Catalyst-free Geminal Aminofluorination of ortho-Sulfonamide-Tethered Alkylidene cyclopropanes via Wagner-Meerwein Rearrangement

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**General Remarks**

$^1$H and $^{13}$C NMR spectra were recorded at 400 MHz, respectively. Multiplicities are reported using the following abbreviations: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad resonance. HRMS spectra were recorded by ESI method. Infrared spectra were recorded on a Perkin-Elmer PE-983 spectrometer with absorption in cm$^{-1}$. Mass spectra were recorded by ESI, and HRMS was measured on a HP-5989 instrument. Melting points were determined on a digital melting point apparatus and temperatures were uncorrected. X-ray structure was determined on a Bruker Smart-1000 X-ray Diffraction meter. The employed solvents were dried up by standard methods when necessary. Commercially obtained reagents such as “F” reagent 2a (Selectfluor et al.), S1 (anthranilic acid derivatives, 2-aminobenzophenone derivatives, 2-aminobenzonitrile derivatives), MeLi, RMgCl or RMgBr, nBuLi, AcOH et al. were used without further purification. All reactions were monitored by TLC with silica gel coated plates (Huanghai GF254). Flash column chromatography was performed by using 300-400 mesh silica gel eluting with ethyl acetate and petroleum ether at increased pressure. Abbreviations are reported as follows: EA = ethyl acetate, DCM = dichloromethane, DCE = 1,2-dichloroethane, MeOH = methanol, THF = tetrahydrofuran, DMF = N,N-dimethylformamide, Ns = 4-nitrobenzenesulfonyl, Ts = 4-methylbenzenesulfonyl, Ms = methanesulfonyl, Bz = Benzoyl, Ac = Acetyl, TFA = trifluoroacetic acid, Tf = trifluoromethanesulfonyl, Nf = perfluoro-1-butanesulfonyl, NFSI = N-fluorobenzensulfonimide.
### Screen of reaction conditions

**Table S1.** Screen of reaction conditions on solvent.\(^{a,b}\)

![Chemical structure](image)

<table>
<thead>
<tr>
<th>entry(^a)</th>
<th>2a (equiv)</th>
<th>solvent</th>
<th>T/°C</th>
<th>time/h</th>
<th>yield (%)(^b)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1.0</td>
<td>MeCN</td>
<td>rt</td>
<td>8</td>
<td>trace</td>
</tr>
<tr>
<td>2</td>
<td>1.5</td>
<td>MeCN</td>
<td>rt</td>
<td>8</td>
<td>35</td>
</tr>
<tr>
<td>3</td>
<td>2.0</td>
<td>MeCN</td>
<td>rt</td>
<td>8</td>
<td>40</td>
</tr>
<tr>
<td>4</td>
<td>3.0</td>
<td>MeCN</td>
<td>rt</td>
<td>8</td>
<td>46</td>
</tr>
<tr>
<td>5</td>
<td>3.0</td>
<td>CH(_2)CH(_2)CN</td>
<td>rt</td>
<td>8</td>
<td>trace</td>
</tr>
<tr>
<td>6</td>
<td>3.0</td>
<td>PhCN</td>
<td>rt</td>
<td>8</td>
<td>trace</td>
</tr>
<tr>
<td>7</td>
<td>3.0</td>
<td>DMF</td>
<td>rt</td>
<td>8</td>
<td>trace</td>
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<tr>
<td>8</td>
<td>3.0</td>
<td>DMSO</td>
<td>rt</td>
<td>8</td>
<td>N.D.</td>
</tr>
<tr>
<td>9</td>
<td>3.0</td>
<td>MeOH</td>
<td>rt</td>
<td>8</td>
<td>&lt;1%</td>
</tr>
<tr>
<td>10</td>
<td>3.0</td>
<td>tBuOH</td>
<td>rt</td>
<td>8</td>
<td>&lt;1%</td>
</tr>
<tr>
<td>11</td>
<td>3.0</td>
<td>CHCl(_3)</td>
<td>rt</td>
<td>8</td>
<td>&lt;1%</td>
</tr>
<tr>
<td>12</td>
<td>3.0</td>
<td>acetone</td>
<td>rt</td>
<td>8</td>
<td>&lt;5%</td>
</tr>
<tr>
<td>13</td>
<td>3.0</td>
<td>EA</td>
<td>rt</td>
<td>8</td>
<td>N.D.</td>
</tr>
<tr>
<td>14</td>
<td>3.0</td>
<td>THF</td>
<td>rt</td>
<td>8</td>
<td>N.D.</td>
</tr>
<tr>
<td>15</td>
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<td>DCE</td>
<td>rt</td>
<td>8</td>
<td>N.D.</td>
</tr>
<tr>
<td>16</td>
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<tr>
<td>17</td>
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<td>MeCN</td>
<td>0</td>
<td>8</td>
<td>19</td>
</tr>
<tr>
<td>18</td>
<td>3.0</td>
<td>MeCN</td>
<td>60</td>
<td>8</td>
<td>N.D.</td>
</tr>
</tbody>
</table>

\[a\] All reactions were carried out with 1r (0.1 mmol) and “F“ source (0.3 mmol) in solvent (1.0 mL) at ambient temperature for 8 h. \[b\] \(^{19}\)F NMR yields using 1-fluoronaphthalene as an internal standard.
Table S2. Screen of reaction conditions on “F” reagent.\textsuperscript{a,b}

\[
\text{PhNHTs} + \text{CH}_3\text{CN, rt, 6 h} \rightarrow \text{TsF}
\]

[a] All reactions were carried out with 1r (0.1 mmol) and “F” source (0.3 mmol) in solvent (1.0 mL) at ambient temperature for 8 h. [b] \textsuperscript{19}F NMR yields using 1-fluoronaphthalene as an internal standard.

Table S3. Screen of reaction conditions on equivalent of water.\textsuperscript{a,b}

<table>
<thead>
<tr>
<th>entry</th>
<th>(\text{H}_2\text{O} \text{ (eq.)} )</th>
<th>solvent</th>
<th>(T/\degree\text{C} )</th>
<th>time/h</th>
<th>yield (%)\textsuperscript{b}</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.5</td>
<td>MeCN</td>
<td>R. T.</td>
<td>8</td>
<td>45</td>
</tr>
<tr>
<td>2</td>
<td>1.0</td>
<td>MeCN</td>
<td>R. T.</td>
<td>8</td>
<td>44</td>
</tr>
<tr>
<td>3</td>
<td>2.0</td>
<td>MeCN</td>
<td>R. T.</td>
<td>8</td>
<td>45</td>
</tr>
<tr>
<td>4</td>
<td>5.0</td>
<td>MeCN</td>
<td>R. T.</td>
<td>8</td>
<td>47</td>
</tr>
<tr>
<td>5</td>
<td>10</td>
<td>MeCN</td>
<td>R. T.</td>
<td>8</td>
<td>42</td>
</tr>
<tr>
<td>6</td>
<td>4Å MS</td>
<td>MeCN</td>
<td>R. T.</td>
<td>8</td>
<td>47</td>
</tr>
</tbody>
</table>

[a] All reactions were carried out with 1r (0.1 mmol) and “F” source (0.3 mmol) in CH\textsubscript{3}CN (1.0 mL) at ambient temperature for 8 h. [b] \textsuperscript{19}F NMR yields using 1-fluoronaphthalene as an internal standard.
Table S4. Screen of reaction conditions on additives.^[a,b]

![Chemical reaction diagram]

<table>
<thead>
<tr>
<th>entry</th>
<th>additive</th>
<th>equiv</th>
<th>yield (%)^[b]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>LnF&lt;sub&gt;3&lt;/sub&gt;</td>
<td>0.1</td>
<td>53</td>
</tr>
<tr>
<td>2</td>
<td>CuBr</td>
<td>0.2</td>
<td>N.R.</td>
</tr>
<tr>
<td>3</td>
<td>Ce(OTf)&lt;sub&gt;3&lt;/sub&gt;</td>
<td>0.2</td>
<td>N.R.</td>
</tr>
<tr>
<td>4</td>
<td>Bi(OTf)&lt;sub&gt;3&lt;/sub&gt;</td>
<td>0.2</td>
<td>N.R.</td>
</tr>
<tr>
<td>5</td>
<td>PhII(OAc)&lt;sub&gt;2&lt;/sub&gt;</td>
<td>3.0</td>
<td>52</td>
</tr>
<tr>
<td>6</td>
<td>PhII(CO&lt;sub&gt;2&lt;/sub&gt;C&lt;sub&gt;2&lt;/sub&gt;)&lt;sub&gt;2&lt;/sub&gt;</td>
<td>0.2</td>
<td>58</td>
</tr>
<tr>
<td>7</td>
<td>SiO&lt;sub&gt;2&lt;/sub&gt;</td>
<td>3.0</td>
<td>45</td>
</tr>
<tr>
<td>8</td>
<td>TiOH</td>
<td>0.2</td>
<td>28</td>
</tr>
<tr>
<td>9</td>
<td>Yb(OTf)&lt;sub&gt;3&lt;/sub&gt;</td>
<td>0.2</td>
<td>35</td>
</tr>
<tr>
<td>10</td>
<td>ZnCl&lt;sub&gt;2&lt;/sub&gt;</td>
<td>0.2</td>
<td>39</td>
</tr>
<tr>
<td>11</td>
<td>Quinine</td>
<td>0.2</td>
<td>35</td>
</tr>
<tr>
<td>12</td>
<td>TsOH</td>
<td>0.2</td>
<td>16</td>
</tr>
<tr>
<td>13</td>
<td>AgNO&lt;sub&gt;3&lt;/sub&gt;</td>
<td>0.2</td>
<td>19</td>
</tr>
<tr>
<td>14</td>
<td>Na&lt;sub&gt;2&lt;/sub&gt;S&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;8&lt;/sub&gt;</td>
<td>3.0</td>
<td>45</td>
</tr>
<tr>
<td>15</td>
<td>tBuOOH</td>
<td>3.0</td>
<td>27</td>
</tr>
<tr>
<td>16</td>
<td>NIS</td>
<td>3.0</td>
<td>N.R.</td>
</tr>
<tr>
<td>17</td>
<td>BF&lt;sub&gt;3&lt;/sub&gt;Et&lt;sub&gt;2&lt;/sub&gt;O</td>
<td>3.0</td>
<td>N.R.</td>
</tr>
<tr>
<td>18</td>
<td>K&lt;sub&gt;2&lt;/sub&gt;CO&lt;sub&gt;3&lt;/sub&gt;</td>
<td>3.0</td>
<td>25</td>
</tr>
<tr>
<td>19</td>
<td>AgNTf&lt;sub&gt;2&lt;/sub&gt;</td>
<td>0.2</td>
<td>46</td>
</tr>
<tr>
<td>20</td>
<td>MgSO&lt;sub&gt;4&lt;/sub&gt;</td>
<td>3.0</td>
<td>41</td>
</tr>
</tbody>
</table>

^[a] All reactions were carried out with 1r (0.1 mmol) and “F” source (0.3 mmol) in CH<sub>3</sub>CN (1.0 mL) at ambient temperature for 8 h. [b] <sup>19</sup>F NMR yields using 1-fluoronaphthalene as an internal standard.
Table S5. Screen of reaction conditions using 1a as template substrate.\textsuperscript{a,b,c}

<table>
<thead>
<tr>
<th>entry\textsuperscript{a}</th>
<th>additive</th>
<th>equiv (x)</th>
<th>yield\textsuperscript{d} (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>AgF</td>
<td>2</td>
<td>30</td>
</tr>
<tr>
<td>2</td>
<td>InF\textsubscript{3}</td>
<td>2</td>
<td>46</td>
</tr>
<tr>
<td>3</td>
<td>PhOH</td>
<td>2</td>
<td>68</td>
</tr>
<tr>
<td>4</td>
<td>PhCOCOOH</td>
<td>2</td>
<td>74</td>
</tr>
<tr>
<td>5</td>
<td>CH\textsubscript{3}COOH</td>
<td>2</td>
<td>76</td>
</tr>
<tr>
<td>6</td>
<td>CF\textsubscript{3}COOH</td>
<td>2</td>
<td>-</td>
</tr>
<tr>
<td>7</td>
<td>adipic acid</td>
<td>2</td>
<td>75</td>
</tr>
<tr>
<td>8</td>
<td>citric acid</td>
<td>2</td>
<td>66</td>
</tr>
<tr>
<td>9</td>
<td>2,6-lutidine</td>
<td>2</td>
<td>31</td>
</tr>
<tr>
<td>10</td>
<td>DABCO</td>
<td>2</td>
<td>17</td>
</tr>
<tr>
<td>11</td>
<td>phenol</td>
<td>2</td>
<td>46</td>
</tr>
<tr>
<td>12</td>
<td>-</td>
<td>-</td>
<td>70</td>
</tr>
<tr>
<td>13</td>
<td>NaHCO\textsubscript{3}</td>
<td>2</td>
<td>36</td>
</tr>
<tr>
<td>14</td>
<td>CH\textsubscript{3}COOH</td>
<td>0.5</td>
<td>76</td>
</tr>
<tr>
<td>15</td>
<td>CH\textsubscript{3}COOH</td>
<td>1</td>
<td>80</td>
</tr>
<tr>
<td>16</td>
<td>CH\textsubscript{3}COOH</td>
<td>5</td>
<td>82</td>
</tr>
<tr>
<td>17</td>
<td>CH\textsubscript{3}COOH</td>
<td>10</td>
<td>85 (81\textsuperscript{c})</td>
</tr>
<tr>
<td>18</td>
<td>CH\textsubscript{3}COOH</td>
<td>100</td>
<td>65</td>
</tr>
<tr>
<td>19</td>
<td>PhCOOH</td>
<td>10</td>
<td>79 (73\textsuperscript{d})</td>
</tr>
</tbody>
</table>

[a] All reactions were carried out with 1a (0.1 mmol), “F” source (0.3 mmol) and additives in CH\textsubscript{3}CN (1.0 mL) at ambient temperature for 6 h. [b] \textsuperscript{19}F NMR yields using 1-fluoronaphthalene as an internal standard. [c] Isolated yields.

