Intramolecular cross coupling of *gem*-dibromoolefins: A mild approach to 2-bromo benzofused heterocycles

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Supporting Information

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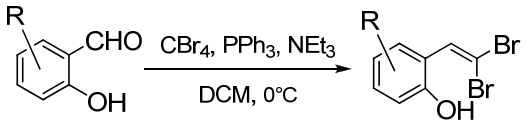
General Experimental Procedures. Unless otherwise noted, all reactions were carried out under an atmosphere of nitrogen or argon in oven-dried glassware equipped with magnetic stirring. Solvents and solutions were transferred by syringe or cannula unless otherwise noted. When required, solvents were degassed by bubbling of nitrogen or argon through a needle. Organic solutions were concentrated by rotary evaporation at reduced pressure (15–30 torr, house vacuum) at 25-50°C. Analytical Thin Layer Chromatography (TLC) was performed using EM Separations pre-coated silica gel 0.2 mm layer UV 254 fluorescent sheets, and visualization was accomplished with 250 nm UV light followed by immersion in an acidic solution of vanillin in ethanol. Flash chromatography was performed using Ultra Pure 230-400 mesh silica gel purchased from Silicycle.

Instrumentation. Melting points were taken on a Fisher-Johns melting point apparatus without correction. IR spectra were obtained using a Shimadzu FTIR-8400S FT-IR spectrometer on NaCl plates. High-resolution mass spectra were obtained by electron impact ionization using a VG 70-250S (double focusing) mass spectrometer at 70eV. ^{1}H, ^{13}C, and ^{19}F NMR spectra were obtained using either a Bruker Avance III 400 MHz, Varian Mercury 400 MHz, or Varian Mercury 300 MHz spectrometer. ^{1}H NMR spectra were referenced to tetramethylsilane (TMS, 0 ppm). ^{13}C NMR spectra were referenced to the carbon resonances of the solvent ($CDCl_3$: δ 77.0 ppm). ^{19}F NMR spectra were unreferenced. Spectral features are tabulated in the following order: chemical shift (δ, ppm); multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad); coupling constant (*J*, Hz); number of protons.

Materials. Dioxane, THF, diethyl ether, and toluene were distilled under nitrogen from Na/benzophenone immediately prior to use. Acetonitrile and Et_3N were distilled from CaH_2. Dichloromethane was purified using an MBraun Solvent Purification System. All reagents, metal catalysts, and ligands were purchased from Sigma-Aldrich, VWR International, or Strem Chemical Company and used as received unless otherwise noted. Copper iodide (98%) was purchased from Sigma-Aldrich. *gem*-Dibromoanilines **10a-10b** were prepared from the corresponding nitro-benzaldehydes.[1] *gem*-Dibromophenols **5c-e** and **5h** were prepared from the corresponding salicylaldehydes.[2] All characterization was consistent with the literature.

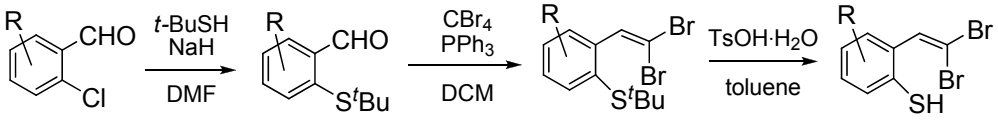
General Procedures

General Procedure 1) Procedure for the synthesis of *gem*-dibromophenols:



In a round-bottomed flask equipped with a magnetic stirrer was added PPh_3 (6 equiv) and DCM (1.0 mL per mmol PPh_3). The vessel was cooled to 0 °C, after which a solution of CBr_4 (3 equiv) in DCM (1.0 mL per mmol PPh_3) was added. After 10 minutes, NEt_3 (6 equiv) was added dropwise and stirred for an additional 5 minutes, after which a solution of the requisite salicylaldehyde (1 equiv) in DCM (1mL per mmol salicylaldehyde) was added dropwise over 10 minutes. The internal temperature was maintained below 10 °C over the addition of all reagents. The vessel was stirred for an additional 30 min at 0 °C, after which it was allowed to warm to room temperature and stirred for an additional 1 h. The reaction was quenched by addition of saturated aqueous NH_4Cl solution. The phases were then separated, and the aqueous layer was extracted with DCM. The combined organic layers were concentrated under reduced pressure to approximately 10% of the original volume. The residue was dissolved in Et_2O and filtered over pad of celite. The resulting solution was concentrated by rotary evaporation and purified by flash column chromatography.

General Procedure 2) First procedure for the synthesis of *gem*-dibromothiophenols:



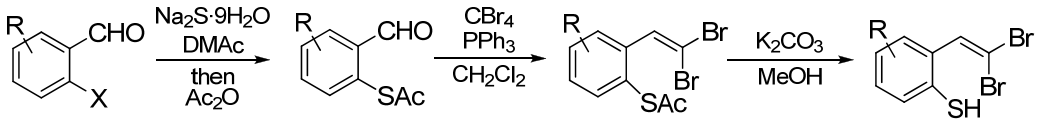
Step 1 - To a flame-dried flask was added NaH (2.0 equiv) and DMF (1.4 mL per mmol NaH). The flask was purged with N_2 and cooled to 0 °C in an ice bath. ^{t}BuSH (2.0 equiv) was added, and the reaction was allowed to stir until all of the solid had reacted (~1h). The requisite aldehyde (1.0 equiv) was then added, and the reaction was allowed to warm to RT and stirred overnight. The reaction was diluted with Et_2O, and the organic phase was washed with HCl (10% aq.), water

and brine, then dried ($MgSO_4$), filtered and concentrated. The crude material was purified by flash chromatography.

Step 2 - The requisite aldehyde (1.0 equiv) and CBr_4 (1.5 equiv) were dissolved in DCM (6 mL per mmol aldehyde) and cooled to 0 °C under N_2. A solution of PPh_3 (3.0 equiv) in DCM (4 mL per mmol aldehyde) was added dropwise over 1 h. The reaction was then warmed to RT and stirred until complete by TLC (usually 0-2 h). Pentane was added to precipitate as much $Ph_3P{=}O$ as possible, and the suspension was filtered through a pad of silica, washing with Et_2O. The solution was concentrated, and the product was purified by flash chromatography.

Step 3 - The requisite dibromide (1.0 equiv) was dissolved in toluene (1.3 mL per mmol dibromide). $TsOH{\cdot}H_2O$ (1.0 equiv) was added, and the reaction heated to 110 °C in an oil bath and stirred overnight. The reaction was cooled, and diluted with Et_2O, and the product was extracted 4 times with NaOH (10% aq.) as the sodium salt. The aqueous layer was acidified (conc. HCl), and the product was extracted with Et_2O. The organic layer was dried ($MgSO_4$), filtered, and concentrated under reduced pressure.

General Procedure 3) Second procedure for the synthesis of *gem*-dibromothiophenols:

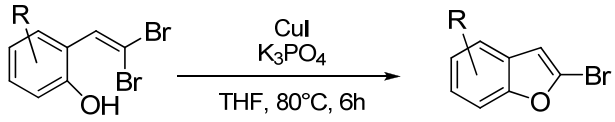


Step 1 - To a flask containing $Na_2S{\cdot}9H_2O$ (1.2 equiv) was added DMAc (3 mL per mmol aldehyde) and the resulting suspension was heated to 90 °C in an oil bath. After stirring for 30 minutes, the aldehyde (1.0 equiv) was added, and the reaction was stirred at 90 °C until the suspension turned from blue/green to reddish brown and TLC indicated consumption of starting material (up to 2.5 hours). The reaction was then cooled to 0 °C in an ice bath, and Ac_2O was added. The reaction was stirred at 0 °C for 1 h, then warmed to RT and stirred until the red colour had disappeared (up to 1 h). The reaction was then diluted with Et_2O and washed with HCl (10% aq.) and water. The organic phase was dried ($MgSO_4$), filtered and concentrated, and the product was purified by flash chromatography.

Step 2 - The same method from general procedure 2, step 2 was followed.

Step 3 - To a suspension of the requisite dibromide (1 equiv) in MeOH (5 mL per mmol dibromide) under N_2 was added K_2CO_3 (1.5 equiv) and the resulting suspension was stirred at RT until starting material was completely consumed, as indicated by TLC (~30 min.). The reaction was then diluted with ether and extracted with a saturated aqueous NaOH solution. The aqueous layer was acidified (conc. HCl) and extracted with Et_2O. The organic layer was dried ($MgSO_4$), filtered and concentrated to give the product.

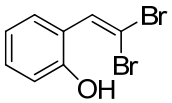
General procedure 4) Procedure for the synthesis of 2-bromobenzofurans and 2-bromobenzothiophenes:



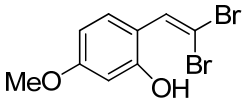
To a 0.5-2 mL microwave reaction vial equipped with a magnetic stir bar was added the requisite *gem*-dibromoolefin (1 equiv), CuI (5 mol%), and K_3PO_4 (2 equiv). The flask was flushed with argon for 5 minutes, after which THF (1 mL per 0.2 mmol olefin) was added and the vial sealed and placed in a pre-heated oil bath at 80°C. The vial was stirred for 6 hours, after which it was removed from the oil bath and allowed to cool to room temperature. The contents were filtered over a pad of silica gel, washing with copious amounts of Et_2O. The resulting solution was concentrated under reduced pressure to afford spectroscopically pure product.

Experimental Data

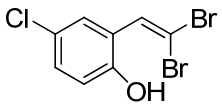
Starting materials:



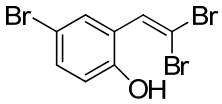
2-(2,2-Dibromovinyl)phenol (5a). General procedure 1 was followed (1 mmol scale). The product was purified by flash chromatography eluting with 15% EtOAc/pentane to provide **5a** as a white solid (225 mg, 81%). Characterization data match those previously reported.[3] **^{1}H NMR** ($CDCl_3$, 400 MHz): δ = 7.51-7.56 (m, 2H), 7.22 (t, *J* = 7.7 Hz, 1H), 6.94 (t, *J* = 7.6 Hz, 1H), 6.81 (d, *J* = 8.1 Hz, 1H), 5.15 (br s, 1H). **^{13}C NMR** ($CDCl_3$, 100 MHz): δ = 152.5, 132.4, 130.1, 129.3, 122.9, 120.7, 115.8, 92.1..



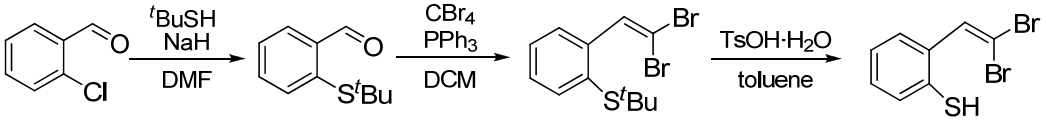
2-(2,2-Dibromovinyl)-5-methoxyphenol (5b). General procedure 1 was followed (0.5 mmol scale). The product was purified by flash chromatography eluting with 15% EtOAc/pentane to provide **5b** as a yellow solid (90 mg, 62%) **mp**: 93-95 °C. **IR** (cm^{-1}, neat): 3408, 2918, 2849, 1616, 1516, 1443, 1298, 1165, 1111. **^{1}H NMR** ($CDCl_3$, 400 MHz): δ = 7.48-7.51 (m, 2H), 6.52 (dd, *J* = 9.0, 2.5 Hz, 1H), 6.38 (d, *J* = 2.5 Hz, 1H), 4.99 (br s, 1H), 3.79 (s, 3H). **^{13}C NMR** ($CDCl_3$, 100 MHz): δ = 161.1, 153.7, 131.9, 130.0, 115.6, 106.5, 101.6, 90.6, 55.4. **HRMS** (EI): Calc'd for $C_9H_8O_2Br_2$, 307.8871; found, 307.8861.



4-Chloro-2-(2,2-dibromovinyl)phenol (5f). General procedure 1 was followed (2 mmol scale). The product was purified by flash chromatography eluting with 15% EtOAc/pentane to provide **5f** as a white solid (460 mg, 74%). Characterization data match those previously reported.[4] **^{1}H NMR** ($CDCl_3$, 400 MHz): δ = 7.52 (d, *J* = 3.2 Hz, 1H), 7.48 (s, 1H), 7.19 (dd, *J* = 11.6, 3.2 Hz, 1H), 6.77 (d, *J* = 11.6 Hz, 1H), 4.95 (br s, 1H). **^{13}C NMR** ($CDCl_3$, 100 MHz): δ = 151.2, 131.2, 129.8, 128.8, 125.5, 117.1, 104.8, 93.4.



4-Bromo-2-(2,2-dibromovinyl)phenol (5g). General procedure 1 was followed (5 mmol scale). The product was purified by flash chromatography eluting with 15% EtOAc/pentane to provide **5g** as an off-white solid (1.35g, 76%). **mp**: 65-67 °C. **IR** (cm^{-1}, neat): 3539, 3437, 3038, 1483, 1408, 1319, 1200, 1167, 1105. **^{1}H NMR** ($CDCl_3$, 400 MHz): δ = 7.65 (d, *J* = 2.4 Hz, 1H), 7.47 (s, 1H), 7.33 (dd, *J* = 8.6, 2.4 Hz), 6.72 (d, *J* = 8.6 Hz, 1H), 4.92 (br s, 1H). **^{13}C NMR** ($CDCl_3$, 100 MHz): δ = 151.5, 132.7, 131.7, 131.0, 124.7, 117.5, 112.7, 93.7. **HRMS** (EI): Calc'd for $C_8H_5OBr_3$, 355.7870; found, 355.7881.



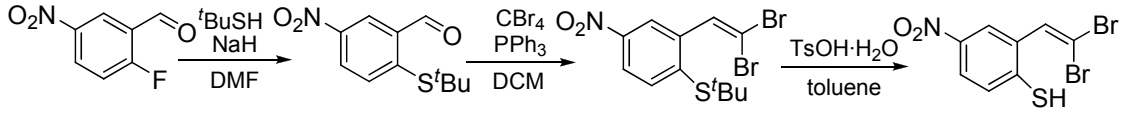
2-(2,2-Dibromovinyl)benzenethiol (8a)

General procedure 2 was followed. The aldehyde ((*2*-tert-*butylsulfanylbenzaldehyde)* was prepared on a 35.6 mmol scale. The product was purified by flash chromatography eluting with 20% DCM/pentane to give 6.65 g (96%) as a slightly yellow oil. The spectral data were identical to a commercial sample.

The dibromide (*1*-tert-*butylsulfanyl)-2-(2,2-dibromovinyl)benzenethiol)* was prepared according to the general procedure (10 mmol scale). The product was purified by flash chromatography eluting with 2% Et_2O/pentane to give 3.18 g (91%) as a colorless oil. **IR** (cm^{-1}, neat): 2960, 2896, 2856, 1601, 1455, 1435, 1363, 1254, 1216, 1165, 1060, 1036, 953, 887, 858, 822, 793, 754, 731, 688. **^{1}H NMR** ($CDCl_3$, 400 MHz): δ = 7.94 (s, 1H), 7.70 – 7.72 (m, 1H), 7.57 (dd, *J* = 7.6, 1.4 Hz, 1H), 7.39 (td, *J* = 7.5, 1.4 Hz, 1H), 7.32 (td, *J* = 7.5, 1.5 Hz, 1H). **^{13}C NMR** ($CDCl_3$, 100 MHz): δ = 141.8, 139.1, 138.2, 132.3, 129.9, 129.1, 128.7, 90.7, 48.1, 31.3. **HRMS** (EI): Calc'd for $C_{12}H_{14}Br_2S$, 269.0000; found, 269.0000.

The title compound **8a** was prepared according to the general procedure (7.6 mmol scale). 1.46 g (65%) was isolated as a yellow oil. **IR** (cm^{-1}, neat): 3057, 3001, 2566, 2357, 1915, 1602, 1585, 1460, 1430, 1277, 1254, 1202, 1161, 1129, 1066, 1037, 944, 876, 854, 790, 745, 715, 682. **^{1}H NMR** ($CDCl_3$, 300 MHz): δ = 7.45-7.48 (m, 2H), 7.33-7.36 (m, 1H), 7.16-7.25 (m, 2H), 3.38 (s, 1H). **^{13}C NMR** ($CDCl_3$, 100 MHz): δ = 135.9, 135.3, 130.8, 130.7, 129.8, 129.2, 126.1, 93.7. **HRMS** (EI): Calc'd for $C_8H_6Br_2S$,

291.8557; found, 291.8561.

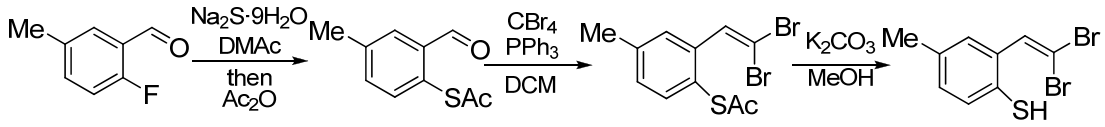


2-(2,2-Dibromovinyl)-4-nitrobenzenethiol (8b)

General procedure 2 was followed. The aldehyde *(2-(*tert-*butylsulfanyl)-5-nitrobenzenaldehyde)* was prepared on a 10 mmol scale. The product was purified by flash chromatography eluting with 3-4% Et_2O/pentane to give 943 mg (39%) as a yellow oil. **IR** (cm^{-1}, neat): 3091, 2966, 2866, 1694, 1600, 1530, 1461, 1400, 1347, 1293, 1243, 1162, 1095, 1052, 967, 916, 848, 818, 743, 708, 641. **^{1}H NMR** ($CDCl_3$, 400 MHz): δ = 10.75 (s, 1H), 8.78 (d, *J* = 2.7 Hz, 1H), 8.38 (dd, *J* = 8.5, 2.7 Hz, 1H), 7.84 (d, *J* = 8.5 Hz, 1H), 1.37 (s, 9H). **^{13}C NMR** ($CDCl_3$, 100 MHz): δ = 191.1, 148.5, 144.8, 140.3, 140.2, 127.1, 123.4, 49.7, 31.3. **HRMS** (EI): Calc'd for $C_{11}H_{13}NO_3S$, 239.0616; found, 239.0618.

The dibromide *((1-*tert-*butylsulfanyl)-2-(2,2-dibromovinyl)-5-nitrobenzene)* was prepared according to the general procedure (3.5 mmol scale). The product was purified by flash chromatography eluting with 1% Et_2O/pentane to give 1.18 g (85%) as a yellow oil. **IR** (cm^{-1}, neat): 2963, 2862, 1597, 1569, 1521, 1471, 1456, 1393, 1365, 1347, 1293, 1261, 1162, 1105, 1052, 944, 911, 838, 798, 743, 722, 704, 572, 482. **^{1}H NMR** ($CDCl_3$, 400 MHz): δ = 8.57 (d, *J* = 2.3 Hz, 1H), 8.14 (d, *J* = 8.5, 2.6 Hz, 1H), 7.86 (s, 1H), 7.73 (d, *J* = 8.5 Hz, 1H), 1.36 (s, 9H). **^{13}C NMR** ($CDCl_3$, 100 MHz): δ = 147.7, 142.2, 141.3, 138.4, 135.8, 124.7, 122.7, 94.0, 49.8, 31.4. **HRMS** (EI): Calc'd for $C_{12}H_{13}BrNO_2S$, 313.9850; found: 313.9850.

The title compound **8b** was prepared according to the general procedure on a 2.0 mmol scale. 183 mg (54%) of the product was isolated as white solid. **mp:** 135-137 °C. **IR** (cm^{-1}, neat): 3089, 2569, 1594, 1571, 1517, 1504, 1456, 1344, 1300, 1272, 1197, 1058, 948, 913, 846, 823, 798, 736, 710. **^{1}H NMR** ($CDCl_3$, 400 MHz): δ = 8.34 (d, *J* = 2.2 Hz, 1H), 8.06 (dd, *J* = 8.7, 2.5, 1H), 7.44 (d, *J* = 8.7 Hz, 1H), 7.41 (s, 1H), 3.76 (s, 1H). **^{13}C NMR** ($CDCl_3$, 100 MHz): δ = 145.8, 141.3, 134.9, 133.4, 129.9, 124.9, 123.7. **HRMS** (EI): Calc'd for $C_8H_5Br_2NO_2S$, 336.8408; found, 336.8418.

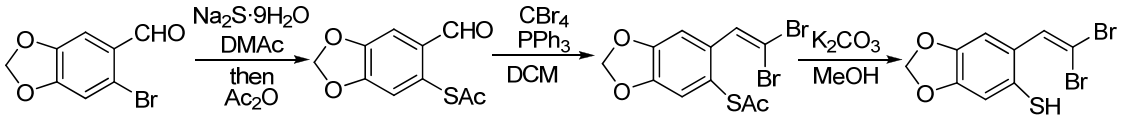


2-(2,2-Dibromovinyl)-4-methylbenzenethiol (8c)

General procedure 3 was followed. The aldehyde *((*S*-2-formyl-4-methylphenyl) ethanethioate)* was prepared on a 6 mmol scale. The product was purified by flash chromatography eluting with 10-20% Et_2O/2% DCM/pentane to give 380 mg (33%) as a white solid. **IR** (cm^{-1}, neat): 3008, 2916, 2886, 1697, 1684, 1595, 1565, 1472, 1417, 1396, 1357, 1275, 1226, 1153, 1138, 1111, 1055, 1005, 959, 938, 900, 823, 751, 707, 675. **^{1}H NMR** ($CDCl_3$, 400 MHz): δ = 10.22 (s, 1H), 7.85 (d, *J* = 1.4 Hz, 1H), 7.44 (dd, *J* = 7.9, 1.5 Hz, 1H), 7.37 (d, *J* = 7.9 Hz, 1H), 2.48 (s, 3H), 2.44 (s, 3H). **^{13}C NMR** ($CDCl_3$, 100 MHz): δ = 193.0, 191.0, 141.0, 136.6, 136.4, 135.1, 129.7, 127.8, 30.3, 21.2. **HRMS** (EI): Calc'd for $C_{10}H_{10}O_2S$, 194.0402; found, 194.0410.

The dibromide *(*S*-[2-(2,2-dibromovinyl)-4-methylphenyl] ethanethioate)* was prepared according to the general procedure (1.91 mmol scale). The product was purified by flash chromatography eluting with 3-4% Et_2O/pentane to give 584 mg (87%) as a white solid. **IR** (cm^{-1}, neat): 3017, 2920, 1918, 1699, 1598, 1462, 1386, 1353, 1286, 1261, 1226, 1165, 1097, 1053, 944, 890, 839, 824, 814, 732, 714. **^{1}H NMR** ($CDCl_3$, 400 MHz): δ = 7.43–7.45 (m, 2H), 7.33 (d, *J* = 7.9 Hz, 1H), 7.20 (dd, *J* = 8.0, 0.8 Hz), 2.42 (s, 3H), 2.40 (s, 3H). **^{13}C NMR** ($CDCl_3$, 100 MHz): δ = 193.2, 140.3, 139.6, 125.9, 130.5, 130.0, 123.6, 92.6, 30.2, 21.3. **HRMS** (EI): Calc'd for $C_{11}H_{10}BrOS$: (M - Br), 268.9636; found, 268.9632.

The title compound **8c** was prepared according to the general procedure (1.57 mmol scale). The product was purified by flash chromatography eluting with pentane to give 402 mg (83%) as a yellow oil. **IR** (cm^{-1}, neat): 3006, 2919, 2566, 1597, 1559, 1471, 1398, 1285, 1256, 1227, 1167, 1145, 1062, 1039, 1008, 952, 892, 827, 809, 730, 709, 639. **^{1}H NMR** ($CDCl_3$, 400 MHz): δ = 7.48 (s, 1H), 7.29 (br s, 1H), 7.25 (d, *J* = 8.4 Hz, 1H), 7.03 (dd, *J* = 8.0, 1.8 Hz, 1H), 3.29 (s, 1H), 2.33 (s, 3H). **^{13}C NMR** ($CDCl_3$, 100 MHz): δ = 136.0, 135.3, 130.8, 130.1, 129.8, 126.5, 92.9, 20.9. **HRMS** (EI): Calc'd for $C_9H_8Br_2S$, 305.8713; found, 305.8710.

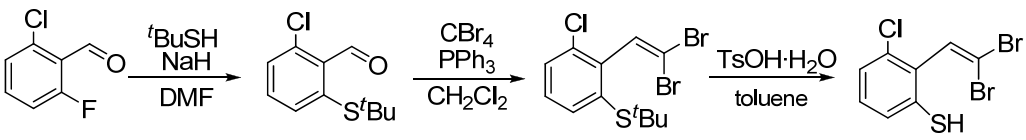


6-(2,2-dibromovinyl)-1,3-benzodioxole-5-thiol (8d)

General procedure 3 was followed. The aldehyde *((*S-*6-formyl-1,3-benzodioxol-5-yl) ethanethioate)* was prepared on a 6 mmol scale. The product was purified by flash chromatography eluting with 10-15% Et_2O/2%CH_2Cl_2/pentane to give 474 mg (35%) as a white solid. **mp**: 112-113 °C. **IR** (cm^{-1}, neat): 2915, 2858, 1709, 1682, 1600, 1503, 1477, 1412, 1393, 1344, 1256, 1116, 1035, 999, 929. **^{1}H NMR** ($CDCl_3$, 400 MHz): δ = 10.14 (s, 1H), 7.48 (s, 1H), 6.90 (s, 1H), 6.11 (s, 2H), 2.48 (s, 3H). **^{13}C NMR** ($CDCl_3$, 100 MHz): δ = 193.1, 189.3, 152.7, 150.2, 132.8, 126.9, 115.9, 108.1, 102.9, 30.4. **HRMS** (EI): Calc'd for $C_{10}H_8O_4S$, 224.0143; found, 224.0134.

The dibromide *(*S-*[6-(2,2-dibromovinyl)-1,3-benzodioxol-5-yl] ethanethioate)* was prepared according to the general procedure (2.25 mmol scale). The product was purified by flash chromatography eluting with 5% Et_2O/pentane to give 670 mg (78%) as a white solid. **mp**: 106-108 °C. **IR** (cm^{-1}, neat): 3018, 2907, 1690, 1604, 1498, 1477, 1413, 1393, 1344, 1272, 1252, 1105, 1036, 951, 930, 870, 854, 832, 759, 717, 657. **^{1}H NMR** ($CDCl_3$, 400 MHz): δ = 7.40 (s, 1H), 7.15 (1H, s), 6.89 (s, 1H), 6.04 (s, 2H), 2.42 (s, 1H). **^{13}C NMR** ($CDCl_3$, 100 MHz): δ = 193.3, 149.2, 148.1, 135.4, 134.1, 119.7, 115.4, 109.7, 102.4, 102.1, 92.2, 30.1. **HRMS** (EI): Calc'd for $C_{11}H_8BrO_3S$, 377.8561; found, 377.8565.

The title compound **8d** was prepared according to the general procedure (1.05 mmol scale). The product was purified by flash chromatography eluting with 1-2% Et_2O/pentane to give 284 mg (80%) as a brown solid. **mp**: 88-90 °C. **IR** (cm^{-1}, neat): 2905, 2527, 1606, 1591, 1496, 1476, 1408, 1386, 1338, 1267, 1241, 1158, 1120, 1037, 994, 928, 876. **^{1}H NMR** ($CDCl_3$, 400 MHz): δ = 7.47 (s, 1H), 7.04 (1H, s), 6.86 (s, 1H), 5.98 (s, 2H), 3.27 (s, 1H). **^{13}C NMR** ($CDCl_3$, 100 MHz): δ = 148.0, 146.7, 135.6, 129.4, 122.3, 111.5, 109.4, 101.7, 92.2. **HRMS** (EI): Calc'd for $C_9H_6B_2rO_2S$, 335.8455; found, 355.8448.

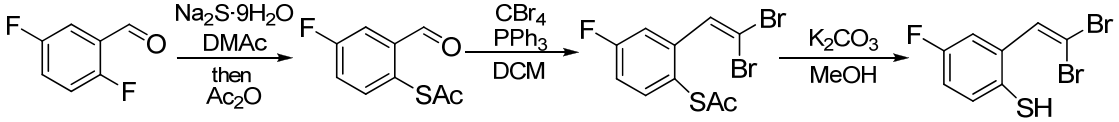


3-Chloro-2-(2,2-dibromovinyl)benzenethiol (**8e**)

General procedure 2 was followed. The aldehyde (*2-(*tert-*butylsulfanyl)-6-chlorobenzaldehyde*) was prepared on a 10 mmol scale. The product was purified by flash chromatography eluting with 2.5% Et_2O/pentane to give 1.08 g (47%) as a slightly yellow oil. **IR** (cm^{-1}, neat): 3069, 2964, 2898, 2864, 2745, 1710, 1572, 1553, 1433, 1385, 1366, 1267, 1163, 1092, 1024, 925, 847, 789, 771, 715, 661. **^{1}H NMR** ($CDCl_3$, 400 MHz): δ = 10.67 (s, 1H), 7.54 (dd, *J* = 7.5, 1.3 Hz, 1H), 7.48-7.50 (m, 1H), 7.42 (t, *J* = 7.9 Hz, 1H), 1.31 (s, 9H). **^{13}C NMR** ($CDCl_3$, 100 MHz): δ = 192.5, 138.3, 137.9, 134.0, 132.3, 132.1, 48.8, 31.3. **HRMS** (EI): Calc'd for $C_{11}H_{13}ClOS$, 228.0376; found, 228.0378.

