Supplementary Material (ESI) for Chemical Communications

Trichlorophenol (TCP) Sulfonate Esters: A Selective Alternative to Pentafluorophenol (PFP) Esters and Sulfonyl Chlorides for the Preparation of Sulfonamides

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Supporting Information

General. Solvents and reagents were commercially available and used without further purification, unless otherwise noted. Anhydrous solvents were used when necessary. Analytical thin layer chromatography (TLC) was performed on SIL G/UV_{254} silica plates and visualisation was achieved by use of UV light and potassium permanganate solution. Flash chromatography was carried out using BDH silica gel (particle size 33microm –70 microm.

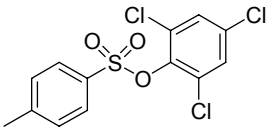
^{1}H NMR spectra were recorded on a Brucker AMX 300 (300 MHz) spectrometer. Chemical shifts are reported in units parts per million (ppm) relative to the singlet at 7.26 ppm for chloroform-d. Spin multiplicities were reported as singlet (s), doublet (d), triplet (t), quartet (q), multiplet (m) and coupling constants (J) are given in Hertz (Hz).

^{13}C NMR spectra were recorded on a Brucker AMX 300 (75 MHz) and standard abbreviations were used (singlet (s), doublet (d), triplet (t), quartet (q)).

Mass spectra were obtained on a Kratos MS25 spectrometer.

Infra red spectra were run on a Shimadzu FTIR 8700 spectrometer or a Perkin-Elmer Spectrum One spectrometer with frequencies given in reciprocal centimetres (cm^{-1}). Major Features of each spectrum are reported and the following abbreviations are used: w, weak; m, medium; s, strong and br, broad.

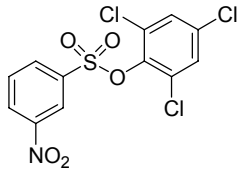
2,4,6-Trichlorophenyltosylate



To a solution of triphenylphosphine oxide (1.1 g, 4 mmol) in anhydrous DCM (20 ml) at 0 °C under nitrogen was added trifluoromethanesulfonic anhydride (0.3 ml, 2 mmol) and the mixture was stirred for 20 minutes. Pyridinium *p*-toluenesulfonate (510 mg, 2 mmol) was added and the mixture was stirred for 20 minutes. A pre-mixed solution of 2,4,6-trichlorophenol (409 mg, 2 mmol) and triethylamine (0.47 ml, 2 mmol) in DCM (5 ml) was added dropwise over a period of 10 minutes. The reaction was allowed to warm to room temperature. It was then diluted with DCM (*ca.* 30 ml) and washed with 2M sodium carbonate solution (2 x 30ml), 2M HCl (2 x 30 ml), water (30 ml), separated, dried ($MgSO_4$) and concentrated *in vacuo*. The crude product was purified by column chromatography (petroleum ether/diethyl ether) to yield the product as a white solid (495 mg, 69%). Data in agreement with literature values.[1]

MP	84-87ºC
^{1}H NMR	δ_H (300 MHz, $CDCl_3$) 7.90 (2H, d, J = 8.6 Hz, Ar**H**), 7.39 (2H, d, J= 8.3 Hz, Ar**H**), 7.35 (2H,s, Ar**H**), 2.48 (3H, s, CH_3)
^{13}C NMR	δ_C (75 MHz, $CDCl_3$) 145.9 (s, **C**(Ar)), 142.4 (s, **C**(Ar)), 134.0 (s, **C**(Ar)), 132.8 (s, **C**(Ar)), 131.0 (s, **C**(Ar)), 129.8 (d, **C**(Ar)), 129.2 (d, **C**(Ar)), 128.6 (d, **C**(Ar)), 21.8 (q, **C**H_3).
FTIR	(CH_3Cl Solution, cm^{-1}) 1558 m, 1437 w, 1387 s, 1275 s, 1256 s, 1192 m, 1180, m 1137 m, 1091 w
HRMS (CI):	calcd for $C_{13}H_9Cl_3O_3S$ (M^+): 349.93380 found 349.93417

3-Nitrophenyl 2,4,6-trichlorophenyl sulfonyl ester



Prepared as for 2,4,6-Trichlorophenyltosylate. The product was purified by column chromatography (petroleum ether/diethyl ether) to yield the product as a white solid (689 mg, 72 %).

