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 ν_{max} in 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 N_2. 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 CH_2Cl_2 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 $MgSO_4$, 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. $NaHCO_3$ and brine, then dried over $MgSO_4$, filtered and concentrated under reduced pressure.

General Procedure V – DBN Salt Phosphonylations

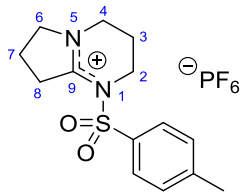
The appropriate DBN salt (1.3 equiv), amine (1 equiv) and the given amount of DBN in acetonitrile (0.07 M) were heated at 80 °C for the given amount of time. Upon completion the reaction mixture was concentrated under reduced pressure and purified by silica plug or silica column chromatography.

General Procedure VI – DBN Salt Phosphonylations 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.

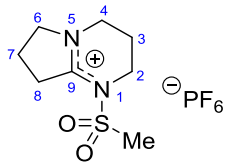
Characterisation of DBN•PF_6 and DABCO•PF_6 Salts

N-Tosyl DBN•PF_6 (1a)



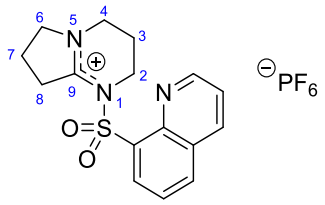
Following general procedure I: DBN (1.85 mL, 15 mmol) was added to *p*-toluenesulfonyl chloride (2.97 g, 15.6 mmol) and KPF_6 (2.76 g, 15 mmol) in MeCN (75 mL). Upon work up and trituration with CH_2Cl_2 the title compound was obtained as a colourless solid (6.03 g, 95%); mp decomposed at 201 °C; δ_H (DMSO-*d6*, 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^8), 3.75-3.83 (4H, m, H^6 and H^4), 7.55 (2H, d, *J* 8.3 Hz, CH_{Ar}) and 7.97 (2H, d, *J* 8.3 Hz, $-SO_2CCH_{Ar}$); δ_C (DMSO-*d6*, 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; δ_F (DMSO-*d6*, 470 MHz) -70.3 (d, J_{P-F} 711.5 Hz, $^-PF_6$); ESI-MS of $[C_{14}H_{19}N_2O_2S]^+$; theoretical m/z of $[M+H]^+$ = 279.1167, measured m/z of $[M+H]^+$ = 279.1232; ν_{max} (thin-film)/cm^{-1} 828, 1173 (RSO_2R stretch) and 1323 (RSO_2R stretch).

N-Mesyl DBN•PF_6 (1b)



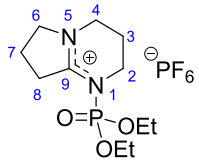
Following general procedure I: DBN (1.85 mL, 15 mmol) was added to methanesulfonyl chloride (1.21 mL, 15.6 mmol) and KPF_6 (2.76 g, 15 mmol) in MeCN (75 mL). Upon work up and trituration with CH_2Cl_2 the title compound was obtained as a colourless solid (5.30 g, 92%); mp 114-116 °C; δ_H (DMSO-*d6*, 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^8), 3.59 (3H, s) and 3.84 (4H, t, *J* 5.9 Hz, H^6 and H^4); δ_C (DMSO-*d6*, 125 MHz) 18.2, 18.9, 34.2, 41.0, 44.3, 44.8, 55.9 and 166.2; δ_F (DMSO-*d6*, 470 MHz) -70.3 (d, J_{P-F} 711.5 Hz, $^-PF_6$); ESI-MS of $[C_8H_{15}N_2O_2S]^+$; theoretical m/z of $[M+H]^+$ = 203.0854, measured m/z of $[M+H]^+$ = 203.0896; ν_{max} (thin-film)/cm^{-1} 1162 (RSO_2R stretch) and 1337 (RSO_2R stretch).

_N_-8-Quinolinesulfonyl DBN•PF_6 (1c)



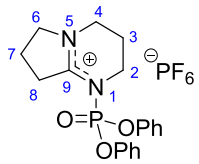
Following general procedure I: DBN (1.85 mL, 15 mmol) was added to 8-quinolinesulfonyl chloride (3.55 g, 15.6 mmol) and KPF_6 (2.76 g, 15 mmol) in MeCN (75 mL). Upon work up and trituration with CH_2Cl_2 the title compound was obtained as a colourless solid (5.06 g, 73%); mp 246-249 °C; δ_H (DMSO-*d6*, 500 MHz) 1.85 (2H, app. quin, *J* 5.8 Hz, H^3), 2.16 (2H, app quin, *J* 7.8 Hz, H^7), 3.45 (2H, t, *J* 5.9 Hz, H^2), 3.51 (2H, t, *J* 7.8 Hz, H^8), 3.85 (2H, t, *J* 7.8 Hz, H^6), 3.98-4.01 (2H, m, H^4), 7.82 (1H, dd, *J* 8.3, 3.9 Hz, CH_{Ar}), 7.91 (1H, t, *J* 7.3 Hz, CH_{Ar}), 8.55 (1H, dd, *J* 8.3, 1.5 Hz, CH_{Ar}), 8.62 (1H, dd, *J* 7.3, 1.5 Hz, CH_{Ar}), 8.67 (1H, dd, *J* 8.3, 2.0 Hz, CH_{Ar}) and 9.11-9.15 (1H, m, CH_{Ar}); δ_C (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, 143.0, 152.9 and 167.0; δ_F (DMSO-*d6*, 470 MHz) -70.3 (d, $J_{P\text{-}F}$ 711.5 Hz, $^-PF_6$); ESI-MS of $[C_{16}H_{18}N_3O_2S]^+$; theoretical m/z of $[M+H]^+$ = 316.1120, measured m/z of $[M+H]^+$ = 316.1196; ν_{max} (thin-film)/cm^{-1} 828, 1172 (RSO_2R stretch) and 1324 (RSO_2R stretch).

_N_-Diethoxyphoshoryl DBN•PF_6 (2a)



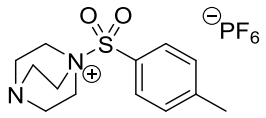
Following general procedure I: DBN (3.70 mL, 30 mmol) was added to diethyl chlorophosphate (4.50 mL, 31.2 mmol) and KPF_6 (5.52 g, 30 mmol) in MeCN (150 mL). Upon work up and trituration with EtOAc the title compound was obtained as a colourless solid (11.42 g, 98%); mp 81-83 °C; δ_H (DMSO-*d6*, 500 MHz) 1.30 (6H, dt, J 1.0, 6.9 Hz, CH_2CH_3), 2.00-2.12 (4H, m, H^3), 3.21 (2H, t, *J* 7.8 Hz, H^7), 3.48 (2H, t, *J* 5.9 Hz, H^4), 3.55-3.60 (2H, m, H^2), 3.77-3.81 (2H, m, H^6) and 4.16-4.23 (4H, m, -O$CH_2$$CH_3$); δ_C (DMSO-*d6*, 125 MHz) 15.7 (d, $J_{P\text{-}C}$ 6.8 Hz), 17.6, 18.2 (d, $J_{P\text{-}C}$ 3.6 Hz), 33.7, 43.9, 43.5, 55.2, 64.7 (d, $J_{P\text{-}C}$ 5.0 Hz) and 167.5 (d, $J_{P\text{-}C}$ 13.7 Hz); δ_F (DMSO-*d6*, 470 MHz) -70.1 (d, $J_{P\text{-}F}$ 711.5 Hz, $^-PF_6$); δ_P (DMSO-*d6*, 121 MHz) -2.09; ESI-MS of $[C_{11}H_{22}N_2O_3P]^+$; 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_-Diphenoxyphoshoryl DBN•PF_6 (2b)



Following general procedure I: DBN (1.85 mL, 15 mmol) was added to diphenyl chlorophosphate (3.23 mL, 15.6 mmol) and KPF_6 (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, H^3 and H^7), 3.31 (2H, t, *J* 7.9 Hz, H^8), 3.54 (2H, t, *J* 5.7 Hz, H^4), 3.81-3.86 (2H, m, H^2), 3.87-4.11 (2H, m, H^6), 7.31-7.35 (6H, m, CH_{Ar}) and 7.45-7.50 (4H, m, CH_{Ar}); δ_C (DMSO-*d6*, 125 MHz) 18.0, 18.7 (d, $J_{P\text{-}C}$ 3.7 Hz), 34.7, 44.4, 44.7, 56.2, 120.5 (d, $J_{P\text{-}C}$ 4.7 Hz), 127.0, 130.9, 149.5 (d, $J_{P\text{-}C}$ 7.0 Hz) and 168.0 (d, $J_{P\text{-}C}$ 15.4 Hz); δ_F (DMSO-*d6*, 470 MHz) -70.0 (d, $J_{P\text{-}F}$ 711.4 Hz, $^-PF_6$); δ_P (DMSO-*d6*, 121 MHz) -11.19; ESI-MS of $[C_{19}H_{22}N_2O_3P]^+$; 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.

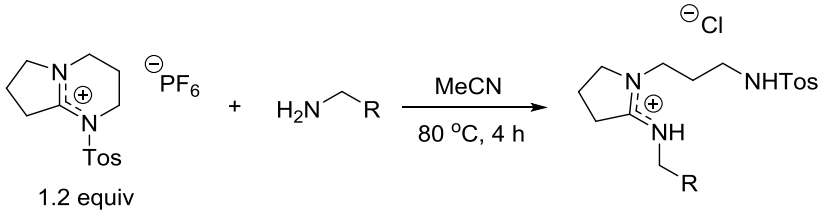
_N_-Tosyl DABCO•PF_6 (5a)

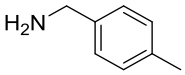
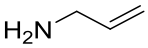
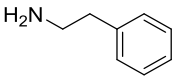


1,4-Diazabicyclo[2.2.2]octane (DABCO) (588 mg, 5.25 mmol) was added to *p*-toluenesulfonyl chloride (953 mg, 5 mmol) and KPF_6 (920 mg, 5 mmol) in MeCN (25 mL) and stirred at rt for 1 h. After this time the reaction mixture was filtered through Celite to remove the white precipitate that had formed, and the filtrate concentrated under reduced pressure. The resulting DABCO•PF_6 salt was purified by trituration with CH_2Cl_2 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, CH_3), 3.45-3.63 (12H, m, CH_2), 7.13 (2H, d, *J* 7.8 Hz, CH_{Ar}) and 7.50 (2H, d, *J* 7.8 Hz, CH_{Ar}); 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, $J_{P\text{-}F}$ 711.5 Hz, $^-PF_6$); ESI-MS of $[C_{13}H_{18}N_2O_2S_2]^+$; 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 (RSO_2R stretch) and 1391.

Sulfonylation of Primary Amines

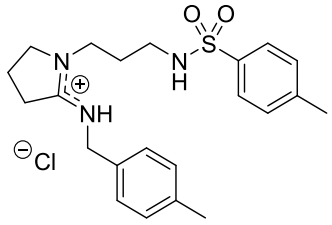
Table 1. The reaction of primary amines with *N*-tosyl DBN•PF_6



Entry	Amine	Product	Conversion (%)[a]	Yield (%)
1		**3a**	100	61
2		**3b**	100	57
3		**3c**	100	>100

[a]Conversion determined by analysis of crude ^{1}H NMR spectra

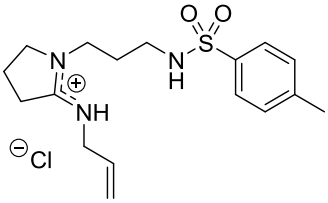
N-(4-Methylbenzyl)-1-tosylhexahydropyrrolo[1,2-*a*]pyrimidin-8a(6*H*)-amine hydrochloride (3a)



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. $NaHCO_3$ 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 (127 mg, 61%); mp 52-55 °C; δ_H (CD_3CN, 500 MHz) 1.74- 1.81 (2H, m, C*H*$_2$), 2.06 (2H, app. quin, *J* 7.8 Hz, C*H*$_2$), 2.31 (3H, s, C*H*$_3$), 2.41 (3H, s, C*H*$_3$), 2.83-2.91 (4H, m, C*H*$_2$), 3.47 (2H, t, *J* 7.8 Hz, C*H*$_2$), 3.62 (2H, t, *J* 7.3 Hz, C*H*$_2$), 4.44 (2H, s, C*H*$_2$Ph), 6.40 (1H, br. s, N*H*), 7.18 (2H, d, *J* 7.8 Hz, C*H*$_{Ar}$), 7.23 (2H, d, *J* 7.8 Hz, C*H*$_{Ar}$), 7.36 (2H, d, *J* 8.3 Hz, C*H*$_{Ar}$), 7.72 (2H, d, *J* 8.3 Hz, -SO_2CC*H*$_{Ar}$) and 8.65 (1H, br. s, N*H*); δ_C (CD_3CN, 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;

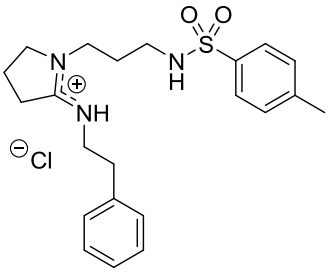
ESI-MS of $[C_{22}H_{30}N_3O_2S]^+$; theoretical m/z of $[M+H]^+$ = 400.2059, measured m/z of $[M+H]^+$ = 400.2166; ν_{max} (thin-film)/cm^{-1} 831, 1154 (RSO_2R stretch), 1324 (RSO_2R stretch), 1667, and 3332 (N-H stretch).

***N*-(3-(2-(Allylimino)pyrrolidin-1-ylpropyl)-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; δ_H ($CDCl_3$, 500 MHz) 1.88 (2H, dt, *J* 13.2, 6.6 Hz, C*H*$_2$), 2.14 (2H, app. q, *J* 7.6 Hz, C*H*$_2$), 2.37 (3H, s, C*H*$_3$), 2.89 (2H, t, *J* 8.1 Hz, C*H*$_2$), 2.94 (2H, t, *J* 2.94 Hz, C*H*$_2$), 3.63 (2H, t, *J* 7.3 Hz, C*H*$_2$), 3.70 (2H, t, *J* 7.1 Hz, C*H*$_2$), 3.94 (2H, d, CH=C*H*$_2$), 5.14-5.22 (2H, m, CHC*H*$_2$), 5.83 (1H, ddt, *J* 16.8, 10.9, 5.5 Hz, C*H*), 7.26 (2H, d, *J* 7.3 Hz, C*H*$_{Ar}$) and 7.73 (2H, d, *J 7.7* Hz, -SO_2CC*H*$_{Ar}$); δ_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 $[C_{17}H_{25}N_3O_2S]^+$; theoretical m/z of $[M+H]^+$ = 336.1746, measured m/z of $[M+H]^+$ = 336.1830; ν_{max} (thin-film)/cm^{-1} 826, 1144 (RSO_2R stretch), 1322 (RSO_2R stretch), 1667, and 3290 (N-H stretch).

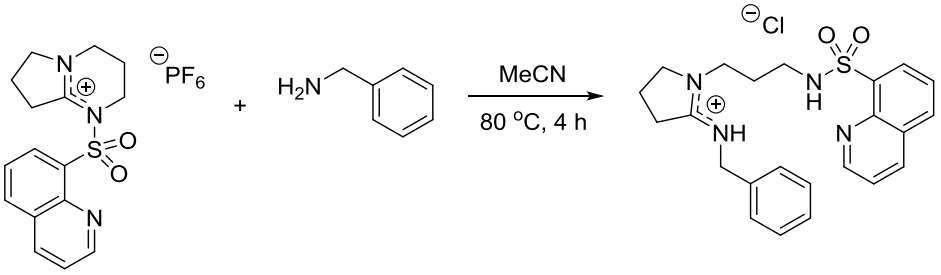
4-Methyl-*N*-(3-(2-phenethylimino)pyrrolidin-1-yl)propyl)benzenesulfonamide hydrochloride (3c)



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; δ_H (CD_3CN, 500 MHz) 1.75 (2H, dt, *J* 14.4, 7.0 Hz, C*H*$_2$), 1.98 (2H, dt, *J* 15.9, 7.7 Hz, C*H*$_2$), 2.44 (3H, s,

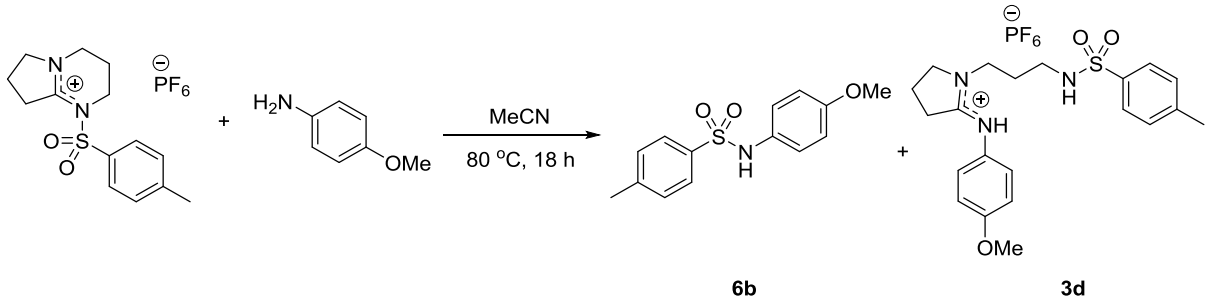
CH_3), 2.65 (2H, t, *J* 8.1 Hz, C*H*$_2$), 2.86 (2H, t, *J* 6.6 Hz, C*H*$_2$), 2.92 (2H, t, *J* 7.1 Hz, C*H*$_2$), 3.32-3.37 (2H, m, C*H*$_2$), 3.55 (2H, t, *J* 7.1 Hz, C*H*$_2$), 3.61 (2H, t, *J* 7.3 Hz, C*H*$_2$), 7.24-7.30 (3H, m, Ph-*H*), 7.33-7.37 (2H, m, Ph-*H*), 7.43 (2H, d, *J* 8.8 Hz, C*H*$_{Ar}$) and 7.75 (2H, d, *J* 8.3 Hz, -SO_2CC*H*$_{Ar}$); δ_C (CD_3CN, 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 $[C_{22}H_{30}N_3O_2S]^+$; theoretical m/z of $[M+H]^+$ = 400.2059, measured m/z of $[M+H]^+$ = 400.2169; ν_{max} (thin-film)/cm^{-1} 826, 1144 (RSO_2R stretch), 1322 (RSO_2R stretch), 1667, and 3290 (N-H stretch).

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



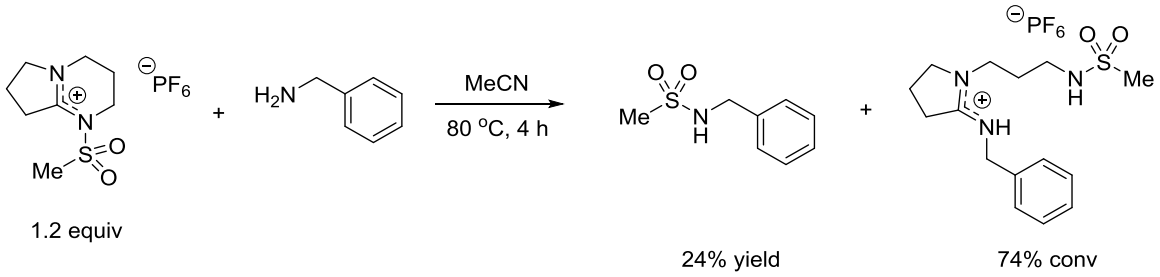
DBN salt **1c** (256 mg, 0.6 mmol) and benzylamine (55 µL, 0.5 mmol) in MeCN (2 mL) were stirred for 1 h at 80 °C. After this time the reaction mixture was taken up in EtOAc and washed with 1 M HCl, aq. sat. $NaHCO_3$ and brine. The organic layer was dried over $MgSO_4$, filtered and concentrated under reduced pressure to yield the title compound as a yellow solid (235 mg, quant.); mp 71-76 °C; δ_H (CD_3CN, 500 MHz) 1.71- 1.79 (2H, m, C*H*$_2$), 2.02-2.11 (2H, m, C*H*$_2$), 2.81 (2H, t, *J* 6.4 Hz, C*H*$_2$), 2.88 (2H, t, *J* 7.8 Hz, C*H*$_2$), 3.38 (2H, t, *J* 7.8 Hz, C*H*$_2$), 3.62 (2H, t, *J* 7.3 Hz, C*H*$_2$), 4.50 (2H, s, C*H*$_2$Ph), 7.30-7.42 (5H, m, Ph-*H*), 7.66 (1H, dd, *J* 3.9, 8.3 Hz, C*H*$_{Ar}$), 7.72 (1H, t, *J* 7.8 Hz, C*H*$_{Ar}$), 8.22 (1H, dd, *J* 1.5, 7.8 Hz, C*H*$_{Ar}$), 8.33 (1H, dd, *J* 1.0, 7.3 Hz, C*H*$_{Ar}$), 8.44 (1H, dd, *J* 1.5, 8.3 Hz, C*H*$_{Ar}$) and 9.03 (1H, d, *J* 1.5, 3.9 Hz, C*H*$_{Ar}$); δ_C ($CDCl_3$, 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 $[C_{23}H_{27}N_4O_2S]^+$; theoretical m/z of $[M+H]^+$ = 423.1855, measured m/z of $[M+H]^+$ = 423.1961; ν_{max} (thin-film)/cm^{-1} 826, 1144 (RSO_2R stretch), 1322 (RSO_2R stretch), 1668 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.

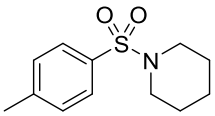
***N*-Benzylmethanesulfonamide[23]**



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]; δ_H ($CDCl_3$, 500 MHz) 2.87 (3H, s, C*H*$_3$), 4.32 (2H, d, *J* 6.0 Hz, C*H*$_2$), 4.76 (1H, br. s, N*H*) and 7.29-7.43 (5H, m, Ph-*H*); δ_C ($CDCl_3$, 125 MHz) 41.1, 47.2, 127.9, 128.2, 129.0 and 136.7; ESI-MS of $[C_8H_{11}NO_2S]^+$; theoretical m/z of $[M+Na]^+$ = 208.0408, measured m/z of $[M+Na]^+$ = 208.0399; ν_{max} (thin-film)/cm^{-1} 834, 1137 (RSO_2R stretch), 1305 (RSO_2R stretch), 1667 (N-H stretch) and 3225 (N-H stretch).

Characterisation of Sulfonamides and Sulfonate Esters

1-Tosylpiperidine[1] (4a)

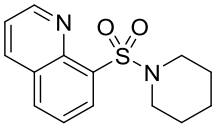


Following general procedure II: DBN salt **1a** (416 mg, 1 mmol) and piperidine (104 µL, 1.05 mmol) in MeCN (7 mL) for 4 h gave the title compound as a colourless crystalline solid (204 mg, 86%).

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

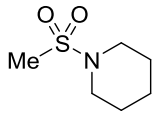
Characterisation: mp 98-100 °C [lit. mp 95-97 °C]; δ_H ($CDCl_3$, 500 MHz) 1.37- 1.44 (5H, m, C*H*$_2$), 1.63 (4H, dt, *J* 11.4, 5.8 Hz, C*H*$_2$), 2.43 (3H, s, C*H*$_3$), 2.93-2.99 (4H, m, C*H*$_2$), 7.31 (2H d, *J* 8.3 Hz, C*H*$_{Ar}$) and 7.63 (2H, d, *J* 8.3 Hz, -SO_2CC*H*$_{Ar}$); δ_C ($CDCl_3$, 125 MHz) 21.5, 23.5, 25.2, 46.9, 127.7, 129.5, 133.3 and 143.3; ESI-MS of $[C_{12}H_{17}NO_2S]^+$; theoretical m/z of $[M+Na]^+$ = 262.0877, measured m/z of $[M+Na]^+$ = 262.0872; ν_{max} (thin-film)/cm^{-1} 1162 (RSO_2R stretch) and 1337 (RSO_2R stretch).

8-(Piperidin-1-ylsulfonyl)quinoline[2] (4b)



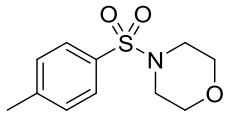
Following general procedure II: DBN salt **1c** (461 mg, 1 mmol) and piperidine (104 µL, 1.05 mmol) in MeCN (7 mL) for 4 h gave the title compound as a colourless crystalline solid (160 mg, 58%); mp 155-156 °C [lit. mp 157-158 °C]; δ_H ($CDCl_3$, 500 MHz) 1.42-1.51 (2H, m, C*H*$_2$), 1.55-1.65 (4H, m, C*H*$_2$), 3.34-3.44 (4H, m, C*H*$_2$), 7.51 (1H, dd, *J* 8.3, 4.4 Hz, C*H*$_{Ar}$), 7.57-7.63 (1H, m, C*H*$_{Ar}$), 8.01 (1H, dd, *J* 7.8, 1.5 Hz, C*H*$_{Ar}$), 8.23 (1H, dd, *J* 8.3, 1.5 Hz, C*H*$_{Ar}$), 8.47 (1H, dd, *J* 7.3, 1.5 Hz, C*H*$_{Ar}$) and 9.03 - 9.10 (1 H, dd, *J* 4.4, 1.5 Hz, C*H*$_{Ar}$); δ_C ($CDCl_3$, 125 MHz) 23.9, 25.9, 47.2, 121.9, 125.4, 128.9, 132.9, 133.1, 136.3, 137.2, 144.3 and 151.0; ESI-MS of $[C_{14}H_{16}N_2O_2S]^+$; theoretical m/z of $[M+Na]^+$ = 299.0830, measured m/z of $[M+H]^+$ = 299.0813; ν_{max} (thin-film)/cm^{-1} 1162 (RSO_2R stretch) and 1318 (RSO_2R stretch).

1-(Methylsulfonyl)piperidine[3] (4c)



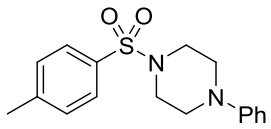
Following general procedure II: DBN salt **1b** (378 mg, 1 mmol) and piperidine (104 µL, 1.05 mmol) in MeCN (7 mL) for 4 h gave the title compound as a colourless crystalline solid (131 mg, 80%); mp 44-46 °C [lit. mp 45-46 °C]; δ_H ($CDCl_3$, 500 MHz) 1.50-1.56 (2H, m, C*H*$_2$), 1.61-1.67 (4H, m, C*H*$_2$), 2.72 (3H, s, C*H*$_3$) and 3.12-3.16 (4H, m, *H*$_2$); δ_C ($CDCl_3$, 125 MHz) 23.6, 25.3, 34.3 and 46.7; ESI-MS of $[C_6H_{13}NO_2S]^+$; theoretical m/z of $[M+Na]^+$ = 186.0564, measured m/z of $[M+Na]^+$ = 186.0563; ν_{max} (thin-film)/cm^{-1} 1159 (RSO_2R stretch) and 1315 (RSO_2R stretch).

4-Tosylmorpholine[4] (4d)



Following general procedure II: DBN salt **1a** (213 mg, 0.5 mmol) and morpholine (46 µL, 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]; δ_H ($CDCl_3$, 500 MHz) 2.40 (3H, s, C*H*$_3$), 2.92-2.97 (4H, m, NC*H*$_2$), 3.67-3.72 (4H, m, OC*H*$_2$), 7.31 (2H, d, *J* 8.3 Hz, C*H*$_{Ar}$) and 7.60 (2H, d, *J* 8.3 Hz, -SO_2CC*H*$_{Ar}$); δ_C ($CDCl_3$, 125 MHz) 21.5, 46.0, 66.0, 127.9, 129.7, 132.0 and 143.9; ESI-MS of $[C_{11}H_{15}NO_3S]^+$; theoretical m/z of $[M+Na]^+$ = 264.0670, measured m/z of $[M+Na]^+$ = 264.0660; ν_{max} (thin-film)/cm^{-1} 1162 (RSO_2R stretch) and 1343 (RSO_2R stretch).

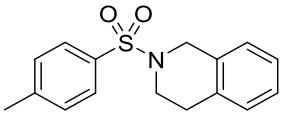
1-Phenyl-4-tosylpiperazine[5] (4e)



Following general procedure II: DBN salt **1a** (213 mg, 0.5 mmol) and 1-phenylpiperazine (80 µL, 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]; δ_H ($CDCl_3$, 500 MHz) 2.48 (3H, s, C*H*$_3$), 3.17-3.23 (4H, m, C*H*$_2$), 3.24-3.31 (4H, m, C*H*$_2$), 6.87-6.96 (3H, m, Ph), 7.26-7.32 (2H, m, Ph), 7.38 (2H, d, *J* 8.3 Hz, C*H*$_{Ar}$) and 7.71 (2H, d, *J* 8.3 Hz, -SO_2CC*H*$_{Ar}$); δ_C ($CDCl_3$, 125 MHz) 21.5, 46.1, 49.1, 116.8, 120.8, 127.9, 129.2, 129.7,

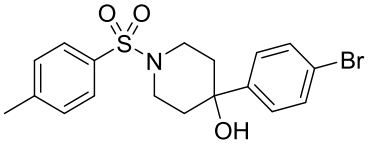
132.4, 143.8 and 150.7; ESI-MS of $[C_{17}H_{20}N_2O_2S]^+$; theoretical m/z of $[M+Na]^+$ = 339.1143, measured m/z of $[M+Na]^+$ = 339.1147; ν_{max} (thin-film)/cm^{-1} 1168 (RSO_2R stretch) and 1345 (RSO_2R stretch).

2-Tosyl-1,2,3,4-tetrahydroisoquinoline[6] (4f)



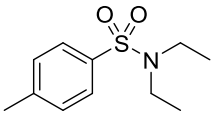
Following general procedure II: DBN salt **1a** (213 mg, 0.5 mmol) and 1,2,3,4-tetrahydroisoquinoline (66 µL, 0.53 mmol) in MeCN (7 mL) for 4 h gave the title compound as an off-white crystalline solid (94 mg, 75%); mp 103-104 °C [lit. mp 95-96 °C]; δ_H ($CDCl_3$, 500 MHz) 2.43 (3H, s, C*H*$_3$), 2.94 (2H, t, *J* 5.9 Hz, NCH_2CH_2), 3.36 (2H, t, *J* 5.9 Hz, NCH_2CH_2), 4.26 (2H, s, NCH_2CH_{Ar}), 7.01-7.06 (1H, m, C*H*$_{Ar}$), 7.06-7.11 (1H, m, C*H*$_{Ar}$), 7.12-7.18 (2H, m, C*H*$_{Ar}$), 7.34 (2H, d, *J* 8.3 Hz, $CH_{Ar}CCH_3$) and 7.74 (2H, d, *J* 8.3 Hz, -SO_2CCH_{Ar}); δ_C ($CDCl_3$, 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 $[C_{16}H_{17}NO_2S]^+$; theoretical m/z of $[M+Na]^+$ = 310.0878, measured m/z of $[M+Na]^+$ = 310.0861; ν_{max} (thin-film)/cm^{-1} 1163 (RSO_2R stretch) and 1332 (RSO_2R stretch).

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



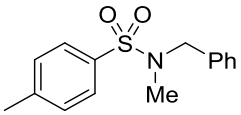
Following general procedure II: DBN salt **1a** (213 mg, 0.5 mmol) and 4-(4-bromophenyl) 4-piperidinol (136 mg, 0.53 mmol) in MeCN (7 mL) for 4 h gave the title compound as an off-white solid (185 mg, 90%); mp 182-184 °C; δ_H ($CDCl_3$, 500 MHz) 1.75 (2H, app d, *J* 12.7 Hz, C*H*$_2$), 2.12 (2H, app t, *J* 13.2 Hz, C*H*$_2$), 2.45 (3H, s, C*H*$_3$), 2.75 (2H, app t, *J* 12.2 Hz, C*H*$_2$), 3.71 (2H, d, *J* 11.3 Hz, C*H*$_2$), 7.29 (2H, d, *J* 8.31 Hz, C*H*$_{Ar}$), 7.34 (2H, d, *J* 8.31 Hz, C*H*$_{Ar}$), 7.46 (2H, d, *J* 8.3 Hz, C*H*$_{Ar}$), 7.66 (2H, d, *J* 8.3 Hz, C*H*$_{Ar}$); δ_C ($CDCl_3$, 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 $[C_{18}H_{20}NO_3SBr]^+$; theoretical m/z of $[M+Na]^+$ = 432.0245, measured m/z of $[M+Na]^+$ = 432.0256; ν_{max} (thin-film)/cm^{-1} 1153 (RSO_2R stretch), 1344 (RSO_2R stretch) and 3538 (O-H stretch).

***N,N*-Diethyl-4-methylbenzenesulfonamide[7] (4h)**



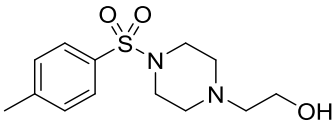
Following general procedure II: DBN salt **1a** (213 mg, 0.5 mmol) and diethylamine (55 µL, 0.53 mmol) in MeCN (7 mL) for 18 h gave the title compound as an off-white solid (54 mg, 48%); mp 55-57 °C [lit. mp 58-59 °C]; δ_H ($CDCl_3$, 500 MHz) 1.11 (6H, t, *J* 7.1 Hz, CH_2CH_3), 2.40 (3H, s, CH_3), 3.21 (4H, q, *J* 7.1 Hz, CH_2CH_3), 7.27 (2H, d, *J 8.3* Hz, CH_{Ar}) and 7.67 (2H, d, *J* 8.31 Hz, $-SO_2CCH_{Ar}$); δ_C ($CDCl_3$, 125 MHz) 14.1, 21.4, 42.0, 127.0, 129.6, 137.4 and 142.9; ESI-MS of $[C_{11}H_{17}NO_2S]^+$; theoretical m/z of $[M+Na]^+$ = 250.0878, measured m/z of $[M+H]^+$ = 250.0867; ν_{max} (thin-film)/cm^{-1} 1166 (RSO_2R stretch) and 1345 (RSO_2R stretch).

***N*-Benzyl-*N*,4-dimethylbenzenesulfonamide[8] (4i)**



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]; δ_H ($CDCl_3$, 500 MHz) 2.45 (3H, s, CH_3), 2.59 (3H, s, NCH_3), 4.14 (2H, s, CH_2), 7.29-7.35 (5H, m, Ph-*H*), 7.37 (2H d, *J* 8.3 Hz, CH_{Ar}) and 7.74 (2H, d, *J* 8.3 Hz, $-SO_2CCH_{Ar}$); δ_C ($CDCl_3$, 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 $[C_{15}H_{17}NO_2S]^+$; theoretical m/z of $[M+Na]^+$ = 298.0877, measured m/z of $[M+Na]^+$ = 298.0894; ν_{max} (thin-film)/cm^{-1} 1161 (RSO_2R stretch) and 1339 (RSO_2R stretch).

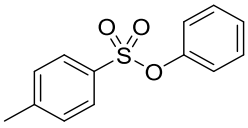
2-(4-Tosylpiperazin-1-yl)ethan-1-ol[9] (4j)



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); δ_H ($CDCl_3$, 250 MHz) 2.37 (3H, s, CH_3), 2.44-2.50 (2H, m, NCH_2CH_2OH), 2.50-2.56 (4H, 2, $-CH_2NCH_2-$), 2.92-3.00 (4H, m, $S-NCH_2$), 3.48-3.55 (2H,

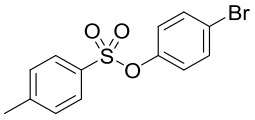
m, C*H*$_2$OH), 7.27 (2H d, *J* 8.1 Hz, C*H*$_{Ar}$) and 7.57 (2H, d, *J* 8.3 Hz, -SO$_2$CC*H*$_{Ar}$); δ_C ($CDCl_3$, 125 MHz) 21.5, 46.1, 52.0, 57.7, 58.9, 127.0, 127.8, 129.7 and 143.8; ESI-MS of $[C_{13}H_{20}N_2O_3S]^+$; theoretical m/z of $[M+Na]^+$ = 307.1092, measured m/z of $[M+Na]^+$ = 307.1112; ν_{max} (thin-film)/cm^{-1} 1174 (RSO$_2$R stretch), 1345 (RSO$_2$R stretch) 3369 (OH stretch).

Phenyl-4-methylbenzenesulfonate[10] (4k)



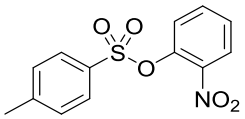
Following general procedure III; DBN salt **1a** (213 mg, 0.5 mmol), phenol (50 mg, 0.53 mmol) and DBN (12 µL, 0.1 mmol) in MeCN (7 mL) gave the title compound as a white crystalline solid (118 mg, 95%) after 4 h; mp 89-94 °C [lit. mp 89-90 °C]; δ_H ($CDCl_3$, 500 MHz) 2.44 (3H, s, C*H*$_3$), 6.98 (2H, d, *J* 8.3 Hz, C*H*$_{Ar}$), 7.22-7.32 (5H, m, C*H*$_{Ar}$) and 7.70 (2H, d, *J* 8.3 Hz, -SO$_2$CC*H*$_{Ar}$); δ_C ($CDCl_3$, 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 $[C_{13}H_{12}O_3S]^+$; theoretical m/z of $[M+Na]^+$ = 271.0405, measured m/z of $[M+Na]^+$ = 271.0373; ν_{max} (thin-film)/cm^{-1} 1152 (RSO$_2$R stretch) and 1345 (RSO$_2$R stretch).

4-Bromophenyl-4-methylbenzenesulfonate[11] (4l)



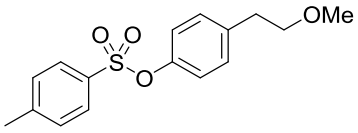
Following general procedure III: DBN salt **1a** (213 mg, 0.5 mmol), 4-bromophenol (92 mg, 0.53 mmol) and DBN (12 µL, 0.1 mmol) in MeCN (7 mL) for 4 h gave the title compound as a colourless crystalline solid (118 mg, 95%); mp 77-79 °C [lit. mp 69-71 °C]; δ_H ($CDCl_3$, 500 MHz) 2.45 (3H, s, C*H*$_3$), 6.87 (2H, d, *J* 9.0 Hz, -OCC*H*$_{Ar}$), 7.32 (2H, d, *J* 7.8 Hz, C*H*$_{Ar}$), 7.40 (2H, d, *J* 9.0 Hz, C*H*$_{Ar}$) and 7.68 (2H, d, *J* 8.3 Hz, -SO$_2$CC*H*$_{Ar}$); δ_C ($CDCl_3$, 125 MHz) 21.7 121.1, 124.1, 128.5, 129.9, 132.0, 132.7, 145.7 and 148.6; ESI-MS of $[C_{13}H_{11}O_3SBr]^+$; theoretical m/z of $[M+Na]^+$ = 348.9510, measured m/z of $[M+Na]^+$ = 348.9489; ν_{max} (thin-film)/cm^{-1} 1158 (RSO$_2$R stretch) and 1374 (RSO$_2$R stretch).

2-Nitrophenyl-4-methylbenzenesulfonate[12] (4m)



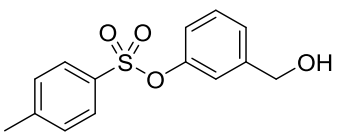
Following general procedure III: DBN salt **1a** (213 mg, 0.5 mmol), 2-nitrophenol (74 mg, 0.53 mmol) and DBN (12 µL, 0.1 mmol) in MeCN (7 mL) for 4 h gave the title compound as a colourless solid (131 mg, 89%); mp 79-82 °C [lit. mp 80-82 °C]; δ_H ($CDCl_3$, 500 MHz) 2.46 (3H, s, C*H*$_3$), 7.34 (2H, d, *J* 8.3 Hz, C*H*$_{Ar}$), 7.36-7.48 (2H, m, C*H*$_{Ar}$), 7.59-7.63 (1H, m, C*H*$_{Ar}$) 7.75 (2H, d, *J* 8.3 Hz, -SO_2CC*H*$_{Ar}$) and 7.89 (1H, dd, *J 1.7,* 8.4 Hz, C*H*$_{Ar}$); δ_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 $[C_{13}H_{11}NO_5S]^+$; theoretical m/z of $[M+Na]^+$ = 316.0256, measured m/z of $[M+Na]^+$ = 316.0240; ν_{max} (thin-film)/cm^{-1} 819, 1158 (RSO_2R 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; δ_H ($CDCl_3$, 500 MHz) 2.44 (3H, s, C*H*$_3$), 2.83 (2H, t, *J* 7.0 Hz, C*H*$_2$), 3.33 (3H, s, OC*H*$_3$), 3.56 (2H, t, *J* 7.0 Hz, C*H*$_2$), 6.89 (2H, d, *J* 8.9 Hz, C*H*$_{Ar}$), 7.13 (2H, d, *J* 8.9 Hz, C*H*$_{Ar}$), 7.30 (2H, d, *J* 8.3 Hz, C*H*$_{Ar}$) and 7.70 (2H, d, *J* 8.3 Hz, -SO_2CC*H*$_{Ar}$); δ_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 $[C_{16}H_{18}O_4S]^+$; theoretical m/z of $[M+Na]^+$ = 329.0823, measured m/z of $[M+Na]^+$ = 329.0839; ν_{max} (thin-film)/cm^{-1} 861, 1049, 1140 (RSO_2R stretch), 1375 (RSO_2R 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 ($CDCl_3$, 500 MHz) 2.43 (3H, s, C*H*$_3$), 4.60 (2H, s, C*H*$_2$), 6.83 (1H, dt, *J* 7.1, 2.3 Hz, C*H*$_{Ar}$), 7.03 (1H, s, C*H*$_{Ar}$), 7.20-7.26 (2H, m, C*H*$_{Ar}$), 7.30 (2H, d, *J* 8.5 Hz, C*H*$_{Ar}$) and 7.69 (2H, d, *J* 8.3 Hz, -SO_2CC*H*$_{Ar}$); δ_C ($CDCl_3$, 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 $[C_{14}H_{14}O_4S]^+$; theoretical m/z of $[M+Na]^+$ = 301.0510, measured m/z of $[M+Na]^+$ = 301.0525; ν_{max} (thin-film)/cm^{-1} 1175 (RSO_2R stretch), 1366 (RSO_2R 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 ^{1}H 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-hyrdoxybenzyl alcohol (rt 14.09 min).

