Supplementary Information

Diastereoselective synthesis of β-aminosulfones from the direct addition to PMP imines

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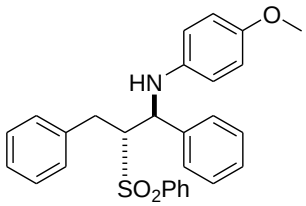
General experimental data:

Infra-red spectra were recorded on Perkin Elmer Spectrum One FT-IR spectrometers, with absorption reported in wavenumbers (cm^{-1}). Proton magnetic resonance spectra (^{1}H NMR) were recorded at 400 or 600 MHz on Bruker Avance 400 or 600 spectrometers respectively. Chemical shifts (δ) are quoted in parts per million (ppm) and referenced to the residual solvent peak. Carbon magnetic resonance spectra (^{13}C NMR) were recorded at 100 or 150 MHz on Bruker Avance 400 or 600 spectrometers respectively. If not specifically stated, the NMR experiments were run at 20 ^{o}C. Chemical shifts (δ) are quoted in parts per million (ppm) and referenced to the residual solvent peak. Coupling constants (*J*) are quoted in Hertz (Hz). High resolution mass spectra (HRMS) were recorded on a Bruker Daltonics micrOTOF spectrometer fitted with an electrospray ionisation (ES) source. "Hydrophobic frits" refers to filtration tubes sold by Whatman. Liquid chromatography was by automation using the Flashmaster II available from Argonaut Technologies Ltd, which utilises disposable, normal phase, pre-packed cartridges SPE cartridges. SPE (solid phase extraction) refers to the use of cartridges sold by International Sorbent Technology Ltd. It provides quaternary on-line solvent mixing to enable gradient methods to be run. Samples are queued using the multi-functional open access software, which manages solvents, flow-rates, gradient profile, and collection conditions. The system is equipped with a Knauer variable wavelength uv-detector and two Gilson FC204 fraction-collectors enabling automated peak cutting, collection and tracking.

General Procedure for synthesis of sulfones

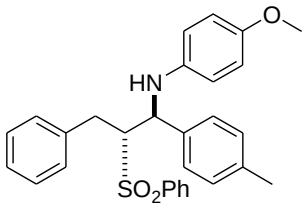
To Sulfone (0.5 mmol, 1 equiv.) in THF (4.0 ml) stirred under nitrogen at -78 °C was added a solution of BuLi (1.0M in hexane, 0.375 mL, 0.600 mmol). The reaction mixture was stirred at -78 ºC for 15 mins to give a yellow solution. Then imine (0.600 mmol, 1.2 equiv.) in THF (1.ml) was added slowly and stirred to 1 hr at -78 °C. The reaction mixture was quenched with saturated ammonium chloride (5 ml), and the aqueous layer was extracted with Et_2O (2 x 20 mL). The organic phase was dried using a hydrophobic frit and evaporated in vacuo to give the crude product which was purified by flash chromatography to isolate the product.

