Diarylamine synthesis via desulfinylative Smiles rearrangement

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1. General Remarks

All solvents and reagents were purchased from Sigma Aldrich, Thermo Fisher Scientific, Apollo Scientific or Fluorochem and were used as received without further purification. Flash column chromatography was performed using either Biotage Snap Ultra cartridges or Biotage Sfar Silica cartridges on a Biotage Isolera automated column. $^1$H, $^{13}$C and $^{19}$F NMR spectroscopy were recorded on either 400 MHz or 500 MHz Bruker Avance NMR spectrometers. Chemical shifts ($\delta$) are reported in parts per million (ppm) and multiplicities are reported as either singlets (s), doublets (d), triplets (t), quartets (q) or multiplets (m). Coupling constants (J) are reported in Hertz (Hz). All $^1$H NMR and $^{13}$C NMR shifts were referenced to the residual solvent peak of CDCl$_3$ ($^1$H referenced to 7.26 ppm and $^{13}$C referenced to 77.16 ppm), DMSO-d$_6$ ($^1$H referenced to 2.50 ppm and $^{13}$C referenced to 39.52 ppm) and acetone-d$_6$ ($^1$H referenced to 2.06 ppm and $^{13}$C referenced to 29.84 ppm). All $^{19}$F chemical shifts were unadjusted from raw data. 2D heteronuclear single quantum coherence (HSQC), heteronuclear multiple bond correlation (HMBC) and homonuclear correlation spectroscopy (COSY) NMR spectroscopy was used to assist the assignment of signals. High resolution mass spectrometry (HRMS) was recorded on a Waters QTOF, using either ESI or APCI as ionisation methods. Thin layer chromatography (TLC) was carried out using commercially available coated TLC plates and spots were illuminated either by UV light (254 nm) or by staining the plate with a KMnO$_4$ solution. Compound names are those generated by ChemBioDraw™ (CambridgeSoft) following International Union of Pure and Applied Chemistry (IUPAC) nomenclature. Novel compounds are labelled in *italics*. Melting points (MPs) were recorded on a Griffin melting point apparatus to the nearest degree. Reactions which proceeded under microwave irradiation were performed in a Biotage Initiator Microwave Synthesizer.
2. General Procedures

General Procedure A for the Synthesis of N-Aryl Sulfinamides

\[
\begin{align*}
\text{Ar}^2 &+ \text{MeSO}_2\text{OMe} &\rightarrow &\text{Ar}^1
\end{align*}
\]

Carried out by adaptation of a literature procedure.\(^1\) A 2-5 mL microwave vial was charged with the corresponding aniline (2.5 mmol) and the vial was evacuated under vacuum and filled with nitrogen. Anhydrous THF (2 mL) was added and the solution was stirred at -78 °C. \(n\)-BuLi (1.6 M in hexanes, 1 mL, 1.6 mmol) was added dropwise and the mixture was stirred at -78 °C for 20 minutes. A second 2-5 mL microwave vial was charged with methyl sulfinate 8 (200 mg, 2 mmol), evacuated under vacuum and filled with nitrogen. Dry THF (1.5 mL) was added, and the resulting solution was added dropwise to the reaction mixture, which was then stirred for 1-2 hours at -78 °C. The reaction mixture was then quenched with saturated aqueous NaHCO\(_3\) (3 mL) and extracted with EtOAc (3 x 20 mL). The organic layer was then washed with saturated aqueous NaHCO\(_3\) (3 x 20 mL) and dried with anhydrous MgSO\(_4\). This was then filtered, and concentrated \textit{in vacuo} to afford the crude product, which was purified by flash column chromatography.

General Procedure B for the Desulfinylative Smiles Rearrangement

\[
\begin{align*}
\text{Ar}^2 &+ \text{Cs}_2\text{CO}_3 &\rightarrow &\text{Ar}^1
\end{align*}
\]

A 2-5 mL microwave vial was charged with the corresponding sulfinamide (0.2 mmol) and Cs\(_2\)CO\(_3\) (392 mg, 1.2 mmol), evacuated under vacuum, and filled with nitrogen. Anhydrous DMF (2 mL) was added, and the mixture was stirred in a pre-warmed oil bath at 70 °C for 16h. The vial was opened, the reaction mixture was dissolved in EtOAc (20 mL), washed with 1M aqueous HCl (2 x 20 mL) and 10% (w/v) aqueous LiCl (2 x 20 mL). The aqueous layer was then extracted with EtOAc (3 x 20 mL), and the combined organic layers were dried with anhydrous MgSO\(_4\), filtered and concentrated \textit{in vacuo}. The crude product was then purified by flash column chromatography, affording the pure product.

General Procedure C for the Intermolecular S\(_n\)Ar Control Reaction

\[
\begin{align*}
\text{Ar}^2 &+ \text{Ar}^1 &\rightarrow &\text{Ar}^2
\end{align*}
\]

Carried out according to a literature procedure.\(^2\) A 2-5 mL microwave vial was charged with 1-fluoro-4-nitrobenzene (141 mg, 1 mmol) and K\(_2\)CO\(_3\) (140 mg, 1 mmol), evacuated under vacuum and filled with nitrogen. Anhydrous DMF (2 mL) and the corresponding aniline (1.1 mmol) were added and the reaction mixture was heated to reflux for 16 h. After 16 h, the reaction was monitored by TLC (30:70
S4

EtOAc:hexane). No product was observed, and this was confirmed by NMR analysis of the crude product. No purification was necessary.

**General Procedure D for the One-Pot Desulfinylative Cross-Coupling**

\[
\text{O}_2\text{N} \quad \text{MeS} \quad \text{H}_2\text{N} \quad \text{H}_2\text{O} \quad \text{O}_2\text{N} \\
\text{O}_2\text{N} \quad \text{MeS} \quad \text{H}_2\text{N} \quad \text{H}_2\text{O} \quad \text{O}_2\text{N}
\]

A 50 mL round-bottomed flask was charged with the corresponding aniline (2.5 mmol), evacuated under vacuum and filled with nitrogen. Anhydrous THF (2 mL) was added and the solution was stirred at -78 °C. n-BuLi (1.6 M in hexanes, 2 mL, 3.2 mmol) was added dropwise and the mixture was stirred at -78 °C for 20 minutes. A second 50 mL round-bottomed flask was charged with methyl sulfinate 8 (200 mg, 2 mmol), evacuated under vacuum and filled with nitrogen. Anhydrous THF (1.5 mL) was added, and the resulting solution was added dropwise to the reaction mixture, which was then stirred for 1 h at -78 °C. The reaction mixture was quenched with MeOH (3 mL) and the crude product was concentrated \textit{in vacuo}. The flask was then filled with nitrogen, and the crude product dissolved in anhydrous DMF (5 mL). The flask was then stirred at 70 °C in a pre-warmed oil bath for 16 h. After this, the mixture was extracted with EtOAc (3x 20 mL), washed with 1M aqueous HCl (2 x 20 mL) and 10% (w/v) aqueous LiCl (3 x 20 mL). The organic layers were combined and dried with anhydrous MgSO\textsubscript{4}. This was filtered, and then concentrated \textit{in vacuo} to afford the crude product, which was purified by flash column chromatography to afford the pure product.

**General Procedure E for the Microwave Reaction**

A sealed 2-5 mL microwave vial was charged with the corresponding sulfinamide (0.2 mmol) and Cs\textsubscript{2}CO\textsubscript{3} (392 mg, 1.2 mmol), evacuated under vacuum and filled with nitrogen. Anhydrous DMA (2 mL) was added, and the mixture was placed in a Biotage Initiator Microwave Synthesizer at 70 °C for 30 min. The vial was then opened, the reaction mixture was dissolved in EtOAc (20 mL), washed with 1M aqueous HCl (2 x 20 mL) and 10% (w/v) aqueous LiCl (2 x 20 mL). The aqueous layer was then extracted with EtOAc (3 x 20 mL), and the combined organic layers were dried with anhydrous MgSO\textsubscript{4}, filtered and concentrated \textit{in vacuo}. The crude product was then purified by flash column chromatography, affording the pure product.
3. Data for Synthesised Compounds

Products from the Desulfinylative Smiles

4-nitro-N-phenylaniline (2a)

![Chemical Structure]

Synthesised according to general procedure B (column conditions: 0-30% EtOAc in hexane). The pure product was afforded as a yellow solid (31 mg, 73% yield).