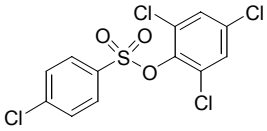
MP 129-130ºC

^{1}H NMR δ_H (300 MHz, $CDCl_3$) 8.88 (1H, app. t, J = 1.9 Hz, Ar**H**), 8.59 (1H, ddd, J = 1.1, 2.2, 8.3 Hz, Ar**H**), 8.37 (1H, ddd, J = 1.1, 1.7, 8.0 Hz, Ar**H**), 7.85(1H, app. t, J = 8.0 Hz, Ar**H**), 7.39(2H, app. t, C**H**$_3$)

FTIR (CH_3Cl Solution, cm^{-1}) 1541 s, 1443 w, 1354 s, 1256 s, 1196 m

HRMS (CI): calcd for $C_{12}H_6Cl_3NO_5S$ (M^+): 380.90268 found 380.89050

4-Chloro-benzenesulfonic acid 2,4,6-trichlorophenyl ester



Prepared as for 2,4,6-Trichlorophenyltosylate. The product was purified by column chromatography (petroleum ether/diethyl ether) to yield the product as a white solid (555mg, 80%). Data in agreement with literature values.[2]

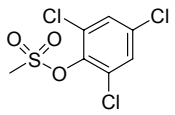
MP 100-103ºC *lit* 97-98ºC (ethanol, benzene)

^{1}H NMR δ_H (300 MHz, $CDCl_3$) 7.96 (2H, d, J = 8.7 Hz, Ar**H**), 7.57 (2H, d, J = 8.7 Hz, Ar**H**), 7.37(1H, s, Ar**H**)

^{13}C NMR δ_C (75 MHz, $CDCl_3$) 130.8 (s, **C**(Ar)), 130.0 (d, **C**(Ar)), 129.6 (d, **C**(Ar)), 129.2 (d, **C**(Ar))

HRMS (CI): calcd for $C_{12}H_6Cl_4O_3S$ (M^+): 370.88700 found 370.88811

Methyl 2,4,6-trichlorophenylsulfonyl ester



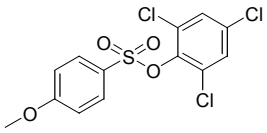
Prepared as for 2,4,6-Trichlorophenyltosylate. The product was purified by column chromatography (petroleum ether/diethyl ether) to yield the product as a white solid (629 mg, 44 %).

MP 63-66ºC

^{1}H NMR δ_H (300 MHz, $CDCl_3$) 7.41 (2H, s, Ar**H**), 3.46, s, C**H$_3$**)

^{13}C NMR δ_C (75 MHz, $CDCl_3$) 142.0 (s, **C**(Ar)), 133.1 (s, **C**(Ar)), 130.6 (s, **C**(Ar)), 129.2 (d, **C**(Ar)), 41.1 (q, **C**H_3)

4-Methoxy-benzenesulfonic acid 2,4,6-trichlorophenyl ester



To a solution of 4-methoxybenzenesulfonyl chloride (12.4 g, 60 mmol) in DCM (150 ml) at 0 °C was added a pre-mixed solution of 2,4,6-trichlorophenol (14.2 g, 72 mmol) and triethylamine (20.9 ml, 150 mmol) in DCM (50 ml) dropwise. The reaction was stirred at 0 °C for a further 15mins and allowed to warm to room temperature over 2h. The reaction mixture was washed with 2M sodium carbonate solution (2 x 50 ml), 2M HCl (2 x 50 ml) and water (50 ml), separated, dried ($MgSO_4$) and the solvent removed *in vacuo*. Recrystallisation from acetone gave the product as white crystals (19g, 86%).

