Supporting information

A facile, catalyst and additive-free, and scalable approach to the photochemical preparation of disulfides from organo sulfenyl chlorides

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Materials and Methods

Materials

All commercially available reagents and solvents were used without further purification except where otherwise stated. CS_2 (AR, 99.5%), Concentrated sulfuric acid (98%), Cyclohexane (AR, 99.5%) and Benzene (HPLC, 500 mL) were purchased from Tianjin Damao Chemical Reagent Factory. Hydrochloric acid (AR) was purchased from Yantai Yuandong Chemical Co. LTD. Chlorine and Chloroform (99.9%) were got from Shandong Dongyue Chemical Co. LTD. Sodium sulfate decahydrate (AR) was purchased from Macklin. Acetic acid (AR, ≥99.5%). Toluene (AR, ≥99.5%) and Isopropanol (≥99.7%) were purchased from Xilong Scientific Co., Ltd.. Methanol (AR), Ethanol (AR, anhydrous) and n-pentane (99%) were purchased from Sino pharma Reagent Co. LTD, Acetonitrile (HPLC) was purchased from Sigma-Aldrich, Acetophenone (AR) was purchased from Tianjin Bodi Chemical Co. LTD.

Methods

Reactions were monitored by thin layer chromatography (TLC) with precoated silica gel plates from Merck Chemicals (TLC Silica gel 60 F254, 250 μm thickness) using UV light as the visualizing agent and/or iodine vapor. All reactions were carried out in NBT-Photoreactor (GXAS335, Beijing NBET Technology Co., Ltd) with a IKA C-MAG HS-7 stirrer under a nitrogen atmosphere.

Nuclear Magnetic Resonance spectra were recorded on a Bruker 400/600 UltraShield spectrometer (400/600 MHz for 1H,376MHz for 19F and 100MHz for 13C) in chloroform-d. Chemical shifts (δ) are quoted in parts per million (ppm) and were internally referenced to residual $CHCl_3$ (7.26 ppm for ^{1}H, 77.16 ppm for ^{13}C). Coupling constants (J) are reported in Hertz (Hz) to the nearest 0.1 Hz. The following abbreviations (or combinations thereof) were used for peak multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, quintet, m = multiplet.

Gas chromatography (GC) was carried out on Agilent 8860. High-performance liquid chromatography (HPLC) was carried out on Agilent 1260. Gas chromatography-mass spectrometry (GC-MS) was performed on Agilent 7890B/5977B. High-resolution mass spectra (HR-MS) were recorded under electron impact (EI-TOF) (70 eV) condition using a MicroMass GCT CA 055 instrument. The Flash chromatographic system used for separation was SepaBean machine U100 from Changzhou Santai Technology Co.,Ltd.

Synthesis of trichloromethyl sulfenyl chloride [1]

A three-necked glass reaction bottle with a stir bar and cooling tube (-20 °C ethanol circulating liquid) was charged with 380.7 g carbon disulfide (AR, 99.5%, 5.00 mol), 12% HCl (aq) (418.8 g, AR), chlorine was Slowly bubbled to react with the slurry solution until carbon disulfide content less than 1% (GC area normalization method). Then the solution was allowed to still stand for 10 minutes, observing that two phases were formed. The organic phases were gathered and the solvent was removed in vacuo (-0.095 mPa), and the fraction with a top temperature of 73-75 °C was collected to afford trichloromethyl sulfenyl chloride (800.5 g) in a yield of 85% and a content of 98.7% (GC area normalization method). GC-MS: m/z: 185.8 [M^+]. ^{13}C NMR (101 MHz, $CDCl_3$) δ 97.55.

Synthesis of 1,2-bis(trichloromethyl)disulfide in a batch photoreactor

A 500 mL Photoreactor (NBT, Fig. 1) with heated magnetic stirring and flat top cover was charged with 0.05 mol trichloromethyl sulfenyl chloride (9.4 g, 98.7 % (GC, area normalization method)) and cyclohexane (53 mL), the LED lamp was placed on the top plate and turned on to modulate the specified current to irradiate the solution. Persistent emission of hydrogen chloride with slight chlorine gas was also detected with a pH test paper and a potassium iodide starch test paper (see Fig. 2). After irradiation, the solution was checked with GC-MS. On completion, the solvent was removed in vacuo, and the residue was distilled in vacuo to afford 1,2-bis(trichloromethyl)disulfide. GC-MS: m/z: 299.8 [M+]. ^{13}C NMR (101 MHz, $CDCl_3$) δ 98.41.

Batch LED-light Reactor：Beijing NBET Technology Co., Ltd NBT-LED100 LED-light Reactor (NBT-LED100-350/365/385/405/420/455).

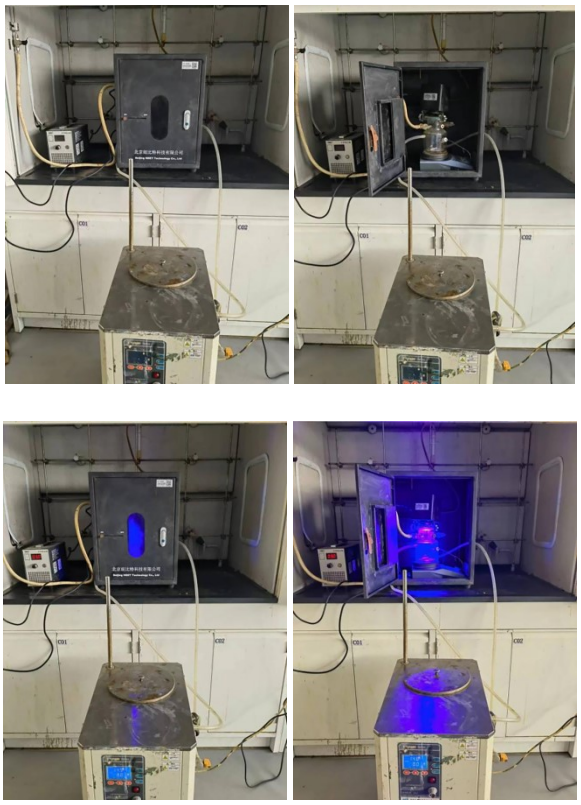


Fig. S1 Batch photoreactor

Left Right

Fig. S2 Test chart for tail gas of trichloromethyl mercaptan

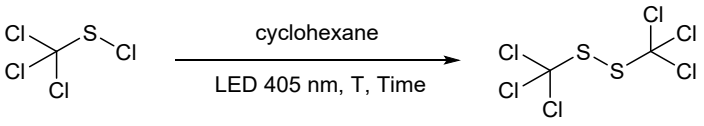
Failed reactions of nearly 100 grams scale amplification in batch reactors

A 1000mL photoreactor (NBT) with heated magnetic stirring and flat top cover was charged with 0.5 mol trichloromethyl sulfenyl chloride (94 g) and cyclohexane (530 mL). After 15 minutes of irradiation at 405 nm at 35 °C, it was found that there was a large amount of reaction raw materials left, and no remarkable improvement was observed after continued irradiation for extra 2 hours, which indicated that there might be an amplification problem with a batch reactor.

The synthesis of bis trichloromethyl disulfide in a Corning G1 flow reactor

The mixture with trichloromethyl sulfenyl chloride in cyclohexane (50 mmol, 0.85 M) and was pumped into a Corning G1 glass reactor (Fig. 3 and Fig. 4) in a volumetric flow rate of 13.7 mL/min to conduct conditional exploration experiments under 405 nm LED at a set temperature and residence time, and the results were shown in Table S1.

Table S1 Reaction condition optimization for the synthesis of bis trichloromethyl disulfide in Corning G1 flow reactor[a]



1a **2a**

Entry	Temp. (°C)	Residence Time (min)	Yield[b] (%)
1	35	1.0	45
2	35	1.5	56
3	35	2.0	80
4	35	2.5	82
5	35	3.0	91
6	35	9.0	91
7	35	12.0	91
8	35	15.0	91
9	35	18.0	91
10	45	3.0	92
11	55	3.0	92
12	65	3.0	93
13	75	3.0	93
14	85	3.0	94

[a] Reaction conditions: **1a** in cyclohexane (0.85 M，13.7 mL/min), LED 405 nm.

[b] Isolated yield.

Fig. S3 Corning G1 photoreactor

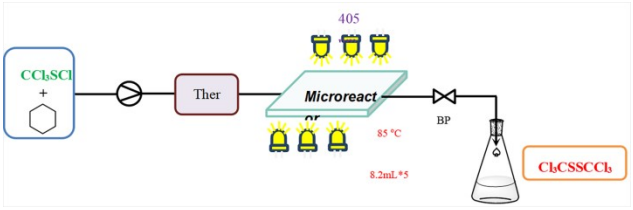
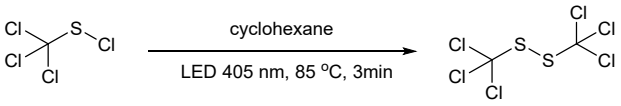


Fig. S4 Continuous process equipment

Kilogram-scale synthesis of 1,2-bis(trichloromethyl)disulfide in a Corning G1 flow reactor



1a **2a**

Trichloromethyl sulfenyl chloride **1a** (1878 g, 99.0% (GC area normalization method), 10.0 mol, 1.0 equiv) and cyclohexane (8416 g, 10639 mL) were mixed homogeneously and pumped into a Corning Advanced-Flow G1-10FM Hybrid glass reactor (5 plates in series with a liquid holding capacity of 41 mL) at a flow rate of 13.7 mL/min at 85 °C for a residence time of 3 minutes. After passing through the standby pressure valve (0.4 MPa), the sample was collected in a 20 L three-port flask with a condensing tube (-20 °C). The resulting solution was checked by GCMS. As a result, only cyclohexane, chlorocyclohexane and 1,2-bis(trichloromethyl)disulfide were found in the solution.

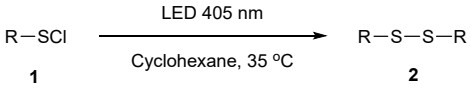
The collected reaction liquid was distilled in vacuo (-0.095 MPa, the temperature gradually increased to 95 °C), and the cyclohexane and chlorocyclohexane were removed to obtain 1410 g bis trichloromethyl disulfide **2a** with a yield of 93.7% and a content of 99.0% (GC area normalization method). The solvent cyclohexane was recovered 7276 g by atmospheric distillation (top temperature 83-85 °C, kettle temperature 100-105 °C) with a purity of 99.6% (GC area normalization method) and in 96.1% recovery. Under vacuum distillation (-0.098 MPa, top temperature 75-80 °C), 1200 g chlorocyclohexane was obtained with a yield of 99.5% and a content of 98.3% (GC area normalization method). Tail gas absorption liquid increased weight by 370 g and the total weight loss during the distillation process was 23 g.

Solvent reuse experiment

Trichloromethyl sulfenyl chloride **1a** (1623 g, 8.6 mol) and recycled cyclohexane from the kilogram-scale synthesis of bis trichloromethyl disulfide in Corning G1 flow reactor (7275 g, 9196 mL) were mixed homogeneously and pumped into a Corning Advanced-Flow G1-10FM Hybrid glass reactor (5 plates in series with a liquid holding capacity of 41 mL) at a flow rate of 13.7 mL/min at 85 °C for a residence time of 3 minutes. After passing through the standby pressure valve (0.4 MPa), the sample was collected in a 20 L three-port flask with a condensing tube (-20 °C).

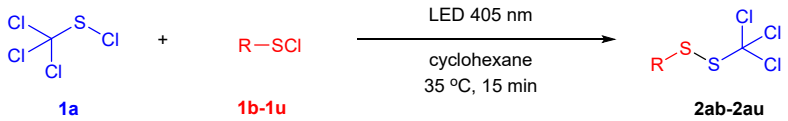
The collected reaction liquid was distilled, and 1228 g bis trichloromethyl disulfide was obtained with a yield of 93.8% and a content of 99.3% after removing cyclohexane and chlorocyclohexane. The solvent cyclohexane was recovered 6320 g by atmospheric distillation (top temperature 83-85 °C, kettle temperature 100-105 °C) with a purity of 99.5% (GC area normalization method) and 96.0% recovery. Under vacuum distillation (-0.098 MPa, top temperature 75-80 °C), 1033 g chlorocyclohexane was obtained with a yield of 99.3% and a content of 98.5% (GC area normalization method). Tail gas absorption liquid increased weight by 310 g and the total weight loss during the distillation process was 7 g.

General procedure for the synthesis of symmetrical disulfides



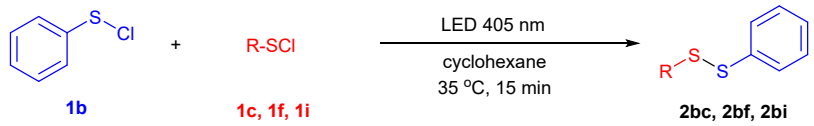
A mixture of compounds **1** (5 mmol) and cyclohexane (5.3 mL) were placed into a 50 mL Photoreactor (NBT) in a nitrogen atmospher, the mixture was allowed to react at 35 °C for 15 minutes. On completion, the solvent was removed by vacuum distillation, and the residue was purified by flash chromatography on silica gel (Petroleum ether/EA) to afford the disulfides **2**.

General procedure for the synthesis of unsymmetrical disulfides with sulfenyl chloride compounds and trichloromethyl sulfenyl chloride



A mixture of sulfenyl chloride compounds **1b-1u** (1 mmol), trichloromethyl sulfenyl chloride **1a** (2 mmol) and cyclohexane (3.3 mL) were placed into a 50 mL photoreactor (NBT) in a nitrogen atmospher, the mixture was allowed to react at 35 °C for 15 minutes. On completion, the solvent was removed in vacuo, and the residue was purified by TLC (thin-layer chromatography) to afford the disulfides **2ab-2au**.

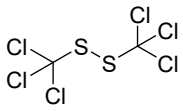
General procedure for the photochemical synthesis of unsymmetrical disulfides from phenyl sulfenyl chloride and aryl sulfenyl chloride



1b **1c, 1f, 1i** **2bc, 2bf, 2bi**

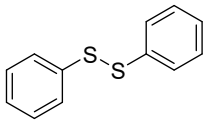
A mixture of aryl sulfenyl chloride compounds **1c, 1f, 1i** (1 mmol), phenyl sulfenyl chloride **1b** (2 mmol) and cyclohexane (3.3 mL) were placed into a 50 mL photoreactor (NBT) in a nitrogen atmospher, the mixture was allowed to react at 35 °C for 15 minutes. On completion, the solvent was removed under reduced pressure, and the residue was purified by TLC (thin-layer chromatography) to afford the corresponding disulfides.

Characterization data of disulfides



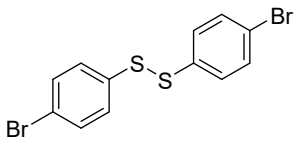
2a

1,2-Bis(trichloromethyl)disulfide (2a) Compound **2a** (colorless liquid) was obtained 700 mg in 93% yield according to the procedure of Synthesis of bis trichloromethyl disulfide in batch photpreactor. ^{13}C NMR (151 MHz, $CDCl_3$) δ 98.41. GC-MS: m/z: 299.8 [M^+].



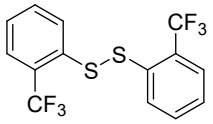
2b

1,2-Bis(phenyl)disulfide (2b) Compound **2b** (white solid, m.p. 61-63 °C) was obtained 373 mg in 73% yield according to the general procedure for the synthesis of symmetrical disulfides (eluent for Thin-layer column chromatography: petroleum ether). ^1H NMR (600 MHz, CDCl3) δ 7.56-7.54 (d, *J*=12.0 Hz, 4H), 7.36-7.33 (t, 4H), 7.28-7.26 (t, 2H). GC-MS: m/z: 218.0 [M^+].



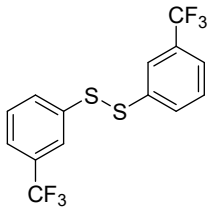
2c

Bis(4-bromophenyl)disulfide (2c) Compound **2c** (yellow solid, m.p. 92-94 °C) was obtained 683 mg in 73% yield according to the general procedure for the synthesis of symmetrical disulfides (eluent for flash column chromatography: n-hexane). ^1H NMR (600 MHz, $CDCl_3$) δ 7.43-7.42 (d, *J*=6.0 Hz, 4H), 7.34-7.33 (d, *J*=6.0 Hz, 4H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 135.88, 132.37, 129.55, 121.69. HRMS (EI-TOF) Calculated ($C_{12}H_8Br_2S_2$) 373.8434 [M^+], Found: 373.8435.



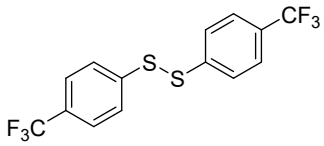
2d

Bis(2-(trifluoromethyl)phenyl)disulfide (2d) Compound **2d** (white solid, m.p. 59-60 °C) was obtained 528 mg in 88% yield according to the general procedure for the synthesis of symmetrical disulfides (eluent for flash column chromatography: petroleum ether) . ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84-7.82 (d, *J*=8.0 Hz, 2H), 7.65-7.63 (d, *J*=8.0 Hz, 2H), 7.51-7.47 (t, 2H), 7.35-7.31 (t, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 132.67, 129.63, 127.31, 126.84, 126.80, 124.87, 122.24. ^{19}F NMR (565 MHz, $CDCl_3$) δ -59.77. HRMS (EI-TOF) Calculated ($C_{14}H_8F_6S_2$) 353.9972 [M^+], Found: 353.9975.



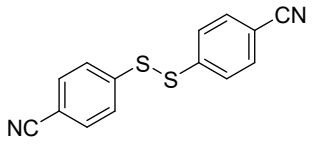
2e

Bis(3-(trifluoromethyl)phenyl)disulfide (2e) Compound **2e** (white solid, m.p. > 250 °C) was obtained 850 mg in 96% yield according to the general procedure for the synthesis of symmetrical disulfides (eluent for flash column chromatography:petroleum ether). ^{1}H NMR (400MHz, $CDCl_3$) δ 7.75 (s, 2H), 7.67 (d, *J*=7.8 Hz, 2H), 7.38 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 137.92, 132.06, 131.73, 130.86, 129.87, 124.48, 122.36. ^{19}F NMR (565 MHz, $CDCl_3$) δ -62.91. HRMS(EI-TOF) Calculated ($C_{14}H_8F_6S_2$)353.9972 [M^+], Found:353.9969.



2f

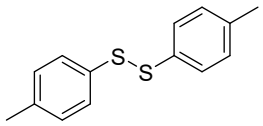
Bis(4-(trifluoromethyl)phenyl)disulfide (2f) Compound **2f** (white solid, m.p. 119-120 °C) was obtained 810 mg in 91% yield according to the general procedure for the synthesis of symmetrical disulfides (eluent for flash column chromatography: petroleum ether:ethyl acetate=8:2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55-7.42 (m, 8H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 140.96, 129.91, 129.70, 129.48, 129.26, 126.74, 126.30, 126.27, 126.25, 124.90, 123.10, 121.29. ^{19}F NMR (565 MHz, $CDCl_3$) δ -62.59. HRMS (EI-TOF) Calculated ($C_{14}H_8F_6S_2$) 353.9972[M^+], Found: 353.9970.



2g

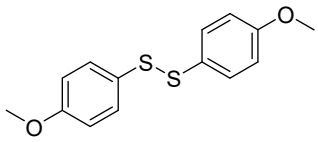
4,4'-Dithiobis(benzonitrile) (2g) Compound **2g** (white solid, m.p. 171-173 °C) was obtained 540 mg in 81% yield according to the general procedure for the synthesis of symmetrical disulfides (eluent for flash column

chromatography:petroleum ether) .^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54-7.61 (m, 8H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 142.12, 132.83, 126.50, 118.24, 110.88. HRMS (EI-TOF) Calculated ($C_{14}H_8N_2S_2$) 268.0129 [M^+], Found: 268.0126.



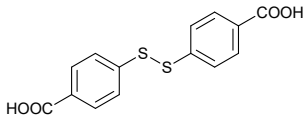
2i

Bis(4-methylphenyl)disulfide (2i) Compound **2i** (purple solid, m.p. 47-48 °C) was obtained 330 mg in 53% yield according to the general procedure for the synthesis of symmetrical disulfides (eluent for flash column chromatography: petroleum ether). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 (dd, *J*=8.4, 2.0 Hz, 4H), 7.10 (m, 4H), 2.32 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 137.48, 133.89, 129.83, 128.53, 21.10. HRMS (EI-TOF) Calculated ($C_{14}H_{14}S_2$) 246.0537 [M^+], Found: 246.0539.



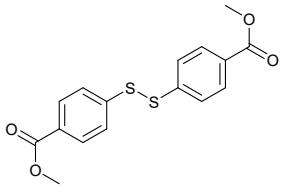
2j

1,2-bis(4-methoxyphenyl)disulfide (2j) Compound **2j** (yellow solid, m.p. 47-48 °C) was obtained 314 mg in 45% yield according to the general procedure for the synthesis of symmetrical disulfides (eluent for flash column chromatography:petroleum ether: ethyl acetate=5:1). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.42-7.40 (d, *J*=12.0 Hz, 4H), 6.85-6.83 (d, *J*=12.0 Hz, 4H), 3.80 (s, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 160.02, 132.76, 128.53, 114.72, 55.46. EI-MS: m/z: 278.0 [M^+].



