

SUPPORTING INFORMATION

Highly Chemoselective NH- and O-Transfer to Thiols Using Hypervalent Iodine Reagents: Synthesis of Sulfonimides and Sulfonamides

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General Experimental Considerations:

All non-aqueous reactions were run under an inert atmosphere (argon) using standard techniques. Anhydrous solvents were obtained by filtration through drying columns (THF, diethyl ether, CH_2Cl_2).

Flash column chromatography was performed using 230-400 mesh silica and 70-230 mesh neutral Al_2O_3 with the indicated solvent system according to standard techniques. Analytical thin-layer chromatography (TLC) was performed on precoated, glass-backed silica gel plates. Visualization of the developed chromatogram was performed by UV absorbance (254 nm), or aqueous potassium permanganate or ninhydrin in ethanol stains.

Infrared spectra (FTIR) were recorded in reciprocal centimeters (cm^{-1}).

Nuclear magnetic resonance spectra were recorded on 300, 400, 500 and 700 MHz spectrometers. Chemical shifts for ^1H NMR spectra are recorded in parts per million from tetramethylsilane with the solvent resonance as the internal standard (chloroform, $\delta = 7.27$ ppm, acetone, $\delta = 2.05, 2.84$ ppm and methanol $\delta = 3.31, 4.87$ ppm, DMSO $\delta = 2.50$). Data were reported as follows: chemical shift [integration, multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet and bs = broad signal), coupling constant in Hz]. ^{13}C NMR spectra were recorded with complete proton decoupling. Chemical shifts are reported in parts per million from tetramethylsilane with the solvent resonance as the internal standard ($^{13}\text{CDCl}_3$: 77.00 ppm, $^{13}\text{CD}_3\text{OD}$: 49.00 ppm and $^{13}\text{C}_3\text{D}_6\text{O}$: 29.84, 206.26 ppm).

Melting points are uncorrected.

The high resolution mass spectrometry (HRMS) analyses were performed using a Bruker microTOF QII mass spectrometer equipped with an electrospray ion source (ESI) operated in positive ion mode. The sample solutions (CH_3OH or $\text{CH}_3\text{OH} + 0.1\% \text{v/v HCOOH}$) were introduced by continuous infusion at a flow rate of 180 mL min^{-1} with the aid of a syringe pump. The instrument was operated with endplate offset and capillary voltages set to -500 V and -4500 V respectively. The nebulizer pressure was 0.4 bar (N_2), and the drying gas (N_2) flow rate was 4.0 L min^{-1} . The capillary exit and skimmer 1 voltages were 90 V and 30 V, respectively. The drying gas temperature was set at 180°C . The calibration was carried out with sodium formate: a solution made up of 10 ml of 98% formic acid, 10 ml of sodium hydroxide (1.0 M), 490 ml of i-propanol and 490 ml of deionized water. The software used for the simulations was Bruker Daltonics DataAnalysis (version 4.0).

Reagents: Commercial reagents were used as supplied or purified by standard techniques where necessary.

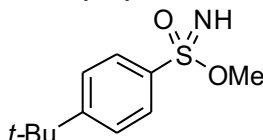
Sulfonimides

General procedure A for the synthesis of sulfonimides

Ammonium carbamate (156 mg, 2.00 mmol) and [(diacetoxy)iodo]benzene (644 mg, 2.00 mmol) were added to a stirred solution of thiol (0.50 mmol, 1 equiv) in MeOH (2.5 mL) at 25 °C for 3 h. The solvent was removed under reduced pressure. Purification by flash column chromatography (neutral Al₂O₃, 20–35% EtOAc/pentane) afforded the title sulfonimides.

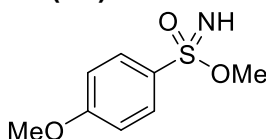
Note: For larger scale preparations a work-up with an aqueous solution of NaHCO₃ is needed in order to remove excess of acetic acid to improve the stability of the sulfonimide.

Methyl 4-(*tert*-butyl)benzenesulfonimide (2a)



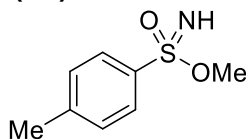
General procedure A was followed using 4-*tert*-butylthiophenol **1a** (83 mg, 0.50 mmol) to afford sulfonimide **2a** as a white solid (69 mg, 65%). *R_f* 0.34 (25% EtOAc/Pentane). mp = 31–33 °C. IR (film)/cm⁻¹ 3283, 2960, 1594, 1277, 1150, 994, 963, 755. ¹H NMR (400 MHz, CDCl₃): δ 7.95–7.88 (m, 2H, 2 × Ar-H), 7.56–7.49 (m, 2H, 2 × Ar-H), 3.63 (s, 3H, OCH₃), 3.24 (bs, 1H, NH), 1.33 (s, 9H, C(CH₃)₃). ¹³C NMR (101 MHz, CDCl₃): δ 156.9 (Ar-C_q), 133.8 (Ar-C_q), 127.5 (Ar-C), 125.9 (Ar-C), 55.4 (OCH₃), 35.1 (Ar-C(CH₃)₃), 31.0 (C(CH₃)₃). HRMS (ESI) *m/z* Calcd for C₁₁H₁₈NO₂S [M+H]⁺: 228.1053; Found: 228.1052.

Methyl 4-methoxybenzenesulfonimide (2b)

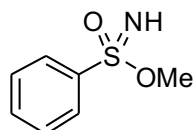


General procedure A was followed using 4-methoxythiophenol **1b** (70 mg, 0.50 mmol) to afford sulfonimide **2b** as a pale yellow wax (54 mg, 54%). *R_f* 0.12 (30% EtOAc/Pentane). IR (film)/cm⁻¹ 3270, 3947, 1594, 1578, 1496, 1461, 1440, 1316, 1258, 1145, 1084. ¹H NMR (400 MHz, CDCl₃): δ 7.97–7.93 (m, 2H, Ar-H), 7.02–6.98 (m, 2H, Ar-H), 3.89 (s, 3H, OCH₃), 3.63 (s, 3H, OCH₃), 3.15 (bs, 1H, NH). ¹³C NMR (101 MHz, CDCl₃): δ 163.3 (Ar-C_q), 130.0 (2 × Ar-C), 128.3 (Ar-C_q), 114.1 (2 × Ar-C), 55.6 (OCH₃), 55.4 (OCH₃). HRMS (ESI) *m/z* Calcd. for C₈H₁₂NO₃S [M+H]⁺: 202.0532; Found: 202.0540.

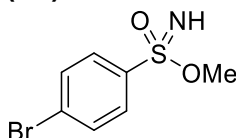
Methyl 4-methylbenzenesulfonimide (2c)



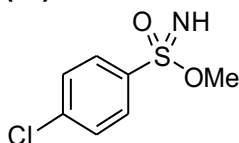
General procedure A was followed using 4-methylthiophenol **1c** (62 mg, 0.50 mmol) to afford sulfonimide **2c** as a pale white solid (54 mg, 58%). *R_f* 0.26 (30% EtOAc/Pentane). mp = 43–45 °C (lit 45–47).¹ IR (film)/cm⁻¹ 3297, 3252, 2949, 1737, 1594, 1492, 1450, 1378, 1265, 1148. ¹H NMR (400 MHz, CDCl₃): δ 7.90 (d, *J* = 8.2 Hz, 2H, Ar-H), 7.34 (d, *J* = 8.2 Hz, 2H, Ar-H), 3.64 (s, 3H, OCH₃), 3.19 (bs, 1H, NH), 2.45 (s, 3H, CH₃). ¹³C NMR (101 MHz, CDCl₃): δ 144.1 (Ar-C_q), 133.9 (Ar-C_q), 129.6 (2 × Ar-C), 127.8 (2 × Ar-C), 55.5 (OCH₃), 21.6 (CH₃). Spectroscopic data for this compound is consistent with the literature.¹

Methyl benzenesulfonimide (2d)

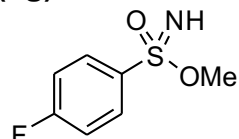
Ammonium carbamate (312 mg, 4.00 mmol) and ([diacetoxy]iodo]benzene (1.29 g, 4.00 mmol) were added to a stirred solution of thiol (110 mg, 1.00 mmol) in MeOH (5.0 mL) at 25 °C for 3 h. The solvent was removed under reduced pressure. Purification by flash column chromatography (neutral Al₂O₃, solvent graded from 20–35% EtOAc/Pentane) afforded sulfonimide **2d** as a colorless oil (70 mg, 41%). *R_f* 0.14 (25% EtOAc/Pentane). IR (film)/cm⁻¹ 3274, 2948, 1478, 1446, 1272, 1147, 955, 733. ¹H NMR (400 MHz, CDCl₃): δ 8.04–7.99 (m, 2H, Ar-H), 7.65–7.59 (m, 1H, Ar-H), 7.59–7.49 (m, 2H, Ar-H), 3.65 (s, 3H, OCH₃), 3.26 (bs, 1H, NH). ¹³C NMR (101 MHz, CDCl₃): δ 136.9 (Ar-C_q), 133.1 (Ar-C), 128.9 (2 × Ar-C), 127.7 (2 × Ar-C), 55.6 (OCH₃). HRMS (ESI) *m/z* Calcd for C₇H₁₀NO₂S [M+H]⁺: 172.0427; Found: 172.0428.

Methyl 4-bromobenzenesulfonimide (2e)

General procedure A was followed using 4-bromothiophenol **1e** (95 mg, 0.50 mmol) to afford sulfonimide **2e** as a pale yellow oil (59 mg, 47%). *R_f* 0.38 (30% EtOAc/Pentane). IR (film)/cm⁻¹ 3962, 3088, 2947, 1737, 1574, 1470, 1388, 1268, 1067. ¹H NMR (400 MHz, CDCl₃): δ 7.90–7.87 (m, 2H, Ar-H), 7.70–7.67 (m, 2H, Ar-H), 3.67 (s, 3H, OCH₃), 3.25 (bs, 1H, NH). ¹³C NMR (101 MHz, CDCl₃): δ 136.1 (Ar-C_q), 132.3 (2 × Ar-C), 129.3 (2 × Ar-C), 128.3 (Ar-C_q), 55.7. HRMS (ESI) *m/z* Calcd. for C₇H₉NO₂S⁷⁹Br [M+H]⁺: 249.9532; Found: 249.9537.

Methyl 4-chlorobenzenesulfonimide (2f)

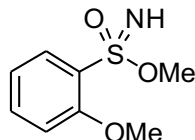
General procedure A was followed using 4-chlorothiophenol **1f** (72 mg, 0.50 mmol) to afford sulfonimide **2f** as a colourless oil (39 mg, 42%). *R_f* 0.29 (25% EtOAc/Pentane). IR (film)/cm⁻¹ 3288, 2948, 1582, 1474, 1395, 1269, 1088, 964, 757. ¹H NMR (400 MHz, CDCl₃): δ 7.98–7.92 (m, 2H, 2 × Ar-H), 7.53–7.47 (m, 2H, 2 × Ar-H), 3.65 (s, 3H, OCH₃), 3.30 (bs, 1H, NH). ¹³C NMR (101 MHz, CDCl₃): δ 139.7 (Ar-C_q), 135.5 (Ar-C_q), 129.22 (Ar-C), 129.18 (Ar-C), 55.6 (OCH₃). HRMS (ESI) *m/z* Calcd for C₇H₉NO₂S³⁵Cl [M+H]⁺: 206.0037; Found: 206.0043.

Methyl 4-fluorobenzenesulfonimide (2g)

General procedure A was followed using 4-fluorothiophenol **1g** (64 mg, 0.50 mmol) to afford sulfonimide **2g** as a yellow solid (15 mg, 41%). *R_f* 0.22 (25% EtOAc/Pentane). mp = 43–45 °C. IR (film)/cm⁻¹ 3281, 3074, 2952, 1589, 1494, 1270, 1153, 956, 714. ¹H NMR (400 MHz, CDCl₃): δ 8.07–8.00 (m, 2H, Ar-H), 7.25–7.18 (m, 2H, Ar-H), 3.66 (s, 3H, OCH₃), 3.25 (bs, 1H, NH). ¹³C NMR (101 MHz, CDCl₃): δ 165.4 (d, ¹*J*_{C-F} = 255.6 Hz, Ar-CF_q), 133.0 (d, ⁴*J*_{C-F} = 2.4 Hz, FAr-C_q), 130.5 (d, ³*J*_{C-F} = 9.5 Hz, 2 × FAr-C), 116.2 (d, ²*J*_{C-F} = 22.7 Hz, 2 × FAr-C), 55.6 (OCH₃). ¹⁹F NMR (377 MHz,

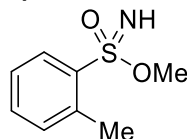
CDCl_3) δ -104.6 (Ar-F). HRMS (ESI) m/z Calcd for $\text{C}_7\text{H}_9\text{NO}_2\text{SF}$ $[\text{M}+\text{H}]^+$: 190.0333; Found: 190.0333.

Methyl 2-methoxybenzenesulfonimide (2h)



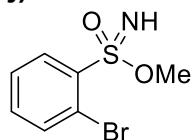
General Procedure A was followed using 2-methoxybenzenethiol **1h** (100 mg, 0.71 mmol) to afford sulfonimide **2h** as yellow oil (70 mg, 50%). R_f 0.42 (30% EtOAc/Hexane). IR (film)/ cm^{-1} 3340, 2945, 1480, 1282, 1162, 1016, 970, 802, 756. ^1H NMR (700 MHz, Acetone- D_6): δ 7.88 (d, J = 7.8 Hz, 1H, Ar-H), 7.64 (t, J = 7.9 Hz, 1H, Ar-H), 7.27 (d, J = 8.4 Hz, 1H, Ar-H), 7.13 (t, J = 7.6 Hz, 1H, Ar-H), 4.27 (bs, 1H, NH), 4.01 (s, 3H, OCH_3), 3.60 (s, 3H, OCH_3). ^{13}C NMR (176 MHz, Acetone- D_6): δ 157.5 (Ar- C_q), 135.5 (Ar-C), 130.2 (Ar-C), 128.0 (Ar- C_q), 121.1 (Ar-C), 113.6 (Ar-C), 56.7 (OCH_3), 55.0 (OCH_3). HRMS (ESI-TOF) m/z : Calcd for $\text{C}_8\text{H}_{12}\text{NO}_3\text{S}$ $[\text{M}+\text{H}]^+$: 202.0532; Found: 202.0555.

Methyl 2-methylbenzenesulfonimide (2i)



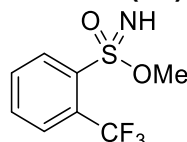
General procedure A was followed using 2-methylthiophenol **1i** (62 mg, 0.50 mmol) to afford sulfonimide **2i** as a colourless oil (26 mg, 28%). R_f 0.31 (25% EtOAc/Pentane). IR (film)/ cm^{-1} 3285, 3062, 2947, 1456, 1268, 1151, 963, 722. ^1H NMR (400 MHz, CDCl_3) δ 8.09 (d, J = 8.4, 1H, Ar-H), 7.51–7.44 (m, 1H, Ar-H), 7.36–7.29 (m, 2H, 2 x Ar-H), 3.64 (s, 3H, OCH_3), 3.34 (bs, 1H, NH), 2.70 (s, 3H, Ar- CH_3). ^{13}C NMR (101 MHz, CDCl_3) δ 138.0 (Ar- C_q), 135.4 (Ar- C_q), 133.0 (Ar-C), 132.6 (Ar-C), 129.7 (Ar-C), 125.9 (Ar-C), 55.1 (OCH_3), 20.4 (Ar- CH_3). HRMS (ESI) m/z Calcd for $\text{C}_8\text{H}_{12}\text{NO}_2\text{S}$ $[\text{M}+\text{H}]^+$: 186.0583; Found: 186.0583.

Methyl 2-bromobenzenesulfonimide (2j)



General Procedure A was followed using 2-bromobenzenethiol **1j** (100 mg, 0.53 mmol) to afford sulfonimide **2j** as a pale yellow oil (26 mg, 20%). R_f 0.25 (30% EtOAc/Hexane). IR (film)/ cm^{-1} 3274, 2922, 2852, 1446, 1425, 1273, 1138, 1023, 961, 751. ^1H NMR (500 MHz, Acetone- D_6): δ 8.22 (dd, J = 7.8, 1.8 Hz, 1H, Ar-H), 7.87 (dd, J = 7.8, 1.3 Hz, 1H, Ar-H), 7.63–7.55 (m, 2H, 2 x Ar-H), 4.70 (bs, 1H, NH), 3.68 (s, 3H, OCH_3). ^{13}C NMR (126 MHz, Acetone- D_6): δ 139.4 (Ar- C_q), 136.4 (Ar-C), 134.9 (Ar-C), 132. (Ar-C), 128.8 (Ar-C), 120.5 (Ar- C_q), 55.4 (OCH_3). HRMS (ESI-TOF) m/z : Calcd for $\text{C}_7\text{H}_8^{79}\text{BrNNaO}_2\text{S}$ $[\text{M}+\text{Na}]^+$: 271.9351; Found: 271.9350.

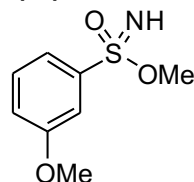
Methyl 2-(trifluoromethyl)benzenesulfonimide (2k)



General procedure A was followed using 2-(trifluoromethyl)benzenethiol **1k** (89 mg, 0.50 mmol) to afford sulfonimide **2k** as a yellow oil (19 mg, 16%). R_f 0.26 (30% EtOAc/Pentane). IR (film)/ cm^{-1}

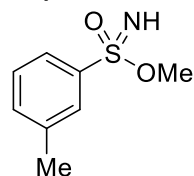
3329, 3079, 2952, 2918, 1597, 1509, 1481, 1432, 1359, 1307, 1264, 1237, 1172, 1134, 1117, 1052, 1031. ^1H NMR (400 MHz, CDCl_3): δ 8.36–8.34 (m, 1H, Ar-H), 7.91–7.89 (m, 1H, Ar-H), 7.76–7.71 (m, 2H, Ar-H), 3.81 (s, 3H, OCH_3), 3.56 (bs, 1H, NH). ^{13}C NMR (101 MHz, CDCl_3): δ 133.0 (Ar-C), 132.3 (Ar-C), 131.3 (Ar-C), 128.5 (q, $^3J_{\text{C-F}} = 6.1$ Hz, Ar-C), 128.2 (q, $^2J_{\text{C-F}} = 34.2$ Hz, Ar-C_q), 122.7 (q, $^1J_{\text{C-F}} = 276.9$ Hz, CF_3), 55.1 (OCH_3). *o*-Ar-C_q signal not observed. ^{19}F NMR (377 MHz, CDCl_3) δ –57.8. HRMS (ESI) m/z Calcd. for $\text{C}_8\text{H}_9\text{NO}_2\text{SF}_3$ $[\text{M}+\text{H}]^+$: 240.0301; Found: 240.0299.

Methyl 3-methoxybenzenesulfonimide (2l)



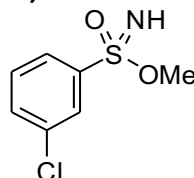
General Procedure A was followed using 3-methoxybenzenethiol **1l** (100 mg, 0.71 mmol) to afford sulfonimide **2l** as a brown oil (114 mg, 80%). R_f 0.31 (30% EtOAc/Hexane). IR (film)/ cm^{-1} 2983, 1598, 1477, 1374, 1243, 1046, 788, 725. ^1H NMR (500 MHz, CDCl_3): δ 7.58 (ddd, $J = 7.8, 1.7, 1.0$ Hz, 1H, Ar-H), 7.51–7.50 (m, 1H, Ar-H), 7.43 (t, $J = 8.0$ Hz, 1H, Ar-H), 7.14 (ddd, $J = 8.3, 2.6, 0.9$ Hz, 1H, Ar-H), 3.87 (s, 3H, OCH_3), 3.66 (s, 3H, OCH_3), 3.22 (bs, 1H, NH). ^{13}C NMR (126 MHz, CDCl_3): δ 160.0 (Ar-C_q), 138.3 (Ar-C_q), 130.1 (Ar-C), 120.1 (Ar-C), 119.9 (Ar-C), 112.4 (Ar-C), 55.8 (OCH_3), 55.7 (OCH_3). HRMS (ESI-TOF) m/z Calcd for $\text{C}_8\text{H}_{12}\text{NO}_3\text{S}$ $[\text{M}+\text{H}]^+$: 202.0532; Found: 202.0533.

Methyl 3-methylbenzenesulfonimide (2m)

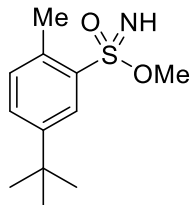


General Procedure A was followed using 3-methylbenzenethiol **1m** (100 mg, 0.81 mmol) to afford sulfonimide **2m** as a yellow oil (103 mg, 69%). R_f 0.25 (30% EtOAc/Hexane). IR (film)/ cm^{-1} 3291, 2948, 1478, 1275, 1138, 1080, 971, 788, 723. ^1H NMR (700 MHz, Acetone- D_6): δ 7.80 (s, 1H, Ar-H), 7.78 (d, $J = 7.2$ Hz, 1H, Ar-H), 7.51–7.47 (m, 2H, 2 x Ar-H), 4.43 (bs, 1H, NH), 3.58 (s, 3H, OCH_3), 2.44 (s, 3H, CH_3). ^{13}C NMR (176 MHz, Acetone- D_6): δ 140.0 (Ar-C_q), 139.1 (Ar-C_q), 134.3 (Ar-C), 129.7 (Ar-C), 128.6 (Ar-C), 125.5 (Ar-C), 55.6 (OCH_3), 21.2 (CH_3). HRMS (ESI-TOF) m/z Calcd for $\text{C}_8\text{H}_{12}\text{NO}_2\text{S}$ $[\text{M}+\text{H}]^+$: 186.0583; Found: 186.0574.

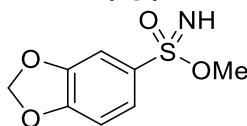
Methyl 3-chlorobenzenesulfonimide (2n)



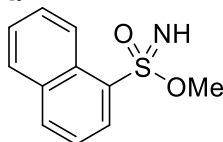
General Procedure A was followed using 3-chlorobenzenethiol **1n** (100 mg, 0.69 mmol) to afford sulfonimide **2n** as a yellow oil (66 mg, 47%). R_f 0.22 (30% EtOAc/Hexane). IR (film)/ cm^{-1} 3294, 2949, 1579, 1462, 1279, 1152, 1075, 969, 790, 719. ^1H NMR (700 MHz, Acetone- D_6): δ 7.97 (s, 1H, Ar-H), 7.94 (d, $J = 7.8$ Hz, 1H, Ar-H), 7.75–7.72 (m, 1H, Ar-H), 7.66 (t, $J = 7.9$ Hz, 1H, Ar-H), 4.73 (bs, 1H, NH), 3.64 (s, 3H, OCH_3). ^{13}C NMR (176 MHz, Acetone- D_6): δ 141.3 (Ar-C_q), 135.7 (Ar-C_q), 133.7 (Ar-C), 131.8 (Ar-C), 128.2 (Ar-C), 126.9 (Ar-C), 56.0 (OCH_3). HRMS (ESI-TOF) m/z Calcd for $\text{C}_7\text{H}_9^{35}\text{ClNO}_2$ $[\text{M}+\text{H}]^+$: 206.0037; Found: 206.0032.

Methyl 5-(*tert*-butyl)-2-methylbenzenesulfonimide (2o)

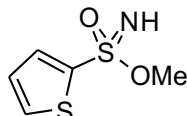
General Procedure A was followed using 5-(*tert*-butyl)-2-methylbenzenethiol **1o** (100 mg, 0.55 mmol) to afford sulfonimide **2o** as a colorless oil (70 mg, 54%). R_f 0.52 (30% EtOAc/Hexane). IR (film)/ cm^{-1} 3300, 2929, 1489, 1264, 1136, 975, 736. ^1H NMR (500 MHz, Acetone- D_6): δ 8.13 (d, J = 2.1 Hz, 1H, Ar-H), 7.59 (dd, J = 8.0, 2.1 Hz, 1H, Ar-H), 7.34 (d, J = 8.0 Hz, 1H, Ar-H), 4.48 (bs, 1H, NH), 3.58 (s, 3H, OCH_3), 2.62 (s, 3H, CH_3), 1.34 (s, 9H, $(\text{C}(\text{CH}_3)_3)$). ^{13}C NMR (176 MHz, Acetone- D_6): δ 149.8 (Ar- C_q), 137.1 (Ar- C_q), 135.5 (Ar- C_q), 133.2 (Ar-C), 130.6 (Ar-C), 127.0 (Ar-C), 54.9 (OCH_3), 35.1 ($\text{C}(\text{CH}_3)_3$), 31.4 ($\text{C}(\text{CH}_3)_3$), 20.0 (CH_3). HRMS (ESI-TOF) m/z Calcd for $\text{C}_{12}\text{H}_{20}\text{NO}_2\text{S}$ $[\text{M}+\text{H}]^+$: 242.1209; Found 242.1209.

Methyl benzo[d][1,3]dioxole-5-sulfonimide (2p)

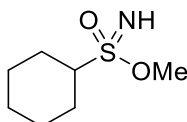
General procedure A was followed using benzo[d][1,3]dioxole-5-thiol **1p** (77 mg, 0.50 mmol) to afford sulfonimide **2p** as a pale yellow solid (58 mg, 54%). R_f 0.19 (30% EtOAc/Pentane). mp = 68–71 °C. IR (film)/ cm^{-1} 3329, 3078, 2951, 2916, 1598, 1509, 1480, 1431, 1358, 1276, 1263, 1236, 1173, 1134, 1117, 1052, 1031. ^1H NMR (400 MHz, CDCl_3): δ 7.59 (dd, J = 8.2, 1.9 Hz, 1H, Ar-H), 7.42 (d, J = 1.9 Hz, 1H, Ar-H), 6.90 (d, J = 8.2 Hz, 1H, Ar-H), 6.09 (s, 2H, CH_2), 3.65 (s, 3H, OCH_3), 3.16 (bs, 1H, NH). ^{13}C NMR (101 MHz, CDCl_3): δ 151.8 (Ar- C_q), 148.2 (Ar- C_q), 131.4 (Ar- C_q), 123.6 (Ar-C), 108.1 (Ar-C), 108.0 (Ar-C), 102.3 (CH_2), 55.5 (OCH_3). HRMS (ESI) m/z Calcd. for $\text{C}_8\text{H}_{10}\text{NO}_4\text{S}$ $[\text{M}+\text{H}]^+$: 216.0325; Found: 216.0330.

Methyl naphthalene-1-sulfonimide (2q)

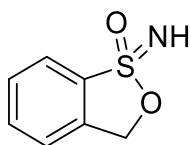
General procedure A was followed using naphthalene-1-thiol **1q** (60 mg, 0.37 mmol) to afford sulfonimide **2q** as a pale orange solid (28 mg, 34%). R_f 0.36 (30% EtOAc/Pentane). mp = 78–80 °C. IR (film)/ cm^{-1} 3284, 2946, 1593, 1506, 1455, 1346, 1274, 1257, 1196, 1156, 1113. ^1H NMR (400 MHz, CDCl_3): δ 8.81 (d, J = 8.5 Hz, 1H, Ar-H), 8.38 (dd, J = 7.4, 1.1 Hz, 1H, Ar-H), 8.11 (d, J = 8.2 Hz, 1H, Ar-H), 7.95 (d, J = 8.2 Hz, 1H, Ar-H), 7.70 (ddd, J = 8.5, 6.9, 1.3 Hz, 1H, Ar-H), 7.64–7.55 (m, 2H, Ar-H), 3.65 (s, 3H, OCH_3), 3.58 (s, 1H, NH). ^{13}C NMR (101 MHz, CDCl_3): δ 134.7 (Ar-C), 134.3 (Ar- C_q), 132.5 (Ar- C_q), 129.9 (Ar-C), 128.7 (Ar-C), 128.4 (Ar- C_q), 128.3 (Ar-C), 127.0 (Ar-C), 125.5 (Ar-C), 123.9 (Ar-C), 55.5 (OCH_3). HRMS (ESI) m/z Calcd. for $\text{C}_{11}\text{H}_{11}\text{NO}_2\text{S}$ $[\text{M}+\text{H}]^+$: 222.0583; Found: 222.0591.

Methyl thiophene-2-sulfonimide (2r)

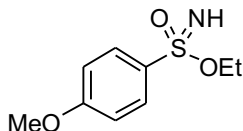
General Procedure A was followed using from thiophene-2-thiol **1r** (80 mg, 0.69 mmol) to afford sulfonimide **2r** as a brown oil (65 mg, 54%). R_f 0.41 (30% EtOAc/Hexane). IR (film)/ cm^{-1} 3350, 2948, 1458, 1285, 1144, 911, 734. ^1H NMR (500 MHz, CDCl_3): δ 7.72 (d, J = 3.7 Hz, 1H, Ar-H), 7.64 (d, J = 5.0 Hz, 1H, Ar-H), 7.12 (t, J = 3.7 Hz, 1H, Ar-H), 3.75 (s, 3H, OCH_3), 3.32 (bs, 1H, NH). ^{13}C NMR (176 MHz, CDCl_3): δ 138.0 (Ar- C_q), 133.6 (Ar-C), 133.3 (Ar-C), 127.6 (Ar-C), 56.4 (OCH_3). HRMS (ESI-TOF) m/z Calcd for $\text{C}_5\text{H}_8\text{NO}_2\text{S}_2$ $[\text{M}+\text{H}]^+$: 177.9991; Found 177.9987.

Methyl cyclohexanesulfonimide (2s)

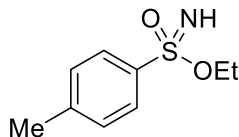
General Procedure A was followed using cyclohexanethiol **1s** (100 mg, 0.86 mmol) to afford sulfonimide **2s** as a yellow oil (60 mg, 40%). R_f 0.22 (30% EtOAc/Hexane). IR (film)/ cm^{-1} 3292, 2930, 1454, 1289, 1255, 1124, 986, 855, 767. ^1H NMR (700 MHz, Acetone- D_6): δ 3.69 (s, 4H, overlapping NH and OCH_3), 3.06 (tt, J = 12.0, 3.4 Hz, 1H, CH), 2.16 (dd, J = 26.5, 12.8 Hz, 2H, 2 $\times$ CH), 1.86-1.83 (m, 2H, 2 $\times$ CH), 1.68-1.67 (m, 1H), 1.56-1.48 (m, 2H, 2 $\times$ CH), 1.35-1.31 (m, 2H, 2 $\times$ CH), 1.23-1.17 (m, 1H). ^{13}C NMR (176 MHz, Acetone- D_6): δ 60.4 (OCH_3), 53.7 (CH), 27.9 (CH_2), 27.3 (CH_2), 25.9 (CH_2), 25.8 (CH_2), 25.7 (CH_2). HRMS (ESI-TOF) m/z Calcd for $\text{C}_7\text{H}_{16}\text{NO}_2\text{S}$ $[\text{M}+\text{H}]^+$: 178.0896; Found: 178.0880.

1-Imino-1,3-dihydro-1 λ^4 -benzo[c][1,2]oxathiole 1-oxide (2t)

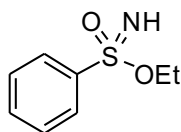
General procedure A was followed using (2-mercaptophenyl)methanol **1t** (350 mg, 2.50 mmol) to afford cyclic sulfonimide **2t** as a white solid (243 mg, 57%). R_f 0.43 (60% EtOAc/Pentane). mp = 121–125 °C. IR (film)/ cm^{-1} 3271 1454, 1262, 1214, 1144, 1104, 1028. ^1H NMR (400 MHz, CDCl_3): δ 7.85–7.83 (m, 1H, Ar-H), 7.66 (td, J = 7.6, 0.8 Hz, 1H, Ar-H), 7.58 (td, J = 7.6, 0.8 Hz, 1H, Ar-H), 7.41–7.39 (m, 1H, Ar-H), 5.48–5.39 (m, 2H, CH_2), 3.67 (bs, 1H, NH). ^{13}C NMR (101 MHz, CDCl_3): δ 136.1 (Ar- C_q), 134.4 (Ar- C_q), 133.3 (Ar-C), 129.8 (Ar-C), 123.1 (Ar-C), 122.5 (Ar-C), 69.8 (CH_2). HRMS (ESI) m/z Calcd. for $\text{C}_7\text{H}_8\text{NO}_2\text{S}$ $[\text{M}+\text{H}]^+$: 170.0270; Found: 170.0282.

Ethyl 4-methoxybenzenesulfonimide (2aa)

General Procedure A was followed using 4-methoxybenzenethiol **1b** (70 mg, 0.50 mmol) but using ethanol as the solvent to afford sulfonimide **2aa** as a yellow oil (48 mg, 45%). R_f 0.43 (30% EtOAc/Hexane). IR (film)/ cm^{-1} 3342, 2983, 1597, 1497, 1261, 1144, 1024, 908, 734. ^1H NMR (500 MHz, CDCl_3): δ 7.93 (d, J = 8.9 Hz, 2H, 2 $\times$ Ar-H), 6.98 (d, J = 8.9 Hz, 2H, 2 $\times$ Ar-H), 4.01-3.92 (m, 2H, OCH_2), 3.87 (s, 3H, OCH_3), 3.14 (bs, 1H, NH), 1.24 (t, J = 7.1 Hz, 3H, CH_3). ^{13}C NMR (126 MHz, CDCl_3): δ 163.3 (Ar- C_q), 129.9 (Ar-C), 129.6 (Ar- C_q), 114.2 (Ar-C), 65.7 (OCH_2), 55.8 (OCH_3), 14.9 (CH_3). HRMS (ESI-TOF) m/z Calcd for $\text{C}_9\text{H}_{13}\text{NNaO}_3\text{S}$ $[\text{M}+\text{Na}]^+$: 238.0508; Found 238.0513.

Ethyl 4-methylbenzenesulfonimide (2ab)

General procedure A was followed using 4-methylthiophenol **1c** (62 mg, 0.50 mmol) but using ethanol as the solvent to afford sulfonimide **2ab** as a colourless oil (64 mg, 64%). R_f 0.28 (30% EtOAc/Pentane). IR (film)/ cm^{-1} 3293, 2983, 1493, 1444, 1388, 1267, 1144, 1004. ^1H NMR (400 MHz, CDCl_3): δ 7.90–7.88 (m, 2H, Ar-H), 7.33–7.31 (m, 2H, Ar-H), 4.05–3.93 (m, 2H, CH_2), 3.18 (bs, 1H, NH), 2.44 (s, 3H, Ar- CH_3), 1.25 (t, $J = 7.1$ Hz, 3H, CH_3). ^{13}C NMR (101 MHz, CDCl_3): δ 143.8 (Ar- C_q), 135.2 (Ar- C_q), 129.5 ($2 \times$ Ar-C), 127.6 ($2 \times$ Ar-C), 65.6 (OCH_2), 21.5 (Ar- CH_3), 14.8 (CH_3). HRMS (ESI) m/z Calcd. for $\text{C}_9\text{H}_{14}\text{NO}_2\text{S}$ $[\text{M}+\text{H}]^+$: 200.0740; Found: 200.0741. Spectroscopic data for this compound is consistent with the literature.¹

Ethyl benzenesulfonimide (2ac)

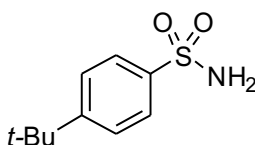
General Procedure A was followed using thiophenol **1d** (50 mg, 0.45 mmol) but using ethanol as the solvent to afford sulfonimide **2ac** as a colorless oil (38 mg, 48%). R_f 0.42 (30% EtOAc/Hexane). IR (film)/ cm^{-1} 3294, 2923, 1447, 1266, 1099, 895, 728. ^1H NMR (300 MHz, CDCl_3): δ 8.01 (d, $J = 7.9$ Hz, 2H, $2 \times$ Ar-H), 7.61 (t, $J = 7.1$ Hz, 1H, Ar-H), 7.52 (t, $J = 7.1$ Hz, 2H, $2 \times$ Ar-H), 4.09–3.95 (m, 2H, OCH_2), 3.23 (bs, 1H, NH), 1.25 (t, $J = 7.1$ Hz, 3H, CH_3). ^{13}C NMR (176 MHz, CDCl_3): δ 140.1 (Ar- C_q), 132.7 (Ar-C), 129.2 (Ar-C), 127.2 (Ar-C), 38.4 (OCH_2), 15.2 (CH_3). HRMS (ESI-TOF) m/z Calcd for $\text{C}_8\text{H}_{11}\text{NNaO}_2\text{S}$ $[\text{M}+\text{Na}]^+$: 208.0403; Found: 208.0402.

Sulfonamides

General procedure B for the synthesis of sulfonamides

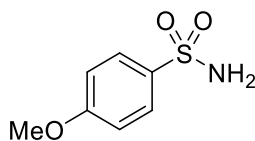
Ammonium carbamate (39 mg, 0.50 mmol) and [(diacetoxy)iodo]benzene (564 mg, 1.75 mmol) were added to a stirred solution of thiol (0.50 mmol, 1 equiv) in MeOH (2.5 mL) at 25 °C for 24 h. The solvent was removed under reduced pressure. Purification by flash column chromatography (SiO₂, 20–35% EtOAc/Pentane) afforded the title sulfonamides.

4-(*tert*-Butyl)benzenesulfonamide (**3a**)



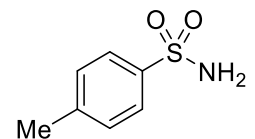
General procedure B was followed using 4-*tert*-butylthiophenol **1a** (83 mg, 0.50 mmol) to afford sulfonamide **3a** as a white solid (85 mg, 80%). *R*_f 0.33 (25% EtOAc/Pentane). mp = 130–132 °C. (lit. = 133–134 °C).² IR (film)/cm⁻¹ 3357, 3262, 2963, 1567, 1397, 1326, 1161, 1091, 830. ¹H NMR (400 MHz, CDCl₃): δ 7.88–7.83 (m, 2H, 2 × Ar-H), 7.53–7.48 (m, 2H, 2 × Ar-H), 5.32 (bs, 2H, NH₂), 1.33 (s, 9H, C(CH₃)₃). ¹³C NMR (101 MHz, CDCl₃): δ 156.4 (Ar-C_q), 139.0 (Ar-C_q), 126.2 (Ar-C), 126.0 (Ar-C), 35.1 (Ar-C(CH₃)₃), 31.0 (C(CH₃)₃). Spectroscopic data for this compound (IR, NMR)³ is consistent with the literature.

4-Methoxybenzenesulfonamide (**3b**)

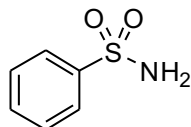


General procedure B was followed using 4-methoxythiophenol **1b** (70 mg, 0.50 mmol) to afford sulfonamide **3b** as a white solid (70 mg, 75%). *R*_f 0.13 (30% EtOAc/Pentane). mp = 104–107 °C (lit. = 113 °C).⁴ IR (film)/cm⁻¹ 3347, 3257, 1597, 1578, 1498, 1458, 1327, 1302, 1259, 1152, 1093, 1021. ¹H NMR (400 MHz, MeOH-D₄): δ 7.84–7.82 (m, 2H, Ar-H), 7.06–7.03 (m, 2H, Ar-H), 4.91 (s, 2H, NH₂), 3.86 (s, 3H, OCH₃). ¹³C NMR (101 MHz, MeOH-D₄): δ 164.0 (Ar-C_q), 136.8 (Ar-C_q), 129.2 (2 × Ar-C), 115.0 (2 × Ar-C), 56.1 (OCH₃). Spectroscopic data for this compound (IR)⁵ is consistent with the literature.

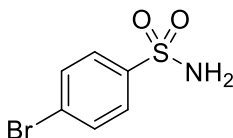
4-Methylbenzenesulfonamide (**3c**)



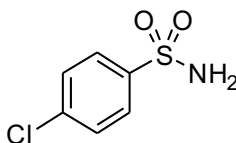
General procedure B was followed using 4-methylthiophenol **1c** (62 mg, 0.50 mmol) to afford sulfonamide **3c** as a white solid (69 mg, 81%). *R*_f 0.26 (30% EtOAc/Pentane). mp = 133–137 °C (lit. = 137.5 °C).⁶ IR (film)/cm⁻¹ 3354, 3259, 1738, 1598, 1526, 1386, 1298, 1154, 1096, 1018. ¹H NMR (400 MHz, CDCl₃): δ 7.82 (d, *J* = 8.2 Hz, 2H, Ar-H), 7.33 (d, *J* = 8.2 Hz, 2H, Ar-H), 4.82 (bs, 2H, NH₂), 2.44 (s, 3H, CH₃). ¹³C NMR (101 MHz, CDCl₃): δ 143.7 (Ar-C_q), 139.0 (Ar-C_q), 129.7 (2 × Ar-C), 126.5 (2 × Ar-C), 21.5 (CH₃). Spectroscopic data for this compound (NMR)⁷ (IR)⁸ is consistent with the literature.

Benzenesulfonamide (3d)

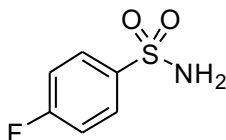
Ammonium carbamate (78 mg, 1.00 mmol) and [(diacetoxy)iodo]benzene (1.13 g, 3.50 mmol) were added to a stirred solution of thiol (110 mg, 1.00 mmol) in MeOH (5.0 mL) at 25 °C for 24 h. The solvent was removed under reduced pressure. Purification by flash column chromatography (SiO₂, solvent graded from 20–35% EtOAc/Pentane) afforded sulfonamide **3d** as a white solid (108 mg, 69%). *R_f* 0.14 (25% EtOAc/Pentane). mp = 150–153 °C. (lit. = 150–152 °C).⁹ IR (film)/cm⁻¹ 3320, 3070, 2922, 2503, 2397, 1479, 1447, 1327, 1310, 1150, 1087, 841, 754. ¹H NMR (400 MHz, MeOH-D₄): δ 7.94–7.88 (m, 2H, 2 × Ar-H), 7.62–7.50 (m, 3H, 3 × Ar-H), 4.90 (bs, 2H, NH₂). ¹³C NMR (101 MHz, MeOH-D₄): δ 145.0 (Ar-C_q), 133.2 (Ar-C), 130.0 (Ar-C), 127.0 (Ar-C). Spectroscopic data for this compound (IR)¹⁰ is consistent with the literature.

