Supporting Information

Metal Free Bi(hetero)aryl Synthesis: A Benzyne Truce–Smiles Rearrangement

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Supporting Information

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1. General Information:

Nuclear Magnetic Resonance (NMR) spectra were recorded on 500 or 400 MHz Bruker NMR spectrometers in CDCl$_3$ at 298 K (unless stated otherwise). All chemical shift values are reported in parts per million (ppm) with coupling constant ($J$) values reported in Hz. All spectra were referenced to CDCl$_3$ the residual solvent peak CHCl$_3$ ($\delta = 7.26$ ppm) for 1H NMR and the CDCl$_3$ solvent peak ($\delta = 77.16$ ppm) for $^{13}$C{$^1$H} NMR. The notation of signals is: Proton: $\delta$ chemical shift in ppm (number of protons, multiplicity, $J$ value(s), proton assignment). Carbon: $\delta$ chemical shift in ppm (carbon assignment). Fluorine: $\delta$ chemical shift in ppm (Fluorine assignment). Splitting patterns are assigned s = singlet, b = broad, d = doublet, td = triplet of doublet, dt = doublet of triplet, t = triplet, q = quartet. Low resolution mass spectrometry was performed on an Agilent 6100 mass spectrometer (ES ionisation) and Hewlett Packard 5971 MSD (GC/MS with EI). High resolution mass spectrometry was performed on a Waters QTOF with ESI/APCI ionisation and a Thermo Finnigan MAT95XP (EI).

Chiral stationary phase HPLC was performed using an Aglient 1200 Series HPLC with a Chirapak IB 4.6 $\times$ 250 mm column and eluted with 1% isopropyl alcohol and 99% hexane at a rate of 1mL/min with absorbance reported at 254 nm.

Melting points were determined using a Kofler hot-stage apparatus or Stuart Scientific SMP10 apparatus and are uncorrected. Thin layer chromatography (TLC) was performed using pre-coated Merck 60F254 silica plates. Visualization was performed using UV light (285 nm) and treatment with acidic potassium permanganate. Flash chromatography was performed using silica gel (Sigma Aldrich, 40-63 $\mu$, 60 Å) and a Biotage® Isoleara™ equipped with 10 g or 25 g Biotage® SNAP Ultra cartridges.

Tetrahydrofuran (THF) was distilled over sodium wire and benzophenone. CH$_2$Cl$_2$ and toluene and distilled over calcium hydride. Diethyl ether was dried using a solvent purification system. All other solvents and reagents were purchased from commercial sources and used as supplied.
2. Synthesis of Sulfonamide Starting Materials

General procedure A for synthesis of N-aryl sulfonamides

N-Aryl sulfonamides were synthesised according to the following modified literature procedure.[1] The sulfonyl chloride (1 eq.) was dissolved in ethanol (0.5 M) and the respective aniline (2 eq.) was added. The reaction mixture was stirred and monitored by TLC analysis (1:3 v/v EtOAc:hexane). Upon completion the reaction mixture was acidified with HCl (1 M) and stirred at 0 °C for 5 minutes and then was then diluted with EtOAc and water. The aqueous phase was washed twice with EtOAc, and the combined organics were washed with brine, dried over magnesium sulfate, filtered and concentrated under vacuum. The crude reaction mixture was then purified by column chromatography.

General procedure B for synthesis of N-aryl sulfonamides

N-Aryl sulfonamides were prepared by following the literature procedure.[2] A solution of sulfonyl chloride (1.0 mmol) in dry CH₂Cl₂ (15 mL) was added over 15 min to a solution of amine (1.1 mmol) and pyridine (1.1 mmol) in dry CH₂Cl₂ (15 mL). The reaction was stirred at ambient temperature for 2 – 3 hours and the progress of the reaction was monitored by TLC (1:3 v/v EtOAc:hexane). Upon completion the reaction mixture was acidified with HCl (1 M, pH 2), the aqueous phase was separated and extracted with CH₂Cl₂ (2 × 10 mL). The combined organic layers were washed with brine, dried over Na₂SO₄, and evaporated to dryness to give sulfonamide as a crystalline solid. The crude material was purified by column chromatography.

General procedure C for the synthesis of N-alkyl sulfonamides

N-Alkyl sulfonamides were synthesised according to modified literature procedures.[3] The sulfonyl chloride (1 mmol, 1 eq.) was dissolved in THF (0.2 M) and appropriate amine (3 eq.) was added to the reaction mixture. The reaction was stirred for 30 minutes at ambient temperature until completion was indicated by TLC (1:3 v/v EtOAc:hexane). The reaction mixture was acidified with 1 M HCl (pH 2) at 0 °C, then diluted with EtOAc and water. The aqueous phase was washed twice with EtOAc and the combined organics were washed with saturated brine and dried over magnesium sulfate, filtered and concentrated under vacuum. The crude product was triturated with EtOAc and hexane, filtered and dried under vacuum or purified by column chromatography.
3. Characterisation data for sulfonamides

**Compound 1b**

![Chemical Structure of Compound 1b]

Chemical Formula: C$_{12}$H$_{10}$N$_2$O$_4$S  
MW = 278

4-Nitro-$N$-phenylbenzenesulfonamide 1b was synthesised according to general procedure A to afford a white crystalline solid (218 mg, 78%). R$_f$ 0.41 (EtOAc:hexanes 1:3); $^1$H NMR (400 MHz, DMSO-$d_6$) δ 10.61 (s, 1H, NH), 8.37 (d, $J$ = 8.9 Hz, 2H, ArH), 7.99 (d, $J$ = 8.9 Hz, 2H, ArH), 7.27 (d, $J$ = 7.2 Hz, 1H, ArH), 7.25 (d, $J$ = 7.2 Hz, 1H, ArH), 7.13 – 7.04 (m, 3H, ArH); $^{13}$C NMR (101 MHz, DMSO-$d_6$) δ 149.8 (C), 144.9 (C), 136.9 (C), 129.4 (2 x CH), 128.3 (2 x CH), 124.8 (CH), 124.7 (2 x CH), 120.7 (2 x CH); m/z (ES$^-$) 277 ([M-H]$^-$, 100%). Data are consistent with literature values.$^{[3]}$

**Compound 1c**

![Chemical Structure of Compound 1c]

Chemical Formula: C$_{13}$H$_{12}$N$_2$O$_5$S  
MW = 308

2-Methoxy-4-nitro-$N$-phenylbenzenesulfonamide 1c was synthesized according to general procedure A (1.19 mmol) to give an off-white crystalline solid (301 mg, 82%). R$_f$ 0.19 (EtOAc: hexane 1:4) = 0.19; $^1$H NMR (400 MHz, CDCl$_3$) δ 8.01 (d, $J$ = 8.6 Hz, 1H, ArH), 7.85 – 7.82 (m, 2H, ArH), 7.24 – 7.20 (m, 2H, ArH), 7.11 (d, $J$ = 7.4 Hz, 1H, ArH), 7.07 – 7.03 (m, 3H, ArH), 4.17 (s, 3H, OCH$_3$); $^{13}$C NMR (101 MHz, CDCl$_3$) δ 156.6 (C), 151.6 (C), 135.6 (C), 132.1 (CH), 131.9 (C), 129.4 (2 x CH), 125.9 (CH), 121.4 (2 x CH), 115.5 (CH), 107.2 (CH), 57.2 (OCH$_3$); HRMS (TOF MS ES$^-$) m/z calculated for C$_{13}$H$_{11}$N$_2$O$_5$S 307.0389 [M-H]$^+$, found 307.0382; mp 154 °C.
Conc. HCl (4 mL) was added to a solution of 2-chloro-4-nitroaniline (2.10 g, 12.1 mmol) in TFA (40 mL). The mixture was cooled to 0 °C and then a solution of sodium nitrite (1.06 g, 15.4 mmol) in water (3 mL) was added over a 20 minute period maintaining the temperature at 0°C. After 20 minutes the reaction mixture was poured into a solution of CuCl (80 mg), CuCl₂ (0.826 g, 6.2 mmol) and H₂SO₃ (40 ml) in acetic acid (40 mL) and kept at 0°C. After the initial effervescence subsided, the reaction mixture was allowed to sit at room temperature. After 30 minutes, the reaction mixture was diluted with 200 mL of water and extracted with hexane (2 × 100 mL). The combined organics were evaporated under vacuum to give the crude sulfonyl chloride as an amber oil (1.75 g). The sulfonyl chloride was used directly in the next step without further purification.

2-Chloro-4-nitro-N-phenylbenzenesulfonamide 1d was synthesized according general procedure A to afford an off-white crystalline solid (1.21 g, 32% over two steps). Rf 0.39 (EtOAc:hexane 1:4); ¹H NMR (400 MHz, CDCl₃) δ 8.36 (d, J = 2.1 Hz, 1H, ArH), 8.19 (d, J = 8.7 Hz, 1H, ArH), 8.14 (d, J = 8.7, 2.1 Hz, 1H, ArH), 7.27 – 7.22 (m, 2H, ArH), 7.16 – 7.10 (m 4H, ArH); ¹³C NMR (126 MHz, DMSO-d₆) δ 150.2 (C), 141.9 (C), 136.3 (C), 132.8 (CH), 131.9 (C), 129.3 (2 x CH), 126.7 (CH), 124.5 (CH), 122.7 (CH), 119.8 (2 x CH); HRMS (TOF MS ES⁻) m/z calculated for C₁₂H₈N₂O₄SCl 310.9893 [M-H]⁻, found 310.9889; Mp: 98 °C.⁴
**Compound 1e**

![Chemical Structure](image)

Chemical Formula: C₁₂H₉FN₂O₄S  
MW = 296

3-Fluoro-4-nitro-N-phenylbenzenesulfonamide 1e was synthesized according to general procedure A (0.835 mmol) to give a yellow crystalline solid (239 mg, 97%). Rf 0.28 (EtOAc: hexane 1:4); ¹H NMR (500 MHz, CDCl₃) δ 8.09 (dd, J = 10.0, 6.9 Hz, 1H, ArH), 7.69 (dd, J = 9.6, 1.8 Hz, 1H, ArH), 7.67 – 7.64 (m, 1H, ArH), 7.34 – 7.30 (m, 2H, ArH), 7.24 – 7.21 (m, 1H, ArH), 7.11 – 7.08 (m, 2H, ArH), 6.78 (brs, 1H, NH); ¹³C NMR (126 MHz, CDCl₃) δ 155.0 (d, J = 271.0 Hz, CF), 145.5 (d, J = 6.6 Hz, meta-C), 139.9 (m, ortho-C), 134.9 (CH), 129.8 (2 x CH), 127.0 (d, J = 2.7 Hz, para-CH), 126.9 (CH), 123.3 (d, J = 5.0 Hz, meta-CH), 122.6 (2 x CH), 117.8 (d, J = 23.7 Hz, ortho-CH); ¹⁹F NMR (500 MHz, CDCl₃) δ -113.54; HRMS (TOF MS ES⁻) m/z calculated for C₁₂H₉N₂O₄SF 295.0189 [M-H]⁻, found 295.0201; mp: 116 °C.

**Compound 1f**

![Chemical Structure](image)

Chemical Formula: C₁₃H₁₀F₃N₂O₄S  
MW = 346

4-Nitro-N-phenyl-3-(trifluoromethyl)benzenesulfonamide 1f was synthesized according to general procedure A (1.05 mmol) to give a white crystalline solid (272 mg, 76%). Rf 0.35 (EtOAc:hexane 1:4); ¹H NMR (500 MHz, CDCl₃) δ 8.18 (d, J = 1.9 Hz, 1H, ArH), 8.08 (dd, J = 8.4, 1.9 Hz, 1H, ArH), 7.90 (d, J = 8.4 Hz, 1H, ArH), 7.35 (brs, 1H, NH), 7.32 – 7.29 (m, 2H, ArH), 7.24 – 7.21 (m, 1H, ArH), 7.12 – 7.10 (m, 2H, ArH); ¹³C NMR (126 MHz, CDCl₃) δ 150.0 (C), 143.0 (C), 134.7 (C), 132.0 (CH), 129.8 (2 x CH), 127.0 (q, J = 5.2 Hz, CH), 126.9 (CH), 125.8 (CH), 124.6 (q, J = 35.3 Hz, C-CF₃), 122.6 (2 x CH), 120.9 (q, J = 275.0 Hz, CF₃); ¹⁹F NMR (500 MHz, CDCl₃) δ -60.26; HRMS (TOF MS AP⁺) m/z calculated for C₁₃H₁₀N₂O₄SF₃ [M+H]⁺ 347.0313, found 347.0303; Mp: 62 °C.
Compound 1g

\[
\text{O=S=O} \quad \text{NHbN} \\
\text{NO}_2
\]

Chemical Formula: C_{13}H_{12}N_2O_4S  
MW = 292

\(N\)-Benzyl-2-nitrobenzenesulfonamide 1g was synthesized according to general procedure A (1 mmol) to give a white crystalline solid (252 mg, 86%). \(R_f\) 0.14 (EtOAc:hexane 1:3); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 8.00 (dd, \(J = 8.0, 1.6\) Hz, 1H, ArH), 7.82 (dd, \(J = 7.8, 1.5\) Hz, 1H, ArH), 7.70 – 7.61 (m, 2H, ArH), 7.23 – 7.20 (m, 5H, ArH), 5.71 (t, \(J = 6.3\) Hz, 1H, NH), 4.32 (d, \(J = 6.3\), 2H, CH\(_2\)); \(^1\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 147.8, 135.6, 134.0, 133.4, 132.7, 131.0, 128.7, 128.0, 127.8, 125.2, 47.9; HRMS (ES\(^+\)) \(m/z\) calculated for C\(_{13}\)H\(_{12}\)N\(_2\)O\(_4\)NaS \([\text{M+Na}]^+\) 315.0415, found : 315.0426; mp: 92 \(^\circ\)C. Data are consistent with literature.\(^5\)

Compound 1h

\[
\begin{align*}
\text{Cl} & \quad \text{Me} \\
\text{NO}_2 & \quad \text{Na}_2\text{S, Sulfur} \\
& \quad \text{NaOH, EtOH} \\
\text{reflux, 10 h} & \quad \text{SH} \\
\text{Me} & \quad \text{30\% H}_2\text{O}_2, \text{AcOH} \\
& \quad \text{reflux, 2 h} \\
\text{SO}_2\text{Cl} & \quad \text{MeNH}_2 \\
\text{reflux, 5 h} & \quad \text{SO}_2\text{NHMe} \\
\text{Me} & \quad \text{NO}_2
\end{align*}
\]

Chemical Formula: C\(_{13}\)H\(_{12}\)N\(_2\)O\(_4\)S  
MW = 230

\(N,2\)-Dimethyl-4-nitrobenzenesulfonamide 1h was synthesised according to modified a modified literature procedure.\(^6\)
A mixture of 2-chloro-5-nitrotoluene (1.0 g, 5.8 mmol), 60% purity grade Na₂S (0.55 g, 4.2 mmol), sulfur (0.136 g, 4.2 mmol), NaOH (0.233 g, 5.8 mmol) in 50 mL ethanol was refluxed for 10 h. The reaction was quenched with 10 mL 10% HCl. The reaction mixture was extracted twice with ethyl acetate (25 mL) and the organic layer was washed with 10% HCl, dried (anhydrous Na₂SO₄), filtered and evaporated in vacuo. The crude product 2-methyl-4-nitrobenzenethiol (0.556 g, 56%) was obtained as a yellow solid which was used in the following step without further purification. Rf 0.36 (EtOAc:hexanes 1:1); ¹H NMR (500 MHz, CDCl₃) δ 8.02 (d, J = 2.4 Hz, 1H, ArH), 7.92 (dd, J = 8.5, 2.4 Hz, 1H, ArH), 7.34 (d, J = 8.5 Hz, 1H, ArH), 3.68 (brs, 1H, SH), 2.39 (s, 3H, CH₃); ¹³C NMR (126 MHz, CDCl₃) δ 145.5, 141.9, 136.0, 129.0, 124.8, 121.6, 20.8; HRMS (TOF MS ES⁻) m/z calculated for C₇H₆NO₂S 168.0119 [M-H]⁻, found 168.0120; mp: 172 °C.

