Supplementary Information

2,6-Bis(1,2,3-triazol-4-yl)pyridine ruthenium(II) complex embedded porous organic polymers as efficient photocatalyst for organic transformations

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Experimental Section

1. materials

2,6-Diethynylpyridine, 1,4-diethynylbenzene, 4,4'-diethynyl-1,1'-biphenyl, 4-iodoaniline, 3-iodoaniline, aniline, ethyl isocyanoacetate, tertbutyl isocyanide, tosylmethyl isocyanide and thiols were purchased from Beijing Inno Chem Science & Technology Co., Ltd. Copper sulfate pentahydrate ($CuSO_4 \cdot 5H_2O$), sodium ascorbate, sodium acetate (NaOAc), ruthenium(III) chloride trihydrate ($RuCl_3 \cdot 3H_2O$), 2,2,6,6-tetramethylpiperidinooxy (TEMPO), trimethylamine (Et_3N), ethyl acetate (EtOAc), tetrahydrofuran (THF), dichloromethane (CH_2Cl_2), acetonitrile (CH_3CN), N,N-dimethylformamide (DMF), 1,4-dioxane, and dimethyl sulfoxide (DMSO) were purchased from Shanghai Aladdin Biochemical Technology Co., Ltd. Ethynyltrimethylsilane, [1,1′-bis(diphenylphosphino)ferrocene]dichloropalladium ($PdCl_2$(dppf)), and tetrakis(triphenylphosphine)palladium ($Pd(PPh_3)_4$) were purchased from TCI. These chemicals were used as received without further purification.

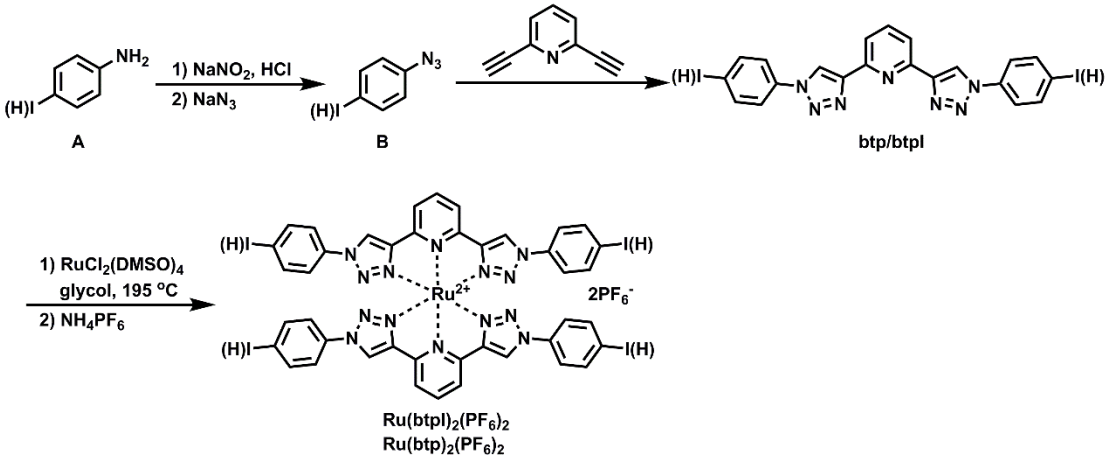
2. Sample characterizations

Fourier transform infrared (FT-IR) spectra were recorded on an IR-spectrum one (Perkin Elmer) spectrometer. NMR spectra were recorded on Varian Unity Inova 400 spectrometer (^1H at 400 MHz and ^{13}C at 100 MHz). ^{13}C cross-polarization magic-angle spinning (CP/MAS) NMR spectra were obtained on Varian Infinity-plus 300 spectrosmeter. Thermogravimetric analysis (TGA) were carried out in a N_2 atmosphere with a heating rate of 20 °C/min on a Diamond TG/DTA thermal analyzer (Perkin Elmer). Powder X-ray diffraction (PXRD) measurements were taken with a Bruker D8 advance with Cu Kα radiation at a scan rate of 10°/min. Scanning electron microscopy (SEM) images were conducted on a JEOL JSM-6510 electron microscope. Elemental distribution was determined by the energy-dispersive X-ray spectroscopy (EDX) mapping technique in field scanning electron microscopy. The specific surface area and pore-size distribution of the sample were tested by nitrogen adsorption-desorption at 77 K on a QDS-MP-30 volumetric gas sorption instrument. Surface areas were calculated from the adsorption data from $0.05 < P/P_0 < 0.30$ by using Brunauer-Emmett-Teller (BET) methods. The pore size distribution curves were obtained from the adsorption branches by using Barrett-Joyner-Halenda (BJH) method. UV-vis diffuse reflectance spectra were recorded on a Lambda 900 spectrophotometer (Perkin-Elmer).