The dibromide (*1*-tert-*butylsulfanyl)-3-chloro-2-(2,2-dibromovinyl)benzene)* was prepared according to the general procedure (4.0 mmol scale). The product was purified by flash chromatography eluting with 1% Et_2O/pentane to give 1.46 g (95%) as a slightly yellow oil. **IR** (cm^{-1}, neat): 2962, 2896, 2861, 1614, 1572, 1550, 1454, 1428, 1391, 1364, 1264, 1249, 1163, 1094, 1071, 1023, 973, 909, 879, 817, 783, 722, 622, 574. **^{1}H NMR** ($CDCl_3$, 400 MHz): δ = 7.50 (dd, *J* = 7.7, 1.2 Hz, 1H), 7.48 (s, 1H), 7.42 (dd, *J* = 8.1, 1.2 Hz, 1H), 7.26 (t, *J* = 7.9 Hz, 1H), 1.32 (s, 9H). **^{13}C NMR** ($CDCl_3$, 100 MHz): δ = 140.9, 136.9, 135.8, 134.7, 133.9, 130.4, 129.1, 95.5, 48.3, 31.5. **HRMS** (EI): Calc'd for $C_{12}H_{13}BrClS$ (M-Br), 245.8906; found, 245.8903.

The title compound **8e** was prepared according to the general procedure (3.0 mmol scale). 505 mg (51%) of the product was obtained as a colorless oil. **IR** (cm^{-1}, neat): 3008, 2567, 1610, 1573, 1553, 1428, 1253, 1197, 1100, 874, 820, 790, 768, 712. **^{1}H NMR** ($CDCl_3$, 400 MHz): δ = 7.31 (s, 1H), 7.20-7.24 (m, 2H), 7.14 (t, *J* = 7.8 Hz, 1H), 3.59 (s, 1H). **^{13}C NMR** ($CDCl_3$, 100 MHz): δ = 134.4, 134.2, 133.83, 133.78, 129.8, 128.0, 126.9, 97.6. **HRMS** (EI): Calc'd for $C_8H_5Br_2ClS$, 325.8167; found. 325.8167.



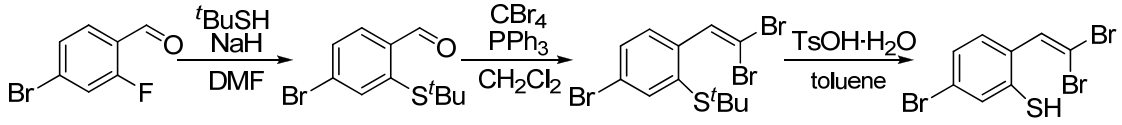
2-(2,2-Dibromovinyl)-4-fluorobenzenethiol (8f)

General procedure 3 was followed. The aldehyde *(*S-*4-fluoro-2-formylphenyl) ethanethioate* was prepared on a 4.5 mmol scale. The product was purified by flash chromatography to give 350 mg (23%) as a yellow oil. **IR** (cm^{-1}, neat): 3070, 2857, 1695, 1597, 1580, 1472, 1413, 1354, 1292, 1263, 1217, 1149, 1122, 1104, 950, 886, 829, 762,

612. **^{1}H NMR** ($CDCl_3$, 400 MHz): δ = 10.17 (d, *J* = 3.0 Hz, 1H), 7.73 (dd, *J* = 8.6, 3.0 Hz, 1H), 7.49 (dd, *J* = 8.6, 5.1 Hz, 1H), 7.34 (ddd, *J* = 8.6, 7.7, 3.0 Hz, 1H), 2.50 (s, 3H). **^{19}F NMR** ($CDCl_3$, 282 MHz): δ = -108.6. **^{13}C NMR** ($CDCl_3$, 100 MHz): δ = 192.6 (d, *J* = 2.0 Hz), 189.7 (d, *J* = 1.9 Hz), 164.0 (d, *J* = 252.2 Hz), 139.0 (d, *J* = 6.7 Hz), 138.8 (d, *J* = 7.7 Hz), 126.6 (d, *J* = 3.4 Hz), 121.7 (d, *J* = 22.3 Hz), 115.9 (d, *J* = 23.4 Hz), 30.4. **HRMS** (EI): Calc'd for $C_9H_7FO_2S$, 198.0151; found, 198.0156.

The dibromide *(*S*-[2-(2,2-dibromovinyl)-4-fluorophenyl] ethanethioate)* was prepared according to the general procedure (1.59 mmol scale). The product was purified by flash chromatography to give 394 mg (73%) as a white solid. **mp**: 80-81 °C. **IR** (cm^{-1}, neat): 3013, 2927, 1894, 17007, 1599, 1573, 1462, 1408, 1355, 1274, 1215, 1159, 1127, 1101, 1055, 971, 945, 879, 832, 814, 736, 710. **^{1}H NMR** ($CDCl_3$, 400 MHz): δ = 7.38-7.44 (m, 3H), 7.10 (td, *J* = 8.4, 2.8 Hz, 1H), 2.44 (s, 3H). **^{19}F NMR** ($CDCl_3$, 376 MHz): δ = -110.0. **^{13}C NMR** ($CDCl_3$, 100 MHz): δ = 192.8 (d, *J* = 1.4 Hz), 163.5 (d, *J* = 251.2 Hz), 138.2 (d, *J* = 8.9 Hz), 134.8 (d, *J* = 8.9 Hz), 122.7 (d, *J* = 1.9 Hz), 117.3 (d, *J* = 23.6 Hz), 116.6 (d, *J* = 22.0 Hz), 94.2, 30.4. **HRMS** (EI): Calc'd for $C_{10}H_7FOS$, 229.9201; found, 229.9208.

The title compound **8f** was prepared according to the general procedure (1.0 mmol scale). The product was purified by flash chromatography eluting with 10% Et_2O/pentane to give 269 mg (86%) as a brown solid. **mp**: 59-61 °C. **IR** (cm^{-1}, neat): 3094, 2997, 2575, 1871, 1598, 1578, 1489, 1458, 1407, 1291, 1271, 1258, 1216, 1157, 1118, 1063, 972, 191, 882, 831, 804, 730, 702. **^{1}H NMR** ($CDCl_3$, 400 MHz): δ = 7.49 (s, 1H), 7.34 (dd, *J* = 8.6, 5.4 Hz, 1H), 7.27 (dd, *J* = 9.2, 2.8 Hz, 1H), 6.96 (td, *J* = 8.2, 2.8 Hz, 1H), 3.31 (s, 1H). **^{19}F NMR** ($CDCl_3$, 376 MHz): δ = -115.7. **^{13}C NMR** ($CDCl_3$, 100 MHz): δ = 161.3 (d, *J* = 246.3 Hz), 137.4 (d, *J* = 8.5 Hz), 135.1 (d, *J* = 2.0 Hz), 132.8 (d, *J* = 8.0 Hz), 125.2 (d, *J* = 3.4 Hz), 116.8 (d, *J* = 23.7 Hz), 116.5 (d, *J* = 22.0 Hz), 94.4. **HRMS** (EI): Calc'd for $C_8H_5Br_2FS$, 309.8463; found: 304.8461.



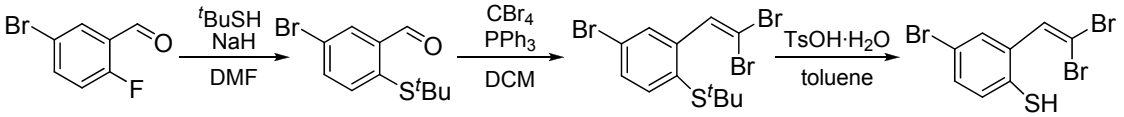
5-Bromo-2-(2,2-dibromovinyl)benzenethiol (**8g**)

General procedure 2 was followed. The aldehyde *(4-bromo-2-(*tert-*butylsulfanyl)benzaldehyde*) was prepared on a 12.9 mmol scale. The product was

purified by flash chromatography eluting with 1% Et_2O/pentane to give 2.14 g (61%) as a white solid. **mp**: 50-53 °C. **IR** (cm^{-1}, neat): 2971, 2864, 1685, 1661, 1565, 1472, 1458, 1386, 1363, 1275, 1456, 1221, 1191, 1168, 1156, 1127, 1074, 1018, 956, 884, 828, 740, 709. **^{1}H NMR** ($CDCl_3$, 300 MHz): δ = 10.71 (d, *J* = 0.7 Hz, 1H), 7.85 (d, *J* = 8.4 Hz, 1H), 7.80 (d, *J* = 1.9 Hz, 1H), 7.65 (ddd, *J* = 8.3, 1.9, 0.7 Hz, 1H), 1.32 (s, 9H). **^{13}C NMR** ($CDCl_3$, 100 MHz): δ = 192.7, 142.3, 138.7, 138.4, 133.1, 129.7, 128.6, 48.5, 31.2. **HRMS** (EI): Calc'd for $C_{17}H_5BrOS$ (M - C_4H_8), 215.9244; found, 215.9245.

The dibromide *(5-bromo-(1-*tert*-butylsulfanyl)-2-(2,2-dibromovinyl)benzene)* was prepared according to the general procedure (2.12 mmol scale). The product was purified by flash chromatography eluting with 1% Et_2O/pentane to give 3.334 g (100%) as a yellow oil. **mp**: 63-65 °C. **IR** (cm^{-1}, neat): 3022, 2961, 2896, 2861, 1588, 1569, 1545, 1471, 1456, 1392, 1363, 1263, 1245, 1218, 1163, 1083, 1058, 1023, 955, 931, 877, 816, 800, 743, 723, 710, 695, 638. **^{1}H NMR** ($CDCl_3$, 300 MHz): δ = 7.84 (s, 1H), 7.73 (d, *J* = 2.0 Hz, 1H), 7.59 (d, *J* = 8.4 Hz, 1H), 7.52 (dd, *J* = 8.4, 2.0 Hz, 1H), 1.30 (s, 9H). **^{13}C NMR** ($CDCl_3$, 75 MHz): δ = 141.2, 140.5, 137.1, 134.4, 132.2, 131.1, 122.1, 91.5, 48.8, 31.3. **HRMS** (EI): Calc'd for $C_8H_4Br_2S$ (M - C_4H_9Br), 289.8400; found, 289.8408.

The title compound **8g** was prepared according to the general procedure (5.0 mmol scale). The product was purified by flash chromatography eluting with 12% Et_2O/pentane to give 1.03 g (55%) as a white solid. **mp:** 95-97 °C. **IR** (cm^{-1}, neat): 3063, 3002, 2570, 1907, 1710, 1597, 1574, 1545, 1459, 1437, 1372, 1285, 1271, 1252, 1202, 1147, 1120, 1082, 1065, 932, 872, 854, 832, 812, 800, 746, 722, 710, 701. **^{1}H NMR** ($CDCl_3$, 400 MHz): δ = 7.50 (d, *J* = 1.6 Hz, 1H), 7.38 (s, 1H), 7.34 (d, *J* = 8.4 Hz,1H), 7.31 (dd, *J* = 8.4, 1.6 Hz, 1H), 3.43 (s, 1H). **^{13}C NMR** ($CDCl_3$, 100 MHz): δ = 136.7, 134.4, 132.2, 131.8, 131.7, 129.7, 119.3, 94.8. **HRMS** (EI): Calc'd for $C_8H_4Br_2S$ (M - HBr), 289.8400; found, 289.8391.



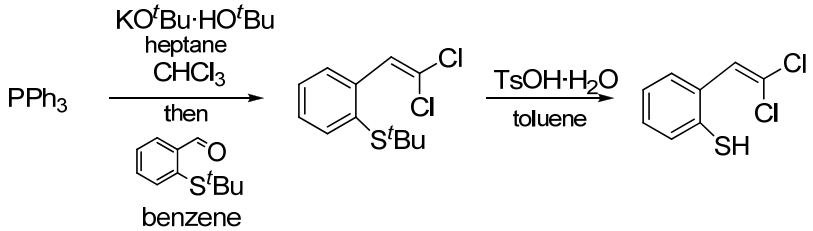
4-Bromo-2-(2,2-dibromovinyl)benzenethiol (**8h**)

General procedure 2 was followed. The aldehyde *(5-bromo-2-(*tert*-butylsulfanyl)benzaldehyde*) was prepared on a 12.9 mmol scale. The product was purified by flash chromatography eluting with 1% Et_2O/pentane to give 1.23 g (35%) as a yellow oil. **IR** (cm^{-1}, neat): 3057, 2963, 2862, 1695, 1570, 1548, 1472, 1456, 1364, 1270,

1246, 1183, 1165, 1083, 1051, 896, 876, 828, 731, 640. **^{1}H NMR** ($CDCl_3$, 400 MHz): δ = 10.69 (s, 1H), 8.11 (d, *J* = 2.4 Hz, 1H), 7.69 (dd, *J* = 8.2, 2.4 Hz, 1H), 7.49 (d, *J* = 8.2Hz, 1H), 1.29 (s, 9H). **^{13}C NMR** ($CDCl_3$, 100 MHz): δ = 192.3, 141.5, 104.8, 136.6, 135.7, 131.4, 124.7, 48.1, 31.1. **HRMS** (EI): Calc'd for $C_{11}H_{13}BrOS$, 271.9870; found, 271.9876.

The dibromide *(4-bromo-(1-*tert*-butylsulfanyl)-2-(2,2-dibromovinyl)benzene)* was prepared according to the general procedure (4.5 mmol scale). The product was purified by flash chromatography eluting with 1% Et_2O/pentane to give 1.69 g (88%) as a white solid. **mp**: 63-65 °C. **IR** (cm^{-1}, neat): 3012, 2968, 2956, 2896, 2859, 1592, 1569, 1541, 1470, 1451, 1389, 1378, 1361, 1274, 1263, 1242, 1216, 1195, 1164, 1088, 1052, 970, 906, 878, 825, 815, 723, 701. **^{1}H NMR** ($CDCl_3$, 300 MHz): δ = 7.86 (br s, 2H), 7.45 (dd, *J* = 8.2, 1.6 Hz, 1H), 7.41 (d, *J* = 8.2 Hz, 1H), 1.28 (s, 9H). **^{13}C NMR** ($CDCl_3$, 75 MHz): δ = 143.3, 140.3, 136.8, 132.7, 131.7, 131.4, 123.4, 92.2, 48.4, 31.2. **HRMS** (EI): Calc'd for $C_8H_4Br_2S$ (M - C_4H_9Br), 289.8400; found, 289.8408.

The title compound **8h** was prepared according to the general procedure (3.71 mmol scale). The product was purified by flash chromatography eluting with 12% Et_2O/pentane to give 760 mg as a pale yellow solid. **mp**: 90-91 °C. **IR** (cm^{-1}, neat): 3057, 2997, 2574, 1883, 1611, 1588, 1549, 1455, 1404, 1386, 1271, 1245, 1197, 1089, 1067, 1055, 943, 928, 895, 876, 831, 814, 803, 705. **^{1}H NMR** ($CDCl_3$, 400 MHz): δ = 7.60 (d, *J* = 2.1 Hz, 1H), 7.41 (s, 1H), 7.34 (dd, *J* = 8.4, 2.1 Hz, 1H), 7.21 (d, *J* = 8.4 Hz, 1H), 3.37 (s, 1H). **^{13}C NMR** ($CDCl_3$, 100 MHz): δ = 134.6, 133.7, 132.9, 132.5, 130.8, 129.0, 122.6, 94.6. **HRMS** (EI): Calculated for $C_{10}H_5Br_2S$ (M - HBr), 289.8400; found, 289.8407.



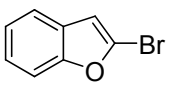
2-(2,2-Dichlorovinyl)benzenethiol (8i)

The dichloride (*1-*tert*-butylsulfanyl)-2-(2,2-dibromovinyl)benzenethiol)* was prepared as follows: To a round-bottom flask was charged KO^{t}Bu·HO^{t}Bu (1.86 g, 10.00 mmol, 2.0 equiv) and powdered PPh_3 (2.62 g, 10 mmol, 2.0 equiv), and the flask was purged with argon for 10 min. After *n*-heptane (15 mL) was added, the mixture was cooled to

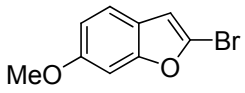
0 °C with an ice bath. To the mixture, a solution of chloroform (1.19 g, 10.00 mmol, 2.0 equiv) in *n*-heptane (5 mL) was added dropwise in such a rate that the internal temperature was maintained under 3 °C. After addition, the mixture was stirred for an additional 30 min. The mixture was concentrated to about 10 mL under vacuum at RT. To the mixture at 0 °C the 2-(*tert*-butylthio)benzaldehyde (971 mg, 5.00 mmol, 1.0 equiv) was added in one portion followed by dry benzene (3 mL), and the resulting mixture was stirred at 0 °C for 1 h then at RT overnight. The reaction was quenched with NH_4Cl solution (20 mL), and extracted with DCM (3 x 20 mL). The combined organic layers were washed with water, brine (which was additionally extracted with DCM (3 x 10 mL)) and dried over $MgSO_4$. The solution was filtered and concentrated at reduced pressure and the product purified by flash chromatography eluting with 1% Et_2O/pentane to afford the product as a slightly yellow oil (805 mg, 62%). **IR** (cm^{-1}, neat): 3055, 2961, 2938, 2922, 2896, 2860, 1607, 1471, 1456, 1436, 1391, 1363, 1198, 1059, 1038, 954, 915, 872, 834, 821, 756, 739, 695, 657. **^{1}H NMR** ($CDCl_3$, 300 MHz): δ = 7.74 (dd, *J* = 7.8, 0.8 Hz, 1H), 7.59 (dd, *J* = 7.6 Hz, 1.3 Hz, 1H), 7.45 (s, 1H), 7.40 (dt, *J* = 7.7, 1.4 Hz, 1H), 7.30 (dt, *J* = 7.7, 1.5 Hz, 1H), 1.28 (s, 9H). **^{13}C NMR** ($CDCl_3$, 100 MHz): δ = 139.7, 139.20, 132.7, 129.8, 129.5, 129.1, 128.6, 121.7, 48.1, 31.2. **HRMS** (EI): Calc'd for $C_{12}H_{14}Cl_2S$, 260.0193; found, 260.0194.

The title compound **8i** was prepared according to the general procedure 2 (2.72 mmol scale). 391 mg (71%) was isolated as a yellow oil. **IR** (cm^{-1}, neat): 3054, 3018, 2915, 2848, 1608, 1463, 1434, 1261, 1065, 1037, 946, 913, 820, 749, 724, 654. **^{1}H NMR** ($CDCl_3$, 300 MHz): δ = 7.49-7.55 (m, 1H), 7.33-7.38 (m, 1H), 7.17-7.23 (m, 2H), 6.95 (s, 1H), 3.37 (s, 1H). **^{13}C NMR** ($CDCl_3$, 100 MHz): δ = 133.1, 131.2, 130.8, 129.9, 129.2, 127.2, 126.1, 124.2. **HRMS** (EI): Calc'd for $C_8H_6Cl_2S$, 203.9567; found, 203.9574

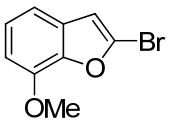
Cyclization products:



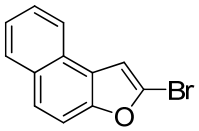
2-Bromobenzofuran (6a). General procedure 4 was followed (0.2 mmol scale). Filtration of the crude reaction mixture provided **6a** as a clear oil (37 mg, 93%). Characterization data match those previously reported.[5] **^{1}H NMR** ($CDCl_3$, 400 MHz): δ = 7.42-7.50 (m, 2H), 7.19-7.27 (m, 2H), 6.71 (d, *J* = 0.9 Hz). **^{13}C NMR** ($CDCl_3$, 100 MHz): δ = 155.8, 128.7, 128.2, 124.2, 123.4, 120.1, 110.9, 108.3.



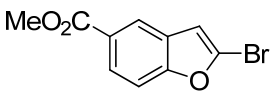
2-Bromo-6-methoxybenzofuran (6b). General procedure 4 was followed (0.2 mmol scale). Filtration of the crude reaction mixture provided **6b** as a clear oil (40 mg, 89%). **IR** (cm^{-1}, neat): 3001, 2955, 2834, 1622, 1493, 1435, 1275, 1234, 1144, 1107, 1059, 1028. **^{1}H NMR** ($CDCl_3$, 400 MHz): δ = 7.35 (d, *J* = 8.6 Hz, 1H), 6.99 (d, *J* = 2.1 Hz, 1H), 6.86 (dd, *J* = 8.6, 2.3 Hz, 1H), 6.64 (s, 1H), 3.84 (s, 3H). **^{13}C NMR** ($CDCl_3$, 100 MHz): δ = 157.8, 156.6, 126.0, 122.0, 120.2, 112.3, 108.0, 95.8, 55.7. **HRMS** (EI): Calc'd for $C_9H_7O_2Br$, 225.9629; found, 225.9627.



2-Bromo-7-methoxybenzofuran (6c). General procedure 4 was followed (0.2 mmol scale). Filtration of the crude reaction mixture provided **6c** as a clear oil (43 mg, 95%). **IR** (cm^{-1}, neat): 3138, 3007, 2940, 2839, 1622, 1589, 1543, 1485, 1429, 1317, 1273, 1177, 1096. **^{1}H NMR** ($CDCl_3$, 400 MHz): δ = 7.15 (t, *J* = 7.8 Hz, 1H), 7.09 (d, *J* = 7.8 Hz, 1H), 6.77 (d, *J* = 7.9 Hz, 1H), 6.71 (s, 1H), 4.00 (br s, 1H). **^{13}C NMR** ($CDCl_3$, 100 MHz): δ = 145.0, 144.6, 130.1, 127.9, 123.9, 112.2, 108.4, 106.3, 55.9. **HRMS** (EI): Calc'd for $C_9H_7O_2Br$, 225.9629; found, 225.9634.

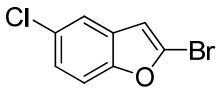


2-Bromonaphtho[2,1-*b*]furan (6d). General procedure 4 was followed (0.2 mmol scale). Filtration of the crude reaction mixture provided **6d** as a clear oil (44 mg, 89%). **IR** (cm^{-1}, neat): 3129, 3053, 1514, 1383, 1250, 1161, 1092. **^{1}H NMR** ($CDCl_3$, 400 MHz): δ = 8.01 (d, *J* = 8.2 Hz, 1H), 7.91 (d, *J* = 8.2 Hz, 1H), 7.67 (d, *J* = 9.0 Hz, 1H), 7.54-7.61 (m, 2H), 7.48 (ddd, *J* = 8.1, 6.9, 1.3 Hz, 1H), 7.17 (d, *J* = 0.8 Hz, 1H). **^{13}C NMR** ($CDCl_3$, 100 MHz): δ = 153.5, 130.4, 128.8, 126.7, 126.6, 126.3, 125.2, 125.0, 124.2, 123.3, 111.8, 107.5. **HRMS** (EI): Calc'd for $C_{12}H_7OBr$, 245.9680; found, 245.9679.

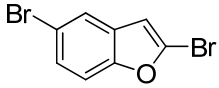


Methyl 2-bromobenzofuran-5-carboxylate (6e). General procedure 4 was followed (0.2 mmol scale). Filtration of the crude reaction mixture provided **6e** as a white solid (47 mg,

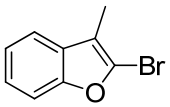
93%). **mp**: 102-104 °C. **IR** (cm^{-1}, neat): 3125, 3013, 2959, 1724, 1441, 1297, 1261, 1163, 1072. **^{1}H NMR** ($CDCl_3$, 400 MHz): δ = 8.25 (d, *J* = 1.7 Hz, 1H), 8.00 (dd, *J* = 8.7, 1.8 Hz, 1H), 7.48 (d, *J* = 8.7 Hz, 1H), 6.81 (d, *J* = 0.9 Hz, 1H), 3.94 (s, 3H). **^{13}C NMR** ($CDCl_3$, 100 MHz): δ = 166.9, 158.2, 129.8, 128.7, 126.0, 125.8, 122.4, 110.8, 108.8, 52.1. **HRMS** (EI): Calc'd for $C_{10}H_7O_3Br$, 253.9579; found, 253.9583.



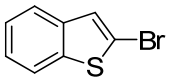
2-Bromo-5-chlorobenzofuran (6f). General procedure 4 was followed (0.2 mmol scale). Filtration of the crude reaction mixture provided **6f** as a clear oil (46 mg, 99%). **IR** (cm^{-1}, neat): 2926, 1724, 1614, 1537, 1439, 1252, 1163, 1074. **^{1}H NMR** ($CDCl_3$, 400 MHz): δ = 7.48 (d, *J* = 2.2 Hz, 1H), 7.36 (d, *J* = 8.7 Hz, 1H), 7.22 (dd, *J* = 8.7, 2.2 Hz, 1H), 6.68 (s, 1H). **^{13}C NMR** ($CDCl_3$, 100 MHz): δ = 154.1, 129.9, 129.8, 129.2, 124.5, 119.7, 111.9, 108.0. **HRMS** (EI): Calc'd for C_8H_4OClBr, 229.9134; found, 229.9137.



2,5-Dibromobenzofuran (6g). General procedure 4 was followed (0.2 mmol scale). Filtration of the crude reaction mixture provided **6g** as a yellow solid (53 mg, 96%). **mp**: 56-58 °C. **IR** (cm^{-1}, neat): 3133, 3090, 2857, 1532, 1447, 1435, 1252, 1227, 1163, 1072, 1049. **^{1}H NMR** ($CDCl_3$, 400 MHz): δ = 7.64 (d, *J* = 1.8 Hz, 1H), 7.30-7.38 (m, 2H), 6.68 (d, *J* = 0.7 Hz, 1H). **^{13}C NMR** ($CDCl_3$, 100 MHz): δ = 154.5, 130.6, 129.7, 127.2, 122.7, 116.6, 112.4, 107.9. **HRMS** (EI): Calc'd for $C_8H_4Obr_2$, 273.8629; found, 273.8625.

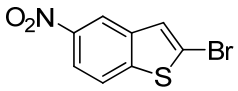


2-Bromo-3-methylbenzofuran (6h). General procedure 4 was followed (0.2 mmol scale). The residue obtained upon filtration was further purified by flash chromatography eluting with pentane to afford **6h** as a yellow oil (22 mg, 52%). Characterization data match those previously reported.[6] **^{1}H NMR** ($CDCl_3$, 400 MHz): δ = 7.38-7.46 (m, 2H), 7.19-7.28 (m, 2H), 2.19 (s, 3H). **^{13}C NMR** ($CDCl_3$, 100 MHz): δ = 155.1, 129.4, 126.3, 124.2, 122.9, 118.7, 115.1, 110.8, 8.8.

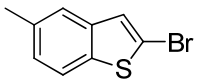


2-Bromobenzo[*b*]thiophene (9a). General procedure 4 was followed (0.2 mmol scale).

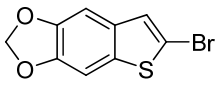
Filtration of the crude reaction mixture provided **9a** as a off-white solid (36 mg, 84%). Characterization data match those previously reported.[7] **^{1}H NMR** ($CDCl_3$, 400 MHz): δ = 7.65-7.74 (m, 2H), 7.24-7.35 (m, 3H). **^{13}C NMR** ($CDCl_3$, 100 MHz): δ = 141.0, 139.6, 126.6, 124.8, 124.5, 122.7, 121.7, 115.4.



2-Bromo-5-nitrobenzo[*b*]thiophene (9b). General procedure 4 was followed (0.1 mmol scale). Filtration of the crude reaction mixture provided **9b** as a yellow solid (23 mg, 88%). **mp**: 121-123 °C. **IR** (cm^{-1}, neat): 3099, 1600, 1512, 1502, 1343, 1279, 1240, 1065. **^{1}H NMR** ($CDCl_3$, 400 MHz): δ = 8.60 (t, *J* = 2.0 Hz, 1H), 8.20 (dt, *J* = 8.9, 2.0 Hz, 1H), 7.86 (dd, *J* = 8.9, 1.6 Hz, 1H), 7.51 (d, *J* = 1.8 Hz, 1H). **^{13}C NMR** ($CDCl_3$, 100 MHz): δ = 146.8, 146.0, 139.5, 127.3, 122.4, 119.4, 119.0, 118.4. **HRMS** (EI): Calc'd for $C_8H_4NO_2SBr$, 256.9146; found, 256.9147.