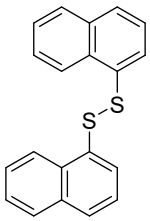
2k

4,4'-disulfanediyldibenzoic acid (2k)[2] Compound **2k** (white solid, m.p. > 250 °C) was obtained 121 mg in 79% yield according to the general procedure for the synthesis of symmetrical disulfides. after reaction, water (500 mg) was added to quench the solution and white solid was filtrated and dried. ^{1}H NMR (400 MHz, MeOD) δ 8.00-7.98(d, *J*=8 Hz, 4H), 7.62-7.60 (d, *J*=8 Hz, 4H). ^{13}C NMR (101 MHz, MeOD) δ 167.72, 141.96, 131.59, 130.89, 127.24.



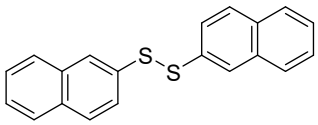
2l

Dimethyl 4,4'-disulfanediyldibenzoate (2l)[3] Compound **2l** (white solid, m.p. 117-118 °C) was obtained 30 mg in 31% yield according to the general procedure for the synthesis of symmetrical disulfides (eluent for flash column chromatography: petroleum ether). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97-7.95 (d, *J*=8 Hz, 4H), 7.53-7.51 (d, *J*=8 Hz, 4H), 3.89(s, 6H). ^{13}C NMR (101 MHz, CDCl3) δ 166.55, 142.27, 130.44, 129.01, 126.16, 52.33.



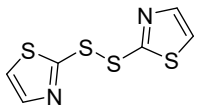
2n

Bis(1-Naphthyl)disulfide (2n) Compound **2n** (white solid, m.p. 71-72 °C) was obtained 550 mg in 71% yield according to the general procedure for the synthesis of symmetrical disulfides (eluent for flash column chromatography: petroleum ether: ethyl acetate=9:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.36-8.33 (m, 2H), 7.89-7.85 (m, 2H), 7.80 (d, *J*=8 Hz, 2H), 7.63-7.61 (m, 2H), 7.54-7.50 (m, 4H), 7.33-7.29 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 134.13, 133.43, 132.76, 130.34, 129.35, 128.61, 126.72, 126.41, 125.48, 125.15. HRMS (EI-TOF) Calculated ($C_{20}H_{14}S_2$) 318.0537 [M^+], Found: 318.0540.



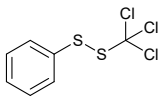
2o

Bis(2-Naphthyl)disulfide (2o) Compound **2o** (white solid, m.p. 138-140 °C) was obtained 570 mg in 72% yield according to the general procedure for the synthesis of symmetrical disulfides (eluent for flash column chromatography: petroleum ether). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (d, *J*=1.7 Hz, 1H), 7.81-7.78 (m, 2H), 7.75-7.73 (m, 1H), 7.64 (dd, *J*=8.7, 1.9Hz, 1H), 7.50-7.43 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 134.29, 133.51, 132.53, 129.02, 127.81, 127.51, 126.78, 126.57, 126.28, 125.69. HRMS (EI-TOF) Calculated ($C_{20}H_{14}S_2$) 318.0537 [M^+], Found: 318.0534.



2p

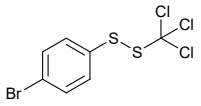
2,2'-Dithiobis(thiazole) (2p) Compound **2p** (green solid, m.p. 177-178 °C) was obtained 350 mg in 60% yield according to the general procedure for the synthesis of symmetrical disulfides (eluent for flash column chromatography: petroleum ether : ethyl acetate=6:4). ^{1}H NMR (400 MHz, $CDCl_3$) δ7.72 (d, *J*=4 Hz, 2H), 7.35 (d, *J*=4Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.71, 144.35, 122.58. HRMS (EI-TOF) Calculated ($C_6H_4N_2S_4$) 231.9257 [M^+], Found:231.9259.



2ab

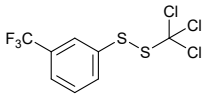
1-phenyl-2-(trichloromethyl)disulfide (2ab) Compound **2ab** (colorless oil) was obtained 127 mg in 49% yield according to the general procedure for the synthesis of unsymmetrical disulfides with sulfenyl chloride

compounds and trichloromethyl sulfenyl chloride (eluent for thin-layer chromatography (TLC): petroleum ether). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66-7.64 (d, *J*=8 Hz, 2H), 7.36 (t, 3H). ^{13}C NMR (101 MHz, CDCl3) δ 135.03, 129.89, 129.38, 128.73, 100.71. HRMS (EI-TOF) Calculated ($C_7H_5Cl_3S_2$) 257.8898 [M^+], Found: 257.8900.



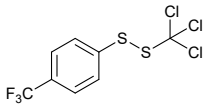
2ac

1-(4-bromophenyl)-2-(trichloromethyl)disulfide (2ac) Compound **2ac** (yellow oil) was obtained 160 mg in 47% yield according to the general procedure for the synthesis of unsymmetrical disulfides with sulfenyl chloride compounds and trichloromethyl sulfenyl chloride (eluent for thin-layer chromatography (TLC): petroleum ether). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.53-7.49 (m, 4H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 134.21, 132.51, 131.35, 123.06, 100.52. HRMS (EI-TOF) Calculated ($C_7H_4BrCl_3S_2$) 335.8003 [M^+], Found: 335.8001.



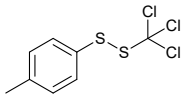
2ae

1-(trichloromethyl)-2-(3-(trifluoromethyl)phenyl)disulfide (2ae) Compound **2ae** (yellow oil) was obtained 170 mg in 52% yield according to the general procedure for the synthesis of unsymmetrical disulfides with sulfenyl chloride compounds and trichloromethyl sulfenyl chloride (eluent for thin-layer chromatography (TLC): petroleum ether). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52-7.48 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 136.49, 132.33, 129.86, 125.98, 125.94, 125.36, 125.32,100.42. ^{19}F NMR (565 MHz, CDCl3) δ -62.81. HRMS (EI-TOF) Calculated ($C_8H_4Cl_3F_3S_2$) 325.8772 [M^+], Found: 325.8770.



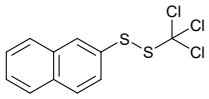
2af

1-(trichloromethyl)-2-(4-(trifluoromethyl)phenyl)disulfide (2af) Compound **2af** (yellow oil) was obtained 167 mg in 51% yield according to the general procedure for the synthesis of unsymmetrical disulfides with sulfenyl chloride compounds and trichloromethyl sulfenyl chloride (eluent for thin-layer chromatography (TLC): petroleum ether). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.77-7.76 (d, *J*=6.0 Hz, 2H), 7.65-7.63 (d, *J*=12.0 Hz, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 139.70, 130.64, 128.49, 126.29, 125.26, 100.41. ^{19}F NMR (565 MHz, CDCl3) δ -62.67. HRMS (EI-TOF) Calculated ($C_8H_4Cl_3F_3S_2$) 325.8772[M^+], Found: 325.8770.



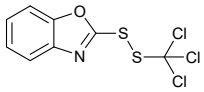
2ai

1-(p-tolyl)-2-(trichloromethyl)disulfide (2ai) Compound **2ai** (yellow oil) was obtained 114mg in 35% yield. After washed with 10% NaoH(aq) 5 mL*2, according to the general procedure for the synthesis of unsymmetrical disulfides with sulfenyl chloride compounds and trichloromethyl sulfenyl chloride (eluent for thin-layer chromatography (TLC): petroleum ether). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55-7.53 (d, *J*=8 Hz, 2H), 7.18-7.16 (d, *J*=8 Hz, 2H), 2.36 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 139.18, 131.45, 130.69, 130.01, 100.64, 21.21. HRMS (EI-TOF) Calculated ($C_8H_7Cl_3S_2$) 271.9055[M^+], Found: 271.9058.



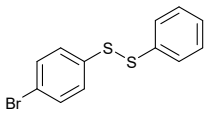
2ao

1-(naphthalen-2-yl)-2-(trichloromethyl)disulfide (2ao) Compound **2ao** (yellow oil) was obtained **140 mg** in 45% yield according to the general procedure for the synthesis of unsymmetrical disulfides with sulfenyl chloride compounds and trichloromethyl sulfenyl chloride (eluent for thin-layer chromatography (TLC): petroleum ether). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.27 (m, 1H), 7.90 (m, 1H), 7.80 (m, 3H), 7.64 (m, 1H), 7.56 (m, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 133.49, 133.16, 132.16, 129.35, 129.32, 128.01, 127.89, 127.16, 127.12, 126.84, 100.75. HRMS (EI-TOF) Calculated ($C_{11}H_7Cl_3S_2$) 307.9055 [M^+], Found: 307.9056.



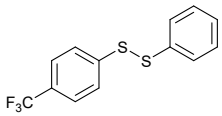
2au

2-((trichloromethyl)disulfaneyl)benzo[d]oxazole (2au) Compound **2au** (yellow oil) was obtained 113 mg in 39% yield according to the general procedure for the synthesis of unsymmetrical disulfides with sulfenyl chloride compounds and trichloromethyl sulfenyl chloride (eluent for thin-layer chromatography (TLC): petroleum ether). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.73-7.71 (m, 1H), 7.56-7.54 (m, 1H), 7.38-7.35 (m, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 159.29, 152.38, 141.99, 125.83, 125.21, 120.12, 110.77, 99.29. HRMS (EI-TOF) Calculated ($C_8H_4Cl_3NS_2$)298.8800 [M^+], Found: 298.8799.



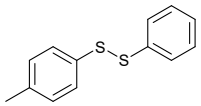
2bc

1-(4-bromophenyl)-2-phenyldisulfide **(2bc)** Compound **2bc** (white solid, m.p. 220-222 °C) was obtained **150 mg** in 50% yield according to the general procedure for the photochemical synthesis of unsymmetrical disulfides from phenyl sulfenyl chloride and aryl sulfenyl chloride (eluent for thin-layer chromatography (TLC): petroleum ether). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 (d, *J*=8Hz, 2H), 7.40 (d, *J*=8Hz, 2H), 7.30 (m, 2H), 7.24 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 136.56, 136.47, 133.55, 131.98, 129.22, 127.71, 127.32, 121.10. HRMS (EI-TOF) Calculated ($C_{12}H_9BrS_2$) 295.9329 [M^+],Found: 295.9332.



2bf

1-phenyl-2-(4-(trifluoromethyl)phenyl)disulfide (2bf) Compound **2bf** (colorless oil) was obtained 198 mg in 43% yield according to the general procedure for the photochemical synthesis of unsymmetrical disulfides from phenyl sulfenyl chloride and aryl sulfenyl chloride (eluent for thin-layer chromatography (TLC): petroleum ether). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.64-7.57(m, 9H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 140.96, 136.18, 129.70, 129.42, 127.74, 126.74, 126.66, 126.29, 126.27. ^{19}F NMR (565 MHz, $CDCl_3$) δ -62.58. HRMS (EI-TOF) Calculated ($C_{13}H_9Cl_3S_2$) 286.0098 [M^+], Found: 286.0096.



2bi

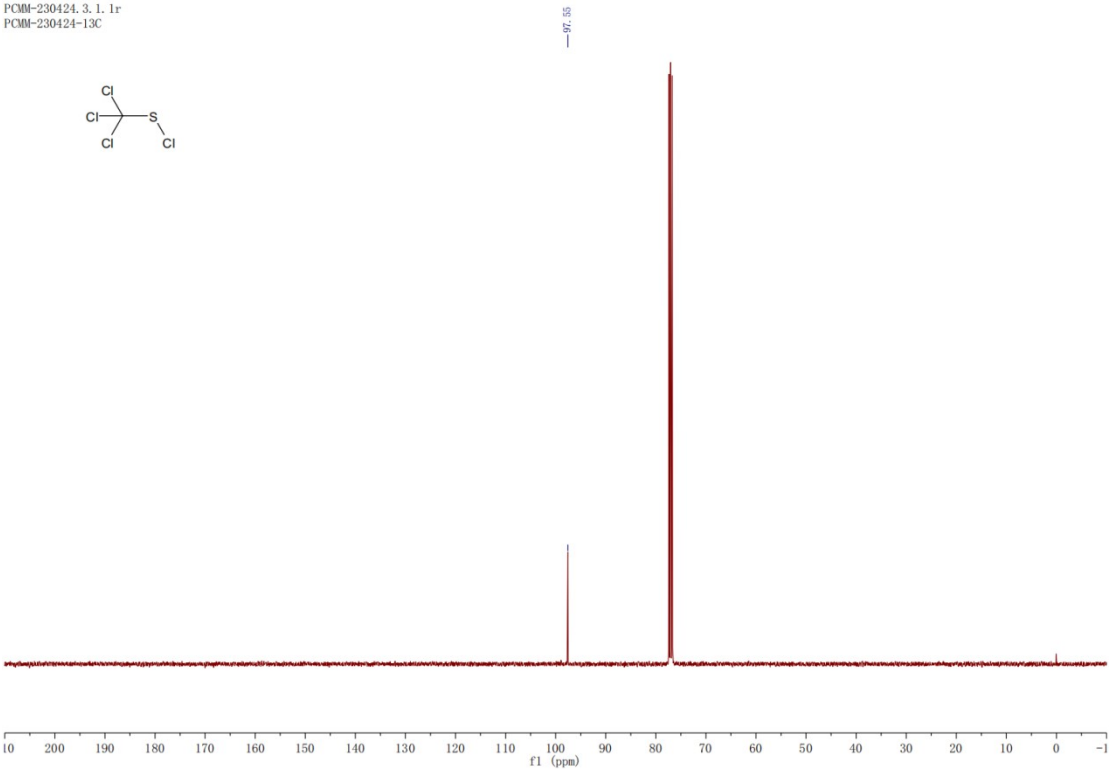
1-phenyl-2-(p-tolyl)disulfide (2bi) Compound **2bi** (colorless oil) was obtained **210 mg** in 40% yield according to the general procedure for the photochemical synthesis of unsymmetrical disulfides from phenyl sulfenyl chloride and aryl sulfenyl chloride (eluent for thin-layer chromatography (TLC): petroleum ether). Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 (m, 2H), 7.37 (m, 2H), 7.30 (m,2H), 7.24 (m,1H), 7.11(m,2H), 2.33 (s, 3H). HRMS (EI-TOF) Calculated ($C_{13}H_{12}S_2$) 232.0380 [M^+], Found: 232.0382.

References

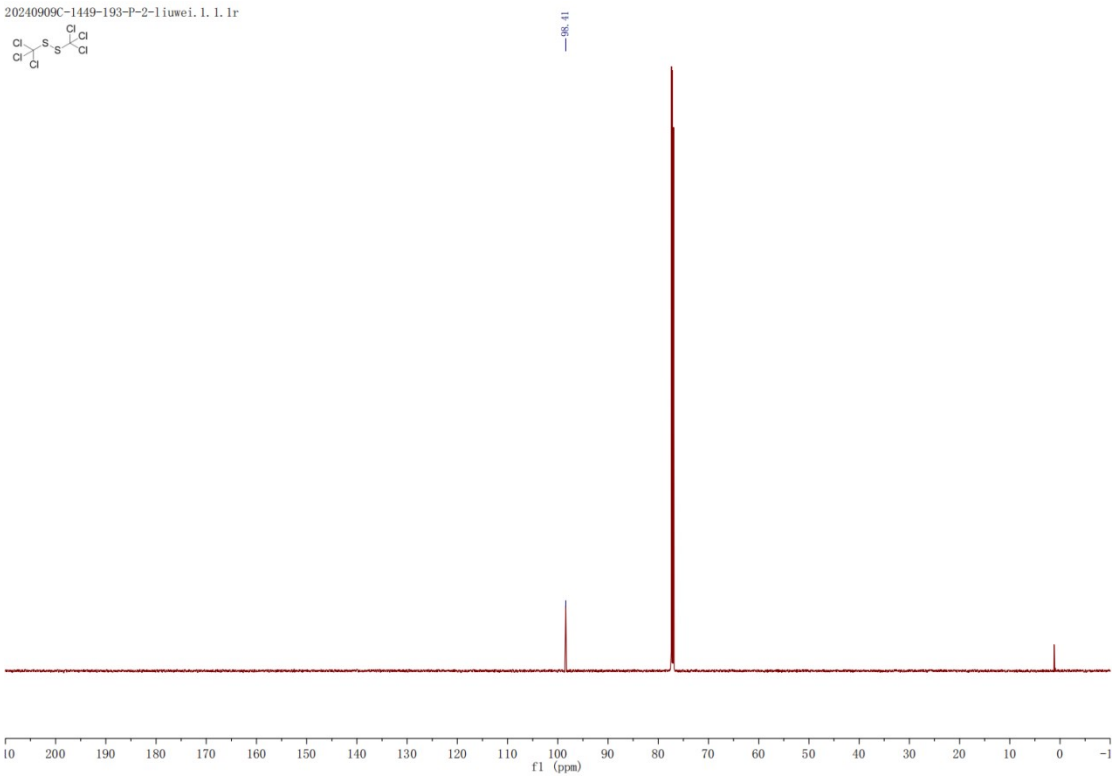
1. D. Q. Cai, R. L. Wang, G. H. Wu, F. C. Jia and H. X. Liu. A device and method for preparation of trichloromethyl sulfenyl chloride. CN201210101219.