A mixture of 2-methyl-4-nitrobenzenethiol (0.556 g), 6% H₂O₂ (14.3 mL, 25.3 mmol) and AcOH (5.4 g, 90.5 mmol) was refluxed for 2 h. The completion of reaction was confirmed by TLC. The crude product 2-methyl-4-nitrobenzenesulfonic acid was obtained upon evaporation of the reaction mixture under reduced pressure. The crude 2-methyl-4-nitrobenzenesulfonic acid appeared as a light yellow crystalline solid (0.657g, 92%) and was used without further purification. Rf 0.74 (MeOH:CHCl₃ 5:95); ¹H NMR (400 MHz, CDCl₃) δ 8.07 (d, J = 2.4 Hz, 1H, ArH), 8.01 (dd, J = 8.8, 2.4, 1H, ArH), 7.58 (d, J = 8.8, 1H, ArH), 2.58 (s, 3H, CH₃); ¹³C NMR (101 MHz, CDCl₃) δ 146.3, 142.2, 137.1, 125.8, 125.0, 122.2, 19.1.

To 2-methyl-4-nitrobenzenesulfonic acid (0.657 g) was added SOCl₂ (1.2 mL, 16.3 mmol) and the mixture was refluxed for 5 hours. Excess SOCl₂ was evaporated in vacuo to give the acid chloride as a black solid which was used in the following step directly.

To a THF (10 mL) solution of 2-methyl-4-nitrobenzenesulfonyl chloride (crude product), was added an ethanolic solution of MeNH₂, (33% solution by wt, 1.7 mL, 18.4 mmol) and the reaction mixture was stirred for 5 hours at ambient temperature. The volatiles were evaporated in vacuo, and the crude material was extracted with ethyl acetate. The organic layer was dried over (anhydrous Na₂SO₄), filtered and evaporated to give the crude sulfonamide. The crude product was subsequently purified by column chromatography (SiO₂, 1:9 v/v EtOAc:hexane). The pure sulfonamide was obtained as a pale yellow crystalline solid (140 mg, 20% over two steps). Rf 0.48 (EtOAc:hexanes 1:1); ¹H NMR (400 MHz, CDCl₃) δ 8.19 (s, 1H, ArH), 8.16 – 8.15 (m, 2H, ArH), 4.51 (brq, J = 5.4 Hz, 1H, ArH), 2.76 (s, 3H,
NCH$_3$), 2.71 (d, $J$ = 5.4, 3H, CH$_3$); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 149.9, 142.9, 139.4, 130.9, 127.2, 121.1, 29.2, 20.6; HRMS (TOF MS ES$^-$) calculated for C$_8$H$_9$N$_2$O$_4$S 229.0283 [M-H]$^+$ found 229.0285; mp: 166 °C.

**Compound 1i**

\[
\begin{align*}
\text{NHMe} & \\
O=SO & \\
\text{O} & \\
\text{NO}_2
\end{align*}
\]

Chemical Formula: C$_7$H$_8$N$_2$O$_4$S
MW = 216

$N$-Methyl-4-nitrobenzenesulfonamide 1i was synthesised according to general procedure C to afford a white crystalline solid (182 mg, 84%). $R_f$ 0.17 (EtOAc:hexane 1:3); $^1$H NMR (400 MHz, DMSO-d$_6$) $\delta$ 8.43 (d, $J$ = 8.8 Hz, 2H, ArH), 8.02 (d, $J$ = 8.8 Hz, 2H, ArH), 7.84 (s, 1H, NH), 2.46 (s, 3H, CH$_3$); $^{13}$C NMR (101 MHz, DMSO-d$_6$) $\delta$ 149.6 (C), 144.9 (C), 128.3 (2 x CH), 124.7 (2 x CH), 28.6 (CH$_3$); $m/z$ (ES$^-$) 215 ([M-H]$^+$, 100%). Data are consistent with literature values.$^{[3]}$

**Compound 1j**

\[
\begin{align*}
\text{NHBu} & \\
O=SO & \\
\text{O} & \\
\text{NO}_2
\end{align*}
\]

Chemical Formula: C$_{13}$H$_{14}$N$_2$O$_4$S
MW = 258

$N$-Butyl-4-nitrobenzenesulfonamide 1j was synthesised according to general procedure C to afford a white crystalline solid (181 mg, 70%). $R_f$ 0.39 (EtOAc:hexane 1:3); $^1$H NMR (400 MHz, DMSO-d$_6$) $\delta$ 8.41 (d, $J$ = 8.7 Hz, 2H, ArH), 8.03 (d, $J$ = 8.7 Hz, 2H, ArH), 7.96 (t, $J$ = 5.9 Hz, 1H, NH), 2.78 (q, $J$ = 6.6 Hz, 2H, NCH$_2$CH$_2$CH$_2$CH$_3$), 1.34 (p, $J$ = 6.9 Hz, 2H, NCH$_2$CH$_2$CH$_2$CH$_3$), 1.22 (h, $J$ = 7.2 Hz, 2H, NCH$_2$CH$_2$CH$_2$CH$_3$), 0.79 (t, $J$ = 7.3 Hz, 3H, NCH$_2$CH$_2$CH$_2$CH$_3$); $^{13}$C NMR (101 MHz, DMSO-d$_6$) $\delta$ 149.5 (C), 146.2 (C), 128.0 (2 x CH), 124.6 (2 x CH), 42.2 (NCH$_2$CH$_2$CH$_2$CH$_3$), 31.1(NCH$_2$CH$_2$CH$_2$CH$_3$), 19.2(NCH$_2$CH$_2$CH$_2$CH$_3$), 13.4 (NCH$_2$CH$_2$CH$_2$CH$_3$); $m/z$ (ES$^-$) 257.1 ([M-H]$^+$, 100%). Data are consistent with literature values.$^{[7]}$
Compound 1k

\[
\begin{array}{c}
\text{NHBn} \\
\text{O=S=O} \\
\text{NO}_2
\end{array}
\]

Chemical Formula: C_{13}H_{12}N_{2}O_{4}S  
MW = 292

\textit{N}-\textit{Benzyl-4-nitrobenzenesulfonamide 1k} was synthesised according to general procedure C to afford a white crystalline solid (225 mg, 77%). \textit{R} \_f \text{ 0.32 (EtOAc:hexanes 1:3); } ^{1}\text{H NMR (400 MHz, DMSO-}\text{d}_6\text{)} \delta 8.57 (t, J = 6.2 Hz, 1H, NH), 8.36 (d, J = 8.9 Hz, 2H, ArH), 8.00 (d, J = 8.9 Hz, 2H, ArH), 7.30 – 7.16 (m, 5H, ArH), 4.06 (d, J = 6.2 Hz, 2H, CH\textsubscript{2}); ^{13}\text{C NMR (101 MHz, DMSO-}\text{d}_6\text{)} \delta 149.4 (C), 146.4 (C), 137.1 (C), 128.3 (2 \times CH), 128.1 (2 \times CH), 127.7 (2 \times CH), 127.3 (CH), 124.5 (2 \times CH), 46.2 (CH\textsubscript{2}); m/z (ES\textsuperscript{-}) 291 ([M-H]\textsuperscript{-}, 100%). Data are consistent with literature values.\textsuperscript{[8]}

Compound 1l

\[
\begin{array}{c}
\text{Br} \\
\text{HN} \\
\text{O=S=O} \\
\text{NO}_2
\end{array}
\]

Chemical Formula: C_{12}H_{8}BrN_{2}O_{4}S  
MW = 357

\textit{N-(2-Bromophenyl)-4-nitrobenzenesulfonamide 1l} was synthesised according to general procedure A to afford a pink solid (191 mg, 54%). \textit{R} \_f \text{ 0.46 (EtOAc:hexane 1:3); } ^{1}\text{H NMR (400 MHz, DMSO-}\text{d}_6\text{)} \delta 10.40 (s, 1H, NH), 8.40 (d, J = 8.9 Hz, 2H, ArH), 7.94 (d, J = 8.9 Hz, 2H, ArH), 7.61 (dd, J = 8.4, 1.5 Hz, 1H, ArH), 7.35 (td, J = 7.6, 1.5 Hz, 1H, ArH), 7.23 – 7.16 (m, 2H, ArH); ^{13}\text{C NMR (101 MHz, DMSO-}\text{d}_6\text{)} \delta 149.8 (C), 146.0 (C), 134.2 (C), 133.4 (CH), 128.9 (CH), 128.9 (CH), 128.6 (CH), 128.3 (2 \times CH), 124.7 (2 \times CH), 120.9 (C); HRMS (TOF MS ES\textsuperscript{-}) m/z calculated for C_{12}H_{8}BrN_{2}O_{4}S 354.9388 [M-H], found 354.9379; mp 136 – 138 °C.
Compound 1m

4-Nitro-N-(o-tolyl)benzenesulfonamide was synthesized according to general procedure B to give a pinkish white crystalline solid (277 mg, 94%). Rf 0.28 (EtOAc:hexanes 1:3); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.28 (d, $J$ = 8.8, 2H, ArH), 7.90 (d, $J$ = 8.8, 2H, ArH), 7.28 – 7.26 (m, 1H, ArH), 7.20 – 7.12 (m, 3H, ArH), 6.52 (brs, 1H, NH), 2.02 (s, 3H, CH$_3$); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 150.2, 145.3, 133.3, 132.1, 131.1, 128.4, 127.3, 127.2, 125.0, 124.3, 17.7; m/z (ES$^-$) 291 ([M-H]$^-$, 100%); Mp: 152 °C. Data are consistent with literature.$^{[3]}$

Compounds 1n

$N$-(2-Methoxyphenyl)-4-nitrobenzenesulfonamide was synthesized according to general procedure B to give a pale yellow crystalline solid (253 mg, 82%). Rf 0.28 (EtOAc:hexane 1:3); $^1$H NMR (400 MHz, DMSO-$d_6$) $\delta$ 9.95 (s, 1H, NH), 8.36 (d, $J$ = 8.7, 2H, ArH), 7.92 (d, $J$ = 8.7, 2H, ArH), 7.21 (dd, $J$ = 8.0, 1.6 Hz, 1H, ArH), 7.17 (t, $J$ = 8.0 Hz, 1H, ArH), 6.91 – 6.88 (m, 2H, ArH), 3.41 (s, 3H, OCH$_3$); $^{13}$C NMR (101 MHz, DMSO-$d_6$) $\delta$ 153.0, 149.5, 146.3, 128.2, 127.7, 126.9, 124.3, 124.1, 120.5, 111.9, 55.2; m/z (ES$^-$) 307 ([M-H]$^-$, 100%); Mp 142 °C.$^{[3]}$
Compound 1o

![Chemical Structure](image)

Chemical Formula: C\textsubscript{13}H\textsubscript{10}N\textsubscript{2}O\textsubscript{4}S

MW = 258

4-Cyano-N-phenylbenzenesulfonamide 1o was synthesised according to general procedure A to afford a white solid (240 mg, 93%). R\textsubscript{f} 0.08 (EtOAc:hexanes 1:9); \textsuperscript{1}H NMR (500 MHz, CDCl\textsubscript{3}) \(\delta\) 7.88 (d, \(J = 8.5\) Hz, 2H, ArH), 7.76 (d, 2H, ArH), 7.33 – 7.27 (m, 3H, ArH), 7.21 (t, \(J = 7.4\) Hz, 1H, ArH), 7.09 (d, \(J = 7.9\) Hz, 2H, ArH), 6.78 (s, 1H, NH); \textsuperscript{13}C NMR (101 MHz, CDCl\textsubscript{3}) \(\delta\) 144.2 (C), 143.0 (C), 140.1 (C), 132.7 (2 x CH), 130.8 (CH), 130.2 (2 x CH), 130.0 (C), 129.5 (2 x CH), 121.9 (CH), 121.5 (CH), 118.9 (C), 118.7 (CH), 118.2 (2 x CH), 111.2 (C); HRMS (TOF MS ES\textsuperscript{-}) \textit{m/z} calculated for C\textsubscript{13}H\textsubscript{9}N\textsubscript{2}SO\textsubscript{2} 257.0385 [\textit{M-H}]\textsuperscript{+}, found 257.0390. Data are consistent with literature values.\textsuperscript{[9]}

Compound 1p

![Chemical Structure](image)

Chemical Formula: C\textsubscript{14}H\textsubscript{13}NO\textsubscript{3}S

MW = 275

4-Acetyl-N-phenylbenzenesulfonamide was synthesised according to general procedure A to afford a pale brown solid (246 mg, 89%). R\textsubscript{f} 0.04 (EtOAc:hexanes 1:9); \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) \(\delta\) 8.07 (d, \(J = 8.4\) Hz, 2H, ArH), 7.95 (d, \(J = 8.5\) Hz, 2H, ArH), 7.38 – 7.29 (m, 3H, ArH), 7.23 (t, \(J = 7.4\) Hz, 2H, ArH), 7.18 (d, \(J = 7.6\) Hz, 2H, ArH), 2.70 (s, 3H, CH\textsubscript{3}); \textsuperscript{13}C NMR (101 MHz, CDCl\textsubscript{3}) \(\delta\) 197.2 (C=O), 142.8 (C), 140.2 (C), 136.0 (C), 129.6 (2 x CH), 129.0 (2 x CH), 127.7 (2 x CH), 126.0 (CH), 122.1 (2 x CH), 27.04 (CH\textsubscript{3}). Data are consistent with literature values.\textsuperscript{[10]}
Compound 1q

![Chemical structure of Compound 1q]

Chemical Formula: C_{12}H_{8}BrCl_{2}NO_{2}S  
MW = 381

4-Bromo-2,6-dichloro-N-phenylbenzenesulfonamide was synthesized according to general procedure A to give a white crystalline solid (248 mg, 70%). R_f 0.55 (EtOAc: hexane 1:4); \textsuperscript{1}H NMR (400 MHz, DMSO-d_{6}) δ 10.90 (s, 1H, NH), 7.96 (s, 2H, ArH), 7.28 – 7.24 (m, 2H, ArH), 7.10 – 7.08 (m, 2H, ArH), 7.06 – 7.02 (m 1H, ArH); \textsuperscript{13}C NMR (101 MHz, DMSO-d_{6}) δ 136.6 (C), 135.3 (2 x C), 134.1 (2 x CH), 133.4 (C), 129.4 (2 x CH), 126.6 (CH), 124.2 (CH), 118.8 (2 x CH); HRMS (TOF MS ES\textsuperscript{−}) m/z calculated for C_{12}H_{7}NO_{2}SCl_{2}Br 377.8758 [M-H\textsuperscript{+}], found 377.8765; Mp: 108 °C.

