Supplementary Information

A practical fluorosulfonylating platform via photocatalytic imidazolium-based SO$_2$F radical reagent

Zhang & Li et al.
**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). \(^1\)H NMR and \(^1\)C NMR spectra were recorded at 400 MHz or 500 MHz and 100 MHz or 125 MHz spectrometers, respectively. \(^1\)F NMR spectra were recorded at 376 MHz or 470 MHz spectrometers. Chemical shifts are reported as \(\delta\) values relative to internal TMS (\(\delta\) 0.00 for \(^1\)H NMR), chloroform (\(\delta\) 7.26 for \(^1\)H NMR), acetonitrile (\(\delta\) 1.94 for \(^1\)H NMR), chloroform (\(\delta\) 77.00 for \(^1\)C NMR), and acetonitrile (\(\delta\) 118.26 for \(^1\)C 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](image1)

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

![Supplementary Figure 2. Cap with Septa](image2)
II. Synthesis of Starting Materials
Substrates 1j-1u, 1w, 1y-1z, 1aa-1ab were purchased from commercial sources (Alfa, TCI, Energy and Macklin) and used as received.
Substrates 1a-1d were prepared according to the literature.¹
Substrates 2f were prepared according to the literature.²
Substrates 5a-5k were prepared according to the literature.³
Substrates 7a-7l were prepared according to the literature.⁴

III. Synthesis of Sulfonyl fluoride imidazolium salt (2a-2e)

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 ℃. 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 × 3) and dried in vacuo to yield the title compound (2a-2e) as a white solid.

1-(fluorosulfonyl)-3-methyl-2-phenyl-1H-benzo[d]imidazol-3-ium trifluoromethanesulfonate (2a)
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, 131.4, 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.

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

69%; white solid: m.p. 165-166 °C; $^1$H NMR (400 MHz, Acetonitrile-$d_3$) 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). $^{13}$C NMR (101 MHz, Acetonitrile-$d_3$) 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$_4$N$_2$O$_2$S$^+$ [M]$^+$ 359.0472; found 359.0471.

**Supplementary Figure 3.** X-ray crystallography for 2b (CCDC number: 2164689)

2-(2-chlorophenyl)-1-(fluorosulfonyl)-3-methyl-1H-benzo[d]imidazol-3-iumtrifluoromethanesulfonate (2c)
65%; white solid: m.p. 145-146 °C; \(^1\)H NMR (400 MHz, Acetonitrile-\(d_3\)) \(\delta\) 8.23 (dt, \(J = 7.4, 0.9\) Hz, 1H), 8.20 – 8.13 (m, 1H), 8.07 – 7.96 (m, 2H), 7.95 – 7.87 (m, 2H), 7.83 (dd, \(J = 8.3, 1.2\) Hz, 1H), 7.75 (td, \(J = 7.6, 1.2\) Hz, 1H), 4.00 (s, 3H). \(^{13}\)C NMR (101 MHz, Acetonitrile-\(d_3\)) \(\delta\) 150.7, 137.3, 135.2, 133.4, 132.6, 132.2, 131.7, 130.8, 130.5, 129.5, 122.0 (q, \(J = 321.0\) Hz), 120.3, 116.4, 116.0, 35.6. \(^{19}\)F NMR (376 MHz, Acetonitrile-\(d_3\)) \(\delta\) 63.52, -79.24. HRMS(ESI): caled for C\(_{14}\)H\(_{11}\)ClF\(_2\)N\(_2\)O\(_2\)S\(^+\) [M]\(^+\) 325.0208; found 325.0207.

2-(4-fluorophenyl)-1-(fluorosulfonyl)-3-methyl-1H-benz[d]imidazol-3-iumtrifluoromethanesulfonate (2d)

60%; white solid: m.p. 148-149 °C; \(^1\)H NMR (400 MHz, Acetonitrile-\(d_3\)) \(\delta\) 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-\(d_3\)) \(\delta\) 168.4, 165.8, 153.4, 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\(_3\)) \(\delta\) 64.65, -79.30, -104.18– -104.25 (m). HRMS(ESI): caled for C\(_{14}\)H\(_{11}\)F\(_2\)N\(_2\)O\(_2\)S\(^+\) [M]\(^+\) 309.0504; found 309.0505.

1-(fluorosulfonyl)-2-(4-methoxyphenyl)-3-methyl-1H-benz[d]imidazol-3-iumtrifluoromethanesulfonate (2e)

43%; white solid: m.p. 162-163 °C; \(^1\)H NMR (400 MHz, Acetonitrile-\(d_3\)) \(\delta\) 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-\(d_3\)) \(\delta\) 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, CDCl\(_3\)) \(\delta\) 64.72, -79.28. HRMS(ESI): caled for C\(_{15}\)H\(_{14}\)FN\(_2\)O\(_3\)S\(^+\) [M]\(^+\) 321.0704; found 321.0704.

IV. Cyclic Voltammetry Studies for 2a-2e

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-AgNO\(_3\) (0.1 M) in
CH$_3$CN as the reference electrode, tetrabutylammonium tetrafluoroborate (0.1 M) was used as the supporting electrolyte, using Fe$^+/\text{Fe}$ as the internal standard, the scan rate was 0.2 V/s.

**Supplementary Figure 4.** Cyclic voltammograms of 2a
Supplementary Figure 5. Cyclic voltammograms of 2b
Supplementary Figure 6. Cyclic voltammograms of 2c

Supplementary Figure 7. Cyclic voltammograms of 2d

Supplementary Figure 8. Cyclic voltammograms of 2e
V. Optimizations of the Reaction Conditions

Supplementary Table 1: Optimization of solvents[\textsuperscript{a}]

<table>
<thead>
<tr>
<th>Entry</th>
<th>Change of conditions</th>
<th>Yield of 3\textsubscript{a}[\textsuperscript{b}]</th>
<th>E/Z ratio[\textsuperscript{c}]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>None</td>
<td>10%</td>
<td>&gt; 20:1</td>
</tr>
<tr>
<td>2</td>
<td>EA(1mL)</td>
<td>41%</td>
<td>&gt; 20:1</td>
</tr>
<tr>
<td>3</td>
<td>DME(1mL)</td>
<td>45%</td>
<td>&gt; 20:1</td>
</tr>
<tr>
<td>4</td>
<td>NMP(1mL)</td>
<td>n.d.</td>
<td>-</td>
</tr>
<tr>
<td>5</td>
<td>2-Me-THF(1mL)</td>
<td>13.4%</td>
<td>&gt; 20:1</td>
</tr>
<tr>
<td>6</td>
<td>hexane(1mL)</td>
<td>n.d.</td>
<td>-</td>
</tr>
<tr>
<td>7</td>
<td>DMSO(1mL)</td>
<td>n.d.</td>
<td>-</td>
</tr>
<tr>
<td>8</td>
<td>DMF(1mL)</td>
<td>n.d.</td>
<td>-</td>
</tr>
<tr>
<td>9</td>
<td>Acetone</td>
<td>8%</td>
<td>&gt; 20:1</td>
</tr>
<tr>
<td>10</td>
<td>2f instead of 2a</td>
<td>n.d.</td>
<td>-</td>
</tr>
</tbody>
</table>

[\textsuperscript{a}] All reactions were carried out with 1\textsubscript{a} (17.5 mg, 0.10 mmol), 2\textsubscript{a} (0.20 mmol, 2equiv), fac-Ir(ppy)\textsubscript{3} (2 mol\%) in solution (1.0 mL) under Ar and 60 W blue LEDs. [\textsuperscript{b}] Yields determined by GC using dodecane as an internal standard. [\textsuperscript{c}] The E/Z ratio was determined by \textsuperscript{1}H NMR.

Supplementary Table 2: Optimization of additives[\textsuperscript{a}]

[\textsuperscript{a}]
<table>
<thead>
<tr>
<th>Entry</th>
<th>Change of additives</th>
<th>Yield of $3a^{[b]}$</th>
<th>$E/Z$ ratio$^{[c]}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>None</td>
<td>45%</td>
<td>&gt; 20:1</td>
</tr>
<tr>
<td>2</td>
<td>DMAP (2.5 equiv)</td>
<td>n.d.</td>
<td>-</td>
</tr>
<tr>
<td>3</td>
<td>Na$_2$HPO$_4$ (2.5 equiv)</td>
<td>46%</td>
<td>&gt; 20:1</td>
</tr>
<tr>
<td>4</td>
<td>K$_2$HPO$_4$ (2.5 equiv)</td>
<td>27%</td>
<td>&gt; 20:1</td>
</tr>
<tr>
<td>5</td>
<td>Na$_3$PO$_4$ (2.5 equiv)</td>
<td>32%</td>
<td>&gt; 20:1</td>
</tr>
<tr>
<td>6</td>
<td>K$_3$PO$_4$ (2.5 equiv)</td>
<td>27%</td>
<td>&gt; 20:1</td>
</tr>
<tr>
<td>7</td>
<td>KH$_2$PO$_4$ (2.5 equiv)</td>
<td>59%</td>
<td>&gt; 20:1</td>
</tr>
<tr>
<td>8</td>
<td>CsF (2.5 equiv)</td>
<td>n.d.</td>
<td>-</td>
</tr>
<tr>
<td>9</td>
<td>LiCl (2.5 equiv)</td>
<td>n.d.</td>
<td>-</td>
</tr>
<tr>
<td>10</td>
<td>Pyridine (2.5 equiv)</td>
<td>12.5%</td>
<td>&gt; 20:1</td>
</tr>
</tbody>
</table>

$^{[a]}$ All reactions were carried out with $1a$ (17.5 mg, 0.10 mmol), $2a$ (0.20 mmol, 2equiv), $fac$-Ir(ppy)$_3$ (2 mol%), additive (2.5 equiv) in DME (1.0 mL) under Ar and 60 W blue LEDs. $^{[b]}$ Yields determined by GC using dodecane as an internal standard. $^{[c]}$ The $E/Z$ ratio was determined by $^1$H NMR.

**Supplementary Table 3: Optimization of photocatalysts and light sources$^{[a]}$**

![Chemical structure](image)

<table>
<thead>
<tr>
<th>Entry</th>
<th>Change of conditions</th>
<th>Yield of $3a^{[b]}$</th>
<th>$E/Z$ ratio$^{[c]}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>None</td>
<td>59%</td>
<td>&gt; 20:1</td>
</tr>
<tr>
<td>2</td>
<td>4CzIPN</td>
<td>62%</td>
<td>&gt; 20:1</td>
</tr>
<tr>
<td>3</td>
<td>Ir$_2$[dF(CF$_3$)ppy)$_2$(dtbbpy)]PF$_6$</td>
<td>38%</td>
<td>&gt; 20:1</td>
</tr>
<tr>
<td>4</td>
<td>4CzIPN (26 W visible light)</td>
<td>57%</td>
<td>&gt; 20:1</td>
</tr>
</tbody>
</table>

S11
5 4CzIPN (90 W blue LED) 55% > 20:1
6 4CzIPN (30 W blue LED) 56% > 20:1

[a] All reactions were carried out with 1a (17.5 mg, 0.10 mmol), 2a (0.20 mmol, 2equiv), photosensitizer (2 mol%), KH2PO4 (0.20 mmol, 2equiv) in DME (1.0 mL) under Ar and light irradiation. [b] Yields determined by GC using dodecane as an internal standard. [c] The E/Z ratio was determined by 1H NMR.

Supplementary Table 4: Optimization of imidazolium reagents[a]

<table>
<thead>
<tr>
<th>Entry</th>
<th>Change of reagents</th>
<th>Yield of 3a[b]</th>
<th>E/Z ratio[d]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>None</td>
<td>62%</td>
<td>&gt; 20:1</td>
</tr>
<tr>
<td>2</td>
<td>2b</td>
<td>71% (65%)[^e]</td>
<td>&gt; 20:1</td>
</tr>
<tr>
<td>3</td>
<td>2c</td>
<td>58%</td>
<td>&gt; 20:1</td>
</tr>
<tr>
<td>4</td>
<td>2d</td>
<td>64%</td>
<td>&gt; 20:1</td>
</tr>
<tr>
<td>5</td>
<td>2e</td>
<td>16%</td>
<td>&gt; 20:1</td>
</tr>
</tbody>
</table>

[a] All reactions were carried out with 1a (16.0 mg, 0.10 mmol), 2 (0.20 mmol, 2equiv), 4CzIPN (2 mol%), in DME (1.0 mL) under Ar and 60 W blue LEDs. [b] Yields determined by GC using dodecane as an internal standard. [c] Isolated yields. [d] The E/Z ratio was determined by 1H NMR.

Supplementary Table 5: Optimization of Z-alkenylsulfonyl fluoride reaction conditions[a]
<table>
<thead>
<tr>
<th>Entry</th>
<th>Change of conditions</th>
<th>Yield of 4c[^b]</th>
<th>E/Z ratio[^d]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>None</td>
<td>39</td>
<td>0.85:1</td>
</tr>
<tr>
<td>2</td>
<td>2a instead of 2b</td>
<td>20</td>
<td>1.15:1</td>
</tr>
<tr>
<td>3</td>
<td>2c instead of 2b</td>
<td>23</td>
<td>0.81:1</td>
</tr>
<tr>
<td>4</td>
<td>fac-Ir[d-F(p-t-Bu)ppy]_3</td>
<td>18.2</td>
<td>2.43:1</td>
</tr>
<tr>
<td>5</td>
<td>Ru(phen)_3(PF_6)_2</td>
<td>0</td>
<td>-</td>
</tr>
<tr>
<td>6</td>
<td>Fluorescein</td>
<td>0</td>
<td>-</td>
</tr>
<tr>
<td>7</td>
<td>w/o PC</td>
<td>0</td>
<td>-</td>
</tr>
<tr>
<td>8</td>
<td>w/o Light</td>
<td>0</td>
<td>-</td>
</tr>
<tr>
<td>9</td>
<td>30°C</td>
<td>40</td>
<td>0.86:1</td>
</tr>
<tr>
<td>10</td>
<td>40°C</td>
<td>37</td>
<td>0.84:1</td>
</tr>
<tr>
<td>11</td>
<td>50°C</td>
<td>44</td>
<td>0.78:1</td>
</tr>
<tr>
<td>12</td>
<td>50°C, Then Ir[(dF(CF_3)ppy)_2(dtbbpy)]PF_6 in 1.5 mL MeCN was injected to the tube, 12h</td>
<td>50 (41)[^e]</td>
<td>0.72:1</td>
</tr>
<tr>
<td>13</td>
<td>50°C, Then Ir(dFppy)_3 in 1.5 mL MeCN was injected to the tube, 12h</td>
<td>33.3</td>
<td>1.10:1</td>
</tr>
</tbody>
</table>
50°C, Then *fac*-Ir\([d-F(p-t-Bu)ppy]_3\) in 1.5 mL MeCN was injected to the tube, 12h

50°C, Then *fac*-Ir\([(3-tBu-phenyl)-4-tBu-ppy]_3\) in 1.5 mL MeCN was injected to the tube, 12h

50°C, Then Ir\([(bpy)_{2}dtbbpy]\)PF\(_6\) in 1.5 mL MeCN was injected to the tube, 12h

50°C, Then Ru\((\text{phen})_3(\text{PF}_6)_2\) in 1.5 mL MeCN was injected to the tube, 12h

[a] All reactions were carried out with 1n (16.0 mg, 0.10 mmol), 2b (0.20 mmol, 2 equiv), PC (2 mol%), in EA:DME = 4:1 (1.0 mL) under Ar and 60W blue LEDs. [b] Yields determined by GC using dodecane as an internal standard. [c] Isolated yields. [d] The E/Z ratio was determined by \(^1\)H NMR.

