Supporting Information

Diastereoselective Johnson-Corey-Chaykovsky Trifluoroethylidenation

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1. General Information

$^1$H, $^{13}$C and $^{19}$F NMR spectra were detected on a 500 MHz, 400 MHz or 300 MHz NMR spectrometer. Data for $^1$H NMR, $^{13}$C NMR and $^{19}$F NMR were recorded as follows: chemical shift ($\delta$, ppm), multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet, q = quartet, coupling constant (s) in Hz). Mass spectra were obtained on GC-MS or LC-MS (ESI). High resolution mass data were recorded on a high resolution mass spectrometer in the EI or ESI mode.

Reagents such as 2,2,2-trifluoroethyl triflate, diphenyl sulfide, TBAF, TBAT and extra dry dichloromethane are commercially available.

2. Screening Reaction Conditions for the Synthesis of Salt 1

2.1 Screening reaction conditions for the synthesis of salt 1

Table S2.1. Screening reaction conditions for the synthesis of salt 1

<table>
<thead>
<tr>
<th>Entry</th>
<th>B</th>
<th>A:B</th>
<th>Temp. (°C)</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>B1</td>
<td>5:1</td>
<td>120 °C</td>
<td>N.R.</td>
</tr>
<tr>
<td>2</td>
<td>B1</td>
<td>10:1</td>
<td>200 °C</td>
<td>N.R.</td>
</tr>
<tr>
<td>3</td>
<td>B2</td>
<td>10:1</td>
<td>120 °C</td>
<td>N.R.</td>
</tr>
<tr>
<td>4</td>
<td>B3</td>
<td>10:1</td>
<td>120 °C</td>
<td>3%</td>
</tr>
<tr>
<td>5</td>
<td>B3</td>
<td>1:5</td>
<td>100 °C</td>
<td>N.R.</td>
</tr>
<tr>
<td>6</td>
<td>B3</td>
<td>1:5</td>
<td>200 °C</td>
<td>82%</td>
</tr>
<tr>
<td>7</td>
<td>B3</td>
<td>1:5</td>
<td>150 °C</td>
<td>80%</td>
</tr>
<tr>
<td>8</td>
<td>B3</td>
<td>1:5</td>
<td>120 °C</td>
<td>32%</td>
</tr>
</tbody>
</table>
2.2 Typical Procedure for the Synthesis of 1

\[
\begin{align*}
\text{Ph-S-Ph} + \text{F}_3\text{C}=-\text{O}+\text{S}=-\text{CF}_3 & \xrightarrow{\text{neat \ 150 \ } ^\circ\text{C}} \text{Ph-S-Ph} \text{OTf} \text{CF}_3 \\
\end{align*}
\]

The mixture of 2,2,2-trifluoroethyl triflate (4.64 g, 20 mmol, 1.0 equiv.) and diphenyl sulfide (18.6 g, 100 mmol, 5.0 equiv.) in a sealed tube was stirred at 150 °C for 30 hours. After the reaction mixture was cooled to room temperature, diethyl ether (10 mL) was added to precipitate the crude product, which was then washed by dry diethyl ether to give the final product 1 (5.9 g, yield 70%).

Diphenyl(2,2,2-trifluoroethyl)sulfonyl triflate (1): White solid. M.P.: 136.6 - 137.8 °C; \(^1\)H NMR (400 MHz, acetone-\(d_6\)) \(\delta\) 8.35 (d, \(J = 7.7\) Hz, 4H), 7.98 - 7.90 (m, 2H), 7.89 - 7.80 (m, 4H), 5.75 (q, \(J = 8.8\) Hz, 2H); \(^1\)F NMR (376 MHz, acetone-\(d_6\)) \(\delta\) -61.20 (t, \(J = 8.8\) Hz, 3F), -78.95 (s, 3F); \(^{13}\)C NMR (101 MHz, acetone-\(d_6\)) \(\delta\) 135.44 (s), 131.67 (s), 131.07 (s), 124.25 (s), 122.58 (q, \(J = 278.2\) Hz), 121.35 (q, \(J = 321.4\) Hz), 45.04 (q, \(J = 33.9\) Hz); IR (neat) \(\nu\) = 3096, 3067, 2999, 2937, 1484, 1450, 1415, 1342, 1244, 1155, 1110, 1029, 761, 740, 690, 679, 639, 541, 517, 507, 467 cm\(^{-1}\); HRMS (ESI) Calcd for C\(_{14}\)H\(_{12}\)F\(_3\)S\(^+\) [M - OTf]\(^+\): 269.0606, Found: 269.0604; Calcd for CF\(_3\)O\(_3\)S\(^-\) [OTf]\(^-\): 148.9526, Found: 148.9522.

3. Screening Reaction Conditions for Exopoxidation, Cyclopropanation and Airdination
3.1 Screening reaction conditions for epoxidation

Screening bases for the epoxidation of 2a (4-nitrobenzaldehyde) with reagent 1 in DCM suggested that TBAT was a suitable base (entries 1-7, Table S3.1). The reaction was sensitive to the solvent, and DCM seemed to be a good choice (entries 8-12 vs Entry 5). Lowering the reaction temperature led to a dramatic decrease in the yield (entry 13, Table S3.1), and elevating the temperature improved the yield slightly to 68% (entry 14). The use of excess aldehyde (2 equiv.) was necessary to efficiently trap the unstable ylide intermediate generated in situ, as evidenced by the observation that decreasing the loading of aldehyde resulted in lower yield (entry 15). Increasing the reaction scale and shortening the time had no negative effect on this transformation (entry 16). Under these optimal reaction conditions (entry 16), the substrate scope of epoxidation was investigated.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Base</th>
<th>Solvent</th>
<th>Temp. (°C)</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>NaF</td>
<td>DCM</td>
<td>r.t.</td>
<td>NR</td>
</tr>
<tr>
<td>2</td>
<td>CsF</td>
<td>DCM</td>
<td>r.t.</td>
<td>NR</td>
</tr>
<tr>
<td>3&lt;sup&gt;c&lt;/sup&gt;</td>
<td>CsF</td>
<td>DCM</td>
<td>r.t.</td>
<td>27</td>
</tr>
<tr>
<td>4</td>
<td>TBAF</td>
<td>DCM</td>
<td>r.t.</td>
<td>35</td>
</tr>
<tr>
<td>5</td>
<td>TBAT</td>
<td>DCM</td>
<td>r.t.</td>
<td>64</td>
</tr>
<tr>
<td>6&lt;sup&gt;d&lt;/sup&gt;</td>
<td>iPr&lt;sub&gt;2&lt;/sub&gt;NH</td>
<td>DCM</td>
<td>r.t.</td>
<td>14</td>
</tr>
<tr>
<td>7</td>
<td>Cs&lt;sub&gt;2&lt;/sub&gt;CO&lt;sub&gt;3&lt;/sub&gt;</td>
<td>DCM</td>
<td>r.t.</td>
<td>30</td>
</tr>
<tr>
<td>8</td>
<td>TBAT</td>
<td>DMF</td>
<td>r.t.</td>
<td>16</td>
</tr>
<tr>
<td>9</td>
<td>TBAT</td>
<td>CH&lt;sub&gt;3&lt;/sub&gt;CN</td>
<td>r.t.</td>
<td>30</td>
</tr>
<tr>
<td>10</td>
<td>TBAT</td>
<td>THF</td>
<td>r.t.</td>
<td>13</td>
</tr>
<tr>
<td>11</td>
<td>TBAT</td>
<td>Toluene</td>
<td>r.t.</td>
<td>11</td>
</tr>
<tr>
<td>12</td>
<td>TBAT</td>
<td>DCE</td>
<td>r.t.</td>
<td>48</td>
</tr>
<tr>
<td>13</td>
<td>TBAT</td>
<td>DCM</td>
<td>0 °C</td>
<td>43</td>
</tr>
</tbody>
</table>

<sup>a</sup> Table S3.1. Screening reaction conditions for epoxidation
3.2 Screening reaction conditions for cyclopropanation

The investigation of the base (entries 1-10, Table S3.2) for the cyclopropanation of 4'-phenyl-phenyl vinyl ketone 4a with reagent 1 showed that TBAF or TBAT was suitable (entries 9 and 10). This transformation was not sensitive to the reaction solvent (entries 11-16). Considering the price of the base and the operational convenience of the solvent, TBAF and DCM were chosen as the base and the solvent respectively (entry 9).

Table S3.2. Screening reaction conditions for cyclopropanation

<table>
<thead>
<tr>
<th>Entry</th>
<th>Base</th>
<th>Solvent</th>
<th>Time</th>
<th>Ratio $^b$</th>
<th>Yield $^c$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Cs$_2$CO$_3$</td>
<td>DCM</td>
<td>1 h</td>
<td>2 : 1 : 1.5</td>
<td>49</td>
</tr>
<tr>
<td>2</td>
<td>Na$_2$CO$_3$</td>
<td>DCM</td>
<td>1 h</td>
<td>2 : 1 : 1.5</td>
<td>N.R.</td>
</tr>
<tr>
<td>3</td>
<td>DBU</td>
<td>DCM</td>
<td>1 h</td>
<td>2 : 1 : 1.5</td>
<td>29</td>
</tr>
<tr>
<td>4</td>
<td>Et$_3$N</td>
<td>DCM</td>
<td>1 h</td>
<td>2 : 1 : 1.5</td>
<td>14</td>
</tr>
<tr>
<td>5</td>
<td>KF</td>
<td>DCM</td>
<td>1 h</td>
<td>2 : 1 : 1.5</td>
<td>N.R.</td>
</tr>
<tr>
<td>6$^d$</td>
<td>KF</td>
<td>DCM</td>
<td>1 h</td>
<td>2 : 1 : 1.5</td>
<td>58</td>
</tr>
<tr>
<td>7</td>
<td>CsF</td>
<td>DCM</td>
<td>1 h</td>
<td>2 : 1 : 1.5</td>
<td>10</td>
</tr>
<tr>
<td>8</td>
<td>TBAF</td>
<td>DCM</td>
<td>1 h</td>
<td>2 : 1 : 1.5</td>
<td>90</td>
</tr>
<tr>
<td>9</td>
<td>TBAF</td>
<td>DCM</td>
<td>2 h</td>
<td>2 : 1 : 1.5</td>
<td>100</td>
</tr>
<tr>
<td>10</td>
<td>TBAT</td>
<td>DCM</td>
<td>2 h</td>
<td>2 : 1 : 1.5</td>
<td>100</td>
</tr>
<tr>
<td>11</td>
<td>TBAT</td>
<td>DCM</td>
<td>2 h</td>
<td>1 : 1.5 : 1.5</td>
<td>92</td>
</tr>
</tbody>
</table>

$^a$Reaction conditions: 1 (0.1 mmol), 2a (2 equiv.), base (1.5 equiv.) and 4Å MS (80 mg) in solvent (2 mL) for 1 h. NR: no reaction; $^b$Determined by $^{19}$F NMR with the use of trifluoromethyl benzene as an internal standard; $^c$18-crown-6 (1.5 equiv.) was used as additive; $^d$The reaction was run for 4 h; $^e$Molar ratio: 1 : 2a : base = 1 : 1.5 : 1; $^f$Reaction conditions: 1 (0.5 mmol), 2a (1 mmol), base (0.75 mmol) and 4Å MS (400 mg) in DCM (10 mL) for 20 minutes.
3.3 Screening reaction conditions for aziridination

Various reaction conditions, including base, solvent and temperature, were examined for aziridination of compound 6a with reagent 1. The optimal reaction conditions (entry 1, Table S3.3) were similar with that for cyclopropanation.