Compound 1r

![Chemical structure of Compound 1r]

Chemical Formula: C_{14}H_{12}BrCl_{2}NO_{2}S  
Molecular Weight: 409

(R)-4-bromo-2,6-dichloro-N-(1-phenylethyl)benzenesulfonamide 1q was synthesised according to general procedure B (4 mmol) to give a white crystalline solid (1.26g, 78%). \textsuperscript{1}H NMR (500 MHz, CDCl\textsubscript{3}) δ 7.36 (s, 2H, ArH), 7.15 – 7.07 (m, 5H, ArH), 5.78 (d, J = 8.5 Hz, 1H, CH), 4.66 – 4.55 (m, 1H, NH), 1.52 (d, J = 7.0 Hz, 3H, CH\textsubscript{3}); \textsuperscript{13}C NMR (126 MHz, CDCl\textsubscript{3}) δ 140.4, 135.3, 135.2, 133.6, 128.5, 127.8, 125.9, 125.5, 54.7, 22.9.

Compound 1s

![Chemical structure of Compound 1s]

Chemical Formula: C_{15}H_{9}N_{2}O_{2}S  
Molecular Weight: 235
N-Phenylpyrimidine-2-sulfonamide was synthesised according to a modified literature procedure.\textsuperscript{[11]} HCl (2 M, 25 mL) and CH\textsubscript{2}Cl\textsubscript{2} (25 mL) were cooled to –5 °C. With rapid stirring cold NaOCl (10 %, 3.3 eq., 11 mL) was added at such a rate than the internal temperature does not exceed 0 °C. The 2-mercaptanpyrimidine (560 mg, 5 mmol) was added in small portions and an internal temperature of -5 to -10 °C was maintained. The reaction was left to stir rapidly for 20 minutes after which time the excess chlorine was quenched by adding Na\textsubscript{2}S\textsubscript{2}O\textsubscript{3} (sat.). The crude reaction was transferred to a cold separating funnel and the organic phase was quickly extracted with cold dichloromethane CH\textsubscript{2}Cl\textsubscript{2} (50 mL). The organic phase was cooled to 0 °C and aniline (1.4 mL, 15 mmol, 3 eq.) was added. The ice bath was then removed and the reaction was stirred for 40 minutes until completion was confirmed by TLC (1:19 Et\textsubscript{2}O:CH\textsubscript{2}Cl\textsubscript{2}). The crude reaction mixture was purified by column chromatography to afford a pale yellow solid (200 mg, 0.11 mmol, 17%). \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) δ 8.79 (t, J = 4.3 Hz, 2H, ArH), 8.11 (d, J = 38.5 Hz, 1H, NH), 7.40 (td, J = 4.9, 1.7 Hz, 1H, ArH), 7.21 (dd, J = 8.6, 1.4 Hz, 2H, ArH), 7.14 (ddd, J = 8.1, 6.6, 3.0 Hz, 2H, ArH), 7.01 (tu, J = 6.9, 1.7 Hz, 1H, ArH); \textsuperscript{13}C NMR (126 MHz, CDCl\textsubscript{3}) δ 164.8, 164.8, 158.6, 136.0, 129.3, 125.7, 123.6, 123.6, 122.1; m/z (ES\textsuperscript{+}) 234 ([M-H]).

**Compound 1t**

\[
\begin{array}{c}
\text{N-SO}_2\text{NHPh} \\
\text{Chemical Formula: C}_{11}\text{H}_{10}\text{N}_2\text{O}_2\text{S} \\
\text{Molecular Weight: 234}
\end{array}
\]

N-Phenylpyridine-2-sulfonamide 1t was synthesised according to a modified literature procedure.\textsuperscript{[11]} HCl (2 M, 25 mL) and CH\textsubscript{2}Cl\textsubscript{2} (25 mL) were cooled to –5 °C. With rapid stirring cold NaOCl (10 %, 3.3 eq., 11 mL) was added at such a rate than the internal temperature does not exceed 0 °C. The 2-mercaptanpyridine (555 mg, 5 mmol) was added in small portions and internal temperature of -5 to -10 °C was maintained. The reaction was left to stir rapidly for 20 minutes after which time the excess chlorine was quenched by adding Na\textsubscript{2}S\textsubscript{2}O\textsubscript{3} (sat.). The crude reaction was transferred to a cold separating funnel and the organic phase was quickly extracted with cold dichloromethane CH\textsubscript{2}Cl\textsubscript{2} (50 mL). The organic phase was cooled to 0 °C and aniline (1.4 mL, 15 mmol, 3 eq.) was added. The ice bath was then removed and the reaction was stirred for 40 minutes until completion was confirmed by TLC (1:19 Et\textsubscript{2}O:CH\textsubscript{2}Cl\textsubscript{2}). The crude reaction mixture was purified by column chromatography to afford a pale yellow solid (820 mg, 3.5 mmol, 70%). \textsuperscript{1}H NMR (400 MHz, Acetone-\textit{d}_6) δ 9.22
(s, 1H, NH), 8.65 (ddd, J = 4.7, 1.7, 0.9 Hz, 1H, ArH), 8.01 – 7.89 (m, 2H, ArH), 7.55 (ddd, J = 7.4, 4.7, 1.4 Hz, 1H, ArH), 7.28 – 7.13 (m, 4H, ArH), 7.03 – 6.97 (m, 1H, ArH); $^{13}$C NMR (101 MHz, Acetone-$d_6$) $\delta$ 157.9 (C), 150.9 (CH), 139.1 (CH), 138.6 (C), 129.8, 127.9, 125.2, 123.5, 121.8; ES $^+$ 233 ([M-H], 100%).

Compound 1u

![Chemical Formula: C$_{13}$H$_{10}$N$_2$O$_2$S$_2$
MW = 290]

N-Phenylbenzo[d]thiazole-2-sulfonamide 1u was synthesised according to modified literature procedure.$^{[12]}$ A stirred suspension of 2-mercaptobenzothiazole (2.0 g, 12 mmol, 1 eq.) in HCl (1M, 30 mL) and CH$_2$Cl$_2$ (0.2 M, 60 mL) was cooled in a salt ice bath and sodium hypochlorite (~10%, 36 mL, 0.36 mmol, 0.03 eq.) was slowly added. The solution continued to be stirred for 1 hour. The reaction mixture was then separated in a pre-cooled separating funnel, and the aqueous layer was extracted with cold CH$_2$Cl$_2$ (10 mL). The organic layers were quickly washed with cold NaHCO$_3$ and saturated brine, and dried over MgSO$_4$ for 30 minutes at -78 °C under a nitrogen atmosphere, then filtered and concentrated under vacuum. Ice cold dry diethyl ether was added (5 mL) and the mixture cooled to -78 °C, filtered and then the solid washed with cold (-78 °C) dry Et$_2$O and dried for 30 minutes. The resulting cream solid was stored under nitrogen at -18 °C.

A portion of the cream solid (500 mg, 2.1 mmol) was then dissolved in ethanol at 0 °C and aniline (0.4 mL, 4.2 mmol) was added. The mixture was warmed to room temperature by which time the reaction appeared complete by TLC. The crude reaction mixture was recrystallized from ethanol, however some aniline remained, and so column chromatography was performed (SiO$_2$ gel, 0:1 to 1:1 EtOAc:hexane) to afford a white crystalline solid (207 mg, 35%). $^1$H NMR (400 MHz, DMSO-$d_6$) $\delta$ 11.24 (s, 1H), 8.28 – 8.21 (m, 1H), 8.18 (d, J = 7.7 Hz, 1H), 7.71 – 7.58 (m, 3H), 7.28 (d, J = 7.7 Hz, 2H), 7.21 (d, J = 7.5 Hz, 2H), 7.11 (t, J = 7.3 Hz, 1H); $^{13}$C NMR (101 MHz, DMSO-$d_6$) $\delta$ 165.6 (C), 151.6 (C), 136.4 (C), 135.9 (C), 129.3 (2 x CH), 127.9 (CH), 127.8 (CH), 125.1 (CH), 124.6 (CH), 123.3 (CH), 121.1 (2 x
CH); HRMS (TOF MS ES\(^+\)) \(m/z\) calculated for 313.0081 \([M+Na]^+\), found 313.0089. Data are consistent with literature values.\(^{13}\)

4. General Procedures for Synthesis of Biaryls

**General Procedure D**

The sulfonamide (1 eq.), potassium fluoride (3 eq.) and 18-crown-6 (3 eq.) were measured into a microwave vial and then THF (0.1M) and the aryne precursor (1 eq.) were added. The vial was sealed with a cap and the solution was then stirred at reflux for 24 hours. The reaction was then cooled, and then diluted with ethyl acetate and water. The aqueous phase was separated and extracted twice with ethyl acetate. The combined organic were washed with brine, dried over anhydrous magnesium sulphate, filtered and concentrated under vacuum. The crude product was then purified using column chromatography (SiO\(_2\) gel, 0:1 to 1:9 v/v EtOAc:hexanes) to afford the title compound.

**General Procedure E**

The sulfonamide (1 eq.), potassium fluoride (6 eq.) and 18-crown-6 (6 eq.) were measured into a microwave vial and then THF (0.1M) and the aryne precursor (2 eq.) were added. The vial was sealed with a cap and the solution was then stirred at reflux for 24 hours. The reaction was then cooled, and then diluted with ethyl acetate and water. The aqueous phase was separated and extracted twice with ethyl acetate. The combined organic were washed with brine, dried over anhydrous magnesium sulphate, filtered and concentrated under vacuum. The crude product was then purified using column chromatography (SiO\(_2\) gel, 0:1 to 1:9 v/v EtOAc:hexanes) to afford the title compound.
Characterisation data for biaryls

Nitro-phenyl sulfonamide scope (Scheme 2)

**Compound 4a**

![Chemical structure of Compound 4a](image)

Chemical Formula: $C_{18}H_{14}N_2O_2$

$\text{MW} = 290$

4’-Nitro-$N$-phenyl-[1,1’-biphenyl]-2-amine 4a was synthesised according to general procedure D (0.25 mmol). The title compound was isolated as a red crystalline solid (40 mg, 56%). $R_f$ 0.83 (EtOAc:hexane, 1:9); $^1H$ NMR (400 MHz, CDCl$_3$) $\delta$ 8.26 (d, $J = 8.8$ Hz, 2H, ArH), 7.65 (d, $J = 8.8$ Hz, 2H, ArH), 7.40 (d, $J = 8.1$ Hz, 1H, ArH), 7.36 – 7.30 (td, $J = 8.3$, 1.1 Hz, 1H, ArH), 7.30 – 7.21 (m, 3H, ArH), 7.07 (td, $J = 7.4$, 1.3 Hz, 1H, ArH), 7.00 (d, $J = 7.7$ Hz, 2H, ArH), 6.95 (tt, $J = 7.4$, 1.1 Hz, 1H, ArH), 5.44 (s, 1H, NH); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 147.1 (C), 146.3 (C), 143.1 (C), 140.3 (C), 130.9 (CH), 130.3 (2 x CH), 129.8 (C), 129.7 (CH), 129.6 (2 x CH), 124.2 (2 x CH), 122.1 (CH), 121.6 (CH), 119.0 (2 x CH), 118.3 (CH); HRMS (TOF MS ES$^+$) $m/z$ calculated for $C_{18}H_{13}N_2O_2$ 289.0977 [M-H], found 289.0991; mp: 93–98 °C.

**Compound 4b**

![Chemical structure of Compound 4b](image)

Chemical Formula: $C_{19}H_{16}N_2O_3$

$\text{MW} = 320$

6-Methoxy-4’-nitro-$N$-phenyl-[1,1’-biphenyl]-2-amine 4b was synthesised according to general procedure D (0.25 mmol) and was isolated as an orange crystalline solid (52 mg, 65%). $R_f$ 0.39 (EtOAc:hexanes, 1:9); $^1H$ NMR (400 MHz, CDCl$_3$) $\delta$ 8.28 (d, $J = 8.6$ Hz, 2H, ArH), 7.54 (d, $J = 8.6$ Hz, 2H, ArH), 7.31 – 7.19 (m, 3H, ArH), 7.0 (t, $J = 7.9$ Hz, 3H, ArH),
6.95 (t, J = 7.3 Hz, 1H, ArH), 6.60 (dd, J = 8.3, 0.9 Hz, 1H, ArH), 5.16 (br s, 1H, ArH), 3.74 (s, 3H, ArH); $^{13}$C NMR (101 MHz, CDCl$_3$) δ 157.5 (C), 147.2 (C), 142.7 (C), 142.3 (C), 141.9 (C), 132.2 (2 x CH), 129.9 (CH), 129.5 (2 x CH), 124.0 (2 x CH), 121.9 (CH), 119.1 (2 x CH), 117.8 (C), 110.4 (CH), 103.6 (CH), 55.8 (OCH$_3$); HRMS (TOF MS ES$^+$) m/z calculated for C$_{19}$H$_{16}$N$_2$O$_3$Na 343.1059 [M+Na]$^+$, found 343.1075; mp 153 - 156 °C.