**Supplementary Table 6: Optimization of radical hydrofluorosulfonylation reaction**

<table>
<thead>
<tr>
<th>Entry</th>
<th>Change of solvents</th>
<th>Yield of 6a[^{[b]}]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>None</td>
<td>69%</td>
</tr>
<tr>
<td>2</td>
<td>MeCN</td>
<td>0%</td>
</tr>
<tr>
<td>3</td>
<td>EA</td>
<td>18%</td>
</tr>
<tr>
<td>4</td>
<td>DCM</td>
<td>trace</td>
</tr>
<tr>
<td>5</td>
<td>DME</td>
<td>37%</td>
</tr>
<tr>
<td>6</td>
<td>Acetone</td>
<td>22%</td>
</tr>
<tr>
<td>7</td>
<td>DMSO</td>
<td>0%</td>
</tr>
<tr>
<td>8</td>
<td>DMF</td>
<td>0%</td>
</tr>
<tr>
<td>9</td>
<td>MeOH</td>
<td>0%</td>
</tr>
<tr>
<td>10</td>
<td>THF:MeCN = 4:1</td>
<td>35%</td>
</tr>
<tr>
<td>11</td>
<td>2-Methyltetrahydrofuran:MeCN = 4:1</td>
<td>53%</td>
</tr>
<tr>
<td>12</td>
<td>2-Methyltetrahydrofuran:Acetone = 4:1</td>
<td>64%</td>
</tr>
</tbody>
</table>
13 2-Methyltetrahydrofuran:Acetone = 3:2 63%
14 2-Methyltetrahydrofuran:Acetone = 5:1 65%

[a] All reactions were carried out with 5a (0.10 mmol), 2a (0.20 mmol, 2.0 equiv), fac-Ir[d-F-(p-t-Bu)pppy]₃ (2 mol%) and cyclohexa-1,4-diene (1.5 equiv) in solution (1 mL) under Ar and 30 W blue LEDs. [b] Yields determined by GC using dodecane as an internal standard.

Supplementary Table 7: Optimization of photocatalysts and light sources

<table>
<thead>
<tr>
<th>Entry</th>
<th>PC</th>
<th>Light sources</th>
<th>Yield of 6a[b]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>fac-Ir[d-F-(p-t-Bu)pppy]₃</td>
<td>30 W Blue LEDs</td>
<td>69%</td>
</tr>
<tr>
<td>2</td>
<td>Ir{[dF(CF₃)ppy]₂(dtbbpy) }PF₆</td>
<td>30 W Blue LEDs</td>
<td>29%</td>
</tr>
<tr>
<td>3</td>
<td>4CzIPN</td>
<td>30 W Blue LEDs</td>
<td>44%</td>
</tr>
<tr>
<td>4</td>
<td>fac-Ir[d-F-(p-t-Bu)pppy]₃</td>
<td>10 W Blue LEDs</td>
<td>27%</td>
</tr>
<tr>
<td>5</td>
<td>fac-Ir[d-F-(p-t-Bu)pppy]₃</td>
<td>60 W Blue LEDs</td>
<td>72% (68)[c]</td>
</tr>
<tr>
<td>6</td>
<td>4CzIPN</td>
<td>90 W Blue LEDs</td>
<td>67%</td>
</tr>
</tbody>
</table>

[a] All reactions were carried out with 5a (0.10 mmol), 2a (0.20 mmol, 2.0 equiv), PC (2 mol%) and cyclohexa-1,4-diene (1.5 equiv) in 2-methyltetrahydrofuran:acetone = 9:1 (1 mL) under Ar and light irradiation. [b] Yields determined by GC using dodecane as an internal standard. [c] Isolated yields.

Supplementary Table 8: Optimization of radical migration fluorosulfonylation reaction

<table>
<thead>
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<tr>
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S15
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<td>6</td>
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[a] All reactions were carried out with 7a (0.10 mmol), 2a (0.20 mmol, 2.0 equiv), fac-Ir(d-F-(p-t-Bu)ppy)₃ (2 mol%) in DME:EA = 4:1 (1.0 mL) under Ar and 60 W blue LEDs. [b] Isolated yields.
VI. General Procedure for the Synthesis of the Products 3, 4, 6 and 8

General Procedure for the synthesis of product 3
Condition A: Under argon, to a solution of 4CzIPN (2 mol%), KH$_2$PO$_4$ (2.5 equiv) and IMSF reagent 2b (0.2 mmol, 2 equiv.) in dried DME (1 mL) was added corresponding alkenes 1 (0.1 mmol) at room temperature. After that, the tube was exposed to a 60 W blue LEDs about 10 h 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 4
Condition B: Under argon, to a solution of PC 1 (2 mol%), KH$_2$PO$_4$ (2.5 equiv) and IMSF reagent 2b (0.2 mmol, 2 equiv.) in dried EA:DME = 4:1 (1 mL) was added corresponding alkenes 1 (0.1 mmol) at room temperature. After that, the tube was exposed to a 60 W blue LEDs about 12 h, then 1.5 ml of acetonitrile containing Ir{[dF(CF$_3$)ppy]$_2$(dtbbpy)}PF$_6$ (2 mol%) was injected into the reaction tube about 12 h 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 6
Condition C: Under argon, to a solution of fac-Ir[d-F-(p-t-Bu)ppy]$_3$ (2 mol%), 1,4-cyclohexadiene (1.5 equiv) and IMSF reagent 2a or 2b (0.2 mmol, 2 equiv.) in dried 2-Methyltetrahydrofuran : Acetone = 9:1 (1 mL) was added corresponding alkenes 5 (0.1 mmol) at room temperature. After that, the tube was exposed to a 60 W blue LEDs 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 8
Condition D: Under argon, to a solution of fac-Ir[d-F-(p-t-Bu)ppy]$_3$ (2 mol%), and IMSF reagent 2a (0.2 mmol, 2 equiv) in dried EA:DME = 7:3 (1 mL) was added corresponding alkenes 7 (0.1 mmol) at room temperature. After that, the tube was exposed to a 60 W blue LEDs 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 studies and synthetic application

Synthetic application (a):
To a solution of 2-Pyrazolin-5-one 9 (0.2 mmol), NaHCO₃ (1.0 equiv) and DBU (5 mol%) in dried DCM (1 mL) was added corresponding alkenes 3m (0.1 mmol) at room temperature about 24 h 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 product 10 in 50% yield.

\[ \text{3m (0.1 mmol)} + \text{9 (0.2 mmol)} \xrightarrow{\text{NaHCO}_3 (1 \text{ equiv}), \text{DBU (5 mol%)}} \text{10 (50%)} \]

Synthetic application (b):
To a solution of 5,5-dimethylcyclohexane-1,3-dione 11 (0.2 mmol), NEt₃ (1.5 equiv) in dried DMSO (1 mL) was added corresponding alkenes 3m (0.1 mmol) at room temperature about 1 h 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 product 12 in 40% yield.

\[ \text{3m (0.1 mmol)} + \text{11 (0.2 mmol)} \xrightarrow{\text{NEt}_3 (1.5 \text{ equiv})} \text{12 (40%)} \]

Synthetic application (c):
To a solution of Estrone 13 (0.2 mmol), KOH (2.0 equiv) in dried CH₃CN (1 mL) was added corresponding alkenes 3m (0.1 mmol) at 50°C about 12 h 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 product 14 in 60% yield.
Synthetic application (d):
To a solution of Vitamin E \(15\) (0.05 mmol), KOH (2.0 equiv) in dried CH\(_3\)CN (1 mL) was added Lumacator intermediate derivative \(6f\) (0.025 mmol) at 50°C about 12 h 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 product \(16\) in 70% yield.

Mechanistic study (a):

Under argon, to a solution of 4CzIPN (2 mol%), KH\(_2\)PO\(_4\) (2.5 equiv), TEMPO (2 equiv) and IMSF reagent \(2b\) (0.2 mmol, 2 equiv.) in dried DME (1 mL) was added corresponding alkenes \(1a\) (0.1 mmol) at room temperature. After that, the tube was exposed to a 60 W blue LEDs about 10 h until the reaction was completed as monitored by TLC analysis. Subsequently, the reaction mixture was analyzed by GC. GC showed that no major product \(3a\) was formed after addition of 0.2 mmol of TEMPO. In addition, we were fortunate to detect product \(17\) in HRMS (ESI). HRMS (ESI): caled for C\(_9\)H\(_{18}\)FNO\(_3\)SNa\(^+\) [M +Na\(^+\)] 262.0883; found 262.0887.

Mechanistic study (b):
Underargon, to a solution of 4CzIPN (2 mol%), KH$_2$PO$_4$ (2.5 equiv), MgCl$_2$ (0.5 equiv) and IMSF reagent 2b (0.2 mmol, 2 equiv.) in dried DME (1 mL) was added corresponding alkenes 18 (0.1 mmol) at room temperature. After that, the tube was exposed to a 60 W blue LEDs about 10 h until the reaction was completed as monitored by TLC analysis. We obtained the product 19 in an isolated yield of 11%.
VIII. Proposed Mechanism

(a) Proposed Mechanism for Alkenylsulfonyl fluoride reaction

As shown below, the mechanism for photocatalytic alkenylsulfonyl fluoride could be proposed. Starting from the oxidation of the excited state of 4CzIPN* by IMSF reagent 2b, 4CzIPN+ species was generated with imidazole B and fluorosulfonyl radical A, which can undergo addition reactions with alkenes I to produce intermediate C. Then the intermediate C was oxidized by 4CzIPN+ to get intermediate D and regenerate 4CzIPN. The intermediate D underwent hydrogen eliminated to get product E-alkenylsulfonyl fluoride 3 in the presence of a weak base. Under photocatalytic conditions, the product 3 underwent isomerisation to produce Z-alkenylsulfonyl fluoride product 4.

(b) Proposed Mechanism for hydrofluorosulfonylation reaction

As shown below, the mechanism for photocatalytic hydrofluorosulfonylation could be proposed. Starting from the oxidation of the excited state of iridium catalyst Ir(III)* by IMSF reagent 2a, Ir(IV) species was generated with imidazole F and fluorosulfonyl radical A. The addition of SO2F radical and olefin 5 afforded intermediate G followed by hydrogen atom transfer with cyclohexa-1,4-diene H to furnish the product 6. The Ir(IV) species was reduced by intermediate I to regenerate Ir(III) catalyst and to give compound J.

Supplementary Figure 9. Proposed Mechanism for Alkenylsulfonyl fluoride reaction
Supplementary Figure 10. Proposed Mechanism for hydrofluorosulfonylation reaction

(c) Proposed Mechanism for migration fluorosulfonylation reaction
As shown below, the mechanism for photocatalytic migration fluorosulfonylation could be proposed. Initially, the oxidation of the excited state of iridium catalyst Ir(III)* by IMSF reagent 2a, Ir(IV) species was generated with sulfonyl fluoride radical A. The addition of SO₂F radical and olefins 7 afforded the carbon radical intermediate K, which rapidly attacks the heteroarene to generate cyclic nitrogen radical intermediate L. The fast ring opening followed by radical β-cleavage furnished a stabilized radical intermediate M, which is oxidized by Ir(IV) to carbocation intermediate N. Finally, deprotonation of intermediate N afforded the heteroaryl migrated products 8a-8h.

Supplementary Figure 11. Proposed Mechanism for migration fluorosulfonylation reaction
IX. Characteristic Data

(E)-2-(N-methylacetamido)-2-phenylethene-1-sulfonyl fluoride (3a)

65% (16.7 mg); white solid: m.p. 95-96 °C; \(^1\)H NMR (400 MHz, Chloroform-\(d\)) \(\delta\) 7.62 – 7.53 (m, 1H), 7.54 – 7.43 (m, 4H), 6.45 (s, 1H), 3.08 (s, 3H), 2.13 (s, 3H). \(^13\)C NMR (101 MHz, Chloroform-\(d\)) \(\delta\) 171.08, 159.33 (\(J = 5.0\) Hz), 132.24, 132.01, 129.36, 129.05, 113.20 (d, \(J = 30.4\) Hz), 36.83, 23.81. \(^19\)F NMR (376 MHz, Chloroform-\(d\)) \(\delta\) 69.87. HRMS (ESI): caled for C\(_{11}\)H\(_{13}\)FNO\(_3\)S\(^+\) [M + H]\(^+\) 258.0595; found 258.0595.

(E)-2-(N-isopropylacetamido)-2-phenylethene-1-sulfonyl fluoride (3b)

82% (23.5 mg); white solid: m.p. 100-101 °C; \(^1\)H NMR (400 MHz, Chloroform-\(d\)) \(\delta\) 7.62 – 7.44 (m, 5H), 6.34 (s, 1H), 4.37 (hept, \(J = 6.9\) Hz, 1H), 2.16 (s, 3H), 1.16 (s, 3H), 1.14 (s, 3H). \(^13\)C NMR (101 MHz, Chloroform-\(d\)) \(\delta\) 169.7, 158.1 (\(J = 5.7\) Hz), 132.9, 132.6, 129.9, 128.8, 117.6 (d, \(J = 29.7\) Hz), 50.8, 24.2, 20.6. \(^19\)F NMR (376 MHz, Chloroform-\(d\)) \(\delta\) 67.54. HRMS (ESI): caled for C\(_{13}\)H\(_{17}\)FNO\(_3\)S\(^+\) [M + H]\(^+\) 286.0908; found 286.0907.

(E)-2-(N-benzylacetamido)-2-phenylethene-1-sulfonyl fluoride (3c)

40% (13.2 mg); white solid: m.p. 103-104 °C; \(^1\)H NMR (400 MHz, Chloroform-\(d\)) \(\delta\) 7.62 – 7.53 (m, 1H), 7.48 (ddd, \(J = 8.0, 6.6, 1.2\) Hz, 2H), 7.43 – 7.38 (m, 2H), 7.35 – 7.28 (m, 3H), 7.12 (dd, \(J = 7.8, 1.8\) Hz, 2H), 6.26 (s, 1H), 4.68 (s, 2H), 2.20 (s, 4H). \(^13\)C NMR (101 MHz, Chloroform-\(d\)) \(\delta\) 170.7, 158.3 (d, \(J = 5.2\) Hz), 135.9, 132.4, 131.7, 129.6, 129.0, 128.9, 128.1, 128.0, 115.5 (d, \(J = 30.0\) Hz), 51.4, 23.6. \(^19\)F NMR \(^19\)F NMR (376 MHz, Chloroform-\(d\)) \(\delta\) 69.01. HRMS (ESI): caled for C\(_{17}\)H\(_{17}\)FNO\(_3\)S\(^+\) [M + H]\(^+\) 334.0908; found 334.0908.

(E)-2-(N-(2-methylbenzyl)acetamido)-2-phenylethene-1-sulfonyl fluoride (3d)
47% (16.5 mg); white solid: m.p. 114-115 °C; \( ^1H \) NMR (400 MHz, Chloroform-\( d \)) \( \delta \) 7.60 – 7.52 (m, 1H), 7.46 (dd, \( J = 8.5, 7.0 \) Hz, 2H), 7.39 – 7.32 (m, 2H), 7.24 – 7.10 (m, 3H), 6.92 (dd, \( J = 6.8, 2.2 \) Hz, 1H), 6.37 (s, 1H), 4.76 (s, 2H), 2.19 (s, 3H), 2.09 (s, 3H).

\( ^{13}C \) NMR (101 MHz, Chloroform-\( d \)) \( \delta \) 170.8, 158.8 (d, \( J = 5.1 \) Hz), 135.6, 133.5, 132.3, 131.8, 130.8, 129.5, 128.9, 127.9, 127.1, 126.4, 114.7 (d, \( J = 30.1 \) Hz), 49.7, 23.9, 19.0.

\( ^{19}F \) NMR (376 MHz, Chloroform-\( d \)) \( \delta \) 69.47. HRMS (ESI): caled for C\(_{18}\)H\(_{19}\)FNO\(_3\)S\(^+\) [M + H]\(^+\) 348.1064; found 348.1064.

**2,2-diphenylethene-1-sulfonyl fluoride (3e)**

82% (21.5 mg); white solid: m.p. 77-78 °C; \( ^1H \) NMR (400 MHz, Chloroform-\( d \)) \( \delta \) 7.52 – 7.42 (m, 4H), 7.39 (t, \( J = 7.7 \) Hz, 2H), 7.34 – 7.28 (m, 4H), 6.83 (s, 1H). \( ^{13}C \) NMR (101 MHz, Chloroform-\( d \)) \( \delta \) 161.3 (d, \( J = 3.7 \) Hz), 138.1 (d, \( J = 2.1 \) Hz), 135.2, 131.5, 130.2, 129.3, 128.9, 128.4, 117.7 (d, \( J = 28.1 \) Hz). \( ^{19}F \) NMR (376 MHz, Chloroform-\( d \)) \( \delta \) 68.15. HRMS (ESI): caled for C\(_{14}\)H\(_{12}\)FO\(_2\)S\(^+\) [M + H]\(^+\) 263.0537; found 263.0537.

