Tandem Thia-Fries Rearrangement – Cyclisation of 2-(Trimethylsilyl)phenyl Trifluoromethanesulfonate Benzyne Precursors

Catherine Hall, Jaclyn L. Henderson, Guillaume Ernouf and Michael F. Greaney[a]

[a]*School of Chemistry, University of Manchester, Oxford Road, Manchester, M13 9PL,UK*

Supporting Information

I. Experimental Procedures

General Methods:

^{1}H NMR spectra were recorded on a 300, 400, or 500 MHz spectrometer. ^{13}C NMR spectra were recorded at 75, 101 or 126 MHz. 19F NMR spectra were recorded at 376 or 471 MHz. All chemical shift values are reported in parts per million (ppm) relative to the solvent signal,[1] with coupling constant (J) values reported in Hz. The notation of signals is: Proton: δ chemical shift in ppm (number of protons, multiplicity, J value(s), proton assignment). Carbon: δ chemical shift in ppm (carbon assignment, J value). Fluorine: δ chemical shift in ppm (Fluorine assignment). If assignment is ambiguous a range of shifts is reported.

Low resolution mass spectrometry (LRMS) was measure using either positive and/or negative electrospray – atmospheric pressure ionisation (ES-API) on an Agilent Technologies 6130 Quadrupole liquid chromatography mass spectrometer (LCMS) or by electron impact ionisation (EI) using a Micromass Platform II. High resolution mass spectrometry (HRMS) was measured using EI using a thermo Finnigan MAT95XP or atmospheric pressure chemical ionisation (APCI) using a LTQ Orbitrap XL. Gas chromatography mass spectrometry (GCMS) used was an Agilent Technologies 7890A GC system with a 5975C inert XL EI/CI MSD Triple Axis Detector using a BP5 – 30m X 0.25 mmx 0.25 µm column. Melting points were measured on a variable heater apparatus and are uncorrected. IR spectra were recorded on an ATR FTIR spectrometer as evaporated films or neat.

All reactions were carried out under an inert nitrogen atmosphere unless otherwise stated. Glassware for inert atmosphere reactions was oven-dried and cooled under a flow of nitrogen. Tetrahydrofuran (THF) was distilled over sodium wire and benzophenone, CH_2Cl_2, toluene and diisopropyl amine (DIPA) were distilled

[1] H. E. Gottlieb, V. Kotlyar and A. Nudelman, *J. Org. Chem.*, 1997, **62**, 7512-7515.

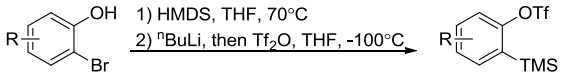
over calcium hydride. Caesium fluoride was thoroughly dried under vacuum with heating. All other solvents and reagents were purchased from commercial sources and used as supplied.

All reactions were carried out under nitrogen in glass microwave vials or a round bottomed flask sealed with a rubber septum and heated in oil baths with a thermocouple temperature control. Routine TLC analysis was carried out on aluminium sheets coated with silica gel 60 Å F_{254}, 0.2 mm thickness. Plates were viewed with a 254 nm ultraviolet lamp and dipped in aqueous potassium permanganate. Flash column chromatography was performed manually on silica gel eluting (40-63 µm) with hexane/ethyl acetate or hexane/CH_2Cl_2 under pressurised air flow.

Preparation of aryne precursors.

2-(Trimethylsilyl)phenyl trifluoromethanesulfonates **1e**, **1g** and **1h** are commercially available, and **1a**,[2] **1b**[3] and **1f**[4] have been previously described. The other aryne precursors used in this study were prepared according to modified literature procedures as follows:

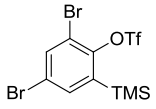
General Procedure A



The appropriate 2-bromophenol (1 eq) and hexamethyldisilazane (1.5 eq) were heated to 70°C in THF (0.3 M) for 2 hours. Residual hexamethyldisilazane and ammonia were removed under reduced pressure to give a (2-bromophenoxy)trimethylsilane, which was used without further purification.

The (2-bromophenoxy)trimethylsilane (1 eq) was dissolved in THF (0.05 M) and cooled to -100°C. ^{n}BuLi (1.6 M, 1.1 eq) was then added dropwise and the reaction was stirred for 30 minutes (reaching a maximum of -80°C). Trifluoromethanesulfonic anhydride (1.2 eq) was then added dropwise and the reaction was stirred for a further 30 minutes at -100 °C. After which time it was allowed to warm to ambient temperature over 2 hours, then quenched with cold $NaHCO_3$ (sat. aq.). The aqueous phase was extracted with Et_2O, and then the combined organics were washed with brine, dried over $MgSO_4$, filtered and concentrated *in vacuo*. The crude reaction mixture was purified by column chromatography.

2,4-Dibromo-(trimethylsilyl)phenyl trifluoromethanesulfonate 1c was synthesised according to general procedure A. The crude reaction mixture was purified by column chromatography to afford a colourless oil (1.6 g, 59% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (d, J = 2.4 Hz, 1H), 7.57 (d, J = 2.4 Hz, 1H), 0.41 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.9, 140.2, 138.4, 138.0, 122.6, 118.7 (q, J = 320.9



[2] D. Peña, A. Cobas, D. Pérez and E. Guitián, *Synthesis*, 2002, 1454-1458.
[3] M. Dai, Z. Wang and S. J. Danishefsky, *Tetrahedron Lett.*, 2008, **49**, 6613-6616.
[4] H. Yoshida, E. Shirakawa, Y. Honda and T. Hiyama, *Angew. Chem. Int. Ed.* 2002, **41**, 3247–3249.

Hz), 117.7, 0.1; ^{19}F NMR (377 MHz, $CDCl_3$) -71.5; LRMS (EI) *m/z* 440.9 (40% [M-CH_3]), 307.9 (100% [M-OSO_2CF_3]); ν_{max} (neat)/cm^{-1} 2956, 1539, 1409, 1362, 1254, 1211, 1166, 1135, 1059.

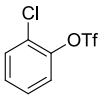
2-Chloro-6-(trimethylsilyl)phenyl trifluoromethanesulfonate 1d was synthesised from 2-bromo-6-chlorophenol according to general procedure A. The crude reaction mixture was purified by column chromatography to afford a colourless oil (1.17g, 37%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.50 (dd, J = 7.8, 1.7 Hz, 1H), 7.46 (dd, J = 7.4, 1.7 Hz, 1H), 7.31 (app. t, J = 7.6 Hz, 1H), 0.40 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 148.3, 137.7, 135.0, 132.6, 129.0, 127.6, 118.9 (q, J = 320.8 Hz), 0.4; ^{19}F NMR (377 MHz, $CDCl_3$) -71.6; LRMS (EI) *m/z* 317.0 (75% [M-CH_3]), 184.0 (100% [M-OSO_2CF_3]); ν_{max} (neat/cm^{-1}) 2959, 2904, 1555, 1401, 1209, 1176, 1135, 1086, 1062.

2-Nitro-6-(trimethylsilyl)phenol was synthesised according to modified literature procedures.[1] 2-Bromo-6-nitrophenol (1.53 g, 7 mmol) and hexamethyldisilazane (2.19 mL, 10.5 mmol) were heated to 70°C in THF (0.3 M) for 2 hours. Residual hexamethyldisilazane and ammonia were removed under reduced pressure to give (2-bromo-6-nitrophenoxy)trimethylsilane, which was used without further purification. The (2-bromo-6-nitrophenoxy)trimethylsilane was dissolved in THF (0.05 M) and cooled to -100°C. ^{n}BuLi (3.08 mL, 1.6 M in hexanes, 7.7 mmol) was then added dropwise and the reaction was stirred for 30 minutes (reaching a maximum of -80°C. Pure fractions were isolated to afford a yellow amorphous solid (239 mg, 16%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 11.01 (s, 1H), 8.10 (dd, J = 8.4, 1.7 Hz, 1H), 7.66 (dd, J = 7.0, 1.7 Hz, 1H), 6.97 (dd, J = 8.4, 7.0 Hz, 1H), 0.34 (s, 9H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 159.2, 143.3, 133.2, 131.9, 126.2, 120.2, -1.1; LRMS (ES-API) *m/z* 210.0 (100% [M-H]$^-$); HRMS (+APCI) *m/z*: Calculated for [M+H]$^+$ $C_9H_{14}NO_3Si$ 212.0737, Found 212.0736; ν_{max} (neat)/cm^{-1} 3186, 2956, 2899, 1592, 1532, 1456, 1425, 1324, 1293, 1246, 1166, 1121, 1089, 1066.

2-Nitro-6-(trimethylsilyl)phenyl trifluoromethanesulfonate 1i was synthesised from 2-nitro-6-(trimethylsilyl)phenol according to modified literature procedures.[2] Trifluoromethanesulfonic anhydride (0.17 mL, 0.98 mmol) was added dropwise to a solution of 2-nitro-6-(trimethylsilyl)phenol (190 mg, 0.9 mmol) in anhydrous pyridine (0.3 mL) at 0 °C and then allowed to warm to ambient temperature over 22 hours. The crude reaction mixture was quenched with 1M HCl (1 mL) and extracted with dichloromethane (2 x 5 mL). The organic phases were combined, washed with brine, dried over $MgSO_4$, filtered and concentrated *in vacuo*. The crude reaction mixture was purified by column chromatography afford a yellow oil (220 mg, 71%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (dd, J = 7.9, 1.8 Hz, 1H), 7.82 (dd, J = 7.5, 1.8 Hz, 1H), 7.58 – 7.50 (m, 1H), 0.44 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.6, 142.0, 141.0, 139.2, 128.8, 127.4, 118.3 (q, J = 320.4 Hz), -0.12. ^{19}F NMR (377 MHz, $CDCl_3$) δ -72.9; LRMS (ES-API) *m/z* 366.01 (100%, [M+Na]$^+$); HRMS (+APCI) *m/z*: Calculated for [M+H]$^+$ $C_{10}H_{13}F_3NO_5SSi$

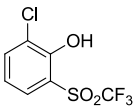
344.0236, Found 344.0230; ν_{max} (neat)/cm^{-1} 2956, 2899, 1594, 1567, 1537, 1405, 1351, 1293, 1254, 1210, 1180, 1131, 1107, 1071.

2-Cholorophenyl trifluoromethylsulfonate 9 was synthesised according to modified literature procedures.[5]



Trifluromethanesulfonic anhydride (1.5 mL, 8.9 mmol) was added dropwise to a solution of 2-chlorophenol (0.84 mL, 8.1 mmol) in anhydrous pyridine (3 mL) at 0 °C. The reaction was allowed to warm to ambient temperature over 24 hours, then quenched with 1M HCl (5 mL) and extracted with dichloromethane (2 x 10 mL). The organic phases were combined, washed with brine, dried over $MgSO_4$, filtered and concentrated *in vacuo*. The crude reaction mixture was purified by column chromatography to afford a colourless oil (2.09 g, 99%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.59 – 7.48 (m, 1H), 7.39 – 7.30 (m, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 145.7, 131.3, 129.2, 128.3, 127.3, 123.0, 118.6 (q, J = 320.6 Hz); ^{19}F NMR (471 MHz, $CDCl_3$) δ -73.5; ν_{max} (neat)/cm^{-1} 1474, 1424, 1248, 1205, 1181, 1159, 1136, 1055, 1035. Data is consistent with literature values.[5]

2-Chloro-6-((trifluomethyl)sulfonyl)phenol 4b was synthesised according to modified literature procedures.[5]



A solution of DIPA (0.56 mL, 4 mmol) in THF (4 mL) under nitrogen was cooled to –78 °C. ^{n}BuLi (1.72 mL, 2.33 M in hexanes, 4 mmol) was added and the solution was transferred to an ice bath for 30 minutes. The lithium di-isopropyl amine (LDA) solution was then cooled to –78 °C and 2-chlorophenyl trifluoromethylsulfonate **9** (1.0 g 3.8 mmol) in THF (20 mL) was added dropwise. The reaction mixture was stirred for 5 hours at –78 °C, after which time the reaction was transferred to an ice bath and quenched with 1M HCl (5 mL) at 0 °C. The acidic phase was extracted with hexane:ethyl acetate 20:1 solution (3 x 10 mL) and the combined organic phases were washed with brine, dried over $MgSO_4$, and then concentrated *in vacuo*. The crude was purified by column chromatography to afford a yellow solid (189 mg, 19%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.64 (br. s, 1H), 7.80 (dd, J = 7.9, 1.7 Hz, 1H), 7.71 (dd, J = 8.0, 1.6 Hz, 1H), 7.11 (app. t, J = 8.0 Hz, 1H).^{13}C NMR (75 MHz, $CDCl_3$) δ 145.7, 131.3, 129.2, 128.3, 127.3, 123.0, 118.6 (q, J = 320.6 Hz); ^{19}F NMR (471 MHz, $CDCl_3$) δ -73.5; LRMS *m/z* 258.8 (100%, $[M-H]^-$); ν_{max} (neat)/cm^{-1} 3441, 1738, 1583, 1464, 1368, 1316, 1274, 1250, 1206, 1188, 1128, 1073. Data consistent with literature values.[5]

Fries rearrangement – Cyclisation Studies

General Procedure B

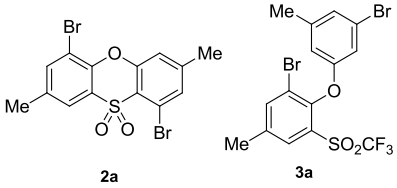
A solution of the aryne precursor (1 eq) in acetonitrile:toluene mixtures (0.5 M) was added to dried caesium fluoride (3 eq). The reaction mixture was stirred vigorously at ambient temperature for 4 to 24

[5] J. P. H. Charmant, A. M. Dyke and G. C. Lloyd-Jones, *Chem. Commun*. 2003, 380-381.

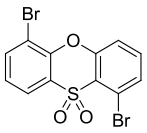
hours. The reaction was then diluted with water and diethyl ether, and the aqueous phase was extracted with diethyl ether. Combined organics were washed with brine, dried over $MgSO_4$, filtered and evaporated to dryness. The crude reaction mixture was then purified by column chromatography.

