Supporting Information

Photoredox catalyzed stereo- and regioselective vicinal fluorosulfonyl-borylation of unsaturated hydrocarbons

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Supplementary Methods

I. General Methods

All reactions were performed in flame-dried glassware with magnetic stirring bar and sealed with a rubber septum. The solvents were distilled by standard methods. Reagents were obtained from commercial suppliers and used without further purification unless otherwise noted. Silica gel column chromatography was carried out using silica Gel 60 (230–400 mesh). Analytical thin layer chromatography (TLC) was done using silica Gel (silica gel 60 F254). TLC plates were analyzed by an exposure to ultraviolet (UV) light and/or submersion in phosphomolybdic acid solution or submersion in KMnO₄ solution or in I₂. NMR experiments were measured on a Bruker AVANCE III-400 or 500 spectrometer and carried out in chloroform-d (CDCl₃) or acetonitrile-d₃ (CD₃CN). ¹H NMR and ¹³C NMR spectra were recorded at 400 MHz or 500 MHz and 100 MHz or 125 MHz spectrometers, respectively. ¹⁹F NMR spectra were recorded at 376 MHz or 470 MHz spectrometers. Chemical shifts are reported as δ values relative to internal TMS (δ 0.00 for ¹H NMR), chloroform (δ 7.26 for ¹H NMR), acetonitrile (δ 1.94 for ¹H NMR), chloroform (δ 77.00 for ¹³C NMR), and acetonitrile (δ 1.32 or 118.26 for ¹³C NMR) in parts per million (ppm). The following abbreviations are used for the multiplicities: s: singlet, d: doublet, dd: doublet of doublet, t: triplet, q: quadruplet, m: multiplet, br: broad signal for proton spectra; Coupling constants (J) are reported in Hertz (Hz). Melting points were uncorrected. Infrared spectra were obtained on agilent Cary630. HRMS were recorded on a Bruker miccOTOF-Q111. GC-MS spectra were performed on Agilent 5977B.

Medium-sized screw-cap test tubes (8 mL) were used for all 0.10 mmol scale reactions: Fisher 13 x 100 mm tubes (Cat. No.1495935C)

Supplementary Figure 1. Fisher 13 x 100 mm tubes

Cap with Septa: Thermo Scientific ASM PHN CAP w/PTFE/SIL (Cat. No.03378316)

Supplementary Figure 2. Cap with Septa
II. Synthesis of Starting Materials

Substrates 1a-1e, 1m-1x, 5a, 5f-5m were purchased from commercial sources (Alfa, TCI, Energy, Bide and Macklin) and used as received.

Substrates 1f-1l, 5n were prepared according to the literature.[1]

Substrates 5b-5e were prepared according to the literature.[2]

III. Synthesis of Sulfonyl fluoride imidazolium salt (2a-2d)[3]

General Procedure:

1) Sodium hydride (60% dispersion in mineral oil.) (36 mmol, 1.2 equiv.) was added to corresponding imidazole (30 mmol, 1 equiv.) in N,N-Dimethylformamide (100 mL). The mixture was stirred at room temperature for 1 hour; A balloon volume of sulfuryl fluoride gas was then added to the reaction system. After the reaction was completed by TLC monitoring, the reaction mixture was evaporated in vacuo. Then, the reaction mixture was quenched with water and extracted with ethyl acetate (60 mL x 3). The organic layer was dried over Na2SO4, and evaporated in vacuo. The product was purified by flash column chromatography on silica gel with n-pentane/ethyl acetate as eluent to give the corresponding intermediate A.

2) To a solution of the corresponding intermediate A in DCM (50 mL) was added dropwise MeOTf (45 mmol) at 0 ºC. Then, the mixture was stirred at room temperature for 12 hours, while monitoring by TLC. After that time, the mixture was concentrated under rotary evaporation to give a white solid (or a viscous liquid) crude product, to which tert-butyl methyl ether (30 mL) was added. With vigorous stirring, a solid precipitate was formed. The precipitate was washed with tert-butyl methyl ether (30 mL x 3) and dried in vacuo to yield the title compound (2a-2d) as a white solid.

1-(fluorosulfonyl)-3-methyl-2-(4-(trifluoromethyl)phenyl)-1H-benzo[d]imidazol-3-ium trifluoromethanesulfonate (2a)

69%; white solid: m.p. 165-166 ºC; 1H NMR (400 MHz, Acetonitrile-d3) δ 8.24 – 8.20 (m, 1H), 8.17 – 8.11 (m, 1H), 8.09 (d, J = 0.9 Hz, 4H), 8.03 – 7.95 (m, 2H), 3.96 (s, 3H). 13C NMR (101 MHz, Acetonitrile-d3) δ 152.5, 136.1 (q, J = 33.1 Hz), 132.8, 132.6, 132.0, 130.7, 130.6, 127.6
(q, J = 3.8 Hz), 125.9, 124.8, 123.1, 122.0 (q, J = 320.8 Hz), 116.0, 115.9, 35.6. $^{19}$F NMR (376 MHz, Acetonitrile-$d_3$) δ 64.62, -63.88, -79.31.; HRMS(ESI): caled for C$_{15}$H$_{11}$F$_2$N$_2$O$_2$S$^+$ [M]$^+$ 359.0472; found 359.0471.

1-(fluorosulfonyl)-3-methyl-2-phenyl-1H-benzo[d]imidazol-3-i um trifluoromethanesulfonate (2b)

$$\text{OTf} + \text{Me} \rightarrow \begin{array}{c} \text{N} \\ \text{Ph} \\ \text{SO}_2F \end{array}$$

73%, white solid: m.p. 169-170 °C; $^1$H NMR (400 MHz, Acetonitrile-$d_3$) δ 8.24 – 8.17 (m, 1H), 8.15 – 8.06 (m, 1H), 8.03 – 7.91 (m, 2H), 7.91 – 7.85 (m, 3H), 7.83 – 7.72 (m, 2H), 3.95 (s, 3H). $^{13}$C NMR (101 MHz, Acetonitrile-$d_3$) δ 154.2, 135.4, 132.7, 131.6, 131.4, 130.6, 130.4, 122.0 (q, J = 320.8 Hz), 120.79, 115.92, 115.90, 35.45. 120.8, 115.9, 115.9, 35.5. $^{19}$F NMR (376 MHz, Acetonitrile-$d_3$) δ 64.76, -79.23. HRMS(ESI): caled for C$_{14}$H$_{12}$FN$_2$O$_2$S$^+$ [M]$^+$ 291.0598; found 291.0596.

2-(4-fluorophenyl)-1-(fluorosulfonyl)-3-methyl-1H-benzo[d]imidazol-3-i um trifluoromethanesulfonate (2c)

$$\text{OTf} + \text{Me} \rightarrow \begin{array}{c} \text{N} \\ \text{SO}_2F \\ \text{F} \end{array}$$

60%; white solid: m.p. 148-149 °C; $^1$H NMR (400 MHz, Acetonitrile-$d_3$) δ 8.24 – 8.16 (m, 1H), 8.14 – 8.04 (m, 1H), 8.01 – 7.95 (m, 2H), 7.94 – 7.89 (m, 2H), 7.59 – 7.48 (m, 2H), 3.95 (s, 3H). $^{13}$C NMR (101 MHz, Acetonitrile-$d_3$) δ 168.4, 165.8, 153.4, 134.6 (d, J = 9.8 Hz), 132.7, 131.8, 130.6, 122.0 (q, J = 320.7 Hz), 118.1, 116.9 (d, J = 3.4 Hz), 116.0, 115.9, 35.49. $^{19}$F NMR (376 MHz, CDCl$_3$) δ 64.65, -70.27, -104.18– -104.25 (m). HRMS(ESI): caled for C$_{14}$H$_{12}$FN$_2$O$_2$S$^+$ [M]$^+$ 309.0504; found 309.0505.

1-(fluorosulfonyl)-2-(4-methoxyphenyl)-3-methyl-1H-benzo[d]imidazol-3-i um trifluoromethanesulfonate (2d)

$$\text{OTf} + \text{Me} \rightarrow \begin{array}{c} \text{N} \\ \text{SO}_2F \\ \text{OMe} \end{array}$$

43%; white solid: m.p. 162-163 °C; $^1$H NMR (400 MHz, Acetonitrile-$d_3$) δ 8.23 – 8.13 (m, 1H), 8.12 – 8.00 (m, 1H), 7.99 – 7.89 (m, 2H), 7.85 – 7.74 (m, 2H), 7.33 – 7.25 (m, 2H), 3.96 (s, 3H), 3.95 (s, 3H). $^{13}$C NMR (101 MHz, Acetonitrile-$d_3$) δ 165.4, 154.7, 133.7, 132.7, 131.4, 130.6, 130.3, 122.1 (q, J = 320.9 Hz), 116.1, 116.0, 115.7, 111.9, 56.8, 35.4. $^{19}$F NMR (376 MHz, Acetonitrile-$d_3$) δ 64.72, -79.28. HRMS(ESI): caled for C$_{15}$H$_{14}$FN$_2$O$_2$S$^+$ [M]$^+$ 321.0704; found 321.0704.
Synthesis of 3,4-Diethyl-3,4-hexanediol[4]

According to the method previously reported by Roberto Sanz et al[4], in an oven dried Schlenck flask (100 mL), the corresponding ketone (20 mmol) and anhydrous THF (50 mL) were added under an inert nitrogen atmosphere. The resulting solution was cooled to -60 °C and TiCl₄ (3.3 mL, 30 mmol) was added slowly via a syringe. The mixture was stirred for 30 min and Zn dust (3.93 g, 60 mmol) was added. Then, the obtained suspension was stirred and refluxed (70 °C) for 3 h. The reaction mixture was cooled to 0 °C, saturated aqueous K₂CO₃ (25 mL) was added slowly and stirred for 30 min. The resulting mixture was filtered through a pad of Celite and washed with EtOAc. The filtrate was extracted with EtOAc. The organic layer was washed with brine, dried over anhydrous Na₂SO₄, filtered and concentrated under reduced pressure. The residue was purified by silica gel flash column chromatography (hexane/EtOAc = 20:1), 3,4-diethyl-3,4-hexanediol which was obtained pure without further purification.

All data matched that reported in the literature.[4]

IV. Cyclic Voltammetry Studies for 2a-2d

Unless otherwise noted, the cyclic voltammetry measurements were conducted on a MPI-A multi-functional electrochemical and chemiluminescent system (Shanghai CH Instrument Ltd. Co., China) at room temperature, with a polished Pt plate as the working electrode, platinum thread as the counter electrode and Ag-AgNO₃ (0.1 M) in CH₃CN as the reference electrode, tetrabutylammonium tetrafluoroborate (0.1 M) was used as the supporting electrolyte, using Fc⁺/Fc as the internal standard, the scan rate was 0.2 V/s.
Supplementary Figure 3. Cyclic voltammograms of 2a

Supplementary Figure 4. Cyclic voltammograms of 2b
Supplementary Figure 5. Cyclic voltammograms of 2c

Supplementary Figure 6. Cyclic voltammograms of 2d
V. Optimizations of the Reaction Conditions

Supplementary Table 1: Optimization of IMSF-reagents[a]

<table>
<thead>
<tr>
<th>Entry</th>
<th>Change of conditions</th>
<th>Yield of 4a[b]</th>
<th>Z/E ratio[c]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>None</td>
<td>23%</td>
<td>&gt; 20:1</td>
</tr>
<tr>
<td>2</td>
<td>2b instead of 2a</td>
<td>8%</td>
<td>&gt; 20:1</td>
</tr>
<tr>
<td>3</td>
<td>2c instead of 2a</td>
<td>9%</td>
<td>&gt; 20:1</td>
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<tr>
<td>4</td>
<td>2d instead of 2a</td>
<td>5%</td>
<td>5.6:1</td>
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</tbody>
</table>

[a] All reactions were carried out with 1a (12.2 mg, 0.10 mmol), 2 (0.25 mmol, 2.5 equiv.), 3 (0.25 mmol, 2.5 equiv.), 4CzIPN (2 mol%) in EA (2.0 mL) under Ar and 60 W blue LEDs, the reaction was completed as monitored by TLC analysis, after which 3,4-diethyl-3,4-hexanediol was added to the reaction system and stirred for 1 hour. [b] Yields determined by GC using dodecane as an internal standard. [c] The Z/E ratio was determined by 1H NMR using 19F NMR.

Supplementary Table 2: Optimization of photocatalysts[a]

<table>
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<th>Entry</th>
<th>Change of conditions</th>
<th>Yield of 4a[b]</th>
<th>Z/E ratio[c]</th>
</tr>
</thead>
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<tr>
<td>1</td>
<td>None</td>
<td>23%</td>
<td>&gt; 20:1</td>
</tr>
<tr>
<td>2</td>
<td>fac-Ir(ppy)₃</td>
<td>11%</td>
<td>&gt; 20:1</td>
</tr>
<tr>
<td>3</td>
<td>fac-Ir[d-F-(p-t-Bu)ppy]₃</td>
<td>9%</td>
<td>5.6:1</td>
</tr>
<tr>
<td>4</td>
<td>Ir[[dF(CF₃)ppy]₂(dtbbpy)]PF₆</td>
<td>8%</td>
<td>6:1</td>
</tr>
</tbody>
</table>

[a] All reactions were carried out with 1a (12.2 mg, 0.10 mmol), 2 (0.25 mmol, 2.5 equiv.), 3 (0.25 mmol, 2.5 equiv.), 4CzIPN (2 mol%) in EA (2.0 mL) under Ar and 60 W blue LEDs, then 3,4-diethyl-3,4-hexanediol 1h.
5 Ir(mppy)$_3$ 11% 1.3:1
6 4-DPA-iPN 7% > 20:1
7 Ir[(bpy)$_2$dtbbpy]PF$_6$ 7% > 20:1
8 2-Isopropylthioxanthone 11% 4.9:1

[a] All reactions were carried out with 1a (12.2 mg, 0.10 mmol), 2a (0.25 mmol, 2.5 equiv.), 3 (0.25 mmol, 2.5 equiv.), photocatalysts (2 mol%) in EA (2.0 mL) under Ar and 60 W blue LEDs, the reaction was completed as monitored by TLC analysis, after which 3,4-diethyl-3,4-hexanediol was added to the reaction system and stirred for 1 hour. [b] Yields determined by GC using dodecane as an internal standard. [c] The Z/E ratio was determined by $^1$H NMR and $^{19}$F NMR.

