Copper-Catalyzed Electrophilic Amination of Sodium Sulfinates
at Room Temperature

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1. **General**

All commercial reagents were used directly without further purification, unless otherwise stated. Dry dimethylsulfoxide (DMSO) was purchased from J & K chemical, stored over 4 Å molecular sieves and handled under N₂. Anhydrous methanol (MeOH) was distilled from anhydrous calcium chloride, Dioxane, Tetrahydrofuran (THF), toluene and m-Xylene were distilled from sodium/benzophenone, 1,2-Dimethoxyethane (DME) and 1,2-Dichloroethane (DCE) were distilled from calcium hydride prior to use. t-BuONa was purchased from J & K chemical. All schlenk tubes and sealed vessels (50 mL) were purchased from Beijing Synthware Glass. CDCl₃ was purchased from Cambridge Isotope Laboratories.¹H NMR and ¹³C NMR spectra were recorded on Jeol ECA-400 and Bruker 400 DRX spectrometers. ¹³C NMR spectra were referenced to the carbon signal of CDCl₃ (77.0 ppm). GC-MS spectra were recorded on Agilent Technologies 1890A GC system and 5975C inert MSD with Triple-Axis Detector.

2. **Experimental sections**

2.1 **General procedure for sulfonamides from O-benzoyl hydroxylamines and sodium sulfinates.**

To a 50 mL schlenk tube containing sodium sulfinate (1.0 mmol) and O-benzoyl hydroxylamine (0.5 mmol) were added and the tube was purged with N₂ for 3 times. Then DCE (4.0 mL), subsequently (Note, if O-benzoyl hydroxylamine was a liquid, it was introduced to the tube after addition of DCE). The resulted mixture was allowed to stir for 12 h at room temperature under atmosphere of N₂, then CuBr₂ (2 mol%) was added and stirred another 12 h. After the completion of the reaction, the resulting mixture was concentrated under the vacuum and directly purified by flash chromatography to give the desired product.
2.2 Optimization of reaction conditions

Table S1. Catalyst and solvent effects (excluded data in the Table 1) $^a$

<table>
<thead>
<tr>
<th>Entry</th>
<th>Solvent</th>
<th>Cat.</th>
<th>Temp. ($^\circ$C)</th>
<th>Yield (%) $^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>EtOH/ H$_2$O (2:1)</td>
<td>CuBr$_2$</td>
<td>100</td>
<td>77</td>
</tr>
<tr>
<td>2</td>
<td>EtOH/ H$_2$O (1:1)</td>
<td>CuBr$_2$</td>
<td>100</td>
<td>56</td>
</tr>
<tr>
<td>3</td>
<td>EtOH/ H$_2$O (1:2)</td>
<td>CuBr$_2$</td>
<td>100</td>
<td>43</td>
</tr>
<tr>
<td>4</td>
<td>DCE</td>
<td>Cu(NO$_3$)$_2$·3H$_2$O</td>
<td>100</td>
<td>71</td>
</tr>
<tr>
<td>5</td>
<td>DCE</td>
<td>CuSO$_4$·5H$_2$O</td>
<td>100</td>
<td>67</td>
</tr>
<tr>
<td>6</td>
<td>DCE</td>
<td>Cu(OAc)$_2$·H$_2$O</td>
<td>100</td>
<td>85</td>
</tr>
<tr>
<td>7</td>
<td>DCE</td>
<td>CuCl$_2$·2H$_2$O</td>
<td>100</td>
<td>88</td>
</tr>
<tr>
<td>8</td>
<td>DCE</td>
<td>FeBr$_2$</td>
<td>100</td>
<td>41</td>
</tr>
<tr>
<td>9</td>
<td>DCE</td>
<td>NiBr$_2$</td>
<td>100</td>
<td>56</td>
</tr>
<tr>
<td>10</td>
<td>DCE</td>
<td>CuCl</td>
<td>100</td>
<td>45</td>
</tr>
</tbody>
</table>

$^a$ Reaction was carried out with 0.5 mmol scale: 2 equiv. 1 and 1equiv. 2 were dissolved in 4 mL solvent and stirred in 12 h under atmosphere of N$_2$, then the catalyst was added and stirred for additional 12 h.

$^b$ Isolate yield based on 2.

2.3 Control experiments of reaction conditions

Scheme S1 Control experiments.
3. Data for the amination products

3\textsuperscript{s1}:

$^1$H NMR (CDCl\textsubscript{3}, 400 MHz, 298 K): $\delta = 7.77-7.75$ (m, 2H, ArH), 7.65-7.61 (m, 1H, ArH), 7.58-7.54 (m, 2H, ArH), 3.74 (t, $J = 5.0$ Hz, 4H, OCH\textsubscript{2}), 3.00 (t, $J = 5.0$ Hz, 4H, NCH\textsubscript{2}); $^{13}$C NMR (100 MHz, CDCl\textsubscript{3}, 298 K, ppm) $\delta$ 134.97 (ArC), 133.06 (ArC), 129.12 (ArC), 127.82 (ArC), 66.08 (OCH\textsubscript{2}), 45.96 (NCH\textsubscript{2}); Yield: >99%, white solid, mp: 115-117 °C; $R_f = 0.50$ (Petrol/EtOAc 4:1).