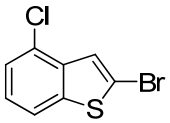


2-Bromo-5-methylbenzo[*b*]thiophene (9c). General procedure 4 was followed (0.2 mmol scale). Filtration of the crude reaction mixture provided **9c** as a yellow solid (45 mg, 99%). **mp**: 67-69 °C. **IR** (cm^{-1}, neat): 3084, 2922, 1431, 1250, 1140, 947. **^{1}H NMR** ($CDCl_3$, 400 MHz): δ = 7.58 (d, *J* = 8.3 Hz, 1H), 7.46 (s, 1H), 7.22 (s, 1H), 7.12 (d, *J* = 8.3 Hz, 1H), 2.43 (s, 3H). **^{13}C NMR** ($CDCl_3$, 100 MHz): δ = 139.6, 137.9, 134.3, 126.1, 125.9, 122.5, 121.0, 115.1, 21.2. **HRMS** (EI): Calc'd for C_9H_7SBr, 225.9452; found, 225.9449.

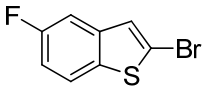


2-bromo-5,6-methylenedioxybenzothiophene (9d)

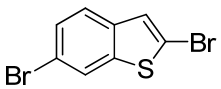
General procedure 4 was followed (0.2 mmol scale). The residue obtained upon filtration was further purified by flash chromatography eluting with pentane to afford **9d** as a white solid (38 mg, 74%). **mp**: 156-158 °C. **IR** (cm^{-1}, neat): 3073, 2922, 1559, 1497, 1468, 1302, 1231, 1111. **^{1}H NMR** ($CDCl_3$, 400 MHz): δ = 7.15 (s, 1H), 7.11 (s, 1H), 7.06 (s, 1H), 6.00 (s, 2H). **^{13}C NMR** ($CDCl_3$, 100 MHz): δ = 147.1, 146.8, 134.5, 134.1, 126.4, 112.2, 101.9, 101.6., 101.3. **HRMS** (EI): Calc'd for $C_9H_5O_2SBr$, 255.9194; found, 255.9197



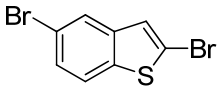
2-Bromo-4-chlorobenzo[*b*]thiophene (9e). General procedure 4 was followed (0.2 mmol scale). Filtration of the crude reaction mixture provided **9e** as an off-white solid (45 mg, 91%) **mp**: 36-38 °C. **IR** (cm^{-1}, neat): 3098, 2922, 1551, 1501, 1445, 1406, 1319, 1283, 1202, 1099. **^{1}H NMR** ($CDCl_3$, 400 MHz): δ = 7.60 (d, *J* = 8.0 Hz, 1H), 7.50 (s, 1H), 7.32 (d, *J* = 7.8 Hz, 1H), 7.23 (t, *J* = 7.9 Hz, 1H). **^{13}C NMR** ($CDCl_3$, 100 MHz): δ = 141.9, 137.9, 127.7, 125.2, 125.0, 124.8, 120.0, 116.6. **HRMS** (EI): Calc'd for C_8H_4SClBr, 245.8906; found, 245.8907.



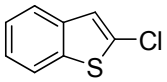
2-Bromo-5-fluorobenzo[*b*]thiophene (9f). General procedure 4 was followed (0.2 mmol scale). Filtration of the crude reaction mixture provided **9f** as a white solid (38 mg, 82%). **mp**: 39-41 °C. **IR** (cm^{-1}, neat): 3096, 1599, 1570, 1427, 1292, 1238, 1202, 1125. **^{1}H NMR** ($CDCl_3$, 400 MHz): δ = 7.63 (dd, *J* = 8.8, 4.8 Hz, 1H), 7.35 (dd, *J* = 9.2, 2.5 Hz, 1H), 7.27 (s, 1H), 7.07 (ddd, *J* = 8.9, 8.8, 2.4 Hz, 1H). **^{19}F NMR** ($CDCl_3$, 282 Hz) δ = -118.1. **^{13}C NMR** (C **^{13}C NMR** ($CDCl_3$, 100 MHz): δ = 160.9 (d, *J* = 242.6 Hz), 140.4 (d, *J* = 9.5 Hz), 136.3 (d, *J* = 1.8 Hz), 126.3 (d, *J* = 4.2 Hz), 122.7 (d, *J* = 9.3 Hz), 117.7, 113.2 (d, *J* = 25.1 Hz), 108.4 (d, *J* = 23.4 Hz). **HRMS** (EI): Calc'd for C_8H_4SFBr, 229.9201; found, 229.9211.



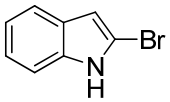
2,6-Dibromobenzo[*b*]thiophene (9g). General procedure 4 was followed (0.2 mmol scale). Filtration of the crude reaction mixture provided **9g** as a yellow solid (53 mg, 91%). **mp**: 50-51 °C. **IR** (cm^{-1}, neat): 3080, 1584, 1549, 1449, 1381, 1319, 1082. **^{1}H NMR** ($CDCl_3$, 400 MHz): δ = 7.83 (s, 1H), 7.51 (d, *J* = 8.5 Hz, 1H), 7.41 (dd, *J* = 8.5, 1.7 Hz). 7.25 (s, 1H). **^{13}C NMR** ($CDCl_3$, 100 MHz): δ = 142.2, 138.1, 128.2, 126.2, 124.1, 123.7, 118.5, 116.0. **HRMS** (EI): Calc'd for $C_8H_4SBr_2$, 289.8400; found, 289.8394.



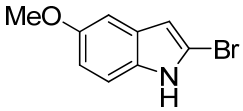
2,5-Dibromobenzo[*b*]thiophene (9h). General procedure 4 was followed (0.2 mmol scale). Filtration of the crude reaction mixture provided **9h** as a yellow solid (56 mg, 96%). **mp**: 54-55 °C. **IR** (cm^{-1}, neat): 3086, 2920, 1580, 1427, 1404, 1167, 1067, 945. **^{1}H NMR** ($CDCl_3$, 400 MHz): δ = 7.81 (d, *J* = 1.8 Hz, 1H), 7.56 (d, *J* = 8.6 Hz, 1H), 7.40 (dd, *J* = 8.6, 1.9 Hz, 1H), 7.24 (s, 1H). **^{13}C NMR** ($CDCl_3$, 100 MHz): δ = 141.0, 139.5, 127.5, 125.8, 125.3, 122.8, 118.9, 117.3. **HRMS** (EI): Calc'd for $C_8H_4SBr_2$, 289.8400; found, 289.8405.



2-Chlorobenzo[*b*]thiophene (9i). General procedure 4 was followed (0.19 mmol scale). The residue obtained upon filtration was further purified by flash chromatography eluting with pentane to afford **9i** as a white solid (20 mg, 62%). **mp**: 31-32 °C. **IR** (cm^{-1}, neat): 3088, 3067, 1510, 1458, 1427, 1327, 1250, 1175, 1153. **^{1}H NMR** ($CDCl_3$, 400 MHz): δ = 7.63-7.71 (m, 2H), 7.28-7.36 (m, 2H), 7.17 (s, 1H). **^{13}C NMR** ($CDCl_3$, 100 MHz): δ = 138.8, 138.6, 131.8, 124.8, 124.5, 122.9, 122.7, 121.8. **HRMS** (EI): Calc'd for C_8H_5SCl, 167.9800; found, 167.9803.



2-bromo-1H-indole (11a). To a 0.5-2 mL microwave vial was added gem-dibromoaniline **10a** (28 mg, 0.1 mmol), $Pd_2(dba)_3$ (2.3 mg, 0.0025 mmol), $PtBu_3HBF_4$ (2.9 mg, 0.01 mmol), and K_3PO_4 (63.7 mg, 0.3 mmol). The vial was purged with argon for 5 minutes, followed by the addition of toluene (0.5 mL). The tube was sealed and placed in a pre-heated oil bath at 100 °C and stirred vigorously for 16 hours. The vessel was cooled to room temperature and the contents added directly on to a flash column, eluting with 10% EtOAc/pentane to provide **11a** as an off-white solid (13 mg, 64%). Characterization data match those previously reported.[8] **^{1}H NMR** ($CDCl_3$, 400 MHz): δ = 8.02 (br s, 1H), 7.52 (d, *J* = 7.5 Hz, 1H), 7.24 (d, *J* = 8.0 Hz, 1H), 7.08-7.18 (m, 2H), 6.52 (s, 1H. **^{13}C NMR** ($CDCl_3$, 100 MHz): δ = 136.5, 128.8, 122.3, 120.6, 119.7, 110.4, 108.8, 104.9.



2-bromo-5-methoxy-1*H*-indole (11b). To a 0.5-2 mL microwave vial was added gem-dibromoaniline **11a** (31 mg, 0.1 mmol), $Pd_2(dba)_3$ (2.3 mg, 0.0025 mmol), $PtBu_3HBF_4$ (2.9 mg, 0.01 mmol), and K_3PO_4 (63.7 mg, 0.3 mmol). The vial was purged with argon for 5 minutes, followed by the addition of toluene (0.5 mL). The tube was sealed and placed in a pre-heated oil bath at 100 °C and stirred vigorously for 16 hours. The vessel was cooled to room temperature and the contents added directly on to a flash column, eluting with 10% EtOAc/pentane to provide **11b** as a white solid (15 mg, 66%). **mp**: 62-63 °C (decomp). **IR** (cm^{-1}, neat): 3393, 3302, 2932, 2832, 1622, 1584, 1435, 1337, 1215, 1157, 1028. **^{1}H NMR** ($CDCl_3$, 400 MHz): δ = 7.97 (br s, 1H), 7.17 (d, *J* = 8.8 Hz, 1H), 6.99 (d, *J* = 2.4 Hz, 1H), 6.82 (dd, *J* = 8.8, 2.5 Hz, 1H), 6.45 (d, *J* = 2.0 Hz, 1H), 3.83 (s, 3H). **^{13}C NMR** ($CDCl_3$, 100 MHz): δ = 154.4, 131.4, 129.0, 112.1, 110.9, 108.7, 104.5, 101.4, 55.6. **HRMS** (EI): Calc'd for C_9H_8NOBr, 224.9789; found, 224.9790.

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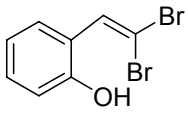
Spectra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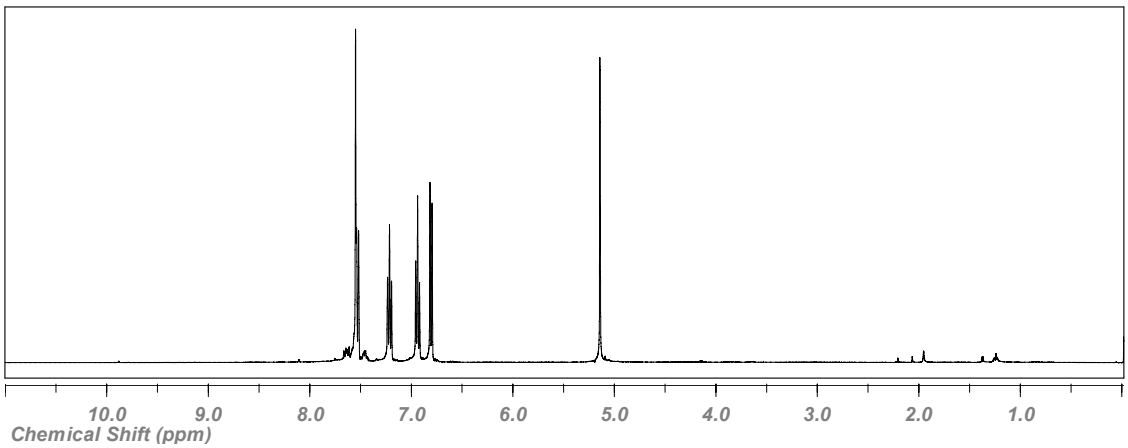
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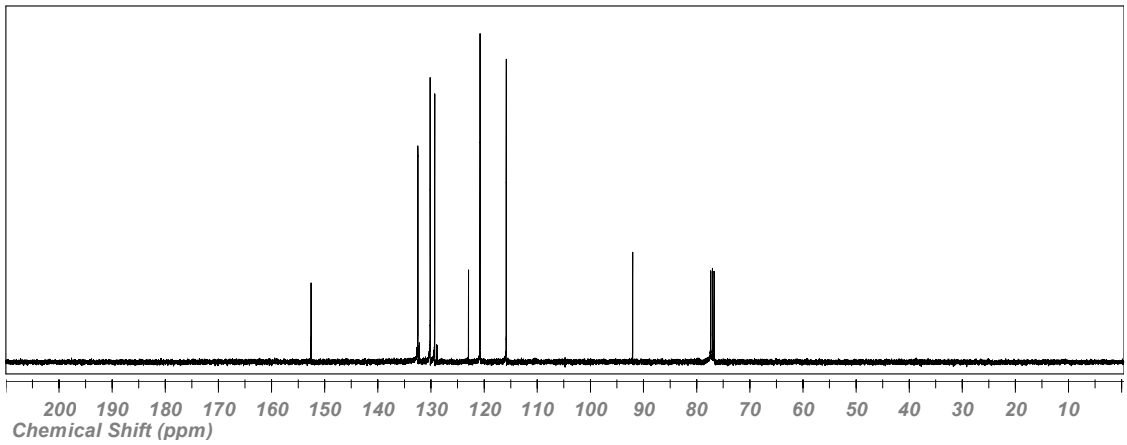
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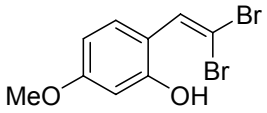
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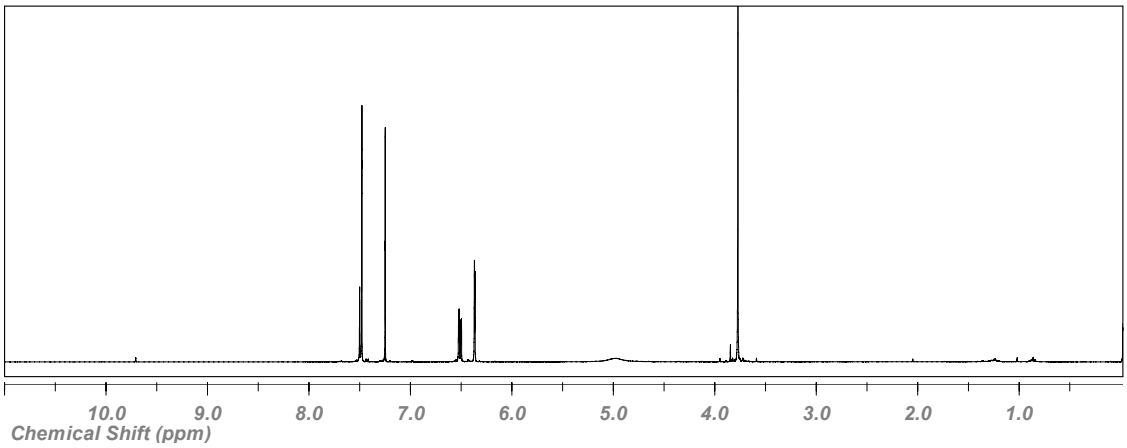
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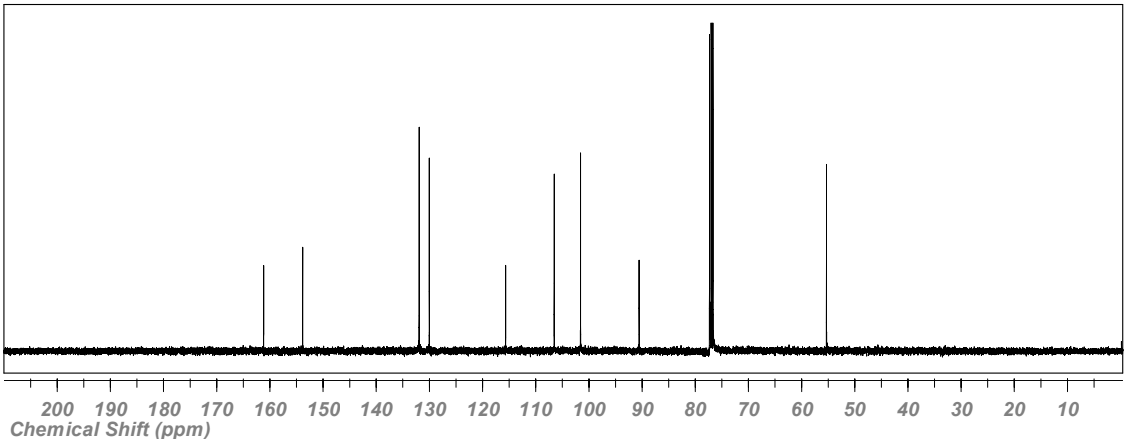
Chemical Shift (ppm)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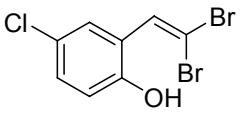
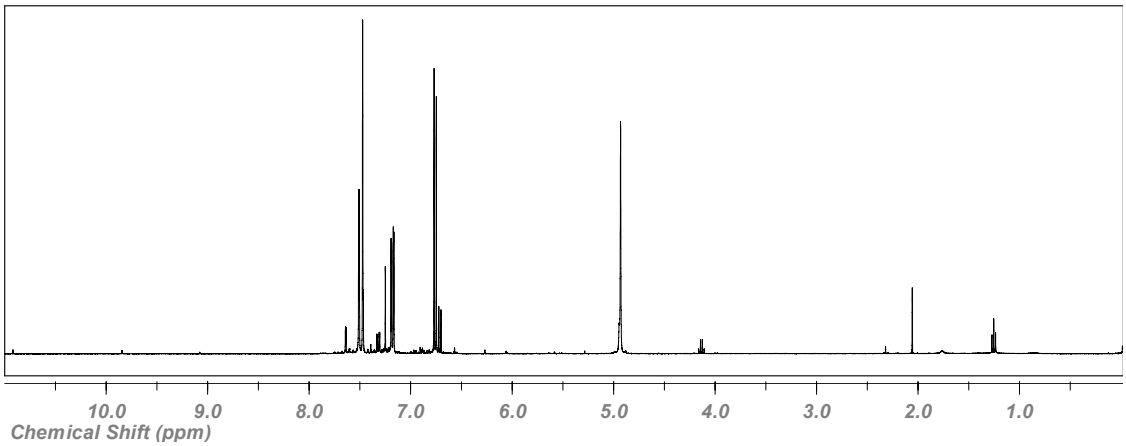
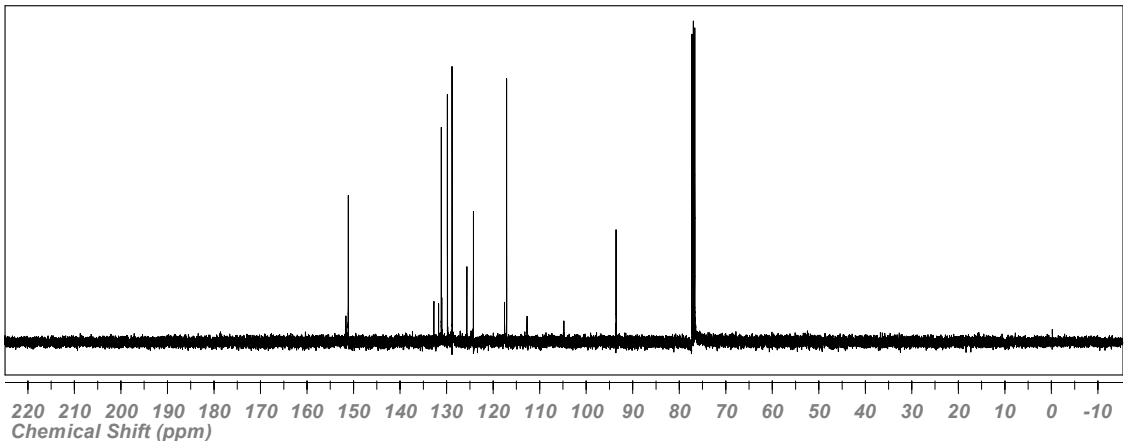
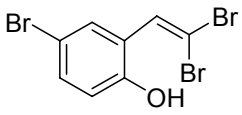
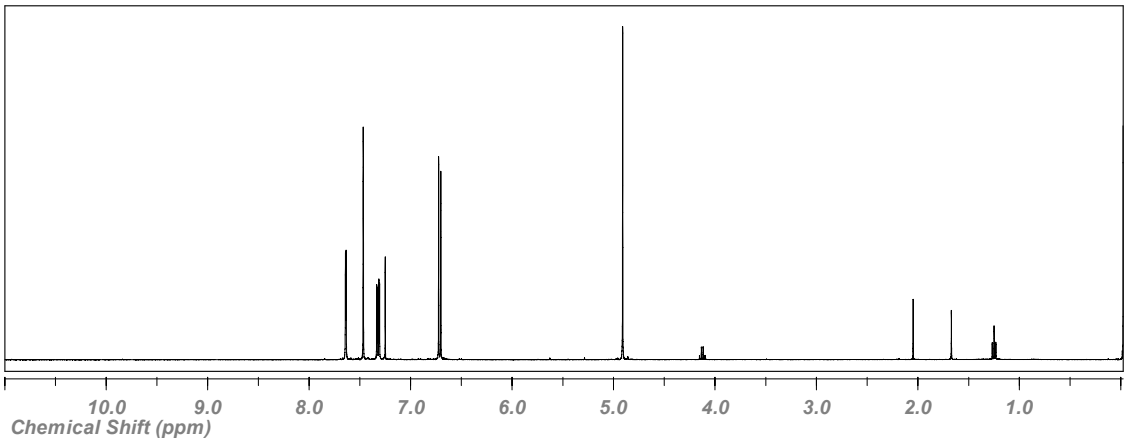
Chemical Shift (ppm)

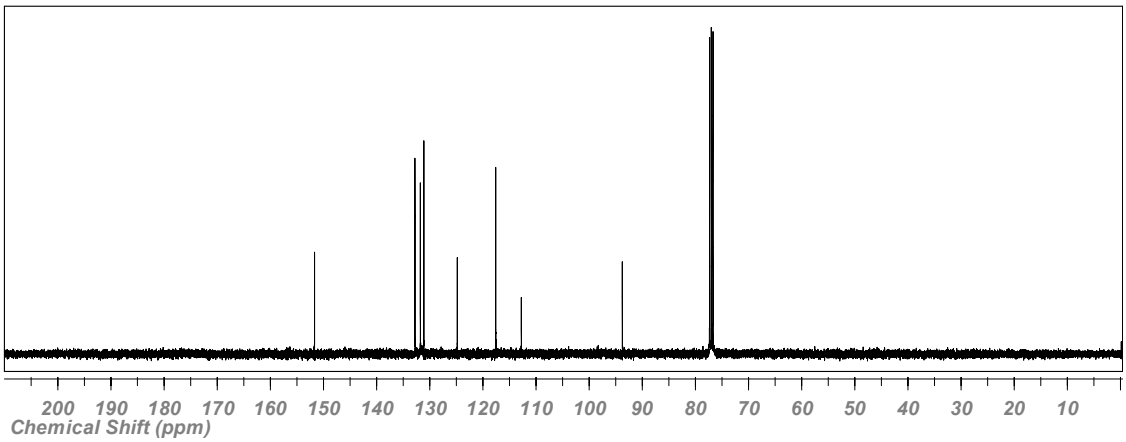

Cl
Br
Br
OH


10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0
Chemical Shift (ppm)


220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
Chemical Shift (ppm)


Br
Br
Br
OH


10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0
Chemical Shift (ppm)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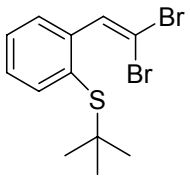
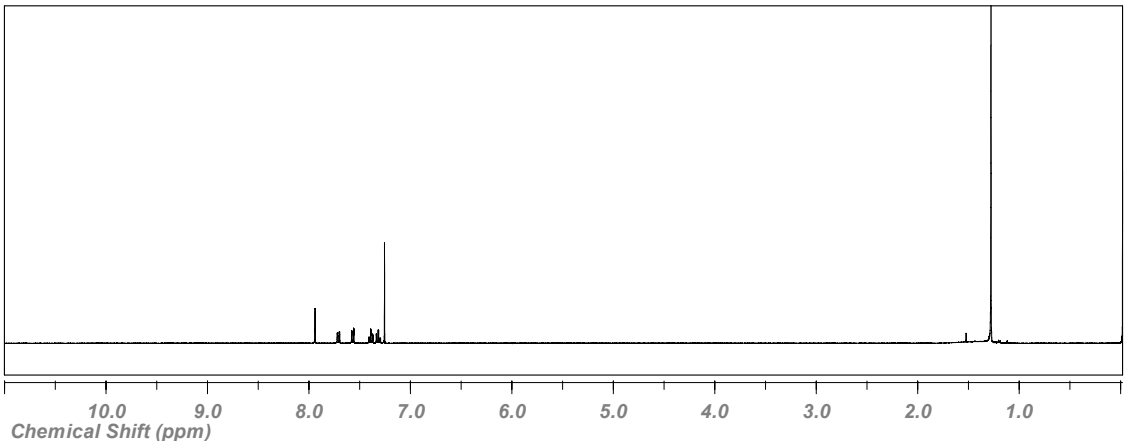
Chemical Shift (ppm)


Br
Br
S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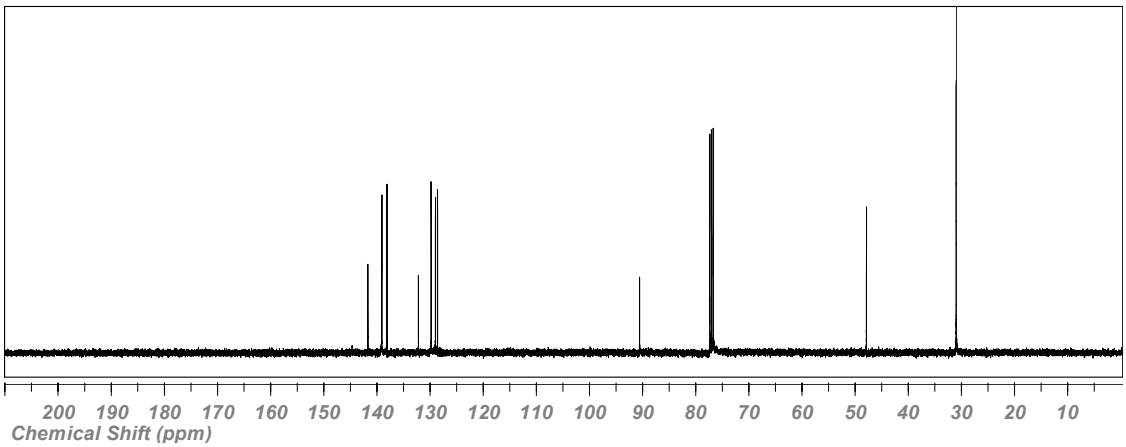
Chemical Shift (ppm)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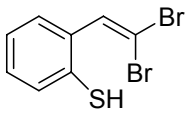
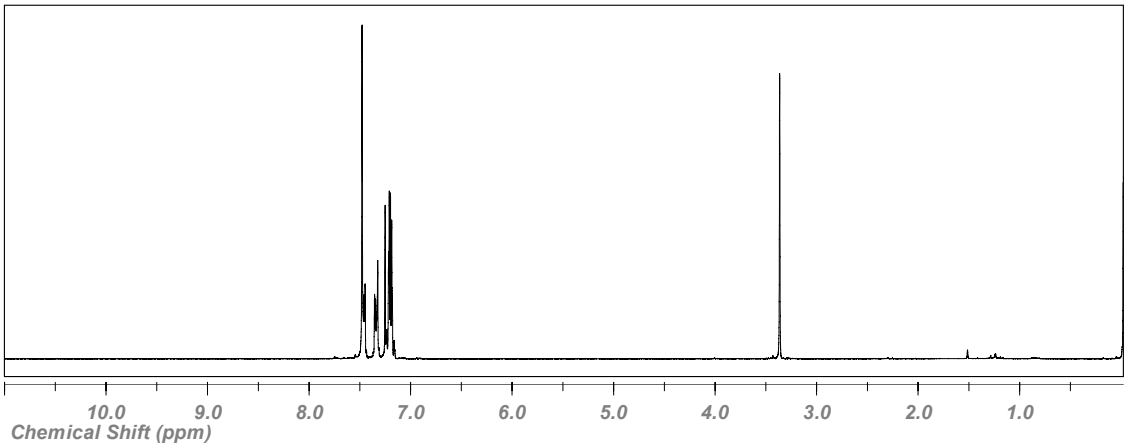
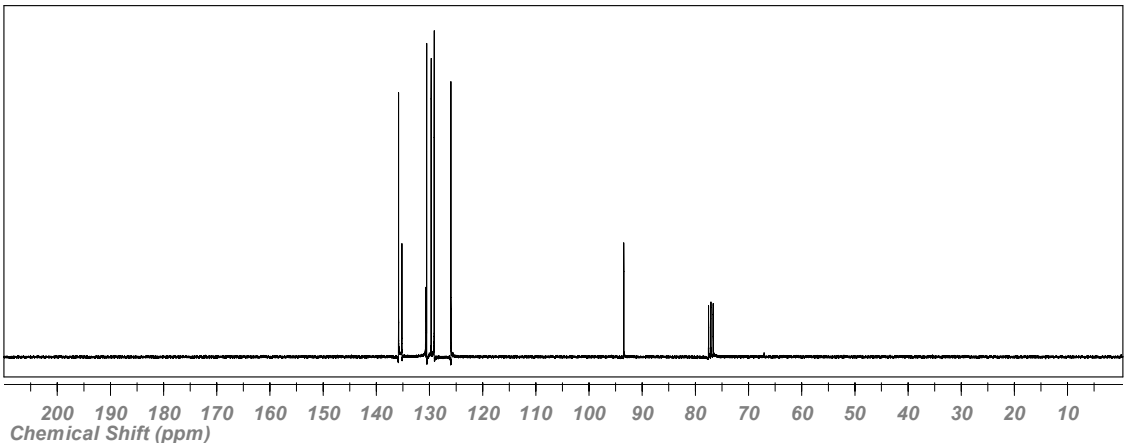
Chemical Shift (ppm)