**2,2-di-p-tolylethene-1-sulfonyl fluoride (3f)**

72% (21.0 mg); white solid: m.p. 82-83 °C; \( ^1H \) NMR (400 MHz, Chloroform-\( d \)) \( \delta \) 7.27 (s, 1H), 7.25 (s, 1H), 7.21 (d, \( J = 10.3 \) Hz, 6H), 2.43 (s, 3H), 2.40 (s, 3H). \( ^{13}C \) NMR (101 MHz, Chloroform-\( d \)) \( \delta \) 161.6 (d, \( J = 3.7 \) Hz), 142.1, 140.4, 135.5 (d, \( J = 2.2 \) Hz), 132.4, 129.5, 129.4, 129.0, 129.0, 116.0 (d, \( J = 27.6 \) Hz), 21.5, 21.4. \( ^{19}F \) NMR (376 MHz, Chloroform-\( d \)) \( \delta \) 68.54. HRMS (ESI): caled for C\(_{16}\)H\(_{16}\)FO\(_2\)S\(^+\) [M + H]\(^+\) 291.0850; found 291.0850.

**2,2-bis(4-fluorophenyl)ethene-1-sulfonyl fluoride (3g)**
74% (22.0 mg); white solid: m.p. 86-87 °C; $^1$H NMR (400 MHz, Chloroform-$d$) $\delta$ 7.31 (ddd, $J = 9.0, 5.3, 3.9$ Hz, 4H), 7.21 – 7.05 (m, 4H), 6.78 (s, 1H). $^{13}$C NMR (101 MHz, Chloroform-$d$) $\delta$ 166.1, 165.2, 163.5, 162.7, 159.0 (d, $J = 4.1$ Hz), 134.1, 131.5 (d, $J = 8.2$ Hz), 131.0 (d, $J = 8.9$ Hz), 117.7 (d, $J = 28.4$ Hz), 116.0 (dd, $J = 43.1, 21.9$ Hz). $^{19}$F NMR (376 MHz, Chloroform-$d$) $\delta$ 68.16, -107.36 (td, $J = 8.6, 3.9$ Hz), -109.34 (tt, $J = 8.6, 5.3$ Hz). HRMS (ESI): caled for C$_{14}$H$_{10}$F$_3$O$_2$S$^+$ [M + H]$^+$ 299.0348; found 299.0349.

2-(thiophen-2-yl)ethyl 3-(fluorosulfonyl)-2-phenylacrylate (3h)

32% (E/Z = 1:1) (11.0 mg); yellow oil; $^1$H NMR (400 MHz, Chloroform-$d$), (E/Z mixture of isomer), $\delta$ 7.57 – 7.39 (m, 4H), 7.31 (dt, $J = 6.8, 1.5$ Hz, 1H), 7.17 (ddd, $J = 6.7, 5.1, 1.3$ Hz, 1H), 7.01 – 6.84 (m, 1H), 6.81 – 6.68 (m, 1H), 4.63 – 4.46 (m, 2H), 3.31 – 3.19 (m, 2H). $^{13}$C NMR (101 MHz, Chloroform-$d$), (E/Z mixture of isomer), $\delta$ 164.0, 151.8, 148.1, 139.0, 138.8, 132.4, 130.8, 130.4, 130.1, 130.0 (d, $J = 31.9$ Hz), 129.5, 128.8, 128.3, 127.1, 127.0, 117.6 (d, $J = 30.8$ Hz), 67.2, 67.0, 29.0, 28.8. $^{19}$F NMR (376 MHz, Chloroform-$d$), (E/Z mixture of isomer), $\delta$ 66.05, 65.87. HRMS (ESI): caled for C$_{15}$H$_{13}$FO$_4$S$_2$Na$^+$ [M + Na]$^+$ 363.0131; found 363.0130.

penty (E)-3-(fluorosulfonyl)-2-phenylacrylate (3i)

53% (16.0 mg); colorless oil; $^1$H NMR (500 MHz, Chloroform-$d$) $\delta$ 7.50 – 7.42 (m, 4H), 7.38 – 7.32 (m, 2H), 4.26 (t, $J = 6.7$ Hz, 2H), 1.68 (p, $J = 6.8$ Hz, 2H), 1.39 – 1.14 (m, 4H), 0.90 (t, $J = 6.9$ Hz, 3H). $^{13}$C NMR (126 MHz, Chloroform-$d$) $\delta$ 163.8 (d, $J = 2.8$ Hz), 148.5 (d, $J = 4.7$ Hz), 130.3, 130.3, 129.5 (d, $J = 31.5$ Hz), 128.7, 128.2, 67.4, 28.0, 27.8, 22.1, 13.9. $^{19}$F NMR (471 MHz, Chloroform-$d$) $\delta$ 65.92. HRMS (ESI): caled for C$_{14}$H$_{17}$FNO$_4$SNa$^+$ [M + Na]$^+$ 323.0724; found 323.0721.
(E)-1,2-diphenylethene-1-sulfonyl fluoride (3j)

\[
\begin{align*}
\text{SO}_2\text{F} & \quad 23\% \ (6.0 \ mg); \ \text{white solid: m.p. 107-108 °C; } ^1\text{H NMR (400 MHz, Chloroform-}d) \ \delta 7.94 (s, 1H), 7.59 – 7.46 (m, 3H), 7.43 (dd, } J = 7.6, 2.0 \ 	ext{Hz, 2H}), 7.38 – 7.30 (m, 1H), 7.23 (t, } J = 7.8 \ 	ext{Hz, 2H}), 7.11 (d, } J = 7.2 \ 	ext{Hz, 2H). } ^{13}\text{C NMR (126 MHz, Chloroform-}d) \ \delta 143.3 (d, } J = 2.2 \ 	ext{Hz), 133.9 (d, } J = 22.5 \ 	ext{Hz), 131.5, 131.3, 131.1, 130.4, 130.3, 129.6, 129.4, 128.8. } ^{19}\text{F NMR (376 MHz, Chloroform-}d) \ \delta 53.03. \ 
\text{HRMS (ESI): caled for C}_{14}\text{H}_{11}\text{FO}_2\text{SNa}^+ [M + Na]^+ 285.0356; found 285.0355. 
\end{align*}
\]

(E)-1-phenylprop-1-ene-2-sulfonyl fluoride (3k)

\[
\begin{align*}
\text{SO}_2\text{F} & \quad 30\% \ (6.0 \ mg); \ \text{white solid: m.p. 50-51 °C; } ^1\text{H NMR (500 MHz, Chloroform-}d) \ \delta 7.78 (s, 1H), 7.51 – 7.41 (m, 5H), 2.40 (s, 3H). \ \text{13C NMR (126 MHz, Chloroform-}d) \ \delta 142.2 (d, } J = 2.7 \ 	ext{Hz), 132.3, 130.7 (d, } J = 21.4 \ 	ext{Hz) 130.5, 129.9, 129.0, 13.7. } ^{19}\text{F NMR (471 MHz, Chloroform-}d) \ \delta 50.53. \ 
\text{HRMS (ESI): caled for C}_{9}\text{H}_{10}\text{FO}_2\text{S}^+ [M + H]^+ 201.0380; found 201.0381. 
\end{align*}
\]

(E)-2-phenylprop-1-ene-1-sulfonyl fluoride (3l)

\[
\begin{align*}
\text{SO}_2\text{F} & \quad 69\% \ (13.7 \ mg); \ \text{white solid: m.p. 55-56 °C; } ^1\text{H NMR (500 MHz, Chloroform-}d) \ \delta 7.55 – 7.43 (m, 5H), 6.62 (s, 1H), 2.64 (s, 3H). \ \text{13C NMR (126 MHz, Chloroform-}d) \ \delta 160.1 (d, } J = 2.4 \ 	ext{Hz), 138.7, 131.0, 129.1, 126.5, 118.3 (d, } J = 25.5 \ 	ext{Hz), 18.59. } ^{19}\text{F NMR (471 MHz, Chloroform-}d) \ \delta 66.09. \ 
\text{HRMS (ESI): caled for C}_{9}\text{H}_{10}\text{FO}_2\text{S}^+ [M + H]^+ 201.0380; found 201.0382. 
\end{align*}
\]

(E)-2-phenylethene-1-sulfonyl fluoride (3m)

\[
\begin{align*}
\text{SO}_2\text{F} & \quad 81\% \ (15.1 \ mg); \ \text{white solid: m.p. 86-87 °C; } ^1\text{H NMR (400 MHz, Chloroform-}d) \ \delta 7.82 (d, } J = 15.6 \ 	ext{Hz, 1H), 7.59 – 7.43 (m, 5H), 6.88 (d, } J = 15.5 \ 	ext{Hz, 1H). } ^{13}\text{C NMR (101 MHz, Chloroform-}d) \ \delta 148.9 (d, } J = 2.7 \ 	ext{Hz), } 
\end{align*}
\]
132.7, 131.0, 129.4, 129.1, 117.9 (d, J = 28.1 Hz). $^{19}$F NMR (376 MHz, Chloroform-$d$) δ 62.30. HRMS (ESI): caled for C$_8$H$_8$FO$_2$S$^+$ [M + H]$^+$ 187.0224; found 187.0231.

(E)-2-(4-(tert-butyl)phenyl)ethene-1-sulfonyl fluoride (3n)

\[
\text{SO}_2F
\]

82% (19.1 mg); white solid: m.p. 46-47 °C; $^1$H NMR (400 MHz, Chloroform-$d$) δ 7.79 (d, J = 16.7 Hz, 1H), 7.49 (s, 4H), 6.82 (d, J = 15.5 Hz, 1H), 1.34 (s, 9H). $^{13}$C NMR (101 MHz, Chloroform-$d$) δ 156.71, 148.83 (d, J = 2.7 Hz), 129.0, 128.2, 126.4, 116.7 (d, J = 27.7 Hz), 35.2, 31.0. $^{19}$F NMR (376 MHz, Chloroform-$d$) δ 62.39, -104.98. HRMS (ESI): caled for C$_{12}$H$_{16}$FO$_2$S$^+$ [M + H]$^+$ 243.0850; found 243.0850.

(E)-2-(4-fluorophenyl)ethene-1-sulfonyl fluoride (3o)

\[
\text{SO}_2F
\]

64% (13 mg); white solid: m.p. 79-80 °C; $^1$H NMR (400 MHz, Chloroform-$d$) δ 7.78 (d, J = 15.5 Hz, 1H), 7.67 – 7.51 (m, 2H), 7.17 (t, J = 8.5 Hz, 2H), 6.81 (d, J = 15.5 Hz, 1H). $^{13}$C NMR (101 MHz, Chloroform-$d$) δ 165.2 (d, J = 255.6 Hz), 147.5 (d, J = 2.7 Hz), 131.3 (d, J = 9.1 Hz), 127.3 (d, J = 3.6 Hz), 117.7 (dd, J = 28.3, 2.6 Hz), 116.8 (d, J = 22.3 Hz). $^{19}$F NMR $^{19}$F NMR (376 MHz, Chloroform-$d$) δ 62.39, -104.98. HRMS (ESI): caled for C$_8$H$_7$F$_2$O$_2$S$^+$ [M + H]$^+$ 205.0130; found 205.0130.

(E)-2-(4-chlorophenyl)ethene-1-sulfonyl fluoride (3p)

\[
\text{Cl}
\]

82% (18.1 mg); white solid: m.p. 114-115 °C; $^1$H NMR (400 MHz, Chloroform-$d$) δ 7.77 (d, J = 15.5 Hz, 1H), 7.48 (q, J = 8.7 Hz, 4H), 6.86 (d, J = 15.5 Hz, 1H). $^{13}$C NMR (101 MHz, Chloroform-$d$) δ 147.4 (d, J = 2.8 Hz), 138.9, 130.2, 129.8, 129.4, 118.5 (d, J = 28.4 Hz). $^{19}$F NMR (376 MHz, Chloroform-$d$) δ 62.33. HRMS (ESI): caled for C$_8$H$_7$ClFO$_2$S$^+$ [M + H]$^+$ 220.9834; found 220.9832.

(E)-2-(m-tolyl)ethene-1-sulfonyl fluoride (3q)

S27
67% (12.4 mg); white solid: m.p. 32-33 °C; $^1$H NMR (400 MHz, Chloroform-$d$) δ 7.78 (d, $J = 15.6$ Hz, 1H), 7.41 – 7.30 (m, 4H), 6.85 (d, $J = 15.5$ Hz, 1H), 2.40 (s, 3H). $^{13}$C NMR (101 MHz, Chloroform-$d$) δ 149.1 (d, $J = 2.8$ Hz), 139.3, 133.5, 130.9, 129.6, 129.3, 126.3, 117.6 (d, $J = 28.0$ Hz), 21.3. $^{19}$F NMR (376 MHz, Chloroform-$d$) δ 62.35. HRMS (ESI): caled for C$_9$H$_{10}$FO$_2$S$^+$ [M + H]$^+$ 201.0380; found 201.0379.

(E)-2-(2,6-dimethylphenyl)ethene-1-sulfonyl fluoride (3r)

70% (15.0 mg); slight yellow oil; $^1$H NMR (400 MHz, Chloroform-$d$) δ 7.79 (d, $J = 15.5$ Hz, 1H), 7.49 (s, 3H), 6.82 (d, $J = 15.5$ Hz, 1H), 1.34 (s, 6H). $^{13}$C NMR (101 MHz, Chloroform-$d$) δ 156.7, 148.8 (d, $J = 2.6$ Hz), 129.0, 128.2, 126.4, 116.7 (d, $J = 27.7$ Hz), 31.0. $^{19}$F NMR (376 MHz, Chloroform-$d$) δ 62.58. HRMS (ESI): caled for C$_{10}$H$_{12}$FO$_2$S$^+$ [M + H]$^+$ 215.0537; found 215.0539.

3,4-dihydronaphthalene-2-sulfonyl fluoride (3s)

35% (35.5 mg); colorless oil; $^1$H NMR (400 MHz, Chloroform-$d$) δ 7.62 (s, 1H), 7.38 (dt, $J = 7.4$, 4.3 Hz, 1H), 7.29 (d, $J = 6.2$ Hz, 2H), 7.23 (d, $J = 8.3$ Hz, 1H), 3.05 ((t, $J = 8.0$ Hz, 2H), 2.79 (t, $J = 8.0$ Hz, 2H). $^{13}$C NMR (101 MHz, Chloroform-$d$) δ 140.20 (d, $J = 3.0$ Hz), 136.03, 131.79, 130.30 (d, $J = 25.0$ Hz), 129.77, 129.67, 128.15, 127.47, 27.20, 21.98. $^{19}$F NMR (376 MHz, Chloroform-$d$) δ 54.17. HRMS (ESI): caled for C$_{10}$H$_{10}$FO$_2$S$^+$ [M + H]$^+$ 213.0380; found 213.0381.

(E)-2-(thiophen-2-yl)ethene-1-sulfonyl fluoride (3t)

65% (12.5 mg); white solid: m.p. 64-65 °C; $^1$H NMR (400 MHz, Chloroform-$d$) δ 7.79 (d, $J = 16.6$ Hz, 1H), 7.73 (d, $J = 2.9$ Hz, 1H), 7.44 (dd, $J = 5.2$, 2.9 Hz, 1H), 7.30 (d, $J = 5.1$ Hz, 1H), 6.69 (d, $J = 15.4$ Hz, 1H). $^{13}$C NMR (101 MHz, Chloroform-$d$) δ 142.0 (d, $J = 2.7$ Hz), 134.0, 132.5, 128.3, 125.0, 124.0, 120.0.
117.1 (d, J = 27.9 Hz). $^{19}$F NMR (376 MHz, Chloroform-$d$) δ 62.86. HRMS (ESI): caled for C$_6$H$_6$FO$_2$S$_2^+$ [M + H]$^+$ 192.9788; found 192.9786.