4-Bromobenzenesulfonamide (3e)

General procedure B was followed using 4-bromothiophenol **1e** (95 mg, 0.50 mmol) to afford sulfonamide **3e** as a white solid (70 mg, 59%). *R_f* 0.29 (30% EtOAc/Pentane). mp = 160–162 °C (lit. = 166–167).¹¹ IR (film)/cm⁻¹ 3322, 3233, 3116, 1737, 1571, 1469, 1390, 1322, 1271, 1145, 1090, 1067, 1010. ¹H NMR (400 MHz, MeOH-D₄): δ 7.81–7.79 (m, 2 H, Ar-C), 7.73–7.71 (m, 2 H, Ar-C), 4.91 (s, 2 H, NH₂). ¹³C NMR (101 MHz, MeOH-D₄): δ 144.4 (Ar-C_q), 133.2 (2 × Ar-C), 129.0 (2 × Ar-C), 127.5 (Ar-C_q). Spectroscopic data for this compound (IR)⁸ is consistent with the literature.

4-Chlorobenzenesulfonamide (3f)

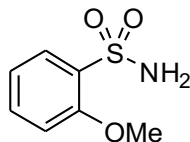
General procedure B was followed using 4-chlorothiophenol **1f** (72 mg, 0.50 mmol) to afford sulfonamide **3f** as a white solid (55 mg, 56%). *R_f* 0.25 (25% EtOAc/Pentane). mp = 141–143 °C. (lit. = 140–144 °C).¹² IR (film)/cm⁻¹ 3277, 3090, 2497, 2353, 2327, 1584, 1474, 1318, 1145, 1086, 819. ¹H NMR (400 MHz, MeOH-D₄): δ 7.92–7.84 (m, 2H, 2 × Ar-H), 7.58–7.49 (m, 2H, 2 × Ar-H), 4.82 (bs, 2H, NH₂). ¹³C NMR (101 MHz, MeOH-D₄): δ 143.7 (Ar-C_q), 139.2 (Ar-C_q), 130.1 (Ar-C), 128.8 (Ar-C). Spectroscopic data for this compound (IR)¹⁰ is consistent with the literature.

4-Fluorobenzenesulfonamide (3g)

General procedure B was followed using 4-fluorothiophenol **1g** (64 mg, 0.50 mmol) to afford sulfonamide **3g** as a white solid (42 mg, 48%). *R_f* 0.24 (25% EtOAc/Pentane). mp = 120–122 °C. (lit. = 122 °C).¹³ IR (film)/cm⁻¹ 3314, 3109, 2516, 2411, 1587, 1493, 1225, 1321, 1145, 836. ¹H NMR (400 MHz, MeOH-D₄): δ 8.02–7.87 (m, 2H, 2 × Ar-H), 7.33–7.20 (m, 2H, 2 × Ar-H), 4.90 (bs, 2H, NH₂). ¹³C NMR (101 MHz, MeOH-D₄): δ 164.0 (d, ¹*J*_{C-F} = 251.4 Hz, Ar-CF_q), 139.3 (d, ⁴*J*_{C-F} =

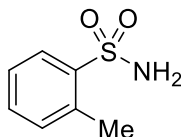
3.2 Hz, FAr-C_q), 128.0 (d, $^3J_{C-F}$ = 9.3 Hz, FAr-C), 114.9 (d, $^2J_{C-F}$ = 22.6 Hz, FAr-C). ^{19}F NMR (377 MHz, MeOD-D₄): δ -109.4 (Ar-F). Spectroscopic data for this compound (IR)¹⁴ is consistent with the literature.

2-Methoxybenzenesulfonamide (3h)



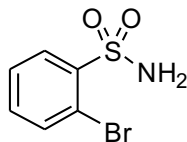
General Procedure B was followed using 2-methoxybenzenethiol **1h** (100 mg, 0.71 mmol) to afford sulfonamide **3h** as white solid (119 mg, 90%). Purification by washing with CH₂Cl₂. mp = 172–173 °C (lit. = 173–174).¹⁵ IR (film)/cm⁻¹ 3464, 2985, 2912, 1466, 1447, 1373, 1241, 1047, 938. ^1H NMR (500 MHz, MeOH-D₄): δ 7.84 (d, J = 7.8 Hz, 1H, Ar-H), 7.58 (t, J = 7.9 Hz, 1H, Ar-H), 7.20 (d, J = 8.4 Hz, 1H, Ar-H), 7.06 (t, J = 7.6 Hz, 1H, Ar-H), 3.98 (s, 3H, OCH₃). ^{13}C NMR (176 MHz, MeOH-D₄): δ 157.9 (Ar-C_q), 135.3 (Ar-C), 132.1 (Ar-C_q), 129.2 (Ar-C), 121.2 (Ar-C), 113.4 (Ar-C), 56.6 (OCH₃). HRMS (ESI-TOF) m/z Calcd for C₇H₉NNaO₃S [M+Na]⁺: 210.0195; Found: 210.0198.

2-Methylbenzenesulfonamide (3i)



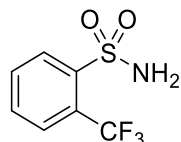
General procedure B was followed using 2-methylthiophenol **1i** (62 mg, 0.50 mmol) to afford sulfonamide **3i** as a white solid (67 mg, 78%). R_f 0.27 (25% EtOAc/Pentane). mp = 153–154 °C. (lit. = 155–157 °C).¹⁵ IR (film)/cm⁻¹ 3373, 3253, 3098, 2601, 1559, 1309, 1148. ^1H NMR (400 MHz, DMSO-D₆) δ 7.84 (d, J = 8.1 Hz, 1H, Ar-H), 7.48 (td, J = 7.7, 7.3, 1.4 Hz, 1H, Ar-H), 7.42–7.31 (m, 2H, 2 x Ar-H), 3.36 (bs, 2H, NH₂), 2.58 (s, 3H, Ar-CH₃). ^{13}C NMR (101 MHz, DMSO-D₆) δ 142.1 (Ar-C_q), 135.9 (Ar-C_q), 132.2 (Ar-C), 131.9 (Ar-C), 127.0 (Ar-C), 126.1 (Ar-C), 19.9 (Ar-CH₃). Spectroscopic data for this compound (IR)¹⁰ (NMR)¹⁶ is consistent with the literature.

2-Bromobenzenesulfonamide (3j)



General Procedure B was followed using 2-bromobenzenethiol **1j** (50 mg, 0.26 mmol) to afford sulfonamide **3j** as white solid (24 mg, 40%). R_f 0.23 (30% EtOAc/Hexane). mp = 190–192 °C (lit. = 194–195).¹⁶ IR (film)/cm⁻¹ 3365, 3260, 2918, 1565, 1447, 1373, 1334, 1241, 1156, 1026, 765. ^1H NMR (500 MHz, Acetone-D₆): δ 8.12 (dd, J = 7.8, 1.7 Hz, 1H, Ar-H), 7.83 (dd, J = 7.8, 1.2 Hz, 1H, Ar-H), 7.59–7.50 (m, 2H, 2 x Ar-H), 6.74 (bs, 2H, NH₂). ^{13}C NMR (126 MHz, Acetone-D₆): δ 143.7 (Ar-C_q), 135.9 (Ar-C), 134.2 (Ar-C), 130.4 (Ar-C), 128.7 (Ar-C), 120.1 (Ar-C_q). HRMS (ESI-TOF) m/z Calcd for C₆H₅⁷⁹BrNO₂S [M-H]⁻: 233.9230; Found: 233.9240.

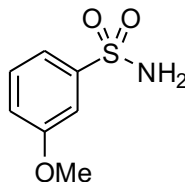
2-(Trifluoromethyl)benzenesulfonamide (3k)



General procedure B was followed using 2-(trifluoromethyl)benzenethiol **1k** (89 mg, 0.50 mmol) to afford sulfonamide **3k** as a white solid (63 mg, 56%). R_f 0.31 (30% EtOAc/Pentane). mp = 183–185

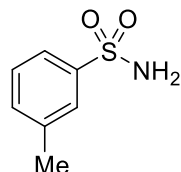
°C (lit. = 184–185 °C).¹⁷ IR (film)/cm⁻¹ 3370, 3321, 3266, 2461, 1566, 1439, 1416, 1341, 1303, 1270, 1183, 1157, 1137, 1119, 1099, 1037. ¹H NMR (400 MHz, MeOH-D₄): δ 8.27–8.25 (m, 1H, Ar-H), 7.92–7.90 (m, 1H, Ar-H), 7.81–7.74 (m, 2H, Ar-H), 4.87 (s, 2H, NH₂). ¹³C NMR (101 MHz, MeOH-D₄): δ 133.8 (Ar-C), 133.5 (Ar-C), 131.0 (Ar-C), 129.14 (q, ³J_{C-F} = 6.3 Hz, Ar-C), 128.2 (q, ²J_{C-F} = 32.8 Hz), 124.5 (q, ¹J_{C-F} = 259.2 Hz). *o*-Ar-C_q signal not observed. ¹⁹F NMR (377 MHz, MeOH-D₄): δ –58.9. Spectroscopic data for this compound (IR)¹⁸ is consistent with the literature.

3-Methoxybenzenesulfonamide (3l)



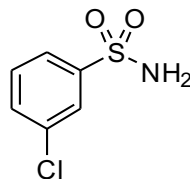
General Procedure B was followed using 3-methoxybenzenethiol **1l** (100 mg, 0.71 mmol) to afford sulfonamide **3l** as a yellow solid (122 mg, 92%). Purification by washing with hexane. mp = 127–129°C (lit. = 130–132).¹⁹ IR (film)/cm⁻¹ 3341, 3267, 2944, 2837, 1491, 1319, 1255, 1170, 1028, 905, 801. ¹H NMR (500 MHz, MeOH-D₄): δ 7.48–7.42 (m, 3H, 3 x Ar-H), 7.14–7.12 (m, 1H, Ar-H), 3.85 (s, 3H, OCH₃). ¹³C NMR (176 MHz, MeOH-D₄): δ 161.3 (Ar-C_q), 146.1 (Ar-C_q), 131.1 (Ar-C), 119.1 (Ar-C), 119.0 (Ar-C), 112.2 (Ar-C), 56.1 (OCH₃). HRMS (ESI-TOF) *m/z* Calcd for C₇H₉NNaO₃S [M+Na]⁺: 210.0195; Found: 210.0194.

3-Methylbenzenesulfonamide (3m)

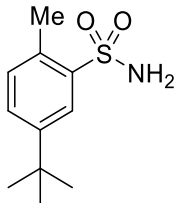


General Procedure B was followed using 3-methylbenzenethiol **1m** (100 mg, 0.81 mmol) to afford sulfonamide **3m** as a white solid (122 mg, 88%). Purification by washing with hexane. mp = 109–111°C (lit. = 107–109).²⁰ IR (film)/cm⁻¹ 3257, 2921, 2851, 1478, 1330, 1305, 1156, 908, 785. ¹H NMR (500 MHz, MeOH-D₄): δ 7.73 (s, 1H, Ar-H), 7.70–7.69 (m, 1H, Ar-H), 7.43–7.40 (m, 2H, 2 x Ar-H), 2.42 (s, 3H, CH₃). ¹³C NMR (176 MHz, MeOH-D₄): δ 144.9 (Ar-C_q), 140.4 (Ar-C_q), 133.8 (Ar-C), 129.9 (Ar-C), 127.4 (Ar-C), 124.2 (Ar-C), 21.3 (CH₃). HRMS (ESI-TOF) *m/z* Calcd for C₇H₉NNaO₂S [M+Na]⁺: 194.0246; Found: 194.0230.

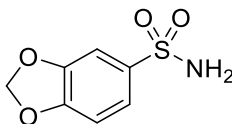
3-Chlorobenzenesulfonamide (3n)



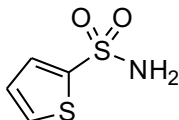
General Procedure B was followed using 3-chlorobenzenethiol **1n** (100 mg, 0.69 mmol) to afford sulfonamide **3n** as a white solid (118 mg, 90%). Purification by washing with CH₂Cl₂. mp = 152–154°C (lit. = 148–150).²¹ IR (film)/cm⁻¹ 3256, 2917, 1566, 1331, 1158, 1122, 1079, 918, 791. ¹H NMR (500 MHz, MeOH-D₄): δ 7.90 (t, *J* = 1.9 Hz, 1H, Ar-H), 7.82 (ddd, *J* = 7.8, 1.6, 1.1 Hz, 1H, Ar-H), 7.61–7.59 (m, 1H, Ar-H), 7.53 (t, *J* = 7.9 Hz, 1H, Ar-H). ¹³C NMR (176 MHz, MeOH-D₄): δ 147.0 (Ar-C_q), 135.9 (Ar-C_q), 133.1 (Ar-C), 131.7 (Ar-C), 127.2 (Ar-C), 125.5 (Ar-C). HRMS (ESI-TOF) *m/z* Calcd for C₆H₅³⁵ClNO₂S [M-H]⁻: 189.9735; Found: 189.9718.

5-(*tert*-Butyl)-2-methylbenzenesulfonamide (3o)

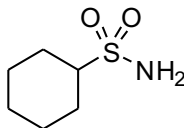
General Procedure B was followed using 5-(*tert*-butyl)-2-methylbenzenethiol **1o** (50 mg, 0.28 mmol) to afford sulfonamide **3o** as a yellow solid (57 mg, 90%). R_f 0.33 (30% EtOAc/Hexane). mp = 140-142°C (lit. = 142-143).²² IR (film)/cm⁻¹ 3400, 2965, 1492, 1334, 1251, 1170, 1035, 963. ¹H NMR (500 MHz, Acetone-D₆): δ 8.02 (d, J = 2.0 Hz, 1H, Ar-H), 7.52 (dd, J = 7.9, 2.1 Hz, 1H, Ar-H), 7.30 (d, J = 8.0 Hz, 1H, Ar-H), 6.54 (bs, 2H, NH₂), 2.63 (s, 3H, CH₃), 1.32 (s, 9H, (C(CH₃)₃)). ¹³C NMR (176 MHz, Acetone-D₆): δ 149.9 (Ar-C_q), 142.7 (Ar-C_q), 134.2 (Ar-C_q), 132.9 (Ar-C), 129.7 (Ar-C), 125.10 (Ar-C), 35.1 (C(CH₃)₃), 31.44 (C(CH₃)₃), 19.8 (CH₃). HRMS (ESI-TOF) m/z Calcd for C₁₁H₁₆NO₂S [M-H]⁻: 226.0907; Found: 226.0905.

Benzo[d][1,3]dioxole-5-sulfonamide (3p)

General procedure B was followed using benzo[d][1,3]dioxole-5-thiol **1p** (77 mg, 0.50 mmol) to afford sulfonamide **3p** as an off-white solid (50 mg, 50%). R_f 0.26 (30% EtOAc/Pentane). mp = 147-149 °C (lit. = 137 °C).²³ IR (film)/cm⁻¹ 3283, 3248, 3110, 2917, 2505, 2437, 2404, 2347, 1603, 1576, 1500, 1484, 1424, 1312, 1244, 1174, 1135, 1111, 1033. ¹H NMR (400 MHz, MeOH-D₄): δ 7.45 (dd, J = 8.2, 1.8 Hz, 1H, Ar-H), 7.31 (d, J = 1.8 Hz, 1H, Ar-H), 6.93 (d, J = 8.2 Hz, 1H, Ar-H), 6.07 (s, 2H, CH₂), 4.88 (s, 2H, NH₂). ¹³C NMR (101 MHz, MeOH-D₄): δ 152.3 (Ar-C_q), 149.5 (Ar-C_q), 138.5 (Ar-C_q), 122.4 (Ar-C), 108.9 (Ar-C), 107.5 (Ar-C), 103.7 (CH₂). HRMS (ESI) m/z Calcd. for C₇H₆NO₄S [M-H]⁻: 200.0023; Found: 200.0023.

Thiophene-2-sulfonamide (3r)

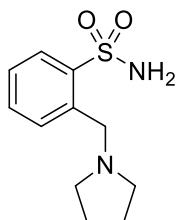
General Procedure B was followed using thiophene-2-thiol **1r** (100 mg, 0.86 mmol) to afford sulfonamide **3r** as a brown solid (133 mg, 95%). Purification by washing with CH₂Cl₂. mp = 142-144°C (lit. = 145-147).²⁰ IR (film)/cm⁻¹ 3350, 3262, 3093, 2918, 1297, 1164, 1020, 904, 725. ¹H NMR (500 MHz, MeOH-D₄): δ 7.70 (dd, J = 5.0, 1.3 Hz, 1H, Ar-H), 7.61 (dd, J = 3.7, 1.3 Hz, 1H, Ar-H), 7.10 (dd, J = 5.0, 3.7 Hz, 1H, Ar-H). ¹³C NMR (176 MHz, MeOH-D₄): δ 146.5 (Ar-C_q), 132.0 (Ar-C), 131.6 (Ar-C), 128.1 (Ar-C). HRMS (ESI-TOF) m/z Calcd for C₄H₄NO₂S₂ 161.9689 [M-H]⁻; Found: 161.9689.

Cyclohexanesulfonamide (3s)

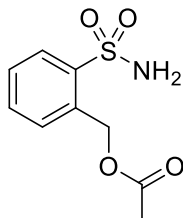
General Procedure B was followed using cyclohexanethiol **1s** (100 mg, 0.86 mmol) to afford sulfonamide **3s** as a white solid (105 mg, 75%). R_f 0.14 (90% EtOAc/Hexane). mp = 158-160°C (lit. = 165-167).²⁴ IR (film)/cm⁻¹ 3351, 3265, 2936, 2858, 1453, 1318, 1273, 1147, 1121, 910, 767. ¹H

NMR (300 MHz, MeOH-D₄): δ 2.92-2.82 (m, 1H, CH), 2.22-2.17 (m, 2H, CH₂), 1.91-1.86 (m, 2H, CH₂), 1.75-1.69 (m, 1H), 1.54-1.18 (m, 5H, 2 x CH₂). ¹³C NMR (176 MHz, MeOH-D₄): δ 63.6 (CH), 27.8 (2 x CH₂), 26.4 (CH₂) 26.2 (2 x CH₂). HRMS (ESI-TOF) m/z Calcd for C₆H₁₃NNaO₂S [M+Na]⁺: 186.0559; Found: 186.0554.

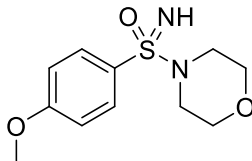
Reaction of sulfonimidates with nucleophiles

2-(Pyrrolidin-1-ylmethyl)benzenesulfonamide (**4**)

Pyrrolidine (42 μ L, 0.5 mmol) was added to a stirred solution of 1-imino-1,3-dihydro-1 λ^4 -benzo[c][1,2]oxathiole 1-oxide **2t** (42 mg, 0.25 mmol) in MeOH (1.25 mL) and the reaction was stirred at 25 °C for 24 h. The solvent was removed under reduced pressure and crude mixture purified by column chromatography (SiO₂, 1–5% MeOH/CH₂Cl₂) to afford the title compound **4** as a pale yellow solid (48 mg, 80%). *R*_f 0.48 (40% Acetone/Pentane). mp = 117–119 °C. IR (film)/cm⁻¹ 3246, 2971, 2818, 1328, 1156, 1130, 1109, 1064. ¹H NMR (400 MHz, CDCl₃): δ 8.06 (dd, *J* = 7.6, 1.6 Hz, 1H, Ar-H), 7.52–7.43 (m, 2H, Ar-H), 7.34 (dd, *J* = 7.3, 1.4 Hz, 1H, Ar-H), 6.96 (bs, 2H, NH₂), 4.07 (s, 2H, CH₂), 2.62–2.54 (m, 4H, 2 $\times$ CH₂), 1.80–1.76 (m, 4H, 2 $\times$ CH₂). ¹³C NMR (101 MHz, CDCl₃): δ 141.9 (Ar-C_q), 135.9 (Ar-C_q), 132.4 (Ar-C), 132.3 (Ar-C), 128.3 (Ar-C), 127.8 (Ar-C), 59.1 (CH₂), 53.4 (2 $\times$ CH₂), 23.4 (2 $\times$ CH₂). HRMS (ES–ToF) *m/z* Calcd. for C₁₁H₁₇N₂O₂S [M+H]⁺: 241.1005; Found: 241.1023.

2-Sulfamoylbenzyl acetate (**5**)

1-Imino-1,3-dihydro-1 λ^4 -benzo[c][1,2]oxathiole 1-oxide **2t** (42 mg, 0.25 mmol) was stirred in AcOH (1.25 mL) at 25 °C for 24 h. The solvent was removed under reduced pressure and crude mixture purified by column chromatography (SiO₂, 50% EtOAc/pentane) to afford the title compound **5** as an off-white solid (44 mg, 77%). *R*_f 0.66 (70% EtOAc/pentane). mp = 136–137 °C. IR (film)/cm⁻¹ 3361, 3258, 1727 (s, C=O), 1367, 1323, 1246, 1151, 1038. ¹H NMR (400 MHz, CDCl₃): δ 8.06 (d, *J* = 7.8 Hz, 1H, Ar-H), 7.61–7.59 (m, 2H, Ar-H), 7.52–7.46 (m, 1H, Ar-H), 5.57 (s, 2H, CH₂), 5.34 (bs, 2H, NH₂), 2.14 (s, 3H, CH₃). ¹³C NMR (101 MHz, CDCl₃): δ 140.2 (Ar-C_q), 134.3 (Ar-C_q), 133.0 (Ar-C), 130.9 (Ar-C), 128.9 (Ar-C), 128.1 (Ar-C), 63.0 (CH₂), 21.0 (CH₃). HRMS (ES–ToF) *m/z* Calcd. for C₉H₁₀NO₄S [M-H]⁻: 228.0336; Found: 228.0324.

4-(4-Methoxyphenylsulfonimidoyl)morpholine (**6**)

A mixture of methyl 4-methoxybenzenesulfonimidate **2b** (50 mg, 0.25 mmol) and morpholine (23.6 mg, 0.27 mmol) was heated at 70 °C with stirring for 24 h in the absence of solvent. The crude product was washed with Et₂O and collected by filtration to afford sulfonimidamide **6** as a yellow oil (51.2 mg, 80%). IR (film)/cm⁻¹ 3300, 2957, 1454, 1263, 1099, 1018, 913, 727. ¹H NMR (500 MHz, CDCl₃): δ 7.86 (d, *J* = 8.9 Hz, 2H, 2 $\times$ Ar-H), 6.97 (d, *J* = 8.9 Hz, 2H, 2 $\times$ Ar-H), 3.86 (s, 3H, OCH₃), 3.69–3.67 (m, 4H, (O(CH₂)₂)), 2.88–2.86 (m, 4H, (N(CH₂)₂)). NH signal not observed. ¹³C NMR (126

MHz, CDCl₃): δ 163.1 (Ar-C_q), 134.0 (Ar-C_q), 128.7 (Ar-C), 114.4 (Ar-C), 68.1 (OCH₃), 55.8 (O(CH₂)₂), 46.5 (N(CH₂)₂). HRMS (ESI-TOF) m/z Calcd. for C₁₁H₁₇N₂O₃S [M+H]⁺: 257.0954; Found: 257.0953.

Control Reactions (Scheme 5)**a) in scheme 5**

[(Diacetoxy)iodo]benzene [70.8 mg, 0.22 mmol] was added to a stirred solution of thiophenol **1d** (50 mg, 0.45 mmol) in MeOH (2.25 mL) at 25°C. After 1 minute a sample was taken and analyzed by gas chromatography (GC) observing complete conversion of the thiol into the corresponding disulfide. Another portion of PhI(OAc)₂ (505.5 mg, 1.57 mmol) was added and the solution stirred at 25°C for 3 h. After this time, the solvent was removed under reduced pressure to afford methyl benzenesulfinate **8** as a pale yellow oil (59 mg, 85%). Spectroscopic data were consistent with the data reported into the literature.²⁵

b) in scheme 5

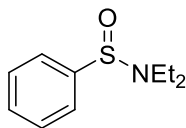
[(Diacetoxy)iodo]benzene [505.5 mg, 1.57 mmol], was added to a stirred solution of thiophenol **1d** (50 mg, 0.45 mmol) in MeOH (2.25 mL) at 25°C. After 1 minute, the solvent was removed under reduced pressure and the crude mixture was purified by flash chromatography (silica gel, 10% EtOAc/hexane) to afford a mixture of diphenyldisulfide **7** (47%) and methyl benzenesulfinate **8** (53%). Spectroscopic data for isolated compounds were consistent with the data reported into the literature.^{25,26}

c) in scheme 5

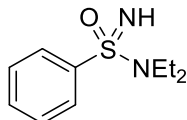
Ammonium carbamate (159.1 mg, 2.04 mmol) and [(diacetoxy)iodo]benzene [408.9 mg, 1.27 mmol] were added to a solution of methyl benzenesulfinate **8** (80 mg, 0.51 mmol) in MeCN (2.55 mL) and stirred at 25°C for 3 h. The solvent was removed under reduced pressure, and the crude mixture was purified by flash chromatography (neutral Al₂O₃, R_f 0.14 (25% EtOAc/Pentane) to afford methyl benzenesulfonimide **2d** as a colorless oil (69.7 mg, 80%).

d) in scheme 5**Methyl 4-methylbenzenesulfonimide (2c)**

Ammonium carbamate (62 mg, 0.80 mmol) and [(diacetoxy)iodo]benzene (196 mg, 0.60 mmol) were added to a stirred solution of 4-methylbenzenesulfinamide **9** (31 mg, 0.20 mmol) in MeOH (1.0 mL) at 25 °C for 3 h. The solvent was removed under reduced pressure. Purification by flash column chromatography (neutral Al₂O₃, 25% EtOAc/pentane) afforded sulfonimide **2c** as a pale yellow oil (16 mg, 43%). Data consistent with that reported above, and previously in the literature.¹

e) in scheme 5***N,N*-Diethylbenzenesulfinamide (10)**

Methyl benzenesulfinate **8** (1.31 mL, 10 mmol) and diethylamine (3.10 mL, 30 mmol) were combined in a 25 mL round bottom flask, purged with argon, sealed with a septum and stirred for 24 h at 60 °C. The reaction mixture was diluted with water (20 mL), extracted with CH₂Cl₂ (3 × 20 mL), dried (MgSO₄), filtered and the solvent removed under reduced pressure. Purification by flash chromatography (SiO₂, 30% EtOAc/pentane) afforded sulfinamide **10** as a pale yellow oil (734 mg, 37%). R_f 0.15 (20% EtOAc/pentane). IR (film)/cm⁻¹ 3422 (br), 3058, 2972, 2934, 2872, 1443, 1379, 1330, 1173, 1145, 1087, 1056, 1008. ¹H NMR (400 MHz, CDCl₃) δ 7.68–7.66 (m, 2H, Ph-H), 7.52–7.46 (m, 3H, Ph-H), 3.21–3.08 (m, 4H, 2 × CH₂), 1.13 (t, J = 7.2 Hz, 6H, 2 × CH₃). ¹³C NMR (101 MHz, CDCl₃) δ 144.3 (Ar-C_q), 130.5 (Ar-C), 128.7 (2 × Ar-C), 126.3 (2 × Ar-C), 42.0 (2 × CH₂), 14.4 (2 × CH₃). Spectroscopic data for this compound is consistent with that shown in the literature.²⁷

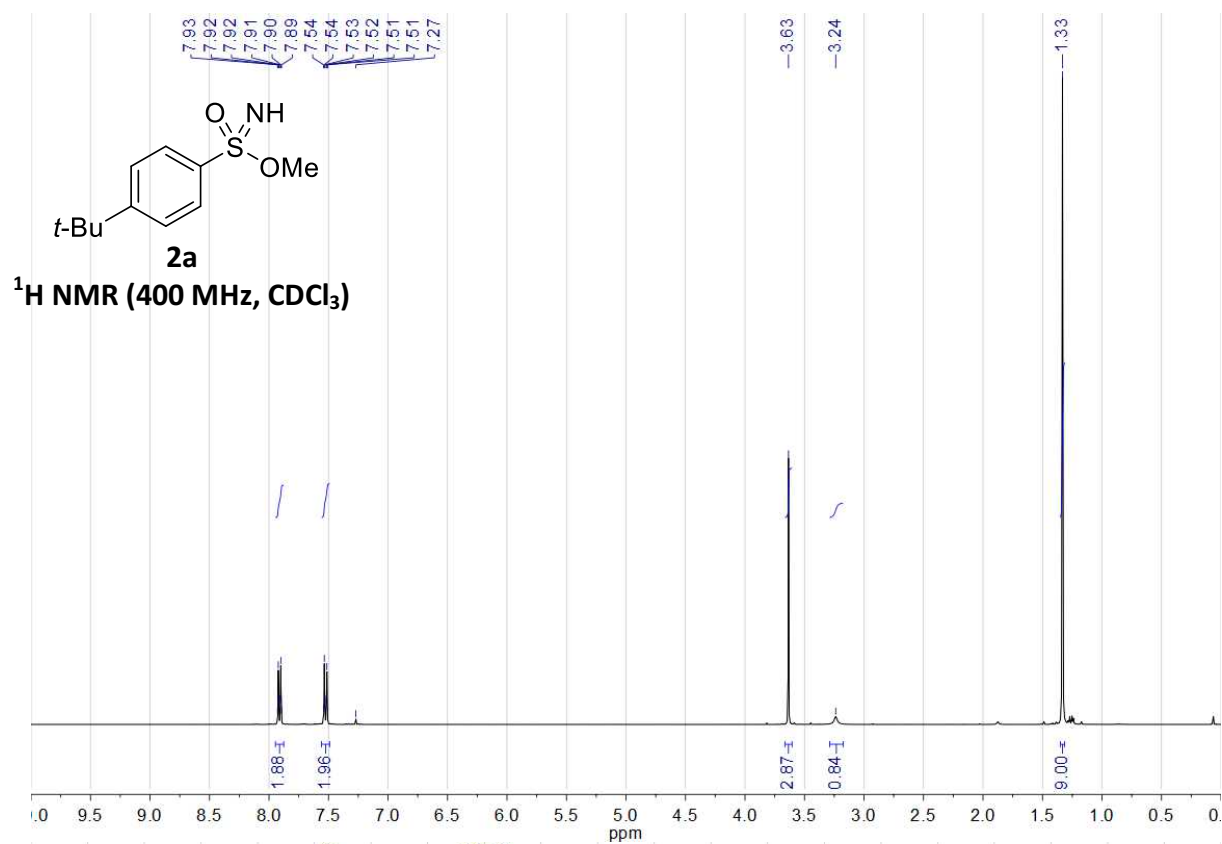
***N,N*-Diethylbenzenesulfonimidamide (11)**

Ammonium carbamate (62 mg, 0.80 mmol) and [(diacetoxy)iodo]benzene (196 mg, 0.60 mmol) were added to a stirred solution of *N,N*-diethylbenzenesulfinamide **10** (40 mg, 0.20 mmol) in MeOH (0.4 mL) at 25 °C. After 3 h, solvent was removed under reduced pressure. Purification by flash column chromatography (SiO₂, 20% EtOAc/pentane) afforded sulfonimidamide **11** as a pale yellow oil (82 mg, 77%). *R*_f 0.17 (30% EtOAc/pentane). IR (film)/cm⁻¹ 3284 (br, C=O), 2974, 2935, 2873, 1445, 1342, 1247, 1130, 996. ¹H NMR (400 MHz, CDCl₃) δ 7.96–7.93 (m, 2H, Ph-H), 7.56–7.46 (m, 3H, Ph-H), 3.36–3.17 (m, 4H, 2 × CH₂), 2.48 (bs, 1H, NH), 1.10 (t, *J* = 7.1 Hz, 6H, 2 × CH₃). ¹³C NMR (101 MHz, CDCl₃) δ 140.7 (Ar-C_q), 131.8 (Ar-C), 128.8 (2 × Ar-C), 127.2 (2 × Ar-C), 42.8 (2 × CH₂), 14.5 (2 × CH₃). Spectroscopic data for this compound is consistent with that shown in the literature.²⁸

References

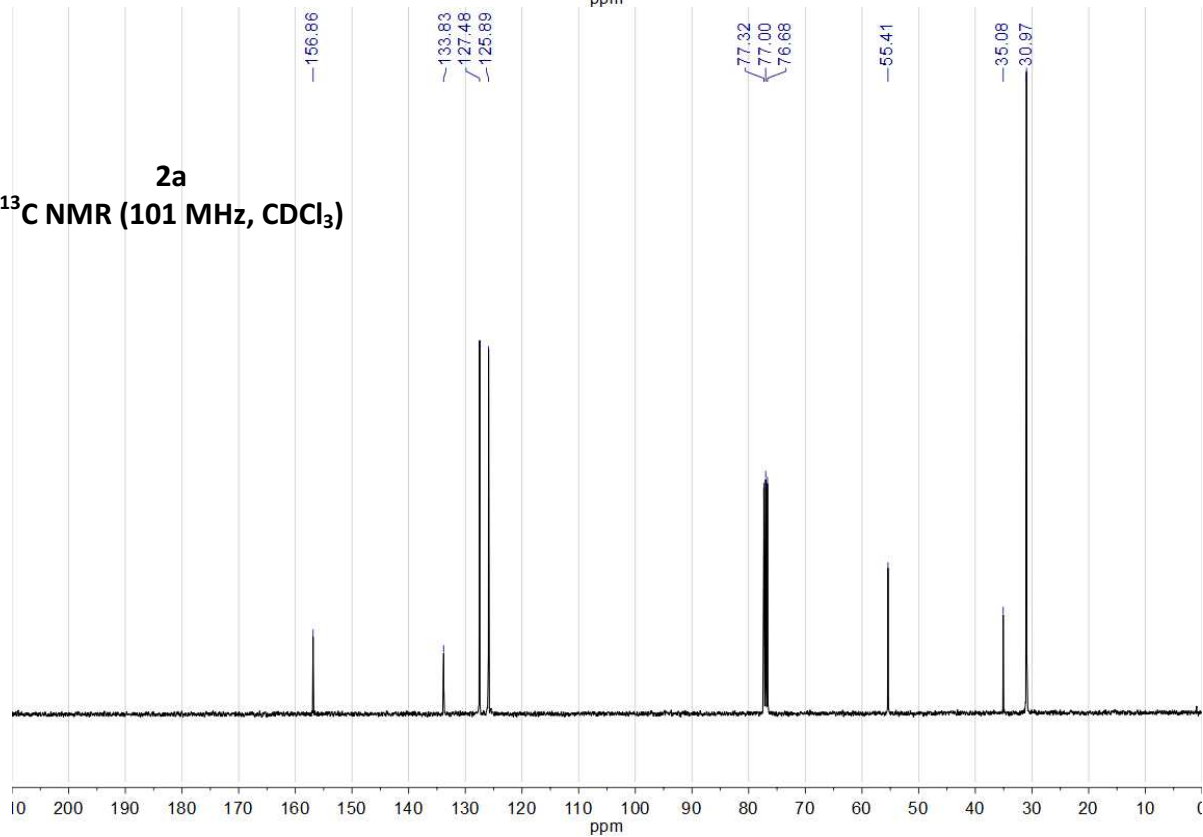
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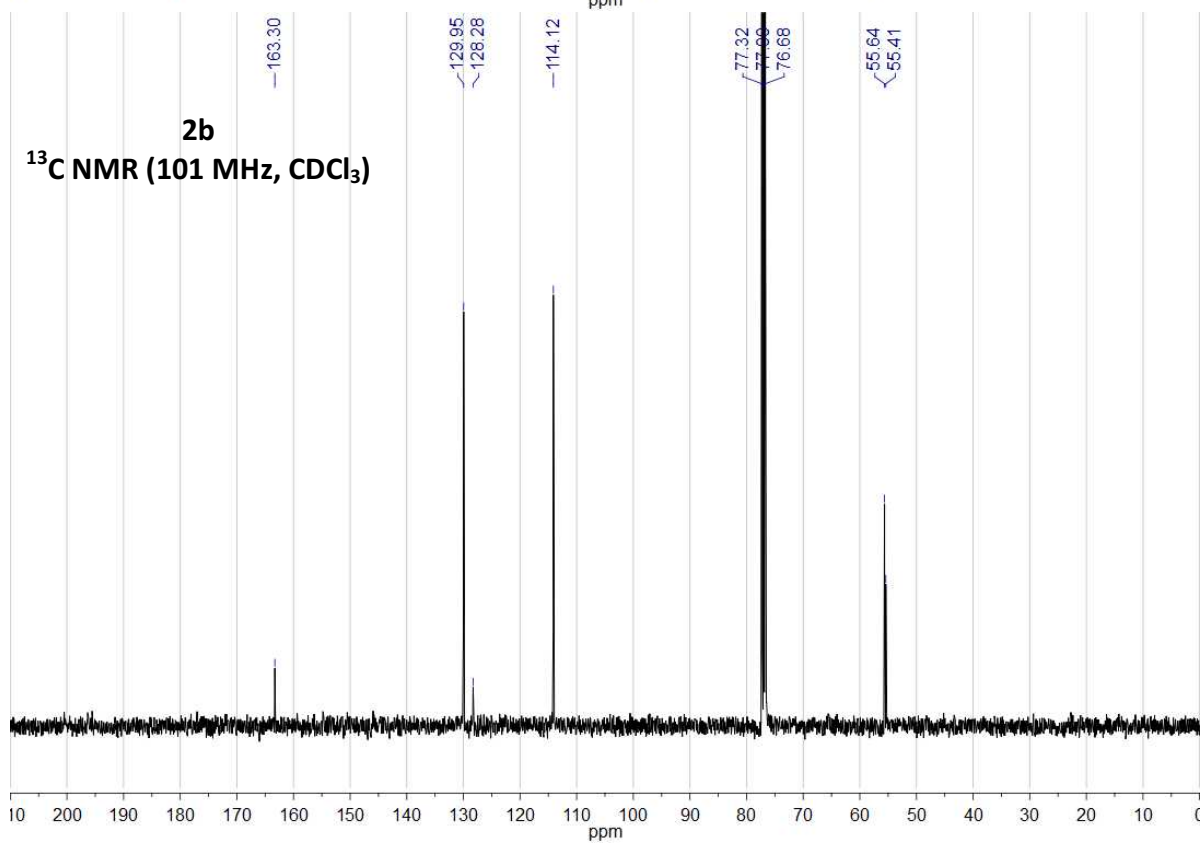
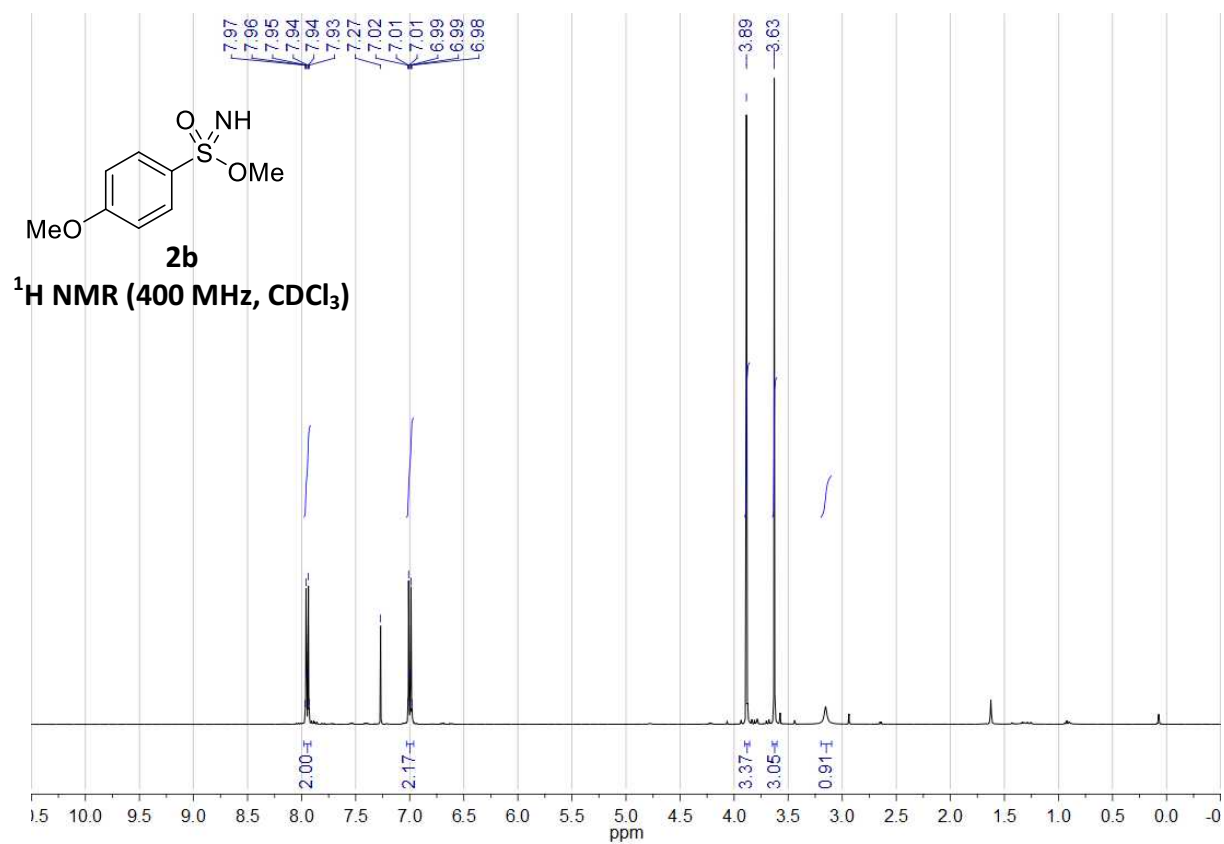
^1H and ^{13}C NMR spectra of novel compounds