1-Bromo2-(3-bromo-5-methylphenoxy)-5-methyl-3-((trifluoromethyl)sulfonyl)benzene 3a and 1,6-dibromo-3,8-dimethylphenoxathiine 10,10-dioxide 2a

2-Bromo-4-methyl-6-(trimethylsilyl)phenyl trifluromethanesulfonate **1a** (419 mg, 1.1 mmol) was subjected to the conditions outlined in general procedure B. The crude reaction mixture was purified by column chromatography to afford **3a** as a white solid (22 mg, 9%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (dd, J = 2.1, 0.9 Hz, 1H), 7.73 (dd, J = 2.1, 0.8 Hz, 1H), 6.90 (td, J = 1.5, 0.7 Hz, 1H), 6.54 (ddd, J = 2.4, 1.7, 0.7 Hz, 1H), 6.40 (ddd, J = 2.3, 1.4, 0.7 Hz, 1H), 2.36 (t, J = 0.7 Hz, 3H), 2.14 (app. q, J = 0.6 Hz, 3H); ^{13}C NMR (400 MHz, $CDCl_3$) δ 157.6, 149.1, 143.2, 141.5, 138.3, 133.1, 127.1, 122.5, 119.8, 116.1, 115.4, 112.8, 21.4, 20.8 (triflone carbon not observed); LRMS (ES-API+) 510.9 (100%, $[M+Na]^+$); HRMS (+APCI) *m/z*: Calculated for $[M+H]^+$ $C_{15}H_{12}Br_2F_3O_3S$ 486.8821, Found 486.8819; ν_{max} (neat)/cm^{-1} 3071, 2927, 2859, 1601, 1576, 1452, 1369, 1302, 1262, 1208, 1123; mp 101-109 °C; and **2a** as a white crystalline solid (98.4 mg, 44%).^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (dd, J = 1.9, 0.9 Hz, 1H), 7.72 – 7.66 (m, 2H), 7.43 (dd, J = 1.6, 0.7 Hz, 1H), 7.26 (d, J = 1.5 Hz, 2H), 2.44 (app. d, J = 1.0 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 151.7, 145.7, 144.2, 138.4, 136.1, 132.1, 125.8, 122.6, 121.1, 118.9, 117.2, 111.3, 21.3, 20.7; LRMS (ES-API+) 419 (100%, $[M+H]^+$); HRMS (+ESI) *m/z*: Calculated for $[M+Na]^+$ $C_{14}H_{10}O_3Br_2SNa^+$ 438.8610, Found 438.8612 ($[M+Na]^+$); ν_{max} (neat)/cm^{-1} 1578, 1555, 1440, 1299, 1249, 1159, 1108; mp 230-234°C.

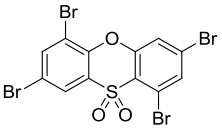


1,6-Dibromophenoxathiine 10,10-dioxide 2b



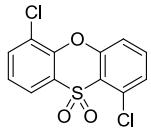
2-Bromo-6-(trimethylsilyl)phenyl trifluoromethanesulfonate **1b** (378 mg, 1.0 mmol) was subjected to conditions outlined in general procedure B. The crude reaction mixture was purified by column chromatography to afford **2b** as a white crystalline solid (43 mg, 29%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.03 (dd, J = 8.0, 1.5 Hz, 1H), 7.89 (dd, J = 7.9, 1.6 Hz, 1H), 7.62 (dd, J = 5.3, 3.7 Hz, 1H), 7.52 – 7.45 (m, 2H), 7.30 (app. t, J = 8.0 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 151.9, 146.4, 137.8, 134.0, 131.4, 126.4, 125.6, 124.1, 123.1, 118.9, 117.6, 111.9; LRMS (ES-API) 391.0 (100%, $[M+H]^+$); HRMS (ES-API) *m/z*: Calculated for $[M+Na]^+$ $C_{12}H_6O_3SNa^+$ 410.8297, Found 410.8282 ($[M+Na]^+$); ν_{max} (neat)/cm^{-1} 1578, 1555, 1441, 1298, 1249, 1158, 1109; mp 205-207°C.

1,3,6,8-Tetrabromophenoxathiine 10,10-dioxide 2c



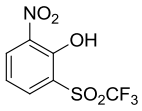
2,4-Bromo-6-(trimethylsilyl)phenyl trifluromethanesulfonate **1c** (136 mg, 0.3 mmol) was subjected to the conditions outlined in general procedure B. The crude reaction mixture was purified by column chromatography to afford **2c** as a white crystalline solid (16 mg, 20%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (d, J = 2.2 Hz, 1H), 8.02 (d, J = 2.2 Hz, 1H), 7.79 (d, J = 1.8 Hz, 1H), 7.68 (d, J = 1.8 Hz, 1H); ^{13}C NMR (101 MHz, CDCl3) δ 151.85, 145.57, 140.40, 134.43, 128.11, 127.57, 125.77, 123.44, 122.23, 118.76, 117.98, 113.32; LRMS (ES-API+) *m/z* 570.7 (100%, $[M+Na]^+$); HRMS (+APCI) *m/z*: Calculated for $[M+H]^+$ $C_{12}H_4Br_4O_3$ 544.6687, Found 544.9976; ν_{max} (neat)/cm^{-1} 3067, 2922, 2852, 1738, 1579, 1564, 1539, 1446, 1380, 1313, 1260, 1244, 1213, 1181, 1157, 1129, 1094, 1017; mp 259-265°C.

1,6-Dichlorophenoxathiine 10,10-dioxide 2d



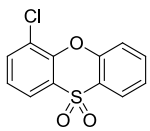
2-Chloro-6-(trimethylsilyl)phenyl trifluromethanesulfonate **1d** (49.9 mg, 0.15 mmol) was subjected to the conditions outlined in general procedure B. The crude reaction mixture was purified by column chromatography to afford **2d** as a white crystalline solid (13.5 mg, 60%).^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (dd, J = 8.1, 1.5 Hz, 1H), 7.73 (dd, J = 7.9, 1.5 Hz, 1H), 7.58 (dd, J = 8.6, 7.9 Hz, 1H), 7.45 – 7.40 (m, 2H), 7.37 (t, J = 8.0 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 151.7, 145.6, 134.6, 133.8, 131.4, 127.8, 126.7, 125.2, 123.2, 122.8, 122.2, 118.26; LRMS (ES-API+) *m/z* 301.1 (100%, $[M+H]^+$); HRMS (+ESI) *m/z*: Calculated for $[M+NH_4]^+$ $C_{12}H_{10}O_3N_1Cl_2S_1$ 317.9753, Found 317.9750; ν_{max} (neat)/cm^{-1} 3079, 2917, 2847, 1738, 1580, 1561, 1444, 1328, 1299, 1254, 1227, 1187, 1162, 1151, 1122, 1081; mp 182-189°C.

2-Nitro-6-((trifluoromethyl)sulfonyl)phenol 4a

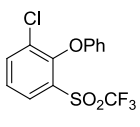


2-Nitro-6-(trimethylsilyl)phenyl trifluoromethanesulfonate **1i** (90 mg, 0.26 mmol) was subjected to the conditions outlined in general procedure B. The crude reaction mixture was purified by column chromatography to afford **4a** as a yellow solid (47.6 mg, 68%)**.** ^{1}H NMR (400 MHz, Methanol-d4) δ 7.64 (dd, J = 8.1, 2.0 Hz, 1H), 7.33 (dd, J = 7.8, 2.0 Hz, 1H), 5.87 (app. t, J = 8.0 Hz, 1H), 4.29 (s, 1H); ^{13}C (75 MHz, Methanol-d4) δ 165.9, 142.2, 141.2, 136.5, 123.9, 121.8 (app. d, J = 326.4 Hz), 110.6; ^{19}F(376 MHz, $CDCl_3$) -73.32; LRMS (ES-API-) *m/z* 270.0 $[M-H]^-$; HRMS (ESI+) *m/z*: $[M + Na]^+$ Calculated for $C_7H_4O_5N_1F_3Na_1S_1$ 293.9654; Found 293.9640; ν_{max} (neat)/cm^{-1} 3565, 2973, 2359, 1600, 1542, 1506, 1474, 1436, 1341, 1324, 1261, 1204, 1163, 1129, 1080; mp decomposition observed.

4-Chlorophenoxathiine 10,10-dioxide 2f and 1-Chloro-2-phenoxyl-3-((trifluoromethyl)sulfonyl)benzene 3c



2f

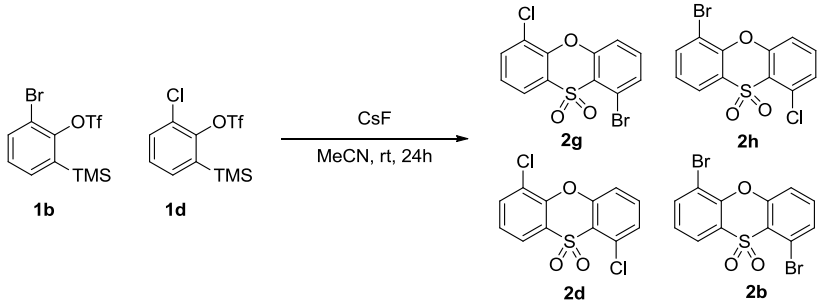


3c

2-Chloro-6-((trifluomethyl)sulfonyl)phenol **4b** (78.2 mg, 0.3 mmol) and 2-(trimethylsilyl)phenyl trifuloromethylsulfonate **1e** (98.5mg, 0.33 mmol) were subjected to the conditions outlined in general procedure B. The

crude reaction mixture was purified by column chromatography to afford **3c** as a yellow oil (17 mg, 16%); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.09 (dd, J = 8.1, 1.6 Hz, 1H), 7.89 (dt, J = 8.0, 1.1 Hz, 1H), 7.48 (app. td, J = 8.1, 0.7 Hz, 1H), 7.36 – 7.28 (m, 2H), 7.13 – 7.05 (m, 1H), 6.85 – 6.77 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 157.1, 151.0, 139.4, 131.8, 131.0, 130.3, 129.6, 126.4, 123.3, 115.6; LRMS (ES-API+) *m/z* 359.0 $[M+Na]^+$; HRMS (ESI+) *m/z*: $[M + NH_4]^+$ Calculated for $C_{13}H_{12}O_3NClF_3S$ 354.0173, Found 354.0173; ν_{max} (neat)/cm^{-1} 3082, 2973, 2359, 1592, 1571, 1490, 1446, 1436, 1369, 1251, 1208, 1189, 1161, 1131, 1085, 1024; and **2f** as a white crystalline solid (23.5 mg, 27%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (dd, J = 8.0, 1.7 Hz, 1H), 7.97 (dd, J = 8.0, 1.6 Hz, 1H), 7.76-7.64 (m, 2H), 7.52 (dd, J = 8.5, 1.1 Hz, 1H), 7.48 – 7.43 (m, 1H), 7.35 (t, J = 8.0 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 151.4, 147.7, 134.7, 134.54 126.7, 125.6, 125.1, 124.8, 123.9, 123.5, 121.9, 119.4.; LRMS (ES-API+) *m/z* 267.0 (100%, $[M+H]^+$); HRMS (+APCI) *m/z*: $[M+H]^+$ Calculated for $C_{12}H_7ClO_3S$ 299.9877, Found 266.9875; ν_{max} (neat)/cm^{-1} 3079, 2918, 2849, 1737, 1601, 1583, 1561, 1473, 1455, 1436, 1377, 1312, 1271, 1247, 1205, 1176, 1153, 1111, 1070; mp 148-152°C.

Crossover reaction



2-Bromo-6-(trimethylsilyl)phenyl trifluoromethanesulfonate **1b** (84.3 mg, 0.25 mmol) of each Cl-SM = 83.2 mg and 2-chloro-6-(trimethylsilyl)phenyl trifluromethanesulfonate **1d** (83.2 mg, 0.25 mmol) were subjected to the conditions outlined in general procedure B. The products were isolated as an inseparable mixture by column chromatography (31 mg) in the relative ratio **2d**:**2g**+**2h**:**2b** 28:49:23 (as determined by GCMS).