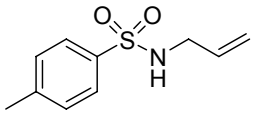
MP 116-120ºC (acetone)

^{1}H NMR δ_H (300 MHz, $CDCl_3$) 7.94 (2H, d, J = 9.1Hz, Ar**H**), 7.03 (2H, d, J= 9.0 Hz, Ar**H**), 7.35 (2H,s, Ar**H**), 3.91 (3H, s, CH_3)

^{13}C NMR δ_C (75 MHz, $CDCl_3$) 164.5 (s, **C**(Ar)), 142.4 (s, **C**(Ar)), 132.7 (s, **C**(Ar)), 130.9 (d, **C**(Ar)), 129.1 (d, **C**(Ar)), 128.2 (s, **C**(Ar)), 114.4 (d, **C**(Ar)), 55.8 (q, **C**H_3)

FTIR (cm^{-1}) 1593 m, 1495 w, 1439 m, 1380 s, 1319 w, 1266 s, 1166 s, 1093 m, 1018 m

***N*-Allyl-4-methylbenzenesulfonamide**



To a solution of TCP sulfonate (100 mg, 0.28 mmol) in NMP (1 ml) was added allylamine (45 µl, 0.56 mmol) and triethylamine (43 µl, 0.31 mmol). The mixture was heated in the microwave for 10 minutes at 140 ºC. The reaction mixture was diluted with diethyl ether (20 ml) and washed with 2M sodium carbonate solution (2 x 10 ml), 2M hydrochloric acid (2 x 10 ml) and 10% Lithium chloride solution (3 x 10 ml). The organic portion was separated, dried ($MgSO_4$) and the solvent removed *in vacuo* to yield a yellow solid (50 mg, 83%). Data in agreement with literature values.[3]

MP 63-64ºC *lit* 63-65ºC (aq. MeOH)

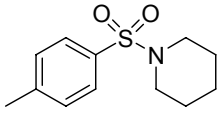
^{1}H NMR δ_H (300 MHz, $CDCl_3$) 7.75 (2H, d, J =8.3 Hz, Ar**H**), 7.27(2H, d, J =8.3 Hz, Ar**H**), 5.71 (1H, ddt, J = 17.1, 10.2, 5.9 Hz, CH_2**H**C=CH_2), 5.15 (1H, app. dq, J = 17.1, 1.6 Hz, CH=C**H**H), 5.08 (1H, app. dq, J = 10.2, 1.1, CH=C**H**H), 4.77 (1H, br t, J = 5.9, N**H**), 3.57 (2H, app. tt, J = 6.2, 1.3 Hz , C**H$_2$**-CH=CH_2), 2.41 (3H, s, C**H$_3$**)

^{13}C NMR δ_C (75 MHz, $CDCl_3$) 143.5 (s, **C**(Ar)), 137.0 (s, **C**(Ar)), 133.0 (d, **C**(Ar)), 129.7 (d, **C**H=CH_2), 117.7 (t, CH_2-CH=**C**H_2), 45.8(t, **C**H_2-CH=CH_2), 21.5 (q, **C**H_3)

FTIR (CH_3Cl Solution, cm^{-1}) 3287 br. S, 2987 m, 1647 w, 1598 m, 1495 w, 1422 s 1328 s, 1265 s, 1161 s, 1094 w

HRMS (ESI): calcd for $C_{10}H_{13}NO_2S$ (M^+): 211.06670 found 211.06644

Toluene-4-sulfonyl-piperidine



Prepared as for *N*-Allyl-4-methylbenzenesulfonamide to yield the product as a white solid (60 mg, 88 %). Data in agreement with literature values.[4]

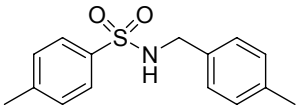
MP 90-95ºC *lit.* 98ºC

^{1}H NMR δ_H (300 MHz, $CDCl_3$) 7.63 (2H, d, J = 8.3 Hz, ArH), 7.28 (2H, d, J = 8.3 Hz, ArH), 2.96 (4H, t, J = 5.6 Hz, CH_2), 2.42 (3H, s, CH_2), 1.59 – 1.66 (4H, m, CH_2), 1.36 – 1.44 (2H, m, CH_2)

^{13}C NMR δ_C (75 MHz, $CDCl_3$) 143.3 (s, **C**(Ar)), 133.3 (s, **C**(Ar)), 129.5 (d, **C**(Ar)), 127.7 (d, **C**(Ar)), 46.9(t, **C**H_2), 29.7(t, **C**H_2), 25.2 (t, **C**H_2), 23.5 (t, **C**H_2), 21.5 (q, **C**H_3)