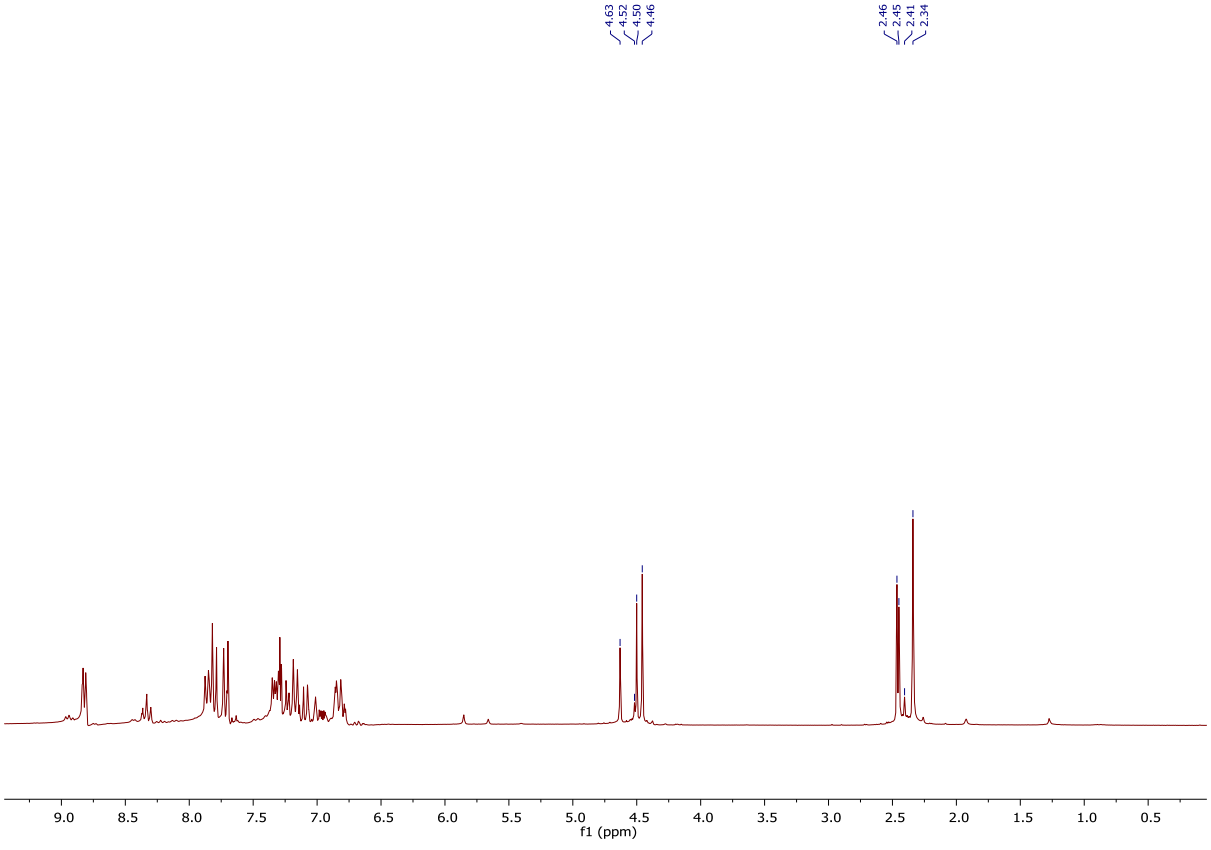
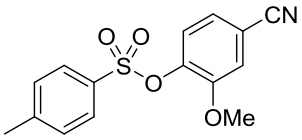


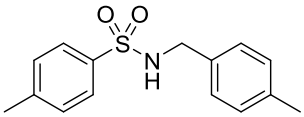
Figure 1. ^{1}H NMR spectrum of crude reaction mixture of tosyl chloride and 3-hydroxybenzyl alcohol

2-Cyano-2-methoxphenyl 4-methylbenzenesulfonate[14] (4p)



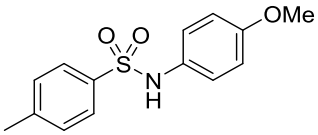
Following general procedure III; DBN salt **1a** (213 mg, 0.5 mmol), 4-hydroxy-3-methoxybenzonitrile (75 mg, 0.53 mmol) and DBN (12 µL, 0.1 mmol) in MeCN (7 mL) gave the title compound as a colourless solid (126 mg, 83%) after 4 h; mp 87-89 °C [lit. mp 91-92 °C]; δ_H ($CDCl_3$, 500 MHz) 2.44 (3H, s, C*H*$_3$), 3.60 (3H, s, OC*H*$_3$), 7.07 (1H, d, *J* 1.5 Hz, C*H*$_{Ar}$), 7.17-7.25 (2H, m, C*H*$_{Ar}$), 7.31 (2H, d, *J* 8.5 Hz, C*H*$_{Ar}$) and 7.72 (2H, d, *J* 8.3 Hz, -SO_2CC*H*$_{Ar}$); δ_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 $[C_{15}H_{13}NO_4S]^+$; theoretical m/z of $[M+Na]^+$ = 326.0463, measured m/z of $[M+Na]^+$ = 326.0444; ν_{max} (thin-film)/cm^{-1} 1173 (RSO_2R stretch), 1374 (RSO_2R 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]; δ_H ($CDCl_3$, 300 MHz) 2.20 (3H, s, C*H*$_3$), 2.33 (3H, s, C*H*$_3$), 3.95 (2H, d, *J* 6.0 Hz, C*H*$_2$), 4.96 (1H, t, *J* 6.0 Hz N*H*), 6.93-7.00 (4H, m, amine C*H*$_{Ar}$), 7.18 (2H, d, *J* 8.3 Hz, C*H*$_{Ar}$) and 7.64 (2H, d, *J* 8.3 Hz, -SO_2CC*H*$_{Ar}$); δ_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 $[C_{15}H_{17}NO_2S]^+$; theoretical m/z of $[M+Na]^+$ = 298.0878, measured m/z of $[M+Na]^+$ = 298.0866; ν_{max} (thin-film)/cm^{-1} 1152 (RSO_2R stretch), 1324 (RSO_2R stretch) and 3263 (N-H).

***N*-(4-Methoxyphenyl)-4-methylbenzenesulfonamide[16] (6b)**

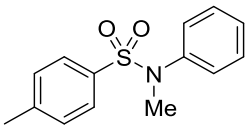


Following general procedure II: DBN salt **1a** (213 mg, 0.5 mmol) and *p*-anisidine (65 mg, 0.53 mmol) in MeCN (7 mL) was stirred at 80 °C for 18 h. Analysis of the crude ^{1}H NMR spectrum showed 0% conversion to the title compound based on the integrals of the methyl peak in starting DBN salt (δ_H 2.46 ppm) and literature product (δ_H 2.39 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]; δ_H ($CDCl_3$, 500 MHz) 2.39 (3H, s, C*H*$_3$), 3.79 (3H, s, OC*H*$_3$), 6.58 (1H, br. s, O*H*), 6.76 (2H, d, *J* 8.8 Hz, -OCC*H*$_{Ar}$), 6.98 (2H, d, *J* 8.8 Hz, -NCC*H*$_{Ar}$), 7.22 (2H, d, *J* 8.3 Hz, C*H*$_{Ar}$) and 7.60 (2H, d, *J* 8.3 Hz, -SO_2CC*H*$_{Ar}$); δ_C ($CDCl_3$, 125 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 $[C_{14}H_{15}NO_3S]^+$; theoretical m/z of $[M+Na]^+$ = 300.0670, measured m/z of $[M+Na]^+$ = 300.0655; ν_{max} (thin-film)/cm^{-1} 1156 (RSO_2R stretch), 1327 (RSO_2R stretch) and 3268 (N-H).

***N*,4-Dimethyl-*N*-phenylbenzenesulfonamide[17] (6c)**



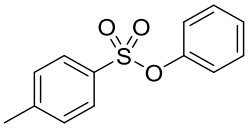
Following general procedure II: DBN salt **1a** (213 mg, 0.5 mmol) and *N*-methylaniline (57 µL, 0.53 mmol) in MeCN (7 mL) was stirred at 80 °C for 18 h. Analysis of the crude ^{1}H NMR spectrum showed 0% conversion to the title compound based on the integrals of the methyl peak in starting DBN salt (δ_H 2.46 ppm) and literature product (δ_H 2.43 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]; δ_H ($CDCl_3$, 500 MHz) 2.41 (3H, s, C*H*$_3$), 3.16 (3H, s, NC*H*$_3$), 2.93-2.99 (4H, m, C*H*$_2$), 7.07-7.11 (2H, m, Ph-*H*), 7.23 (2H, d, *J* 8.3 Hz, C*H*$_{Ar}$), 7.25-7.32 (3H, m, Ph-*H*) and 7.42 (2H, d, *J* 8.3 Hz, -SO_2CC*H*$_{Ar}$); δ_C ($CDCl_3$, 125 MHz) 21.5, 38.06, 126.6, 127.2, 127.9, 128.8, 129.3, 133.5, 141.6 and 143.5; ESI-MS of $[C_{14}H_{15}NO_2S]^+$; theoretical m/z of $[M+Na]^+$ = 284.0721,

measured m/z of $[M+Na]^+$ = 284.0721; ν_{max} (thin-film)/cm^{-1} 1150 (RSO_2R stretch) and 1342 (RSO_2R stretch).

Phenyl-4-methylbenzenesulfonate[17] (4k)

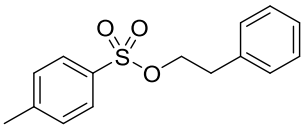


Following general procedure II: DBN salt **1a** (213 mg, 0.5 mmol), phenol (50 mg, 0.53 mmol) and DBN (12 µL, 0.1 mmol) in MeCN (7 mL) for 4 h gave the title compound as a colourless crystalline solid (118 mg, 95%).

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 ($CDCl_3$, 500 MHz) 2.44 (3H, s, C*H*$_3$), 6.98 (2H, d, *J* 8.3 Hz, C*H*$_{Ar}$), 7.22-7.32 (5H, m, C*H*$_{Ar}$) and 7.70 (2H, d, *J* 8.3 Hz, -SO_2CC*H*$_{Ar}$); δ_C ($CDCl_3$, 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 $[C_{13}H_{12}O_3S]^+$; theoretical m/z of $[M+Na]^+$ = 271.0405, measured m/z of $[M+Na]^+$ = 271.0373; ν_{max} (thin-film)/cm^{-1} 1152 (RSO_2R stretch) and 1345 (RSO_2R stretch).

Phenethyl-4-methylbenzenesulfonate[18] (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 ^{1}H NMR spectrum showed 0% conversion to the title compound by the absence of peaks at 3.87 ($CDCl_3$, t, *J* 6.6 Hz, CH_2) and 2.88 ($CDCl_3$, t, *J* 6.6 Hz, CH_2) ppm.[18]

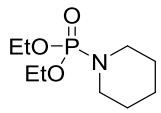
Following general procedure IV: DABCO salt **5a** (248 mg, 0.6 mmol) and 2-phenylethanol (72 µL, 0.5 mmol) in MeCN (7 mL) for 4 h gave the title compound as a colourless solid (113 mg, 82%).

Characterisation: mp 35-37 °C [lit. mp 36.5-37°C][19]; δ_H (MeCN-*d3*, 500 MHz) 2.42 (3H, s, C*H*$_3$), 2.90 (2H, t, *J* 6.4 Hz, C*H*$_2$), 4.22 (2H, t, *J* 6.4 Hz, C*H*$_2$), 7.10-7.15 (2H, m, Ph), 7.20-7.30 (3H, m, Ph), 7.36 (2H, d, *J*

8.8 Hz, CH_{Ar}), 7.66 (2H, d, *J* 8.80 Hz, -SO_2CCH_{Ar}); δ_C (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 $[C_{15}H_{16}O_3S]^+$; theoretical m/z of $[M+Na]^+$ = 299.0718, measured m/z of $[M+Na]^+$ = 299.0781; ν_{max} (thin-film)/cm^{-1} 1171 (RSO_2R stretch) and 1343 (RSO_2R stretch).

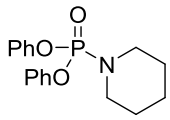
Characterisation of Phosphoramidates and Phosphonates

Diethyl piperidin-1-ylphoshonate[20] (7a)



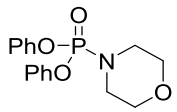
Following general procedure V: DBN salt **2a** (264 mg, 0.65 mmol) and piperidine (50 µL, 0.5 mmol) in MeCN (7 mL) for 2 h gave the title compound as a yellow oil (95 mg, 86%) after purification by silica column chromatography (5% MeOH/EtOAc); δ_H ($CDCl_3$, 500 MHz) 1.63 (6H, dt, *J* 1.0, 7.0 Hz, CH_2CH_3), 1.42-1.59 (6H, m, CH_2), 2.98-3.15 (4H, m, $-NCH_2$) and 3.90-4.11 (4H, m, $-OCH_2CH_3$); 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 $[C_9H_{20}NO_3P]^+$; 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-*d6*, 500 MHz) 1.34-1.42 (4H, m, CH_2), 1.46-1.53 (2H, m, CH_2), 3.17-3.25 (4H, m, $-NCH_2$), 7.17-7.22 (2H, m, CH_{Ar}) and 7.26-7.44 (8H, m, CH_{Ar}); δ_C (Acetone-*d6*, 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-*d6*, 121 MHz) -1.03; ESI-MS of $[C_{17}H_{20}NO_3P]^+$; 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.

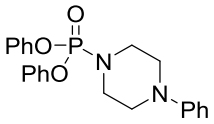
Diphenyl morpholinophosphonate (7c)



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

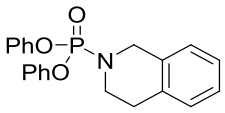
purification by silica plug (50% EtOAc/petroleum ether); mp 67-69 °C [lit. mp 71-72 °C][21]; δ_H (Acetone-*d6*, 500 MHz) 3.15-3.32 (4H, m, CH_2), 3.38-3.56 (4H, m, CH_2) and 7.16-7.52 (10H, m, CH_{Ar}); δ_C (Acetone-*d6*, 125 MHz) 44.7, 66.3 (d, $J_{P\text{-}C}$ 4.8 Hz), 120.2 (d, $J_{P\text{-}C}$ 2.9 Hz), 120.2 (d, $J_{P\text{-}C}$ 4.8 Hz), 125.0, 129.8 and 151.0 (d, $J_{P\text{-}C}$ 6.7 Hz); δ_P (Acetone-*d6*, 121 MHz) -1.95; ESI-MS of $[C_{16}H_{18}NO_4P]^+$; theoretical m/z of $[M+Na]^+$ = 342.0871, measured m/z of $[M+Na]^+$ = 342.0855; ν_{max} (thin-film)/cm^{-1} 781, 924, 1189, 1486 and 2858.

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



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; δ_H (Acetone-*d6*, 500 MHz) 3.01-3.06 (4H, m, CH_2), 3.39-3.45 (4H, m, CH_2), 6.84 (1H, tt, *J* 1.0, 7.3 Hz, CH_{Ar}), 6.89-6.93 (2H, m, CH_{Ar}), 7.18-7.26 (4H, m, CH_{Ar}) and 7.35-7.44 (8H, m, CH_{Ar}); δ_C (Acetone-*d6*, 125 MHz) 44.7, 49.3 (d, $J_{P\text{-}C}$ 5.7 Hz), 116.4, 119.9, 120.3 (d, $J_{P\text{-}C}$ 4.8 Hz), 125.0, 129.0, 130.0, 151.1 (d, $J_{P\text{-}C}$ 5.7 Hz) and 151.6; δ_P (Acetone-*d6*, 121 MHz) -1.46; ESI-MS of $[C_{22}H_{23}N_2O_3P]^+$; theoretical m/z of $[M+H]^+$ = 395.1524, measured m/z of $[M+H]^+$ = 395.1503; ν_{max} (thin-film)/cm^{-1} 656, 749, 929, 1143, 1484 and 2853.

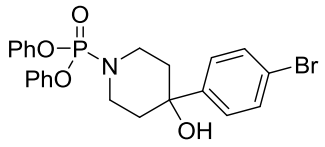
Diphenyl (1,2,3,4-tetrahydroisoquinoline-2-yl)phosphonate (7e)



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); δ_H (Acetone-*d6*, 500 MHz) 2.68 (2H, t, *J* 5.9 Hz, CH_2), 3.53 (2H, dt, *J* 5.9, 9.8 Hz, CH_2), 4.48 (2H, d, *J* 6.9 Hz, -NCH_2), 7.02-7.07 (1H, m, CH_{Ar}), 7.09-7.20 (5H, m, CH_{Ar}) and 7.27-7.37 (8H, m, CH_{Ar}); δ_C (Acetone-*d6*, 125 MHz) 28.4 (d, $J_{P\text{-}C}$ 2.9 Hz), 42.3 (d, $J_{P\text{-}C}$ 2.9 Hz), 46.1 (d, $J_{P\text{-}C}$ 3.8 Hz), 120.2 (d, $J_{P\text{-}C}$ 4.8 Hz), 124.9, 126.0, 126.1, 126.4, 129.2, 129.7, 133.1 (d, $J_{P\text{-}C}$ 5.7 Hz), 134.0 and 151.1 (d, $J_{P\text{-}C}$ 5.7 Hz); δ_P (Acetone-*d6*, 121 MHz) -0.92; ESI-MS of $[C_{21}H_{20}NO_3P]^+$;

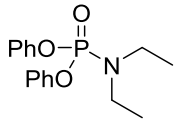
theoretical m/z of $[M+Na]^+$ = 388.1079, measured m/z of $[M+H]^+$ = 388.1058; ν_{max} (thin-film)/cm^{-1} 686, 748, 928, 1143, 1485 and 2831.

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



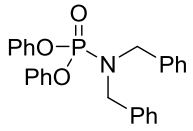
Following general procedure V: DBN salt **2b** (326 mg, 0.65 mmol) and 4-(4-bromophenyl)-4-piperidinol (128 mg, 0.5 mmol) in MeCN (7 mL) for 2 h gave the title compound as a pale yellow solid (213 mg, 87%) after purification by silica plug (50% EtOAc/petroleum ether); mp 141-144 °C; δ_H ($CDCl_3$, 500 MHz) 1.54-1.61 (2H, m, C*H*$_2$), 1.71 (2H, dt, *J* 4.4, 13.4, C*H*$_2$), 2.50 (1H, br. s, O*H*), 3.19-3.32 (2H, m, C*H*$_2$), 3.56-3.65 (2H, m, C*H*$_2$), 7.11 (2H, d, *J* 8.6 Hz, C*H*$_{Ar}$), 7.18 (2H, t, *J* 7.4 Hz, C*H*$_{Ar}$), 7.22-7.29 (4H, m, C*H*$_{Ar}$), 7.34 (4H, t, *J* 7.9 Hz, C*H*$_{Ar}$) and 7.40 (2H, d, *J* 8.6 Hz, BrCC*H*$_{Ar}$); δ_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} 2.9 Hz) and 150.9 (d, J_{P-C} 6.7 Hz); δ_P ($CDCl_3$, 121 MHz) -1.40; ESI-MS of $[C_{23}H_{23}NO_4PBr]^+$; theoretical m/z of $[M+Na]^+$ = 510.0446, measured m/z of $[M+Na]^+$ = 510.0439; ν_{max} (thin-film)/cm^{-1} 784, 928, 1191, 1485, 2925 and 3382.

Diphenyl diethylphosphoramidate (7g)



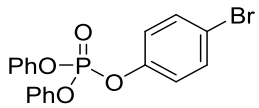
Following general procedure V: DBN salt **2b** (326 mg, 0.65 mmol) and diethylamine (52 µL, 0.5 mmol) in MeCN (7 mL) for 24 h gave the title compound as a pale yellow oil (117 mg, 77%) after purification by silica column chromatography (10-20% EtOAc/petroleum ether); mp 51-52 °C [lit. mp 61-62 °C][21]; δ_H (Acetone-*d6*, 500 MHz) 1.03 (6H, t, *J* 7.1 Hz, C*H*$_3$), 3.24 (4H, dq, *J* 7.1, 12.1 Hz, C*H*$_2$), 7.17-7.22 (2H, m, C*H*$_{Ar}$), 7.29-7.35 (4H, m, C*H*$_{Ar}$) and 7.36-7.42 (4H, m, C*H*$_{Ar}$); δ_C (Acetone-*d6*, 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); δ_P (Acetone-*d6*, 121 MHz) -0.76; ESI-MS of $[C_{16}H_{20}NO_3P]^+$; theoretical m/z of $[M+Na]^+$ = 328.1079, measured m/z of $[M+Na]^+$ = 328.1069; ν_{max} (thin-film)/cm^{-1} 755, 916, 1190, 1487, 1590 and 2976.

Diphenyl dibenzylphosphoramidate (7h)



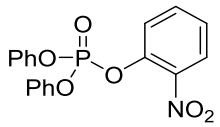
Following general procedure V; DBN salt **2b** (326 mg, 0.65 mmol) and dibenzylamine (96 µL, 0.5 mmol) in MeCN (5 mL) for 24 h gave the title compound as a pale yellow solid (52 mg, 25%) after purification by silica column chromatography (10% EtOAc/petroleum ether); mp 78-79 °C; δ_H (Acetone-*d6*, 500 MHz) 4.28 (4H, d, *J* 10.8 Hz, C*H*$_2$), 7.15-7.20 (4H, m, C*H*$_{Ar}$), 7.22-7.29 (8H, m, C*H*$_{Ar}$), 7.32-7.36 (4H, m, C*H*$_{Ar}$) and 7.38-7.42 (4H, m, C*H*$_{Ar}$); 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 $[C_{26}H_{24}NO_3P]^+$; 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 diphenylphosphate[22] (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, C*H*$_{Ar}$), 7.32-7.37 (4H, m, C*H*$_{Ar}$), 7.40-7.46 (4H, m, C*H*$_{Ar}$) and 7.59 (4H, d, *J* 8.4 Hz, BrCC*H*$_{Ar}$); 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 $[C_{18}H_{14}NO_4PBr]^+$; 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.

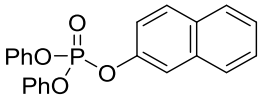
2-Nitrophenyl diphenylphosphate (7j)



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

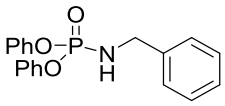
(184 mg, 99%) after purification by silica plug (50% EtOAc/petroleum ether); δ_H (Acetone-*d6*, 500 MHz) 7.26-7.31 (2H, m, CH_{Ar}), 7.33-7.36 (4H, m, CH_{Ar}), 7.41-7.51 (6H, m, CH_{Ar}), 7.66 (1H, dt, *J* 1.3, 8.4 Hz, CH_{Ar}) and 7.74 (1H, ddd, *J* 1.7, 7.5, 8.4 Hz, CH_{Ar}); δ_C (Acetone-*d6*, 125 MHz) 120.1 (d, $J_{P\text{-}C}$ 4.9 Hz), 122.7 (d, $J_{P\text{-}C}$ 2.9 Hz), 125.9, 126.1 (d, $J_{P\text{-}C}$ 1.3 Hz), 126.5 (d, $J_{P\text{-}C}$ 1.2 Hz), 130.1, 134.8 (d, $J_{P\text{-}C}$ 1.3 Hz), 141.7 (d, $J_{P\text{-}C}$ 0.5 Hz), 142.6 (d, $J_{P\text{-}C}$ 6.3 Hz) and 150.3 (d, $J_{P\text{-}C}$ 7.5 Hz); δ_P (Acetone-*d6*, 121 MHz) -18.11; ESI-MS of $[C_{18}H_{14}NO_6P]^+$; theoretical m/z of $[M+Na]^+$ = 394.0456, measured m/z of $[M+Na]^+$ = 394.0465; ν_{max} (thin-film)/cm^{-1} 744, 946, 1181, 1483, 1530 and 2923.

Naphthalen-2-yl diphenylphosphate[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_H (Acetone-*d6*, 500 MHz) 7.22-7.30 (2H, m, CH_{Ar}), 7.38-7.55 (11H, m, CH_{Ar}), 7.87-7.94 (3H, m, CH_{Ar}) and 7.97 (1H, d, *J* 8.9 Hz, CH_{Ar}); δ_C (Acetone-*d6*, 125 MHz) 116.8 (d, $J_{P\text{-}C}$ 5.1 Hz), 119.9 (d, $J_{P\text{-}C}$ 5.1 Hz), 120.2 (d, $J_{P\text{-}C}$ 5.0 Hz), 125.8 (d, $J_{P\text{-}C}$ 1.1 Hz), 126.0, 127.1, 127.6, 127.9, 130.1, 130.8, 131.3, 134.0, 148.3 (d, $J_{P\text{-}C}$ 7.6 Hz) and 150.7 (d, $J_{P\text{-}C}$ 7.3 Hz); δ_P (Acetone-*d6*, 121 MHz) -17.27; ESI-MS of $[C_{22}H_{17}O_6P]^+$; theoretical m/z of $[M+Na]^+$ = 399.0762, measured m/z of $[M+Na]^+$ = 399.0757; ν_{max} (thin-film)/cm^{-1} 749, 946, 1152, 1296, 1487, 1589 and 3061.

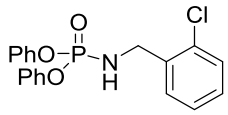
Diphenyl benzylphosphoramidate[23] (8a)



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_H (Acetone-*d6*, 500 MHz) 4.28 (2H, dd, *J* 7.1, 11.8, -NCH_2Ph), 5.31 (1H, dt, *J* 6.9, 13.3 Hz, N*H*), 7.16-7.31 (11H, m, CH_{Ar}) and 7.33-7.40 (4H, m, CH_{Ar}); δ_C (Acetone-*d6*, 125 MHz) 45.2, 120.3 (d, $J_{P\text{-}C}$ 4.9 Hz), 124.7, 127.0, 127.7, 128.2, 129.6, 139.9 (d, $J_{P\text{-}C}$ 5.3 Hz) and 151.2 (d, $J_{P\text{-}C}$ 6.7 Hz); δ_P (Acetone-*d6*,

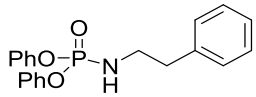
121 MHz) -0.21; ESI-MS of $[C_{19}H_{18}NO_3P]^+$; theoretical m/z of $[M+H]^+$ = 340.1103, measured m/z of $[M+H]^+$ = 340.1076; ν_{max} (thin-film)/cm^{-1} 751, 839, 1188, 1487 and 3394.

Diphenyl (2-chlorobenzyl)phosphoramidate (8b)



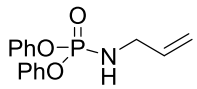
Following general procedure VI: DBN salt **2b** (452 mg, 0.9 mmol) and 2-chlorobenzylamine (61 µL, 0.5 mmol) in MeCN (15 mL) for 4 h gave the title compound as a colourless solid (146 mg, 78%) after purification by silica column chromatography (5-20% EtOAc/petroleum ether); mp 90-91 °C; δ_H (Acetone-*d6*, 500 MHz) 4.40 (2H, dd, *J* 7.2, 12.5, -NC*H*$_2$Ph), 5.42-5.63 (1H, m, N*H*), 7.14-7.31 (8H, m, C*H*$_{Ar}$), 7.32-7.38 (5H, m, C*H*$_{Ar}$) and 7.47 (1H, dd, *J* 1.6, 7.5 Hz, C*H*$_{Ar}$); δ_C (Acetone-*d6*, 125 MHz) 42.8, 120.3 (d, J_{P-C} 4.9 Hz), 124.8, 127.0, 128.6, 129.1, 129.2, 129.6, 132.5, 137.1 (d, J_{P-C} 5.1 Hz) and 151.2 (d, J_{P-C} 6.6 Hz); δ_P (Acetone-*d6*, 121 MHz) -0.19; ESI-MS of $[C_{19}H_{17}NO_3PCl]^+$; theoretical m/z of $[M+H]^+$ = 340.1103, measured m/z of $[M+H]^+$ = 340.1076; ν_{max} (thin-film)/cm^{-1} 743, 930, 1191, 1488, 1589 and 3250.

Diphenyl phenethylphosphoramidate[24] (8c)



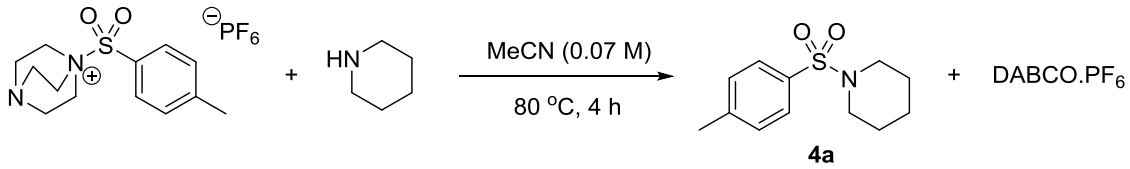
Following general procedure VI: DBN salt **2b** (452 mg, 0.9 mmol) and 2-phenethylamine (63 µL, 0.5 mmol) in MeCN (15 mL) for 4 h gave the title compound as a colourless solid (117 mg, 66%) after purification by silica column chromatography (5-30% EtOAc/petroleum ether); mp 73-74 °C [lit. mp 77.5-78 °C]; δ_H (Acetone-*d6*, 250 MHz) 2.69 (2H, m, C*H*$_2$), 3.22-3.44 (2H, m, C*H*$_2$), 4.80-5.22 (2H, m, -N*H*) and 7.13-7.47 (15H, m, C*H*$_{Ar}$); δ_C (Acetone-*d6*, 125 MHz) 37.8 (d, J_{P-C} 5.8 Hz), 43.3, 120.3 (d, J_{P-C} 4.8 Hz), 124.7, 126.2, 128.4, 128.8, 129.6, 139.1 and 151.3 (d, J_{P-C} 6.4 Hz); δ_P (Acetone-*d6*, 121 MHz) -0.11; ESI-MS of $[C_{20}H_{20}NO_3P]^+$; theoretical m/z of $[M+Na]^+$ = 376.1079, measured m/z of $[M+Na]^+$ = 376.1053; ν_{max} (thin-film)/cm^{-1} 748, 924, 1195, 1488, 1589 and 3243.

Diphenyl allylphosphoramidate[25] (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_H (Acetone-*d6*, 300 MHz) 3.61-3.76 (2H, m, -NHC*H*$_2$), 5.01 (1H, dd, *J* 1.1, 10.4 Hz, -CHC*H*H), 5.05-5.24 (2H, m, -CHCH*H* and N*H*), 5.82 (1H, ddt, *J* 5.4, 10.6, 15.8 Hz, -CH$_2$C*H*CH$_2$), 7.20 (2H, t, *J* 7.1 Hz, C*H*$_{Ar}$) and 7.28-7.42 (8H, m, C*H*$_{Ar}$); δ_C (Acetone-*d6*, 125 MHz) 43.9, 114.8, 120.4 (d, $J_{P\text{-}C}$ 4.8 Hz), 124.7, 129.6, 136.2 (d, $J_{P\text{-}C}$ 5.7 Hz) and 151.3 (d, $J_{P\text{-}C}$ 6.5 Hz); δ_P (Acetone-*d6*, 121 MHz) -0.12; ESI-MS of $[C_{15}H_{16}NO_3P]^+$; theoretical m/z of $[M+Na]^+$ = 312.0765, measured m/z of $[M+Na]^+$ = 312.0654; ν_{max} (thin-film)/cm^{-1} 754, 921, 1184, 1487, 1590 and 3251.

Stability of *N*-Tosyl DABCO•PF_6 Salts

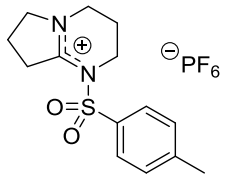


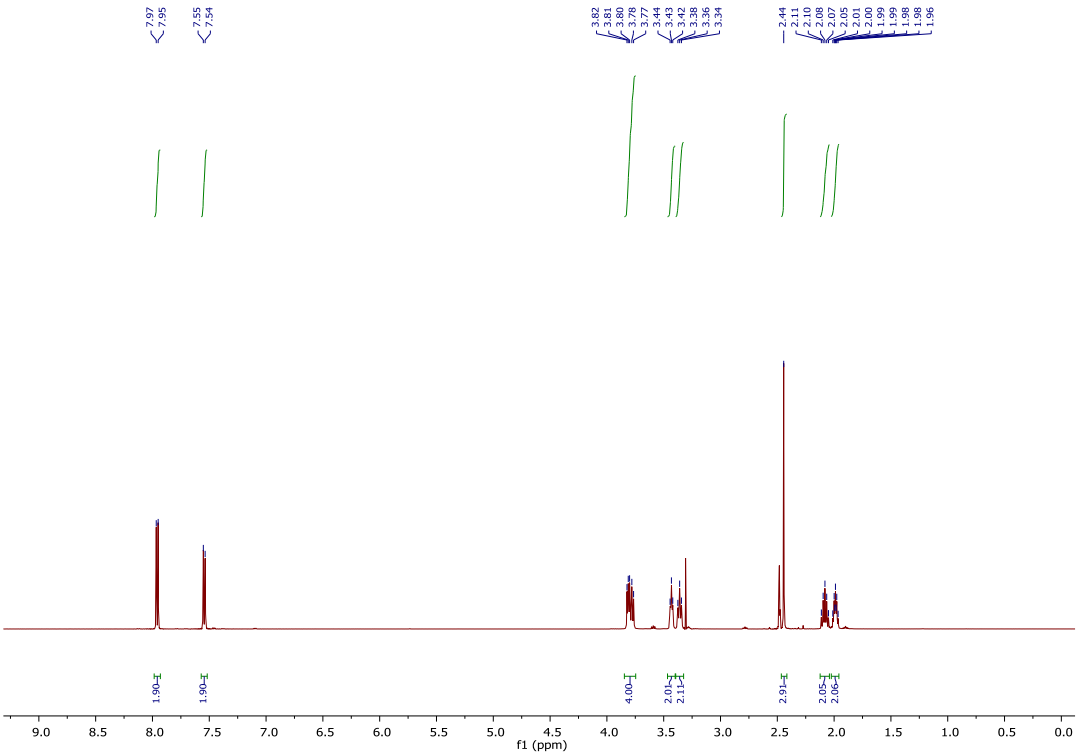
DABCO salt **5a** (207 mg, 0.5 mmol) and piperidine (49 µL, 0.5 mmol) were added to MeCN (7 mL) and heated at 80 °C for 4 h. After this time the reaction mixture was concentrated under reduced pressure and an ^{1}H NMR taken of the crude mixture. Conversion to product **4a** was determined by relative 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 N_2 at rt during this test, results are given below.

