DBN Hexafluorophosphate Salts as Convenient Sulfonylating and Phosphonylating Agents

Supplementary Information

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**General Experimental**

Starting materials and solvents were obtained from commercial sources without further purification; chemicals were purchased from Acros Organics, Sigma Aldrich, Alfa Aesar, Fluka and Lancaster. Thin layer chromatography was carried out on aluminium or plastic backed silica plates (Fisher). Plates were visualised under UV (254 nm) light, followed by staining with potassium permanganate and gentle heating. Compound separations were carried out using column chromatography on 60 micron dry silica (Aldrich), solvents were concentrated using a Büchi rotary evaporator.

$^1$H, $^{13}$C, $^{39}$P and $^{19}$F NMR spectra were run in deuterated (>99.5%) solvent and recorded on a Bruker Avance 250 (250 MHz, 62.5 MHz), a Bruker Avance (300 MHz, 75 MHz) or Agilent (500 MHz, 125 MHz) spectrometer at 303 K. Chemical shifts are reported as parts per million (ppm) with reference to residual solvent signals. Coupling constants are reported in Hz and signal multiplicities are reported as singlet (s), doublet (d), triplet (t), quintet (quin), doublet of doublets (dd), doublet of triplets (dt), doublet of quartets (dq), triplet of triplets (tt), multiplet (m) or a broad singlet (br. s).

Mass spectra were recorded using an electrospray Time-of-Flight MicroTOFTM (ESI-TOF) mass spectrometer (Bruker Daltonik, GmbH, Bremen, Germany), coupled with an Agilent 1200 LC system (Agilent Technologies, Waldbronn, Germany). The observed isotope pattern matched the corresponding theoretical values as calculated from the expected elemental formula. Samples were diluted with HPLC grade methanol or acetonitrile. Gas chromatography mass spectrometry was performed using an Agilent Technologies 78908 GC-MS system.

Infra-red spectra were recorded on a PerkinElmer 100 FT-IR spectrometer, using a Universal ATR accessory for sampling; relevant absorbance quoted as $v_{\text{max}}$ in $\text{cm}^{-1}$. Melting points were determined using Stuart SMP10 melting point equipment using closed end capillary tubes and are uncorrected.
General Procedures

General Procedure I – Synthesis of DBN Salts

1,5-Diazabicyclo[4.3.0]non-5-ene (DBN) (1 equiv) was added to the appropriate sulfonyl chloride or chlorophosphate (1.05 equiv) and potassium hexafluorophosphate (1 equiv) in dry MeCN under N₂. The reaction was stirred at room temperature for 1 h. After this time the reaction mixture was filtered through Celite to remove the KCl precipitate, and the filtrate concentrated under reduced pressure. The resulting DBN salt was purified by trituration with CH₂Cl₂ or EtOAc.

General Procedure II – DBN Salt Sulfonylations

The appropriate DBN salt (1 equiv), amine (1.05 equiv) in acetonitrile (0.07 M) were heated at 80 °C for the given amount of time. Upon completion the reaction mixture was concentrated under reduced pressure and purified by silica plug (40% EtOAc/petroleum ether).

General Procedure III – DBN Salt Sulfonylation of Phenols

The appropriate DBN salt (1 equiv), amine (1.05 equiv), DBN (0.2 equiv) and acetonitrile (0.07 M) were added to a Radley’s carousel tube. The reaction tube was sealed and heated at 80 °C for the given amount of time. Upon completion the reaction mixture was concentrated under reduced pressure and purified by silica plug (50% EtOAc/petroleum ether), taken up in EtOAc, washed with 1 M NaOH, dried over MgSO₄, filtered and concentrated under reduced pressure.

General Procedure IV – DABCO Salt Sulfonylations

The appropriate DABCO salt (1.2 equiv), amine (1 equiv) and acetonitrile (0.07 M) were added to a Radley’s carousel tube. The reaction tube was sealed and heated at 80 °C for 4 h. Upon completion the reaction mixture was concentrated, taken up in EtOAc and the insoluble material removed by filtration. The organic layer was washed successively with 1 M HCl, aq. sat. NaHCO₃ and brine, then dried over MgSO₄, filtered and concentrated under reduced pressure.
**General Procedure V – DBN Salt Phosphorylations**

The appropriate DBN salt (1.3 equiv), amine (1 equiv) and the given amount of DBN in acetonitrile (0.07 M) were heated at 80 °C for the given amount of time. Upon completion the reaction mixture was concentrated under reduced pressure and purified by silica plug or silica column chromatography.

**General Procedure VI – DBN Salt Phosphorylations of Primary Amines**

The appropriate DBN salt (1.8 equiv), amine (1 equiv) and acetonitrile (0.033 M) were added to a Radley’s carousel tube. The reaction tube was sealed and heated at 80 °C for the given amount of time. Upon completion the reaction mixture was concentrated under reduced pressure and purified by silica column chromatography.
Characterisation of DBN·PF$_6$ and DABCO·PF$_6$ Salts

**N-Tosyl DBN·PF$_6$ (1a)**

Following general procedure I: DBN (1.85 mL, 15 mmol) was added to $p$-toluenesulfonyl chloride (2.97 g, 15.6 mmol) and KPF$_6$ (2.76 g, 15 mmol) in MeCN (75 mL). Upon work up and trituration with CH$_2$Cl$_2$ the title compound was obtained as a colourless solid (6.03 g, 95%); mp decomposed at 201 °C; $\delta$$_H$(DMSO-d$_6$, 500 MHz) 1.96-2.02 (2H, m, $H^3$), 2.08 (2H, app. quin, $J$ 7.8 Hz, $H^7$), 2.44 (3H, s, CH$_3$), 3.36 (2H, t, $J$ 7.8 Hz, $H^2$), 3.43 (2H, t, $J$ 5.9 Hz, $H^6$), 3.75-3.83 (4H, m, $H^6$ and $H^4$), 7.55 (2H, d, $J$ 8.3 Hz, CH$_2$) and 7.97 (2H, d, $J$ 8.3 Hz, -SO$_2$CCH$_2$); $\delta$$_C$(DMSO-d$_6$, 125 MHz) 17.7, 18.5, 21.1, 33.7, 44.0, 44.5, 55.5, 110.0, 128.0, 130.6, 132.8, 146.8 and 165.1; $\delta_f$ (DMSO-d$_6$, 470 MHz) -70.3 (d, $J_{PF}$ 711.5 Hz, PF$_6$); ESI-MS of [C$_{14}$H$_{19}$N$_2$O$_2$S]$^+$; theoretical m/z of [M+H]$^+$ = 279.1167, measured m/z of [M+H]$^+$ = 279.1232; $\nu$$_{max}$ (thin-film)/cm$^{-1}$ 828, 1173 (RSO$_2$R stretch) and 1323 (RSO$_2$R stretch).

**N-Mesityl DBN·PF$_6$ (1b)**

Following general procedure I: DBN (1.85 mL, 15 mmol) was added to methanesulfonyl chloride (1.21 mL, 15.6 mmol) and KPF$_6$ (2.76 g, 15 mmol) in MeCN (75 mL). Upon work up and trituration with CH$_2$Cl$_2$ the title compound was obtained as a colourless solid (5.30 g, 92%); mp 114-116 °C; $\delta$$_H$(DMSO-d$_6$, 500 MHz) 2.07-2.15 (4H, m, $H^3$ and $H^7$), 3.34 (2H, t, $J$ 7.8 Hz, $H^2$), 3.51 (2H, t, $J$ 5.9 Hz, $H^6$), 3.59 (3H, s) and 3.84 (4H, t, $J$ 5.9 Hz, $H^6$ and $H^4$); $\delta$$_C$(DMSO-d$_6$, 125 MHz) 18.2, 18.9, 34.2, 41.0, 44.3, 44.8, 55.9 and 166.2; $\delta_f$ (DMSO-d$_6$, 470 MHz) -70.3 (d, $J_{PF}$ 711.5 Hz, PF$_6$); ESI-MS of [C$_8$H$_{15}$N$_2$O$_2$S]$^+$; theoretical m/z of [M+H]$^+$ = 203.0854, measured m/z of [M+H]$^+$ = 203.0896; $\nu$$_{max}$ (thin-film)/cm$^{-1}$ 1162 (RSO$_2$R stretch) and 1337 (RSO$_2$R stretch).
**N-8-Quinolinesulfonyl DBN•PF₆ (1c)**

Following general procedure I: DBN (1.85 mL, 15 mmol) was added to 8-quinolinesulfonyl chloride (3.55 g, 15.6 mmol) and KPF₆ (2.76 g, 15 mmol) in MeCN (75 mL). Upon work up and trituration with CH₂Cl₂ the title compound was obtained as a colourless solid (5.06 g, 73%); mp 246-249 °C; δₓ (DMSO-d₆, 500 MHz) 1.85 (2H, ap. quin, J 5.8 Hz, H₃), 2.16 (2H, app quin, J 7.8 Hz, H₇), 3.45 (2H, t, J 5.9 Hz, H₂), 3.51 (2H, J 7.8 Hz, H₇), 3.85 (2H, t, J 7.8 Hz, H₆), 3.98-4.01 (2H, m, H₄), 7.82 (1H, dd, J 8.3, 3.9 Hz, CH₆Ar), 7.91 (1H, t, J 7.3 Hz, CH₃), 8.55 (1H, dd, J 8.3, 1.5 Hz, CH₃), 8.62 (1H, dd, J 7.3, 1.5 Hz, CH₃), 8.67 (1H, dd, J 8.3, 2.0 Hz, CH₃) and 9.11-9.15 (1H, m, CH₃); δₓ (DMSO-d₆, 125 MHz) 18.4, 18.7, 34.8, 44.5, 45.5, 56.0, 123.8, 126.5, 129.3, 132.2, 134.7, 137.4, 138.1, 152.9 and 167.0; δ₁ (DMSO-d₆, 470 MHz) -70.3 (d, J₁-PF 711.5 Hz, PF₆); ESI-MS of [C₁₆H₁₈N₃O₂S]⁺; theoretical m/z of [M+H]⁺ = 316.1120, measured m/z of [M+H]⁺ = 316.1196; ν max (thin-film)/cm⁻¹ 828, 1172 (RSO₂R stretch) and 1324 (RSO₂R stretch).

