Electronic Supplementary Material (ESI) for ChemComm.

SUPPORTING INFORMATION

Controlled α-Mono- and α,α-Di-Halogenation of Alkyl Sulfones using Reagent-Solvent Halogen Bonding

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GENERAL EXPERIMENTAL CONDITIONS

General: Unless stated otherwise, all non-aqueous reactions were performed in oven-dried glassware sealed with microwave caps or rubber septa under a nitrogen atmosphere, and were stirred with Teflon-coated magnetic stir bars.[1] Liquid reagents and solvents were transferred by syringe using standard Schlenk techniques. Tetrahydrofuran (THF), diethyl ether (Et_2O), dichloromethane (CH_2Cl_2), toluene (PhMe), acetonitrile (MeCN), and methanol (MeOH) were dried by passage over a column of activated alumina (JC Meyers Solvent System). Anhydrous 1,4-dioxane, dimethyl sulfoxide (DMSO), *tert*-butyl methyl ether (*t*-BuOMe), and diisopropyl ether (*i*-Pr_2O) were obtained in Sure Seal bottles from Aldrich and used as received. Anhydrous 1,2-dichloroethane (DCE) and 1,2-dimethoxyethane (DME) were obtained in Sure Seal bottles from Acros Organics and used as received. All other solvents and reagents were used as received unless otherwise noted. Thin layer chromatography was performed using Silicycle silica gel 60 F-254 precoated plates (0.25 mm) and visualised by UV irradiation and anisaldehyde, CAM, potassium permanganate, or iodine stain. Sorbent silica gel (particle size 40-63 μm) was used for flash chromatography of the indicated solvent system according to standard techniques.[2] Flash chromatography was performed on a Biotage Isolera One. Nuclear magnetic resonance (NMR) spectra (^1H, ^{13}C) were recorded on Varian or Bruker spectrometers operating at either 300 or 700 MHz for ^1H and 175 MHz for ^{13}C experiments. Chemical shifts (δ) for ^1H NMR spectra are recorded in parts per million from tetramethylsilane with the solvent resonance as the internal standard (chloroform, δ 7.26 ppm). Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, qn = quintet, m = multiplet and br = broad), coupling constant in Hz, and integration. Chemical shifts for ^{13}C NMR spectra are recorded in parts per million from tetramethylsilane using the central peak of deuterochloroform (δ 77.16 ppm) as the internal standard. All spectra were obtained with complete proton decoupling. Only select ^1H and ^{13}C spectra are reported. Infrared (IR) spectra were collected on a Thermo Scientific Nicolet iS5 FTIR instrument using attenuated total reflectance (ATR) mode and signals are reported in reciprocal centimeters (cm^{-1}). Only selected IR frequencies are reported. High-resolution mass spectral data were obtained from the NC State University Mass Spectrum Facility, using a Thermo Fisher Scientific Exactive Plus for ESI.

Reagents: NFSI, I_2, 2,3,4,5,6,6-Hexachlorohexa-2,4-dienone, NBS, 1,3-Dibromo-5,5-dimethylhydantoin, and Bromotrichloromethane were purchased from commercial sources and used without further purification. Carbon tetrabromide was purchased from Alfa Aesar and contained up to ca 6% water. Bromine was purchased from from Alfa Aesar (99.5%). Solid LiHMDS (97%) was purchased from Sigma-Aldrich and LDA (2.0 M in THF/*n*-heptane/ethylbenzene) was purchased from Acros Organics. Most alkyl sulfones used as starting materials were prepared according to literature procedures (see specific procedures, pages S4-S5).[3,4]

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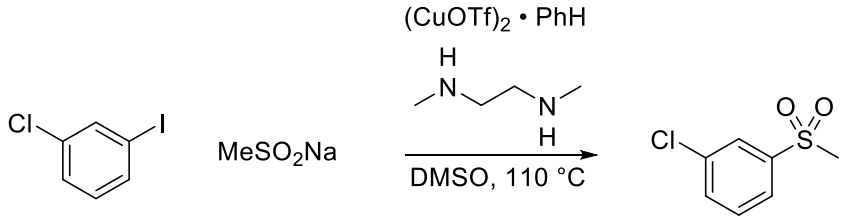
[1] D. F. Shriver, M. A. Drezdzon, *The manipulation of air-sensitive compounds*. Wiley: New York; Chichester, 1986.
[2] W. C. Still, M. Kahn and A. Mitra, *J. Org. Chem.*, 1978, **43**, 2923-2925.
[3] J. M. Baskin and Z. Wang, *Org. Lett.*, 2002, **4**, 4423-4425.
[4] B. Yu, A.-H. Liu, L.-N. He, B. Li, Z.-F. Diao and Y.-N. Li, *Green Chem.*, 2012, **14**, 957-962.

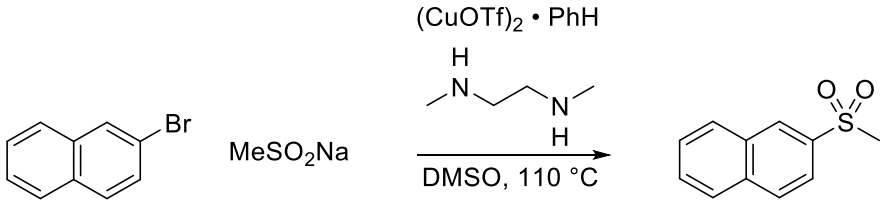
EXPERIMENTAL PROCEDURES AND CHARACTERISATION DATA

Synthesis of alkyl sulfones 1a-1m

Sulfone **1a** was prepared according to a known procedure.[4] Sulfones **1b**, **1c**, **1d** and **1g** were synthesised via a cross-coupling reaction.[3] Compound **1j** was prepared by following a literature S_N2 procedure with benzene sulfinic acid sodium salt and chlorodiphenylmethane.[5,6] Compound **1l** was prepared by following a literature S_N2 procedure with methyl sulfinic acid sodium salt and benzyl chloride.[7,8]



1-Chloro-3-(methylsulfonyl)benzene (1e). To a microwave vial containing 1-chloro-3-iodobenzene (1.0 g, 4.2 mmol, 1.0 equiv), methanesulfinic acid sodium salt (514 mg, 5.0 mmol, 1.2 equiv), and copper(I) trifluoromethanesulfonate benzene complex 90% (117 mg, 0.23 mmol, 0.05 equiv) under N_2 was added DMSO (4 mL) and *N*,*N*'-dimethylethylenediamine (45 µL, 0.42 mmol, 0.10 equiv) and heated to 110 °C for 20 hours. After this time, the reaction was cooled to room temperature, diluted with ethyl acetate, and filtered through a pad of SiO_2. The filtrate was washed twice with H_2O, once with brine, dried with Na_2SO_4, and concentrated under vacuum to afford sulfone **1e** (638 mg, 80%) after purification by flash chromatography (10-50% EtOAc in Hexanes, elution gradient). All analyses were consistent with the previously reported data.[9]



2-(Methylsulfonyl)naphthalene (1f). To a microwave vial containing 2-bromonaphthalene (1.0 g, 4.8 mmol, 1.0 equiv), methanesulfinic acid sodium salt (592 mg, 5.8 mmol, 1.2 equiv), and copper(I) trifluoromethanesulfonate benzene complex 90% (134 mg, 0.24 mmol, 0.05 equiv) under N_2 was added DMSO (4 mL) and *N*,*N*'-dimethylethylenediamine (52 µL, 0.48 mmol, 0.10 equiv) and heated to 110 °C for 20 hours. After this time, the reaction was cooled to room temperature, diluted with ethyl acetate, and filtered through a pad of SiO_2. The filtrate was washed twice with H_2O, once with brine, dried with Na_2SO_4, and concentrated under vacuum to afford sulfone **1f** (683 mg, 69%) after purification by flash chromatography (10-60% EtOAc in Hexanes, elution gradient). All analyses were consistent with the previously reported data.[9]

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[5] W. Wei, R. K. Khangarot, L. Stahl, C. Veresmortean, P. Pradhan, L. Yang and B. Zajc, *Org. Lett.*, 2018, **20**, 3574-3578.
[6] M. Baidya, S. Kobayashi and H. Mayr, *J. Am. Chem. Soc.*, 2010, **132**, 4796-4805.
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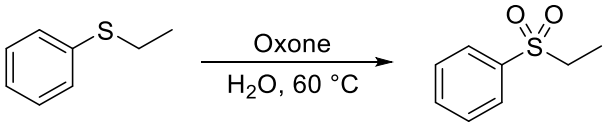
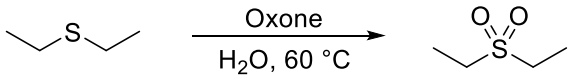
[9] A. Kar, I. A. Sayyed, W. F. Lo, H. M. Kaiser, M. Beller and M. K. Tse, *Org. Lett.*, 2007, **9**, 3405-3408.

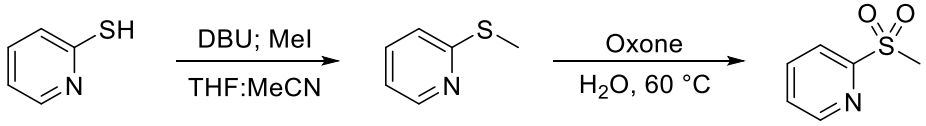


(Ethylsulfonyl)benzene (1h). A 100 mL round bottom flask was charged with ethyl(phenyl)sulfane (1.0 g, 7.2 mmol, 1.0 equiv) open to air. H_2O (30 mL) and Oxone (6.6 g, 21.7 mmol, 3.0 equiv.) were added sequentially and the resulting solution was heated to 60 °C for 16 hours. After this time, the reaction was cooled to room temperature and extracted three times with ethyl acetate. The organic layers were combined, dried with Na_2SO_4, and concentrated under vacuum to afford sulfone **1h** (1.2 g, 95%) after purification by flash chromatography (10-45% EtOAc in Hexanes, elution gradient). All analyses were consistent with the previously reported data.[10]

(Benzylsulfonyl)benzene (1i). A 100 mL round bottom flask was charged with benzenesulfinic acid sodium salt (2.0 g, 12.2 mmol, 1.0 equiv) and flushed with N_2. DMF (40 mL) was added, followed by benzyl bromide (2.17 mL, 18.3 mmol, 1.5 equiv), and the resulting solution was heated to 80 °C for 4 hours. After this time, the reaction was cooled to room temperature, diluted with H_2O, and extracted twice with ethyl acetate. The organic layers were combined, washed with brine, dried with Na_2SO_4, and concentrated under vacuum to afford sulfone **1i** (2.6 g, 93%) after purification by flash chromatography (0-90% EtOAc in Hexanes, elution gradient). All analyses were consistent with the previously reported data.[11]



(Ethylsulfonyl)ethane (1k). A 100 mL round bottom flask was charged with diethyl sulfide (1.0 g, 11.1 mmol, 1.0 equiv) open to air. H_2O (30 mL) and Oxone (10.2 g, 32.2 mmol, 3.0 equiv) were added sequentially and the resulting solution was heated to 60 °C for 16 hours. After this time, the reaction was cooled to room temperature and extracted three times with ethyl acetate. The organic layers were combined, dried with Na_2SO_4, and concentrated under vacuum to afford sulfone **1k** (902 mg, 67%) after purification by flash chromatography (5-40% EtOAc in Hexanes, elution gradient). All analyses were consistent with the previously reported data.[12]



2-(methylsulfonyl)pyridine (1m). 2-(Methylthio)pyridine was prepared according to a reported procedure.[13] A round bottom flask was charged with 2-(methylthio)pyridine (450 mg, 3.6 mmol, 1.0 equiv) open to air. H_2O (15 mL) and Oxone (2.9 g, 9.6 mmol, 3.0 equiv.) were added sequentially and the resulting solution was heated to 60 °C for 16 hours. After this time, the reaction was cooled to room temperature and extracted three times with ethyl acetate. The organic layers were combined, dried with Na_2SO_4, and concentrated under vacuum to afford sulfone **1m** (419 mg, 74%) as a colorless oil after purification by flash chromatography (10-60% EtOAc in Hexanes, elution gradient). All analyses were consistent with the previously reported data.[13]

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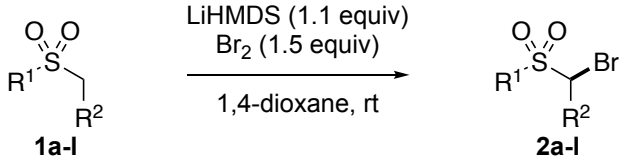
[10] M. Ishida, T. Minami and T. Agawa, *J. Org. Chem.*, 1979, **44**, 2067-2073.
[11] R. Kuwano, Y. Kondo and T. Shirahama, *Org. Lett.*, 2005, **7**, 2973-2975.
[12] A. Shaabani, P. Mirzaei, S. Naderi and D. G. Lee, *Tetrahedron*, 2004, **60**, 11415-11420.
[13] P. H. Bos, B. Macia, M. A. Fernandez-Ibanez, A. J. Minnaard and B. L. Feringa, *Org. Biomol. Chem.*, 2010, **8**, 47-49.

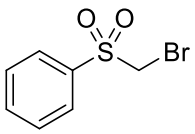
GENERAL PROCEDURE A: Synthesis of α-bromosulfones 2a-2l



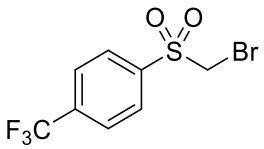
An oven-dried microwave vial equipped with a magnetic stirbar was charged with the alkyl sulfone **1** (1.0 mmol, 1.0 equiv), capped and flushed with N_2. Anhydrous dioxane (5 mL) was added and to the resulting solution was added solid LiHMDS (184 mg, 1.1 mmol, 1.1 equiv) and stirred for 1.5 hours. After this time, the deprotonated sulfone solution was transferred via syringe to a separate oven-dried microwave vial containing Br_2 (77 μL, 1.5 mmol, 1.5 equiv) in dioxane (2 mL). The reaction mixture was stirred for 2 h and then quenched by slow addition of aqueous sat. Na_2SO_3 (5 mL) and extracted with CH_2Cl_2 (2 x 30 mL). The combined organic fractions were washed with aqueous sat. Na_2SO_3 (2 x 30 mL), dried over Na_2SO_4, and concentrated under vacuum to give the crude α-brominated sulfone **2**, which was purified by flash chromatography (10-50% EtOAc in Hexanes, elution gradient) to afford the pure product. **Important note:** Using wet dioxane will result in lower yields and loss of selectivity.

On gram scale: The reaction was carried out by dissolving the alkyl sulfone **1** (7.68 mmol, 1.0 equiv) in anhydrous dioxane (36 mL) and adding solid LiHMDS (1.4 g, 8.45 mmol, 1.1 equiv), allowing to stir for 1.5 h at room temperature. After this time, the deprotonated sulfone solution was transferred to a separate oven-dried round bottom flask containing Br_2 (0.59 mL, 11.55 mmol, 1.5 equiv) in anhydrous dioxane (15 mL) and stirred for an additional 2 h at room temperature.

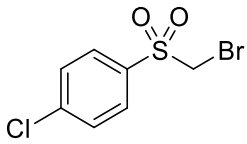
Specific procedures and characterisation data of α-bromosulfones 2a-2l



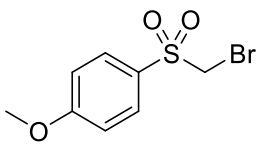
((Bromomethyl)sulfonyl)benzene (2a). General procedure A was followed, starting with (methylsulfonyl)benzene (**1a**)[4] (156 mg, 1.0 mmol, 1.0 equiv), LiHMDS (184 mg, 1.1 mmol, 1.1 equiv), and Br_2 (77 μL, 1.5 mmol, 1.5 equiv) in dioxane for 3.5 h, affording sulfone **2a** (134 mg, 57% yield) as a white solid after purification by flash chromatography, eluting with 10-50% EtOAc in hexanes (elution gradient). The reaction can also be carried out on gram scale, starting with (methylsulfonyl)benzene (1.2 g, 7.68 mmol, 1.0 equiv), LiHMDS (1.4 g, 8.45 mmol, 1.1 equiv), and Br_2 (0.59 mL, 11.55 mmol, 1.5 equiv) in dioxane for 3.5 h, affording sulfone **2a** (1.0 g, 56% yield) as a white solid after purification by flash chromatography, eluting with 0-65% EtOAc in hexanes (elution gradient). **mp** 52-53 °C. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 8.01-7.96 (m, 2H), 7.79-7.69 (m, 1H), 7.69-7.54 (m, 2H), 4.44 (s, 2H). **^{13}C NMR** (175 MHz, $CDCl_3$) δ 135.9, 134.7, 129.3, 129.3, 44.5. **IR** (neat) 3018, 2947, 1582, 1447, 1304, 1210, 1080, 836. **HRMS** (HESI) calcd for $[C_7H_7BrO_2S+H]^+$: *m/z*, 234.9423 found 234.9420.



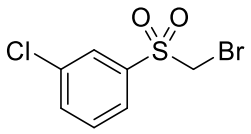
1-((Bromomethyl)sulfonyl)-4-(trifluoromethyl)benzene (2b). General procedure A was followed, starting with 1-(methylsulfonyl)-4-(trifluoromethyl)benzene (**1b**)[3] (224 mg, 1.0 mmol, 1.0 equiv), LiHMDS (184 mg, 1.1 mmol, 1.1 equiv), and Br_2 (77 μL, 1.5 mmol, 1.5 equiv) in dioxane for 3.5 h, affording sulfone **2b** (165 mg, 54% yield) as a white solid after purification by flash chromatography, eluting with 10-65% EtOAc in hexanes (elution gradient). **mp** 154-155 °C. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 8.13 (d, J = 8.1 Hz, 2H), 7.89 (d, J = 8.6 Hz, 2H), 4.47 (s, 2H). **^{13}C NMR** (175 MHz, $CDCl_3$) δ 139.3, 136.4 (q, J = 33.0 Hz), 130.1, 126.5, 123.7 (q, J = 272 Hz), 44.0. **IR** (neat) 3036, 2960, 1405, 1189, 1121, 1062, 839, 754, 709, 600. **HRMS** (HESI) calcd for $[C_8H_6BrF_3O_2S+H]^+$: *m/z*, 302.9297 found 302.9297.



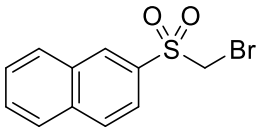
1-((Bromomethyl)sulfonyl)-4-chlorobenzene (2c). General procedure A was followed, starting with 1-chloro-4-(methylsulfonyl)benzene (**1c**)[3] (191 mg, 1.0 mmol, 1.0 equiv), LiHMDS (184 mg, 1.1 mmol, 1.1 equiv), and Br_2 (77 μL, 1.5 mmol, 1.5 equiv) in dioxane for 3.5 h, affording sulfone **2c** (157 mg, 58% yield) as a white solid after purification by flash chromatography, eluting with 10-70% EtOAc in hexanes (elution gradient). **mp** 122-123 °C. **^{1}HNMR** (300 MHz, $CDCl_3$) δ 7.98-7.82 (m, 2H), 7.68-7.50 (m, 2H), 4.44 (s, 2H). **^{13}C NMR** (175 MHz, $CDCl_3$) δ 141.6, 134.2, 130.8, 129.7, 44.5. **IR** (neat) 3039, 2961, 1582, 1475, 1314, 1144, 1082, 765, 736, 602. **HRMS** (HESI) calcd for $[C_7H_6BrClO_2S+H]^+$: *m/z*, 268.9033 found 268.9033.



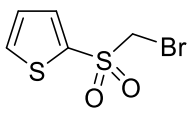
1-((Bromomethyl)sulfonyl)-4-methoxybenzene (2d). General procedure A was followed, starting with 1-methoxy-4-(methylsulfonyl)benzene (**1d**)[4] (186 mg, 1.0 mmol, 1.0 equiv), LiHMDS (184 mg, 1.1 mmol, 1.1 equiv), and Br_2 (77 μL, 1.5 mmol, 1.5 equiv) in dioxane for 3.5 h, affording sulfone **2d** (131 mg, 49% yield) as a white solid after purification by flash chromatography, eluting with 10-70% EtOAc in hexanes (elution gradient). **mp** 66-68 °C. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.94-7.86 (m, 2H), 7.09-7.01 (m, 2H), 4.42 (s, 2H), 3.91 (s, 3H). **^{13}C NMR** (175 MHz, $CDCl_3$) δ 165.2, 133.5, 123.0, 114.5, 55.9, 51.2. **IR** (neat) **HRMS** (HESI) calcd for $[C_8H_9BrO_3S+H]^+$: *m/z*, 264.9529 found 264.9524. **IR** (neat) 3037, 2964, 2839, 1574, 1200, 1095, 1024, 832, 803, 503. **HRMS** (HESI) calcd for $[C_8H_9BrO_3S+H]^+$: *m/z*, 264.9529 found 264.9524.



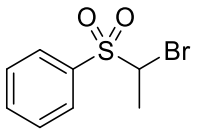
1-((Bromomethyl)sulfonyl)-3-chlorobenzene (2e). General procedure A was followed, starting with 1-chloro-3-(methylsulfonyl)benzene (**1e**) (191 mg, 1.0 mmol, 1.0 equiv), LiHMDS (184 mg, 1.1 mmol, 1.1 equiv), and Br_2 (77 µL, 1.5 mmol, 1.5 equiv) in dioxane for 3.5 h, affording sulfone **2e** (127 mg, 47% yield) as a white solid after purification by flash chromatography, eluting with 10-65% EtOAc in hexanes (elution gradient). **mp** 82-84 °C. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.97 (t, *J* = 1.9 Hz, 1H), 7.92-7.84 (m, 1H), 7.75-7.65 (m, 1H), 7.56 (t, *J* = 7.9 Hz, 1H), 4.45 (s, 2H). **^{13}C NMR** (175 MHz, $CDCl_3$) δ 137.5, 135.7, 134.9, 130.6, 129.3, 127.5, 44.3. **IR** (neat) 3068, 3030, 2955, 1455, 1316, 1148, 785, 734, 578. **HRMS** (HESI) calcd for $[C_7H_6BrClO_2S\text{-}H]^-$: *m/z*, 266.8888 found 266.8892.



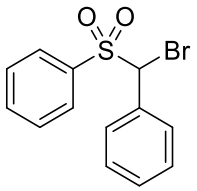
2-((Bromomethyl)sulfonyl)naphthalene (2f). General procedure A was followed, starting with 2-(methylsulfonyl)naphthalene (**1f**) (206 mg, 1.0 mmol, 1.0 equiv), nBuLi (1.1 mmol, 1.1 equiv), and Br_2 (77 µL, 1.5 mmol, 1.5 equiv) in dioxane for 3.5 h, affording sulfone **2f** (171 mg, 60% yield) as a white solid after purification by flash chromatography, eluting with 10-65% EtOAc in hexanes (elution gradient). **mp** 113-114 °C. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 8.57 (s, 1H), 8.12-8.00 (m, 2H), 8.00-7.87 (m, 2H), 7.77-7.65 (m, 2H), 4.52 (s, 2H). **^{13}C NMR** (175 MHz, $CDCl_3$) δ 135.8, 132.7, 132.0, 131.7, 129.8, 129.7, 129.6, 128.1, 128.0, 123.3, 44.6. **IR** (neat) 3020, 2950, 1313, 1103, 1070, 878, 825, 761, 671. **HRMS** (HESI) calcd for $[C_{11}H_9BrO_2S+Na]^+$: *m/z*, 306.9399 found 306.9403.



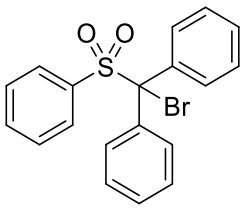
2-((Bromomethyl)sulfonyl)thiophene (2g). General procedure A was followed, starting with 2-(methylsulfonyl)thiophene (**1g**)[3] (162 mg, 1.0 mmol, 1.0 equiv), LiHMDS (184 mg, 1.1 mmol, 1.1 equiv), and Br_2 (77 µL, 1.5 mmol, 1.5 equiv) in dioxane for 3.5 h, affording sulfone **2g** (118 mg, 49% yield) as a white solid after purification by flash chromatography, eluting with 10-60% EtOAc in hexanes (elution gradient). **mp** 48-49 °C. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.87-7.79 (m, 2H), 7.25-7.20 (m, 1H), 4.53 (s, 2H). **^{13}C NMR** (175 MHz, $CDCl_3$) δ 136.5, 135.9, 128.2, 45.8. **IR** (neat) 3112, 3092, 3026, 2955, 1397, 1312, 1145, 1019, 859, 749, 724, 574, 551, 503. **HRMS** (HESI) calcd for $[C_5H_5BrO_2S_2+H]^+$: *m/z*, 240.8987 found 240.8989.



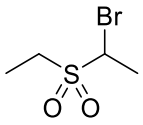
((1-Bromoethyl)sulfonyl)benzene (2h). General procedure A was followed, starting with (ethylsulfonyl)benzene (**1h**) (170 mg, 1.0 mmol, 1.0 equiv), *n*-BuLi (1.1 mmol, 1.1 equiv), and Br_2 (77 µL, 1.5 mmol, 1.5 equiv) in dioxane for 3.5 h, affording sulfone **2h** (141 mg, 57% yield) as a white solid after purification by flash chromatography, eluting with 10-50% EtOAc in hexanes (elution gradient). **mp** 45-46 °C. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.97 (d, *J* = 7.8 Hz, 2H), 7.76-7.67 (m, 1H), 7.60 (t, *J* = 7.5 Hz, 2H), 4.85 (q, *J* = 6.9 Hz, 1H), 1.97 (d, *J* = 6.9 Hz, 3H). **^{13}C NMR** (175 MHz, $CDCl_3$) δ 134.7, 134.6, 130.1, 129.1, 59.0, 19.4. **IR** (neat) 2964, 1445, 1289, 1188, 1047, 765, 694. **HRMS** (HESI) calcd for $[C_8H_9BrO_2S+H]^+$: *m/z*, 248.9579 found 248.9577.



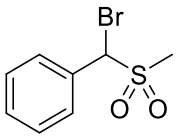
((Bromo(phenyl)methyl)sulfonyl)benzene (2i). General procedure A was followed, starting with (benzylsulfonyl)benzene (**1i**) (232 mg, 1.0 mmol, 1.0 equiv), LiHMDS (184 mg, 1.1 mmol, 1.1 equiv), and Br_2 (77 µL, 1.5 mmol, 1.5 equiv) in dioxane for 3.5 h, affording sulfone **2i** (200 mg, 64% yield) as a white solid after purification by flash chromatography, eluting with 10-65% EtOAc in hexanes (elution gradient). **mp** 188-190 °C. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.74-7.59 (m, 3H), 7.51-7.41 (m, 2H), 7.41-7.33 (m, 3H), 7.33-7.27 (m, 2H), 5.70 (s, 1H). **^{13}C NMR** (175 MHz, $CDCl_3$) δ 134.9, 134.4, 131.0, 130.4, 130.2, 130.1, 128.8, 128.5, 65.7. **IR** (neat) 2969, 1445, 1307, 1143, 1081, 731, 693. **HRMS** (HESI) calcd for $[C_{13}H_{11}BrO_2S+Na]^+$: *m/z*, 332.9555 found 332.9550.



(Bromo(phenylsulfonyl)methylene)dibenzene (2j). General procedure A was followed, starting with ((phenylsulfonyl)methylene)dibenzene (**1j**)[6] (500 mg, 1.6 mmol, 1.0 equiv), LiHMDS (301 mg, 1.8 mmol, 1.1 equiv), and Br_2 (130 µL, 2.4 mmol, 1.5 equiv) in dioxane for 3.5 h, affording sulfone **2j** (171 mg, 73% yield) as a white solid after purification by flash chromatography, eluting with 0-45% EtOAc in hexanes (elution gradient). **mp** 178-179 °C. **^{1}H NMR** (300 MHz, DMSO-d_6) δ 7.70-7.62 (m, 1H), 7.57-7.50 (m, 4H), 7.45-7.28 (m, 10H). **^{13}C NMR** (175 MHz, DMSO-d_6) δ 137.2, 135.2, 134.8, 131.4, 130.6, 130.1, 128.8, 128.6, 86.7. **IR** (neat) 3065, 1443, 1142, 1080, 752, 712, 681, 576. **HRMS** (HESI) calcd for $[C_{19}H_{15}BrO_2S+Na]^+$: *m/z*, 408.9868 found 408.9867.

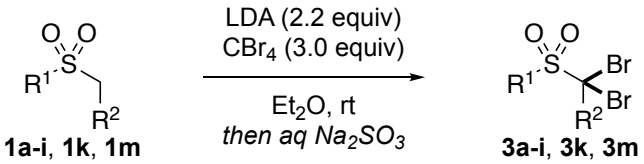


1-Bromo-1-(ethylsulfonyl)ethane (2k). General procedure A was followed, starting with (ethylsulfonyl)ethane (**1k**) (122 mg, 1.0 mmol, 1.0 equiv), LiHMDS (184 mg, 1.1 mmol, 1.1 equiv), and Br_2 (77 µL, 1.5 mmol, 1.5 equiv) in dioxane for 3.5 h, affording sulfone **2k** (59 mg, 29% yield) as a colorless oil after purification by flash chromatography, eluting with 10-65% EtOAc in hexanes (elution gradient). **^{1}H NMR** (300 MHz, $CDCl_3$) δ 4.78 (q, *J* = 7.0 Hz, 1H), 3.44-3.17 (m, 2H), 2.03 (d, *J* = 7.0 Hz, 3H), 1.45 (t, *J* = 7.5 Hz, 3H). **^{13}C NMR** (175 MHz, $CDCl_3$) δ 55.1, 43.9, 17.5, 6.3. **IR** (neat) 2981, 2944, 1445, 1310, 1131, 784, 736. **HRMS** (HESI) calcd for $[C_4H_9BrO_2S+H]^+$: *m/z*, 200.9579 found 200.9582.