1 mmol scale procedure:

A 50 mL round-bottomed flask was charged with sulfinamide 3a (262 mg, 1 mmol) and Cs₂CO₃ (1.96 g, 6 mmol), evacuated under vacuum and filled with nitrogen. Anhydrous DMF (8 mL) was added and the reaction mixture was left to stir for in a pre-warmed oil bath at 70 °C for 16 h. The reaction mixture was dissolved in EtOAc (30 mL), washed with 1M aqueous HCl (2 x 40 mL) and 10% (w/v) aqueous LiCl (2 x 40 mL). The aqueous layer was then extracted with EtOAc (3 x 40 mL), and the combined organic layers were dried with anhydrous MgSO₄, filtered and concentrated in vacuo. The crude product was then purified by flash column chromatography, affording the pure product as a yellow solid (130 mg, 61% yield).

^H NMR (500 MHz, CDCl₃) δ 8.12 (d, J = 9.2 Hz, 2H), 7.39 (t, J = 7.8 Hz, 2H), 7.21 (d, J = 7.9 Hz, 2H), 7.19 (t, J = 7.4 Hz, 1H), 6.94 (d, J = 9.2 Hz, 2H), 6.34 (s, 1H).

^13C NMR (126 MHz, CDCl₃) δ 150.2, 139.8, 139.5, 129.8, 126.3, 124.7, 122.0, 113.7.

HRMS (ESI) Calculated for C₁₂H₁₀N₂O₂Na : 237.0634. Found: 237.0627 [M+Na]^+

Data is in accordance with literature.¹

2-methyl-N-(4-nitrophenyl)aniline (2b)

![Chemical Structure]

Synthesised according to general procedure B (column conditions: 5-30% EtOAc in hexane). The pure product was afforded as a yellow solid (26 mg, 56% yield).

^H NMR (400 MHz, Acetone-d₆) δ 8.09 (d, J = 9.3 Hz, 2H), 8.02 (s, 1H), 7.38 – 7.15 (m, 4H), 6.85 (d, J = 9.2 Hz, 2H), 2.26 (s, 3H).

^13C NMR (101 MHz, Acetone-d₆) δ 153.5, 139.4, 139.2, 134.6, 132.2, 127.9, 126.8, 126.1, 113.6, 18.0.

HRMS (APCI) Calculated for C₁₃H₁₃N₂O₂ : 229.0972. Found: 229.0964 [M+H]^+
Data is in accordance with literature.4

3-methyl-N-(4-nitrophenyl)aniline (2c)

Synthesised according to general procedure B (column conditions: 5-30% EtOAc in hexane). The pure product was afforded as a yellow solid (27 mg, 59% yield).

$^1$H NMR (400 MHz, Acetone-$d_6$) δ 8.36 (s, 1H), 8.11 (d, $J = 9.2$ Hz, 2H), 7.28 (t, $J = 7.7$ Hz, 1H), 7.18 – 7.07 (m, 4H), 7.00 – 6.93 (m, 1H), 2.34 (s, 3H).

$^{13}$C NMR (101 MHz, Acetone-$d_6$) δ 152.0, 141.2, 140.2, 139.9, 130.2, 126.8, 125.4, 122.8, 119.3, 114.4, 21.4.

HRMS (APCI) Calculated for C$_{13}$H$_{13}$N$_2$O$_2$: 229.0972. Found: 229.0964 [M+H]$^+$

Data is in accordance with literature.4

4-methyl-N-(4-nitrophenyl)aniline (2d)

Synthesised according to general procedure B (column conditions: 0-30% EtOAc in hexane). The pure product was afforded as an orange solid (29 mg, 64% yield).

$^1$H NMR (400 MHz, CDCl$_3$) δ 8.10 (d, $J = 9.1$ Hz, 2H), 7.20 (d, $J = 8.3$ Hz, 2H), 7.10 (d, $J = 8.0$ Hz, 2H), 6.87 (d, $J = 9.3$ Hz, 2H), 6.29 (s, 1H), 2.36 (s, 3H).

$^{13}$C NMR (101 MHz, CDCl$_3$) δ 151.0, 139.5, 136.8, 134.9, 130.4, 126.4, 122.8, 113.3, 21.1.

HRMS (ESI) Calculated for C$_{13}$H$_{11}$N$_2$O$_2$: 227.0821 Found: 227.0815 [M-H]$^-$

Data is in accordance with literature.4

4-chloro-N-(4-nitrophenyl)aniline (2e)

Synthesised according to general procedure B (column conditions: 0-30% EtOAc in hexane). The pure product was afforded as an orange solid (25 mg, 50% yield).
1H NMR (500 MHz, CDCl₃) δ 8.14 (d, J = 9.2 Hz, 2H), 7.35 (d, J = 8.8 Hz, 2H), 7.15 (d, J = 8.8 Hz, 2H), 6.92 (d, J = 9.3 Hz, 2H), 6.21 (s, 1H).

13C NMR (101 MHz, CDCl₃) δ 149.8, 140.3, 138.3, 130.0, 129.8, 126.4, 123.2, 114.0.

HRMS (ESI) Calculated for C₁₂H₈ClN₂O₂: 247.0280. Found: 247.0266 [M-H]^−

Data is in accordance with literature.⁴

4-fluoro-N-(4-nitrophenyl)aniline (2f)

Synthesised according to general procedure B (column conditions: 0-30% EtOAc in hexane). The pure product was afforded as an orange solid (23 mg, 50% yield).

1H NMR (400 MHz, CDCl₃) δ 8.11 (d, J = 9.4 Hz, 2H), 7.22 – 7.16 (m, 2H), 7.13 – 7.05 (m, 2H), 6.83 (d, J = 9.5 Hz, 2H), 6.16 (s, 1H).

13C NMR (101 MHz, CDCl₃) δ 160.2 (d, J = 245.0 Hz), 150.8, 143.4, 140.3, 135.5 (d, J = 2.8 Hz), 126.4, 125.0 (d, J = 8.0 Hz), 116.6 (d, J = 22.6 Hz), 113.3.

19F NMR (376 MHz, CDCl₃) δ -116.63 (s).

HRMS (APCI) Calculated for C₁₂H₉FN₂O₂: 232.0643. Found: 232.0646 [M]^+ 

Data is in accordance with literature.⁴

3-bromo-N-(4-nitrophenyl)aniline (2g)

Synthesised according to general procedure B (column conditions: 0-30% EtOAc in hexane). The pure product was afforded as an orange solid (46 mg, 78% yield).

1H NMR (400 MHz, acetone-d₆) δ 8.55 (s, 1H), 8.15 (d, J = 9.2 Hz, 2H), 7.47 (s, 1H), 7.37 – 7.31 (m, 2H), 7.29 – 7.24 (m, 1H), 7.22 (d, J = 9.4 Hz, 2H).

13C NMR (101 MHz, acetone-d₆) δ 150.8, 143.4, 140.8, 132.1, 126.9, 126.7, 123.9, 123.4, 120.0, 115.4.

HRMS (APCI) Calculated for C₁₂H₁₀BrN₂O₂: 292.9920. Found: 292.9922 [M+H]^+ 

Data is in accordance with literature.⁴

2-fluoro-N-(4-nitrophenyl)aniline (2h)
Synthesised according to general procedure B (column conditions: 0-30% EtOAc in hexane). The pure product was afforded as a yellow solid (32 mg, 68% yield).