**((E)-2-(pyridin-2-yl)ethene-1-sulfonyl fluoride (3u))**

![Chemical structure of (E)-2-(pyridin-2-yl)ethene-1-sulfonyl fluoride](image)

53% (11.6 mg); yellow solid: m.p. 48-49 °C; $^1$H NMR (500 MHz, Chloroform-$d$) δ 8.73 (d, J = 7.2 Hz, 1H), 7.83 (td, J = 7.7, 1.8 Hz, 1H), 7.80 (d, J = 16.1 Hz, 1H), 7.55 (d, J = 17.1 Hz, 1H), 7.49 (d, J = 7.7 Hz, 1H), 7.43 (dd, J = 7.7, 4.7 Hz, 1H). $^{13}$C NMR (126 MHz, Chloroform-$d$) δ 150.7, 149.4, 146.7 (d, J = 3.3 Hz), 137.3, 126.4, 126.2, 122.7 (d, J = 28.9 Hz). $^{19}$F NMR (471 MHz, Chloroform-$d$) δ 61.59. HRMS (ESI): caled for C$_7$H$_7$FNO$_2$S$^+$ [M + H]$^+$ 188.0176; found 188.0176.

**Phenethyl (E)-4-(2-(fluorosulfonyl)vinyl)benzoate (3v)**

![Chemical structure of Phenethyl (E)-4-(2-(fluorosulfonyl)vinyl)benzoate](image)

33% (11.0 mg); white solid: m.p. 92-93 °C; $^1$H NMR (400 MHz, Chloroform-$d$) δ 8.13 – 8.04 (m, 2H), 7.84 (d, J = 15.6 Hz, 1H), 7.65 – 7.58 (m, 2H), 7.38 – 7.21 (m, 4H), 6.96 (dd, J = 15.6, 2.5 Hz, 1H), 4.57 (t, J = 7.0 Hz, 2H), 3.10 (t, J = 6.9 Hz, 2H). $^{13}$C NMR (101 MHz, Chloroform-$d$) δ 165.3, 147.3 (d, J = 2.8 Hz), 137.6, 134.8, 133.6, 130.4, 128.9, 128.9, 128.6, 126.7, 120.3 (d, J = 28.8 Hz), 66.0, 35.1. $^{19}$F NMR (376 MHz, Chloroform-$d$) δ 62.10. HRMS (ESI): caled for C$_{17}$H$_{15}$FO$_4$SNa$^+$ [M + Na]$^+$ 357.0567; found 357.0567.

**(2R,8R,9R,10S,13S,14R,17S)-10,13-dimethyl-17-((S)-6-methylheptan-2-yl)-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthren-2-yl 4-((E)-2-(fluorosulfonyl)vinyl)benzoate (3w)**

![Chemical structure of (2R,8R,9R,10S,13S,14R,17S)-10,13-dimethyl-17-((S)-6-methylheptan-2-yl)-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthren-2-yl 4-((E)-2-(fluorosulfonyl)vinyl)benzoate](image)

42% (25.0 mg); white solid: m.p. 176-177 °C; $^1$H NMR (400 MHz, Chloroform-$d$) δ 8.13 (d, J = 8.4 Hz, 2H), 7.84
(E)-2-((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)ethene-1-sulfonyl fluoride (3x)

33% (12.0 mg); white solid: m.p. 81-82 °C; \(^1\)H NMR (500 MHz, Chloroform-\(d\)) \(\delta\) 7.76 (d, \(J = 15.5\) Hz, 1H), 7.39 (d, \(J = 8.2\) Hz, 1H), 7.34 (d, \(J = 10.1\) Hz, 1H), 7.28 (s, 1H), 2.98 – 2.87 (m, 2H), 2.53 (dd, \(J = 18.9, 9.4\) Hz, 1H), 2.47 – 2.41 (m, 1H), 2.38 – 2.32 (m, 1H), 2.25 – 2.09 (m, 1H), 2.12 – 2.03 (m, 2H), 2.00 (dt, \(J = 12.6, 2.8\) Hz, 1H), 1.68 – 1.61 (m, 2H), 1.57 – 1.45 (m, 4H), 0.93 (s, 3H). \(^{13}\)C NMR (126 MHz, Chloroform-\(d\)) \(\delta\) 220.4, 146.98 (d, \(J = 3.8\) Hz), 145.3, 131.25, 131.06, 129.8, 128.9, 128.5, 126.5, 126.4, 116.9, 50.5, 47.9, 44.7, 37.8, 35.8, 31.5, 29.2, 26.1, 25.5, 21.6, 13.8. \(^{19}\)F NMR (471 MHz, Chloroform-\(d\)) \(\delta\) 62.55. HRMS (ESI): caled for C\(_{36}\)H\(_{52}\)FO\(_4\)S\(^+\) [M + H]\(^+\) 599.3565; found 599.3617.

(Z)-2-phenylethene-1-sulfonyl fluoride (4a)

42% (7.8 mg); white solid: m.p. 56-57 °C; \(^1\)H NMR (400 MHz, Chloroform-\(d\)) \(\delta\) 7.65 – 7.56 (m, 2H), 7.51 – 7.41 (m, 3H), 7.39 (dd, \(J = 11.9, 5.8\) Hz, 1H), 6.51 (dd, \(J = 11.9, 2.6\) Hz, 1H). \(^{13}\)C NMR (101 MHz, Chloroform-\(d\)) \(\delta\) 146.68 (d, \(J = 3.8\) Hz), 131.25, 131.06, 130.05 (d, \(J = 1.7\) Hz), 128.69, 120.27 (d,
$J = 28.6 \text{ Hz}$). $^{19}$F NMR (376 MHz, Chloroform-$d$) δ 64.00; HRMS (ESI): caled for C$_8$H$_7$FO$_2$Na$^+$ [M + Na]$^+$ 209.0043; found 209.0039.

(Z)-2-(m-tolyl)ethene-1-sulfonyl fluoride (4b)

\[
\begin{align*}
\text{45\% (9.0 mg); slight yellow solid: m.p. 47-48 \degree C; } & \text{ \textit{^1H NMR (400 MHz, Chloroform-$d$) } \delta 7.42 (d, J = 7.6 \text{ Hz, 1H}), 7.39 – 7.31 (m, 3H), 7.28 (d, J = 7.7 \text{ Hz, 1H}), 6.48 (dd, J = 11.9, 2.6 \text{ Hz, 1H}), 2.39 (s, 3H). } \\
& \text{\textit{^13C NMR (101 MHz, Chloroform-$d$) } \delta 146.9 \text{ (d, } J = 3.9 \text{ Hz), 138.5, 132.1, 131.0, 130.7 (d, J = 1.6 Hz), 128.6, 127.2 (d, } J = 1.8 \text{ Hz), 120.0 (d, } J = 28.7 \text{ Hz), 21.3. } \\
& \text{\textit{^19F NMR (376 MHz, Chloroform-$d$) } \delta 63.98. } \\
& \text{HRMS (ESI): caled for C$_9$H$_{10}$FO$_2$S$^+$ [M + H]$^+$ 201.0380; found 201.0381.}
\end{align*}
\]

(Z)-2-(4-(tert-butyl)phenyl)ethene-1-sulfonyl fluoride (4c)

\[
\begin{align*}
\text{41\% (10.0 mg); colorless oil; } & \text{ \textit{^1H NMR (400 MHz, Chloroform-$d$) } \delta 7.59 (d, J = 8.4 \text{ Hz, 2H}), 7.47 (d, J = 8.5 \text{ Hz, 2H}), 7.31 (dd, J = 12.0, 5.6 \text{ Hz, 1H}), 6.43 (dd, J = 12.0, 3.0 \text{ Hz, 1H}), 1.34 (s, 9H). } \\
& \text{\textit{^13C NMR (101 MHz, Chloroform-$d$) } \delta 155.2, 146.6 (d, J = 3.6 \text{ Hz), 130.5, 128.1, 125.8, 118.6 (d, } J = 28.4 \text{ Hz), 35.0, 31.0. } \\
& \text{\textit{^19F NMR (376 MHz, Chloroform-$d$) } \delta 63.77. } \\
& \text{HRMS (ESI): caled for C$_{12}$H$_{15}$FO$_2$SNa$^+$ [M + Na]$^+$ 265.0669; found 265.0669.}
\end{align*}
\]

(Z)-2-(2,6-dimethylphenyl)ethene-1-sulfonyl fluoride (4d)

\[
\begin{align*}
\text{50\% (10.7 mg); slight yellow oil; } & \text{ \textit{^1H NMR (500 MHz, Chloroform-$d$) } \delta 7.56 (dd, J = 11.4, 6.4 \text{ Hz, 1H}), 7.25 (s, 1H), 7.14 (q, J = 7.8 \text{ Hz, 2H}), 6.57 (dd, J = 11.4, 1.1 \text{ Hz, 1H}), 2.35 (s, 3H), 2.28 (s, 3H). } \\
& \text{\textit{^13C NMR (126 MHz, Chloroform-$d$) } \delta 146.9 \text{ (d, } J = 3.9 \text{ Hz), 135.5, 133.2, 131.3, 130.8, 130.0, 129.4 (d, } J = 2.3 \text{ Hz), 122.0 (d, } J = 27.8 \text{ Hz), 20.8, 19.4. } \\
& \text{\textit{^19F NMR (471 MHz, Chloroform-$d$) } \delta 64.96. } \\
& \text{HRMS (ESI): caled for C$_{10}$H$_{12}$FO$_2$S$^+$ [M + H]$^+$ 215.0537; found 215.0536.}
\end{align*}
\]
(Z)-2-mesitylene-1-sulfonyl fluoride (4e)

57% (12.9 mg); white solid: m.p. 115-116 °C; \(^1\)H NMR (400 MHz, Chloroform-\(d\)) \(\delta\) 7.53 (dd, \(J = 11.2, 6.3\) Hz, 1H), 6.91 (s, 2H), 6.71 (d, \(J = 11.1\) Hz, 1H), 2.30 (s, 3H), 2.22 (s, 6H). \(^1^3\)C NMR (101 MHz, Chloroform-\(d\)) \(\delta\) 148.2, 148.1, 138.6, 134.4, 128.2, 124.7 (d, \(J = 27.2\) Hz), 21.1, 20.0. \(^1^9\)F NMR (376 MHz, Chloroform-\(d\)) \(\delta\) 62.49. HRMS (ESI): caled for C\(_{11}\)H\(_{14}\)FO\(_2\)S\(^+\) [M + H\(^+\)] 229.0693; found 229.0680.

(Z)-2-(4-chlorophenyl)prop-1-ene-1-sulfonyl fluoride (4f)

33% (7.7 mg); colorless oil; \(^1\)H NMR (400 MHz, Chloroform-\(d\)) \(\delta\) 7.44 – 7.35 (m, 2H), 7.27 – 7.13 (m, 2H), 6.49 (s, 1H), 2.31 (s, 3H). \(^1^3\)C NMR (101 MHz, Chloroform-\(d\)) \(\delta\) 159.6 (d, \(J = 3.6\) Hz), 135.9, 135.0, 128.9, 128.1, 119.5 (d, \(J = 27.5\) Hz), 27.3 (d, \(J = 2.3\) Hz). \(^1^9\)F NMR (376 MHz, Chloroform-\(d\)) \(\delta\) 66.36. HRMS (ESI): caled for C\(_9\)H\(_9\)ClFO\(_2\)S\(^+\) [M + H\(^+\)] 234.9991; found 234.9989.

(Z)-2-(4-bromophenyl)ethene-1-sulfonyl fluoride (4g)

25% (6.5 mg); yellow solid: m.p. 53-54 °C; \(^1\)H NMR (500 MHz, Chloroform-\(d\)) \(\delta\) 7.59 (d, \(J = 8.6\) Hz, 2H), 7.46 (d, \(J = 8.4\) Hz, 2H), 7.31 (dd, \(J = 11.9, 5.7\) Hz, 1H), 6.54 (dd, \(J = 11.9, 2.4\) Hz, 1H). \(^1^3\)C NMR (126 MHz, Chloroform-\(d\)) \(\delta\) 145.3 (d, \(J = 3.9\) Hz), 132.0, 131.5, 129.9, 126.1, 121.0 (d, \(J = 28.9\) Hz). \(^1^9\)F NMR (471 MHz, Chloroform-\(d\)) \(\delta\) 64.14. HRMS (ESI): caled for C\(_9\)H\(_7\)FO\(_2\)S\(_2\)Na\(^+\) [M + Na\(^+\)] 286.9148; found 286.9146.

(3R,5R)-3-isopropyl-5-methylcyclohexyl (Z)-3-(fluorosulfonyl)-2-phenylacrylate (4h)

S32
41% (15.0 mg); white solid: m.p. 124-125 °C; \(^1\)H NMR (500 MHz, Chloroform-\(d\)) \(\delta\) 7.60 – 7.45 (m, 5H), 6.71 (s, 1H), 4.97 (td, \(J = 10.9, 4.4\) Hz, 1H), 2.36 – 2.29 (m, 1H), 1.87 (td, \(J = 7.0, 2.7\) Hz, 1H), 1.77 – 1.69 (m, 2H), 1.62 (s, 1H), 1.56 (tdd, \(J = 12.0, 6.6, 3.4\) Hz, 1H), 1.46 (ddt, \(J = 12.5, 10.8, 3.1\) Hz, 1H), 1.10 (tdd, \(J = 12.1, 10.4, 7.9\) Hz, 2H), 0.97 (d, \(J = 6.6\) Hz, 3H), 0.85 (d, \(J = 7.0\) Hz, 3H), 0.80 (d, \(J = 6.9\) Hz, 3H). \(^{13}\)C NMR (126 MHz, Chloroform-\(d\)) \(\delta\) 163.8, 152.5 (d, \(J = 3.8\) Hz), 132.3, 132.2, 131.3, 129.4, 127.4, 117.0 (d, \(J = 30.7\) Hz), 78.2, 46.9, 39.8, 34.1, 31.5, 25.6, 23.0, 22.0, 20.8, 15.7. \(^{19}\)F NMR (471 MHz, Chloroform-\(d\)) \(\delta\) 66.10. HRMS (ESI): caled for C\(_{19}\)H\(_{25}\)FO\(_4\)SNa\(^+\) [M + Na\(^+\)] 391.1350; found 391.1348.

**Methyl (Z)-4-(2-(fluorosulfonyl)-1-(3,5,5,8,8-pentamethyl-5,6,7,8-tetrahydronaphthalen-2-yl)vinyl)benzoate (4i)**

\(~\text{69\%}~(Z:E=1.6:1)~(31.0~\text{mg})~;~\text{yellow~oil;}~\) \(^1\)H NMR (500 MHz, Chloroform-\(d\)) \(\delta\) 8.09 – 8.01 (m, 1H), 7.42 – 7.36 (m, 1H), 7.17 (s, 0H), 7.12 (s, 1H), 6.99 (s, 0H), 3.93 (s, 1H), 1.90 (s, 1H), 1.71 (s, 2H), 1.29 (d, \(J = 9.2\) Hz, 6H).

\(^{13}\)C NMR (126 MHz, Chloroform-\(d\)) \(\delta\) 166.2, 160.6 (d, \(J = 3.6\) Hz), 146.8, 142.4, 141.1 (d, \(J = 2.1\) Hz), 132.4, 132.2, 130.8, 130.2, 128.5, 127.8, 127.6, 120.2 (d, \(J = 27.7\) Hz), 52.5, 35.1, 35.0, 34.2, 34.0, 31.8, 31.7, 19.4. \(^{19}\)F NMR (471 MHz, Chloroform-\(d\)) \(\delta\) 67.04. HRMS (ESI): caled for C\(_{25}\)H\(_{30}\)FO\(_4\)S\(^+\) [M + H\(^+\)] 445.1844; found 445.1841.

**5-(fluorosulfonyl)pentyl benzoate (6a)**

\(~\text{69\%}~(18.8~\text{mg})~;~\text{colorless~oil;}~\) \(^1\)H NMR (400 MHz, Chloroform-\(d\)) \(\delta\) 8.06 – 8.00 (m, 1H), 7.61 – 7.52 (m, 2H), 7.45 (t, \(J = 7.7\) Hz, 1H), 4.35 (t, \(J = 6.3\) Hz, 2H), 3.45 – 3.35 (m, 2H), 2.04 (p, \(J = 7.7\) Hz, 2H), 1.92 – 1.79 (m, 2H), 1.66 (p, \(J = 7.8, 7.3\) Hz, 2H). \(^{13}\)C NMR (101 MHz, Chloroform-\(d\)) \(\delta\) 166.5, 133.0, 130.1, 129.5, 128.4, 64.1,
50.7 (d, $J = 16.5$ Hz), 28.1, 24.6, 23.5. $^{19}$F NMR (376 MHz, Chloroform-$d$) $\delta$ 59.62 (t, $J = 4.7$ Hz). HRMS (ESI): caleed for C$_{12}$H$_{16}$FO$_4$S$^+$ [M + H]$^+$ 275.0748; found 275.0747.

