Electronic Supplementary Information

for

Functionalized Geminal-diborylalkanes from Various Electron-Deficient Alkynes and $\text{B}_2\text{pin}_2$

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1. General information

All reactions were accomplished in Schlenk tubes under an atmosphere of N₂. Column chromatography was performed over silica gel (200-300 mesh). ¹H NMR spectra were recorded on a 500 M spectrometer and chemical shifts (in ppm) were referred to CDCl₃ (δ=7.26 ppm), d₆-DMSO (δ=2.5 ppm) (as an internal standard. ¹³C NMR spectra were obtained by using the same NMR spectrometer and were calibrated with CDCl₃ (δ=77.0 ppm), d₆-DMSO (δ=40.0 ppm). ¹⁹F NMR spectrometers were operated on the same NMR spectrometer with CDCl₃ or d₆-DMSO. The following abbreviations were used to illuminate the diversities: δ= chemical shifts, J = coupling constant, s=singlet, d=doublet, t=triplet, q=quartet, m=multiplet. HRMS (ESI) were measured with a quadrupole and TOF mass spectrometers. The X-ray single-crystal determination was performed on a Bruker APEX II X-ray single crystal diffractometer. All reagents and solvents were obtained from commercial suppliers, and used without further purification. Reactions were monitored by thin-layer chromatography (TLC). The products were purified by column chromatography on silica gel using petroleum ether and ethyl acetate as the eluent.
2. Screening of conditions

Table S1. Base effect on the reaction.\textsuperscript{a}

\[
\begin{align*}
1b + \text{B}_{2}\text{pin}_2 & \quad \text{Base, Et}_2\text{O, CH}_3\text{OH} \quad 50^\circ\text{C}, 12 \text{ h} \\
& \rightarrow \text{Bpin-O} \quad \text{Bpin-O} \\
\end{align*}
\]

<table>
<thead>
<tr>
<th>Entry</th>
<th>Base (0.1 equiv)</th>
<th>Yield (%)\textsuperscript{a}</th>
</tr>
</thead>
<tbody>
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<td>Na\textsubscript{2}CO\textsubscript{3}</td>
<td>23</td>
</tr>
<tr>
<td>2</td>
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<td>3</td>
<td>K\textsubscript{3}PO\textsubscript{4}</td>
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<td>56</td>
</tr>
<tr>
<td>6</td>
<td>NaO-tBu</td>
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<tr>
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</tr>
<tr>
<td>14</td>
<td>KOH</td>
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</tbody>
</table>

Conditions\textsuperscript{a}: alkyne (0.2 mmol), CH\textsubscript{3}OH (10 equiv.), Et\textsubscript{2}O (1 mL), 12 h, N\textsubscript{2}, GC yield.

Table S2. The amount of base effect on the reaction.\textsuperscript{a}

\[
\begin{align*}
1b + \text{B}_{2}\text{pin}_2 & \quad \text{K}_{2}\text{CO}_3, \text{Et}_2\text{O, CH}_3\text{OH} \quad 50^\circ\text{C}, 12 \text{ h} \\
& \rightarrow \text{Bpin-O} \quad \text{Bpin-O} \\
\end{align*}
\]

<table>
<thead>
<tr>
<th>Entry</th>
<th>K\textsubscript{2}CO\textsubscript{3} (X equiv)</th>
<th>Yield (%)\textsuperscript{a}</th>
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</thead>
<tbody>
<tr>
<td>1</td>
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<td>2</td>
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<td>77</td>
</tr>
<tr>
<td>3</td>
<td>0.3</td>
<td>\textbf{92 (88)}\textsuperscript{b}</td>
</tr>
<tr>
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<tr>
<td>7</td>
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Conditions\textsuperscript{a}: alkyne (0.2 mmol), CH\textsubscript{3}OH (10 equiv), Et\textsubscript{2}O (1 mL), 12 h, N\textsubscript{2}, GC yield. \textsuperscript{b} Isolated yield.
Table S3. The amount of B<sub>2</sub>pin<sub>2</sub> effect on the reaction.<sup>a</sup>

\[
\begin{align*}
\text{1b} & \quad + \quad \text{B<sub>2</sub>pin<sub>2</sub>} \quad \xrightarrow{\text{K<sub>2</sub>CO<sub>3</sub> (0.3 equiv)}} \\
& \quad \text{Et<sub>2</sub>O, CH<sub>3</sub>OH, 50 °C, 12 h} \\
\end{align*}
\]

<table>
<thead>
<tr>
<th>Entry</th>
<th>B&lt;sub&gt;2&lt;/sub&gt;pin&lt;sub&gt;2&lt;/sub&gt; (x equiv)</th>
<th>Yield (%)&lt;sup&gt;a&lt;/sup&gt;</th>
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Conditions<sup>a</sup>: alkyne (0.2 mmol), CH<sub>3</sub>OH (10 equiv), Et<sub>2</sub>O (1 mL), 12 h, N<sub>2</sub>, GC yield.

Table S4. Temperature effect on the reaction.<sup>a</sup>

\[
\begin{align*}
\text{1b} & \quad + \quad \text{B<sub>2</sub>pin<sub>2</sub>} \quad \xrightarrow{\text{K<sub>2</sub>CO<sub>3</sub> (0.3 equiv)}} \\
& \quad \text{Et<sub>2</sub>O, CH<sub>3</sub>OH, Temp, 12h} \\
\end{align*}
\]

<table>
<thead>
<tr>
<th>Entry</th>
<th>Temp (°C)</th>
<th>Yield (%)&lt;sup&gt;a&lt;/sup&gt;</th>
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<tr>
<td>5</td>
<td>70</td>
<td>72</td>
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</tbody>
</table>

Conditions<sup>a</sup>: alkyne (0.2 mmol), CH<sub>3</sub>OH (10 equiv), Et<sub>2</sub>O (1 mL), 12h, N<sub>2</sub>, GC yield.

Table S5. Time effect on the reaction.<sup>a</sup>

\[
\begin{align*}
\text{1b} & \quad + \quad \text{B<sub>2</sub>pin<sub>2</sub>} \quad \xrightarrow{\text{K<sub>2</sub>CO<sub>3</sub> (0.3 equiv)}} \\
& \quad \text{Et<sub>2</sub>O, CH<sub>3</sub>OH, 50 °C, Time} \\
\end{align*}
\]

<table>
<thead>
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<th>Entry</th>
<th>Time (h)</th>
<th>Yield (%)&lt;sup&gt;a&lt;/sup&gt;</th>
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<td>92</td>
</tr>
<tr>
<td>5</td>
<td>16</td>
<td>89</td>
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</tbody>
</table>

Conditions<sup>a</sup>: alkyne (0.2 mmol), CH<sub>3</sub>OH (10 equiv), Et<sub>2</sub>O (1 mL), N<sub>2</sub>, GC yield.
Table S6. Summarizing of the reaction\textsuperscript{a}

\[
\text{OEt} \quad \text{Bpin} \quad \text{K}_2\text{CO}_3, \text{Et}_2\text{O}, \text{CH}_3\text{OH} \quad \text{Temp, 12h} \quad \text{OEt} \\
1a \quad 2 \quad 3a \quad (\text{Bpin}) \quad (\text{Bpin}) \\
\]

<table>
<thead>
<tr>
<th>entry</th>
<th>B\textsubscript{2}pin\textsubscript{2} (equiv)</th>
<th>K\textsubscript{2}CO\textsubscript{3} (equiv)</th>
<th>Temp (\textdegree C)</th>
<th>Yield (%)\textsuperscript{a}</th>
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<td>92 (88)\textsuperscript{b}</td>
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<td>4</td>
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<td>89</td>
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<tr>
<td>10\textsuperscript{e}</td>
<td>2</td>
<td>0.3</td>
<td>50</td>
<td>30</td>
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</table>

\textsuperscript{a}Conditions: alkyne (0.2 mmol), CH\textsubscript{3}OH (10 equiv), Et\textsubscript{2}O (1 mL), 12 h, N\textsubscript{2}, GC yield.

\textsuperscript{b}Isolated yield.

\textsuperscript{c}6 h. \textsuperscript{d}16 h. \textsuperscript{e}air.
3. General procedure for starting materials

1). General procedure for the preparation of propiolates

\[
\begin{align*}
\text{PhBr} + \text{HOAc} & \xrightarrow{\text{K}_2\text{CO}_3, \text{DMF}, \text{rt}} \text{Ph}(\text{O})\text{COCl} \\
\end{align*}
\]

To a suspension of potassium carbonate (4.47 g, 32.3 mmol) in DMF (15 mL), propionic acid (2.00 mL, 32.3 mmol) in DMF (8 mL) was added and stirred at 0 °C. After 10 min, benzyl bromide (3.20 mL, 26.9 mmol) was added and the reaction mixture was warmed to 25 °C. The resulting solution was stirred for 2 h and then water was added (45 mL). The mixture was extracted with EtOAc–hexanes 1:1 (3 × 30 mL). The combined organic layers were washed with brine and then dried (Na$_2$SO$_4$). After evaporation of the solvent under reduced pressure, the residue was purified through FCC (SiO$_2$; 30% EtOAc in hexanes) to yield a colorless oil (1.79 g, 90%).

2). General procedure for the preparation of propiolamides

A solution of DMAP (15 mg, 0.13 mmol) and DCC (2.58 g, 13 mmol) in CH$_2$Cl$_2$ (15 mL) was added slowly over 1 h to a solution of propionic acid (0.77 mL, 13 mmol) and aniline (1.4 mL, 14 mmol) in CH$_2$Cl$_2$ (15 mL) at 0°C. The suspension was then stirred for 5 h at room temperature, monitoring through TLC (30% EtOAc in hexanes). Upon completion, the mixture was filtered through a layer of Celite and the filtrate concentrated in vacuo. The residue was purified through FCC (SiO$_2$; 30% EtOAc in hexanes) to yield a colorless oil (1.79 g, 90%). Spectral data matched those reported in the literature.