**Compound 4c**

\[
\text{Chemical Formula: } C_{24}H_{18}N_2O_3
\]

MW = 366

4''-Nitro-N-phenyl-[1,1':2',1''-terphenyl]-3'-amine 4c was synthesised according to general procedure D (0.25 mmol) and isolated as an orange solid (65 mg, 71%). R$_f$ 0.41 (EtOAc:hexanes, 1:9); $^1$H NMR (500 MHz, CDCl$_3$) δ 8.07 (d, J = 8.8 Hz, 2H, ArH), 7.38 (dd, J = 8.2, 1.3 Hz, 1H, ArH), 7.34 (d, J = 7.4 Hz, 1H, ArH), 7.30 (dt, J = 9.1, 2.5 Hz, 2H, ArH), 7.25 (dd, J = 8.5, 7.4 Hz, 2H, ArH), 7.14 (dt, J = 4.1, 1.6 Hz, 2H, ArH), 7.04 – 6.98 (m, 4H, ArH), 6.95 (t, J = 7.4 Hz, 1H, ArH), 5.17 (s, 1H, NH); $^{13}$C NMR (126 MHz, CDCl$_3$) δ 146.9 (C), 144.9 (C), 142.9 (C), 142.8 (C), 140.9 (C), 132.3 (2 x CH), 129.7 (2 x CH), 129.6 (2 x CH), 129.2 (CH), 128.0 (2 x CH), 127.9 (C), 126.9 (CH), 123.8 (2 x CH), 123.3 (CH), 121.9 (CH), 119.0 (2 x CH), 116.7 (C); HRMS (TOF MS APCI$^+$) m/z calculated for C$_{24}$H$_{18}$N$_2$O$_2$ 367.1447 [M+H]$^+$, found 367.1429; Mp 148 °C.
2',6-Dimethoxy-4'-nitro-N-phenyl-[1,1'-biphenyl]-2-amine 4d was synthesised according to general procedure D (0.46 mmol) and was isolated as red crystalline solid (99 mg, 62%). Rf 0.2 (EtOAc:hexanes 1:9); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.83 (d, \(J = 8.3\) Hz, 1H, ArH), 7.75 (s, 1H, ArH), 7.33 (d, \(J = 8.3\) Hz, 1H, ArH), 7.21 – 7.11 (m, 3H, ArH), 6.94 (d, \(J = 8.2\) Hz, 1H, ArH), 6.88 (d, \(J = 7.9\) Hz, 2H, ArH), 6.82 (t, \(J = 7.4\) Hz, 1H, ArH), 6.54 (d, \(J = 8.2\) Hz, 1H, ArH), 5.16 (brs, 1H, NH), 3.72 (s, 3H, OCH\(_3\)), 3.65 (s, 3H, OCH\(_3\)); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 157.8 (C), 157.6 (C), 148.4 (C), 143.1 (C), 142.1 (C), 133.2 (CH), 131.0 (C), 129.5 (CH), 129.2 (2 x CH), 121.2 (CH), 118.4 (2 x CH), 116.0 (CH), 114.9 (C), 110.7 (CH), 106.2 (C), 103.7 (CH), 56.1 (OCH\(_3\)), 55.7 (OCH\(_3\)); HRMS (TOF MS ES\(^{+}\)) \(m/z\) calculated for C\(_{20}\)H\(_{18}\)N\(_2\)O\(_4\)Na 373.1164 [M+Na]\(^{+}\), found 373.1179; mp: 162°C; rt (HPLC) 16.17, 17.39.
Compound 4e':

\[
\begin{align*}
\text{Chemical Formula: } & C_{22}H_{16}N_2O_2 \\
\text{MW = } & 340
\end{align*}
\]

1-(4-Nitrophenyl)-N-phenynaphthalen-2-amine 4e' was synthesised according to general procedure D (0.25 mmol) and was isolated as a red crystalline solid (43 mg, 51%). R\textsubscript{f} 0.42 (EtOAc:hexanes, 1:9); \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) δ 8.43 – 8.36 (m, 2H, ArH), 7.86 – 7.79 (m, 2H, ArH), 7.63 – 7.55 (m, 3H, ArH), 7.36 (ddd, \(J = 6.7, 4.8, 3.3\) Hz, 2H, ArH), 7.32 – 7.22 (m, 3H, ArH), 7.05 – 6.92 (m, 3H, ArH), 5.34 (br s, 1H, NH); \textsuperscript{13}C NMR (101 MHz, CDCl\textsubscript{3}) δ 147.7 (C), 144.4 (C), 143.1 (C), 133.1 (C), 132.4 (2 x CH), 129.7 (CH), 129.6 (2 x CH), 129.5 (C), 128.4 (CH), 127.1 (CH), 124.6 (2 x CH), 124.2 (CH), 124.0 (CH), 123.3 (C), 122.0 (CH), 119.4 (CH), 118.8 (2 x CH); \(m/z\) (EI\textsuperscript{+}) 340 ([M]\textsuperscript{+}, 100%); HRMS (TOF MS ES\textsuperscript{+}) \(m/z\) calculated for C\textsubscript{22}H\textsubscript{16}O\textsubscript{2}N\textsubscript{2} 340.1206 [M]\textsuperscript{+}, found 340.1197; mp: 162-164 °C.

Compound 4e'':

\[
\begin{align*}
\text{Chemical Formula: } & C_{22}H_{16}N_2O_2 \\
\text{MW = } & 340
\end{align*}
\]

2-(4-Nitrophenyl)-N-phenynaphthalen-1-amine 4e'' was synthesised according to general procedure D (0.25 mmol scale) and was isolated as a yellow solid (14 mg, 17%). R\textsubscript{f} 0.3 (EtOAc:hexanes, 1:9); \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) δ 8.22 (d, \(J = 8.5\) Hz, 2H, ArH), 8.02 (d, \(J = 8.4\) Hz, 1H, ArH), 7.93 (d, \(J = 8.1\) Hz, 1H, ArH), 7.84 (d, \(J = 8.5\) Hz, 1H, ArH), 7.56 (dd, \(J = 9.2, 2.6\) Hz, 3H, ArH), 7.54 – 7.43 (m, 2H, ArH), 7.15 (dd, \(J = 8.4, 7.1\) Hz, 2H, ArH), 6.81 (t, \(J = 7.3\) Hz, 1H, ArH), 6.61 – 6.49 (m, 2H, ArH), 5.52 (s, 1H, NH); \textsuperscript{13}C NMR (101...
MHz, CDCl₃) δ 147.3 (C), 147.2 (C), 146.8 (C), 134.8 (C), 134.7 (C), 132.6 (C), 130.7 (C), 130.2 (2 x CH), 129.5 (2 x CH), 128.5 (CH), 127.7 (CH), 127.0 (CH), 126.9 (CH), 126.5 (CH), 125.0 (CH), 123.9 (2 x CH), 119.7 (CH), 114.9 (2 x CH); HRMS (El, +ve) m/z Calculated for C₂₂H₁₆O₂N₂ 340.1206 [M]⁺, found 340.1214; mp: decomposition at 202 °C.

Compounds 4f

5-Methoxy-4′-nitro-N-phenyl-[1,1′-biphenyl]-2-amine and 4-methoxy-4′-nitro-N-phenyl-[1,1′-biphenyl]-2-amine 4f were synthesised, as an inseparable mixture, according to general procedure D (0.48 mmol) and were isolated as a red solid (77 mg, 67%). Rᵣ 0.25 (EtOAc: hexanes, 1:9); ¹H NMR (400 MHz, CDCl₃) δ ¹H NMR (400 MHz, CDCl₃) δ 8.31 – 8.18 (m, 4H, ArH), 7.70 – 7.52 (m, 4H, ArH), 7.36 (d, J = 8.8 Hz, 1H, ArH), 7.31 – 7.27 (m, 1H, ArH), 7.24 – 7.14 (m, 3H, ArH), 7.09 – 7.01 (m, 2H, ArH), 7.01 – 6.90 (m, 3H, ArH), 6.90 – 6.76 (m, 5H, ArH), 6.62 (dd, J = 8.5, 2.5 Hz, 1H, ArH), 5.47 (s, 1H, NH), 5.11 (s, 1H, NH), 3.85 (s, 3H, OCH₃), 3.80 (s, 3H, OCH₃); ¹³C NMR (101 MHz, CDCl₃) δ 160.9 (C), 155.9 (C), 147.0 (C), 146.7 (C), 146.1 (C), 146.0 (C), 145.2 (C), 142.5 (C), 141.5 (C), 133.9 (C), 132.5 (C), 131.7 (C), 130.1 (C), 130.0 (2 x CH), 129.5 (2 x CH), 129.4 (2 x CH), 124.7 (CH), 124.1 (2 x CH), 123.8 (2 x CH), 122.0 (C), 121.8 (CH), 119.8 (C), 118.7 (2 x CH), 115.7 (CH), 115.5 (2 x CH), 115.2 (CH), 107.4 (CH), 103.6 (C), 55.7 (OCH₃), 55.4 (OCH₃); HRMS (TOF MS ES⁺) calculated for C₁₉H₁₆N₂O₃Na 343.1059 [M+Na]⁺, found 343.1074.
Compounds 4g

4-Methyl-4'-nitro-N-phenyl-[1,1'-biphenyl]-2-amine and 5-methyl-4'-nitro-N-phenyl-[1,1'-biphenyl]-2-amine 4g were synthesised, as an inseparable mixture, of isomers according to general procedure D (0.46 mmol) and were isolated as a red crystalline solid (89 mg, 64%).

Rf 0.45 (EtOAc:hexanes 1:9); H NMR (400 MHz, CDCl₃) δ 8.30 – 8.20 (m, 4H, ArH), 7.68 – 7.56 (m, 4H, ArH), 7.35 – 7.28 (m, 1H, ArH), 7.26 – 7.19 (m, 4H, ArH), 7.17 (dd, J = 8.1, 5.4 Hz, 2H, ArH), 7.11 (s, 1H, ArH), 6.99 (dt, J = 6.9, 1.2 Hz, 2H, ArH), 6.97 – 6.83 (m, 5H, ArH), 5.38 (s, 1H, NH), 5.28 (s, 1H, NH), 2.37 (s, 3H, CH₃), 2.35 (s, 3H, CH₃); C NMR (101 MHz, CDCl₃) δ 146.9 (C), 146.8 (C), 146.3 (C), 146.2 (C), 143.8 (C), 143.0 (C), 139.9 (C), 139.9 (C), 137.2 (C), 132.1 (CH), 131.2 (CH), 130.7 (C), 130.6 (CH), 130.3 (CH), 130.1 (2 x CH), 130.1 (2 x CH), 129.4 (2 x CH), 129.4 (2 x CH), 127.0 (C), 124.0 (2 x CH), 123.9 (2 x CH), 122.9 (CH), 121.4 (CH), 120.7 (CH), 120.5 (CH), 119.4 (CH), 118.1 (2 x CH), 117.0 (2 x CH), 21.4 (CH₃), 20.7 (CH₃); HRMS (TOS MS ES⁺) calculated for C₁₉H₁₇N₂O₂ 305.1290 [M+H]⁺, found 305.1298.
Compounds 4h

\[
\begin{align*}
\text{Ph} & \text{NHPh} \\
\text{N} & \text{Ph} \\
\text{NO}_2 & \text{NO}_2
\end{align*}
\]

Chemical Formula: C\textsubscript{24}H\textsubscript{18}N\textsubscript{2}O\textsubscript{2}  
MW = 366

4''-Nitro-N-phenyl-[1,1':3',1''-terphenyl]-4'-amine and 4-nitro-N-phenyl-[1,1':4',1''-terphenyl]-2'-amine were synthesised 4h, as an inseparable mixture of isomers, according to general procedure D (0.48 mmol) and were isolated as a red crystalline solid (111 mg, 66%). R\textsubscript{f} 0.37 (EtOAc:hexanes 1:9); \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) \textsuperscript{8} 8.36 – 8.23 (m, 4H, ArH), 7.77 – 7.67 (m, 4H, ArH), 7.63 (d, J = 1.7 Hz, 1H, ArH), 7.62 – 7.53 (m, 5H, ArH), 7.52 – 7.42 (m, 6H, ArH), 7.41 – 7.33 (m, 3H, ArH), 7.33 – 7.21 (m, 9H, ArH), 7.06 (td, J = 5.6, 4.9, 2.5 Hz, 4H, ArH), 7.02 – 6.91 (m, 2H, ArH), 5.50 (s, 1H, NH), 5.47 (s, 1H, NH); \textsuperscript{13}C NMR (101 MHz, CDCl\textsubscript{3}) \textsuperscript{8} 147.1 (C), 147.0 (C), 146.0 (C), 145.8 (C), 142.8 (C), 142.7 (C), 142.6 (C), 140.5 (C), 140.3 (C), 140.1 (C), 139.5 (C), 134.7 (C), 131.2 (CH), 130.3 (2 x CH), 130.1 (2 x CH), 129.7 (C), 129.6 (2 x CH), 129.5 (2 x CH), 129.3 (C), 128.9 (2 x CH), 128.8 (2 x CH), 128.5 (CH), 128.2 (CH), 127.7 (CH), 127.1 (2 x CH), 126.6 (2 x CH), 124.2 (2 x CH), 124.2 (2 x CH), 121.7 (CH), 121.6 (CH), 120.7 (CH), 118.7 (CH), 118.5 (2 x CH), 118.2 (2 x CH), 117.3 (CH); HRMS (TOF MS ES\textsuperscript{+}) calculated for C\textsubscript{24}H\textsubscript{17}N\textsubscript{2}O\textsubscript{2} 365.1290 [M-H], found 365.1273.
Compounds 4i

5-Bromo-4'-nitro-N-phenyl-[1,1'-biphenyl]-2-amine and 4-bromo-4'-nitro-N-phenyl-[1,1'-biphenyl]-2-amine 4i were synthesised, as an inseparable mixture, according to general procedure D (0.25 mmol) and were isolated as red solid (38 mg, 63%). Rf 0.43 (EtOAc:hexanes 1:9); $^1$H NMR (400 MHz, CDCl$_3$) δ ppm 8.28 (d, $J$ = 8.1 Hz, 2 H, ArH) 7.58 - 7.69 (m, 2 H, ArH) 7.58 - 7.53 (m, 2 H, ArH) 7.21 - 7.35 (m, 3 H, ArH) 6.94 - 7.19 (m, 4 H, ArH) 5.49 (s, 1 H, NH) 5.41 (s, 1 H, NH); $^{13}$C NMR (101 MHz, CDCl$_3$) δ 147.2, 147.1, 145.0, 144.6, 142.1, 141.9, 141.4, 139.5, 133.1, 132.3, 131.9, 130.9, 130.1, 130.1, 129.6, 129.5, 127.3, 124.3, 124.2, 124.1, 123.6, 122.7, 122.1, 119.7, 119.7, 119.5, 118.6, 113.5; $m/z$ (TOF MS AP$^+$) 369 ([M+H]$^+$, 100%), 371 ([M+H]$^+$, 100%); HRMS (TOF MS AP$^+$) $m/z$ calculated for C$_{18}$H$_{14}$N$_2$O$_2$Br 369.0239 [M+H]$^+$ found 369.0251.

