl$_2$ (10 mL), and pyridine (1.80 mL, 1.68 g, 21.3 mmol, 2.00 equiv) at 0°C.
After dropwise addition of a solution of triflic anhydride (2.15 mL, 3.61 g, 12.8 mmol, 1.20 equiv) in CH$_2$Cl$_2$ (5 mL), the reaction mixture was stirred at room temperature for 1.5 h and quenched with the addition of Et$_2$O (15 mL) and aqueous HCl (10%, 5 mL). The reaction mixture was washed successively with aqueous saturated NaHCO$_3$ (10 mL) and brine (10 mL). Drying over MgSO$_4$, evaporation of the solvents under reduced pressure and purification by Kugelrohr distillation afforded the desired product (2.3 g, 95%) as a colorless liquid (b.p.= 95°C, 10 mbar). 1H NMR (400 MHz, CDCl$_3$): $\delta=7.27$–7.30 (m, 2H), 7.37–7.50 (m, 3H) ppm. 13C NMR (100 MHz, CDCl$_3$): $\delta=118.9$ (q, JC,F = 320 Hz), 121.5, 128.5, 130.4, 149.8 ppm.

b. Preparation of 1,1-Diborylalkanes.

1,1-Diborylalkanes were prepared according to literature procedure.[2]

**Method A.** In air, Cu-catalyst (10 mmol), base (250 mmol), and diboron reagent (220 mmol) were added to a Schlenk tube equipped with a stir bar. The vessel was evacuated and filled with argon (three cycles). DMF (300 mL), and Dibromomethane (100 mmol) were added via syringe under an argon atmosphere. The reaction mixture was stirred at 40 °C for 24 h, and then diluted with EtOAc, filtered through silica gel with copious washings (Et$_2$O or EtOAc), concentrated, and purified by column chromatography.

**Method B.** In air, Cu-catalyst (20 mmol), base (60 mmol), and diboron reagent (44 mmol) were added to a Schlenk tube equipped with a stir bar. The vessel was evacuated and filled with argon (three cycles). DMF (120 mL), and 1,1-Dibromoethane (20 mmol) were added via syringe under an argon atmosphere. The reaction mixture was stirred at 40 °C for 24 h, and then diluted with EtOAc, filtered through silica gel with copious washings (Et$_2$O or EtOAc), concentrated, and purified by column chromatography.

**Method C.**[3] In air, diborylmethane (10 mmol) was added to a Schlenk tube equipped with a stir bar. The vessel was evacuated and filled with argon (three cycles). THF (30 mL), and LDA (11 mmol Acros) were added via syringe under an argon atmosphere at 0 °C. The reaction mixture was stirred for 5 min, and then alkyl halide (10 mmol) was added at the same temperature. The reaction mixture was allowed to warm to room
temperature and stirred for 2 hours. When reaction completed, reaction mixture diluted with \( \text{Et}_2\text{O} \), and quenched by the \( \text{NH}_4\text{Cl} \) (aq). The organic layer was dried over \( \text{Na}_2\text{SO}_4 \) (s), filtered and concentrated in vacuo and purified by column chromatography.

### III. Pd-catalyzed Cross-coupling of 1,1-Diborylalkanes with Phenyl Triflate

**Table 1.** Various conditions for the reaction of phenyl triflate and diborylmethane

<table>
<thead>
<tr>
<th>Entry</th>
<th>( Y ) (mmol)</th>
<th>Solvent</th>
<th>Base</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1(^b)</td>
<td>0.15</td>
<td>( \text{H}_2\text{O/dioxane} )</td>
<td>KOH</td>
<td>5</td>
</tr>
<tr>
<td></td>
<td>H₂O/dioxane</td>
<td>Base</td>
<td>Yield (%)</td>
<td></td>
</tr>
<tr>
<td>---</td>
<td>-------------</td>
<td>-------------</td>
<td>-----------</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>NaOH</td>
<td>4</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>LiOH</td>
<td>20</td>
<td></td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>TBAOH</td>
<td>65</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>TMAOH</td>
<td>50</td>
<td></td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>TBAOH</td>
<td>85 (90%)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>TRITON B</td>
<td>54</td>
<td></td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>TBAOH</td>
<td>trace</td>
<td></td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>TBAOH</td>
<td>58</td>
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</tr>
<tr>
<td>10</td>
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<tr>
<td>15</td>
<td>TBAOH</td>
<td>43</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

a Reaction conditions: 1a (0.1 mmol), 2a (y mmol), Pd(OAc)₂ (5 mol%), PPh₃ (10 mol%), base (3 equiv) in 0.5 mL dioxane at rt under an Ar atmosphere for 3h. The yield was determined by GC using benzophenone as the internal standard (average of two GC runs).  

