Supporting Information

Transition-metal-free Persulfuration to Construct Unsymmetrical Disulfides and Mechanistic Study of Sulfur Redox Process

Xiao Xiao,[†] Minghao Feng,[†] and Xuefeng Jiang*,[†]

[†] Shanghai Key Laboratory of Green Chemistry and Chemical Process, Department of Chemistry, East China Normal University, 3663 North Zhongshan Road, Shanghai 200062, P. R. China

xfjiang@chem.ecnu.edu.cn

Index

I. General Information

NMR spectrum:

^{1}H and ^{13}C NMR spectra were collected on 400 MHz NMR spectrometers (Bruker AVANCE) using $CDCl_3$. Chemical shifts are reported in parts per million (ppm). Chemical shifts for protons are reported in parts per million downfield and are referenced to residual protium in the NMR solvent ($CHCl_3$ = δ 7.26). Chemical shifts for carbon are reported in parts per million downfield and are referenced to the carbon resonances of the solvent ($CDCl_3$ = δ 77.0). Data are represented as follows: chemical shift, multiplicity (br = broad, s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constants in Hertz (Hz), integration.

Mass spectroscopy:

Mass spectra were in general recorded on a Shimadzu GCMS-QP2010 Ultra and a HP 5989A mass selective detector.

Chromatography:

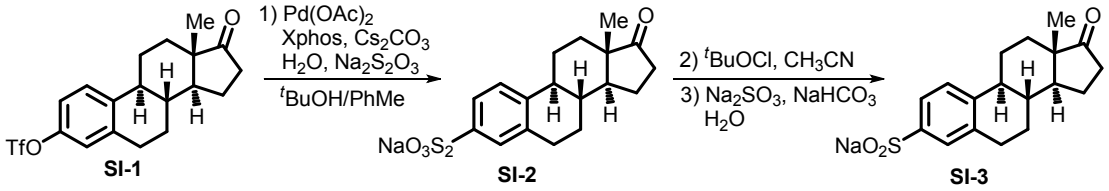
Column chromatography was performed with silica gel (200-300 mesh ASTM).

IR:

TENSOR (27) Series FT-IR Spectrometers.

II. Starting Materials Synthetic Procedure

Most of the thiosulfate and sulfinate sodium are prepared according to the reported literatures.[1, 2]

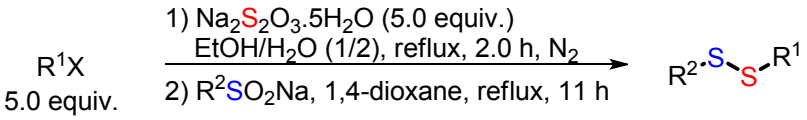


SI-1 (483.0 mg, 1.2 mmol, 1.0 equiv.), $Pd(OAc)_2$ (26.9 mg, 0.12 mmol, 10 mol%), Xphos (171.6 mg, 0.36 mmol, 30 mol%), Cs_2CO_3 (782.0 mg, 2.4 mmol, 2.0 equiv.), H_2O (43.2mg, 2.4 mmol, 2.0 equiv.), $Na_2S_2O_3$ (474.3 mg, 3.0 mmol, 2.5 equiv.) was added to solvent of ^{t}BuOH/PhMe (1.2/1.8 mL) at N_2 atmosphere. Then the mixture was heated to 80 ^{o}C for 8 h [1c] before Et_2O was added to this mixture, which was then filterd at atmosphere pressure, MeOH (20 mL) was added to the filter cake, which was then filtered at atmosphere pressure. The filtrate was collected and removed the solvent under vacuum to give the crude **SI-2**.

The crude product **SI-2** was dissolved in CH_3CN (10 mL) and treated with H_2O (108.0 mg, 6.0 mmol, 5.0 equiv.), ^{t}BuOCl (651.4 mg, 6.0 mmol, 5.0 equiv.) at 0 ^{o}C for 30 min. Then removed the solvent under vacuum and purified by silica gel to give the corresponding sulfonyl chloride.

The corresponding sulfonyl chloride (113.0 mg, 0.32 mmol), Na_2SO_3 (80.7 mg, 0.64 mmol, 2.0 equiv.) and $NaHCO_3$ (53.8 mg, 0.64 mmol, 2.0 equiv.) was added to the solvent of water (1.0 mL), then the mixture was heated to 80 ^{o}C for 8 h. Removed the solvent under vacuum, then added MeOH to dissolved the residue. Then the mixture was filtered at atmosphere pressure. The filtrate was collected and concentrated to give **SI-3** (82 mg, 0.24 mmol, 20% over three steps) as a colorless solid.

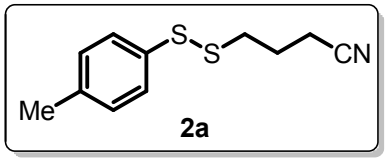
III. General procedure:



Step 1: To a Schlenk tube were added $Na_2S_2O_3{\cdot}5H_2O$ (248.2 mg, 1.0 mmol, 5.0 equiv.), alkyl halide (1.0 mmol, 5.0 equiv.), $EtOH/H_2O$ (0.25 mL/0.5 mL), the mixture was stirred at reflux for 2 hours under N_2 atmosphere, then removed the solvent to proceed step 2.

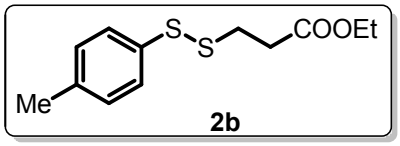
Step 2: R^2SO_2Na (0.2 mmol, 1.0 equiv.), 1,4-dioxane (1.0 mL) were added to the reaction, then the mixture was stirred at 110 °C (reflux) for 11 hours. When the reaction was finished, the mixture was cooled to room temperature. The desired product was obtained after work up and purification.

VI. Disulfides Synthesis and Spectra Data



2a

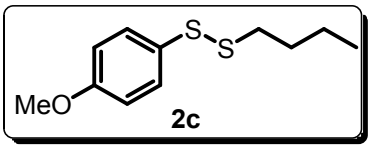
Compound **2a**: The reaction was conducted according to the general procedure. After the reaction was finished, PPh_3 (31.5 mg, 0.12 mmol, 0.6 equiv.) was added. The reaction system was stirred at 50 °C for 4 hours before it was concentrated under vacuum. Purification by column chromatography afforded the title product (41.9 mg, 0.188 mmol, 94%) as a yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.43 (d, J = 8.0 Hz, 2H), 7.15 (d, J = 8.0 Hz, 2H), 2.81 (t, J = 6.8 Hz, 2H), 2.44 (t, J = 7.2 Hz, 2H), 2.34 (s, 3H), 2.09-2.03 (m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 137.74, 133.11, 129.90, 129.06, 118.94, 36.41, 24.08, 21.04, 15.59; **IR** (film) 3028, 2924, 2247, 1900, 1488, 1424, 1260, 1206, 1110, 1017, 805, 761 cm^{-1}; **HRMS (EI)** Calcd for $C_{11}H_{13}NS_2$ 223.0489, Found 223.0491.



2b

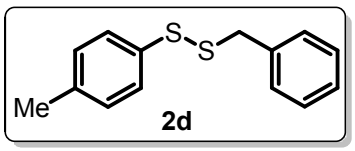
Compound **2b**: The reaction was conducted according to the general procedure.

Concentration under vacuum and purification by column chromatography gave the title compound (44.6 mg, 0.174 mmol, 87%) as a yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.43 (d, *J* = 8.0 Hz, 2H), 7.14 (d, *J* = 8.0 Hz, 2H), 4.13 (q, *J* = 7.2 Hz, 2H), 2.95 (t, *J* = 7.2 Hz, 2H), 2.72 (t, *J* = 7.2 Hz, 2H), 2.34 (s, 3H), 1.25 (t, *J* = 7.2 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 171.61, 137.26, 133.43, 129.77, 128.49, 60.70, 33.73, 33.04, 20.99, 14.12; **IR** (film) 2978, 1733, 1487, 1372, 1235, 1181, 1023, 932, 849, 804 cm^{-1}; **HRMS (EI)** Calcd for $C_{12}H_{16}O_2S_2$ 256.0592, Found 256.0594.



2c

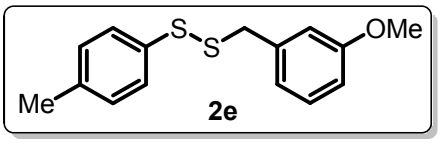
Compound **2c**: To a Schlenk tube were added ^{n}BuS_2O_3Na (1.0 mmol, 5.0 equiv.), 4-MeOPhSO_2Na (0.2 mmol, 1.0 equiv.) and 1,4-dioxane (1.0 mL), the mixture was stirred at 110 ^{o}C (reflux) for 11 hours. When the reaction was finished, the mixture was cooled to room temperature, worked up with tri-*o*-tolylphosphine (0.12 mmol, 0.6 equiv.) at 100 ^{o}C for 4 hours. The mixture was then concentrated and purified by column chromatography to afford desired product（24.2 mg, 0.106 mmol, 53%）as a yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.49-7.47 (m, 2H), 6.88-6.85 (m, 2H), 3.81 (s, 3H), 2.73 (t, *J* = 7.2 Hz, 2H), 1.69-1.62 (m, 2H), 1.43-1.33 (m, 2H), 0.89 (t, *J* = 7.2 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 159.40, 131.59, 128.44, 114.55, 55.36, 38.43, 30.72, 21.58, 13.64; **IR** (film) 2955, 1588, 1490, 1458, 1287, 1244, 1175, 1097, 1031, 823, 738 cm^{-1}; **HRMS (EI)** Calcd for $C_{11}H_{16}OS_2$ 228.0643, Found 228.0645.



2d

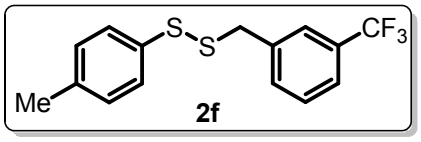
Compound **2d**[3]: The reaction was conducted according to the general procedure. Concentration under vacuum and purification by column chromatography gave the title compound (38.4 mg, 0.156 mmol, 78%) as a colorless solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.42 (dd, *J* = 8.0, 2.0 Hz, 2H), 7.35 (m, 5H) 7.17 (d, *J* = 8.0 Hz, 2H) 4.00 (d, *J* = 2.0 Hz, 2H), 2.40 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 137.11, 136.62, 133.51, 129.68, 129.36, 128.59, 128.48, 127.44, 43.19, 21.02; **IR** (film) 3027, 2921, 1892,

1597, 1488, 1451, 1262, 1203, 1073, 1022, 914, 803, 763, 698 cm^{-1}; **MS (EI)** m/z 246 (M+).



2e

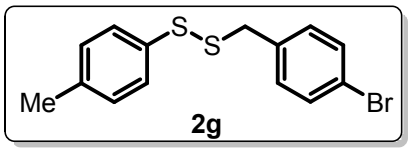
Compound **2e**: The reaction was conducted according to the general procedure. Concentration under vacuum and purification by column chromatography gave the title compound (50.3 mg, 0.182 mmol, 91%) as a colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.40 (d, *J* = 8.0 Hz, 2H), 7.24 (t, *J* = 8.0 Hz, 1H), 7.14 (d, *J* = 8.0 Hz, 2H), 6.90 (d, *J* = 8.4 Hz, 1H), 6.84-6.82 (m, 2H), 3.95 (s, 2H), 3.80 (s, 3H), 2.37 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 159.60, 138.11, 137.13, 133.53, 129.67, 129.46, 128.66, 121.70, 114.69, 113.13, 55.14, 43.36, 21.02; **IR** (film) 2919, 2834, 1894, 1599, 1489, 1453, 1435, 1296, 1263, 1222, 1151, 1115, 1078, 1043, 1016, 996, 934, 871, 804, 782, 735, 700 cm^{-1}; **HRMS (EI)** Calcd for $C_{15}H_{16}OS_2$ 276.0643, Found 276.0645.



2f

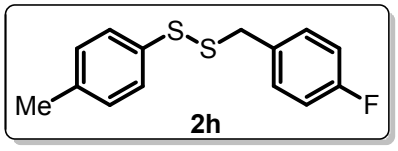
Compound **2f**: The reaction was conducted according to the general procedure. After the reaction was finished, tri-*o*-tolylphosphine (36.5 mg, 0.12 mmol, 0.6 equiv.) was added. The reaction system was stirred at 100 °C for 4 hours before it was cooled to room temperature. Then DDQ (27.2 mg, 0.12 mmol, 0.6 equiv.) was added (to obtain the purified unsymmetrical disulfide, DDQ was added to oxidize a small amount of 3-CF_3BnSH), and the system was stirred at room temperature for 4 hours before it was concentrated under vacuum. Purification by column chromatography afforded the title product (49.0 mg, 0.156 mmol, 78%) as a red oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.50-7.36 (m, 4H), 7.30 (d, *J* = 8.0 Hz, 2H), 7.08 (d, *J* = 8.0 Hz, 2H), 3.96 (s, 2H), 2.33 (s, 3H); **^{19}F NMR** (377 MHz, $CDCl_3$) δ 62.65; **^{13}C NMR** (100 MHz, $CDCl_3$) δ 137.77, 137.41, 133.01, 132.70, 130.71 (q, $^{2}J_{C\text{-}F}$ = 32.1 Hz), 129.70, 128.84, 128.83, 126.13 (q, $^{3}J_{C\text{-}F}$ = 3.8 Hz), 124.16 (q, $^{3}J_{C\text{-}F}$ = 3.8 Hz), 123.94 (q, $^{1}J_{C\text{-}F}$ = 270.6 Hz),

42.57, 20.98; **IR** (film) 3028, 1489, 1448, 1327, 1166, 1124, 1075, 899, 801, 744, 699 cm^{-1}; **HRMS (EI)** Calcd for $C_{15}H_{13}F_3S_2$ 314.0411, Found 314.0409.



2g

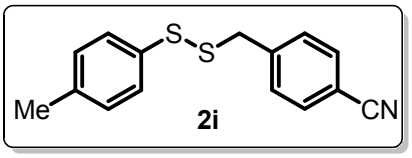
Compound **2g**: The reaction was conducted according to the general procedure. After the reaction was finished, DDQ (27.2 mg, 0.12 mmol, 0.6 equiv.) was added. The reaction system was stirred at room temperature for 4 hours before it was concentrated under vacuum. Purification by column chromatography afforded the title product (48.8 mg, 0.150 mmol, 75%) as a white solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.39 (d, *J* = 8.4 Hz, 2H), 7.32 (d, *J* = 8.0 Hz, 2H), 7.12 (m, 4H), 3.87 (s, 2H), 2.35 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 137.29, 135.74, 133.20, 131.49, 131.01, 129.68, 128.73, 121.43, 42.40, 21.03; **IR** (film) 3027, 2920, 1896, 1589, 1485, 1404, 1193, 1071, 1012, 873, 805, 731 cm^{-1}; **HRMS (EI)** Calcd for $C_{14}H_{13}BrS_2$ 323.9642, Found 323.9639.



2h

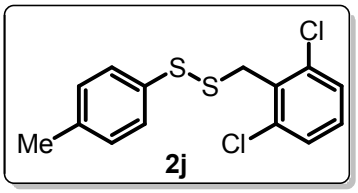
Compound **2h**: The reaction was conducted according to the general procedure. After the reaction was finished, tri-*o*-tolylphosphine (36.5 mg, 0.12 mmol, 0.6 equiv.) was added. The reaction system was stirred at 100 °C for 4 hours before it was cooled to room temperature. Then DDQ (27.2 mg, 0.12 mmol, 0.6 equiv.) was added, and the system was stirred at room temperature for 4 hours before it was concentrated under vacuum. Purification by column chromatography afforded the title product (37.5 mg, 0.142 mmol, 71%) as a red oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.38 (d, *J* = 8.4 Hz, 2H), 7.30-7.25 (m, 2H)，7.14 (d, *J* = 8.0 Hz, 2H), 7.03-6.97 (m, 2H), 3.94 (s, 2H), 2.38 (s, 3H); **^{19}F NMR** (377 MHz, $CDCl_3$) δ 114.83;**^{13}C NMR** (100 MHz, $CDCl_3$) δ 162.16 (d, $^1J_{C\text{-}F}$ = 244.7 Hz), 137.24, 133.35, 132.47 (d, $^4J_{C\text{-}F}$ = 3.2 Hz), 130.97 (d, $^3J_{C\text{-}F}$ = 8.1 Hz), 129.70, 128.63, 115.34 (d, $^2J_{C\text{-}F}$ = 21.4 Hz), 42.30, 21.02; **IR** (film) 2919, 1897, 1599, 1502, 1423, 1300, 1226, 1155, 1086, 1016, 835, 806, 747, 680 cm^{-1};

HRMS (EI) Calcd for $C_{14}H_{13}FS_2$ 264.0443, Found 264.0446.



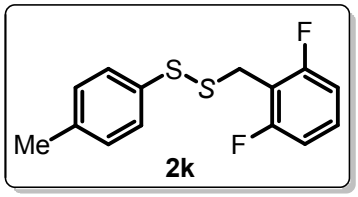
2i

Compound **2i**: Step 1 was according to the general procedure. Removed the solvent after step 1 was finished, $TolSO_2Na$ (0.2 mmol), 1,4-dioxane (1.0 mL) were added, the mixture was stirred at 90 °C for 11 hours. After the reaction was finished, the mixture was concentrated, purified by column chromatography to afford desired product (29.3 mg, 0.108 mmol, 54%) as a white solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.54 (d, *J* = 8.0 Hz, 2H), 7.36 (d, *J* = 8.0 Hz, 2H), 7.29 (d, *J* = 8.0 Hz, 2H), 7.09 (d, *J* = 8.0 Hz, 2H), 3.93 (s, 2H), 2.35 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 142.36, 137.58, 132.79, 132.11, 130.07, 129.72, 128.82, 118.66, 111.10, 42.53, 21.01; **IR** (film) 2922, 2228, 1902, 1604, 1490, 1413, 1178, 1103, 1021, 841, 804, 741 cm^{-1}; **HRMS (EI)** Calcd for $C_{15}H_{13}NS_2$ 271.0489, Found 271.0490.



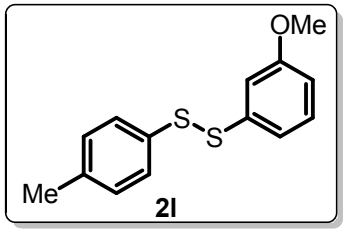
2j

Compound **2j**: The reaction was conducted according to the general procedure. After the reaction was finished, DDQ (27.2 mg, 0.12 mmol, 0.6 equiv.) was added. The reaction system was stirred at room temperature for 4 hours before it was concentrated under vacuum. Purification by column chromatography afforded the title product (46.7 mg, 0.148 mmol, 74%) as a white solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.44 (d, *J* = 8.0 Hz, 2H), 7.29 (d, *J* = 8.0 Hz, 2H), 7.15-7.11 (m, 3H), 4.34 (s, 2H), 2.37 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 136.88, 135.95, 133.67, 133.03, 129.54, 128.95, 128.24, 127.97 38.58, 21.01; **IR** (film) 2921, 1894, 1567, 1488, 1434, 1299, 1209, 1089, 1018, 872, 804, 769, 733, 674 cm^{-1}; **HRMS (EI)** Calcd for $C_{14}H_{12}Cl_2S_2$ 313.9757, Found 313.9754.



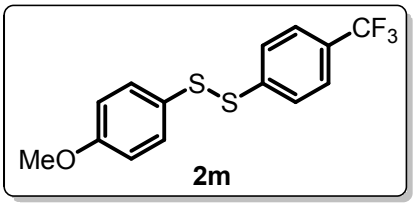
2k

Compound **2k**: The reaction was conducted according to general procedure. Concentration under vacuum and purification by column chromatography gave the title compound (48.5 mg, 0.172 mmol, 86%) as a colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.40 (d, *J* = 8.0 Hz, 2H), 7.23-7.15 (m, 1H), 7.11 (d, *J* = 8.0 Hz, 2H), 6.88-6.82 (m, 2H), 4.01 (s, 2H), 2.34 (s, 3H); **^{19}F NMR** (377 MHz, $CDCl_3$) δ 114.13; **^{13}C NMR** (100 MHz, $CDCl_3$) δ 161.40 (dd, $^1J_{C\text{-}F}$ = 248.2 Hz, $^3J_{C\text{-}F}$ = 7.7 Hz), 137.20, 133.39, 129.62, 129.07 (t, $^3J_{C\text{-}F}$ = 10.2 Hz), 128.57, 113.45 (t, $^2J_{C\text{-}F}$ = 19.1 Hz) 111.13 (dd, $^2J_{C\text{-}F}$ = 19.0 Hz, $^4J_{C\text{-}F}$ = 6.1 Hz), 29.61, 21.02; **IR** (film) 2924, 1905, 1624, 1590, 1470, 1272, 1235, 1173, 1135, 994, 788, 734, 695 cm^{-1}; **HRMS (EI)** Calcd for $C_{14}H_{12}F_2S_2$ 282.0348, Found 282.0347.



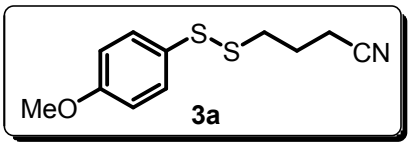
2l

Compound **2l**: To a Schlenk tube were added 3-MeOPhS_2O_3Na (1.0 mmol, 5.0 equiv.), TolSO_2Na (0.2 mmol, 1.0 equiv.) and 1,4-dioxane (1.0 mL), the mixture was stirred at 110 °C (reflux) for 11 hours. When the reaction was finished, the mixture was concentrated and purified by column chromatography to afford the desired product (26.7 mg, 0.102 mmol, 51%) as a white solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.42 (d, *J* = 8.0 Hz, 2H) 7.24-7.20 (m, 1H), 7.13-7.08 (m, 4H), 6.78-6.75 (m, 1H), 3.78 (s, 3H), 2.34 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 159.96, 138.54, 137.54, 133.54, 129.81, 128.40,119.51, 112.98, 112.40, 55.26, 21.03; **IR** (film) 2937, 1584, 1477, 1426, 1282, 1239, 1178, 1039, 851, 803, 772, 685 cm^{-1}; **HRMS (EI)** Calcd for $C_{14}H_{14}OS_2$ 262.0486, Found 262.0488.



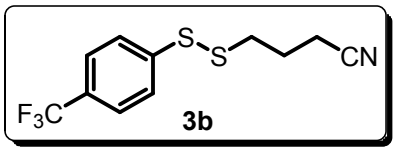
2m

Compound **2m**: To a Schlenk tube were added, 4-$CF_3PhS_2O_3Na$ (1.0 mmol, 5.0 equiv.), 4-$MeOPhSO_2Na$ (0.2 mmol, 1.0 equiv.), and 1,4-dioxane (1.0 mL), the mixture was stirred at 110 ^oC (reflux) for 11 hours. When the reaction was finished, the mixture was concentrated and purified by column chromatography to afford the desired product (37.9 mg, 0.12 mmol, 60%) as a yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.63 (d, J = 8.0 Hz, 2H), 7.56 (d, J = 8.4 Hz, 2H), 7.43 (d, J = 8.8 Hz, 2H), 6.84 (d, J = 8.8 Hz, 2H), 3.79 (s, 3H); **^{19}F NMR** (377 MHz, $CDCl_3$) δ 62.40;**^{13}C NMR** (100 MHz, $CDCl_3$) δ 160.04, 142.31, 131.81, 128.80 (q, $^2J_{C\text{-}F}$ = 32.5 Hz), 126.95, 126.86, 126.68 (q, $^1J_{C\text{-}F}$ = 270.2 Hz), 125.82(q, $^3J_{C\text{-}F}$ = 3.7 Hz), 114.84, 55.36; **IR** (film) 2949, 2838, 1595, 1490, 1400, 1321, 1247, 1167, 1120, 1022, 824, 705 cm^{-1}; **HRMS (EI)** Calcd for $C_{14}H_{11}F_3OS_2$ 316.0203, Found 316.0201.

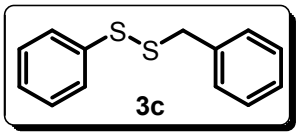


3a

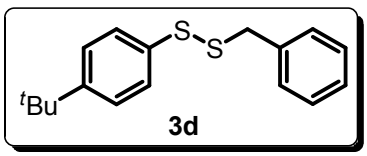
Compound **3a**: The reaction was conducted according to the general procedure. After the reaction was finished, tri-*m*-tolylphosphine (36.5 mg, 0.12 mmol, 0.6 equiv.) was added. The reaction system was stirred at room temperature for 4 hours before it was concentrated under vacuum. Purification by column chromatography afforded the title product (30.6 mg, 0.128mmol, 64%) as a colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.50-7.46 (m, 2H), δ 6.89-6.85 (m, 2H), 3.81 (s, 3H), 2.81 (t, J = 6.4 Hz, 2H), 2.43 (t, J = 7.2 Hz, 2H), 2.11-2.04 (m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 159.85, 132.41, 127.35, 118.99, 114.75, 55.36, 36.32, 24.07, 15.57; **IR** (film) 2941, 2837, 2247, 2043, 1588, 1490, 1452, 1288, 1245, 1175, 1101, 1027, 825 cm^{-1}; **HRMS (EI)** Calcd for $C_{11}H_{13}NOS_2$ 239.0439, Found 239.0438.



Compound **3b**: The reaction was conducted according to the general procedure. After the reaction was finished, tri-*m*-tolylphosphine (36.5 mg, 0.12 mmol, 0.6 equiv.) was added. The reaction system was stirred at room temperature for 4 hours before it was concentrated under vacuum. Purification by column chromatography afforded the title product (34.4 mg, 0.124mmol, 62%) as a yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.63 (d, J = 8.4 Hz, 2H), 7.58 (d, J = 8.8 Hz, 2H), 2.84 (t, J = 6.8 Hz, 2H), 2.48 (t, J = 6.8 Hz, 2H), 2.09-2.0 (m, 2H); **^{19}F NMR** (377 MHz, $CDCl_3$) δ 62.47; **^{13}C NMR** (100 MHz, $CDCl_3$) δ 141.5, 128.95 (q, $^2J_{C\text{-}F}$ = 32.5 Hz), 126.70, 125.94 (q, $^3J_{C\text{-}F}$ = 3.8 Hz) 123.88 (q, $^1J_{C\text{-}F}$ = 270.2 Hz), 118.64, 36.42, 24.27, 15.73; **IR** (film) 2929, 2248, 1603, 1496, 1401, 1323, 1261, 1163, 1120, 1080, 1061, 1012, 829, 777, 724, 699 cm^{-1}; **HRMS (EI)** Calcd for $C_{11}H_{10}F_3NS_2$ 277.0207, Found 277.0205.

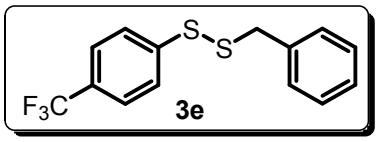


Compound **3c**[3]: The reaction was conducted according to the general procedure. After the reaction was finished, DDQ (27.2 mg, 0.12 mmol, 0.6 equiv.) was added. The reaction system was stirred at room temperature for 4 hours before it was concentrated under vacuum. Purification by column chromatography afforded the title product (40.0 mg, 0.172mmol, 86%) as a red oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.51 (d, J = 7.6 Hz, 2H), 7.36-7.24 (m, 8H), 4.0 (s, 2H), **^{13}C NMR** (100 MHz, $CDCl_3$) δ 136.94, 136.50, 129.36, 128.89, 128.50, 127.58, 127.52,126.6, 43.28; **IR** (film) 3062, 2922, 1580, 1478, 1443, 1301, 1230, 1069, 1024, 910, 740, 693 cm^{-1}; **MS (EI)** m/z 232 (M+).



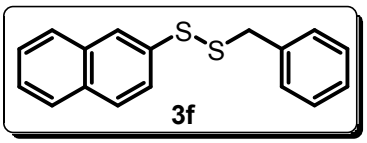
Compound **3d**: The reaction was conducted according to the general procedure. After

the reaction was finished, DDQ (27.2 mg, 0.12 mmol, 0.6 equiv.) was added. The reaction system was stirred at room temperature for 4 hours before it was concentrated under vacuum. Purification by column chromatography afforded the title product (38.0 mg, 0.132mmol, 66%) as a red oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.47-7.45 (m, 2H), 7.9-7.30 (m, 7H), 4.01 (s, 2H), 1.38 (s, 9H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 150.27, 136.65, 133.56, 129.37, 128.48, 128.15, 127.45, 126.00, 43.35, 34.50, 31.25; **IR** (film) 3029, 2959, 1596, 1489, 1397, 1268, 1196, 1115, 1071, 1016, 916, 824, 763, 698 cm^{-1}; **HRMS (EI)** Calcd for $C_{17}H_{20}S_2$ 288.1006, Found 288.1004.



3e

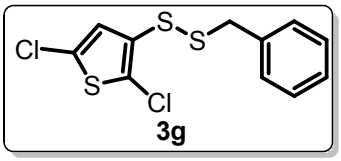
Compound **3e**: The reaction was conducted according to the general procedure. After the reaction was finished, DDQ (27.2 mg, 0.12 mmol, 0.6 equiv.) was added. The reaction system was stirred at room temperature for 4 hours before it was concentrated under vacuum. Purification by column chromatography afforded the title product (36.6 mg, 0.122mmol, 61%) as a white solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ7.53 (s, 4H), 7.31-7.29 (m, 5H), 4.00 (s, 2H); **^{19}F NMR** (377 MHz, $CDCl_3$) δ 62.42;**^{13}C NMR** (100 MHz, $CDCl_3$) δ 141.98, 136.13, 129.34, 128.57, 128.40 (q, $^2J_{C\text{-}F}$ = 32.5 Hz), 127.73, 126.41, 125.55 (q, $^3J_{C\text{-}F}$ = 3.7 Hz), 124.01 (q, $^1J_{C\text{-}F}$ = 270.1 Hz), 43.42; **IR** (film) 3031, 1603, 1494, 1453, 1401, 1323, 1165, 1121, 1071, 1013, 829, 764, 698 cm^{-1}; **HRMS (EI)** Calcd for $C_{14}H_{11}F_3S_2$ 300.0254, Found 300.0252.



3f

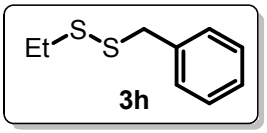
Compound **3f**[4]: The reaction was conducted according to the general procedure. Concentration under vacuum and purification by column chromatography gave the title compound (44.0 mg, 0.156 mmol, 78%) as a white solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.92 (s, 1H), 7.87-7.79 (m, 3H), 7.60-7.49 (m, 3H), 7.36-7.28 (m, 5H), 4.03 (s, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 136.59, 134.18, 133.41, 132.24, 129.39, 128.68, 128.52, 127.71, 127.55, 127.31, 126.61, 126,24, 126.00, 125.72, 43.28; **IR**

(film) 3052, 1947, 1586, 1496, 1452, 1344, 1231, 1195, 1134, 1067, 1020, 946, 888, 851, 810, 745, 697 cm^{-1}; **MS (EI)** m/z 282 (M+).



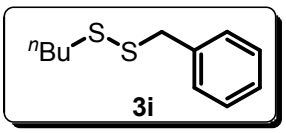
3g

Compound **3g**: Step 1 was according to the general procedure. Removed the solvent after step 1 was finished, sodium 2,5-dichlorothiophene-3-sulfinate (0.2 mmol, 1.0 equiv.), 1,4-dioxane (1.0 mL) were added, the mixture was stirred at 90 °C for 11 hours. After the reaction was finished, DDQ (27.2 mg, 0.12 mmol, 0.6 equiv.) was added. The reaction system was stirred at room temperature for 4 hours before it was concentrated under vacuum. Purification by column chromatography afforded the title product (44.2 mg, 0.144 mmol, 72%) as a colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.30-7.26 (m, 5H), 6.56 (s, 1H), 3.99 (s, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 136.3, 131.50, 129.35, 128.58, 128.31, 127.74, 126.33, 125.94, 43.99; **IR** (film) 3092, 3028, 2920, 1947, 1878, 1598, 1504, 1452, 1415, 1303, 1231, 1195, 1138, 1032, 913, 823, 761, 697 cm^{-1}; **HRMS (EI)** Calcd for $C_{11}H_8Cl_2S_3$ 305.9165, Found 305.9168.



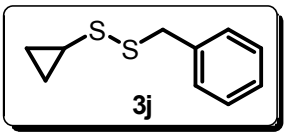
3h

Compound **3h**[5]: The reaction was conducted according to the general procedure. After the reaction was finished, DDQ (27.2 mg, 0.12 mmol, 0.6 equiv.) was added. The reaction system was stirred at room temperature for 4 hours before it was concentrated under vacuum. Purification by column chromatography afforded the title product (22.8 mg, 0.124mmol, 62%) as a red oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.39-7.30 (m, 5H), 3.94 (s, 2H), 2.47 (q, J = 7.2 Hz, 2H) 1.26 (t, J = 7.2 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 137.54, 129.25, 128.45, 127.34, 43.73, 32.39, 14.26; **IR** (film) 3028, 2967, 2922, 1600, 1494, 1450, 1252, 1195, 1067, 1031, 968, 913, 763, 698, 668 cm^{-1}; **MS (EI)** m/z 184 (M+).



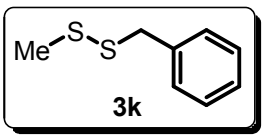
3i

Compound **3i**[6]: The reaction was conducted according to the general procedure. After the reaction was finished, DDQ (27.2 mg, 0.12 mmol, 0.6 equiv.) was added. The reaction system was stirred at room temperature for 4 hours before it was concentrated under vacuum. Purification by column chromatography afforded the title product (32.7 mg, 0.154mmol, 77%) as a red oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.26-7.17 (m, 5H), 3.8 (s, 2H), 2.32 (t, *J* = 7.2 Hz, 2H), 1.49-1.42 (m, 2H), 1.28-1.19 (m, 2H), 0.78 (t, *J* = 7.2, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 137.59, 129.25, 128.43, 127.31, 43.69, 38.33, 31.07, 21.57, 13.61; **IR** (film) 3032, 2946, 1598, 1453, 1279, 1216, 1069, 911, 761, 698 cm^{-1}; **MS (EI)** m/z 212 (M+).



3j

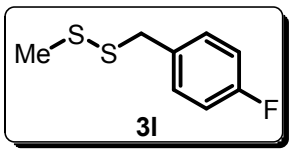
Compound **3j**: The reaction was conducted according to the general procedure. After the reaction was finished, DDQ (27.2 mg, 0.12 mmol, 0.6 equiv.) was added. The reaction system was stirred at room temperature for 4 hours before it was concentrated under vacuum. Purification by column chromatography afforded the title product (34.5 mg, 0.176mmol, 88%) as a colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.40-7.28 (m, 5H), 3.99 (s, 2H), 1.91-1.85 (m, 1H), 0.87-0.82 (m, 2H), 0.65-0.61 (m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 137.71, 129.32, 128.44, 127.29, 43.28, 18.63, 9.61; **IR** (film) 3071, 3021, 1598, 1493, 1451, 1420, 1272, 1230, 1192, 1060, 1024, 912, 868, 817, 764, 698 cm^{-1}; **HRMS (EI)** Calcd for $C_{10}H_{12}S_2$ 196.0380, Found 196.0382.



3k

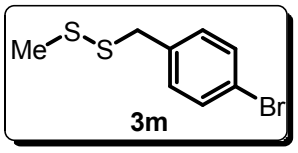
Compound **3k**[5]: The reaction was conducted according to the general procedure. After the reaction was finished, tri-*m*-tolylphosphine (36.5 mg, 0.12 mmol, 0.6 equiv.)

was added. The reaction system was stirred at room temperature for 4 hours before it was concentrated under vacuum. Purification by column chromatography afforded the title product (23.8 mg, 0.140mmol, 70%) as a colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.42-7.31 (m, 5H), 3.96 (s, 2H), 2.16 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 137.57, 129.35, 128.55, 127.42, 43.02, 23.02; **IR** (film) 3028, 2915, 1600, 1493, 1451, 1418, 1306, 1231, 1067, 1027, 953, 764, 698 cm^{-1}; **MS (EI)** m/z 170 (M+).



3l

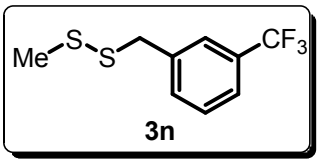
Compound **3l**: The reaction was conducted according to the general procedure. After the reaction was finished, DDQ (27.2 mg, 0.12 mmol, 0.6 equiv.) was added. The reaction system was stirred at room temperature for 4 hours before it was concentrated under vacuum. Purification by column chromatography afforded the title product (28.2 mg, 0.15 mmol, 75%) as a colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.33-7.29 (m, 2H), 7.04-6.99 (m, 2H), 3.87 (s, 2H), 2.12 (s, 3H); **^{19}F NMR** (377 MHz, $CDCl_3$) δ 114.96; **^{13}C NMR** (100 MHz, $CDCl_3$) δ 162.25 (d, $^1J_{C\text{-}F}$ = 244.5 Hz), 133.37 (d, $^4J_{C\text{-}F}$ = 3.1 Hz) 130.88 (d, $^3J_{C\text{-}F}$ = 8.1 Hz), 115.43 (d, $^2J_{C\text{-}F}$ = 21.3 Hz), 42.08, 23.06; **IR** (film) 2918, 1887, 1601, 1507, 1420, 1304, 1225, 1156, 1089, 1016, 952, 834, 749 cm^{-1}; **HRMS (EI)** Calcd for $C_8H_9FS_2$ 188.0130, Found 188.0128.



3m

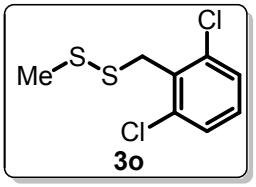
Compound **3m**: The reaction was conducted according to the general procedure. After the reaction was finished, DDQ (27.2 mg, 0.12 mmol, 0.6 equiv.) was added. The reaction system was stirred at room temperature for 4 hours before it was concentrated under vacuum. Purification by column chromatography afforded the title product (45.8 mg, 0.184 mmol, 92%) as a red oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.45 (d, J = 8.4 Hz, 2H), 7.22 (d, J = 8.4 Hz, 2H) 3.84 (S, 2H), 2.14 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 135.88, 133.72, 128.90, 128.32, 37.78, 23.62; **IR** (film) 2914, 1897, 1652, 1585, 1485, 1412, 1412, 1305, 1195, 1070, 1011, 953, 874, 821, 729 cm^{-1};

HRMS (EI) Calcd for $C_8H_9BrS_2$ 247.9329, Found 247.9327.



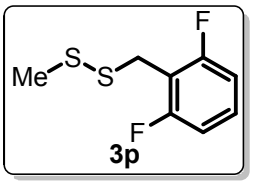
3n

Compound **3n**: The reaction was conducted according to the general procedure. After the reaction was finished, DDQ (27.2 mg, 0.12 mmol, 0.6 equiv.) was added. The reaction system was stirred at room temperature for 4 hours before it was concentrated under vacuum. Purification by column chromatography afforded the title product (35.7 mg, 0.15 mmol, 75%) as a colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.61 (s, 1H), 7.56-7.53 (m, 2H), 7.47-7.43 (m, 1H), 3.93 (s, 2H), 2.11 (s, 3H); **^{19}F NMR** (377 MHz, $CDCl_3$) δ 62.62; **^{13}C NMR** (100 MHz, $CDCl_3$) δ 138.67, 132.61, 130.84 (q, $^2J_{C\text{-}F}$ = 32.2 Hz), 128.95, 125.99 (q, $^3J_{C\text{-}F}$ = 3.7 Hz), 124.16 (q, $^3J_{C\text{-}F}$ = 3.7 Hz), 123.98 (q, $^1J_{C\text{-}F}$ = 270.7 Hz), 42.24, 22.91; **IR** (film) 2923, 1735, 1448, 1330, 1169, 1128, 1077, 901, 803, 702 cm^{-1}; **HRMS (EI)** Calcd for $C_9H_9F_3S_2$ 238.0098, Found 238.0096.

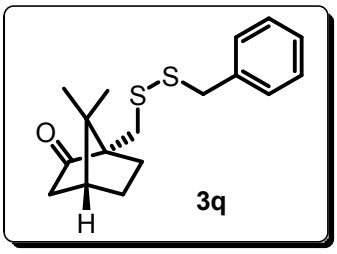


3o

Compound **3o**: The reaction was conducted according to the general procedure. After the reaction was finished, DDQ (27.2 mg, 0.12 mmol, 0.6 equiv.) was added. The reaction system was stirred at room temperature for 4 hours before it was concentrated under vacuum. Purification by column chromatography afforded the title product (25.3 mg, 0.106 mmol, 53%) as a colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.32 (d, J = 8.0 Hz, 2H), 7.15 (dd, J = 8.4 Hz, J = 7.6 Hz, 1H), 4.29 (s, 2H), 2.36 (s, 3H), **^{13}C NMR** (100 MHz, $CDCl_3$) δ 135.88, 133.72, 128.90, 128.32, 37.79, 23.62; **IR** (film) 2917, 1565, 1432, 1304, 1215, 1090, 953, 874, 768 cm^{-1}; **HRMS (EI)** Calcd for $C_8H_8Cl_2S_2$ 237.9444, Found 237.9443.

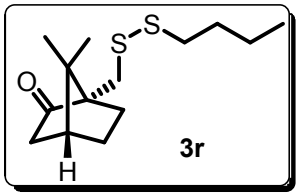


Compound **3p**: The reaction was conducted according to the general procedure. After the reaction was finished, DDQ (27.2 mg, 0.12 mmol, 0.6 equiv.) was added. The reaction system was stirred at room temperature for 4 hours before it was concentrated under vacuum. Purification by column chromatography afforded the title product (21.0 mg, 0.102 mmol, 51%) as a yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.31-7.24 (m, 1H), 6.97-6.91 (m, 2H), 4.03 (s, 2H), 2.32 (s, 3H); **^{19}F NMR** (377 MHz, $CDCl_3$) δ 114.50; **^{13}C NMR** (100 MHz, $CDCl_3$) δ 161.48 (dd, $^{1}J_{C\text{-}F}$ = 247.9 Hz, $^{3}J_{C\text{-}F}$ = 7.7 Hz), 129.01 (t, $^{3}J_{C\text{-}F}$ = 10.1 Hz), 114.06 (t, $^{2}J_{C\text{-}F}$ = 18.9 Hz), 111.19 (dd, $^{2}J_{C\text{-}F}$ = 219.0 Hz, $^{4}J_{C\text{-}F}$ = 6.3 Hz), 28.93, 22.99; **IR** (film) 2919, 1624, 1589, 1470, 1422, 1271, 1235, 1170, 1059, 995, 955, 786, 736, 694 cm^{-1}; **HRMS (EI)** Calcd for $C_8H_8F_2S_2$ 206.0035, Found 206.0034.