Supplementary Table 3: Optimization of solutions$^{[a]}$

<table>
<thead>
<tr>
<th>Entry</th>
<th>Change of additives</th>
<th>Yield of 4a$^{[b]}$</th>
<th>Z/E ratio$^{[c]}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>None</td>
<td>23%</td>
<td>&gt; 20:1</td>
</tr>
<tr>
<td>2</td>
<td>Methyl acetate</td>
<td>7%</td>
<td>&gt; 20:1</td>
</tr>
<tr>
<td>3</td>
<td>1,4-dioxane</td>
<td>0</td>
<td>-</td>
</tr>
<tr>
<td>4</td>
<td>CH$_3$CN</td>
<td>6%</td>
<td>&gt; 20:1</td>
</tr>
<tr>
<td>5</td>
<td>Mesitylene</td>
<td>trace</td>
<td>-</td>
</tr>
<tr>
<td>6</td>
<td>Acetone</td>
<td>0</td>
<td>-</td>
</tr>
<tr>
<td>7</td>
<td>CH$_3$CH$_2$OH</td>
<td>0</td>
<td>-</td>
</tr>
</tbody>
</table>

[a] All reactions were carried out with 1a (12.2 mg, 0.10 mmol), 2a (0.25 mmol, 2.5 equiv.), 3 (0.25 mmol, 2.5 equiv.), 4CzIPN (2 mol%) in solution (2.0 mL) under Ar and 60 W blue LEDs, the reaction was completed as monitored by TLC analysis, after which 3,4-diethyl-3,4-hexanediol was added to the reaction system and stirred for 1 hour. [b] Yields determined by GC using dodecane as an internal standard. [c] The Z/E ratio was determined by $^1$H NMR and $^{19}$F NMR.
**Supplementary Table 4: Optimization of conditions**

<table>
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<th>Entry</th>
<th>Change of conditions</th>
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<th>Z/E ratio$^c$</th>
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<td>None</td>
<td>23%</td>
<td>&gt; 20:1</td>
</tr>
<tr>
<td>2</td>
<td>30W Blue LEDs</td>
<td>32%</td>
<td>&gt; 20:1</td>
</tr>
<tr>
<td>3</td>
<td>90W Blue LEDs</td>
<td>46%</td>
<td>&gt; 20:1</td>
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<tr>
<td>4</td>
<td>EA (1 mL)</td>
<td>36%</td>
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<tr>
<td>5</td>
<td>EA (1.5 mL)</td>
<td>33%</td>
<td>&gt; 20:1</td>
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<tr>
<td>6</td>
<td>EA (2.5 mL)</td>
<td>25%</td>
<td>&gt; 20:1</td>
</tr>
<tr>
<td>7</td>
<td>Isopropyl acetate (1 mL), 90W Blue LEDs</td>
<td>60%</td>
<td>&gt; 20:1</td>
</tr>
<tr>
<td>8</td>
<td>Isopropyl acetate (0.6 mL), 90W Blue LEDs</td>
<td>95% (70%)$^d$</td>
<td>&gt; 20:1</td>
</tr>
<tr>
<td>9</td>
<td>Isopropyl acetate (0.8 mL), 90W Blue LEDs</td>
<td>49%</td>
<td>&gt; 20:1</td>
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<tr>
<td>10</td>
<td>Isopropyl acetate (1.2 mL), 90W Blue LEDs</td>
<td>31%</td>
<td>&gt; 20:1</td>
</tr>
<tr>
<td>11</td>
<td>In darkness</td>
<td>0</td>
<td>-</td>
</tr>
<tr>
<td>12</td>
<td>w/o 4CzIPN</td>
<td>0</td>
<td>-</td>
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</table>

$^a$ All reactions were carried out with 1a (12.2 mg, 0.10 mmol), 2a (0.25 mmol, 2.5 equiv.), 3 (0.25 mmol, 2.5 equiv.), 4CzIPN (2 mol%) in solution (X mL) under Ar and light irradiation, the reaction was completed as monitored by TLC analysis, after which 3,4-diethyl-3,4-hexanediol was added to the reaction system and stirred for 1 hour. $^b$ Yields determined by GC using dodecane as an internal standard. $^c$ The Z/E ratio was determined by $^1$H NMR and $^{19}$F NMR. $^d$ Isolated yield.

**Supplementary Table 5: Optimization of solvents under the optimal condition**

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<td>2</td>
<td>30W Blue LEDs</td>
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<td>3</td>
<td>90W Blue LEDs</td>
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<tr>
<td>4</td>
<td>EA (1 mL)</td>
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<tr>
<td>5</td>
<td>EA (1.5 mL)</td>
</tr>
<tr>
<td>6</td>
<td>EA (2.5 mL)</td>
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<tr>
<td>7</td>
<td>Isopropyl acetate (1 mL), 90W Blue LEDs</td>
</tr>
<tr>
<td>8</td>
<td>Isopropyl acetate (0.6 mL), 90W Blue LEDs (95% (70%)$^d$)</td>
</tr>
<tr>
<td>9</td>
<td>Isopropyl acetate (0.8 mL), 90W Blue LEDs</td>
</tr>
<tr>
<td>10</td>
<td>Isopropyl acetate (1.2 mL), 90W Blue LEDs</td>
</tr>
<tr>
<td>11</td>
<td>In darkness</td>
</tr>
<tr>
<td>12</td>
<td>w/o 4CzIPN</td>
</tr>
<tr>
<td>Entry</td>
<td>Change of additives</td>
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<td>1</td>
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<tr>
<td>2</td>
<td>EtOH</td>
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<td>3</td>
<td>CH₃CN</td>
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<td>Methyl acetate (MA)</td>
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<td>10</td>
<td>DME</td>
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[a] All reactions were carried out with 1a (12.2 mg, 0.10 mmol), 2a (0.25 mmol, 2.5 equiv.), 3 (0.25 mmol, 2.5 equiv.), 4CzIPN (2 mol%) in solvents (0.6 mL) under Ar and 90 W blue LEDs, the reaction was completed as monitored by TLC analysis, after which 3,4-diethyl-3,4-hexanediol was added to the reaction system and stirred for 1 hour. [b] Yields determined by GC using dodecane as an internal standard. [c] Isolated yield.

Supplementary Table 6: Optimization of conditions for aryl alkynes[a]

<table>
<thead>
<tr>
<th>Entry</th>
<th>Change of conditions</th>
<th>Yield of 4r[b]</th>
<th>Z/E ratio[c]</th>
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<tr>
<td>1</td>
<td>None</td>
<td>41</td>
<td>&gt; 20:1</td>
</tr>
<tr>
<td>2</td>
<td>30W, 24h</td>
<td>41</td>
<td>&gt; 20:1</td>
</tr>
<tr>
<td>3</td>
<td>60W, 24h</td>
<td>38</td>
<td>&gt; 20:1</td>
</tr>
<tr>
<td>4</td>
<td>2b, 90W, 24h</td>
<td>34</td>
<td>&gt; 20:1</td>
</tr>
<tr>
<td></td>
<td>Reaction</td>
<td>Time</td>
<td>Yield</td>
</tr>
<tr>
<td>---</td>
<td>----------</td>
<td>------</td>
<td>-------</td>
</tr>
<tr>
<td>5</td>
<td>2b, 60W, 24h</td>
<td>32</td>
<td>&gt; 20:1</td>
</tr>
<tr>
<td>6</td>
<td>2b, 30W, 24h</td>
<td>30</td>
<td>&gt; 20:1</td>
</tr>
<tr>
<td>7</td>
<td>4CzIPN 30W, 12h</td>
<td>31</td>
<td>&gt; 20:1</td>
</tr>
<tr>
<td>8</td>
<td>4CzIPN 90W, 12h</td>
<td>7</td>
<td>&gt; 20:1</td>
</tr>
<tr>
<td>9</td>
<td>2a, 4CzIPN 30W, 12h</td>
<td>24</td>
<td>&gt; 20:1</td>
</tr>
<tr>
<td>10</td>
<td>2a, 4CzIPN 90W, 12h</td>
<td>42</td>
<td>&gt; 20:1</td>
</tr>
<tr>
<td>11</td>
<td>2a, 4CzIPN 90W, 24h</td>
<td>36</td>
<td>&gt; 20:1</td>
</tr>
<tr>
<td>12</td>
<td>2a, 4CzIPN 30W, 24h</td>
<td>50</td>
<td>&gt; 20:1</td>
</tr>
<tr>
<td>13</td>
<td>2a, 4CzIPN 60W, 24h</td>
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</tr>
<tr>
<td>14</td>
<td>2a (3.0 equiv), 4CzIPN 30W, 24h</td>
<td>40</td>
<td>&gt; 20:1</td>
</tr>
<tr>
<td>15</td>
<td>2a, 4CzIPN 60W, 12h</td>
<td>54</td>
<td>&gt; 20:1</td>
</tr>
<tr>
<td>16</td>
<td>2a, 4CzIPN 60W, 6h</td>
<td>49</td>
<td>&gt; 20:1</td>
</tr>
<tr>
<td>17</td>
<td>2a:3=3:3, 60W, 12h</td>
<td>52</td>
<td>&gt; 20:1</td>
</tr>
<tr>
<td>18</td>
<td>2a:3=3:3, 60W, 24h</td>
<td>44</td>
<td>&gt; 20:1</td>
</tr>
<tr>
<td>19</td>
<td>Isopropyl acetate instead EA</td>
<td>26</td>
<td>&gt; 20:1</td>
</tr>
<tr>
<td>20</td>
<td>Methyl acetate instead EA</td>
<td>48</td>
<td>&gt; 20:1</td>
</tr>
<tr>
<td>21</td>
<td>2a, Isopropyl acetate (0.6 mL), 4CzIPN 90W, 13h</td>
<td>69(50)^d</td>
<td>&gt; 20:1</td>
</tr>
</tbody>
</table>

[a] All reactions were carried out with 1r (10.2 mg, 0.10 mmol), 2a (0.25 mmol, 2.5 equiv.), 3 (0.25 mmol, 2.5 equiv.), 4CzIPN (2 mol%) in solution (X mL) under Ar and light irradiation, the reaction was completed as monitored by TLC analysis, after which 3,4-diethyl-3,4-hexanediol was added to the reaction system and stirred for 1 hour. [b] Yields determined by GC using dodecane as an internal standard. [c] The E/Z ratio was determined by ^1H NMR and ^19F NMR. [d] Isolated yield.

Supplementary Table 7: Optimization of solvents for fluorosulfonyl-borylation of olefins[^]
<table>
<thead>
<tr>
<th>Entry</th>
<th>Change of reagents</th>
<th>Yield of 6a[b]</th>
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<tbody>
<tr>
<td>1</td>
<td>None</td>
<td>54</td>
</tr>
<tr>
<td>2</td>
<td>Methyl acetate</td>
<td>49</td>
</tr>
<tr>
<td>3</td>
<td>Isopropyl acetate(IA)</td>
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<tr>
<td>4</td>
<td>DCM</td>
<td>nd</td>
</tr>
<tr>
<td>5</td>
<td>THF</td>
<td>nd</td>
</tr>
<tr>
<td>6</td>
<td>CH$_3$CN</td>
<td>13</td>
</tr>
<tr>
<td>7</td>
<td>DME</td>
<td>7</td>
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<tr>
<td>8</td>
<td>Acetone</td>
<td>11</td>
</tr>
<tr>
<td>9</td>
<td>DCE</td>
<td>3</td>
</tr>
</tbody>
</table>

[a] All reactions were carried out with 5a (13.2 mg, 0.10 mmol), 2b (0.25 mmol, 2.5 equiv.), 3 (0.3 mmol, 3.0 equiv.), BE$_3$ (0.03 mmol, 0.3 equiv.), fac-Ir(ppy)$_3$ (2 mol%), in Solvents (2.0 mL) under Ar and 90 W blue LEDs, the reaction was completed as monitored by TLC analysis, after which pinacol and triethylamine was added to the reaction system and stirred for 1-2 h. [b] Yields determined by GC using dodecane as an internal standard.

Supplementary Table 8: Optimization of photocatalysts for fluorosulfonyl-borylation of olefins$^a$

<table>
<thead>
<tr>
<th>Entry</th>
<th>Change of Photocatalysts</th>
<th>Yield of 6a$^b$</th>
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<tr>
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<td>None</td>
<td>68</td>
</tr>
<tr>
<td>2</td>
<td>fac-Ir[d-F-((p-t-Bu)ppy)$_3$</td>
<td>46</td>
</tr>
<tr>
<td>3</td>
<td>Ir[(dF(CF$_3$)ppy)$_2$(dtbbpy)]PF$_6$</td>
<td>38</td>
</tr>
</tbody>
</table>
4

4CzIPN

5

Ir(mppy)$_3$

6

4-DPA-iPN

7

Ir[dF(CF$_3$)ppy]$_3$

8

Ir[dFppy]$_3$

[a] All reactions were carried out with 5a (13.2 mg, 0.10 mmol), 2b (0.25 mmol, 2.5 equiv.), 3 (0.3 mmol, 3.0 equiv.), BEt$_3$ (0.03 mmol, 0.3 equiv.), photocatalysts (2 mol%), in IA (2.0 mL) under Ar and 90 W blue LEDs, the reaction was completed as monitored by TLC analysis, after which pinacol and triethylamine was added to the reaction system and stirred for 1-2 h. [b] Yields determined by GC using dodecane as an internal standard.

Supplementary Table 9: Optimization of material ratio for fluorosulfonyl-borylation of olefins$^{[a]}$

<table>
<thead>
<tr>
<th>Entry</th>
<th>Change of material ratio(5a:2a:3:BEt$_3$)</th>
<th>Yield of 6a$^{[b]}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>None</td>
<td>68</td>
</tr>
<tr>
<td>2</td>
<td>1:1.5:2:0.2</td>
<td>28</td>
</tr>
<tr>
<td>3</td>
<td>1:2:2:0.2</td>
<td>19</td>
</tr>
<tr>
<td>4</td>
<td>1:2.5:2:0.2</td>
<td>28</td>
</tr>
<tr>
<td>5</td>
<td>1:2.5:1.5:0.2</td>
<td>10</td>
</tr>
<tr>
<td>6</td>
<td>1:2.5:2.5:0.2</td>
<td>23</td>
</tr>
<tr>
<td>7</td>
<td>1:2.5:3:0.2</td>
<td>64</td>
</tr>
<tr>
<td>8</td>
<td>1:2.5:3:0.15</td>
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</tr>
<tr>
<td>9</td>
<td>1:2.5:3:0.25</td>
<td>69</td>
</tr>
<tr>
<td>10</td>
<td>1:2.5:3:0.35</td>
<td>66</td>
</tr>
<tr>
<td>11</td>
<td>1:2:2:0.15</td>
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<td>12</td>
<td>1:2:3:0.3</td>
<td>19</td>
</tr>
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<td>13</td>
<td>1:2:2:0.3</td>
<td>49</td>
</tr>
<tr>
<td>14</td>
<td>1:2:3:0.2</td>
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</tr>
<tr>
<td>15</td>
<td>1:1.5:3:0.3</td>
<td>17</td>
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</table>

[a] All reactions were carried out with 5a (13.2 mg, 0.10 mmol), 2b (x mmol, x equiv.), 3 (y mmol, y equiv.), BEt$_3$ (z mmol, z equiv.), fac-Ir(pppy)$_3$ (2 mol%), in IA (2.0 mL) under Ar and 90 W blue LEDs, the reaction was completed as monitored by TLC analysis, after which pinacol and
triethylamine was added to the reaction system and stirred for 1-2 h. [b] Yields determined by GC using dodecane as an internal standard.

