Supporting Information for:

One-Pot Synthesis of N-Substituted Benzannulated Triazoles
via Stable Arene Diazonium Salts

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1. **Synthesis of Starting Materials**

2-Aminobenzamides 6a–6e and 6h–6n were all commercially available.

2-Amino-5-iodobenzamide (6f)^1

Iodine (0.373 g, 1.47 mmol) was added in portions over 1 h to a stirred solution of 2-aminobenzamide (0.200 g, 1.47 mmol) and sodium hydrogen carbonate (0.123 g, 1.47 mmol) in water (49 mL). The reaction mixture was then heated to 60 °C and stirred for 18 h. The reaction mixture was cooled to room temperature, washed with 1 M aqueous sodium thiosulfate (10 mL) and then extracted with ethyl acetate (3 × 50 mL). The combined organic layers were dried (MgSO₄), filtered and concentrated in vacuo. Recrystallisation from water:methanol (10:1) gave 2-amino-5-iodobenzamide (6f) (0.277 g, 72%) as a brown solid. Mp 191–194 °C (lit.¹ 193–194 °C); δ_H (400 MHz, DMSO-d₆) 6.54 (1H, d, J 8.7 Hz, 3-H), 6.69 (2H, br s, NH₂), 7.13 (1H, br s, NH), 7.37 (1H, dd, J 8.7, 2.1 Hz, 4-H), 7.80 (1H, d, J 2.1 Hz, 6-H); δ_C (101 MHz, DMSO-d₆) 74.4 (C), 116.1 (C), 118.9 (CH), 136.5 (CH), 139.8 (CH), 149.7 (C), 169.9 (C); m/z (EI) 262 (M⁺, 50%), 244 (100), 117 (48), 90 (33).

2-Amino-5-nitrobenzamide (6g)^2

To a stirred solution of 2-amino-5-nitrobenzoic acid (0.150 g, 0.820 mmol) and hydroxybenzotriazole (0.122 g, 0.910 mmol) in N,N'-dimethylformamide (3 mL) was added N-(3-dimethylaminopropyl)-N'-ethylcarbodiimide hydrochloride (0.184 g, 0.910 mmol). The reaction mixture was stirred at room temperature for 2 h, cooled to 0 °C and 28% aqueous ammonia solution (83 µL) was added. The mixture was allowed to warm to room temperature and stirred for a further 2 h. The reaction mixture was diluted in ethyl acetate (30 mL) and washed with 5% aqueous sodium bicarbonate (30 mL). The organic layer was then washed with water (3 × 20 mL) and brine (3 × 20 mL). The organic layer was dried (MgSO₄), filtered and concentrated in vacuo. The reaction mixture was triturated with ethyl acetate:hexane (1:1) and the resulting solid was filtered to give 2-amino-5-nitrobenzamide (6g) (0.116 g, 78%) as a yellow solid. Mp 232–236 °C (lit.² 236 °C); δ_H (400 MHz, DMSO-d₆) 6.79 (1H, d, J 9.2 Hz, 3-H), 7.42 (1H, br s, NH), 7.91 (2H, br s, NH₂), 8.03 (1H, dd, J 9.2, 2.6 Hz, 4-H), 8.22 (1H, br s, NH), 8.55 (1H, d, J 2.6 Hz, 6-H); δ_C (101 MHz, DMSO-d₆) 112.1 (C), 116.0 (CH), 126.4 (CH), 127.6 (CH), 134.8 (C), 155.7 (C), 169.7 (C); m/z (EI) 181 (M⁺, 82%), 164 (57), 133 (53), 90 (61), 78 (100), 63 (84).
2-Amino-N-benzylbenzamide (6o)<sup>3</sup>

To a stirred solution of benzylamine (0.0910 mL, 0.0830 mmol) in ethyl acetate (0.6 mL) was added isatoic anhydride (0.150 g, 0.910 mmol). The reaction mixture was heated to 90 °C and stirred for 18 h. After cooling to room temperature, the reaction mixture was concentrated in vacuo. Purification by flash column chromatography, eluting with 30% ethyl acetate in hexane gave 2-amino-N-benzylbenzamide (6o) (0.169 g, 90%) as a white solid. Mp 124‒127 °C (lit.3 123‒125 °C); δ<sub>H</sub> (400 MHz, CDCl<sub>3</sub>) 4.61 (2H, d, J 5.6 Hz, PhCH<sub>2</sub>), 5.56 (2H, br s, NH<sub>2</sub>), 6.32 (1H, br s, NH), 6.63 (1H, td, J 8.2, 0.9 Hz, 5-H), 6.69 (1H, dd, J 8.2, 0.9 Hz, 3-H), 7.21 (1H, td, J 8.2, 1.4 Hz, 4-H), 7.27‒7.39 (6H, m, 6-H and Ph); δ<sub>C</sub> (101 MHz, CDCl<sub>3</sub>) 43.9 (CH<sub>2</sub>), 116.3 (C), 117.1 (CH), 117.8 (CH), 127.2 (CH), 127.7 (CH), 128.0 (2 × CH), 128.9 (2 × CH), 132.6 (CH), 138.4 (C), 148.5 (C), 169.2 (C); m/z (ESI) 249 (MNa<sup>+</sup>. 100%).

2-Amino-N-(methoxycarbonylmethyl)benzamide (6p)<sup>4</sup>

To a stirred solution of glycine methyl ester hydrochloride (0.240 g, 1.92 mmol) in ethyl acetate (4.2 mL) was added isatoic anhydride (0.344 g, 2.11 mmol) and triethylamine (0.227 µL, 1.92 mmol). The reaction mixture was heated to 90 °C and stirred for 18 h. After cooling to room temperature, the reaction mixture was concentrated in vacuo. Purification by flash column chromatography, eluting with 20% ethyl acetate in dichloromethane gave 2-amino-N-(methoxycarbonylmethyl)benzamide (6p) (0.320 g, 80%) as a white solid. Mp 73‒77 °C (lit.4 73‒74 °C); δ<sub>H</sub> (400 MHz, CDCl<sub>3</sub>) 3.80 (3H, s OCH<sub>3</sub>), 4.20 (2H, d, J 5.1 Hz, CH<sub>2</sub>CO<sub>2</sub>CH<sub>3</sub>), 5.50 (2H, br s, NH<sub>2</sub>), 6.59 (1H, br s, NH), 6.63‒6.70 (2H, m, 3-H and 5-H), 7.19‒7.25 (1H, m, 4-H), 7.40 (1H, dd, J 8.4, 1.6 Hz, 6-H); δ<sub>C</sub> (101 MHz, CDCl<sub>3</sub>) 41.6 (CH<sub>2</sub>), 52.6 (CH<sub>3</sub>), 115.2 (C), 116.8 (CH), 117.5 (CH), 127.6 (CH), 132.8 (CH), 149.0 (C), 169.4 (C), 170.8 (C); m/z (ESI) 231 (MNa<sup>+</sup>. 100%).

2-Amino-N-phenylbenzamide (6q)<sup>5</sup>

To a stirred solution of aniline (0.0920 mL, 1.10 mmol) in ethyl acetate (0.6 mL) was added isatoic anhydride (0.150 g, 0.920 mmol). The reaction mixture was heated to 90 °C and stirred for 18 h. After cooling to room temperature, the reaction mixture was concentrated in vacuo. Purification by flash column chromatography, eluting with 25‒40% ethyl acetate in hexane gave 2-amino-N-phenylbenzamide (6q) (0.143 g, 73%) as a white solid. Mp 125‒127 °C (lit.5 125‒127 °C); δ<sub>H</sub> (500 MHz, CDCl<sub>3</sub>) 2.80 (2H, d, J 5.1 Hz, PhCH<sub>2</sub>), 4.20 (2H, d, J 5.1 Hz, PhCH<sub>2</sub>), 5.50 (2H, br s, NH<sub>2</sub>), 6.59 (1H, br s, NH), 6.63‒6.70 (2H, m, 3-H and 5-H), 7.19‒7.25 (1H, m, 4-H), 7.40 (1H, dd, J 8.4, 1.6 Hz, 6-H); δ<sub>C</sub> (101 MHz, CDCl<sub>3</sub>) 41.6 (CH<sub>2</sub>), 52.6 (CH<sub>3</sub>), 115.2 (C), 116.8 (CH), 117.5 (CH), 127.6 (CH), 132.8 (CH), 149.0 (C), 169.4 (C), 170.8 (C); m/z (ESI) 231 (MNa<sup>+</sup>. 100%).
MHz, CD$_3$OD) 6.67–6.71 (1H, m, 5-H), 6.79 (1H, dd, J 8.2, 0.8 Hz, 3-H), 7.12 (1H, tt, J 7.4, 1.1 Hz, 4'-H), 7.20–7.25 (1H, m, 4-H), 7.31–7.36 (2H, m, 3'-H and 5'-H), 7.59 (1H, dd, J 7.9, 1.4 Hz, 6-H), 7.60–7.64 (2H, m, 2'-H and 6'-H); δ$_C$ (126 MHz, CD$_3$OD) 117.4 (CH), 118.0 (C), 118.2 (CH), 122.5 (2 × CH), 125.3 (CH), 129.4 (CH), 129.7 (2 × CH), 133.4 (CH), 140.0 (C), 150.6 (C); m/z (ESI) 235 (MNa$^+$, 100%).