Conditions for GCMS: Back injector temperature at 300 °C with 20:1 split ratio using a helium carrier gas at 1 mL per minute. Initial temperature of 50 °C with a 3 minute hold followed by an increase of 25 °C per minute to 300 °C and then a 5 minute hold at 300 °C. The auxiliary heater to MS set to 300 °C. **2d** (14.641 minutes, m/z 299.9), **2h**+**2g** (15.232 minutes, m/z 345.9) and **2b** (15.911, m/z 389.8)

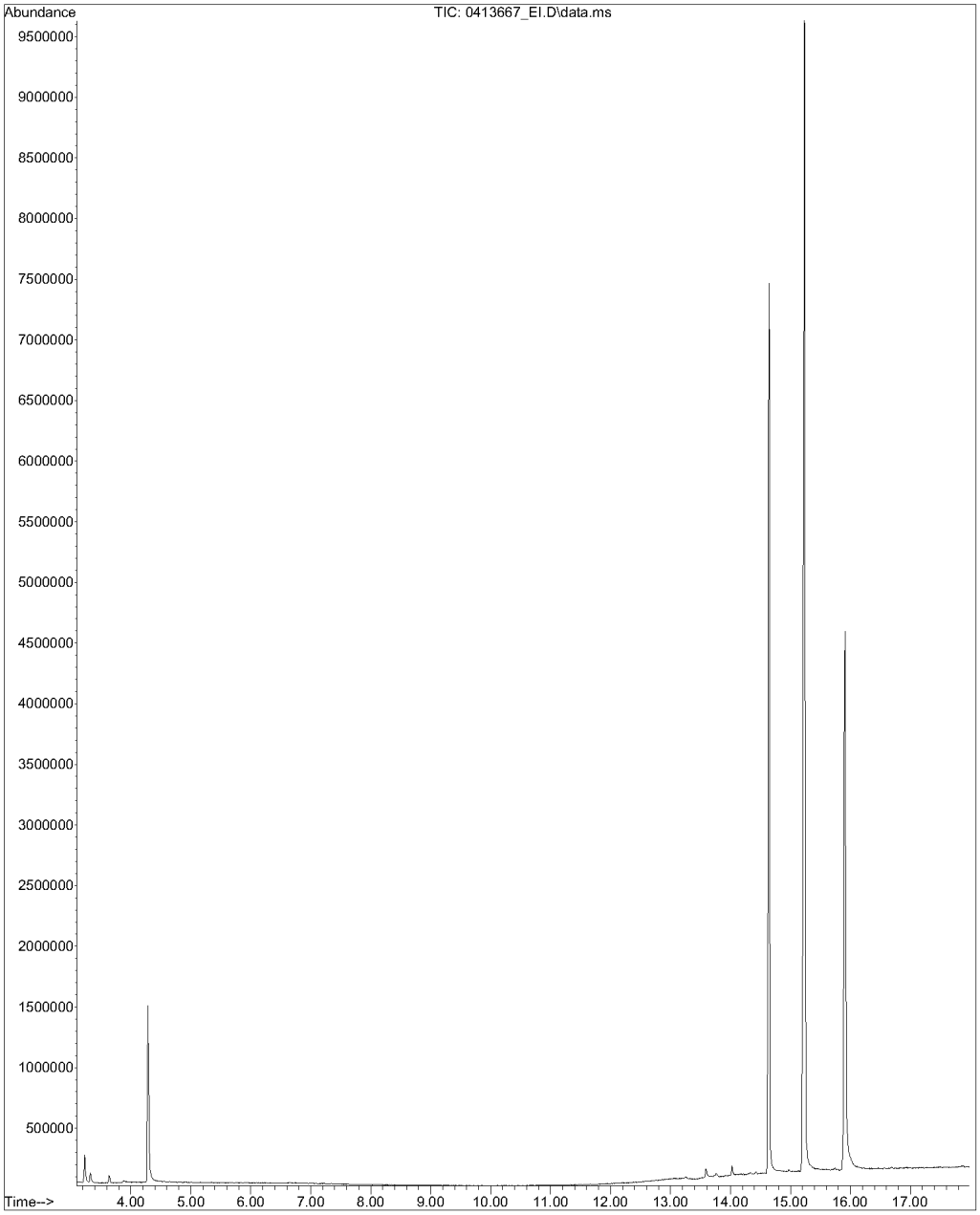
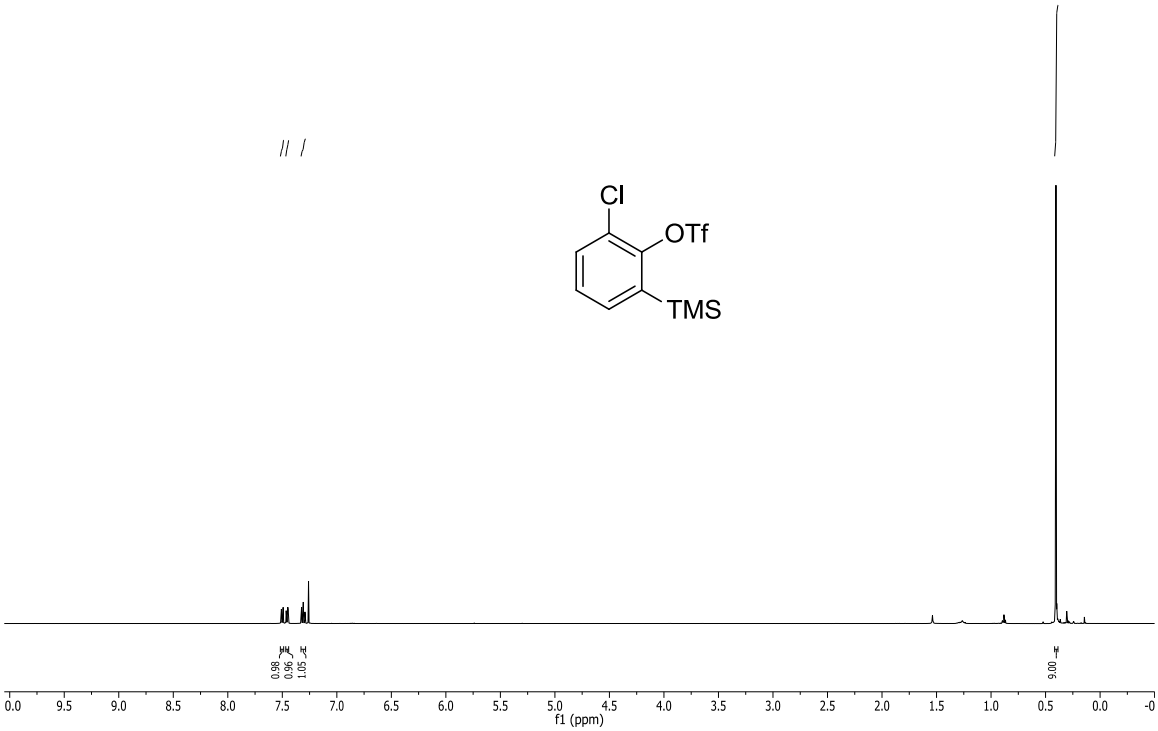


Fig. 1: GCMS trace of products from crossover reaction

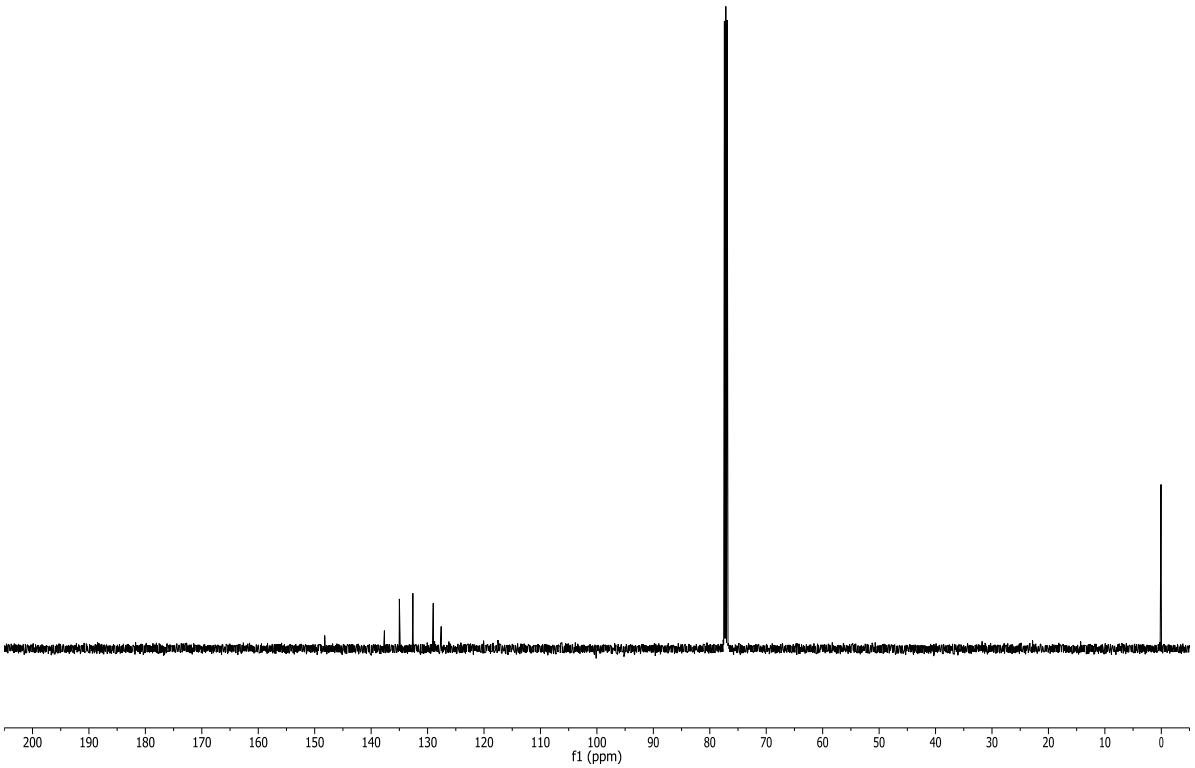
II. NMR Spectra

2-Chloro-6-(trimethylsilyl)phenyl trifluoromethanesulfonate 1d

^{1}H NMR (500 MHz, $CDCl_3$)

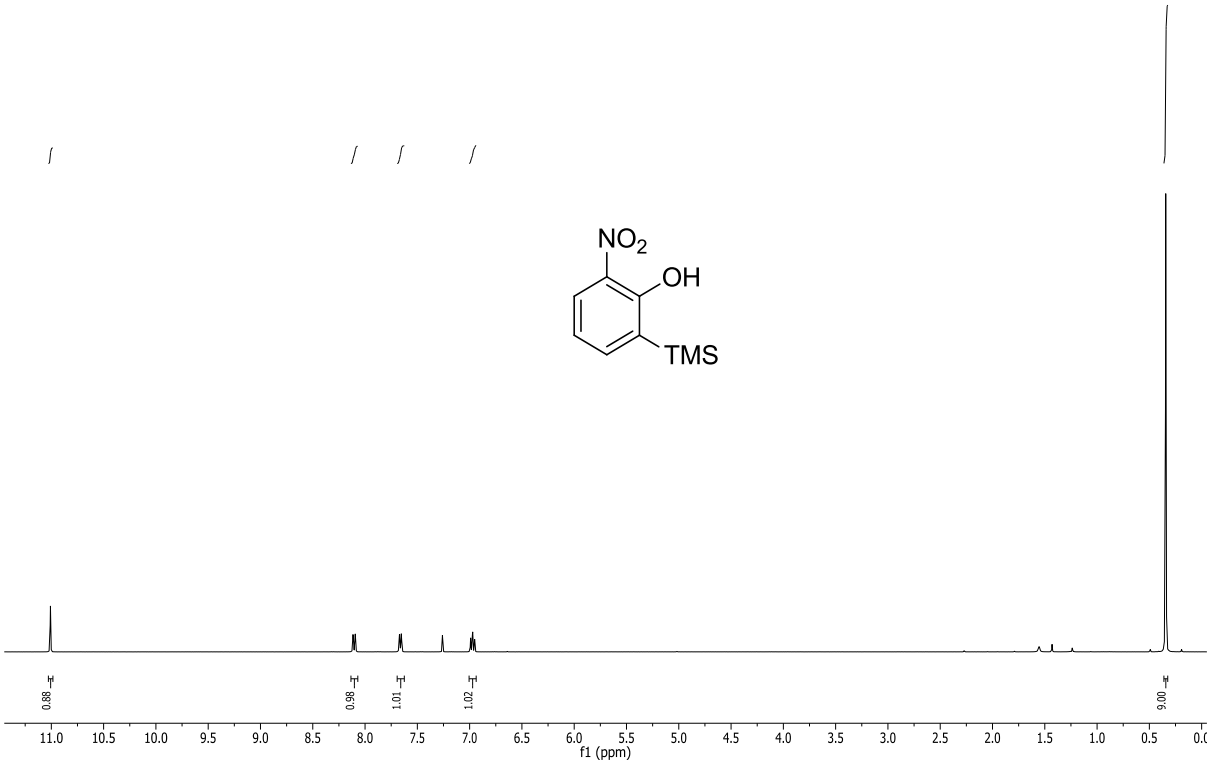


^{13}C NMR (126 MHz, $CDCl_3$)