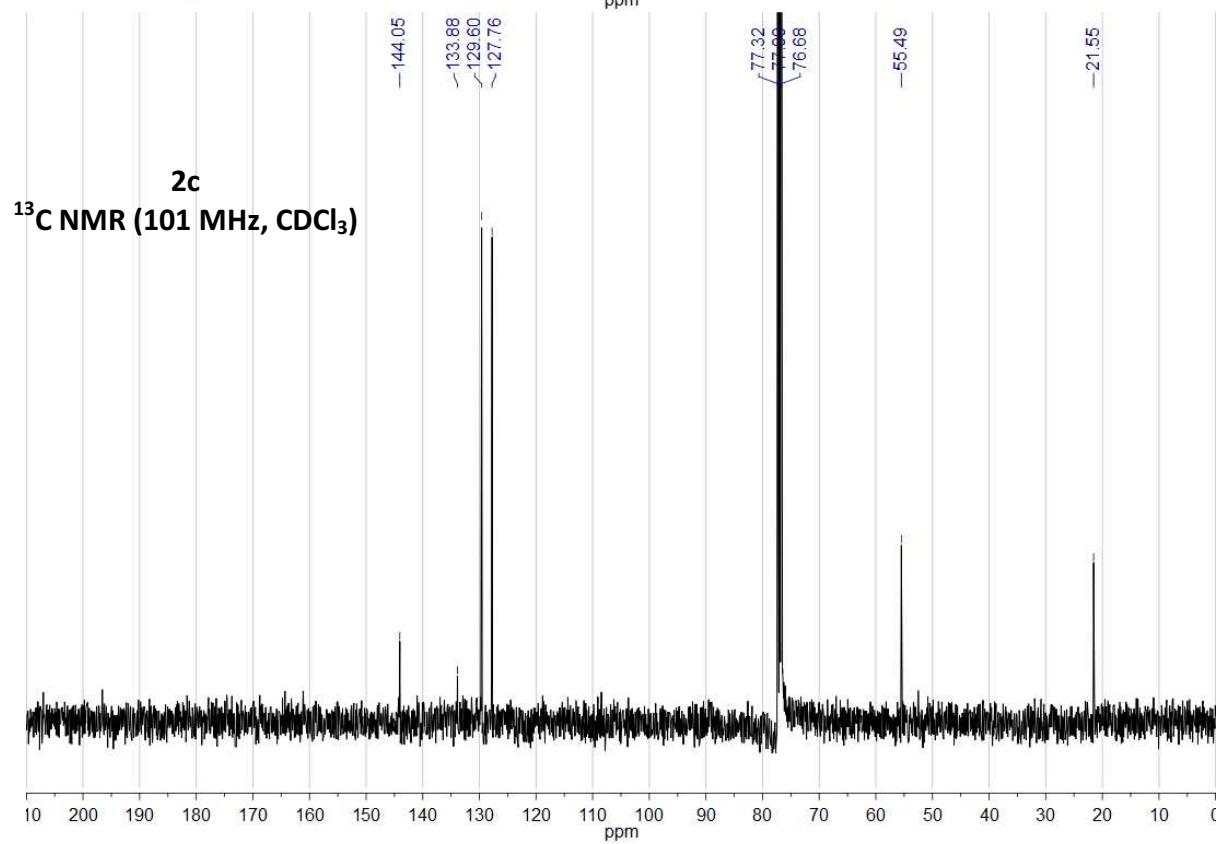
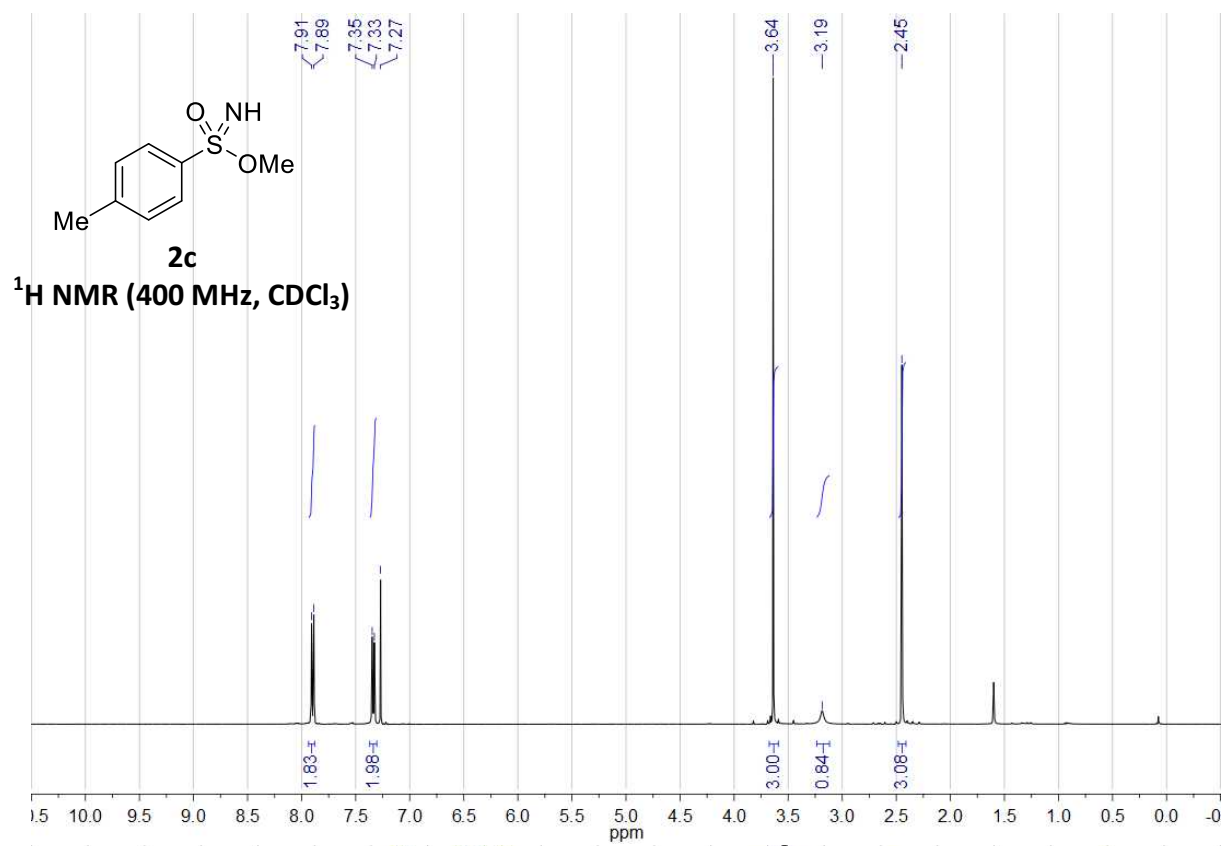


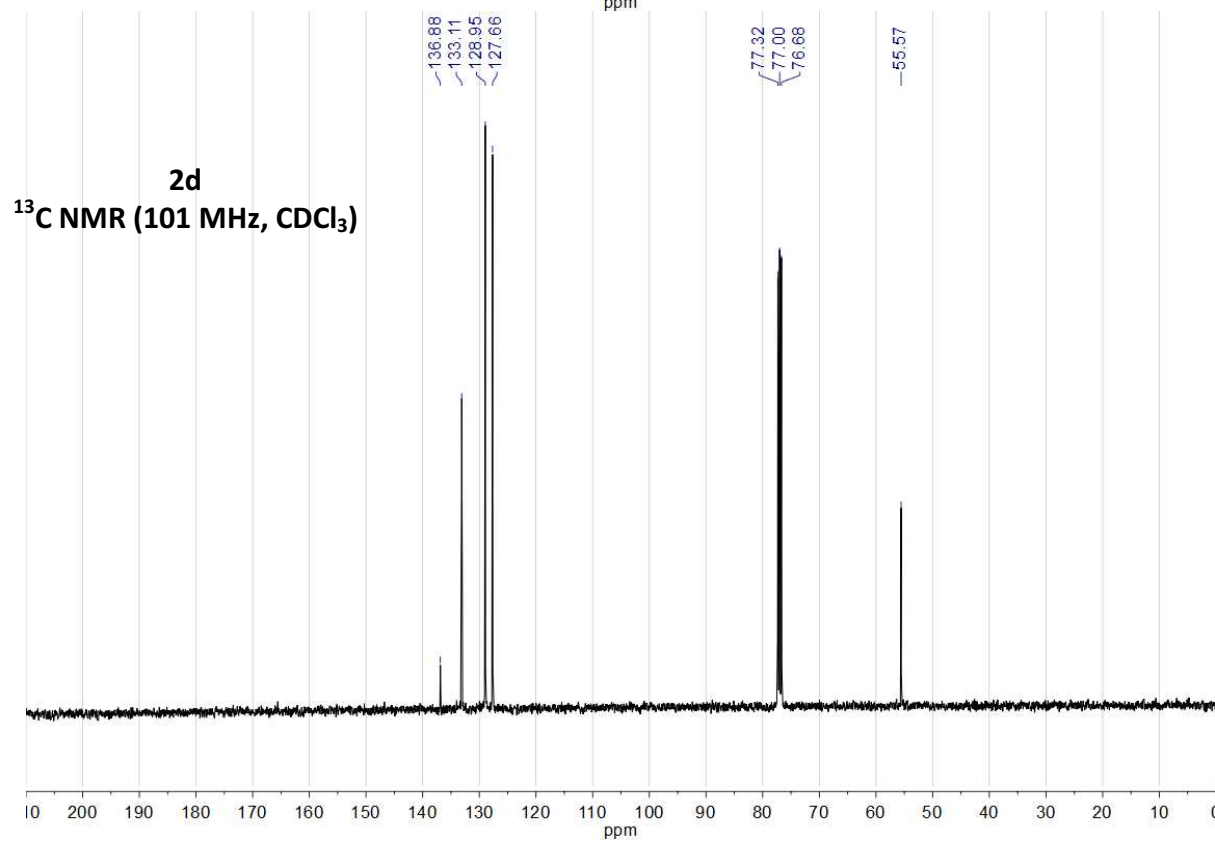
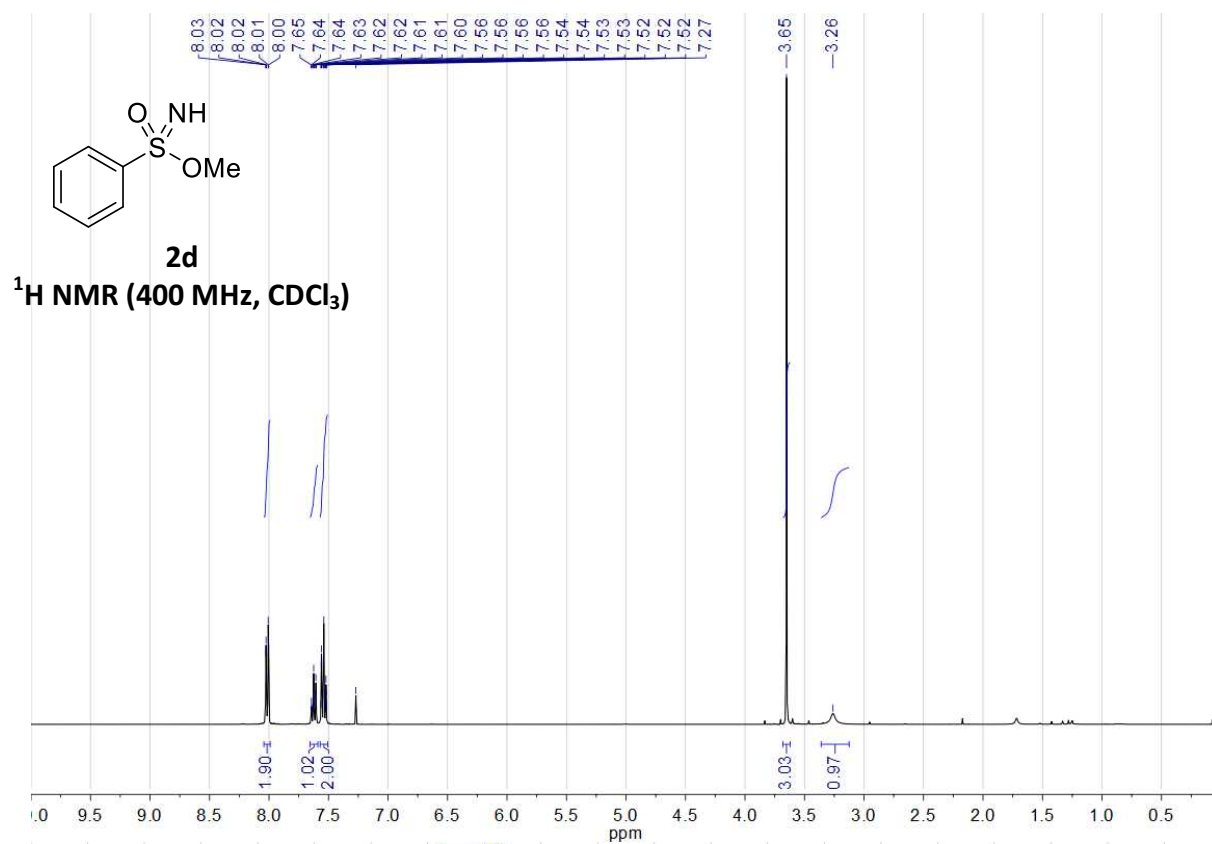
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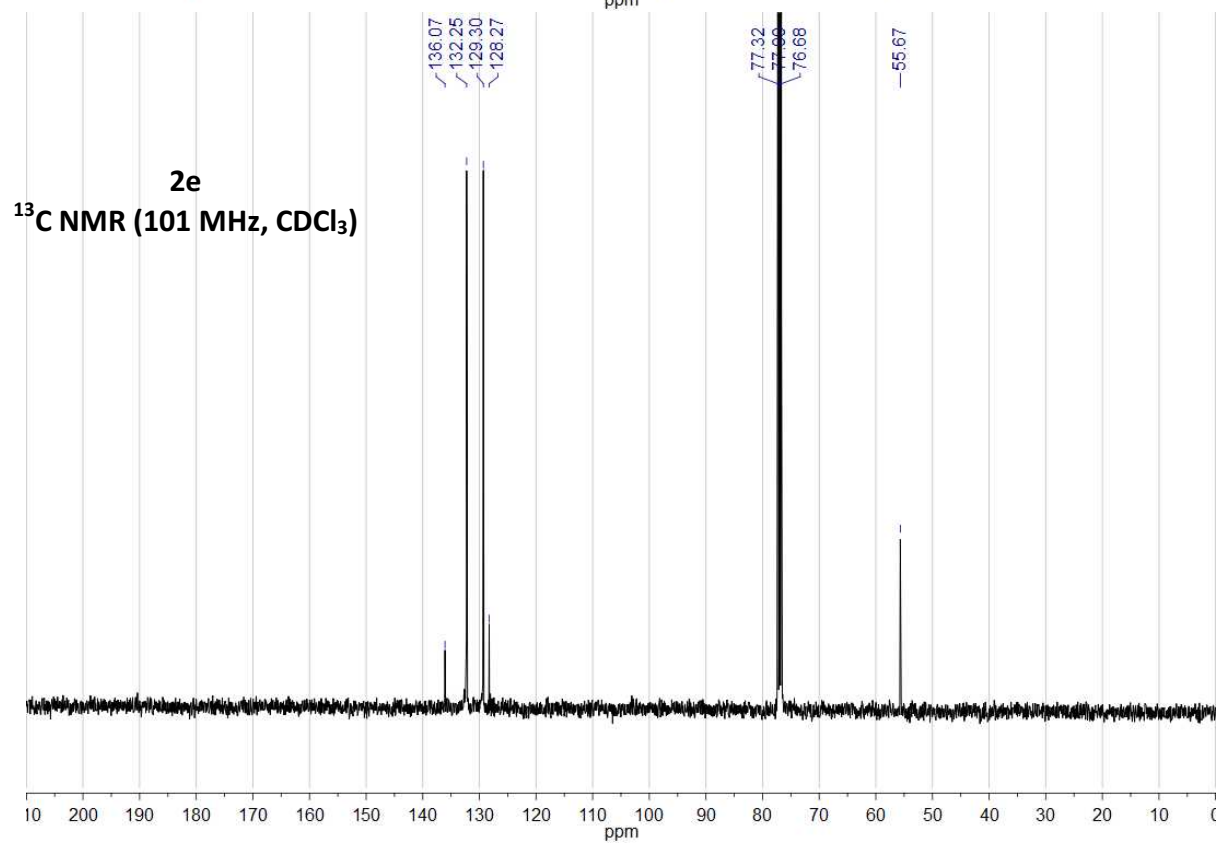
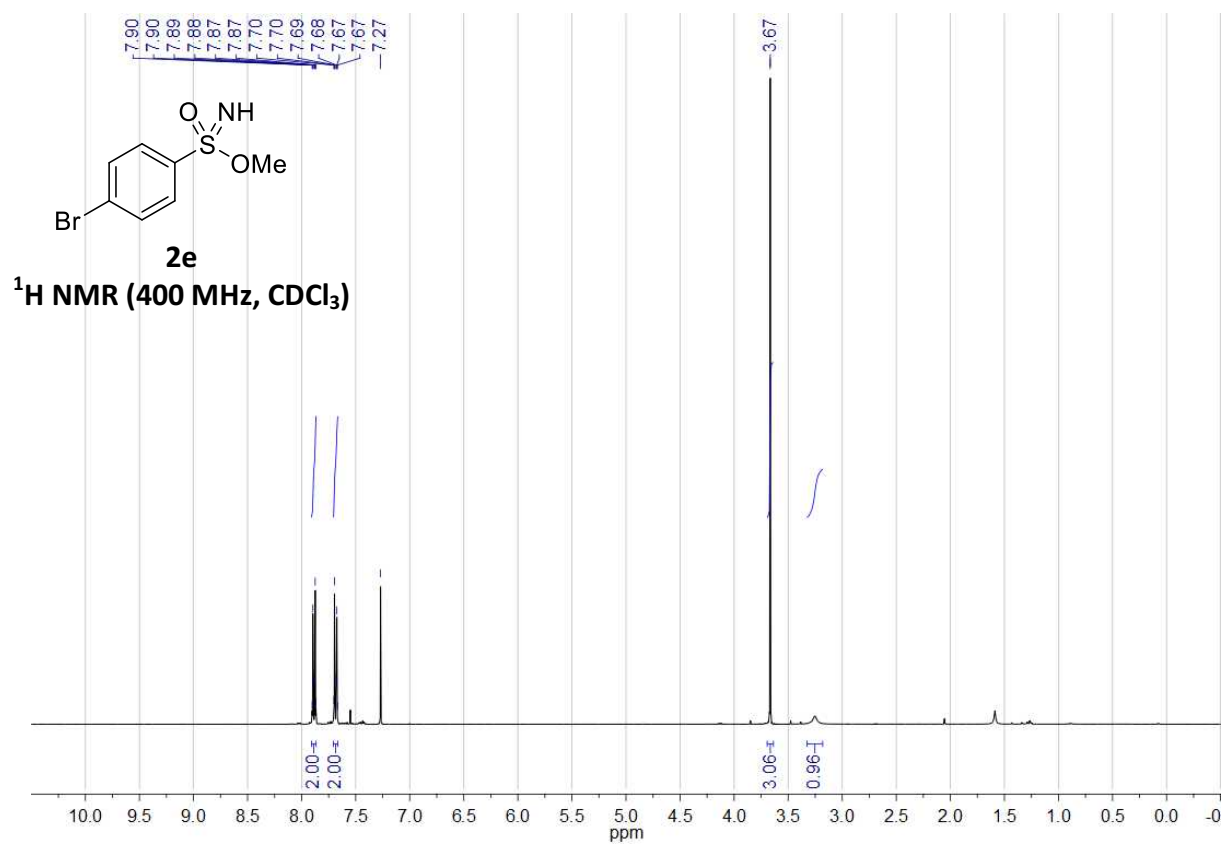
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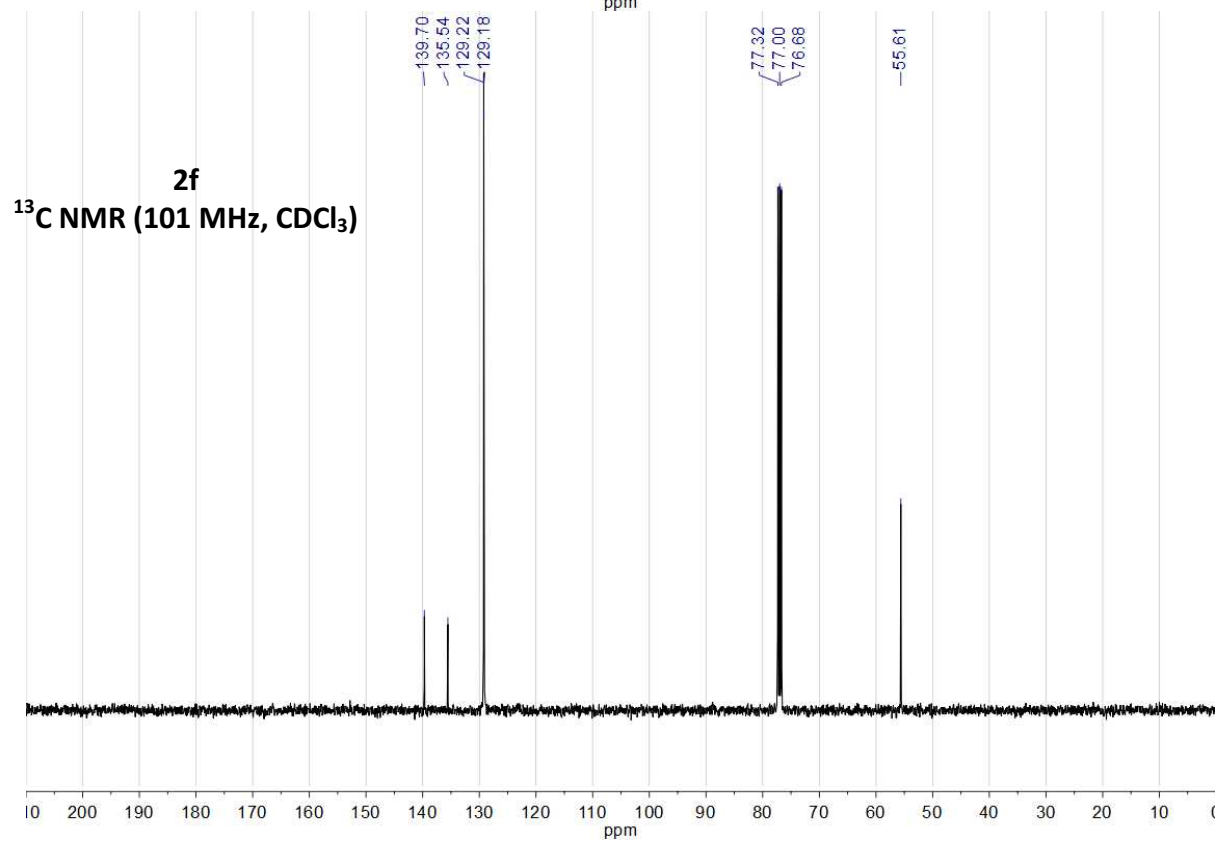
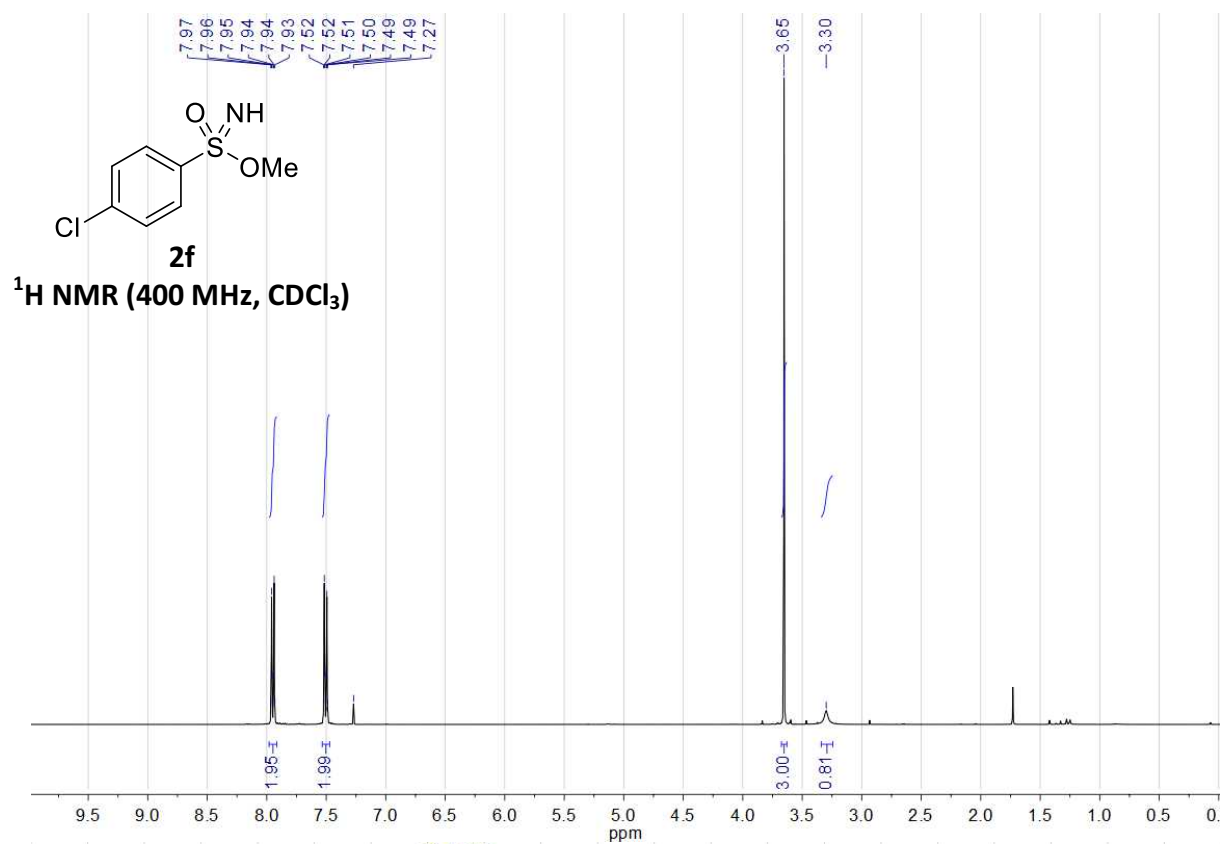


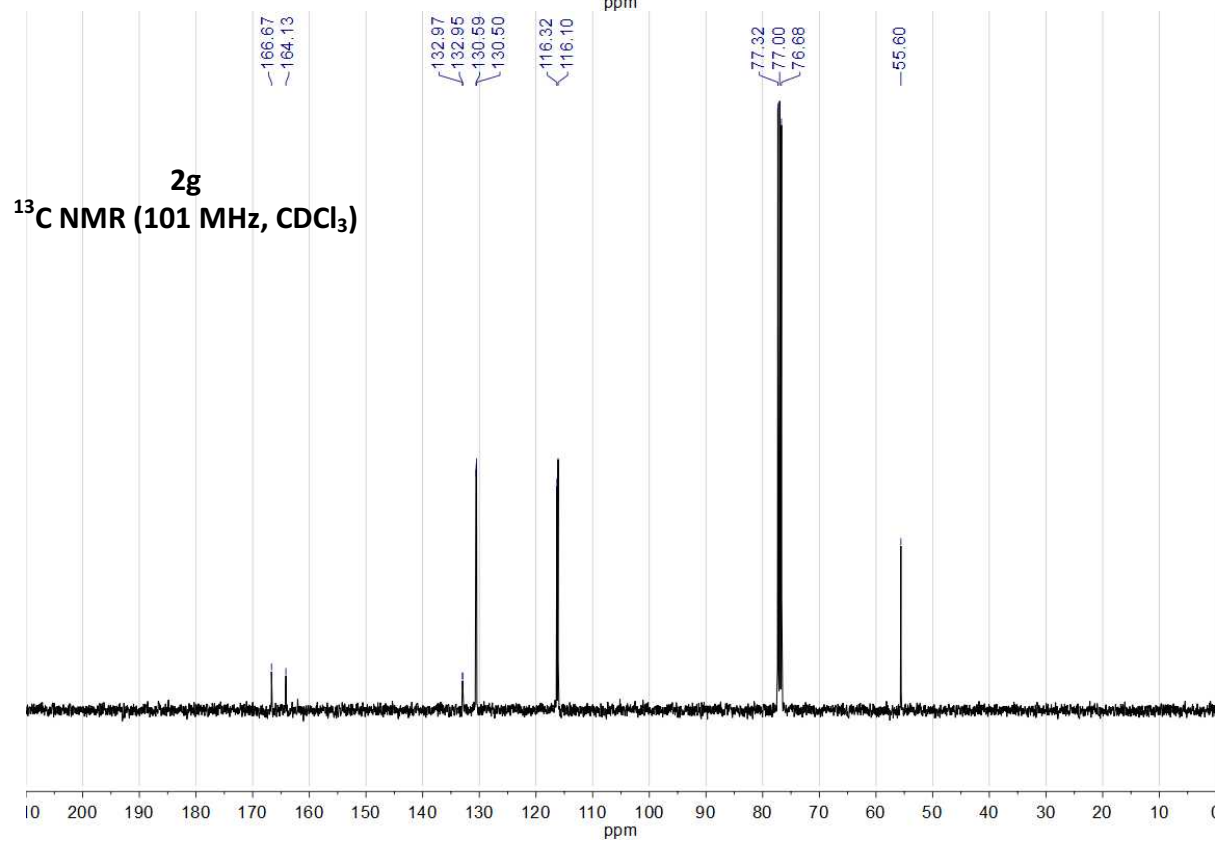
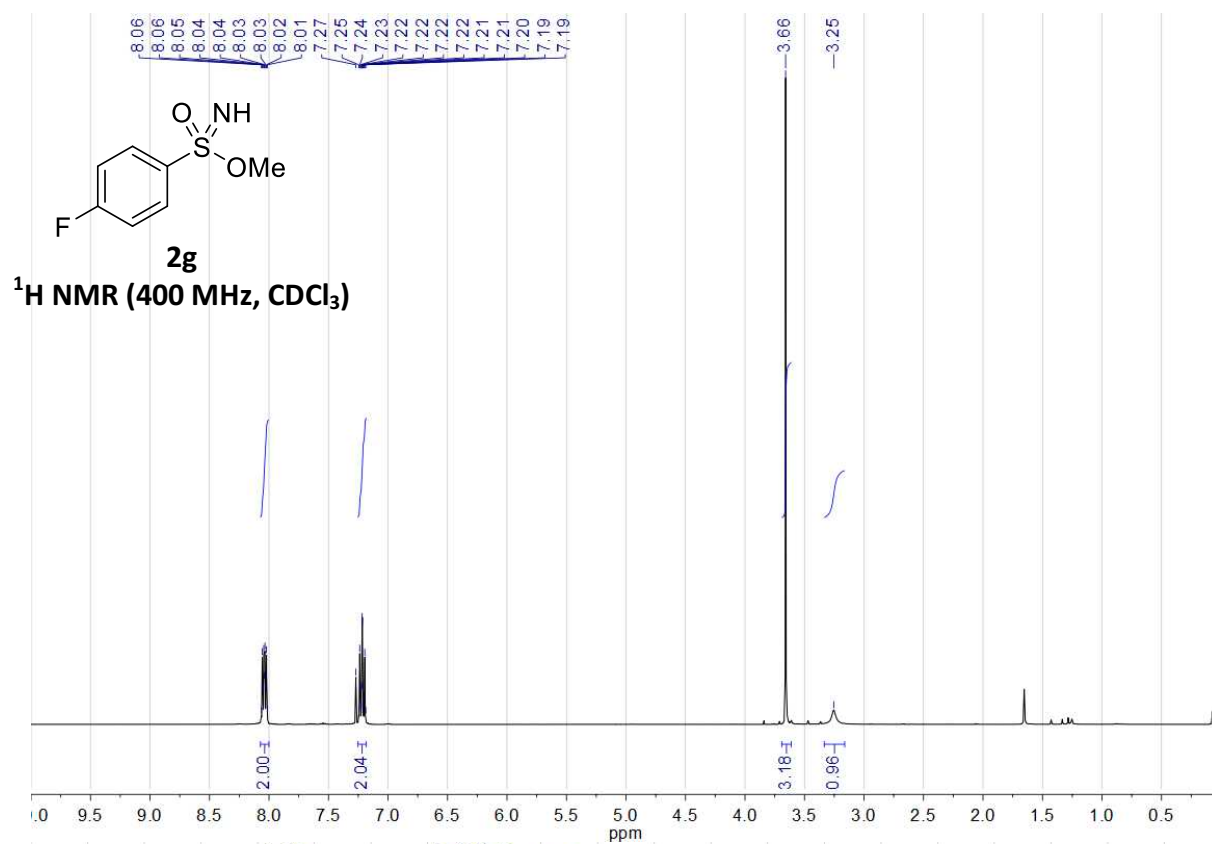


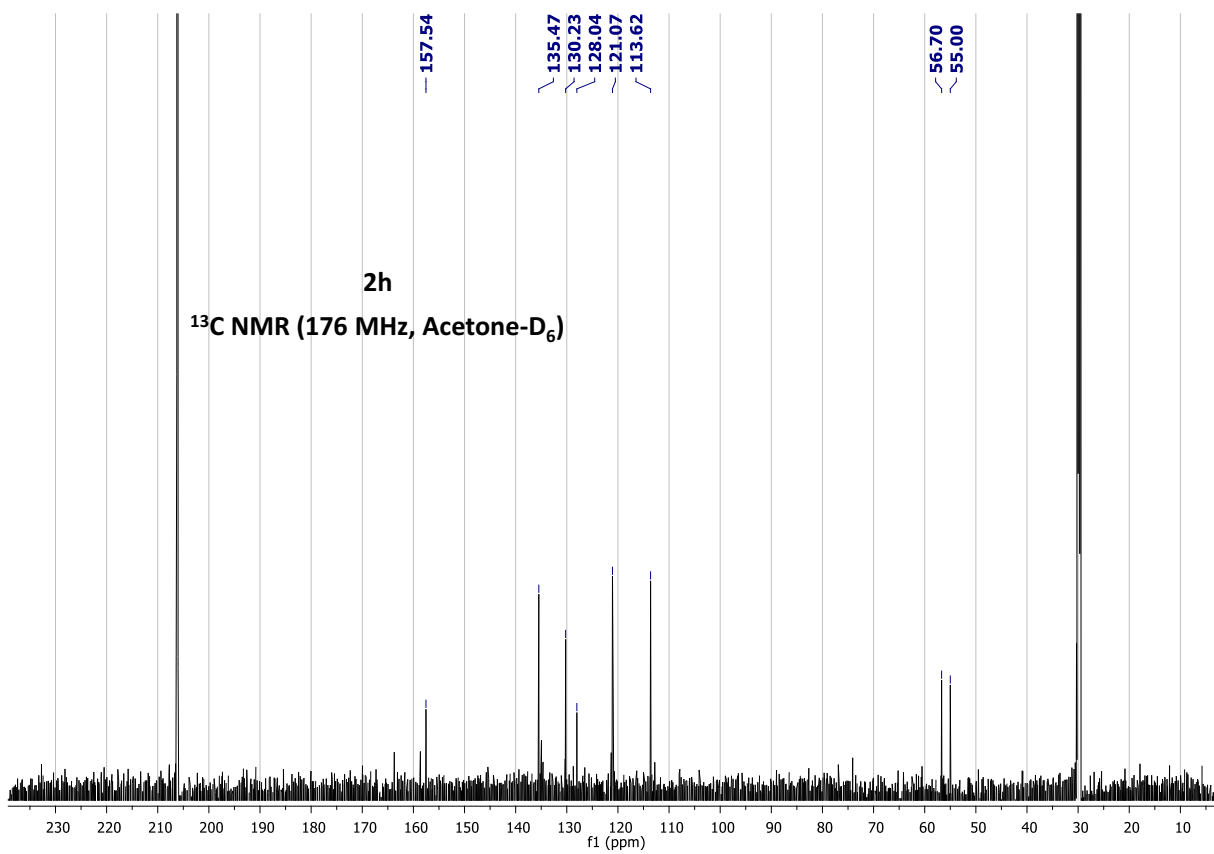
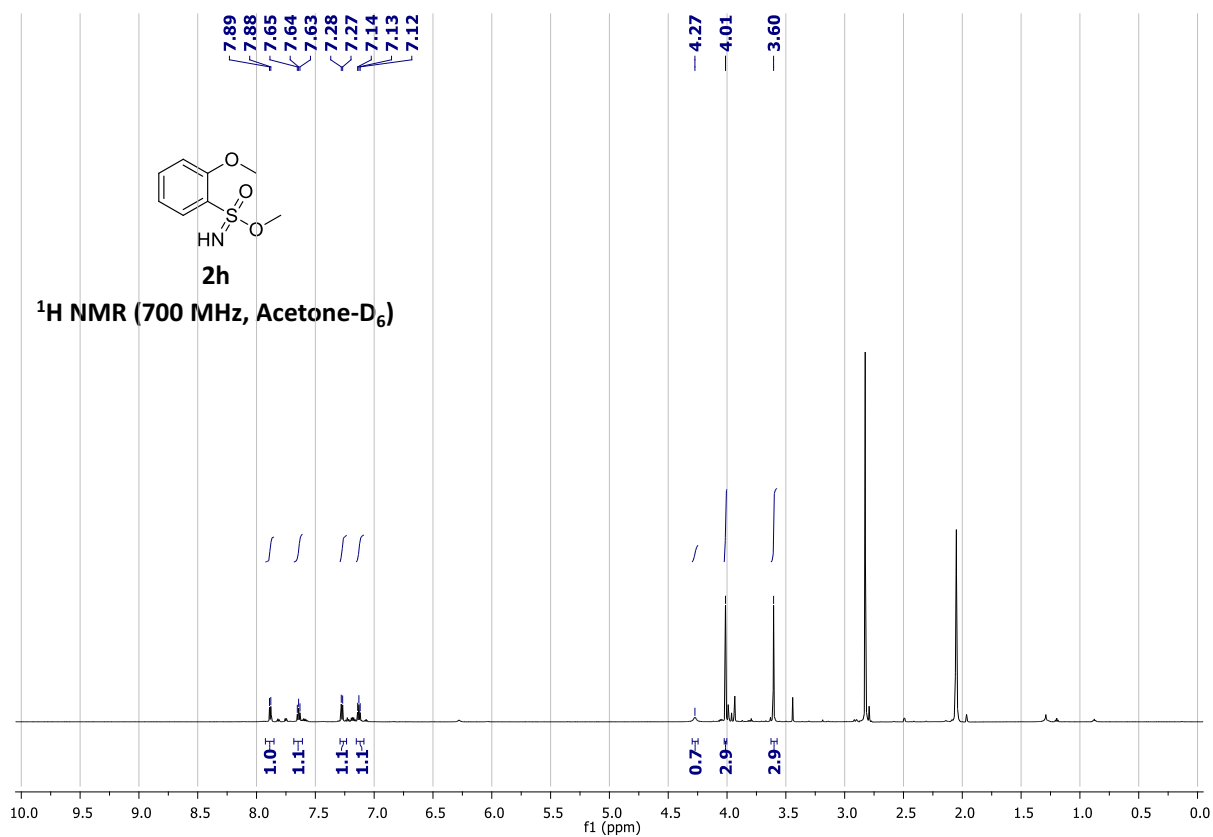