Table S3.3. Screening reactions conditions for aziridination

<table>
<thead>
<tr>
<th>Entry</th>
<th>Base</th>
<th>Solvent</th>
<th>Ratio</th>
<th>Yield</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>DCM</td>
<td>TBAF</td>
<td>rt.</td>
<td>100%</td>
</tr>
<tr>
<td>2</td>
<td>DCM</td>
<td>TBAT</td>
<td>rt.</td>
<td>100%</td>
</tr>
<tr>
<td>3</td>
<td>DCM</td>
<td>Et3N</td>
<td>rt.</td>
<td>89%</td>
</tr>
<tr>
<td>4</td>
<td>DCM</td>
<td>DBU</td>
<td>rt.</td>
<td>78%</td>
</tr>
<tr>
<td>5</td>
<td>DCM</td>
<td>Cs2CO3</td>
<td>rt.</td>
<td>90%</td>
</tr>
<tr>
<td>6</td>
<td>DCM</td>
<td>CsF</td>
<td>rt.</td>
<td>62%</td>
</tr>
<tr>
<td>7d</td>
<td>DCM</td>
<td>KF</td>
<td>rt.</td>
<td>76%</td>
</tr>
<tr>
<td>8</td>
<td>THF</td>
<td>TBAF</td>
<td>rt.</td>
<td>95%</td>
</tr>
<tr>
<td>9</td>
<td>CH3CN</td>
<td>TBAF</td>
<td>rt.</td>
<td>76%</td>
</tr>
<tr>
<td>10</td>
<td>Dioxane</td>
<td>TBAF</td>
<td>rt.</td>
<td>100%</td>
</tr>
<tr>
<td>11</td>
<td>DMF</td>
<td>TBAF</td>
<td>rt.</td>
<td>72%</td>
</tr>
<tr>
<td>12</td>
<td>DMSO</td>
<td>TBAF</td>
<td>rt.</td>
<td>84%</td>
</tr>
<tr>
<td>13</td>
<td>DMA</td>
<td>TBAF</td>
<td>rt.</td>
<td>76%</td>
</tr>
<tr>
<td>14</td>
<td>NMP</td>
<td>TBAF</td>
<td>rt.</td>
<td>86%</td>
</tr>
</tbody>
</table>

Notes:

a Reaction conditions: 1 (0.1 mmol), 4a (2 equiv.), base (1.5 equiv.) and 4Å MS (80 mg) in solvent (2 mL); b Molar ratio: 1 : 4a : base = 1 : 2 : 1.5; c Determined by 19F NMR with the use of trifluoromethyl benzene as an internal standard. d 18-crown-6 (1.5 equiv.) was used as additive.
4. Typical Procedure for the Preparation of 4, 6

4.1 Procedure for the Preparation of 4

4 were synthesized according to the procedure reported in literature.[1]

\[
\begin{align*}
&\text{R} \quad \text{O} \\
\begin{array}{c}
\text{\text{+}} \\
\text{(HCHO)}_n \\
\text{TAMA} \\
\text{THF, reflux} \\
\text{4}
\end{array}
\end{align*}
\]

Into the solution of paraformaldehyde (7.5 g, 250/n mmol, 5.0 equiv.) and N-methylanilinium trifluoroacetate (TAMA, 11.05 g, 50 mmol, 1.0 equiv.) in THF (50 mL) was added aryl methyl ketone (50 mmol, 1.0 equiv.) under N\textsubscript{2} atmosphere. The mixture was refluxed for 10 h. After being cooled to room temperature, the solvent was removed by concentration under vacuum. The residue was dissolved in ethyl acetate (100 mL). The organic phase was washed with H\textsubscript{2}O (100 mL × 2), HCl solution (1M) and H\textsubscript{2}O (100 mL), and then dried over Na\textsubscript{2}SO\textsubscript{4}. After filtration and concentration, the residue was subjected to flash column chromatography with hexane/ethyl acetate to afford the product 4.

\[
\begin{align*}
\text{O} \\
\text{4a}
\end{align*}
\]

1-(1,1'-Biphenyl]-4-yl)prop-2-en-1-one (4a)[2]: 56%; \textsuperscript{1}H NMR (300 MHz, CDCl\textsubscript{3}) δ 8.04 (d, J = 7.8 Hz, 2H), 7.71 (d, J = 7.8 Hz, 2H), 7.64 (d, J = 7.8 Hz, 2H), 7.48 (t, J = 7.2 Hz, 2H), 7.41 (t, J = 7.2 Hz, 1H), 7.24 (dd, J = 17.1, 10.5 Hz, 1H), 6.48 (dd, J = 17.1, 1.5 Hz, 1H), 5.96 (dd, J = 10.5, 1.5 Hz, 1H).
1-(4-Methoxyphenyl)prop-2-en-1-one (4b): 40%; $^1$H NMR (300 MHz, CDCl$_3$) δ 7.97 (d, $J$ = 8.6 Hz, 2H), 7.18 (dd, $J$ = 17.1, 10.6 Hz, 1H), 6.97 (d, $J$ = 8.6 Hz, 2H), 6.43 (d, $J$ = 17.1 Hz, 1H), 5.88 (d, $J$ = 10.6 Hz, 1H), 3.88 (s, 3H).

1-(3-Methoxyphenyl)prop-2-en-1-one (4c): 26%; $^1$H NMR (400 MHz, CDCl$_3$) δ 7.50 - 7.39 (m, 2H), 7.31 (t, $J$ = 7.8 Hz, 1H), 7.16 - 7.01 (m, 2H), 6.38 (d, $J$ = 17.1 Hz, 1H), 5.85 (d, $J$ = 10.5 Hz, 1H), 3.78 (s, 3H).

1-(Naphthalen-2-yl)prop-2-en-1-one (4d): 45%; $^1$H NMR (300 MHz, CDCl$_3$) δ 8.47 (s, 1H), 8.04 (d, $J$ = 8.6 Hz, 1H), 8.00 - 7.85 (m, 3H), 7.67 - 7.51 (m, 2H), 7.33 (dd, $J$ = 17.1, 10.6 Hz, 1H), 6.51 (d, $J$ = 17.1 Hz, 1H), 5.98 (d, $J$ = 10.6 Hz, 1H).
1-(4-Fluorophenyl)prop-2-en-1-one (4e): 37%; $^1$H NMR (300 MHz, CDCl$_3$) δ 8.09 - 7.87 (m, 2H), 7.22 - 7.04 (m, 3H), 6.44 (d, $J = 17.1$ Hz, 1H), 5.94 (d, $J = 10.6$ Hz, 1H); $^{19}$F NMR (282 MHz, CDCl$_3$) δ -105.06 - -105.56 (m, 1F).

1-(4-Chlorophenyl)prop-2-en-1-one (4g): 72%; $^1$H NMR (300 MHz, CDCl$_3$) δ 7.90 (d, $J = 8.1$ Hz, 2H), 7.46 (d, $J = 8.1$ Hz, 2H), 7.12 (dd, $J = 17.1$, 10.6 Hz, 1H), 6.45 (d, $J = 17.1$ Hz, 1H), 5.96 (d, $J = 10.6$ Hz, 1H).

1-(3-Chlorophenyl)prop-2-en-1-one (4g): 44%; $^1$H NMR (300 MHz, CDCl$_3$) δ 7.79 (s, 1H), 7.73 - 7.66 (m, 1H), 7.46 - 7.38 (m, 1H), 7.36 - 7.26 (m, 1H), 7.00 (dd, $J = 17.1$, 10.6 Hz, 1H), 6.34 (dd, $J = 17.1$, 1.3 Hz, 1H), 5.85 (dd, $J = 10.6$, 1.3 Hz, 1H).

1-(4-Bromophenyl)prop-2-en-1-one (4h): 59%; Colorless liquid. $^1$H NMR (300 MHz, CDCl$_3$) δ 7.82 (d, $J = 8.6$ Hz, 2H), 7.63 (d, $J = 8.6$ Hz, 2H), 7.12 (dd, $J = 17.1$, 10.6 Hz, 1H), 6.45 (dd, $J = 17.1$, 1.5 Hz, 1H), 5.96 (dd, $J = 10.6$, 1.5 Hz, 1H).
1-(2-Bromophenyl)prop-2-en-1-one (4i)\(^{[2]}\): 31%; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.60 (d, \(J = 8.3\) Hz, 1H), 7.41 - 7.27 (m, 3H), 6.71 (dd, \(J = 17.5, 10.5\) Hz, 1H), 6.09 (d, \(J = 17.5\) Hz, 1H), 6.06 (d, \(J = 10.5\) Hz, 1H).

1-(4-Nitrophenyl)prop-2-en-1-one (4j)\(^{[1]}\): 27%; \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) 8.26 (d, \(J = 8.6\) Hz, 2H), 8.01 (d, \(J = 8.6\) Hz, 2H), 7.06 (dd, \(J = 17.1, 10.6\) Hz, 1H), 6.41 (d, \(J = 17.1\) Hz, 1H), 6.00 (d, \(J = 10.6\) Hz, 1H).

1-(3-Nitrophenyl)prop-2-en-1-one (4d)\(^{[3]}\): 31%; \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) 8.77 (s, 1H), 8.45 (d, \(J = 7.4\) Hz, 1H), 8.28 (d, \(J = 7.4\) Hz, 1H), 7.71 (t, \(J = 7.4\) Hz, 1H), 7.18 (dd, \(J = 17.1, 9.7\) Hz, 1H), 6.53 (d, \(J = 17.1\) Hz, 1H), 6.08 (d, \(J = 9.7\) Hz, 1H).

1-(2-Nitrophenyl)prop-2-en-1-one (4l)\(^{[4]}\): 52%; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.91 - 7.79 (m, 2H), 7.45 - 7.34 (m, 2H), 7.07 (dd, \(J = 17.1, 10.6\) Hz, 1H), 6.40 (dd, \(J = 17.1, 1.6\) Hz, 1H), 5.90
1-(Furan-2-yl)prop-2-en-1-one (4m): 29%; ^1H NMR (400 MHz, CDCl$_3$) δ 7.61 (d, $J = 0.9$ Hz, 1H), 7.32 - 7.20 (m, 1H), 7.04 (dd, $J = 17.2$, 10.5 Hz, 1H), 6.60 - 6.43 (m, 2H), 5.84 (dd, $J = 10.5$, 1.6 Hz, 1H).

1-Cyclohexylprop-2-en-1-one (4n): 23%; ^1H NMR (400 MHz, CDCl$_3$) δ 6.43 (dd, $J = 17.5$, 10.5 Hz, 1H), 6.25 (dd, $J = 17.5$, 1.2 Hz, 1H), 5.75 (dd, $J = 10.5$, 1.2 Hz, 1H), 2.62 (ddd, $J = 11.0$, 8.7, 2.3 Hz, 1H), 1.86 - 1.78 (m, 4H), 1.69 (d, $J = 11.6$ Hz, 1H), 1.40 - 1.25 (m, 5H).