5a\textsuperscript{s1}:

$^1$H NMR (CDCl\textsubscript{3}, 400 MHz, 298 K): $\delta = 7.85-7.83$ (m, 2H, ArH), 7.62-7.51 (m, 3H, ArH), 3.27-3.23 (m, 4H, NCH\textsubscript{2}), 1.80-1.72 (m, 4H, CH\textsubscript{2}); $^{13}$C NMR (100 MHz, CDCl\textsubscript{3}, 298 K, ppm) $\delta$ 136.79 (ArC), 132.48 (ArC), 128.90 (ArC), 127.33 (ArC), 47.82 (NCH\textsubscript{2}), 25.10 (CH\textsubscript{2}); Yield: >99%, white solid, mp: 156-157 °C; $R_f = 0.60$ (Petrol/EtOAc 8:1).

5b\textsuperscript{s1}:

$^1$H NMR (CDCl\textsubscript{3}, 400 MHz, 298 K): $\delta = 7.77-7.75$ (m, 2H, ArH), 7.62-7.57 (m, 1H, ArH), 7.55-7.51 (m, 2H, ArH), 2.99 (t, $J = 5.6$ Hz, 4H, NCH\textsubscript{2}), 1.67-1.61 (m, 4H, CH\textsubscript{2}), 1.44-1.39 (m, 2H, CH\textsubscript{2}); $^{13}$C NMR (100 MHz, CDCl\textsubscript{3}, 298 K, ppm) $\delta = 136.36$ (ArC), 132.51 (ArC), 128.88 (ArC), 127.61 (ArC), 46.90 (NCH\textsubscript{2}), 25.14 (CH\textsubscript{2}), 23.47 (CH\textsubscript{2}); Yield: >99%, white solid, mp: 90-92 °C; $R_f = 0.60$ (Petrol/EtOAc 8:1).

5c\textsuperscript{s2}:
$^1$H NMR (CDCl$_3$, 400 MHz, 298 K): $\delta$ = 7.79-7.77 (m, 2H, ArH), 7.56-7.47 (m, 3H, ArH), 3.26 (t, $J$ = 5.6 Hz, 4H, NCH$_2$), 1.70-1.57 (m, 4H, CH$_2$), 1.56-1.55 (m, 4H, CH$_2$); $^{13}$C NMR (100 MHz, CDCl$_3$, 298 K, ppm) $\delta$ = 139.50 (ArC), 132.13 (ArC), 128.90 (ArC), 126.81 (ArC), 48.17 (NCH$_2$), 29.06 (CH$_2$), 26.80 (CH$_2$); Yield: 88%, colourless liquid, $R_f$ = 0.70 (Petrol/EtOAc 8:1).

5d$^{53}$:

$^1$H NMR (CDCl$_3$, 400 MHz, 298 K): $\delta$ = 7.80-7.78 (m, 2H, ArH), 7.58-7.48 (m, 3H, ArH), 3.14 (t, $J$ = 5.6 Hz, 4H, NCH$_2$), 1.73-1.64 (m, 10H, CH$_2$); $^{13}$C NMR (100 MHz, CDCl$_3$, ppm) $\delta$ = 142.72 (ArC), 132.19 (ArC), 128.92 (ArC), 127.06 (ArC), 48.70 (NCH$_2$), 29.68 (CH$_2$), 27.75 (CH$_2$), 26.61 (CH$_2$), 25.04 (CH$_2$); Yield: 79%, colourless liquid, $R_f$ = 0.75 (Petrol/EtOAc 8:1).

6a$^{54}$:

$^1$H NMR (400 MHz, CDCl$_3$, 298 K) $\delta$ = 7.74-7.74 (m, 2H, ArH), 7.642-7.61 (m, 1H, ArH), 7.57-7.53 (m, 2H, ArH), 3.51 (t, $J$ = 4.8 Hz, 4H, NCH$_2$), 2.98 (t, $J$ = 4.8 Hz, 4H, NCH$_2$), 1.40 (s, 9H, CH$_3$); $^{13}$C NMR (100 MHz, CDCl$_3$, ppm) $\delta$ = 154.07 (C=O), 132.95 (ArC), 129.07 (ArC), 127.59 (ArC), 80.32 (C-O), 45.75 (NCH$_2$), 28.16 (CH$_3$); Yield: >99%, yellow solid, mp: 127-128 °C; $R_f$ = 0.60 (Petrol/EtOAc 4:1).