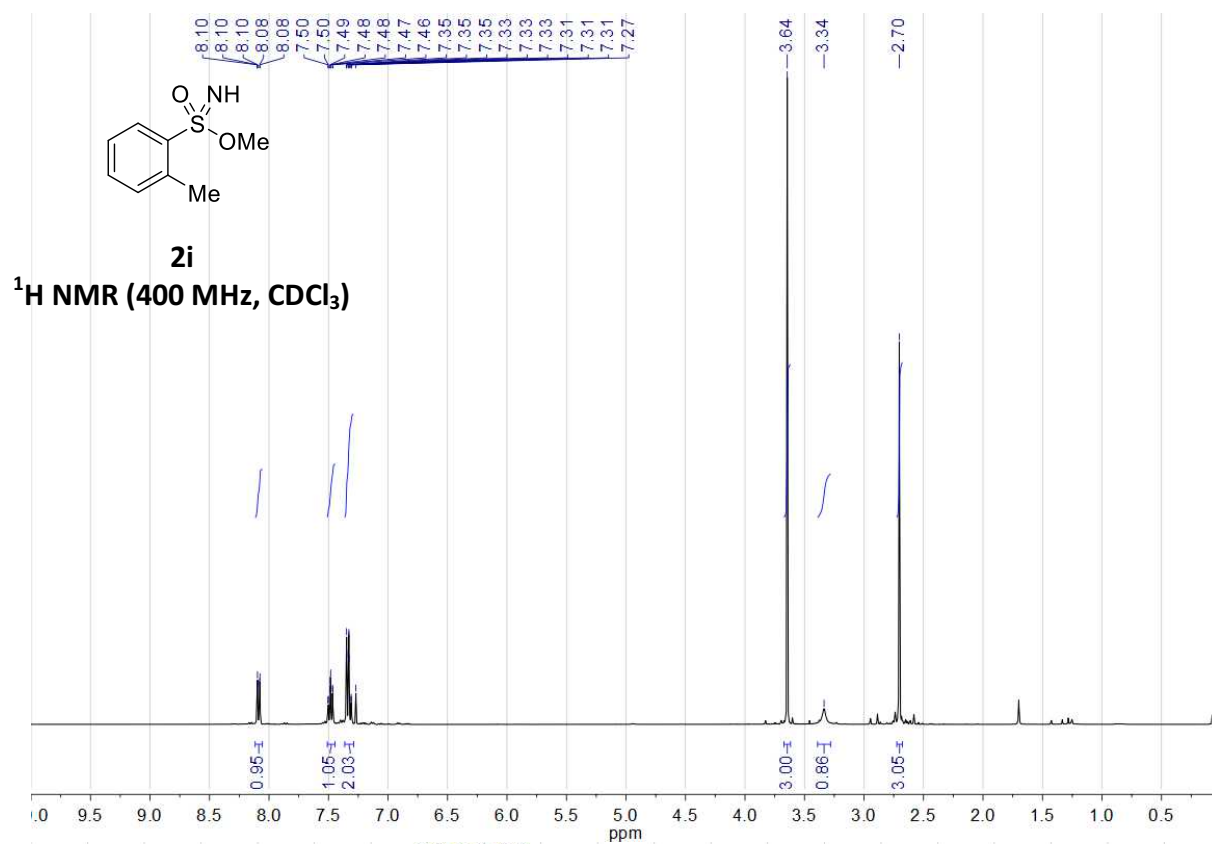






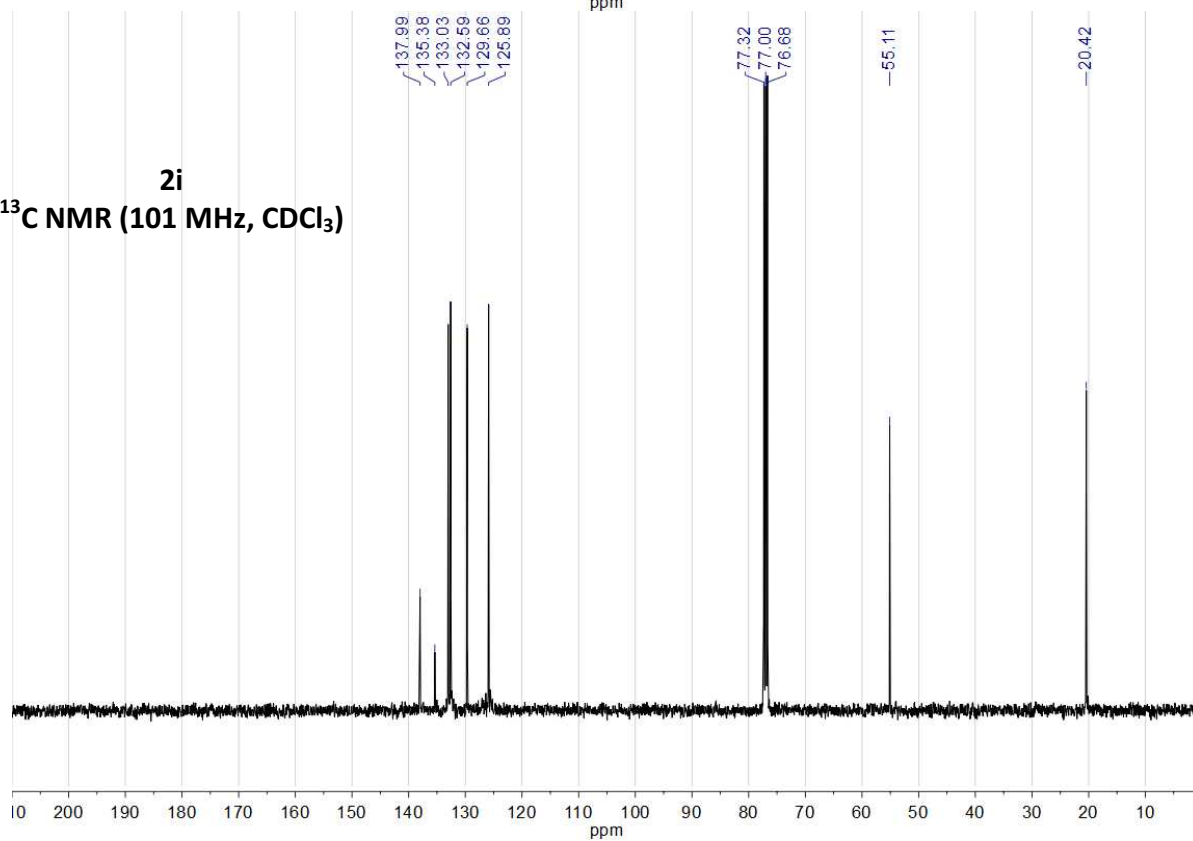


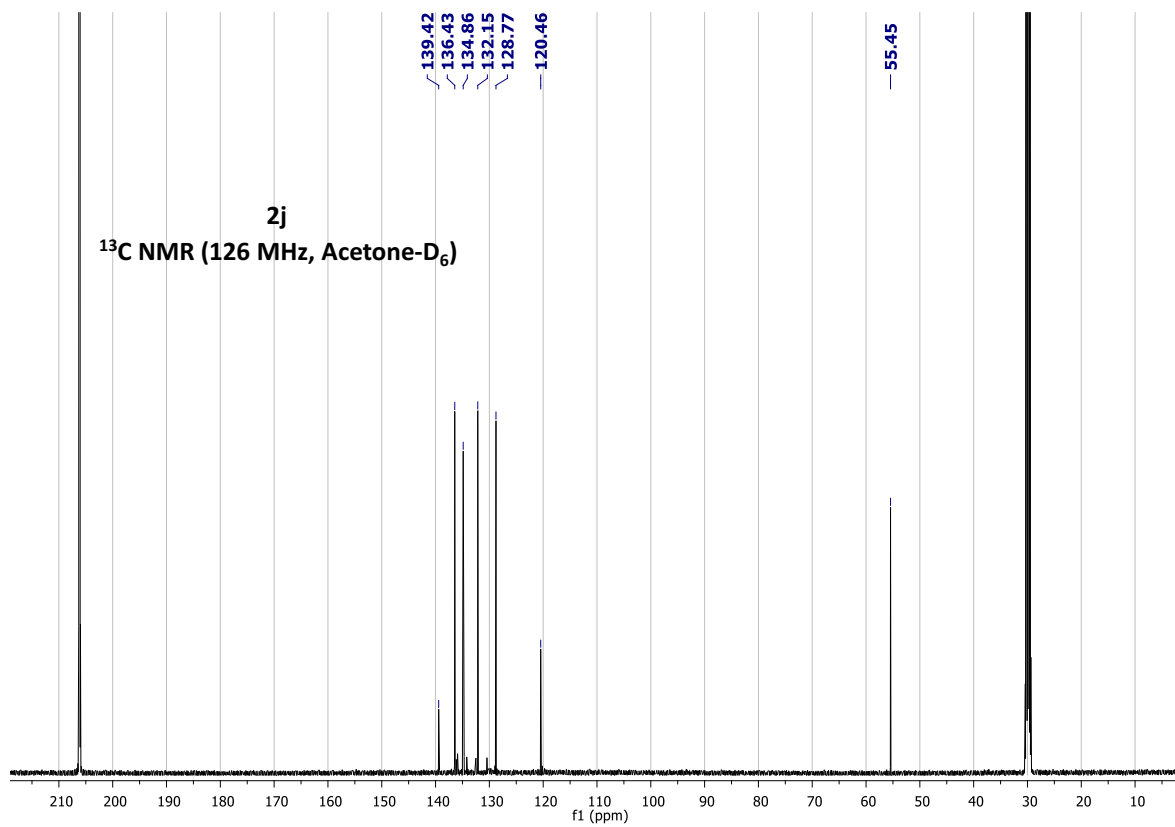
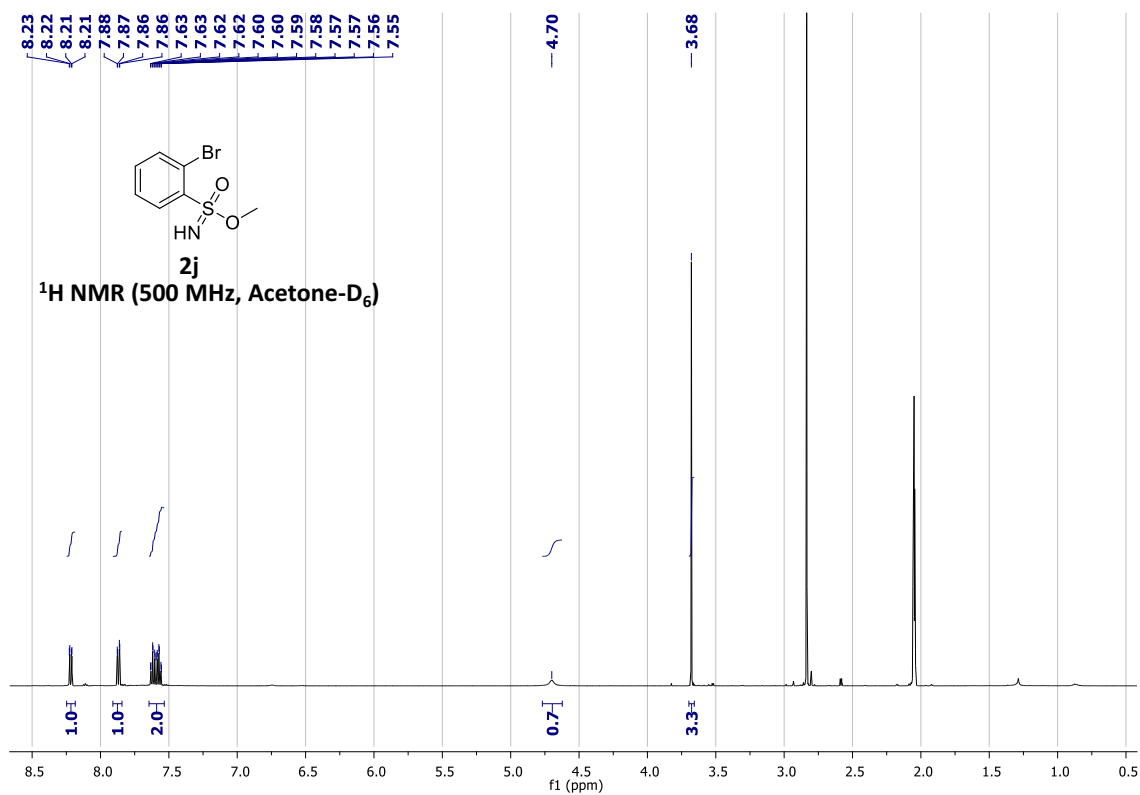


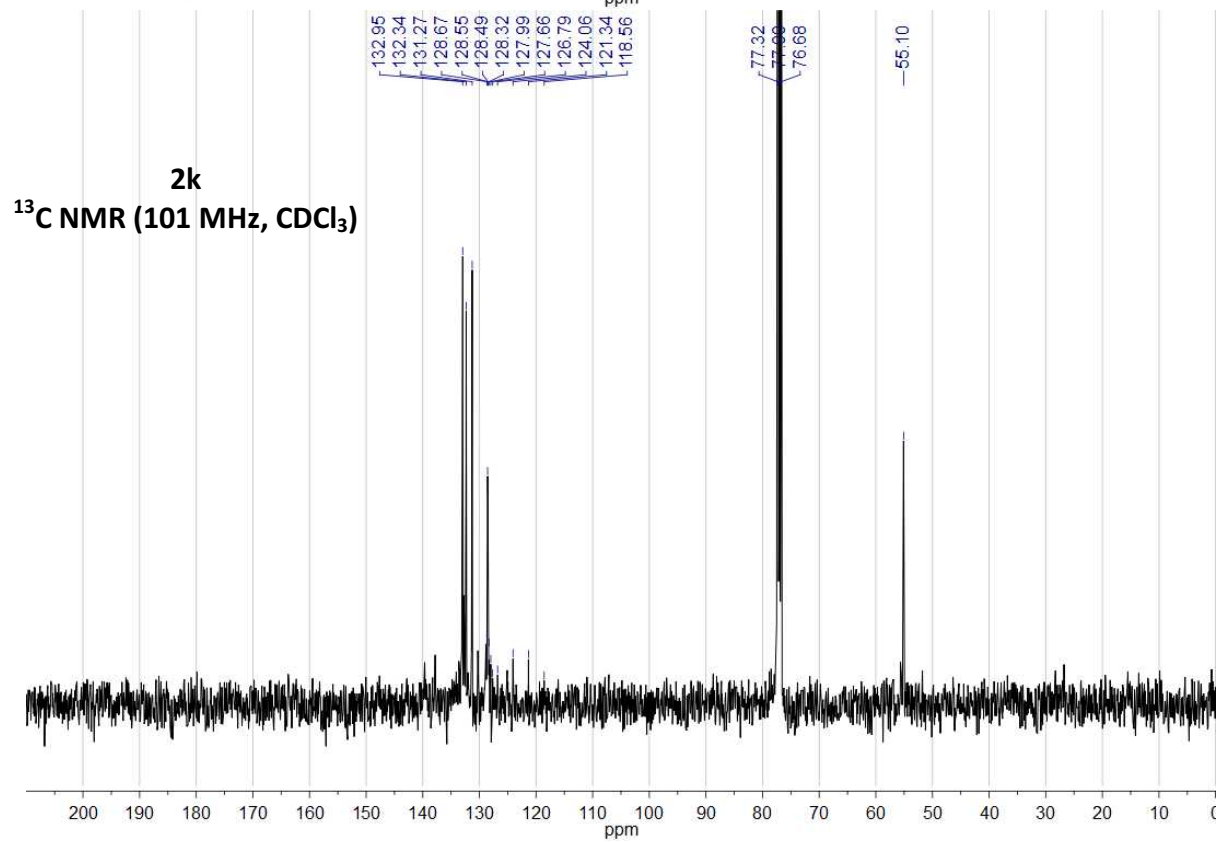
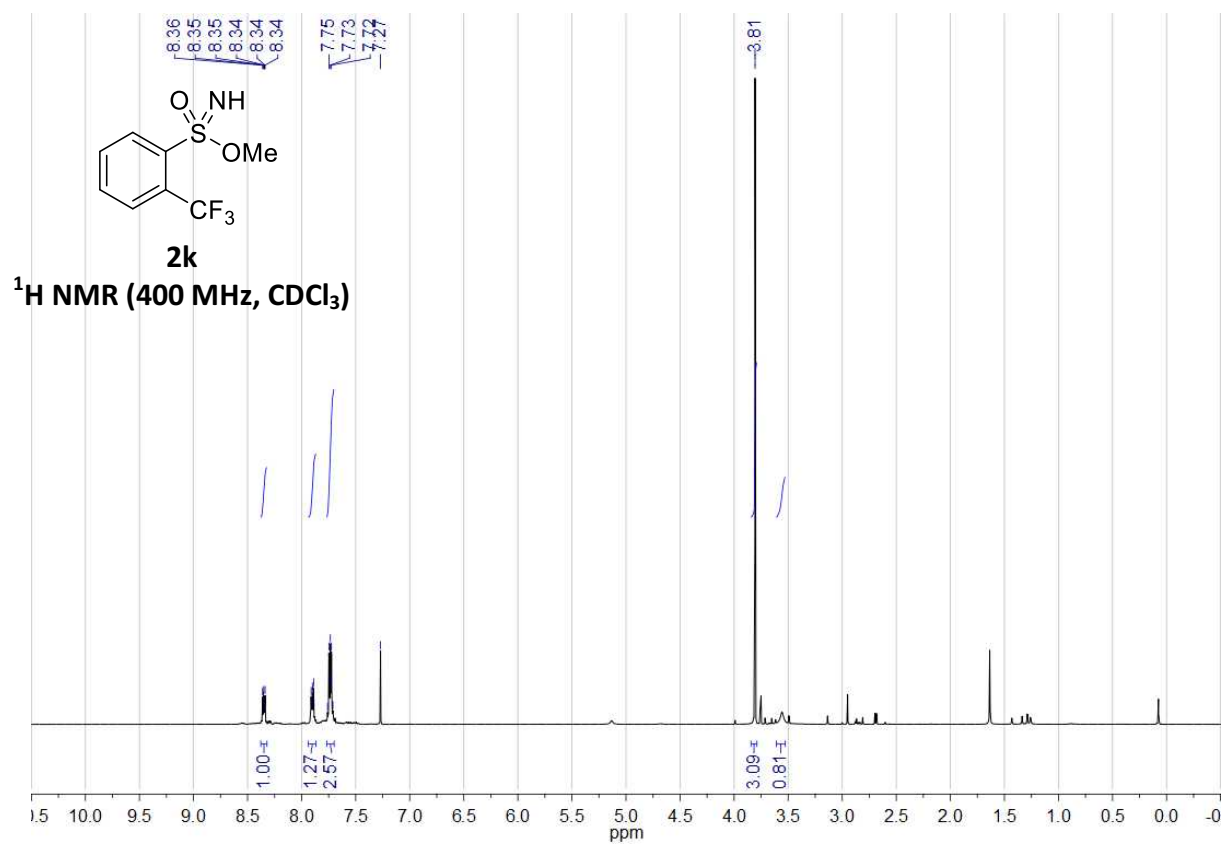


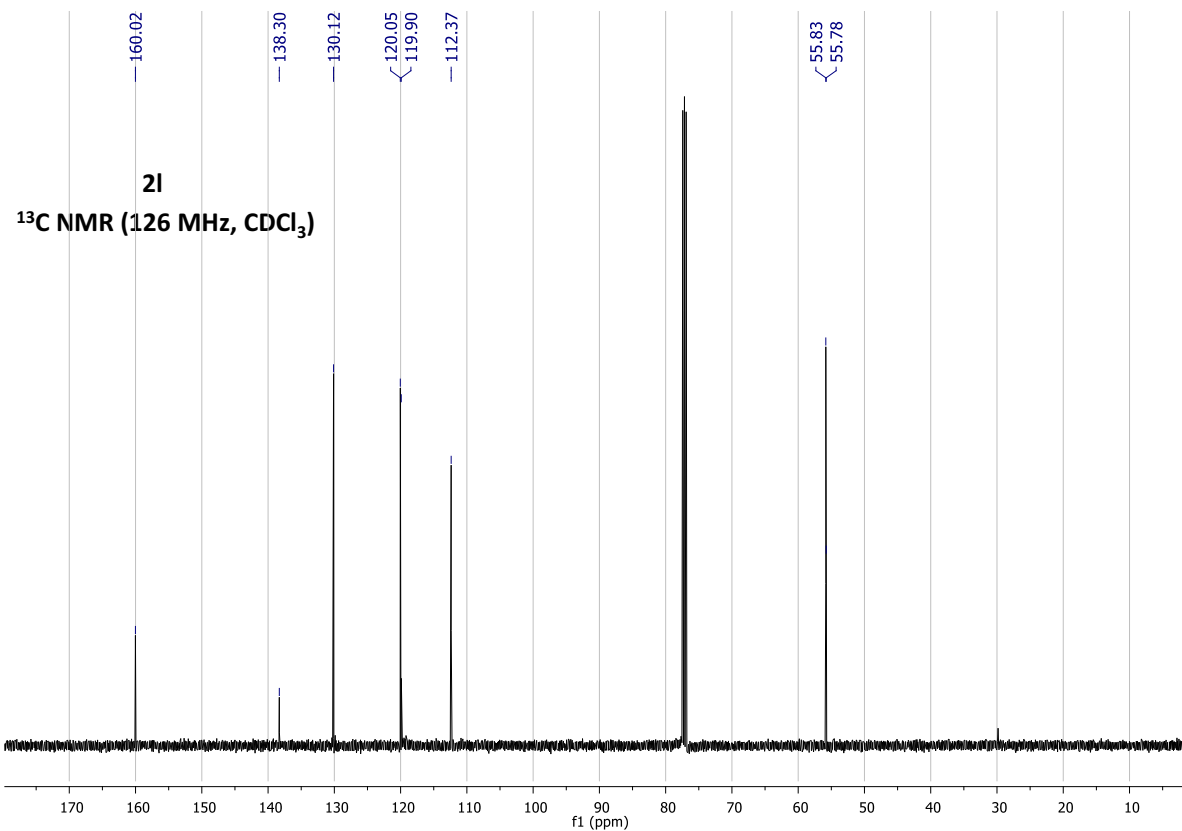
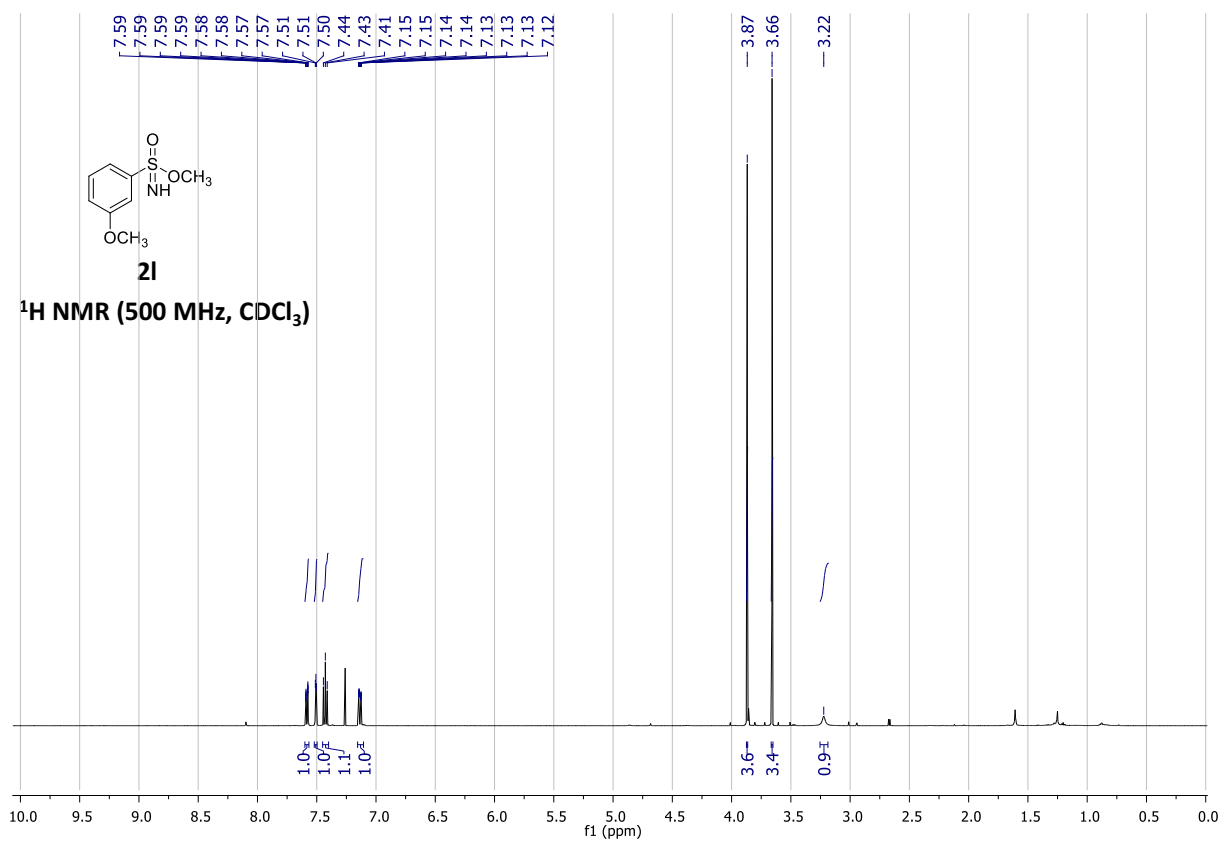
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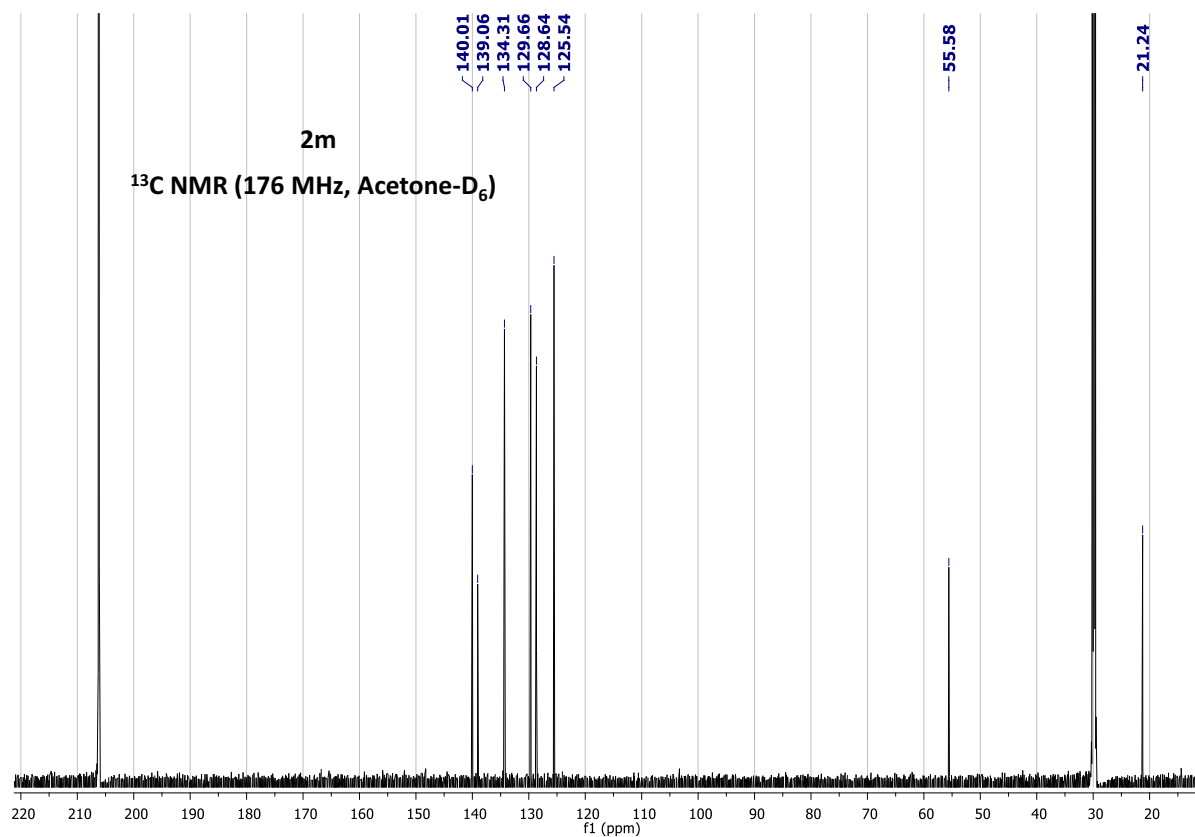
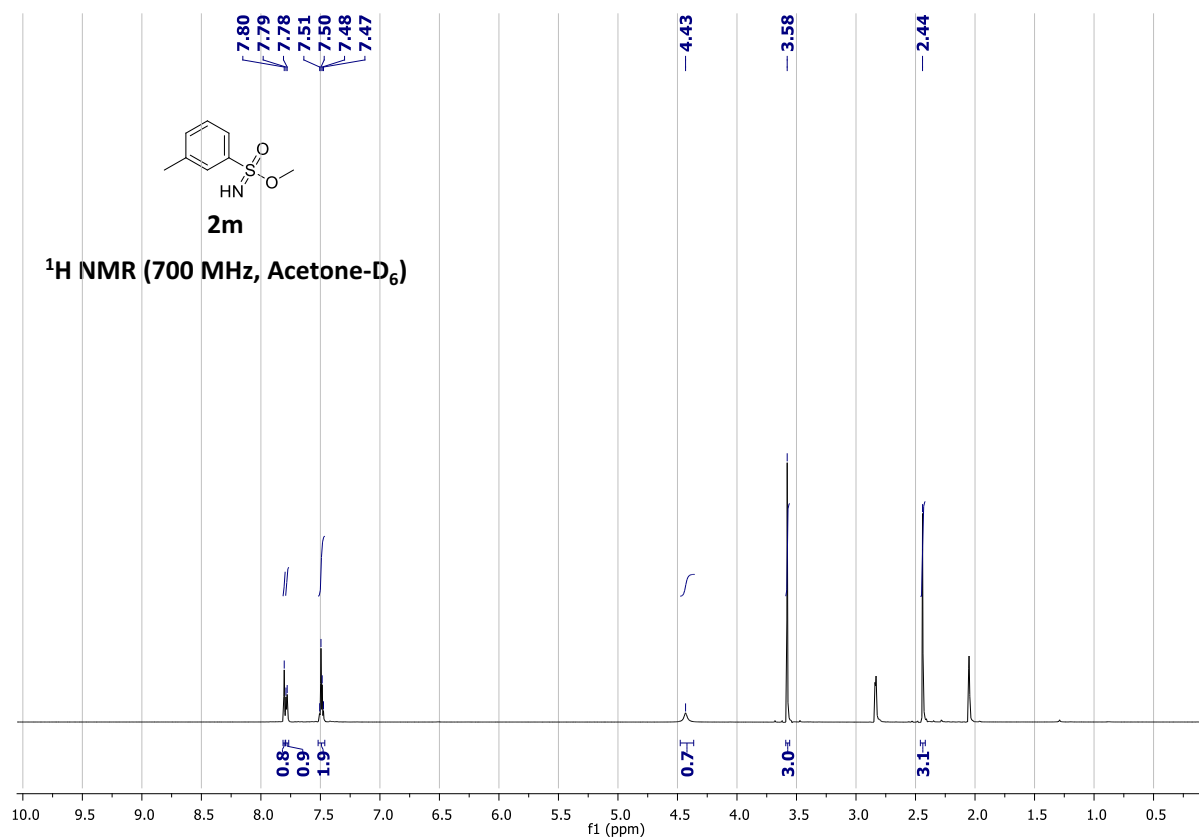
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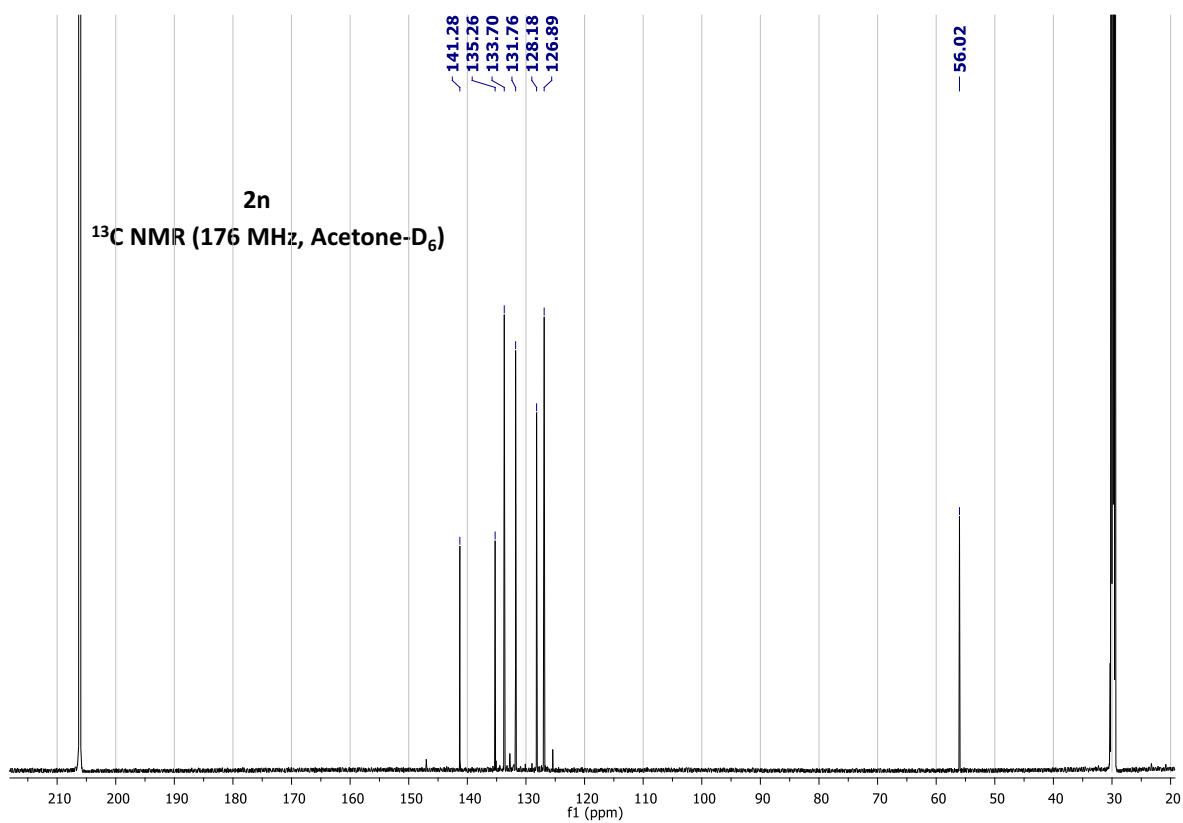
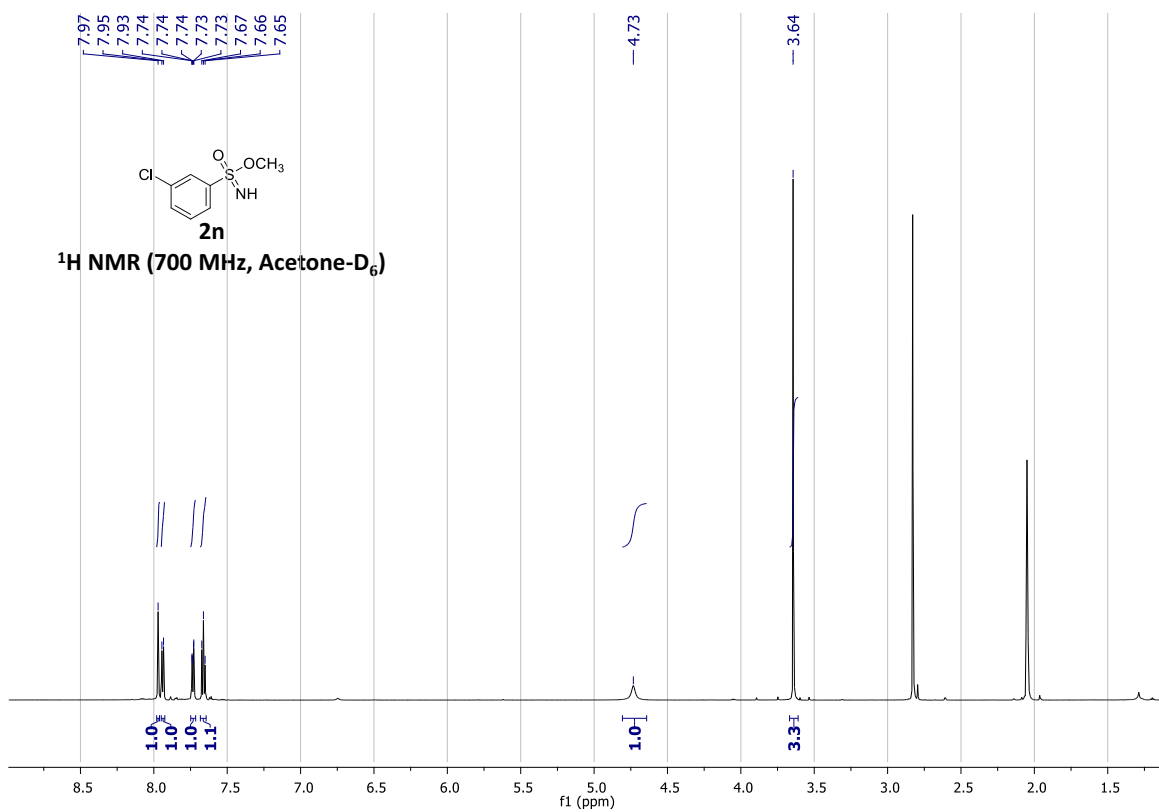


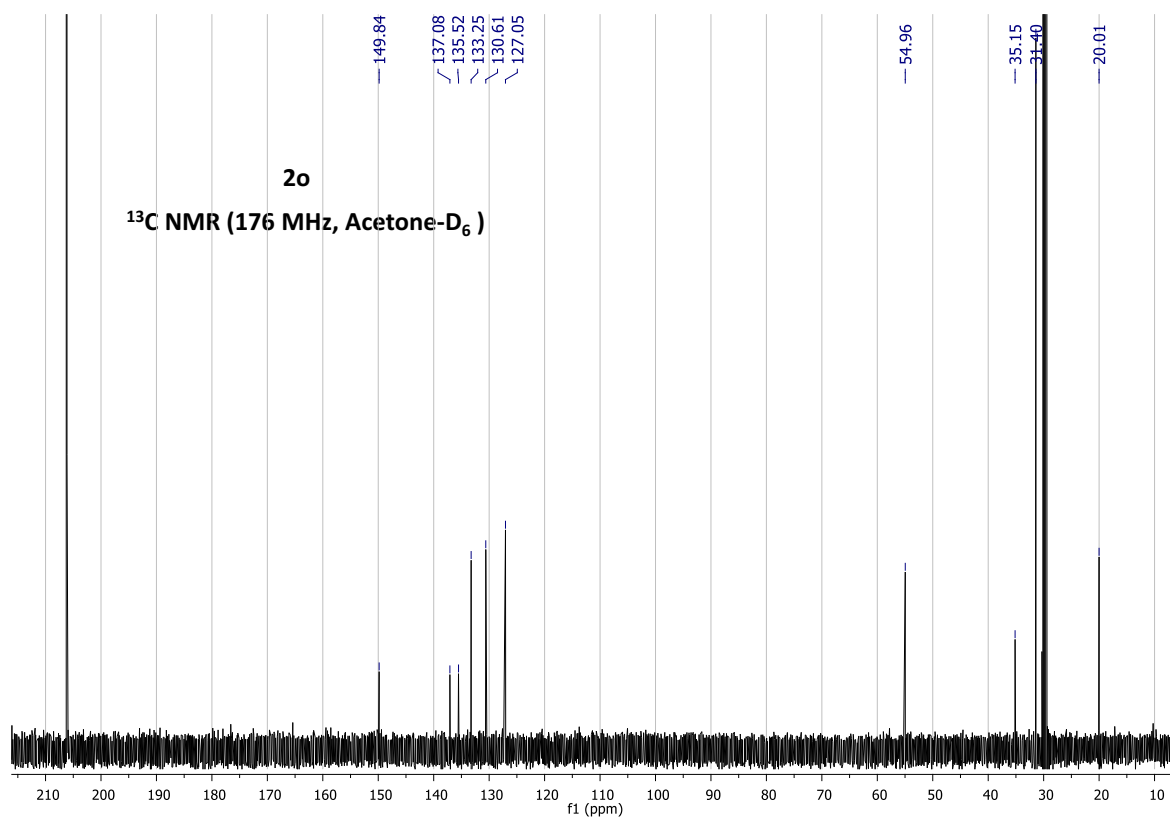
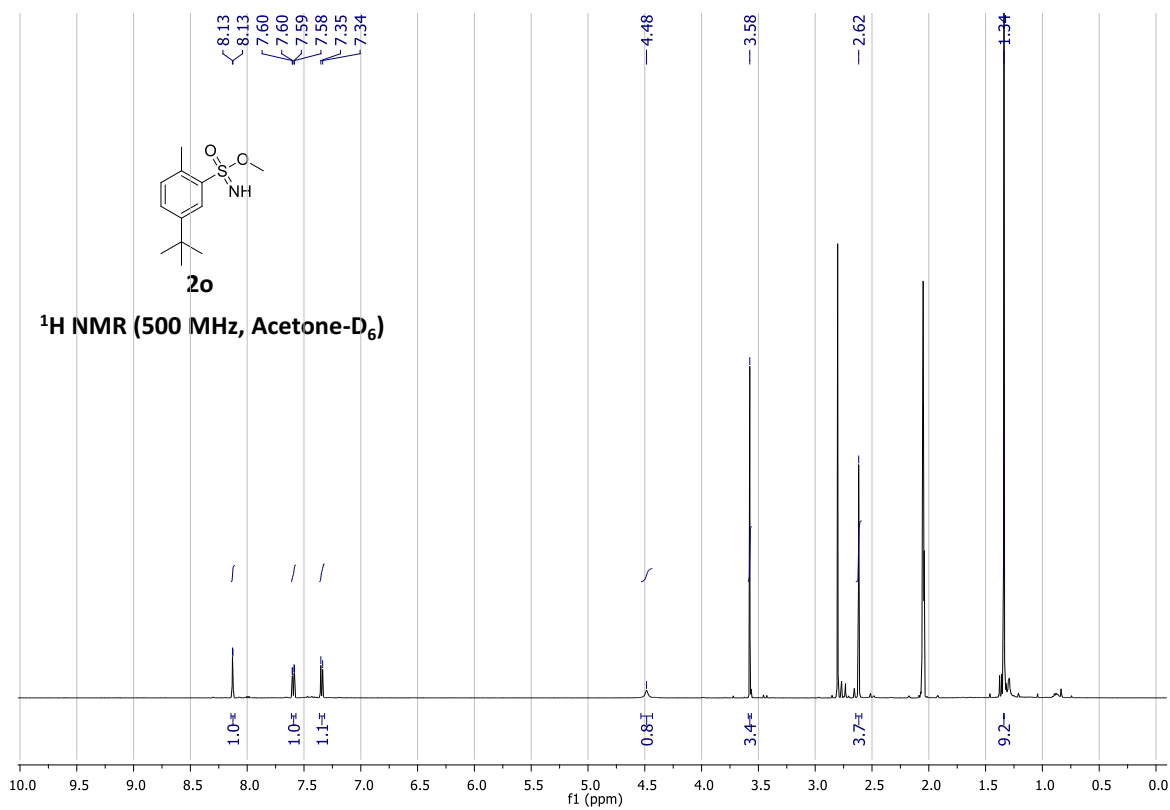