2-Amino-N-(2'-methylphenyl)benzamide (6r)$^6$

To a stirred solution of o-toluamide (0.236 mL, 2.21 mmol) in ethyl acetate (4 mL) was added isatoic anhydride (0.400 g, 2.45 mmol). The reaction mixture was heated to 90 °C and stirred for 18 h. After cooling to room temperature, the reaction mixture was concentrated in vacuo. Purification by flash column chromatography, eluting with 20% ethyl acetate in hexane gave 2-amino-N-(2'-methylphenyl)benzamide (6r) (0.252 g, 50%) as a white solid. Mp 115–120 °C (lit.$^6$ 113–115 °C); δ$_H$ (400 MHz, CDCl$_3$) 2.33 (3H, s, 2'-CH$_3$), 5.54 (2H, br s, NH$_2$), 6.69–6.78 (2H, m, 3-H and 5'-H), 7.13 (1H, td, J 7.6, 1.2 Hz, 4-H), 7.20–7.32 (3H, m, 5-H, 3'-H and 4'-H), 7.50 (1H, dd, J 8.4, 1.2 Hz, 6'-H), 7.60 (1H, br s, NH), 7.83 (1H, br d, J 8.4 Hz, 6-H); δ$_C$ (101 MHz, CDCl$_3$) 18.1 (CH$_3$), 116.3 (C), 117.0 (CH), 117.8 (CH), 123.7 (CH), 125.6 (CH), 127.0 (CH), 127.3 (CH), 130.0 (C), 130.8 (CH), 132.9 (CH), 135.9 (C), 149.3 (C), 167.7 (C); m/z (ESI) 225 ([M‒H$^-$]$, 100%).

2-Amino-N-(4'-methylphenyl)benzamide (6s)$^3$

To a stirred solution of p-toluidine (0.0890 mL, 0.830 mmol) in ethyl acetate (0.6 mL) was added isatoic anhydride (0.150 g, 0.920 mmol). The reaction mixture was heated to 90 °C and stirred for 18 h. After cooling to room temperature, the reaction mixture was concentrated in vacuo. Purification by flash column chromatography, eluting with 20–30% ethyl acetate in hexane gave 2-amino-N-(4'-methylphenyl)benzamide (6s) (0.157 g, 84%) as a white solid. Mp 149–152 °C (lit.$^3$ 148–150 °C); δ$_H$ (500 MHz, CDCl$_3$) 2.34 (3H, s, 4'-CH$_3$), 5.49 (2H, br s, NH$_2$), 6.69–6.74 (2H, m, 3-H and 5-H), 7.17 (2H, br d, J 8.3 Hz, 3'-H and 5'-H), 7.23–7.28 (1H, m, 4-H), 7.42–7.48 (3H, m, 6-H, 2'-H and 6'-H), 7.67 (1H, br s, NH); δ$_C$ (126 MHz, CDCl$_3$) 21.0 (CH$_3$), 116.5 (C), 116.9 (CH), 117.6 (CH), 120.8 (2 × CH), 127.3 (CH), 129.6 (2 × CH), 132.7 (CH), 134.3 (C), 135.4 (C), 149.0 (C), 167.7 (C); m/z (ESI) 249 (MNa$^+$, 100%).

2-Amino-N-(4'-methoxyphenyl)benzamide (6t)$^3$

To a stirred solution of 4-methoxyaniline (0.103 g, 0.830 mmol) in ethyl acetate (0.6 mL) was added isatoic anhydride (0.150 g, 0.910 mmol). The reaction mixture was heated to 90 °C and stirred for 18 h. After cooling to room temperature, the reaction mixture was concentrated in vacuo. Purification
by flash column chromatography, eluting with 40% ethyl acetate in hexane gave 2-amino-N-(4′-methoxyphenyl)benzamide (6t) (0.170 g, 84%) as a brown solid. Mp 113‒116 °C (lit.3 114–116 °C); δH (400 MHz, CDCl3) 3.81 (3H, s, 4′-OCH3), 5.49 (2H, br s, NH2), 6.68–6.74 (2H, m, 6-H and 5-H), 6.88–6.94 (2H, m, 3′-H and 5′-H), 7.22–7.28 (1H, m, 4-H), 7.43–7.49 (3H, m, 6-H, 2′-H and 6′-H), 7.64 (1H, br s, NH); δC (101 MHz, CDCl3) 55.7 (CH3), 114.4 (2 × CH), 116.5 (C), 117.0 (CH), 117.7 (CH), 122.7 (2 × CH), 127.2 (CH), 131.0 (C), 132.8 (CH), 149.1 (C), 156.9 (C), 167.7 (C); m/z (ESI) 265 (MNa+. 100%).

2-Amino-N-(4′-fluorophenyl)benzamide (6u)

To a stirred solution of 4′-fluoroaniline (0.0800 mL, 0.830 mmol) in ethyl acetate (0.6 mL) was added isatoic anhydride (0.150 g, 0.920 mmol). The reaction mixture was heated to 90 °C and stirred for 18 h. After cooling to room temperature, the reaction mixture was concentrated in vacuo. Purification by flash column chromatography, eluting with 25% ethyl acetate in hexane gave 2-amino-N-(4′-fluorophenyl)benzamide (6u) (0.143 g, 75%) as a white solid. Mp 122‒125 °C (lit.6 125‒127 °C); δH (400 MHz, DMSO-d6) 6.31 (2H, br s, NH2), 6.59 (1H, td, J 8.0, 1.0 Hz, 5-H), 6.75 (1H, dd, J 8.2, 1.0 Hz, 3-H), 7.12‒7.23 (3H, m, 4-H, 2′-H and 6′-H), 7.61 (1H, dd, J 8.0, 1.3 Hz, 6-H), 7.68–7.76 (2H, m, 3′-H and 5′-H), 10.03 (1H, br s, NH); δC (101 MHz, DMSO-d6) 114.8 (2 × CH, d, 3JCF = 23.8 Hz), 115.0 (C), 115.1 (CH), 116.4 (CH), 122.3 (2 × CH, d, 3JCF = 7.7 Hz), 128.6 (CH), 132.1 (CH), 135.5 (C, d, 4JCF = 2.6 Hz), 149.7 (C), 158.1 (C, d, 1JCF = 240.1 Hz), 167.7 (C); m/z (ESI) 253 (MNa+. 100%).