3. Electrochemical measurements

Cyclic voltammetry (CV) experiments were performed using a CH Instruments Model 760E electrochemical work station (CH Instruments Inc.). The three-electrode-cell system consisted of a glassy carbon working electrode, a platinum plate counter electrode and a SCE reference electrode. The samples were prepared by first mixing sample with 5 wt% Nafion to give a homogeneous suspension, then a 10 μL drop was placed on top of a glassy carbon working electrode and let the solvent evaporate in a vacuum chamber for 60 min. The measurement was carried out in a Bu_4NPF_6 solution (0.1 M in acetonitrile) as supporting electrolyte (pH 3.87) with a scan rate of 0.1 V s^{-1} in the range of -2.0 V to 2.0 V.

4. Synthesis of building blocks



4.1. Synthesis of B

In a round-bottom flask equipped with a magnetic stirring bar, 4-iodoaniline **A1** or aniline **A2** (5.0 mmol) was suspended in HCl (6 M, 10 mL) cooled in an ice bath. Then 5 mL of aqueous solution of $NaNO_2$ (0.69 g, 10.0 mmol) was added dropwise. The reaction mixture was stirred for 0.5 h and 3 mL of aqueous solution of NaN_3 (0.65 g, 10.0 mmol) was added dropwise. After that, the mixture was allowed to stir for another 12 h at room temperature. Then the mixture was extracted with ethyl acetate (15 mL × 3). The combined organic extracts were washed with brine and dried over $MgSO_4$. The volatiles were removed under vacuum to give crude product, which was purified by column chromatography on silica gel (petroleum ether) to afford azidobenzene **B**.

Following the above synthetic procedure and using 4-iodoaniline **A1** as the starting material, the product 1-azido-4-iodobenzene **B1** was obtained as a yellow oil (1.12 g, 91%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51-7.41 (m, 2H), 6.94-6.87 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 140.00,

138.73, 121.06, 88.23.

Following the above synthetic procedure and using aniline **A2** as the starting material, the product 1-azido-3-iodobenzene **B2** was obtained as a yellow oil (1.11 g, 90%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49-7.45 (m, 1H), 7.38 (t, *J* = 1.9 Hz, 1H), 7.07 (t, *J* = 7.9 Hz, 1H), 7.02-6.96 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.39, 133.97, 131.09, 127.95, 118.44, 94.66.

4.2. Synthesis of btp

2,6-Diethynylpyridine (305 mg, 2.4 mmol), **B** (5.0 mmol), $CuSO_4$ $5H_2O$ (0.25 g, 1.0 mmol) and sodium ascorbate (0.198 g, 1.0 mmol) in dry DMF (10 mL) was stirred under a nitrogen atmosphere at 90 °C for 48 h.

For **btpI**, the reaction mixture was cooled to room temperature and 20 mL of diethyl ether was added. The resulting precipitate was filtered and the solid was washed with diethyl ether, dichloromethane, water and ethanol to give the product.

For **btp**, the reaction mixture was cooled to room temperature and 10 mL of water was added. The mixture was extracted with dichloromethane (20 mL × 3). The organic phases were washed with brine and dried over $MgSO_4$. The volatiles were removed under vacuum to give crude product, which was purified by column chromatography on silica gel (dichloromethane) to afford the product.

Following the above synthetic procedure and using 1-azido-4-iodobenzene **B1** as the starting material, the product 2,6-bis(1-(4-iodophenyl)-1,2,3-triazol-4-yl)pyridine **btpI** was obtained as a gray powder (1.18 g, 80%). ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.40 (s, 2H), 8.19-7.97 (m, 7H), 7.85 (d, *J* = 7.9 Hz, 4H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 149.82, 139.59, 138.15, 137.92, 132.32, 128.85, 122.46, 120.26, 96.04.