3). General procedure for the preparation of ynones

\[
\begin{align*}
\text{PhCl} + \text{C} & \xrightarrow{\text{Pd(Ph$_3$)$_2$Cl}_2 (2\%), Cul (4\%), Et$_3$N (1equiv), dry THF, rt, 1h, N}_2 \text{Ph} \text{C} \quad \text{O} \\
\end{align*}
\]


Ketones were prepared according to a literature procedure. Using standard Schlenk line, to a flame-dried round bottom flask equipped with stir bar under N2 atmosphere was added acid chloride (10.0 mmol, 1.0 equiv), PdCl2(PPh3)2 (140 mg, 0.2 mmol, 2.0 mol%), CuI (76 mg, 0.4 mmol, 4.0 mol%), Et3N (1.4 mL, 10.0 mmol, 1.0 equiv), and alkyne (1.0 equiv) in dry THF (50 mL) at 25°C. The resulting reaction mixture was stirred at room temperature for 1 h. The reaction was quenched with water (30 mL). The aqueous layer was extracted with EtOAc (3*30 mL). The combined organic layers were washed with brine (30 mL), dried over MgSO4, filtered, and concentrated in vacuo. The resulting crude solid was purified by silica gel flash column chromatography using an elution gradient from 100% hexanes to 10% EtOAc in hexanes. Product-containing fractions were combined and concentrated in vacuo to afford target product.

4). General procedure for the preparation of 2-ethynylazoles

Under a nitrogen atmosphere, to a solution of 2-Bromobenzothiazole (346 mg, 2.1 mmol) in DCE (10 mL) and Et3N (2 equiv) were added ethynyltrimethylsilane (0.4 mL, 251 mg, 2.6 mmol) and trans-dichlorobis(triphenylphosphine)palladium(II) (30 mg, 0.04 mmol). The reaction was stirred at rt for 15 min, and then CuI (4 mg, 0.023 mmol) was added. The reaction mixture was stirred at 80°C for 12.0 h until no more starting product was detected by TLC analysis. The solvent was then evaporated under reduced pressure, and the crude material was purified by flash chromatography over a silica gel column using Hex/EtOAc (85:15) to afford the desired product as a pale yellow solid (489 mg, 91%). Then to a stirred solution of trimethyl(oxazole)silane (322 mg, 1.58 mmol) in EtOH (10 mL) was added KF (123 mg, 2.3 equiv) and 18-crown-6 (10 mol%). The reaction was stirred at rt for 2.0 h. The residue was poured into H2O (100 mL) and extracted with CH2Cl2 (3 × 150 mL), washed with brine, and dried over Na2SO4. The solvent was removed at reduced pressure to give the desired product as an orange solid (145 mg, 44%).

8
5). General procedure for the preparation of aryl alkynes

\[
\begin{align*}
\text{Under a nitrogen atmosphere, to a solution of 1-bromo-4-}
\text{(methylsulfonyl)benzene (500 mg, 2.13 mmol) in Et}_3\text{N (10 mL) were added ethynyltrimethylsilane (0.35 mL, 251 mg, 2.56 mmol) and } trans\text{-dichlorobis(triphenylphosphine)palladium(II) (30 mg, 0.04 mmol). The reaction was stirred at rt for 15 min, and then CuI (4 mg, 0.023 mmol) was added. The reaction mixture was stirred at rt for 12.0 h until no more starting product was detected by TLC analysis. The solvent was then evaporated under reduced pressure, and the crude material was purified by flash chromatography over a silica gel column using Hex/EtOAc (85:15) to afford the desired trimethyl((4-(methylsulfonyl)phenyl)ethynyl)silane as a pale yellow solid (489 mg, 91%). Then to a stirred solution of trimethyl((4-(methylsulfonyl)phenyl)-ethynyl)silane (400 mg, 1.58 mmol) in MeOH (11 mL) was added K}_2\text{CO}_3 (438 mg, 3.16 mmol). The reaction was stirred at rt for 2.0 h. The residue was poured into H}_2\text{O (100 mL) and extracted with CH}_2\text{Cl}_2 (3 × 150 mL), washed with brine, and dried over Na}_2\text{SO}_4. The solvent was removed at reduced pressure to give the desired product as an orange solid (279 mg, 98%).}
\end{align*}
\]

6). General procedure for the preparation of 1-aryl-1-propynes

\[
\begin{align*}
1\text{-Aryl-1-propynes were prepared according to literature procedure. Reactions were performed in a schlenk tube equipped with a stirring bar and capped with a rubber septum. The followings were placed in the tube in order: 21.1 mg (1 mol%) of Pd, 25.6 mg of dppb (2 mol%), 6 ml of TBAF, 3.0 mmol (252.2 mg) of 2-butynoic acid and 3.0 mmol of arylbromobenzene. The mixture was stirred at 110°C for 3 h. The reaction mixture was extracted with aqueous NH}_4\text{Cl solution and diethyl ether. The}
\end{align*}
\]
ether extract was dried over anhydrous MgSO$_4$, filtered, and evaporated under reduced pressures. The reaction mixture was purified by flash chromatography on silica gel ($n$-hexane/ethyl acetate) to afford the product.\footnote{7}

**General procedure for the preparation of medicinally relevant substrates**

![Chemical structure](image)

A round-bottom flask was charged with 4-bromobenzoyl chloride (720 mg, 1.1 equiv), 1,2,3,4-di-$O$-isopropylpseudilene-$\alpha$-$D$-galactopyranose (775 mg, 2.98 mmol), Et$_3$N (452 mg, 1.50 equiv), DMAP (36 mg, 0.03 equiv) and CH$_2$Cl$_2$ (20 mL). The reaction mixture was then filtered, and the filtrate was washed with 1M HCl. The organic layer was dried over anhydrous Na$_2$SO$_4$, and concentrated in vacuo, which was further purified by column chromatography to give a pure alkyl 4-bromobenzoate. The followings were placed in the tube in order: 21.1 mg (1 mol %) of Pd, 25.6 mg of dppb (2 mol %), 6 ml of TBAF, 3.0 mmol (252.2 mg) of 2-butynoic acid and 3.0 mmol of arylbromobenzene. The mixture was stirred at 110 $^\circ$C for 3 h. The reaction mixture was extracted with aqueous NH$_4$Cl solution and diethyl ether. The ether extract was dried over anhydrous MgSO$_4$, filtered, and evaporated under reduced pressures. The reaction mixture was purified by flash chromatography on silica gel ($n$-hexane/ethyl acetate) to afford the product.\footnote{7}

**General procedure for the preparation of vinyl(boronate)**

![Chemical structure](image)

To an oven dried schlenk tube equipped with a stir bar were added A$_1$ (0.25 mmol), B$_2$pin$_2$ (1.1 equiv), CuCl (2.5 mg, 0.025 mmol), NaOt-Bu (9.6 mg, 0.10 mmol), and
THF (2 mL) under nitrogen. After the mixture was stirred at room temperature for 4h, the reaction mixture was filtered through a pad of Celite and concentrated. The product was purified by silica gel chromatography.13

4. General procedure for the synthesis of diborylalkanes

\[
\begin{align*}
\text{EWG-} & \quad \text{R} = \text{H, CH}_3 \\
\text{B}_{2}\text{pin}_2 & \quad \text{2 equiv} \\
\text{K}_2\text{CO}_3, \text{Et}_2\text{O}, \text{CH}_3\text{OH} & \quad \text{50 °C, N}_2, 12 \text{ h}
\end{align*}
\]

General procedure A: the synthesis of Geminal-diborylalkanes from aromatic acetylenes and B\textsubscript{2}pin\textsubscript{2}: In air, a 25 mL Schlenk tube was charged with B\textsubscript{2}pin\textsubscript{2} (2.0 equiv) and K\textsubscript{2}CO\textsubscript{3} (0.3 equiv). The flask was evacuated and filled with nitrogen for three cycles. Et\textsubscript{2}O (1 mL), alkynes (0.2 mmol) and CH\textsubscript{3}OH (80 uL, 10 equiv) were added. The reaction was allowed to stir at 50 °C for 12 hours. Upon completion, the reaction mixture was diluted with ethyl acetate, filtered through a silica gel plug, rinsed with ethyl acetate, and concentrated in vacuo. The crude reaction mixture was purified on silica gel to afford the desired product.

Or a 25 mL Young’s tube was charged with B\textsubscript{2}pin\textsubscript{2} (2.0 equiv) and K\textsubscript{2}CO\textsubscript{3} (0.3 equiv), and filled with nitrogen. Then, Et\textsubscript{2}O (0.1 mL), alkynes (0.2 mmol) and CH\textsubscript{3}OH (80 uL, 10 equiv) were added. The reaction was allowed to stir at 50 °C for 12 hours. (3a-3h, 3o-3q)

General procedure B: the synthesis of Geminal-diborylalkanes from carbonyl group-containing alkynes and B\textsubscript{2}pin\textsubscript{2}: In air, a 25 mL Schlenk tube was charged with B\textsubscript{2}pin\textsubscript{2} (2.0 equiv) and K\textsubscript{2}CO\textsubscript{3} (0.5 equiv). The flask was evacuated and filled with nitrogen for three cycles. Et\textsubscript{2}O (1 mL), alkynes (0.2 mmol) and CH\textsubscript{3}OH (80 uL, 10 equiv) were added. The reaction was allowed to stir at 60 °C for 16 hours. Upon completion, the reaction mixture was diluted with ethyl acetate, filtered through a silica gel plug, rinsed with ethyl acetate, and concentrated in vacuo. The crude reaction mixture was purified on silica gel to afford the desired product.

Or a 25 mL Young’s tube was charged with B\textsubscript{2}pin\textsubscript{2} (2.0 equiv) and K\textsubscript{2}CO\textsubscript{3} (0.3 equiv), and filled with nitrogen. Then, Et\textsubscript{2}O (0.1 mL), alkynes (0.2 mmol) and CH\textsubscript{3}OH (80 uL,
10 equiv) were added. The reaction was allowed to stir at 60 °C for 12 hours. (3i-3n, 6a-6s)

5. General procedure for the transformation of diborylalkanes

(1). Typical procedure for Silver-Catalyzed Fluorination of Secondary Alkylboronic Esters.

Geminal-diborylalkanes (0.2 mmol), AgNO₃ (14 mg, 0.08 mmol), Selectfluor (424 mg, 0.6 mmol) were placed in a Schlenk tube. The reaction vessel was evacuated and filled with nitrogen for three times. Then dichloromethane (1 mL), water (1 mL), and TFA (0.4 ml), H₃PO₄ (0.2 ml) were added successively at rt. The reaction mixture was stirred at 60 °C for 8 h. The resulting mixture was extracted with CH₂Cl₂ (15 mL × 3). The combined organic phases were dried over anhydrous Na₂SO₄. After removal of solvent under reduced pressure, the crude product was purified by column chromatography on silica gel with hexane/ethyl acetate (50:1 - 40:1, v:v) as the eluent to give the pure product.