NMR spectra

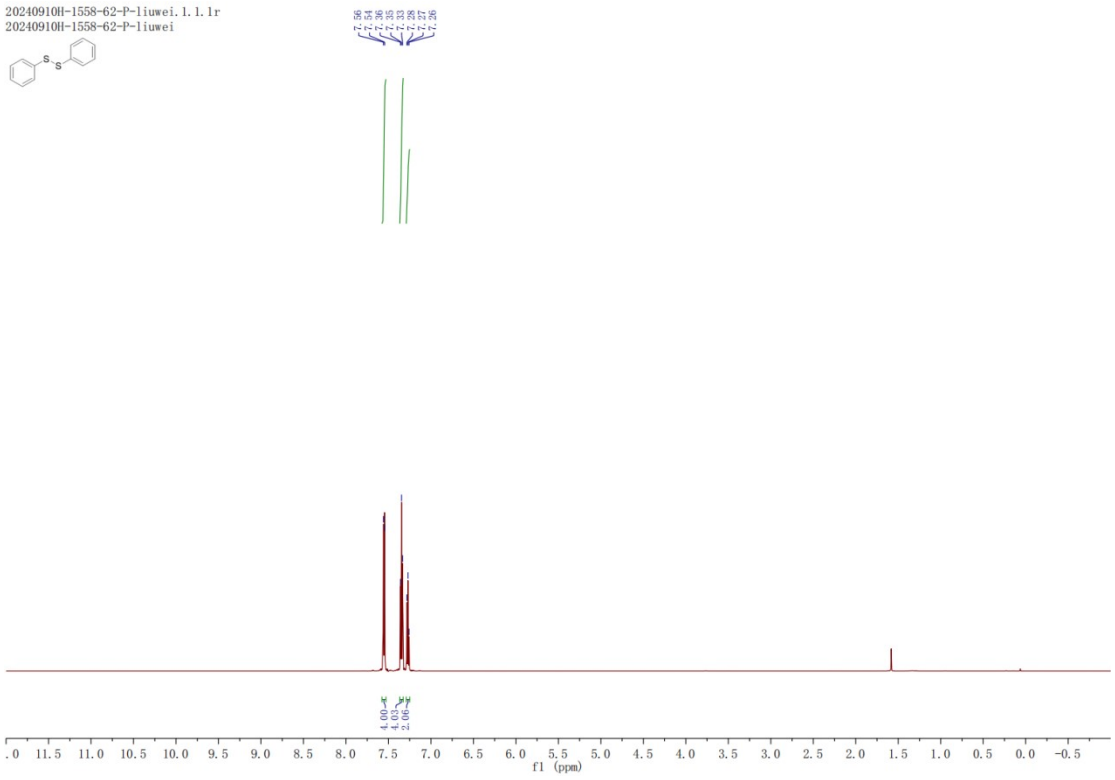
^{13}CNMR spectra of **1a**



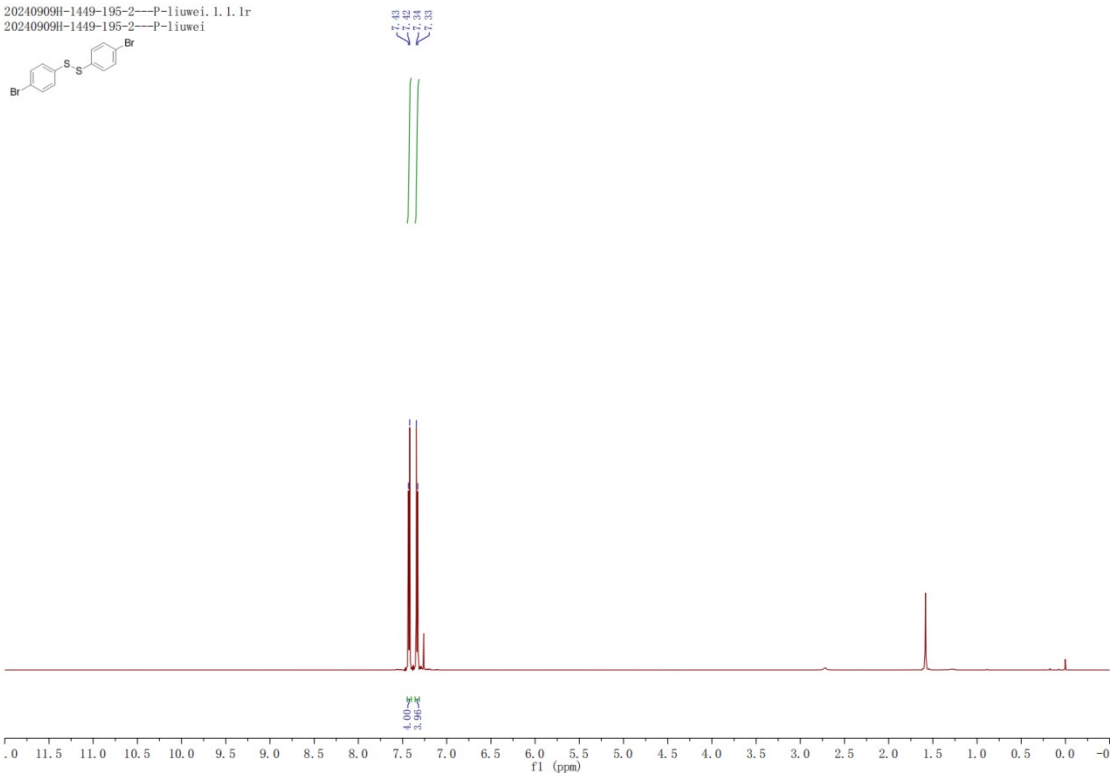
^{13}CNMR spectra of **2a**



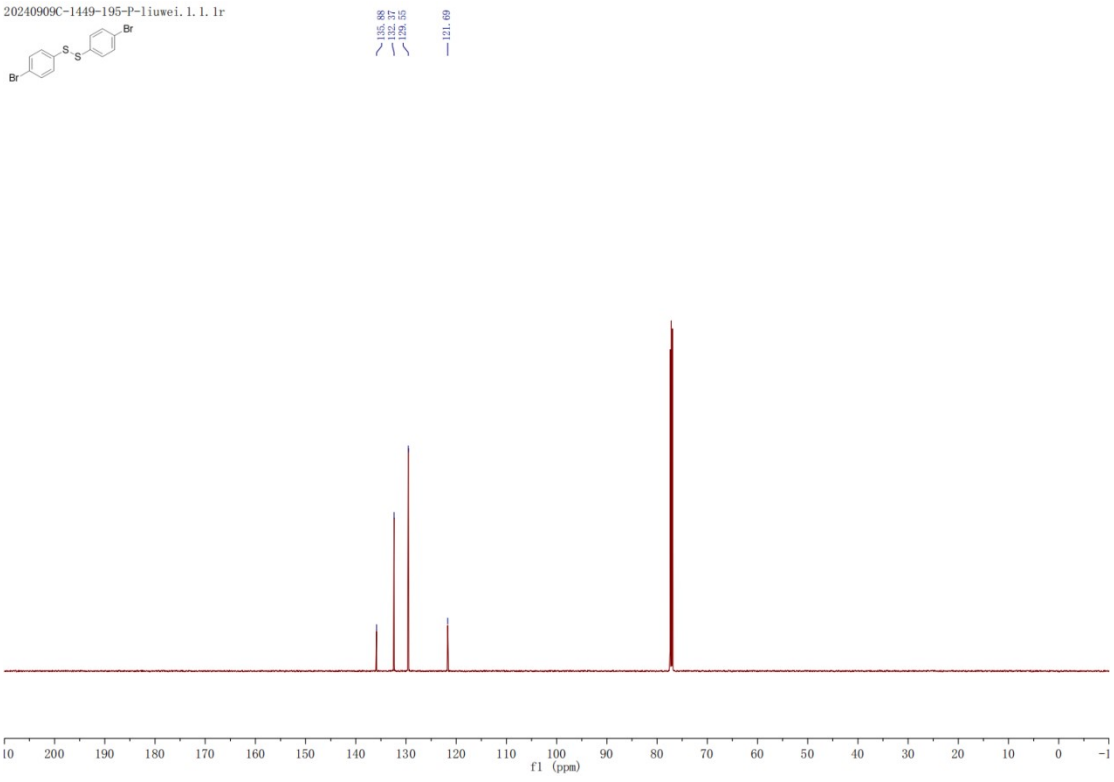
^{1}HNMR spectrum of **2b**



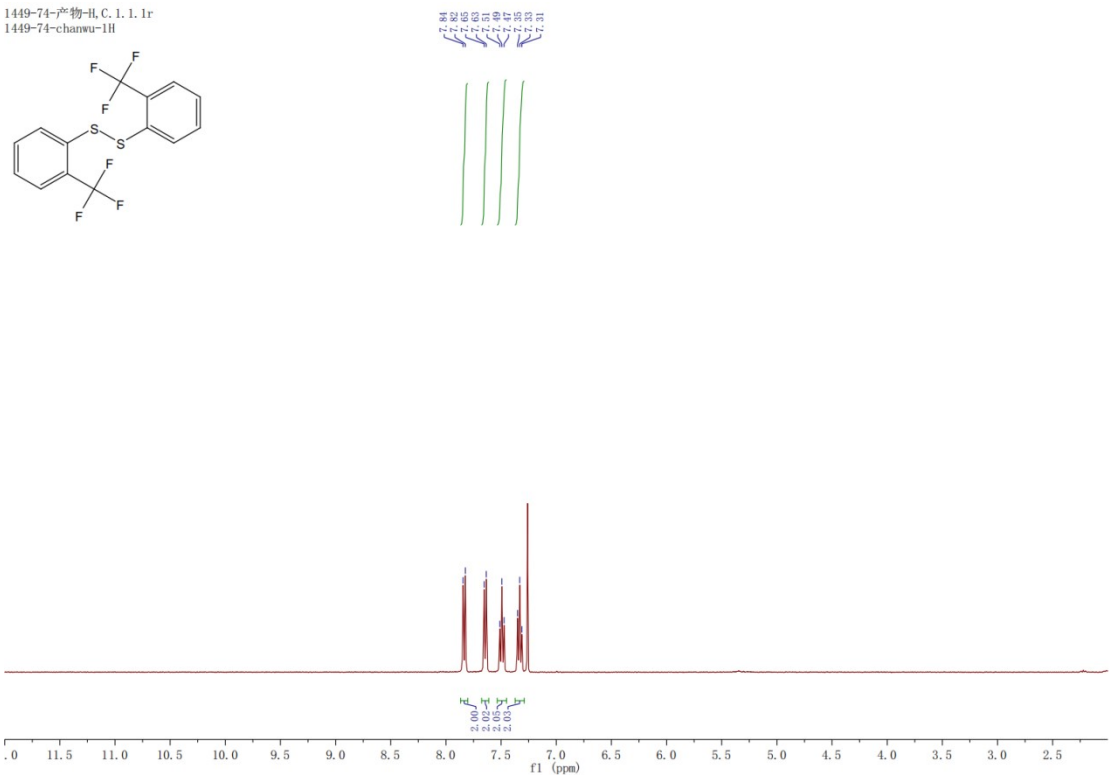
^{1}HNMR spectrum of **2c**



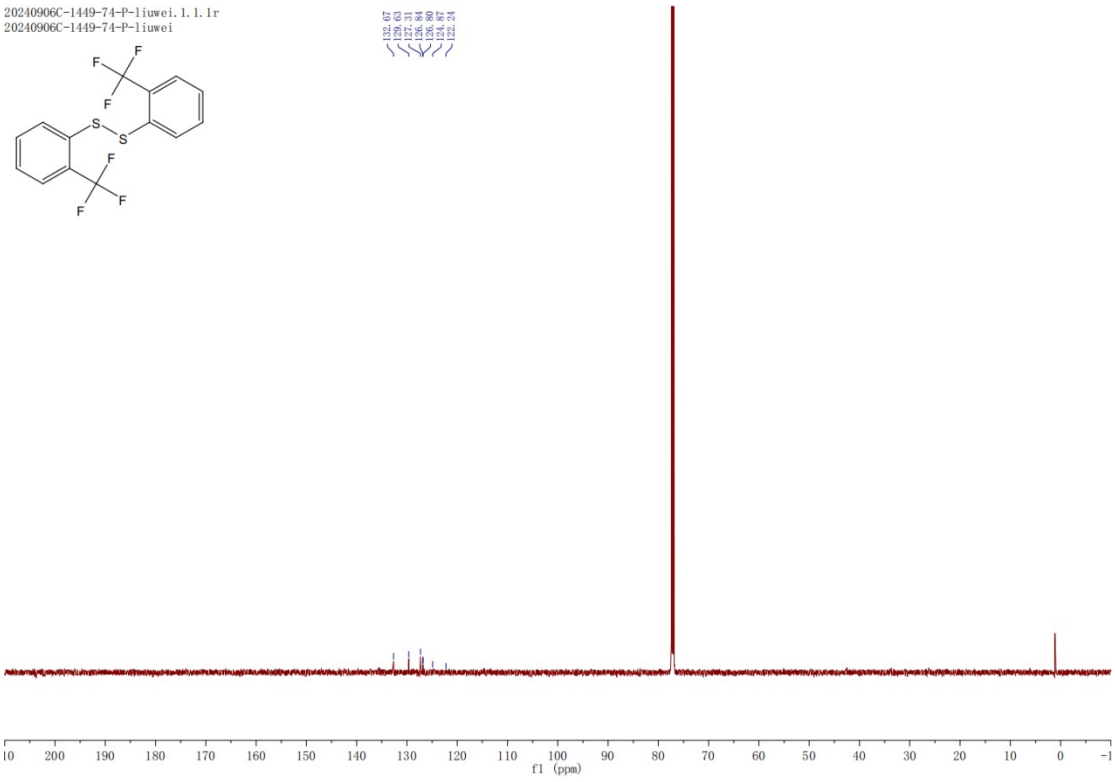
^{13}CNMR spectrum of **2c**



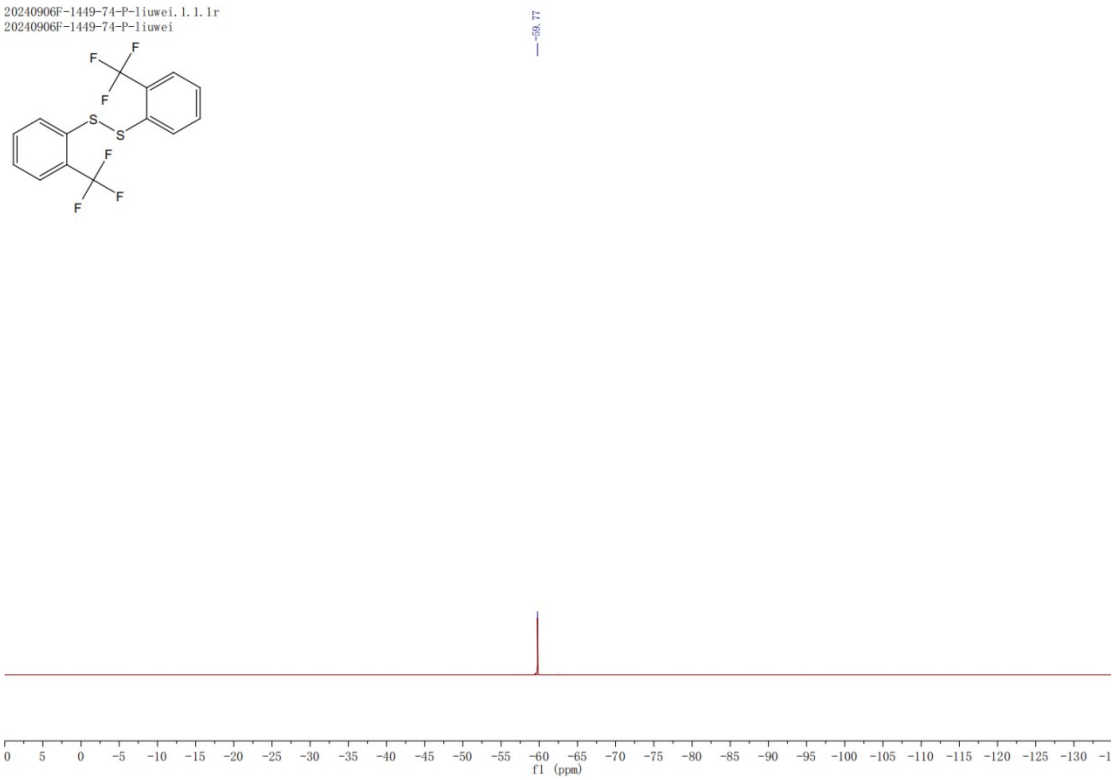
^{1}HNMR spectrum of **2d**



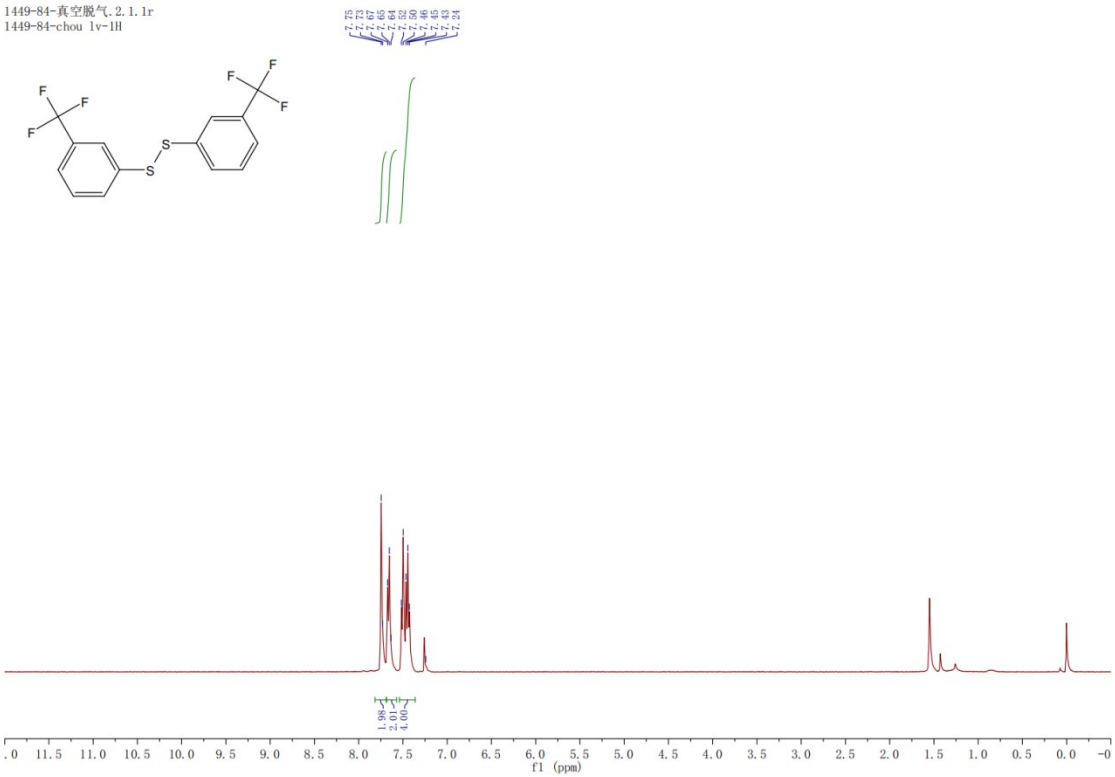
^{13}CNMR spectrum of **2d**



^{19}FNMR spectrum of **2d**



^{1}HNMR spectra of **2e**



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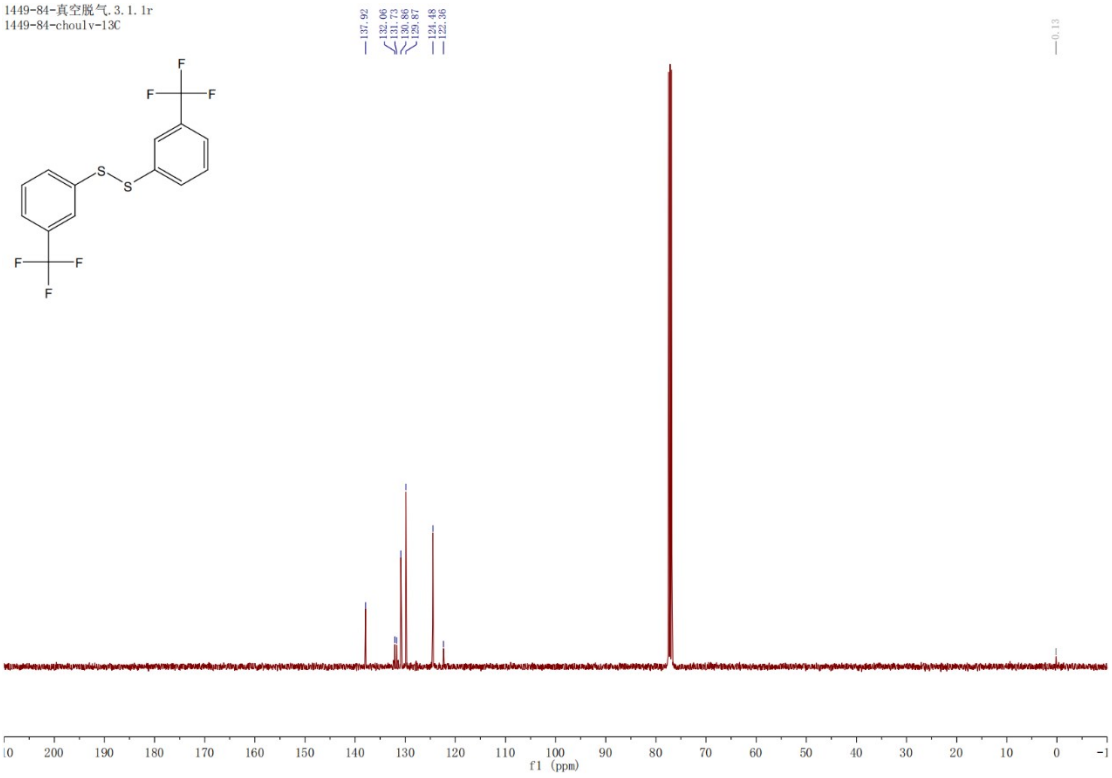
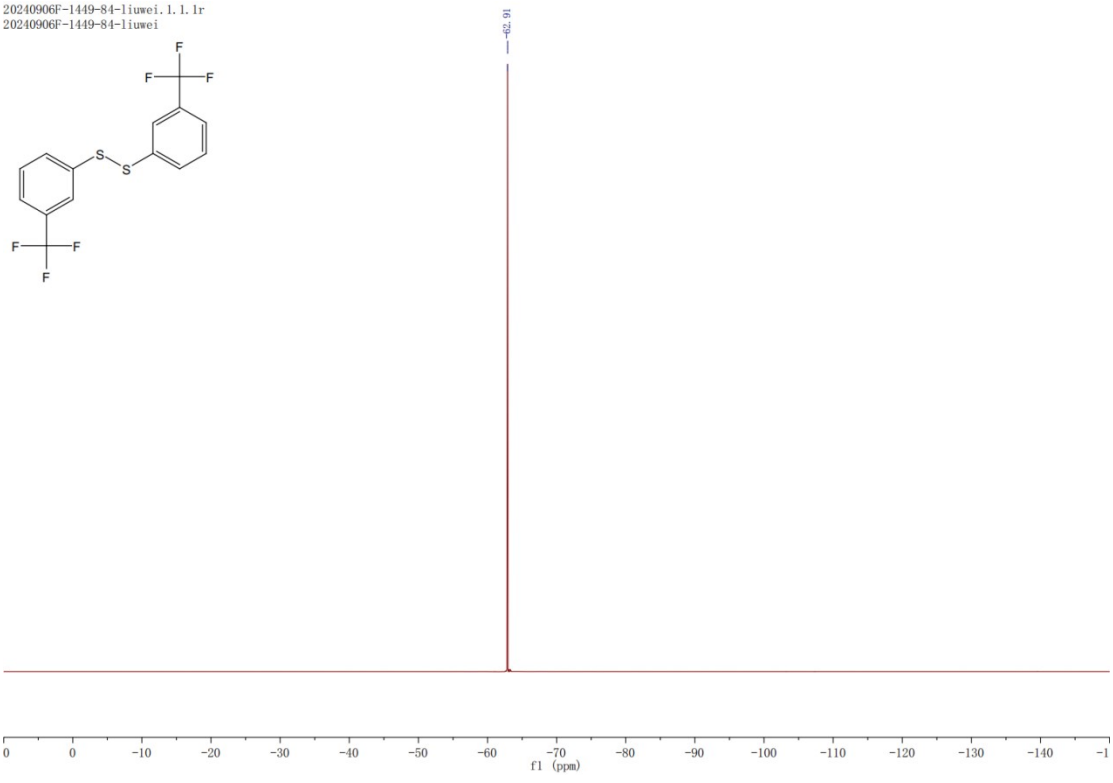
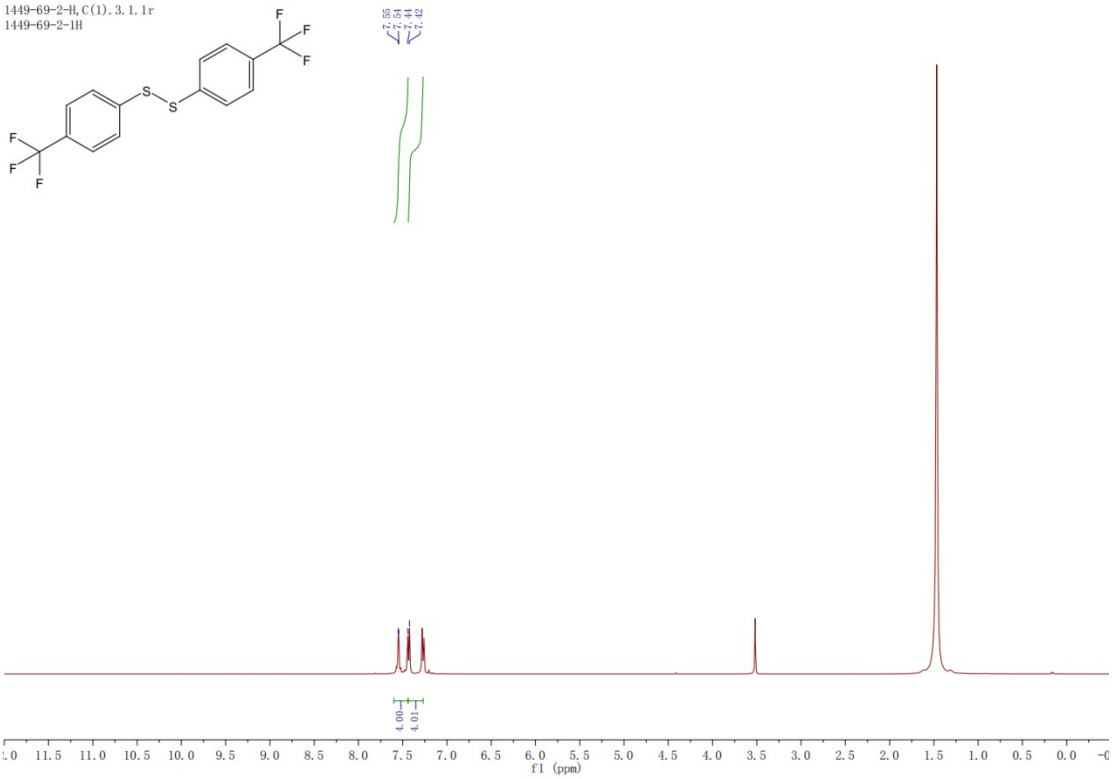