5-(fluorosulfonyl)pentyl benzo[d][1,3]dioxole-5-carboxylate (6b)

46% (14.5 mg); yellow solid; m.p. 48-49 °C; $^1$H NMR (400 MHz, Chloroform-$d$) $\delta$ 7.63 (dd, $J = 8.2$, 1.7 Hz, 1H), 7.45 (d, $J = 1.7$ Hz, 1H), 6.84 (d, $J = 8.2$ Hz, 1H), 6.04 (s, 2H), 4.31 (t, $J = 6.3$ Hz, 2H), 3.44 – 3.35 (m, 2H), 2.10 – 1.98 (m, 2H), 1.88 – 1.77 (m, 2H), 1.71 – 1.60 (m, 2H). $^{13}$C NMR (101 MHz, Chloroform-$d$) $\delta$ 165.8, 151.7, 147.8, 125.3, 124.1, 109.4, 108.0, 101.8, 64.0, 50.7 (d, $J = 16.6$ Hz), 28.1, 24.6, 23.2. $^{19}$F NMR (376 MHz, Chloroform-$d$) $\delta$ 53.67 (t, $J = 3.6$ Hz.). HRMS (ESI): caleed for C$_{13}$H$_{16}$FO$_6$S$^+$ [M + H]$^+$ 319.0646; found 319.0646.

5-(fluorosulfonyl)pentyl 2-(4-isobutylphenyl)propanoate (6c)

60% (21.5 mg); colorless oil; $^1$H NMR (400 MHz, Chloroform-$d$) $\delta$ 7.19 (d, $J = 8.2$ Hz, 2H), 7.10 (d, $J = 8.2$ Hz, 2H), 4.19 – 3.99 (m, 2H), 3.68 (q, $J = 7.1$ Hz, 1H), 3.24 (ddd, $J = 9.5$, 6.9, 4.2 Hz, 2H), 2.45 (d, $J = 7.2$ Hz, 2H), 1.94 – 1.77 (m, 3H), 1.62 (dq, $J = 8.2$, 6.1 Hz, 2H), 1.49 (d, $J = 7.2$ Hz, 3H), 1.45 – 1.33 (m, 2H), 0.90 (d, $J = 6.7$ Hz, 6H). $^{13}$C NMR (101 MHz, Chloroform-$d$) $\delta$ 174.7, 140.6, 137.8, 129.3, 127.1, 63.7, 50.6 (d, $J = 16.5$ Hz), 45.2, 45.0, 30.2, 27.8, 24.3, 23.0, 22.4, 18.3. $^{19}$F NMR (376 MHz, Chloroform-$d$) $\delta$ 53.53 (t, $J = 4.0$ Hz). HRMS (ESI): caleed for C$_{18}$H$_{28}$FO$_4$S$^+$ [M + H]$^+$ 359.1687; found 359.1687.

(4-methyl-1-tosylpyrrolidin-3-yl)methanesulfonyl fluoride (6d)

40% (13.4 mg); slight yellow solid; m.p. 94-95 °C; $^1$H NMR (400 MHz, Chloroform-$d$) $\delta$ 7.73 (d, $J = 8.3$ Hz, 2H), 7.35 (d, $J = 8.0$ Hz, 2H), 3.56 (dd, $J = 10.7$, 7.2 Hz, 1H), 3.44 – 3.31 (m, 2H), 3.27 (dd, $J = 10.5$, 7.7 Hz, 1H), 3.09 (tt, $J = 8.6$, 4.0 Hz, 2H),
2.70 – 2.57 (m, 1H), 2.41 – 2.47 (m, 4H), 0.87 (d, J = 7.1 Hz, 3H). $^{13}$C NMR (101 MHz, Chloroform-$d$) δ 144.0, 133.5, 129.9, 127.4, 53.9, 50.0 (d, J = 2.0 Hz), 49.6 (d, J = 17.2 Hz), 36.9, 35.2, 21.5, 13.2. $^{19}$F NMR (376 MHz, Chloroform-$d$) δ 56.56 (t, J = 3.7 Hz).

HRMS (ESI): caled for C$_{13}$H$_{19}$FNO$_4$S$_2^+$ [M + H]$^+$ 336.0734; found 336.0735.

5-(fluorosulfonyl)pentyl 4-(N,N-dipropylsulfamoyl)benzoate (6e)

42% (18.4 mg); slight yellow oil; $^1$H NMR (400 MHz, Chloroform-$d$) δ 8.14 (d, J = 8.4 Hz, 2H), 7.87 (d, J = 8.5 Hz, 2H), 4.38 (t, J = 6.4 Hz, 2H), 3.41 (td, J = 7.7, 4.0 Hz, 2H), 3.14 – 3.06 (m, 4H), 2.05 (p, J = 7.7 Hz, 2H), 1.92 – 1.81 (m, 2H), 1.73 – 1.61 (m, 2H), 1.55 (h, J = 7.4 Hz, 4H), 0.87 (t, J = 7.4 Hz, 6H). $^{13}$C NMR (101 MHz, Chloroform-$d$) δ 165.2, 144.4, 133.4, 130.2, 127.0, 64.7, 50.7 (d, J = 16.7 Hz), 49.9, 28.0, 24.5, 23.2, 21.9, 11.1. $^{19}$F NMR (376 MHz, Chloroform-$d$) δ 53.89 (t, J = 4.6 Hz). HRMS (ESI): caled for C$_{18}$H$_{29}$FNO$_6$S$_2^+$ [M + H]$^+$ 438.1415; found 438.1414.

5-(fluorosulfonyl)pentyl 1-(2,2-difluorobenzo[d][1,3]dioxol-5-yl)cyclopropane-1-carboxylate (6f)

61% (24.1 mg); colorless oil; $^1$H NMR (400 MHz, Chloroform-$d$) δ 7.06 (s, 1H), 7.04 (d, J = 1.7 Hz, 1H), 7.00 – 6.97 (m, 1H), 4.06 (t, J = 6.3 Hz, 2H), 3.34 – 3.27 (m, 2H), 1.98 – 1.85 (m, 2H), 1.66 – 1.54 (m, 4H), 1.51 – 1.38 (m, 2H), 1.19 (q, J = 4.0 Hz, 2H). $^{13}$C NMR (101 MHz, Chloroform-$d$) δ 173.9, 143.4, 142.8, 135.7, 131.7 (t, J = 255.0 Hz), 125.6, 112.0, 108.9, 64.4, 50.6 (d, J = 16.6 Hz), 29.0, 27.8, 24.3, 23.0, 16.9. $^{19}$F NMR (376 MHz, Chloroform-$d$) δ 53.89 (t, J = 3.9 Hz). HRMS (ESI): caled for C$_{16}$H$_{18}$F$_3$O$_6$S$^+$ [M + H]$^+$ 395.0771; found 395.0772.

5-((4-methyl-2-oxo-2H-chromen-7-yl)oxy)pentane-1-sulfonyl fluoride (6g)

S35
45% (14.8 mg); colorless oil; $^1$H NMR (400 MHz, Chloroform-$d$) δ 7.49 (d, $J$ = 8.8 Hz, 1H), 6.84 (dd, $J$ = 8.8, 2.5 Hz, 1H), 6.79 (d, $J$ = 2.6 Hz, 1H), 6.14 (q, $J$ = 1.2 Hz, 1H), 4.05 (t, $J$ = 6.0 Hz, 2H), 3.47 – 3.38 (m, 2H), 2.40 (d, $J$ = 1.2 Hz, 3H), 2.06 (p, $J$ = 7.7 Hz, 2H), 1.95 – 1.82 (m, 2H), 1.72 (ddd, $J$ = 15.3, 9.1, 6.1 Hz, 2H). $^{13}$C NMR (101 MHz, Chloroform-$d$) δ 161.8, 161.2, 155.3, 152.5, 125.6, 113.7, 112.5, 112.1, 101.3, 67.7, 50.7 (d, $J$ = 16.6 Hz), 28.3, 24.7, 23.3, 18.6. $^{19}$F NMR (376 MHz, Chloroform-$d$) δ 53.74 (t, $J$ = 4.6 Hz.). HRMS (ESI): caled for C$_{15}$H$_{18}$FO$_5$S$^+$ [M + H]$^+$ 329.0854; found 329.0855.

(8R,9S,10R,13S,14S,17S)-10,13-dimethyl-3-oxo-2,3,6,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthren-17-yl 5-(fluorosulfonyl)pentanoate (6h)

34% (16.0 mg); yellow solid: m.p. 96-97 °C;

$^1$H NMR (400 MHz, Chloroform-$d$) δ 5.73 (s, 1H), 4.62 (dd, $J$ = 9.2, 7.7 Hz, 1H), 3.44 – 3.35 (m, 2H), 2.45 – 2.33 (m, 3H), 2.33 – 2.24 (m, 1H), 2.24 – 2.14 (m, 1H), 2.01 (ddt, $J$ = 11.9, 9.5, 6.4 Hz, 2H), 1.89 – 1.64 (m, 5H), 1.63 – 1.52 (m, 3H), 1.45 – 1.32 (m, 2H), 1.25 (s, 8H), 1.19 (s, 3H), 0.84 (s, 3H).

$^{13}$C NMR (101 MHz, Chloroform-$d$) δ 172.4, 170.8, 124.0, 82.8, 53.7, 50.6 (d, $J$ = 16.7 Hz), 50.2, 42.5, 38.6, 36.7, 35.7, 35.4, 33.9, 33.4, 32.7, 31.5, 29.7, 27.5, 23.5, 23.2, 22.9, 20.5, 17.4, 12.1. $^{19}$F NMR (376 MHz, Chloroform-$d$) δ 53.74 (t, $J$ = 4.7 Hz.). HRMS (ESI): caled for C$_{24}$H$_{36}$FO$_5$S$^+$ [M + H]$^+$ 455.2262; found 455.2261.

(8S,9R,13R,14R)-13-methyl-17-oxo-7,8,9,11,12,13,14,15,16,17-decahydro-6H-cyclopenta[a]phenanthren-3-yl 5-(fluorosulfonyl)pentanoate (6i)
56% (24.5 mg); slight yellow solid: m.p. 97-98 °C; $^1$H NMR (400 MHz, Chloroform-$d$) δ 7.29 (d, $J = 8.6$ Hz, 1H), 6.88 – 6.78 (m, 2H), 3.44 (td, $J = 7.5, 4.2$ Hz, 2H), 2.91 (dd, $J = 8.7, 3.9$ Hz, 2H), 2.64 (t, $J = 7.1$ Hz, 2H), 2.51 (dd, $J = 18.8, 8.6$ Hz, 1H), 2.45 – 2.36 (m, 1H), 2.29 (td, $J = 10.7, 4.1$ Hz, 1H), 2.22 – 2.03 (m, 4H), 1.96 (ddt, $J = 12.6, 8.5, 4.7$ Hz, 3H), 1.69 – 1.54 (m, 3H), 1.57 – 1.40 (m, 4H), 0.91 (s, 3H). $^{13}$C NMR (101 MHz, Chloroform-$d$) δ 220.7, 171.3, 148.3, 138.1, 137.6, 126.5, 121.4, 118.6, 50.6, 50.4 (d, $J = 2.8$ Hz), 47.9, 44.1, 38.0, 35.8, 33.3, 31.5, 29.4, 26.3, 25.7, 23.0, 22.9, 21.6, 13.8. $^{19}$F NMR (376 MHz, Chloroform-$d$) δ 53.80 (t, $J = 4.7$ Hz.). HRMS (ESI): caled for C$_{23}$H$_{30}$FO$_5$S$^+$ [M + H]$^+$ 437.1793; found 437.1794.

(R)-2,5,7,8-tetramethyl-2-((4R,8R)-4,8,12-trimethyltridecyl)chroman-6-yl 5-(fluorosulfonyl)pentanoate (6j)

25% (15.0 mg); slight yellow oil; $^1$H NMR (400 MHz, Chloroform-$d$) δ 3.44 (td, $J = 7.6, 4.2$ Hz, 2H), 2.69 (t, $J = 7.1$ Hz, 2H), 2.59 (t, $J = 6.8$ Hz, 2H), 2.09 (s, 2H), 1.98 (d, $J = 16.5$ Hz, 7H), 1.78 (ddq, $J = 20.1, 13.4, 6.8$ Hz, 2H), 1.62 – 1.49 (m, 4H), 1.43 (s, 1H), 1.26 (s, 16H), 1.24 (s, 4H), 0.86 (tt, $J = 7.6, 4.6$ Hz, 15H). $^{13}$C NMR (101 MHz, Chloroform-$d$) δ 171.1, 149.5, 140.3, 126.5, 124.7, 123.2, 117.5, 75.1, 50.6 (d, $J = 17.0$ Hz), 39.4, 37.4 (d, $J = 3.2$ Hz), 37.3, 33.0, 32.8, 32.7, 31.9, 30.3, 29.7, 28.0, 24.8, 24.5, 23.2, 23.1, 22.7 (d, $J = 2.7$ Hz), 22.6, 21.0, 20.6, 19.8, 19.7, 14.1, 13.0, 12.2, 11.8. $^{19}$F NMR (376 MHz, Chloroform-$d$) δ 53.73 (t, $J = 4.9$ Hz.). HRMS (ESI): caled for C$_{34}$H$_{57}$FO$_5$SNa$^+$ [M + Na]$^+$ 619.3803; found 619.3805.

((10R,13S)-10,13-dimethyl-3-oxo-2,3,6,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthren-17-yl)methyl 5-(fluorosulfonyl)pentanoate (6k)
31% (14.0 mg); colorless oil; $^1$H NMR (400 MHz, Chloroform-$d$) δ 7.17 (d, $J = 8.2$ Hz, 1H), 7.00 (dd, $J = 8.2, 2.1$ Hz, 1H), 6.90 (s, 1H), 5.43 (t, $J = 6.6$ Hz, 1H), 3.34 (td, $J = 7.6, 4.3$ Hz, 2H), 3.25 (dd, $J = 13.7, 6.4$ Hz, 1H), 3.10 (dd, $J = 13.7, 6.5$ Hz, 1H), 2.93 (ddd, $J = 17.3, 6.9, 1.9$ Hz, 1H), 2.81 (td, $J = 17.8, 11.2, 10.0, 4.8$ Hz, 2H), 2.34 – 2.26 (m, 1H), 2.22 (t, $J = 7.1$ Hz, 2H), 2.01 – 1.91 (m, 2H), 1.88 – 1.62 (m, 7H), 1.45 – 1.31 (m, 3H), 1.23 (d, $J = 7.1$ Hz, 9H), 0.94 (s, 3H). 13C NMR (101 MHz, Chloroform-$d$) δ 171.5, 147.1, 145.7, 134.7, 126.9, 124.1, 123.9, 50.5 (d, $J = 16.5$ Hz), 49.7, 45.2, 38.3, 37.4, 37.3, 36.2, 35.5, 33.4, 30.1, 25.2, 23.9 (d, $J = 2.3$ Hz), 23.7, 23.0, 18.9, 18.7, 18.5. 19F NMR (376 MHz, Chloroform-$d$) δ 53.67 (t, $J = 4.6$ Hz.). HRMS (ESI): caled for C$_{25}$H$_{39}$FNO$_3$S$^+$ [M + H]$^+$ 452.2629; found 452.2627.