2-Amino-N-(4′-chlorophenyl)benzamide (6v)

To a stirred solution of 4-chloroaniline (0.212 g, 1.64 mmol) in ethyl acetate (1.2 mL) was added isatoic anhydride (0.300 g, 1.84 mmol). The reaction mixture was heated to 90 °C and stirred for 18 h. After cooling to room temperature, the reaction mixture was concentrated in vacuo. Purification by flash column chromatography, eluting with 20–40% ethyl acetate in hexane gave 2-amino-N-(4′-chlorophenyl)benzamide (6v) (0.277 g, 69%) as a white solid. Mp 197–200 °C (lit.7 198–200 °C); δH (500 MHz, DMSO-d6) 6.32 (2H, br s, NH2), 6.59 (1H, br t, J 7.9 Hz, 5-H), 6.75 (1H, br d, J 8.2 Hz, 3-H), 7.18–7.23 (1H, m, 4-H), 7.35–7.41 (2H, m, 2′-H and 6′-H), 7.61 (1H, dd, J 7.9, 1.1 Hz, 6-H), 7.72–7.78 (2H, m, 3′-H and 5′-H), 10.10 (1H, br s, NH); δC (126 MHz, DMSO-d6) 114.7 (CH), 114.9 (C), 116.4 (CH), 122.0 (2 × CH), 126.9 (C), 128.4 (2 × CH), 128.7 (CH), 132.3 (CH), 138.3 (C), 149.8 (C), 167.9 (C); m/z (ESI) 269 (MNa+. 100%).
2-Amino-N-(4'-iodophenyl)benzamide (6w)
To a stirred solution of 4-idoaniline (0.181 g, 0.830 mmol) in ethyl acetate (0.6 mL) was added isatoic anhydride (0.150 g, 0.920 mmol). The reaction mixture was heated to 90 °C and stirred for 18 h. An additional portion of isatoic anhydride (0.0300 g, 0.180 mmol) was then added. After 3 h, a final portion of isatoic anhydride (0.0300 g, 0.180 mmol) was added and the reaction mixture was stirred for 2.5 h. After cooling to room temperature, the reaction mixture was concentrated in vacuo. Purification by flash column chromatography, eluting with 25% ethyl acetate in hexane gave 2-amino-N-(4'-iodophenyl)benzamide (6w) (0.145 g, 52%) as a yellow solid. Mp 120‒122 °C; ν_max/cm⁻¹ (neat) 3285 (NH), 2529 (CH), 1622 (C=O), 1574 (C=C), 1522, 1481, 1385, 812; δ_H (500 MHz, CD₃OD) 6.64–6.70 (1H, m, 5-H), 6.78 (1H, br d, J 8.1 Hz, 3-H), 7.19–7.25 (1H, m, 4-H), 7.45–7.50 (2H, m, 2'-H and 6'-H), 7.58 (1H, dd, J 7.9, 1.3 Hz, 6-H), 7.63–7.68 (2H, m, 3'-H and 5'-H); δ_C (126 MHz, CD₃OD) 87.8 (C), 117.3 (CH), 117.6 (C), 118.2 (CH), 124.1 (2 × CH), 129.4 (CH), 133.6 (CH), 138.8 (2 × CH), 140.1 (C), 150.8 (C), 170.4 (C); m/z (ESI) 360.9809 (MNa⁺). C₁₃H₁₁IN₂NaO requires 360.9808).

N-(2-Aminobenzoyl)-2'-aminothiazole (6x)⁸
To a stirred solution of 2-aminothiazole (0.166 g, 1.65 mmol) in ethyl acetate (1.2 mL) was added isatoic anhydride (0.300 g, 1.84 mmol). The reaction mixture was heated to 90 °C and stirred for 18 h. After cooling to room temperature, the reaction mixture was concentrated in vacuo. Purification by flash column chromatography, eluting with 20–30% ethyl acetate in hexane gave N-(2-aminobenzoyl)-2'-aminothiazole (6x) (0.300 g, 83%) as an orange solid. Mp 157–159 °C (lit.⁸ 151–153 °C); δ_H (500 MHz, CDCl₃) 5.68 (2H, br s, NH₂), 6.67–6.72 (1H, m, 5-H), 6.76 (1H, dd, J 8.2, 0.7 Hz, 3-H), 6.90 (1H, d, J 3.7 Hz, 5'-H), 7.12 (1H, d, J 3.7 Hz, 4'-H), 7.29–7.34 (1H, m, 4-H), 7.70 (1H, dd, J 8.0, 1.3 Hz, 6-H), 12.26 (1H, br s, NH); δ_C (126 MHz, CDCl₃) 113.1 (CH), 113.7 (C), 116.8 (CH), 117.5 (CH), 128.8 (CH), 133.8 (CH), 137.5 (CH), 149.9 (C), 160.1 (C), 167.4 (C); m/z (ESI) 242 (MNa⁺. 100%).

2-Nitro-N-methylbenzenesulfonamide⁹
2-Nitrobenzenesulfonyl chloride (0.500 g, 2.26 mmol) was added in portions to a mixture of methylamine hydrochloride (0.183 g, 2.71 mmol) and triethylamine (0.626 mL, 4.51 mmol) in dichloromethane (25 mL) at 0 °C. The reaction mixture was warmed to room temperature and stirred
for 2 h. Methanol (5 mL) was then added and the reaction mixture stirred for a further 1 h. The reaction mixture was concentrated in vacuo, diluted with dichloromethane (25 mL) and washed with brine (2 × 25 mL). The organic layer was dried (MgSO$_4$), filtered and concentrated in vacuo. Purification by flash column chromatography, eluting with 25% ethyl acetate in hexane gave 2-nitro-N-methylbenzenesulfonamide (0.342 g, 70%) as a yellow solid. Mp 100‒104 °C (lit. 9106 °C); δ$_{\text{H}}$ (400 MHz, CDCl$_3$) 2.80 (3H, d, $J$ 5.2 Hz, NCH$_3$), 5.22 (1H, br s, NH), 7.72–7.79 (2H, m, 4-H and 5-H), 7.84–7.90 (1H, m, 6-H), 8.11–8.17 (1H, m, 3-H); δ$_{\text{C}}$ (101 MHz, CDCl$_3$) 29.9 (CH$_3$), 125.6 (CH), 131.7 (CH), 132.7 (C), 132.8 (CH), 133.8 (CH), 148.5 (C); m/z (ESI) 239 (MNa$^+$). 100%.

2-Nitro-N-ethylbenzenesulfonamide$_{10}$

2-Nitrobenzenesulfonyl chloride (0.500 g, 2.26 mmol) was dissolved in dichloromethane (2 mL) and added dropwise to a stirred solution of ethylamine (0.125 mL, 1.88 mmol) and triethylamine (0.315 mL, 2.26 mmol) in dichloromethane (4 mL) at 0 °C. The reaction mixture was warmed to room temperature and stirred for 4 h. The reaction mixture was then concentrated in vacuo. Purification by flash column chromatography, eluting with 70% diethyl ether in hexane gave 2-nitro-N-ethylbenzenesulfonamide (0.433 g, 100%) as a white solid. Mp 96‒98 °C (lit. 1098–100 °C); δ$_{\text{H}}$ (400 MHz, CDCl$_3$) 1.17 (3H, t, $J$ 7.3 Hz, NCH$_2$CH$_3$), 3.16 (2H, qd, $J$ 7.3, 6.0 Hz, NCH$_2$CH$_3$), 5.22 (1H, d, $J$ 6.0 Hz, NH), 7.71–7.78 (2H, m, 4-H and 5-H), 7.83–7.89 (1H, m, 6-H), 8.11–8.17 (1H, m, 3-H); δ$_{\text{C}}$ (101 MHz, CDCl$_3$) 15.3 (CH$_3$), 39.0 (CH$_2$), 125.5 (CH), 131.2 (CH), 132.9 (CH), 133.7 (CH), 133.9 (C), 148.2 (C); m/z (ESI) 253 (MNa$^+$). 100%.