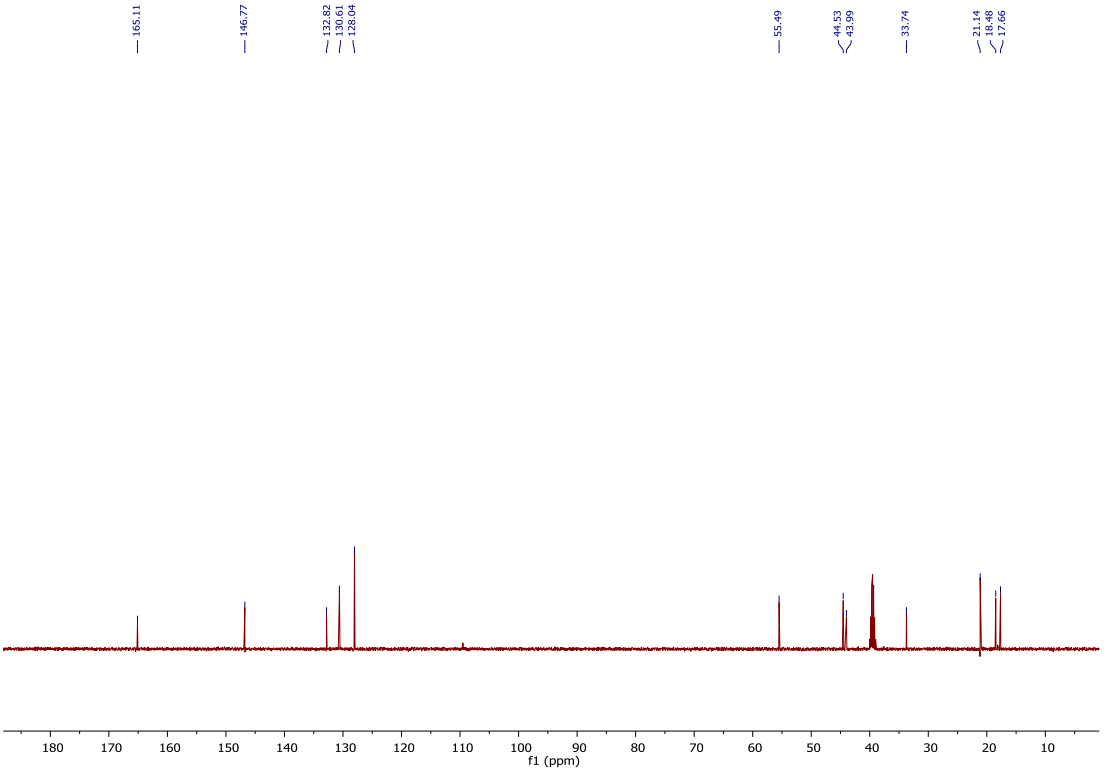
Age of Salt (d)	Conversion to 4a (%)
0	76
2	66
4	55
6	26

^{1}H and ^{13}C NMR Spectra

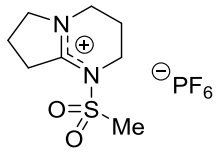
N-Tosyl DBN•PF_6 (1a)

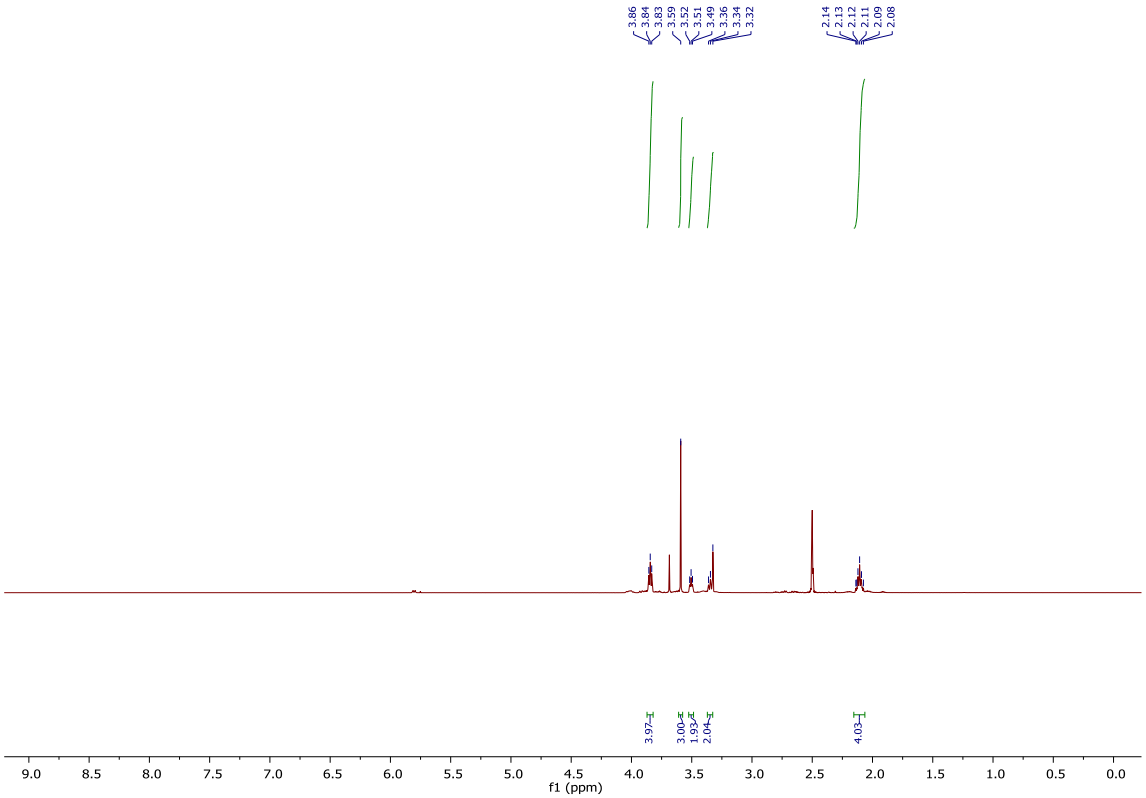


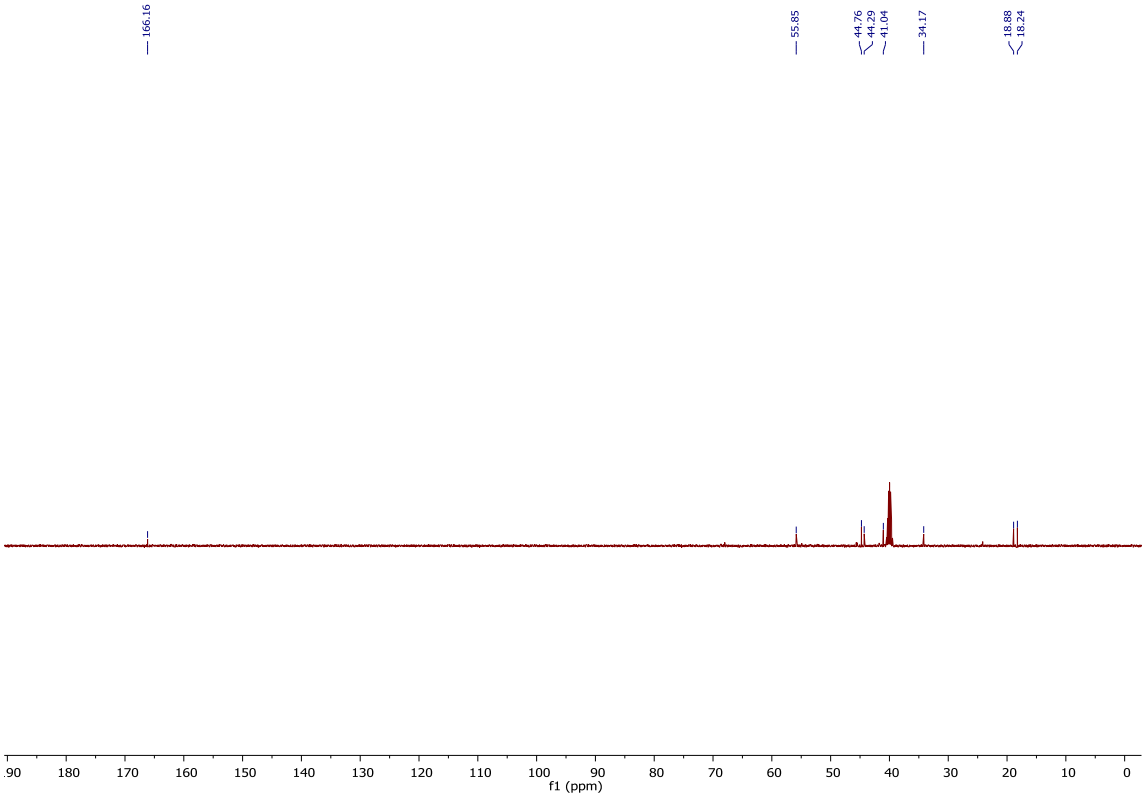




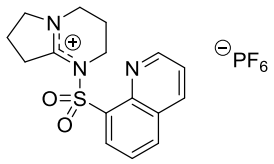
_N_-Mesyl DBN•PF_6 (1b)

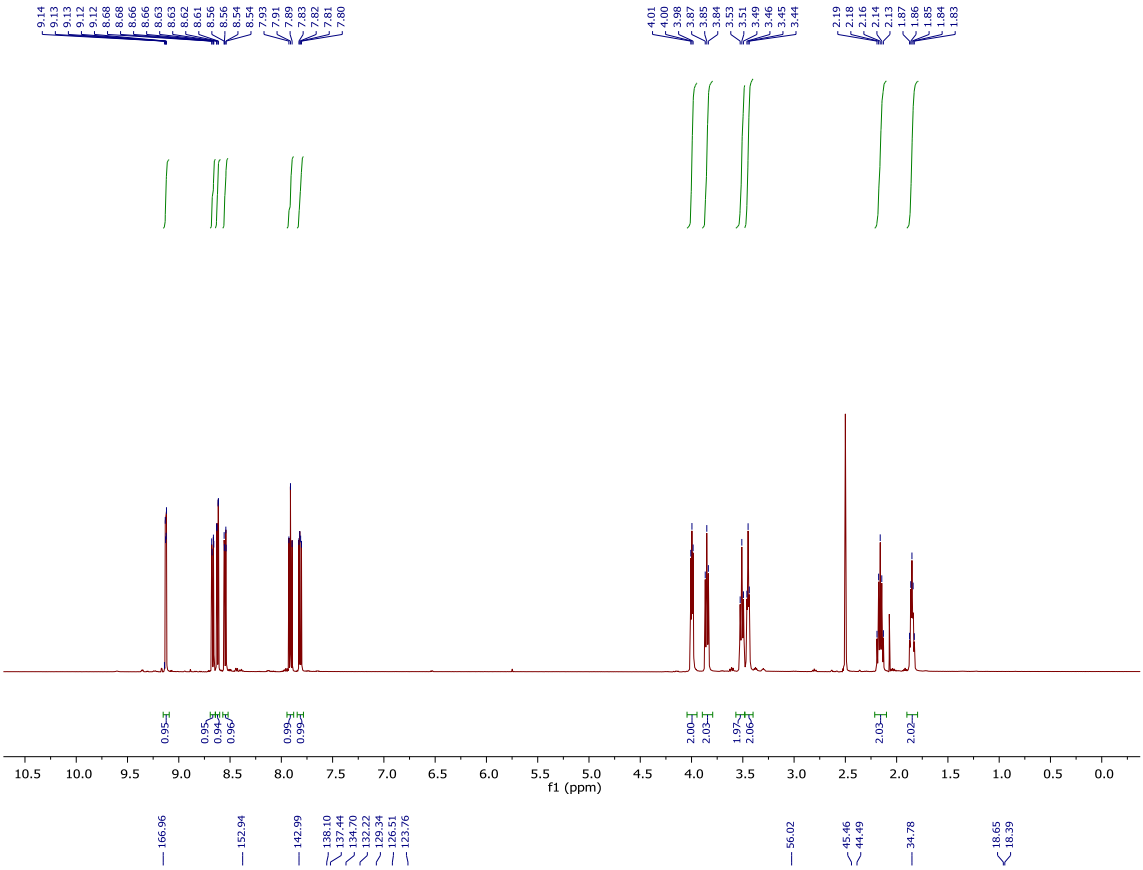


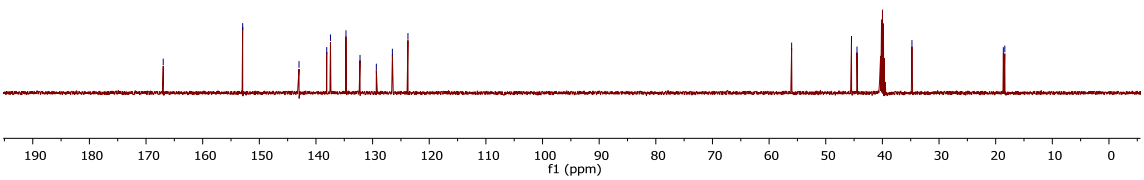




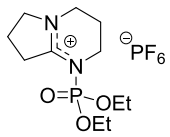
N-8-Quinolinesulfonyl DBN•PF_6 (1c)

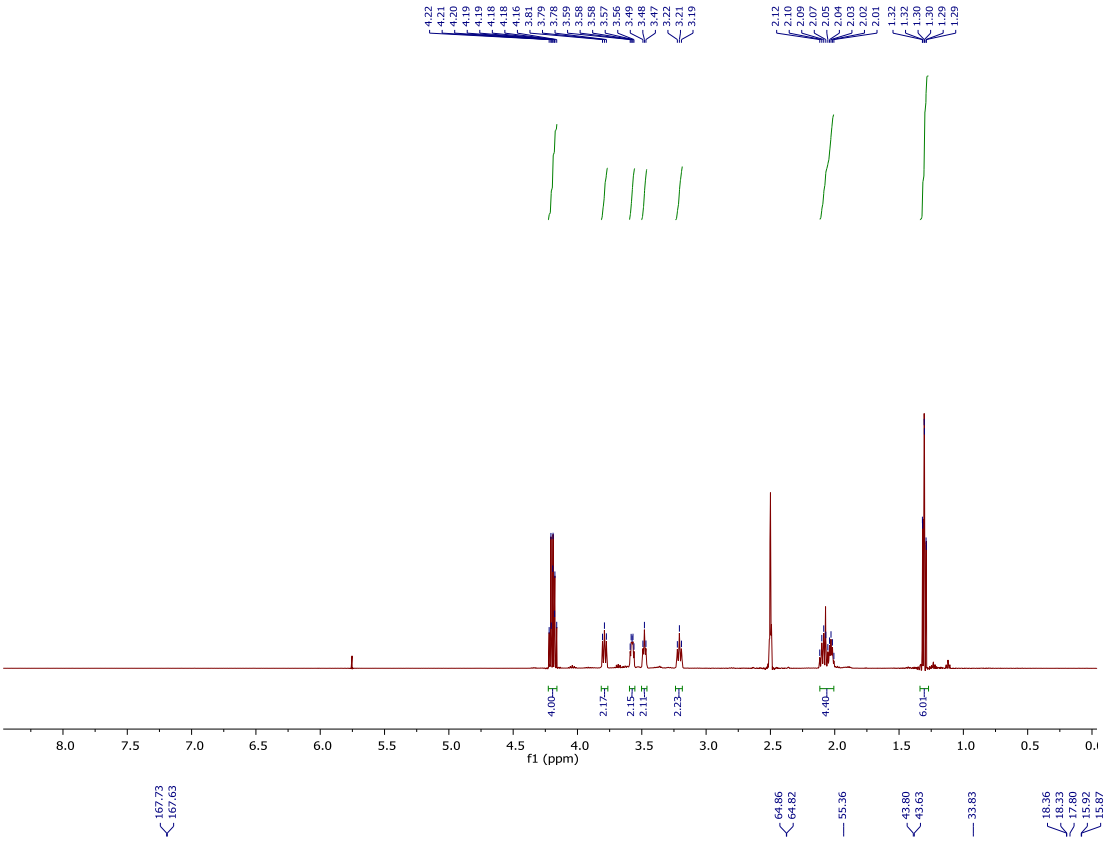


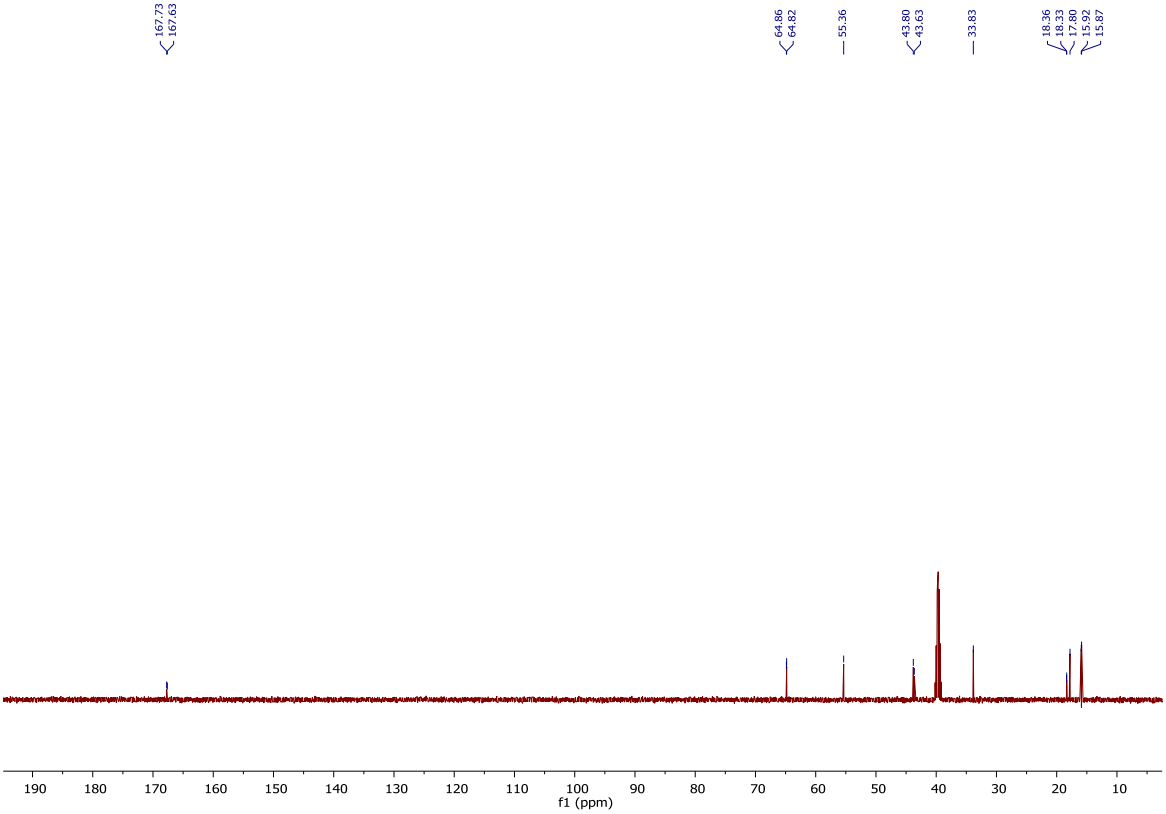




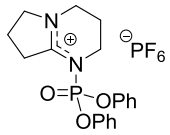
N-Diethoxyphoshoryl DBN•PF_6 (2a)

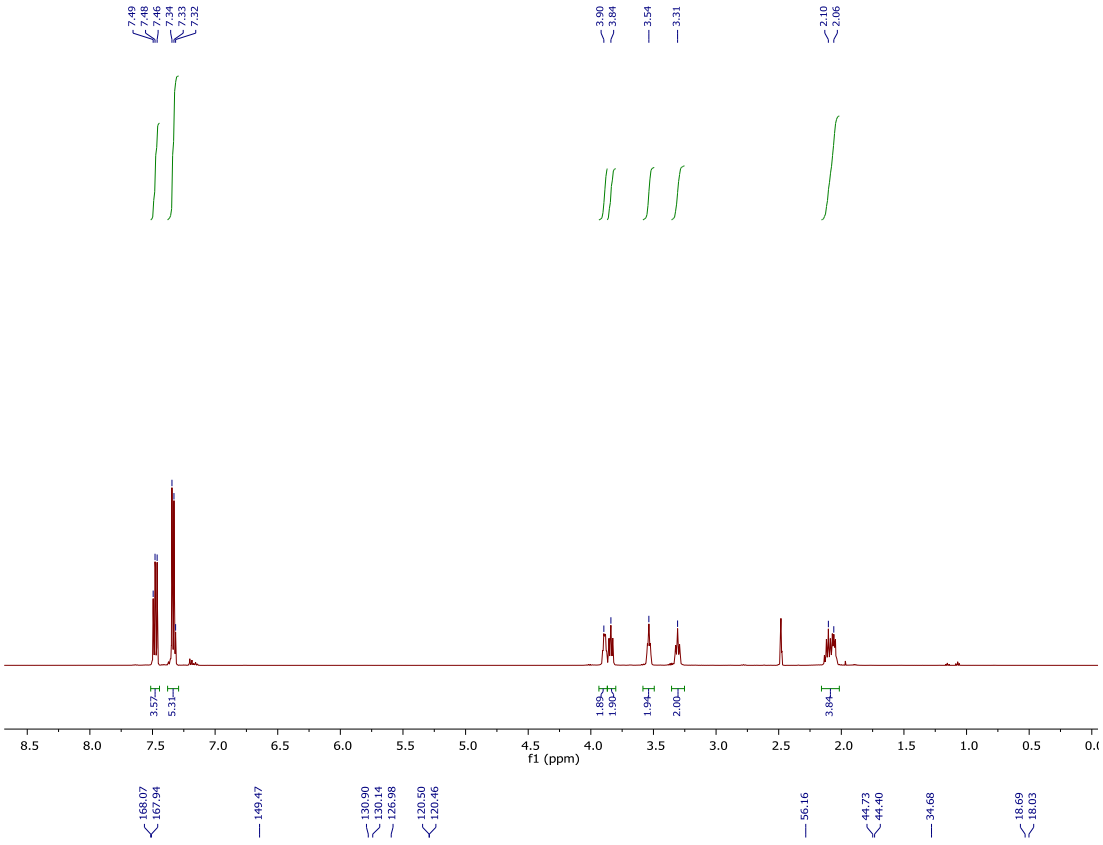




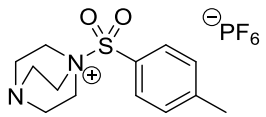


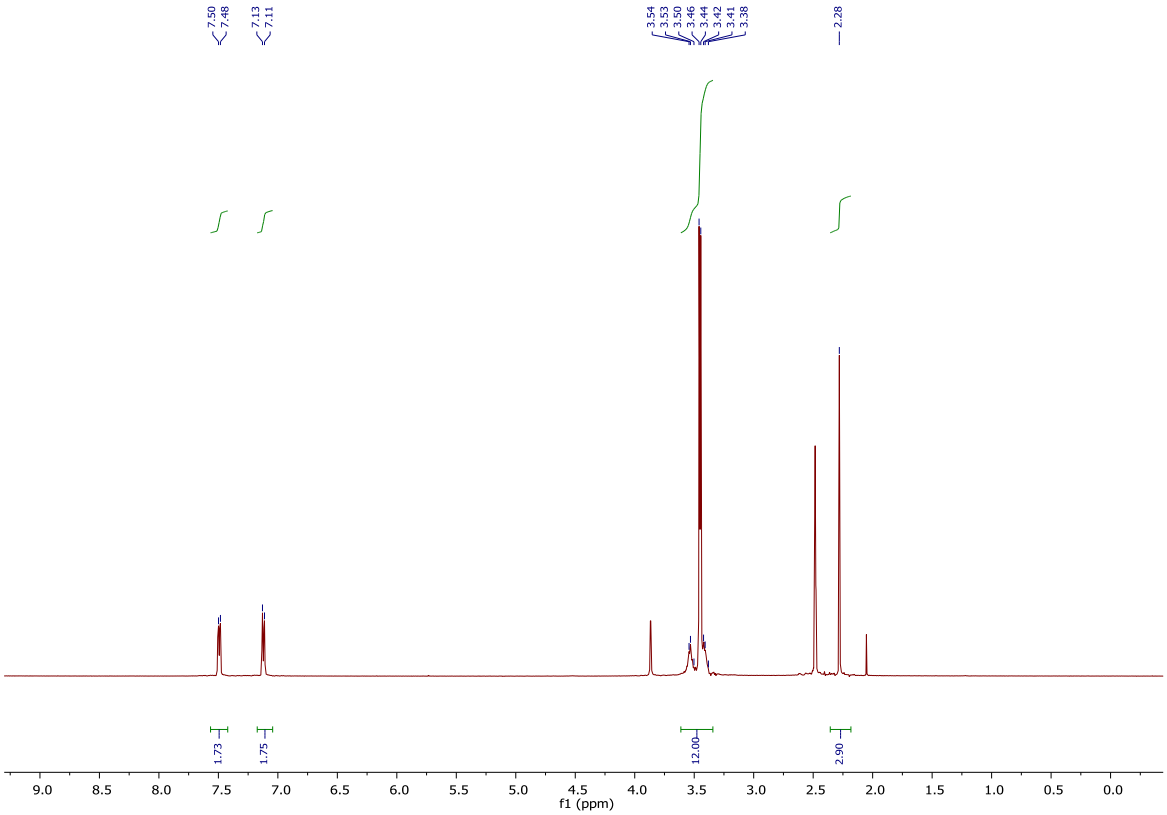
N-Diphenoxyphoshoryl DBN•PF_6 (2b)

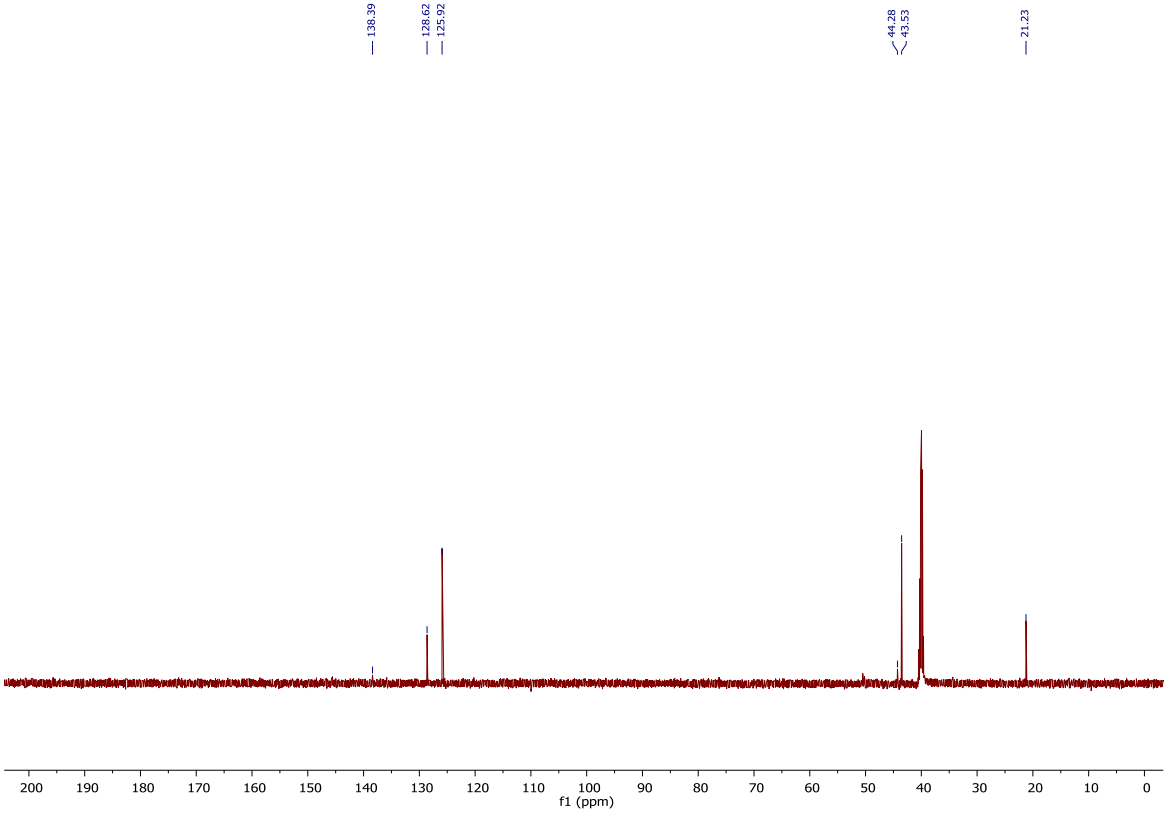




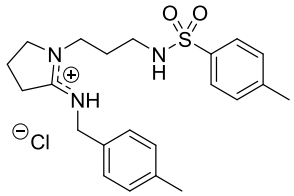
_N_-Tosyl DABCO•PF_6 (5a)

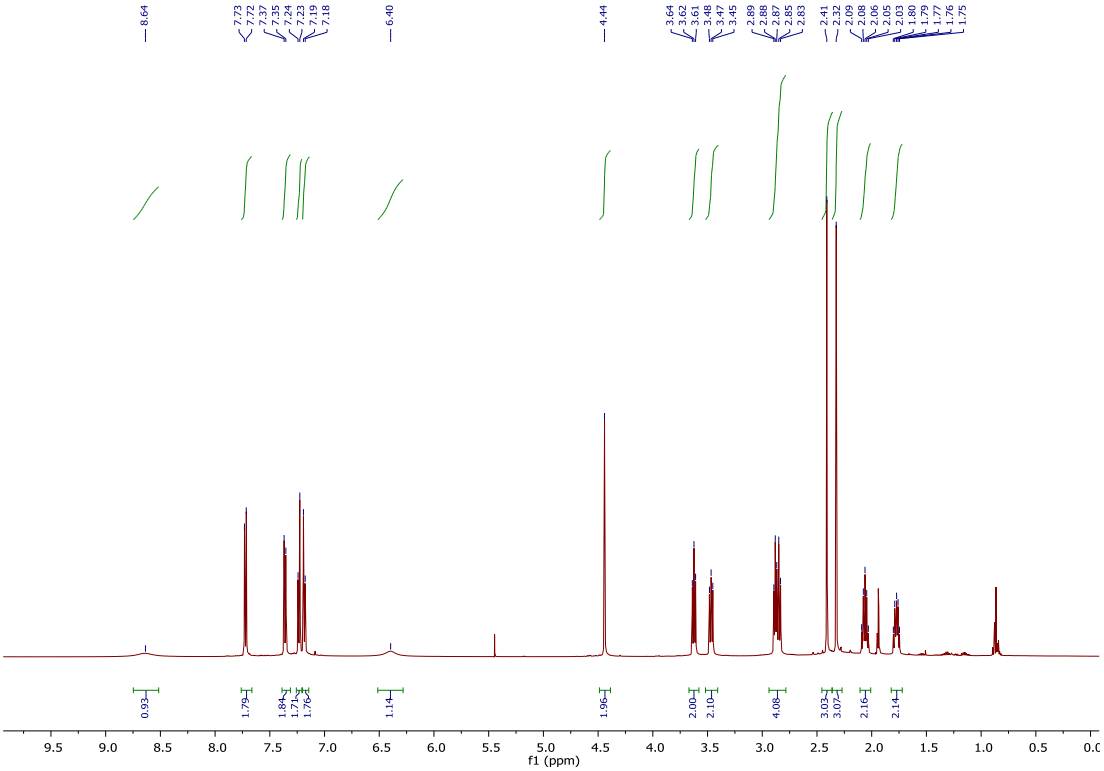


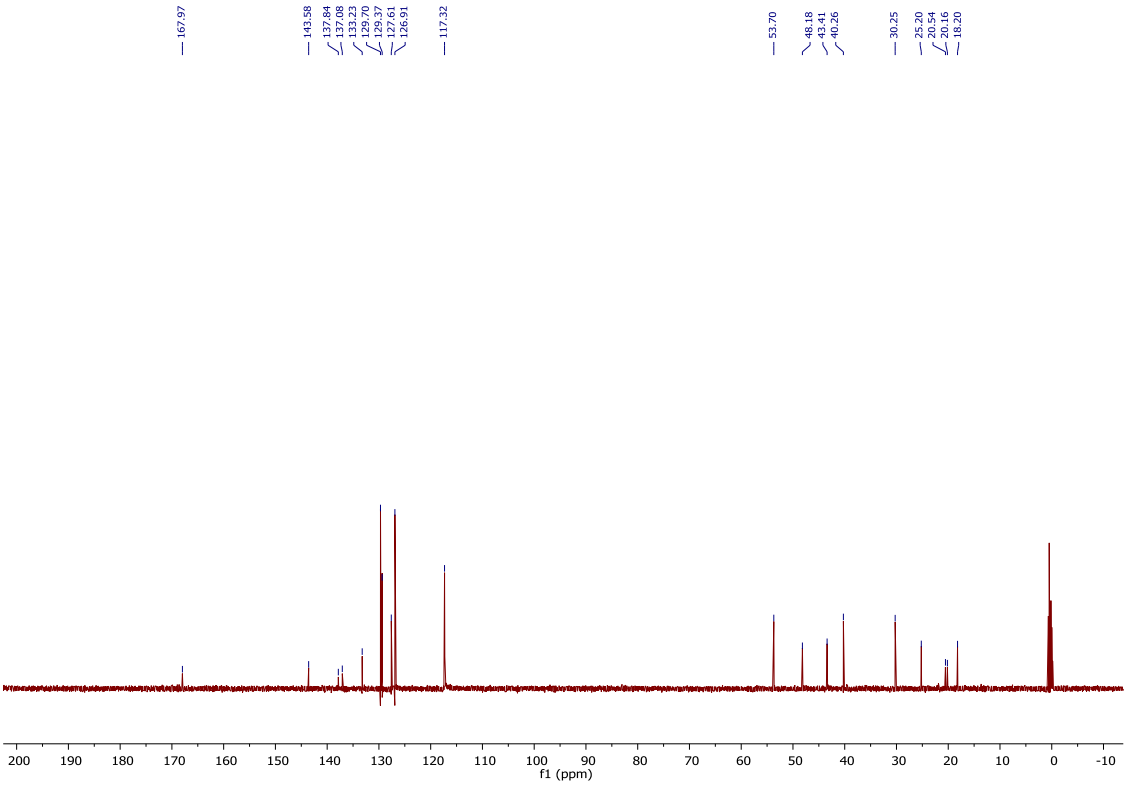




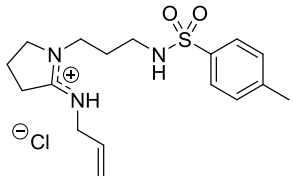
_N_-(4-Methylbenzyl)-1-tosylhexahydropyrrolo[1,2-_a_]pyrimidin-8a(6_H_)-amine hydrochloride (3a)

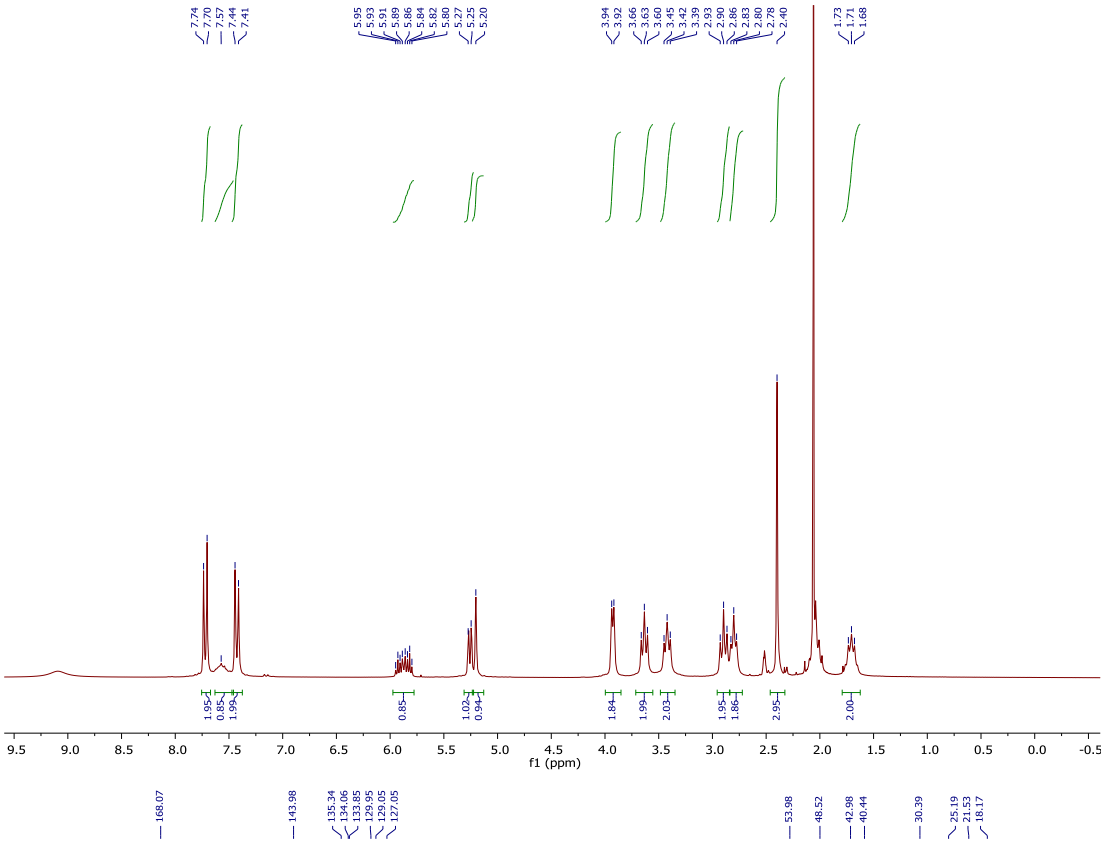


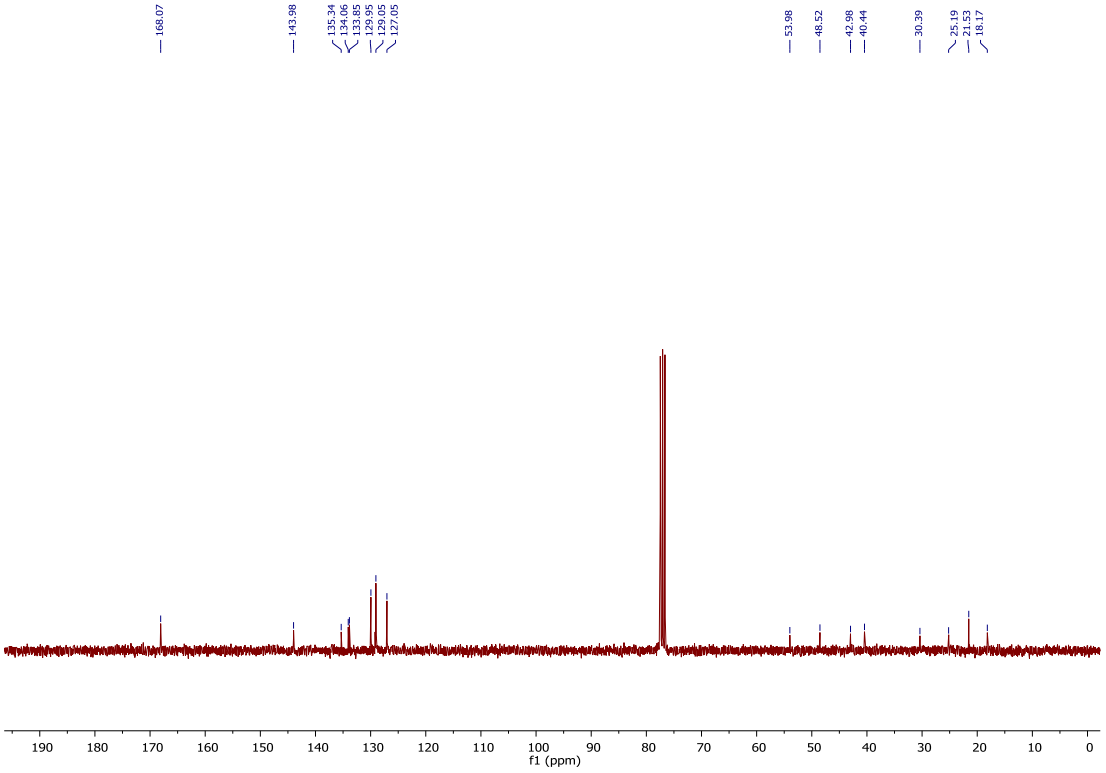




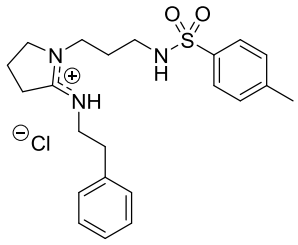
_N_-(3-(2-(Allylimino)pyrrolidin-1-ylpropyl)-4-methylbenzenesulfonamide hydrochloride (3b)

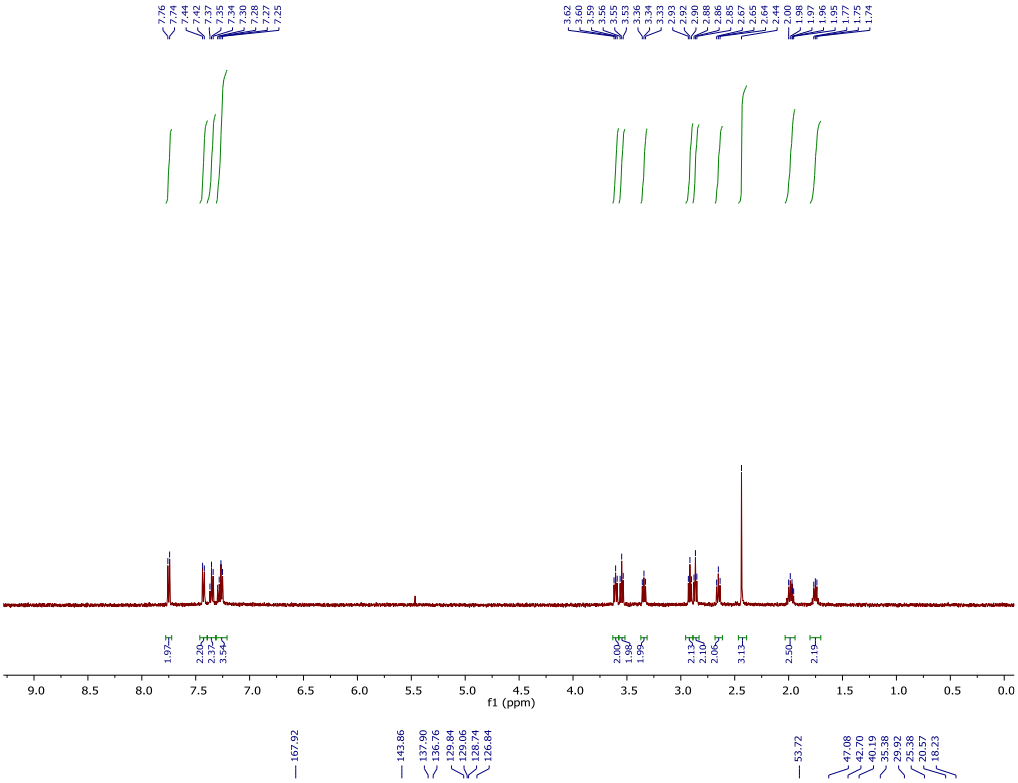


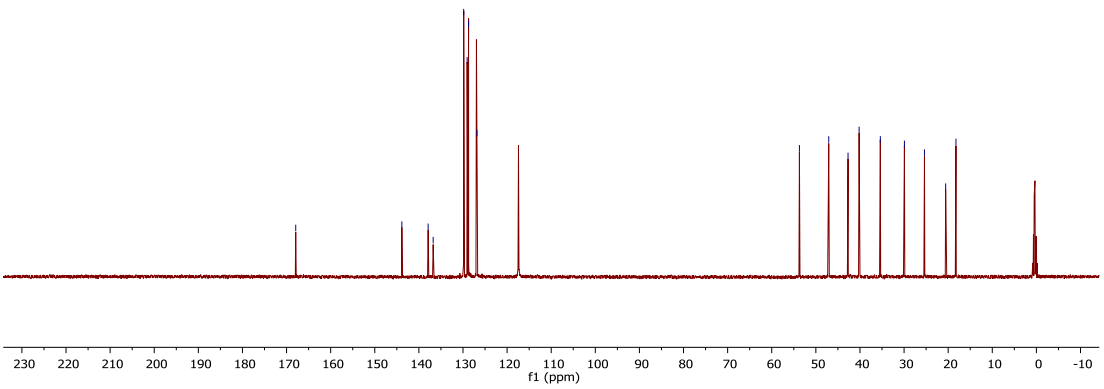




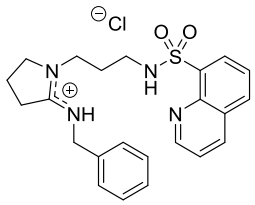
4-Methyl-*N*-(3-(2-phenethylimino)pyrrolidin-1-yl)propyl)benzenesulfonamide hydrochloride (3c)