(Bromo(methylsulfonyl)methyl)benzene (2l). General procedure A was followed, starting with ((methylsulfonyl)methyl)benzene (**1l**)[7,8] (170 mg, 1.0 mmol, 1.0 equiv), LiHMDS (184 mg, 1.1 mmol, 1.1 equiv), and Br_2 (77 µL, 1.5 mmol, 1.5 equiv) in dioxane for 3.5 h, affording sulfone **2l** (138 mg, 55% yield) as a white solid after purification by flash chromatography, eluting with 10-65% EtOAc in hexanes (elution gradient). **mp** 94-95 °C. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.70-7.56 (m, 2H), 7.54-7.36 (m, 3H), 5.68 (s, 1H), 3.03 (s, 3H). **^{13}C NMR** (175 MHz, $CDCl_3$) δ 130.8, 130.4, 130.1, 129.0, 63.8, 37.5. **IR** (neat) 3116, 3041, 2963, 1398, 1304, 1134, 781. **HRMS** (HESI) calcd for $[C_8H_9BrO_2S+H]^+$: *m/z*, 270.9399 found 270.9403.

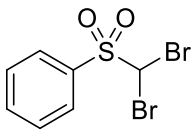
GENERAL PROCEDURE B: Synthesis of α,α-dibromosulfones 3a-3i, 3k, 3m



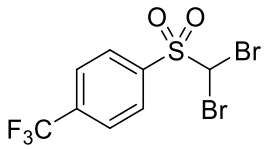
An oven-dried microwave vial equipped with a magnetic stirbar was charged with alkyl sulfone **1** (0.32 mmol, 1.0 equiv), capped and flushed with N_2. Anhydrous Et_2O (2.5 mL) was added and to the resulting solution was added LDA (2.0 M in THF/*n*-heptane/ethylbenzene, 0.35 mL, 0.70 mmol, 2.2 equiv) and stirred for 1.5 hours. After this time, the deprotonated sulfone solution was transferred via syringe to a separate microwave vial containing CBr_4 (318 mg, 0.96 mmol, 3.0 equiv) in Et_2O (5 mL). The reaction mixture was stirred for 2 h and then quenched by slow addition of aqueous sat. Na_2SO_3 (5 mL) and extracted with CH_2Cl_2 (2 x 30 mL). The combined organic fractions were washed with aqueous sat. Na_2SO_3 (2 x 30 mL), dried over Na_2SO_4, and concentrated under vacuum to give the crude α,α-dibrominated sulfone **3**, which was purified by flash chromatography (10-50% EtOAc in Hexanes, elution gradient) to afford the pure product.

On gram scale: The reaction was also carried out by dissolving the alkyl sulfone **1** (9.6 mmol, 1.0 equiv) in anhydrous Et_2O (50 mL) and adding LDA (2.0 M in THF/*n*-heptane/ethylbenzene, 10.85 mL, 21.1 mmol, 2.2 equiv), allowing to stir for 1.5 h at room temperature. After this time, the deprotonated sulfone was transferred to a separate vial containing CBr_4 (9.5 g, 28.8 mmol, 3.0 equiv) in Et_2O (100 mL) and stirred for an additional 2 h at room temperature.

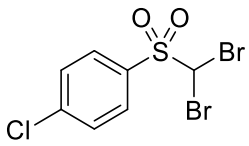
Specific procedures and characterisation data for α,α-dibromosulfones 3a-3i, 3k, 3m



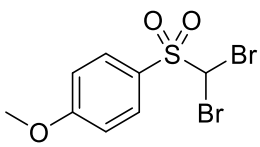
((Dibromomethyl)sulfonyl)benzene (3a). General procedure B was followed, starting with (methylsulfonyl)benzene (**1a**)[4] (50 mg, 0.32 mmol, 1.0 equiv), LDA (2.0 M in THF/*n*-heptane/ethylbenzene, 0.36 mL, 0.70 mmol, 2.2 equiv), carbon tetrabromide (318 mg, 0.96 mmol, 3.0 equiv) and H_2O (3 μL, 0.16 mmol, 0.5 equiv) in Et_2O for 3.5 h, affording sulfone **3a** (66 mg, 64% yield) as a white solid after purification by flash chromatography, eluting with 0-55% EtOAc in hexanes (elution gradient). The reaction can also be carried out on gram scale, starting with (methylsulfonyl)benzene (**1a**) (1.5 g, 9.6 mmol, 1.0 equiv), LDA (2.0 M in THF/*n*-heptane/ethylbenzene, 10.85 mL, 21.1 mmol, 2.2 equiv), carbon tetrabromide (9.5 g, 28.8 mmol, 3.0 equiv) and H_2O (90 μL, 4.8 mmol, 0.5 equiv) in Et_2O for 3.5 h, affording sulfone **3a** (1.8 g, 60% yield) as a white solid after purification by flash chromatography, eluting with 0-40% EtOAc in hexanes (elution gradient). **mp** 72-73 °C. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 8.10-8.01 (m, 2H), 7.83-7.72 (m, 1H), 7.69-7.58 (m, 2H), 6.24 (s, 1H). **^{13}C NMR** (175 MHz, $CDCl_3$) δ 135.4, 132.2, 131.2, 129.2, 50.5. **IR** (neat) 3067, 2986, 2922, 2851, 1446, 1325, 1147, 1079, 739, 682, 522. **HRMS** (HESI) calcd for $[C_7H_6Br_2O_2S+Na]^+$: *m/z*, 334.8348 found 334.8352.



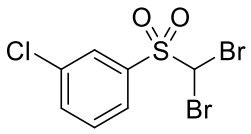
1-((Dibromomethyl)sulfonyl)-4-(trifluoromethyl)benzene (3b). General procedure B was followed, starting with 1-(methylsulfonyl)-4-(trifluoromethyl)benzene (**1b**)[3] (72 mg, 0.32 mmol, 1.0 equiv), LDA (2.0 M in THF/*n*-heptane/ethylbenzene, 0.36 mL, 0.70 mmol, 2.2 equiv), and carbon tetrabromide (318 mg, 0.96 mmol, 3.0 equiv) in Et_2O for 3.5 h, affording sulfone **3b** (78 mg, 64% yield) as a white solid after purification by flash chromatography, eluting with 0-55% EtOAc in hexanes (elution gradient). **mp** 97-99 °C. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 8.21 (d, J = 8.2 Hz, 2H), 7.90 (d, J = 8.2 Hz, 2H), 6.27 (s, 1H). **^{13}C NMR** (175 MHz, $CDCl_3$) δ 136.9 (q, J = 33.2 Hz) 135.8, 131.9, 126.3, 122.9 (q, J = 273.5 Hz), 49.8. **IR** (neat) 2988, 2952, 1319, 1135, 833, 699, 526. **HRMS** (HESI) calcd for $[C_8H_5Br_2F_3O_2S-H]^-$: *m/z*, 378.8256 found 378.8256.



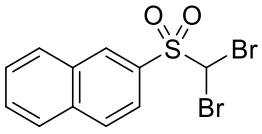
1-Chloro-4-((dibromomethyl)sulfonyl)benzene (3c). General procedure B was followed, starting with 1-Chloro-4-(methylsulfonyl)benzene (**1c**)[3] (61 mg, 0.32 mmol, 1.0 equiv), LDA (2.0 M in THF/*n*-heptane/ethylbenzene, 0.36 mL, 0.70 mmol, 2.2 equiv), and carbon tetrabromide (318 mg, 0.96 mmol, 3.0 equiv) in Et_2O for 3.5 h, affording sulfone **3c** (65 mg, 58% yield) as a white solid after purification by flash chromatography, eluting with 0-55% EtOAc in hexanes (elution gradient). **mp** 123-124 °C. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 8.00 (d, J = 8.6 Hz, 2H), 7.61 (d, J = 8.6 Hz, 2H), 6.24 (s, 1H). **^{13}C NMR** (175 MHz, $CDCl_3$) δ 142.6, 132.6, 130.4, 129.6, 50.2. **IR** (neat) 3091, 2955, 1575, 1329, 1177, 1078, 827, 777, 712, 648, 554. **HRMS** (HESI) calcd for $[C_7H_5Br_2ClO_2S-H]^-$: *m/z*, 344.7993 found 344.7991.



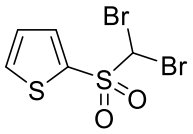
1-((Dibromomethyl)sulfonyl)-4-methoxybenzene (3d). General procedure B was followed, starting with 1-methoxy-4-(methylsulfonyl)benzene (**1d**)[4] (60 mg, 0.32 mmol, 1.0 equiv), LDA (2.0 M in THF/*n*-heptane/ethylbenzene, 0.36 mL, 0.70 mmol, 2.2 equiv), and carbon tetrabromide (318 mg, 0.96 mmol, 3.0 equiv) with 3 μL of H_2O in Et_2O (2.5/5 mL) for 3.5 h, affording sulfone **3d** (67 mg, 60% yield) as a white solid after purification by flash chromatography, eluting with 0-55% EtOAc in hexanes (elution gradient). **mp** 77-79 °C. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.97 (d, J = 9.1 Hz, 2H), 7.06 (d, J = 9.1 Hz, 2H), 6.23 (s, 1H), 3.92 (s, 3H). **^{13}C NMR** (175 MHz, $CDCl_3$) δ 165.2, 133.5, 122.9, 114.5, 55.9, 51.1. **IR** (neat) 2986, 2952, 2844, 1591, 1496, 1117, 1056, 1018, 832, 804, 550. **HRMS** (HESI) calcd for $[C_8H_8Br_2O_3S+Na]^+$: *m/z*, 364.8453 found 364.8449.



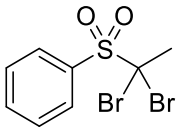
1-Chloro-3-((dibromomethyl)sulfonyl)benzene (3e). General procedure B was followed, starting with 1-Chloro-3-(methylsulfonyl)benzene (**1e**) (61 mg, 0.32 mmol, 1.0 equiv), LDA (2.0 M in THF/*n*-heptane/ethylbenzene, 0.36 mL, 0.70 mmol, 2.2 equiv), and carbon tetrabromide (318 mg, 0.96 mmol, 3.0 equiv) in Et_2O for 3.5 h, affording sulfone **3e** (57 mg, 51% yield) as a white solid after purification by flash chromatography, eluting with 0-60% EtOAc in hexanes (elution gradient). **mp** 67-68 °C. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 8.03 (t, *J* = 1.9 Hz, 1H), 7.95 (d, *J* = 7.8 Hz, 1H), 7.73 (d, *J* = 8.1 Hz, 1H), 7.58 (t, *J* = 8.0 Hz, 1H), 6.25 (s, 1H). **^{13}C NMR** (175 MHz, $CDCl_3$) δ 135.6, 133.9, 131.0, 130.4, 129.3, 50.1. **IR** (neat) 3090, 2953, 1326, 1182, 1104, 790, 745, 629, 571. **HRMS** (HESI) calcd for $[C_7H_5Br_2ClO_2S\text{-}H]^-$: *m/z*, 344.7993 found 344.7991.



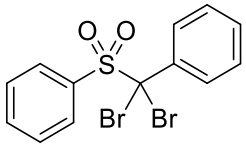
2-((Dibromomethyl)sulfonyl)naphthalene (3f). General procedure B was followed, starting with 2-(methylsulfonyl)naphthalene (**1f**) (66 mg, 0.32 mmol, 1.0 equiv), LDA (2.0 M in THF/*n*-heptane/ethylbenzene, 0.36 mL, 0.70 mmol, 2.2 equiv), carbon tetrabromide (318 mg, 0.96 mmol, 3.0 equiv) and H_2O (3 μL, 0.16 mmol, 0.5 equiv) in Et_2O for 3.5 h, affording sulfone **3f** (78 mg, 66% yield) as a white solid after purification by flash chromatography, eluting with 0-50% EtOAc in hexanes (elution gradient). **mp** 109-110 °C. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 8.64 (s, 1H), 8.10-7.92 (m, 4H), 7.75-7.66 (m, 2H), 6.34 (s, 1H). **^{13}C NMR** (175 MHz, $CDCl_3$) δ 136.1, 133.8, 131.9, 130.3, 129.7, 129.4, 129.1, 128.1, 128.1, 124.8, 50.8. **IR** (neat) 3076, 3056, 2981, 1318, 1144, 1066, 858, 814, 745, 648, 541. **HRMS** (HESI) calcd for $[C_{11}H_8Br_2O_2S\text{+}Na]^+$: *m/z*, 384.8504 found 384.8498.



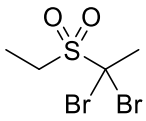
2-((Dibromomethyl)sulfonyl)thiophene (3g). General procedure B was followed, starting with 2-(methylsulfonyl)thiophene (**1g**)[3] (52 mg, 0.32 mmol, 1.0 equiv), LDA (2.0 M in THF/*n*-heptane/ethylbenzene, 0.36 mL, 0.70 mmol, 2.2 equiv), and carbon tetrabromide (318 mg, 0.96 mmol, 3.0 equiv) in Et_2O for 3.5 h, affording sulfone **3g** (65 mg, 63% yield) as a white solid after purification by flash chromatography, eluting with 0-55% EtOAc in hexanes (elution gradient). **mp** 47-49 °C. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.96-7.89 (m, 2H), 7.30-7.23 (m, 1H), 6.33 (s, 1H). **^{13}C NMR** (175 MHz, $CDCl_3$) δ 139.0, 137.5, 131.3, 128.2, 51.0. **IR** (neat) 3107, 3091, 2986, 1396, 1334, 1154, 1016, 858, 744, 573. **HRMS** (HESI) calcd for $[C_5H_4Br_2O_2S_2\text{-}H]^-$: *m/z*, 316.7947 found 316.7946.



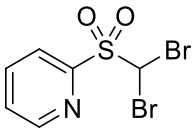
((1,1-Dibromoethyl)sulfonyl)benzene (3h). General procedure B was followed, starting with (ethylsulfonyl)benzene (**1h**) (55 mg, 0.32 mmol, 1.0 equiv), LDA (2.0 M in THF/*n*-heptane/ethylbenzene, 0.36 mL, 0.70 mmol, 2.2 equiv), and carbon tetrabromide (318 mg, 0.96 mmol, 3.0 equiv) in Et_2O for 3.5 h, affording sulfone **3h** (47 mg, 45% yield) as a white solid after purification by flash chromatography, eluting with 0-55% EtOAc in hexanes (elution gradient). **mp** 91-92 °C. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 8.20-8.09 (m, 2H), 7.83-7.71 (m, 1H), 7.66-7.58 (m, 2H), 2.73 (s, 3H). **^{13}C NMR** (175 MHz, $CDCl_3$) δ 135.2, 132.6, 131.3, 128.7, 70.7, 34.2. **IR** (neat) 2921, 1444, 1321, 1152, 1067, 735, 681, 541. **HRMS** (HESI) calcd for $[C_8H_8Br_2O_2S\text{+}Na]^+$: *m/z*, 348.8504 found 348.8501.



((Dibromo(phenyl)methyl)sulfonyl)benzene (3i). General procedure B was followed, starting with (benzylsulfonyl)benzene (**1i**) (74 mg, 0.32 mmol, 1.0 equiv), LDA (2.0 M in THF/*n*-heptane/ethylbenzene, 0.36 mL, 0.70 mmol, 2.2 equiv), and carbon tetrabromide (318 mg, 0.96 mmol, 3.0 equiv) in Et_2O for 3.5 h, affording sulfone **3i** (45 mg, 36% yield) as a white solid after purification by flash chromatography, eluting with 0-60% EtOAc in hexanes (elution gradient). **mp** 116-117 °C. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.83-7.75 (m, 2H), 7.67-7.59 (m, 3H), 7.45-7.37 (m, 3H), 7.34-7.27 (m, 2H). **^{13}C NMR** (175 MHz, $CDCl_3$) δ 134.8, 133.8, 132.4, 131.4, 131.1, 130.9, 128.2, 127.9, 79.2. **IR** (neat) 2973, 2922, 2865, 2844, 1443, 1322, 1147, 1059, 1016, 683, 564, 539. **HRMS** (HESI) calcd for $[C_{13}H_{10}Br_2O_2S\text{+}Na]^+$: *m/z*, 410.8661 found 410.8655.

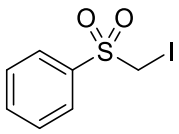


1,1-Dibromo-1-(ethylsulfonyl)ethane (3k). General procedure B was followed, starting with (ethylsulfonyl)ethane (**1k**) (39 mg, 0.32 mmol, 1.0 equiv), LDA (2.0 M in THF/*n*-heptane/ethylbenzene, 0.36 mL, 0.70 mmol, 2.2 equiv), and carbon tetrabromide (318 mg, 0.96 mmol, 3.0 equiv) in Et_2O for 3.5 h, affording sulfone **3k** (27 mg, 30% yield) as a light brown solid after purification by flash chromatography, eluting with 0-55% EtOAc in hexanes (elution gradient). **mp** 49-50 °C. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 3.64 (q, J = 7.5 Hz, 2H), 2.72 (s, 3H), 1.54 (t, J = 7.5 Hz, 3H). **^{13}C NMR** (175 MHz, $CDCl_3$) δ 68.6, 40.7, 32.5, 6.2. **IR** (neat) 2992, 2951, 1308, 1141, 1070, 741, 675, 571, 488. **HRMS** (HESI) calcd for $[C_4H_8Br_2O_2S+H]^+$: *m/z*, 278.8685 found 278.8681.

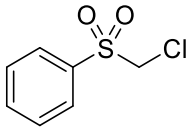


2-((Dibromomethyl)sulfonyl)pyridine (3m). General procedure B was followed, starting with 2-(methylsulfonyl)pyridine (**1m**) (50 mg, 0.32 mmol, 1.0 equiv), LDA (2.0 M in THF/*n*-heptane/ethylbenzene, 0.36 mL, 0.70 mmol, 2.2 equiv), and carbon tetrabromide (318 mg, 0.96 mmol, 3.0 equiv) in Et_2O for 3.5 h, affording sulfone **3m** (27 mg, 27% yield) as a white solid after purification by flash chromatography, eluting with 0-55% EtOAc in hexanes (elution gradient). **mp** 100-102 °C. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 8.79 (d, J = 4.7 Hz, 1H), 8.26-8.18 (m, 1H), 8.07-7.99 (m, 1H), 7.68-7.60 (m, 1H), 6.86 (s, 1H). **^{13}C NMR** (175 MHz, $CDCl_3$) δ 152.7, 150.8, 138.3, 128.4, 125.1, 48.4. **IR** (neat) 2922, 2850, 1579, 1336, 1166, 1106, 752, 559, 526. **HRMS** (HESI) calcd for $[C_6H_5Br_2NO_2S+H]^+$: *m/z*, 313.8481 found 313.8477.

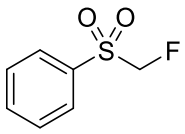
Specific procedures and characterisation data of α-halosulfones 4-6 and α,α,α-tribromosulfone 7



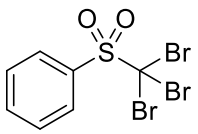
((Iodomethyl)sulfonyl)benzene (4). General procedure A was followed, starting with (methylsulfonyl)benzene (**1a**)[4] (156 mg, 1.0 mmol, 1.0 equiv), LiHMDS (184 mg, 1.1 mmol, 1.1 equiv), and I_2 (381 mg, 1.5 mmol, 1.5 equiv) in dioxane for 3.5 h, affording sulfone **4** (142 mg, 50% yield) as a white solid after purification by flash chromatography, eluting with 10-65% EtOAc in hexanes (elution gradient). The reaction can also be carried out on gram scale, starting with (methylsulfonyl)benzene (**1a**)[4] (1.2 g, 7.68 mmol, 1.0 equiv), LiHMDS (1.4 g, 8.45 mmol, 1.1 equiv), and I_2 (2.9 g, 11.55 mmol, 1.5 equiv) in dioxane for 3.5 h, affording sulfone **4** (968 mg, 45% yield) as a white solid after purification by flash chromatography, eluting with 0-45% EtOAc in hexanes (elution gradient). **mp** 63-65 °C. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.98 (d, *J* = 8.3 Hz, 2H), 7.72 (t, *J* = 7.4 Hz, 1H), 7.67-7.54 (m, 2H), 4.46 (s, 2H). **^{13}C NMR** (175 MHz, $CDCl_3$) δ 135.9, 134.6, 129.4, 129.0, 17.0. **IR** (neat) 3061, 3003, 2934, 1446, 1288, 1175, 1135, 1075, 800, 736, 678, 616, 517. **HRMS** (HESI) calcd for $[C_7H_7IO_2S+Na]^+$: *m/z*, 304.9104 found 304.9098.



((Chloromethyl)sulfonyl)benzene (5). General procedure A was followed, starting with (methylsulfonyl)benzene (**1a**)[4] (156 mg, 1.0 mmol, 1.0 equiv), LiHMDS (184 mg, 1.1 mmol, 1.1 equiv), and 2,3,4,5,6,6-hexachlorocyclo-2,4-dienone (451 mg, 1.5 mmol, 1.5 equiv) in dioxane for 3.5 h, affording sulfone **5** (90 mg, 47% yield) as a white solid after purification by flash chromatography, eluting with 10-65% EtOAc in hexanes (elution gradient). **mp** 48-50 °C. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 8.06-7.93 (m, 2H), 7.74 (t, *J* = 7.5 Hz, 1H), 7.62 (t, *J* = 7.5 Hz, 2H), 4.53 (s, 2H). **^{13}C NMR** (175 MHz, $CDCl_3$) δ 135.6, 134.8, 129.4, 129.3, 58.5. **IR** (neat) 3011, 2947, 2865, 1448, 1306, 1156, 1132, 1071, 865, 737, 684, 516. **HRMS** (HESI) calcd for $[C_7H_7ClO_2S+Na]^+$: *m/z*, 212.9748 found 212.9745.



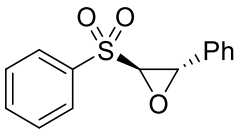
((Fluoromethyl)sulfonyl)benzene (6). General procedure A was followed, starting with (methylsulfonyl)benzene (**1a**)[4] (156 mg, 1.0 mmol, 1.0 equiv), LiHMDS (184 mg, 1.1 mmol, 1.1 equiv), and *N*-fluorobenzenesulfonimide (NFSI, 473 mg, 1.5 mmol, 1.5 equiv) in dioxane for 3.5 h, affording sulfone **6** (23 mg, 13% yield) as a white solid after purification by flash chromatography, eluting with 10-65% EtOAc in hexanes (elution gradient). **mp** 52-54 °C. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 8.0-7.95 (m 2H), 7.80-7.69 (m, 1H), 7.68-7.56 (m, 2H), 5.13 (d, *J* = 47.1 Hz, 2H). **^{13}C NMR** (175 MHz, $CDCl_3$) δ 135.9, 134.9, 129.5, 129.0, 92.0 (d, *J* = 220 Hz). **IR** (neat) 3014, 2950, 1448, 1316, 1145, 1050, 938, 751, 684, 523. **HRMS** (HESI) calcd for $[C_7H_7FO_2S+H]^+$: *m/z*, 175.0224 found 175.0221.



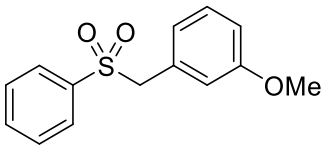
((Tribromomethyl)sulfonyl)benzene (7). To a solution of KOH (281 mg, 5.0 mmol, 5.0 equiv) in dry methanol (3 mL) was added ((dibromomethyl)sulfonyl)benzene (**3a**) (314 mg, 1.0 mmol, 1.0 equiv) and cooled to 0 °C. A solution of Br_2 (0.13 mL, 2.6 mmol, 2.6 equiv) in CCl_4 (0.5 mL) was added dropwise and the reaction was slowly warmed to room temperature. After 1.0 h, the precipitate was filtered and washed twice with hexanes. The filtrate was dried with $MgSO_4$, filtered, and concentrated. The crude sample was then recrystallized from 2-propanol to afford sulfone **7** (40 mg, 10% yield) as a white solid. All analyses were consistent with the previously reported data.[14]

[14] D. L. Fields and H. Shechter, *J. Org. Chem.*, 1986, **51**, 3369-3371.

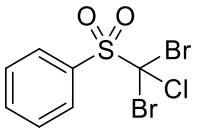
Specific procedures and characterisation data of sulfones 8-10



***trans*-2-phenyl-3-(phenylsulfonyl)oxirane (8).** Prepared following literature procedure[15], starting with ((Bromomethyl)sulfonyl)benzene (**2a**) (50 mg, 0.21 mmol, 1.0 equiv), benzaldehyde (22 µL, 0.21 mmol, 1.0 equiv), and potassium *tert*-butoxide (24 mg, 0.21 mmol, 1.0 equiv), affording product **8** (54 mg, 97% yield) as a white solid after recrystallisation from hexanes/$CHCl_3$. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.00 (d, J = 8.4 Hz, 2H), 7.77-7.72 (m, 1H), 7.64 (t, J = 7.8 Hz, 2H), 7.37 (dt, J = 5.4, 3.0 Hz, 3H), 7.27 (d, J = 2.1 Hz, 2H), 4.59 (d, J = 1.6 Hz, 1H), 4.18 (d, J = 1.6 Hz, 1H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 136.9, 134.6, 132.7, 129.6, 129.5, 128.9, 128.8, 126.1, 71.0, 57.5. All analyses were consistent with the previously reported data.[15]



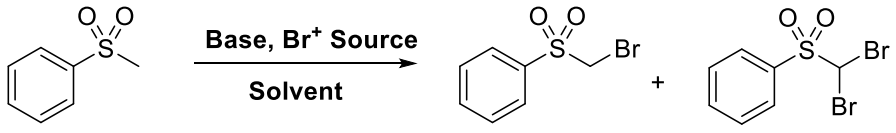
((1-methoxy-3-((phenylsulfonyl)methyl)benzene (9). Prepared following literature procedure[16], starting with ((Bromomethyl)sulfonyl)benzene (**2a**) (82 mg, 0.35 mmol, 1.0 equiv), ZnI_2 (145 mg, 0.46 mmol, 1.3 equiv), 3-methoxyphenylmagnesium bromide (1M in THF, 0.46 mL, 0.46 mmol, 1.3 equiv), $NiCl_2$•glyme (8 mg, 0.04 mmol, 0.1 equiv), and (*S*,*S*)-PhBOX (15 mg, 0.05 mmol, 0.13 equiv), affording sulfone **9** (43 mg, 46% yield) as a white solid after purification by flash chromatography, eluting with 0-35% EtOAc in hexanes (elution gradient). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.65 (d, J = 6.8 Hz, 2H), 7.60 (t, J = 7.5 Hz, 1H), 7.45 (t, J = 7.8 Hz, 2H), 7.15 (t, J = 7.9 Hz, 1H), 6.84 (dd, J = 8.4, 2.6 Hz, 1H), 6.64 (d, J = 7.6 Hz, 1H), 6.60 (t, J = 2.1 Hz, 1H), 4.28 (s, 2H), 3.70 (s, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 159.6, 137.9, 133.7, 129.5, 129.4, 128.9, 128.7, 123.2, 115.9, 114.8, 62.9, 55.2. All analyses were consistent with the previously reported data.[17]



((Dibromochloromethyl)sulfonyl)benzene (10). Prepared following literature procedure,[18] starting with ((dibromomethyl)sulfonyl)benzene (**3a**) (100 mg, 0.32 mmol, 1.0 equiv) and 8% NaOCl in H_2O (0.80 mL, 0.96 mmol, 3.0 equiv) neat at 75 °C for 4 h, affording sulfone **10** (97 mg, 87% yield) as a white solid after purification by flash chromatography, eluting with 0-50% EtOAc in hexanes (elution gradient). **mp** 104-106 °C. **^{1}H NMR** (700 MHz, DMSO-d_6) δ 8.17-8.11 (m, 2H), 7.98-7.88 (m, 1H), 7.76 (t, J = 6.9 Hz, 2H). **^{13}C NMR** (175 MHz, DMSO-d_6) δ 136.8, 133.4, 129.9, 129.0, 69.3. **IR** (neat) 3065, 2918, 1448, 1331, 1155, 1075, 680, 543. **HRMS** (HESI) calcd for $[C_7H_5Br_2ClO_2S+Na]^+$: *m/z*, 368.7958 found 368.7957.

[15] P. F. Vogt and D. F. Tavares, *Can. J. Chem.*, 1969, **47**, 2875-2881.
[16] J. Choi, P. Martín-Gago and G. C. Fu, *J. Am. Chem. Soc.*, 2014, **136**, 12161-12165.
[17] A. Orita, H. Taniguchi and J. Otera, *Chem. Asian J.*, 2006, **1**, 430-437.
[18] K. M. Borys, M. D. Korzyński and Z. Ochal, *Tetrahedron Lett.*, 2012, **53**, 6606-6610.