Table 1
Entry1. *N*-(1,3-diphenyl-2-(phenylsulfonyl)propyl)-4-methoxyaniline



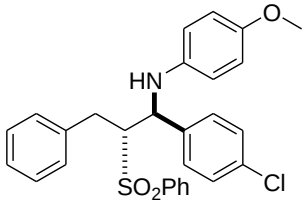
White solid, yield: (78%) m.p. 183-185 ^{o}C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ_H 3.21 (1H, dd, *J*=15.6, 4.3, CH_α), 3.46 (1H, dd, *J*=15.6, 6.5, CH_a), 3.69-3.74 (1H, m, C*H*SO_2), 3.72 (3H, s, OCH_3), 4.76 (1H, app. br, s, C*H*NH),4.87 (1H, br,s , CHN*H*), 6.44 (2H, d, *J*=9.0, Ar*H*), 6.52-6.64 (2H, m, Ar*H*), 6.70 (2H, d, *J*=9.0, Ar*H*), 6.94-7.10 (3H, m, Ar*H*), 7.14-7.36 (6H, m, Ar*H*), 7.37-7.48 (2H, m, Ar*H*), 7.52-7.64 (1H, m, Ar*H*), 7.79 (2H, d, *J*=7.2, Ar*H*); **^{13}C NMR** (101 MHz, $CDCl_3$): δ_C 28.6 (*C*H_2), 55.7 (O*C*H_3), 57.9 (*C*HNH), 71.6 (*C*HSO_2), 114.6 (2C, *Ar*), 115.5 (2C, *Ar*), 126.3 (*Ar*), 127.1 (2C, *Ar*), 127.8 (*Ar*), 128.2 (2C, *Ar*), 128.4 (2C, *Ar*), 128.7 (2C, *Ar*), 128.9 (2C, *Ar*), 129.2 (2C, *Ar*), 133.8 (*Ar*), 137.9 (q), 138.3 (q), 139.1 (q), 140.8 (q), 152.7 (q); **IR** (NEAT) 3383 (N-H), 3029 (C-H), 2931 (C-H), 1510 (C=C), 1142 (S=O); **HRMS** (ES) calcd. for $C_{28}H_{28}NO_3S^+$, [M + H^+] 458.1784 found 458.1781.

Entry 2. 4-methoxy-*N*-(3-phenyl-2-(phenylsulfonyl)-1-(p-tolyl)propyl)aniline



White solid, yield: (60%) m.p. 142-144 ^{o}C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ_H 2.39 (3H, s, C*H*$_3$), 3.25 (1H, dd, *J*=15.3, 4.3, C*H*$_{2\alpha}$), 3.46 (1H, dd, *J*=15.3 6.7, C*H*$_{2\beta}$), 3.73-3.79 (1H, m, C*H*SO_2), 3.77 (3H, s, OC*H*$_3$), 4.78 (1H, d *J*=2.3, C*H*NH), 4.92 (1H, br,s , CHN*H*), 6.49 (2H, d, *J*=8.8, Ar*H*), 6.67 (2H, dd, *J*=7.0, 2.3, Ar*H*), 6.71-6.81 (2H, m, Ar*H*), 7.01-7.13 (3H, m, Ar*H*), 7.17 (2H, d, *J*=7.8, Ar*H*), 7.26 (2H, d, *J*=8.0, Ar*H*), 7.46 (2H, t, *J*=7.8, Ar*H*), 7.62 (1H, t, *J*=7.5, Ar*H*), 7.83 (2H, d, *J*=7.3, Ar*H*); **^{13}C NMR** (101 MHz, $CDCl_3$): δ_C 21.1 (*C*H_2), 28.7 (*C*H_2), 55.7 (O*C*H_3), 57.7 (*C*HNH), 71.5 (*C*HSO_2), 114.6 (2C, *Ar*), 115.5 (2C, *Ar*), 126.3 (*Ar*), 127.0 (2C, *Ar*), 128.2 (2C, *Ar*), 128.5 (2C, *Ar*), 128.7 (2C, *Ar*), 129.1 (2C, *Ar*), 129.6 (2C, *Ar*), 133.8 (*Ar*), 136.0 (q), 137.5 (q), 138.0 (q), 138.3 (q), 140.9 (q), 152.6 (q); **IR** (NEAT) 3383 (N-H), 3029 (C-H), 2931 (C-H), 1511 (C=C), 1142 (S=O) ; **HRMS** (ES) calcd. for $C_{29}H_{30}NO_3S^+$, [M + H^+] 472.1945 found 472.1941

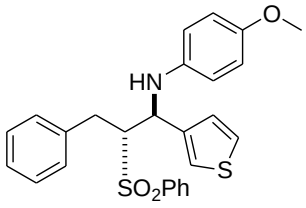
Entry 3. *N*-(1-(4-chlorophenyl)-3-phenyl-2-(phenylsulfonyl)propyl)-4-methoxyaniline