**N-Diethoxyphosphoryl DBN•PF₆ (2a)**

Following general procedure I: DBN (3.70 mL, 30 mmol) was added to diethyl chlorophosphate (4.50 mL, 31.2 mmol) and KPF₆ (5.52 g, 30 mmol) in MeCN (150 mL). Upon work up and trituration with EtOAc the title compound was obtained as a colourless solid (11.42 g, 98%); mp 81-83 °C; δₓ (DMSO-d₆, 500 MHz) 1.30 (6H, dt, J 1.0, 6.9 Hz, CH₂CH₃), 2.00-2.12 (4H, m, H₂), 3.21 (2H, t, J 7.8 Hz, H₇), 3.48 (2H, t, J 5.9 Hz, H₇), 3.55-3.60 (2H, m, H₂), 3.77-3.81 (2H, m, H₆) and 4.16-4.23 (4H, m, -OCH₂CH₃); δₓ (DMSO-d₆, 125 MHz) 15.7 (d, Jₓ-P 6.8 Hz), 17.6, 18.2 (d, Jₓ-P 3.6 Hz), 33.7, 43.9, 43.5, 55.2, 64.7 (d, Jₓ-P 5.0 Hz) and 167.5 (d, Jₓ-P 13.7 Hz); δ₁ (DMSO-d₆, 470 MHz) -70.1 (d, J₁-PF 711.5 Hz, PF₆); δ₁ (DMSO-d₆, 121 MHz) -2.09; ESI-MS of [C₁₁H₁₈N₂O₃P]⁺; theoretical m/z of [M+H]⁺ = 261.1368, measured m/z of [M+H]⁺ = 261.1440; ν max (thin-film)/cm⁻¹ 824, 1184 and 1484.
N-Diphenoxyposphoryl DBN•PF₆ (2b)

Following general procedure I: DBN (1.85 mL, 15 mmol) was added to diphenyl chlorophosphate (3.23 mL, 15.6 mmol) and KPF₆ (2.76 g, 15 mmol) in MeCN (75 mL). Upon work up and trituration with EtOAc the title compound was obtained as a colourless solid (6.93 g, 92%); mp 94-97 °C; δ_H (DMSO-d₆, 500 MHz) 2.03-2.14 (4H, m, H₃ and H⁷), 3.31 (2H, t, J 7.9 Hz, H⁸), 3.54 (2H, t, J 5.7 Hz, H⁴), 3.81-3.86 (2H, m, H₂), 3.87-4.11 (2H, m, H⁶), 7.31-7.35 (6H, m, C_H Ar) and 7.45-7.50 (4H, m, C_H Ar); δ_C (DMSO-d₆, 125 MHz) 18.0, 18.7 (d, J_P-C 3.7 Hz), 34.7, 44.4, 44.7, 56.2, 120.5 (d, J_P-C 4.7 Hz), 127.0, 130.9, 149.5 (d, J_P-C 7.0 Hz) and 168.0 (d, J_P-C 15.4 Hz); δ_F (DMSO-d₆, 470 MHz) -70.0 (d, J_P-F 711.4 Hz, ^PF₆); δ_P (DMSO-d₆, 121 MHz) -11.19; ESI-MS of [C₁₉H₂₂N₂O₃P]^+; theoretical m/z of [M+H]^+ = 357.1368, measured m/z of [M+H]^+ = 357.1454; ν_max (thin-film)/cm⁻¹ 832, 989 and 1652.

N-Tosyl DABCO•PF₆ (5a)

1,4-Diazabicyclo[2.2.2]octane (DABCO) (588 mg, 5.25 mmol) was added to p-toluenesulfonyl chloride (953 mg, 5 mmol) and KPF₆ (920 mg, 5 mmol) in MeCN (25 mL) and stirred at rt for 1 h. After this time the reaction mixture was filtered through Celite to remove the white precipitate that had formed, and the filtrate concentrated under reduced pressure. The resulting DABCO•PF₆ salt was purified by trituration with CH₂Cl₂ the title compound was obtained as a colourless solid (1.78 g, 86%); mp decomposed at 178 °C; δ_H (DMSO-d₆, 500 MHz) 2.29 (3H, s, CH₃), 3.45-3.63 (12H, m, CH₂), 7.13 (2H, d, J 7.8 Hz, CH₆) and 7.50 (2H, d, J 7.8 Hz, CH₆); δ_C (DMSO-d₆, 125 MHz) 21.2, 43.6, 44.4, 125.9, 128.7, 138.5 and 145.5; δ_F (DMSO-d₆, 470 MHz) -70.0 (d, J_P-F 711.5 Hz, ^PF₆); ESI-MS of [C₁₃H₁₈N₂O₂S₂]^+; theoretical m/z of [M+H]^+ = 267.1167, measured m/z of [M+H]^+ = 267.1138; ν_max (thin-film)/cm⁻¹ 668, 831, 1175 (RSO₂R stretch) and 1391.
Sulfonylation of Primary Amines

Table 1. The reaction of primary amines with N-tosyl DBN•PF₆

<table>
<thead>
<tr>
<th>Entry</th>
<th>Amine</th>
<th>Product</th>
<th>Conversion (%)</th>
<th>Yield (%)</th>
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<tr>
<td>1</td>
<td>H₂N-</td>
<td>3a</td>
<td>100</td>
<td>61</td>
</tr>
<tr>
<td>2</td>
<td>H₂N-</td>
<td>3b</td>
<td>100</td>
<td>57</td>
</tr>
<tr>
<td>3</td>
<td>H₂N-</td>
<td>3c</td>
<td>100</td>
<td>&gt;100</td>
</tr>
</tbody>
</table>

*Conversion determined by analysis of crude ¹H NMR spectra

N-(4-Methylbenzyl)-1-tosylhexahydropyrrolo[1,2-α]pyrimidin-8a(6H)-amine hydrochloride (3a)

DBN salt 1a (256 mg, 0.6 mmol) and 4-methylbenzylamine (62 μL, 0.53 mmol) in MeCN (2 mL) were stirred for 1 h at 80 °C. After this time the reaction mixture was taken up in EtOAc and washed with 1 M HCl, aq. sat. NaHCO₃ and brine. The organic layer was dried over MgSO₄, filtered and concentrated under reduced pressure to yield the title compound as a pale yellow solid (127 mg, 61%); mp 52-55 °C; δ (CD₃CN, 500 MHz) 1.74-1.81 (2H, m, CH₂), 2.06 (2H, app. quin, J 7.8 Hz, CH₂), 2.31 (3H, s, CH₃), 2.41 (3H, s, CH₃), 2.83-2.91 (4H, m, CH₂), 3.47 (2H, t, J 7.8 Hz, CH₂), 3.62 (2H, t, J 7.3 Hz, CH₂), 4.44 (2H, s, CH₃Ph), 6.40 (1H, br. s, NH), 7.18 (2H, d, J 7.8 Hz, CH₂), 7.23 (2H, d, J 7.8 Hz, CH₂), 7.36 (2H, d, J 8.3 Hz, CH₃), 7.72 (2H, d, J 8.3 Hz, -SO₂CCCH₃) and 8.65 (1H, br. s, NH); δC (CD₃CN, 125 MHz) 18.2, 20.2, 20.5, 25.2, 30.3, 40.3, 43.4, 48.2, 53.7, 126.9, 127.6, 129.4, 129.7, 133.2, 137.1, 137.9, 143.6 and 168.0;
ESI-MS of $[\text{C}_{22}\text{H}_{30}\text{N}_{3}\text{O}_{2}\text{S}]^+$; theoretical m/z of $[\text{M}+\text{H}]^+$ = 400.2059, measured m/z of $[\text{M}+\text{H}]^+$ = 400.2166; $\nu_{\text{max}}$ (thin-film)/cm$^{-1}$ 831, 1154 (RSO$_2$R stretch), 1324 (RSO$_2$R stretch), 1667, and 3332 (N-H stretch).

$N$-(3-(2-(Allylimino)pyrrolidin-1-yl)propyl)-4-methylbenzenesulfonamide hydrochloride (3b)

DBN salt 1a (256 mg, 0.6 mmol) and allylamine (38 µL, 0.53 mmol) in MeCN (2 mL) were stirred for 1 h at 80 °C. After this time the reaction mixture was taken up in EtOAc and washed with 1 M HCl, aq. sat. NaHCO$_3$ and brine. The organic layer was dried over MgSO$_4$, filtered and concentrated under reduced pressure to yield the title compound as a pale yellow solid (106 mg, 57%); mp 73-75 °C; $\delta_{\text{H}}$ (CDCl$_3$, 500 MHz) 1.88 (2H, dt, $J_{13.2}$, 6.6 Hz, CH$_2$), 2.14 (2H, app. q, $J_{7.6}$ Hz, CH$_2$), 2.37 (3H, s, CH$_3$), 2.89 (2H, t, $J_{8.1}$ Hz, CH$_2$), 2.94 (2H, t, $J_{7.3}$ Hz, CH$_2$), 3.63 (2H, t, $J_{7.1}$ Hz, CH$_2$), 3.70 (2H, t, $J_{7.3}$ Hz, CH$_2$), 3.94 (2H, d, CH=C), 5.14-5.22 (2H, m, CH=CH$_2$), 5.83 (1H, ddt, $J_{16.8}$, 10.9, 5.5 Hz, CH), 7.26 (2H, d, $J_{7.3}$ Hz, CH$_{Ar}$) and 7.73 (2H, d, $J_{7.7}$ Hz, -SO$_2$CC$_{Ar}$); $\delta_{\text{C}}$ (CDCl$_3$, 125 MHz) 18.5, 21.4, 25.0, 29.9, 47.5, 53.6, 117.9, 127.1, 129.7, 132.3, 136.5, 143.3 and 167.6; ESI-MS of $[\text{C}_{17}\text{H}_{25}\text{N}_{3}\text{O}_{2}\text{S}]^+$; theoretical m/z of $[\text{M}+\text{H}]^+$ = 336.1746, measured m/z of $[\text{M}+\text{H}]^+$ = 336.1830; $\nu_{\text{max}}$ (thin-film)/cm$^{-1}$ 826, 1144 (RSO$_2$R stretch), 1322 (RSO$_2$R stretch), 1667, and 3290 (N-H stretch).

4-Methyl-$N$-(3-(2-phenethylimino)pyrrolidin-1-yl)propylbenzenesulfonamide hydrochloride (3c)

DBN salt 1a (256 mg, 0.6 mmol) and 2-phenethylamine (63 µL, 0.5 mmol) in MeCN (2 mL) were stirred for 1 h at 80 °C. After this time the reaction mixture was taken up in EtOAc and washed with 1 M HCl, aq. sat. NaHCO$_3$ and brine. The organic layer was dried over MgSO$_4$, filtered and concentrated under reduced pressure to yield the title compound as an off-white solid (255 mg, quant.); mp 147-149 °C; $\delta_{\text{H}}$ (CD$_3$CN, 500 MHz) 1.75 (2H, dt, $J_{14.4}$, 7.0 Hz, CH$_2$), 1.98 (2H, dt, $J_{15.9}$, 7.7 Hz, CH$_2$), 2.44 (3H, s,
CH₃), 2.65 (2H, t, J 8.1 Hz, CH₂), 2.86 (2H, t, J 6.6 Hz, CH₂), 2.92 (2H, t, J 7.1 Hz, CH₂), 3.32-3.37 (2H, m, CH₂), 3.55 (2H, t, J 8.1 Hz, CH₂), 3.61 (2H, t, J 7.3 Hz, CH₂), 7.24-7.30 (3H, m, Ph-H); δC (CD₃CN, 125 MHz) 18.2, 20.6, 25.4, 29.9, 35.4, 40.2, 42.7, 47.1, 53.7, 117.4, 127.0, 128.7, 129.1, 129.8, 136.8, 137.9, 143.9 and 167.9; ESI-MS of [C₂₂H₃₀N₃O₂S]+; theoretical m/z of [M+H]+ = 400.2059, measured m/z of [M+H]+ = 400.2169; νmax (thin-film)/cm⁻¹ 826, 1144 (RSO₂R stretch), 1322 (RSO₂R stretch), 1667, and 3290 (N-H stretch).