Following the above synthetic procedure and using azidobenzene **B2** as the starting material, the product 2,6-bis(1-phenyl-1,2,3-triazol-4-yl)pyridine **btp** as a white solid (683 mg, 78%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.67 (s, 2H), 8.17 (d, *J* = 7.8 Hz, 2H), 7.89 (t, *J* = 7.8 Hz, 1H), 7.78 (d, *J* = 8.0 Hz, 4H), 7.50 (t, *J* = 7.6 Hz, 4H), 7.42 (t, *J* = 7.4 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 149.78, 148.83, 137.94, 136.92, 129.82, 128.94, 120.44, 120.22, 119.76.

4.3. Synthesis of $RuCl_2(DMSO)_4$

The product was synthesized by a similar procedure to that previously reported [1]. To a 100 mL three necked flask was added $RuCl_3 \cdot 3H_2O$ (1.0 g, 3.8 mmol), isopropanol (15 mL) and DMSO (5 mL). The mixture was degassed and filled with N_2 for three times. After heating at 85 ºC for 48

h, the mixture was cooled to room temperature. The resulting precipitate was filtered and washed with acetone, toluene and diethyl ether in turn. After dried in vacuum, the product was obtained as a yellow solid (1.2 g, 65%), which was used directly without further purification.

4.4. Synthesis of Ru(II) complexes

The product was synthesized by a similar procedure to that previously reported [2]. To a suspension of **btpI/btp** (810 μmol) in ethylene glycol (300 mL) was added dropwise a solution of $[RuCl_2(DMSO)_4]$ (196 mg, 405 μmol) in ethylene glycol (20 mL). The reaction mixture was heated under reflux for 2 h and a yellow colored solution was obtained. A saturated aqueous NH_4PF_6 solution (3 mL) was added, which led to the precipitation of a yellow colored solid. After cooling to room temperature, the suspension was filtered. The residue was thoroughly washed with water and dried in vacuum. Then the solid was redissolved in acetonitrile (50 mL) and filtered to separate impurities. The solvent was removed, and the residue was dried in vacuum to afford the product.

Following the above synthetic procedure and using **btpI** as the starting material, the product $[Ru(btpI)_2](PF_6)_2$ was obtained as a lemon yellow solid (349 mg, 53 %). ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.02 (s, 4H), 8.71-8.40 (m, 6H), 7.91 (d, *J* = 8.1 Hz, 8H), 7.47 (d, *J* = 8.1 Hz, 8H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 150.63, 150.38, 139.20, 135.64, 125.00, 122.71, 121.06, 120.97, 96.80. HRMS (ESI, CH_3OH): m/z = 667.8834, (calcd. 667.8838 for $[Ru(btpI)_2]^{2+}$).

Following the above synthetic procedure and using **btp** as the starting material, the product $[Ru(btp)_2](PF_6)_2$ was obtained as a white solid (227 mg, 50 %). ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.02 (s, 4H), 8.67-8.49 (m, 6H), 7.76-7.62 (m, 8H), 7.61-7.44 (m, 12H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 150.58, 150.52, 139.19, 135.99, 130.64, 130.53, 125.13, 121.03, 120.96. HRMS (ESI, CH_3OH): m/z = 416.0901, (calcd 416.0905 for $[Ru(btp)_2]^{2+}$).

4.5. Synthesis of the polymers POP-Ru-3

A flask was charged with $Ru(btpI)_2(PF_6)_2$ (195 mg, 0.12 mmol), 1, 4-benzenediboronic acid (40 mg, 0.24 mmol), tetrakis(triphenylphosphine)palladium (30 mg, 0.024 mmol), potassium carbonate (325 mg, 2.4 mmol), dimethylformamide (15 mL) and H_2O (5 mL). The mixture was heated to 80 °C and stirred for 72 h under a nitrogen atmosphere. After cooling to room temperature, the reaction mixture was filtered and the resulting solid material was washed with CH_3OH, THF and CH_2Cl_2. Further purification of the polymer was carried out by Soxhlet extraction with CH_3OH and CH_2Cl_2 successively for 24 h each time. The residue was dried under vacuum for 24 h at 100

°C to give POP-Ru-3 in 89% yield as a yellow solid.