Optimisation of the α-monobromination reaction

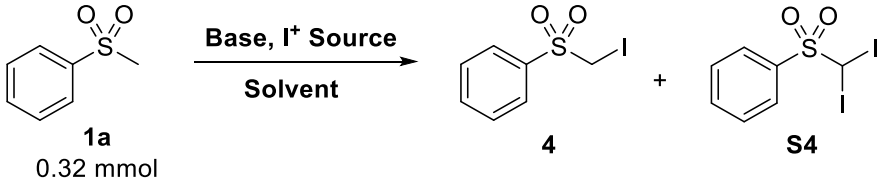


1a 0.32 mmol **2a** **3a**

Entry	Br^+ Source (equiv)	Temp.	Base (equiv)	Solvent	2a[a]	3a[a]	Remaining 1a[a]
1	Br_2 (1.5)	rt	*n*-BuLi (1.1)	THF	12%	15%	47%
2	Br_2 (1.5)	0 °C	*n*-BuLi (1.1)	THF	11%	18%	57%
3	Br_2 (1.5)	rt	*n*-BuLi (1.1)	Et_2O	59%	22%	32%
4	Br_2 (1.5)	–78 °C	*n*-BuLi (1.1)	Et_2O	33%	21%	45%
5	Br_2 (1.5)	40 °C	*n*-BuLi (1.1)	Et_2O	51%	16%	31%
6[c]	Br_2 (1.5)	rt	*n*-BuLi (1.1)	Et_2O	1%	9%	59%
7	NBS (1.5)	rt	*n*-BuLi (1.1)	Et_2O	21%	5%	61%
8	$CBrCl_3$ (1.5)	rt	*n*-BuLi (1.1)	Et_2O	15%	16%	23%
9	DBDMH (1.5)	rt	*n*-BuLi (1.1)	Et_2O	34%	0%	39%
10	CBr_4 (1.5)	rt	*n*-BuLi (1.1)	Et_2O	5%	45%	8%
11	Br_2 (1.5)	rt	*n*-BuLi (2.2)	Et_2O	29%	37%	10%
12	Br_2 (5.0)	rt	*n*-BuLi (1.1)	Et_2O	56%	18%	24%
13	Br_2 (1.5)	rt	LDA (1.1)	Et_2O	36%	7%	57%
14	Br_2 (1.5)	rt	LiHMDS (1.1)	Et_2O	51%	18%	29%
15	Br_2 (1.5)	rt	NaHMDS (1.1)	Et_2O	37%	18%	42%
16	Br_2 (1.5)	rt	KHMDS (1.1)	Et_2O	23%	19%	58%
17	Br_2 (1.5)	rt	LiTMP (1.1)	Et_2O	36%	9%	49%
18	Br_2 (1.5)	rt	NaH (1.1)	Et_2O	0%	0%	100%
19	Br_2 (1.5)	rt	LiO*t*-Bu (1.1)	Et_2O	0%	0%	100%
20	Br_2 (1.5)	rt	KO*t*-Bu (1.1)	Et_2O	4%	20%	76%
21	Br_2 (1.5)	rt	*n*-BuLi (1.1)	*i*-Pr_2O	42%	14%	32%
22	Br_2 (1.5)	rt	*n*-BuLi (1.1)	*t*-BuOMe	48%	21%	24%
23	Br_2 (1.5)	rt	*n*-BuLi (1.1)	DME	56%	3%	34%
24	Br_2 (1.5)	rt	*n*-BuLi (1.1)	Dioxane	68%	0%	37%
25	Br_2 (1.5)	rt	*n*-BuLi (1.1)	DMSO	0%	0%	100%
26	Br_2 (1.5)	rt	*n*-BuLi (1.1)	DMF	0%	0%	100%
27	Br_2 (1.5)	rt	*n*-BuLi (1.1)	PhMe	0%	0%	100%
28	Br_2 (1.5)	rt	KOH (1.1)	*t*-BuOH	0%	0%	100%
29	Br_2 (1.5)	rt	*s*-BuLi (1.1)	Dioxane	14%	0%	79%
30	Br_2 (1.5)	rt	*t*-BuLi (1.1)	Dioxane	27%	0%	71%
31[d]	Br_2 (1.5)	rt	*n*-BuLi (1.1)	Dioxane	67%	8%	30%
32[d]	Br_2 (1.5)	rt	LiHMDS (1.1)	Dioxane	64%	0%	36%
33[d]	**Br_2 (1.5)**	**rt**	**LiHMDS (1.1)**	**Dioxane**	**57%[b]**	**0%**	-
34[e]	Br_2 (1.5)	rt	LiHMDS (1.1)	Dioxane	56%[b]	0%	-

[a] NMR yield determined using 1,3,5-trimethoxybenzene as internal standard. [b] Isolated yield. [c] Reverse addition [d] 1.0 mmol scale. [e] 7.7 mmol scale

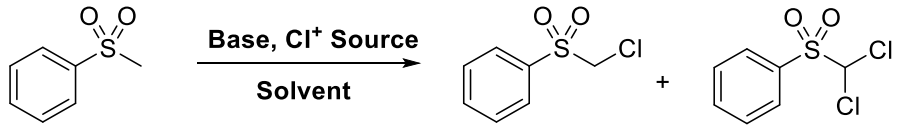
Optimisation of the α-monoiodination reaction



Entry	I^+ Source (equiv)	Temp.	Base (equiv)	Solvent	4[a]	S4[a]	Remaining 1a[a]
1	I_2 (1.5)	rt	*n*-BuLi (1.1)	Dioxane	48%	0%	52%
2	I_2 (3.0)	rt	*n*-BuLi (1.1)	Dioxane	57%	0%	44%
3	NIS (1.5)	rt	*n*-BuLi (1.1)	Dioxane	57%	0%	42%
4	NIS (3.0)	rt	*n*-BuLi (1.1)	Dioxane	56%	0%	40%
5	NIS (1.5)	100 °C	*n*-BuLi (1.1)	Dioxane	16%	0%	48%
6	NIS (1.5)	40 °C	*n*-BuLi (1.1)	Dioxane	51%	0%	45%
7[c]	NIS (1.5)	rt	LiHMDS (1.1)	Dioxane	51%	0%	52%
8[c]	I_2 (1.5)	rt	LiHMDS (1.1)	Dioxane	56%	0%	44%
9[c]	**I_2 (1.5)**	**rt**	**LiHMDS (1.1)**	**Dioxane**	**50%[b]**	**0%**	-
10[c]	DIH (1.5)	rt	LiHMDS (1.1)	Dioxane	26%	23%	50%
11[d]	I_2 (1.5)	rt	LiHMDS (1.1)	Dioxane	45%[b]	0%	-

[a] NMR yield determined using 1,3,5-trimethoxybenzene as internal standard. [b] Isolated yield. [c] 1.0 mmol scale. [d] 7.7 mmol scale.

Optimisation of the α-monochlorination reaction



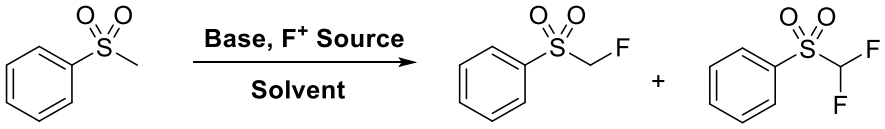
1a
0.32 mmol

5 **S5**

Entry	Cl^+ Source (equiv)	Temp.	Base (equiv)	Solvent	5[a]	S5[a]	Remaining 1a[a]
1	CCl_4 (1.5)	rt	*n*-BuLi (1.1)	Dioxane	0%	9%	64%
2	CCl_4 (20.3)	80 °C	KOH (12.0)	*t*-BuOH	0%	0%	61%
3	CCl_4 (1.5)	80 °C	KOH (1.1)	*t*-BuOH	0%	0%	90%
4	NCS (1.5)	rt	*n*-BuLi (1.1)	Dioxane	0%	0%	100%
5	2,3,4,5,6,6-hexachloro-2,4-dien-1-one (1.5)	rt	*n*-BuLi (1.1)	Dioxane	48%	10%	38%
6	2,3,4,5,6,6-hexachloro-2,4-dien-1-one (3.0)	rt	*n*-BuLi (1.1)	Dioxane	47%	0%	30%
7	2,3,4,5,6,6-hexachloro-2,4-dien-1-one (1.5)	100 °C	*n*-BuLi (1.1)	Dioxane	11%	8%	56%
8	2,3,4,5,6,6-hexachloro-2,4-dien-1-one (1.5)	40 °C	*n*-BuLi (1.1)	Dioxane	43%	6%	38%
9	C_2Cl_6 (1.5)	rt	*n*-BuLi (1.1)	Dioxane	0%	10%	54%
10[c]	2,3,4,5,6,6-hexachloro-2,4-dien-1-one (1.5)	rt	*n*-BuLi (1.1)	Dioxane	46%	4%	32%
11[c]	**2,3,4,5,6,6-hexachloro-2,4-dien-1-one (1.5)**	**rt**	**LiHMDS (1.1)**	**Dioxane**	**47%[b]**	**0%**	-
12[c]	DCDMH (1.5)	rt	LiHMDS (1.1)	Dioxane	30%	0%	62%

[a] NMR yield determined using 1,3,5-trimethoxybenzene as internal standard. [b] Isolated yield. [c] 1.0 mmol scale

Optimisation of the α-monofluorination reaction

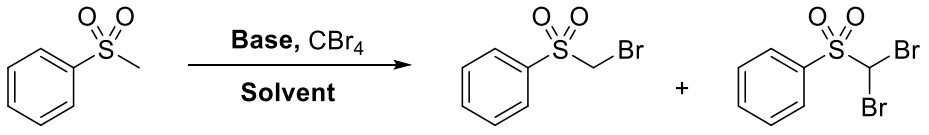


Entry	F^+ Source (equiv)	Temp.	Base (equiv)	Solvent	6[a]	S6[a]	Remaining 1a[a]
1	NFSI (1.5)	rt	*n*-BuLi (1.1)	Dioxane	12%	0%	34%
2	Selectfluor (1.5)	rt	*n*-BuLi (1.1)	Dioxane	4%	0%	61%
3	NFSI (1.5)	100 °C	*n*-BuLi (1.1)	Dioxane	17%	0%	57%
4	1-Fluoro-2,4,6-trimethylpyridinium triflate (1.5)	rt	*n*-BuLi (1.1)	Dioxane	0%	0%	50%
5	1-Fluoropyridinium triflate (1.5)	rt	*n*-BuLi (1.1)	Dioxane	0%	0%	62%
6	Fluoro-*N*,*N*,*N'*,*N'*-tetramethylformamidinium hexafluorophosphate (1.5)	rt	*n*-BuLi (1.1)	Dioxane	0%	0%	56%
7[c]	**NFSI (1.5)**	**rt**	**LiHMDS (1.1)**	**Dioxane**	**13%[b]**	**0%**	-
8	NFSI (1.5)	40 °C	LiHMDS (1.1)	Dioxane	21%	0%	58%
9	NFSI (1.5)	rt	LiHMDS (1.1)	THF	13%[b]	0%	61%
10[19]	NFSI (1.4)	–78 °C to rt	LDA (1.2)	PhMe	10%	0%	71%

[a] NMR yield determined using 1,3,5-trimethoxybenzene as internal standard. [b] Isolated yield. [c] 1.0 mmol scale

[19] W. Wei, R. K. Khangarot, L. Stahl, C. Veresmortean, P. Pradhan, L. Yang and B. Zajc, *Org. Lett.*, 2018, **20**, 3574-3578.

Optimisation of the α,α-dibromination reaction

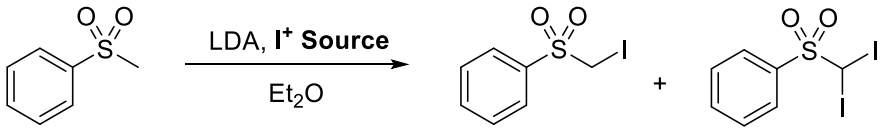


1a 0.32 mmol **2a** **3a**

Entry	Base (equiv)	Solvent	H_2O	Temp.	CBr_4 equiv	2a[a]	3a[a]	Remaining 1a[a]
1	*n*-BuLi (1.1)	Et_2O	No	rt	1.5	5%	45%	8%
2	*n*-BuLi (1.1)	Et_2O	No	–78 °C	1.5	15%	43%	6%
3	*n*-BuLi (1.1)	Et_2O	No	0 °C	1.5	18%	41%	5%
4	*n*-BuLi (2.2)	Et_2O	No	rt	3.0	0%	52%	5%
5	LiTMP (2.2)	Et_2O	No	rt	3.0	0%	48%	6%
6	LDA (2.2)	Et_2O	No	rt	3.0	0%	67%	1%
7	LiHMDS (2.2)	Et_2O	No	rt	3.0	0%	36%	6%
8	NaHMDS (2.2)	Et_2O	No	rt	3.0	0%	36%	10%
9	KHMDS (2.2)	Et_2O	No	rt	3.0	0%	40%	4%
10	KOH (2.2)	Et_2O	No	rt	3.0	0%	0%	100%
11	NaH (2.2)	Et_2O	No	rt	3.0	0%	26%	68%
12	*t*-BuOK (2.2)	Et_2O	No	rt	3.0	0%	29%	0%
13	*t*-BuOLi (2.2)	Et_2O	No	rt	3.0	0%	62%	1%
14	*t*-BuLi (2.2)	Et_2O	No	rt	3.0	0%	20%	1%
15	LDA (2.2)	Dioxane	No	rt	3.0	54%	2%	25%
16	LDA (2.2)	THF	No	rt	3.0	17%	43%	20%
17	LDA (2.2)	DME	No	rt	3.0	66%	2%	19%
18	LDA (2.2)	*i*-Pr_2O	No	rt	3.0	16%	59%	11%
19	LDA (2.2)	*t*-BuOMe	No	rt	3.0	13%	55%	12%
20	LDA (2.2)	PhMe	No	rt	3.0	2%	55%	3%
21	LDA (2.2)	DMSO	No	rt	3.0	14%	0%	66%
22	LDA (2.2)	DMF	No	rt	3.0	2%	0%	0%
23	LDA (2.2)	Et_2O	No	–20 °C	3.0	0%	55%	2%
24	LDA (2.2)	Et_2O	No	40 °C	3.0	1%	54%	3%
25	LDA (2.2)	Et_2O	No	rt	6.0	2%	52%	12%
26	LDA (2.2)	Et_2O	3 µL	rt	3.0	1%	75%	4%
27	**LDA (2.2)**	**Et_2O**	**3 µL**	**rt**	**3.0**	**1%**	**64%[b]**	-
28	LDA (2.2)	Et_2O	2 µL	rt	3.0	1%	58%	4%
29	LDA (2.2)	Et_2O	4 µL	rt	3.0	19%	54%	12%
30[c]	LDA (2.2)	Et_2O	90 µL	rt	3.0	< 1%	60%[b]	-

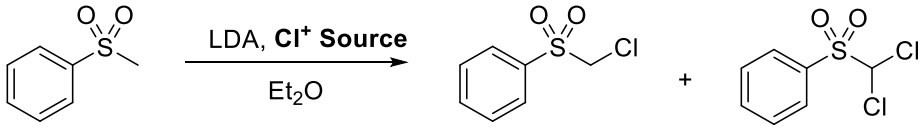
[a] NMR yield determined using 1,3,5-trimethoxybenzene as internal standard. [b] Isolated yield.
[c] 9.6 mmol scale.

Attempted controlled syntheses of α,α-diiodosulfones, α,α-dichlorosulfones and α,α-difluorosulfones



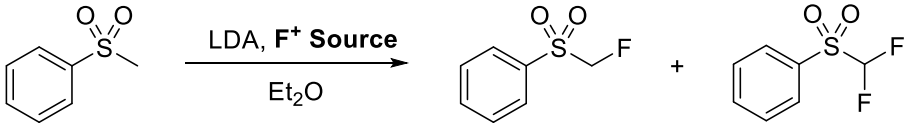
Entry	I^+ Source (equiv)	Temp.	LDA equiv	4[a]	S4[a]	Remaining 1a[a]
1	NIS (6.0)	rt	4.0	18%	37%	17%
2	NIS (3.0)	rt	2.2	13%	26%	35%
3	NIS (3.0)	40 °C	2.2	13%	27%	29%
4	I_2 (3.0)	rt	2.2	22%	19%	16%
5	CI_4 (3.0)	rt	2.2	6%	7%	14%
6	DIH (3.0)	rt	2.2	20%	17%	39%

[a] NMR yield determined using 1,3,5-trimethoxybenzene as internal standard.



Entry	Cl^+ Source (equiv)	Temp.	LDA equiv	5[a]	S5[a]	Remaining 1a[a]
1	CCl_4 (3.0)	rt	2.2	0%	4%	73%
2	DCDMH (3.0)	rt	2.2	18%	3%	71%
3	2,3,4,5,6,6-hexachloro-2,4-dien-1-one (3.0)	rt	2.2	13%	24%	51%

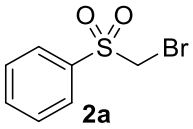
[a] NMR yield determined using 1,3,5-trimethoxybenzene as internal standard.



Entry	F^+ Source (equiv)	Temp.	LDA equiv	6[a]	S6[a]	Remaining 1a[a]
1	NFSI (3.0)	rt	2.2	15%	0%	55%
2	Selectfluor (3.0)	rt	2.2	0%	0%	100%

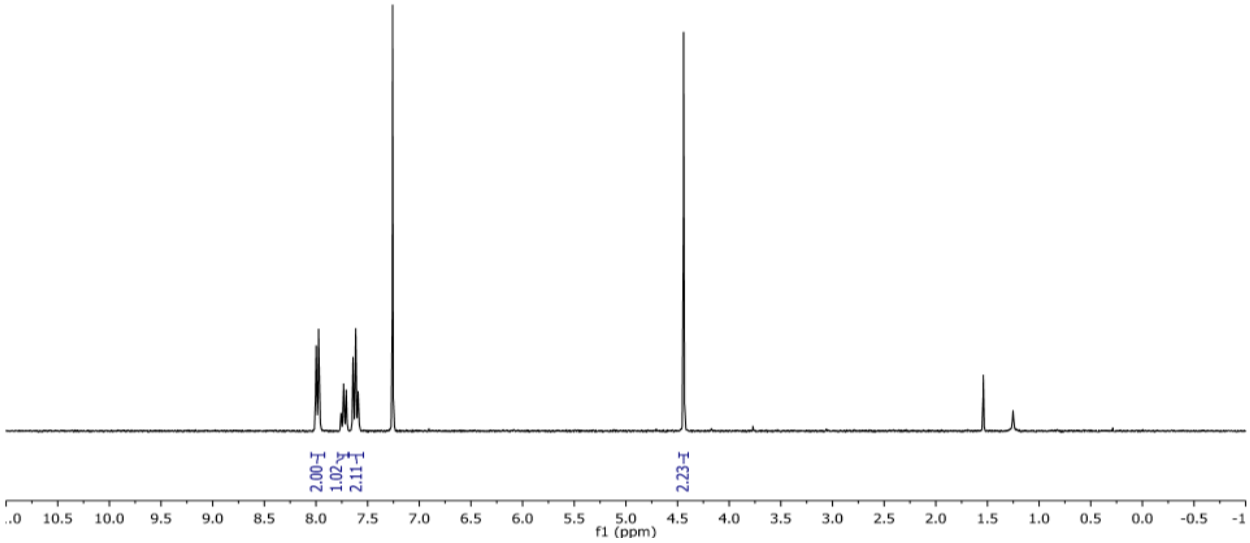
[a] NMR yield determined using 1,3,5-trimethoxybenzene as internal standard.

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

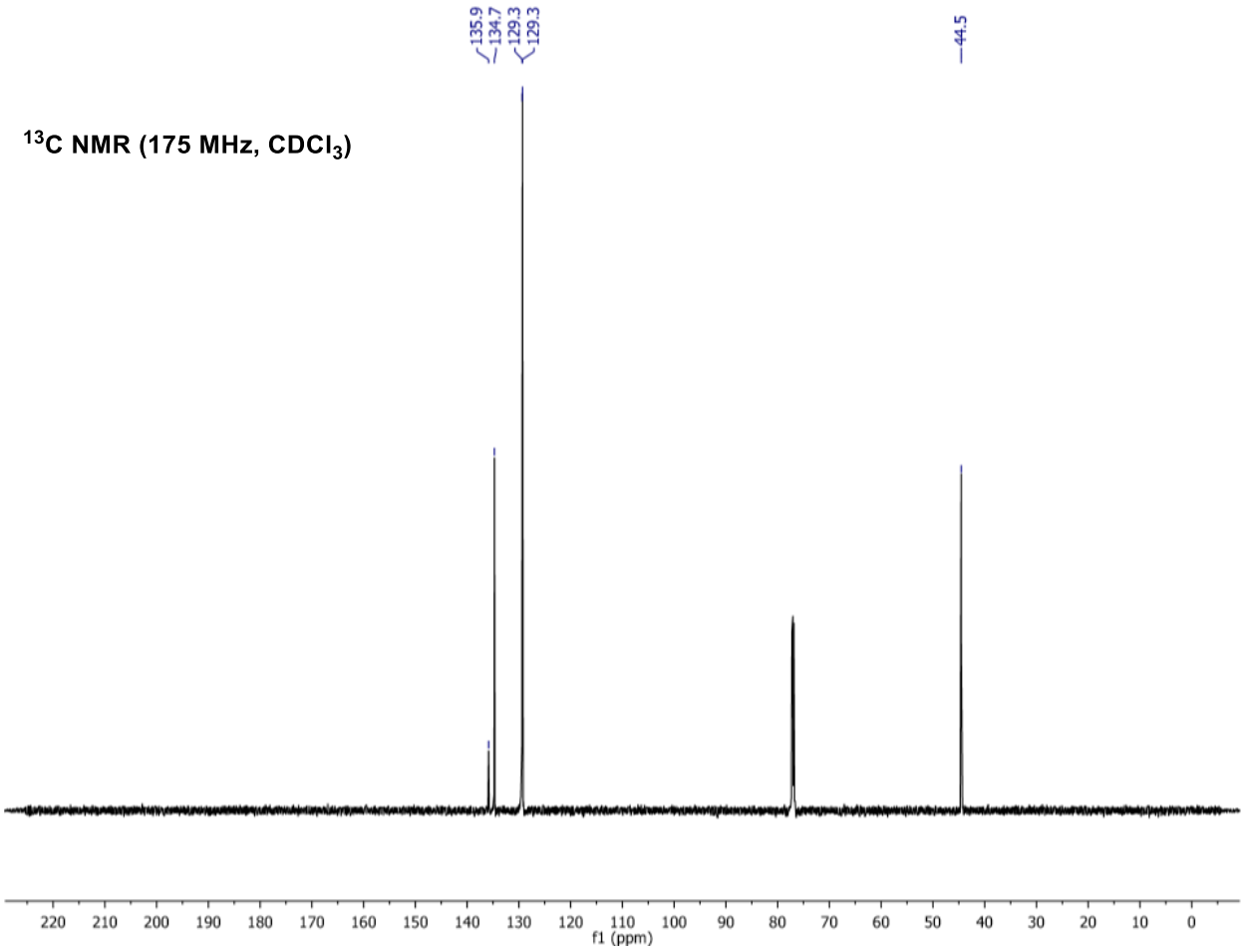


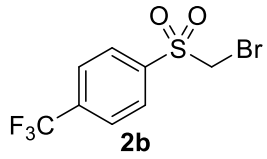
2a

^{1}H NMR (300 MHz, $CDCl_3$)



^{13}C NMR (175 MHz, $CDCl_3$)

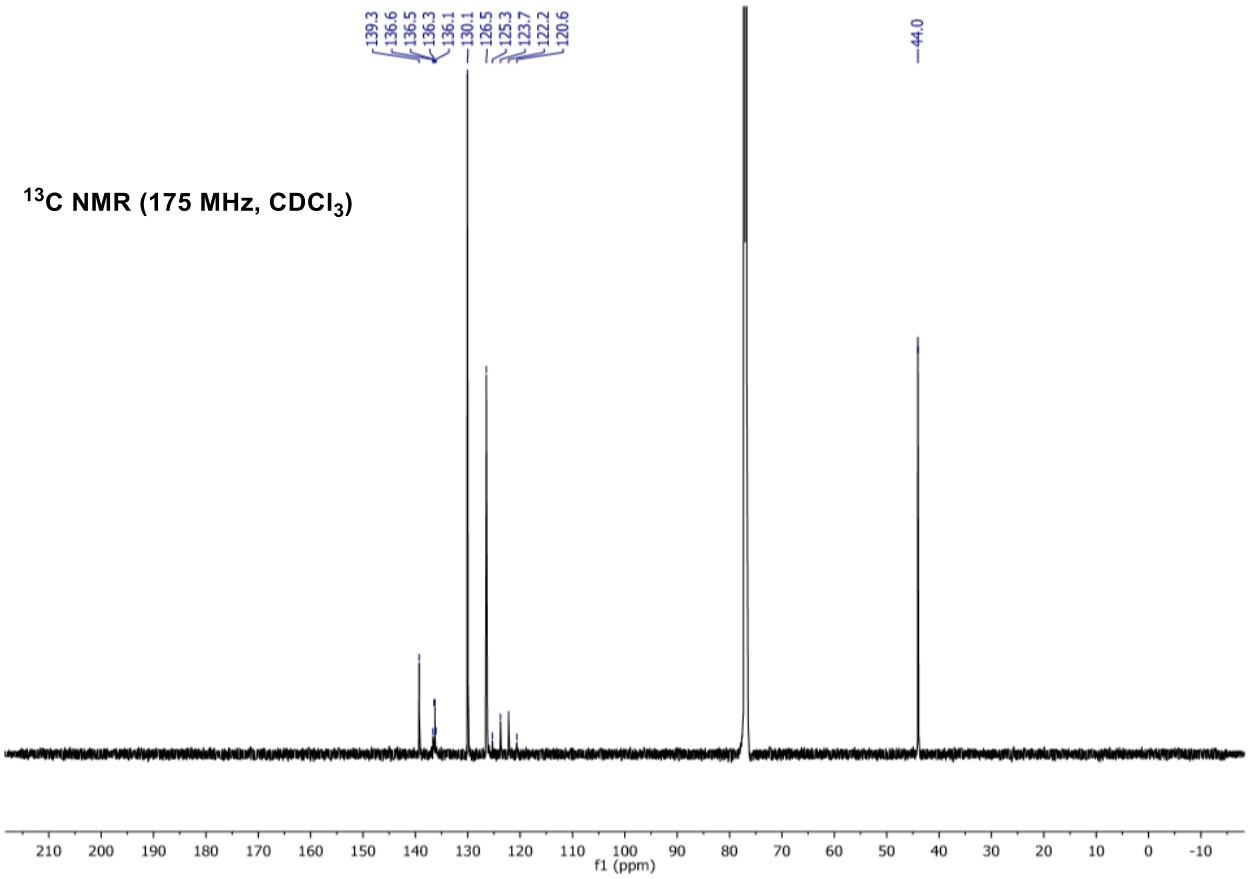


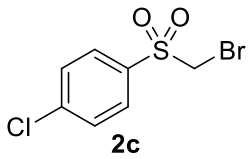


2b

^{1}H NMR (300 MHz, $CDCl_3$)

^{13}C NMR (175 MHz, $CDCl_3$)

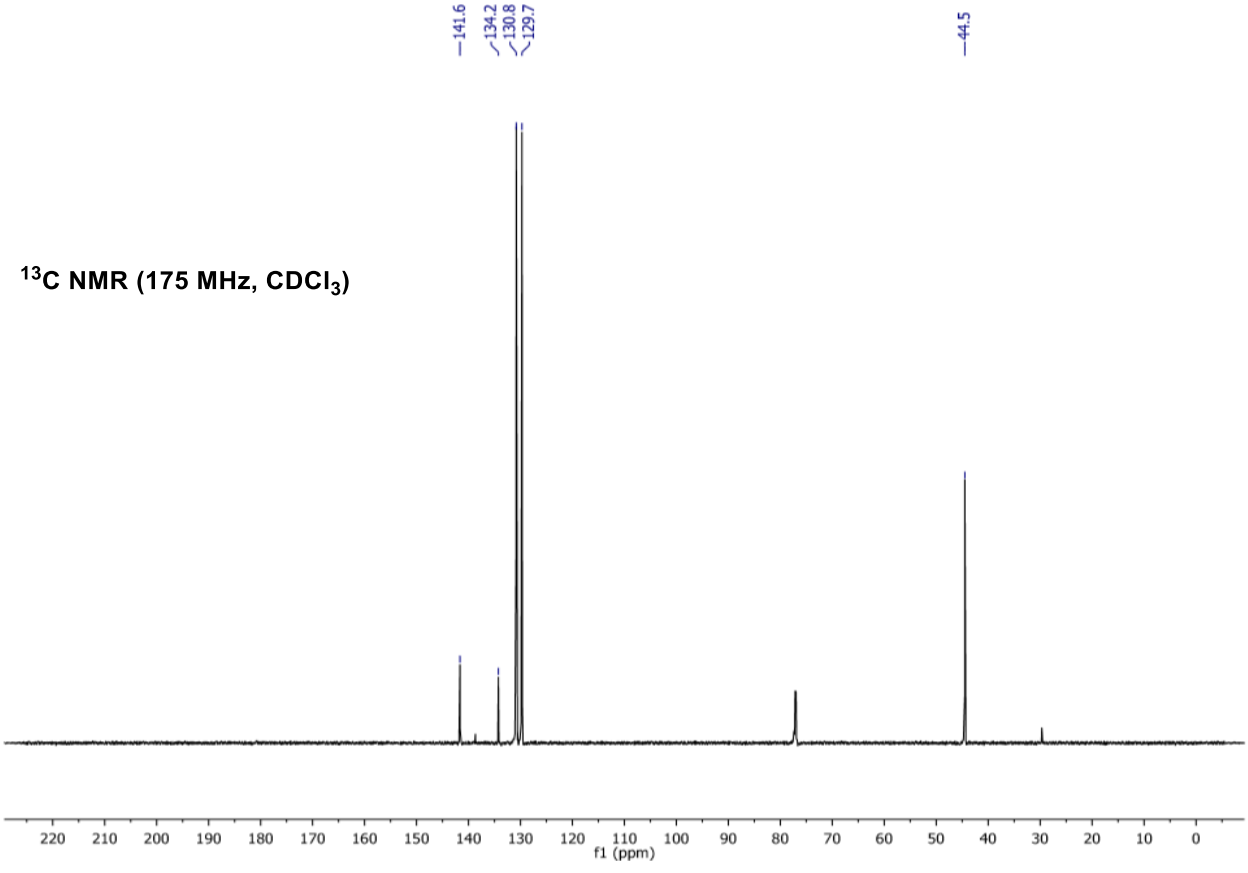


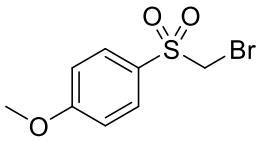


2c

^{1}H NMR (300 MHz, $CDCl_3$)