Compound 4j

2'-Methoxy-4'-nitro-N-phenyl-[1,1'-biphenyl]-2-amine 4j was synthesised according to general procedure D (0.46 mmol) and was isolated as bright red solid (120 mg, 82%). Rf 0.3 (EtOAc:hexanes, 1:9); $^1$H NMR (400 MHz, CDCl$_3$) δ 7.93 (dd, $J$ = 8.3, 2.0 Hz, 1H, ArH), 7.83 (d, $J$ = 2.0 Hz, 1H, ArH), 7.45 (d, $J$ = 8.3 Hz, 1H, ArH), 7.40 (dd, $J$ = 8.3, 1.3 Hz, 1H, ArH), 7.35 - 7.31 (m, 1H, ArH), 7.23 - 7.20 (m, 3H, ArH), 7.06 (dt, $J$ = 7.4, 1.5 Hz, 1H, ArH), 6.96 - 6.93 (m, 2H, ArH), 6.90 - 6.87 (m, 1H, ArH), 3.54 (brs, 1H, NH), 3.85 (s, 3H,
OCH₃); $^{13}$C NMR (101 MHz, CDCl₃) δ 156.9 (C), 148.3 (C), 143.4 (C), 141.0 (C), 135.3 (C), 132.2 (CH), 131.2 (CH), 129.3 (C), 129.2 (× 2 CH), 127.4 (C), 121.5 (CH), 120.8 (CH), 118.8 (CH), 117.6 (× 2 CH), 116.3 (CH), 105.9 (CH), 56.1 (OCH₃); HRMS (TOF MS ES⁺) m/z calculated for C₁₉H₁₈N₂O₃Na 343.1059 [M+Na]⁺, found 343.1071; mp: 82 °C.

**Compound 4k**

![Chemical Structure](image)

Chemical Formula: C₁₅H₁₃ClN₂O₂
MW = 325

2'-Chloro-4'-nitro-N-phenyl-[1,1'-biphenyl]-2-amine 4j was synthesised according to general procedure D (0.46 mmol) and was isolated as red crystalline solid (86 mg, 58%). Rf 0.3 (EtOAc:hexanes, 1:9); $^1$H NMR (400 MHz, CDCl₃) δ 8.28 (d, $J$ = 2.3 Hz, 1H, ArH), 8.09 (dd, $J$ = 8.4, 2.3 Hz, 1H, ArH), 7.48 (d, $J$ = 8.4 Hz, 1H, ArH), 7.32 – 7.25 (m, 2H, ArH), 7.17 – 7.13 (m, 2H, ArH), 7.10 – 7.28 (m, 1H, ArH), 7.00 – 6.96 (m, 1H, ArH), 6.91 – 6.88 (m, 2H, ArH), 6.87 – 6.83 (m, 1H, ArH), 5.10 (brs, 1H, NH); $^{13}$C NMR (100 MHz, CDCl₃) δ 147.7 (C), 144.8 (C), 142.6 (C), 140.7 (C), 135.2 (C), 132.7 (CH), 130.4 (CH), 129.9 (CH), 129.3 (× 2 CH), 127.4 (C), 125.1 (CH), 122.1 (CH), 121.7 (CH), 121.3 (CH), 118.6 (× 2 CH), 118.2 (CH); HRMS (TOF MS AP⁺) m/z calculated for C₁₈H₁₄N₂O₂Cl 325.0744 [M+H]⁺, found 325.0755; mp: 102 °C.

**Compound 4l**

![Chemical Structure](image)

Chemical Formula: C₁₅H₁₂Cl₂N₂O₂
MW = 358

2',6'-Dichloro-4'-nitro-N-phenyl-[1,1'-biphenyl]-2-amine 4l was synthesised according to general procedure D (0.25 mmol) and was isolated as a deep red crystalline solid (72 mg,
81%). Rf 0.56 (EtOAc:hexanes 1:9); 1H NMR (400 MHz, DMSO-d6) δ 8.37 (s, 2H, ArH), 7.34 – 7.26 (m, 2H, ArH), 7.21 (brs, 1H, NH), 7.13 (t, J = 7.8 Hz, 2H, ArH), 7.09 – 7.06 (m, 1H, ArH), 7.02 – 6.97 (m, 1H, ArH), 6.95 (d, J = 7.7 Hz, 2H, ArH), 6.76 (t, J = 7.3 Hz, 1H, ArH); 13C NMR (101 MHz, DMSO-d6) δ 147.3 (C), 143.7 (C), 143.6 (C), 141.5 (C), 136.5 (2 x CH), 130.4 (C), 130.0 (C), 129.0 (2 x CH), 125.4 (CH), 123.4 (2 x CH), 120.8 (CH), 120.3 (CH), 118.5 (CH), 117.9 (2 x CH); HRMS (TOF MS AP+) m/z calculated for C18H13N2O2Cl2 359.0354 [M+H]+, found 359.0346; mp 172-174 °C.

Compounds 4m

![Chemical Structure](image)

Chemical Formula: C18H13FN2O2
MW = 308

3'-Fluoro-4'-nitro-N-phenyl-[1,1'-biphenyl]-2-amine 4m was synthesised according to general procedure D (0.46 mmol) and was isolated as red crystalline (58 mg, 41%). Rf 0.26 (EtOAc:hexanes, 1:9); 1H NMR (400 MHz, CDCl3) δ 8.0 (t, J = 8.3 Hz, 1H, ArH), 7.34 – 7.28 (m, 2H, ArH), 7.22 (t, J = 7.8 Hz, 1H, ArH), 7.17 – 7.13 (m, 4H, ArH), 6.95 (t, J = 7.4 Hz, 1H, ArH), 6.89 – 6.83 (m, 3H, ArH), 5.30 (brs, 1H, NH); 13C NMR (126 MHz, CDCl3) δ 155.9 (d, J = 265.7 Hz, CF), 147.9 (d, J = 8.5 Hz, C), 142.8 (C), 140.4 (C), 136.2 (d, J = 7.5 Hz, C), 130.8 (CH), 130.3 (CH), 129.6 (2 x CH), 128.7 (d, J = 1.5 Hz, C), 126.7 (d, J = 2.3 Hz, CH), 125.5 (d, J = 3.8 Hz, CH), 122.2 (CH), 121.9 (CH), 119.3 (C), 119.2 (CH), 119.1 (C), 118.5 (2 x CH); 19F NMR (500 MHz, CDCl3) δ -116.97; HRMS (TOF MS AP+) m/z calculated for C18H14N2O2F 309.1039 [M+H]+, found 309.1037; mp: 62 °C.
Compound 4n

\[
\begin{align*}
&\text{Chemical Formula: } C_{19}H_{13}F_3N_2O_2 \\
&MW = 358
\end{align*}
\]

4'-Nitro-N-phenyl-3'-(trifluoromethyl)-[1,1'-biphenyl]-2-amine \textbf{4n} was synthesised according to general procedure D (0.46 mmol) and was isolated as yellow solid (44 mg, 27%). R\textsubscript{f} 0.27 (EtOAc:hexanes, 1:9); \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) \ δ 7.87 – 7.85 (m, 2H, ArH), 7.77 (dd, \( J = 8.3, 1.8 \) Hz, 1H, ArH), 7.33 – 7.27 (m, 2H, ArH), 7.21 – 7.16 (m, 3H, ArH), 7.06 – 7.02 (m, 1H, ArH), 6.90 – 6.86 (m, 3H, ArH), 5.26 (brs, 1H, NH); \textsuperscript{13}C NMR (101 MHz, CDCl\textsubscript{3}) \ δ 146.7 (C), 146.6 (C), 142.6 (C), 140.2 (C), 133.6 (C), 130.7 (CH), 130.3 (C), 129.5 (2 x CH), 128.8 (q, \( J = 5.2 \) Hz, CH=C-CF\textsubscript{3}), 128.6 (C), 125.6 (CH), 124.4 (q, \( J = 34.0 \) Hz, C-CF\textsubscript{3}), 121.8 (q, \( J = 274.0 \) Hz, CF\textsubscript{3}), 122.4 (CH), 121.7 (C), 119.5 (CH), 118.2 (2 x CH); \textsuperscript{19}F NMR (400 MHz, CDCl\textsubscript{3}) \ δ -59.93; HRMS (TOF MS AP\textsuperscript{+}) \textsuperscript{m/z} calculated for C\textsubscript{19}H\textsubscript{14}N\textsubscript{2}O\textsubscript{2}F\textsubscript{3} 359.1007 [M+H]\textsuperscript{+}, found 359.0999; mp: 56 °C.

Compound 4o

\[
\begin{align*}
&\text{Chemical Formula: } C_{19}H_{13}BrN_2O_2 \\
&MW = 369
\end{align*}
\]

\(N\)-(2-Bromophenyl)-4'-nitro-[1,1'-biphenyl]-2-amine \textbf{4o} was synthesised according to general procedure D (0.25 mmol) was isolated as a yellow crystalline solid (68 mg, 73%). R\textsubscript{f} 0.47 (EtOAc:hexanes, 1:9); \textsuperscript{1}H NMR (500 MHz, CDCl\textsubscript{3}) \ δ 8.30 – 8.21 (m, 2H, ArH), 7.65 – 7.59 (m, 2H, ArH), 7.51 – 7.45 (m, 1H, ArH), 7.41 – 7.36 (m, 2H, ArH), 7.34 (dt, \( J = 7.4, 1.1 \) Hz, 1H, ArH), 7.21 – 7.16 (m, 1H, ArH), 7.16 – 7.10 (m, 2H, ArH), 6.76 – 6.72 (m, 1H, ArH), 5.90 (s, 1H, NH); \textsuperscript{13}C NMR (126 MHz, CDCl\textsubscript{3}) \ δ 147.3 (C), 146.0 (C), 141.2 (C), 138.9 (C), 133.2 (CH), 132.0 (C), 131.0 (CH), 130.1 (2 x CH), 129.9 (CH), 128.3 (CH), 124.1 (2 x CH), 118.2 (2 x CH).
123.7 (CH), 121.6 (CH), 121.5 (CH), 116.3 (CH), 112.8 (C); HRMS (TOF MS AP+) m/z calculated for C_{18}H_{14}N_{2}O_{2}Br 369.0239 [M+H]^+, found 369.0241; mp 109-112 °C.

**Compound 4p**

![Chemical structure of 4p](image)

Chemical Formula: C_{18}H_{18}N_{2}O_{2}
MW = 304

4’-Nitro-N-(o-tolyl)-[1,1’-biphenyl]-2-amine **4p** was synthesised according to general procedure D (0.54 mmol) and was isolated as an orange crystalline solid (87 mg, 62%). R_{f} 0.38 (EtOAc:hexanes, 1:9); \textsuperscript{1}H NMR (400 MHz, CD_{2}Cl_{2}) \delta 8.26 (d, J = 8.7, 2H, ArH), 7.70 (d, J = 8.7, 2H, ArH), 7.31–7.27 (m, 2H, ArH), 7.18 (d, J = 7.50, 1H, ArH), 7.12 – 7.11 (m, 2H, ArH), 7.06 – 7.01 (m, 2H, ArH) 6.95 – 6.92 (m, 1H, ArH), 5.33 (brs, 1H, NH), 2.12 (s, 3H, CH_{3}); \textsuperscript{13}C NMR (101 MHz, CD_{2}Cl_{2}) \delta 147.4 (C), 146.8 (C), 141.6 (C), 141.4 (C), 131.3 (CH), 131.0 (CH), 130.6 (2 x CH), 130.0 (CH), 129.6 (C), 129.4 (C), 127.2 (CH), 124.4 (2 x CH), 122.9 (CH), 121.5 (CH), 119.9 (CH), 118.4 (CH), 18.0 (CH_{3}); HRMS (ES\textsuperscript{+}) calculated for C_{19}H_{17}N_{2}O_{2} 305.1290 [M+H]^+, found 305.1279; mp: 120 °C.

**Compound 4q**

![Chemical structure of 4q](image)

Chemical Formula: C_{19}H_{18}N_{2}O_{3}
MW = 320

N-(2-Methoxyphenyl)-4’-nitro-[1,1’-biphenyl]-2-amine **4q** was synthesised according to general procedure D (0.23 mmol) and as isolated as a dark yellow solid (71 mg, 49%). R_{f} 0.25 (EtOAc:hexanes, 1:9); \textsuperscript{1}H NMR (400 MHz, CDCl_{3}) \delta 8.17 (d, J = 8.7, 2H, ArH), 7.56 (d, J = 8.7, 2H, ArH), 7.38 (d, J = 8.3, 1H, ArH), 7.27–7.23 (m, 1H, ArH), 7.20 (dd, J = 7.7, 1.6 Hz, 1H, ArH), 7.17 – 7.13 (m, 1H, ArH), 6.99 (dt, J = 7.5, 1.2 Hz, 1H, ArH), 6.80 – 6.70 (m, 3H, ArH), 5.79 (brs, 1H, NH), 3.68 (s, 3H, OCH_{3}); \textsuperscript{13}C NMR (101 MHz, CDCl_{3}) \delta 148.6 (C),
146.9 (C), 146.3 (C), 139.8 (C), 132.6 (C), 130.7 (CH), 130.5 (C), 130.1 (2 x CH), 129.5 (CH), 123.9 (2 x CH), 122.0 (CH), 120.7 (CH), 120.5 (CH), 119.4 (CH), 115.2 (CH), 110.6 (CH), 55.5 (OCH₃); HRMS (ES⁺) calculated for C₁₉H₁₇N₂O₃ 321.1239 [M+H]⁺, found 321.1255; mp: 86 °C.