(2). General procedure for the preparation of synthesis of alkyl mono(boronate)

To a dried 10mL reaction tube was added geminal-diborylalkanes (0.26 mmol), NaOMe (14.2 mg, 0.26 mmol), MeOH (32.0 μL, 0.78 mmol) and toluene (2.0 mL). The mixture was stirred at 90 °C for 12 h. The reaction was quenched by HCl aquerous (1%, 5 mL) and extracted with EtOAc (3 × 10 ml). The combined organic phase was washed with saturated brine, dried over Na₂SO₄ and concentrated in vacuo. The residue was purified by flash chromatography on silica gel using PE/EtOAc (40:1) as the eluent to give the pure product.
(3). General procedure for the preparation of synthesis of secondary alkylated N-heteroaromatic compounds

To an oven-dried 4-dram vial equipped with a Teflon coated magnetic stirring bar were added N-heteroaromatic N-oxide (0.20 mmol), NaOMe (3.0 equiv), geminal-diborylalkanes (2.0 equiv) and anhydrous toluene (2.0 mL). The vial was sealed with a PTFE/silicone-lined septum cap and the reaction mixture was stirred at the indicated temperature for 3 h. The reaction mixture was filtered through celite pad and washed with CH$_2$Cl$_2$ (20 mL). The filtrate was concentrated under reduced pressure. To remove unreacted internal gem-bis[(pinacolato)boryl]alkane, NaBO$_3$•4H$_2$O (93 mg, 0.60 mmol) and THF/H$_2$O (3.0 mL, 1:1) were added to the above obtained crude mixture in a 20 mL vial and stirred for 3 h at room temperature. The reaction mixture was quenched with brine (5.0 mL) and extracted with EtOAc (10 mL x 3). The combined organic layers were dried over MgSO$_4$, filtered and concentrated under reduced pressure. The crude reaction mixture was purified by silica gel column chromatography to yield the desired product.$^{11}$
6. Crystal data of 3n and 6a-para

Crystallographic data for compound 3n (CCDC-1570208) has been deposited with the Cambridge Crystallographic Data Centre. Copies of the data can be obtained, free of charge, on application to CCDC (Email: deposit@ccdc.cam.ac.uk).
Crystallographic data for compound 6a-para (CCDC-1523638) has been deposited with the Cambridge Crystallographic Data Centre, Copies of the data can be obtained, free of charge, on application to CCDC (Email:deposit@ccdc.cam.ac.uk).

Bond precision: C-C = 0.0044 Å

Wavelength = 0.71073 Å

Cell:
- a = 9.6906(9) Å
- b = 10.9669(11) Å
- c = 11.5436(13) Å
- alpha = 70.045(10)°
- beta = 86.183(8)°
- gamma = 84.832(8)°

Temperature: 295 K

Volume: 1147.6(2) Å³

Space group: P -1

Hall group: -P 1

Moiety formula: C21 H31 B2 N O4

Sum formula: C21 H31 B2 N O4

Mr: 383.09

Dx, g cm⁻³: 1.109

Z: 2

Mμ (mm⁻¹): 0.074

F(000): 412.0

F(000)' = 412.18

h, k, l max: 13, 15, 15

Nref: 6196

 Tmin, Tmax: 0.965, 0.978

Tmin': 0.964

Correction method = # Reported T Limits: Tmin=0.489 Tmax=1.000
AbsCorr = MULTI-SCAN

Data completeness = 0.846

Theta (max) = 29.172

R(reflections) = 0.0724 (2923)

wR2(reflections) = 0.2056 (5241)

S = 1.032

Npar= 261
7. The in situ $^1$H NMR of compound 3a from alkyne 1a
8. Extra contents for reviews comments

\[ \text{CN} \quad \xrightarrow{\text{standard conditions}} \quad \text{CN} \]

0.4 mmol

\[ \text{Bpin} \quad \text{Bpin} \quad + \quad \text{Bpin} \quad \text{Bpin} \]

\[ \text{Bpin} \quad \text{CN} \]

\[ \text{Bpin} \quad \text{Bpin} \]

\[ \text{6w}, 19\% \]

\[ \text{6'd}, 62\% \]

\[ \text{NC} \quad \text{Bpin} \quad \text{Bpin} \quad + \quad \text{Bpin} \quad \text{Bpin} \]

\[ \text{NC} \quad \text{Bpin} \]

\[ \text{6x}, 75\% \]

\[ \text{trace by GCMS} \]

\[ \text{CN} \quad \xrightarrow{\text{standard conditions}} \quad \text{CN} \]

0.4 mmol
9. Characterization data for products

Ethyl 3,3-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propanoate (3a) (CAS: No. 1302132-95-1)\(^4\)

The reaction was performed following the general procedure A. Colorless oil, 88% yield (62.3 mg). \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 4.08 (q, \(J = 7.1\) Hz, 2H), 2.54 (d, \(J = 8.3\) Hz, 2H), 1.24 – 1.20 (m, 15H), 1.20 (s, 12H), 1.09 – 1.03 (m, 1H). \(^1^3\)C NMR (126 MHz, CDCl\(_3\)) \(\delta\) 174.9, 83.2, 60.2, 30.6, 24.8, 24.4, 14.3.

Methyl 3,3-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propanoate (3b) (CAS: No. 1800103-38-1)\(^1\)

The reaction was performed following the general procedure A. Colorless oil, 80% yield (54.4 mg). \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 3.62 (s, 3H), 2.55 (d, \(J = 8.3\) Hz, 2H), 1.22 (s, 12H), 1.20 (s, 12H), 1.06 (dd, \(J = 10.7, 5.7\) Hz, 1H). \(^1^3\)C NMR (126 MHz, CDCl\(_3\)) \(\delta\) 175.3, 83.2, 51.5, 30.3.

Tert-butyl 3,3-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propanoate (3c)(CAS: No. 1812184-92-1)\(^1\)

The reaction was performed following the general procedure A. Colorless oil, 78% yield (59.3 mg). \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 2.48 (d, \(J = 8.5\) Hz, 2H), 2.30 (s, 6H), 1.40 (s, 9H), 1.22 (s, 12H), 1.19 (s, 12H), 1.03 (t, \(J = 8.4\) Hz, 1H). \(^1^3\)C NMR (126 MHz, CDCl\(_3\)) \(\delta\) 174.2, 83.1, 79.6, 31.7, 28.1, 25.0, 24.8, 24.4.

3,5-Dimethylbenzyl 3,3-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propanoate (3d)

The reaction was performed following the general procedure A. Colorless oil, 50% yield (44.4 mg). \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 6.95 (s, 2H), 6.92 (s, 1H), 5.02 (s, 2H), 2.63 (d, \(J = 8.3\) Hz, 2H), 2.30 (s, 6H), 1.22 (s, 12H), 1.19 (s, 12H), 1.11 (t, \(J = 8.3\) Hz,
1H). $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 174.7, 137.9, 136.1, 129.5, 125.8, 124.8, 83.2, 66.1, 30.6, 24.8, 24.4, 21.2.

HRMS (ESI, m/z) calcd for $^{12}$C$_{24}$H$_{38}$B$_2$O$_6$[M+H]$^+$: 443.3000; found: 443.3002.

Ethyl 3,3-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butanoate (3e)(CAS: No. 1009307-15-6)$^{13}$

The reaction was performed following the general procedure A. Colorless oil, 84% yield (61.3 mg). $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 4.09 (q, $J = 7.1$ Hz, 2H), 2.56 (s, 2H), 1.28 – 1.25 (m, 3H), 1.23 (s, 12H), 1.21 (s, 12H), 1.09 (s, 3H). $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 174.1, 83.2, 60.0, 39.1, 24.6, 24.8, 16.7, 14.3.

Ethyl 3,3-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)heptanoate (3f)

The reaction was performed following the general procedure A. Colorless oil, 64% yield (52.5 mg). $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 4.08 (t, $J = 7.1$ Hz, 2H), 2.64 (s, 2H), 1.63 (dd, $J = 10.2$, 6.6 Hz, 2H), 1.25 (d, $J = 2.3$ Hz, 5H), 1.22 (s, 12H), 1.21 (s, 12H), 1.18 – 1.13 (m, 2H), 0.84 (t, $J = 7.3$ Hz, 3H). $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 174.2, 83.1, 59.9, 34.9, 29.6, 29.8, 24.9, 24.7, 24.5, 23.3, 14.3, 14.1.

HRMS (ESI, m/z) calcd for $^{12}$C$_{21}$H$_{40}$B$_2$O$_6$[M+H]$^+$: 409.3156; found: 409.3157.

Benzyl 3,3-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butanoate (3g)

The reaction was performed following the general procedure A. Colorless oil, 78% yield (67.1 mg). $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.32 (d, $J = 4.5$ Hz, 4H), 7.30 – 7.27 (m, 1H), 5.09 (s, 2H), 2.64 (s, 2H), 1.21 (s, 12H), 1.19 (s, 12H), 1.11 (s, 3H). $^{13}$C
NMR (125 MHz, CDCl$_3$) δ 173.9, 136.3, 128.4, 128.0, 127.9, 83.2, 65.9, 39.0, 24.9, 24.6, 16.6.
HRMS (ESI, m/z) calcd for $^{12}$C$_{23}$H$_{36}$B$_2$O$_6$[M+H]$^+$: 429.2843; found: 429.2845.

2-Bromobenzyl3,3-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butanoate (3h)

The reaction was performed following the general procedure A. Colorless oil, 68% yield (74.8 mg).

$^1$H NMR (500 MHz, CDCl$_3$) δ 7.53 (d, $J$ = 8.7 Hz, 1H), 7.38 (d, $J$ = 6.4 Hz, 1H), 7.29 (d, $J$ = 7.5 Hz, 1H), 7.15 (t, $J$ = 8.5 Hz, 1H), 5.17 (s, 2H), 2.68 (s, 2H), 1.21 (s, 12H), 1.20 (s, 12H), 1.13 (s, 3H).

$^{13}$C NMR (125 MHz, CDCl$_3$) δ 173.6, 135.7, 132.6, 129.4, 129.3, 127.3, 122.9, 83.5, 83.2, 65.4, 38.9, 24.9, 24.6, 24.5, 16.7.

HRMS (ESI, m/z) calcd for $^{12}$C$_{23}$H$_{35}$B$_2$O$_6$Br$^+$: 507.1949; found: 507.1950.

4,4-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butan-2-one (3i)(CAS: No. 1175712-38-5)$^{14}$

The reaction was performed following the general procedure A. Colorless oil, 73% yield (46.7 mg).