2-Nitro-N-propylbenzenesulfonamide$_{11}$

2-Nitrobenzenesulfonyl chloride (0.500 g, 2.26 mmol) was dissolved in dichloromethane (2 mL) and added dropwise to a stirred solution of $n$-propylamine (0.161 mL, 1.96 mmol) and triethylamine (0.315 mL, 2.26 mmol) in dichloromethane (4 mL) at 0 °C. The reaction mixture was warmed to room temperature and stirred for 2 h. The reaction mixture was then concentrated in vacuo, diluted with dichloromethane (25 mL) and washed with water (3 × 30 mL), sodium bicarbonate (2 × 20 mL), 1 M hydrochloric acid (2 × 15 mL) and brine (2 × 15 mL). The organic layer was dried (MgSO$_4$), filtered and concentrated in vacuo to give 2-nitro-N-propylbenzenesulfonamide (0.392 g, 82%) as a white solid. Mp 72‒76 °C (lit. 1170 °C); δ$_{\text{H}}$ (400 MHz, CDCl$_3$) 0.91 (3H, t, $J$ 7.4 Hz, 3'-H$_3$), 1.55 (2H, sextet, $J$ 7.4 Hz, 2'-H$_2$), 3.07 (2H, td, $J$ 7.4, 6.2 Hz, 1'-H$_2$), 5.25 (1H, br t, $J$ 6.3 Hz, NH), 7.70–7.77 (2H, m, 4-H and 5-H), 7.83–7.89 (1H, m, 6-H), 8.11–8.18 (1H, m, 3-H); δ$_{\text{C}}$ (101 MHz, CDCl$_3$) 11.2 (CH$_3$), 23.1 (CH$_2$), 45.7 (CH$_2$), 125.5 (CH), 131.2 (CH), 132.9 (CH), 133.6 (CH), 134.0 (C), 148.3 (C); m/z (ESI) 267 (MNa$^+$). 100%).
2-Nitro-N-(tert-butyl)benzenesulfonamide

2-Nitrobenzenesulfonyl chloride (0.500 g, 2.26 mmol) was dissolved in dichloromethane (2 mL) and added dropwise to a stirred solution of tert-butylamine (0.197 mL, 1.88 mmol) and triethylamine (0.315 mL, 2.26 mmol) in dichloromethane (4 mL) at 0 °C. The reaction mixture was stirred at 0 °C for 1 h, warmed to room temperature and stirred for a further 5 h. The reaction mixture was concentrated in vacuo, diluted with dichloromethane (25 mL) and washed with water (3 × 30 mL), sodium bicarbonate (2 × 20 mL), 1 M hydrochloric acid (2 × 15 mL) and brine (2 × 15 mL). The organic layer was dried (MgSO₄), filtered and concentrated in vacuo to give 2-nitro-N-(tert-butyl)benzenesulfonamide (0.243 g, 50%) as a white solid. Mp 121‒123 °C; ν_{max}/cm⁻¹ (neat) 3264 (NH), 2974 (CH), 1541, 1368, 1323, 1153, 997; δ_H (400 MHz, CDCl₃) 1.32 (9H, s, NHC(C₃H₃)₃), 5.25 (1H, br s, NH), 7.66‒7.76 (2H, m, 4-H and 5-H), 7.85 (1H, dd, J 7.3, 2.0 Hz, 6-H), 8.20 (1H, dd, J 7.3, 2.0 Hz, 3-H); δ_C (101 MHz, CDCl₃) 30.4 (3 × CH₃), 55.9 (C), 125.4 (CH), 130.6 (CH), 133.0 (CH), 133.2 (CH), 137.4 (C), 148.0 (C); m/z (ESI) 281.0566 (MNa⁺. C₁₀H₁₄N₂NaO₄S requires 281.0566).

N-Benzylation 2-nitrobenzenesulfonamide

2-Nitrobenzenesulfonyl chloride (0.500 g, 2.26 mmol) was dissolved in dichloromethane (2 mL) and added dropwise to a stirred solution of benzylamine (0.206 mL, 1.88 mmol) and triethylamine (0.315 mL, 2.26 mmol) in dichloromethane (4 mL) at 0 °C. The reaction mixture was warmed to room temperature and stirred for 2 h. The reaction mixture was concentrated in vacuo, diluted with dichloromethane (20 mL) and washed with water (3 × 20 mL), sodium bicarbonate (2 × 10 mL), 1 M hydrochloric acid (2 × 15 mL) and brine (2 × 15 mL). The organic layer was dried (MgSO₄), filtered and concentrated in vacuo. Purification by flash column chromatography, eluting with 60% diethyl ether in hexane gave N-benzylation 2-nitrobenzenesulfonamide (0.415 g, 75%) as a white solid. Mp 86‒91 °C (lit. 92 °C); δ_H (400 MHz, CDCl₃) 4.32 (2H, d, J 6.3 Hz, PhCH₂), 5.71 (1H, t, J 6.3 Hz, NH), 7.17–7.25 (5H, m, Ph), 7.63 (1H, td, J 7.8, 1.6 Hz, 5-H), 7.68 (1H, td, J 7.8, 1.5 Hz, 4-H), 7.82 (1H, dd, J 7.8, 1.5 Hz, 6-H), 8.01 (1H, dd, J 7.8, 1.6 Hz, 3-H); δ_C (101 MHz, CDCl₃) 48.0 (CH₂), 125.4 (CH), 128.0 (2 × CH), 128.2 (CH), 128.8 (2 × CH), 131.2 (CH), 132.8 (CH), 133.5 (CH), 134.2 (C), 135.8 (C), 148.0 (C); m/z (ESI) 315 (MNa⁺. 100%).

N-(4′-Methoxybenzyl)-2-nitrobenzenesulfonamide

2-Nitrobenzenesulfonyl chloride (0.500 g, 2.26 mmol) was dissolved in dichloromethane (2 mL) and added dropwise to a stirred solution of 4-methoxybenzylamine (0.246 mL, 1.88 mmol) and triethylamine (0.315 mL, 2.26 mmol) in dichloromethane (4 mL) at 0 °C. The reaction mixture was
warmed to room temperature and stirred for 2 h. The reaction mixture was concentrated in vacuo, diluted with dichloromethane (20 mL) and washed with water (3 × 20 mL), sodium bicarbonate (2 × 10 mL), 1 M hydrochloric acid (2 × 15 mL) and brine (2 × 15 mL). The organic layer was dried (MgSO₄), filtered and concentrated in vacuo. Purification by flash column chromatography, eluting with 50–70% dichloromethane in hexane gave N-(4’-methoxybenzyl)-2-nitrobenzenesulfonamide (X) (0.458 g, 76%) as a white solid. Mp 112–116 °C (lit.¹³ 117–119 °C); δH (400 MHz, CDCl₃) 3.75 (3H, s, OCH₃), 4.24 (2H, d, J 6.2 Hz, NCH₂), 5.64 (1H, t, J 6.2 Hz, NH), 6.75 (2H, br d, J 8.4 Hz, 3’-H and 5’-H), 7.12 (2H, d, J 8.4 Hz, 2’-H and 6’-H), 7.64 (1H, td, J 7.6, 1.7 Hz, 5-H), 7.68 (1H, td, J 7.6, 1.5 Hz, 4-H), 7.82 (1H, dd, J 7.6, 1.5 Hz, 6-H), 8.01 (1H, dd, J 7.6, 1.7 Hz, 3-H); δC (101 MHz, CDCl₃) 47.6 (CH₂), 55.4 (CH₃), 114.2 (2 × CH), 125.4 (CH), 127.8 (C), 129.4 (2 × CH), 131.2 (CH), 132.8 (CH), 133.5 (CH), 134.2 (C), 148.0 (C), 159.5 (C); m/z (ESI) 345 (MNa⁺. 100%).

**N-Phenyl-2-nitrobenzenesulfonamide**¹⁴

2-Nitrobenzenesulfonyl chloride (0.300 g, 1.35 mmol) was added in portions over 0.5 h to a stirred solution of aniline (0.148 mL, 1.62 mmol) in 50% aqueous methanol (3 mL) and sodium acetate (0.156 g, 1.90 mmol). The reaction mixture was then heated to 60 °C and stirred for 1 h. The reaction mixture was allowed to cool to room temperature, diluted in water (7 mL) and acidified to pH 2 using 1 M hydrochloric acid. The precipitate was filtered, washed with excess water and then recrystallised from 4:1 ethanol:water to give N-phenyl-2-nitrobenzenesulfonamide (0.295 g, 79%) as a white solid. Mp 106–110 °C (lit.¹⁴ 109–110 °C); δH (400 MHz, CDCl₃) 7.15–7.31 (6H, m, Ph and NH), 7.57 (1H, td, J 7.9, 1.3 Hz, 5-H), 7.69 (1H, td, J 7.9, 1.3 Hz, 4-H), 7.82 (1H, dd, J 7.9, 1.3 Hz, 6-H), 7.86 (1H, dd, J 7.9, 1.3 Hz, 3-H); δC (101 MHz, CDCl₃) 123.5 (2 × CH), 125.4 (CH), 126.8 (CH), 129.6 (2 × CH), 132.0 (CH), 132.4 (C), 132.7 (CH), 134.1 (CH), 135.7 (C), 148.4 (C); m/z (ESI) 301 (MNa⁺. 100%).