\textbf{1H NMR (400 MHz, Acetone-d$_6$)} \(\delta 8.24\) (s, 1H), \(8.14\) (d, \(J = 9.2\) Hz, 2H), \(7.55 - 7.46\) (m, 1H), \(7.35 - 7.19\) (m, 3H), \(7.06\) (d, \(J = 8.5\) Hz, 2H).

\textbf{13C NMR (101 MHz, Acetone-d$_6$)} \(\delta 156.9\) (d, \(J = 245.3\) Hz), \(151.9, 140.4, 128.9\) (d, \(J = 11.8\) Hz), \(126.7\) (d, \(J = 7.9\) Hz), \(126.6, 25.9\) (d, \(J = 3.7\) Hz), \(125.5\) (d, \(J = 1.7\) Hz), \(117.3\) (d, \(J = 19.8\) Hz), \(114.6\).

\textbf{19F NMR (376 MHz, Acetone-d$_6$)} \(\delta -124.76\) (s).

\textbf{HRMS (ESI)} Calculated for C$_{12}$H$_9$FN$_2$O$_2$Na: 255.0546. Found: 255.0540 [M+Na]$^+$

\textbf{4-methoxy-N-(4-nitrophenyl)aniline (2i)}

Synthesised according to general procedure B (column conditions: 0-30% EtOAc in hexane). The pure product was afforded as a red solid (25 mg, 51% yield).

\textbf{1H NMR (400 MHz, CDCl$_3$)} \(\delta 8.08\) (d, \(J = 9.2\) Hz, 2H), \(7.16\) (d, \(J = 9.0\) Hz, 2H), \(6.94\) (d, \(J = 8.9\) Hz, 2H), \(6.75\) (d, \(J = 9.2\) Hz, 2H), \(6.15\) (s, 1H), \(3.83\) (s, 3H).

\textbf{13C NMR (101 MHz, CDCl$_3$)} \(\delta 157.6, 151.8, 139.2, 132.1, 126.5, 125.7, 115.1, 112.8, 55.7\).

\textbf{HRMS (ESI)} Calculated for C$_{13}$H$_{12}$N$_2$O$_2$Na: 267.0740. Found: 267.0736 [M+Na]$^+$

Data is in accordance with literature.$^4$

\textbf{3-methoxy-N-(4-nitrophenyl)aniline (2j)}

Synthesised according to general procedure B, on a 0.1 mmol scale (column conditions: 0-30% EtOAc in hexane). The pure product was afforded as an orange solid (9 mg, 54% yield).

\textbf{1H NMR (500 MHz, CDCl$_3$)} \(\delta 8.12\) (d, \(J = 9.2\) Hz, 2H), \(7.29\) (t, \(J = 8.1\) Hz, 1H), \(6.97\) (d, \(J = 9.1\) Hz, 2H), \(6.81 - 6.78\) (m, 1H), \(6.75\) (t, \(J = 2.3\) Hz, 1H), \(6.73 - 6.68\) (m, 1H), \(3.82\) (s, 3H).

\textbf{13C NMR (126 MHz, CDCl$_3$)} \(\delta 160.9, 150.0, 140.9, 140.1, 130.7, 126.4, 114.2, 114.1, 109.9, 107.8, 55.5\).

\textbf{HRMS (ESI)} Calculated for C$_{13}$H$_{12}$N$_2$O$_2$Na: 267.0740. Found: 267.0736 [M+Na]$^+$

S8
Data is in accordance with literature.4

3,5-dimethoxy-N-(4-nitrophenyl)aniline (2k)

Synthesised according to general procedure B (column conditions: 0-30% EtOAc in hexane). The pure product was afforded as a red solid (33 mg, 61% yield).

$^1$H NMR (500 MHz, DMSO-d$_6$) $\delta$ 9.27 (s, 1H), 8.09 (d, $J$ = 9.5 Hz, 2H), 7.10 (d, $J$ = 9.5 Hz, 2H), 6.37 (d, $J$ = 2.2 Hz, 2H), 6.25 (t, $J$ = 2.2 Hz, 1H), 3.74 (s, 6H).

$^{13}$C NMR (126 MHz, DMSO-d$_6$) $\delta$ 161.2, 150.5, 141.9, 138.1, 126.1, 114.0, 98.7, 95.3, 55.2.

HRMS (APCI) Calculated for C$_{24}$H$_{15}$N$_2$O$_4$: 275.1026. Found: 275.1015 [M+H]$^+$

MP 150-152 °C

4-nitro-N-(4-(trifluoromethyl)phenyl)aniline (2l)

Synthesised according to general procedure B (column conditions: 0-30% EtOAc in hexane). The pure product was afforded as a yellow solid (40 mg, 70% yield).

$^1$H NMR (400 MHz, Acetone-d$_6$) $\delta$ 8.76 (s, 1H), 8.18 (d, $J$ = 8.8 Hz, 2H), 7.70 (d, $J$ = 8.6 Hz, 2H), 7.48 (d, $J$ = 8.3 Hz, 2H), 7.33 (d, $J$ = 9.2 Hz, 2H).

$^{13}$C NMR (101 MHz, Acetone-d$_6$) $\delta$ 150.0, 145.5, 141.4, 127.6 (q, $J$ = 3.8 Hz), 126.6, 124.3 (q, $J$ = 32.6 Hz), 121.5, 120.0, 116.3.

$^{19}$F NMR (376 MHz, Acetone-d$_6$) $\delta$ -62.28 (s).

HRMS (APCI) Calculated for C$_{16}$H$_{10}$F$_3$N$_2$O$_2$: 283.0689. Found: 283.0686 [M+H]$^+$

Data is in accordance with literature.5

N-(4-nitrophenyl)naphthalen-1-amine (2m)
Synthesised according to general procedure B (column conditions: 0-25% EtOAc in hexane). The pure product was afforded as a brown solid (33 mg, 61% yield).

$^1$H NMR (400 MHz, Acetone-$_d_6$) $\delta$ 9.41 (s, 1H), 8.06 (d, $J = 9.0$ Hz, 2H), 8.02 – 7.96 (m, 2H), 7.84 (d, $J = 7.9$ Hz, 1H), 7.62 – 7.48 (m, 4H), 6.89 (d, $J = 9.4$ Hz, 2H).

$^{13}$C NMR (101 MHz, Acetone-$_d_6$) $\delta$ 153.0, 137.6, 135.6, 134.4, 128.8, 128.4, 126.5, 126.3, 126.2, 126.1, 125.7, 122.8, 121.3, 113.0.

HRMS (ESI) Calculated for C$_{16}$H$_{11}$N$_2$O$_2$: 263.0815. Found: 263.0812 [M-H]$^-$

Data is in accordance with literature.$^4$

N-(4-nitrophenyl)pyridin-2-amine (2n)

Synthesised according to general procedure B (column conditions: 0-50% EtOAc in hexane). The pure product was afforded as an orange solid (17 mg, 40% yield).

$^1$H NMR (500 MHz, Acetone-$_d_6$) $\delta$ 9.12 (s, 1H), 8.36 – 8.31 (m, 1H), 8.18 (d, $J = 9.4$ Hz, 2H), 8.01 (d, $J = 9.3$ Hz, 2H), 7.69 (t, $J = 8.7$ Hz, 1H), 7.01 (d, $J = 8.3$ Hz, 1H), 6.97 – 6.93 (m, 1H).

$^{13}$C NMR (126 MHz, Acetone-$_d_6$) $\delta$ 154.9, 148.2, 147.4, 140.3, 137.8, 125.0, 116.7, 116.6, 112.2.

HRMS (ESI) Calculated for C$_{13}$H$_9$N$_3$O$_2$Na: 238.0587. Found: 238.0581 [M+Na]$^+$

Data is in accordance with literature.$^6$

N-(4-nitrophenyl)quinolin-8-amine (2o)

Synthesised according to general procedure B (column conditions: 0-50% EtOAc in hexane). The pure product was afforded as an orange solid (26 mg, 50% yield).

