SUPPORTING INFORMATION

2-Sulfinyl-Oxetanes: Synthesis, Stability and Reactivity

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General Experimental Conditions:

All non-aqueous reactions were carried out under an inert atmosphere (argon) with oven-dried (160 ºC) or flame dried glassware using standard techniques. Anhydrous solvents were obtained by filtration through drying columns (THF, Et_2O, CH_2Cl_2, PhMe) or obtained from commercial suppliers and used without further purification (DMF). H_2O was distilled before use.
Flash column chromatography was performed using 230-400 mesh silica, 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), aqueous potassium permanganate stain or PMA (phosphomolybdic acid).
Infrared spectra were recorded using a Perkin-Elmer spectrum 100 FT-IR Spectrometer and the absorbencies were reported in wavenumbers (cm^{-1}).
Nuclear magnetic resonance spectra were recorded on a Bruker AV 400 (400 MHz) or AV 500 (500 MHz) spectrometer. Data were reported as follows: chemical shift, integration, multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet, br = broad), coupling constant in Hz and assignment. Chemical shifts are reported in parts per million from tetramethylsilane with the solvent resonance as an internal standard (^{1}H NMR spectra: $CDCl_3$: δ = 7.27 ppm, $(CD_3)_2CO$: δ = 2.05 ppm, CD_3OD: δ = 3.31 ppm, $(CD_3)_2SO$: δ = 2.50 ppm. ^{13}C NMR spectra: $CDCl_3$: δ = 77.00 ppm, $(CD_3)_2CO$: δ = 29.84, 206.26 ppm, CD_3OD: δ = 49.00 ppm, $(CD_3)_2SO$: δ = 39.52 ppm) or using chloroform with 1% tetramethylsilane as the internal standard. ^{13}C NMR spectra were recorded with complete proton decoupling. ^{19}F NMR spectra were recorded with complete proton decoupling. Chemical shifts are reported in parts per million referenced to the standard monofluorobenzene: −113.5 ppm. Assignments of ^{1}H and ^{13}C spectra were made by the analysis of δ/*J* values and COSY, HSQC and HMBC experiments as appropriate.
High resolution mass spectrometry were recorded on VG Platform II, Waters Xevo G2-S, VG Autospec or Thermofisher LTQ Orbitrap XL spectrometers. Melting points are uncorrected

Reagents: For the preparation of LDA or LiHMDS solutions, diisopropylamine or hexamethyldisilazane were distilled over potassium hydroxide immediately before use. Unless otherwise stated *m*CPBA was washed prior to use: dissolved in CH_2Cl_2, washed with a phosphate buffer (pH 7.5) and dried ($MgSO_4$) then the solvent removed under reduced pressure. All commercially available organometallic solutions were titrated against salicylaldehyde phenylhydrazone.[i] All other commercially available reagents were used without further purification.

Preparation of a 0.61M solution of LiHMDS:
A solution of HMDS (1.27 ml, 6.0 mmol) in THF (5.38 mL) was cooled to –78 ºC for 10 min then *n*BuLi (2.35 mL, 5.49 mmol, 2.3 M in hexane) was added dropwise. The solution was stirred at –78 ºC for 30 min then warmed to 0 ºC for 30 min prior to immediate use.

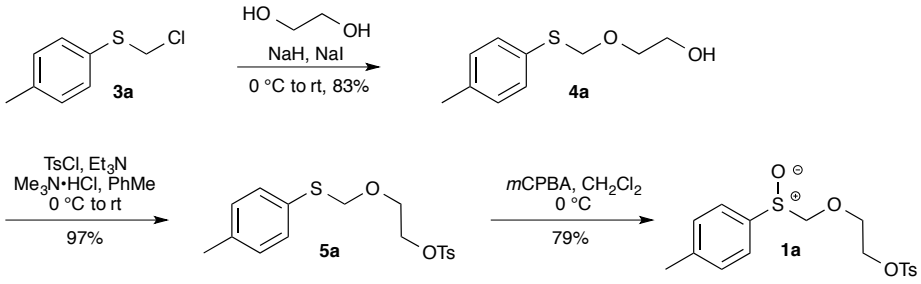
General Procedure for the preparation of a 1 M solution of LDA:
A solution of diisopropylamine (0.92 mL, 6.60 mmol) in THF (2.68 mL) was cooled to –78 ºC for 10 min then *n*BuLi (2.40 mL, 6.00 mmol, 2.5 M in hexane) was added dropwise. Solution stirred at –78 ºC for 1 h prior to use.

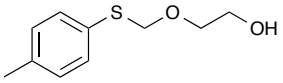
Compound Handling/Purification/Storage: All synthetic intermediates were stored under argon at –20 ºC for short periods of time. Instability of sulfoxide compounds meant that in some cases appropriate molecular ions (HRMS) could not be obtained.

Sulfinyl-oxetane diastereoisomers: The relative configuration of the oxetane diastereoisomers was not assigned. For consistency, diastereoisomers are denoted **A** or **B** based on polarity, with compound **A** eluting first on flash chromatography.

i. B. E. Love and E. G. Jones, *J. Org. Chem.*, 1999, **64**, 3755–3756.

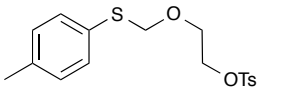
Synthesis of 1-methyl-4-({2-[(4-methylbenzenesulfonyl)oxy]ethoxy}methanesulfinyl)benzene (1a)





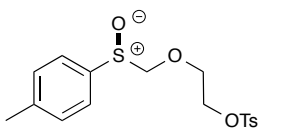
2-{[(4-Methylphenyl)sulfanyl]methoxy}ethan-1-ol (4a)[1]

Sodium hydride (60% in mineral oil, 2.57 g, 64.25 mmol) was added to ethylene glycol (400 mL) at 0 ºC and stirred for 1 h 15 min. Sodium iodide (9.62 g, 64.18 mmol) was added followed by a solution of chloromethylsulfide **3a** (10.04 g, 58.37 mmol) in ethylene glycol (5 mL). The resulting solution was stirred at 0 ºC for 1 h then warmed to rt for 4 h. Water (300 mL) was added and the product was extracted with ethyl acetate (10 × 50 mL). The combined organic layers were dried ($MgSO_4$), filtered and the solvent removed under reduced pressure. Purification by flash chromatography (50% EtOAc/hexane) afforded alcohol **4a** (9.60 g, 83%) as a yellow oil. R_f = 0.34 (50% EtOAc/hexane). IR (film)/cm^{-1} 3449 (OH), 2926, 2872, 1734, 1493, 1461, 1373, 1250, 1052, 1017, 806, 734. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (2 H, d, *J* = 8.1 Hz, 2 × Ar-H), 7.13 (2 H, d, *J* = 8.1 Hz, 2 × Ar-H), 5.00 (2 H, s, SCH_2O), 3.78–3.72 (4 H, m, OCH_2CH_2OH), 2.34 (3 H, s, CH_3), 1.94 (1 H, s, OH). ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.2 (Ar-C_q), 131.5 (Ar-C_q), 131.1 (2 × Ar-C), 129.8 (2 × Ar-C), 77.0 (SCH_2O), 69.7 (OCH_2), 61.7 (OCH_2), 21.1 (CH_3). HRMS (ESI) *m/z* Calculated for $C_{10}H_{14}NaO_2S^+$ $[M+Na]^+$: 221.0607; Found: 221.0607 $[M+Na]^+$, Δ 0 ppm.



2-{[(4-Methylphenyl)sulfanyl]methoxy}ethyl-4-methylbenzene-1-sulfonate (5a)[1]

Triethylamine (3.14 mL, 22.34 mmol) and trimethylamine hydrochloride (70 mg, 0.75 mmol) were added to a solution of alcohol **4a** (1.50 g, 7.56 mmol) in toluene (10 mL) at 0 ºC and stirred for 10 min. A suspension of 4-toluenesulfonyl chloride (2.86 g, 15.00 mmol) in toluene (10 mL) was added dropwise. The mixture was stirred at 0 ºC for 30 min then allowed to warm to rt slowly over 40 min and stirred for a further 1 h 20 min. Water (100 mL) was added to the reaction and the product was extracted with EtOAc (4 × 50 mL). The combined organic layers were washed with H_2O (30 mL) and brine (50 mL) then dried ($MgSO_4$), filtered and the solvent removed under reduced pressure. Purification by flash chromatography (40% EtOAc/hexane) afforded tosylate **5a** (2.52 g, 97%) as a yellow oil. R_f = 0.34 (40% EtOAc/hexane). IR (film)/cm^{-1} 2984, 2891, 1734, 1596, 1499, 1362, 1237, 1175, 1095, 1011, 915, 807. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (2 H, d, *J* = 8.2 Hz, 2 × Ts-H), 7.34–7.30 (4 H, m, 2 × Ts-H + 2 × Tol-H), 7.10 (2 H, d, *J* = 8.2 Hz, 2 × Tol-H), 4.90 (2 H, s, SCH_2O), 4.22–4.18 (2 H, m, $TsOCH_2$), 3.83–3.78 (2 H, m, CH_2OCH_2), 2.45 (3 H, s, Ts-CH_3), 2.33 (3 H, s, Tol-CH_3). ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.8 (Ts-C_q), 137.1 (Tol-C_q), 132.9 (Ts-C_q), 131.4 (Tol-C_q), 131.0 (2 × Ar-C), 129.8 (2 × Ar-C), 129.7 (2 × Ar-C), 127.9 (2 × Ar-C), 76.8 (SCH_2O), 68.7 (SCH_2OCH_2), 65.5 ($TsOCH_2$), 21.6 (Ts-CH_3), 21.0 (Tol-CH_3). HRMS (ESI) *m/z* Calculated for $C_{17}H_{24}NO_4S_2^+$ $[M+NH_4]^+$: 370.1141; Found: 370.1134 $[M+NH_4]^+$, Δ 1.9 ppm.

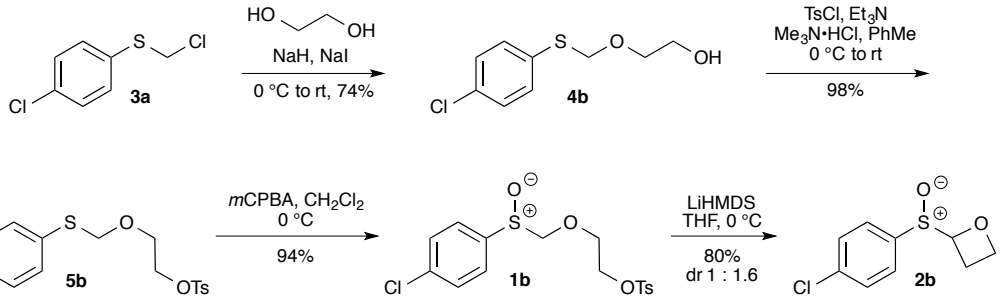


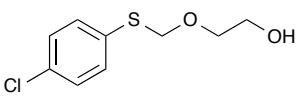
1-Methyl-4-({2-[(4-methylbenzenesulfonyl)oxy]ethoxy}methanesulfinyl) benzene (1a)

meta-Chloroperbenzoic acid (70%, 1.18 g, 4.80 mmol) was added to a solution of sulfide **5a** (1.54 g, 4.37 mmol) in dichloromethane (20 mL) at 0 ºC and the mixture stirred at 0 ºC for 3 h. The reaction was quenched with sat. aq. Na_2SO_3 (20 mL) and extracted with dichloromethane (7 × 20 mL). The combined organic layers were washed with 5% NaOH (3 × 10 mL) and sat. aq. NH_4Cl (50 mL) then dried ($MgSO_4$), filtered and the solvent removed under reduced pressure. Purification by flash chromatography (60% EtOAc/hexane)

afforded a sample of sulfoxide **1a** as pale yellow oil. R_f = 0.30 (60% EtOAc/hexane). IR (film)/cm^{-1} 2970, 1599, 1496, 1355, 1189, 1175, 1142, 1096, 1004, 915, 810. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (2 H, d, *J* = 8.5 Hz, 2 × Ts-H), 7.48 (2 H, d, *J* = 8.2 Hz, 2 × Ar-H), 7.36–7.30 (4 H, m, 2 × Ts-H + 2 × Ar-H), 4.40 (1 H, d, *J* = 10.6 Hz, SC*H*HO), 4.35 (1 H, d, *J* = 10.6 Hz, SCH*H*O), 4.21–4.14 (2 H, m, OCH_2), 4.10–3.95 (2 H, m, OCH_2), 2.43 (3 H, s, CH_3), 2.40 (3 H, s, CH_3). This compound rapidly decomposed on isolation on each attempt and ^{13}C NMR could not be obtained.

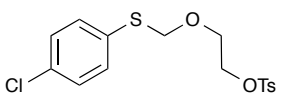
Synthesis of 2-(4-chlorobenzenesulfinyl)oxetane (2b)





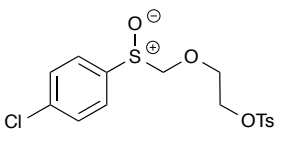
2-{[(4-Chlorophenyl)sulfanyl]methoxy}ethan-1-ol (4b)[1]

Sodium hydride (60% in mineral oil, 1.56 g, 39.01 mmol) was added to ethylene glycol (200 mL) at 0 ºC and stirred for 30 min. Sodium iodide (5.83 g, 38.90 mmol) was added followed by chloromethyl sulfide **3b** (6.26 g, 32.42 mmol) using DMF (5 mL) to aid transfer. The resulting solution was stirred at 0 ºC for 3 h then warmed to rt for 12 h. The reaction was quenched by the addition of sat. aq. NH_4Cl (200 mL) and the mixture extracted with EtOAc (4 × 75 mL). The combined organic layers were dried ($MgSO_4$), filtered and the solvent removed under reduced pressure. Purification by flash chromatography (50% EtOAc/hexane) afforded alcohol **4b** (5.27 g, 74%) as a colourless oil. R_f = 0.31 (50% EtOAc/hexane). IR (film)/cm^{-1} 3388 (OH), 2934, 2872, 1481, 1392, 1313, 1095, 1059, 1013, 816, 683. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 (2 H, d, *J* = 8.6 Hz, 2 × Ar-H), 7.27 (2 H, d, *J* = 8.6 Hz, 2 × Ar-H), 5.01 (2 H, s, SCH_2O), 3.80–3.69 (4 H, m, OCH_2CH_2OH), 2.08 (1 H, s, OH). ^{13}C NMR (100 MHz, $CDCl_3$) δ 133.9 (Ar-C_q), 133.0 (Ar-C_q), 131.6 (2 × Ar-C), 129.1 (2 × Ar-C), 76.4 (SCH_2O), 69.8 (OCH_2), 61.5 (OCH_2). HRMS (ESI) *m/z* Calculated for $C_9H_{11}{}^{35}ClNaO_2S^+$ $[M+Na]^+$: 241.0060; Found: 241.0060 $[M+Na]^+$, Δ 0 ppm.



2-{[(4-Chlorophenyl)sulfanyl]methoxy}ethyl-4-methylbenzene-1-sulfonate (5b)[1]

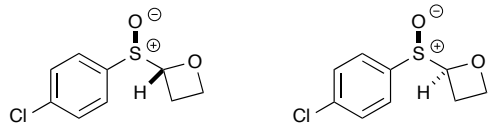
Triethylamine (6.19 mL, 44.04 mmol) and trimethylamine hydrochloride (141 mg, 1.48 mmol) were added to a solution of alcohol **4b** (3.24 g, 14.82 mmol) in toluene (40 mL) at 0 ºC and stirred for 20 min. 4-Toluenesulfonyl chloride (5.65 g, 29.64 mmol) was added portionwise. The mixture was stirred at 0 ºC for 30 min then at rt for 2h. The reaction was quenched by the addition of sat. aq. $NaHCO_3$ (200 mL) and the mixture extracted with EtOAc (3 × 100 mL). The combined organic layers were washed with sat. aq. NH_4Cl (100 mL) then dried ($MgSO_4$), filtered and the solvent removed under reduced pressure. Purification by flash chromatography (40% EtOAc/hexane) afforded tosylate **5b** (5.39 g, 98%) as a colourless oil. R_f = 0.24 (20% EtOAc/hexane). IR (film)/cm^{-1} 2920, 1601, 1482, 1358, 1180, 1095, 1093, 1017, 922, 820, 776, 668, 559. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (2 H, d, *J* = 8.3 Hz, 2 × Ts-H), 7.38–7.31 (4 H, m, 2 × Ts-H + 2 × Ar-H), 7.26–7.20 (2 H, m, 2 × Ar-H), 4.92 (2 H, s, SCH_2O), 4.23–4.19 (2 H, m, $TsOCH_2$), 3.84–3.80 (2 H, m, CH_2OCH_2), 2.45 (3 H, s, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.9 (Ts-C_q), 133.7 (Ar-C_q), 133.0 (Ts-C_q), 132.8 (Ar-C_q), 131.7 (2 × Ar-C), 129.8 (2 × Ts-C), 129.0 (2 × Ar-C), 127.9 (2 × Ts-C), 76.3 (SCH_2O), 68.6 (SCH_2OCH_2), 65.6 ($TsOCH_2$), 21.7 (CH_3). HRMS (ESI) *m/z* Calculated for $C_{16}H_{21}{}^{35}ClNO_4S_2^+$ $[M+NH_4]^+$: 390.0595; Found: 390.0595 $[M+NH_4]^+$, Δ 0 ppm.



2-(((4-Chlorophenyl)sulfinyl)methoxy)ethyl-4-methylbenzenesulfonate (1b)

meta-Chloroperbenzoic acid (1.11 g, 6.43 mmol) was added slowly to a solution of sulfide **5b** (2.00 g, 5.36 mmol) in dichloromethane (50 mL) at 0 ºC and the mixture stirred at 0 ºC for 1 h then warmed to rt for 1 h. The reaction was quenched with sat. aq. Na_2SO_3 (80 mL) and $NaHCO_3$ (80 mL) then extracted with dichloromethane (4 × 40 mL). The combined organic layers were washed with sat. aq. $NaHCO_3$ (80 mL) then dried ($MgSO_4$), filtered and the solvent removed under reduced pressure. Purification by flash chromatography (70% EtOAc/hexane) afforded sulfoxide **1b** (1.95 g, 94%) as a colourless

oil. R_f = 0.19 (70% EtOAc/hexane). IR (film)/cm^{-1} 3060, 2954, 2932, 1597, 1475, 1452, 1391, 1353, 1244, 1174, 1086, 1010, 909, 815, 772, 740. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (2 H, d, *J* = 8.5 Hz, 2 × Ts-H), 7.54 (2 H, d, *J* = 8.6 Hz, 2 × Ar-H), 7.49 (2 H, d, *J* = 8.6 Hz, 2 × Ar-H), 7.33 (2 H, d, *J* = 8.5 Hz, 2 × Ts-H), 4.45 (1 H, d, *J* = 10.5 Hz, SC*H*HO), 4.38 (1 H, d, *J* = 10.5 Hz, SCH*H*O), 4.18–4.16 (2 H, m, OCH_2), 4.10–3.89 (2 H, m, OCH_2), 2.44 (3 H, s, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.1 (Ts-C_q), 138.9 (Ar-C_q), 137.6 (Ar-C_q), 132.5 (Ts-C_q), 129.9 (2 × Ts-C), 129.5 (2 × Ar-C), 127.8 (2 × Ts-C), 125.8 (2 × Ar-C), 91.7 (SCH_2O), 71.0 (OCH_2CH_2O), 68.5 (OCH_2CH_2O), 21.6 (CH_3). HRMS (ESI) *m/z* Calculated for $C_{16}H_{18}{}^{35}ClO_5S_2^+$ $[M+H]^+$: 389.0279; Found: Accurate mass could not be found due to compound degradation.



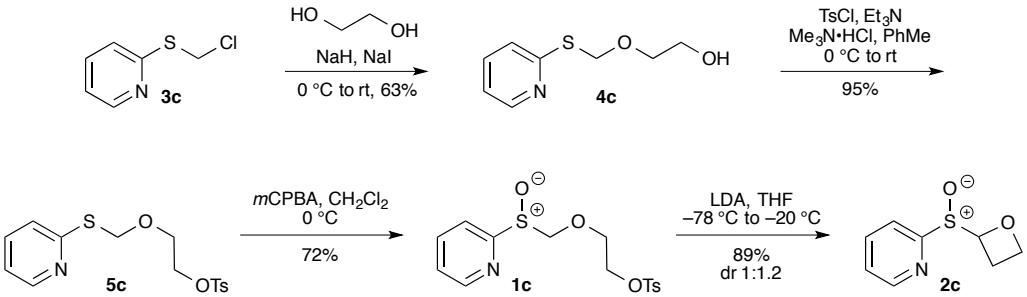
2-((4-Chlorobenzenesulfinyl)oxetane (2b)

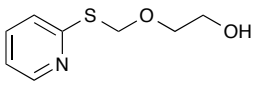
A solution of LiHMDS (1 M in THF, 0.16 mL, 0.16 mmol) was added dropwise to a solution of sulfoxide **1b** (50 mg, 0.13 mmol) in THF (5 mL) at 0 ºC and stirred for 1 h. The reaction was quenched with sat. aq. NH_4Cl (10 mL) and extracted with CH_2Cl_2 (5 × 6 mL). The combined organics were dried ($MgSO_4$), filtered and the solvent removed under reduced pressure. Purification by flash chromatography (70% EtOAc/hexane) afforded the oxetane as a mixture of two diastereoisomers **2b-A** (10 mg, 36%) followed by **2b-B** (12 mg, 44%) both as colourless oils.

Minor Diastereoisomer 2b-A: R_f = 0.30 (70% EtOAc/hexane). IR (film)/cm^{-1} 3079, 2965, 2897, 1574, 1475, 1391, 1256, 1235, 1176, 1090, 1079, 1052, 975, 931, 913, 822, 741, 702. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54–7.49 (4 H, m, 4 × Ar-H), 5.26 (1 H, dd, *J* = 7.6, 5.2 Hz, OCHS), 4.80 (1 H, ddd, *J* = 9.0, 6.8, 5.4 Hz, OCH*H*), 4.68 (1 H, ddd, *J* = 8.4, 6.0, 5.4 Hz, OC*H*H), 3.26–3.18 (1 H, m, OCH_2CH*H*), 2.73–2.63 (1 H, m, OCH_2C*H*H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.7 (Ar-C_q), 137.4 (Ar-C_q), 129.3 (2 × Ar-C), 126.5 (2 × Ar-C), 96.8 (OCHS), 71.1 (OCH_2), 22.5 (OCH_2CH_2).

Major Diastereoisomer 2b-B: R_f = 0.13 (70% EtOAc/hexane). IR (film)/cm^{-1} 3079, 2965, 2897, 1574, 1475, 1391, 1256, 1235, 1176, 1090, 1079, 1052, 975, 931, 913, 822, 741, 702. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (2 H, dt, *J* = 8.4, 2.0 Hz, 2 × Ar-H), 7.51 (2 H, dt, *J* = 8.4, 2.0 Hz, 2 × Ar-H), 5.38 (1 H, dd, *J* = 7.4, 5.7 Hz, OCHS), 4.65–4.55 (2 H, m, OCH_2), 3.07–3.98 (2 H, m, OCH_2CH_2). ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.7 (Ar-C_q), 137.4 (Ar-C_q), 129.3 (2 × Ar-C), 126.5 (2 × Ar-C), 96.8 (OCHS), 71.1 (OCH_2), 22.5 (OCH_2CH_2).

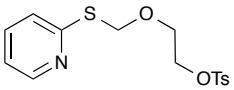
Synthesis of 2-(oxetan-2-ylsulfinyl)pyridine (2c)





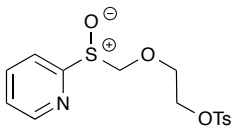
2-[(Pyridin-2-ylsulfanyl)methoxy]ethan-1-ol (4c)[1]

Sodium hydride (60% in mineral oil, 0.55 g, 13.78 mmol) was added to ethylene glycol (120 mL) at 0 ºC and stirred for 55 min. Sodium iodide (2.06 g, 13.78 mmol) was added followed by chloromethyl sulfide **3c** (2.00 g, 12.53 mmol) using ethylene glycol (1 mL) to aid transfer. The resulting solution was stirred at 0 ºC for 25 min then warmed to rt for 19 h 20 min. Water (150 mL) was added to the reaction and the product was extracted with EtOAc (10 × 35 mL). The combined organic layers were dried ($MgSO_4$), filtered and the solvent removed under reduced pressure. Purification by flash chromatography (0–80% EtOAc/heptane) afforded alcohol **4c** (1.46 g, 63%) as a colourless oil. R_f = 0.59 (80% EtOAc/heptane). IR (film)/cm^{-1} 3344 (OH), 2925, 1656, 1577, 1454, 1416, 1281, 1102, 1060, 908, 824, 758, 721, 678. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.46–8.44 (1 H, m, Py-H), 7.52 (1 H, ddd, *J* = 8.0, 7.3, 1.9 Hz, Py-H), 7.29 (1 H, ddd, *J* = 8.0, 1.0, 0.9 Hz, Py-H), 7.04 (1 H, ddd, *J* = 7.3, 5.0, 1.0 Hz, Py-H), 5.38 (2 H, s, SCH_2O), 3.77–3.72 (4 H, m, OCH_2CH_2OH), 2.95 (1 H, br s, OH). ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.4 (Py-C_q), 149.5 (Py-C), 136.5 (Py-C), 123.2 (Py-C), 120.4 (Py-C), 71.9 (SCH_2O), 70.5 (OCH_2), 61.6 (OCH_2). HRMS (ESI) *m/z* Calculated for $C_8H_{12}NO_2S^+$ $[M+H]^+$: 186.0583; Found: 186.0582 $[M+H]^+$, Δ 0.5 ppm.



2-[(Pyridin-2-ylsulfanyl)methoxy]ethyl-4-methylbenzene-1-sulfonate (5c)[1]

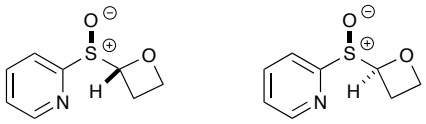
Triethylamine (4.06 mL, 28.89 mmol) and trimethylamine hydrochloride (93 mg, 0.97 mmol) were added to a solution of alcohol **4c** (0.90 g, 4.86 mmol) in toluene (30 mL) at 0 ºC and stirred for 30 min. A solution of 4-toluenesulfonyl chloride (3.71 g, 19.46 mmol) in toluene (10 mL) was added and the mixture was stirred at 0 ºC for 35 min then at rt for 2 h 35 min. Water (50 mL) was added to the reaction and the product was extracted with EtOAc (7 × 30 mL). The combined organic layers were washed with H_2O (30 mL) and brine (30 mL) then dried ($MgSO_4$), filtered and the solvent removed under reduced pressure. Purification by flash chromatography (0–40% EtOAc/heptane) afforded tosylate **5c** (1.57 g, 95%) as a colourless oil. R_f = 0.36 (40% EtOAc/heptane). IR (film)/cm^{-1} 2924, 1610, 1533, 1494, 1453, 1419, 1353, 1281, 1216, 1172, 1119, 1032, 1009, 916, 816, 767, 680. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.43–8.41 (1 H, m, Py-H), 7.76 (2 H, d, *J* = 8.3 Hz, 2 × Ts-H), 7.50 (1 H, ddd, *J* = 8.0, 7.4, 1.9 Hz, Py-H), 7.31 (2 H, d, *J* = 8.3 Hz, 2 × Ts-H), 7.24 (1 H, d, *J* = 8.0 Hz, Py-H), 7.02 (1 H, ddd, *J* = 7.4, 4.9, 1.0 Hz, Py-H), 5.32 (2 H, s, SCH_2O), 4.18–4.16 (2 H, m, OCH_2CH_2), 3.79–3.76 (2 H, m, OCH_2CH_2), 2.42 (3 H, s, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.2 (Py-C_q), 149.4 (Py-C), 144.7 (Ts-C_q), 136.4 (Py-C), 133.0 (Ts-C_q), 129.7 (2 × Ts-C), 127.8 (2 × Ts-C), 122.8 (Py-C), 120.3 (Py-C), 71.8 (SCH_2O), 68.7 (OCH_2CH_2), 66.2 (OCH_2CH_2), 21.5 (CH_3). HRMS (NSI) *m/z* Calculated for $C_{15}H_{18}NO_4S_2^+$ $[M+H]^+$: 340.0672; Found: 340.0674 $[M+H]^+$, Δ 0.6 ppm.



2-({2-[(4-Methylbenzenesulfonyl)oxy]ethoxy}methanesulfinyl)pyridine (1c)

meta-Chloroperbenzoic acid (2.06 g, 11.93 mmol) was added portionwise to a solution of sulfide **5c** (3.37 g, 9.93 mmol) in dichloromethane (150 mL) at 0 ºC and the mixture stirred whilst warming to rt for 2 h 30 min. The reaction was quenched with sat. aq. Na_2SO_3 (40 mL) and sat. aq. $NaHCO_3$ (40 mL) then extracted with dichloromethane (5 × 40 mL). The combined organic layers were washed with sat. aq. $NaHCO_3$ (50 mL) then dried ($MgSO_4$), filtered and the solvent removed under reduced pressure. Purification by flash chromatography

(90–100% EtOAc/hexane) afforded sulfoxide **1c** (2.54 g, 72%) as a yellow solid, m.p. = 81–83 ºC. R_f = 0.30 (100% EtOAc). IR (film)/cm^{-1} 1577, 1445, 1421, 1347, 1240, 1172, 1145, 1110, 1035, 1009, 947, 914, 805, 770, 664. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.62–8.59 (1 H, m, Py-H), 7.99–7.90 (2 H, m, Py-H), 7.75 (2 H, d, *J* = 8.3 Hz, 2 × Ts-H), 7.38 (1 H, ddd, *J* = 7.0, 4.7, 1.8 Hz, Py-H), 7.32 (2 H, d, *J* = 8.3 Hz, 2 × Ts-H), 4.85 (1 H, d, *J* = 10.8 Hz, SC*H*HO), 4.57 (1 H, d, *J* = 10.8 Hz, SCH*H*O), 4.17–3.99 (4 H, m, OCH_2CH_2O), 2.42 (3 H, s, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.6 (Py-C_q), 149.6 (Py-C), 145.0 (Ts-C_q), 138.0 (Py-C), 132.7 (Ts-C_q), 129.8 (2 × Ts-C), 127.9 (2 × Ts-C), 124.7 (Py-C), 120.8 (Py-C), 91.1 (SCH_2O), 71.1 (OCH_2), 68.6 (OCH_2), 21.6 (CH_3). HRMS (ES) *m/z* Calculated for $C_{15}H_{17}NNaO_5S_2$ [M+Na]: 378.0446; Found: 378.0457 [M+Na], Δ 2.9 ppm.



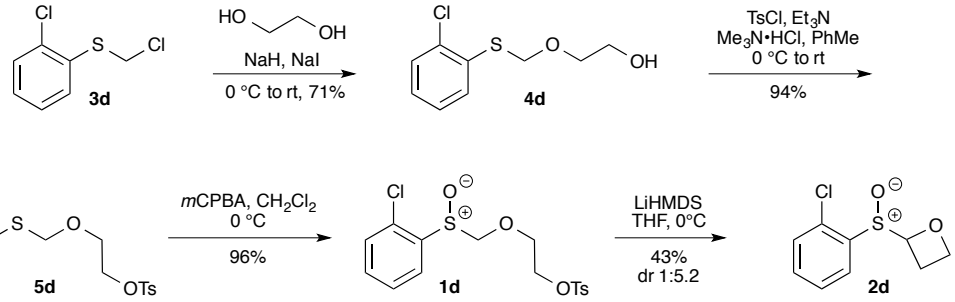
2-(Oxetan-2-ylsulfinyl)pyridine (2c)

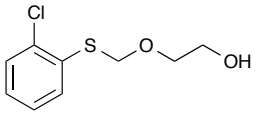
A solution of LDA (1 M in THF, 1.08 mL, 1.08 mmol) was added dropwise to a solution of sulfoxide **1c** (0.26 g, 0.71 mmol) in THF (28 mL) at –78 °C and stirred for 15 min. The reaction flask was transferred to a –20 ºC bath and stirred for a further 20 min. The reaction was quenched with sat. aq. NH_4Cl (50 mL) and extracted with CH_2Cl_2 (5 × 30 mL). The combined organics were dried ($MgSO_4$), filtered and the solvent removed under reduced pressure. Purification by flash chromatography afforded the oxetane as a mixture of two diastereoisomers **2c-A** (50 mg, 38%) (20% EtOAc/hexane) followed by **2c-B** (68 mg, 51%) (20% CH_2Cl_2/Et_2O) both as white solids.

Minor Diastereoisomer 2c-A: m.p. = 71–73 ºC. R_f = 0.10 (20% CH_2Cl_2/Et_2O). IR (film)/cm^{-1} 3502, 2970, 2912, 1575, 1449, 1421, 1240, 1088, 1053, 1009, 975, 915, 774, 739. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.61 (1 H, d, *J* = 4.7 Hz, Py-H), 8.04 (1 H, d, *J* = 7.8 Hz, Py-H), 7.94 (1 H, ddd, *J* = 7.8, 7.5, 1.7 Hz, Py-H), 7.37 (1 H, ddd, *J* = 7.5, 4.7, 1.1 Hz, Py-H), 5.78 (1 H, dd, *J* = 7.9, 5.6 Hz, OCHS), 4.82 (1 H, ddd, *J* = 8.8, 6.9, 5.4 Hz, OCH*H*), 4.65 (1 H, ddd, *J* = 8.4, 6.0, 5.4 Hz, OC*H*H), 3.39–3.28 (1 H, m, OCH_2CH*H*), 3.17–3.05 (1 H, m, OCH_2C*H*H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.0 (Py-C_q), 149.5 (Py-C), 137.7 (Py-C), 124.6 (Py-C), 121.4 (Py-C), 97.2 (OCHS), 71.4 (OCH_2), 22.7 (OCH_2*C*H_2). HRMS (CI) *m/z* Calculated for $C_8H_{10}NO_2S$ [M+H]: 184.0432; Found: 184.0430 [M+H], Δ 1.1 ppm.

Major Diastereoisomer 2c-B: m.p. = 71–73 ºC. R_f = 0.15 (20% CH_2Cl_2/Et_2O). IR (film)/cm^{-1} 3398, 2956, 1573, 1564, 1447, 1418, 1332, 1222, 1113, 1083, 1042, 988, 764, 712. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.63–8.61 (1 H, d, *J* = 4.6 Hz, Py-H), 7.98–7.90 (2 H, m, 2 × Py-H), 7.38 (1 H, ddd, *J* = 6.8, 4.8, 2.2 Hz, Py-H), 5.82 (1 H, dd, *J* = 7.4, 5.3 Hz, OCHS), 4.80 (1 H, ddd, *J* = 12.0, 6.8, 5.4 Hz, OCH*H*), 4.69 (1 H, ddd, *J* = 11.4, 6.0, 5.4 Hz, OC*H*H), 3.58–3.47 (1 H, m, OCH_2C*H*H), 3.22–3.12 (1 H, m, OCH_2CH*H*). ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.0 (Py-C_q), 149.7 (Py-C), 137.9 (Py-C), 124.6 (Py-C), 120.5 (Py-C), 100.0 (OCHS), 71.5 (OCH_2), 18.7 (OCH_2*C*H_2). HRMS (CI) *m/z* Calculated for $C_8H_{10}NO_2S$ [M+H]: 184.0432; Found: 184.0430 [M+H], Δ 1.1 ppm.

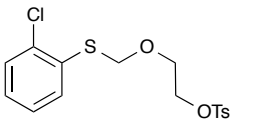
Synthesis of 2-(2-chlorobenzenesulfinyl)oxetane (2d)





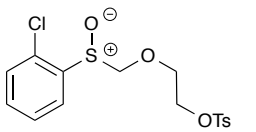
2-(((2-Chlorophenyl)thio)methoxy)ethanol (4d)[2]

Sodium hydride (60% in mineral oil, 1.60 g, 40.01 mmol) was added to ethylene glycol (350 mL) at 0 ºC and stirred for 1 h 30 min. Sodium iodide (6.01 g, 40.10 mmol) was added followed by chloromethylsulfide **3d** (6.88 g, 35.63 mmol). The resulting solution was stirred at 0 ºC for 2 h then warmed to rt for 17 h. Water (175 mL) was added and the product was extracted with ethyl acetate (10 × 30 mL). The combined organic layers were dried ($MgSO_4$), filtered and the solvent removed under reduced pressure. Purification by flash chromatography (30% EtOAc/hexane) afforded alcohol **4d** (5.60 g, 71%) as a pale yellow oil. R_f = 0.42 (100% EtOAc). IR (film)/cm^{-1} 3380 (OH), 2927, 1575, 1454, 1431, 1309, 1253, 1100, 1055, 1033, 1018, 887, 824, 745, 656. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (1 H, dd, *J* = 7.8, 1.6 Hz, Ar-H), 7.38 (1 H, dd, *J* = 7.8, 1.5 Hz, Ar-H), 7.23 (1 H, ddd, *J* = 9.1, 7.8, 1.5 Hz, Ar-H), 7.16 (1 H, ddd, *J* = 9.1, 7.8, 1.6 Hz, Ar-H), 5.10 (2 H, s, SCH_2O), 3.75 (4 H, br s, SCH_2CH_2OH), 2.05 (1 H, br s, OH). ^{13}C NMR (100 MHz, $CDCl_3$) δ 134.8 (C_q), 134.0 (C_q), 130.2 (Ar-C), 129.7 (Ar-C), 127.5 (Ar-C), 127.3 (Ar-C), 74.8 (SCH_2O), 70.0 (OCH_2), 61.5 (OCH_2). HRMS (EI) *m/z* Calculated for $C_9H_{15}NO_2S^{35}Cl$ [M+NH_4]: 236.0512; Found: 236.0521 [M+NH_4], Δ 3.8 ppm.



2-{[(2-Chlorophenyl)sulfanyl]methoxy}ethyl-4-methylbenzene-1-sulfonate (5d)[2]

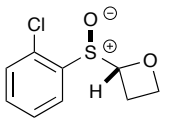
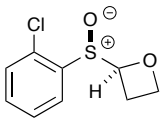
Triethylamine (9.59 mL, 68.24 mmol) and trimethylamine hydrochloride (0.22 g, 2.29 mmol) were added to a solution of alcohol **4d** (5.02 g, 22.93 mmol) in toluene (100 mL) at 0 ºC and stirred for 1 h. 4-Toluenesulfonyl chloride (8.74 g, 45.87 mmol) was added portionwise. The mixture was stirred at 0 ºC for 50 min then allowed to warm to rt and stirred for a further 1 h 30 min. Water (75 mL) was added to the reaction and the product was extracted with EtOAc (5 × 25 mL). The combined organic layers were dried ($MgSO_4$), filtered and the solvent removed under reduced pressure. Purification by flash chromatography (20% EtOAc/hexane) afforded tosylate **5d** (8.03 g, 94%) as a white solid; m.p. = 40–42 ºC. R_f = 0.15 (20% EtOAc/hexane). IR (film)/cm^{-1} 3069, 2876, 1596, 1573, 1450, 1357, 1314, 1230, 1175, 1123, 1085, 1018, 924, 835, 759, 730, 661. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (2 H, d, *J* = 8.0 Hz, 2 × Ts-H), 7.55 (1 H, dd, *J* = 7.9, 1.7 Hz, Ar-H), 7.37 (1 H, dd, *J* = 7.9, 1.6 Hz, Ar-H), 7.32 (2 H, d, *J* = 8.0 Hz, 2 × Ts-H), 7.25–7.14 (2 H, m, 2 × Ar-H), 5.00 (2 H, s, SCH_2O), 4.23–4.18 (2 H, m, $TsOCH_2$), 3.80–3.80 (2 H, m, CH_2OCH_2), 2.45 (3 H, s, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.9 (C_q), 134.6 (C_q), 133.8 (C_q), 132.9 (C_q), 130.3 (Ar-C), 129.8 (2 × Ts-C), 129.6 (Ar-C), 127.9 (2 × Ts-C), 127.5 (Ar-C), 127.4 (Ar-C), 74.6 (SCH_2O), 68.6 (OCH_2), 65.8 (OCH_2), 21.6 (CH_3). HRMS (ES) *m/z* Calculated $C_{18}H_{21}NO_4S_2^{35}Cl$ [M+H+CH_3CN]: 414.0601; Found: 414.0605 [M+H+CH_3CN], Δ 1.0 ppm.



1-Chloro-2-({2-[(4-methylbenzenesulfonyl)oxy]ethoxy}methane sulfinyl)benzene (1d)

meta-Chloroperbenzoic acid (0.26 g, 1.51 mmol) was added portionwise to a solution of sulfide **5d** (0.51 g, 1.37 mmol) in dichloromethane (20 mL) at 0 ºC and the mixture for 1 h 45 min. The reaction was quenched with sat. aq. Na_2SO_3 (20 mL) and sat. aq. $NaHCO_3$ (20 mL) then extracted with dichloromethane (3 × 15 mL). The combined organic layers were washed with sat. aq. Na_2SO_3 (2 × 10 mL) and sat. aq. $NaHCO_3$ (10 mL) then dried ($MgSO_4$), filtered and the solvent removed under reduced pressure. Purification by flash

chromatography (70% EtOAc/hexane) afforded sulfoxide **1d** (0.51 g, 96%) as a colourless oil. R_f = 0.30 (70% EtOAc/hexane). IR (film)/cm^{-1} 2953, 1598, 1448, 1355, 1175, 1095, 1018, 910, 814, 733, 661. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (1 H, dd, *J* = 7.6, 1.7 Hz, Ar-H), 7.89 (2 H, d, *J* = 8.4 Hz, 2 × Ts-H), 7.55 (1 H, ddd, *J* = 9.0, 7.6, 1.3 Hz, Ar-H), 7.48 (1 H, ddd, *J* = 9.0, 7.9, 1.7 Hz, Ar-H), 7.41 (1 H, dd, *J* = 7.9, 1.3 Hz, Ar-H), 7.35 (2 H, d, *J* = 8.4 Hz, 2 × Ts-H), 4.79 (1 H, d, *J* = 10.8 Hz, SC*H*HO), 4.39 (1 H, d, *J* = 10.8 Hz, SCH*H*O), 4.23–4.19 (2 H, m, OCH_2), 4.14–4.09 (2 H, m, OCH_2), 2.45 (3 H, s, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.1 (C_q), 138.1 (C_q), 132.8 (C_q), 132.6 (C_q), 130.2 (Ar-C), 130.0 (2 × Ts-C), 129.9 (Ar-C), 128.2 (Ar-C), 128.1 (2 × Ts-C), 126.9 (Ar-C), 91.2 (SCH_2O), 71.2 (OCH_2), 68.8 (OCH_2), 21.8 (CH_3).

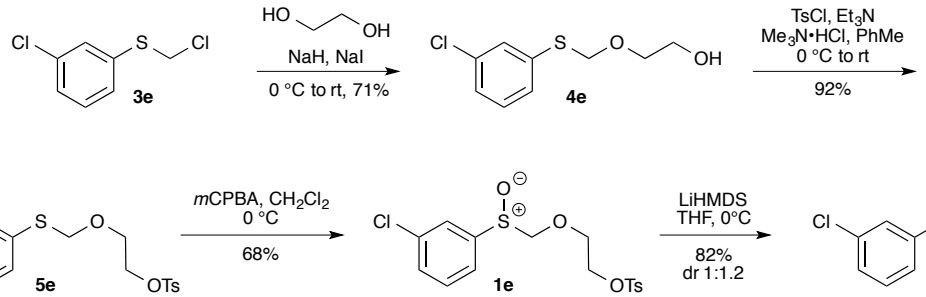



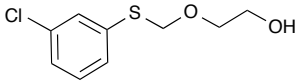
2-(2-Chlorobenzenesulfinyl)oxetane (2d)
A solution of LiHMDS (1.0 M in THF, 0.94 mL, 0.94 mmol) was added dropwise to a solution of sulfoxide **1d** (0.30 g, 0.78 mmol) in THF (30 mL) at 0 ºC and stirred for 1 h 15 min. The reaction was quenched with sat. aq. NH_4Cl (20 mL) and extracted with CH_2Cl_2 (5 × 15 mL). The combined organics were dried ($MgSO_4$), filtered and the solvent removed under reduced pressure. Purification by flash chromatography (40% EtOAc/hexane) afforded the sulfinyl oxetane as a mixture of two diastereoisomers **2d-A** (12 mg, 6%) followed by **2d-B** (62 mg, 37%) both as colourless oils.

Minor Diastereoisomer 2d-A: R_f = 0.22 (40% EtOAc/hexane). IR (film)/cm^{-1} 2965, 1724, 1573, 1433, 1357, 1248, 1176, 1103, 1026, 914, 815, 752, 660. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (1 H, dd, *J* = 7.3, 1.8 Hz, Ar-H), 7.50 (1 H, ddd, *J* = 8.9, 7.3, 1.3 Hz, Ar-H), 7.44 (1 H, ddd, *J* = 8.9, 7.8, 1.8 Hz, Ar-H), 7.39 (1 H, dd, *J* = 7.8, 1.3 Hz, Ar-H), 5.79 (1 H, dd, *J* = 7.4, 5.3 Hz, OCHS), 4.81 (1 H, ddd, *J* = 8.9, 6.7, 5.3 Hz, OCH*H*), 4.68 (1 H, ddd, *J* = 8.3, 6.1, 5.3 Hz, OC*H*H), 3.27–3.18 (1 H, m, OCH_2CH*H*), 2.56–2.47 (1 H, m, OCH_2C*H*H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.9 (C_q), 132.2 (Ar-C), 130.3 (C_q), 129.8 (Ar-C), 127.9 (Ar-C), 126.4 (Ar-C), 97.5 (SCHO), 71.5 (OCH_2), 18.2 (OCH_2CH_2). HRMS (ES) *m/z* Calculated $C_9H_{10}{}^{35}ClO_2S$ [M+H]: 217.0090; Found: 217.0104, [M+H], Δ 6.5 ppm.