b The used bases were 8N aqueous solution.  
c Organic bases were 1N aqueous solution or methanol solution.  
d 2 equiv TBAOH was used.  
e 4 equiv TBAOH was used.  

TBAOH = Tetrabutylammonium hydroxide. TMAOH = Tetramethylammonium hydroxide. TBOH = Tetrabutylphosphonium hydroxide. TRITON B = Benzyltrimethylammonium hydroxide. DMF = N,N-dimethylformamide. DMSO = Dimethylsulfoxide. THF = Tetrahydrofuran.

### General Procedure for Examples Described in Table 1 and Table 2.

**General Procedure A** In air, Pd(OAc)₂ (1.1 mg, 0.005 mmol), PPh₃ (2.6 mg, 0.01 mmol), and diborylmethanes (40.2 mg, 0.15 mmol) were added to a Schlenk tube equipped with a stir bar. The vessel was evacuated and filled with argon (this process was repeated three times). Dioxane (0.5 mL), 1 M TBAOH (0.3 mL, 0.3 mmol) were added in turn by syringe under argon atmosphere at room temperature, and then stirred at rt for 1 min. And aryl triflate (0.1 mmol) was added in turn by syringe under argon atmosphere. The resulting reaction mixture was stirred vigorously at rt over night. The reaction mixture was then diluted with EtOAc, filtered through silica gel with copious washings (Et₂O or EtOAc), concentrated, and purified by column chromatography.

![4,4,5,5-tetramethyl-2-(2-methylbenzyl)-1,3,2-dioxaborolane](image)

4,4,5,5-tetramethyl-2-(2-methylbenzyl)-1,3,2-dioxaborolane (3b, 17.8 mg, 77% yield, CAS: 390381-02-9)

Synthesized according to typical procedure and purified by column chromatography (petroleum ether : ethyl acetate = 30 : 1) to give colorless oil; ¹H NMR (400 MHz, CDCl₃) δ 7.15 – 7.00 (m, 4H), 2.26 (s, 3H), 2.25 (s, 2H), 1.22 (s, 12H) ppm. ¹³C NMR (101 MHz, CDCl₃) δ 137.49, 135.88, 129.75, 129.43, 125.83, 125.12, 83.33, 24.71, 20.08 ppm.
**4,4,5,5-tetramethyl-2-(3-methylbenzyl)-1,3,2-dioxaborolane (3c, 17.4mg, 75% yield, CAS: 356570-54-2)**:[4]  
Synthesized according to typical procedure and purified by column chromatography (petroleum ether : ethyl acetate = 30 : 1) to give colorless oil;  
$^1$H NMR (400 MHz, CDCl$_3$) δ 7.12 (t, $J = 7.6$ Hz, 1H), 7.01 – 6.96 (m, 2H), 6.95 – 6.90 (m, 1H), 2.30 (s, 3H), 2.25 (s, 2H), 1.23 (s, 12H) ppm.  
$^{13}$C NMR (101 MHz, CDCl$_3$) δ 138.50, 137.73, 129.90, 128.17, 126.01, 125.64, 83.41, 24.75, 21.45 ppm.