**N-(3-(2-(Benzylimino)pyrrolidin-1-yl)propyl)quinolone-8-sulfonamide hydrochloride**

![Reaction Scheme]

DBN salt 1c (256 mg, 0.6 mmol) and benzylamine (55 μL, 0.5 mmol) in MeCN (2 mL) were stirred for 1 h at 80 °C. After this time the reaction mixture was taken up in EtOAc and washed with 1 M HCl, aq. sat. NaHCO₃ and brine. The organic layer was dried over MgSO₄, filtered and concentrated under reduced pressure to yield the title compound as a yellow solid (235 mg, quant.); mp 71-76 °C; δH (CD₃CN, 500 MHz) 1.71-1.79 (2H, m, CH₂), 2.02-2.11 (2H, m, CH₂), 2.81 (2H, t, J 6.4 Hz, CH₂), 2.88 (2H, t, J 7.8 Hz, CH₂), 3.38 (2H, t, J 7.8 Hz, CH₂), 3.62 (2H, t, J 7.3 Hz, CH₂), 4.50 (2H, s, CH₂Ph), 7.30-7.42 (5H, m, Ph-H), 7.66 (1H, dd, J 3.9, 8.3 Hz, CH₃), 7.72 (1H, t, J 7.8 Hz, CH₃), 8.22 (1H, dd, J 1.5, 7.8 Hz, CH₃), 8.33 (1H, dd, J 1.0, 7.3 Hz, CH₃), 8.44 (1H, dd, J 1.5, 8.3 Hz, CH₃) and 9.03 (1H, d, J 1.5, 3.9 Hz, CH₃); δC (CDCl₃, 125 MHz) 18.3, 25.8, 30.2, 40.7, 43.6, 48.8, 53.8, 122.6, 125.6, 127.5, 128.1, 128.7, 129.0, 131.2, 133.8, 134.8, 135.7, 137.0, 143.0, 151.8 and 167.9; ESI-MS of [C₂₃H₂₇N₄O₂S]+; theoretical m/z of [M+H]+ = 423.1855, measured m/z of [M+H]+ = 423.1961; νmax (thin-film)/cm⁻¹ 826, 1144 (RSO₂R stretch), 1322 (RSO₂R stretch), 1667, and 3288 (N-H stretch).
Reaction of p-Anisidine with N-Tosyl DBN•PF$_6$

DBN salt 1a (256 mg, 0.6 mmol) and p-anisidine (62 mg, 0.5 mmol) in MeCN (2 mL) were heated at 80 °C for 18 h. After this time the reaction was concentrated under reduced pressure and the crude reaction mixture analysed. Analysis of the crude $^1$H NMR showed complete consumption of DBN salt 1a by the disappearance of peaks at 7.55 and 7.97 ppm. The reaction mixture was taken up in EtOAc and washed with 1 M HCl, aq. sat. NaHCO$_3$ then brine, the organic layer dried over MgSO$_4$, filtered then concentrated under reduced pressure. Mass spectroscopy showed the presence of a peak at 402.1959 corresponding to the expected adduct product 3d. The $^1$H NMR spectrum showed the presence of a mixture of compounds, with the major product being the ring-opened product 3d; neither product was isolated from this mixture.

N-Benzylmethanesulphonamide$^{23}$

Following general procedure II; DBN salt 1b (209 mg, 0.6 mmol) and benzylamine (55 μL, 0.5 mmol) in MeCN (2 mL) were heated at 80 °C for 1 h to give the title compound as an orange solid (22 mg, 24%); mp 57-60 °C [lit. mp 58-59 °C]; $\delta$H (CDCl$_3$, 500 MHz) 2.87 (3H, s, C$_3$H$_3$), 4.32 (2H, d, J 6.0 Hz, CH$_2$), 4.76 (1H, br. s, NH) and 7.29-7.43 (5H, m, Ph-H); $\delta$C (CDCl$_3$, 125 MHz) 41.1, 47.2, 127.9, 128.2, 129.0 and 136.7; ESI-MS of [C$_8$H$_{11}$NO$_2$S]$^+$; theoretical m/z of [M+Na]$^+$ = 208.0408, measured m/z of [M+Na]$^+$ = 208.0399; $\nu_{\text{max}}$ (thin-film)/cm$^{-1}$ 834, 1137 (RSO$_2$R stretch), 1305 (RSO$_2$R stretch), 1667 (N-H stretch) and 3225 (N-H stretch).
Characterisation of Sulfonamides and Sulfonate Esters

1-Tosylpiperidine\(^1\) (4a)

Following general procedure II: DBN salt 1a (416 mg, 1 mmol) and piperidine (104 \(\mu\)L, 1.05 mmol) in MeCN (7 mL) for 4 h gave the title compound as a colourless crystalline solid (204 mg, 86%).

Following general procedure IV: DABCO salt 5a (248 mg, 0.6 mmol) and piperidine (49 \(\mu\)L, 0.5 mmol) in MeCN (7 mL) for 4 h gave the title compound as a colourless crystalline solid (92 mg, 82%).

Characterisation: mp 98-100 °C [lit. mp 95-97 °C]; \(\delta\)\(_{\text{H}}\) (CDCl\(_3\), 500 MHz) 1.37-1.44 (5H, m, \(\text{CH}_2\)), 1.63 (4H, dt, \(J\) 11.4, 5.8 Hz, \(\text{CH}_2\)), 2.43 (3H, s, \(\text{CH}_3\)), 2.93-2.99 (4H, m, \(\text{CH}_2\)), 7.31 (2H, d, \(J\) 8.3 Hz, \(\text{CH}_ar\)) and 7.63 (2H, d, \(J\) 8.3 Hz, -SO\(_2\)CC\(_{\text{H}}\text{Ar}\)); \(\delta\)\(_{\text{C}}\) (CDCl\(_3\), 125 MHz) 21.5, 23.5, 25.2, 46.9, 127.7, 129.5, 133.3 and 143.3; ESI-MS of [C\(_{12}\)H\(_{17}\)N\(_2\)O\(_2\)S]\(^+\); theoretical m/z of [M+Na]\(^+\) = 262.0877, measured m/z of [M+Na]\(^+\) = 262.0872; \(\nu_{\text{max}}\) (thin-film)/cm\(^{-1}\) 1162 (RSO\(_2\)R stretch) and 1337 (RSO\(_2\)R stretch).

8-(Piperidin-1-ylsulfonyl)quinoline\(^2\) (4b)

Following general procedure II: DBN salt 1c (461 mg, 1 mmol) and piperidine (104 \(\mu\)L, 1.05 mmol) in MeCN (7 mL) for 4 h gave the title compound as a colourless crystalline solid (160 mg, 58%); mp 155-156 °C [lit. mp 157-158 °C]; \(\delta\)\(_{\text{H}}\) (CDCl\(_3\), 500 MHz) 1.42-1.51 (2H, m, \(\text{CH}_2\)), 1.55-1.65 (4H, m, \(\text{CH}_2\)), 3.34-3.44 (4H, m, \(\text{CH}_2\)), 7.51 (1H, dd, \(J\) 8.3, 4.4 Hz, \(\text{CH}_al\)), 7.57-7.63 (1H, m, \(\text{CH}_al\)), 8.01 (1H, dd, \(J\) 7.8, 1.5 Hz, \(\text{CH}_al\)), 8.23 (1H, dd, \(J\) 8.3, 1.5 Hz, \(\text{CH}_al\)), 8.47 (1H, dd, \(J\) 7.3, 1.5 Hz, \(\text{CH}_al\)) and 9.03 - 9.10 (1 H, dd, \(J\) 4.4, 1.5 Hz, \(\text{CH}_al\)); \(\delta\)\(_{\text{C}}\) (CDCl\(_3\), 125 MHz) 23.9, 25.0, 47.2, 121.9, 125.4, 128.9, 132.9, 133.1, 136.3, 137.2, 144.3 and 151.0; ESI-MS of [C\(_{14}\)H\(_{16}\)N\(_2\)O\(_2\)S]\(^+\); theoretical m/z of [M+Na]\(^+\) = 299.0830, measured m/z of [M+H]\(^+\) = 299.0813; \(\nu_{\text{max}}\) (thin-film)/cm\(^{-1}\) 1162 (RSO\(_2\)R stretch) and 1318 (RSO\(_2\)R stretch).
1-(Methylsulfonyl)piperidine\(^3\) (4c)

Following general procedure II: DBN salt 1b (378 mg, 1 mmol) and piperidine (104 \(\mu\)L, 1.05 mmol) in MeCN (7 mL) for 4 h gave the title compound as a colourless crystalline solid (131 mg, 80%); mp 44-46 °C [lit. mp 45-46 °C]; \(\delta_H\) (CDCl\(_3\), 500 MHz) 1.50-1.56 (2H, m, CH\(_2\)), 1.61-1.67 (4H, m, CH\(_2\)), 2.72 (3H, s, CH\(_3\)) and 3.12-3.16 (4H, m, CH\(_2\)); \(\delta_C\) (CDCl\(_3\), 125 MHz) 23.6, 25.3, 34.3 and 46.7; ESI-MS of [C\(_6\)H\(_{13}\)N\(_2\)O\(_2\)S]\(^+\); theoretical m/z of [M+Na\(^+\)] = 186.0564, measured m/z of [M+Na\(^+\)] = 186.0563; \(\nu_{\text{max}}\) (thin-film)/cm\(^{-1}\) 1159 (RSO\(_2\)R stretch) and 1315 (RSO\(_2\)R stretch).

4-Tosylmorpholine\(^4\) (4d)

Following general procedure II: DBN salt 1a (213 mg, 0.5 mmol) and morpholine (46 \(\mu\)L, 0.53 mmol) in MeCN (7 mL) for 4 h gave the title compound as a yellow solid (105 mg, 87%); mp 147-149 °C [lit. mp 148-150 °C]; \(\delta_H\) (CDCl\(_3\), 500 MHz) 2.40 (3H, s, CH\(_3\)), 2.92-2.97 (4H, m, NCH\(_2\)), 3.67-3.72 (4H, m, OCH\(_2\)), 7.31 (2H, d, J 8.3 Hz, CH\(_2\)) and 7.60 (2H, d, J 8.3 Hz, -SO\(_2\)CC\(_6\)H\(_5\)); \(\delta_C\) (CDCl\(_3\), 125 MHz) 21.5, 46.0, 66.0, 127.9, 129.7, 132.0 and 143.9; ESI-MS of [C\(_{11}\)H\(_{15}\)NO\(_3\)S]\(^+\); theoretical m/z of [M+Na\(^+\)] = 264.0670, measured m/z of [M+Na\(^+\)] = 264.0660; \(\nu_{\text{max}}\) (thin-film)/cm\(^{-1}\) 1162 (RSO\(_2\)R stretch) and 1343 (RSO\(_2\)R stretch).

1-Phenyl-4-tosylpiperazine\(^5\) (4e)

Following general procedure II: DBN salt 1a (213 mg, 0.5 mmol) and 1-phenylpiperazine (80 \(\mu\)L, 0.53 mmol) in MeCN (7 mL) for 4 h gave the title compound as a colourless crystalline solid (119 mg, 75%); mp 200-202 °C [lit. mp 199-201 °C]; \(\delta_H\) (CDCl\(_3\), 500 MHz) 2.48 (3H, s, CH\(_3\)), 3.17-3.23 (4H, m, CH\(_2\)), 3.24-3.31 (4H, m, CH\(_2\)), 6.87-6.96 (3H, m, Ph), 7.26-7.32 (2H, m, Ph), 7.38 (2H, d, J 8.3 Hz, CH\(_2\)) and 7.71 (2H, d, J 8.3 Hz, -SO\(_2\)CC\(_6\)H\(_5\)); \(\delta_C\) (CDCl\(_3\), 125 MHz) 21.5, 46.1, 49.1, 116.8, 120.8, 127.9, 129.2, 129.7,
132.4, 143.8 and 150.7; ESI-MS of [C<sub>17</sub>H<sub>20</sub>N<sub>2</sub>O<sub>2</sub>S]<sup>+</sup>; theoretical m/z of [M+Na]<sup>+</sup> = 339.1143, measured m/z of [M+Na]<sup>+</sup> = 339.1147; ν<sub>max</sub> (thin-film)/cm<sup>-1</sup> 1168 (RSO<sub>R</sub>R stretch) and 1345 (RSO<sub>R</sub>R stretch).