2-(benzo[d]thiazol-2-yl)-5-oxo-5-(m-tolyl)pentane-1-sulfonyl fluoride (8a)

66% (26.0 mg); yellow solid: m.p. 107-108 °C; $^1$H NMR (400 MHz, Chloroform-$d$) $^1$H NMR (400 MHz, Chloroform-$d$) δ 8.00 (dt, $J = 8.3, 0.9$ Hz, 1H), 7.91 – 7.84 (m, 1H), 7.65 (d, $J = 11.1$ Hz, 2H), 7.50 (ddd, $J = 8.3, 7.2, 1.3$ Hz, 1H), 7.41 (ddd, $J = 8.2, 7.2, 1.2$ Hz, 1H), 7.37 – 7.28 (m, 2H), 4.32 (ddd, $J = 14.8, 7.6, 4.1$ Hz, 1H), 4.04 (dt, $J = 8.8, 7.5, 5.2$ Hz, 1H), 3.89 (dt, $J = 14.8, 5.0$ Hz, 1H), 3.11 – 2.93 (m, 2H), 2.63 – 2.38 (m, 2H), 2.37 (s, 3H). 13C NMR (101 MHz, Chloroform-$d$) δ 198.3, 169.0, 152.9, 138.5, 136.4, 134.8, 134.1, 131.6, 128.5 (d, $J = 4.6$ Hz), 126.5, 125.6, 125.2, 123.2, 121.8, 54.9 (d, $J = 16.1$ Hz), 38.8, 34.8, 29.4, 21.3. 19F NMR (376 MHz, Chloroform-$d$) δ 58.23. (t, $J = 4.2$ Hz). HRMS (ESI): caled for C$_{19}$H$_{19}$FNO$_3$S$_2$ $^+$ [M + H]$^+$ 392.0785; found 392.0786.

2-(benzo[d]thiazol-2-yl)-5-(4-fluorophenyl)-5-oxopentane-1-sulfonyl fluoride (8b)
75% (29.5 mg); yellow solid: m.p. 105-106 °C; $^1$H NMR (400 MHz, Chloroform-$d$) δ 8.03 – 7.96 (m, 1H), 7.88 (m, 3H), 7.46 (m, 2H), 7.14 – 7.04 (m, 2H), 4.31 (m, 1H), 4.04 (m, 1H), 3.89 (m, 1H), 3.09 – 2.91 (m, 2H), 2.49 (m, 2H). $^{13}$C NMR (101 MHz, Chloroform-$d$) δ 196.5, 168.0 (d, $J = 172.0$ Hz), 164.6, 152.9, 134.7, 132.8, 130.6 (d, $J = 9.2$ Hz), 126.5, 125.7, 123.2, 121.8, 115.8 (d, $J = 21.8$ Hz), 54.9 (d, $J = 16.3$ Hz), 38.8, 34.7, 29.3. $^{19}$F NMR (376 MHz, Chloroform-$d$) δ 58.28 (t, $J = 4.8$ Hz), -95.97 – -112.81 (m). HRMS (ESI): caled for C$_{18}$H$_{16}$F$_2$NO$_3$S$_2$+ [M + H]$^+$ 396.0489; found 396.0488.

2-(benzo[d]thiazol-2-yl)-5-(furan-2-yl)-5-oxopentane-1-sulfonyl fluoride (8c)

27% (10.0 mg); yellow solid: m.p. 123-124 °C; $^1$H NMR (400 MHz, Chloroform-$d$) δ 8.20 – 8.13 (m, 1H), 8.00 – 7.95 (m, 1H), 7.62 – 7.49 (m, 2H), 7.39 (dd, $J = 1.8$, 0.8 Hz, 1H), 6.27 (ddd, $J = 19.8$, 3.3, 1.3 Hz, 2H), 3.86 (m, 1H), 3.78 – 3.60 (m, 2H), 3.26 (t, $J = 7.2$ Hz, 2H), 2.43 – 2.18 (m, 2H). $^{13}$C NMR (101 MHz, Chloroform-$d$) δ 193.7, 165.7, 153.4, 151.0, 142.7, 137.2, 127.8, 127.1, 125.4, 122.5, 110.5, 108.5, 54.6 (d, $J = 14.7$ Hz), 35.6, 34.3, 27.3 (d, $J = 2.0$ Hz). $^{19}$F NMR (376 MHz, Chloroform-$d$) δ 58.17 (d, $J = 5.4$ Hz). HRMS (ESI): caled for C$_{16}$H$_{15}$FNO$_4$S$_2$+ [M + H]$^+$ 368.0421; found 368.0420.

2-(benzo[d]thiazol-2-yl)-5-oxo-5-(thiophen-2-yl)pentane-1-sulfonyl fluoride (8d)

26% (10.0 mg); yellow oil; $^1$H NMR (400 MHz, Chloroform-$d$) δ 8.03 – 7.97 (m, 1H), 7.91 – 7.84 (m, 1H), 7.65 – 7.58 (m, 2H), 7.46 (m, 2H), 7.08 (dd, $J = 4.9$, 3.8 Hz, 1H), 4.31 (m, 1H), 4.04 (m, 1H), 3.88 (ddd, $J = 14.8$, 5.5, 4.6 Hz, 1H), 3.10 – 2.88 (m, 2H), 2.59 – 2.38 (m, 2H). $^{13}$C NMR (101 MHz, Chloroform-$d$) δ 190.9, 168.8, 152.9, 143.5, 134.8, 134.0, 132.0, 128.1, 126.5, 125.6, 123.2, 121.8, 54.8 (d, $J = 16.3$ Hz), 38.8, 35.4, 29.5. $^{19}$F NMR (376 MHz, Chloroform-$d$) δ 58.17 (d, $J = 5.4$ Hz). HRMS (ESI): caled for C$_{16}$H$_{15}$FNO$_4$S$_2$+ [M + H]$^+$ 368.0421; found 368.0420.
MHz, Chloroform-d) δ 58.27 (t, J = 3.2 Hz). HRMS (ESI): caled for C_{16}H_{15}FNO_{3}S_{3}^{+} [M + H]^+ 384.0193; found 384.0192.

5-oxo-5-phenyl-2-(thiazol-2-yl)pentane-1-sulfonyl fluoride (8e)

70% (23.0 mg); white solid: m.p. 102-103 °C; \(^{1}H\) NMR (400 MHz, Chloroform-d) δ 7.90 – 7.85 (m, 2H), 7.79 (d, J = 3.3 Hz, 1H), 7.63 – 7.50 (m, 1H), 7.44 (m, 2H), 7.30 (d, J = 3.3 Hz, 1H), 4.19 (m, 1H), 3.99 (m, 1H), 3.83 (dt, J = 14.6, 5.0 Hz, 1H), 3.06 – 2.88 (m, 2H), 2.52 – 2.29 (m, 2H). \(^{13}C\) NMR (101 MHz, Chloroform-d) δ 198.1, 168.0, 143.1, 136.4, 133.4, 128.7, 127.9, 119.3, 55.4 (d, J = 15.8 Hz), 37.9, 34.7, 29.6 (d, J = 1.6 Hz). \(^{19}F\) NMR (376 MHz, Chloroform-d) δ 58.21 (t, J = 4.7 Hz). HRMS (ESI): caled for C_{14}H_{14}FNO_{3}S_{2}^{+} [M + H]^+ 328.0472; found 328.0471.

2-(benzo[d]thiazol-2-yl)-6,6-dimethyl-5-oxoheptane-1-sulfonyl fluoride (8f)

57% (20.5 mg); slight yellow oil; \(^{1}H\) NMR (400 MHz, Chloroform-d) δ 7.94 (dd, J = 46.6, 7.3 Hz, 2H), 7.47 (m, 2H), 4.27 (m, 1H), 3.93 (m, 1H), 3.87 – 3.77 (m, 1H), 2.61 – 2.44 (m, 2H), 2.38 – 2.17 (m, 2H), 1.09 (s, 9H). \(^{13}C\) NMR (101 MHz, Chloroform-d) δ 214.2, 169.1, 152.9, 147.5, 126.5, 125.6, 123.2, 121.8, 54.9 (d, J = 16.2 Hz), 44.1, 38.7, 32.7, 29.4, 26.5. \(^{19}F\) NMR (376 MHz, Chloroform-d) δ 58.08 (t, J = 4.2 Hz) HRMS (ESI): caled for C_{16}H_{21}FN_{2}O_{3}S_{2}^{+} [M + H]^+ 358.0942; found 358.0941.

2-(benzo[d]thiazol-2-yl)-5-cyclopropyl-5-oxopentane-1-sulfonyl fluoride (8g)
73% (25.0 mg); slight yellow oil; $^1$H NMR (400 MHz, Chloroform-$d$) $\delta$ 7.95 (dd, $J = 50.0$, 7.5 Hz, 2H), 7.60 – 7.38 (m, 2H), 4.28 (m, 1H), 3.97 – 3.88 (m, 1H), 3.83 (dt, $J = 14.7$, 5.0 Hz, 1H), 2.76 – 2.52 (m, 2H), 2.42 – 2.20 (m, 2H), 1.83 (ddd, $J = 12.4$, 7.8, 4.5 Hz, 1H), 1.05 – 0.96 (m, 2H), 0.91 – 0.81 (m, 2H). $^{13}$C NMR (101 MHz, Chloroform-$d$) $\delta$ 208.7, 169.0, 152.9, 134.7, 126.4, 125.6, 123.1, 121.8, 54.7 (d, $J = 16.1$ Hz), 39.4, 38.6, 29.1, 20.6, 11.1 (d, $J = 3.2$ Hz). $^{19}$F NMR (376 MHz, Chloroform-$d$) $\delta$ 58.10 (t, $J = 4.3$ Hz). HRMS (ESI): caled for C$_{15}$H$_{17}$FNO$_3$S$_2$ $^+$ [M + H]$^+$ 342.0629; found 342.0628.

2-(benzo[d]thiazol-2-yl)-5-oxohexane-1-sulfonyl fluoride (8h)

48% (15.0 mg); slight yellow oil; $^1$H NMR (400 MHz, Chloroform-$d$) $\delta$ 7.94 (dd, $J = 47.4$, 7.9 Hz, 2H), 7.47 (m, 2H), 4.26 (m, 1H), 3.97 – 3.87 (m, 1H), 3.82 (ddd, $J = 14.7$, 5.6, 4.6 Hz, 1H), 2.58 – 2.45 (m, 2H), 2.38 – 2.21 (m, 2H), 2.10 (s, 3H). $^{13}$C NMR (101 MHz, Chloroform-$d$) $\delta$ 206.5, 168.8, 152.9, 134.7, 126.5, 125.6, 123.2, 121.8, 54.7 (d, $J = 16.5$ Hz), 39.6, 38.6, 30.0, 28.9. $^{19}$F NMR (376 MHz, Chloroform-$d$) $\delta$ 58.14 (t, $J = 4.5$ Hz). HRMS (ESI): caled for C$_{13}$H$_{15}$FNO$_3$S$_2$ $^+$ [M + H]$^+$ 316.0472; found 316.0471.

2-cyano-2-methyl-5-oxo-5-phenylpentane-1-sulfonyl fluoride (8i)

42% (12.0 mg); slight yellow oil; $^1$H NMR (400 MHz, Chloroform-$d$) $\delta$ 7.99 (d, $J = 7.2$ Hz, 2H), 7.62 (t, $J = 7.4$ Hz, 1H), 7.50 (t, $J = 7.7$ Hz, 1H), 3.71 (ddd, $J = 55.4$, 15.0, 3.2 Hz, 2H), 3.29 (t, $J = 7.9$ Hz, 2H), 2.43 – 2.20 (m, 2H), 1.71 (s, 3H). $^{13}$C NMR (101 MHz, Chloroform-$d$) $\delta$ 197.0, 136.0, 133.8, 128.9, 128.1, 119.9, 57.8 (d, $J = 17.2$ Hz), 34.6, 33.8, 33.1 (d, $J = 1.9$ Hz), 23.7. $^{19}$F NMR (376 MHz, Chloroform-$d$) $\delta$ 65.35 (t, $J = 3.8$ Hz). HRMS (ESI): caled for C$_{13}$H$_{15}$FNO$_3$S $^+$ [M + H]$^+$ 284.0751; found 284.0750.
2-cyano-5-oxo-5-(p-tolyl)pentane-1-sulfonyl fluoride (8j)

71% (20.0 mg); slight yellow solid: m.p. 88-89 °C; $^1$H NMR (400 MHz, Chloroform-$d$) δ 7.77 (d, $J$ = 7.2 Hz, 2H), 7.46 – 7.34 (m, 2H), 3.80 (m, 1H), 3.68 (dt, $J$ = 15.0, 5.3 Hz, 1H), 3.54 (ddt, $J$ = 10.0, 8.5, 4.8 Hz, 1H), 3.35 – 3.27 (m, 2H), 2.43 (s, 3H), 2.36 (m, 1H), 2.22 – 2.09 (m, 1H). $^{13}$C NMR (101 MHz, Chloroform-$d$) δ 197.5, 138.8, 136.0, 134.7, 128.7 (d, $J$ = 17.7 Hz), 125.3, 117.6, 52.3 (d, $J$ = 19.1 Hz), 34.8, 26.9, 26.0, 21.4. $^{19}$F NMR (376 MHz, Chloroform-$d$) δ 58.03 (t, $J$ = 6.4 Hz). HRMS (ESI): caled for C$_{13}$H$_{15}$FNO$_3$S$^+$ [M + H]$^+$ 284.0751; found 284.0750.

5-(4-bromophenyl)-2-cyano-5-oxopentane-1-sulfonyl fluoride (8k)

58% (20.1 mg); slight yellow solid: m.p. 107-108 °C; $^1$H NMR $^1$H NMR (400 MHz, Chloroform-$d$) δ 7.83 (d, $J$ = 8.6 Hz, 2H), 7.65 (d, $J$ = 8.6 Hz, 2H), 3.81 (ddd, $J$ = 15.0, 8.3, 3.2 Hz, 1H), 3.68 (dt, $J$ = 15.0, 5.3 Hz, 1H), 3.54 (ddt, $J$ = 10.1, 8.2, 4.9 Hz, 1H), 3.37 – 3.18 (m, 2H), 2.44 – 2.31 (m, 1H), 2.26 – 2.09 (m, 1H). $^{13}$C NMR (101 MHz, Chloroform-$d$) δ 196.3, 134.6, 132.2, 129.5, 129.2, 52.2 (d, $J$ = 19.1 Hz), 34.7, 26.8, 25.8. $^{19}$F NMR (376 MHz, Chloroform-$d$) δ 59.13 (t, $J$ = 5.6 Hz). HRMS (ESI): caled for C$_{12}$H$_{12}$BrFNO$_3$S$^+$ [M + H]$^+$ 347.9700; found 347.9703.

2-cyano-5-(furan-2-yl)-5-oxopentane-1-sulfonyl fluoride (8l)

69% (18.0 mg); slight yellow oil; $^1$H NMR (400 MHz, Chloroform-$d$) δ 7.78 (dd, $J$ = 3.8, 1.2 Hz, 1H), 7.71 (dd, $J$ = 4.9, 1.1 Hz, 1H), 7.18 (dd, $J$ = 4.9, 3.8 Hz, 1H), 3.80 (ddd, $J$ = 15.0, 8.5, 3.3 Hz, 1H), 3.68 (dt, $J$ = 15.1, 5.3 Hz, 1H), 3.54 (ddt, $J$ = 9.9, 8.4, 4.9 Hz, 1H), 3.36 – 3.16 (m, 2H), 2.44 – 2.31 (m, 1H), 2.26 – 2.07 (m, 1H). $^{13}$C NMR (101 MHz, Chloroform-$d$) δ 190.1, 143.0, 134.6, 132.5, 128.4, 117.4, 52.1 (d, $J$ = 19.1 Hz), 35.2, 26.8, 25.90. $^{19}$F NMR (376 MHz, Chloroform-$d$) δ 59.10 (t, $J$ = 4.8 Hz). HRMS (ESI): caled for C$_{10}$H$_{11}$FNO$_4$S$^+$ [M + H]$^+$ 260.0388; found 260.0363.
5-methyl-4,7-diphenyl-4,7-dihydro-3H-[1,2]oxathiino[6,5-c]pyrazole 2,2-dioxide (10)

50% (17.2 mg); White solid; $^1$H NMR (400 MHz, Chloroform-$d$) δ 7.69 – 7.63 (m, 2H), 7.51 – 7.30 (m, 8H), 4.53 (dd, $J = 11.4$, 5.9 Hz, 1H), 3.74 (dd, $J = 14.2$, 5.9 Hz, 1H), 3.41 (dd, $J = 14.2$, 11.4 Hz, 1H), 1.72 (s, 3H). $^{13}$C NMR (101 MHz, Chloroform-$d$) δ 147.0, 144.0, 138.1, 137.1, 129.4, 129.3, 128.5, 128.0, 127.2, 99.0, 52.1, 37.9, 13.6. HRMS (ESI): caled for C$_{18}$H$_{17}$N$_2$O$_3$S$^+$ [M + H]$^+$ 341.0955; found 341.0953.