FTIR (CH_3Cl Solution, cm^{-1}) 2944 s, 2925 s, 2859 m, 1596 w, 1466 m, 1439, 1357 s, 1312 s, 1184 s, 1149 m, 1068 m, 1028 m

4-Methyl-*N*-(4-methyl-benzyl)-benzenesulfonamide



Prepared as for *N*-Allyl-4-methylbenzenesulfonamide to yield the product as a white solid (73 mg, 94 %). Data in agreement with literature values.[5]

MP 93-96 ºC *lit.* 94.7-95.5ºC

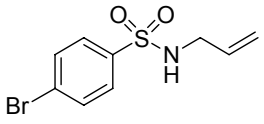
^{1}H NMR δ_H (300 MHz, $CDCl_3$) 7.76 (2H, d, J = 8.3 Hz, Ar**H**), 7.31 (2H, d, J = 8.3, Ar**H**), 7.08 (4H, 2, Ar**H**), 4.57 (1H, br, N**H**), 4.20 (2H, d, J = 7.3 Hz, C**H$_2$**), 2.51 (3H, s, C**H$_3$**), 2.31 (3H, s, C**H$_3$**)

^{13}C NMR δ_C (75 MHz, $CDCl_3$) 143.5 (s, **C**(Ar)), 137.7 (s, **C**(Ar)), 136.9 (s, **C**(Ar)), 133.2 (s, **C**(Ar)), 129.4 (d, **C**(Ar)), 129.7 (d, **C**(Ar)), 127.9 (d, **C**(Ar)), 127.2 (d, **C**(Ar)), 47.1 (t, **C**H_2), 21.5 (q, **C**H_3), 21.1(q, **C**H_3)

FTIR (CH_3Cl Solution, cm^{-1}) 3361 m, 3027 w, 2926 w, 1595 w, 1516 w, 1416 m, 1323 s, 1184 w, 1161 s, 1094 m, 1056 m, 1020 w

HRMS (ESI): calcd for $C_{15}H_{17}NO_2S$ (M^+): 275.09799 found 275.09805

***N*-Allyl-4-bromobenzenesulfonamide**



Prepared as for *N*-Allyl-4-methylbenzenesulfonamide to yield the product as a brown solid (57 mg, 78 %). Data in agreement with literature values.[6]

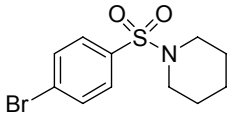
MP 62-64ºC *lit.* 60-61ºC

^{1}H NMR δ_H (300 MHz, $CDCl_3$) 7.73 (2H, d, J =8.8, Ar**H**), 7.65(2H, d, J =8.8 Hz, Ar**H**), 5.70 (1H, ddt, J = 17.1, 10.2, 5.6 Hz, CH_2**H**C=CH_2), 5.16 (1H, app. dq, J = 17.1, 1.7 Hz, CH=C**H**H), 5.10 (1H, app. dq, J = 10.12, 1.4 Hz, CH=C**H**H), 4.83 (1H, t, J = 6.0 Hz, N**H**), 3.60 (2H, app. tt, J = 6.1, 1.4 Hz , C**H$_2$**-CH=CH_2)

^{13}C NMR δ_C (75 MHz, $CDCl_3$) 139.1 (s, **C**(Ar)), 132.7 (d, **C**(Ar)), 132.4 (d, **C**(Ar)), 128.7(d, **C**H=CH_2), 127.7 (s, **C**(Ar)), 118.0 (t, CH_2-CH=**C**H_2), 45.8(t, **C**H_2-CH=CH_2)

HRMS (ESI): calcd for $C_{11}H_{14}BrNO_2S$ (M^+): 274.96101 found 274.96101

1-(4-Bromo-benzenesulfonyl)-piperidine



Prepared as for *N*-Allyl-4-methylbenzenesulfonamide to yield the product as a white solid (60 mg, 82 %). Data in agreement with literature values.[7]

MP 87-90ºC *lit.* 90-91ºC

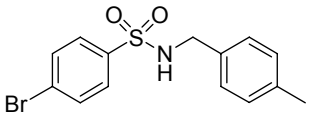
^{1}H NMR δ_H (300 MHz, $CDCl_3$) 7.58-7.67 (4H, m, Ar**H**), 2.97 (4H, t, J = 5.6 Hz), 1.58 -1.66 (4H, m, C**H$_2$**), 1.37-1.45 (2H, m, C**H$_2$**)