**N-(4’-Methylphenyl)-2-nitrobenzenesulfonamide**¹⁵

2-Nitrobenzenesulfonyl chloride (0.500 g, 2.26 mmol) was dissolved in dichloromethane (2 mL) and added dropwise to a stirred solution of p-toluidine (0.227 g, 2.12 mmol) and triethylamine (0.315 mL, 2.26 mmol) in dichloromethane (4 mL) at 0 °C. The reaction mixture was stirred at 0 °C for 1 h, warmed to room temperature and stirred for a further 5 h. The reaction mixture was concentrated in vacuo, diluted with dichloromethane (20 mL) and washed with water (3 × 30 mL), sodium bicarbonate (2 × 20 mL), 1 M hydrochloric acid (2 × 15 mL) and brine (2 × 15 mL). The organic layer was dried (MgSO₄), filtered and concentrated in vacuo to give N-(4’-methylphenyl)-2-nitrobenzenesulfonamide (0.390 g, 63%) as a yellow solid. Mp 104–108 °C (lit.¹⁵ 110 °C); δH (400
MHz, CDCl$_3$) 2.28 (3H, s, 4'-CH$_3$), 7.06 (4H, br s, 2'-H, 3'-H, 5'-H and 6'-H), 7.15 (1H, br s, NH), 7.56 (1H, td, J 7.9, 1.3 Hz, 5'-H), 7.68 (1H, td, J 7.9, 1.3 Hz, 4'-H), 7.80 (1H, dd, J 7.9, 1.3 Hz, 6'-H), 7.85 (1H, dd, J 7.9, 1.3 Hz, 3'-H); δ$_C$ (101 MHz, CDCl$_3$) 21.1 (CH$_3$), 123.9 (2 × CH), 125.4 (CH), 130.2 (2 × CH), 132.1 (CH), 132.5 (C), 132.6 (CH), 132.9 (C), 133.9 (CH), 136.9 (C), 148.4 (C); m/z (ESI) 315 (MNa$^+$, 100%).

**N-(4'-Methoxyphenyl)-2-nitrobenzenesulfonamide**

2-Nitrobenzenesulfonyl chloride (0.500 g, 2.26 mmol) was dissolved in dichloromethane (2 mL) and added dropwise to a stirred solution of p-anisidine (0.261 g, 2.12 mmol) and triethylamine (0.315 mL, 2.26 mmol) in dichloromethane (4 mL) at 0 °C. The reaction mixture was warmed to room temperature and stirred for 6 h. The reaction mixture was concentrated in vacuo, diluted with dichloromethane (30 mL) and washed with water (3 × 50 mL), sodium bicarbonate (2 × 30 mL), 1 M hydrochloric acid (2 × 30 mL) and brine (2 × 30 mL). The organic layer was dried (MgSO$_4$), filtered and concentrated in vacuo to give N-(4'-methoxyphenyl)-2-nitrobenzenesulfonamide (0.403 g, 62%) as a brown solid. Mp 106‒108 °C (lit.$^{16}$ 106‒107 °C); δ$_H$ (400 MHz, CDCl$_3$) 3.76 (3H, s, OCH$_3$), 6.75‒6.80 (2H, m, 3'-H and 5'-H), 7.06‒7.12 (3H, m, NH, 2'-H and 6'-H), 7.56 (1H, td, J 7.8, 1.3 Hz, 5'-H), 7.70 (1H, td, J 7.8, 1.4 Hz, 4'-H), 7.74 (1H, dd, J 7.8, 1.4 Hz, 6'-H), 7.86 (1H, dd, J 7.8, 1.3 Hz, 3'-H); δ$_C$ (101 MHz, CDCl$_3$) 55.6 (CH$_3$), 114.7 (2 × CH), 125.3 (CH), 126.4 (2 × CH), 128.0 (C), 132.1 (CH), 132.4 (C), 132.6 (CH), 133.9 (CH), 148.4 (C), 158.7 (C); m/z (ESI) 331 (MNa$^+$, 100%).

**N-(4'-Bromophenyl)-2-nitrobenzenesulfonamide**

2-Nitrobenzenesulfonyl chloride (0.500 g, 2.26 mmol) was dissolved in dichloromethane (2 mL) and added dropwise to a stirred solution of 4-bromoaniline (0.364 g, 2.12 mmol) and triethylamine (0.315 mL, 2.26 mmol) in dichloromethane (4 mL) at 0 °C. The reaction mixture was warmed to room temperature and stirred for 18 h. The reaction mixture was concentrated in vacuo, diluted with dichloromethane (20 mL) and washed with water (3 × 20 mL), sodium bicarbonate (2 × 10 mL), 1 M hydrochloric acid (2 × 15 mL) and brine (2 × 15 mL). The organic layer was dried (MgSO$_4$), filtered and concentrated in vacuo. Purification by flash column chromatography, eluting with 60% diethyl ether in hexane gave N-(4'-bromophenyl)-2-nitrobenzenesulfonamide (0.348 g, 46%) as an off-white solid. Mp 106—110 °C (lit.$^{15}$ 105 °C); δ$_H$ (400 MHz, CDCl$_3$) 7.06–7.12 (2H, m, 2'-H and 6'-H), 7.26 (1H, br s, NH), 7.36–7.42 (2H, m, 3'-H and 5'-H), 7.61 (1H, td, J 7.8, 1.3 Hz, 5'-H), 7.71 (1H, td, J 7.8, 1.3 Hz, 4'-H), 7.83 (1H, dd, J 7.8, 1.3 Hz, 6'-H), 7.86 (1H, dd, J 7.8, 1.3 Hz, 3'-H); δ$_C$ (101 MHz, CDCl$_3$) 120.3 (C), 125.0 (2 × CH), 125.6 (CH), 132.0 (CH), 132.1 (C), 132.7 (2 × CH), 132.9 (CH), 134.3 (CH), 134.8 (C), 148.4 (C); m/z (ESI) 381 (MNa$^+$, 100%).
N-(4’-Iodophenyl)-2-nitrobenzenesulfonamide\textsuperscript{17}

2-Nitrobenzenesulfonyl chloride (0.500 g, 2.26 mmol) was added in portions to a stirred solution of 4-iodoaniline (0.495 g, 2.26 mmol) in dry pyridine (1.5 mL) at 0 °C. The reaction mixture was warmed to room temperature and stirred for 2 h. The reaction mixture was diluted with 2 M aqueous hydrochloric acid (50 mL) and extracted with chloroform (2 × 50 mL). The organic layers were combined and washed with brine (2 × 50 mL). The organic layer was dried (MgSO\textsubscript{4}), filtered and concentrated in vacuo. Purification by flash column chromatography, eluting with 60% diethyl ether in hexane gave N-(4’-iodophenyl)-2-nitrobenzenesulfonamide (0.766 g, 84%) as an orange solid. Mp 95‒100 °C (lit.\textsuperscript{17} 92‒94 °C); δ\textsubscript{H} (400 MHz, CDCl\textsubscript{3}) 6.93‒7.00 (2H, m, 2’-H and 6’-H), 7.23 (1H, br s, NH), 7.56‒7.65 (3H, m, 5-H, 3’-H and 5’-H), 7.71 (1H, td, J 7.8, 1.4 Hz, 4-H), 7.82‒7.88 (2H, m, 3-H and 6-H); δ\textsubscript{C} (101 MHz, CDCl\textsubscript{3}) 91.2 (C), 125.1 (2 × CH), 125.6 (CH), 132.0 (CH), 132.2 (C), 132.9 (CH), 134.3 (CH), 135.5 (C), 138.7 (2 × CH), 148.4 (C); m/z (ESI) 427 (MNa\textsuperscript{+} 100%).