$^1$H NMR (500 MHz, CDCl$_3$) δ 2.73 (d, $J$ = 8.1 Hz, 2H), 2.10 (s, 3H), 1.23 (s, 12H), 1.20 (s, 12H), 0.96 (t, $J$ = 8.0 Hz, 1H).

$^{13}$C NMR (125 MHz, CDCl$_3$) δ 209.03, 83.1, 40.7, 29.1, 25.0, 24.7, 24.5.

4,4-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexan-2-one (3j)

The reaction was performed following the general procedure A. Colorless oil, 70% yield (49.3 mg).

$^1$H NMR (500 MHz, CDCl$_3$) δ 2.83 (s, 2H), 2.09 (s, 3H), 1.64 (q, $J$ = 7.5 Hz, 2H), 1.24 (s, 12H), 1.22 (s, 12H), 0.78 (t, $J$ = 7.5 Hz, 3H).

$^{13}$C NMR (125 MHz, CDCl$_3$) δ 208.9, 83.09, 44.39, 29.6, 24.9, 24.8, 24.7, 22.8, 11.7.

HRMS (ESI, m/z) calcd for $^{12}$C$_{18}$H$_{34}$B$_2$O$_5$[M+Na]$^+$: 373.2506; found: 373.2506.

1-Phenyl-3,3-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)heptan-1-one (3k)

The reaction was performed following the general procedure B. Colorless oil, 74% yield (65.4 mg).

$^1$H NMR (500 MHz, CDCl$_3$) δ 7.99 (dd, $J$ = 8.3, 1.2 Hz, 2H), 7.52 (t,
$J = 7.4$ Hz, 1H), 7.42 (t, $J = 7.7$ Hz, 2H), 3.37 (s, 2H), 1.68 (dd, $J = 10.1$, 6.6 Hz, 2H), 1.26 (s, 12H), 1.24 (s, 12H), 1.22 – 1.19 (m, 2H), 1.15 – 1.10 (m, 2H), 0.79 (t, $J = 7.3$ Hz, 3H). $^{13}$C NMR (125 MHz, CDCl$_3$) δ 200.5, 137.1, 132.7, 128.4, 127.9, 82.9, 41.0, 31.3, 30.2, 24.7, 24.6, 22.9, 14.1.

HRMS (ESI, m/z) calcd for $^{12}$C$_2$$_5$H$_{30}$B$_2$O$_5$[M+Na]$^+$: 463.3027; found: 463.3027.

3-Cyclopropyl-1-phenyl-3,3-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propan-1-one (3l)

The reaction was performed following the general procedure B. Colorless oil, 67% yield (57.1 mg). $^1$H NMR (500 MHz, CDCl$_3$) δ 8.00 (dd, $J = 8.3$, 1.2 Hz, 2H), 7.52 (t, $J = 7.4$ Hz, 1H), 7.43 (t, $J = 7.6$ Hz, 2H), 3.29 (s, 2H), 1.26 (s, 12H), 1.24 (s, 12H), 1.11 – 1.06 (m, 1H), 0.35 (ddd, $J = 8.4$, 5.8, 4.4 Hz, 2H), 0.22 – 0.18 (m, 2H).

$^{13}$C NMR (125 MHz, CDCl$_3$) δ 200.3, 137.2, 132.6, 128.3, 128.1, 82.9, 42.5, 24.7, 24.6, 12.9, 3.5.

HRMS (ESI, m/z) calcd for $^{12}$C$_2$$_4$H$_{36}$B$_2$O$_5$[M+H]$^+$: 425.2894; found: 425.28.

1-Phenyl-3,3-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)decan-1-one (3m)

The reaction was performed following the general procedure B. Colorless oil, 78% yield (75.5 mg). $^1$H NMR (500 MHz, CDCl$_3$) δ 8.02 – 7.96 (m, 2H), 7.51 (t, $J = 6.7$ Hz, 1H), 7.42 (t, $J = 7.6$ Hz, 2H), 3.37 (s, 2H), 1.71 – 1.64 (m, 2H), 1.26 (s, 12H), 1.24 (s, 12H), 1.16 (dt, $J = 19.0$, 11.4 Hz, 10H), 0.81 (t, $J = 7.1$ Hz, 3H). $^{13}$C NMR (125 MHz, CDCl$_3$) δ 200.2, 137.3, 132.5, 128.3, 128.1, 83.0, 40.1, 31.8, 30.0, 29.2, 27.7, 24.8, 24.7, 22.6, 14.1.

HRMS (ESI, m/z) calcd for $^{12}$C$_{28}$H$_{46}$B$_2$O$_5$[M+Na]$^+$: 505.3496; found: 505.3498.

1,6-Diphenyl-3,3-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexan-1-one (3n)

The reaction was performed following the general procedure B. Colorless oil, 70% yield (75.6 mg). $^1$H NMR (500 MHz, CDCl$_3$) δ 7.98 (d, $J = 7.1$ Hz, 2H), 7.53 (t, $J = 8.0$ Hz, 1H), 7.43 (t, $J = 7.7$ Hz, 2H), 7.20 (t, $J = 7.4$ Hz, 2H), 7.10 (dd, $J = 12.0$, 6.5 Hz, 3H), 3.38 (s, 2H), 2.56 – 2.50 (m, 2H), 1.84 – 1.80 (m, 2H), 1.54 – 1.45 (m, 2H), 1.28 (s, 12H), 1.25 (s, 12H). $^{13}$C NMR (125 MHz, CDCl$_3$) δ 200.0, 143.0, 137.1,
132.6, 128.2, 128.1, 125.4, 83.1, 77.3, 77.0, 76.8, 40.0, 36.7, 31.6, 30.2, 30.1, 24.8, 24.7, 22.6, 14.1.

HRMS (ESI, m/z) calcd for \( ^{12}C_{30}H_{42}B_2O_5\)[M+H]^+: 503.3364; found: 503.3367.

N-phenyl-3,3-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butanamide (3o)

\[
\begin{align*}
\text{H} & \quad \text{N} \\
\text{O} & \quad \text{Bpin} \\
\text{Bpin} & \quad \text{Bpin}
\end{align*}
\]

The reaction was performed following the general procedure A. Colorless oil, 66% yield (54.8 mg). \(^1H\) NMR (500 MHz, CDCl\(_3\)) \(\delta\) 7.69 (s, 1H), 7.49 (d, \(J = 7.9\) Hz, 2H), 7.27 (dd, \(J = 10.5, 5.0\) Hz, 2H), 7.04 (t, \(J = 7.3\) Hz, 1H), 2.61 (s, 2H), 1.24 (s, 24H), 1.16 (s, 3H). \(^{13}C\) NMR (125 MHz, CDCl\(_3\)) \(\delta\) 171.4, 138.3, 128.8, 123.56, 119.4, 83.4, 42.3, 24.7, 24.6, 16.6.

HRMS (ESI, m/z) calcd for \( ^{12}C_{22}H_{35}B_2O_5\)[M+H]^+: 414.2847; found: 414.2848.

N-methyl-N-phenyl-3,3-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butanamide (3p)

\[
\begin{align*}
\text{N} & \quad \text{O} \\
\text{Bpin} & \quad \text{Bpin} \\
\text{Bpin} & \quad \text{Bpin}
\end{align*}
\]

The reaction was performed following the general procedure A. Colorless oil, 78% yield (67.1 mg). \(^1H\) NMR (500 MHz, CDCl\(_3\)) \(\delta\) 7.40 (t, \(J = 7.5\) Hz, 2H), 7.33 (d, \(J = 6.9\) Hz, 1H), 7.17 (d, \(J = 7.4\) Hz, 2H), 3.27 (s, 3H), 2.35 (s, 2H), 1.20 (d, \(J = 4.5\) Hz, 24H), 0.98 (s, 3H). \(^{13}C\) NMR (125 MHz, CDCl\(_3\)) \(\delta\) 143.5, 129.7, 129.1, 127.8, 127.2, 82.4, 41.1, 38.2, 29.7, 24.8, 18.0.

HRMS (ESI, m/z) calcd for \( ^{12}C_{23}H_{35}B_2O_5\)[M+Na]^+: 450.2823; found: 450.2825.

N-(4-(tert-butyl)phenyl)-3,3-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butanamide (3q)

\[
\begin{align*}
\text{H} & \quad \text{N} \\
\text{O} & \quad \text{Bpin} \\
\text{Bpin} & \quad \text{Bpin}
\end{align*}
\]

The reaction was performed following the general procedure A. Colorless oil, 66% yield (62.2 mg). \(^1H\) NMR (500 MHz, CDCl\(_3\)) \(\delta\) 7.60 (s, 1H), 7.41 (d, \(J = 8.6\) Hz, 2H), 7.30 (d, \(J = 8.6\) Hz, 2H), 2.60 (s, 2H), 1.29 (s, 9H), 1.25 (s, 24H), 0.07 (s, 3H). \(^{13}C\) NMR (125 MHz, CDCl\(_3\)) \(\delta\) 171.2, 146.4, 135.7, 125.6, 119.2, 83.3, 42.2, 34.3, 31.3, 25.0, 24.7, 24.6, 16.5.

HRMS (ESI, m/z) calcd for \( ^{12}C_{26}H_{43}B_2O_5\)[M+H]^+: 470.3473; found: 470.3473.

1,3-diphenyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propan-1-one (3r)

\[
\begin{align*}
\text{N} & \quad \text{O} \\
\text{Bpin} & \quad \text{Bpin}
\end{align*}
\]
The reaction was performed following the general procedure A. Colorless oil, 60% yield. \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 7.97 (dd, \(J = 8.3, 1.1\) Hz, 2H), 7.54 (t, \(J = 7.4\) Hz, 1H), 7.44 (t, \(J = 7.7\) Hz, 2H), 7.30 (dt, \(J = 15.2, 7.4\) Hz, 4H), 7.17 (t, \(J = 6.9\) Hz, 1H), 3.56 (dd, \(J = 18.3, 10.9\) Hz, 1H), 3.43 (dd, \(J = 18.3, 5.0\) Hz, 1H), 2.80 (dd, \(J = 10.9, 5.0\) Hz, 1H), 1.25 (s, 6H), 1.17 (s, 6H). \(^{13}\)C NMR (125 MHz, CDCl\(_3\)) \(\delta\) 199.7, 141.9, 136.7, 132.9, 128.5, 128.4, 128.3, 128.0, 125.6, 83.4, 43.2, 24.53, 24.50.

