Supporting Information

NaClO-Promoted Atroposelective Couplings of 3-Substituted Indoles with Amino Acid Derivatives

Zhaojie Li, Hao Zhang, Shouyun Yu*

State Key Laboratory of Analytical Chemistry for Life Science, Jiangsu Key Laboratory of Advanced Organic Materials, School of Chemistry and Chemical Engineering, Nanjing University, Nanjing 210023 (China)

E-mail: yushouyun@nju.edu.cn; Websites: http://hysz.nju.edu.cn/yusy/

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1. General Methods.

NaClO (Sodium hypochlorite solution reagent grade, available chlorine 4.00 - 4.99 %) was purchased from Sigma Aldrich. Benzotrifluoride, Toluene, Anisole, THF, DCM, 1,4-Dioxane, CH\textsubscript{3}CN and DMF were dried according to Purification of Common Laboratory Chemicals. Other reagents were used without further purification. Thin layer chromatography (TLC) was performed on EMD precoated plates (silica gel 60 F254, Art 5715) and visualized by fluorescence quenching under UV light and by staining with phosphomolybdic acid or potassium permanganate, respectively. Column chromatography was performed on EMD Silica Gel 60 (300–400 Mesh) using a forced flow of 0.5–1.0 bar. \textsuperscript{1}H NMR (400 MHz), \textsuperscript{13}C NMR (100 MHz) and \textsuperscript{19}F (376 MHz) were measured on a Bruker AVANCE III-400 spectrometer. Chemical shifts are expressed in parts per million (ppm) with respect to the residual solvent peak. Coupling constants are reported as Hertz (Hz), signal shapes and splitting patterns are indicated as follows: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet. Infrared (IR) spectra were recorded on a Nicolet 6700 spectrophotometer and are reported as wavenumber (cm\textsuperscript{-1}).
2. Racemization Studies

Thermal racemization of 3a: A solution of 3a (50 mg, dr = 80:1) in toluene (5 mL) was heated at the indicated temperatures (Table S1). At intervals, small samples (0.2 mL) were taken and the solvent was removed by evaporation. The dr value was determined by $^{19}$F NMR. The rates and energy barrier for the isomerization of 3a in toluene was calculated as shown in Table S2 and Table S3.

Table S1. Thermal Racemization of 3a.

<table>
<thead>
<tr>
<th>Temperature °C</th>
<th>Time/h</th>
<th>0 h</th>
<th>2 h</th>
<th>4 h</th>
<th>8 h</th>
<th>12 h</th>
<th>24 h</th>
<th>36 h</th>
<th>48 h</th>
<th>60 h</th>
<th>-</th>
</tr>
</thead>
<tbody>
<tr>
<td>40 °C</td>
<td>dr</td>
<td>80:1</td>
<td>68:1</td>
<td>46:1</td>
<td>33:1</td>
<td>31:1</td>
<td>28:1</td>
<td>22:1</td>
<td>16:1</td>
<td>13:1</td>
<td>-</td>
</tr>
<tr>
<td>60 °C</td>
<td>Time/h</td>
<td>0 h</td>
<td>2 h</td>
<td>4 h</td>
<td>6 h</td>
<td>8 h</td>
<td>12 h</td>
<td>15 h</td>
<td>24 h</td>
<td>30 h</td>
<td>48 h</td>
</tr>
<tr>
<td></td>
<td>dr</td>
<td>80:1</td>
<td>19:1</td>
<td>16:1</td>
<td>13:1</td>
<td>10:1</td>
<td>7.5:1</td>
<td>6.5:1</td>
<td>5:1</td>
<td>4.5:1</td>
<td>4:1</td>
</tr>
<tr>
<td>80 °C</td>
<td>Time/min</td>
<td>0</td>
<td>30</td>
<td>60</td>
<td>120</td>
<td>150</td>
<td>210</td>
<td>240</td>
<td>360</td>
<td>480</td>
<td>720</td>
</tr>
<tr>
<td></td>
<td>dr</td>
<td>80:1</td>
<td>12:1</td>
<td>8.9:1</td>
<td>6.3:1</td>
<td>5.2:1</td>
<td>4.7:1</td>
<td>4.5:1</td>
<td>4.0:1</td>
<td>4.0:1</td>
<td>4.0:1</td>
</tr>
</tbody>
</table>

Figure S1.1. The racemization plot of 3a at 313.15 K
For reversible first order kinetics, the rate law is: \( \frac{d[3a]}{dt} = k_f[3a] \cdot [3a^*] \)

And since \( K_{eq} = \frac{k_f}{k_b} = \frac{[3a]_{eq}}{[3a]_{eq} - [3a]_{eq}} = \frac{[3a]_0 - [3a]_{eq}}{[3a]_{eq}} \) and \( K_{eq} = \frac{1}{4} \), it can be used to eliminate \([3a^*]\), integration of the rate law gives \( \ln\left(\frac{[3a]_0 - [3a]_{eq}}{[3a]_0 - [3a]_{eq}}\right) = -(k_f + k_b)t \)

By plotting \( \ln\left(\frac{[3a]_0 - [3a]_{eq}}{[3a]_0 - [3a]_{eq}}\right) \) against \( t \), a linear equation is obtained, with the slope =
\[-(k_f + k_b)\].

**Figure S2.1.** The plot of \(\ln(\frac{[3a]_t-[3a]_{eq}}{[3a]_0-[3a]_{eq}})\) versus time \(t\) at 313.15 K

**Figure S2.2.** The plot of \(\ln(\frac{[3a]_t-[3a]_{eq}}{[3a]_0-[3a]_{eq}})\) versus time \(t\) at 333.15 K
Figure S2.3. The plot of $\ln \left( [3a]_t - [3a]_{eq} \right)$ versus time $t$ at 353.15 K

Table S2. Rates for the Racemization of 3a

<table>
<thead>
<tr>
<th>T (K)</th>
<th>$k_{obs}$/h$^{-1}$</th>
<th>$k_f$/h$^{-1}$</th>
<th>$k_b$/h$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>313.15 K</td>
<td>0.00565</td>
<td>0.00113</td>
<td>0.00452</td>
</tr>
<tr>
<td>333.15 K</td>
<td>0.07530</td>
<td>0.01506</td>
<td>0.06024</td>
</tr>
<tr>
<td>353.15 K</td>
<td>0.57000</td>
<td>0.11400</td>
<td>0.45600</td>
</tr>
</tbody>
</table>

The calculation of energy barrier $\Delta$$^G_{\theta_m}$ for racemization:

Insertion of $k_f$ and $k_b$ into the Eyring equation $\Delta G^{\dagger} = RT \cdot \ln \left( \frac{k_BT}{k_B h} \right)$ give $\Delta G^{\dagger}_{k_f}$ and $\Delta G^{\dagger}_{k_b}$.

The half-life of racemization of 3a $\tau_{1/2rac} = \frac{\ln 2}{k_{obs}}$

Table S3. Rates, half-life and energy barrier for the racemization of 3a.

<table>
<thead>
<tr>
<th>T (K)</th>
<th>$\tau_{1/2rac}$</th>
<th>$\Delta G^{\dagger}_{k_f}$ (kcal·mol$^{-1}$)</th>
<th>$\Delta G^{\dagger}_{k_b}$ (kcal·mol$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>313.15 K</td>
<td>122.68 h</td>
<td>27.66</td>
<td>26.80</td>
</tr>
<tr>
<td>333.15 K</td>
<td>9.21 h</td>
<td>27.75</td>
<td>26.84</td>
</tr>
<tr>
<td>353.15 K</td>
<td>1.22 h</td>
<td>28.04</td>
<td>27.07</td>
</tr>
</tbody>
</table>
3. General procedures for synthesis of starting materials

**Indoles:** (1a, 1b, 1c, 1d) are known compounds and were synthesized according to the literature.²)

![Indole structures](image)

**General procedures A for the synthesis of 3-alkyl-1-aryl-1H-indole.**

$$ \begin{array}{ccc}
    \text{R}^2 & \text{R}^3 & \text{I} \\
    \text{s1} & & \text{DMF, } 120 \, ^\circ \text{C, } 16 \, \text{h} \\
    \rightarrow & \text{Cul, Cs}_2\text{CO}_3 & \rightarrow \\
    & \text{R}^2 & \text{R}^3 \\
\end{array} $$

According to literature precedent,² to a flame-dried flask containing indole s1 (1.2 eq.), iodobenzene (1.0 eq.), copper (I) iodide (20 mol %) and cesium carbonate (2.0 eq.) were stirred for 16 h at 120 °C in DMF. After cooling down to room temperature, the reaction mixture was diluted with EtOAc (30 mL) and washed with water (2 x 50 mL). The combined aqueous layer was extracted with EtOAc (2 x 50 mL). The combined
organic layer was dried over Na$_2$SO$_4$, filtered and concentrated in vacuo. Purification by silica-gel chromatography ($n$-pentane) afforded the product 1.

1-(3,5-dimethylphenyl)-3-methyl-1H-indole (1e): by following the general procedure A, 3-methyl-1H-indole (1.57 g, 12 mmol, 1.2 eq.), 1-iodo-3,5-dimethylbenzene (2.32 g, 10 mmol, 1.0 eq.), copper(I) iodide (380.90 mg, 2 mmol, 20 mol %) and cesium carbonate (6.52 g, 20 mmol, 2.0 eq.) in DMF (30 mL), flash chromatography (EtOAc/$n$-Hexane 10:90) afforded 1e (1.86 g, 79 %) as a white solid. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.61 (d, $J = 7.2$ Hz, 1H), 7.55 (d, $J = 8.1$ Hz, 1H), 7.23-7.13 (m, 2H), 7.11-7.09 (m, 3H), 6.94 (s, 1H), 2.38 (s, 9H). $^{13}$C NMR (101 MHz, CDCl$_3$): $\delta$ 139.90, 139.33, 135.98, 127.72, 127.66, 125.64, 122.19, 121.77, 119.62, 119.15, 112.45, 110.59, 21.43, 9.65. IR (neat, cm$^{-1}$): 2913.54, 1598.22, 1462.52, 1359.80, 1194.19, 848.02, 734.80, 694.17. HRMS (ESI) ([M+Na]$^+$) Calcd. for C$_{17}$H$_{17}$NNa$: 258.1253; found: 258.1261.

3-benzyl-1-(4-methoxyphenyl)-1H-indole (1f): by following the general procedure A, 3-benzyl-1H-indole (1.66 g, 8 mmol, 1.2 eq.), 1-iodo-4-methoxybenzene (1.57 g, 6.7 mmol, 1.0 eq.), copper(I) iodide (255 mg, 1.3 mmol, 20 mol %) and cesium carbonate (4.37 g, 13.4 mmol, 2.0 eq.) in DMF (30 mL), flash chromatography (EtOAc/$n$-Hexane 10:90) afforded 1f (1.25 g, 70 %) as a white solid. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.61 (d, $J = 7.7$ Hz, 1H), 7.49 (d, $J = 8.2$ Hz, 1H), 7.45-7.30 (m, 6H), 7.27-7.20 (m, 2H), 7.20-7.13 (m, 1H), 7.09-6.99 (m, 3H), 4.20 (s, 2H), 3.89 (s, 3H).
\[^{13}\text{C} \text{NMR}\ (101 \text{ MHz}, \text{CDCl}_3) \ \delta \ 158.03, 141.01, 136.72, 132.93, 128.82, 128.43, 126.54, 126.01, 125.78, 122.33, 119.72, 119.42, 116.29, 114.71, 110.41, 55.62, 31.60. \]

IR (neat, cm\(^{-1}\)):
3025.06, 2906.55, 1599.42, 1510.80, 1457.24, 1245.94, 1029.82, 833.74, 734.11.

HRMS (ESI) ([M+Na]\(^+\)) Calcd. for C\(_{22}\)H\(_{19}\)NNaO\(_2\): 336.135; found: 336.1348.

5-methoxy-1-(4-methoxyphenyl)-3-methyl-1\(H\)-indole (1j): by following the general procedure A, 5-methoxy-3-methyl-1\(H\)-indole (1.29 g, 8.0 mmol, 1.2 eq.), 1-iodo-4-methoxybenzene (1.62 g, 6.7 mmol, 1.0 eq.), copper(I) iodide (255 mg, 1.3 mmol, 20 mol %) and cesium carbonate (4.37 g, 13.4 mmol, 2.0 eq.) in DMF (30 mL), flash chromatography (EtOAc/n-Hexane 10:90) afforded 1j (1.29 g, 72 %) as a white solid. \(^1\text{H} \text{NMR}\ (400 \text{ MHz}, \text{CDCl}_3): \ \delta \ 7.41-7.33 (m, 3H), 7.07-7.04 (m, 2H), 7.03-6.99 (m, 2H), 6.87 (dd, \(J = 8.9, 2.5 \text{ Hz}, 1H\)), 3.90 (s, 3H), 3.87 (s, 3H), 2.36 (s, 3H). \[^{13}\text{C} \text{NMR}\ (101 \text{ MHz}, \text{CDCl}_3): \ \delta \ 157.75, 154.12, 133.21, 131.64, 129.72, 126.41, 125.35, 114.69, 112.19, 111.67, 111.10, 100.86, 55.98, 55.60, 9.67. \text{IR (neat, cm}^{-1}\)\): 3127.57, 1913.23, 1729.31, 1598.81, 1508.87, 1460.42, 1224.41, 1029.54, 831.89, 738.34. HRMS (ESI) ([M+Na]\(^+\)) Calcd. for \ C\(_{17}\)H\(_{17}\)NNaO\(_2\): 290.1151; found: 290.1160.