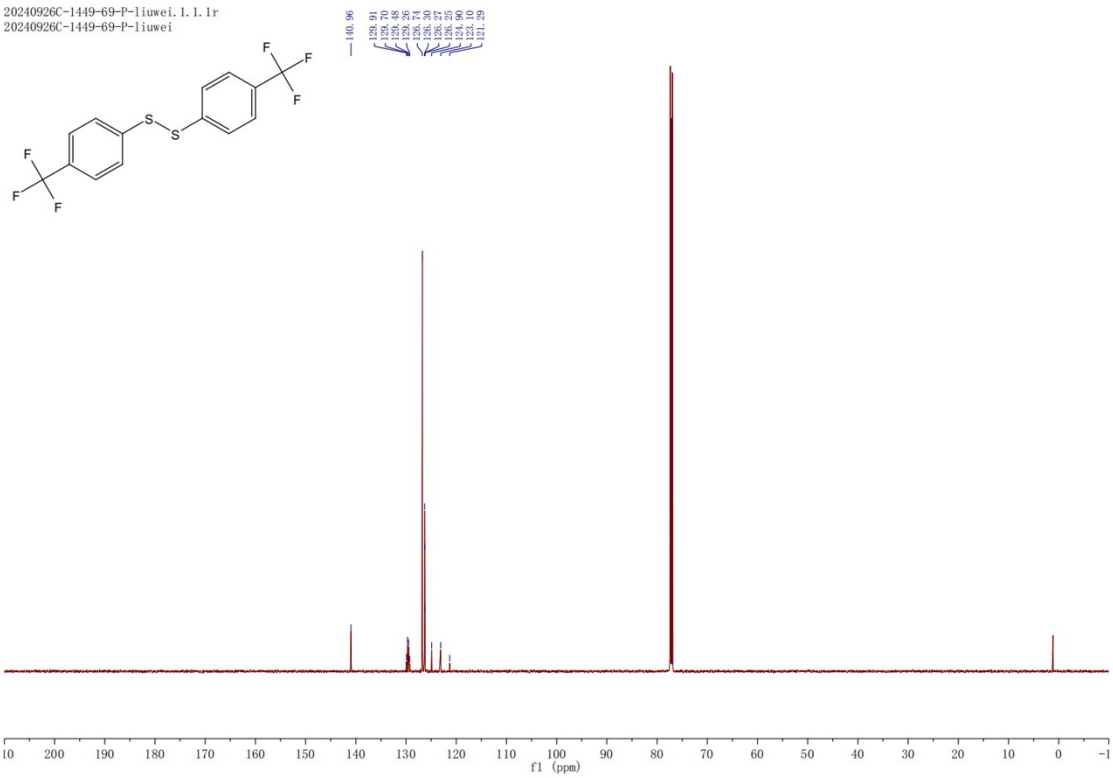
^{19}FNMR spectra of **2e**



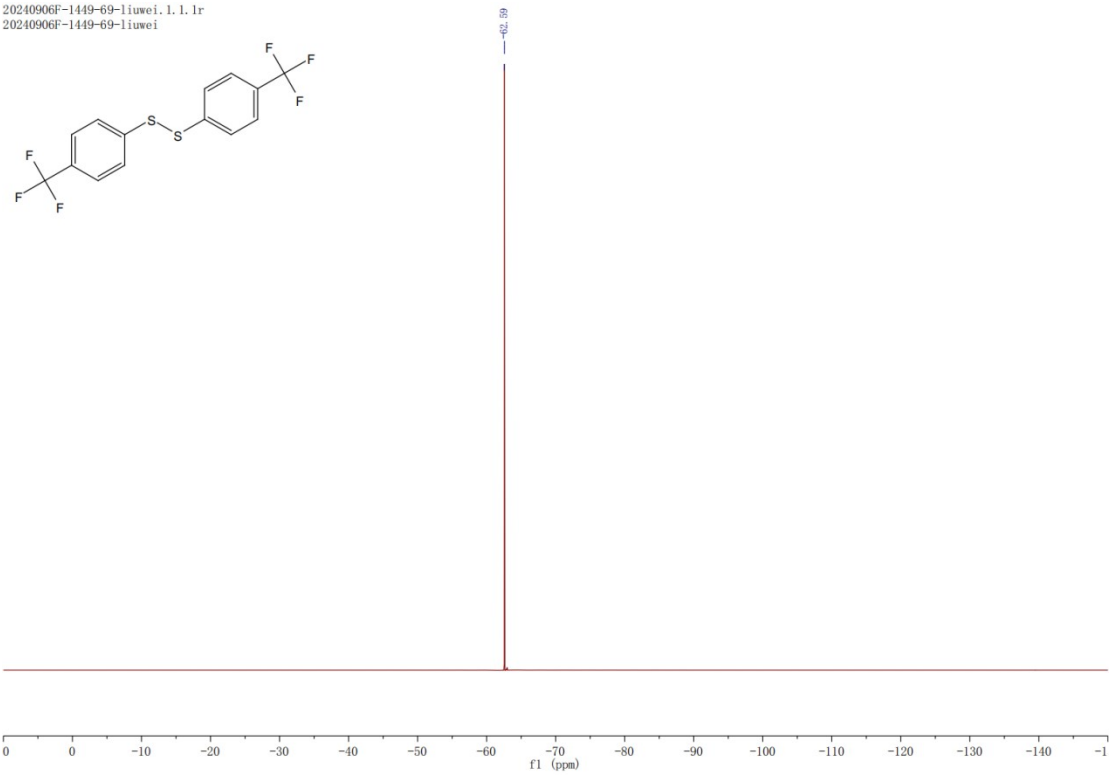
^{1}HNMR spectrum of **2f**



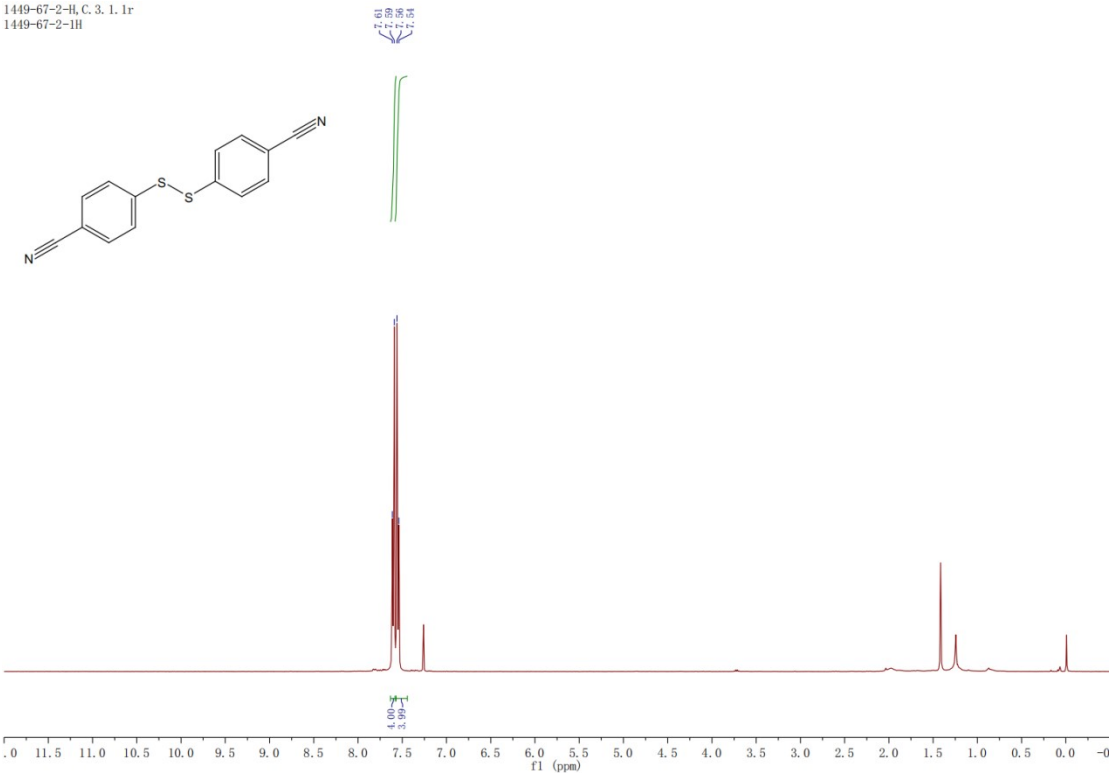
^{13}CNMR spectrum of **2f**



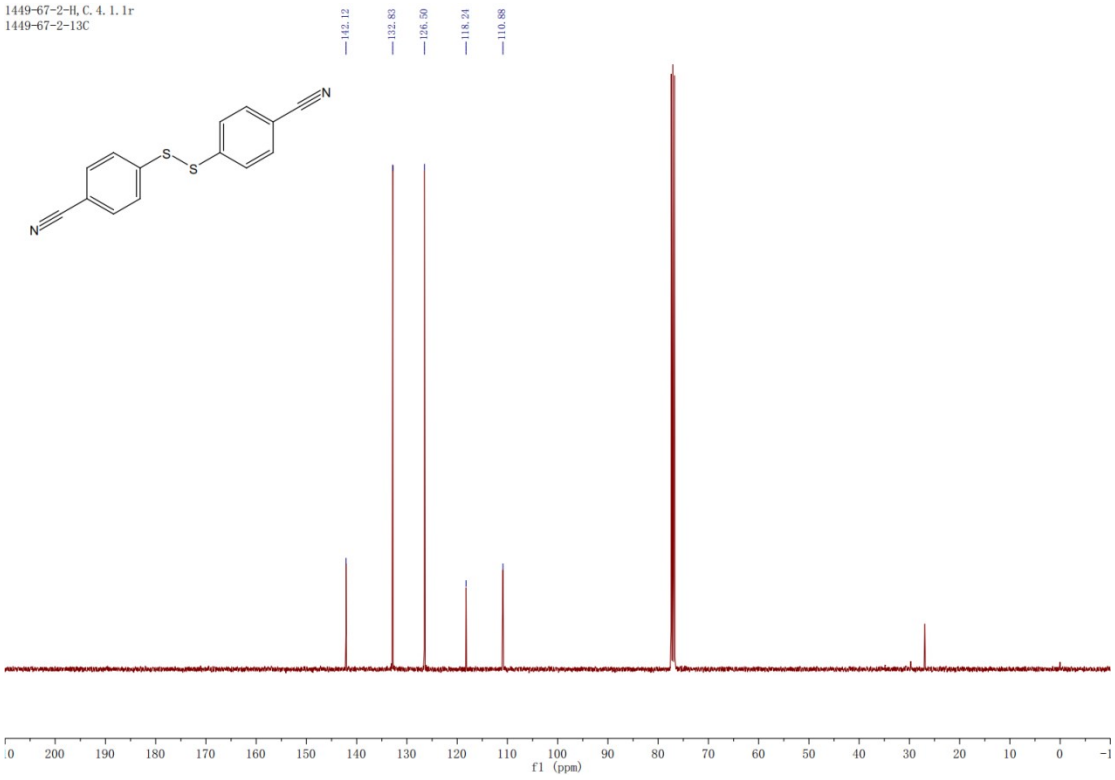
^{19}FNMR spectrum of **2f**



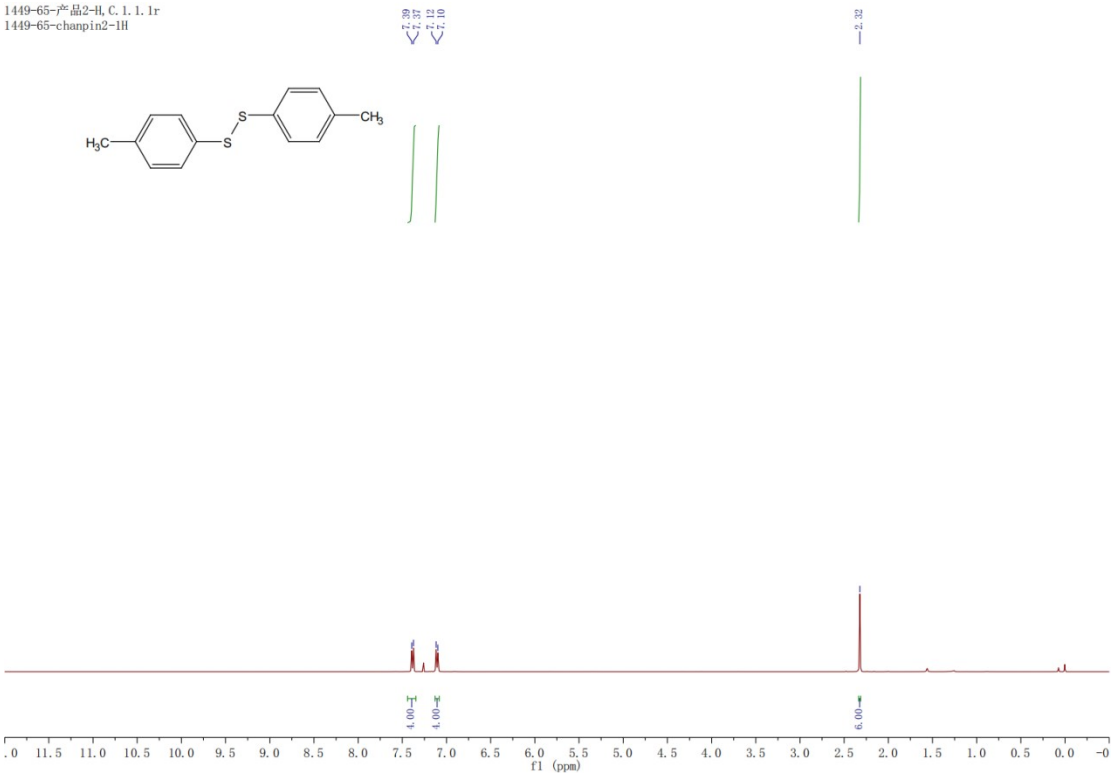
[1]HNMR spectra of **2g**



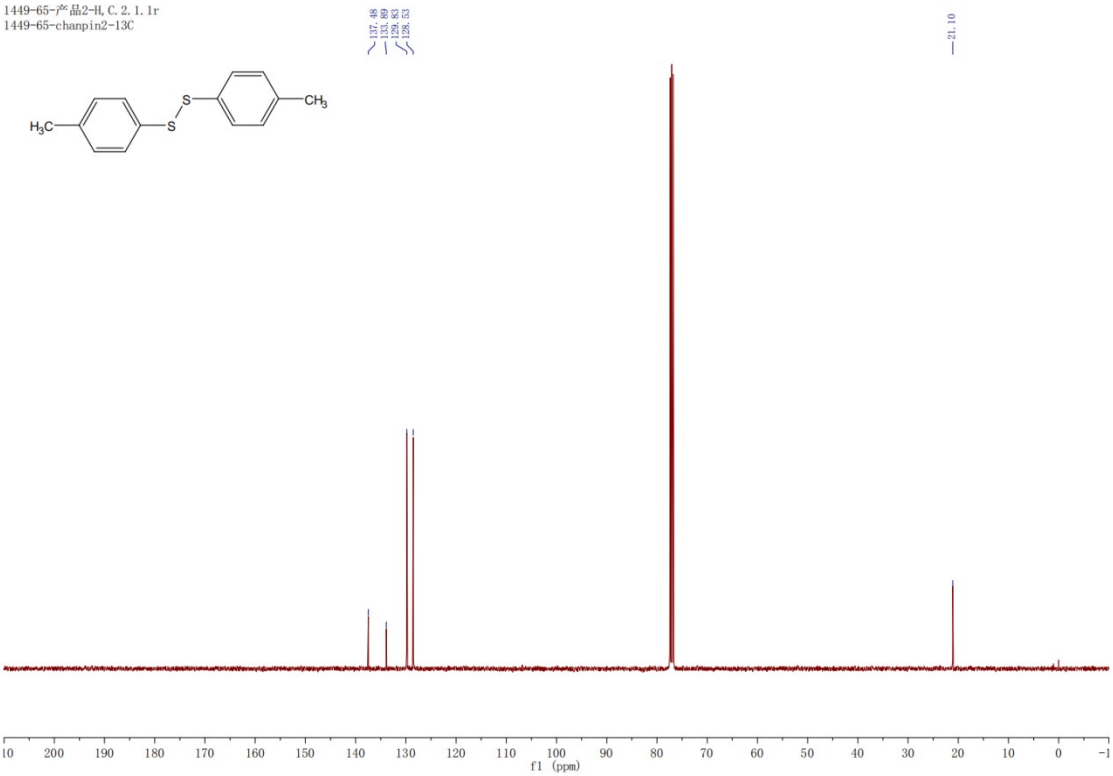
^{13}CNMR spectra of **2g**



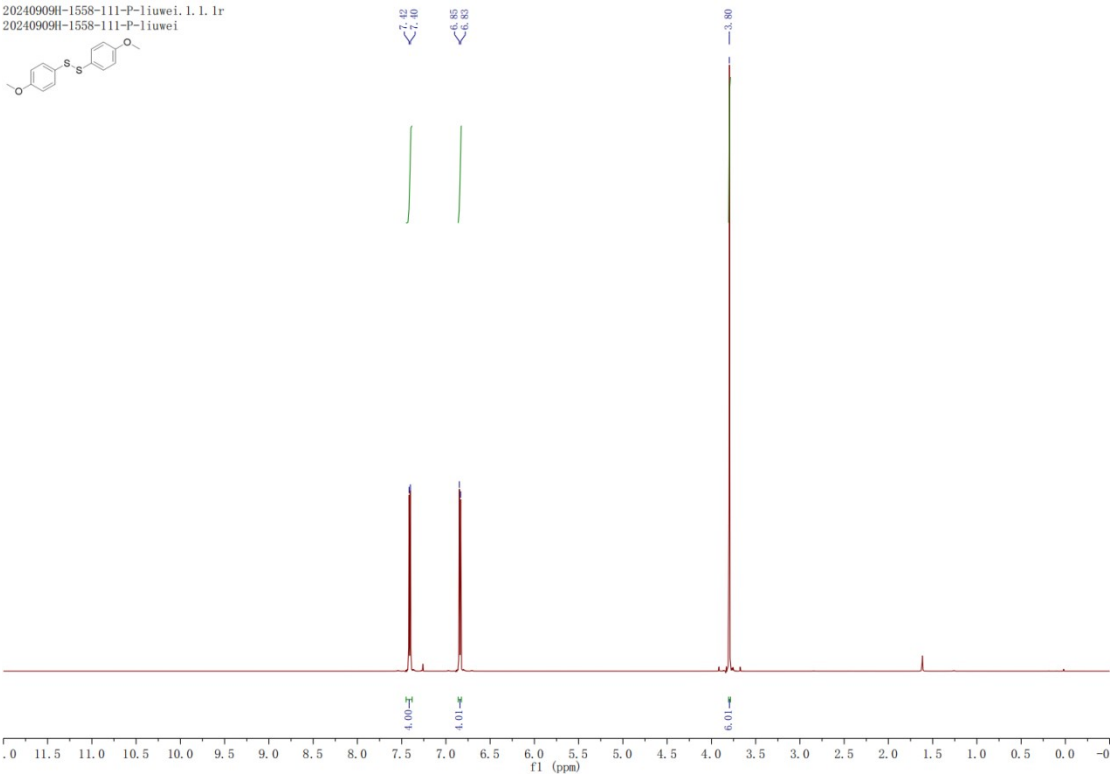
^{1}HNMR spectrum of **2i**



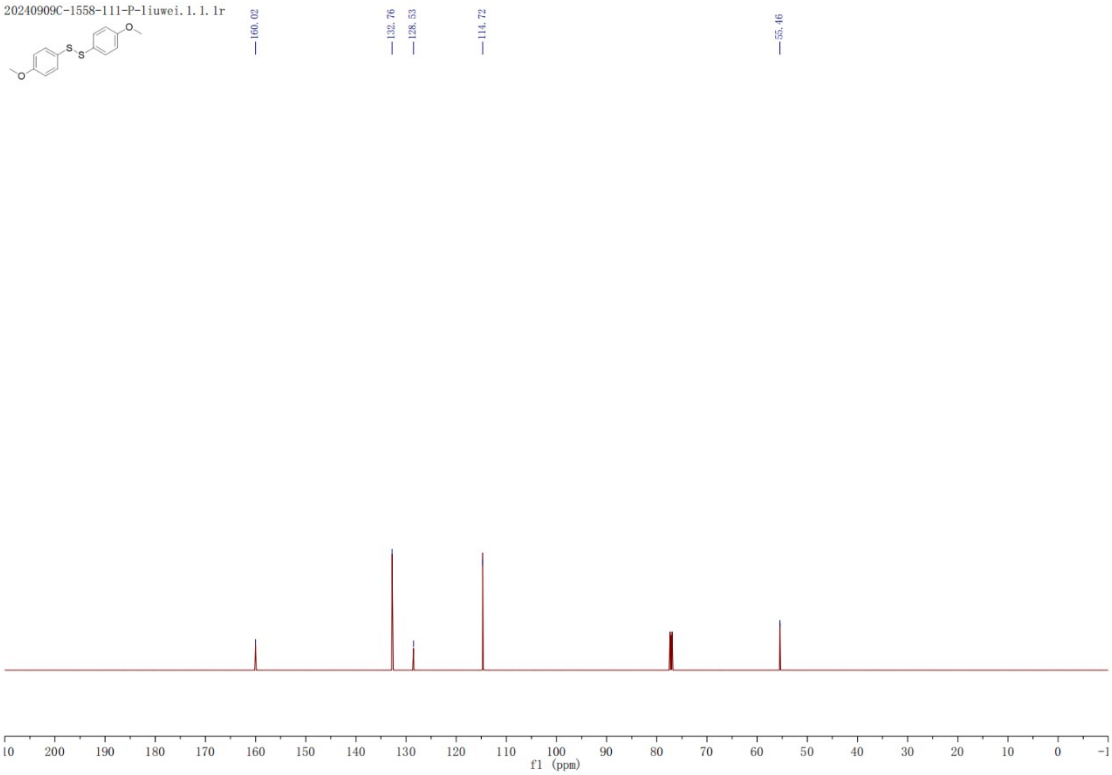
^{13}CNMR spectrum of **2i**



^{1}HNMR spectrum of **2j**



^{13}CNMR spectrum of **2j**



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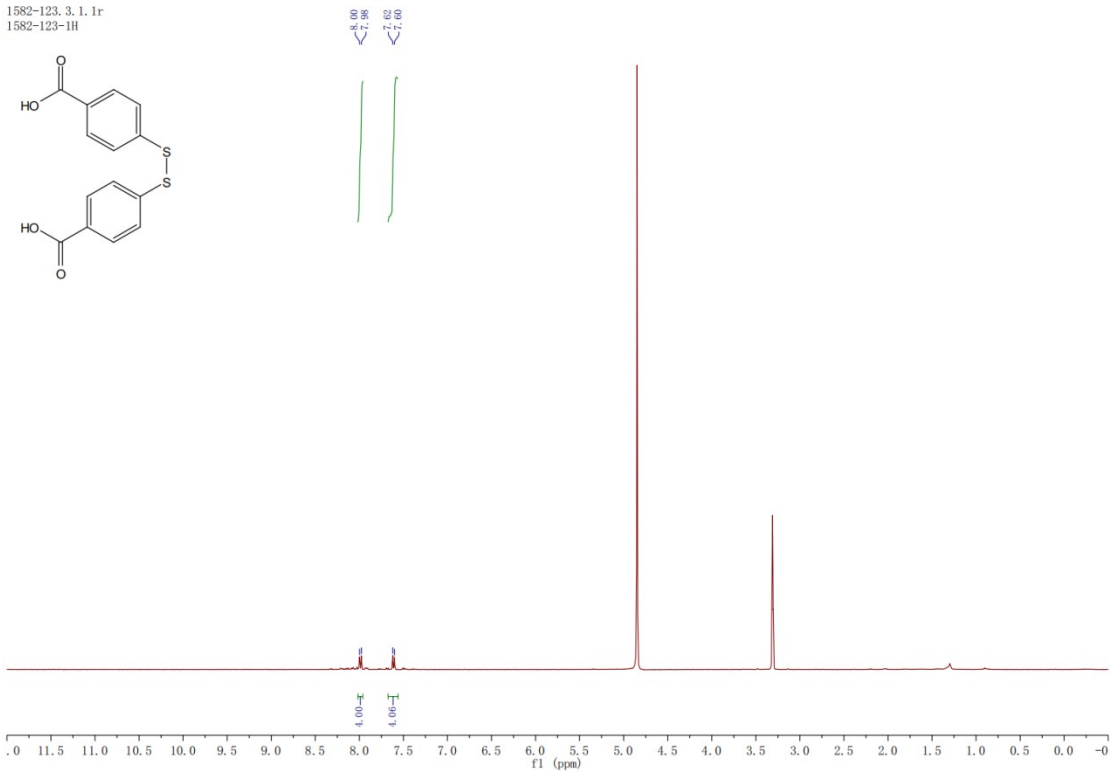
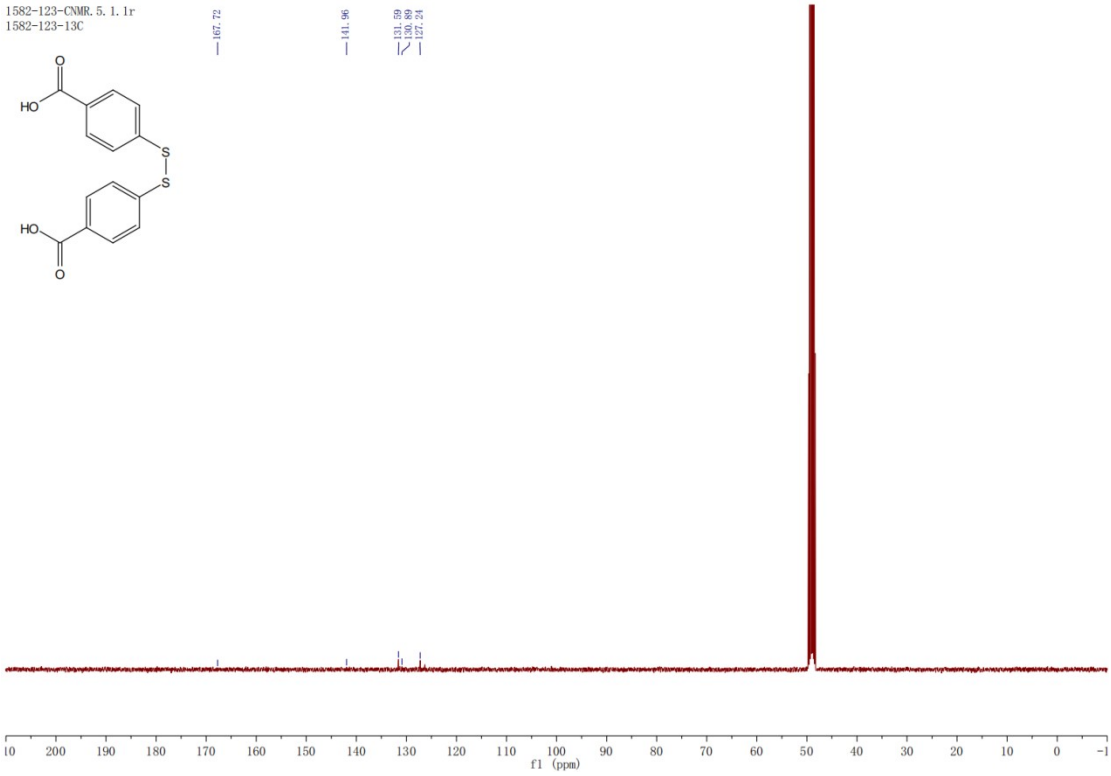
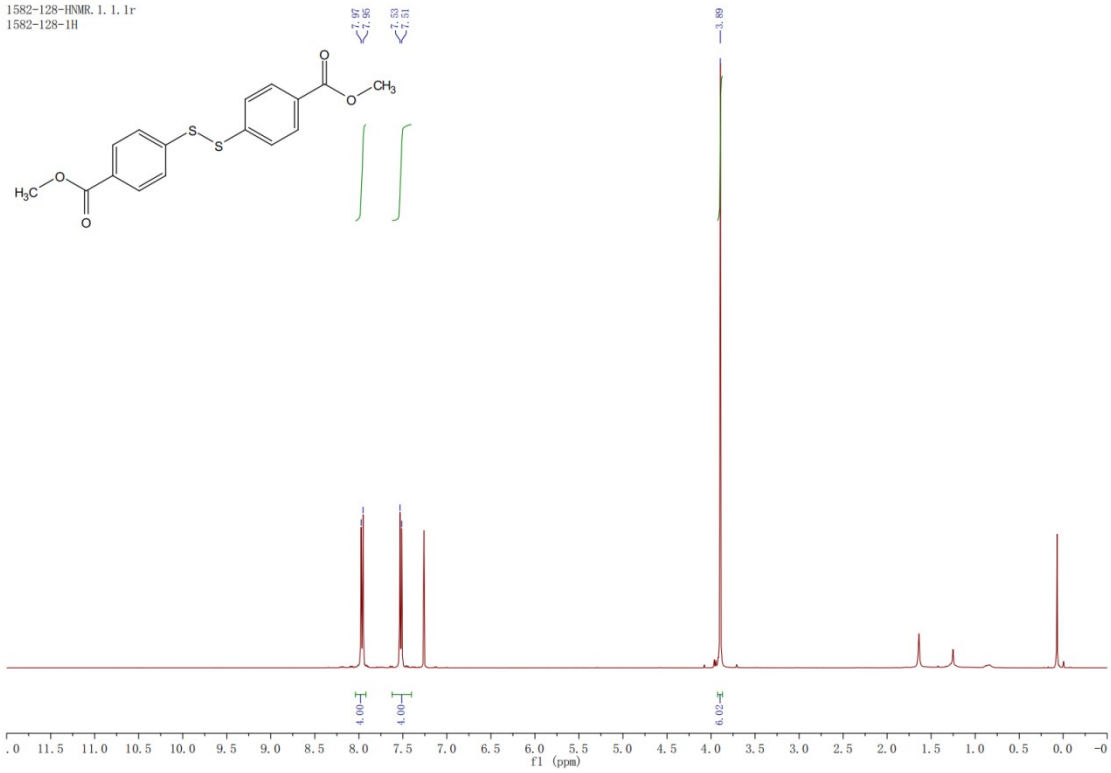