6b$^{55}$:

$^1$H NMR (400 MHz, CDCl$_3$, 298 K) $\delta$ = 7.81-7.79 (m, 2H, ArH), 7.64-7.61 (m, 1H, ArH), 7.58-7.54 (m, 2H, ArH), 7.27-7.23 (m, 2H, ArH), 6.91-6.86 (m, 3H, ArH), 3.26-3.23 (m, 4H, NCH$_2$), 3.19-3.17 (m, 4H, NCH$_2$); $^{13}$C NMR (100 MHz, CDCl$_3$, 298 K, ppm) $\delta$ = 135.48 (ArC), 132.98 (ArC), 129.24 (ArC), 129.11 (ArC), 127.84 (ArC), 122.73 (ArC), 120.86 (ArC), 116.90 (ArC), 49.18 (NCH$_2$), 46.08 (NCH$_2$); Yield: >99%, white solid, mp: 133-135 °C; $R_f$ = 0.50
(Petrol/EtOAc 4:1).

**7**

$^1$H NMR (400 MHz, CDCl$_3$, 298 K) $\delta$ = 7.86-7.84 (m, 2H, ArH), 7.62-7.52 (m, 3H, ArH), 7.17-7.12 (m, 2H, ArH), 7.09-7.02 (m, 2H, ArH), 4.27 (s, 2H, NCH$_2$), 3.38 (t, $J$ = 5.6 Hz, 2H, NCH$_2$), 2.93 (t, $J$ = 6.0 Hz, 2H, NCH$_2$CH$_2$); $^{13}$C NMR (100 MHz, CDCl$_3$, 298 K, ppm) $\delta$ = 136.30 (ArC), 133.40 (ArC), 132.97 (ArC), 133.81 (ArC), 131.15 (ArC), 129.05 (ArC), 128.78 (ArC), 127.62 (ArC), 126.73 (ArC), 126.31 (ArC), 47.47 (NCH$_2$), 43.68 (NCH$_2$), 28.77 (NCH$_2$CH$_2$); Yield: 61%, white solid, mp: 155-157 °C; $R_f$ = 0.65 (Petrol/EtOAc 8:1).

**8**

$^1$H NMR (400 MHz, CDCl$_3$, 298 K) $\delta$ = 7.79 (d, $J$ = 6.8 Hz, 2H, ArH), 7.53-7.44 (m, 3H, ArH), 4.23-4.20 (m, 1H, NCH$_2$), 3.71-3.68 (m, 1H, NCH$_2$), 2.96 (td, $J$ = 12.8 Hz, $J$ = 2.0 Hz, 1H, NCH), 1.56-1.31 (m, 6H, CH$_2$CH$_2$CH$_2$), 1.03 (d, $J$ = 6.8 Hz, 3H, CH$_3$); $^{13}$C NMR (100 MHz, CDCl$_3$, 298 K, ppm) $\delta$ = 141.20 (ArC), 132.04 (ArC), 128.87 (ArC), 126.77 (ArC), 48.40 (NCH$_2$), 40.20 (NCH), 30.22 (CH$_2$), 25.09 (CH$_2$), 18.02 (CH$_2$), 15.22 (CH$_3$); Yield: 74%, yellow oil, $R_f$ = 0.67 (Petrol/EtOAc 8:1).

**9**

$^1$H NMR (400 MHz, CDCl$_3$, 298 K) $\delta$ = 7.83-7.80 (m, 2H, ArH), 7.54-7.45 (m, 3H, ArH), 4.22-4.15 (m, 2H, NCH), 1.46-1.33 (m, 12H, CH$_2$, CH$_3$); $^{13}$C NMR (100 MHz, CDCl$_3$, 298 K, ppm) $\delta$ = 141.88 (ArC), 131.91 (ArC), 128.89 (ArC), 126.52 (ArC), 47.98 (NCH), 29.57 (CH$_2$), 22.31 (CH$_2$), 13.28 (CH$_3$); Yield: 41%, white solid, mp: 99-102 °C; $R_f$ = 0.65 (Petrol/EtOAc 8:1).
$^1$H NMR (400 MHz, CDCl$_3$, 298K) $\delta$ = 7.78-7.75 (m, 2H, ArH), 7.62-7.58 (m, 1H, ArH), 7.55-7.51 (m, 2H, ArH), 2.69 (s, 6H, Me); $^{13}$C NMR (100 MHz, CDCl$_3$, 298K, ppm) $\delta$ = 135.41 (ArC), 132.64 (ArC), 128.95 (ArC), 127.63 (ArC), 37.85 (Me); Yield: 93%, white solid, mp: 45-46 °C; $R_f$ = 0.45 (Petrol/EtOAc 8:1).