Supplementary Table 10: Optimization of IMSF reagents and control experiments for fluorosulfonyl-borylation of olefins

![Chemical structures]

<table>
<thead>
<tr>
<th>Entry</th>
<th>PC</th>
<th>Yield of 6a[b]</th>
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<tbody>
<tr>
<td>1</td>
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<tr>
<td>2</td>
<td>2a instead of 2b</td>
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<tr>
<td>3</td>
<td>2c instead of 2b</td>
<td>59</td>
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<tr>
<td>4</td>
<td>2d instead of 2b</td>
<td>8</td>
</tr>
<tr>
<td>5</td>
<td>w/o Ir(ppy)3</td>
<td>nd</td>
</tr>
<tr>
<td>6</td>
<td>In the darkness</td>
<td>nd</td>
</tr>
</tbody>
</table>

[a] All reactions were carried out with 5a (13.2 mg, 0.10 mmol), 2 (0.25 mmol, 2.5 equiv.), 3 (0.3 mmol, 3 equiv.), BEt3 (0.025 mmol, 0.25 equiv.), fac-Ir(ppy)3 (2 mol%), in IA (2.0 mL) under Ar and 90 W blue LEDs, the reaction was completed as monitored by TLC analysis, after which pinacol and triethylamine was added to the reaction system and stirred for 1-2 h. [b] Yields determined by GC using dodecane as an internal standard.

Supplementary Table 11: Optimization of IMSF reagents and other conditions for fluorosulfonyl-borylation of olefins

![Chemical structures]

<table>
<thead>
<tr>
<th>Entry</th>
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<tbody>
<tr>
<td>1</td>
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<td>69</td>
</tr>
<tr>
<td>2</td>
<td>30W, 12h</td>
<td>67</td>
</tr>
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<td></td>
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<tr>
<td>---</td>
<td>----------</td>
<td>-------</td>
</tr>
<tr>
<td>3</td>
<td>60W, 12h</td>
<td>62</td>
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<tr>
<td>4</td>
<td>90W, 24h</td>
<td>25</td>
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<tr>
<td>5</td>
<td>2a, 90W, 24h</td>
<td>80</td>
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<tr>
<td>6</td>
<td>3 equiv of 2b, 12h</td>
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<td>7</td>
<td>3.5 equiv of 2b, 12h</td>
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<td>3.0 equiv of 2b, 12h, 30W</td>
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</tr>
<tr>
<td>11</td>
<td>3.0 equiv of 2b, 12h, 60W</td>
<td>50</td>
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</table>

[a] All reactions were carried out with 5a (13.2 mg, 0.10 mmol), 2 (x mmol, x equiv.), 3 (0.3 mmol, 3 equiv.), BEt3 (0.025 mmol, 0.25 equiv.), fac-Ir(ppy)3 (2 mol%), in IA (2.0 mL) under Ar and Light irradiation, the reaction was completed as monitored by TLC analysis, after which pinacol and triethylamine was added to the reaction system and stirred for 1-2 h. [b] Yields determined by GC using dodecane as an internal standard. [c] Isolated Yields.

General Procedure for the synthesis of products 4a, 4c-4e. Condition A: Under argon, to a solution of 4CzIPN (2 mol%), 2,2'-Bis-1,3,2-benzodioxaborole 3 (0.25 mmol, 2.5 equiv.) and IMSF reagent 2a (0.2 mmol, 2 equiv.) in dried isopropyl acetate (0.6 mL) was added corresponding alkynes 1a, 1c-1e (0.1 mmol) at room temperature. After that, the tube was exposed to a 90 W blue LEDs about 40min-12h, after which 3,4-diethyl-3,4-hexanediol was added to the reaction system and stirred for 1 h. The reaction was completed as monitored by TLC analysis and the reaction mixture was evaporated in vacuo. The crude products were directly purified by flash chromatography on silica gel to give the desired products.

General Procedure for the synthesis of products 4b, 4f-4l. Condition B: Under argon, to a solution of 4CzIPN (2 mol%), 2,2'-Bis-1,3,2-benzodioxaborole 3 (0.25 mmol, 2.5 equiv.) and IMSF reagent 2a (0.2 mmol, 2 equiv.) in dried isopropyl acetate : ethyl acetate= 2:1 (0.8 mL) was added corresponding alkynes 1b, 1f-1l (0.1 mmol) at room temperature. After that, the tube was exposed to a 90 W blue LEDs about 40min-12h, after which 3,4-diethyl-3,4-hexanediol was added to the reaction system and stirred for 1 h. The reaction was completed as monitored by TLC analysis and the reaction mixture was evaporated in vacuo. The crude products were directly purified by flash chromatography on silica gel to give the desired products.

General Procedure for the synthesis of products 4m-4x. Condition C: Under argon, to a solution of 4CzIPN (2 mol%), 2,2'-Bis-1,3,2-benzodioxaborole 3 (0.25 mmol, 2.5 equiv.) and IMSF reagent 2a (0.2 mmol, 2 equiv.) in dried isopropyl acetate (0.6 mL) was added corresponding alkynes 1m-1x (0.1 mmol) at room temperature. After that, the tube was
exposed to a 90 W blue LEDs about 13 h, after which 3,4-diethyl-3,4-hexanediol was added to the reaction system and stirred for 1 h. The reaction was completed as monitored by TLC analysis and the reaction mixture was evaporated in vacuo. The crude products were directly purified by flash chromatography on silica gel to give the desired products.

**General Procedure for the synthesis of product 6. Condition D:** Under argon, to a solution of fac-Ir(ppy)$_3$ (2 mol%), BEt$_3$ (0.025 mmol, 0.25 equiv.), 2,2'-Bis-1,3,2-benzodioxaborole 3 (0.3 mmol, 3.0 equiv.) and IMSF reagent 2a (0.3 mmol, 3.0 equiv.) in dried isopropyl acetate (2 mL) was added corresponding olefins 5 (0.1 mmol) at room temperature. After that, the tube was exposed to a 30 W blue LEDs about 12 h, after which pinacol and triethylamine was added to the reaction system and stirred for 1-2 h. The reaction was completed as monitored by TLC analysis and the reaction mixture was evaporated in vacuo. The crude products were directly purified by flash chromatography on silica gel to give the desired products.

**General Procedure for the synthesis of product 7 and 8**\[5\]. **Condition E:** Under argon, to a solution of 4m (0.05 mmol) in dried MeOH (1 mL) was added CuX$_2$ (1.0 equiv.) at room temperature. After that, the tube was heated to 80 ºC about 12 h, then until the reaction was completed as monitored by TLC analysis. The reaction mixture was evaporated in vacuo. The crude products were directly purified by flash chromatography on silica gel to give the desired products.

**General Procedure for the synthesis of product 9**\[6\]. **Condition F:** Under argon, to a solution of 4m (0.05 mmol), Pd(OAc)$_2$ (5 mol%), P(o-Tol)$_3$ (10 mol%), in dried toluene (0.5 mL) was added H$_2$O (2.5 equiv.) at room temperature. After that, the tube was heated to 80 ºC about 12
h, then until the reaction was completed as monitored by TLC analysis. The reaction mixture was evaporated in *vacuo*. The crude products were directly purified by flash chromatography on silica gel to give the desired products.

**General Procedure for the synthesis of product 11, 13, 17, 20**[7]. **Condition G:** Under argon, to a solution of 4m (0.05 mmol), Pd(OAc)$_2$ (15 mol%), SPhos (35 mol%), K$_3$PO$_4$ (1.5 equiv.) in dried toluene (0.5 mL) was added corresponding aryl bromides 12, 16, 19 (0.06 mmol) or 3,6-dihydro-2H-pyran-4-yl trifluoromethanesulfonate 10 (0.06 mmol) at room temperature. After that, the tube was heated to 80 ºC about 12 h, then until the reaction was completed as monitored by TLC analysis. The reaction mixture was evaporated in *vacuo*. The crude products were directly purified by flash chromatography on silica gel to give the desired products.

**General Procedure for the synthesis of product 14**[8]. **Condition H:** To a solution of sesamol (1.0 equiv.), HMDS (1.0 equiv.), and BTMG (20 mol%) in dried MeCN (0.5 mL) was added corresponding alkenes 13 at room temperature. After that, the tube was heated to a 60 ºC about 1 h, then until the reaction was completed as monitored by TLC analysis. The reaction mixture was evaporated in *vacuo*. The crude products were directly purified by flash chromatography on silica gel to give the desired products.

**General Procedure for the synthesis of product 15, 21**[9]. **Condition I:** To a solution of amines (2.0 equiv.), Ca(NTf)$_2$ (1.0 equiv.) in t-amylOH (0.5 mL) was added corresponding alkenes 13 or 20 at room temperature. After that, the tube was heated to a 60 ºC about 24 h, then until the reaction was completed as monitored by TLC analysis. The reaction mixture was
evaporated in vacuo. The crude products were directly purified by flash chromatography on silica gel to give the desired products.

**General Procedure for the synthesis of product 18**

**Condition J:** To a solution of estrone (2.0 equiv.), KOH (2.0 equiv.) in MeCN (0.5 mL) was added corresponding alkene 17 at room temperature. After that, the tube was heated to a 50 ºC about 12 h, then until the reaction was completed as monitored by TLC analysis. The reaction mixture was evaporated in vacuo. The crude products were directly purified by flash chromatography on silica gel to give the desired products.
VII. Mechanistic experiments

A. Luminescence quenching experiment

The luminescence quenching experiment was taken using a F-4600 FL Spectrophotometer (Hitachi, Japan). The experiments were carried out in 5 x 10^{-4} mol/L of Ir(ppy)$_3$ in CH$_3$CN at 25 ºC with an excitation wavelength of 380 nm and an excitation and emission bandwidth of 5 nm. The scanspeed was set at 1200 nm/min and the PMT voltage was set to 500 V. The concentrations of quencher (5a, IMSF-2a, B$_2$Cat$_2$) in CH$_3$CN were 0.01 mmol/mL. The concentrations of quencher IMSF-2a in CH$_3$CN was 4 mmol/L, 8 mmol/L, 12 mmol/L, 16 mmol/L. (see supplementary figure 7 and supplementary figure 8-9)

To determine whether a reductive or oxidative quenching cycle is operative in the reaction, fluorescence quenching studies were conducted. Based on the above data, photoexcited Ir(ppy)$_3^*$ can be quenched by IMSF-2a, which involving a oxidative quenching cycle.

![Supplementary Figure 7. The data of fluorescence quenching of Ir(ppy)$_3$, B$_2$Cat$_2$, 5a, IMSF-2a](image-url)
Supplementary Figure 8. The data of fluorescence quenching of Ir(ppy)$_3$ by different concentrations of IMSF-2a

Supplementary Figure 9. Stern-Volmer plot of Ir(ppy)$_3$ at different concentrations of IMSF-2a
B. $^{11}\text{B}$ NMR experiments

All $^{11}\text{B}$ NMR data was recorded at 25 °C. See supplementary figure 10-13 for details of reagents and solvents; supplementary figure 10 shows $\text{B}_2\text{Cat}_2$ in $\text{CD}_3\text{CN}$; supplementary figure 11 shows $\text{B}_2\text{Cat}_2$ : Isopropyl acetate (IA) = 1:1 in $\text{CD}_3\text{CN}$; supplementary figure 12 shows $\text{B}_2\text{Cat}_2$ : IMSF-2a = 1:1 in $\text{CD}_3\text{CN}$; supplementary Figure 13 shows $\text{B}_2\text{Cat}_2$ : 1-methyl-2-(4-(trifluoromethyl)phenyl)-1H-benzo[d]imidazole = 1:1 in $\text{CD}_3\text{CN}$.

Supplementary Figure 10. $\text{B}_2\text{Cat}_2$ in $\text{CD}_3\text{CN}$
Supplementary Figure 11. B\textsubscript{2}Cat\textsubscript{2} : Isopropyl acetate =1:1 in CD\textsubscript{3}CN

Supplementary Figure 12. B\textsubscript{2}Cat\textsubscript{2} : IMSF-2a =1:1 in CD\textsubscript{3}CN
Supplementary Figure 13. B$_2$Cat$_2$: 1-methyl-2-(4-(trifluoromethyl)phenyl)-1H-benzo[d]imidazole = 1:1 in CD$_3$CN

$^1$B NMR experiments reveal that there is just a single signal whether only B$_2$Cat$_2$ in CD$_3$CN, mix isopropyl acetate with B$_2$Cat$_2$ in CD$_3$CN or mix IMSF-2a with B$_2$Cat$_2$ in CD$_3$CN (supplementary figure 10-12); when mix imidazole residue with B$_2$Cat$_2$ in CD$_3$CN, the latter shows one upfield signal (supplementary figure 13). The upfield shifting supports the ligation of imidazole residue with diboron species.

C. Control Experiment

(a)

Under argon, to a solution of 4CzIPN (2 mol%), B$_2$Cat$_2$ (2.5 equiv.), TEMPO (3.0 equiv.) and IMSF-2a (0.25 mmol, 2.5 equiv.) in dried IA (0.6 mL) was added corresponding alkyne 1a (0.1 mmol) at room temperature. After that, the tube was exposed to a 90 W blue LEDs about 40min until the reaction was completed as monitored by TLC analysis. Subsequently, the reaction mixture was analyzed by GC. GC showed that no major product 4a was formed after addition of 0.3 mmol of TEMPO.
Under argon, to a solution of 4CzIPN (2 mol%), B$_2$Cat$_2$ (2.5 equiv), 1,1-diphenylethylene (0.2 mmol, 2.0 equiv.) and IMSF- 2a (0.25 mmol, 2.5 equiv.) in dried IA (0.6 mL) was added corresponding alkyne 1a (0.1 mmol) at room temperature. After that, the tube was exposed to a 90 W blue LEDs about 40 min until the reaction was completed as monitored by TLC analysis. Subsequently, the reaction mixture was analyzed by GC. GC showed that trace product 4a was formed after addition of 0.2 mmol of 1,1-diphenylethylene. In addition, product 13 can be obtained with a 66% separation yield.

D. Proposed mechanism

From the above mechanistic experiments, we speculate on the possible mechanism of the reaction: First, under the irradiation, the cationic reagent 2a can be reduced by excited state photocatalyst (PC*) to generate radical intermediate I and releases SO$_2$F radical and imidazole residue II. Then the addition of SO$_2$F radical to the alkynes regioselectively furnishes vinylic radical intermediate III. Subsequent addition of vinyl radical III to B$_2$Cat$_2$ afforded a Z-vinyl diboron radical species IV. The control of stereoselectivity is governed by steric repulsion between the fluorosulfonyl group and the boronates. Then, the activation of diboron reagent by in situ generated imidazole residues II forms a highly reactive B–N heteroleptic intermediate V, which leads to the desired bifunctional products 4 or 6 and imidazole stabilized boryl radical species VI. Finally, photo-oxidation of VI followed by coupling with -OTf affords boryl imidazolium salt VII and regenerates PC. (supplementary figure 14).