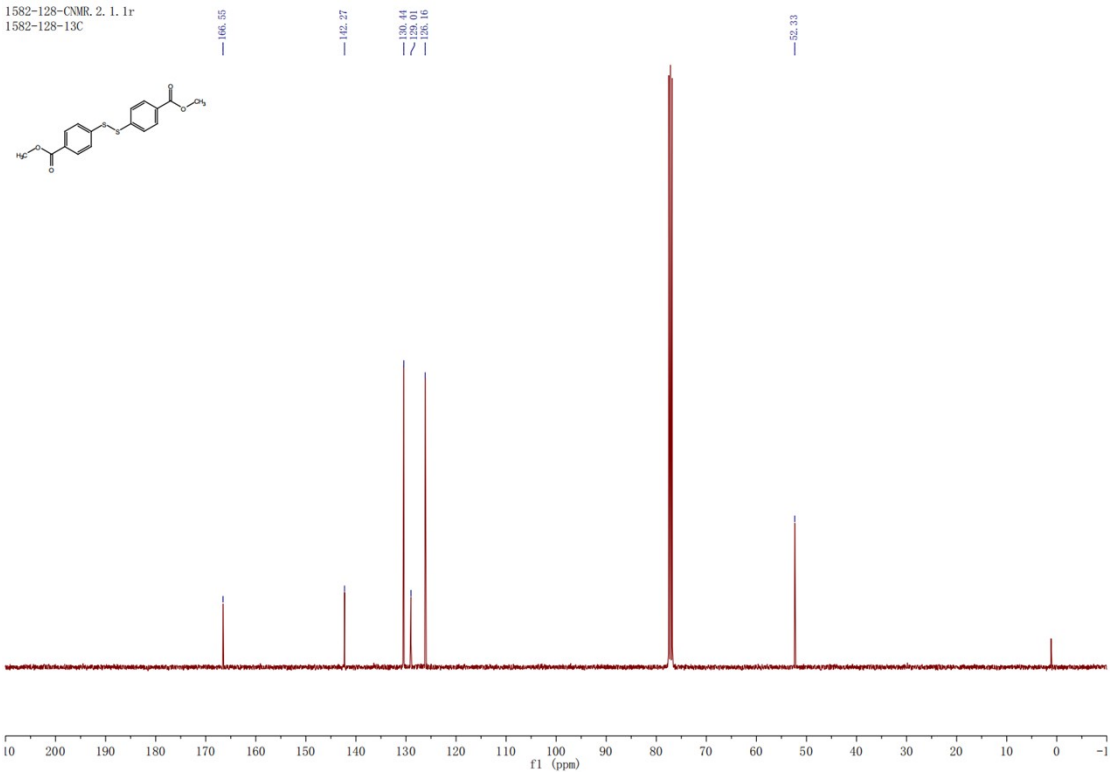
^{13}CNMR spectrum of **2k**



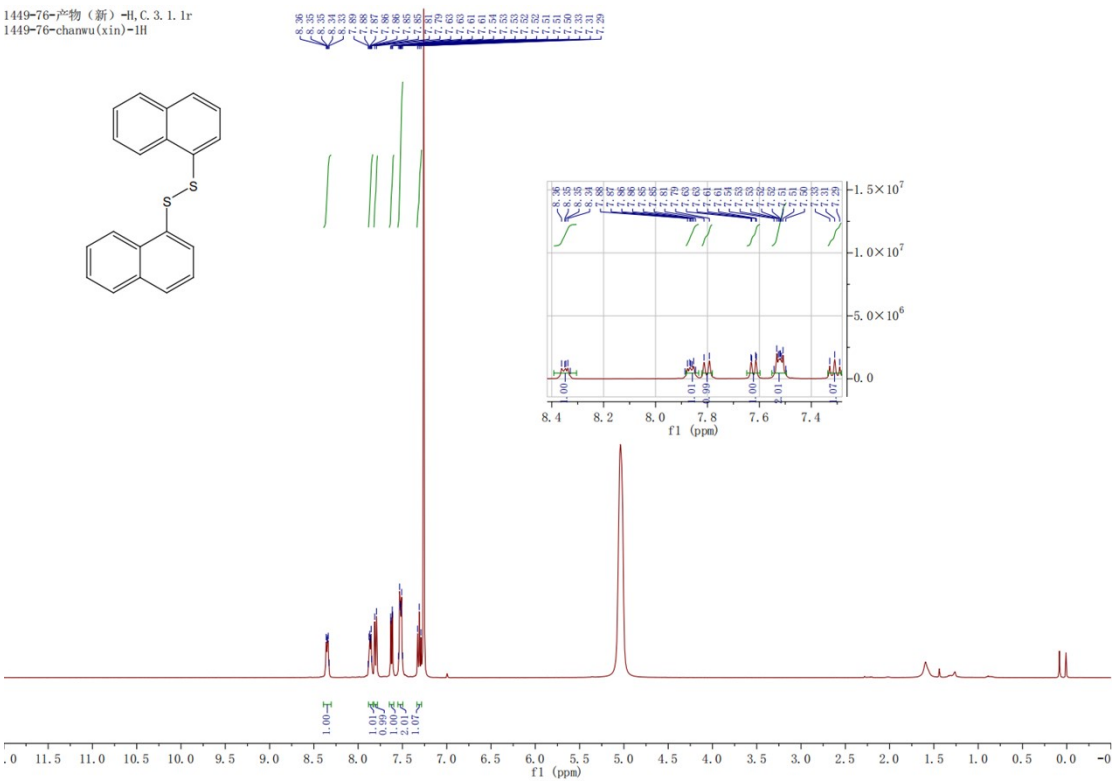
^{1}HNMR spectrum of **2l**



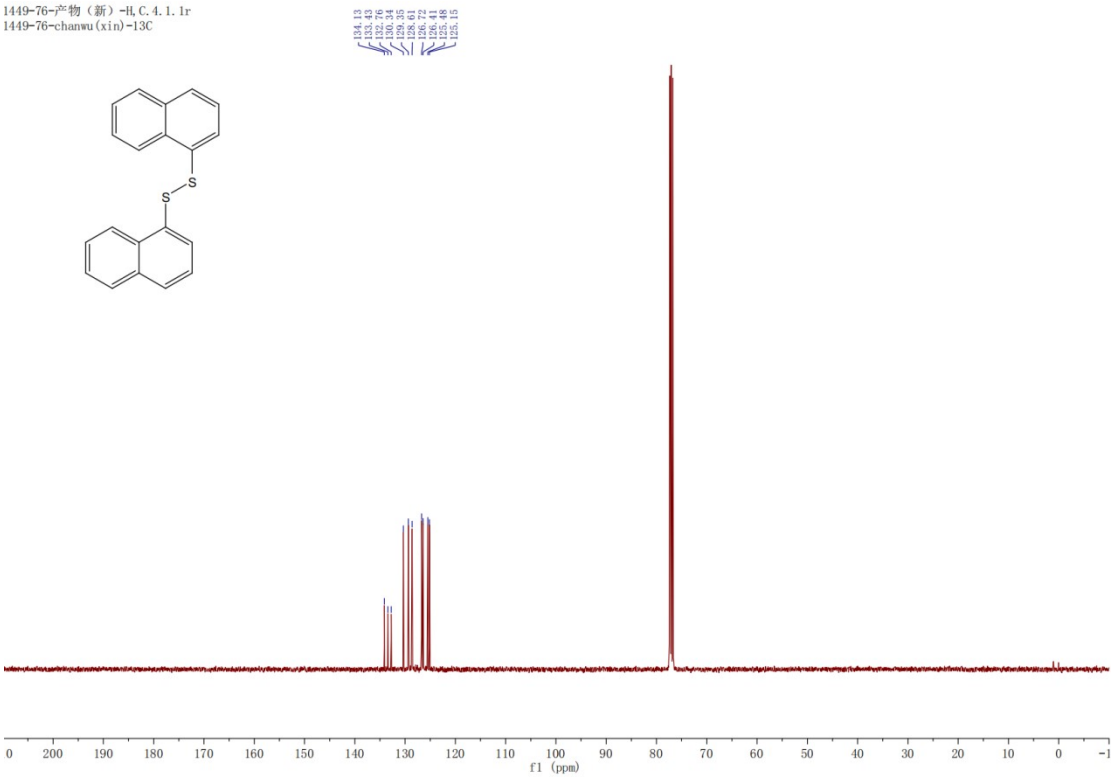
^{13}CNMR spectrum of **2l**



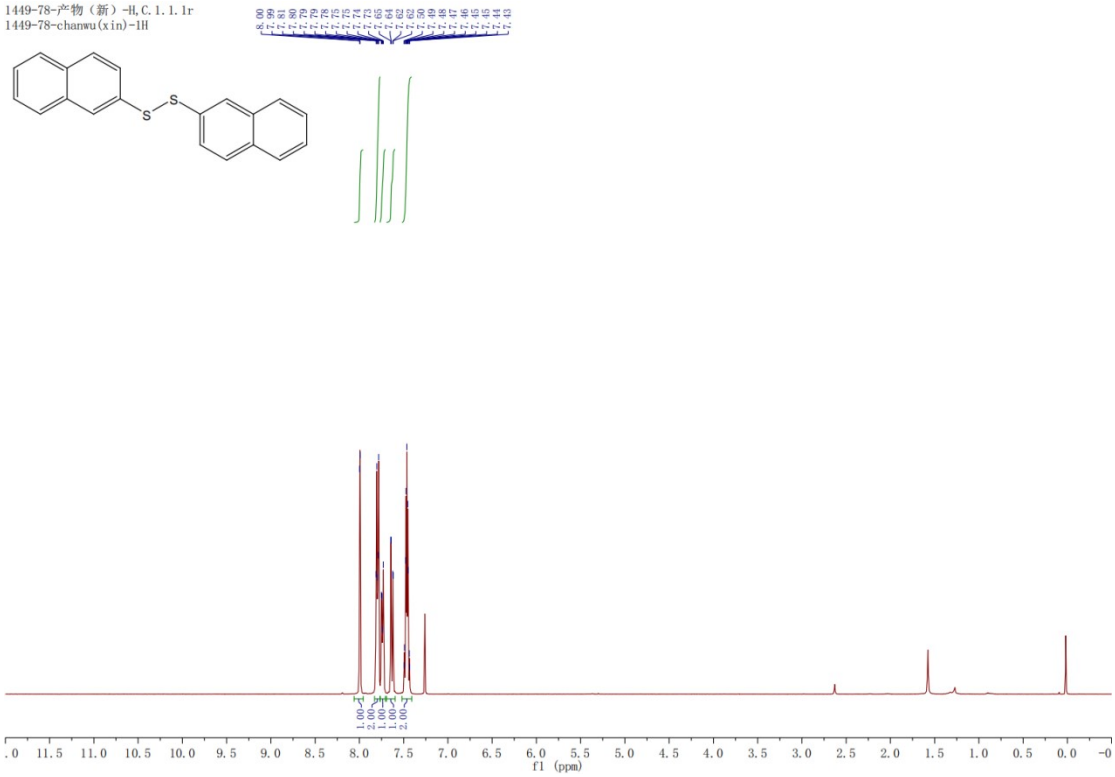
^{1}HNMR spectrum of **2n**



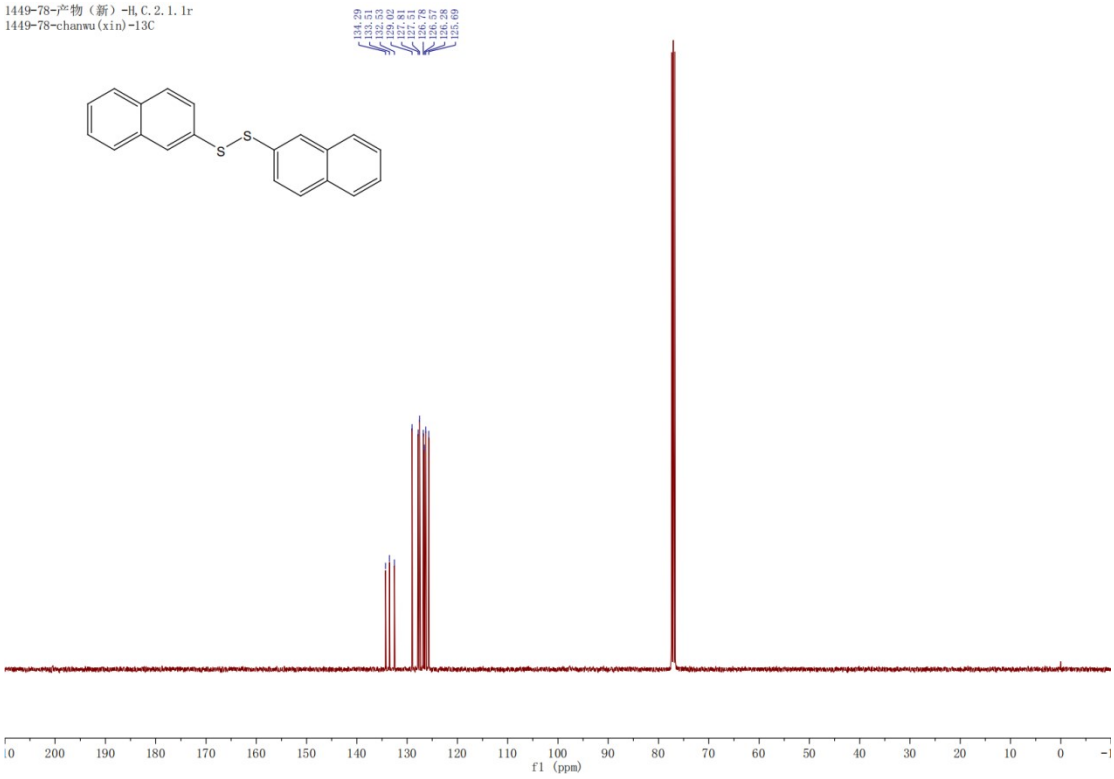
^{13}CNMR spectrum of **2n**



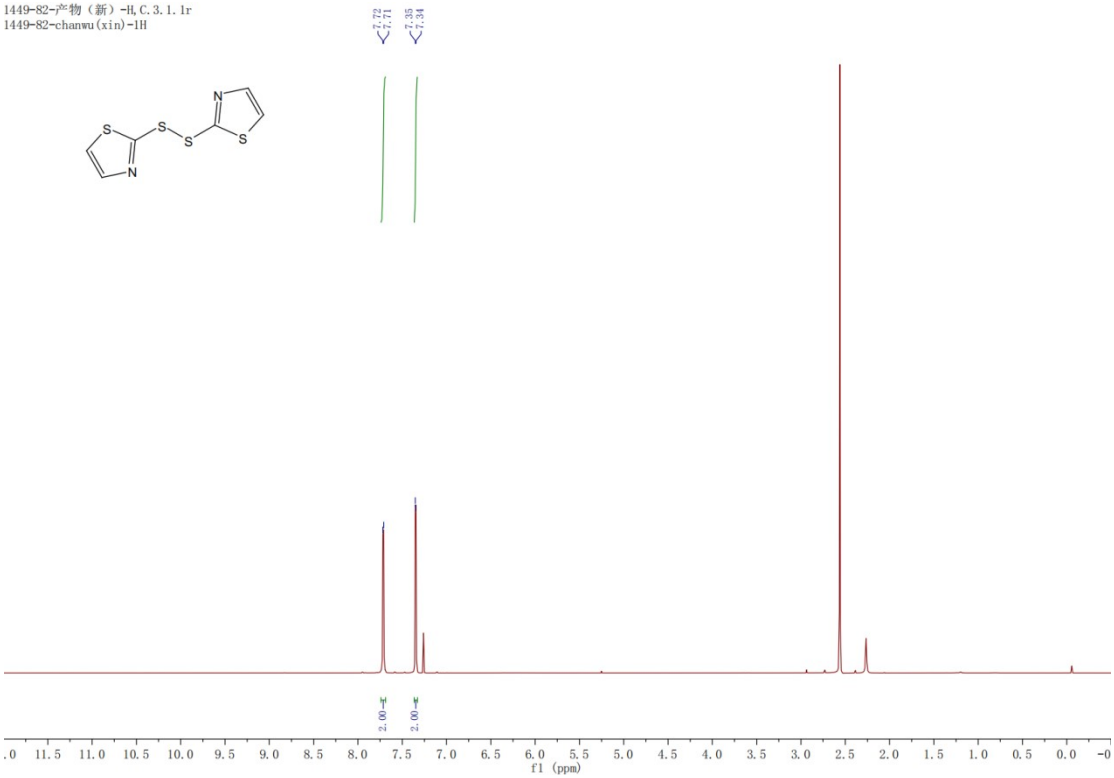
^{1}HNMR spectrum of **2o**



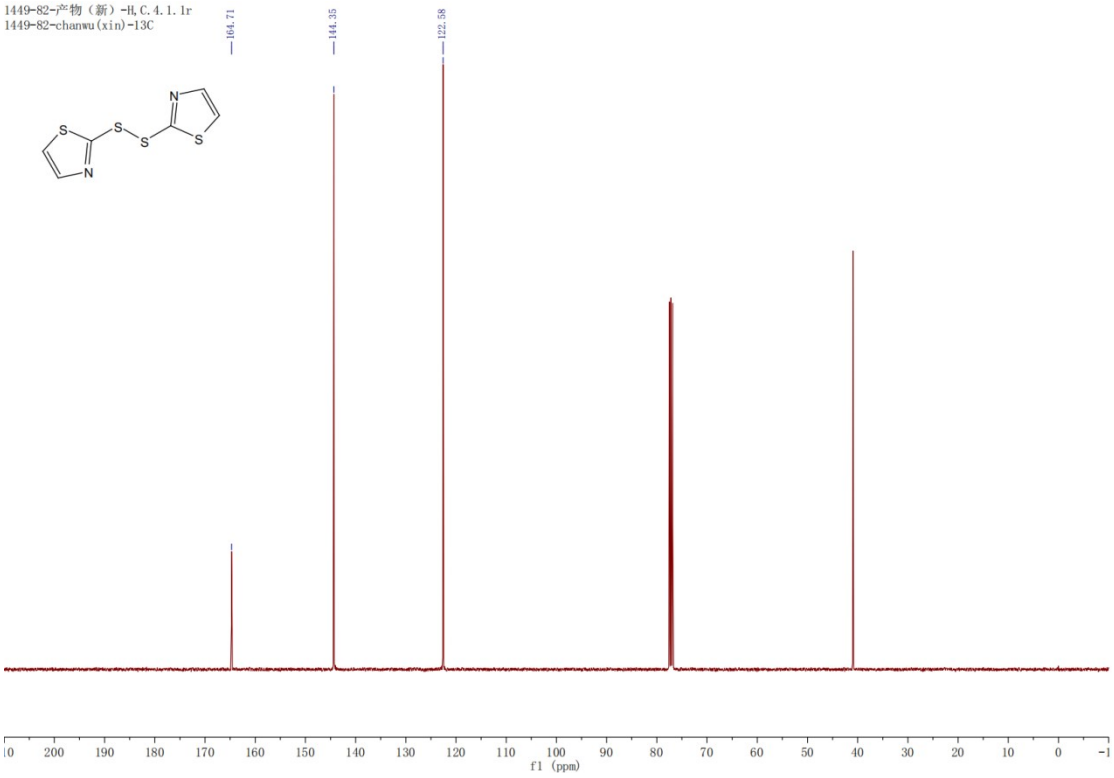
^{13}CNMR spectrum of **2o**



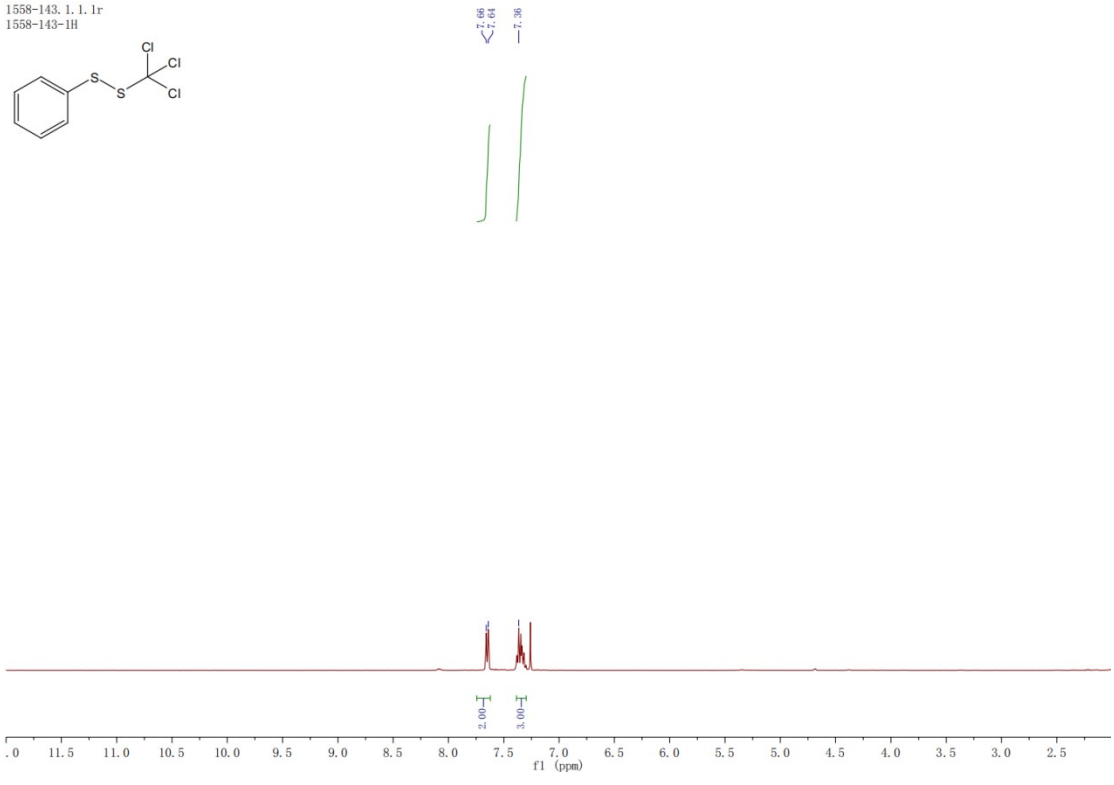
^{1}HNMR spectrum of **2p**