$^1$H NMR (400 MHz, CDCl$_3$, 298K) $\delta$ = 7.81-7.79 (m, 2H, ArH), 7.57-7.52 (m, 1H, ArH), 7.50-7.46 (m, 2H, ArH), 3.26-3.21 (m, 4H, NCH$_2$), 1.11 (t, $J$ = 7.2 Hz, 6H, CH$_2$CH$_3$); $^{13}$C NMR (100 MHz, CDCl$_3$, 298K, ppm) $\delta$ = 140.38 (ArC), 132.19 (ArC), 128.95 (ArC), 126.93 (ArC), 41.98 (NCH$_2$), 14.08 (CH$_2$CH$_3$); Yield: 85%, yellow solid, mp: 35-37 °C; $R_f$ = 0.50 (Petrol/EtOAc 8:1).

$^1$H NMR (400 MHz, CDCl$_3$, 298K) $\delta$ = 7.76-7.74 (m, 2H, ArH), 7.57-7.47 (m, 3H, ArH), 2.97 (t, $J$ = 7.2 Hz, 2H, NCH$_2$), 2.69 (s, 3H, NCH$_3$), 1.50-1.45 (m, 2H, NCH$_2$CH$_3$), 1.25-1.23 (m, 10H), 0.85 (t, $J$ = 6.4 Hz, 3H, CH$_2$CH$_3$); $^{13}$C NMR (100 MHz, CDCl$_3$, 298K, ppm) $\delta$ = 137.50 (ArC), 132.33 (ArC), 128.88 (ArC), 127.18 (ArC), 50.00 (NCH$_2$), 34.41 (NCH$_3$), 31.63 (NCH$_2$CH$_3$), 29.04, 27.45, 26.37, 22.50, 13.96; Yield: 89%, yellow oil, $R_f$ = 0.70 (Petrol/EtOAc 8:1).

$^1$H NMR (400 MHz, CDCl$_3$, 298K) $\delta$ = 7.84-7.82 (m, 2H, ArH), 7.59-7.49 (m, 3H, ArH),
5.65-5.55 (m, 2H, CH₂=CH), 5.16-5.12 (m, 4H, NCH₂), 3.82 (d, J = 6.0 Hz, 4H, CH₂=CH); ¹³C NMR (100 MHz, CDCl₃, 298K, ppm) δ = 140.41 (ArC), 132.49 (ArC), 129.04 (ArC), 127.07 (CH₂=CH), 119.01 (NCH₂), 49.28 (CH₂=CH); Yield: 50%, yellow oil, Rᵣ = 0.55 (Petrol/EtOAc 8:1).

![S11](image1)

¹H NMR (400 MHz, CDCl₃, 298K) δ = 7.87-7.84 (m, 2H, ArH), 7.65-7.55 (m, 3H, ArH), 7.36-7.28 (m, 5H, ArH), 4.15 (s, 2H, NCH₂), 2.61 (s, 3H, Me); ¹³C NMR (100 MHz, CDCl₃, 298K, ppm) δ = 137.43 (ArC), 135.55 (ArC), 132.65 (ArC), 129.12 (ArC), 128.62 (ArC), 128.33 (ArC), 127.90 (ArC), 127.42 (ArC), 54.10 (NCH₂), 34.30 (Me); Yield: 89%, white solid, mp: 86-89 ºC; Rᵣ = 0.55 (Petrol/EtOAc 8:1).

![S12](image2)

¹H NMR (400 MHz, CDCl₃, 298K) δ = 7.78-7.75 (m, 2H, ArH), 7.58-7.55 (m, 1H, ArH), 7.52-7.49 (m, 2H, ArH), 7.31-7.28 (m, 2H, ArH), 7.24-7.17 (m, 3H, ArH), 3.29-3.25 (m, 2H, NCH₂), 2.88-2.84 (m, 2H, NCH₂CH₂), 2.76 (s, 3H, Me); ¹³C NMR (100 MHz, CDCl₃, 298K, ppm) δ = 138.10 (ArC), 132.42 (ArC), 129.99 (ArC), 128.93 (ArC), 128.64 (ArC), 127.11 (ArC), 126.42 (ArC), 51.64 (NCH₂), 35.00 (NCH₂CH₂), 34.64 (Me); Yield: 96%, colourless oil, Rᵣ = 0.62 (Petrol/EtOAc 4:1).

![S13](image3)

¹H NMR (400 MHz, CDCl₃, 298K) δ = 7.86-7.84 (m, 2H, ArH), 7.61-7.58 (m, 1H, ArH), 7.53-7.49 (m, 2H, ArH), 7.22-7.21 (m, 6H, ArH), 7.05-7.03 (m, 4H, ArH), 4.34 (s, 4H, NCH₂); ¹³C NMR (100 MHz, CDCl₃, 298K, ppm) δ = 135.52 (ArC), 132.48 (ArC), 129.10 (ArC), 128.54 (ArC), 128.42 (ArC), 127.66 (ArC), 127.14 (ArC), 50.42 (NCH₂); Yield: 54%, white solid, mp:
72-74 °C; \( R_f = 0.70 \) (Petrol/EtOAc 4:1).