**4-(3-oxo-3-phenylpropyl)benzonitrile (3s)**

The reaction was performed following the general procedure A. Colorless oil, 78% yield. \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 7.94 (d, \(J = 7.6\) Hz, 2H), 7.57 (t, \(J = 7.2\) Hz, 3H), 7.46 (t, \(J = 7.7\) Hz, 2H), 7.37 (d, \(J = 8.1\) Hz, 2H), 3.33 (t, \(J = 7.4\) Hz, 2H), 3.14 (t, \(J = 7.4\) Hz, 2H). \(^{13}\)C NMR (125 MHz, CDCl\(_3\)) \(\delta\) 198.2, 147.0, 136.5, 133.3, 132.2, 129.3, 128.7, 118.9, 110.0, 39.4, 29.9.

**4-(2,2-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)benzonitrile (6a-para)**

The reaction was performed following the general procedure A. White solid (mp: 168.2-169.3 °C), 88% yield (67.4 mg). \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 7.51 (d, \(J = 8.2\) Hz, 2H), 7.33 (d, \(J = 8.2\) Hz, 2H), 2.91 (d, \(J = 8.3\) Hz, 2H), 1.16 (d, \(J = 10.5\) Hz, 24H), 1.12 (d, \(J = 8.4\) Hz, 1H). \(^{13}\)C NMR (125 MHz, CDCl\(_3\)) \(\delta\) 150.3, 131.8, 129.1, 119.3, 109.1, 83.3, 31.5, 24.8, 24.5. HRMS-(DART) for: \(^{12}\)C\(_2\)\(^{1}\)H\(_3\)\(^{10}\)B\(_2\)^{14}\)N\(_{16}\)O\(_{4}\)[M+H]\(^+\): calculated: 382.2585, found: 382.2585.

**3-(2,2-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)benzonitrile (6a-meta)**

The reaction was performed following the general procedure A. Colorless oil, 19% yield. \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 7.55 (s, 1H), 7.47 – 7.40 (m, 2H), 7.31 (t, \(J = 7.7\) Hz, 1H), 2.88 (d, \(J = 8.3\) Hz, 2H), 1.25 (d, \(J = 3.0\) Hz, 1H), 1.18 (s, 12H), 1.17 (s, 12H). \(^{13}\)C NMR (125 MHz, CDCl\(_3\)) \(\delta\) 145.9, 133.0, 132.1, 129.3, 128.8, 119.2, 111.8, 83.4, 31.0, 25.0, 24.8, 24.6, 24.5.
HRMS(ESI, m/z) calcd for $^{12}$C$_{21}$H$_{31}$B$_{14}$N$_{16}$O$_{4}$Na[Na][M+Na]$: 406.2331; found: 406.2329.

2-(2,2-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)benzonitrile (6a-ortho)

![Chemical Structure]

The reaction was performed following the general procedure A. Colorless oil, 75% yield. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.54 (dd, $J$ = 7.7, 0.9 Hz, 1H), 7.46 – 7.38 (m, 2H), 7.21 (td, $J$ = 7.5, 1.5 Hz, 1H), 3.08 (d, $J$ = 8.2 Hz, 2H), 1.25 (t, $J$ = 4.0 Hz, 1H), 1.17 (d, $J$ = 8.1 Hz, 24H). $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 148.4, 132.6, 132.2, 129.2, 126.0, 118.1, 112.4, 83.3, 29.8, 25.0, 24.8, 24.4. HRMS(ESI, m/z) calcd for $^{12}$C$_{21}$H$_{31}$B$_{14}$N$_{16}$O$_{4}$Na[Na]: 406.2332; found: 406.2332.

1-(4-(2,2-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)phenyl)ethan-1-one (6b)

![Chemical Structure]

The reaction was performed following the general procedure A. White solid (mp: 174.2-175.3 °C), 78% yield (62.4 mg). $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.89 (d, $J$ = 8.2 Hz, 2H), 7.29 (d, $J$ = 8.2 Hz, 2H), 3.87 (s, 3H), 2.91 (d, $J$ = 8.3 Hz, 2H), 1.30 (d, $J$ = 1.9 Hz, 1H), 1.16 (d, $J$ = 8.4 Hz, 24H). $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 167.3, 150.1, 129.4, 128.3, 127.3, 83.2, 51.9, 31.4, 24.8, 24.5. HRMS-(DART) for: $^{12}$C$_{22}$H$_{34}$B$_{16}$O$_{5}$[M+H]: calculated: 398.2664, found: 398.2665.

Methyl 4-(2,2-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)benzoate (6c)

![Chemical Structure]

The reaction was performed following the general procedure A. White solid (mp: 183.2-184.8 °C), 80% yield (66.6 mg). $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.89 (d, $J$ = 8.2 Hz, 2H), 7.29 (d, $J$ = 8.2 Hz, 2H), 3.87 (s, 3H), 2.91 (d, $J$ = 8.3 Hz, 2H), 1.39 – 1.21 (m, 1H), 1.17 (s, 12H), 1.15 (s, 12H). $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 167.3, 150.1, 129.4, 128.3, 127.3, 83.2, 51.9, 31.4, 24.8, 24.5. HRMS (ESI, m/z) calcd for $^{12}$C$_{22}$H$_{34}$B$_{16}$O$_{6}$[M+Na]: 437.2506; found: 437.2509.
2,2'-(2-(4-(Methylsulfonyl)phenyl)ethane-1,1-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (6d)

The reaction was performed following the general procedure A. White solid (mp: 177.2-178.3 °C), 80% yield (66.6 mg). $^1$H NMR (500 MHz, CDCl$_3$) δ 7.78 (d, $J = 8.3$ Hz, 2H), 7.41 (d, $J = 8.3$ Hz, 2H), 2.99 (s, 3H), 2.93 (d, $J = 8.3$ Hz, 2H), 1.16 (s, 12H), 1.15 (s, 12H), 1.12 (d, $J = 8.4$ Hz, 1H). $^{13}$C NMR (125 MHz, CDCl$_3$) δ 151.3, 137.6, 129.3, 127.1, 83.3, 44.6, 31.3, 24.8, 24.5.

HRMS (ESI, m/z) calcd for $^{12}$C$_{21}$H$_{34}$B$_2$O$_6$S$^{[M+Na]^+}$: 457.2227; found: 457.2227.

4-(2,2-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propyl)benzonitrile (6e)

The reaction was performed following the general procedure A. White solid (mp: 177.2-178.3 °C), 84% yield (67.2 mg). $^1$H NMR (500 MHz, CDCl$_3$) δ 7.50 (d, $J = 8.3$ Hz, 2H), 7.35 (d, $J = 8.2$ Hz, 2H), 2.91 (s, 2H), 1.22 (s, 12H), 1.19 (s, 12H), 0.96 (s, 3H). $^{13}$C NMR (125 MHz, CDCl$_3$) δ 147.7, 131.4, 130.7, 119.3, 109.3, 83.4, 39.4, 24.8, 24.6, 15.8.

HRMS (ESI, m/z) calcd for $^{12}$C$_{21}$H$_{34}$B$_2$O$_6$N$^{[M+Na]^+}$: 418.2561; found: 418.2563.

1-(4-(2,2-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propyl)phenyl)ethan-1-one (6f)

The reaction was performed following the general procedure A. White solid (mp: 177.0-178.6 °C), 90% yield (74.5 mg). $^1$H NMR (500 MHz, CDCl$_3$) δ 7.81 (d, $J = 8.2$ Hz, 2H), 7.33 (d, $J = 8.2$ Hz, 2H), 2.92 (s, 2H), 2.55 (s, 3H), 1.23 (s, 12H), 1.19 (s, 12H), 0.96 (s, 3H). $^{13}$C NMR (125 MHz, CDCl$_3$) δ 198.1, 147.9, 134.7, 130.0, 127.8, 83.3, 39.2, 26.5, 24.8, 24.6, 15.8.

HRMS (ESI, m/z) calcd for $^{12}$C$_{22}$H$_{36}$B$_2$O$_5$N$^{[M+H]^+}$: 413.2894; found: 413.2896.

1-(4-(2,2-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propyl)phenyl)propan-1-one (6g)
The reaction was performed following the general procedure A. White solid (mp: 169.2-171.3 °C), 87% yield (74.8 mg). \textsuperscript{1}H NMR (500 MHz, CDCl\textsubscript{3}) \(\delta\) 7.82 (d, \(J = 8.2\) Hz, 2H), 7.32 (d, \(J = 8.2\) Hz, 2H), 2.96 (q, \(J = 7.2\) Hz, 2H), 2.91 (s, 2H), 1.23 (s, 12H), 1.21 – 1.17 (m, 15H), 0.96 (s, 3H). \textsuperscript{13}C NMR (125 MHz, CDCl\textsubscript{3}) \(\delta\) 200.7, 147.6, 134.4, 130.0, 127.5, 83.3, 39.2, 31.6, 24.8, 24.6, 15.8, 8.3. HRMS (ESI, m/z) calcd for \textsuperscript{12}C\textsubscript{24}H\textsubscript{38}B\textsubscript{2}O\textsubscript{5}\textsuperscript{[M+H]+}: 427.3051; found: 427.3051.

\textbf{2,2'-(1-(4-(Methylsulfonyl)phenyl)propane-2,2-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (6h)}

The reaction was performed following the general procedure A. White solid (mp: 188.2-190.3 °C), 90% yield (81.1 mg). \textsuperscript{1}H NMR (500 MHz, CDCl\textsubscript{3}) \(\delta\) 7.80 – 7.76 (m, 2H), 7.45 (d, \(J = 8.4\) Hz, 2H), 3.02 (s, 3H), 2.95 (s, 2H), 1.23 (s, 12H), 1.20 (s, 12H), 0.97 (s, 3H). \textsuperscript{13}C NMR (125 MHz, CDCl\textsubscript{3}) \(\delta\) 148.8, 137.6, 130.8, 126.7, 83.4, 44.6, 39.2, 24.8, 24.7, 15.8. HRMS (ESI, m/z) calcd for \textsuperscript{12}C\textsubscript{22}H\textsubscript{36}B\textsubscript{2}O\textsubscript{6}\textsuperscript{[M+Na]+}: 471.2384; found: 471.2386.