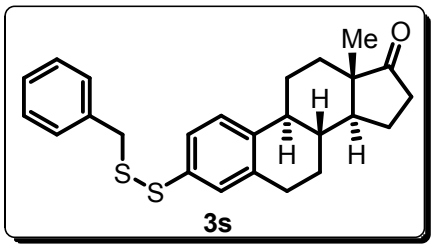


Compound **3q**: To a Schlenk tube were added BnS_2O_3Na (1.0 mmol, 5.0 equiv.), the sodium sulfinate (0.2 mmol, 1.0 equiv.) and 1,4-dioxane (1.0 mL), the mixture was stirred at 110 ^{o}C (reflux) for 11 hours. After the reaction was finished, The mixture was concentrated and purified by column chromatography to afford the desired product（38.0 mg, 0.124 mmol, 62%）as a colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.33-7.20 (m, 5H), 3.88 (s, 2H), 2.84 (d, *J* = 13.2 Hz, 1H), 2.55 (d, *J* = 13.2 Hz, 1H), 2.27 (ddd, *J* = 18.4, 4.7, 1.8 Hz, 1H), 2.00-1.97 (m, 1H), 1.92-1.88 (m, 2H), 1.78 (d, *J* = 18.3 Hz, 1H), 1.50-1.43 (m, 1H), 1.36-1.28 (m, 1H), 0.88 (s, 3H), 0.76 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 216.76, 137.55, 129.37, 128.46, 127.30, 61.12, 47.72, 43.50, 43.40, 42.97, 38.17, 26.77, 26.38, 20.03, 19.93; **IR** (film) 2956, 1739, 1453, 1239, 1045, 912, 764, 732, 697 cm^{-1}; **HRMS (EI)** Calcd for $C_{17}H_{22}OS_2$ 306.1112,

Found 306.1110.

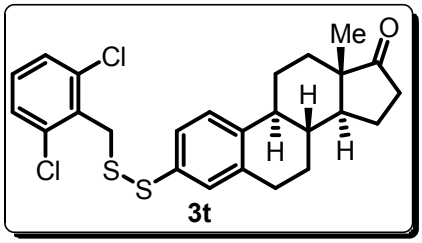


Compound **3r**: To a Schlenk tube were added $^{n}BuS_2O_3Na$ (1.0 mmol, 5.0 equiv.), the sodium sulfinate (0.2 mmol, 1.0 equiv.) and 1,4-dioxane (1.0 mL), the mixture was stirred at 110 °C (reflux) for 11 hours. After the reaction was finished, The mixture was concentrated and purified by column chromatography to afford the desired product（34.8 mg, 0.128 mmol, 64%）as a colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 3.18 (d, *J* = 13.2 Hz, 1H), 2.75-2.69 (m, 3H), 2.38-2.32 (m, 1H), 2.10-1.98 (m, 3H), 1.85 (d, *J* = 18.3 Hz, 1H), 1.71-1.63 (m, 2H), 1.60-1.54 (m, 1H), 1.45-1.35 (m, 3H), 1.04 (s, 3H),0.93-0.89 (m, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 216.95, 61.26, 47.77, 43.49, 43.01, 38.95, 38.50, 31.14, 26.79, 26.51, 21.59, 20.17, 20.10, 13.65; **IR** (film) 2954, 1741, 1416, 1045 cm^{-1}; **HRMS (EI)** Calcd for $C_{14}H_{24}OS_2$ 272.1269, Found 272.1269.



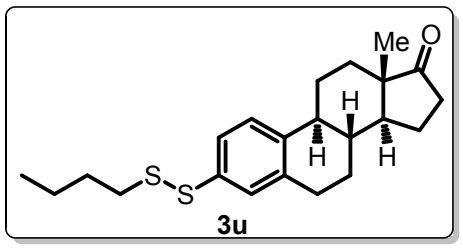
Compound **3s**: To a Schlenk tube were added BnS_2O_3Na (0.7 mmol, 5.0 equiv.), the sodium sulfinate (0.14 mmol, 1.0 equiv.) and 1,4-dioxane (0.7 mL), the mixture was stirred at 110 °C (reflux) for 11 hours. After the reaction was finished, The mixture was concentrated and purified by column chromatography to afford the desired product（35.4 mg, 0.0868 mmol, 62%）as a yellow solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.24-7.12 (m, 7H), 7.05 (s, 1H), 3.86 (s, 2H), 2.78 (dd, *J* = 8.8, 4.2 Hz, 2H), 2.45 (dd, *J* = 19.0, 8.8 Hz, 1H), 2.23-2.16 (m, 1H), 2.19 (td, *J* = 10.7, 4.0 Hz, 1H), 2.11-1.88 (m, 4H), 1.60-1.30 (m, 6H), 0.83 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 220.61, 138.94, 137.38, 136.79, 133.97, 129.34, 128.68, 128.48, 127.43, 126.00,

125.71, 50.44, 47.89, 44.22, 43.47, 38.00, 35.79, 31.52, 29.26, 26.33, 25.65, 21.54, 13.79; **IR** (film) 2928, 1737, 1561, 1436, 1088, 1007, 909, 817, 778, 761, 733 cm^{-1}; **HRMS (EI)** Calcd for $C_{25}H_{28}OS_2$ 408.1582, Found 408.1580.



3t

Compound **3t**: To a Schlenk tube were added sodium 2,6-dichlorobenzyl sulfothioate (0.35 mmol, 5.0 equiv.), the sodium sulfinate (0.07 mmol, 1.0 equiv.) and 1,4-dioxane (0.7 mL), the mixture was stirred at 110 °C (reflux) for 11 hours. After the reaction was finished, The mixture was concentrated and purified by column chromatography to afford the desired product（16.7 mg, 0.035 mmol, 50%）as a yellow solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.21-7.12 (m, 5H), 7.05-7.01 (m, 1H), 4.26 (s, 2H), 2.81 (dd, *J* = 8.9, 4.2 Hz, 2H), 2.44 (dd, *J* = 19.0, 8.9 Hz, 1H), 2.36-2.31 (m, 1H), 2.23-2.17 (m, 1H), 2.13-1.88 (m, 4H), 1.61-1.33 (m, 6H), 0.85 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 220.76, 138.70, 137.26, 136.02, 134.09, 133.08, 128.97, 128.27, 127.91, 125.90, 125.08, 50.45,47.94, 44.24, 38.80, 38.05, 35.82, 31.53, 29.30, 26.38, 25.70, 21.57, 13.80 ; **IR** (film) 2928, 1737, 1561, 1436, 1088, 1007, 909, 817, 778, 761, 733 cm^{-1}; **HRMS (EI)** Calcd for $C_{25}H_{26}Cl_2OS_2$ 476.0802, Found 476.0805.



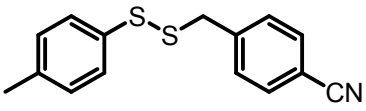
3u

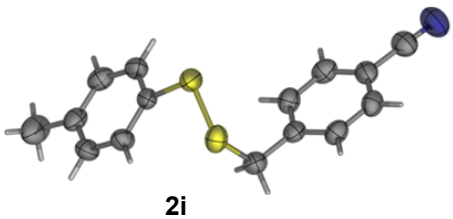
Compound **3u**: To a Schlenk tube were added sodium S-2,6-dichlorobenzyl sulfothioate (0.35 mmol, 5.0 equiv.), the sodium sulfinate (0.07 mmol, 1.0 equiv.) and 1,4-dioxane (0.7 mL), the mixture was stirred at 110 °C (reflux) for 11 hours. After the reaction was finished, the mixture was concentrated and purified by column chromatography to afford the desired product（14.4 mg, 0.0385 mmol, 55%）as a yellow solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.25 (dd, *J* = 8.1, 2.0 Hz, 1H), 7.19-7.17

(m, 2H), 2.84 (dd, J = 8.9, 4.2 Hz, 2H), 2.67 (t, J = 7.4 Hz, 2H), 2.44 (dd, J = 19.0, 8.9 Hz, 1H), 2.36-2.31 (m, 1H), 2.22 (td, J = 10.6, 4.3 Hz, 1H), 2.12-1.88 (m, 4H), 1.63-1.56 (m, 3H), 1.48-1.40 (m, 4H), 1.38-1.28 (m, 3H), 0.84-0.81 (m, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 220.76, 138.73, 137.42, 134.57, 128.23, 126.05, 125.28, 50.45, 47.93, 44.24, 38.58, 38.04, 35.82, 31.53, 30.83, 29.34, 26.37, 25.68, 21.60, 21.56, 13.81,13.63; **IR** (film) 2927, 1735, 1456, 910,733 cm^{-1}; **HRMS (EI)** Calcd for $C_{22}H_{30}OS_2$ 374.1738, Found 374.1740.

V. X-ray Crystallography Analysis of Compound 2i, 4 and 5

Compound **2i** (CCDC-1017450):





2i

Datablock: z

```
Bond precision:        C-C = 0.0035 A                Wavelength=0.71073
Cell:          a=6.1546(2)       b=15.4938(6)      c=28.9800(11)
               alpha=90          beta=90           gamma=90
Temperature: 296 K
                      Calculated                        Reported
Volume                2763.48(17)                       2763.48(17)
Space group           P b c a                           Pbca
Hall group            -P 2ac 2ab                        ?
Moiety formula        C15 H13 N S2                      ?
Sum formula           C15 H13 N S2                      C15 H13 N S2
Mr                    271.40                            271.38
Dx,g cm-3             1.305                             1.305
Z                     8                                 8
Mu (mm-1)             0.366                             0.366
F000                  1136.0                            1136.0
F000'                 1138.29
h,k,lmax              7,18,34                           7,18,34
Nref                  2441                              2439
Tmin,Tmax             0.932,0.954                       0.911,0.954
Tmin'                 0.909
Correction method= MULTI-SCAN
Data completeness= 0.999          Theta(max)= 25.010
R(reflections)= 0.0380( 1730)         wR2(reflections)= 0.1029( 2439)
S = 1.021               Npar= Npar = 163
```

The following ALERTS were generated. Each ALERT has the format
test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.

Alert level C

ABSTY02_ALERT_1_C An _exptl_absorpt_correction_type has been given without a literature citation. This should be contained in the _exptl_absorpt_process_details field.
Absorption correction given as multi-scan

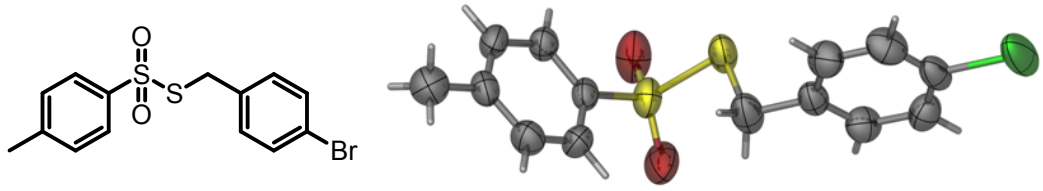
Alert level G

PLAT005_ALERT_5_G No _iucr_refine_instructions_details in the CIF Please Do !
PLAT066_ALERT_1_G Predicted and Reported Tmin&Tmax Range Identical ? Check
PLAT710_ALERT_4_G Delete 1-2-3 or 2-3-4 Linear Torsion Angle ... # 27 Do !
C2 -C3 -C14 -N1 -78.00 11.00 1.555 1.555 1.555 1.555
PLAT710_ALERT_4_G Delete 1-2-3 or 2-3-4 Linear Torsion Angle ... # 28 Do !
C4 -C3 -C14 -N1 98.00 11.00 1.555 1.555 1.555 1.555

0 **ALERT level A** = Most likely a serious problem - resolve or explain
0 **ALERT level B** = A potentially serious problem, consider carefully
1 **ALERT level C** = Check. Ensure it is not caused by an omission or oversight
4 **ALERT level G** = General information/check it is not something unexpected

2 ALERT type 1 CIF construction/syntax error, inconsistent or missing data
0 ALERT type 2 Indicator that the structure model may be wrong or deficient
0 ALERT type 3 Indicator that the structure quality may be low
2 ALERT type 4 Improvement, methodology, query or suggestion
1 ALERT type 5 Informative message, check

Compound **4** (CCDC-1017451):



4

Datablock: z

Bond precision: C-C = 0.0056 A Wavelength=0.71073

Cell: a=10.1609(11) b=14.3305(15) c=10.5313(11)
alpha=90 beta=94.541(4) gamma=90

Temperature: 296 K

	Calculated	Reported
Volume	1528.7(3)	1528.7(3)
Space group	P 21/n	P2(1)/n
Hall group	-P 2yn	?
Moiety formula	C14 H13 Br O2 S2	?
Sum formula	C14 H13 Br O2 S2	C14 H13 Br O2 S2
Mr	357.28	357.27
Dx,g cm-3	1.552	1.552
Z	4	4
Mu (mm-1)	2.956	2.956
F000	720.0	720.0
F000'	720.11	
h,k,lmax	12,17,12	12,17,12
Nref	2687	2684
Tmin,Tmax	0.629,0.661	0.649,0.682
Tmin'	0.617	

Correction method= MULTI-SCAN

Data completeness= 0.999 Theta(max)= 25.000

R(reflections)= 0.0406(1963) wR2(reflections)= 0.0990(2684)

S = 0.983 Npar= Npar = 172

The following ALERTS were generated. Each ALERT has the format
test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.

Alert level C

PLAT241_ALERT_2_C High Ueq as Compared to Neighbors for ..... C7 Check
PLAT242_ALERT_2_C Low Ueq as Compared to Neighbors for ..... C11 Check
PLAT334_ALERT_2_C Small Average Benzene C-C Dist. C8 -C13 1.37 Ang.

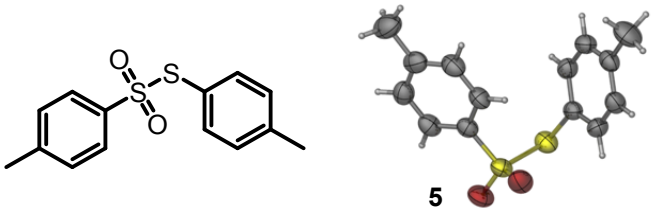
Alert level G

PLAT005_ALERT_5_G No _iucr_refine_instructions_details in the CIF Please Do !
PLAT380_ALERT_4_G Incorrectly? Oriented X(sp2)-Methyl Moiety ..... C14 Check

0 ALERT level A = Most likely a serious problem - resolve or explain
0 ALERT level B = A potentially serious problem, consider carefully
3 ALERT level C = Check. Ensure it is not caused by an omission or oversight
2 ALERT level G = General information/check it is not something unexpected

0 ALERT type 1 CIF construction/syntax error, inconsistent or missing data
3 ALERT type 2 Indicator that the structure model may be wrong or deficient
0 ALERT type 3 Indicator that the structure quality may be low
1 ALERT type 4 Improvement, methodology, query or suggestion
1 ALERT type 5 Informative message, check

Compound **5** (CCDC-1017452):



5

Datablock: z

```
Bond precision:        C-C = 0.0056 A                Wavelength=0.71073
Cell:         a=15.245(4)       b=6.6576(17)      c=15.228(4)
              alpha=90          beta=118.268(7)   gamma=90
Temperature: 296 K
                      Calculated                        Reported
Volume                1361.3(6)                         1361.3(6)
Space group           P 21/c                            P2(1)/c
Hall group            -P 2ybc                           ?
Moiety formula        C14 H14 O2 S2                     ?
Sum formula           C14 H14 O2 S2                     C14 H14 O2 S2
Mr                    278.39                            278.37
Dx,g cm-3             1.358                             1.358
Z                     4                                 4
Mu (mm-1)             0.382                             0.382
F000                  584.0                             584.0
F000'                 585.21
h,k,lmax              18,7,18                           18,7,18
Nref                  2383                              2380
Tmin,Tmax             0.925,0.959                       0.881,0.959
Tmin'                 0.878
Correction method= MULTI-SCAN
Data completeness= 0.999          Theta(max)= 25.010
R(reflections)= 0.0473( 1531)         wR2(reflections)= 0.1301( 2380)
S = 1.032               Npar= Npar = 163
```

The following ALERTS were generated. Each ALERT has the format
test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.

Alert level C

PLAT340_ALERT_3_C Low Bond Precision on C-C Bonds ..... 0.0056 Ang.

Alert level G

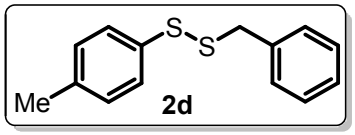
PLAT005_ALERT_5_G No _iucr_refine_instructions_details in the CIF Please Do !
PLAT066_ALERT_1_G Predicted and Reported Tmin&Tmax Range Identical ? Check
PLAT380_ALERT_4_G Incorrectly? Oriented X(sp2)-Methyl Moiety ..... C13 Check
PLAT380_ALERT_4_G Incorrectly? Oriented X(sp2)-Methyl Moiety ..... C14 Check

0 **ALERT level A** = Most likely a serious problem - resolve or explain
0 **ALERT level B** = A potentially serious problem, consider carefully
1 **ALERT level C** = Check. Ensure it is not caused by an omission or oversight
4 **ALERT level G** = General information/check it is not something unexpected

1 ALERT type 1 CIF construction/syntax error, inconsistent or missing data
0 ALERT type 2 Indicator that the structure model may be wrong or deficient
1 ALERT type 3 Indicator that the structure quality may be low
2 ALERT type 4 Improvement, methodology, query or suggestion
1 ALERT type 5 Informative message, check

All these data can be obtained free of charge from Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/ data_request/ci.

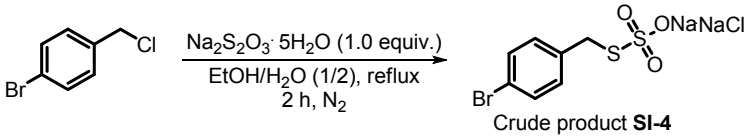
VI. Gram Scale Reaction



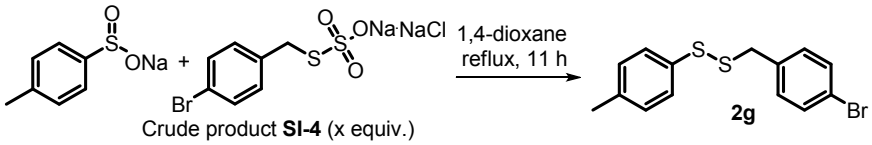
To a Schlenk tube were added $Na_2S_2O_3{\cdot}5H_2O$ (1.24 g, 5.0 mmol, 5.0 equiv.), BnCl (580 uL, 5.0 mmol, 5.0 equiv.), EtOH/H_2O (1.3 mL/2.5 mL), the mixture was stirred at reflux for 2 h under N_2 atmosphere before the solvent was removed. TolSO_2Na (178.2 mg, 1.0 mmol, 1.0 equiv.), 1,4-dioxane (2.5 mL) were added, the mixture was stirred at 110 ^oC (reflux) for 11 hour. After the reaction was finished, DDQ (136 mg, 0.6 mmol, 0.6 equiv.) was added, the reaction system was stirred at room temperature for 4 hours before it was concentrated under vacuum. Purification by column chromatography afforded the title product **2d** (172.0 mg, 0.7 mmol, 70%) as a colorless solid.

To a Schlenk tube were added, $Na_2S_2O_3{\cdot}5H_2O$ (12.4 g, 50 mmol, 5.0 equuiv.), BnCl (5.8 mL, 50 mmol, 5.0 equiv.), EtOH/H_2O (12.5 mL/25 mL), the mixture was stirred at reflux for 2 h under N_2 atmosphere, before the solvent was removed. TolSO_2Na (1.78 g, 10 mmol, 1.0 equiv.), 1,4-dioxane (25 mL or 13 mL) were added, the mixture was stirred at 110 ^oC (reflux) for 11 hours. After the reaction was finished, DDQ (1.36 g, 6.0 mmol, 0.6 equiv.) was added, the reaction system was stirred at room temperature for 4 hours before it was concentrated under vacuum. Purification by column chromatography afforded the title product **2d** (1.89 g, 7.7 mmol, 77%) as a colorless solid.

VII. Control Experiments



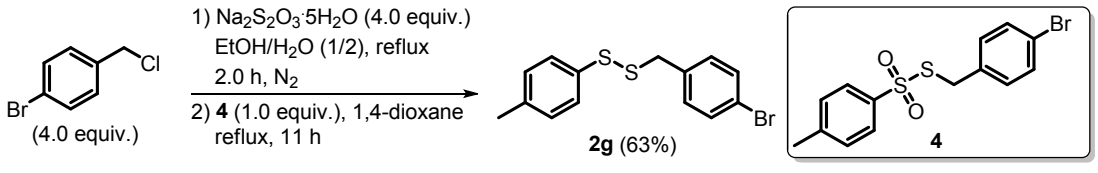
Prepared for **SI-4** following as step 1: To a Schlenk tube were added $Na_2S_2O_3 \cdot 5H_2O$ (2.48 g, 10 mmol, 1.0 equiv.), 1-bromo-4-(chloromethyl)benzene (2.05 g, 10 mmol, 1.0 equiv.), EtOH/H_2O (2.5 mL/5.0 mL), the mixture was stirred at reflux for two hours under N_2 atmosphere before the solvent was removed. The crude product **SI-4** was obtained as a white solid.



Entry	**SI-5** /equiv.	Yield/%	Entry	**SI-5** /equiv.	Yield/%
1[a]	1.0	13	5	5.0	75
2	2.0	53	6	6.0	75
3	3.0	68	7	7.0	72
4	4.0	72	8	8.0	64

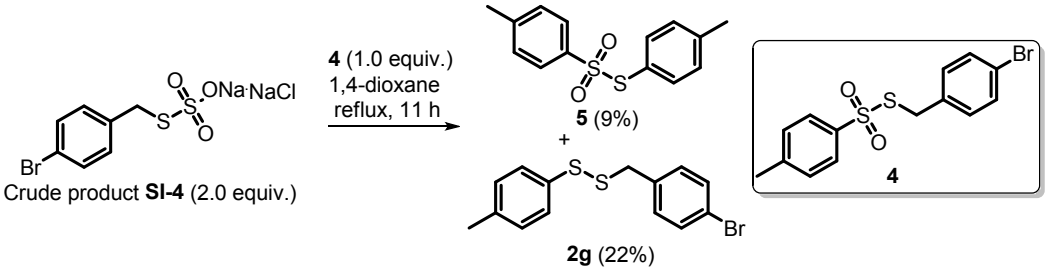
[a] The yields of intermediates : $TolSO_2STol$ (16%), 4-$BrC_6H_4CH_2SSO_2Tol$ (10%), (4-$BrC_6H_4CH_2S)_2$ (34%)

Procedures of disulfide obtained by equivalents of halide and $Na_2S_2O_3$: To a Schlenk tube were added $TolSO_2Na$ (0.2 mmol) and crude product **SI-4**, the mixture was stirred at 110 °C (reflux) for 11 hours before it was concentrated, purified by column chromatography to afford the desired product **2g**. When the amount of **SI-4** was 1.0 equiv., compound **2g** (13%), **4** (10%) and **5** (16%), **6** (34%) were obtained.

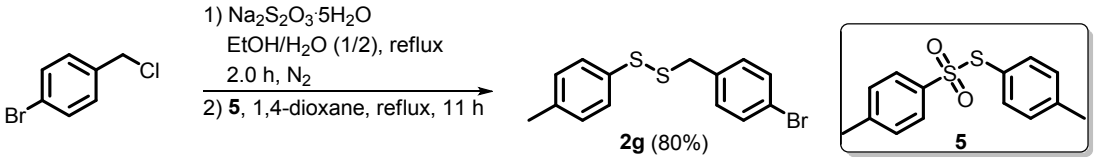


To a Schlenk tube were added $Na_2S_2O_3 \cdot 5H_2O$ (198.6 mg, 0.8 mmol, 4.0 equiv.), 1-bromo-4-(chloromethyl)benzene (164.4 mg, 0.8 mmol, 4.0 equiv.), EtOH/H_2O (0.2 mL/0.4 mL), the mixture was stirred at reflux for two hours under N_2 atmosphere, then the solvent was removed. Compound **4** (71.5 mg, 0.2 mmol, 1.0 equiv.) and 1,4-dioxane (1.0 mL) were added to the reaction, then the mixture was stirred at 110 °C

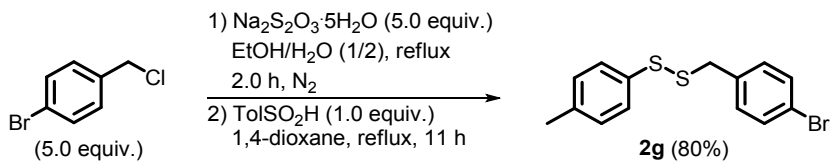
(reflux) for 11 hours before it was concentrated, purified by column chromatography to afford the desired product **2g** (40.9 mg, 0.126 mmol, 63%).



To a Schlenk tube were added **4** (71.5 mg, 0.2 mmol, 1.0 equiv.) and the crude **SI-4** (144.6 mg, 0.4 mmol, 1.0 equiv.), then the mixture was stirred at 110 °C (reflux) for 11 hours before it was concentrated, purified by column chromatography to afford the desired product. Compound **5** (2.5 mg, 0.009 mmol, 9%) and **2g** (14.3mg, 0.044 mmol, 22%) was obtained, starting material **4** (56%) was recovered simultaneously.

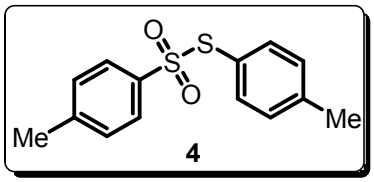


To a Schlenk tube were added $Na_2S_2O_3 \cdot 5H_2O$ (248.2 mg, 1.0 mmol), 1-bromo-4-(chloromethyl)benzene (205.5 mg, 1.0 mmol), EtOH/H_2O (0.25 mL/0.5 mL), the mixture was stirred at reflux for 2 h under N_2 atmosphere before the solvent was removed. **5** (27.8 mg, 0.1 mmol), 1,4-dioxane (1.0 mL) were added, the mixture was stirred at 110 °C (reflux) for 11 hours before it was concentrated, purified by column chromatography to afford the desired product **2g** (52.0 mg, 0.16 mmol, 80%).



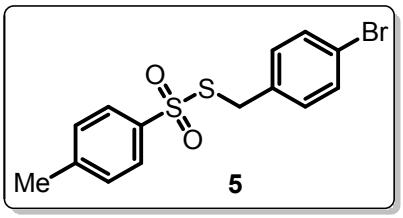
To a Schlenk tube were added $Na_2S_2O_3 \cdot 5H_2O$ (248.2 mg, 1.0 mmol, 5.0 equiv.), 1-bromo-4-(chloromethyl)benzene (205.5 mg, 1.0 mmol, 5.0 equiv.), EtOH/H_2O (0.25 mL/0.5 mL), the mixture was stirred at reflux for 2 hours under N_2 atmosphere, then removed the solvent. $TolSO_2H$ (52.4 mg, 0.2 mmol, 1.0 equiv.), 1,4-dioxane (1.0 mL)

were added, the mixture was stirred at 110 °C (reflux) for 11 hours before it was concentrated, purified by column chromatography to afford the desired product **2g** (52.0 mg, 0.16 mmol, 80%).



4

Compound **4**[7]: A colorless solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.46 (dd, *J* = 8.4, 2.0 Hz, 2H), 7.25-7.20 (m, 4H), 7.14 (d, *J* = 8.0 Hz, 2H), 2.42 (s, 3H), 2.37 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ144.56, 142.01, 140.43, 136.45, 130.16, 129.33, 127.55, 124.56, 21.61, 21.43; **IR** (film) 2920, 1912, 1742, 1591, 1486, 1322, 1135, 1076, 883, 807, 737 cm^{-1}; **MS (EI)** m/z 278 (M+).



5

Compound **5**: To a 25 mL flask were added sodium 4-methylbenzenesulfonothioate[8] (526 mg, 2.5 mmol, 1.0 equiv.), 1-bromo-4-(chloro- methyl)benzene (565 mg, 2.75 mmol, 1.1 equiv.), TBAI (92 mg, 0.25 mmol, 0.1 equiv.) CH_3CN (12 mL), the mixture was heated to 50 °C. After 24 hours, the mixture was cooled to room temperature, then concentrated, purified by column chromatography to afford the desired product (643.1 mg, 1.8 mmol, 72%) as a red solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.68 (d, *J* = 8.4 Hz, 2H), δ 7.34 (d, *J* = 8.4 Hz, 2H), δ 7.27 (d, *J* = 8.4 Hz, 2H), δ 7.06 (d, *J* = 8.4 Hz, 2H), δ 4.22 (s, 2H), δ 2.47 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 144.80, 142.02, 132.96, 131.77, 130.69, 129.69, 126.94, 121.93, 39.61, 21.63; **IR** (film) 2923, 2857, 1592, 1485, 1406, 1323, 1139, 1075, 1013, 810, 708 cm^{-1}; **HRMS (EI)** Calcd for $C_{14}H_{13}BrO_2S_2$ 355.9540, Found 355.9539.

VIII. References

1. Prepared for thiosulfate salts: (a) W. Fan, Y. Wu, X. K. Li, N. Yao, X. Li, Y. G. Yu and L. Hai, *Eur. J. Med. Chem.* 2011, **46**, 365; (b) J. T. Reeves, K. Camara, Z. S. Han, Y. Xu, H. Lee, C. A. Busacca and C. H. Senanayake, *Org. Lett.* 2014, **16**, 1196; (c) J. Yi, Y. Fu, B. Xiao, W. C. Cui and Q. X. Guo, *Tetrahedron Lett.*, 2011 , **52**, 205.

2. Prepared for sodium sulfinate salts: (a) X. Zhou, J. Luo, J. Liu, S. Peng and G. J. Deng, *Org. Lett.*, 2011, **13**, 1432; (b) Z. Huang and J. Xu, *RSC Adv.* 2013, **3**, 15114.

3. D. N. Harpp and R. A. Smith, *J. Am Chem. Soc.* 1982, **104**, 6045.

4. R.G. Hiskey and M.A. Harpold, *Tetrahedron*, 1967, **23**, 3923.

5. C. Remi, R. Martin, V. Pornrapee, B. Tore and R. Olof, *Chem. Comm.* 2008, **48**, 6603.

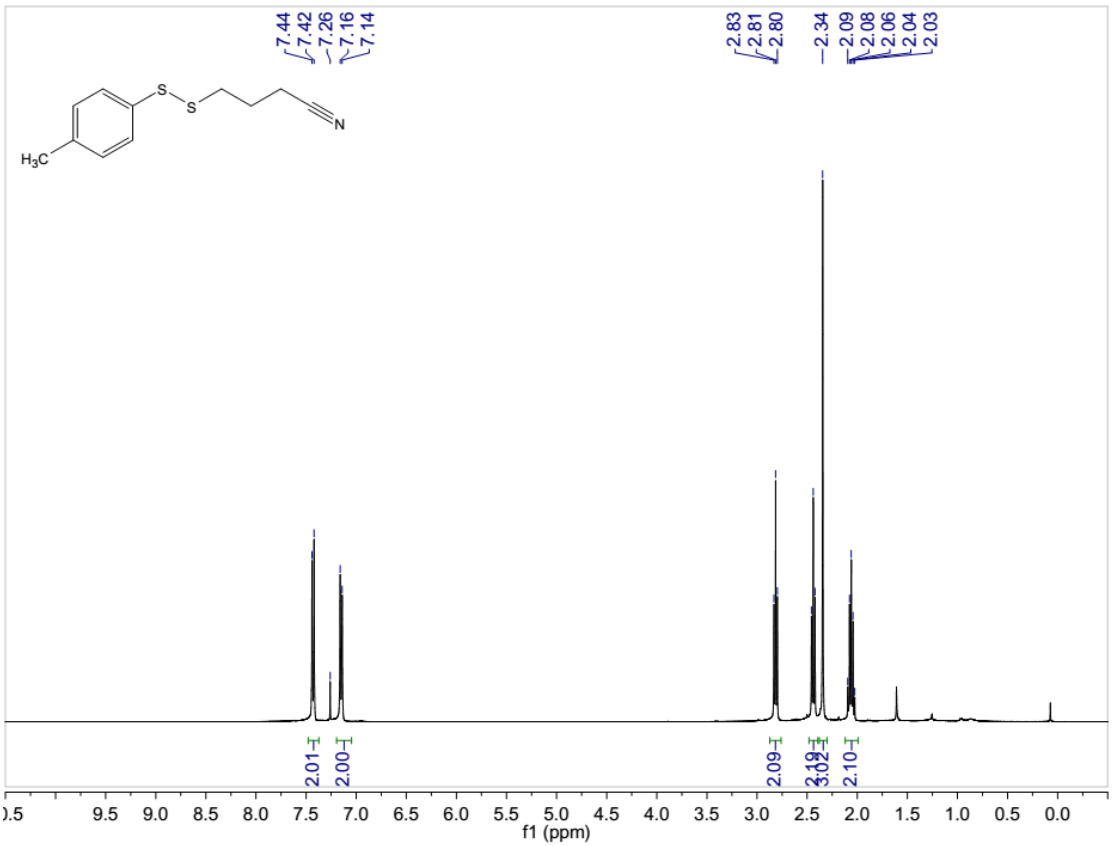
6. M. Arisawa and M. Yamaguchi, *J. Am Chem. Soc.* 2003, **125**, 6624.

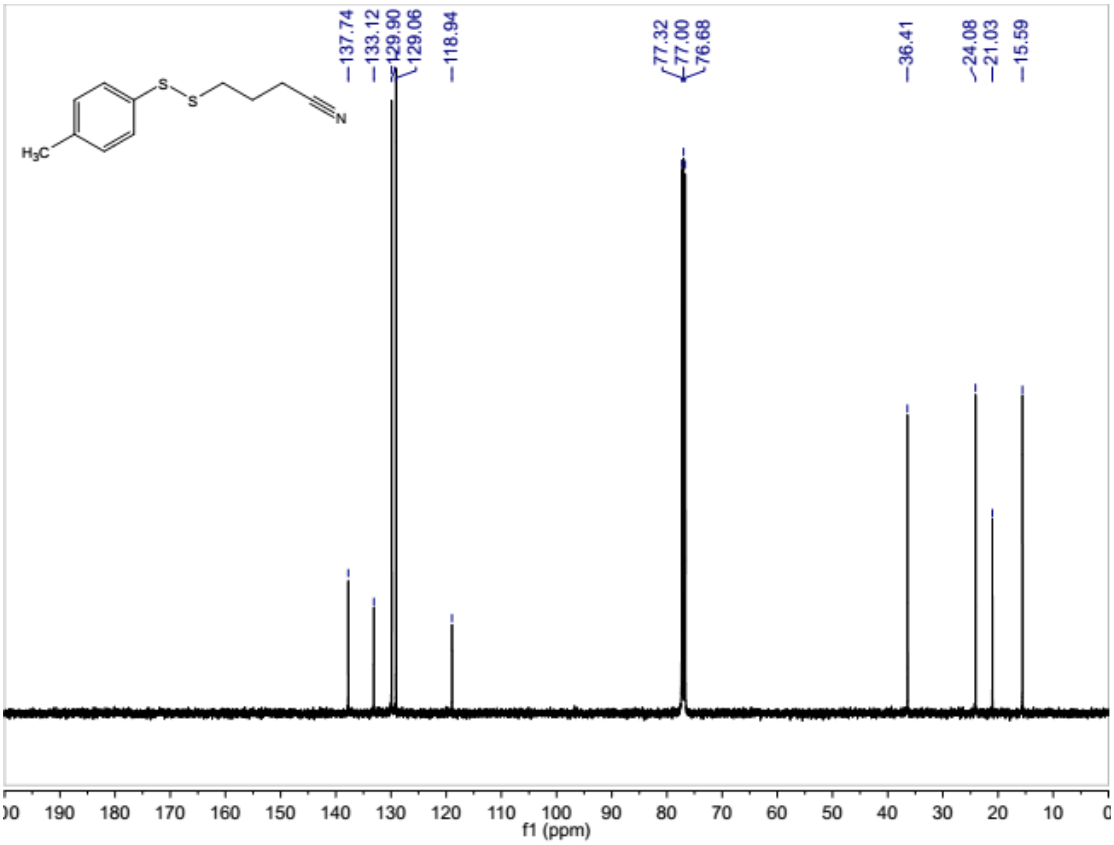
7. F. L.Yang and S. K. Tian, *Angew. Chem., Int. Ed.* 2013, **52**, 4929.

8. (a) J. P. Harmon and L. Field, *J. Org. Chem.* 1986, **51**, 5235; (b) G. E. P. Kruger and T. Gunnlaugsson, *Dalton Trans.* 2011, **40**, 12310.