White solid, yield: (71%) m.p. 150-153 ^{o}C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ_H 3.15 (1H, dd, *J*=15.4, 5.0, C*H*$_\alpha$), 3.46 (1H, dd, *J*=15.4 6.3, C*H*$_\beta$), 3.68-3.80 (1H, m, C*H*SO_2), 3.74 (3H, s, OC*H*$_3$), 4.76 (1H, d *J*=2.5, C*H*NH), 4.91 (1H, br,s , CHN*H*), 6.34-6.50 (2H, m, Ar*H*), 6.55 (2H, dd, *J*=7.3, 2.3, Ar*H*), 6.69-6.77 (2H, m, Ar*H*), 7.01-7.12 (3H, m, Ar*H*), 7.23-7.30 (4H, m, Ar*H*), 7.38-7.50 (2H, m, Ar*H*), 7.55-7.66 (1H, m, Ar*H*), 7.75-7.86 (2H, m, Ar*H*); **^{13}C NMR** (101 MHz, $CDCl_3$): δ_C 28.9 (*C*H_2), 55.7 (O*C*H_3), 57.4 (*C*HNH), 71.2 (*C*HSO_2), 114.7 (2C, *Ar*), 115.5 (2C, *Ar*), 126.5 (*Ar*), 128.4 (2C, *Ar*), 128.4 (2C, *Ar*),

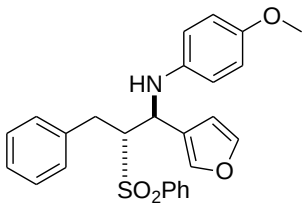
128.6 (2C, *Ar*), 128.7 (2C, *Ar*), 129.0 (2C, *Ar*), 129.2 (2C, *Ar*), 133.6 (q), 134.0 (*Ar*), 137.6 (q), 137.7 (q), 137.8 (q), 140.4 (q), 152.9 (q); **IR** (NEAT) 3385 (N-H), 3063 (C-H), 2934 (C-H), 1511 (C=C), 1143 (S=O); **HRMS** (CI) calcd. for $C_{28}H_{27}NO_3SCl^+$, [M + H^+] 492.1400 found 492.1404.

Entry 4. 4-methoxy-*N*-(3-phenyl-2-(phenylsulfonyl)-1-(thiophen-3-yl)propyl)aniline



White solid, yield: (78%) m.p. 162-164 ^oC; **^{1}H NMR** (400 MHz, $CDCl_3$): δ_H 3.39 (2H, d, *J*=6.0, C*H*$_2$), 3.79 (3H, s, OC*H*$_3$), 3.87 (1H, app td, *J*=5.8, 2.6, C*H*SO_2), 4.98 (1H, br,s , CHN*H*), 5.12 (1H, app br. s, C*H*NH), 6.53-6.62 (2H, m, Ar*H*), 6.73-6.81 (2H, m, Ar*H*), 6.85 (2H, dd, *J*=6.5, 2.8, Ar*H*), 7.03 (1H, dd, *J*=5.0, 3.8, Ar*H*), 7.09 (1H, d, *J*=3.3, Ar*H*), 7.14-7.23 (3H, m, Ar*H*), 7.28 (1H, dd, *J*=5.0, 1.0, Ar*H*), 7.42-7.52 (2H, m, Ar*H*), 7.60-7.66 (1H, m, Ar*H*), 7.76-7.84 (2H, m, Ar*H*); **^{13}C NMR** (101 MHz, $CDCl_3$): δ_C 30.1 (*C*H_2), 54.5 (*C*HNH), 55.6 (O*C*H_3), 71.4 (*C*HSO_2), 114.7 (2C, *Ar*), 115.7 (2C, *Ar*), 125.1 (*Ar*), 125.2 (*Ar*), 126.6 (*Ar*), 127.3 (*Ar*), 128.4 (2C, *Ar*), 128.6 (2C, *Ar*), 128.6 (2C, *Ar*), 129.1 (2C, *Ar*), 133.8 (*Ar*), 137.7 (q), 138.1 (q), 140.4 (q), 143.7 (q), 153.0 (q); **IR** (NEAT) 3377 (N-H), 3063 (C-H), 2833 (C-H), 1511 (C=C), 1144 (S=O); **HRMS** (CI) calcd. for $C_{26}H_{26}NO_3S_2^+$, [M + H^+] 464.1348 found 464.1354.