$^1$H NMR (400 MHz, Acetone-$_d_6$) $\delta$ 9.19 (s, 1H), 8.90 (dd, $J = 4.2$, 1.7 Hz, 1H), 8.38 (dd, $J = 8.3$, 1.7 Hz, 1H), 8.25 (d, $J = 9.1$ Hz, 2H), 7.87 (dd, $J = 5.9$, 2.9 Hz, 1H), 7.69 – 7.55 (m, 5H).

$^{13}$C NMR (101 MHz, Acetone-$_d_6$) $\delta$ 150.0, 149.4, 140.4, 138.1, 137.4, 129.9, 127.8, 126.6, 123.2, 121.3, 116.9, 116.9, 113.8.

HRMS (ESI) Calculated for C$_{15}$H$_{11}$N$_3$O$_2$Na: 288.0743. Found: 288.0731 [M+Na]$^+$

Data is in accordance with literature.$^4$
2,4,6-trimethyl-N-(4-nitrophenyl)aniline (2p)

![Chemical structure](image)

Synthesised according to general procedure B (column conditions: 0-25% EtOAc in hexane). The pure product was afforded as a yellow solid (37 mg, 71% yield).

$^1$H NMR (500 MHz, CDCl$_3$) δ 8.06 (d, $J = 8.7$ Hz, 2H), 6.97 (s, 2H), 6.44 (d, $J = 8.7$ Hz, 2H), 5.86 (s, 1H), 2.32 (s, 3H), 2.16 (s, 6H).

$^{13}$C NMR (126 MHz, CDCl$_3$) δ 152.6, 138.7, 137.5, 136.5, 133.1, 129.6, 126.6, 111.7, 21.1, 18.2.

HRMS (APCI) Calculated for C$_{25}$H$_{27}$N$_2$O$_2$: 257.1285. Found: 257.1272 [M+H]$^+$

MP 125-127°C

2,6-diisopropyl-N-(4-nitrophenyl)aniline (2q)

![Chemical structure](image)

Synthesised according to general procedure B (column conditions: 0-25% EtOAc in hexane). The pure product was afforded as a yellow solid (31 mg, 51% yield).

$^1$H NMR (400 MHz, DMSO-d$_6$) δ 8.76 (s, 1H), 7.99 (d, $J = 34.0$ Hz, 2H), 7.39 – 7.32 (m, 1H), 7.27 (d, $J = 7.1$ Hz, 2H), 6.99 (s, 1H), 5.90 (s, 1H), 3.00 (h, $J = 6.9$ Hz, 2H), 1.13 (d, $J = 6.8$ Hz, 6H), 1.05 (d, $J = 6.9$ Hz, 6H).

$^{13}$C NMR (101 MHz, DMSO-d$_6$) δ 154.8, 146.9, 136.4, 133.2, 128.2, 126.8, 124.0, 113.2, 108.8, 27.9, 24.1, 23.0.

HRMS (APCI) Calculated for C$_{20}$H$_{25}$N$_2$O$_2$: 297.1603. Found: 297.1609 [M-H]$^-$

MP 140-142°C

2-(tert-butyl)-N-(4-nitrophenyl)aniline (2r)

![Chemical structure](image)

Synthesised according to general procedure B (column conditions: 0-30% EtOAc in hexane). The pure product was afforded as an orange solid (38 mg, 69% yield).

$^1$H NMR (500 MHz, DMSO-d$_6$) δ 8.64 (s, 1H), 8.01 (d, $J = 9.3$ Hz, 2H), 7.55 – 7.48 (m, 1H), 7.34 – 7.27 (m, 2H), 7.16 – 7.09 (m, 1H), 6.58 (d, $J = 9.3$ Hz, 2H), 1.31 (s, 9H).
**13C NMR** (126 MHz, DMSO-d$_6$) δ 154.6, 147.7, 138.1, 136.6, 130.9, 127.6, 127.5, 127.4, 126.2, 112.3, 34.9, 30.6.

**HRMS (APCI)** Calculated for C$_{16}$H$_{19}$N$_2$O$_2$: 271.1441. Found: 271.1435 [M+H]$^+$

**MP** 91-94°C

2-methoxy-4-nitro-N-phenylaniline (2s)

![2-methoxy-4-nitro-N-phenylaniline](image)

Synthesised according to general procedure B (column conditions: 0-30% EtOAc in hexane). The pure product was afforded as a yellow solid (32 mg, 65% yield).

**1H NMR** (400 MHz, CDCl$_3$) δ 7.80 – 7.70 (m, 1H), 7.66 (s, 1H), 7.31 (t, $J = 8.1$ Hz, 2H), 7.21 – 7.13 (m, 2H), 7.12 – 7.06 (m, 1H), 7.04 (d, $J = 9.0$ Hz, 1H), 3.93 (s, 3H).

**13C NMR** (101 MHz, CDCl$_3$) δ 146.0, 140.8, 139.5, 139.0, 129.8, 124.6, 122.2, 119.2, 109.5, 105.7, 56.3.

**HRMS (APCI)** Calculated for C$_{13}$H$_{13}$N$_2$O$_2$: 245.0921. Found: 245.0914 [M+H]$^+$

Data is in accordance with literature.7

5-nitro-N-phenylpyridin-2-amine (2t)

![5-nitro-N-phenylpyridin-2-amine](image)

Synthesised according to general procedure B, 0.1 mmol scale (column conditions: 0-40% EtOAc in hexane). The pure product was afforded as a yellow solid (14 mg, 63% yield).

**1H NMR** (500 MHz, Acetone-d$_6$) δ 9.07 (d, $J = 2.7$ Hz, 1H), 8.31 (dd, $J = 9.3$, 2.8 Hz, 1H), 7.76 (d, $J = 8.1$ Hz, 2H), 7.39 (t, $J = 7.6$ Hz, 2H), 7.13 (t, $J = 7.4$ Hz, 1H), 6.99 (d, $J = 9.3$ Hz, 1H).

**13C NMR** (126 MHz, Acetone-d$_6$) δ 160.0, 146.3, 140.3, 137.7, 133.5, 129.8, 124.6, 121.5, 110.4.

**HRMS (APCI)** Calculated for C$_{11}$H$_{10}$N$_3$O$_2$: 216.0768. Found: 216.0761 [M+H]$^+$

Data is in accordance with literature.8
Sulfinamide Starting Materials

4-nitro-N-phenylbenzenesulfinamide (3a)

Prepared according to general procedure A, 4 mmol scale (column conditions: 0-40% EtOAc in hexane). The pure product was afforded as a yellow solid (519 mg, 49% yield).

$^1$H NMR (500 MHz, DMSO-d$_6$) δ 9.59 (s, 1H), 8.40 (d, $J$ = 9.1 Hz, 2H), 7.98 (d, $J$ = 9.1 Hz, 2H), 7.25 (t, $J$ = 7.7 Hz, 2H), 7.07 (d, $J$ = 7.4 Hz, 2H), 6.97 (t, $J$ = 7.4 Hz, 1H).

$^{13}$C NMR (126 MHz, DMSO-d$_6$) δ 151.5, 149.1, 141.2, 129.4, 127.4, 124.2, 122.7, 118.2.

HRMS (ESI) Calculated for C$_{12}$H$_9$N$_2$O$_3$S: 261.0339. Found: 261.0334 [M-H]⁻.

Data is in accordance with literature.$^9$

4-nitro-N-(o-tolyl)benzenesulfinamide (3b)

Prepared according to general procedure A (column conditions: 5-40% EtoAc in hexane). The pure product was afforded as an orange solid (83 mg, 30% yield).

$^1$H NMR (500 MHz, Acetone-d$_6$) δ 8.40 (d, $J$ = 9.0 Hz, 2H), 8.12 – 8.03 (m, 3H), 7.39 – 7.33 (m, 1H), 7.19 (d, $J$ = 7.2 Hz, 1H), 7.11 (t, $J$ = 7.7 Hz, 1H), 7.01 (t, $J$ = 7.5 Hz, 1H), 2.32 (s, 3H).