^{13}C NMR δ_C (75 MHz, $CDCl_3$) 135.5 (s, **C**(Ar)), 132.3(d, **C**(Ar)), 129.2(d, **C**(Ar)), 127.6(s, **C**(Ar)), 46.9(t, **C**H_2), 25.1(t, **C**H_2), 23.4(t, **C**H_2)

FTIR (CH_3Cl Solution, cm^{-1}) 3053 m, 2987 w, 1575 m, 1471 w, 1464 w, 1388 s, 1282 w, 1193 s, 1104 m, 1067 m, 1031 m

HRMS (ESI): calcd for $C_{11}H_{14}BrNO_2S$ (M^+): 302.99231 found 302.99278

4-Bromo-*N*-(4-methyl-benzyl)-benzenesulfonamide



Prepared as for *N*-Allyl-4-methylbenzenesulfonamide to yield the product as a yellow solid (69 mg, 84 %). Data in agreement with literature values.[5]

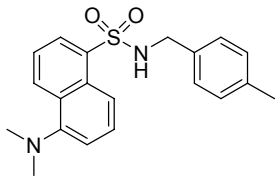
MP 124-128ºC *lit.* 126.5-127.5ºC

^{1}H NMR δ_H (300 MHz, $CDCl_3$) 7.68 (2H, d, J = 10.8 Hz, Ar**H**), 7.60 (2H, d, J = 10.9 Hz, Ar**H**), 7.09(4H, s, Ar**H**), 4.93 (1H, t, J = 6.0 Hz, N**H**), 4.09 (2H, d, J = 6.1 Hz, C**H$_2$**), 2.31 (3H, s, C**H$_3$**)

^{13}C NMR δ_C (75 MHz, $CDCl_3$) 139.1 (s, Ar**H**), 137.9 (s, Ar**H**), 132.8 (s, Ar**H**), 132.3 (d, Ar**H**), 129.4 (d, Ar**H**), 128.7 (d, Ar**H**), 127.9 (d, Ar**H**), 127.6(s, Ar**H**), 47.1 (t, C**H$_2$**), 21.1 (q, C**H$_3$**)

HRMS (ESI): calcd for $C_{14}H_{14}BrNO_2S$ (M^+): 338.99231 found 338.99096

5-Dimethylamino-naphthalene-1-sulfonic acid 4-methyl-benzylamide



To a solution of TCP sulfonate (100 mg, 0.23 mmol) in NMP (1 ml) was added 4-methylbenzylamine (59 µl, 0.46 mmol) and triethylamine (36 µl, 0.26 mmol). The mixture was heated in the microwave for 10 minutes at 140 ºC. The reaction mixture was diluted with diethyl ether (20 ml) and washed with 2M sodium carbonate solution

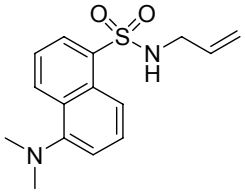
(2 x 10 ml), and 10% Lithium chloride solution (3 x 10 ml). The organic portion was separated, dried ($MgSO_4$), filtered and the solvent removed *in vacuo*. The crude product was purified by column chromatography (Petroleum ether 40-60 ºC /diethyl ether) to yield a yellow oil (74 mg, 91 %).

^{1}H NMR δ_H (300 MHz, $CDCl_3$ 8.54(1H, d, J = 8.5 Hz, Ar**H**), 8.25-8.31 (2H, m, Ar**H**), 7.48-7.57 (2H, m, Ar**H**), 7.19 (1H, d, J = 7.5 Hz, Ar**H**), 6.95 (4H, s, Ar**H**), 4.97 (1H, t, J = 6.0 Hz, N**H**), 4.02 (2H, d, J = 6.1 Hz, C**H$_2$**), 2.90 (6H, s, C**H$_3$**), 2.24 (3H, s, C**H$_3$**)