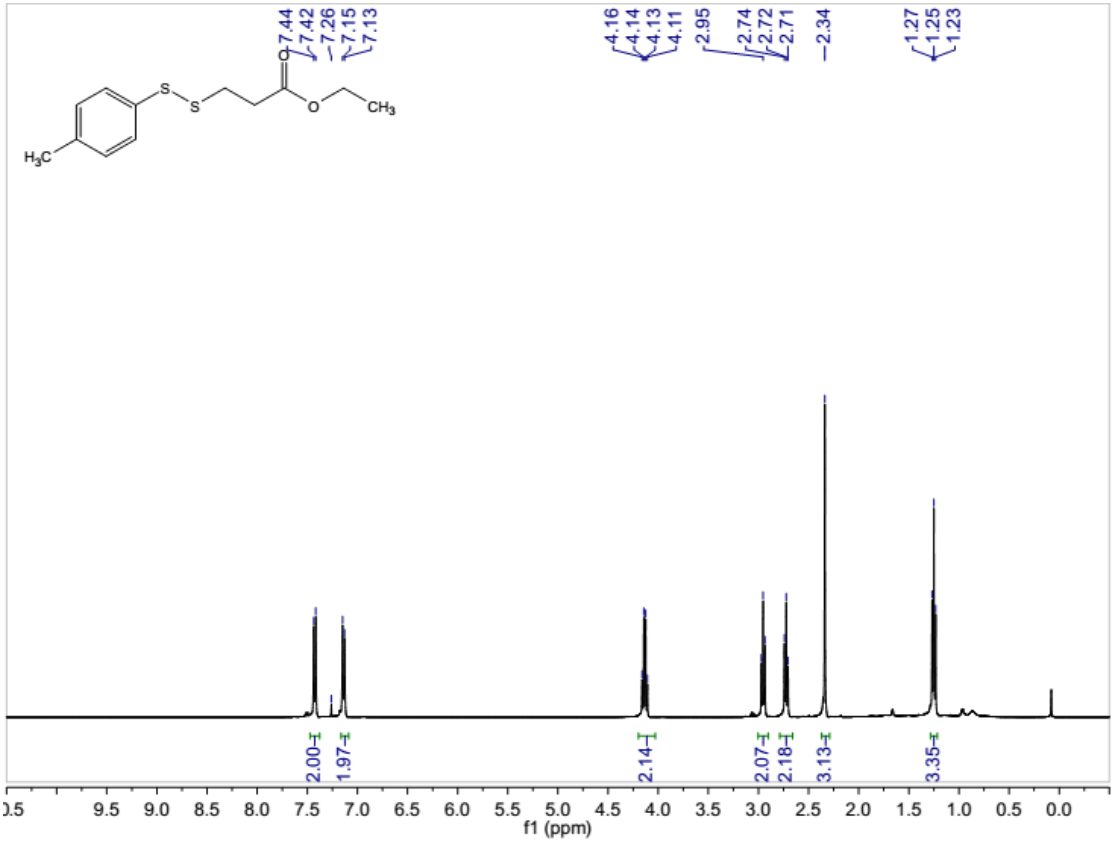
IX. NMR Spectra

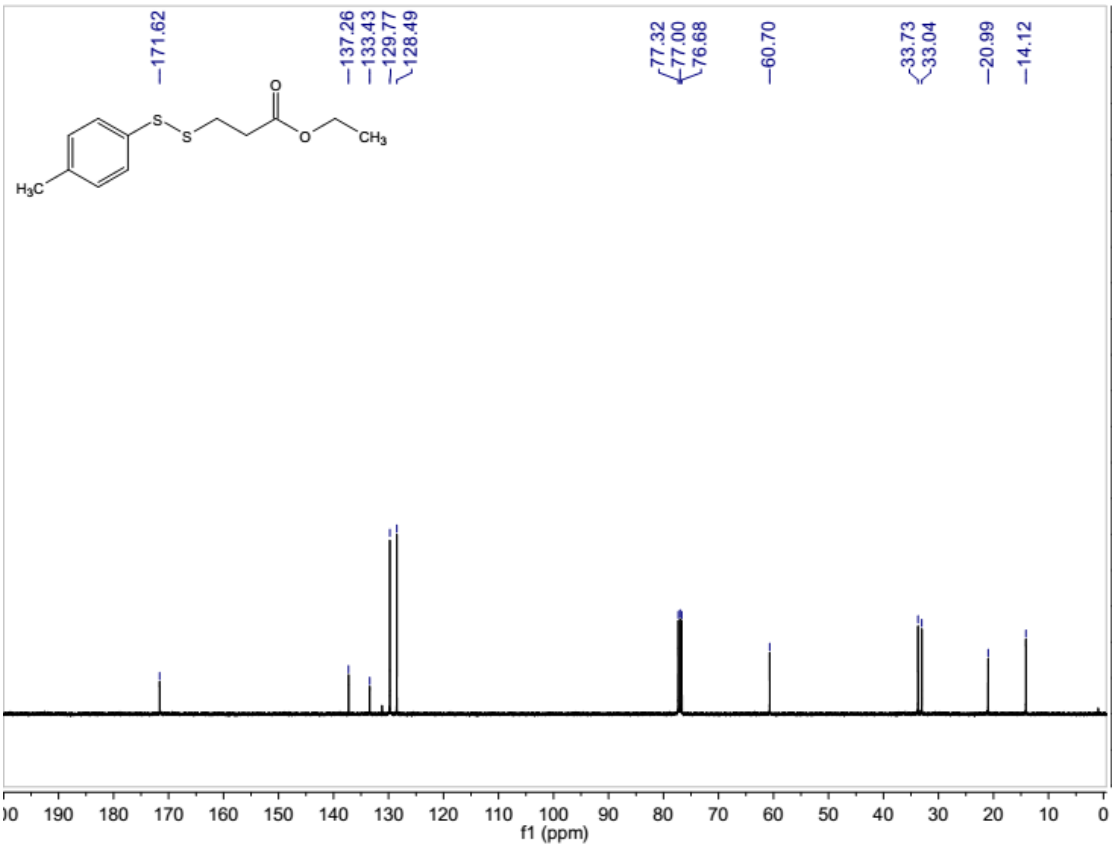
Compound **2a**:



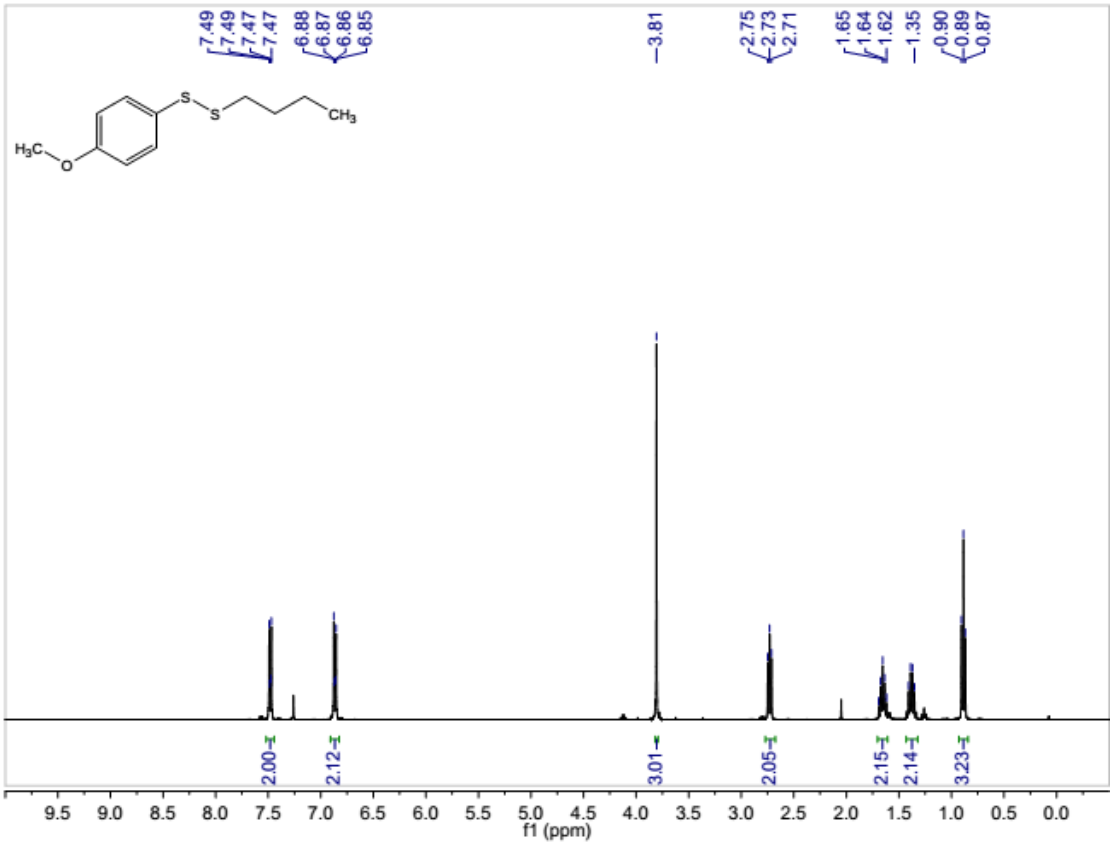


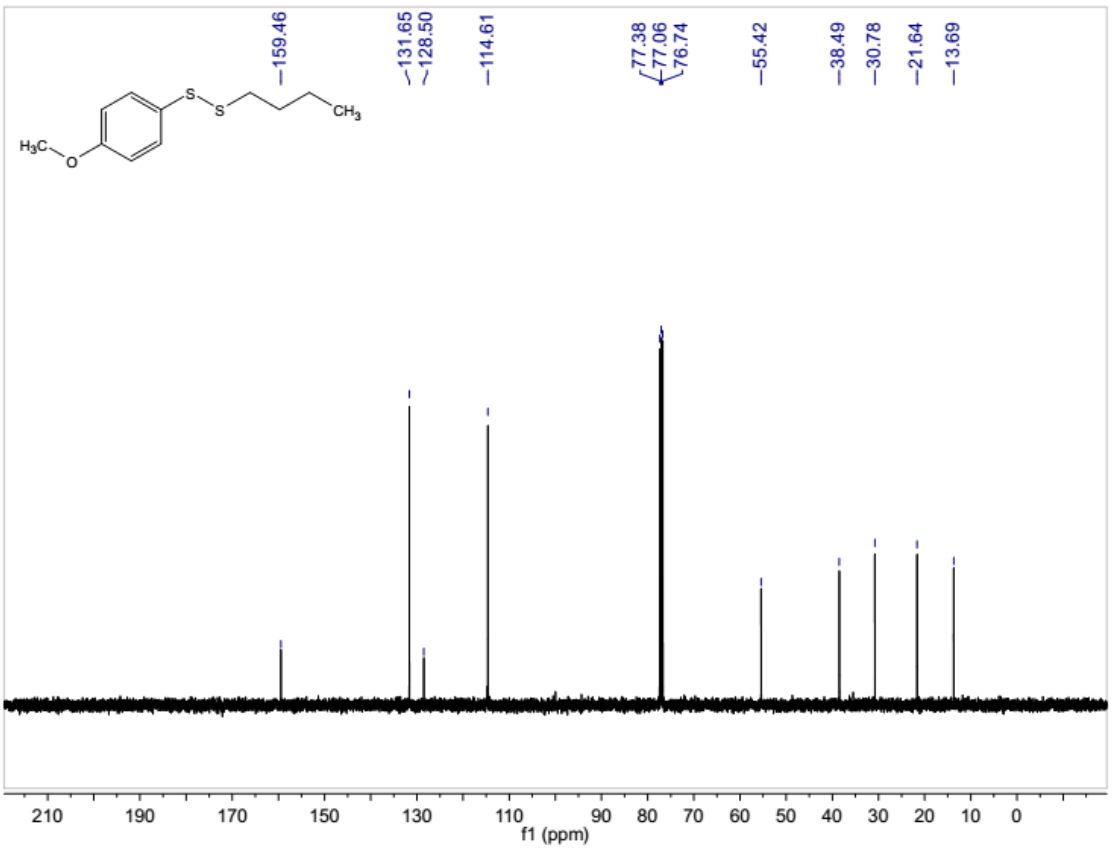
Compound **2b**:


7.44
7.42
7.26
7.15
7.13
4.16
4.14
4.13
4.11
2.95
2.74
2.72
2.71
2.34
1.27
1.25
1.23
2.00
1.97
2.14
2.07
2.18
3.13
3.35
f1 (ppm)

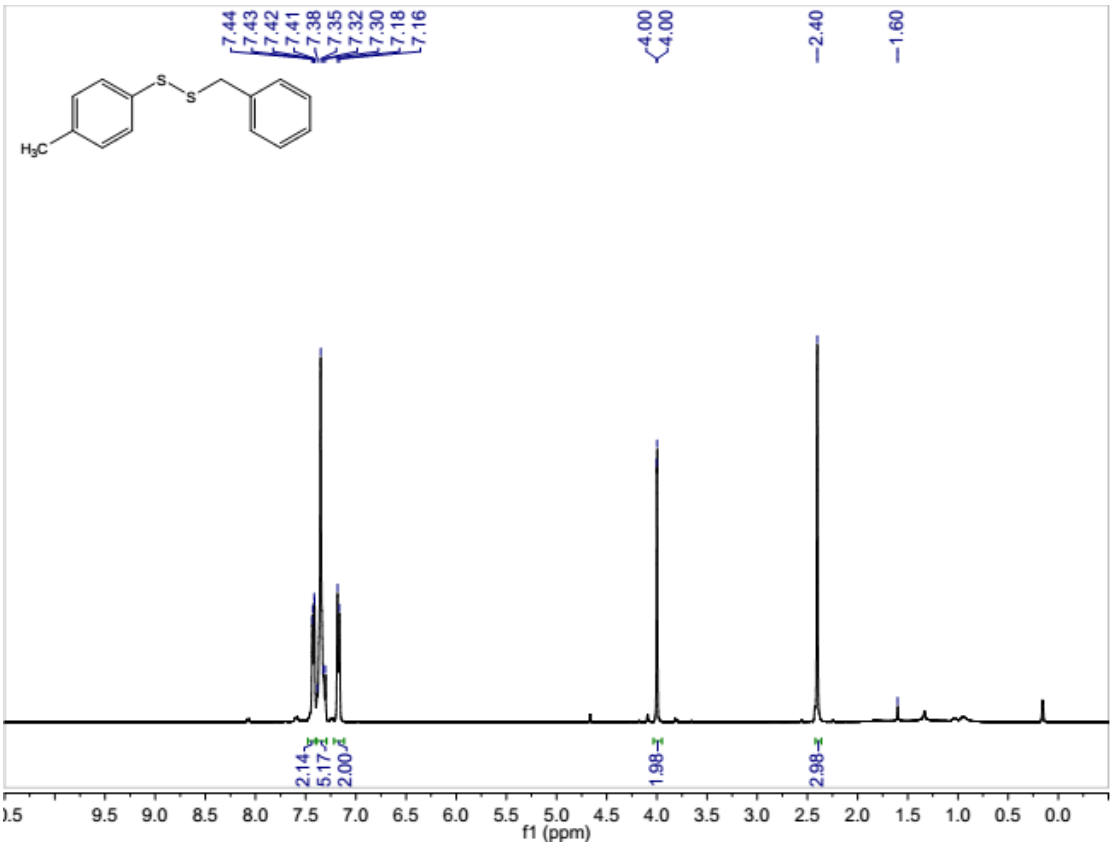

171.62
137.26
133.43
129.77
128.49
77.32
77.00
76.68
60.70
33.73
33.04
20.99
14.12
f1 (ppm)

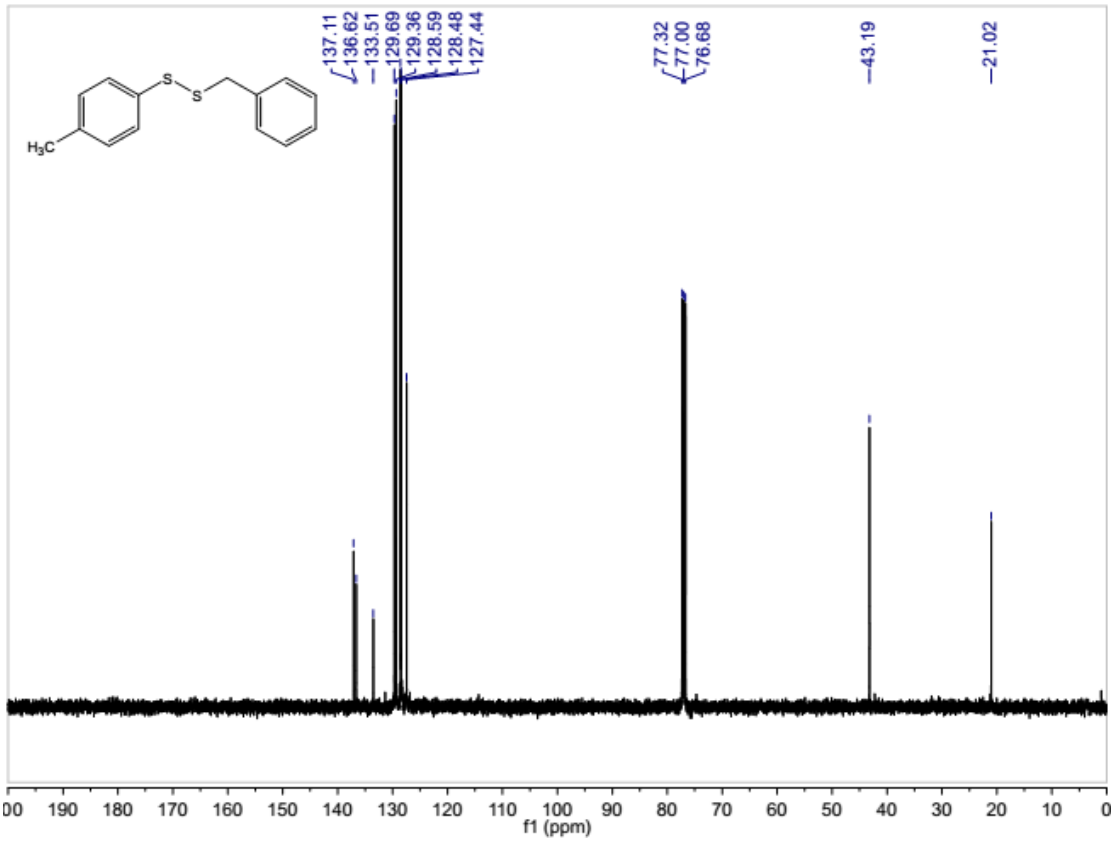
Compound **2c**:


7.49
7.49
7.47
7.47
6.88
6.87
6.86
6.85
3.81
2.75
2.73
2.71
1.65
1.64
1.62
1.35
0.90
0.89
0.87
S
S
CH3
H3C
O
2.00
2.12
3.01
2.05
2.15
2.14
3.23
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

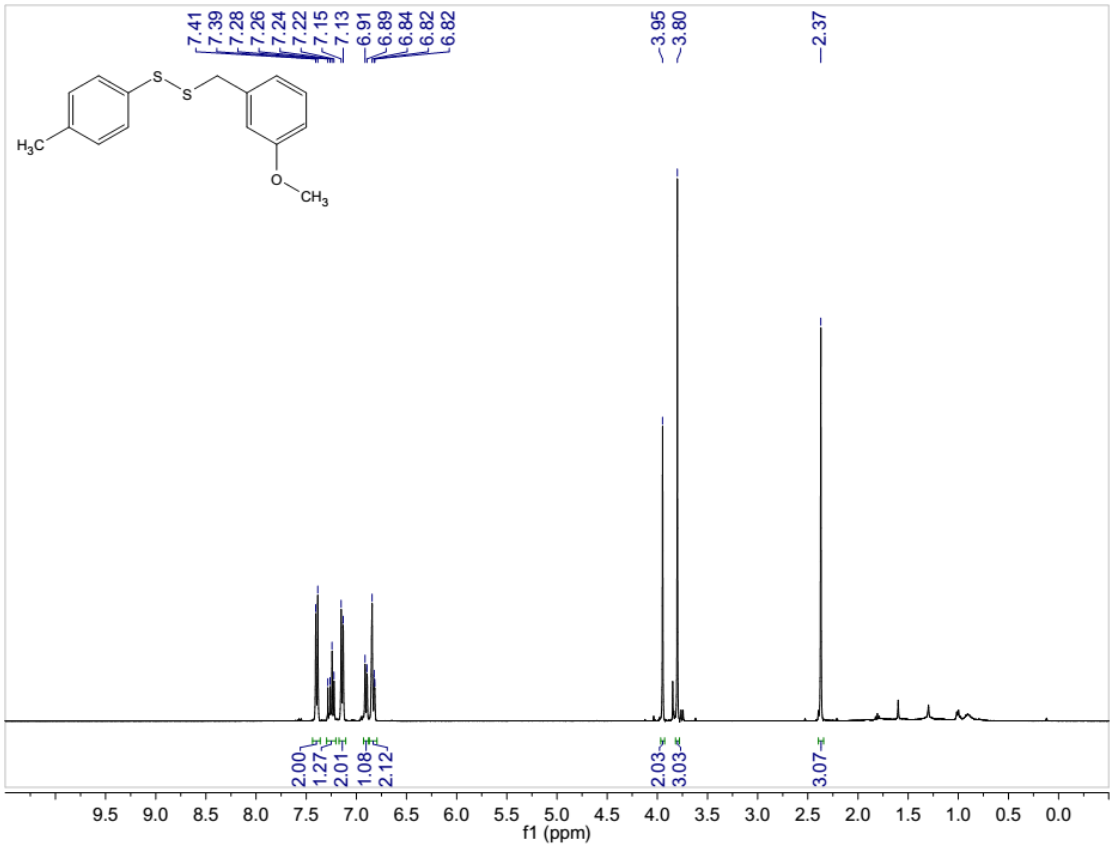

159.46
131.65
128.50
114.61
77.38
77.06
76.74
55.42
38.49
30.78
21.64
13.69
S
S
CH3
H3C
O
210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

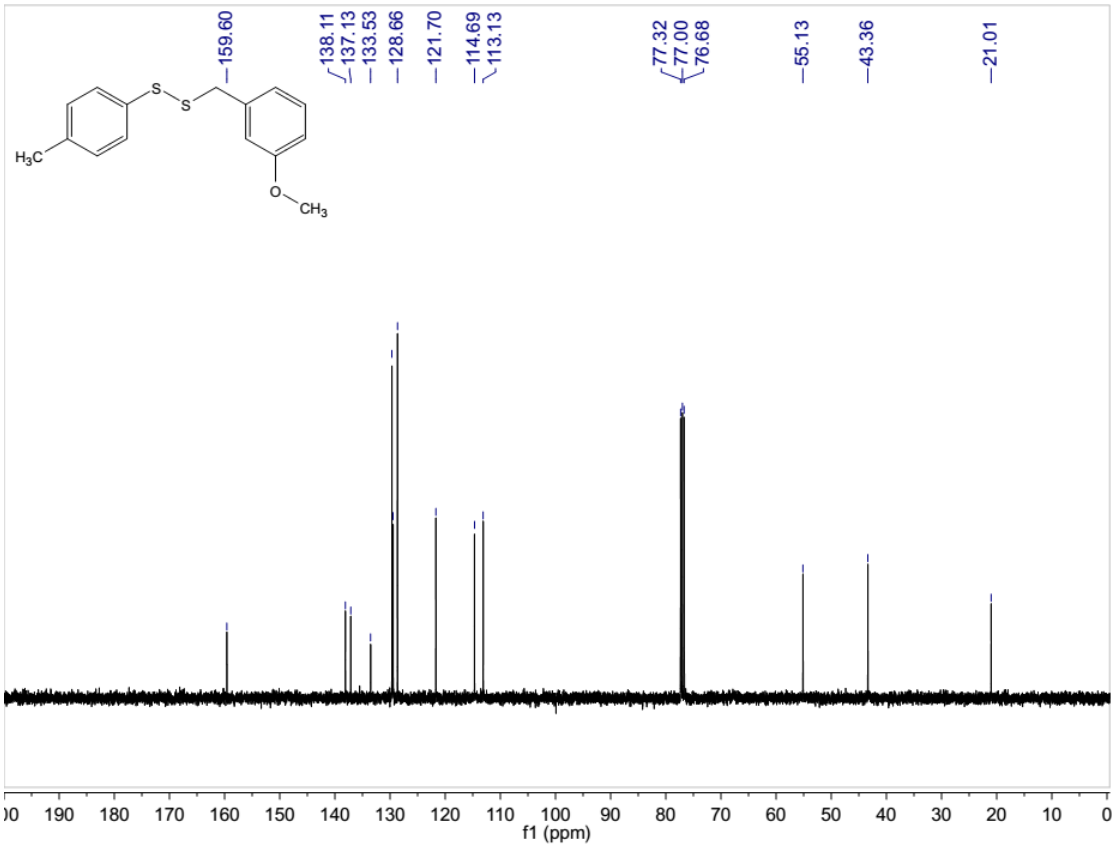
Compound **2d**:


7.44
7.43
7.42
7.41
7.38
7.35
7.32
7.30
7.18
7.16
4.00
4.00
2.40
1.60
S
S
H3C
2.14
5.17
2.00
1.98
2.98
f1 (ppm)

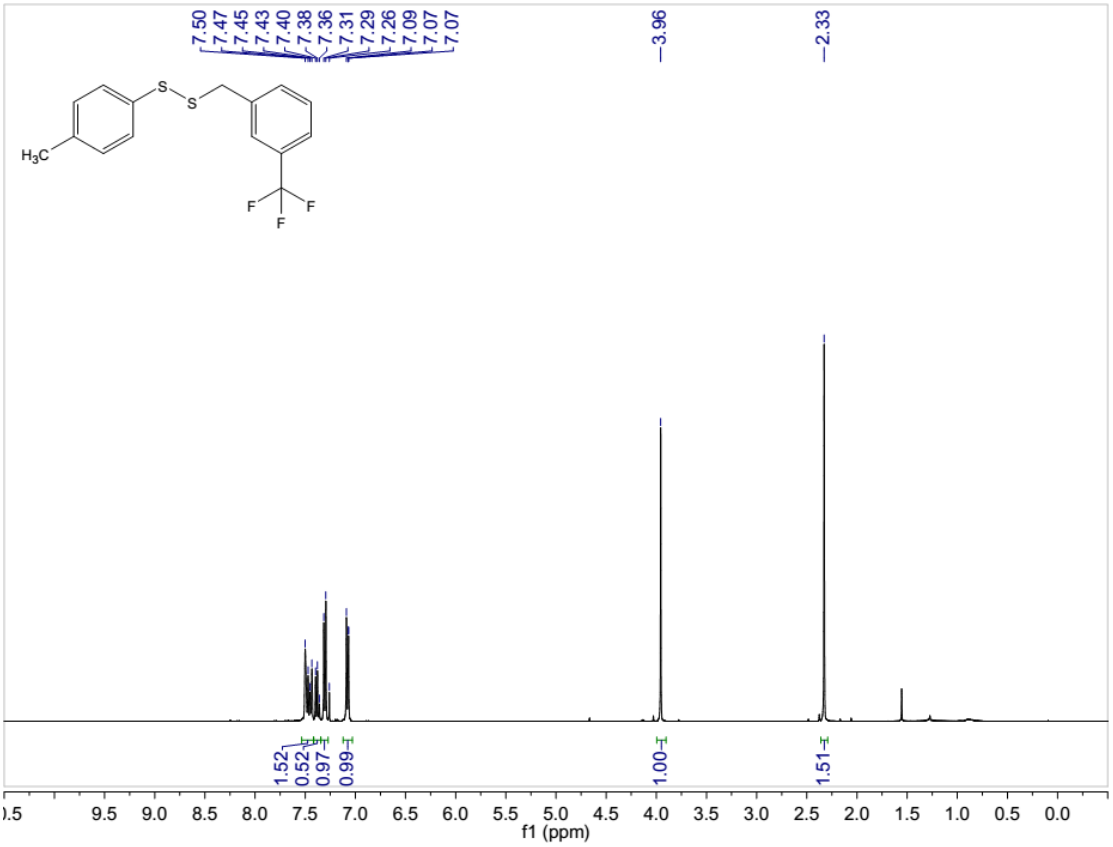

137.11
136.62
133.51
129.69
129.36
128.59
128.48
127.44
77.32
77.00
76.68
43.19
21.02
S
S
H3C
f1 (ppm)

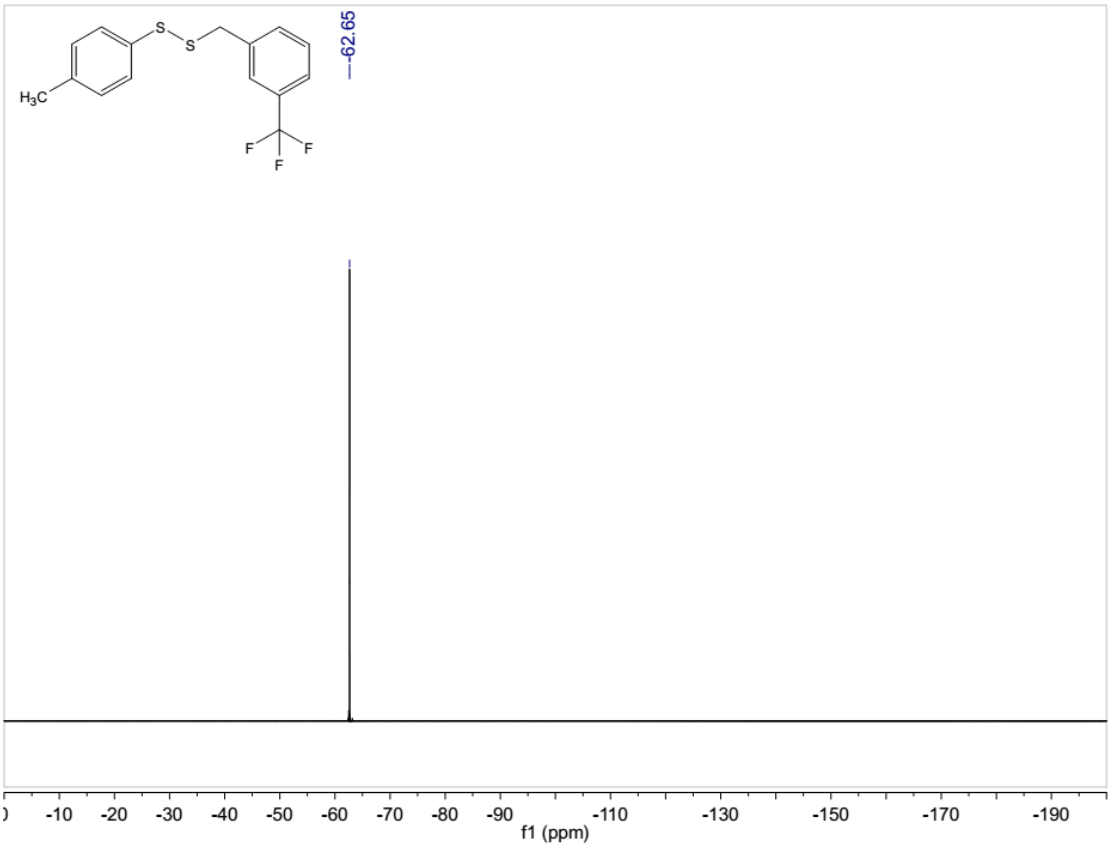
Compound **2e**:

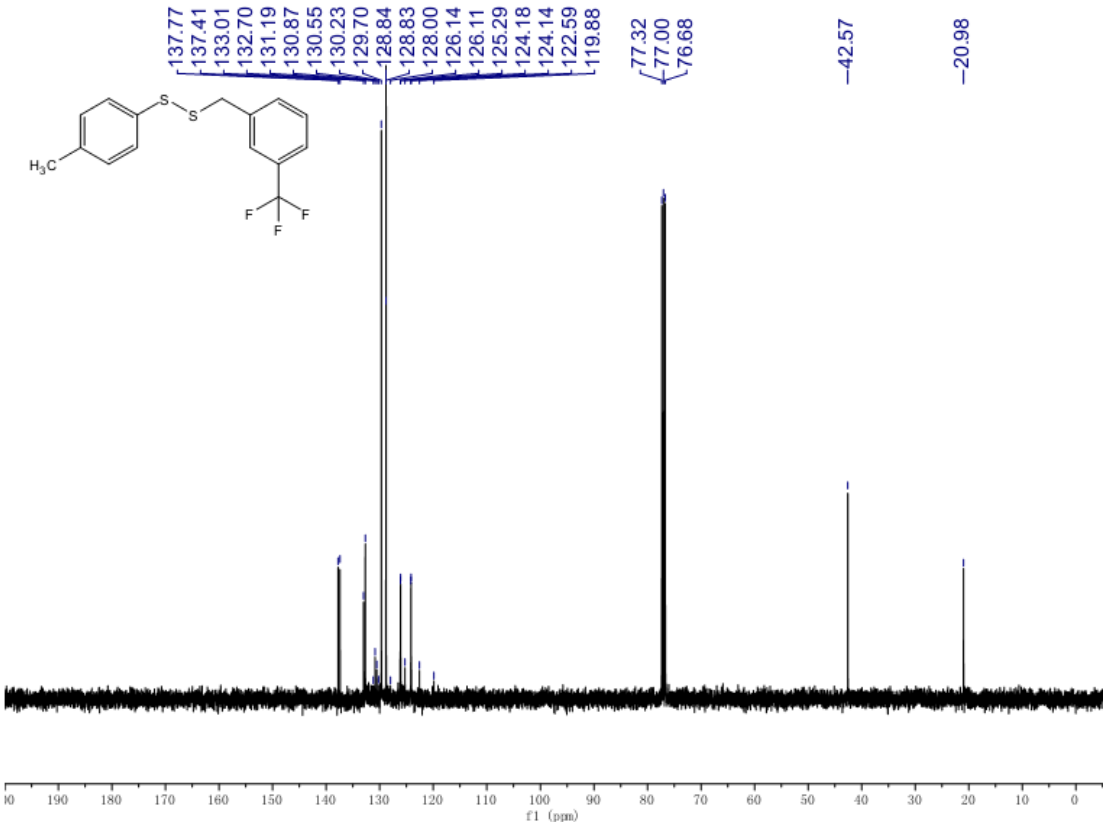

7.41
7.39
7.28
7.26
7.24
7.22
7.15
7.13
6.91
6.89
6.84
6.82
6.82
3.95
3.80
2.37
S
S
H3C
O
CH3
2.00
1.27
2.01
1.08
2.12
2.03
3.03
3.07
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


159.60
138.11
137.13
133.53
128.66
121.70
114.69
113.13
77.32
77.00
76.68
55.13
43.36
21.01
S
S
H3C
O
CH3
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

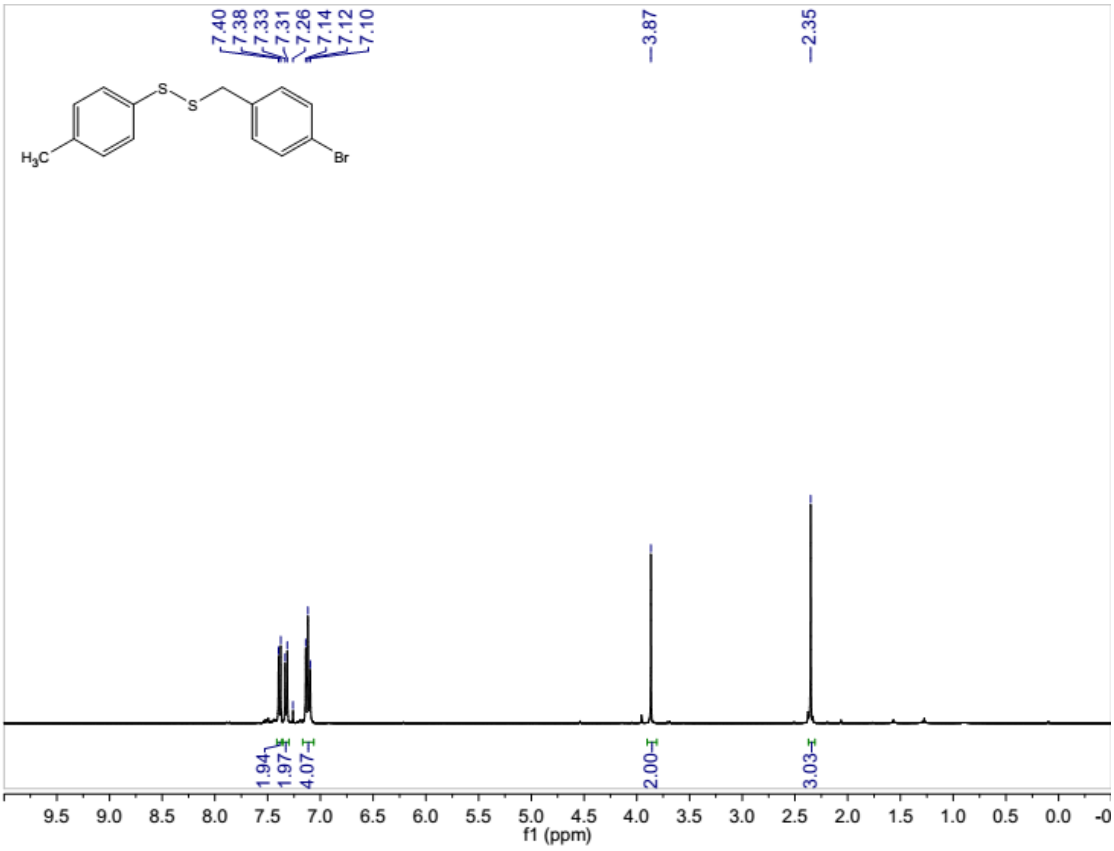
Compound **2f**:

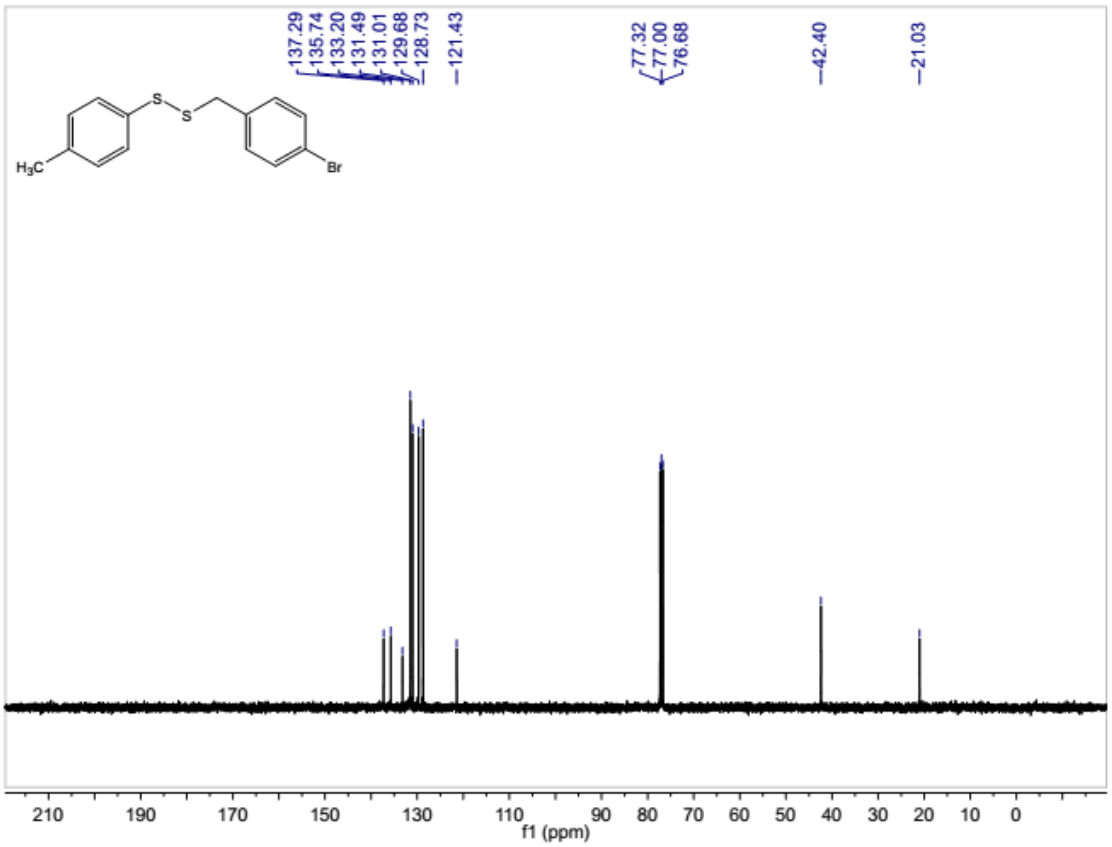

7.50
7.47
7.45
7.43
7.40
7.38
7.36
7.31
7.29
7.26
7.09
7.07
7.07
3.96
2.33
S
S
H3C
F
F
F
1.52
0.52
0.97
0.99
1.00
1.51
f1 (ppm)


-62.65
S
S
H3C
F
F
F
f1 (ppm)

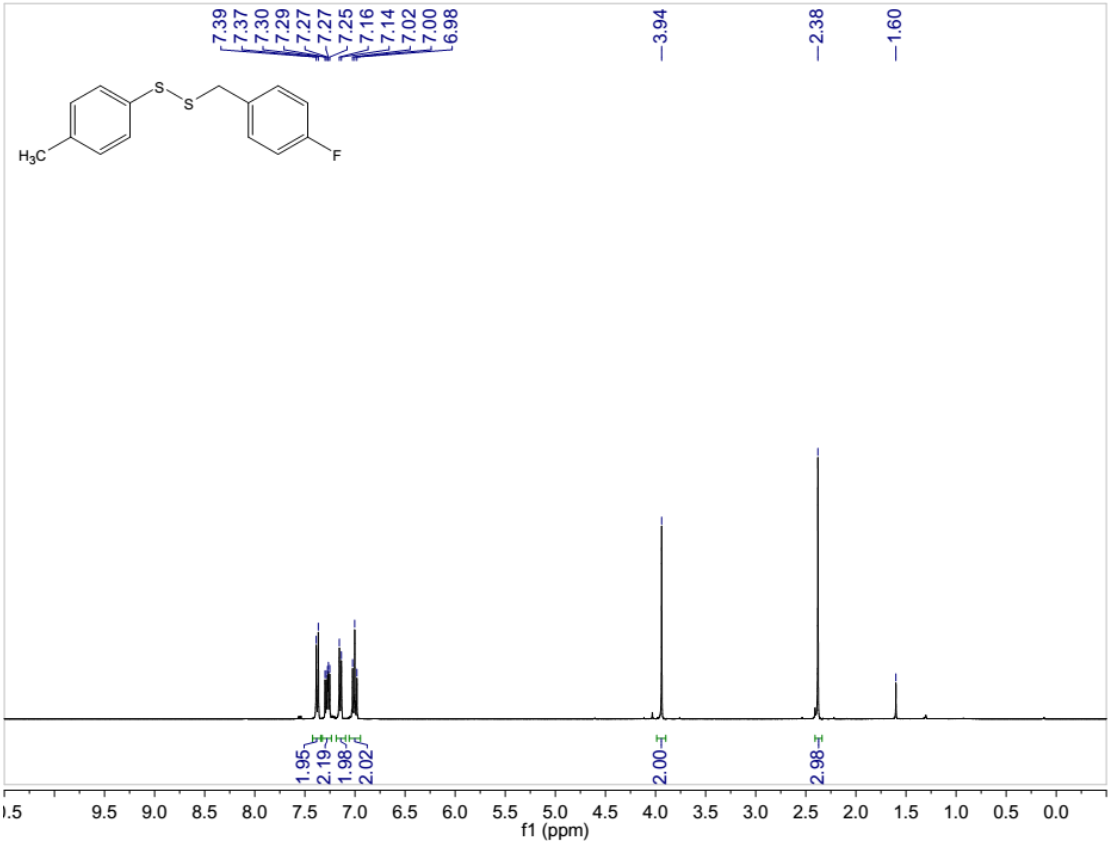

137.77
137.41
133.01
132.70
131.19
130.87
130.55
130.23
129.70
128.84
128.83
128.00
126.14
126.11
125.29
124.18
124.14
122.59
119.88
77.32
77.00
76.68
42.57
20.98
f1 (ppm)

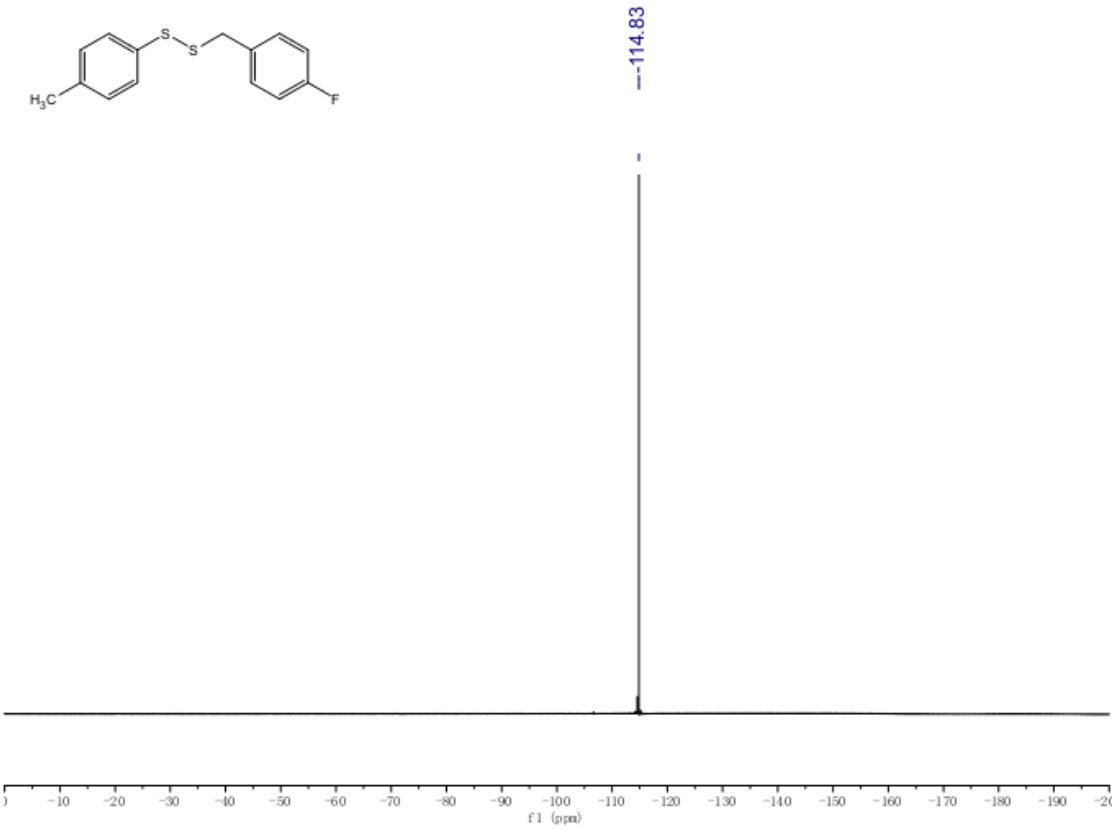
Compound **2g**:

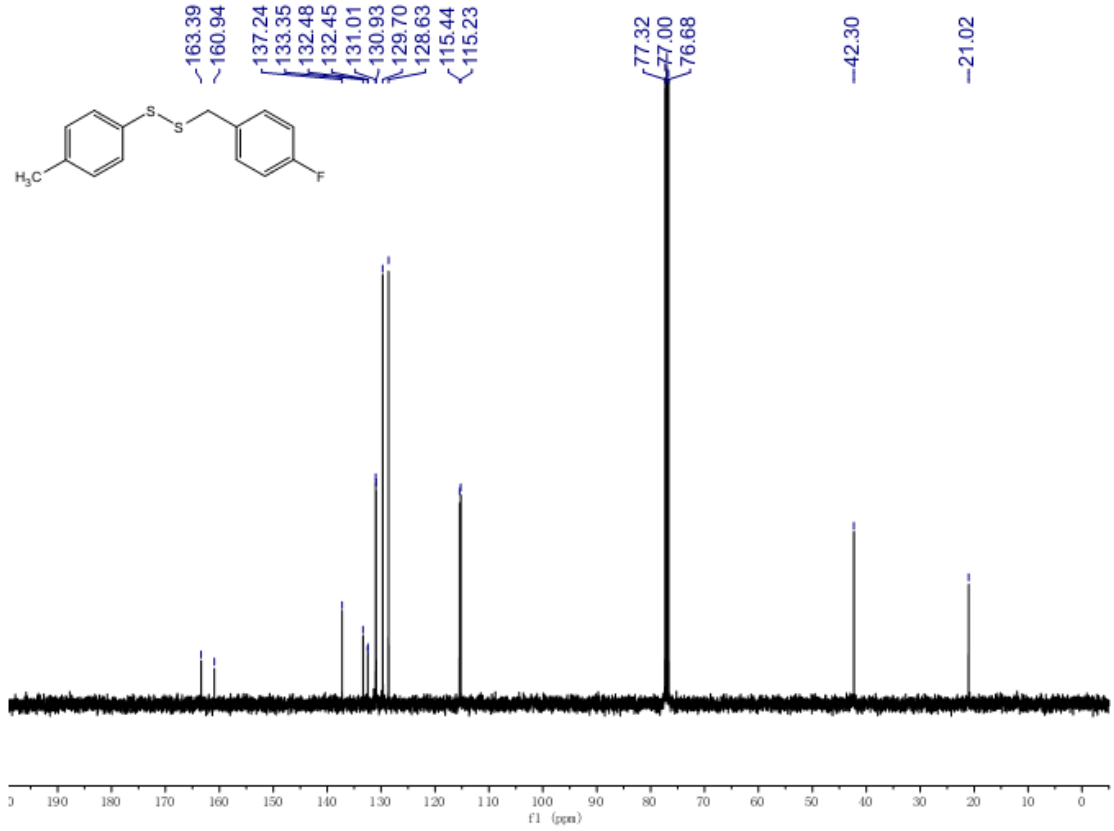

7.40
7.38
7.33
7.31
7.26
7.14
7.12
7.10
3.87
2.35
1.94
1.97
4.07
2.00
3.03
f1 (ppm)


137.29
135.74
133.20
131.49
131.01
129.68
128.73
121.43
77.32
77.00
76.68
42.40
21.03
S
S
H3C
Br
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

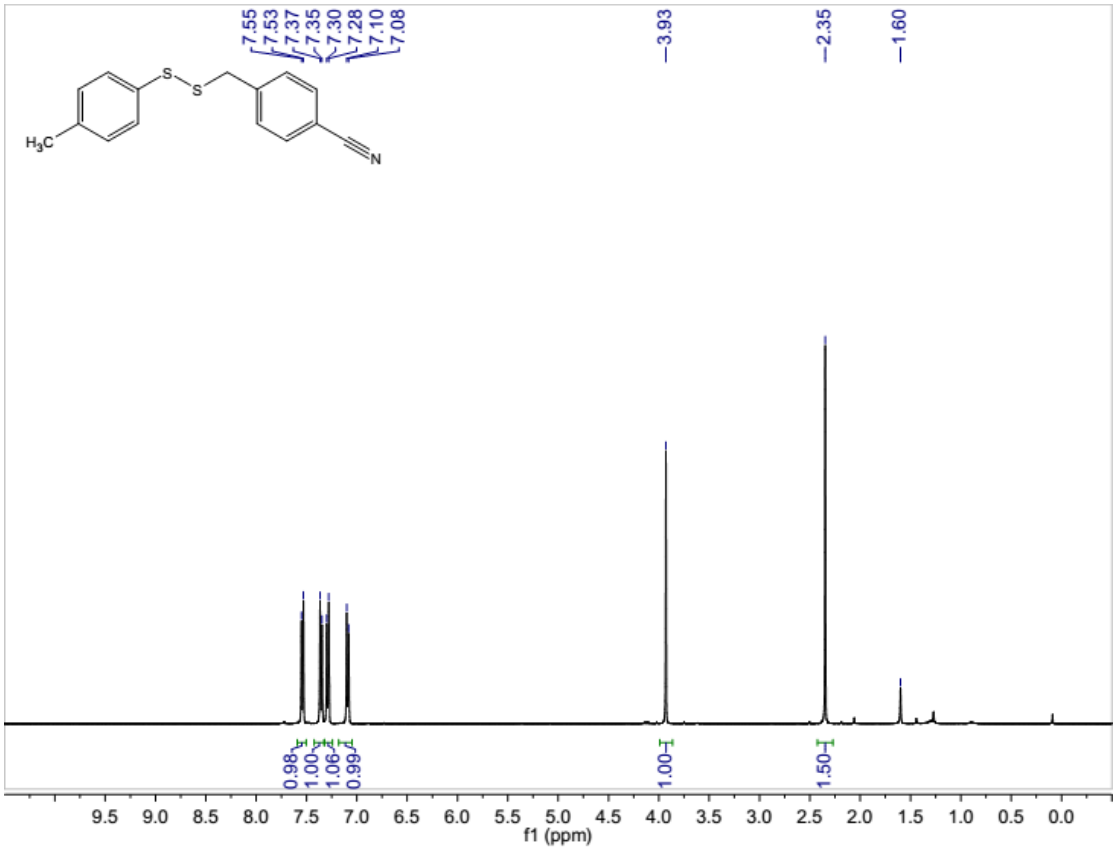
Compound **2h**:

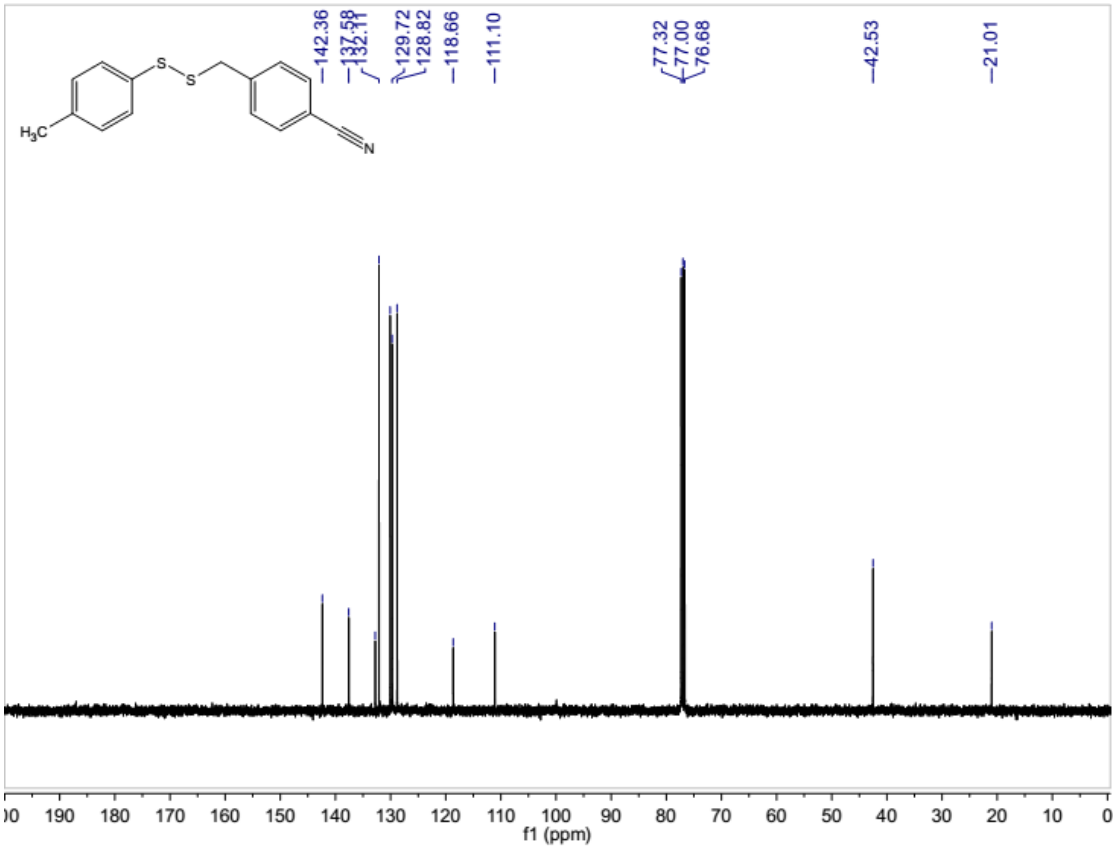

7.39
7.37
7.30
7.29
7.27
7.27
7.25
7.16
7.14
7.02
7.00
6.98
3.94
2.38
1.60
S
S
H3C
F
1.95
2.19
1.98
2.02
2.00
2.98
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


-114.83
f1 (ppm)

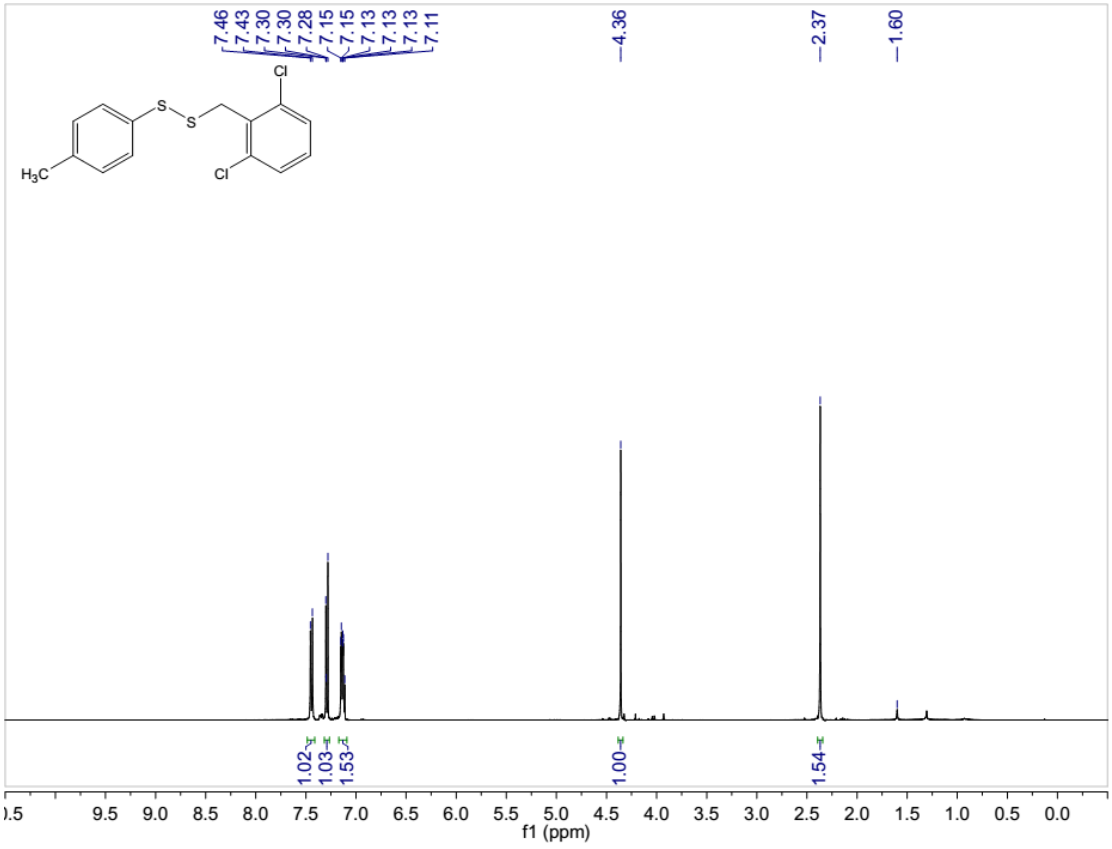

163.39
160.94
137.24
133.35
132.48
132.45
131.01
130.93
129.70
128.63
115.44
115.23
77.32
77.00
76.68
42.30
21.02
f1 (ppm)

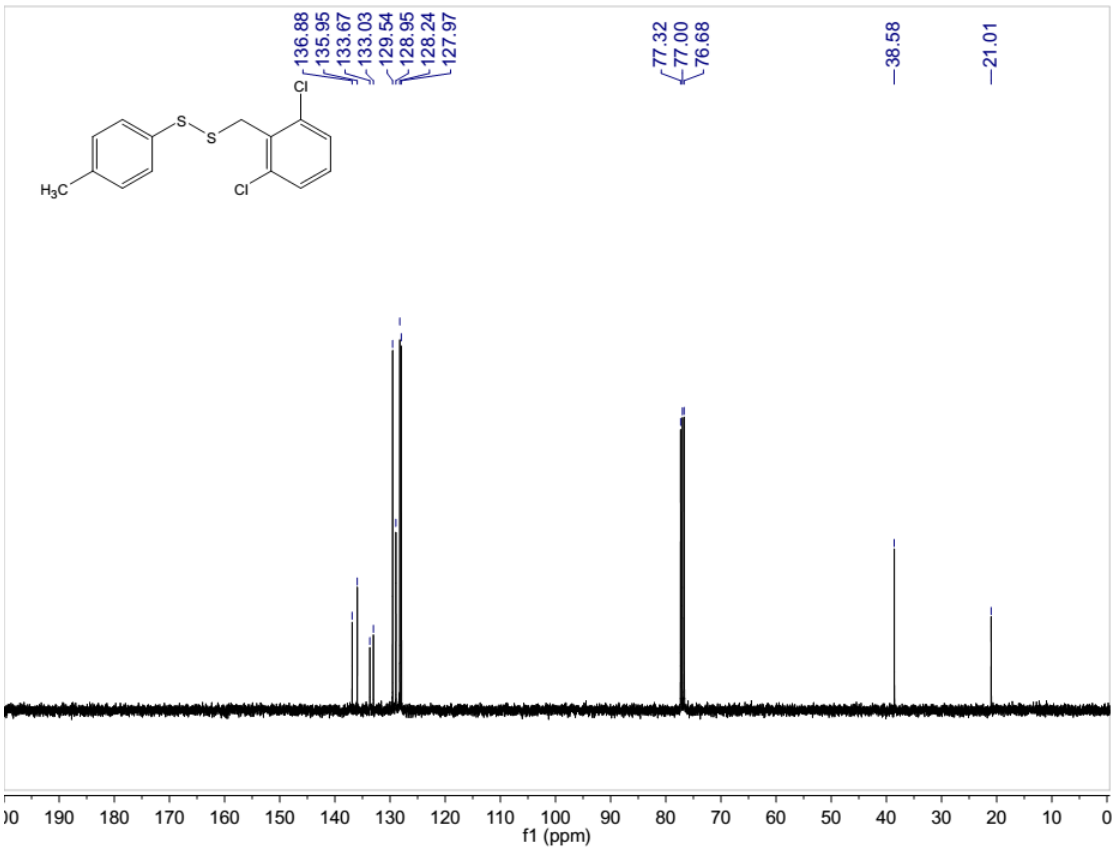
Compound **2i**:


7.55
7.53
7.37
7.35
7.30
7.28
7.10
7.08
3.93
2.35
1.60
0.98
1.00
1.06
0.99
1.00
1.50
f1 (ppm)

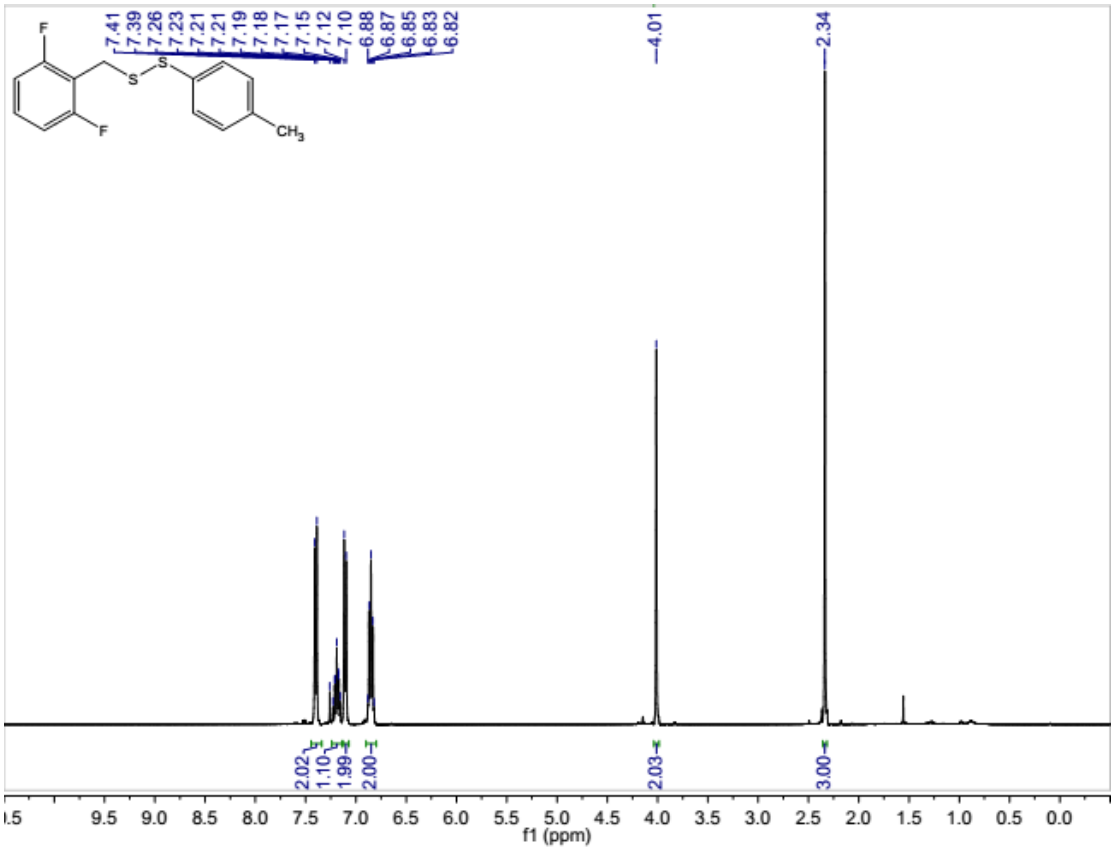

142.36
132.11
129.72
128.82
118.66
111.10
77.32
77.00
76.68
42.53
21.01
f1 (ppm)

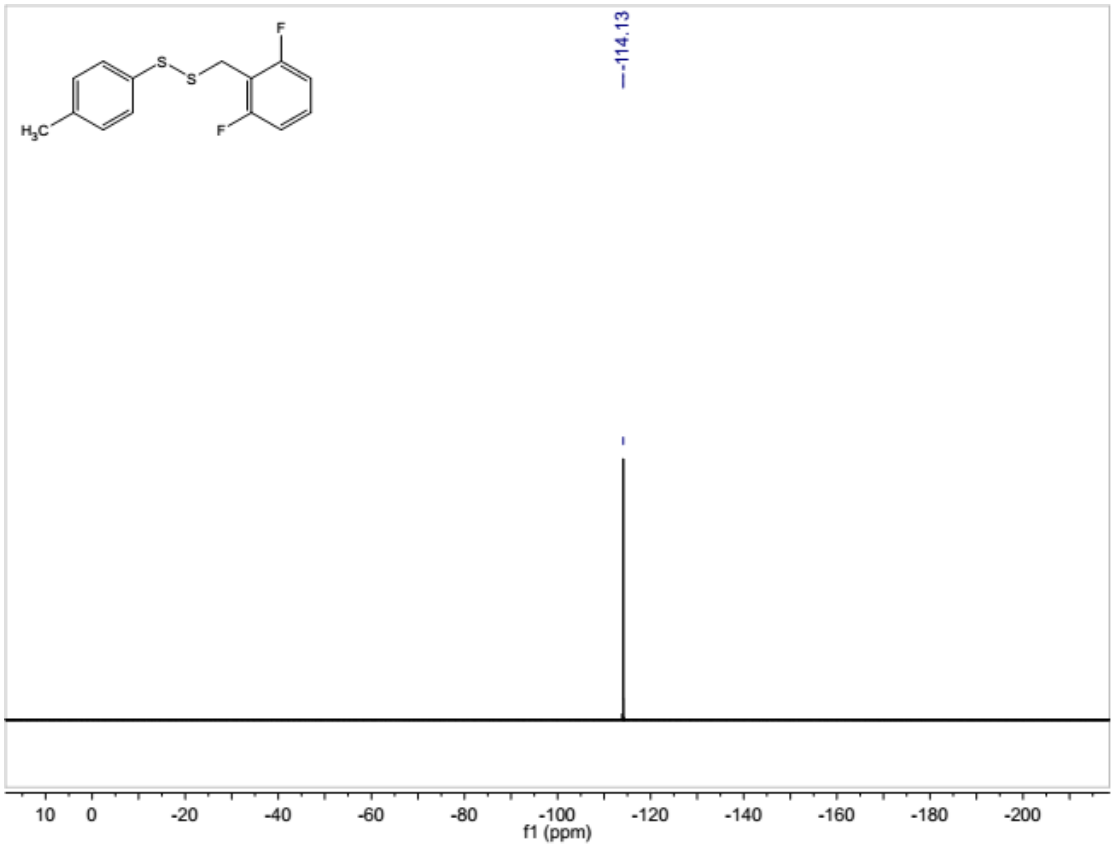
Compound **2j**:

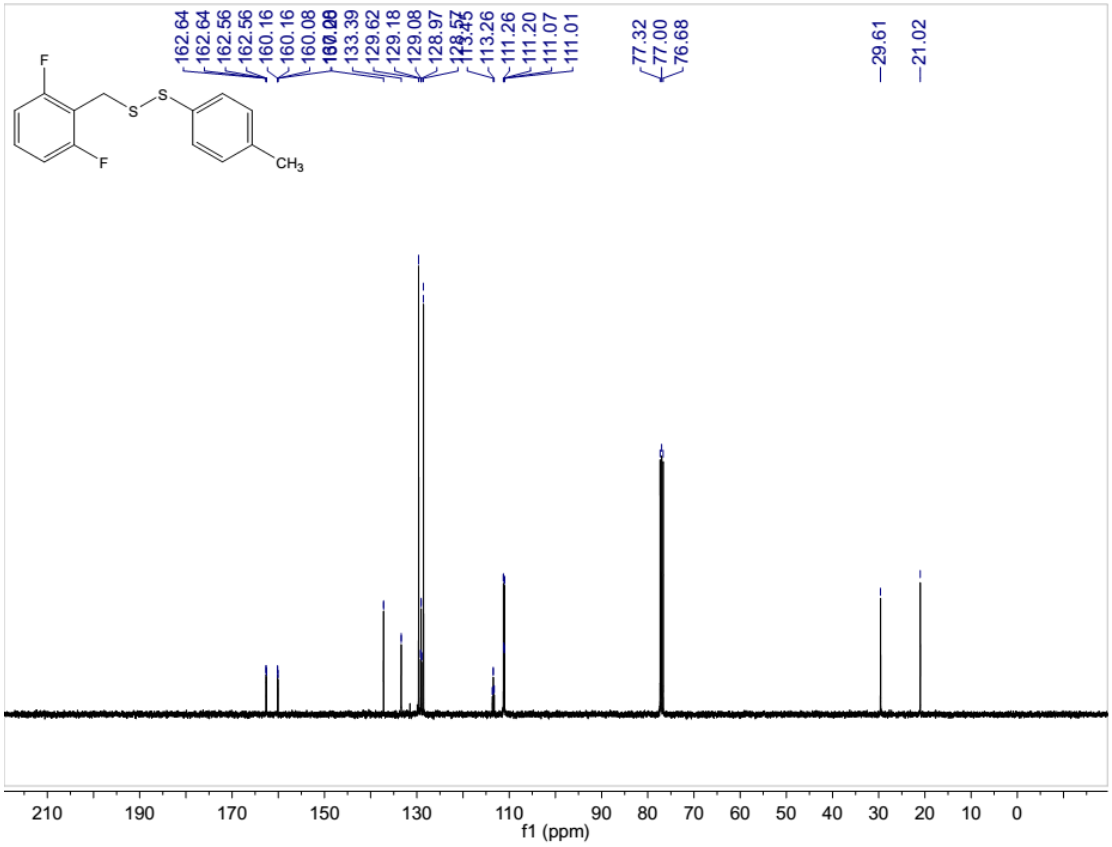

7.46
7.43
7.30
7.30
7.28
7.15
7.15
7.13
7.13
7.13
7.11
4.36
2.37
1.60
Cl
S
S
H3C
Cl
1.02
1.03
1.53
1.00
1.54
f1 (ppm)


136.88
135.95
133.67
133.03
129.54
128.95
128.24
127.97
77.32
77.00
76.68
38.58
21.01
Cl
S
S
H3C
Cl
f1 (ppm)

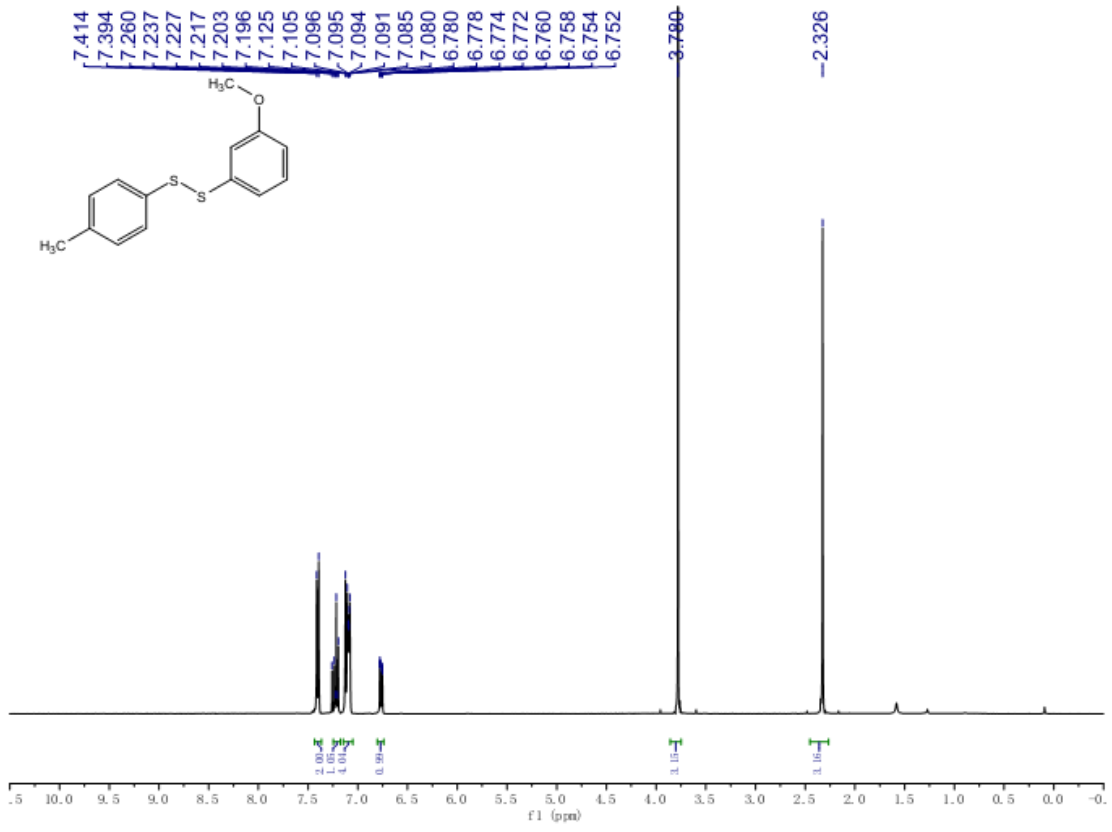
Compound **2k**:

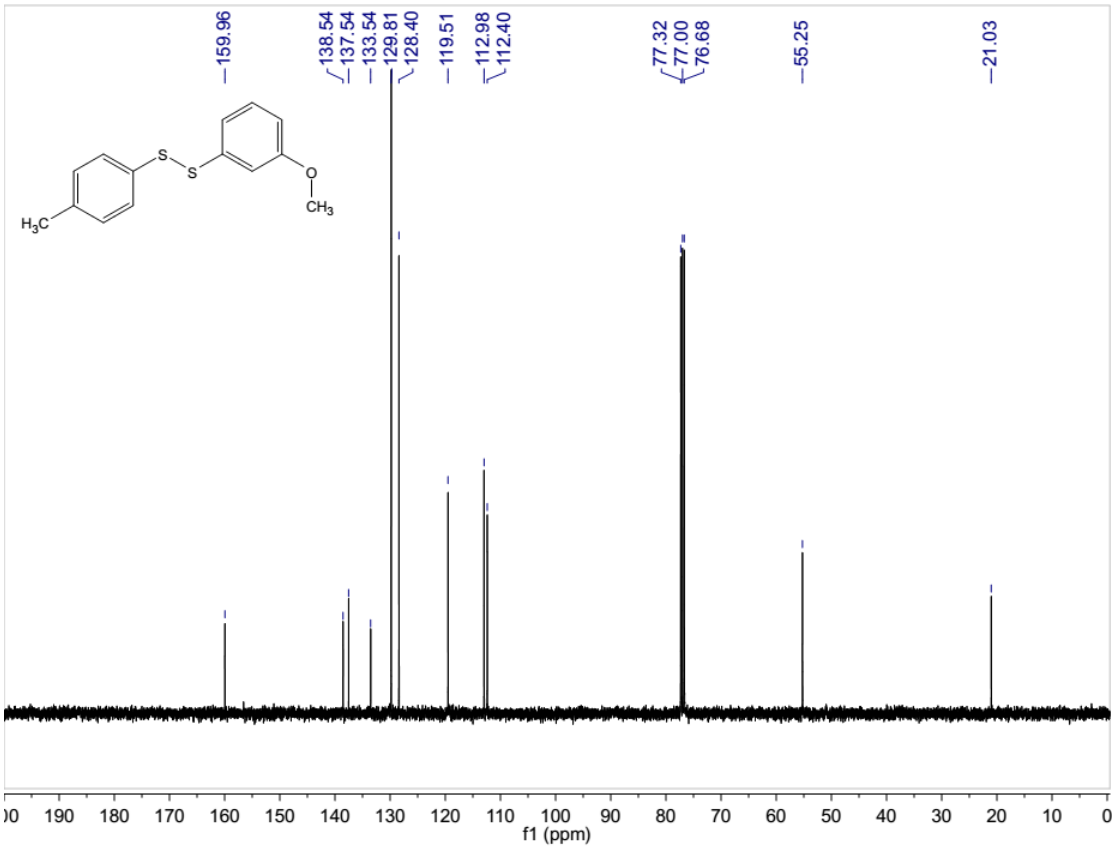

F
F
S
S
CH3
7.41
7.39
7.26
7.23
7.21
7.21
7.19
7.18
7.17
7.15
7.12
7.10
6.88
6.87
6.85
6.83
6.82
4.01
2.34
2.02
1.10
1.99
2.00
2.03
3.00
f1 (ppm)


F
S
S
H3C
F
-114.13
f1 (ppm)

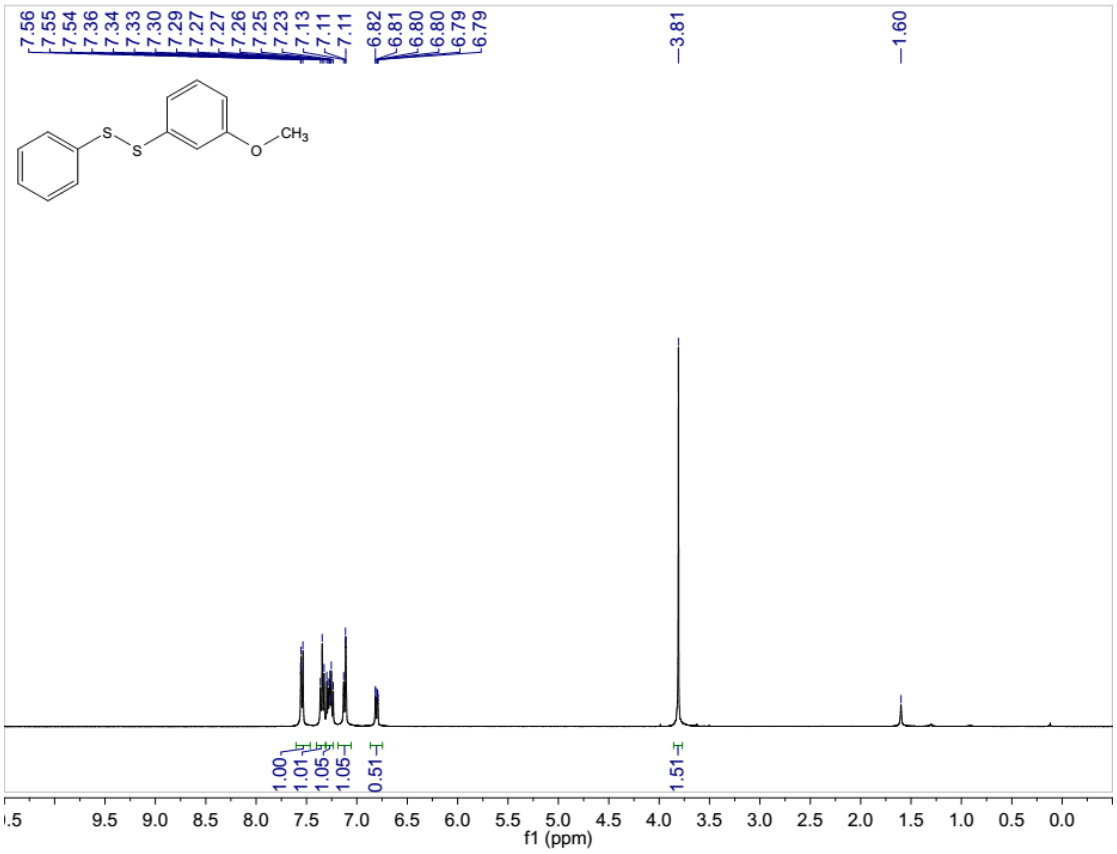

F
F
S
S
CH3
162.64
162.64
162.56
162.56
160.16
160.16
160.08
133.39
129.62
129.18
129.08
128.97
113.45
113.26
111.26
111.20
111.07
111.01
77.32
77.00
76.68
29.61
21.02
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

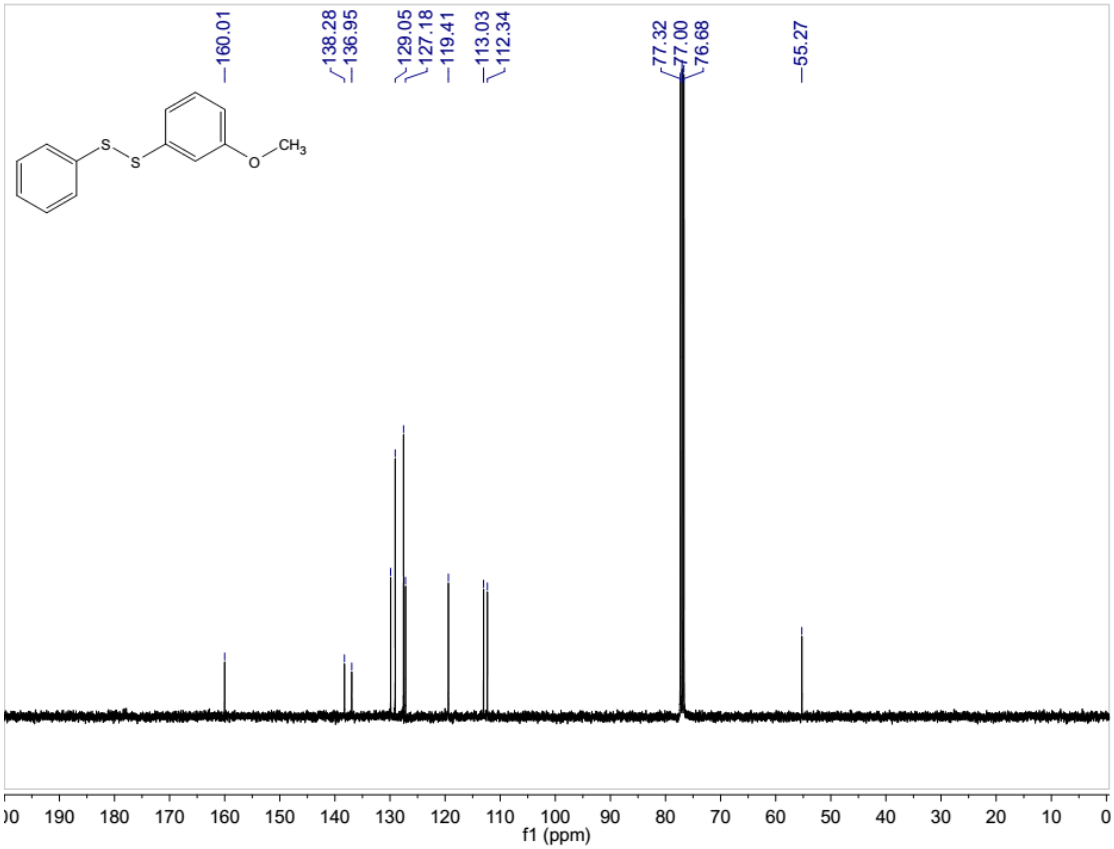
Compound **2l**:


7.414
7.394
7.260
7.237
7.227
7.217
7.203
7.196
7.125
7.105
7.096
7.095
7.094
7.091
7.085
7.080
6.780
6.778
6.774
6.772
6.760
6.758
6.754
6.752
3.780
2.326
H3C
O
S
S
H3C
f1 (ppm)

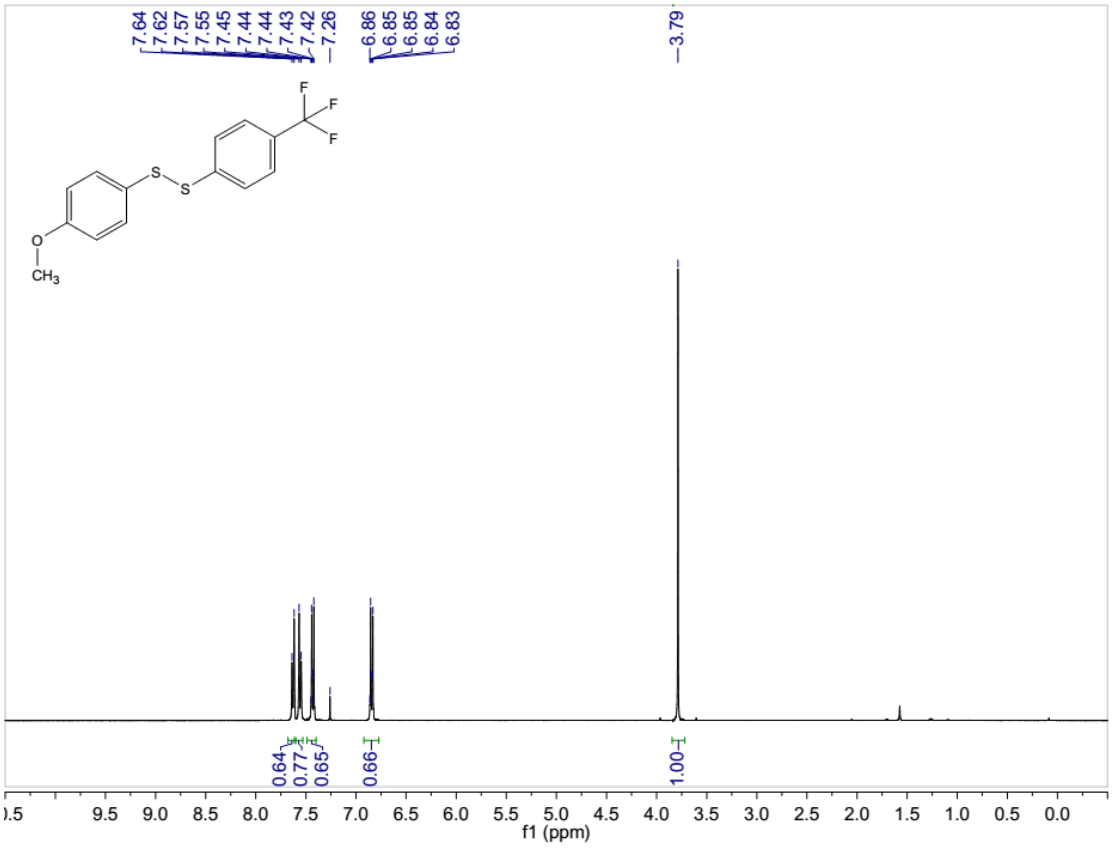

159.96
138.54
137.54
133.54
129.81
128.40
119.51
112.98
112.40
77.32
77.00
76.68
55.25
21.03
S
S
O
CH3
H3C
f1 (ppm)