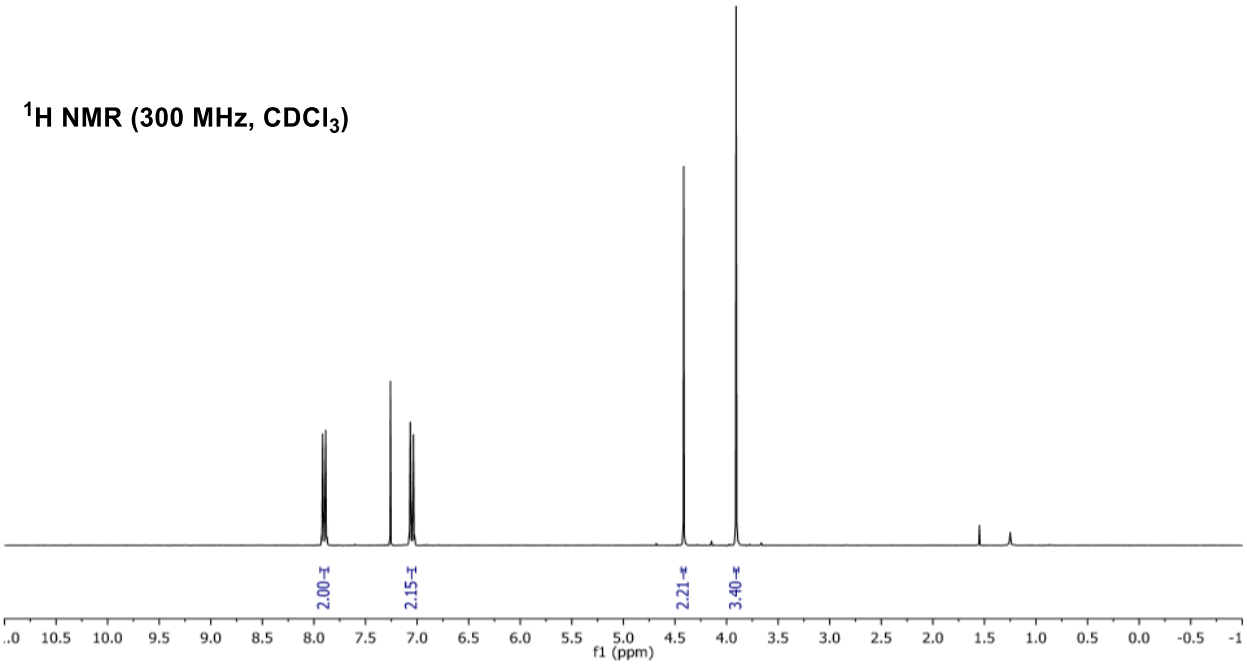
^{13}C NMR (175 MHz, $CDCl_3$)



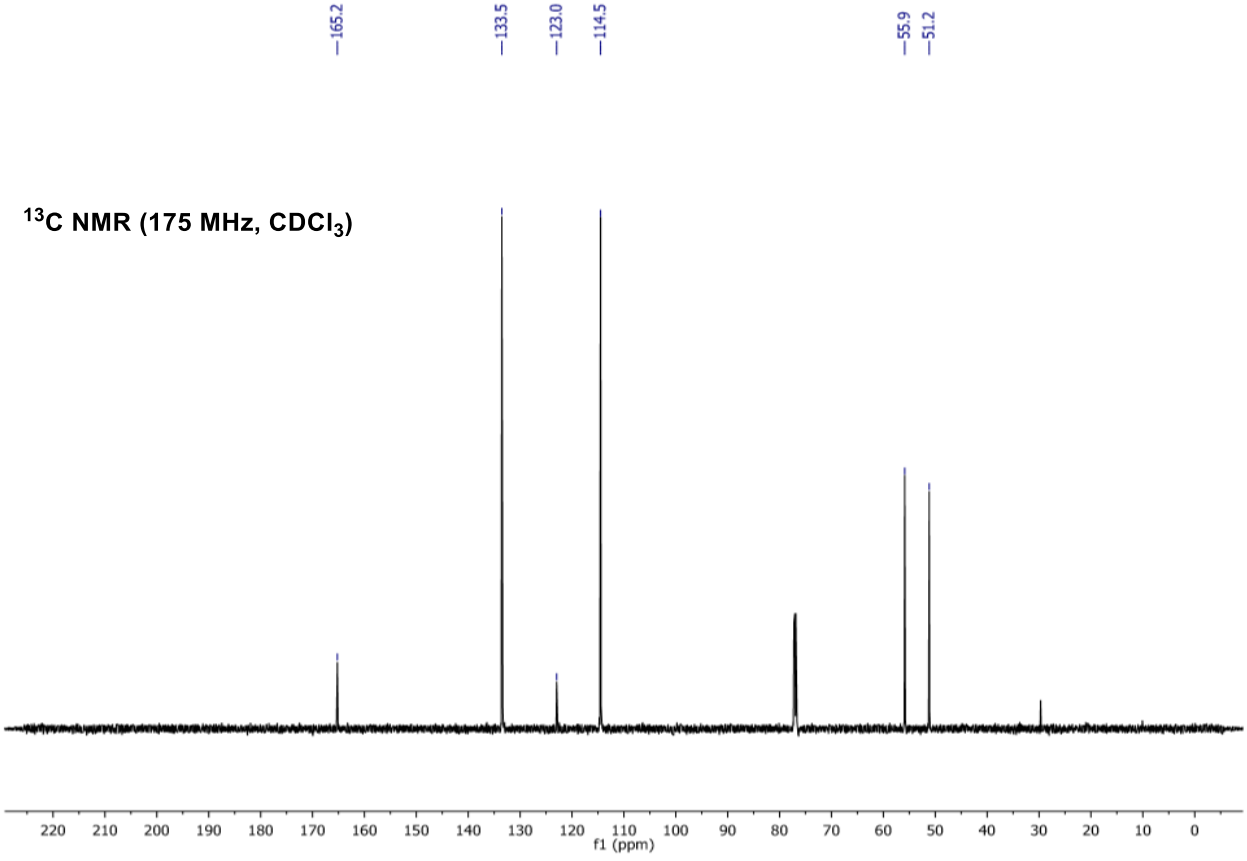


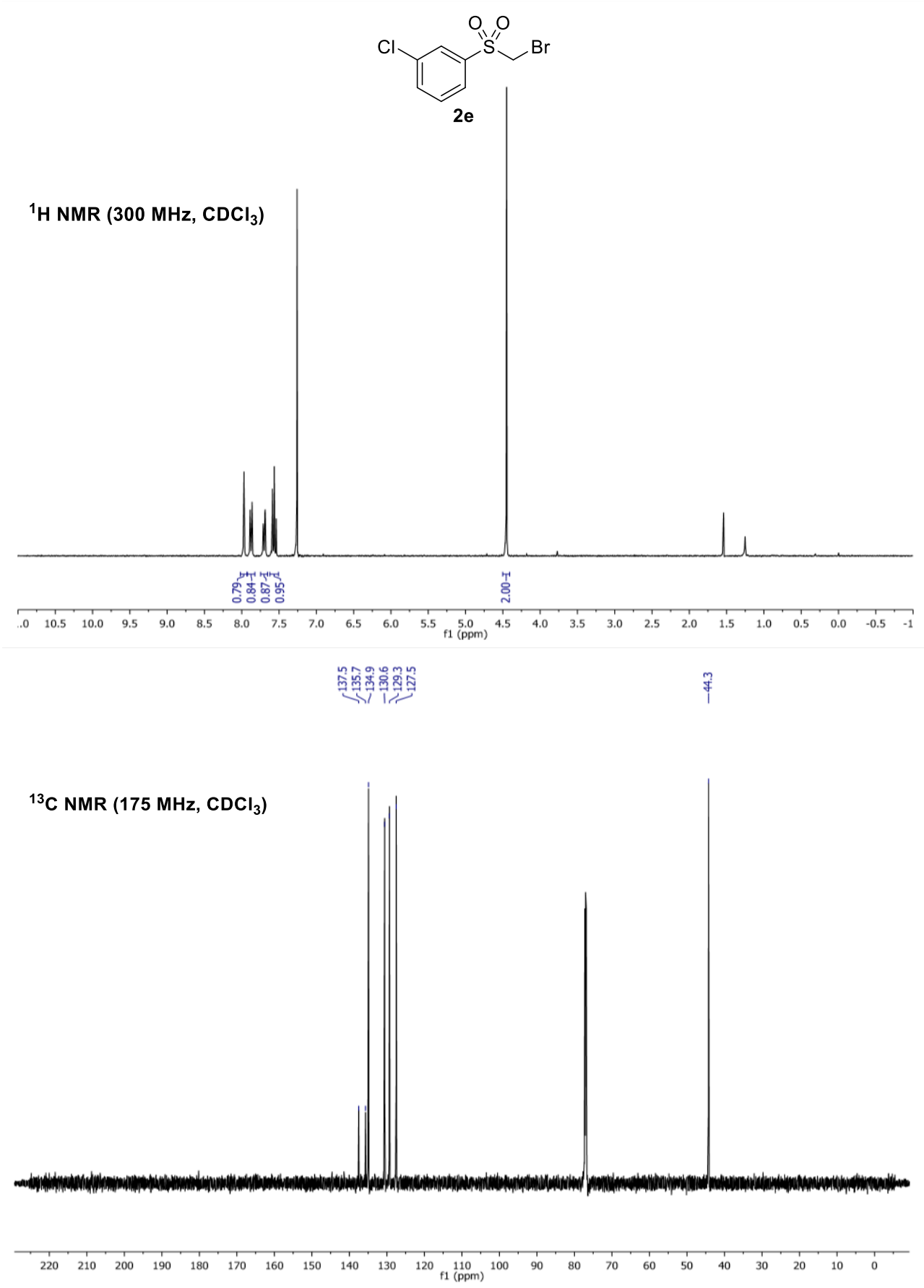
2d

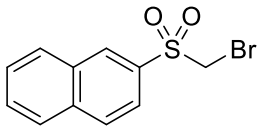
^{1}H NMR (300 MHz, $CDCl_3$)



^{13}C NMR (175 MHz, $CDCl_3$)

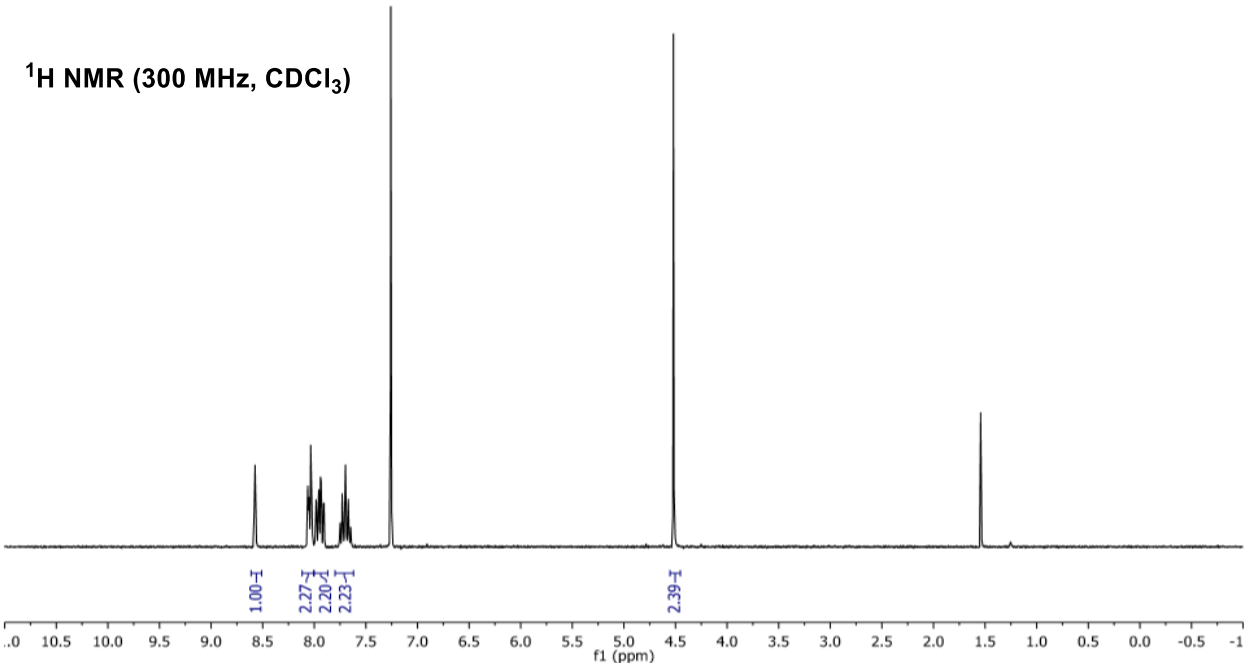



Cl
O
O
S
Br
2e
^{1}H NMR (300 MHz, CDCl$_3$)
0.79
0.84
0.87
0.95
2.00
f1 (ppm)
137.5
135.7
134.9
130.6
129.3
127.5
44.3
^{13}C NMR (175 MHz, CDCl$_3$)
f1 (ppm)

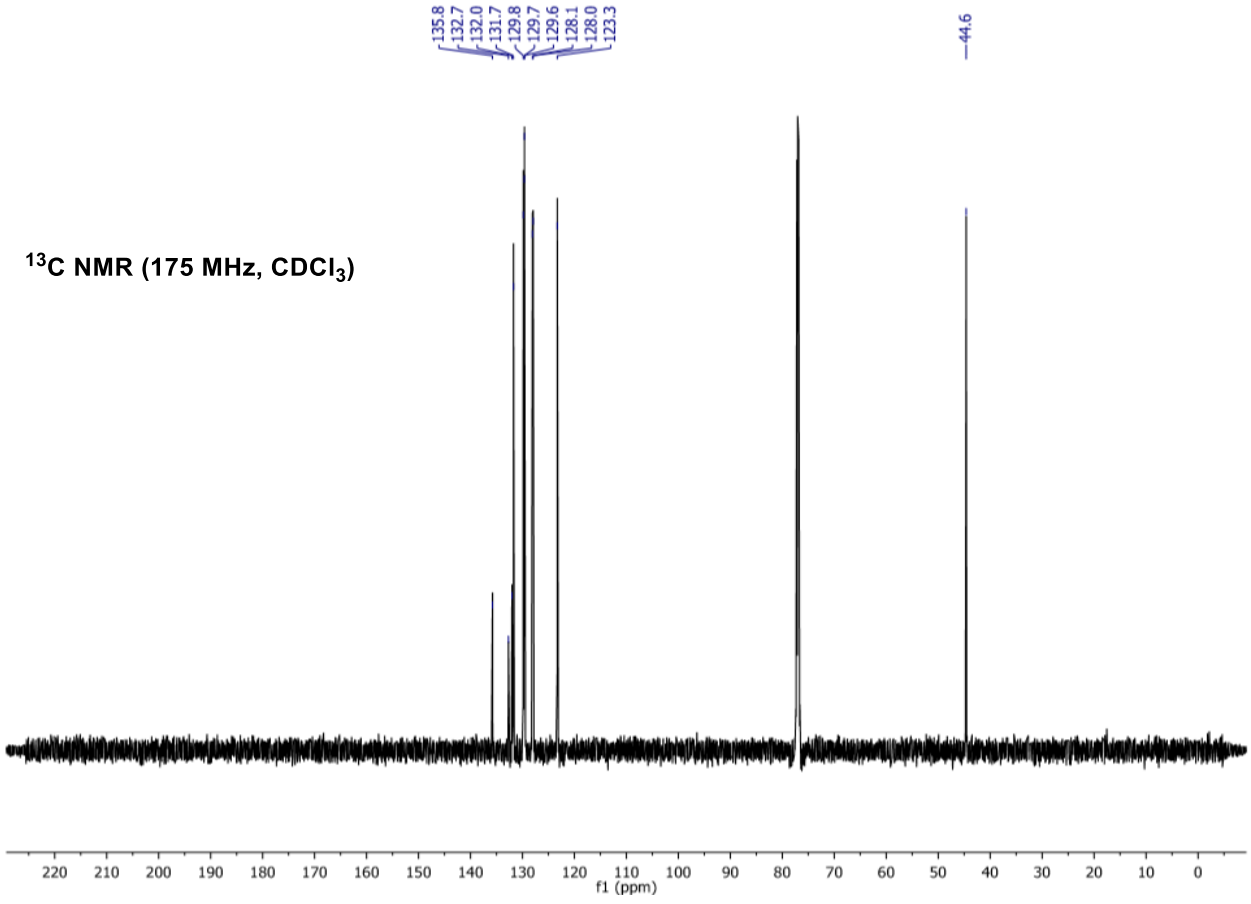


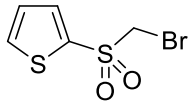
2f

^{1}H NMR (300 MHz, $CDCl_3$)



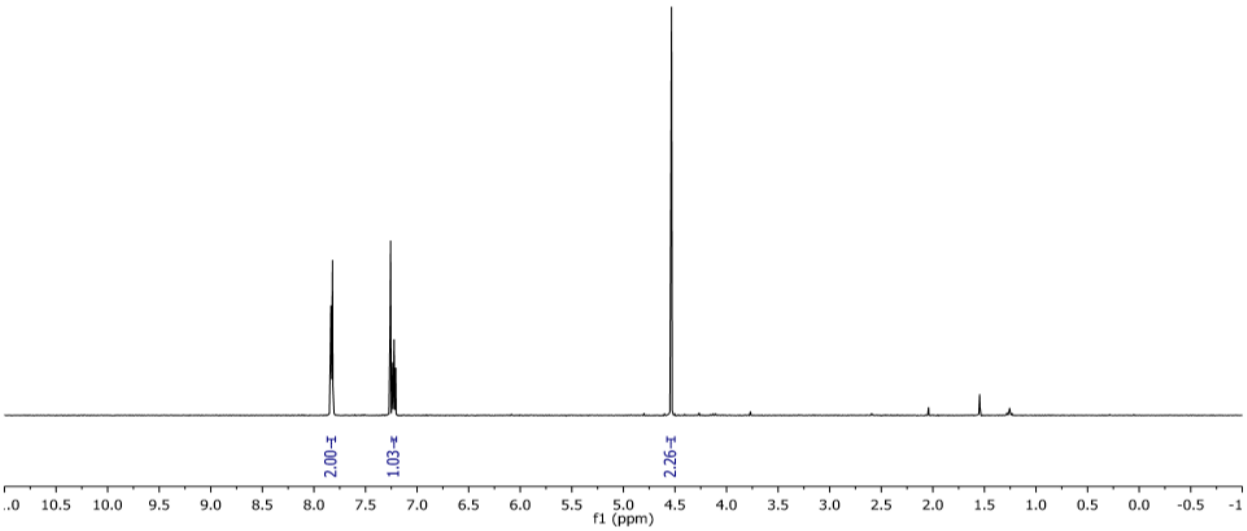
^{13}C NMR (175 MHz, $CDCl_3$)



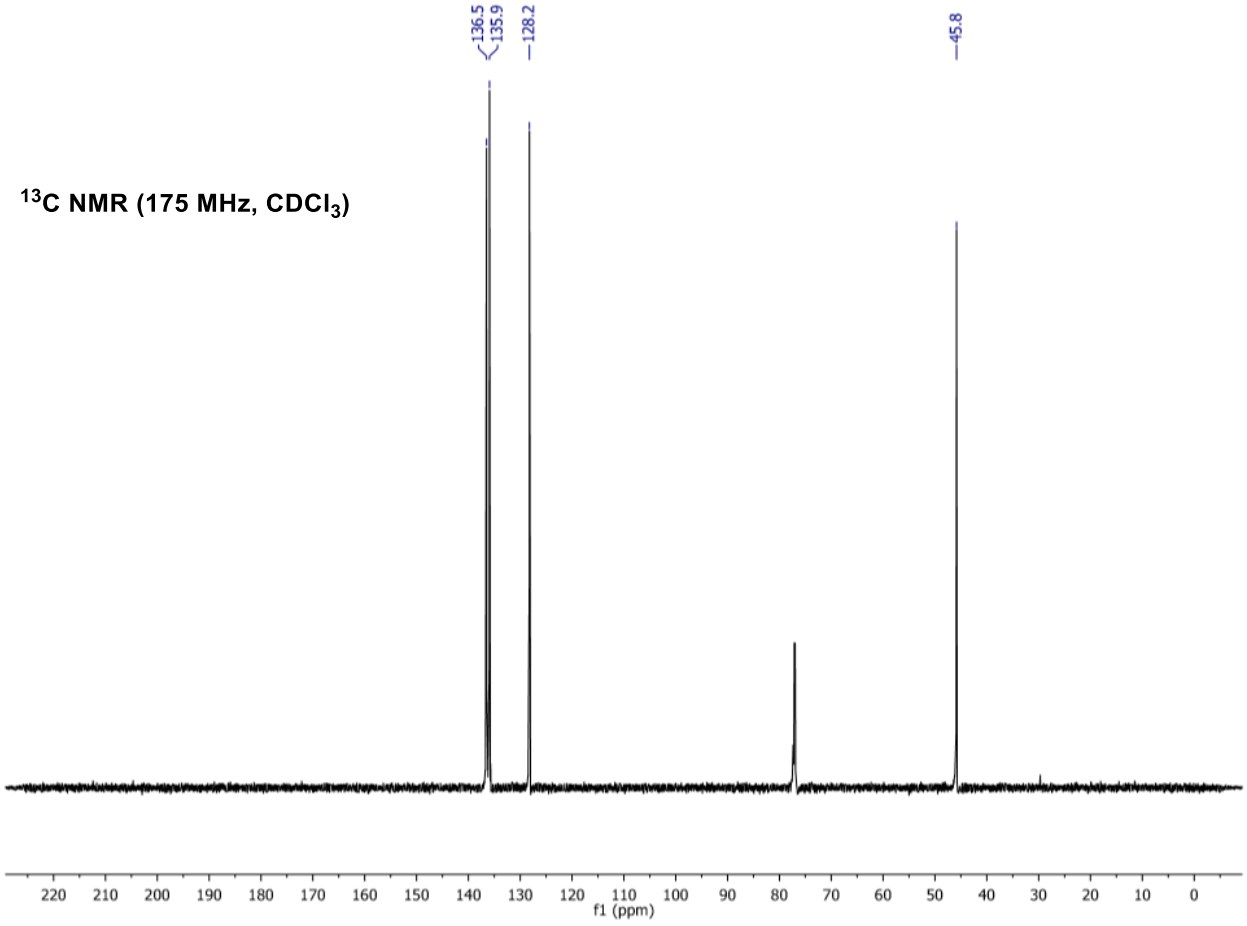


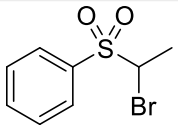
2g

^{1}H NMR (300 MHz, $CDCl_3$)



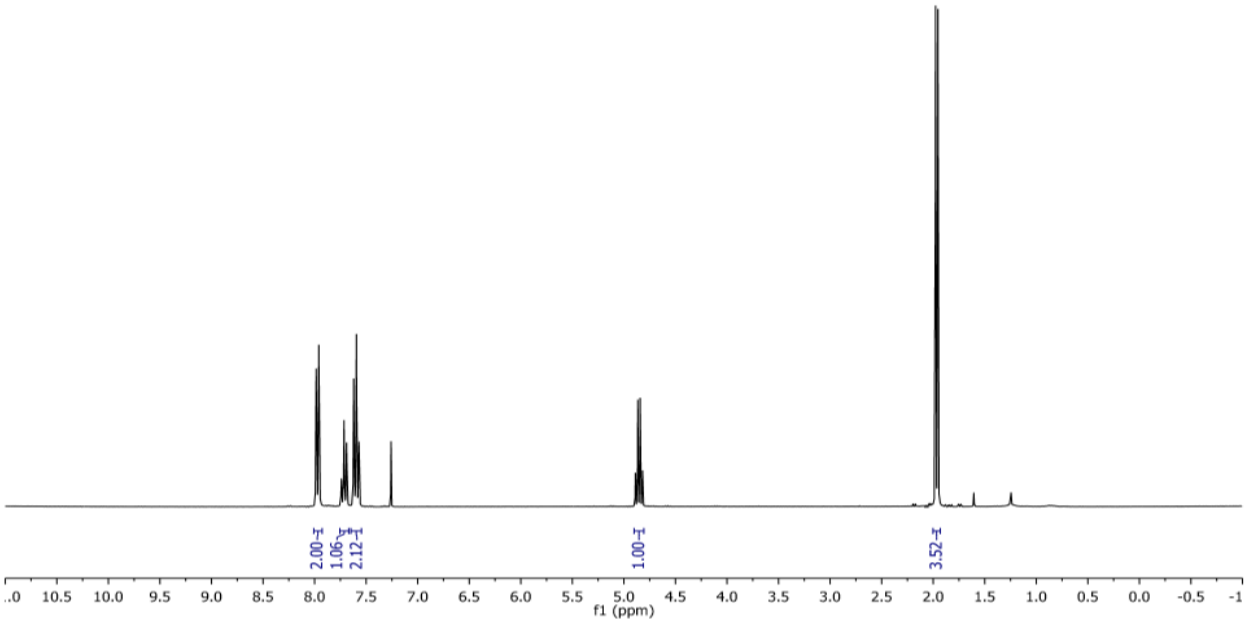
^{13}C NMR (175 MHz, $CDCl_3$)



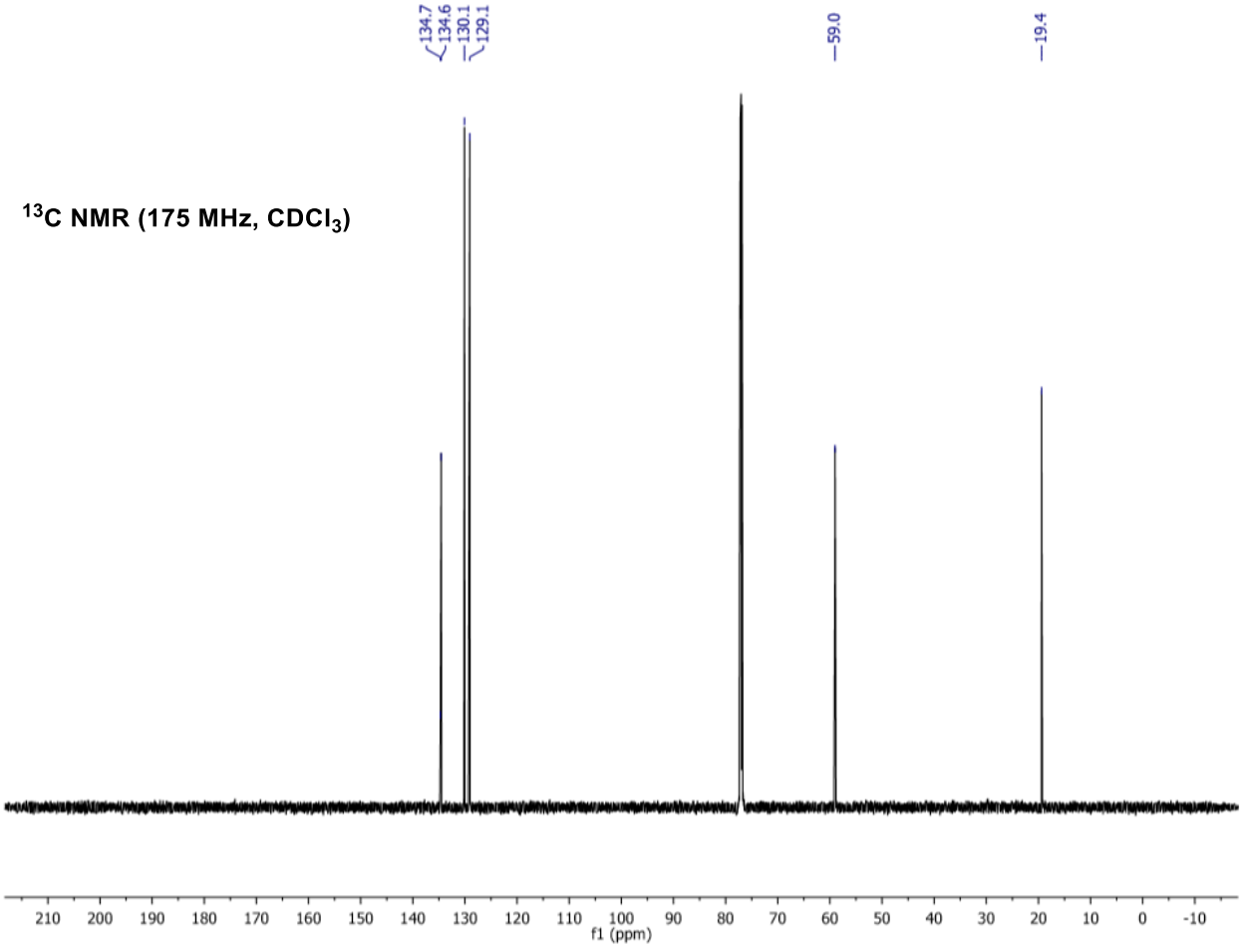


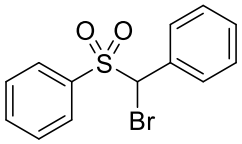
2h

^{1}H NMR (300 MHz, $CDCl_3$)



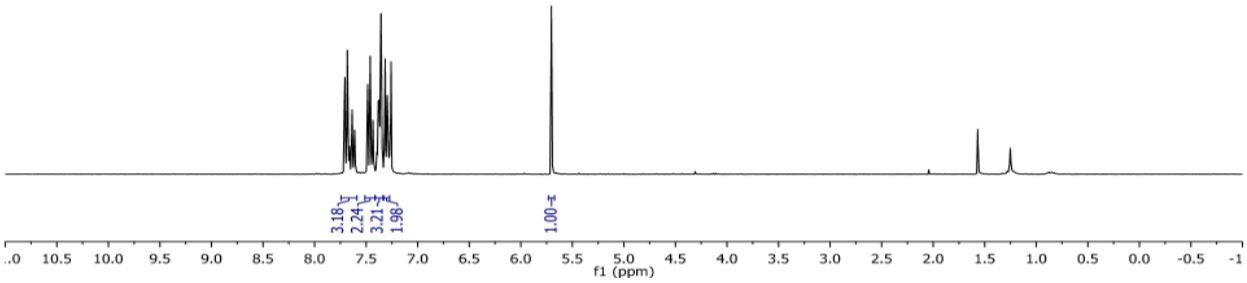
^{13}C NMR (175 MHz, $CDCl_3$)