**Compound 4r**

![Chemical formula](image)

Chemical Formula: C₁₉H₁₄N₂O₂

MW = 290

2'-Nitro-N-phenyl-[1,1'-biphenyl]-2-amine 4r was synthesised according to general procedure E from sulfonamide (0.33 mmol) and 2-trimethylsilylphenyl triflate (0.66 mmol) and was as isolated as a dark yellow oil (41 mg, 31%). Rf 0.39 (EtOAc:hexanes 2:8); ¹H NMR (400 MHz, CDCl₃) δ 8.11 (d, J = 8.1, 1H, ArH), 7.81 (t, J = 7.6 Hz, 1H, ArH), 7.68 (t, J = 7.8 Hz, 1H, ArH), 7.62 (d, J = 7.7 Hz, 1H, ArH), 7.52 – 7.47 (m, 2H, ArH), 7.39 (t, J = 7.8 Hz, 2H, ArH), 7.34 (d, J = 7.6 Hz, 1H, ArH), 7.24 – 7.21 (m, 1H, ArH), 7.10– 7.06 (m, 3H, ArH), 5.37 (brs, 1H, NH); ¹³C NMR (101 MHz, CDCl₃) δ 149.5 (C), 143.1 (C), 140.8 (C), 133.7 (C), 133.0 (CH), 132.7 (CH), 129.6 (CH), 129.3 (2 x CH), 129.2 (C), 128.7 (2 x CH), 124.3 (CH), 122.0 (CH), 121.2 (CH), 118.9 (CH), 118.1 (2 x CH); HRMS (ES⁺) calculated for C₁₈H₁₅N₂O₂ 291.1134 [M+H]⁺, found 291.1125.

**Compound 7a**

![Chemical formula](image)

Chemical formula: C₂₅H₂₀N₂O₂

MW = 380

N-Benzyl-2'-nitro-N-phenyl-[1,1'-biphenyl]-2-amine 7a was synthesised according to general procedure E (0.4 mmol) and was isolated as a red brown crystalline solid (109 mg, 72%). Rf 0.39 (EtOAc:hexanes, 1:9); ¹H NMR (500 MHz, CDCl₃) δ 7.78 (dd, J = 8.1, 1.3 Hz, 1H, ArH), 7.44 – 7.36 (m, 3H, ArH), 7.33 – 7.27 (m, 4H, ArH), 7.19 – 7.13 (m, 3H, ArH),
7.08 – 7.06 (m, 2H, ArH), 7.02 – 6.99 (m, 2H, ArH), 6.66 (tt, J = 7.3, 1.1 Hz, 1H, ArH), 6.61 – 6.59 (m, 2H, ArH), 4.64 (d, J = 17.2 Hz, 1H, CHaHb), 4.55 (d, J = 17.2 Hz, 1H, CHaHb);

13C NMR (126 MHz, CDCl3) δ 148.7 (C), 147.7 (C), 145.5 (C), 138.7 (C), 135.6 (C), 134.6 (C), 132.5 (CH), 132.3 (CH), 130.5 (CH), 129.8 (CH), 128.6 (2 x CH), 128.4 (CH), 128.3 (2 x CH), 128.1 (CH), 126.6 (2 x CH), 126.4 (CH), 126.0 (CH), 124.2 (CH), 118.5 (CH), 115.7 (2 x CH), 55.0 (CH2); HRMS (ES+) calculated for C25H20N2O2Na 403.1422 [M+Na]+, found 403.1419; mp: 96 °C.

**Compound 7b**

![Chemical structure of compound 7b](image)

Chemical formula: C25H18N2O2

MW = 318

N,2’-Dimethyl-4’-nitro-N-phenyl-[1,1’-biphenyl]-2-amine 7b was synthesised according to general procedure E (0.46 mmol) and was isolated as an amorphous yellow solid (77 mg, 53%). Rf 0.47 (EtOAc:hexanes, 1:9); 1H NMR (400 MHz, CDCl3) δ 7.95 (d, J = 2.3 Hz, 1H, ArH), 7.81 (dd, J = 8.5, 2.3 Hz, 1H, ArH), 7.36 – 7.32 (m, 1H, ArH), 7.27 (d, J = 8.0 Hz, 1H, ArH), 7.20 (dt, J = 7.4, 1.4 Hz, 1H, ArH), 7.17 – 7.14 (m, 1H, ArH), 7.11 (d, J = 8.5 Hz, 1H, ArH), 7.02 (t, J = 8.0 Hz, 2H, ArH), 6.64 (t, J = 7.4 Hz, 1H, ArH), 6.53 (t, J = 7.4 Hz, 2H, ArH), 2.81 (s, 3H, NCH3), 2.18 (s, 3H, CH3); 13C NMR (101 MHz, CDCl3) δ 149.0 (C), 146.8 (C), 146.6 (C), 137.7 (C), 137.1 (C), 131.3 (CH), 130.9 (CH), 129.6 (CH), 128.8 (2 x CH), 127.7 (CH), 125.3 (CH), 124.8 (CH), 120.4 (CH), 118.4 (CH), 115.0 (2 x CH), 39.8 (NCH3), 20.4 (CH3); HRMS (ES+) calculated for C20H18N2O2Na 341.1266 [M+Na]+, found 341.1277.
**Compound 7c**

![Chemical structure of Compound 7c](image)

Chemical formula: $C_{19}H_{16}N_2O_2$

$\text{MW} = 304$

$N$-Methyl-4'-nitro-$N$-phenyl-[1,1'-biphenyl]-2-amine 7c was synthesised according to general procedure E (0.25 mmol) and was isolated as a yellow solid (44 mg, 58%). $R_f$ 0.60 (EtOAc:hexanes, 1:9); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.16 (d, $J = 8.7$ Hz, 2H, ArH), 7.54 (d, $J = 8.7$ Hz, 2H, ArH), 7.45 (t, $J = 8.4$ Hz, 2H, ArH), 7.38 – 7.31 (m, 2H, ArH), 7.18 (t, $J = 7.9$ Hz, 2H, ArH), 6.76 (t, $J = 7.3$ Hz, 1H, ArH), 6.67 (d, $J = 8.1$ Hz, 2H, ArH), 2.90 (s, 3H, CH$_3$); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 149.1 (C), 147.1 (C), 146.8 (C), 146.5 (C), 137.7 (C), 131.3 (CH), 130.4 (CH), 129.5 (2 x CH), 129.2 (2 x CH), 129.1 (CH), 126.6 (CH), 123.7 (2 x CH), 118.1 (CH), 114.1 (2 x CH), 39.6 (CH$_3$); HRMS (TOF MS El$^+$) $m/z$ Calculated for $C_{19}H_{16}O_2N_2$ 304.1206 [M$^+$], found 304.1198; mp 126 – 130 °C.

**Compound 7d**

![Chemical structure of Compound 7d](image)

Chemical formula: $C_{22}H_{22}N_2O_2$

$\text{MW} = 346$

$N$-Butyl-4'-nitro-$N$-phenyl-[1,1'-biphenyl]-2-amine 7d was synthesised according to general procedure E (0.25 mmol) and was isolated as a yellow solid (36 mg, 42%). $R_f$ 0.63 (EtOAc:hexanes, 1:9); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.15 (d, $J = 8.8$ Hz, 2H, ArH), 7.50 (d, $J = 8.8$ Hz, 2H, ArH), 7.45 (t, $J = 7.8$ Hz, 2H, ArH), 7.38 (d, $J = 7.4$ Hz, 1H, ArH), 7.32 (d, $J = 7.9$ Hz, 1H, ArH), 7.17 (t, $J = 7.3$ Hz, 2H, ArH), 6.74 (t, $J = 7.3$ Hz, 1H, ArH), 6.64 (d, $J = 8.0$ Hz, 2H, ArH), 3.11 (t, $J = 8.0$ Hz, 2H, NCH$_2$CH$_2$CH$_2$CH$_3$), 1.53 – 1.41 (p, $J = 7.5$ Hz, 2H, NCH$_2$CH$_2$CH$_2$CH$_3$), 1.17 (h, $J = 7.4$ Hz, 2H, NCH$_2$CH$_2$CH$_2$CH$_3$), 0.81 (t, $J = 7.3$ Hz, 3H, NCH$_2$CH$_2$CH$_2$CH$_3$); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 148.9 (C), 147.1 (C), 146.9 (C), 146.5 (C), 137.7 (C), 131.3 (CH), 130.4 (CH), 129.5 (2 x CH), 129.2 (2 x CH), 129.1 (CH), 126.6 (CH), 123.7 (2 x CH), 118.1 (CH), 114.1 (2 x CH), 39.6 (CH$_3$); HRMS (TOF MS El$^+$) $m/z$ Calculated for $C_{22}H_{22}O_2N_2$ 346.1670 [M$^+$], found 346.1654; mp 146 – 148 °C.
145.0 (C), 138.2 (C), 131.5 (CH), 130.7 (CH), 130.2 (CH), 129.6 (2 x CH), 129.3 (2 x CH),
126.7 (CH), 123.7 (2 x CH), 117.7 (CH), 114.2 (2 x CH), 51.4 (NCH2CH2CH2CH3), 28.8
(NCH2CH2CH2CH3), 20.3 (NCH2CH2CH2CH3), 14.0 NCH2CH2CH2CH3); HRMS (TOF MS
EI+) m/z Calculated for C22H22O2N2 346.1676 [M]+, found 346.1667.

**Compound 7e**

![Chemical structure of Compound 7e](image)

Chemical formula: C25H20N2O2
MW = 380

*N*-Benzyl-4'-nitro-*N*-phenyl-[1,1'-biphenyl]-2-amine *7e* was synthesised according to general
procedure E (0.25 mmol) and was isolated as a yellow solid (43 mg, 45%). Rf 0.43
(EtOAc:hexanes, 1:9); 1H NMR (500 MHz, CDCl3) δ 8.17 – 8.12 (m, 2H, ArH), 7.50 – 7.41
(m, 5H, ArH) 7.38 – 7.32 (m, 1H, ArH), 7.24 – 7.07 (m, 7H, ArH), 6.75 (tt, J = 7.3, 1.1 Hz,
1H, ArH), 6.70 – 6.60 (m, 2H, ArH), 4.39 (s, 2H, CH2); 13C NMR (126 MHz, CDCl3) δ 149.2
(C), 147.2 (C), 146.9 (C), 145.2 (C), 138.4 (C), 138.2 (C), 131.7 (CH), 130.6 (2 x CH), 130.3
(2 x CH), 129.7 (2 x CH), 129.3 (CH), 128.5 (2 x CH), 127.0 (CH), 126.9 (2 x CH), 126.8
(CH), 123.8 (2 x CH), 118.4 (CH), 114.6 (2 x CH), 56.2 (CH2); HRMS (TOF MS EI+) m/z
calculated for C25H20O2N2 380.1519 [M]+, found 380.1506; mp 132 - 136 °C.

**Compound 7f**

![Chemical structure of Compound 7f](image)

Chemical formula: C22H22N2O4
MW = 378

6-Methoxy-*N*-(3-methoxyphenyl)-*N*,2’-dimethyl-4’nitro-[1,1’-biphenyl]-2-amine *7f* was
synthesised according to general procedure E (0.46 mmol) and was isolated as an amorphous
yellow solid (82 mg, 48%). Rf 0.14 (EtOAc:hexanes, 1:9); 1H NMR (400 MHz, CDCl3) δ
8.05 (d, J = 2.5 Hz, 1H, ArH), 7.90 (dd, J = 8.5, 2.5 Hz, 1H, ArH), 7.40 (t, J = 8.2 Hz, 1H,
ArH), 7.16 (d, J = 8.5, Hz, 1H, ArH), 7.02 (t, J = 8.2, Hz, 1H, ArH), 6.97 (d, J = 8.0, Hz, 1H, ArH), 6.89 (d, J = 8.4 Hz, 1H, ArH), 6.29 (dd, J = 8.0, 2.4 Hz, 1H, ArH), 6.17 (dd, J = 8.4, 2.4 Hz, 1H, ArH), 6.11 (t, J = 2.4 Hz, 1H, ArH), 3.77 (s, 3H, OCH$_3$), 3.72 (s, 3H, OCH$_3$), 2.78 (s, 3H, NCH$_3$), 2.22 (s, 3H, CH$_3$); $^{13}$C NMR (101 MHz, CDCl$_3$) δ 160.3 (C), 157.2 (C), 150.5 (C), 147.6 (C), 146.9 (C), 142.7 (C), 139.1 (C), 131.1 (CH), 130.2 (CH), 129.4 (CH), 126.8 (C), 124.3 (CH), 120.8 (CH), 120.3 (CH), 108.2 (CH), 107.4 (CH), 102.3 (CH), 100.9 (CH), 55.7 (OCH$_3$), 55.0 (OCH$_3$), 39.3 (NCH$_3$), 19.9 (CH$_3$); HRMS (ES$^+$) calculated for C$_{22}$H$_{22}$N$_2$O$_4$Na 401.1477 [M+Na]$^+$, found 401.1477; rt (HPLC) 13.19, 14.46

Sulfonamide Scope (Scheme 4)

Compound 4s

![Chemical structure of Compound 4s]

Chemical Formula: C$_{19}$H$_{14}$N$_2$

MW = 270

2’-(Phenylamino)-[1,1’-biphenyl]-4-carbonitrile 4s was synthesized according to general procedure D (0.25 mmol) and was isolated as a yellow oil (34 mg, 50%). R$_f$ 0.38 (EtOAc:hexanes, 1:9); $^1$H NMR (400 MHz, CDCl$_3$) δ 7.71 – 7.65 (m, 2H ArH), 7.60 – 7.55 (m, 2H, ArH), 7.38 (dd, J = 8.3, 1.3 Hz, 1H, ArH), 7.29 (td, J = 8.5, 8.0, 1.9 Hz, 1H, ArH), 7.25 – 7.19 (m, 3H, ArH), 7.03 (td, J = 7.4, 1.2 Hz, 1H, ArH), 7.01 – 6.96 (m, 2H, ArH), 6.93
1-(2′-(Phenylamino)−[1,1′-biphenyl]-4-yl)ethan-1-one 4t was synthesized according to general procedure D (0.25 mmol) and was isolated as a white solid (50 mg, 69%). R<sub>f</sub> 0.23 (EtOAc:hexanes 1:9) ¹H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.08 – 8.01 (m, 2H, ArH), 7.63 – 7.57 (m, 2H, ArH), 7.45 (dd, J = 8.2, 1.2 Hz, 1H, ArH), 7.37 – 7.24 (m, 4H, ArH), 7.11 – 7.03 (m, 3H, ArH), 7.00 – 6.95 (m, 1H, ArH), 5.58 (s, 1H, NH), 2.66 (s, 3H, CH<sub>3</sub>); ¹³C NMR (101 MHz, CDCl<sub>3</sub>) δ 197.8 (C=O), 144.2 (C), 143.1 (C), 140.1 (C), 136.0 (C), 130.8 (CH), 130.6 (C), 129.6 (2 x CH), 129.5 (2 x CH), 129.1 (2 x CH), 129.0 (CH), 121.6 (CH), 121.3 (CH), 118.2 (2 x CH), 118.2 (CH), 26.81 (CH<sub>3</sub>); HRMS (TOF MS ES⁺) m/z calculated for C<sub>20</sub>H<sub>17</sub>NONa 310.1208 [M+Na]<sup>+</sup>, found 310.12136; mp 138 °C.