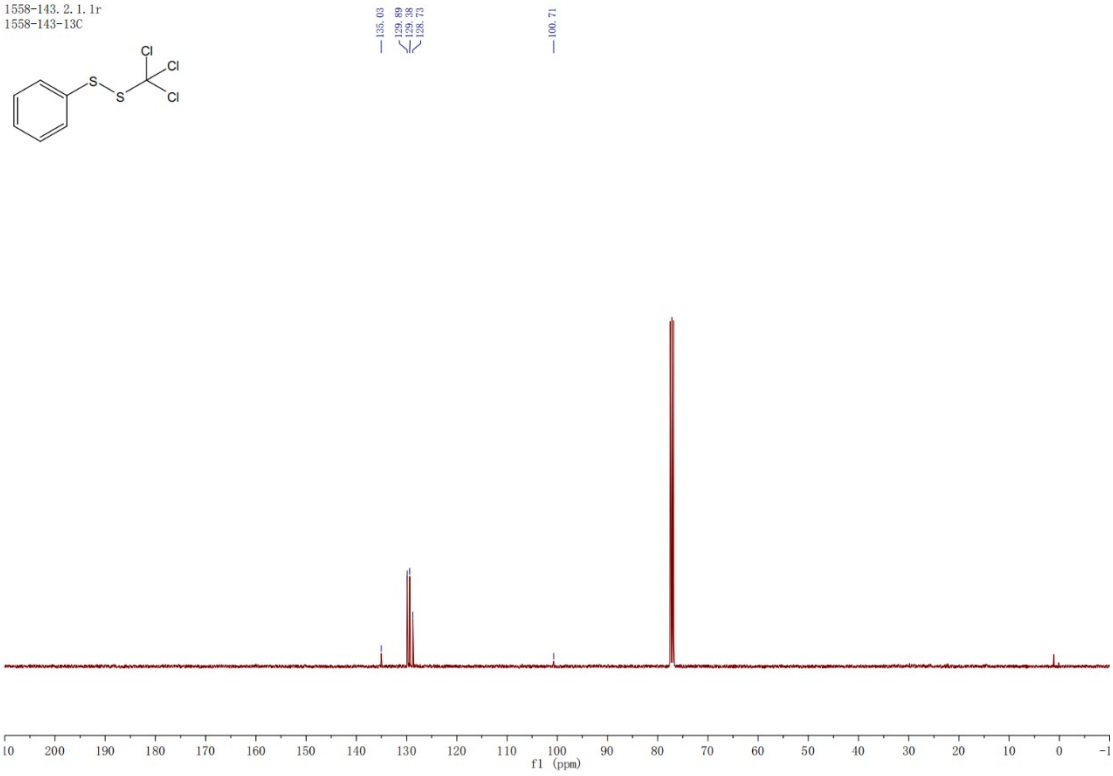
^{13}CNMR spectrum of **2p**



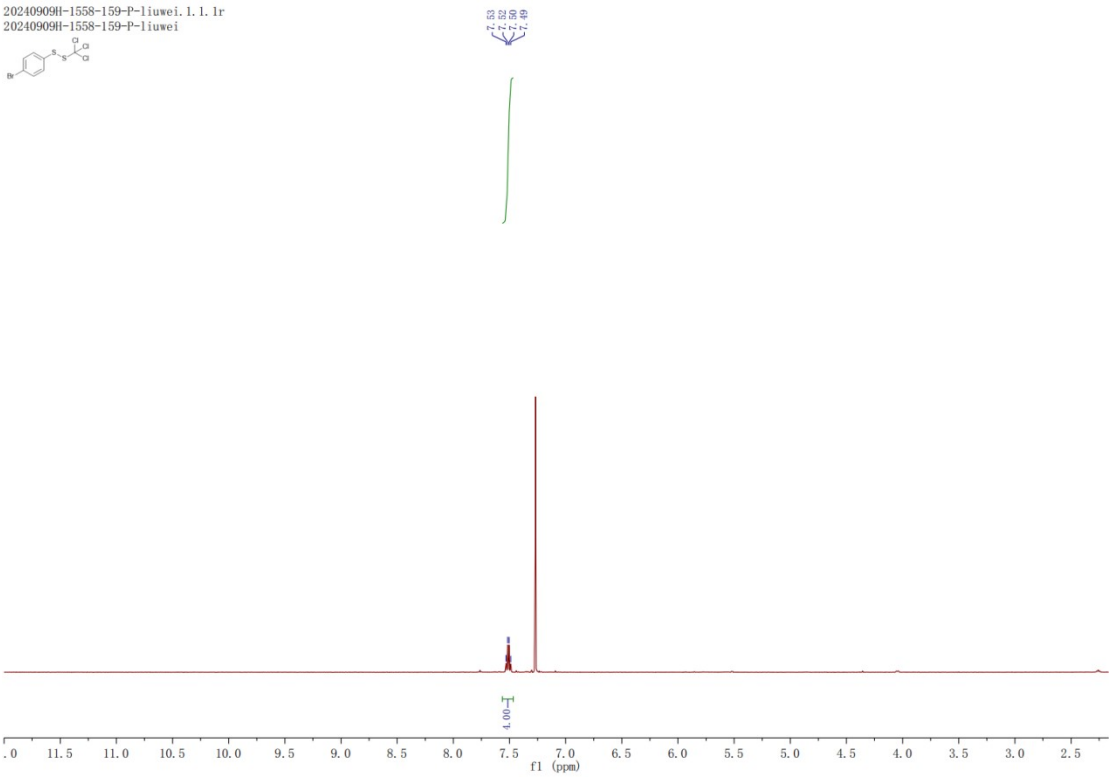
^{1}HNMR spectrum of **2ab**



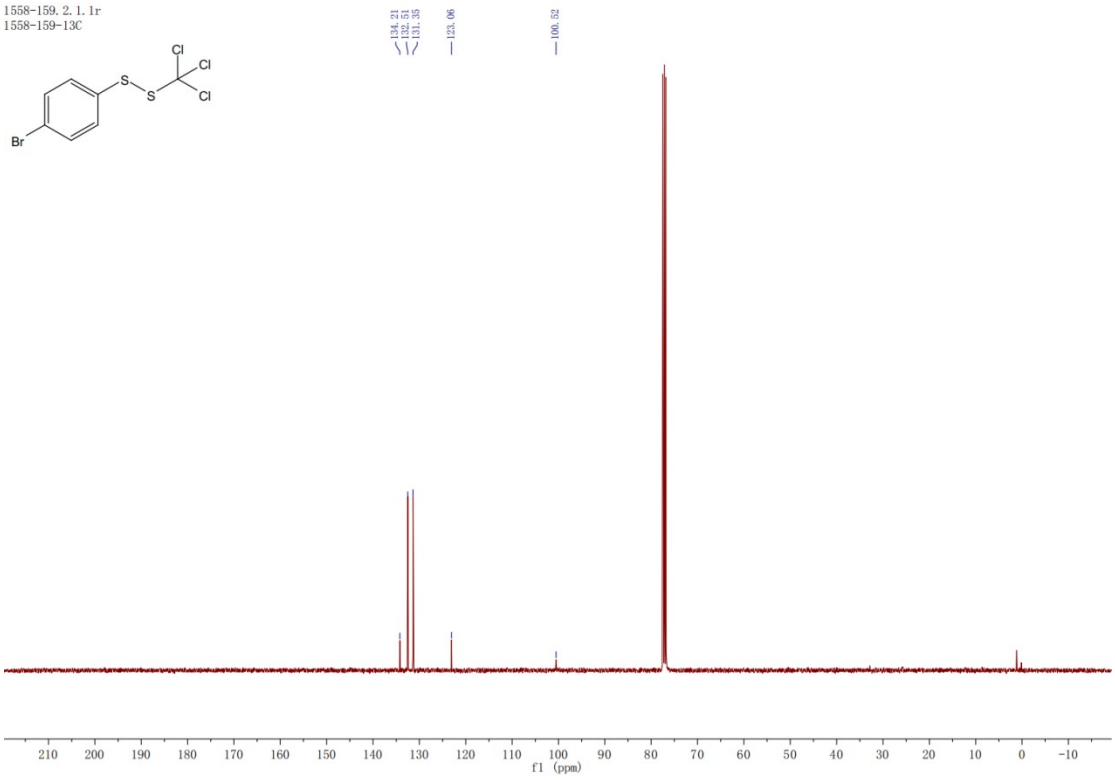
^{13}CNMR spectrum of **2ab**



^{1}HNMR spectrum of **2ac**

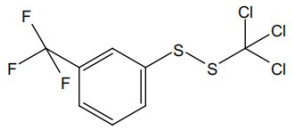


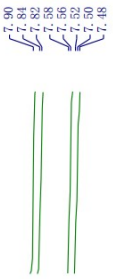
^{13}CNMR spectrum of **2ac**

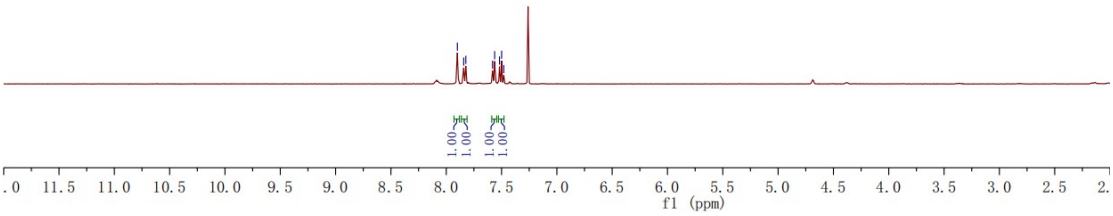


^{1}HNMR spectrum of **2ae**

1558-157. 1. 1. 1r
1558-157-1H

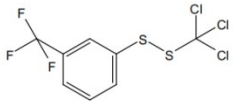




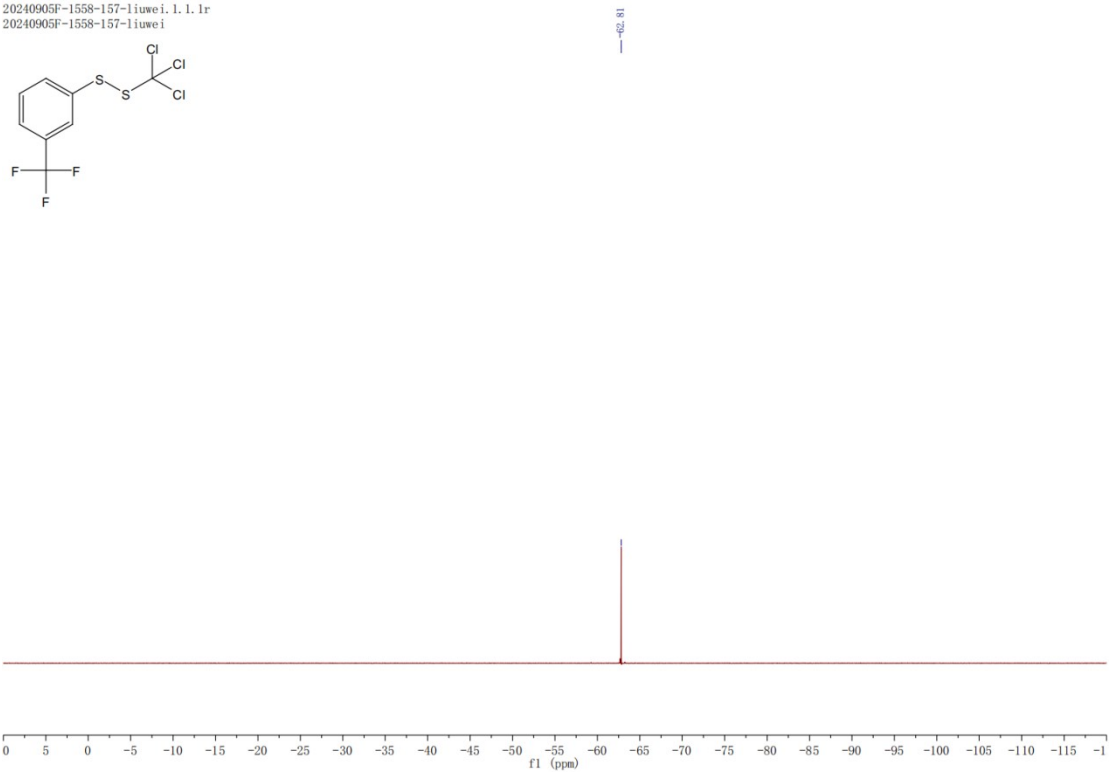