^{13}C NMR δ_C (75 MHz, $CDCl_3$) 152.0 (s, **C**(Ar)), 137.5 (s, **C**(Ar)), 134.6 (s, **C**(Ar)), 133.2 (s, **C**(Ar)), 130.5 (d, **C**(Ar)), 129.9 (d, **C**(Ar)), 129.7 (s, **C**(Ar)), 129.2 (d, **C**(Ar)), 128.4 (d, **C**(Ar)), 127.8 (d, **C**(Ar)), 123.2 (d, **C**(Ar)), 118.8 (d, **C**(Ar)), 115.2 (d, **C**(Ar)), 47.1 (t, **C**H_2), 45.5 (q, **C**H_3), 21.0 (q, **C**H_3)

HRMS (ESI): calcd for $C_{20}H_{22}BrN_2O_2S$ (M^+): 354.13965 found 354.13877

5-Dimethylamino-naphthalene-1-sulfonic acid allylamide



Prepared as for 5-Dimethylamino-naphthalene-1-sulfonic acid 4-methyl-benzylamide to yield the product as a yellow oil (51 mg, 77 %). Data in agreement with literature values.[8]

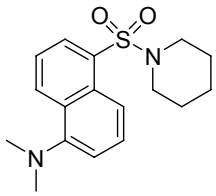
^{1}H NMR δ_H (300 MHz, $CDCl_3$) 8.55 (1H, d, J = 8.5 Hz, Ar**H**), 8.30(1H, d, J = 8.6 Hz, ArH), 8.25(1H, dd, J = 7.2, 1.3 Hz, Ar**H**), 7.50-7.59 (2H, m, Ar**H**), 7.19 (1H, d, J = 7.5, Ar**H**), 5.62 (1H, ddt, J = 17.1, 10.2, 5.9 Hz, C**H**=CH_2), 5.08 (1H, app. dq, J = 17.1, 1.3, CH=C(**H**)H), 5.00 (1H, app. dq, J = 10.3, 1.3, CH=C(**H**)H), 4.80 (1H, br. S , N**H**), 3.55 (2H, app. tt, J = 6.0, 1.5 Hz, C**H$_2$**)

^{13}C NMR δ_C (75 MHz, $CDCl_3$) 134.7 (s, **C**(Ar)), 133.1(d, **C**(Ar)), 130.5(d, **C**(Ar)), 129.9 (s, **C**(Ar)), 129.8(d, **C**(Ar)), 129.7, 129.5(s, **C**(Ar)), 123.2 (d, **C**(Ar)), 118.8 (d, **C**(Ar)), 117.7 (t, **C**H_2), 115.3 (d, **C**H=CH_2), 45.9(t, **C**H_2), 45.4(q, **C**H_3)

FTIR (CH_3Cl Solution, cm^{-1}) 3584 w, 3299 s, 2943 m, 2833 m, 2789 m, 1646 w, 1612 w, 1588 m, 1574 m, 1504 w, 1455 m, 1409 m 1318 s, 1318 s, 1231 w, 1161 s, 1144 s

HRMS (ESI): calcd for $C_{15}H_{18}N_2O_2S$ (M^+): 290.10835 found 290.10697

Dimethyl-[5-(piperidine-1-sulfonyl)-napthalen-1-yl]-amine



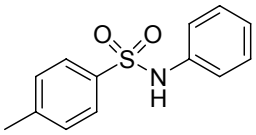
Prepared as for 5-Dimethylamino-naphthalene-1-sulfonic acid 4-methyl-benzylamide to yield the product as a yellow oil (65 mg, 89 %).

^{1}H NMR δ_H (300 MHz, $CDCl_3$) 8.82 (1H, d, J = 8.5 Hz, Ar**H**), 8.55 (1H, d, J = 8.5 Hz, Ar**H**), 8.42 (1H, d, J = 8.7 Hz, Ar**H**), 7.53 (2H, app. dt, J = 7.8, 1.3 Hz, Ar**H**), 7.18 (1H, d, J = 7.5, Ar**H**), 3.17(4H, t, J = 5.1 Hz, C**H$_2$**), 2.89(6H, s, C**H$_3$**), 1.54-1.61 (4H, m, C**H$_2$**), 1.40-1.47 (2H, m, C**H$_2$**)

^{13}C NMR δ_C (75 MHz, $CDCl_3$) 135.5, 130.5, 130.4, 130.0, 127.8, 123.2, 120.1, 115.2, 46.3, 45.5, 25.4, 23.7