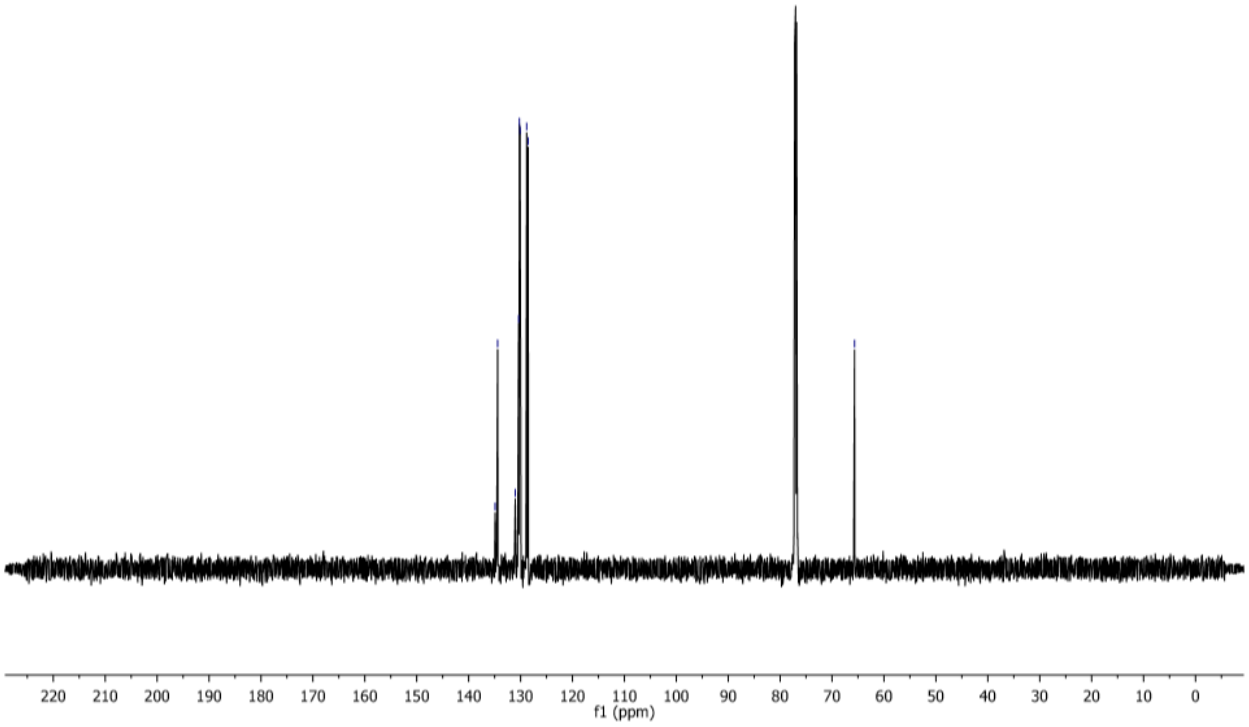


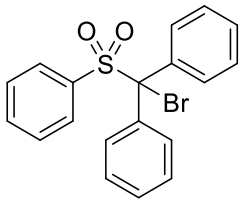
2i

^{1}H NMR (300 MHz, $CDCl_3$)



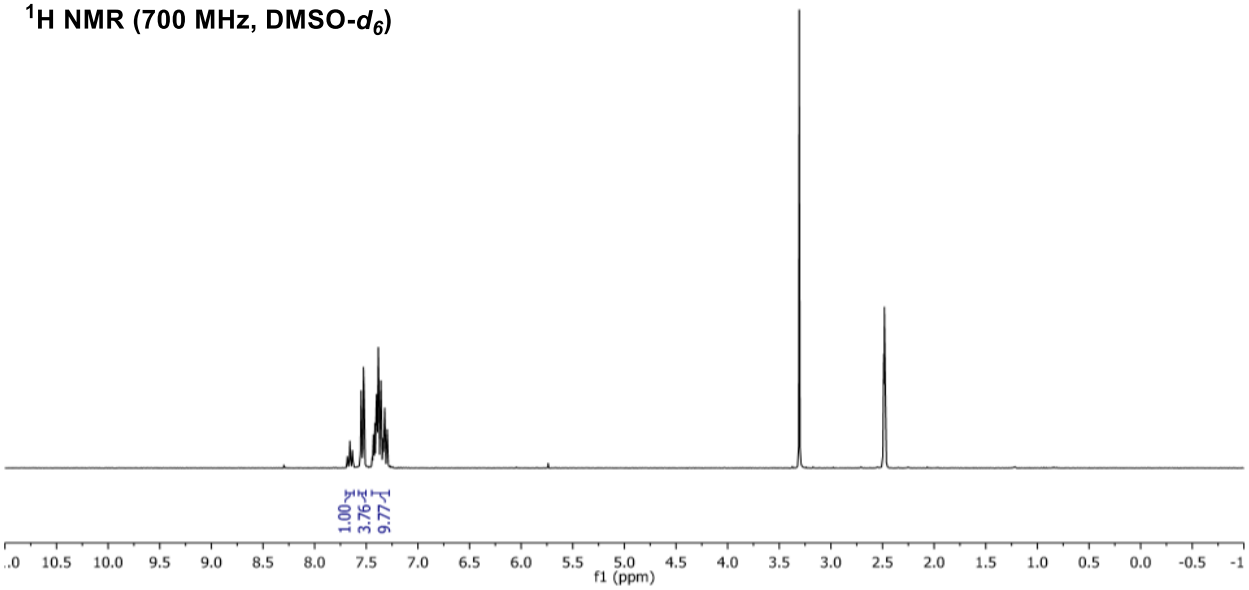
^{13}C NMR (175 MHz, $CDCl_3$)



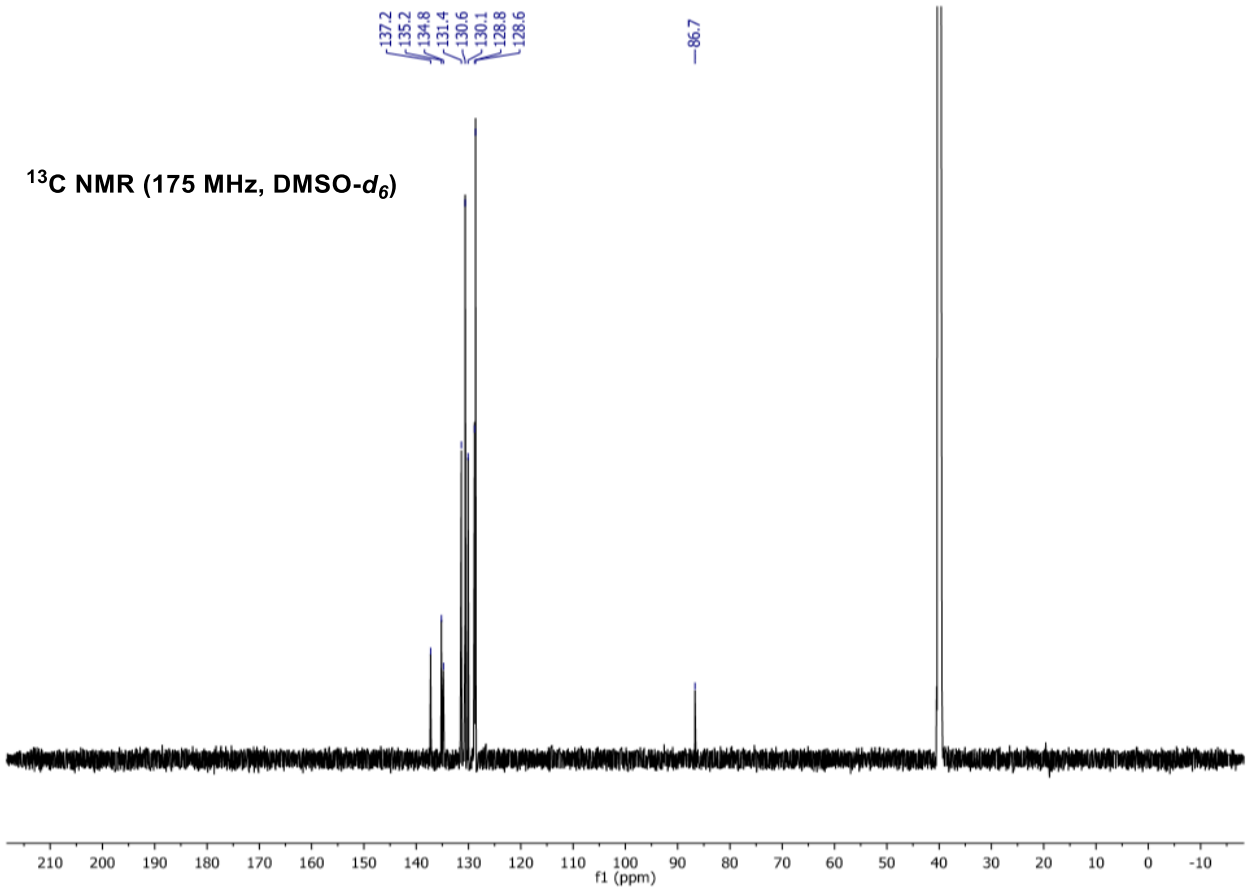


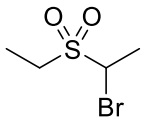
2j

^{1}H NMR (700 MHz, DMSO-d_6)



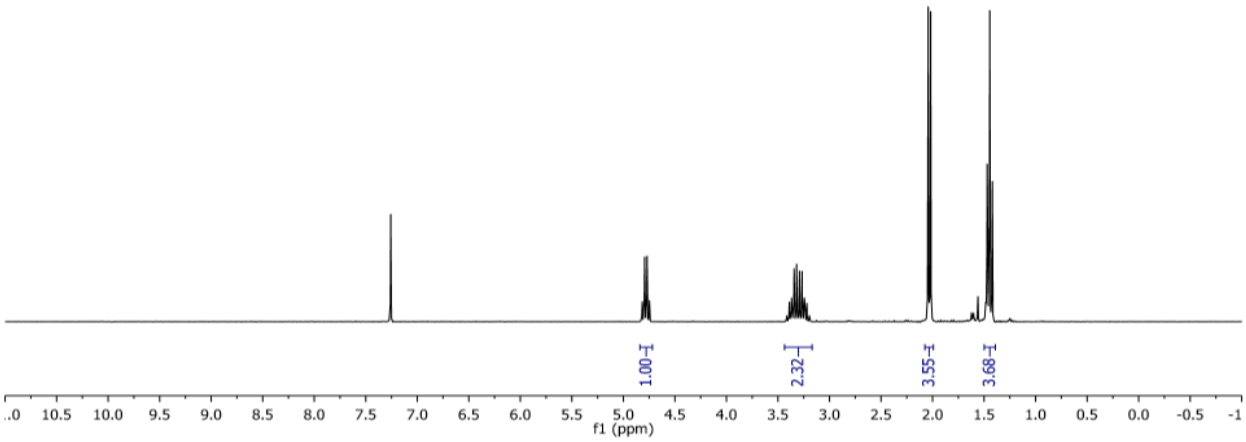
^{13}C NMR (175 MHz, DMSO-d_6)



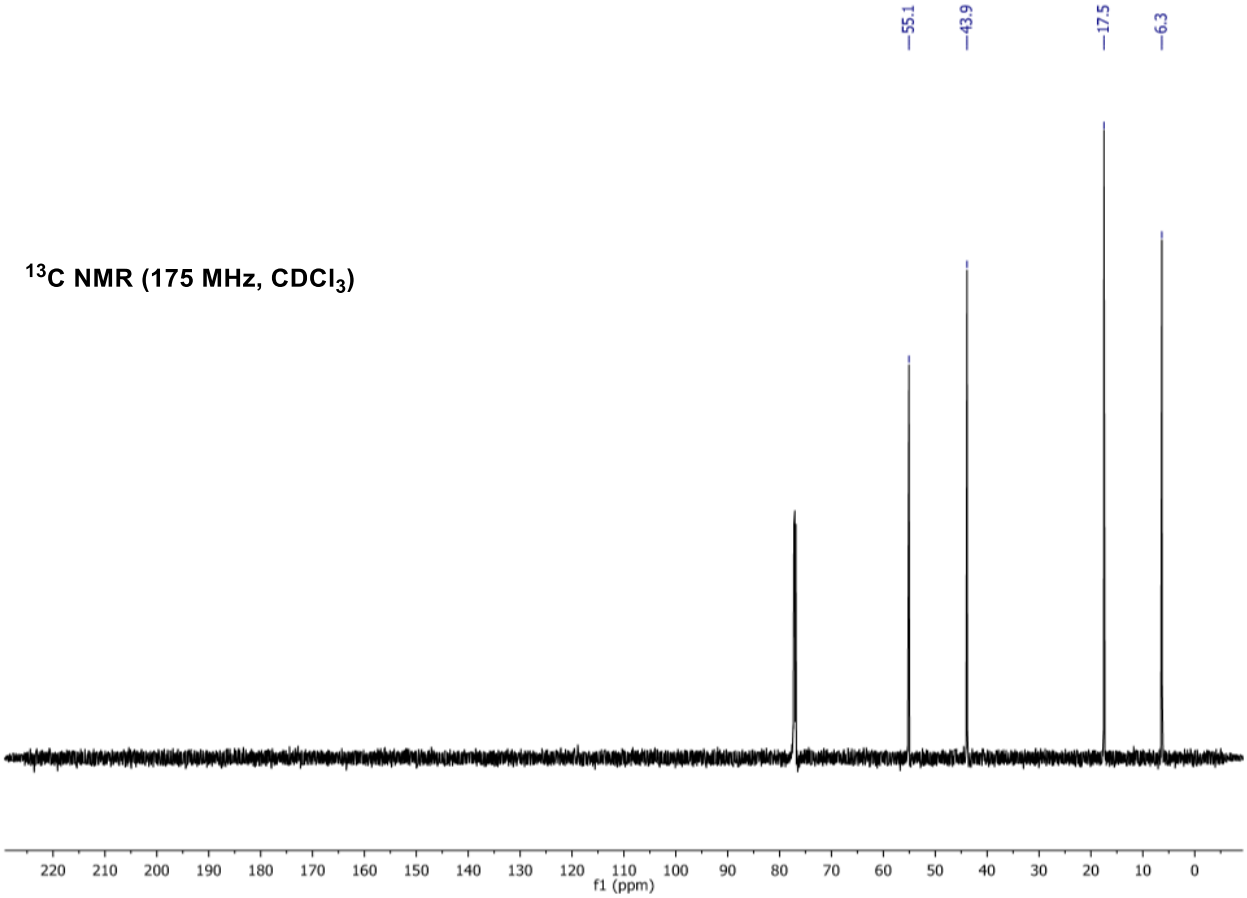


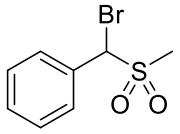
2k

^{1}H NMR (300 MHz, $CDCl_3$)



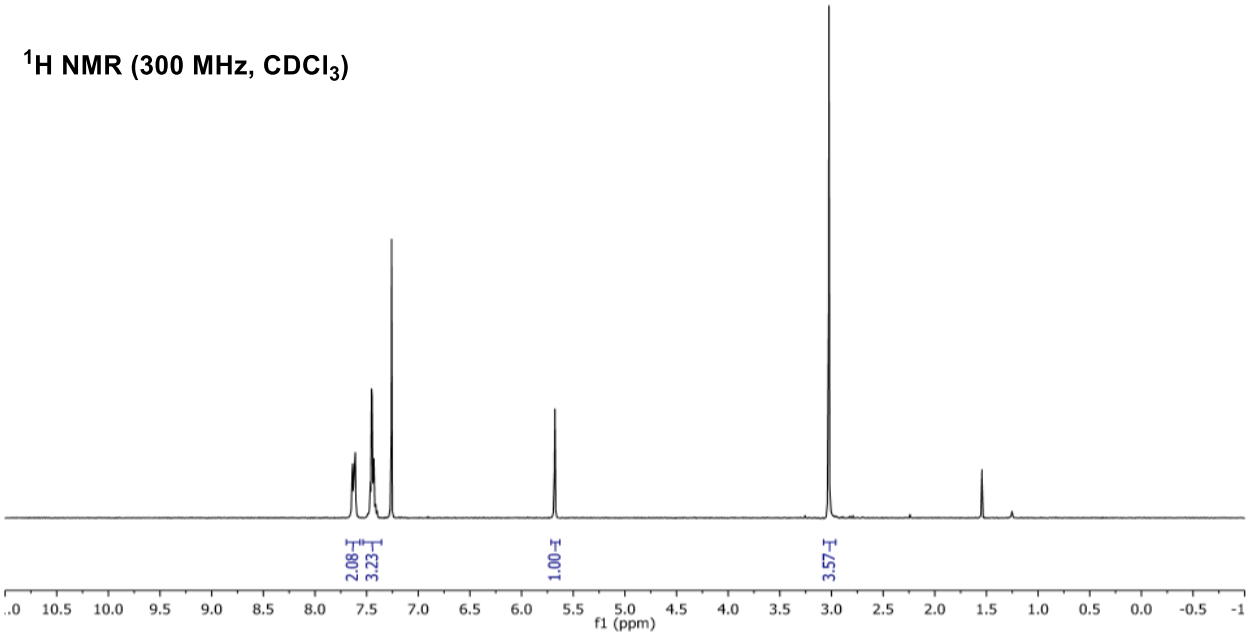
^{13}C NMR (175 MHz, $CDCl_3$)



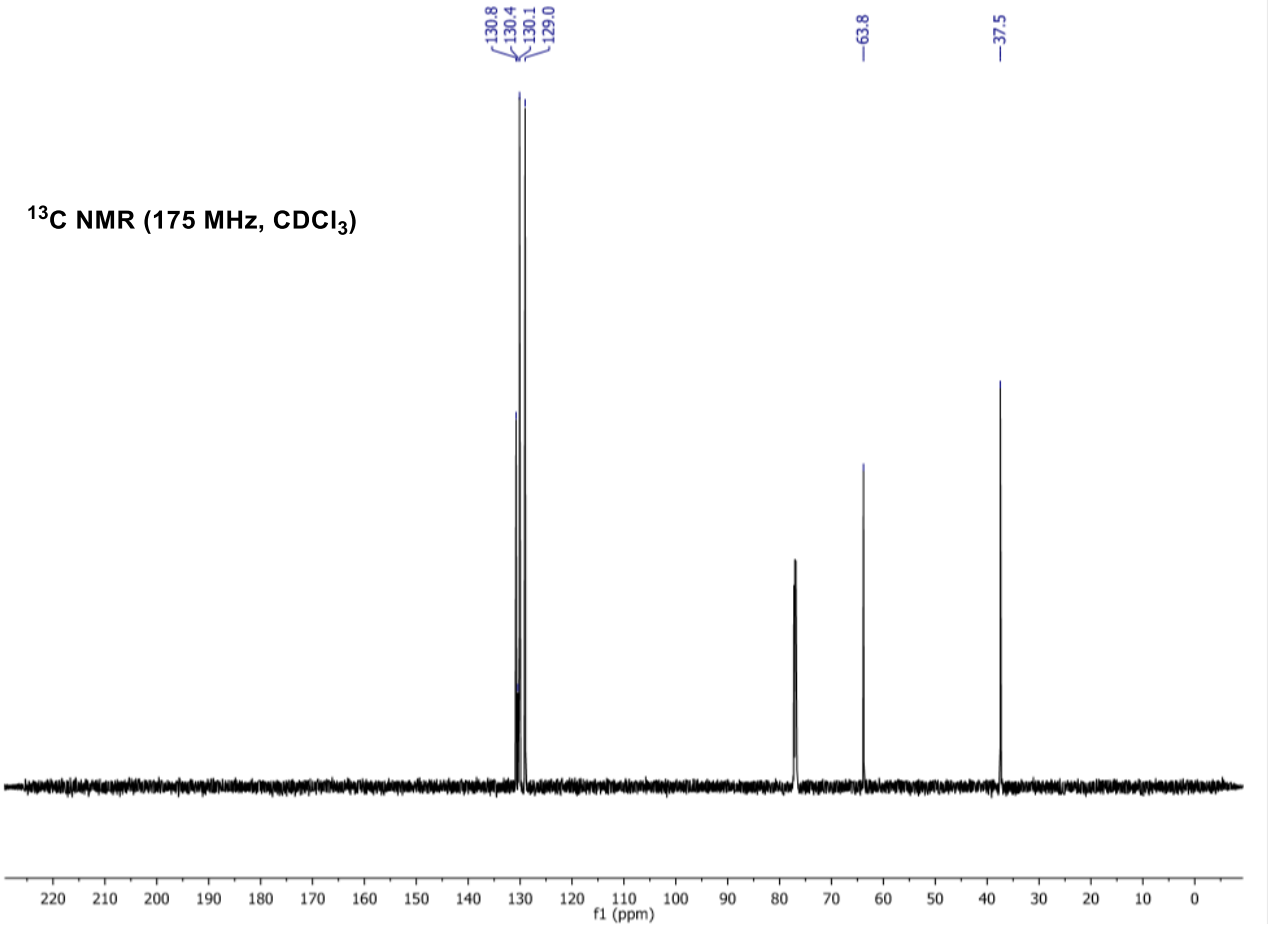


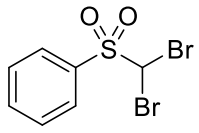
2l

^{1}H NMR (300 MHz, $CDCl_3$)



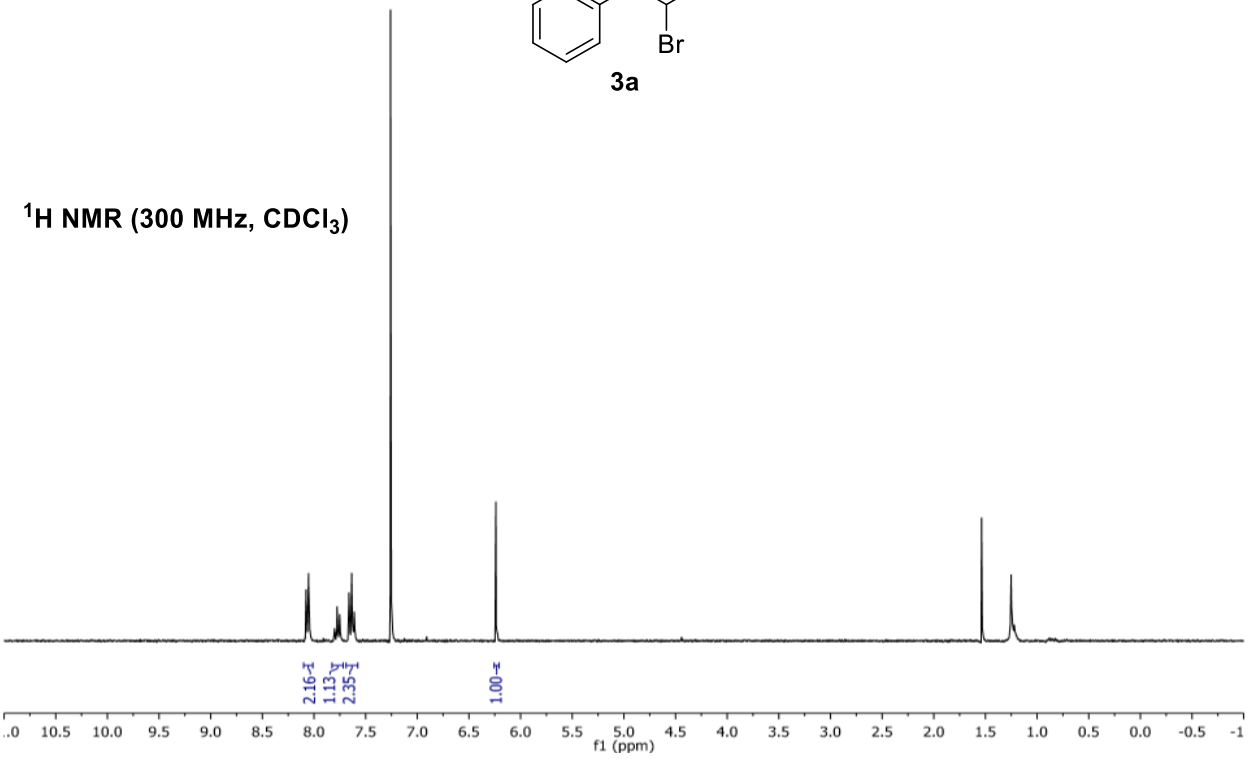
^{13}C NMR (175 MHz, $CDCl_3$)



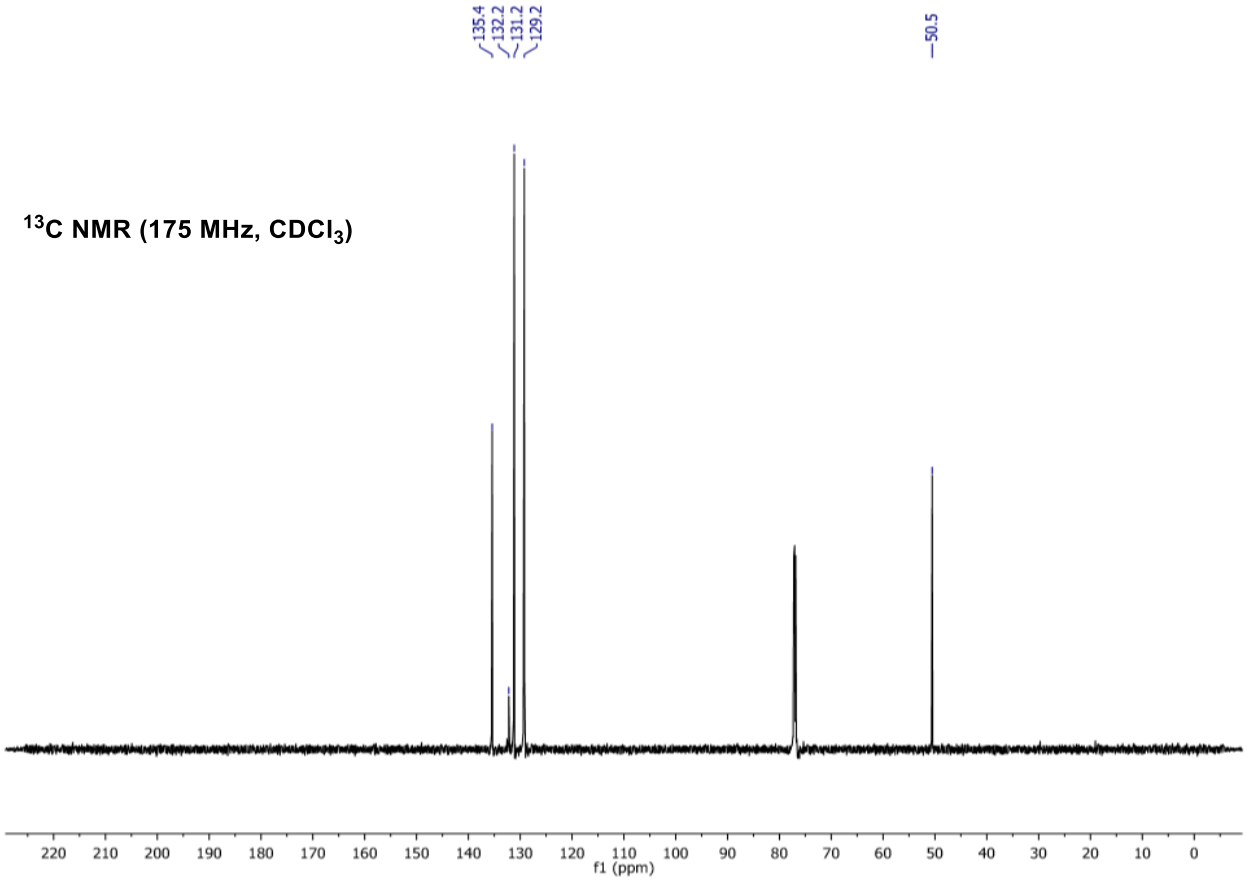


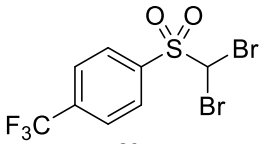
3a

^{1}H NMR (300 MHz, $CDCl_3$)