4-(benzyloxy)-1-(4-methoxyphenyl)-3-methyl-1\(H\)-indole (1i): by following the general procedure A, 4-(benzyloxy)-3-methyl-1\(H\)-indole (1.90 g, 8. mmol, 1.2 eq.), 1-iodo-4-methoxybenzene (1.62 g, 6.7 mmol, 1.0 eq.), copper(I) iodide (255 mg, 1.3 mmol, 20 mol %) and cesium carbonate (4.37 g, 13.4 mmol, 2.0 eq.) in DMF (30 mL),
flash chromatography (EtOAc/n-Hexane 10:90) afforded 1i (1.17 g, 51 %) as a white solid. $^1$H NMR (400 MHz, CDCl$_3$): δ 7.72 (s, 1H), 7.34-7.29 (m, 2H), 7.29-7.21 (m, 2H), 7.04 (s, 1H), 7.02-6.97 (m, 2H), 3.85 (s, 3H), 2.33 (s, 3H); $^{13}$C NMR (101 MHz, CDCl$_3$): δ 158.18, 135.13, 132.51, 131.06, 127.08, 125.66, 124.88, 121.74, 114.79, 112.70, 111.77, 111.65, 55.62, 9.49. IR (neat, cm$^{-1}$): 2964.09, 2914.07, 1511.64, 1444.89, 1245.76, 1029.45, 833.92, 741.74. HRMS (ESI) ([M+Na$^+$]) Calcd. for C$_{23}$H$_{21}$NNaO$_2$: 366.1465; found: 366.1470.

![Image](image1)

**5-bromo-1-(4-methoxyphenyl)-3-methyl-1H-indole (1k):** by following the general procedure A, 5-bromo-3-methyl-1H-indole (1.67 g, 8.0 mmol, 1.2 eq.), 1-iodo-4-methoxybenzene (1.62 g, 6.7 mmol, 1.0 eq.), copper(I) iodide (255 mg, 1.3 mmol, 20 mol %) and cesium carbonate (4.37 g, 13.4 mmol, 2.0 eq.) in DMF (30 mL), flash chromatography (EtOAc/n-Hexane 10:90) afforded 1k (1.01 g, 48 %) as a white solid. $^1$H NMR (400 MHz, CDCl$_3$): δ 7.72 (s, 1H), 7.34-7.29 (m, 2H), 7.29-7.21 (m, 2H), 7.04 (s, 1H), 7.02-6.97 (m, 2H), 3.85 (s, 3H), 2.33 (s, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$): δ 158.18, 135.13, 132.51, 131.06, 127.08, 125.66, 124.88, 121.74, 114.79, 112.70, 111.77, 111.65, 55.62, 9.49. IR (neat, cm$^{-1}$): 3130.68, 2913.65, 1729.73, 1508.81, 1453.82, 1223.78, 1029.43, 833.17, 738.98. HRMS (ESI) ([M+Na$^+$]) Calcd. for C$_{16}$H$_{14}$BrNNaO$^+$: 338.0151; found: 338.0163.

![Image](image2)

**1-(4-methoxyphenyl)-3-methyl-5-(trifluoromethyl)-1H-indole (1l):** by following the general procedure A, 3-methyl-5-(trifluoromethyl)-1H-indole (1.59 g, 8.0 mmol,
1.2 eq.), 1-iodo-4-methoxybenzene (1.62 g, 6.7 mmol, 1.0 eq.), copper(I) iodide (255 mg, 1.3 mmol, 20 mol %) and cesium carbonate (4.37 g, 13.4 mmol, 2.0 eq.) in DMF (30 mL), flash chromatography (EtOAc/n-Hexane 10:90) afforded 1 (1.18 g, 58 %) as a white solid. 1H NMR (400 MHz, CDCl3): δ 7.91 (d, J = 0.7 Hz, 1H), 7.50-7.39 (m, 2H), 7.39-7.33 (m, 2H), 7.16 (d, J = 1.0 Hz, 1H), 7.08-7.01 (m, 2H), 3.89 (s, 3H), 2.41 (s, 3H). 19F NMR (376 MHz, CDCl3): δ -60.16 (s). 13C NMR (101 MHz, CDCl3): δ 158.42, 138.21, 137.75, 132.26, 128.66, 127.67, 125.88, 121.95, 121.63, 119.55, 118.84 (d, J = 3), 116.89 (d, J = 4), 114.84, 112.99, 110.46, 55.62, 9.45. IR (neat, cm⁻¹): 3049.18, 2912.75, 1730.27, 1598.18, 1509.00, 1459.87, 1223.27, 1029.30, 834.25, 739.75. HRMS (ESI) ([M+Na]+) Calcd. for C17H14F3NNaO+: 328.0920; found: 328.0928.

1-(4-methoxyphenyl)-3-methyl-5-nitro-1H-indole (1m): by following the general procedure A, 3-methyl-5-nitro-1H-indole (1.41 g, 8.0 mmol, 1.2 eq.), 1-iodo-4-methoxybenzene (1.62 g, 6.7 mmol, 1.0 eq.), copper(I) iodide (255 mg, 1.3 mmol, 20 mol %) and cesium carbonate (4.37 g, 13.4 mmol, 2.0 eq.) in DMF (30 mL), flash chromatography (EtOAc/n-Hexane 10:90) afforded 1m (0.85 g, 45 %) as a yellow solid. 1H NMR (400 MHz, CDCl3): δ 8.59 (d, J = 2.1 Hz, 1H), 8.08 (dd, J = 9.1, 2.2 Hz, 1H), 7.45-7.31 (m, 3H), 7.19 (s, 1H), 7.10-6.99 (m, 2H), 3.89 (s, 3H), 2.42 (s, 3H). 13C NMR (101 MHz, CDCl3): δ 158.85, 141.50, 139.28, 131.62, 129.12, 128.70, 125.98, 117.80, 116.60, 114.99, 114.64, 110.18, 55.66, 9.43. IR (neat, cm⁻¹): 3130.50, 2913.34, 1729.60, 1599.18, 1508.69, 1460.38, 1222.64, 1029.42, 834.16, 741.58. HRMS (ESI) ([M+Na]+) Calcd. for C16H14N2NaO3+: 305.0897; found: 305.0893.
6-fluoro-1-(4-methoxyphenyl)-3-methyl-1H-indole (1n): by following the general procedure A, 6-fluoro-3-methyl-1H-indole (1.19 g, 8.0 mmol, 1.2 eq.), 1-iodo-4-methoxybenzene (1.62 g, 6.7 mmol, 1.0 eq.), copper(I) iodide (255 mg, 1.3 mmol, 20 mol %) and cesium carbonate (4.37 g, 13.4 mmol, 2.0 eq.) in DMF (30 mL), flash chromatography (EtOAc/n-Hexane 10:90) afforded 1n (0.80 g, 47 %) as a white solid.

^1H NMR (400 MHz, CDCl₃): δ 7.49 (m, 1H), 7.36-7.28 (m, 2H), 7.10 (dd, J = 10.2, 2.2 Hz, 1H), 7.04-6.96 (m, 3H), 6.95 - 6.84 (m, 1H), 3.84 (s, 3H), 2.35 (s, 3H).

^19F NMR (376 MHz, CDCl₃): δ -120.68 -120.78 (m).

^13C NMR (101 MHz, CDCl₃): δ 161.54, 159.18, 158.15, 136.45 (d, J = 12.1 Hz), 132.68, 126.22 (d, J = 3.6 Hz), 125.94, 125.53, 119.86 (d, J = 10.1 Hz), 114.83, 112.27, 108.13 (d, J = 24 Hz), 96.73 (d, J = 27 Hz), 55.60, 9.59. IR (neat, cm⁻¹): 3048.68, 2912.73, 1731.21, 1509.88, 1453.66, 1243.71, 1029.84, 848.03, 740.85. HRMS (ESI) ([M+Na]+) Calcd. for C₁₆H₁₄FNNaO⁺: 278.0952; found: 278.0963.

6-chloro-1-(4-methoxyphenyl)-3-methyl-1H-indole (1o): by following the general procedure A, 6-chloro-3-methyl-1H-indole (1.32 g, 8.0 mmol, 1.2 eq.), 1-iodo-4-methoxybenzene (1.62 g, 6.7 mmol, 1.0 eq.), copper(I) iodide (255 mg, 1.3 mmol, 20 mol %) and cesium carbonate (4.37 g, 13.4 mmol, 2.0 eq.) in DMF (30 mL), flash chromatography (EtOAc/n-Hexane 10:90) afforded 1o (0.91 g, 50 %) as a white solid.

^1H NMR (400 MHz, CDCl₃): δ 7.53 (dd, J = 8.4, 0.8 Hz, 1H), 7.46-7.41 (m, 1H), 7.38-7.31 (m, 2H), 7.18-7.12 (m, 1H), 7.08-7.00 (m, 3H), 3.89 (s, 3H), 2.38 (s, 3H).
$^{13}$C NMR (101 MHz, CDCl$_3$): $\delta$ 158.27, 138.23, 136.87, 132.42, 128.28, 127.92, 126.62, 125.75, 120.12, 120.03, 116.40, 114.85, 112.25, 110.23, 55.62, 9.53. IR (neat, cm$^{-1}$): 2932.19, 2835.05, 1608.19, 1510.62, 1464.24, 1245.22, 1031.66, 832.65, 799.80. HRMS (ESI) ([M+Na]$^+$) Calcd. for C$_{16}$H$_{14}$ClNNaO$^+$: 294.0656; found: 294.0659.

1-(4-methoxyphenyl)-3,7-dimethyl-1H-indole (1p): by following the general procedure A, 3,7-dimethyl-1H-indole (1.16 g, 8.0 mmol, 1.2 eq.), 1-iodo-4-methoxybenzene (1.62 g, 6.7 mmol, 1.0 eq.), copper(I) iodide (255 mg, 1.3 mmol, 20 mol %) and cesium carbonate (4.37 g, 13.4 mmol, 2.0 eq.) in DMF (30 mL), flash chromatography (EtOAc/n-Hexane 10:90) afforded 1p (0.87 g, 52 %) as a white solid. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.47 (d, $J = 7.6$ Hz, 1H), 7.30-7.26 (m, 2H), 7.08-7.02 (m, 1H), 6.96-6.89 (m, 3H), 6.87 (s, 1H), 3.87 (s, 3H), 2.35 (s, 3H), 2.01 (s, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$): $\delta$ 158.94, 134.52, 129.58, 129.19, 128.53, 124.49, 121.55, 119.38, 116.90, 113.54, 111.23, 55.54, 19.51, 9.54. IR (neat, cm$^{-1}$): 2963.43, 2913.87, 1511.14, 1444.12, 1245.88, 1220.91, 1030.31, 835.13, 782.98, 593.58. HRMS (ESI) ([M+Na]$^+$) Calcd. for C$_{17}$H$_{17}$NNaO$^+$: 274.1202; found: 274.1210.

3-chloro-1-(4-methoxyphenyl)-1H-indole (1g): synthesized according to literature precedent.$^2$ 1,3-dichloro-5,5-dimethylhydantoin (DCDMH) (2.17 g, 11 mmol, 1.1 eq.) was added to a solution of 1-(4-methoxyphenyl)-1H-indole (2.23 g, 10 mmol, 1 eq.) in 1.4-dioxane (30 mL) at room temperature, and the resulting solution was stirred up to transform completely. The reaction solution was poured into the saturated NaHCO$_3$
solution (30 mL), the mixtures was extracted by ethyl acetate (2 x 30 mL). The organic phase was dried over Na₂SO₄, filtered, concentrated under reduced pressure. The residue was then purified by flash chromatography (EtOAc/n-Hexane 5:95) to provide the corresponding product 1g as a brown solid (2.14 g, 83 %). ¹H NMR (400 MHz, CDCl₃): δ 7.71-7.64 (m, 1H), 7.41 (d, J = 7.9 Hz, 1H), 7.38-7.33 (m, 2H), 7.27-7.18 (m, 3H), 7.05-6.98 (m, 2H), 3.87 (s, 3H). ¹³C NMR (101 MHz, CDCl₃): δ 158.57, 135.48, 131.98, 126.07, 124.78, 123.30, 120.70, 118.54, 114.84, 110.66, 106.86, 77.37, 77.05, 76.74, 55.63. IR (neat, cm⁻¹): 3125.92, 1915.27, 1598.98, 1508.73, 1454.28, 1242.56, 1223.71, 1030.02, 834.04, 741.00. HRMS (ESI) ([M+Na]⁺) Calcd. for C₁₅H₁₂ClNNaO⁺: 280.0500; found: 280.0514.

