# Supplementary Material (ESI) for Chemical Communications


# Observations on the Reactivity of Pentafluorophenylsulfonate Esters

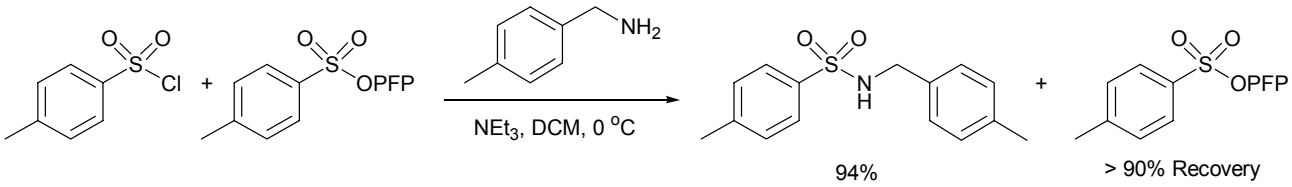
**Caddick, Wilden & Judd**

## Supporting Information

# Supplementary Material (ESI) for Chemical Communications


**MECHANISTIC STUDIES**

**Bimolecular Competition Studies 1: Preparation of 4-Methyl-*N*-(4-methyl-benzyl)-benzenesulfonamide.**




A solution of *p*-toluenesulfonyl chloride (381 mg, 2.0 mmol) and pentafluorophenyl-*p*-toluenesulfonate (676 mg, 2.0 mmol) in DCM (30 mL) were cooled to 0 $^{o}$C and triethylamine (303 mg, 0.40 mL, 6.0 mmol) was added. A solution of 4-methylbenzylamine (242 mg, 2.0 mmol) in DCM (5 mL) was added dropwise to the cooled solution over a period of 5 minutes. The solution was then allowed to stir for a further 1h after which time the reaction was diluted with DCM (20 mL) and washed with 2M HCl (3 x 30 mL). The organic fraction was dried ($MgSO_4$), filtered, and the solvent removed from the filtrate *in vacuo*. The crude residue was subjected to flash column chromatography (20% ether/petroleum ether 40-60 $^{o}$C) to yield the product sulfonamide as a pale yellow solid (517 mg, 1.88 mmol, 94%) and recovered PFP ester as an off white solid (612 mg, 1.81 mmol, 90% recovery).

**MP** 93-95 $^{o}$C (DCM / hexane).

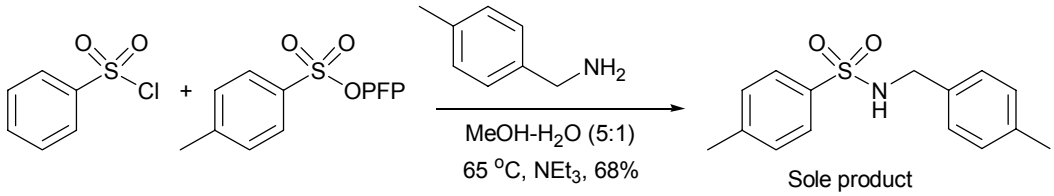
**$^{1}$H NMR** $\delta_H$ ($CDCl_3$, 300 MHz) 7.78 (2H, d, *J* = 8.0 Hz, 2 x Ar**H**), 7.30 (2H, d, *J* = 8.0 Hz, 2 x Ar**H**), 7.08 (4H, app. s, 4 x Ar**H**), 4.87 (1H, br. t, *J* = N**H**), 4.09 (2H, d, *J* = 6.1 Hz, C**H$_2$**NH), 2.46 (3H, s, ArC**H$_3$**), 2.31 (3H, s, ArC**H$_3$**).

**$^{13}$C NMR** $\delta_c$ ($CDCl_3$, 75 MHz) 143.8 (s, **C** (Ar)), 138.0 (s, **C** (Ar)), 137.2 (s, **C** (Ar)), 133.6 (s, **C** (Ar)), 130.1 (d, 2 x **C**H (Ar)), 129.7 (d, 2 x **C**H (Ar)), 128.3 (d, 2 x **C**H (Ar)), 127.6 (d, 2 x **C**H (Ar)), 47.4 (t, **C**$H_2$NH), 21.9 (q, Ar**C**$H_3$), 21.5 (q, Ar**C**$H_3$).