HRMS (ESI): calcd for $C_{17}H_{22}N_2O_2S$ (M^+): 318.13965 found 318.13789

4-Methyl-*N*-phenyl-benzenesulfonamide



To a solution of TCP sulfonate (100 mg, 0.28 mmol) in anhydrous THF (2 ml) under nitrogen was added aniline (59.6 µl, 0.56 mmol) and LHMDS (1M soln in THF) (570 µl, 0.56 mmol). The mixture was stirred for 4h at 50 ºC. The reaction mixture was diluted with Et_2O (20 ml) and washed with 2M sodium carbonate solution (2 x 10 ml), 2M hydrochloric acid (2 x 10 ml) and water (10 ml). The organic portion was separated, dried ($MgSO_4$), filtered and the solvent removed *in vacuo*. The crude product was purified by column chromatography (Petroleum ether/diethyl ether) to yield a white solid (54mg , 78%). Data in agreement with literature values.[9]

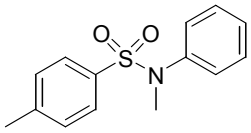
MP 93-96ºC *lit.* 103ºC

^{1}H NMR δ_H (300 MHz, $CDCl_3$) 7.68 (2H, d, J = 8.3 Hz, Ar**H**), 7.20-7.26 (4H, m,), 7.04-7.12 (3H, m), 2.37 (3H, s, C**H$_3$**).

^{13}C NMR δ_C (75 MHz, $CDCl_3$) 143.9 (s, **C**(Ar)), 136.6 (s, **C**(Ar)), 136.1 (s, **C**(Ar)), 129.7 (d, **C**(Ar)), 129.3 (d, **C**(Ar)), 127.3 (d, **C**(Ar)), 125.3 (d, **C**(Ar)), 121.5 (d, **C**(Ar)), 21.5 (q, **C**H_3)

HRMS (ESI): calcd for $C_{13}H_{13}NO_2S$ (M^+): 274.06615 found 274.06581

4,*N*-Dimethyl-*N*-phenyl-benzenesulfonamide



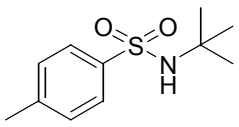
Prepared as for 4-Methyl-*N*-phenyl-benzenesulfonamide to yield the product as a white solid (67.5 mg, 92 %). Data in agreement with literature values.[10]

MP 92-94ºC *lit.* 93-95ºC

^{1}H NMR δ_H (300 MHz, $CDCl_3$) 7.42 (2H, d, J = 8.3 Hz, Ar**H**), 7.22-7.30 (5H, m,), 7.08-7.11 (2H, m), 3.16 (3H, s, C**H$_3$**), 2.41 (3H, s, C**H$_3$**).

^{13}C NMR δ_C (75 MHz, $CDCl_3$) 143.5 (s, **C**(Ar)), 141.6 (s, **C**(Ar)), 133.6 (s, **C**(Ar)), 129.3 (d, **C**(Ar)), 128.8 (d, **C**(Ar)), 127.9 (d, **C**(Ar)), 127.3 (d, **C**(Ar)), 126.6 (d, **C**(Ar)), 38.1(q, **C**H_3), 21.5 (q, **C**H_3)

***N*-tert-Butyl-4-methyl-benzenesulfonamide**



Prepared as for 4-Methyl-*N*-phenyl-benzenesulfonamide to yield the product as a brown solid (48.6mg, 75%).

MP 111-114ºC

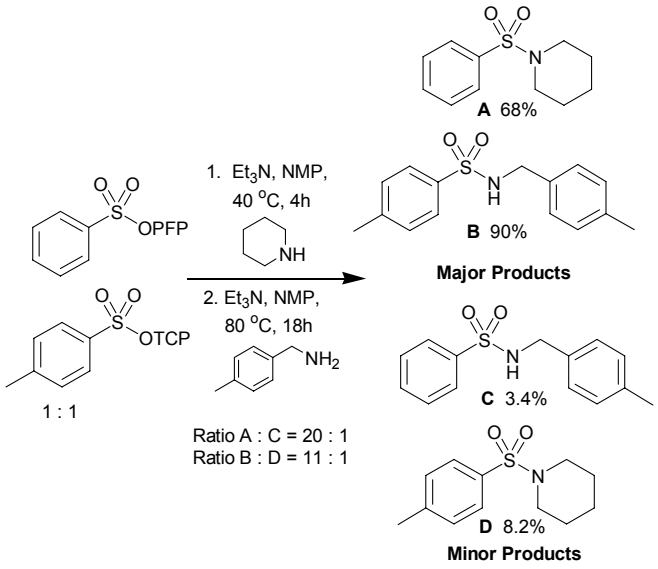
^{1}H NMR δ_H (300 MHz, $CDCl_3$) 7.77 (2H, d, J= 7.8 Hz, ArH), 7.26 (2H, d, J= 7.3 Hz, ArH), 4.70 (1H, br s, NH), 2.45 (3H, s, ArCH3), 1.24 (9H, s, 9 H, $C(CH_3)_3$)