4.6. General Procedure for the photosynthesis of thiocarbamates

To a glass tube was added thiols (0.2 mmol), isocyanides (0.5 mmol), photocatalyst (1.0 mol%), H_2O (0.1 mL) and EtOAc (3 mL). The mixture was degassed and filled with O_2 for three times, and then irradiated with blue LED light (6 W) at room temperature and O_2 atmosphere with an O_2 balloon. After reaction, the catalyst was isolated by centrifugation and thoroughly washed with methanol and dichloromethane. The combined organic phases were concentrated under reduced pressure, and the residue was purified by silica gel column chromatography to give the desired product. For reuse studies, the isolated catalyst was dried in vacuum before being reused in further reactions under the same conditions.

4.7. General Procedure for the coupling of thiols

To a glass tube was added thiols (0.4 mmol), photocatalyst (1.0 mol%), CH_3CN (3 mL). The mixture was then irradiated with blue LED light (6 W) at room temperature. After reaction, the catalyst was isolated by centrifugation and thoroughly washed with methanol and dichloromethane. The combined organic phases were concentrated under reduced pressure, and the residue was purified by silica gel column chromatography to give the desired product. For reuse studies, the isolated catalyst was dried in vacuum before being reused in further reactions under the same conditions.

[1] Z. Li, Y. Li, Y. Zhao, H. Wang, Y. Zhang, B. Song, X. Li, S. Lu, X.-Q. Hao, S.-W. Hla, Y. Tu, X. Li, J. Am. Chem. Soc. 142 (2020) 6196-6205.

[2] M. Ostermeier, M.-A. Berlin, R. M. Meudtner, S. Demeshko, F. Meyer, C. Limberg, S. Hecht, Chem. Eur. J. 16 (2010) 10202-10213.

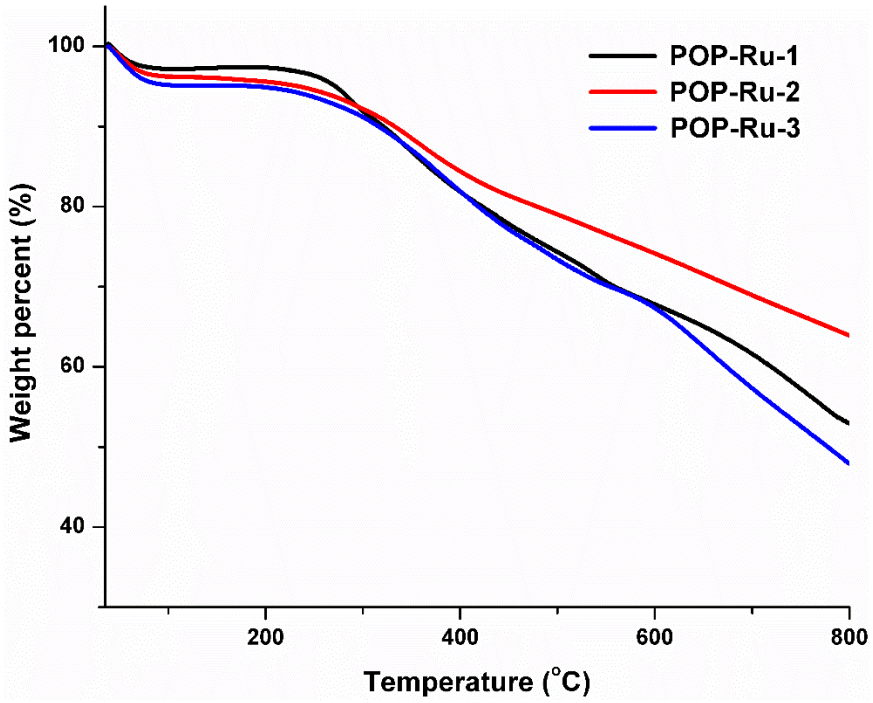


Fig. S1. TGA curves of POP-Ru.