4.2 Procedure for the Synthesis of 6

6 were synthesized according to the procedure reported in literature[^6].

**Method A:**

![Method A diagram]

**Method B:**

![Method B diagram]

**Method A[^6b, 6c]:** Aldehyde (31.5 mmol, 1.05 equiv), sulfonamide (30.0 mmol, 1.0 equiv) and tetraethyl orthosilicate (120 mmol, 25 g, 4.0 equiv) were combined in a flask equipped with a still head and the mixture was stirred at 160°C until no ethanol was produced. After the reaction
system was cooled to room temperature, ethyl acetate/n-hexane (1:3) was added to precipitate the crude product. After filtration, the solid was washed by ethyl acetate/n-hexane(1:3) followed by ethanol to give the pure product 6a-j, l-m.

**Method B**\textsuperscript{[6a]}: Aldehyde (30.0 mmol, 1.0 equiv), sodium \(p\)-tolylsulfinate (30.0 mmol, 1.0 equiv) and sulfonamide (30 mmol, 1.0 equiv) were mixed in formic acid/H\(_2\)O (1:1, 100 mL) and stirred for 72 h at room temperature. The resulting white precipitate was filtered off, washed with H\(_2\)O (2 x 30 mL), then pentane (30 mL), and dissolved in CH\(_2\)Cl\(_2\) (150 mL). Sat. aq NaHCO\(_3\) was added and the solution was well stirred overnight at room temperature. The organic phase was decanted, then washed with brine and dried over Na\(_2\)SO\(_4\). Filtered off and the solvent removed under vacuum to yield the corresponding product 6k.

\(\text{N}^\text{Ts}\) 6a (\((E)\)-N-Benzylidene-4-methylbenzenesulfonamide (6a)\textsuperscript{[7]}: \(1^H\) NMR (300 MHz, CDCl\(_3\)) \(\delta\) 9.03 (s, 1H), 7.95 - 7.86 (m, 4H), 7.65 - 7.58 (m, 1H), 7.49 (t, \(J = 7.5\) Hz, 2H), 7.35 (d, \(J = 8.0\) Hz, 2H), 2.44 (s, 3H).

\(\text{N}^\text{Ts}\) 6b (\((E)\)-4-Methyl-N-(4-methylbenzylidene)benzenesulfonamide (6b)\textsuperscript{[7]}: \(1^H\) NMR (400 MHz, CDCl\(_3\)) \(\delta\) 8.97 (s, 1H), 7.86 (d, \(J = 8.1\) Hz, 2H), 7.79 (d, \(J = 7.6\) Hz, 2H), 7.32 (d, \(J = 7.9\) Hz, 2H), 7.26 (d, \(J = 7.8\) Hz, 2H), 2.41 (s, 6H).

\(\text{N}^\text{Ts}\) 6c (\((E)\)-N-(4-Methoxybenzylidene)-4-methylbenzenesulfonamide (6c)\textsuperscript{[7]}: \(1^H\) NMR (300 MHz, CDCl\(_3\)) \(\delta\) 8.94 (s, 1H), 7.94 - 7.83 (m, 4H), 7.33 (d, \(J = 8.3\) Hz, 2H), 6.97 (d, \(J = 8.3\) Hz, 2H), 3.89 (s, 3H), 2.43 (s, 3H).
(E)-N-([1,1'-Biphenyl]-4-ylmethylene)-4-methylbenzenesulfonamide (6d): \(^1\)H NMR (400 MHz, CDCl\(_3\)) δ 9.05 (s, 1H), 7.98 (d, \(J = 8.0\) Hz, 2H), 7.89 (d, \(J = 8.0\) Hz, 2H), 7.70 (d, \(J = 7.9\) Hz, 2H), 7.61 (d, \(J = 7.3\) Hz, 2H), 7.50 - 7.37 (m, 3H), 7.34 (d, \(J = 7.9\) Hz, 2H), 2.43 (s, 3H).

(\(E\))-4-Methyl-N-(naphthalen-2-ylmethylene)benzenesulfonamide (6e): \(^1\)H NMR (400 MHz, CDCl\(_3\)) δ 9.16 (s, 1H), 8.32 (s, 1H), 8.02 (d, \(J = 8.3\) Hz, 1H), 7.96 - 7.84 (m, 5H), 7.62 (t, \(J = 7.2\) Hz, 1H), 7.56 (t, \(J = 7.6\) Hz, 1H), 7.34 (d, \(J = 7.6\) Hz, 2H), 2.43 (s, 3H).

(\(E\))-N-(4-Fluorobenzylidene)-4-methylbenzenesulfonamide (6f): \(^1\)H NMR (400 MHz, CDCl\(_3\)) δ 8.98 (s, 1H), 7.94 (dd, \(J = 8.5, 5.5\) Hz, 2H), 7.87 (d, \(J = 8.2\) Hz, 2H), 7.33 (d, \(J = 8.2\) Hz, 2H), 7.16 (t, \(J = 8.5\) Hz, 2H), 2.42 (s, 3H); \(^19\)F NMR (376 MHz, CDCl\(_3\)) δ -101.03 - -101.13 (m, 1F).

(\(E\))-N-(4-Chlorobenzylidene)-4-methylbenzenesulfonamide (6g): \(^1\)H NMR (300 MHz, CDCl\(_3\)) δ 8.99 (s, 1H), 7.94 - 7.81 (m, 4H), 7.46 (d, \(J = 8.3\) Hz, 2H), 7.35 (d, \(J = 8.3\) Hz, 2H), 2.44 (s, 3H).
\((E)-N-(4\text{-}Bromobenzylidene)\text{-}4\text{-}methylbenzenesulfonamide (6h)\):
\(^{1}\text{H} \text{NMR} (400 \text{ MHz, CDCl}_3) \delta 8.95 (s, 1H), 7.86 (d, J = 8.2 \text{ Hz, 2H}), 7.75 (d, J = 8.4 \text{ Hz, 2H}), 7.60 (d, J = 8.4 \text{ Hz, 2H}), 7.33 (d, J = 8.0 \text{ Hz, 2H}), 2.41 (s, 3H).

\((E)-N-(4\text{-}Cyanobenzylidene)\text{-}4\text{-}methylbenzenesulfonamide (6i)\):
\(^{1}\text{H} \text{NMR} (400 \text{ MHz, CDCl}_3) \delta 9.04 (s, 1H), 8.01 (d, J = 8.2 \text{ Hz, 2H}), 7.88 (d, J = 8.2 \text{ Hz, 2H}), 7.76 (d, J = 8.2 \text{ Hz, 2H}), 7.36 (d, J = 8.2 \text{ Hz, 2H}), 2.44 (s, 3H).

\((E)-4\text{-}Methyl-N-(3\text{-}(\text{trifluoromethyl})benzylidene)benzenesulfonamide (6j)\):
\(^{1}\text{H} \text{NMR} (300 \text{ MHz, CDCl}_3) \delta 9.08 (s, 1H), 8.20 (s, 1H), 8.10 (d, J = 7.8 \text{ Hz, 1H}), 7.90 (d, J = 8.1 \text{ Hz, 2H}), 7.86 (d, J = 8.1 \text{ Hz, 1H}), 7.65 (t, J = 7.8 \text{ Hz, 1H}), 7.37 (d, J = 8.1 \text{ Hz, 2H}), 2.45 (s, 3H); \(^{19}\text{F} \text{NMR} (376 \text{ MHz, CDCl}_3) \delta -63.04 (s, 3F).

\((E)-N-(\text{Cyclohexylmethylene})\text{-}4\text{-}methylbenzenesulfonamide (6k)\):
\(^{1}\text{H} \text{NMR} (400 \text{ MHz, CDCl}_3) \delta 8.45 (d, J = 4.4 \text{ Hz, 1H}), 7.77 (d, J = 8.2 \text{ Hz, 2H}), 7.30 (d, J = 8.2 \text{ Hz, 2H}), 2.48 - 2.36 (br s, 4H), 1.91 - 1.80 (m, 5H), 1.76 - 1.70 (m, 2H), 1.68 - 1.62 (m, 1H), 1.36 - 1.12 (m, 5H).
(E)-N-(4-Fluorobenzylidene)methanesulfonamide (6l)\textsuperscript{[12]}: \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) \(\delta\) 8.98 (s, 1H), 7.98 (dd, \(J = 8.3, 5.5\) Hz, 2H), 7.20 (t, \(J = 8.3\) Hz, 2H), 3.12 (s, 3H); \textsuperscript{19}F NMR (376 MHz, CDCl\textsubscript{3}) \(\delta\) -99.07 - -101.73 (m).

(E)-N-(4-Bromobenzylidene)methanesulfonamide (6m)\textsuperscript{[13]}: \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) \(\delta\) 8.97 (s, 1H), 7.80 (d, \(J = 8.4\) Hz, 2H), 7.67 (d, \(J = 8.4\) Hz, 2H), 3.12 (s, 3H).

5. Procedure for the Synthesis of 3, 5, 7

5.1 Procedure for the Synthesis of 3

\[
\begin{align*}
\text{Ph}_2\text{SCH}_2\text{CF}_3 + \text{R} & \xrightarrow{\text{TBAT, 4Å MS, DCM, reflux, 20 min}} \text{R} \text{CF}_3
\end{align*}
\]

Into the mixture of diphenyl(2,2,2-trifluoroethyl)sulfonium triflate 1 (0.5 mmol, 0.2092 g, 1.0 equiv.), aldehyde 2 (1.0 mmol, 2.0 equiv.), TBAT (0.75 mmol, 0.4048 g, 1.5 equiv.) and 4Å MS (0.4 g) was added dichloromethane (8 mL) under N\textsubscript{2} atmosphere. The resulting mixture was refluxed for 20 min. After filtration, the solvent was removed by concentration under vacuum and the residue was subjected to flash column chromatography with hexane/ethyl acetate (100:1-20:1) as the eluent to afford the final product.
(2SR,3RS)-2-(4-Nitrophenyl)-3-(trifluoromethyl)oxirane (3a): 61%; White solid. M.P. 55.0-56.1 oC; ¹H NMR (400 MHz, CDCl₃) δ 8.25 (d, J = 8.6 Hz, 2H), 7.49 (d, J = 8.6 Hz, 2H), 4.25 (s, 1H), 3.57 - 3.44 (m, 1H); ¹³C NMR (101 MHz, CDCl₃) δ 148.44 (s), 140.65 (s), 126.72 (s), 123.97 (s), 121.71 (q, J = 276.3 Hz), 57.06 (q, J = 41.3 Hz), 53.95 (q, J = 2.8 Hz); IR (neat) ν = 3087, 2973, 1936, 1608, 1525, 1465, 1351, 1285, 1159, 872, 698 cm⁻¹; HRMS (EI) Calcd for C₉H₆NO₃F₃ [M]⁺: 233.0300, Found: 233.0298.