Major Diastereoisomer 2d-B: R_f = 0.15 (40% EtOAc/hexane). IR (film)/cm^{-1} 2965, 1724, 1573, 1433, 1357, 1248, 1176, 1103, 1026, 914, 815, 752, 660. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (1 H, dd, *J* = 7.7, 1.7 Hz, Ar-H), 7.50 (1 H, ddd, *J* = 9.0, 7.7, 1.3 Hz, Ar-H), 7.43 (1 H, ddd, *J* = 9.0, 7.9, 1.7 Hz, Ar-H), 7.36 (1 H, dd, *J* = 7.9, 1.3 Hz, Ar-H), 5.75 (1 H, dd, *J* = 7.7, 5.5 Hz, OCHS), 4.79 (1 H, ddd, *J* = 8.8, 6.9, 5.2 Hz, OCH*H*), 4.64 (1 H, ddd, *J* = 8.3, 5.9, 5.2 Hz, OCH*H*), 3.31–3.23 (1 H, m, OCH_2CH*H*), 3.13–3.04 (1 H, m, OCH_2C*H*H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.8 (C_q), 132.1 (Ar-C), 129.9 (C_q), 129.5 (Ar-C), 128.0 (Ar-C), 127.5 (Ar-C), 94.5 (SCHO), 71.5 (OCH_2), 22.7 (OCH_2CH_2). HRMS (ES) *m/z* Calculated $C_9H_{10}{}^{35}ClO_2S$ [M+H]: 217.0090; Found: 217.0104, [M+H], Δ 6.5 ppm.

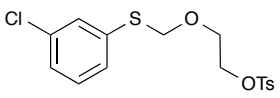
Synthesis of 2-(3-chlorobenzenesulfinyl)oxetane (2e)





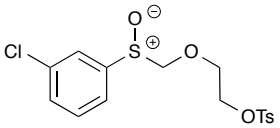
2-{[(3-Chlorophenyl)sulfanyl]methoxy}ethan-1-ol (4e)[2]

Sodium hydride (60% in mineral oil, 0.27 g, 6.87 mmol) was added to ethylene glycol (55 mL) at 0 ºC and stirred for 1 h 20 min. Sodium iodide (1.03 g, 6.87 mmol) was added followed by chloromethylsulfide **3e** (1.20 g, 6.25 mmol). The resulting solution was stirred at 0 ºC for 1 h then warmed to rt and stirred for a further 17 h. Water (30 mL) was added and the product was extracted with ethyl acetate (10 × 15 mL). The combined organic layers were dried ($MgSO_4$), filtered and the solvent removed under reduced pressure. Purification by flash chromatography (30% EtOAc/hexane) afforded alcohol **4e** (0.97 g, 71%) as a colourless oil. R_f = 0.10 (30% EtOAc/hexane). IR (film)/cm^{-1} 3381 (OH), 2929, 1576, 1562, 1460, 1400, 1307, 1052, 1017, 886, 823, 773, 677. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49–7.46 (1 H, m, Ar-H), 7.35 (1 H, ddd, *J* = 6.6, 1.9, 1.7 Hz, Ar-H), 7.26–7.19 (2 H, m, 2 × Ar-H), 5.07 (2 H, s, SCH_2O), 3.83–3.73 (4 H, m, OCH_2CH_2OH), 1.87 (1 H, br s, OH). ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.6 (C_q), 134.5 (C_q), 129.9 (Ar-C), 129.4 (Ar-C), 127.9 (Ar-C), 126.8 (Ar-C), 75.9 (SCH_2O), 69.9 (OCH_2), 61.4 (OCH_2). HRMS (CI) *m/z* Calculated $C_9H_{12}O_2S^{35}Cl$ [M+H]: 219.0247; Found: 219.0253 [M+H], Δ 2.7 ppm.



2-{[(3-Chlorophenyl)sulfanyl]methoxy}ethyl-4-methylbenzene-1-sulfonate (5e)[2]

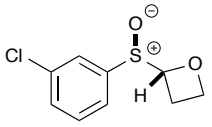
Triethylamine (1.66 mL, 11.83 mmol) and trimethylamine hydrochloride (38 mg, 0.39 mmol) were added to a solution of alcohol **4e** (0.86 g, 3.94 mmol) in toluene (18 mL) at 0 ºC and stirred for 30 min. 4-Toluenesulfonyl chloride (1.50 g, 7.87 mmol) was added portionwise. The mixture was stirred at 0 ºC for 20 min then allowed to warm to rt and stirred for a further 1 h 30 min. Water (20 mL) was added to the reaction and the product was extracted with EtOAc (5 × 15 mL). The combined organic layers were dried ($MgSO_4$), filtered and the solvent removed under reduced pressure. Purification by flash chromatography (20% EtOAc/hexane) afforded tosylate **5e** (1.35 g, 92%) as a colourless oil. R_f = 0.15 (20% EtOAc/hexane). IR (film)/cm^{-1} 2921, 1576, 1453, 1431, 1251, 1117, 1034, 954, 907, 735, 658. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (2 H, d, *J* = 8.2 Hz, 2 × Ts-H), 7.40 (1 H, br s, Ar-H), 7.33 (2 H, d, *J* = 8.2 Hz, 2 × Ts-H), 7.31–7.26 (1 H, m, Ar-H), 7.23–7.18 (2 H, m, 2 × Ar-H), 4.95 (2 H, s, SCH_2O), 4.24–4.18 (2 H, m, $TsOCH_2$), 3.84–3.78 (2 H, m, CH_2OCH_2), 2.44 (3 H, s, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.9 (Ts-C_q), 137.4 (Ar-C_q), 134.6 (Ar-C_q), 132.8 (Ts-C_q), 129.9 (Ar-C), 129.8 (2 × Ts-C), 129.4 (2 × Ar-C), 127.9 (2 × Ts-C), 126.9 (Ar-C), 75.8 (SCH_2O), 68.6 (OCH_2), 65.8 (OCH_2), 21.6 (CH_3). HRMS (APCI) *m/z* Calculated $C_{16}H_{21}{}^{35}ClNO_4S_2^+$ $[M+NH_4]^+$: 390.0595; Found: 390.0587 $[M+NH_4]^+$, Δ 2.1 ppm.

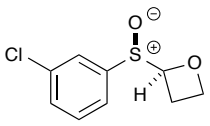


1-Chloro-3-({2-[(4-methylbenzenesulfonyl)oxy]ethoxy}methane sulfinyl)benzene (1e)

meta-Chloroperbenzoic acid (0.36 g, 2.09 mmol) was added to a solution of sulfide **4e** (0.71 g, 1.91 mmol) in dichloromethane (28 mL) at 0 ºC and the mixture stirred at 0 ºC for 2 h. The reaction was quenched with sat. aq. Na_2SO_3 (25 mL) and extracted with dichloromethane (5 × 20 mL). The combined organic layers were washed with 1 M NaOH (2 × 10 mL) and sat. aq. NH_4Cl (15 mL) then dried ($MgSO_4$), filtered and the solvent removed under reduced pressure. Purification by flash chromatography (70% EtOAc/hexane) afforded sulfoxide **1e** (0.50 g, 68%) as a white solid, m.p. = 81–82 ºC. R_f = 0.30 (70%

EtOAc/hexane). IR (film)/cm^{-1} 3060, 2957, 1597, 1588, 1457, 1406, 1352, 1249, 1186, 1172, 1121, 1041, 1015, 937, 915, 887, 775, 664. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (2 H, d, *J* = 8.3 Hz, 2 × Ts-H), 7.63–7.60 (1 H, m, Ar-H), 7.51–7.44 (3 H, m, 3 × Ar-H), 7.34 (2 H, d, *J* = 8.3 Hz, 2 × Ts-H), 4.49 (1 H, d, *J* = 10.6 Hz, SC*H*HO), 4.39 (1 H, d, *J* = 10.6 Hz, SCH*H*O), 4.23–3.99 (4 H, m, OCH_2CH_2O), 2.44 (3 H, s, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.1 (Ts-C_q), 142.6 (Ar-C_q), 135.7 (Ar-C_q), 132.6 (Ts-C_q), 131.5 (Ar-C), 130.5 (Ar-C), 129.9 (2 × Ts-C), 127.9 (2 × Ts-C), 124.3 (Ar-C), 122.5 (Ar-C), 92.1 (SCH_2O), 71.1 (OCH_2), 68.8 (OCH_2), 21.6 (CH_3). HRMS (ES) *m/z* Calculated $C_{17}H_{18}O_5S_2{}^{35}Cl$ [M+H]: 389.0284; Found 389.0300 [M+H], Δ 4.1 ppm.





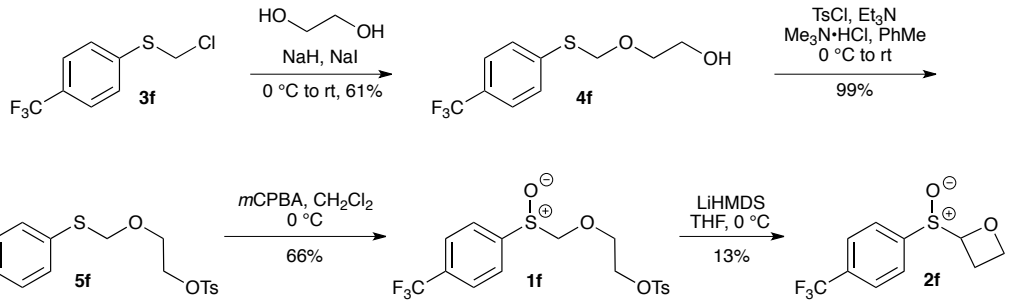
2-(3-Chlorobenzenesulfinyl)oxetane (2e)

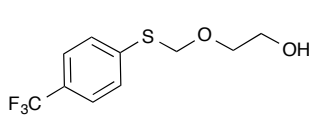
A solution of LiHMDS (1.0 M in THF, 5.04 mL, 5.04 mmol) was added dropwise to a solution of sulfoxide **1e** (1.78 g, 4.58 mmol) in THF (175 mL) at 0 ºC and stirred for 1 h 25 min. The reaction was quenched with sat. aq. NH_4Cl (50 mL) and extracted with CH_2Cl_2 (5 × 15 mL). The combined organics were dried ($MgSO_4$), filtered and the solvent removed under reduced pressure. Purification by flash chromatography (50% EtOAc/hexane) afforded the oxetane as a mixture of two diastereoisomers **2e-A** (0.45 g, 45%) followed by **2e-B** (0.37 g, 37%) both as off-white solids.

Major Diastereoisomer 2e-A: m.p. = 65–66 ºC. R_f = 0.17 (50% EtOAc/hexane). IR (film)/cm^{-1} 3025, 2970, 2937, 1756, 1738, 1438, 1336, 1228, 1217, 1208, 914, 650. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60–7.58 (1 H, m, Ar-H), 7.49–7.41 (3 H, m, 3 × Ar-H), 5.31 (1 H, dd, *J* = 7.5, 5.0 Hz, OCHS), 4.81 (1 H, ddd, *J* = 8.8, 6.7, 5.4 Hz, OCH*H*), 4.68 (1 H, ddd, *J* = 8.5, 6.2, 5.4 Hz, OC*H*H), 3.28–3.16 (1 H, m, OCH_2CH*H*), 2.74–2.62 (1 H, m, OCH_2C*H*H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.3 (C_q), 135.7 (C_q), 131.4 (Ar-C), 130.4 (Ar-C), 124.2 (Ar-C), 122.2 (Ar-C), 99.9 (SCHO), 71.3 (OCH_2), 19.5 (OCH_2*C*H_2). HRMS (ES) *m/z* Calculated $C_9H_{10}{}^{35}ClO_2S^+$ $[M+H]^+$: 217.0085; Found: 217.0079, $[M+H]^+$, Δ 2.8 ppm.

Minor Diastereoisomer 2e-B: m.p. = 65–66 ºC. R_f = 0.09 (50% EtOAc/hexane). IR (film)/cm^{-1} 3025, 2970, 2937, 1756, 1738, 1438, 1336, 1228, 1217, 1208, 914, 650. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69–7.67 (1 H, m, Ar-H), 7.55–7.44 (3 H, m, 3 × Ar-H), 5.42 (1 H, dd, *J* = 7.6, 5.6 Hz, OCHS), 4.67–4.59 (2 H, m, OCH_2), 3.10–2.99 (2 H, m, OCH_2C*H*$_2$). ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.1 (C_q), 135.5 (C_q), 131.5 (Ar-C), 130.2 (Ar-C), 125.2 (Ar-C), 123.2 (Ar-C), 97.0 (SCHO), 71.2 (OCH_2), 22.6 (OCH_2*C*H_2). HRMS (ES) *m/z* Calculated $C_9H_{10}{}^{35}ClO_2S^+$ $[M+H]^+$: 217.0085; Found: 217.0079, $[M+H]^+$, Δ 2.8 ppm.

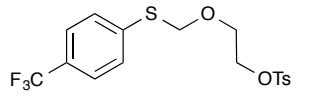
Synthesis of 2-[4-(trifluoromethyl)benzenesulfinyl]oxetane (2f)





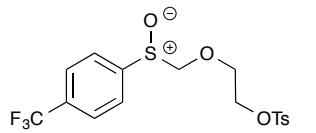
2-({[4-(Trifluoromethyl)phenyl]sulfanyl}methoxy)ethan-1-ol (4f)[2]

Sodium hydride (60% in mineral oil, 76 mg, 1.92 mmol) was added to ethylene glycol (16 mL) at 0 ºC and stirred for 40 min. Sodium iodide (0.29 g, 1.95 mmol) was added followed by chloromethyl sulfide **3f** (0.40 g, 1.77 mmol). The resulting solution was stirred at 0 ºC for 2 h then warmed to rt for 15 h. Water (20 mL) was added and the product was extracted with ethyl acetate (10 × 10 mL). The combined organic layers were dried ($MgSO_4$), filtered and the solvent removed under reduced pressure. Purification by flash chromatography (30% EtOAc/hexane) afforded alcohol **4f** (0.28 g, 61%) as a pale yellow oil. R_f = 0.10 (30% EtOAc/hexane). IR (film)/cm^{-1} 2927, 2296, 1607, 1403, 1321, 1162, 1060, 1013, 888, 825, 779, 677. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59–7.52 (4 H, m, 4 × Ar-H), 5.12 (2 H, s, SCH_2O), 3.83–3.75 (4 H, m, OCH_2CH_2OH), 2.03 (1 H, br s, OH). ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.0 (Ar-C_q), 128.7 (2 × Ar-C), 128.2 (C_q, q, J_{CF} = 32.9 Hz, *C*-CF_3), 125.5 (q, J_{CF} = 3.3 Hz, 2 × Ar-C), 123.9 (C_q, q, J_{CF} = 272.0 Hz, CF_3), 75.0 (SCH_2O), 69.9 (OCH_2), 61.2 (OCH_2). ^{19}F NMR (400 MHz, $CDCl_3$) δ –62.57 (CF_3). HRMS (CI) *m/z* Calculated $C_{10}H_{15}NF_3O_2S$ $[M+NH_4]^+$: 270.0770; Found: 270.0770 $[M+NH_4]^+$, Δ 0 ppm.



2-({[4-(Trifluoromethyl)phenyl]sulfanyl}methoxy)ethyl-4-methylbenzene-1-sulfonate (5f)[2]

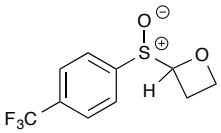
Triethylamine (0.33 mL, 2.37 mmol) and trimethylamine hydrochloride (7 mg, 0.07 mmol) were added to a solution of alcohol **4f** (0.20 g, 0.79 mmol) in toluene (4 mL) at 0 ºC and stirred for 30 min. 4-Toluenesulfonyl chloride (0.31 g, 1.61 mmol) was added portionwise. The mixture was stirred at 0 ºC for 20 min then allowed to warm to rt and stirred for a further 1 h 30 min. Water (20 mL) was added to the reaction and the product was extracted with EtOAc (5 × 10 mL). The combined organic layers were dried ($MgSO_4$), filtered and the solvent removed under reduced pressure. Purification by flash chromatography (20% EtOAc/hexane) afforded tosylate **5f** (0.32 g, 99%) as an off white solid; m.p. = 70–71 ºC. R_f = 0.15 (20% EtOAc/hexane). IR (film)/cm^{-1} 2926, 1603, 1317, 1161, 1097, 1083, 1028, 996, 909, 826, 811, 759, 683. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (2 H, d, *J* = 8.3 Hz, 2 × Ts-H), 7.52–7.48 (4 H, m, 4 × Ar-H), 7.33 (2 H, d, *J* = 8.3 Hz, 2 × Ts-H), 5.02 (2 H, s, SCH_2O), 4.26–4.29 (2 H, m, $TsOCH_2$), 3.86–3.81 (2 H, m, CH_2OCH_2), 2.45 (3 H, s, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.9 (Ts-C_q), 140.7 (Ar-C_q), 132.9 (Ts-C_q), 129.8 (2 x Ts-C), 129.0 (2 × Ar-C), 128.5 (C_q, q, J_{CF} = 32.1 Hz, *C*-CF_3), 127.9 (2 x Ts-C), 125.6 (q, J_{CF} = 3.5 Hz, 2 × Ar-C), 124.0 (C_q, q, J_{CF} = 272.6 Hz, CF_3), 75.1 (SCH_2O), 68.5 (OCH_2), 65.8 (OCH_2), 21.6 (CH_3). ^{19}F NMR (400 MHz, $CDCl_3$) δ –62.5 (CF_3). HRMS (APCI) *m/z* Calculated $C_{17}H_{21}F_3NO_4S_2^+$ $[M+NH_4]^+$: 424.0859; Found: 424.0854 $[M+NH_4]^+$, Δ 1.2 ppm.



1-({2-[(4-Methylbenzenesulfonyl)oxy]ethoxy}methanesulfinyl)-4-(trifluoromethyl)benzene (1f)

meta-Chloroperbenzoic acid (79 mg, 0.46 mmol) was added to a solution of sulfide **5f** (0.17 g, 0.42 mmol) in dichloromethane (6 mL) at 0 ºC and the mixture stirred at 0 ºC for 2 h 15 min. The reaction was quenched with sat. aq. Na_2SO_3 (10 mL) and extracted with dichloromethane (5 × 10 mL). The combined organic layers were washed with 1 M NaOH (2 × 10 mL) and sat. aq. NH_4Cl (10 mL) then dried ($MgSO_4$), filtered and the solvent removed under reduced pressure. Purification by flash chromatography (70% EtOAc/hexane)

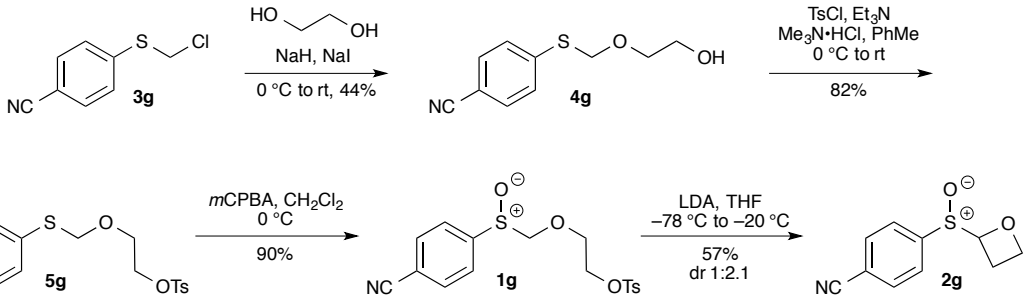
afforded sulfoxide **1f** (0.12 g, 66%) as a colourless oil. R_f = 0.21 (70% EtOAc/hexane). IR (film)/cm^{-1} 2914, 1599, 1452, 1404, 1359, 1322, 1170, 1102, 1037, 1013, 946, 811, 700, 659. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83–7.70 (6 H, m, 4 × Ar-H + 2 × Ts-H), 7.34 (2 H, d, *J* = 8.3 Hz, 2 × Ts-H), 4.53 (1 H, d, *J* = 10.4 Hz, SC*H*HO), 4.44 (1 H, d, *J* = 10.4 Hz, SCH*H*O), 4.22–4.00 (4 H, m, OCH_2CH_2O), 2.44 (3 H, s, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.2 (Ts-C_q), 133.6 (Ar-C_q), 132.6 (Ts-C_q), 131.9 (C_q, q, J_{CF} = 31.2 Hz, *C*-CF_3), 129.9 (2 × Ts-C), 127.9 (2 × Ts-C), 126.3 (q, J_{CF} = 3.6 Hz, 2 × Ar-C), 124.9 (2 × Ar-C), 123.5 (C_q, q, J_{CF} = 248.9 Hz, CF_3), 91.8 (SCH_2O), 71.3 (OCH_2), 68.5 (OCH_2), 21.6 (CH_3). ^{19}F NMR (400 MHz, $CDCl_3$) δ –62.5 (CF_3). HRMS (ES) *m/z* Calculated $C_{17}H_{17}O_5F_3NaS_2$ [M+Na]: 445.0367; Found 445.0373 [M+Na], Δ 1.3 ppm.

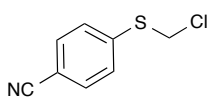


2-[4-(Trifluoromethyl)benzenesulfinyl]oxetane (2f)

A solution of LiHMDS (1 M in THF, 0.21 mL, 0.21 mmol) was added dropwise to a solution of sulfoxide **1f** (74 mg, 0.17 mmol) in THF (7 mL) at 0 ºC and stirred for 1 h 45 min. The reaction was quenched with sat. aq. NH_4Cl (20 mL) and extracted with CH_2Cl_2 (5 × 10 mL). The combined organics were dried ($MgSO_4$), filtered and the solvent removed under reduced pressure. Purification by flash chromatography (50% EtOAc/hexane) afforded oxetane **2f** (6 mg, 13%) as a colourless oil. Only one diastereoisomer isolated. R_f = 0.22 (50% EtOAc/hexane). IR (film)/cm^{-1} 2929, 1730, 1605, 1402, 1321, 1169, 1128, 1102, 1061, 1014, 952, 836, 698, 666. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (2 H, d, *J* = 7.7 Hz, 2 × Ar), 7.72 (2 H, d, *J* = 7.7 Hz, 2 × Ar), 5.32 (1 H, dd, *J* = 7.4, 5.2 Hz, SCHO), 4.84 (1 H, ddd, *J* = 8.8, 6.8, 5.4 Hz, OCH*H*), 4.70 (1 H, ddd, *J* = 8.8, 6.2, 5.4, Hz, OC*H*H), 3.28–3.18 (1 H, m, OCH_2CHH), 2.75–2.64 (1 H, m, OCH_2CHH). ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.7 (Ar-C_q), 133.2 (C_q, q, J_{CF} = 32.3 Hz, *C*-CF_3), 126.2 (q, J_{CF} = 4.2 Hz, 2 × Ar-C), 124.7 (2 × Ar-C), 123.5 (q, J_{CF} = 274.4 Hz, CF_3), 99.9 (OCHS), 71.4 (OCH_2), 19.8 (OCH_2CH_2). ^{19}F NMR (400 MHz, $CDCl_3$) δ –62.9 (CF_3). HRMS (EI) *m/z* Calculated $C_{10}H_9F_3O_2S$ [M]: 250.0275; Found 250.0287 [M], Δ 4.8 ppm.

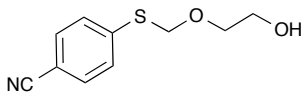
Synthesis of 4-(oxetane-2-sulfinyl)benzonitrile (2g)





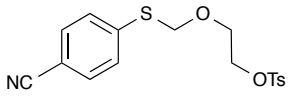
4-4-[(Chloromethyl)sulfanyl]benzonitrile (3g)

N-Chlorosuccinimide (2.46 g, 18.42 mmol) was added portionwise to a solution of 4-(methylthio)benzonitrile (2.50 g, 16.75 mmol) in dichloroethane (25 mL). The reaction was stirred at rt for 18 h then filtered through a short pad of silica, eluting with dichloromethane (50 mL). The solvent was removed under reduced pressure to afford chloromethyl sulfide **3g** (3.00 g, 97%) as an off white solid, which was used without further purification; m.p. = 146–147 ºC. R_f = 0.51 (40% EtOAc/hexane). IR(film)/cm^{-1} 3034, 2224 (CN), 1590, 1486, 1403, 1224, 1140, 1123, 1085, 1016, 831, 811, 736. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67–7.65 (2 H, d, *J* = 8.6 Hz, 2 × Ar-H), 7.55–7.52 (2 H, d, *J* = 8.6 Hz, 2 × Ar-H), 5.04 (2 H, s, SCH_2Cl). ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.6 (Ar-C_q), 132.6 (2 × Ar-C), 128.4 (2 × Ar-C), 118.4 (CN), 110.5 (Ar-C_q), 47.8 (SCH_2Cl). HRMS (EI) *m/z* Calculated for $C_8H_6NS_2{}^{35}Cl$ [M]: 182.9909; Found: 182.9908 [M], Δ 0.5 ppm. The observed data (^{1}H and ^{13}C) is consistent with that reported in the literature.[3]



4-{[(2-Hydroxyethoxy)methyl]sulfanyl}benzonitrile (4g)

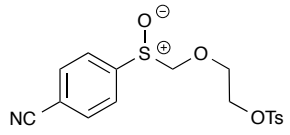
Potassium *t*-butoxide (1.01 g, 9.00 mmol) was added to a solution of ethylene glycol (4.6 mL, 82.50 mmol) in DMF (67 mL) at 0 ºC and stirred for 1 h. Potassium iodide (1.49 g, 8.98 mmol) was added followed by chloromethylsulfide **3g** (1.50 g, 8.17 mmol). DMF (2 mL) was added to aid solubility. The resulting solution was stirred at 0 ºC for 1 h then warmed to rt for 14 h. Water (100 mL) was added and the product was extracted with ethyl acetate (7 × 20 mL). The combined organic layers were dried ($MgSO_4$), filtered and the solvent removed under reduced pressure. Purification by flash chromatography (40% EtOAc/hexane) afforded alcohol **4g** (0.76 g, 44%) as a colourless oil. R_f = 0.09 (40% EtOAc/hexane). IR (film)/cm^{-1} 3411 (OH), 2925, 2226 (CN), 1592, 1457, 1432, 1402, 1316, 1303, 1273, 1181, 1106, 1085, 1058, 1016, 975, 888, 822, 778, 760, 680. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (2 H, d, *J* = 8.7 Hz, 2 × Ar-H), 7.54 (2 H, d, *J* = 8.7 Hz, 2 × Ar-H), 5.16 (2 H, s, SCH_2O), 3.83–3.76 (4 H, m, OCH_2CH_2OH), 1.77 (1 H, br s, OH). ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.4 (Ar-C_q), 132.3 (2 × Ar-C), 128.4 (2 × Ar-C), 118.7 (CN), 109.5 (Ar-C_q), 74.7 (SCH_2O), 70.1 (OCH_2), 61.5 (OCH_2). HRMS (CI) *m/z* Calculated for $C_{10}H_{12}NO_2S^+$ $[M+H]^+$: 210.0583; Found: 210.0579 $[M+H]^+$, Δ 1.9 ppm.



2-{[(4-Cyanophenyl)sulfanyl]methoxyethyl-4-methylbenzene-1-sulfonate (5g)

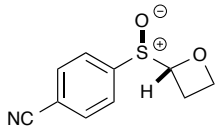
Triethylamine (2.52 mL, 17.93 mmol) and trimethylamine hydrochloride (57 mg, 0.60 mmol) were added to a solution of alcohol **4g** (1.26 g, 6.03 mmol) in toluene (20 mL) at 0 ºC and stirred for 30 min. 4-Toluenesulfonyl chloride (2.30 g, 12.06 mmol) was added portionwise. The mixture was stirred at 0 ºC for 35 min then allowed to warm to rt slowly and stirred for a further 3 h. Water (75 mL) was added to the reaction and the product was extracted with EtOAc (4 × 25 mL). The combined organic layers were washed with brine (25 mL) then dried ($MgSO_4$), filtered and the solvent removed under reduced pressure. Purification by flash chromatography (30% EtOAc/hexane) afforded tosylate **5g** (1.79 g, 82%) as an off white solid; m.p. = 86–87 ºC. R_f = 0.18 (30% EtOAc/hexane). IR (film)/cm^{-1} 2221 (CN), 1590, 1487, 1430, 1317, 1292, 1240, 1188, 1171, 1118, 1081, 1029, 995, 907, 822, 761, 683. ^{1}H NMR (400 MHz,

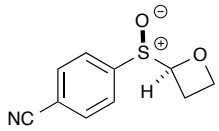
$CDCl_3$) δ 7.77 (2 H, d, *J* = 8.4 Hz, 2 × Ts-H), 7.54–7.46 (4 H, m, 4 × Ar-H), 7.34 (2 H, d, *J* = 8.4 Hz, 2 × Ts-H), 5.04 (2 H, s, SCH_2O), 4.24–4.20 (2 H, m, $TsOCH_2$), 3.85–3.82 (2 H, m, CH_2OCH_2), 2.46 (3 H, s, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.0 (Ts-C_q), 143.0 (Ar-C_q), 132.8 (Ts-C_q), 132.3 (2 × Ar-C), 129.8 (2 × Ts-C), 128.5 (2 × Ar-C), 127.9 (2 × Ts-C), 118.6 (CN), 109.5 (Ar-C_q), 74.5 (SCH_2O), 68.4 (OCH_2), 65.9 (OCH_2), 21.7 (CH_3). HRMS (NSI) *m/z* Calculated for $C_{17}H_{21}N_2O_4S_2^+$ $[M+NH_4]^+$: 381.0937; Found: 381.0940 $[M+NH_4]^+$, Δ 0.8 ppm.



4-({2-[(4-Methylbenzenesulfonyl)oxy]ethoxy)methanesulfinyl) benzonitrile (1g)

meta-Chloroperbenzoic acid (0.26 g, 1.51 mmol) was added to a solution of sulfide **5g** (0.50 g, 1.38 mmol) in dichloromethane (20 mL) at 0 ºC and the mixture stirred at 0 ºC for 2 h 30 min. The reaction was quenched with sat. aq. Na_2SO_3 (30 mL) and extracted with dichloromethane (5 × 15 mL). The combined organic layers were washed with 1 M NaOH (2 × 15 mL) and sat. aq. NH_4Cl (15 mL) then dried ($MgSO_4$), filtered and the solvent removed under reduced pressure. Purification by flash chromatography (70% EtOAc/hexane) afforded sulfoxide **1g** (0.47 g, 90%) as pale yellow solid, m.p. = 85–87 ºC. R_f = 0.20 (70% EtOAc/hexane). IR (film)/cm^{-1} 2929, 2231, 1596, 1487, 1445, 1397, 1351, 1309, 1295, 1247, 1189, 1120, 1080, 1042, 939, 834, 811, 775, 719, 704, 663. ^1H NMR (400 MHz, $CDCl_3$) δ 7.86–7.73 (6 H, m, 4 × Ar-H + 2 × Ts-H), 7.37 (2 H, d, *J* = 8.4 Hz, 2 × Ts-H), 4.56 (1 H, d, *J* = 10.6 Hz, SC*H*HO), 4.47 (1 H, d, *J* = 10.6 Hz, SCH*H*O), 4.24–4.03 (4 H, m, OCH_2CH_2O), 2.47 (3 H, s, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.5 (Ar-C_q), 145.2 (Ts-C_q), 132.9 (2 × Ar-C), 132.9 (Ts-C_q), 130.0 (2 × Ts-C), 127.9 (2 × Ts-C), 125.2 (2 × Ar-C), 117.7 (CN), 115.2 (Ar-C_q), 91.4 (SCH_2O), 71.4 (OCH_2), 68.5 (OCH_2), 21.7 (CH_3). HRMS (ES) *m/z* Calculated for $C_{17}H_{18}NO_5S_2^+$ $[M+H]^+$: 380.0621; Found: 380.0624 $[M+H]^+$, Δ 0.8 ppm.





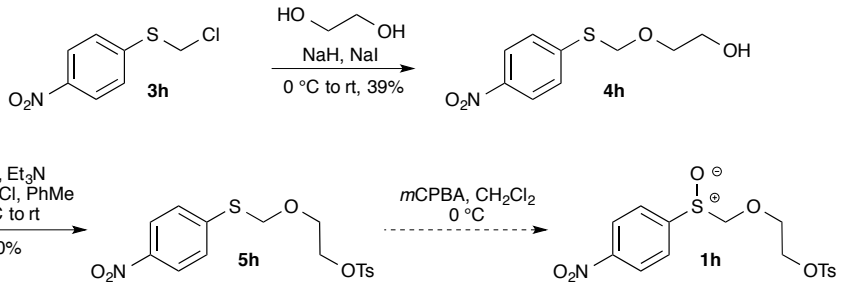
4-(Oxetane-2-sulfinyl)benzonitrile (2g)

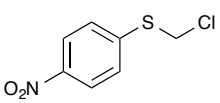
A solution of LDA (1 M in THF, 0.29 mL, 0.29 mmol) was added dropwise to a solution of sulfoxide **1g** (72.2 mg, 0.190 mmol) in THF (7.6 mL) at –78 ºC and stirred for 15 min. The reaction flask was transferred to a –20 ºC bath and stirred for a further 20 min. The reaction was quenched with sat. aq. NH_4Cl (10 mL) and extracted with CH_2Cl_2 (5 × 10 mL). The combined organics were dried ($MgSO_4$), filtered and the solvent removed under reduced pressure. Purification by flash chromatography (60-70% EtOAc/pentane) afforded the oxetane as a mixture of two diastereoisomers, **2g-A** (7.2 mg, 18%) followed by **2g-B** (19.5 mg, 50%); both as colourless oils.

Minor Diastereoisomer 2g-A: R_f = 0.45 (70% EtOAc/pentane). IR (film)/cm^{-1} 3090, 2967, 2881, 2229, 1731, 1589, 1483, 1397, 1338, 1245, 1177, 1144, 1073, 1015, 953, 828, 778, 715, 663. ^1H NMR (400 MHz, $CDCl_3$) δ 7.82 (2 H, d, *J* = 8.5 Hz, 2 × Ar-H), 7.72 (2 H, d, *J* = 8.5 Hz, 2 × Ar-H), 5.31 (1 H, dd, *J* = 7.3, 5.0 Hz, OCHS), 4.84 (1 H, ddd, *J* = 8.8, 7.0, 5.5 Hz, OCH*H*), 4.71 (1 H, ddd, *J* = 8.5, 5.9, 5.5 Hz, OC*H*H), 3.25–3.15 (1 H, m, OCH_2CHH), 2.78–2.68 (1 H, m, OCH_2CHH). ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.2 (C_q), 132.8 (2 × Ar-C), 124.9 (2 × Ar-C), 117.6 (CN), 115.0 (C_q), 99.9 (OCHS), 71.5 (OCH_2), 20.1 (OCH_2CH_2). HRMS (ASAP) *m/z* Calculated for $C_{10}H_{10}NO_2S$ [M+H]: 208.0432; Found: 208.0432 [M], Δ 0 ppm.

Major Diastereoisomer 2g-B: R_f = 0.13 (70% EtOAc/pentane). IR (film)/cm^{-1} 3090, 2967, 2881, 2229, 1731, 1589, 1483, 1397, 1338, 1245, 1177, 1144, 1073, 1015, 953, 828, 778, 715, 663. ^1H NMR (400 MHz, $CDCl_3$) δ 7.83 (2 H, d, *J* = 8.3 Hz, 2 × Ar-H), 7.78 (2 H, d, *J* = 8.3 Hz, 2 × Ar-H), 5.44 (1 H, dd, *J* = 7.6, 5.4 Hz, OCHS), 4.66–4.60 (2 H, m, OCH_2), 3.18–3.02 (2 H, m, OCH_2CH_2). ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.9 (C_q), 132.5 (2 × Ar-C), 125.8 (2 × Ar-C), 117.8 (CN), 115.0 (C_q), 97.1 (OCHS), 71.5 (OCH_2), 22.7 (OCH_2CH_2). HRMS (ASAP) *m/z* Calculated for $C_{10}H_{10}NO_2S$ [M+H]: 208.0432; Found: 208.0432 [M], Δ 0 ppm.

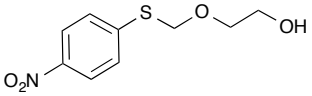
Synthesis of 2-{[(4-nitrophenyl)sulfanyl]methoxy}ethyl-4-methylbenzene-1-sulfonate (5h)





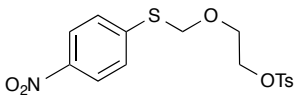
1-[(Chloromethyl)sulfanyl]-4-nitrobenzene (3h)

N-Chlorosuccinimide (2.17 g, 16.25 mmol) was added portionwise to a solution of 4-nitrothioanisole (2.50 g, 14.78 mmol) in dichloroethane (25 mL). The reaction was stirred at rt for 17 h then filtered through a short pad of silica, eluting with dichloromethane (25 mL). The solvent was removed under reduced pressure to afford chloromethyl sulfide **82k** (3.04 g, quant) as a pale yellow solid, which was used without further purification; m.p. = 58–59 ºC (lit m.p. 63–64 ºC).[4] R_f = 0.81 (100% EtOAc). IR (film)/cm^{-1} 3098, 3022, 2964, 2829, 1593, 1575, 1500 (NO_2), 1479, 1401, 1319 (NO_2), 1235, 1186, 1110, 1089, 964, 836, 735, 720. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.23 (2 H, d, *J* = 9.0 Hz, 2 × Ar-H), 7.57 (2 H, d, *J* = 9.0 Hz, 2 × Ar-H), 5.07 (2 H, s, SCH_2Cl). ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.7 (C_q), 141.3 (C_q), 127.5 (2 × Ar-C), 123.9 (2 × Ar-C), 47.1 (SCH_2Cl). HRMS (CI) *m/z* Calculated for $C_7H_7{}^{35}ClNO_2S^+$ $[M+H]^+$: 203.9881; Found: 203.9879 $[M+H]^+$, Δ 1.0 ppm. The observed data (^{1}H) was consistent with that reported in the literature.[5]



2-{[(4-Nitrophenyl)sulfanyl]methoxy}ethan-1-ol (4h)

Sodium hydride (60% in mineral oil, 0.11 g, 2.70 mmol) was added to ethylene glycol (25 mL) at 0 ºC and stirred for 1 h 30 min. Sodium iodide (0.41 g, 2.71 mmol) was added followed by chloromethyl sulfide **3h** (0.50 g, 2.46 mmol). DMF (1 mL) was added to aid solubility. The resulting solution was stirred at 0 ºC for 30 min then warmed to rt for 15 h 30 min. Water (50 mL) was added and the product was extracted with ethyl acetate (10 × 30 mL). The combined organic layers were dried ($MgSO_4$), filtered and the solvent removed under reduced pressure. Purification by flash chromatography (50% EtOAc/hexane) afforded alcohol **4h** (0.22 g, 39%) as a pale yellow solid; m.p. = 40–41 ºC. R_f = 0.15 (50% EtOAc/hexane). IR (film)/cm^{-1} 2923, 1595, 1578, 1510 (NO), 1479, 1338 (NO), 1109, 1080, 1062, 888, 853, 742, 683. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 (2 H, d, *J* = 8.9 Hz, 2 × Ar-H), 7.57 (2 H, d, *J* = 8.9 Hz, 2 × Ar-H), 5.18 (2 H, s, SCH_2O), 3.82–3.75 (4 H, m, OCH_2CH_2OH), 1.84 (1 H, br s, OH). ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.0 (C_q), 145.8 (C_q), 127.8 (2 × Ar-C), 124.0 (2 × Ar-C), 74.5 (SCH_2O), 70.2 (OCH_2), 61.5 (OCH_2). HRMS (APCI) *m/z* Calculated for $C_9H_{15}N_2O_4S^+$ $[M+NH_4]^+$: 247.0747; Found: 247.0749 $[M+NH_4]^+$, Δ 0.8 ppm.

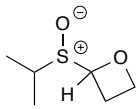


2-{[(4-Nitrophenyl)sulfanyl]methoxy}ethyl-4-methylbenzene-1-sulfonate (5h)

Triethylamine (0.24 mL, 1.71 mmol) and trimethylamine hydrochloride (6 mg, 0.06 mmol) were added to a solution of alcohol **4h** (0.13 g, 0.57 mmol) in toluene (2 mL) at 0 ºC and stirred for 30 min. 4-Toluenesulfonyl chloride (0.22 g, 1.15 mmol) was added portionwise. The mixture was stirred at 0 ºC for 30 min then allowed to warm to rt slowly over 30 min and stirred for a further 1 h 30 min. Water (20 mL) was added to the reaction and the product was extracted with EtOAc (4 × 20 mL). The combined organic layers were washed with brine (25 mL) and H_2O (20 mL) then dried ($MgSO_4$), filtered and the solvent removed under reduced pressure. Purification by flash chromatography (40% EtOAc/hexane) afforded tosylate **5h** (0.19 g, 90%) as a white solid; m.p. = 82–83 ºC. R_f = 0.29 (40% EtOAc/hexane). IR (film)/cm^{-1} 2925, 1593, 1577, 1505 (NO), 1454, 1345 (NO), 1332, 1280, 1188, 1172, 1103, 1085, 1013, 946, 852, 837, 810, 781, 739, 682. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (2 H, d, *J* = 8.7 Hz, 2 × Ar-H), 7.78 (2 H, d, *J* = 8.2 Hz, 2 × Ts-H), 7.50 (2 H, d, *J* = 8.7 Hz, 2 × Ar-H), 7.34 (2 H, d, *J* =

8.2 Hz, 2 × Ts-H), 5.08 (2 H, s, SCH_2O), 4.25–4.21 (2 H, m, $TsOCH_2$), 3.88–3.84 (2 H, m, CH_2OCH_2), 2.46 (3 H, s, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.9 (Ar-C_q), 145.6 (Ar-C_q), 145.1 (Ts-C_q), 132.8 (Ts-C_q), 129.8 (2 × Ts-C), 128.0 (2 × Ts-C), 127.9 (2 × Ar-C), 123.9 (2 × Ar-C), 74.3 (SCH_2O), 68.3 ($TsOCH_2$), 66.0 (CH_2OCH_2), 21.6 (CH_3). HRMS (NSI) *m/z* Calculated for $C_{16}H_{21}N_2O_6S_2^+$ $[M+NH_4]^+$: 401.0836; Found: 401.0834 $[M+NH_4]^+$, Δ 0.5 ppm.

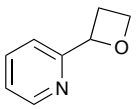
Sulfoxide-magnesium exchange on oxetane 2e to give 6



2-(Propane-2-sulfinyl)oxetane (6)

*i*PrMgCl (2 M in Et_2O, 0.13 mL, 0.26 mmol) was added dropwise to a solution of 2-(3-chlorobenzenesulfinyl)oxetane **2e** (28 mg, 0.13 mmol) in THF (1.5 mL) at –78 ºC and stirred for 5 min. The reaction was quenched with sat. aq. NH_4Cl (10 mL) and extracted with CH_2Cl_2 (5 × 10 mL). The combined organics were dried ($MgSO_4$), filtered and the solvent removed under reduced pressure. Purification by flash chromatography (100% EtOAc) afforded oxetane **6** (16 mg, 86%) as a colourless oil. R_f = 0.14 (100% EtOAc). IR (film)/cm^{-1} 2967, 1646, 1471, 1368, 1241, 1051, 1009, 975, 916, 764. ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.57 (1 H, dd, *J* = 8.1, 6.0 Hz, SCHO), 4.84–4.77 (1 H, m, OCH*H*), 4.76–4.70 (1 H, m, OC*H*H), 3.30–3.22 (1 H, m, OCH_2CH*H*), 3.19 (1 H, sept, *J* = 7.0 Hz, (SC*H*$(CH_3)_2$), 3.06–2.95 (1 H, m, OCH_2C*H*H), 1.42 (3 H, d, *J* = 7.0 Hz, CH_3), 1.14 (3 H, d, *J* = 7.0 Hz, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$) δ 91.3 (SCHO), 71.6 (OCH_2), 46.0 (S*C*H$(CH_3)_2$), 22.2 (OCH_2*C*H_2), 16.7 (CH_3), 15.9 (CH_3).

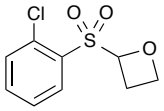
Sulfoxide-magnesium exchange on oxetane 2c to give 7



2-(Oxetan-2-yl)pyridine (7)

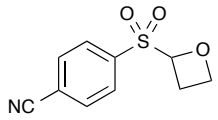
*i*PrMgCl·LiCl (1.3 M in THF, 0.35 mL, 0.46 mmol) was added dropwise to a solution of 2-(oxetan-2-ylsulfinyl)pyridine **2c** (41 mg, 0.23 mmol) in THF (4.5 mL) at –78 ºC and stirred for 5 min. 3-Pentanone (75 µL, 0.69 mmol) was added and the reaction stirred at –78 ºC for a further 5 min. Reaction quenched with sat. aq. NH_4Cl (10 mL) and extracted with CH_2Cl_2 (5 × 10 mL). Combined organics were dried ($MgSO_4$), filtered and the solvent removed under reduced pressure. Purification by flash chromatography (100% EtOAc) afforded oxetane **7** (18 mg, 60%) as a colourless oil. R_f = 0.48 (100% EtOAc). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.60 (1 H, d, *J* = 4.7 Hz, Py-H), 7.78 (1 H, ddd, *J* = 9.4, 7.7, 1.6 Hz, Py-H), 7.62 (1 H, d, *J* = 7.7 Hz, Py-H), 7.23 (1 H, dd, *J* = 7.2, 4.7 Hz, Py-H), 5.87 (1 H, t, *J* = 7.5 Hz, OCHPy), 4.91–4.85 (1 H, m, OCH*H*), 4.72 (1 H, dt, *J* = 9.2, 5.9 Hz, OC*H*H), 3.19–3.08 (1 H, m, OCH_2CH*H*), 2.80–2.69 (1 H, m, OCH_2C*H*H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.4 (C_q), 149.3 (Py-C), 136.8 (Py-C), 122.5 (Py-C), 119.8 (Py-C), 83.0 (OCHPy), 69.0 (OCH_2), 28.9 (OCH_2*C*H_2).