No reaction occurred for these substrates:
General procedure for the preparation of compounds 1a-1ac

**For the synthesis of S2**

\[
\begin{align*}
\text{S1}' & \quad \text{commercial available} \\
\text{O} & \quad \text{MeLi (3.3 equiv)} \\
\text{OH} & \quad \text{DMA, 0 }^\circ\text{C, 2 h} \\
\text{NH}_2 & \quad \text{X'} \\
\text{S2}' & \quad \text{MeO} \\
\end{align*}
\]

**For the synthesis of S3 and 1**

\[
\begin{align*}
\text{S2} & \quad \text{commercial available} \\
\text{O} & \quad \text{Br} \\
\text{OH} & \quad \text{THF, reflux, 24 h} \\
\text{NH}_2 & \quad \text{X'} \\
\text{S3} & \quad \text{X'} \\
\text{R(Ar)} & \quad \text{TsCl, pyridine, DCM, rt} \\
\text{S3} & \quad \text{or MsCl, TEA, DCM, 0 }^\circ\text{C} \\
\text{R(Ar)} & \quad \text{or ArSO}_2\text{Cl, pyridine, rt} \\
\text{1} & \quad \text{X'} \\
\end{align*}
\]

There are some substrates S3 unable to obtain:

\[
\begin{align*}
\text{S2} & \quad \text{X'} \\
\text{S3} & \quad \text{X'} \\
\text{R(Ar)} & \quad \text{NaH} \\
\text{S3} & \quad \text{THF, reflux, 24 h} \\
\end{align*}
\]

Compounds S2,\textsuperscript{1,2,3} S3\textsuperscript{4} and several compounds 1\textsuperscript{5} were prepared according to the previous literature.

*General procedure A:* For the synthesis of S2\textsuperscript{1:}

To a solution of S1' (30 mmol, 1.0 equiv) in DMA (50 mL, superdry) was added MeLi (49.5 mL, 99 mmol, 3.3 equiv, 2.0 M) dropwise at 0 °C and then the mixture was stirred at 0 °C for 2 h, then 100 mL 1.0 N HCl was added for quenching the reaction. After separation, the resulting aqueous mixture was extracted with EA (3 x 30 mL), and the combined extracts were washed with brine,
dried over anhydrous Na₂SO₄. After the solution was filtered and the solvent was evaporated under vacuum, the residue was purified by a flash chromatograph on silica gel using PE/EA (30:1) as the eluent to yield the products S₂'.

General procedure B: For the synthesis of S₂'':
To a solution of S₁'' (30 mmol, 1.0 equiv) in THF (50 mL, superdry) was added RMgBr or RMgCl (90 mmol, 3.0 equiv) dropwise at 0 °C and then the mixture was stirred at rt for 6 h, then 100 mL saturated NH₄Cl aqueous solution was added for quenching the reaction, after separation, the resulting aqueous mixture was extracted with EA (3 x 30 mL), and the combined extracts were washed with brine, dried over anhydrous Na₂SO₄. After the solution was filtered and the solvent was evaporated under vacuum, the residue was purified by a flash chromatograph on silica gel using PE/EA (30:1) as the eluent to yield the products S₂''.

General procedure C: For the synthesis of S₂''':
A solution of S₁''' (30 mmol, 1.0 equiv) and CDI (30 mmol, 1.0 equiv) in dry THF (100 mL) was stirred at rt for 2 h, then, a solution of N,O-dimethylhydroxylamine hydrochloride (2.93 g, 30 mmol, 1.0 equiv) and NEt₃ (5 mL, 36 mmol, 1.2 equiv) in 50 mL dry THF was added and the mixture was stirred at rt overnight. The reaction mixture was then poured onto an equal volume of ice and saturated Na₂CO₃. The THF was then removed by rotary evaporation, and the resulting aqueous mixture was extracted with EA (3 x 30 mL), and the combined extracts were washed with water and brine, dried over anhydrous Na₂SO₄. After the solution was filtered and the solvent was evaporated under vacuum, the residue was purified by a flash chromatograph on silica gel using PE/EA (1:1) as the eluent to yield the products S₂'''.

Then, n-BuLi (2.0 equiv) was added slowly to a mixture of S₂''' and ArBr (1.0 equiv) in dry THF over 1.0 h in a flamed-dried 100 mL Schlenk tube at -78 °C under the protection of Ar atmosphere, and 1.0 N HCl (2.0 equiv) was added at -78 °C. The mixture was extracted with EA (3 x 20 mL), and the combined extracts were washed with saturated Na₂CO₃, dried over anhydrous Na₂SO₄. After the solution was filtered and the solvent was evaporated under vacuum, the residue was purified by a flash chromatograph on silica gel using PE/EA (30:1) as the eluent to yield the products S₂'''.

General procedure D: For the synthesis of S₃⁴:
A solution of (4-bromobutyl)triphenylphosphonium bromide (1.3 equiv) and NaH (2.6 equiv) in THF (25 mL) was stirred at 75 °C under Ar atmosphere for 12 h. Afterwards, compound S₂ in THF
(10 mL) was added and the reaction solution was stirred at 75 °C until compound S2 was consumed completely. The reaction mixture was cooled to room temperature, and the mixture was filtered through a celite pad. The filtrate was concentrated under reduced pressure and the residue was purified by a silica gel flash chromatography (PE/EA (100:1-20:1) to afford the product S3.

**General procedure E:** For the synthesis of 15:

R(Ar)SO2Cl (1.05-1.5 equiv) was added slowly to a solution of S3 in dry DCM or pyridine at 0 °C followed the addition of NEt3 or pyridine, and then the mixture was stirred at room temperature for 12 h (TsCl), and 0 °C for 2 h (MsCl), at rt for 6 h (BsCl, PhSO2Cl). The reaction mixture was concentrated under reduced pressure and the residue was purified by a silica gel flash chromatography (PE/EA (10:1) to afford the product 1.
Spectroscopic data for products 1g-1y

Compound 1g: A white solid (547.3 mg, 85%); M.p. 111-112 °C. \(^1\)H NMR (400 MHz, Chloroform-\(d\)) \(\delta\) 0.84 (t, \(J = 7.4\) Hz, 3H), 0.96 (t, \(J = 7.7\) Hz, 2H), 1.29 (t, \(J = 7.7\) Hz, 2H), 2.19 (q, \(J = 7.7\) Hz, 2H), 2.36 (s, 3H), 6.93 (s, 1H), 6.96 – 7.09 (m, 2H), 7.13 – 7.23 (m, 3H), 7.56 – 7.69 (m, 3H). \(^13\)C NMR (100 MHz, Chloroform-\(d\)) \(\delta\) 2.7, 3.4, 12.4, 21.5, 29.8, 41.8, 119.2, 122.6, A 123.9, 127.1, 127.4, 127.6, 128.3, 129.5, 132.7, 133.8, 136.4, 143.8. IR (neat) \(\nu\) 3259, 1598, 1580, 1484, 1387, 1335, 1165, 1085, 934, 901, 814, 751, 679 cm\(^{-1}\). HRMS (ESI) Calcd. for C\(_{19}\)H\(_{25}\)N\(_2\)O\(_2\)S requires (M\(^{+}\)+NH\(_4\))\(^{+}\): 345.1631, Found: 345.1625.
Compound 1i: A white solid (327.6 mg, 59%); M.p. 78-79 °C. $^1$H NMR (400 MHz, Chloroform-$d$) δ 0.86 – 0.91 (m, 3H), 0.97 – 1.02 (m, 2H), 1.13 – 1.33 (m, 25H), 2.15 (t, $J = 7.1$ Hz, 2H), 2.36 (s, 3H), 6.92 (s, 1H), 7.00 – 7.05 (m, 2H), 7.17 – 7.22 (m, 3H), 7.60 – 7.67 (m, 3H). $^{13}$C NMR (100 MHz, Chloroform-$d$) δ 3.2, 3.4, 14.2, 21.5, 22.7, 27.8, 29.4, 29.5, 29.66, 29.69, 29.72, 32.0, 36.7, 119.1, 123.2, 123.8, 126.3, 127.2, 127.6, 128.5, 129.5, 132.8, 133.9, 136.6, 143.7. IR (neat) ν 3267, 2977, 2954, 2922, 2850, 1600, 1571, 1487, 1459, 1378, 1340, 1166, 1093, 908, 813, 752, 723, 706, 683 cm$^{-1}$. HRMS (ESI) Calcd. for C$_{29}$H$_{45}$N$_2$O$_2$S requires (M$^+$+NH$_4$): 485.3196, Found: 485.3191.
Compound 1j: A pale yellow solid (389.1 mg, 54%); M.p. 141-142 °C. ¹H NMR (400 MHz, Chloroform-­d) δ 1.11 (d, J = 7.5 Hz, 2H), 1.21 (d, J = 7.5 Hz, 2H), 1.68 (s, 3H), 2.37 (s, 3H), 6.77
(d, \( J = 9.5 \) Hz, 1H), 6.84 – 7.09 (m, 2H), 7.09 – 7.31 (m, 2H), 7.44 – 7.55 (m, 2H), 7.59 (dd, \( J = 9.1, 5.3 \) Hz, 1H). \(^{13}\text{C}\) NMR (101 MHz, Chloroform-\( d \)) \( \delta \) 3.1, 4.8, 21.5, 22.0, 114.3, 114.5, 114.8, 121.4, 123.9 (d, \( J = 8.6 \) Hz), 124.1, 127.1, 129.2, 129.5, 135.9, 136.7 (d, \( J = 7.7 \) Hz), 143.8, 159.8 (d, \( J = 244.9 \) Hz). \(^{19}\text{F}\) NMR (376 MHz, Chloroform-\( d \)) \( \delta \) -117.4. IR (neat) \( \nu \) 3255, 2978, 2919, 2845, 1609, 1598, 1494, 1378, 1329, 1162, 1091, 896, 874, 815, 676 cm\(^{-1}\). HRMS (ESI) Calcd. for \( \text{C}_{18}\text{H}_{22}\text{FN}_{2}\text{O}_{2}\text{S} \) requires (M\(^+\) + NH\(_4\)): 349.1381, Found: 349.1376.
**Compound 1k**: A yellow solid (395.4 mg, 35%); M.p. 81-82 °C. $^1$H NMR (400 MHz, Chloroform-$d$) $\delta$ 0.69 – 0.86 (m, 3H), 0.89 – 1.01 (m, 2H), 1.13 (h, $J = 3.0$ Hz, 4H), 1.25 (t, $J = 7.9$ Hz, 2H),
2.05 (t, $J = 6.9$ Hz, 2H), 2.34 (s, 3H), 6.74 (dd, $J = 9.2$, 3.0 Hz, 1H), 6.87 (s, 1H), 6.90 (ddd, $J = 8.4$, 4.2 Hz, 1H), 7.11 – 7.23 (m, 2H), 7.53 – 7.60 (m, 2H), 7.63 (dd, $J = 9.0$, 5.2 Hz, 1H). $^{13}$C NMR (101 MHz, Chloroform-$d$) δ 3.1, 3.6, 13.9, 21.5, 22.6, 29.8, 36.0, 114.2, 114.4, 115.0, 115.3, 121.8 (d, $J = 8.3$ Hz), 124.1, 125.6, 127.1, 129.6, 129.9 (d, $J = 2.7$ Hz), 135.5 (d, $J = 7.6$ Hz), 136.2, 143.9, 159.3 (d, $J = 244.1$ Hz). $^{19}$F NMR (376 MHz, CDCl$_3$, TMS) δ -118.4. IR (neat) ν 3232, 2977, 2941, 1657, 1592, 1478, 1376, 1332, 1166, 1091, 901, 814, 707, 682 cm$^{-1}$. HRMS (ESI) Calcd. for C$_{21}$H$_{28}$FN$_2$O$_2$S requires (M$^+$+NH$_4$): 391.1850, Found: 391.1842.
Compound 1: A yellow solid (451.5 mg, 73%); M.p. 119-120 °C. 1H NMR (400 MHz, Chloroform-d) δ 1.03 – 1.15 (m, 2H), 1.19 – 1.27 (m, 2H), 1.75 (s, 3H), 2.38 (s, 3H), 6.94 (s, 1H),
7.04 (d, J = 2.1 Hz, 1H), 7.19 – 7.24 (m, 2H), 7.26 (s, 2H), 7.54 – 7.57 (m, 2H). $^{13}$C NMR (100 MHz, Chloroform- $d$) δ 3.1, 4.6, 21.5, 22.2, 120.9, 122.3, 124.7, 127.2, 127.6, 128.1, 129.6, 129.8, 132.1, 135.8, 136.0, 144.0. IR (neat) ν 3249, 2975, 2938, 1657, 1600, 1478, 1377, 1333, 1166, 1090, 901, 814, 707, 682 cm$^{-1}$. HRMS (ESI) Calcd. for C$_{18}$H$_{22}$ClN$_2$O$_2$S requires (M$^+$+NH$_4$): 365.1085, Found: 365.1085.
**Compound 1m:** A yellow solid (691.2 mg, 64%); M.p. 121-122 °C. $^1$H NMR (400 MHz, Chloroform-$d$) δ 0.83 (t, $J = 7.5$ Hz, 3H), 0.96 (t, $J = 8.4$ Hz, 2H), 1.25 – 1.33 (m, 2H), 1.57 (s, 1H), 2.15 (q, $J = 7.5$ Hz, 2H), 2.37 (s, 3H), 6.83 (s, 1H), 7.01 (d, $J = 2.5$ Hz, 1H), 7.16 (dd, $J = 8.8, 2.5$ Hz, 1H), 7.21 (s, 1H), 7.23 (s, 1H), 7.56 – 7.63 (m, 3H). $^{13}$C NMR (100 MHz, Chloroform-$d$) δ 2.6, 3.6, 12.3, 21.5, 29.5, 120.8, 123.9, 126.3, 127.1, 127.6, 128.4, 129.2, 129.6, 132.6, 134.7, 136.1, 144.1. IR (neat) ν 3259, 2978, 2875, 1661, 1594, 1484, 1377, 1333, 1159, 1089, 904, 814, 708 cm$^{-1}$. HRMS (ESI) Calcd. for C$_{19}$H$_{24}$ClN$_2$O$_2$S requires (M$^+$+NH$_4$): 379.1242, Found: 379.1237.
### Compound 1n