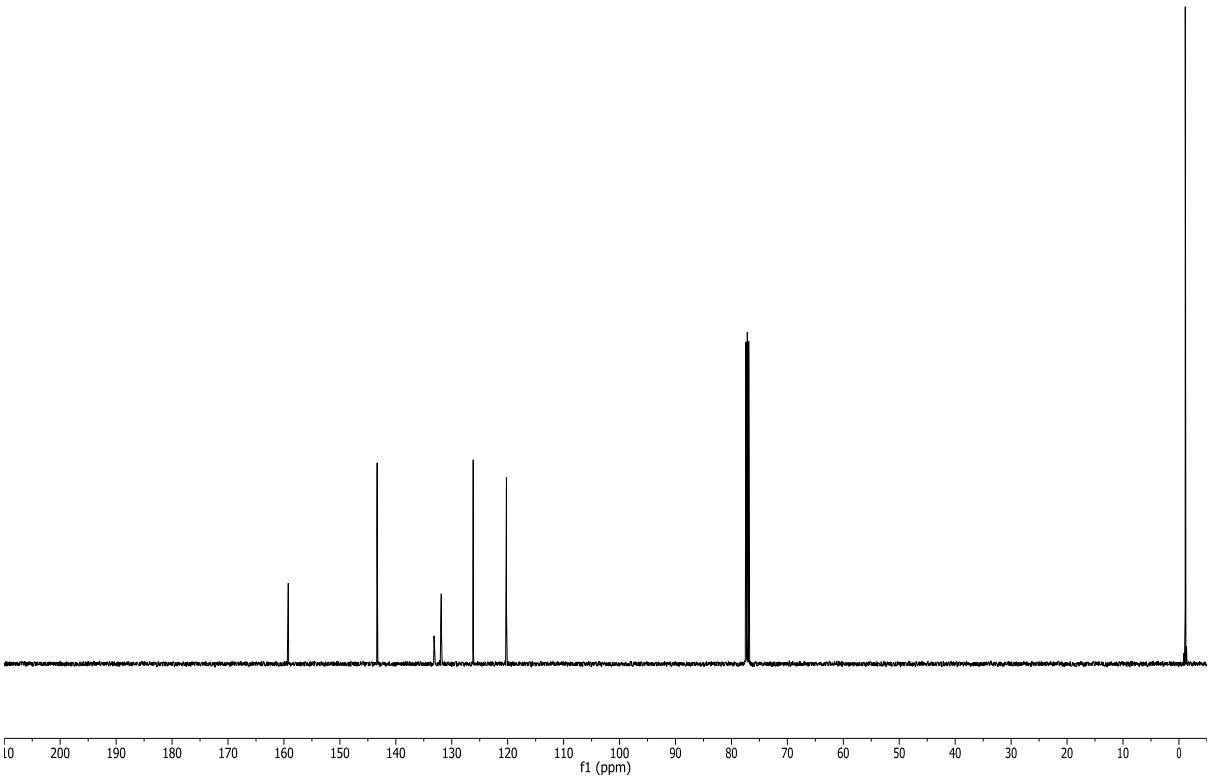


2-Nitro-6-(trimethylsilyl)phenol

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

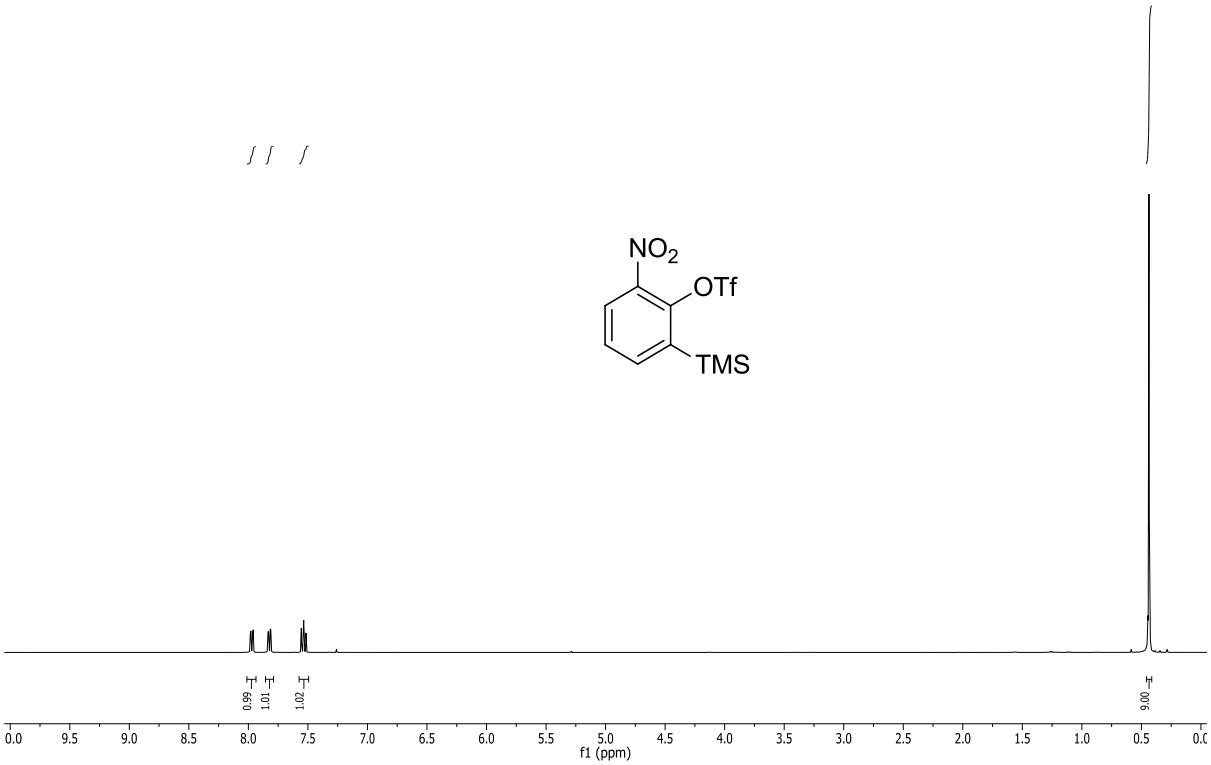


^{13}C NMR (126 MHz, $CDCl_3$)

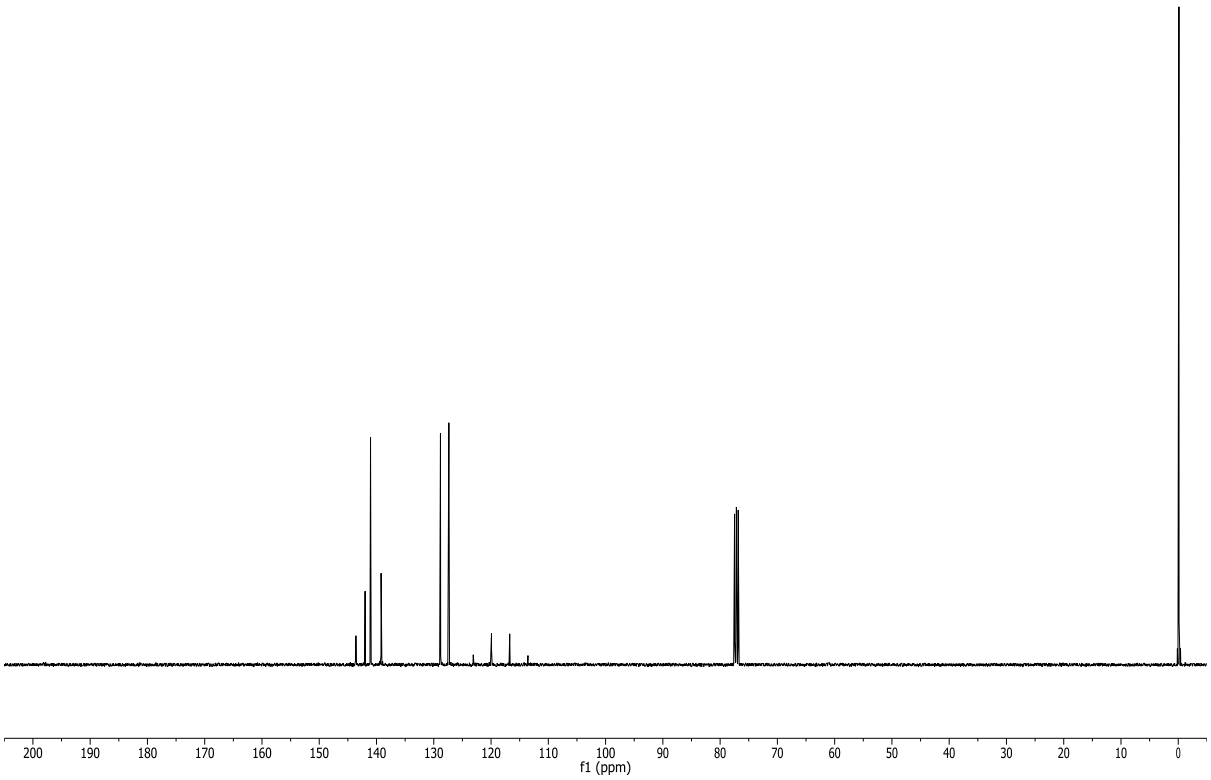


2-Nitro-6-(trimethylsilyl)phenyl trifluoromethanesulfonate 1i

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

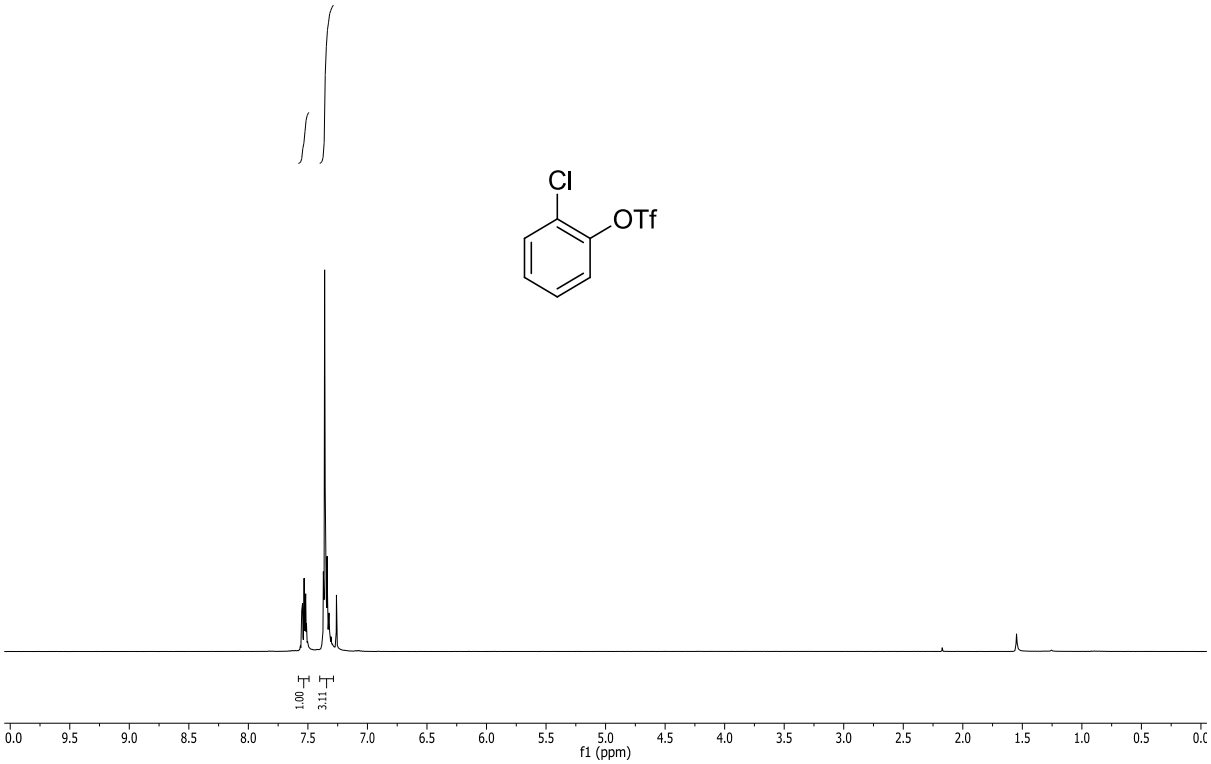


^{13}C NMR (101 MHz, $CDCl_3$)

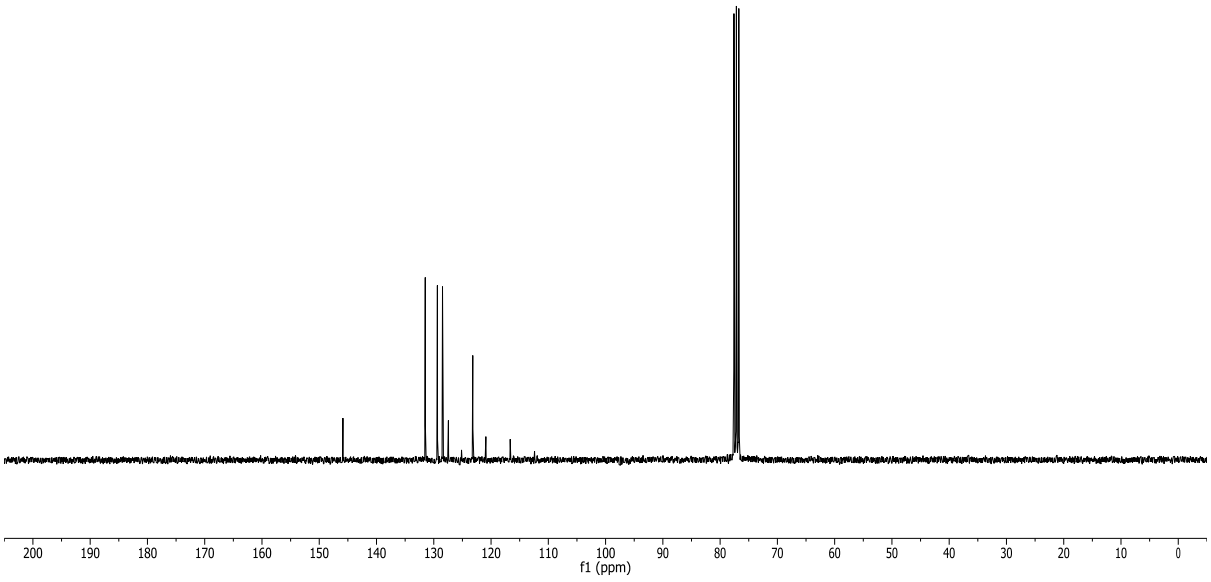


2-Cholorophenyl trifluoromethylsulfonate 9

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

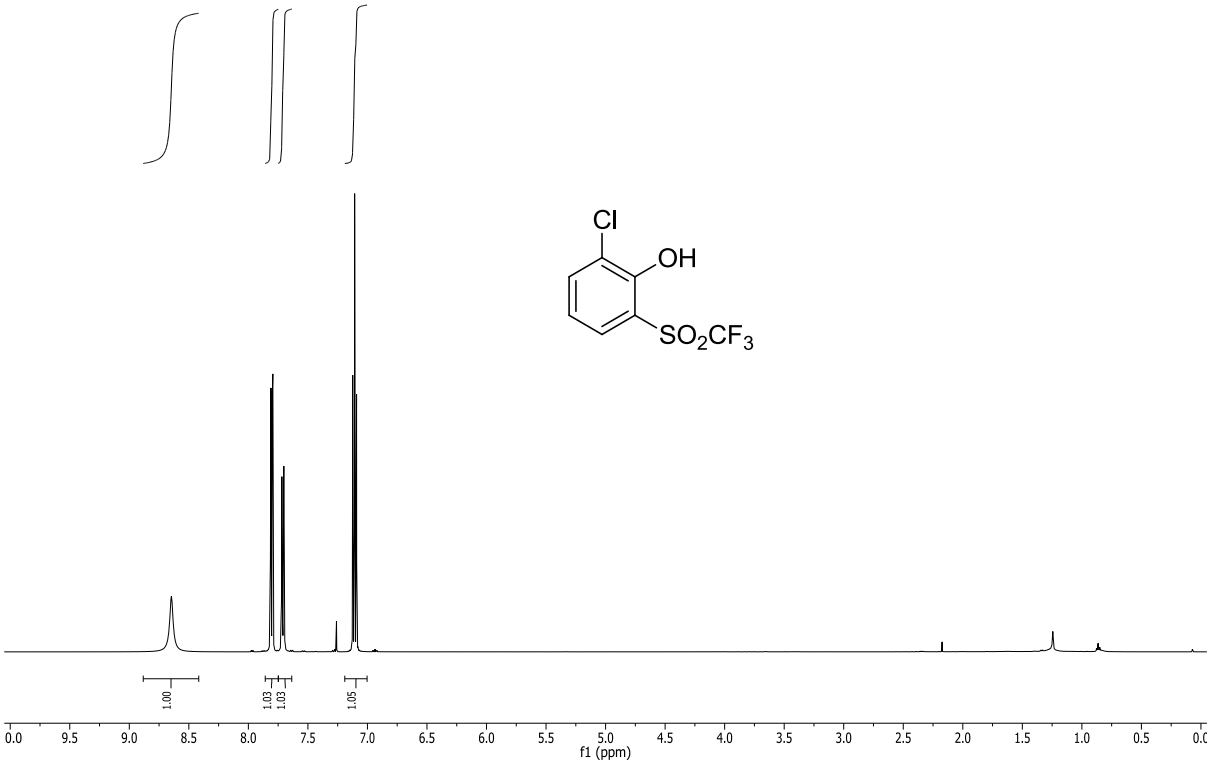


^{13}C NMR (75 MHz, $CDCl_3$)