\textbf{Ethyl 4-(2,2-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propyl)benzoate (6i)}

The reaction was performed following the general procedure A. White solid (mp: 168.2-169.3 °C), 88% yield (78.1 mg). \textsuperscript{1}H NMR (500 MHz, CDCl\textsubscript{3}) \(\delta\) 7.81 (d, \(J = 8.3\) Hz, 2H), 7.31 (d, \(J = 8.0\) Hz, 2H), 4.33 (q, \(J = 7.0\) Hz, 2H), 2.91 (s, 2H), 1.36 (t, \(J = 7.0\) Hz, 3H), 1.22 (s, 12H), 1.19 (s, 12H), 0.96 (s, 3H). \textsuperscript{13}C NMR (125 MHz, CDCl\textsubscript{3}) \(\delta\) 166.8, 147.4, 129.8, 128.9, 127.7, 83.2, 60.6, 39.2, 24.9, 24.8, 24.6, 15.8, 14.3. HRMS (ESI, m/z) calcd for \textsuperscript{12}C\textsubscript{24}H\textsubscript{38}B\textsubscript{2}O\textsubscript{6}\textsuperscript{[M+Na]+}: 465.2819; found: 465.2824.

\textbf{Ethyl 3-(4-(2,2-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propyl)phenyl)-3-oxopropanoate (6j)}

The reaction was performed following the general procedure A. White solid (mp: 168.2-169.3 °C), 85% yield (78.1 mg). \textsuperscript{1}H NMR (500 MHz, CDCl\textsubscript{3}) \(\delta\) 7.81 (d, \(J = 8.3\) Hz, 2H), 7.31 (d, \(J = 8.0\) Hz, 2H), 4.33 (q, \(J = 7.0\) Hz, 2H), 2.91 (s, 2H), 1.36 (t, \(J = 7.0\) Hz, 3H), 1.22 (s, 12H), 1.19 (s, 12H), 0.96 (s, 3H). \textsuperscript{13}C NMR (125 MHz, CDCl\textsubscript{3}) \(\delta\) 166.8, 147.4, 129.8, 128.9, 127.7, 83.2, 60.6, 39.2, 24.9, 24.8, 24.6, 15.8, 14.3. HRMS (ESI, m/z) calcd for \textsuperscript{12}C\textsubscript{24}H\textsubscript{38}B\textsubscript{2}O\textsubscript{6}\textsuperscript{[M+Na]+}: 465.2819; found: 465.2824.
Hz, 2H), 7.34 (d, J = 8.3 Hz, 2H), 2.93 (s, 2H), 2.56 (s, 3H), 1.25 (s, 2H), 1.23 (s, 12H), 1.20 (s, 12H), 0.97 (s, 3H). $^{13}$C NMR (125 MHz, CDCl$_3$) δ 198.1, 147.9, 134.8, 130.1, 127.8, 83.3, 39.2, 29.7, 26.5, 24.8, 24.7, 15.8. HRMS (ESI, m/z) caleld for $^{12}$C$_{25}$H$_{38}$B$_2$O$_7$[M+Na]$^+$: 473.2874; found: 473.2876.

2,2'-(2-(4-(trifluoromethyl)phenyl)ethane-1,1-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane)(6k)

The reaction was performed following the general procedure A. Colorless oil, 24% yield (20.3 mg). $^1$H NMR (500 MHz, CDCl$_3$) δ 7.47 (d, J = 8.1 Hz, 2H), 7.34 (d, J = 8.1 Hz, 2H), 2.92 (d, J = 8.4 Hz, 2H), 1.28 (t, J = 2.9 Hz, 1H), 1.18 (s, 12H), 1.16 (s, 12H).

$^{13}$C NMR (125 MHz, CDCl$_3$) δ 148.6 (d, J = 1.2 Hz), 128.6, 127.1, 124.9 (q, J = 3.8 Hz), 83.3, 31.2, 24.80, 24.77, 24.5.

HRMS (ESI, m/z) caleld for $^{12}$C$_{21}$H$_{31}$B$_2$O$_4$F$_3$[M+H]$^+$: 427.2442; found: 427.2433.

2,2',2''-(2-(4-(trifluoromethyl)phenyl)ethane-1,1,2-triyl)tris(4,4,5,5-tetramethyl-1,3,2-dioxaborolane)(6a)

The reaction was performed following the general procedure A. Colorless oil, 64% yield (62.3 mg). $^1$H NMR (500 MHz, CDCl$_3$) δ 7.42 (d, J = 8.1 Hz, 2H), 7.31 (d, J = 8.1 Hz, 2H), 2.74 (d, J = 12.6 Hz, 1H), 1.44 (d, J = 12.6 Hz, 1H), 1.23 (d, J = 5.5 Hz, 12H), 1.14 (d, J = 8.6 Hz, 12H), 0.92 (d, J = 20.6 Hz, 12H).

$^{13}$C NMR (125 MHz, CDCl$_3$) δ 149.92, 128.6, 127.1, 124.71 (q, J = 3.7 Hz), 83.2, 83.1, 82.8, 31.6, 25.0, 24.81, 24.80, 24.6, 24.4, 24.22, 24.20, 22.6.

HRMS (ESI, m/z) caleld for $^{12}$C$_{27}$H$_{42}$B$_3$O$_6$F$_3$[M+Na]$^+$: 575.3104; found: 575.3105.

2,2',2''-(2-(4-fluorophenyl)ethane-1,1,2-triyl)tris(4,4,5,5-tetramethyl-1,3,2-dioxaborolane)(6b)

The reaction was performed following the general procedure A. Colorless oil, 80% yield (81.2 mg). $^1$H NMR (500 MHz, CDCl$_3$) δ 7.15 (dd, J = 8.7, 5.6 Hz, 2H), 6.86 (t,
$J = 8.8$ Hz, 2H), 2.64 (d, $J = 12.8$ Hz, 1H), 1.42 – 1.37 (m, 1H), 1.23 (d, $J = 6.0$ Hz, 12H), 1.13 (d, $J = 9.1$ Hz, 12H), 0.95 (d, $J = 12.4$ Hz, 12H). $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 161.7, 159.8, 140.9, 129.7, 114.5, 114.4, 83.1, 83.0, 82.7, 25.0, 24.82, 24.80 24.6, 24.5, 24.4. 24.2. HRMS-(DART) for: $^{12}$C$_{26}$H$_{42}$B$_3$F$_{16}$O$_6$[M+H]$^+$: calculated: 500.3426, found: 500.3425.

2,2',2''-(2-(4-bromophenyl)ethane-1,1,2-triy)tris(4,4,5,5-tetramethyl-1,3,2-dioxaborolane)(6'c)

![Image of compound 6'c]

The reaction was performed following the general procedure A. Colorless oil, 84% yield (84.3 mg). $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.29 (d, $J = 8.4$ Hz, 2H), 7.09 (d, $J = 8.4$ Hz, 2H), 2.63 (d, $J = 12.7$ Hz, 1H), 1.27 (d, $J = 6.6$ Hz, 1H), 1.23 (d, $J = 5.5$ Hz, 12H), 1.14 (d, $J = 7.5$ Hz, 12H), 0.96 (d, $J = 16.7$ Hz, 12H). $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 144.5, 130.8, 130.2, 118.3, 83.2, 83.1, 82.8, 25.0, 24.82, 24.80, 24.6, 24.5, 24.3, 24.2. HRMS(ESI,m/z) calcd for $^{12}$C$_{26}$H$_{42}$B$_3$F$_{16}$O$_6$Br[M+Na]$^+$: 563.2526; found: 563.2517.

3-(1,2,2-tris(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)benzonitrile (6'd)

![Image of compound 6'd]

The reaction was performed following the general procedure A. Colorless oil, 62% yield. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.52 (s, 1H), 7.46 – 7.42 (m, 1H), 7.35 (dt, $J = 7.5$, 1.2 Hz, 1H), 7.27 (dd, $J = 10.5$, 4.9 Hz, 1H), 2.71 (d, $J = 12.5$ Hz, 1H), 1.41 – 1.35 (m, 1H), 1.23 (d, $J = 4.4$ Hz, 12H), 1.14 (d, $J = 8.9$ Hz, 12H), 0.97 (s, 6H), 0.93 (s, 6H). $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 147.2, 133.0, 132.2, 128.61, 128.55, 119.34, 111.6, 83.5, 83.3, 82.9, 24.8, 24.7, 24.6, 24.5, 24.3. HRMS(ESI,m/z) calcd for $^{12}$C$_{26}$H$_{42}$B$_3$F$_{16}$O$_6$N$_1$Na[M+Na]$^+$: 532.3184; found: 532.3191.

2-(2,2-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)benzo[d]oxazole

(6l)

![Image of compound 6l]

The reaction was performed following the general procedure A. Colorless oil, 87% yield (69.6 mg). $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.63 – 7.59 (m, 1H), 7.43 – 7.39 (m,
1H), 7.25 – 7.21 (m, 2H), 3.16 (d, J = 8.2 Hz, 2H), 1.40 (t, J = 8.1 Hz, 1H), 1.23 (s, 12H), 1.19 (s, 12H). 13C NMR (125 MHz, CDCl3) δ 168.8, 150.8, 141.4, 123.9, 123.7, 119.4, 110.1, 83.4, 24.8, 24.4.

2-(2,2-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)benzo[d]thiazole (6m)

The reaction was performed following the general procedure A. Colorless oil, 72% yield (59.8 mg). 1H NMR (500 MHz, CDCl3) δ 7.91 (d, J = 8.1 Hz, 1H), 7.80 (d, J = 7.9 Hz, 1H), 7.30 (t, J = 7.6 Hz, 1H), 3.36 (d, J = 8.0 Hz, 2H), 1.43 (t, J = 7.9 Hz, 1H), 1.24 (s, 12H), 1.20 (s, 12H). 13C NMR (125 MHz, CDCl3) δ 173.9, 153.1, 135.4, 125.5, 124.2, 122.4, 121.4, 83.4, 30.34, 24.8, 24.5.

4,4,5,5-tetramethyl-2-(1-(4-(methylsulfonyl)phenyl)hex-1-en-2-yl)-1,3,2-dioxaborolane (6n)

1H NMR (500 MHz, CDCl3) δ 7.88 (d, J = 8.4 Hz, 2H), 7.45 (d, J = 8.3 Hz, 2H), 7.18 (s, 1H), 3.05 (s, 3H), 2.34 – 2.29 (m, 2H), 1.48 – 1.39 (m, 3H), 1.29 (s, 12H), 1.26 (dd, J = 7.1, 3.7 Hz, 1H), 0.85 (t, J = 7.3 Hz, 3H). 13C NMR (125 MHz, CDCl3) δ 143.6, 139.2, 138.4, 129.5, 127.1, 83.6, 44.5, 31.9, 26.8, 24.9, 24.7, 22.7, 13.9. HRMS(ESI,m/z) calcd for 12C19H3011B16O432S[M+H]+: 365.1952; found: 365.1951.