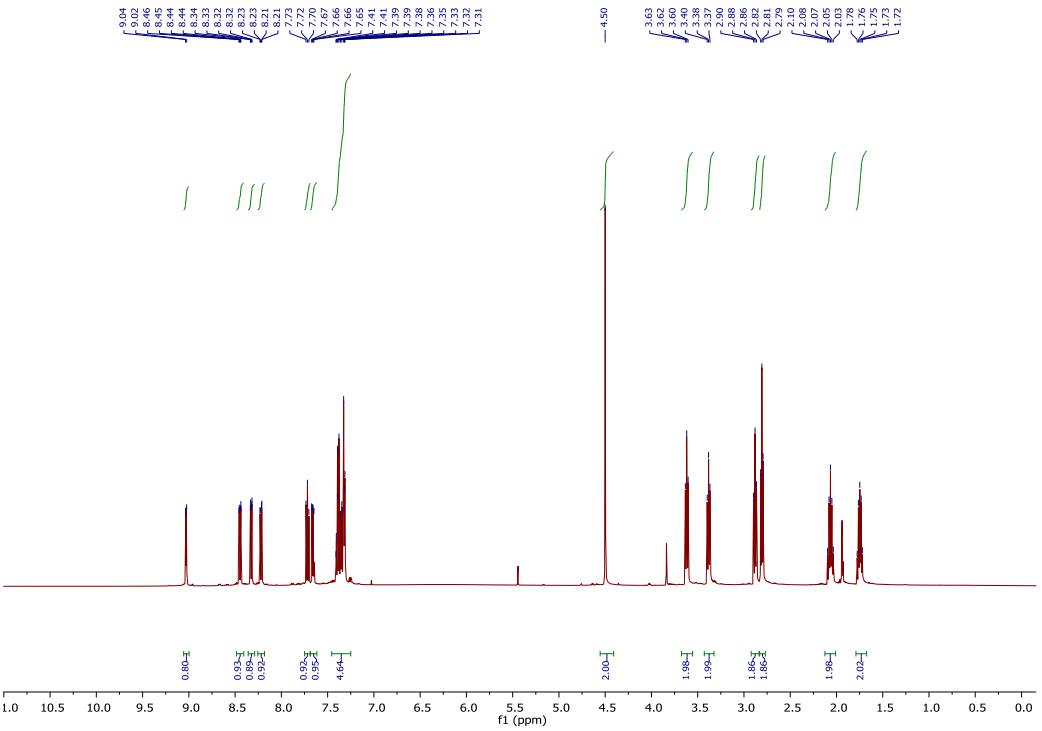


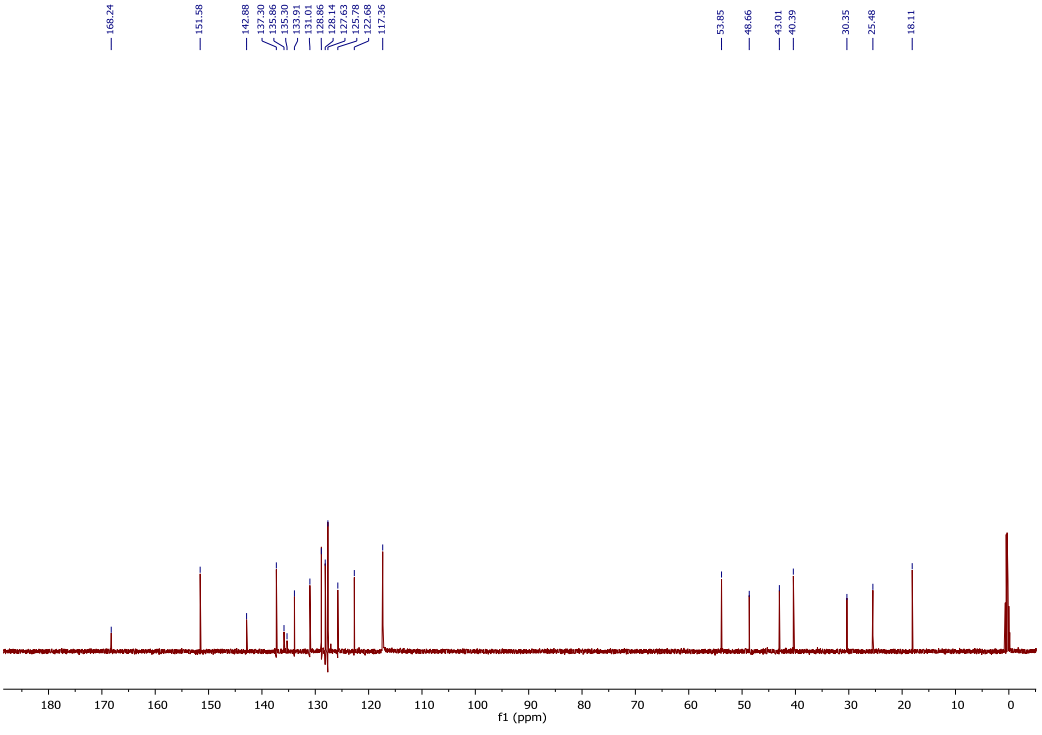




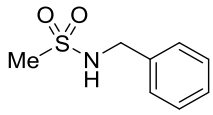
***N*-(3-(2-(Benzylimino)pyrrolidin-1-yl)propyl)quinolone-8-sulfonamide hydrochloride**

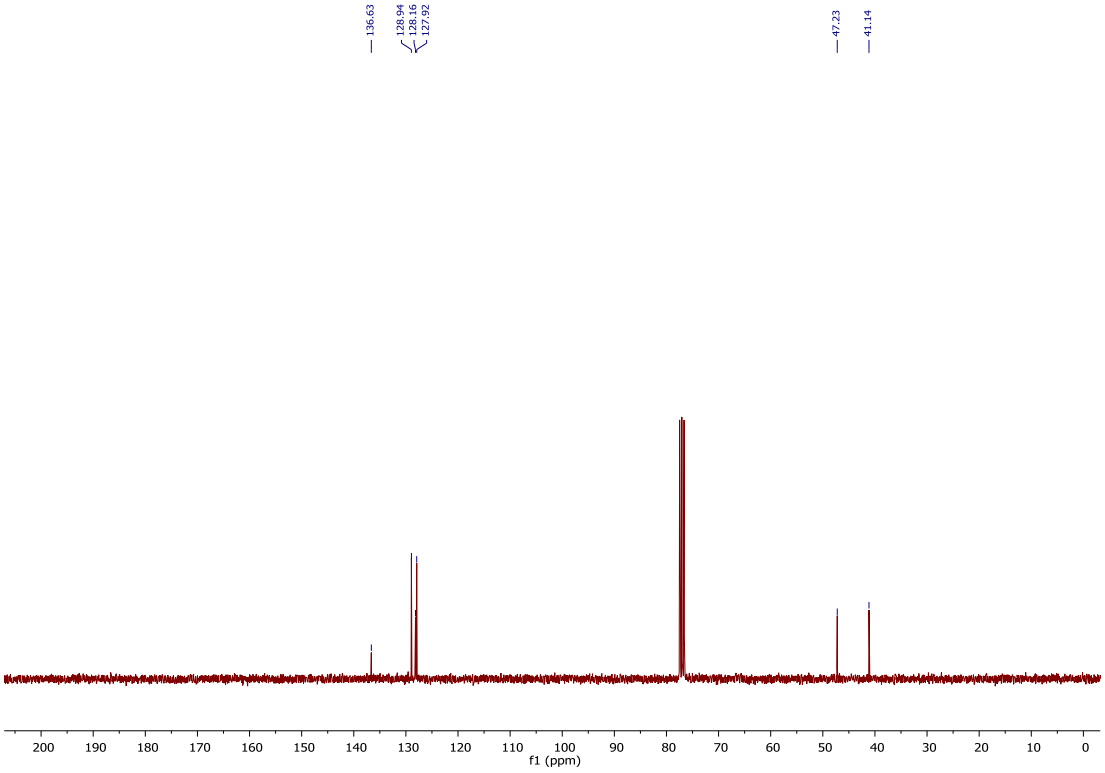


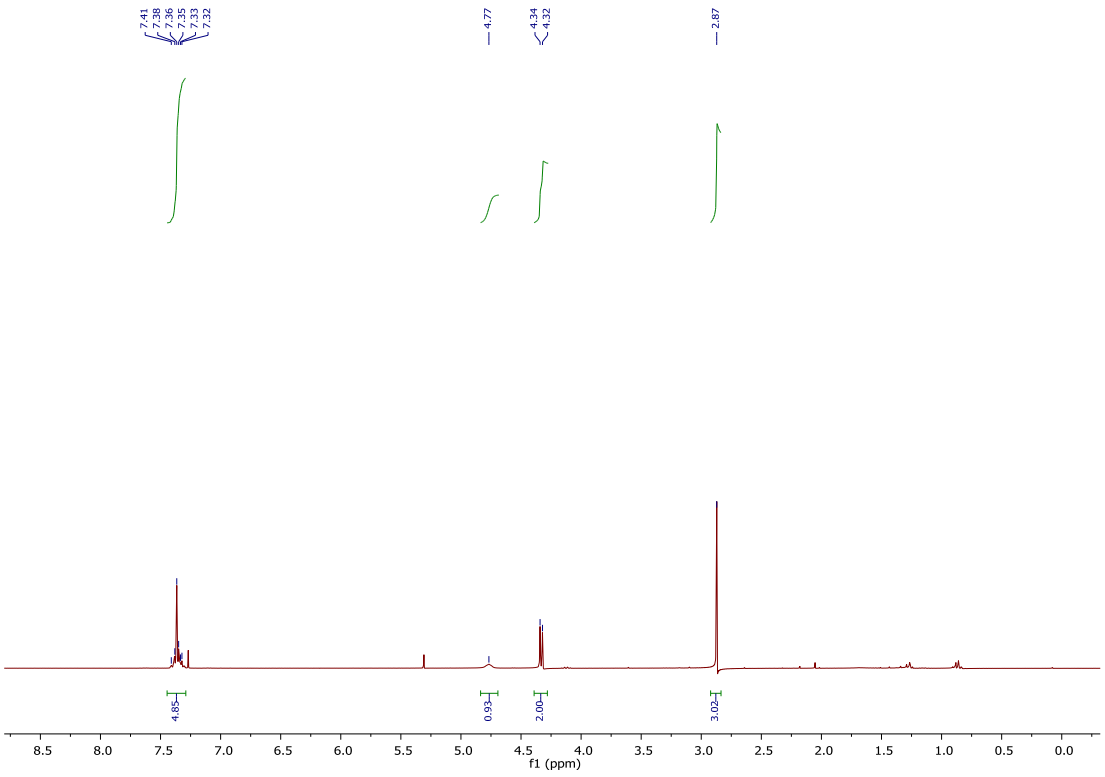




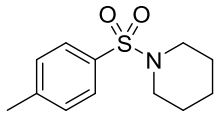
***N*-Benzylmethanesulfonamide**

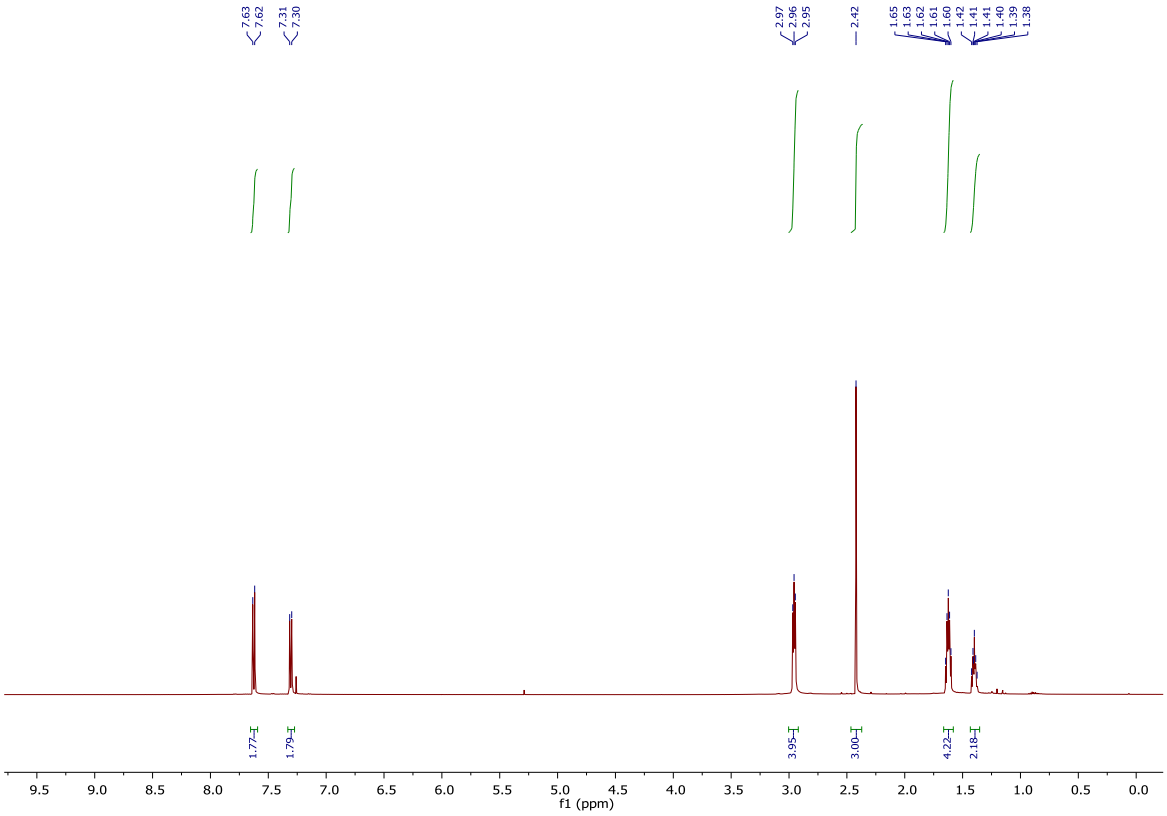


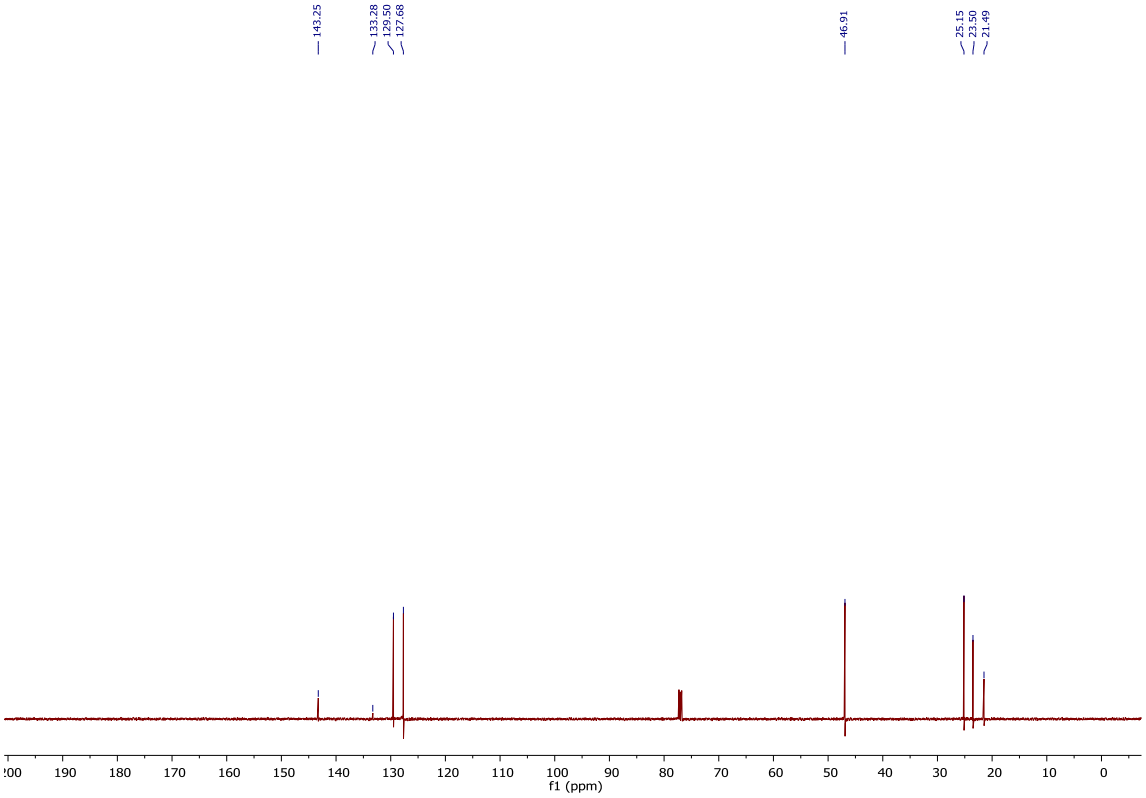




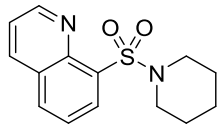
1-Tosylpiperidine (4a)

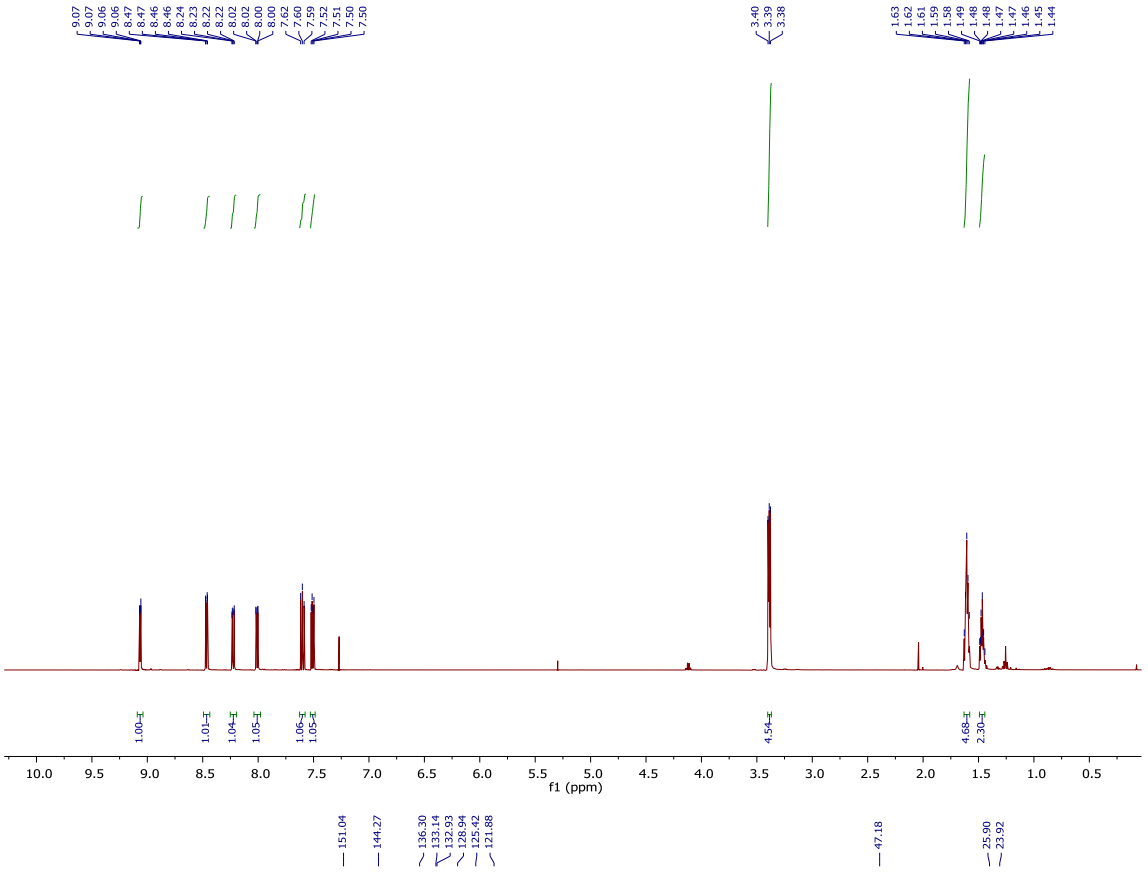


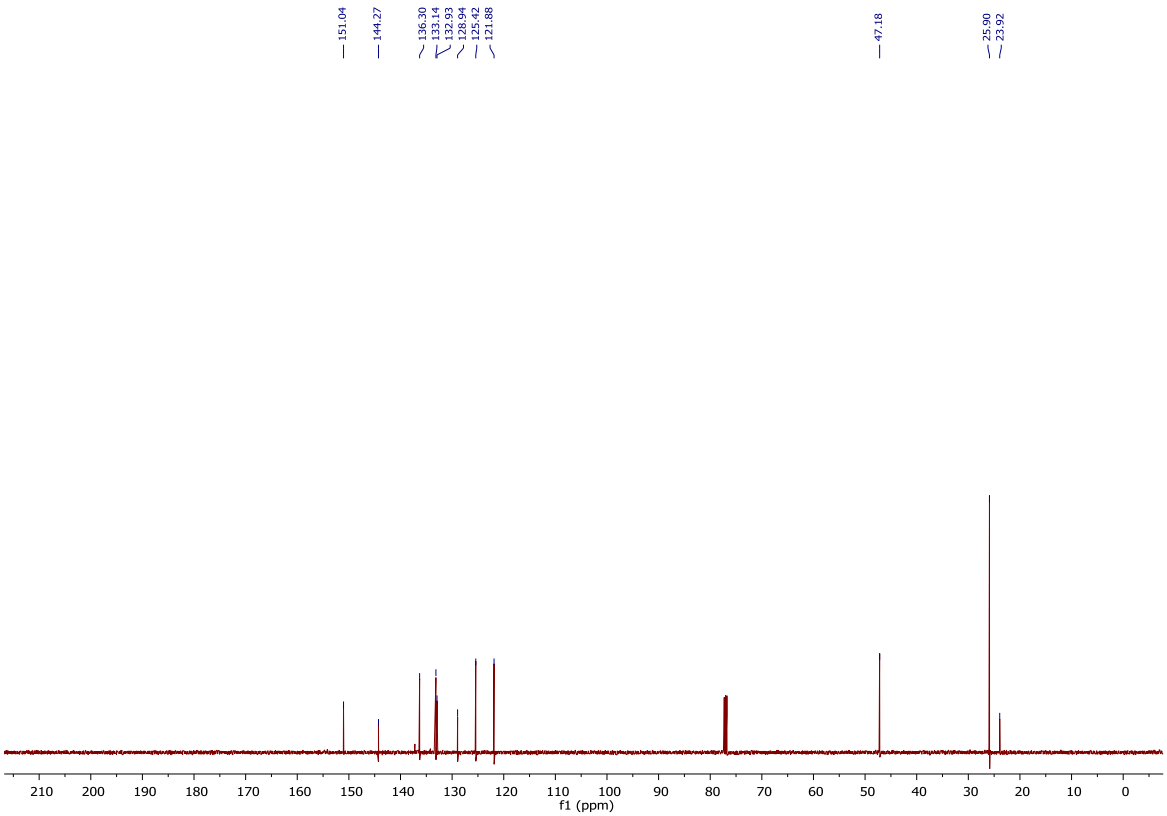




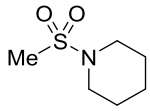
8-(Piperidin-1-ylsulfonyl)quinoline (4b)

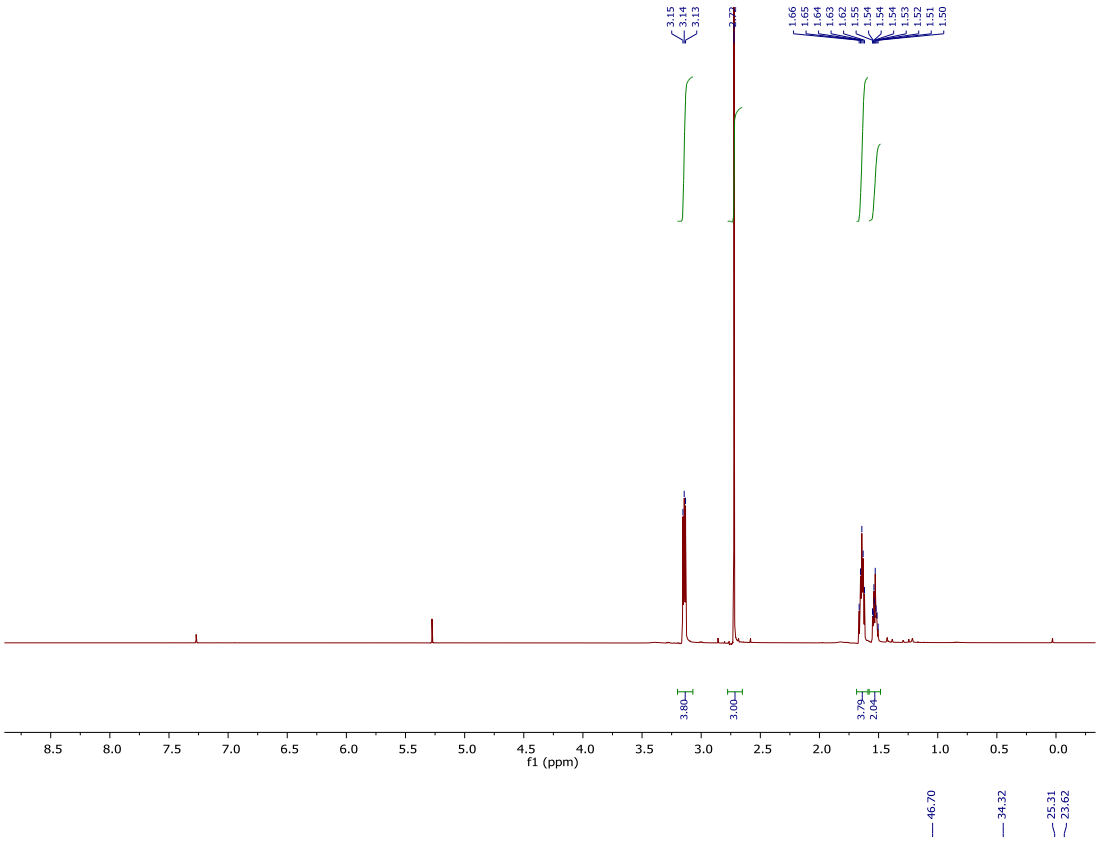


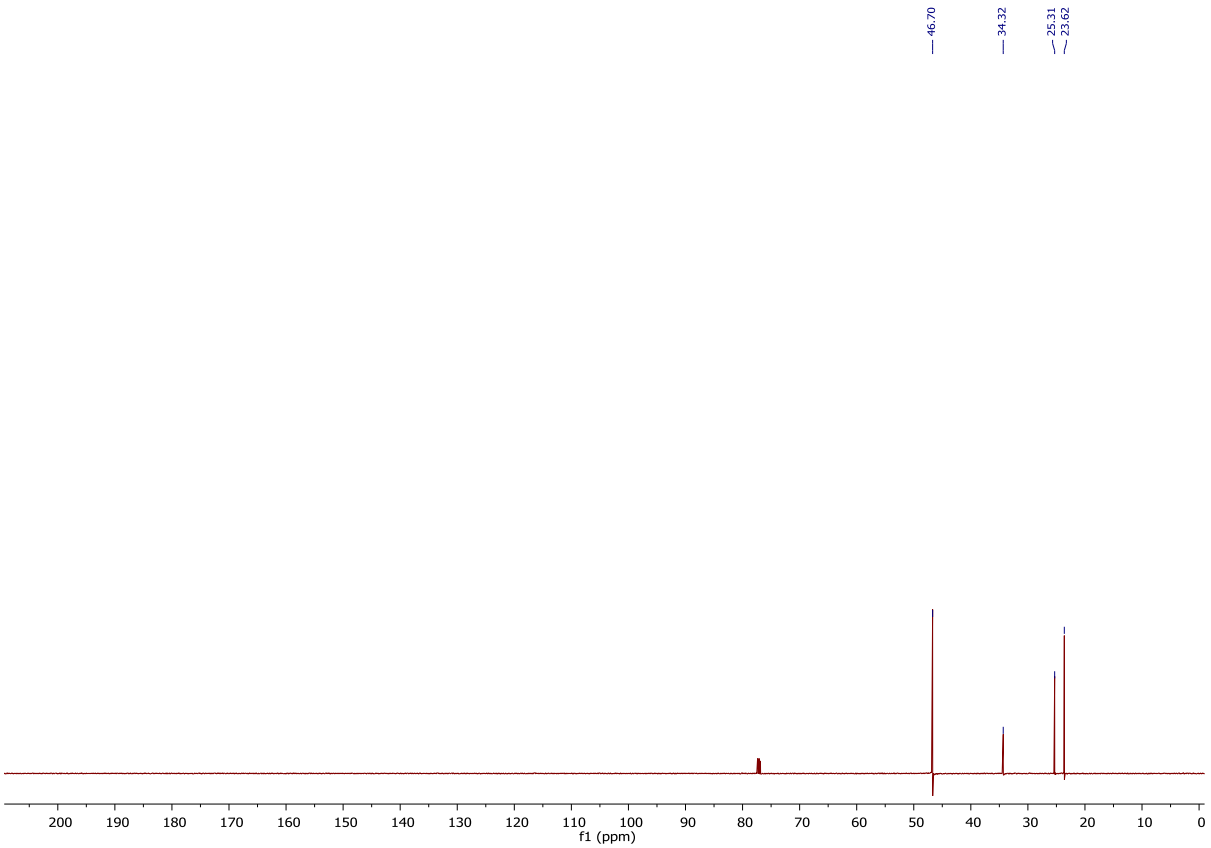




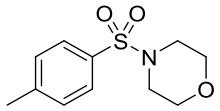
1-(Methylsulfonyl)piperidine (4c)

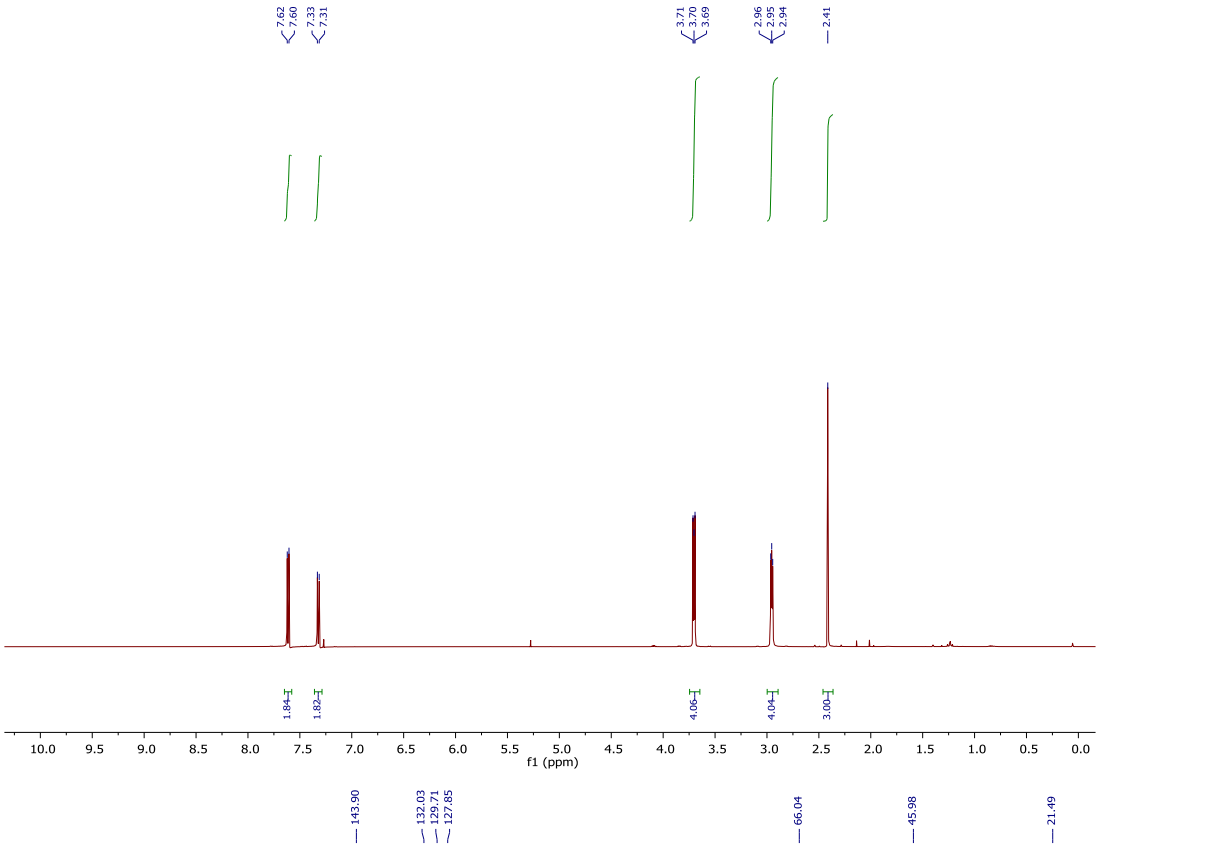


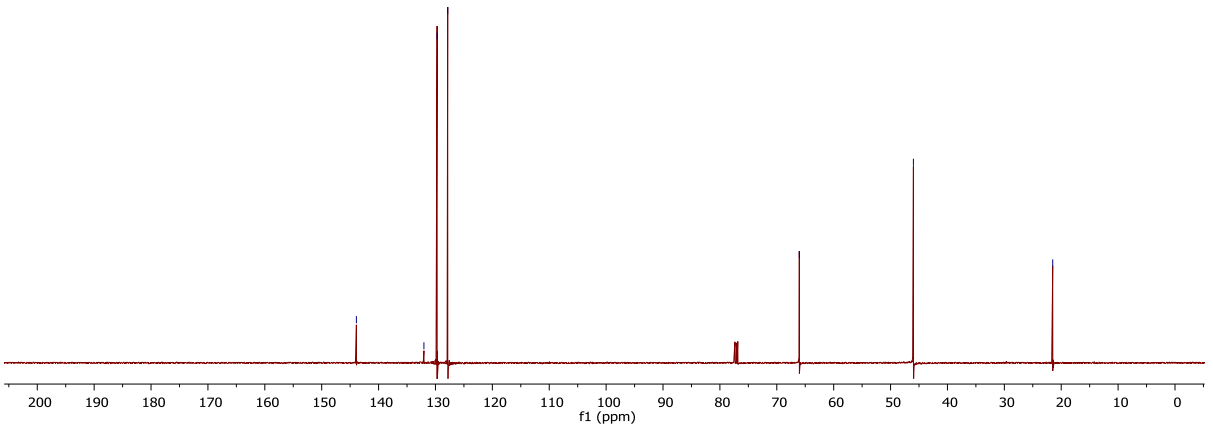




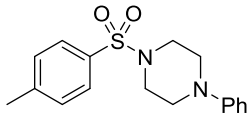
4-Tosylmorpholine (4d)

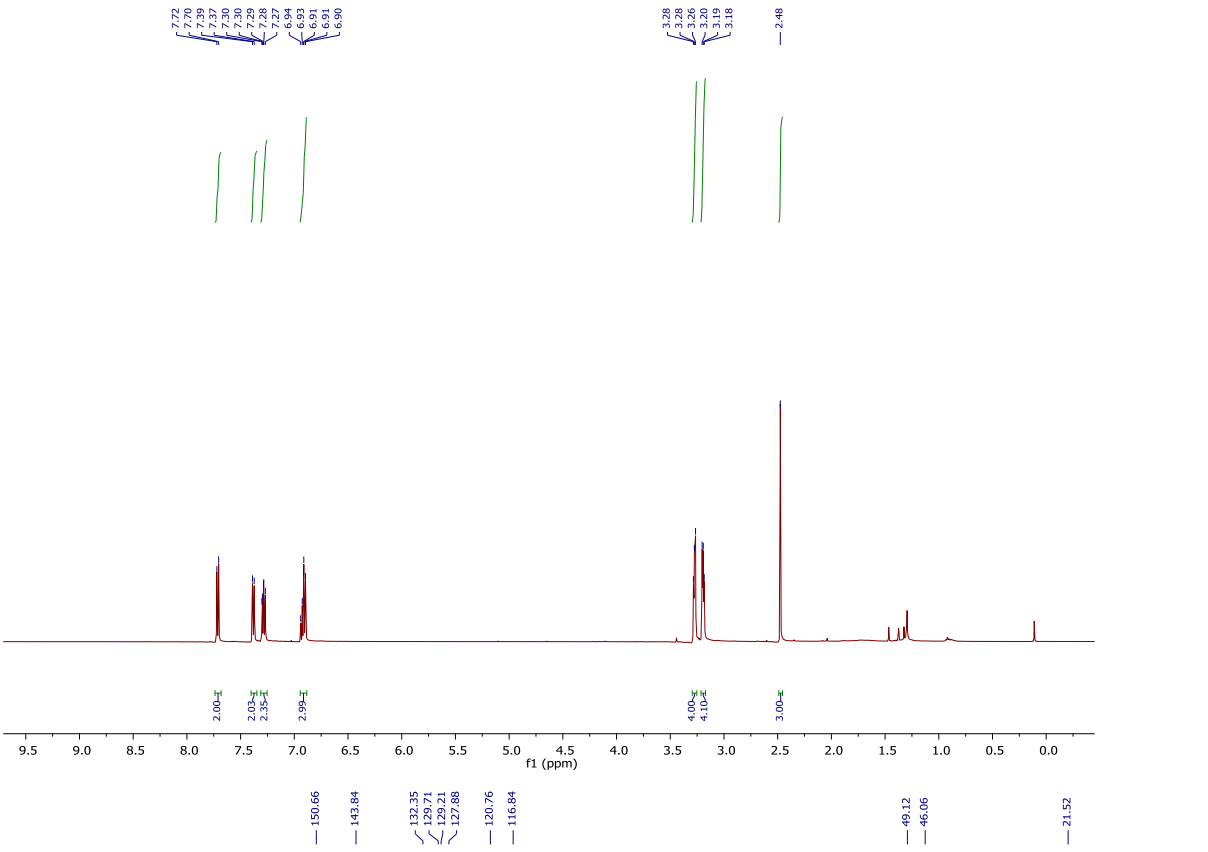


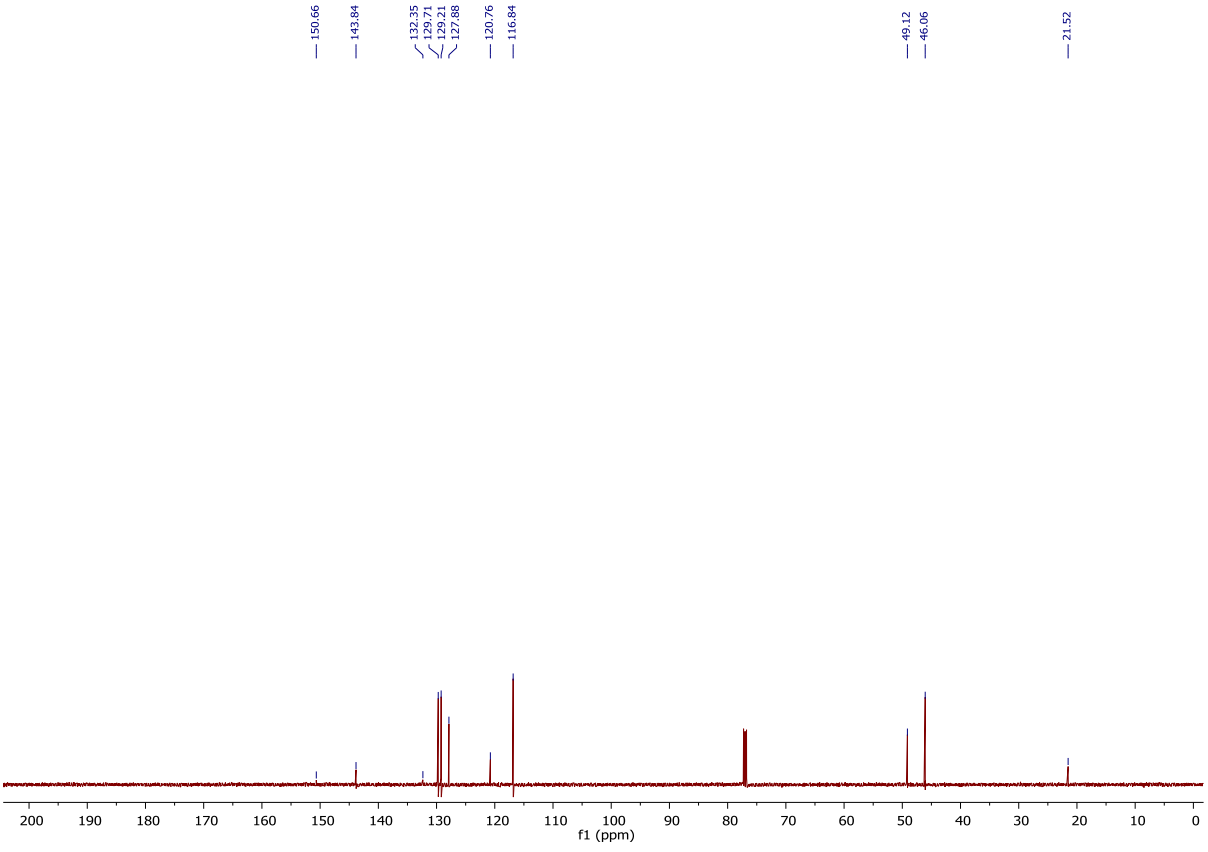




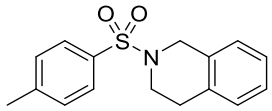
1-Phenyl-4-tosylpiperazine (4e)