3-bromo-1-(4-methoxyphenyl)-1H-indole (1h): synthesized according to literature precedent, a mixture of 1-(4-methoxyphenyl)-1H-indole (2.23 g, 10 mmol, 1 eq.) and 1,3-Dibromo-5,5-dimethylhydantoin (DBDMH) (3.15 g, 11 mmol, 1.1 eq.) in 1.4-dioxane (30 mL), flash chromatography (EtOAc/n-Hexane 5:95) afforded 1h as a brown solid (2.05 g, 68 %). ¹H NMR (400 MHz, CDCl₃): δ 7.66-7.55 (m, 1H), 7.43-7.37 (m, 1H), 7.34 (d, J = 8.7 Hz, 2H), 7.29 (s, 1H), 7.25-7.18 (m, 2H), 7.00 (d, J = 8.7 Hz, 2H), 3.85 (s, 3H); ¹³C NMR (101 MHz, CDCl₃): δ 158.64, 135.97, 131.97, 127.70, 127.21, 126.09, 123.31, 120.88, 119.49, 114.87, 110.62, 92.04, 77.38, 77.06, 76.75, 55.64. IR (neat, cm⁻¹): 3125.82, 2913.72, 1599.36, 1507.87, 1453.59, 1222.65, 1029.43, 834.80, 741.86. HRMS (ESI) ([M+Na]⁺) Calcd. for C₁₅H₁₂BrNNaO⁺: 323.9994; found: 323.9998.
Amino acid derivatives:

General procedures B for the synthesis of N-[(trifluoromethyl)sulfonyl] amino acids derivatives.

Synthesized according to literature precedent, amino acid tert-butyl esters were suspended in dichloromethane, and trimethylamine (2 eq.) was added with stirring. A solution of trifluoromethanesulfonic anhydride (1.2 eq.) in dichloromethane was added to the mixture under a dry nitrogen gas atmosphere at -78 °C. The mixture was then stirred overnight at room temperature. The resulting solution was washed with dilute hydrochloric acid and then with saturated aqueous sodium chloride. The concentrated dichloromethane solution was shaken with diethyl ether under reduced pressure. The extract was purified on silica gel (MeOH/CHCl₃ 1:5) to provide the corresponding N-trifluoromethanesulfonyl amino acids derivatives (50-60% yields).
(S)-tert-butyl-3-methyl-2-(trifluoromethylsulfonylamido)butanoate (2a): by following the general procedure B, tert-butyl L-valinate (1.73 g, 10 mmol, 1.0 eq.), trimethylamine (2.02 g, 20 mmol, 2 eq.) and trifluoromethanesulfonic anhydride (3.39 g, 12 mmol 1.2 eq.) in dichloromethane, flash chromatography (EtOAc/n-Hexane 10:90) afforded 2a (1.67 g, 55 %) as a white solid. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 5.46 (s, 1H), 3.94 (dd, $J = 8.4, 4.3$ Hz, 1H), 2.26-2.11 (m, 1H), 1.49 (s, 9H), 1.04 (d, $J = 6.8$ Hz, 3H), 0.92 (d, $J = 6.9$ Hz, 3H). $^{19}$F NMR (376 MHz, CDCl$_3$): $\delta$ -76.98. $^{13}$C NMR (101 MHz, CDCl$_3$): $\delta$ 169.48, 119.61(q, $J = 323$ Hz), 83.63, 62.82, 31.62, 27.83, 18.82, 16.92. IR (neat, cm$^{-1}$): 3220.82, 2976.63, 1713.00, 1507.48, 1370.16, 1183.62, 1148.09, 836.44, 595.50. HRMS (ESI) ([M - H]$^+$) Calcd. for C$_{10}$H$_{17}$F$_3$NO$_4$S: 304.0836; found: 304.0823.

(S)-ethyl-3-methyl-2-(trifluoromethylsulfonylamido)butanoate (2b): by following the general procedure B, ethyl L-valinate (1.45 g, 10 mmol, 1.0 eq.), trimethylamine (2.02 g, 20 mmol, 2 eq.) and trifluoromethanesulfonic anhydride (3.39 g, 12 mmol 1.2 eq.) in dichloromethane, flash chromatography (EtOAc/n-Hexane 10:90) afforded 2b (1.66 g, 60 %) as a white solid. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 5.85 (s, 1H), 4.34-4.19 (m, 2H), 4.05 (d, $J = 4.7$ Hz, 1H), 2.18-2.26 (m, 1H), 1.31 (td, $J = 7.1, 0.5$ Hz, 3H), 1.04 (d, $J = 6.8$ Hz, 3H), 0.94 (d, $J = 6.9$ Hz, 3H). $^{19}$F NMR (376 MHz, CDCl$_3$): $\delta$ -77.04. $^{13}$C NMR (101 MHz, CDCl$_3$): $\delta$ 170.47, 119.56 (q, $J = 323$ Hz), 62.44, 62.28, 31.60, 18.76, 16.98, 14.04. IR (neat, cm$^{-1}$): 3165.08, 2975.39, 1712.57, 1461.51, 1369.44, 1296.67, 1177.41, 1022.47, 613.88. HRMS (ESI) ([M-H]$^+$) Calcd. for C$_8$H$_{13}$F$_3$NO$_4$S: 276.0523; found:276.0516.
(S)-**tert**-butyl-3-phenyl-2-(trifluoromethylsulfonamido)propanoate (2c): by following the general procedure B, **tert**-butyl L-phenylalaninate (2.21 g, 10 mmol, 1.0 eq.), trimethylamine (2.02 g, 20 mmol, 2 eq.) and trifluoromethanesulfonic anhydride (3.39 g, 12 mmol 1.2 eq.) in dichloromethane, flash chromatography (EtOAc/n-Hexane 10:90) afforded 2c as a white solid (1.77 g, 50 %).\(^1\)H NMR (400 MHz, CDCl\(_3\)): δ 7.38-7.24 (m, 3H), 7.21-7.13 (m, 2H), 5.58 (s, 1H), 4.38 (dd, \(J = 13.2, 6.2\) Hz, 1H), 3.25-2.96 (m, 2H), 1.42 (s, 9H). \(^{19}\)F NMR (376 MHz, CDCl\(_3\)): δ -77.37. \(^{13}\)C NMR (101 MHz, CDCl\(_3\)): δ 168.88, 134.23, 129.66, 128.74, 127.64, 119.46 (q, \(J = 323\) Hz), 84.00, 58.21, 39.77, 27.78. IR (neat, cm\(^{-1}\)): 3211.91, 2914.13, 1722.67, 1511.68, 1458.33, 1182.87, 1145.84, 835.17, 604.84. HRMS (ESI) ([M-H]^-) Calcd. for C\(_{14}\)H\(_{17}\)F\(_3\)NO\(_4\)S-: 352.0836; found: 352.0840.

(S)-**tert**-butyl-4-methyl-2-(trifluoromethylsulfonamido)pentanoate (2d): by following the general procedure B, **tert**-butyl L-leucinate (1.87 g, 10 mmol, 1.0 eq.), trimethylamine (2.02 g, 20 mmol, 2 eq.) and trifluoromethanesulfonic anhydride (3.39 g, 12 mmol 1.2 eq.) in dichloromethane, flash chromatography (EtOAc/n-Hexane 10:90) afforded 2d (1.69 g, 53 %) as a white solid. \(^1\)H NMR (400 MHz, CDCl\(_3\)): δ 5.74 (d, \(J = 8.7\) Hz, 1H), 4.23-3.78 (m, 1H), 1.86-1.75 (m, 1H), 1.66-1.54 (m, 2H), 1.48 (s, 9H), 0.97 (d, \(J = 6.6\) Hz, 6H). \(^{19}\)F NMR (376 MHz, CDCl\(_3\)): δ -77.19. \(^{13}\)C NMR (101 MHz, CDCl\(_3\)): δ 170.63, 119.51 (q, \(J = 323\) Hz), 83.57, 56.42, 42.67, 27.78, 24.37, 22.67, 21.45. IR (neat, cm\(^{-1}\)): 3213.91, 2967.83, 1715.30, 1383.70, 1179.70, 1142.65, 837.54, 605.30. HRMS (ESI) ([M-H]^-) Calcd. for C\(_{11}\)H\(_{19}\)F\(_3\)NO\(_4\)S-:
(2S, 3R)-tert-butyl-3-methyl-2-(trifluoromethylsulfonamido)pentanoate (2f): by following the general procedure B, tert-butyl L-alloisoleucinate (1.87 g, 10 mmol, 1.0 eq.), trimethylamine (2.02 g, 20 mmol, 2 eq.) and trifluoromethanesulfonic anhydride (3.39 g, 12 mmol 1.2 eq.) in dichloromethane, flash chromatography (EtOAc/n-Hexane 10:90) afforded 2f (1.79 g, 53 %) as a white solid. ¹H NMR (400 MHz, CDCl₃): δ 5.72 (s, 1H), 3.99 (dd, J = 9.6, 4.8 Hz, 1H), 1.99-1.80 (m, 1H), 1.48 (s, 9H), 1.47-1.41 (m, 1H), 1.24-1.13 (m, 1H), 0.99 (d, J = 6.9 Hz, 3H), 0.94 (t, J = 7.4 Hz, 3H). ¹³C NMR (101 MHz, CDCl₃): δ 169.39, 119.58 (q, J = 323 Hz), 83.66, 62.07, 38.71, 27.84, 24.56, 15.21, 11.47. IR (neat, cm⁻¹): 3209.28, 1977.15, 1708.10, 1371.84, 1180.83, 1146.85. HRMS (ESI) ([M-H]⁻) Calcd. for C₁₁H₁₉F₃NO₄S⁻: 318.0992; found: 318.0990.

(S)-tert-butyl-3-(tert-butoxy)-2-(trifluoromethylsulfonamido)propanoate (2g): by following the general procedure B, tert-butyl O-(tert-butyl)-L-serinate (2.17 g, 10 mmol, 1.0 eq.), trimethylamine (2.02 g, 20 mmol, 2 eq.) and trifluoromethanesulfonic anhydride (3.39 g, 12 mmol 1.2 eq.) in dichloromethane, flash chromatography (EtOAc/n-Hexane 10:90) afforded 2g (1.96 g, 53 %) as a white solid. ¹H NMR (400 MHz, CDCl₃): δ 5.82 (s, 1H), 4.20 (s, 1H), 3.83 (dd, J = 8.9, 4.8 Hz, 1H), 3.58 (dd, J = 8.9, 3.0 Hz, 1H), 1.48 (s, 9H), 1.16 (s, 9H). ¹³C NMR (101 MHz, CDCl₃): δ 167.56, 119.48 (q, J = 323 Hz), 83.30, 73.67, 63.10, 57.82, 27.85, 27.20. IR (neat, cm⁻¹): 3213.96, 2978.03, 1725.55, 1459.62, 1371.37, 1180.07, 1146.93, 1092.98, 837.05, 604.77. HRMS (ESI) ([M-H]⁻) Calcd. for
(S)-**tert-buty1-2-cyclohexyl-2-(trifluoromethylsulphonamido)acetate** (2h): by following the general procedure B, **tert-buty1 (S)-2-amino-2-cyclohexylacetate** (2.13 g, 10 mmol, 1.0 eq.), trimethylamine (2.02 g, 20 mmol, 2 eq.) and trifluoromethanesulfonyl anhydride (3.39 g, 12 mmol 1.2 eq.) in dichloromethane, flash chromatography (EtOAc/n-Hexane 10:90) afforded 2h (2.07 g, 60 %) as a white solid. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 5.56 (s, 1H), 3.91 (d, $J$ = 4.4 Hz, 1H), 1.87- .57 (m, 6H), 1.53-1.44 (m, 9H), 1.36-0.97 (m, 5H). $^{19}$F NMR (376 MHz, CDCl$_3$): $\delta$ -77.00. $^{13}$C NMR (101 MHz, CDCl$_3$): $\delta$ 169.39, 119.60 (q, $J$ = 323 Hz), 83.58, 62.49, 41.11, 29.23, 27.88, 27.52, 25.79, 25.78. IR (neat, cm$^{-1}$): 3235.49, 2929.83, 1712.61, 1383.73, 1180.13, 1141.63, 834.16, 595.69. HRMS (ESI) ([M-H]$^-$) Calcd. for C$_{12}$H$_{21}$F$_3$NO$_5$S: 348.1098; found:348.1110.

(S)-**N-(1-((tert-butyldimethylsilyl)oxy)-3-phenylpropan-2-yl)-1,1,1-trifluoromethanesulphonamide** (2i): synthesized according to literature precedent, $^4$ **tert-buty1 L-threoninate** (3.5 g, 20 mmol) and imidazole (2.6 g, 38.5 mmol) were dissolved in 20 mL of MeCN. **Tert-butyldimethylsilyl chloride** (3.5 mL, 20 mmol) was added to the mixture and the reaction was allowed to stir overnight. The reaction was diluted with 40 mL Et$_2$O and poured into 50 mL of water. The organic layer was extracted with Et$_2$O (2 x 40 mL), washed with brine (1 x 50 mL) and dried using MgSO$_4$. The crude product was used in the next step without further purification.