4,4,5,5-tetramethyl-2-(1-(4-(methylsulfonyl)phenyl)-5-phenylpent-1-en-2-yl)-1,3,2-dioxaborolane (6o)

1H NMR (500 MHz, CDCl3) δ 7.79 (d, J = 8.4 Hz, 2H), 7.33 (d, J = 8.2 Hz, 2H), 7.26 (t, J = 7.3 Hz, 2H), 7.19 (dd, J = 13.2, 5.8 Hz, 2H), 7.14 (d, J = 6.9 Hz, 2H), 3.05 (s, 3H), 2.62 (t, J = 7.5 Hz, 2H), 2.40 – 2.35 (m, 2H), 1.85 – 1.78 (m, 2H), 1.31 (s, 12H). 13C NMR (125 MHz, CDCl3) δ 143.1, 142.0, 139.6, 138.4, 129.5, 128.3, 128.1, 127.0, 125.6, 83.6, 44.2, 35.6, 31.1, 28.8, 24.6, 20.8. HRMS(ESI,m/z) calcd for 12C24H3111BNa16O432S[M+Na]+: 449.1928; found: 449.1926.

ethyl -4-(2,4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pent-1-en-1-yl)benzoate (6p)
(3aS,5S,5aR,8aR,8bS)-2,2,7,7-tetramethyltetrahydro-5H-bis([1,3]dioxolo)[4,5-b:4',5'-d]pyran-5-yl)methyl4-(2,2-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propyl)benzoate (6q)

The reaction was performed following the general procedure A. Colorless oil, 84% yield (101.6 mg). \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 7.89 (d, \(J = 8.3\) Hz, 2H), 7.31 (d, \(J = 8.3\) Hz, 2H), 5.55 (d, \(J = 4.9\) Hz, 1H), 4.64 (dd, \(J = 7.9, 2.5\) Hz, 1H), 4.50 (dd, \(J = 11.4, 5.1\) Hz, 1H), 4.38 (dd, \(J = 11.4, 7.4\) Hz, 1H), 4.35 – 4.30 (m, 2H), 4.16 (ddd, \(J = 4.9, 4.3, 1.6\) Hz, 1H), 2.91 (s, 2H), 1.50 (s, 3H), 1.46 (s, 3H), 1.34 (s, 3H), 1.32 (s, 3H), 1.23 (s, 12H), 1.19 (s, 12H), 0.96 (s, 3H). \(^1\)^C NMR (125 MHz, CDCl\(_3\)) \(\delta\) 170.9, 147.6, 129.8, 129.0, 109.5, 108.7, 96.2, 83.2, 71.0, 70.6, 66.1, 63.5, 60.3, 25.8, 24.7, 24.5, 24.4, 20.9, 15.7, 14.1. HRMS (ESI, m/z) calcd for \(^{12}\)C\(_{34}\)^{1}H\(_{52}\)^{16}B\(_2\)^{16}O\(_{11}\)[M+H\(^{+}\)]: 657.3841; found: 657.3841.

2-((1S,4R)-7,7-dimethylbicyclo[2.2.1]hept-2-en-2-yl)ethyl 4-(2,2-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propyl)benzoate (6r)

The reaction was performed following the general procedure A. Colorless oil, 80% yield (89.6 mg). \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 7.87 (d, \(J = 8.3\) Hz, 2H), 7.31 (d, \(J = 8.3\) Hz, 2H), 5.55 (d, \(J = 4.9\) Hz, 1H), 4.64 (dd, \(J = 7.9, 2.5\) Hz, 1H), 4.50 (dd, \(J = 11.4, 5.1\) Hz, 1H), 4.38 (dd, \(J = 11.4, 7.4\) Hz, 1H), 4.35 – 4.30 (m, 2H), 4.16 (ddd, \(J = 4.9, 4.3, 1.6\) Hz, 1H), 2.91 (s, 2H), 2.40 (dd, \(J = 11.8, 5.0\) Hz, 2H), 2.38 – 2.34 (m, 1H), 2.21 (t, \(J = 17.2\) Hz, 2H), 2.11 (t, \(J = 6.3\) Hz, 1H), 2.09 – 2.06 (m, 1H), 1.33 (s, 1H), 1.26 (s, 3H), 1.23 (s, 12H), 1.19 (s, 12H), 0.98 (s, 3H), 0.82 (s, 3H). \(^1\)^C NMR (125 MHz, CDCl\(_3\)) \(\delta\) 129.5, 128.5, 118.4, 82.8, 62.6, 45.4, 40.4, 38.9, 35.7, 31.2, 30.9, 25.8, 24.4, 24.2, 20.7, 20.4, 15.5, 13.7. HRMS (ESI, m/z) calcd for \(^{12}\)C\(_{33}\)^{1}H\(_{50}\)^{16}B\(_2\)^{16}O\(_{6}\)[M+Na\(^{+}\)]: 585.3758; found: 585.3757.

(E)-3,7-dimethylocta-2,6-dien-1-yl4-(2,2-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)benzoate (6s)
The reaction was performed following the general procedure A. Colorless oil, 62% yield (66.9 mg). \( ^1H \) NMR (500 MHz, CDCl\(_3\)) \( \delta \) 7.88 (d, \( J = 8.2 \) Hz, 2H), 7.28 (d, \( J = 8.2 \) Hz, 2H), 5.43 (t, \( J = 7.2 \) Hz, 1H), 5.08 (t, \( J = 6.4 \) Hz, 1H), 4.08 (d, \( J = 7.2 \) Hz, 2H), 3.86 (s, 3H), 2.90 (d, \( J = 8.3 \) Hz, 2H), 2.09 – 2.04 (m, 4H), 1.73 (s, 3H), 1.59 (s, 3H), 1.37 – 1.31 (m, 1H), 1.16 (s, 12H), 1.15 (s, 12H). \( ^{13}C \) NMR (125 MHz, CDCl\(_3\)) \( \delta \) 167.3, 150.1, 139.9, 129.4, 128.3, 127.3, 124.4, 123.8, 83.5, 83.2, 58.9, 51.9, 31.9, 31.4, 26.5, 24.9, 24.7, 24.5, 23.4, 17.6. HRMS (ESI, m/z) calcd for \( ^{12}C_{31}^{11}H_{48}^{10}B_2^{16}O_6^{[M+Na]^+}: 561.3527 \); found: 561.3529.

(1R,2S,5R)-2-isopropyl-5-methylcyclohexyl4-(2,2-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propyl)benzoate (6t)

The reaction was performed following the general procedure A. Colorless oil, 65% yield (76.7 mg). \( ^1H \) NMR (500 MHz, CDCl\(_3\)) \( \delta \) 7.88 (d, \( J = 8.3 \) Hz, 2H), 7.31 (d, \( J = 8.3 \) Hz, 2H), 4.90 (td, \( J = 10.9, 4.4 \) Hz, 1H), 2.95 – 2.89 (m, 2H), 2.10 (d, \( J = 11.7 \) Hz, 1H), 1.98 – 1.91 (m, 1H), 1.73 – 1.69 (m, 2H), 1.53 (t, \( J = 11.7 \) Hz, 2H), 1.33 (s, 1H), 1.24 (s, 12H), 1.20 (s, 12H), 1.10 (dd, \( J = 21.8, 9.9 \) Hz, 2H), 0.97 (s, 3H), 0.90 (t, \( J = 6.4 \) Hz, 6H), 0.77 (d, \( J = 6.9 \) Hz, 3H). \( ^{13}C \) NMR (125 MHz, CDCl\(_3\)) \( \delta \) 165.6, 146.9, 129.4, 128.5, 127.7, 82.7, 73.8, 46.9, 40.6, 38.7, 33.9, 30.9, 26.0, 24.3, 24.1, 23.2, 21.4, 15.9, 15.2. HRMS (ESI, m/z) calcd for \( ^{12}C_{31}^{11}H_{48}^{10}B_2^{16}O_6^{[M+Na]^+}: 575.3915 \); found: 575.3914.

(3S,8R,9S,10R,13S,14S)-10,13-dimethyl-17-oxo2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthren-3-yl4-(2,2-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propyl)benzoate (6u)

The reaction was performed following the general procedure A. Colorless oil, 74% yield (102.1 mg). \( ^1H \) NMR (500 MHz, CDCl\(_3\)) \( \delta \) 7.88 (d, \( J = 8.2 \) Hz, 2H), 7.31 (d, \( J = 8.2 \) Hz, 2H), 5.44 (d, \( J = 5.0 \) Hz, 1H), 4.83 (dq, \( J = 16.3, 5.3 \) Hz, 1H), 2.92 (s, 2H), 2.46 (dd, \( J = 18.9, 9.3 \) Hz, 3H), 2.14 – 2.05 (m, 2H), 1.95 (ddd, \( J = 17.2, 14.8, 7.0 \) Hz, 3H), 1.87 – 1.83 (m, 1H), 1.78 – 1.63 (m, 6H), 1.52 (ddd, \( J = 16.7, 12.8, 3.7 \) Hz, 2H), 1.23 (s, 12H), 1.20 (s, 12H), 1.08 (s, 3H), 0.96 (s, 3H), 0.89 (s, 3H). \( ^{13}C \) NMR (125 MHz, CDCl\(_3\)) \( \delta \) 171.1, 166.2, 147.4, 140.0, 129.8, 128.9, 128.0, 121.8, 83.2, 73.9,
(3S,8S,9S,10R,13R,14S,17R)-10,13-dimethyl-17-((R)-6-methylheptan-2-yl)-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1Hcyclopenta[a]phenanthren-3-yl 4-(2,2-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propyl)benzoate (6v)

The reaction was performed following the general procedure A. Colorless oil, 74% yield (102.1 mg). $^1$H NMR (500 MHz, CDCl$_3$) δ 7.89 (d, $J = 8.3$ Hz, 2H), 7.31 (d, $J = 8.3$ Hz, 2H), 5.41 (d, $J = 3.6$ Hz, 1H), 4.87 – 4.79 (m, 1H), 2.92 (s, 2H), 2.44 (d, $J = 7.7$ Hz, 2H), 1.98 (d, $J = 17.1$ Hz, 3H), 1.93 – 1.69 (m, 4H), 1.57 – 1.43 (m, 6H), 1.36 – 1.31 (m, 4H), 1.24 (s, 12H), 1.20 (s, 12H), 1.17 – 1.08 (m, 6H), 1.06 (s, 3H), 1.01 (dd, $J = 16.9$, 6.4 Hz, 3H), 0.96 (s, 3H), 0.92 (d, $J = 6.5$ Hz, 3H), 0.86 (dd, $J = 6.6$, 2.3 Hz, 6H), 0.68 (s, 3H).