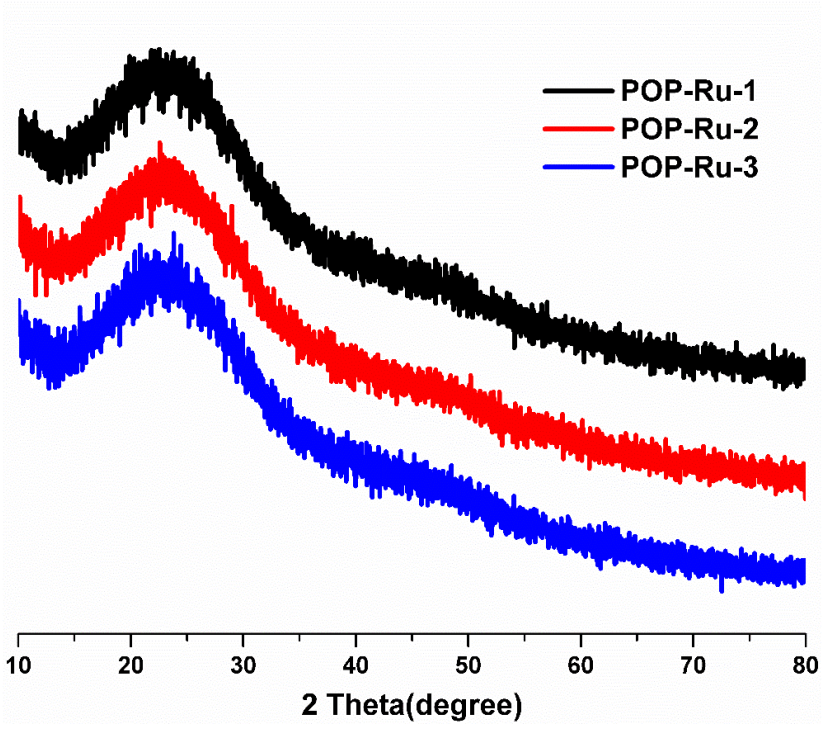


Fig. S2. PXRD curves of POP-Ru.

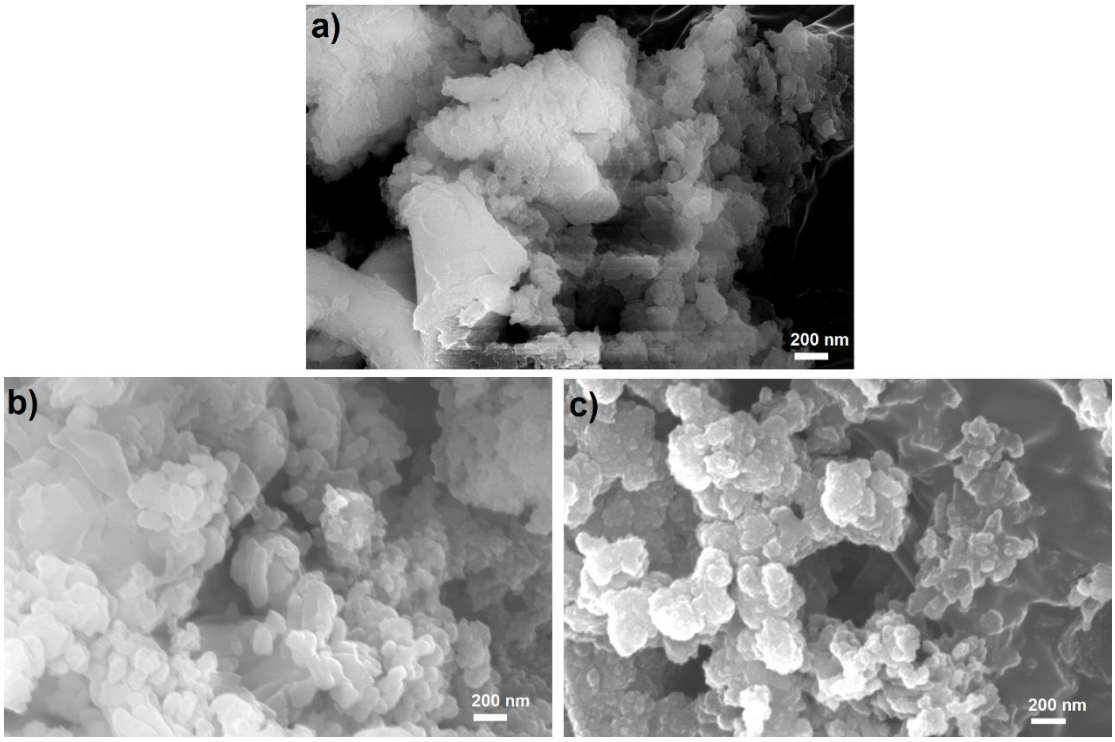


Fig. S3. SEM images of (a) POP-Ru-1, (b) POP-Ru-2 and POP-Ru-3.