2-Tosyl-1,2,3,4-tetrahydroisoquinoline<sup>6</sup> (4f)

![Image of 2-Tosyl-1,2,3,4-tetrahydroisoquinoline](image.png)

Following general procedure II: DBN salt 1a (213 mg, 0.5 mmol) and 1,2,3,4-tetrahydroisoquinoline (66 μL, 0.53 mmol) in MeCN (7 mL) for 4 h gave the title compound as an off-white crystalline solid (94 mg, 75%); mp 103-104 °C [lit. mp 95-96 °C]; δ<sub>H</sub> (CDCl<sub>3</sub>, 500 MHz) 2.43 (3H, s, CH<sub>3</sub>), 2.94 (2H, t, J 5.9 Hz, NCH<sub>2</sub>C<sub>H</sub>), 3.36 (2H, t, J 5.9 Hz, NC<sub>H</sub>CH<sub>2</sub>), 4.26 (2H, s, NC<sub>H</sub>CH<sub>Ar</sub>), 7.01-7.06 (1H, m, CH<sub>Ar</sub>), 7.06-7.11 (1H, m, CH<sub>Ar</sub>), 7.12-7.18 (2H, m, CH<sub>Ar</sub>) and 7.34 (2H, d, J 8.3 Hz, CH<sub>Ar</sub>CCH<sub>3</sub>); δ<sub>C</sub> (CDCl<sub>3</sub>, 125 MHz) 21.5, 28.9, 43.7, 47.5, 126.3, 126.3, 126.7, 127.7, 127.8, 129.7, 131.6, 133.1, 133.3 and 143.7; ESI-MS of [C<sub>17</sub>H<sub>20</sub>N<sub>2</sub>O<sub>2</sub>S]<sup>+</sup>; theoretical m/z of [M+Na]<sup>+</sup> = 310.0878, measured m/z of [M+Na]<sup>+</sup> = 310.0861; ν<sub>max</sub> (thin-film)/cm<sup>-1</sup> 1163 (RSO<sub>R</sub>R stretch) and 1332 (RSO<sub>R</sub>R stretch).

4-(4-Bromophenyl)-1-tosylpiperidin-4-ol (4g)

![Image of 4-(4-Bromophenyl)-1-tosylpiperidin-4-ol](image.png)

Following general procedure II: DBN salt 1a (213 mg, 0.5 mmol) and 4-(4-bromophenyl) 4-piperidinol (136 mg, 0.53 mmol) in MeCN (7 mL) for 4 h gave the title compound as an off-white solid (185 mg, 90%); mp 182-184 °C; δ<sub>H</sub> (CDCl<sub>3</sub>, 500 MHz) 1.75 (2H, app d, J 12.7 Hz, CH<sub>2</sub>), 2.12 (2H, app t, J 13.2 Hz, CH<sub>2</sub>), 2.45 (3H, s, CH<sub>3</sub>), 2.75 (2H, app t, J 12.2 Hz, CH<sub>2</sub>), 3.71 (2H, d, J 11.3 Hz, CH<sub>2</sub>), 7.29 (2H, d, J 8.31 Hz, CH<sub>Ar</sub>), 7.34 (2H, d, J 8.31 Hz, CH<sub>Ar</sub>), 7.46 (2H, d, J 8.3 Hz, CH<sub>Ar</sub>), 7.66 (2H, d, J 8.3 Hz, CH<sub>Ar</sub>); δ<sub>C</sub> (CDCl<sub>3</sub>, 125 MHz) 21.5, 37.6, 42.2, 70.4, 121.4, 126.2, 127.7, 129.7, 131.6, 133.2, 143.6 and 146.4; ESI-MS of [C<sub>18</sub>H<sub>20</sub>NO<sub>3</sub>SBr]<sup>+</sup>; theoretical m/z of [M+Na]<sup>+</sup> = 432.0245, measured m/z of [M+Na]<sup>+</sup> = 432.0256; ν<sub>max</sub> (thin-film)/cm<sup>-1</sup> 1153 (RSO<sub>R</sub>R stretch), 1344 (RSO<sub>R</sub>R stretch) and 3538 (O-H stretch).
**N,N-Diethyl-4-methylbenzenesulfonamide** (4h)

![Chemical structure](image)

Following general procedure II: DBN salt 1a (213 mg, 0.5 mmol) and diethylamine (55 μL, 0.53 mmol) in MeCN (7 mL) for 18 h gave the title compound as an off-white solid (54 mg, 48%); mp 55-57 °C [lit. mp 58-59 °C]; δH (CDCl3, 500 MHz) 1.11 (6H, t, J 7.1 Hz, CH2CH3), 2.40 (3H, s, CH3), 3.21 (4H, q, J 7.1 Hz, C2H5CH3), 7.27 (2H, d, J 8.3 Hz, CHAr) and 7.67 (2H, d, J 8.31 Hz, -SO2CClAr); δC (CDCl3, 125 MHz) 14.1, 21.4, 42.0, 127.0, 129.6, 137.4 and 142.9; ESI-MS of [C11H17NO2S]+; theoretical m/z of [M+Na]+ = 250.0878, measured m/z of [M+Na]+ = 250.0867; νmax (thin-film)/cm⁻¹ 1166 (RSO2R stretch) and 1345 (RSO2R stretch).

**N-Benzyl-N,4-dimethylbenzenesulfonamide** (4i)

![Chemical structure](image)

Following general procedure II; DBN salt 1a (213 mg, 0.5 mmol) and N-methylbenzylamine (68 μL, 0.53 mmol) and DBN (12 μL, 0.1 mmol) in MeCN (7 mL) gave the title compound as a white solid (78 mg, 60%) after 18 h; mp 90-93 °C [lit. mp 86-88 °C]; δH (CDCl3, 500 MHz) 2.45 (3H, s, CH3), 2.59 (3H, s, NCH3), 4.14 (2H, s, CH2), 7.29-7.35 (5H, m, Ph-H), 7.37 (2H d, J 8.3 Hz, CHAr) and 7.74 (2H, d, J 8.3 Hz, -SO2CClAr); δC (CDCl3, 125 MHz) 21.5, 34.3, 54.1, 127.5, 127.9, 128.4, 128.6, 129.7, 134.4, 135.7 and 143.5; ESI-MS of [C15H17NO2S]+; theoretical m/z of [M+Na]+ = 298.0877, measured m/z of [M+Na]+ = 298.0894; νmax (thin-film)/cm⁻¹ 1161 (RSO2R stretch) and 1349 (RSO2R stretch).

**2-(4-Tosylpiperazin-1-yl)ethan-1-ol** (4j)

![Chemical structure](image)

Following general procedure II; DBN salt 1a (213 mg, 0.5 mmol) and 1-(hydroxyethyl)-piperazine (65 μL, 0.53 mmol) in MeCN (7 mL) gave the title compound as a colourless oil (88 mg, 62%) after 4 h and purification by silica gel plug (80% EtOAc/Pet. ether); δH (CDCl3, 250 MHz) 2.37 (3H, s, CH3), 2.44-2.50 (2H, m, NCH2CH2OH), 2.50-2.56 (4H, 2, -CH2NCH2-), 2.92-3.00 (4H, m, S-NCH2), 3.48-3.55 (2H,
m, CH₂OH), 7.27 (2H d, J 8.1 Hz, CH₆) and 7.57 (2H, d, J 8.3 Hz, -SO₂CCH₆); δC (CDCl₃, 125 MHz) 21.5, 46.1, 52.0, 57.7, 58.9, 127.0, 127.8, 129.7 and 143.8; ESI-MS of [C₁₃H₂₀N₂O₃S]; theoretical m/z of [M+Na]⁺ = 307.1092, measured m/z of [M+Na]⁺ = 307.1112; νmax (thin-film)/cm⁻¹ 1174 (RSO₂R stretch), 1345 (RSO₂R stretch) and 3369 (OH stretch).

**Phenyl-4-methylbenzenesulfonate** (4k)

![Phenyl-4-methylbenzenesulfonate](image)

Following general procedure III; DBN salt 1a (213 mg, 0.5 mmol), phenol (50 mg, 0.53 mmol) and DBN (12 μL, 0.1 mmol) in MeCN (7 mL) gave the title compound as a white crystalline solid (118 mg, 95%) after 4 h; mp 89-94 °C [lit. mp 89-90 °C]; δH (CDCl₃, 500 MHz) 2.44 (3H, s, CH₃), 6.98 (2H, d, J 8.3 Hz, CH₆), 7.22-7.32 (5H, m, CH₆) and 7.70 (2H, d, J 8.3 Hz, -SO₂CCH₆); δC (CDCl₃, 125 MHz) 21.7, 115.3, 122.4, 127.1, 128.5, 129.6, 129.7, 132.4, 145.3 and 149.6; ESI-MS of [C₁₃H₁₂O₃S]; theoretical m/z of [M+Na]⁺ = 271.0405, measured m/z of [M+Na]⁺ = 271.0373; νmax (thin-film)/cm⁻¹ 1152 (RSO₂R stretch) and 1345 (RSO₂R stretch).

**4-Bromophenyl-4-methylbenzenesulfonate** (4l)

![4-Bromophenyl-4-methylbenzenesulfonate](image)

Following general procedure III; DBN salt 1a (213 mg, 0.5 mmol), 4-bromophenol (92 mg, 0.53 mmol) and DBN (12 μL, 0.1 mmol) in MeCN (7 mL) for 4 h gave the title compound as a colourless crystalline solid (118 mg, 95%); mp 77-79 °C [lit. mp 69-71 °C]; δH (CDCl₃, 500 MHz) 2.45 (3H, s, CH₃), 6.87 (2H, d, J 9.0 Hz, -OCCH₆), 7.32 (2H, d, J 7.8 Hz, CH₆), 7.40 (2H, d, J 9.0 Hz, CH₆) and 7.68 (2H, d, J 8.3 Hz, -SO₂CCH₆); δC (CDCl₃, 125 MHz) 21.7 121.1, 124.1, 128.5, 129.9, 132.0, 132.7, 145.7 and 148.6; ESI-MS of [C₁₃H₁₁O₃SBr]; theoretical m/z of [M+Na]⁺ = 348.9510, measured m/z of [M+Na]⁺ = 348.9489; νmax (thin-film)/cm⁻¹ 1158 (RSO₂R stretch) and 1374 (RSO₂R stretch).
2-Nitrophenyl-4-methylbenzenesulfonate\(^{12}\) (4m)

Following general procedure III: DBN salt 1a (213 mg, 0.5 mmol), 2-nitrophenol (74 mg, 0.53 mmol) and DBN (12 μL, 0.1 mmol) in MeCN (7 mL) for 4 h gave the title compound as a colourless solid (131 mg, 89%); mp 79-82 °C [lit. mp 80-82 °C]; \(\delta_H\) (CDCl\(_3\), 500 MHz) 2.46 (3H, s, CH\(_3\)), 7.34 (2H, d, J 8.3 Hz, CH\(_{Ar}\)), 7.36-7.48 (2H, m, CH\(_{Ar}\)), 7.59-7.63 (1H, m, CH\(_{Ar}\)), 7.75 (2H, d, J 8.3 Hz, -SO\(_2\)CC\(_{HAr}\)) and 7.89 (1H, dd, J 1.7, 8.4 Hz, CH\(_{Ar}\)); \(\delta_C\) (CDCl\(_3\), 125 MHz) 21.8, 125.3, 125.8, 127.6, 128.6, 130.0, 131.5, 134.2, 141.4, 142.9 and 146.3; ESI-MS of [C\(_{13}\)H\(_{11}\)N\(_{O}\)\(_5\)S\(^+\)]; theoretical m/z of [M+Na\(^+\)] = 316.0256, measured m/z of [M+Na\(^+\)] = 316.0240; \(\nu_{\text{max}}\) (thin-film)/cm\(^{-1}\) 819, 1158 (RSO\(_2\)R stretch), 1353, 1374 and 1532 (ArNO\(_2\) stretch).