![Structure of 4,4,5,5-tetramethyl-2-(3-methylbenzyl)-1,3,2-dioxaborolane (3c)](image)

**4,4,5,5-tetramethyl-2-(4-methylbenzyl)-1,3,2-dioxaborolane (3d, 18.5mg, 81% yield, CAS: 356570-52-0)**:[4]  
Synthesized according to typical procedure and purified by column chromatography (petroleum ether : ethyl acetate = 30 : 1) to give colorless oil;  
$^1$H NMR (400 MHz, CDCl$_3$) δ 7.09 – 7.05 (m, 2H), 7.05 – 7.01 (m, 2H), 2.28 (s, 3H), 2.24 (s, 2H), 1.22 (s, 12H) ppm.  
$^{13}$C NMR (101 MHz, CDCl$_3$) δ 135.40, 134.12, 129.02, 128.89, 83.38, 24.77, 21.01 ppm.

![Structure of 4,4,5,5-tetramethyl-2-(4-methylbenzyl)-1,3,2-dioxaborolane (3d)](image)

**2-(2-chlorobenzyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3e, 10.3mg, 41% yield, CAS: 136565-82-1)**:[5]  
Synthesized according to typical procedure and purified by column chromatography (petroleum ether : ethyl acetate = 30 : 1) to give colorless oil;  
$^1$H NMR (400 MHz, CDCl$_3$) δ 7.33 – 7.29 (td, $J = 7.6$, 1.5 Hz, 1H), 7.22 (td, $J = 7.5$, 1.2 Hz, 1H), 7.14 (td, $J = 7.4$, 1.2 Hz, 1H), 7.08 (td, $J = 7.6$, 1.5 Hz, 1H), 2.38 (s, 2H), 1.24 (s, 12H) ppm.  
$^{13}$C NMR (101 MHz, CDCl$_3$) δ 137.53, 133.87, 129.41, 129.07, 127.20, 125.08, 83.62, 24.72 ppm.

![Structure of 2-(2-chlorobenzyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3e)](image)

**2-(3-chlorobenzyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3f, 9.8mg, 39% yield, CAS: 517920-59-1)**:[5]  
Synthesized according to typical procedure and purified by column chromatography (petroleum ether : ethyl acetate = 30 : 1) to give colorless oil;  
$^1$H NMR (400 MHz, CDCl$_3$) δ 7.20 – 7.13 (m, 2H), 7.10 (d, $J = 8.1$ Hz, 1H), 7.05 (d, $J = 7.4$ Hz, 1H), 2.27 (s, 2H), 1.23 (s, 12H) ppm.  
$^{13}$C NMR (101 MHz, CDCl$_3$) δ 140.78, 133.92, 129.41, 129.07, 127.20, 125.08, 83.62, 24.72 ppm.

![Structure of 2-(3-chlorobenzyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3f)](image)
2-(4-chlorobenzyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3g, 10.8mg, 43% yield, CAS: 475250-49-8)\(^5\):
Synthesized according to typical procedure and purified by column chromatography (petroleum ether : ethyl acetate = 30 : 1) to colorless oil; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta 7.20 (d, J = 8.4 \text{ Hz}, 2\text{H}), 7.10 (d, J = 8.3 \text{ Hz}, 2\text{H}), 2.25 (s, 2\text{H}), 1.23 (s, 12\text{H}) \text{ ppm.} \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta 136.12, 129.54, 129.25, 127.28, 82.53, 23.68 \text{ ppm.}\)

2-(3-methoxybenzyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3h, 16.3mg, 66% yield, 797762-23-3)\(^4\):
Synthesized according to typical procedure and purified by column chromatography (petroleum ether : ethyl acetate = 20 : 1) to colorless oil; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta 7.14 (t, J = 7.9 \text{ Hz}, 1\text{H}), 6.80 – 6.72 (m, 2\text{H}), 6.67 (dd, J = 8.2, 2.2 \text{ Hz}, 1\text{H}), 3.77 (s, 3\text{H}), 2.27 (s, 2\text{H}), 1.23 (s, 12\text{H}) \text{ ppm.} \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta 159.52, 140.35, 129.13, 121.50, 114.59, 83.41, 55.03, 24.71 \text{ ppm.}\)