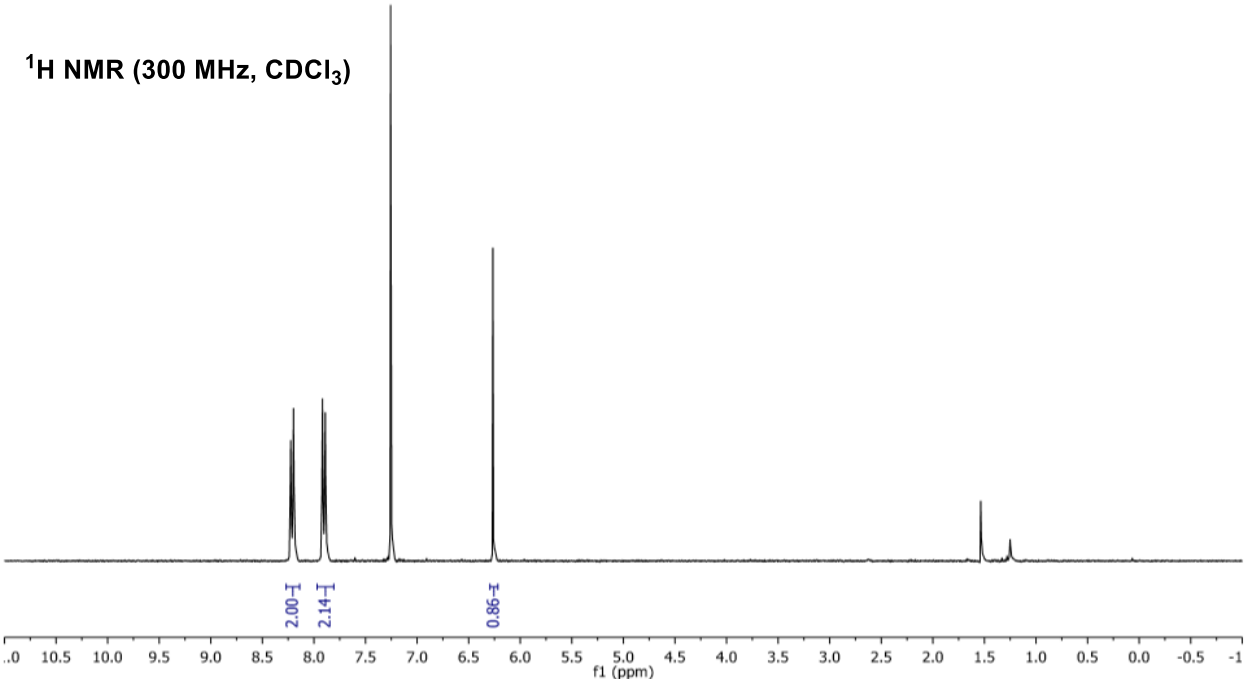
^{13}C NMR (175 MHz, $CDCl_3$)



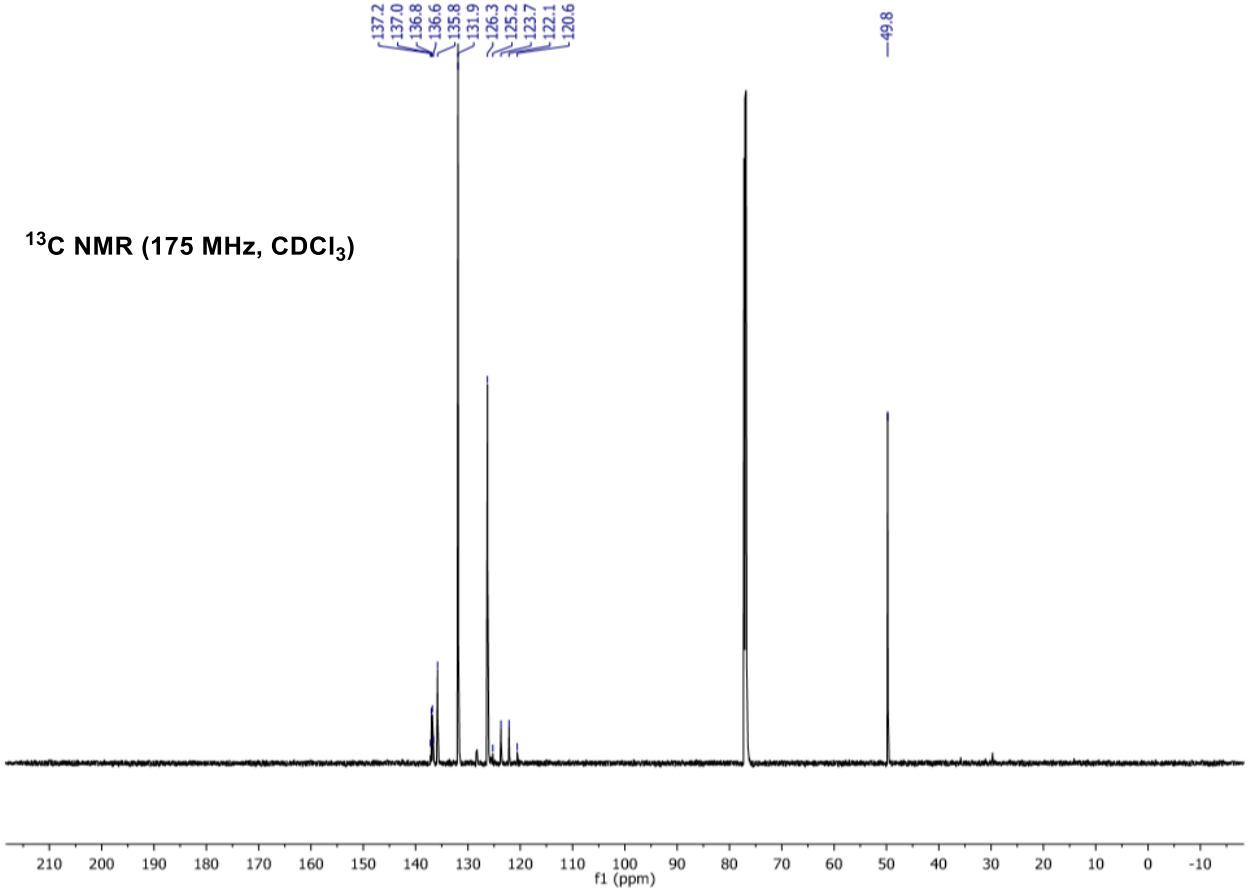


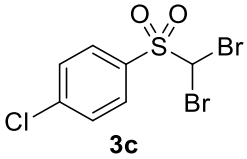
3b

^{1}H NMR (300 MHz, $CDCl_3$)



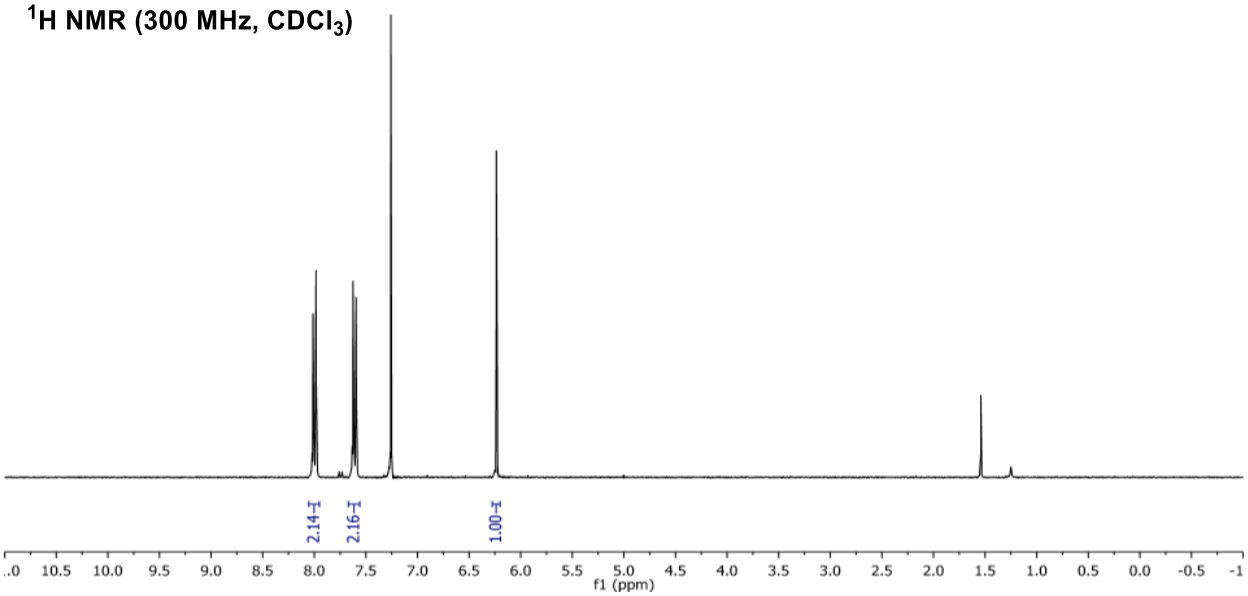
^{13}C NMR (175 MHz, $CDCl_3$)



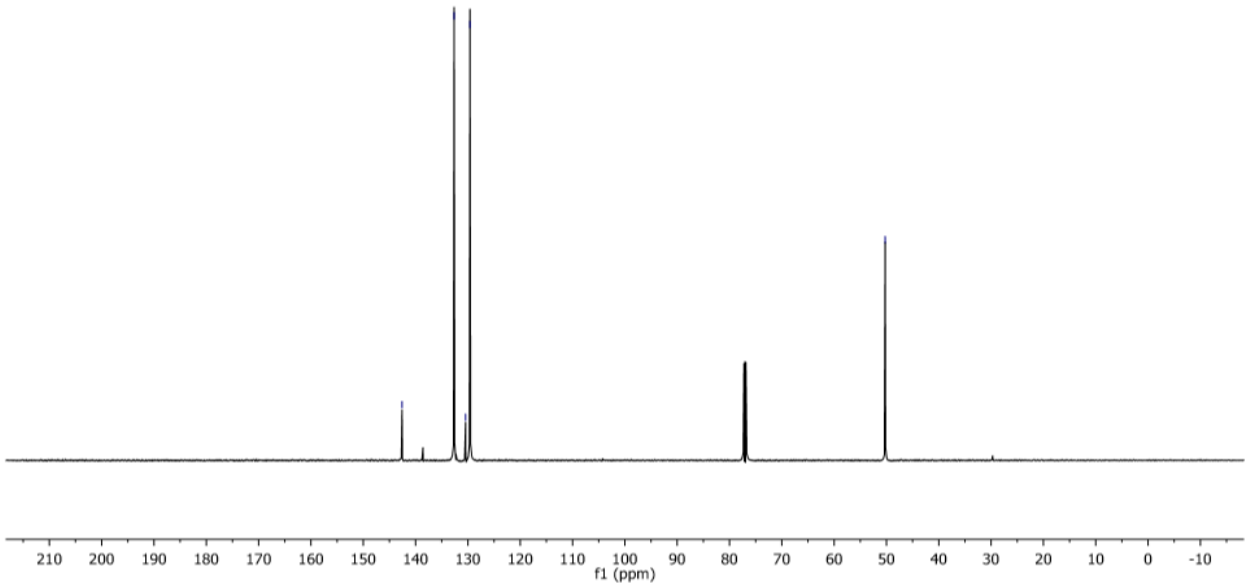


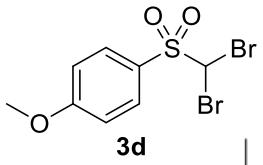
3c

^{1}H NMR (300 MHz, $CDCl_3$)



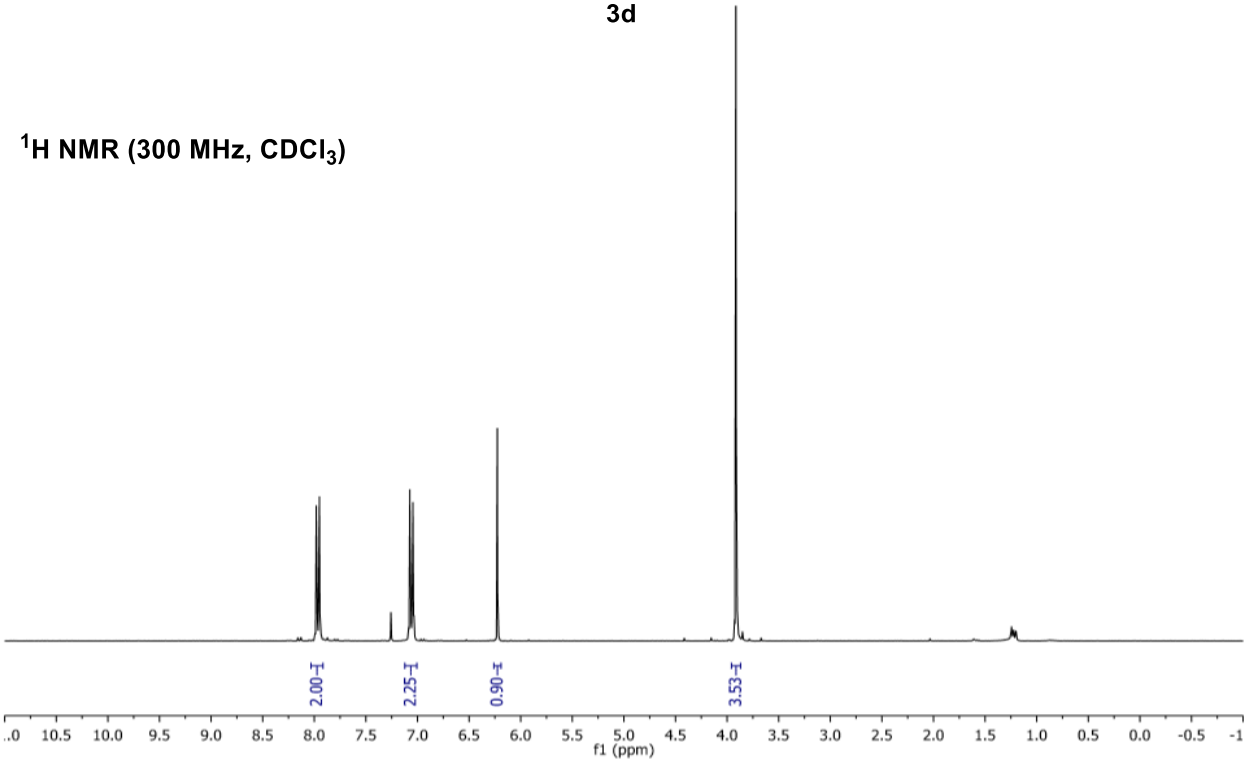
^{13}C NMR (175 MHz, $CDCl_3$)



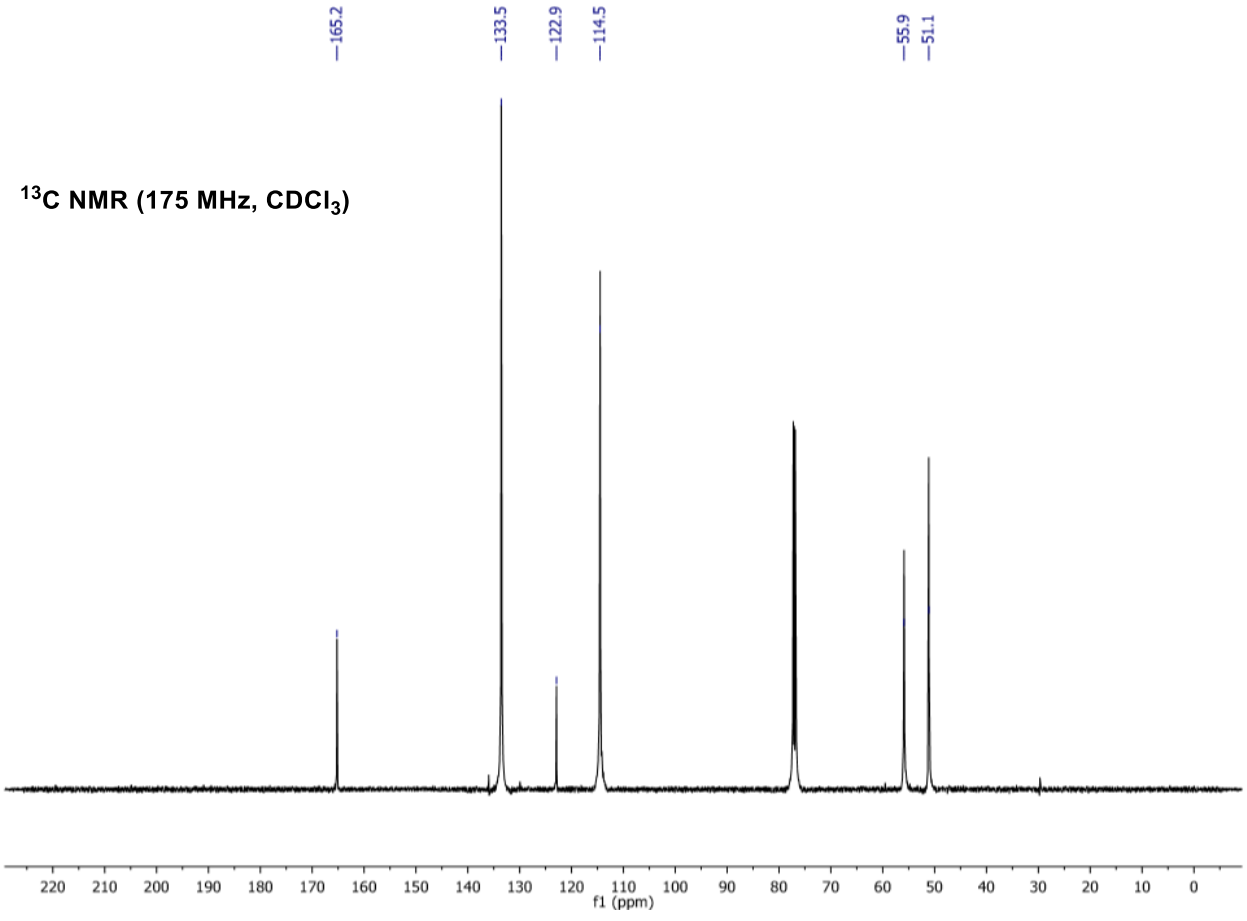


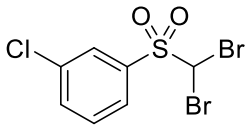
3d

^{1}H NMR (300 MHz, $CDCl_3$)



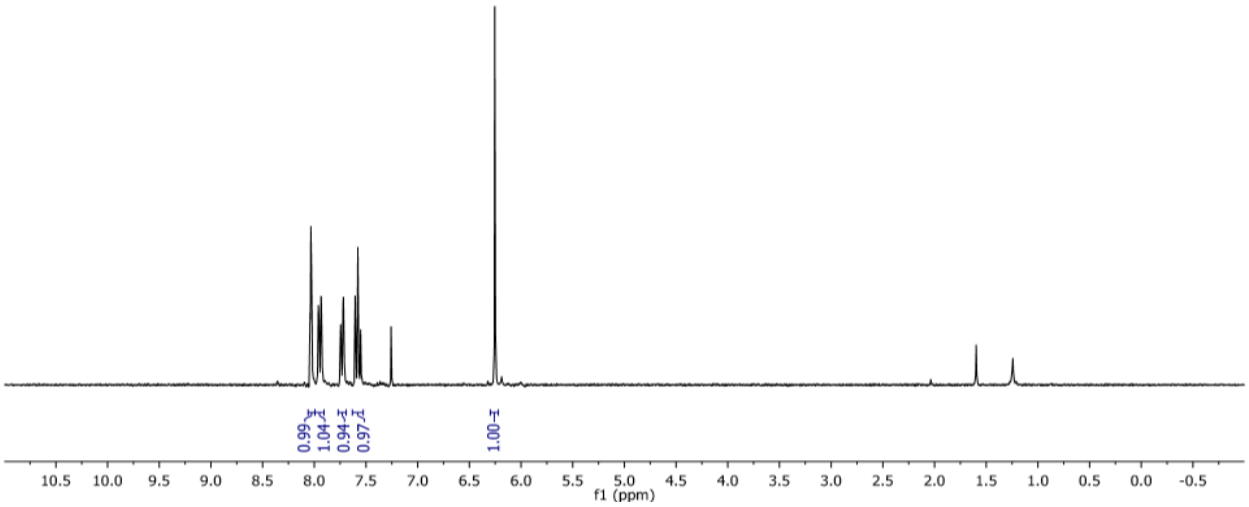
^{13}C NMR (175 MHz, $CDCl_3$)



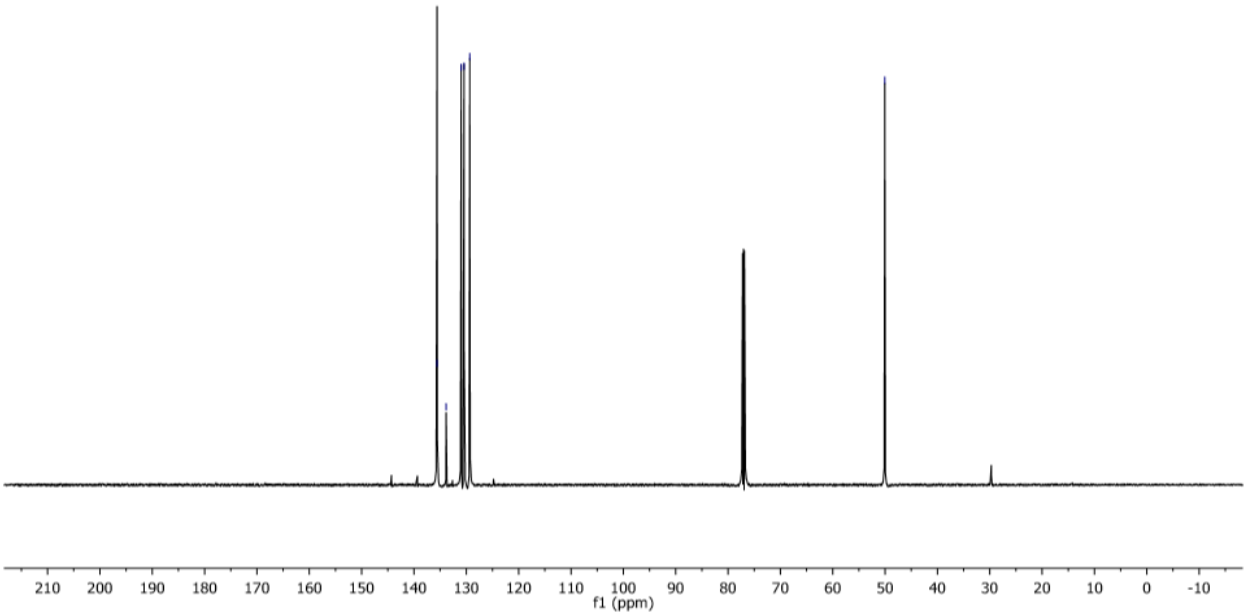


3e

^{1}H NMR (300 MHz, $CDCl_3$)

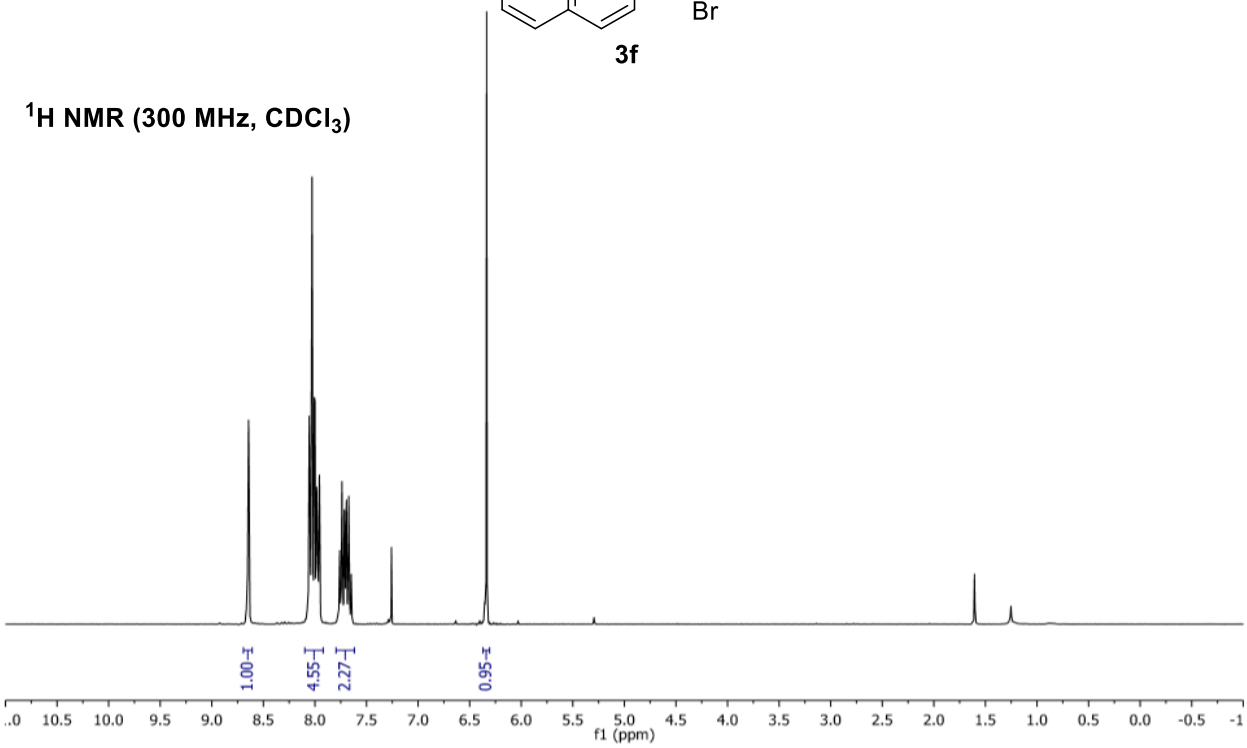


^{13}C NMR (175 MHz, $CDCl_3$)

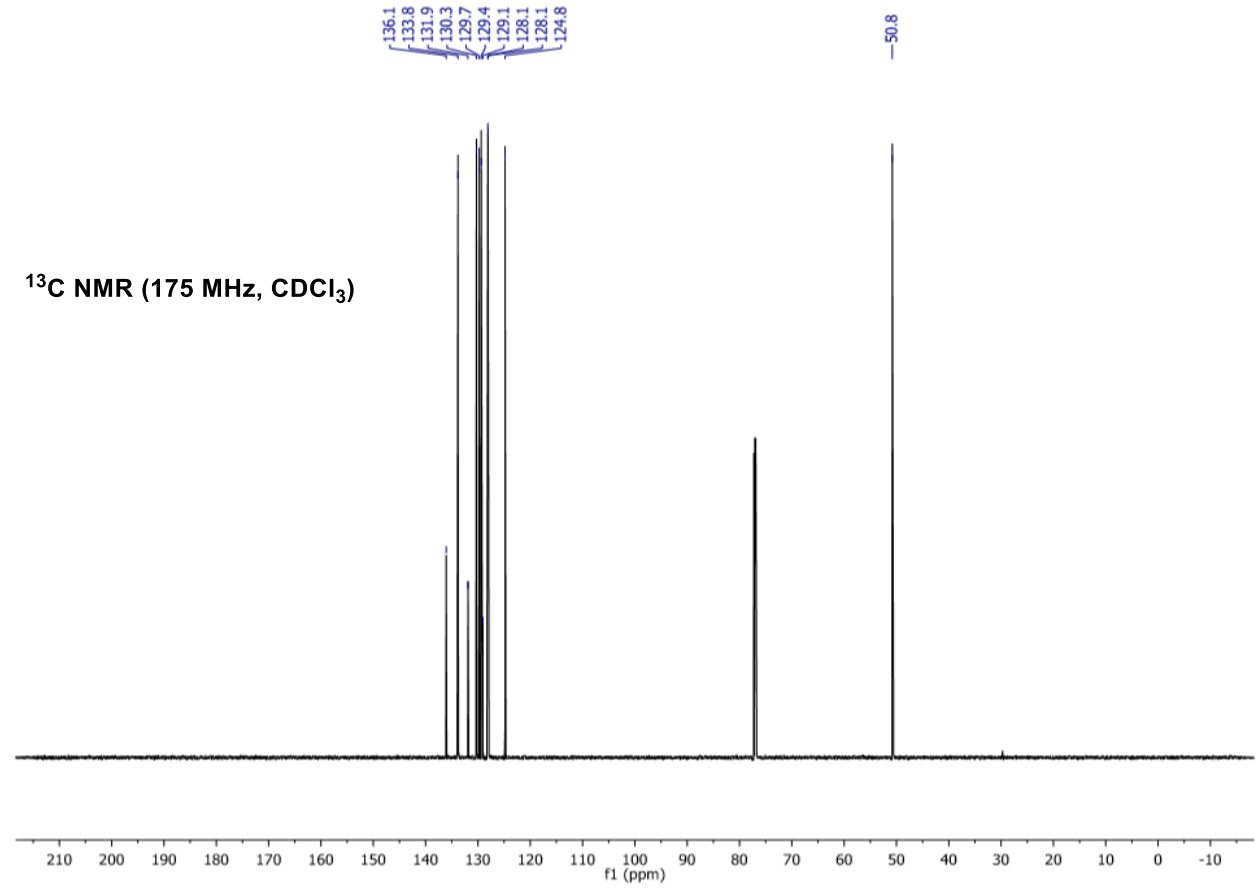


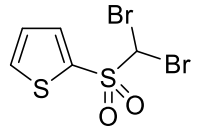
3f

^{1}H NMR (300 MHz, $CDCl_3$)



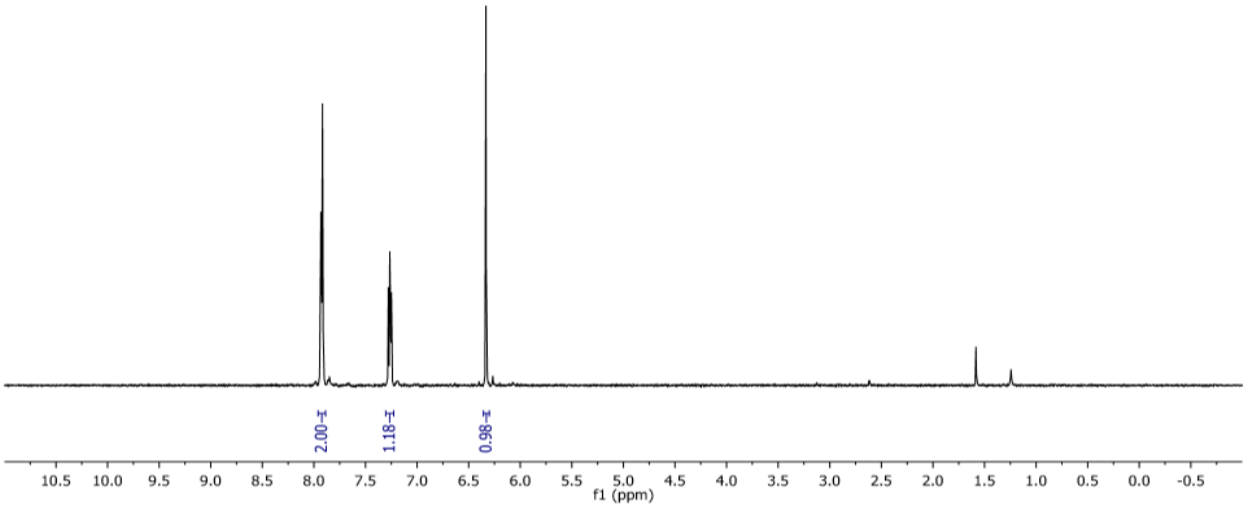
^{13}C NMR (175 MHz, $CDCl_3$)