2-Amino-N-methylbenzenesulfonamide (8a)\textsuperscript{18}

To a stirred solution of 2-nitro-N-methylbenzenesulfonamide (0.126 g, 0.583 mmol) in ethyl acetate (6 mL) was added tin(II) dichloride dihydrate (0.658 g, 2.91 mmol). The reaction mixture was heated under reflux for 18 h. The mixture was cooled to room temperature and sodium bicarbonate (100 mL) was added. The reaction mixture was filtered through a pad of Celite\textsuperscript{®} and diluted with ethyl acetate (40 mL). The organic layer was washed with sodium bicarbonate (3 × 60 mL), dried (MgSO\textsubscript{4}), filtered and concentrated in vacuo. Purification by flash column chromatography, eluting with 65% diethyl ether in hexane gave 2-amino-N-methylbenzenesulfonamide (8a) (0.0850 g, 78%) as a yellow oil. Spectroscopic data were consistent with the literature.\textsuperscript{18} δ\textsubscript{H} (400 MHz, CDCl\textsubscript{3}) 2.58 (3H, d, J 5.5 Hz, NCH\textsubscript{3}), 4.66 (1H, br s, NH), 4.85 (2H, br s, NH\textsubscript{2}), 6.77 (1H, dd, J 8.1, 1.0 Hz, 3-H), 6.79‒6.86 (1H, m, 5-H), 7.31‒7.37 (1H, m, 4-H), 7.71 (1H, dd, J 8.0, 1.5 Hz, 6-H); δ\textsubscript{C} (101 MHz, CDCl\textsubscript{3}) 29.5 (CH\textsubscript{3}), 117.9 (CH), 118.1 (CH), 120.7 (C), 130.2 (CH), 134.4 (CH), 145.2 (C); m/z (ESI) 209 (MNa\textsuperscript{+} 100%).

2-Amino-N-ethylbenzenesulfonamide (8b)

To a stirred solution of 2-nitro-N-ethylbenzenesulfonamide (0.142 g, 0.617 mmol) in ethyl acetate (6 mL) was added tin(II) dichloride dihydrate (0.696 g, 3.08 mmol). The reaction mixture was heated under reflux for 18 h. The mixture was cooled to room temperature and sodium bicarbonate (150 mL) was added. The reaction mixture was filtered through a pad of Celite\textsuperscript{®} and diluted with ethyl acetate (50 mL). The organic layer was washed with sodium bicarbonate (3 × 50 mL), dried (MgSO\textsubscript{4}), filtered and concentrated in vacuo. Purification by flash column chromatography, eluting with 60% diethyl ether in hexane gave 2-amino-N-ethylbenzenesulfonamide (8b) (0.104 g, 84%) as a yellow oil.
ν<sub>max</sub>/cm<sup>−1</sup> (neat) 3379 (NH), 2967 (CH), 1618 (C=C), 1481, 1315, 1134, 752; δ<sub>H</sub> (400 MHz, CDCl<sub>3</sub>) 0.83 (3H, t, J 7.4 Hz, 3'-H<sub>3</sub>), 1.37–1.49 (2H, m, 2'-H<sub>2</sub>), 2.82 (2H, q, J 6.9 Hz, 1'-H<sub>2</sub>), 4.82–4.96 (3H, m, NH and NH<sub>2</sub>), 6.72–6.81 (2H, m 3-H and 5-H), 7.27–7.33 (1H, m, 4-H), 7.69 (1H, dd, J 8.0, 1.4 Hz, 6-H); δ<sub>C</sub> (101 MHz, CDCl<sub>3</sub>) 11.2 (CH<sub>3</sub>), 22.8 (CH<sub>2</sub>), 45.1 (CH<sub>2</sub>), 117.8 (CH), 117.8 (CH), 121.7 (C), 129.7 (CH), 134.1 (CH), 145.1 (C); m/z (ESI) 237.0664 (MNa<sup>+</sup>). C<sub>9</sub>H<sub>14</sub>N<sub>2</sub>NaO<sub>2</sub>S requires 237.0668.

2-Amino-N-(tert-butyl)benzenesulfonamide (8d)
To a stirred solution of 2-nitro-N-(tert-butyl)benzenesulfonamide (0.222 g, 0.859 mmol) in ethyl acetate (9 mL) was added tin(II) dichloride dihydrate (0.970 g, 4.30 mmol). The reaction mixture was heated under reflux for 18 h. The mixture was cooled to room temperature and sodium bicarbonate (150 mL) was added. The reaction mixture was filtered through a pad of Celite<sup>®</sup> and diluted with ethyl acetate (100 mL). The organic layer was washed with sodium bicarbonate (3 × 60 mL), dried (MgSO<sub>4</sub>), filtered and concentrated in vacuo. Purification by flash column chromatography, eluting with 20% ethyl acetate in hexane gave 2-amino-N-(tert-butyl)benzenesulfonamide (8d) (0.0330 g, 17%) as a beige solid. Mp 83–87 °C; ν<sub>max</sub>/cm<sup>−1</sup> (neat) 3383 (NH), 2974 (CH), 1620 (C=C), 1483, 1315, 1136, 752; δ<sub>H</sub> (400 MHz, CDCl<sub>3</sub>) 1.18 (9H, s, NHC(CH<sub>3</sub>)<sub>3</sub>), 4.75–4.90 (3H, m, NH and NH<sub>2</sub>), 6.73 (1H, br d, J 8.1 Hz, 3-H), 6.76–6.82 (1H, m, 5-H), 7.26–7.32 (1H, m, 4-H), 7.74 (1H, dd, J 8.0, 1.4 Hz, 6-H); δ<sub>C</sub> (101 MHz, CDCl<sub>3</sub>) 11.2 (CH<sub>3</sub>), 22.8 (CH<sub>2</sub>), 45.1 (CH<sub>2</sub>), 117.8 (CH), 117.8 (CH), 121.7 (C), 129.7 (CH), 134.1 (CH), 145.1 (C); m/z (ESI) 237.0664 (MNa<sup>+</sup>). C<sub>9</sub>H<sub>14</sub>N<sub>2</sub>NaO<sub>2</sub>S requires 237.0668.
1.4 Hz, 6-H); δC (101 MHz, CDCl3) 30.0 (3 × CH3), 54.8 (C), 117.8 (CH), 118.0 (CH), 125.3 (C), 129.4 (CH), 133.8 (CH), 144.9 (C); m/z (ESI) 251.0824 (M+NaC10H16N2NaO2S requires 251.0825).

2-Amino-N-benzylbenzenesulfonamide (8e)
To a stirred solution of 2-nitro-N-benzylbenzenesulfonamide (0.176 g, 0.602 mmol) in ethyl acetate (6 mL) was added tin(II) dichloride dihydrate (0.679 g, 3.01 mmol). The reaction mixture was heated under reflux for 18 h. The mixture was cooled to room temperature and sodium bicarbonate (60 mL) was added. The reaction mixture was filtered through a pad of Celite® and diluted with ethyl acetate (30 mL). The organic layer was washed with sodium bicarbonate (3 × 60 mL), dried (MgSO4), filtered and concentrated in vacuo. Purification by flash column chromatography, eluting with 30% ethyl acetate in hexane gave 2-amino-N-benzylbenzenesulfonamide (8e) (0.134 g, 85%) as a yellow oil; vmax/cm−1 (neat) 3375 (NH), 1616 (C=C), 1481, 1454, 1315, 1138, 841; δH (400 MHz, CDCl3) 4.05 (2H, d, J 6.2 Hz, PhCH2), 4.84 (2H, br s, NH2), 4.96 (1H, t, J 6.2 Hz, NH), 6.77 (1H, dd, J 8.1, 0.8 Hz, 3-H), 6.79–6.85 (1H, m, 5-H), 7.16–7.20 (2H, m, 2’-H and 6’-H), 7.24–7.37 (4H, m, 4-H, 3’-H, 4’-H and 5’-H), 7.74 (1H, dd, J 8.0, 1.5 Hz, 6-H); δC (101 MHz, CDCl3) 47.5 (CH2), 117.9 (CH), 118.2 (CH), 121.8 (C), 128.0 (2 × CH), 128.0 (CH), 128.8 (2 × CH), 129.9 (CH), 134.4 (CH), 136.4 (C), 145.2 (C); m/z (ESI) 285.0670 (M+NaC13H14N2NaO2S requires 285.0668).