17\textsuperscript{\textsuperscript{14}}: 

$\text{H NMR (400 MHz, CDCl}_3$, 298K $\delta = 7.74$-$7.72 \ (m, \ 2H, \ ArH), \ 7.56$-$7.52 \ (m, \ 1H, \ ArH), \ 7.48$-$7.41 \ (m, \ 2H, \ ArH), \ 6.77$-$6.68 \ (m, \ 3H, \ ArH), \ 3.82 \ (d, \ J = 4.8 \ Hz, \ 6H, \ OCH}_3), \ 3.24$-$3.21 \ (m, \ 2H; \text{NCH}_2), \ 2.72 \ (s, \ 3H; \text{Me})$; \textsuperscript{13}C NMR (100 MHz, CDCl\textsubscript{3}, 298K, ppm) $\delta = 148.75$ (ArC), 147.51 (ArC), 137.56 (ArC), 132.35 (ArC), 130.60 (ArC), 128.87 (ArC), 127.05 (ArC), 120.56 (ArC), 111.85 (ArC), 111.16 (ArC), 55.69 (OCH\textsubscript{3}), 51.69 (NCH\textsubscript{2}), 34.95 (NCH\textsubscript{2}CH\textsubscript{2}), 34.19 (NCH\textsubscript{3}); Yield: 83%, yellow oil, \( R_f = 0.60 \) (Petrol/EtOAc 2:1).

18\textsuperscript{\textsuperscript{14}}: 

$\text{H NMR (400 MHz, CDCl}_3$, 298K $\delta = 7.75 \ (d, \ J = 7.6 \ Hz, \ 2H, \ ArH), \ 7.58$-$7.55 \ (m, \ 1H, \ ArH), \ 7.51$-$7.48 \ (m, \ 2H, \ ArH), \ 7.15$-$7.12 \ (m, \ 2H, \ ArH), \ 6.96 \ (t, \ J = 8.4 \ Hz, \ 2H, \ ArH), \ 3.23 \ (t, \ J = 11.6 \ Hz, \ 2H, \ NCH\textsubscript{2}); \ 2.82 \ (t, \ J = 8.0 \ Hz, \ 2H, \ NCH\textsubscript{2}CH\textsubscript{2}); \ 2.74 \ (s, \ 3H, \ Me)$; \textsuperscript{13}C NMR (100 MHz, CDCl\textsubscript{3}, 298K, ppm) $\delta = 162.76$ (ArC), 160.33 (ArC), 137.62 (ArC), 133.83 (ArC), 132.50 (ArC), 130.18 (ArC), 130.10 (ArC), 128.99 (ArC), 127.13 (ArC), 115.35 (ArC), 115.14 (ArC), 51.64 (NCH\textsubscript{2}), 35.06 (NCH\textsubscript{2}CH\textsubscript{2}), 33.84 (Me); \textsuperscript{19}F NMR (CDCl\textsubscript{3}, 376 MHz, 298 K): $\delta = -116.43$; Yield: 95%, yellow oil; \( R_f = 0.65 \) (Petrol/EtOAc 4:1).

19\textsuperscript{\textsuperscript{15}}: 

$\text{H NMR (400 MHz, CDCl}_3$, 298K $\delta = 7.78$-$7.76 \ (m, \ 2H, \ ArH), \ 7.60$-$7.56 \ (m, \ 1H, \ ArH), \ 7.53$-$7.49 \ (m, \ 2H, \ ArH), \ 7.14 \ (dd, \ J = 4.8 \ Hz, \ J = 0.8 \ Hz, \ 1H, \ ArH), \ 6.93$-$6.91 \ (m, \ 1H, \ ArH), \ 6.84 \ (d, \ J = 3.6 \ Hz, \ 1H, \ ArH), \ 3.30 \ (t, \ J = 7.2 \ Hz, \ 2H, \ NCH\textsubscript{2}); \ 3.07 \ (t, \ J = 8.0 \ Hz, \ 2H, \ NCH\textsubscript{2}CH\textsubscript{2}); \ 2.76 \ (s, \ 3H, \ Me)$; \textsuperscript{13}C NMR (100 MHz, CDCl\textsubscript{3}, 298K, ppm) $\delta = 140.13$ (ArC), 137.53 (ArC), 130.14 (ArC), 128.99 (ArC), 127.13 (ArC), 115.35 (ArC), 115.14 (ArC), 51.64 (NCH\textsubscript{2}), 35.06 (NCH\textsubscript{2}CH\textsubscript{2}), 33.84 (Me); Yield: 95%, yellow oil; \( R_f = 0.65 \) (Petrol/EtOAc 4:1).
132.50 (ArC), 128.98 (ArC), 127.11 (ArC), 126.85 (ArC), 125.37 (ArC), 123.82 (ArC), 51.66 (NCH₂), 35.15 (NCH₂CH₂), 28.80 (Me); Yield: 95%, yellow oil, R_f = 0.55 (Petrol/EtOAc 4:1).