The product of the first step was suspended in dichloromethane, and trimethylamine (4.04 g, 40 mmol, 2 eq.) was added with stirring. A solution of trifluoromethanesulfonyl anhydride (6.78 g, 24 mmol, 1.2 eq.) in dichloromethane
was added to the mixture under a dry nitrogen gas atmosphere at -78 °C. The mixture was then stirred overnight at room temperature. The resulting solution was washed with dilute hydrochloric acid and then with saturated aqueous sodium chloride. The concentrated dichloromethane solution was shaken with diethyl ether under reduced pressure. The extract was purified on silica gel (MeOH/CHCl₃ 1:5) to provide the corresponding product (2.02 g, 51 %). ¹H NMR (400 MHz, CDCl₃): δ 7.28-7.21 (m, 2H), 7.21-7.16 (m, 1H), 7.11 (d, J = 7.9 Hz, 2H), 5.13 (s, 1H), 3.71 (d, J = 5.2 Hz, 1H), 3.57-3.41 (m, 2H), 2.89 (d, J = 6.9 Hz, 2H), 0.86 (s, 10H), 0.00 (s, 6H). ¹⁹F NMR (376 MHz, CDCl₃): δ -77.93. ¹³C NMR (101 MHz, CDCl₃): δ 136.41, 129.46, 128.75, 127.09, 119.56 (q, J = 323 Hz), 62.79, 58.00, 38.50, 25.84, 18.26, -5.53, -5.64. IR (neat, cm⁻¹): 3307.43, 2930.28, 1421.28, 1373.04, 1189.16, 831.33, 777.49, 616.82. HRMS (ESI) ([M-H]⁻) Calcd. for C₁₆H₂₅F₃NO₃SSi⁻: 396.1282; found: 396.1278.

(2S,3R)-tert-butyl-3-((tert-butyldimethylsilyl)oxy)-2-(trifluoromethylsulfonamido)butanoate (2e): synthesized according to the method for 2i, 2e (2.86 g, 68 %) was prepared as a white solid by flash chromatography (EtOAc/n-Hexane 10:90). ¹H NMR (400 MHz, CDCl₃): δ 5.40 (d, J = 9.3 Hz, 1H), 4.39-4.21 (m, 1H), 3.78 (d, J = 9.3 Hz, 1H), 1.40 (s, 9H), 1.19 (d, J = 6.3 Hz, 3H), 0.78 (s, 9H), 0.00 (s, 3H), -0.04 (s, 3H). ¹⁹F NMR (376 MHz, CDCl₃): δ -77.23. ¹³C NMR (101 MHz, CDCl₃): δ 168.02, 119.50 (q, J = 323 Hz), 83.56, 68.58, 63.48, 27.94, 25.73, 20.98, 17.90, -4.02, -5.02. IR (neat, cm⁻¹): 3302.89, 2930.29, 1727.11, 1376.00, 1145.09, 990.67, 836.76, 777.02, 613.84. HRMS (ESI) ([M-H]⁻) Calcd. for C₁₅H₂₉F₃NO₅SSi⁻: 420.1493; found: 420.1487.
tert-butyl ((4-nitrophenyl)sulfonyl)-L-valinate (2j): synthesized according to literature precedent, tert-butyl L-valinate (1.73 g, 10 mmol, 1.0 eq.), trimethylamine (2.02 g, 20 mmol, 2 eq.) and 4-nitrobenzenesulfonyl chloride (2.65 g, 12 mmol 1.2 eq.) in dichloromethane, flash chromatography (EtOAc/n-Hexane 10:90) afforded 2j (2.86 g, 80 %) as a yellow solid. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.33 (d, $J$ = 8.9 Hz, 2H), 8.04 (d, $J$ = 8.9 Hz, 2H), 5.26 (d, $J$ = 9.9 Hz, 1H), 3.70 (dd, $J$ = 9.9, 4.4 Hz, 1H), 2.16-2.03 (m, 1H), 1.24 (s, 9H), 1.01 (d, $J$ = 6.8 Hz, 3H), 0.85 (d, $J$ = 6.9 Hz, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 169.96, 150.04, 145.68, 128.65, 124.19, 82.90, 61.43, 31.54, 27.69, 19.09, 16.88. HRMS (ESI) ([M-H]$^-$) Calcd. for C$_{15}$H$_{21}$N$_2$O$_6$S$: 357.1120; found: 357.1132.

A 10 mL round bottom flask was equipped with a rubber septum and magnetic stir bar. It was charged with indole 1 (0.2 mmol, 2.0 eq.) and amino acid derivative 2 (0.1 mmol, 1.0 eq.). Benzotrifluoride (2.0 mL, 0.05 M) and NaClO (0.3 mmol, 3.0 eq.) was added via syringe. The mixture was then stirred for 12 h. After the reaction was complete (as judged by TLC analysis), the mixture was poured into a separatory funnel containing 10 mL of H₂O and 10 mL of EtOAc. The layers were separated and the aqueous layer was extracted with EtOAc (2 × 10 mL). The combined organic layers were dried over Na₂SO₄ and concentrated under reduced pressure after filtration. The residue was purified by flash chromatography on silica gel to afford the desired product 3.

Notes:

NaClO (Sodium hypochlorite solution reagent grade, available chlorine 4.00-4.99 %) was purchased from Sigma-Aldrich.

Product Number: 239305

CAS Number: 7681-52-9

MDL: MFCD00011120

Formula: NaClO

Formula Weight: 74.44 g/mol

Composition available chlorine, 4.00 - 4.99%

Density 1.097 g/mL at 25 °C

Storage Temperature: 2 - 8 °C

\[ M \ [\text{ClO}^-] = \text{available chlorine} \times d / 0.070906 \]

\[ M \ [\text{ClO}^-] = 0.05 \times 1.097 / 0.070906 = 0.775 \text{ M} \]

(The above data was provided by Sigma-Aldrich)
5. Date for products.

(S)-tert-buty1-2-(N-(1,3-dimethyl-1H-indol-2-yl)-1,1,1-trifluoromethylsulfonamido)-3-methylbutanoate (3a): According to the general procedure, purification by flash chromatography (EtOAc/n-Hexane 5:95), 3a (16.3 mg, 36 %, 7.7:1 dr) was obtained as a white solid from 1a, 2a and NaClO. m.p. 61-63 °C. 

$^1$H NMR (400 MHz, DMSO): \( \delta \) 7.59 (d, \( J = 7.9 \) Hz, 1H), 7.46 (d, \( J = 8.3 \) Hz, 1H), 7.37-7.27 (m, 1H), 7.21-7.08 (m, 1H), 4.55 (d, \( J = 2.6 \) Hz, 1H), 3.92 (s, 3H), 2.26 (s, 3H), 2.11-1.98 (m, 1H), 1.51 (s, 9H), 1.13 (d, \( J = 7.1 \) Hz, 3H). 

$^{19}$F NMR (377 MHz, CDCl$_3$): \( \delta -73.26 \). 

$^{13}$C NMR (101 MHz, DMSO): \( \delta \) 167.81, 134.88, 125.18, 123.83, 119.56 (d, \( J = 8 \) Hz), 119.46 (q, \( J = 323 \) Hz), 111.23, 110.28, 82.75, 69.49, 29.82, 27.89, 27.57, 21.35, 16.04, 9.26. IR (neat, cm$^{-1}$): 2975.18, 2913.04, 1745.98, 1393.79, 1190.46, 1149.86, 1028.78, 741.70, 594.19. HRMS (ESI) ([M+Na]$^+$) Calcd. for C$_{20}$H$_{27}$F$_3$N$_2$NaO$_4$S$^+$: 471.1536; found: 471.1554.

(S)-tert-buty1-2-(N-(1,3-dimethyl-1H-indol-2-yl)-1,1,1-trifluoromethylsulfonamido)-3-methylbutanoate (3a): According to the general procedure, purification by flash chromatography (EtOAc/n-Hexane 5:95), 3a (2.1 mg, 5 %) was obtained as a white solid from 1a, 2a and NaClO. 

$^1$H NMR (400 MHz, DMSO): \( \delta \) 7.58 (d, \( J = 7.9 \) Hz, 1H), 7.44 (d, \( J = 8.3 \) Hz, 1H), 7.33-7.26 (m, 1H), 7.16-7.08 (m, 1H), 4.71 (d, \( J = 2.9 \) Hz, 1H), 3.64 (s, 3H), 2.40 (s, 3H), 1.86-1.74 (m, 1H), 1.47 (s, 9H), 1.13 (d, \( J = 7.0 \) Hz, 3H), 0.55 (d, \( J = 6.7 \) Hz, 3H). 

$^{19}$F NMR (377 MHz, CDCl$_3$): \( \delta -73.26 \). 

$^{13}$C NMR (101 MHz, DMSO): \( \delta \) 166.98, 134.82, 125.49, 124.63, 123.70, 119.57 (d, \( J = 8 \) Hz), 119.06 (q, \( J = 323 \) Hz), 112.21, 110.21, 82.55, 69.62, 40.09, 39.88, 39.67, 39.46, 39.25, 39.04, 38.83, 29.84, 28.39, 27.55, 21.45, 16.84, 9.13. IR (neat, cm$^{-1}$): 2977.05,
(S)-tert-butyl-3-methyl-2-(1,1,1-trifluoro-N-(1-(4-methoxyphenyl)-3-methyl-1H-indol-2-yl)methylsulfonamido)butanoate (3b): According to the general procedure, purification by flash chromatography (EtOAc/n-Hexane 5:95), 3b (47.5 mg, 88 %, 13:1 dr) was obtained as a white solid from 1b, 2a and NaClO. m.p. 85 - 87 °C. $^1$H NMR (400 MHz, DMSO): $\delta$ 7.64 (d, $J = 7.7$ Hz, 1H), 7.45 (d, $J = 7.1$ Hz, 2H), 7.26-7.21 (m, 1H), 7.21-7.14 (m, 3H), 6.83 (d, $J = 8.2$ Hz, 1H), 3.97 (d, $J = 7.2$ Hz, 1H), 3.86 (s, 3H), 2.30 (s, 3H), 1.90-1.75 (m, 1H), 1.39 (s, 9H), 0.70 (d, $J = 6.6$ Hz, 3H), 0.48 (d, $J = 6.7$ Hz, 3H). $^{19}$F NMR (376 MHz, CDCl$_3$): $\delta$ -71.62. $^{13}$C NMR (101 MHz, DMSO): $\delta$ 165.93, 159.48, 136.83, 130.67, 128.19, 125.51, 125.40, 124.51, 120.16, 119.60, 119.17(q, $J = 323$ Hz), 114.83, 113.47, 110.53, 82.66, 70.43, 55.46, 29.34, 27.34, 19.52, 17.70, 9.86. IR (neat, cm$^{-1}$): 2974.45, 1934.25, 1738.96, 1609.08, 1512.77, 1456.60, 1218.47, 1150.29, 1027.90, 780.68, 632.77. HRMS (ESI) ([M+Na$^+$]) Calcd. for C$_{26}$H$_{31}$F$_3$N$_2$NaO$_5$S$^+$: 563.1798; found: 563.1808.

(S)-tert-butyl-3-methyl-2-(1,1,1-trifluoro-N-(3-methyl-1-phenyl-1H-indol-2-yl)methylsulfonamido)butanoate (3c): According to the general procedure, purification by flash chromatography (EtOAc/n-Hexane 5:95), 3c (43.9 mg, 86 %, 12.3:1 dr) was obtained as a colourless liquid from 1c, 2a and NaClO. $^1$H NMR (400 MHz, DMSO): $\delta$ 7.69-7.62 (m, 3H), 7.60 (d, $J = 7.1$ Hz, 1H), 7.54 (d, $J = 7.3$ Hz, 2H), 7.29-7.21 (m, 1H), 7.22-7.14 (m, 1H), 6.87 (d, $J = 8.2$ Hz, 1H), 3.96 (d, $J = 7.2$ Hz, 1H), 2.32 (s, 3H), 1.88-1.76 (m, 1H), 1.39 (s, 9H), 0.69 (d, $J = 6.6$ Hz, 3H), 0.41 (d, $J = 6.7$ Hz,
(S)-tert-butyl-2-(N-(1-benzyl-3-methyl-1H-indol-2-yl)-1,1,1-trifluoromethylsulfonamido)-3-methylbutanoate (3d): According to the general procedure, purification by flash chromatography (EtOAc/n-Hexane 5:95), 3d (24.1 mg, 46 %, 9.6:1 dr) was obtained as a colourless liquid from 1d, 2a and NaClO. $^1$H NMR (400 MHz, DMSO): $\delta$ 7.72-7.58 (m, 1H), 7.30-7.22 (m, 3H), 7.13-7.07 (m, 4H), 6.86-6.70 (m, 1H), 6.06 (d, $J = 17.0$ Hz, 1H), 5.42 (d, $J = 17.0$ Hz, 1H), 4.58 (d, $J = 2.4$ Hz, 1H), 2.32 (s, 3H), 2.12-2.02 (m, 1H), 1.48 (s, 9H), 1.17 (dd, $J = 11.9, 7.1$ Hz, 3H), 0.34 (d, $J = 6.7$ Hz, 3H). $^{19}$F NMR (377 MHz, CDCl$_3$): $\delta$ -72.96. $^{13}$C NMR (101 MHz, DMSO): $\delta$ 168.38, 137.76, 135.02, 128.60, 127.29, 127.22, 126.18, 124.95, 124.30, 123.02 (q, $J = 323$ Hz), 120.28, 112.81, 112.29, 83.45, 70.42, 47.42, 40.63, 40.42, 40.21, 40.00, 39.79, 39.58, 39.37, 28.47, 28.08, 22.18, 16.90, 10.03. IR (neat, cm$^{-1}$): 2977.05, 2930.69, 1741.38, 1401.10, 1187.51, 1147.29, 1026.10, 741.62, 612.62. HRMS (ESI) ([M+Na]$^+$) Calcd. for C$_{26}$H$_{31}$F$_3$N$_2$NaO$_4$S$: 547.1849; found: 547.1847.