2-(4-methoxybenzyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3i, 16.4mg, 67% yield, 475250-52-3)\(^4\):
Synthesized according to typical procedure and purified by column chromatography (petroleum ether : ethyl acetate = 20 : 1) to colorless oil; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta 7.09 (d, J = 8.6 \text{ Hz}, 2\text{H}), 6.79 (d, J = 8.6 \text{ Hz}, 2\text{H}), 3.76 (s, 3\text{H}), 2.22 (s, 2\text{H}), 1.23 (s, 12\text{H}) \text{ ppm.} \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta 157.08, 130.48, 129.82, 113.76, 83.37, 55.21, 24.74 \text{ ppm.}\)

2-(3-fluorobenzyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3j, 17.0mg, 72% yield, CAS: 1310048-95-3)\(^4\):
Synthesized according to typical procedure and purified by column chromatography (petroleum ether : ethyl acetate = 30 : 1) to colorless oil; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta 7.18 (dd, J = 14.2, 7.8 \text{ Hz}, 1\text{H}), 6.92 (dd, J = 16.2, 8.9 \text{ Hz}, 2\text{H}), 6.81 (td, J = 8.5, 2.2 \text{ Hz}, 1\text{H}), 2.29 (s, 2\text{H}), 1.23 (s, 12\text{H}) \text{ ppm.} \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta 162.86 (d, J = 244.4 \text{ Hz}), 141.26 (d, J = 7.8 \text{ Hz}), 129.51 (d, J = 8.5 \text{ Hz}), 124.68 (d, J = 2.6 Hz), 115.84 (d, J = 21.0 Hz), 111.74 (d, J = 21.0 Hz), 83.58, 24.72 \text{ ppm.}\)
4,4,5,5-tetramethyl-2-(4-(trifluoromethyl)benzyl)-1,3,2-dioxaborolane (3k, 17.1mg, 60% yield, CAS: 475250-46-5)[5]:

Synthesized according to typical procedure and purified by column chromatography (petroleum ether : ethyl acetate = 30 : 1) to colorless oil; ¹H NMR (400 MHz, CDCl₃) δ 7.48 (d, J = 8.0 Hz, 2H), 7.28 (d, J = 8.1 Hz, 2H), 2.35 (s, 2H), 1.23 (s, 12H) ppm. ¹³C NMR (101 MHz, CDCl₃) δ 143.11, 129.17, 127.21 (q, J = 32.3 Hz), 125.15 (q, J = 3.7 Hz), 124.53 (q, J = 271.9 Hz), 83.69, 24.71 ppm.

4,4,5,5-tetramethyl-2-(4-(trifluoromethoxy)benzyl)-1,3,2-dioxaborolane (3l, 19.0 mg, 63% yield, CAS: 872038-32-9)[5]:

Synthesized according to typical procedure and purified by column chromatography (petroleum ether : ethyl acetate = 20 : 1) to colorless oil; ¹H NMR (400 MHz, CDCl₃) δ 7.19 (d, J = 8.7 Hz, 2H), 7.08 (d, J = 7.9 Hz, 2H), 2.29 (s, 2H), 1.24 (s, 12H) ppm. ¹³C NMR (101 MHz, CDCl₃) δ 146.79, 137.46, 130.11, 120.83, 120.55 (q, J = 255.0 Hz), 83.61, 24.72 ppm. ¹⁴C NMR δ 146.79, 137.46, 130.11, 124.10, 121.82, 119.27, 116.73, 83.61, 24.72.

2-((2,3-dihydro-1H-inden-5-yl)methyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3m, 19.1mg, 74% yield):

Synthesized according to typical procedure and purified by column chromatography (petroleum ether : ethyl acetate = 30 : 1) to colorless oil; ¹H NMR (400 MHz, CDCl₃) δ 7.09 (d, J = 7.6 Hz, 1H), 7.04 (s, 1H), 6.95 (d, J = 7.6 Hz, 1H), 2.85 (dd, J = 12.7, 7.1 Hz, 4H), 2.08 – 1.99 (m, 2H), 2.03 (dd, J = 14.8, 7.4 Hz, 2H), 1.24 (s, 12H) ppm. ¹³C NMR (101 MHz, CDCl₃) δ 144.36, 140.59, 136.13, 126.70, 125.10, 124.10, 83.37, 32.84, 32.44, 25.51, 24.75 ppm. HRMS (EI) m/z calc. C₁₆H₂₃BO₂: 281.1697, found: 281.1704.