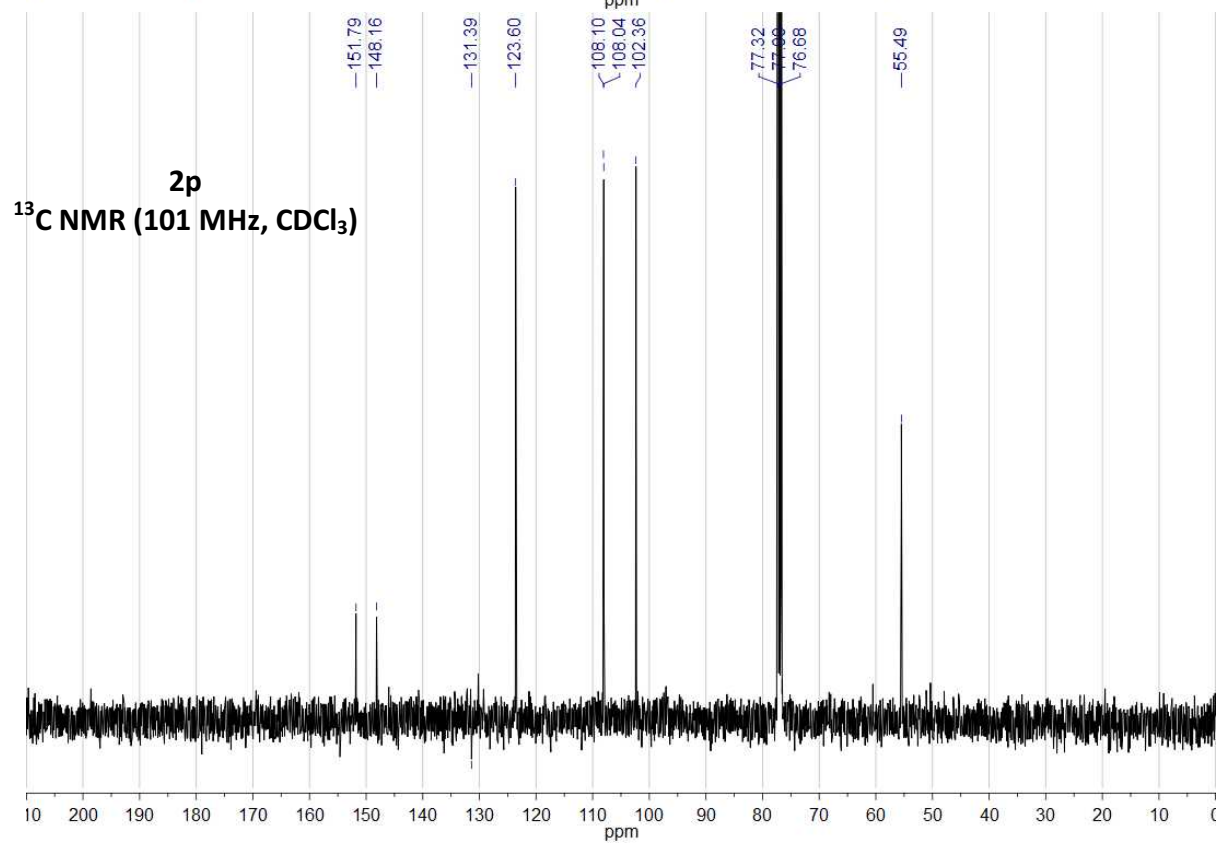
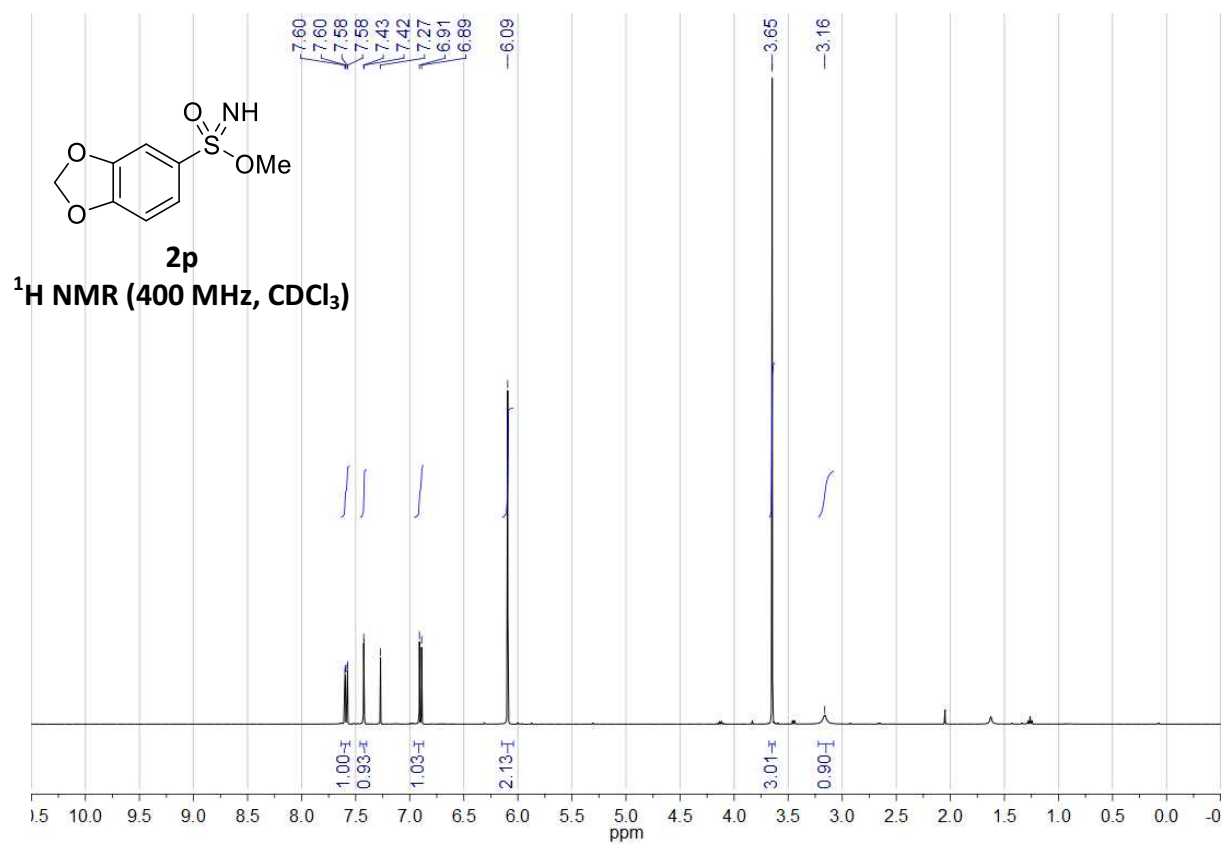


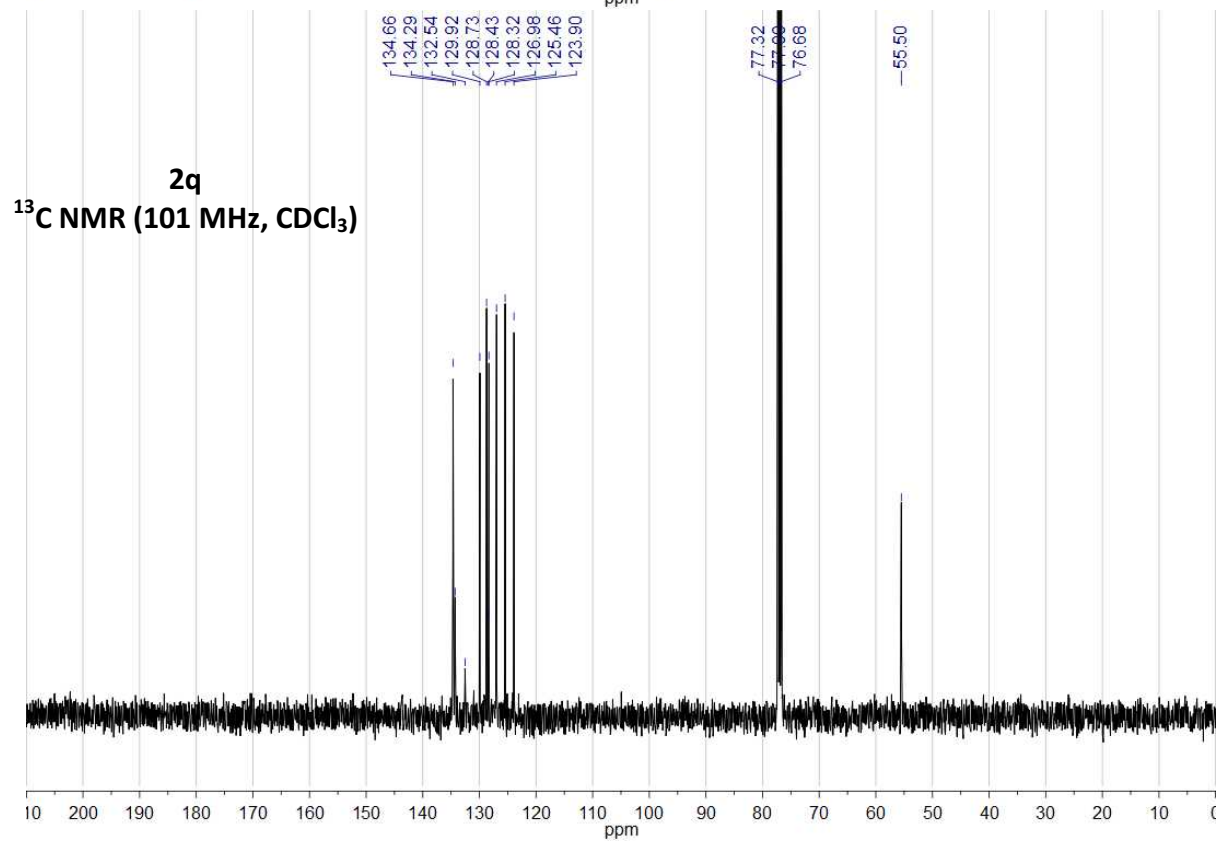
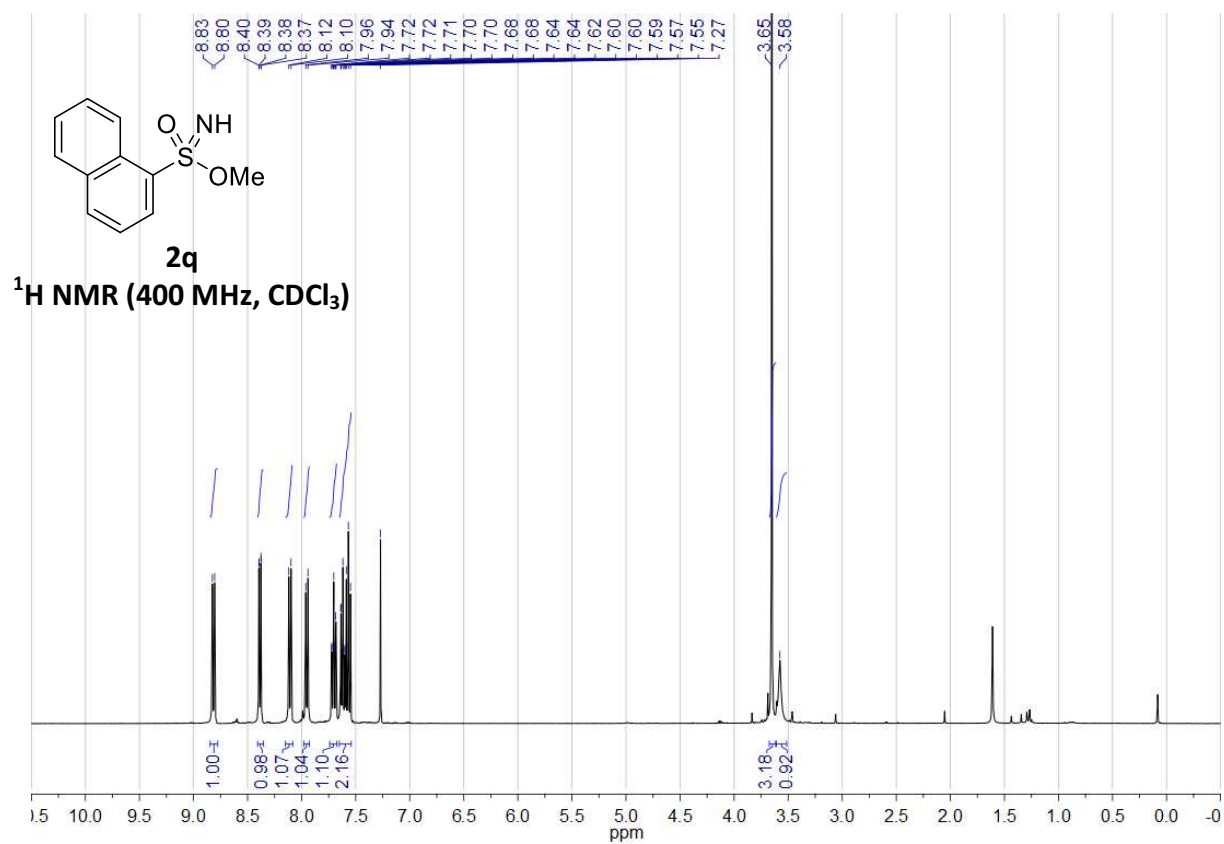


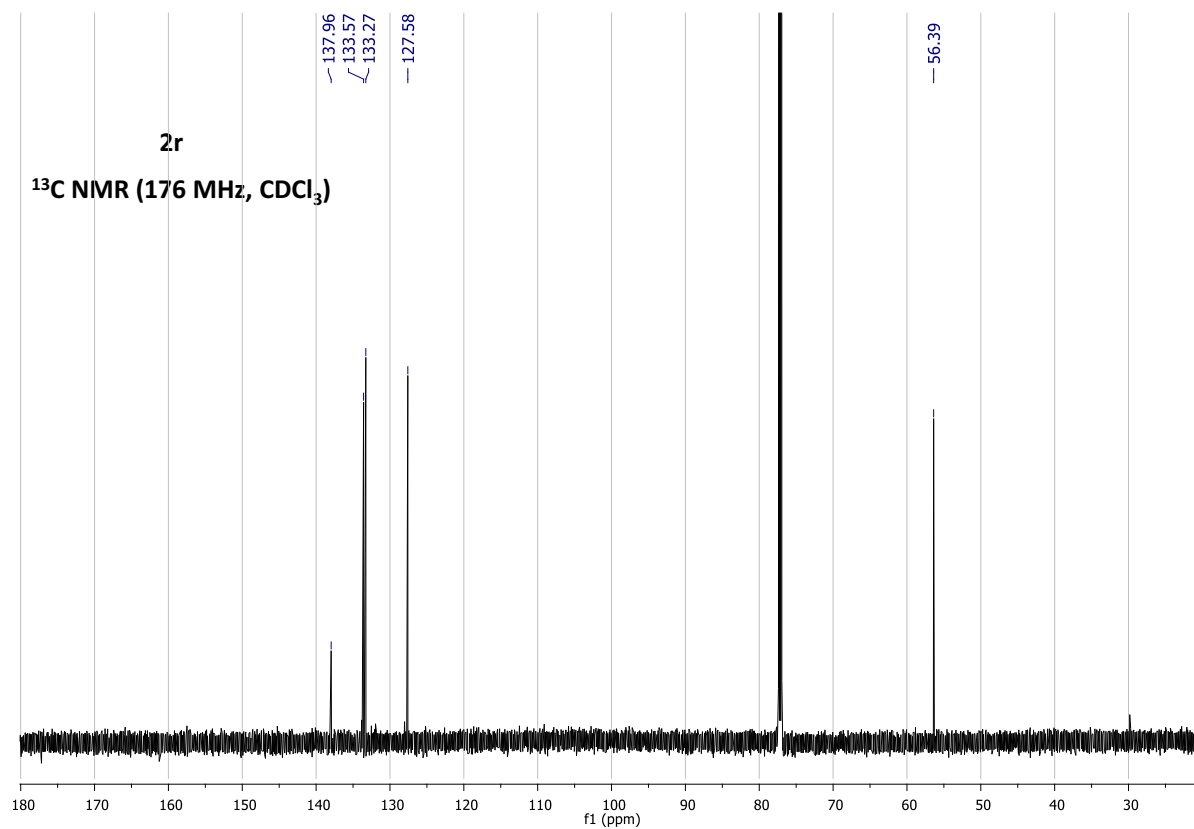
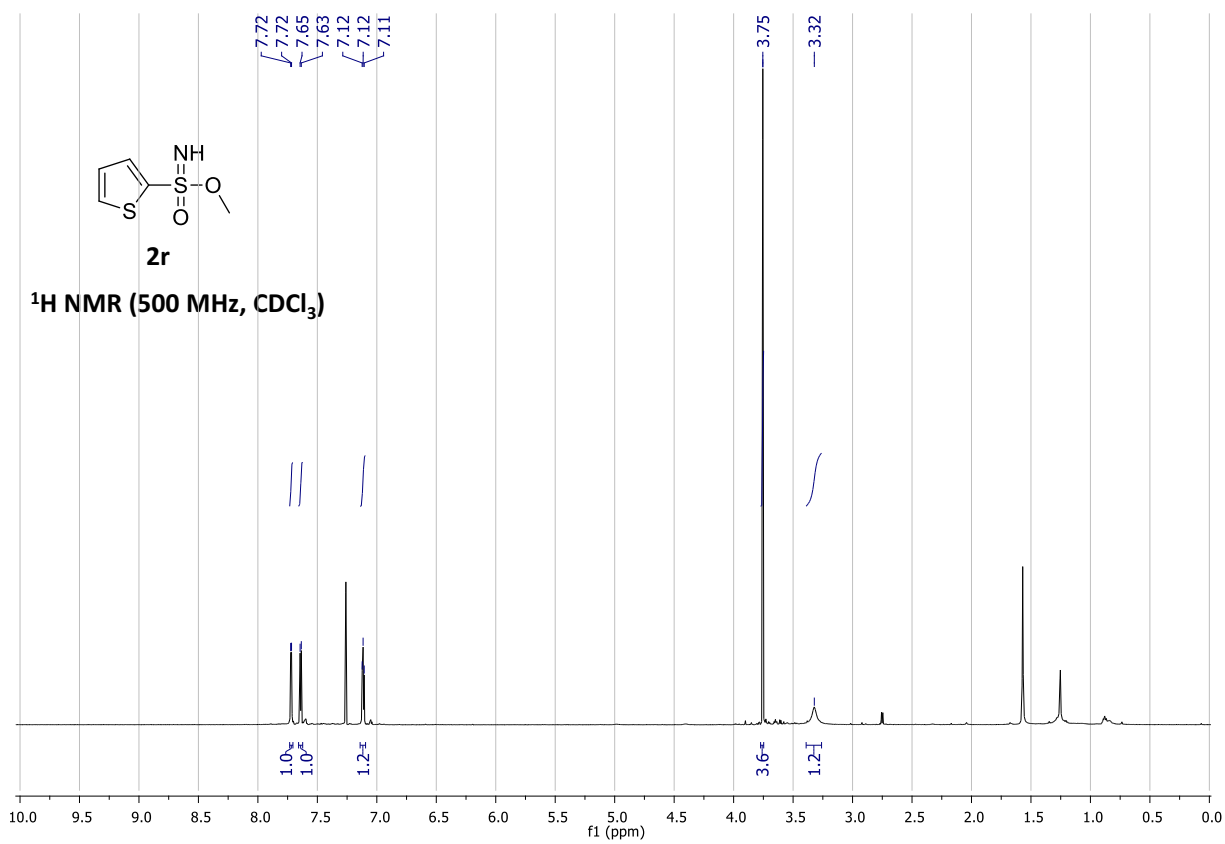


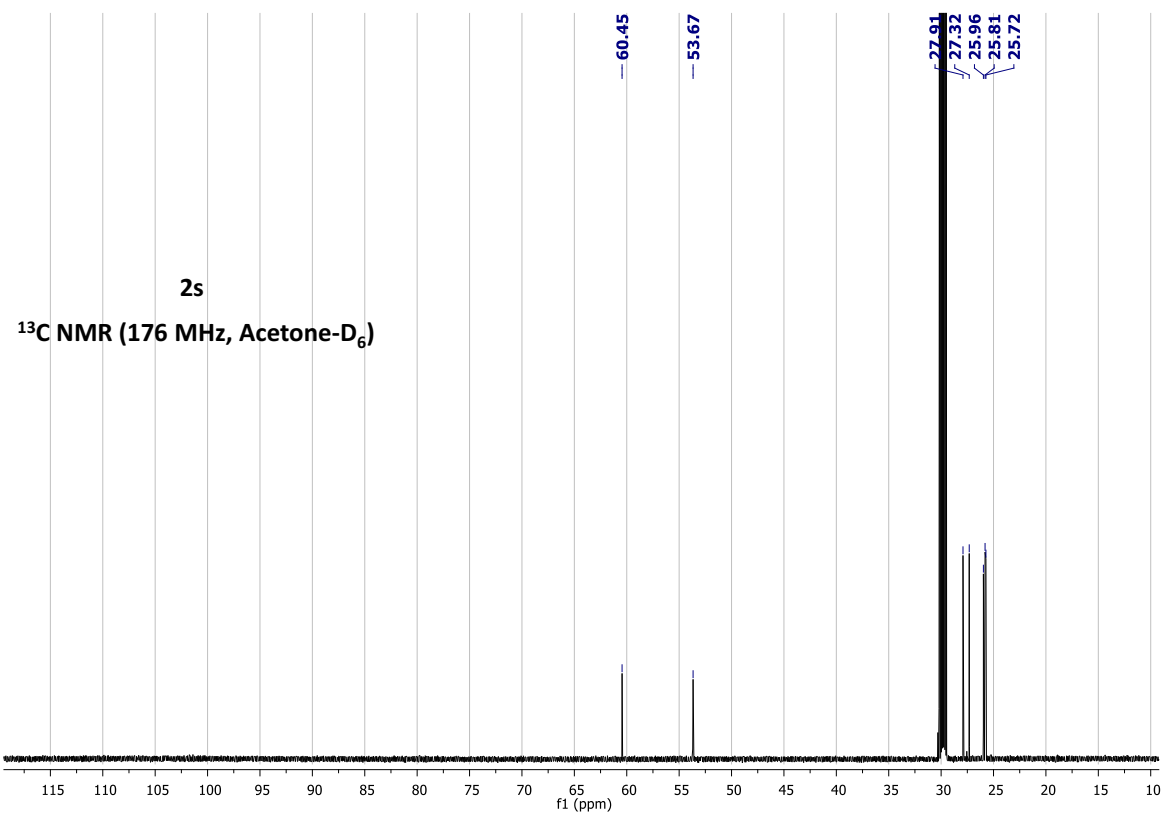
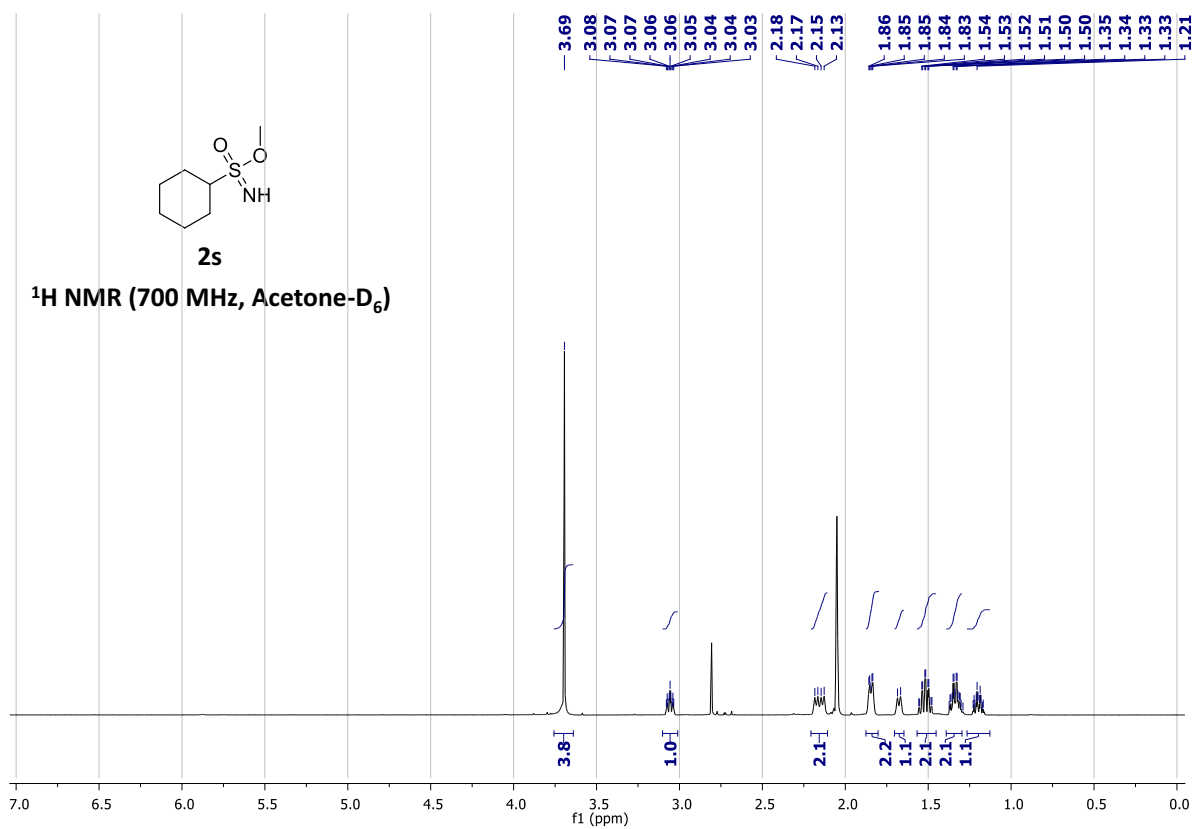


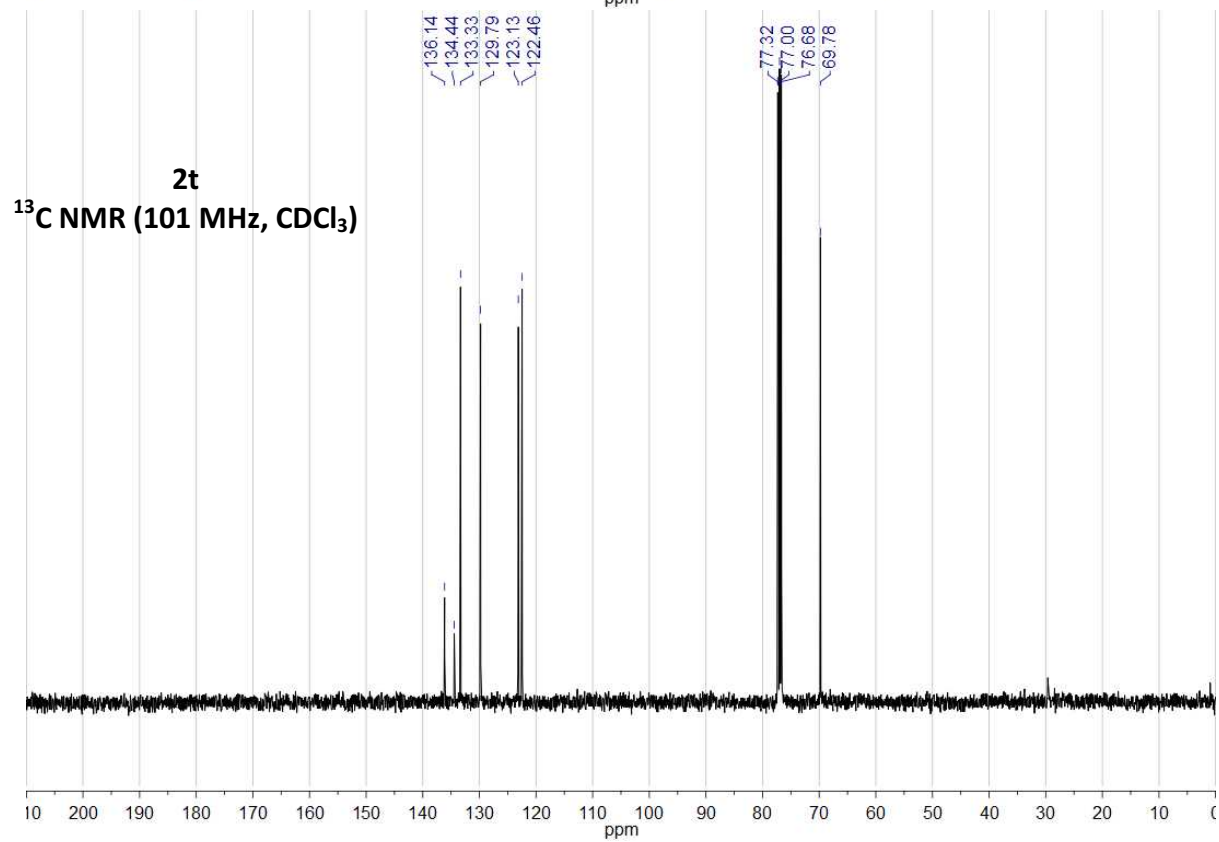
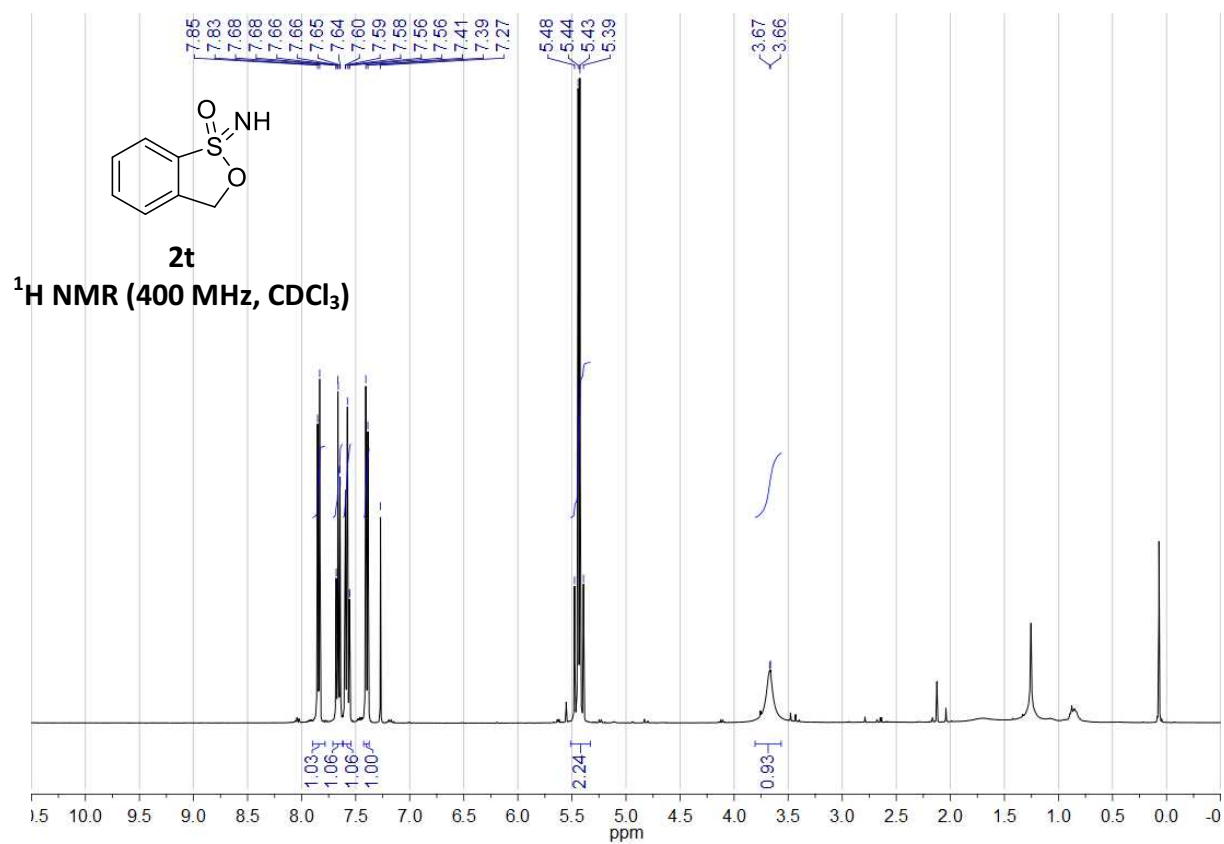


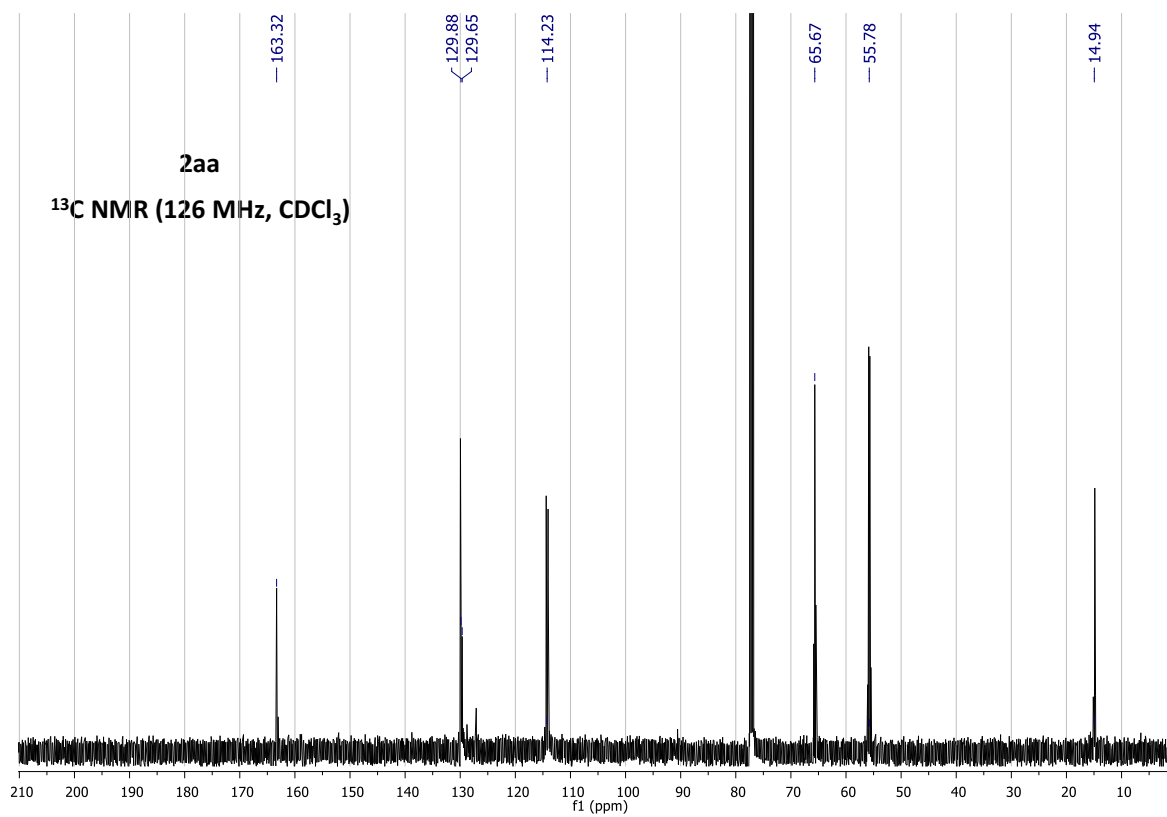
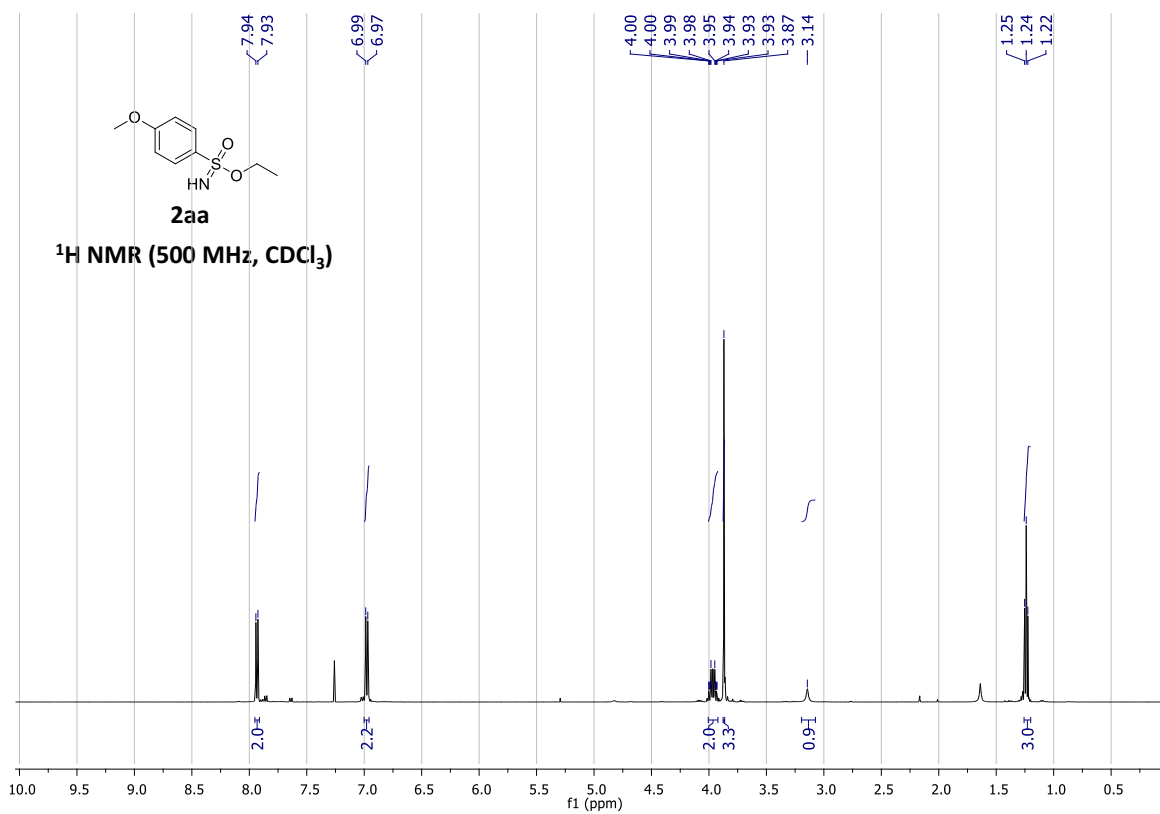


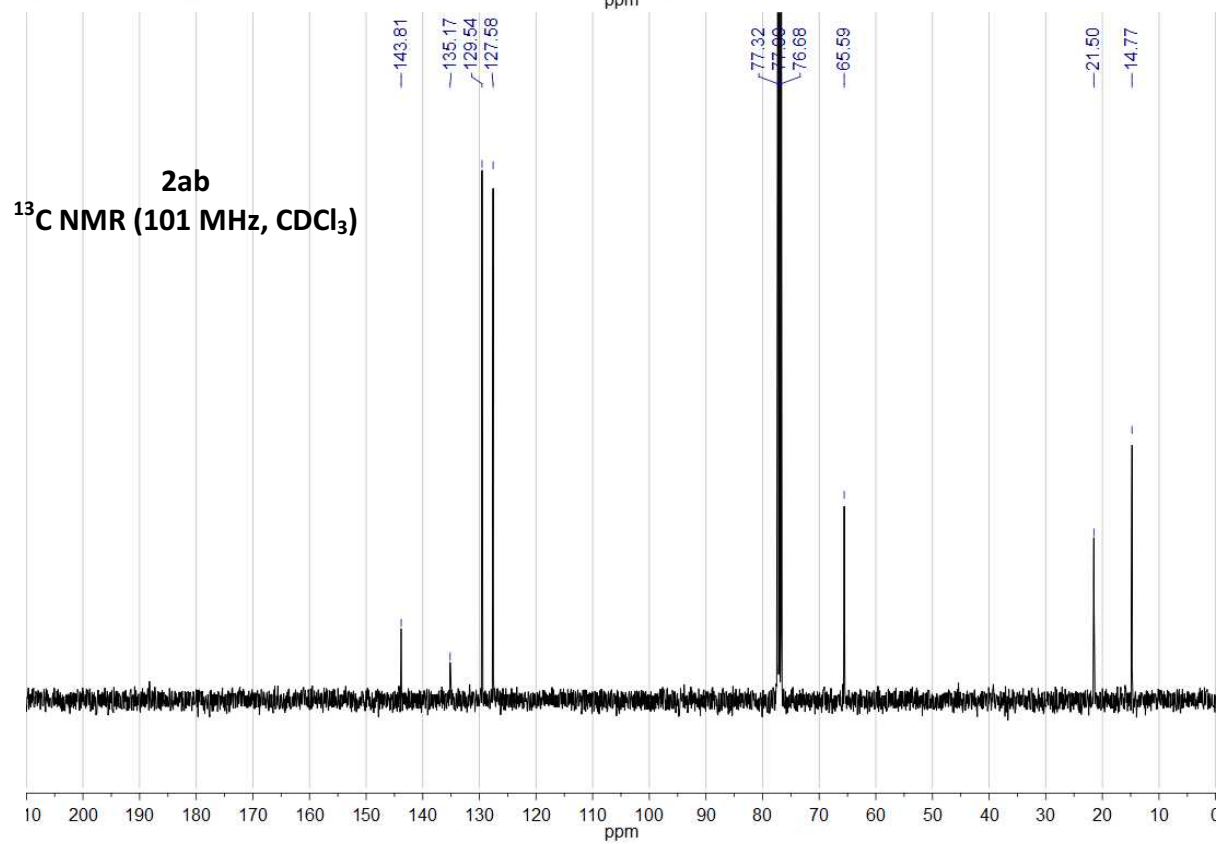
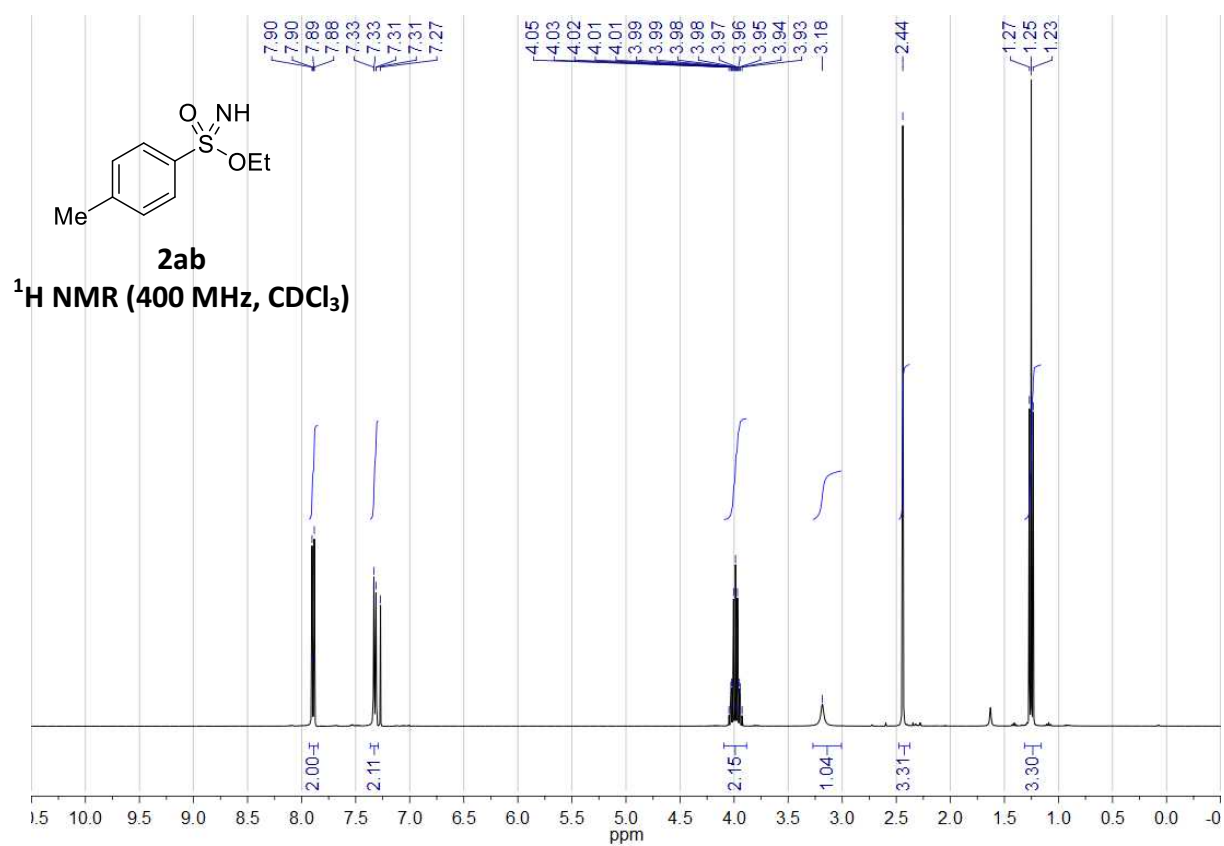