(S)-tert-butyl-2-(N-(1-(3,5-dimethylphenyl)-3-methyl-1H-indol-2-yl)-1,1,1-trifluoromethylsulfonamido)-3-methylbutanoate (3e): According to the general procedure,
puriﬁcation by ﬂash chromatography (EtOAc/n-Hexane 5:95), 3e (28.0 mg, 52 %,10.4:1 dr) was obtained as a colourless liquid from 1e, 2a and NaClO. $^1$H NMR (400 MHz, DMSO): δ 7.64 (d, J = 7.7 Hz, 1H), 7.28-7.20 (m, 2H), 7.19-7.11 (m, 3H), 6.91 (d, J = 8.2 Hz, 1H), 3.91 (d, J = 6.7 Hz, 1H), 2.35 (s, 6H), 2.31 (s, 3H), 1.90-1.73 (m, 1H), 1.39 (s, 9H), 0.70 (d, J = 6.6 Hz, 3H), 0.46 (d, J = 6.7 Hz, 3H). $^{19}$F NMR (376 MHz, CDCl$_3$): δ -71.47. $^{13}$C NMR (101 MHz, CDCl$_3$): δ 171.20, 144.26, 141.59, 140.93, 135.51, 131.93, 130.88, 129.78, 125.45, 124.88, 124.40 (q, J = 323 Hz), 119.00, 115.94, 87.91, 75.59, 34.55, 32.61, 25.95, 24.89, 22.88, 15.01. IR (neat, cm$^{-1}$): 2971.76, 2927.50, 1732.13, 1597.40, 1459.87, 1367.54, 1150.42, 1026.83, 845.27, 743.64. HRMS (ESI) ([M+Na]$^+$) Calcd. for C$_{27}$H$_{33}$F$_3$N$_2$NaO$_4$S$: 561.2005; found: 561.1997.

$\text{(S)-}^{\text{tert}}\text{-butyl-3-methyl-2-(1,1,1-triﬂuoro-N-(1-(4-methoxyphenyl)-3-benzyl-1H-indol-2-yl)methylsulfonyl)butanoate (3f):}$ According to the general procedure, puriﬁcation by ﬂash chromatography (EtOAc/n-Hexane 5:95), 3f (21.6 mg, 35 %,12.6:1 dr) was obtained as a white solid from 1f, 2a and NaClO. m.p. 55-57 °C. $^1$H NMR (400 MHz, DMSO): δ 7.53 (s, 2H), 7.29-7.25 (m, 2H), 7.23-7.17 (m, 6H), 7.01-6.94 (m, 2H), 6.86 (d, J = 8.3 Hz, 1H), 4.27-4.15 (m, 2H), 3.93 (d, J = 5.8 Hz, 1H), 3.88 (s, 3H), 1.96-1.83 (m, 1H), 1.42 (s, 9H), 0.72 (d, J = 6.6 Hz, 3H), 0.59 (d, J = 6.7 Hz, 3H). $^{19}$F NMR (376 MHz, CDCl$_3$): δ -70.93. $^{13}$C NMR (101 MHz, DMSO): δ 166.19, 159.59, 139.64, 137.14, 130.62, 128.21 (d, J = 18 Hz), 128.01, 126.51, 125.98, 124.66, 124.30, 120.36 (d, J = 47 Hz), 119.10 (q, J = 323 Hz), 115.83, 114.96, 110.76, 82.89, 69.69, 55.51, 40.09, 39.88, 39.67, 39.46, 39.25, 39.04, 38.83, 30.70, 29.08, 27.44, 20.08, 17.57. IR (neat, cm$^{-1}$): 2969.02, 2920.52, 1740.92, 1512.33, 1455.75, 1389.49, 1209.50, 1149.62, 1028.74, 827.77, 744.6. HRMS (ESI) ([M+Na]$^+$) Calcd. for C$_{32}$H$_{35}$F$_3$N$_2$NaO$_4$S$: 639.2111; found: 639.2096.
(S)-**tert**-butyl-2-(N-(3-chloro-1-(4-methoxyphenyl)-1H-indol-2-yl)-1,1,1-trifluoromethylsulfonamido)-3-methylbutanoate (3g): According to the general procedure, purification by flash chromatography (EtOAc/n-Hexane 5:95), 3g (49.3 mg, 88 %, 7.6:1 dr) was obtained as a white solid from 1g, 2a and NaClO. m.p. 113-115 °C.  
\[ ^1\text{H NMR (400 MHz, DMSO)}: \delta 7.65 \text{(dd, } J = 7.1, 0.8 \text{ Hz, 1H}), 7.51 \text{(s, 2H)}, 7.38-7.26 \text{(m, 2H)}, 7.20 \text{(d, } J = 9.1 \text{ Hz, 2H}), 6.92 \text{(d, } J = 8.1 \text{ Hz, 1H}), 3.95 \text{(d, } J = 8.9 \text{ Hz, 1H)}, 3.87 \text{(s, 3H)}, 1.96-1.75 \text{(m, 1H)}, 1.37 \text{(s, 9H)}, 0.76 \text{(d, } J = 6.6 \text{ Hz, 3H}), 0.33 \text{(d, } J = 6.6 \text{ Hz, 3H)}. \]  
\[ ^{19}\text{F NMR (377 MHz, CDCl}_3): \delta -71.06. \]  
\[ ^{13}\text{C NMR (101 MHz, DMSO): } \delta 165.24, 159.97, 135.62, 131.06, 130.42, 127.22, 125.72, 124.74, 122.40, 121.73, 118.39, 119.14 \text{(q, } J = 323 \text{ Hz}), 115.32, 114.78, 111.29, 107.93, 82.69, 71.03, 55.56, 29.90, 27.31, 18.80, 17.95. \]  
IR (neat, cm\(^{-1}\)): 2972.00, 2935.14, 1736.24, 1514.39, 1396.09, 1214.07, 1129.22, 1000.29, 835.72, 741.46, 588.83. HRMS (ESI) ([M+Na\(^+\)]: Calcd. for C\(_{25}\)H\(_{28}\)ClF\(_3\)N\(_2\)O\(_5\)S\(^+\): 583.1252; found: 583.1254.

(S)-**tert**-butyl-2-(N-(3-bromo-1-(4-methoxyphenyl)-1H-indol-2-yl)-1,1,1-trifluoromethylsulfonamido)-3-methylbutanoate (3h): According to the general procedure, purification by flash chromatography (EtOAc/n-Hexane 5:95), 3h (46.5 mg, 77 %, 5.0:1 dr) was obtained as colourless liquid from 1h, 2a and NaClO.  
\[ ^1\text{H NMR (400 MHz, DMSO)}: \delta 7.58 \text{(dd, } J = 6.8, 1.1 \text{ Hz, 2H}), 7.39-7.23 \text{(m, 3H)}, 7.23-7.17 \text{(m, 2H)}, 6.90 \text{(d, } J = 7.7 \text{ Hz, 1H}), 4.00 \text{(d, } J = 7.0 \text{ Hz, 1H}), 3.87 \text{(s, 3H)}, 1.98-1.84 \text{(m, 1H)}, 1.36 \text{(s, 9H)}, 0.81 \text{(d, } J = 6.6 \text{ Hz, 3H}), 0.51 \text{(d, } J = 6.7 \text{ Hz, 3H)}. \]  
\[ ^{19}\text{F NMR (376 MHz, CDCl}_3): \delta -70.22. \]  
\[ ^{13}\text{C NMR (101 MHz, DMSO): } \delta 165.63, 160.44, 136.80, 131.29, \]
127.89, 127.74, 126.13, 124.88, 122.32, 120.01, 119.53 (q, $J = 323$ Hz), 114.75, 111.75, 95.91, 83.24, 71.39, 56.06, 30.23, 27.91, 19.87, 18.08. IR (neat, cm$^{-1}$): 2979.67, 2933.89, 1735.60, 1513.82, 1396.61, 1213.86, 1128.72, 999.54, 835.49, 588.90. HRMS (ESI) ([M+Na]$^+$) Calcd. for C$_{25}$H$_{28}$BrF$_3$N$_2$NaO$_5$S$^+$: 627.0747; found: 627.1753.

(S)-tert-buty1-2-(N-(4-(benzyloxy)-1-(4-methoxyphenyl)-3-methyl-1H-indol-2-yl)-1,1,1-trifluoromethylsulfonamido)-3-methylbutanoate (3i): According to the general procedure, purification by flash chromatography (EtOAc/n-Hexane 5:95), 3i (57.5 mg, 89 %, 12.3:1 dr) was obtained as a colourless liquid from 1i, 2a and NaClO. 

$^1$H NMR (400 MHz, DMSO): $\delta$ 7.60-7.54 (m, 2H), 7.54-7.49 (m, 1H), 7.50-7.37 (m, 5H), 7.31 (d, $J = 8.8$ Hz, 1H), 7.18 (dd, $J = 7.8$, 1.4 Hz, 2H), 6.64 (d, $J = 8.8$ Hz, 1H), 5.15-5.02 (m, 2H), 3.94 (d, $J = 6.8$ Hz, 1H), 3.86 (s, 3H), 2.36 (s, 3H), 1.90-1.77 (m, 1H), 1.39 (s, 10H), 0.71 (d, $J = 6.6$ Hz, 3H), 0.50 (d, $J = 6.7$ Hz, 3H). $^{19}$F NMR (376 MHz, CDCl$_3$): $\delta$ -71.54. $^{13}$C NMR (101 MHz, DMSO): $\delta$ 165.89, 159.75, 148.46, 137.30, 136.53, 130.68, 128.46, 128.19, 128.08, 126.47, 125.97, 120.10, 117.46, 112.90, 108.41, 82.79, 75.97, 70.39, 55.50, 29.33, 27.35, 19.62, 17.62, 11.57. IR (neat, cm$^{-1}$): 2975.73, 2935.25, 1738.02, 1513.24, 1393.00, 1203.41, 1027.74, 833.02, 594.63. HRMS (ESI) ([M+Na]$^+$) Calcd. for C$_{33}$H$_{37}$F$_3$N$_2$NaO$_6$S$^+$: 669.2217; found: 669.2230.
(S)-tert-butyl-3-methyl-2-(1,1,1-trifluoro-N-(5-methoxy-1-(4-methoxyphenyl)-3-methyl-1H-indol-2-yl)methylsulfonamido)butanoate (3j): According to the general procedure, purification by flash chromatography (EtOAc/Hexane 10:90), 3j (53.5 mg, 94%, 13.7:1 dr) was obtained as a white solid from 1j, 2a and NaClO. m.p. 121-123 °C. $^1$H NMR (400 MHz, DMSO): δ 7.44-7.40 (m, 2H), 7.16 (d, J = 9.2 Hz, 2H), 7.10 (d, J = 2.4 Hz, 1H), 6.88 (dd, J = 8.9, 2.4 Hz, 1H), 6.74 (d, J = 9.0 Hz, 1H), 3.95 (d, J = 7.1 Hz, 1H), 3.85 (s, 3H), 3.80 (s, 3H), 2.27 (s, 3H), 1.87-1.75 (m, 1H), 1.40 (s, 9H), 0.69 (d, J = 6.6 Hz, 3H), 0.47 (d, J = 6.7 Hz, 3H). $^{19}$F NMR (377 MHz, CDCl$_3$): δ -71.65. $^{13}$C NMR (101 MHz, DMSO): δ 165.94, 159.37, 154.12, 131.96, 130.54, 128.44, 125.76, 125.49, 125.22, 119.17 (q, J = 323 Hz), 115.00, 114.79, 113.14, 111.60, 100.80, 82.65, 70.43, 55.47, 29.32, 27.37, 27.27, 19.55, 17.72, 9.97. IR (neat, cm$^{-1}$): 2971.16, 2934.11, 1735.32, 1513.85, 1396.53, 1213.89, 1128.85, 999.65, 835.49, 589.31. HRMS (ESI) ([M+Na]$^+$) Calcd. for C$_{27}$H$_{33}$F$_3$N$_2$NaO$_6$S$: 593.1904; found: 593.1889.