^{13}C NMR δ_C (75 MHz, $CDCl_3$) 142.8 (s, **C**(Ar)), 140.5 (s, **C**(Ar)), 129.5 (d, **C**(Ar)), 127.0 (d, **C**(Ar)), 54.6 (s, $C(CH_3)_3$), 30.2 (q, CH_3), 21.5 (q, CH_3)

HRMS (ESI): calcd for $C_{11}H_{17}NO_2S$ (M^+): 228.10582 found 228.10549

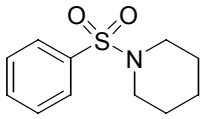
Supplementary Material (ESI) for Chemical Communications

Selective Sulfonamide formation from TCP Sulfonate Esters and PFP Sulfonate Esters



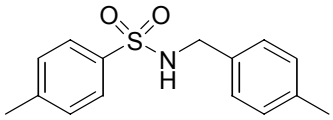
To a solution of TCP tosylate (250 mg, 0.71 mmol, 1 eq) and phenyl PFP sulfonate (230 mg, 0.71 mmol, 1 eq) in NMP (2 ml) was added 4-methylbenzylamine (90 µl, 0.71 mmol, 1 eq) and triethylamine (119 µl, 0.84 mmol, 1.2 eq) and the mixture was stirred at 40°C for 4h. Piperidine (140 µl, 1.42 mmol, 2 eq) and triethylamine (119 µl, 0.84 mmol, 1.2 eq) were added to mixture and it was heated to 100°C for 3 hours and then cooled to rt. The reaction mixture was diluted with DCM (50 ml) and washed with 2M sodium carbonate solution (2 x 15 ml), 2M hydrochloric acid (2 x 15 ml) and 10% lithium chloride solution (3 x 15 ml). The organic portion was separated, dried ($MgSO_4$), filtered and the solvent removed *in vacuo*. The crude products were separated by column chromatography (Petroleum ether/diethyl ether) to yield a 20:1 mixture of 1-Benzenesulfonylpiperidine: (1-(Toluene-4-sulfonyl)-piperidine) as a pale brown solid (131mg, 68%, 8.2%) and a 11:1 mixture of 1-(Toluene-4-sulfonyl)-piperidine: (N-(4-Methyl-benzyl)-benzenesulfonamide) as a pale brown solid (163mg, 90%, 3.4%).

1-Benzenesulfonylpiperidine



^{1}H NMR δ_H (300 MHz, $CDCl_3$) **Major Product:** 7.73-7.76 (2H, m, ArH), 7.49-7.61 (3H, m, ArH), 2.96 (4H, t, J = 5.5 Hz, CH_2), 1.59 – 1.66 (4H, m, CH_2), 1.36 – 1.44 (2H, m, CH_2) **Minor Product** (1-(Toluene-4-sulfonyl)-piperidine)

4-Methyl-*N*-(4-Methyl-benzyl)-benzenesulfonamide



^{1}H NMR δ_H (300 MHz, $CDCl_3$) **Major Product** 7.77 (2H, d, J = 8.3 Hz, Ar**H**), 7.30 (2H, d, J = 8.0, Ar**H**), 7.07 (4H, 2, Ar**H**), 4.86 (1H, t, J = 5.9 Hz, N**H**), 4.06 (2H, d, J = 6.1 Hz, C**H$_2$**), 2.43 (3H, s, C**H$_3$**), 2.30 (3H, s, C**H$_3$**); **Minor Product** (N-(4-Methyl-benzyl)-benzenesulfonamide)

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