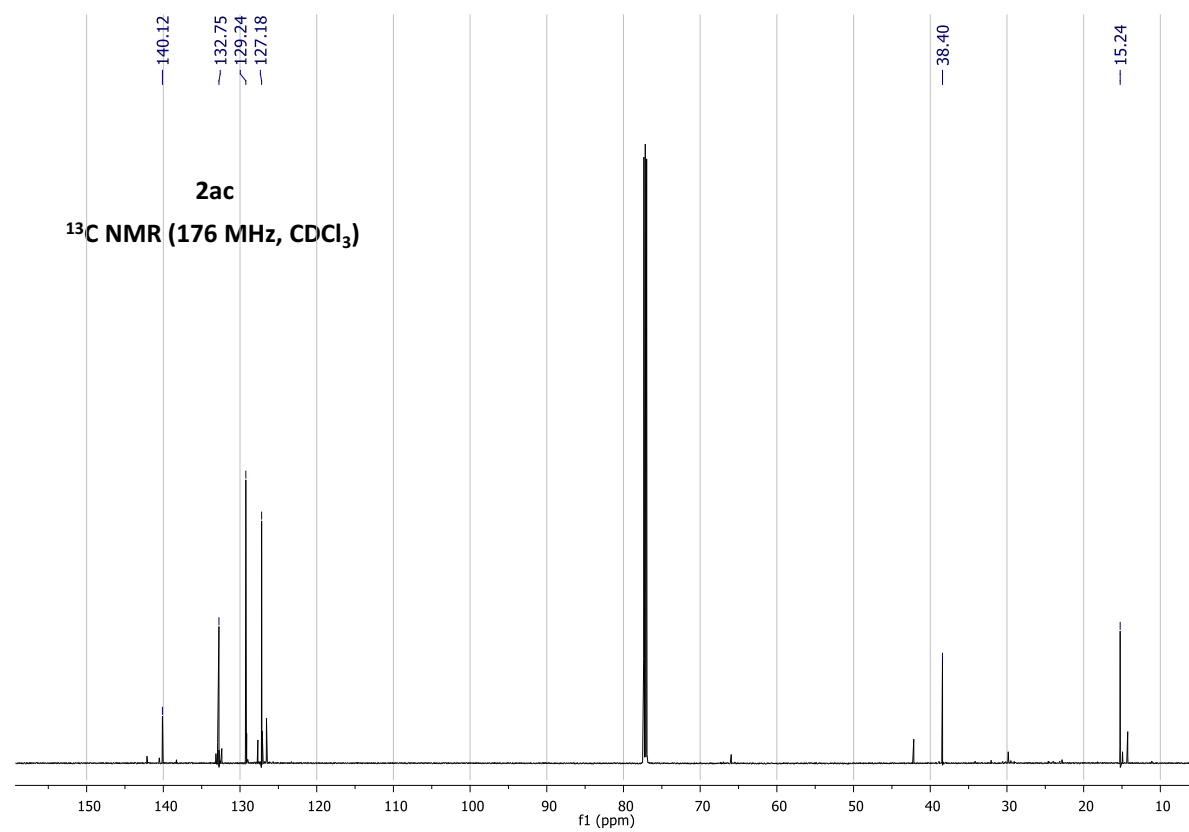
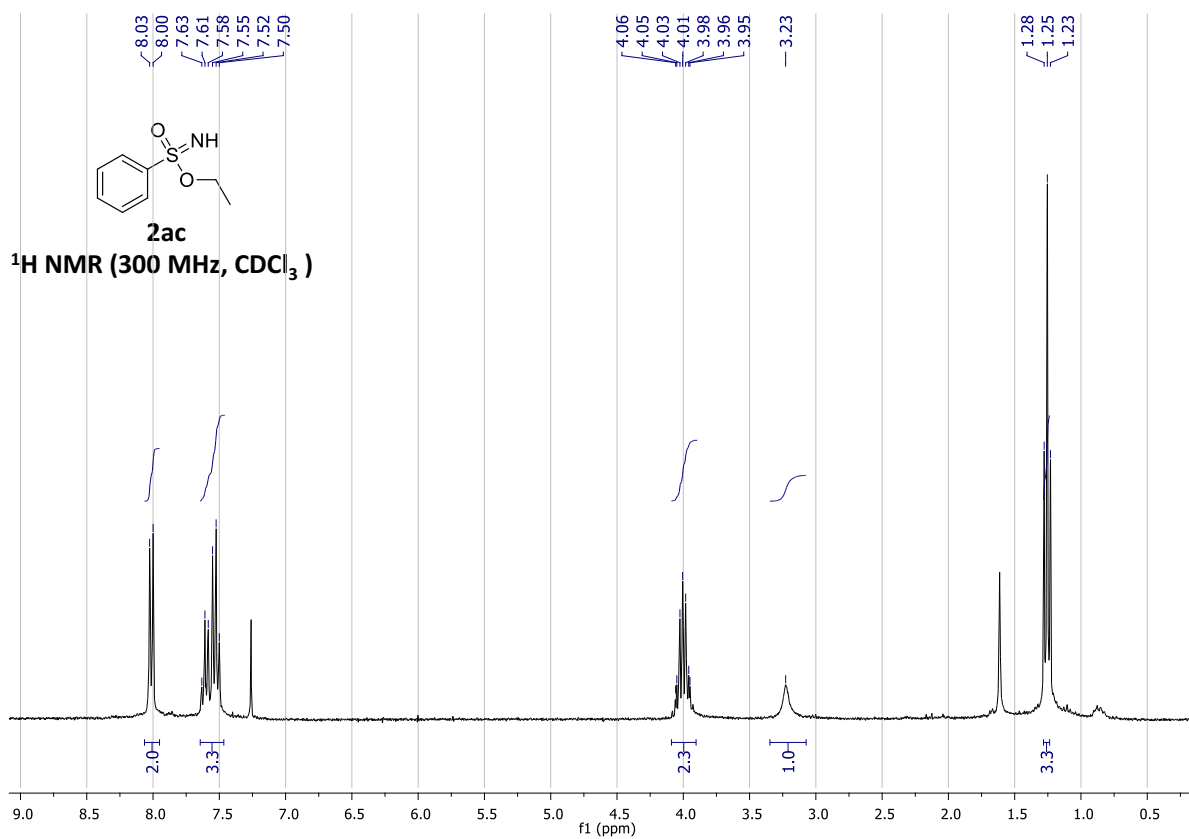


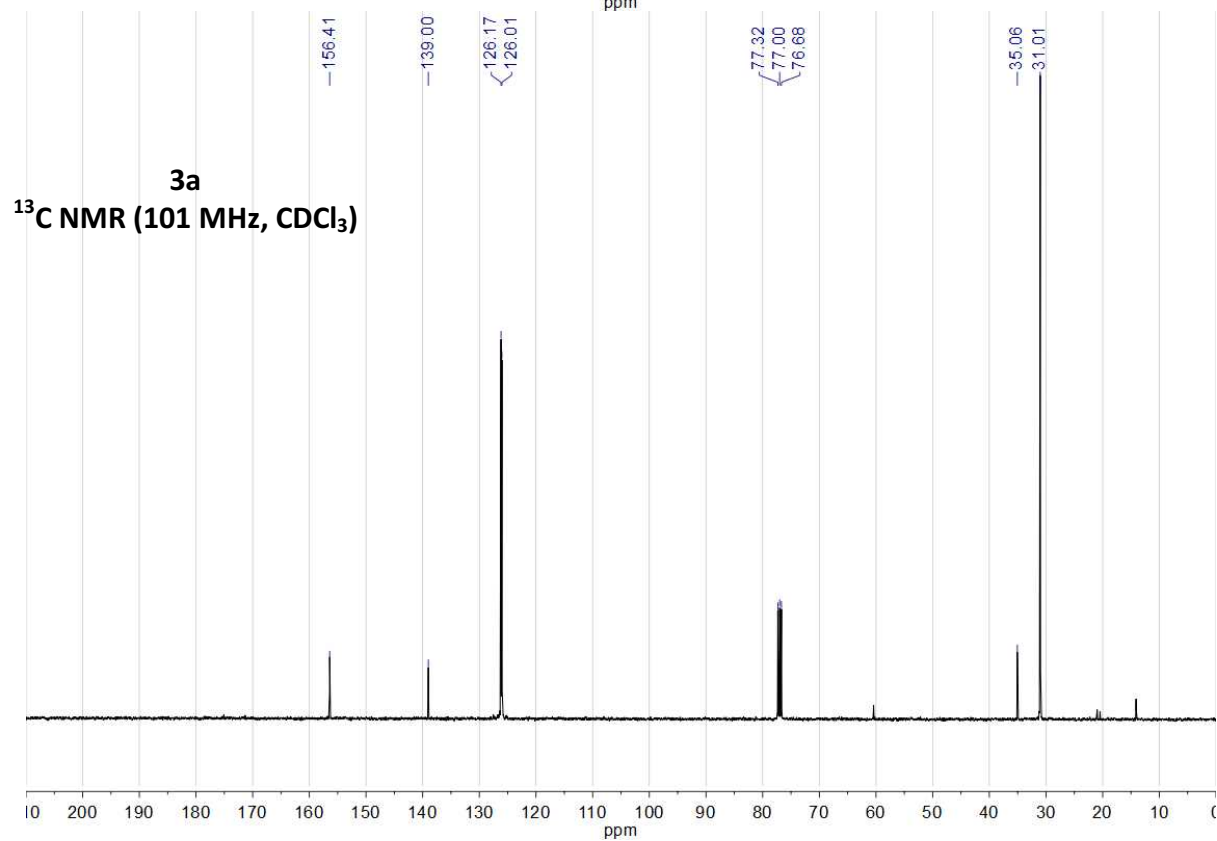
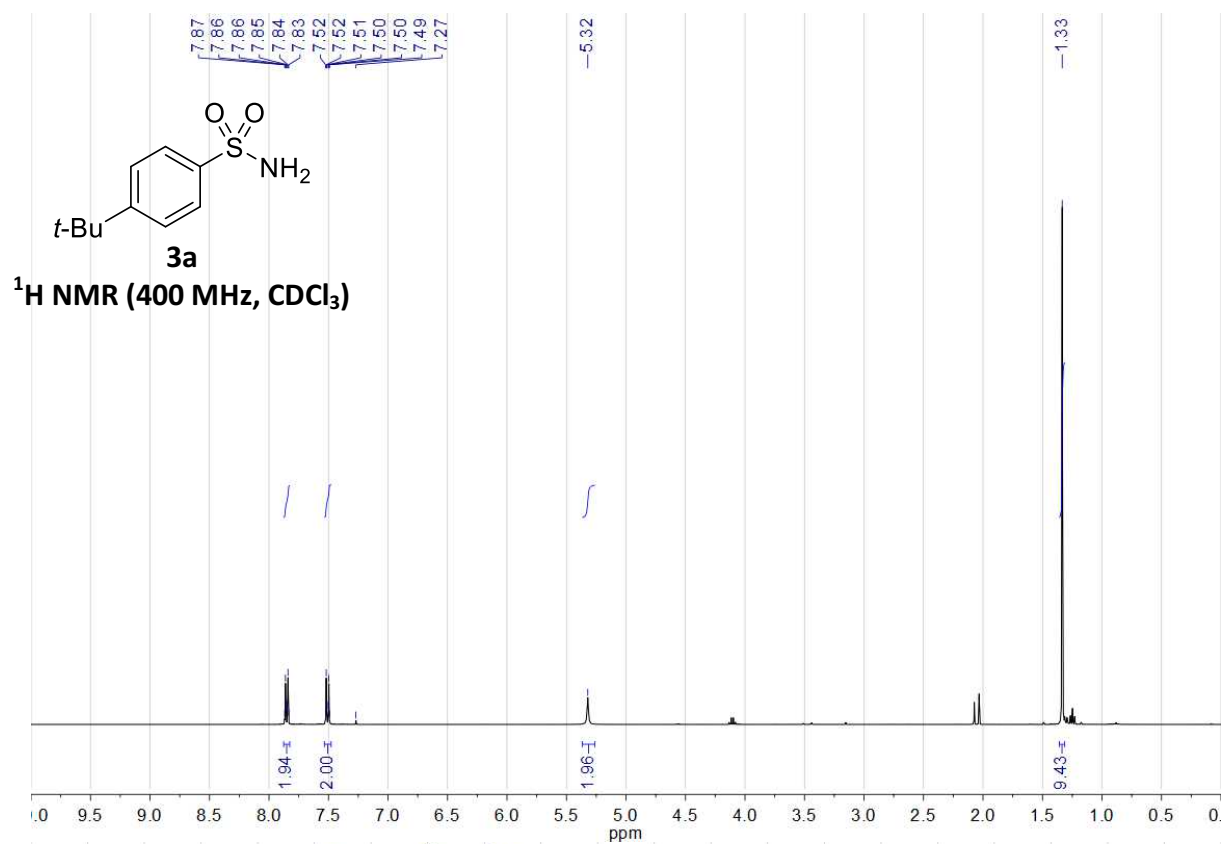


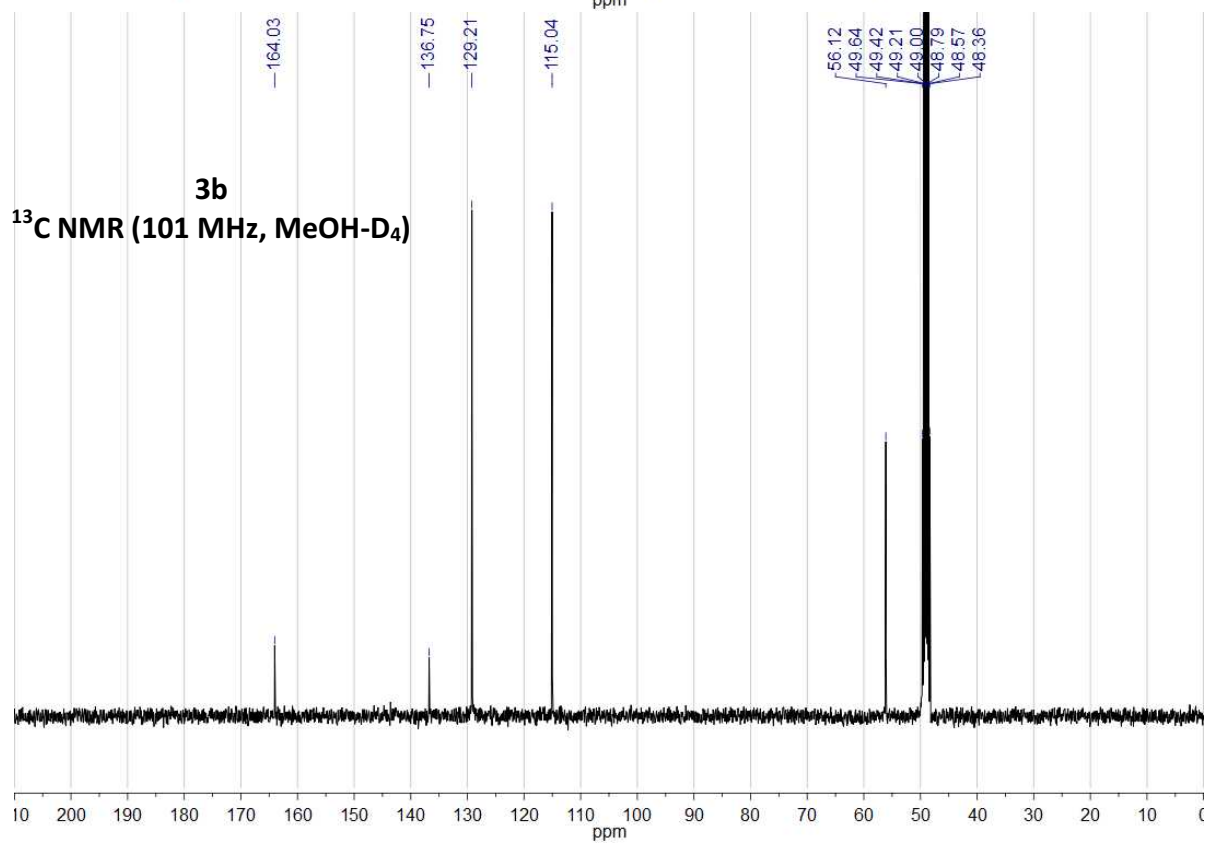
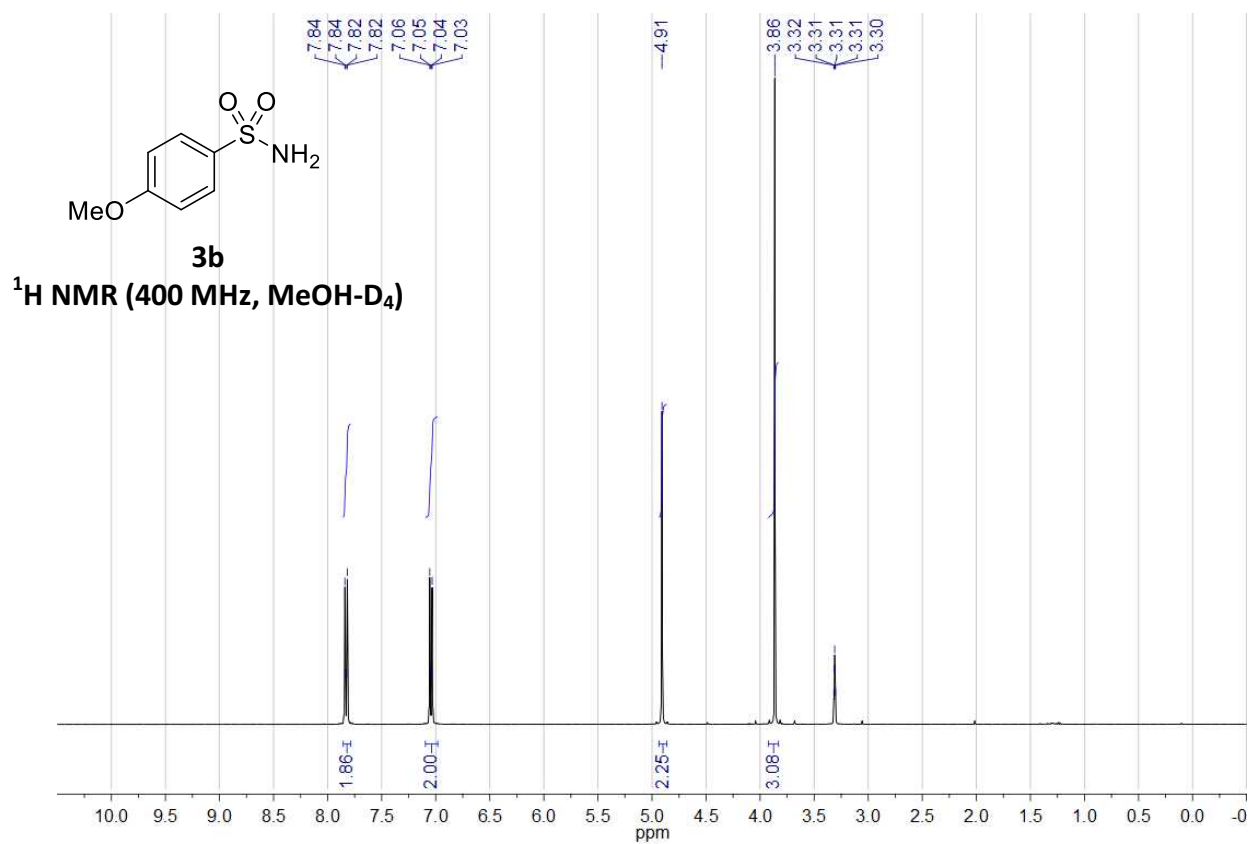


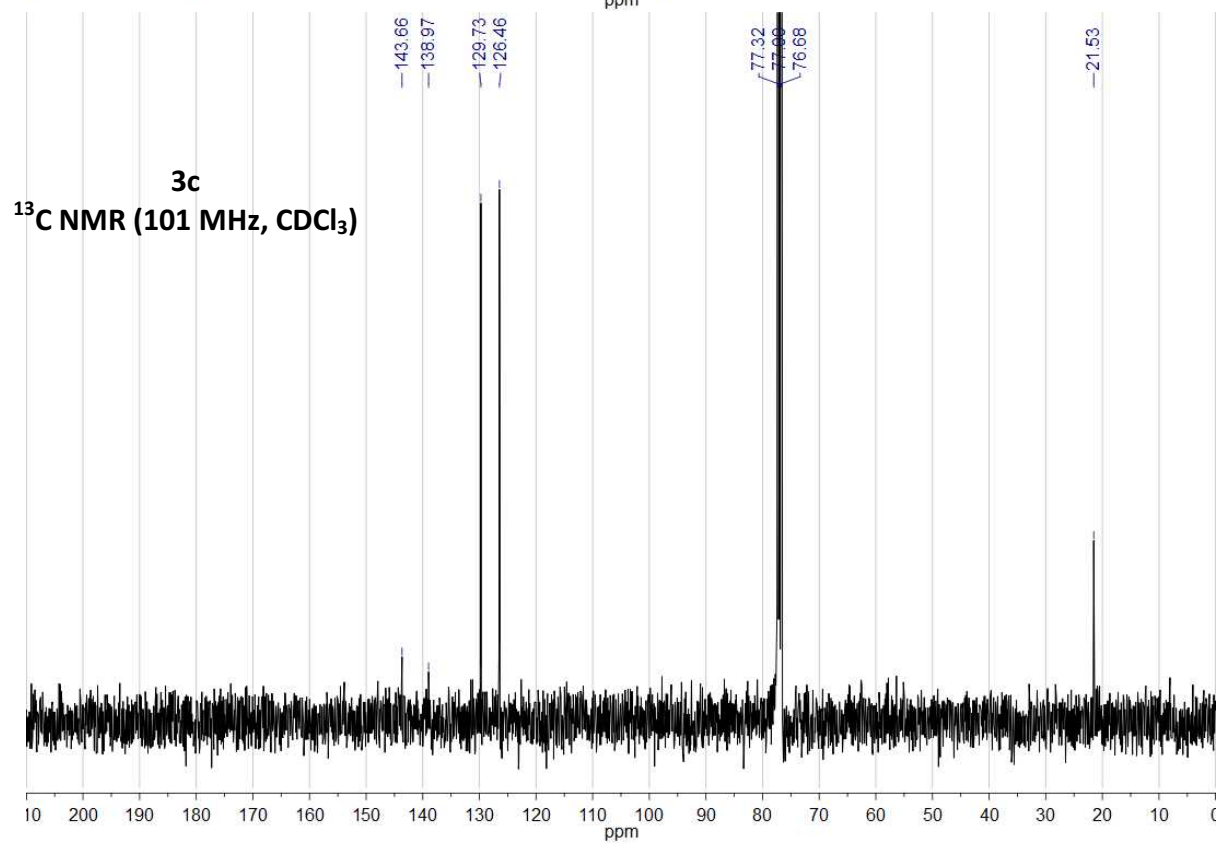
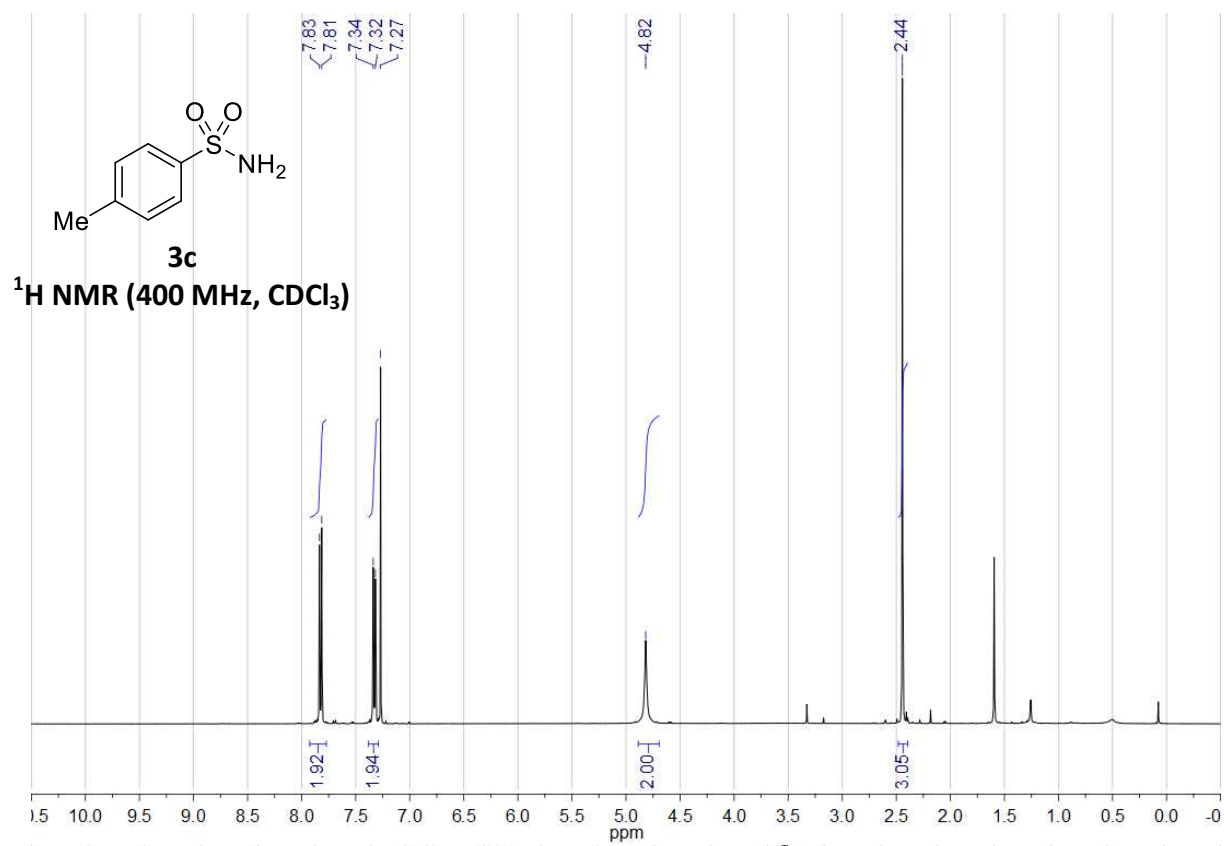


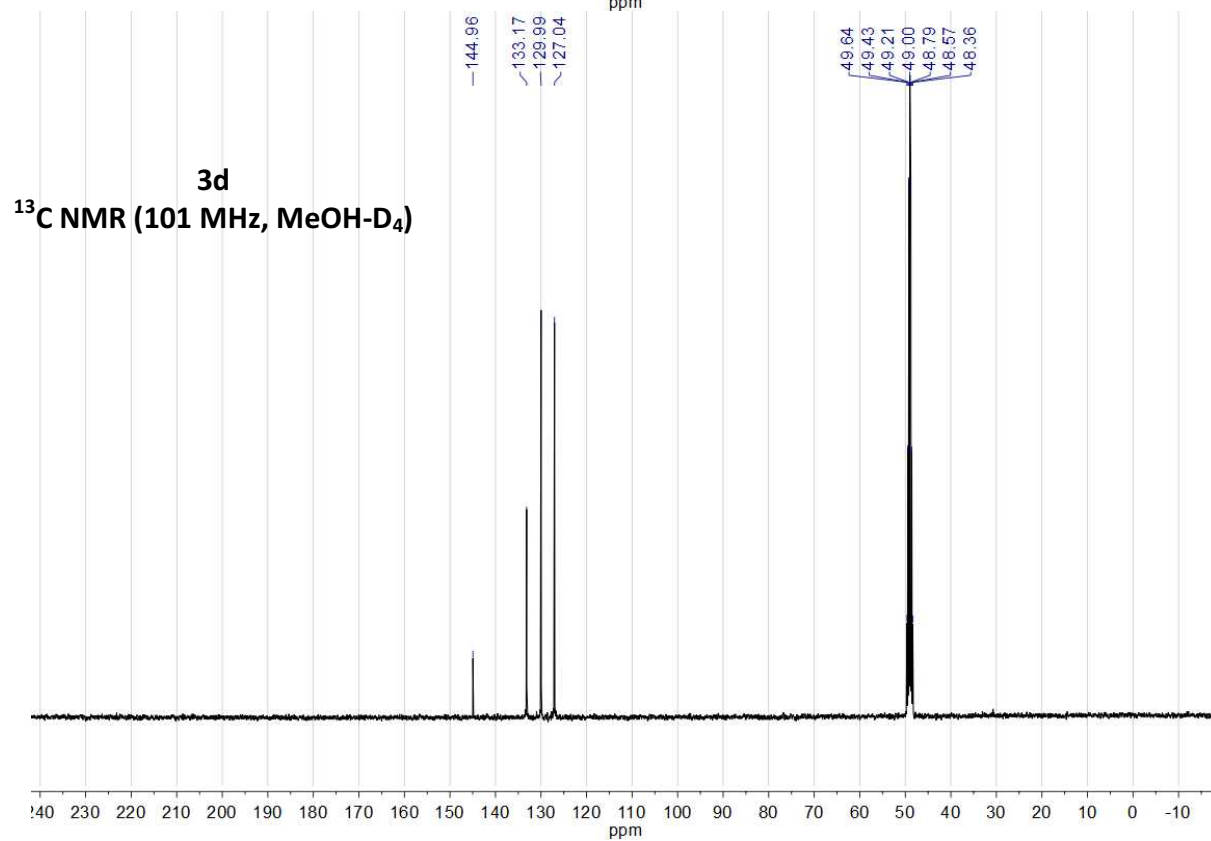
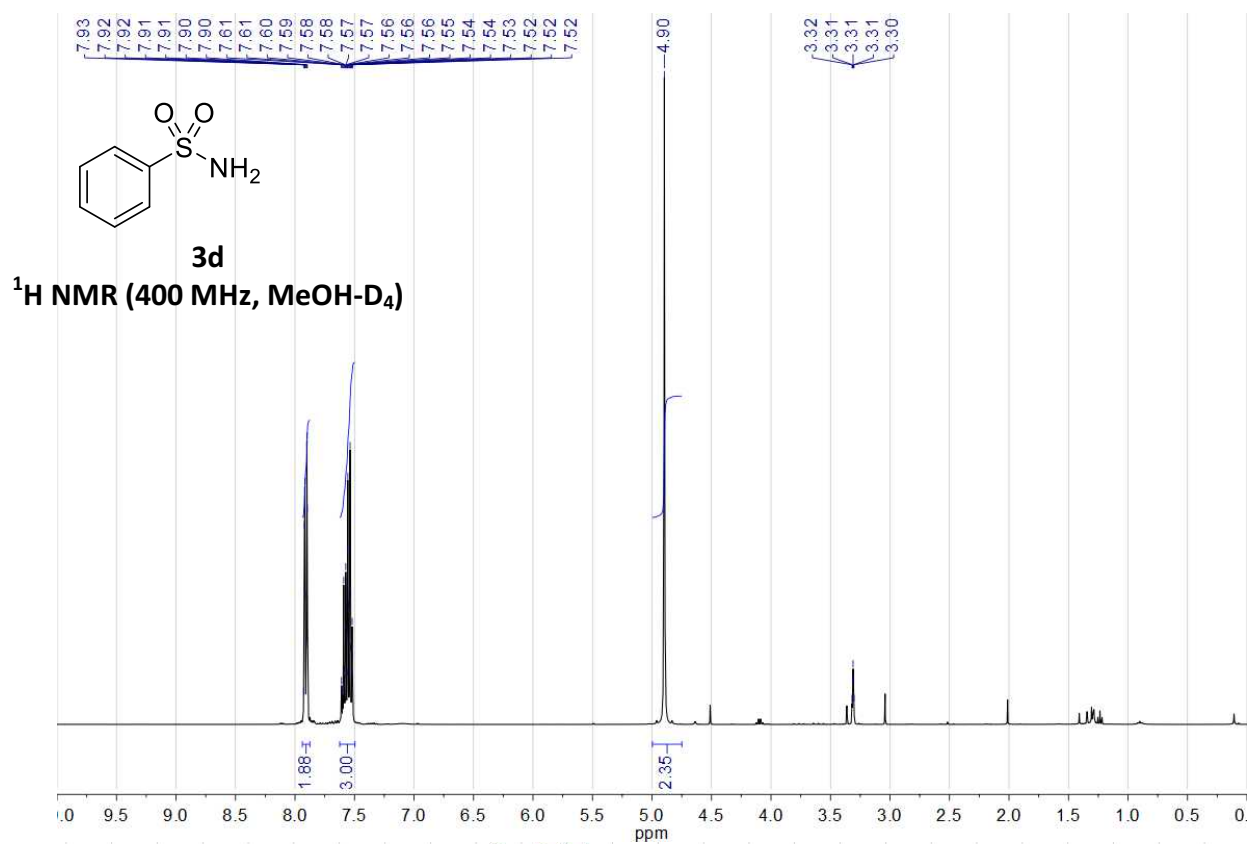


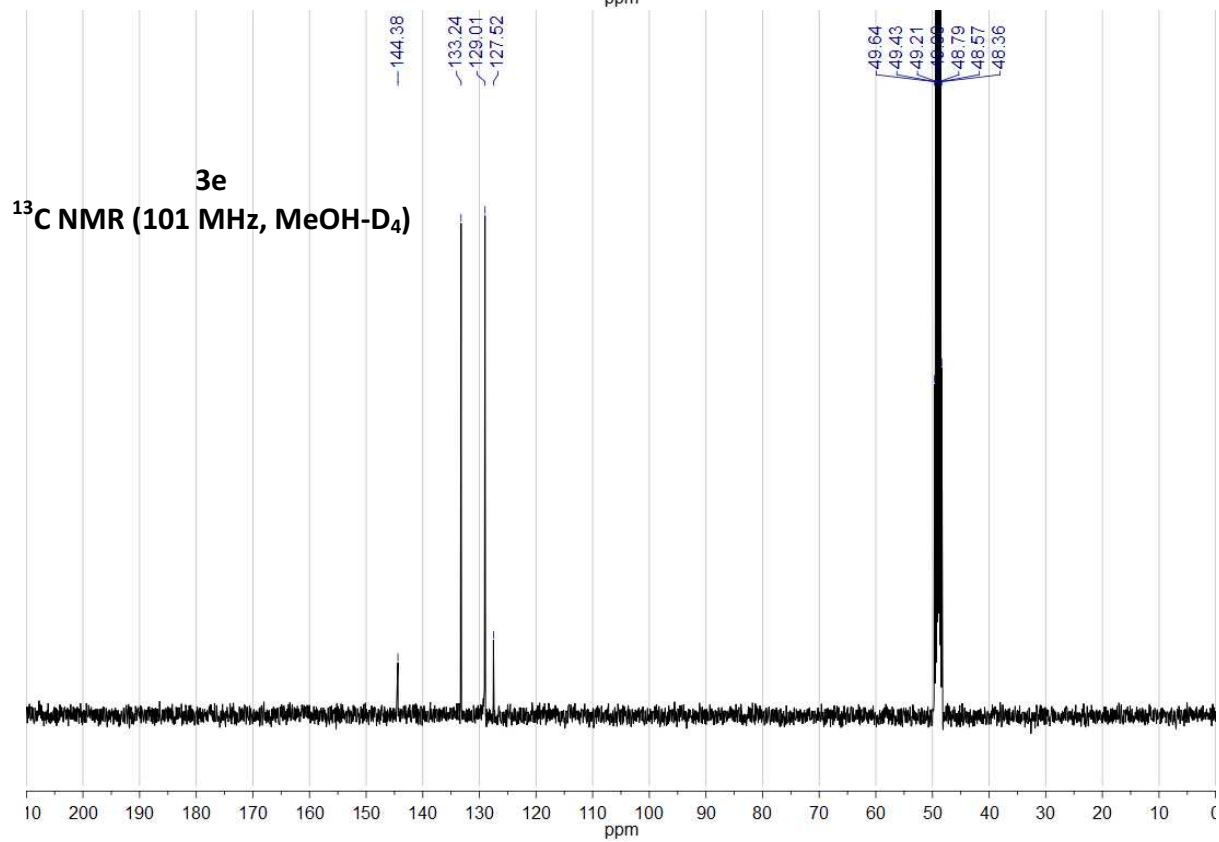
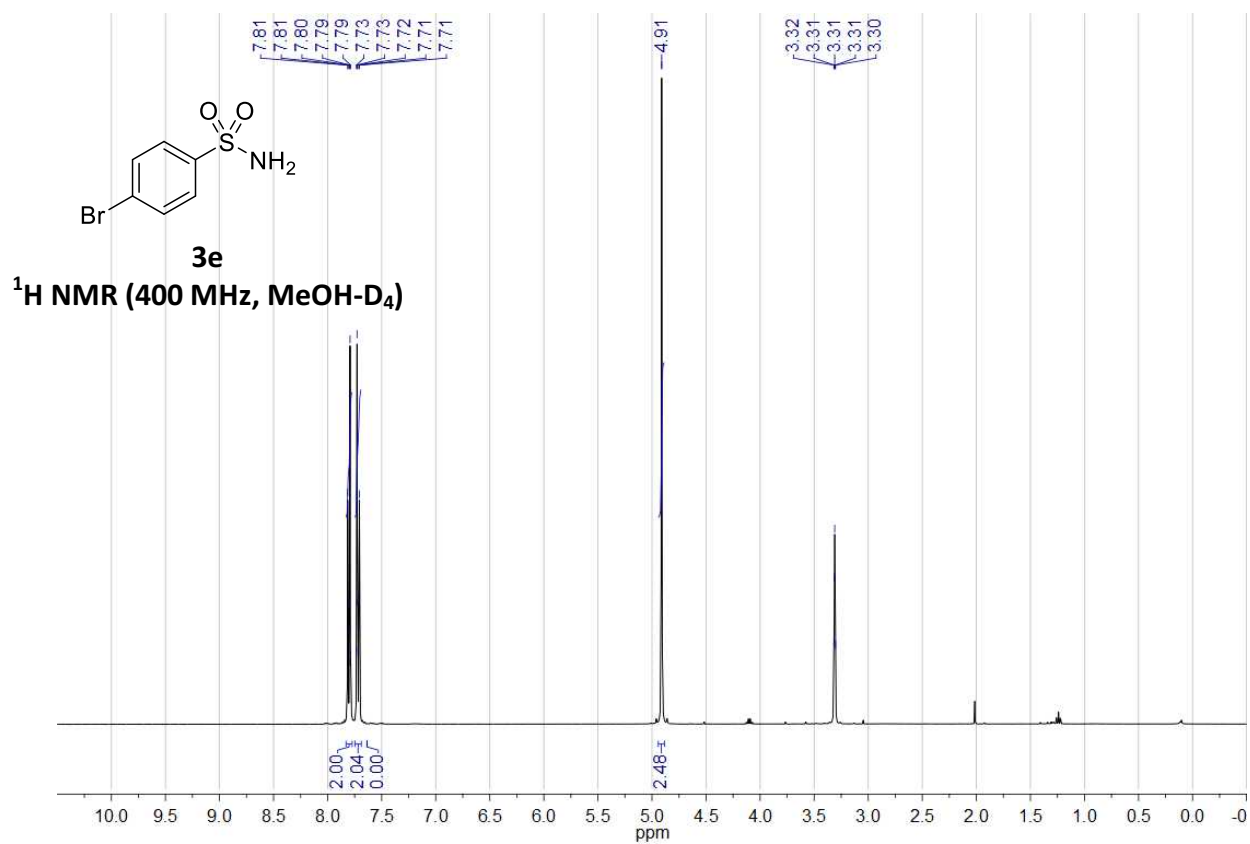