(S)-tert-butyl-2-(N-(5-bromo-1-(4-methoxyphenyl)-3-methyl-1H-indol-2-yl)-1,1,1-trifluoromethylsulfonamido)-3-methylbutanoate (3k): According to the general procedure, purification by flash chromatography (EtOAc/Hexane 5:95), 3k (52.5 mg, 85%, 12.6:1 dr) was obtained as a colourless liquid from 1k, 2a and NaClO. $^1$H NMR (400 MHz, DMSO): δ 7.88 (d, J = 1.8 Hz, 1H), 7.45 (d, J = 8.6 Hz, 2H), 7.37 (dd, J = 8.8, 1.9 Hz, 1H), 7.18 (d, J = 9.1 Hz, 2H), 6.79 (d, J = 8.8 Hz, 1H), 3.97 (d, J = 7.1 Hz, 1H), 3.86 (s, 3H), 2.28 (s, 3H), 1.88-1.75 (m, 1H), 1.39 (s, 9H), 0.70 (d, J = 6.6 Hz, 3H), 0.47 (d, J = 6.7 Hz, 3H). $^{19}$F NMR (376 MHz, CDCl$_3$): δ -71.68. $^{13}$C NMR (101 MHz, DMSO): δ 165.88, 159.68, 135.47, 130.61, 127.69, 127.18, 126.58, 122.02, 119.11 (q, J = 323 Hz), 114.92, 114.30, 113.34, 112.80, 112.68, 82.81, 70.43,
(S)-tert-butyl-3-methyl-2-(1,1,1-trifluoro-N-(1-(4-methoxyphenyl)-3-methyl-5-(trifluoromethyl)-1H-indol-2-yl)methylsulfonamido)butanoate (3l): According to the general procedure, purification by flash chromatography (EtOAc/n-Hexane 5:95), 3l (51.1 mg, 84 %, 14.0:1 dr) was obtained as a white solid from 1l, 2a and NaClO. m.p. 97-99 °C. 1H NMR (400 MHz, DMSO): δ 8.08 (s, 1H), 7.54 (dd, J = 8.8, 1.6 Hz, 1H), 7.49 (d, J = 8.4 Hz, 1H), 7.20 (d, J = 9.1 Hz, 2H), 7.01 (d, J = 8.7 Hz, 1H), 6.92 (d, J = 0.4 Hz, 1H), 3.97 (d, J = 7.2 Hz, 1H), 3.87 (s, 3H), 2.36 (s, 3H), 1.90-1.74 (m, 1H), 1.40 (s, 9H), 0.70 (d, J = 6.6 Hz, 3H), 0.47 (d, J = 6.7 Hz, 3H). 19F NMR (376 MHz, CDCl3): δ -60.59, -71.67; 13C NMR (101 MHz, DMSO): δ 165.90, 159.83, 138.14, 130.96, 130.68, 127.44, 127.38, 126.43, 124.83, 123.74, 121.29, 120.98, 120.89, 119.32, 117.70, 114.91, 111.66, 82.86, 70.36, 55.52, 29.38, 27.34, 19.50, 17.65, 9.81. IR (neat, cm⁻¹): 2971.70, 2918.75, 1738.13, 1513.89, 1394.20, 1214.06, 1028.26, 835.66, 741.49, 590.58. HRMS (ESI) ([M+Na]⁺) Calcd. for C27H30F6N2NaO5S⁺: 631.1672; found: 631.1683.

(S)-tert-butyl-3-methyl-2-(1,1,1-trifluoro-N-(1-(4-methoxyphenyl)-3-methyl-5-nitro-1H-indol-2-yl)methylsulfonamido)butanoate (3m): According to the general
procedure, purification by flash chromatography (EtOAc/n-Hexane 15:85), 3m (36.3 mg, 62 %, 15.0:1 dr) was obtained as a yellow solid from 1m, 2a and NaClO. m.p. 119-121 °C. 1H NMR (400 MHz, DMSO): δ 8.69 (d, J = 2.2 Hz, 1H), 8.13 (dd, J = 9.1, 2.3 Hz, 1H), 7.51 (d, J = 8.8 Hz, 2H), 7.22 (d, J = 9.0 Hz, 2H), 7.01 (d, J = 9.1 Hz, 1H), 4.00 (d, J = 7.1 Hz, 1H), 3.88 (s, 3H), 2.41 (s, 3H), 1.92 - 1.79 (m, 1H), 1.41 (s, 9H), 0.72 (d, J = 6.6 Hz, 3H), 0.49 (d, J = 6.7 Hz, 3H). 19F NMR (376 MHz, CDCl3): δ -71.70. 13C NMR (101 MHz, DMSO): δ 166.38, 160.56, 141.98, 139.98, 131.15, 129.13, 127.58, 125.21, 120.23, 119.58 (q, J = 323 Hz), 117.61, 117.04, 115.62, 112.09, 83.52, 70.93, 56.09, 29.93, 27.88, 20.02, 18.13, 10.35. IR (neat, cm⁻¹): 3424.59, 2972.85, 2933.58, 1739.10, 1513.19, 1338.17, 1209.43, 1026.94, 836.29, 593.07. HRMS (ESI) ([M+Na]⁺) Calcd. for C26H30F3N3NaO7S⁺: 608.1649; found: 608.1638.

(S)-tert-butyl-3-methyl-2-(1,1,1-trifluoro-N-(6-fluoro-1-(4-methoxyphenyl)-3-methyl-1H-indol-2-yl)methylsulfonamido)butanoate (3n): According to the general procedure, purification by flash chromatography (EtOAc/n-Hexane 5:95), 3n (51.3 mg, 92 %, 13.0:1 dr) was obtained as a colourless liquid from 1n, 2a and NaClO. 1H NMR (400 MHz, DMSO): δ 7.69 (dd, J = 8.7, 5.4 Hz, 1H), 7.46 (d, J = 8.6 Hz, 2H), 7.18 (d, J = 9.1 Hz, 2H), 7.05 (td, J = 9.6, 2.3 Hz, 1H), 6.56 (dd, J = 9.9, 2.2 Hz, 1H), 3.96 (d, J = 7.2 Hz, 1H), 3.87 (s, 3H), 2.30 (s, 3H), 1.89 - 1.78 (m, 1H), 1.40 (s, 9H), 0.71 (d, J = 6.6 Hz, 3H), 0.48 (d, J = 6.7 Hz, 3H). 19F NMR (376 MHz, CDCl3): δ -71.71. 13C NMR (101 MHz, DMSO): δ 166.42, 162.35, 160.16, 159.98, 137.36 (d, J = 12 Hz), 131.05, 128.30, 126.41, 126.37, 122.78, 122.03 (d, J = 10 Hz), 119.64 (q, J = 323 Hz), 115.48, 114.87, 114.48, 109.52 (d, J = 25 Hz), 97.12 (d, J = 26 Hz), 83.25, 70.94, 56.00, 29.85, 27.87, 20.03, 18.20, 10.38. IR (neat, cm⁻¹): 2974.58, 2933.61,
According to the general procedure, purification by flash chromatography (EtOAc/n-Hexane 5:95), 3o (47.6 mg, 83 %.12.0:1 dr) was obtained as a white solid from 1o, 2a and NaClO. m.p. 41-43 °C. 1H NMR (400 MHz, DMSO): δ 7.69 (d, J = 8.5 Hz, 1H), 7.46 (d, J = 8.8 Hz, 2H), 7.24-7.14 (m, 3H), 6.80 (d, J = 1.7 Hz, 1H), 3.96 (d, J = 7.2 Hz, 1H), 3.87 (s, 3H), 2.29 (s, 3H), 1.91-1.75 (m, 1H), 1.39 (s, 9H), 0.70 (d, J = 6.6 Hz, 3H), 0.47 (d, J = 6.7 Hz, 3H). 19F NMR (376 MHz, CDCl3): δ -71.69. 13C NMR (101 MHz, DMSO): δ 165.89, 159.73, 137.08, 130.66, 129.35, 127.50, 126.30, 124.24, 121.52, 119.11 (q, J = 323 Hz), 114.99, 114.22, 110.04, 82.79, 70.42, 55.50, 29.36, 27.35, 19.49, 17.70, 9.85. IR (neat, cm⁻¹): 2975.21, 2933.39, 1739.72, 1512.75, 1392.67, 1206.20, 1127.59, 1027.54, 835.69, 601.68. HRMS (ESI) ([M+Na]⁺) Calcd. for C26H30ClF3N2NaO5S⁺: 597.1408; found: 597.1418.

(S)-1H-indol-2-yl)methylsulfonamido)butanoate (3p): According to the general procedure, purification by flash chromatography (EtOAc/n-Hexane 5:95), 3p (50.9 mg, 92 %, 10.5:1 dr) was obtained as a white solid from 1p, 2a and NaClO. m.p.
85-87 °C. $^1$H NMR (400 MHz, DMSO): δ 7.57 (dd, $J = 8.6$, 2.6 Hz, 1H), 7.48 (d, $J = 7.6$ Hz, 1H), 7.37 (dd, $J = 8.5$, 2.6 Hz, 1H), 7.13-6.99 (m, 4H), 3.86 (d, $J = 3.0$ Hz, 3H), 3.84 (d, $J = 2.0$ Hz, 1H), 2.32 (s, 3H), 1.93-1.84 (m, 1H), 1.74 (s, 3H), 1.39 (d, $J = 10.5$ Hz, 9H), 0.72 (d, $J = 6.6$ Hz, 3H), 0.62 (d, $J = 6.8$ Hz, 3H). $^{19}$F NMR (377 MHz, CDCl$_3$): δ -71.19. $^{13}$C NMR (101 MHz, DMSO): δ 166.57, 160.25, 135.43, 132.81, 132.71, 130.00, 127.62, 126.94, 126.84, 121.28, 120.55, 118.18, 119.66 (q, $J = 323$ Hz), 114.27, 114.07, 113.82, 83.15, 70.67, 55.98, 29.73, 27.92, 20.53, 18.85, 17.77, 10.32, 10.29. IR (neat, cm$^{-1}$): 2922.40, 2931.90, 1738.86, 1511.88, 1391.97, 1219.34, 1152.22, 1027.09, 838.85, 594.17. HRMS (ESI) ([M+Na]$^+$) Calcd. for C$_{27}$H$_{33}$F$_3$N$_2$NaO$_5$S$: 577.1954; found: 577.1965.

(S)-tert-butyl-2-(N-(1-(4-methoxyphenyl)-3-methyl-1H-indol-2-yI)-4-nitrophenylsulfonamido)-3-methylbutanoate (3q): According to the general procedure, purification by flash chromatography (EtOAc/n-Hexane 10:90), 3q (38.5 mg, 65 %, 13.0:1 dr) was obtained as a white solid from 1b, 2j and NaClO. m.p. 126-128 °C. $^1$H NMR (400 MHz, DMSO): δ 8.44 (d, $J = 8.9$ Hz, 2H), 8.03 (d, $J = 11.4$ Hz, 2H), 7.52 (d, $J = 7.7$ Hz, 3H), 7.21-7.08 (m, 4H), 6.88 (d, $J = 8.2$ Hz, 1H), 4.09 (d, $J = 6.4$ Hz, 1H), 3.87 (s, 3H), 1.81-1.71 (m, 1H), 1.67 (s, 3H), 1.30 (s, 9H), 0.61 (d, $J = 6.6$ Hz, 3H), 0.53 (d, $J = 6.8$ Hz, 3H). $^{13}$C NMR (101 MHz, DMSO): δ 167.51, 159.61, 150.68, 145.59, 137.14, 130.96, 130.60, 129.43, 128.46, 126.47, 124.84, 124.41, 120.29, 119.87, 115.08, 112.80, 110.94, 82.48, 69.83, 55.96, 29.74, 27.98, 20.19, 17.99, 10.62. IR (neat, cm$^{-1}$): 2973.36, 2934.56, 1738.82, 1513.11, 1396.43, 1218.09, 1037.54, 836.58, 633.26. HRMS (ESI) ([M+Na]$^+$) Calcd. for C$_{31}$H$_{33}$N$_3$NaO$_5$S$: 616.2088; found: 616.2096.
(S)-ethyl-3-methyl-2-(1,1,1-trifluoro-N-(1-(4-methoxyphenyl)-3-methyl-1H-indol-2-yl)methylsulfonamido)butanoate (3r): According to the general procedure, purification by flash chromatography (EtOAc/n-Hexane 5:95), 3r (46.1 mg, 90 %, 11.0:1 dr) was obtained as a white solid from 1b, 2b and NaClO. m.p. 139-141 °C. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.79-7.65 (m, 1H), 7.59 (d, $J = 7.5$ Hz, 1H), 7.26-7.08 (m, 3H), 7.03 (d, $J = 8.2$ Hz, 2H), 6.87 (d, $J = 8.1$ Hz, 1H), 4.22-4.10 (m, 3H), 3.89 (s, 3H), 2.29 (d, $J = 1.0$ Hz, 3H), 1.92-1.78 (m, 1H), 1.23 (t, $J = 7.2$ Hz, 3H), 0.72 (d, $J = 6.6$ Hz, 3H), 0.43 (d, $J = 6.7$ Hz, 3H). $^{19}$F NMR (377 MHz, CDCl$_3$): $\delta$ -71.99. $^{13}$C NMR (101 MHz, CDCl$_3$): $\delta$ 167.38, 159.86, 137.65, 129.16, 126.06, 125.84, 124.30, 120.08, 119.62, 119.73 (q, $J = 323$ Hz), 114.07, 111.00, 70.70, 61.42, 55.59, 29.64, 19.40, 18.68, 13.87, 9.54, 9.51. IR (neat, cm$^{-1}$): 2925.38, 1744.65, 1513.29, 1397.14, 1191.16, 839.99, 749.25, 590.90. HRMS (ESI) ([M+Na$^+$]) Calcd. for C$_{24}$H$_{27}$F$_{3}$N$_{2}$NaO$_{5}$S$^+$: 535.1485; found: 535.1497.