Br
Br
SH


10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0
Chemical Shift (ppm)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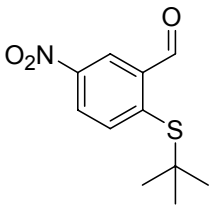
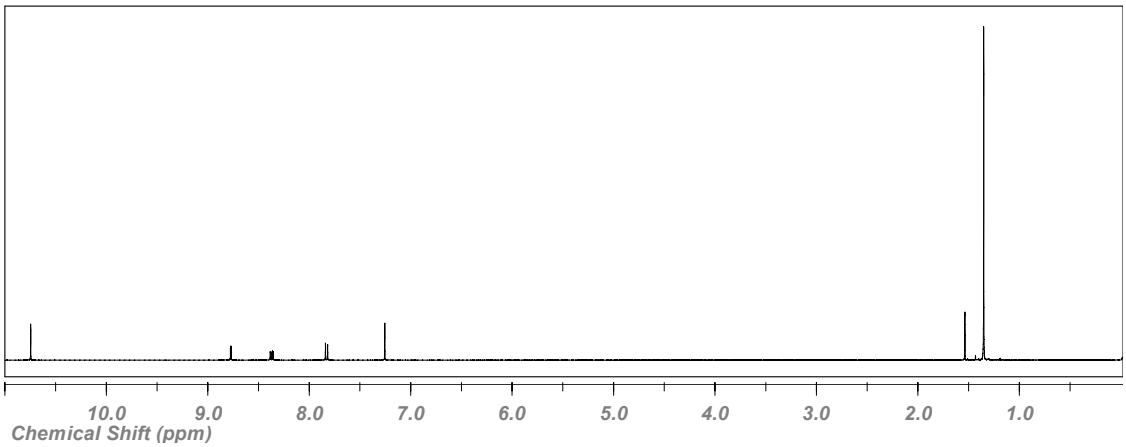
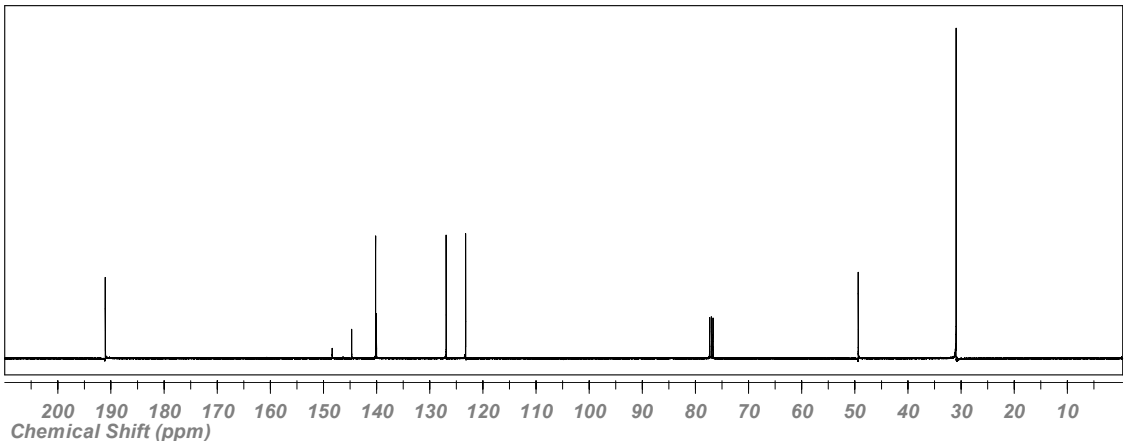
Chemical Shift (ppm)


O
O2N
S


10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0
Chemical Shift (ppm)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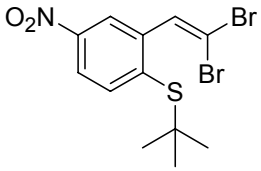
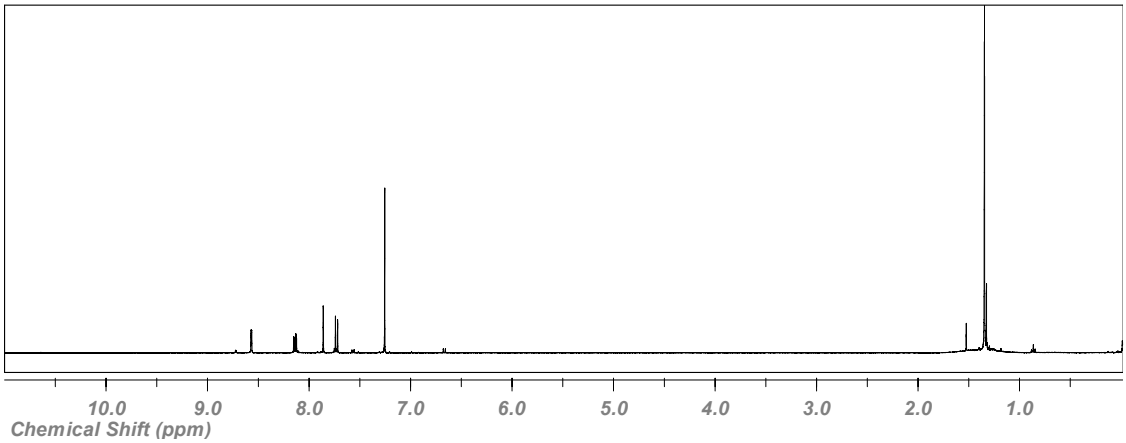
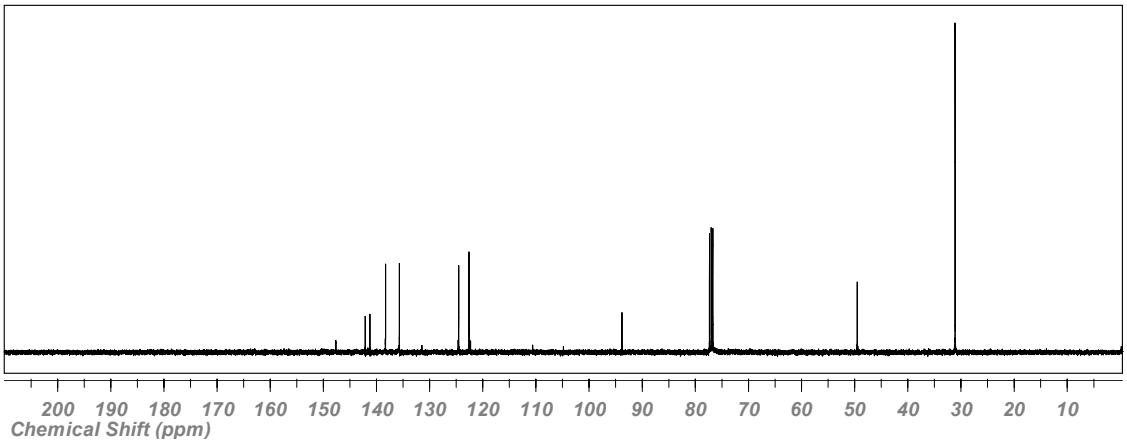
Chemical Shift (ppm)


O2N
Br
Br
S


10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0
Chemical Shift (ppm)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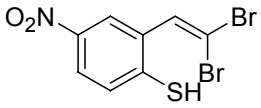
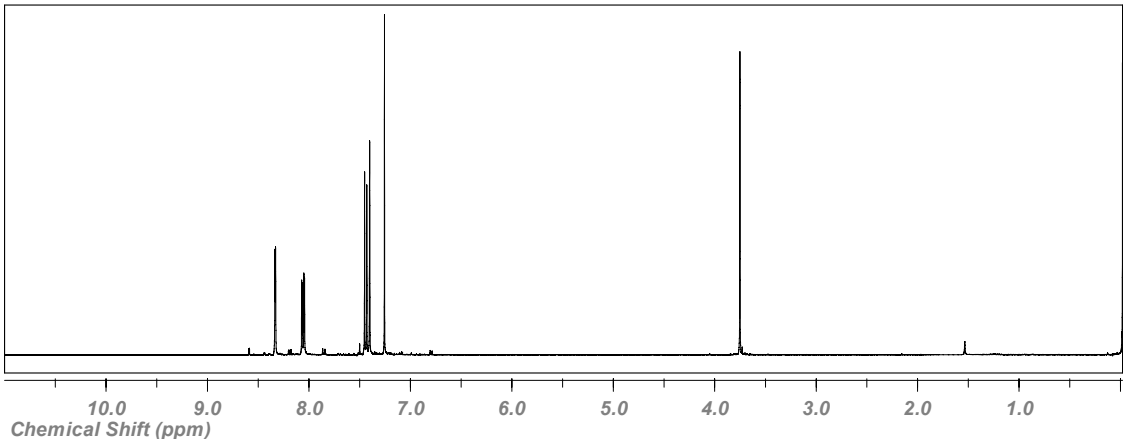
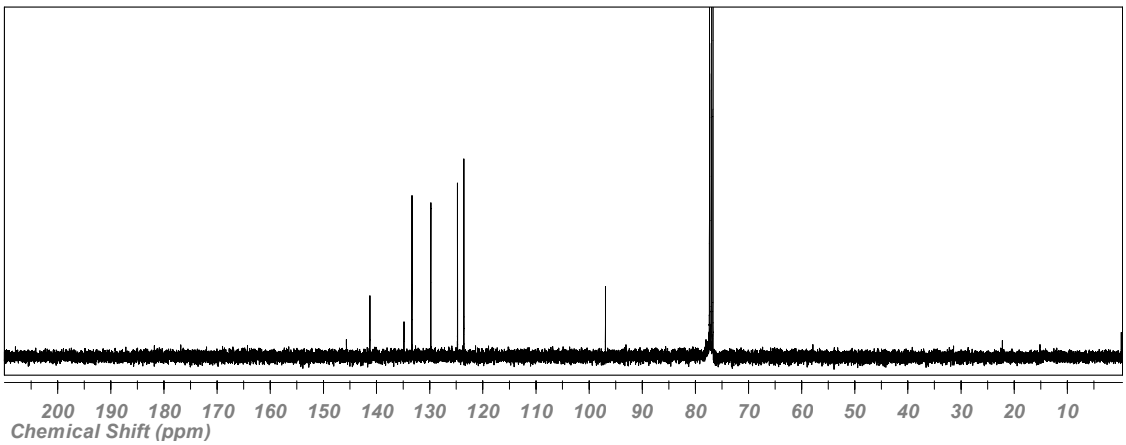
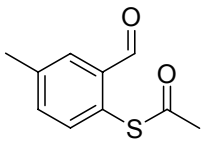
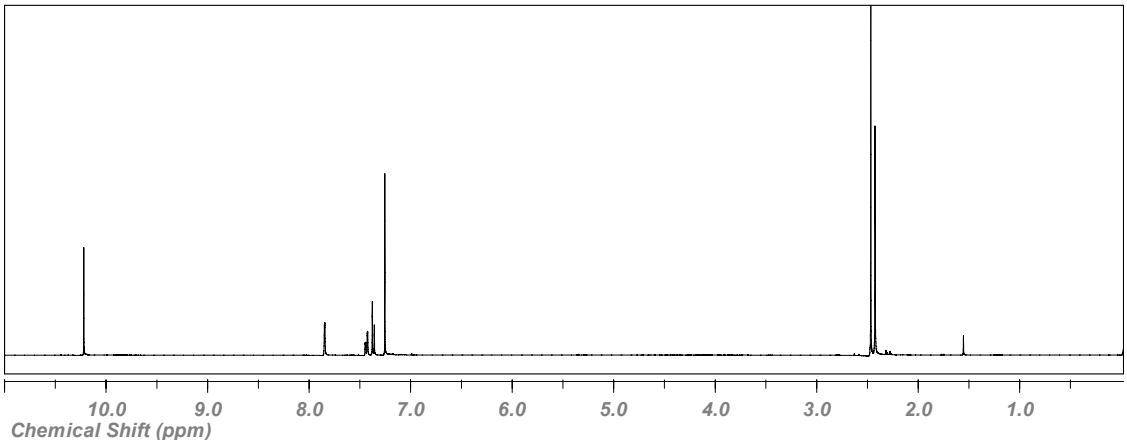
Chemical Shift (ppm)

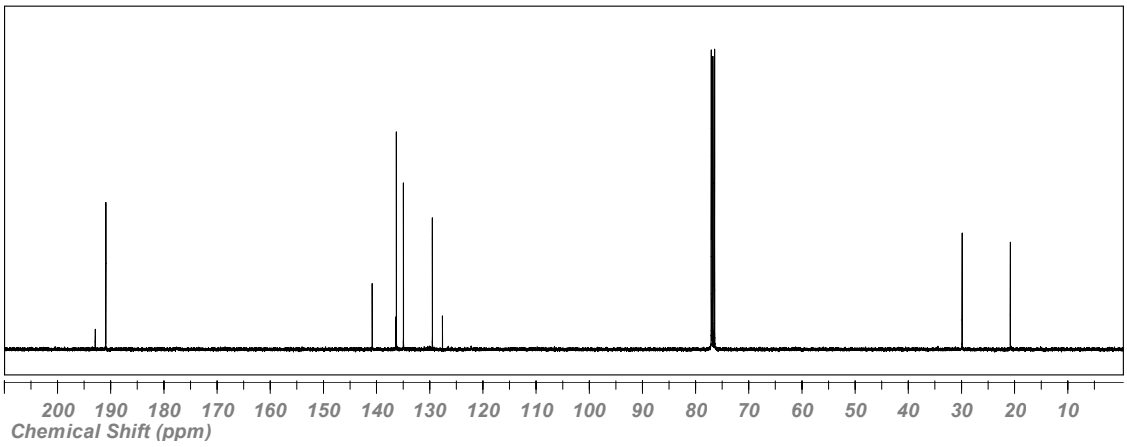

O2N
Br
Br
SH


10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0
Chemical Shift (ppm)


200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
Chemical Shift (ppm)


O
O
S


10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0
Chemical Shift (ppm)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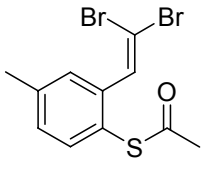
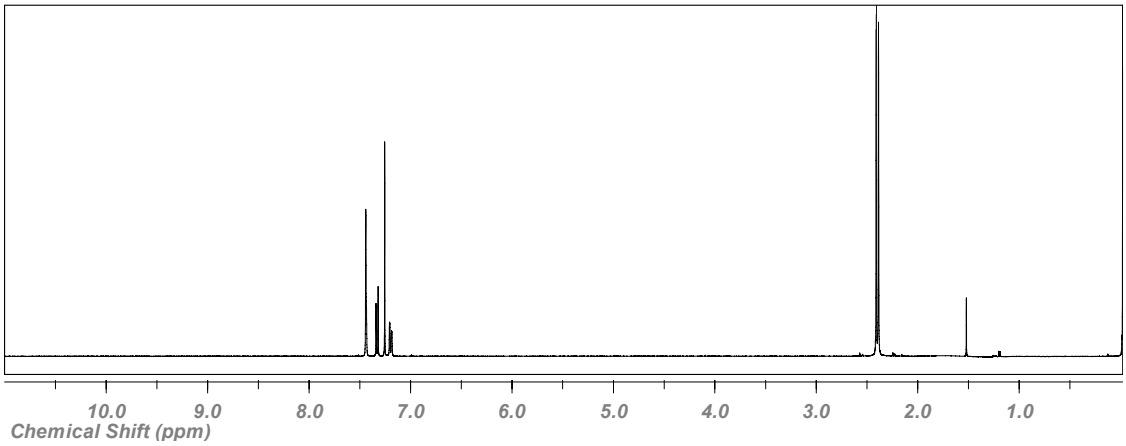
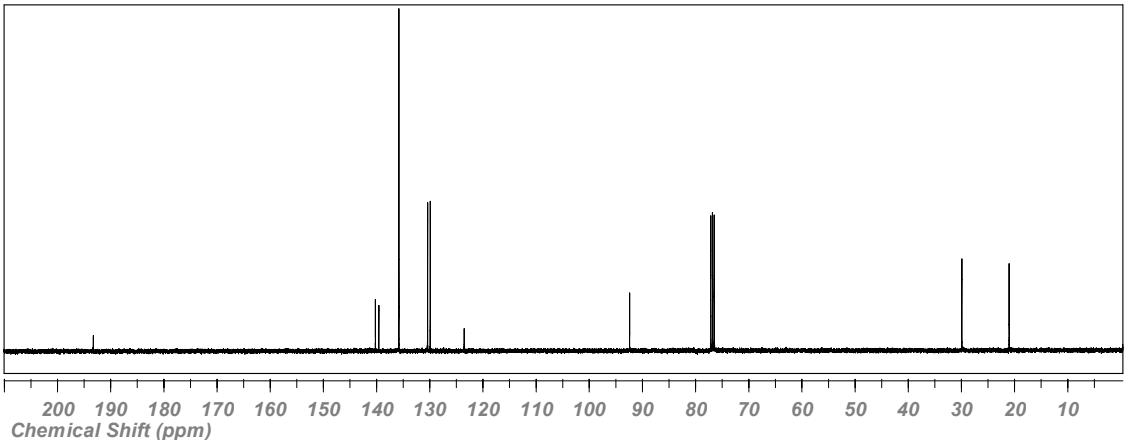
Chemical Shift (ppm)


Br
Br
O
S


10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0
Chemical Shift (ppm)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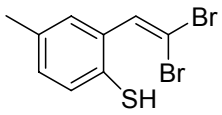
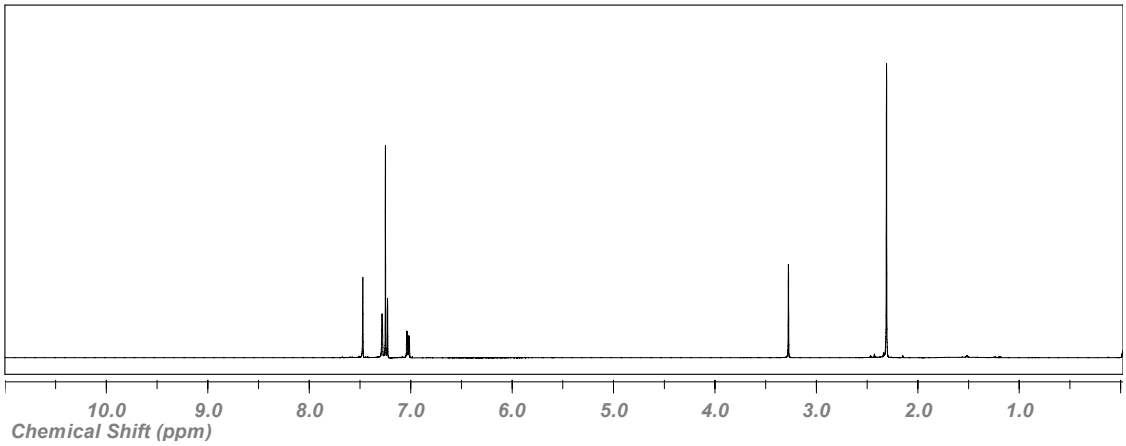
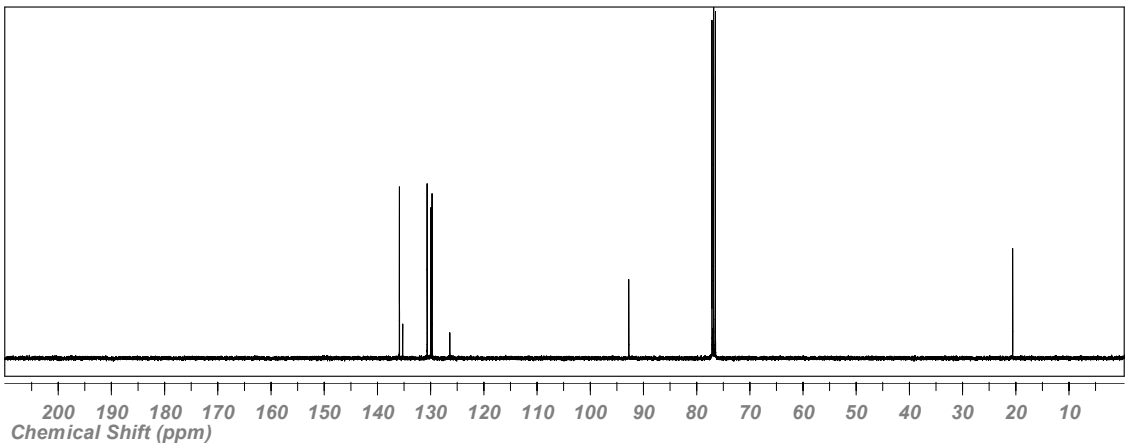
Chemical Shift (ppm)


Br
Br
SH


10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0
Chemical Shift (ppm)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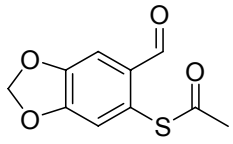
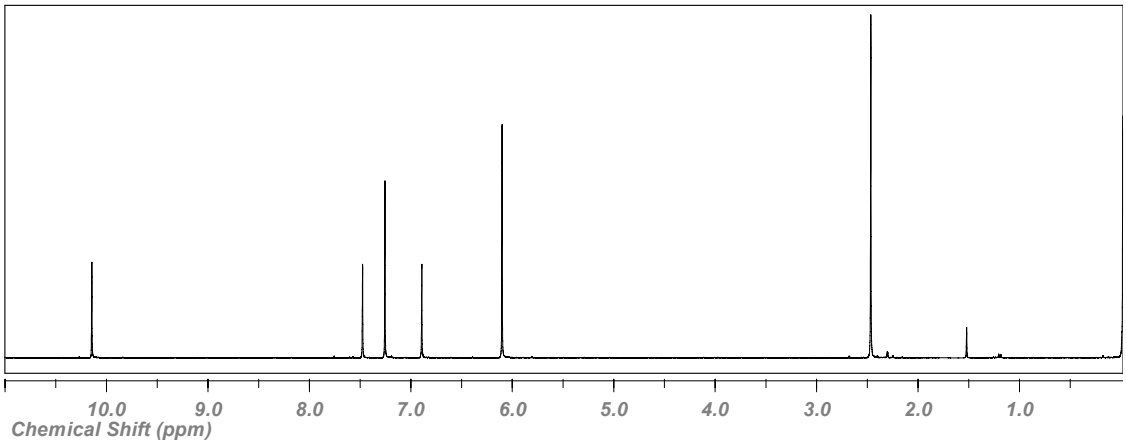
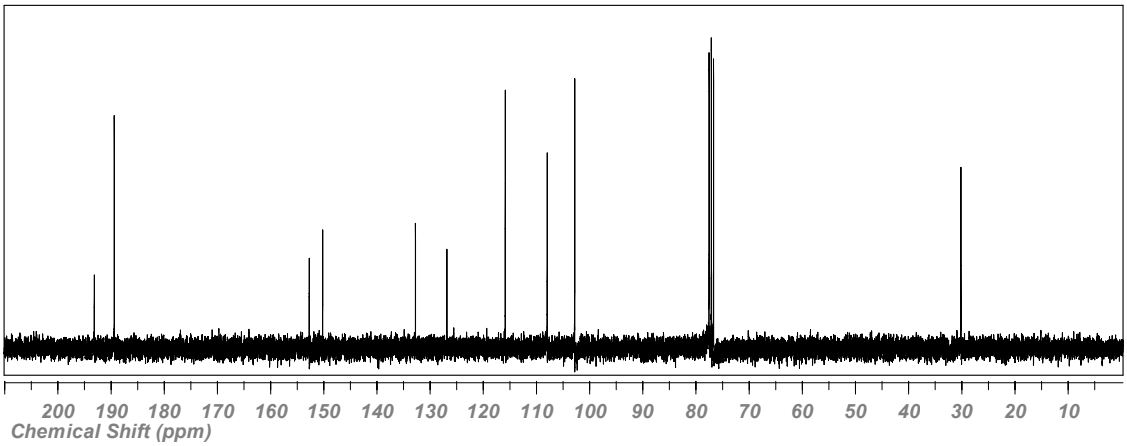
Chemical Shift (ppm)


O
O
O
O
S


10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0
Chemical Shift (ppm)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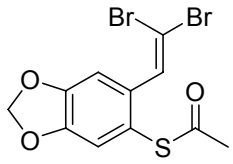
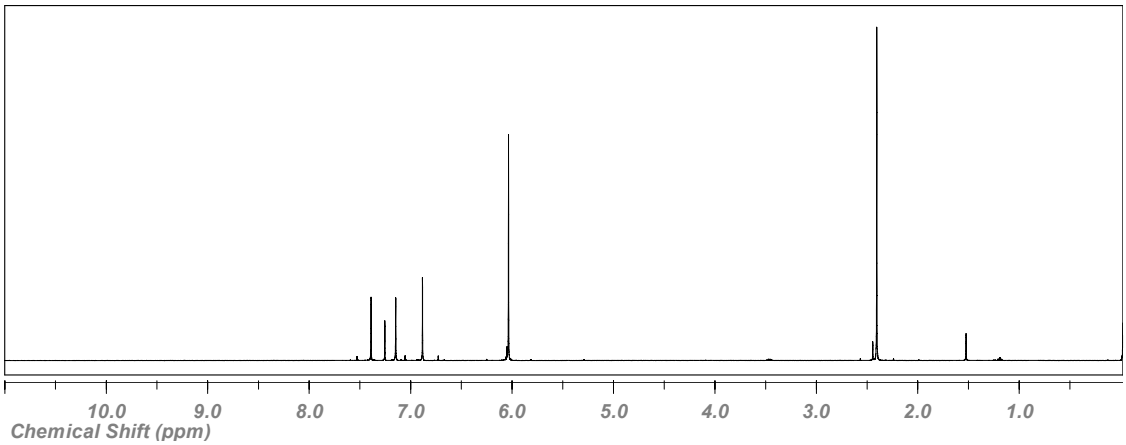
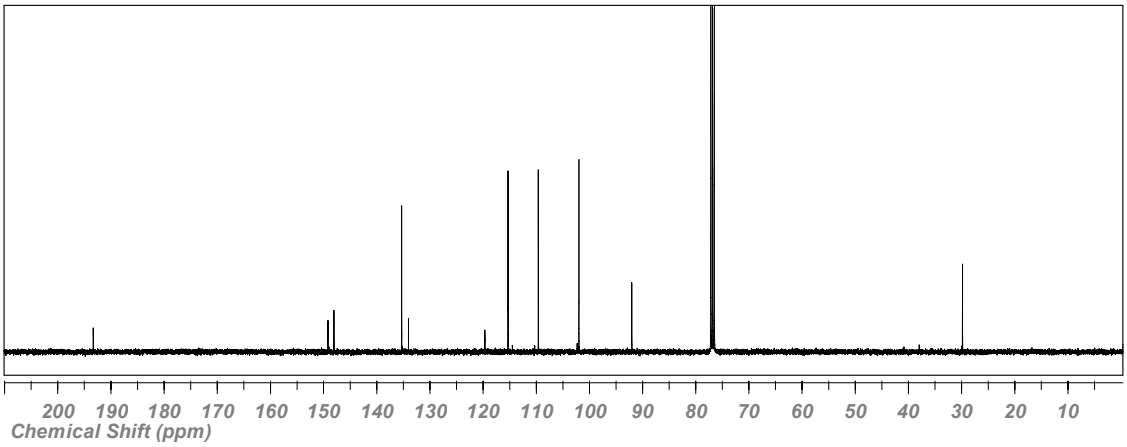
Chemical Shift (ppm)