Formation of sulfonyl-oxetanes 8d and 8g



2-((2-Chlorophenyl)sulfonyl)oxetane (8d)

meta-Chloroperbenzoic acid (25.9 mg, 0.15 mmol) was added portionwise to a solution of sulfide **2d-B** (21.7 mg, 0.10 mmol) in dichloromethane (1.0 mL) at 0 ºC and the mixture stirred for 1 h at 0 ºC followed by 1 h at rt. The reaction was quenched with sat. aq. Na_2SO_3 (1.0 mL) and extracted with dichloromethane (5 × 3 mL). The combined organic layers were dried (Na_2SO_4), filtered and the solvent removed under reduced pressure. Purification by flash chromatography (20% EtOAc/pentane) afforded sulfone **8d** (21.2 mg, 91%) as a colourless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20 (dd, *J* = 7.9, 1.7 Hz, 1H, Ar-H), 7.61-7.51 (m, 2H, 2 × Ar-H), 7.48 (ddd, *J* = 7.9, 7.0, 1.5 Hz, 1H, Ar-H), 5.94 (dd, *J* = 7.9, 5.0 Hz, 1H, OCHS), 4.95 (ddd, *J* = 8.5, 7.6, 5.5 Hz, 1H, OC*H*H), 4.69 (dt, *J* = 8.5, 5.5 Hz, 1H, OC*H*H), 3.30-3.13 (m, 2H, OCH_2CH_2). All other data was consistent with that previously reported in the literature.[2]



4-(Oxetan-2-ylsulfonyl)benzonitrile (8g)

meta-Chloroperbenzoic acid (19.9 mg, 0.12 mmol) was added portionwise to a solution of sulfide **2g-B** (15.9 mg, 0.077 mmol) in dichloromethane (0.8 mL) at 0 ºC and the mixture stirred for 1 h at 0 ºC. The reaction was quenched with sat. aq. Na_2SO_3 (1.0 mL) and extracted with dichloromethane (5 × 3 mL). The combined organic layers were dried (Na_2SO_4), filtered and the solvent removed under reduced pressure. Purification by flash chromatography (70% Et_2O/pentane) afforded sulfone **8g** (10.8 mg, 63%) as a colourless oil. R_f = 0.26 (70% Et_2O/pentane). IR (film)/cm^{-1} 3095, 2977, 2905, 2235, 1443, 1396, 1322, 1285, 1150, 1086, 1031, 983, 908, 842, 726, 689. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14-8.04 (m, 2H, 2 ×Ar-H), 7.91-7.83 (m, 2H, 2 × Ar-H), 5.39 (dd, *J* = 7.3, 5.8 Hz, 1H, OCHS), 4.86 (app. td, *J* = 8.0, 5.5 Hz, 1H, OC*H*H), 4.72-4.65 (m, 1H, OC*H*H), 3.25-3.07 (m, 2H, OCH_2CH_2). ^{13}C NMR (101 MHz, $CDCl_3$) δ 139.8 (C_q), 132.9 (2 × Ar-C), 130.2 (2 × Ar-C), 118.1 (CN), 117.1 (C_q), 94.2 (OCHS), 71.9 (OCH_2), 22.1 (OCH_2CH_2). HRMS (NSI) *m/z* Calculated for $C_{10}H_9NaO_3NS^+$ $[M+Na]^+$: 246.0195; Found: 246.0197 $[M+Na]^+$, Δ 0.7 ppm.

References

1. K. F. Morgan, I. A. Hollingsworth and J. A. Bull, *Chem. Commun.*, 2014, **50**, 5203.
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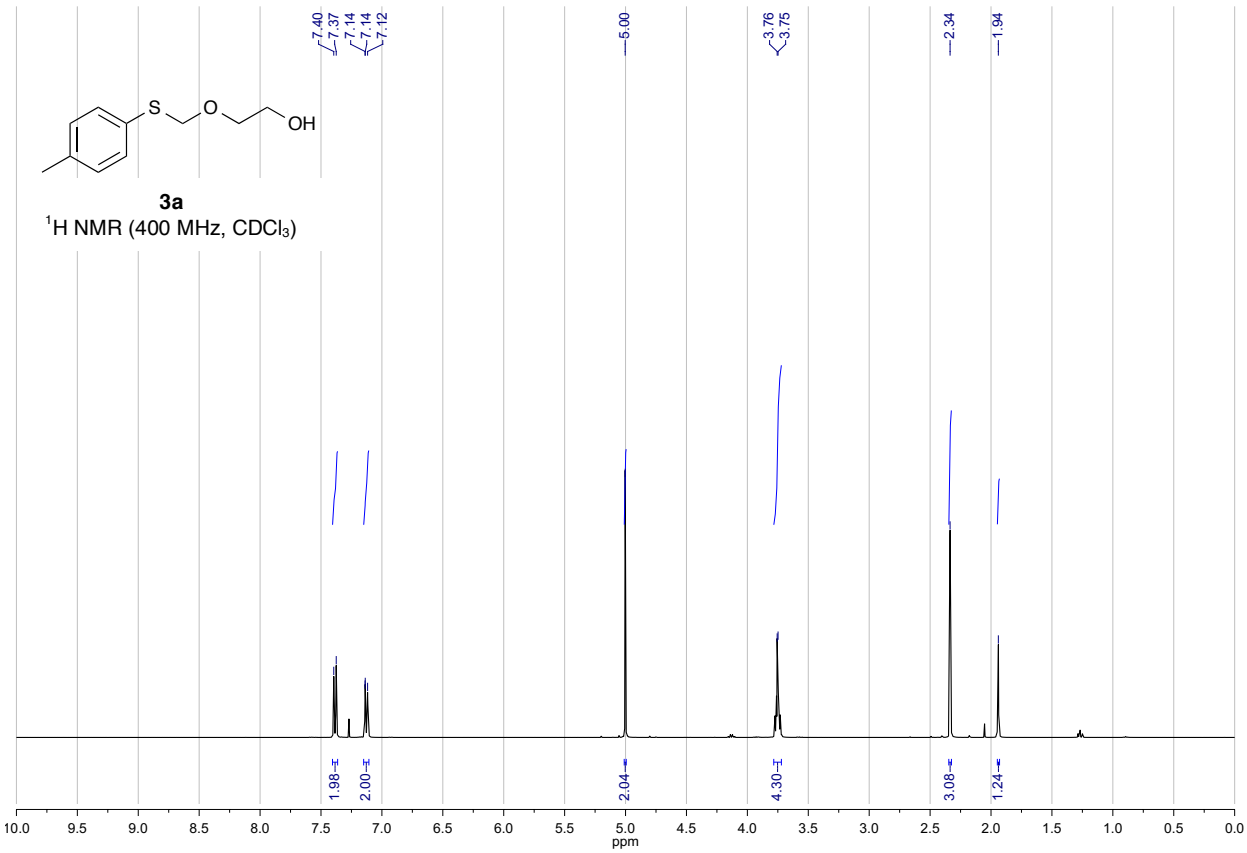
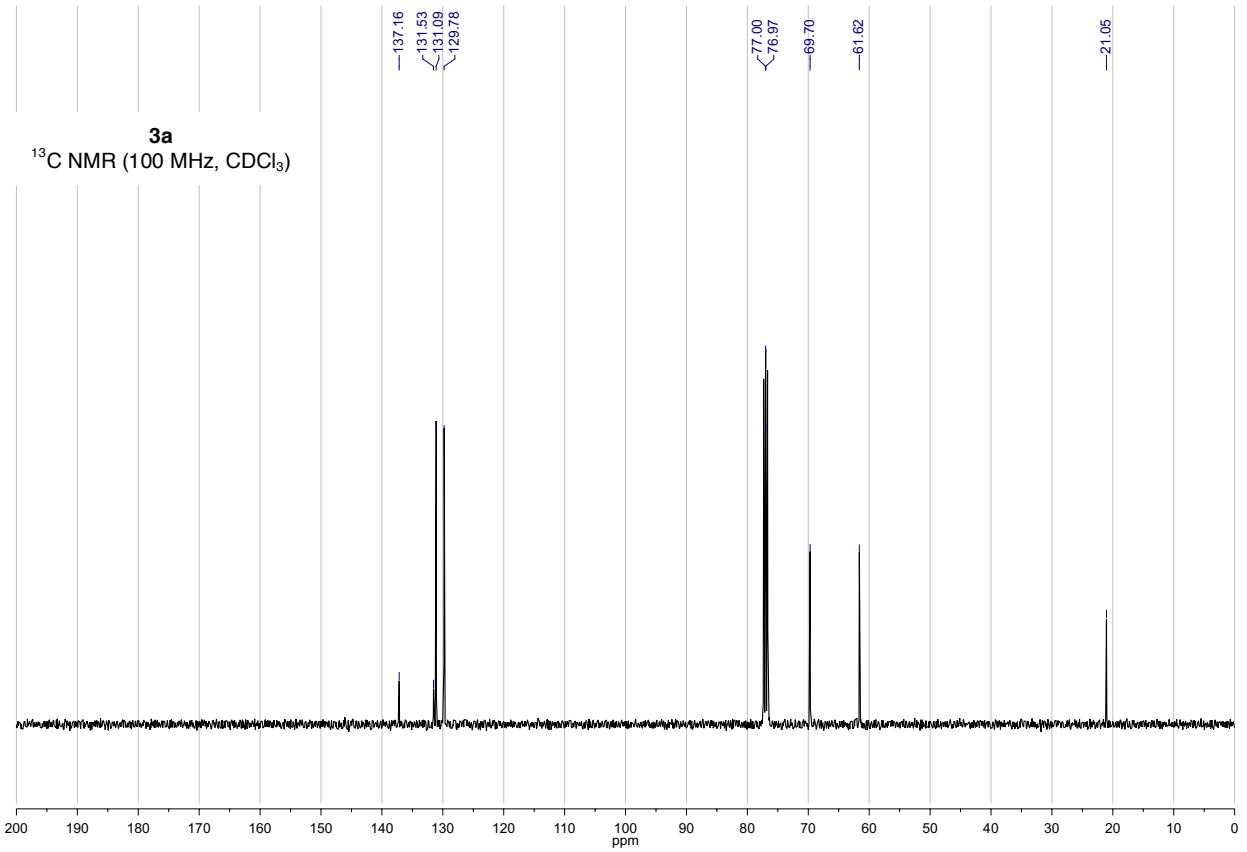
5. Y. Tamura, H. Annoura, M. Fuji, M. Okura and H. Ishibashi, *Chem. Pharm. Bull*, 1986, **34**, 540.

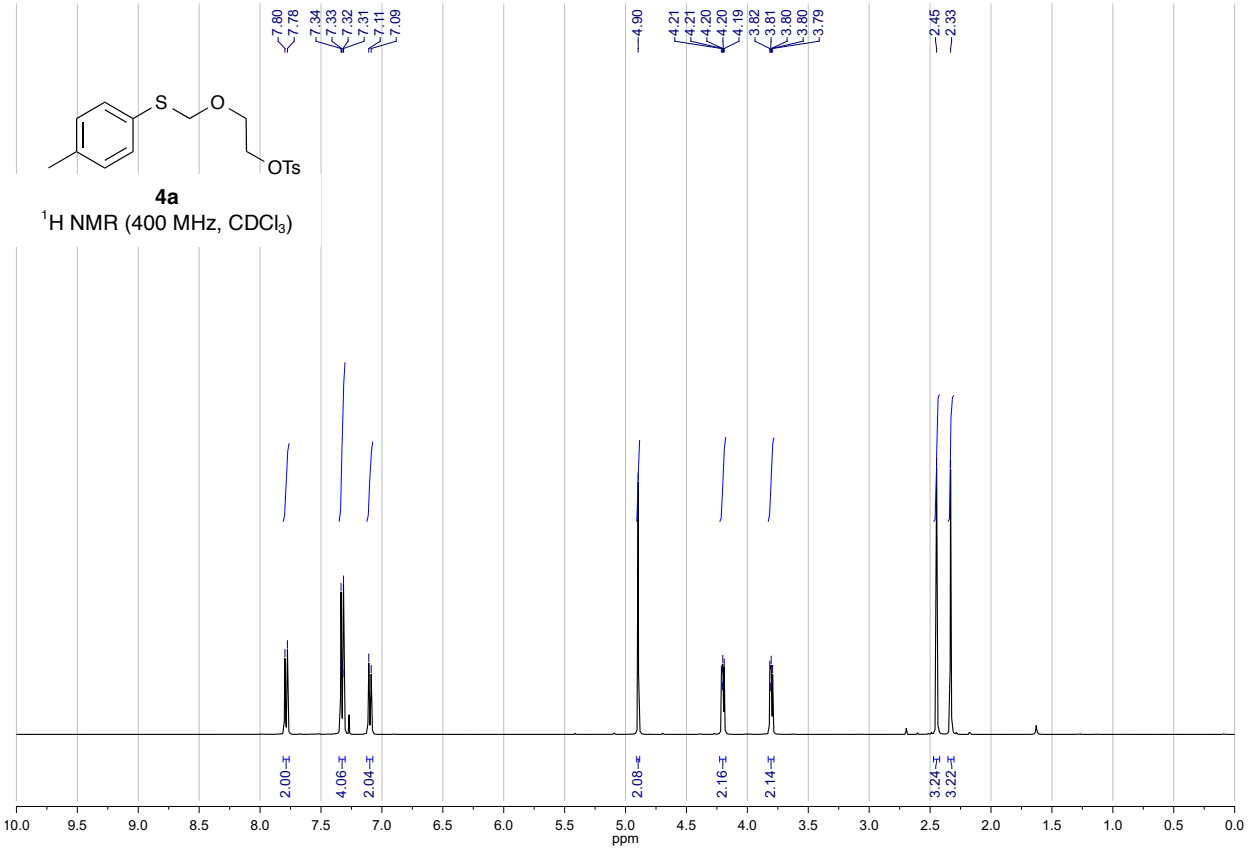
^{1}H and ^{13}C NMR spectra of selected compounds



3a
^{1}H NMR (400 MHz, $CDCl_3$)

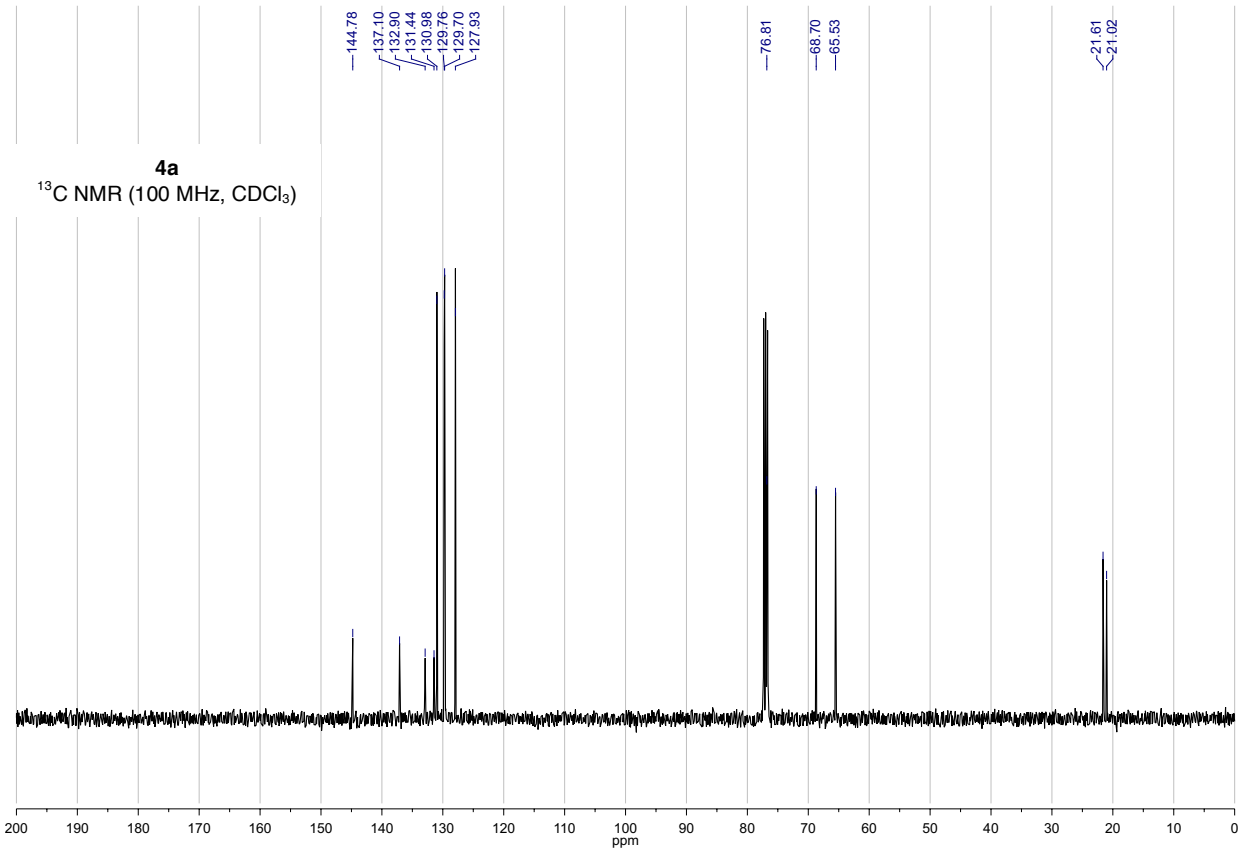


3a
^{13}C NMR (100 MHz, $CDCl_3$)



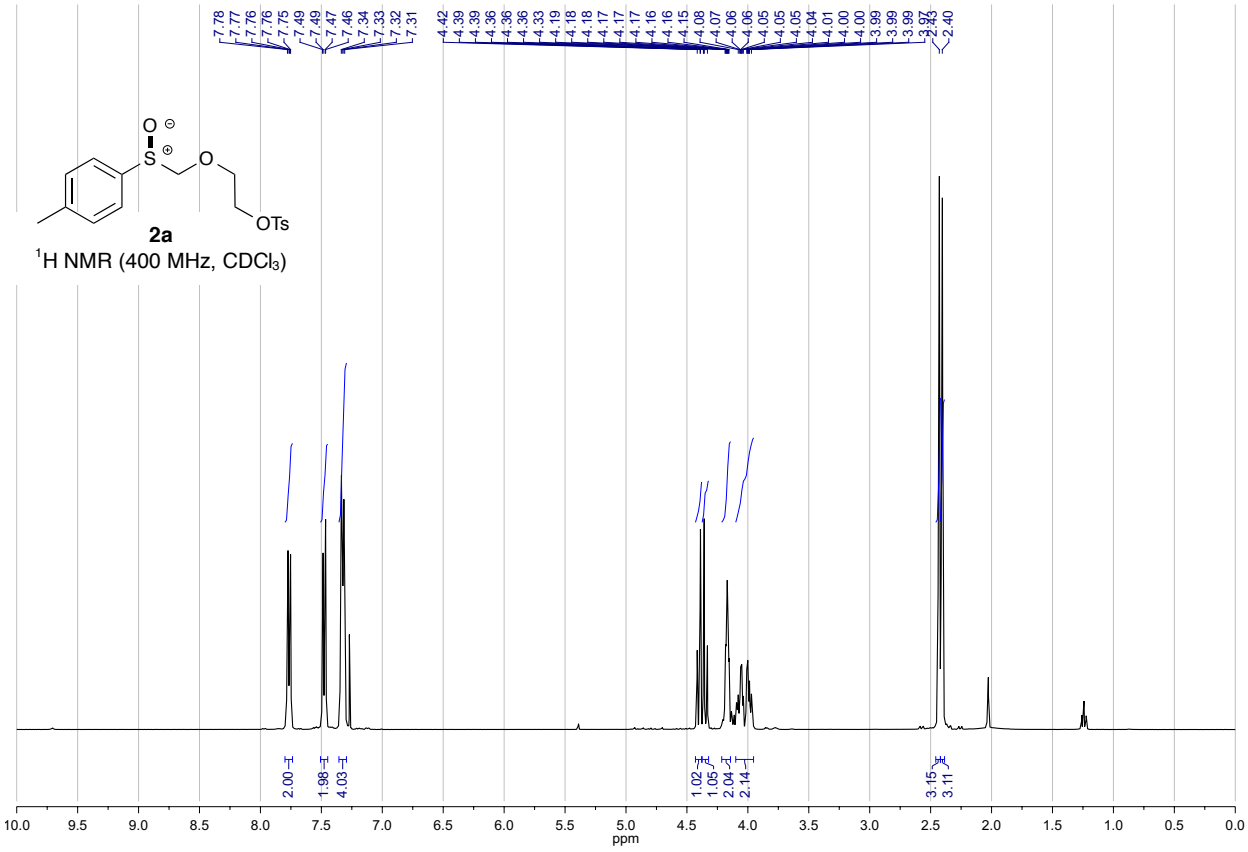
4a

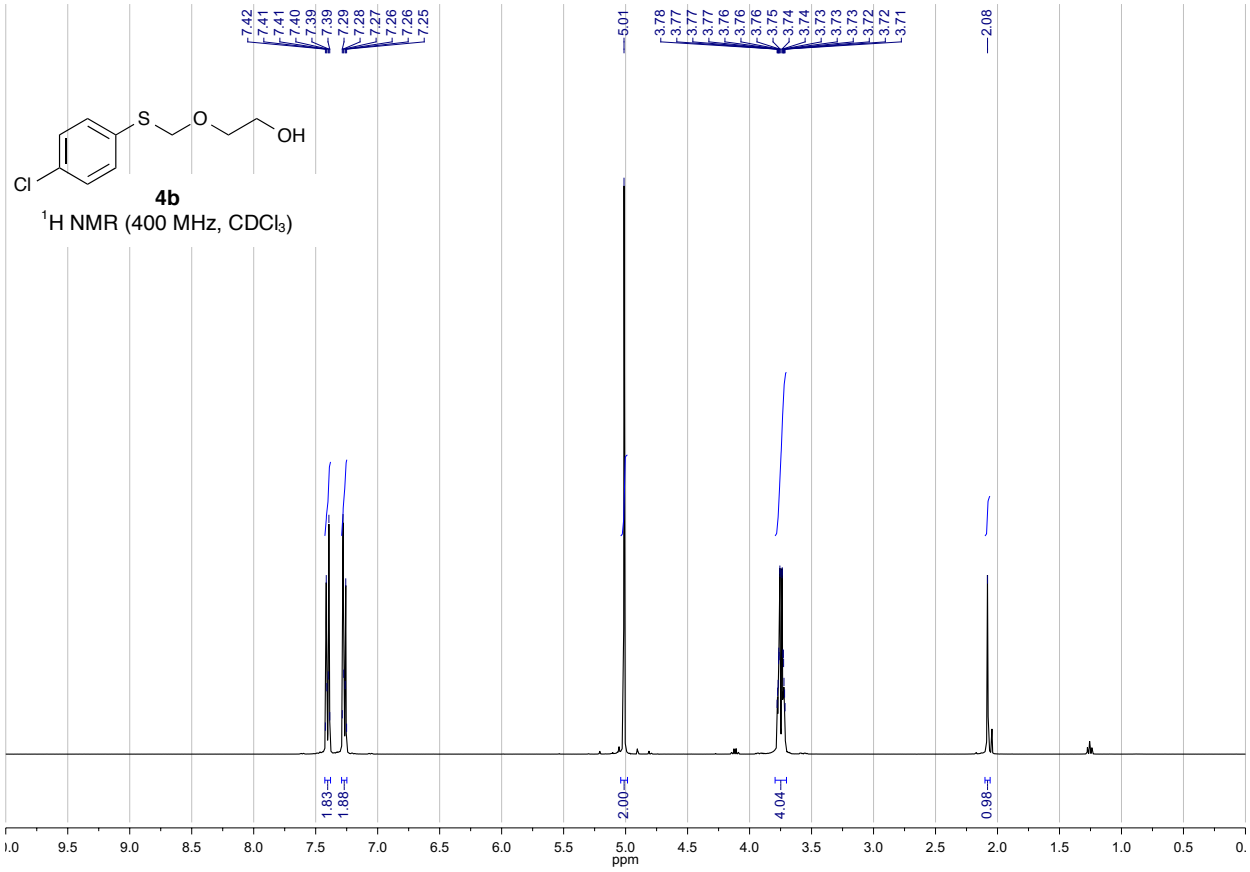
^{1}H NMR (400 MHz, $CDCl_3$)

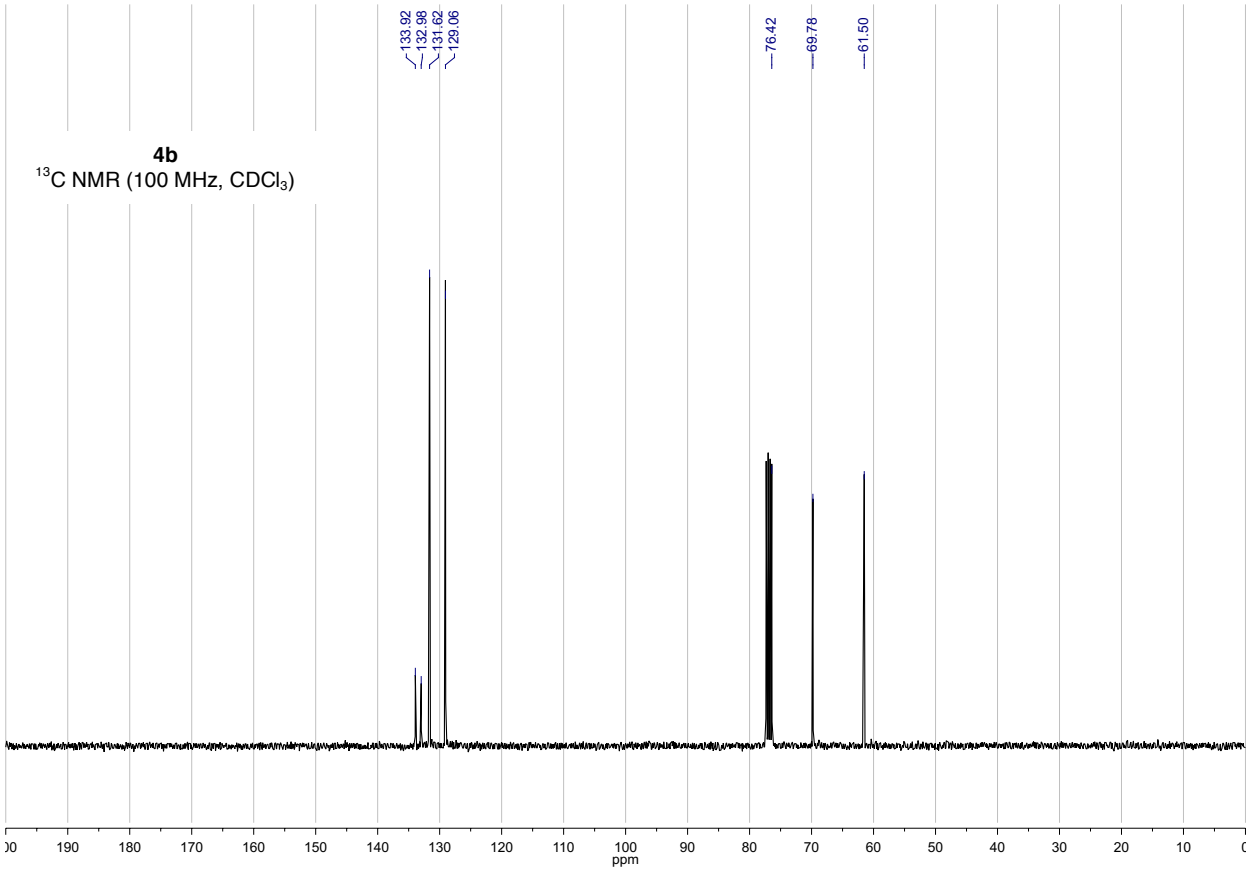


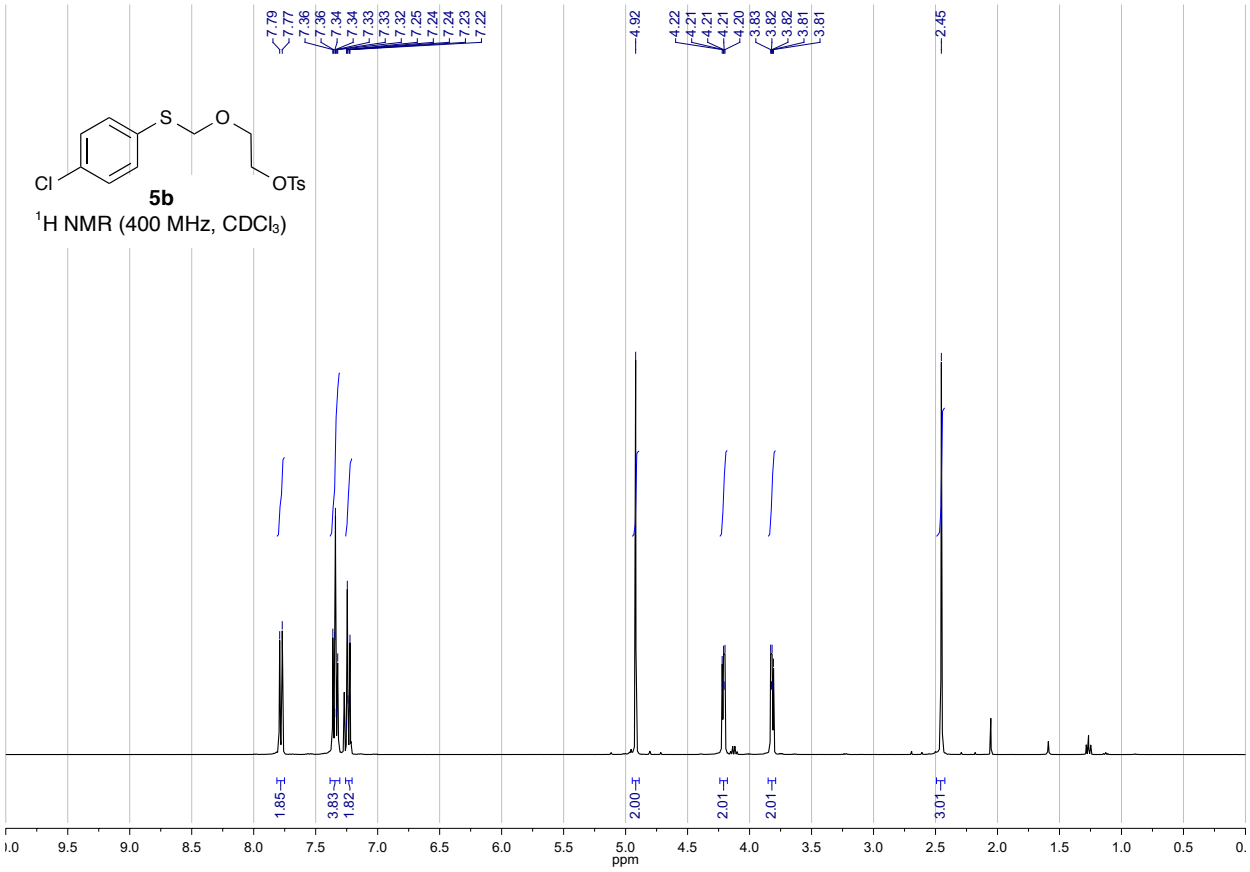
4a

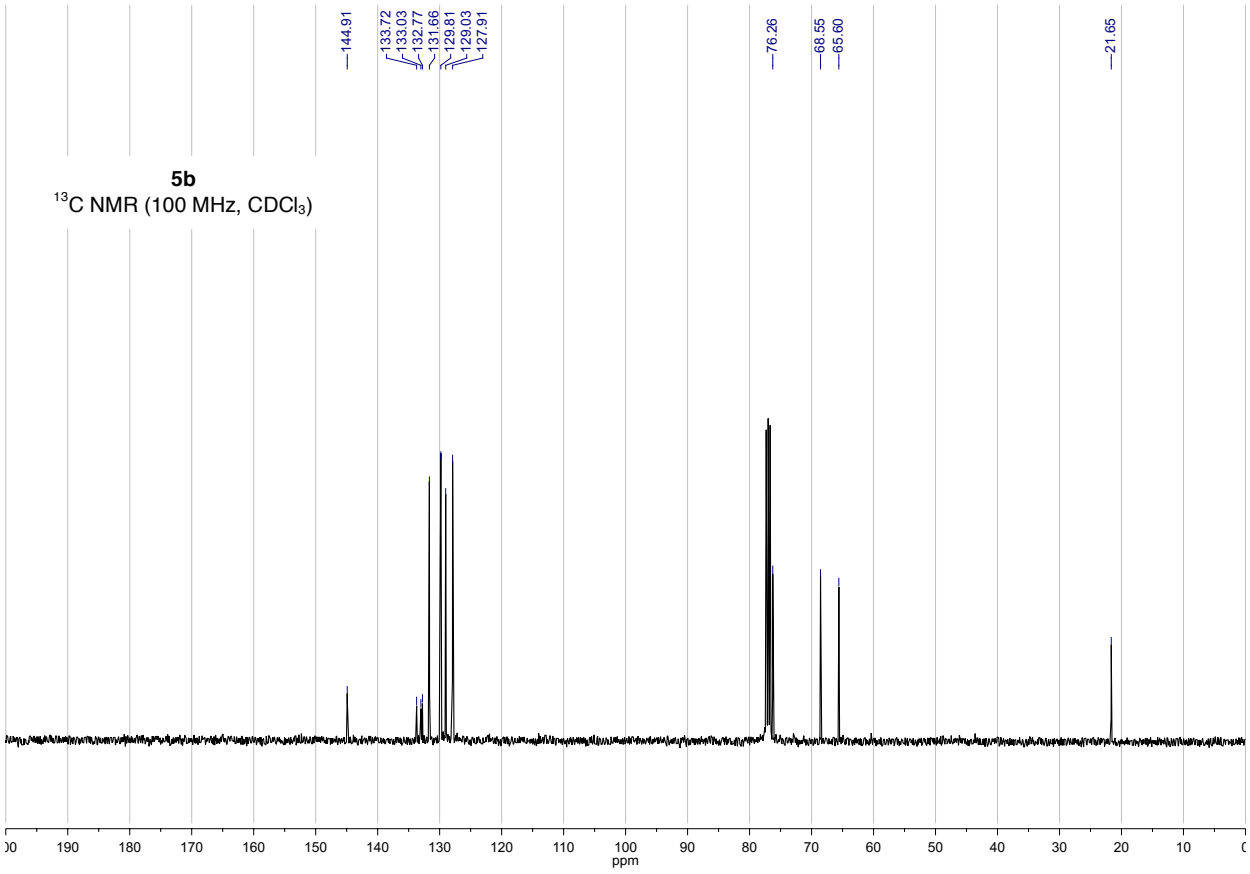
^{13}C NMR (100 MHz, $CDCl_3$)

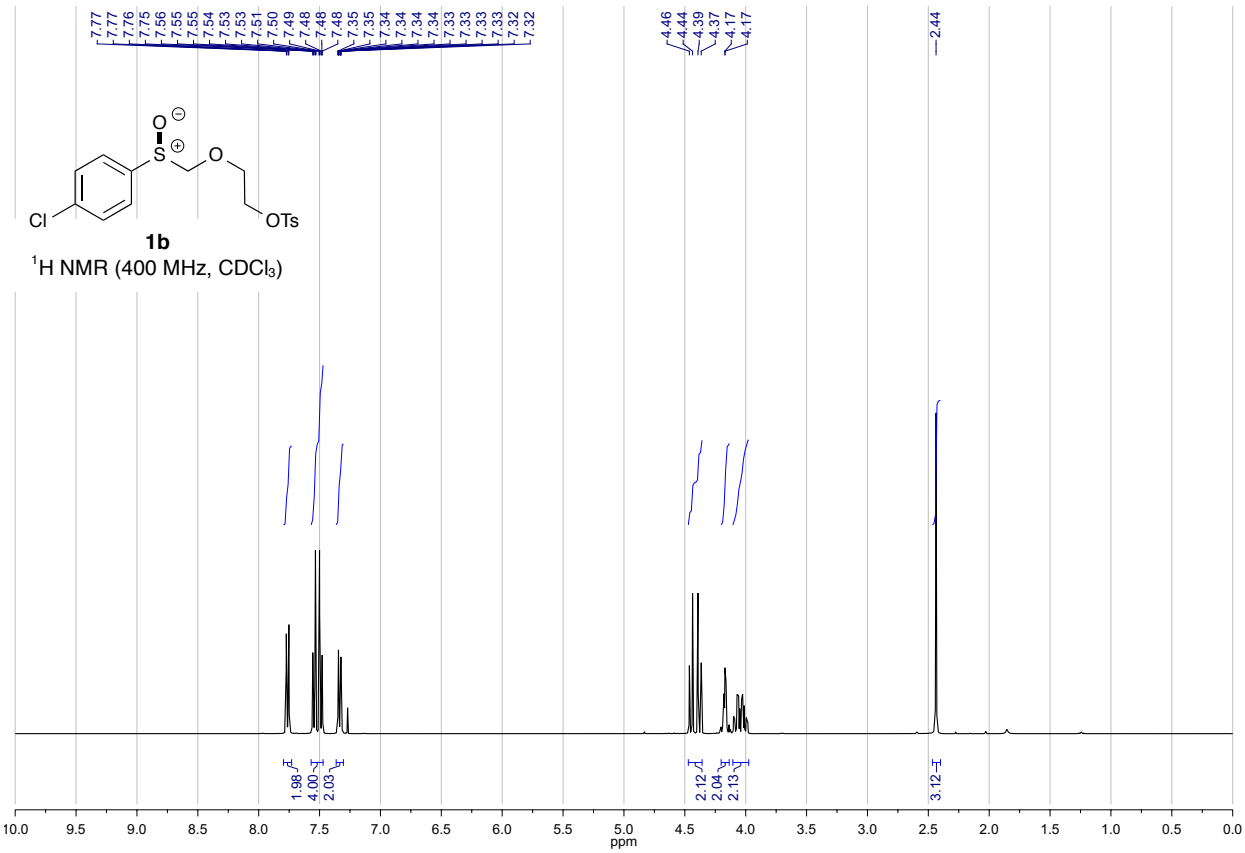

7.78
7.77
7.76
7.76
7.75
7.49
7.49
7.47
7.46
7.34
7.33
7.32
7.31
4.42
4.39
4.39
4.36
4.36
4.36
4.33
4.19
4.18
4.18
4.17
4.17
4.17
4.16
4.16
4.15
4.08
4.07
4.06
4.06
4.05
4.05
4.05
4.04
4.01
4.00
4.00
3.99
3.99
3.99
3.43
2.40
O
S
O
OTs
2a
^{1}H NMR (400 MHz, $CDCl_3$)
2.00
1.98
4.03
1.02
1.05
2.04
2.14
3.15
3.11
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm

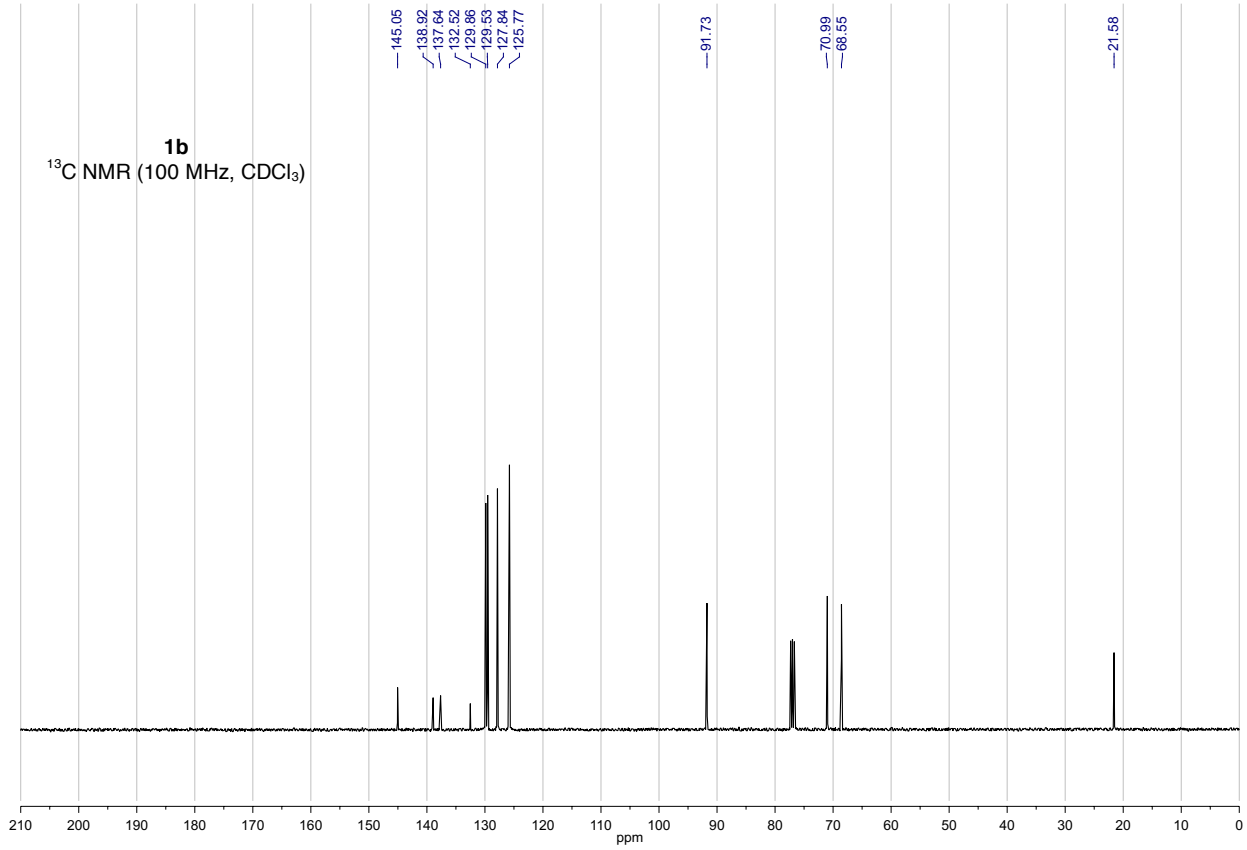

7.42
7.41
7.41
7.40
7.39
7.39
7.29
7.28
7.27
7.26
7.26
7.25
5.01
3.78
3.77
3.77
3.77
3.76
3.76
3.76
3.75
3.74
3.74
3.73
3.73
3.73
3.72
3.72
3.71
2.08
S
O
OH
Cl
4b
^{1}H NMR (400 MHz, $CDCl_3$)
1.83
1.88
2.00
4.04
0.98
ppm

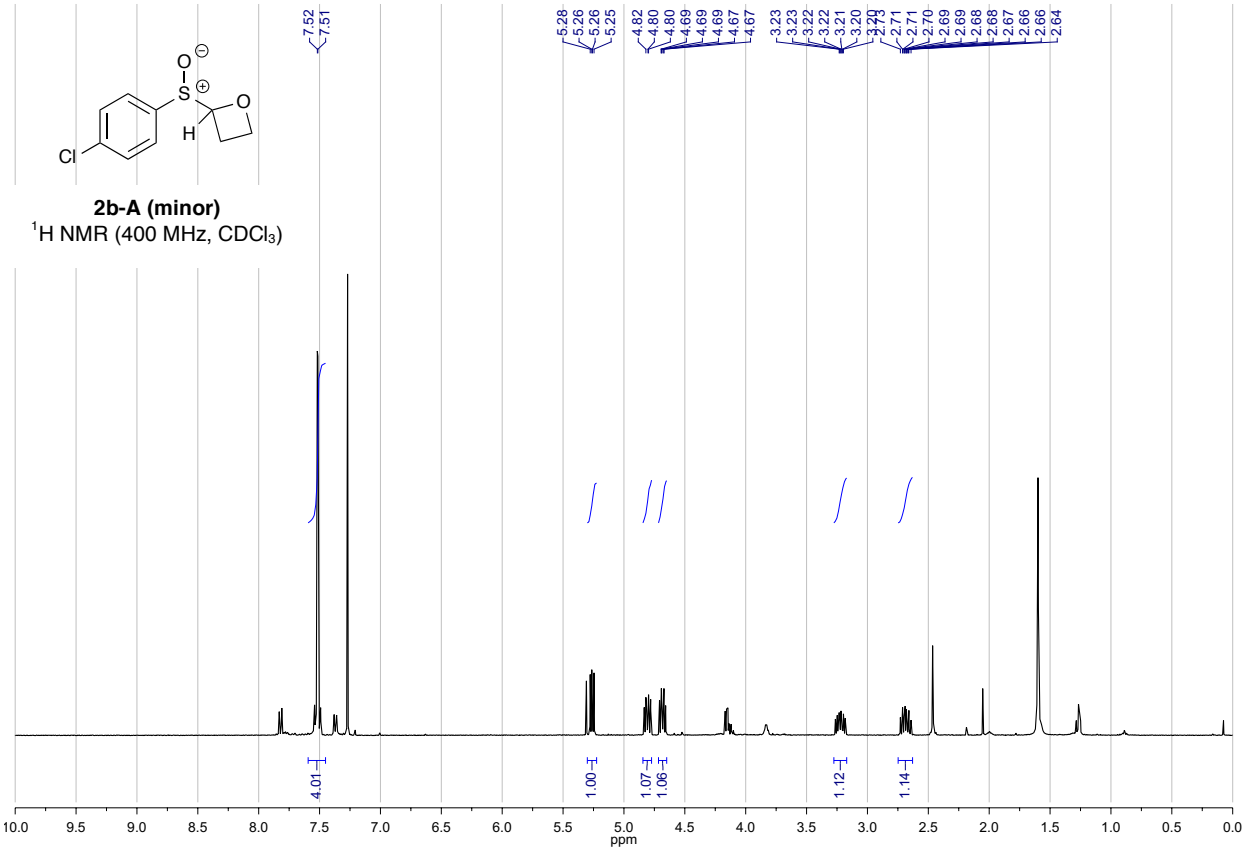

133.92
132.98
131.62
129.06
76.42
69.78
61.50
4b
^{13}C NMR (100 MHz, $CDCl_3$)
ppm