4,4,5,5-tetramethyl-2-(3-nitrobenzyl)-1,3,2-dioxaborolane (3n, 13.7mg, 52% yield):

Synthesized according to typical procedure and purified by column chromatography (petroleum ether : ethyl acetate = 10 : 1) to colorless oil; ¹H NMR (400 MHz, CDCl₃) δ 8.06 (s, 1H), 7.99 (d, J = 8.1 Hz, 1H), 7.51 (d, J = 7.6 Hz, 1H), 7.40 (t, J = 7.9 Hz, 1H), 2.40 (s, 2H), 1.24 (s, 12H) ppm. ¹³C NMR (101 MHz, CDCl₃) δ 148.25, 140.92, 135.33, 128.97, 123.79, 120.19, 83.87, 24.72 ppm.
2-((1,1'-biphenyl)-2-ylmethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3o, 17.9mg, 61% yield, CAS: 792923-26-3)\[4]\: Synthesized according to typical procedure and purified by column chromatography (petroleum ether : ethyl acetate = 30 : 1) to colorless oil;\[^1\]H NMR (400 MHz, CDCl\textsubscript{3}) \(\delta\) 7.41 – 7.25 (m, 7H), 7.20 (dq, \(J = 3.6, 2.8\) Hz, 2H), 2.28 (s, 2H), 1.14 (s, 12H) ppm. \[^1\]C NMR (101 MHz, CDCl\textsubscript{3}) \(\delta\) 142.25, 141.66, 136.55, 130.15, 129.99, 129.51, 128.00, 127.26, 126.68, 125.13, 83.31, 24.73 ppm.

3-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)benzaldehyde (3p, 11.6mg, 47% yield): Synthesized according to typical procedure and purified by column chromatography (petroleum ether : ethyl acetate =10 : 1) to colorless oil;\[^1\]H NMR (400 MHz, CDCl\textsubscript{3}) \(\delta\) 9.98 (s, 1H), 7.69 (s, 1H), 7.65 (d, \(J = 7.4\) Hz, 1H), 7.46 (d, \(J = 7.6\) Hz, 1H), 7.40 (t, \(J = 7.5\) Hz, 1H), 2.38 (s, 2H), 1.24 (s, 12H) ppm. \[^1\]C NMR (101 MHz, CDCl\textsubscript{3}) \(\delta\) 192.72, 139.95, 136.50, 135.27, 130.32, 128.88, 126.51, 83.69, 24.72 ppm. HRMS (EI) m/z calc (M+Na\textsuperscript{+}). C\textsubscript{14}H\textsubscript{19}BO\textsubscript{3}: 269.1325, found: 269.1320.

2-(4-chloro-3-methylbenzyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3q, 18.4mg, 69% yield): Synthesized according to typical procedure and purified by column chromatography (petroleum ether : ethyl acetate = 30 : 1) to colorless oil;\[^1\]H NMR (400 MHz, CDCl\textsubscript{3}) \(\delta\) 7.18 (d, \(J = 8.1\) Hz, 1H), 7.03 (d, \(J = 2.0\) Hz, 1H), 6.94 (ddd, \(J = 8.1, 2.3, 0.5\) Hz, 1H), 2.32 (s, 3H), 2.22 (s, 2H), 1.23 (s, 12H) ppm. \[^1\]C NMR (101 MHz, CDCl\textsubscript{3}) \(\delta\) 137.14, 135.54, 131.61, 130.77, 128.75, 127.68, 83.52, 24.71, 19.99 ppm. HRMS (EI) m/z calc (M+Na\textsuperscript{+}). C\textsubscript{14}H\textsubscript{20}BClO\textsubscript{2}: 289.1143, found: 289.1149.