Br
Br
O
O
O
S


10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0
Chemical Shift (ppm)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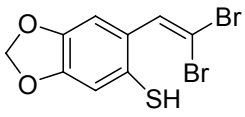
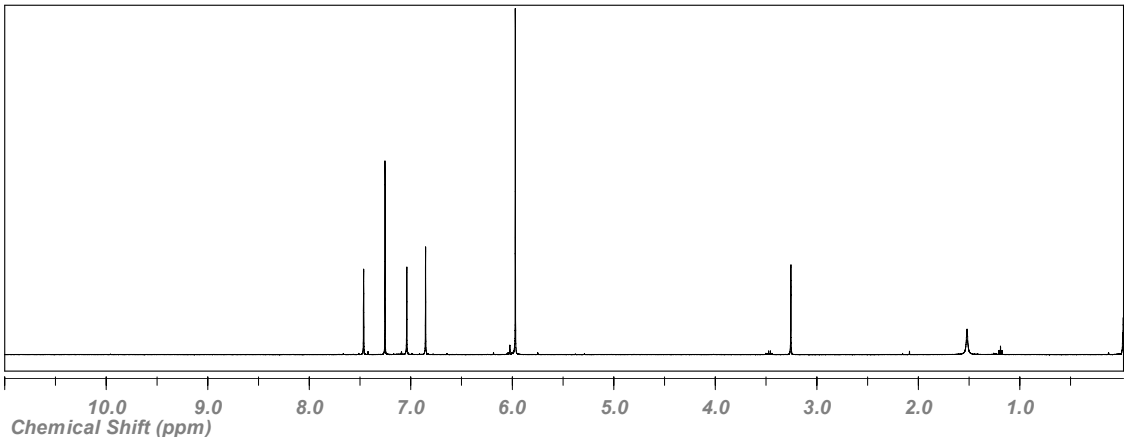
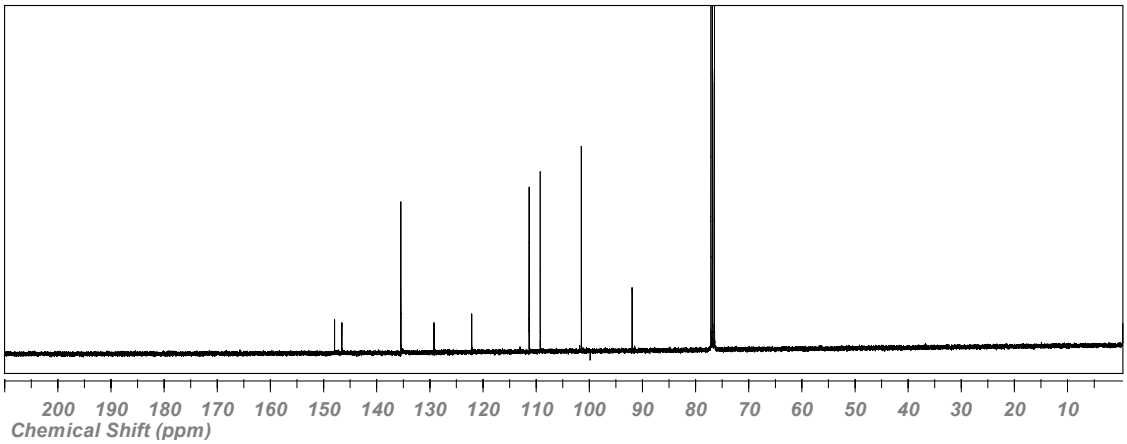
Chemical Shift (ppm)


O
O
Br
Br
SH


10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0
Chemical Shift (ppm)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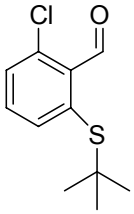
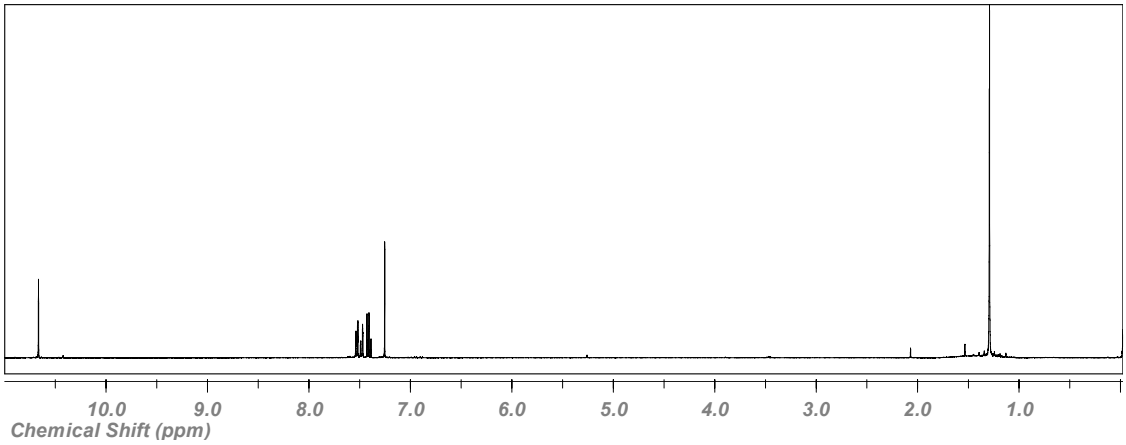
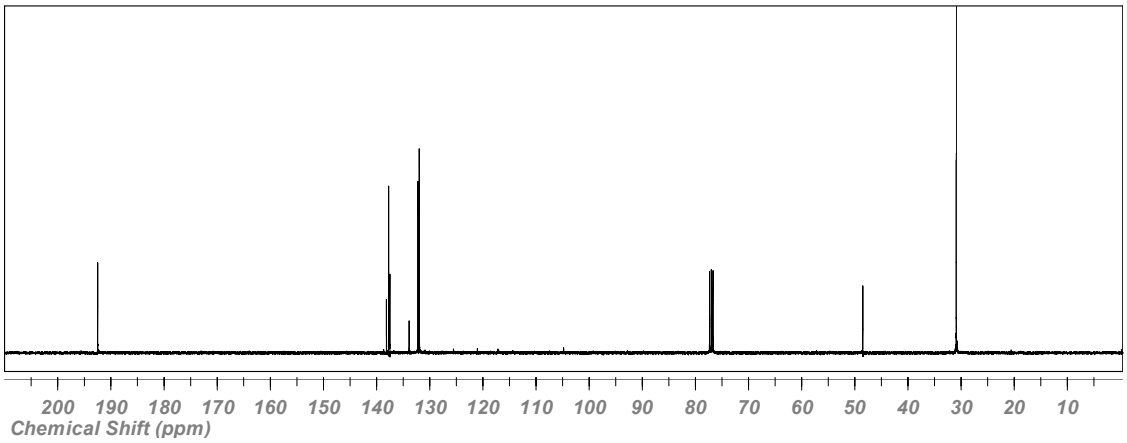
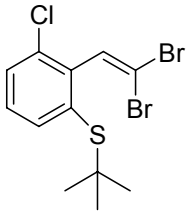
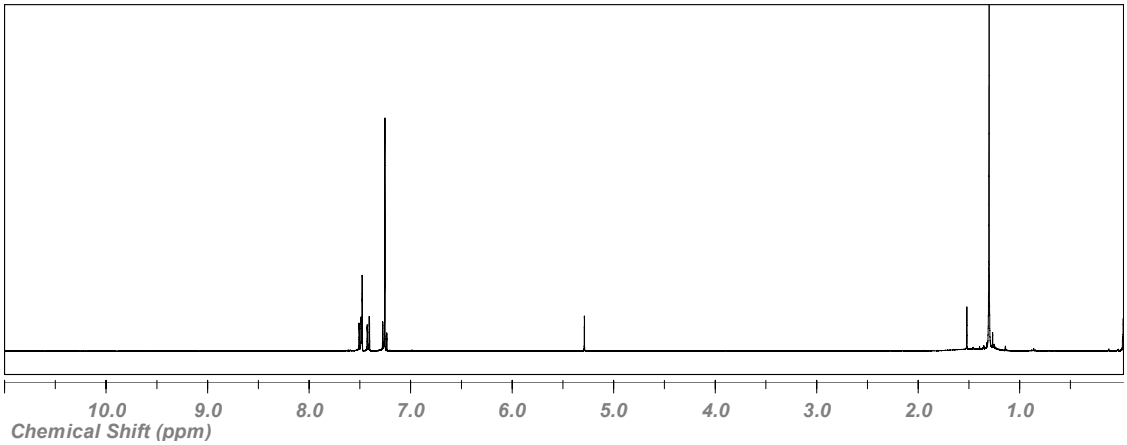
Chemical Shift (ppm)

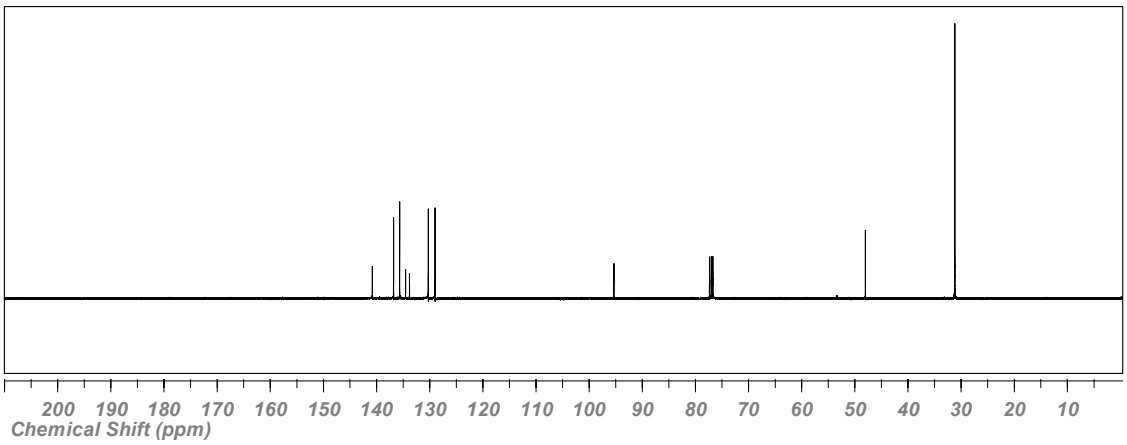

Cl
O
S


10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
Chemical Shift (ppm)


200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
Chemical Shift (ppm)


Cl
Br
Br
S


10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0
Chemical Shift (ppm)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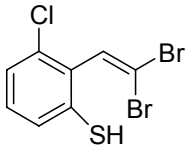
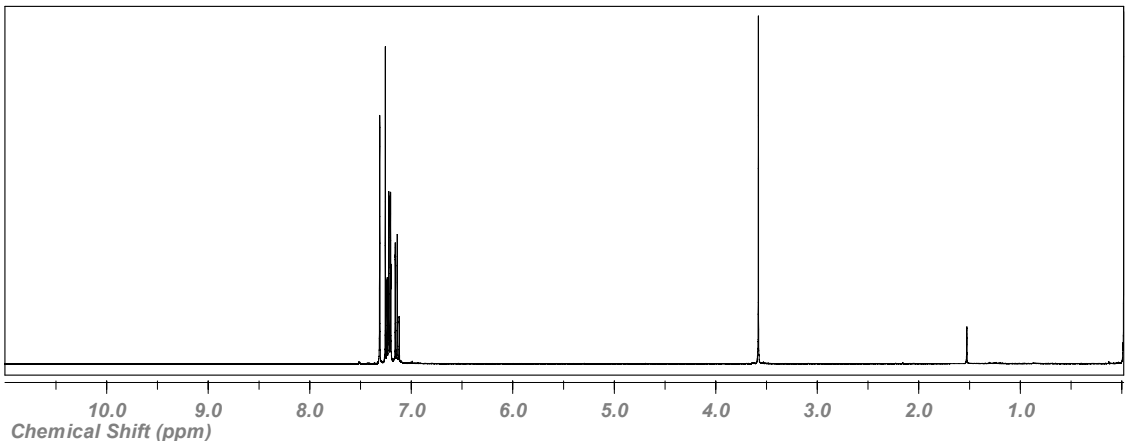
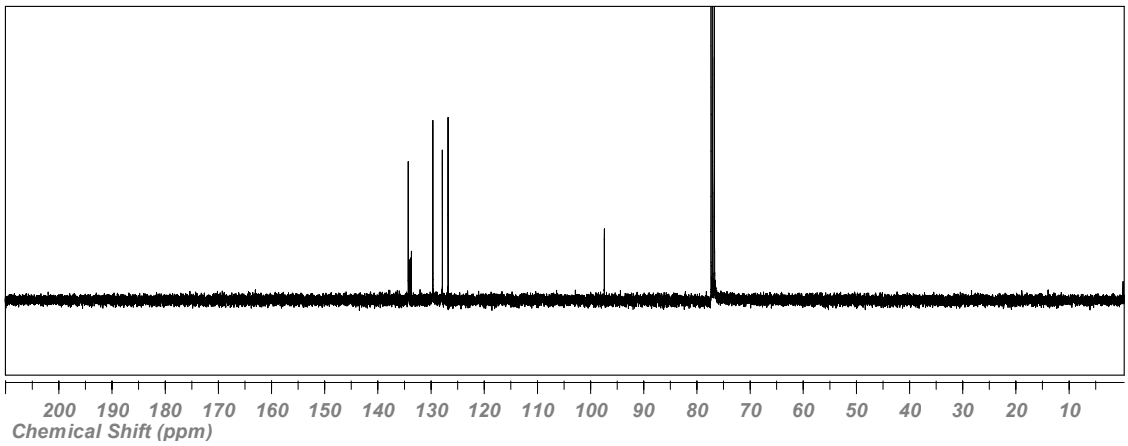
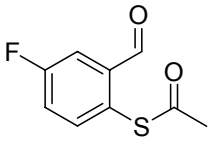
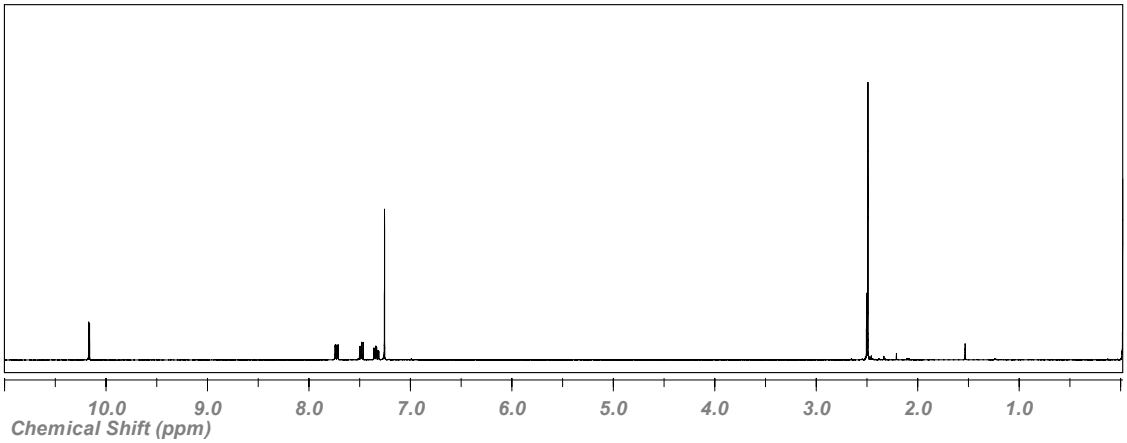
Chemical Shift (ppm)

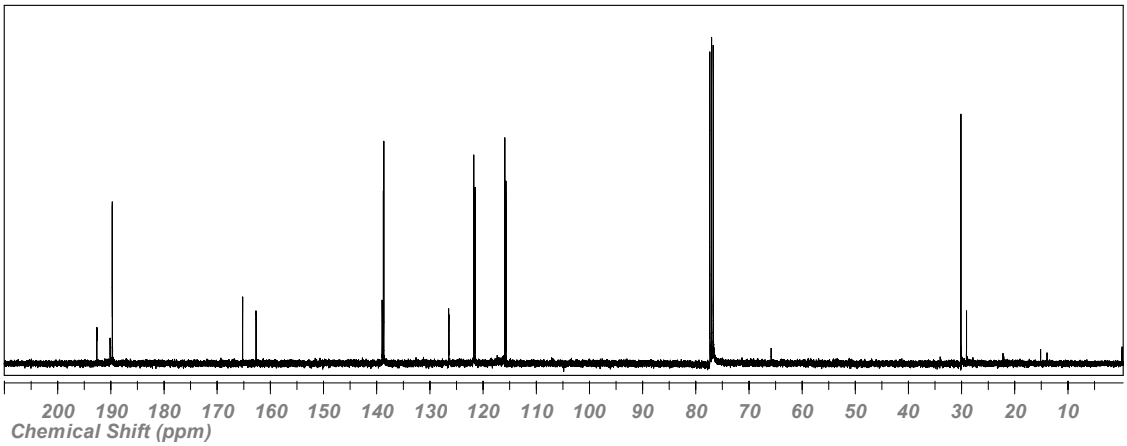

Cl
Br
Br
SH


10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0
Chemical Shift (ppm)


200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
Chemical Shift (ppm)


O
F
O
S


10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0
Chemical Shift (ppm)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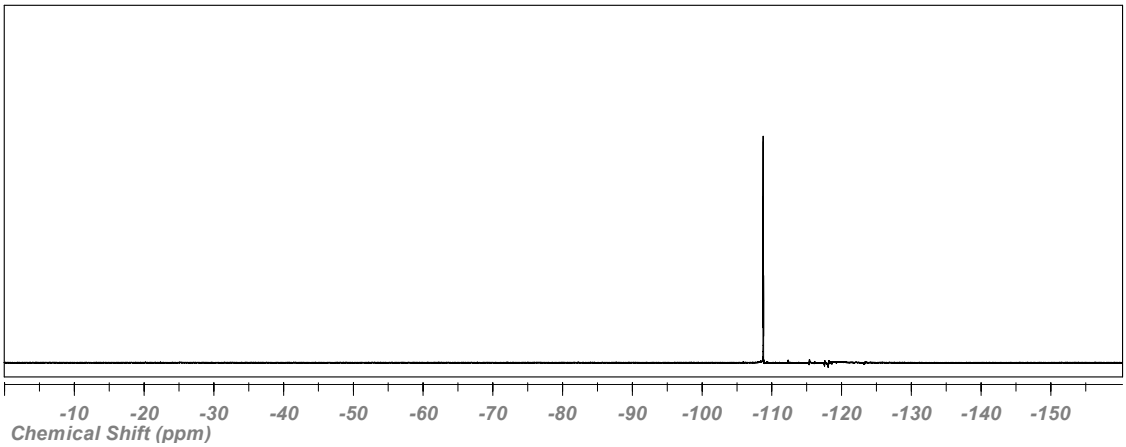
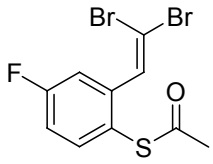
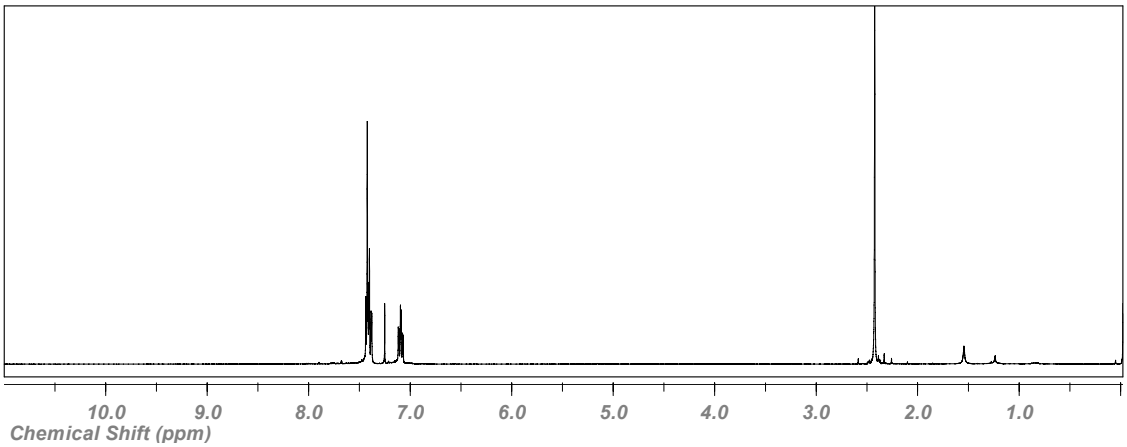
Chemical Shift (ppm)


-10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150
Chemical Shift (ppm)


Br
Br
F
O
S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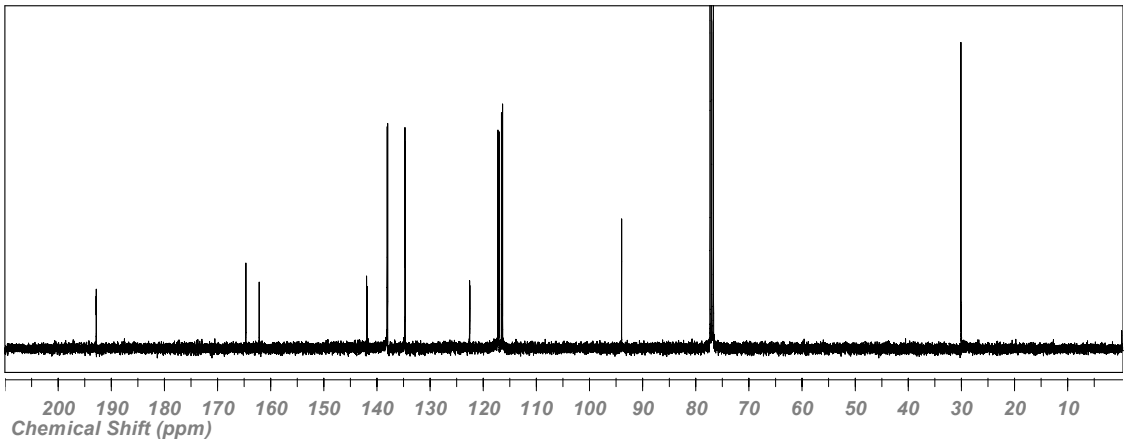
Chemical Shift (ppm)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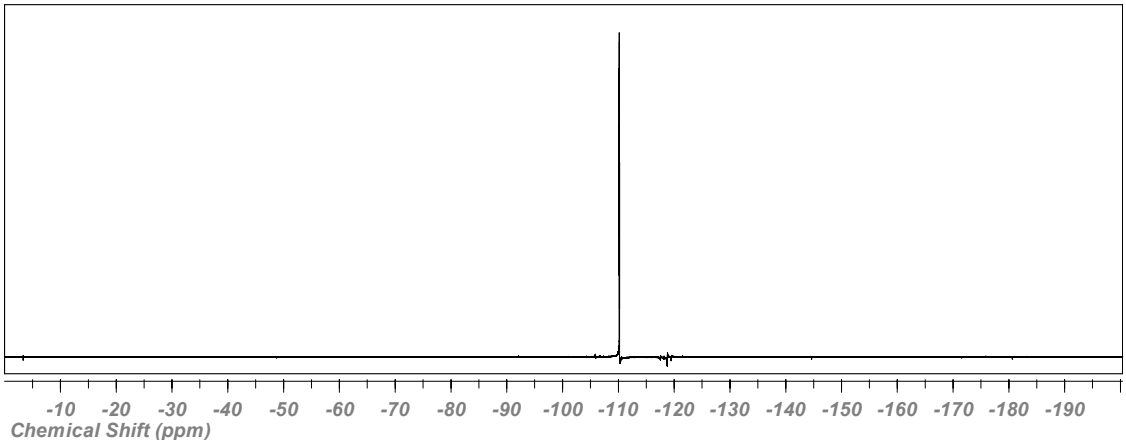
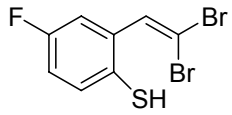
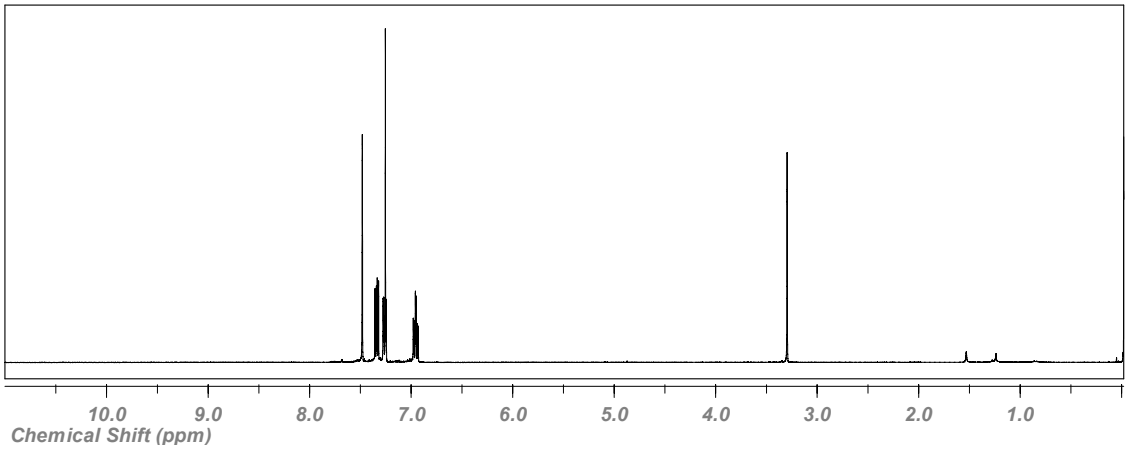
Chemical Shift (ppm)


-10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190
Chemical Shift (ppm)


F
Br
Br
SH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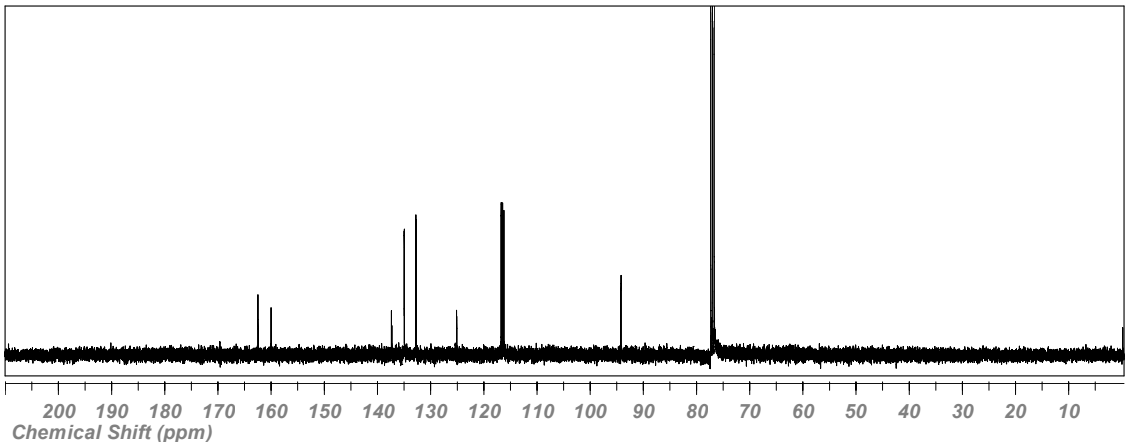
Chemical Shift (ppm)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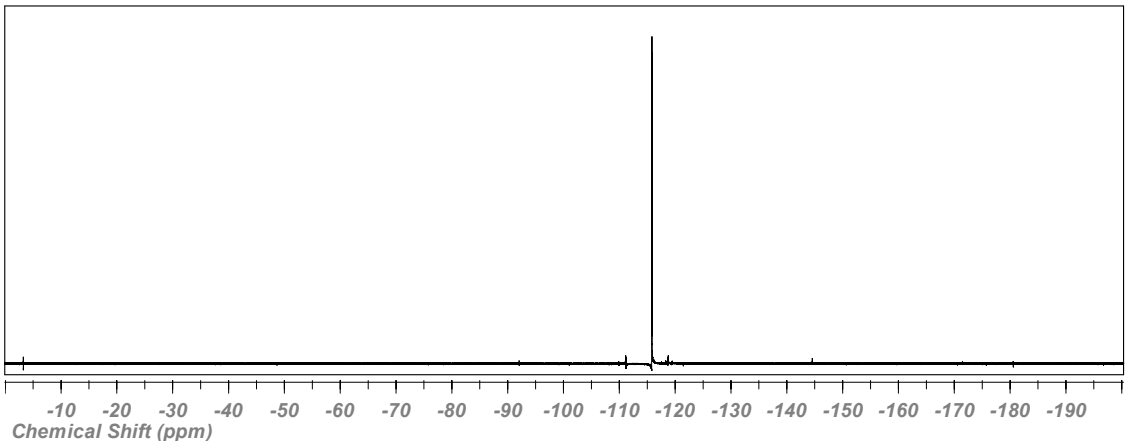
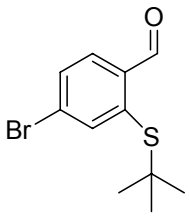
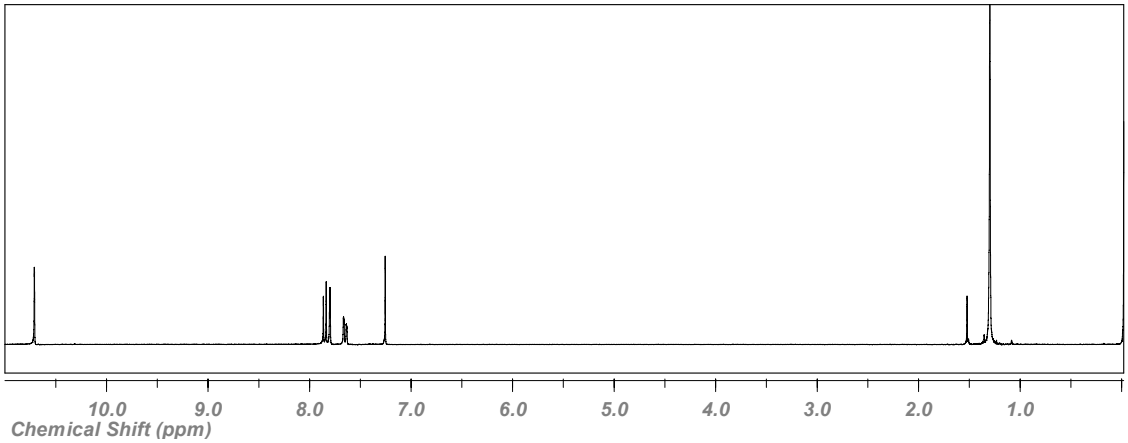
Chemical Shift (ppm)