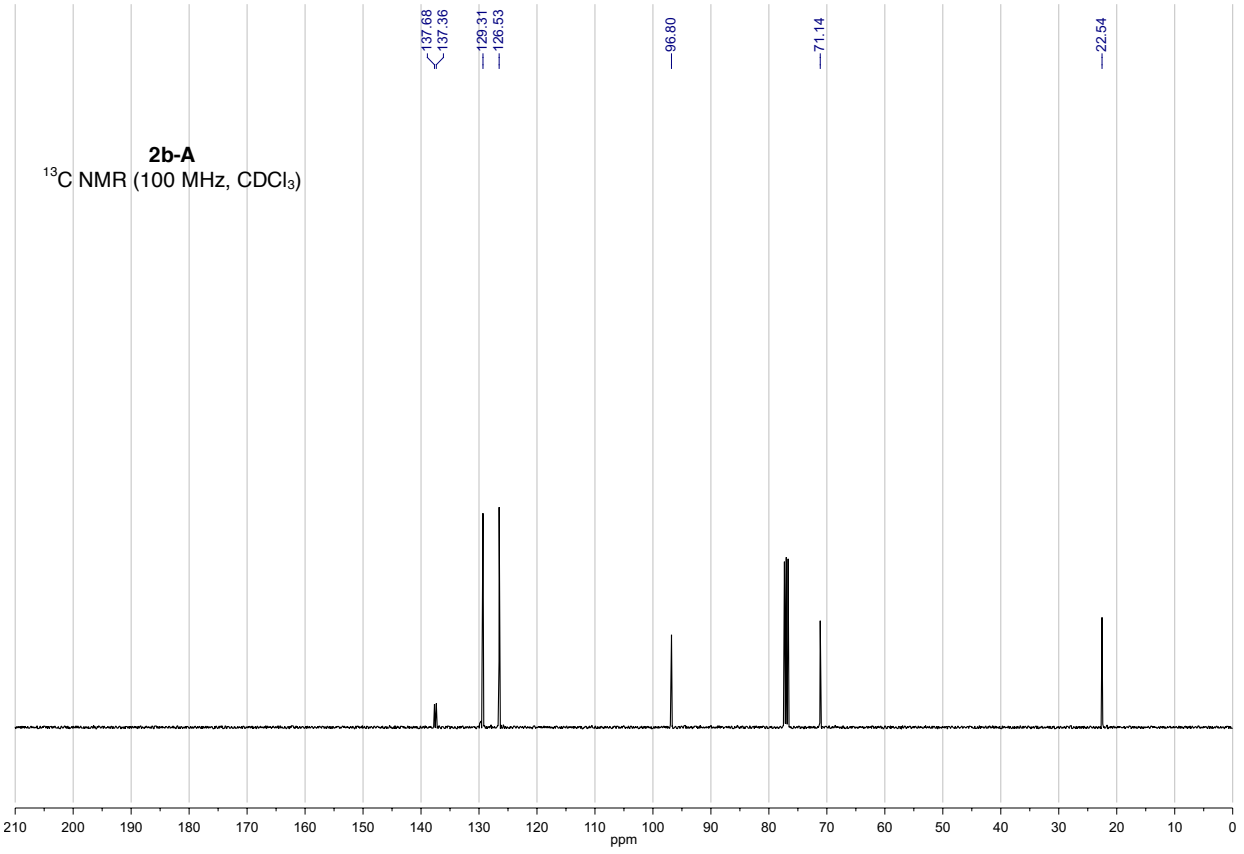

7.79
7.77
7.36
7.36
7.34
7.34
7.33
7.33
7.32
7.25
7.24
7.24
7.23
7.22
4.92
4.22
4.21
4.21
4.21
4.20
3.83
3.82
3.82
3.81
3.81
2.45
S
O
Cl
OTs
5b
1H NMR (400 MHz, CDCl3)
1.85
3.83
1.82
2.00
2.01
2.01
3.01
ppm

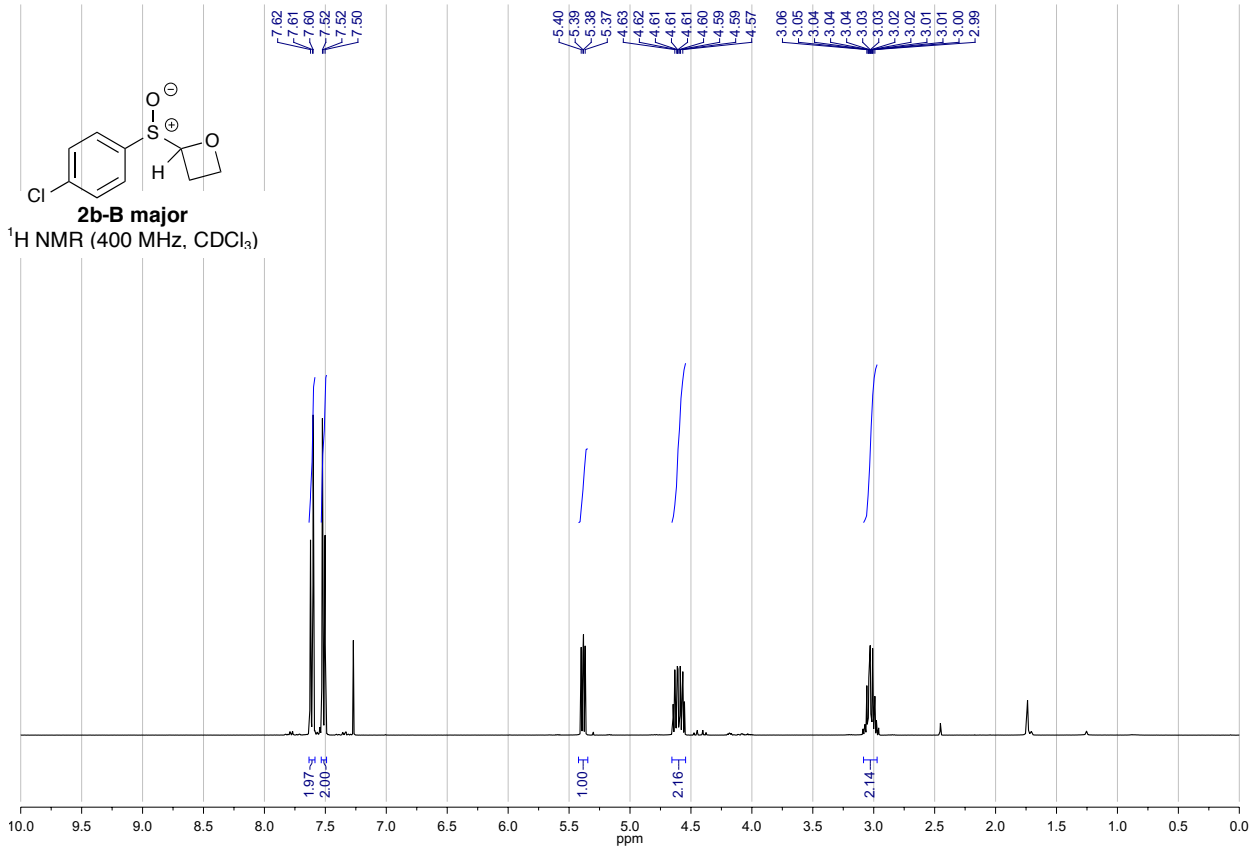

144.91
133.72
133.03
132.77
131.66
129.81
129.03
127.91
76.26
68.55
65.60
21.65
5b
13C NMR (100 MHz, CDCl3)
ppm

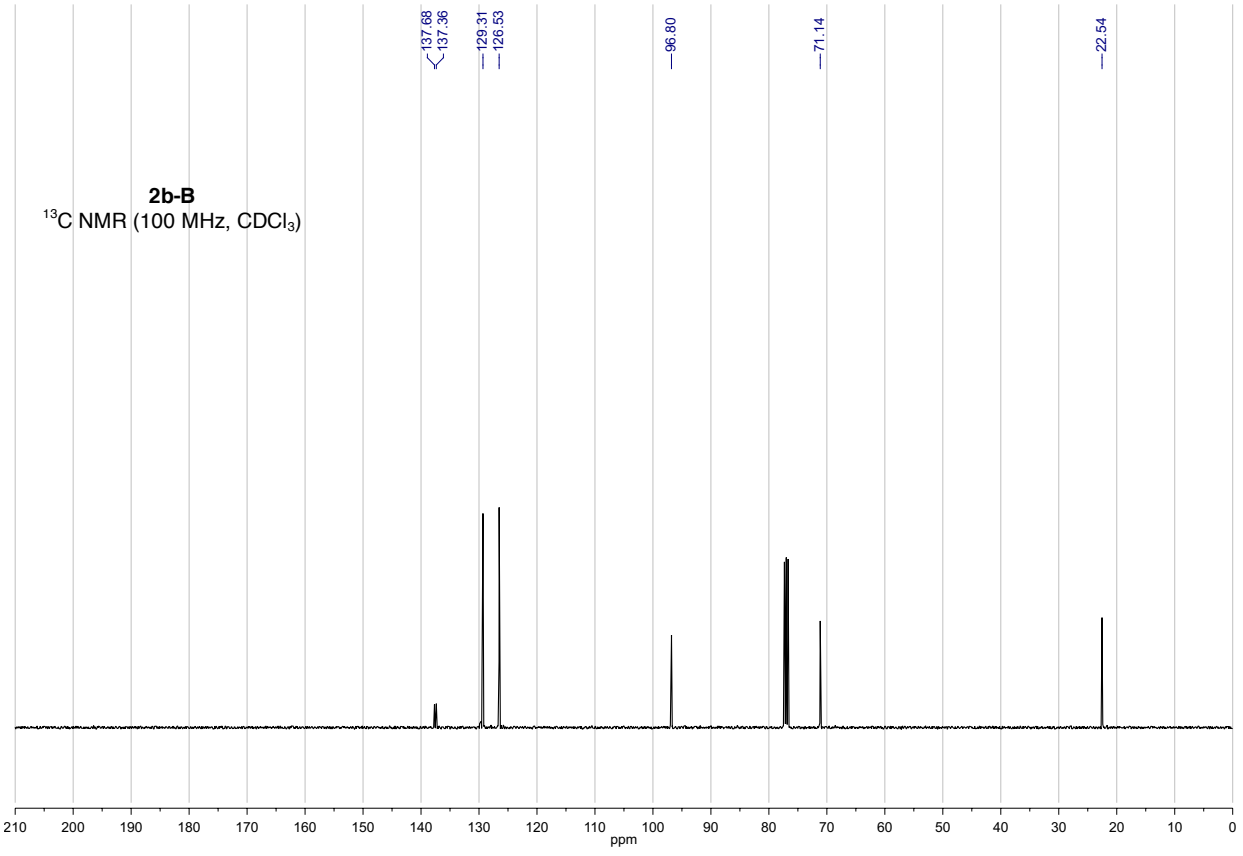

7.77
7.77
7.76
7.75
7.56
7.55
7.55
7.54
7.53
7.53
7.51
7.50
7.49
7.48
7.48
7.48
7.35
7.35
7.34
7.34
7.34
7.34
7.33
7.33
7.33
7.33
7.32
7.32
4.46
4.44
4.39
4.37
4.17
4.17
2.44
O
S
O
Cl
OTs
1b
^{1}H NMR (400 MHz, CDCl$_3$)
1.98
4.00
2.03
2.12
2.04
2.13
3.12
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
ppm

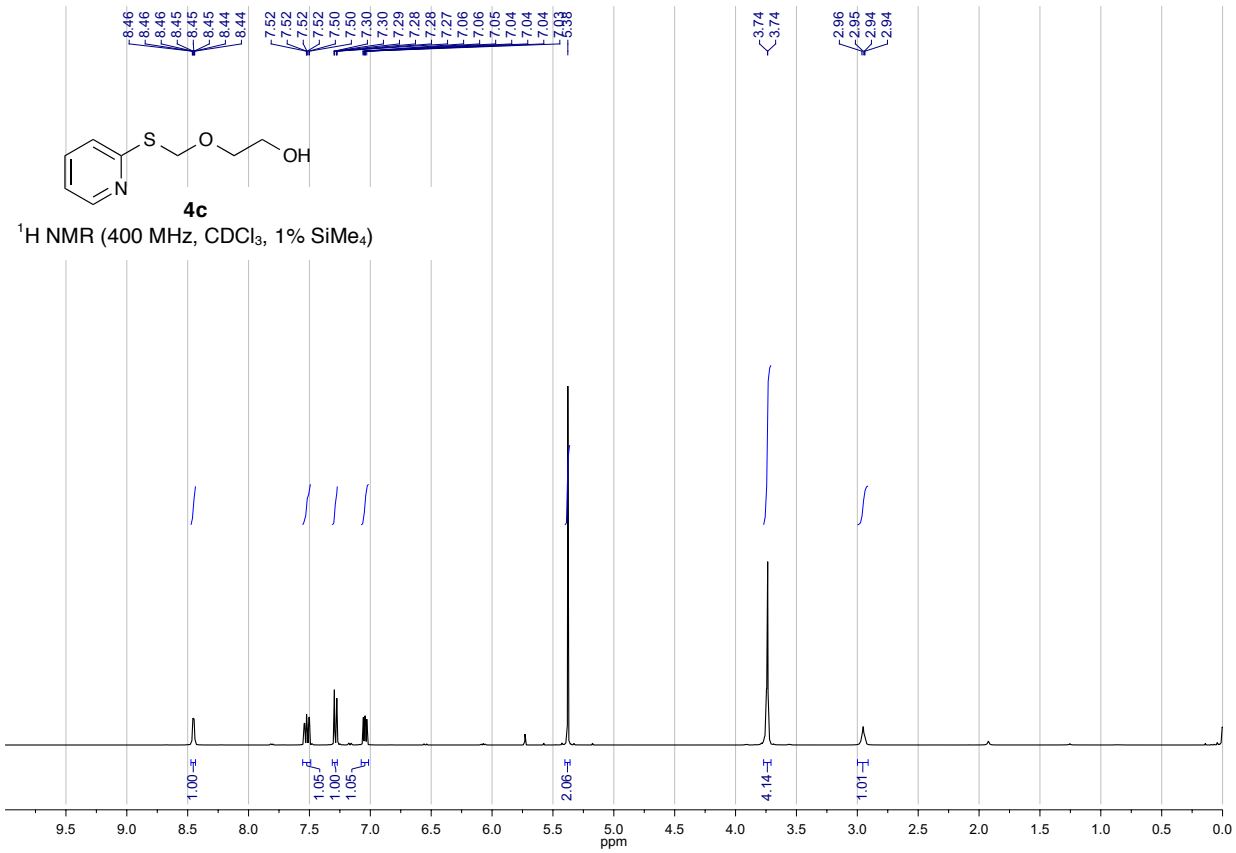

145.05
138.92
137.64
132.52
129.86
129.53
127.84
125.77
91.73
70.99
68.55
21.58
1b
^{13}C NMR (100 MHz, CDCl$_3$)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm


2b-A (minor)
^{1}H NMR (400 MHz, CDCl$_3$)
7.52
7.51
5.28
5.26
5.26
5.25
4.82
4.80
4.80
4.69
4.69
4.69
4.67
4.67
3.23
3.23
3.22
3.22
3.21
3.20
2.71
2.71
2.70
2.69
2.69
2.68
2.68
2.67
2.66
2.66
2.64
4.01
1.00
1.07
1.06
1.12
1.14
ppm


2b-A
^{13}C NMR (100 MHz, CDCl$_3$)
137.68
137.36
129.31
126.53
96.80
71.14
22.54
ppm

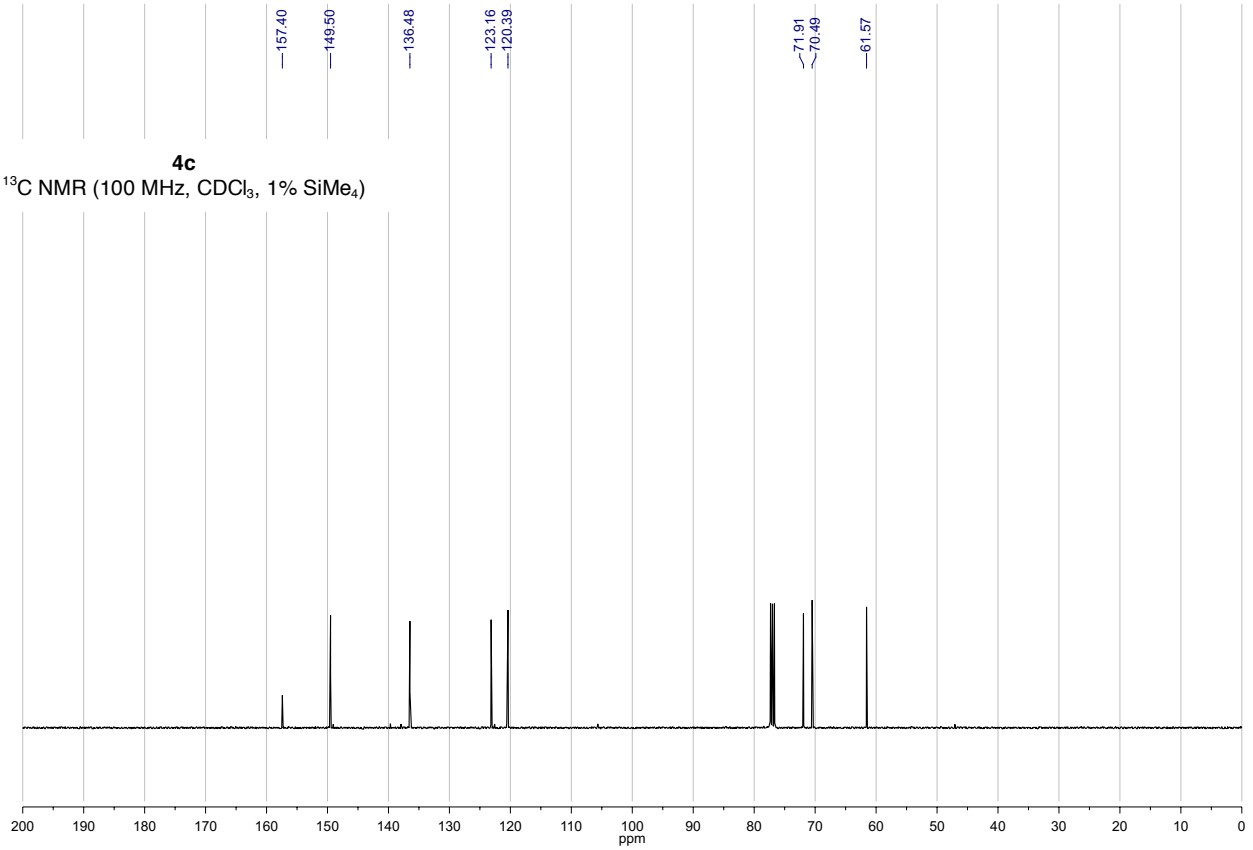

7.62
7.61
7.60
7.52
7.52
7.50
5.40
5.39
5.38
5.37
4.63
4.62
4.61
4.61
4.61
4.60
4.59
4.59
4.57
3.06
3.05
3.04
3.04
3.04
3.03
3.03
3.02
3.02
3.01
3.01
3.00
2.99
1.97
2.00
1.00
2.16
2.14
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
O
S
O
H
Cl
2b-B major
^{1}H NMR (400 MHz, $CDCl_3$)


137.68
137.36
129.31
126.53
96.80
71.14
22.54
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm
2b-B
^{13}C NMR (100 MHz, $CDCl_3$)



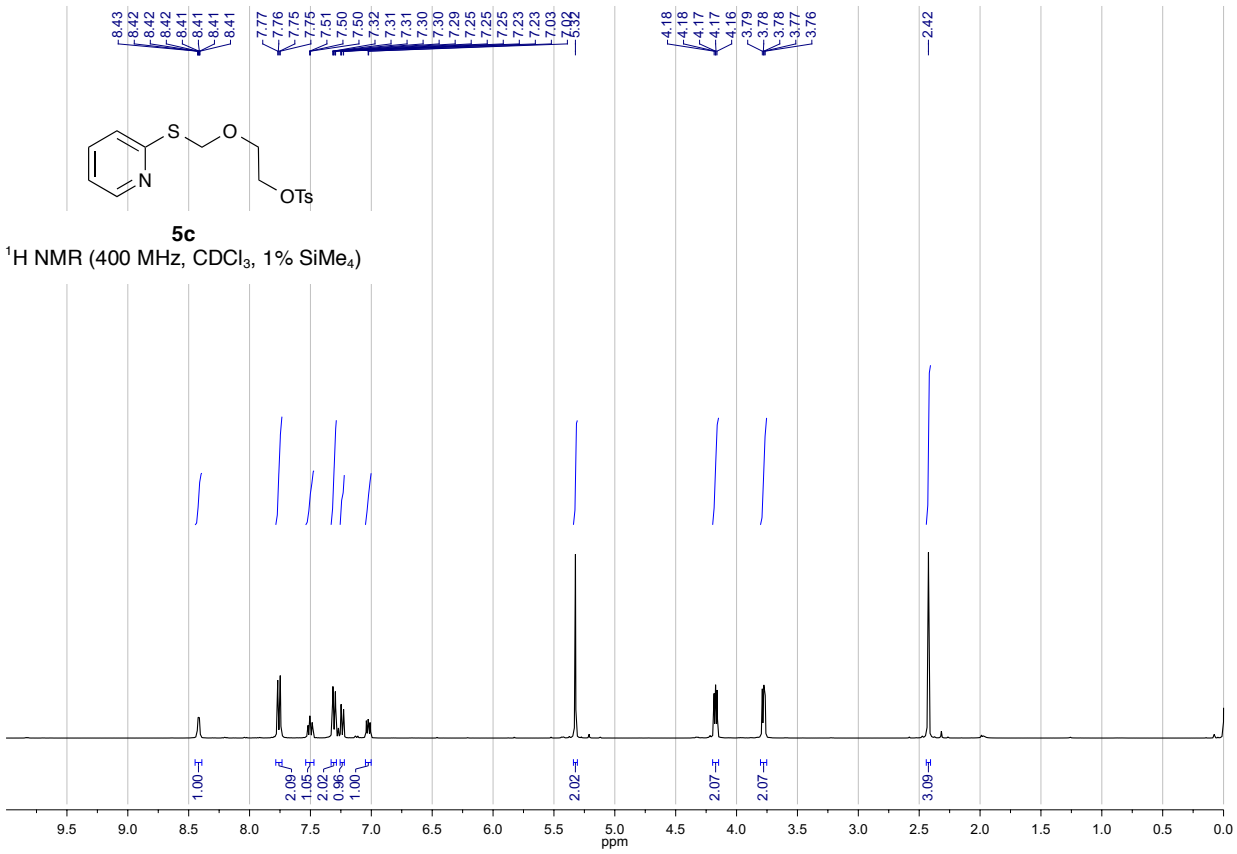
4c

^{1}H NMR (400 MHz, $CDCl_3$, 1% $SiMe_4$)



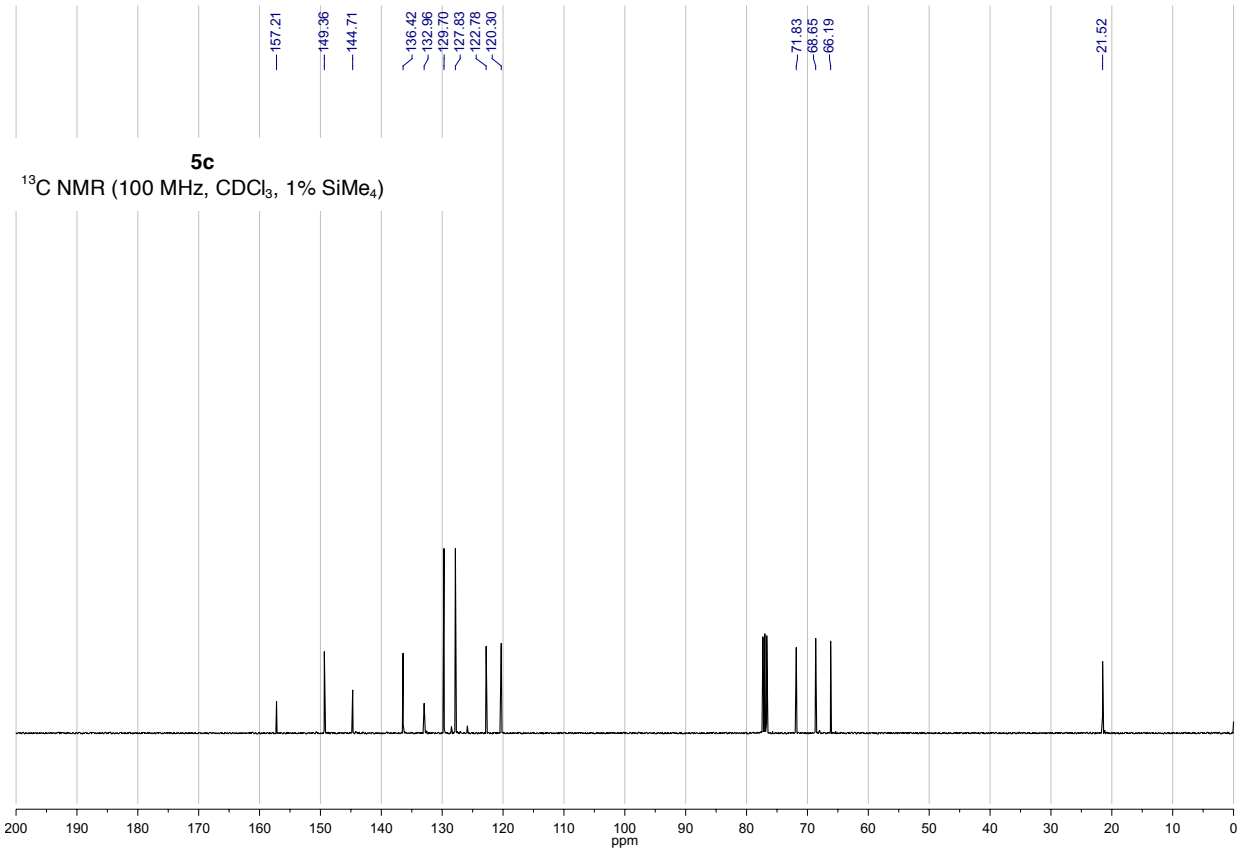
4c

^{13}C NMR (100 MHz, $CDCl_3$, 1% $SiMe_4$)



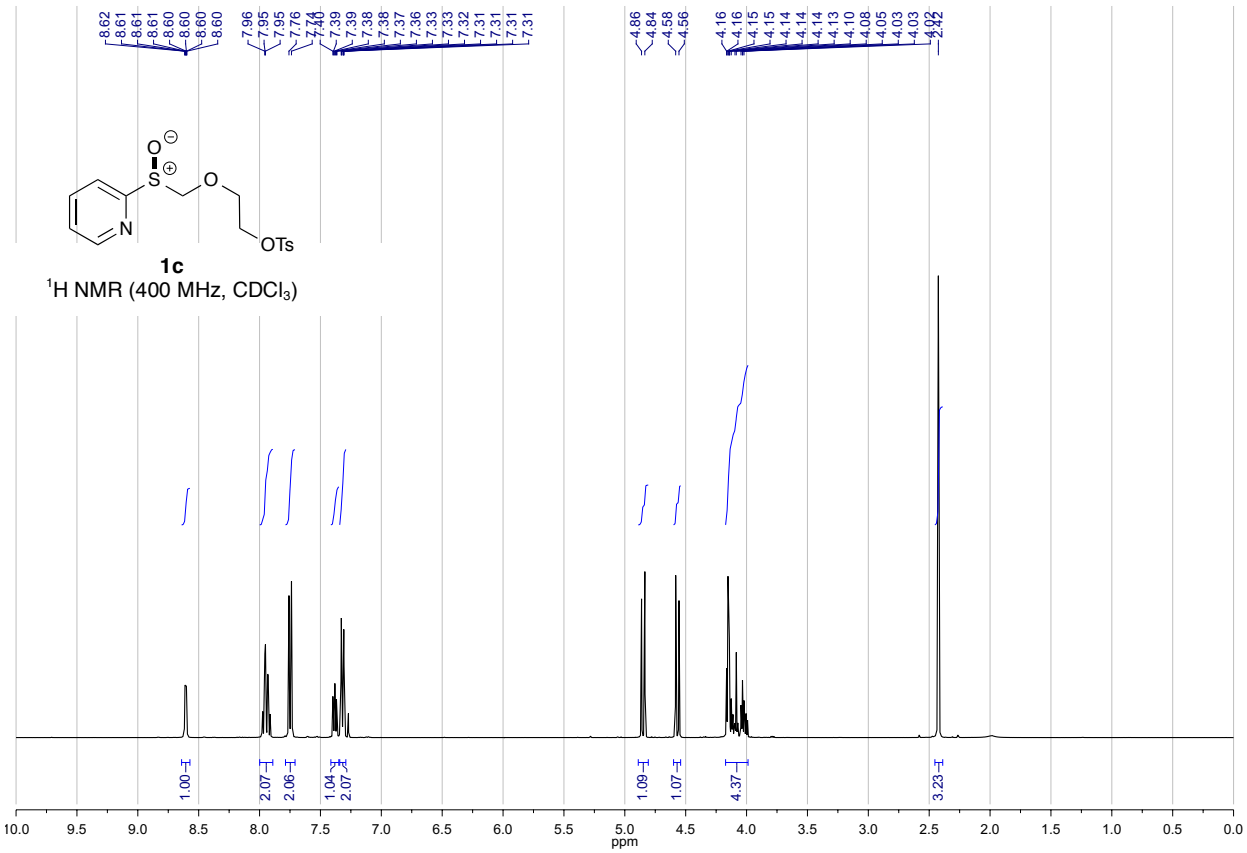
5c

^{1}H NMR (400 MHz, $CDCl_3$, 1% $SiMe_4$)



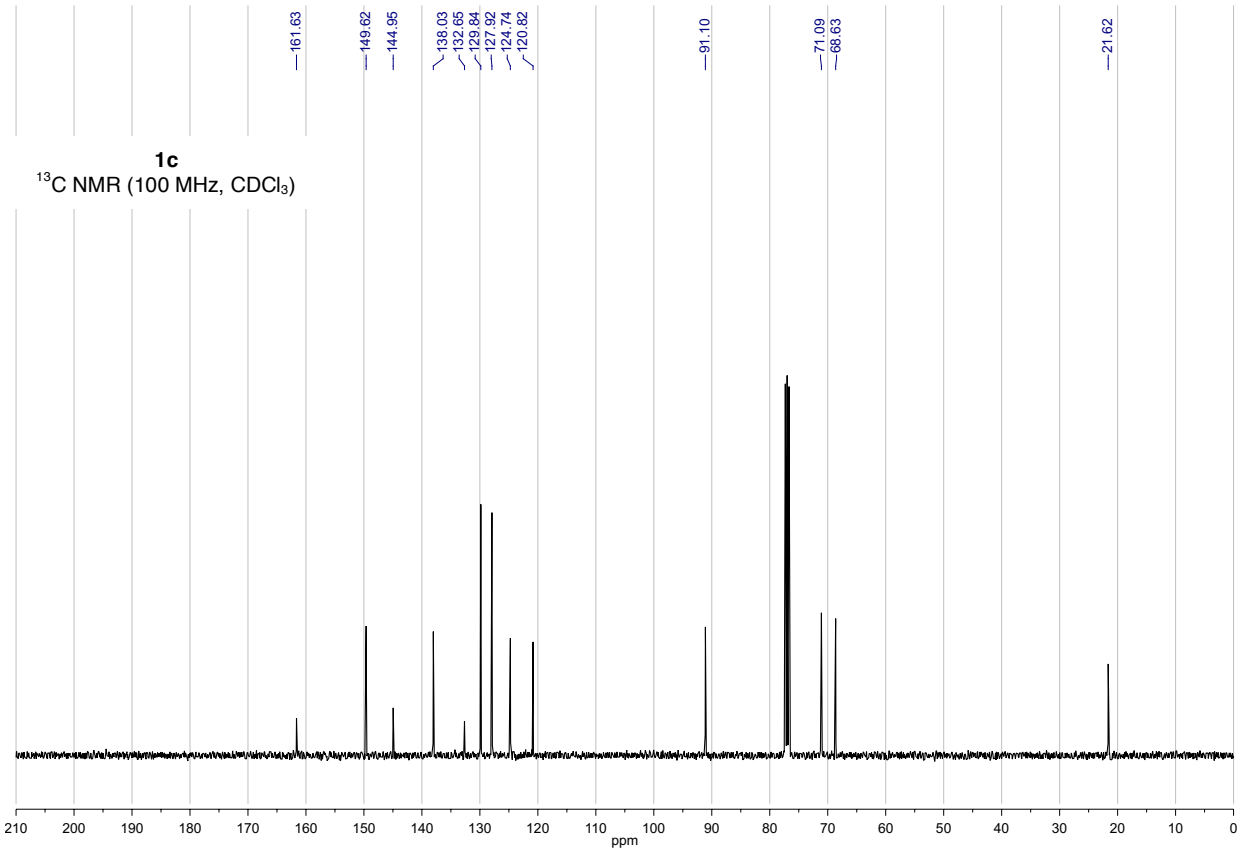
5c

^{13}C NMR (100 MHz, $CDCl_3$, 1% $SiMe_4$)



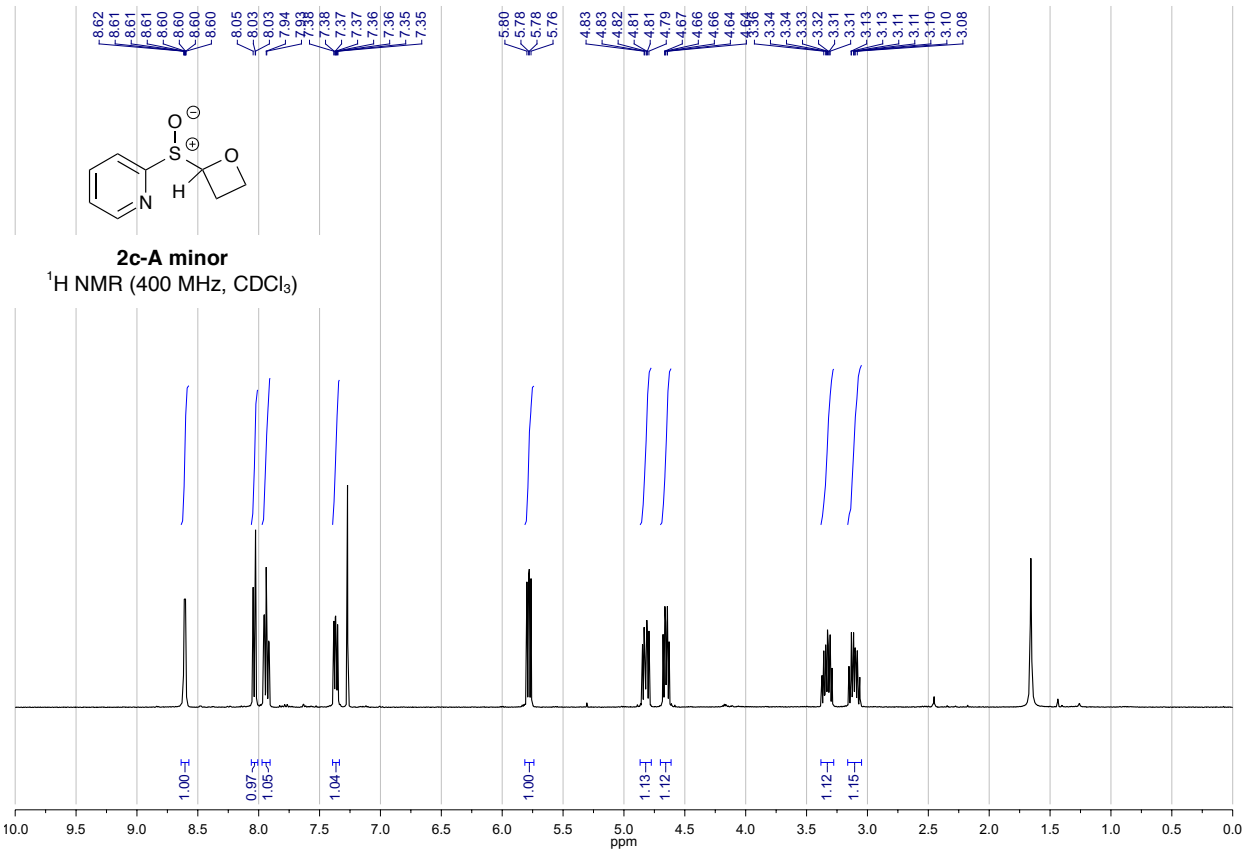
1c

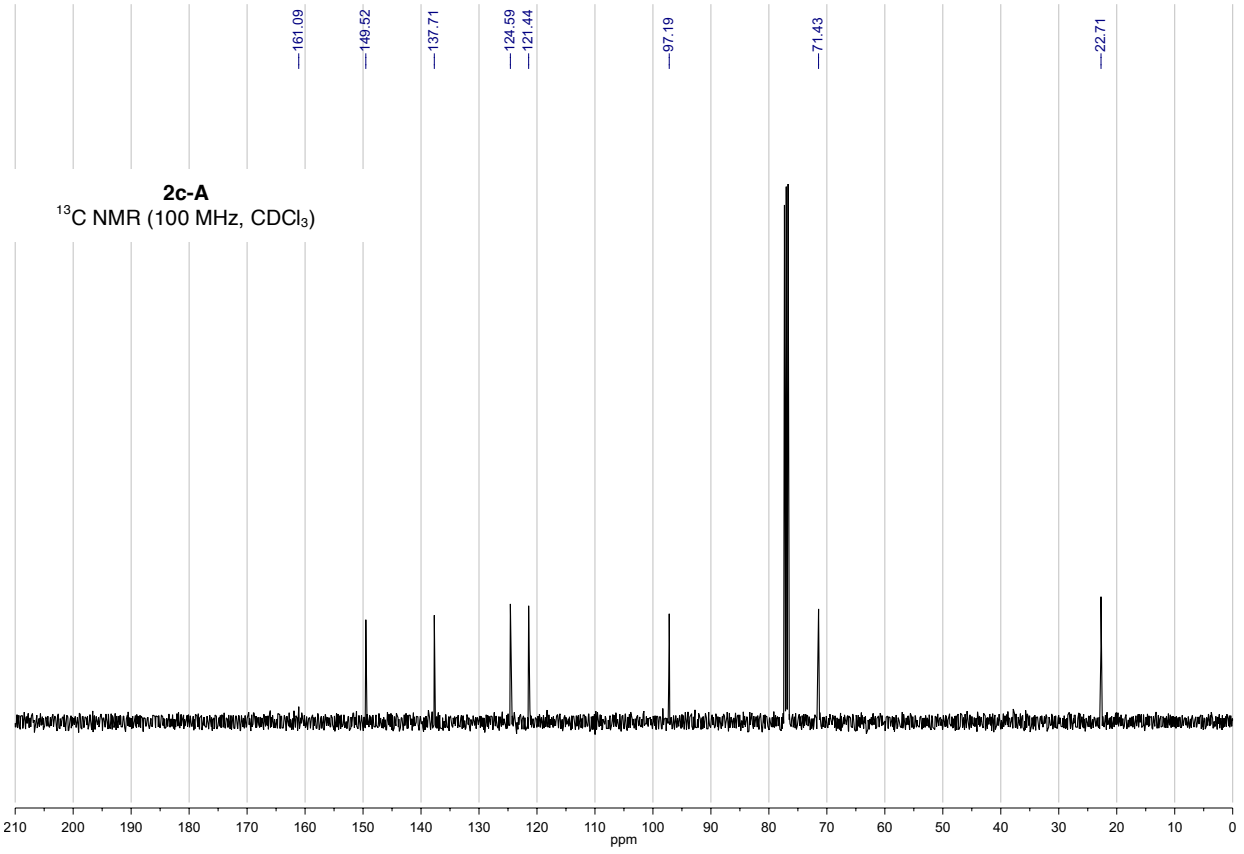
^{1}H NMR (400 MHz, $CDCl_3$)

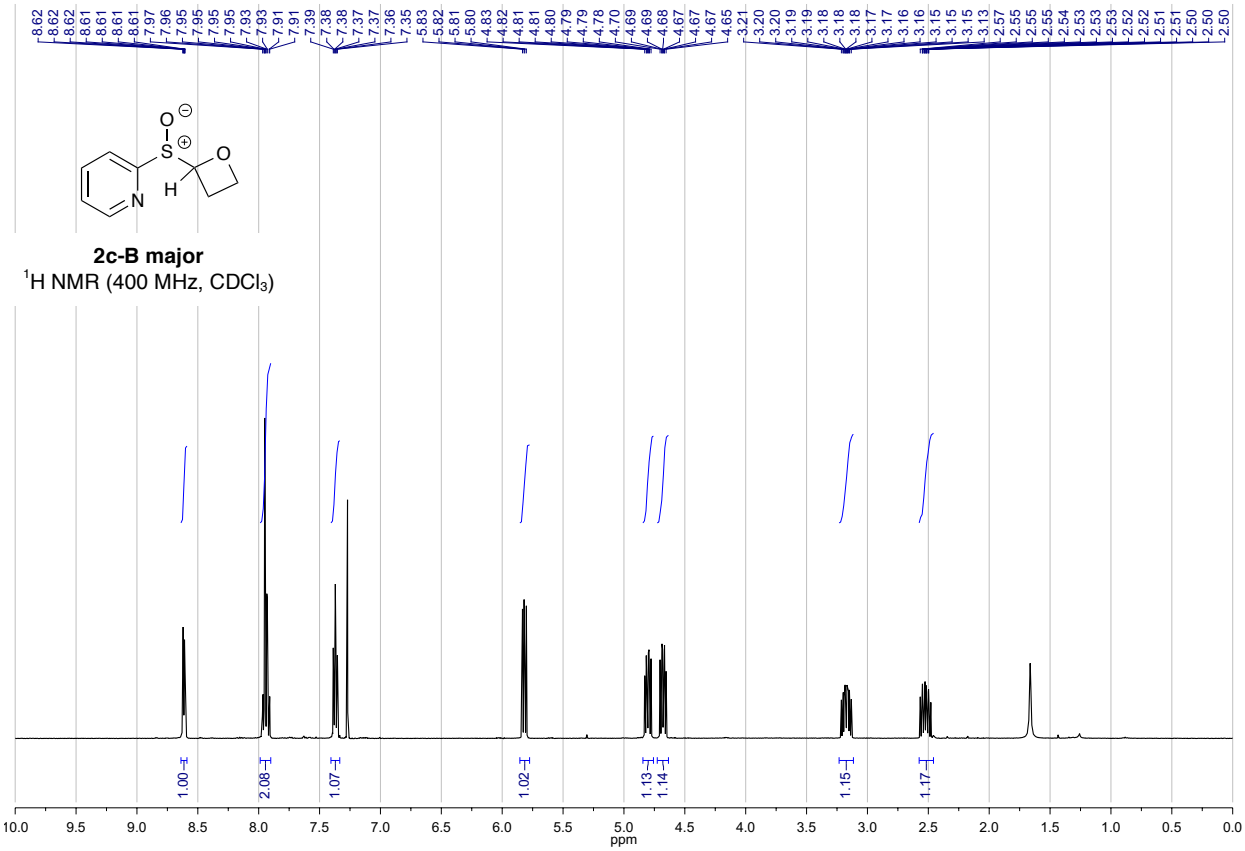


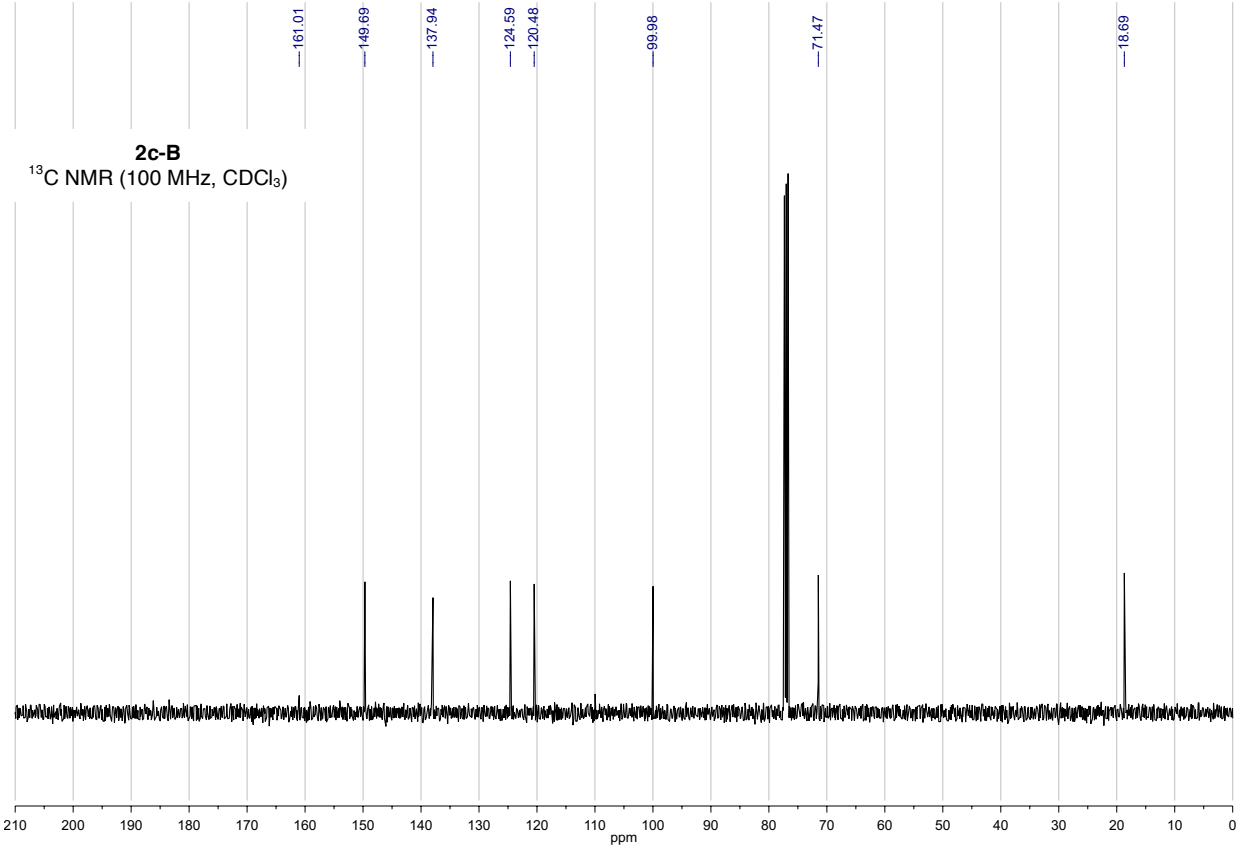
1c

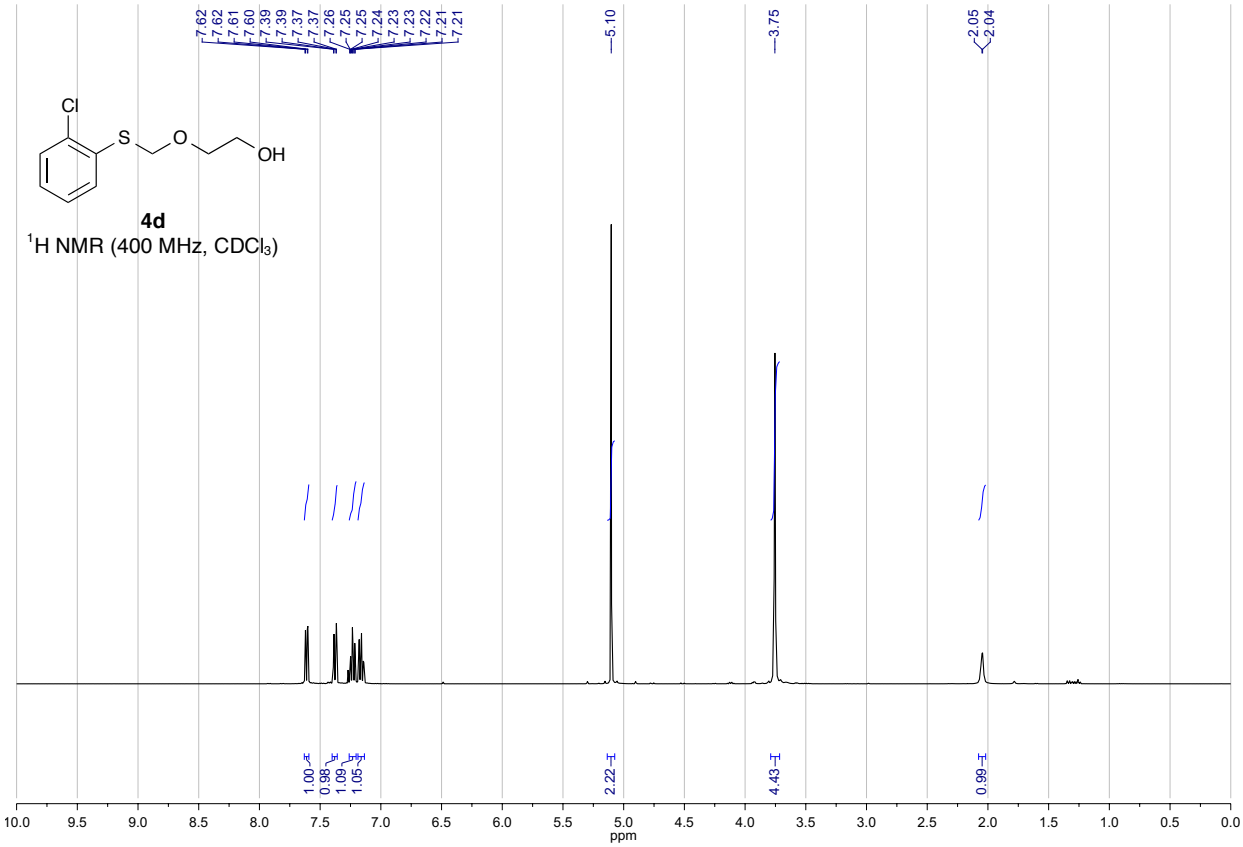
^{13}C NMR (100 MHz, $CDCl_3$)