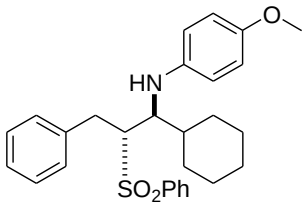
Entry 5. *N*-(1-(furan-3-yl)-3-phenyl-2-(phenylsulfonyl)propyl)-4-methoxyaniline



White solid, yield: (87%) m.p. 147-149 ^oC; **^{1}H NMR** (400 MHz, $CDCl_3$): δ_H 3.25 (1H, dd, *J*=14.6, 8.3, C*H*$_\alpha$), 3.35 (1H, dd, *J*=14.6 5.1, C*H*$_\beta$), 3.80 (3H, s, OC*H*$_3$), 3.90-4.02 (1H, m, C*H*SO_2), 4.75-5.02 (2H, m , CHN*H* and C*H*NH), 6.32-6.43 (2H, m, Ar*H*), 6.45-

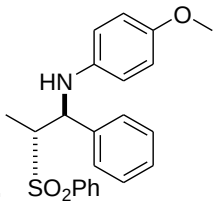
6.56 (2H, m, Ar*H*), 6.71-6.83 (2H, m, Ar*H*), 7.02 (2H, dd, *J*=7.4, 1.6, Ar*H*), 7.19-7.30 (3H, m, Ar*H*), 7.32-7.38 (1H, m, Ar*H*), 7.51 (2H, t, *J*=7.8, Ar*H*), 7.65 (1H, t, *J*=7.5, Ar*H*), 7.76-7.86 (2H, m, Ar*H*); **^{13}C NMR** (101 MHz, $CDCl_3$): δ_C 31.5 (*C*H_2), 52.4 (*C*HNH), 55.7 (O*C*H_3), 68.8 (*C*HSO_2), 109.0 (*Ar*), 110.6 (*Ar*), 114.8 (2C, *Ar*), 115.7 (2C, *Ar*), 126.9 (*Ar*), 128.6 (2C, *Ar*), 128.7 (2C, *Ar*), 128.9 (2C, *Ar*), 129.1 (2C, *Ar*), 133.6 (*Ar*), 137.1 (q), 138.3 (q), 140.1 (q), 142.0 (*Ar*), 151.8 (q), 153.0 (q); **IR** (NEAT) 3378 (N-H), 3063 (C-H), 2834 (C-H), 1511 (C=C), 1144 (S=O); **HRMS** (ES) calcd. for $C_{26}H_{26}NO_4S^+$, [M + H^+] 448.1577 found 448.1572.

Entry 6. *N*-(1-(furan-3-yl)-3-phenyl-2-(phenylsulfonyl)propyl)-4-methoxyaniline



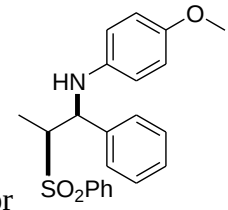
White solid, yield: (73%) m.p. 110-112 ^oC; **^{1}H NMR** (400 MHz, $CDCl_3$): δ_H 0.83-1.02 (1H, m, C*H* cyclo), 1.10-1.28 (4H, m, C*H* cyclo), 1.65-1.84 (5H, m, C*H* cyclo), 1.99 (1H, d, *J*=12.3, Ar*H*), 3.05 (1H, dd, *J*=14.6, 9.3, CH_a), 3.15 (1H, dd, *J*=14.6, 4.3, CH_a), 3.61-3.77 (2H, m, C*H*SO_2 and CHN*H*), 3.81 (3H, s, OCH_3), 3.86 (1H, app. br, s *CHNH*), 6.42-6.57 (2H,m, Ar*H*), 6.70-6.84 (2H, m, Ar*H*), 6.91-7.05 (2H, m, Ar*H*), 7.20-7.31 (3H, m, Ar*H*), 7.52 (2H, t, *J*=7.8, Ar*H*), 7.65 (1H, t, *J*=7.5, Ar*H*), 7.79-7.91 (2H, m, Ar*H*); **^{13}C NMR** (101 MHz, $CDCl_3$): δ_C 26.2 (*C*H_2), 26.2 (*C*H_2), 26.3 (*C*H_2), 28.9 (*C*H_2), 31.9 (*C*H_2), 32.4 (*C*H_2Ph), 42.1 (*C*H), 55.8 (O*C*H_3), 58.2 (*C*HNH), 67.6 (*C*HSO_2), 114.7 (2C, *Ar*), 114.9 (2C, *Ar*), 126.8 (*Ar*), 128.5 (2C, *Ar*), 128.6 (2C, *Ar*), 128.7 (2C, *Ar*), 129.1 (2C, *Ar*), 133.5 (*Ar*), 137.6 (q), 139.2 (q), 141.8 (q), 152.1 (q); **IR** (NEAT) 3385 (N-H), 3030 (C-H), 2933 (C-H), 1511 (C=C); **HRMS** (CI) calcd. for $C_{28}H_{34}NO_3S^+$, [M + H^+] 464.1354 found 464.1352.