2-(3,5-dimethylbenzyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3r, 19.4mg, 79% yield, 356570 -54-2): Synthesized according to typical procedure and purified by column chromatography (petroleum ether : ethyl acetate = 30 : 1) to colorless oil; \[^1\]H NMR (400 MHz, CDCl\textsubscript{3}) \(\delta\) 6.80 (s, 2H), 6.76 (s, 1H), 6.26 (s, 6H), 2.21 (s, 2H), 1.24 (s, 12H) ppm. \[^1\]C NMR (101 MHz, CDCl\textsubscript{3}) \(\delta\) 138.39, 137.62, 126.87, 126.58, 83.37, 24.72, 21.29 ppm.
4,4,5,5-tetramethyl-2-(naphthalen-1-ylmethyl)-1,3,2-dioxaborolane (3s, 16.6mg, 62% yield, CAS: 475250-57-8)[5]:
Synthesized according to typical procedure and purified by column chromatography (petroleum ether : ethyl acetate = 20 : 1) to colorless oil; 1H NMR (400 MHz, CDCl₃) δ 8.00 (d, J = 7.8 Hz, 1H), 7.85 – 7.80 (m, 1H), 7.66 (d, J = 7.6 Hz, 1H), 7.51 – 7.42 (m, 2H), 7.36 (q, J = 7.3 Hz, 2H), 2.69 (s, 2H), 1.19 (s, 12H) ppm. 13C NMR (101 MHz, CDCl₃) δ 135.59, 133.75, 132.43, 128.50, 126.44, 125.76, 125.36, 125.33, 124.51, 83.53, 24.66 ppm.

(8R,9S,13S,14S)-13-methyl-3-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)-7,8,9,11,12,13,15,16-octahydro-6H-cyclopenta[a]phenanthren-17(14H)-one (3t, 20.5 mg, 54% yield): Synthesized according to typical procedure and purified by column chromatography (petroleum ether : ethyl acetate = 30 : 1) to white solid; 1H NMR (400 MHz, CDCl₃) δ 7.16 (d, J = 8.0 Hz, 1H), 6.98 (d, J = 8.2 Hz, 1H), 6.91 (s, 1H), 2.91 – 2.84 (m, 2H), 2.50 (dd, J = 18.7, 8.6 Hz, 1H), 2.44 – 2.37 (m, 1H), 2.27 (d, J = 10.4 Hz, 1H), 2.23 (s, 2H), 2.15 (dd, J = 18.4, 9.3 Hz, 1H), 2.10 – 1.95 (m, 3H), 1.68 – 1.39 (m, 7H), 1.25 (s, 12H), 0.90 (s, 3H) ppm. 13C NMR (101 MHz, CDCl₃) δ 136.19, 136.13, 135.88, 129.67, 126.49, 125.25, 83.39, 50.51, 48.03, 44.25, 38.24, 35.88, 31.62, 29.34, 26.60, 25.72, 24.75, 21.59, 13.86 ppm. HRMS (EI) m/z calc (M+Na⁺). C₂₅H₃₅BO₃: 417.2577, found: 417.2578.

Experimental Procedures for Examples Described in Table 3.

**General Procedure B** In air, Pd(OAc)₂(2.2mg, 0.01mmol), PPh₃(5.2mg, 0.02mmol), and 1,1-diborylalkanes (40.2mg, 0.15mmol) were added to a Schlenk tube equipped with a stir bar. The vessel was evacuated and filled with argon (this process was repeated three times). Dioxane (0.5 mL), 1M TBAOH (0.3ml,0.3mmol) were added in turn by syringe under argon atmosphere at room temperature, and then stirred at rt for 1 min. And aryl triflate (0.1 mmol) was added in turn by syringe under argon atmosphere. The resulting reaction mixture was stirred vigorously at rt over night. The reaction mixture was then diluted with EtOAc, filtered through silica gel with copious washings (Et₂O or EtOAc), concentrated, and purified by column chromatography.
3-(1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)benzaldehyde (4a, 17.4 mg, 67% yield):
Following general procedure B, 1,1-diborylene and 3-formylphenyl triflates were used; The product was isolated by flash chromatography (10% ethyl acetate/hexane) as a pale colorless oil. ^1H NMR (400 MHz, CDCl\textsubscript{3}) \(\delta\) 9.99 (s, 1H), 7.74 (s, 1H), 7.67 (dt, \(J = 7.4, 1.3\) Hz, 1H), 7.50 (d, \(J = 7.7\) Hz, 1H), 7.43 (t, \(J = 7.6\) Hz, 1H), 2.54 (q, \(J = 7.5\) Hz, 1H), 1.37 (d, \(J = 7.5\) Hz, 3H), 1.21 (d, \(J = 4.3\) Hz, 12H) ppm. ^13C NMR (101 MHz, CDCl\textsubscript{3}) \(\delta\) 192.84, 146.15, 136.53, 134.22, 129.05, 128.90, 126.76, 83.56, 24.61, 24.57, 16.76 ppm. HRMS (EI) m/z calc (M+Na\textsuperscript{+}). C\textsubscript{18}H\textsubscript{23}BO\textsubscript{3}: 283.1545, found: 269.1551.