4-(2-Methoxyethyl)phenyl-4-methylbenzenesulfonate (4n)

Following general procedure III; DBN salt 1a (213 mg, 0.5 mmol), 4-(2-methoxyethyl)phenol (81 mg, 0.53 mmol) and DBN (12 μL, 0.1 mmol) in MeCN (7 mL) gave the title compound as a colourless oil (129 mg, 84%) after 4 h; \(\delta_H\) (CDCl\(_3\), 500 MHz) 2.44 (3H, s, CH\(_3\)), 2.83 (2H, t, J 7.0 Hz, CH\(_2\)), 3.33 (3H, s, OCH\(_3\)), 3.56 (2H, t, J 7.0 Hz, CH\(_2\)), 6.89 (2H, d, J 8.9 Hz, CH\(_{Ar}\)), 7.13 (2H, d, J 8.9 Hz, CH\(_{Ar}\)), 7.30 (2H, d, J 8.3 Hz, CH\(_{Ar}\)) and 7.70 (2H, d, J 8.3 Hz, -SO\(_2\)CC\(_{HAr}\)); \(\delta_C\) (CDCl\(_3\), 125 MHz) 21.7, 35.5, 58.6, 73.1, 122.2, 128.5, 129.7, 129.9, 132.5, 138.2, 145.2 and 148.0; ESI-MS of [C\(_{16}\)H\(_{18}\)O\(_4\)S\(^+\)]; theoretical m/z of [M+Na\(^+\)] = 329.0823, measured m/z of [M+Na\(^+\)] = 329.0839; \(\nu_{\text{max}}\) (thin-film)/cm\(^{-1}\) 861, 1049, 1140 (RSO\(_2\)R stretch), 1375 (RSO\(_2\)R stretch), 1412 and 1705.

3-(Hydroxymethyl)phenyl 4-methylbenzenesulfonate\(^{13}\) (4o)

Following general procedure III; DBN salt 1a (213 mg, 0.5 mmol), 3-hydroxybenzyl alcohol (62 mg, 0.53 mmol) and DBN (12 μL, 0.1 mmol) in MeCN (7 mL) gave the title compound as a colourless solid...
(121 mg, 87%) after 4 h; mp 62-65 °C [lit. mp 65-67 °C]; δ_H (CDCl₃, 500 MHz) 2.43 (3H, s, CH₃), 4.60 (2H, s, CH₂), 6.83 (1H, dt, J 7.1, 2.3 Hz, CH₃), 7.03 (1H, s, CH₃), 7.20-7.26 (2H, m, CH₂), 7.30 (2H, d, J 8.5 Hz, CH₂) and 7.69 (2H, d, J 8.3 Hz, -SO₂CCH₃); δ_C (CDCl₃, 125 MHz) 21.7, 64.2, 120.7, 121.1, 125.3, 128.4, 129.6, 129.8, 132.4, 143.2, 145.4 and 149.7; ESI-MS of [C₁₄H₁₄O₄S]+; theoretical m/z of [M+Na]+ = 301.0510, measured m/z of [M+Na]+ = 301.0525; ν_max (thin-film)/cm⁻¹: 1175 (RSO₂R stretch), 1366 (RSO₂R stretch) and 3369 (OH stretch).

**Reaction of 3-Hydroxybenzyl alcohol with Tosyl Chloride**

Tosyl chloride (101 mg, 0.53 mmol) was added to 3-hydroxybenzyl alcohol (62 mg, 0.5 mmol) and pyridine (61 μL, 0.75 mmol) in CH₂Cl₂ (5 mL). The reaction was stirred at rt for 18 h then concentrated under reduced pressure. Analysis by ¹H NMR spectroscopy showed a complex mixture (Figure 1), whilst analysis by GC-MS showed that the main components of the mixture were 3-hydroxybenzyl chloride (rt 12.38 min) and 3-hydroxybenzyl alcohol (rt 14.09 min).

![Figure 1. ¹H NMR spectrum of crude reaction mixture of tosyl chloride and 3-hydroxybenzyl alcohol](image-url)
2-Cyano-2-methoxphenyl 4-methylbenzenesulfonate$^{14}$ (4p)

Following general procedure III; DBN salt 1a (213 mg, 0.5 mmol), 4-hydroxy-3-methoxybenzonitrile (75 mg, 0.53 mmol) and DBN (12 μL, 0.1 mmol) in MeCN (7 mL) gave the title compound as a colourless solid (126 mg, 83%) after 4 h; mp 87-89 °C [lit. mp 91-92 °C]; $\delta_H$ (CDCl$_3$, 500 MHz) 2.44 (3H, s, C$_3$H$_3$), 3.60 (3H, s, OCH$_3$), 7.07 (1H, d, $J_{1.5}$ Hz, CH$_{ar}$), 7.17-7.25 (2H, m, CH$_{ar}$), 7.31 (2H, d, $J_{8.5}$ Hz, CH$_{ar}$) and 7.72 (2H, d, $J_{8.3}$ Hz, -SO$_2$CCH$_{ar}$); $\delta_C$ (CDCl$_3$, 125 MHz) 21.7, 56.0, 111.7, 116.0, 117.9, 124.9, 125.1, 128.5, 129.6, 132.7, 141.8, 145.7 and 152.3; ESI-MS of [C$_{15}$H$_{13}$NO$_4$S]$^+$; theoretical m/z of [M+Na]$^+$ = 326.0463, measured m/z of [M+Na]$^+$ = 326.0444; $\nu_{\text{max}}$ (thin-film)/cm$^{-1}$ 1173 (RSO$_2$R stretch), 1374 (RSO$_2$R stretch), 1597 and 2233 (CN stretch).

4-Methyl-N-(4-methylbenzyl)benzenesulfonamide$^{15}$ (6a)

Following general procedure IV: DABCO salt 5a (248 mg, 0.6 mmol) and 4-methylbenzylamine (64 μL, 0.5 mmol) in MeCN (7 mL) for 4 h gave the title compound as a yellow crystalline solid (104 mg, 74%); mp 90-93 °C [lit. mp 90-91 °C]; $\delta_H$ (CDCl$_3$, 300 MHz) 2.20 (3H, s, CH$_3$), 2.33 (3H, s, CH$_3$), 3.95 (2H, d, $J_{6.0}$ Hz, CH$_3$), 4.96 (1H, t, $J_{6.0}$ Hz NH), 6.93-7.00 (4H, m, amine CH$_{ar}$), 7.18 (2H, d, $J_{8.3}$ Hz, CH$_{ar}$) and 7.64 (2H, d, $J_{8.3}$ Hz, -SO$_2$CCH$_{ar}$); $\delta_C$ (CDCl$_3$, 125 MHz) 21.1, 21.5, 47.0, 127.2, 127.8, 129.3, 129.7, 133.2, 136.9, 137.6 and 143.4; ESI-MS of [C$_{15}$H$_{13}$NO$_2$S]$^+$; theoretical m/z of [M+Na]$^+$ = 298.0878, measured m/z of [M+Na]$^+$ = 298.0866; $\nu_{\text{max}}$ (thin-film)/cm$^{-1}$ 1152 (RSO$_2$R stretch), 1324 (RSO$_2$R stretch) and 3263 (N-H).
**N-(4-Methoxyphenyl)-4-methylbenzenesulfonamide**\(^6\) (6b)

![Chemical Structure of N-(4-Methoxyphenyl)-4-methylbenzenesulfonamide]

Following general procedure II: DBN salt 1a (213 mg, 0.5 mmol) and \(p\)-anisidine (65 mg, 0.53 mmol) in MeCN (7 mL) was stirred at 80 °C for 18 h. Analysis of the crude \(^1\)H NMR spectrum showed 0% conversion to the title compound based on the integrals of the methyl peak in starting DBN salt (\(\delta_H 2.46 \text{ ppm}\)) and literature product (\(\delta_H 2.39 \text{ ppm}\)).

Following general procedure IV: DABCO salt 5a (248 mg, 0.6 mmol) and \(p\)-anisidine (65 mg, 0.5 mmol) in MeCN (7 mL) for 4 h gave the title compound as a pale brown solid (124 mg, 89%).

Characterisation: mp 111-113 °C [lit. mp 114-116 °C]; \(\delta_H (\text{CDCl}_3, 500 \text{ MHz})\) 2.39 (3H, s, CH\(_3\)), 3.79 (3H, s, OCH\(_3\)), 6.58 (1H, br. s, OH), 6.76 (2H, d, J 8.8 Hz, -OCCH\(_2\)), 6.98 (2H, d, J 8.8 Hz, -NCCH\(_2\)), 7.22 (2H, d, J 8.3 Hz, CH\(_2\)) and 7.60 (2H, d, J 8.3 Hz, -SO\(_2\)CCH\(_2\)); \(\delta_C (\text{CDCl}_3, 125 \text{ MHz})\) 21.5, 55.4, 114.4, 125.4, 127.3, 128.9, 129.5, 136.0, 143.6 and 157.9; ESI-MS of \([\text{C}_{14}\text{H}_{15}\text{NO}_3\text{S}]^+\); theoretical m/z of \([\text{M+Na}]^+ = 300.0670\), measured m/z of \([\text{M+Na}]^+ = 300.0655\); \(\nu_{\text{max}}\) (thin-film)/cm\(^{-1}\) 1156 (RSO\(_2\)R stretch), 1327 (RSO\(_2\)R stretch) and 3268 (N-H).

**N,4-Dimethyl-N-phenylbenzenesulfonamide**\(^7\) (6c)

![Chemical Structure of N,4-Dimethyl-N-phenylbenzenesulfonamide]

Following general procedure II: DBN salt 1a (213 mg, 0.5 mmol) and \(N\)-methylaniline (57 µL, 0.53 mmol) in MeCN (7 mL) was stirred at 80 °C for 18 h. Analysis of the crude \(^1\)H NMR spectrum showed 0% conversion to the title compound based on the integrals of the methyl peak in starting DBN salt (\(\delta_H 2.46 \text{ ppm}\)) and literature product (\(\delta_H 2.43 \text{ ppm}\)).