Supplementary Figure 14. Proposed mechanism
VIII. References
IX. Characteristic Data

(Z)-3-cyclohexyl-2-(4,4,5,5-tetraethyl-1,3,2-dioxaborolan-2-yl)prop-1-ene-1-sulfonyl fluoride (4a)

70% (27.2 mg); colorless oil; ¹H NMR (400 MHz, Chloroform-d) δ 6.86 (s, 1H), 2.59 (d, J = 6.8 Hz, 2H), 1.79 – 1.60 (m, 13H), 1.34 – 1.11 (m, 6H), 0.92 (t, J = 7.5 Hz, 12H). ¹³C NMR (101 MHz, Chloroform-d) δ 129.8 (d, J = 23.2 Hz), 90.3, 38.1, 37.9, 33.2, 32.8, 26.3, 26.2, 8.7. The signal of the α-B-carbon was not observed. ¹⁹F NMR (376 MHz, Chloroform-d) δ 65.06. ¹¹B NMR (128 MHz, Chloroform-d) δ 29.09. HRMS(ESI): caled for C₁₉H₃₅BFO₄S + [M + H]+ 389.2328; found 389.2326.

(Z)-5-chloro-2-(4,4,5,5-tetraethyl-1,3,2-dioxaborolan-2-yl)pent-1-ene-1-sulfonyl fluoride (4b)

57% (20.9 mg); colorless oil; ¹H NMR (400 MHz, Chloroform-d) δ 6.91 (s, 1H), 3.56 (t, J = 6.7 Hz, 2H), 2.80 (ddt, J = 9.2, 5.9, 1.3 Hz, 2H), 2.07 – 1.93 (m, 2H), 1.71 (qd, J = 7.3, 4.5 Hz, 8H), 0.92 (t, J = 7.5 Hz, 12H). ¹³C NMR (101 MHz, Chloroform-d) δ 130.8 (d, J = 23.6 Hz), 90.6, 44.3, 31.6, 28.5, 26.3, 8.7. The signal of the α-B-carbon was not observed. ¹⁹F NMR (376 MHz, Chloroform-d) δ 64.99. ¹¹B NMR (128 MHz, Chloroform-d) δ 28.87. HRMS(ESI): caled for C₁₅H₂₉ClBFO₄S + [M + H]+ 369.1469; found 369.1466.

(Z)-2-(4,4,5,5-tetraethyl-1,3,2-dioxaborolan-2-yl)pent-1-ene-1-sulfonyl fluoride (4c)

54% (18.0 mg); colorless oil; ¹H NMR (400 MHz, Chloroform-d) δ 6.86 (s, 1H), 2.69 – 2.61 (m, 2H), 1.70 (qd, J = 7.3, 4.3 Hz, 8H), 1.59 – 1.49 (m, 2H), 0.97 (t, J = 7.4 Hz, 3H), 0.92 (t, J = 7.5 Hz, 12H). ¹³C NMR (101 MHz, Chloroform-d) δ 129.7 (d, J = 23.2 Hz), 90.3, 32.6, 26.3, 22.3, 14.1, 8.7. The signal of the α-B-carbon was not observed. ¹⁹F NMR (376 MHz, Chloroform-d) δ 64.92. ¹¹B NMR (160 MHz, Chloroform-d) δ 28.94. HRMS(ESI): caled for C₁₅H₂₉BFO₄S + [M + H]+ 335.1858; found 335.1856.
(Z)-4-phenyl-2-(4,4,5,5-tetraethyl-1,3,2-dioxaborolan-2-yl)but-1-ene-1-sulfonyl fluoride

(4d)

\[
\begin{align*}
\text{SO}_2\text{F} & \quad \text{Et} \quad \text{Et} \\
\text{O} & \quad \text{O} \\
\end{align*}
\]

40% (15.8 mg); colorless oil; \(^1\)H NMR (500 MHz, Chloroform-\(d\)) \(\delta\) 7.32 (dd, \(J = 8.0, 6.9\) Hz, 2H), 7.24 (dd, \(J = 5.8, 2.7\) Hz, 3H), 6.92 (s, 1H), 3.03 – 2.96 (m, 2H), 2.85 – 2.79 (m, 2H), 1.72 (qd, \(J = 7.3, 4.3\) Hz, 8H), 0.96 (t, \(J = 7.4\) Hz, 12H). \(^{13}\)C NMR (126 MHz, Chloroform-\(d\)) \(\delta\) 140.7, 130.3 (d, \(J = 23.3\) Hz), 128.5, 128.5, 126.3, 125.3, 90.5, 35.1, 32.9, 26.3, 8.7. The signal of the \(\alpha\)-B-carbon was not observed. \(^{19}\)F NMR (471 MHz, Chloroform-\(d\)) \(\delta\) 64.98. \(^{11}\)B NMR (160 MHz, Chloroform-\(d\)) \(\delta\) 28.27. HRMS(ESI): caled for C\(_{20}\)H\(_{31}\)BF\(_4\)O\(_4\)S\(^+\) [M + H\(^+\)] 397.2015; found 397.2016.

(Z)-2-(4,4,5,5-tetraethyl-1,3,2-dioxaborolan-2-yl)dodec-1-ene-1-sulfonyl fluoride (4e)

\[
\begin{align*}
\text{Me} & \quad \text{SO}_2\text{F} \\
\text{Et} & \quad \text{Et} \\
\end{align*}
\]

51% (22.0 mg); colorless oil; \(^1\)H NMR (500 MHz, Chloroform-\(d\)) \(\delta\) 6.83 (s, 1H), 2.68 – 2.60 (m, 2H), 1.76 – 1.63 (m, 8H), 1.48 (ddd, \(J = 11.4, 8.6, 6.2\) Hz, 2H), 1.37 – 1.22 (m, 14H), 0.92 (t, \(J = 7.5\) Hz, 12H), 0.88 (t, \(J = 6.9\) Hz, 3H). \(^{13}\)C NMR (126 MHz, Chloroform-\(d\)) \(\delta\) 129.4 (d, \(J = 22.9\) Hz), 90.3, 31.9, 30.8, 29.6, 29.6, 29.4, 29.3, 29.2, 28.8, 26.3, 22.7, 14.1, 8.7. The signal of the \(\alpha\)-B-carbon was not observed. \(^{19}\)F NMR (471 MHz, Chloroform-\(d\)) \(\delta\) 64.94. \(^{11}\)B NMR (160 MHz, Chloroform-\(d\)) \(\delta\) 29.41. HRMS(ESI): caled for C\(_{22}\)H\(_{43}\)BF\(_4\)O\(_4\)S\(^+\) [M + H\(^+\)] 433.2954; found 433.2952.

(Z)-5-(fluorosulfonyl)-4-(4,4,5,5-tetraethyl-1,3,2-dioxaborolan-2-yl)pent-4-en-1-yl 1-fluorocyclopropane-1-carboxylate (4f)

\[
\begin{align*}
\text{SO}_2\text{F} & \quad \text{Et} \\
\end{align*}
\]

50% (21.8 mg); colorless oil; \(^1\)H NMR (500 MHz, Chloroform-\(d\)) \(\delta\) 6.91 (s, 1H), 4.23 (t, \(J = 6.2\) Hz, 2H), 2.77 – 2.71 (m, 2H), 1.89 (ddt, \(J = 9.3, 7.8, 6.2\) Hz, 2H), 1.70 (m, 8H), 1.39 (s, 2H), 1.37 – 1.35 (m, 2H), 0.92 (t, \(J = 7.4\) Hz, 12H). \(^{13}\)C NMR (126 MHz, Chloroform-\(d\)) \(\delta\) 170.5 (d, \(J = 24.2\) Hz), 130.8 (d, \(J = 23.6\) Hz), 90.6, 73.8, 64.8, 27.8, 27.3, 26.3, 14.6, 14.5, 8.7. The signal
of the α-B-carbon was not observed. $^{19}$F NMR (471 MHz, Chloroform-$d$) δ 64.96, -197.85. $^{11}$B NMR (160 MHz, Chloroform-$d$) δ 28.99. HRMS(ESI): caled for C$_{19}$H$_{32}$BF$_2$O$_6$S$^+$ [M + H]$^+$ 437.1975; found 437.1977.

(Z)-5-(fluorosulfonyl)-4-(4,4,5,5-tetraethyl-1,3,2-dioxaborolan-2-yl)pent-4-en-1-yl 3,3-difluorocyclobutane-1-carboxylate (4g)

$^{13}$C NMR (101 MHz, Chloroform-$d$) δ 173.2, 130.8 (d, $J = 23.8$ Hz), 90.6, 64.4, 38.7 (t, $J = 24.5$ Hz), 27.8, 27.3, 26.5 (dd, $J = 14.5$, 5.0 Hz), 26.3, 8.7.

$^{19}$F NMR (376 MHz, Chloroform-$d$) δ 64.93, -82.69 -83.26 (m), -96.99 -97.67 (m).

$^{11}$B NMR (128 MHz, Chloroform-$d$) δ 29.01.

HRMS(ESI): caled for C$_{20}$H$_{33}$BF$_3$O$_6$S$^+$ [M + H]$^+$ 469.2038; found 469.2036.

(Z)-5-(fluorosulfonyl)-4-(4,4,5,5-tetraethyl-1,3,2-dioxaborolan-2-yl)pent-4-en-1-yl cyclobutane-carboxylate (4h)

$^{13}$C NMR (126 MHz, Chloroform-$d$) δ 175.4, 130.5 (d, $J = 23.3$ Hz), 90.5, 63.6, 38.1, 28.0, 27.5, 26.3, 25.3, 18.4, 8.7. The signal of the α-B-carbon was not observed. $^{19}$F NMR (376 MHz, Chloroform-$d$) δ 64.93, -82.69 -83.26 (m), -96.99 -97.67 (m). $^{11}$B NMR (128 MHz, Chloroform-$d$) δ 29.01. HRMS(ESI): caled for C$_{20}$H$_{35}$BF$_3$O$_6$S$^+$ [M + H]$^+$ 433.2226; found 433.2224.

(Z)-5-(fluorosulfonyl)-4-(4,4,5,5-tetraethyl-1,3,2-dioxaborolan-2-yl)pent-4-en-1-yl cyclopentane-carboxylate (4i)
51% (22.8 mg); colorless oil; $^1$H NMR (400 MHz, Chloroform-$d$) δ 6.89 (s, 1H), 4.11 (t, $J = 6.2$ Hz, 2H), 2.80 – 2.68 (m, 3H), 1.93 – 1.76 (m, 6H), 1.70 (qd, $J = 7.3$, 3.7 Hz, 9H), 1.58 (tdt, $J = 6.3$, 4.7, 2.2 Hz, 3H), 0.92 (t, $J = 7.5$ Hz, 12H). $^{13}$C NMR (101 MHz, Chloroform-$d$) δ 176.7, 130.5 (d, $J = 23.4$ Hz), 90.5, 63.6, 43.9, 30.0, 28.0, 27.6, 26.3, 25.8, 8.7. The signal of the α-B-carbon was not observed. $^{19}$F NMR (376 MHz, Chloroform-$d$) δ 64.98. $^{11}$B NMR (128 MHz, Chloroform-$d$) δ 28.98. HRMS(ESI): caled for C$_{21}$H$_{37}$BFO$_6$S$^+$ [M + H]$^+$ 447.2383; found 447.2380.

(Z)-5-(fluorosulfonyl)-4-(4,4,5,5-tetraethyl-1,3,2-dioxaborolan-2-yl)pent-4-en-1-yl (1R,2R)-2-phenylcyclopropane-1-carboxylate (4j)

41% (20.3 mg); colorless oil; $^1$H NMR (400 MHz, Chloroform-$d$) δ 7.32 – 7.25 (m, 2H), 7.24 – 7.15 (m, 1H), 7.14 – 7.07 (m, 2H), 6.89 (s, 1H), 4.15 (t, $J = 6.2$ Hz, 2H), 2.77 (t, $J = 7.7$ Hz, 2H), 2.53 (ddd, $J = 9.3$, 6.5, 4.1 Hz, 1H), 1.95 – 1.82 (m, 3H), 1.77 – 1.62 (m, 8H), 1.60 (ddd, $J = 9.6$, 5.3, 4.5 Hz, 1H), 1.32 (ddd, $J = 8.4$, 6.5, 4.5 Hz, 1H), 0.90 (td, $J = 7.5$, 2.4 Hz, 12H). $^{13}$C NMR (101 MHz, Chloroform-$d$) δ 173.2, 140.1, 130.5 (d, $J = 23.6$ Hz), 128.4, 126.5, 126.2, 90.5, 27.9, 27.5, 26.3, 26.2, 24.1, 17.0, 8.7. The signal of the α-B-carbon was not observed. $^{19}$F NMR (376 MHz, Chloroform-$d$) δ 65.03. $^{11}$B NMR (128 MHz, Chloroform-$d$) δ 29.06. HRMS(ESI): caled for C$_{25}$H$_{37}$BFO$_6$S$^+$ [M + H]$^+$ 495.2383; found 495.2386.

S30
(Z)-5-(fluorosulfonyl)-4-(4,4,5,5-tetraethyl-1,3,2-dioxaborolan-2-yl)pent-4-en-1-yl 4-
methylcyclohexane-1-carboxylate (4k)

\[
\begin{align*}
\text{Me} & \quad \text{SO}_{2}F \\
\text{Et} & \quad \text{O} \\
\text{B} & \quad \text{O} \\
\text{Et} & \quad \text{Et} \\
\text{Et} & \quad \text{Et}
\end{align*}
\]

50% (23.7 mg); colorless oil; \(^1\)H NMR (400 MHz, Chloroform-\(d\)) \(\delta\) 6.89 (s, 1H), 4.10 (t, \(J = 6.1\) Hz, 2H), 2.74 (t, \(J = 7.8\) Hz, 2H), 2.20 (tt, \(J = 12.3, 3.6\) Hz, 1H), 1.95 (dq, \(J = 12.4, 3.5, 3.0\) Hz, 2H), 1.89 – 1.79 (m, 2H), 1.80 – 1.63 (m, 11H), 1.50 – 1.28 (m, 4H), 0.92 (t, \(J = 7.5\) Hz, 12H), 0.89 (d, \(J = 6.5\) Hz, 3H). \(^{13}\)C NMR (101 MHz, Chloroform-\(d\)) \(\delta\) 176.2, 130.5 (d, \(J = 23.5\) Hz), 90.5, 63.4, 43.2, 34.3, 32.0, 29.0, 28.0, 27.6, 26.3, 22.5, 8.7. The signal of the \(\alpha\)-B-carbon was not observed. \(^{19}\)F NMR (376 MHz, Chloroform-\(d\)) \(\delta\) 64.98. \(^{11}\)B NMR (128 MHz, Chloroform-\(d\)) \(\delta\) 28.88. HRMS(ESI): caled for \(\text{C}_{23}\text{H}_{41}\text{BF}_{6}\text{O}_{6}\text{S}^+ [M + H]^+\) 475.2696; found 475.2699.