$^{13}$C NMR (126 MHz, Acetone-d$_6$) δ 153.2, 150.5, 140.1, 131.7, 131.0, 128.3, 127.5, 125.3, 124.7, 122.6, 18.2.

HRMS (APCI) Calculated for C$_{13}$H$_{13}$N$_2$O$_3$S: 277.0641. Found: 277.0631 [M+H]$^+$

MP 120-123°C

4-nitro-N-(m-tolyl)benzenesulfonamide (3c)

Prepared according to general procedure A (column conditions: 5-40% EtOAc in hexane). The pure product was afforded as a yellow solid (202 mg, 73% yield).
**1H NMR** (500 MHz, Acetone-\(\text{d}_6\)) \(\delta\) 8.45 – 8.39 (m, 3H), 8.07 (d, \(J = 8.2\) Hz, 2H), 7.15 (t, \(J = 7.8\) Hz, 1H), 7.02 (s, 1H), 6.97 (d, \(J = 8.5\) Hz, 1H), 6.86 (d, \(J = 7.5\) Hz, 1H), 2.28 (s, 3H).

**13C NMR** (126 MHz, Acetone-\(\text{d}_6\)) \(\delta\) 153.1, 150.5, 142.2, 140.0, 130.0, 128.2, 124.8, 124.8, 120.2, 116.8, 21.4.

**HRMS (APCI)** Calculated for C_{13}H_{13}N_{2}O_{3}S: 277.0641. Found: 277.0634 [M+H]^+.

**MP** 119-121 °C

4-nitro-N-(p-tolyl)benzenesulfinamide (3d)

Synthesised according to general procedure A (column conditions: 5-40% EtOAc in hexane). The pure product was afforded as a yellow solid (185 mg, 67% yield).

**1H NMR** (400 MHz, Acetone-\(\text{d}_6\)) \(\delta\) 8.39 (d, \(J = 8.8\) Hz, 2H), 8.37 (s, 1H), 8.06 (d, \(J = 8.8\) Hz, 2H), 7.12 – 7.02 (m, 4H), 2.25 (s, 3H).

**13C NMR** (101 MHz, Acetone-\(\text{d}_6\)) \(\delta\) 153.2, 150.6, 141.0, 130.1, 128.7, 128.2, 124.9, 20.7.

**HRMS (ESI)** Calculated for C_{13}H_{11}N_{2}O_{3}S: 275.0496. Found: 275.0487 [M-H]^-

Data is in accordance with literature.\(^{10}\)

**N-(4-chlorophenyl)-4-nitrobenzenesulfinamide (3e)**

Synthesised according to general procedure A (column conditions: 5-40% EtOAc in hexane). The pure product was afforded as a red solid (85 mg, 29% yield).

**1H NMR** (400 MHz, Acetone-\(\text{d}_6\)) \(\delta\) 8.66 (s, 1H), 8.43 (d, \(J = 9.1\) Hz, 2H), 8.07 (d, \(J = 9.1\) Hz, 2H), 7.29 (d, \(J = 9.1\) Hz, 2H), 7.19 (d, \(J = 8.9\) Hz, 2H).

**13C NMR** (101 MHz, Acetone-\(\text{d}_6\)) \(\delta\) 152.6, 150.6, 141.0, 130.1, 128.7, 128.2, 124.9, 121.4.

**HRMS (ESI)** Calculated for C_{13}H_{9}ClN_{2}O_{3}S: 294.9950. Found: 294.9942 [M-H]^-

**MP** 154-156 °C
**N-(4-fluorophenyl)-4-nitrobenzenesulfinamide (3f)**

![Structure of 3f]

Synthesised according to general procedure A (column conditions: 5-40% EtOAc in hexane). The pure product was afforded as a yellow solid (144 mg, 52% yield).

**^1H NMR** (400 MHz, Acetone-\(\text{d}_6\)) \(\delta\) 8.51 (s, 1H), 8.41 (d, \(J = 8.9\) Hz, 2H), 8.06 (d, \(J = 8.9\) Hz, 2H), 7.25 – 7.15 (m, 2H), 7.11 – 7.00 (m, 2H).

**^13C NMR** (101 MHz, Acetone-\(\text{d}_6\)) \(\delta\) 159.2 (d, \(J = 240.2\) Hz), 151.8, 149.6, 137.0, 127.3, 123.9, 121.8 (d, \(J = 8.2\) Hz), 115.7 (d, \(J = 22.9\) Hz).

**^19F NMR** (376 MHz, Acetone-\(\text{d}_6\)) \(\delta\) -121.16 (s).

**HRMS (APCI)** Calculated for C\(_{12}\)H\(_{10}\)FN\(_2\)O\(_3\)S: 281.0391. Found: 281.0383 [M+H]^+.

**MP** 132-134°C

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**N-(3-bromophenyl)-4-nitrobenzenesulfinamide (3g)**

![Structure of 3g]

Synthesised according to general procedure A (column conditions: 5-40% EtOAc in hexane). The pure product was afforded as a yellow solid (241 mg, 71% yield).

**^1H NMR** (500 MHz, DMSO-\(\text{d}_6\)) \(\delta\) 9.81 (s, 1H), 8.41 (d, \(J = 8.5\) Hz, 2H), 8.00 (d, \(J = 8.9\) Hz, 2H), 7.25 (t, \(J = 2.0\) Hz, 1H), 7.21 (t, \(J = 7.9\) Hz, 1H), 7.18 – 7.13 (m, 1H), 7.11 – 7.05 (m, 1H).

**^13C NMR** (126 MHz, DMSO-\(\text{d}_6\)) \(\delta\) 151.0, 149.3, 143.1, 131.4, 127.4, 125.2, 124.2, 122.1, 120.3, 116.8.

**HRMS (APCI)** Calculated for C\(_{12}\)H\(_{8}\)BrN\(_2\)O\(_3\)S: 338.9444. Found: 338.9442 [M-H]^−.

**MP** 108-109°C

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**N-(2-fluorophenyl)-4-nitrobenzenesulfinamide (3h)**

![Structure of 3h]

Synthesised according to general procedure A (column conditions: 5-40% EtOAc in hexane). The pure product was afforded as an off-white solid (189 mg, 68% yield).
1H NMR (500 MHz, DMSO-d6) δ 9.59 (s, 1H), 8.39 (d, J = 9.1 Hz, 2H), 7.95 (d, J = 8.8 Hz, 2H), 7.31 – 7.15 (m, 2H), 7.09 – 7.00 (m, 2H).

13C NMR (126 MHz, DMSO-d6) δ 153.7 (d, J = 243.6 Hz), 151.2, 149.1, 128.2 (d, J = 12.6 Hz), 127.4, 124.8 – 124.6 (m), 124.1, 122.2 (d, J = 1.9 Hz), 116.0 (d, J = 19.2 Hz).

19F NMR (471 MHz, DMSO-d6) δ -126.15 – -126.23 (m).

HRMS (APCI) Calculated for C12H10FN2O3S: 281.0391. Found: 281.0387 [M+H]+

MP 142-144°C

N-(4-methoxyphenyl)-4-nitrobenzenesulfinamide (3i)

Synthesised according to general procedure A (column conditions: 5-40% EtOAc in hexane). The pure product was afforded as a bronze solid (161 mg, 55% yield).

1H NMR (400 MHz, Acetone-d6) δ 8.39 (d, J = 9.1 Hz, 2H), 8.20 (s, 1H), 8.03 (d, J = 9.1 Hz, 2H), 7.09 (d, J = 9.0 Hz, 2H), 6.84 (d, J = 8.5 Hz, 2H), 3.74 (s, 3H).