Following general procedure IV: DABCO salt 5a (248 mg, 0.6 mmol) and \(N\)-methylaniline (54 µL, 0.5 mmol) in MeCN (7 mL) for 4 h gave the title compound as a pale yellow solid (103 mg, 79%).

Characterisation: mp 90-93 °C [lit. mp 90-92 °C]; \(\delta_H (\text{CDCl}_3, 500 \text{ MHz})\) 2.41 (3H, s, CH\(_3\)), 3.16 (3H, s, NCH\(_3\)), 2.93-2.99 (4H, m, CH\(_2\)), 7.07-7.11 (2H, m, Ph-H), 7.23 (2H, d, J 8.3 Hz, CH\(_2\)), 7.25-7.32 (3H, m, Ph-H) and 7.42 (2H, d, J 8.3 Hz, -SO\(_2\)CCH\(_2\)); \(\delta_C (\text{CDCl}_3, 125 \text{ MHz})\) 21.5, 38.06, 126.6, 127.2, 127.9, 129.3, 133.5, 141.6 and 143.5; ESI-MS of \([\text{C}_{14}\text{H}_{15}\text{NO}_2\text{S}]^+\); theoretical m/z of \([\text{M+Na}]^+ = 284.0721\),
measured m/z of [M+Na]^+ = 284.0721; ν_max (thin-film)/cm⁻¹ 1150 (RSO₂R stretch) and 1342 (RSO₂R stretch).

**Phenyl-4-methylbenzenesulfonate** (4k)

Following general procedure II: DBN salt 1a (213 mg, 0.5 mmol), phenol (50 mg, 0.53 mmol) and DBN (12 μL, 0.1 mmol) in MeCN (7 mL) for 4 h gave the title compound as a colourless crystalline solid (118 mg, 95%).

Following general procedure IV: DABCO salt 5a (248 mg, 0.6 mmol) and phenol (48 mg, 0.5 mmol) in MeCN (7 mL) for 4 h gave the title compound as a colourless solid (93 mg, 75%).

Characterisation: mp 89-94 °C [lit. mp 89-90 °C]; δ_H (CDCl₃, 500 MHz) 2.44 (3H, s, CH₃), 6.98 (2H, d, J 8.3 Hz, CHAr), 7.22-7.32 (5H, m, CHAr) and 7.70 (2H, d, J 8.3 Hz, -SO₂CC₄H₆); δ_C (CDCl₃, 125 MHz) 21.7, 115.3, 122.4, 127.1, 128.5, 129.6, 129.7, 132.4, 145.3 and 149.6; ESI-MS of [C₁₃H₁₂O₃S]⁺; theoretical m/z of [M+Na]^+ = 271.0405, measured m/z of [M+Na]^+ = 271.0373; ν_max (thin-film)/cm⁻¹ 1152 (RSO₂R stretch) and 1345 (RSO₂R stretch).

**Phenethyl-4-methylbenzenesulfonate** (6d)

Following general procedure II: DBN salt 1a (213 mg, 0.5 mmol) and 2-phenylethanol (63 μL, 0.53 mmol) in MeCN (7 mL) was stirred at 80 °C for 18 h. Analysis of the crude ¹H NMR spectrum showed 0% conversion to the title compound by the absence of peaks at 3.87 (CDCl₃, t, J 6.6 Hz, CH₂) and 2.88 (CDCl₃, t, J 6.6 Hz, CH₂) ppm.¹⁸

Following general procedure IV: DABCO salt 5a (248 mg, 0.6 mmol) and 2-phenylethanol (72 μL, 0.5 mmol) in MeCN (7 mL) for 4 h gave the title compound as a colourless solid (113 mg, 82%).

Characterisation: mp 35-37 °C [lit. mp 36.5-37°C]¹⁹; δ_H (MeCN-d3, 500 MHz) 2.42 (3H, s, CH₃), 2.90 (2H, t, J 6.4 Hz, CH₂), 4.22 (2H, t, J 6.4 Hz, CH₂), 7.10-7.15 (2H, m, Ph), 7.20-7.30 (3H, m, Ph), 7.36 (2H, d, J
8.8 Hz, CH₃), 7.66 (2H, d, J 8.80 Hz, -SO₂CCH₃); δC (MeCN-d3, 125 MHz) 21.7, 35.7, 72.1, 127.7, 128.6
129.5, 129.9, 131.0, 133.8, 138.0 and 146.2; ESI-MS of [C₁₅H₁₆O₃S]⁺; theoretical m/z of
[M+Na]⁺ = 299.0718, measured m/z of [M+Na]⁺ = 299.0781; νmax (thin-film)/cm⁻¹ 1171 (RSO₂R stretch)
and 1343 (RSO₂R stretch).
Characterisation of Phosphoramidates and Phosphonates

Diethyl piperidin-1-ylphosphonate (7a)

Following general procedure V: DBN salt 2a (264 mg, 0.65 mmol) and piperidine (50 μL, 0.5 mmol) in MeCN (7 mL) for 2 h gave the title compound as a yellow oil (95 mg, 86%) after purification by silica column chromatography (5% MeOH/EtOAc); δ_H (CDCl_3, 500 MHz) 1.63 (6H, dt, J 1.0, 7.0 Hz, CH_2CH_3), 1.42-1.59 (6H, m, CH_2), 2.98-3.15 (4H, m, -NC_2H); δ_C (CDCl_3, 125 MHz) 16.2 (d, J_P-C 6.7 Hz), 24.5, 26.1 (d, J_P-C 4.8 Hz), 45.4 (d, J_P-C 1.9 Hz) and 62.0 (d, J_P-C 5.7 Hz); δ_P (CDCl_3, 121 MHz) 8.89; ESI-MS of [C_9H_20N_3O_3P]^+; theoretical m/z of [M+Na]^+ = 244.1079, measured m/z of [M+Na]^+ = 244.1075; ν_max (thin-film)/cm^-1 832, 1022, 1214 and 2937.

Diphenyl piperidin-1-ylphosphonate (7b)

Following general procedure V: DBN salt 2b (326 mg, 0.65 mmol) and piperidine (50 μL, 0.5 mmol) in MeCN (7 mL) for 2 h gave the title compound as a colourless oily solid (154 mg, 97%) after purification by silica plug (50% EtOAc/petroleum ether); mp 72-73 °C [lit. mp 75-76 °C]^{21}; δ_H (Acetone-d_6, 500 MHz) 1.34-1.42 (4H, m, CH_2), 1.46-1.53 (2H, m, CH_2), 3.17-3.25 (4H, m, -NC_2H); δ_C (Acetone-d_6, 125 MHz) 24.0, 25.6 (d, J_P-C 3.8 Hz), 45.3 (d, J_P-C 2.9 Hz), 120.2 (d, J_P-C 4.8 Hz), 124.8, 129.7 and 151.2 (d, J_P-C 5.7 Hz); δ_P (Acetone-d_6, 121 MHz) - 1.03; ESI-MS of [C_17H_20N_3O_3P]^+; theoretical m/z of [M+Na]^+ = 340.1079, measured m/z of [M+Na]^+ = 340.1057; ν_max (thin-film)/cm^-1 919, 1189, 1487 and 2937.

Diphenyl morpholinophosphonate (7c)

Following general procedure V: DBN salt 2b (326 mg, 0.65 mmol) and morpholine (46 μL, 0.5 mmol) in MeCN (7 mL) for 2 h gave the title compound as a colourless oily solid (150 mg, 94%) after...
purification by silica plug (50% EtOAc/petroleum ether); mp 67-69 °C [lit. mp 71-72 °C]1; δH (Acetone-
-d6, 500 MHz) 3.15-3.32 (4H, m, CH2), 3.38-3.56 (4H, m, CH2) and 7.16-7.52 (10H, m, CHar); δC (Acetone-
d6, 125 MHz) 44.7, 66.3 (d, JPC 4.8 Hz), 120.2 (d, JPC 2.9 Hz), 120.2 (d, JPC 4.8 Hz), 125.0, 129.8 and
151.0 (d, JPC 6.7 Hz); δP (Acetone-d6, 121 MHz) -1.95; ESI-MS of [C16H18NO4P]+; theoretical m/z of
[M+Na]+ = 342.0871, measured m/z of [M+Na]+ = 342.0855; νmax (thin-film)/cm⁻¹ 781, 924, 1189, 1486
and 2858.

Diphenyl (4-phenylpiperazin-1-yl)phosphonate (7d)

\[
\text{PhO-} \quad \text{P} \quad \text{N} \quad \text{Ph}
\]

Following general procedure V: DBN salt 2b (326 mg, 0.65 mmol) and N-phenylpiperazine (76 μL, 0.5 mmol) in MeCN (7 mL) for 2 h gave the title compound as a pale yellow solid (167 mg, 85%) after
purification by silica plug (50% EtOAc/petroleum ether); mp 84-86 °C; δH (Acetone-d6, 500 MHz)
3.01-3.06 (4H, m, CH2), 3.39-3.45 (4H, m, CH2), 6.84 (1H, tt, J 1.0, 7.3 Hz, CHar), 6.89-6.93 (2H, m, CHar),
7.18-7.26 (4H, m, CHar) and 7.35-7.44 (8H, m, CHar); δC (Acetone-d6, 125 MHz) 44.7, 49.3 (d, JPC 5.7 Hz),
116.4, 119.9, 120.3 (d, JPC 4.8 Hz), 125.0, 129.0, 130.0, 151.1 (d, JPC 5.7 Hz) and 151.6;
δP (Acetone-d6, 121 MHz) -1.46; ESI-MS of [C22H23N2O3P]+; theoretical m/z of [M+H]+ = 395.1524, measured m/z of
[M+H]+ = 395.1503; νmax (thin-film)/cm⁻¹ 656, 749, 929, 1143, 1484 and 2853.

Diphenyl (1,2,3,4-tetrahydroisoquinoline-2-yl)phosphonate (7e)

\[
\text{PhO-} \quad \text{P} \quad \text{N}
\]

Following general procedure V: DBN salt 2b (326 mg, 0.65 mmol) and 1,2,3,4-tetrahydroisoquinoline
(62 μL, 0.5 mmol) in MeCN (7 mL) for 2 h gave the title compound as a yellow oil (157 mg, 86%) after
purification by silica plug (50% EtOAc/petroleum ether); δH (Acetone-d6, 500 MHz) 2.68 (2H, t, J 5.9 Hz,
CH2), 3.53 (2H, dt, J 5.9, 9.8 Hz, CH2), 4.48 (2H, d, J 6.9 Hz, -NC2H5), 7.02-7.07 (1H, m, CHar), 7.09-7.20
(5H, m, CHar) and 7.27-7.37 (8H, m, CHar); δC (Acetone-d6, 125 MHz) 28.4 (d, JPC 2.9 Hz), 42.3 (d, JPC 2.9 Hz),
46.1 (d, JPC 3.8 Hz), 120.2 (d, JPC 4.8 Hz), 124.9, 126.0, 126.1, 126.4, 129.2, 129.7, 133.1 (d, JPC 5.7 Hz),
134.0 and 151.1 (d, JPC 5.7 Hz); δP (Acetone-d6, 121 MHz) -0.92; ESI-MS of [C23H20NO4P]+;
theoretical m/z of [M+Na]$^+$ = 388.1079, measured m/z of [M+H]$^+$ = 388.1058; $\nu_{\text{max}}$ (thin-film)/cm$^{-1}$: 686, 748, 928, 1143, 1485 and 2831.