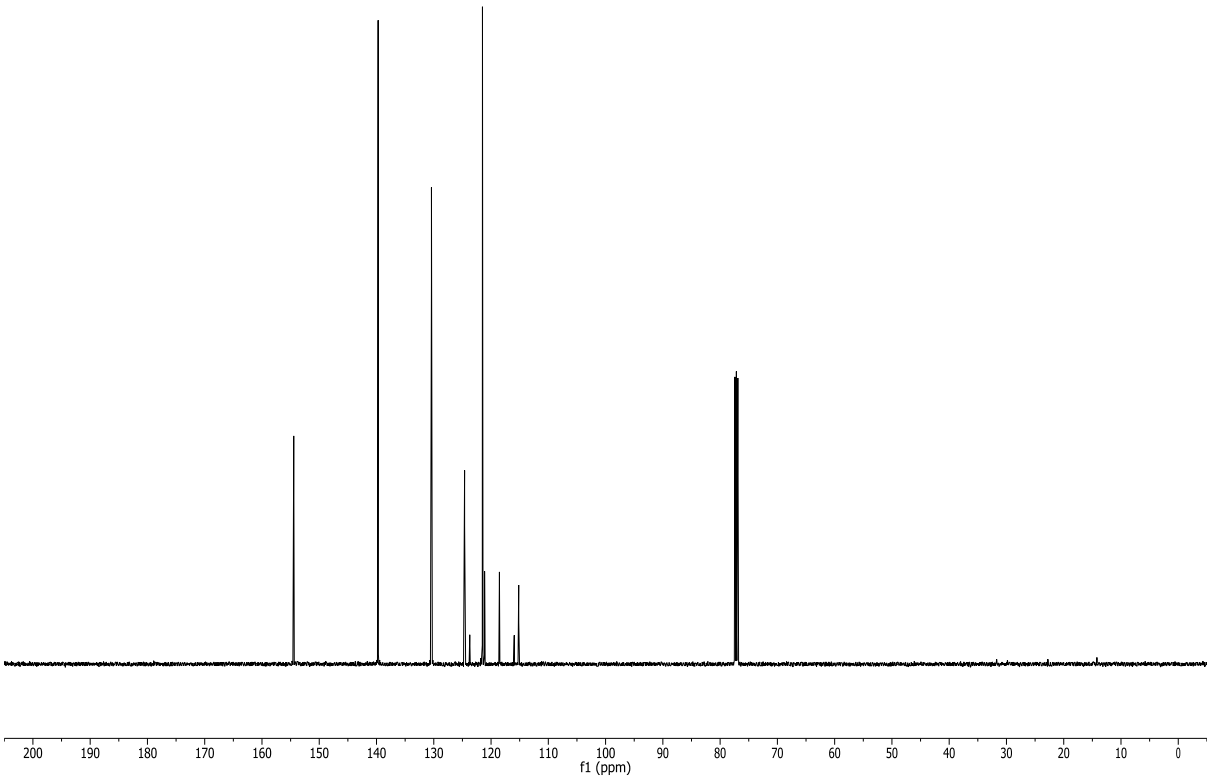


2-Chloro-6-((trifluomethyl)sulfonyl)phenol 4b

^{1}H NMR (500 MHz, $CDCl_3$)

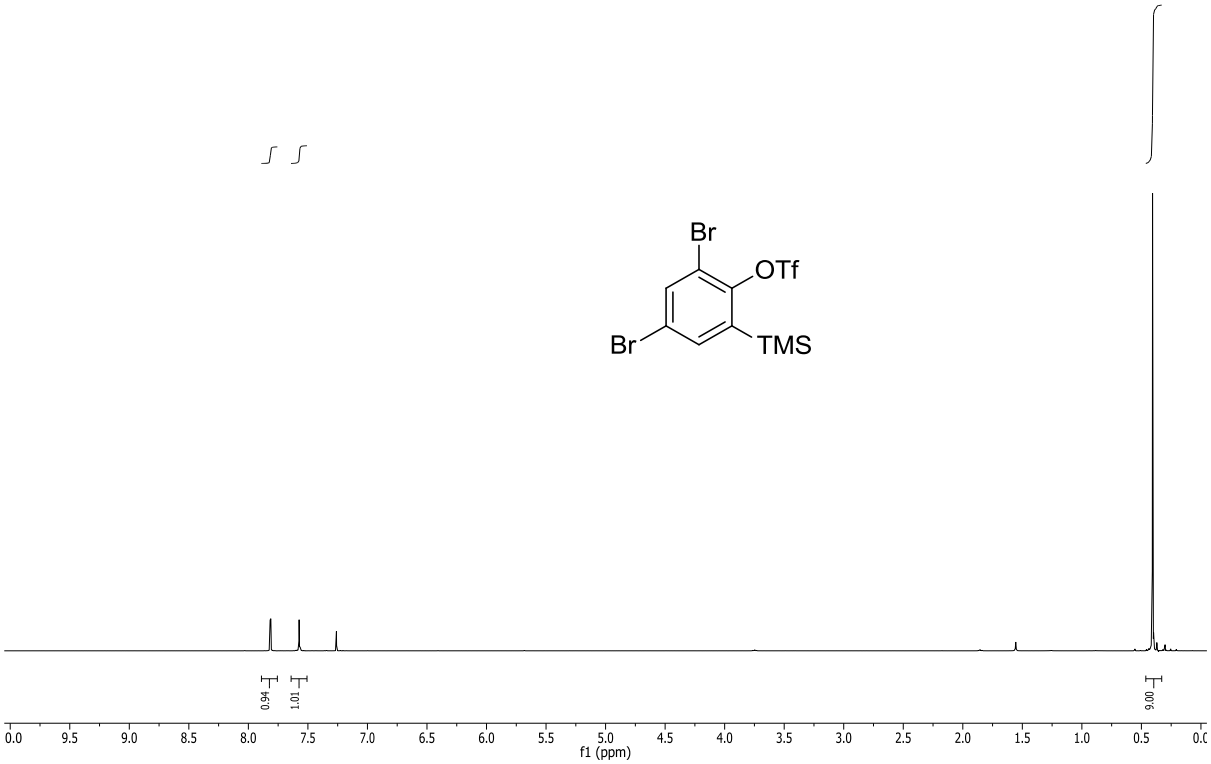


^{13}C NMR (126 MHz, $CDCl_3$)

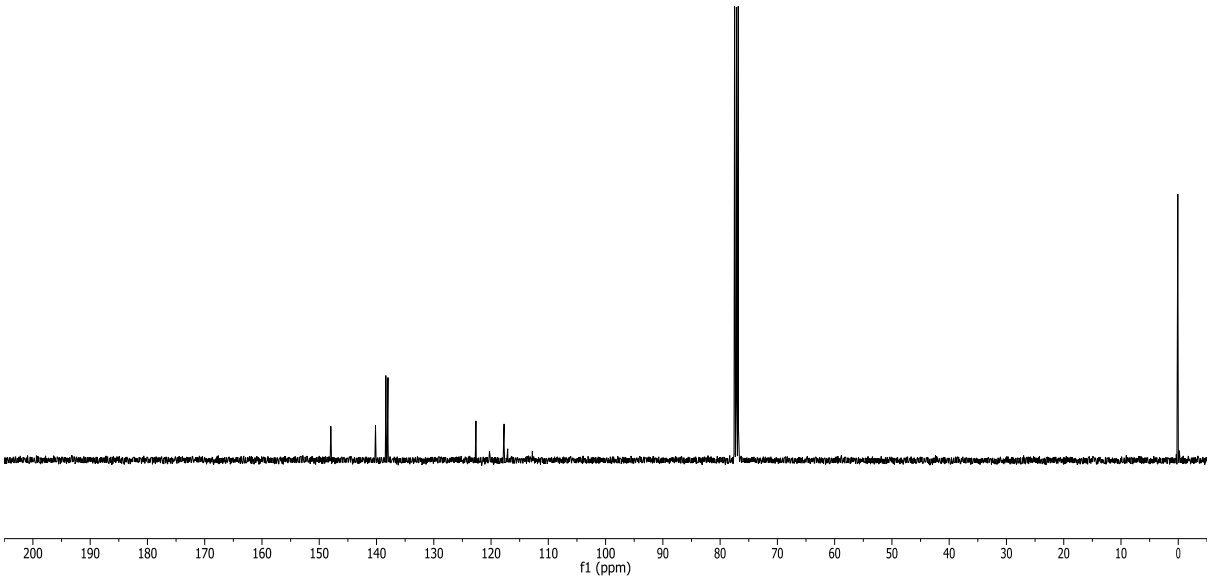


2,4-Dibromo-(trimethylsilyl)phenyl trifluoromethanesulfonate 1c

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

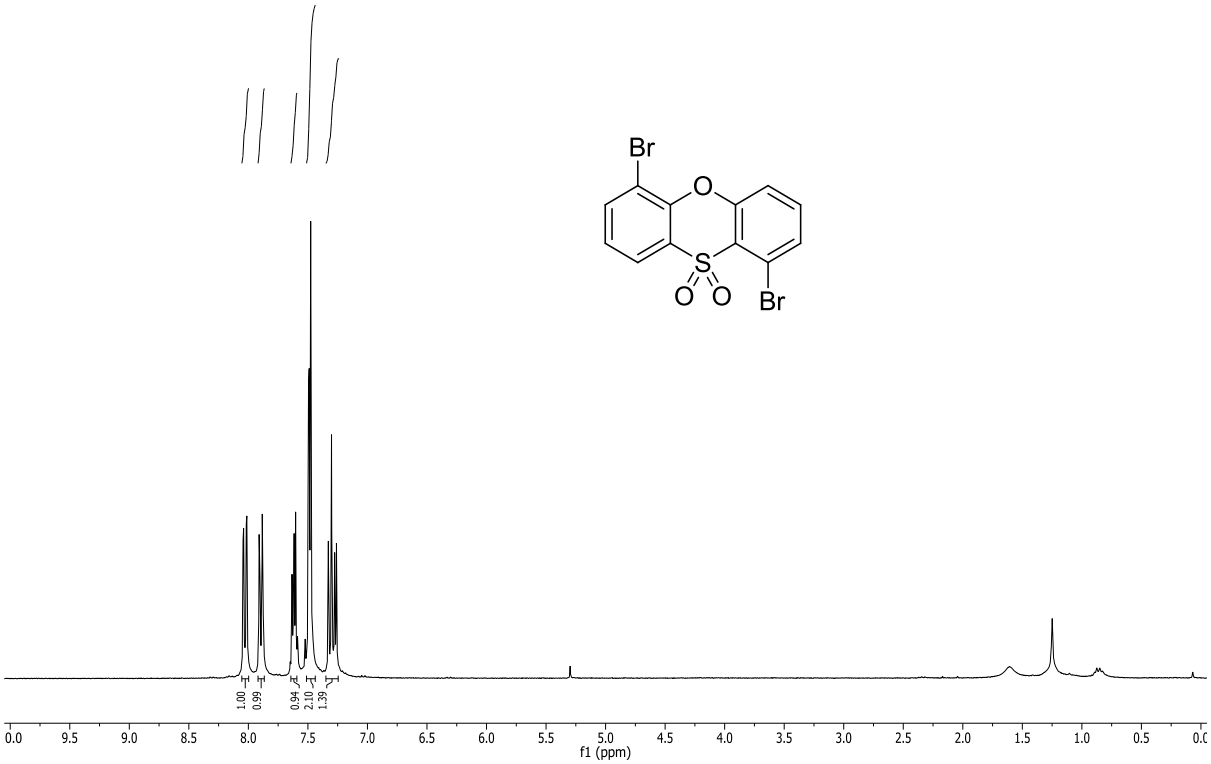


^{13}C NMR (101 MHz, $CDCl_3$)