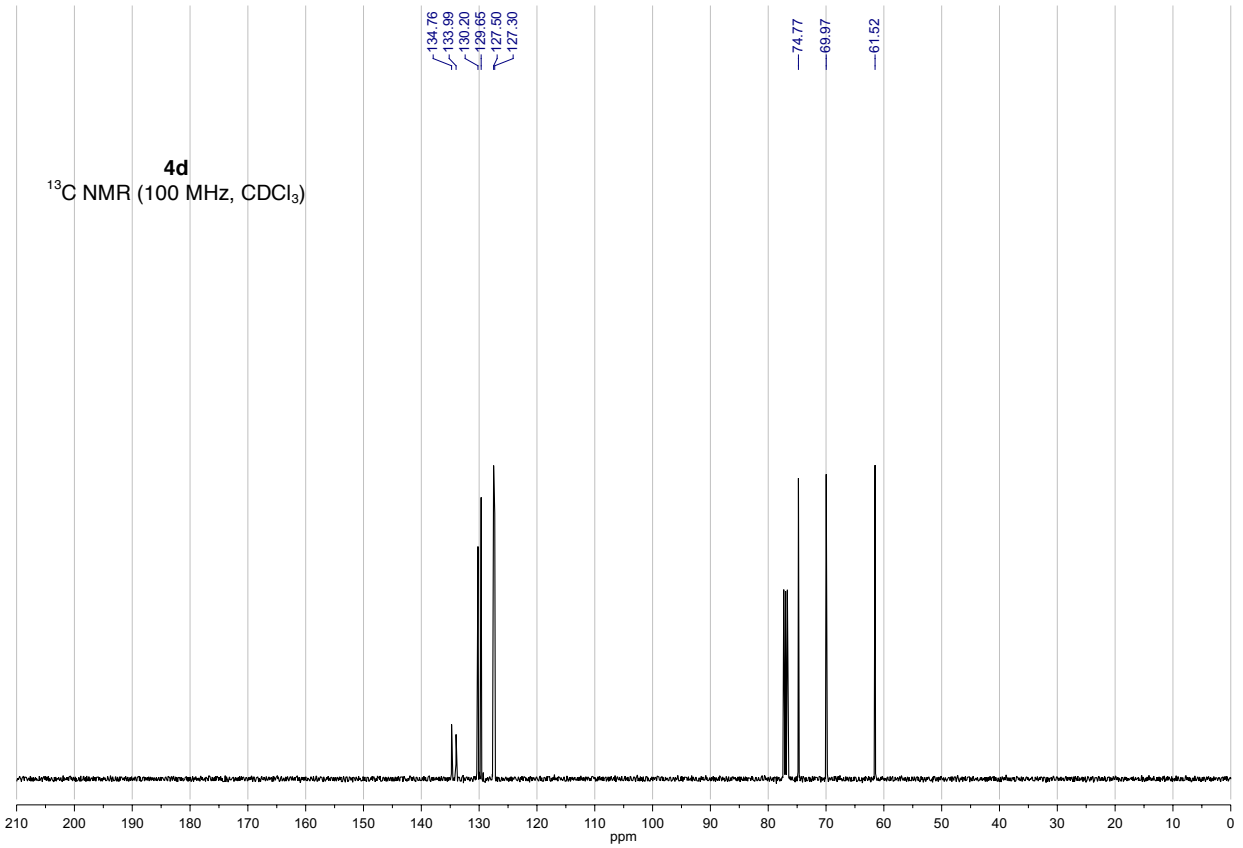

8.62
8.61
8.61
8.61
8.60
8.60
8.60
8.60
8.05
8.03
8.03
7.94
7.38
7.37
7.37
7.36
7.36
7.35
7.35
5.80
5.78
5.78
5.76
4.83
4.83
4.82
4.81
4.81
4.79
4.67
4.66
4.66
4.64
4.64
3.36
3.34
3.34
3.33
3.32
3.31
3.31
3.13
3.13
3.11
3.11
3.10
3.10
3.08
O
S
O
H
N
2c-A minor
^{1}H NMR (400 MHz, CDCl$_3$)
1.00
0.97
1.05
1.04
1.00
1.13
1.12
1.12
1.15
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
ppm

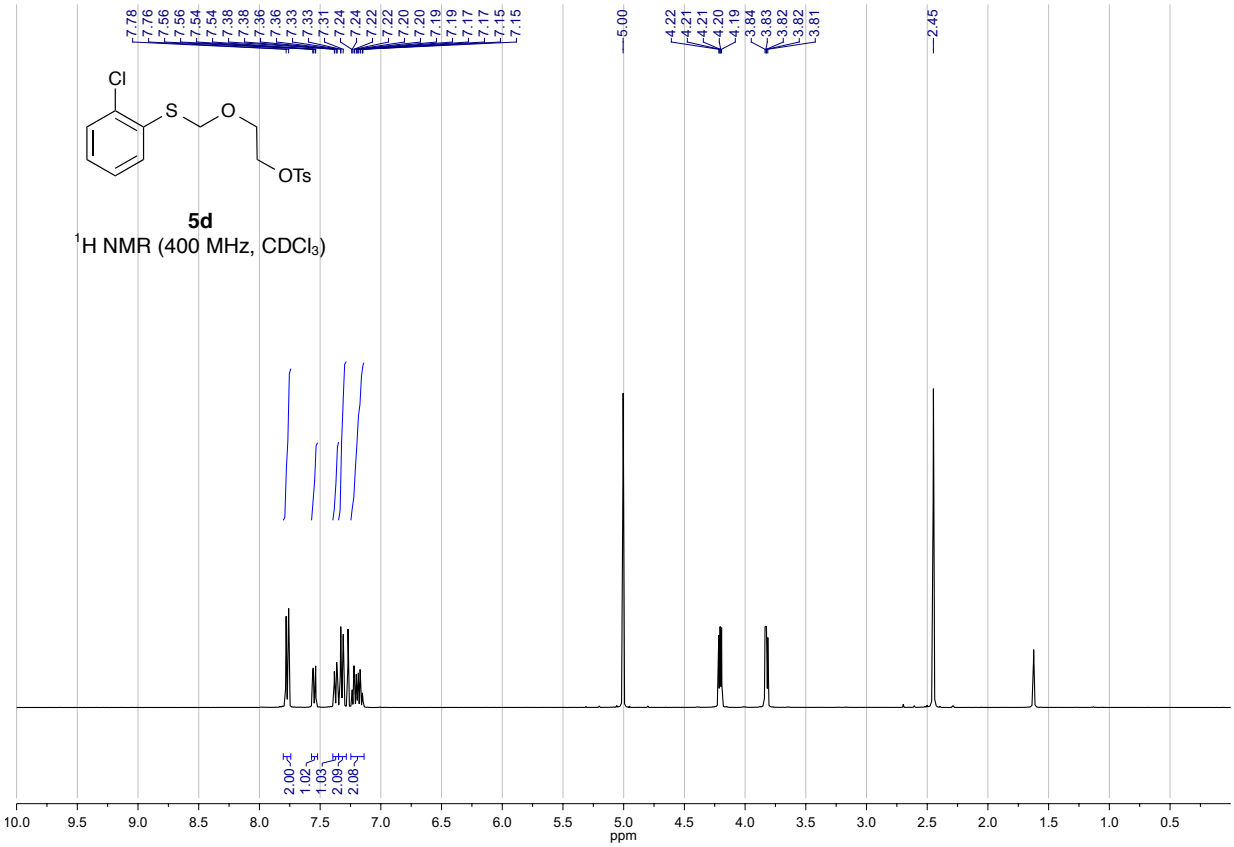

161.09
149.52
137.71
124.59
121.44
97.19
71.43
22.71
2c-A
^{13}C NMR (100 MHz, CDCl$_3$)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm

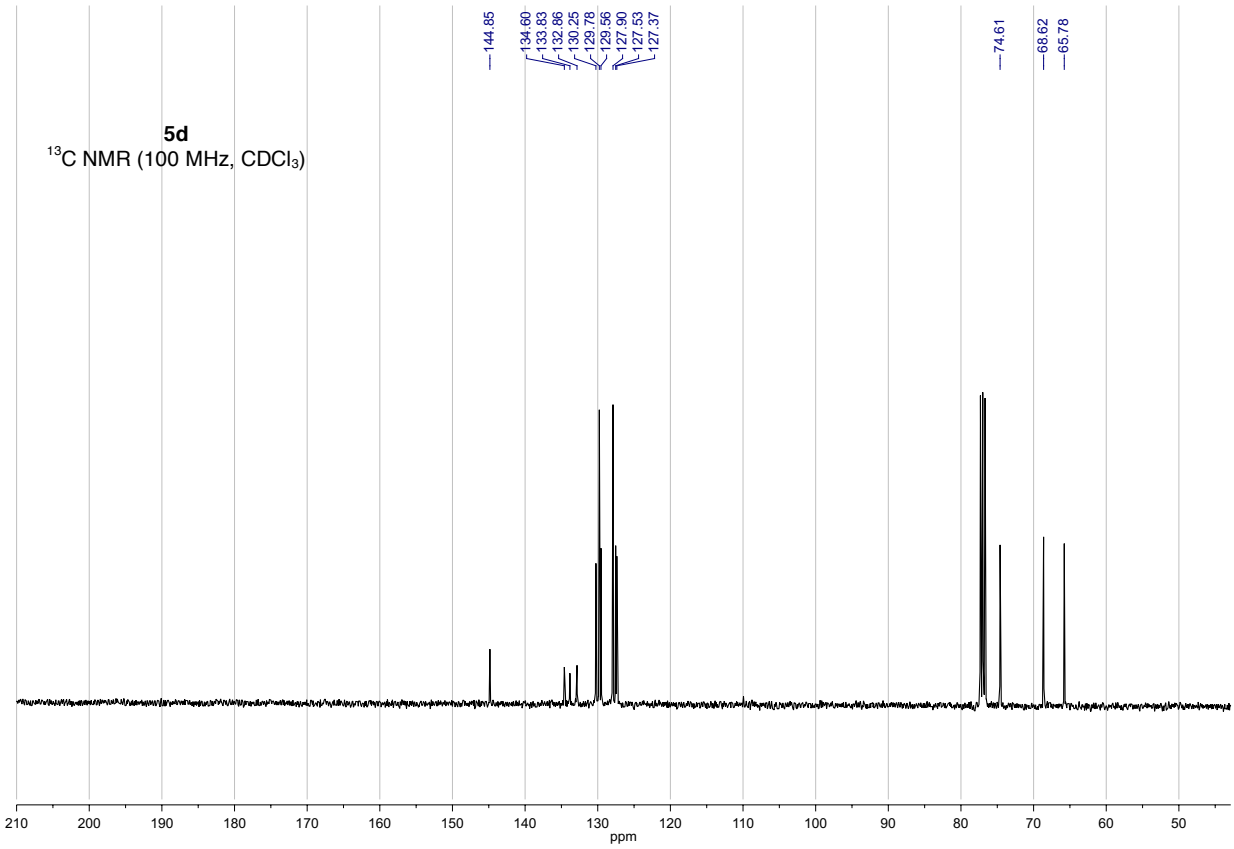

2c-B major
1H NMR (400 MHz, CDCl3)
ppm

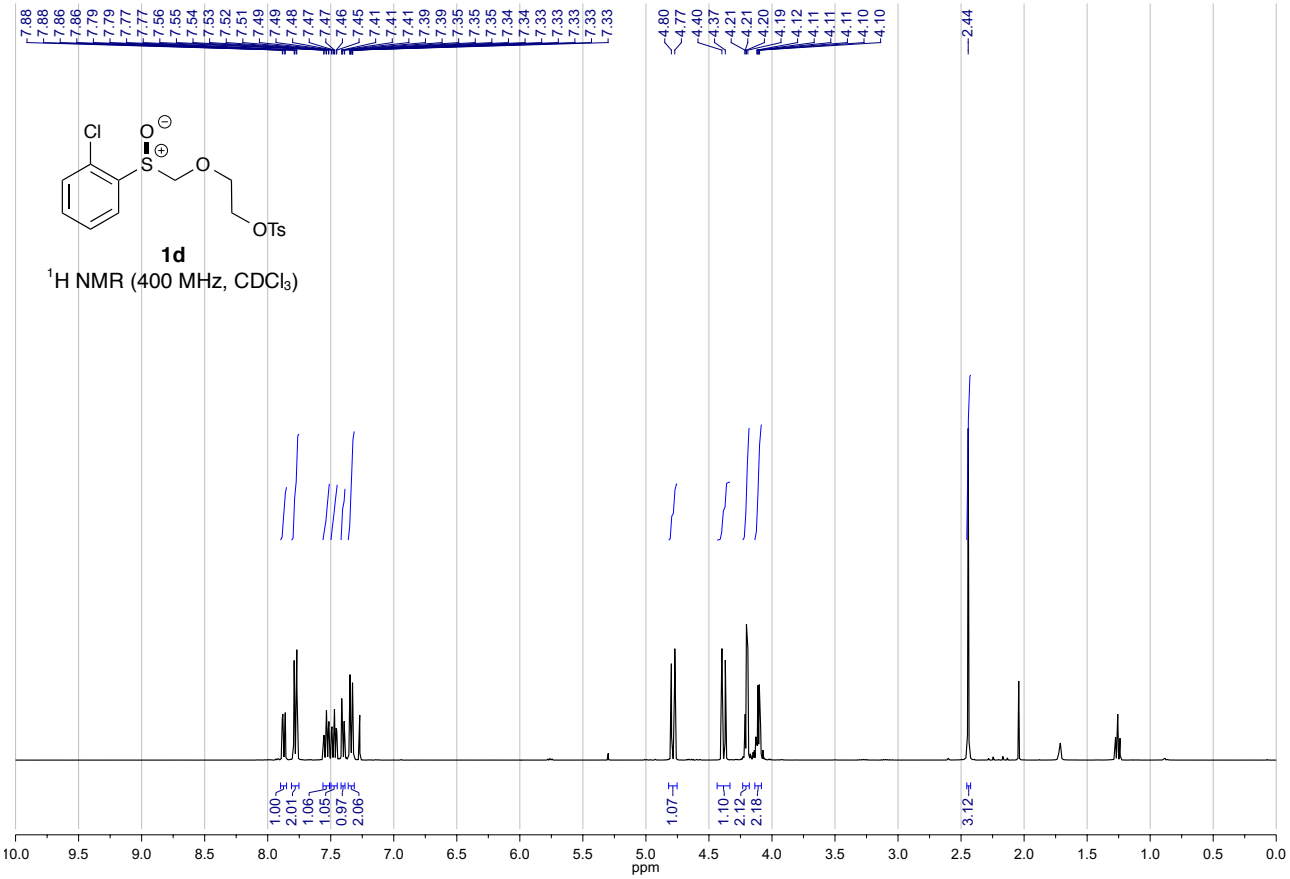

2c-B
13C NMR (100 MHz, CDCl3)
ppm

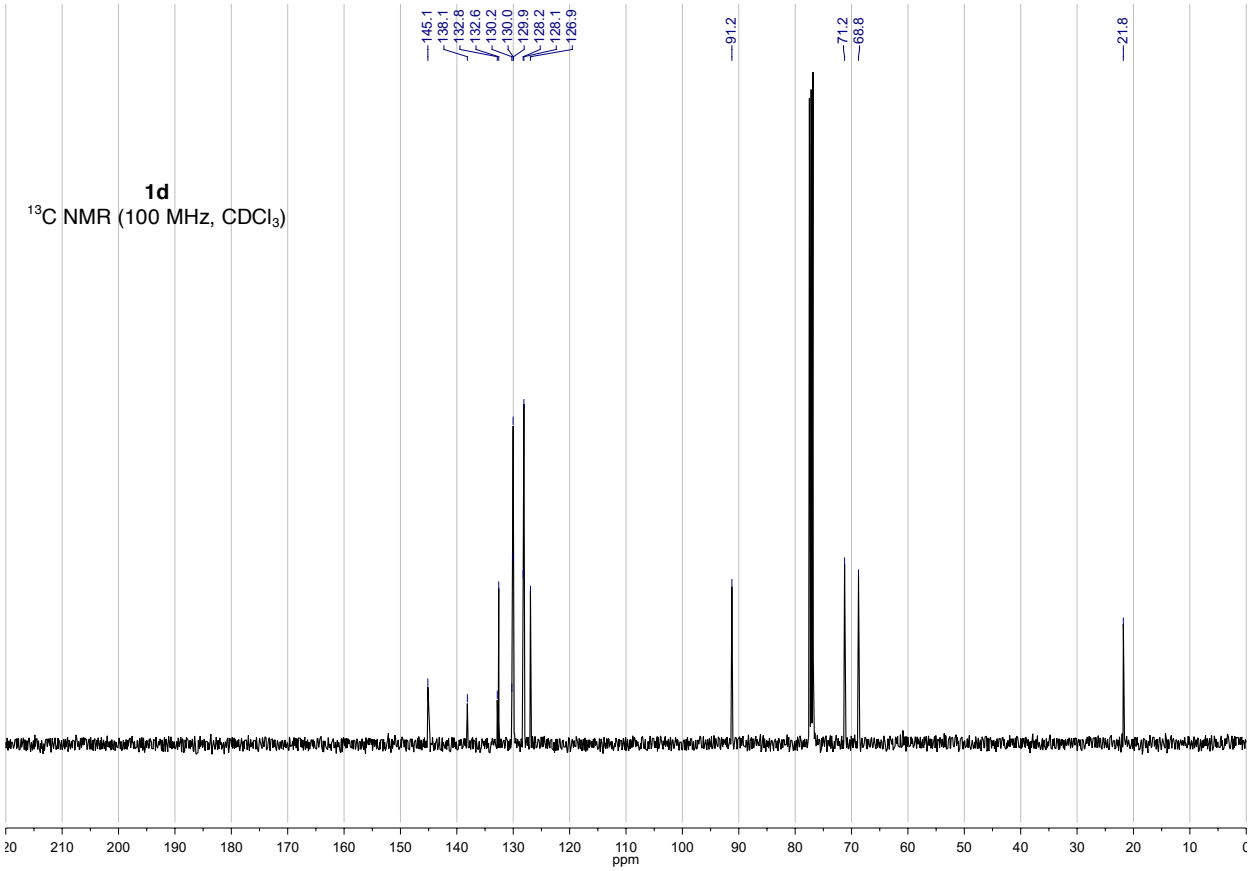

7.62
7.62
7.61
7.60
7.39
7.39
7.37
7.37
7.26
7.25
7.25
7.24
7.23
7.23
7.22
7.21
7.21
5.10
3.75
2.05
2.04
Cl
S
O
OH
4d
1H NMR (400 MHz, CDCl3)
1.00
0.98
1.09
1.05
2.22
4.43
0.99
ppm

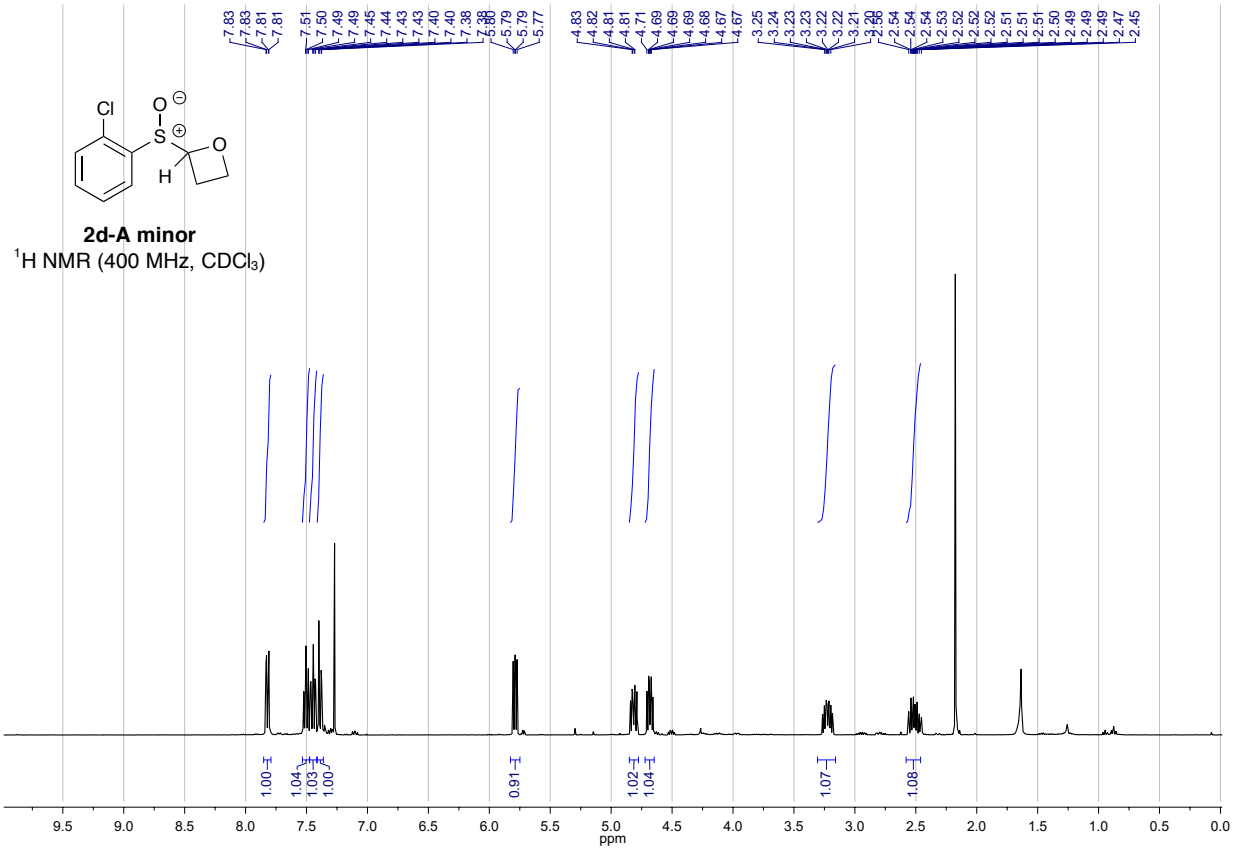

134.76
133.99
130.20
129.65
127.50
127.30
74.77
69.97
61.52
4d
13C NMR (100 MHz, CDCl3)
ppm

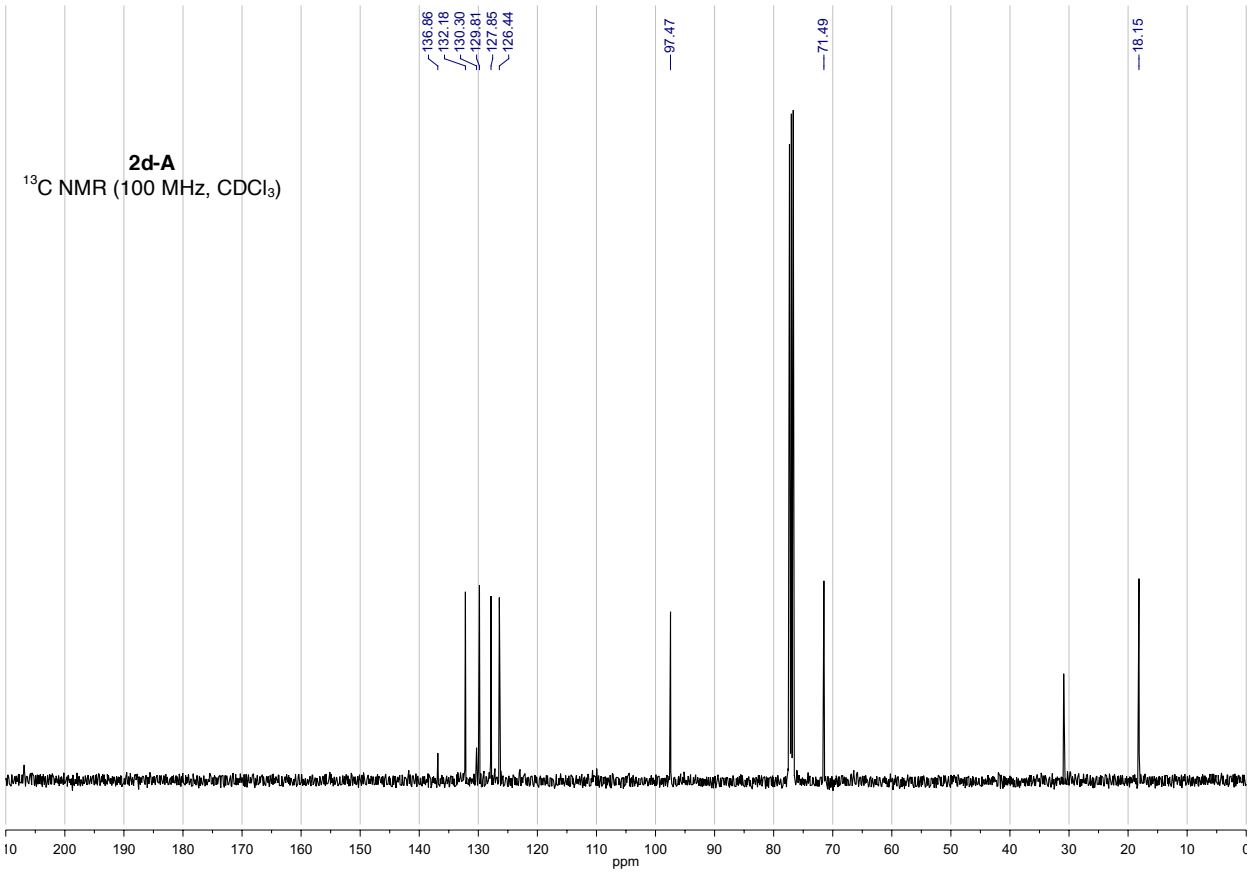

7.78
7.76
7.56
7.56
7.54
7.54
7.38
7.38
7.36
7.36
7.33
7.33
7.31
7.24
7.24
7.22
7.22
7.20
7.20
7.19
7.19
7.17
7.17
7.15
7.15
5.00
4.22
4.21
4.21
4.20
4.19
3.84
3.83
3.82
3.82
3.81
2.45
Cl
S
O
OTs
5d
1H NMR (400 MHz, CDCl3)
2.00
1.02
1.03
2.09
2.08
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm

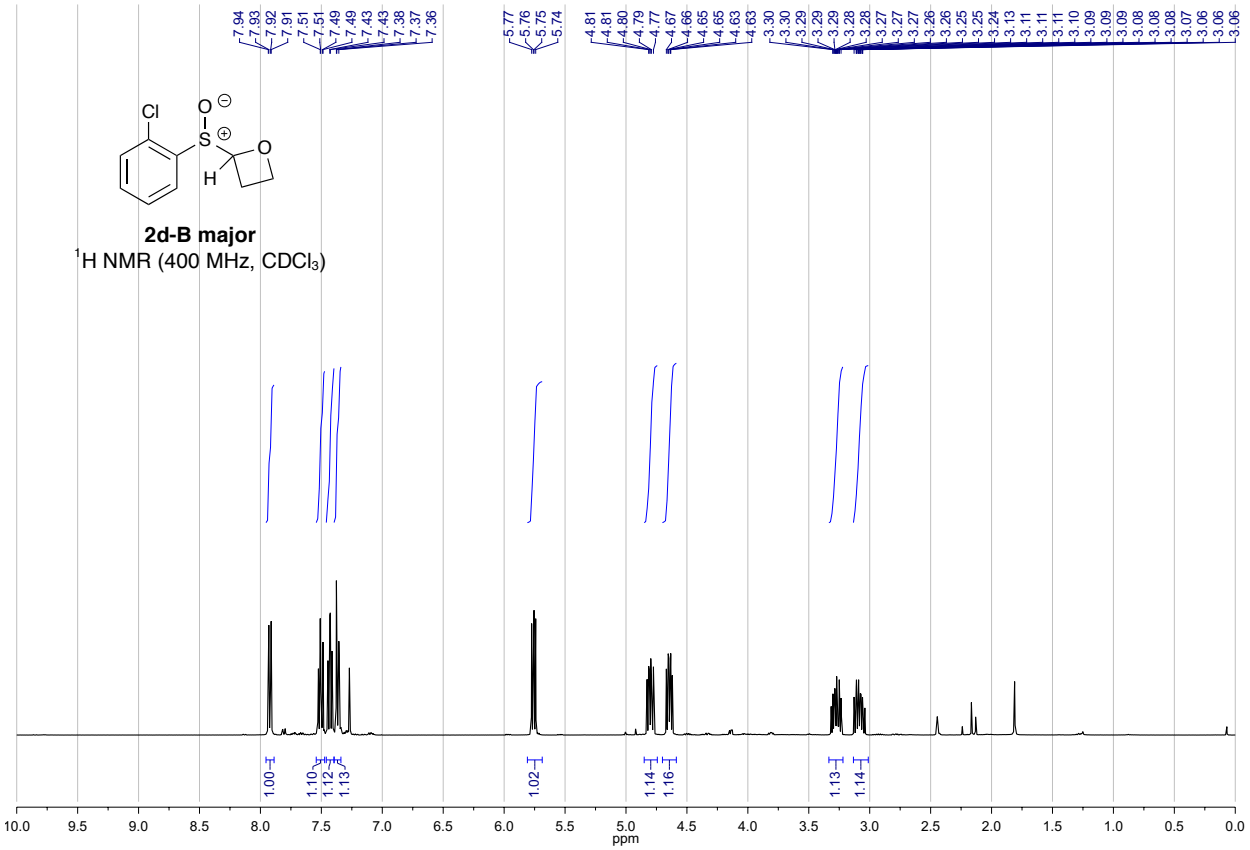

144.85
134.60
133.83
132.86
130.25
129.78
129.56
127.90
127.53
127.37
74.61
68.62
65.78
5d
13C NMR (100 MHz, CDCl3)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
ppm

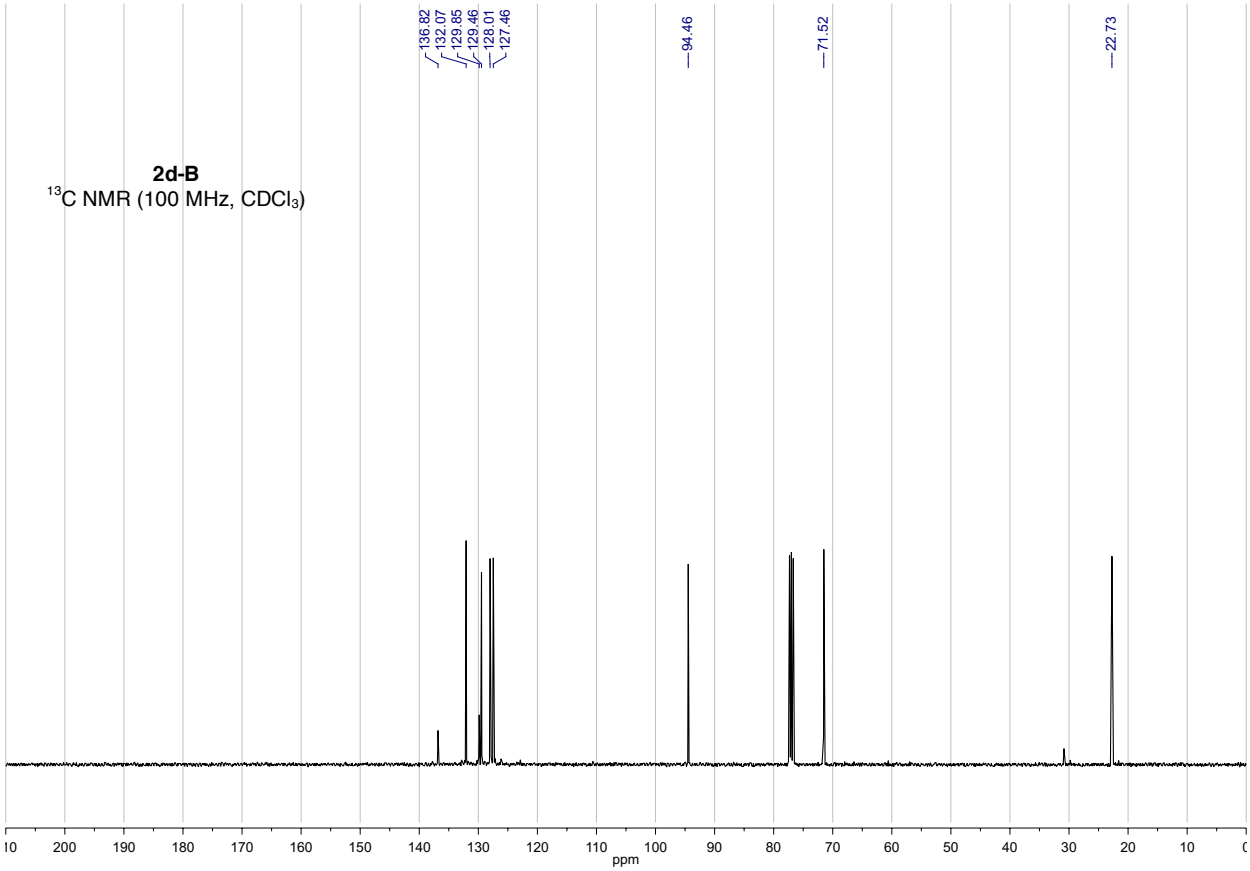

Cl
O
S
O
OTs
1d
^{1}H NMR (400 MHz, $CDCl_3$)
ppm

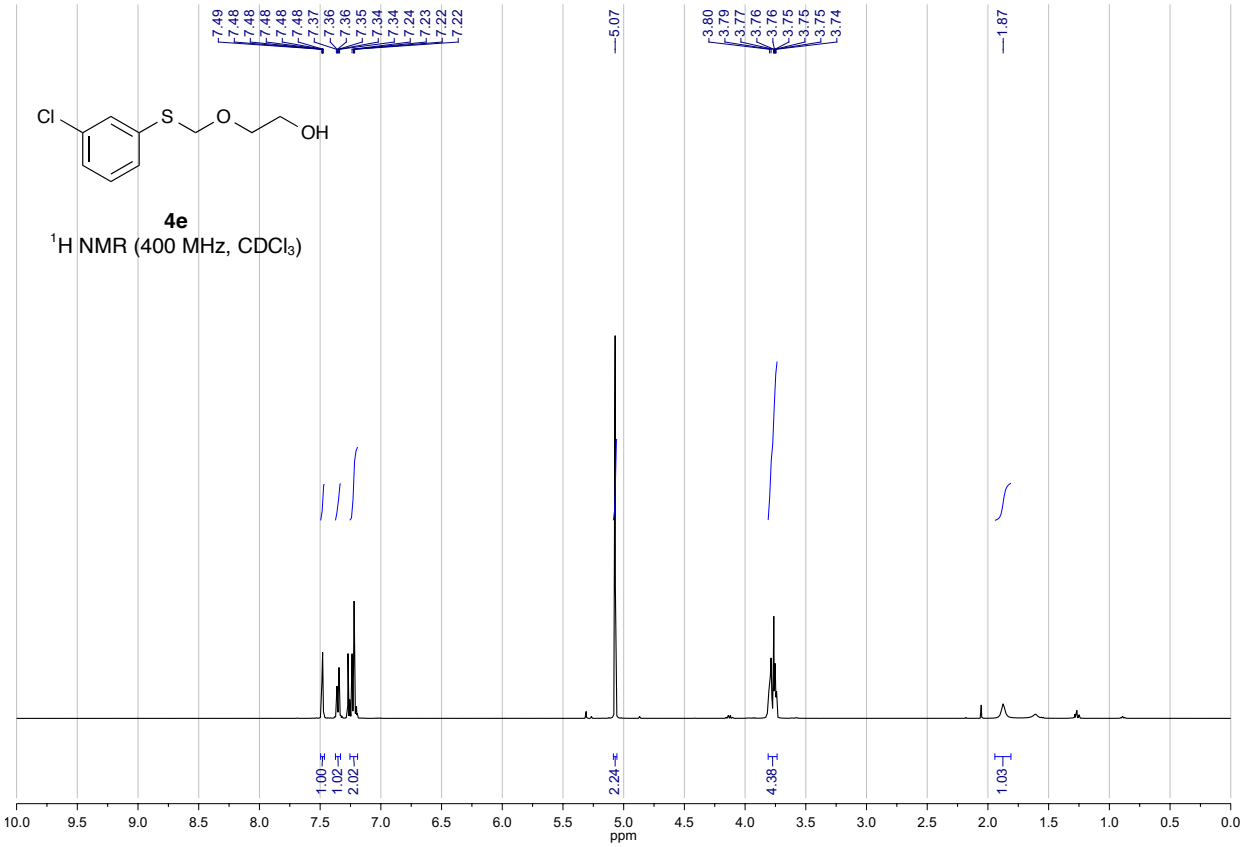

1d
^{13}C NMR (100 MHz, $CDCl_3$)
ppm

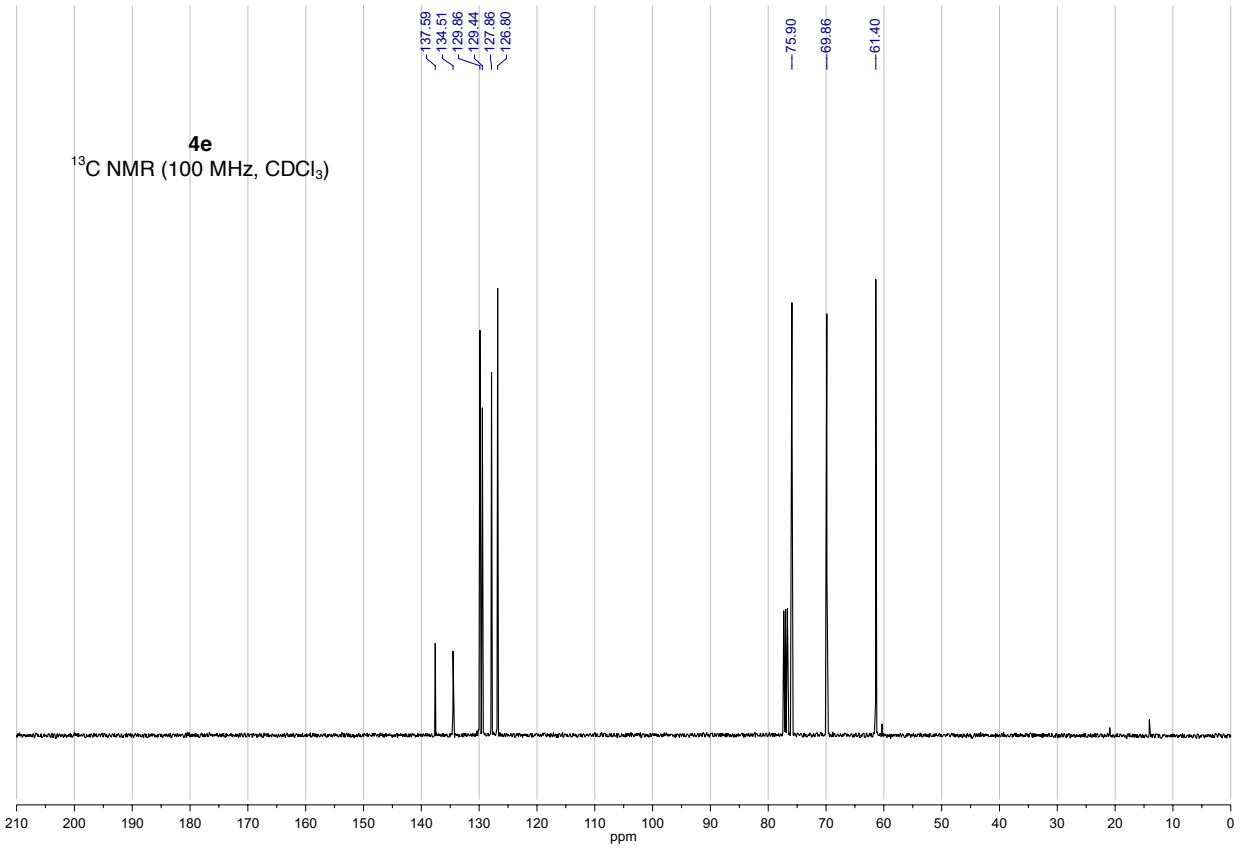

Cl
O
S
O
H
2d-A minor
1H NMR (400 MHz, CDCl3)
7.83
7.83
7.81
7.81
7.51
7.50
7.49
7.49
7.45
7.44
7.43
7.43
7.40
7.40
7.38
5.80
5.79
5.79
5.77
4.83
4.82
4.81
4.81
4.71
4.69
4.69
4.68
4.67
4.67
3.25
3.24
3.23
3.23
3.22
3.21
2.54
2.54
2.54
2.53
2.52
2.52
2.52
2.51
2.51
2.51
2.50
2.49
2.49
2.49
2.47
2.45
1.00
1.04
1.03
1.00
0.91
1.02
1.04
1.07
1.08
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm

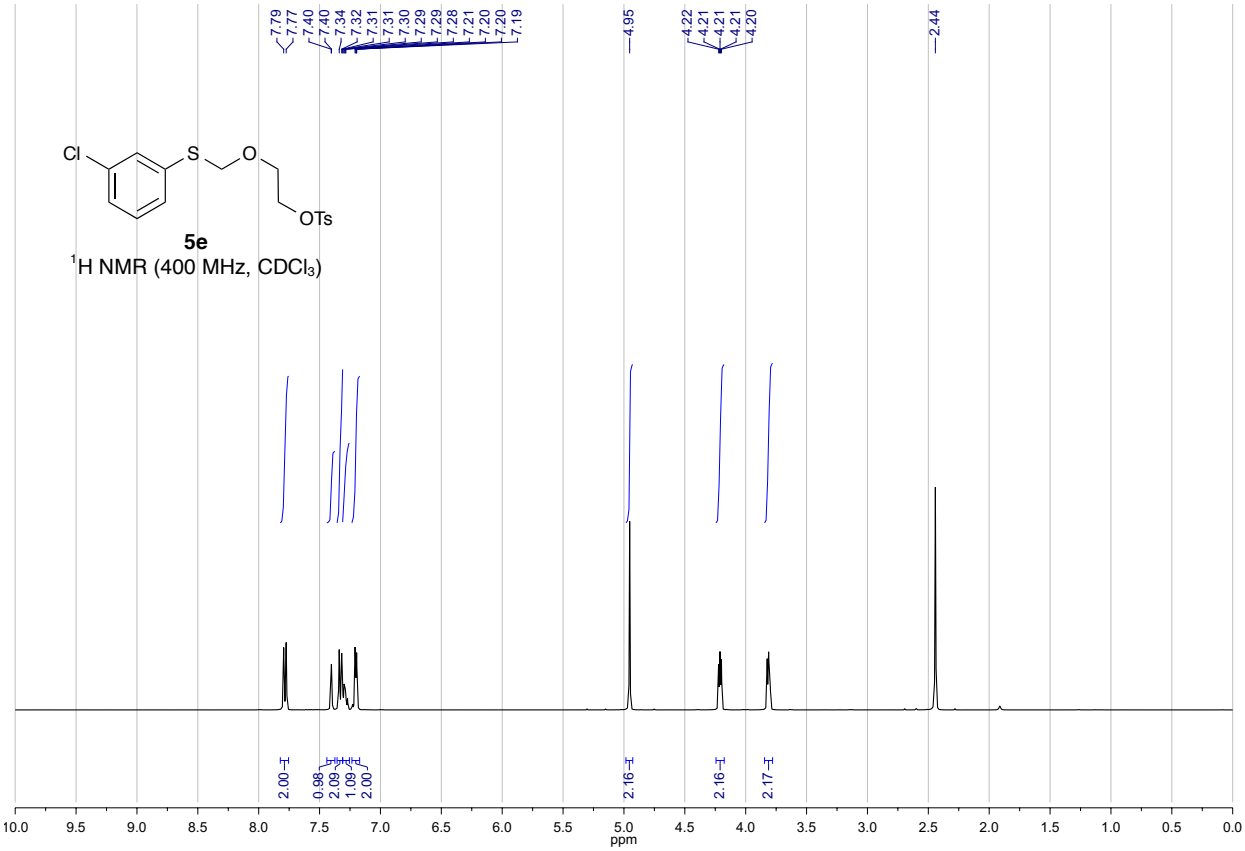

2d-A
13C NMR (100 MHz, CDCl3)
136.86
132.18
130.30
129.81
127.85
126.44
97.47
71.49
18.15
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

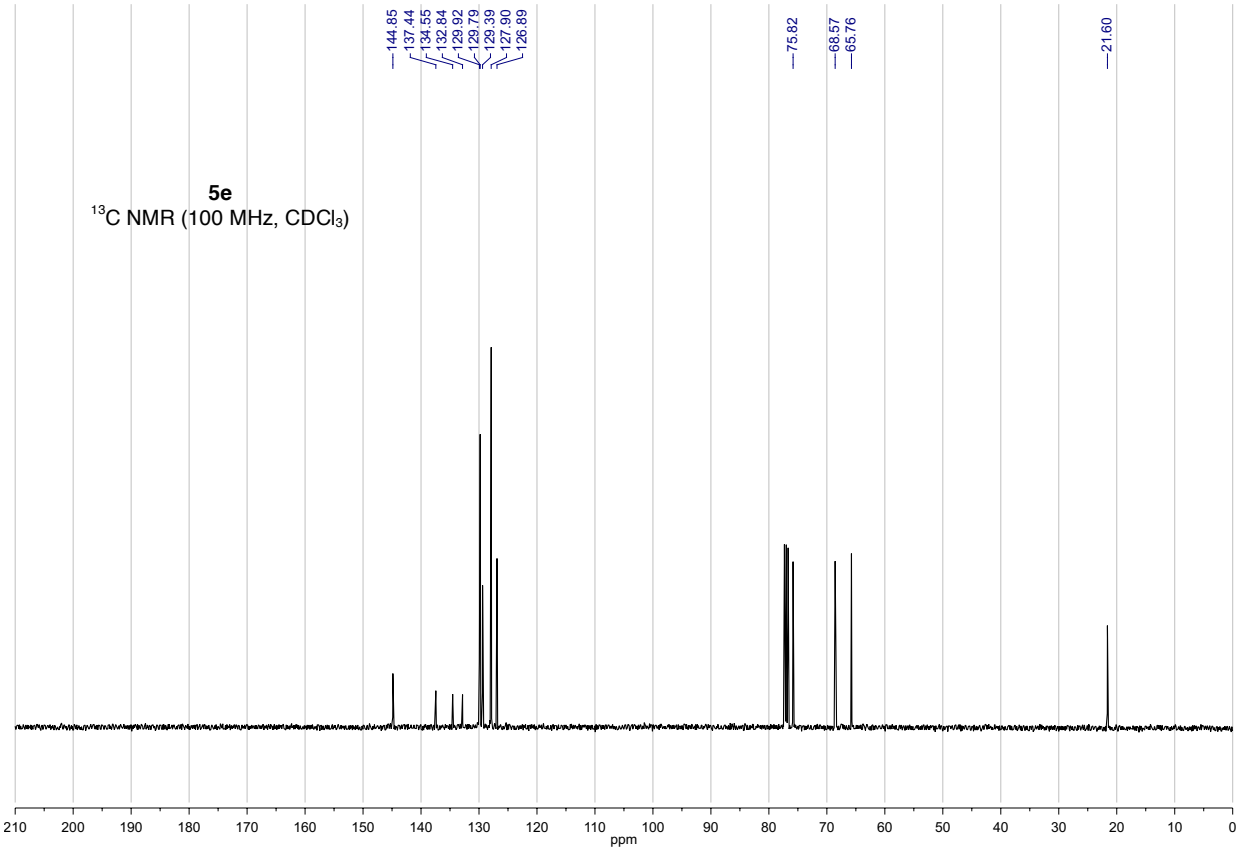

Cl
O
S
O
H
2d-B major
1H NMR (400 MHz, CDCl3)
ppm

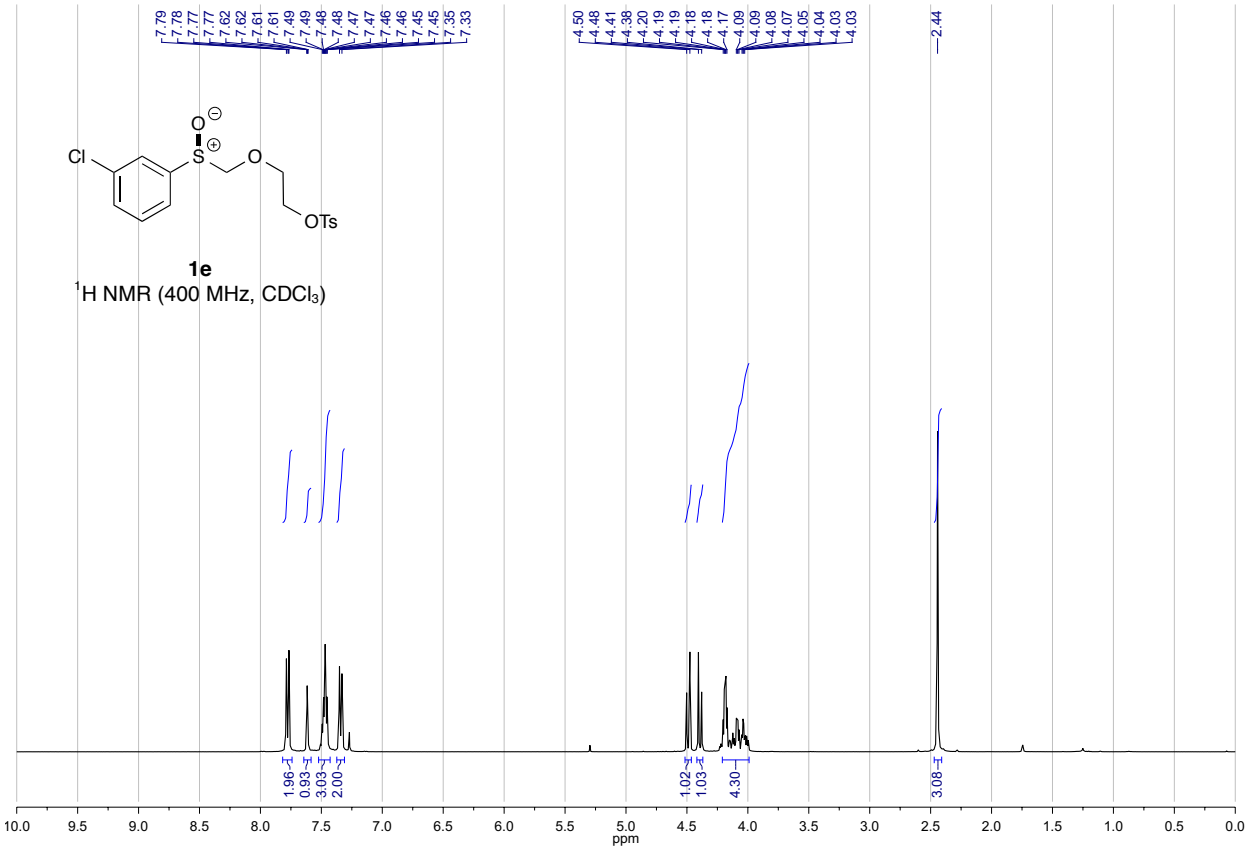

2d-B
13C NMR (100 MHz, CDCl3)
136.82
132.07
129.85
129.46
128.01
127.46
94.46
71.52
22.73
ppm

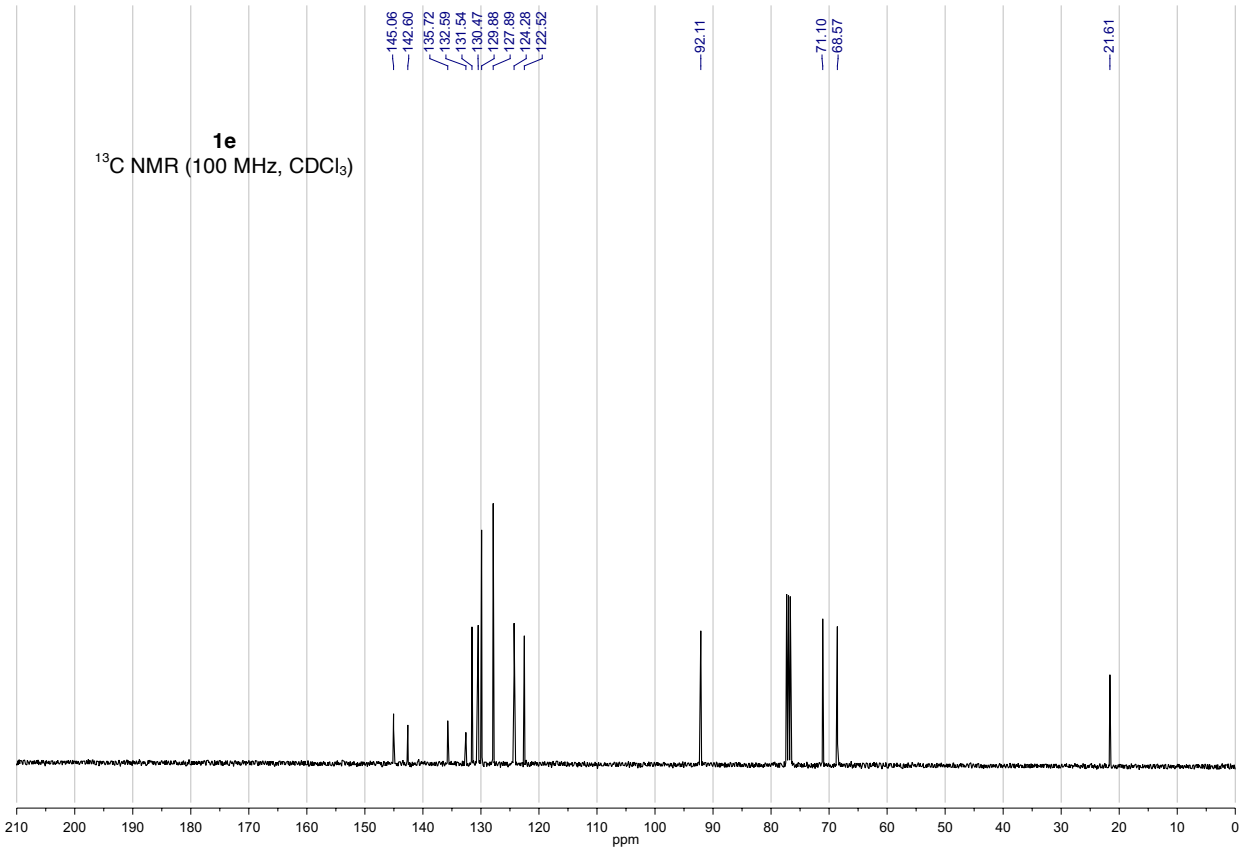

7.49
7.48
7.48
7.48
7.48
7.48
7.37
7.36
7.36
7.35
7.34
7.34
7.24
7.23
7.22
7.22
5.07
3.80
3.79
3.77
3.76
3.76
3.75
3.75
3.75
3.74
1.87
Cl
S
O
OH
4e
1H NMR (400 MHz, CDCl3)
1.00
1.02
2.02
2.24
4.38
1.03
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
ppm

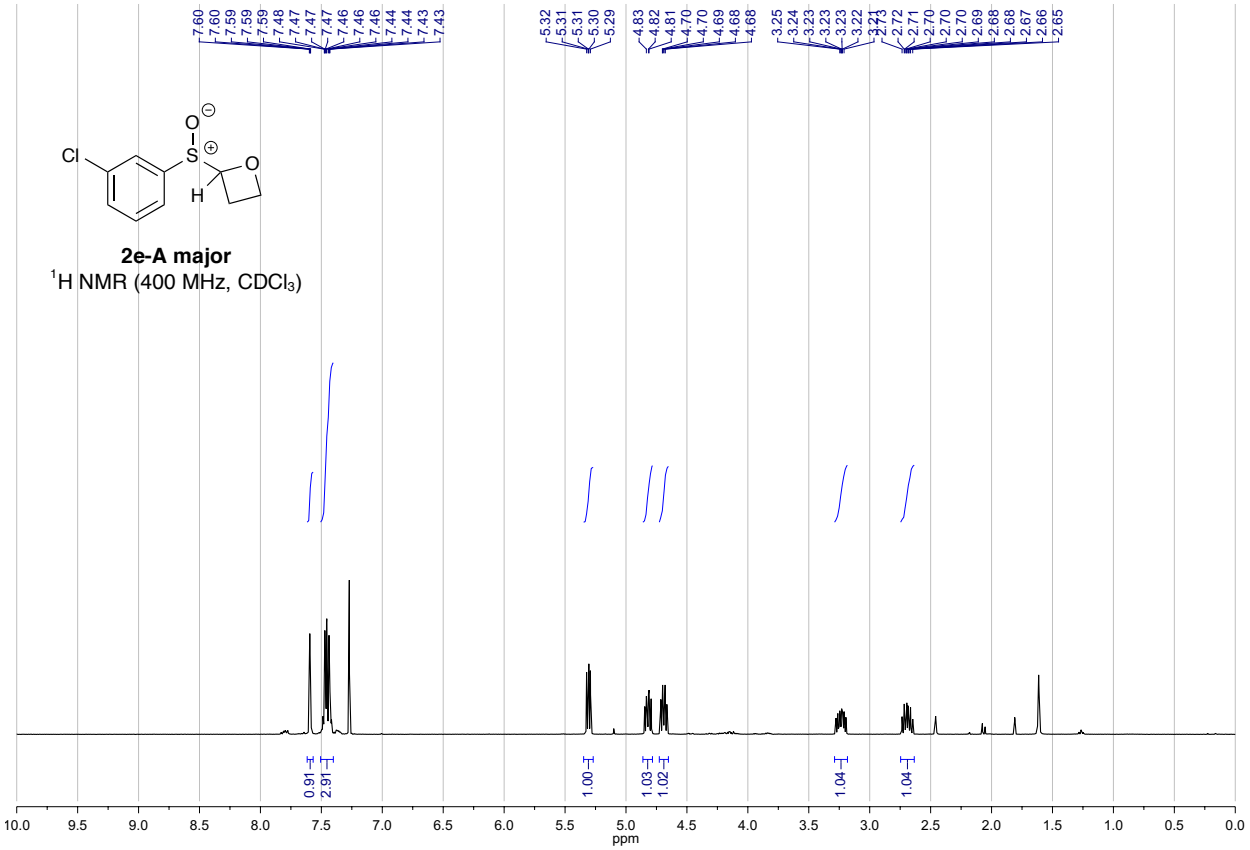

137.59
134.51
129.86
129.44
127.86
126.80
75.90
69.86
61.40
4e
13C NMR (100 MHz, CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm

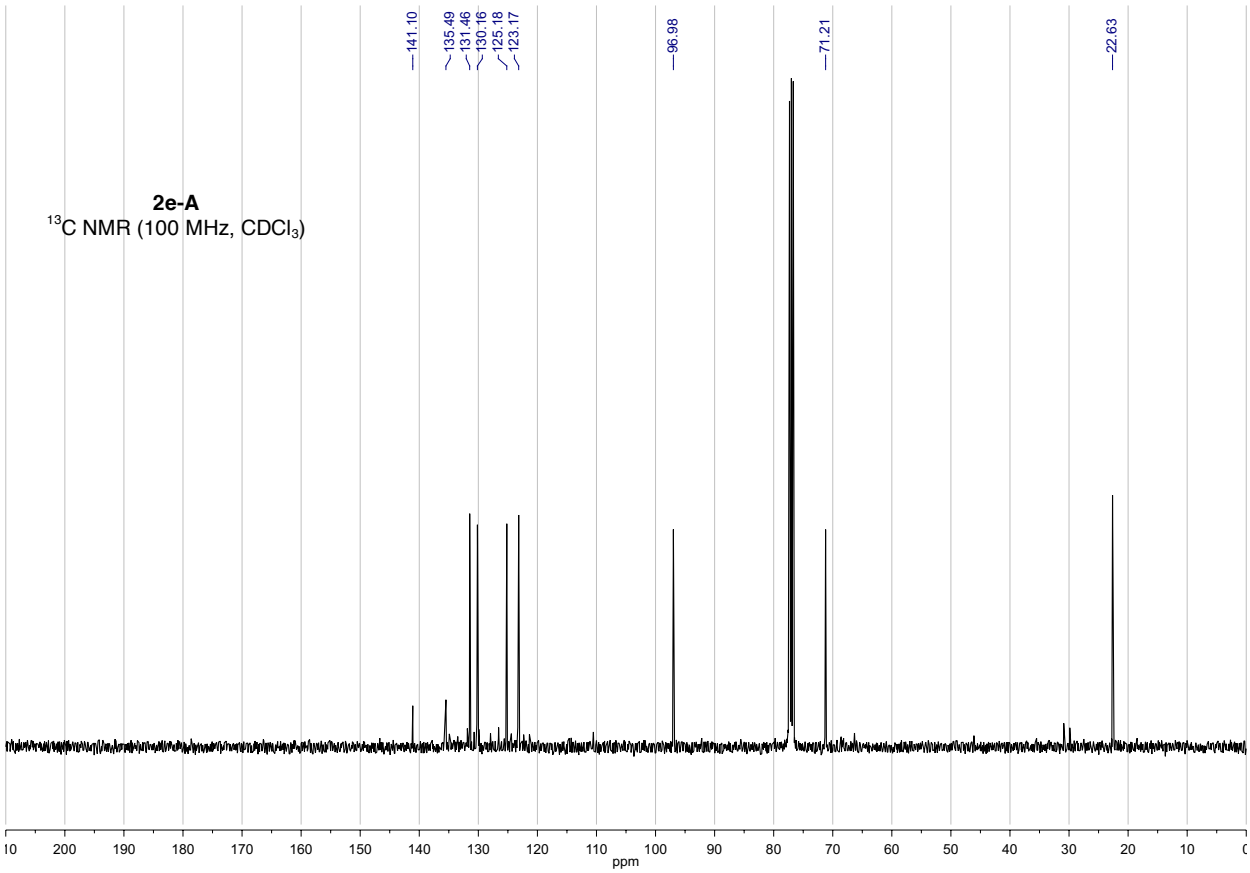

7.79
7.77
7.40
7.40
7.34
7.32
7.31
7.31
7.30
7.29
7.29
7.28
7.21
7.20
7.20
7.19
4.95
4.22
4.21
4.21
4.21
4.20
2.44
Cl
S
O
OTs
5e
1H NMR (400 MHz, CDCl3)
2.00
0.98
2.09
1.09
2.00
2.16
2.16
2.17
ppm

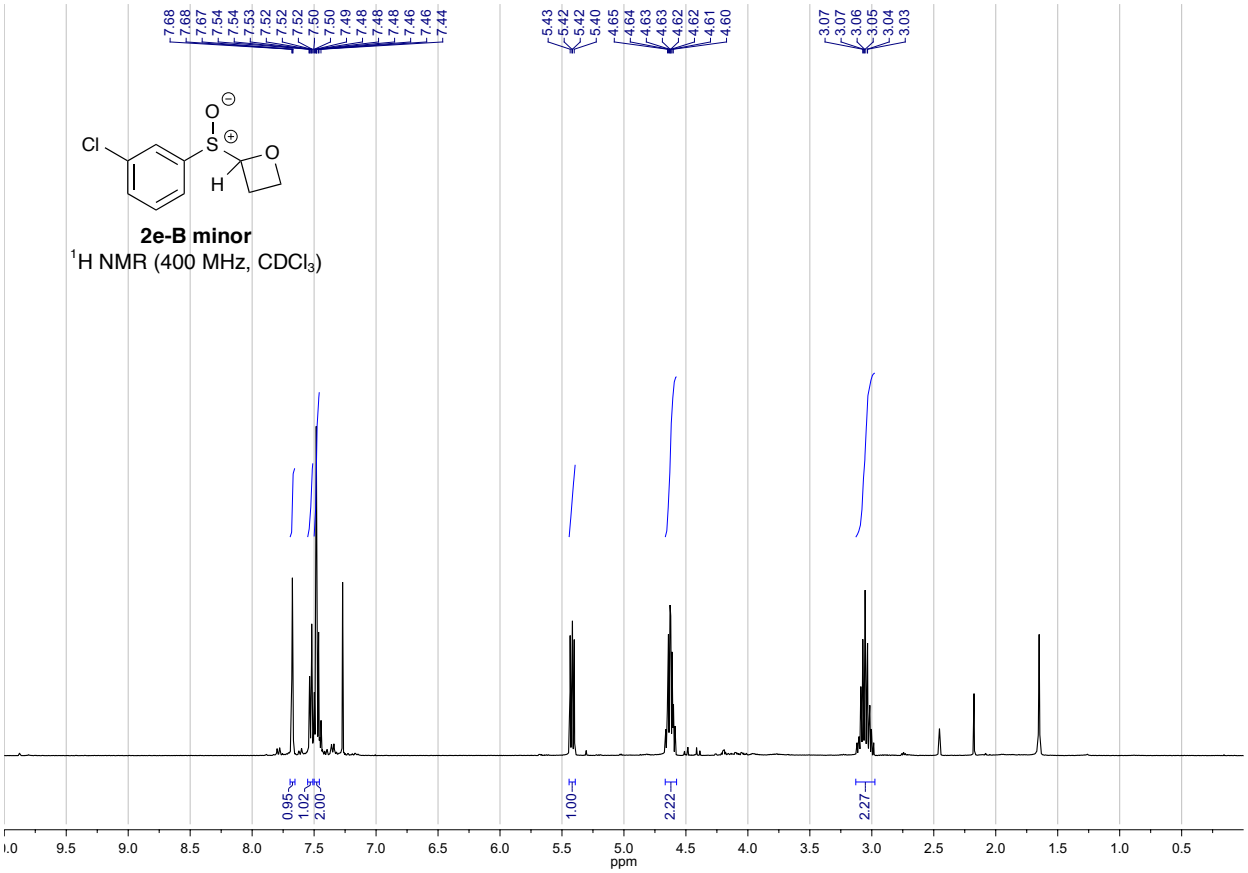

144.85
137.44
134.55
132.84
129.92
129.79
129.39
127.90
126.89
75.82
68.57
65.76
21.60
5e
13C NMR (100 MHz, CDCl3)
ppm

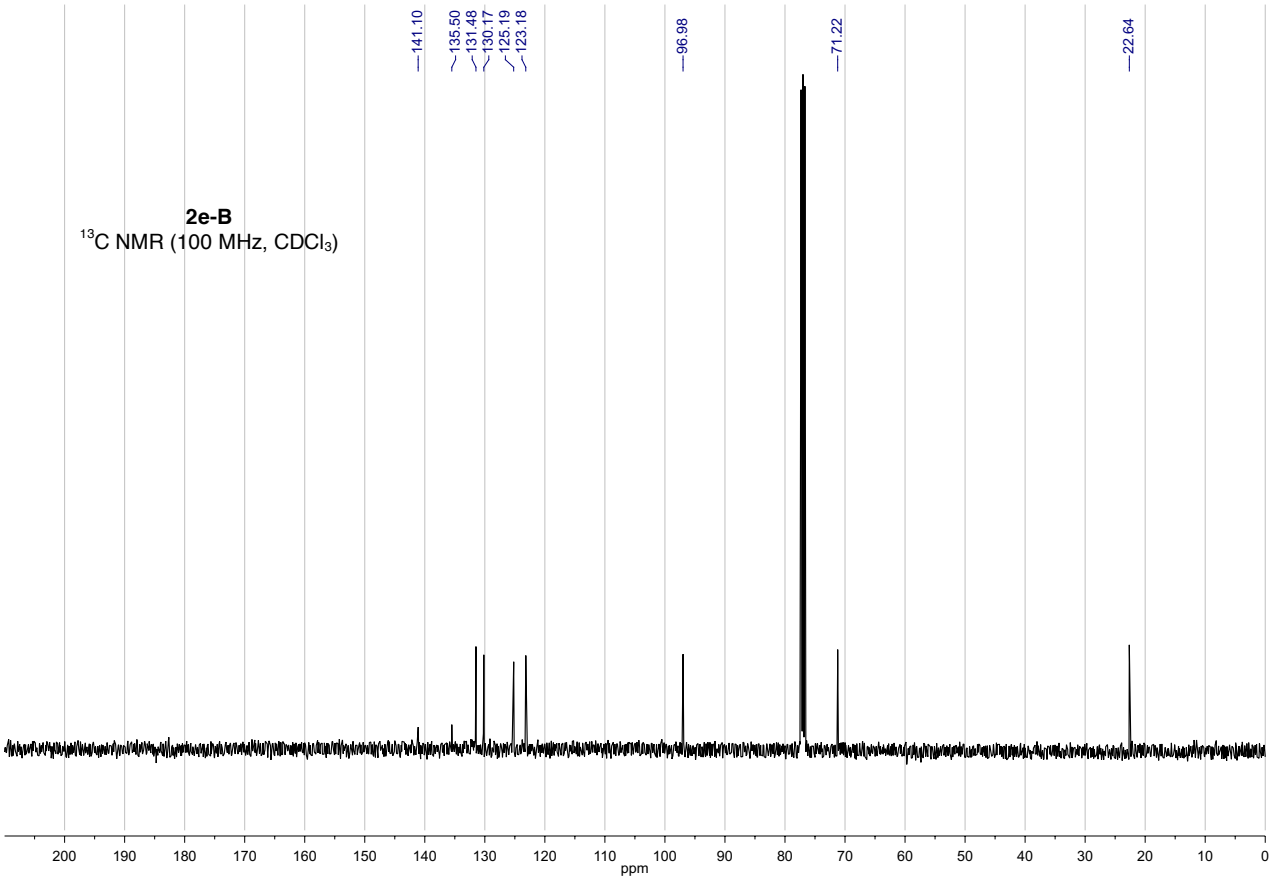

7.79
7.78
7.77
7.77
7.62
7.62
7.61
7.61
7.49
7.49
7.48
7.48
7.47
7.47
7.46
7.46
7.45
7.45
7.35
7.33
4.50
4.48
4.41
4.38
4.20
4.19
4.19
4.18
4.17
4.09
4.09
4.08
4.07
4.05
4.04
4.03
4.03
2.44
Cl
O
S
O
OTs
1e
1H NMR (400 MHz, CDCl3)
1.96
0.93
3.03
2.00
1.02
1.03
4.30
3.08
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm

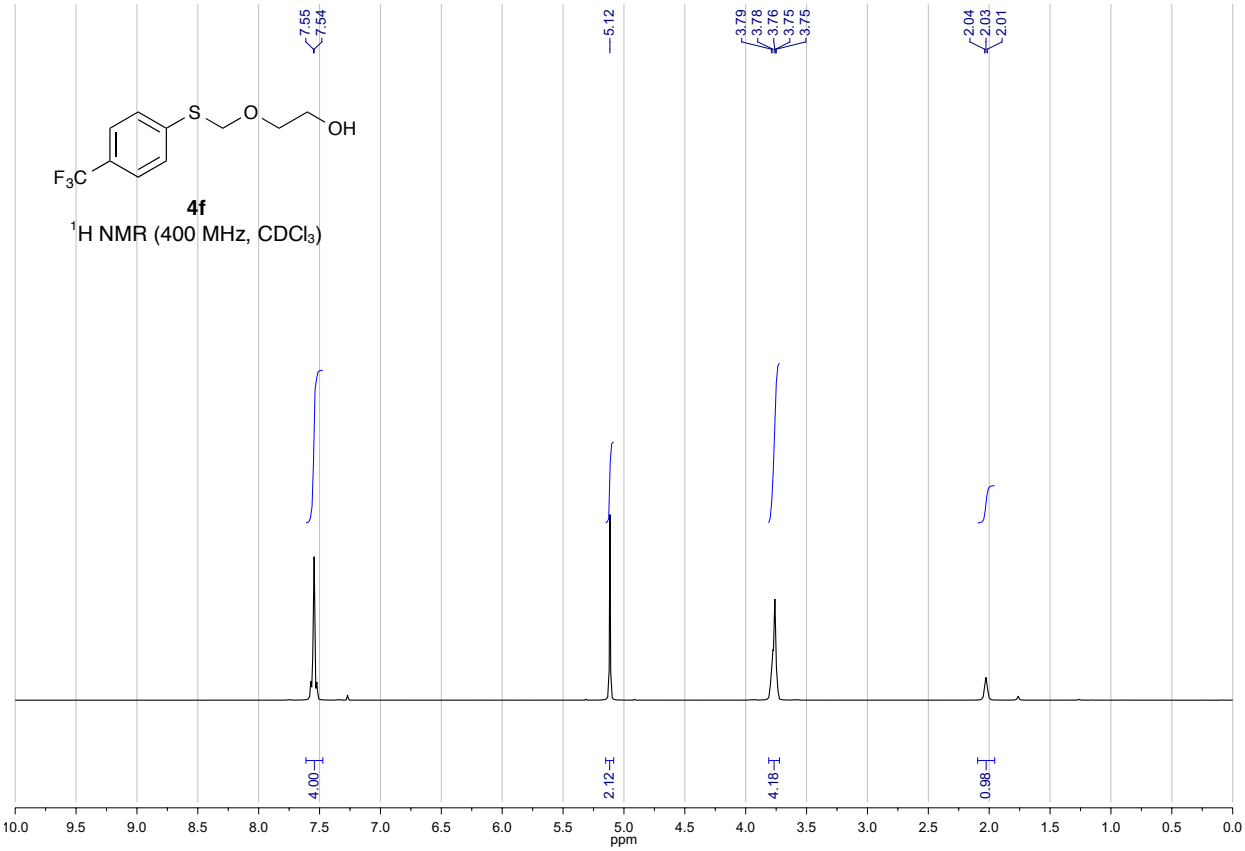

145.06
142.60
135.72
132.59
131.54
130.47
129.88
127.89
124.28
122.52
92.11
71.10
68.57
21.61
1e
13C NMR (100 MHz, CDCl3)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

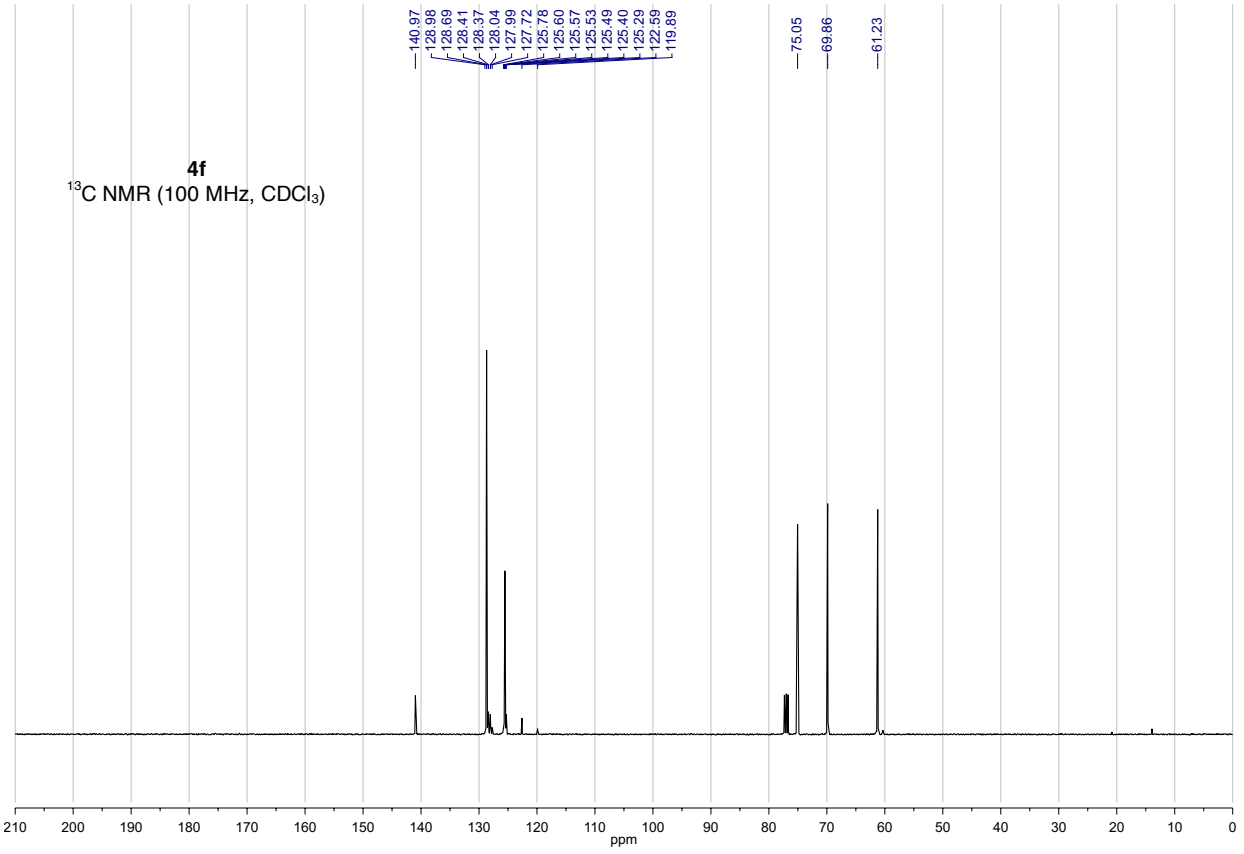

Cl
O
S
O
H
2e-A major
^{1}H NMR (400 MHz, CDCl$_3$)
ppm

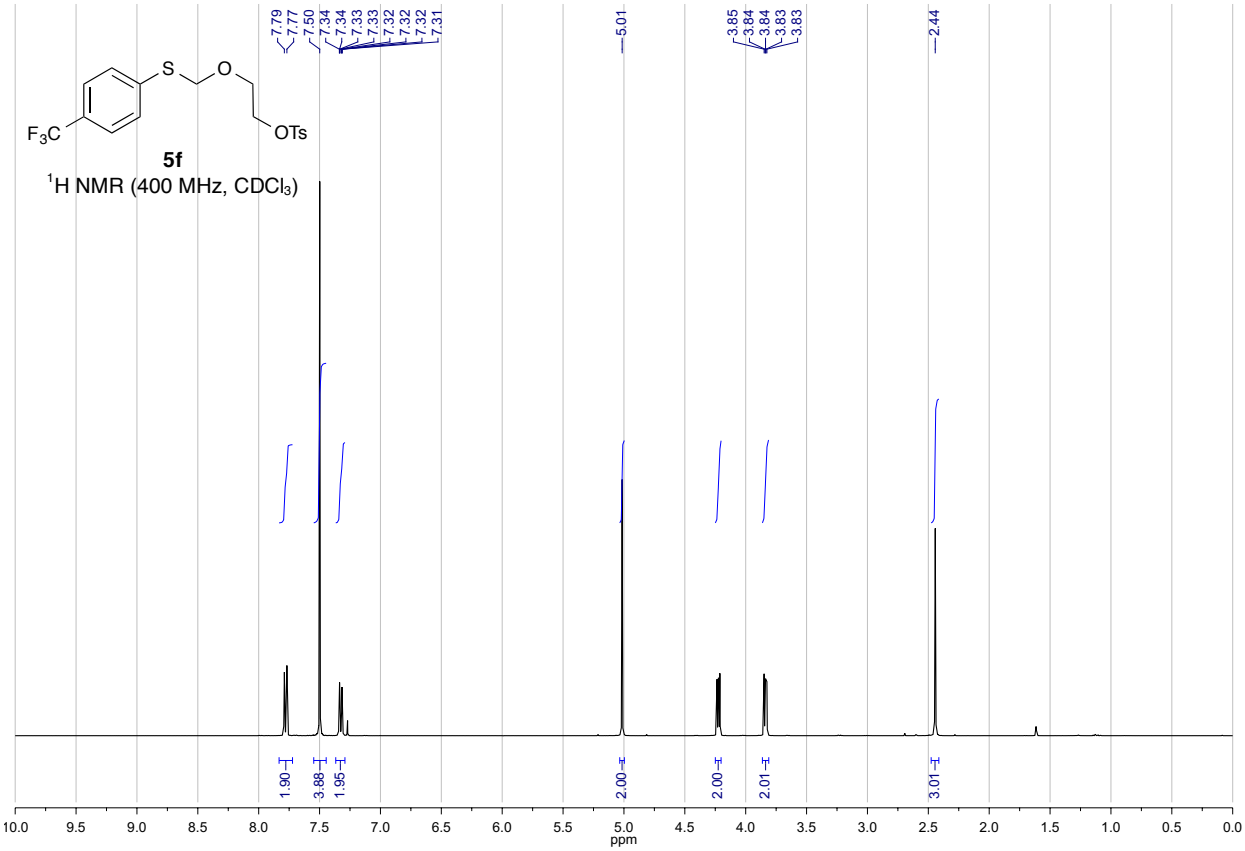

2e-A
^{13}C NMR (100 MHz, CDCl$_3$)
141.10
135.49
131.46
130.16
125.18
123.17
96.98
71.21
22.63
ppm

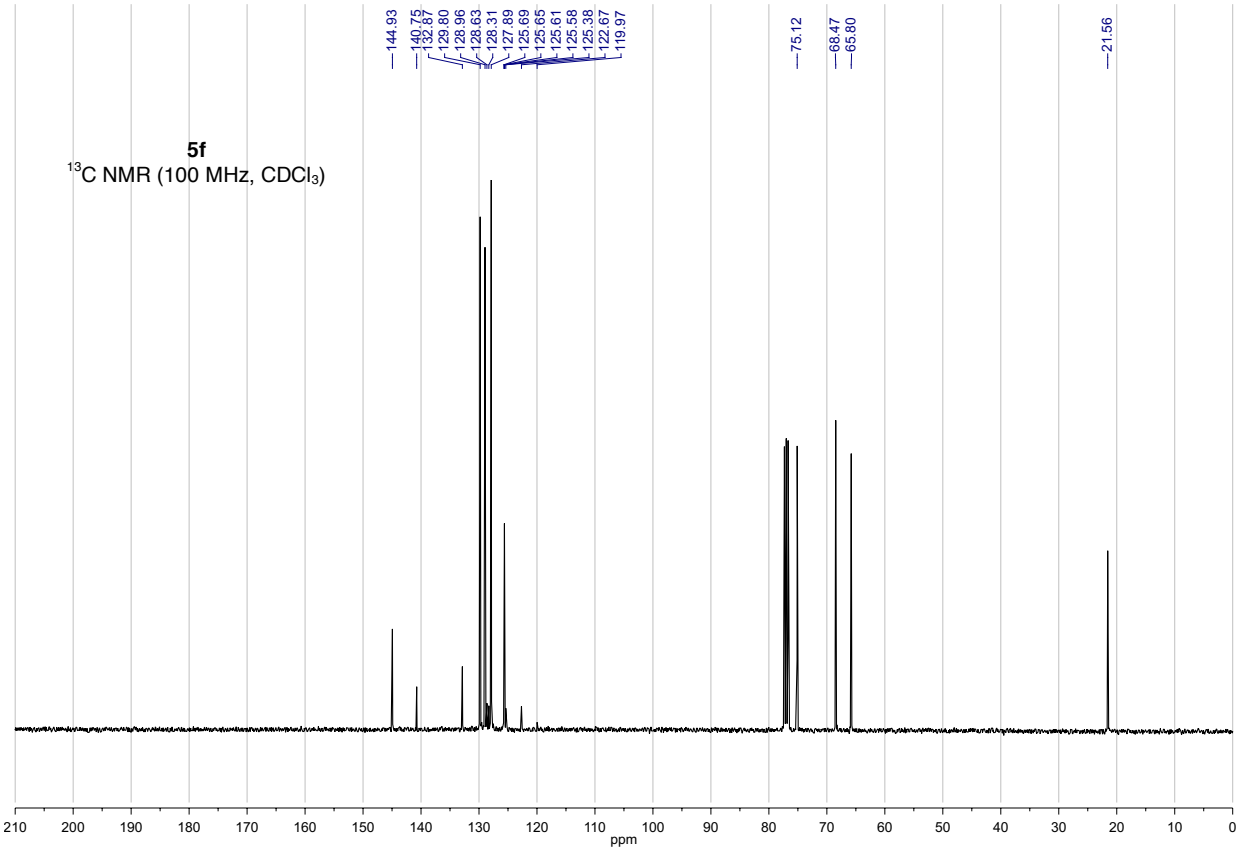

7.68
7.68
7.67
7.54
7.54
7.53
7.52
7.52
7.52
7.50
7.50
7.49
7.48
7.48
7.48
7.46
7.46
7.44
5.43
5.42
5.42
5.40
4.65
4.64
4.63
4.63
4.62
4.62
4.61
4.60
3.07
3.07
3.06
3.05
3.04
3.03
Cl
O
S
O
H
2e-B minor
1H NMR (400 MHz, CDCl3)
0.95
1.02
2.00
1.00
2.22
2.27
ppm

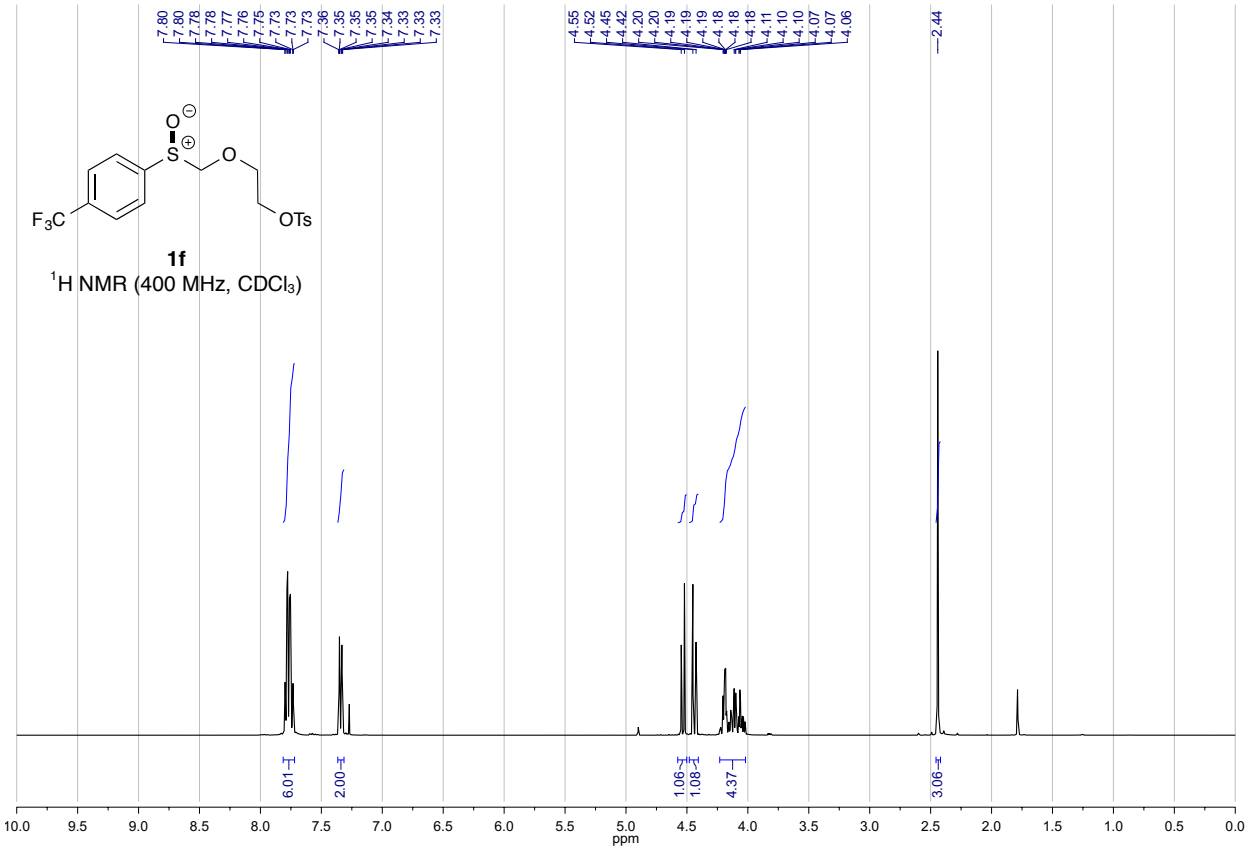

141.10
135.50
131.48
130.17
125.19
123.18
96.98
71.22
22.64
2e-B
13C NMR (100 MHz, CDCl3)
ppm