-10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190
Chemical Shift (ppm)


O
Br
S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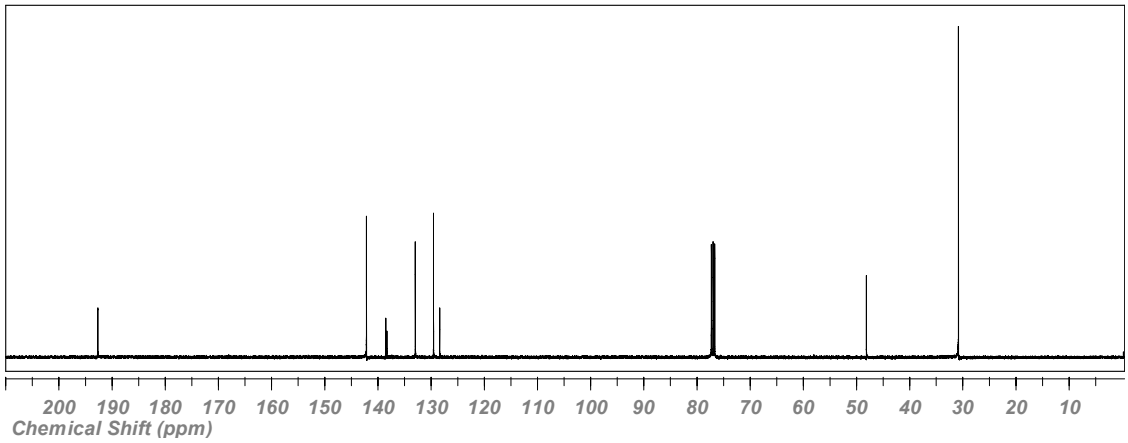
Chemical Shift (ppm)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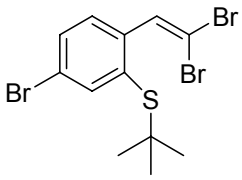
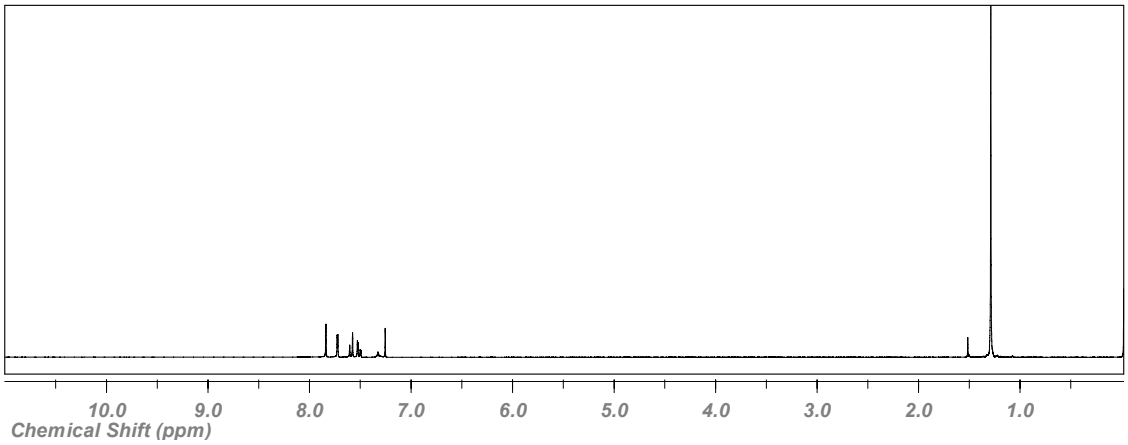
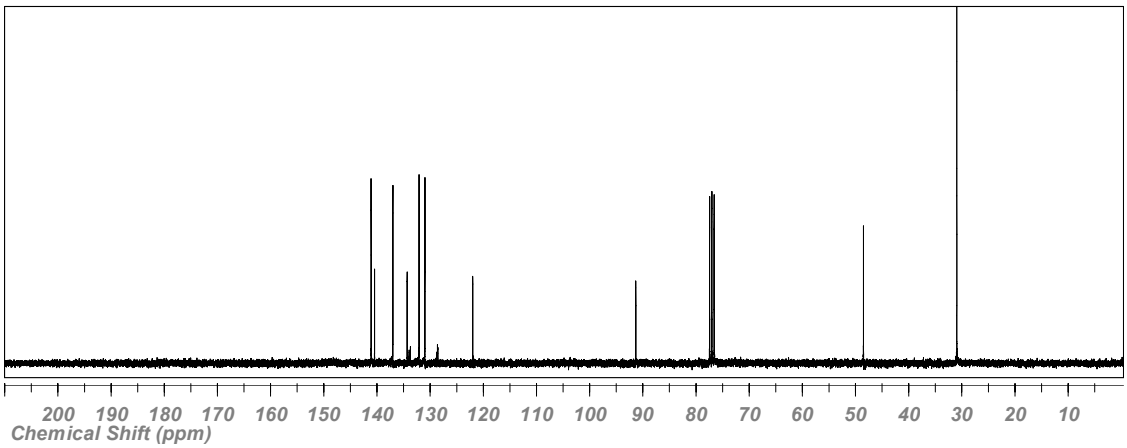
Chemical Shift (ppm)


Br
Br
Br
S


10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0
Chemical Shift (ppm)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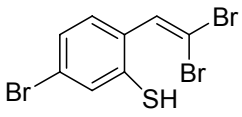
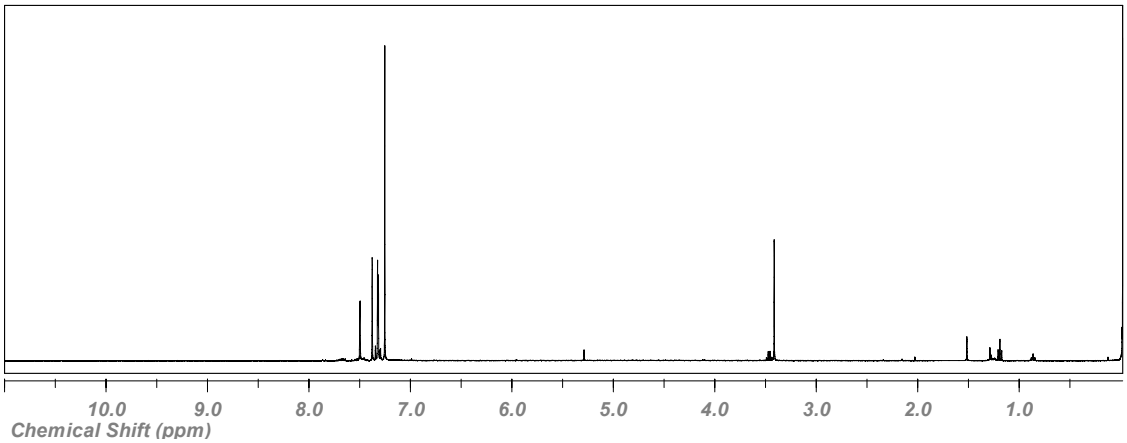
Chemical Shift (ppm)


Br
Br
Br
SH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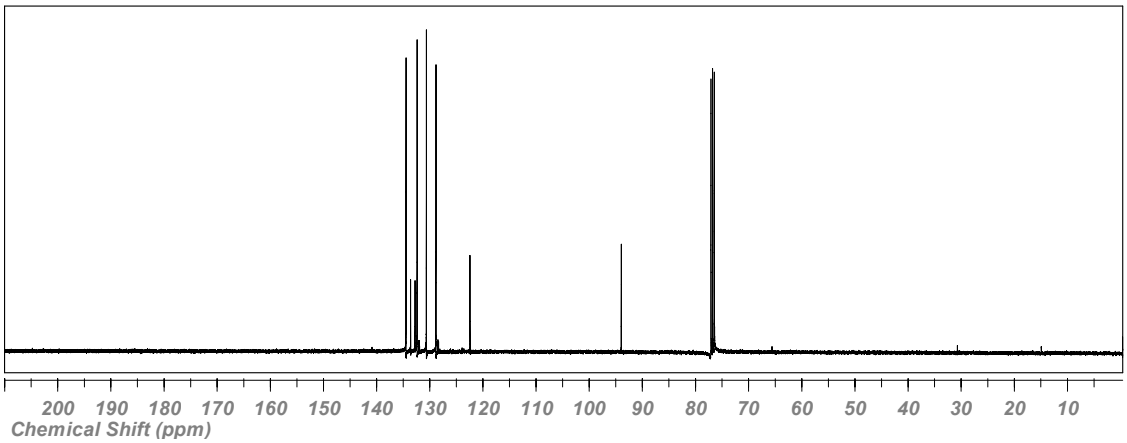
Chemical Shift (ppm)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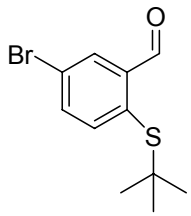
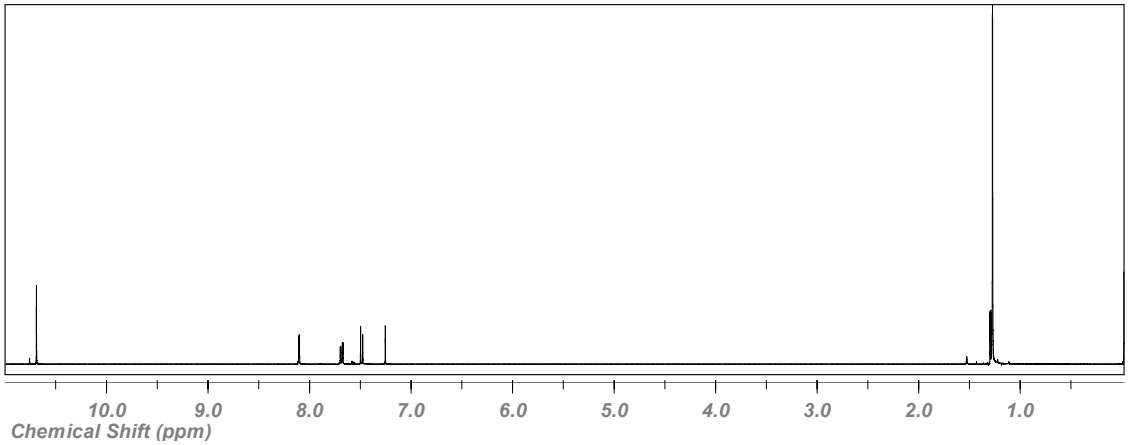
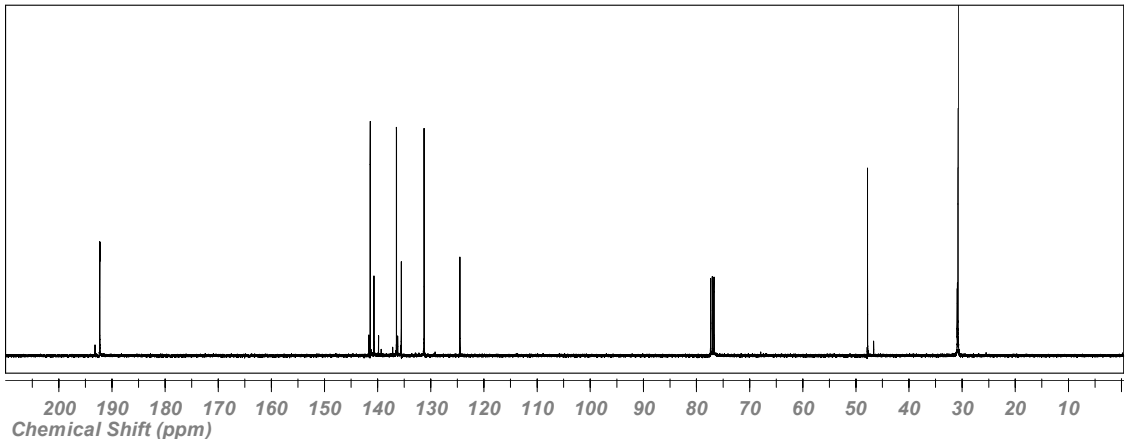
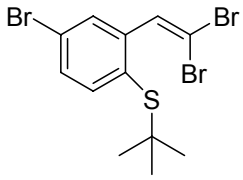
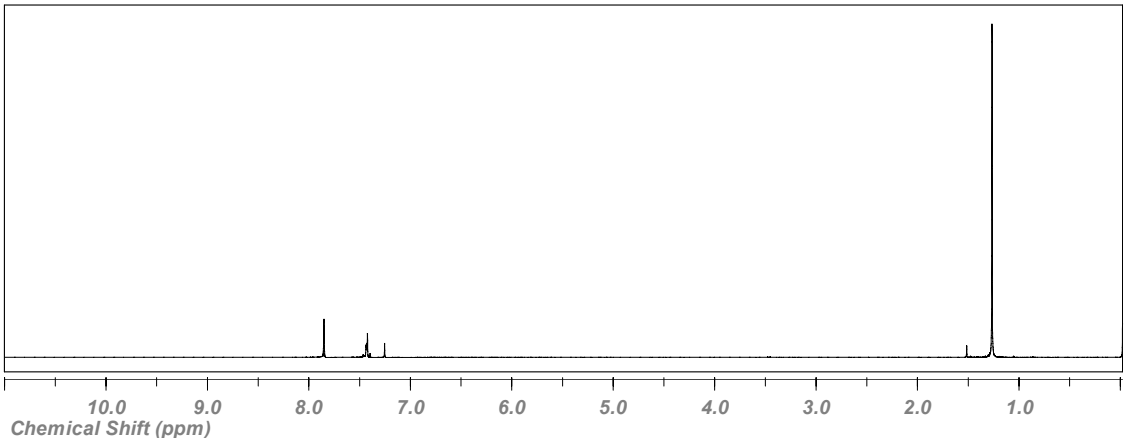
Chemical Shift (ppm)

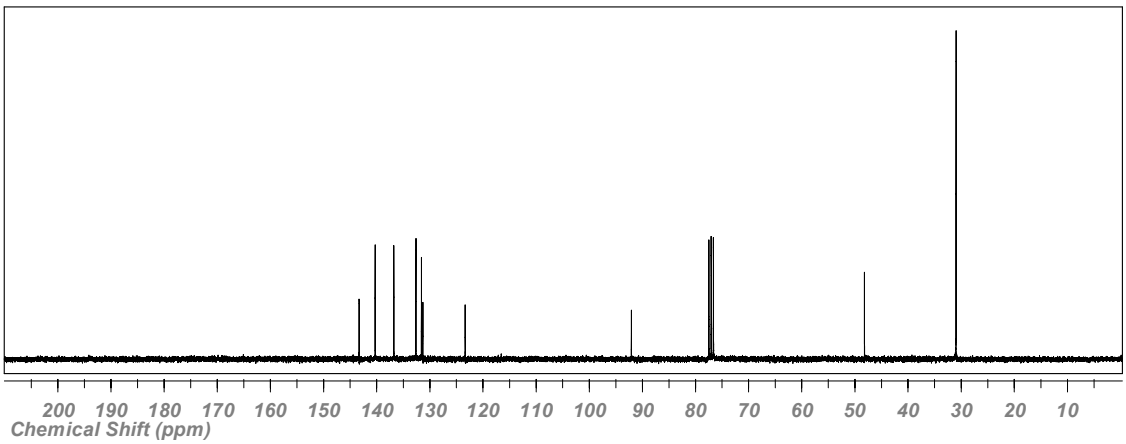

O
Br
S


10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
Chemical Shift (ppm)


200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
Chemical Shift (ppm)


Br
Br
Br
S


10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0
Chemical Shift (ppm)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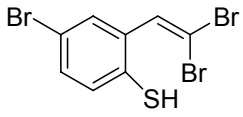
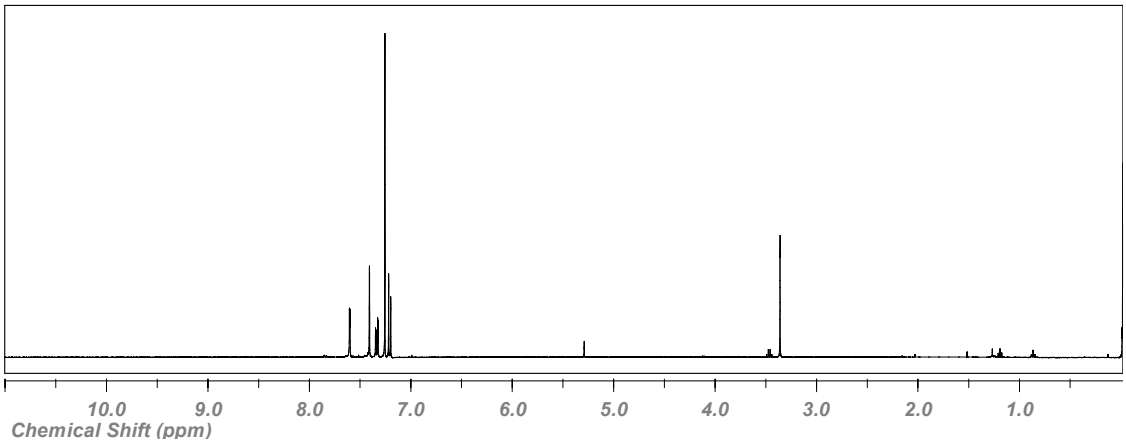
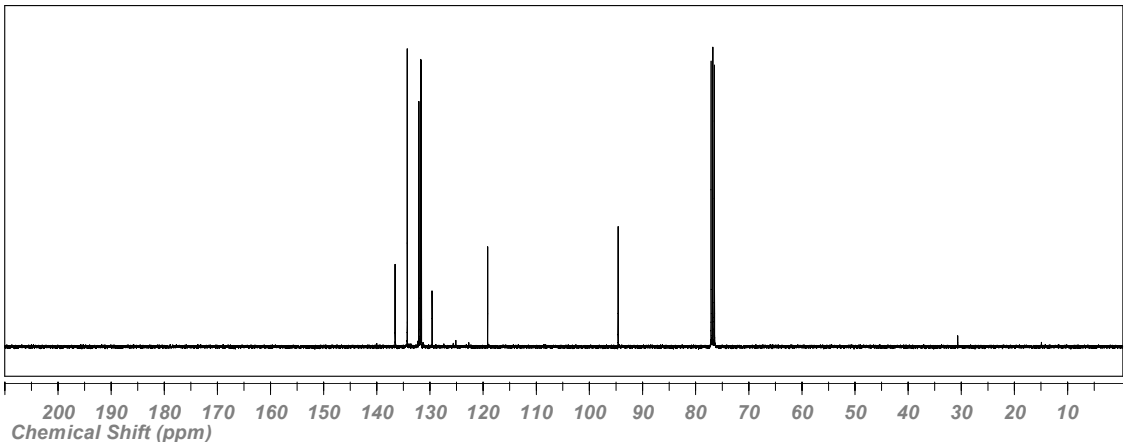
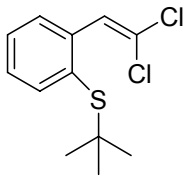
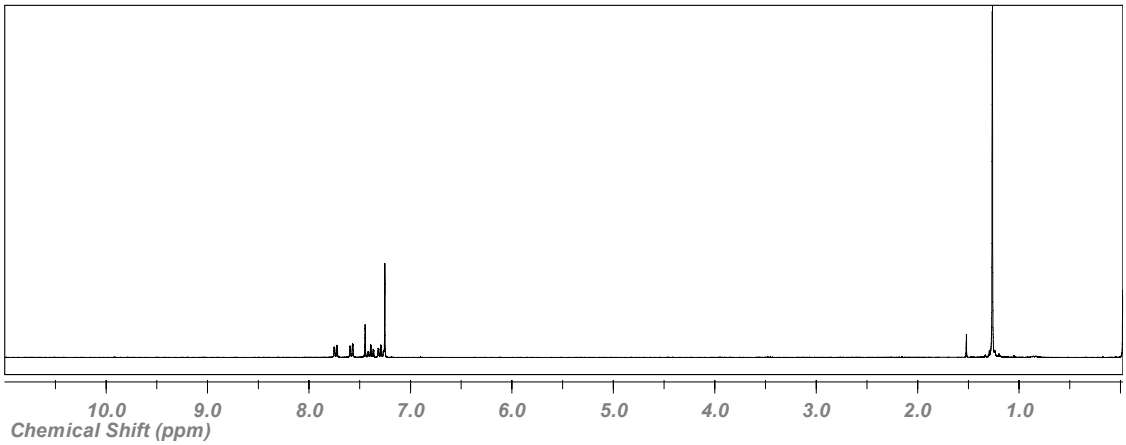
Chemical Shift (ppm)

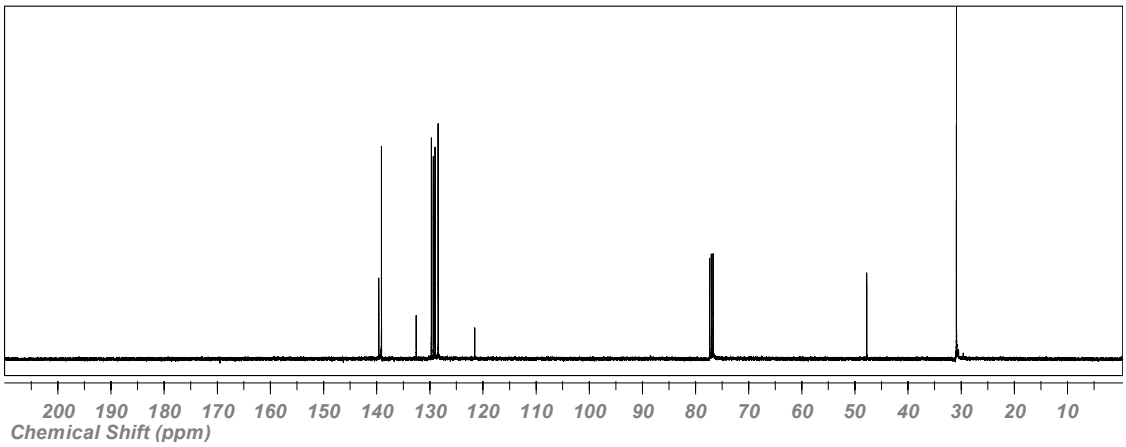

Br
Br
Br
SH


10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0
Chemical Shift (ppm)


200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
Chemical Shift (ppm)


Cl
Cl
S


10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0
Chemical Shift (ppm)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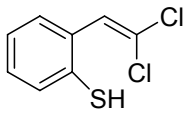
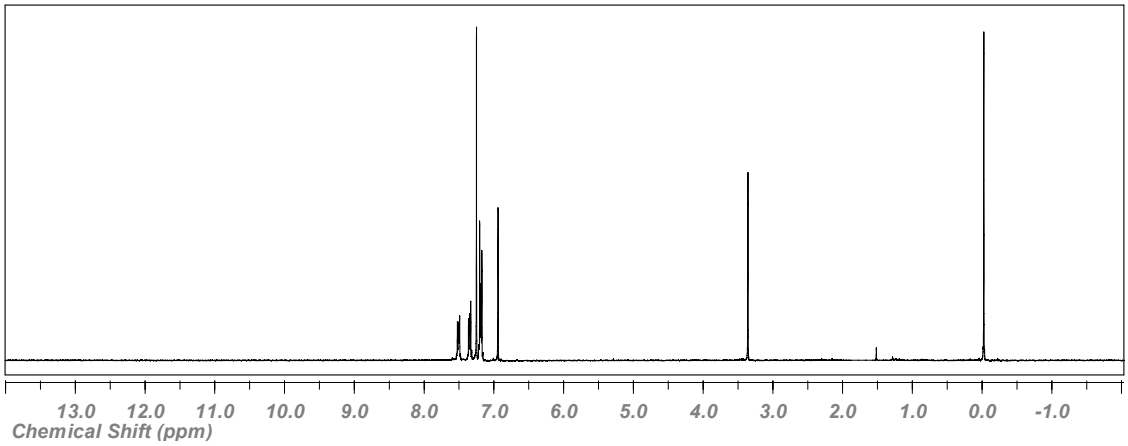
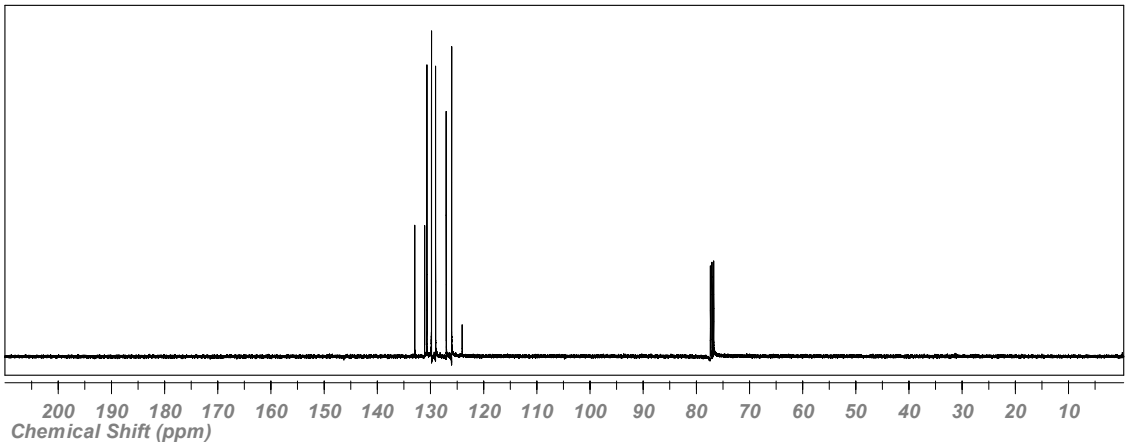
Chemical Shift (ppm)