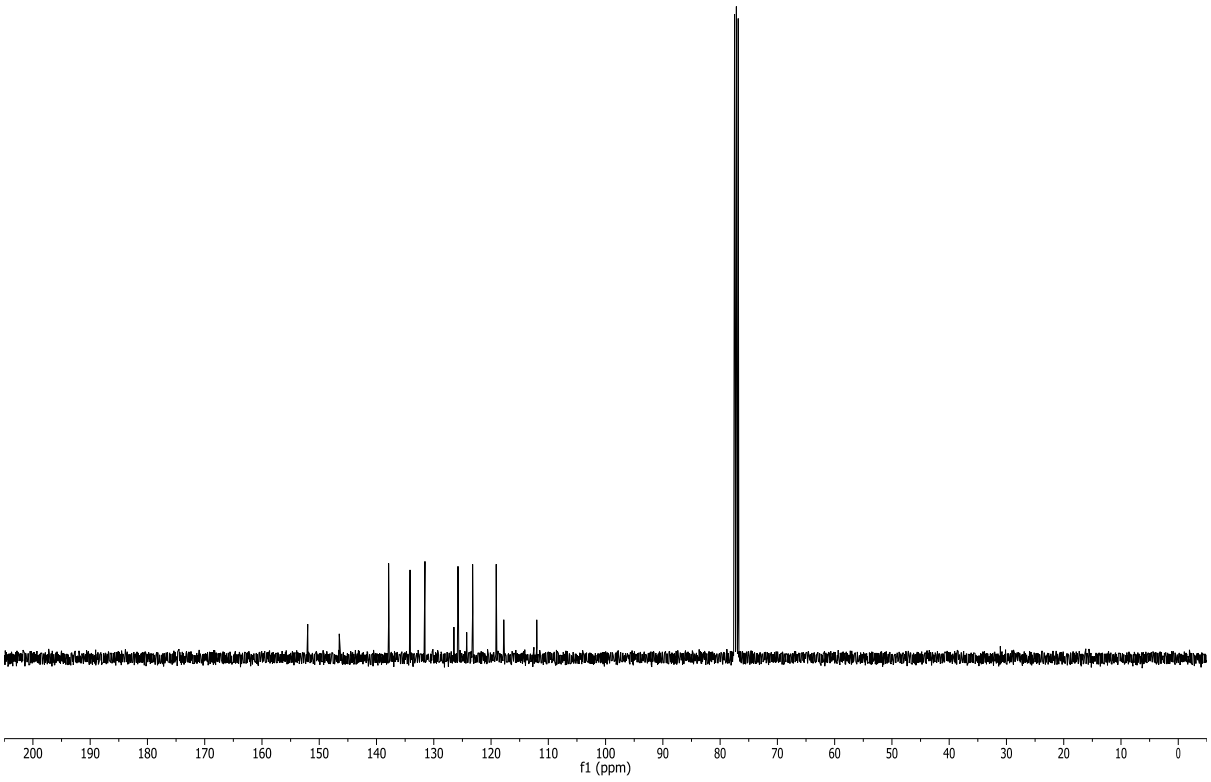


1,6-Dibromophenoxathiine 10,10-dioxide 2b

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

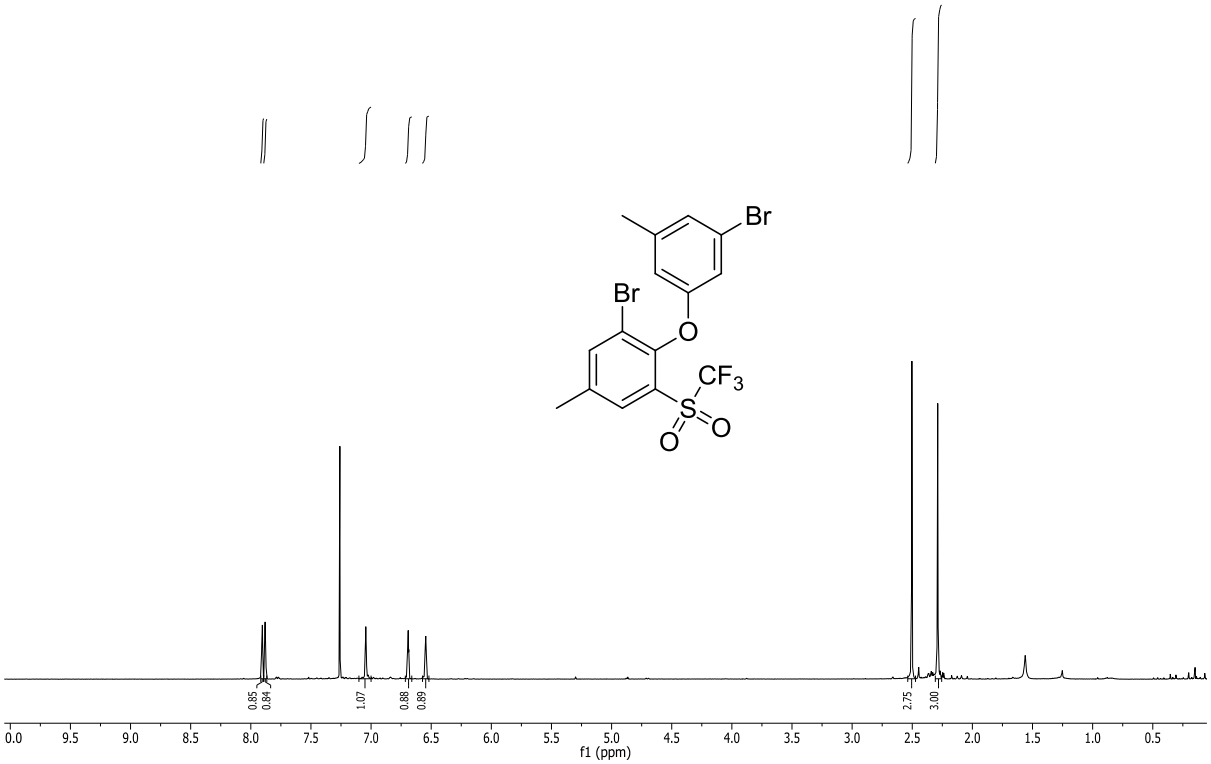


^{13}C NMR (75 MHz, $CDCl_3$)

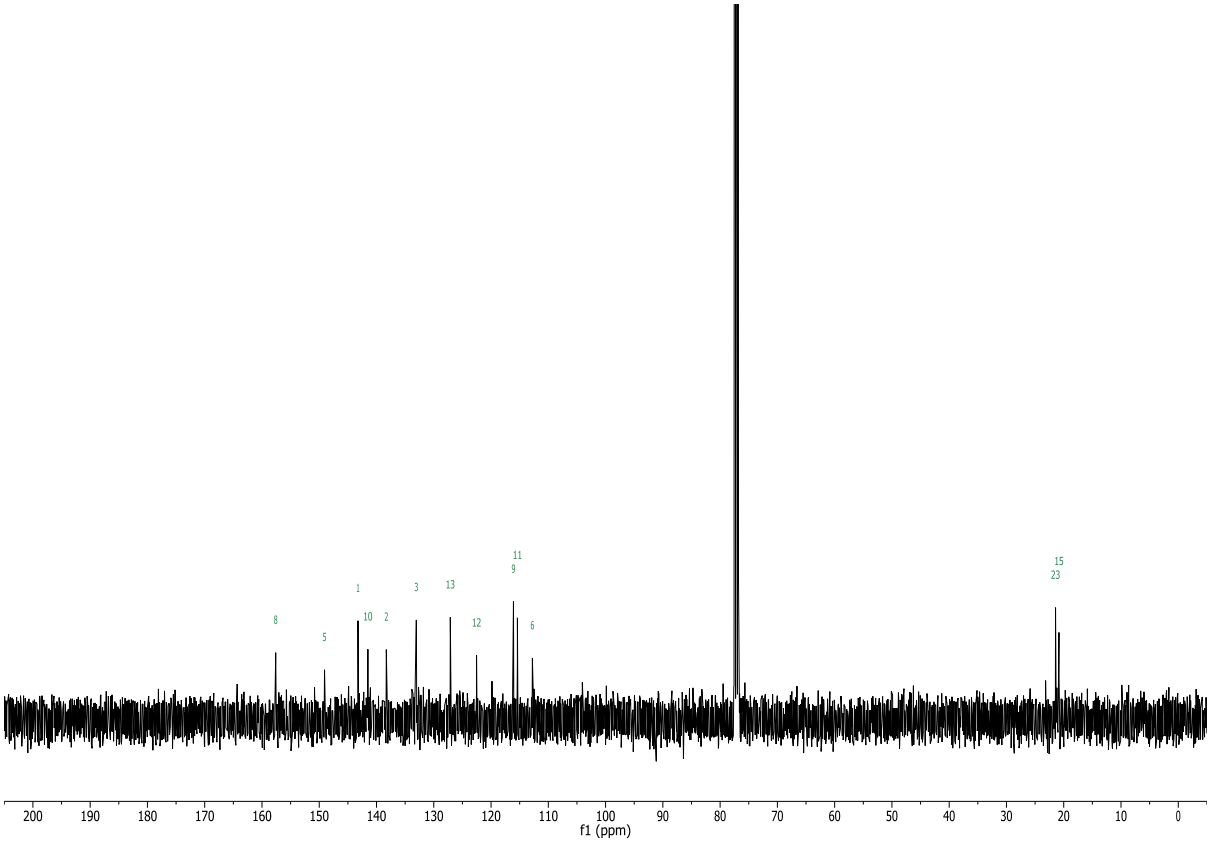


1-Bromo2-(3-bromo-5-methylphenoxy)-5-methyl-3-((trifluoromethyl)sulfonyl)benzene 3a

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

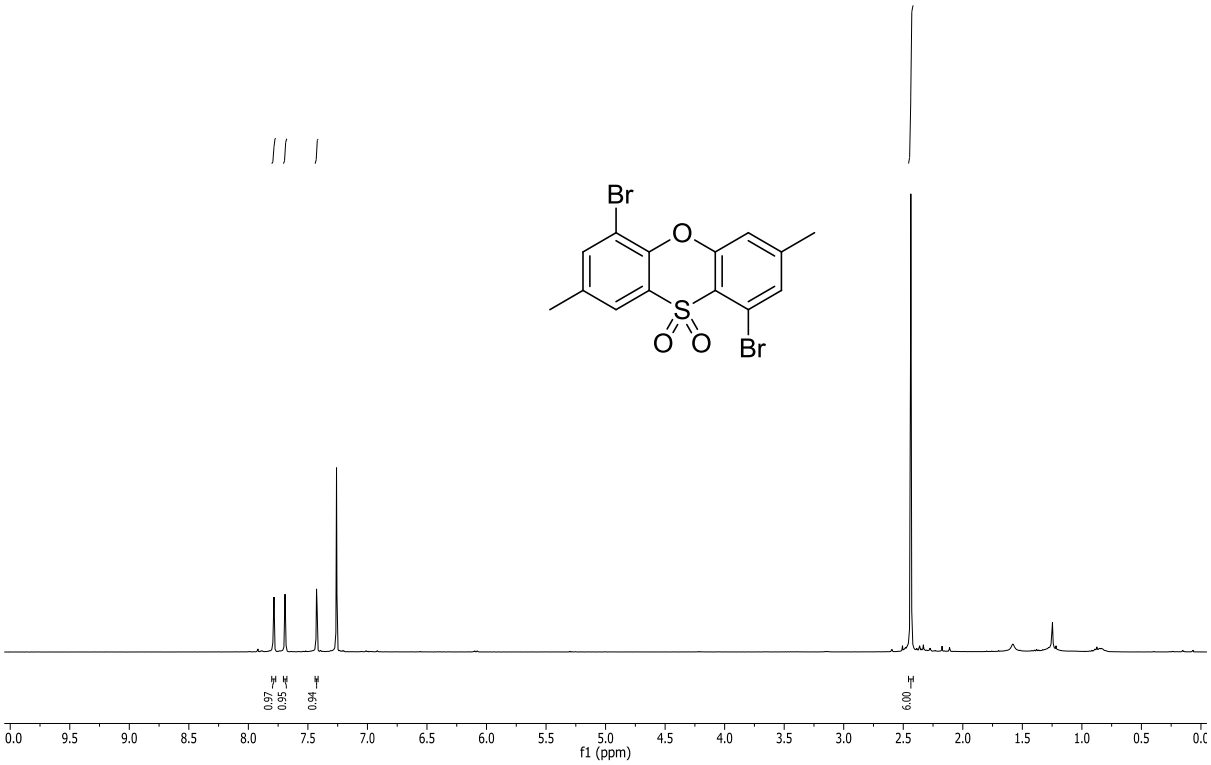


^{13}C NMR (101 MHz, $CDCl_3$)