20a:

^1^H NMR (400 MHz, CDCl₃, 298K) δ = 7.91-7.88 (m, 1H, ArH), 7.50-7.46 (m, 1H, ArH), 7.35-7.32 (m, 2H, ArH), 3.72 (t, J = 4.4 Hz, 4H, OCH₂), 3.15 (t, J = 4.8 Hz, 4H, NCH₂), 2.65 (s, 3H, Me); ^1^C NMR (100 MHz, CDCl₃, 298K, ppm) δ = 138.05 (ArC), 134.88 (ArC), 133.00 (ArC), 132.83 (ArC), 130.33 (ArC), 126.08 (ArC), 66.21 (OCH₂), 45.22 (NCH₂), 20.74 (Me); Yield: 98%, white solid, mp: 89-91 °C; R_f = 0.54 (Petrol/EtOAc 4:1).

20b:

^1^H NMR (400 MHz, CDCl₃, 298K) δ = 7.56-7.55 (m, 2H, ArH), 7.44-7.43 (m, 2H, ArH), 3.75 (t, J = 4.4 Hz, 4H, OCH₂), 3.00 (t, J = 4.8 Hz, 4H, NCH₂), 2.45 (s, 3H, Me); ^1^C NMR (100 MHz, CDCl₃, 298K, ppm) δ = 139.26 (ArC), 134.77 (ArC), 133.78 (ArC), 128.87 (ArC), 127.99 (ArC), 124.91 (ArC), 65.97 (OCH₂), 45.90 (NCH₂), 21.27 (Me); Yield: >99%, white solid, mp: 121-123 °C; R_f = 0.54 (Petrol/EtOAc 4:1).

20c:

^1^H NMR (400 MHz, CDCl₃, 298K) δ = 7.64 (d, J = 8.0 Hz, 2H, ArH), 7.35 (d, J = 8.0 Hz, 2H, ArH), 3.74 (t, J = 4.4 Hz, 4H, OCH₂), 2.98 (t, J = 4.4 Hz, 4H, NCH₂), 2.45 (s, 3H, Me); ^1^C NMR (100 MHz, CDCl₃, 298K, ppm) δ = 143.86 (ArC), 132.00 (ArC), 129.67 (ArC), 127.81 (ArC), 66.01 (OCH₂), 45.92 (NCH₂), 21.45 (Me); Yield: >99%, white solid, mp: 149-151 °C; R_f = 0.55 (Petrol/EtOAc 4:1).
$^{21}$

\begin{figure}
\centering
\includegraphics[width=0.2\textwidth]{image1.png}
\caption{Structure of compound $S_{1}$.}
\end{figure}

$^{1}$H NMR (400 MHz, CDCl$_3$, 298K) $\delta$ = 7.70-7.68 (m, 2H, ArH), 7.02-7.00 (m, 2H, ArH), 3.88 (s, 3H, OMe), 3.74 (t, $J$ = 4.8 Hz, 4H, OCH$_2$), 2.98 (t, $J$ = 4.4 Hz, 4H, NCH$_2$); $^{13}$C NMR (100 MHz, CDCl$_3$, 298K, ppm) $\delta$ = 163.15 (ArC), 129.88 (ArC), 126.53 (ArC), 114.21 (ArC), 65.97 (OCH$_2$), 55.56 (OCH$_3$), 45.92 (NCH$_2$); Yield: 97%, white solid, mp: 112-114 °C; $R_f$ = 0.65 (Petrol/EtOAc 2:1).

$^{22a}$

\begin{figure}
\centering
\includegraphics[width=0.2\textwidth]{image2.png}
\caption{Structure of compound $S_{1}$.}
\end{figure}

$^{1}$H NMR (400 MHz, CDCl$_3$, 298K) $\delta$ = 7.71-7.69 (m, 2H, ArH), 7.55-7.53 (m, 2H, ArH), 3.75 (t, $J$ = 4.8 Hz, 4H, OCH$_2$), 3.00 (t, $J$ = 4.8 Hz, 4H, NCH$_2$); $^{13}$C NMR (100 MHz, CDCl$_3$, 298K, ppm) $\delta$ = 139.63 (ArC), 133.67 (ArC), 129.41 (ArC), 129.15 (ArC), 65.95 (OCH$_2$), 45.86 (NCH$_2$); Yield: 99%, white solid, mp: 149-151 °C; $R_f$ = 0.45 (Petrol/EtOAc 4:1).