Compound 4u

4′-Bromo-2′,6′-dichloro-N-phenyl-[1,1′-biphenyl]-2-amine 4u was synthesised according to general procedure D (0.46 mmol) and isolated as a white solid (158 mg, 88%). R<sub>f</sub> 0.52 (EtOAc:hexanes 1:9); ¹H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.61 (s, 2H, ArH), 7.38 – 7.32 (m, 2H,
ArH), 7.25 – 7.22 (m, 2H, ArH), 7.09 (dd, J = 7.6, 1.7 Hz, 1H, ArH), 7.06 – 7.04 (m, 1H, ArH), 7.03 – 7.01 (m, 2H, ArH), 6.96 – 6.92 (m, 1H, Ar), 5.07 (brs, 1H, NH); $^{13}$C NMR (125 MHz, CDCl$_3$) δ 142.8 (C), 141.2 (C), 136.8 (2 x C), 135.7 (C), 131.1 (2 x CH), 130.5 (CH), 129.6 (CH), 129.2 (2 x CH), 125.8 (C), 121.9 (C), 121.6 (CH), 121.0 (CH), 119.0 (2 x CH), 117.7 (CH); HRMS (TOF MS AP$^+$) m/z calculated for C$_{18}$H$_{13}$NCl$_2$Br 391.9608 [M+H]$^+$, found 391.9615; mp: 72 °C.

**Compound 4v**

![Chemical structure of Compound 4v](image)

Chemical Formula: C$_{19}$H$_{14}$BrCl$_2$NO
MW = 423

4'-Bromo-2',6'-dichloro-6-methoxy-N-phenyl-[1,1'-biphenyl]-2-amine 4v was synthesised according to general procedure D (0.25 mmol) and was isolated as a white solid (78 mg, 79%). R$_f$ 0.52 (EtOAc:hexanes 1:9); $^1$H NMR (400 MHz, CDCl$_3$) δ 7.60 (s, 2H, ArH), 7.29 (t, J = 8.3 Hz, 1H, ArH), 7.23 (tt, J = 7.4, 2.0 Hz, 2H, ArH), 7.06 – 7.02 (m, 2H, ArH), 6.98 (dd, J = 8.4, 0.9 Hz, 1H, ArH), 6.97 – 6.92 (m, 1H, ArH), 6.58 (dd, J = 8.3, 0.9 Hz, 1H, ArH), 5.02 (s, 1H, NH), 3.75 (s, 3H, OCH$_3$); $^{13}$C NMR (101 MHz, CDCl$_3$) δ 157.6 (C), 142.7 (C), 142.4 (C), 137.5 (CH), 132.6 (C), 131.2 (2 x CH), 130.3 (CH), 129.3 (2 x CH), 122.0 (CH), 121.9 (C), 119.8 (2 x CH), 114.2 (C), 109.8 (CH), 103.3 (CH), 56.0 (OCH$_3$); HRMS (TOF MS AP$^+$) m/z calculated for C$_{19}$H$_{15}$NOCl$_2$Br 421.9714 [M+H], found 421.9749; Mp 120 °C.
Compound 4w

Chemical Formula: C_{22}H_{14}BrCl_{2}N
MW = 443

1-(4-Bromo-2,6-dichlorophenyl)-N-phenylnaphthalen-2-amine and 2-(4-bromo-2,6-dichlorophenyl)-N-phenylnaphthalen-1-amine 4w were synthesised, as an inseparable mixture, according to general procedure D (0.25 mmol) and were isolated as a colourless crystalline solid (71 mg, 65%, 2.5:1). Rf 0.62 (EtOAc:hexanes 1:9); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.91 (d, $J$ = 8.5 Hz, 1H, ArH), 7.81 (d, $J$ = 8.2 Hz, 1H, ArH), 7.71 (dd, $J$ = 9.1, 5.6 Hz, 9H, ArH), 7.58 (s, 8H, ArH), 7.50 – 7.37 (m, 7H, ArH), 7.32 (ddd, $J$ = 8.3, 6.9, 1.3 Hz, 1H, ArH), 7.26 – 7.19 (m, 8H, ArH), 7.19 – 7.08 (m, 10H, ArH), 6.94 (dq, $J$ = 8.7, 2.3 Hz, 14H, ArH), 6.86 (tt, $J$ = 7.2, 1.2 Hz, 4H, ArH), 6.60 (tt, $J$ = 7.2, 1.2 Hz, 1H, ArH), 6.48 – 6.36 (m, 2H, ArH), 5.15 (s, 4H, NH); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 146.4, 142.8, 139.0, 137.9, 136.7, 136.2, 135.9, 134.8, 133.9, 132.3, 131.6, 131.0, 130.7, 130.0, 129.9, 129.5, 129.3, 129.0, 128.5, 128.5, 127.7, 127.2, 126.9, 126.5, 126.1, 125.0, 123.9, 123.3, 122.5, 122.1, 121.7, 119.5, 119.18, 119.17, 119.0, 115.3; HRMS (TOF MS AP$^+$) m/z calculated for C$_{22}$H$_{15}$NCl$_2$Br 441.9765 [M$^+$], found 441.9751.

Compound 4x

Chemical Formula: C$_{23}$H$_{16}$BrCl$_2$N
MW = 421

(R)-4'-Bromo-2',6'-dichloro-N-(1-phenylethyl)-[1,1'-biphenyl]-2-amine 4x was synthesised according to general procedure E (0.25 mmol) and was isolated as a pale yellow oil (66 mg,
63%). R_f = 0.63 (EtOAc:hexanes, 1:9); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta 7.68 (d, J = 1.9\) Hz, 1H, ArH), 7.66 (d, \(J = 1.9\) Hz, 1H, ArH), 7.37 – 7.26 (m, 5H, ArH), 7.25 – 7.20 (m, 1H, ArH), 7.15 (dd, \(J = 8.2, 7.4, 1.6\) Hz, 1H, ArH), 6.92 (dd, \(J = 7.5, 1.7\) Hz, 1H, ArH), 6.76 (td, \(J = 7.4, 1.1\) Hz, 1H, ArH), 6.51 – 6.45 (m, 1H, ArH), 4.58 – 4.48 (m, 1H, NHCH), 3.52 (brs, 1H, NHCH), 1.41 (d, \(J = 6.7\) Hz, 3H, CH\(_3\)); \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta 145.1\) (C), 144.0 (C), 137.5 (C), 137.1 (C), 135.9 (C), 131.5 (CH), 131.3 (CH), 129.9 (CH), 129.7 (CH), 128.7 (2 x CH), 127.0 (CH), 125.9 (2 x CH), 122.1 (C), 121.5 (C), 117.1 (CH), 112.2 (CH), 53.4 (NCH), 25.3 (CH\(_3\)); HRMS (FTMS APCI\(^+\)) \(m/z\) calculated for C\(_{20}\)H\(_{17}\)BrCl\(_2\)N 419.9916 [M+H]\(^+\), found 419.9917.

**Compound 4y**

![Chemical Structure](image)

**Chemical Formula:** C\(_{17}\)H\(_{14}\)N\(_2\)

**MW = 246**

\(N\)-Phenyl-2-(pyridin-2-yl)aniline 4y was synthesised according to general procedure D (0.25 mmol) was isolated as a white solid (29 mg, 42%). R_f 0.46 (EtOAc:hexanes, 1:9); \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta 10.14\) (s, 1H, NH), 8.57 – 8.52 (m, 1H, ArH), 7.70 (td, \(J = 7.8, 1.9\) Hz, 1H, ArH), 7.63 (dt, \(J = 8.1, 1.1\) Hz, 1H, ArH), 7.53 (dd, \(J = 7.8, 1.6\) Hz, 1H, ArH), 7.39 (dd, \(J = 8.3, 1.2\) Hz, 1H, ArH), 7.18 (dt, \(J = 8.5, 6.9, 1.8\) Hz, 3H, ArH), 7.15 – 7.09 (m, 3H, ArH), 6.88 – 6.81 (m, 2H, ArH); \(^{13}\)C NMR (126 MHz, CDCl\(_3\)) \(\delta 159.2\) (C), 147.6 (CH), 143.1 (C), 142.9 (C), 137.2 (CH), 130.0 (CH), 129.8 (CH), 129.4 (2 x CH), 124.9 (C), 122.9 (CH), 121.4 (CH), 121.3 (CH), 119.6 (2 x CH), 119.4 (CH), 116.8 (CH); HRMS (FTMS ESI\(^+\)) calculated for C\(_{17}\)H\(_{15}\)N\(_2\) 247.1230 [M+H]\(^+\), found 247.1234. Data are consistent with literature values.\(^{[14]}\)
**Compound 4z**

![Chemical structure of 4z](image)

**Chemical Formula:** C$_{16}$H$_{14}$N$_3$

**MW = 247**

*N*-Phenyl-2-(pyrimidin-2-yl)aniline 4z was synthesised according to general procedure D (0.35 mmol) and was isolated as a yellow oil (48 mg, 55%). R$_f$ 0.27 (EtOAc:hexanes, 1:9); $^1$H NMR (400 MHz, CDCl$_3$) δ 10.67 (s, 1H, NH), 8.69 (d, $J$ = 4.9 Hz, 2H, ArH), 8.44 (dd, $J$ = 8.0, 1.7 Hz, 1H, ArH), 7.32 (dd, $J$ = 8.5, 1.2 Hz, 1H, ArH), 7.28 – 7.13 (m, 5H, ArH), 7.03 (t, $J$ = 4.9 Hz, 1H, ArH), 6.93 (tt, $J$ = 7.0, 1.6 Hz, 1H, ArH), 6.81 (ddd, $J$ = 8.2, 7.0, 1.3 Hz, 1H, ArH); $^{13}$C NMR (101 MHz, CDCl$_3$) δ 165.8 (C), 156.3 (2 x CH), 145.7 (C), 142.2 (C), 131.7 (CH), 131.4 (CH), 129.4 (2 x CH), 122.4 (CH), 121.4 (2 x CH), 120.8 (C), 118.4 (CH), 117.7 (CH), 115.5 (CH); HRMS (TOF MS AP$^+$) Calculated for C$_{16}$H$_{15}$N$_3$ 248.1188 [M+H]$^+$, found 248.1181.

**Compound 4zz**

![Chemical structure of 4zz](image)

**Chemical Formula:** C$_{16}$H$_{14}$N$_2$S

**MW = 302**

2-(Benzo[d]thiazol-2-yl)-N-phenylaniline 4zz was synthesised according to general procedure D (0.25 mmol) and was isolated as a yellow solid (22 mg, 74%). R$_f$ 0.74 (EtOAc:hexane, 1:9); $^1$H NMR (400 MHz, CDCl$_3$) δ 10.69 (s, 1H, NH), 7.88 (d, $J$ = 8.1 Hz, 1H, ArH), 7.78 (d, $J$ = 7.9 Hz, 1H, ArH), 7.70 (d, $J$ = 7.9 Hz, 1H, ArH), 7.36 (t, $J$ = 7.9 Hz, 1H, ArH), 6.73 (t, $J$ = 7.5 Hz, 1H, ArH); $^{13}$C NMR (101 MHz, CDCl$_3$) δ 169.1 (C), 153.5 (C), 144.2 (C), 141.5 (C), 133.4 (C), 131.6 (CH), 130.9 (CH), 129.5 (2 x CH), 126.3 (CH), 125.2 (CH), 123.3 (CH), 122.6 (CH), 122.4 (2 x CH), 121.3 (CH), 118.0 (CH), 116.7 (C), 114.6
1-(4-Nitrophenyl)-9H-carbazole 8a was synthesised according to a modified literature procedure.\textsuperscript{15} N-(2-Bromophenyl)-4'-nitro-[1,1'-biphenyl]-2-amine 4o (50 mg, 0.13 mmol, 1 eq.), palladium acetate (2.2 mg, 0.01 mmol, 10 mol%), PCy\textsubscript{3}HBF\textsubscript{4} (7.4 mg, 0.02 mmol, 20 mol%), oven dried potassium carbonate (37 mg, 0.27 mmol, 2 eq.) were dissolved in degassed DMA (0.65 mL, 0.2M) and heated to reflux for 24 hours. The crude reaction mixture was filtered through a pad of Celite\textsuperscript{©} and then purified by column chromatography (SiO\textsubscript{2}, 0 – 10% EtOAc:hexanes) to afford the title compound as a yellow solid (33 mg, 86%). R\textsubscript{f} 0.40 (EtOAc:hexanes, 1:9); \textsuperscript{1}H NMR (400 MHz, DMSO-\textit{d}\textsubscript{6}) δ 7.38 (d, \textit{J} = 8.5 Hz, 2H), 7.00 (d, \textit{J} = 8.5 Hz, 2H), 6.34 (d, \textit{J} = 8.2 Hz, 2H), 6.29 – 6.25 (m, 3H), 6.22 (d, \textit{J} = 7.7 Hz, 1H), 6.07 (dd, \textit{J} = 10.5, 7.6 Hz, 5H), 5.76 (d, \textit{J} = 7.9 Hz, 2H), 5.66 (t, \textit{J} = 7.3 Hz, 1H); \textsuperscript{13}C NMR (101 MHz, DMSO-\textit{d}\textsubscript{6}) δ 149.9, 145.3, 145.2, 139.86, 136.0, 135.9, 133.5, 131.0, 129.8, 129.0, 128.4, 124.8, 123.1, 122.4, 120.5, 118.6, 115; \textit{m/z} (ES\textsuperscript{+}) 287 ([M-H]\textsuperscript{-}, 100%). Data are consistent with the literature values.\textsuperscript{16}

The preparation procedure of 9-phenyl-9H-carbazole 8b from 2'-nitro-N-phenyl-[1,1'-biphenyl]-2-amine 4r was adapted from a literature procedure describing a synthesis of
dibenzo[\textit{b,d}]furan from 2'-nitro-[1,1'-biphenyl]-2-ol.\textsuperscript{[17]} To a suspension of NaH (11.5 mg, 0.48 mmol) in hexamethylphosphoric triamide (1.0 mL) was added a solution of 2'-nitro-\textit{N}-phenyl-[1,1'-biphenyl]-2-amine (70 mg, 0.24 mmol) in hexamethylphosphoric triamide (1.0 mL). The reaction mixture was heated at 70°C with vigorous stirring. After 22 hours the starting material had been consumed (TLC analysis). The reaction mixture was cooled and poured into 5% HCl followed by extraction of the aqueous layer with EtOAc. The organic layer was washed with water and brine, dried over Na\textsubscript{2}SO\textsubscript{4}, filtered and evaporated. The crude product was purified by column chromatography (SiO\textsubscript{2}, 1:1 v/v EtOAc:hexane) to give the pure compound as greenish crystalline solid (41 mg, 71%). R\textsubscript{f} 0.39 (1:19 EtOAc:hexane); \textsuperscript{1}H NMR (400 MHz, CD\textsubscript{2}Cl\textsubscript{2}) \(\delta\) 8.15(dt, \(J = 7.8, 1.1\) Hz, 2H), 7.65 – 7.61 (m, 2H), 7.59 – 7.57 (m, 2H), 7.51 – 7.47 (m, 1H), 7.42 – 7.41 (m, 4H), 7.30 – 7.26 (m, 2H); \textsuperscript{13}C NMR (101 MHz, CDCl\textsubscript{3}) \(\delta\) 140.8, 137.6, 129.8, 127.4, 127.1, 125.9, 123.3, 120.3, 119.8, 109.7; HRMS (TOF MS AP\textsuperscript{+}) calculated for C\textsubscript{18}H\textsubscript{13}N\textsubscript{2}\textsuperscript{[M+H]\textsuperscript{+}} 244.1126, found 244.1114; Mp: 96°C. The analytical data are consistent with commercial sample (CAS 1150-62-5).