A pale yellow solid (856.8 mg, 82%); M.p. 74-75 °C. ¹H NMR (400 MHz, Chloroform-­d) δ 0.77 – 0.85 (m, 3H), 0.91 – 0.98 (m, 2H), 1.15 (q, J = 7.3, 5.5 Hz, 4H), 1.25 (t, J = 7.7 Hz, 2H), 2.12 (d, J = 8.6 Hz, 2H), 2.34 (s, 3H), 6.95 (s, 1H), 7.00 (d, J = 2.5 Hz, 1H), 7.14 (dd, J = 8.8, 2.5 Hz, 1H), 7.17 – 7.23 (m, 2H), 7.57 – 7.68 (m, 3H). ¹³C NMR (100 MHz, Chloroform-d) δ 3.1, 3.5, 13.9, 21.5, 22.6, 29.8, 36.1, 120.6, 124.5, 125.2, 127.1, 127.5, 128.4, 129.1, 129.7, 132.6, 134.7, 136.2, 144.0. IR (neat) ν 3266, 2956, 2922, 2860, 1598, 1481, 1377, 1331, 1166, 1090, 923, 860, 813, 669 cm⁻¹. HRMS (ESI) Calcd. for C₂₁H₂₈ClN₂O₂S requires (M⁺+NH₄⁺): 407.1555, Found: 407.1552.
**Compound 1o**: A white solid (418.2 mg, 67%); M.p. 121-122 °C. $^1$H NMR (400 MHz, Chloroform-$d$) $\delta$ 1.08 (d, $J = 6.8$ Hz, 2H), 1.16 – 1.27 (m, 2H), 1.75 (s, 3H), 2.37 (s, 3H), 6.98 (s,
1H), 7.13 – 7.25 (m, 3H), 7.30 (d, \(J = 8.6\) Hz, 1H), 7.49 (d, \(J = 8.7\) Hz, 1H), 7.53 – 7.60 (m, 2H).

\(^{13}\)C NMR (100 Mhz, Chloroform-\(d\)) \(\delta\) 3.1, 4.7, 21.5, 22.2, 117.5, 120.9, 122.3, 124.8, 127.1, 129.6, 130.6, 130.9, 132.6, 135.9, 136.0, 144.0. IR (neat) \(\nu\) 3249, 1484, 1470, 1376, 1335, 1185, 1169, 1134, 1119, 1091, 1066, 908, 844, 816, 740, 705, 688, 673, 653 cm\(^{-1}\). HRMS (ESI) Calcd. for C\(_{18}\)H\(_{19}\)BrNO\(_2\)S requires (M\(^+\)+H): 392.0314, Found: 392.0316.
**Compound 1p**: A white solid (921.3 mg, 76%); M.p. 120-121 °C. $^1$H NMR (400 MHz, Chloroform-$d$) $\delta$ 0.83 (t, $J = 7.5$ Hz, 3H), 0.91 – 0.98 (m, 2H), 1.24 – 1.33 (m, 2H), 2.15 (q, $J = 8.7$, 8.1 Hz, 2H), 2.37 (s, 3H), 6.86 (d, $J = 21.8$ Hz, 1H), 7.16 (d, $J = 2.3$ Hz, 1H), 7.18 – 7.24 (m, 2H), 7.30 (dd, $J = 8.7$, 2.3 Hz, 1H), 7.52 (d, $J = 8.8$ Hz, 1H), 7.60 (s, 1H), 7.62 (s, 1H). $^{13}$C NMR (100 Mhz, Chloroform-$d$) $\delta$ 2.6, 3.6, 12.3, 21.5, 29.6, 116.9, 121.0, 124.0, 126.1, 127.2, 129.7, 130.5, 131.3, 133.2, 135.1, 136.1, 144.1. IR (neat) $\nu$ 3251, 2974, 1591, 1474, 1371, 1332, 1168, 1090, 900, 856, 814, 737, 706, 699, 676, 652 cm$^{-1}$. HRMS (ESI) Calcd. for C$_{19}$H$_{24}$BrN$_{2}$O$_{2}$S requires (M$^+$+NH$_4$): 423.0736, Found: 423.0732.
Compound 1q: A yellow oil (1051.4 mg, 81%). $^1$H NMR (400 MHz, Chloroform-$d$) $\delta$ 0.81 (t, $J = 6.3$ Hz, 3H), 0.99 (d, $J = 7.6$ Hz, 2H), 1.07 – 1.24 (m, 4H), 1.26 (t, $J = 7.5$ Hz, 2H), 2.17 (d, $J = 7.2$ Hz, 2H), 2.35 (s, 3H), 6.96 (s, 1H), 7.04 (s, 1H), 7.15 – 7.25 (m, 3H), 7.56 – 7.74 (m, 3H). $^{13}$C NMR (100 Mhz, Chloroform-$d$) $\delta$ 3.3, 3.4, 13.9, 21.5, 22.6, 29.9, 36.4, 119.0, 123.2, 123.8, 126.2, 127.2, 127.6, 128.4, 129.6, 132.6, 133.9, 136.4, 143.8. IR (neat) $\nu$ 3254, 2977, 2933, 1654, 1597, 1479, 1377, 1333, 1305, 1289, 1196, 1185, 1166, 1120, 1090, 1009, 902, 879, 842, 814, 741, 707, 682 cm$^{-1}$. HRMS (DART) Calcd. for C$_{21}$H$_{25}$BrNO$_2$S requires (M$^+$+H): 434.0784, Found: 434.0782.
Compound 1u: A yellow solid (374.1 mg, 72%); M.p. 143-144 °C. $^1$H NMR (400 MHz, Chloroform-$d$) $\delta$ 1.03 – 1.12 (m, 2H), 1.15 – 1.22 (m, 2H), 1.62 (s, 3H), 2.36 (s, 3H), 3.76 (s, 3H),
6.59 (d, $J = 2.9$ Hz, 1H), 6.78 (dd, $J = 8.9$, 2.9 Hz, 1H), 6.81 (s, 1H), 7.16 (s, 1H), 7.18 (s, 1H), 7.45 (s, 1H), 7.47 (s, 1H), 7.54 (d, $J = 8.9$ Hz, 1H). $^{13}$C NMR (100 Mhz, Chloroform-$d$) $\delta$ 3.0, 4.7, 21.5, 22.1, 55.4, 112.6, 113.4, 122.2, 122.9, 124.5, 126.1, 127.2, 129.4, 136.2, 136.7, 143.5, 156.9. IR (neat) $\nu$ 3313, 1609, 1591, 1491, 1386, 1333, 1292, 1214, 1163, 1089, 1045, 1034, 895, 867, 817, 797, 666 cm$^{-1}$. HRMS (ESI) Calcd. for C$_{19}$H$_{22}$NO$_3$S requires (M$^+$+H): 344.1315, Found: 344.1312.
Compound 1v: A yellow solid (141.8 mg, 47%); M.p. 114-115 °C. \(^1\)H NMR (400 MHz, Chloroform-\(d\)) \(\delta\) 1.05 (s, 2H), 1.19 (s, 2H), 1.72 (s, 3H), 2.24 (s, 3H), 2.32 (s, 3H), 6.87 (s, 1H), 6.95 – 7.05 (m, 2H), 7.11 – 7.19 (m, 2H), 7.50 (d, \(J = 8.2\) Hz, 1H), 7.52 – 7.59 (m, 2H). \(^{13}\)C NMR (100 Mhz, Chloroform-\(d\)) \(\delta\) 2.9, 4.6, 20.8, 21.4, 22.4, 121.5, 122.1, 122.9, 127.1, 128.3, 128.5, 129.4, 130.7, 134.2, 134.3, 136.3, 143.6. IR (neat) \(\nu\) 3249, 2975, 2920, 1600, 1495, 1381, 1333, 1167, 1091, 912, 888, 813, 706, 677 cm\(^{-1}\). HRMS (ESI) Calcd. for C\(_{19}\)H\(_{25}\)N\(_2\)O\(_2\)S requires (M\(^+\)+NH\(_4\))\(^+\): 345.1631, Found: 345.1626.
Compound 1w: A white solid (663.4 mg, 61%); M.p. 139-140 °C. $^1$H NMR (400 MHz, Chloroform- $d$) $\delta$ 1.11 (t, $J$ = 7.4 Hz, 2H), 1.24 – 1.32 (m, 2H), 1.93 (s, 3H), 2.33 (s, 3H), 7.10 – 7.20 (m, 3H), 7.38 (dd, $J$ = 7.1 Hz, 1H), 7.44 (dd, $J$ = 7.1 Hz, 1H), 7.54 (s, 1H), 7.59 – 7.66 (m, 2H), 7.69 (d, $J$ = 8.0 Hz, 1H), 7.79 (d, $J$ = 8.1 Hz, 1H), 8.03 (s, 1H). $^{13}$C NMR (100 Mhz, Chloroform- $d$) $\delta$ 3.2, 4.7, 21.5, 23.0, 117.2, 121.9, 124.2, 125.5, 126.4, 127.25, 127.29, 127.41, 127.44, 129.6, 130.4, 131.8, 132.7, 133.7, 136.3, 143.9. IR (neat) v 3262, 2974, 1590, 1506, 1402, 1346, 1319, 1154, 1092, 902, 811, 745 cm$^{-1}$. HRMS (ESI) Calcd. for C$_{22}$H$_{25}$N$_2$O$_2$S requires (M$^+$+NH$_4$): 381.1631, Found: 381.1630.
Compound 1x: A white solid (1250 mg, 49%); M.p. 116-117 °C. $^1$H NMR (400 MHz, Chloroform-$d$) $\delta$ 0.74 – 0.90 (m, 2H), 1.24 – 1.38 (m, 4H), 1.37 – 1.49 (m, 2H), 1.51 – 1.69 (m, 4H), 2.36 (s,
3H), 2.41 (s, 1H), 6.81 (s, 1H), 6.93 – 7.07 (m, 2H), 7.14 – 7.29 (m, 3H), 7.59 – 7.74 (m, 3H). $^{13}$C NMR (100 Mhz, Chloroform-$d$) δ 1.2, 4.5, 21.5, 24.5, 31.4, 46.7, 118.4, 122.3, 123.5, 127.1, 127.5, 128.9, 129.5, 133.2, 133.9, 136.6, 143.8. IR (neat) ν 3262, 2971, 2856, 1598, 1572, 1491, 1380, 1338, 1167, 1093, 908, 815, 756, 708, 679 cm$^{-1}$. HRMS (ESI) Calcd. for C$_{22}$H$_{29}$N$_2$O$_2$S requires (M$^+$$+$NH$_4$): 385.1944, Found: 385.1939.
**Compound 1y**: A yellow solid (653.4 mg, 49%); M.p. 122-123 °C. $^1$H NMR (400 MHz, Chloroform-<em>d</em>) $\delta$ 0.74 – 0.82 (m, 2H), 1.00 – 1.20 (m, 5H), 1.32 – 1.39 (m, 2H), 1.55 – 1.69 (m, 5H), 2.00 (t, $J = 10.5$ Hz, 1H), 2.36 (s, 3H), 6.79 (s, 1H), 6.96 – 7.03 (m, 2H), 7.15 – 7.24 (m, 3H), 7.62 – 7.72 (m, 3H). $^{13}$C NMR (100 Mhz, Chloroform-<em>d</em>) $\delta$ 0.8, 4.7, 21.5, 26.1, 26.5, 31.8, 45.0, 118.0, 122.3, 123.4, 127.2, 127.5, 128.9, 129.6, 130.5, 132.8, 134.2, 136.6, 143.9. IR (neat) ν 3262, 2982, 2849, 1639, 1613, 1598, 1580, 1484, 1447, 1406, 1377, 1337, 1167, 1089, 898, 747, 706, 665 cm$^{-1}$. HRMS (ESI) Calcd. for C$_{23}$H$_{31}$N$_2$O$_2$S requires (M$^+$+NH$_4$): 399.2101, Found: 399.2096.
fx-11-cyclo6-sub-c
Std carbon