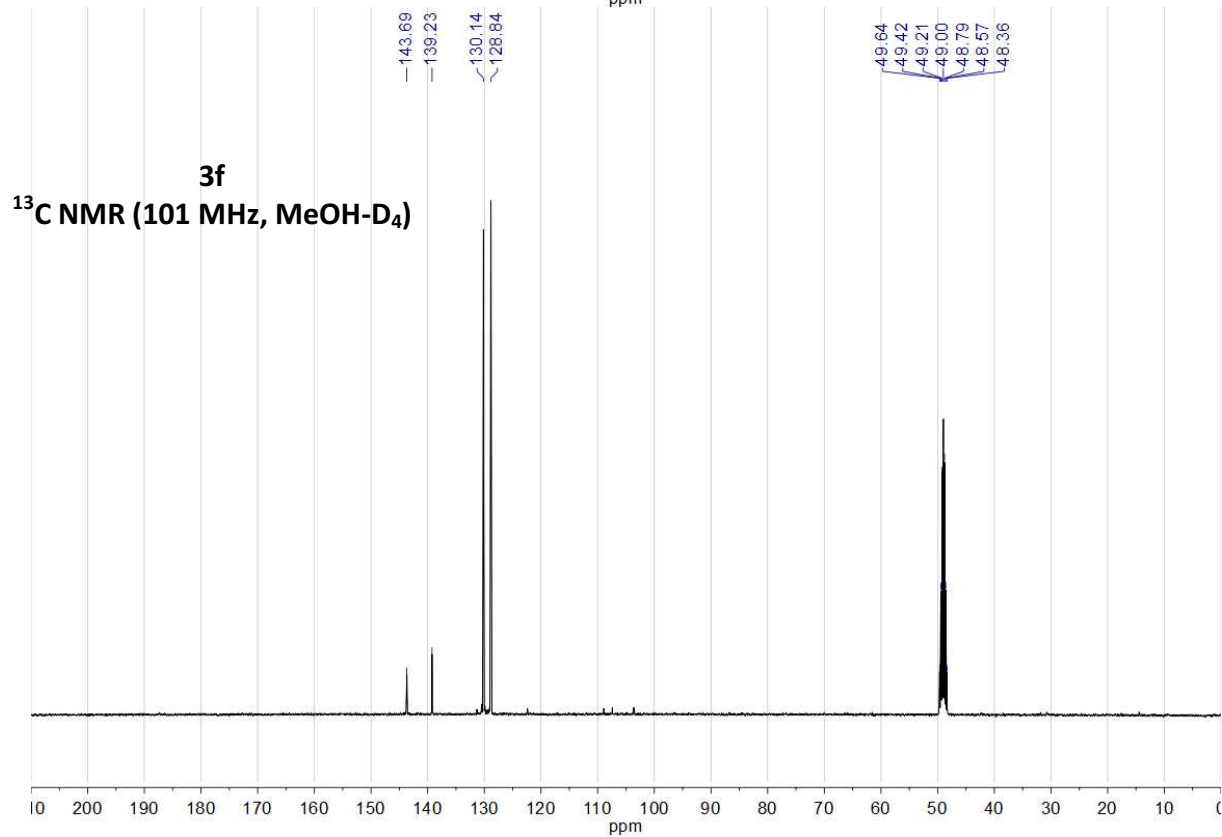
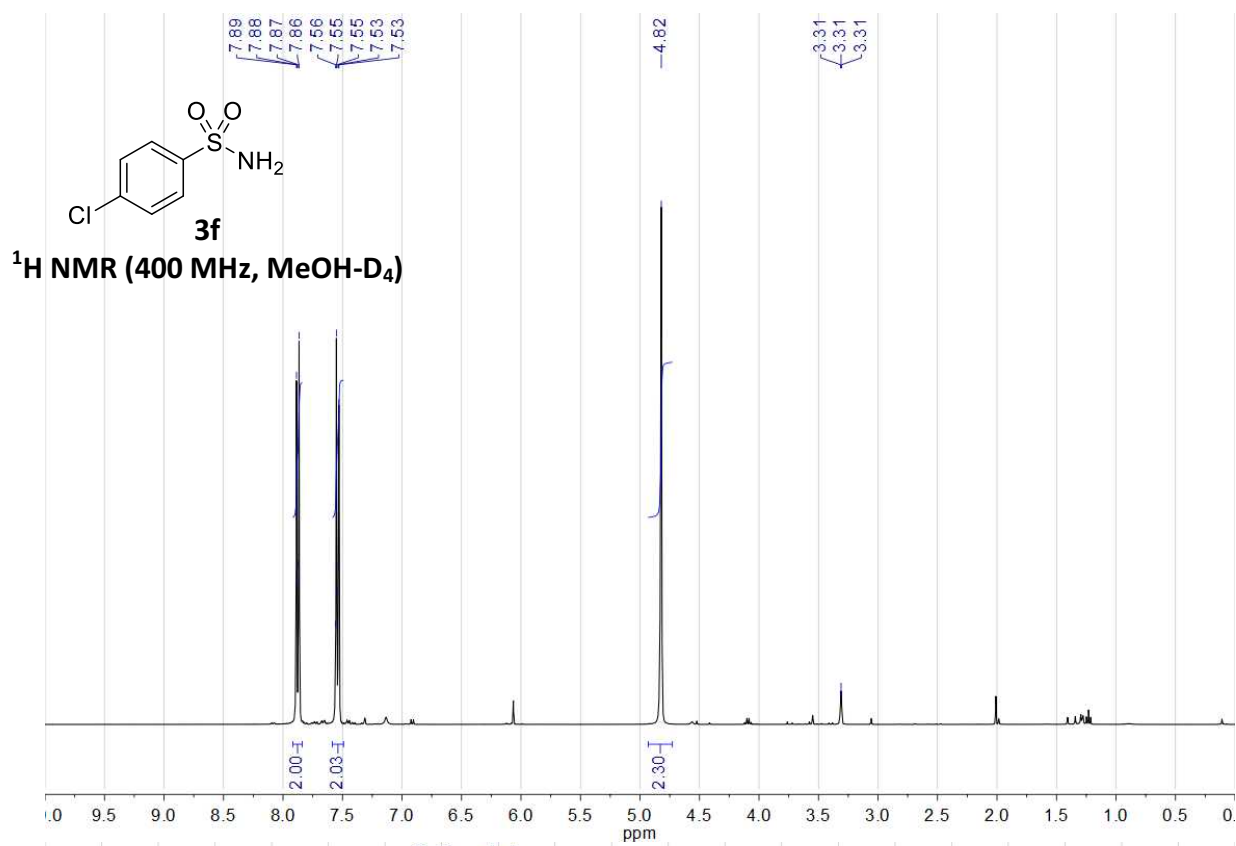


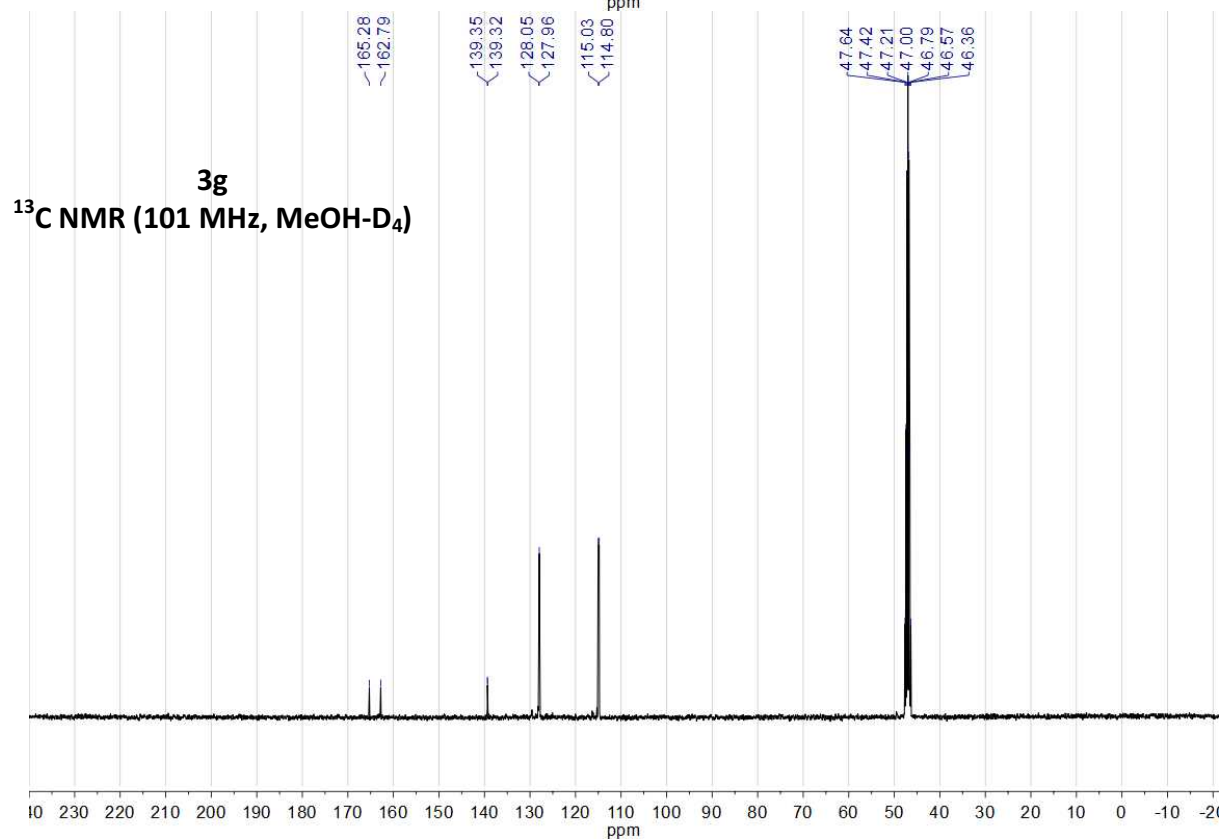
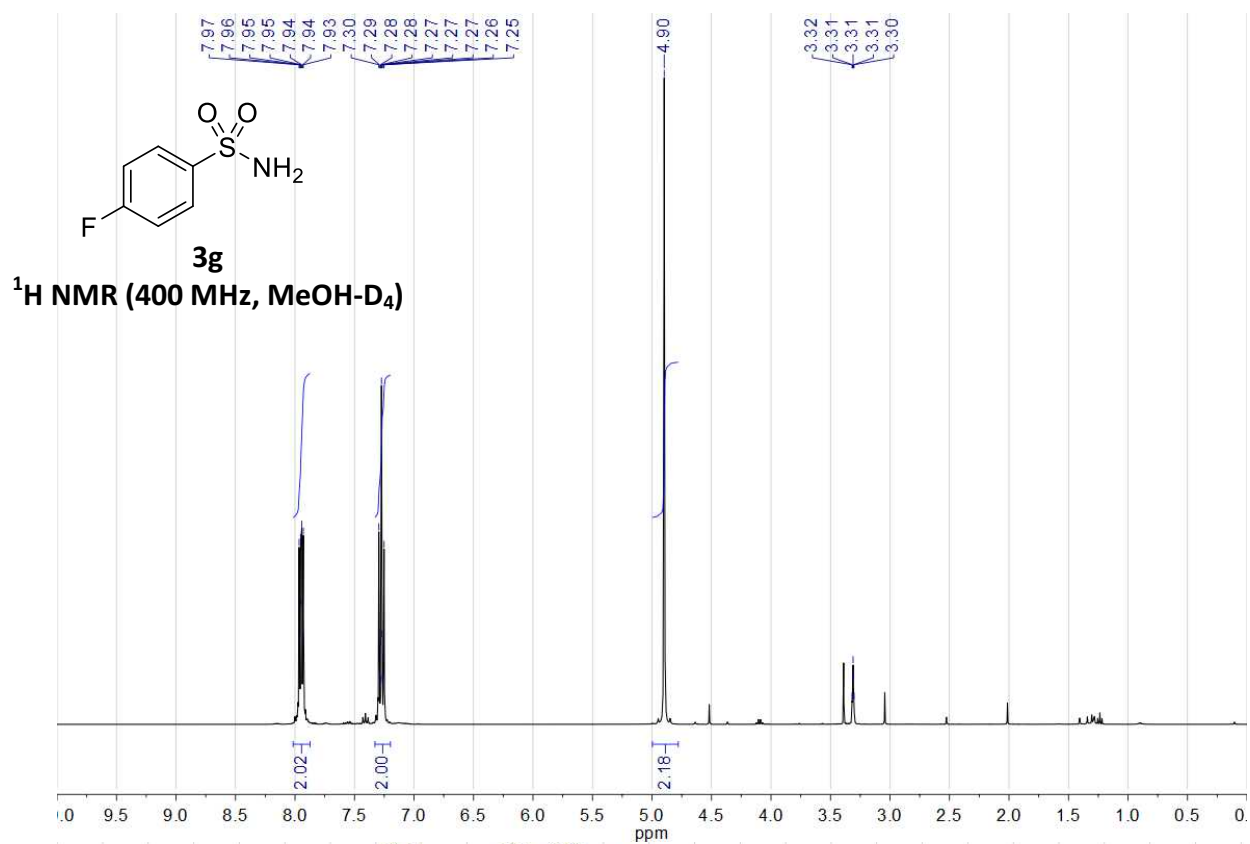


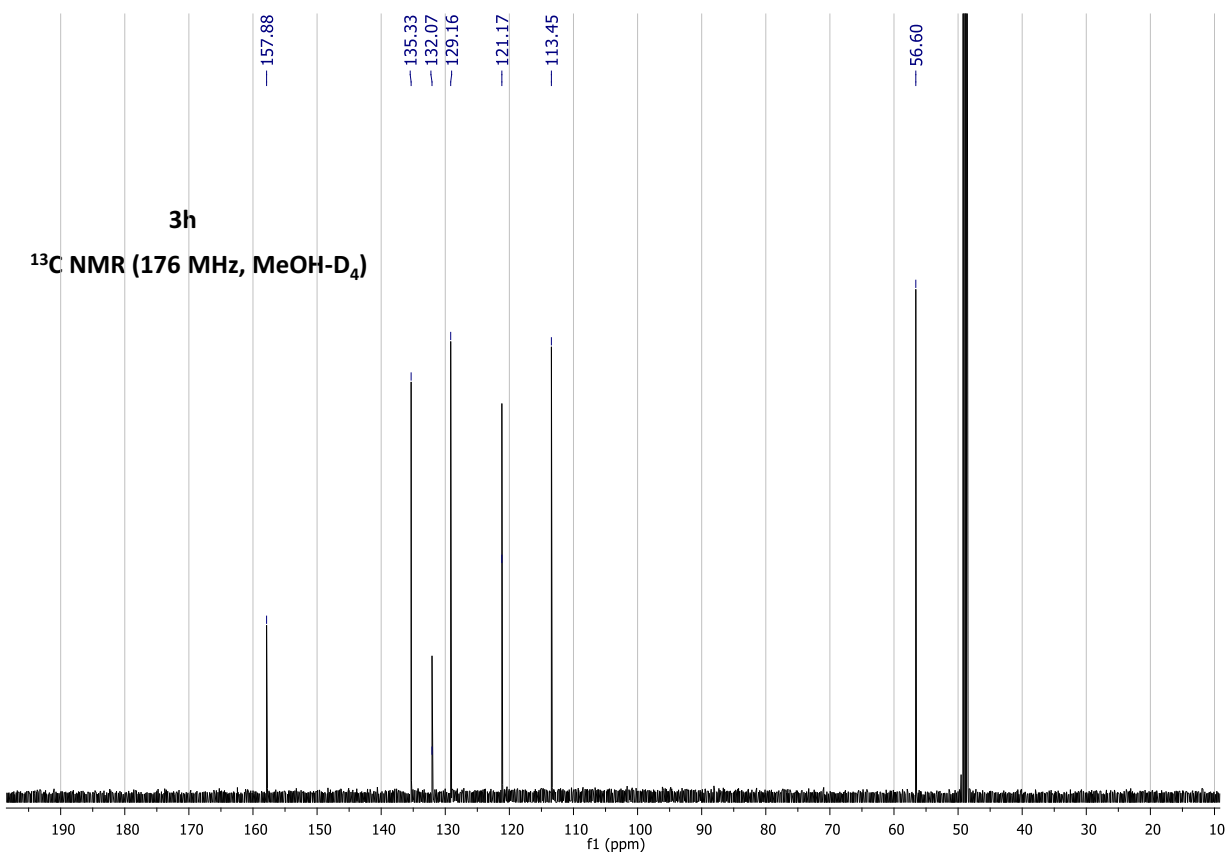
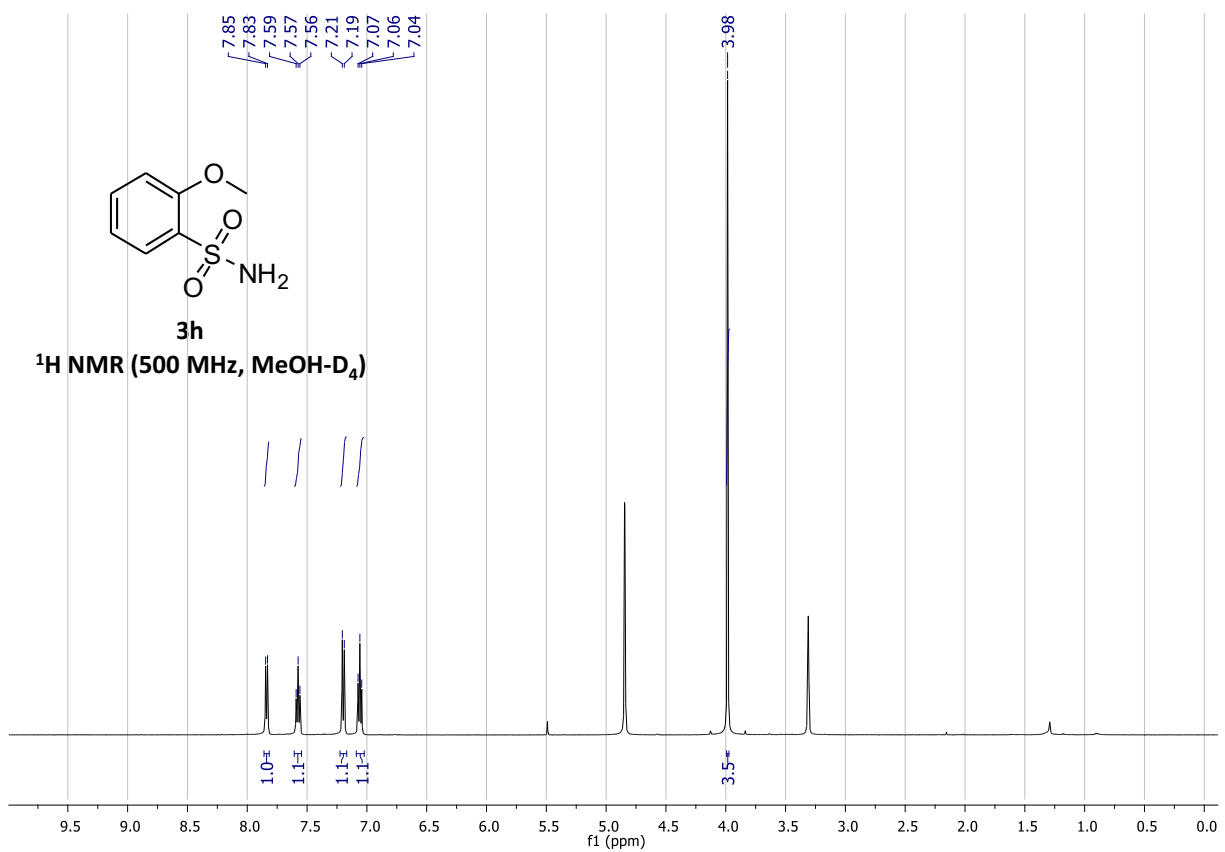


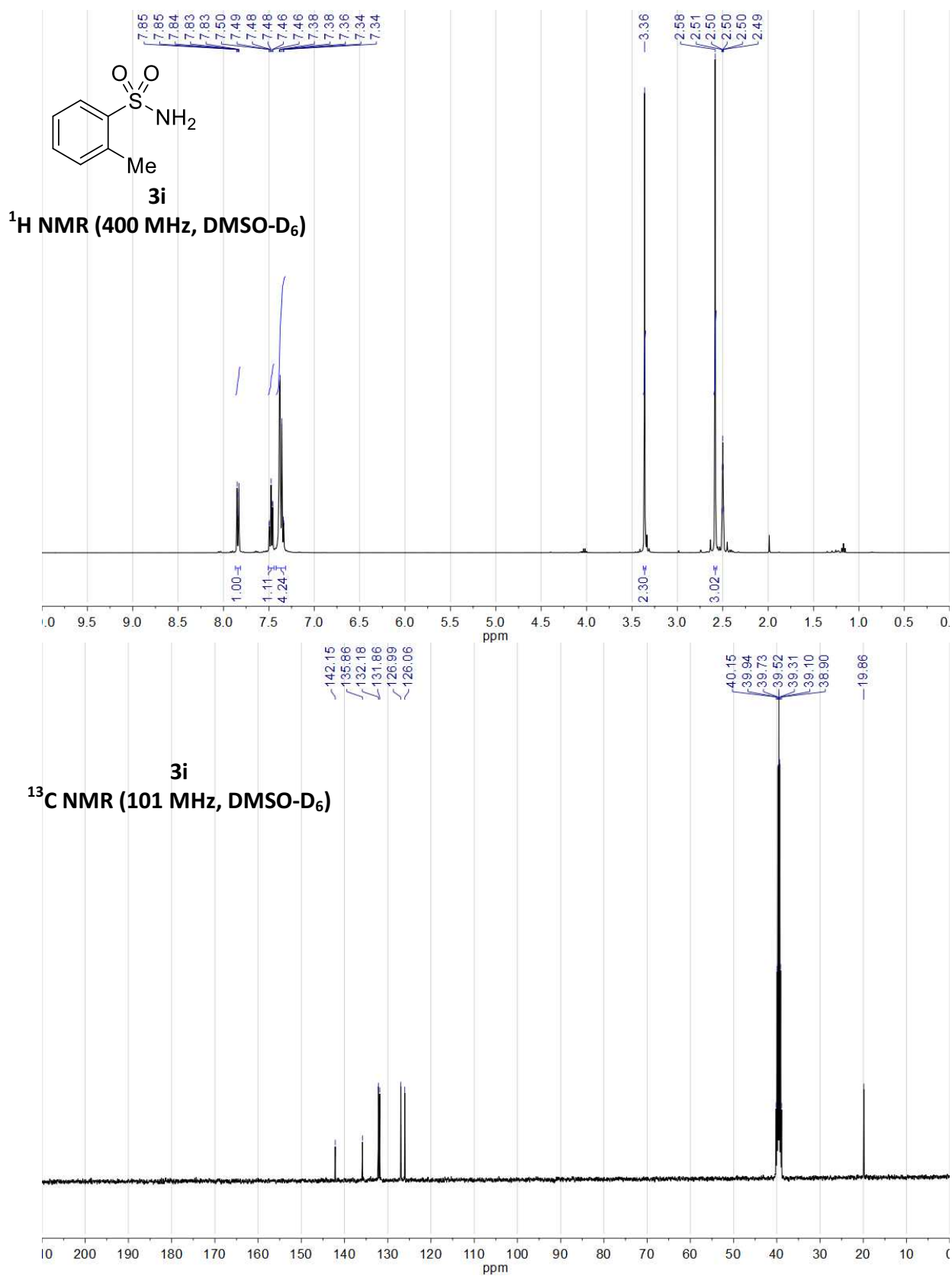


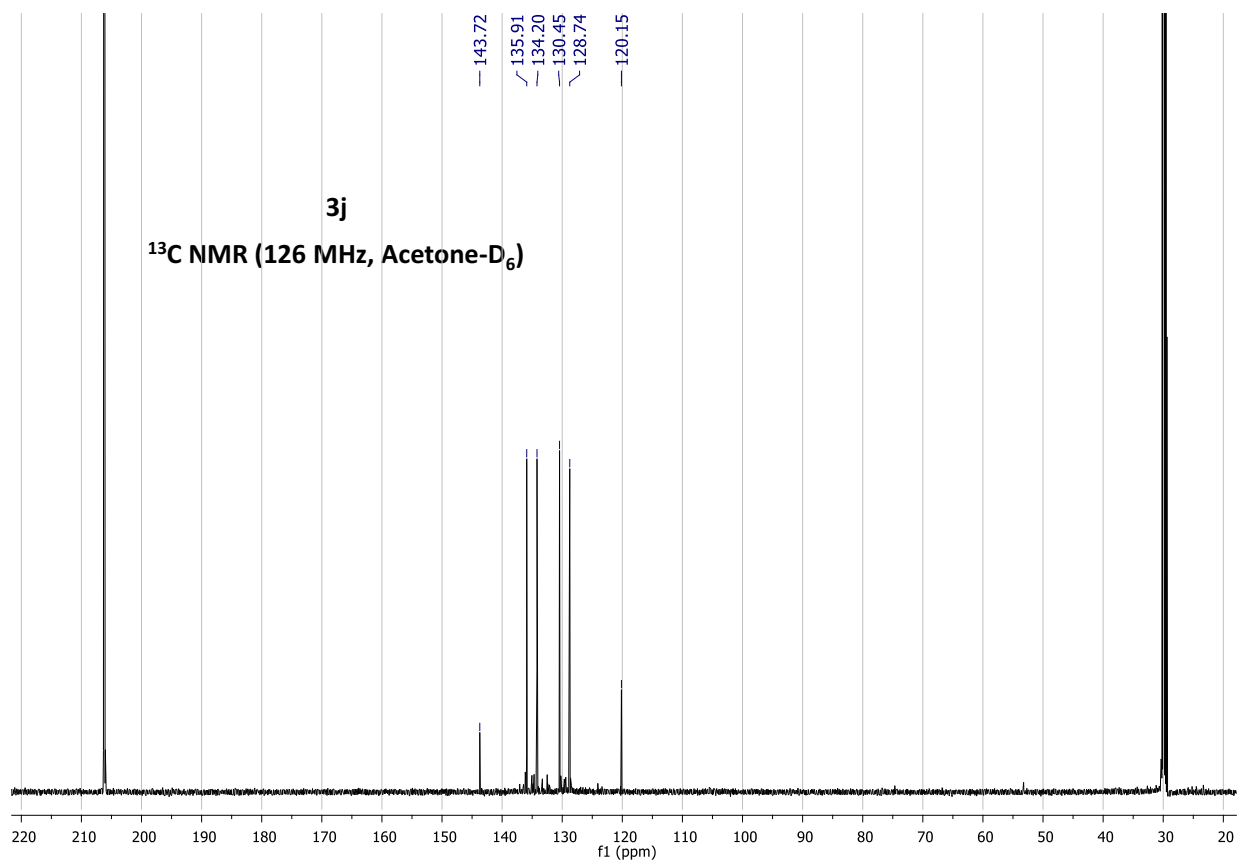
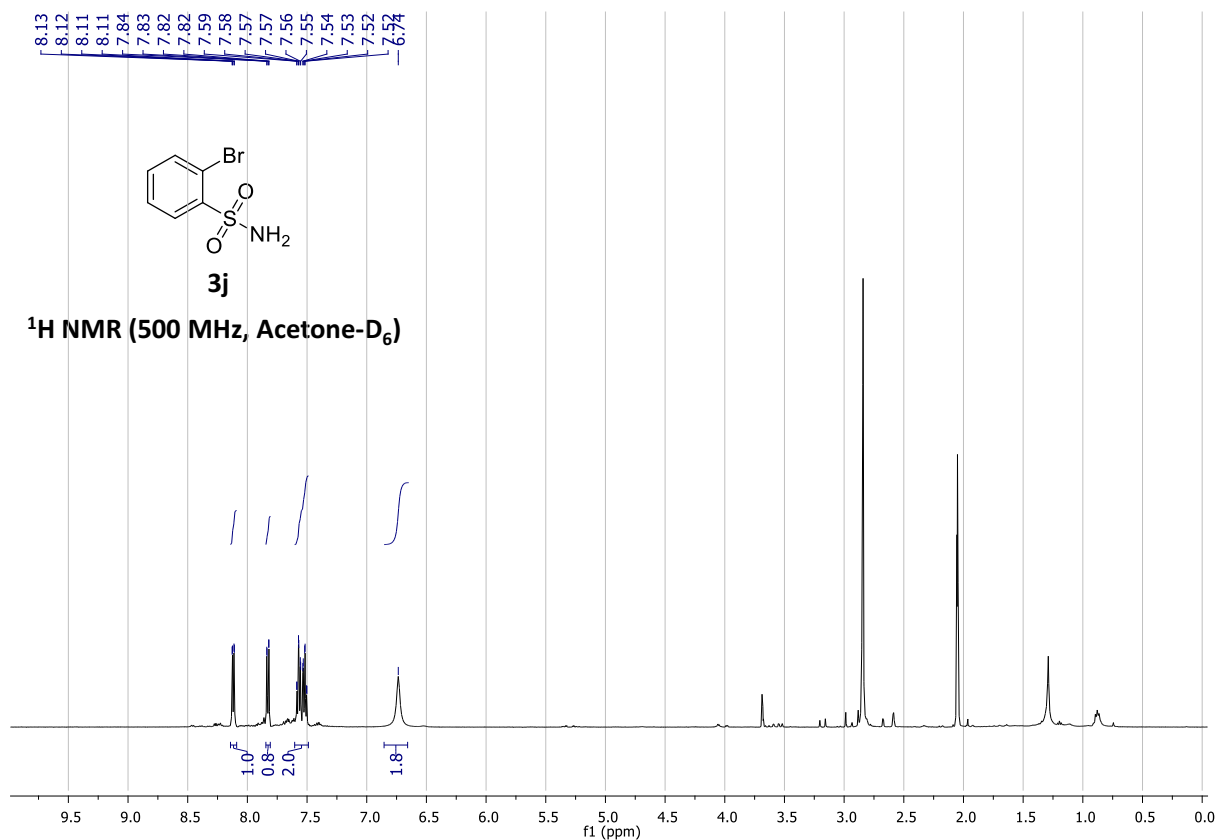


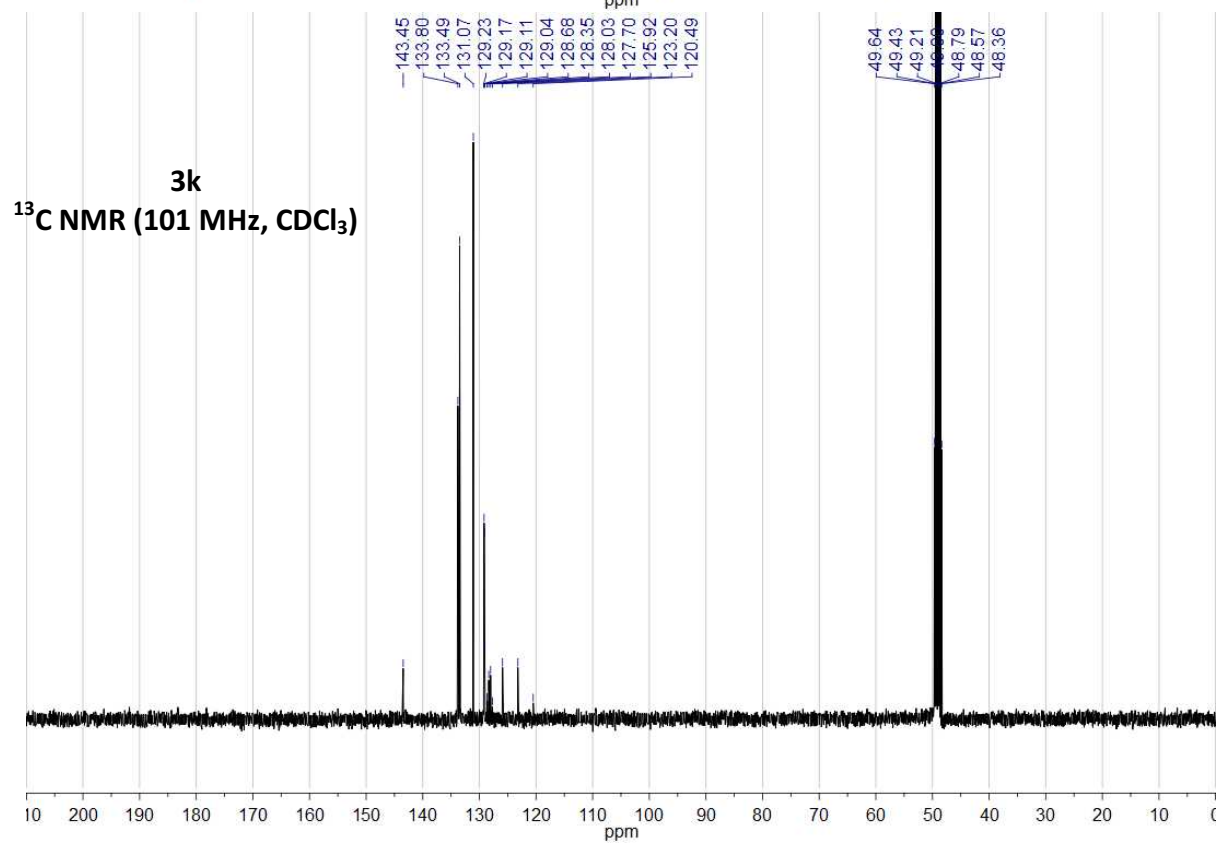
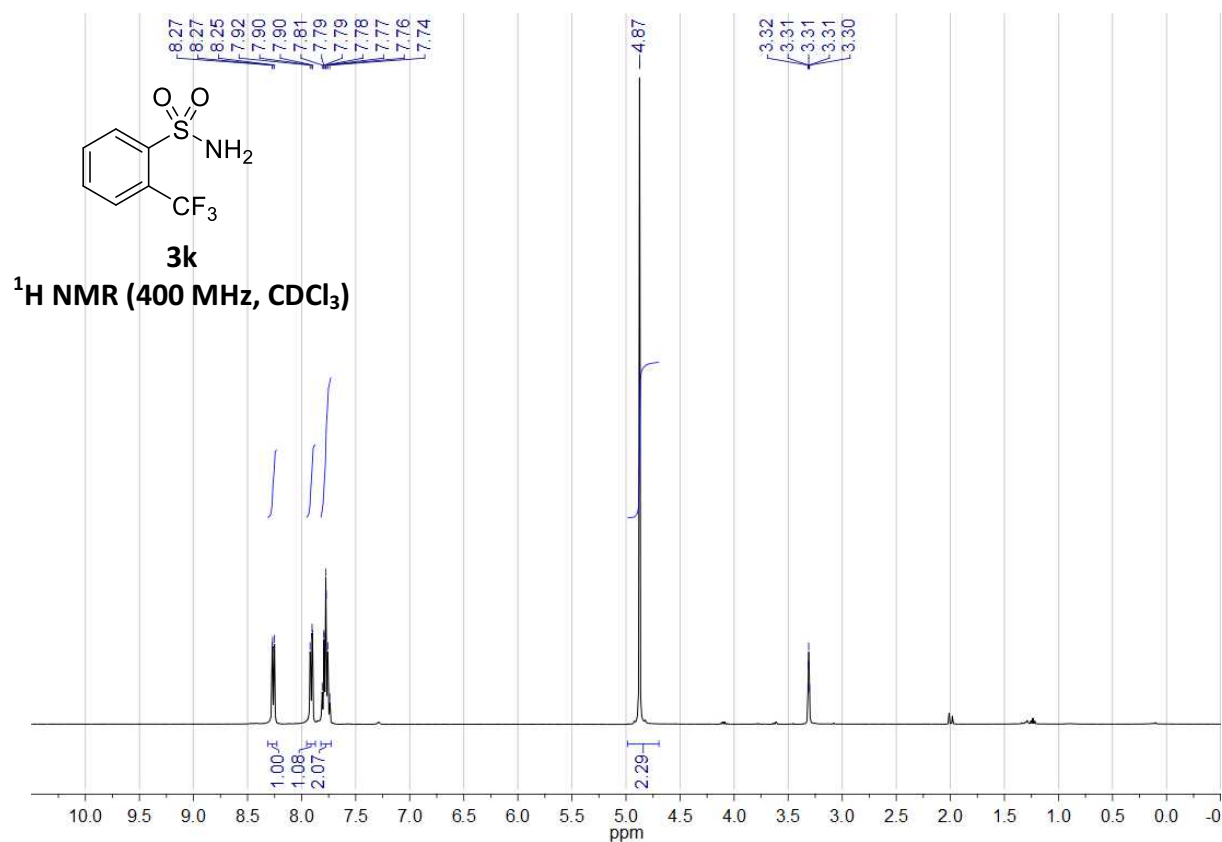


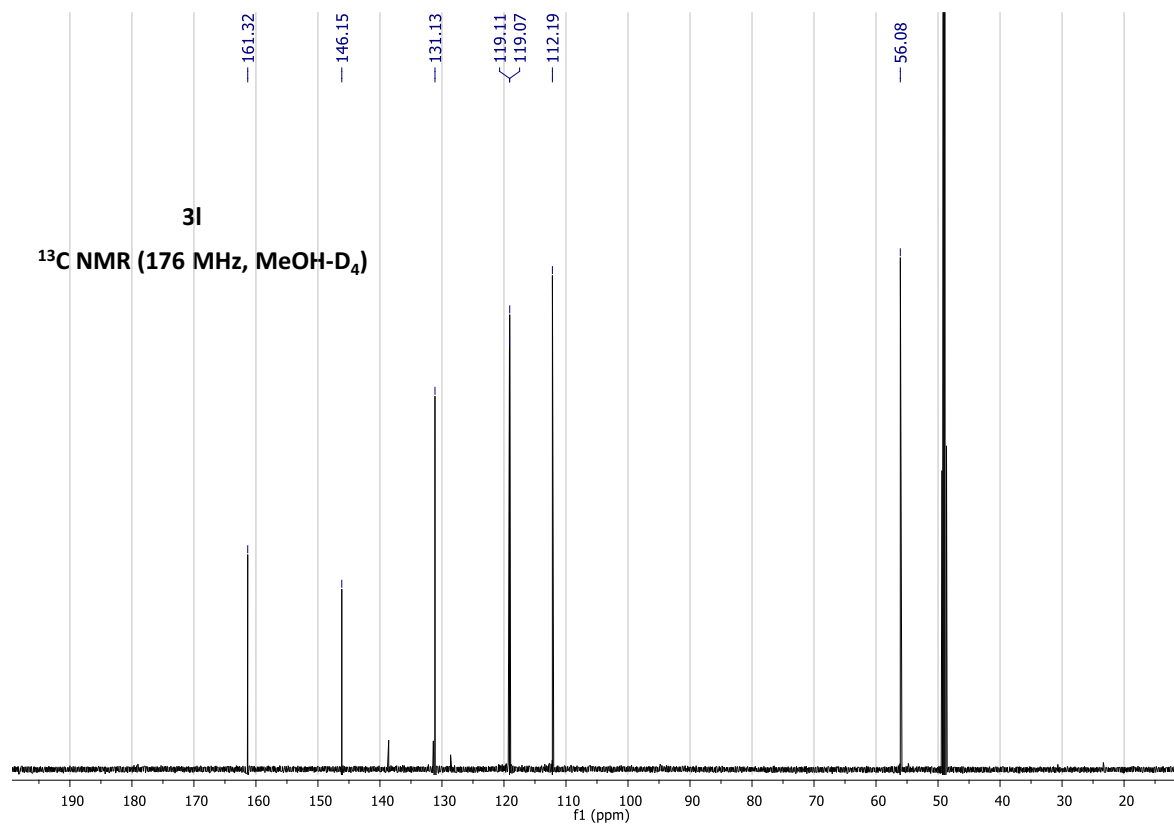
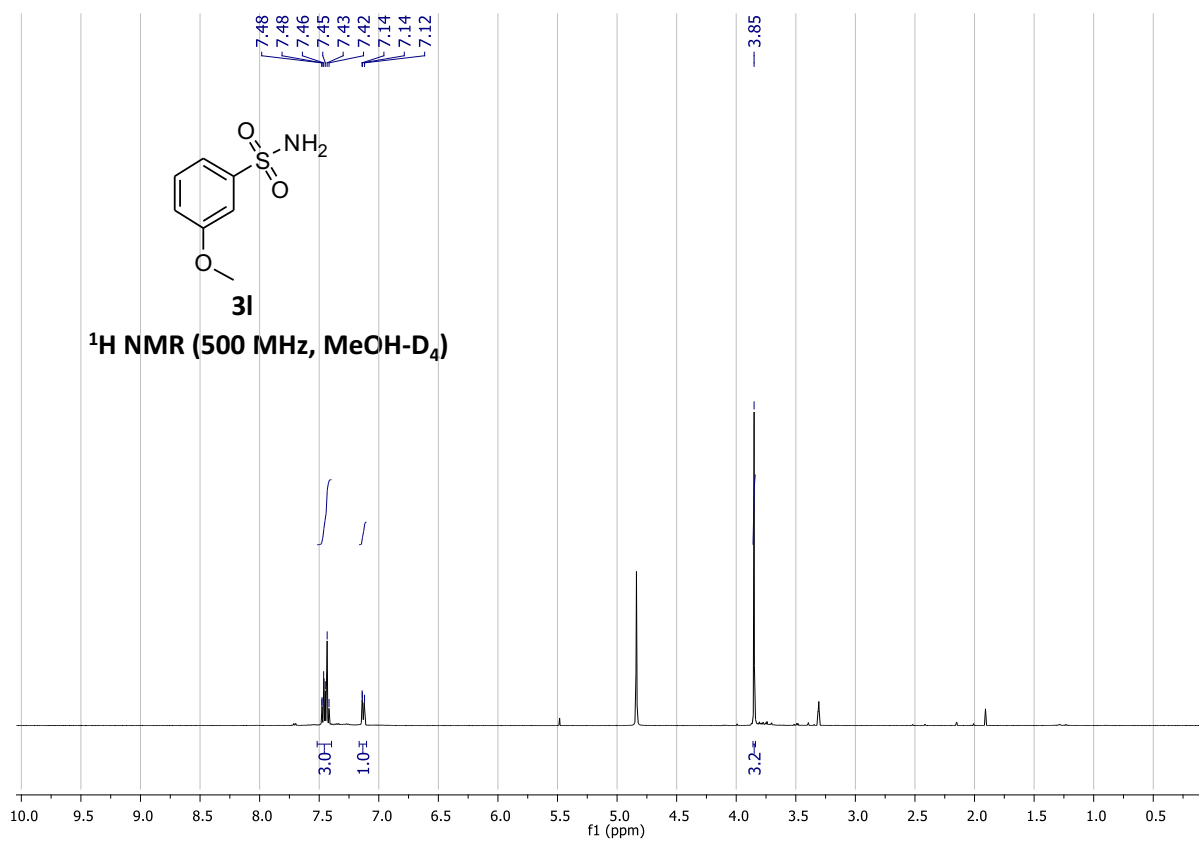