13C NMR (101 MHz, Acetone-d6) δ 157.6, 153.2, 150.4, 134.2, 128.3, 124.7, 123.6, 115.2, 55.7.

HRMS (ESI) Calculated for C13H11N2O4S: 291.0445. Found: 291.0435 [M-H]-

MP 162-163°C

N-(3-methoxyphenyl)-4-nitrobenzenesulfinamide (3j)

Synthesised according to general procedure A (column conditions: 0-40% EtOAc in hexane). The pure product was afforded as a brown solid (37 mg, 13% yield).

1H NMR (400 MHz, Acetone-d6) δ 8.52 (s, 1H), 8.43 (d, J = 8.9 Hz, 2H), 8.08 (d, J = 8.9 Hz, 2H), 7.23 – 7.14 (m, 1H), 6.80 – 6.73 (m, 2H), 6.64 – 6.57 (m, 1H), 3.75 (s, 3H).

13C NMR (101 MHz, Acetone-d6) δ 161.6, 53.1, 143.5, 131.0, 128.2, 126.2, 124.8, 111.8, 109.4, 105.5, 55.5.

HRMS (ESI) Calculated for C13H11N2O4S: 291.0445. Found: 291.0435 [M-H]-

MP 100-102°C
**N-(3,5-dimethoxyphenyl)-4-nitrobenzenesulfinamide (3k)**

![Chemical Structure](image)

Synthesised according to general procedure A (column conditions: 0-50% EtOAc in hexane). The pure product was afforded as an orange solid (170 mg, 53% yield).

**NMR**

^1H NMR (400 MHz, DMSO-d$_6$) δ 9.56 (s, 1H), 8.42 (d, J = 8.9 Hz, 2H), 7.98 (d, J = 8.7 Hz, 2H), 6.23 (d, J = 2.2 Hz, 2H), 6.13 (t, J = 2.2 Hz, 1H), 3.67 (s, 6H).

^13C NMR (101 MHz, DMSO-d$_6$) δ 161.0, 151.4, 149.1, 143.1, 127.3, 124.2, 96.2, 94.4, 55.1.

HRMS (APCI) Calculated for C$_{14}$H$_{15}$N$_2$O$_5$S: 323.0696. Found: 323.0688 [M+H]$^+$

**MP** 130-132 °C

**4-nitro-N-(4-(trifluoromethyl)phenyl)benzenesulfinamide (3l)**

![Chemical Structure](image)

Synthesised according to general procedure A (column conditions: 5-40% EtOAc in hexane). The pure product was afforded as a yellow solid (204 mg, 62% yield).

**NMR**

^1H NMR (400 MHz, Acetone-d$_6$) δ 9.03 (s, 1H), 8.44 (d, J = 9.1 Hz, 2H), 8.11 (d, J = 8.7 Hz, 2H), 7.64 (d, J = 8.3 Hz, 2H), 7.37 (d, J = 8.4 Hz, 2H).

^13C NMR (101 MHz, Acetone-d$_6$) δ 152.3, 150.8, 146.0, 128.2, 127.5 (q, J = 3.9 Hz), 125.0, 124.8 – 124.0 (m), 118.6.

^19F NMR (376 MHz, Acetone-d$_6$) δ -62.36 (s).

HRMS (APCI) Calculated for C$_{13}$H$_9$F$_3$N$_2$O$_3$S: 330.0280. Found: 330.0280 [M]$^+$

**MP** 148-152 °C

**N-(naphthalen-1-yl)-4-nitrobenzenesulfinamide (3m)**

![Chemical Structure](image)
Synthesised according to general procedure A (column conditions: 0-40% EtOAc in hexane). The pure product was afforded as a brown solid (113 mg, 18% yield).

$^1$H NMR (500 MHz, DMSO-d$_6$) $\delta$ 9.79 (s, 1H), 8.36 (d, $J = 8.9$ Hz, 2H), 8.22 – 8.16 (m, 1H), 8.04 (d, $J = 8.8$ Hz, 2H), 7.92 – 7.87 (m, 1H), 7.65 (d, $J = 8.1$ Hz, 1H), 7.59 – 7.50 (m, 2H), 7.46 (d, $J = 7.5$ Hz, 1H), 7.38 (t, $J = 7.8$ Hz, 1H).

$^{13}$C NMR (126 MHz, DMSO-d$_6$) $\delta$ 151.5, 149.0, 136.6, 133.8, 128.1, 127.5, 126.4, 126.0, 125.7, 124.4, 124.0, 122.6, 117.8.

HRMS (ESI) Calculated for C$_{16}$H$_{12}$N$_2$O$_3$SNa: 335.0466. Found: 335.0461 [M+Na]$^+$

MP 120-122 °C

4-nitro-N-(pyridin-2-yl)benzenesulfinamide (3n)

Synthesised according to general procedure A (column conditions: 0-40% EtOAc in hexane). The pure product was afforded as a white solid (144 mg, 55% yield).

$^1$H NMR (400 MHz, DMSO-d$_6$) $\delta$ 10.23 (s, 1H), 8.43 (d, $J = 8.6$ Hz, 2H), 8.29 – 8.22 (m, 1H), 8.04 (d, $J = 9.1$ Hz, 2H), 7.73 – 7.64 (m, 1H), 7.03 – 6.96 (m, 1H), 6.77 (d, $J = 8.2$ Hz, 1H).

$^{13}$C NMR (101 MHz, DMSO-d$_6$) $\delta$ 154.3, 152.0, 149.1, 147.7, 138.6, 127.1, 124.1, 117.7, 110.7.

HRMS (ESI) Calculated for C$_{11}$H$_9$N$_3$O$_3$SNa: 286.0257. Found: 286.0251 [M+Na]$^+$

MP 132-134 °C

4-nitro-N-(quinolin-8-yl)benzenesulfinamide (3o)

Synthesised according to general procedure A (column conditions: 0-60% EtOAc in hexane). The pure product was afforded as a brown solid (113 mg, 36% yield).

$^1$H NMR (400 MHz, DMSO-d$_6$) $\delta$ 9.99 (s, 1H), 8.90 (dd, $J = 4.2$, 1.7 Hz, 1H), 8.43 – 8.31 (m, 3H), 8.00 (d, $J = 8.9$ Hz, 2H), 7.64 – 7.56 (m, 1H), 7.56 – 7.49 (m, 1H), 7.44 – 7.34 (m, 2H).

$^{13}$C NMR (101 MHz, DMSO-d$_6$) $\delta$ 151.6, 149.0, 139.0, 136.8, 136.4, 128.3, 127.6, 127.5, 126.6, 124.2, 122.2, 121.3, 114.7.

HRMS (ESI) Calculated for C$_{15}$H$_{11}$N$_3$O$_3$SNa: 336.0413. Found: 336.0410 [M+Na]$^+$
MP 154-156 °C

N-mesityl-4-nitrobenzenesulfinamide (3p)

Synthesised according to general procedure A (column conditions: 0-30% EtOAc in hexane). The pure product was afforded as an off-white solid (166 mg, 55% yield).

$^1$H NMR (500 MHz, DMSO-d$_6$) δ 8.45 (d, $J = 8.8$ Hz, 2H), 8.35 (s, 1H), 8.11 (d, $J = 9.0$ Hz, 2H), 6.91 (s, 2H), 2.32 (s, 6H), 2.22 (s, 3H).

$^{13}$C NMR (126 MHz, DMSO-d$_6$) δ 152.6, 149.1, 135.5, 135.1, 134.5, 129.1, 127.2, 124.1, 20.4, 19.0.

HRMS (ESI) Calculated for C$_{15}$H$_{15}$N$_2$O$_3$S: 303.0798. Found: 303.0798 [M-H]$^-$

MP 150-152 °C

$N$-(2,6-diisopropylphenyl)-4-nitrobenzenesulfinamide (3q)

Synthesised according to general procedure A (column conditions: 0-30% EtOAc in hexane). The pure product was afforded as a yellow solid (167 mg, 24% yield).