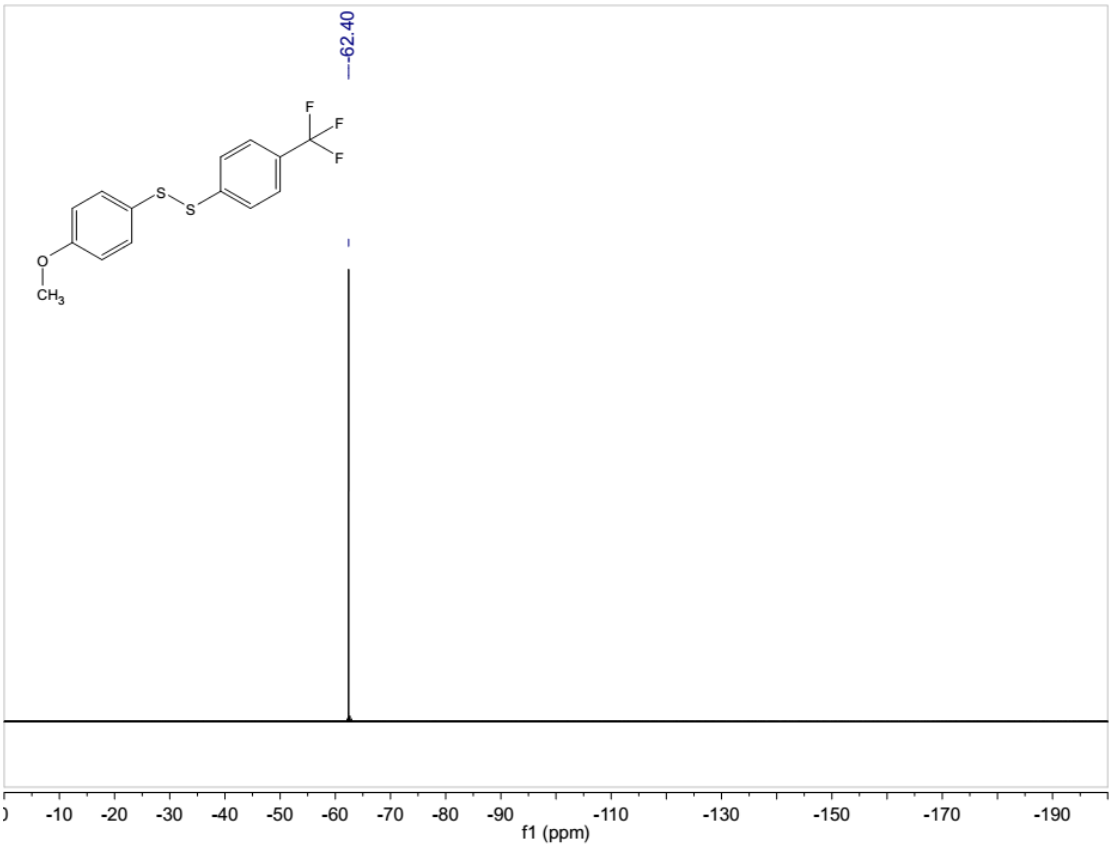
Compound **2m**:

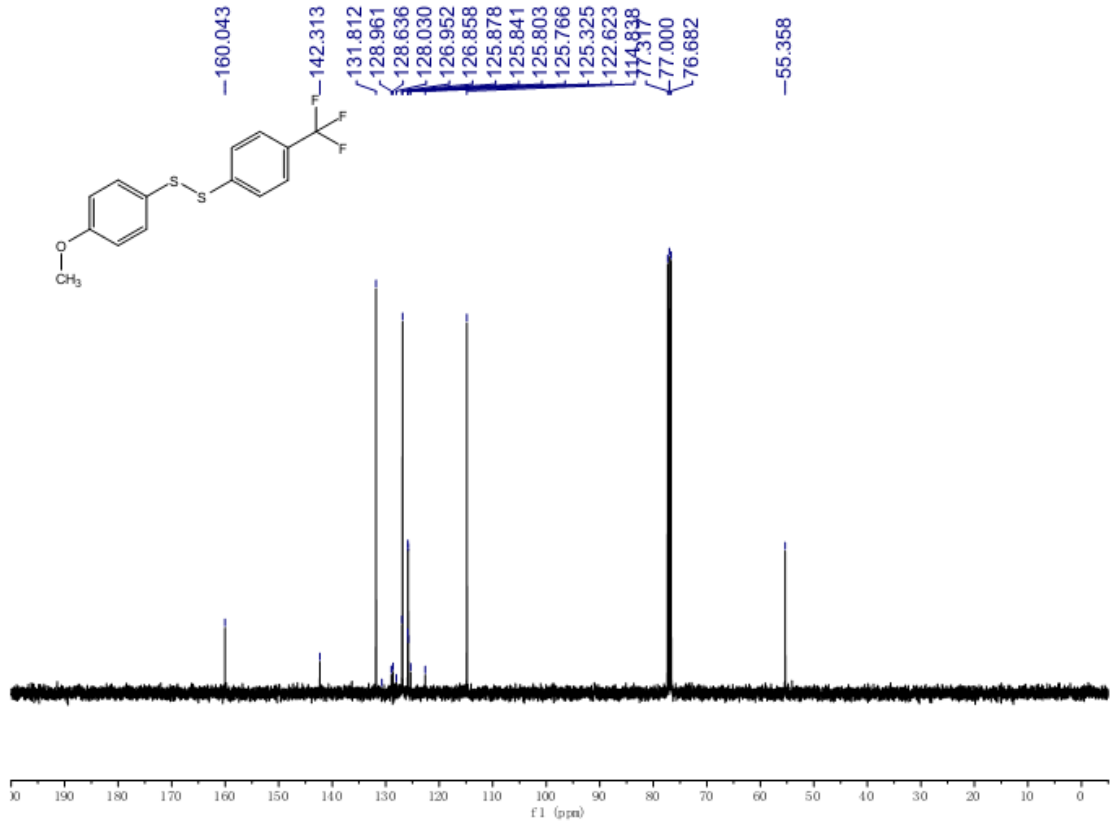

7.56
7.55
7.54
7.36
7.34
7.33
7.30
7.29
7.27
7.27
7.26
7.25
7.23
7.13
7.11
7.11
6.82
6.81
6.80
6.80
6.79
6.79
3.81
1.60
S
S
O
CH3
1.00
1.01
1.05
1.05
0.51
1.51
f1 (ppm)


160.01
138.28
136.95
129.05
127.18
119.41
113.03
112.34
77.32
77.00
76.68
55.27
S
S
O
CH3
f1 (ppm)

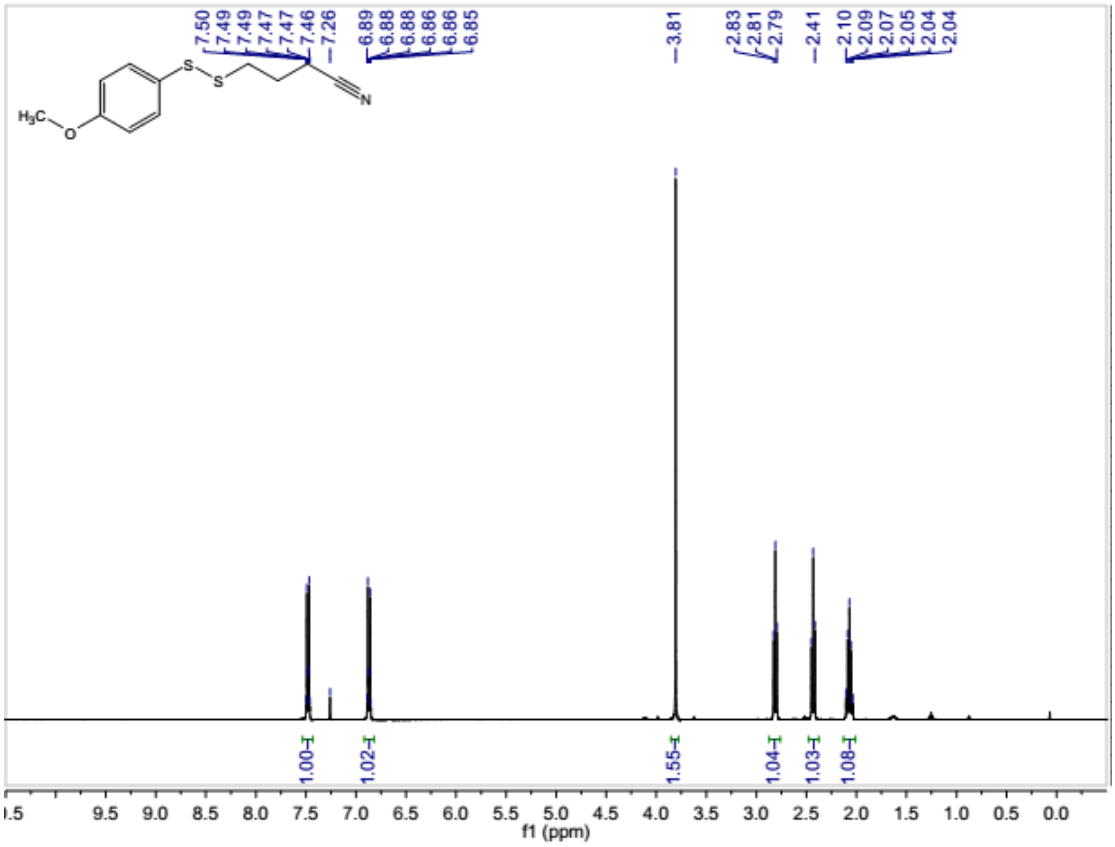
Compound **2n**:

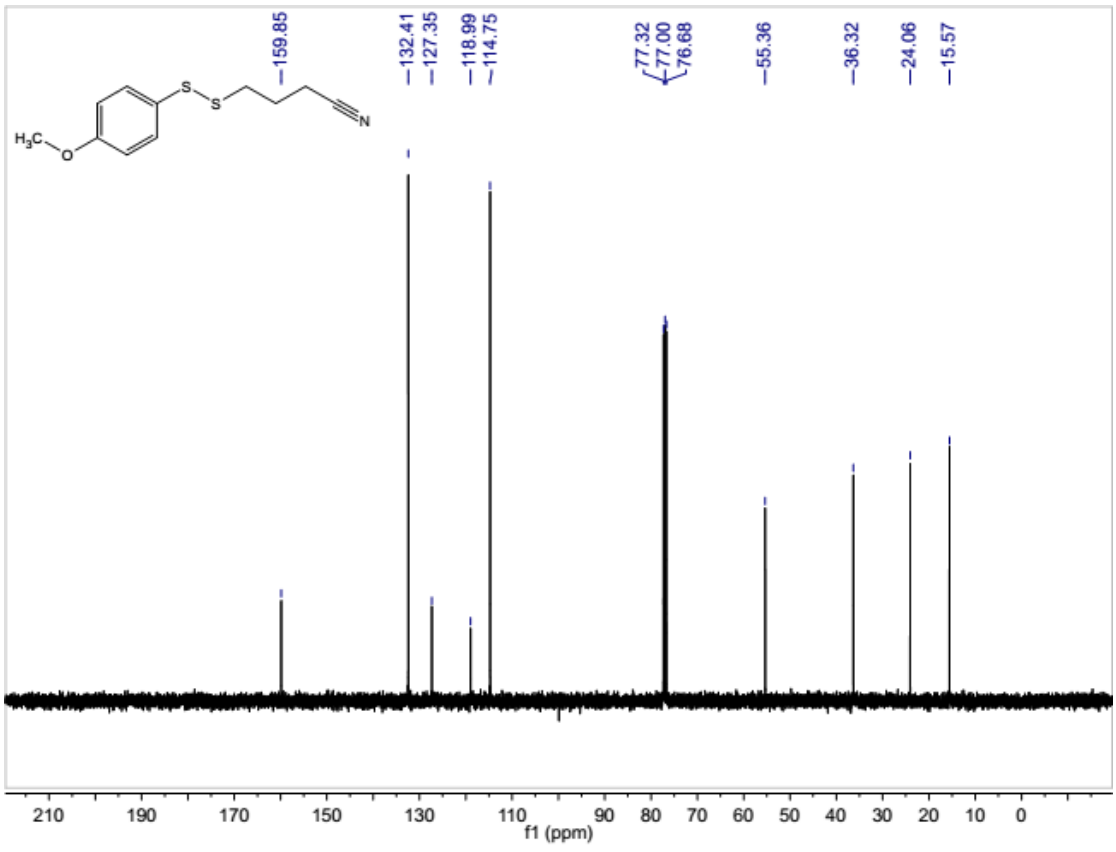

7.64
7.62
7.57
7.55
7.45
7.44
7.44
7.43
7.42
7.26
6.86
6.85
6.85
6.84
6.83
3.79
F
F
F
S
S
O
CH3
0.64
0.77
0.65
0.66
1.00
f1 (ppm)


-62.40
F
F
F
S
S
O
CH3
-10
-20
-30
-40
-50
-60
-70
-80
-90
-110
-130
-150
-170
-190
f1 (ppm)

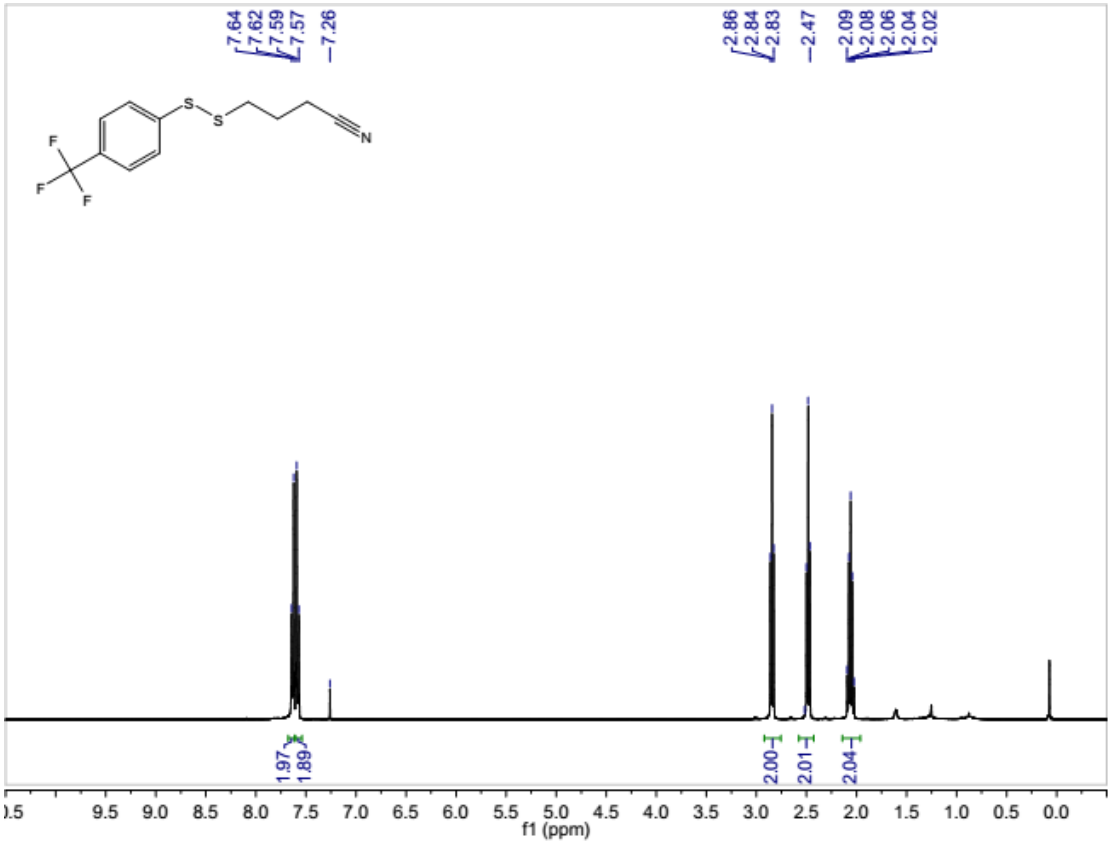

160.043
142.313
131.812
128.961
128.636
128.030
126.952
126.858
125.878
125.841
125.803
125.766
125.325
122.623
77.317
77.000
76.682
55.358
F
F
F
S
S
O
CH3
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

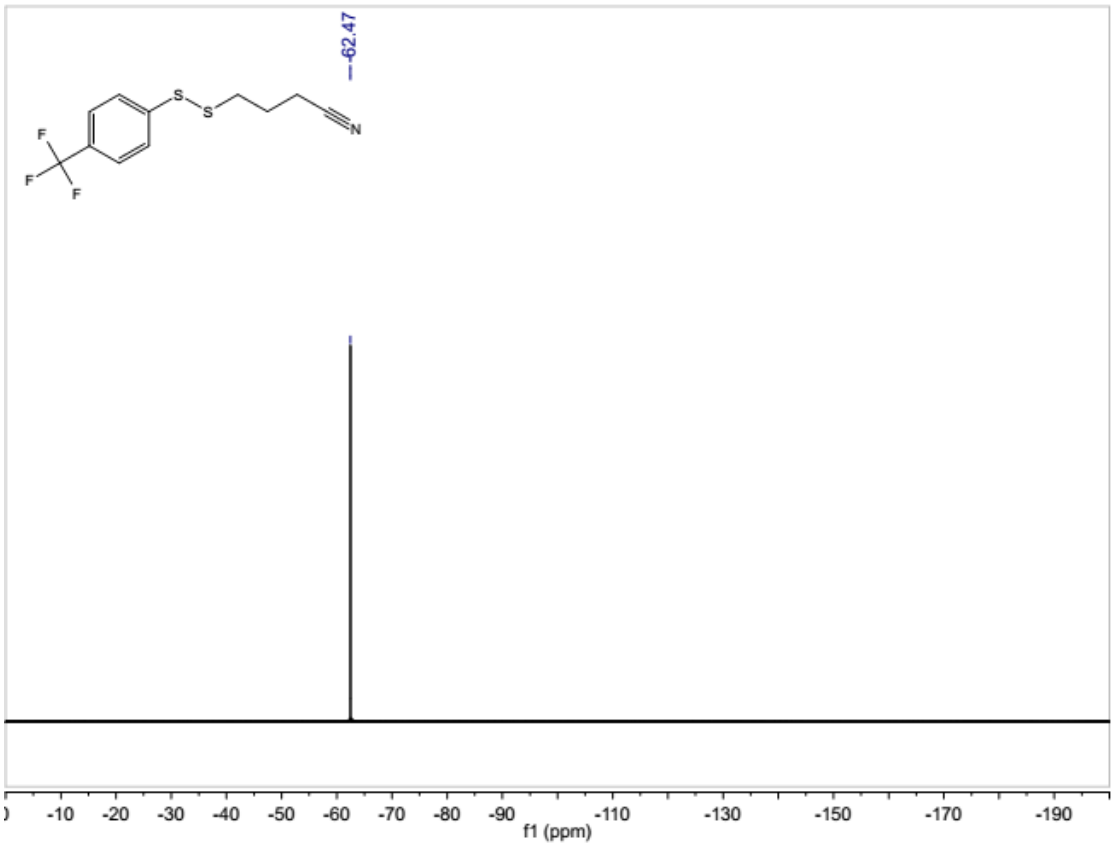
Compound **3a**:

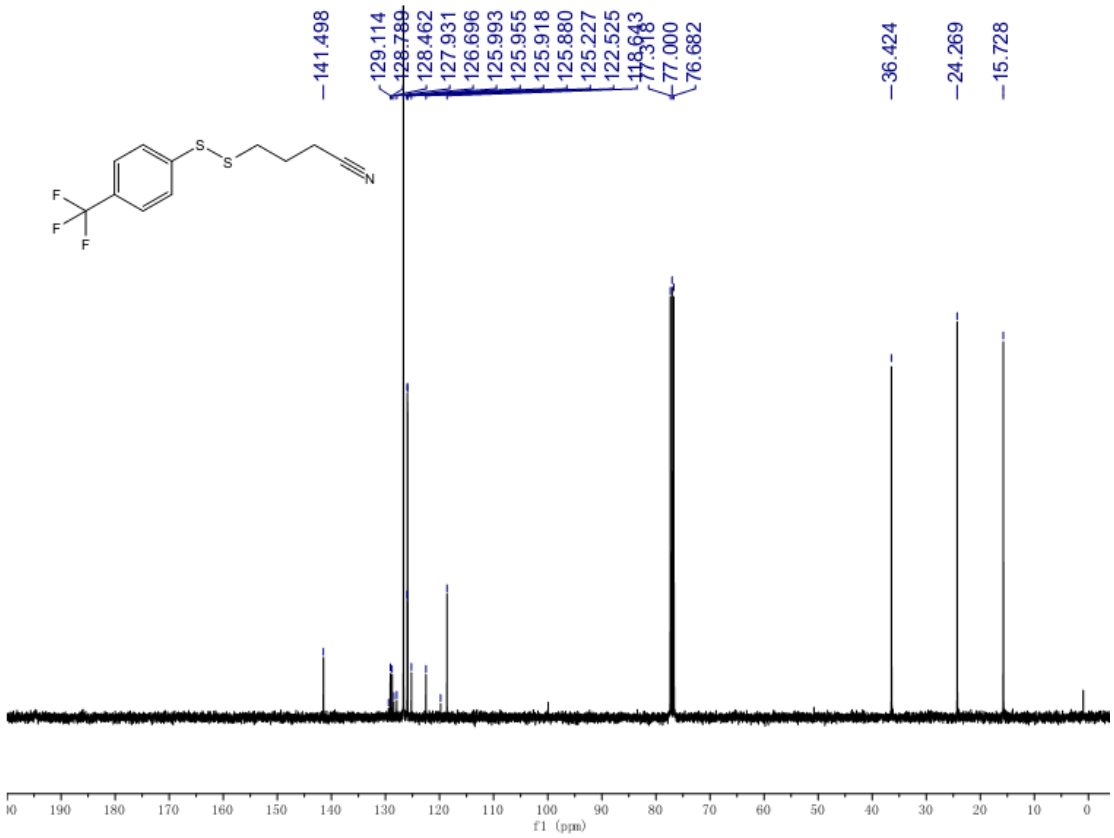

7.50
7.49
7.49
7.47
7.47
7.46
7.26
6.89
6.88
6.88
6.86
6.86
6.85
3.81
2.83
2.81
2.79
2.41
2.10
2.09
2.07
2.05
2.04
2.04
1.00
1.02
1.55
1.04
1.03
1.08
f1 (ppm)


159.85
132.41
127.35
118.99
114.75
77.32
77.00
76.68
55.36
36.32
24.06
15.57
f1 (ppm)

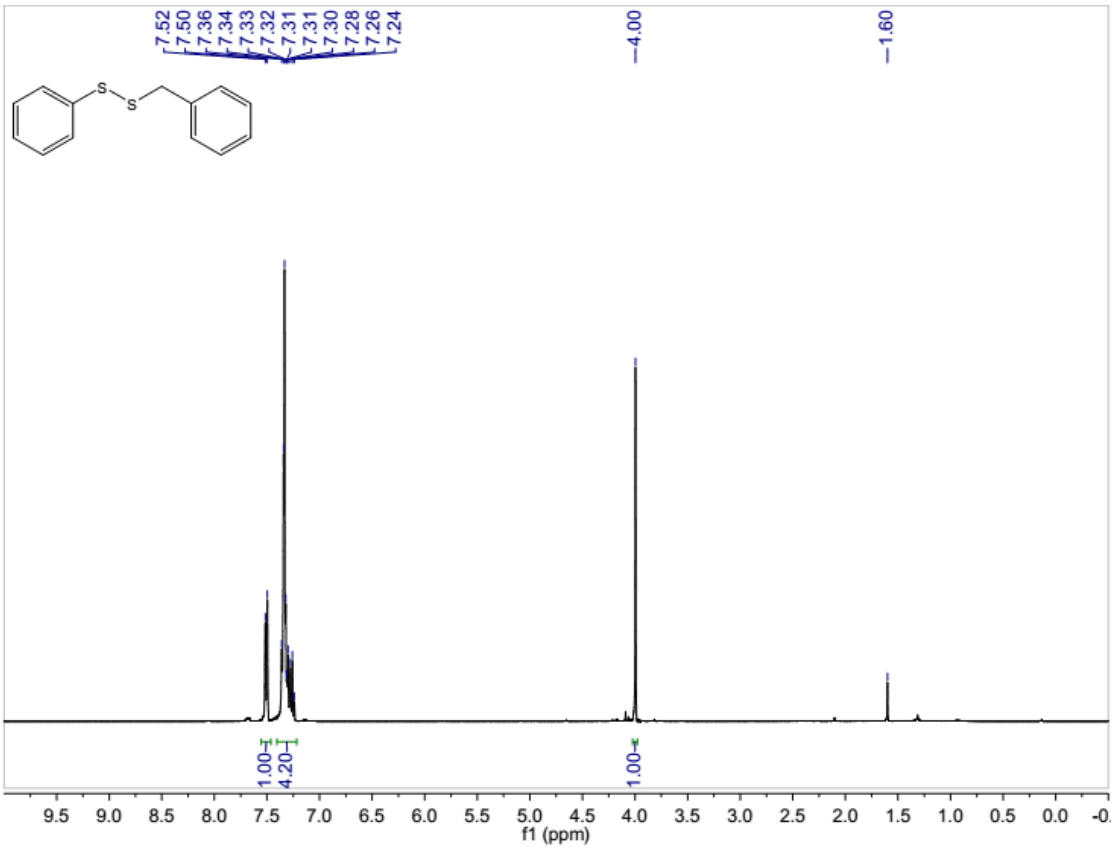
Compound **3b**:

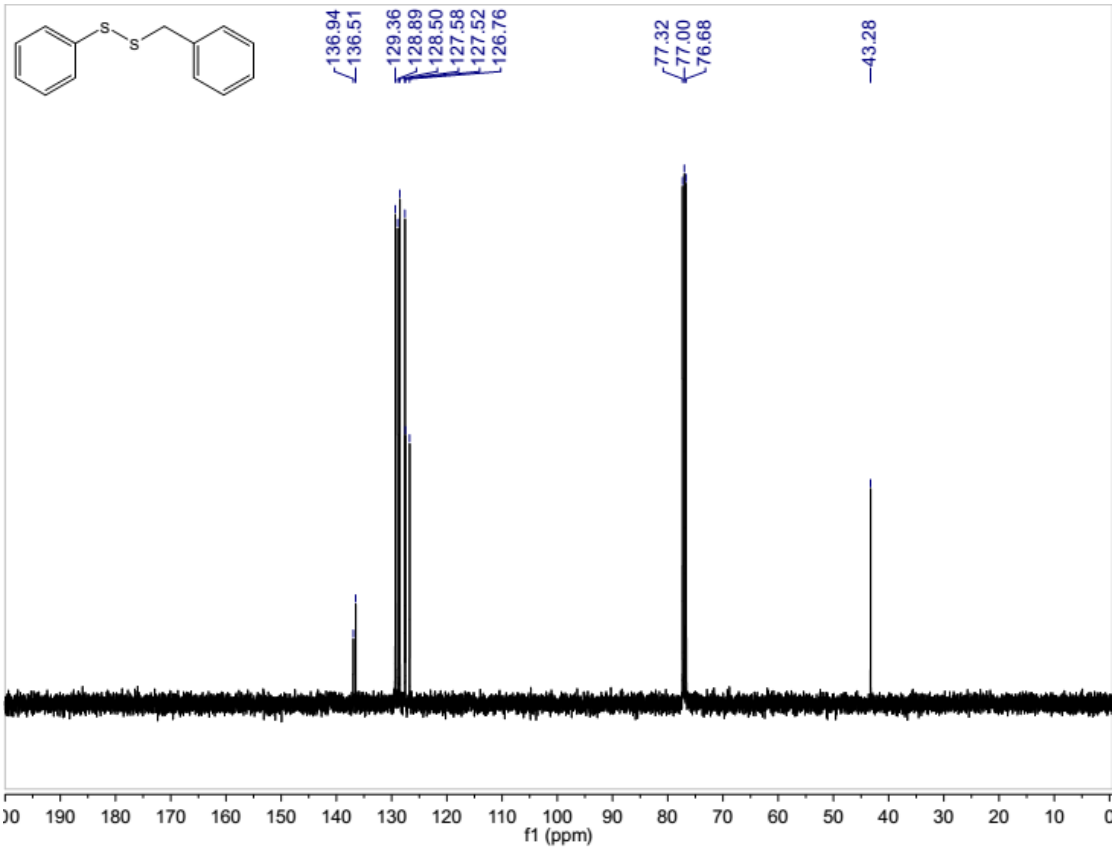

7.64
7.62
7.59
7.57
7.26
2.86
2.84
2.83
2.47
2.09
2.08
2.06
2.04
2.02
1.97
1.89
2.00
2.01
2.04
f1 (ppm)


62.47
f1 (ppm)

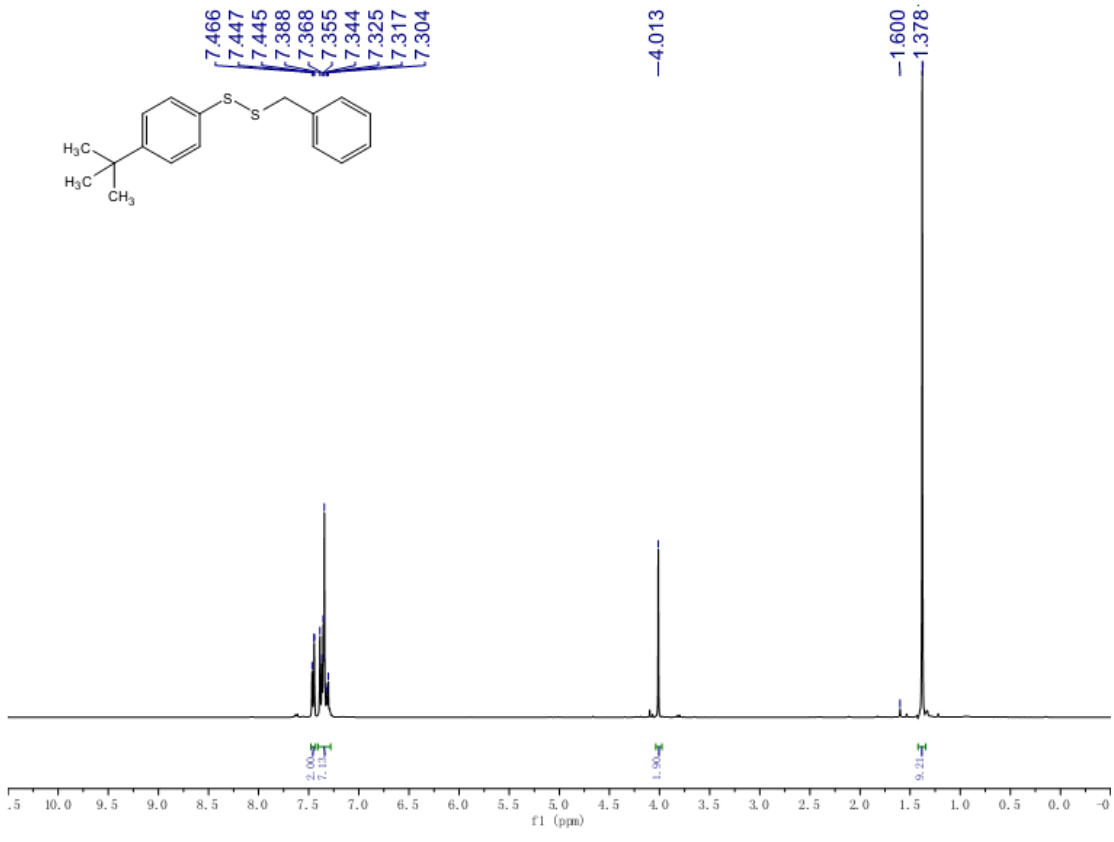

141.498
129.114
128.789
128.462
127.931
126.696
125.993
125.955
125.918
125.880
125.227
122.525
118.643
77.318
77.000
76.682
36.424
24.269
15.728
f1 (ppm)

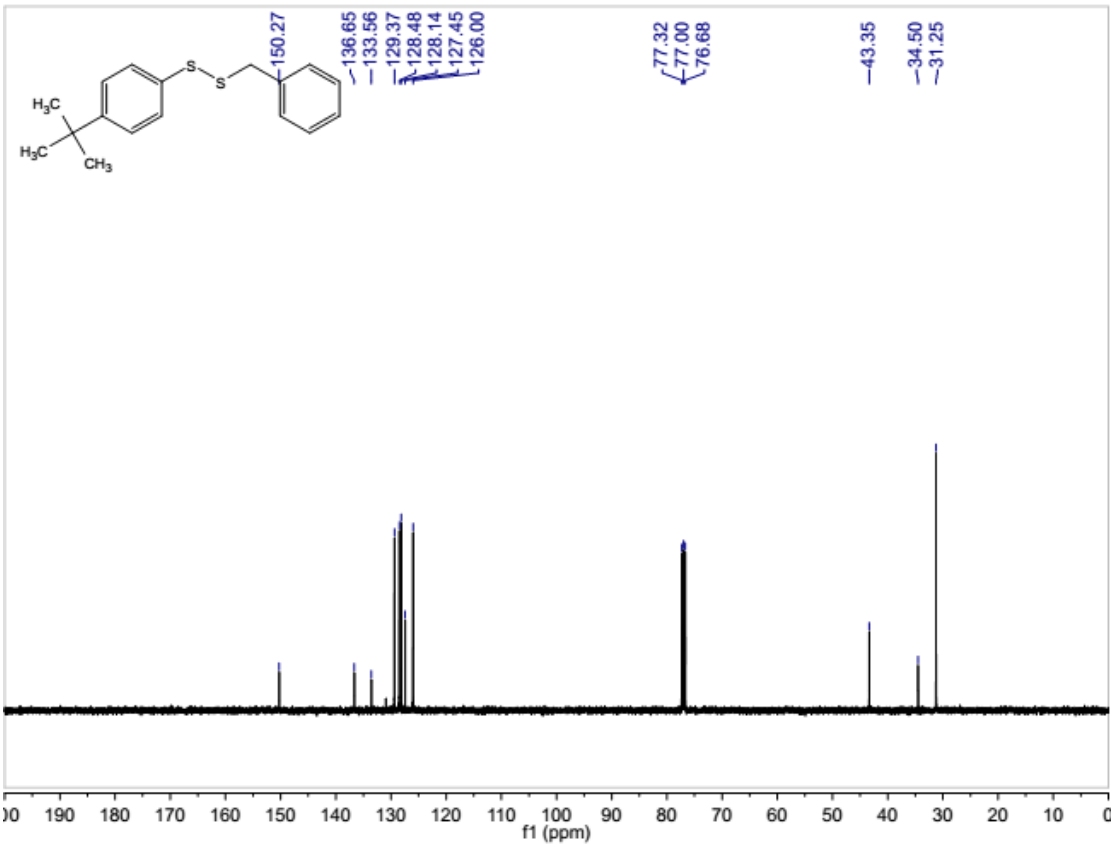
Compound **3c**:


7.52
7.50
7.36
7.34
7.33
7.32
7.31
7.31
7.30
7.28
7.26
7.24
4.00
1.60
1.00
4.20
1.00
f1 (ppm)

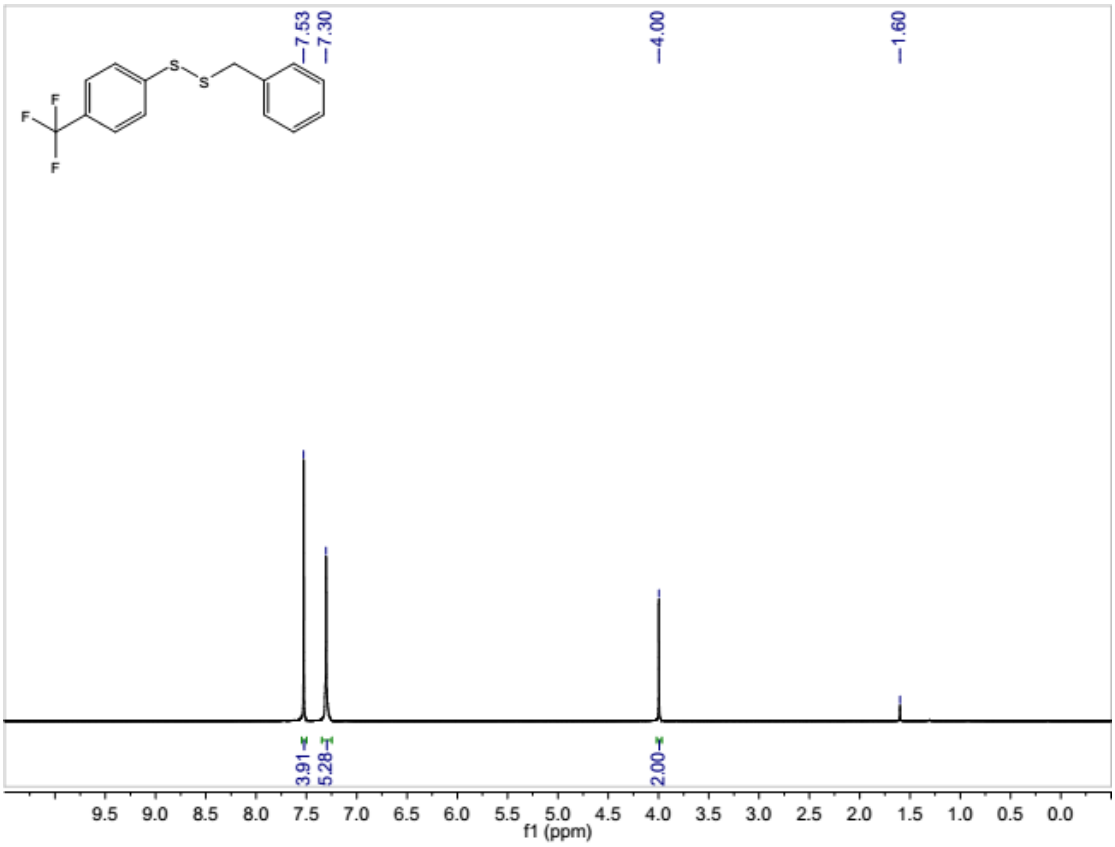

136.94
136.51
129.36
128.89
128.50
127.58
127.52
126.76
77.32
77.00
76.68
43.28
f1 (ppm)

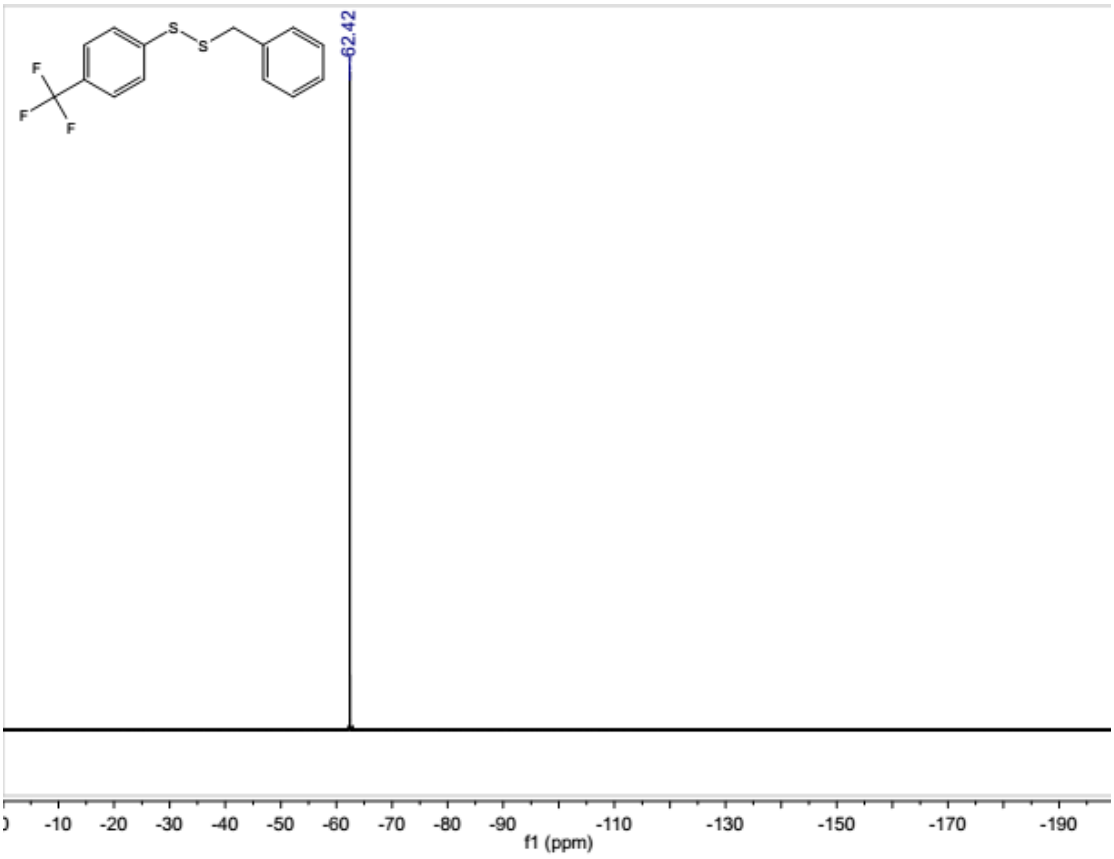
Compound **3d**:

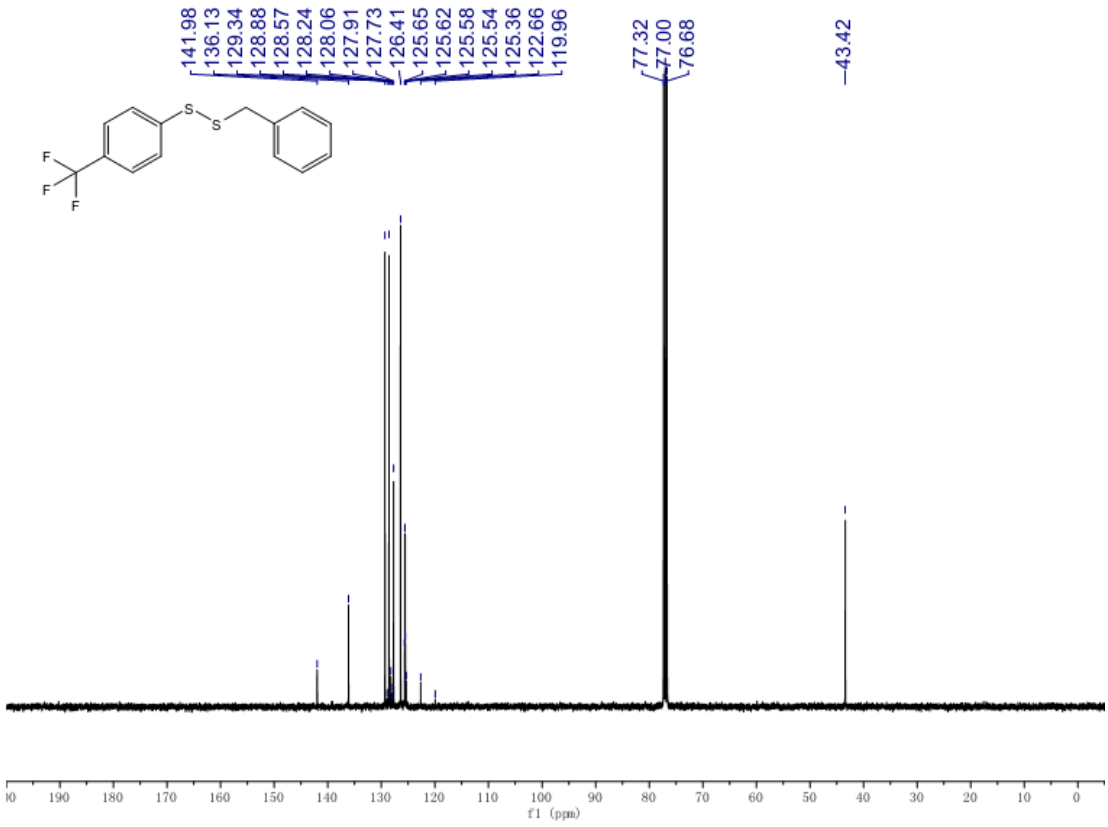

7.466
7.447
7.445
7.388
7.368
7.355
7.344
7.325
7.317
7.304
4.013
1.600
1.378
f1 (ppm)