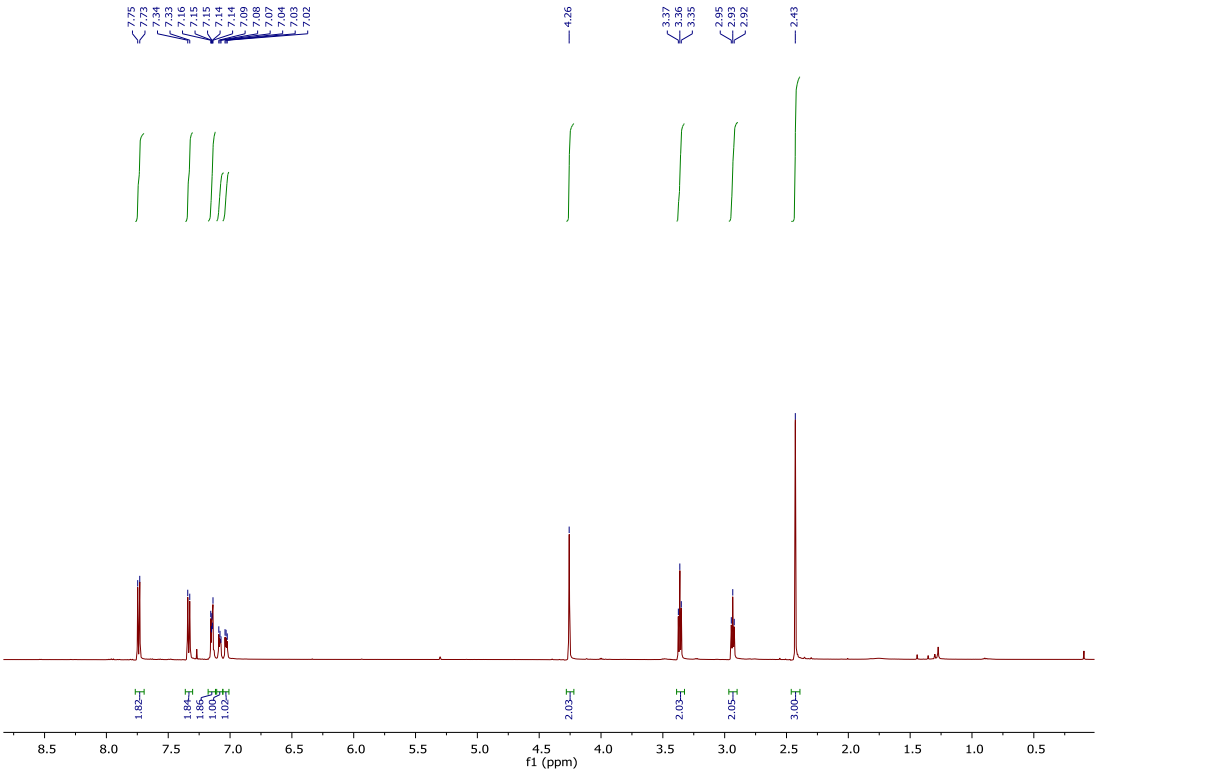


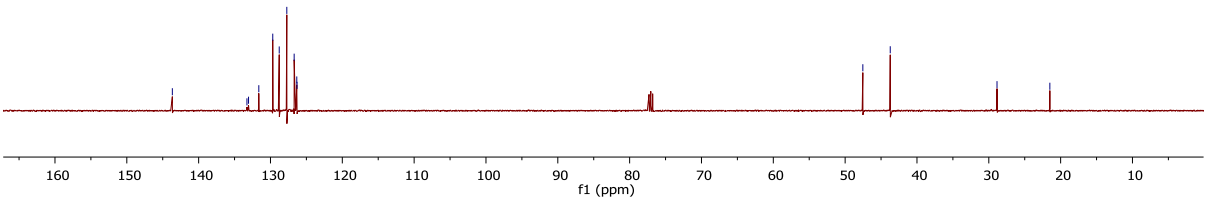




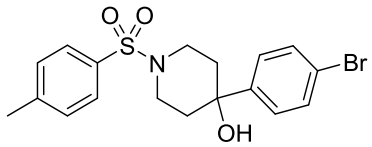
2-Tosyl-1,2,3,4-tetrahydroisoquinoline (4f)

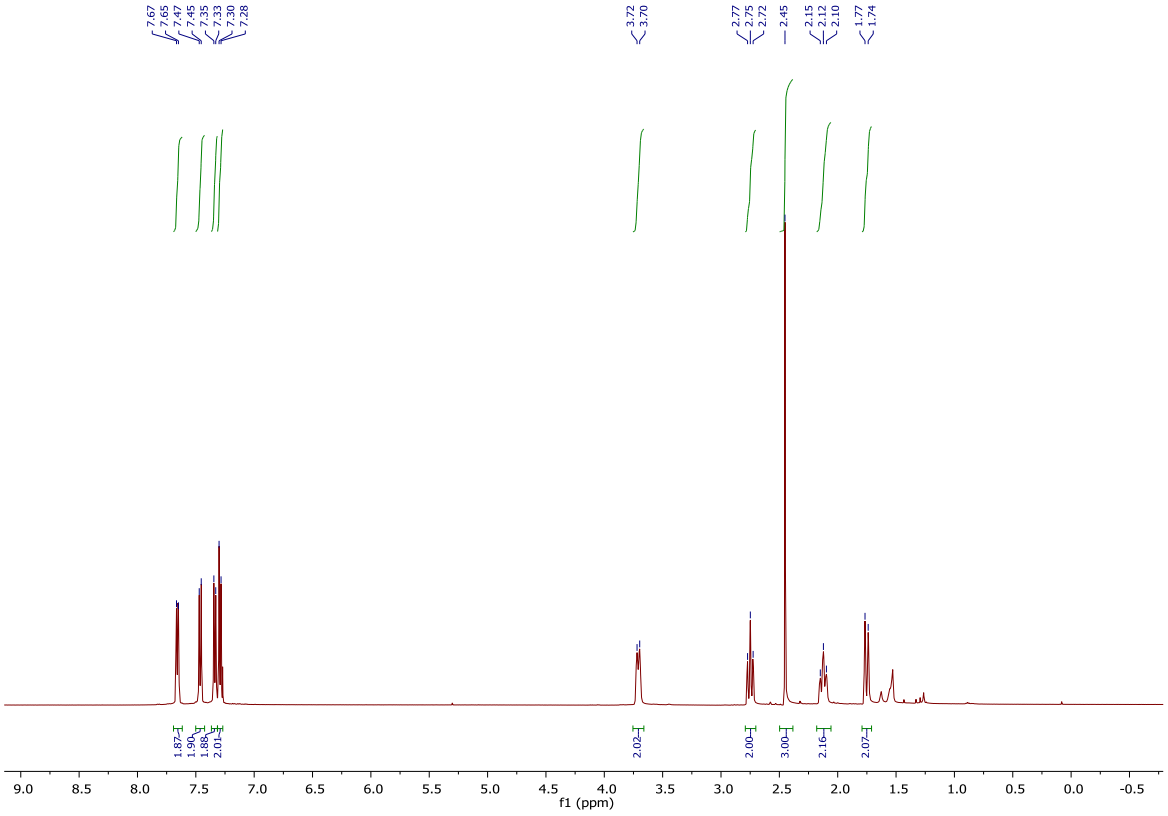


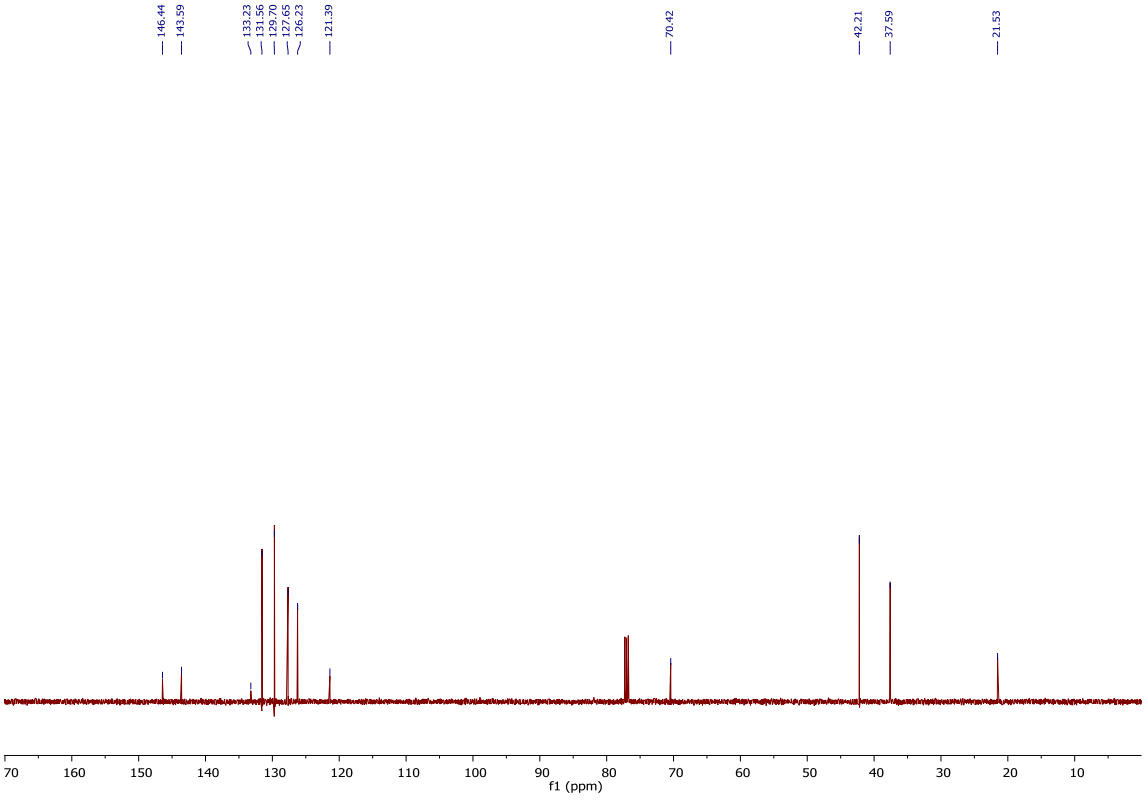




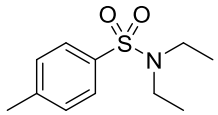
4-(4-Bromophenyl)-1-tosylpiperidin-4-ol (4g)

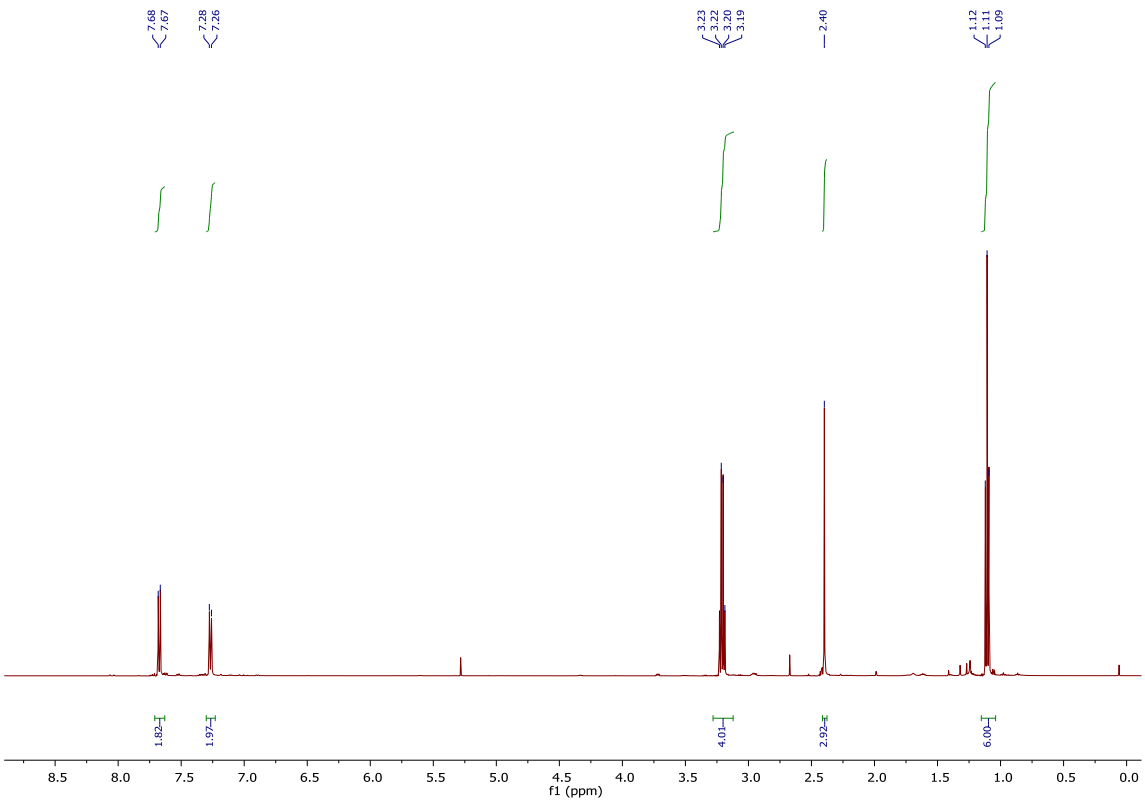


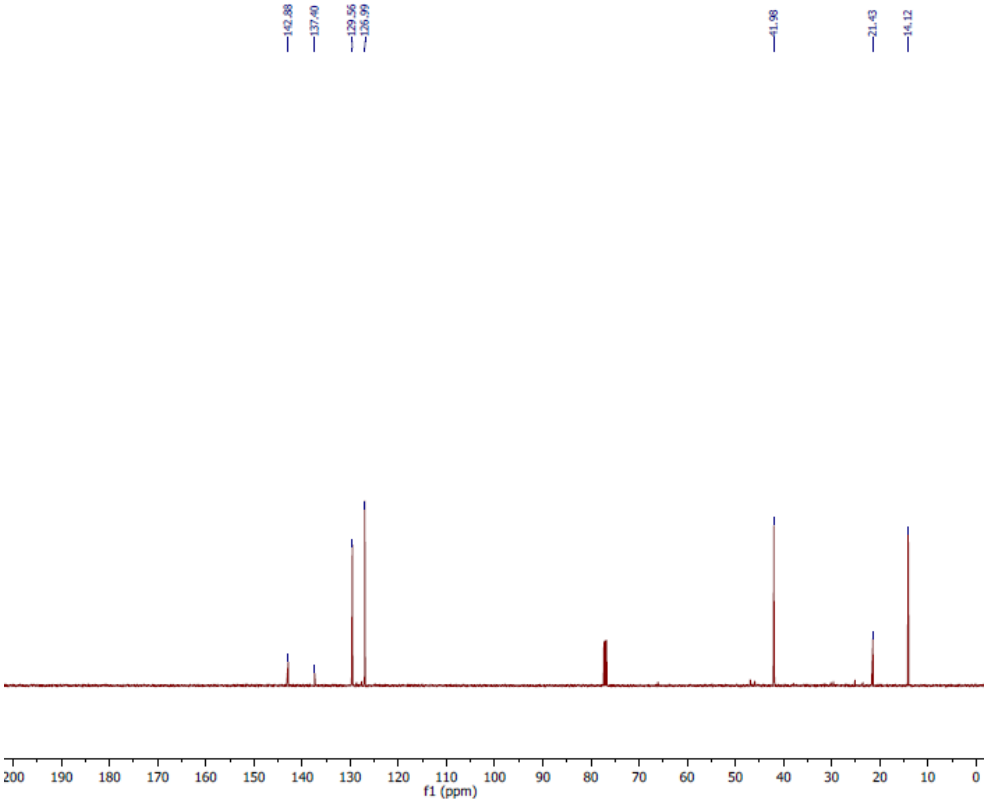




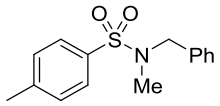
_N,N_-Diethyl-4-methylbenzenesulfonamide (4h)

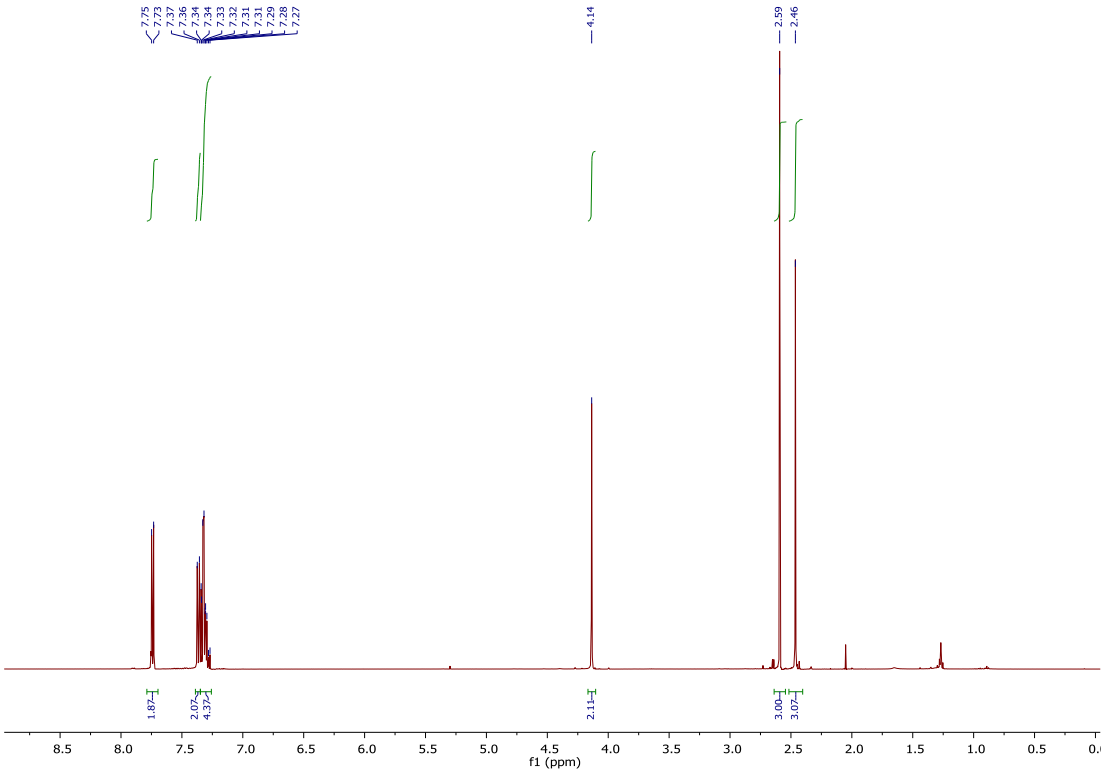


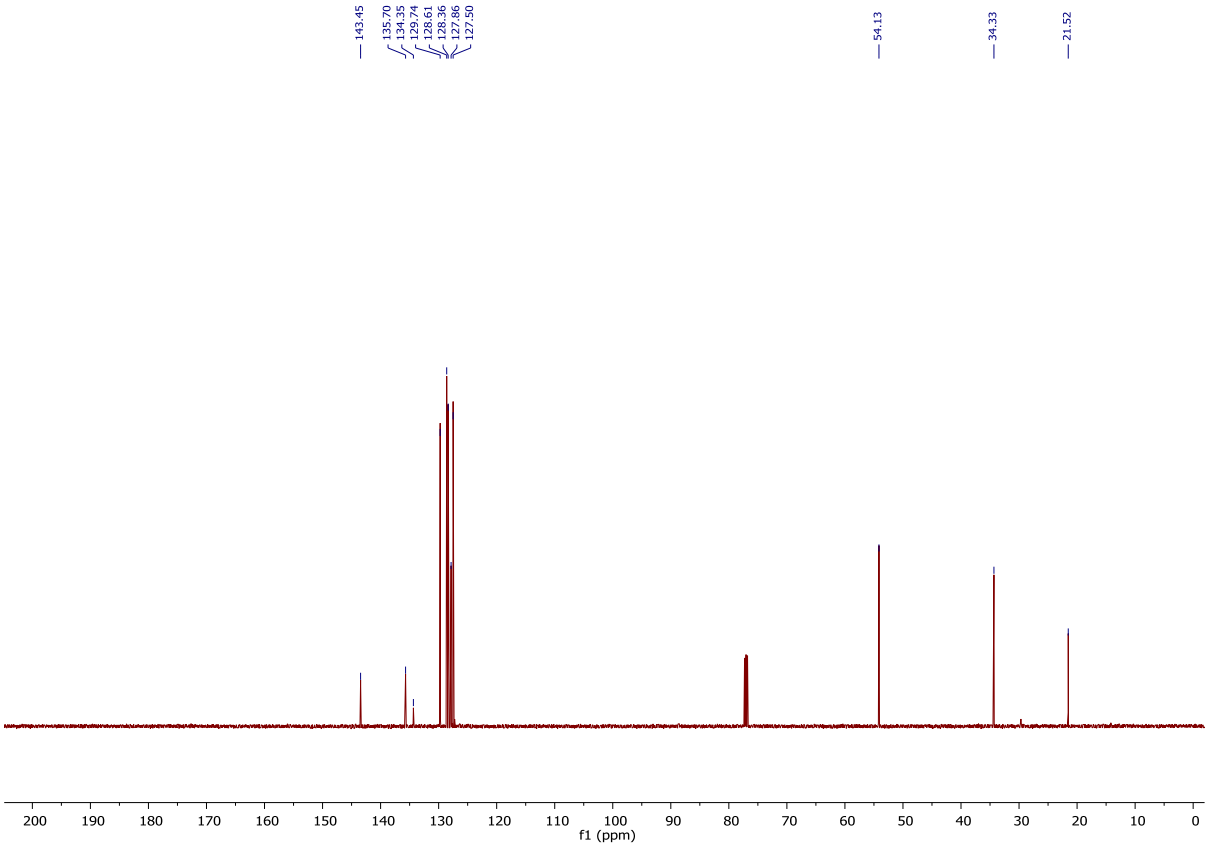




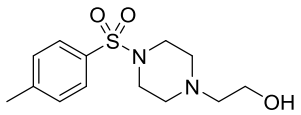
_N_-Benzyl-_N_,4-dimethylbenzenesulfonamide (4i)

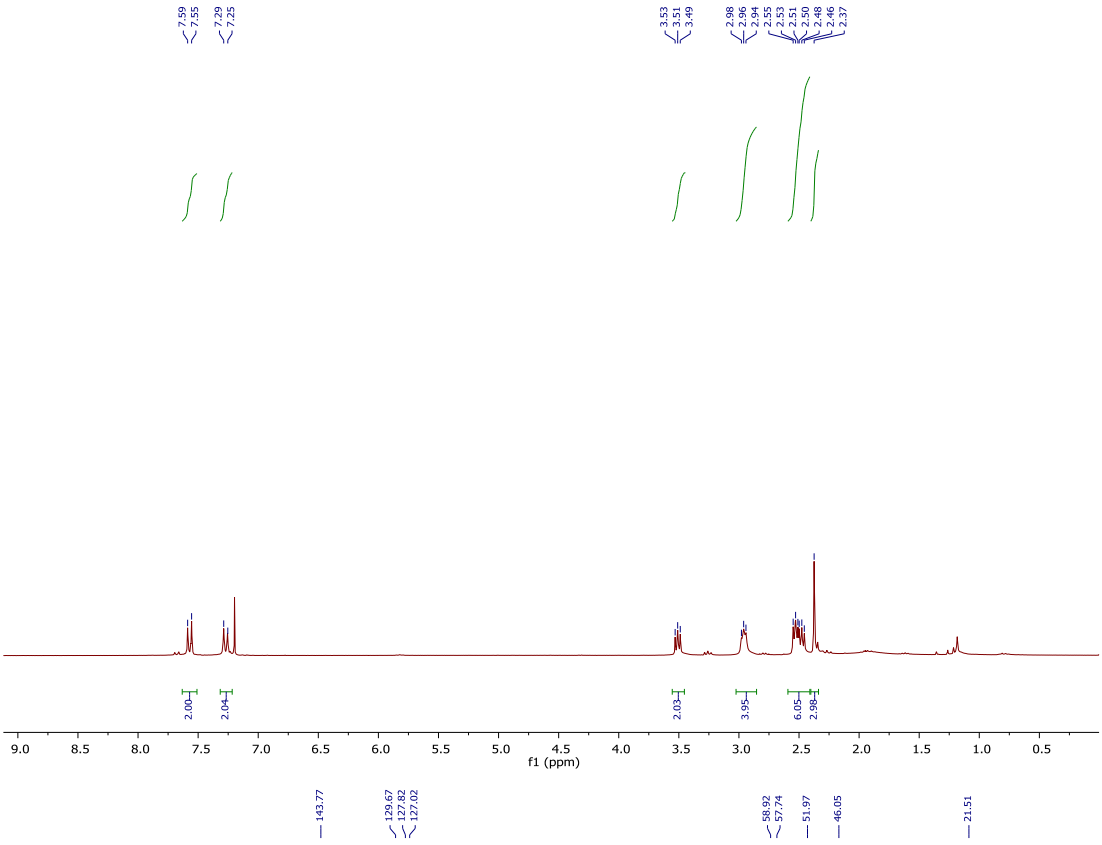


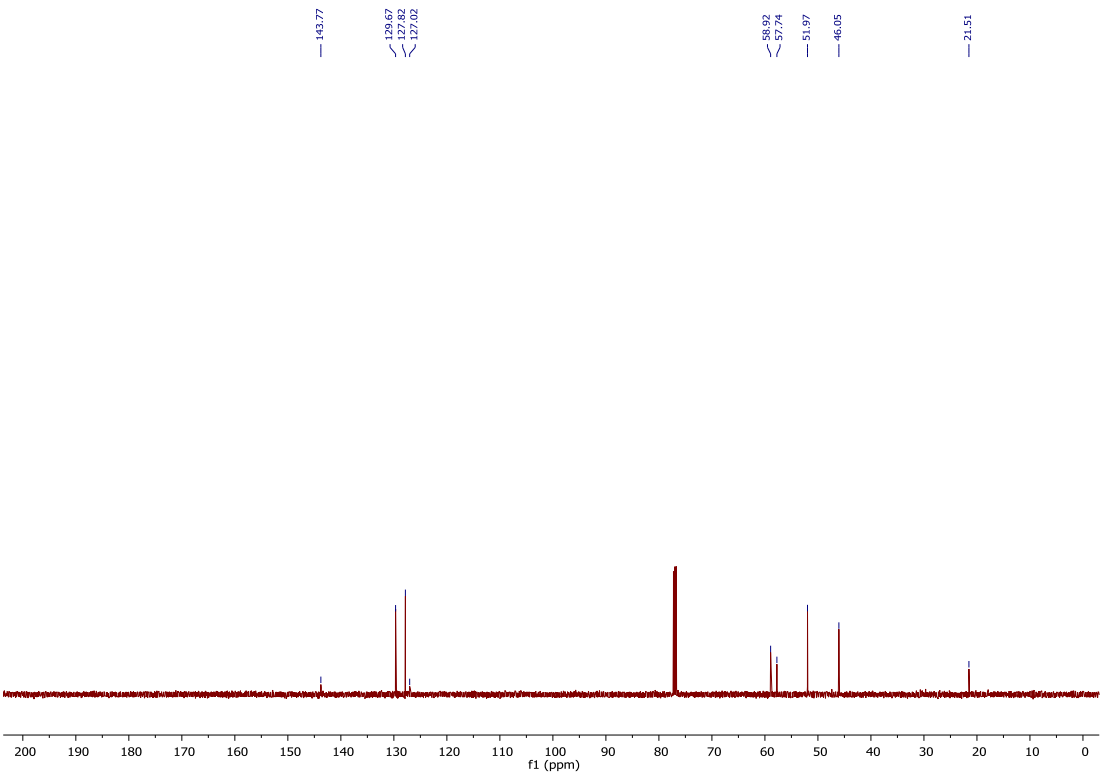




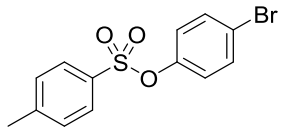
2-(4-Tosylpiperazin-1-yl)ethan-1-ol (4j)

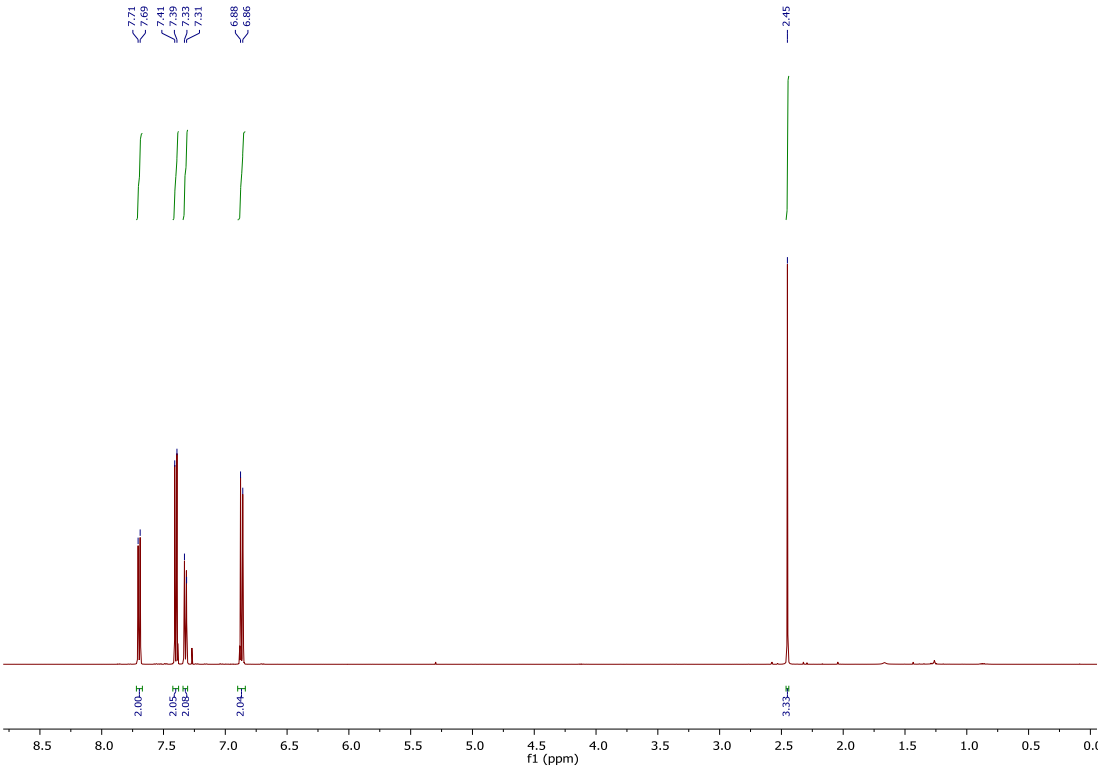


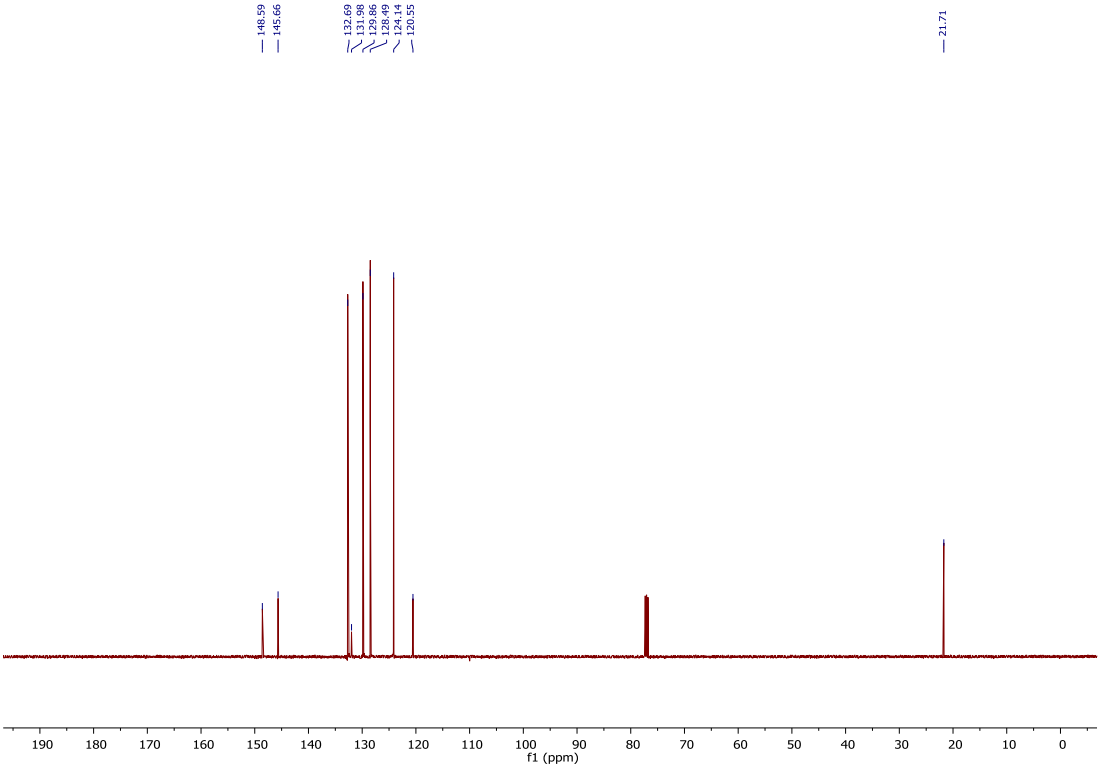




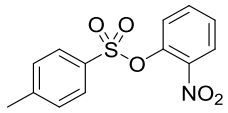
4-Bromophenyl-4-methylbenzenesulfonate (4l)

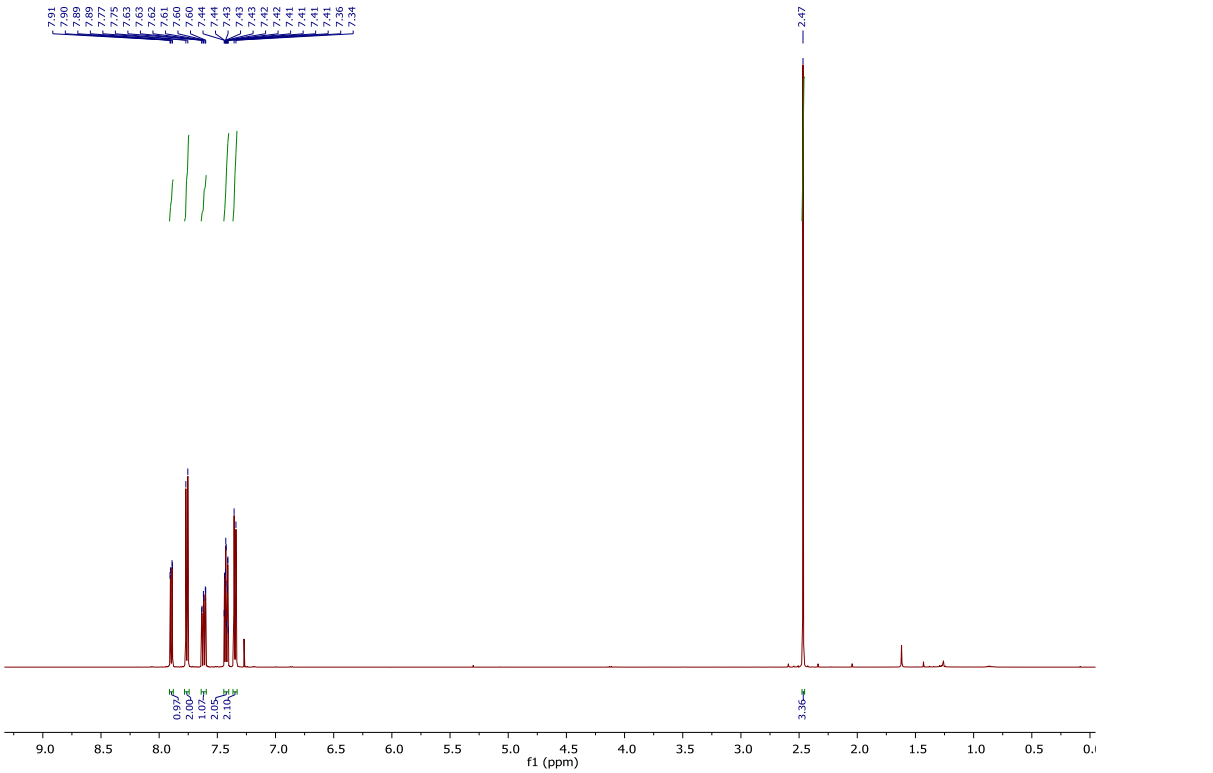


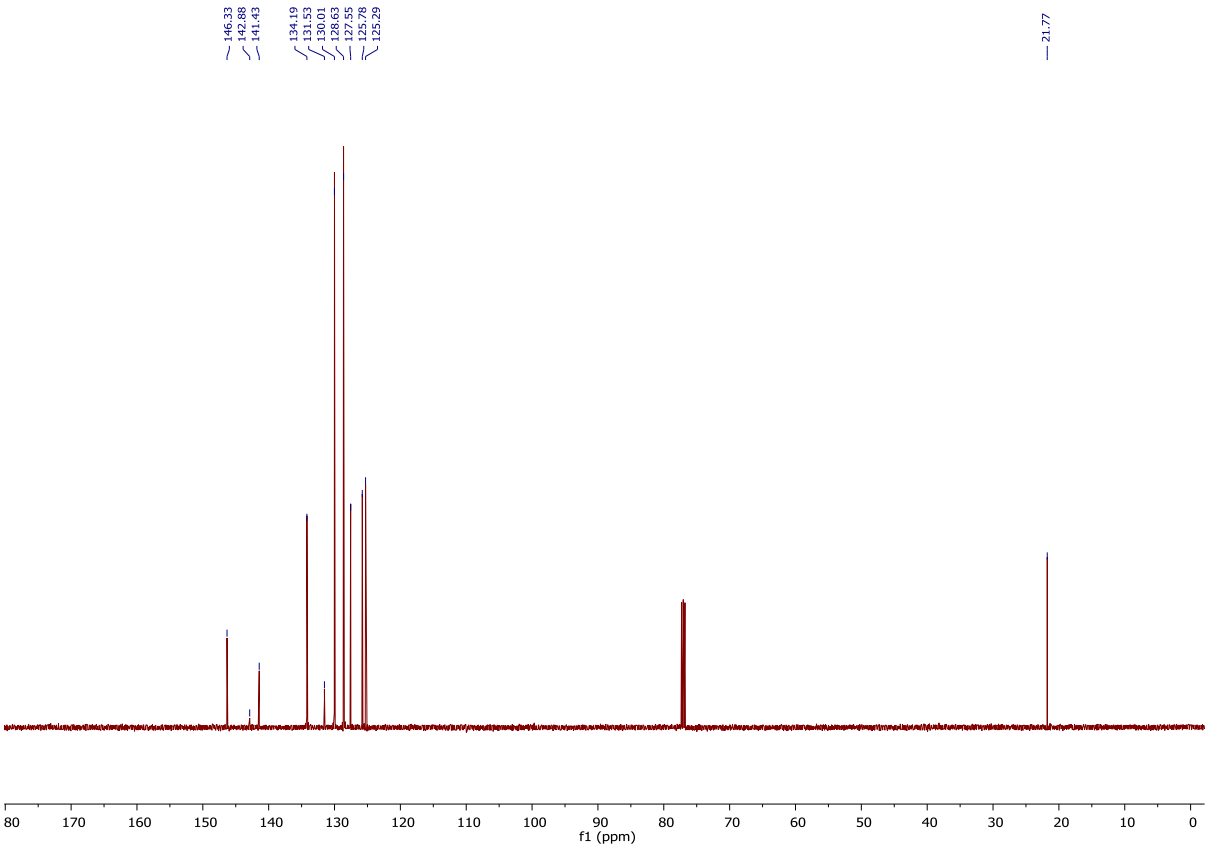




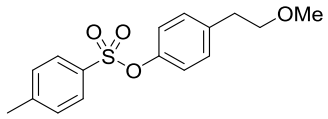
2-Nitrophenyl-4-methylbenzenesulfonate (4m)