Diphenyl (4-(4-bromophenyl)-4-hydroxypiperidin-1-yl)phosphonate (7f)

Following general procedure V: DBN salt 2b (326 mg, 0.65 mmol) and 4-(4-bromophenyl)-4-piperidinol (128 mg, 0.5 mmol) in MeCN (7 mL) for 2 h gave the title compound as a pale yellow solid (213 mg, 87%) after purification by silica plug (50% EtOAc/petroleum ether); mp 141-144 °C; $\delta_H$ (CDCl$_3$, 500 MHz) 1.54-1.61 (2H, m, $\text{CH}_2$), 1.71 (2H, dt, $J$ 4.4, 13.4, $\text{CH}_2$), 2.50 (1H, br. s, $\text{O}$H), 3.19-3.32 (2H, m, $\text{CH}_2$), 3.56-3.65 (2H, m, $\text{CH}_2$), 7.11 (2H, d, $J$ 8.6 Hz, $\text{CH}_2$), 7.18 (2H, t, $J$ 7.4 Hz, $\text{CH}_2$), 7.22-7.29 (4H, m, $\text{CH}_2$), 7.34 (4H, t, $J$ 7.9 Hz, $\text{CH}_2$) and 7.40 (2H, d, $J$ 8.6 Hz, Br$\text{CH}_2$); $\delta_C$ (CDCl$_3$, 125 MHz) 37.9 (d, $J_{P-C}$ 3.8 Hz), 40.8 (d, $J_{P-C}$ 2.9 Hz), 71.0 (d, $J_{P-C}$ 1.9 Hz), 120.1 (d, $J_{P-C}$ 5.7 Hz), 121.0 (d, $J_{P-C}$ 2.9 Hz), 124.9, 126.2, 129.7, 131.4, 147.2 (d, $J_{P-C}$ 6.7 Hz); $\delta_P$ (CDCl$_3$, 121 MHz) -1.40; ESI-MS of [C$_{23}$H$_{23}$N$_2$O$_4$PBr]$^+$; theoretical m/z of [M+Na]$^+$ = 510.0446, measured m/z of [M+Na]$^+$ = 510.0439; $\nu_{\text{max}}$ (thin-film)/cm$^{-1}$: 784, 928, 1191, 1485, 2925 and 3382.

Diphenyl diethylphosphoramidate (7g)

Following general procedure V: DBN salt 2b (326 mg, 0.65 mmol) and diethylamine (52 μL, 0.5 mmol) in MeCN (7 mL) for 24 h gave the title compound as a pale yellow oil (117 mg, 77%) after purification by silica column chromatography (10-20% EtOAc/petroleum ether); mp 51-52 °C [lit. mp 61-62 °C]$^{22}$; $\delta_H$ (Acetone-d$_6$, 500 MHz) 1.03 (6H, t, $J$ 7.1 Hz, $\text{CH}_3$), 3.24 (4H, dq, $J$ 7.1, 12.1 Hz, $\text{CH}_2$), 7.17-7.22 (2H, m, $\text{CH}_2$), 7.29-7.35 (4H, m, $\text{CH}_2$) and 7.36-7.42 (4H, m, $\text{CH}_2$); $\delta_C$ (Acetone-d$_6$, 125 MHz) 13.3 (d, $J_{P-C}$ 2.0 Hz), 39.6 (d, $J_{P-C}$ 4.4 Hz), 120.2 (d, $J_{P-C}$ 5.2 Hz), 124.6 (d, $J_{P-C}$ 0.8 Hz), 129.6 and 151.3 (d, $J_{P-C}$ 6.4 Hz); $\delta_P$ (Acetone-d$_6$, 121 MHz) -0.76; ESI-MS of [C$_{16}$H$_{20}$N$_2$O$_3$P]$^+$; theoretical m/z of [M+Na]$^+$ = 328.1079, measured m/z of [M+Na]$^+$ = 328.1069; $\nu_{\text{max}}$ (thin-film)/cm$^{-1}$: 755, 916, 1190, 1487, 1590 and 2976.
Diphenyl dibenzylphosphoramidate (7h)

Following general procedure V; DBN salt 2b (326 mg, 0.65 mmol) and dibenzylamine (96 μL, 0.5 mmol) in MeCN (5 mL) for 24 h gave the title compound as a pale yellow solid (52 mg, 25%) after purification by silica column chromatography (10% EtOAc/petroleum ether); mp 78-79 °C; δ_H (Acetone-d6, 500 MHz) 4.28 (4H, d, J 10.8 Hz, CH2), 7.15-7.20 (4H, m, CHAr), 7.32-7.36 (4H, m, CHAr) and 7.38-7.42 (4H, m, CHAr); δ_C (Acetone-d6, 125 MHz) 48.4 (d, J_P-C 4.7 Hz), 120.4 (d, J_P-C 4.9 Hz), 124.9, 127.5, 128.4, 128.6, 129.7, 136.7 (d, J_P-C 2.9 Hz) and 151.3 (d, J_P-C 7.1 Hz); δ_P (Acetone-d6, 121 MHz) 0.49; ESI-MS of [C26H24NO3P]+; theoretical m/z of [M+Na]+ = 452.1392, measured m/z of [M+Na]+ = 452.1392; ν_max (thin-film)/cm⁻¹ 742, 919, 1188, 1488, 1591 and 3030.

4-Bromophenyl diphenylphosphate22 (7i)

Following general procedure V: DBN salt 2b (326 mg, 0.65 mmol), 4-bromophenol (87 mg, 0.5 mmol) and DBN (12 μL, 0.1 mmol) in MeCN (7 mL) for 4 h gave the title compound as a colourless oil (198 mg, 98%) after purification by silica plug (50% EtOAc/petroleum ether); δ_H (Acetone-d6, 500 MHz) 7.24-7.32 (4H, m, CHAr), 7.32-7.37 (4H, m, CHAr), 7.40-7.46 (4H, m, CHAr) and 7.59 (4H, d, J 8.4 Hz, BrCCCHAr); δ_C (Acetone-d6, 125 MHz) 118.3 (d, J_P-C 1.6 Hz), 120.1 (d, J_P-C 4.9 Hz), 122.2 (d, J_P-C 4.9 Hz), 125.9 (d, J_P-C 1.2 Hz), 130.1, 133.0, 149.8 (d, J_P-C 6.7 Hz) and 150.5 (d, J_P-C 7.3 Hz); δ_P (Acetone-d6, 121 MHz) -17.67; ESI-MS of [C18H14NO3PBr]+; theoretical m/z of [M+Na]+ = 426.9711, measured m/z of [M+Na]+ = 426.9706; ν_max (thin-film)/cm⁻¹ 752, 948, 1182, 1300, 1481, 1588 and 3072.

2-Nitrophenyl diphenylphosphate (7j)

Following general procedure V: DBN salt 2b (326 mg, 0.65 mmol), 2-nitrophenol (70 mg, 0.5 mmol) and DBN (12 μL, 0.1 mmol) in MeCN (7 mL) for 4 h gave the title compound as a pale yellow oil.
(184 mg, 99%) after purification by silica plug (50% EtOAc/petroleum ether); δ\textsubscript{H} (Acetone-\textit{d}6, 500 MHz) 7.26-7.31 (2H, m, \textit{CH\textsubscript{Ar}}), 7.33-7.36 (4H, m, \textit{CH\textsubscript{Ar}}), 7.41-7.51 (6H, m, \textit{CH\textsubscript{Ar}}), 7.66 (1H, dt, \textit{J} 1.3, 8.4 Hz, \textit{CH\textsubscript{Ar}}) and 7.74 (1H, ddd, \textit{J} 1.7, 7.5, 8.4 Hz, \textit{CH\textsubscript{Ar}}); δ\textsubscript{C} (Acetone-\textit{d}6, 125 MHz) 120.1 (d, \textit{J}_{\text{P-C}} 4.9 Hz), 122.7 (d, \textit{J}_{\text{P-C}} 2.9 Hz), 125.9, 126.1 (d, \textit{J}_{\text{P-C}} 1.3 Hz), 126.5 (d, \textit{J}_{\text{P-C}} 1.2 Hz), 130.1, 134.8 (d, \textit{J}_{\text{P-C}} 1.3 Hz), 141.7 (d, \textit{J}_{\text{P-C}} 0.5 Hz), 142.6 (d, \textit{J}_{\text{P-C}} 6.3 Hz) and 150.3 (d, \textit{J}_{\text{P-C}} 7.5 Hz); δ\textsubscript{P} (Acetone-\textit{d}6, 121 MHz) -18.11; ESI-MS of [C\textsubscript{18}H\textsubscript{14}N\textsubscript{6}O\textsubscript{6}P]\textsuperscript{+}; theoretical m/z of [M+Na]\textsuperscript{+} = 394.0456, measured m/z of [M+Na]\textsuperscript{+} = 394.0465; ν\textsubscript{max} (thin-film)/cm\textsuperscript{-1} 744, 946, 1181, 1483 and 2923.

Naphthalen-2-yl diphenylphosphosphate\textsuperscript{22} (7k)

Following general procedure V: DBN salt 2b (326 mg, 0.65 mmol), 2-naphthol (72 mg, 0.5 mmol) and DBN (12 μL, 0.1 mmol) in MeCN (7 mL) for 4 h gave the title compound as a colourless oil (184 mg, 98%) after purification by silica plug (50% EtOAc/petroleum ether); δ\textsubscript{H} (Acetone-\textit{d}6, 500 MHz) 7.22-7.30 (2H, m, \textit{CH\textsubscript{Ar}}), 7.38-7.55 (11H, m, \textit{CH\textsubscript{Ar}}), 7.87-7.94 (3H, m, \textit{CH\textsubscript{Ar}}) and 7.97 (1H, d, \textit{J} 8.9 Hz, \textit{CH\textsubscript{Ar}}); δ\textsubscript{C} (Acetone-\textit{d}6, 125 MHz) 116.8 (d, \textit{J}_{\text{P-C}} 5.1 Hz), 119.9 (d, \textit{J}_{\text{P-C}} 5.1 Hz), 120.2 (d, \textit{J}_{\text{P-C}} 5.0 Hz), 125.8 (d, \textit{J}_{\text{P-C}} 1.1 Hz), 126.0, 127.1, 127.6, 127.9, 130.1, 130.8, 131.3, 134.0, 148.3 (d, \textit{J}_{\text{P-C}} 7.6 Hz) and 150.7 (d, \textit{J}_{\text{P-C}} 7.3 Hz); δ\textsubscript{P} (Acetone-\textit{d}6, 121 MHz) -17.27; ESI-MS of [C\textsubscript{22}H\textsubscript{17}O\textsubscript{6}P]\textsuperscript{+}; theoretical m/z of [M+Na]\textsuperscript{+} = 399.0762, measured m/z of [M+Na]\textsuperscript{+} = 399.0757; ν\textsubscript{max} (thin-film)/cm\textsuperscript{-1} 749, 946, 1152, 1296, 1487, 1589 and 3061.