150.27
136.65
133.56
129.37
128.48
128.14
127.45
126.00
77.32
77.00
76.68
43.35
34.50
31.25
H3C
H3C
CH3
S
S
f1 (ppm)

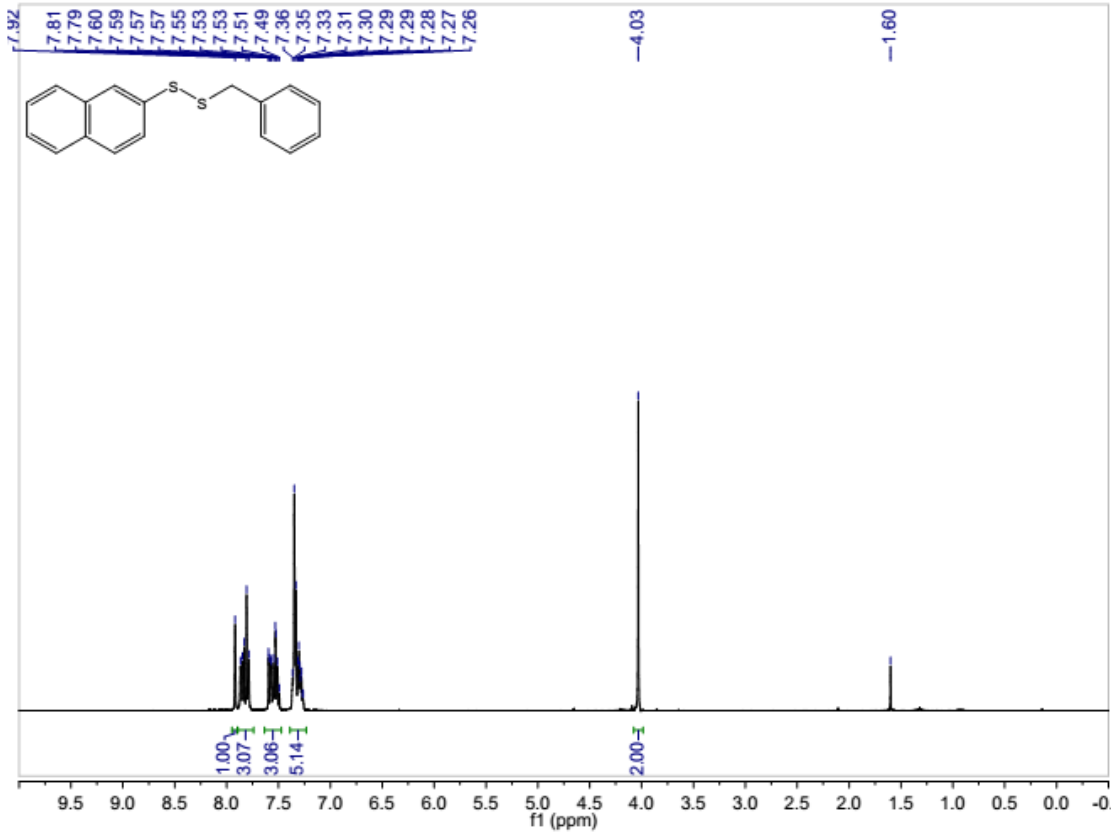
Compound **3e**:

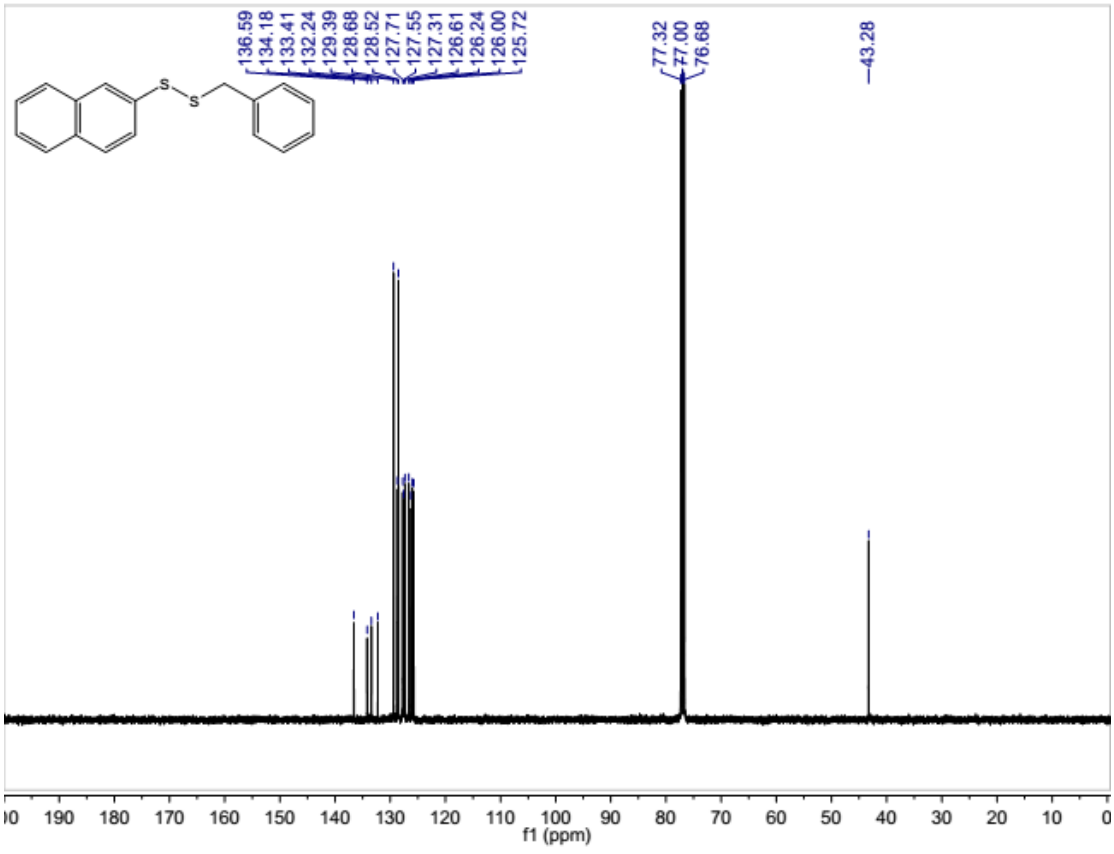

7.53
7.30
4.00
1.60
F
F
F
S
S
3.91
5.28
2.00
f1 (ppm)


62.42
F
F
F
S
S
-10
-20
-30
-40
-50
-60
-70
-80
-90
-110
-130
-150
-170
-190
f1 (ppm)

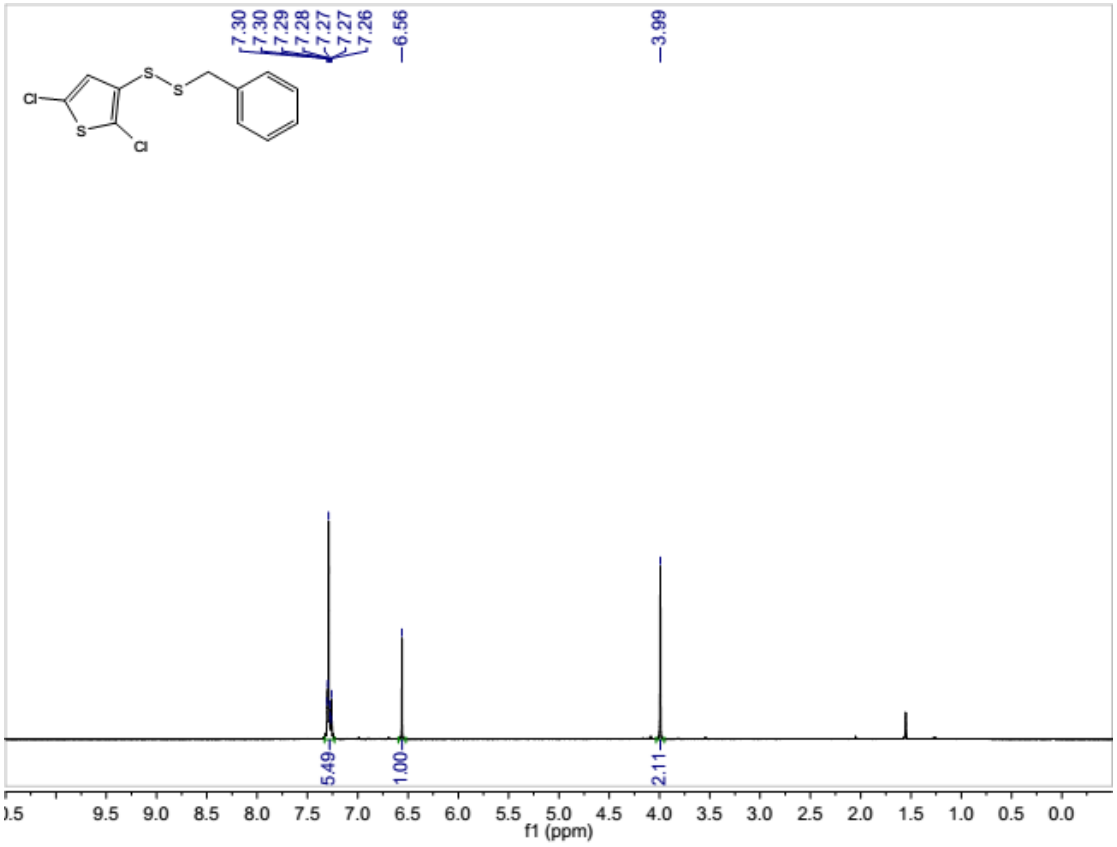

141.98
136.13
129.34
128.88
128.57
128.24
128.06
127.91
127.73
126.41
125.65
125.62
125.58
125.54
125.36
122.66
119.96
77.32
77.00
76.68
43.42
F
F
F
S
S
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

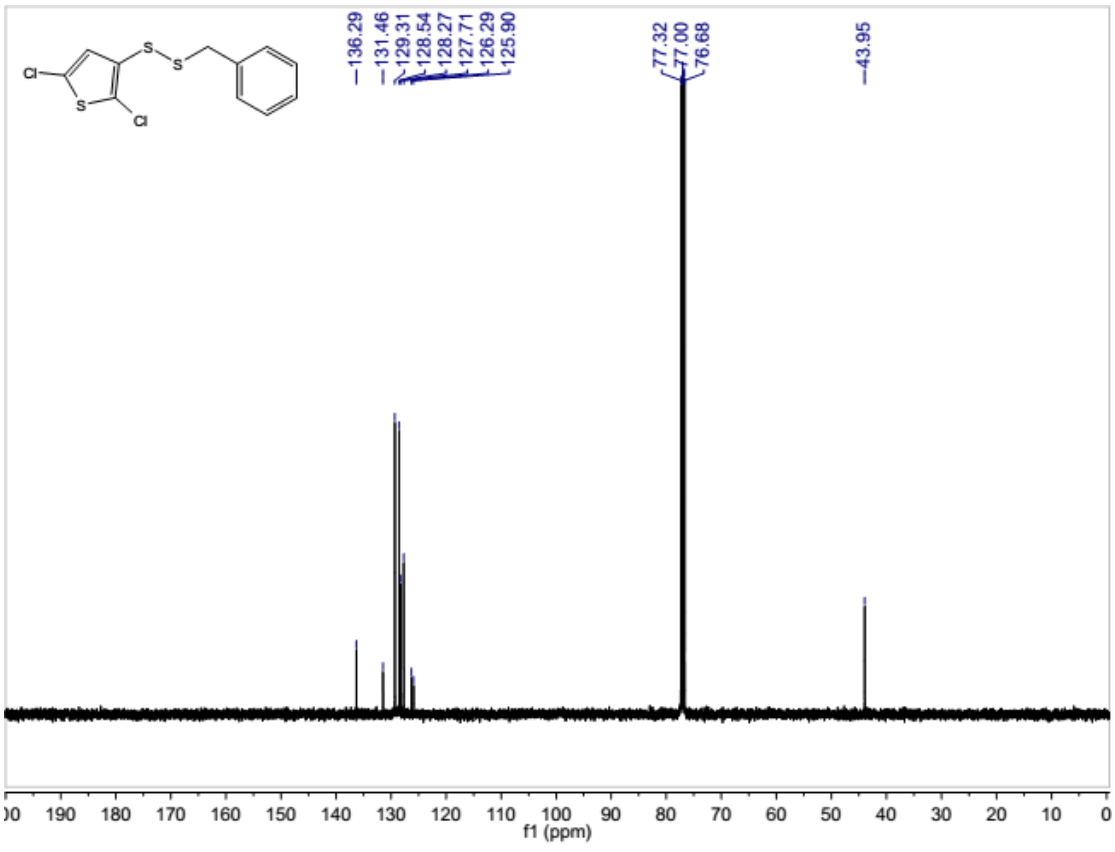
Compound **3f**:


7.81
7.79
7.60
7.59
7.57
7.57
7.55
7.53
7.53
7.51
7.49
7.36
7.35
7.33
7.31
7.30
7.29
7.29
7.28
7.27
7.26
4.03
1.60
1.00
3.07
3.06
5.14
2.00
f1 (ppm)

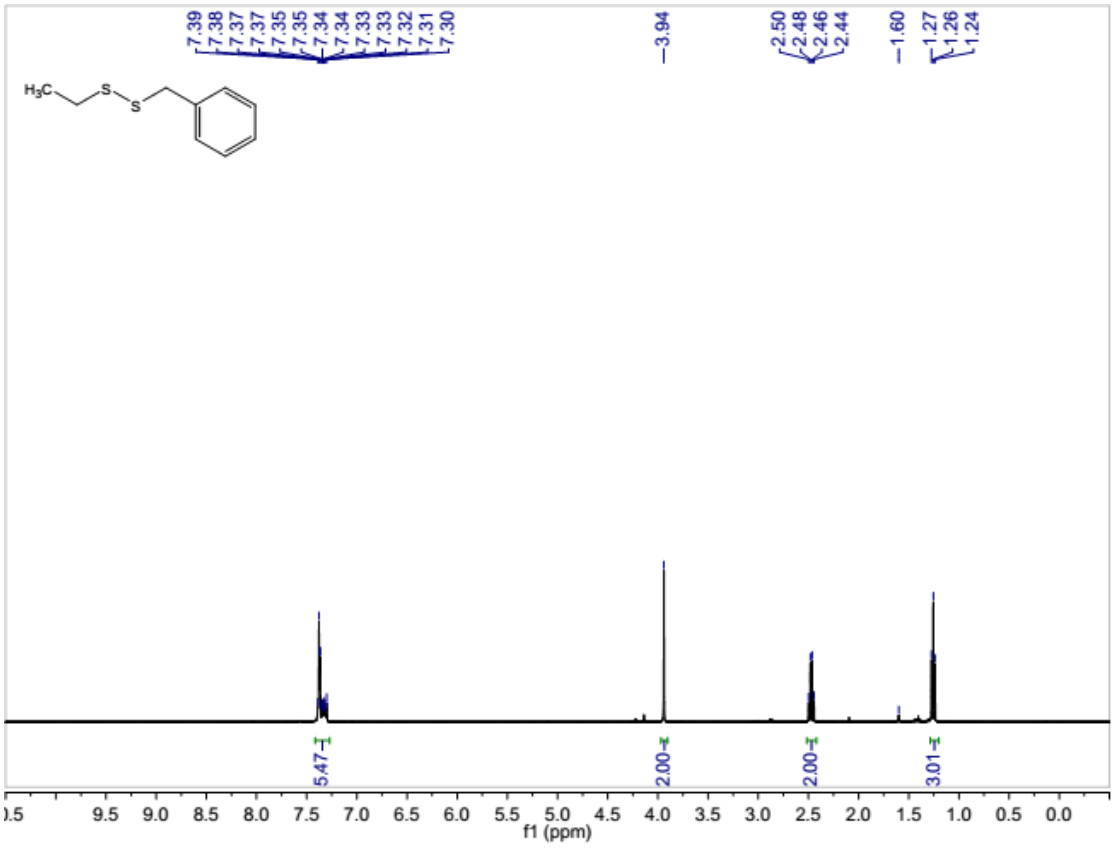

136.59
134.18
133.41
132.24
129.39
128.68
128.52
127.71
127.55
127.31
126.61
126.24
126.00
125.72
77.32
77.00
76.68
43.28
f1 (ppm)

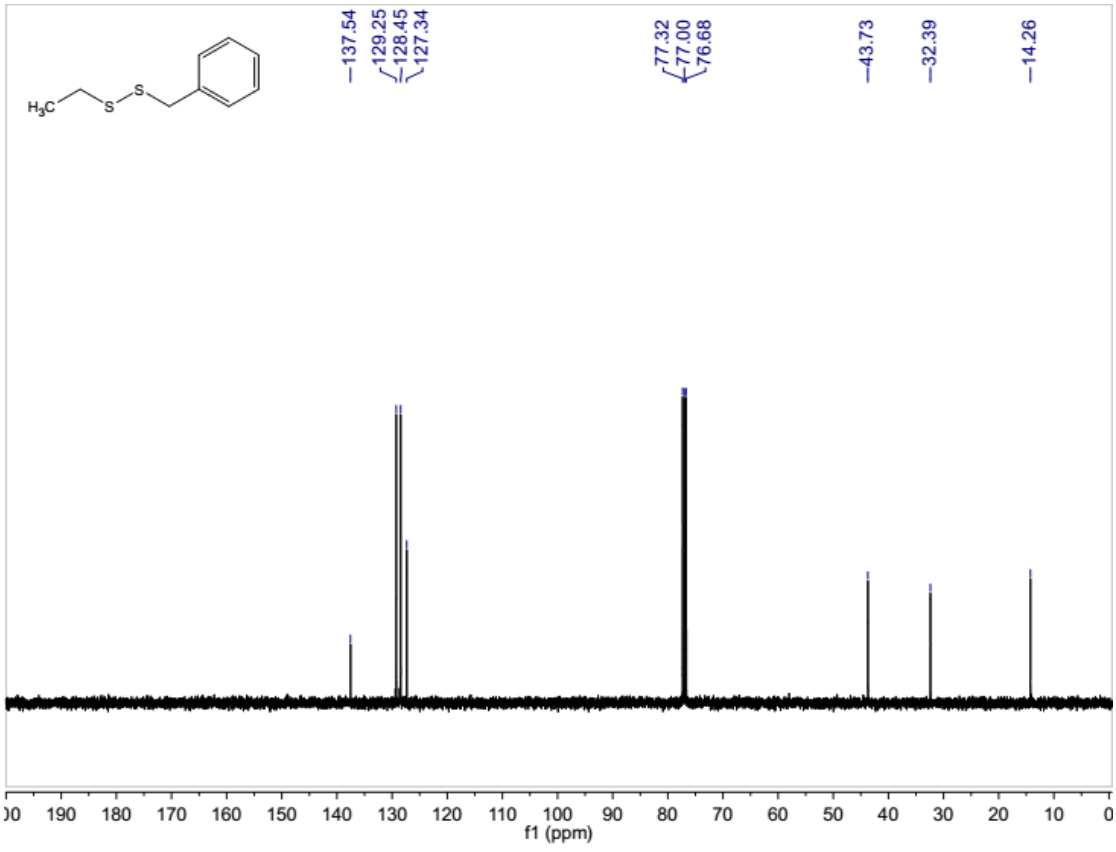
Compound **3g**:


7.30
7.30
7.29
7.28
7.27
7.27
7.26
6.56
3.99
Cl
S
S
Cl
5.49
1.00
2.11
f1 (ppm)

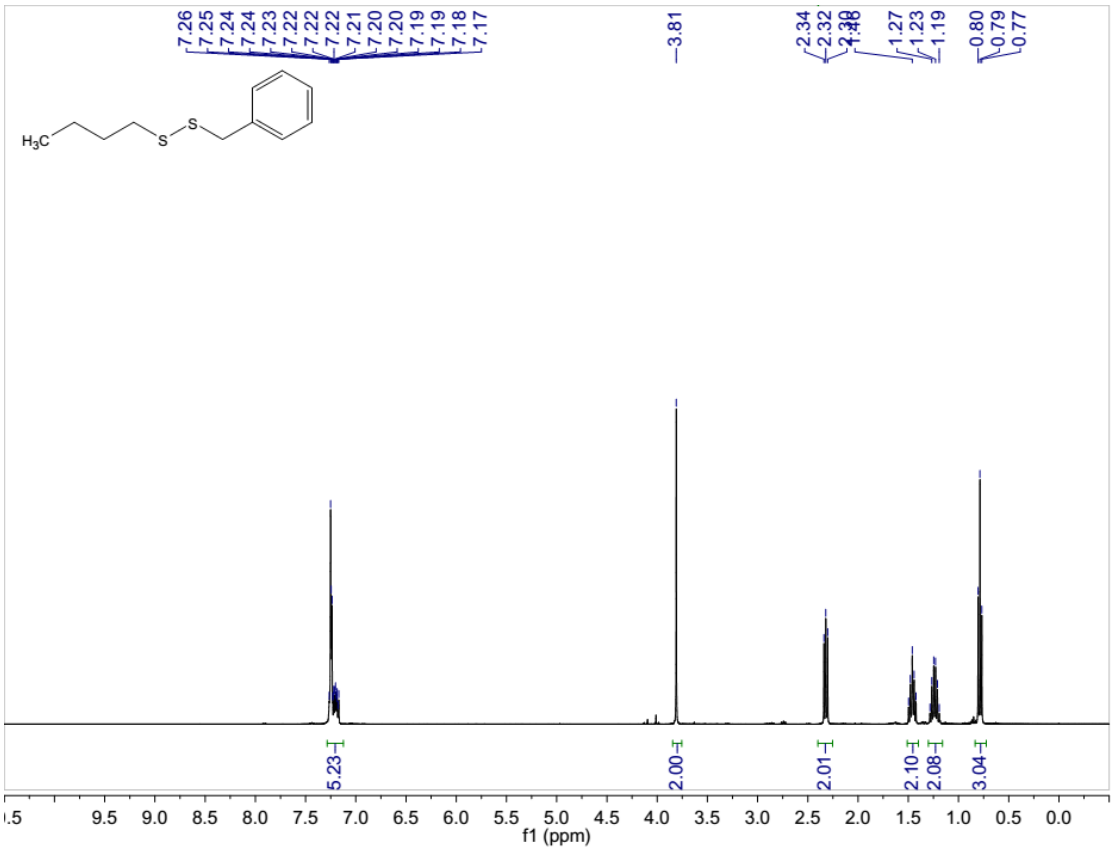

136.29
131.46
129.31
128.54
128.27
127.71
126.29
125.90
77.32
77.00
76.68
43.95
Cl
S
S
Cl
f1 (ppm)

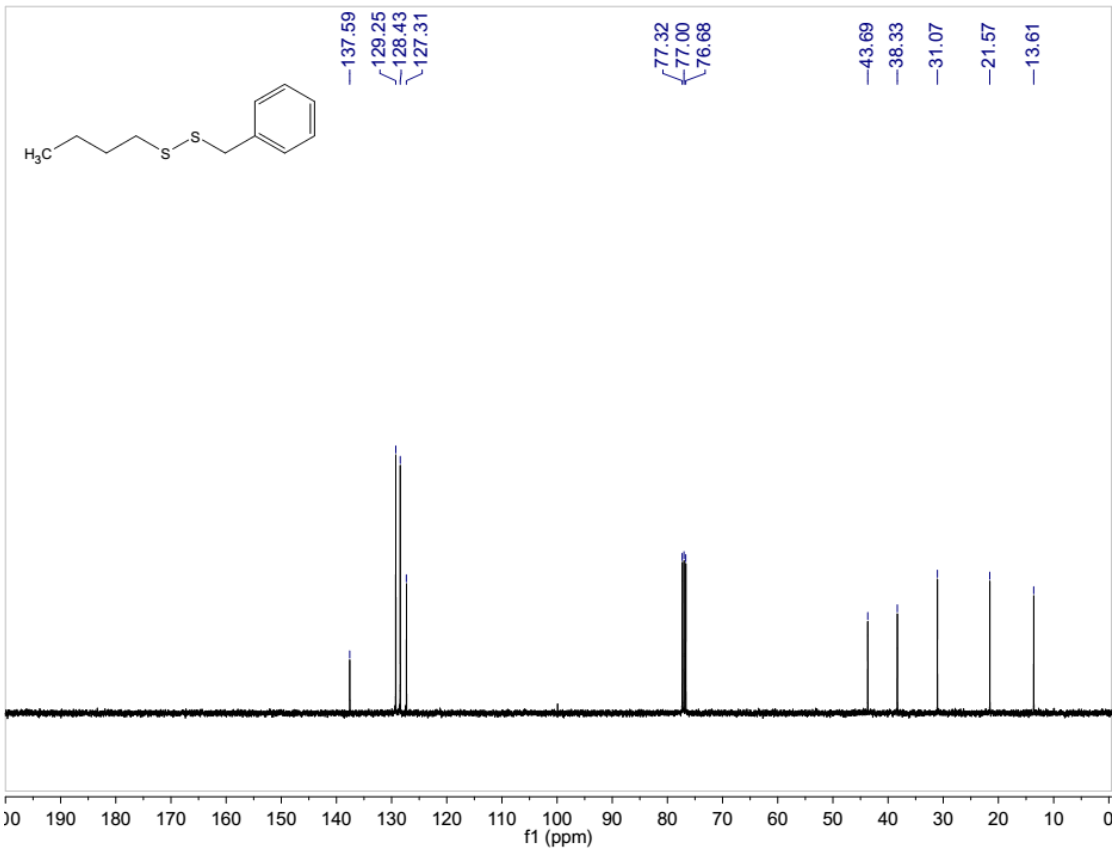
Compound **3h**:


7.39
7.38
7.37
7.37
7.35
7.35
7.34
7.34
7.33
7.33
7.32
7.31
7.30
3.94
2.50
2.48
2.46
2.44
1.60
1.27
1.26
1.24
5.47
2.00
2.00
3.01
f1 (ppm)

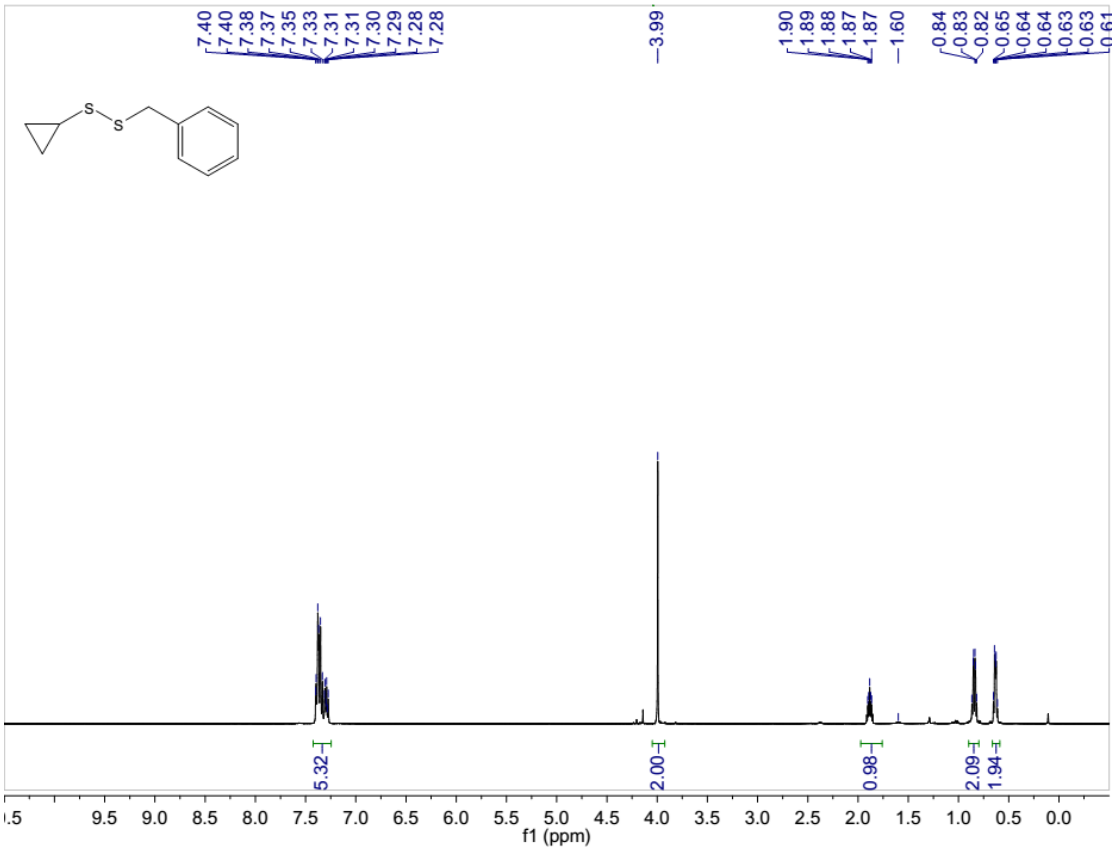

137.54
129.25
128.45
127.34
77.32
77.00
76.68
43.73
32.39
14.26
f1 (ppm)

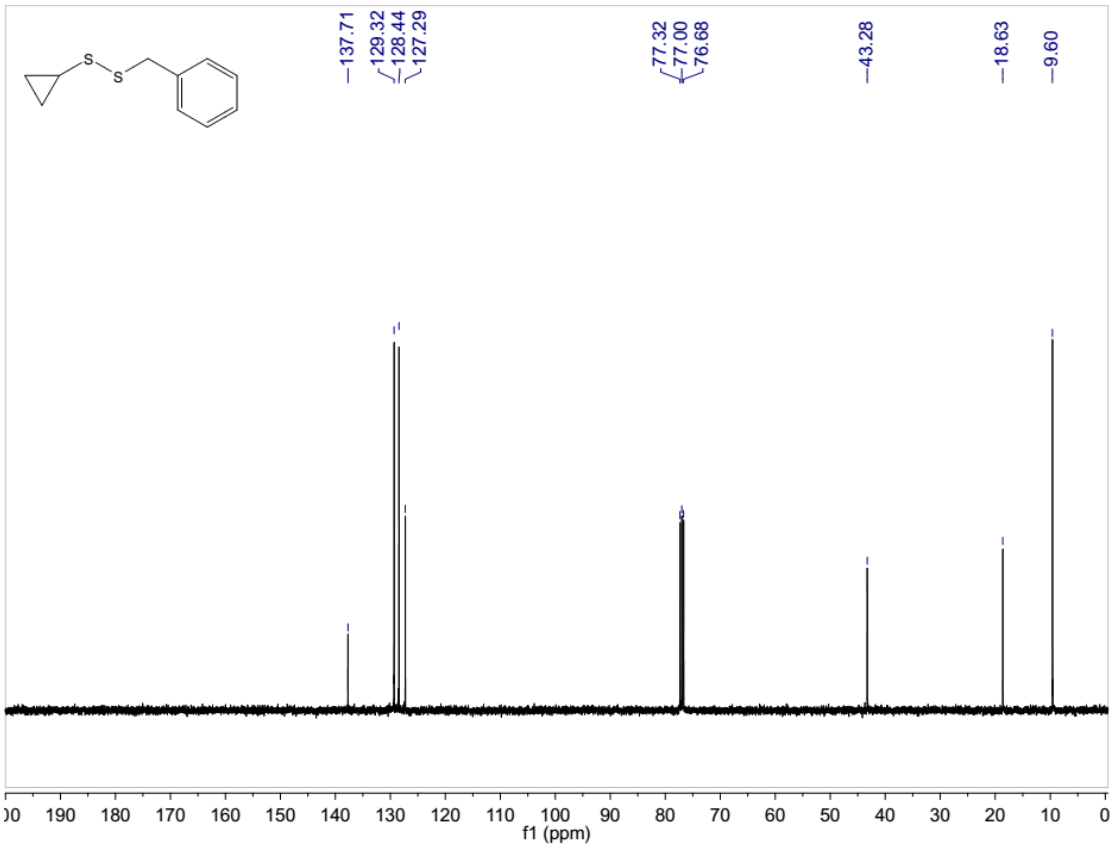
Compound **3i**:


7.26
7.25
7.24
7.24
7.23
7.22
7.22
7.22
7.21
7.20
7.20
7.19
7.19
7.18
7.17
3.81
2.34
2.32
1.27
1.23
1.19
0.80
0.79
0.77
5.23
2.00
2.01
2.10
2.08
3.04
f1 (ppm)

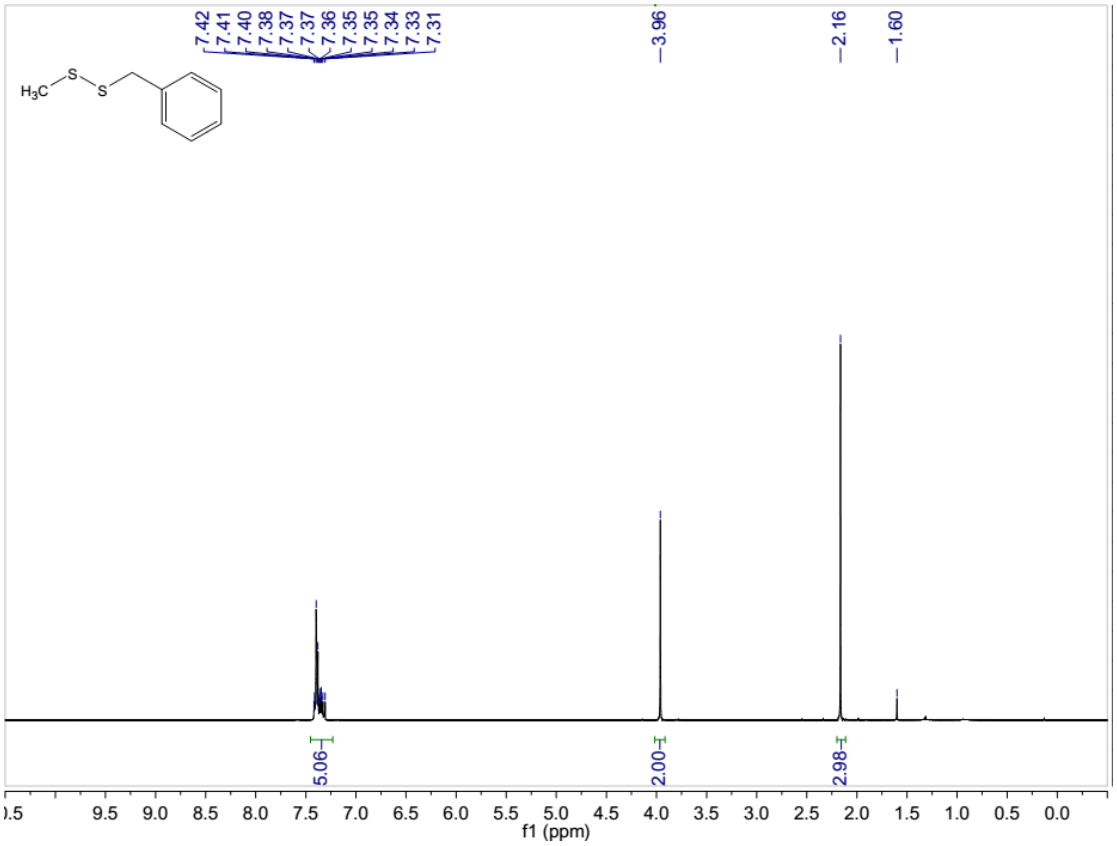

137.59
129.25
128.43
127.31
77.32
77.00
76.68
43.69
38.33
31.07
21.57
13.61
f1 (ppm)

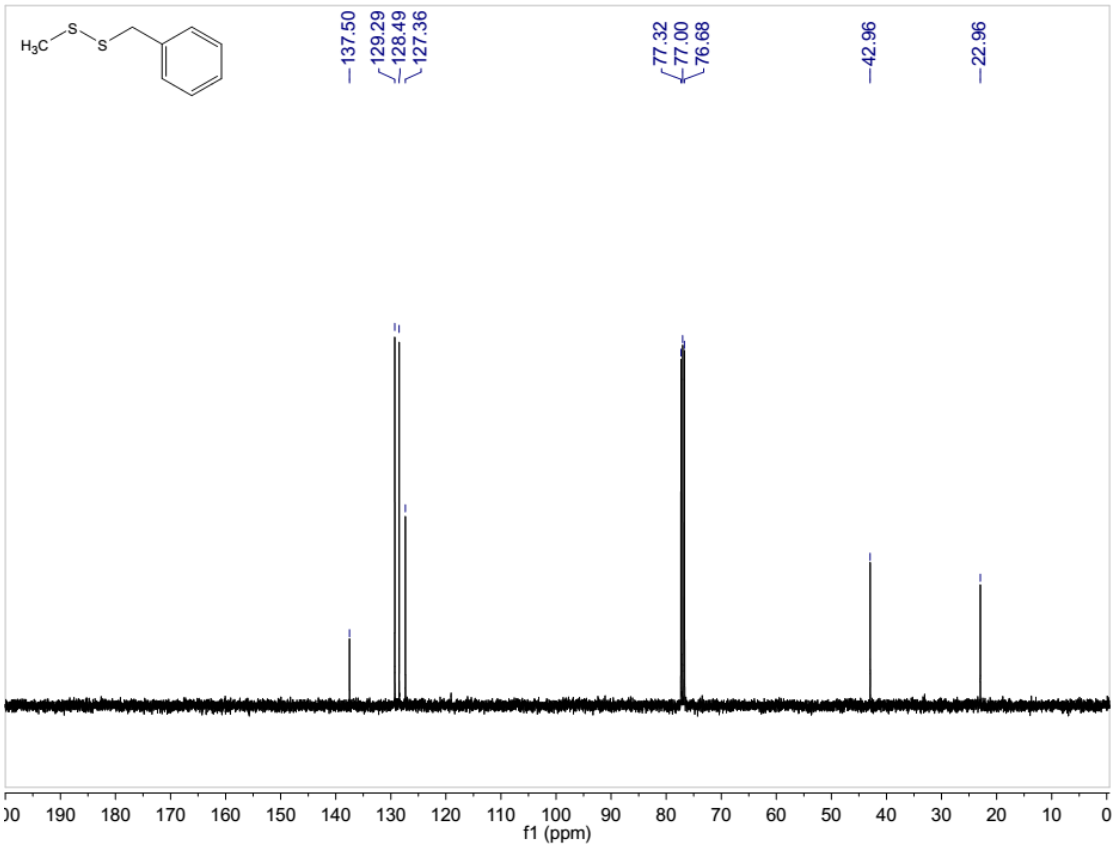
Compound **3j**:


7.40
7.40
7.38
7.37
7.35
7.33
7.31
7.31
7.30
7.29
7.28
7.28
3.99
1.90
1.89
1.88
1.87
1.87
1.60
0.84
0.83
0.82
0.65
0.64
0.64
0.63
0.63
0.61
S
S
5.32
2.00
0.98
2.09
1.94
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

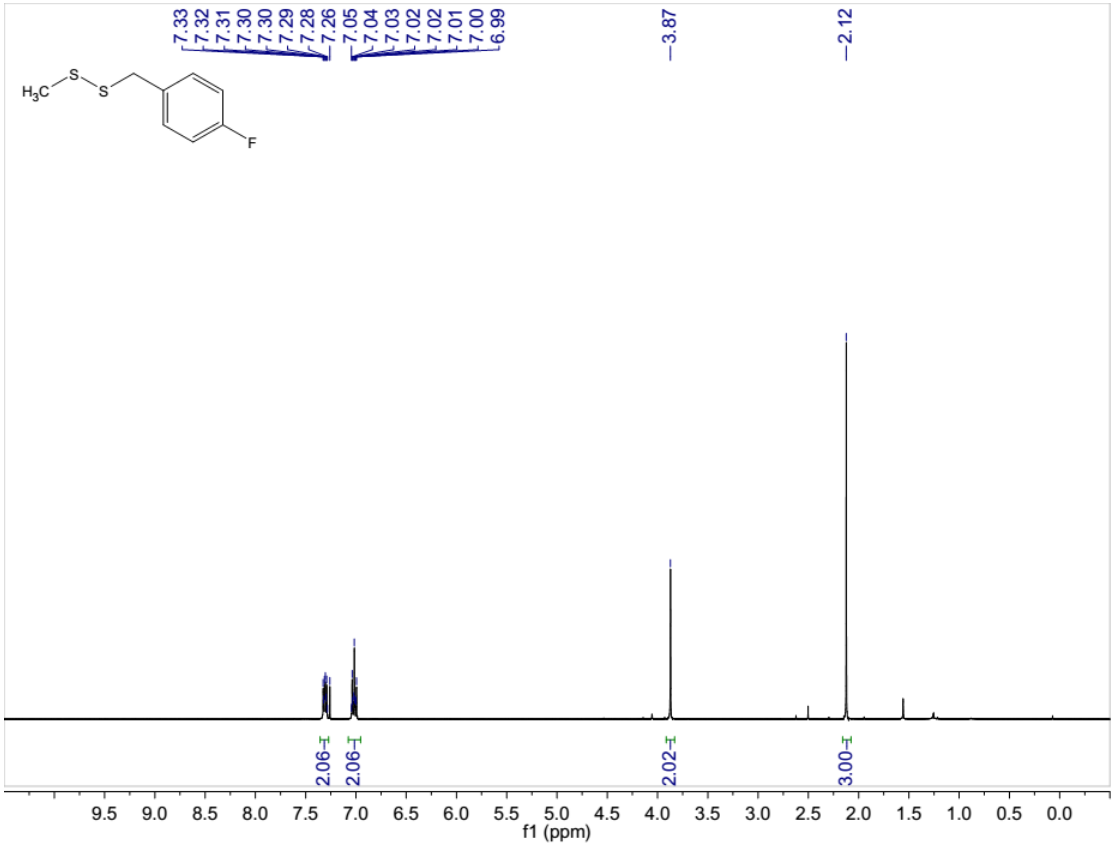

137.71
129.32
128.44
127.29
77.32
77.00
76.68
43.28
18.63
9.60
S
S
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