(2SR,3RS)-2-(3-Nitrophenyl)-3-(trifluoromethyl)oxirane (3b): 50%; Colourless liquid; ¹H NMR (400 MHz, CDCl₃) δ 8.26 (d, J = 7.9 Hz, 1H), 8.20 (s, 1H), 7.73 - 7.58 (m, 2H), 4.29 (s, 1H), 3.56 (dq, J = 4.6, 1.3 Hz, 1H); ¹⁹F NMR (376 MHz, CDCl₃) δ -74.01 (d, J = 4.6 Hz, 3F); HRMS (EI) calcd. for C₉H₆F₃NO₃ [M]⁺: 233.0300, Found: 233.0297.

(2SR,3RS)-2-(2-Nitrophenyl)-3-(trifluoromethyl)oxirane (3c): 62%; Light yellow liquid; ¹H NMR (400 MHz, CDCl₃) δ 8.24 (dd, J = 8.2, 0.9 Hz, 1H), 7.78 - 7.68 (m, 1H), 7.64 - 7.52 (m, 2H), 4.75 (d, J = 1.9 Hz, 1H), 3.37 (qd, J = 4.7, 1.9 Hz, 1H); ¹⁹F NMR (376 MHz, CDCl₃) δ -74.36 (d, J = 4.7 Hz, 3F); ¹³C NMR (101 MHz, CDCl₃) δ 147.26 (s), 134.63 (s), 130.64 (s), 129.76 (s), 127.19 (s), 125.02 (s), 121.85 (q, J = 276.1 Hz), 56.21 (q, J = 41.4 Hz), 53.79 (q, J = 3.3 Hz); IR (neat) ν = 3091, 2864, 1621, 1579, 1533, 1489, 1459, 1445, 1347, 1313, 1282, 1247, 1199, 1166, 1093,
973, 932, 890, 875, 861, 844, 794, 739, 702, 685, 675, 629, 571, 503 cm\(^{-1}\); HRMS (EI): calcd. for C\(_9\)H\(_6\)F\(_3\)NO\(_3\) [M\(^+\)]: 233.0300, Found: 233.0298.

(2SR,3RS)-2-(4-(Methylsulfonyl)phenyl)-3-(trifluoromethyl)oxirane (3d): 56%; White solid. M.P. 103.5-104.8 °C; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.96 (d, \(J = 8.4\) Hz, 2H), 7.51 (d, \(J = 8.4\) Hz, 2H), 4.22 (d, \(J = 1.7\) Hz, 1H), 3.49 (qd, \(J = 4.6, 1.7\) Hz, 1H), 3.04 (s, 3H); \(^{19}\)F NMR (376 MHz, CDCl\(_3\)) \(\delta\) -74.02 (d, \(J = 4.6\) Hz, 3F); \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 141.52 (s), 139.75 (s), 127.99 (s), 126.80 (s), 121.76 (q, \(J = 276.2\) Hz), 57.09 (q, \(J = 41.3\) Hz), 54.10 (q, \(J = 2.8\) Hz), 44.43 (s); IR (neat) \(\nu\) = 3033, 2943, 1607, 1466, 1413, 1354, 1304, 1290, 1252, 1155, 1119, 1086, 968, 926, 867, 836, 799, 767, 722, 675, 558, 544, 535 cm\(^{-1}\); HRMS (EI): calcd. for C\(_{10}\)H\(_9\)F\(_3\)O\(_3\)S [M\(^+\)]: 266.0224, Found: 266.0225.

(2SR,3RS)-2-(3-(Methylsulfonyl)phenyl)-3-(trifluoromethyl)oxirane (3e): 49%; White solid. M.P. 68.1-69.3 °C; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.98 (dt, \(J = 7.0, 1.8\) Hz, 1H), 7.91 (s, 1H), 7.70 -7.58 (m, 2H), 4.26 (d, \(J = 1.5\) Hz, 1H), 3.56 (qd, \(J = 4.6, 1.5\) Hz, 1H); \(^{19}\)F NMR (376 MHz, CDCl\(_3\)) \(\delta\) -74.02 (d, \(J = 4.6\) Hz, 3F); \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 141.58 (s), 135.64 (s), 131.00 (s), 130.09 (s), 128.20 (s), 124.83 (s), 121.78 (q, \(J = 276.2\) Hz), 56.99 (q, \(J = 41.3\) Hz), 54.16 (q, \(J = 2.8\) Hz), 44.39 (s); IR (neat) \(\nu\) = 3070, 3039, 2941, 1721, 1473, 1426, 1345, 1211, 1146, 1088, 998, 971, 961, 926, 905, 891, 860, 792, 767, 691, 680, 633, 588, 542, 533, 490 cm\(^{-1}\); HRMS (EI): calcd. for C\(_{10}\)H\(_6\)F\(_2\)O\(_3\)S [M\(^+\)]: 213.0224, Found: 213.0220.
4-((2SR,3RS)-3-(Trifluoromethyl)oxiran-2-yl)benzonitrile (3f): 56%; White solid. M.P. 53.8 - 54.6 °C; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.68 (d, $J = 8.5$ Hz, 2H), 7.42 (d, $J = 8.5$ Hz, 2H), 4.19 (s, 1H), 3.47 (qd, $J = 4.7$, 1.7 Hz, 1H); $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ -74.03 (d, $J = 4.7$ Hz, 3F); $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 138.76 (s), 132.61 (s), 126.51 (s), 121.74 (q, $J = 276.2$ Hz), 118.11 (s), 113.25 (s), 57.06 (q, $J = 41.2$ Hz), 54.13 (q, $J = 2.8$ Hz); IR (neat) $\nu$ = 3048, 2230, 1615, 1511, 1465, 1352, 1285, 1155, 925, 869, 680 cm$^{-1}$; HRMS (EI): Calcd for C$_9$H$_6$NO$_2$F$_3$ [M$^+$]: 213.0401, Found: 213.0403.

3-((2SR,3RS)-3-(Trifluoromethyl)oxiran-2-yl)benzonitrile (3g): 50%; White solid. M.P. 49.8-50.3 °C; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.68 (d, $J = 6.7$ Hz, 1H), 7.60 (s, 1H), 7.57 - 7.45 (m, 2H), 4.18 (d, 1.5 Hz, 1H), 3.47 (qd, $J = 4.6$, 1.5 Hz, 1H); $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ -74.03 (d, $J = 4.6$ Hz, 3F); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 135.29 (s), 132.86 (s), 130.05 (s), 129.75 (s), 129.33 (s), 121.70 (q, $J = 276.2$ Hz), 117.94 (s), 113.29 (s), 56.94 (q, $J = 41.3$ Hz), 53.90 (q, $J = 2.8$ Hz); IR (neat) $\nu$ = 3093, 2231, 1614, 1588, 1485, 1474, 1425, 1341, 1291, 1252, 1233, 1176, 1142, 1110, 1087, 934, 914, 894, 862, 815, 795, 745, 694, 680, 641, 606, 549, 543, 479 cm$^{-1}$; HRMS (EI): calcd. for C$_{10}$H$_6$F$_3$NO [M$^+$]: 213.0401, Found: 213.0397.

(2SR,3RS)-2-(3,5-Dibromophenyl)-3-(trifluoromethyl)oxirane (3h): 59%; White solid. M.P. 69.2-70.4 °C; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.67 (t, $J = 1.4$ Hz, 1H), 7.38 (d, $J = 1.4$ Hz, 2H),
4.07 (d, $J = 1.6$ Hz, 1H), 3.44 (qd, $J = 4.6$, 1.6 Hz, 1H); $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ -74.04 (d, $J = 4.6$ Hz, 3F); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 137.53 (s), 135.03 (s), 127.64 (s), 123.52 (s), 121.71 (q, $J = 276.3$ Hz), 56.90 (q, $J = 41.3$ Hz), 53.50 (q, $J = 2.8$ Hz); IR (neat) $\nu$ = 3068, 1590, 1560, 1466, 1428, 1414, 1341, 1288, 1153, 1103, 1078, 991, 930, 884, 867, 857, 816, 745, 696, 670, 650, 528 cm$^{-1}$; HRMS (EI): calcd. for C$_9$H$_5$Br$_2$F$_3$O $[M]^{+}$: 343.8659, Found: 343.8664.

(2SR,3RS)-2-(2-Bromo-5-(trifluoromethyl)phenyl)-3-(trifluoromethyl)oxirane (3i): 60%; Colourless liquid; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.72 (d, $J = 8.0$ Hz, 1H), 7.59 - 7.39 (m, 2H), 4.42 (d, $J = 1.5$ Hz, 1H), 3.38 (qd, $J = 4.6$, 1.5 Hz, 1H); $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ -62.98 (s, 3F), -74.17 (d, $J = 4.6$ Hz, 3F); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 134.82 (s), 133.24 (s), 130.66 (q, $J = 33.4$ Hz), 127.01 (q, $J = 3.6$ Hz), 126.18 (d, $J = 1.5$ Hz), 123.45 (q, $J = 3.8$ Hz), 123.41 (q, $J = 272.4$ Hz), 121.76 (q, $J = 276.1$ Hz), 56.46 (q, $J = 41.5$ Hz), 54.63 (q, $J = 3.0$ Hz); IR (neat) $\nu$ = 3040, 2920, 1611, 1584, 1484, 1458, 1418, 1347, 1327, 1287, 1264, 1246, 1163, 1135, 1079, 1033, 934, 922, 908, 871, 831, 756, 725, 688, 642, 626 cm$^{-1}$; HRMS (EI): calcd. for C$_{10}$H$_5$BrF$_6$O $[M]^{+}$: 333.9428, Found: 333.9427.

2-Bromo-6-((2SR,3RS)-3-(trifluoromethyl)oxiran-2-yl)pyridine (3j): 56%; Colourless liquid; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.63 - 7.54 (m, 1H), 7.52 - 7.45 (m, 1H), 7.28 (d, $J = 7.5$ Hz, 1H), 4.22 (d, $J = 1.4$ Hz, 1H), 3.79 (qd, $J = 4.8$, 1.4 Hz, 1H); $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ -73.90 (d, $J = 4.8$ Hz, 3F); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 154.25 (s), 142.36 (s), 139.22 (s), 128.79 (s), 121.90 (q, $J = 276.1$ Hz), 120.07 (s), 55.75 (q, $J = 41.4$ Hz), 54.49 (q, $J = 2.6$ Hz); IR (neat) $\nu$ =
3050, 2923, 1581, 1476, 1442, 1405, 1349, 1275, 1238, 1161, 1124, 1112, 1085, 
1071, 988, 927, 892, 860, 793, 736, 699, 682, 632, 598, 536 cm⁻¹; HRMS (EI): calcd. for 
C₈H₅BrF₃NO [M]⁺: 266.9507, Found: 266.9506.