$^{13}$C NMR (125 MHz, CDCl$_3$) δ 171.1, 166.2, 147.3, 139.8, 129.8, 128.9, 122.6, 83.3, 74.2, 60.4, 56.7, 56.1, 50.0, 42.3, 39.5, 38.2, 37.1, 36.7, 36.2, 35.8, 31.9, 28.2, 28.0, 24.8, 24.3, 23.8, 22.8, 22.6, 21.0, 19.4, 18.7, 15.8, 14.2, 11.9.

HRMS (ESI, m/z) calcd for $^{12}$C$_{41}$H$_{60}$B$_{2}$O$_{7}$[M+Na]$^+$: 707.4490; found: 707.4491.

1-(4-(2,2-difluoropropyl)phenyl)ethan-1-one (7) (CAS: No. 1785555-40-9)

The reaction was performed following the general procedure (1). Colorless oil, 45% yield (17.8 mg). $^1$H NMR (500 MHz, CDCl$_3$) δ 7.92 (d, $J = 8.3$ Hz, 2H), 7.37 (d, $J =...
8.1 Hz, 2H), 3.20 (t, J = 15.5 Hz, 2H), 2.60 (s, 3H), 1.55 (t, J = 18.3 Hz, 3H). \(^{13}\)C NMR (125 MHz, CDCl\(_3\)) \(\delta\) 197.8, 139.0, 136.2, 130.5, 128.4, 122.9 (t, J = 240.0 Hz), 44.3 (t, J = 26.5 Hz), 26.6, 23.0 (t, J = 27.4 Hz). \(^{19}\)F NMR (471 MHz, CDCl\(_3\)) \(\delta\) -89.07. HRMS (ESI, m/z) calcd for \(^{12}\)C\(_{11}\)H\(_{13}\)F\(_2\)O\([M+H]^+\): 199.0929; found: 199.0932.

1-(4-(2-(6-phenylpyridin-2-yl)propyl)phenyl)ethan-1-one (9)

![Chemical Structure](image1)

The reaction was performed following the general procedure (3). Colorless oil, 74% yield (46.6 mg). \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 9.21 (d, J = 2.1 Hz, 1H), 8.41 (d, J = 2.1 Hz, 1H), 8.21 (d, J = 8.5 Hz, 1H), 8.12 (d, J = 8.5 Hz, 2H), 8.06 (d, J = 8.5 Hz, 1H), 7.93 (d, J = 8.1 Hz, 1H), 7.83 (d, J = 8.5 Hz, 2H), 7.79 (ddd, J = 8.4, 6.9, 1.4 Hz, 1H), 7.72 (d, J = 8.6 Hz, 1H), 7.65 – 7.62 (m, 1H), 2.67 (s, 3H), 2.65 (s, 1H), 1.33 (s, 1H), 1.28 (s, 1H), 1.25 (s, 3H). \(^{13}\)C NMR (125 MHz, CDCl\(_3\)) \(\delta\) 197.5, 148.9, 142.1, 136.6, 134.4, 132.6, 129.6, 128.9, 128.8, 128.2, 127.5, 127.4, 31.4, 30.2, 29.7, 26.7. HRMS (ESI, m/z) calcd for \(^{12}\)C\(_{22}\)H\(_{22}\)N\(_16\)O\([M+H]^+\): 316.1696; found: 316.1695.

4,4,5,5-tetramethyl-2-(1-(4-(methylsulfonyl)phenyl)prop-1-en-2-y1)-1,3,2-dioxaborolane (B-1)

![Chemical Structure](image2)

The reaction was performed following the general procedure (8). Colorless oil, 94% yield (60.5 mg). \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 7.88 (d, J = 8.4 Hz, 2H), 7.50 (d, J = 8.4 Hz, 2H), 7.21 (s, 1H), 3.05 (s, 3H), 1.96 (d, J = 1.6 Hz, 3H), 1.29 (s, 12H). \(^{13}\)C NMR (125 MHz, CDCl\(_3\)) \(\delta\) 143.3, 139.9, 138.4, 132.6, 129.9, 127.1, 83.8, 44.4, 24.8, 15.9. HRMS (ESI, m/z) calcd for \(^{12}\)C\(_{16}\)H\(_{24}\)B\(_{16}\)O\(_4\)S\([M+H]^+\): 323.1483; found: 323.1482.

Ethyl (E)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)acrylate (B-2) (CAS: No. 1009307-13-4)

![Chemical Structure](image3)

The reaction was performed following the general procedure (8). Colorless oil, 89% yield (40.1 mg). \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 6.76 (d, J = 18.2 Hz, 1H), 6.61 (d, J = 18.2 Hz, 1H), 4.20 (q, J = 7.1 Hz, 2H), 1.27 (s, 12H), 1.25 (s, 3H). \(^{13}\)C NMR (125 MHz, CDCl\(_3\)) \(\delta\) 165.9, 138.7, 83.9, 60.6, 24.9, 24.7, 14.1.
10. NMR spectrum

Ethyl 3,3-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propanoate (3a)

coming from substrates

H$_2$O

$\text{Bpin}$ $\text{Bpin}$

$\text{Bpin}$ $\text{Bpin}$

H$_2$O

$\text{Bpin}$ $\text{Bpin}$

Methyl3,3-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2yl)propanoate (3b)

![Chemical Structure](image-url)
Tert-butyl 3,3-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propanoate (3c)
3,5-Dimethylbenzyl3,3-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2yl)propanoate (3d)
Ethyl 3,3-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butanoate (3e)
Ethyl 3,3-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)heptanoate (3f)
Benzyl 3,3-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butanoate (3g)

coming from petroleum ether
2-Bromobenzyl3,3-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butanoate (3h)
4,4-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butan-2-one (3i)
4,4-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexan-2-one (3j)
1-Phenyl-3,3-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)heptan-1-one (3k)
3-Cyclopropyl-1-phenyl-3,3-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propan-1-one (3l)
1-Phenyl-3,3-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)decan-1-one (3m)
1,6-Diphenyl-3,3-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexan-1-one (3n)
N-phenyl-3,3-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butanamide (3o)
N-methyl-N-phenyl-3,3-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butanamide (3p)

coming from petroleum ether
N-(4-(tert-butyl)phenyl)-3,3-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butanamide (3q)
1,3-diphenyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propan-1-one (3r)
4-(3-oxo-3-phenylpropyl)benzonitrile (3s)

coming from petroleum ether

H₂O
4-(2,2-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)benzonitrile (6a-para)
3-(2,2-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)benzonitrile (6-meta)
2-(2,2-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)benzonitrile (6-ortho)
1-(4-(2,2-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)phenyl)ethan-1-one (6b)
Methyl 4-(2,2-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)benzoate (6c)
2.2’-(2-(4-(Methylsulfonyl)phenyl)ethane-1,1-diyl)bis(4,4,5,5-tetramethyl-1,3,2-
dioxaborolane) (6d)
4-(2,2-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propyl)benzonitrile (6e)
1-(4-(2,2-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propyl)phenyl)ethan-1-one (6f)
1-(4-(2,2-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propyl)phenyl)propan-1-one (6g)
2,2'-(1-(4-(Methylsulfonyl)phenyl)propane-2,2-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (6h)
Ethyl 4-(2,2-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propyl)benzoate (6i)
Ethyl 3-(4-(2,2-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propyl)phenyl)-3-oxopropanoate (6j)
2,2'-(2-(4-(trifluoromethyl)phenyl)ethane-1,1-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane)(6k)
2,2',2''-(2-(4-(trifluoromethyl)phenyl)ethane-1,1,2-triyl)tris(4,4,5,5-tetramethyl-1,3,2-dioxaborolane)(6'a)
2,2',2''-(2-(4-fluorophenyl)ethane-1,1,2-triyl)tris(4,4,5,5-tetramethyl-1,3,2-dioxaborolane)(6 b)
2,2',2''-(2-(4-bromophenyl)ethane-1,1,2-triyl)tris(4,4,5,5-tetramethyl-1,3,2-dioxaborolane)(6'c)
3-(1,2,2-tris(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)benzonitrile (6'd)
2-(2,2-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)benzo[d]oxazole (6l)\textsuperscript{15}
2-(2,2-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)benzo[d]thiazole (6m)
4,4,5,5-tetramethyl-2-(1-(4-(methylsulfonyl)phenyl)hex-1-en-2-yl)-1,3,2-dioxaborolane (6n)
4,4,5,5-tetramethyl-2-(1-(4-(methylsulfonyl)phenyl)-5-phenylpent-1-en-2-yl)-1,3,2-dioxaborolane (6o)
ethyl 4-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pent-1-en-1-yl)benzoate (6p)
2-((1S,4R)-7,7-dimethylbicyclo[2.2.1]hept-2-en-2-yl)ethyl 4-(2,2-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propyl)benzoate (6r)
(E)-3,7-dimethylocta-2,6-dien-1-yl 4-(2,2-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)benzoate (6s)
(1R,2S,5R)-2-isopropyl-5-methylcyclohexyl4-(2,2-bis(4,4,5,5-tetramethyl-1,3,2-
dioxaborolan-2-yl)propyl)benzoate (6t)
(3S,8R,9S,10R,13S,14S)-10,13-dimethyl-17-oxo2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthren-3-yl4-(2,2-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propyl)benzoate (6u)
(3S,8S,9S,10R,13R,14S,17R)-10,13-dimethyl-17-((R)-6-methylheptan-2-yl)-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1Hcyclopenta[a]phenanthren-3-yl 4-(2,2-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propyl)benzoate (6v)
1-(4-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolayl)propyl)phenyl)ethan-1-one (8)

coming from petroleum ether
1-(4-(2,2-difluoropropyl)phenyl)ethan-1-one (7)
1-(4-(2-(6-phenylpyridin-2-yl)propyl)phenyl)ethan-1-one (9)
4,4,5,5-tetramethyl-2-(1-(4-(methylsulfonyl)phenyl)prop-1-en-2-yl)-1,3,2-dioxaborolane (B-1)

coming from petroleum ether
Ethyl (E)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)acrylate (B-2)
11. References