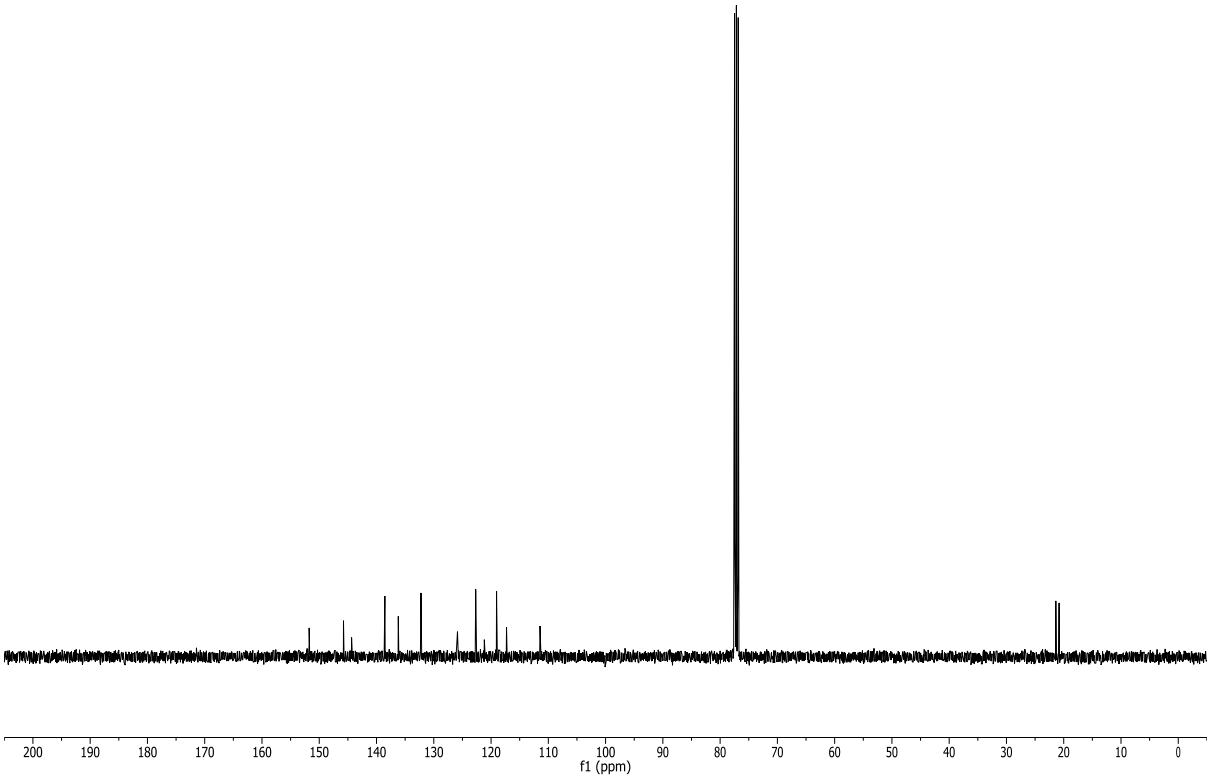


1,6-Dibromo-3,8-dimethylphenoxathiine 10,10-dioxide 2a

^{1}H NMR (400 MHz, $CDCl_3$) δ

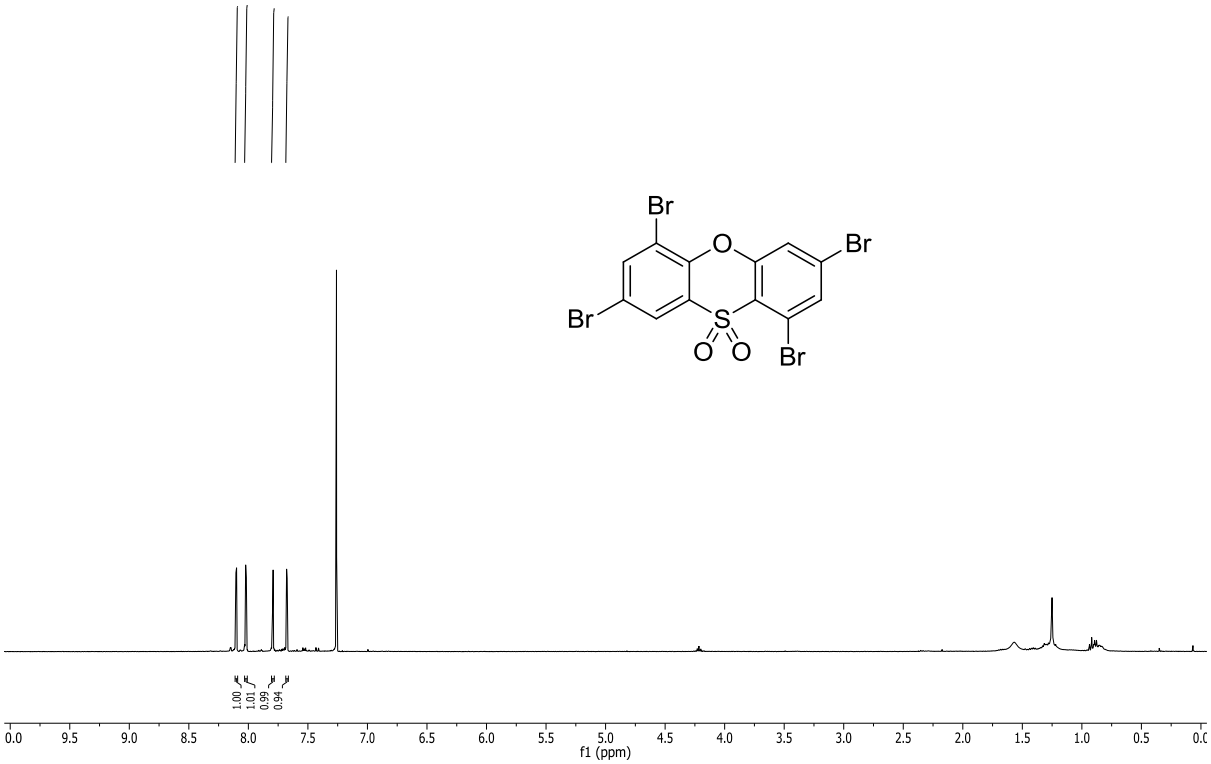


^{13}C NMR (101 MHz, $CDCl_3$

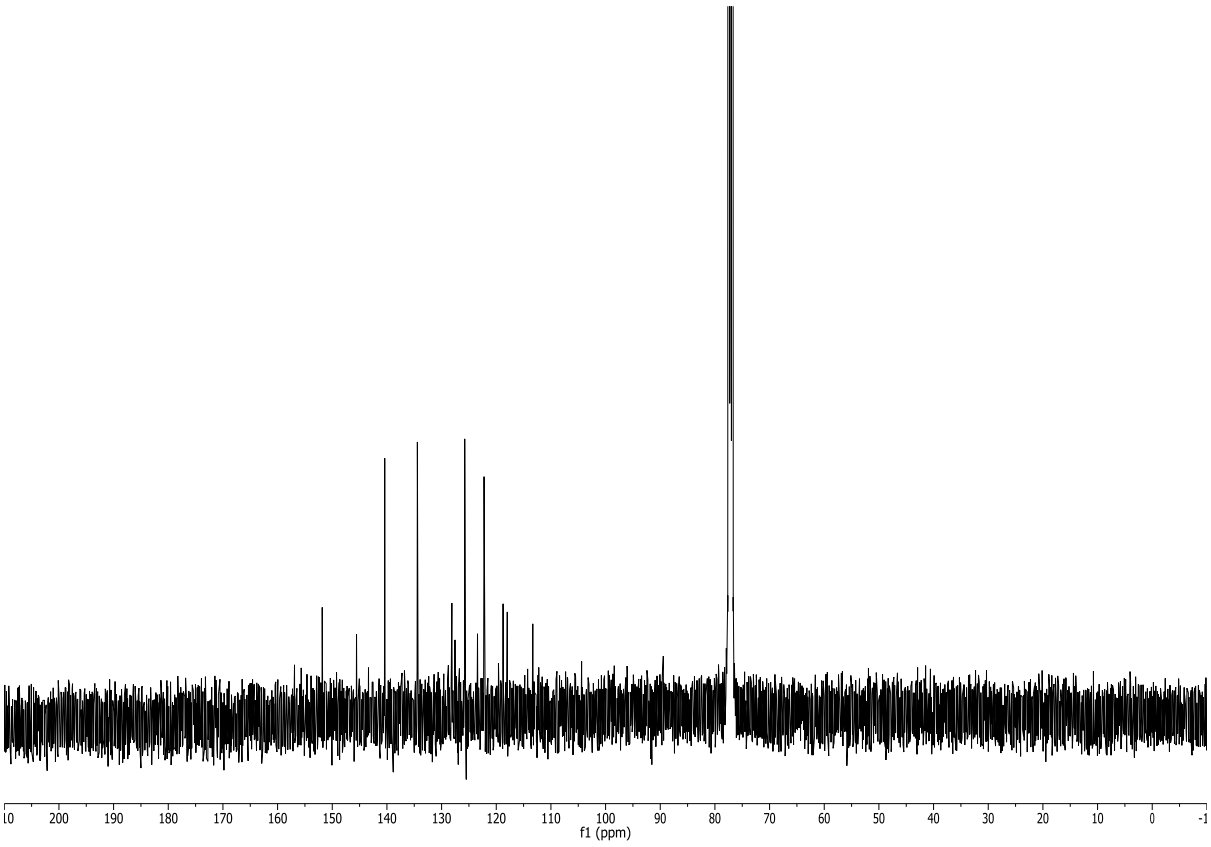


1,3,6,8-Tetrabromophenoxathiine 10,10-dioxide 2c

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

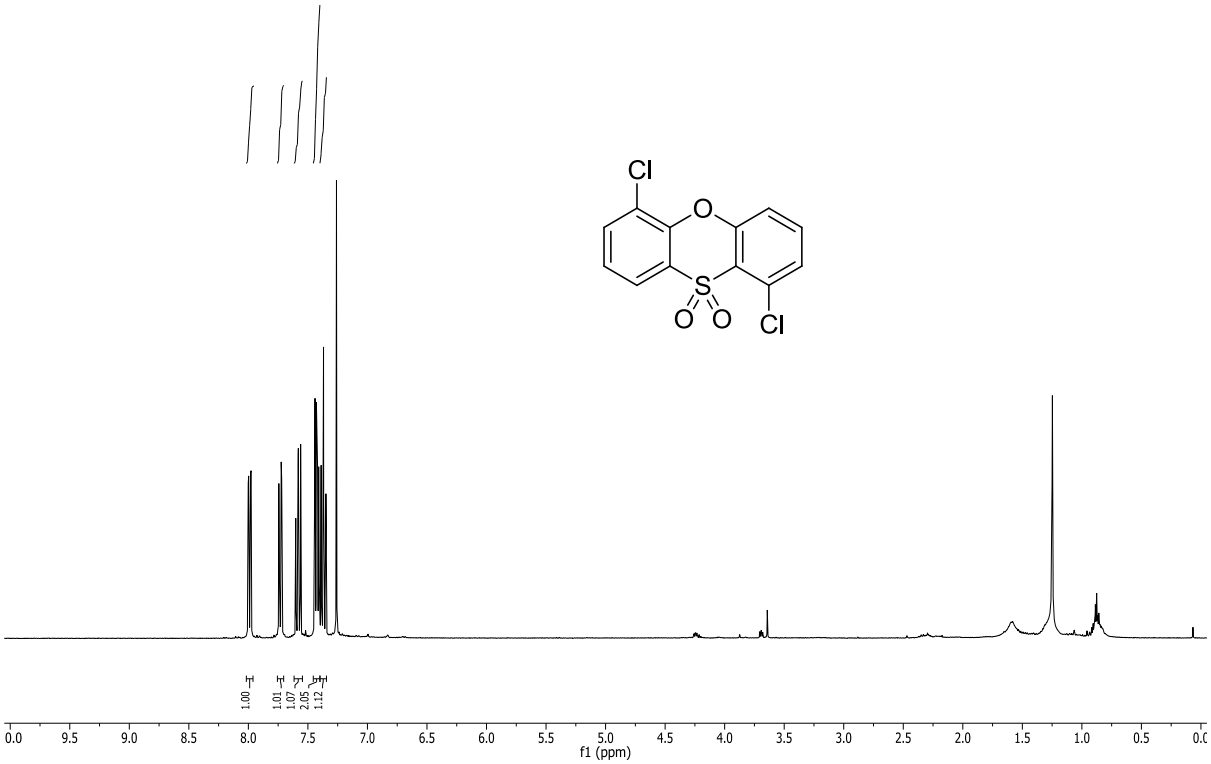


^{13}C NMR (101 MHz, CDCl3)

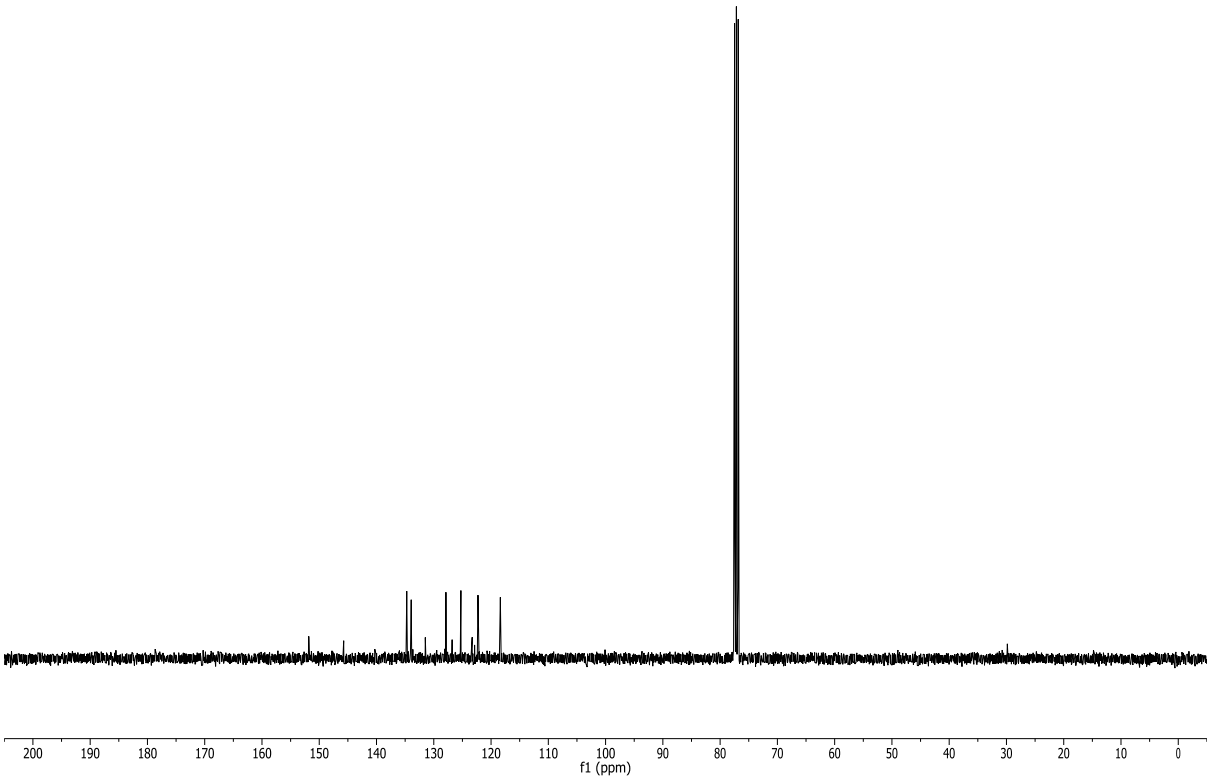


1,6-Dichlorophenoxathiine 10,10-dioxide 2d

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

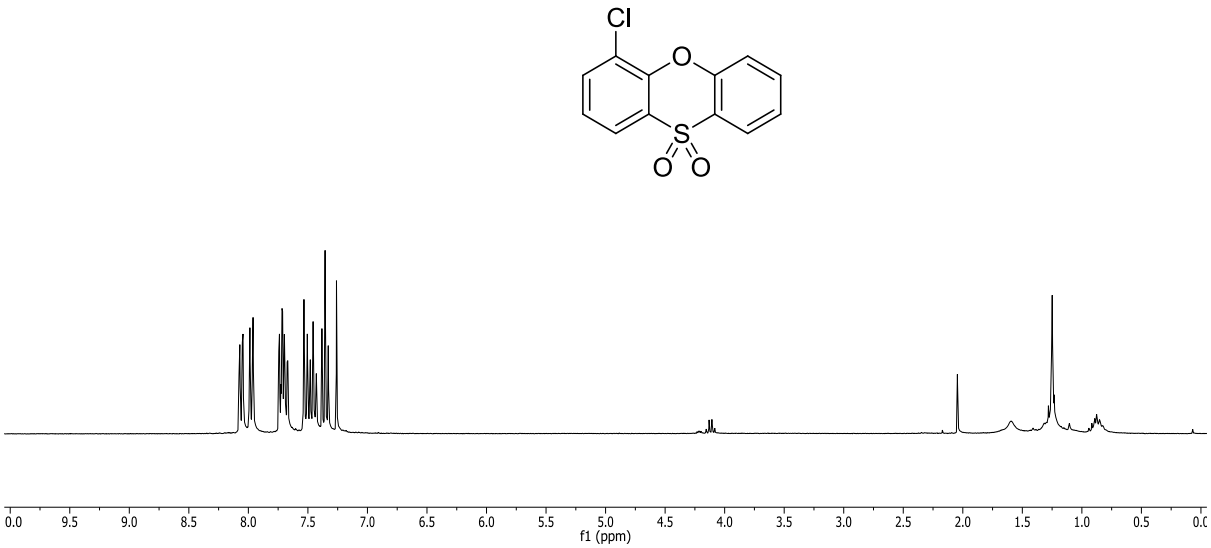


^{13}C NMR (101 MHz, $CDCl_3$)