5.2 The Procedure for the Synthesis of 5

\[
\begin{array}{c}
\text{Ph}_2\text{SCH}_2\text{CF}_3 \quad \text{TBAF, 4Å MS} \\
\text{1} \quad \text{DCM, rt, 2 h} \\
\text{Ar} \quad \text{2.0 equiv.} \\
\text{4} \quad \text{4Å MS (160 mg)} \\
\text{Ar} \quad \text{5} \\
\end{array}
\]

Into the mixture of diphenyl(2,2,2-trifluoroethyl)sulfonium triflate 1 (0.2 mmol, 83.7 mg, 
1.0 equiv.), compound 4 (0.4 mmol, 2.0 equiv.) and 4Å MS (160 mg) in dichloromethane(2 mL) 
was added TBAF (0.3 mmol, 0.3 mL, 1.5 equiv.) dropwise under N₂ atmosphere. The reaction 
mixture was stirred at room temperature for 2 h. After concentration, the residue was subjected to 
flash column chromatography with hexane/ethyl acetate (100:1-20:1) as the eluent to afford the 
final product 5.

\[5a\]

[1,1'-Biphenyl]-4-yl((1SR,2SR)-2-(trifluoromethyl)cyclopropyl)methanone (5a): 90%; White 
solid. M.P.: 108.7-110.3 °C; ¹H NMR (400 MHz, CDCl₃) δ 8.09 (d, \(J = 7.9\) Hz, 2H), 7.72 (d, \(J = \\
7.9\) Hz, 2H), 7.63 (d, \(J = 7.5\) Hz, 2H), 7.48 (t, \(J = 7.1\) Hz, 2H), 7.41 (t, \(J = 7.1\) Hz, 1H), 3.08 - 
3.02 (m, 1H), 2.42 - 2.33 (m, 1H), 1.58 - 1.51 (m, 1H), 1.47 - 1.41 (m, 1H); ¹³C NMR (376 MHz, 
CDCl₃) δ -66.65 (d, \(J = 6.2\) Hz, 3F); ¹⁹F NMR (376 MHz, CDCl₃) δ 195.79 (s), 146.33 (s), 
139.65 (s), 135.39 (s), 128.99 (s), 128.85 (s), 128.39 (s), 127.38 (s), 127.27 (s), 125.24 (q, \(J = \\
271.1\) Hz), 23.82 (q, \(J = 37.8\) Hz), 20.08 (q, \(J = 2.0\) Hz), 12.50 (q, \(J = 2.6\) Hz); IR (neat) ν = 2925, 
2361, 1673, 1603, 560, 1509, 1341, 1264, 1150, 1063, 1305, 936, 849, 772, 739 cm⁻¹; HRMS (EI) 
Naphthalen-2-yl((1SR,2SR)-2-(trifluoromethyl)cyclopropyl)methanone (5b): 89%; Light yellow solid. M.P.: 42.4-44.4°C; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.56 (s, 1H), 8.04 (d, $J = 8.8$ Hz, 1H), 8.01 (d, $J = 8.3$ Hz, 1H), 7.93 (d, $J = 8.8$ Hz, 1H), 7.90 (d, $J = 8.3$ Hz, 1H), 7.66 - 7.55 (m, 2H), 3.22 - 3.14 (m, 1H), 2.49 - 2.37 (m, 1H), 1.63 - 1.54 (m, 1H), 1.53 - 1.45 (m, 1H); $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ -66.66 (d, $J = 6.6$ Hz, 3F); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 196.22 (s), 135.78 (s), 134.04 (s), 132.44 (s), 130.23 (s), 129.67 (s), 128.83 (s), 128.72 (s), 127.82 (s), 127.01 (s), 125.24 (q, $J = 271.1$ Hz), 123.69 (s), 23.86 (q, $J = 37.8$ Hz), 20.13 (q, $J = 1.9$ Hz), 12.70 (q, $J = 2.6$ Hz); IR (neat) $\nu = 3059, 2361, 1673, 1628, 1597, 1471, 1357, 1333, 1107, 756$ cm$^{-1}$; HRMS (EI) Calcd for C$_{15}$H$_{11}$OF$_3$ [M]$^+$: 264.0762, Found: 264.0767.

(4-Nitrophenyl)((1SR,2SR)-2-(trifluoromethyl) cyclopropyl) methanone (5c): 97%; White solid. M.P.: 57.6-59.1°C; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.35 (d, $J = 7.6$ Hz, 2H), 8.16 (d, $J = 7.6$ Hz, 2H), 3.02 - 2.98 (m, 1H), 2.54 - 2.31 (m, 1H), 1.65 - 1.55 (m, 1H), 1.55 - 1.50 (m, 1H); $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ -66.91 (d, $J = 6.4$ Hz, 3F); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 195.11 (s), 150.59 (s), 141.04 (s), 129.26 (s), 124.80 (q, $J = 271.0$ Hz), 123.99 (s), 24.52 (q, $J = 38.0$ Hz), 20.63 (q, $J = 2.1$ Hz), 13.28 (q, $J = 2.7$ Hz); IR (neat) $\nu = 3113, 1686, 1605, 1529, 1420, 1266, 1221, 1151, 1064, 852, 715, 635$ cm$^{-1}$; HRMS (EI) Calcd for C$_{11}$H$_8$NO$_3$F$_3$ [M]$^+$: 259.0456, Found: 259.0455.
(3-Nitrophenyl)((JSR, 2SR)-2-(trifluoromethyl)cyclopropyl)methanone (5d): Quantitative; White solid. M.P.: 29.9-32.0 °C; $^1$H NMR (400 MHz, CDCl$_3$) δ 8.84 (s, 1H), 8.49 (d, $J$ = 8.0 Hz, 1H), 8.35 (d, $J$ = 8.0 Hz, 1H), 7.84 - 7.69 (m, 1H), 3.17 - 2.98 (m, 1H), 2.54 - 2.36 (m, 1H), 1.74 - 1.51 (m, 2H); $^{19}$F NMR (376 MHz, CDCl$_3$) δ -66.88 (d, $J$ = 6.4 Hz, 3F); $^{13}$C NMR (101 MHz, CDCl$_3$) δ 194.42 (s), 148.50 (s), 137.85(s), 133.70 (s), 130.11 (s), 127.81 (s), 124.84 (q, $J$ = 271.4 Hz), 123.30 (s), 24.35 (q, $J$ = 38.1 Hz), 20.32 (q, $J$ = 1.3 Hz), 13.35 (q, $J$ = 2.0 Hz); IR (neat) ν = 3089, 2360, 1687, 1612, 1536, 1340, 1266, 1224, 1151, 1001, 940, 716 cm$^{-1}$; HRMS (EI) Calcd for C$_{11}$H$_8$NO$_3$F$_3$ [M]$^+$: 259.0456, Found: 259.0461.

(2-Nitrophenyl)((JSR, 2SR)-2-(trifluoromethyl)cyclopropyl)methanone (5e): Quantitative; Yellow liquid. $^1$H NMR (400 MHz, CDCl$_3$) δ 8.14 (d, $J$ = 7.5 Hz, 1H), 7.76 (t, $J$ = 7.5 Hz, 1H), 7.65 (t, $J$ = 7.8 Hz, 1H), 7.47 (d, $J$ = 7.8 Hz, 1H), 2.54 - 2.51 (m, 1H), 2.49 - 2.38 (m, 1H), 1.72 - 1.61 (m, 1H), 1.51 - 1.46(m, 1H); $^{19}$F NMR (376 MHz, CDCl$_3$) δ -67.13 (d, $J$ = 6.4 Hz, 3F); $^{13}$C NMR (101 MHz, CDCl$_3$) δ 198.94 (s), 145.93 (s), 137.00 (s), 134.39 (s), 131.25 (s), 127.74 (s), 124.70 (q, $J$ = 271.5 Hz), 124.53 (s), 25.18 (q, $J$ = 38.1 Hz), 24.30 (q, $J$ = 2.1 Hz), 13.78 (q, $J$ = 2.6 Hz); IR (neat) ν = 3066, 1701, 1608, 1575, 1477, 1348, 1265, 1152, 945, 753 cm$^{-1}$; HRMS (EI) Calcd for C$_{11}$H$_8$NOF$_3$ [M]$^+$: 259.0456, Found: 259.0458.
(4-Bromophenyl)((1SR, 2SR)-2-(trifluoromethyl)cyclopropyl)methanone (5f): Quantitative; White solid. M.P.: 28.8-29.9 °C; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.87 (d, \(J = 8.4\) Hz, 2H), 7.61 (d, \(J = 8.4\) Hz, 2H), 2.98 - 2.92 (m, 1H), 2.32 - 2.38 (m, 1H), 1.60 - 1.48 (m, 1H), 1.48 - 1.39(m, 1H); \(^1\)F NMR (376 MHz, CDCl\(_3\)) \(\delta\) -66.83 (d, \(J = 6.5\) Hz, 3F); \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 195.34 (s), 135.39 (s), 132.10 (s), 129.70 (s), 129.08 (s), 125.03 (q, \(J = 271.2\) Hz), 23.97 (q, \(J = 37.9\) Hz), 20.00 (q, \(J = 2.1\) Hz), 12.69 (q, \(J = 2.7\) Hz); IR (neat) \(\nu\) = 3059, 1681, 1587, 1506, 1397, 1341, 1263, 1150, 1071, 995, 838, 739 cm\(^{-1}\); HRMS (EI) Calcd for C\(_{11}\)H\(_8\)OF\(_3\)Br [M]\(^+\): 291.9711, Found: 291.9713.

![5f](image)

(4-Chlorophenyl)((1SR, 2SR)-2-(trifluoromethyl)cyclopropyl)methanone (5g): Quantitative; White solid. M.P.: 25.7-26.1 °C; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.95 (d, \(J = 8.5\) Hz, 2H), 7.47 (d, \(J = 8.5\) Hz, 2H), 2.97 - 2.93 (m, 1H), 2.56 - 2.19 (m, 1H), 1.56 - 1.49 (m, 1H), 1.47 - 1.39 (m, 1H); \(^1\)F NMR (376 MHz, CDCl\(_3\)) \(\delta\) -66.82 (d, \(J = 6.5\) Hz, 3F); \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 195.19 (s), 140.20 (s), 134.95 (s), 129.64 (s), 129.11 (s), 125.05 (q, \(J = 271.2\) Hz), 23.96 (q, \(J = 37.9\) Hz), 20.00 (q, \(J = 2.0\) Hz), 12.72 (q, \(J = 2.5\) Hz); IR (neat) \(\nu\) = 3059, 2360, 1681, 1592, 1490, 1400, 1344, 1264, 1224, 1151, 1116, 1063, 996, 840, 775 cm\(^{-1}\); HRMS (EI) Calcd for C\(_{11}\)H\(_8\)OF\(_3\)Cl [M]\(^+\): 248.0216, Found: 248.0214; Anal. Calcd. for C\(_{11}\)H\(_8\)OF\(_3\)Cl [M]\(^+\): C, 53.14; H, 3.24; Found: C, 52.99; H, 3.43.