7,7-dimethyl-4-phenyl-4,6,7,8-tetrahydrobenzo[e][1,2]oxathiin-5(3H)-one 2,2-dioxide (12)

40% (12.0 mg); white solid; $^1$H NMR (400 MHz, Chloroform-$d$) δ 7.32 (t, $J = 7.3$ Hz, 2H), 7.26 (d, $J = 7.1$ Hz, 1H), 7.19 (dd, $J = 7.1$, 1.8 Hz, 2H), 4.47 (ddt, $J = 9.2$, 7.2, 2.2 Hz, 1H), 3.70 (dd, $J = 14.4$, 7.3 Hz, 1H), 3.45 (dd, $J = 14.4$, 8.9 Hz, 1H), 2.59 – 2.47 (m, 2H), 2.28 (d, $J = 3.3$ Hz, 2H), 1.18 (s, 3H), 1.13 (s, 3H). $^{13}$C NMR (101 MHz, Chloroform-$d$) δ 195.5, 165.6, 139.6, 129.0, 127.6, 116.9, 52.0, 50.7, 42.4, 39.8, 28.6, 27.9. HRMS (ESI): caled for C$_{16}$H$_{19}$O$_4$S$^+$ [M + H]$^+$ 307.0999; found 307.0995.

(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-phenylethene-1-sulfonate (14)

60% (26.3 mg); white solid; $^1$H NMR (400 MHz, Chloroform-$d$) δ 7.56 (d, $J = 15.6$ Hz, 1H), 7.51 – 7.39 (m, 5H), 7.26 (d, $J = 9.3$ Hz, 1H), 7.01 (dd, $J = 6.1$, 2.8 Hz, 2H), 6.88 (d, $J = 15.5$ Hz, 1H), 2.90 (dd, $J = 9.0$, 4.3 Hz, 2H), 2.50 (dd, $J = 18.9$, 8.7 Hz, 1H), 2.37 (dt, $J = 9.0$, 3.2 Hz, 1H), 2.32 – 2.23 (m, 1H), 2.21 – 1.92 (m, 4H), 1.70 – 1.36 (m, 6H), 0.90 (s, 3H). $^{13}$C NMR (101 MHz, Chloroform-$d$) δ 220.6, 147.4, 145.8, 139.0, 138.7, 131.9, 131.7, 129.3, 128.6, 126.7, 122.5, 121.0, 119.3, 50.4, S43
47.9, 44.1, 37.9, 35.8, 31.5, 29.4, 26.2, 25.7, 21.6, 13.8. HRMS (ESI): C_{26}H_{29}O_{4}S^{+} [M + H]^+ 437.1781, found 437.1780.

5-((((R)-2,5,7,8-tetramethyl-2-((4R,8R)-4,8,12-trimethyltridecyl)chroman-6-yl)oxy)sulfonyl)pentyl 2,2-difluorobenzo[d][1,3]dioxole-5-carboxylate (16)

70% (0.025 mmol) (13.4 mg); colorless oil; \(^1H\) NMR (400 MHz, Chloroform-\(d\)) \(\delta\) 7.09 – 7.02 (m, 2H), 6.99 – 6.95 (m, 1H), 4.07 (t, \(J = 6.4\) Hz, 2H), 3.34 – 3.26 (m, 2H), 2.59 (t, \(J = 6.8\) Hz, 2H), 2.21 (d, \(J = 12.8\) Hz, 6H), 2.09 (s, 3H), 2.06 – 1.97 (m, 2H), 1.79 (dh, \(J = 20.0, 6.7\) Hz, 2H), 1.70 – 1.58 (m, 4H), 1.58 – 1.46 (m, 7H), 1.34 – 1.22 (m, 10H), 1.22 – 1.07 (m, 5H), 0.90 – 0.81 (m, 14H). \(^{13}C\) NMR (101 MHz, Chloroform-\(d\)) \(\delta\) 173.9, 150.2, 143.4, 142.8, 139.0, 135.8, 131.7, 128.7, 127.3, 125.7, 123.8, 118.0, 112.0, 108.9, 75.4, 64.6, 51.5, 40.0, 39.4, 37.5, 37.3, 32.8, 32.7, 31.0, 29.0, 28.1, 28.0, 24.8, 24.5, 23.9, 23.3, 22.7, 22.6, 21.0, 20.7, 19.8, 19.7, 16.9, 14.5, 13.6, 12.0. \(^{19}F\) NMR (376 MHz, Chloroform-\(d\)) \(\delta\) -49.92. HRMS (ESI): caled for C_{42}H_{63}F_{2}O_{8}S^{+} [M + H]^+ 765.4206; found 765.4205.

5-chloro-2-phenylpent-2-ene-1-sulfonyl fluoride (19)

11% (2.9 mg); colorless oil; \(^1H\) NMR (400 MHz, Chloroform-\(d\)) \(\delta\) 7.38 – 7.21 (m, 5H), 6.18 (t, \(J = 7.4\) Hz, 1H), 4.53 (d, \(J = 2.5\) Hz, 2H), 3.63 (t, \(J = 6.4\) Hz, 2H), 2.76 (q, \(J = 6.7\) Hz, 2H). \(^{13}C\) NMR (101 MHz, Chloroform-\(d\)) \(\delta\) 135.3, 128.8, 128.8, 128.5, 128.4, 126.5, 52.5 (d, \(J = 16.8\) Hz), 43.2, 32.6. \(^{19}F\) NMR (376 MHz, Chloroform-\(d\)) \(\delta\) 56.81. HRMS (ESI): caled for C_{11}H_{12}ClFO_{2}SNa^{+} [M + Na]^+ 285.0123; found 285.0127.
X. X-ray crystallography data for 2b

Table 9 Crystal data and structure refinement for 2b.

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<th>Identification code</th>
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Crystal structure determination of 2b

Crystal Data for C_{16}H_{11}F_{6.955}N_{2}O_{5}S_{2} (M = 507.53 g/mol): orthorhombic, space group Pnma (no. 62), a = 17.4014 (3) Å, b= 8.0234 (2) Å, c= 14.1405(3) Å, V= 1974.27(7)
$\AA^3$, $Z=4$, $T=193.0$ K, $\mu(\text{GaK\textalpha})=2.191$ mm$^{-1}$, $D_{calc}=1.708$ g/cm$^3$, 17641 reflections measured ($7.008^\circ \leq 2\Theta \leq 107.992^\circ$), 1946 unique ($R_{int}=0.0560$, $R_{sigma}=0.0329$) which were used in all calculations. The final $R_1$ was 0.0640 ($I > 2\sigma(I)$) and $wR_2$ was 0.1765 (all data).
XI. NMR Spectra of 2, 3, 4, 6, 8, 10, 12, 14, 16, 19

Supplementary Figure 12. $^1$H NMR (400 MHz, room temperature, CD$_3$CN) spectra of product 2a

Supplementary Figure 13. $^{13}$C NMR (101 MHz, room temperature, CD$_3$CN) spectra of product 2a
**Supplementary Figure 14.** $^{19}$F NMR (376 MHz, room temperature, CD$_3$CN) spectra of product 2a

**Supplementary Figure 15.** $^1$H NMR (400 MHz, room temperature, CD$_3$CN) spectra of product 2b
Supplementary Figure 16. $^{13}$C NMR (101 MHz, room temperature, CD$_3$CN) spectra of product 2b

Supplementary Figure 17. $^{19}$F NMR (376 MHz, room temperature, CD$_3$CN) spectra of product 2b
Supplementary Figure 18. $^1$H NMR (400 MHz, room temperature, CD$_3$CN) spectra of product 2c

Supplementary Figure 19. $^{13}$C NMR (101 MHz, room temperature, CD$_3$CN) spectra of product 2c
Supplementary Figure 20. $^{19}$F NMR (376 MHz, room temperature, CD$_3$CN) spectra of product 2c

Supplementary Figure 21. $^1$H NMR (400 MHz, room temperature, CD$_3$CN) spectra of product 2d
Supplementary Figure 22. $^{13}$C NMR (101 MHz, room temperature, CD$_3$CN) spectra of product 2d

Supplementary Figure 23. $^{19}$F NMR (376 MHz, room temperature, CD$_3$CN) spectra of product 2d
Supplementary Figure 24. $^1$H NMR (400 MHz, room temperature, CD$_3$CN) spectra of product 2e

Supplementary Figure 25. $^{13}$C NMR (101 MHz, room temperature, CD$_3$CN) spectra of product 2e
**Supplementary Figure 26.** $^{19}$F NMR (376 MHz, room temperature, CD$_3$CN) spectra of product 2e

**Supplementary Figure 27.** $^1$H NMR (400 MHz, room temperature, CDCl$_3$) spectra of product 3a
Supplementary Figure 28. $^{13}$C NMR (101 MHz, room temperature, CDCl$_3$) spectra of product 3a

Supplementary Figure 29. $^{19}$F NMR (101 MHz, room temperature, CDCl$_3$) spectra of product 3a
Supplementary Figure 30. NOESY (400 MHz, room temperature, CDCl₃) spectra of product 3a

Supplementary Figure 31. ¹H NMR (400 MHz, room temperature, CDCl₃) spectra of product 3b
Supplementary Figure 32. $^{13}$C NMR (101 MHz, room temperature, CDCl$_3$) spectra of product 3b.

Supplementary Figure 33. $^{19}$F NMR (376 MHz, room temperature, CDCl$_3$) spectra of product 3b.
Supplementary Figure 34. NOESY (400 MHz, room temperature, CDCl3) spectra of product 3b

Supplementary Figure 35. 1H NMR (400 MHz, room temperature, CDCl3) spectra of product 3c
**Supplementary Figure 36.** $^{13}$C NMR (101 MHz, room temperature, CDCl$_3$) spectra of product 3c

**Supplementary Figure 37.** $^{19}$F NMR (376 MHz, room temperature, CDCl$_3$) spectra of product 3c
Supplementary Figure 38. NOESY (400 MHz, room temperature, CDCl₃) spectra of product 3c

Supplementary Figure 39. ¹H NMR (400 MHz, room temperature, CDCl₃) spectra of product 3d
Supplementary Figure 40. $^{13}$C NMR (101 MHz, room temperature, CDCl$_3$) spectra of product 3d

Supplementary Figure 41. $^{19}$F NMR (376 MHz, room temperature, CDCl$_3$) spectra of product 3d
Supplementary Figure 42. NOESY (400 MHz, room temperature, CDCl₃) spectra of product 3d

Supplementary Figure 43. ¹H NMR (400 MHz, room temperature, CDCl₃) spectra of product 3e
Supplementary Figure 44. $^{13}$C NMR (101 MHz, room temperature, CDCl$_3$) spectra of product 3e

Supplementary Figure 45. $^{19}$F NMR (376 MHz, room temperature, CDCl$_3$) spectra of product 3e
**Supplementary Figure 46.** $^1$H NMR (400 MHz, room temperature, CDCl$_3$) spectra of product 3f

**Supplementary Figure 47.** $^{13}$C NMR (101 MHz, room temperature, CDCl$_3$) spectra of product 3f
Supplementary Figure 48. $^{19}$F NMR (376 MHz, room temperature, CDCl$_3$) spectra of product 3f

Supplementary Figure 49. $^1$H NMR (400 MHz, room temperature, CDCl$_3$) spectra of product 3g
Supplementary Figure 50. $^{13}$C NMR (101 MHz, room temperature, CDCl$_3$) spectra of product 3g

Supplementary Figure 51. $^{19}$F NMR (376 MHz, room temperature, CDCl$_3$) spectra of product 3g
Supplementary Figure 52. $^1$H NMR (400 MHz, room temperature, CDCl$_3$) spectra of product 3h

Supplementary Figure 53. $^{13}$C NMR (101 MHz, room temperature, CDCl$_3$) spectra of product 3h
Supplementary Figure 54. $^{19}$F NMR (376 MHz, room temperature, CDCl$_3$) spectra of product 3h.

Supplementary Figure 55. $^1$H NMR (500 MHz, room temperature, CDCl$_3$) spectra of product 3i.
**Supplementary Figure 56.** $^{13}$C NMR (126 MHz, room temperature, CDCl$_3$) spectra of product $3i$

**Supplementary Figure 57.** $^{19}$F NMR (471 MHz, room temperature, CDCl$_3$) spectra of product $3i$
Supplementary Figure 58. $^1$H NMR (400 MHz, room temperature, CDCl$_3$) spectra of product 3i'.

Supplementary Figure 59. $^{13}$C NMR (101 MHz, room temperature, CDCl$_3$) spectra of product 3i'.
Supplementary Figure 60. $^{19}$F NMR (376 MHz, room temperature, CDCl$_3$) spectra of product 3i’

Supplementary Figure 61. NOESY (400 MHz, room temperature, CDCl$_3$) spectra of product 3i’
Supplementary Figure 62. $^1$H NMR (400 MHz, room temperature, CDCl$_3$) spectra of product 3j

Supplementary Figure 63. $^{13}$C NMR (101 MHz, room temperature, CDCl$_3$) spectra of product 3j

S72
Supplementary Figure 64. $^{19}$F NMR (376 MHz, room temperature, CDCl$_3$) spectra of product 3j

Supplementary Figure 65. $^1$H NMR (500 MHz, room temperature, CDCl$_3$) spectra of product 3k
Supplementary Figure 66. $^{13}$C NMR (126 MHz, room temperature, CDCl$_3$) spectra of product 3k

Supplementary Figure 67. $^{19}$F NMR (471 MHz, room temperature, CDCl$_3$) spectra of product 3k
Supplementary Figure 68. NOESY (400 MHz, room temperature, CDCl₃) NMR spectra of product 3k

Supplementary Figure 69. ¹H NMR (500 MHz, room temperature, CDCl₃) spectra of product 3l
Supplementary Figure 70. $^{13}$C NMR (126 MHz, room temperature, CDCl$_3$) spectra of product 3l

Supplementary Figure 71. $^{19}$F NMR (471 MHz, room temperature, CDCl$_3$) spectra of product 3j
Supplementary Figure 72. NOESY (400 MHz, room temperature, CDCl₃) spectra of product 3j.

Supplementary Figure 73. ¹H NMR (400 MHz, room temperature, CDCl₃) spectra of product 3m.
Supplementary Figure 74. $^{13}$C NMR (101 MHz, room temperature, CDCl$_3$) spectra of product 3m

Supplementary Figure 75. $^{19}$F NMR (376 MHz, room temperature, CDCl$_3$) spectra of product 3m
Supplementary Figure 76. $^1$H NMR (400 MHz, room temperature, CDCl$_3$) spectra of product 3n

Supplementary Figure 77. $^{13}$C NMR (101 MHz, room temperature, CDCl$_3$) spectra of product 3n
Supplementary Figure 78. $^{19}$F NMR (376 MHz, room temperature, CDCl$_3$) spectra of product 3n

Supplementary Figure 79. $^1$H NMR (400 MHz, room temperature, CDCl$_3$) spectra of product 3o
Supplementary Figure 80. $^{13}$C NMR (101 MHz, room temperature, CDCl$_3$) spectra of product 3o

Supplementary Figure 81. $^{19}$F NMR (376 MHz, room temperature, CDCl$_3$) spectra of product 3o
**Supplementary Figure 82.** $^1$H NMR (400 MHz, room temperature, CDCl$_3$) spectra of product 3p

**Supplementary Figure 83.** $^{13}$C NMR (101 MHz, room temperature, CDCl$_3$) spectra of product 3p
Supplementary Figure 84. $^{19}$F NMR (376 MHz, room temperature, CDCl$_3$) spectra of product 3p

Supplementary Figure 85. $^1$H NMR (400 MHz, room temperature, CDCl$_3$) spectra of product 3q
Supplementary Figure 86. $^{13}$C NMR (101 MHz, room temperature, CDCl$_3$) spectra of product 3q

Supplementary Figure 87. $^{19}$F NMR (376 MHz, room temperature, CDCl$_3$) spectra of product 3q
Supplementary Figure 88. $^1$H NMR (400 MHz, room temperature, CDCl$_3$) spectra of product 3r

Supplementary Figure 89. $^{13}$C NMR (101 MHz, room temperature, CDCl$_3$) spectra of product 3r
Supplementary Figure 90. $^{19}$F NMR (376 MHz, room temperature, CDCl$_3$) spectra of product 3r

Supplementary Figure 91. $^1$H NMR (400 MHz, room temperature, CDCl$_3$) spectra of product 3s
**Supplementary Figure 92.** $^{13}$C NMR (101 MHz, room temperature, CDCl$_3$) spectra of product 3s

**Supplementary Figure 93.** $^{19}$F NMR (376 MHz, room temperature, CDCl$_3$) spectra of product 3s
**Supplementary Figure 94.** $^1$H NMR (400 MHz, room temperature, CDCl$_3$) spectra of product 3t

**Supplementary Figure 95.** $^{13}$C NMR (101 MHz, room temperature, CDCl$_3$) spectra of product 3t
Supplementary Figure 96. $^{19}$F NMR (376 MHz, room temperature, CDCl$_3$) spectra of product 3t

Supplementary Figure 97. $^1$H NMR (500 MHz, room temperature, CDCl$_3$) spectra of product 3u
**Supplementary Figure 98.** $^{13}$C NMR (126 MHz, room temperature, CDCl$_3$) spectra of product 3u

**Supplementary Figure 99.** $^{19}$F NMR (471 MHz, room temperature, CDCl$_3$) spectra of product 3u
Supplementary Figure 100. $^1$H NMR (400 MHz, room temperature, CDCl$_3$) spectra of product 3v

Supplementary Figure 101. $^{13}$C NMR (101 MHz, room temperature, CDCl$_3$) spectra of product 3v
Supplementary Figure 102. $^{19}$F NMR (376 MHz, room temperature, CDCl$_3$) spectra of product 3v.