(S)-tert-butyl-3-phenyl-2-(1,1,1-trifluoro-N-(1-(4-methoxyphenyl)-3-methyl-1H-indol-2-yl)methylsulfonamido)propanoate (3s): According to the general procedure, purification by flash chromatography (EtOAc/n-Hexane 5:95), 3s (54.1 mg, 92 %, 6.6:1 dr) was obtained as a white solid from 1b, 2c and NaClO. m.p. 98-100 °C. $^1$H NMR (400 MHz, DMSO): $\delta$ 7.67 (d, $J = 7.8$ Hz, 1H), 7.54 (d, $J = 9.0$ Hz, 2H), 7.30-7.20 (m, 7H), 7.05-6.96 (m, 3H), 4.54 (dd, $J = 12.0$, 4.3 Hz, 1H), 3.85 (s, 3H),
2.62-2.51 (m, 2H), 2.31 (s, 3H), 0.98 (s, 9H). $^{19}$F NMR (377 MHz, CDCl$_3$): $\delta$ -72.46.

$^{13}$C NMR (101 MHz, DMSO): $\delta$ 165.60, 159.93, 137.00, 134.90, 131.32, 130.77, 129.85, 129.57, 129.05, 128.78, 127.77, 126.22, 126.04, 125.28, 120.92, 120.29, 119.70 (q, $J = 323$ Hz), 115.36, 113.76, 111.23, 83.16, 68.08, 56.01, 38.15, 27.28, 9.58. IR (neat, cm$^{-1}$): 2921.29, 1733.36, 1512.92, 1392.22, 1195.59, 1133.99, 1027.48, 838.60, 739.33, 590.43. HRMS (ESI) ([M+Na$^+$]) Calcd. for C$_{30}$H$_{31}$F$_{3}$N$_{2}$NaO$_{5}$S$^+$: 611.1798; found: 611.1808.

(3t):

(S)-tert-butyl-4-methyl-2-(1,1,1-trifluoro-N-(1-(4-methoxyphenyl)-3-methyl-1H-indol-2-yl)methylsulfonamido)pentanoate (3t): According to the general procedure, purification by flash chromatography (EtOAc/n-Hexane 5:95), 3t (49.4 mg, 94 %, 5.4:1 dr) was obtained as a white solid from 1b, 2d and NaClO. m.p. 70-72 °C.

$^1$H NMR (400 MHz, DMSO): $\delta$ 7.66 (d, $J = 7.8$ Hz, 1H), 7.46-7.38 (m, 2H), 7.31-7.23 (m, 1H), 7.21-7.16 (m, 3H), 6.97 (d, $J = 8.2$ Hz, 1H), 4.28 (dd, $J = 12.4$, 3.3 Hz, 1H), 3.86 (s, 3H), 2.30 (s, 3H), 1.51-1.42 (m, 1H), 1.29 (s, 9H), 1.27 - 1.21 (m, 1H), 0.83-0.78 (m, 1H), 0.75 (d, $J = 6.5$ Hz, 3H), 0.70 (d, $J = 6.6$ Hz, 3H). $^{19}$F NMR (377 MHz, CDCl$_3$): $\delta$ -72.58. $^{13}$C NMR (101 MHz, DMSO): $\delta$ 166.83, 159.91, 136.91, 131.18, 130.69, 128.83, 126.81, 126.00, 125.14, 120.81, 120.23, 119.61 (q, $J = 323$ Hz), 115.17, 113.83, 111.18, 83.31, 65.62, 56.03, 27.60, 24.98, 23.82, 20.66, 9.57, 9.54. IR (neat, cm$^{-1}$): 2962.87, 2923.41, 1751.61, 1735.76, 1513.14, 1392.85, 1187.41, 1023.30, 831.04, 592.18. HRMS (ESI) ([M+Na$^+$]) Calcd. for C$_{27}$H$_{33}$F$_{3}$NaO$_{5}$S$^+$: 577.1954; found: 577.1960.
(2S,3R)-tert-butyl-3-((tert-butyldimethylsilyl)oxy)-2-(1,1,1-trifluoro-N-(1-(4-methoxyphenyl))-3-methyl-1H-indol-2-yl)methylsulfonamido)butanoate (3u): According to the general procedure, purification by flash chromatography (EtOAc/n-Hexane 5:95), 3u (32.0 mg, 51%, 7.1:1 dr) was obtained as a white solid from 1b, 2e and NaClO. m.p. 85-87 °C. 1H NMR (400 MHz, DMSO): δ 7.76 (d, J = 7.7 Hz, 1H), 7.60 (d, J = 9.0 Hz, 2H), 7.38-7.33 (m, 1H), 7.31-7.25 (m, 3H), 7.03 (d, J = 8.2 Hz, 1H), 4.61 (d, J = 3.7 Hz, 1H), 3.95 (s, 3H), 3.93-3.89 (m, 1H), 2.49 (s, 3H), 1.43 (s, 9H), 0.90 (s, 9H), -0.01 (d, J = 11.4 Hz, 6H). 19F NMR (377 MHz, CDCl3): δ -71.85. 13C NMR (101 MHz, DMSO): δ 165.56, 159.78, 1590, 128.85, 126.18, 125.20, 120.88, 120.21, 119.52 (q, J = 323 Hz), 115.28, 113.94, 111.17, 82.80, 68.11, 67.99, 55.97, 27.70, 25.81, 19.24, 17.93, 10.07, -4.62, -5.20. IR (neat, cm⁻¹): 2929.89, 1742.23, 1513.49, 1392.22, 1211.95, 1150.19, 1028.41, 828.01, 592.31. HRMS (ESI) ([M+Na]^+): Calcd. for C31H43F3N2O6SSi^+: 679.2455; found: 679.2437.

(2S,3R)-tert-butyl-3-methyl-2-(1,1,1-trifluoro-N-(1-(4-methoxyphenyl))-3-methyl-1H-indol-2-yl)methylsulfonamido)pentanoate (3v): According to the general procedure, purification by flash chromatography (EtOAc/n-Hexane 5:95), 3v (43.1 mg, 82%, 5.9:1 dr) was obtained as a white solid from 1b, 2f and NaClO. m.p. 119-121 °C. 1H NMR (400 MHz, DMSO): δ 7.65 (d, J = 7.8 Hz, 1H), 7.45 (d, J = 6.9 Hz, 2H), 7.27-7.22 (m, 1H), 7.20-7.16 (m, 3H), 6.88 (d, J = 8.2 Hz, 1H), 4.12 (d, J =
4.7 Hz, 1H), 3.86 (s, 3H), 2.40 (s, 3H), 1.65-1.58 (m, 1H), 1.38 (s, 9H), 1.05-0.99 (m, 2H), 0.63-0.58 (m, 6H). \(^{19}\)F NMR (376 MHz, CDCl\(_3\)): \(\delta -71.38\). \(^{13}\)C NMR (101 MHz, DMSO): \(\delta 166.62, 159.87, 137.13, 130.68, 128.77, 126.29, 126.20, 125.09, 120.74, 120.19, 119.56 \text{ (q, } J = 323 \text{ Hz)}\), 115.39, 114.67, 114.09, 111.13, 83.17, 68.97, 56.01, 35.64, 27.87, 27.20, 14.60, 11.57, 10.06. IR (neat, cm\(^{-1}\)): 2919.54, 1747.26, 1512.52, 1184.05, 1027.73, 838.38, 745.37, 590.81. HRMS (ESI) ([M+Na\(^+\)]): Calcd. for C\(_{27}\)H\(_{33}\)F\(_3\)N\(_2\)N\(_2\)O\(_5\)S\(^+\): 577.1954; found: 577.1960.

(S)-\(\text{tert-butyl-3-\(\text{tert-butoxy)-2-(1,1,1-trifluoro-N-\text{-}(4-methoxyphenyl)-3-methyl-1H-indol-2-yl)}\text{methylsulfonamido)propanoate (3w):}\) According to the general procedure, purification by flash chromatography (EtOAc/n-Hexane 5:95), 3w (50.0 mg, 90 \%, 5.5:1 dr) was obtained as a white solid from 1b, 2g and NaClO. m.p. 72-74 °C. \(^{1}\)H NMR (400 MHz, DMSO): \(\delta 7.65 \text{ (d, } J = 7.8 \text{ Hz, 1H)}\), 7.45 (s, 2H), 7.32-7.17 (m, 4H), 7.03 (d, \(J = 8.2 \text{ Hz, 1H})\), 4.29 (dd, \(J = 10.2, 4.2 \text{ Hz, 1H})\), 3.86 (s, 3H), 3.04-2.95 (m, 1H), 2.83-2.71 (m, 1H), 2.26 (s, 3H), 1.20 (s, 9H), 0.88 (s, 9H). \(^{19}\)F NMR (377 MHz, CDCl\(_3\)): \(\delta -72.27\). \(^{13}\)C NMR (101 MHz, DMSO): \(\delta 165.00, 159.89, 136.63, 128.65, 126.03, 125.27, 120.95, 120.23, 119.74 \text{ (q, } J = 323 \text{ Hz)}\), 115.39, 114.04, 113.44, 111.14, 82.95, 73.76, 66.45, 61.22, 56.01, 27.49, 27.21, 9.56, 9.53. IR (neat, cm\(^{-1}\)): 2973.36, 1739.50, 1513.67, 1191.49, 1026.73, 820.64, 738.18, 593.17. HRMS (ESI) ([M+Na\(^+\)]): Calcd. for C\(_{28}\)H\(_{35}\)F\(_3\)N\(_2\)O\(_6\)S\(^+\): 607.2060; found: 607.2080.
(S)-**tert**-butyl-2-cyclohexyl-2-(1,1,1-trifluoro-N-(1-(4-methoxyphenyl)-3-methyl-1H-indol-2-yl)methylsulfonamido)acetate (3x): According to the general procedure, purification by flash chromatography (EtOAc/n-Hexane 5:95), 3x (49.1 mg, 89 %, 12.0:1 dr) was obtained as a white solid from **1b**, **2h** and NaClO. m.p. 89-91 °C. **1H** NMR (400 MHz, DMSO): δ 7.64 (d, J = 7.8 Hz, 1H), 7.50 - 7.41 (m, 2H), 7.29-7.21 (m, 1H), 7.21-7.14 (m, 3H), 6.84 (d, J = 8.2 Hz, 1H), 4.01 (d, J = 7.4 Hz, 1H), 3.85 (s, 3H), 2.29 (s, 3H), 1.58-1.38 (m, 5H), 1.37 (s, 9H), 0.96-0.77 (m, 6H). **19F** NMR (377 MHz, CDCl₃): δ -71.49. **13C** NMR (101 MHz, DMSO): δ 166.33, 159.87, 137.29, 130.89, 128.74, 126.04, 125.91, 125.03, 120.71, 120.08, 119.71 (q, J = 323 Hz), 115.48, 114.04, 111.08, 83.17, 70.85, 56.01, 38.60, 30.47, 28.76, 27.85, 25.95, 25.80, 25.65, 10.48, 10.45. IR (neat, cm⁻¹): 2931.26, 1738.07, 1513.24, 1393.23, 1217.22, 1027.33, 841.81, 742.28, 594.29. HRMS (ESI) ([M+Na]⁺) Calcd. for C₂₉H₃₅F₃N₂NaO₅S⁺: 603.2111; found: 603.2127.

![Chemical Structure](image)

(S)-**N**-(1-((**tert**-butyldimethylsilyl)oxy)-3-phenylpropan-2-yl)-1,1,1-trifluoro-N-(1-(4-methoxyphenyl)-3-methyl-1H-indol-2-yl)methanesulfonamide (3y): According to the general procedure, purification by flash chromatography (EtOAc/n-Hexane 5:95), 3y (31.6 mg, 50 %, 5.1:1 dr) was obtained as a colourless liquid from **1b**, **2i** and NaClO. **1H** NMR (400 MHz, DMSO): δ 7.69 (d, J = 7.6 Hz, 1H), 7.58 (d, J = 7.4 Hz, 1H), 7.30-7.23 (m, 4H), 7.20-7.12 (m, 4H), 7.03 (d, J = 7.1 Hz, 2H), 6.90 (d, J = 8.2 Hz, 1H), 4.08-3.98 (m, 1H), 3.80 (s, 3H), 3.56-3.43 (m, 2H), 2.43 (s, 3H), 2.36-2.31 (m, 1H), 2.04-1.99 (m, 1H), 0.65 (s, 10H), -0.28 (d, J = 6.4 Hz, 6H). **19F** NMR (376 MHz, DMSO): δ -72.73. **13C** NMR (101 MHz, DMSO): δ 159.36, 137.43, 137.05, 128.65, 128.59, 128.30, 126.85, 125.70, 125.06, 124.75, 124.39, 120.13, 119.64, 119.33 (q, J = 323 Hz), 114.85, 113.59, 110.67, 69.39, 59.92, 55.44, 37.89, 25.39, 17.74, 8.64, -6.00, -6.16. IR (neat, cm⁻¹): 2936.37, 1746.58, 1514.33, 1179.66,
1038.41, 836.55, 748.87, 593.67. HRMS (ESI) ([M+Na]+) Calcd. for C_{32}H_{39}F_{3}N_{2}NaO_{4}SSi+: 655.2244; found: 655.2243.