![5g](image)

(4-Fluorophenyl)((1SR,2SR)-2-(trifluoromethyl)cyclopropyl)methanone (5h): 65%; Colorless liquid. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 8.06 - 8.02 (m, 2H), 7.23 - 7.10 (m, 2H), 3.04 - 2.87 (m, 1H), 2.43 - 2.25 (m, 1H), 1.54 - 1.50(m, 1H), 1.45 - 1.40(m, 1H); \(^1\)F NMR (376 MHz, CDCl\(_3\)) \(\delta\)
(3-Chlorophenyl)((1SR,2SR)-2-(trifluoromethyl)cyclopropyl)methanone (5i): 94%; Colorless liquid. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.96 (s, 1H), 7.88 (d, $J = 7.7$ Hz, 1H), 7.58 (d, $J = 7.7$ Hz, 1H), 7.45 (t, $J = 7.7$ Hz, 1H), 2.99 - 2.94 (m, 1H), 2.59 - 2.14 (m, 1H), 1.57 - 1.49 (m, 1H), 1.49 - 1.40 (m, 1H); $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ -66.84 (d, $J = 6.4$ Hz, 3F); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 196.18 (s), 138.18 (s), 135.16 (s), 133.51 (s), 130.08 (s), 128.30 (s), 126.34 (s), 124.99 (q, $J = 271.2$ Hz), 24.03 (q, $J = 37.9$ Hz), 20.16 (q, $J = 2.1$ Hz), 12.87 (q, $J = 2.7$ Hz); IR (neat) $\nu$ = 3070, 2360, 1683, 1573, 1417, 1340, 1264, 1222, 1150, 1000, 941, 787, 734, 708 cm$^{-1}$; HRMS (EI) Calcd for C$_{11}$H$_8$OF$_3$Cl [M]$^+$: 248.0216, Found: 248.0215.

(2-Bromophenyl)((1SR, 2SR)-2-(trifluoromethyl)cyclopropyl)methanone (5j): 82%; Yellow liquid. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.64 (d, $J = 7.0$ Hz, 1H), 7.46 (d, $J = 7.1$ Hz, 1H), 7.39 (t, $J = 7.1$ Hz, 1H), 7.34 (t, $J = 7.0$ Hz, 1H), 2.90 - 2.85 (m, 1H), 2.45 - 2.39 (m, 1H), 1.62 - 1.54 (m, 1H), 1.49 - 1.44 (m, 1H); $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ -66.76 (d, $J = 6.3$ Hz, 3F); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 200.01 (s), 140.72 (s), 133.80 (s), 132.35 (s), 129.32 (s), 127.54 (s), 124.88 (q, $J = 270.9$ Hz), 119.31 (s), 25.37 (q, $J = 38.2$ Hz), 24.24 (q, $J = 1.4$ Hz), 14.20 (q, $J = 2.3$ Hz); IR
(neat) $\nu = 3059, 1694, 1588, 1466, 1389, 1263, 1109, 739$ cm$^{-1}$; HRMS (EI) Calcd for C$_{11}$H$_8$OF$_3$Br [M]$^+$: 291.9711, Found: 291.9715.

![Structure 5k](image)

(4-Methoxyphenyl)((RS,2SR)-2-(trifluoromethyl)cyclopropyl)methanone (5k): 87%; Colorless liquid. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.00 (d, $J = 8.1$ Hz, 2H), 6.97 (d, $J = 8.1$ Hz, 2H), 3.88 (s, 3H), 2.99 - 2.94 (m, 1H), 2.32 - 2.27 (m, 1H), 1.49 (m, 1H), 1.38 (m, 1H); $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ -66.70 (d, $J = 6.1$ Hz, 3F); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 194.60 (s), 163.95 (s), 130.57 (s), 129.75 (s), 125.27 (q, $J = 271.0$ Hz), 113.93 (s), 55.53 (s), 23.50 (q, $J = 37.8$ Hz), 19.66 (q, $J = 1.8$ Hz), 12.18 (q, $J = 2.7$ Hz); IR (neat) $\nu = 2940, 2843, 1669, 1601, 1576, 1513, 1481, 1345, 1234, 1149, 1209, 841$ cm$^{-1}$; HRMS (EI) Calcd for C$_{12}$H$_{11}$O$_2$F$_3$ [M]$^+$: 244.0711, Found: 244.0715.

![Structure 5l](image)

(3-Methoxyphenyl)((RS,2SR)-2-(trifluoromethyl)cyclopropyl)methanone (5l): 88%; Light yellow liquid. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.61 (d, $J = 7.5$ Hz, 1H), 7.49 (s, 1H), 7.41 (t, $J = 7.5$ Hz, 1H), 7.15 (d, $J = 7.5$ Hz, 1H), 3.85 (s, 3H), 3.12 - 2.80 (m, 1H), 2.37 - 2.31 (m, 1H), 1.52 - 1.49 (m, 1H), 1.46 - 1.36 (m, 1H); $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ -66.80 (d, $J = 6.5$ Hz, 3F); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 196.15 (s), 159.91 (s), 138.04 (s), 129.74 (s), 125.15 (q, $J = 271.0$ Hz), 120.90 (s), 120.06 (s), 112.41 (s), 55.42 (s), 23.83 (q, $J = 37.8$ Hz), 20.18 (q, $J = 2.0$ Hz), 12.55 (q, $J = 2.6$ Hz); IR (neat) $\nu = 3058, 2943, 1680, 1598, 1583, 1467, 1432, 1343, 1262, 1151, 1033, 942, 786, 745$ cm$^{-1}$; HRMS (EI) Calcd for C$_{12}$H$_{11}$O$_2$F$_3$ [M]$^+$: 244.0711, Found: 244.0707.
Furan-2-yl((1RS,2RS)-2-(trifluoromethyl)cyclopropyl)methanone (5m): 88%; White solid. M.P.: 46.5-48.5°C; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.67 (d, \(J = 1.7\) Hz, 1H), 7.31 (d, \(J = 3.4\) Hz, 1H), 6.6 (dd, \(J = 3.4\), 1.7 Hz, 1H), 3.17 - 2.74 (m, 1H), 2.66 - 2.17 (m, 1H), 1.56 - 1.45 (m, 1H), 1.43 - 1.36 (m, 1H); \(^{19}\)F NMR (376 MHz, CDCl\(_3\)) \(\delta\) -66.97 (d, \(J = 6.5\) Hz, 3F); \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 184.77 (s), 152.36 (s), 147.14 (s), 125.03 (q, \(J = 271.1\) Hz), 117.86 (s), 112.59 (s), 23.33 (q, \(J = 37.9\) Hz), 19.99 (q, \(J = 2.1\) Hz), 12.08 (q, \(J = 2.6\) Hz); IR (neat) \(\nu\) = 3138, 2360, 1674, 1572, 1469, 1420, 1345, 1268, 1151, 1086, 1017, 763, 642 cm\(^{-1}\); HRMS (EI) Calcd for C\(_9\)H\(_7\)O\(_2\)F\(_3\) [M]+: 204.0398, Found: 204.0396.

### 5.3 The Procedure for The Synthesis of 7

Into the mixture of diphenyl(2,2,2-Trifluoroethyl)sulfonium triflate 1 (1.0 mmol, 0.4184 g, 1.0 equiv.), imine 6 (2.0 mmol, 2.0 equiv.) and 4Å MS (0.8 g) in dichloromethane(10 mL) was added TBAF (1.5 mmol, 1.5 mL, 1.5 equiv.) dropwise under N\(_2\) atmosphere. The reaction mixture was stirred at room temperature for 1 h. After filtration, the solid was washed with DCM (10 mL). The combined organic phase was washed with water, sat. sodium bisulfite and water in sequence and then dried over Na\(_2\)SO\(_4\). The solvent was removed by concentration, and the residue was subjected to flash column chromatography with hexane/ethyl acetate (50:1-20:1) as the eluent to afford the final product 7.
(2RS,3RS)-2-Phenyl-1-tosyl-3-(trifluoromethyl)aziridine (7a): 86%; White solid. M.P. 69.0 - 70.4 °C; \(^{1}\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.91 (d, \(J = 8.2\) Hz, 2H), 7.38 (d, \(J = 8.2\) Hz, 2H), 7.28 (s, 5H), 4.19 (d, \(J = 7.0\) Hz, 1H), 3.49 (dq, \(J = 7.0, 5.4\) Hz, 1H), 2.45 (s, 3H); \(^{19}\)F NMR (376 MHz, CDCl\(_3\)) \(\delta\) -65.82 (d, \(J = 5.4\) Hz, 3F); \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 145.74 (s), 133.55 (s), 130.08 (s), 128.63 (s), 128.43 (s), 128.28 (s), 127.35 (s), 127.35 (s), 122.11 (q, \(J = 275.7\) Hz), 43.51 (q, \(J = 1.1\) Hz), 42.55 (q, \(J = 40.2\) Hz), 21.77 (s); IR (neat) \(\nu\) = 3064, 3034, 1698, 1597, 1489, 1458, 1442, 1384, 1347, 1299, 1237, 1181, 1085, 1050, 1013, 954, 933, 923, 825, 805, 787, 700, 663, 605, 545 cm\(^{-1}\); HRMS (ESI) Calcd for C\(_{16}\)H\(_{15}\)F\(_3\)NO\(_2\)S [M+H]\(^+\): 342.0770, Found: 342.0766.

(2RS,3RS)-2-(p-Tolyl)-1-tosyl-3-(trifluoromethyl)aziridine (7b): 88%; White solid. M.P. 90.3 - 91.3 °C; \(^{1}\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.95 (d, \(J = 8.2\) Hz, 2H), 7.42 (d, \(J = 8.2\) Hz, 2H), 7.20 (d, \(J = 8.2\) Hz, 2H), 7.13 (d, \(J = 8.2\) Hz, 2H), 4.19 (d, \(J = 7.0\) Hz, 1H), 3.51 (dq, \(J = 7.0, 5.4\) Hz, 1H), 2.49 (s, 3H), 2.34 (s, 3H); \(^{19}\)F NMR (376 MHz, CDCl\(_3\)) \(\delta\) -65.69 (d, \(J = 5.4\) Hz, 3F); \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 145.66 (s), 138.48 (s), 133.64 (s), 130.04 (s), 129.11 (s), 128.26 (s), 127.22 (s), 127.04 (s), 122.26 (q, \(J = 275.7\) Hz), 43.50 (q, \(J = 1.2\) Hz), 42.53 (q, \(J = 40.0\) Hz), 21.75 (s), 21.19 (s); IR (neat) \(\nu\) = 3037, 2927, 1598, 1519, 1494, 1435, 1377, 1335, 1292, 1187, 1165, 1150, 1091, 1052, 1041, 945, 910, 880, 814, 777, 683, 666, 609, 558, 539 cm\(^{-1}\); HRMS (ESI) Calcd for C\(_{17}\)H\(_{17}\)F\(_3\)NO\(_2\)S [M+H]\(^+\): 356.0927, Found: 356.0921.
(2RS,3RS)-2-(4-Methoxyphenyl)-1-tosyl-3-(trifluoromethyl)aziridine (7c): 72%; White solid. 
M.P.: 104.5 - 106.1 °C; \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) 7.91 (d, \(J = 8.2\) Hz, 2H), 7.38 (d, \(J = 8.2\) Hz, 2H), 7.20 (d, \(J = 8.7\) Hz, 2H), 6.82 (d, \(J = 8.7\) Hz, 2H), 4.14 (d, \(J = 7.0\) Hz, 1H), 3.76 (s, 3H), 3.45 (dq, \(J = 7.0, 5.5\) Hz, 1H), 2.46 (s, 3H); \(^1\)F NMR (376 MHz, CDCl\(_3\)) \(\delta\) -65.69 (d, \(J = 5.5\) Hz, 3F); \(^1\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 159.82 (s), 145.67 (s), 133.67 (s), 130.04 (s), 128.59 (s), 128.24 (s), 122.31 (q, \(J = 276.1\) Hz), 121.97 (s), 113.87 (s), 55.21 (s), 43.27 (s), 42.60 (q, \(J = 39.9\) Hz), 21.70 (s); IR (neat) \(\nu\) = 3021, 2968, 2842, 1917, 1598, 1519, 1495, 1436, 1377, 1339, 1293, 1259, 1188, 1146, 1051, 1032, 936, 877, 838, 806, 778, 681, 665, 577, 549 cm\(^{-1}\); HRMS (ESI) Calcd for C\(_{17}\)H\(_{16}\)F\(_3\)NNaO\(_3\)S [M+Na]\(^+\): 394.0695, Found: 394.0702.