2-Amino-N-(4’-methoxybenzyl)benzenesulfonamide (8f)
To a stirred solution of 2-nitro-N-(4’-methoxybenzyl)benzenesulfonamide (0.250 g, 0.776 mmol) in ethyl acetate (7.5 mL) was added tin(II) dichloride dihydrate (0.875 g, 3.88 mmol). The reaction mixture was heated under reflux for 18 h. The mixture was cooled to room temperature and sodium bicarbonate (100 mL) was added. The reaction mixture was filtered through a pad of Celite® and diluted with ethyl acetate (60 mL). The organic layer was washed with sodium bicarbonate (3 × 60 mL), dried (MgSO4), filtered and concentrated in vacuo. Purification by flash column chromatography, eluting with 65% diethyl ether in hexane gave 2-amino-N-(4’-methoxybenzyl)benzenesulfonamide (8f) (0.0760 g, 33%) as a colourless oil; vmax/cm−1 (neat) 3372 (NH), 1612 (C=C), 1483, 1317, 1248, 1142, 752; δH (400 MHz, CDCl3) 3.77 (3H, s, 4’-OCH3), 3.98 (2H, d, J 6.1 Hz, NHCH2), 4.83 (2H, br s, NH2), 4.87 (2H, t, J 6.1 Hz, NHCH2), 6.75–6.85 (4H, m, 3-H, 5-H, 3’-H and 5’-H), 7.06–7.12 (2H, m, 2’-H and 6’-H), 7.31–7.37 (1H, m, 4-H), 7.74 (1H, dd, J 8.0, 1.5 Hz, 6-H); δC (101 MHz, CDCl3) 47.0 (CH2), 55.4 (CH3), 114.2 (2 × CH), 117.9 (CH), 118.1 (CH), 121.8 (C), 128.4 (C), 129.4 (2 × CH), 130.0 (CH), 134.4 (CH), 145.1 (C), 159.4 (C); m/z (ESI) 315.0770 (M+NaC13H14N2NaO2S requires 315.0668).
2-Amino-N-phenylbenzenesulfonamide (8g)<sup>10</sup>
To a stirred solution of 2-nitro-N-phenylbenzenesulfonamide (0.265 g, 0.952 mmol) in ethyl acetate (10 mL) was added tin(II) dichloride dihydrate (1.07 g, 4.76 mmol). The reaction mixture was heated under reflux for 18 h. The mixture was cooled to room temperature and sodium bicarbonate (150 mL) was added. The reaction mixture was filtered through a pad of Celite® and diluted with ethyl acetate (100 mL). The organic layer was washed with sodium bicarbonate (3 × 50 mL), dried (MgSO<sub>4</sub>), filtered and concentrated in vacuo. Purification by flash column chromatography, eluting with 60% diethyl ether in hexane gave 2-amino-N-phenylbenzenesulfonamide (8g) (0.195 g, 83%) as a white solid. Mp 120‒122 °C (lit.19 123‒124 °C); δ<sup>H</sup> (400 MHz, CDCl<sub>3</sub>) 4.86 (2H, br s, NH<sub>2</sub>), 6.63‒6.70 (1H, m, 5'-H), 6.74 (1H, dd, J 8.2, 1.0 Hz, 3'-H), 6.77 (1H, br s, NH), 7.01‒7.06 (2H, m, 2'-H and 6'-H), 7.12 (1H, tt, J 6.7, 1.2 Hz, 4'-H), 7.17‒7.22 (2H, m, 3'-H and 5'-H), 7.24‒7.28 (1H, m, 4-H), 7.48 (1H, dd, J 8.0, 1.5 Hz, 6-H); δ<sup>C</sup> (101 MHz, CDCl<sub>3</sub>) 117.8 (CH), 118.1 (CH), 121.2 (C), 123.0 (2 × CH), 126.1 (CH), 129.3 (2 × CH), 130.1 (CH), 134.6 (CH), 136.4 (C), 145.1 (C); m/z (ESI) 271 (MNa<sup>+</sup> 100%).

2-Amino-N-(4'-methylphenyl)benzenesulfonamide (8h)<sup>20</sup>
To a stirred solution of N-(4'-methylphenyl)-2-nitrobenzenesulfonamide (0.193 g, 0.660 mmol) in ethyl acetate (7 mL) was added tin(II) dichloride dihydrate (0.745 g, 3.30 mmol). The reaction mixture was heated under reflux for 18 h. The mixture was cooled to room temperature and sodium bicarbonate (100 mL) was added. The reaction mixture was filtered through a pad of Celite® and diluted with ethyl acetate (30 mL). The organic layer was washed with sodium bicarbonate (3 × 50 mL), dried (MgSO<sub>4</sub>), filtered and concentrated in vacuo. Purification by flash column chromatography, eluting with 60% diethyl ether in hexane gave 2-amino-N-(4'-methylphenyl)benzenesulfonamide (8h) (0.134 g, 77%) as a beige solid. Mp 123‒125 °C (lit.20 125–126 °C); δ<sup>H</sup> (400 MHz, CDCl<sub>3</sub>) 2.25 (3H, s, 4'-CH<sub>3</sub>), 4.85 (2H, br s, NH<sub>2</sub>), 6.63–6.71 (2H, m, 5-H and NH), 6.74 (1H, dd, J 8.1, 0.8 Hz, 3-H), 6.88–6.94 (2H, m, 2'-H and 6'-H), 6.97–7.02 (2H, m, 3'-H and 5'-H), 7.23–7.29 (1H, m, 4-H), 7.46 (1H, dd, J 8.0, 1.5 Hz, 6-H); δ<sup>C</sup> (101 MHz, CDCl<sub>3</sub>) 21.0 (CH<sub>3</sub>), 117.8 (CH), 118.1 (CH), 121.3 (C), 123.6 (2 × CH), 129.9 (2 × CH), 130.2 (CH), 133.7 (C), 134.5 (CH), 136.1 (C), 145.1 (C); m/z (ESI) 285 (MNa<sup>+</sup> 100%).

2-Amino-N-(4'-methoxyphenyl)benzenesulfonamide (8i)<sup>21</sup>
To a stirred solution of N-(4'-methoxyphenyl)-2-nitrobenzenesulfonamide (0.133 g, 0.431 mmol) in ethyl acetate (5 mL) was added tin(II) dichloride dihydrate (0.487 g, 2.16 mmol). The reaction mixture was heated under reflux for 18 h. The mixture was cooled to room temperature and sodium
bicarbonate (100 mL) was added. The reaction mixture was filtered through a pad of Celite® and
diluted with ethyl acetate (50 mL). The organic layer was washed with sodium bicarbonate (3 × 50
mL), dried (MgSO₄), filtered and concentrated in vacuo. Purification by flash column
chromatography, eluting with 60% diethyl ether in hexane gave 2-amino-N-(4'-methoxyphenyl)benzenesulfonamide (8i) (0.110 g, 92%) as an off-white solid. Mp 98‒103 °C (lit.²¹
98‒99 °C); δH (400 MHz, CDCl₃) 3.73 (3H, s, 4’-OCH₃), 4.84 (2H, br s, NH₂), 6.59 (1H, br s, NH),
6.63–6.77 (4H, m, 3-H, 5-H, 3’-H and 5’-H), 6.90–6.97 (2H, m, 2’-H and 6’-H), 7.26–7.31 (1H, m,
4-H), 7.40 (1H, dd, J 8.0, 1.4 Hz, 6-H); δC (101 MHz, CDCl₃) 55.5 (CH₃), 114.4 (2 × CH), 117.7
(CH), 118.1 (CH), 121.1 (C), 126.5 (2 × CH), 128.8 (C), 130.2 (CH), 134.5 (CH), 145.0 (C), 158.4
(C); m/z (ESI) 301 (MNa⁺. 100%).