(Z)-5-(fluorosulfonyl)-4-(4,4,5,5-tetraethyl-1,3,2-dioxaborolan-2-yl)pent-4-en-1-yl 1-(2,2-
difluorobenzo[d][1,3]dioxol-5-yl)cyclopropane-1-carboxylate (4l)

\[
\begin{align*}
\text{F} & \quad \text{O} \\
\text{O} & \quad \text{SO}_{2}F \\
\text{B} & \quad \text{O} \\
\text{Et} & \quad \text{Et} \\
\text{Et} & \quad \text{Et}
\end{align*}
\]

32% (18.4 mg); colorless oil; \(^1\)H NMR (400 MHz, Chloroform-\(d\)) \(\delta\) 7.10 – 7.03 (m, 2H), 6.97 (dd, \(J = 7.8, 0.8\) Hz, 1H), 6.88 (s, 1H), 4.08 (t, \(J = 6.0\) Hz, 2H), 2.66 – 2.58 (m, 2H), 1.78 – 1.62 (m, 12H), 1.17 (q, \(J = 4.0\) Hz, 2H), 0.91 (t, \(J = 7.5\) Hz, 12H). \(^{13}\)C NMR (101 MHz, Chloroform-\(d\)) \(\delta\) 173.9, 135.8, 131.7, 130.8 (d, \(J = 23.6\) Hz), 125.8, 112.0, 108.9, 90.6, 64.5, 29.7, 29.0, 27.9, 27.5, 26.3, 16.9, 8.7. The signal of the \(\alpha\)-B-carbon was not observed. \(^{19}\)F NMR (376 MHz, Chloroform-\(d\)) \(\delta\) 64.87, -49.90. \(^{11}\)B NMR (128 MHz, Chloroform-\(d\)) \(\delta\) 29.30; HRMS(ESI): caled for \(\text{C}_{26}\text{H}_{35}\text{BF}_{3}\text{O}_{8}\text{S}^+ [M + H]^+\) 575.2093; found 575.2091.
(Z)-2-phenyl-2-(4,4,5,5-tetraethyl-1,3,2-dioxaborolan-2-yl)ethene-1-sulfonyl fluoride (4m)

50% (18.4 mg); colorless oil; $^1$H NMR (400 MHz, Chloroform-$d$) $\delta$ 7.39 (dd, $J$ = 5.1, 2.0 Hz, 3H), 7.37 – 7.30 (m, 2H), 7.08 (s, 1H), 1.71 (hept, $J$ = 7.0 Hz, 8H), 0.91 (t, $J$ = 7.5 Hz, 12H). $^{13}$C NMR (101 MHz, Chloroform-$d$) $\delta$ 134.8, 130.4 (d, $J$ = 25.8 Hz), 129.2, 128.1, 127.8 (d, $J$ = 1.3 Hz), 90.8, 26.3, 8.7. The signal of the $\alpha$-B-carbon was not observed. $^{19}$F NMR (376 MHz, Chloroform-$d$) $\delta$ 64.47. $^{11}$B NMR (128 MHz, Chloroform-$d$) $\delta$ 28.98. HRMS(ESI): caled for C$_{18}$H$_{27}$BFO$_4$S$^+$ [M + H]$^+$ 369.1702; found 369.1705.

(Z)-2-(4-(tert-butyl)phenyl)-2-(4,4,5,5-tetraethyl-1,3,2-dioxaborolan-2-yl)ethene-1-sulfonyl fluoride (4n)

52% (22.0 mg); white solid; $^1$H NMR (400 MHz, Chloroform-$d$) $\delta$ 7.44 – 7.29 (m, 4H), 7.03 (s, 1H), 1.72 (hept, $J$ = 7.4 Hz, 8H), 1.33 (s, 9H), 0.92 (t, $J$ = 7.5 Hz, 12H). $^{13}$C NMR (101 MHz, Chloroform-$d$) $\delta$ 152.5, 131.6, 129.4 (d, $J$ = 25.9 Hz), 128.1, 125.1, 90.7, 34.8, 31.2, 26.3, 8.7. The signal of the $\alpha$-B-carbon was not observed. $^{19}$F NMR (376 MHz, Chloroform-$d$) $\delta$ 64.17. $^{11}$B NMR (128 MHz, Chloroform-$d$) $\delta$ 29.87. HRMS(ESI): caled for C$_{22}$H$_{35}$BFO$_4$S$^+$ [M + H]$^+$ 425.2328; found 425.2325.

(Z)-2-(4,4,5,5-tetraethyl-1,3,2-dioxaborolan-2-yl)-2-(p-tolyl)ethene-1-sulfonyl fluoride (4o)

62% (23.6 mg); colorless oil; $^1$H NMR (500 MHz, Chloroform-$d$) $\delta$ 7.35 – 7.29 (m, 2H), 7.24 (d, $J$ = 8.0 Hz, 2H), 7.08 (s, 1H), 2.42 (s, 3H), 1.83 – 1.69 (m, 8H), 0.96 (t, $J$ = 7.5 Hz, 12H). $^{13}$C NMR (101 MHz, Chloroform-$d$) $\delta$ 139.4, 131.8, 129.7 (d, $J$ = 25.8 Hz), 128.9, 128.1, 90.7, 26.3, 21.4, 8.7. The signal of the $\alpha$-B-carbon was not observed. $^{19}$F NMR (376 MHz, Chloroform-$d$) $\delta$ 64.38. $^{11}$B NMR (128 MHz, Chloroform-$d$) $\delta$ 29.18. HRMS(ESI): caled for C$_{19}$H$_{29}$BFO$_4$S$^+$ [M + H]$^+$ 383.1858; found 383.1859.
(Z)-2-([1,1′-biphenyl]-4-yl)-2-(4,4,5,5-tetraethyl-1,3,2-dioxaborolan-2-yl)ethene-1-sulfonyl fluoride (4p)

51% (22.6 mg); colorless oil; 1H NMR (400 MHz, Chloroform-d) δ 7.63 (dd, J = 7.8, 1.6 Hz, 4H), 7.48 – 7.40 (m, 4H), 7.40 – 7.31 (m, 1H), 7.10 (s, 1H), 1.72 (dq, J = 14.6, 7.3 Hz, 8H), 0.93 (t, J = 7.5 Hz, 12H). 13C NMR (101 MHz, Chloroform-d) δ 142.0, 140.3, 133.6, 130.1 (d, J = 25.9 Hz), 128.8, 128.6 (d, J = 1.3 Hz), 127.7, 127.1, 126.8, 90.9, 26.3, 8.7. The signal of the α-B-carbon was not observed. 19F NMR (376 MHz, Chloroform-d) δ 64.40. 11B NMR (128 MHz, Chloroform-d) δ 29.23. HRMS(ESI): caled for C24H31BFO4S+ [M + H]+ 445.2015; found 445.2018.

(Z)-2-(4-pentylphenyl)-2-(4,4,5,5-tetraethyl-1,3,2-dioxaborolan-2-yl)ethene-1-sulfonyl fluoride (4q)

44% (19.3 mg); colorless oil; 1H NMR (400 MHz, Chloroform-d) δ 7.31 – 7.27 (m, 2H), 7.21 – 7.18 (m, 2H), 7.03 (s, 1H), 2.69 – 2.55 (m, 2H), 1.78 – 1.66 (m, 8H), 1.66 – 1.59 (m, 2H), 1.37 – 1.30 (m, 4H), 0.98 – 0.87 (m, 15H). 13C NMR (101 MHz, Chloroform-d) δ 144.4, 131.9, 129.48 (d, J = 25.7 Hz), 128.1, 128.1, 90.7, 35.8, 31.6, 30.7, 26.3, 22.5, 14.0, 8.7. The signal of the α-B-carbon was not observed. 19F NMR (376 MHz, Chloroform-d) δ 64.27. 11B NMR (128 MHz, Chloroform-d) δ 28.42. HRMS(ESI): caled for C28H37BFO4S+ [M + H]+ 439.2484; found 439.2483.
(Z)-2-(4-fluorophenyl)-2-(4,4,5,5-tetraethyl-1,3,2-dioxaborolan-2-yl)ethene-1-sulfonyl fluoride (4r)

52% (20.0 mg); colorless oil; $^1$H NMR (400 MHz, Chloroform-$d$) $\delta$ 7.40 – 7.31 (m, 2H), 7.14 – 7.05 (m, 3H), 2.00 – 1.62 (m, 8H), 0.91 (t, $J = 7.5$ Hz, 12H). $^{13}$C NMR (101 MHz, Chloroform-$d$) $\delta$ 164.5, 162.0, 130.6 (d, $J = 26.1$ Hz), 130.1 (d, $J = 9.6$ Hz), 115.3 (d, $J = 21.8$ Hz), 90.9, 26.3, 8.7. The signal of the $\alpha$-B-carbon was not observed.

$^{19}$F NMR (376 MHz, Chloroform-$d$) $\delta$ 64.37, -111.54 – -111.66 (m). $^{11}$B NMR (128 MHz, Chloroform-$d$) $\delta$ 29.33. HRMS(ESI): caled for C$_{18}$H$_{26}$BF$_2$O$_4$S $\left[\text{M + H}\right]^+$ 387.1608; found 387.1610.

(Z)-2-(4-chlorophenyl)-2-(4,4,5,5-tetraethyl-1,3,2-dioxaborolan-2-yl)ethene-1-sulfonyl fluoride (4s)

50% (20.0 mg); colorless oil; $^1$H NMR (400 MHz, Chloroform-$d$) $\delta$ 7.40 – 7.33 (m, 2H), 7.30 – 7.26 (m, 2H), 7.09 (s, 1H), 1.79 – 1.63 (m, 8H), 0.91 (t, $J = 7.5$ Hz, 12H). $^{13}$C NMR (101 MHz, Chloroform-$d$) $\delta$ 135.4, 133.1, 130.9 (d, $J = 26.0$ Hz), 129.3 (d, $J = 1.4$ Hz), 128.5, 91.0, 26.3, 8.7. The signal of the $\alpha$-B-carbon was not observed. $^{19}$F NMR (376 MHz, Chloroform-$d$) $\delta$ 64.50. $^{11}$B NMR (128 MHz, Chloroform-$d$) $\delta$ 29.19. HRMS(ESI): caled for C$_{19}$H$_{28}$BClFO$_4$S $\left[\text{M + H}\right]^+$ 403.1312; found 403.1314.

(Z)-2-(4,4,5,5-tetraethyl-1,3,2-dioxaborolan-2-yl)-2-(o-tolyl)ethene-1-sulfonyl fluoride (4t)

56% (21.4 mg); colorless oil; $^1$H NMR (400 MHz, Chloroform-$d$) $\delta$ 7.27 – 7.13 (m, 4H), 7.03 – 6.97 (m, 1H), 2.19 (s, 3H), 1.78 – 1.61 (m, 8H), 0.88 (t, $J = 7.5$ Hz, 12H). $^{13}$C NMR (101 MHz, Chloroform-$d$) $\delta$ 135.0, 134.0, 131.8 (d, $J = 24.5$ Hz), 129.8, 128.3, 126.4, 125.5, 90.6, 26.3, 19.9, 8.6. The signal of the $\alpha$-B-carbon was not observed. $^{19}$F NMR (376 MHz, Chloroform-$d$) $\delta$ 64.22. $^{11}$B NMR (128 MHz, Chloroform-$d$) $\delta$ 28.76. HRMS(ESI): caled for C$_{19}$H$_{28}$BFO$_4$S $\left[\text{M + H}\right]^+$ 383.1858; found 383.1860.
(Z)-2-(4-methoxyphenyl)-2-(4,4,5,5-tetraethyl-1,3,2-dioxaborolan-2-yl)ethene-1-sulfonyl fluoride (4u)

52% (18.8 mg); yellow solid; $^1$H NMR (400 MHz, Chloroform-$d$) δ 7.41 – 7.34 (m, 2H), 6.99 (s, 1H), 6.95 – 6.88 (m, 2H), 3.83 (s, 3H), 1.81 – 1.64 (m, J = 7.4 Hz, 8H), 0.92 (t, J = 7.4 Hz, 12H). $^{13}$C NMR (101 MHz, Chloroform-$d$) δ 160.7, 130.2 (d, J = 1.7 Hz), 128.6 (d, J = 25.7 Hz), 126.9, 113.6, 90.7, 55.2, 28.8. The signal of the α-B-carbon was not observed. $^{19}$F NMR (376 MHz, Chloroform-$d$) δ 64.19. $^{11}$B NMR (128 MHz, Chloroform-$d$) δ 29.66. HRMS(ESI): caled for C$_{19}$H$_{29}$BFO$_5$S$^+$ [M + H]$^+$ 399.1808; found 399.1805.

(Z)-2-(4-phenoxynaphthyl)-2-(4,4,5,5-tetraethyl-1,3,2-dioxaborolan-2-yl)ethene-1-sulfonyl fluoride (4v)

44% (20.2 mg); colorless oil; $^1$H NMR (400 MHz, Chloroform-$d$) δ 7.41 – 7.32 (m, 4H), 7.20 – 7.11 (m, 1H), 7.07 (dt, J = 7.7, 1.1 Hz, 2H), 7.03 (s, 1H), 7.02 – 6.94 (m, 2H), 1.83 – 1.62 (m, J = 7.4 Hz, 8H), 0.92 (t, J = 7.5 Hz, 12H). $^{13}$C NMR (101 MHz, Chloroform-$d$) δ 158.8, 156.1, 130.1 (d, J = 1.5 Hz), 129.9, 129.4 (d, J = 25.9 Hz), 129.0, 124.0, 119.9, 117.5, 90.8, 26.3, 8.7. The signal of the α-B-carbon was not observed. $^{19}$F NMR (376 MHz, Chloroform-$d$) δ 64.31. $^{11}$B NMR (128 MHz, Chloroform-$d$) δ 29.21. HRMS(ESI): caled for C$_{24}$H$_{31}$BFO$_5$S$^+$ [M + H]$^+$ 461.1964; found 461.1967.