(2RS,3RS)-2-[[1,1'-Biphenyl]-4-yl]-1-tosyl-3-(trifluoromethyl)aziridine (7d): 95%; White solid. 
M.P. 103.9 - 105.1 °C; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.96 (d, \(J = 8.3\) Hz, 2H), 7.63 - 7.50 (m, 4H), 7.49 - 7.32 (m, 7H), 4.25 (d, \(J = 7.0\) Hz, 1H), 3.56 (dq, \(J = 7.0, 5.4\) Hz, 1H), 2.46 (s, 3H); \(^1\)F NMR (376 MHz, CDCl\(_3\)) \(\delta\) -65.62 (d, \(J = 5.4\) Hz, 3F); \(^1\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 145.77 (s), 141.55 (s), 140.31 (s), 133.62 (s), 130.11 (s), 129.10 (s), 128.85 (s), 128.30 (s), 127.86 (s), 127.63 (s), 127.14 (s), 127.08 (s), 122.30 (q, \(J = 275.7\) Hz), 43.42 (q, \(J = 1.8\) Hz), 42.70 (q, \(J = 40.1\) Hz), 21.74 (s); IR (neat) \(\nu\) = 3075, 3024, 1597, 1489, 1442, 1353, 1300, 1163, 1087, 1056, 960, 935, 803, 816, 766, 690, 662, 605, 559, 849, 530 cm\(^{-1}\); HRMS (ESI) Calcd for C\(_{22}\)H\(_{19}\)F\(_3\)NO\(_2\)S [M+H]\(^+\): 418.1083, Found: 418.1079.
(2RS,3RS)-2-(Naphthalen-2-yl)-1-tosyl-3-(trifluoromethyl)aziridine (7e): 96%; White solid. M.P. 100.6 - 102.2 °C; \( ^1 {H} \) NMR (400 MHz, CDCl\(_3\)) \( \delta \) 8.01 (d, \( J = 8.3 \) Hz, 2H), 7.87 - 7.78 (m, 4H), 7.55 - 7.49 (m, 2H), 7.46 - 7.40 (m, 3H), 4.39 (d, \( J = 7.0 \) Hz, 1H), 3.61 (dq, \( J = 7.0, 5.4 \) Hz, 1H), 2.50 (s, 3H); \(^{19}\)F NMR (376 MHz, CDCl\(_3\)) \( \delta \) -65.62 (d, \( J = 5.4 \) Hz, 3F); \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \( \delta \) 145.80 (s), 133.56 (s), 133.24 (s), 132.90 (s), 130.11 (s), 128.34 (s), 128.31 (s), 127.98 (s), 127.78 (s), 127.51 (s), 126.94 (s), 126.59 (s), 126.53 (s), 124.54 (s), 122.24 (q, \( J = 275.7 \) Hz), 43.64 (q, \( J = 1.1 \) Hz), 42.81 (q, \( J = 40.2 \) Hz), 21.78 (s); IR (neat) \( \nu \) = 3055, 1599, 1436, 1388, 1338, 1293, 1223, 1171, 1148, 1090, 1055, 974, 941, 906, 842, 820, 776, 761, 684, 661, 559, 544 cm\(^{-1}\); HRMS (ESI) Calcd for C\(_{20}\)H\(_{17}\)F\(_3\)NO\(_2\)S [M+H]\(^+\): 392.0927, Found: 392.0919.

(2RS,3RS)-2-(4-Fluorophenyl)-1-tosyl-3-(trifluoromethyl)aziridine (7f): Quantitative; White solid. M.P.: 116.2 - 116.5 °C; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta \) 7.90 (d, \( J = 8.2 \) Hz, 2H), 7.38 (d, \( J = 8.2 \) Hz, 2H), 7.30 - 7.21 (m, 2H), 6.98 (t, \( J = 8.6 \) Hz, 2H), 4.14 (d, \( J = 7.0 \) Hz, 1H), 3.45 (dq, \( J = 7.0, 5.4 \) Hz, 1H), 2.46 (s, 3H); \(^{19}\)F NMR (376 MHz, CDCl\(_3\)) \( \delta \) -65.62 (d, \( J = 5.4 \) Hz, 3F), -112.64 - -113.03 (m, 1F); \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \( \delta \) 162.81 (d, \( J = 247.7 \) Hz), 145.87 (s), 133.42 (s), 130.12 (s), 129.20 (d, \( J = 8.4 \) Hz), 128.25 (s), 125.92 (d, \( J = 3.2 \) Hz), 122.15 (q, \( J = 275.6 \) Hz), 115.53 (d, \( J = 21.9 \) Hz), 42.75 (s), 42.63 (q, \( J = 40.1 \) Hz), 21.73 (s); IR (neat) \( \nu \) = 3037, 1599, 1514, 1452, 1376, 1338, 1282, 1236, 1190, 1170, 1147, 1091, 1058, 952, 905, 885, 831, 817, 784, 750, 703, 682, 669 cm\(^{-1}\); HRMS (ESI) Calcd for C\(_{16}\)H\(_{14}\)F\(_4\)NO\(_2\)S [M+H]\(^+\): 360.0676, Found: 360.0670.
(2RS,3RS)-2-(4-Chlorophenyl)-1-tosyl-3-(trifluoromethyl)aziridine (7g): 89%; White solid. M.P.: 86.8 - 88.4 °C; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.89 (d, \(J = 8.2\) Hz, 2H), 7.38 (d, \(J = 8.2\) Hz, 2H), 7.26 (d, \(J = 8.5\) Hz, 2H), 7.21 (d, \(J = 8.5\) Hz, 2H), 4.13 (d, \(J = 7.0\) Hz, 1H), 3.48 (dq, \(J = 7.0, 5.4\) Hz, 1H), 2.45 (s, 3H); \(^1^9\)F NMR (376 MHz, CDCl\(_3\)) \(\delta\) -65.80 (d, \(J = 5.4\) Hz, 3F); \(^1^3\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 145.90 (s), 134.69 (s), 133.38 (s), 130.13 (s), 128.77 (s), 128.72 (s), 128.66 (s), 128.26 (s), 122.08 (q, \(J = 275.7\) Hz), 42.72 (s), 42.65 (q, \(J = 40.2\) Hz), 21.78 (s); IR (neat) \(\nu = 3032, 1599, 1495, 1437, 1375, 1341, 1293, 1166, 1091, 1053, 1017, 943, 882, 789, 697, 557, 542\) cm\(^{-1}\); HRMS (ESI) Calcd for C\(_{16}\)H\(_{14}\)ClF\(_3\)NO\(_2\)S [M+H]: 376.0380, Found: 376.0373.

(2RS,3RS)-2-(4-Bromophenyl)-1-tosyl-3-(trifluoromethyl)aziridine (7h): 92%; White solid. M.P. 80.4 - 83.3 °C; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.89 (d, \(J = 8.3\) Hz, 2H), 7.41 (d, \(J = 8.3\) Hz, 2H), 7.37 (d, \(J = 8.2\) Hz, 2H), 7.15 (d, \(J = 8.2\) Hz, 2H), 4.11 (d, \(J = 7.0\) Hz, 1H), 3.48 (dq, \(J = 7.0, 5.4\) Hz, 1H), 2.44 (s, 3H). \(^1^9\)F NMR (376 MHz, CDCl\(_3\)) \(\delta\) -65.77 (d, \(J = 5.4\) Hz, 3F); \(^1^3\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 145.91 (s), 133.39 (s), 131.66 (s), 130.13 (s), 129.23 (s), 129.07 (s), 128.25 (s), 122.85 (s), 122.09 (q, \(J = 275.7\) Hz), 42.80 (s), 42.60 (q, \(J = 39.9\) Hz), 21.74 (s); IR (neat) \(\nu = 3090, 3030, 1598, 1491, 1437, 1402, 1372, 1335, 1292, 1162, 1090, 1043, 1013, 939, 826, 819, 788, 757, 694, 673, 614, 571, 549, 528\) cm\(^{-1}\); HRMS (ESI) Calcd for C\(_{16}\)H\(_{14}\)BrF\(_3\)NO\(_2\)S [M+H]: 419.9875, Found: 419.9872.
4-((2RS,3RS)-1-Tosyl-3-(trifluoromethyl)aziridin-2-yl)benzonitrile (7i): 94%; White solid. M.P. 135.9 - 136.4 °C; \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) 7.92 (d, \(J = 8.3\) Hz, 2H), 7.62 (d, \(J = 8.2\) Hz, 2H), 7.43 (d, \(J = 8.3\) Hz, 2H), 7.42 (d, \(J = 8.2\) Hz, 2H), 4.21 (d, \(J = 6.0\) Hz, 1H), 3.55 (dq, \(J = 7.0\), 5.4 Hz, 1H), 2.49 (s, 3H); \(^{19}\)F NMR (376 MHz, CDCl\(_3\)) \(\delta\) -65.94 (d, \(J = 5.4\) Hz, 3F); \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 146.14 (s), 135.45 (s), 133.16 (s), 132.28 (s), 130.21 (s), 128.30 (s), 128.27 (s), 121.89 (q, \(J = 275.7\) Hz), 118.20 (s), 112.82 (s), 42.88 (q, \(J = 40.5\) Hz), 42.48 (q, \(J = 1.3\) Hz), 21.79 (s); IR (neat) \(\nu\) = 3060, 3042, 2231, 1613, 1598, 1509, 1437, 1374, 1339, 1295, 1190, 1167, 1145, 1089, 1040, 934, 849, 796, 772, 678, 601, 573, 560 cm\(^{-1}\); HRMS (ESI) Calcd for C\(_{17}\)H\(_{14}\)F\(_3\)N\(_2\)O\(_2\)S [M+H]\(^+\): 367.0723, Found: 367.0718.