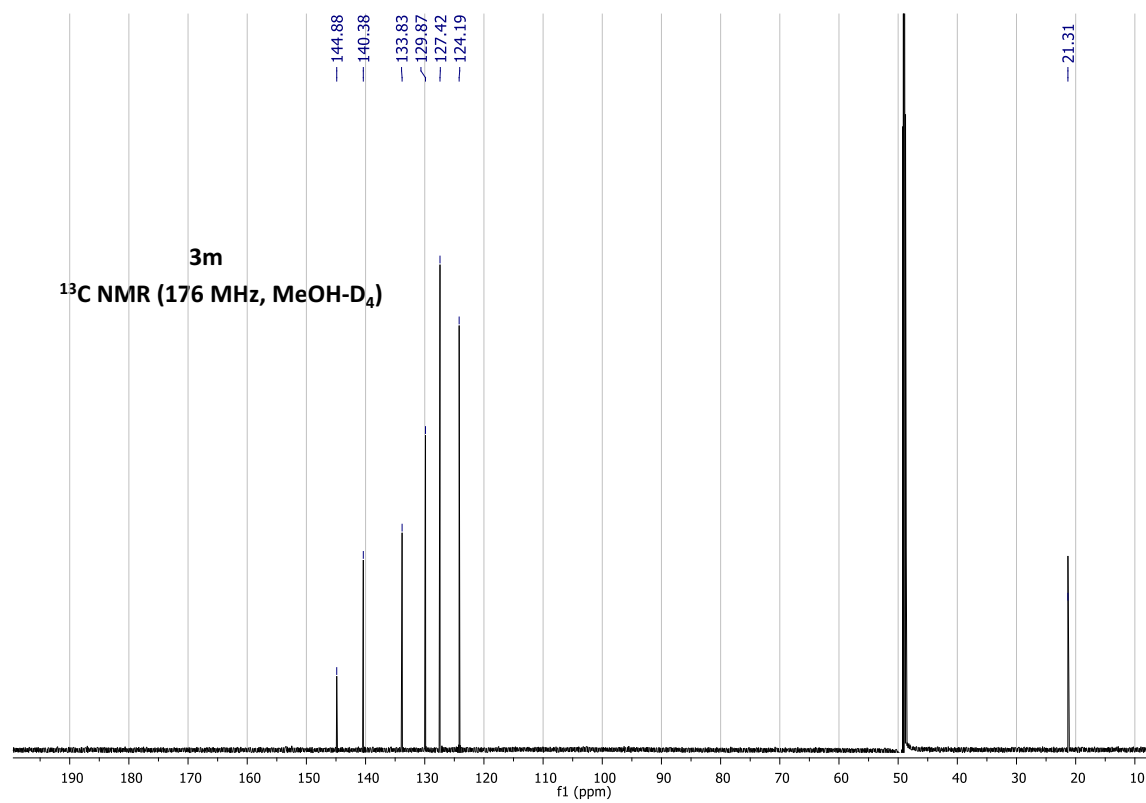
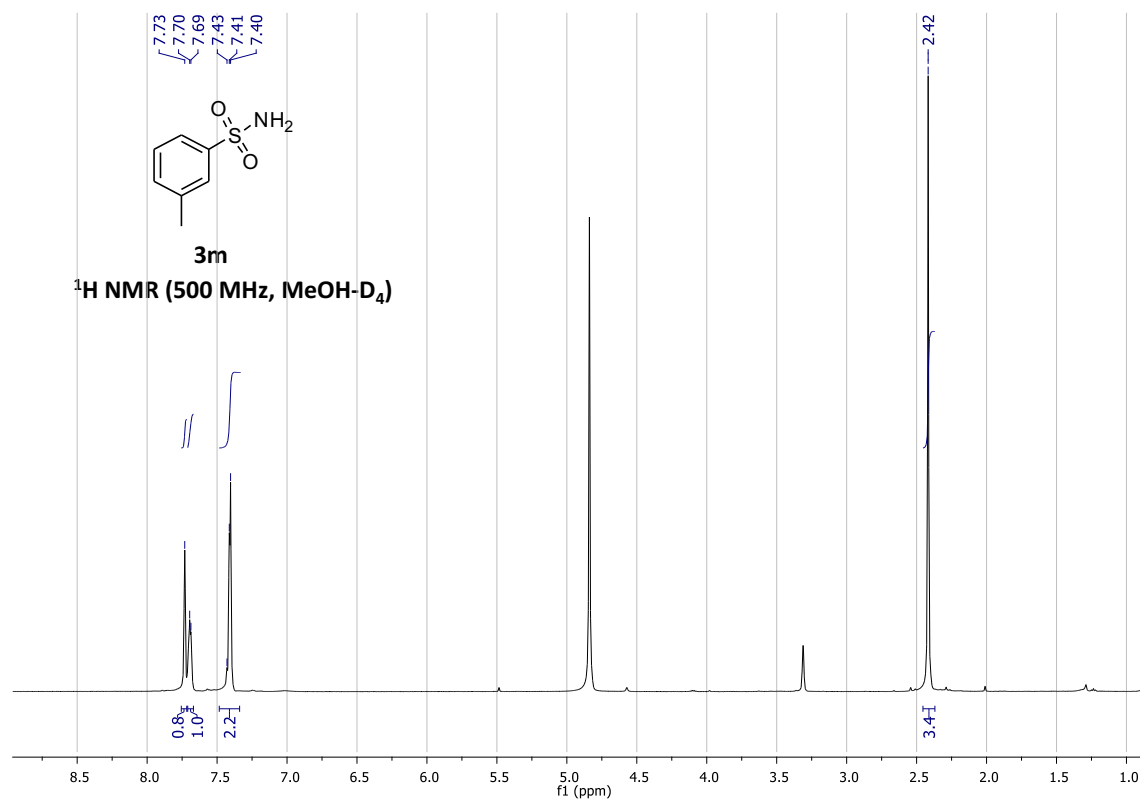


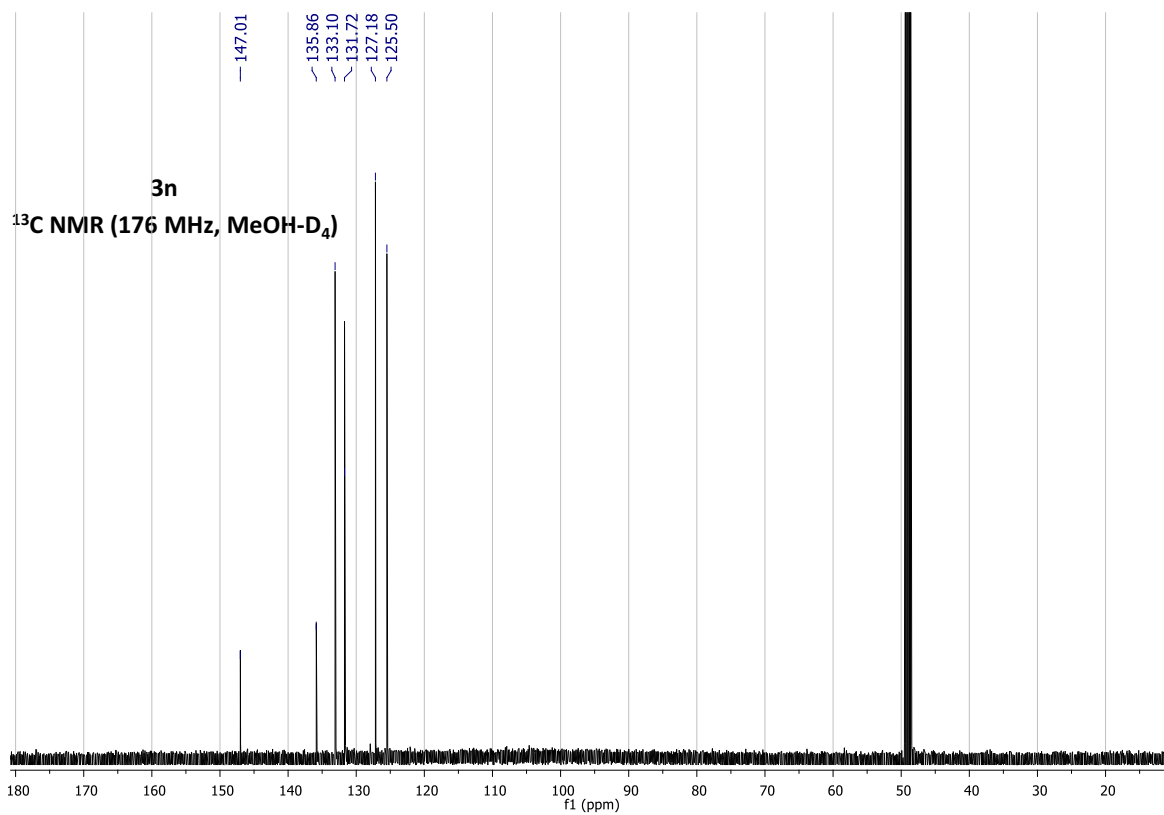
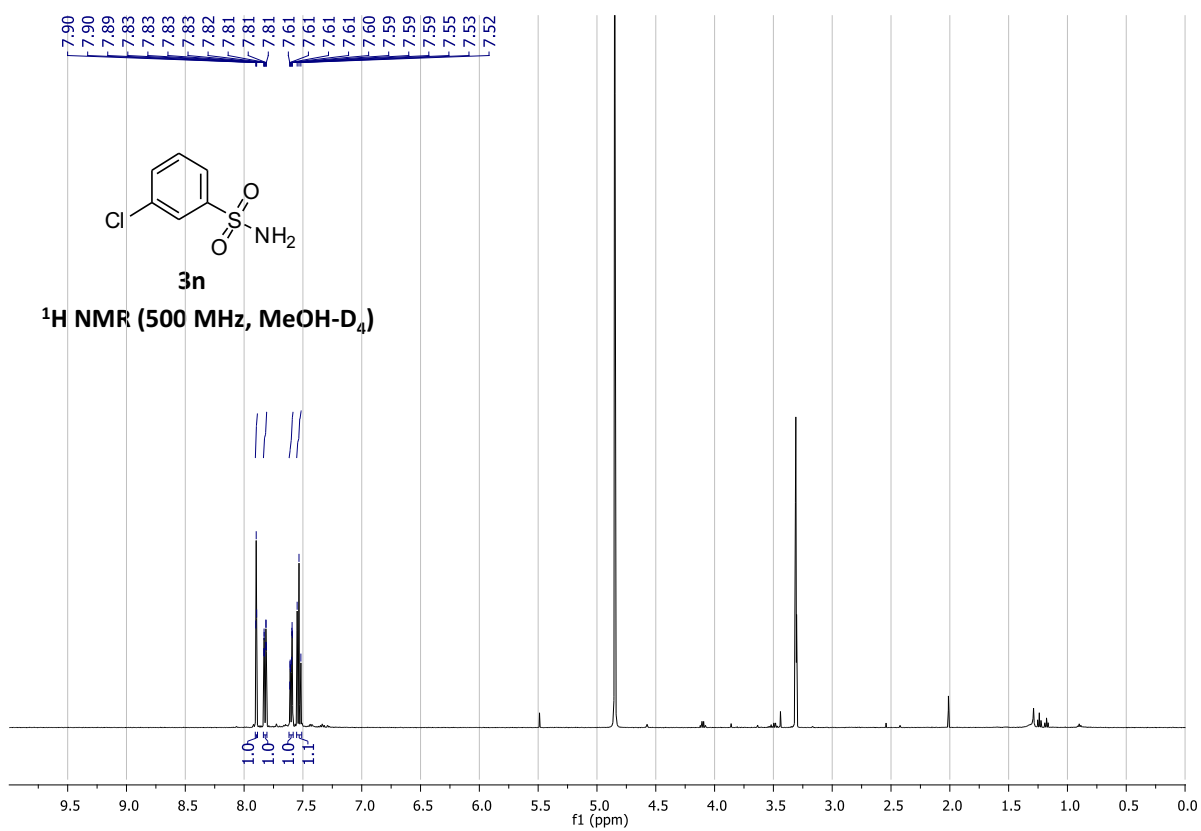


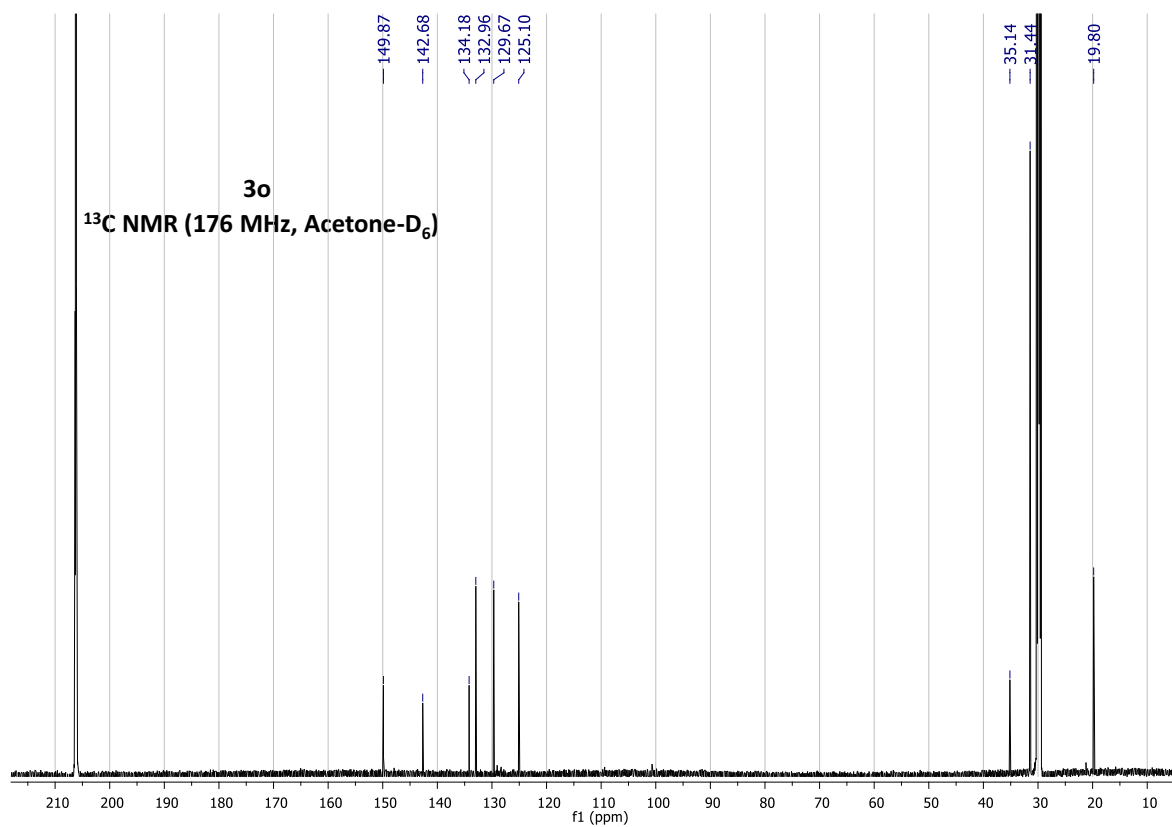
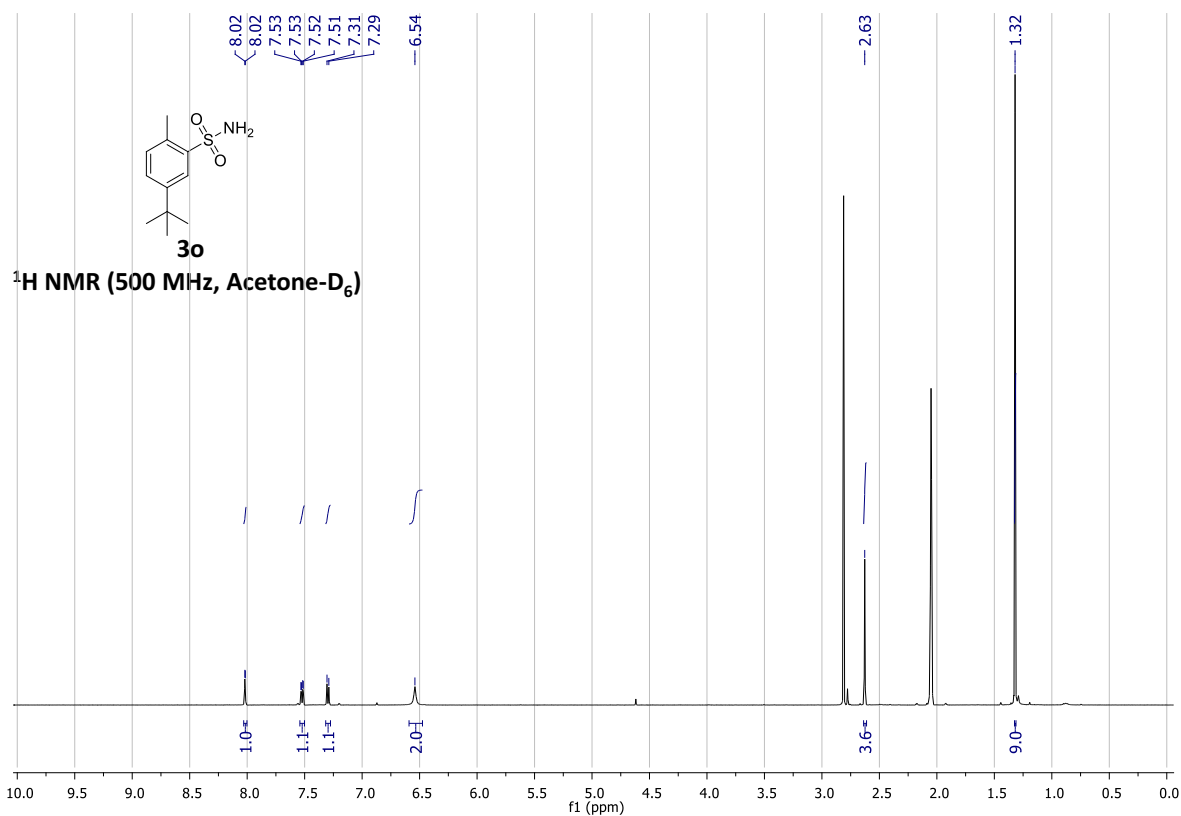


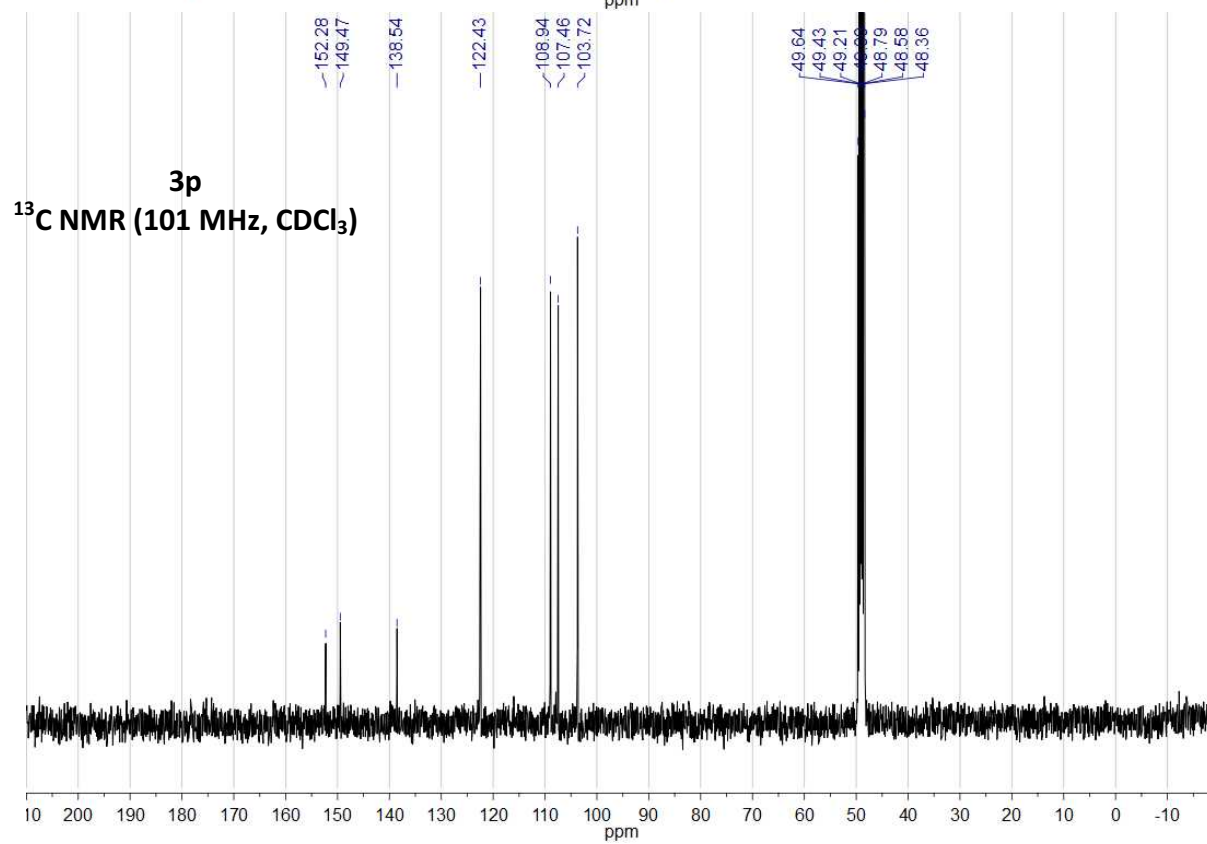
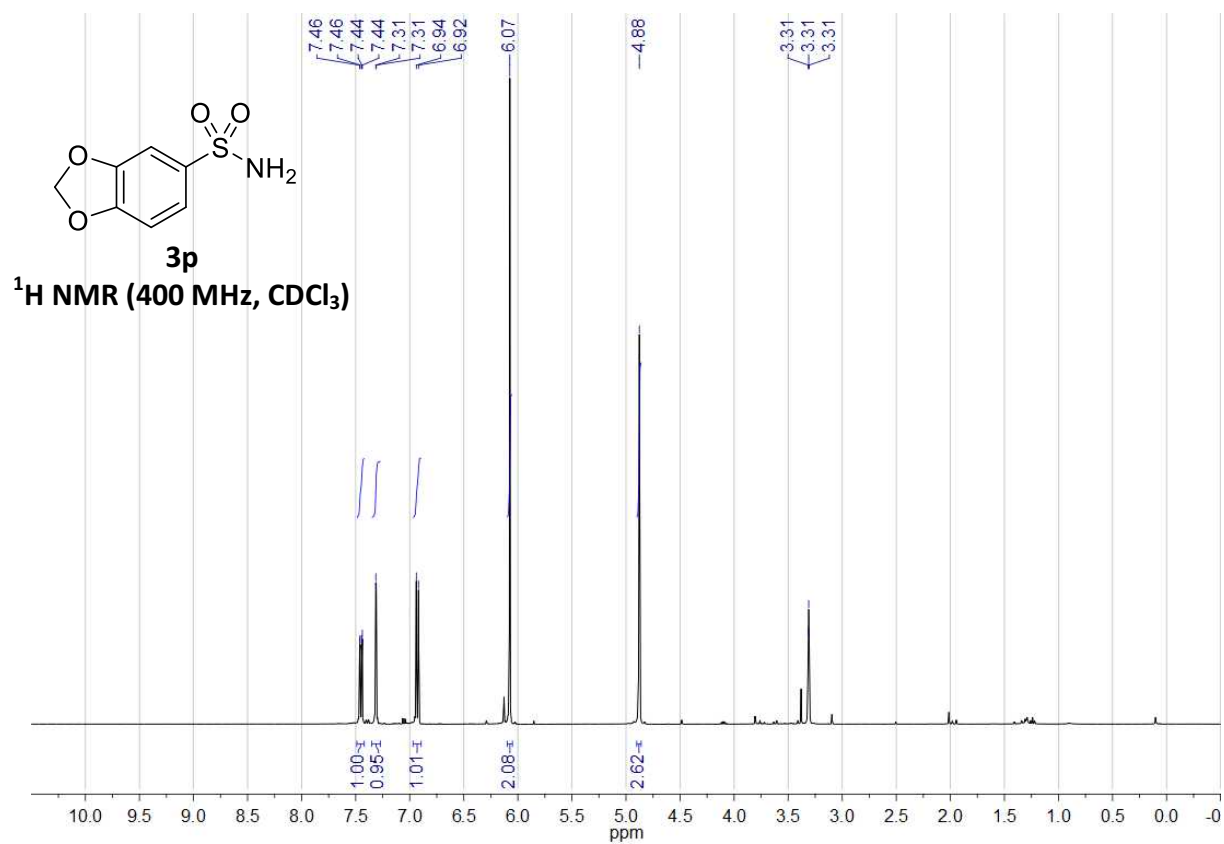


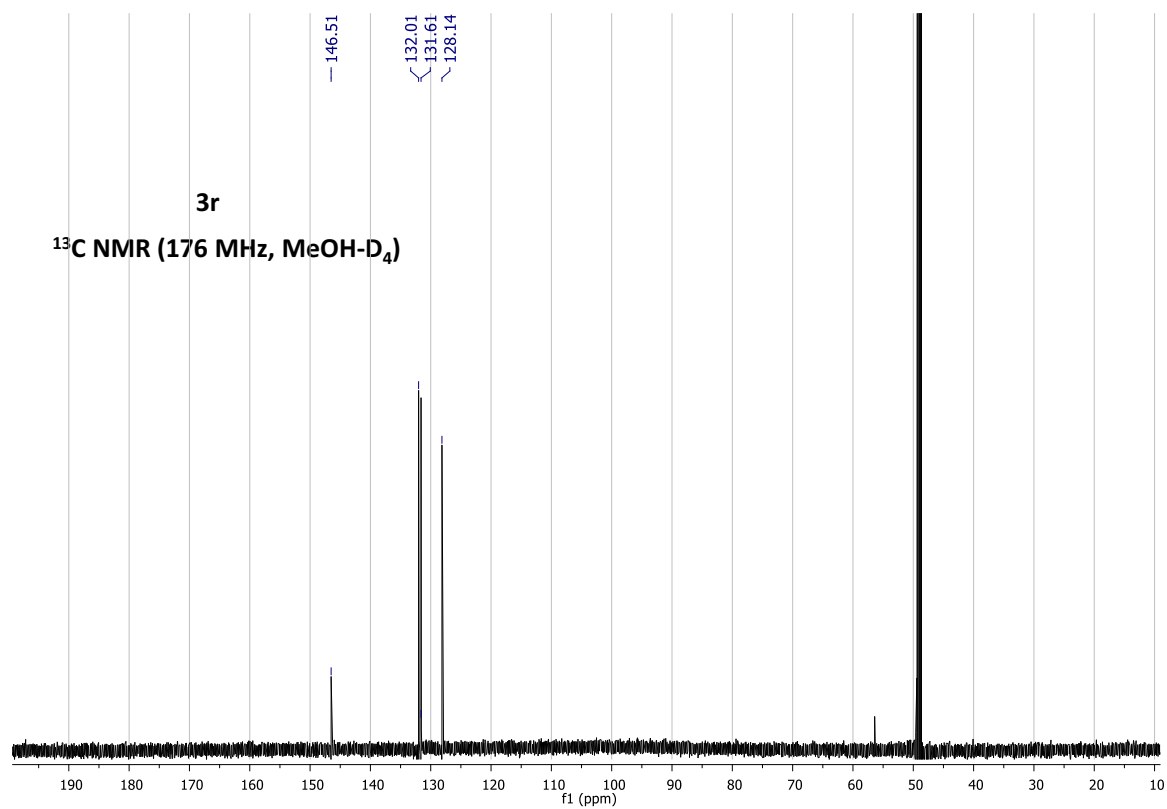
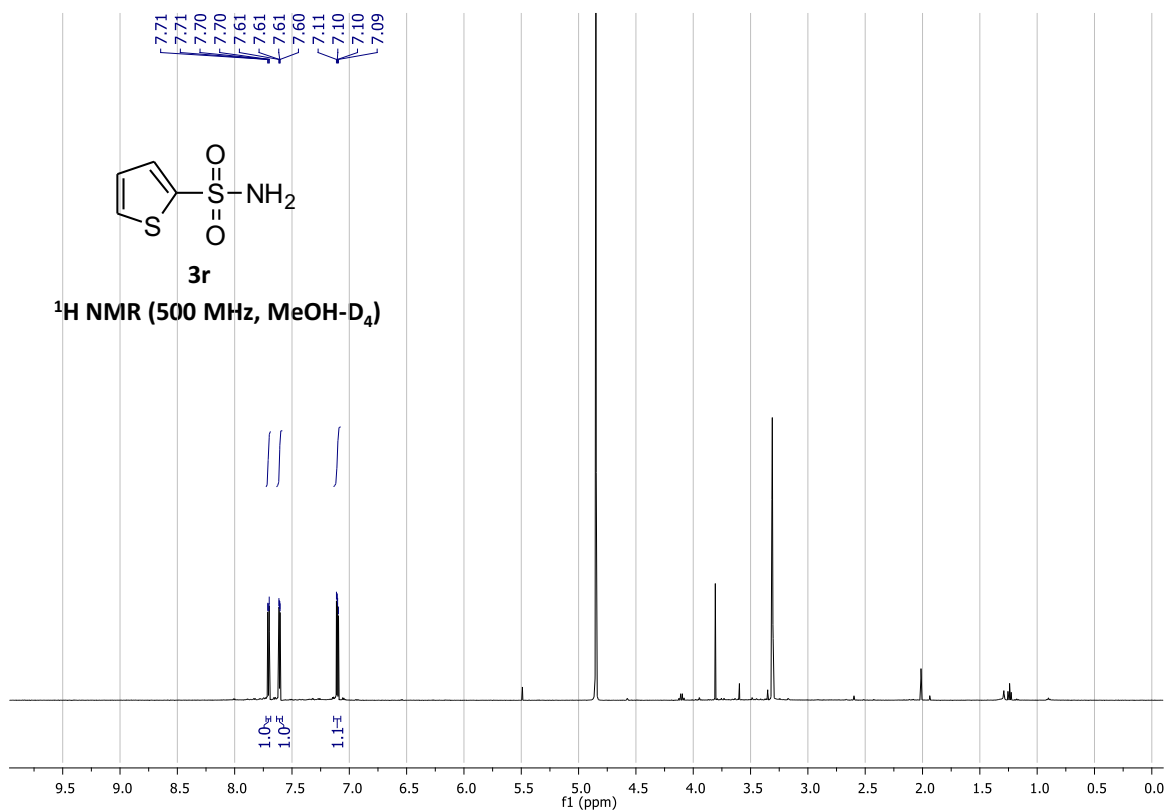


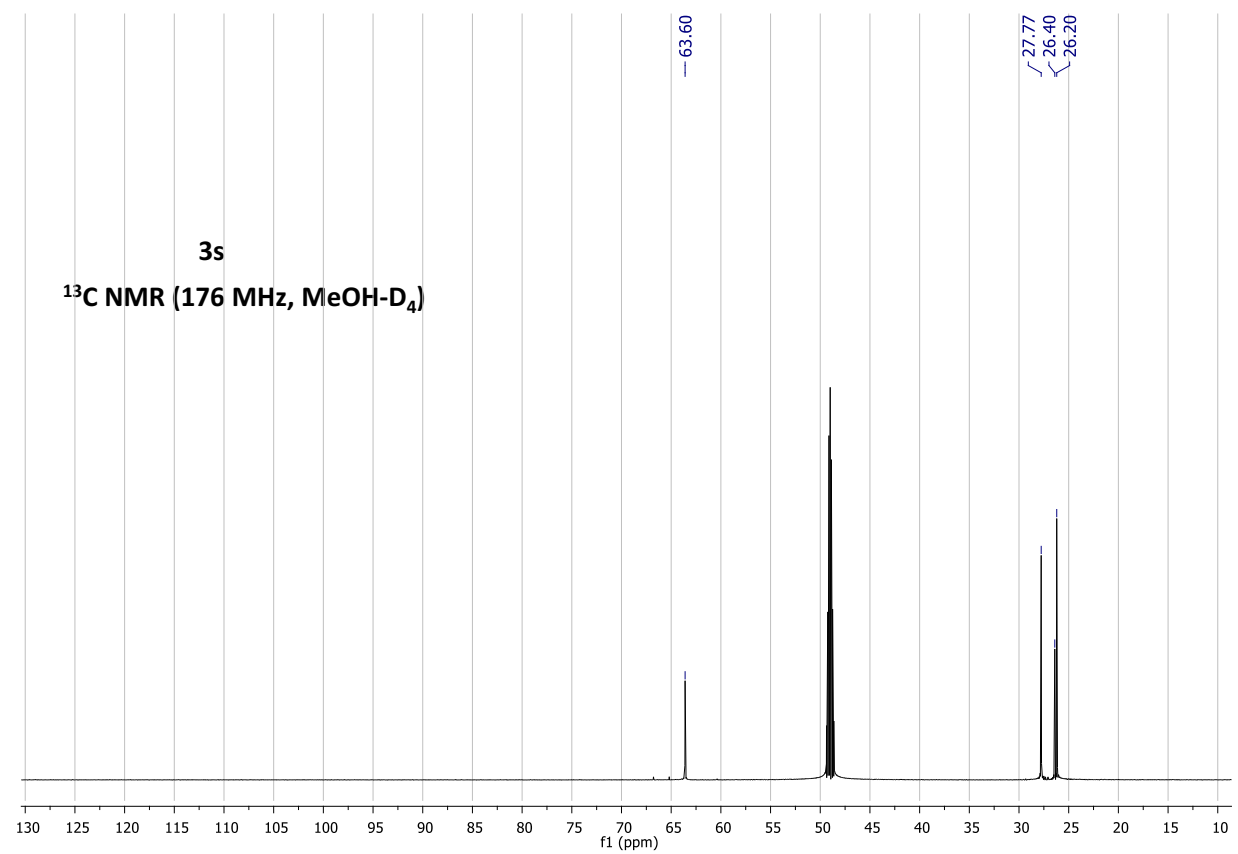
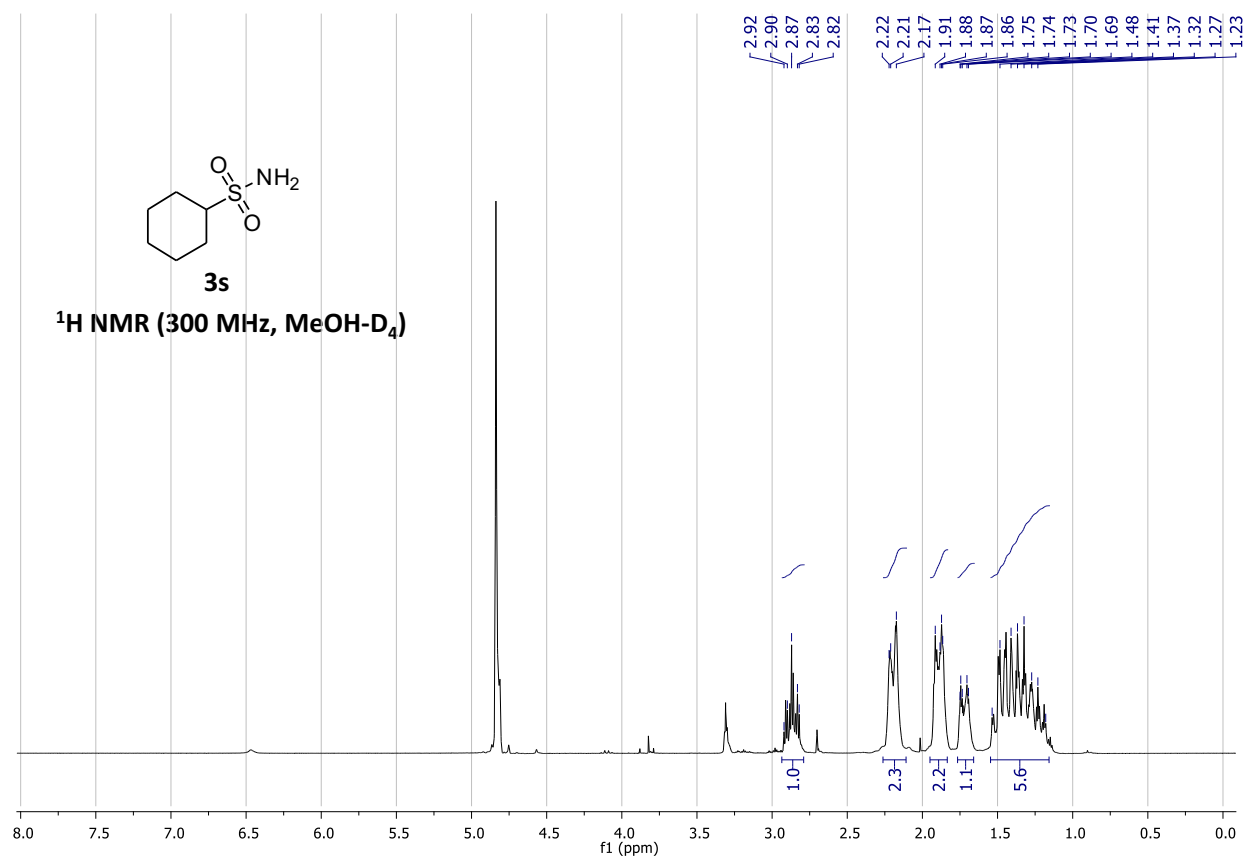


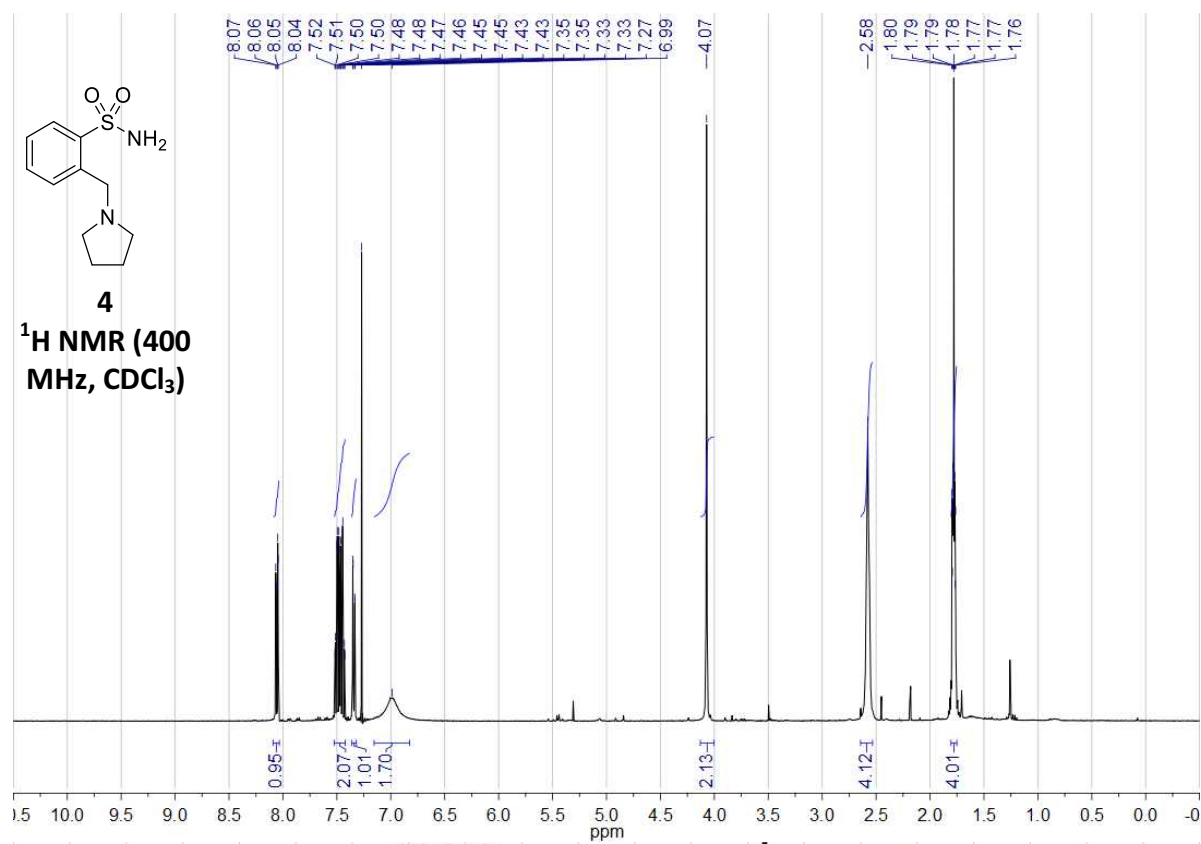












4
¹³C NMR (101 MHz, CDCl₃)