(Z)-2-(naphthalen-2-yl)-2-(4,4,5,5-tetraethyl-1,3,2-dioxaborolan-2-yl)ethene-1-sulfonyl fluoride (4w)

51% (21.3 mg); colorless oil; $^1$H NMR (400 MHz, Chloroform-$d$) δ 7.88 – 7.80 (m, 4H), 7.53 – 7.38 (m, 3H), 7.15 (s, 1H), 1.82 – 1.62 (m, 8H), 0.92 (t, J = 7.4 Hz, 12H). $^{13}$C NMR (101 MHz, Chloroform-$d$) δ 133.4, 132.8, 132.4, 130.5 (d, J = 25.9 Hz), 128.6, 127.8 (d, J = 1.7 Hz), 127.7, 126.9, 126.4, 125.4, 125.3, 90.9, 26.3, 8.7. The signal of the α-B-carbon was not observed. $^{19}$F NMR (376 MHz, Chloroform-$d$) δ 64.46. $^{11}$B
NMR (128 MHz, Chloroform-\(d\)) \(\delta\) 29.26. HRMS(ESI): caleed for C\(_{22}\)H\(_{29}\)BFO\(_4\)S\(_2\) \([\text{M + H}]^+\) 419.1858; found 419.1859.

(Z)-2-(4,4,5,5-tetraethyl-1,3,2-dioxaborolan-2-yl)-2-(thiophen-3-yl)ethene-1-sulfonyle fluoride (4x)

43% (16.0 mg); colorless oil; \(^1\)H NMR (500 MHz, Chloroform-\(d\)) \(\delta\) 7.79 (dd, \(J = 2.9, 1.3\) Hz, 1H), 7.38 (dd, \(J = 5.1, 1.3\) Hz, 1H), 7.33 (dd, \(J = 5.1, 3.0\) Hz, 1H), 6.99 (s, 1H), 1.80 – 1.67 (m, 8H), 0.94 (t, \(J = 7.5\) Hz, 12H). \(^{13}\)C NMR (126 MHz, Chloroform-\(d\)) \(\delta\) 134.5, 129.0, 128.5, 128.0 (d, \(J = 26.1\) Hz), 125.4, 90.8, 26.3, 8.8. The signal of the \(\alpha\)-B-carbon was not observed.

\(^{19}\)F NMR (376 MHz, Chloroform-\(d\)) \(\delta\) 62.81. \(^{11}\)B NMR (128 MHz, Chloroform-\(d\)) \(\delta\) 29.09. HRMS(ESI): caleed for C\(_{16}\)H\(_{25}\)BFO\(_4\)S\(_2\) \([\text{M + H}]^+\) 375.1266; found 375.1264.

4-phenyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butane-1-sulfonyle fluoride (6a)

73% (25.0 mg); white solid; \(^1\)H NMR (400 MHz, Chloroform-\(d\)) \(\delta\) 7.30 (t, \(J = 7.3\) Hz, 2H), 7.25 – 7.12 (m, 3H), 3.63 (ddd, \(J = 14.4, 8.1, 6.0\) Hz, 1H), 3.48 – 3.34 (m, 1H), 2.78 – 2.59 (m, 2H), 2.03 – 1.80 (m, 2H), 1.76 (ddd, \(J = 14.0, 8.1, 5.9\) Hz, 1H), 1.30 (s, 12H). \(^{13}\)C NMR (101 MHz, Chloroform-\(d\)) \(\delta\) 141.2, 128.5, 128.3, 126.1, 84.3, 52.3 (d, \(J = 14.6\) Hz), 34.4, 31.5, 24.8 (d, \(J = 13.0\) Hz). The signal of the \(\alpha\)-B-carbon was not observed. \(^{19}\)F NMR (376 MHz, Chloroform-\(d\)) \(\delta\) 56.00. \(^{11}\)B NMR (128 MHz, Chloroform-\(d\)) \(\delta\) 33.53. HRMS(ESI): caleed for C\(_{16}\)H\(_{25}\)BFO\(_4\)SNa\(_{2}\) \([\text{M + Na}]^+\) 365.1364; found 365.1362.

2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-4-(p-tolyl)butane-1-sulfonyle fluoride (6b)

50% (17.8 mg); white solid; \(^1\)H NMR (400 MHz, Chloroform-\(d\)) \(\delta\) 7.20 – 6.98 (m, 4H), 3.62 (ddd, \(J = 14.4, 8.2, 6.1\) Hz, 1H), 3.42 (ddd, \(J = 14.6, 5.8, 2.9\) Hz, 1H), 2.75 – 2.50 (m, 2H), 2.32 (s, 3H), 1.98 – 1.79 (m, 2H), 1.75 (ddd, \(J = 14.0, 8.1, 5.8\) Hz, 1H), 1.29 (s, 12H). \(^{13}\)C
NMR (101 MHz, Chloroform-d) δ 138.1, 135.6, 129.2, 128.2, 84.3, 52.4 (d, J = 14.9 Hz), 33.9, 31.7, 24.8 (d, J = 13.3 Hz), 21.0. The signal of the α-B-carbon was not observed. ^19F NMR (376 MHz, Chloroform-d) δ 55.88 (d, J = 8.4 Hz). ^11B NMR (128 MHz, Chloroform-d) δ 33.37. HRMS(ESI): caled for C_{17}H_{27}BO_4S^+ [M + H]^+ 357.1702; found 357.1704.

4-(3,5-dimethylphenyl)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butane-1-sulfonyl fluoride (6c)

| 54% (20.0 mg); colorless oil; | ^1H NMR (400 MHz, Chloroform-d) δ 6.99 – 6.71 (m, 3H), 3.62 (ddd, J = 14.5, 8.2, 6.1 Hz, 1H), 3.47 – 3.33 (m, 1H), 2.59 (qdd, J = 13.5, 10.0, 6.3 Hz, 2H), 2.29 (s, 6H), 2.00 – 1.81 (m, 2H), 1.75 (tt, J = 8.1, 5.8 Hz, 1H), 1.28 (s, 12H). |
| 13C NMR (101 MHz, Chloroform-d) δ 141.1, 138.0, 127.8, 126.2, 84.3, 52.4 (d, J = 14.8 Hz), 34.2, 31.6, 24.8 (d, J = 13.0 Hz), 21.2. The signal of the α-B-carbon was not observed. | ^19F NMR (376 MHz, Chloroform-d) δ 55.88 (d, J = 8.9 Hz). ^11B NMR (128 MHz, Chloroform-d) δ 33.79. HRMS(ESI): caled for C_{18}H_{29}BO_4S^+ [M + H]^+ 371.1858; found 371.1856. |

4-((1,1'-biphenyl)-4-yl)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butane-1-sulfonyl fluoride (6d)

| 36% (15.0 mg); colorless oil; | ^1H NMR (400 MHz, Chloroform-d) δ 7.61 – 7.49 (m, 4H), 7.46 – 7.39 (m, 2H), 7.35 – 7.30 (m, 1H), 7.25 (d, J = 8.2 Hz, 2H), 3.64 (ddd, J = 14.2, 8.0, 5.9 Hz, 1H), 3.44 (ddd, J = 14.7, 6.0, 2.9 Hz, 1H), 2.81 – 2.62 (m, 2H), 1.95 (dddd, J = 23.6, 17.3, 13.6, 7.8 Hz, 2H), 1.78 (tt, J = 8.1, 5.9 Hz, 1H), 1.29 (s, 12H). | ^13C NMR (101 MHz, Chloroform-d) δ 141.0, 140.3, 139.2, 128.8, 128.7, 127.3, 127.1, 127.0, 84.4, 52.4 (d, J = 14.8 Hz), 34.0, 31.5, 24.8 (d, J = 12.7 Hz). The signal of the α-B-carbon was not observed. | ^19F NMR (376 MHz, Chloroform-d) δ 56.07 (d, J = 6.3 Hz). ^11B NMR (128 MHz, Chloroform-d) δ 33.74. HRMS(ESI): caled for C_{22}H_{29}BO_4S^+ [M + H]^+ 419.1858; found 419.1859. |
4-(4-(tert-butyl)phenyl)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butane-1-sulfonyl fluoride (6e)

\[
\begin{align*}
\text{Me} & \quad \text{Me} & \quad \text{SO}_2\text{F} \\
\text{B} & \quad \text{O} & \quad \text{O}
\end{align*}
\]

40% (15.9 mg); colorless oil; \(^1\text{H}\) NMR (500 MHz, Chloroform-\(d\)) \(\delta\) 7.33 – 7.30 (m, 2H), 7.12 (d, \(J = 8.3\) Hz, 2H), 3.63 (ddd, \(J = 14.5, 8.3, 6.1\) Hz, 1H), 3.43 (ddd, \(J = 14.7, 5.8, 2.8\) Hz, 1H), 2.74 – 2.56 (m, 2H), 1.98 – 1.82 (m, 2H), 1.76 (tt, \(J = 8.2, 5.8\) Hz, 1H), 1.31 (s, 9H), 1.28 (s, 12H).

\(^{13}\text{C}\) NMR (101 MHz, Chloroform-\(d\)) \(\delta\) 149.0, 138.1, 128.0, 125.4, 84.3, 52.4 (d, \(J = 14.9\) Hz), 34.4, 33.8, 31.5, 31.4, 24.8 (d, \(J = 12.9\) Hz). The signal of the \(\alpha\)-B-carbon was not observed.

\(^{19}\text{F}\) NMR (471 MHz, Chloroform-\(d\)) \(\delta\) 55.84.

\(^{11}\text{B}\) NMR (128 MHz, Chloroform-\(d\)) \(\delta\) 33.68. HRMS(ESI): caled for \(\text{C}_{20}\text{H}_{32}\text{BFO}_4\text{SNa}^+ [\text{M} + \text{Na}]^+ 421.1990\); found 421.1989.

2-cyclohexyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethane-1-sulfonyl fluoride (6f)

\[
\begin{align*}
\text{O} & \quad \text{B} & \quad \text{SO}_2\text{F} \\
\text{Me} & \quad \text{Me} & \quad \text{Me}
\end{align*}
\]

30% (9.6 mg); colorless oil; \(^1\text{H}\) NMR (500 MHz, Chloroform-\(d\)) \(\delta\) 3.65 (ddd, \(J = 14.6, 10.0, 7.2\) Hz, 1H), 3.40 (ddd, \(J = 14.5, 3.9, 2.2\) Hz, 1H), 1.82 – 1.61 (m, 5H), 1.29 (d, \(J = 2.1\) Hz, 12H), 1.17 – 1.05 (m, 3H), 0.97 – 0.85 (m, 4H). \(^{13}\text{C}\) NMR (126 MHz, Chloroform-\(d\)) \(\delta\) 84.2, 51.2 (d, \(J = 15.0\) Hz), 39.3, 32.2, 31.3, 26.5, 26.3 (d, \(J = 13.3\) Hz), 24.9 (d, \(J = 25.5\) Hz). The signal of the \(\alpha\)-B-carbon was not observed. \(^{19}\text{F}\) NMR (471 MHz, Chloroform-\(d\)) \(\delta\) 53.86. \(^{11}\text{B}\) NMR (160 MHz, Chloroform-\(d\)) \(\delta\) 32.62. HRMS(ESI): caled for \(\text{C}_{14}\text{H}_{27}\text{BFO}_4\text{S}^+ [\text{M} + \text{H}]^+ 321.1702\); found 321.1701.

2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexane-1-sulfonyl fluoride (6g)

\[
\begin{align*}
\text{Me} & \quad \text{B} & \quad \text{SO}_2\text{F} \\
\text{Me} & \quad \text{Me}
\end{align*}
\]

70% (20.6 mg); colorless oil; \(^1\text{H}\) NMR (400 MHz, Chloroform-\(d\)) \(\delta\) 3.58 (ddd, \(J = 14.7, 8.3, 6.4\) Hz, 1H), 3.37 (ddd, \(J = 14.7, 5.8, 2.7\) Hz, 1H), 1.75 – 1.62 (m, 1H), 1.61 – 1.52 (m, 2H), 1.38 – 1.29 (m, 4H), 1.25 (s, 12H). 0.89 (t, \(J = 6.9\) Hz, 3H). \(^{13}\text{C}\) NMR (101 MHz, Chloroform-\(d\)) \(\delta\) 84.2, 52.4 (d, \(J = 14.6\) Hz), 30.2, 29.3, 24.7 (d, \(J = 15.5\) Hz), 22.6,
The signal of the \( \alpha \)-B-carbon was not observed. \(^{19}\)F NMR (376 MHz, Chloroform-\( d \)) \( \delta \) 55.35 (d, \( J = 6.1 \) Hz). \(^{11}\)B NMR (128 MHz, Chloroform-\( d \)) \( \delta \) 33.33. HRMS(ESI): caled for \( \text{C}_{12}\text{H}_{25}\text{BFO}_4\text{S}^+ [\text{M} + \text{H}]^+ \) 295.1545; found 295.1543.

6-bromo-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexane-1-sulfonyl fluoride (6h)

\[
\begin{align*}
\text{Br} & \quad \text{SO}_2\text{F} \\
\text{O} & \quad \text{O} \\
\text{B} & \quad \text{B}
\end{align*}
\]

60% (22.3 mg); colorless oil; \(^1\)H NMR (400 MHz, Chloroform-\( d \)) \( \delta \) 3.60 (ddd, \( J = 14.7, 7.6, 5.8 \) Hz, 1H), 3.45 – 3.34 (m, 3H), 2.97 (dd, \( J = 9.7, 8.0, 6.5 \) Hz, 2H), 1.75 – 1.67 (m, 1H), 1.66 – 1.50 (m, 4H), 1.26 (s, 12H). \(^{13}\)C NMR (101 MHz, Chloroform-\( d \)) \( \delta \) 84.4, 52.3 (d, \( J = 14.8 \) Hz), 33.4, 32.4, 28.7, 26.5, 24.8 (d, \( J = 14.0 \) Hz). The signal of the \( \alpha \)-B-carbon was not observed. \(^{19}\)F NMR (376 MHz, Chloroform-\( d \)) \( \delta \) 55.89. \(^{11}\)B NMR (128 MHz, Chloroform-\( d \)) \( \delta \) 33.28. HRMS(ESI): caled for \( \text{C}_{12}\text{H}_{23}\text{BBrFO}_4\text{SNa}^+ [\text{M} + \text{Na}]^+ \) 395.0470; found 395.0471.

3-phenyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propane-1-sulfonyl fluoride (6i)

\[
\begin{align*}
\text{Me} & \quad \text{SO}_2\text{F} \\
\text{O} & \quad \text{O} \\
\text{B} & \quad \text{B}
\end{align*}
\]

63% (20.8 mg); colorless oil; \(^1\)H NMR (400 MHz, Chloroform-\( d \)) \( \delta \) 7.30 (tt, \( J = 7.0, 1.1 \) Hz, 2H), 7.25 – 7.19 (m, 3H), 3.52 (ddd, \( J = 14.5, 8.4, 6.0 \) Hz, 1H), 3.36 – 3.28 (m, 1H), 2.97 (dd, \( J = 14.0, 6.6 \) Hz, 1H), 2.86 – 2.75 (m, 1H), 2.11 – 1.99 (m, 1H), 1.22 (d, \( J = 6.8 \) Hz, 12H). \(^{13}\)C NMR (101 MHz, Chloroform-\( d \)) \( \delta \) 138.7, 129.0, 128.7, 126.8, 84.4, 51.3 (d, \( J = 15.2 \) Hz), 34.8, 24.8 (d, \( J = 8.0 \) Hz). The signal of the \( \alpha \)-B-carbon was not observed. \(^{19}\)F NMR (376 MHz, Chloroform-\( d \)) \( \delta \) 55.73. \(^{11}\)B NMR (128 MHz, Chloroform-\( d \)) \( \delta \) 33.25. HRMS(ESI): caled for \( \text{C}_{15}\text{H}_{22}\text{BFO}_4\text{SNa}^+ [\text{M} + \text{Na}]^+ \) 329.1389; found 329.1390.