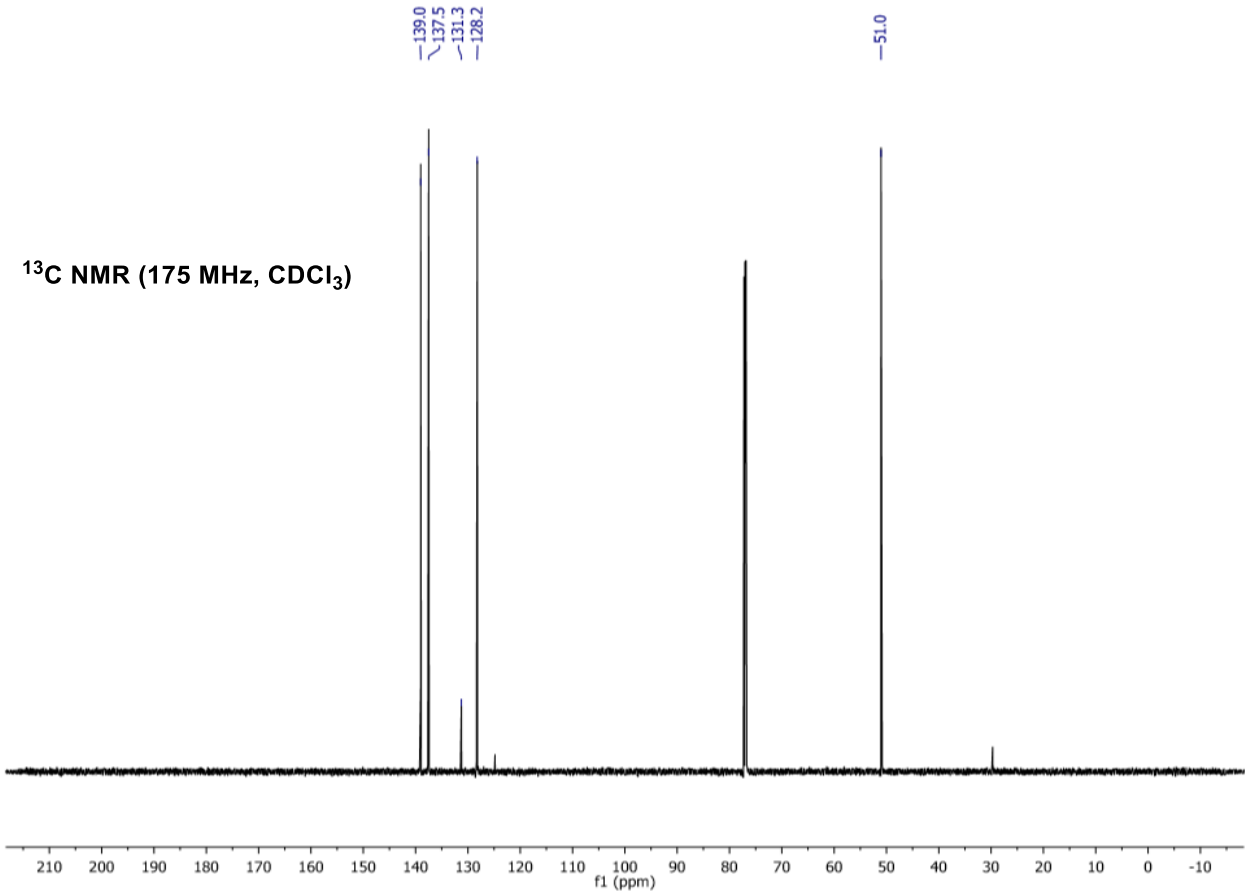


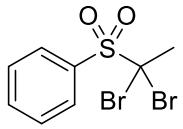
3g

^{1}H NMR (300 MHz, $CDCl_3$)



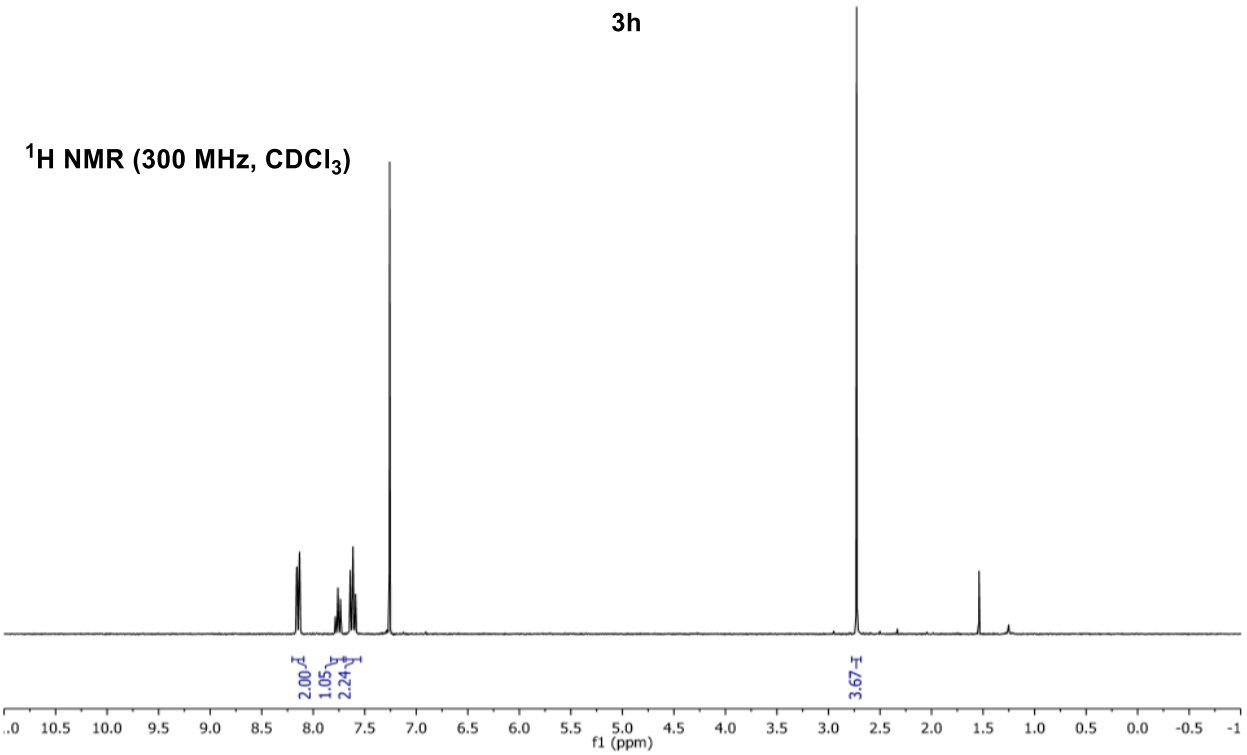
^{13}C NMR (175 MHz, $CDCl_3$)



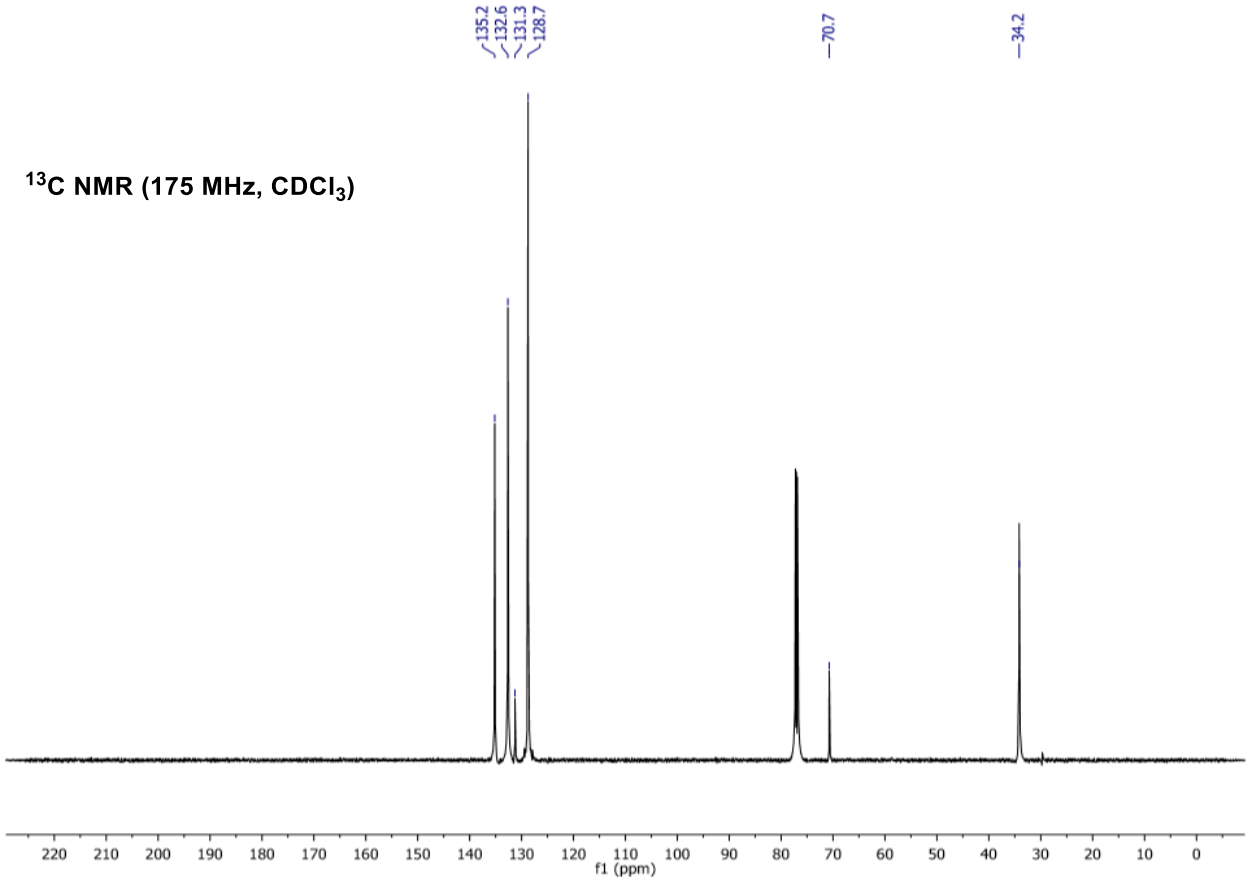


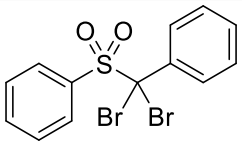
3h

^{1}H NMR (300 MHz, $CDCl_3$)



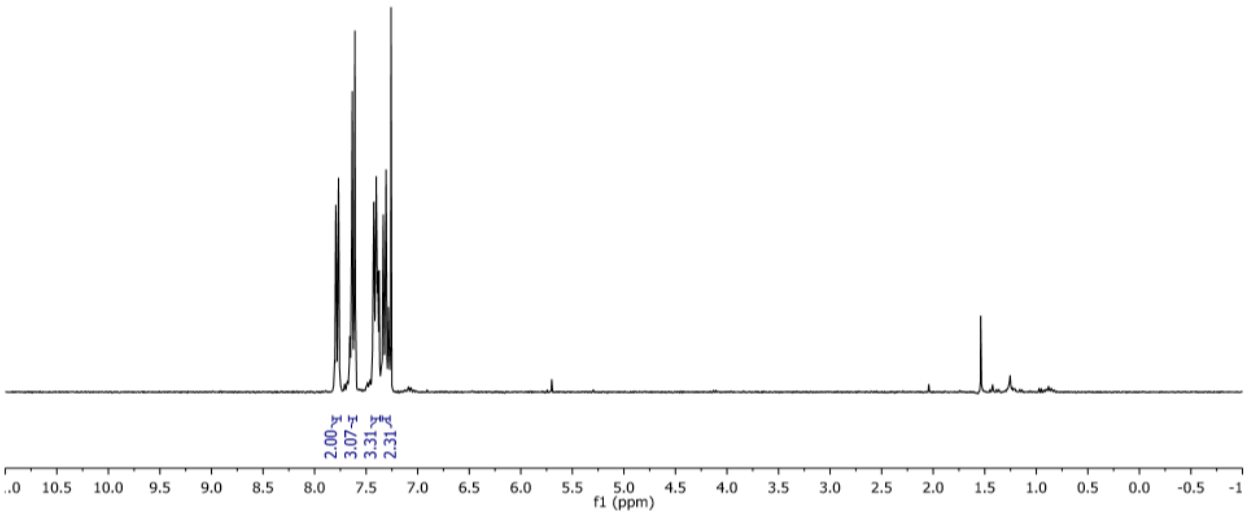
^{13}C NMR (175 MHz, $CDCl_3$)



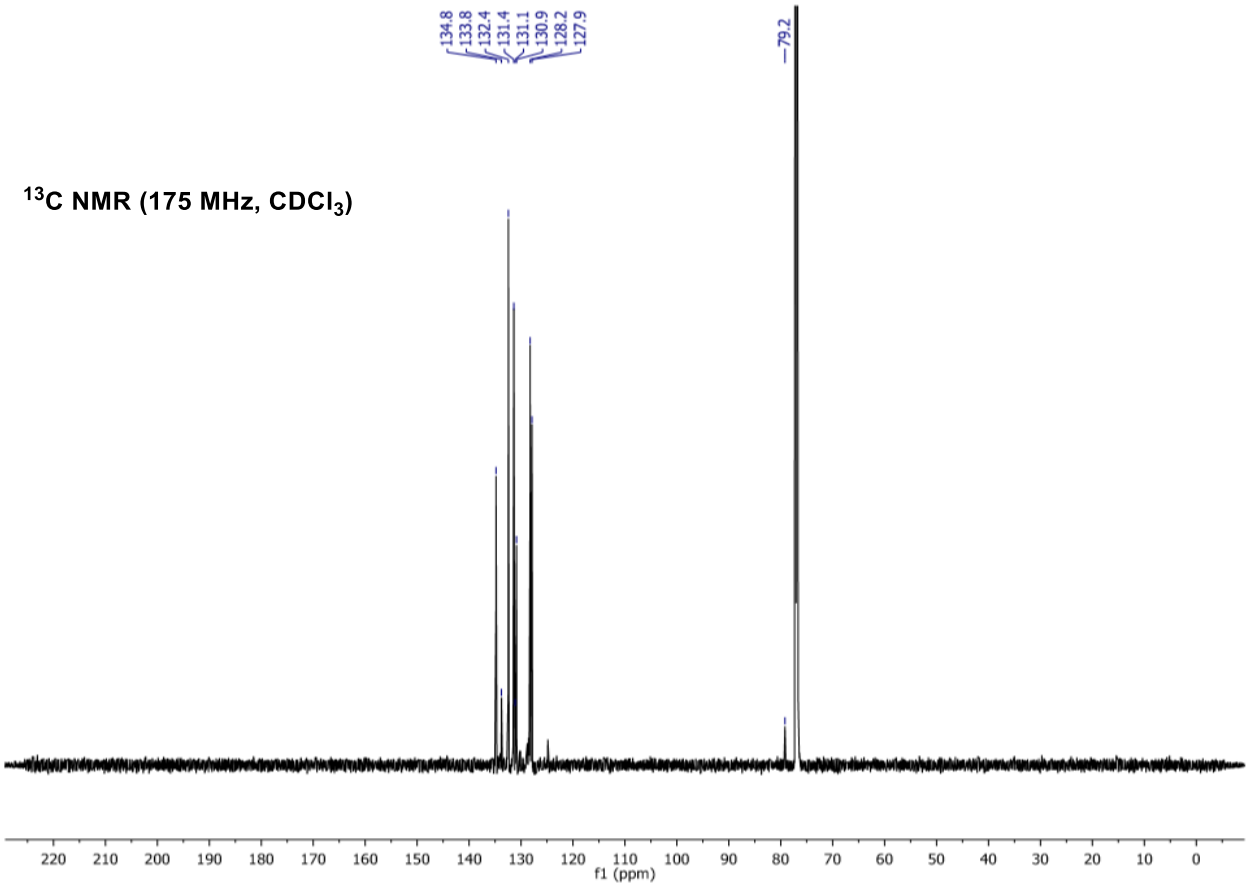


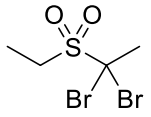
3i

^{1}H NMR (300 MHz, $CDCl_3$)



^{13}C NMR (175 MHz, $CDCl_3$)

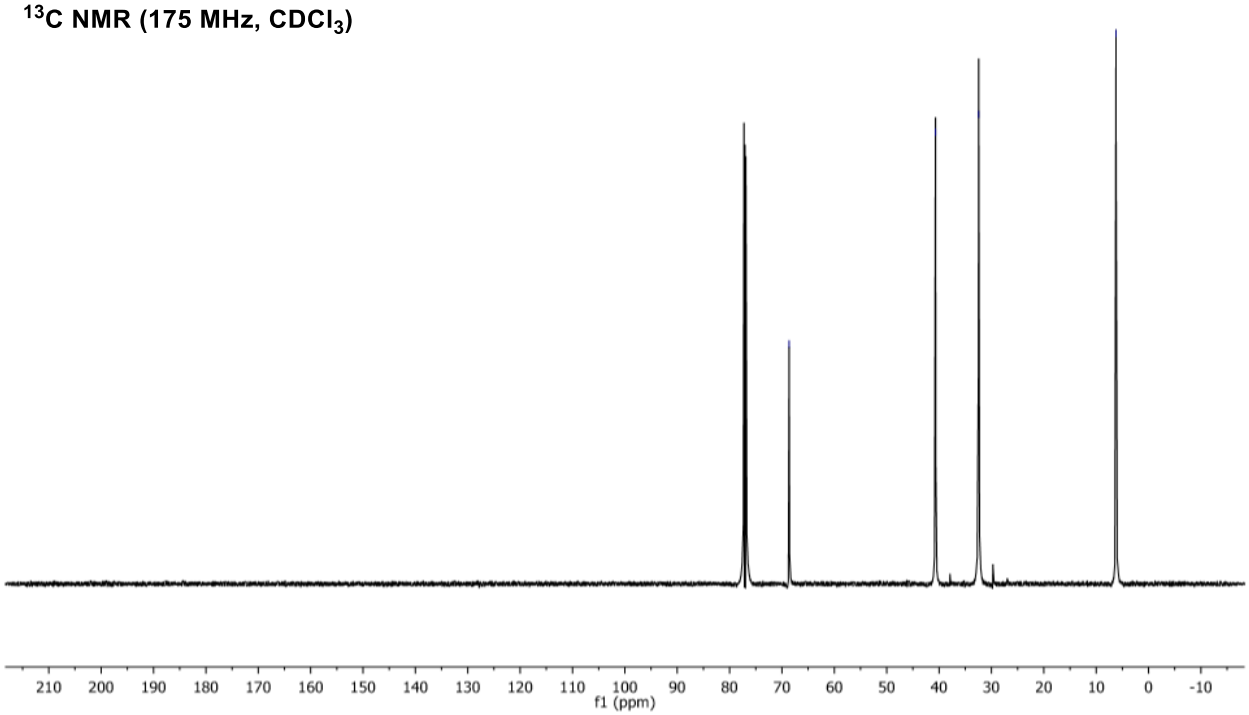


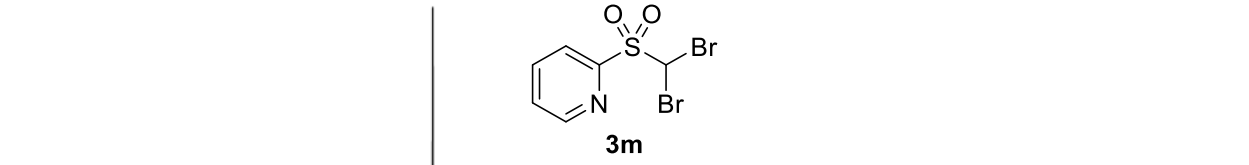


3k

^{1}H NMR (300 MHz, $CDCl_3$)

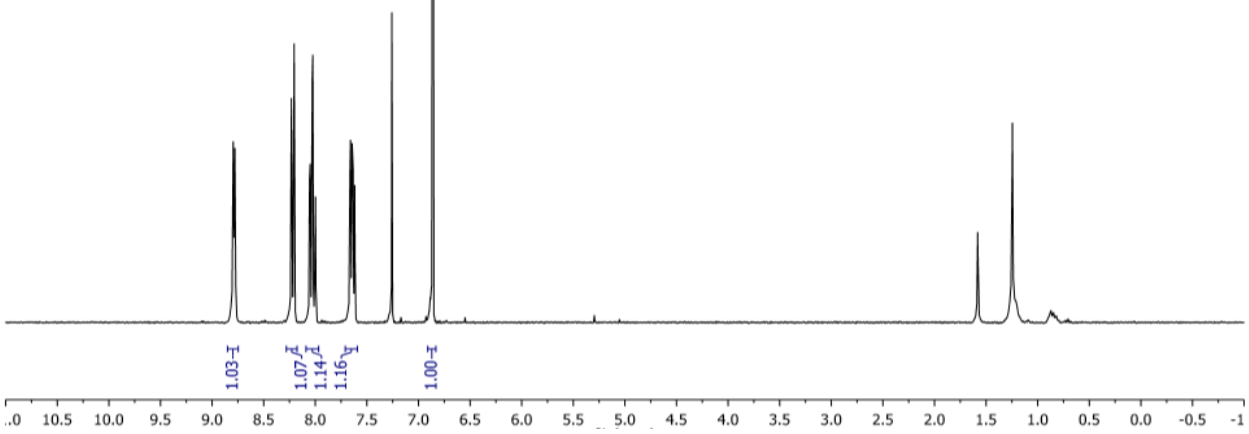
^{13}C NMR (175 MHz, $CDCl_3$)



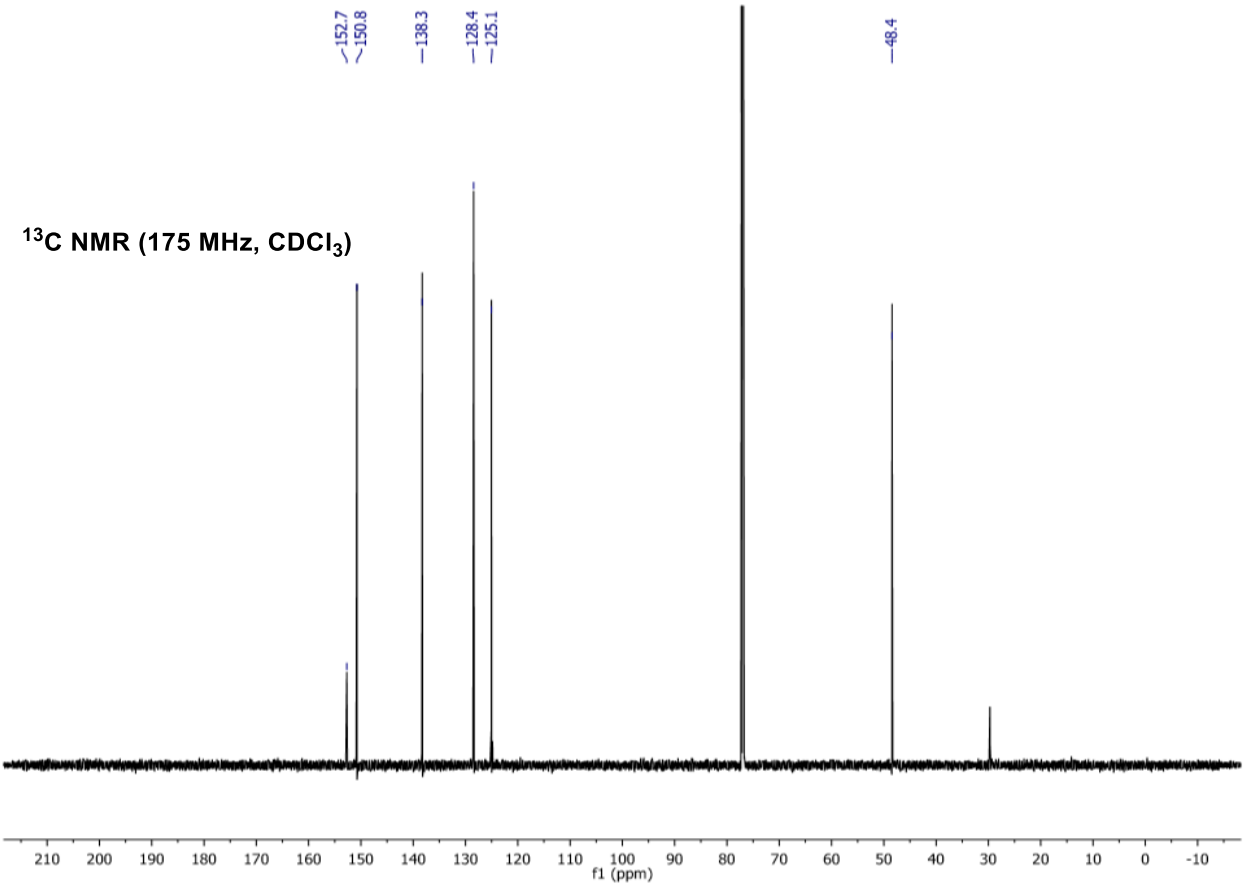


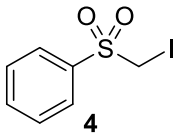
3m

^{1}H NMR (300 MHz, $CDCl_3$)



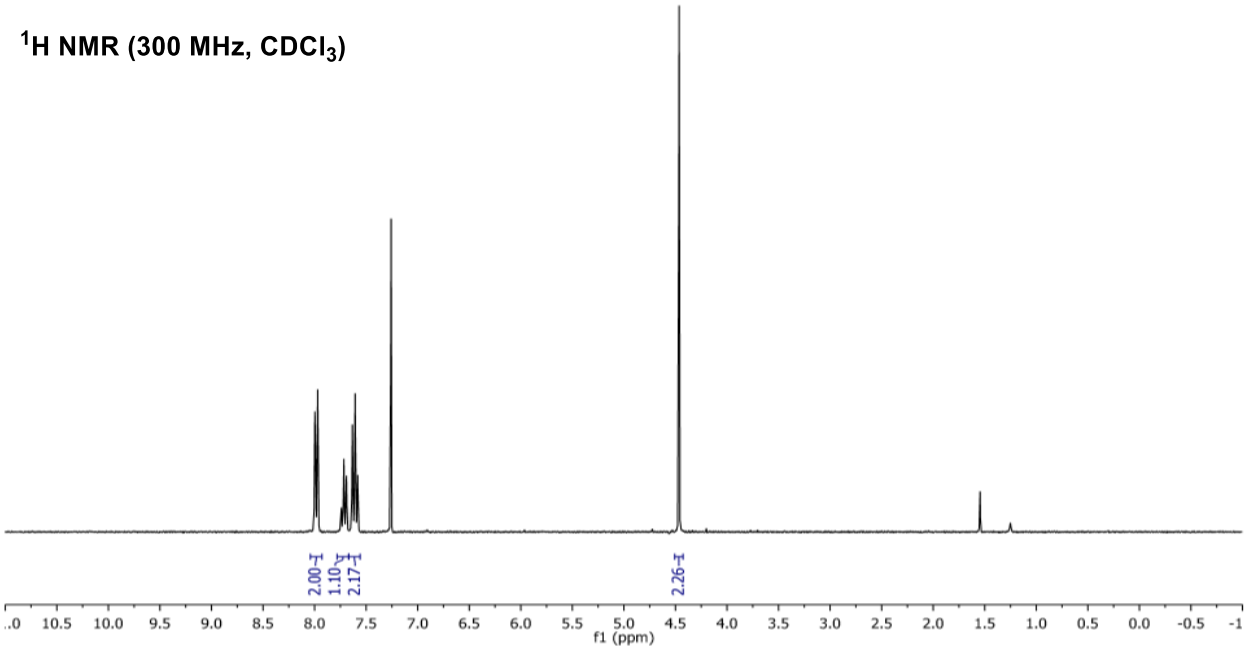
^{13}C NMR (175 MHz, $CDCl_3$)