(2RS,3RS)-1-Tosyl-2-(trifluoromethyl)-3-(3-(trifluoromethyl)phenyl)aziridine (7j): 85%; Colourless liquid. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.96 (d, \(J = 8.2\) Hz, 2H), 7.59 (d, \(J = 7.6\) Hz, 1H), 7.55 - 7.50 (m, 2H), 7.47 (d, \(J = 8.0\) Hz, 1H), 7.44 (d, \(J = 8.2\) Hz, 2H), 4.23 (d, \(J = 6.9\) Hz, 1H), 3.57 (dq, \(J = 6.9\), 5.4 Hz, 1H), 2.50 (s, 3H); \(^{19}\)F NMR (376 MHz, CDCl\(_3\)) \(\delta\) -62.87 (s, 3F), -65.87 (d, \(J = 5.4\) Hz, 3F); \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 146.10 (s), 133.20 (s), 131.32 (s), 131.14 (s), 130.81 (s), 130.17 (s), 129.06 (s), 128.30 (s), 125.56 (q, \(J = 3.7\) Hz), 124.36 (q, \(J = 3.6\) Hz), 123.71 (q, \(J = 272.4\) Hz), 122.01 (q, \(J = 275.6\) Hz), 42.67 (q, \(J = 40.4\) Hz), 42.62 (q, \(J = 0.5\) Hz), 21.72 (s); IR (neat) \(\nu\) = 3033, 1598, 1433, 1379, 1329, 1292, 1230, 1166, 1092, 1074, 955, 916, 814, 771, 743, 701, 679, 543 cm\(^{-1}\); HRMS (ESI) Calcd for C\(_{17}\)H\(_{14}\)F\(_6\)NO\(_2\)S [M+H]\(^+\): 410.0644, Found: 410.0637.
(2RS,3RS)-2-cyclohexyl-1-tosyl-3-(trifluoromethyl)aziridine (7k): 83%; White solid. M.P. 62.5 - 64.1 °C; $^1$H NMR (400 MHz, CDCl$_3$) δ 7.84 (d, $J = 8.2$ Hz, 2H), 7.37 (d, $J = 8.2$ Hz, 2H), 3.23 (dq, $J = 6.9, 6.1$ Hz, 1H), 2.76 - 2.69 (m, 1H), 2.46 (s, 3H), 1.78 - 1.62 (m, 5H), 1.50 - 1.38 (m, 1H), 1.28 - 0.99 (m, 5H); $^{19}$F NMR (376 MHz, CDCl$_3$) δ -65.45 (d, $J = 6.0$ Hz, 3F). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 145.38 (s), 133.70 (s), 129.83 (s), 128.28 (s), 122.97 (q, $J = 275.1$ Hz), 48.05 (s), 41.29 (q, $J = 40.5$ Hz), 35.29 (q, $J = 1.2$ Hz), 31.53 (s), 29.47 (s), 25.89 (s), 25.24 (s), 25.17 (s), 21.68 (s); IR (neat) ν = 3060, 2936, 2852, 1599, 1456, 1408, 1349, 1305, 1283, 1248, 1156, 1119, 1087, 1047, 933, 888, 826, 811, 748, 659, 604, 558, 549, 528 cm$^{-1}$; HRMS (ESI) Calcd for C$_{16}$H$_{20}$F$_3$NNaO$_2$S [M+Na]$^+$: 370.1059, Found: 370.1058.

(2RS,3RS)-2-(4-fluorophenyl)-1-(methylsulfonyl)-3-(trifluoromethyl)aziridine (7l): 90%; White solid. M.P. 76.7 - 78.2 °C; $^1$H NMR (400 MHz, CDCl$_3$) δ 7.40 (dd, $J = 8.5, 5.4$ Hz, 2H), 7.09 - 7.02 (m, 2H), 4.14 (d, $J = 7.0$ Hz, 1H), 3.48 (dq, $J = 7.0, 5.4$ Hz, 1H), 3.23 (s, 3H), IR (neat) ν = 3060, 2936, 2852, 1599, 1456, 1408, 1349, 1305, 1283, 1248, 1156, 1119, 1087, 1047, 933, 888, 826, 811, 748, 659, 604, 558, 549, 528 cm$^{-1}$; HRMS (EI) Calcd for C$_{10}$H$_9$F$_4$NO$_2$S [M]$^+$: 283.0290, Found: 283.0294.
(2RS,3RS)-2-(4-bromophenyl)-1-(methylsulfonyl)-3-(trifluoromethyl)aziridine (7m): 92%; White solid. M.P. 74.4 - 75.9 °C; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.49 (d, $J = 8.3$ Hz, 2H), 7.27 (d, $J = 8.3$ Hz, 2H), 4.09 (d, $J = 7.0$ Hz, 1H), 3.47 (dq, $J = 6.8$, 5.5 Hz, 1H), 3.22 (s, 3H); $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ -65.75 (d, $J = 5.5$ Hz, 3F); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 131.80 (s), 129.09 (s), 128.89 (s), 123.10 (s), 122.13 (q, $J = 275.5$ Hz), 42.85 (q, $J = 40.2$ Hz), 41.97 (q, $J = 0.9$ Hz), 39.72 (s); IR (neat) $\nu$ = 3021, 2945, 1492, 1436, 1408, 1331, 1290, 1236, 1182, 1162, 1143, 1049, 1011, 972, 942, 913, 877, 819, 799, 538, 525 cm$^{-1}$; HRMS (EI) Calcd for C$_{10}$H$_{9}$BrF$_3$NO$_2$S [M]$^+$: 342.9489, Found: 342.9490.
6. NOESY Spectrum and Structure Refinement for 5a
7. X-Ray Diffraction Data and Structure Refinement for 3a, 7i

**Empirical formula**: C9 H6 F3 N O3  
**Formula weight**: 233.15  
**Temperature**: 293(2) K  
**Wavelength**: 0.71073 Å  
**Crystal system, space group**: Orthorhombic, P2(1)2(1)2(1)  
**Unit cell dimensions**:  
\[ \begin{align*} 
    a &= 4.8359(6) \text{ Å} & \alpha &= 90 \text{ deg.} \\
    b &= 6.4223(8) \text{ Å} & \beta &= 90 \text{ deg.} \\
    c &= 30.645(4) \text{ Å} & \gamma &= 90 \text{ deg.}
\end{align*} \]  
**Volume**: 951.8(2) Å³  
**Z, Calculated density**: 4, 1.627 Mg/m³  
**Absorption coefficient**: 0.159 mm⁻¹  
**F(000)**: 472  
**Crystal size**: 0.311 x 0.167 x 0.086 mm  
**Theta range for data collection**: 2.66 to 25.99 deg.  
**Limiting indices**: -5≤h≤5, -7≤k≤5, -35≤l≤37  
**Reflections collected / unique**: 5407 / 1850 [R(int) = 0.0309]  
**Completeness to theta = 25.99**: 99.7 %  
**Absorption correction**: Empirical  
**Max. and min. transmission**: 1.00000 and 0.14145  
**Refinement method**: Full-matrix least-squares on F²  
**Data / restraints / parameters**: 1850 / 6 / 145  
**Goodness-of-fit on F²**: 1.060  
**Final R indices [I>2sigma(I)]**: R1 = 0.0483, wR2 = 0.1313  
**R indices (all data)**: R1 = 0.0559, wR2 = 0.1383  
**Absolute structure parameter**: 0.1(15)  
**Largest diff. peak and hole**: 0.278 and -0.281 e. Å⁻³
Empirical formula  C17 H13 F3 N2 O2 S
Formula weight  366.35
Temperature  293(2) K
Wavelength  0.71073 Å
Crystal system  Monoclinic
Space group  C 2/c
Unit cell dimensions  a = 17.549(4) Å,  \( \alpha = 90^\circ \)
                   b = 11.355(2) Å,  \( \beta = 111.289(4)^\circ \)
                   c = 18.820(4) Å,  \( \gamma = 90^\circ \)
Volume  3494.2(12) Å³
Z  8
Density (calculated)  1.393 Mg/m³
Absorption coefficient  0.228 mm⁻¹
F(000)  1504
Crystal size  0.211 x 0.166 x 0.123 mm³
Theta range for data collection  2.184 to 25.995°
Index ranges  -21<=h<=21, -14<=k<=12, -23<=l<=20
Reflections collected  10399
Independent reflections  3430 [R(int) = 0.0353]
Completeness to theta = 25.242°  100.0 %
Absorption correction  Semi-empirical from equivalents
Max. and min. transmission  0.7457 and 0.6295
Refinement method  Full-matrix least-squares on F²
Data / restraints / parameters  3430 / 36 / 255
Goodness-of-fit on F²  1.058
Final R indices [I>2sigma(I)]  R1 = 0.0465, wR2 = 0.1261
R indices (all data)  R1 = 0.0579, wR2 = 0.1363
Extinction coefficient  0.0041(5)
Largest diff. peak and hole  0.282 and -0.289 e.Å⁻³
8. References

9. Copies of $^1$H NMR, $^{19}$F NMR and $^{13}$C NMR Spectra of 1, 3, 5 and 7
3a

3b
The image contains two sections of a document page with a chemical structure labeled as 3b. The structures show a chemical compound with functional groups and ppm values indicated in the spectrum below the structures. The ppm values range from -74.02 to 148.63. The compound appears to have oxygen, nitrogen, and fluorine atoms.
$\text{H}_3\text{CO}_2\text{S}$

$\text{CF}_3$

$\text{3e}$

$\text{NC}$

$\text{CF}_3$

$\text{3f}$
BrN\_O\_CF\_3

3j
F
O
CF₃
5h

F
O
CF₃
5h
\[
\begin{align*}
&\begin{array}{c}
\text{Cl} \\
\end{array} \\
&\begin{array}{c}
\text{O} \\
\end{array} \\
&\begin{array}{c}
\text{CF}_3 \\
\end{array} \\
&\begin{array}{c}
\text{5i} \\
\end{array} \\
&\begin{array}{c}
\text{Br} \\
\end{array} \\
&\begin{array}{c}
\text{O} \\
\end{array} \\
&\begin{array}{c}
\text{CF}_3 \\
\end{array} \\
&\begin{array}{c}
\text{5j} \\
\end{array}
\end{align*}
\]
7d

Ph

Ts

N

CF3

Ph

Ts

N

CF3

7d

f1 (ppm)

3.02

1.08

1.03

7.04

4.09

2.00

2.46

3.53

3.54

3.56

3.56

3.58

4.24

4.26

7.33

7.35

7.37

7.39

7.41

7.43

7.45

7.53

7.55

7.57

7.57

7.95

7.97

f1 (ppm)

3.00

-65.62

-65.61

Ph

N

Ts

CF3

7d

Ph

Ts

N

CF3

7d

f1 (ppm)

3.00

-65.62

-65.61

Ph

N

Ts

CF3

7d

Ph

Ts

N

CF3

7d

f1 (ppm)

3.00

-65.62

-65.61

Ph

N

Ts

CF3

7d

Ph

Ts

N

CF3

7d

f1 (ppm)

3.00

-65.62

-65.61

Ph

N

Ts

CF3

7d
\[ \text{Ts} \quad \text{CF}_3 \]

7e
-65.93, -100, 112.82, 117.78, 118.20, 120.52, 123.26, 126.00, 128.27, 128.30, 130.21, 132.28, 133.16, 135.45, 146.14, 21.79, 42.28, 42.47, 42.49, 42.68, 43.09, 43.49

$7i\quad \text{N} \quad \text{CF}_3$

$\text{Ts}$

$\text{NC}$

$\text{Ts}$

$\text{NC}$

$\text{CF}_3$

$\text{Ts}$

$\text{NC}$

$\text{CF}_3$

$\text{Ts}$
**S92**

**7i**

**7m**