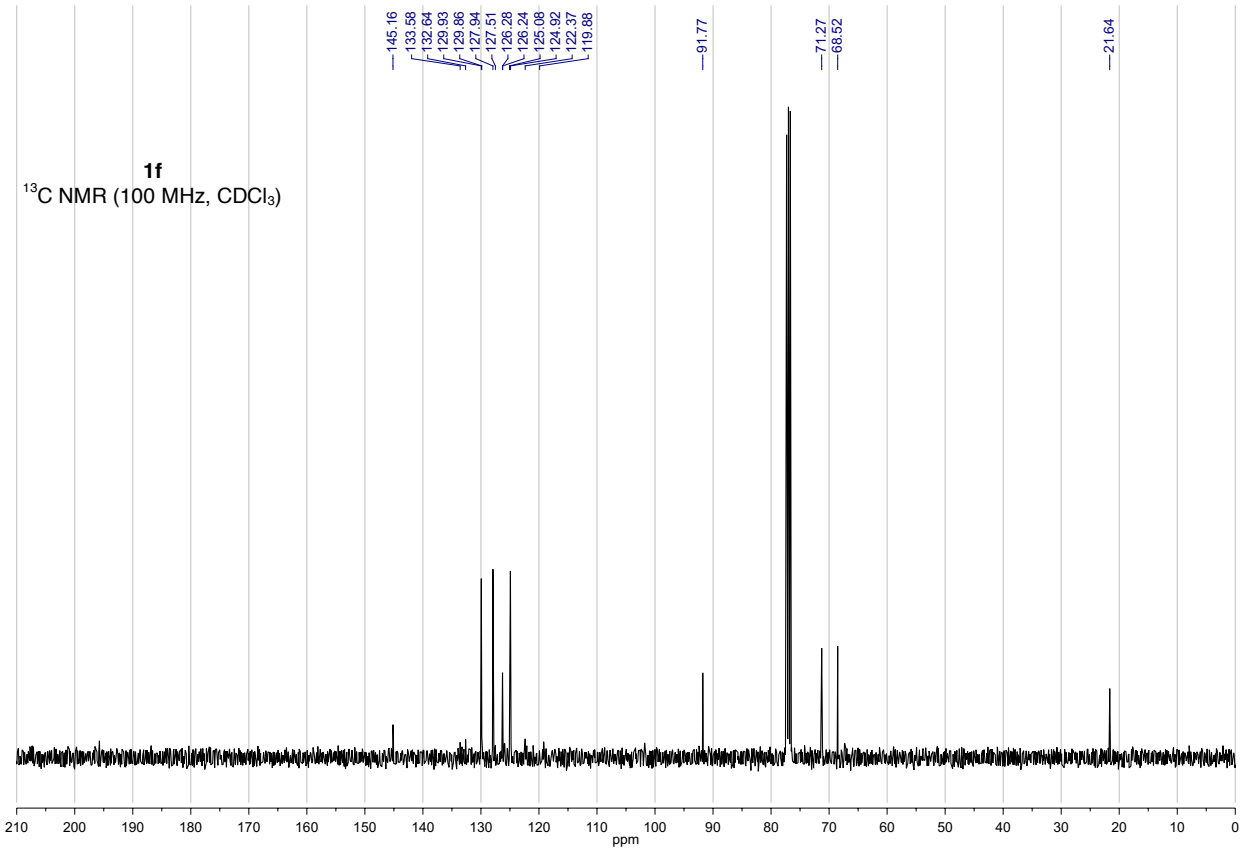

7.55
7.54
5.12
3.79
3.78
3.76
3.75
3.75
2.04
2.03
2.01
S
O
OH
F3C
4f
1H NMR (400 MHz, CDCl3)
4.00
2.12
4.18
0.98
ppm

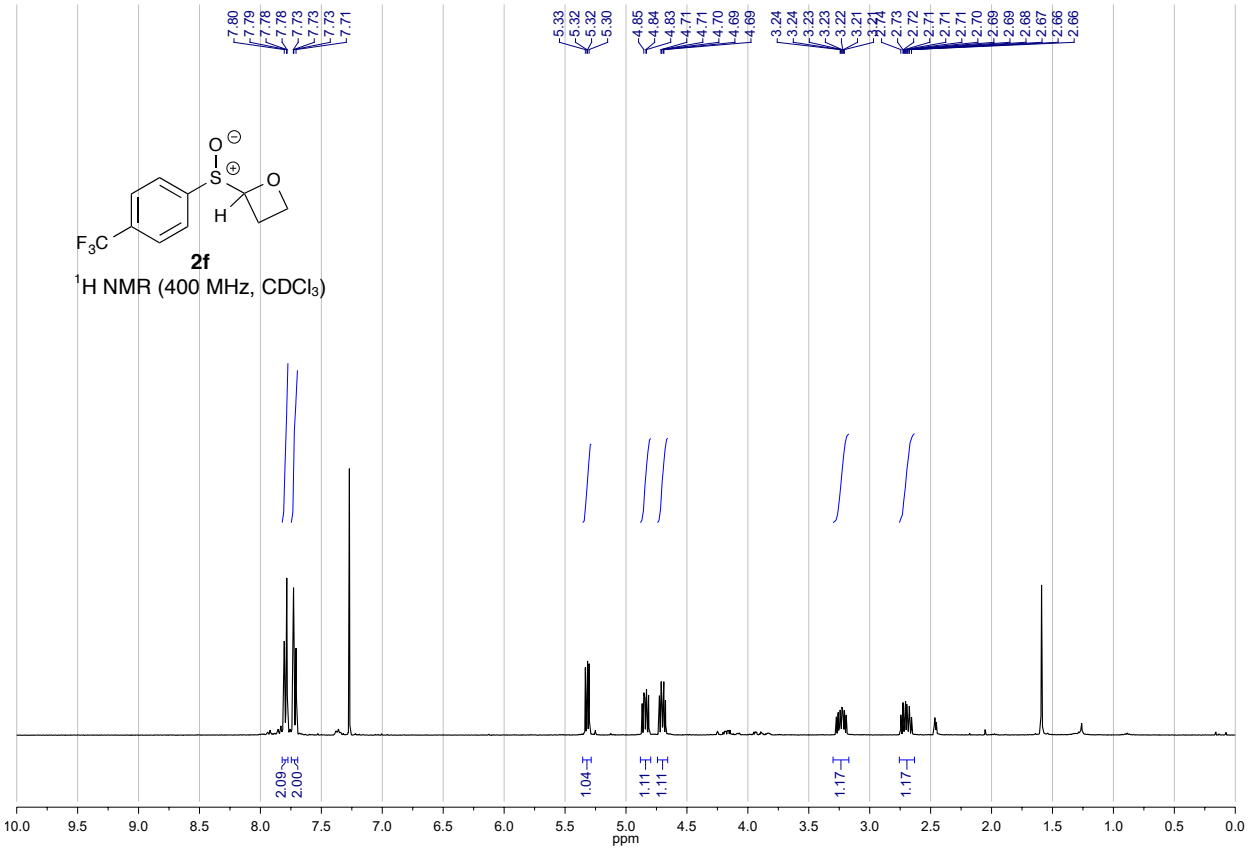

140.97
128.98
128.69
128.41
128.37
128.04
127.99
127.72
125.78
125.60
125.57
125.53
125.49
125.40
125.29
122.59
119.89
75.05
69.86
61.23
4f
13C NMR (100 MHz, CDCl3)
ppm

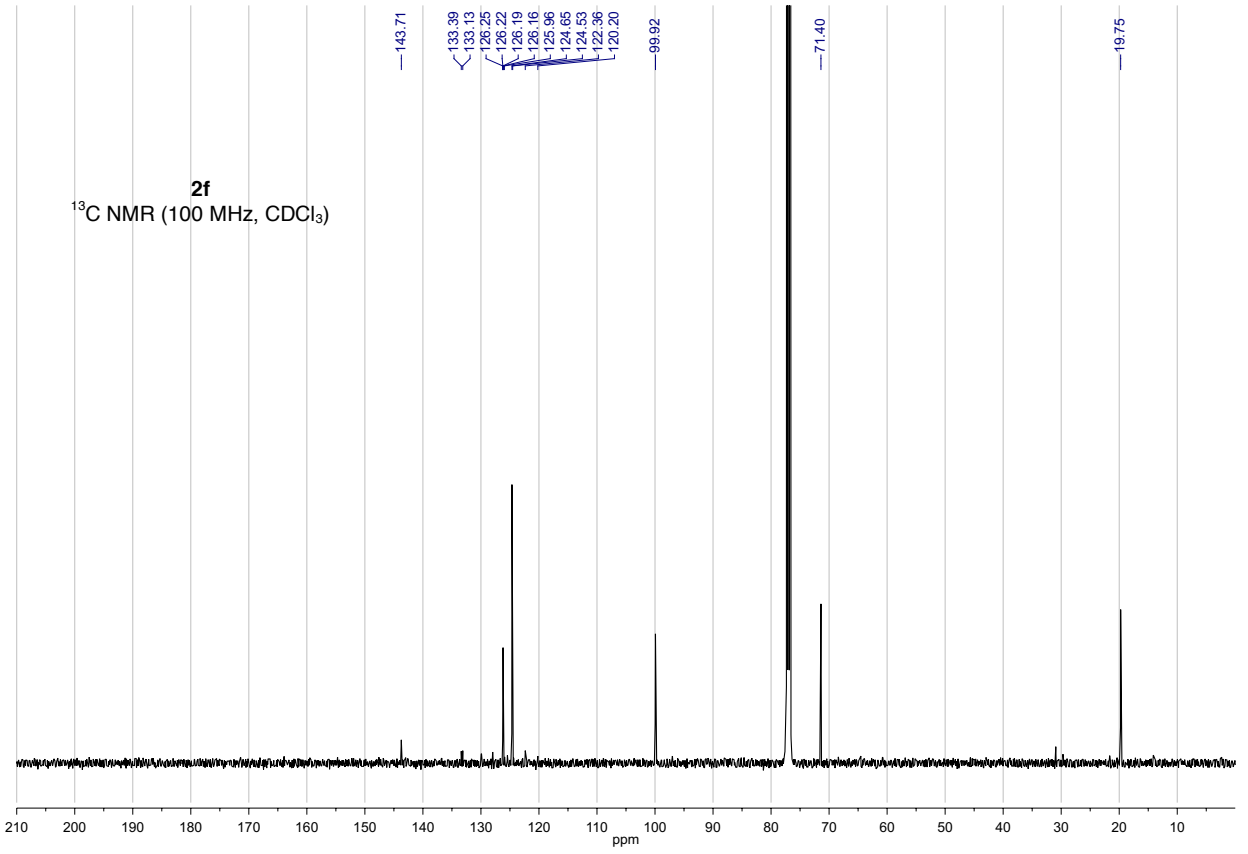

7.79
7.77
7.50
7.34
7.34
7.33
7.33
7.32
7.32
7.32
7.32
7.31
5.01
3.85
3.84
3.84
3.83
3.83
2.44
S
O
F3C
OTs
5f
1H NMR (400 MHz, CDCl3)
1.90
3.88
1.95
2.00
2.00
2.01
3.01
ppm

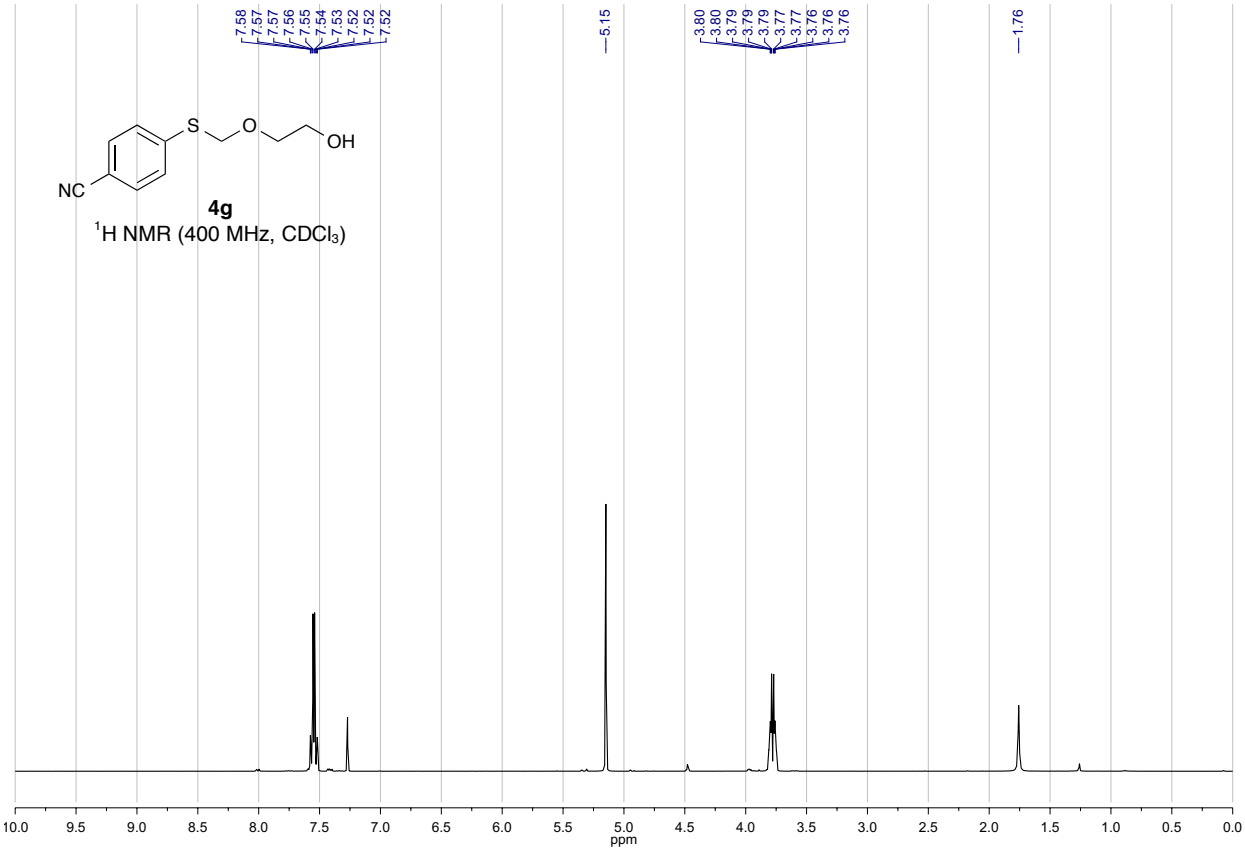

144.93
140.75
132.87
129.80
128.96
128.63
128.31
127.89
125.69
125.65
125.61
125.58
125.38
122.67
119.97
75.12
68.47
65.80
21.56
5f
13C NMR (100 MHz, CDCl3)
ppm

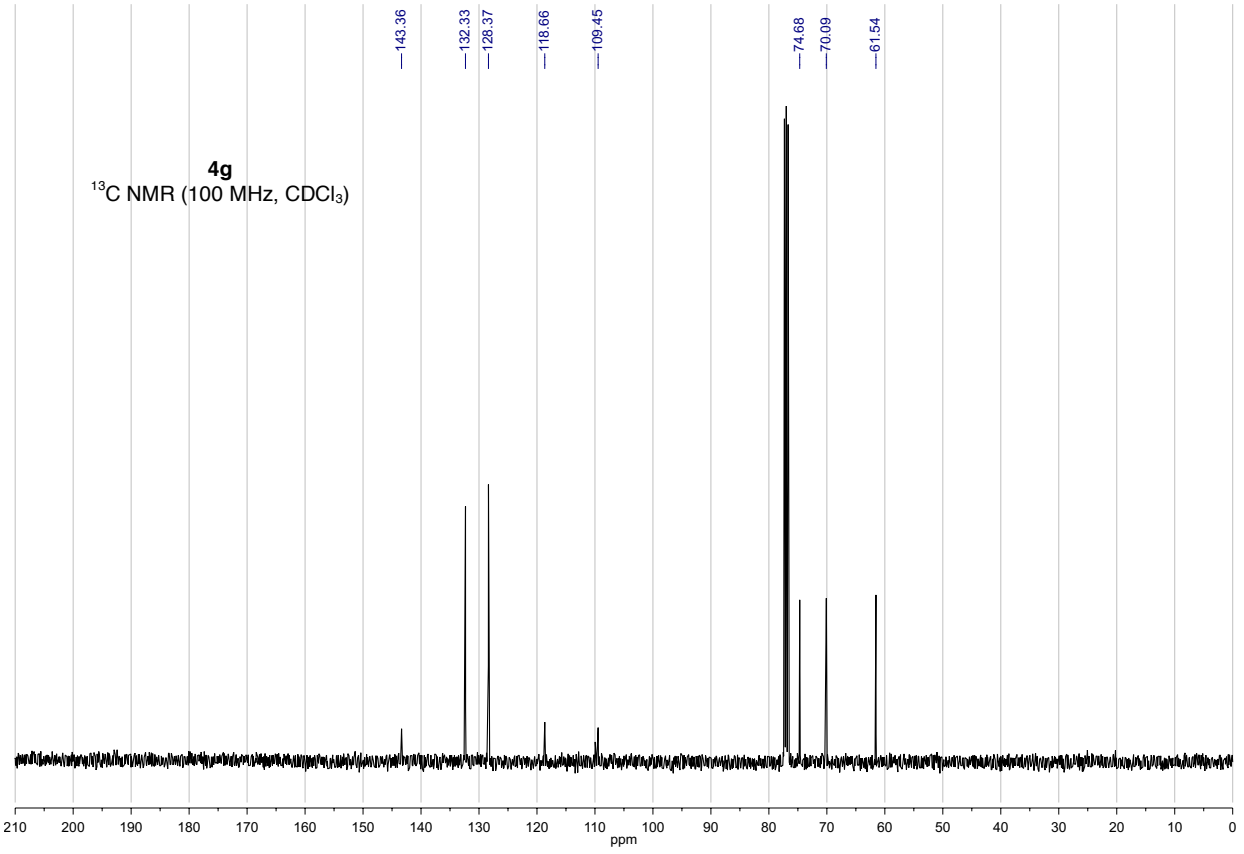

7.80
7.80
7.78
7.78
7.77
7.76
7.75
7.73
7.73
7.36
7.35
7.35
7.35
7.34
7.33
7.33
4.55
4.52
4.45
4.42
4.20
4.20
4.19
4.19
4.19
4.18
4.18
4.18
4.11
4.10
4.10
4.07
4.07
4.06
2.44
O
S
O
F3C
OTs
1f
1H NMR (400 MHz, CDCl3)
6.01
2.00
1.06
1.08
4.37
3.06
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm

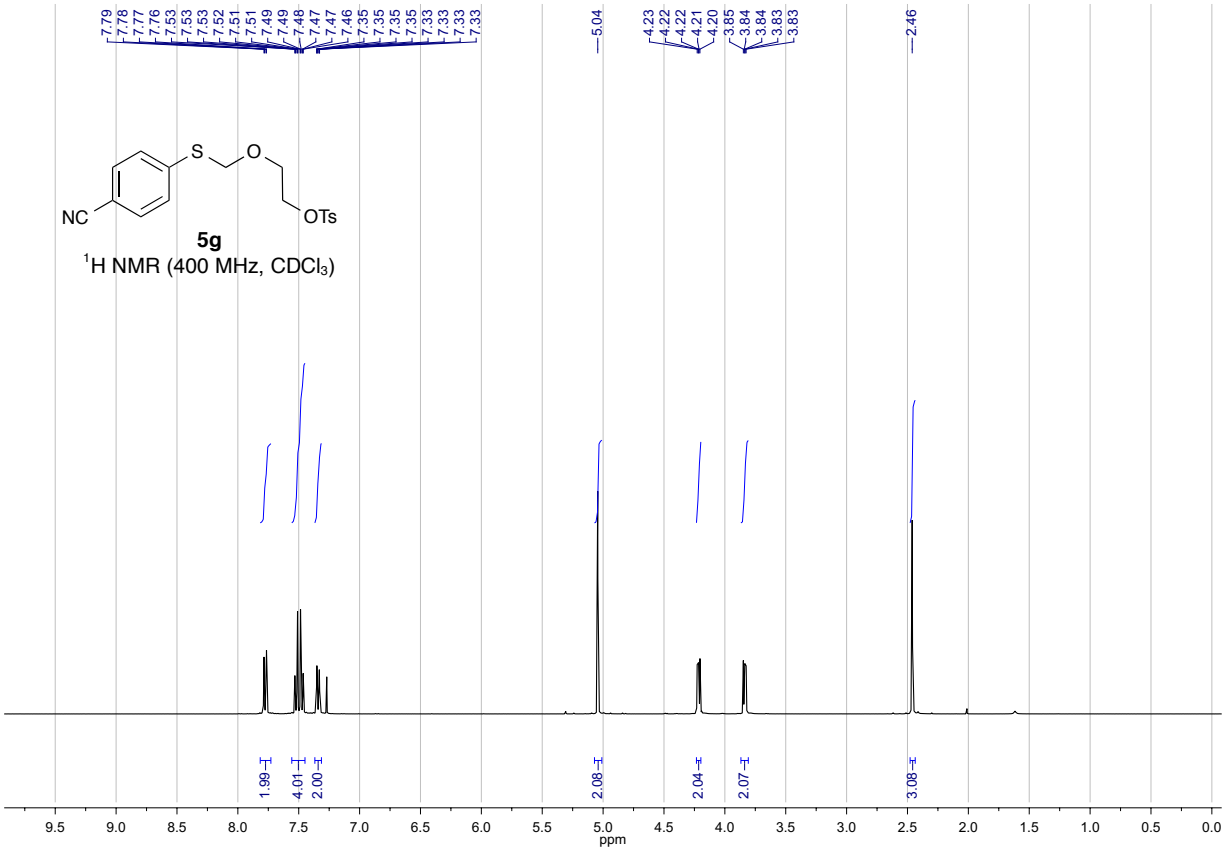

145.16
133.58
132.64
129.93
129.86
127.94
127.51
126.28
126.24
125.08
124.92
122.37
119.88
91.77
71.27
68.52
21.64
1f
13C NMR (100 MHz, CDCl3)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

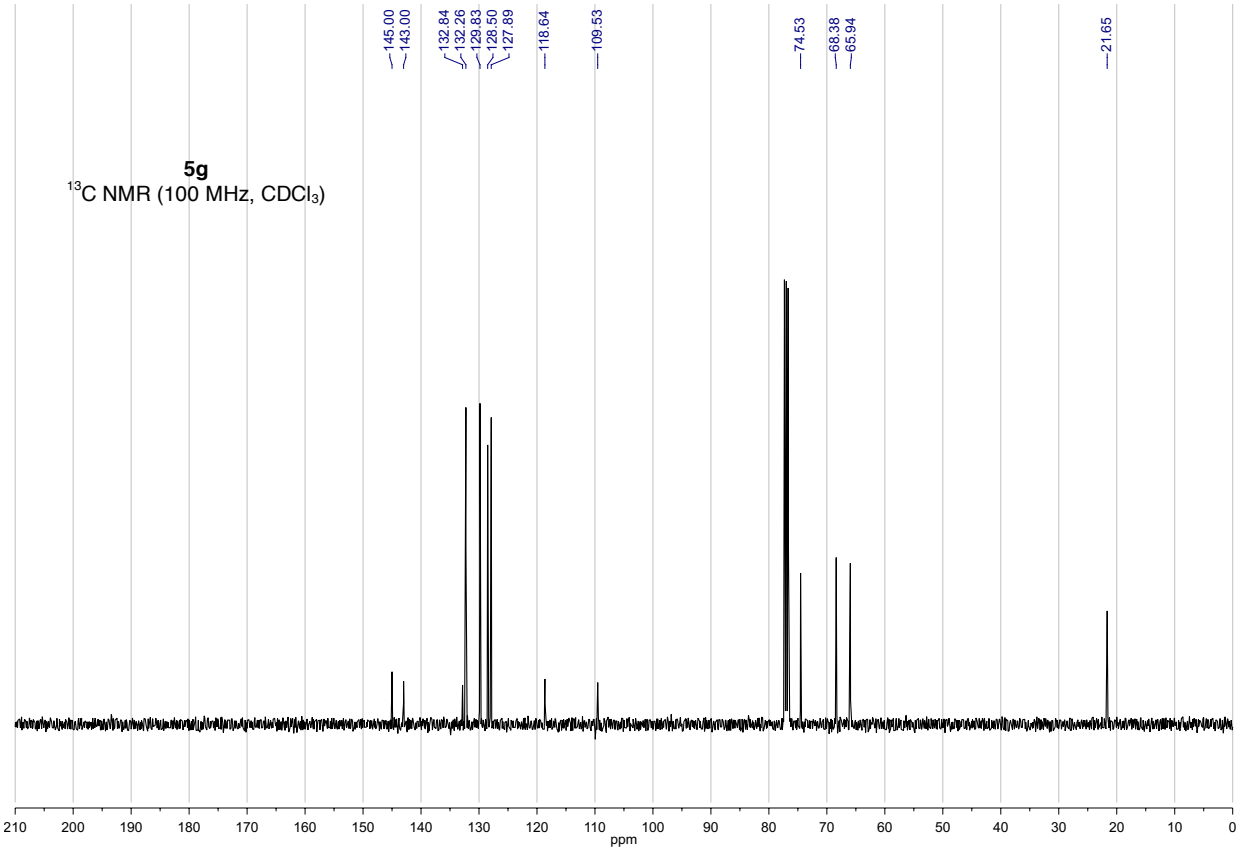

7.80
7.79
7.78
7.78
7.73
7.73
7.71
5.33
5.32
5.32
5.30
4.85
4.84
4.83
4.71
4.71
4.70
4.69
4.69
3.24
3.24
3.23
3.23
3.22
3.21
3.21
2.73
2.72
2.71
2.71
2.71
2.70
2.69
2.69
2.68
2.67
2.66
2.66
O
S
O
H
F3C
2f
1H NMR (400 MHz, CDCl3)
2.09
2.00
1.04
1.11
1.11
1.17
1.17
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
ppm

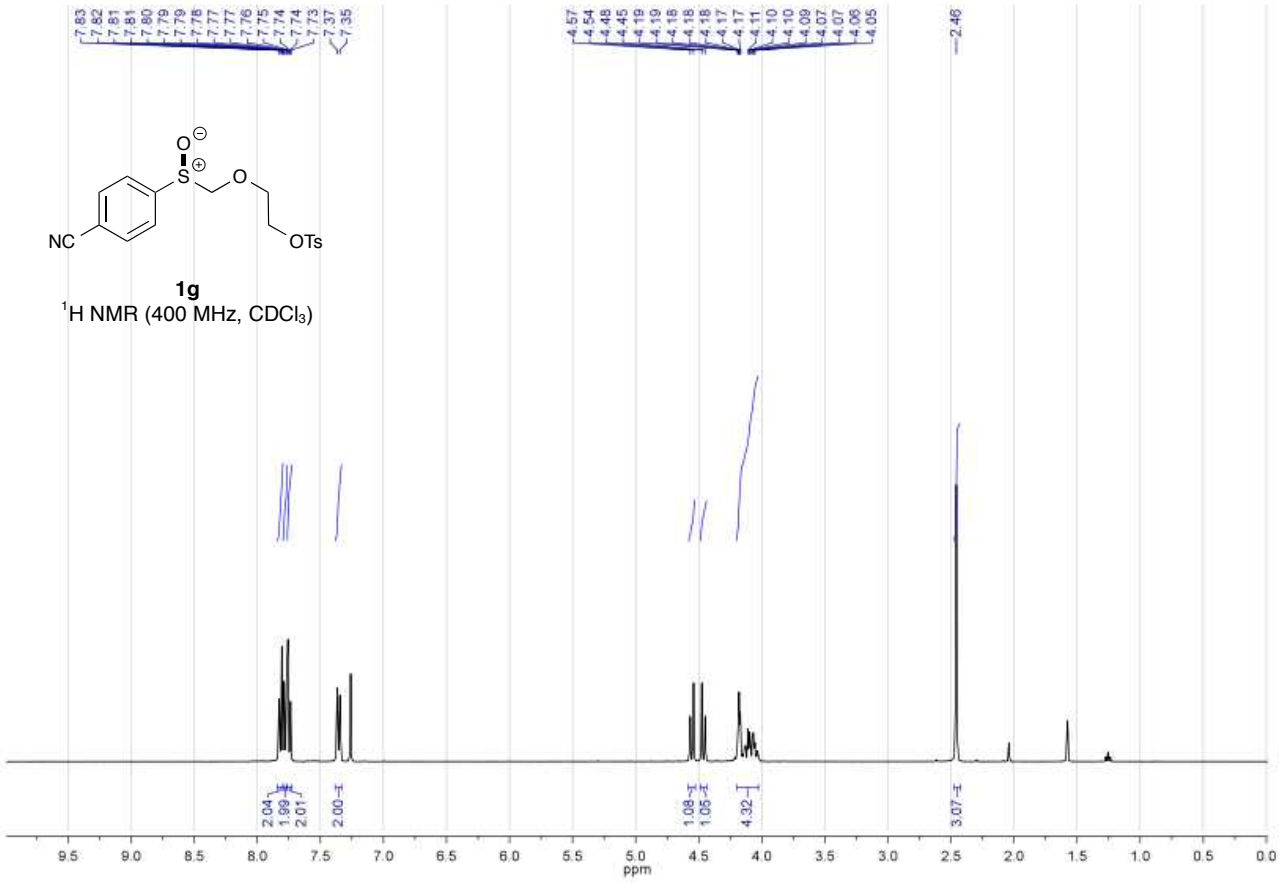

143.71
133.39
133.13
126.25
126.22
126.19
126.16
125.96
124.65
124.53
122.36
120.20
99.92
71.40
19.75
2f
13C NMR (100 MHz, CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
ppm

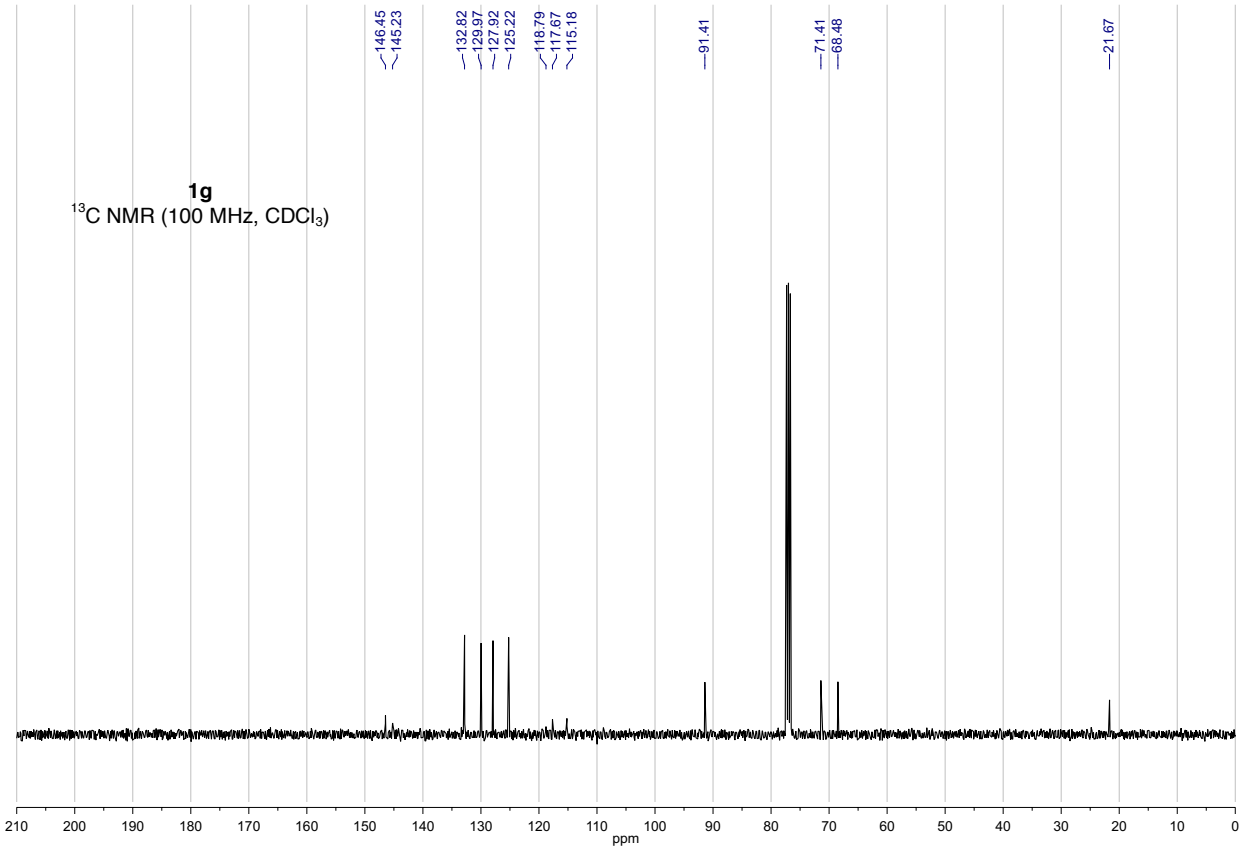

7.58
7.57
7.57
7.56
7.55
7.54
7.53
7.52
7.52
7.52
5.15
3.80
3.80
3.79
3.79
3.79
3.77
3.77
3.76
3.76
3.76
1.76
S
O
OH
NC
4g
^{1}H NMR (400 MHz, CDCl$_3$)
ppm

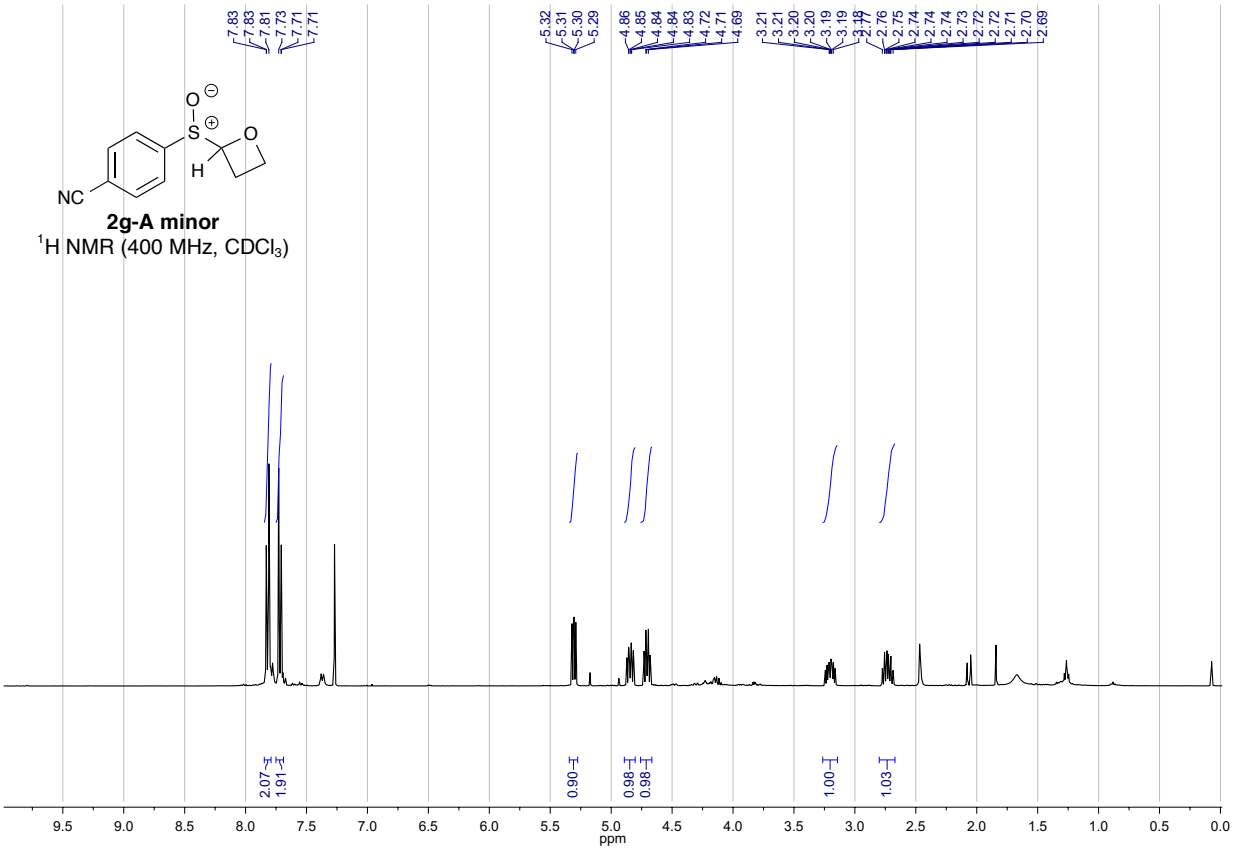

143.36
132.33
128.37
118.66
109.45
74.68
70.09
61.54
4g
^{13}C NMR (100 MHz, CDCl$_3$)
ppm

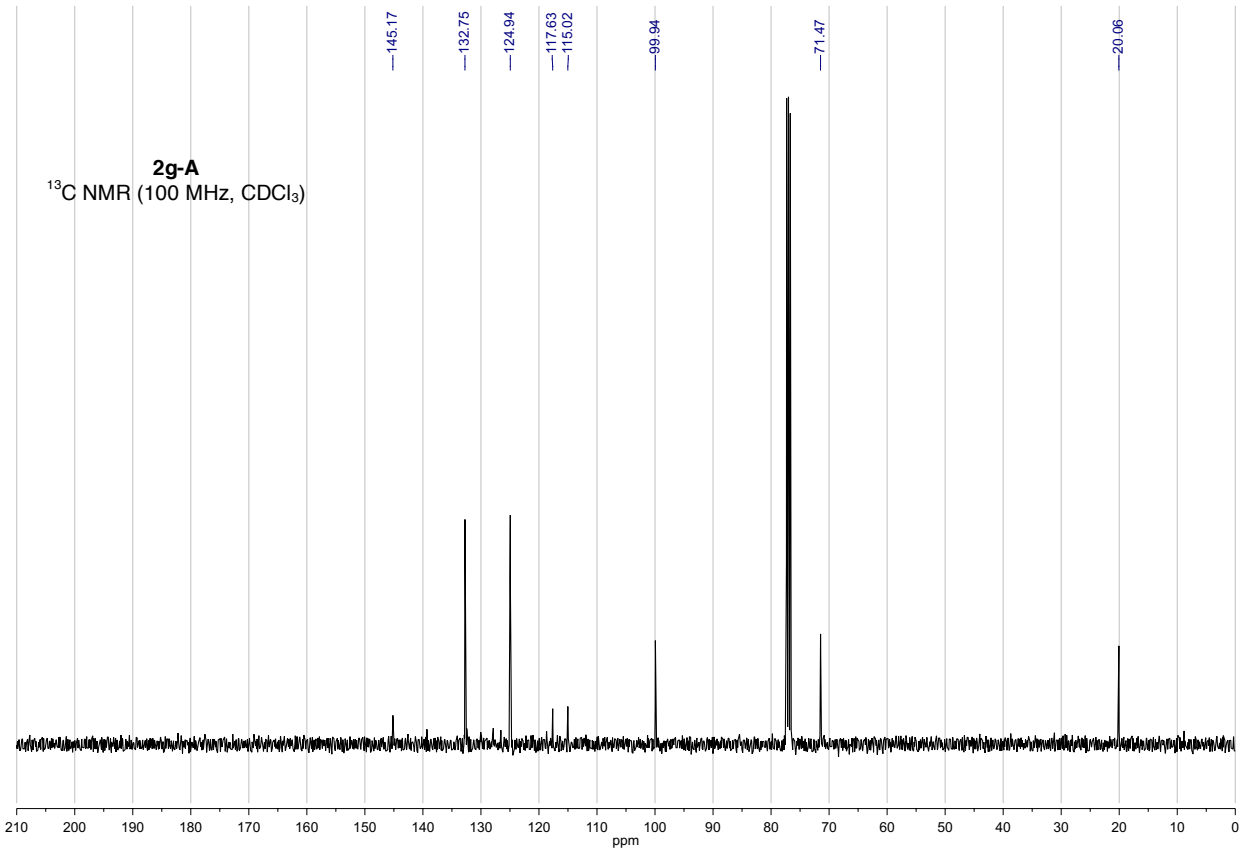

7.79
7.78
7.77
7.76
7.53
7.53
7.52
7.51
7.51
7.49
7.49
7.48
7.47
7.47
7.46
7.35
7.35
7.35
7.35
7.33
7.33
7.33
7.33
5.04
4.23
4.22
4.22
4.21
4.20
3.85
3.84
3.84
3.83
3.83
2.46
S
O
NC
OTs
5g
^{1}H NMR (400 MHz, $CDCl_3$)
1.99
4.01
2.00
2.08
2.04
2.07
3.08
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
ppm

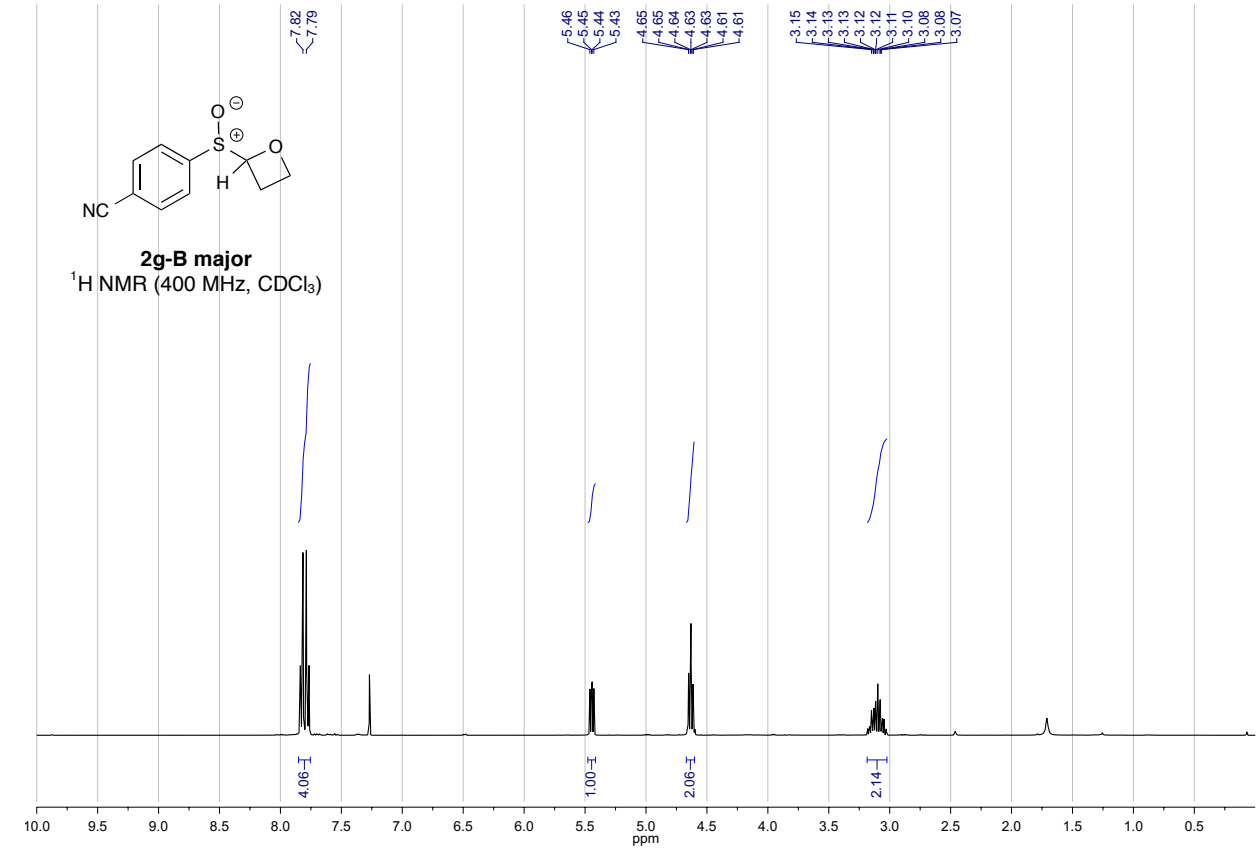

145.00
143.00
132.84
132.26
129.83
128.50
127.89
118.64
109.53
74.53
68.38
65.94
21.65
5g
^{13}C NMR (100 MHz, $CDCl_3$)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm

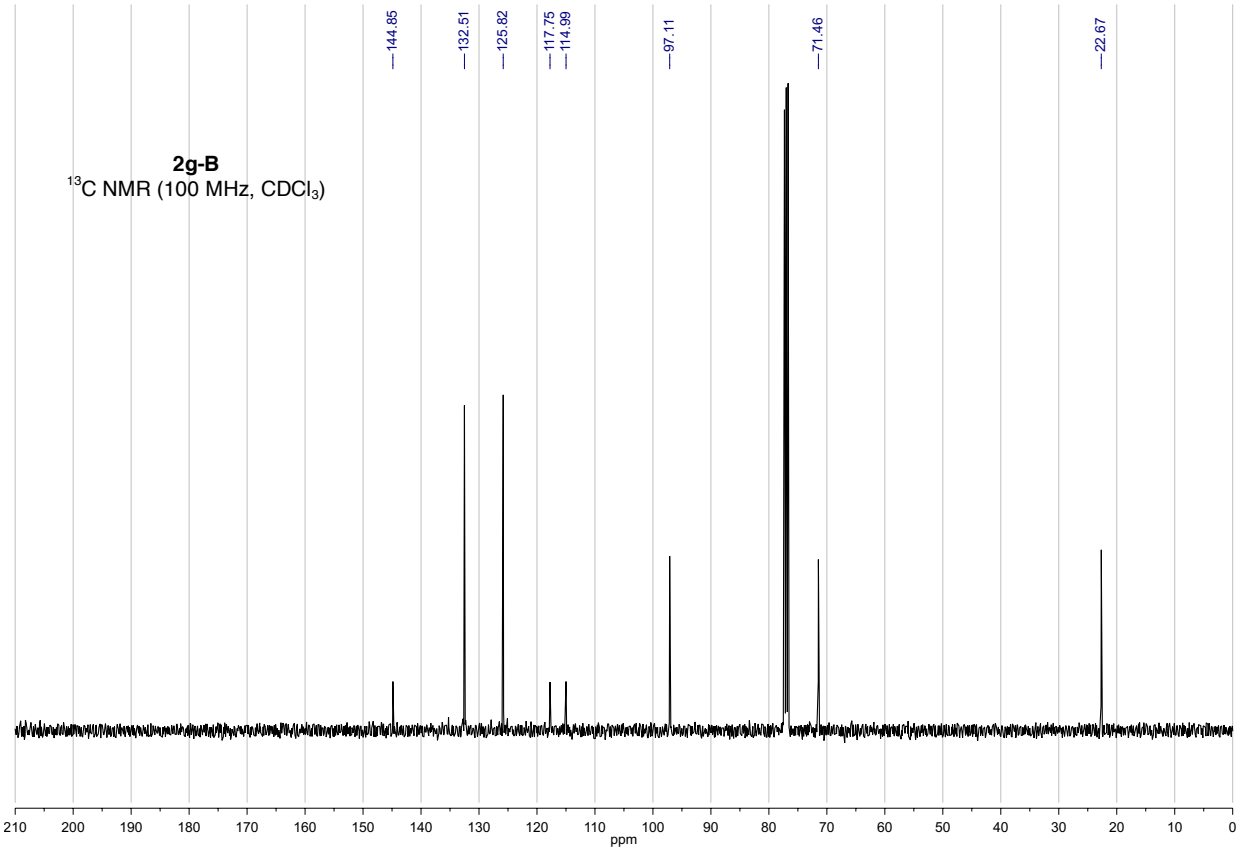

NC
OTs
1g
^{1}H NMR (400 MHz, CDCl$_3$)
ppm

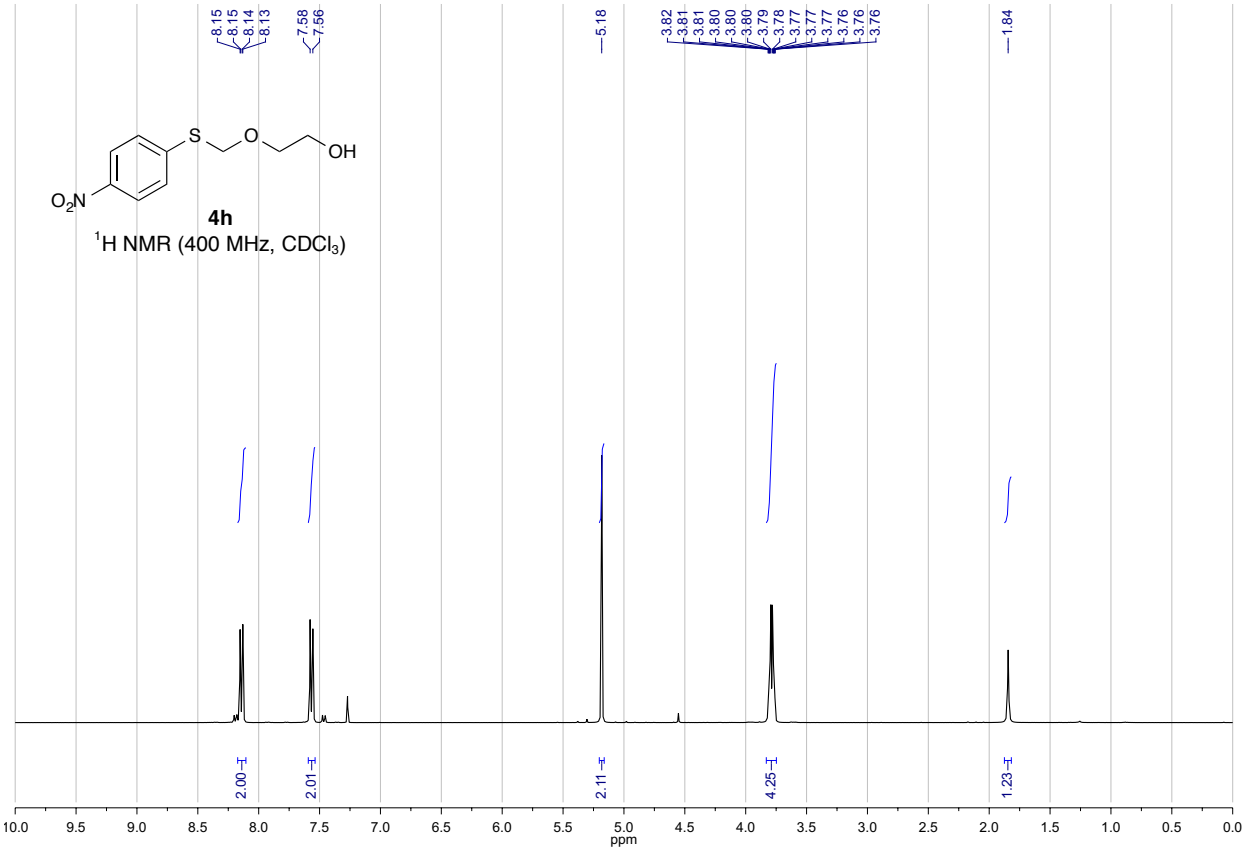

1g
^{13}C NMR (100 MHz, CDCl$_3$)
ppm


7.83
7.83
7.81
7.73
7.71
7.71
5.32
5.31
5.30
5.29
4.86
4.85
4.84
4.84
4.83
4.72
4.71
4.69
3.21
3.21
3.20
3.20
3.19
3.19
2.76
2.75
2.74
2.74
2.74
2.73
2.72
2.72
2.71
2.70
2.69
O
S
O
H
NC
2g-A minor
^{1}H NMR (400 MHz, CDCl$_3$)
2.07
1.91
0.90
0.98
0.98
1.00
1.03
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
ppm


145.17
132.75
124.94
117.63
115.02
99.94
71.47
20.06
2g-A
^{13}C NMR (100 MHz, CDCl$_3$)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm

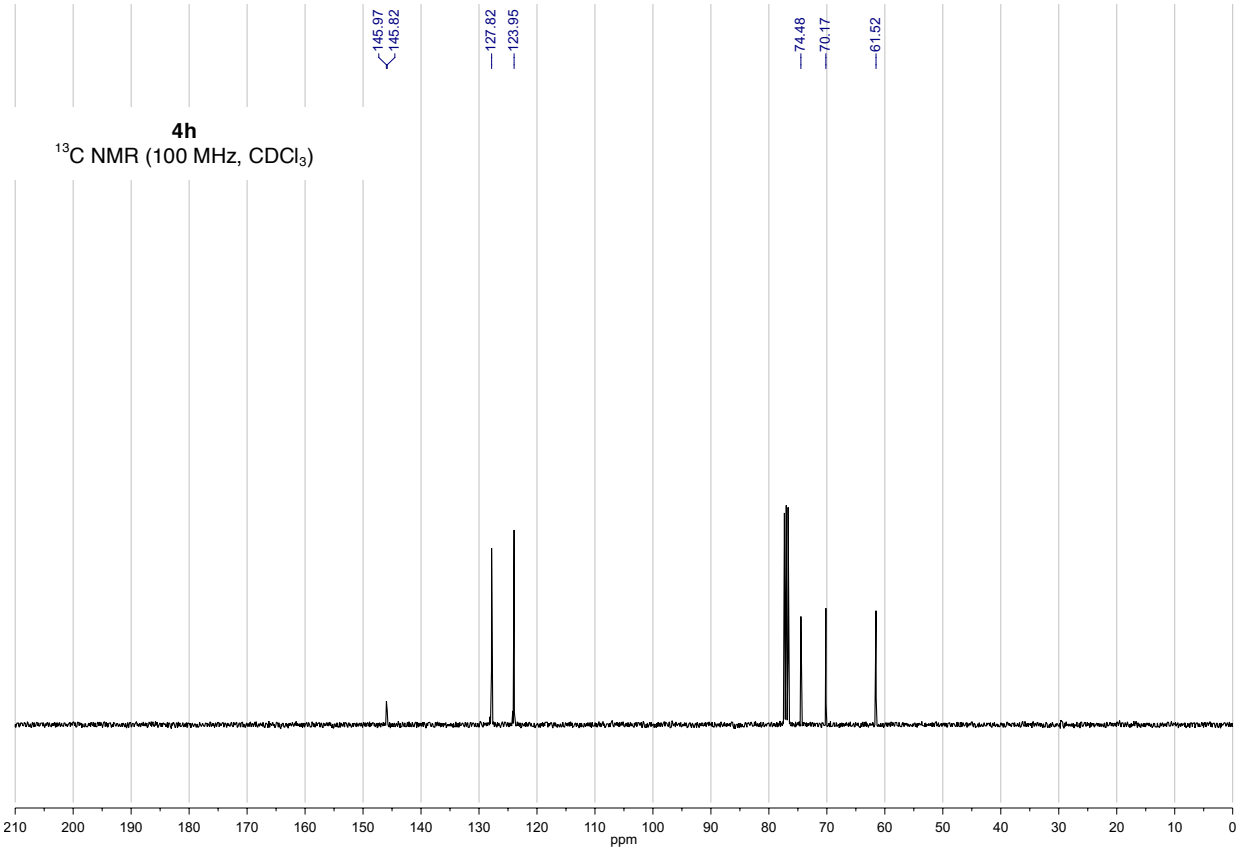

7.82
7.79
5.46
5.45
5.44
5.43
4.65
4.65
4.64
4.63
4.63
4.61
4.61
3.15
3.14
3.13
3.13
3.12
3.12
3.11
3.10
3.08
3.08
3.07
O
S
O
H
NC
2g-B major
1H NMR (400 MHz, CDCl3)
4.06
1.00
2.06
2.14
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm


144.85
132.51
125.82
117.75
114.99
97.11
71.46
22.67
2g-B
13C NMR (100 MHz, CDCl3)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm



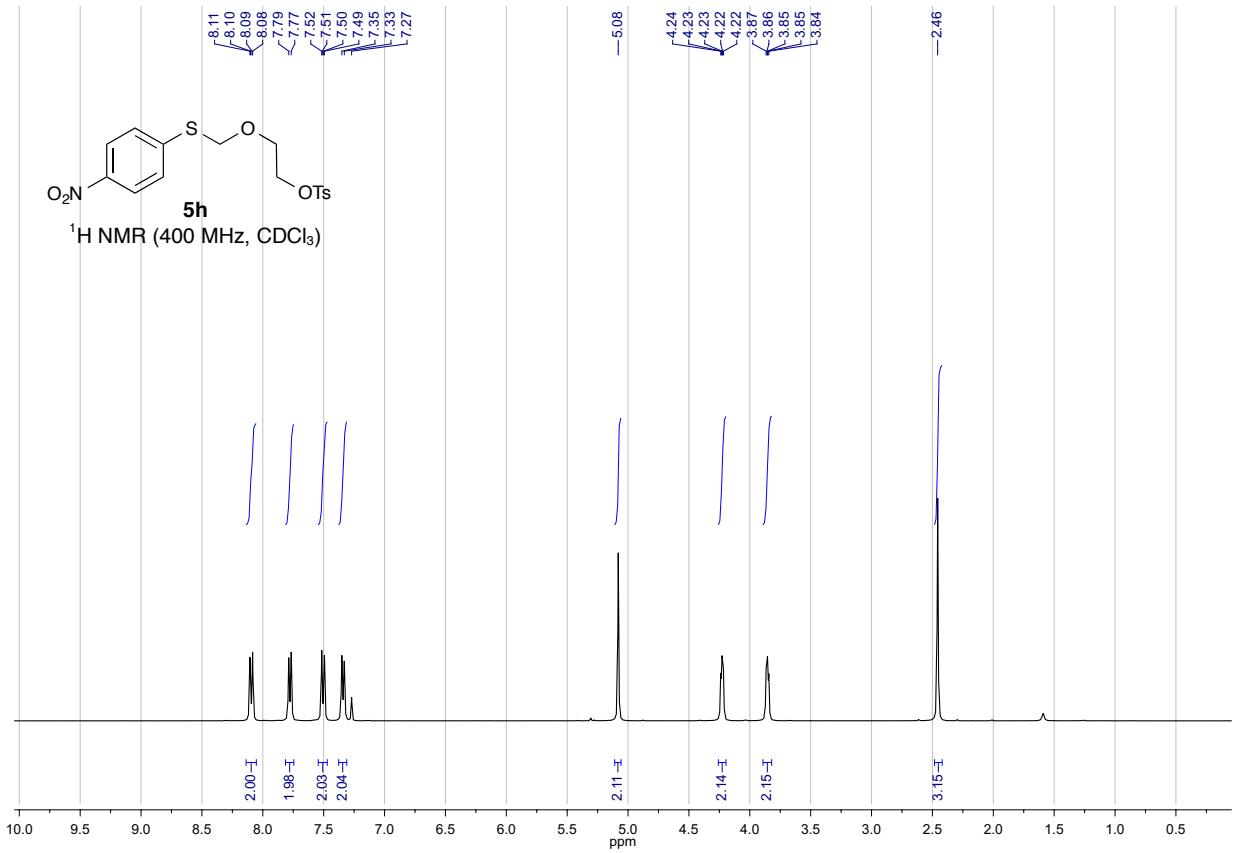
4h

^{1}H NMR (400 MHz, $CDCl_3$)



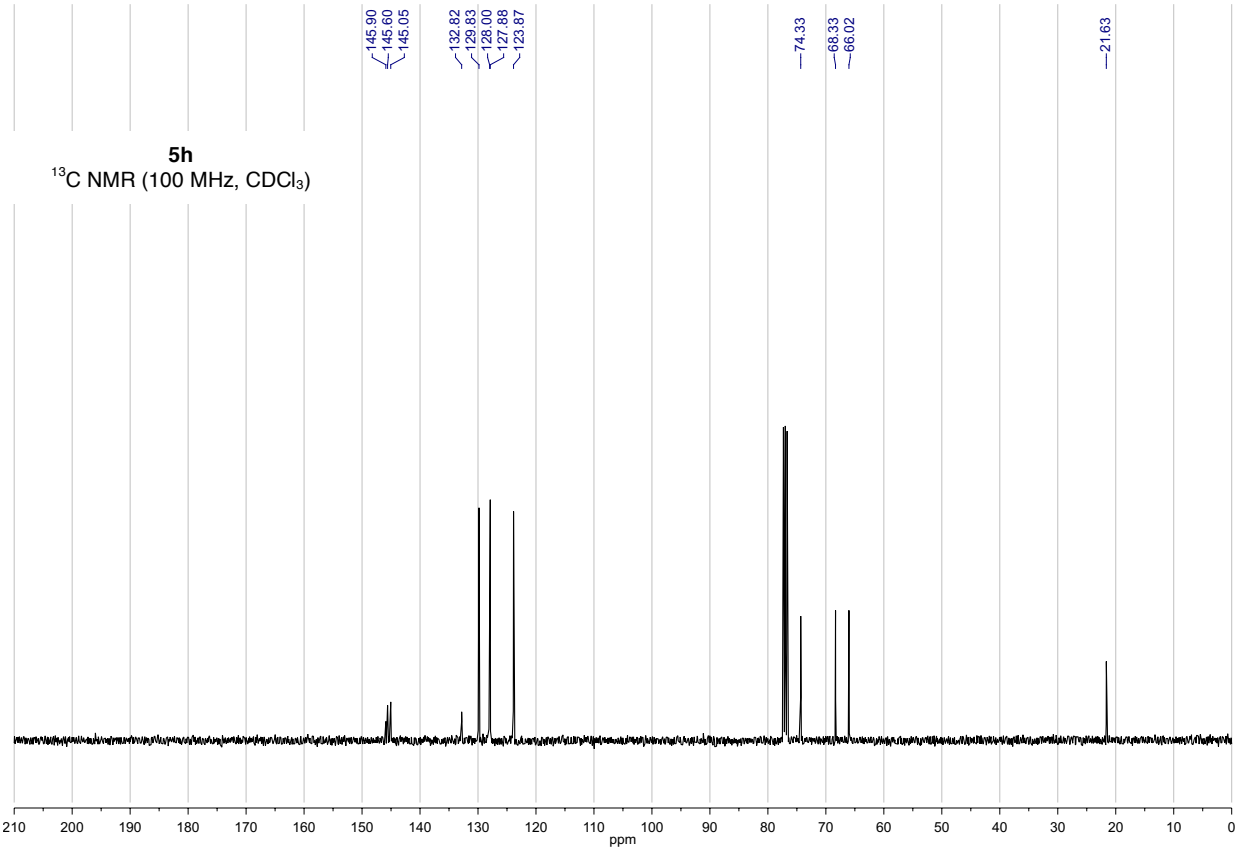
4h

^{13}C NMR (100 MHz, $CDCl_3$)



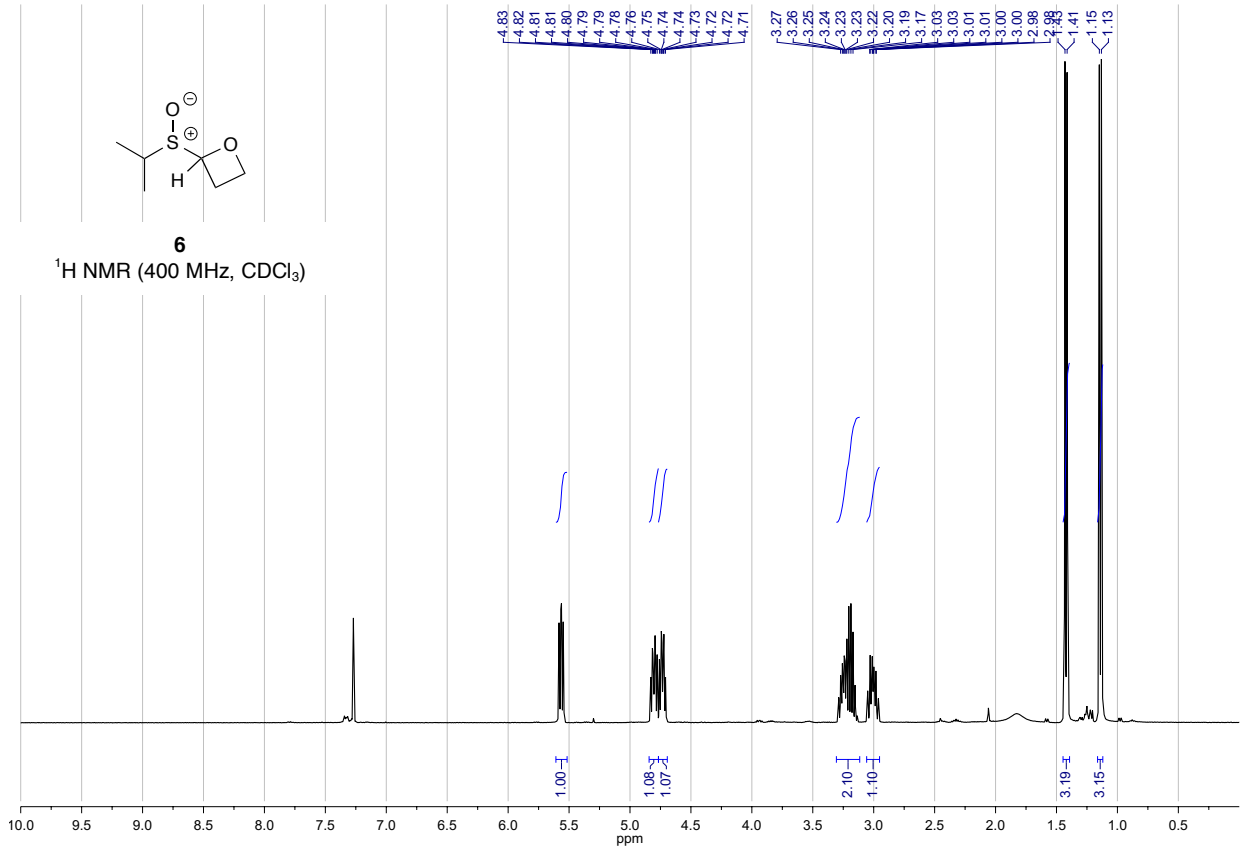
5h

^{1}H NMR (400 MHz, $CDCl_3$)



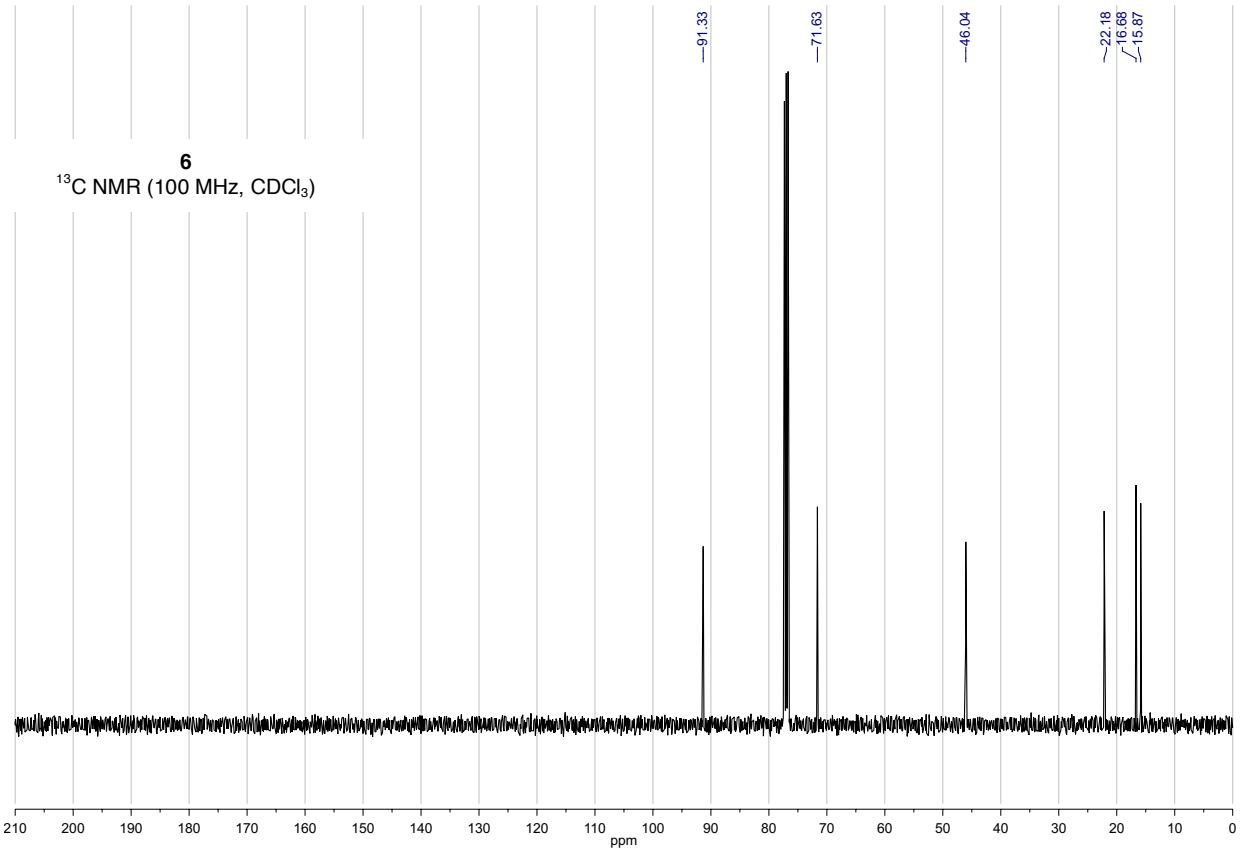
5h

^{13}C NMR (100 MHz, $CDCl_3$)



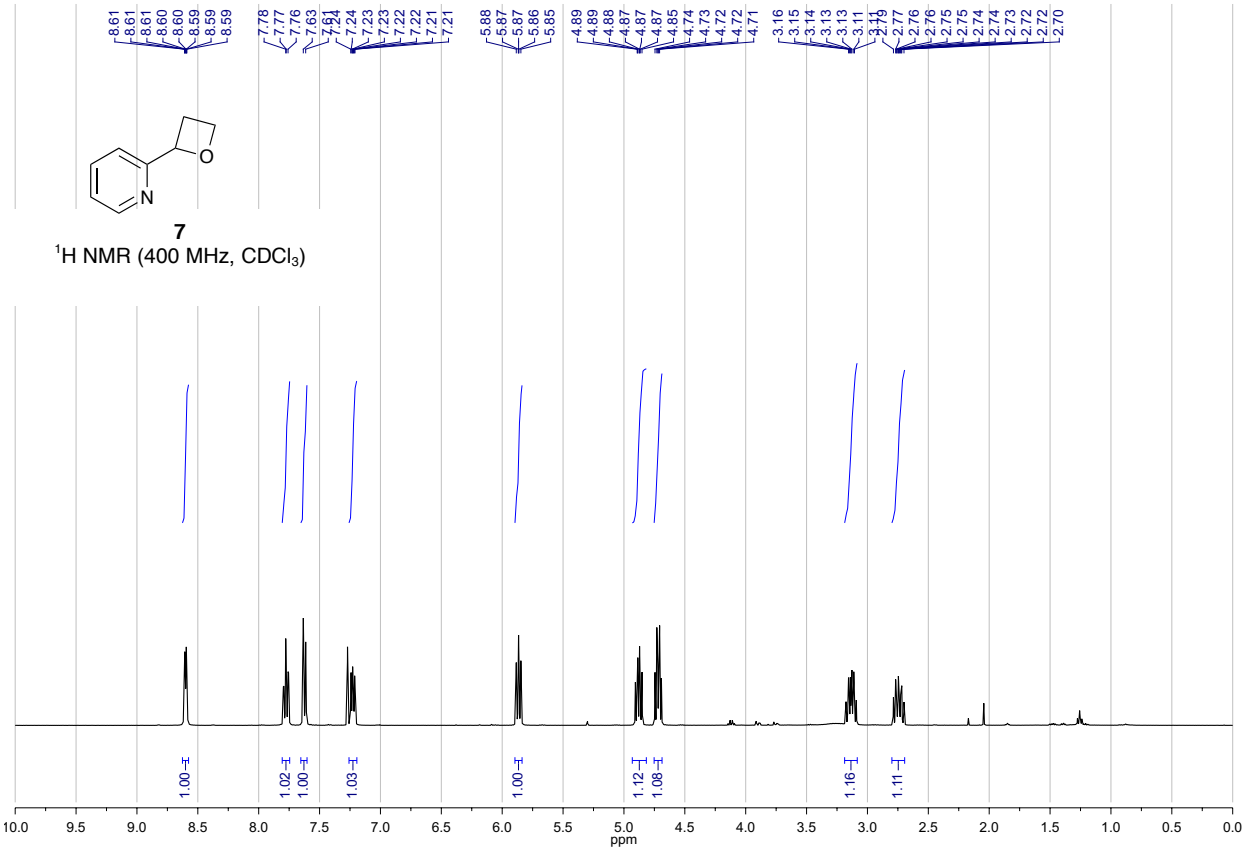
6

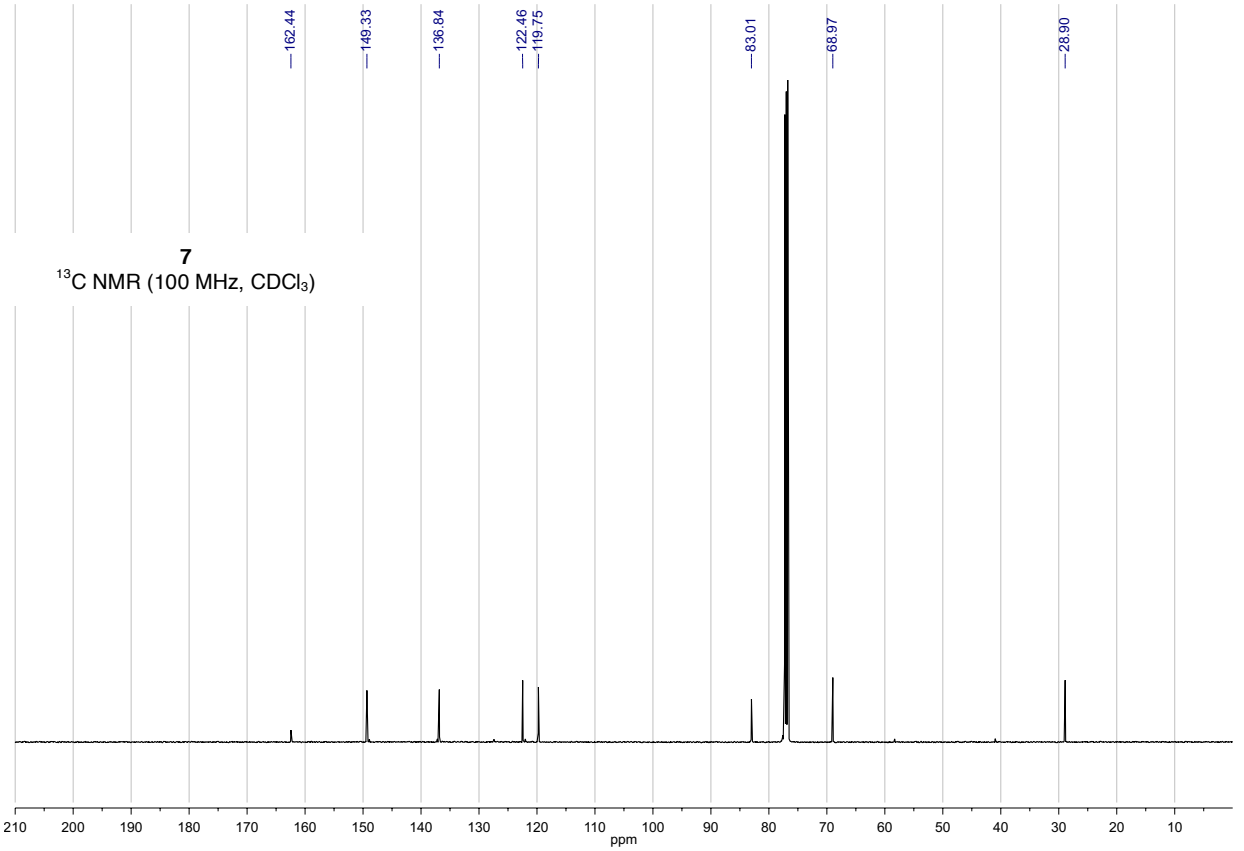
^{1}H NMR (400 MHz, $CDCl_3$)

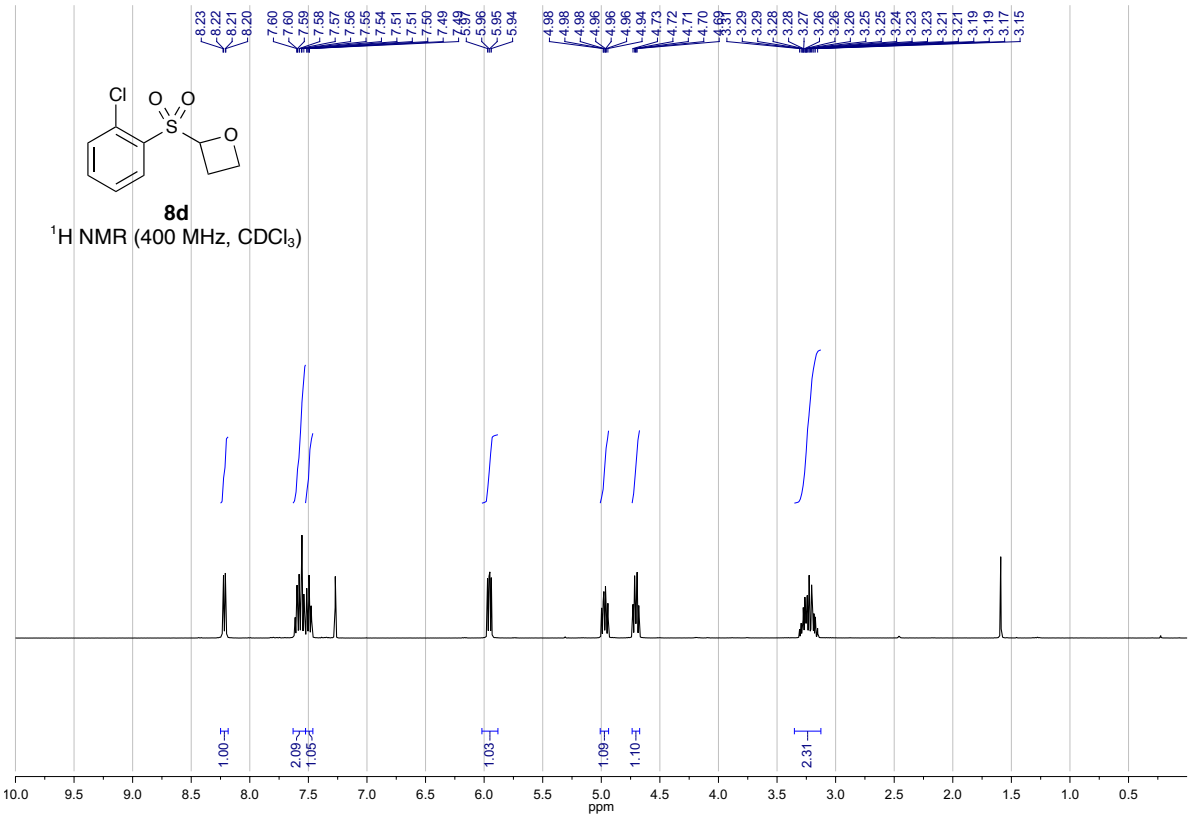


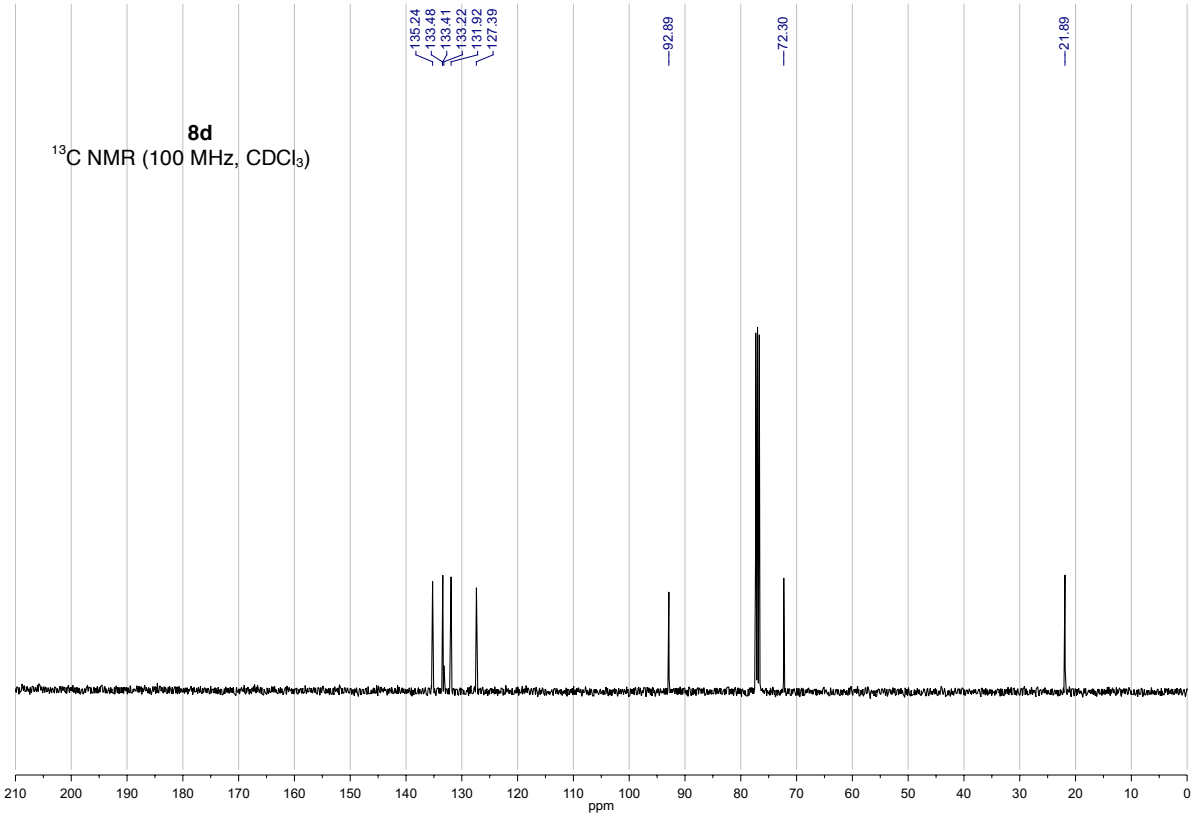
6

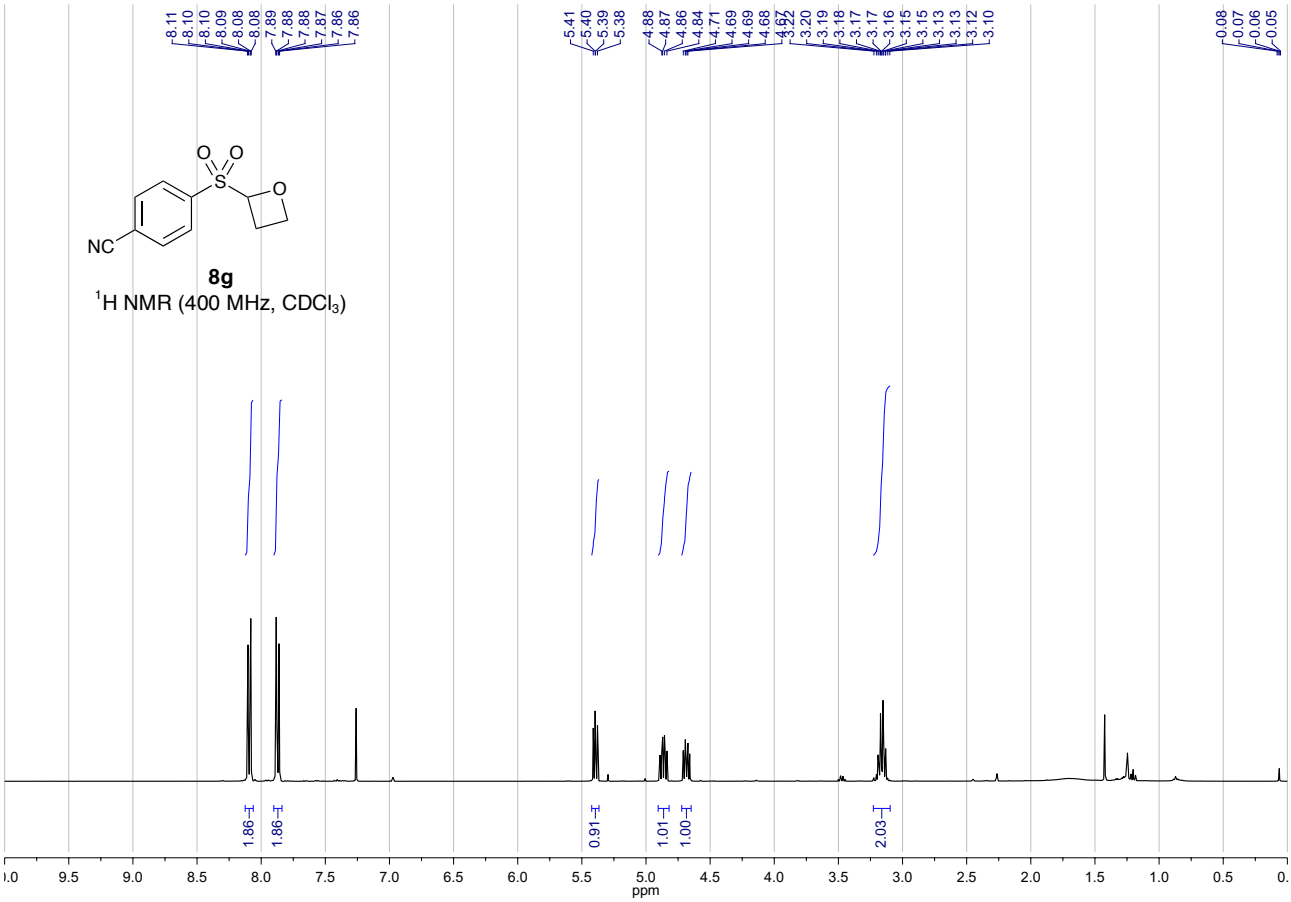
^{13}C NMR (100 MHz, $CDCl_3$)

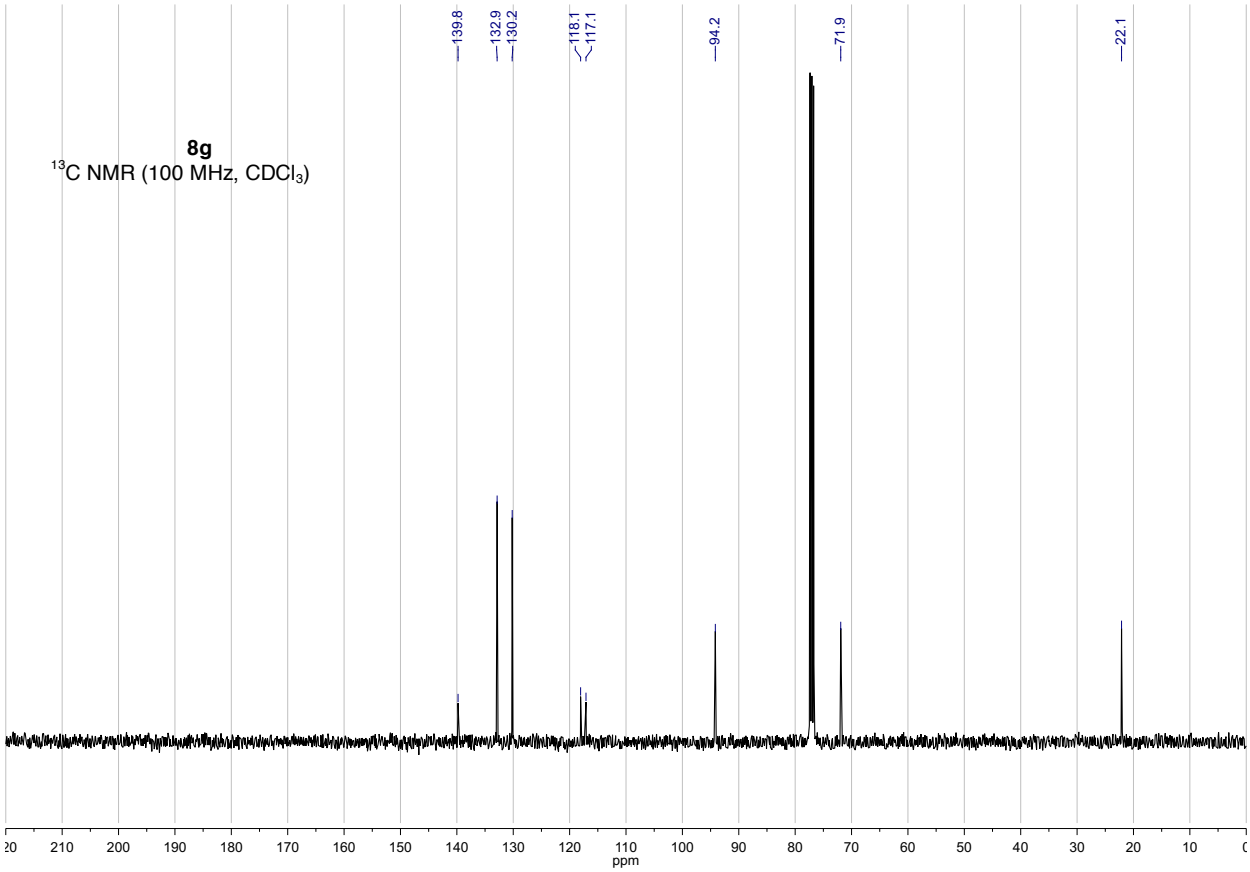

8.61 8.61 8.61 8.60 8.60 8.59 8.59 8.59
7.78 7.77 7.76 7.63 7.24 7.23 7.22 7.21 7.21
5.88 5.87 5.87 5.86 5.85
4.89 4.89 4.88 4.87 4.87 4.85 4.74 4.73 4.72 4.72 4.71
3.16 3.15 3.14 3.13 3.13 3.11 2.77 2.76 2.76 2.75 2.75 2.74 2.74 2.73 2.72 2.72 2.70
O
N
7
1H NMR (400 MHz, CDCl3)
1.00 1.02 1.00 1.03 1.00 1.12 1.08 1.16 1.11
ppm


162.44
149.33
136.84
122.46
119.75
83.01
68.97
28.90
7
13C NMR (100 MHz, CDCl3)
ppm


8.23
8.22
8.21
8.20
7.60
7.60
7.59
7.58
7.57
7.56
7.55
7.54
7.51
7.51
7.50
7.49
5.97
5.96
5.95
5.94
4.98
4.98
4.98
4.96
4.96
4.96
4.94
4.73
4.72
4.71
4.70
3.31
3.29
3.29
3.28
3.28
3.27
3.26
3.26
3.26
3.25
3.25
3.24
3.23
3.23
3.21
3.21
3.19
3.19
3.17
3.15
Cl
O
O
S
O
8d
^{1}H NMR (400 MHz, CDCl$_3$)
1.00
2.09
1.05
1.03
1.09
1.10
2.31
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm


135.24
133.48
133.41
133.22
131.92
127.39
92.89
72.30
21.89
8d
^{13}C NMR (100 MHz, CDCl$_3$)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm


8.11
8.10
8.10
8.09
8.08
8.08
7.89
7.88
7.88
7.87
7.86
7.86
5.41
5.40
5.39
5.38
4.88
4.87
4.86
4.84
4.71
4.69
4.69
4.68
3.22
3.20
3.19
3.18
3.17
3.17
3.16
3.15
3.15
3.13
3.13
3.12
3.10
0.08
0.07
0.06
0.05
O
O
S
O
NC
8g
^{1}H NMR (400 MHz, $CDCl_3$)
1.86
1.86
0.91
1.01
1.00
2.03
ppm


139.8
132.9
130.2
118.1
117.1
94.2
71.9
22.1
8g
^{13}C NMR (100 MHz, $CDCl_3$)
ppm