General procedure for the preparation of compounds 3a-4ac

**General procedure F:** For the synthesis of 3 and 4:

A solution of 1 (0.2 mmol, 1.0 eq) and 2a (212.6 mg, 0.6 mmol, 3.0 eq) in 2 mL of CH$_3$CN, AcOH (0.1 mL, 2.0 mmol, 10 eq) was added by a syringe, and the mixture was stirred at room temperature for 6-8 h. The reaction mixture was concentrated under reduced pressure and the residue was purified by a silica gel flash chromatography (PE/EA = 10:1 to 5:1) to afford the products 3 and 4.

**Scale up experiment on 3.0 mmol of 1r:**

A solution of 1r (1.13 g, 3 mmol, 1.0 eq) and 2a (3.19 g, 9 mmol, 3.0 eq) in 30 mL of CH$_3$CN, AcOH (1.5 mL, 2.0 mmol, 10 eq) was added by a syringe, and the mixture was stirred at room temperature for 8 h. The reaction mixture was concentrated under reduced pressure and the residue was purified by a silica gel flash chromatography (PE/EA = 10:1) to afford the product 3r in 51% yield (605 mg).
Spectroscopic data for products 3a-4ac as following

**Compound 3a**: A white solid (53.7 mg, 81%); M.p. 89-90 °C. $^1$H NMR (400 MHz, Chloroform-$d$) δ 1.53 (s, 3H), 1.62 – 1.74 (m, 1H), 1.85 – 2.00 (m, 1H), 2.39 (s, 3H), 2.85 – 3.00 (m, 1H), 3.12 – 3.25 (m, 1H), 6.97 (dd, $J$ = 7.4 Hz, 1H), 7.06 (d, $J$ = 7.1 Hz, 1H), 7.14 (dd, $J$ = 7.4 Hz, 1H), 7.29 (d, $J$ = 7.6 Hz, 3H), 7.94 (d, $J$ = 8.2 Hz, 2H). $^{13}$C NMR (101 MHz, Chloroform-$d$) δ 16.3 (d, $J$ = 7.7 Hz), 21.6, 27.4 (d, $J$ = 17.2 Hz), 32.9 (d, $J$ = 30.2 Hz), 52.2 (d, $J$ = 19.3 Hz), 107.7 (d, $J$ = 278.4 Hz), 112.1, 122.4, 123.3, 127.7 (d, $J$ = 3.0 Hz), 127.9, 129.7, 135.4, 136.8, 142.0, 144.3. $^{19}$F NMR (376 MHz, Chloroform-$d$) δ -109.8. IR (neat) ν 3050, 2975, 1670, 1595, 1491, 1444, 1431, 1314, 1286, 1249, 1151, 1116, 1042, 1022, 1015, 927, 904, 766, 753, 738, 692, 665 cm$^{-1}$. HRMS (ESI) Calcd. for C$_{18}$H$_{18}$NO$_2$S requires (M$^+$-F): 312.1053, Found: 312.1055.
Compound 3b: A colorless oil (35.1 mg, 69%). $^1$H NMR (400 MHz, Chloroform-$d$) $\delta$ 1.58 (s, 3H), 1.63 – 1.77 (m, 1H), 1.87 – 2.01 (m, 1H), 2.79 – 2.93 (m, 1H), 2.97 – 3.09 (m, 1H), 3.14 (s, 3H),
7.06 (dd, $J = 7.4$ Hz, 1H), 7.15 (d, $J = 7.2$ Hz, 1H), 7.24 (dd, $J = 7.9$ Hz, 1H), 7.39 (d, $J = 8.1$ Hz, 1H). $^{13}$C NMR (101 MHz, Chloroform-$d$) $\delta$ 16.3 (d, $J = 7.6$ Hz), 27.2 (d, $J = 17.7$ Hz), 32.7 (d, $J = 29.5$ Hz), 41.0 (d, $J = 1.5$ Hz), 52.3 (d, $J = 19.2$ Hz), 108.0 (d, $J = 278.5$ Hz), 111.9, 122.8, 123.6, 128.3, 135.1, 142.4 (d, $J = 3.0$ Hz). $^{19}$F NMR (376 MHz, Chloroform-$d$) $\delta$ -114.8. IR (neat) $\nu$ 2964, 2927, 2867, 1604, 1479, 1453, 1354, 1247, 1185, 1168, 1154, 1095, 1017, 963, 943, 809, 767, 747 cm$^{-1}$. HRMS (ESI) Calcd. for C$_{12}$H$_{14}$NO$_2$S requires (M$^+$-F): 236.0740, Found: 236.0741.
**Compound 3c**: A white solid (50.9 mg, 32%); M.p. 115-116 °C. $^1$H NMR (400 MHz, Chloroform-d) $\delta$ 1.53 (s, 3H), 1.65 – 1.75 (m, 1H), 1.95 (tdd, $J$ = 10.9, 7.2, 3.1 Hz, 1H), 2.93 (dq, $J$ = 13.1, 10.1 Hz, 1H), 3.17 (ddt, $J$ = 13.7, 8.7, 2.7 Hz, 1H), 7.01 (dd, $J$ = 7.4 Hz, 1H), 7.08 (d, $J$ = 7.3 Hz, 1H), 7.14 – 7.20 (m, 1H), 7.29 (d, $J$ = 8.1 Hz, 1H), 7.59 – 7.69 (m, 2H), 7.88 – 7.98 (m, 2H). $^{13}$C NMR (101 MHz, Chloroform-d) $\delta$ 16.4 (d, $J$ = 7.7 Hz), 27.5 (d, $J$ = 17.3 Hz), 33.0 (d, $J$ = 29.7 Hz), 52.2 (d, $J$ = 19.4 Hz), 108.0 (d, $J$ = 278.7 Hz), 112.1, 122.6, 123.6, 128.1, 128.5, 129.3 (d, $J$ = 3.5 Hz), 132.4, 135.5, 138.8, 141.7 (d, $J$ = 2.7 Hz). $^{19}$F NMR (377 MHz, Chloroform-d) -110.7. IR (neat) $\nu$ 2990, 2954, 2920, 2844, 1607, 1576, 1469, 1388, 1246, 1171, 1159, 1138, 1094, 1085, 1069, 1007, 937, 819, 812, 759, 750, 740 cm$^{-1}$. HRMS (ESI) Calcd. for C$_{17}$H$_{15}$BrNO$_2$S requires (M'-F): 376.0001, Found: 375.9999.
**Compound 3d**: A pale yellow oil (25.9 mg, 41%). $^1$H NMR (400 MHz, Chloroform-<em>d</em>) $\delta$ 1.52 (s, 3H), 1.63 – 1.71 (m, 1H), 1.92 (tdd, $J = 10.9, 7.2, 3.0$ Hz, 1H), 2.93 (dq, $J = 13.2, 10.4$ Hz, 1H),
3.19 (ddt, J = 13.7, 8.7, 2.6 Hz, 1H), 6.98 (dd, J = 7.4 Hz, 1H), 7.06 (d, J = 7.3 Hz, 1H), 7.15 (ddd, J = 8.1, 7.8, 1.4 Hz, 1H), 7.31 (d, J = 8.1 Hz, 1H), 7.44 – 7.51 (m, 2H), 7.55 (dd, J = 7.3 Hz, 1H), 8.01 – 8.11 (m, 2H). 13C NMR (101 MHz, Chloroform-d) δ 16.4 (d, J = 7.7 Hz), 27.5 (d, J = 17.1 Hz), 33.0 (d, J = 29.9 Hz), 52.2 (d, J = 19.5 Hz), 107.8 (d, J = 278.4 Hz), 112.2, 122.5, 123.4, 127.6 (d, J = 3.0 Hz), 128.0, 129.1, 133.4, 135.4, 139.8, 142.0 (d, J = 2.8 Hz). 19F NMR (376 MHz, Chloroform-d) δ -149.8. IR (neat) ν 3071, 2964, 2925, 2865, 1602, 1474, 1459, 447, 1360, 1248, 1185, 1157, 1141, 1118, 1097, 1086, 1013, 936, 809, 747, 732, 718, 686 cm\(^{-1}\). HRMS (ESI) Calcd. for C\(_{17}\)H\(_{16}\)NO\(_2\)S requires (M\(^+\)-F): 298.0896, Found: 298.0891.
**Compound 3e**: A colorless oil (31.3 mg, 47%). $^1$H NMR (400 MHz, Chloroform-$d$) $\delta$ 1.61 (s, 3H), 1.62 – 1.69 (m, 1H), 1.92 (dq, $J$ = 14.0, 7.5 Hz, 1H), 2.86 (dd, $J$ = 9.2, 6.0 Hz, 2H), 4.49 (d, $J$ = 13.8 Hz, 1H), 4.58 (d, $J$ = 13.8 Hz, 1H), 7.01 (ddd, $J$ = 8.6, 4.6, 4.6 Hz, 1H), 7.06 – 7.13 (m, 3H), 7.27 – 7.36 (m, 3H), 7.37 – 7.43 (m, 2H). $^{13}$C NMR (101 MHz, Chloroform-$d$) $\delta$ $^{13}$C NMR (101 MHz, Chloroform-$d$) $\delta$ 16.6 (d, $J$ = 8.0 Hz), 27.3 (d, $J$ = 17.4 Hz), 32.7 (d, $J$ = 30.0 Hz), 52.3 (d, $J$ = 19.1 Hz), 60.5 (d, $J$ = 2.3 Hz), 108.2 (d, $J$ = 277.2 Hz), 111.9, 122.4, 123.3, 127.5, 128.0, 128.8, 129.0, 131.2, 134.5, 142.8 (d, $J$ = 2.9 Hz). $^{19}$F NMR (377 MHz, Chloroform-$d$) $\delta$ -111.5. IR (neat) $\nu$ 2959, 2923, 2849, 1686, 1594, 1477, 1451, 1358, 1247, 1188, 1180, 1158, 1141, 1097, 1086, 1022, 1014, 945, 833, 811, 690, 665 cm$^{-1}$. HRMS (ESI) Calcd. for C$_{18}$H$_{18}$NO$_2$S requires (M$^+$-F): 312.1053, Found: 312.1049.
**Compound 3g:** A colorless oil (62.2 mg, 90%). $^1$H NMR (400 MHz, Chloroform- $d$) δ 0.95 (t, $J = 7.4$ Hz, 3H), 1.63 (q, $J = 10.3$, 9.4 Hz, 1H), 1.99 (dt, $J = 14.5$, 7.7 Hz, 2H), 2.11 (dq, $J = 14.6$, 7.3 Hz, 1H), 2.37 (s, 3H), 2.82 – 2.99 (m, 1H), 3.15 (dd, $J = 12.7$, 9.5 Hz, 1H), 6.96 (dd, $J = 7.4$ Hz, 1H), 7.05 (d, $J = 7.2$ Hz, 1H), 7.14 (dd, $J = 7.7$ Hz, 1H), 7.24 – 7.32 (m, 3H), 7.88 – 7.97 (m, 2H).