2-(1-(3,5-dimethylphenyl)-3-(naphthalen-2-yl)propyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (4b, 32.4mg, 81% yield):
Following general procedure B, 1,1-diborylnaphthylethyl and 3,5-dimethylphenyl triflates were used; The product was isolated by flash chromatography (20% ethyl acetate/hexane) as a pale colorless oil. ^1H NMR (400 MHz, CDCl\textsubscript{3}) \(\delta\) 8.06 – 7.99 (m, 1H), 7.81 (td, \(J = 6.8, 3.7\) Hz, 1H), 7.67 (d, \(J = 8.1\) Hz, 1H), 7.48 – 7.41 (m, 2H), 7.39 – 7.33 (m, 1H), 7.29 (d, \(J = 6.6\) Hz, 1H), 6.88 (s, 2H), 6.80 (s, 1H), 3.11 – 2.95 (m, 2H), 2.41 (dd, \(J = 14.8, 6.9\) Hz, 1H), 2.33 – 2.21 (m, 7H), 2.12 – 2.00 (m, 1H), 1.23 (t, \(J = 7.1\) Hz, 12H) ppm. ^13C NMR (101 MHz, CDCl\textsubscript{3}) \(\delta\) 142.65, 138.96, 137.64, 133.83, 131.90, 128.59, 127.05, 126.38, 126.24, 125.99, 125.52, 125.27, 124.18, 83.33, 34.04, 32.96, 24.65, 24.64, 21.35 ppm. (M+Na\textsuperscript{+}). C\textsubscript{27}H\textsubscript{33}BO\textsubscript{2}: 423.3615, found: 423.3622. HRMS (EI) m/z calc (M+H\textsuperscript{+}). C\textsubscript{17}H\textsubscript{17}BO\textsubscript{2}, found: 275.2181.

2-(1-(3,5-dimethylphenyl)propyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (4c, 19.6mg, 72%): Following general procedure B, 2,2’-(propane-1,1-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) and 3,5-dimethylphenyl triflates were used; The product was isolated by flash chromatography (10% ethyl acetate/hexane) as a pale colorless oil. ^1H NMR (400 MHz, CDCl\textsubscript{3}) \(\delta\) 6.82 (s, 2H), 6.77 (s, 1H), 2.27 (s, 6H), 2.14 (t, \(J = 7.9\) Hz, 1H), 1.90 – 1.78 (m, 1H), 1.63 (tt, \(J = 14.6, 7.3\) Hz, 1H), 1.21 (d, \(J = 7.8\) Hz, 12H), 0.90 (t, \(J = 7.3\) Hz, 3H) ppm. ^13C NMR (101 MHz, CDCl\textsubscript{3}) \(\delta\) 143.18 (s), 137.51 (s), 126.87 (s), 126.25 (s), 83.18 (s), 25.94 (s), 24.62 (s), 24.61 (s), 21.35 (s), 14.05 (s) ppm. HRMS (EI) m/z calc (M+H\textsuperscript{+}). C\textsubscript{18}H\textsubscript{29}BO\textsubscript{2}, found: 289.2337.
2-(1-(3,5-dimethylphenyl)-2-methylpropyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (4d, 18.7 mg, 65%):