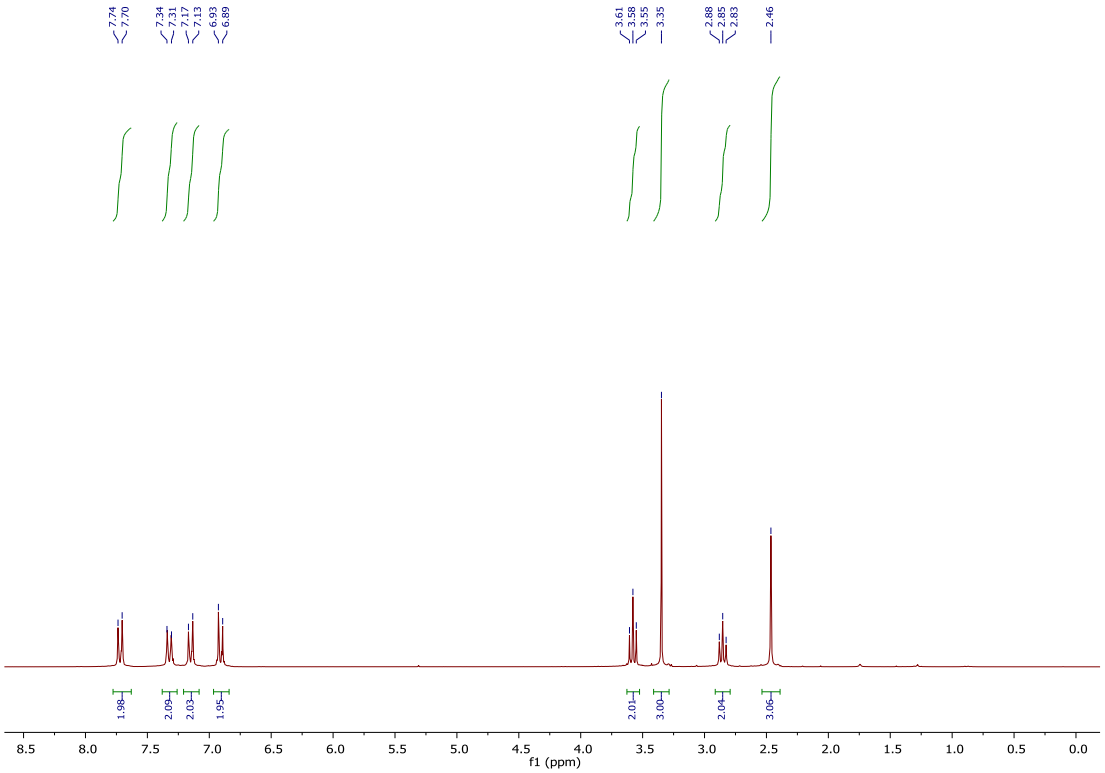


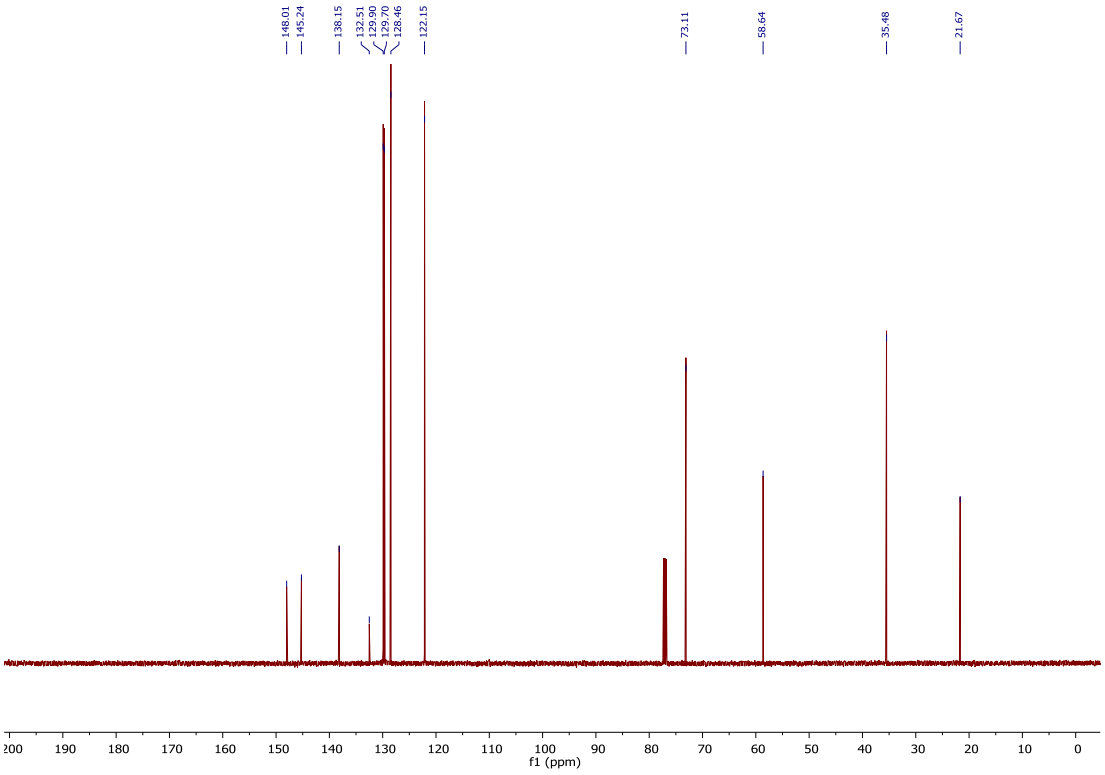




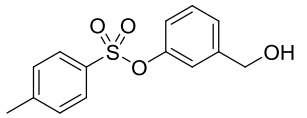
4-(2-Methoxyethyl)phenyl-4-methylbenzenesulfonate (4n)

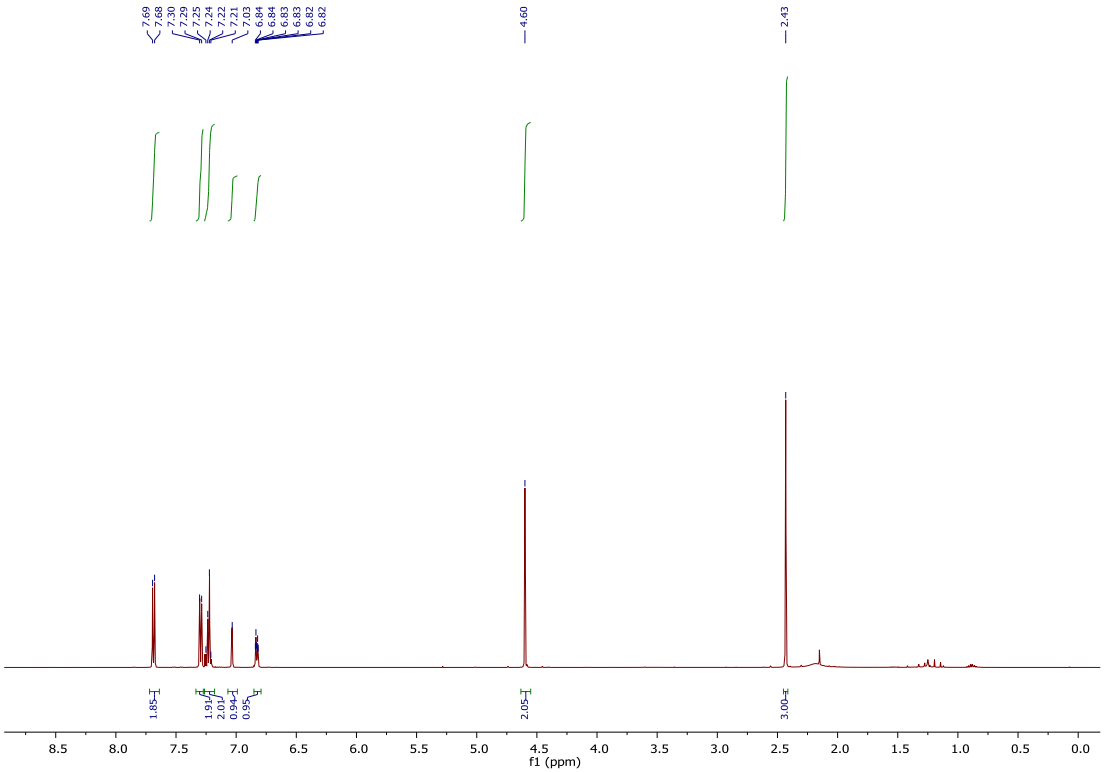


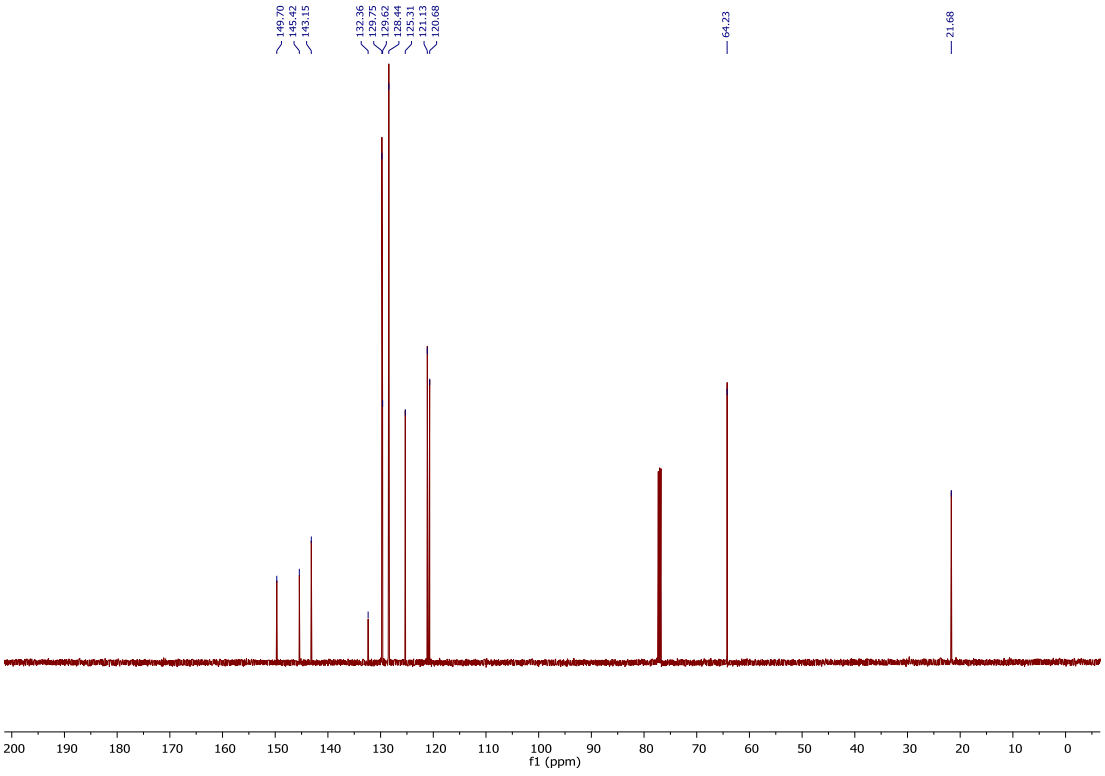




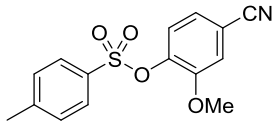
3-(Hydroxymethyl)phenyl 4-methylbenzenesulfonate (4o)

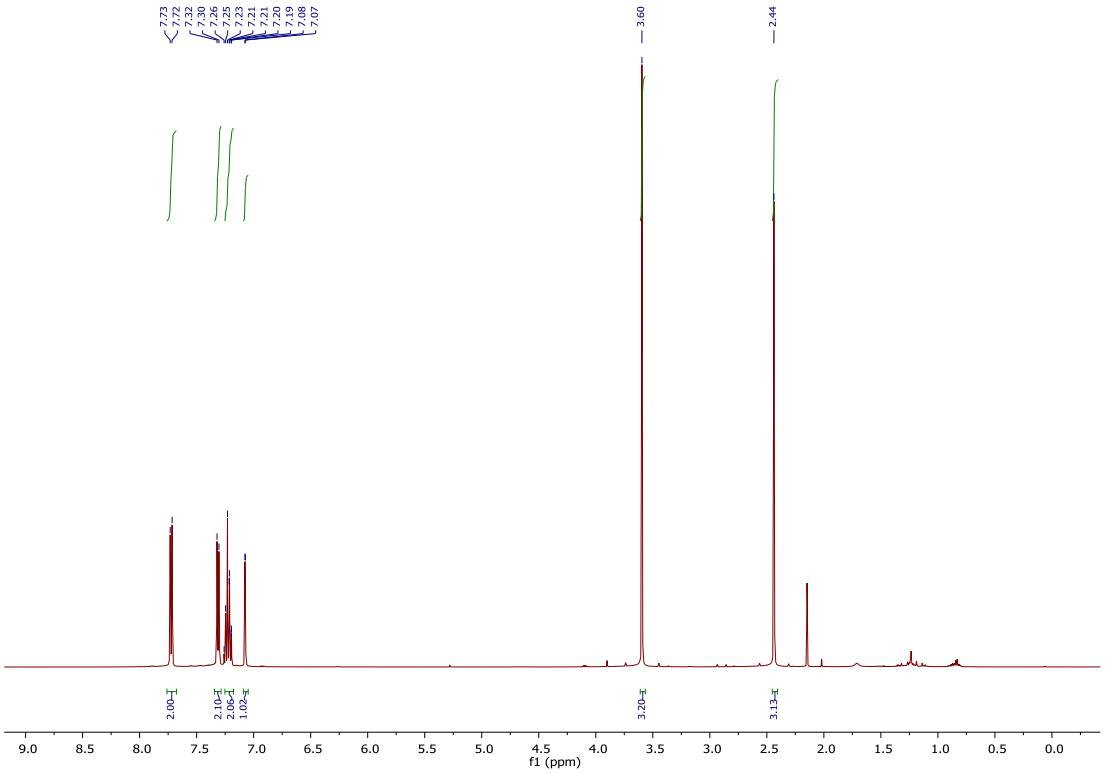


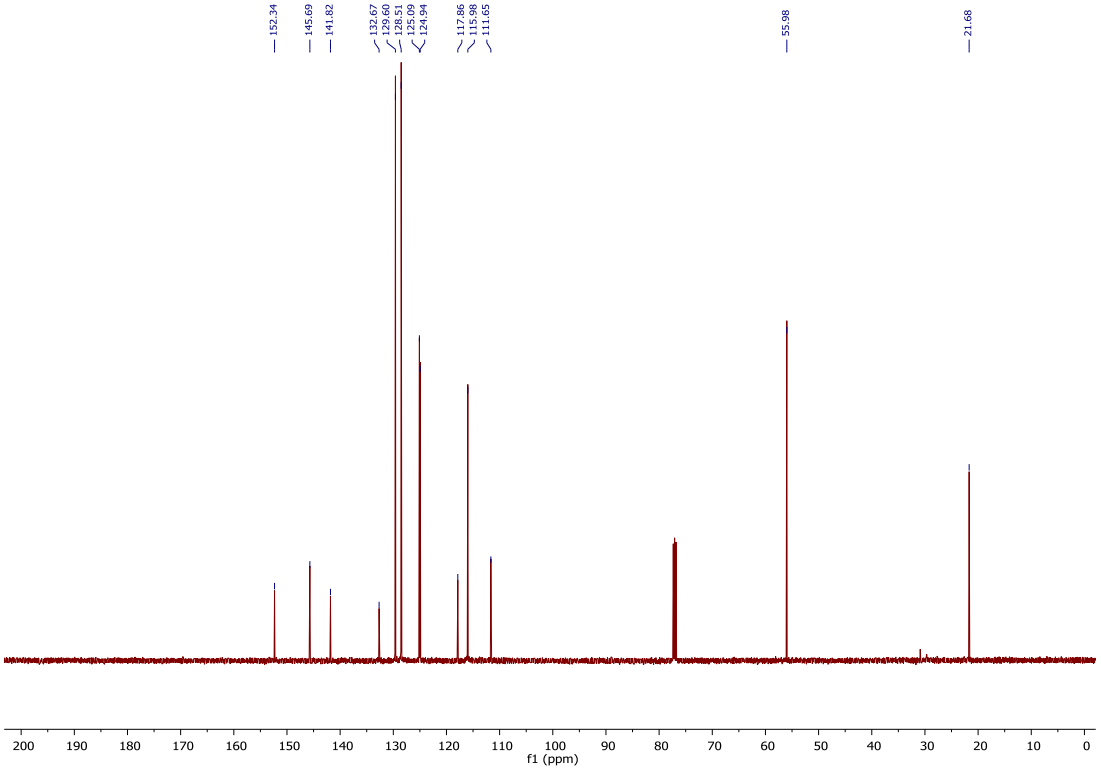




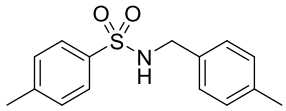
2-Cyano-2-methoxphenyl 4-methylbenzenesulfonate (4p)

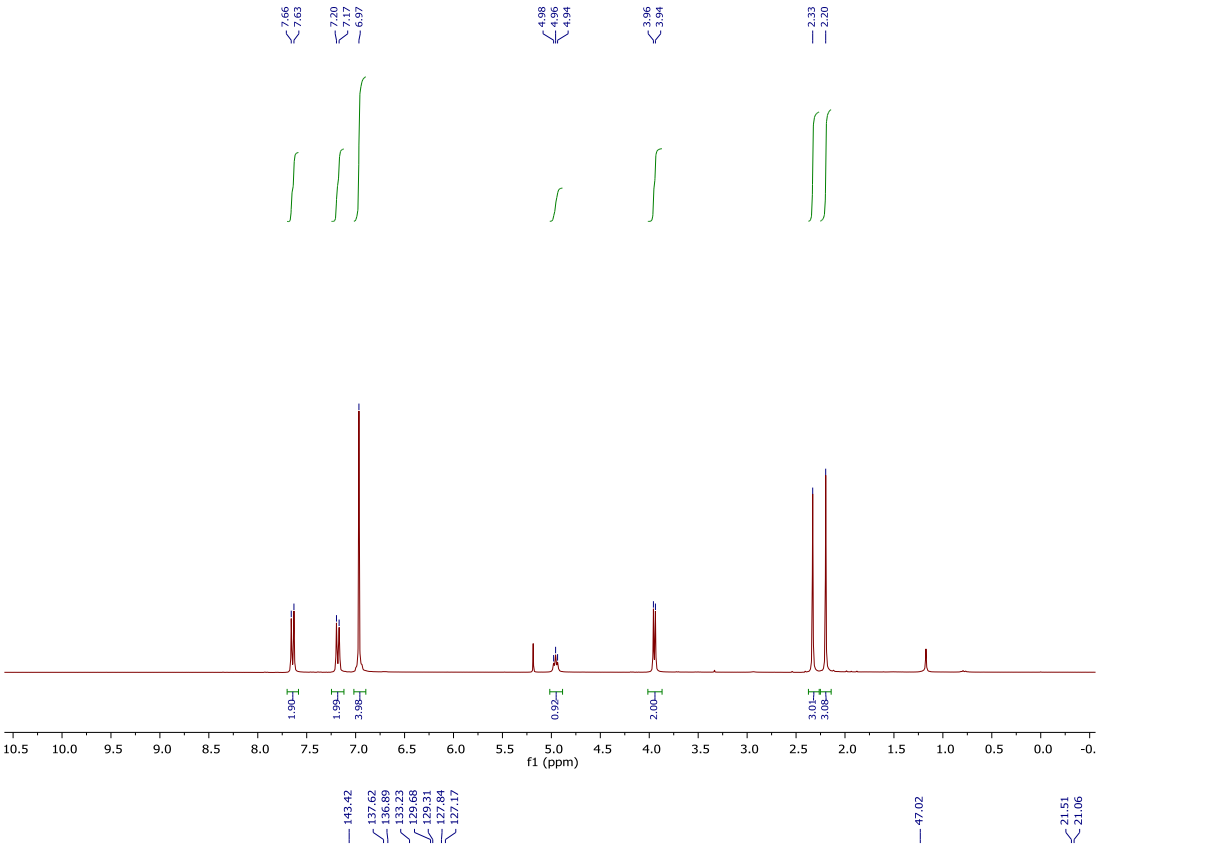


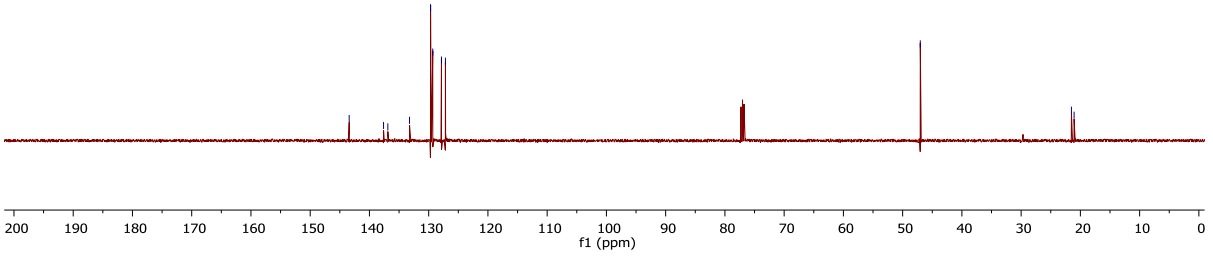




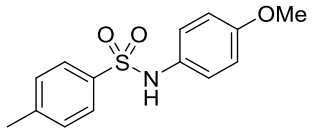
4-Methyl-*N*-(4-methylbenzyl)benzenesulfonamide (6a)

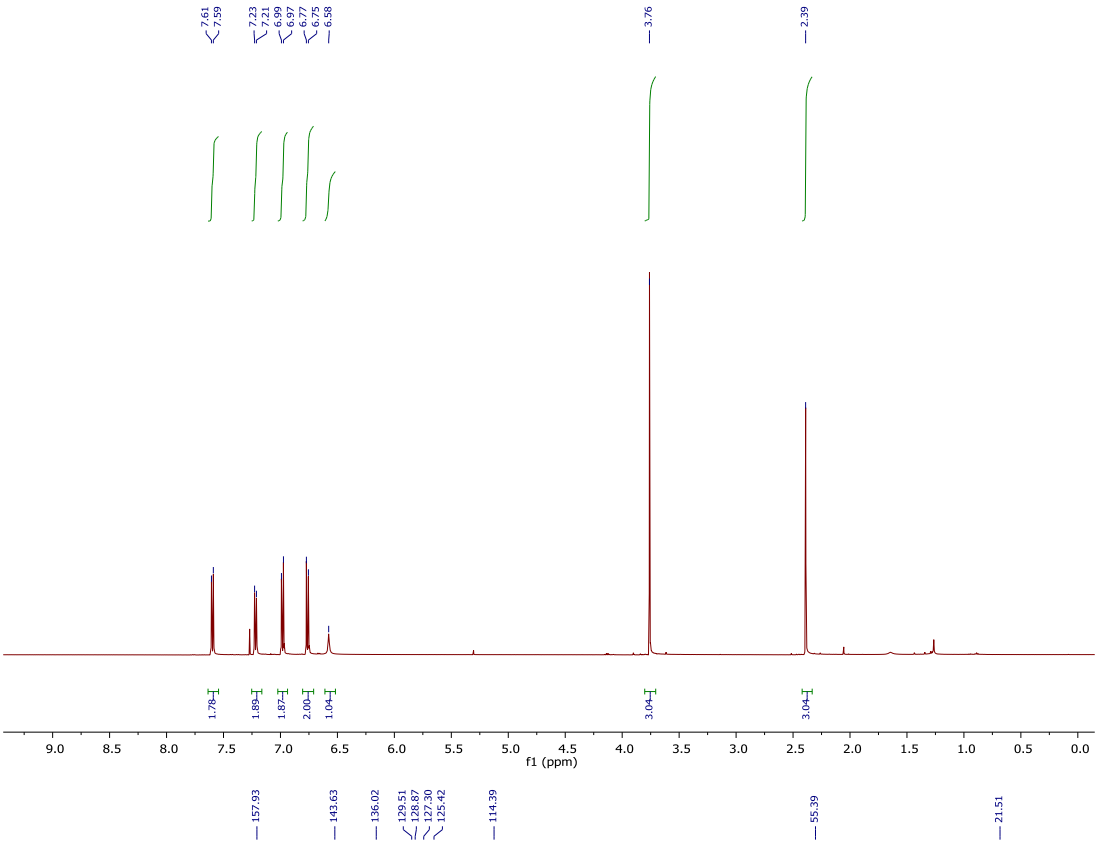


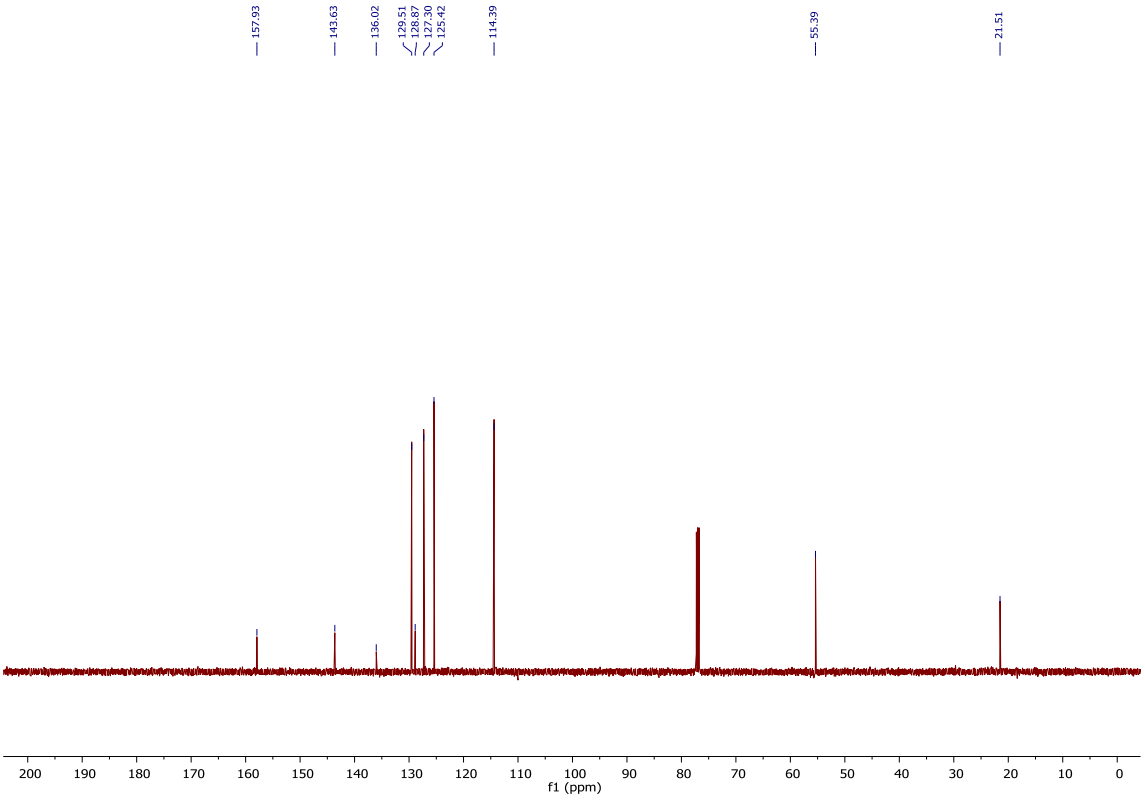




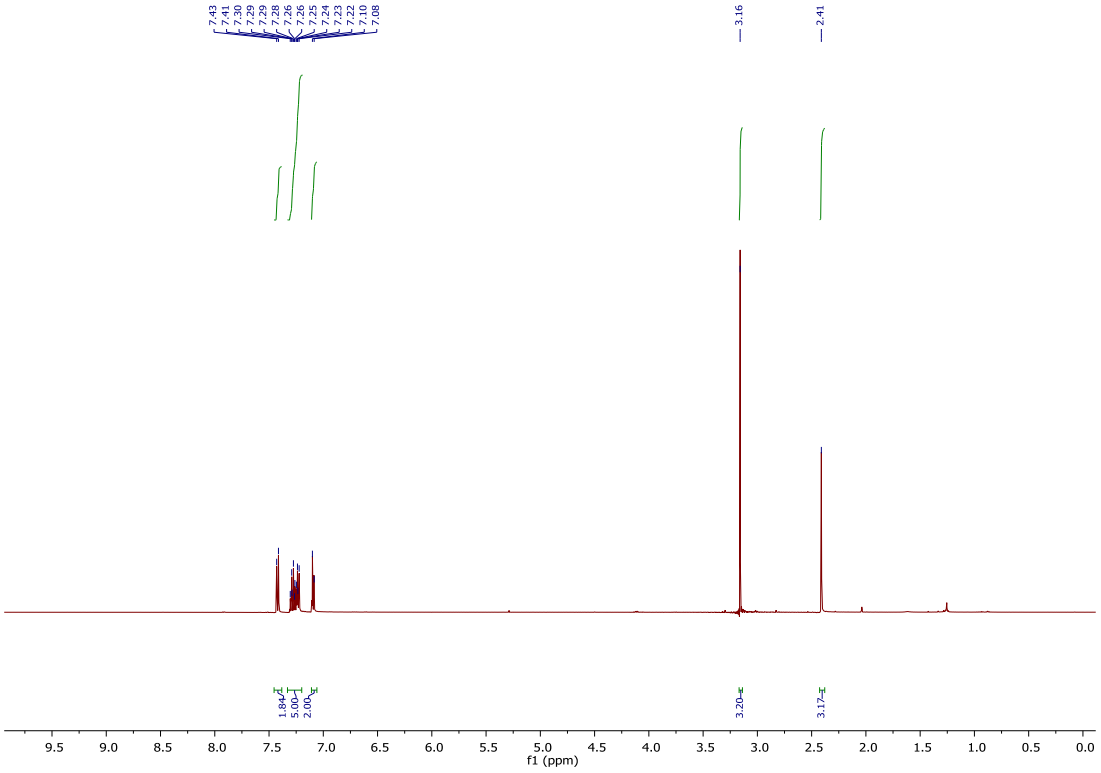
N-(4-Methoxyphenyl)-4-methylbenzenesulfonamide (6b)

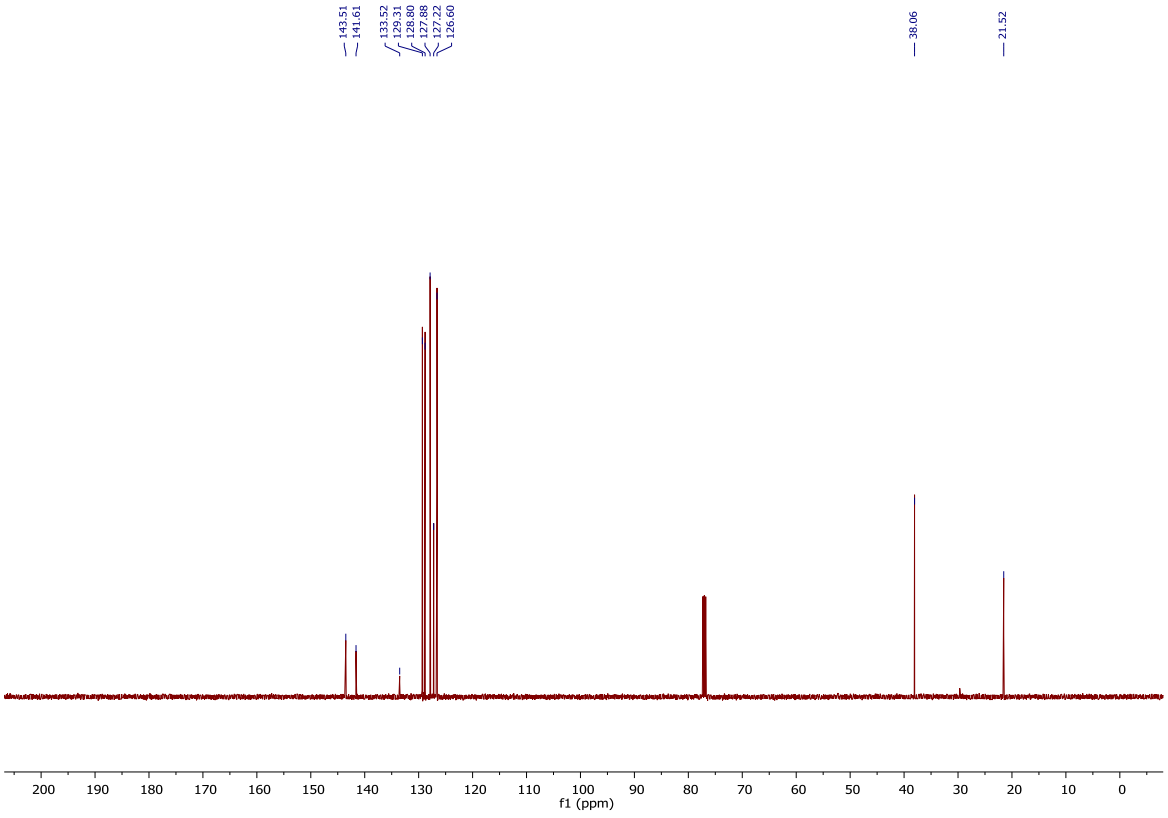




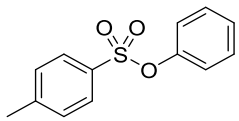


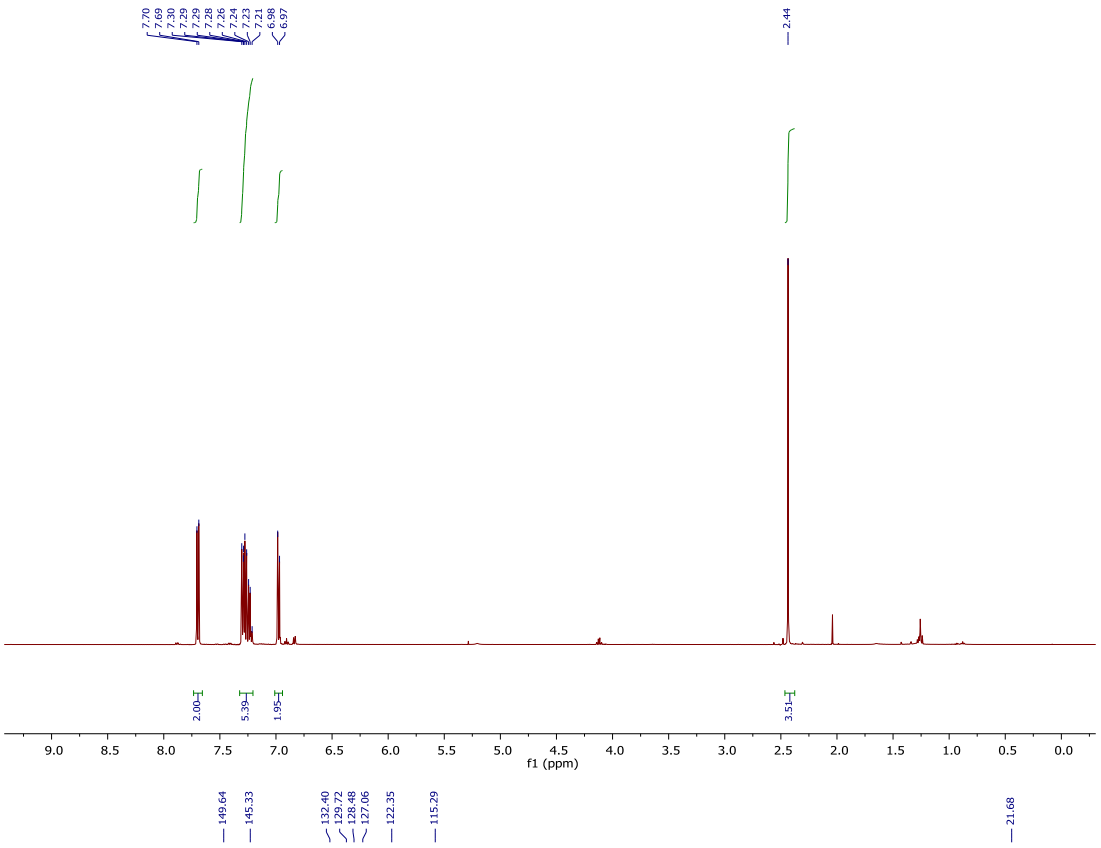
N,4-Dimethyl-*N*-phenylbenzenesulfonamide (6c)

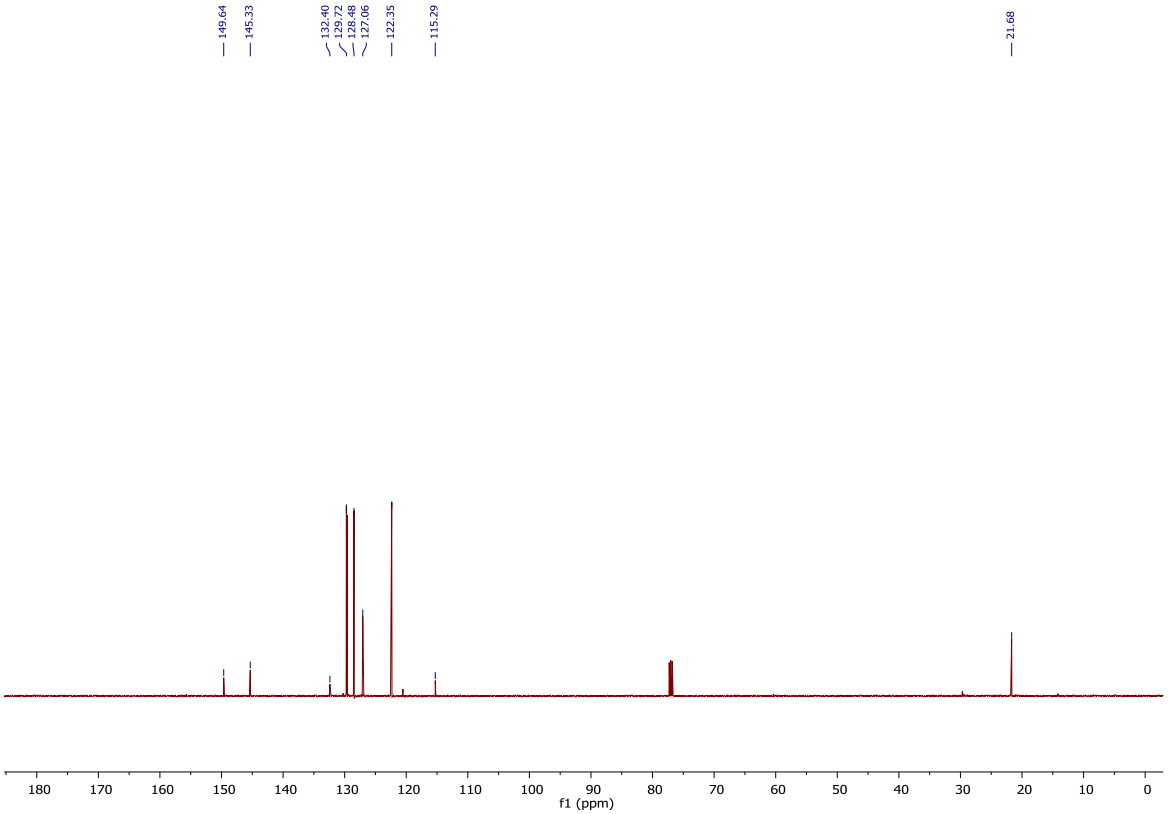




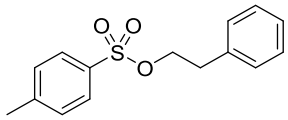
Phenyl-4-methylbenzenesulfonate (4k)