2-Amino-N-(4'-bromophenyl)benzenesulfonamide (8j)
To a stirred solution of N-(4’-bromophenyl)-2-nitrobenzenesulfonamide (0.0940 g, 0.263 mmol) in
ethyl acetate (3 mL) was added tin(II) dichloride dihydrate (0.297 g, 1.32 mmol). The reaction
mixture was heated under reflux for 18 h. The mixture was cooled to room temperature and sodium
bicarbonate (100 mL) was added. The reaction mixture was filtered through a pad of Celite® and
diluted with ethyl acetate (50 mL). The organic layer was washed with sodium bicarbonate (3 × 50
mL), dried (MgSO₄), filtered and concentrated in vacuo. Purification by flash column
chromatography, eluting with 60% diethyl ether in hexane gave 2-amino-N-(4'-bromophenyl)benzenesulfonamide (8j) (0.0730 g, 85%) as a white solid. Mp 105‒110 °C; νmax/cm⁻¹
(neat) 3225 (NH), 1616 (C=C), 1481, 1312, 1134, 910; δH (400 MHz, CDCl₃) 4.84 (2H, br s, NH₂),
6.67–6.72 (1H, m, 5-H), 6.75 (1H, dd, J 8.2, 0.8 Hz, 3-H), 6.83 (1H, br s, NH), 6.89–6.94 (2H, m, 2’-
H and 6’-H), 7.26–7.34 (3H, m, 4-H, 3’-H and 5’-H), 7.48 (1H, dd, J 8.0, 1.5 Hz, 6-H); δC (101 MHz,
CDCl₃) 118.0 (CH), 118.4 (CH), 119.4 (C), 121.0 (C), 124.6 (2 × CH), 130.1 (CH), 132.4 (2 × CH),
134.8 (CH), 135.6 (C), 145.0 (C); m/z (ESI) 348.9615 (MNa⁺. C₁₂H₁₁⁷⁹BrN₂NaO₂S requires
348.9617).

2-Amino-N-(4'-iodophenyl)benzenesulfonamide (8k)
To a stirred solution of N-(4’-iodophenyl)-2-nitrobenzenesulfonamide (0.200 g, 0.495 mmol) in ethyl
acetate (5 mL) was added tin(II) dichloride dihydrate (0.297 g, 1.32 mmol). The reaction mixture was
heated under reflux for 18 h. The mixture was cooled to room temperature and sodium bicarbonate
(150 mL) was added. The reaction mixture was filtered through a pad of Celite® and diluted with
ethyl acetate (60 mL). The organic layer was washed with sodium bicarbonate (3 × 60 mL), dried
(MgSO₄), filtered and concentrated in vacuo. Purification by flash column chromatography, eluting
with 60% diethyl ether in hexane gave 2-amino-N-(4’-iodophenyl)benzenesulfonamide (8k) (0.149 g, 80%) as a yellow solid. Mp 116‒120 °C; νmax/cm–1 (neat) 3383 (NH), 2916 (CH), 1620 (C=C), 1485, 1319, 1141; δH (400 MHz, CDCl3) 4.84 (2H, br s, NH2), 6.70 (1H, td, J 8.2, 1.0 Hz, 5-H), 6.73 (1H, dd, J 8.1, 1.0 Hz, 3-H), 6.77‒6.84 (3H, m, NH, 2’-H and 6’-H), 7.26‒7.32 (1H, m, 4-H), 7.47‒7.53 (3H, m, 6-H, 3’-H and 5’-H); δC (101 MHz, CDCl3) 90.2 (C), 118.0 (CH), 118.4 (CH), 121.0 (C), 124.6 (2 × CH), 130.1 (CH), 134.8 (CH), 136.4 (C), 138.4 (2 × CH), 145.0 (C); m/z (ESI) 396.9481 (MNa+). C12H11IN2NaO2S requires 396.9478).

2-[2’-(4’’-Benzoylpiperazin-1-yl)ethyl]isoindole-1,3-dione

To an oven dried flask containing N-benzyloypiperazine (0.900 g, 4.73 mmol) in acetonitrile (30 mL) was added 2-(2-bromoethyl)isoindoline-1,3-dione (1.20 g, 4.73 mmol) and potassium carbonate (2.29 g, 16.6 mmol). The reaction mixture was heated under reflux for 24 h. The reaction mixture was cooled to room temperature and concentrated in vacuo. The reaction mixture was diluted with water (60 mL) and extracted with ethyl acetate (5 × 60 mL). The organic layer was dried (MgSO4), filtered and concentrated in vacuo. Purification by flash column chromatography, eluting with 70–80% ethyl acetate in hexane gave 2-[2’-(4’’-benzoylpiperazin-1-yl)ethyl]isoindole-1,3-dione (1.09 g, 63%) as a white solid. Mp 151‒156 °C; νmax/cm–1 (neat) 2813 (CH), 2359, 1765, 1702 (C=O), 1617, 1578 (C=C), 1432, 1399, 1288, 1009, 709; δH (500 MHz, CD3OD) 2.50 (2H, br s, 2’’-H2), 2.63 (2H, br s, 6’’-H2), 2.69 (2H, br t, J 6.3 Hz, 2’-H2), 3.38 (2H, br s, 3’’-H2), 3.70 (2H, br s, 5’’-H2), 3.84 (2H, br t, J 6.3 Hz, 1’-H2), 7.36‒7.49 (5H, m, Ph), 7.77‒7.88 (4H, m, 4-H, 5-H, 6-H and 7-H); δC (126 MHz, CD3OD) 35.9 (CH2), 43.2 (CH2), 53.7 (CH2), 54.2 (CH2), 56.6 (2 × CH2), 124.1 (2 × CH), 128.0 (2 × CH), 129.7 (2 × CH), 131.1 (CH), 133.5 (2 × C), 135.3 (2 × CH), 136.8 (C), 169.9 (2 × C), 172.4 (C); m/z (ESI) 386.1476 (MNa+). C21H21N3NaO3 requires 386.1475).
1-Benzoyl-4-[2''-aminoethyl]piperazine (12)

To a stirred solution of 2-[2''-(4''-benzoylpiperazin-1-yl)ethyl]isoindole-1,3-dione (0.200 g, 0.550 mmol) in ethanol (5.5 mL) was added hydrazine monohydrate (0.149 mL, 0.605 mmol). The reaction was heated under reflux for 4 h. The reaction mixture was cooled to room temperature. The resulting white solid was filtered and washed with ethanol (50 mL). The filtrate was concentrated in vacuo. The solid was dissolved in 1 M aqueous sodium hydroxide (25 mL) and saturated with sodium chloride. The mixture was extracted with ethyl acetate (5 × 25 mL). The combined organic layers were dried (MgSO₄), filtered and concentrated in vacuo to give 1-benzoyl-4-[2''-aminoethyl]piperazine (12) (0.110 g, 86%) as a yellow oil. ν max/cm⁻¹ (neat) 3372 (NH), 2941 (CH), 1628 (C=O), 1576 (C=C), 1433, 1293, 1002, 761; δH (500 MHz, CD3OD) 2.44 (2H, br s, 3-H2), 2.50 (2H, br t, J 6.2 Hz, 1'-H2), 2.57 (2H, br s, 5-H2), 2.77 (2H, br t, J 6.2 Hz, 2'-H2), 3.47 (2H, br s, 2-H2), 3.79 (2H, br s, 6-H2), 7.38–7.51 (5H, m, Ph); δC (126 MHz, CD3OD) 38.8 (CH2), 43.2 (CH2), 53.9 (CH2), 54.4 (CH2), 60.7 (2 × CH2), 128.0 (2 × CH), 129.7 (2 × CH), 131.1 (CH), 136.8 (C), 172.4 (C); m/z (ESI) 256.1418 (MNa⁺). C13H19N3NaO requires 256.1420.

2. References
3. $^1$H NMR and $^{13}$C NMR Spectra of All Compounds
6q

NH₂

O

Ph
N\_N\_Ph

70

[Chemical structure image]

[1H NMR spectrum image]
8b
\[ \text{NH}_2 \text{S} \text{NH}_2 \text{Bz} \]
CO₂Me

NH₂

NH

NHBoc

16

The spectrum shows several peaks at different ppm values, indicating the presence of various chemical shifts associated with the compound. The peaks are labeled with their respective chemical shifts, providing information about the structure's proton environments.
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