Following general procedure B, 2,2′-(2-methylpropane-1,1-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) and 3,5-dimethylphenyl triflates were used; The product was isolated by flash chromatography (10% ethyl acetate/hexane) as a pale white solid. \( ^1 \)H NMR (400 MHz, CDCl\(_3\)) \( \delta \) 6.81 (s, 2H), 6.76 (s, 1H), 2.26 (s, 6H), 2.07 (tt, \( J = 17.0, 6.5 \) Hz, 1H), 1.88 (d, \( J = 10.4 \) Hz, 1H), 1.19 (d, \( J = 7.0 \) Hz, 12H), 1.02 (d, \( J = 6.5 \) Hz, 3H), 0.73 (d, \( J = 6.5 \) Hz, 3H) ppm. \( ^{13} \)C NMR (101 MHz, CDCl\(_3\)) \( \delta \) 142.02 (s), 137.29 (s), 126.96 (s), 126.84 (s), 83.10 (s), 30.94 (s), 24.67 (s), 24.49 (s), 23.17 (s), 22.08 (s), 21.35 (s) ppm.

**Experimental Procedures for Examples Described in Scheme 3.**

**General Procedure C** In air, Pd(OAc)\(_2\) (2.2 mg, 0.01 mmol), PPh\(_3\) (5.2 mg, 0.02 mmol), and diborylmethanes (40.2 mg, 0.15 mmol) were added to a Schlenk tube equipped with a stir bar. The vessel was evacuated and filled with argon (this process was repeated three times). Dioxane (0.5 mL), 1M TBAOH (0.3 ml, 0.3 mmol) were added in turn by syringe under argon atmosphere at room temperature, and then stirred at rt for 1 min. And 4-bromophenyl triflate (0.1 mmol) was added in turn by syringe under argon atmosphere. The resulting reaction mixture was stirred vigorously at rt over night. The reaction mixture was then diluted with EtOAc, filtered through silica gel with copious washings (Et\(_2\)O or EtOAc), concentrated, and purified by column chromatography.

**IV. References**


V. NMR Spectra
$^1$H NMR spectra for 3b

$^{13}$C NMR spectra for 3b
$^1$H NMR spectra for 3c

$^{13}$C NMR spectra for 3c
$^1$H NMR spectra for 3d

$^{13}$C NMR spectra for 3d
$^1$H NMR spectra for 3e

$^{13}$C NMR spectra for 3e
H NMR spectra for 3f

\[
\begin{align*}
\text{Cl} & \quad \text{B} \quad \text{O} \\
\text{B} & \quad \text{O} \\
\end{align*}
\]

\[f_1 \text{ (ppm)}
\]

\[\begin{align*}
24.72 & \\
76.72 & \\
77.04 & \\
77.35 & \\
83.62 & \\
125.08 & \\
127.20 & \\
129.07 & \\
129.41 & \\
133.92 & \\
140.78 &
\end{align*}\]

\[f_1 \text{ (ppm)}
\]

\[\begin{align*}
13 \text{ C} \text{ NMR spectra for 3f}
\end{align*}\]
\[ \text{H NMR spectra for 3g} \]

\[ \text{1C NMR spectra for 3g} \]
$^1$H NMR spectra for 3h

$^{13}$C NMR spectra for 3h
$^{1}H$ NMR spectra for 3i

$^{13}C$ NMR spectra for 3i
$^{1}$H NMR spectra for 3j

$^{13}$C NMR spectra for 3j
$^{1}$H NMR spectra for 3k

$^{13}$C NMR spectra for 3k
\( ^1\text{H NMR spectra for 3l} \)

\( ^13\text{C NMR spectra for 3l} \)
$^1$H NMR spectra for 3m

$^{13}$C NMR spectra for 3m
$\textsc{H NMR spectra for 3o}$

$\textsc{C NMR spectra for 3o}$
$^{1}H$ NMR spectra for 3r

$^{13}C$ NMR spectra for 3r
$^1$H NMR spectra for 3s

$^{13}$C NMR spectra for 3s
$^{1}H$ NMR spectra for 3t

$^{13}C$ NMR spectra for 3t
$\text{H NMR spectra for 4a}$

$\text{C NMR spectra for 4a}$
$^1$H NMR spectra for 4b

$^{13}$C NMR spectra for 4b
$^1$H NMR spectra for 4c

$^{13}$C NMR spectra for 4c
$^1$H NMR spectra for 4d

$^{13}$C NMR spectra for 4d