2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)dodecane-1-sulfonyl fluoride (6j)

\[
\begin{align*}
\text{Me} & \quad \text{SO}_2\text{F} \\
\text{O} & \quad \text{O} \\
\text{B} & \quad \text{B}
\end{align*}
\]

79% (30.0 mg); colorless oil; \(^1\)H NMR (400 MHz, Chloroform-\( d \)) \( \delta \) 3.58 (ddd, \( J = 14.8, 8.4, 6.4 \) Hz, 1H), 3.37 (ddd, \( J = 14.7, 5.8, 2.6 \) Hz, 1H), 1.75 – 1.64 (m, 1H), 1.26 (s, 29H), 0.88 (t, \( J = 6.8 \) Hz, 4H). \(^{13}\)C NMR (101 MHz, Chloroform-\( d \)) \( \delta \) 84.2, 52.4 (d, \( J = 14.7 \) Hz),
The signal of the α-B-carbon was not observed. $^{19}$F NMR (376 MHz, Chloroform-$d$) δ 55.33 (d, $J = 9.6$ Hz). $^{11}$B NMR (128 MHz, Chloroform-$d$) δ 33.50. HRMS(ESI): caled for C$_{18}$H$_{37}$BFO$_4$S$^+$ [M + H]$^+$ 379.2484; found 379.2487.

**2,4-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butane-1-sulfonyl fluoride (6k)**

38% (15.0 mg); colorless oil; $^1$H NMR (500 MHz, Chloroform-$d$) δ 3.57 (ddd, $J = 14.9$, 8.4, 6.6 Hz, 1H), 3.40 (dq, $J = 14.2$, 2.5 Hz, 1H), 1.68 (dt, $J = 7.4$, 3.5 Hz, 3H), 1.25 (s, 12H), 1.24 (s, 12H), 0.88 – 0.79 (m, 2H). $^{13}$C NMR (126 MHz, Chloroform-$d$) δ 84.2, 83.2, 52.3 (d, $J = 14.7$ Hz), 24.8. The signal of the α-B-carbon was not observed. $^{19}$F NMR (471 MHz, Chloroform-$d$) δ 54.97. $^{11}$B NMR (128 MHz, Chloroform-$d$) δ 34.02. HRMS(ESI): caled for C$_{16}$H$_{32}$BFO$_6$S$^+$ [M + H]$^+$ 393.2084; found 393.2085.

(S)-2-(1R,1's,4S,4'R)-4'-butyl-[1',1'-bi(cyclohexan)]-4-yl)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethane-1-sulfonyl fluoride (6l)

33% (15.1 mg); white solid; $^1$H NMR (500 MHz, Chloroform-$d$) δ 3.64 (ddd, $J = 14.5$, 10.2, 7.2 Hz, 1H), 3.39 (ddd, $J = 14.6$, 4.1, 2.1 Hz, 1H), 1.77 (d, $J = 13.5$ Hz, 4H), 1.73 – 1.68 (m, 2H), 1.63 (dt, $J = 9.8$, 4.6 Hz, 1H), 1.29 (d, $J = 2.1$ Hz, 12H), 1.22 – 1.11 (m, 3H), 1.03 – 0.94 (m, 6H), 0.95 – 0.83 (m, 14H). $^{13}$C NMR (126 MHz, Chloroform-$d$) δ 84.2, 51.3 (d, $J = 15.0$ Hz), 43.3, 43.1, 39.5, 37.9, 37.2, 33.6, 32.4, 31.4, 30.1, 30.0, 29.8, 29.3, 24.9 (d, $J = 24.8$ Hz), 23.0, 14.2. The signal of the α-B-carbon was not observed. $^{19}$F NMR (471 MHz, Chloroform-$d$) δ 53.88. $^{11}$B NMR (160 MHz, Chloroform-$d$) δ 32.83. HRMS(ESI): caled for C$_{24}$H$_{45}$BFO$_4$S$^+$ [M + H]$^+$ 459.3110; found 459.3113.
(2S)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2-((1R,4s)-4'-((p-tolyl)-[1,1']bi(cyclohexan))-4-yl)ethane-1-sulfonyl fluoride (6m)

32% (15.6 mg); white solid; \(^1\)H NMR (400 MHz, Chloroform-\(d\)) \(\delta\) 7.09 (d, \(J = 1.6\) Hz, 4H), 3.63 (ddd, \(J = 14.5, 10.0, 7.1\) Hz, 1H), 3.38 (ddd, \(J = 14.6, 4.2, 2.2\) Hz, 1H), 2.39 (tq, \(J = 7.1, 3.5\) Hz, 1H), 2.31 (s, 3H), 1.96 – 1.72 (m, 10H), 1.27 (s, 12H), 1.19 – 0.99 (m, 10H). \(^{13}\)C NMR (101 MHz, Chloroform-\(d\)) \(\delta\) 144.8, 135.2, 129.0, 126.6, 84.2, 51.2 (d, \(J = 15.0\) Hz), 44.2, 43.0, 42.7, 39.4, 34.6, 32.4, 31.3, 30.3, 30.0, 29.8, 24.9 (d, \(J = 19.6\) Hz), 21.0. The signal of the \(\alpha\)-B-carbon was not observed. \(^{19}\)F NMR (471 MHz, Chloroform-\(d\)) \(\delta\) 53.93. \(^{11}\)B NMR (128 MHz, Chloroform-\(d\)) \(\delta\) 33.20. HRMS(ESI): caled for \(\text{C}_{27}\text{H}_{43}\text{BFO}_4\text{S}^+ [M + H]^+\) 493.2954; found 493.2957.

5-(fluorosulfonyl)-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pentyl benzoate (6n)

35% (14.0 mg); colorless oil; \(^1\)H NMR (400 MHz, Chloroform-\(d\)) \(\delta\) 8.12 – 8.00 (m, 2H), 7.61 – 7.52 (m, 1H), 7.44 (dd, \(J = 8.3, 7.1\) Hz, 2H), 4.33 (t, \(J = 4.9\) Hz, 2H), 3.73 – 3.57 (m, 1H), 3.47 – 3.37 (m, 1H), 1.94 – 1.71 (m, 5H), 1.25 (s, 12H). \(^{13}\)C NMR (126 MHz, Chloroform-\(d\)) \(\delta\) 166.5, 132.9, 130.3, 129.6, 128.4, 84.4, 64.4, 52.3 (d, \(J = 15.0\) Hz), 27.4, 26.2, 24.8 (d, \(J = 14.8\) Hz). The signal of the \(\alpha\)-B-carbon was not observed. \(^{19}\)F NMR (376 MHz, Chloroform-\(d\)) \(\delta\) 56.11. \(^{11}\)B NMR (128 MHz, Chloroform-\(d\)) \(\delta\) 33.37. HRMS(ESI): caled for \(\text{C}_{18}\text{H}_{27}\text{BFO}_4\text{S}^+ [M + H]^+\) 401.1600; found 401.1603.

(E)-2-bromo-2-phenylethene-1-sulfonyl fluoride (7)

76% (10.0 mg); colorless oil; \(^1\)H NMR (500 MHz, Chloroform-\(d\)) \(\delta\) 7.50 – 7.44 (m, 5H), 7.11 (s, 1H). \(^{13}\)C NMR (126 MHz, Chloroform-\(d\)) \(\delta\) 146.0, 135.3, 131.7, 128.5, 128.2, 123.6 (d, \(J = 29.6\) Hz). \(^{19}\)F NMR (471 MHz, Chloroform-\(d\)) \(\delta\) 66.19. HRMS(ESI): caled for \(\text{C}_{9}\text{H}_{6}\text{BrFO}_2\text{SN}^+ [M + Na]^+\) 286.9148; found 286.9145.
(E)-2-chloro-2-phenylethene-1-sulfonyl fluoride (8)

73% (8.0 mg); colorless oil; $^1$H NMR (500 MHz, Chloroform-$d$) δ 7.53 (dq, $J = 6.4$, 1.4 Hz, 3H), 7.51 – 7.44 (m, 2H), 6.90 (s, 1H). $^{13}$C NMR (126 MHz, Chloroform-$d$) δ 155.4, 133.5, 132.0, 128.6, 128.4, 120.4 (d, $J = 31.1$ Hz). $^{19}$F NMR (471 MHz, Chloroform-$d$) δ 67.08.

All data matched that reported in the literature.$^{[10]}$

(Z)-2-phenylethene-1-sulfonyl fluoride (9)

54% (5.0 mg); white solids; $^1$H NMR (400 MHz, Chloroform-$d$) δ 7.60 (dd, $J = 7.6$, 2.0 Hz, 2H), 7.50 – 7.42 (m, 3H), 7.38 (dd, $J = 11.9$, 5.8 Hz, 1H), 6.51 (dd, $J = 11.9$, 2.6 Hz, 1H). $^{13}$C NMR (101 MHz, Chloroform-$d$) δ 146.7, 131.3, 130.1 (d, $J = 1.8$ Hz), 128.7, 120.3 (d, $J = 28.5$ Hz). $^{19}$F NMR (376 MHz, Chloroform-$d$) δ 64.00.

All data matched that reported in the literature.$^{[3]}$

(Z)-2-(3,6-dihydro-2H-pyran-4-yl)-2-phenylethene-1-sulfonyl fluoride (11)

60% (8.1 mg); light yellow solids; $^1$H NMR (400 MHz, Chloroform-$d$) δ 7.47 – 7.40 (m, 3H), 7.24 – 7.17 (m, 2H), 6.46 (s, 1H), 5.84 (s, 1H), 4.24 (d, $J = 2.7$ Hz, 2H), 3.90 (t, $J = 5.5$ Hz, 2H), 2.39 (dddt, $J = 6.7$, 4.0, 2.5, 1.1 Hz, 2H). $^{13}$C NMR (101 MHz, Chloroform-$d$) δ 159.2, 139.4, 133.9, 133.2, 129.3, 128.7, 128.1, 116.7 (d, $J = 27.5$ Hz), 66.1, 63.7, 25.5. $^{19}$F NMR (376 MHz, Chloroform-$d$) δ 68.89. HRMS(ESI): caled for C_{15}H_{19}FO_{3}SNa$^+$ [M + Na]$^+$ 291.0461; found 291.0465.

2,2-diphenylethene-1-sulfonyl fluoride (13)

61% (8.0 mg); white solids; $^1$H NMR (400 MHz, Chloroform-$d$) δ 7.53 – 7.44 (m, 4H), 7.40 (dd, $J = 8.6$, 6.9 Hz, 2H), 7.32 (ddd, $J = 8.7$, 6.9, 1.5 Hz, 4H), 6.84 (s, 1H). $^{13}$C NMR (101 MHz, Chloroform-$d$) δ 161.3 (d, $J = 3.9$ Hz), 138.1 (d, $J = 2.2$ Hz), 135.2, 131.5, 130.2, 129.3, 128.9, 128.8, 128.4, 117.7 (d, $J = 28.1$ Hz). $^{19}$F NMR (376 MHz, Chloroform-$d$) δ 68.08.
All data matched that reported in the literature.\textsuperscript{[3]}

**Benzo[d][1,3]dioxol-5-yl 2,2-diphenylethene-1-sulfonate (14)**

89\% (17.0 mg); Light yellow solids; \textsuperscript{1}H NMR (400 MHz, Chloroform-\textit{d}) \(\delta\) 7.48 – 7.33 (m, 6H), 7.28 – 7.21 (m, 4H), 6.81 (s, 1H), 6.74 (d, \(J = 8.3\) Hz, 1H), 6.71 – 6.61 (m, 2H), 5.98 (s, 2H). \textsuperscript{13}C NMR (101 MHz, Chloroform-\textit{d}) \(\delta\) 158.5, 148.2, 146.5, 143.4, 139.0, 135.7, 130.8, 129.5, 128.8, 128.6, 128.0, 120.4, 115.2, 108.0, 104.6, 102.0. HRMS(ESI): caled for C\textsubscript{21}H\textsubscript{16}O\textsubscript{5}S\textsubscript{Na} \([M + Na]^+\) 403.0610; found 403.0608.

**4-((2,2-diphenylvinyl)sulfonyl)morpholine (15)**

94\% (15.6 mg); White solids; \textsuperscript{1}H NMR (400 MHz, Chloroform-\textit{d}) \(\delta\) 7.43 – 7.36 (m, 5H), 7.35 – 7.31 (m, 3H), 7.27 – 7.22 (m, 2H), 6.63 (s, 1H), 3.89 – 3.50 (m, 4H), 3.35 – 2.84 (m, 4H). \textsuperscript{13}C NMR (101 MHz, Chloroform-\textit{d}) \(\delta\) 155.5, 139.8, 136.4, 130.2, 129.8, 129.1, 128.6, 128.3, 127.9, 121.9, 66.4, 45.5. HRMS(ESI): caled for C\textsubscript{18}H\textsubscript{20}N\textsubscript{O}\textsubscript{3}S \([M + H]^+\) 330.1159; found 330.1160.