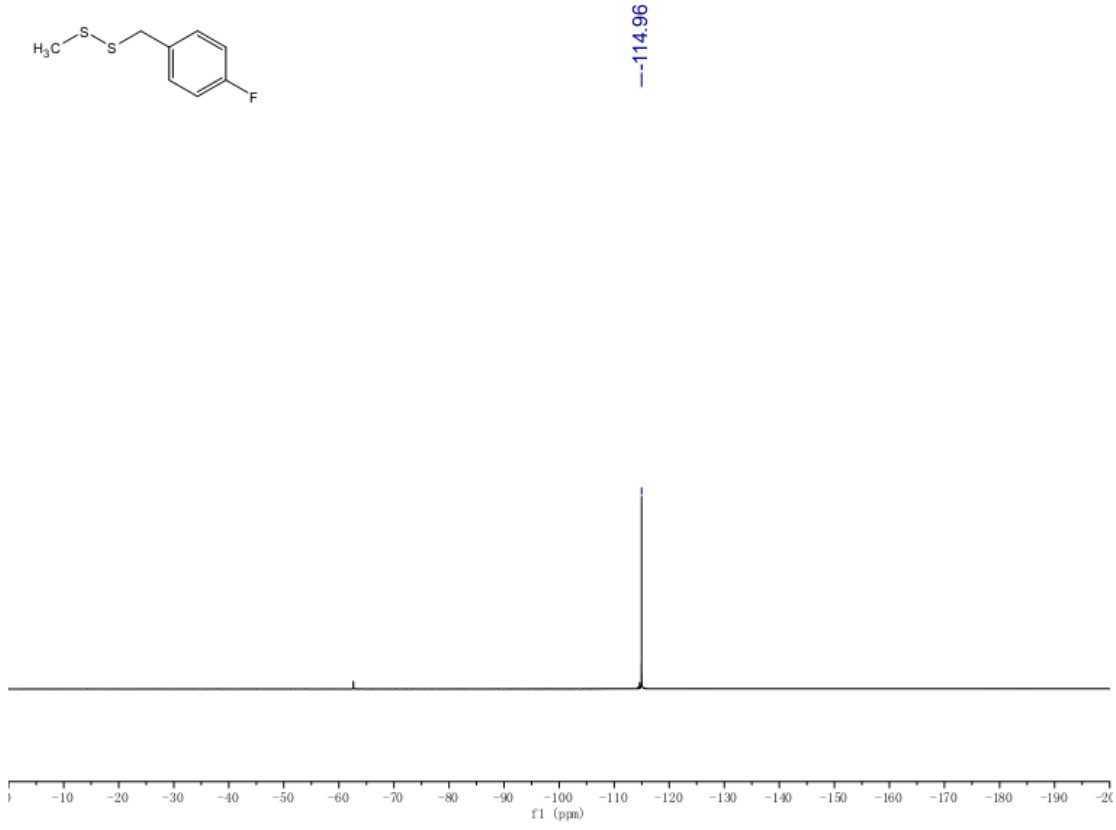
Compound **3k**:

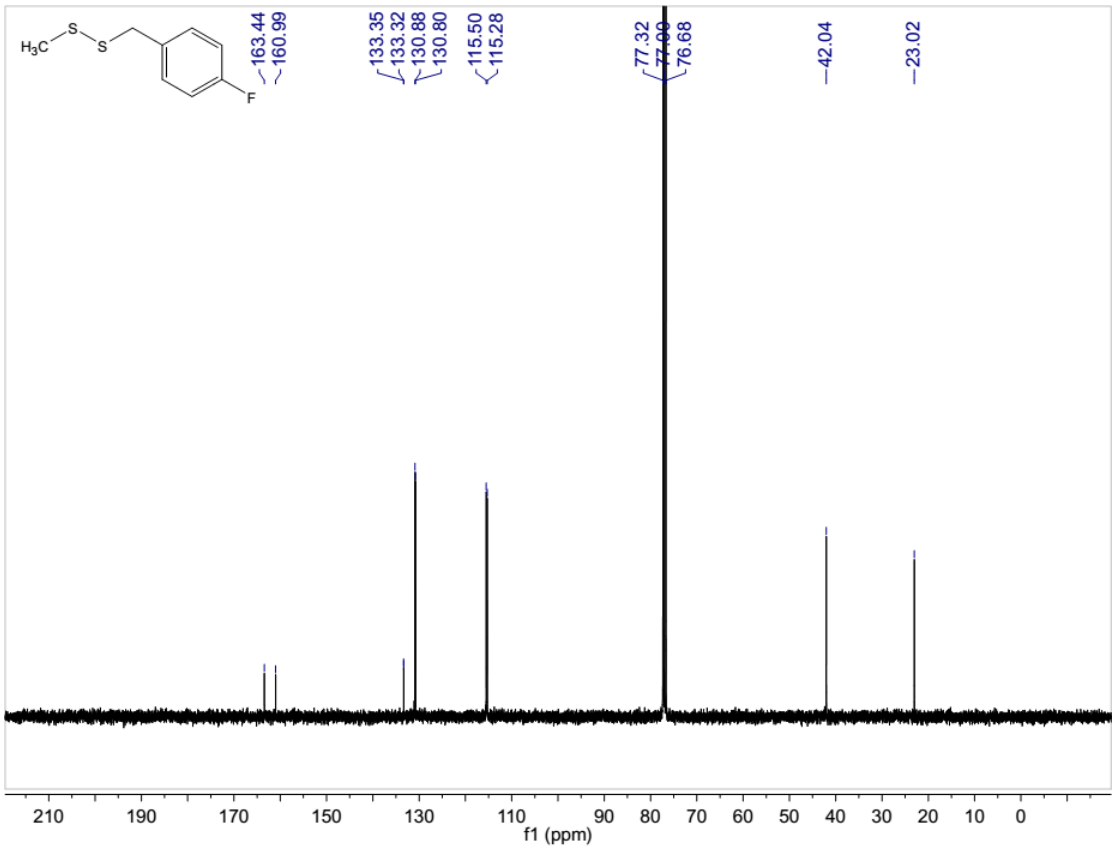

7.42
7.41
7.40
7.38
7.37
7.37
7.36
7.35
7.35
7.34
7.33
7.31
3.96
2.16
1.60
5.06
2.00
2.98
f1 (ppm)


137.50
129.29
128.49
127.36
77.32
77.00
76.68
42.96
22.96
f1 (ppm)

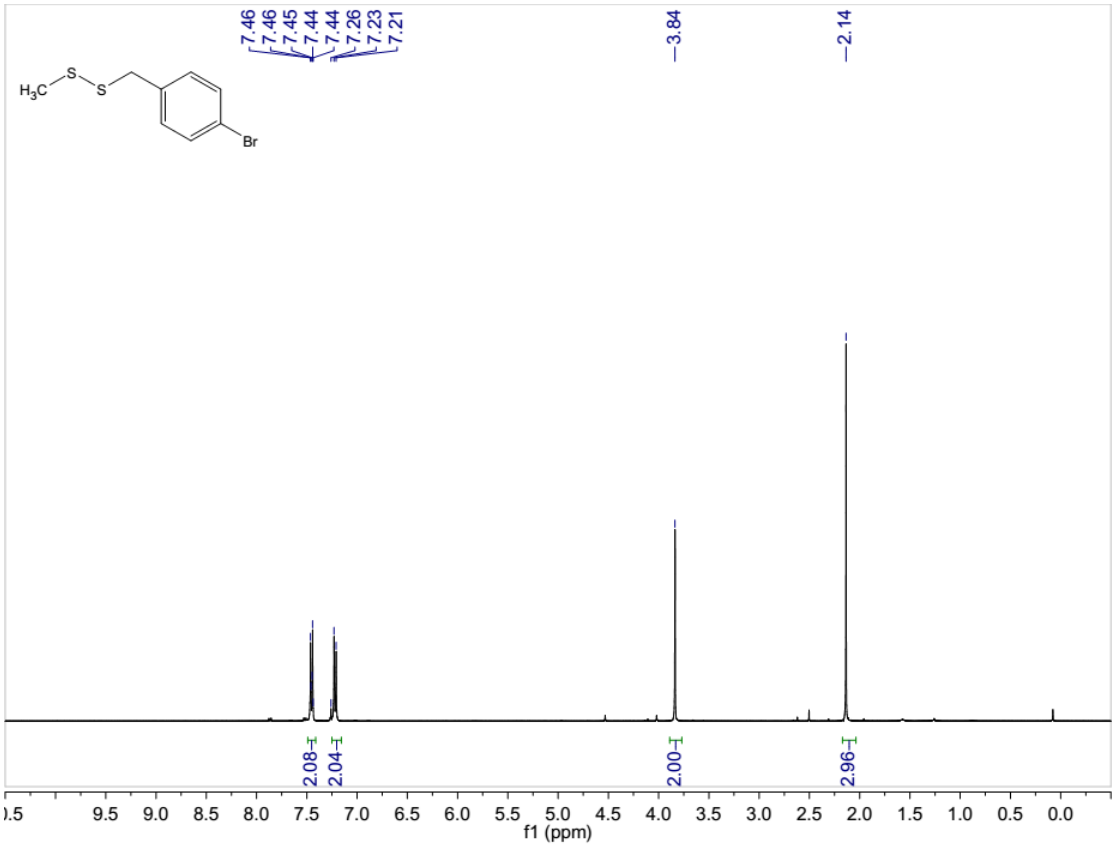
Compound **3l**:

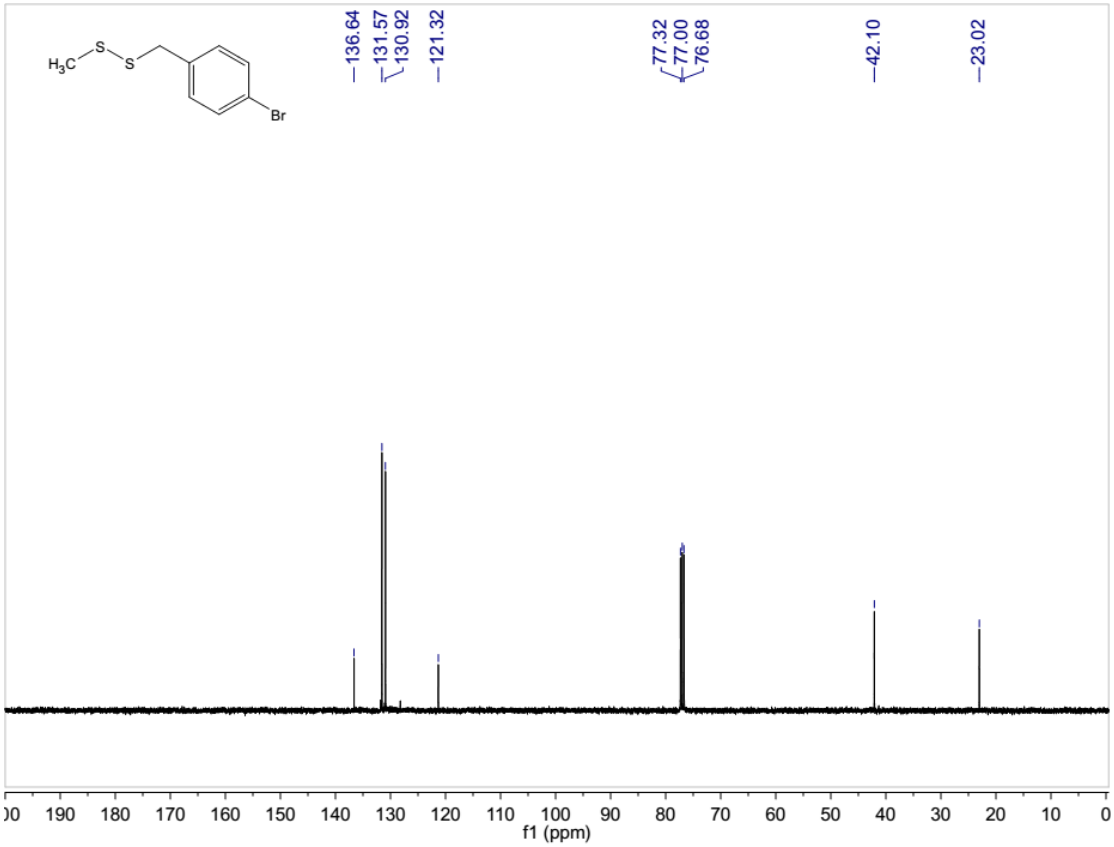

7.33
7.32
7.31
7.30
7.30
7.29
7.28
7.26
7.05
7.04
7.03
7.02
7.02
7.01
7.00
6.99
3.87
2.12
H3C
S
S
F
2.06
2.06
2.02
3.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


H3C
S
S
F
-114.96
-10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190
f1 (ppm)

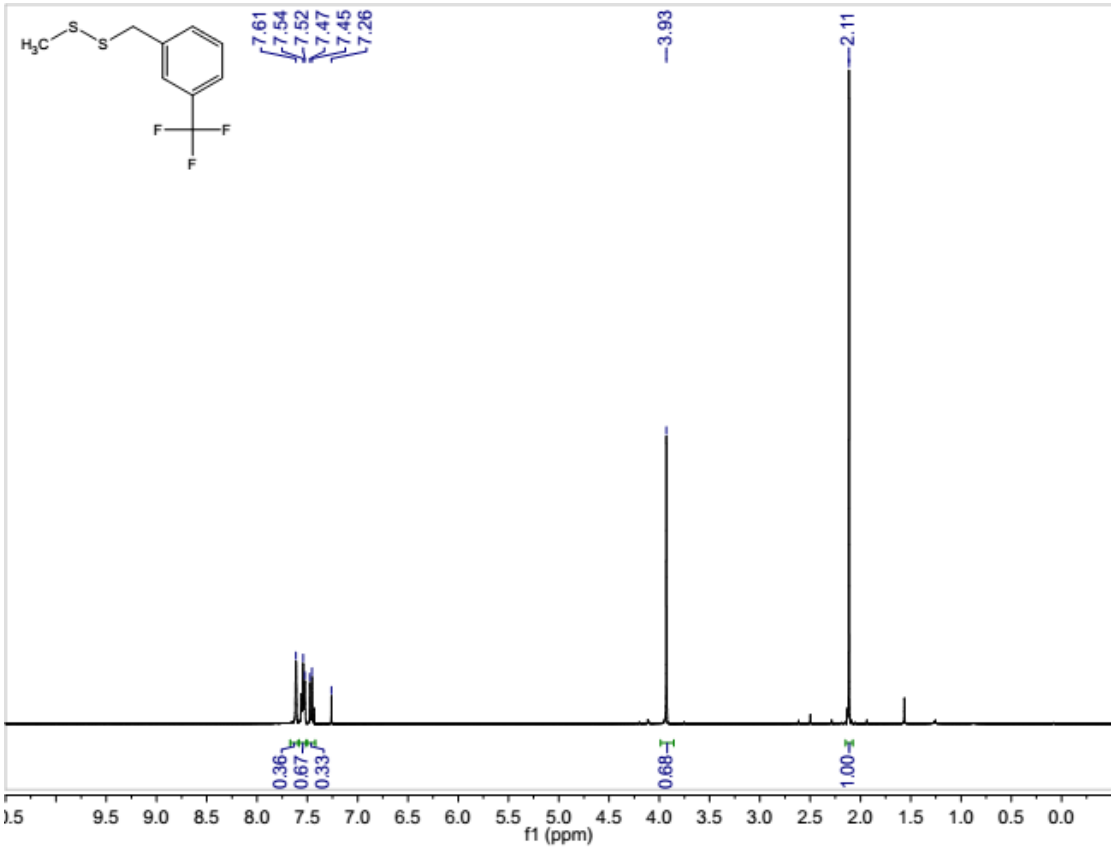

163.44
160.99
133.35
133.32
130.88
130.80
115.50
115.28
77.32
77.00
76.68
42.04
23.02
f1 (ppm)

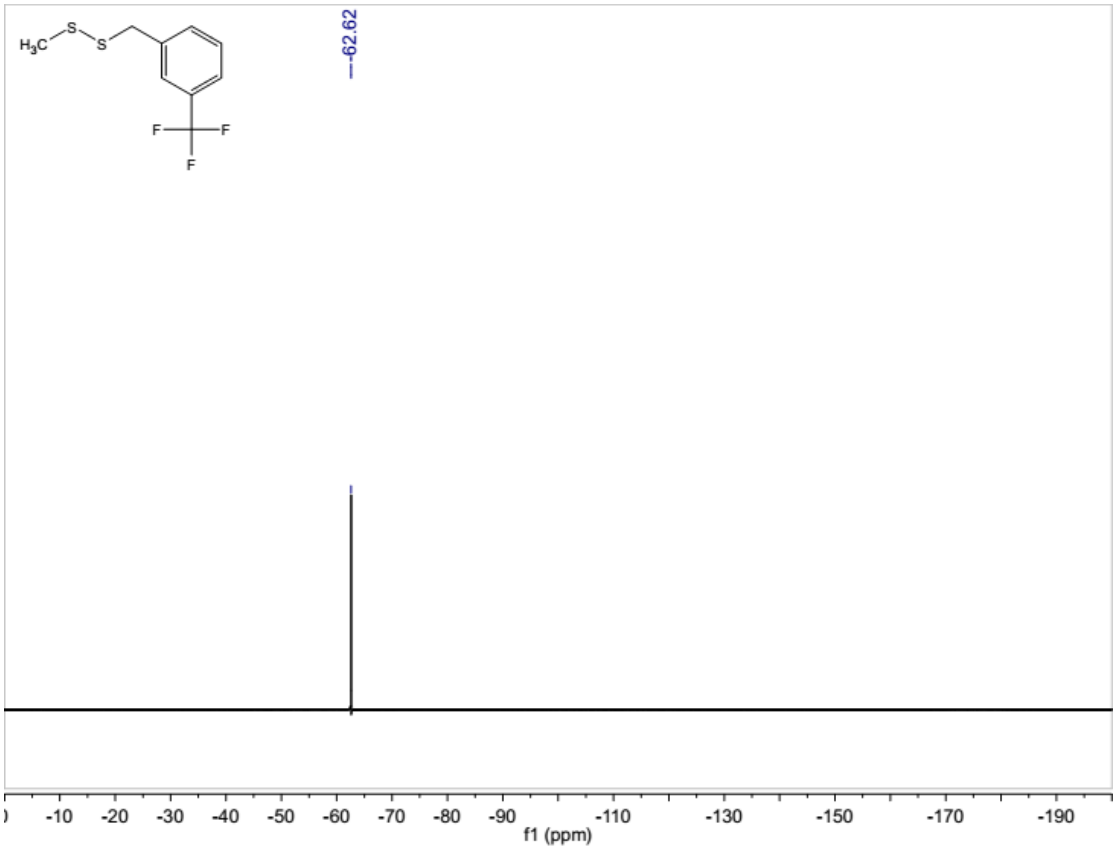
Compound **3m**:

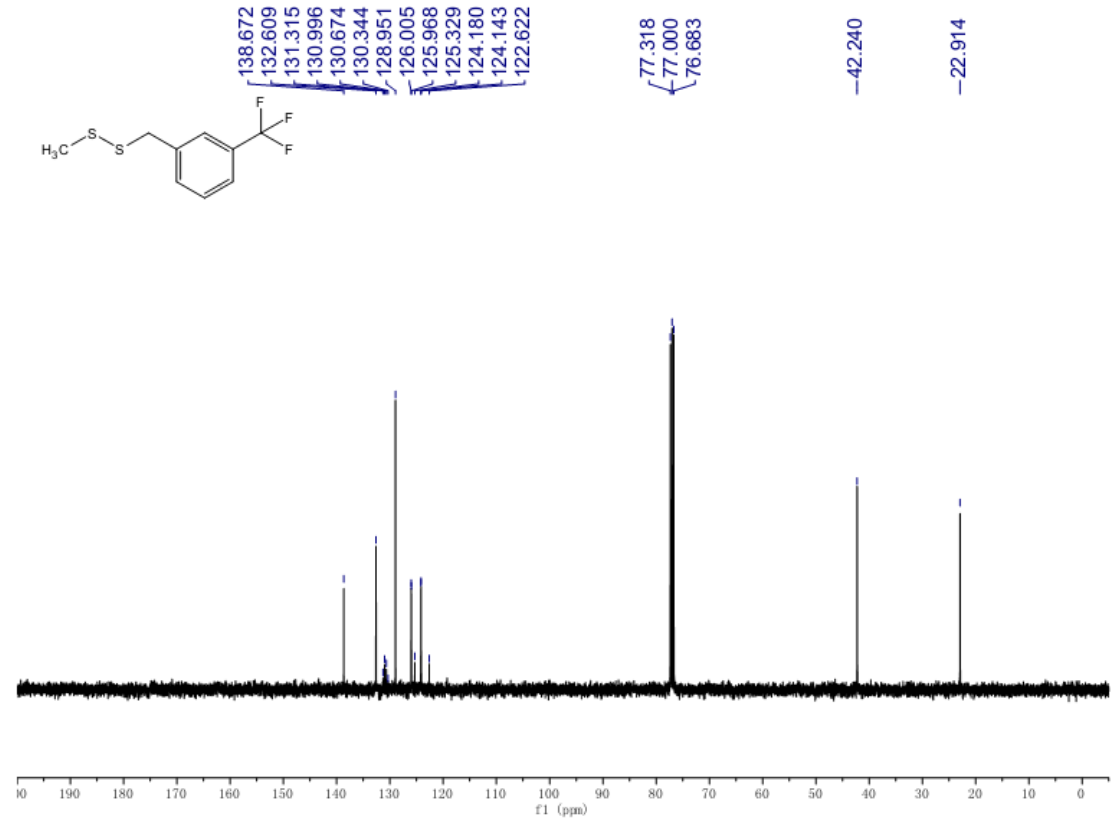

7.46
7.46
7.45
7.44
7.44
7.26
7.23
7.21
3.84
2.14
2.08
2.04
2.00
2.96
f1 (ppm)


136.64
131.57
130.92
121.32
77.32
77.00
76.68
42.10
23.02
f1 (ppm)

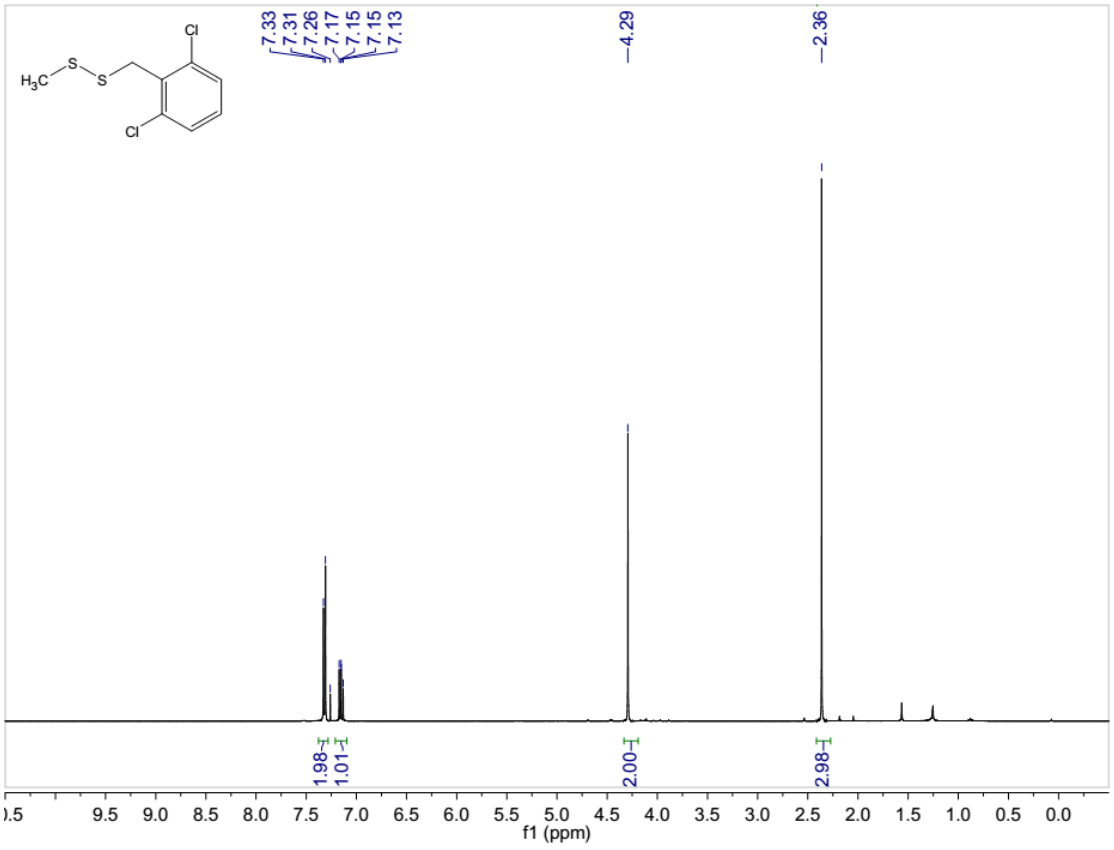
Compound **3n**:

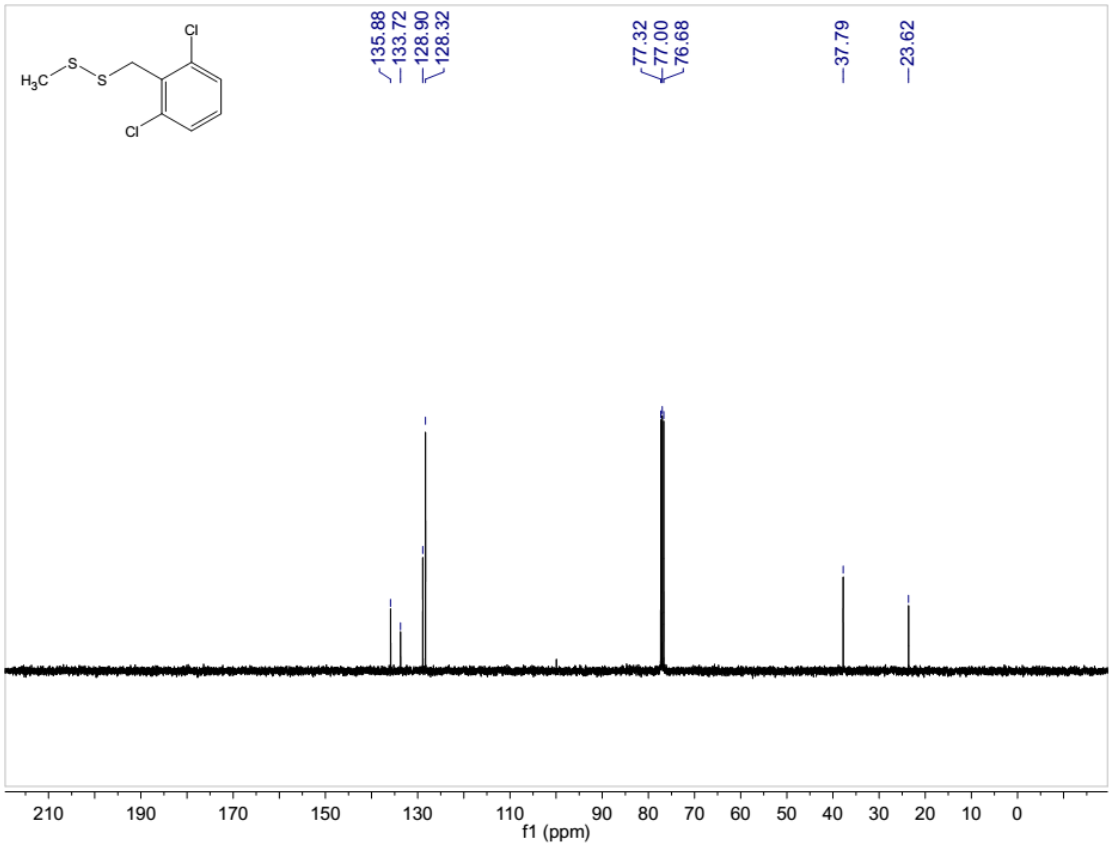

7.61
7.54
7.52
7.47
7.45
7.26
3.93
2.11
0.36
0.67
0.33
0.68
1.00
f1 (ppm)


-62.62
-10 -20 -30 -40 -50 -60 -70 -80 -90 -110 -130 -150 -170 -190
f1 (ppm)

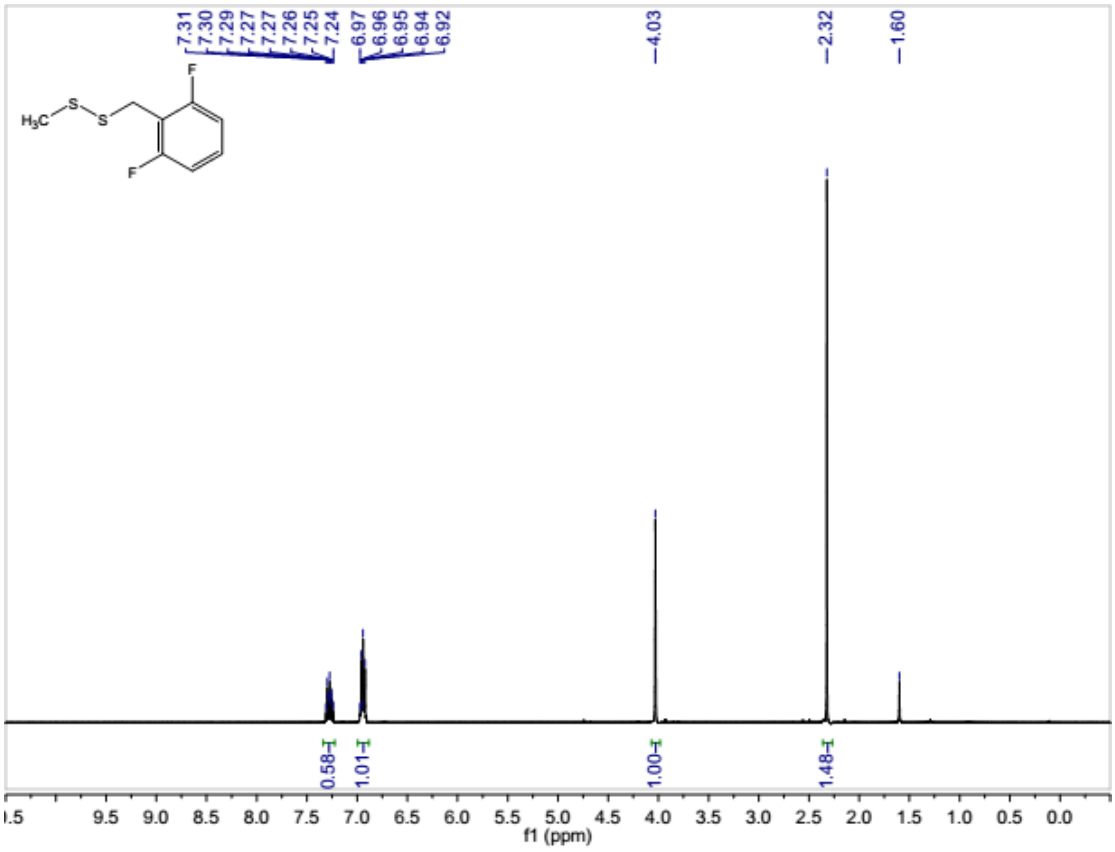

138.672
132.609
131.315
130.996
130.674
130.344
128.951
126.005
125.968
125.329
124.180
124.143
122.622
77.318
77.000
76.683
42.240
22.914
f1 (ppm)

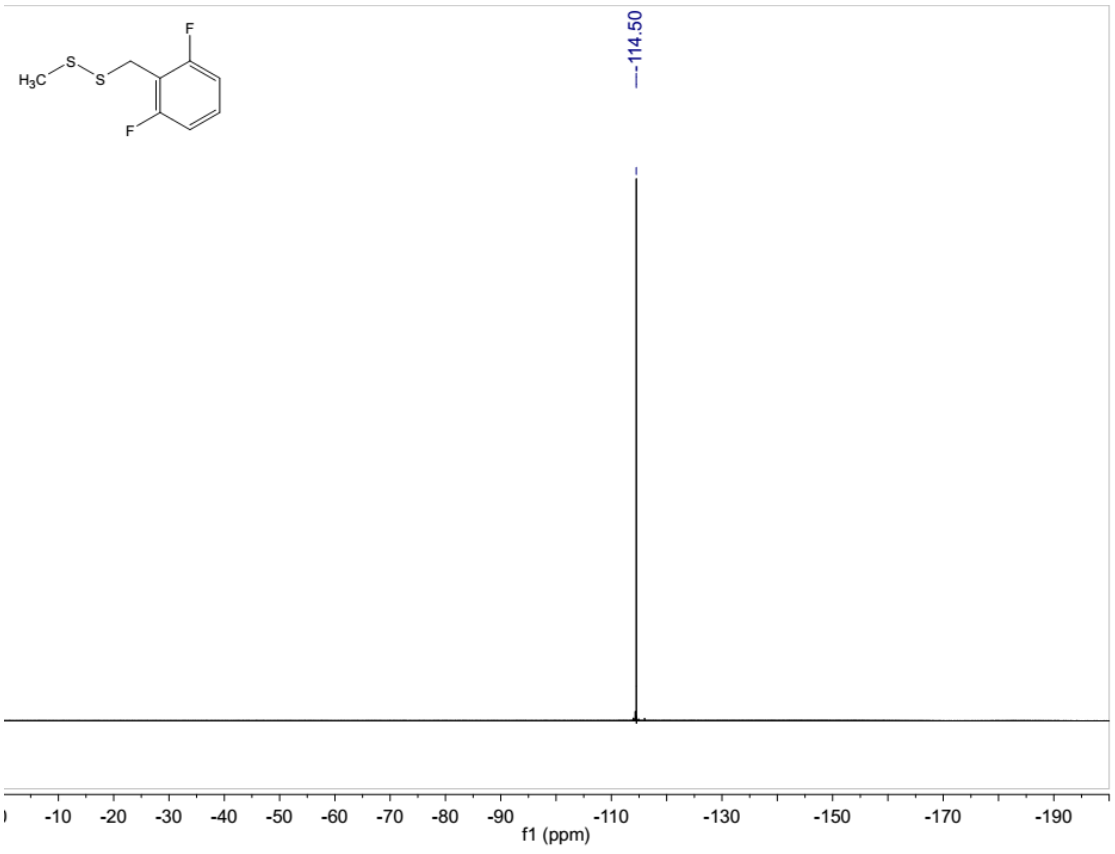
Compound **3o**:

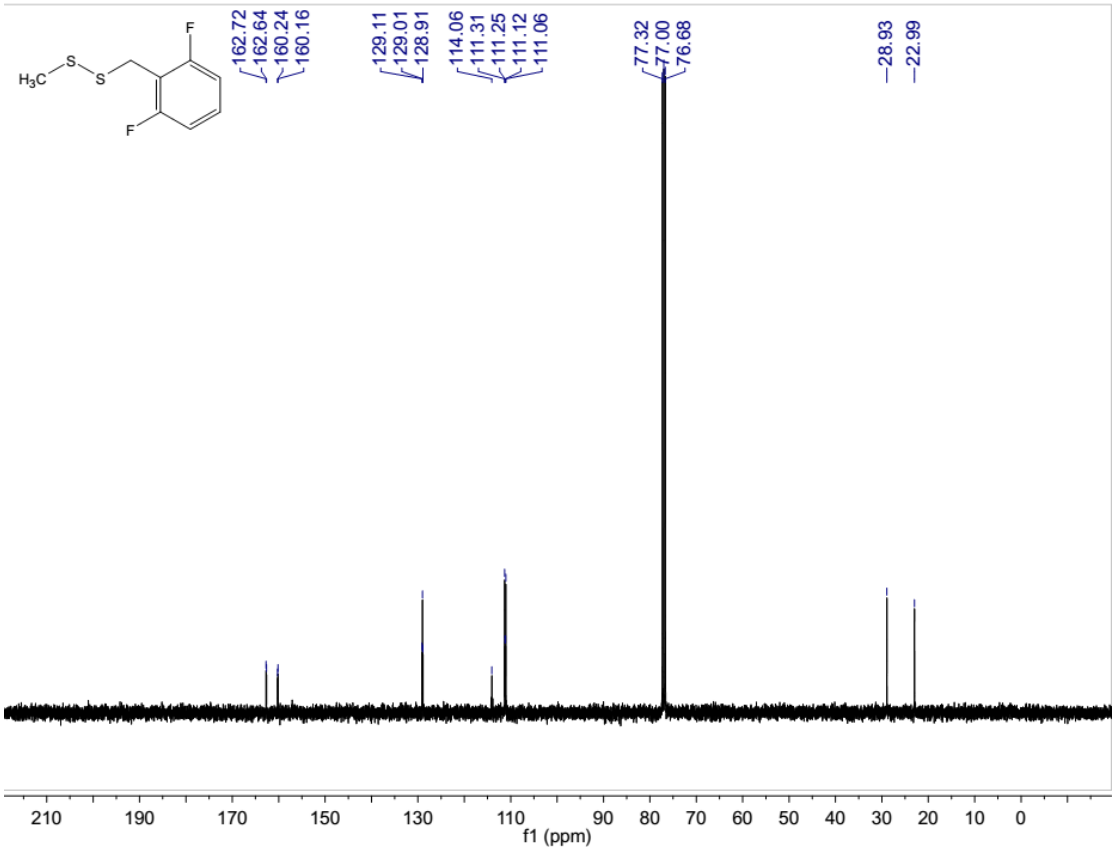

7.33
7.31
7.26
7.17
7.15
7.15
7.13
4.29
2.36
1.98
1.01
2.00
2.98
f1 (ppm)


135.88
133.72
128.90
128.32
77.32
77.00
76.68
37.79
23.62
f1 (ppm)

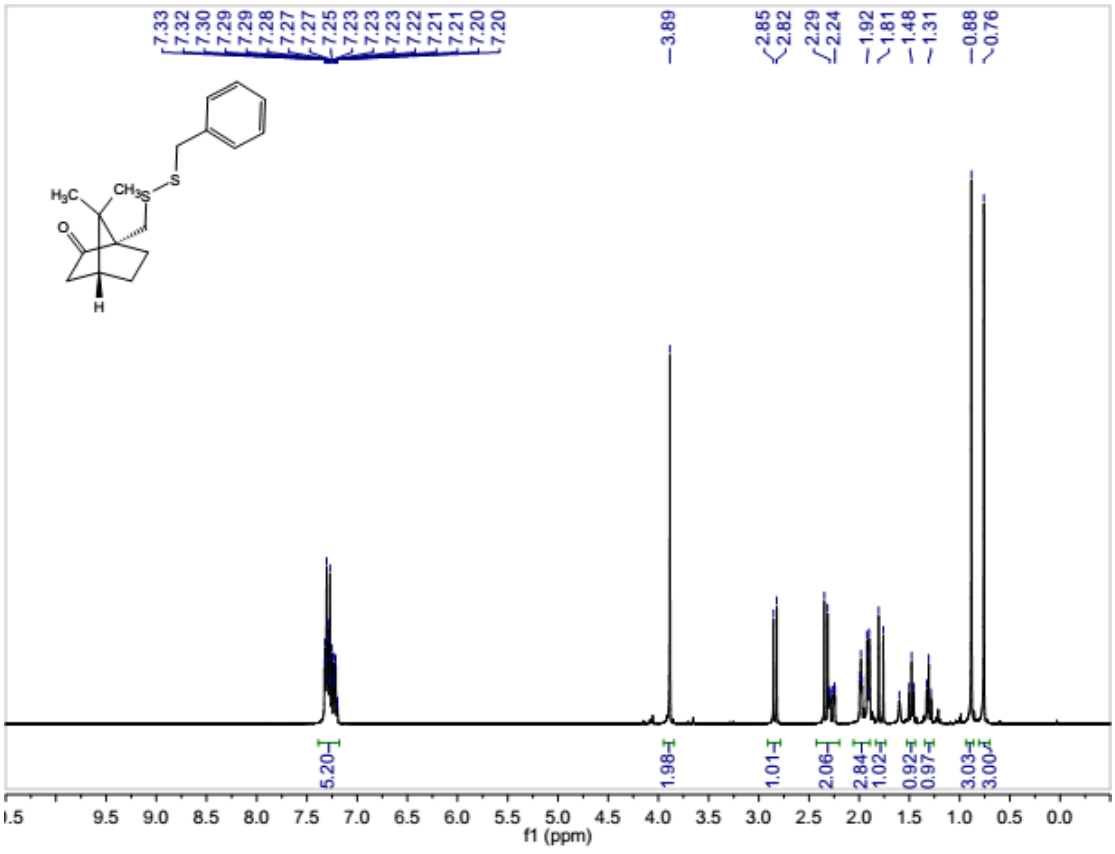
Compound **3p**:

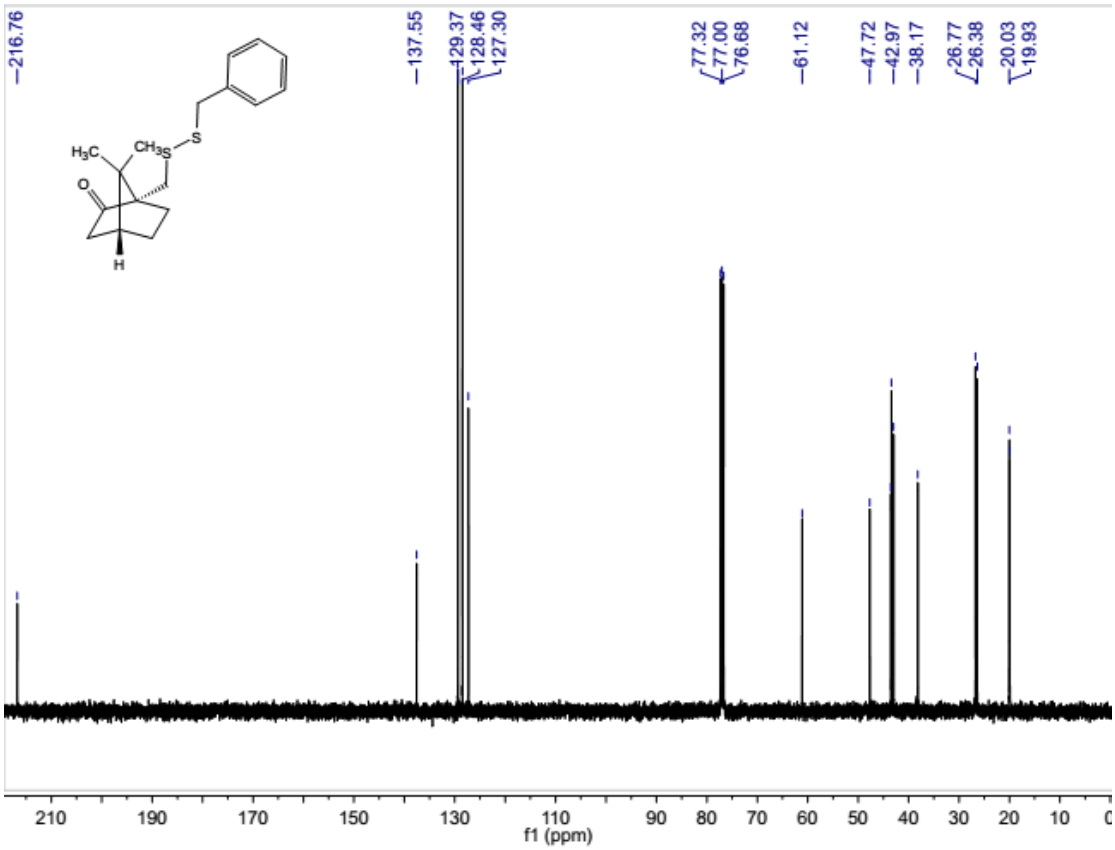

7.31
7.30
7.29
7.27
7.27
7.26
7.25
7.24
6.97
6.96
6.95
6.94
6.92
4.03
2.32
1.60
F
H3C
S
S
F
0.58
1.01
1.00
1.48
f1 (ppm)


F
H3C
S
S
F
-114.50
f1 (ppm)

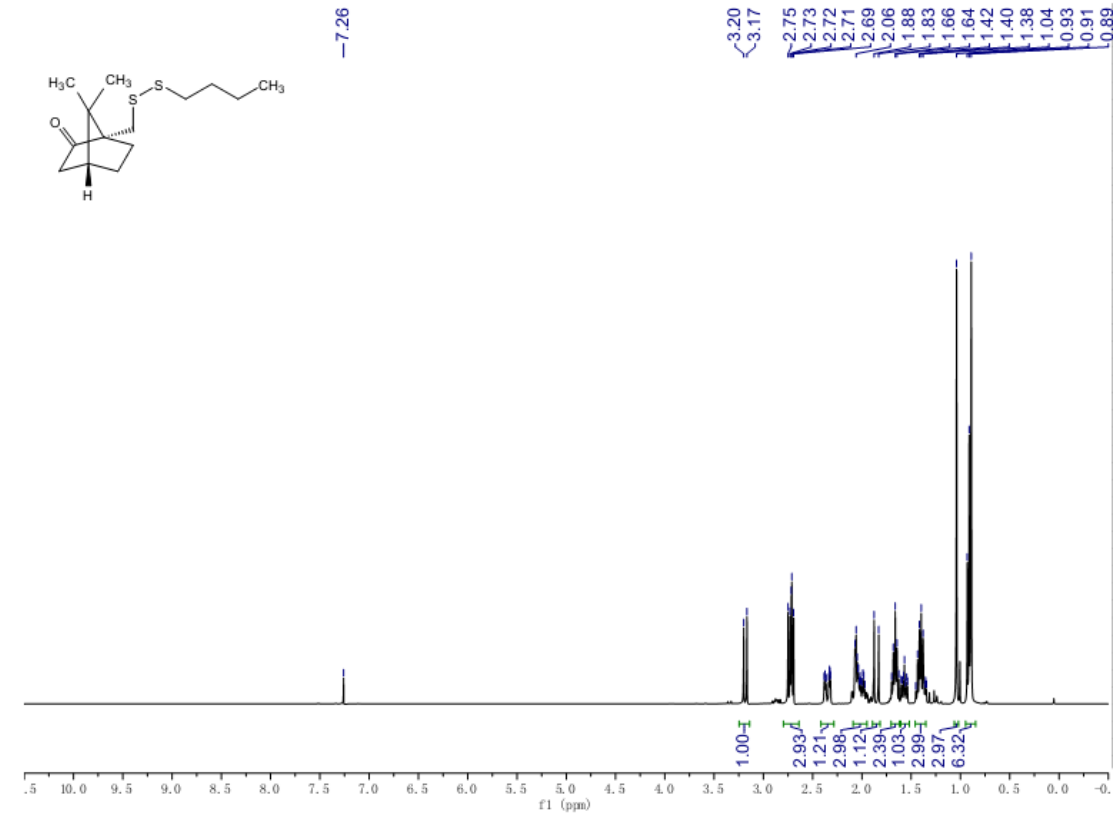

F
H3C
S
S
F
162.72
162.64
160.24
160.16
129.11
129.01
128.91
114.06
111.31
111.25
111.12
111.06
77.32
77.00
76.68
28.93
22.99
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

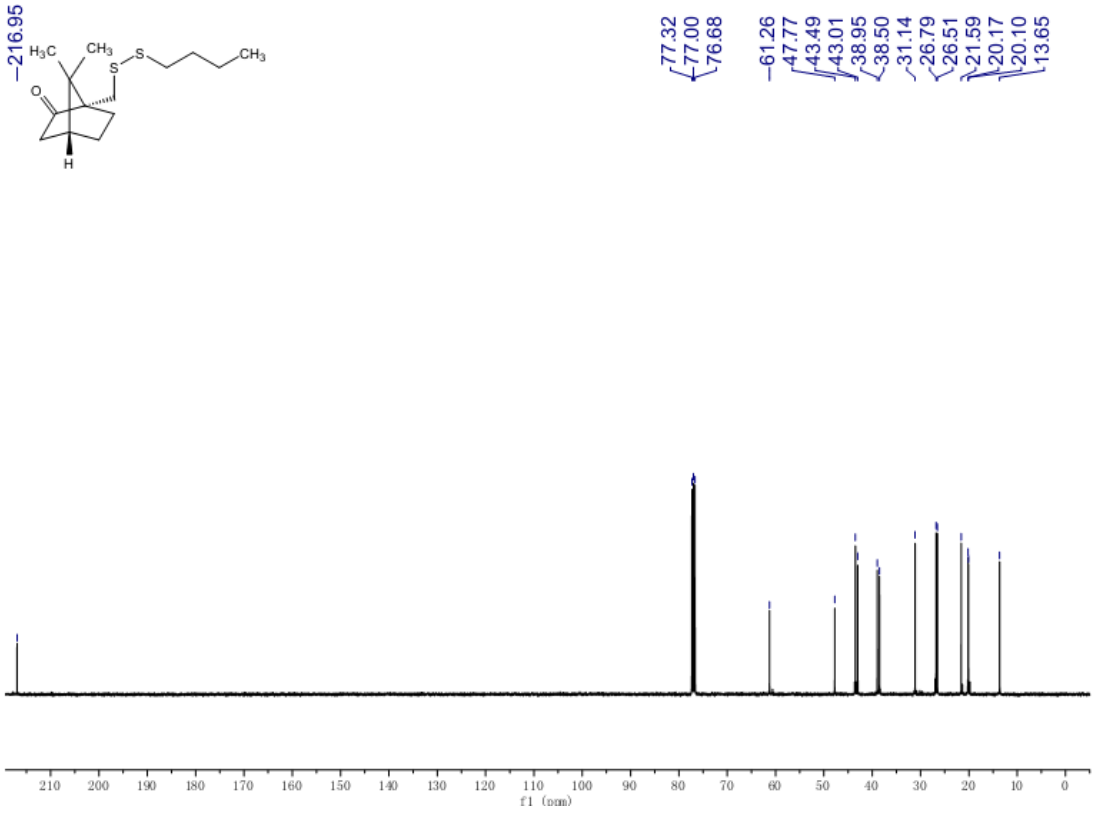
Compound **3q**:


7.33
7.32
7.30
7.29
7.29
7.28
7.27
7.27
7.25
7.23
7.23
7.23
7.22
7.21
7.21
7.20
7.20
3.89
2.85
2.82
2.29
2.24
1.92
1.81
1.48
1.31
0.88
0.76
H3C
CH3
S
S
O
H
5.20
1.98
1.01
2.06
2.84
1.02
0.92
0.97
3.03
3.00
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

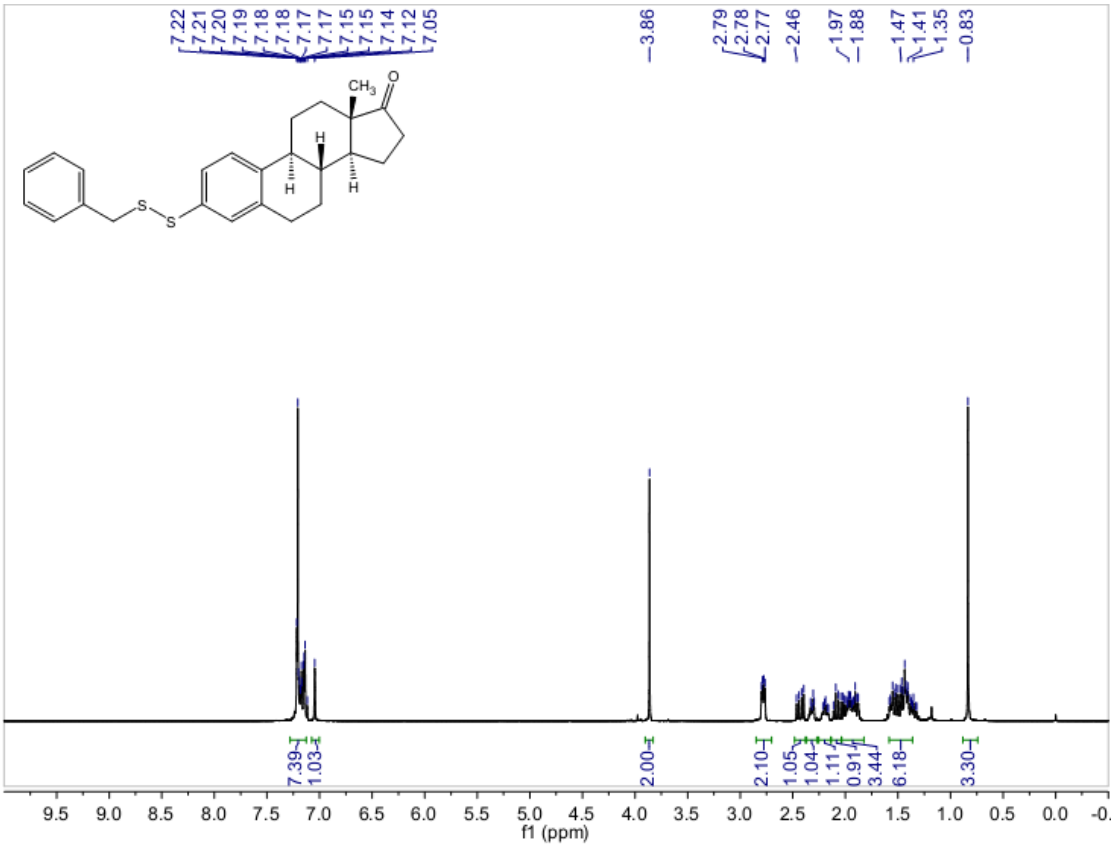

216.76
137.55
129.37
128.46
127.30
77.32
77.00
76.68
61.12
47.72
42.97
38.17
26.77
26.38
20.03
19.93
f1 (ppm)

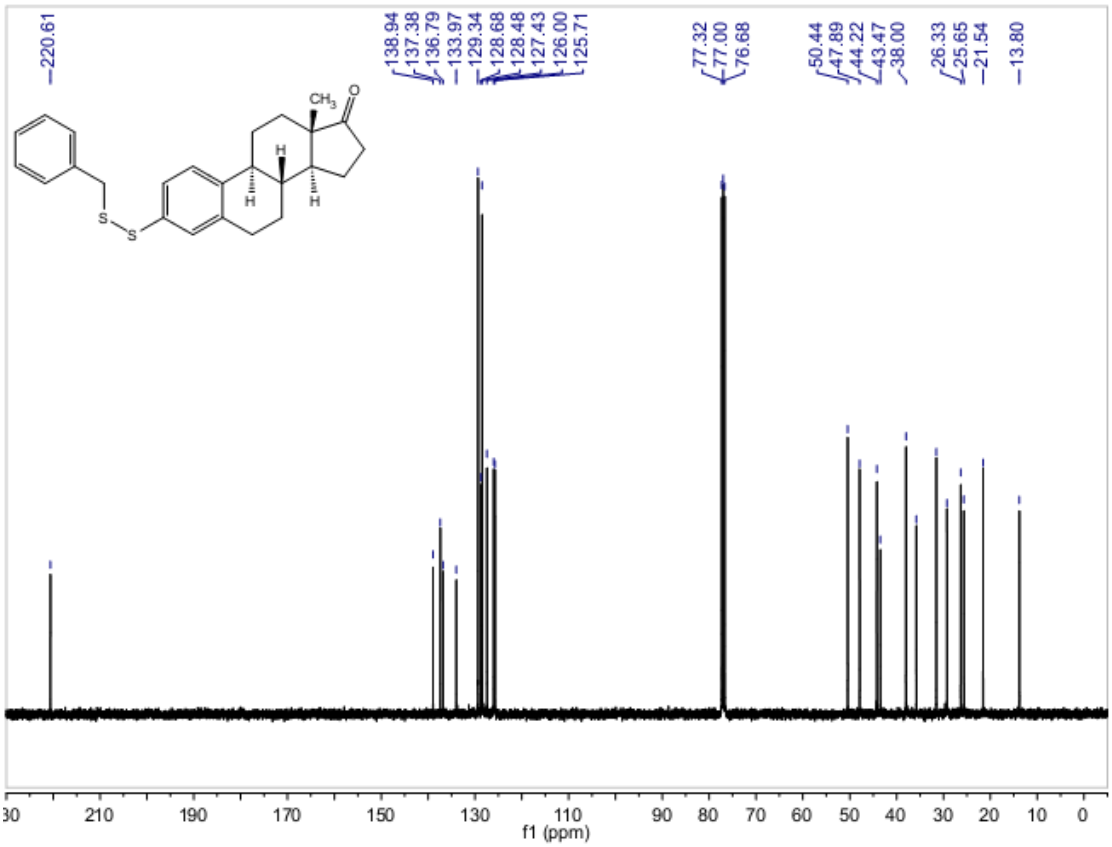
Compound **3r**:


7.26
3.20
3.17
2.75
2.73
2.72
2.71
2.69
2.06
1.88
1.83
1.66
1.64
1.42
1.40
1.38
1.04
0.93
0.91
0.89
1.00
2.93
1.21
2.98
1.12
2.39
1.03
2.99
2.97
6.32
f1 (ppm)

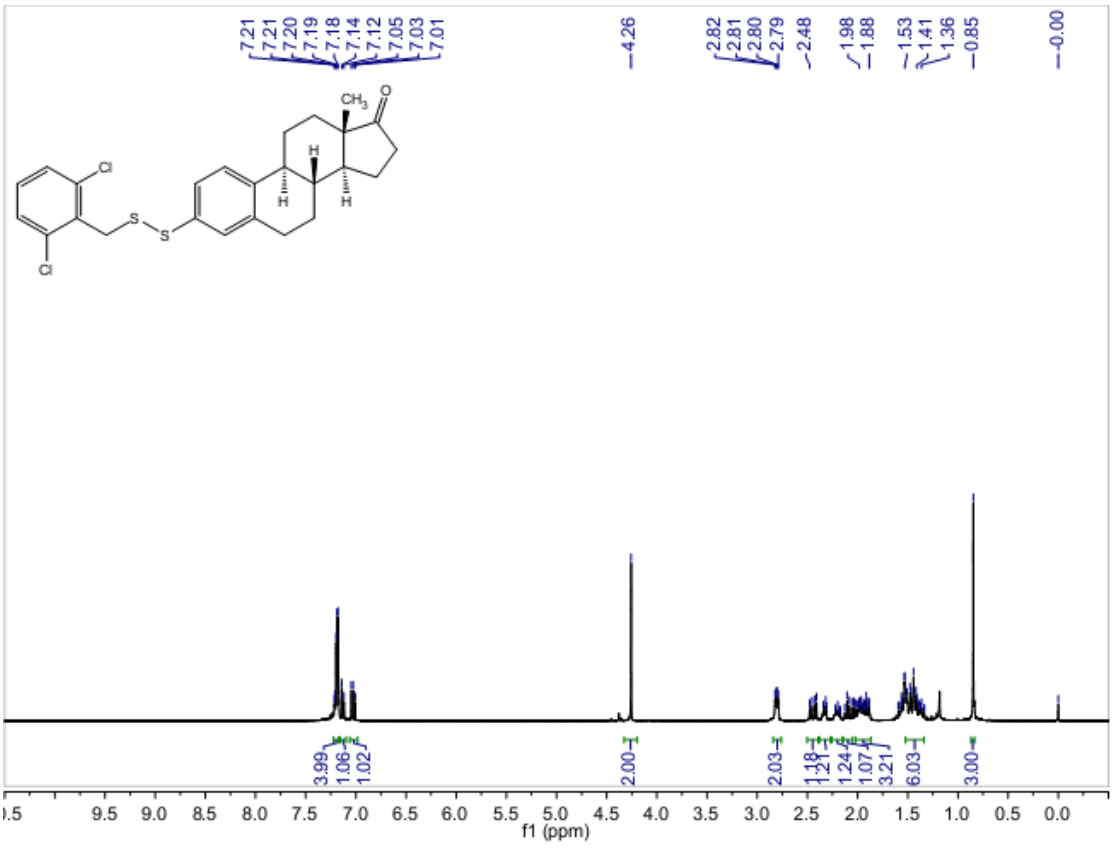

216.95
77.32
77.00
76.68
61.26
47.77
43.49
43.01
38.95
38.50
31.14
26.79
26.51
21.59
20.17
20.10
13.65
f1 (ppm)

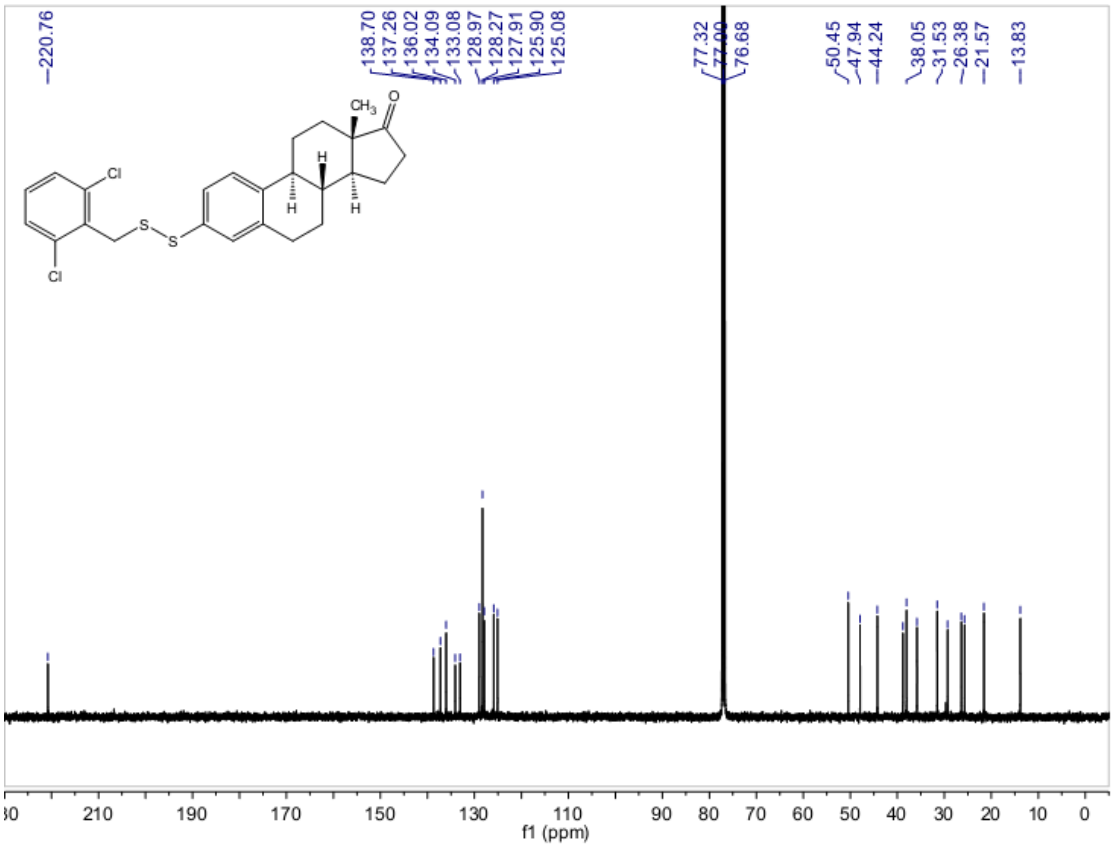
Compound **3s:**


7.22
7.21
7.20
7.19
7.18
7.18
7.17
7.17
7.15
7.15
7.14
7.12
7.05
3.86
2.79
2.78
2.77
2.46
1.97
1.88
1.47
1.41
1.35
0.83
7.39
1.03
2.00
2.10
1.05
1.04
1.11
0.91
3.44
6.18
3.30
f1 (ppm)

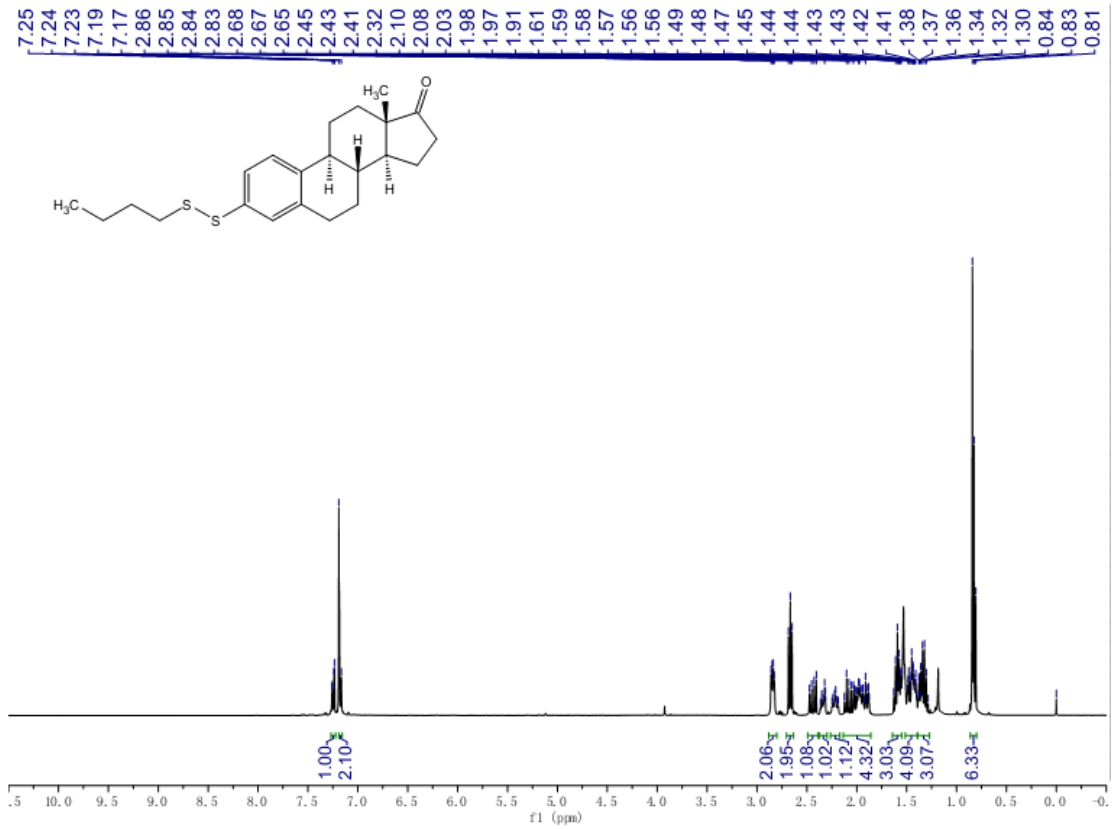

220.61
138.94
137.38
136.79
133.97
129.34
128.68
128.48
127.43
126.00
125.71
77.32
77.00
76.68
50.44
47.89
44.22
43.47
38.00
26.33
25.65
21.54
13.80
CH3
O
H
H
H
S
S
f1 (ppm)

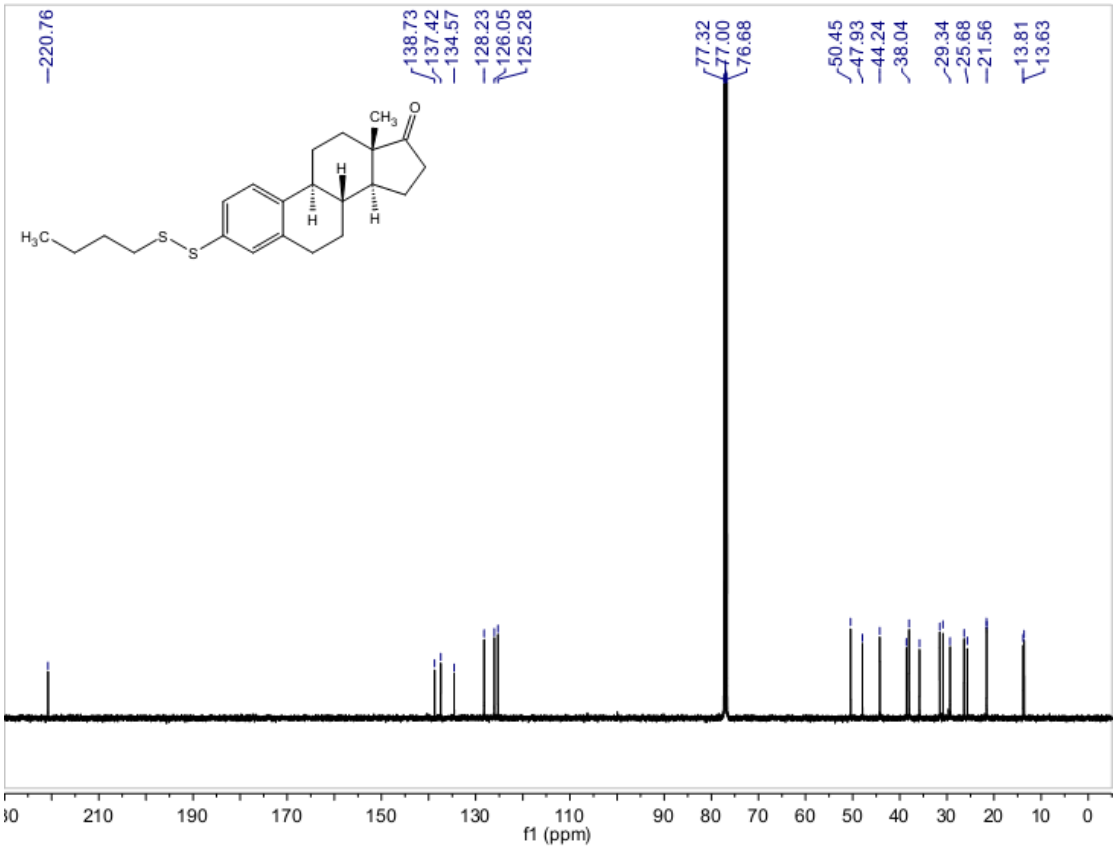
Compound **3t:**


7.21
7.21
7.20
7.19
7.18
7.14
7.12
7.05
7.03
7.01
4.26
2.82
2.81
2.80
2.79
2.48
1.98
1.88
1.53
1.41
1.36
0.85
0.00
CH3
O
H
H
H
Cl
Cl
S
S
3.99
1.06
1.02
2.00
2.03
1.18
1.21
1.24
1.07
3.21
6.03
3.00
f1 (ppm)

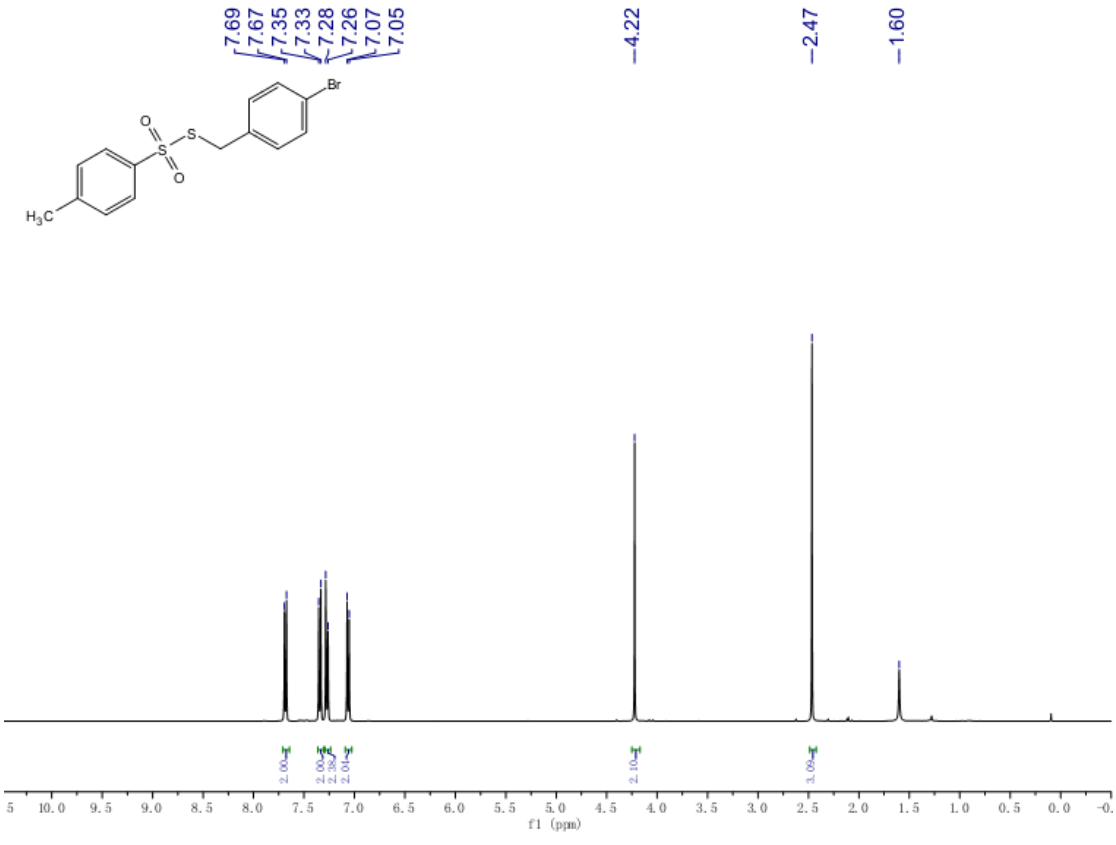

220.76
138.70
137.26
136.02
134.09
133.08
128.97
128.27
127.91
125.90
125.08
77.32
77.00
76.68
50.45
47.94
44.24
38.05
31.53
26.38
21.57
13.83
CH3
O
H
H
H
Cl
Cl
S
S
f1 (ppm)

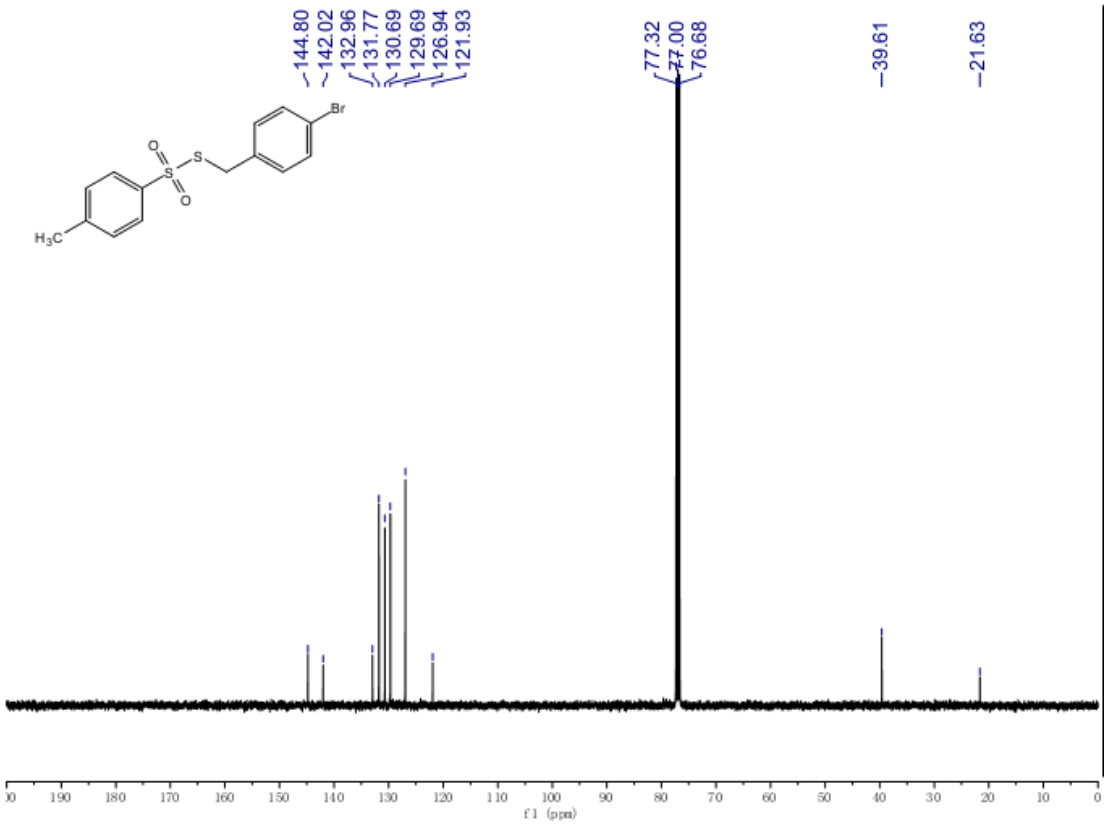
Compound **3u:**


7.25
7.24
7.23
7.19
7.17
2.86
2.85
2.84
2.83
2.68
2.67
2.65
2.45
2.43
2.41
2.32
2.10
2.08
2.03
1.98
1.97
1.91
1.61
1.59
1.58
1.57
1.56
1.56
1.49
1.48
1.47
1.45
1.44
1.44
1.43
1.43
1.42
1.41
1.38
1.37
1.36
1.34
1.32
1.30
0.84
0.83
0.81
H3C
O
H
H
H
H3C
S
S
1.00
2.10
2.06
1.95
1.08
1.02
1.12
4.32
3.03
4.09
3.07
6.33
f1 (ppm)

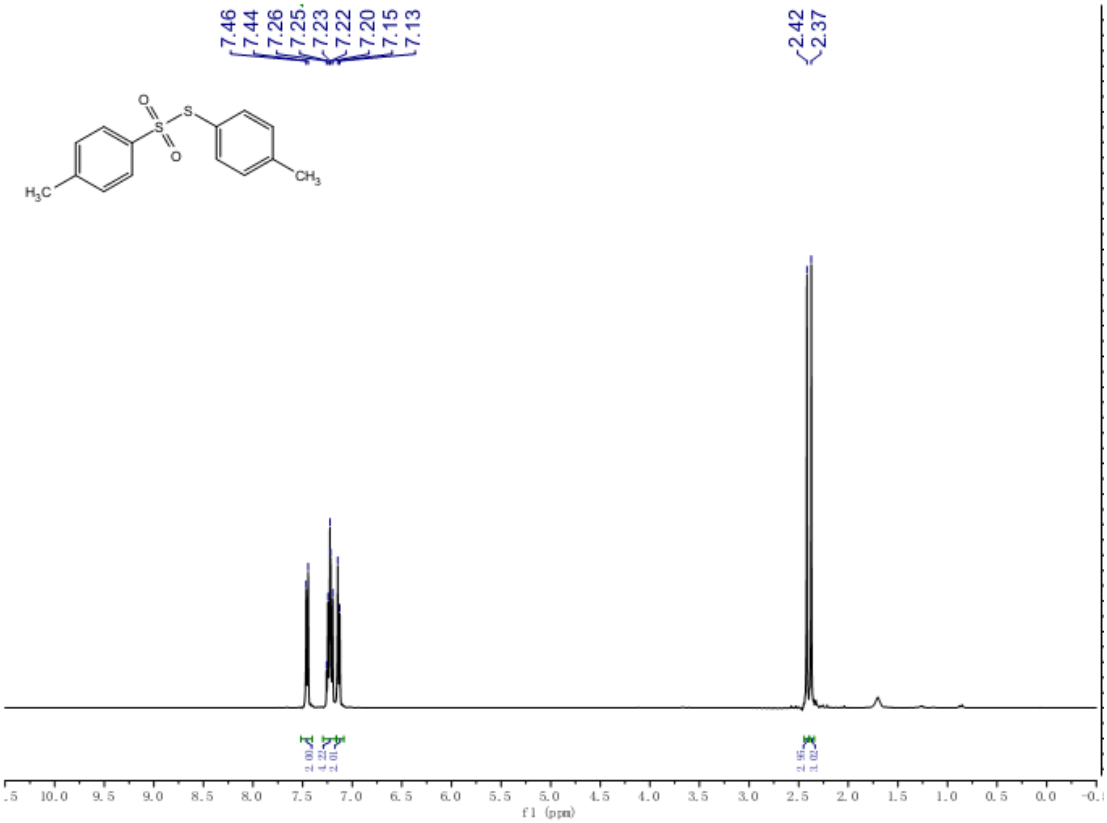

220.76
138.73
137.42
134.57
128.23
126.05
125.28
77.32
77.00
76.68
50.45
47.93
44.24
38.04
29.34
25.68
21.56
13.81
13.63
CH3
O
H
H
H
H3C
S
S
f1 (ppm)

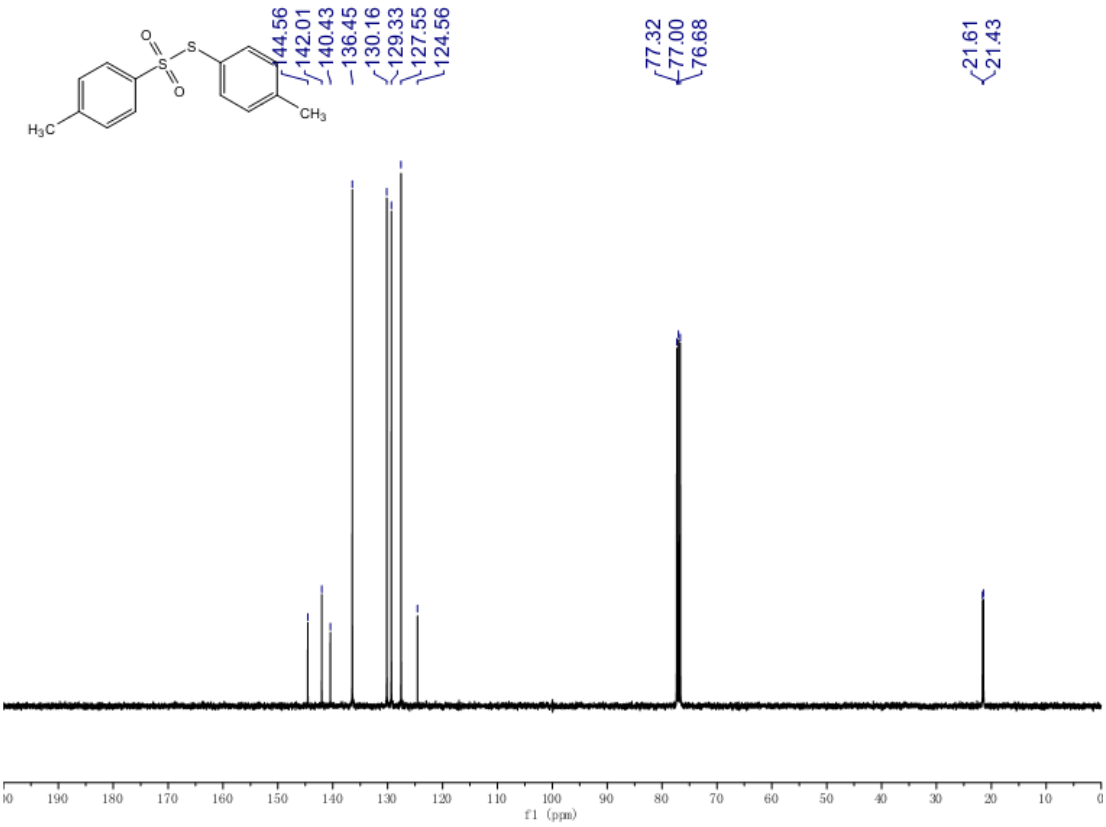
Compound **4**:


7.69
7.67
7.35
7.33
7.28
7.26
7.07
7.05
4.22
2.47
1.60
Br
O
S
O
S
H3C
f1 (ppm)


144.80
142.02
132.96
131.77
130.69
129.69
126.94
121.93
77.32
77.00
76.68
39.61
21.63
Br
S
O
O
H3C
f1 (ppm)

Compound **5**:


7.46
7.44
7.26
7.25
7.23
7.22
7.20
7.15
7.13
2.42
2.37
S
O
O
H3C
CH3
f1 (ppm)


144.56
142.01
140.43
136.45
130.16
129.33
127.55
124.56
77.32
77.00
76.68
21.61
21.43
O
S
S
O
H3C
CH3
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)