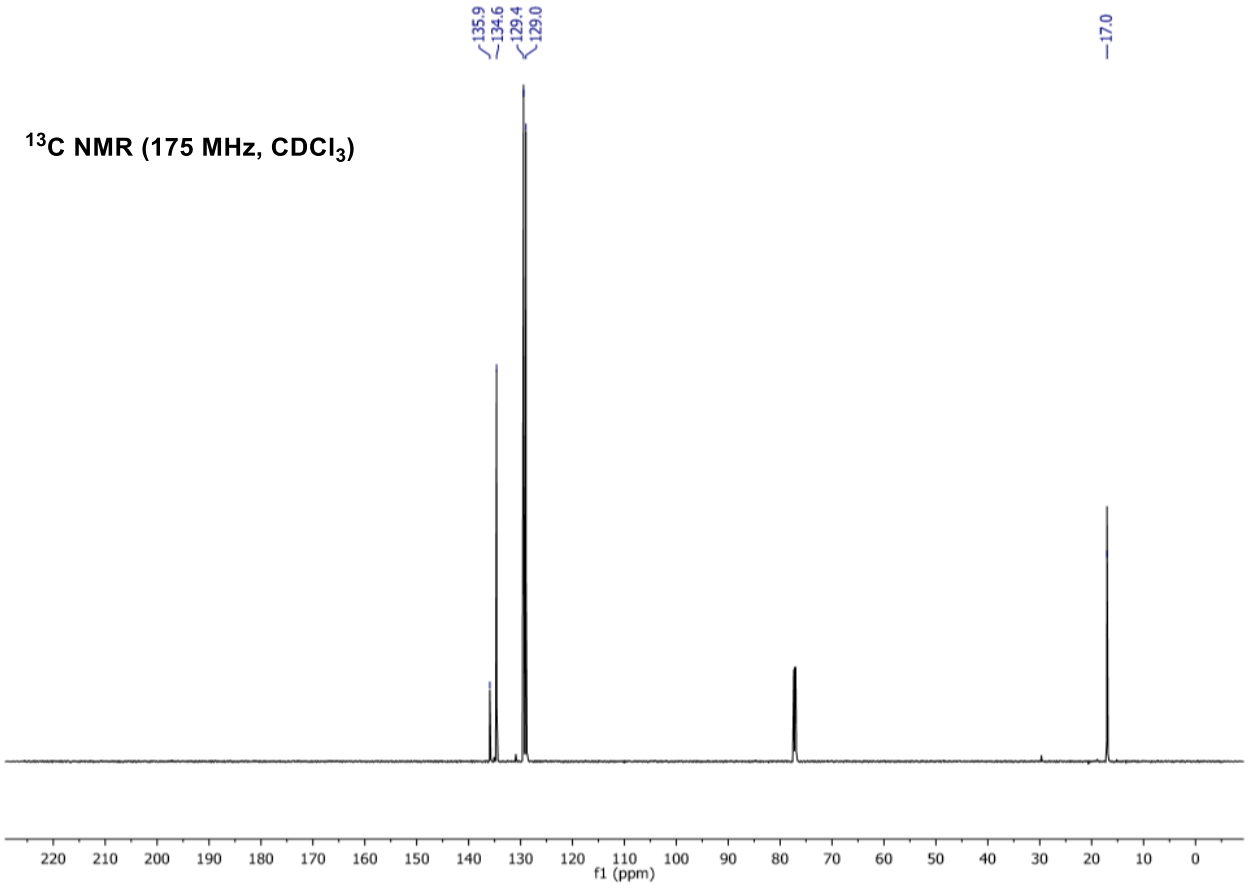


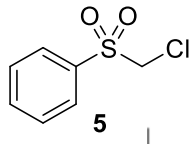
4

^{1}H NMR (300 MHz, $CDCl_3$)



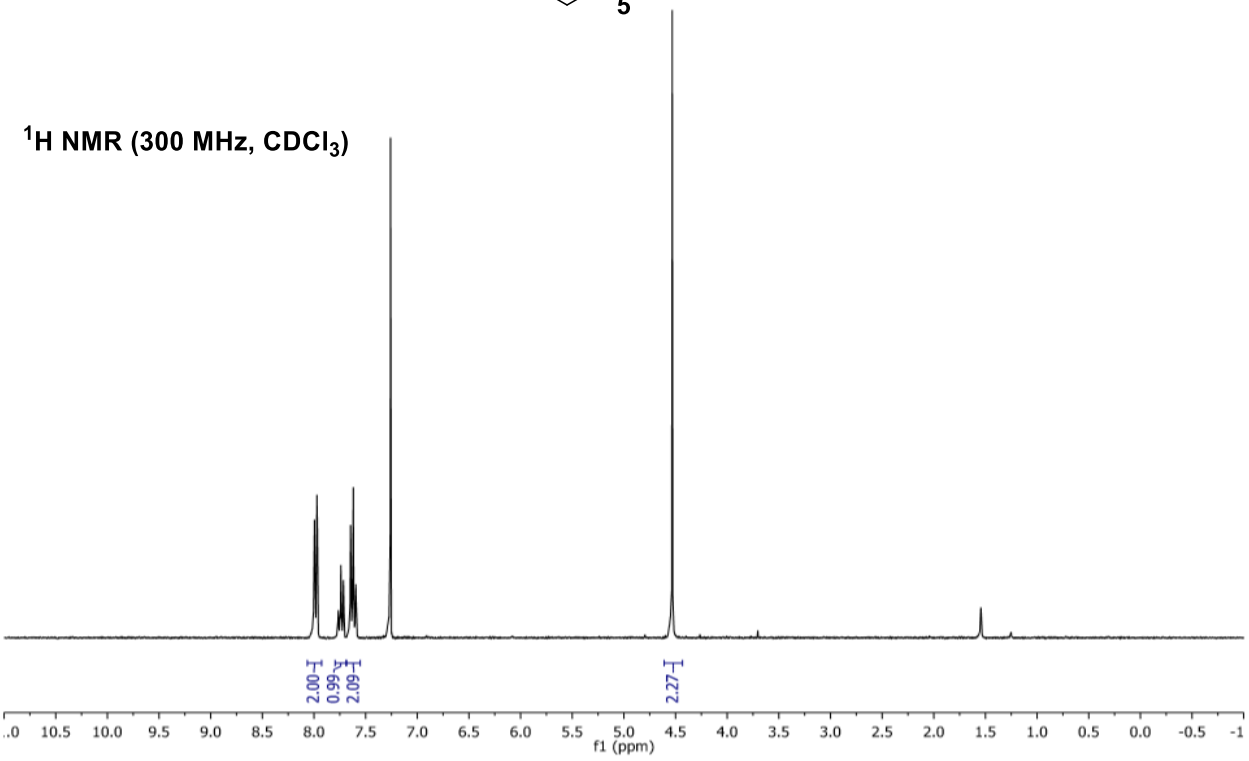
^{13}C NMR (175 MHz, $CDCl_3$)



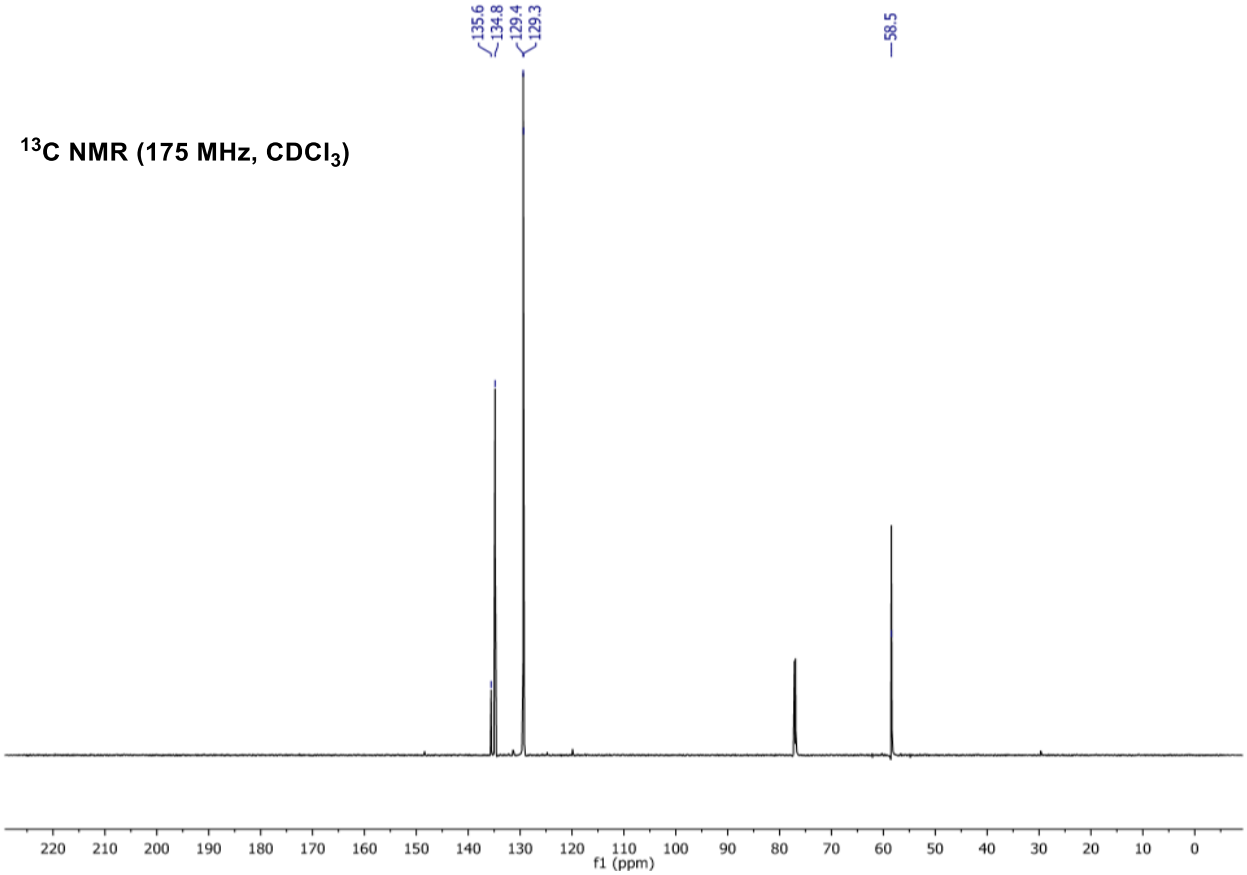


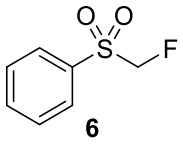
5

^{1}H NMR (300 MHz, $CDCl_3$)



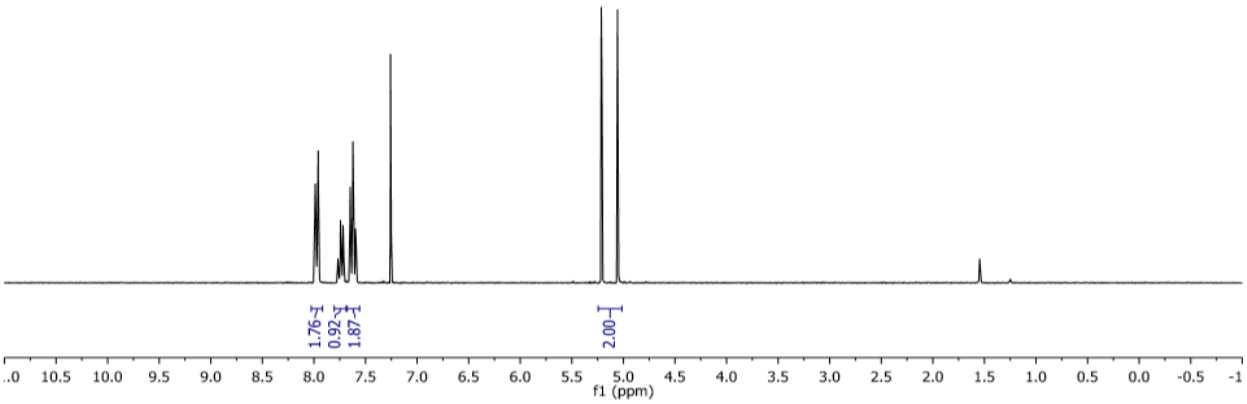
^{13}C NMR (175 MHz, $CDCl_3$)



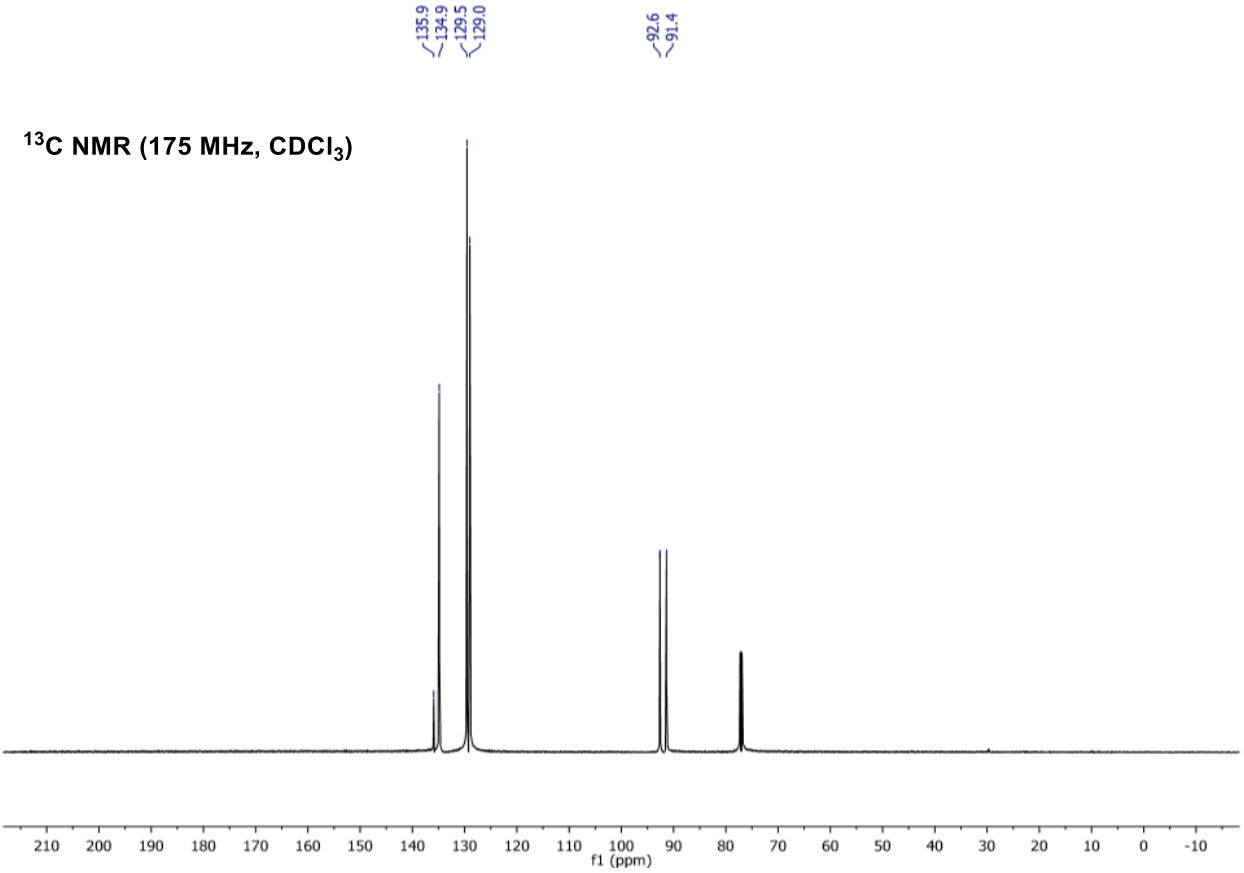


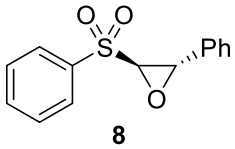
6

^{1}H NMR (300 MHz, $CDCl_3$)



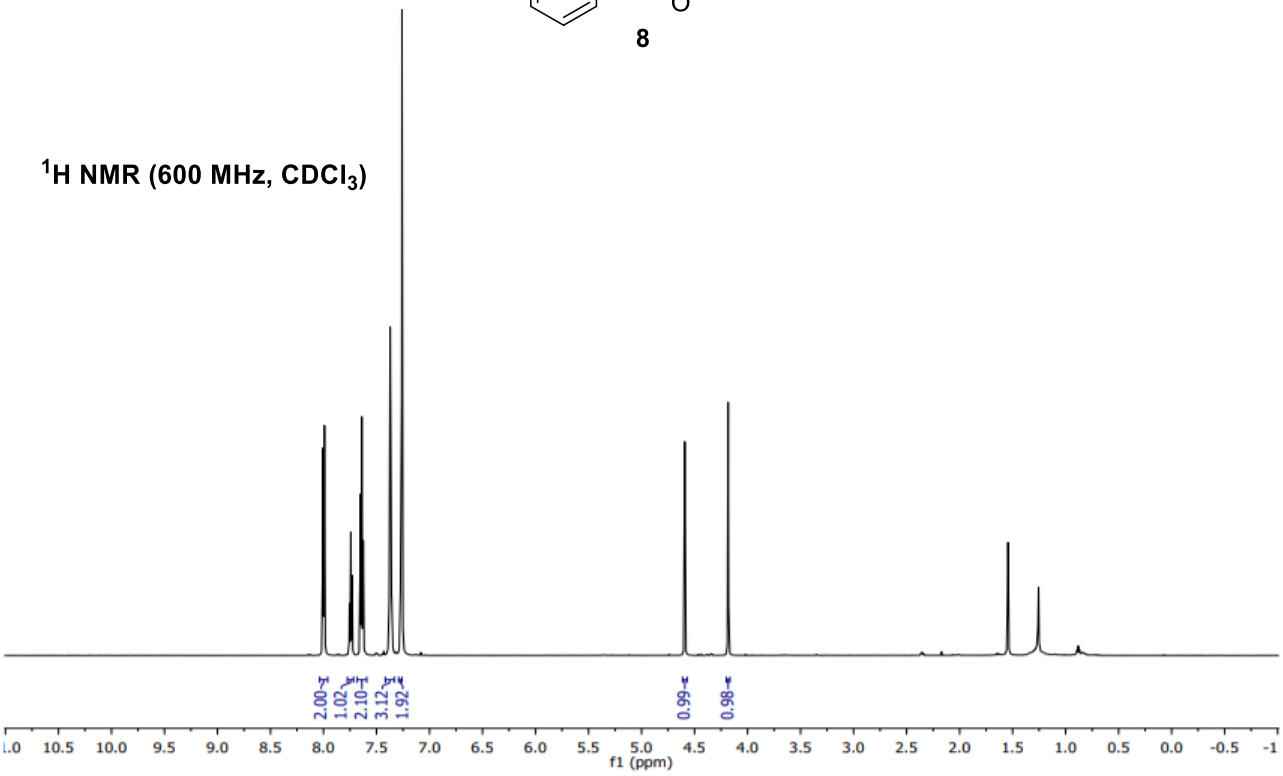
^{13}C NMR (175 MHz, $CDCl_3$)



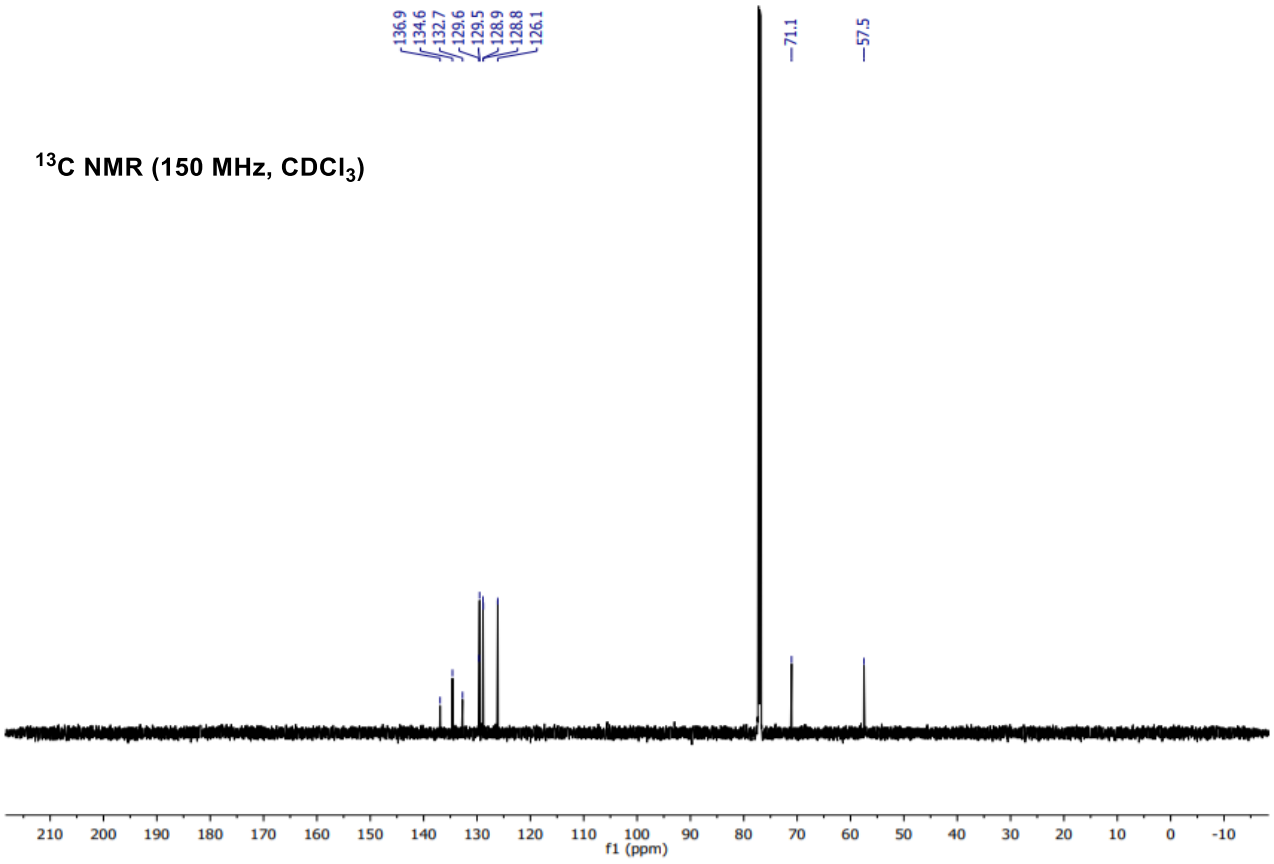


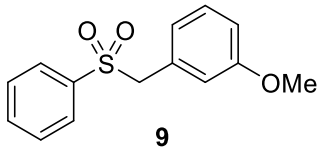
8

^{1}H NMR (600 MHz, $CDCl_3$)



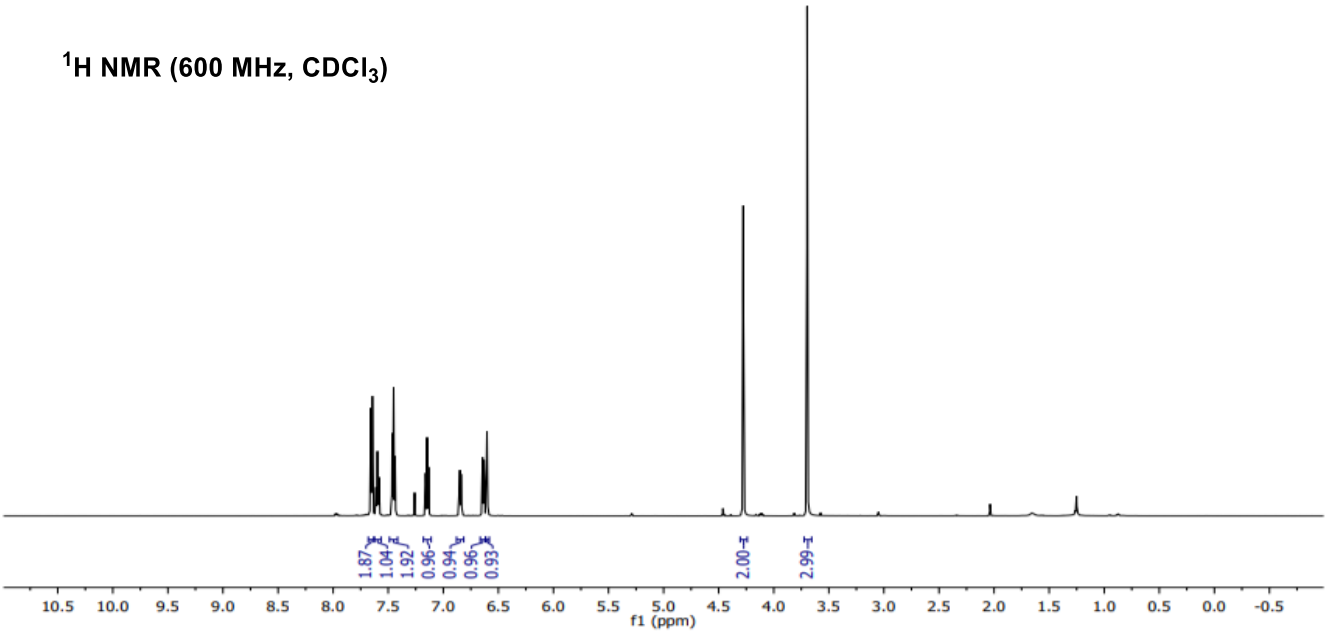
^{13}C NMR (150 MHz, $CDCl_3$)



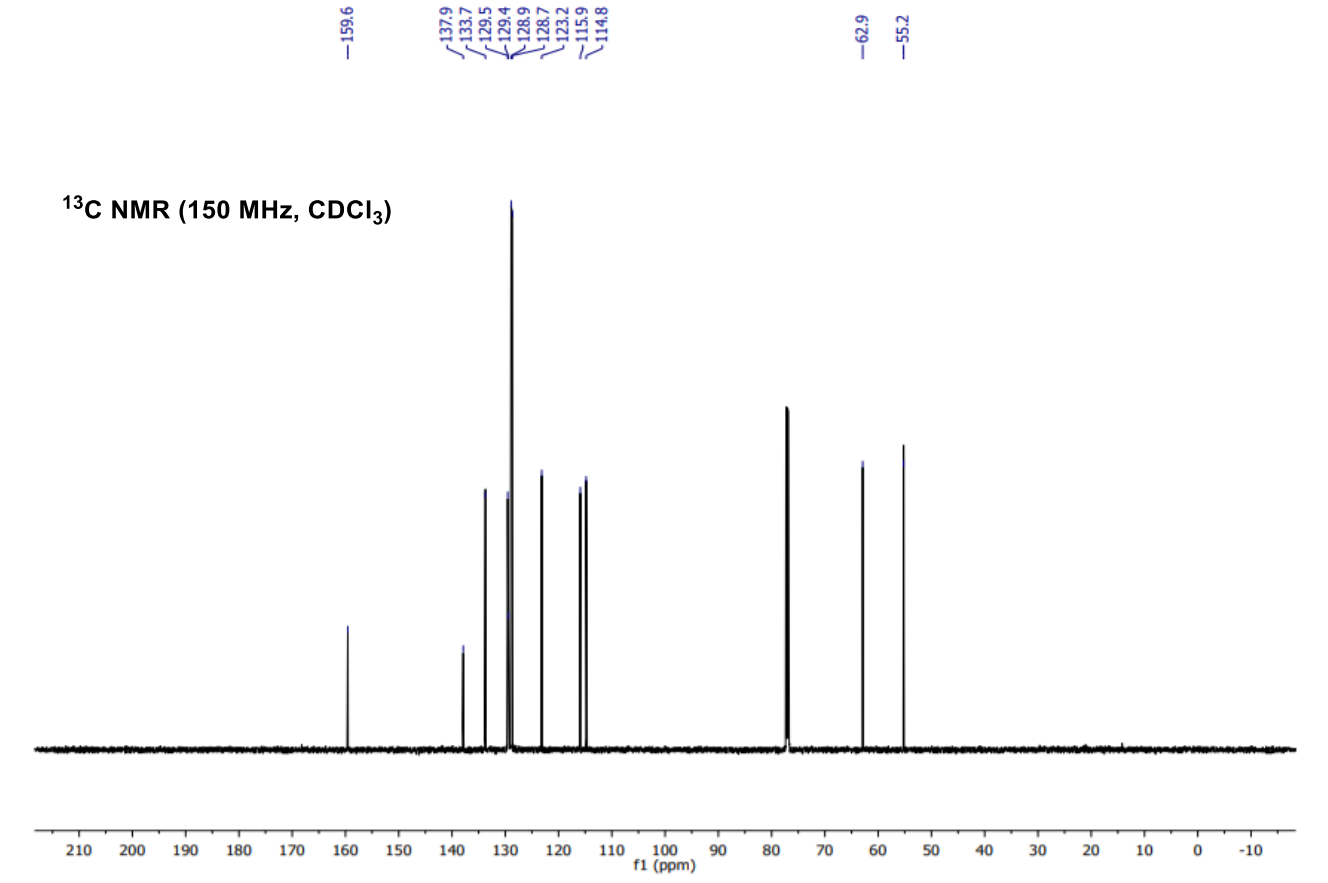


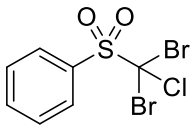
9

^{1}H NMR (600 MHz, $CDCl_3$)



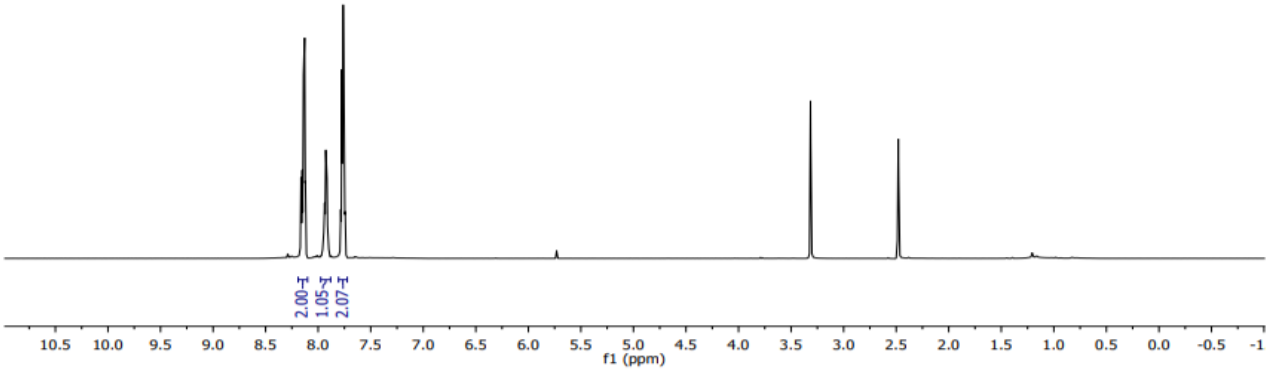
^{13}C NMR (150 MHz, $CDCl_3$)





10

^{1}H NMR (700 MHz, DMSO-d_6)



^{13}C NMR (175 MHz, DMSO-d_6)