**E)-2-(2-methylquinolin-6-yl)-2-phenylethene-1-sulfonyle fluoride (17)**

50\% (8.2 mg); White solids; \textsuperscript{1}H NMR (400 MHz, Chloroform-\textit{d}) \(\delta\) 8.02 (t, \(J = 8.1\) Hz, 2H), 7.72 – 7.61 (m, 2H), 7.57 – 7.47 (m, 3H), 7.41 – 7.32 (m, 3H), 6.97 (s, 1H), 2.77 (s, 3H). \textsuperscript{13}C NMR (126 MHz, Chloroform-\textit{d}) \(\delta\) 161.5, 137.0, 135.1, 135.0, 130.3, 129.6, 129.5, 129.3, 128.5, 128.4, 126.0, 123.2, 120.8, 118.3 (d, \(J = 28.3\) Hz), 115.2, 25.5. \textsuperscript{19}F NMR (471 MHz, Chloroform-\textit{d}) \(\delta\) 68.18. HRMS(ESI): caled for C\textsubscript{18}H\textsubscript{15}FNO\textsubscript{2}S\textsubscript{F} \([M + H]^+\) 328.0802; found 328.0803.
(8R,9S,13S,14S)-13-methyl-17-oxo-7,8,9,11,12,13,14,15,16,17-decahydro-6H-cyclopenta[a]phenanthren-3-yl (E)-2-(2-methylquinolin-6-yl)-2-phenylethene-1-sulfonate (18)

51% (7.4 mg); white solids; \(^1\)H NMR (400 MHz, Chloroform-\(d\)) \(\delta\) 8.00 (t, \(J = 8.4\) Hz, 2H), 7.63 – 7.57 (m, 2H), 7.50 – 7.27 (m, 7H), 7.00 – 6.92 (m, 3H), 2.89 (dd, \(J = 9.1, 4.3\) Hz, 1H), 2.77 (s, 3H), 2.51 (dd, \(J = 18.8, 8.7\) Hz, 1H), 2.39 (d, \(J = 11.9\) Hz, 1H), 2.28 (t, \(J = 10.0\) Hz, 1H), 2.21 – 2.08 (m, 1H), 2.08 – 1.94 (m, 3H), 1.54 (dddd, \(J = 34.4, 27.9, 22.3, 11.5\) Hz, 7H), 0.91 (s, 3H). \(^{13}\)C NMR (101 MHz, Chloroform-\(d\)) \(\delta\) 220.5, 161.0, 147.2, 138.8, 138.6, 136.9, 135.5, 129.6, 129.6, 129.3, 129.0, 128.9, 128.7, 128.5, 128.1, 126.7, 126.2, 123.0, 122.4, 121.6, 119.3, 50.4, 47.9, 44.2, 38.0, 35.8, 31.5, 29.7, 29.4, 26.2, 25.8, 25.5, 21.6, 13.8. HRMS(ESI): caled for C\(_{36}\)H\(_{36}\)N\(_2\)O\(_4\)S\(_2\) \([\text{M} + \text{H}]^+\) 578.2360; found 578.2364.

(E)-2-(9H-fluoren-3-yl)-2-phenylethene-1-sulfonyl fluoride (20)

54% (9.5 mg); white solids; \(^1\)H NMR (400 MHz, Chloroform-\(d\)) \(\delta\) 7.87 – 7.75 (m, 2H), 7.61 – 7.46 (m, 5H), 7.45 – 7.31 (m, 5H), 6.89 (s, 1H), 3.90 (s, 2H). \(^{13}\)C NMR (101 MHz, Chloroform-\(d\)) \(\delta\) 161.6, 145.2, 144.0, 143.7, 140.3, 136.3, 135.5, 130.1, 129.4, 128.4, 128.1, 128.0, 127.1, 125.5, 125.2, 120.7, 129.0, 116.7 (d, \(J = 27.8\) Hz), 36.9. \(^{19}\)F NMR (376 MHz, Chloroform-\(d\)) \(\delta\) 68.69. HRMS(ESI): caled for C\(_{21}\)H\(_{15}\)FO\(_2\)S\(_2\)Na\(^+\) \([\text{M + Na}]^+\) 373.0669; found 373.0666.
(E)-11-((4-((2-(9H-fluoren-3-yl)-2-phenylvinyl)sulfonyl)piperazin-1-yl)-2-chlorodibenzo[b,f][1,4]oxazepine (21)

63% (10.0 mg); white solids; $^1$H NMR (400 MHz, Chloroform-$d$) δ 7.82 – 7.75 (m, 1H), 7.72 (d, $J$ = 8.0 Hz, 1H), 7.58 – 7.51 (m, 1H), 7.48 – 7.29 (m, 9H), 7.28 (d, $J$ = 1.8 Hz, 1H), 7.25 (d, $J$ = 2.6 Hz, 1H), 7.19 (d, $J$ = 8.7 Hz, 1H), 7.14 – 7.06 (m, 3H), 7.01 (td, $J$ = 7.4, 2.0 Hz, 1H), 6.74 (s, 1H), 3.86 (s, 2H), 3.50 (s, 4H), 3.19 (s, 4H). $^{13}$C NMR (101 MHz, Chloroform-$d$) δ 159.4, 158.4, 155.7, 151.7, 144.0, 143.9, 143.6, 140.6, 138.0, 136.8, 132.9, 130.5, 129.9, 128.8, 128.1, 127.6, 127.5, 127.1, 127.1, 125.9, 125.2, 125.0, 124.7, 122.9, 121.7, 120.5, 120.2, 119.9, 47.2, 45.0, 36.9. HRMS(ESI): caled for C$_{38}$H$_{31}$ClN$_3$O$_3$S $^+$ [M + H]$^+$ 644.1769; found 644.1767.

Supplementary Figure 15. $^1$H NMR spectra of product 4a

Supplementary Figure 16. $^{13}$C NMR spectra of product 4a
Supplementary Figure 17. $^{19}$F NMR spectra of product 4a

Supplementary Figure 18. $^{11}$B NMR spectra of product 4a
Supplementary Figure 19. NOESY spectra of product 4a

Supplementary Figure 20. $^1$H NMR spectra of product 4b
Supplementary Figure 21. $^{13}$C NMR spectra of product 4b

Supplementary Figure 22. $^{19}$F NMR spectra of product 4b
Supplementary Figure 23. $^1$H NMR spectra of product 4c

Supplementary Figure 24. $^{13}$C NMR spectra of product 4c
Supplementary Figure 25. $^{19}$F NMR spectra of product 4c

Supplementary Figure 26. $^1$H NMR spectra of product 4d
Supplementary Figure 27. $^{13}$C NMR spectra of product 4d

Supplementary Figure 28. $^{19}$F NMR spectra of product 4d
Supplementary Figure 29. $^1$H NMR spectra of product 4e

Supplementary Figure 30. $^{13}$C NMR spectra of product 4e
Supplementary Figure 31. $^{19}$F NMR spectra of product 4e

Supplementary Figure 32. $^1$H NMR spectra of product 4f
Supplementary Figure 33. $^{13}$C NMR spectra of product 4f

Supplementary Figure 34. $^{19}$F NMR spectra of product 4f
Supplementary Figure 35. $^1$H NMR spectra of product 4g

Supplementary Figure 36. $^{13}$C NMR spectra of product 4g
Supplementary Figure 37. $^{19}$F NMR spectra of product 4g

Supplementary Figure 38. $^1$H NMR spectra of product 4h
Supplementary Figure 39. $^{13}$C NMR spectra of product 4h.

Supplementary Figure 40. $^{19}$F NMR spectra of product 4h.
Supplementary Figure 41. $^1$H NMR spectra of product 4i

Supplementary Figure 42. $^{13}$C NMR spectra of product 4i
Supplementary Figure 43. $^{19}$F NMR spectra of product 4i

Supplementary Figure 44. $^1$H NMR spectra of product 4j
Supplementary Figure 45. $^{13}$C NMR spectra of product 4j

Supplementary Figure 46. $^{19}$F NMR spectra of product 4j
Supplementary Figure 47. $^1$H NMR spectra of product 4k

Supplementary Figure 48. $^{13}$C NMR spectra of product 4k
Supplementary Figure 49. $^{19}$F NMR spectra of product 4k

Supplementary Figure 50. $^1$H NMR spectra of product 4l
Supplementary Figure 51. $^{13}$C NMR spectra of product 4I

Supplementary Figure 52. $^{19}$F NMR spectra of product 4I
Supplementary Figure 53. $^1$H NMR spectra of product 4m

Supplementary Figure 54. $^{13}$C NMR spectra of product 4m
Supplementary Figure 55. $^{19}$F NMR spectra of product 4m

Supplementary Figure 56. $^{11}$B NMR spectra of product 4m
Supplementary Figure 57. NOESY spectra of product 4m

Supplementary Figure 58. $^1$H NMR spectra of product 4n
Supplementary Figure 59. $^{13}$C NMR spectra of product 4n

Supplementary Figure 60. $^{19}$F NMR spectra of product 4n
Supplementary Figure 61. $^1$H NMR spectra of product 4o

Supplementary Figure 62. $^{13}$C NMR spectra of product 4o
Supplementary Figure 63. $^{19}$F NMR spectra of product 4o

Supplementary Figure 64. $^1$H NMR spectra of product 4p
Supplementary Figure 65. $^{13}$C NMR spectra of product 4p

Supplementary Figure 66. $^{19}$F NMR spectra of product 4p
Supplementary Figure 67. $^1$H NMR spectra of product 4q

Supplementary Figure 68. $^{13}$C NMR spectra of product 4q
Supplementary Figure 69. $^{19}$F NMR spectra of product 4q

Supplementary Figure 70. $^1$H NMR spectra of product 4r
Supplementary Figure 71. $^{13}$C NMR spectra of product 4r

Supplementary Figure 72. $^{19}$F NMR spectra of product 4r
Supplementary Figure 73. $^1$H NMR spectra of product 4s

Supplementary Figure 74. $^{13}$C NMR spectra of product 4s
Supplementary Figure 75. $^{19}$F NMR spectra of product 4s

Supplementary Figure 76. $^1$H NMR spectra of product 4t
Supplementary Figure 77. $^{13}$C NMR spectra of product 4t

Supplementary Figure 78. $^{19}$F NMR spectra of product 4t
Supplementary Figure 79. $^1$H NMR spectra of product 4u

Supplementary Figure 80. $^{13}$C NMR spectra of product 4u
Supplementary Figure 81. $^{19}$F NMR spectra of product 4u

Supplementary Figure 82. $^1$H NMR spectra of product 4v
Supplementary Figure 83. $^{13}$C NMR spectra of product 4v

Supplementary Figure 84. $^{19}$F NMR spectra of product 4v
Supplementary Figure 85. $^1$H NMR spectra of product 4w

Supplementary Figure 86. $^{13}$C NMR spectra of product 4w
Supplementary Figure 87. $^{19}$F NMR spectra of product 4w

Supplementary Figure 88. $^1$H NMR spectra of product 4x
Supplementary Figure 89. $^{13}$C NMR spectra of product 4x

Supplementary Figure 90. $^{19}$F NMR spectra of product 4x
Supplementary Figure 91. $^1$H NMR spectra of product $6a$

Supplementary Figure 92. $^{13}$C NMR spectra of product $6a$
Supplementary Figure 93. $^{19}$F NMR spectra of product 6a

Supplementary Figure 94. $^1$H NMR spectra of product 6b
Supplementary Figure 95. $^{13}$C NMR spectra of product 6b

Supplementary Figure 96. $^{19}$F NMR spectra of product 6b
Supplementary Figure 97. $^1$H NMR spectra of product 6c

Supplementary Figure 98. $^{13}$C NMR spectra of product 6c
Supplementary Figure 99. $^{19}\text{F}$ NMR spectra of product 6c

Supplementary Figure 100. $^1\text{H}$ NMR spectra of product 6d
**Supplementary Figure 101.** $^{13}$C NMR spectra of product 6d

**Supplementary Figure 102.** $^{19}$F NMR spectra of product 6d
Supplementary Figure 103. $^1$H NMR spectra of product 6e

Supplementary Figure 104. $^{13}$C NMR spectra of product 6e
Supplementary Figure 105. $^{19}\text{F}$ NMR spectra of product 6e

Supplementary Figure 106. $^1\text{H}$ NMR spectra of product 6f
Supplementary Figure 107. $^{13}$C NMR spectra of product 6f

Supplementary Figure 108. $^{19}$F NMR spectra of product 6f
Supplementary Figure 109. $^1$H NMR spectra of product 6g

Supplementary Figure 110. $^{13}$C NMR spectra of product 6g
Supplementary Figure 111. $^{19}$F NMR spectra of product 6g

Supplementary Figure 112. $^1$H NMR spectra of product 6h
Supplementary Figure 113. $^{13}$C NMR spectra of product 6h

Supplementary Figure 114. $^{19}$F NMR spectra of product 6h
Supplementary Figure 115. $^1$H NMR spectra of product 6i

Supplementary Figure 116. $^{13}$C NMR spectra of product 6i
Supplementary Figure 117. $^{19}$F NMR spectra of product 6i

Supplementary Figure 118. $^1$H NMR spectra of product 6j
Supplementary Figure 119. $^{13}$C NMR spectra of product 6j

Supplementary Figure 120. $^{19}$F NMR spectra of product 6j
Supplementary Figure 121. $^1$H NMR spectra of product 6k

Supplementary Figure 122. $^{13}$C NMR spectra of product 6k
Supplementary Figure 123. $^{19}$F NMR spectra of product 6k

Supplementary Figure 124. $^1$H NMR spectra of product 6l
Supplementary Figure 125. $^{13}$C NMR spectra of product 6l

Supplementary Figure 126. $^{19}$F NMR spectra of product 6l
Supplementary Figure 127. $^1$H NMR spectra of product 6m

Supplementary Figure 128. $^{13}$C NMR spectra of product 6m
Supplementary Figure 129. $^{19}$F NMR spectra of product 6m

Supplementary Figure 130. $^1$H NMR spectra of product 6n
Supplementary Figure 131. $^{13}$C NMR spectra of product 6n

Supplementary Figure 132. $^{19}$F NMR spectra of product 6n
Supplementary Figure 133. $^1$H NMR spectra of product 7

Supplementary Figure 134. $^{13}$C NMR spectra of product 7
Supplementary Figure 135. $^{19}$F NMR spectra of product 7

Supplementary Figure 136. $^1$H NMR spectra of product 8
Supplementary Figure 137. $^{13}$C NMR spectra of product 8

Supplementary Figure 138. $^{19}$F NMR spectra of product 8
Supplementary Figure 139. $^1$H NMR spectra of product 9

Supplementary Figure 140. $^{13}$C NMR spectra of product 9
Supplementary Figure 141. $^{19}$F NMR spectra of product 9

Supplementary Figure 142. $^1$H NMR spectra of product 11
Supplementary Figure 143. $^{13}$C NMR spectra of product 11

Supplementary Figure 144. $^{19}$F NMR spectra of product 11
Supplementary Figure 145. $^1$H NMR spectra of product 13

Supplementary Figure 146. $^{13}$C NMR spectra of product 13
Supplementary Figure 147. $^{19}$F NMR spectra of product 13

Supplementary Figure 148. $^1$H NMR spectra of product 14
Supplementary Figure 149. $^{13}$C NMR spectra of product 14

Supplementary Figure 150. $^1$H NMR spectra of product 15
Supplementary Figure 151. $^{13}$C NMR spectra of product 15

Supplementary Figure 152. $^1$H NMR spectra of product 17
Supplementary Figure 153. $^{13}$C NMR spectra of product 17

Supplementary Figure 154. $^{19}$F NMR spectra of product 17
Supplementary Figure 155. $^1$H NMR spectra of product 18

Supplementary Figure 156. $^{13}$C NMR spectra of product 18
Supplementary Figure 157. $^1$H NMR spectra of product 20

Supplementary Figure 158. $^{13}$C NMR spectra of product 20
Supplementary Figure 159. $^{19}$F NMR spectra of product 20

Supplementary Figure 160. $^1$H NMR spectra of product 21
Supplementary Figure 161. $^{13}$C NMR spectra of product 21