Supplementary Figure 103. $^1$H NMR (400 MHz, room temperature, CDCl$_3$) spectra of product 3w.
**Supplementary Figure 104.** $^{13}$C NMR (101 MHz, room temperature, CDCl$_3$) spectra of product 3w

**Supplementary Figure 105.** $^{19}$F NMR (376 MHz, room temperature, CDCl$_3$) spectra of product 3w
Supplementary Figure 106. $^1$H NMR (500 MHz, room temperature, CDCl$_3$) spectra of product 3x

Supplementary Figure 107. $^{13}$C NMR (126 MHz, room temperature, CDCl$_3$) spectra of product 3x
**Supplementary Figure 108.** $^{19}$F NMR (471 MHz, room temperature, CDCl$_3$) spectra of product 3x

**Supplementary Figure 109.** $^1$H NMR (400 MHz, room temperature, CDCl$_3$) spectra of product 4a
Supplementary Figure 110. $^{13}$C NMR (101 MHz, room temperature, CDCl$_3$) spectra of product 4a

Supplementary Figure 111. $^{19}$F NMR (376 MHz, room temperature, CDCl$_3$) spectra of product 4a
**Supplementary Figure 112.** $^1$H NMR (400 MHz, room temperature, CDCl$_3$) spectra of product 4b

**Supplementary Figure 113.** $^{13}$C NMR (101 MHz, room temperature, CDCl$_3$) spectra of product 4b
Supplementary Figure 114. $^{19}$F NMR (376 MHz, room temperature, CDCl$_3$) spectra of product 4b

Supplementary Figure 115. $^1$H NMR (400 MHz, room temperature, CDCl$_3$) spectra of product 4c
Supplementary Figure 116. $^{13}$C NMR (101 MHz, room temperature, CDCl$_3$) spectra of product 4c

Supplementary Figure 117. $^{19}$F NMR (376 MHz, room temperature, CDCl$_3$) spectra of product 4c
Supplementary Figure 118. $^1$H NMR (500 MHz, room temperature, CDCl$_3$) spectra of product 4d

Supplementary Figure 119. $^{13}$C NMR (126 MHz, room temperature, CDCl$_3$) spectra of product 4d
Supplementary Figure 120. $^{19}$F NMR (471 MHz, room temperature, CDCl$_3$) spectra of product 4d

Supplementary Figure 121. $^1$H NMR (400 MHz, room temperature, CDCl$_3$) spectra of product 4e
**Supplementary Figure 122.** $^{13}$C NMR (101 MHz, room temperature, CDCl$_3$) spectra of product $4e$

**Supplementary Figure 123.** $^{19}$F NMR (376 MHz, room temperature, CDCl$_3$) spectra of product $4e$
Supplementary Figure 124. $^1$H NMR (400 MHz, room temperature, CDCl$_3$) spectra of product 4f

Supplementary Figure 125. $^{13}$C NMR (101 MHz, room temperature, CDCl$_3$) spectra of product 4f
Supplementary Figure 126. $^{19}$F NMR (376 MHz, room temperature, CDCl$_3$) spectra of product 4f

Supplementary Figure 127. NOESY (400 MHz, room temperature, CDCl$_3$) spectra of product 4f
Supplementary Figure 128. $^1$H NMR (500 MHz, room temperature, CDCl$_3$) spectra of product 4g

Supplementary Figure 129. $^{13}$C NMR (126 MHz, room temperature, CDCl$_3$) spectra of product 4g
Supplementary Figure 130. $^{19}$F NMR (471 MHz, room temperature, CDCl$_3$) spectra of product 4g

Supplementary Figure 131. $^1$H NMR (500 MHz, room temperature, CDCl$_3$) spectra of product 4h
Supplementary Figure 132. $^{13}$C NMR (126 MHz, room temperature, CDCl$_3$) spectra of product 4h

Supplementary Figure 133. $^{19}$F NMR (471 MHz, room temperature, CDCl$_3$) spectra of product 4h
**Supplementary Figure 134.** NOESY NMR (400 MHz, room temperature, CDCl₃) spectra of product 4h

**Supplementary Figure 135.** ¹H NMR (500 MHz, room temperature, CDCl₃) spectra of product 4i
Supplementary Figure 136. $^{13}$C NMR (126 MHz, room temperature, CDCl$_3$) spectra of product 4i

Supplementary Figure 137. $^{19}$F NMR (471 MHz, room temperature, CDCl$_3$) spectra of product 4i
**Supplementary Figure 138.** NOESY (400 MHz, room temperature, CDCl₃) spectra of product 4i

**Supplementary Figure 139.** ¹H NMR (500 MHz, room temperature, CDCl₃) spectra of product 4i’
Supplementary Figure 140. $^{13}$C NMR (126 MHz, room temperature, CDCl$_3$) spectra of product 4i’

Supplementary Figure 141. $^{19}$F NMR (471 MHz, room temperature, CDCl$_3$) spectra of product 4i’
**Supplementary Figure 142.** NOESY (400 MHz, room temperature, CDCl₃) spectra of product 4i'

**Supplementary Figure 143.** ¹H NMR (400 MHz, room temperature, CDCl₃) spectra of product 6a
**Supplementary Figure 144.** $^{13}$C NMR (101 MHz, room temperature, CDCl$_3$) spectra of product 6a

**Supplementary Figure 145.** $^{19}$F NMR (376 MHz, room temperature, CDCl$_3$) spectra of product 6a
Supplementary Figure 146. $^1$H NMR (400 MHz, room temperature, CDCl$_3$) spectra of product 6b

Supplementary Figure 147. $^{13}$C NMR (101 MHz, room temperature, CDCl$_3$) spectra of product 6b
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Supplementary Figure 151. $^{19}$F NMR (376 MHz, room temperature, CDCl$_3$) spectra of product 6c
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Supplementary Figure 153. $^{13}$C NMR (101 MHz, room temperature, CDCl$_3$) spectra of product 6d
Supplementary Figure 154. $\text{^{19}F NMR}$ (376 MHz, room temperature, CDCl$_3$) spectra of product 6d

Supplementary Figure 155. $\text{^{1}H NMR}$ (400 MHz, room temperature, CDCl$_3$) spectra of product 6e
Supplementary Figure 156. $^{13}$C NMR (101 MHz, room temperature, CDCl$_3$) spectra of product 6e

Supplementary Figure 157. $^{19}$F NMR (376 MHz, room temperature, CDCl$_3$) spectra of product 6e
Supplementary Figure 158. $^1$H NMR (400 MHz, room temperature, CDCl$_3$) spectra of product 6f

Supplementary Figure 159. $^{13}$C NMR (101 MHz, room temperature, CDCl$_3$) spectra of product 6f
Supplementary Figure 160. $^{19}$F NMR (376 MHz, room temperature, CDCl₃) spectra of product 6f

Supplementary Figure 161. $^1$H (400 MHz, room temperature, CDCl₃) NMR spectra of product 6g
Supplementary Figure 162. $^{13}$C NMR (101 MHz, room temperature, CDCl$_3$) spectra of product 6g

Supplementary Figure 163. $^{19}$F NMR (376 MHz, room temperature, CDCl$_3$) spectra of product 6g
Supplementary Figure 164. $^1$H NMR (400 MHz, room temperature, CDCl$_3$) spectra of product 6h

Supplementary Figure 165. $^{13}$C NMR (101 MHz, room temperature, CDCl$_3$) spectra of product 6h
Supplementary Figure 166. $^{19}$F NMR (376 MHz, room temperature, CDCl$_3$) spectra of product 6h

Supplementary Figure 167. $^1$H NMR (400 MHz, room temperature, CDCl$_3$) spectra of product 6i
Supplementary Figure 168. $^{13}$C NMR (101 MHz, room temperature, CDCl$_3$) spectra of product 6i

Supplementary Figure 169. $^{19}$F NMR (376 MHz, room temperature, CDCl$_3$) spectra of product 6i
Supplementary Figure 170. $^1$H NMR (400 MHz, room temperature, CDCl$_3$) spectra of product 6j

Supplementary Figure 171. $^{13}$C NMR (101 MHz, room temperature, CDCl$_3$) spectra of product 6j
Supplementary Figure 172. $^{19}$F NMR (376 MHz, room temperature, CDCl$_3$) spectra of product 6j

Supplementary Figure 173. $^1$H NMR (400 MHz, room temperature, CDCl$_3$) spectra of product 6k
Supplementary Figure 174. $^{13}$C NMR (101 MHz, room temperature, CDCl$_3$) spectra of product 6k

Supplementary Figure 175. $^{19}$F NMR (376 MHz, room temperature, CDCl$_3$) spectra of product 6k
Supplementary Figure 176. $^1$H NMR (400 MHz, room temperature, CDCl$_3$) spectra of product 8a

Supplementary Figure 177. $^{13}$C NMR (101 MHz, room temperature, CDCl$_3$) spectra of product 8a
Supplementary Figure 178. $^{19}$F NMR (376 MHz, room temperature, CDCl$_3$) spectra of product 8a

Supplementary Figure 179. $^1$H NMR (400 MHz, room temperature, CDCl$_3$) spectra of product 8b
Supplementary Figure 180. $^{13}$C NMR (101 MHz, room temperature, CDCl$_3$) spectra of product 8b

Supplementary Figure 181. $^{19}$F NMR (376 MHz, room temperature, CDCl$_3$) spectra of product 8b
Supplementary Figure 182. $^1$H NMR (400 MHz, room temperature, CDCl$_3$) spectra of product 8c

Supplementary Figure 183. $^{13}$C NMR (101 MHz, room temperature, CDCl$_3$) spectra of product 8c
Supplementary Figure 184. $^{19}$F NMR (376 MHz, room temperature, CDCl$_3$) spectra of product 8c

Supplementary Figure 185. $^1$H NMR (400 MHz, room temperature, CDCl$_3$) spectra of product 8d
**Supplementary Figure 186.** $^{13}$C (101 MHz, room temperature, CDCl$_3$) NMR spectra of product 8d

**Supplementary Figure 187.** $^{19}$F NMR (376 MHz, room temperature, CDCl$_3$) spectra of product 8d
Supplementary Figure 188. $^1$H NMR (400 MHz, room temperature, CDCl$_3$) spectra of product 8e

Supplementary Figure 189. $^{13}$C NMR (101 MHz, room temperature, CDCl$_3$) spectra of product 8e
Supplementary Figure 190. $^{19}$F NMR (376 MHz, room temperature, CDCl$_3$) spectra of product 8e

Supplementary Figure 191. $^1$H NMR (400 MHz, room temperature, CDCl$_3$) spectra of product 8f
**Supplementary Figure 192.** $^{13}$C NMR (101 MHz, room temperature, CDCl$_3$) spectra of product 8f

**Supplementary Figure 193.** $^{19}$F NMR (376 MHz, room temperature, CDCl$_3$) spectra of product 8f
Supplementary Figure 194. $^1$H NMR (400 MHz, room temperature, CDCl$_3$) spectra of product 8g

Supplementary Figure 195. $^{13}$C NMR (101 MHz, room temperature, CDCl$_3$) spectra of product 8g
**Supplementary Figure 196.** $^{19}$F NMR (376 MHz, room temperature, CDCl$_3$) spectra of product 8g

**Supplementary Figure 197.** $^1$H NMR (400 MHz, room temperature, CDCl$_3$) spectra of product 8h
Supplementary Figure 198. $^{13}$C NMR (101 MHz, room temperature, CDCl$_3$) spectra of product $8h$

Supplementary Figure 199. $^{19}$F NMR (376 MHz, room temperature, CDCl$_3$) spectra of product $8h$
Supplementary Figure 200. $^1$H NMR (400 MHz, room temperature, CDCl$_3$) spectra of product 8i

Supplementary Figure 201. $^{13}$C NMR (101 MHz, room temperature, CDCl$_3$) spectra of product 8i
Supplementary Figure 202. $^{19}$F NMR (376 MHz, room temperature, CDCl$_3$) spectra of product 8i

Supplementary Figure 203. $^1$H NMR (400 MHz, room temperature, CDCl$_3$) spectra of product 8j
Supplementary Figure 204. $^{13}$C NMR (101 MHz, room temperature, CDCl$_3$) spectra of product 8j

Supplementary Figure 205. $^{19}$F NMR (376 MHz, room temperature, CDCl$_3$) spectra of product 8j
Supplementary Figure 206. $^1$H NMR (400 MHz, room temperature, CDCl$_3$) spectra of product 8k

Supplementary Figure 207. $^{13}$C NMR (101 MHz, room temperature, CDCl$_3$) spectra of product 8k

S144
**Supplementary Figure 208.** $^{19}$F NMR (376 MHz, room temperature, CDCl$_3$) spectra of product 8k

**Supplementary Figure 209.** $^1$H NMR (400 MHz, room temperature, CDCl$_3$) spectra of product 8l
Supplementary Figure 210. $^{13}$C NMR (101 MHz, room temperature, CDCl$_3$) spectra of product 8l

Supplementary Figure 211. $^{19}$F NMR (376 MHz, room temperature, CDCl$_3$) spectra of product 8l
Supplementary Figure 212. $^1$H NMR (400 MHz, room temperature, CDCl$_3$) spectra of product 10

Supplementary Figure 213. $^{13}$C NMR (101 MHz, room temperature, CDCl$_3$) spectra of product 10
Supplementary Figure 214. $^1$H NMR (400 MHz, room temperature, CDCl$_3$) spectra of product 12

Supplementary Figure 215. $^{13}$C NMR (101 MHz, room temperature, CDCl$_3$) spectra of product 12
Supplementary Figure 216. $^1$H NMR (400 MHz, room temperature, CDCl$_3$) spectra of product 14

Supplementary Figure 217. $^{13}$C NMR (101 MHz, room temperature, CDCl$_3$) spectra of product 14
Supplementary Figure 218. $^1$H NMR (400 MHz, room temperature, CDCl$_3$) spectra of product 16

Supplementary Figure 219. $^{13}$C NMR (101 MHz, room temperature, CDCl$_3$) spectra of product 16
Supplementary Figure 220. $^{19}$F NMR (376 MHz, room temperature, CDCl₃) spectra of product 16

Supplementary Figure 221. $^1$H NMR (400 MHz, room temperature, CDCl₃) spectra of product 19
Supplementary Figure 222. $^{13}$C NMR (101 MHz, room temperature, CDCl$_3$) spectra of product 19

Supplementary Figure 223. $^{19}$F NMR (376 MHz, room temperature, CDCl$_3$) spectra of product 19
XII. References