Cl
Cl
SH


13.0 12.0 11.0 10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0 -1.0
Chemical Shift (ppm)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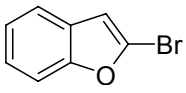
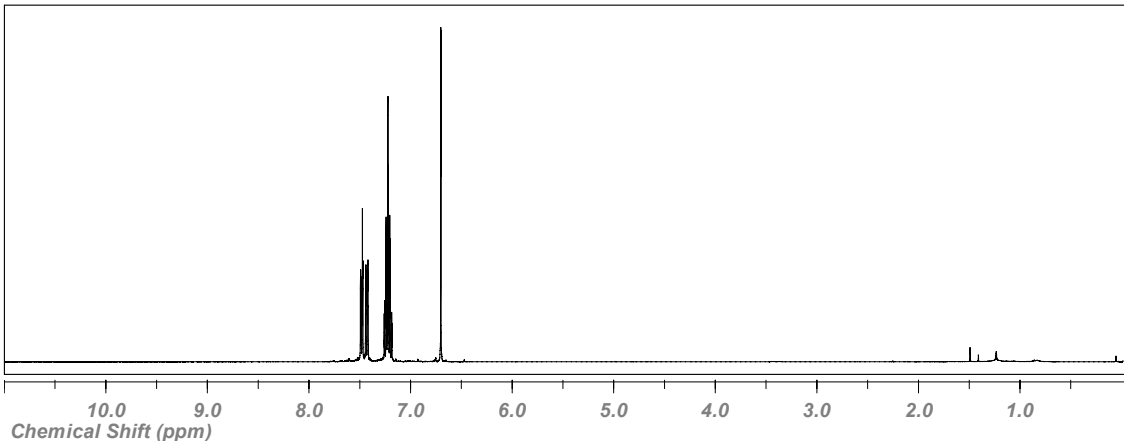
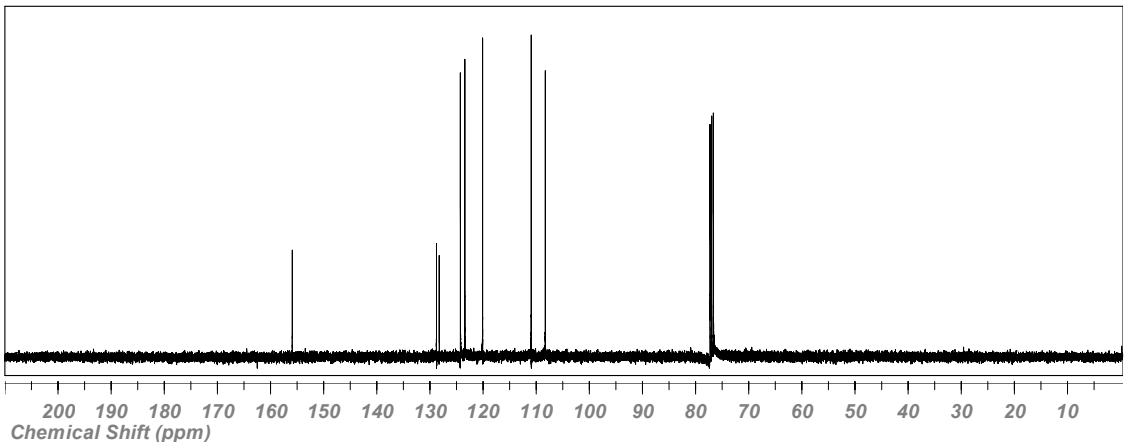
Chemical Shift (ppm)


Br
O


10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0
Chemical Shift (ppm)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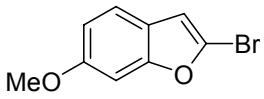
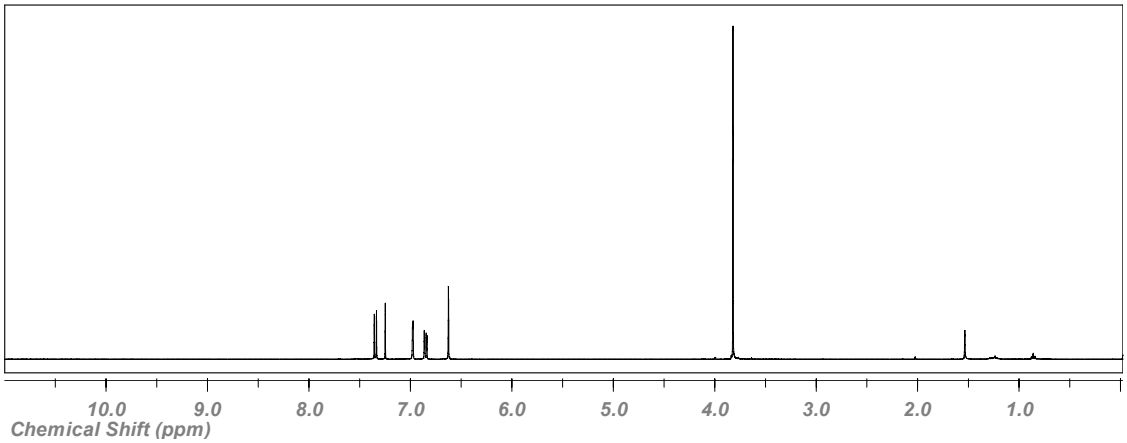
Chemical Shift (ppm)


Br
MeO
O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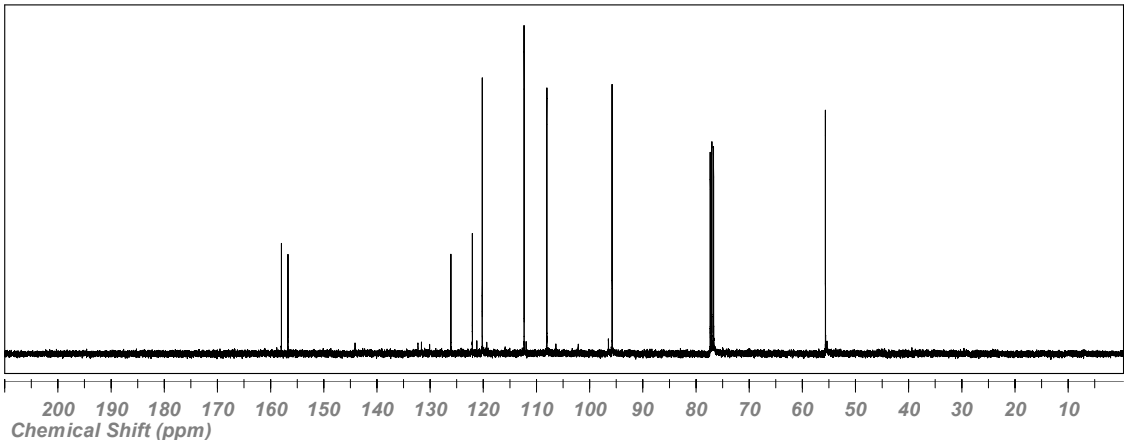
Chemical Shift (ppm)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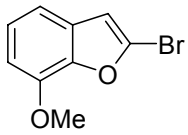
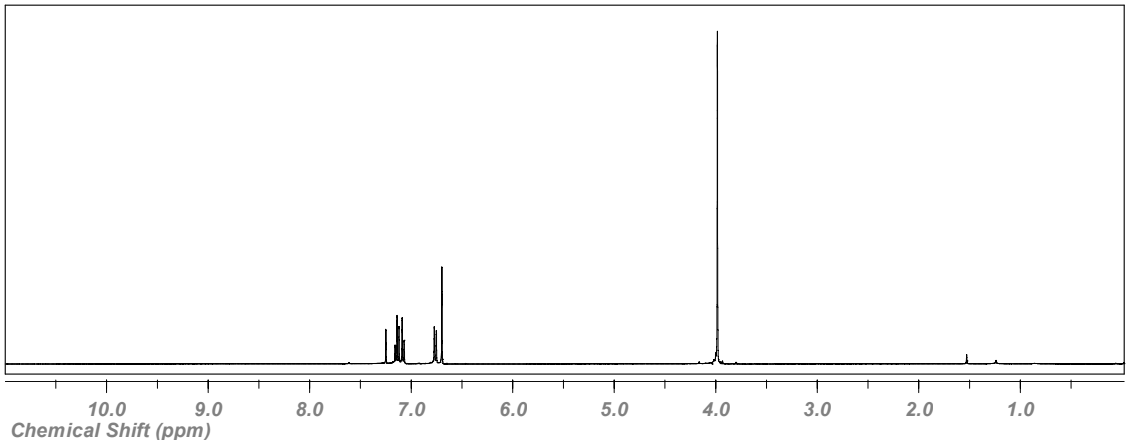
Chemical Shift (ppm)


Br
O
OMe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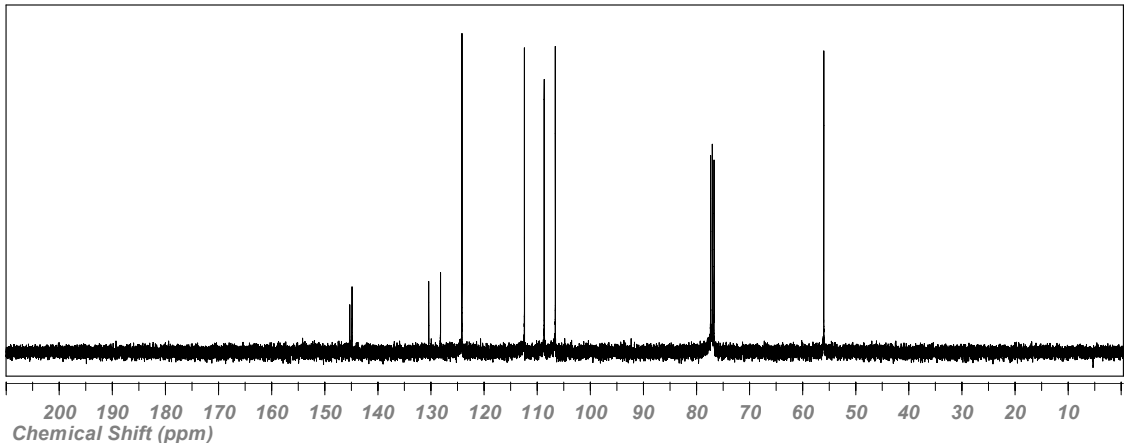
Chemical Shift (ppm)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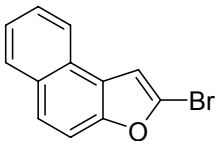
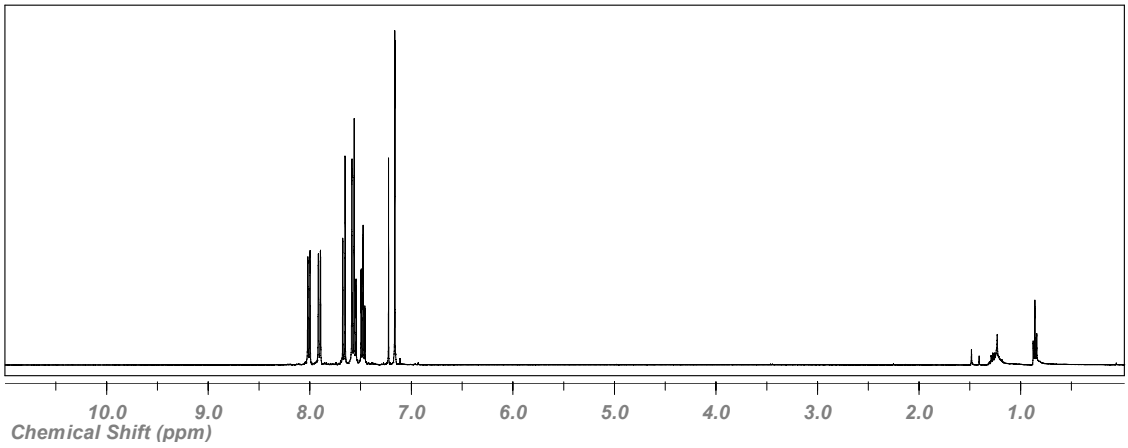
Chemical Shift (ppm)


Br
O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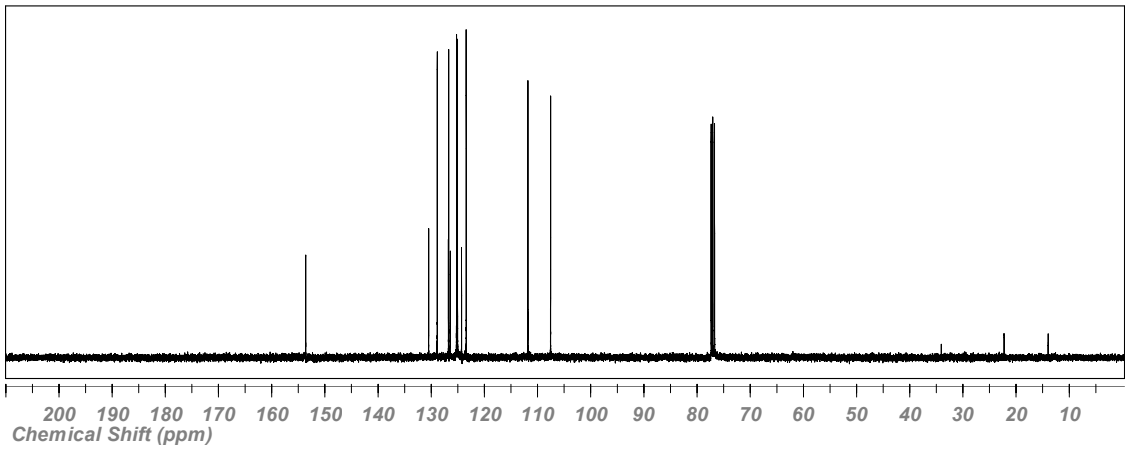
Chemical Shift (ppm)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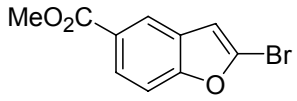
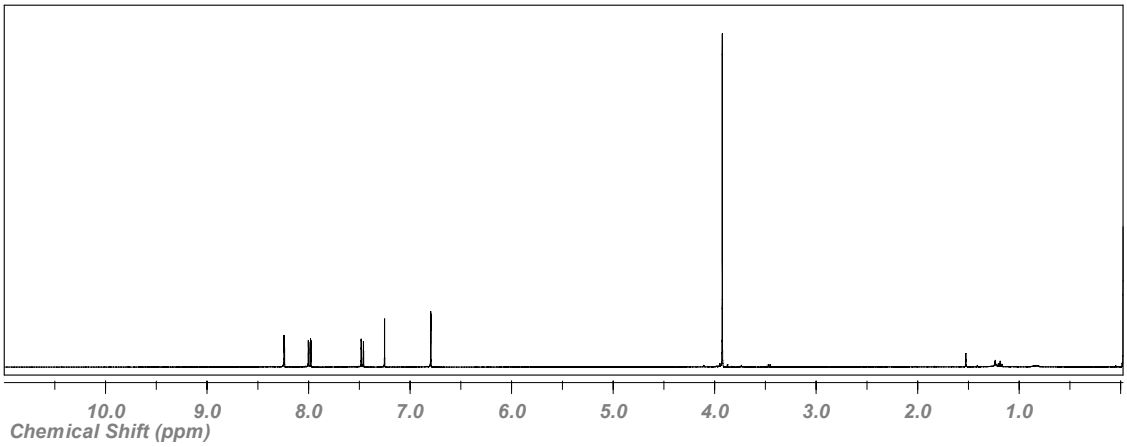
Chemical Shift (ppm)


MeO2C
Br
O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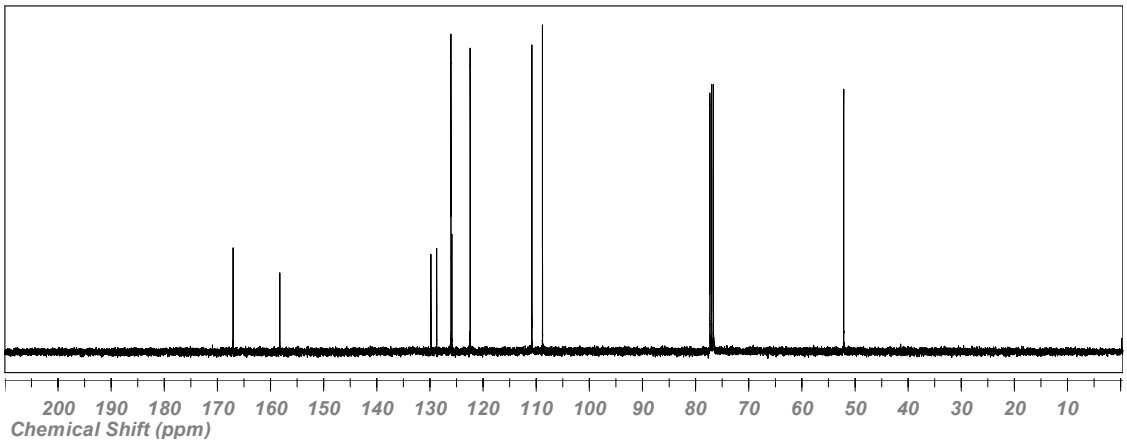
Chemical Shift (ppm)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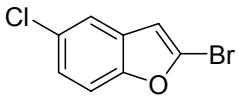
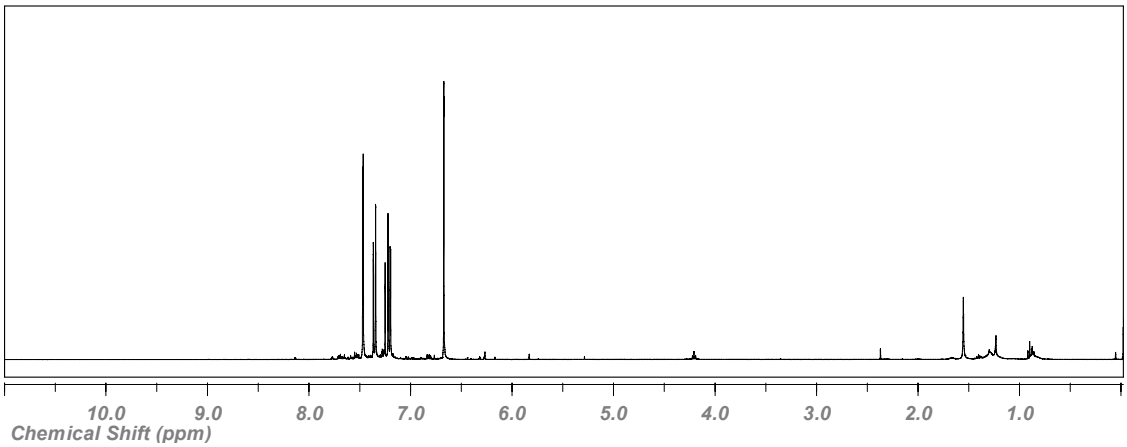
Chemical Shift (ppm)


Cl
Br
O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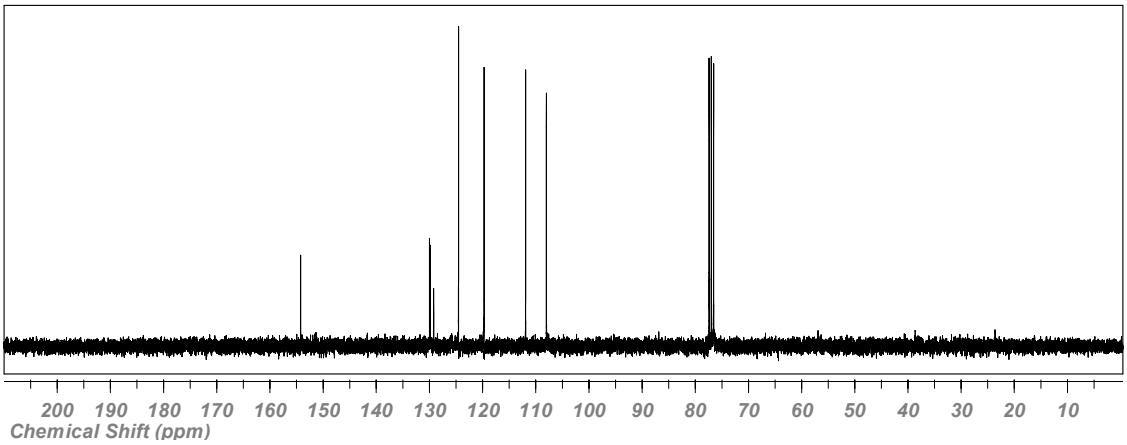
Chemical Shift (ppm)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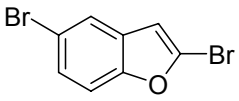
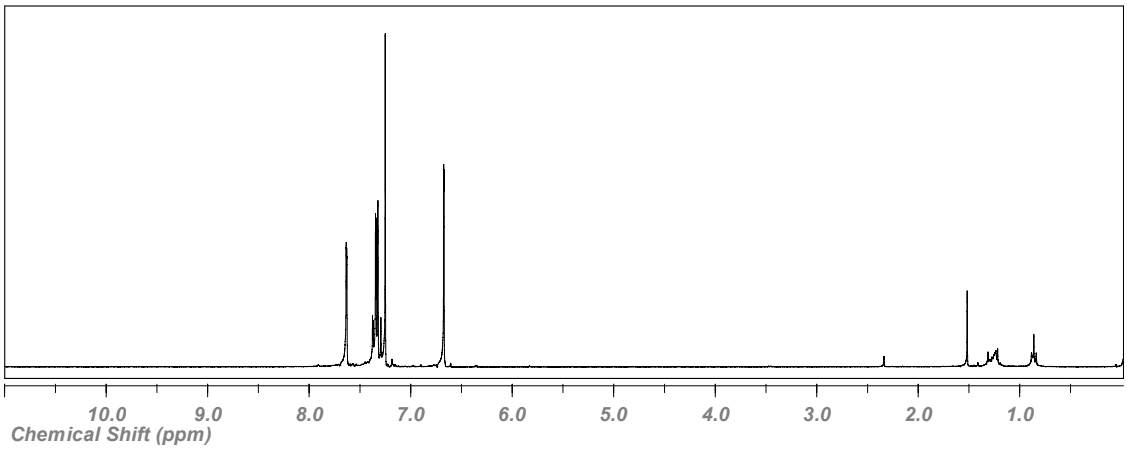
Chemical Shift (ppm)


Br
Br
O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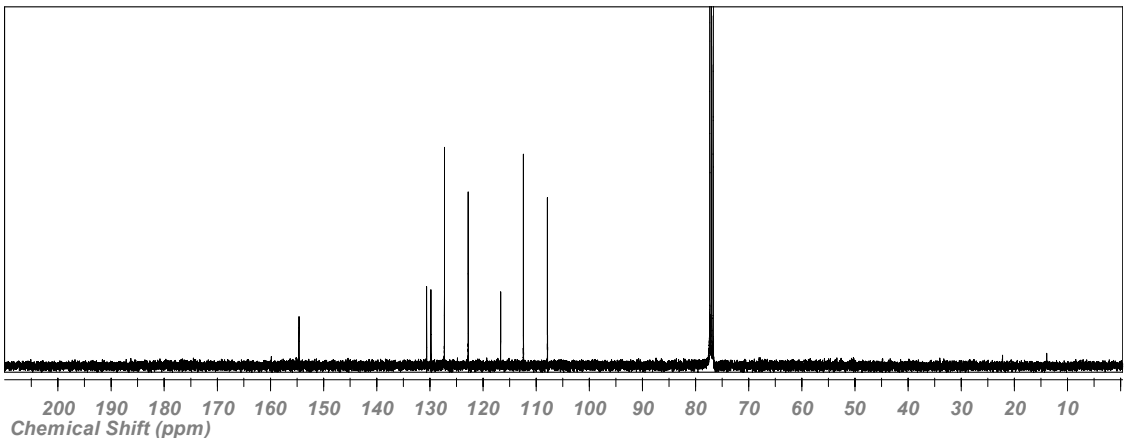
Chemical Shift (ppm)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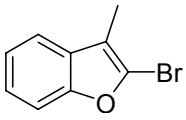
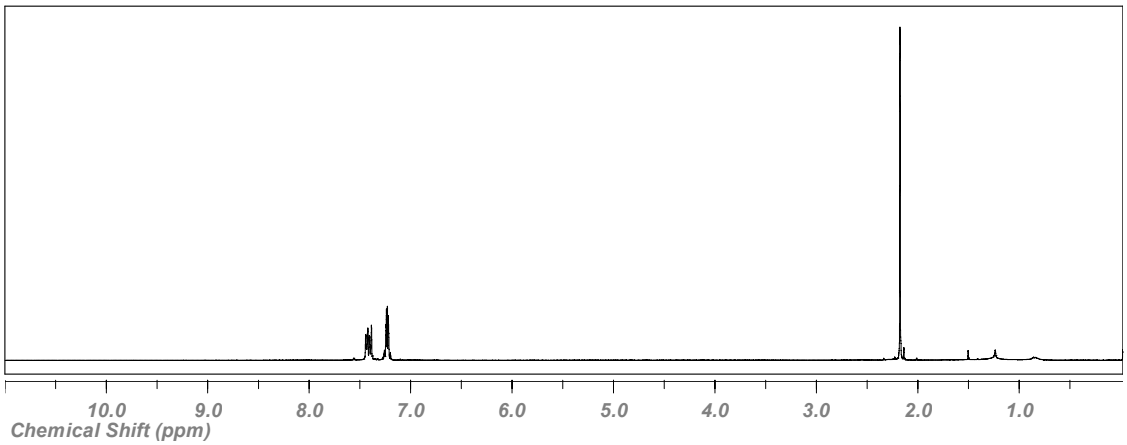
Chemical Shift (ppm)


Br
O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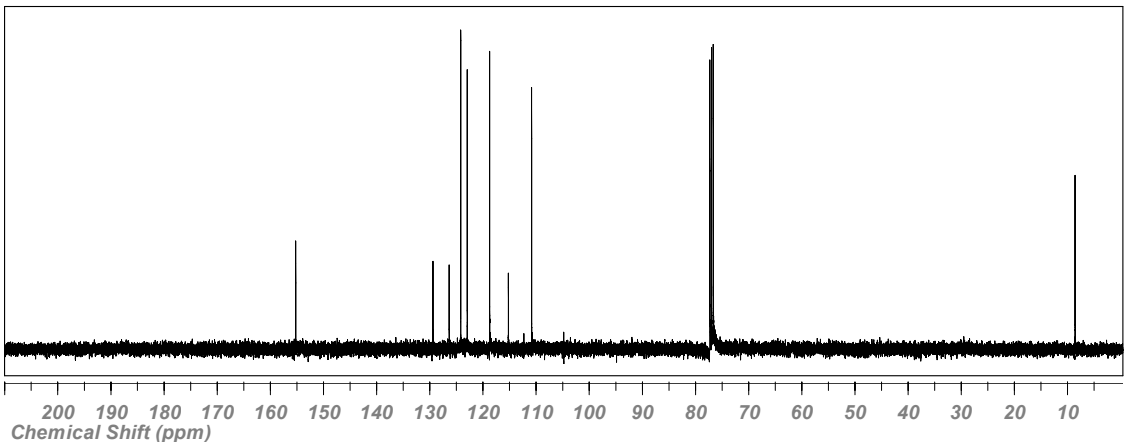
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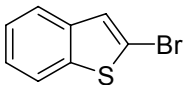
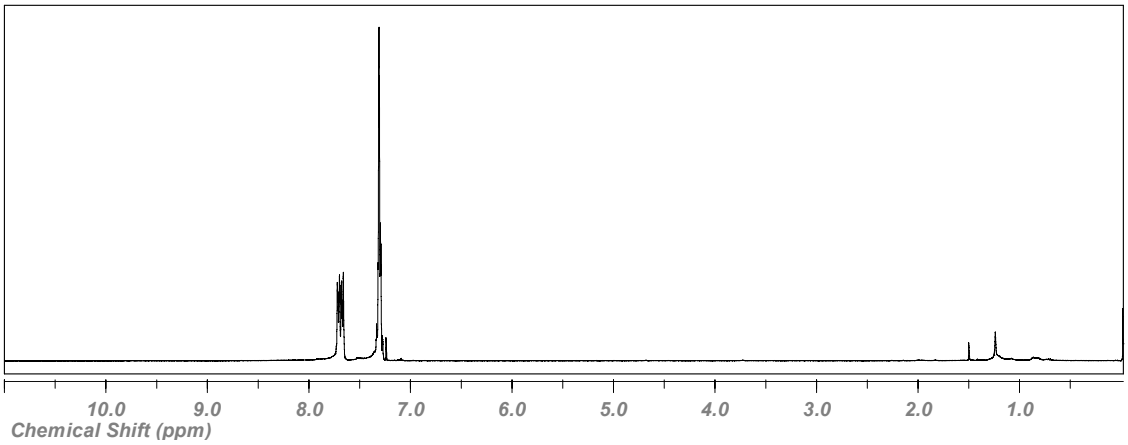
Chemical Shift (ppm)