$^{13}$C NMR (101 MHz, Chloroform- $d$) δ 9.6, 21.6, 24.2 (d, $J = 5.3$ Hz), 25.9 (d, $J = 17.6$ Hz), 33.4 (d, $J = 30.5$ Hz), 56.2 (d, $J = 18.6$ Hz), 108.5 (d, $J = 277.0$ Hz), 112.2, 123.0 (d, $J = 14.6$ Hz), 127.6 (d, $J = 2.9$ Hz), 127.8, 129.7, 134.1, 136.9, 142.4, 144.2. $^{19}$F NMR (376 MHz, Chloroform- $d$) δ -110.0.

IR (neat) υ 2972, 2920, 1654, 1618, 1584, 1545, 1459, 1359, 1244, 1188, 1179, 1157, 1111, 1087, 993, 813, 748, 704, 654 cm$^{-1}$. HRMS (ESI) Calcd. for C$_{19}$H$_{20}$NO$_2$S requires (M$^+$-F): 326.1209, Found: 326.1203.
**Compound 3h**: A colorless oil (58.0 mg, 78%). $^1$H NMR (400 MHz, Chloroform-$d$) $\delta$ 0.88 (d, $J = 6.9$ Hz, 3H), 1.31 (dt, $J = 21.2$, 10.3 Hz, 4H), 1.62 (q, $J = 11.2$ Hz, 1H), 1.88 – 2.11 (m, 3H), 2.36 (s, 3H), 2.83 – 2.99 (m, 1H), 3.09 – 3.22 (m, 1H), 6.96 (dd, $J = 7.4$ Hz, 1H), 7.05 (d, $J = 7.2$ Hz, 1H), 7.13 (dd, $J = 7.7$ Hz, 1H), 7.24 – 7.33 (m, 3H), 7.88 – 7.97 (m, 2H). $^{13}$C NMR (101 MHz, Chloroform-$d$) $\delta$ 13.9, 21.6, 23.5, 26.3 (d, $J = 17.6$ Hz), 27.1 (d, $J = 2.6$ Hz), 31.3 (d, $J = 4.5$ Hz), 33.3 (d, $J = 30.4$ Hz), 55.9 (d, $J = 18.6$ Hz), 108.4 (d, $J = 277.0$ Hz), 112.2, 123.1 (d, $J = 9.6$ Hz), 127.6 (d, $J = 2.8$ Hz), 127.8, 129.7, 134.4, 137.0, 142.3, 144.2. $^{19}$F NMR (376 MHz, Chloroform-$d$) $\delta$ -109.4. IR (neat) $\nu$ 2956, 2920, 2873, 2849, 1644, 1594, 1479, 1463, 1365, 1257, 1188, 1170, 1114, 1089, 1042, 1032, 1012, 813, 749, 702, 679, 657 cm$^{-1}$. HRMS (ESI) Calcd. for C$_{21}$H$_{24}$NO$_2$S requires (M$^+$-F): 354.1522, Found: 354.1514.
**Compound 3i**: A colorless oil (68.9 mg, 71%). $^1$H NMR (400 MHz, Chloroform-$d$) $\delta$ 0.87 (t, $J$ = 6.7 Hz, 3H), 1.18 (s, 20H), 1.62 (q, $J$ = 10.3, 9.5 Hz, 1H), 1.88 – 2.08 (m, 3H), 2.37 (s, 3H), 2.84 – 2.97 (m, 1H), 3.15 (dd, $J$ = 12.8, 9.4 Hz, 1H), 6.95 (dd, $J$ = 7.4 Hz, 1H), 7.05 (d, $J$ = 7.3 Hz, 1H), 7.12 (dd, $J$ = 7.8 Hz, 1H), 7.22 – 7.34 (m, 3H), 7.89 – 7.97 (m, 2H). $^{13}$C NMR (101 MHz, Chloroform-$d$) $\delta$ 14.2, 21.6, 22.7, 24.9 (d, $J$ = 2.5 Hz), 26.3 (d, $J$ = 17.6 Hz), 29.37, 29.38, 29.62, 29.65, 29.67, 29.69, 30.4, 31.6 (d, $J$ = 4.5 Hz), 31.9, 33.3 (d, $J$ = 30.3 Hz), 55.9 (d, $J$ = 18.7 Hz), 108.4 (d, $J$ = 277.2 Hz), 112.2, 123.0 (d, $J$ = 9.8 Hz), 127.6 (d, $J$ = 2.8 Hz), 127.7, 129.7, 134.4, 137.0, 142.3 (d, $J$ = 2.4 Hz), 144.2. $^{19}$F NMR (376 MHz, Chloroform-$d$) $\delta$ -109.6. IR (neat) $\nu$ 2923, 2852, 1597, 1459, 1363, 1248, 1179, 1158, 1140, 1119, 1088, 1026, 1010, 932, 812, 747, 669, 684, 654 cm$^{-1}$. HRMS (ESI) Calcd. for C$_{29}$H$_{40}$NO$_2$S requires (M$^+$-F): 466.2774, Found: 466.2767.
**Compound 3j**: A white solid (68.5 mg, 98%); M.p. 97-98 °C. \(^1\)H NMR (400 MHz, Chloroform-\(d\)) \(\delta\) 1.69 (q, \(J = 10.5, 9.7\) Hz, 1H), 1.88 – 1.99 (m, 1H), 2.40 (s, 3H), 2.86 – 2.98 (m, 1H), 3.19 (dd, \(J = \))
13.1, 8.9 Hz, 1H), 6.77 (dd, $J = 7.4$, 3.3 Hz, 1H), 6.83 (ddd, $J = 10.0$, 9.9, 2.7 Hz, 1H), 7.23 (dd, $J = 9.4$, 4.9 Hz, 1H), 7.27 – 7.33 (m, 2H), 7.87 – 7.96 (m, 2H). $^{13}$C NMR (101 MHz, Chloroform-$d$) $\delta$ 16.0 (d, $J = 7.2$ Hz), 21.4, 27.1 (d, $J = 17.2$ Hz), 32.7 (d, $J = 30.1$ Hz), 51.8, 107.8 (d, $J = 278.9$ Hz), 110.0 (d, $J = 24.4$ Hz), 112.6 (d, $J = 8.4$ Hz), 114.0 (d, $J = 23.3$ Hz), 127.5 (d, $J = 3.1$ Hz), 128.3, 129.6, 130.0, 133.6, 136.5, 137.2 (d, $J = 7.6$ Hz), 137.8, 144.3, 159.1 (d, $J = 241.9$ Hz). $^{19}$F NMR (376 MHz, Chloroform-$d$) $\delta$ -120.2, -109.4. IR (neat) v 3056, 2975, 1670, 1595, 1495, 1469, 1448, 1430, 1314, 1287, 1249, 1151, 1114, 1023, 927, 803, 765, 753, 722, 654 cm$^{-1}$. HRMS (ESI) Calcd. for C$_{18}$H$_{17}$F$_2$NaNO$_2$S requires (M$^+$+Na): 372.0840, Found: 372.0840.
**Compound 3k:** A pale yellow oil (51.1 mg, 65%). $^1$H NMR (400 MHz, Chloroform-$d$) $\delta$ 0.88 (t, $J$ = 6.9 Hz, 3H), 1.34 (t, $J$ = 12.9 Hz, 3H), 1.61 – 1.72 (m, 1H), 1.82 – 1.94 (m, 1H), 1.94 – 2.06 (m, 2H), 2.40 (s, 3H), 2.84 – 2.97 (m, 1H), 3.10 – 3.20 (m, 1H), 6.76 (dd, $J$ = 8.1, 2.6 Hz, 1H), 6.83 (dd, $J$ = 8.8, 8.8, 2.6 Hz, 1H), 7.22 (dd, $J$ = 8.8, 4.3 Hz, 1H), 7.27 – 7.35 (m, 2H), 7.86 – 7.95 (m, 2H). $^{13}$C NMR (101 MHz, Chloroform-$d$) $\delta$ 13.8, 21.5, 23.4, 26.2 (d, $J$ = 17.4 Hz), 27.0 (d, $J$ = 2.6 Hz), 31.2 (d, $J$ = 4.3 Hz), 33.3 (d, $J$ = 30.5 Hz), 55.8 (dd, $J$ = 18.9, 1.8 Hz), 108.7 (d, $J$ = 277.6 Hz), 110.6 (d, $J$ = 24.2 Hz), 112.9 (d, $J$ = 8.4 Hz), 114.0 (d, $J$ = 23.5 Hz), 127.5 (d, $J$ = 2.8 Hz), 129.8, 136.4 (d, $J$ = 7.7 Hz), 136.8, 138.3 (dd, $J$ = 2.3 Hz), 144.4, 159.2 (d, $J$ = 241.7 Hz). $^{19}$F NMR (376 MHz, Chloroform-$d$) $\delta$ -120.2, -109.0. IR (neat) v 3048, 2967, 1667, 1594, 1490, 1440, 1419, 1315, 1281, 1250, 1059, 1039, 1022, 1015, 906, 830, 766, 753, 723, 692, 665, 653 cm$^{-1}$. HRMS (ESI) Calcd. for C$_{21}$H$_{23}$FNO$_2$S requires (M$^+$-F): 372.1428, Found: 372.1420.
**Compound 3l**: A white solid (53.6 mg, 73%); M.p. 123-124 °C. $^1$H NMR (400 MHz, Chloroform-$d$) δ 1.49 (s, 3H), 1.66 (q, $J = 10.7$ Hz, 1H), 1.85 – 1.97 (m, 1H), 2.38 (s, 3H), 2.83 – 2.97 (m, 1H),
3.11 – 3.23 (m, 1H), 7.00 (s, 1H), 7.09 (d, J = 8.6 Hz, 1H), 7.21 (d, J = 8.6 Hz, 1H), 7.25 – 7.32 (m, 2H), 7.83 – 7.93 (m, 2H). ¹³C NMR (101 MHz, Chloroform-d) δ 16.1 (d, J = 7.5 Hz), 21.6, 27.3 (d, J = 17.0 Hz), 32.9 (d, J = 29.8 Hz), 52.0 (d, J = 19.6 Hz), 107.8 (d, J = 279.2 Hz), 113.1, 122.9, 127.6 (d, J = 2.9 Hz), 127.8, 128.4, 129.8, 136.5, 137.3, 140.7 (d, J = 2.8 Hz), 144.6. ¹⁹F NMR (376 MHz, Chloroform-d) δ -109.6. IR (neat) ν 2993, 2946, 2923, 2847, 1594, 1480, 1461, 1357, 1248, 1179, 1162, 1138, 1122, 1089, 1022, 931, 880, 866, 817, 809, 687, 664 cm⁻¹. HRMS (ESI) Calcd. for C₁₈H₁₇ClNO₂S requires (M⁺-F): 346.0663, Found: 346.0661.
Compound 3m: A yellow solid (42.0 mg, 55%); M.p. 99-100 °C. $^1$H NMR (400 MHz, Chloroform-$d$) $\delta$ 0.96 (t, $J$ = 7.5 Hz, 3H), 1.59 – 1.71 (m, 1H), 1.97 (tq, $J$ = 14.9, 7.7 Hz, 2H), 2.11 (dt, $J$ = 14.7,
7.4 Hz, 1H), 2.40 (s, 3H), 2.82 – 2.97 (m, 1H), 3.09 – 3.21 (m, 1H), 7.01 (d, \( J = 2.1 \) Hz, 1H), 7.11 (dd, \( J = 8.6, 2.2 \) Hz, 1H), 7.23 (d, \( J = 8.6 \) Hz, 1H), 7.27 – 7.32 (m, 2H), 7.86 – 7.94 (m, 2H). \(^{13}\)C NMR (101 MHz, Chloroform-\( d \)) \( \delta \) 9.5 (d, \( J = 3.0 \) Hz), 21.6, 24.1 (d, \( J = 5.0 \) Hz), 25.9 (d, \( J = 17.4 \) Hz), 33.4 (d, \( J = 30.3 \) Hz), 56.1 (d, \( J = 18.9 \) Hz), 108.6 (d, \( J = 277.8 \) Hz), 113.2, 123.3, 127.6 (d, \( J = 2.9 \) Hz), 127.7, 128.3, 129.8, 136.0, 136.7, 141.1 (d, \( J = 2.3 \) Hz), 144.5. \(^{19}\)F NMR (376 MHz, Chloroform-\( d \)) \( \delta \) -109.5. IR (neat) \( \nu \) 2959, 2922, 2852, 1600, 1464, 1356, 1242, 1176, 1157, 1141, 1119, 1089, 1029, 995, 979, 813, 687, 663 cm\(^{-1}\). HRMS (ESI) Calcd. for \( \text{C}_{19}\text{H}_{19}\text{NClO}_{2}\text{S} \) requires (\( M^+ \)-F): 360.0820, Found: 360.0820.
Compound 3n: A pale yellow oil (34.5 mg, 42%). $^1$H NMR (400 MHz, Chloroform-d) δ 0.89 (t, $J$ = 7.0 Hz, 3H), 1.29 – 1.41 (m, 3H), 1.64 (q, $J$ = 10.7, 9.6 Hz, 1H), 1.83 – 1.95 (m, 1H), 1.95 – 2.06
(m, 2H), 2.39 (s, 3H), 2.91 (dt, \( J = 20.4 \), 9.7 Hz, 1H), 3.09 – 3.21 (m, 1H), 7.02 (d, \( J = 2.1 \) Hz, 1H), 7.10 (dd, \( J = 8.6 \), 2.1 Hz, 1H), 7.23 (d, \( J = 8.6 \) Hz, 1H), 7.27 – 7.33 (m, 2H), 7.87 – 7.94 (m, 2H).