**Compound 12**

\[
\begin{array}{c}
\text{Chemical formula: C}_{18}\text{H}_{17}\text{N}_2 \\
\text{MW = 260}
\end{array}
\]

4'-Nitro-\textit{N}-phenyl-[1,1'-biphenyl]-2-amine 9 (145 mg, 0.5 mmol) was dissolved in EtOH (25 mL) and was reduced using a Thales Nano H-Cube flow reactor with 10% Pd/C at ambient temperature (30 bar, 1 mL/min). The crude reaction mixture was purified by column chromatography (SiO\textsubscript{2} gel, 0 – 1:1 v/v EtOAc:hexanes) to afford the title compound as a light brown oil (113 mg, 86%). R\textsubscript{f} 0.11 (EtOAc:hexane 1:9); \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) \(\delta\) 7.26 (d, \(J = 8.1\) Hz, 1H, ArH), 7.17 – 7.05 (m, 6H, ArH), 6.95 – 6.89 (m, 2H, ArH), 6.88 – 6.83 (m, 1H, ArH), 6.79 (t, \(J = 7.3\) Hz, 1H, ArH), 6.59 (d, \(J = 8.5\) Hz, 2H, ArH), 5.56 (s, 1H, NH), 3.54 (s, 2H, NH\textsubscript{2}); \textsuperscript{13}C NMR (101 MHz, CDCl\textsubscript{3}) \(\delta\) 145.9 (C), 143.7 (C), 140.2 (C), 131.8 (C), 130.9 (CH), 130.4 (2 x CH), 129.4 (2 x CH), 128.9 (C), 127.6 (CH), 121.1 (CH), 120.9 (CH), 118.0 (2 x CH), 117.4 (CH), 115.4 (2 x CH); HRMS (TOF MS ES\textsuperscript{+}) \(m/z\) Calculated for C\textsubscript{18}H\textsubscript{17}N\textsubscript{2} 261.1392 [M+H]\textsuperscript{+}, found 261.1399.
4-Nitrobenzenesulfonyl chloride (94 mg, 0.42 mmol) was dissolved in dry CH$_2$Cl$_2$ (7 mL) and added to N$^2$-phenyl-[1,1'-biphenyl]-2,4'-diamine 12 (110 mg, 0.42 mmol) and dry pyridine (34 μL, 0.46 mmol, 1.1 eq.) in dry CH$_2$Cl$_2$ (7 mL). The reaction mixture was stirred at ambient temperature for 4 hours and then acidified with 1 M HCl. The aqueous phase was extracted with CH$_2$Cl$_2$ (2 mL x 3); the combined organics were washed with brine (10 mL) and dried over MgSO$_4$, filtered and concentrated under vacuum. The crude reaction mixture was purified by column chromatography (SiO$_2$, 10 - 40% v/v EtOAc:hexanes) to afford the title compound as a yellow solid (82 mg, 44%). $R_f$ 0.09 (EtOAc:hexanes 1:9); $^1$H NMR (400 MHz, DMSO-$d_6$) δ 7.38 (d, $J$ = 8.5 Hz, 2H, ArH), 7.00 (d, $J$ = 8.5 Hz, 2H, ArH), 6.34 (d, $J$ = 8.2 Hz, 2H, ArH), 6.29 – 6.24 (m, 3H, ArH), 6.22 (d, $J$ = 7.7 Hz, 1H, ArH), 6.07 (dd, $J$ = 10.5, 7.6 Hz, 5H, ArH), 5.76 (d, $J$ = 7.9 Hz, 1H, NH), 5.66 (t, $J$ = 7.3 Hz, 1H, NH); $^{13}$C NMR (101 MHz, DMSO) δ 149.9 (C), 145.3 (C), 145.2 (C), 139.8 (C), 136.0 (C), 135.9 (C), 133.5 (C), 131.0 (C), 129.8 (2 x CH), 129.0 (2 x CH), 128.4 (2 x CH), 124.8 (2 x CH), 123.1 (CH), 122.4 (CH), 120.5 (2 x CH), 118.6 (CH), 115.4 (2 x CH); HRMS (TOF MS ES$^-$) m/z calculated For 444.1018 [M-H$^-$], found 444.1003; mp 218 – 220°C.

**Compound 10**

2-(Trimethylsilyl)phenyl trifluoromethanesulfonate (44 μL, 0.18 mmol, 1 eq.) was added to 4-nitro-$N$-(2'-(phenylamino)-[1,1'-biphenyl]-4-yl)benzenesulfonamide (82 mg, 0.18 mmol),
KF (31 mg, 0.54 mmol, 3 eq.), 18-crown-6 (143 mg, 0.54 mmol, 3 eq.) in THF (1.8 mL, 0.1 M). The reaction mixture was stirred at reflux for 24 hours and then cooled to ambient temperature. The crude reaction mixture was purified by column chromatography (SiO₂, 0 to 1:9 v/v EtOAc:hexanes) to afford the title compound as a red solid (55 mg, 67%). R₉ 0.25 (EtOAc:hexane 1:9); ¹H NMR (400 MHz, CDCl₃) δ 8.28 (d, J = 8.7 Hz, 2H, ArH), 7.65 (d, J = 8.7 Hz, 2H, ArH), 7.47 (d, J = 8.1 Hz, 1H, ArH), 7.36 (d, J = 7.7 Hz, 2H, ArH), 7.32 (d, J = 8.4 Hz, 2H, ArH), 7.30 – 7.19 (m, 5H, ArH), 7.09 (t, J = 7.4 Hz, 1H, ArH), 7.06 – 7.02 (m, 4H, ArH), 6.98 (t, J = 7.4 Hz, 1H, ArH), 6.92 (t, J = 7.3 Hz, 1H, ArH), 5.63 (s, 1H, ArH), 5.49 (s, 1H, ArH); ¹³C NMR (101 MHz, CDCl₃) δ 147.2, 146.2, 143.6, 142.5, 140.3, 139.8, 131.8, 131.4, 131.0, 130.9, 130.5, 130.4, 130.2, 129.8, 129.5, 128.0, 124.3, 122.5, 121.3, 121.1, 119.5, 118.2, 118.0, 117.7; HRMS (TOF MS ES⁺) m/z calculated for C₃₀H₂₄N₃O₂ 458.1869 [M+H]⁺, found 458.1865; Mp 214 – 216 °C.

**Compound 11**

![Chemical structure of Compound 11](image)

4′-Bromo-2′,6′-dichloro-[1,1′-biphenyl]-2-amine 11 was synthesised according to modified literature procedure. [¹⁸] Conc. HCl (4mL) was added to (R)-4′-bromo-2′,6′-dichloro-N-(1-phenylethyl)-[1,1′-biphenyl]-2-amine 4x (122 mg, 0.29 mmol) in a microwave vial and then sealed then the mixture was heated to 100 °C for 24 hours. The reaction was cooled to 0 °C, quenched with sat. NaHCO₃, and then diluted with EtOAc (20 mL). The aqueous phase was washed thrice with EtOAc and then the combined organics were washed with sat. brine and dried over MgSO₄, filtered and concentrated under vacuum. The crude reaction mixture was purified by column chromatography (SiO₂, 10% EtOAc:hexane) to afford a white solid (65%, 64 mg, 0.19 mmol). R₉ 0.44 (EtOAc:Hexane, 1:9); ¹H NMR (400 MHz, CDCl₃) δ 7.62 (s, 2H, ArH), 7.29 – 7.22 (m, 1H, ArH), 6.96 (ddd, J = 7.7, 1.6, 0.5 Hz, 1H, ArH), 6.87 (td, J = 7.4, 1.1 Hz, 1H, ArH), 6.82 (ddd, J = 7.9, 1.1, 0.5 Hz, 1H, ArH), 3.32 (brs, 2H, NH); ¹³C NMR (101 MHz, CDCl₃) δ 143.5, 136.9, 135.8, 131.3, 130.1, 130.0, 122.0, 121.9, 118.8, 115.9;
HRMS (FTMS, ESI+) calculated for C_{12}H_{8}BrCl_{2}N [M+H]^+ 315.9290, found 315.9195; Mp 106-108 °C.

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7. NMR Spectra for biaryls

$^1$H and $^{13}$C Spectra (CDCl$_3$, 400 and 101 MHz) for compound 4a
$^1$H and $^{13}$C Spectra (CDCl$_3$, 400 and 101 MHz) for compound 4b

![NMR Spectra Image]

[Chemical Structure Image]

MeO  NHPh  NO$_2$
$^1$H and $^{13}$C Spectra (CDCl$_3$, 500 and 126 MHz) for compound 4c
$^1$H and $^{13}$C Spectra (CDCl$_3$, 400 and 101 MHz) for compound 4d
$^1$H and $^{13}$C Spectra (CDCl$_3$, 400 and 101 MHz) for compound 4e'
$^1$H and $^{13}$C Spectra (CDCl$_3$, 400 and 101 MHz) for compound 4e’’

PhHN

NO$_2$
$^1$H and $^{13}$C Spectra (CDCl$_3$, 400 and 101 MHz) for compounds 4f
$^1$H and $^{13}$C Spectra (CDCl$_3$, 400 and 101 MHz) for compounds 4g
$^1$H and $^{13}$C Spectra (CDCl$_3$, 400 and 101 MHz) for compounds 4i
$^1$H and $^{13}$C Spectra (CDCl$_3$, 400 and 101 MHz) for compound 4j
$^1$H and $^{13}$C Spectra (CDCl$_3$, 400 and 101 MHz) for compound 4k
$^1$H and $^{13}$C Spectra (DMSO-d$_6$, 400 and 101 MHz) for compound 4l
$^1$H and $^{13}$C Spectra (CDCl$_3$, 400 and 126 MHz) for compound 4m
$^1$H and $^{13}$C Spectra (CDCl$_3$, 400 and 101 MHz) for compound 4n
$^1$H and $^{13}$C Spectra (CDCl$_3$, 400 and 101 MHz) for compound 4p
$^1$H and $^{13}$C Spectra (CDCl$_3$, 400 and 101 MHz) for compound 4q
$^1$H and $^{13}$C Spectra (CDCl$_3$, 400 and 101 MHz) for compound 4r
$^1$H and $^{13}$C Spectra (CDCl$_3$, 400 and 101 MHz) for compound 4s
$^1\text{H}$ and $^{13}\text{C}$ Spectra (CDCl$_3$, 400 and 101 MHz) for compound 4t
$^1$H and $^{13}$C Spectra (CDCl$_3$, 500 and 126 MHz) for compound 4u
$^1$H and $^{13}$C Spectra (CDCl$_3$, 400 and 101 MHz) for compound 4v
$^1$H and $^{13}$C Spectra (CDCl$_3$, 400 and 101 MHz) for compounds 4w
$^1$H and $^{13}$C Spectra (CDCl$_3$, 400 and 101 MHz) for compound 4x
$^1$H and $^{13}$C Spectra (CDCl$_3$, 500 and 126 MHz) for compound 4y
$^1$H and $^{13}$C Spectra (CDCl$_3$, 400 and 101 MHz) for compound 4z
$^1$H and $^{13}$C Spectra (CDCl$_3$, 400 and 101 MHz) for compound 4zz
$^1$H and $^{13}$C Spectra (CDCl$_3$, 400 and 101 MHz) for compound 7a
$^1$H and $^{13}$C Spectra (CDCl$_3$, 400 and 101 MHz) for compound 7b
$^1$H and $^{13}$C Spectra (CDCl$_3$, 400 and 101 MHz) for compound 7c
$^1$H and $^{13}$C Spectra (CDCl$_3$, 400 and 101 MHz) for compound 7d
$^1$H and $^{13}$C Spectra (CDCl$_3$, 500 and 126 MHz) for compound 7e
$^1$H and $^{13}$C Spectra (CDCl$_3$, 400 and 101 MHz) for compound 7f
$^1$H and $^{13}$C Spectra (DMSO-d$_6$, 400 and 101 MHz) for compound 8a
$^1$H and $^{13}$C Spectra (CD$_2$Cl$_2$, 400 and 101 MHz) for compound 8b
$^1$H and $^{13}$C Spectra (CDCl$_3$, 400 and 101 MHz) for compound 12
$^1$H and $^{13}$C Spectra (DMSO-$d_6$, 400 and 101 MHz) for compound 9

\[
\text{O}_2\text{N} \quad \text{S} \quad \text{N} \\
\text{H} \quad \text{PhN} \quad \text{PhN}
\]
$^1$H and $^{13}$C Spectra (CDCl$_3$, 400 and 101 MHz) for compound 10
$^1$H and $^{13}$C Spectra (CDCl$_3$, 400 and 101 MHz) for compound 11