^{13}CNMR spectrum of **2ae**

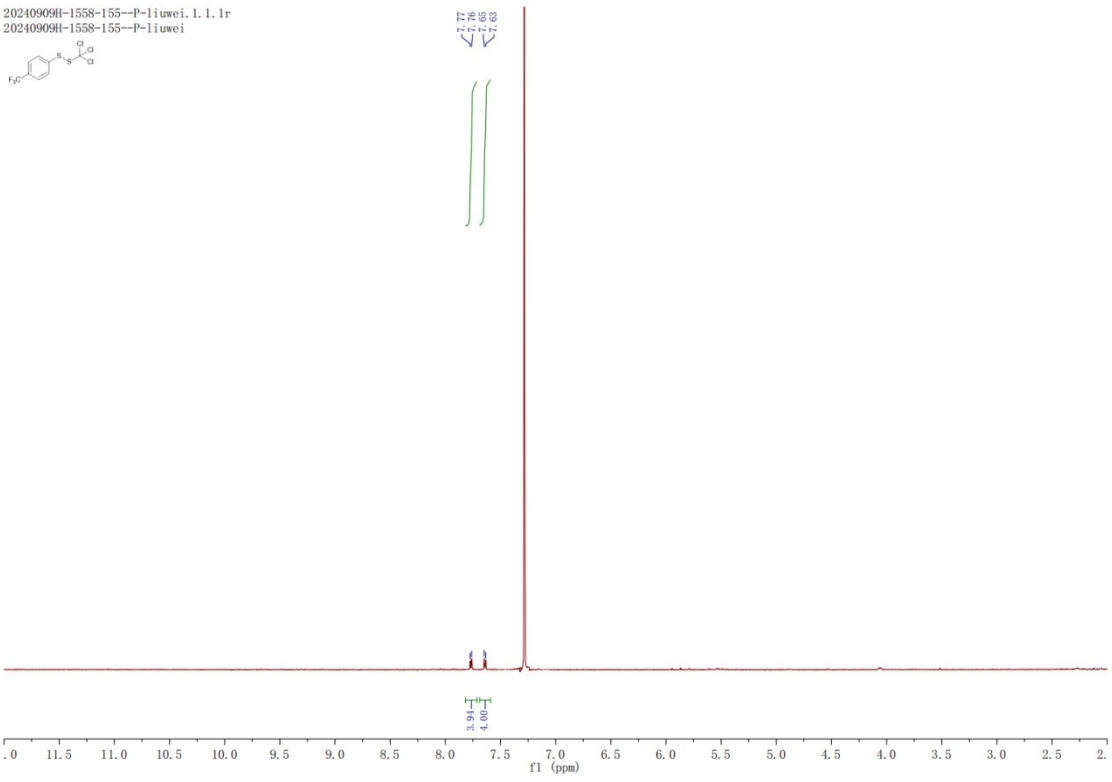
1558-157. 2. 1. 1r
1558-157-13C



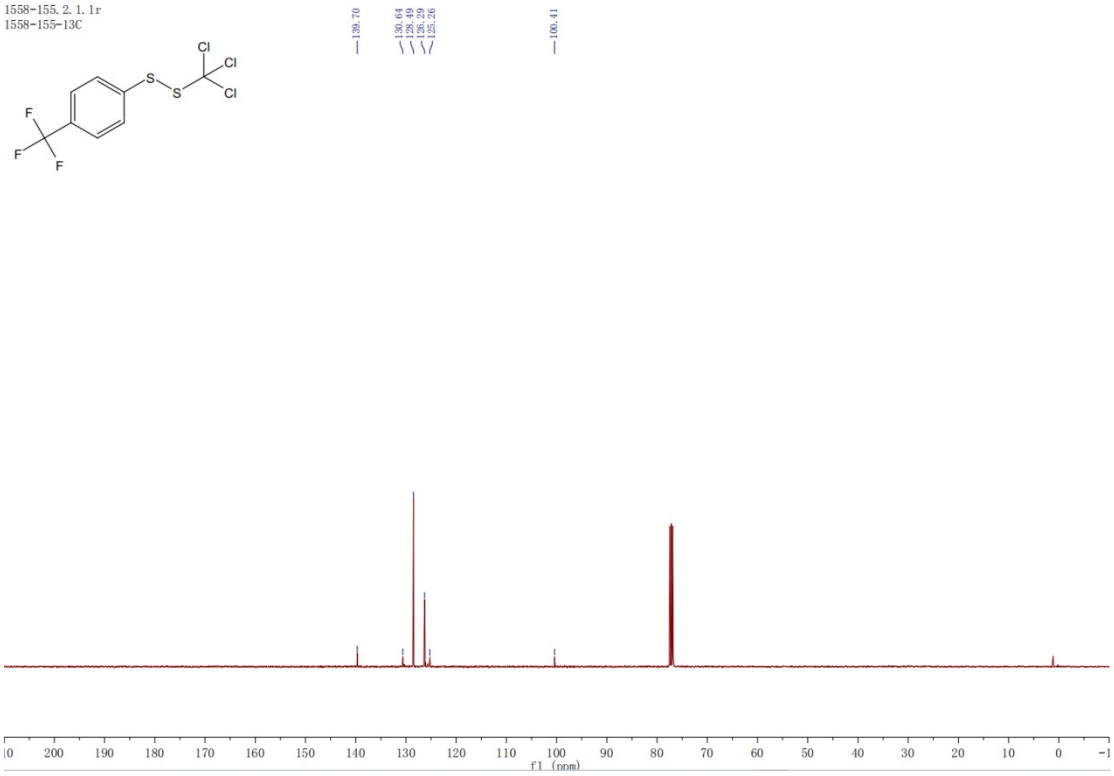
^{19}FNMR spectrum of **2ae**



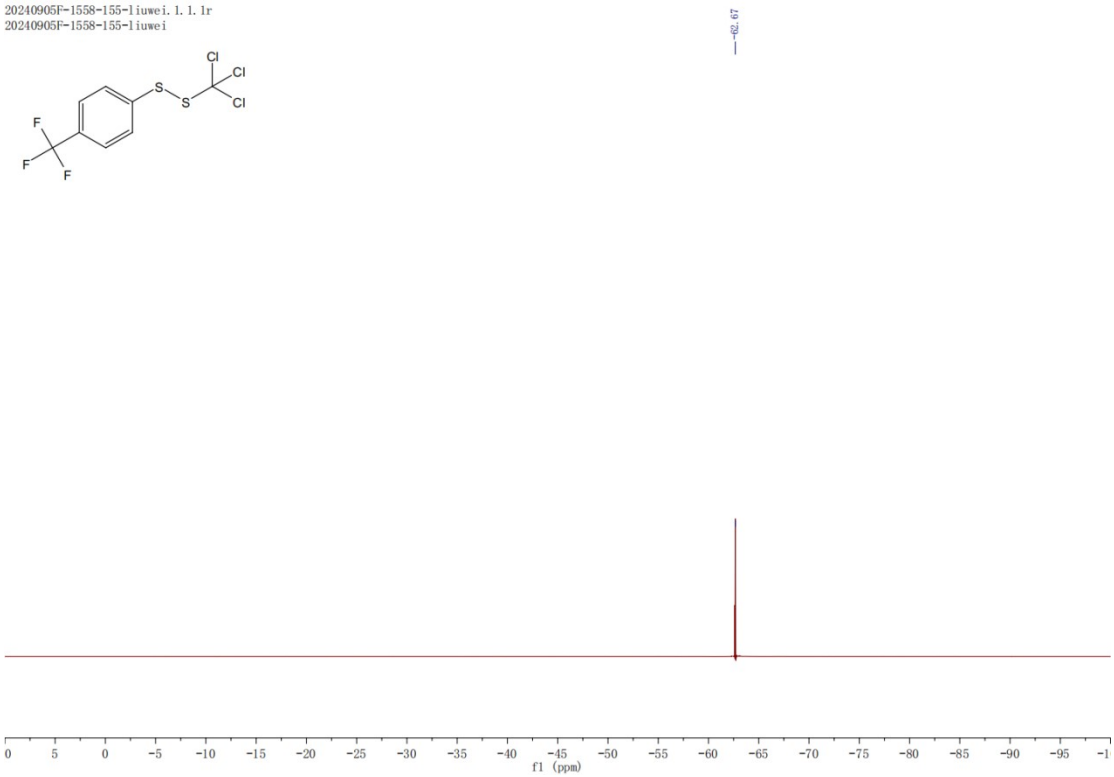
^{1}HNMR spectrum of **2af**



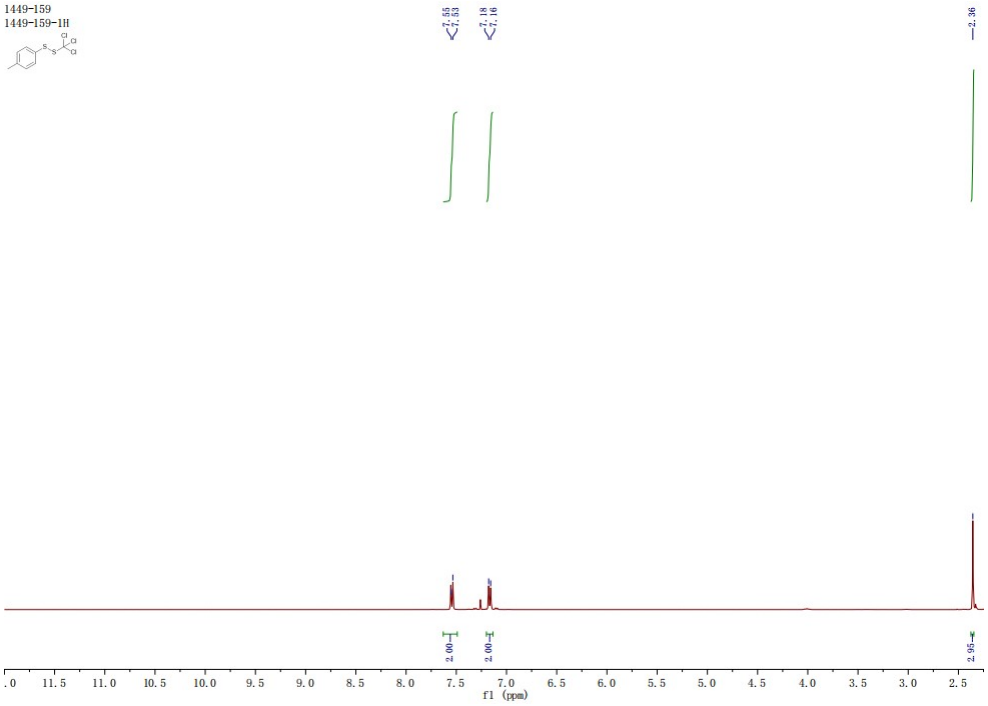
^{13}CNMR spectrum of **2af**



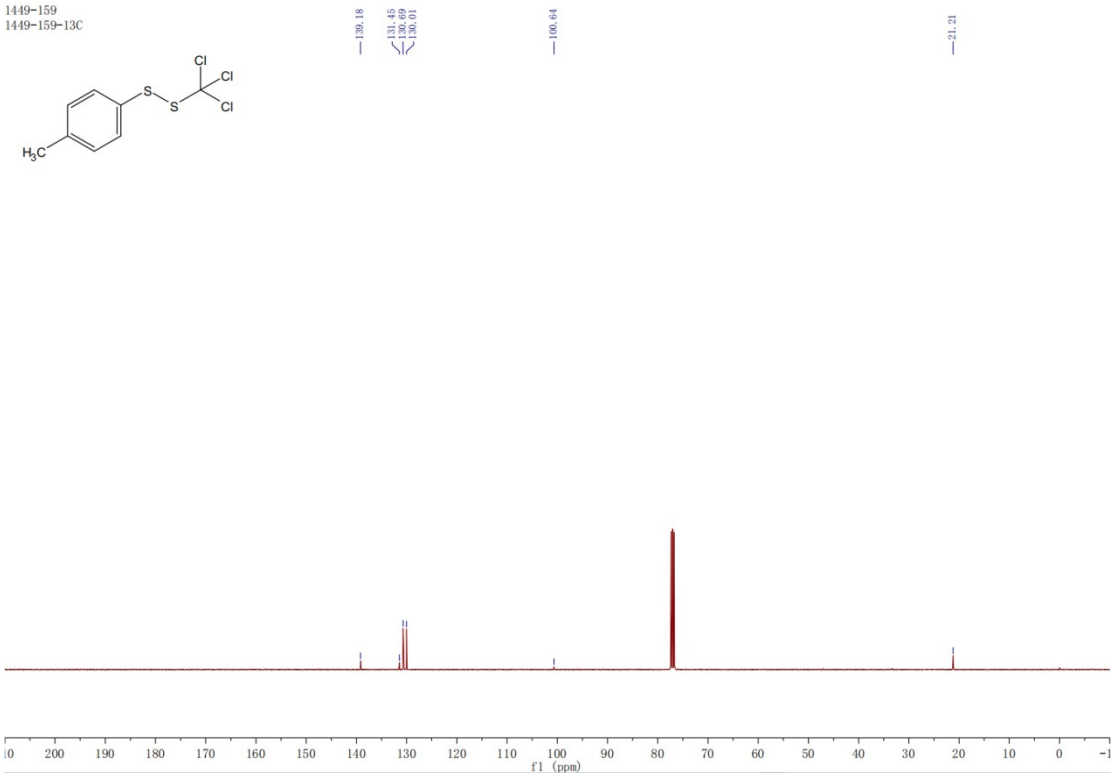
^{19}FNMR spectrum of **2af**



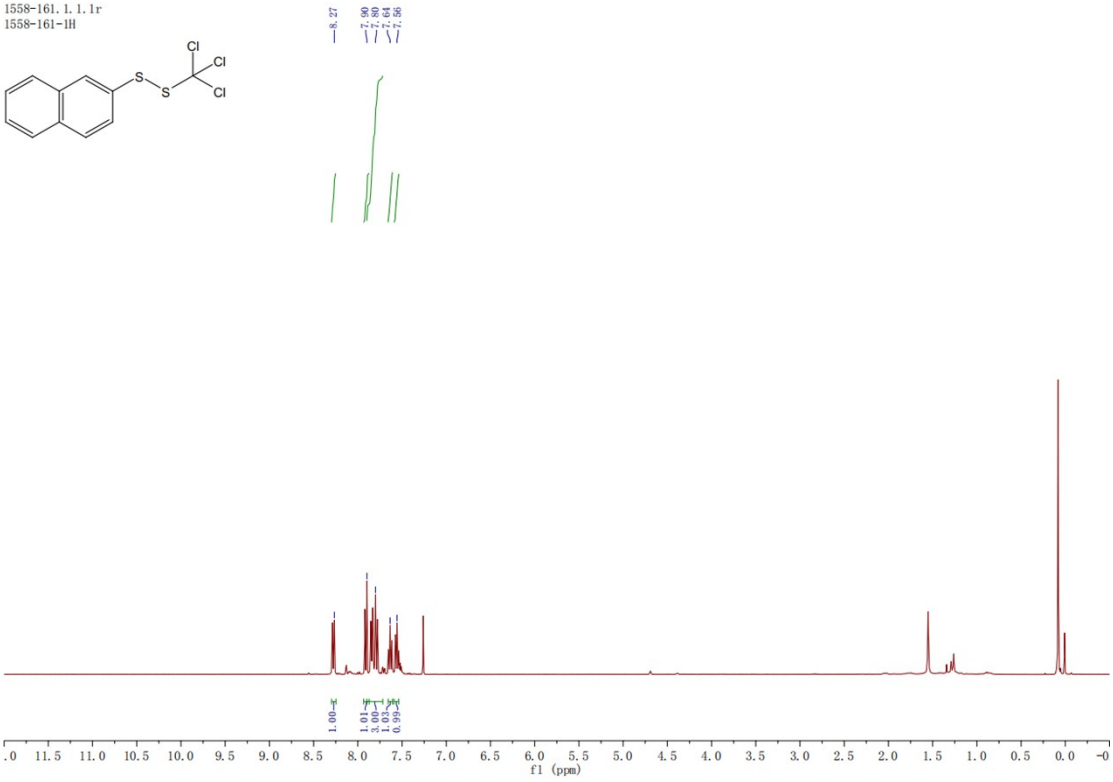
^{1}HNMR spectrum of **2ai**



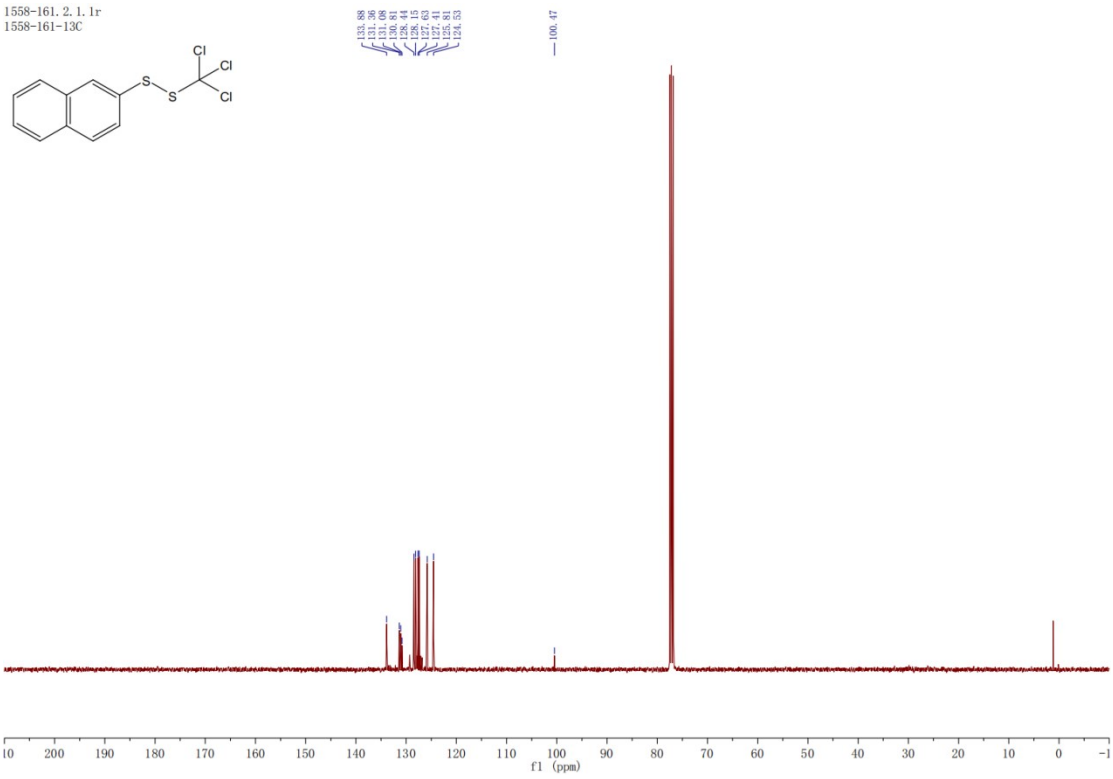
^{13}CNMR spectrum of **2ai**



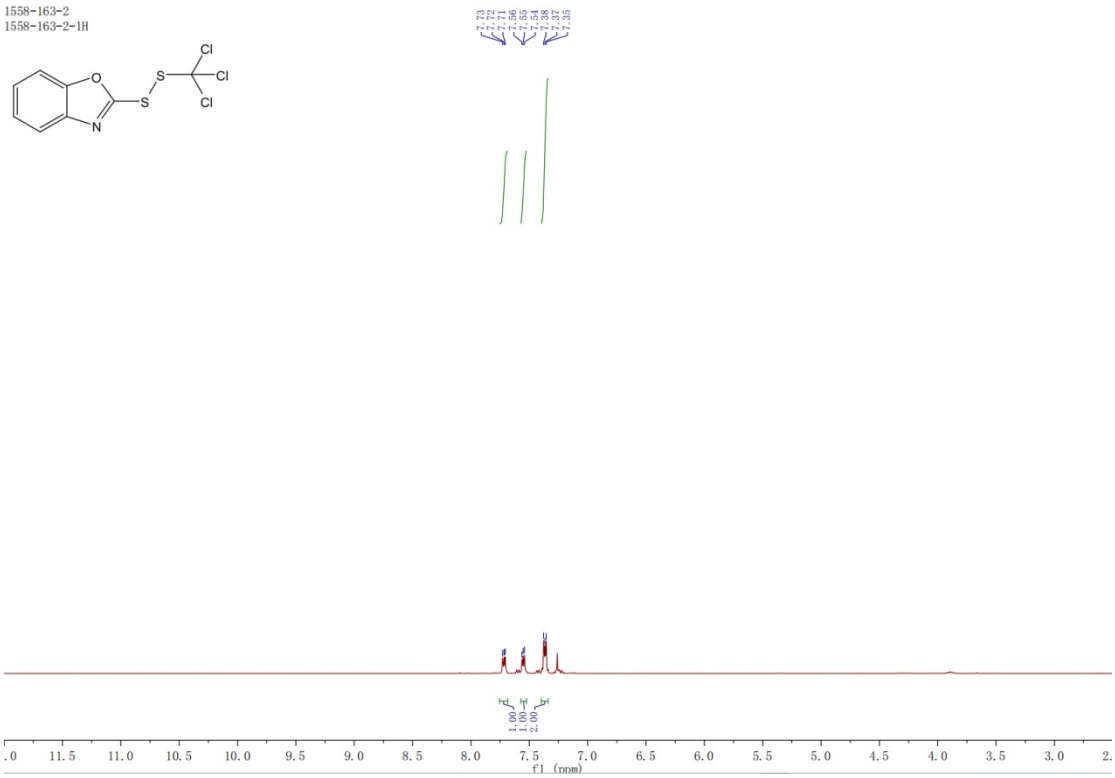