\(^{13}\)C NMR (101 MHz, Chloroform-\( d \)) \( \delta \) 13.8, 21.6, 23.4, 26.2 (d, \( J = 17.4 \) Hz), 26.9 (d, \( J = 2.5 \) Hz), 31.1 (d, \( J = 4.5 \) Hz), 33.4 (d, \( J = 30.3 \) Hz), 55.8 (d, \( J = 18.7 \) Hz), 108.5 (d, \( J = 278.0 \) Hz), 113.1, 123.3, 127.6 (d, \( J = 2.8 \) Hz), 127.6, 128.3, 129.8, 136.3, 136.7, 140.9, 144.5. \(^{19}\)F NMR (376 MHz, Chloroform-\( d \)) \( \delta \) -109.1. IR (neat) \( \nu \) 2954, 2928, 2868, 1597, 1466, 1362, 1244, 1179, 1158, 1144, 1120, 1092, 1032, 1010, 933, 811, 705, 689, 664 cm\(^{-1}\). HRMS (ESI) Calcd. for C\(_{21}\)H\(_{23}\)ClNO\(_2\)S requires (M\(^+\)-F): 388.1133, Found: 388.1129.
**Compound 3o**: A white solid (56.2 mg, 68%); M.p. 170-171 °C. $^1$H NMR (400 MHz, Chloroform- $d$) $\delta$ 1.49 (s, 3H), 1.66 (q, $J = 11.0$ Hz, 1H), 1.86 – 1.96 (m, 1H), 2.38 (s, 3H), 2.82 – 2.97 (m, 1H), 3.10 – 3.21 (m, 1H), 7.12 – 7.18 (m, 2H), 7.23 (d, $J = 2.0$ Hz, 1H), 7.26 – 7.31 (m, 2H), 7.85 – 7.92 (m, 2H). $^{13}$C NMR (101 MHz, Chloroform- $d$) $\delta$ 16.1 (d, $J = 7.4$ Hz), 21.6, 27.3 (d, $J = 16.9$ Hz), 32.9 (d, $J = 29.9$ Hz), 52.0 (d, $J = 19.8$ Hz), 107.8 (d, $J = 279.2$ Hz), 113.6, 115.8, 125.8, 127.6 (d, $J = 2.9$ Hz), 129.8, 130.7, 136.4, 137.6, 141.2, 144.6. $^{19}$F NMR (376 MHz, Chloroform- $d$) $\delta$ -109.2. IR (neat) $\nu$ 3056, 2972, 1670, 1589, 1490, 1444, 1317, 1287, 1244, 1022, 1015, 927, 838, 766, 753, 723, 692, 665, 654 cm$^{-1}$. HRMS (ESI) Calcd. for C$_{18}$H$_{17}$BrNO$_2$S requires (M$^+$-F): 390.0158, Found: 390.0157.
**Compound 3p**: A white solid (46.1 mg, 54%); M.p. 123-124 °C. $^1$H NMR (400 MHz, Chloroform-$d$) $\delta$ 0.85 – 1.07 (m, 3H), 1.57 – 1.70 (m, 1H), 1.89 – 2.03 (m, 2H), 2.08 (dt, $J = 14.7$, 7.4 Hz, 1H),
2.39 (s, 3H), 2.83 – 3.00 (m, 1H), 3.14 (td, J = 12.1, 4.5 Hz, 1H), 7.10 – 7.24 (m, 2H), 7.24 – 7.33 (m, 3H), 7.81 – 7.98 (m, 2H). $^1$H NMR (101 MHz, Chloroform-$d$) δ 9.6 (d, J = 2.9 Hz), 21.6, 24.1 (d, J = 5.0 Hz), 25.9 (d, J = 17.3 Hz), 33.5 (d, J = 30.2 Hz), 56.1 (d, J = 18.7 Hz), 108.5 (d, J = 277.9 Hz), 113.7, 115.7, 126.2, 127.6 (d, J = 2.9 Hz), 129.8, 130.6, 136.4, 136.7, 141.6 (d, J = 2.4 Hz), 144.5. $^1$F NMR (376 MHz, Chloroform-$d$) δ -109.6. IR (neat) ν 2969, 2925, 2857, 1594, 1465, 1358, 1242, 1187, 1178, 1159, 1142, 1119, 1089, 1027, 981, 874, 812, 775, 749, 688, 664 cm$^{-1}$. HRMS (ESI) Calcd. for $C_{19}H_{19}$BrNO$_2$S requires (M$^+$-F): 404.0314, Found: 404.0314.
Compound 3q: A yellow oil (35.7 mg, 39%). $^1$H NMR (400 MHz, Chloroform-$d$) $\delta$ 0.89 (s, 4H), 1.29 (d, $J = 30.1$ Hz, 5H), 1.64 (q, $J = 9.6$ Hz, 1H), 1.80 – 1.94 (m, 1H), 1.94 – 2.07 (m, 2H), 2.40
(s, 3H), 2.90 (dt, $J = 22.0, 10.2$ Hz, 1H), 3.04 – 3.24 (m, 1H), 7.05 – 7.21 (m, 2H), 7.25 (d, $J = 8.6$ Hz, 1H), 7.27 – 7.37 (m, 2H), 7.83 – 7.97 (m, 2H). $^{13}$C NMR (101 MHz, Chloroform-$d$) δ 13.9, 21.6, 23.4, 26.2 (d, $J = 17.4$ Hz), 29.7, 31.1 (d, $J = 4.3$ Hz), 33.4 (d, $J = 30.4$ Hz), 55.7 (d, $J = 18.8$ Hz), 108.4 (d, $J = 278.1$ Hz), 113.6, 115.7, 126.1, 127.6 (d, $J = 2.9$ Hz), 129.8, 130.5, 136.6, 136.7, 141.4 (d, $J = 2.3$ Hz), 144.5. $^{19}$F NMR (376 MHz, Chloroform-$d$) δ -109.0. IR (neat) ν 2959, 2920, 2846, 1597, 1461, 1362, 1257, 1245, 1179, 1158, 1114, 1089, 1012, 934, 809, 749, 689, 663 cm$^{-1}$. HRMS (ESI) Caled. for C$_{21}$H$_{23}$BrNO$_2$S requires (M$^+$-F): 432.0627, Found: 432.0623.
**Compound 3r:** A white solid (45.8 mg, 58%); M.p. 113-114 °C. $^1$H NMR (400 MHz, Chloroform-$d$) $\delta$ 1.89 – 2.00 (m, 1H), 2.41 (s, 3H), 2.90 (q, $J = 6.9$ Hz, 2H), 3.29 (t, $J = 10.6$ Hz, 1H), 6.74 (dd,
$J = 7.5, 1.3 \text{ Hz}, 1\text{H}), 6.92 \text{ (dd, } J = 7.5 \text{ Hz}, 1\text{H}), 7.17 \text{ (dd, } J = 7.8 \text{ Hz}, 1\text{H}), 7.26 – 7.44 \text{ (m, 8H), 7.93 – 8.02 \text{ (m, 2H).}^{13}\text{C NMR (101 MHz, Chloroform-d)}}$ δ 21.6, 25.4 (d, $J = 16.0 \text{ Hz}$), 34.4 (d, $J = 30.1 \text{ Hz}$), 61.1 (d, $J = 18.6 \text{ Hz}$), 107.4 (d, $J = 281.1 \text{ Hz}$), 112.3, 123.4, 124.4, 127.8, 128.1, 128.5, 129.8, 135.4, 136.1, 136.9, 142.6, 144.4. $^{19}\text{F NMR (376 MHz, Chloroform-d)} \delta -101.6. \text{ IR (neat) v 3066, 3032, 2962, 2949, 1602, 1495, 1477, 1459, 1366, 1330, 1236, 1188, 1162, 1143, 1121, 1086, 1007, 955, 924, 807, 760, 693, 669, 652 \text{ cm}^{-1}. \text{ HRMS (ESI) Calcd. for } \text{C}_{23}\text{H}_{20}\text{NO}_{2}\text{S requires (M}^{-}\text{F): 374.1209, Found: 374.1211.}$
**Compound 3s**: A white solid (25.3 mg, 40%); M.p. 111-12 °C. $^1$H NMR (400 MHz, Chloroform-$d$) δ 1.96 (q, $J = 10.5, 10.1$ Hz, 1H), 2.76 – 2.97 (m, 2H), 3.08 – 3.18 (m, 1H), 3.20 (s, 3H), 6.82 (d, $J$
= 8.2 Hz, 1H), 7.01 (dd, J = 7.5 Hz, 1H), 7.24 – 7.30 (m, 1H), 7.33 – 7.40 (m, 3H), 7.39 – 7.46 (m, 2H), 7.49 (d, J = 8.2 Hz, 1H). 13C NMR (101 MHz, Chloroform-d) δ 25.2 (d, J = 16.4 Hz), 34.1 (d, J = 29.8 Hz), 41.3, 61.3 (d, J = 17.9 Hz), 107.7 (d, J = 281.5 Hz), 112.0, 123.8, 124.8, 127.9, 128.5, 128.6, 135.1 (d, J = 3.1 Hz), 135.8, 142.9 (d, J = 3.1 Hz). 19F NMR (376 MHz, Chloroform-d) δ -105.6. IR (neat) ν 2959, 2925, 1602, 1474, 1360, 1448, 1352, 1234, 1183, 1155, 1136, 1012, 822, 766, 703 cm⁻¹. HRMS (ESI) Calcd. for C17H16NO2S requires (M⁺-F): 298.0896, Found: 298.0893.
**Compound 3t**: A white solid (20.4 mg, 45%); M.p. 137-138 °C. $^1$H NMR (400 MHz, Chloroform-$d$) $\delta$ 2.00 (dd, $J = 15.8, 9.4$ Hz, 1H), 2.84 – 3.03 (m, 2H), 3.29 (t, $J = 9.5$ Hz, 1H), 6.78 (d, $J = 7.4$ Hz, 1H).
Hz, 1H), 6.97 (dd, J = 7.4 Hz, 1H), 7.12 – 7.54 (m, 7H), 7.56 – 7.77 (m, 2H), 7.86 – 8.08 (m, 2H).