$^{22b}$

\begin{figure}
\centering
\includegraphics[width=0.2\textwidth]{image3.png}
\caption{Structure of compound $S_{1}$.}
\end{figure}

$^{1}$H NMR (400 MHz, CDCl$_3$, 298K) $\delta$ = 7.70 (d, $J$ = 8.8 Hz, 2H, ArH), 7.62 (d, $J$ = 8.8 Hz, 2H, ArH), 3.75 (t, $J$ = 4.8 Hz, 4H, OCH$_2$), 3.00 (t, $J$ = 4.8 Hz, 4H, NCH$_2$); $^{13}$C NMR (100 MHz, CDCl$_3$, 298K, ppm) $\delta$ = 134.20 (ArC), 132.41 (ArC), 129.41 (ArC), 129.15 (ArC), 65.95 (OCH$_2$), 45.87 (NCH$_2$); Yield: 99%, white solid, mp: 154-157 °C; $R_f$ = 0.42 (Petrol/EtOAc 4:1).

$^{22c}$

\begin{figure}
\centering
\includegraphics[width=0.2\textwidth]{image4.png}
\caption{Structure of compound $S_{1}$.}
\end{figure}

$^{1}$H NMR (400 MHz, CDCl$_3$, 298K) $\delta$ = 7.80-7.76 (m, 2H, ArH), 7.24-7.22 (m, 2H, ArH), 3.75 (t, $J$ = 4.8 Hz, 4H, OCH$_2$), 3.00 (t, $J$ = 4.8 Hz, 4H, NCH$_2$); $^{13}$C NMR (100 MHz, CDCl$_3$, 298K, ppm) $\delta$ = 166.60, 164.05 (ArC), 131.23 (ArC), 130.52 (ArC), 130.43 (ArC), 116.51 (ArC), 116.28 (ArC), 65.99 (OCH$_2$), 45.91 (NCH$_2$); $^{19}$F NMR (CDCl$_3$, 376 MHz, 298 K): $\delta$ = -104.51; Yield:
93%, white solid, mp: 104-105 °C; \( R_f = 0.45 \) (Petrol/EtOAc 4:1).

\[
\begin{align*}
\text{23}^{131} & : & \text{F}_3C & \text{O} & \text{S} & \text{O} & \text{N} & \text{O} \\
\text{1}^H \text{ NMR (400 MHz, CDCl}_3, 298K) & \delta = 7.89 \text{ (d, } J = 8.4 \text{ Hz, 2H, ArH), 7.83 \text{ (d, } J = 8.4 \text{ Hz, 2H, ArH), 3.76 \text{ (t, } J = 4.8 \text{ Hz, 4H, OCH}_2), 3.04 \text{ (t, } J = 4.4 \text{ Hz, 4H, NCH}_2); 13^C \text{ NMR (100 MHz, CDCl}_3, 298K, ppm) } \delta = 139.00 \text{ (ArC), 134.92 \text{ (ArC), 134.59 \text{ (ArC), 128.28 \text{ (ArC), 126.31 \text{ (ArC), 126.28 \text{ (ArC), 66.01 \text{ (OCH}_2), 45.89 \text{ (NCH}_2); 19^F \text{ NMR (CDCl}_3, 376 MHz, 298 K): } \delta = -63.15; \text{Yield: 88%, white solid, mp: 131-133 °C; } R_f = 0.44 \text{ (Petrol/EtOAc 4:1).} }
\end{align*}
\]

\[
\begin{align*}
\text{24}^{131} & : & \text{O} & \text{S} & \text{O} & \text{N} & \text{O} \\
\text{1}^H \text{ NMR (400 MHz, CDCl}_3, 298K) & \delta = 8.34 \text{ (s, 1H, ArH), 8.01-7.99 \text{ (m, 2H, ArH), 7.95-7.93 \text{ (m, 1H, ArH), 7.76-7.74 \text{ (m, 1H, ArH), 7.70-7.62 \text{ (m, 2H, ArH), 3.75 \text{ (t, } J = 4.8 \text{ Hz, 4H, OCH}_2), 3.07 \text{ (t, } J = 4.8 \text{ Hz, 4H, NCH}_2); 13^C \text{ NMR (100 MHz, CDCl}_3, 298K, ppm) } \delta = 134.97 \text{ (ArC), 132.34 \text{ (ArC), 132.29 \text{ (ArC), 132.18 \text{ (ArC), 129.30 \text{ (ArC), 129.23 \text{ (ArC), 128.97 \text{ (ArC), 127.94 \text{ (ArC), 127.67 \text{ (ArC), 122.95 \text{ (ArC), 66.11 \text{ (OCH}_2), 46.06 \text{ (NCH}_2); Y} & \text{Yield: 93%, white solid, mp: 159-161 °C; } R_f = 0.62 \text{ (Petrol/EtOAc 4:1).} \\
\end{align*}
\]