^{1}HNMR spectrum of **2ao**



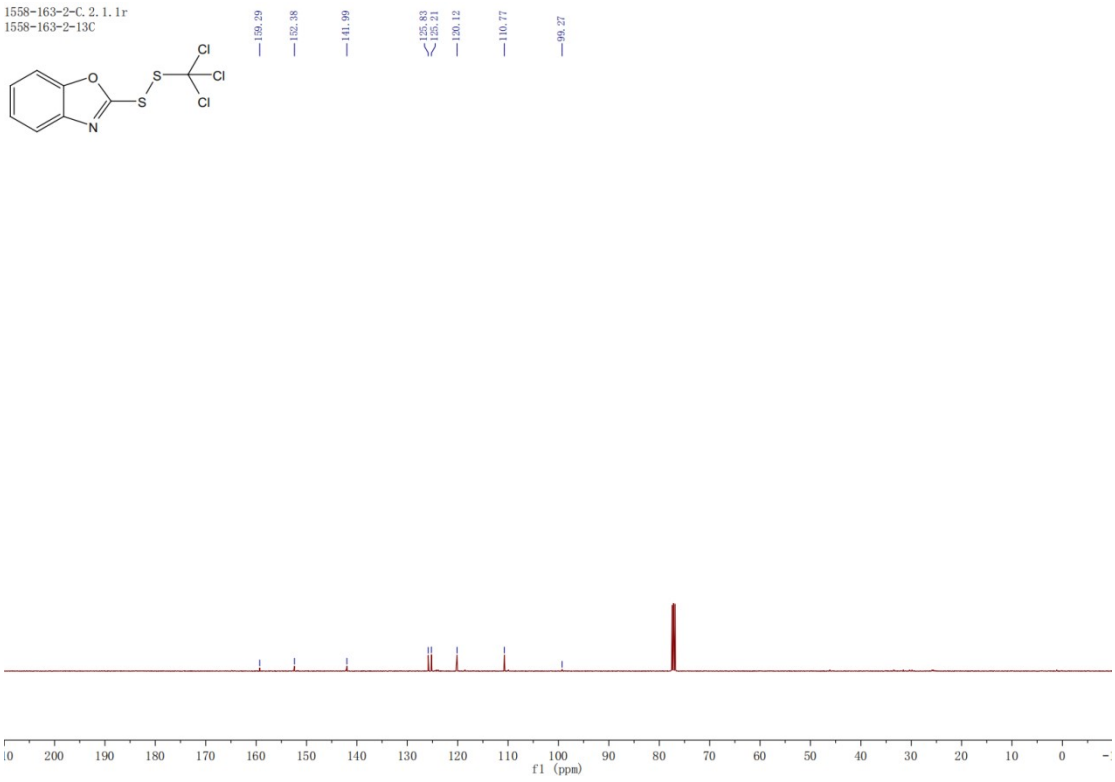
^{13}CNMR spectrum of **2ao**



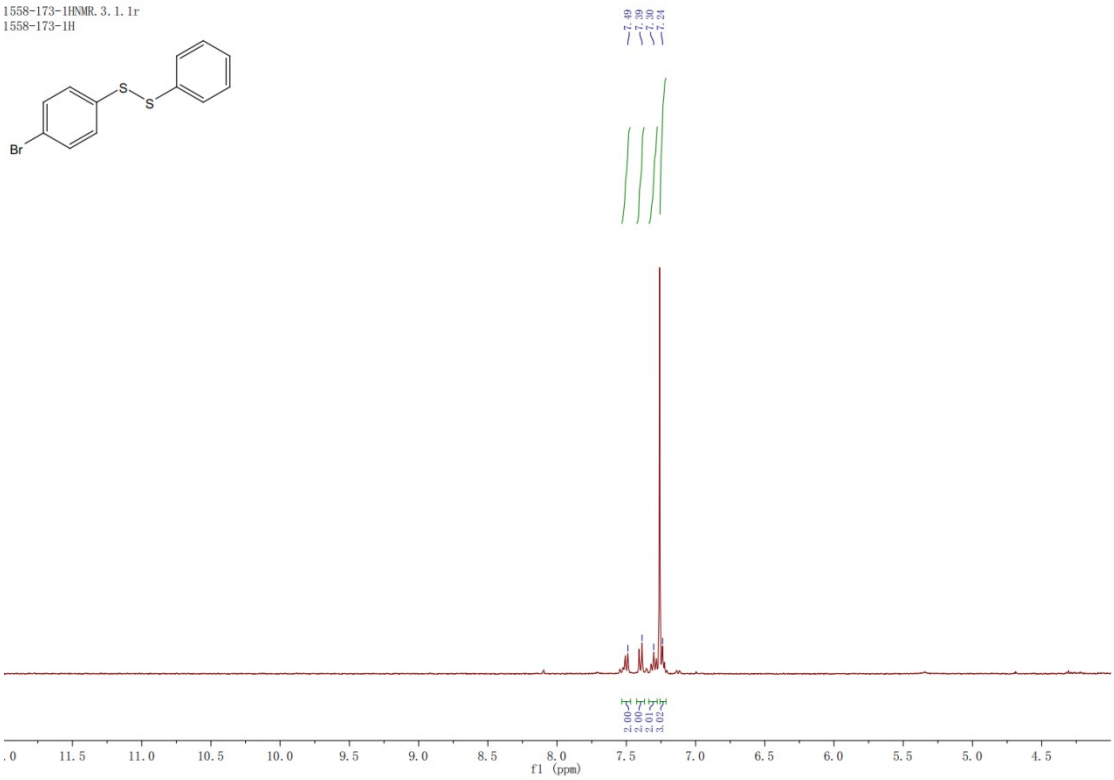
^{1}HNMR spectrum of **2au**



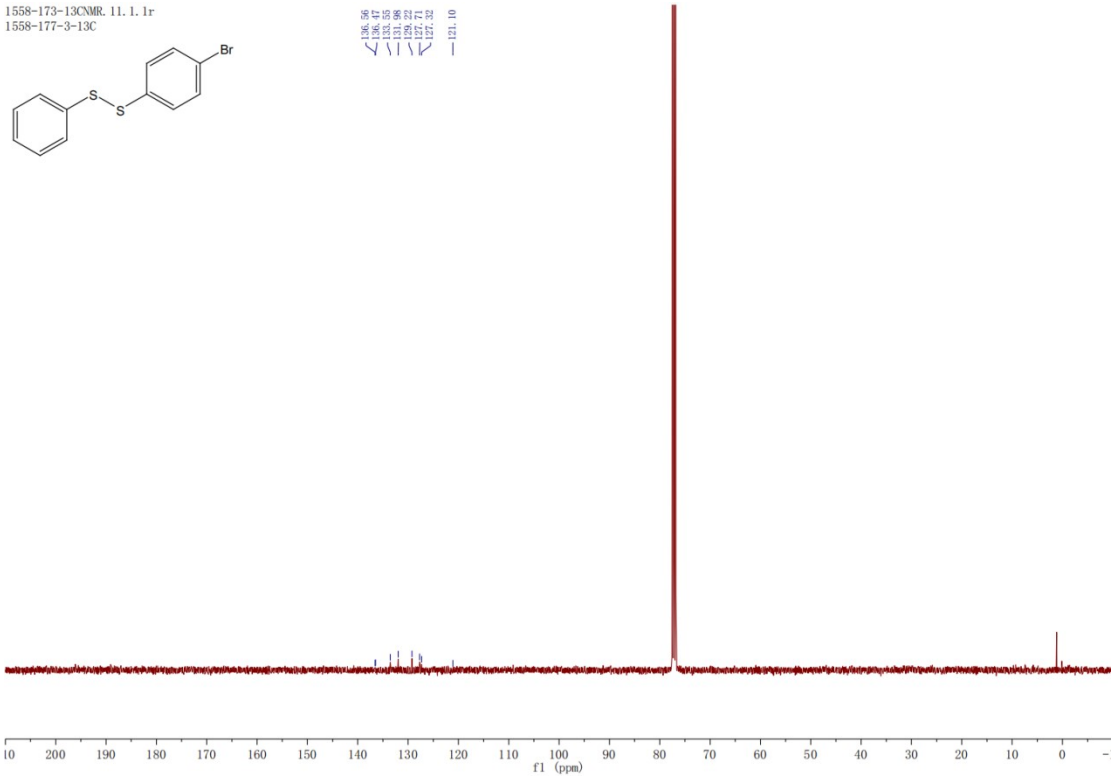
^{13}CNMR spectrum of **2au**



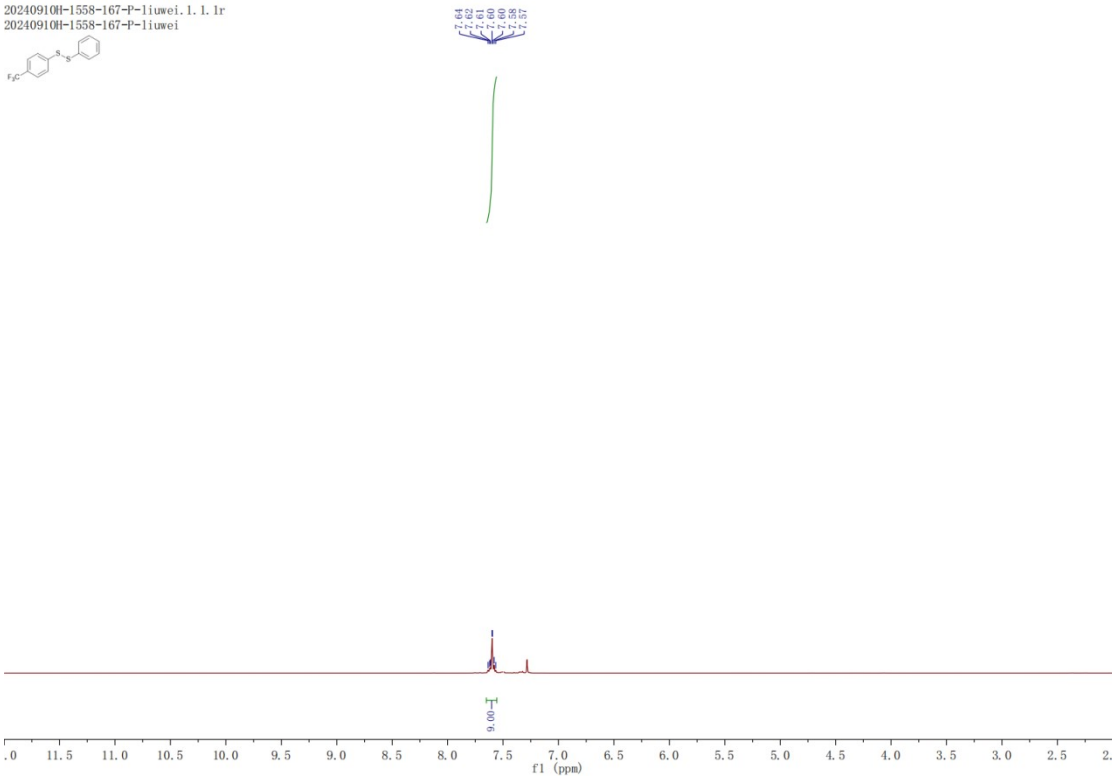
^{1}HNMR spectrum of **2bc**



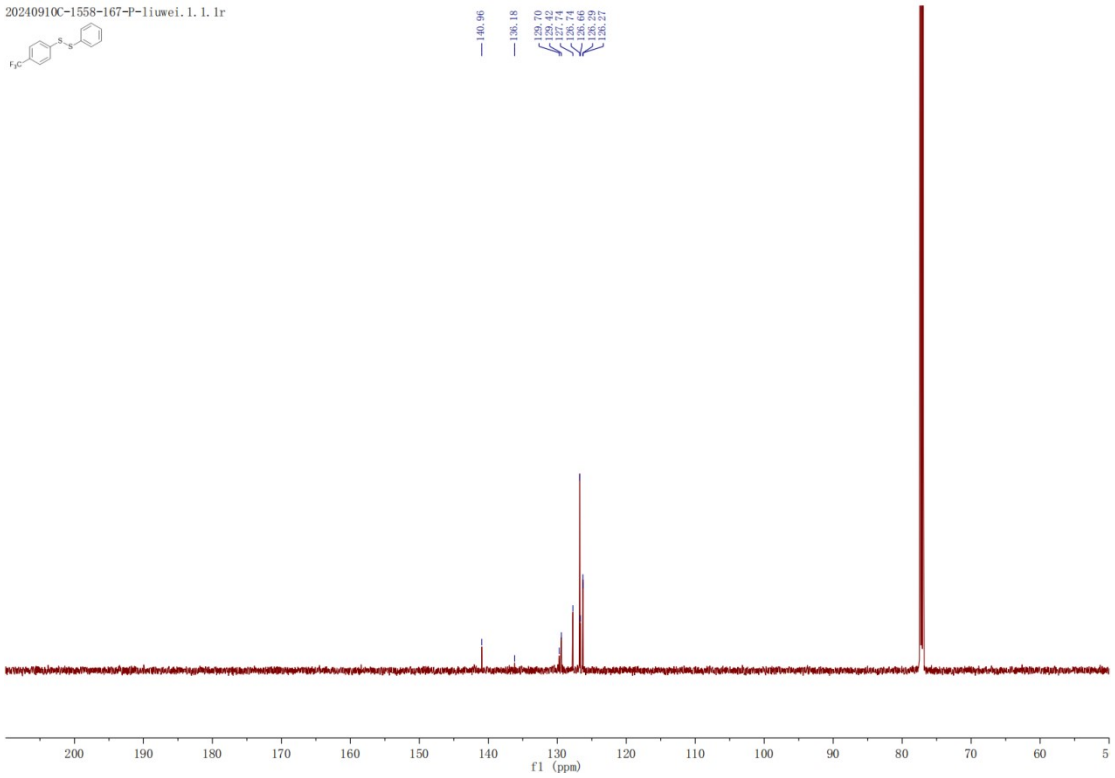
^{13}CNMR spectrum of **2bc**



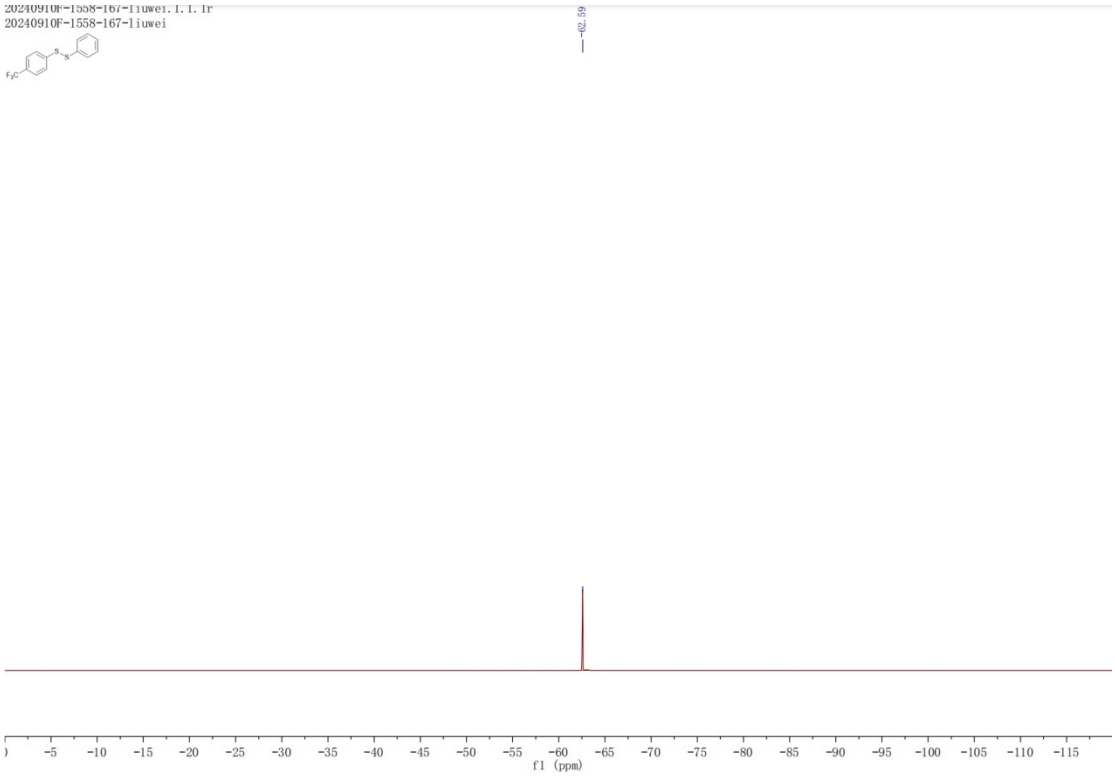
^{1}HNMR spectrum of **2bf**



^{13}CNMR spectrum of **2bf**



^{19}F NMR spectrum of **2bf**



^{1}HNMR spectrum of **2bi**