$^{13}$C NMR (101 MHz, Chloroform-$d$) δ 25.5 (d, $J = 16.0$ Hz), 34.5 (d, $J = 30.1$ Hz), 61.1 (d, $J = 18.3$ Hz), 107.7 (d, $J = 281.5$ Hz), 112.2, 123.8, 124.6, 127.9, 128.3, 128.45, 128.53, 128.6, 129.3 (d, $J = 3.4$ Hz), 132.5, 135.1 (d, $J = 3.1$ Hz), 136.1, 138.9, 142.2 (d, $J = 2.3$ Hz).

$^{19}$F NMR (376 MHz, Chloroform-$d$) δ -102.5. IR (neat) v 3087, 3024, 2944, 1602, 1568, 1496, 1472, 1456, 1369, 1235, 1187, 1162, 1142, 1122, 1069, 1004, 958, 925, 820, 812, 758, 744, 692, 664 cm$^{-1}$. HRMS (ESI) Calcd. for C$_{22}$H$_{17}$BrNO$_2$S requires (M$^+$-F): 438.0158, Found: 438.0159.
**Compound 3v**: A colorless oil (23.9 mg, 36%). $^1$H NMR (400 MHz, Chloroform-\(d\)) $\delta$ 1.66 (dd, $J = 9.5$ Hz, 1H), 1.85 – 1.96 (m, 1H), 2.26 (s, 3H), 2.38 (s, 3H), 2.84 – 2.97 (m, 1H), 3.11 – 3.22 (m,
1H), 6.86 (s, 1H), 6.94 (d, $J = 8.3$ Hz, 1H), 7.18 (d, $J = 8.2$ Hz, 1H), 7.28 (s, 1H), 7.86 – 7.97 (m, 2H). $^{13}$C NMR (101 MHz, Chloroform-$d$) $\delta$ 16.3 (d, $J = 7.6$ Hz), 21.2 (d, $J = 70.5$ Hz), 27.4 (d, $J = 17.3$ Hz), 29.7, 32.8 (d, $J = 30.1$ Hz), 52.2 (d, $J = 19.5$ Hz), 107.9 (d, $J = 278.3$ Hz), 111.9, 123.1, 127.7 (d, $J = 3.0$ Hz), 128.3, 128.5, 129.6, 130.2, 132.9, 133.8, 135.5, 136.9, 139.8 (d, $J = 2.5$ Hz), 144.1. $^{19}$F NMR (376 MHz, Chloroform-$d$) $\delta$ -110.0. IR (neat) $\nu$ 2975, 2920, 1600, 1494, 1381, 1167, 1091, 912, 813, 706, 677 cm$^{-1}$. HRMS (ESI) Calcd. for C$_{19}$H$_{20}$FNNaO$_2$S requires (M$^+$Na)$^+$: 368.1091, Found: 368.1090.
Compound 3w: A yellow oil (3w+3w' = 41.5 mg, 3w:3w' = 4.5:1, it is an inseparable mixture). \(^1\)H
NMR (400 MHz, Chloroform-\textit{d}) $\delta$ 1.64 (s, 3H), 1.67 – 1.78 (m, 1H), 1.87 – 2.02 (m, 1H), 2.37 (s, 3H), 2.96 (dt, $J = 21.7$, 10.2 Hz, 1H), 3.12 – 3.32 (m, 1H), 7.27 (dd, $J = 8.2$, 6.5 Hz, 2H), 7.30 – 7.36 (m, 1H), 7.37 – 7.44 (m, 1H), 7.47 (s, 1H), 7.63 (s, 1H), 7.69 (d, $J = 8.0$ Hz, 1H), 7.74 (d, $J = 8.1$ Hz, 1H), 7.95 – 8.06 (m, 2H). $^{13}$C NMR (101 MHz, Chloroform-\textit{d}) $\delta$ 16.5 (d, $J = 6.8$ Hz), 21.5, 27.5 (d, $J = 15.7$ Hz), 32.6 (d, $J = 29.9$ Hz), 51.7 (d, $J = 19.7$ Hz), 107.9 (d, $J = 277.4$ Hz), 108.3, 120.1 (d, $J = 6.5$ Hz), 121.3, 124.7, 125.7, 126.2, 127.6 (d, $J = 5.0$ Hz), 127.7 (d, $J = 2.9$ Hz), 127.9, 129.6, 129.9 (d, $J = 94.0$ Hz), 133.4, 136.4, 136.6, 140.1 (d, $J = 3.0$ Hz), 144.4. $^{19}$F NMR (376 MHz, Chloroform-\textit{d}) $\delta$ -109.3.
from prolonging the reaction time to 24 h