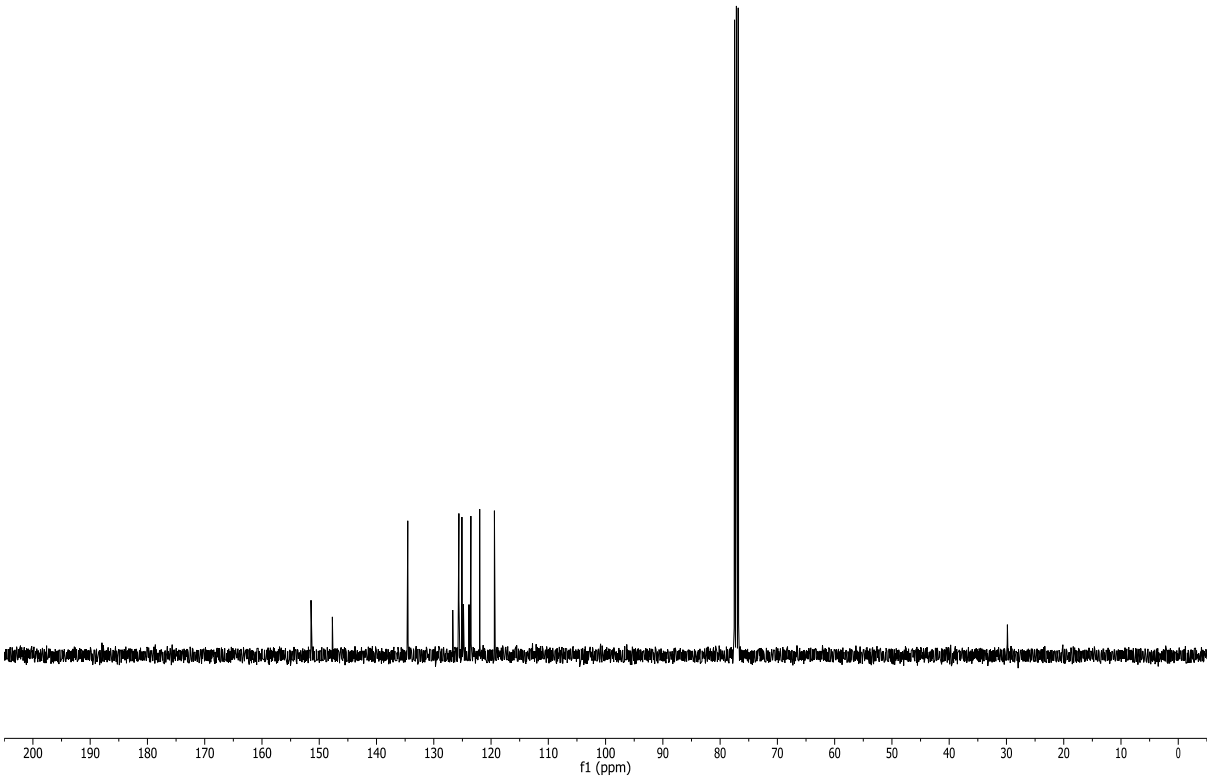


4-Chlorophenoxathiine 10,10-dioxide 2f

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

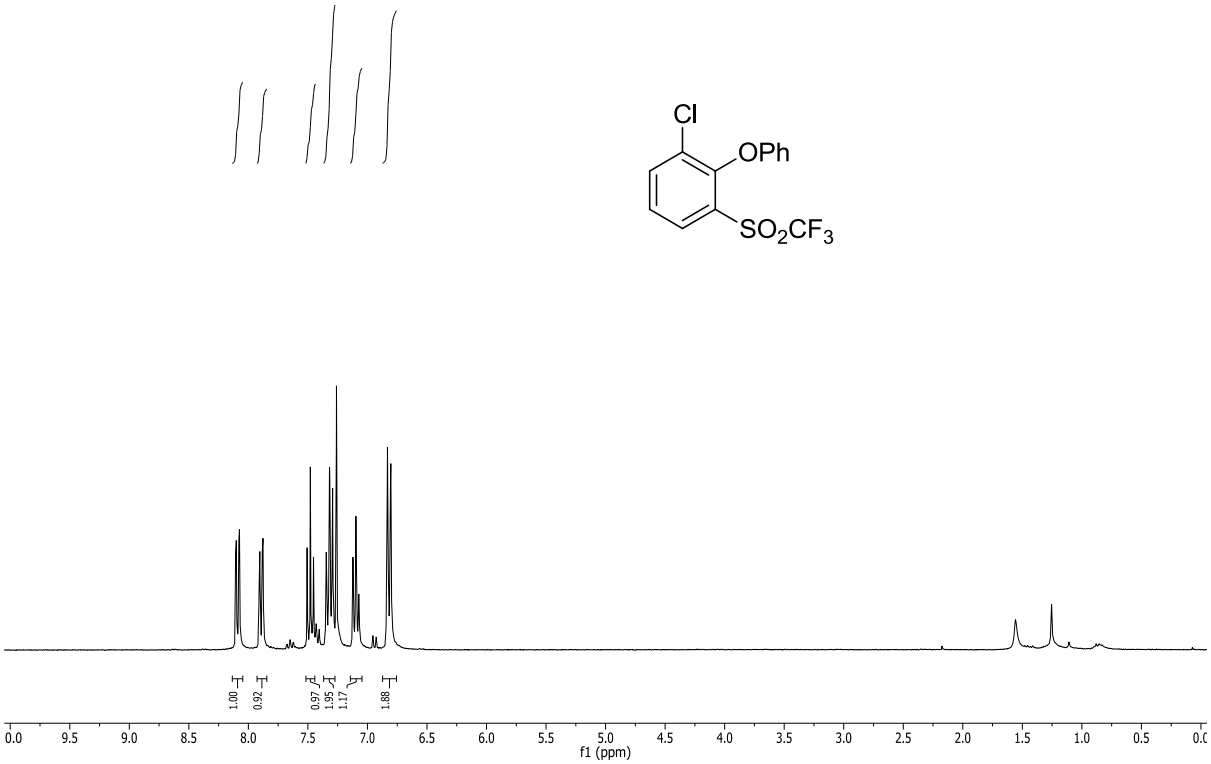


^{13}C NMR (101 MHz, $CDCl_3$)

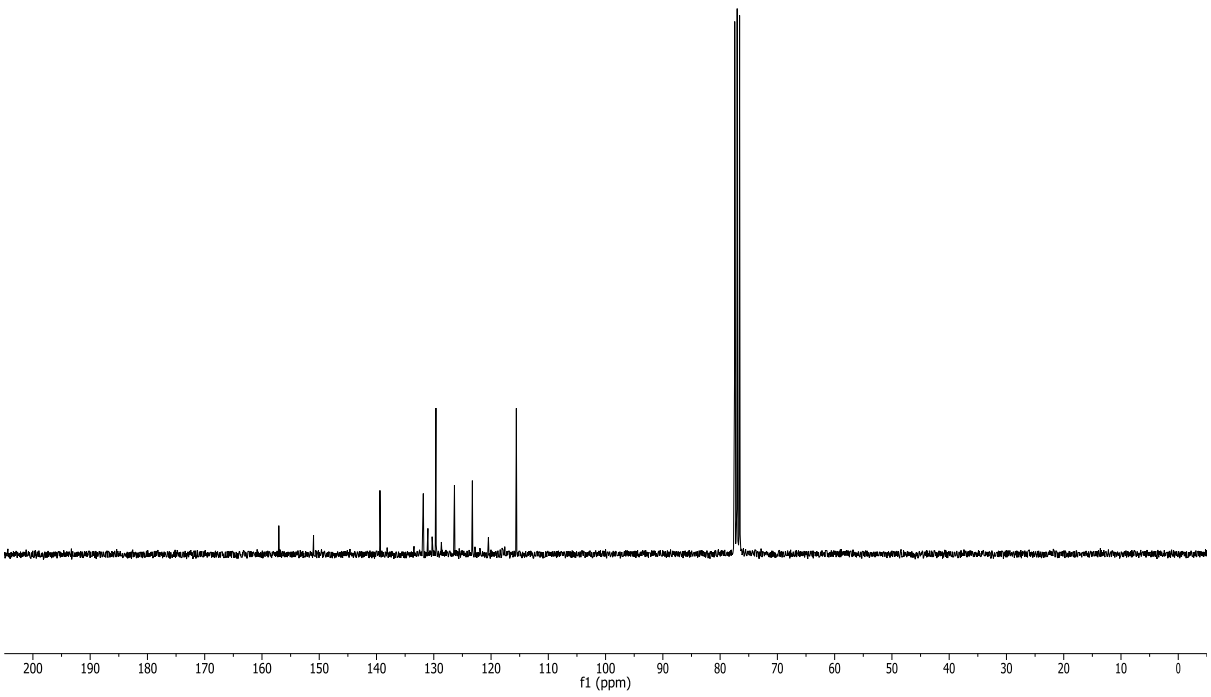


1-Chloro-2-phenoxyl-3-((trifluoromethyl)sulfonyl)benzene 3c

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

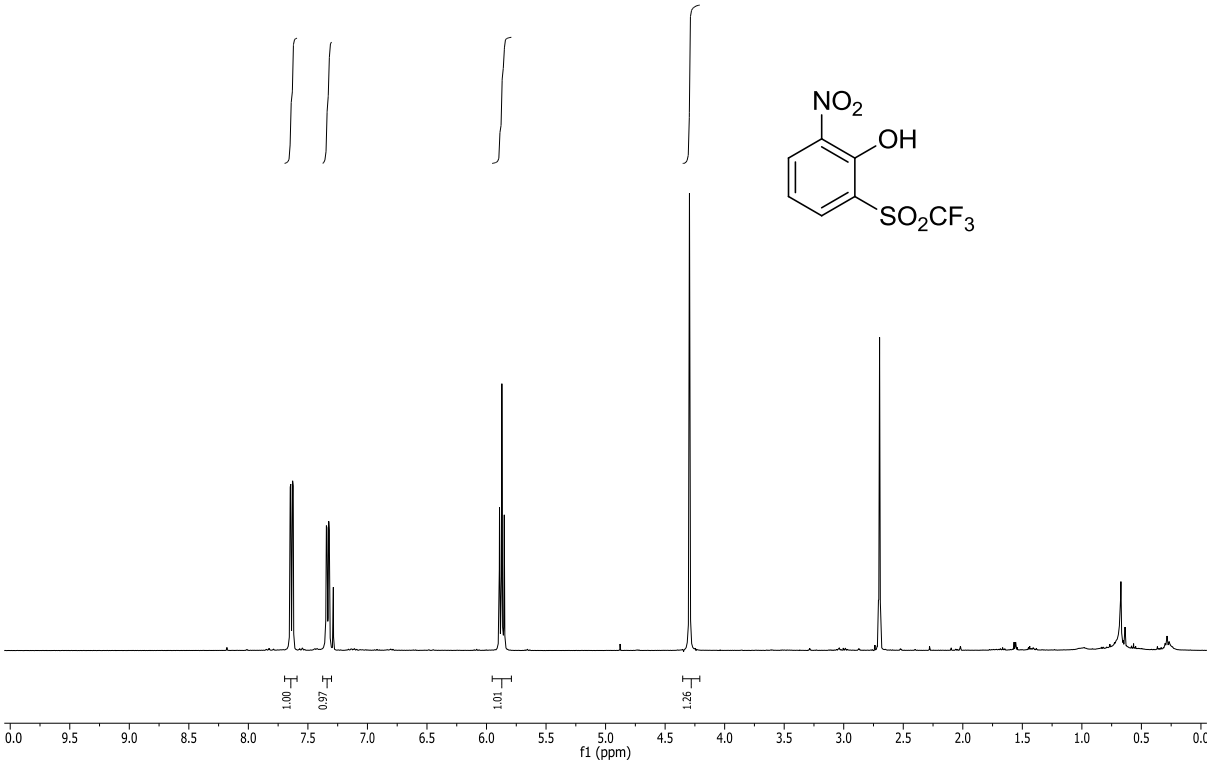


^{13}C NMR (75 MHz, $CDCl_3$)



2-Nitro-6-((trifluoromethyl)sulfonyl)phenol 4a

^{1}H NMR (400 MHz, Methanol-d4)



^{13}C NMR (75 MHz, Methanol-d4)