**FTIR** ($CH_2Cl_2$ 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.

# Supplementary Material (ESI) for Chemical Communications

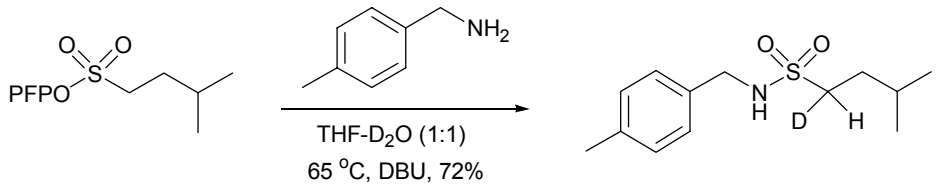

**Bimolecular Competition Studies 2: Preparation of 4-Methyl-*N*-(4-methyl-benzyl)-benzenesulfonamide.**




A solution of benzenesulfonyl chloride (353 mg, 2.0 mmol) and pentafluorophenyl-*p*-toluenesulfonate (676 mg, 2.0 mmol) in methanol-water (5:1 v/v, 30 mL) was warmed to 50 $^{o}$C and a mixture of 4-methylbenzylamine (0.21 mL, 2.5 mmol) and triethylamine (303 mg, 0.40 mL, 6.0 mmol) was added dropwise over a period of 10 minutes. The solution was then allowed to stir for a further 1h after which time the reaction was diluted with DCM (20 mL) and washed with 2M HCl (3 x 30 mL). The organic fraction was dried ($MgSO_4$), filtered, and the solvent removed from the filtrate *in vacuo*. The crude residue was subjected to flash column chromatography (20% ether/petroleum ether 40-60 $^{o}$C) to yield the product sulfonamide as a pale yellow solid (374 mg, 1.36 mmol, 68%) Spectral data reported previously.

# Supplementary Material (ESI) for Chemical Communications


**Preparation of 1-Deutero-3-methyl-butane-1-sulfonic acid 4-methyl-benzylamide**




To a solution of the PFP sulfonate ester (636 mg, 2.0 mmol) in THF-$D_2O$ (1:1 v/v, 20 mL) was added DBU (276 mg, 2.0 mmol) and 4-methylbenzylamine (242 mg, 2.0 mmol). The resulting solution was heated to 65 °C for 2h after which time the reaction was diluted with DCM (20 mL) and washed with 2M HCl (3 x 30 mL), water (30 mL) and brine (30 mL). The organic fraction was dried ($MgSO_4$), filtered, and the filtrate concentrated *in vacuo*. The crude product was purified by flash column chromatography (20% ether/petroleum ether 40-60 °C) to yield the product as a pale yellow solid (333 mg, 1.30 mmol, 72%).

**MP** 78-80 °C (DCM / hexane).

**$^1$H NMR** $\delta_H$ ($CDCl_3$, 300 MHz) 7.23 (2H, d, $J$ = 8.1 Hz, 2 x Ar**H**), 7.16 (2H, d, $J$ = 8.1 Hz, 2 x Ar**H**), 4.49 (1H, br. t, $J$ = 6.0 Hz, N**H**), 4.24 (2H, d, $J$ = 5.9 Hz, C**H$_2$**NH), 2.95-2.82 (1H, m, $SO_2$C**H**D), 2.34 (3H, s, ArC**H$_3$**), 1.65-1.55 (3H, m, $(CH_3)_2$C**H**C**H$_2$**), 0.86 (6H, d, $J$ = 6.4 Hz, (C**H$_3$**)$_2$CH).

**$^{13}$C NMR** $\delta_C$ ($CDCl_3$, 75 MHz) 138.0 (s, **C** (Ar)), 134.2 (s, **C** (Ar)), 129.7 (d, 2 x **C**H (Ar)), 128.2 (d, 2 x **C**H (Ar)), 51.8, 51.5, 51.2 ($J_{CD}$ = 20.8 Hz, **C**HD$SO_2$), 47.1 (t, **C**$H_2$NH), 32.1 (t, **C**$H_2$), 27.3 (d, $(CH_3)_2$**C**H), 22.2 (q, 2 x **C**$H_3$), 21.3 (q, Ar**C**$H_3$).

**FTIR** (Thin film, $cm^{-1}$) 3272 s, 2924 vs, 2854 s, 1516 w, 1459 s, 1366 m, 1326 w, 1300 s, 1142 s, 1124 s, 1070 m.