Br
S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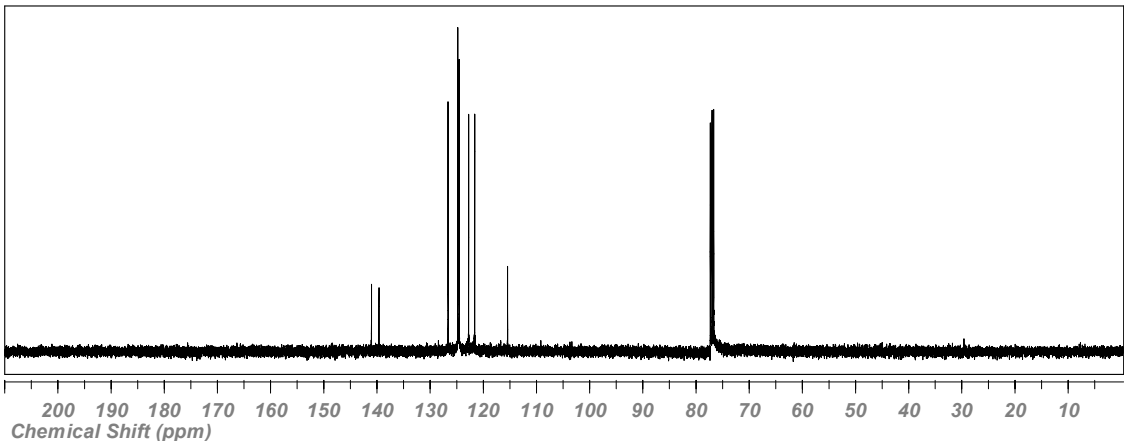
Chemical Shift (ppm)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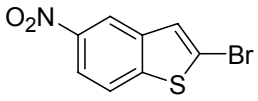
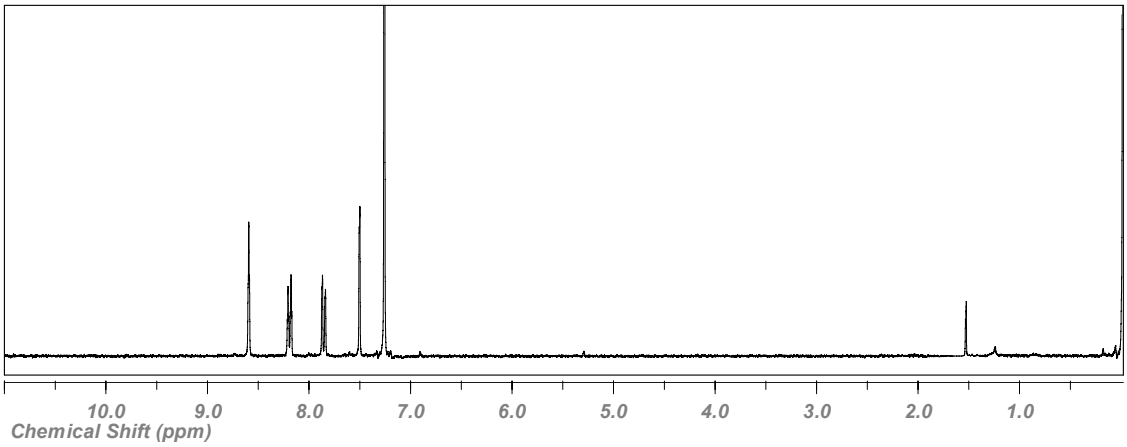
Chemical Shift (ppm)


O2N
Br
S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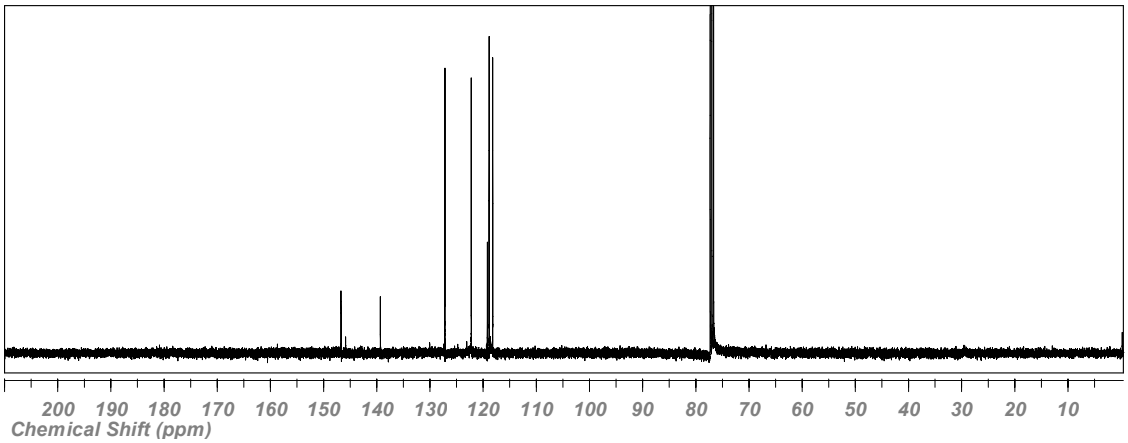
Chemical Shift (ppm)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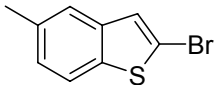
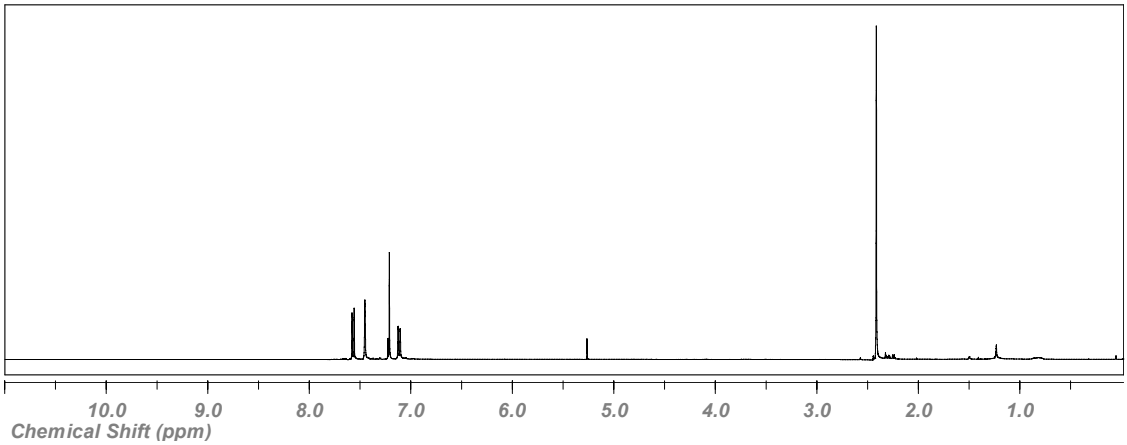
Chemical Shift (ppm)


Br
S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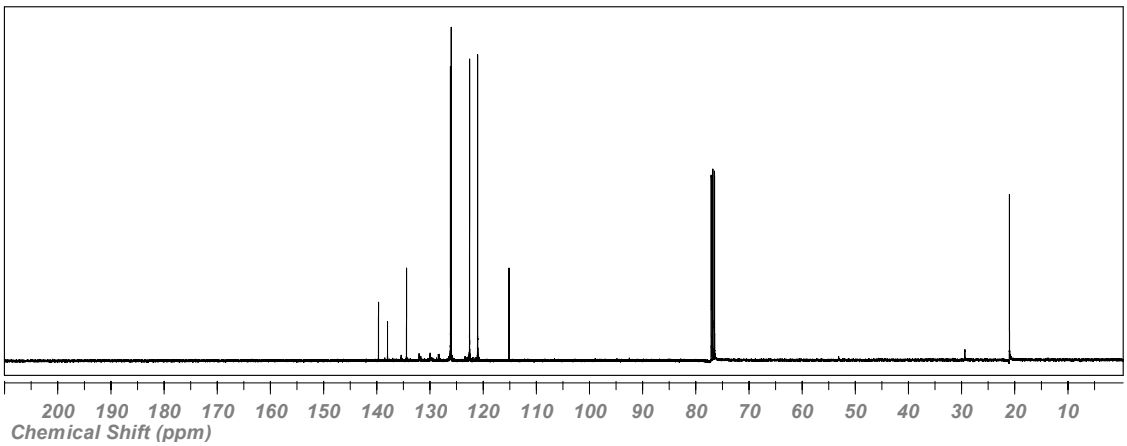
Chemical Shift (ppm)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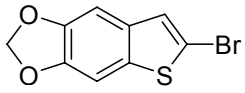
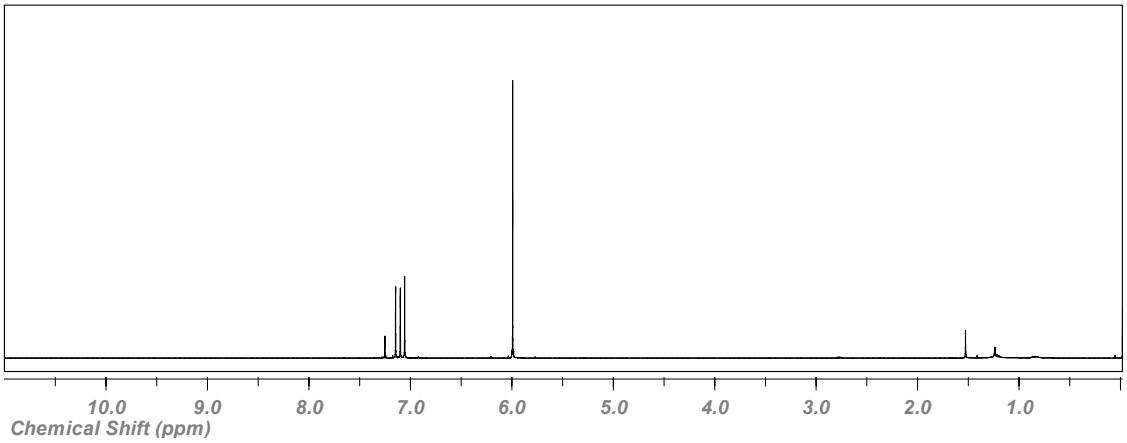
Chemical Shift (ppm)


O
O
S
Br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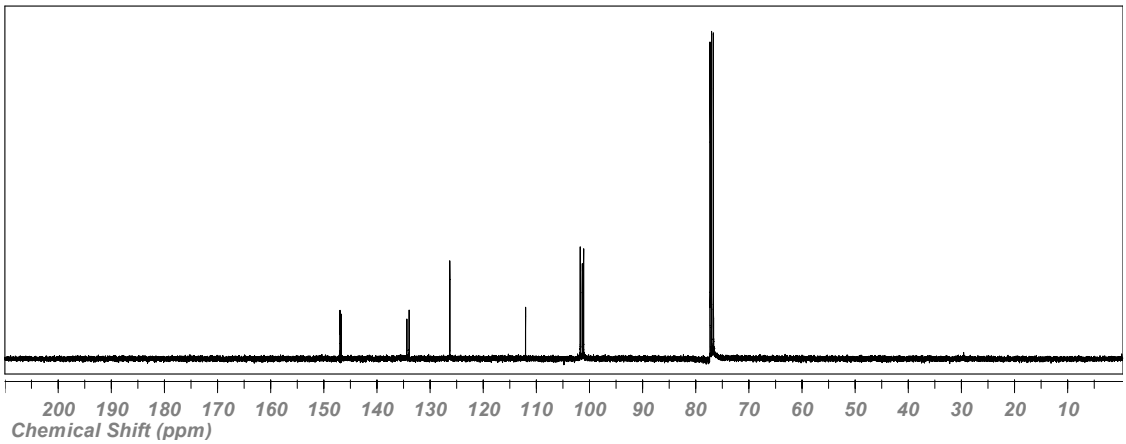
Chemical Shift (ppm)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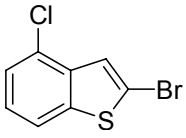
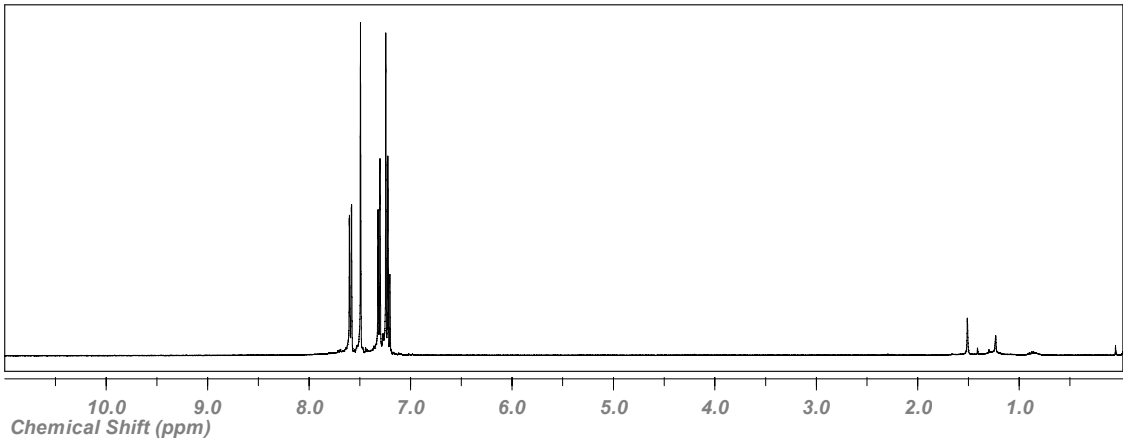
Chemical Shift (ppm)


Cl
Br
S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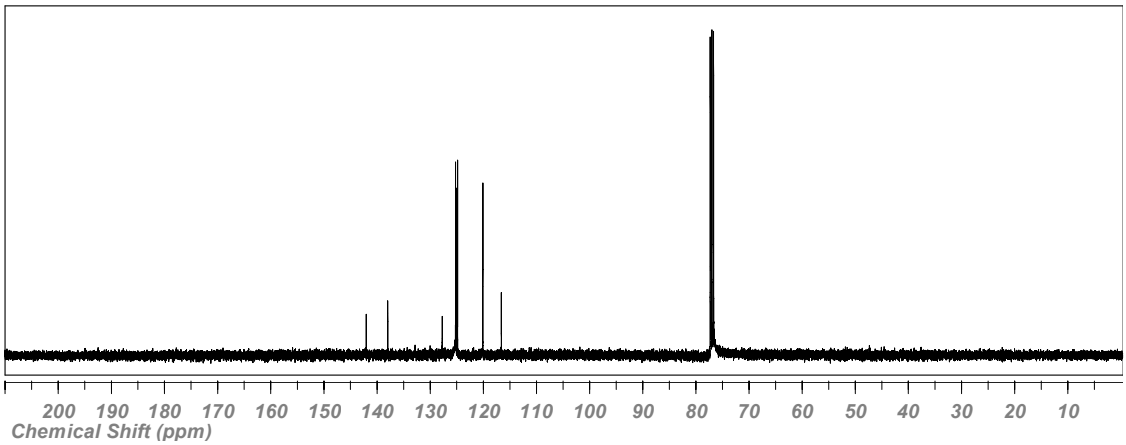
Chemical Shift (ppm)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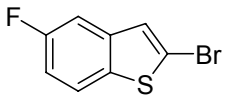
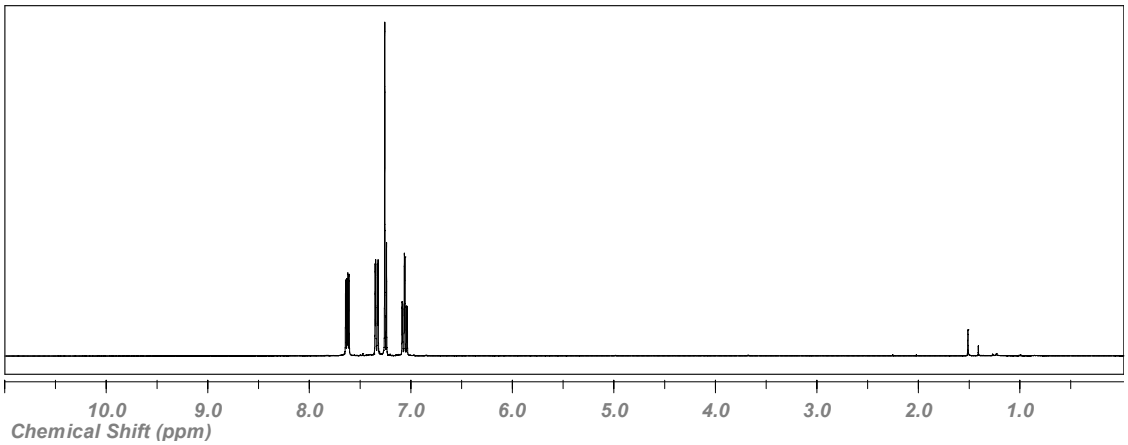
Chemical Shift (ppm)


F
Br
S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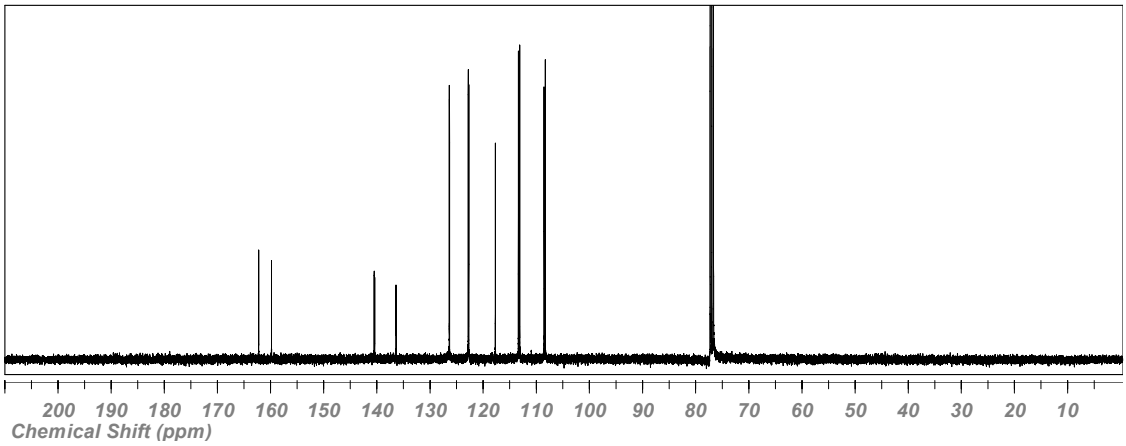
Chemical Shift (ppm)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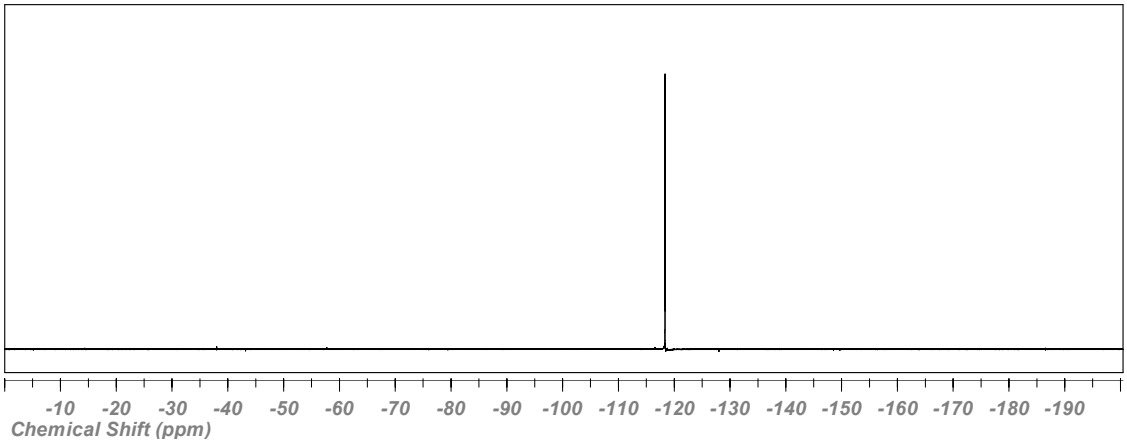
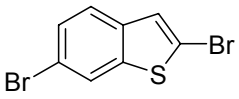
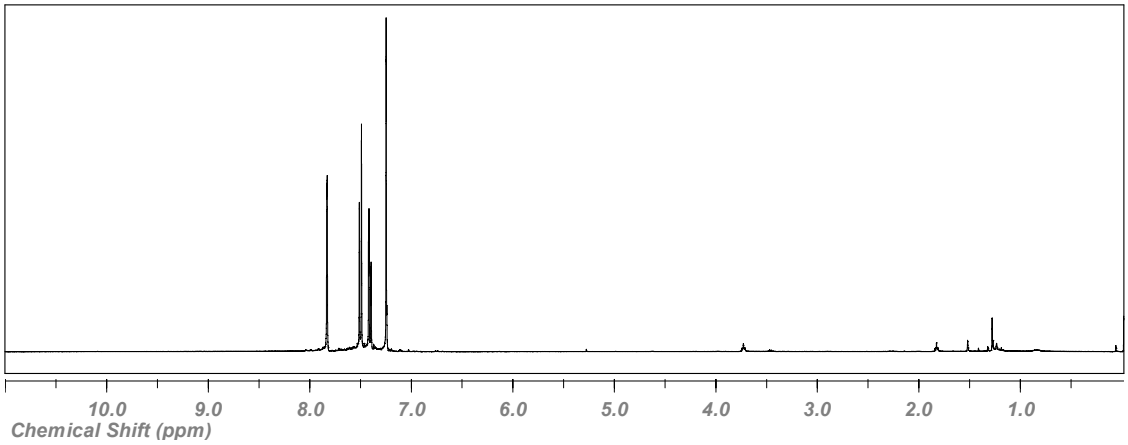
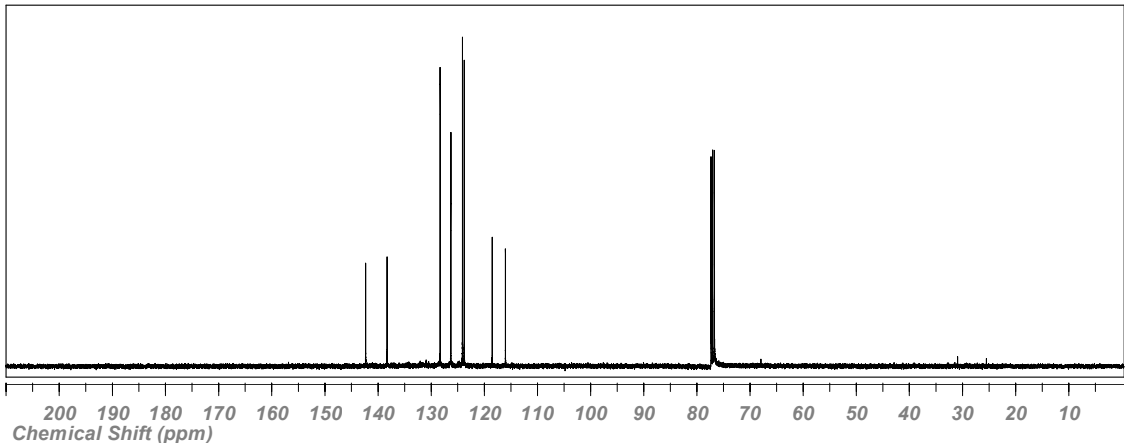
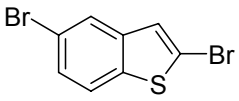
Chemical Shift (ppm)

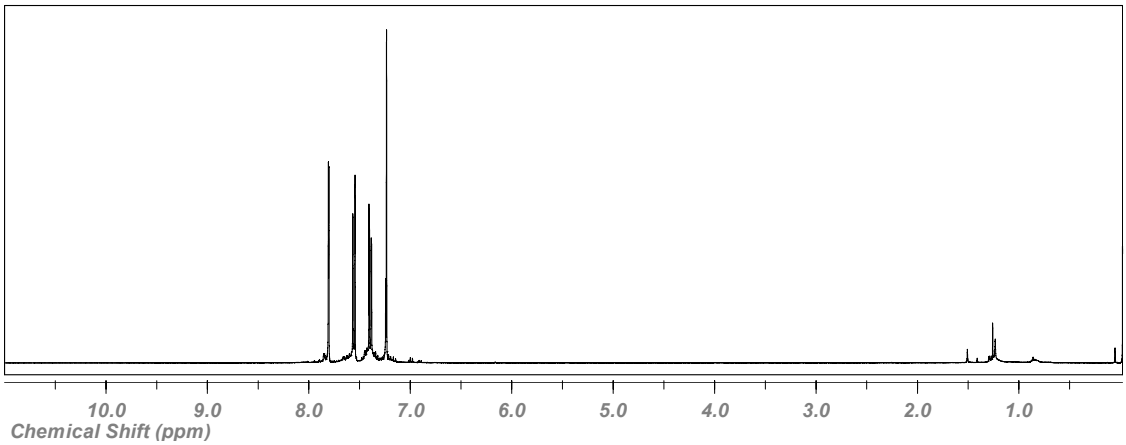

-10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190
Chemical Shift (ppm)


Br
S
Br


10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
Chemical Shift (ppm)


200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
Chemical Shift (ppm)


Br
Br
S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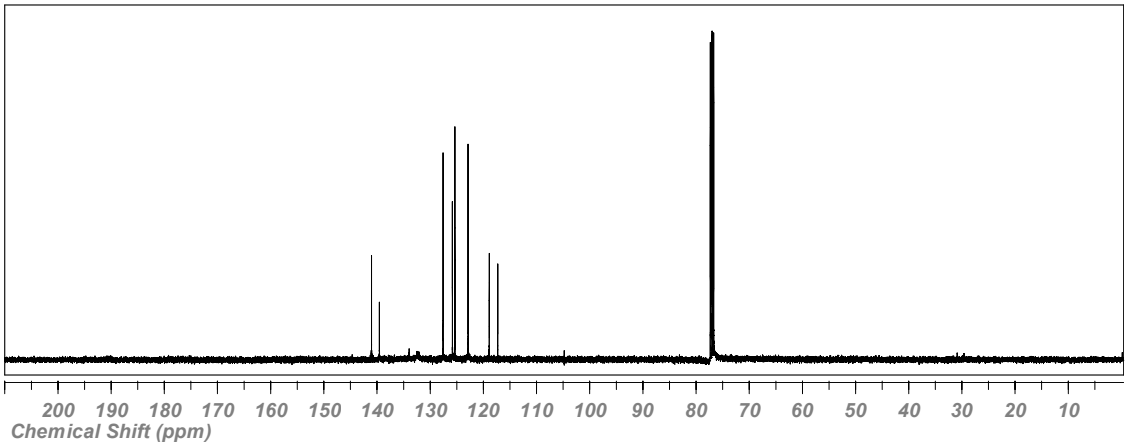
Chemical Shift (ppm)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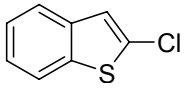
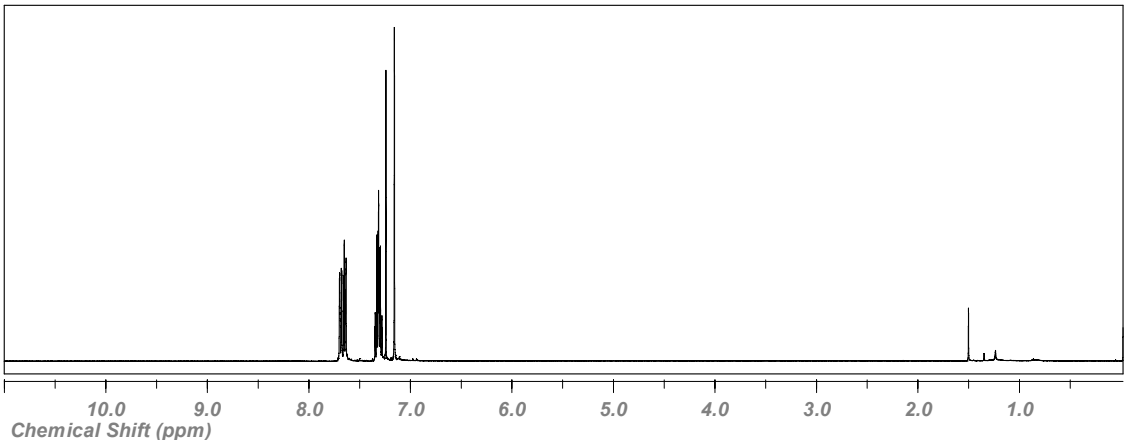
Chemical Shift (ppm)


Cl
S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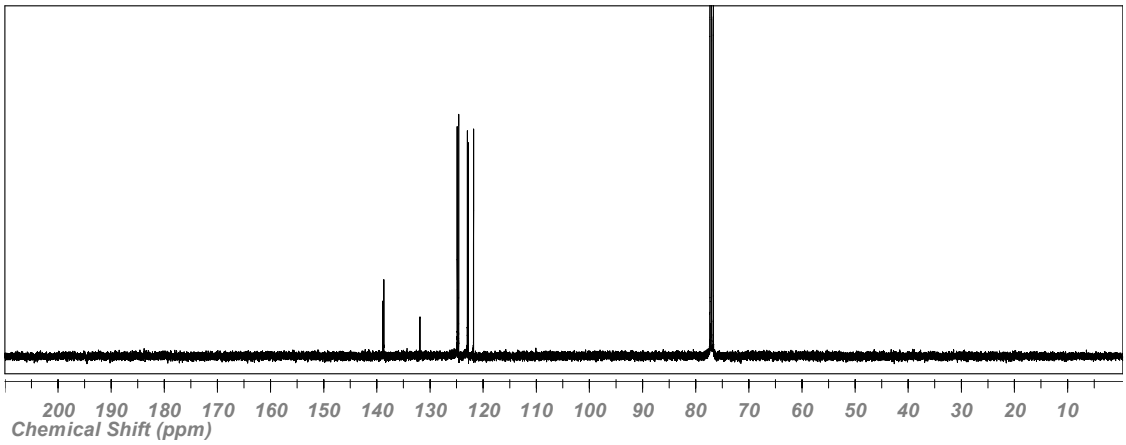
Chemical Shift (ppm)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Chemical Shift (ppm)