$^1$H NMR (400 MHz, DMSO-d$_6$) δ 8.56 (s, 1H), 8.48 (d, $J = 9.3$ Hz, 2H), 8.08 (d, $J = 9.2$ Hz, 2H), 7.30 – 7.17 (m, 3H), 3.52 (p, $J = 6.8$ Hz, 2H), 1.17 (dd, $J = 9.9$, 6.8 Hz, 12H).

$^{13}$C NMR (101 MHz, DMSO-d$_6$) δ 152.6, 149.1, 146.7, 133.6, 127.5, 127.0, 124.2, 123.8, 27.6, 24.1, 24.0.

HRMS (ESI) Calculated for C$_{18}$H$_{21}$N$_2$O$_3$S: 345.1273. Found: 345.1278 [M-H]$^-$

MP 90-92 °C

$N$-(2-(tert-butyl)phenyl)-4-nitrobenzenesulfinamide (3r)

Synthesised according to general procedure A (column conditions: 0-40% EtOAc in hexane). The pure product was afforded as a beige solid (179 mg, 56% yield).
$^1$H NMR (400 MHz, DMSO-$d_6$) $\delta$ 8.51 (s, 1H), 8.42 (d, $J = 9.0$ Hz, 2H), 8.03 (d, $J = 8.6$ Hz, 2H), 7.50 (dd, $J = 7.5$, 1.9 Hz, 1H), 7.39 – 7.33 (m, 1H), 7.21 – 7.08 (m, 2H), 1.38 (s, 9H).

$^{13}$C NMR (101 MHz, DMSO-$d_6$) $\delta$ 151.8, 149.0, 143.9, 139.1, 127.31, 127.3, 126.9, 126.6, 125.8, 124.1, 34.9, 30.8.

HRMS (ESI) Calculated for C$_{16}$H$_{18}$N$_2$O$_3$SNa: 341.0930. Found: 341.0917 [M+Na]$^+$.  

MP 96-98 °C

2-methoxy-4-nitro-N-phenylbenzenesulfinamide (3s)

Synthesised by adaptation of a literature procedure.$^{11}$ A 100 mL round-bottomed flask was charged with 2-methoxy-4-nitrobenzenesulfonyl chloride (1 g, 4 mmol), evacuated under vacuum and filled with nitrogen. Anhydrous DCM (10 mL) was added, alongside NEt$_3$ (8 mmol, 1.12 mL) and the solution was stirred at 0 °C. A separate 100 mL round-bottomed flask was charged with PPh$_3$ (1.052 g, 4 mmol), evacuated under vacuum and filled with nitrogen. Anhydrous DCM (10 mL) and aniline (365 µL, 4 mmol) was added and the solution was stirred at 0°C. The contents of the second flask were added dropwise to the first flask over ice, and the reaction mixture was left stirring for 16 hours. The reaction mixture was extracted with DCM (20 mL), washed with H$_2$O (3 x 20 mL), dried with anhydrous MgSO$_4$. The organic layers were then filtered, concentrated in vacuo and purified by flash column chromatography (0-40% EtOAc in hexane). The pure product was afforded as a yellow solid (247 mg, 21% yield).

$^1$H NMR (500 MHz, DMSO-$d_6$) $\delta$ 9.28 (s, 1H), 8.07 – 7.97 (m, 2H), 7.89 (d, $J = 1.9$ Hz, 1H), 7.24 (t, 2H), 7.02 (d, $J = 7.7$ Hz, 2H), 6.95 (t, $J = 7.4$ Hz, 1H), 3.94 (s, 3H).

$^{13}$C NMR (126 MHz, DMSO-$d_6$) $\delta$ 156.3, 150.6, 142.0, 138.6, 129.2, 127.1, 122.3, 117.7, 115.5, 106.9, 57.0.

HRMS (ESI) Calculated for C$_{13}$H$_{12}$N$_2$O$_3$SNa: 315.0410. Found: 315.0405 [M+Na]$^+$.  

MP 104-106 °C

5-nitro-N-phenylpyridine-2-sulfinamide (3t)

Synthesised by adaptation of a literature procedure.$^{10}$ A 50 mL round-bottomed flask was charged with KF (1 mmol, 59 mg). CH$_3$CN (4.2 mL) and H$_2$O (0.8 mL) were added and the flask was stirred at 0 °C. Meta-chloroperoxybenzoic acid, 70% (m-CBPA) (1 mmol, 172 mg) was added slowly and the mixture was left to stir for 30 min. Sulfenamide 3tp (0.5 mmol, 132 mg) was added portion-wise and
the reaction mixture was stirred at 0 °C for 30 min. The reaction mixture was then extracted with EtOAc (20 mL), washed with saturated aqueous NaHCO_3 (3 x 20 mL) and dried with anhydrous MgSO_4. The organic layers were then filtered, concentrated *in vacuo* and purified by flash column chromatography (0-50% EtOAc in hexane). The pure product was afforded as a white solid (58 mg, 45% yield).

\^H NMR (500 MHz, DMSO-d_6) δ 9.71 (s, 1H), 9.48 – 9.40 (m, 1H), 8.84 (dd, *J* = 8.7, 2.6 Hz, 1H), 8.26 (dd, *J* = 8.5, 0.7 Hz, 1H), 7.22 (t, *J* = 7.9 Hz, 2H), 7.04 (d, *J* = 7.4 Hz, 2H), 6.93 (t, *J* = 7.4 Hz, 1H).

\^C NMR (126 MHz, DMSO-d_6) δ 168.8, 145.1, 144.9, 141.2, 133.5, 129.3, 122.5, 121.9, 117.7.

HRMS (APCI) Calculated for C_{11}H_{10}N_{3}O_{3}S: 264.0437. Found: 264.0430 [M+H]^+.

MP 155-158 °C

Compounds Synthesised for Mechanistic investigations

4-nitro-N-phenylbenzenesulfonamide (1a)

Prepared according to a literature procedure.\[^{12}\] A 50 mL round-bottomed flask was charged with 4-nitrobenzenesulfonyl chloride (244 mg, 1.1 mmol), which was evacuated under vacuum and filled with nitrogen. Pyridine (5 mL) was added, alongside aniline (91 µL, 1 mmol), and the reaction mixture was stirred at room temperature for 3 hours. Toluene (10 mL) was added to the reaction mixture and the solvent was evaporated *in vacuo*. The reaction mixture was then dissolved in DCM (20 mL), extracted from H_2O (2 x 20 mL), dried with anhydrous MgSO_4, filtered and concentrated *in vacuo*. The crude product was then purified by flash column chromatography (10-30% EtOAc in hexane) affording the pure product as a white solid (126 mg, 45%).

\^H NMR (500 MHz, Acetone-d_6) δ 9.29 (s, 1H), 8.38 (d, *J* = 8.6 Hz, 2H), 8.05 (d, *J* = 9.0 Hz, 2H), 7.29 (t, *J* = 7.2 Hz, 2H), 7.23 (d, *J* = 7.6 Hz, 2H), 7.14 (t, *J* = 6.9 Hz, 1H).

\^C NMR (126 MHz, Acetone-d_6) δ 151.2, 146.2, 137.9, 130.2, 129.5, 126.2, 125.2, 122.4.

HRMS (APCI) Calculated for C_{12}H_{10}N_{2}O_{4}S: 277.0289. Found: 277.0280 [M-H].

Data is in accordance with literature.\[^{12}\]

\(N\)-methyl-4-nitro-N-phenylbenzenesulfinamide (3u)
Synthesised according to general procedure A (column conditions: 5-40% EtOAc in hexane). The pure product was afforded as a brown solid (138 mg, 50% yield).

$^1$H NMR (500 MHz, Acetone-$d_6$) $\delta$ 8.46 (d, $J = 9.0$ Hz, 2H), 8.03 (d, $J = 8.2$ Hz, 2H), 7.45 – 7.36 (m, 4H), 7.23 – 7.16 (m, 1H), 2.90 (s, 3H).