**Compound 3w':** A white solid (3w+3w' = 22.9 mg, 3w:3w' = 1:4 in 6 h and 3w' 7.1 mg, 9% in 24 h); M.p. 79-80 °C. ¹H NMR (400 MHz, Chloroform-<sup>d</sup>) δ 1.67 (s, 3H), 1.87 – 1.97 (m, 1H), 2.01 – 2.09 (m, 1H), 2.40 (s, 3H), 2.98 – 3.09 (m, 1H), 3.38 – 3.46 (m, 1H), 7.28 – 7.34 (m, 3H), 7.36 – 7.46 (m, 2H), 7.69 (d, J = 8.0 Hz, 1H), 7.86 – 7.92 (m, 1H), 8.01 (d, J = 1.5 Hz, 1H), 8.02 – 8.05 (m, 1H). ¹³C NMR (101 MHz, Chloroform-<sup>d</sup>) δ 17.17 (d, J = 7.2 Hz), 21.58, 27.34 (d, J = 14.9 Hz), 33.27 (d, J = 29.6 Hz), 52.17 (d, J = 18.3 Hz), 108.31, 108.89 (d, J = 277.2 Hz), 116.66 (d, J = 3.9 Hz), 120.14 (d, J = 6.5 Hz), 121.27, 125.68, 126.31 (d, J = 2.1 Hz), 127.06, 127.90, 129.45, 131.31 (d, J = 3.6 Hz), 137.64 (d, J = 2.5 Hz), 138.51 (d, J = 2.7 Hz), 143.95 (d, J = 92.0 Hz), 144.00. ¹⁹F NMR (376 MHz, Chloroform-<sup>d</sup>) δ -107.6, -133.2. IR (neat) ν 2974, 1591, 1506, 1402, 1346, 1319, 1154, 1092, 902, 811, 745 cm⁻¹. HRMS (ESI) Calcd. for C<sub>22</sub>H<sub>19</sub>FNO<sub>2</sub>S requires (M⁺-F): 380.1115, Found: 380.1112.
A slight difference between 3w and 3w' (comparison diagram)
**Compound 3x:** A colorless oil (41.4 mg, 54%). $^1$H NMR (400 MHz, Chloroform-$d$) $\delta$ 1.37 – 1.48 (m, 1H), 1.49 – 1.73 (m, 6H), 1.83 – 1.93 (m, 2H), 2.08 – 2.22 (m, 1H), 2.38 (s, 3H), 2.55 (p, $J = 8.9$ Hz, 1H), 2.91 (dt, $J = 22.6$, 11.4 Hz, 1H), 3.06 – 3.21 (m, 1H), 6.93 (dd, $J = 7.5$ Hz, 1H), 7.09 – 7.18 (m, 2H), 7.23 – 7.33 (m, 3H), 7.86 – 7.99 (m, 2H). $^{13}$C NMR (101 MHz, Chloroform-$d$) $\delta$ 21.3, 25.1 (d, $J = 17.2$ Hz), 25.6 (d, $J = 86.1$ Hz), 28.1 (d, $J = 47.0$ Hz), 33.7 (d, $J = 30.4$ Hz), 41.1 (d, $J = 3.3$ Hz), 58.3 (d, $J = 18.5$ Hz), 108.3 (d, $J = 276.3$ Hz), 111.9, 122.7, 123.3, 127.4 (d, $J = 3.0$ Hz), 127.4, 129.5, 134.3, 136.8, 142.0 (d, $J = 2.2$ Hz), 144.0. $^{19}$F NMR (376 MHz, Chloroform-$d$) $\delta$ -108.2. IR (neat) $\nu$ 2971, 2856, 1598, 1572, 1491, 1380, 1338, 1167, 1092, 908, 815, 756, 679 cm$^{-1}$. HRMS (ESI) Calcd. for C$_{22}$H$_{24}$FNNaO$_2$S requires (M$^+$+Na): 408.1404, Found: 408.1403.
**Compound 3y**: A colorless oil (35.9 mg, 45%). $^1$H NMR (400 MHz, Chloroform-d) $\delta$ 1.06 – 1.21 (m, 2H), 1.21 – 1.41 (m, 3H), 1.52 – 1.89 (m, 6H), 1.98 (t, $J = 11.5$ Hz, 1H), 2.16 – 2.31 (m, 1H), 2.39 (s, 3H), 2.85 (dt, $J = 23.0$, 11.5 Hz, 1H), 3.00 – 3.16 (m, 1H), 6.94 (dd, $J = 7.4$ Hz, 1H), 7.03 – 7.18 (m, 2H), 7.20 – 7.35 (m, 3H), 7.82 – 7.98 (m, 2H). $^{13}$C NMR (101 MHz, Chloroform-d) $\delta$ 21.6, 24.6 (d, $J = 16.1$ Hz), 26.5, 26.6, 27.2, 27.9, 28.9 (d, $J = 3.3$ Hz), 33.8 (d, $J = 31.0$ Hz), 40.1 (d, $J = 3.0$ Hz), 59.1 (d, $J = 17.7$ Hz), 109.0 (d, $J = 275.0$ Hz), 112.3, 122.9, 123.7, 127.5 (d, $J = 2.6$ Hz), 127.6, 129.7, 134.0, 137.2, 142.3, 144.1. $^{19}$F NMR (376 MHz, Chloroform-d) $\delta$ -110.9. IR (neat) ν 2982, 2919, 2849, 1639, 1612, 1598, 1580, 1484, 1447, 1406, 1377, 1337, 1167, 1089, 898, 807, 747, 706, 689, 665 cm$^{-1}$. HRMS (ESI) Calcd. for C$_{23}$H$_{26}$NO$_2$S requires (M$^+$-F): 380.1679, Found: 380.1673.
**Compound 3z**: A white solid (72.7 mg, 87%); M.p. 128-129 °C. $^1$H NMR (400 MHz, Chloroform-$d$) δ 1.65 – 1.80 (m, 1H), 1.95 – 2.16 (m, 2H), 2.39 (s, 3H), 2.47 (dd, $J = 22.7, 8.8$ Hz, 1H), 2.77 –
2.89 (m, 1H), 3.11 (dt, $J = 13.2$, 6.8 Hz, 1H), 6.88 (d, $J = 7.3$ Hz, 1H), 6.92 – 7.04 (m, 3H), 7.16 – 7.23 (m, 4H), 7.23 – 7.28 (m, 2H), 7.48 (d, $J = 8.2$ Hz, 1H), 7.82 – 7.95 (m, 2H). $^{13}$C NMR (101 MHz, Chloroform-$d$) $\delta$ 21.6, 22.7 (d, $J = 5.8$ Hz), 38.9 (d, $J = 3.5$ Hz), 39.8 (d, $J = 31.6$ Hz), 60.4, 63.2 (d, $J = 18.1$ Hz), 112.5, 120.2 (d, $J = 238.4$ Hz), 123.8, 125.3, 127.1, 127.8 (d, $J = 3.6$ Hz), 127.9, 128.4 (d, $J = 1.6$ Hz), 128.4, 129.5, 135.8, 136.9, 139.6 (d, $J = 7.1$ Hz), 140.7, 144.1. $^{19}$F NMR (376 MHz, Chloroform-$d$) $\delta$ -114.0. IR (neat) $\nu$ 2969, 2927, 2870, 1597, 1456, 1360, 1234, 1187, 1168, 1155, 1131, 1091, 1007, 963, 912, 775, 756, 701, 677, 654 cm$^{-1}$. HRMS (ESI) Calcd. for C$_{24}$H$_{22}$NO$_2$S requires (M$^+$-F): 388.1366, Found: 388.1360.
**Compound 3aa:** A white solid (30.4 mg, 39%); M.p. 182-183 °C. $^1$H NMR (400 MHz, Chloroform-d) $\delta$ 1.88 – 2.00 (m, 1H), 2.42 (s, 3H), 2.87 (tt, $J = 18.9$, 10.4 Hz, 2H), 3.21 – 3.36 (m, 1H), 6.73 (d, $J = 7.5$ Hz, 1H), 6.93 (ddd, $J = 7.6$, 7.5, 2.9 Hz, 1H), 7.00 – 7.12 (m, 2H), 7.19 (ddd, $J = 8.2$, 7.9, 2.8 Hz, 1H), 7.24 – 7.29 (m, 2H), 7.29 – 7.35 (m, 2H), 7.39 (dd, $J = 8.2$, 2.9 Hz, 1H), 7.89 – 8.05 (m, 2H). $^{13}$C NMR (101 MHz, Chloroform-d) $\delta$ 21.6, 25.7 (d, $J = 15.9$ Hz), 34.3 (d, $J = 30.3$ Hz), 60.6 (d, $J = 18.1$ Hz), 107.2 (d, $J = 280.9$ Hz), 112.4, 115.4 (d, $J = 21.4$ Hz), 123.5, 124.3, 127.8 (d, $J = 3.0$ Hz), 128.3, 129.8, 130.2 (d, $J = 8.2$ Hz), 131.2, 131.2 (d, $J = 6.3$ Hz), 136.4 (d, $J = 100.2$ Hz), 142.5 (d, $J = 2.4$ Hz), 144.5, 162.3 (d, $J = 247.1$ Hz). $^{19}$F NMR (376 MHz, Chloroform-d) $\delta$ -114.6, -101.6. IR (neat) $\nu$ 3022, 2962, 2949, 1597, 1510, 1463, 1366, 1232, 1189, 1160, 1143, 1123, 1093, 1006, 919, 831, 809, 766, 674, 667 cm$^{-1}$. HRMS (ESI) Calcd. for C$_{23}$H$_{19}$FNO$_2$S requires (M$^-$-F): 392.1115, Found: 392.1112.
**Compound 3ab:** A white solid (36.0 mg, 45%); M.p. 194-195 °C. $^1$H NMR (400 MHz, Chloroform-$d$) $\delta$ 1.84 – 2.04 (m, 1H), 2.42 (s, 3H), 2.91 (h, $J = 7.7$, 7.0 Hz, 2H), 3.30 (t, $J = 10.2$ Hz, 1H), 6.71 (d, $J = 2.2$ Hz, 1H), 7.16 (dd, $J = 8.7$, 2.2 Hz, 1H), 7.18 – 7.61 (m, 8H), 7.84 – 8.04 (m, 2H). $^{13}$C NMR (101 MHz, Chloroform-$d$) $\delta$ 21.6, 25.2 (d, $J = 16.0$ Hz), 34.3 (d, $J = 30.0$ Hz), 60.8 (d, $J = 18.3$ Hz), 107.5 (d, $J = 282.0$ Hz), 113.2, 124.5, 127.6 (d, $J = 3.1$ Hz), 128.0 (d, $J = 2.7$ Hz), 128.3, 128.5, 128.6, 129.8, 134.5 (d, $J = 2.3$ Hz), 136.4, 137.9, 141.12, 141.14, 144.6. $^{19}$F NMR (376 MHz, Chloroform-$d$) $\delta$ -100.8. IR (neat) ν 3008, 2967, 2920, 2849, 1597, 1460, 1357, 1247, 1231, 1177, 1160, 1133, 1121, 1085, 1040, 1012, 1001, 925, 818, 794, 754, 720, 705, 681 cm$^{-1}$. HRMS (ESI) Calcd. for C$_{23}$H$_{19}$ClNO$_2$S requires (M$^+$-F): 408.0820, Found: 408.0819.
**Compound 3ac**: A white solid (36.4 mg, 39%); M.p. 218 °C. $^1$H NMR (400 MHz, Chloroform-$d$) $\delta$ 1.96 (d, $J$ = 8.0 Hz, 1H), 2.42 (s, 3H), 2.86 (dt, $J$ = 15.5, 8.4 Hz, 2H), 3.19 – 3.36 (m, 1H), 6.71 (dd, $J$ = 7.5, 1.3 Hz, 1H), 6.89 – 6.97 (m, 1H), 7.10 – 7.22 (m, 3H), 7.27 – 7.35 (m, 2H), 7.38 (d, $J$ = 8.2 Hz, 1H), 7.41 – 7.53 (m, 2H), 7.81 – 8.11 (m, 2H). $^{13}$C NMR (101 MHz, Chloroform-$d$) $\delta$ 21.5, 25.3 (d, $J$ = 15.6 Hz), 34.2 (d, $J$ = 30.1 Hz), 60.6 (d, $J$ = 17.7 Hz), 107.1 (d, $J$ = 280.8 Hz), 112.3, 121.9, 123.5, 124.2, 127.7 (d, $J$ = 3.0 Hz), 128.3, 129.7, 130.2, 131.5, 134.5, 135.4, 136.7, 142.5, 144.4. $^{19}$F NMR (376 MHz, Chloroform-$d$) $\delta$ -101.8. IR (neat) v 2069, 2927, 1602, 1492, 1469, 1561, 1363, 1257, 1243, 1187, 1179, 1161, 1143, 1121, 1090, 1005, 926, 822, 813, 751, 704, 687 cm$^{-1}$. HRMS (ESI) Calcd. for C$_{23}$H$_{19}$BrNO$_2$S requires (M$^+$-F): 452.0314, Found: 452.0312.
**Compound 4ac:** A white solid (9.8 mg, 9%); M.p. 172-173 °C. $^1$H NMR (400 MHz, Chloroform-$d$) δ 1.90 – 2.07 (m, 1H), 2.07 (dt, $J = 7.3$, 5.4 Hz, 1H), 2.13 (d, $J = 7.7$ Hz, 3H), 2.26 (s, 3H), 3.20 (dd, $J = 25.2$, 12.8 Hz, 1H), 3.53 (t, $J = 12.1$ Hz, 1H), 6.60 – 6.75 (m, 2H), 6.98 – 7.14 (m, 4H), 7.15 – 7.25 (m, 2H), 7.42 (ddd, $J = 7.7$, 7.7, 1.4 Hz, 1H), 7.53 (ddd, $J = 8.2$, 7.8, 1.5 Hz, 1H), 7.63 (ddd, $J = 8.0$, 1.9, 1.9 Hz, 1H), 7.95 (dd, $J = 8.2$, 1.4 Hz, 1H). $^{13}$C NMR (101 MHz, Chloroform-$d$) δ 19.3 (d, $J = 15.4$ Hz), 21.7, 29.7, 33.3 (td, $J = 26.3$, 20.1 Hz), 47.4 (t, $J = 11.6$ Hz), 101.5 (d, $J = 13.2$ Hz), 122.3, 126.3 – 126.4 (m), 126.5, 127.2, 127.3 – 127.4 (m), 128.8, 129.3, 129.6 (d, $J = 2.2$ Hz), 130.4, 130.6, 134.3, 135.6, 136.4, 144.2. $^{19}$F NMR (376 MHz, Chloroform-$d$) δ -107.89 (d, $J = 206.9$ Hz, 1F), -101.29 (d, $J = 255.2$ Hz, 1F), -44.54 (s, 1F). IR (neat) ν 2959, 2923, 2854, 1600, 1490, 1446, 1396, 1363, 1176, 1108, 1091, 1066, 1007, 983, 807, 764, 745, 680, 656 cm$^{-1}$. HRMS (ESI) Calcd. for C$_{25}$H$_{23}$BrF$_3$N$_2$O$_3$S requires (M$^+$+H): 567.0559, Found: 567.0556.
Control experiments

1. Darkness conditions:

![Chemical structure](image)

A solution of 1a (62.6 mg, 0.2 mmol, 1.0 equiv) and 2a (212.6 mg, 0.6 mmol, 3.0 equiv) in 2 mL CH$_3$CN at a vial encapsulated completely by aluminum foil, AcOH (0.1 mL, 2.0 mmol, 10 equiv) was added by a syringe, and the mixture was stirred at room temperature for 6 h. The reaction mixture was concentrated under reduced pressure and the residue was purified by a silica gel flash chromatography (PE/EA = 10:1) to afford the product 3a (62.6 mg) in the isolated yield of 81%.

2. Radical trapping experiments:

![Chemical structure and table](image)

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A solution of 1a (62.6 mg, 0.2 mmol, 1.0 equiv), 2a (212.6 mg, 0.6 mmol, 3.0 equiv) and TEMPO (x equiv) (for entry A, 6.3 mg, 0.04 mmol, 0.2 equiv) (for entry B, 31.3 mg, 0.2 mmol, 1.0 equiv) (for entry C, 93.8 mg, 0.6 mmol, 3.0 equiv) in 2 mL CH$_3$CN at three vials, AcOH (0.1 mL, 2.0 mmol, 10 equiv) was added by a syringe, and the mixture was stirred at rt for 6 h. The reaction mixture was concentrated, and the residue was purified by a flash chromatograph on silica gel using PE/EA (10:1) as the eluent to yield the product 3a in 77% yield along with the recovery of 1a in 15% for entry A, and 3a in 55% yield along with the recovery of 1a in 32% for entry B, and the recovery of 1a in 95% without product 3a for entry C. In addition, the $^{19}$F NMR signal of Selectfluor disappeared in entry C.
The decomposition of Selectfluor for the formation of compound 5a has been confirmed by HRMS.

**Compound 5a:** Its structure has been confirmed by HRMS (ESI) (Calcd. for C₇H₁₄ClN₂ requires (M⁺): 161.0840, Found: 161.0840).
The crystal data of 3t have been deposited in CCDC with number 1474587. Empirical Formula: C_{22}H_{17}BrFNO_2S; Formula Weight: 458.33; Crystal Dimensions: 0.210 x 0.170 x 0.130 mm³; Crystal System: Orthorhombic; Lattice Parameters: a = 10.0581(11)Å, b = 11.3410(12)Å, c = 17.3605(19)Å, α = 90°, β = 90°, γ = 90°, V = 1980.3(4)Å³; Space group: 21 21 21; Z = 4; D_{calc} = 1.537 g/cm³; F_{000} = 928; Final R indices [I>2sigma(I)] R1 = 0.0399, wR2 = 0.0839.
The crystal data of $3w'$ have been deposited in CCDC with number 1838252. Empirical Formula: $\text{C}_{22}\text{H}_{19}\text{F}_2\text{NO}_2\text{S}$; Formula Weight: 399.44; Crystal Dimensions: 0.200 x 0.160 x 0.130 mm$^3$; Crystal System: Monoclinic; Lattice Parameters: $a = 14.943(3)\text{Å}$, $b = 11.511(2)\text{Å}$, $c = 11.392(2)\text{Å}$, $\alpha = 90^\circ$, $\beta = 98.266(6)^\circ$, $\gamma = 90^\circ$, $V = 1939.0(6)\text{Å}^3$; Space group: P 21/c; $Z = 4$; $D_{\text{calc}} = 1.368 \text{ g/cm}^3$; $F_{000} = 832$; Final R indices [I>2\sigma(I)] $R1 = 0.0651$, $wR2 = 0.1539$. 

The crystal structure of $3w'$ is depicted above, showing the molecular arrangement and bond distances.
The crystal data of 4ac have been deposited in CCDC with number 1504263. Empirical formula: C_{25}H_{22}BrF_{3}N_{2}O_{3}S, Formula weight: 567.41, Crystal system: Monoclinic, Space group: P 21/n, Unit cell dimensions: a = 14.399(2) Å, α = 90°; b = 9.6415(16) Å, β = 93.004(4)°; c = 17.024(3) Å, γ = 90°. Volume: 2360.2(7) Å³, Z = 4, Density (calculated): 1.597 Mg/m³, F(000) = 1152, Crystal size: 0.200 x 0.150 x 0.100 mm³, Final R indices [I>2σ(I)]: R1 = 0.0428, wR2 = 0.1007.
References