\[
\begin{align*}
\text{25}^{1316} & : & \text{O} & \text{S} & \text{O} & \text{N} & \text{O} \\
\text{1}^H \text{ NMR (400 MHz, CDCl}_3, 298K) & \delta = 7.65 \text{ (dd, } J = 5.2 \text{ Hz, } J = 1.2 \text{ Hz, 1H, ArH), 7.55 \text{ (dd, } J = 3.6 \text{ Hz, } J = 1.2 \text{ Hz, 1H, ArH), 7.19-7.17 \text{ (m, 1H, ArH), 3.78 \text{ (t, } J = 4.8 \text{ Hz, 4H, OCH}_2), 3.06 \text{ (t, } J = 4.8 \text{ Hz, 4H, NCH}_2); 13^C \text{ NMR (100 MHz, CDCl}_3, 298K, ppm) } \delta = 135.27 \text{ (ArC), 132.75 \text{ (ArC), 132.46 \text{ (ArC), 127.76 \text{ (ArC), 65.95 \text{ (OCH}_2), 45.95 \text{ (NCH}_2); Y} & \text{Yield: 98%, white solid, mp: 106-107 °C; } R_f = 0.52 \text{ (Petrol/EtOAc 4:1).} \\
\end{align*}
\]
26\textsuperscript{17}: 

\begin{align*}
^1\text{H NMR} (400 \text{ MHz, CDCl}_3, 298\text{K}) &\delta = 8.99 \text{ (d, } J = 2.0 \text{ Hz, 1H, ArH)}, 8.86 \text{ (dd, } J = 4.8 \text{ Hz, } J = 1.6 \\
& \text{Hz, 1H, ArH)}, 8.06-8.04 \text{ (m, 1H, ArH)}, 7.54-7.50 \text{ (m, 1H, ArH)}, 3.77 \text{ (t, } J = 4.8 \text{ Hz, 4H, OCH}_2), \\
& 3.05 \text{ (t, } J = 4.8 \text{ Hz, 4H, NCH}_2); \\
^13\text{C NMR} (100 \text{ MHz, CDCl}_3, 298\text{K, ppm}) &\delta = 153.58 \text{ (ArC)}, 148.42 \text{ (ArC)}, 135.34 \text{ (ArC)}, 131.94 \text{ (ArC)}, 123.71 \text{ (ArC)}, 65.86 \text{ (OCH}_2), 45.73 \text{ (NCH}_2); \\
\text{Yield: 83\%, white solid, mp: 115-117} \text{ °C}; R_f = 0.48 \text{ (Petrol/EtOAc 1:1).}
\end{align*}

27\textsuperscript{18}: 

\begin{align*}
^1\text{H NMR} (400 \text{ MHz, CDCl}_3, 298\text{K}) &\delta = 9.06 \text{ (dd, } J = 4.0 \text{ Hz, } J = 1.6 \text{ Hz, 1H, ArH)}, 8.48 \text{ (dd, } J = \\
& 7.6 \text{ Hz, } J = 1.2 \text{ Hz, 1H, ArH)}, 8.25 \text{ (dd, } J = 8.4 \text{ Hz, } J = 1.6 \text{ Hz, 1H, ArH)}, 8.05 \text{ (dd, } J = 8.4 \text{ Hz, } J = \\
& 1.2 \text{ Hz, 1H, ArH)}, 7.62 \text{ (t, } J = 7.6\text{Hz, 1H, ArH)}, 7.55-7.52 \text{ (m, 1H, ArH)}, 3.71 \text{ (t, } J = 4.4 \text{ Hz, 4H,} \\
& \text{OCH}_2), 3.45 \text{ (t, } J = 4.8 \text{ Hz, 4H, NCH}_2); \\
^13\text{C NMR} (100 \text{ MHz, CDCl}_3, 298\text{K, ppm}) &\delta = 151.18 \text{ (ArC)}, 144.16 \text{ (ArC)}, 136.43 \text{ (ArC)}, 133.60 \text{ (ArC)}, 133.30 \text{ (ArC)}, 128.98 \text{ (ArC)}, 125.48 \text{ (ArC)}, \\
& 122.06 \text{ (ArC), 66.87 (OCH}_2), 46.38 \text{ (NCH}_2); \\
\text{Yield: 72\%, white solid, mp: 183-187} \text{ °C}; R_f = 0.55 \text{ (Petrol/EtOAc 1:1).}
\end{align*}

28a\textsuperscript{18}: 

\begin{align*}
^1\text{H NMR} (400 \text{ MHz, CDCl}_3, 298\text{K}) &\delta = 3.77 \text{ (t, } J = 4.8 \text{ Hz, 4H, OCH}_2), 3.20 \text{ (t, } J = 4.8 \text{ Hz, 4H,} \\
& \text{NCH}_2), 2.78 \text{ (s, 3H, Me); } ^13\text{C NMR} (100 \text{ MHz, CDCl}_3, 298\text{K, ppm}) &\delta = 66.25 \text{ (OCH}_2), 45.80 \\
& \text{(NCH}_2), 33.93 \text{ (Me); white solid, Yield: 32\%, mp: 92-93} \text{ °C}; R_f = 0.35 \text{ (Petrol/EtOAc 4:1).}
\end{align*}
4. $^1$H NMR, $^{13}$C NMR and MS spectra for important compounds
5. References