Entry 7. 4-methoxy-*N*-(1-phenyl-2-(phenylsulfonyl)propyl)aniline



Major

White solid, yield: (55%) m.p. 110-112 ^{o}C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ_H 1.31 (3H, d, *J*=7.3, C*H*$_3$), 3.36 (1H, qd, *J*=7.3, 2.3, C*H*SO_2), 3.69 (3H, s, OC*H*$_3$), 4.59 (1H, br,s , CHN*H*), 4.73 (1H, d, *J*=2.3, C*H*NH), 6.32-6.42 (2H, m, Ar*H*), 6.60-6.71 (2H, m, Ar*H*), 7.20-7.37 (5H, m, Ar*H*), 7.51 (2H, t, *J*=7.8, Ar*H*), 7.65 (1H, t, *J*=7.4, Ar*H*), 7.82-7.95 (2H, m, Ar*H*); **^{13}C NMR** (101 MHz, $CDCl_3$): δ_C 6.8 (CH3), 55.5 (OCH3), 57.3 (CHNH), 65.2 ($CHSO_2$), 114.6 (2C, Ar), 115.3 (2C, Ar), 126.7 (2C, Ar), 127.7 (Ar), 128.8 (2C, Ar), 128.9 (2C, Ar), 129.2 (2C, Ar), 134.0 (Ar), 137.3 (q), 139.9 (q), 140.8 (q), 152.6 (q); **IR** (NEAT) 3388 (N-H), 2934 (C-H), 1512 (C=C); **HRMS** (ES) calcd. for $C_{22}H_{24}NO_3S^+$, [M + H^+] 382.1477 found 382.1481.



Minor

White solid, yield: (30%) m.p. 110-112 ^{o}C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ_H 1.10 (3H, d, *J*=7.0, C*H*$_3$), 3.39-3.57 (1H, m, C*H*SO_2), 3.71 (3H, s, OC*H*$_3$), 4.34 (1H, d, *J*=8.8, C*H*NH), 5.18 (1H, br,s , CHN*H*), 6.37-6.54 (2H, m, Ar*H*), 6.61-6.78 (2H, m, Ar*H*), 7.19-7.39 (5H, m, Ar*H*), 7.51 (2H, t, *J*=7.8, Ar*H*), 7.65 (1H, t, *J*=7.4, Ar*H*), 7.75-7.92 (2H, m, Ar*H*); **^{13}C NMR** (101 MHz, $CDCl_3$): δ_C 13.5 (CH3), 55.7 (OCH3), 60.5 (CHNH), 64.9 ($CHSO_2$), 114.7 (2C, Ar), 115.3 (2C, Ar), 126127.6 (2C, Ar), 128.0 (Ar), 128.8 (2C, Ar), 129.0 (2C, Ar), 129.1 (2C, Ar), 133.8 (Ar), 137.5 (q), 140.4 (q), 140.6 (q), 152.5 (q); **IR** (NEAT) 3388 (N-H), 2934 (C-H), 1512 (C=C); **HRMS** (ES) calcd. for $C_{22}H_{24}NO_3S^+$, [M + H^+] 382.1477 found 382.1490.