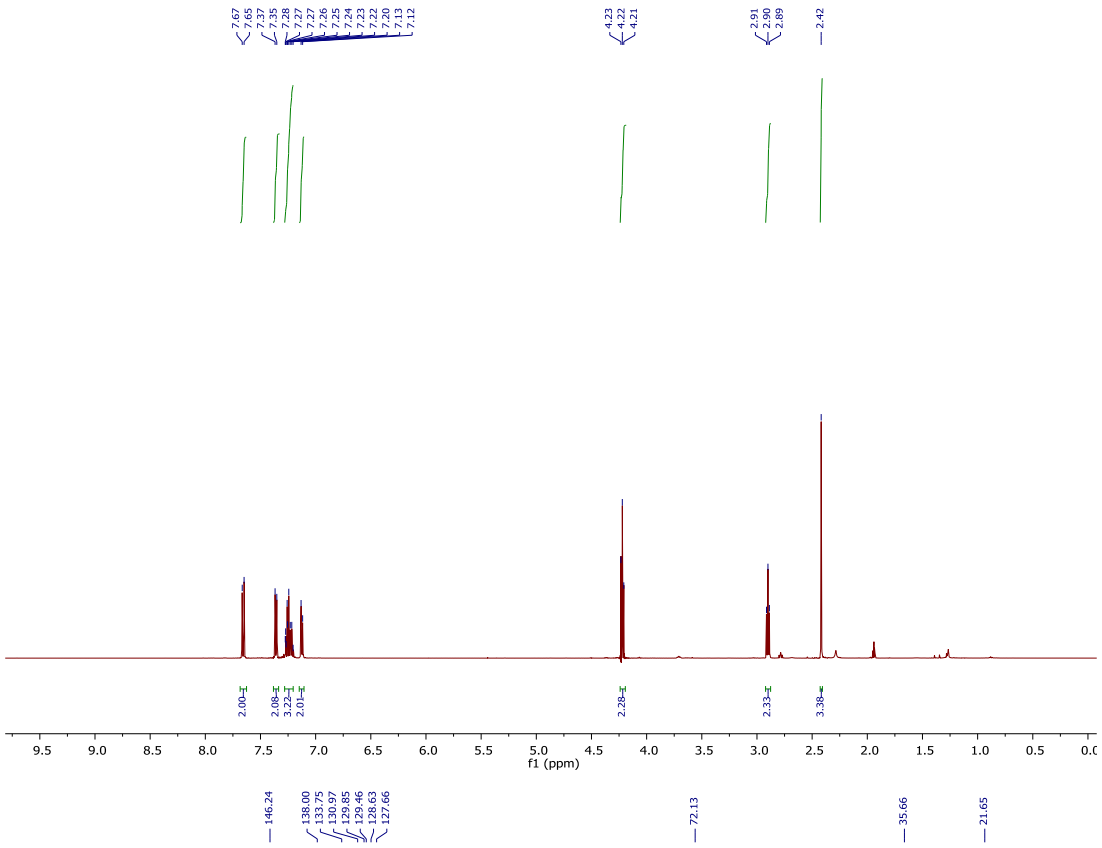


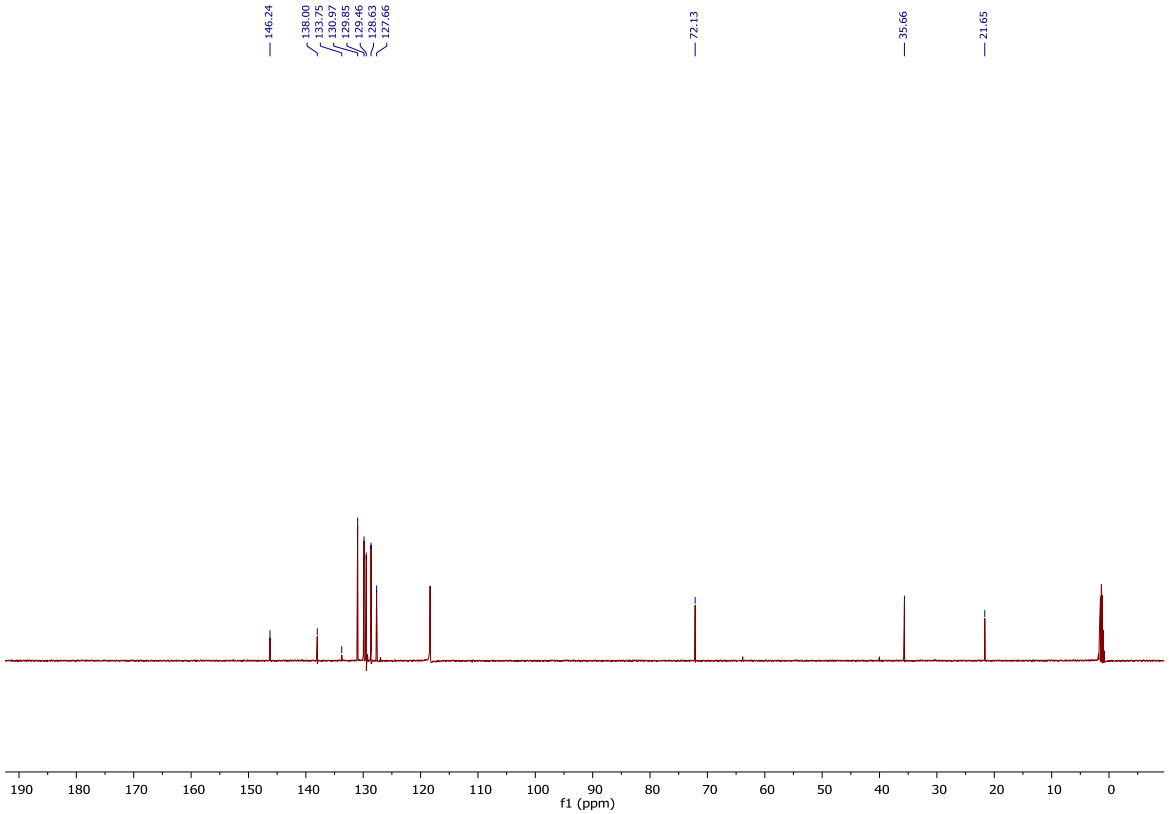




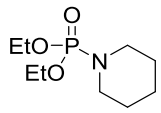
Phenethyl-4-methylbenzenesulfonate (6d)

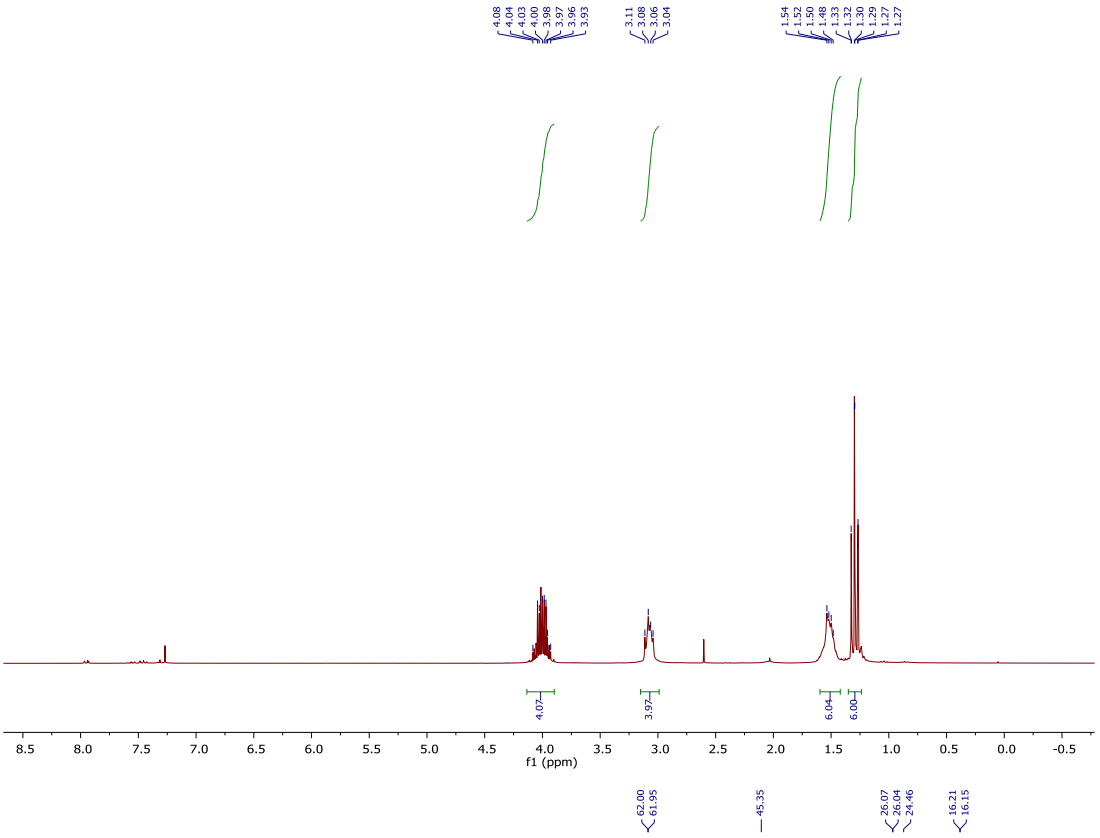


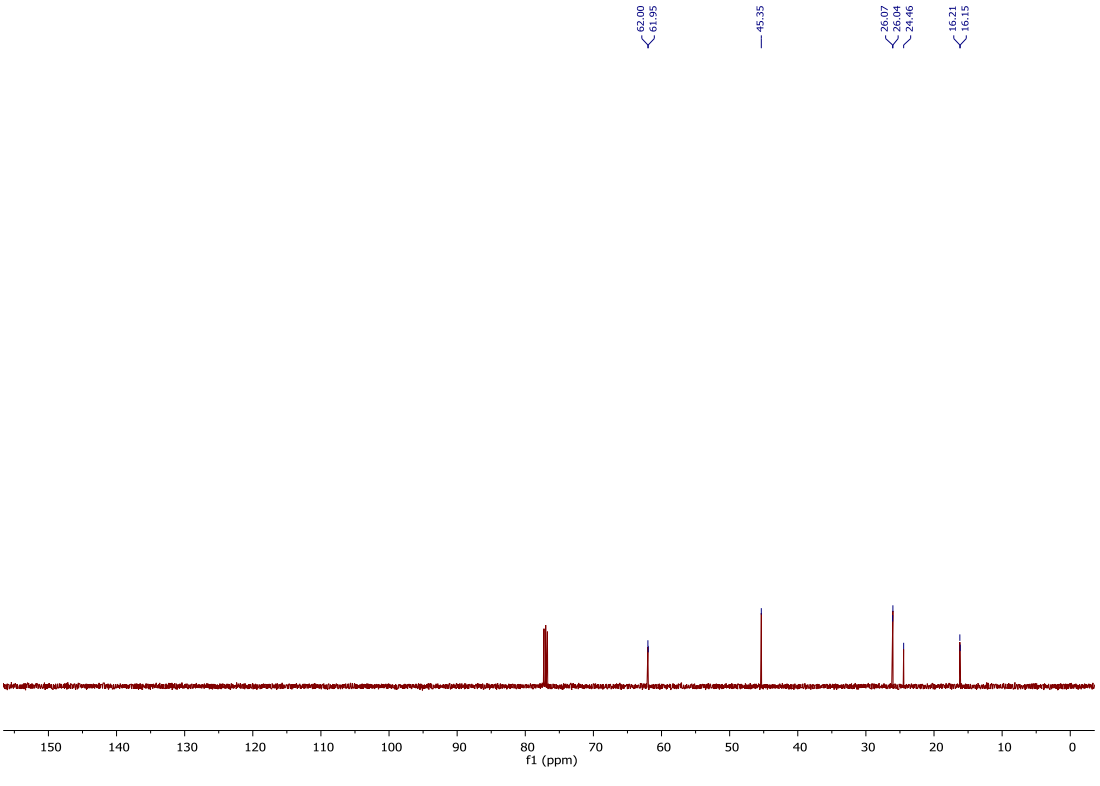




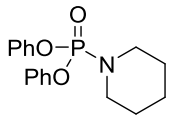
Diethyl piperidin-1-ylphoshonate (7a)

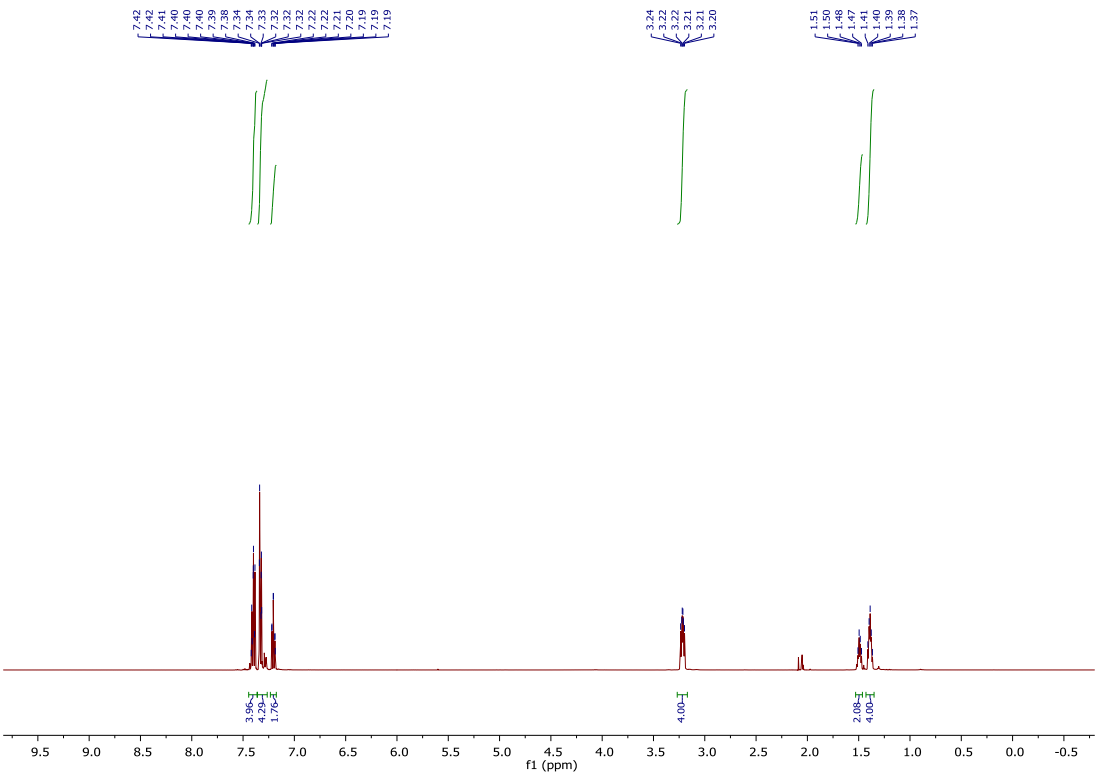


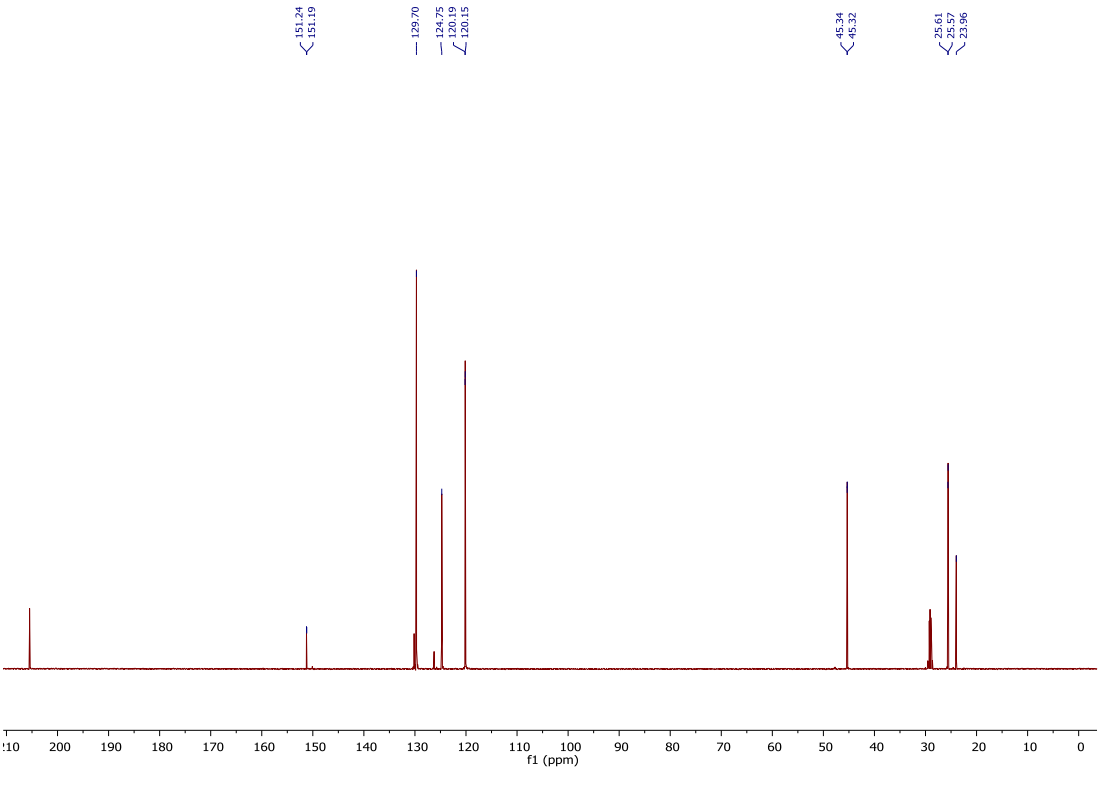




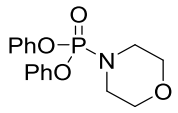
Diphenyl piperidin-1-ylphosphonate (7b)

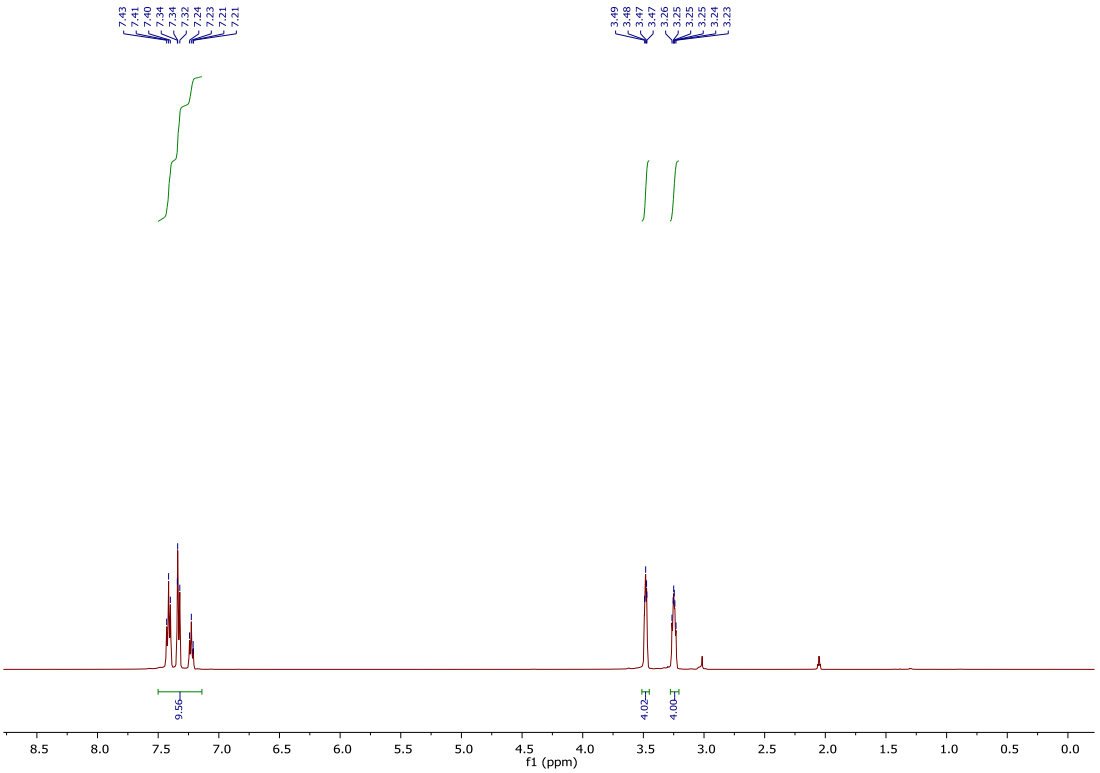


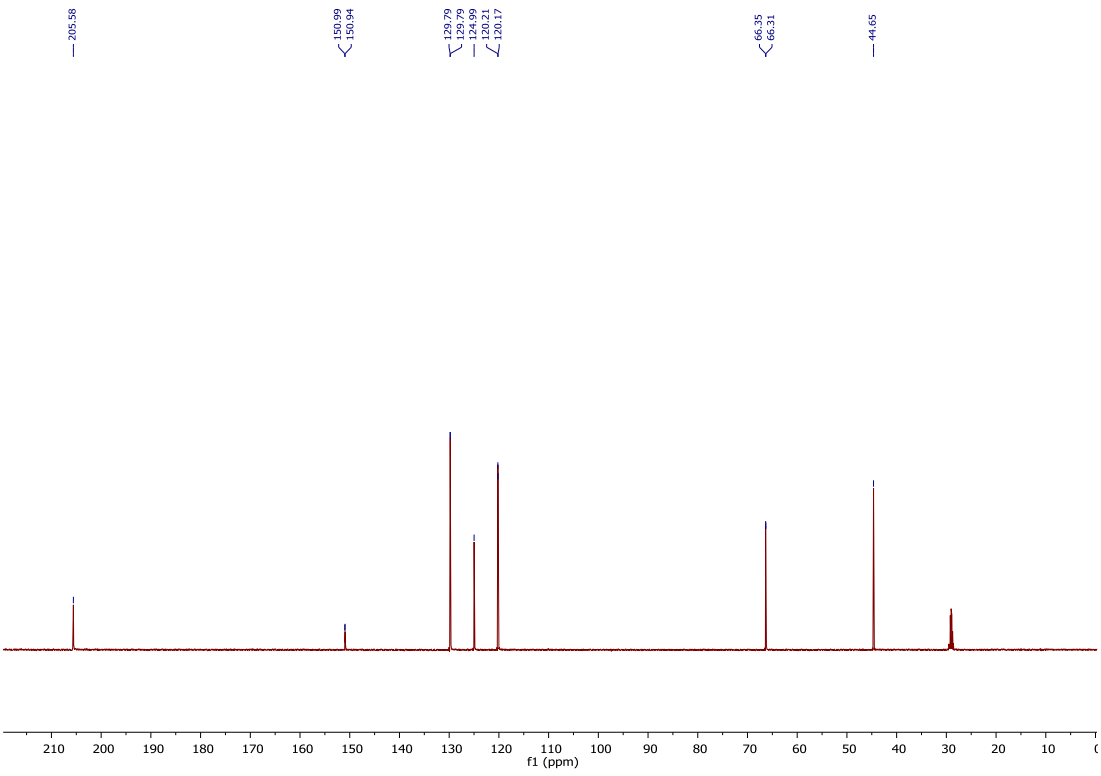




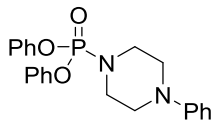
Diphenyl morpholinophosphonate (7c)

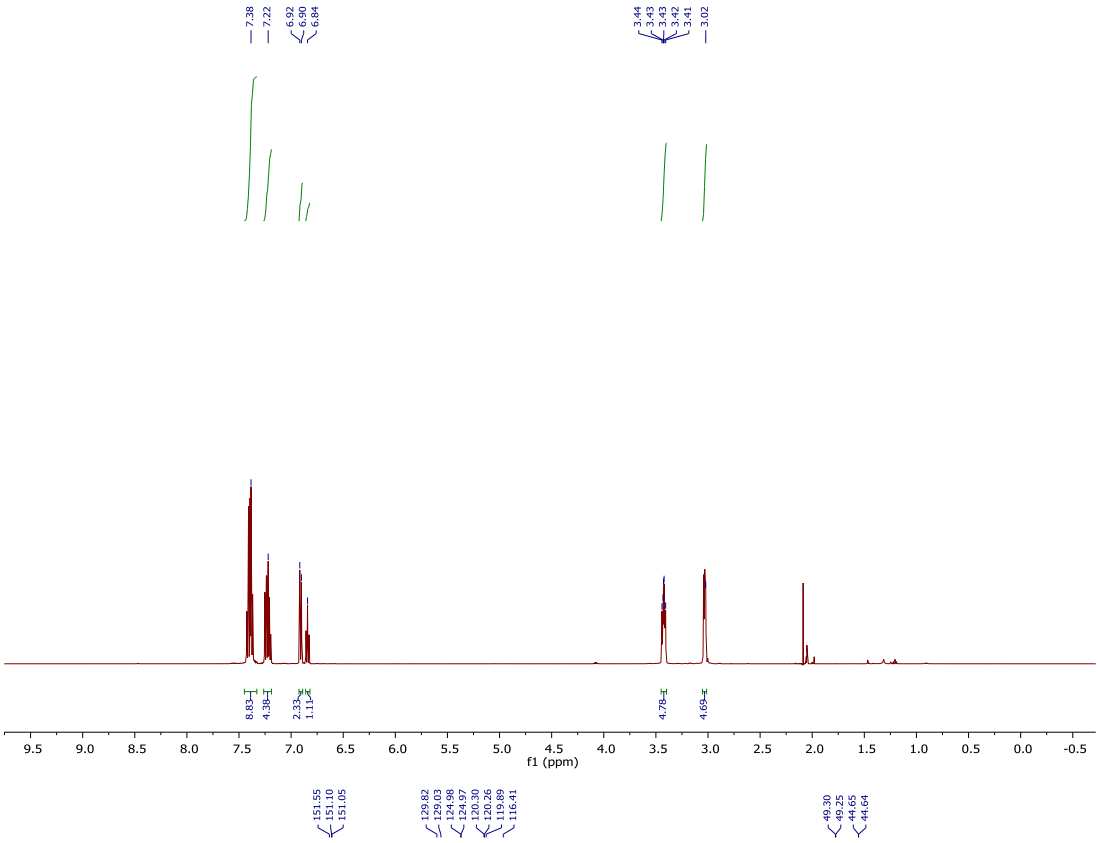


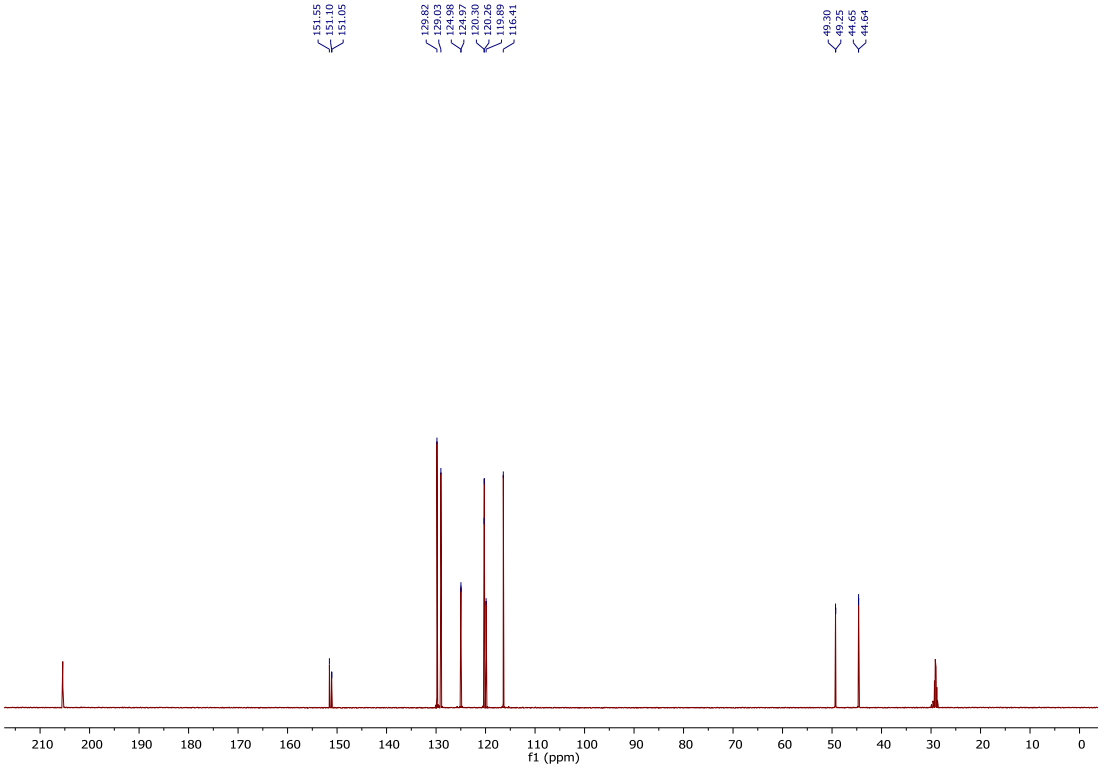




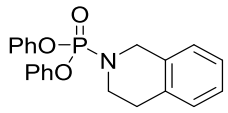
Diphenyl (4-phenylpiperazin-1-yl)phosphonate (7d)

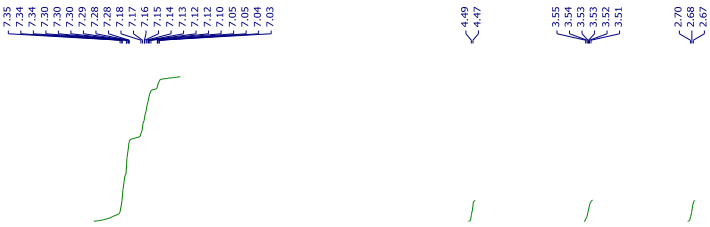


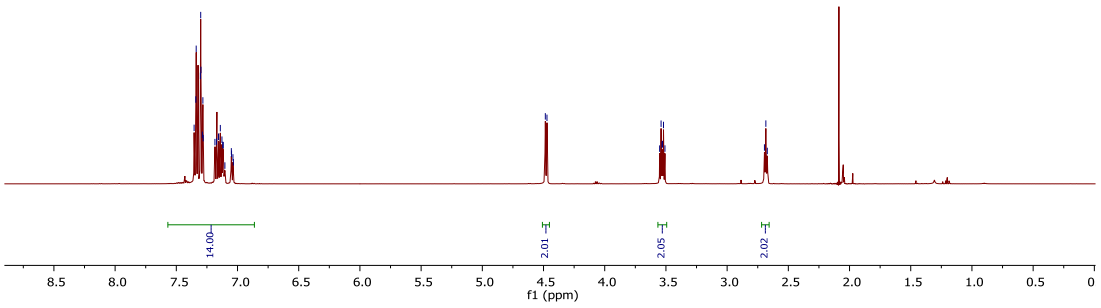


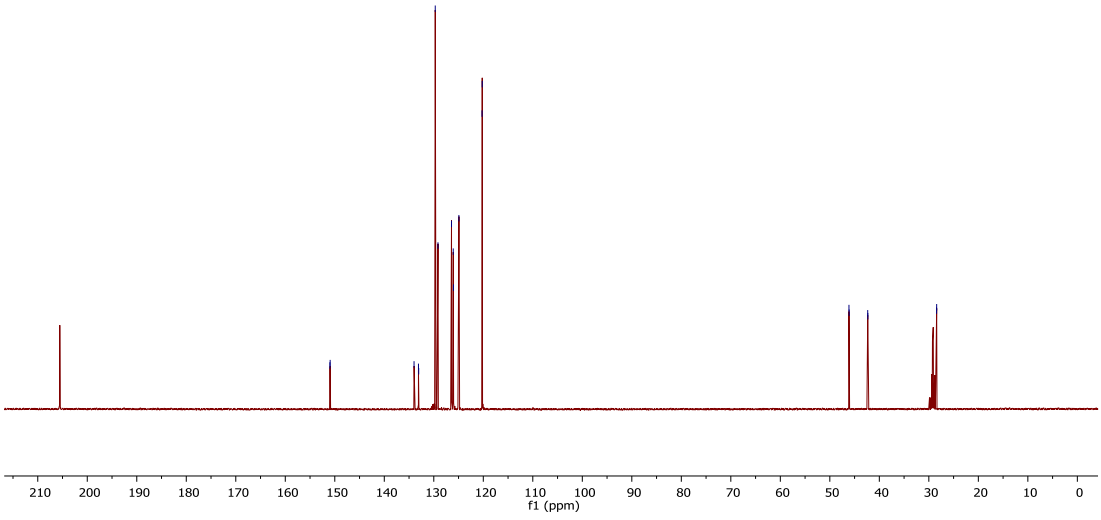


Diphenyl (1,2,3,4-tetrahydroisoquinoline-2-yl)phosphonate (7e)

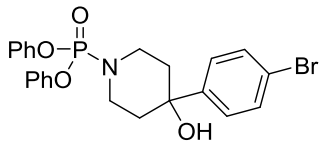


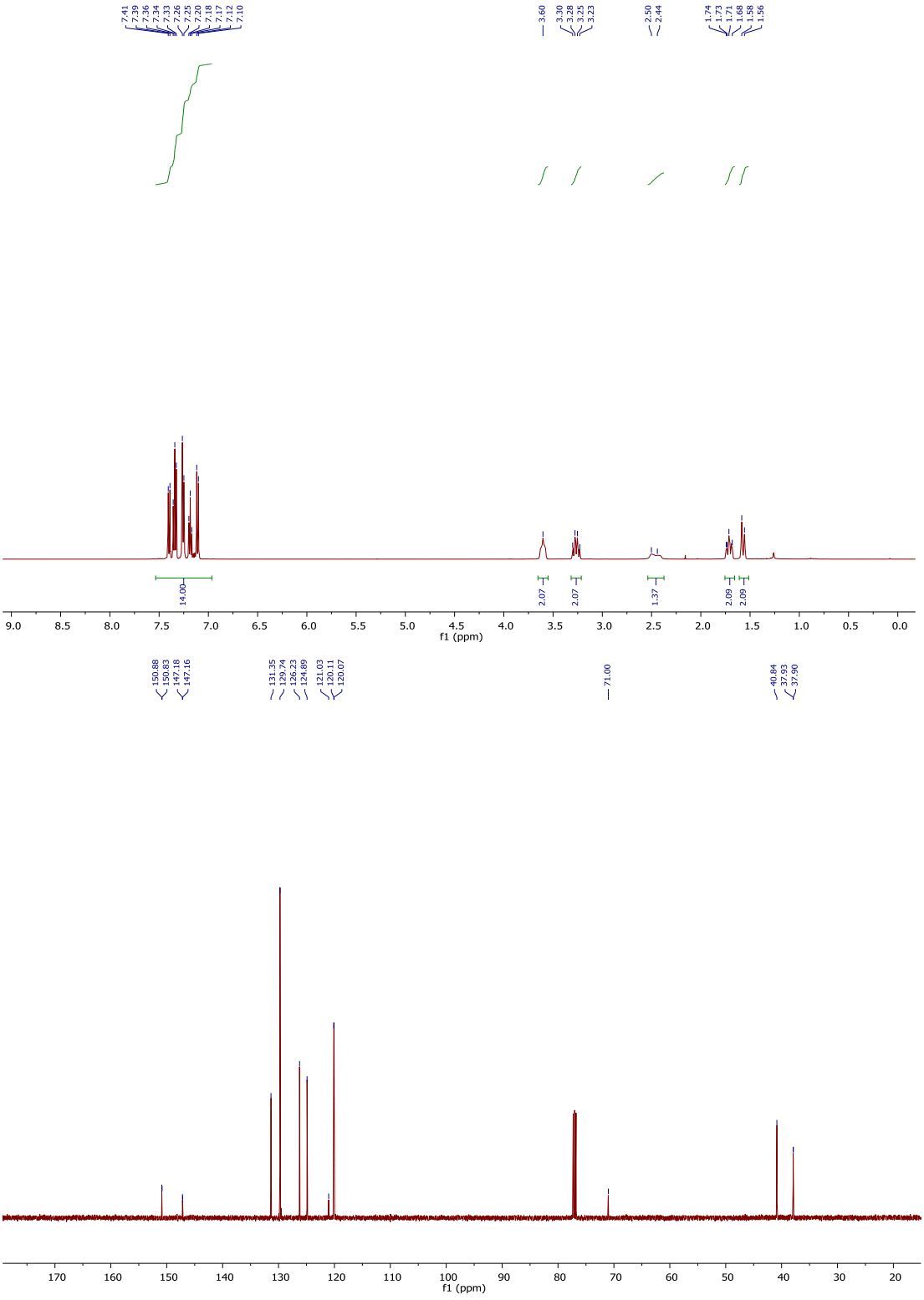




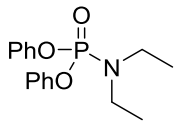


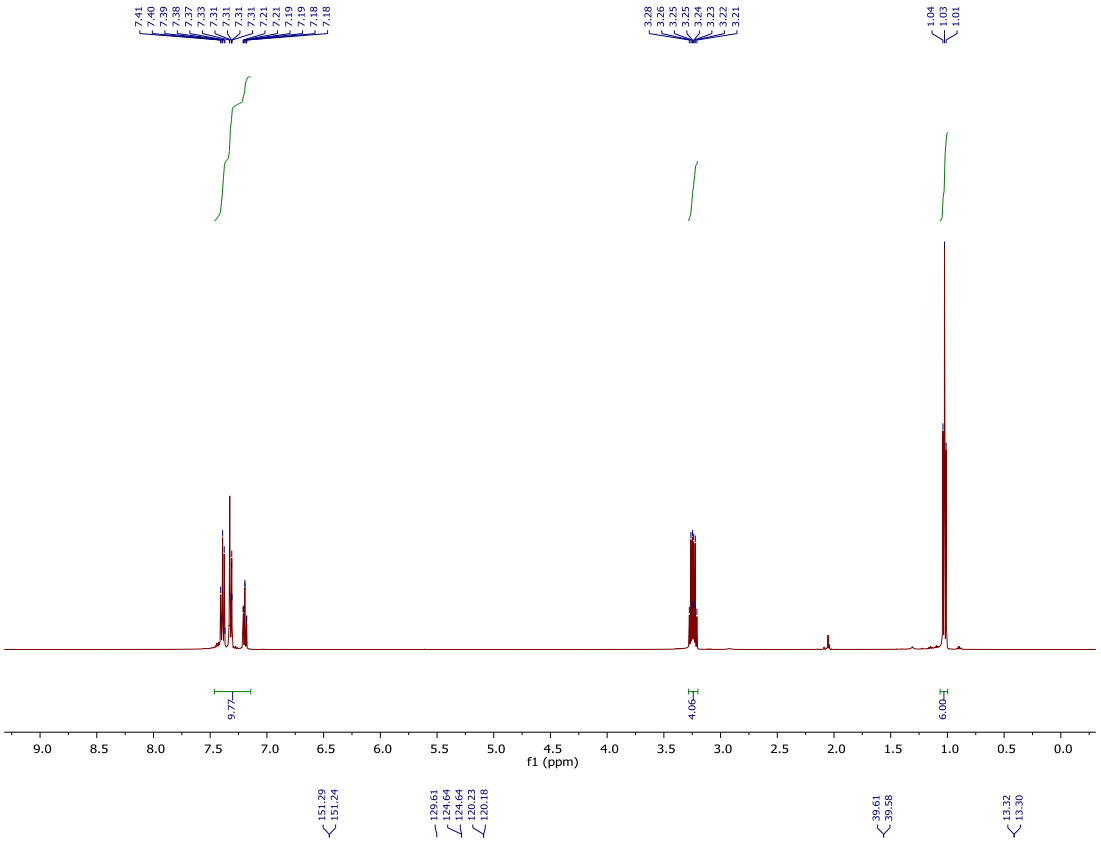
Diphenyl (4-(4-bromophenyl)-4-hydroxypiperidin-1-yl)phosphonate (7f)

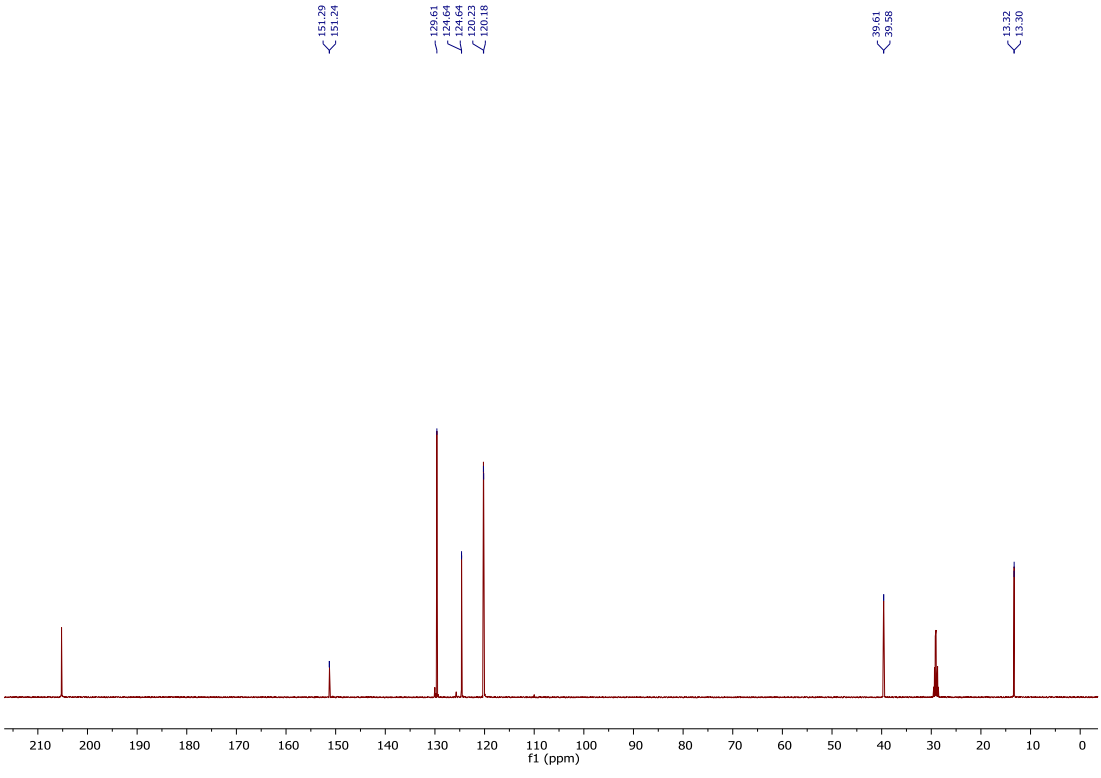




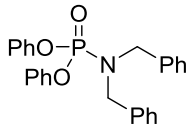
Diphenyl diethylphosphoramidate (7g)