$^{13}$C NMR (126 MHz, Acetone-$d_6$) $\delta$ 151.6, 146.6, 130.3, 128.3, 125.4, 125.1, 122.1, 31.6.

HRMS (APCI) Calculated for C$_{13}$H$_{13}$N$_2$O$_3$S: 277.0641. Found: 277.0640 [M+H]$^+$

MP 90-95 °C

2-((4-nitrophenyl)thio)aniline (11)

A 100 mL round-bottomed flask was charged with 4-fluoronitrobenzene (282 mg, 2 mmol) and K$_2$CO$_3$ (553 mg, 4 mmol), which was evacuated under vacuum and filled with nitrogen. Anhydrous DMF (10 mL) was added to the mixture which was stirred in a pre-warmed oil bath at 70 °C. 2-aminobenzenethiol (0.207 mL, 2 mmol) was added dropwise and the mixture was left to stir at 70 °C for 1 h. The reaction mixture was dissolved in EtOAc (20 mL) and washed with 10% (w/v) aqueous LiCl (3 x 20 mL). The aqueous layer was then extracted with EtOAc (3 x 20 mL) and the combined organic layers were dried with anhydrous MgSO$_4$, filtered and concentrated in vacuo. The crude product was then purified by flash column chromatography (0-40% EtOAc in hexane), affording the pure product as a brown solid (456 mg, 93% yield).

$^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 8.06 (d, $J = 9.2$ Hz, 2H), 7.47 – 7.42 (m, 1H), 7.36 – 7.29 (m, 1H), 7.11 (d, $J = 9.1$ Hz, 2H), 6.86 – 6.83 (m, 1H), 6.83 – 6.78 (m, 1H), 4.29 (s, 2H).

$^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 149.2, 147.3, 145.4, 137.8, 132.5, 125.6, 124.2, 119.3, 115.8, 111.4.

HRMS (ESI) Calculated for C$_{12}$H$_{10}$N$_2$O$_2$SNa: 269.0355. Found: 269.0347 [M+Na]$^+$

Data is in accordance with literature.$^{13}$

2-((4-nitrophenyl)sulfinyl)aniline (10)

A 100 mL round-bottomed flask was charged with 2-((4-nitrophenyl)thio)aniline 11 (440 mg, 1.78 mmol), evacuated under vacuum and filled with nitrogen. DCM (10 mL) was added and the mixture was stirred at 0 °C. A second 100 mL round-bottomed flask was charged with Meta-chloroperoxybenzoic acid, 70% (m-CBPA) (230 mg, 1.9 mmol), evacuated under vacuum and filled with nitrogen. DCM (10 mL) was added and the contents of this flask were added slowly to the first flask. The reaction mixture was stirred at 0 °C for 1 h, at which point the ice bath was removed and the mixture was allowed to warm to room temperature. On consumption of starting material (monitored
by TLC) the reaction was quenched with saturated aqueous NaHCO₃ (20 mL) and extracted with DCM (2 x 20 mL). The combined organic layers were then dried with anhydrous MgSO₄, filtered, and concentrated in vacuo. The crude product was then purified by flash column chromatography (20-60% EtOAc in hexane), affording the pure product as a yellow solid (163 mg, 35% yield).

**¹H NMR** (500 MHz, CDCl₃) δ 8.29 (d, J = 9.1 Hz, 2H), 7.72 (d, J = 8.8 Hz, 2H), 7.49 (dd, J = 7.7, 1.5 Hz, 1H), 7.32 – 7.25 (m, 1H), 6.82 (td, J = 7.6, 1.1 Hz, 1H), 6.64 – 6.58 (m, 1H), 4.89 (s, 2H).

**¹³C NMR** (126 MHz, CDCl₃) δ 150.9, 149.1, 148.0, 134.0, 128.6, 125.9, 124.0, 122.6, 118.0, 117.8.

**HRMS (ESI)** Calculated for C₁₁H₁₀N₂O₃SNa: 285.0304. Found: 285.0296 [M+Na]⁺

### Sulfonamide Starting Material Precursors

#### Methyl 4-nitrobenzenesulfinate (4)

![Methyl 4-nitrobenzenesulfinate](image)

Prepared according to a literature procedure. A 250 ml round-bottomed flask was charged with 1,2-bis(4-nitrophenyl)disulfane (2.48 g, 8 mmol), which was then dissolved in MeOH (50 mL) and DCM (50 mL). The solution was stirred at 0 °C, and then N-bromosuccinimide (7.2 g, 40 mmol) was added slowly. The reaction mixture was stirred overnight. The reaction mixture was then extracted with DCM (50 mL), washed with saturated aqueous NaHCO₃ (2 x 50 mL), dried with anhydrous Na₂SO₄, filtered, and concentrated in vacuo. The crude product was purified by flash column chromatography (0-30% EtOAc in hexane) to afford a light yellow solid (2.752 g, 85% yield).

**¹H NMR** (400 MHz, CDCl₃) δ 8.40 (d, J = 8.7 Hz), 7.90 (d, J = 8.6 Hz, 2H), 3.54 (s, 3H).

**¹³C NMR** (101 MHz, CDCl₃) δ 150.3, 150.2, 126.9, 124.3, 50.7.

**HRMS (ESI)** Calculated for C₇H₇NO₄S: 201.0096 Found: 201.0101 [M⁺]

Data is in accordance with literature.

#### S-(5-nitropyridin-2-yl)-N-phenylthiohydroxylamine (7b)

![S-(5-nitropyridin-2-yl)-N-phenylthiohydroxylamine](image)

Prepared by adaptation of a literature procedure. A 100 mL round-bottomed flask was charged with AgNO₃ (350 mg, 2 mmol) and 5-methyl-2-[(5-nitropyridin-2-yl)disulfany]pyridine (612 mg, 2 mmol) and the flask was evacuated under vacuum and filled with nitrogen. Anhydrous DCM (10 mL) and MeOH (20 mL) were added and the flask was stirred at 0 °C. Aniline (0.9 mL, 10 mmol) was added dropwise and the reaction mixture was stirred overnight. The reaction mixture was then filtered and concentrated in vacuo. The concentrated product was then extracted with DCM (30 mL), washed with
H$_2$O (2 x 20 mL), dried with anhydrous MgSO$_4$, filtered and concentrated in vacuo. The crude product was purified by flash column chromatography (0-30% EtOAc in hexane) to afford a yellow solid (189 mg, 38% yield).

$^1$H NMR (500 MHz, DMSO-d$_6$) δ 9.23 (d, $J = 2.4$ Hz, 1H), 8.49 (dd, $J = 8.9$, 2.6 Hz, 1H), 8.30 (s, 1H), 7.35 (d, $J = 8.4$ Hz, 1H), 7.23 (t, $J = 8.3$ Hz, 2H), 7.01 (d, $J = 7.6$ Hz, 2H), 6.84 (t, $J = 7.3$ Hz, 1H).

$^{13}$C NMR (126 MHz, DMSO-d$_6$) δ 173.1, 146.0, 145.1, 141.5, 132.3, 129.4, 120.3, 117.0, 114.4.

HRMS (APCI) Calculated for C$_{23}$H$_{18}$N$_2$O$_2$S: 248.0488. Found: 248.0477 [M+H]$^+$

MP 112-114 °C
4. Poor-yielding and Unsuccessful Substrates

**N-Aryl Scope**

- O₂N
  - 25%

- O₂N
  - 0%

- O₂N
  - 0%

- O₂N
  - 0%

**S-Aryl Scope**

- NO₂
  - 16%

- 0%

- 0%

- 0%

- NC
  - 0%

- Cl
  - 0%

- trace
5. NMR Spectra for Synthesised Compounds

2a
500 MHz

2a
126 MHz
378 MHz

400 MHz

S56
3I
101 MHz

3I
376 MHz
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