3-chloro-1-(4-methoxyphenyl)-3-methylindolin-2-one (5). $^1$H NMR (400 MHz, CDCl$_3$) δ 7.49 (dd, $J = 7.5$, 0.9 Hz, 1H), 7.36-7.31 (m, 2H), 7.29 -7.23 (m, 1H), 7.14 (td, $J = 7.6$, 1.0 Hz, 1H), 7.07-7.02 (m, 2H), 6.77 (d, $J = 7.9$ Hz, 1H), 3.86 (s, 3H), 2.00 (s, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 173.92, 159.44, 142.66, 130.81, 130.09, 127.85, 126.35, 124.06, 123.72, 115.01, 109.93, 62.00, 55.58, 26.17.

1-(4-methoxyphenyl)-3-methylindolin-2-one (6). $^1$H NMR (400 MHz, CDCl$_3$) δ 7.34-7.24 (m, 3H), 7.21-7.13 (m, 1H), 7.08 (td, $J = 7.6$, 0.9 Hz, 1H), 7.03 (d, $J = 8.9$ Hz, 2H), 6.75 (d, $J = 7.8$ Hz, 0.5 H), 6.67 (d, $J = 8.4$ Hz, 0.5 H), 3.86 (d, $J = 0.6$ Hz, 3H), 3.62-3.57 (m, $J = 7.6$, 3.8 Hz, 1H), 1.58 (dd, $J = 7.6$, 3.9 Hz, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 178.30, 177.68, 159.27, 159.12, 144.40, 142.94, 127.97, 127.85, 127.78, 127.74, 124.22, 123.74, 122.71, 115.01, 114.92, 110.12, 109.18, 55.55, 40.72, 15.69, 15.58.
6. Gram scale synthesis of 3b

A 100 mL round bottom flask was equipped with a rubber septum and magnetic stir bar. It was charged with indole 1b (6 mmol, 1.42 g, 2.0 eq.) and amino acid derivative 2a (3 mmol, 0.92 g, 1.0 eq.). Benzotrifluoride (60 mL, 0.05 M) and NaClO (9 mmol, 11.6 mL, 3.0 eq.) was added via syringe. The mixture was then stirred for 12 h. After the reaction was complete (as judged by TLC analysis), the mixture was poured into a separatory funnel containing 50 mL of H2O and 50 mL of EtOAc. The layers were separated and the aqueous layer was extracted with EtOAc (2 × 30 mL). The combined organic layers were dried over Na2SO4 and concentrated under reduced pressure after filtration. The residue was purified by flash chromatography on silica gel (EtOAc/n-Hexane 10:90) to afford the desired product 3b (1.39 g, 86%, 13.0:1 dr) as a white solid.

References:
7. NMR spectra for all compounds
S70
inseparable diastereomers (12:3:1 dr)

Me\textsuperscript{Pr} COO\textsubscript{Bu}

3c

-66.0 -65.5 -65.0 -64.5 -64.0 -63.5 -63.0 -62.5 -62.0 -61.5 -61.0 -60.5 -60.0 -59.5 -59.0 -58.5 -58.0 -57.5 -57.0 -56.5 -56.0

-72.0 -71.5 -71.0 -70.5 -70.0 -69.5 -69.0 -68.5 -68.0 -67.5 -67.0 -66.5 -66.0

-1.0 -0.5 0.0 0.5 1.0 1.5 2.0 2.5 3.0 3.5 4.0

-6.0 -5.5 -5.0 -4.5 -4.0 -3.5 -3.0 -2.5 -2.0 -1.5 -1.0 -0.5 0.0 0.5 1.0 1.5 2.0 2.5 3.0 3.5 4.0

-7.0 -6.5 -6.0 -5.5 -5.0 -4.5 -4.0 -3.5 -3.0 -2.5 -2.0 -1.5 -1.0 -0.5 0.0 0.5 1.0 1.5 2.0 2.5 3.0 3.5 4.0

-11.0 -10.5 -10.0 -9.5 -9.0 -8.5 -8.0 -7.5 -7.0 -6.5 -6.0 -5.5 -5.0 -4.5 -4.0 -3.5 -3.0 -2.5 -2.0 -1.5 -1.0 -0.5 0.0 0.5 1.0 1.5 2.0 2.5 3.0 3.5 4.0

-22.0 -21.5 -21.0 -20.5 -20.0 -19.5 -19.0 -18.5 -18.0 -17.5 -17.0 -16.5 -16.0 -15.5 -15.0 -14.5 -14.0 -13.5 -13.0 -12.5 -12.0 -11.5 -11.0 -10.5 -10.0 -9.5 -9.0 -8.5 -8.0 -7.5 -7.0 -6.5 -6.0 -5.5 -5.0 -4.5 -4.0 -3.5 -3.0 -2.5 -2.0 -1.5 -1.0 -0.5 0.0 0.5 1.0 1.5 2.0 2.5 3.0 3.5 4.0

-71.5 -72.0 -72.5 -73.0 -73.5 -74.0 -74.5 -75.0 -75.5 -76.0 -76.5 -77.0 -77.5 -78.0 -78.5 -79.0 -79.5 -80.0 -80.5 -81.0 -81.5 -82.0 -82.5 -83.0 -83.5 -84.0 -84.5 -85.0 -85.5 -86.0 -86.5 -87.0 -87.5 -88.0 -88.5 -89.0 -89.5 -90.0 -90.5 -91.0 -91.5 -92.0 -92.5 -93.0 -93.5 -94.0 -94.5 -95.0 -95.5 -96.0 -96.5 -97.0 -97.5 -98.0 -98.5 -99.0 -99.5 -100.0
inseparable diastereomers (9.6:1 dr)

$\text{Me}^{\text{Pr}}$  
$
\text{COO}^{\text{Bu}}$

3d

$\text{Me}^{\text{Pr}}$  
$
\text{COO}^{\text{Bu}}$

3d

$-72.55$

$r_1$ (ppm)

$-66.0 -50.0 -34.0 -18.0 -10.0 -8.0 -6.0 -4.0 -2.0$

$1.00$

$r_1$ (ppm)

$-66.0 -50.0 -34.0 -18.0 -10.0 -8.0 -6.0 -4.0 -2.0$

$-72.56$

$-1.25$

$r_2$ (ppm)

$140 130 120 110 100 90 80 70 60 50 40 30 20 10 0$

$r_2$ (ppm)

$140 130 120 110 100 90 80 70 60 50 40 30 20 10 0$
inseparable diastereomers (12:7:1 dr)
inseparable diastereomers (12:7:1 dr)

![NMR spectrum of compound 3f](image)

*Note: The image contains a chemical structure and an NMR spectrum for compound 3f.*
inseparable diastereomers (12:3:1 dr)

inseparable diastereomers (13:7:1 dr)
Inseparable diastereomers (13:1:1 dr)

$\text{MePt-COOBu}$

$\text{OMe}$

$\text{3n}$

$\text{δ}$

$\text{F}$ (ppm)

$\text{δ}$

$\text{F}$ (ppm)

$\text{δ}$

$\text{F}$ (ppm)

$\text{δ}$

$\text{F}$ (ppm)
inseparable diastereomers (10:6:1 dr)

\[ \text{Diagram} \]

\[ \text{Diagram} \]

S93
inseparable diastereomers (11:0:1 dr)

`MePr` COOEt

1H (ppm)

1H (ppm)

13C (ppm)

13C (ppm)

S95
inseparable diastereomers (11:0:1 dr)

[Chemical structure image]

inseparable diastereomers (6:6:1 dr)

[Chemical structure image]
inseparable diastereomers (6.6:1 dr)
inseparable diastereomers (7:1:1 dr)

TBSO Me COO\textsubscript{Bu}

3u

\[ \text{\textsuperscript{1}H NMR (DMSO-d\textsubscript{6})} \]

\textsuperscript{13}C NMR (DMSO-d\textsubscript{6})
8. X-ray single crystal data for compounds 3a and 3a’

3a (CCDC1909079)

Computing details
Program(s) used to refine structure: SHELXL2014/7 (Sheldrick, 2014).

Crystal data

<table>
<thead>
<tr>
<th>Compound</th>
<th>Formula</th>
<th>$F(000)$</th>
<th>$M_r$</th>
<th>$D_x$</th>
<th>Space group</th>
<th>Radiation</th>
<th>$\mu$</th>
<th>Refinement range</th>
<th>Temperature</th>
<th>Volume</th>
<th>$Z$</th>
</tr>
</thead>
<tbody>
<tr>
<td>CHClF$_6$NOS$_2$</td>
<td>$C_{24}H_{13}ClF_6NOS_2$</td>
<td>8375</td>
<td>256.60</td>
<td>8.546 Mg m$^{-3}$</td>
<td>P$_3_1$</td>
<td>Mo Kα radiation, $\lambda = 0.71073$ Å</td>
<td>4.24 mm$^{-1}$</td>
<td>9.4985 (9) Å</td>
<td>42.753 (3) Å</td>
<td>3340.5 (7) Å$^3$</td>
<td>67</td>
</tr>
</tbody>
</table>

Data collection

<table>
<thead>
<tr>
<th>Reflections</th>
<th>$\theta_{\text{max}}$</th>
<th>$\theta_{\text{min}}$</th>
<th>$h$ range</th>
<th>$k$ range</th>
<th>$l$ range</th>
<th>$R_{int}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>16691 measured</td>
<td>27.5°</td>
<td>2.5°</td>
<td>-12 → 7</td>
<td>-11 → 12</td>
<td>-50 → 52</td>
<td>0.039</td>
</tr>
<tr>
<td>9833 independent</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>8194 reflections with $I &gt; 2\sigma(I)$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Refinement

<table>
<thead>
<tr>
<th>Refinement on $F^2$</th>
<th>Hydrogen site location: inferred from neighbouring sites</th>
</tr>
</thead>
<tbody>
<tr>
<td>Least-squares matrix: full</td>
<td>H-atom parameters constrained</td>
</tr>
<tr>
<td>$R[F^2 &gt; 2\sigma(F^2)] = 0.052$</td>
<td>$w = 1/[\sigma^2(F_o^2) + (0.1P)^2]$</td>
</tr>
<tr>
<td>$wR(F^2) = 0.148$</td>
<td>where $P = (F_o^2 + 2F_c^2)/3$</td>
</tr>
<tr>
<td>$S = 0.96$</td>
<td>$(\Delta/\sigma)_{\text{max}} = 0.006$</td>
</tr>
<tr>
<td>9833 reflections</td>
<td>$\Delta \rho_{\text{max}} = 0.24$ e Å$^{-3}$</td>
</tr>
<tr>
<td>555 parameters</td>
<td>$\Delta \rho_{\text{min}} = -0.30$ e Å$^{-3}$</td>
</tr>
<tr>
<td></td>
<td>Absolute structure parameter: 0.11 (4)</td>
</tr>
</tbody>
</table>

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ($\AA^2$)
Computing details

Program(s) used to refine structure: \textit{SHELXL2014/7} (Sheldrick, 2014).

\textbf{Crystal data}

\begin{tabular}{|l|l|}
\hline
 CHClF$_5$NOS$_2$ & $F(000) = 8250$ \\
$M_r = 256.60$ & $D_x = 8.586 \text{ Mg m}^{-3}$ \\
Trigonal, $P3_1$ & Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å \\
$a = 9.4247$ (11) Å & $\mu = 4.26$ mm$^{-1}$ \\
$c = 42.577$ (6) Å & $T = 296$ K \\
$V = 3275.2$ (9) Å$^3$ & \text{xxxmm} \\
$Z = 66$ & \\
\hline
\end{tabular}

\textbf{Data collection}

\begin{tabular}{|l|l|}
\hline
19768 measured reflections & $\theta_{\text{max}} = 27.5^\circ$, $\theta_{\text{min}} = 2.5^\circ$ \\
6489 independent reflections & $h = -12\rightarrow 11$ \\
5500 reflections with $I > 2\sigma(I)$ & $k = -12\rightarrow 12$ \\
$R_{\text{int}} = 0.072$ & $l = -55\rightarrow 29$ \\
\hline
\end{tabular}
Refinement

Refinement on $F^2$

Hydrogen site location: inferred from neighbouring sites

Least-squares matrix: full

H-atom parameters constrained

$R[F^2 > 2\sigma(F^2)] = 0.055$

$w = 1/[\sigma^2(F_c^2) + (0.0542P)^2 + 2.6465P]$

where $P = (F_o^2 + 2F_c^2)/3$

$wR(F^2) = 0.142$

$(\Delta/\sigma)_{\text{max}} < 0.001$

$S = 1.06$

$\Delta\rho_{\text{max}} = 0.44$ e Å$^{-3}$

6489 reflections

$\Delta\rho_{\text{min}} = -0.40$ e Å$^{-3}$

555 parameters

Absolute structure: Flack $x$
determined using 1080 quotients


1 restraint

Absolute structure parameter: 0.11 (12)

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å$^2$)