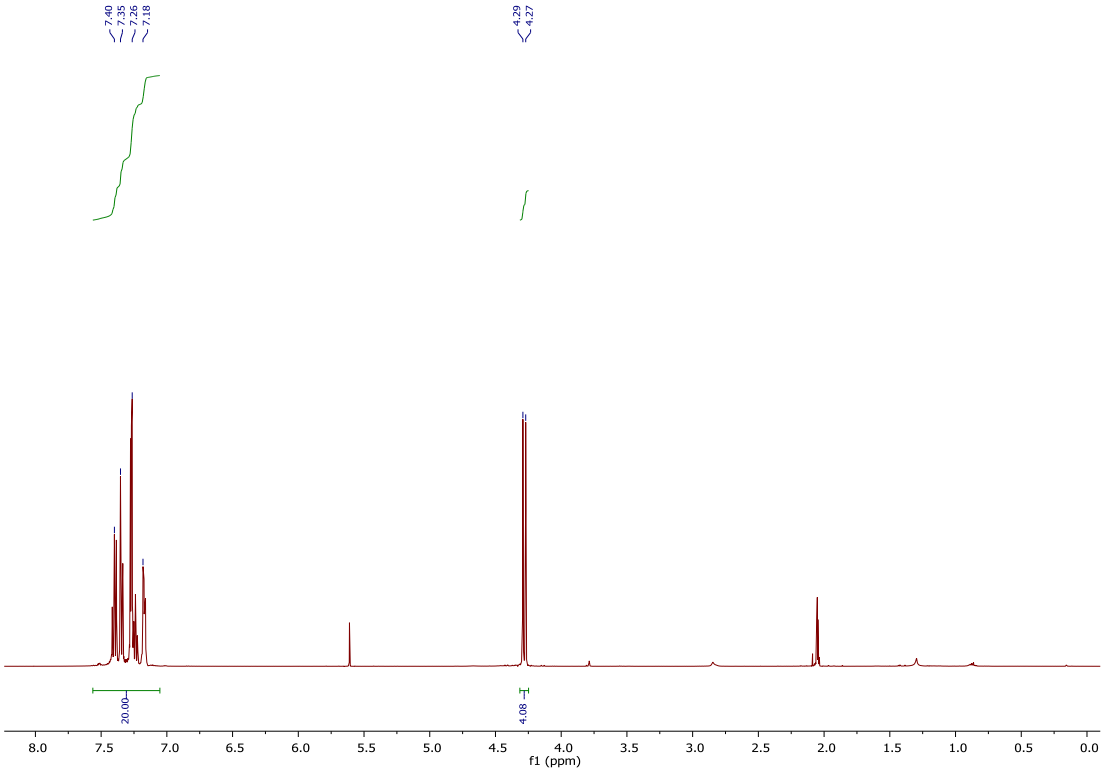


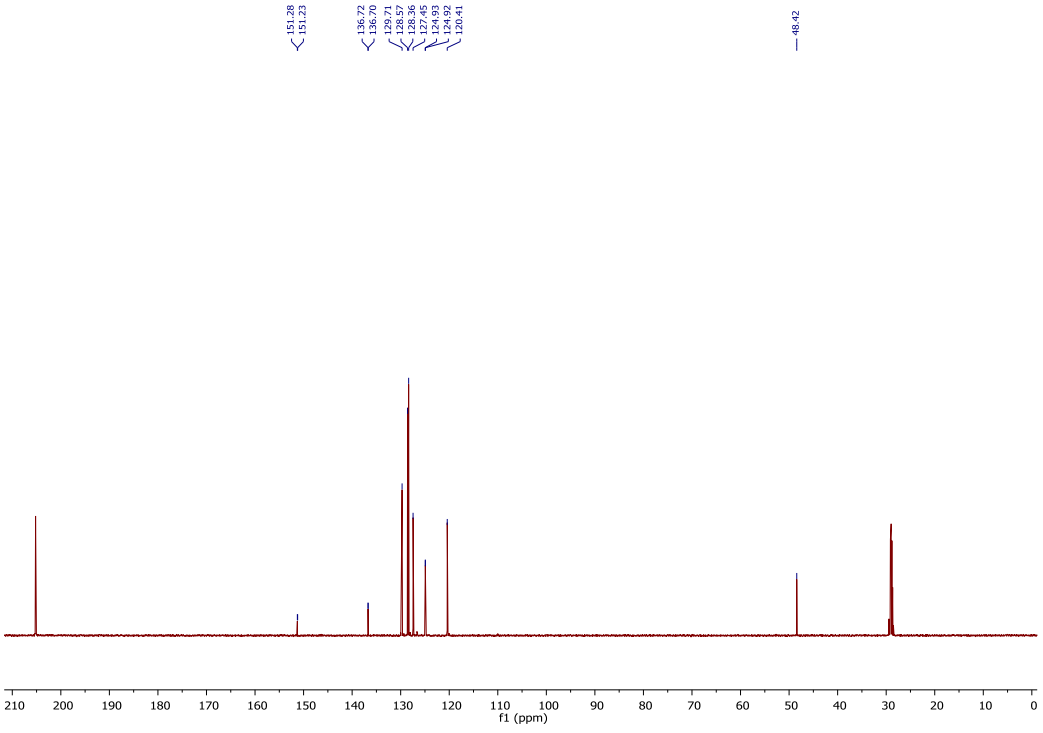




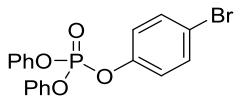
Diphenyl dibenzylphosphoramidate (7h)

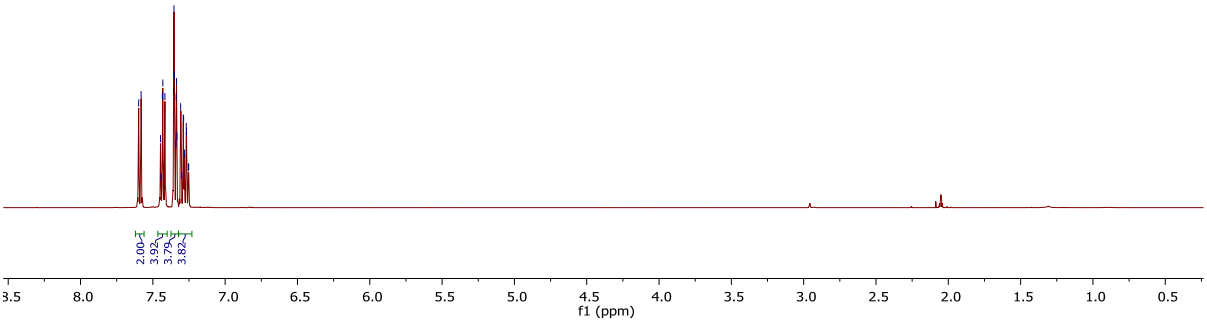


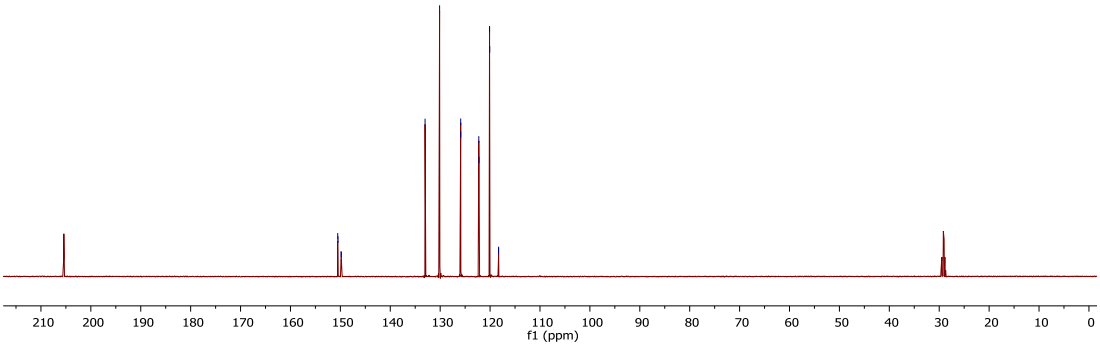




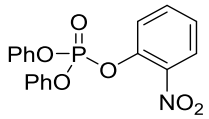
4-Bromophenyl diphenylphosphate (7i)

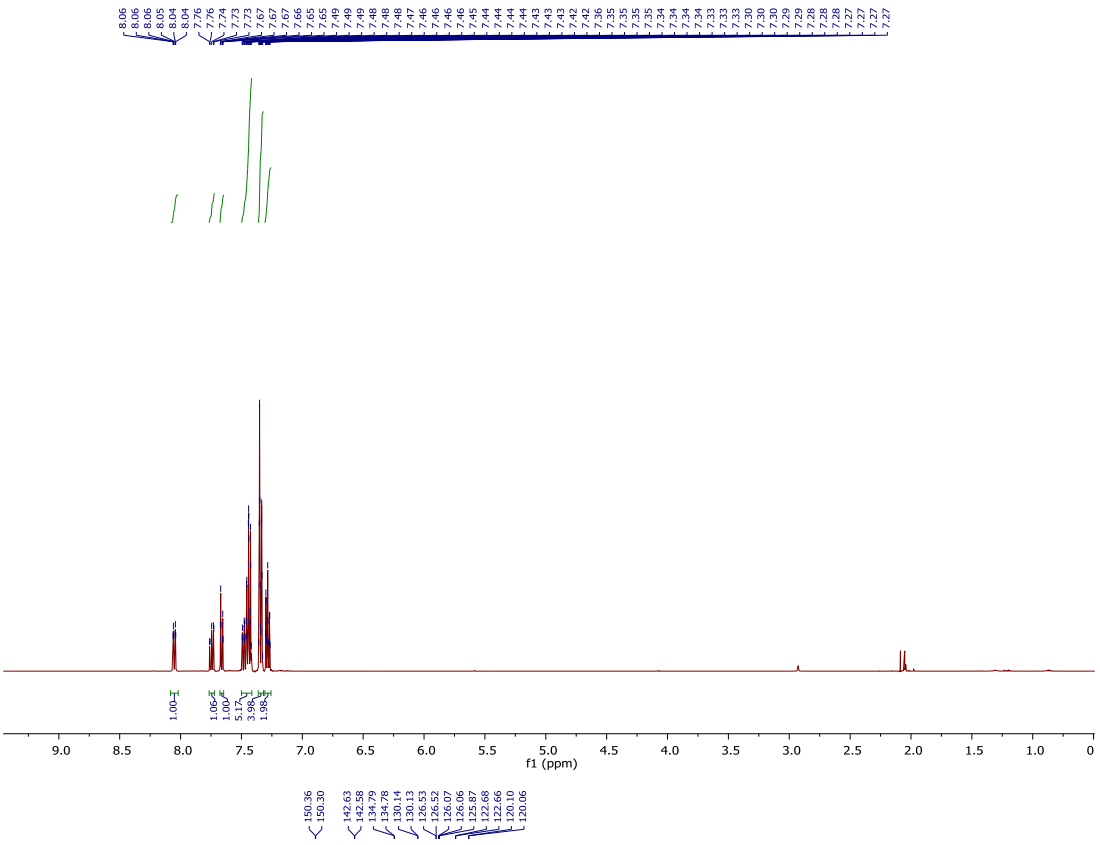


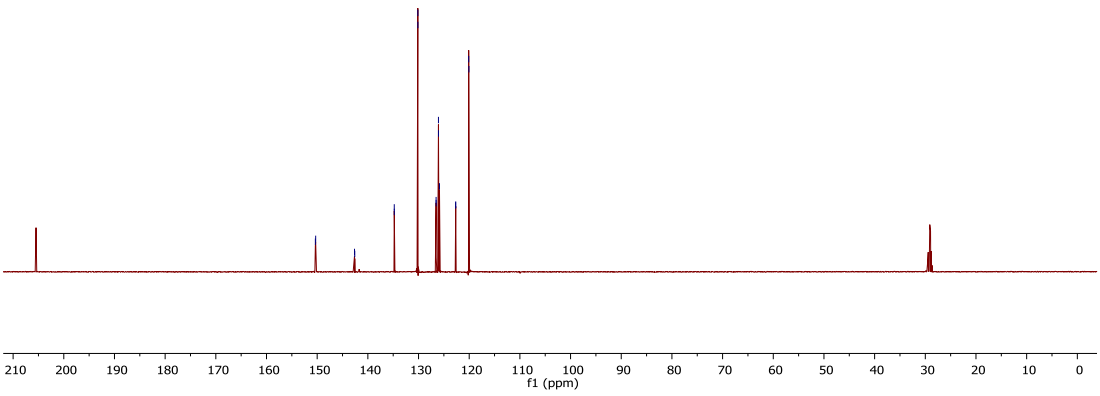




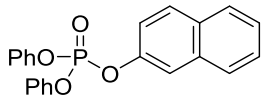
2-Nitrophenyl diphenylphosphate (7j)

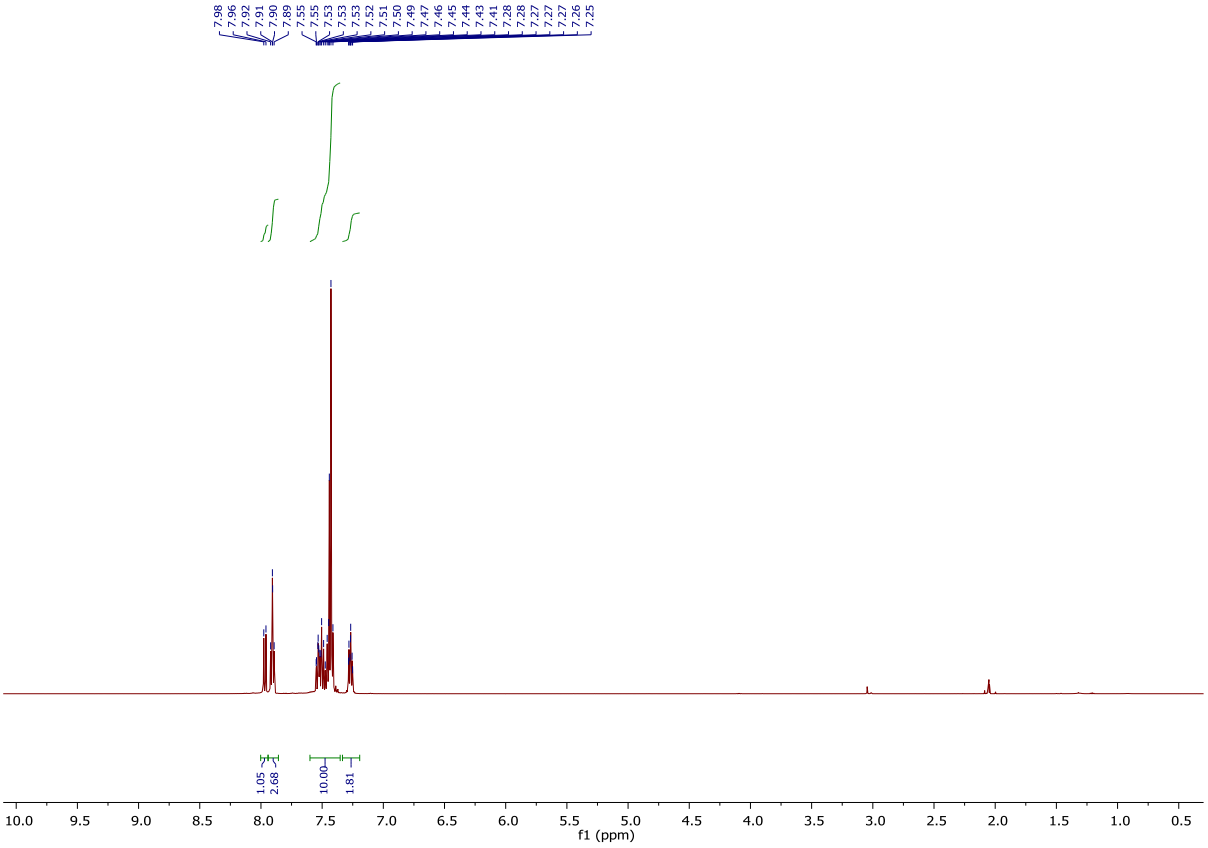


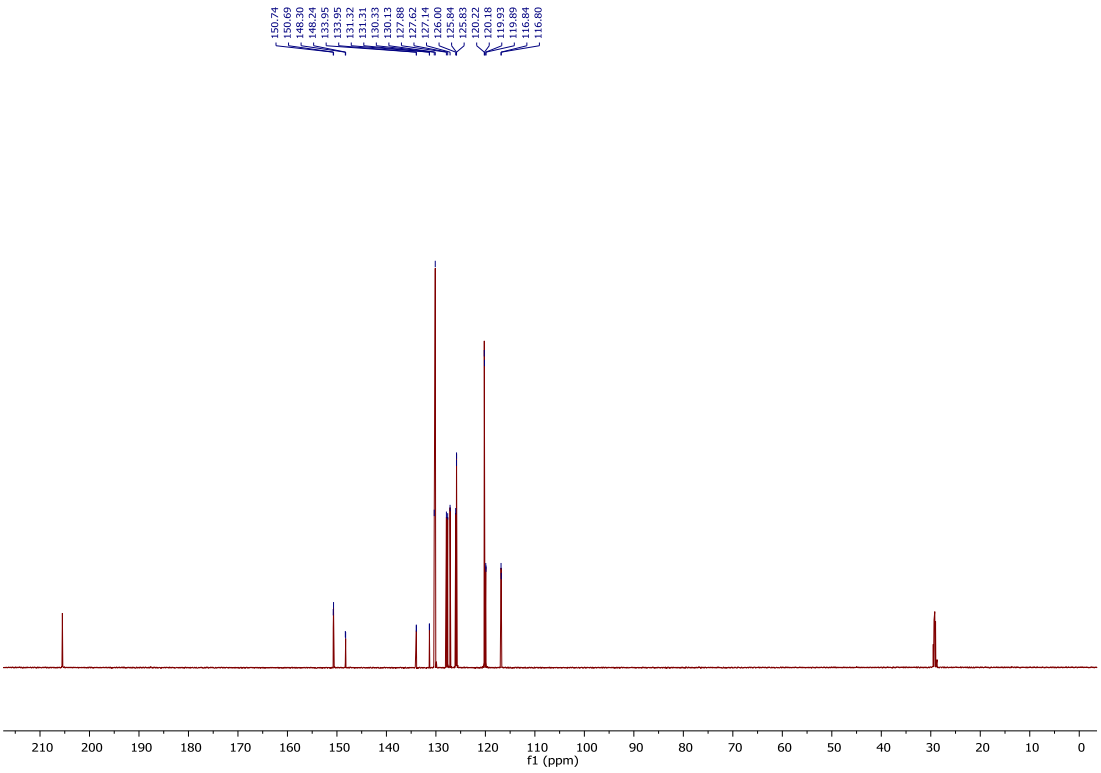




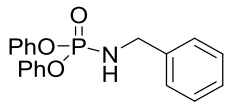
Naphthalen-2-yl diphenylphosphate (7k)

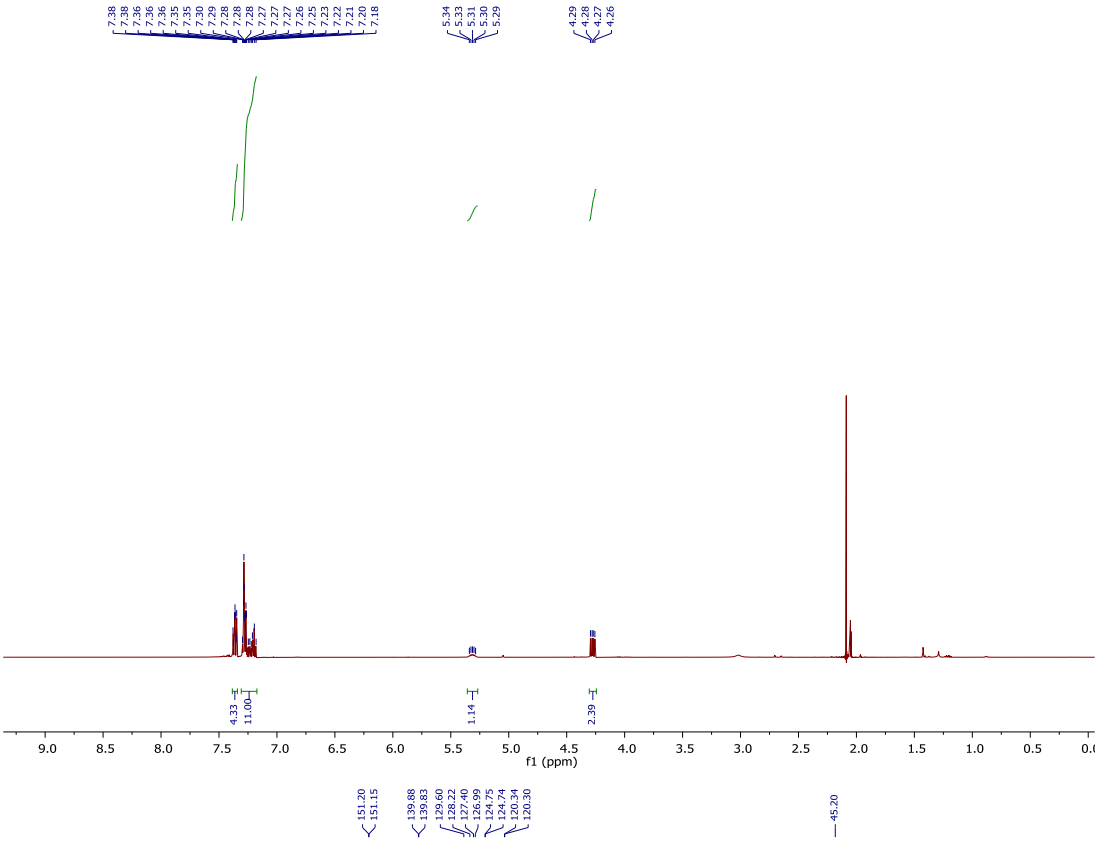


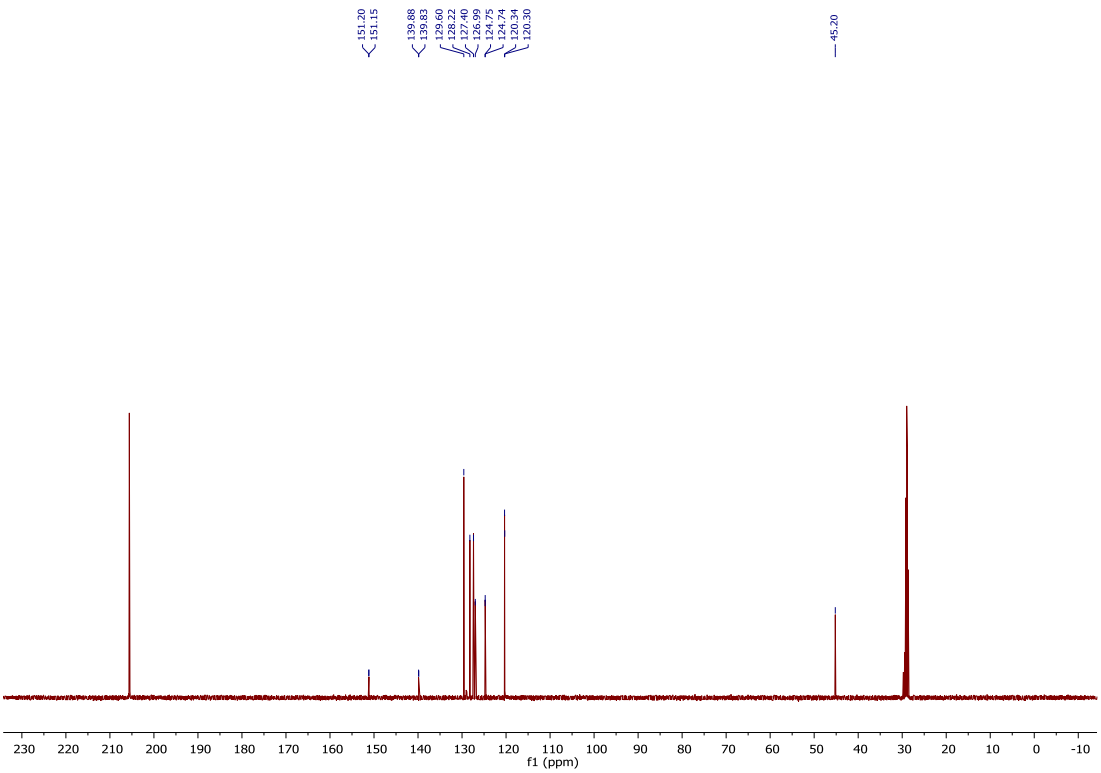




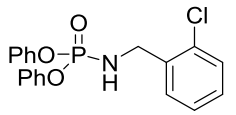
Diphenyl benzylphosphoramidate (8a)

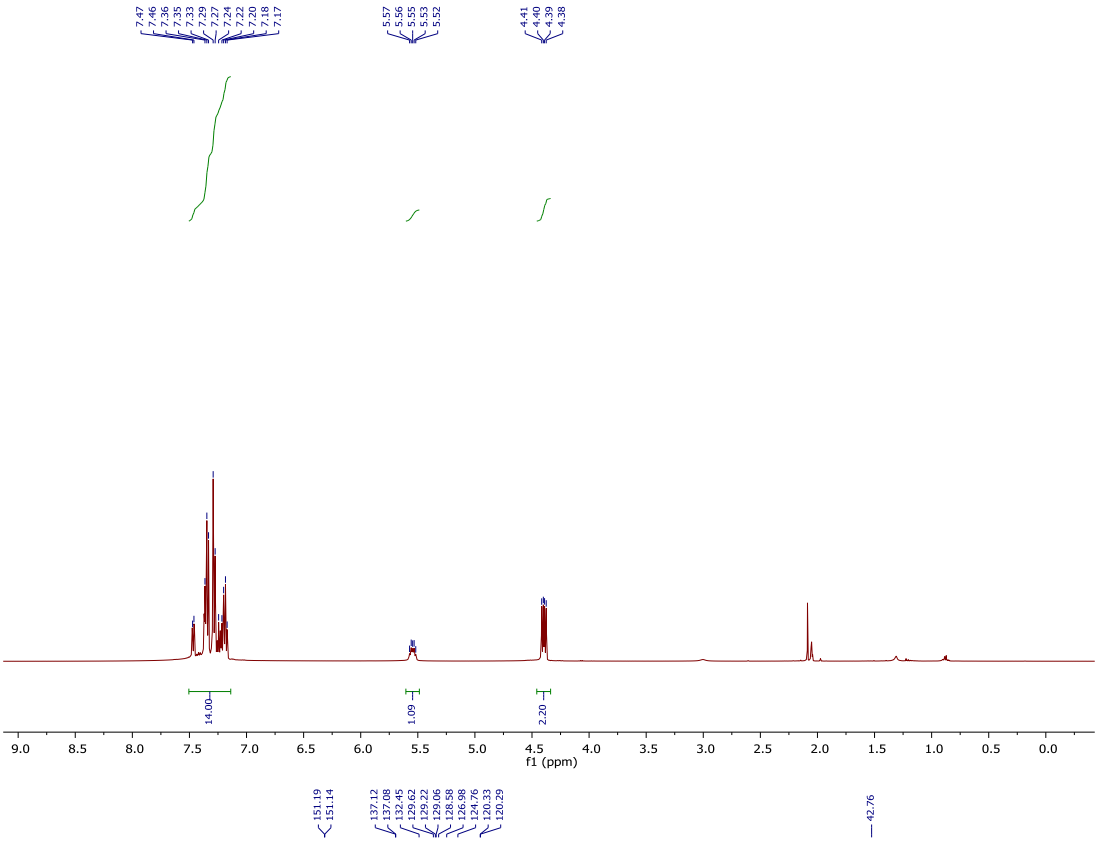


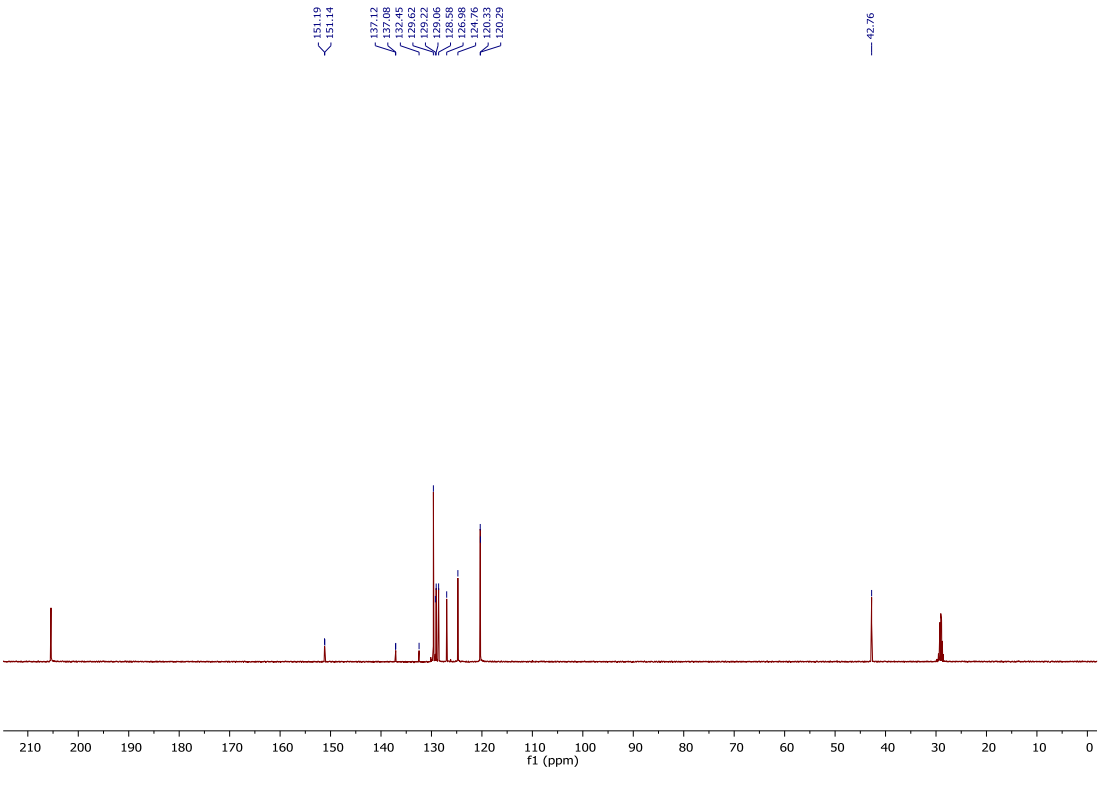




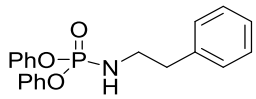
Diphenyl (2-chlorobenzyl)phosphoramidate (8b)

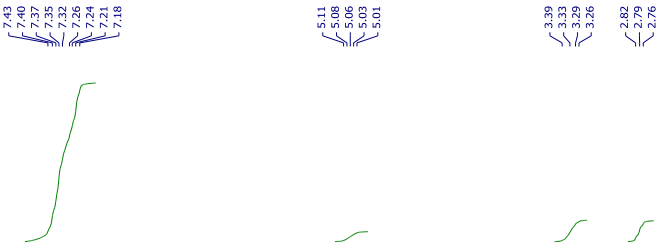


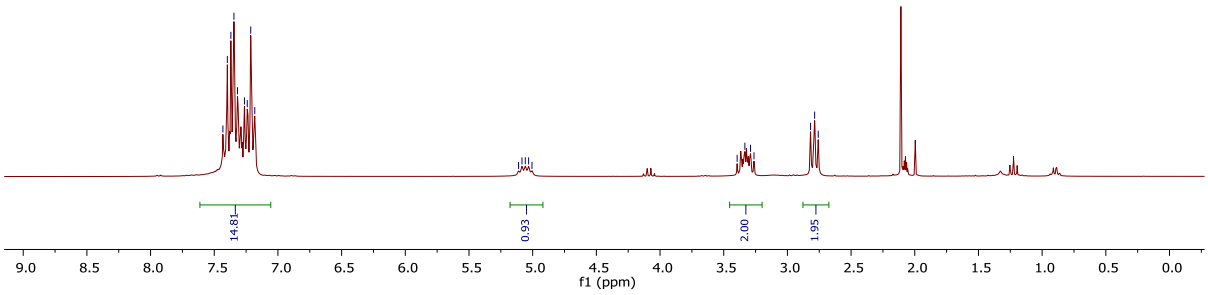


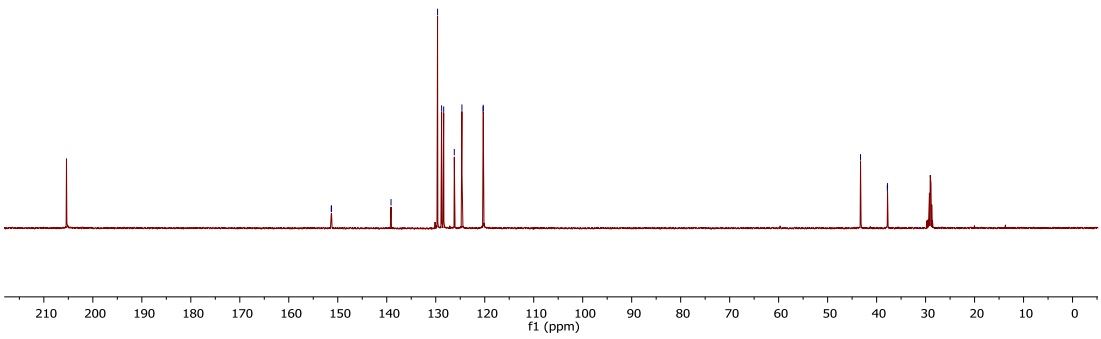


Diphenyl phenethylphosphoramidate (8c)

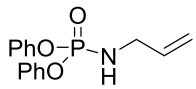


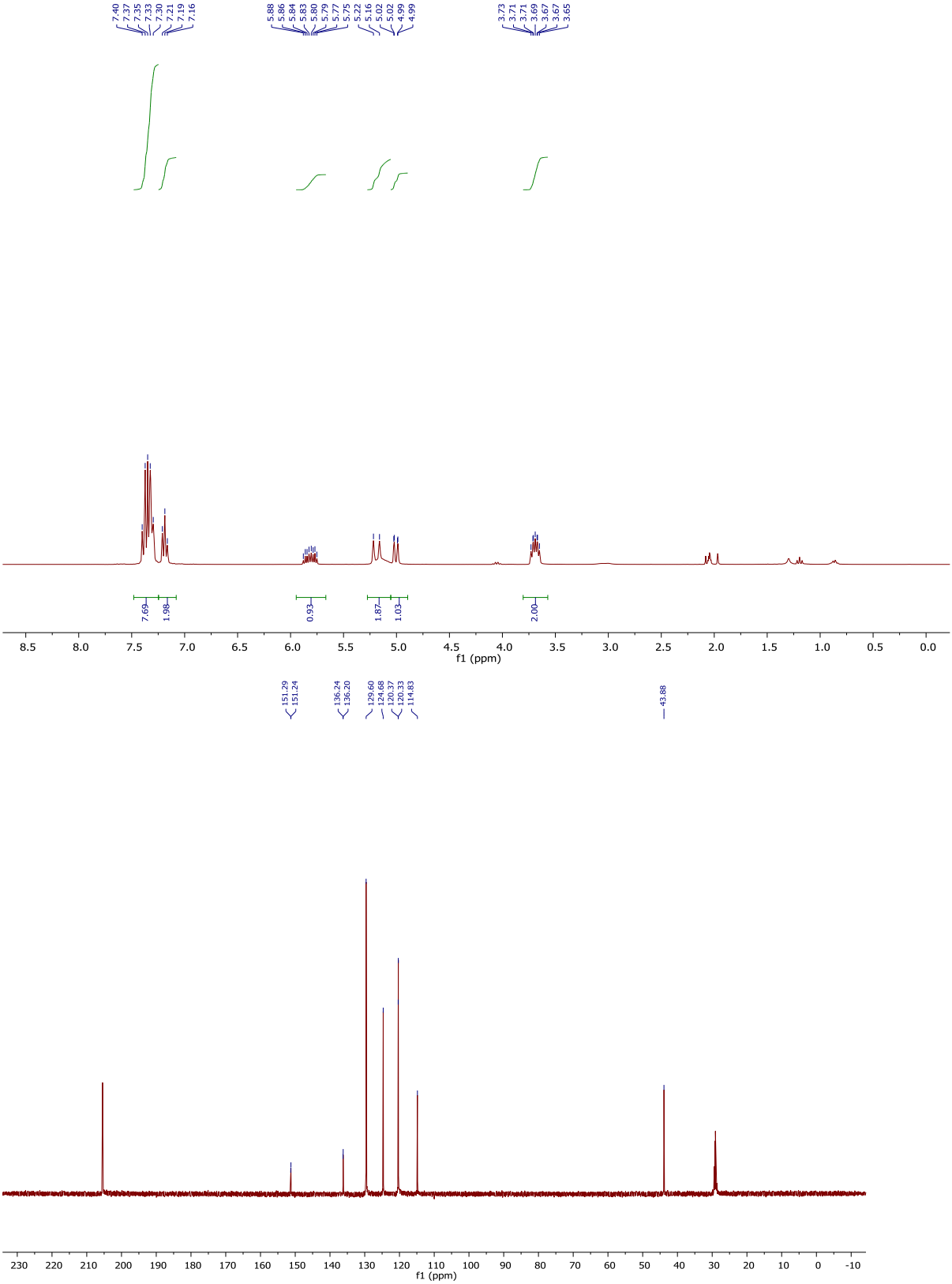






Diphenyl allylphosphoramidate (8d)





References

1. W. Shi, C. M. Bai, K. Zhu, D. M. Cui, and C. Zhang, *Tetrahedron*, 2014, **70**, 434-438.
2. N. M. Vinokurova and I. K. Fel'dman, *Pharm. Chem.*, 1968, **2**, 561-563.
3. G. Zhou, P. Ting, R. Aslanian and J. J. Piwinski, *Org. Lett.*, 2008, **10**, 2517-2520.
4. R. Sridhar, B. Srinivas, V. P. Kumar, M. Narender and K. R. Rao, *Adv. Synth. Catal.*, 2007, **349**, 1873-1876.
5. D. Prelog, *Collect. Czech. Chem. Commun.*, 1933, **5**, 497-501.
6. H. Yamamoto, G. Pandey, Y. Asai, M. Nakano, A. Kinoshita, K. Namba, H. Imagawa and M. Nishizawa, *Org. Lett.*, 2007, **9**, 4029-4032.
7. M. Inman, A. Carbone and C. J. Moody, *J. Org. Chem.*, 2012, **77**, 1217-1232.
8. A. García-Rubia, B. Urones, R. Gómez Arrayás and J. C. Carretero, *Angew. Chem. Int. Ed.*, 2011, **50**, 10927-10931.
9. J. Huang, W. Xu, H. Xie and S. Li, *J. Org. Chem.*, 2012, **77**, 7506-7511.
10. J. K. Laha, K. P. Jethava and N. Dayal, *J. Org. Chem.*, 2014, **79**, 8010-8019
11. D. Zim, V. R. Lando, J. Dupont and A. L. Monteiro, *Org. Lett.*, 2001, **3**, 3049-3051.
12. X. Lei, A. Jalla, M. A. Abou Shama, J. M. Stafford and B. Cao, *Synthesis*, 2015, **47**, 2578-2585.
13. Y. Vida and E. Perez-Inestrosa, *Photochem. Photobiol. Sci.*, 2012, **11**, 1645-1651.
14. O. R'Kyek, N. Halland, A. Lindenschmidt, J. Alonso, P. Lindemann, M. Urmann and M. Nazaré, *Chem. Eur. J.*, 2010, **16**, 9986-9989.
15. P. Qu, C. Sun, J. Ma and F. Li, *Adv. Synth. Catal.*, 2014, **356**, 447-459.
16. W. Zhang, J. Xie, B. Rao and M. Luo, *J. Org. Chem.*, 2015, **80**, 3504-3511.
17. J. K. Laha, K. P. Jethava and N. Dayal, *J. Org. Chem.*, 2014, **79**, 8010-8019.
18. M. E. Sergeev, F. Morgia, M. Lazari, C. Wang, and R. M. van Dam, *J. Am. Chem. Soc.*, 2015, **137**, 5686-5694.
19. I. L. Reich, A. F. Diaz and S. Winstein, *J. Am. Chem. Soc.*, 1972, **94**, 2256-2262.
20. J. Dhineshkumar and K. R. Prabhu, *Org. Lett.*, 2013, **15**, 6062-6065.
21. J. A. Stock, W. J. Hopwood and P. D. Regan, *J. Chem. Soc. (C)*, 1966, 637-639.
22. J. I. Murray, R. Woscholski and A. C. Spivey, *Synlett*, 2015, **26**, 985-990.
23. L. Wang, C. Du, X. Wang, H. Zeng, J. Yao, and B. Chen, *J. Chem. Eng. Data*, 2015, **60**, 1814-1822.
24. S. J. Benkovic, E. J. Sampson, *J. Am. Chem. Soc.*, 1971, **93**, 4009-4016.
25. R. S. Edmundson and T. A. Moran, *J. Chem. Soc. (C)*, 1970, 1009-1012.