Diphenyl benzylphosphoramidate\textsuperscript{23} (8a)

Following general procedure VI: DBN salt 2b (452 mg, 0.9 mmol) and benzylamine (55 μL, 0.5 mmol) in MeCN (15 mL) for 4 h gave the title compound as an off-white solid (120 mg, 71%) after purification by silica column chromatography (5-30% EtOAc/petroleum ether); mp 95-97 °C [lit. mp 107.9 °C]; δ\textsubscript{H} (Acetone-\textit{d}6, 500 MHz) 4.28 (2H, dd, \textit{J} 7.1, 11.8, -N\textsubscript{CH\textsubscript{2}}Ph), 5.31 (1H, dt, \textit{J} 6.9, 13.3 Hz, NH), 7.16-7.31 (11H, m, \textit{CH\textsubscript{Ar}}) and 7.33-7.40 (4H, m, \textit{CH\textsubscript{Ar}}); δ\textsubscript{C} (Acetone-\textit{d}6, 125 MHz) 45.2, 120.3 (d, \textit{J}_{\text{P-C}} 4.9 Hz), 124.7, 127.0, 127.7, 128.2, 129.6, 139.9 (d, \textit{J}_{\text{P-C}} 5.3 Hz) and 151.2 (d, \textit{J}_{\text{P-C}} 6.7 Hz); δ\textsubscript{P} (Acetone-\textit{d}6,
121 MHz) -0.21; ESI-MS of [C_{19}H_{18}NO_{3}P]^+; theoretical m/z of [M+H]^+ = 340.1103, measured m/z of [M+H]^+ = 340.1076; \nu_{\max} (\text{thin-film})/\text{cm}^{-1} 751, 839, 1188, 1487 and 3394.

**Diphenyl (2-chlorobenzyl)phosphoramidate (8b)**

![Diphenyl (2-chlorobenzyl)phosphoramidate (8b)](image)

Following general procedure VI: DBN salt 2b (452 mg, 0.9 mmol) and 2-chlorobenzylamine (61 \text{ \mu L}, 0.5 mmol) in MeCN (15 mL) for 4 h gave the title compound as a colourless solid (146 mg, 78%) after purification by silica column chromatography (5-20% EtOAc/petroleum ether); mp 90-91 °C; \delta_H (Acetone-d6, 500 MHz) 4.40 (2H, dd, J 7.2, 12.5, -NCH$_2$Ph), 5.42-5.63 (1H, m, NH), 7.14-7.31 (8H, m, CH$_{Ar}$), 7.32-7.38 (5H, m, CH$_{Ar}$) and 7.47 (1H, dd, J 1.6, 7.5 Hz, CH$_{Ar}$); \delta_C (Acetone-d6, 125 MHz) 42.8, 120.3 (d, J$_C$P 4.9 Hz), 124.8, 127.0, 128.6, 129.1, 129.2, 129.6, 132.5, 137.1 (d, J$_C$P 5.1 Hz) and 151.2 (d, J$_C$P 6.6 Hz); \delta_P (Acetone-d6, 121 MHz) -0.19; ESI-MS of [C$_{19}$H$_{17}$NO$_3$PCl]$^+$; theoretical m/z of [M+H]^+ = 340.1103, measured m/z of [M+H]^+ = 340.1076; \nu_{\max} (\text{thin-film})/\text{cm}^{-1} 743, 930, 1191, 1488, 1589 and 3250.

**Diphenyl phenethylphosphoramidate (8c)**

![Diphenyl phenethylphosphoramidate (8c)](image)

Following general procedure VI: DBN salt 2b (452 mg, 0.9 mmol) and 2-phenethylamine (63 \text{ \mu L}, 0.5 mmol) in MeCN (15 mL) for 4 h gave the title compound as a colourless solid (117 mg, 66%) after purification by silica column chromatography (5-30% EtOAc/petroleum ether); mp 73-74 °C [lit. mp 77.5-78 °C]; \delta_H (Acetone-d6, 250 MHz) 2.69 (2H, m, CH$_2$), 3.22-3.44 (2H, m, CH$_2$), 4.80-5.22 (2H, m, -NH) and 7.13-7.47 (15H, m, CH$_{Ar}$); \delta_C (Acetone-d6, 125 MHz) 37.8 (d, J$_C$P 5.8 Hz), 43.3, 120.3 (d, J$_C$P 4.8 Hz), 124.7, 126.2, 128.4, 128.8, 129.6, 139.1 and 151.3 (d, J$_C$P 6.4 Hz); \delta_P (Acetone-d6, 121 MHz) -0.11; ESI-MS of [C$_{20}$H$_{20}$NO$_3$P]$^+$; theoretical m/z of [M+Na]^+ = 376.1079, measured m/z of [M+Na]^+ = 376.1053; \nu_{\max} (\text{thin-film})/\text{cm}^{-1} 748, 924, 1195, 1488, 1589 and 3243.
Diphenyl allylphosphoramidate\textsuperscript{(8d)}

Following general procedure VI: DBN salt 2b (452 mg, 0.9 mmol) and allylamine (38 μL, 0.5 mmol) in MeCN (15 mL) for 4 h gave the title compound as a colourless solid (91 mg, 63%) after purification by silica column chromatography (5-30% EtOAc/petroleum ether); mp 52-53 °C [lit. mp 51-53 °C]; δ\textsubscript{H} (Acetone-\textit{d}6, 300 MHz) 3.61-3.76 (2H, m, -NHCH\textsubscript{2}), 5.01 (1H, dd, J 1.1, 10.4 Hz, -CHCH\textsubscript{2}), 5.05-5.24 (2H, m, -CHCH\textsubscript{2} and NH), 5.82 (1H, ddt, J 5.4, 10.6, 15.8 Hz, -CH\textsubscript{2}CHCH\textsubscript{2}), 7.20 (2H, t, J 7.1 Hz, CH\textsubscript{Ar}) and 7.28-7.42 (8H, m, CH\textsubscript{Ar}); δ\textsubscript{C} (Acetone-\textit{d}6, 125 MHz) 43.9, 114.8, 120.4 (d, J\textsubscript{PC} 4.8 Hz), 124.7, 129.6, 136.2 (d, J\textsubscript{PC} 5.7 Hz) and 151.3 (d, J\textsubscript{PC} 6.5 Hz); δ\textsubscript{P} (Acetone-\textit{d}6, 121 MHz) -0.12; ESI-MS of [C\textsubscript{15}H\textsubscript{16}N\textsubscript{O}\textsubscript{3}P]\textsuperscript{+}; theoretical m/z of [M+Na]\textsuperscript{+} = 312.0765, measured m/z of [M+Na]\textsuperscript{+} = 312.0654; ν\textsubscript{max} (thin-film)/cm\textsuperscript{-1} 754, 921, 1184, 1487, 1590 and 3251.
Stability of \(N\)-Tosyl DABCO•PF\(_6\) Salts

\[
\text{O} \quad \text{O} \quad \text{PF}_6
\]
\[+\]
\[
\text{HNN}
\]
\[
\xrightarrow{\text{MeCN (0.07 M)}} \quad 80 \degree \text{C, 4 h} \quad 4a
\]
\[
\text{DABCO.PF}_6
\]

DABCO salt 5a (207 mg, 0.5 mmol) and piperidine (49 μL, 0.5 mmol) were added to MeCN (7 mL) and heated at 80 °C for 4 h. After this time the reaction mixture was concentrated under reduced pressure and an \(^1\)H NMR taken of the crude mixture. Conversion to product 4a was determined by relative integrals of DBN salt (2.38 (3H, s) and 7.41 (2H, d, \(J\) 7.7 Hz) ppm) and product 4a (2.29 (3H, s) and 7.16 (2H, d, \(J\) 7.6 Hz) ppm). Reactions were carried out on the day that DABCO salt 5a was synthesized (day 0) and subsequent days to test the stability of the salt. 5a was stored in a sealed vial purged with \(\text{N}_2\) at rt during this test, results are given below.

<table>
<thead>
<tr>
<th>Age of Salt (d)</th>
<th>Conversion to 4a (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>76</td>
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<tr>
<td>2</td>
<td>66</td>
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<tr>
<td>4</td>
<td>55</td>
</tr>
<tr>
<td>6</td>
<td>26</td>
</tr>
</tbody>
</table>
$^1$H and $^{13}$C NMR Spectra

$N$-Tosyl DBN$\cdot$PF$_6$ (1a)
N-Mesyl DBN•PF$_6$ (1b)
N-8-Quinolinesulfonyl DBN•PF$_6$ (1c)
$N$-Diethoxyphosphoryl $\text{DBN}\cdot\text{PF}_6$ (2a)
N-Diphenoxypyosphoryl DBN•PF₆ (2b)
$N$-Tosyl DABCO•PF$_6$ (5a)
N-(4-Methylbenzyl)-1-tosylhexahydropyrrolo[1,2-α]pyrimidin-8a(6H)-amine hydrochloride (3a)
N-(3-(2-(Allylimino)pyrrolidin-1-ylpropyl)-4-methylbenzenesulfonamide hydrochloride (3b)
4-Methyl-N-(3-(2-phenethylimino)pyrrolidin-1-yl)propyl)benzenesulfonamide hydrochloride (3c)
N-\{3-\{2-(Benzylimino)pyrrolidin-1-yl\}propyl\}quinolone-8-sulfonamide hydrochloride
1-Tosylpiperidine (4a)
8-(Piperidin-1-ylsulfonyl)quinoline (4b)
1-(Methylsulfonyl)piperidine (4c)
4-Tosylmorpholine (4d)
1-Phenyl-4-tosylpiperazine (4e)
2-Tosyl-1,2,3,4-tetrahydroisoquinoline (4f)
4-(4-Bromophenyl)-1-tosylpiperidin-4-ol (4g)
$N,N$-Diethyl-4-methylbenzenesulfonamide (4h)
$N$-Benzyl-$N,4$-dimethylbenzenesulfonamide (4i)
2-(4-Tosylpiperazin-1-yl)ethan-1-ol (4j)
4-Bromophenyl-4-methylbenzenesulfonate (4l)
2-Nitrophenyl-4-methylbenzenesulfonate (4m)
4-(2-Methoxyethyl)phenyl-4-methylbenzenesulfonate (4n)

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\text{Structure Image}
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\text{NMR Spectrum Image}
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3-(Hydroxymethyl)phenyl 4-methylbenzenesulfonate (4o)
2-Cyano-2-methoxphenyl 4-methylbenzenesulfonate (4p)
4-Methyl-N-(4-methylbenzyl)benzenesulfonamide (6a)
N-(4-Methoxyphenyl)-4-methylbenzenesulfonamide (6b)
N,4-Dimethyl-N-phenylbenzenesulfonamide (6c)
Phenyl-4-methylbenzenesulfonate (4k)
Phenethyl-4-methylbenzenesulfonate (6d)
Diethyl piperidin-1-ylphosphonate (7a)
Diphenyl piperidin-1-ylphosphonate (7b)
Diphenyl morpholinophosphonate (7c)
Diphenyl (4-phenylpiperazin-1-yl)phosphonate (7d)
Diphenyl (1,2,3,4-tetrahydroisoquinoline-2-yl)phosphonate (7e)
Diphenyl (4-(4-bromophenyl)-4-hydroxypiperidin-1-yl)phosphonate (7f)
Diphenyl diethylphosphoramidate (7g)
Diphenyl dibenzylphosphoramidate (7h)
4-Bromophenyl diphenylphosphate (7i)
2-Nitrophenyl diphenylphosphate (7j)
Naphthalen-2-yl diphenylphosphate (7k)
Diphenyl benzylphosphoramidate (8a)
Diphenyl (2-chlorobenzyl)phosphoramidate (8b)
Diphenyl phenethylphosphoramidate (8c)
Diphenyl allylphosphoramidate (8d)
References