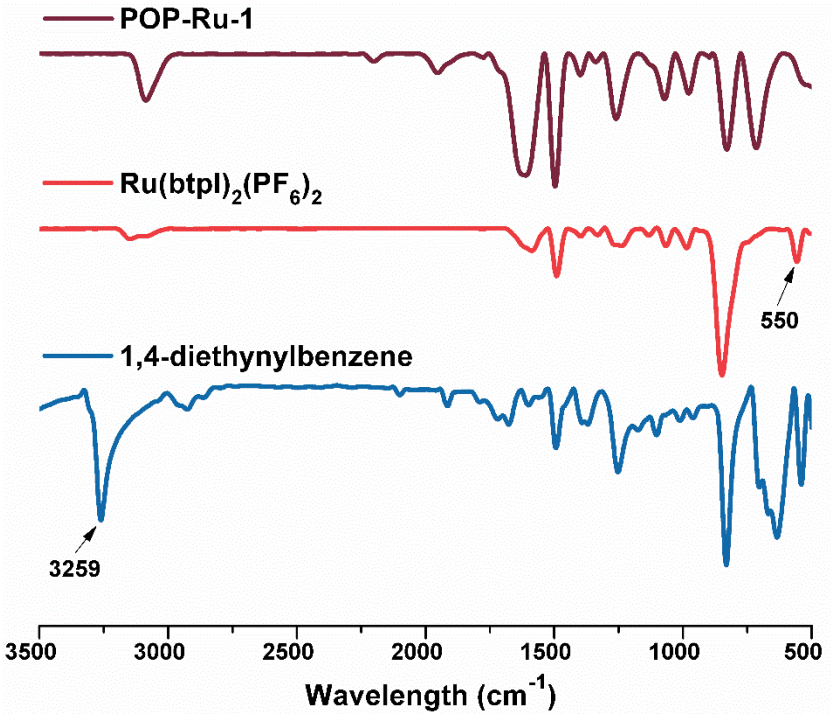


Fig. S4. FT-IR spectra of POP-Ru-1 and corresponding monomers.

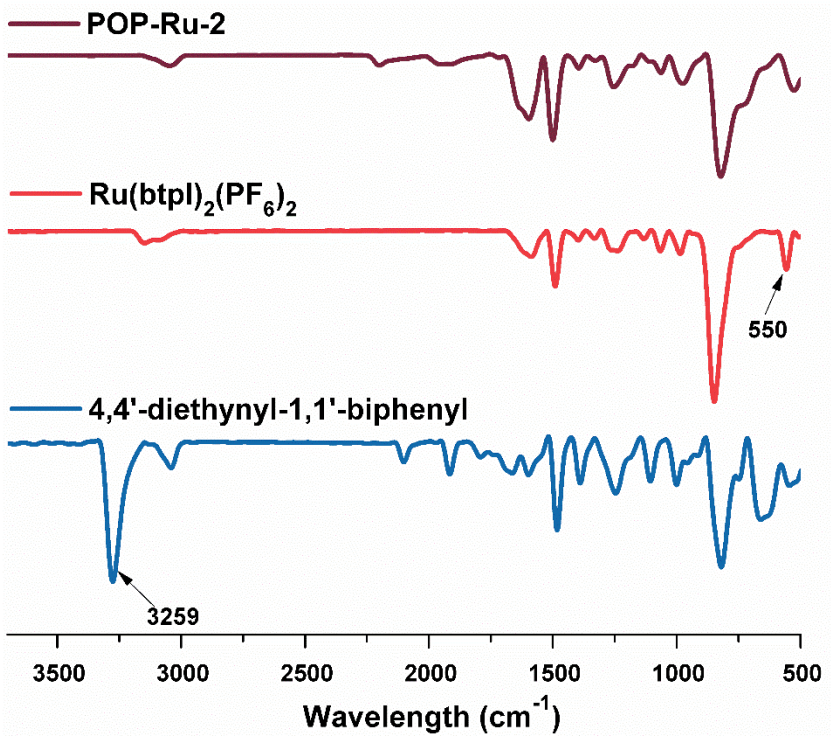


Fig. S5. FT-IR spectra of POP-Ru-2 and corresponding monomers.

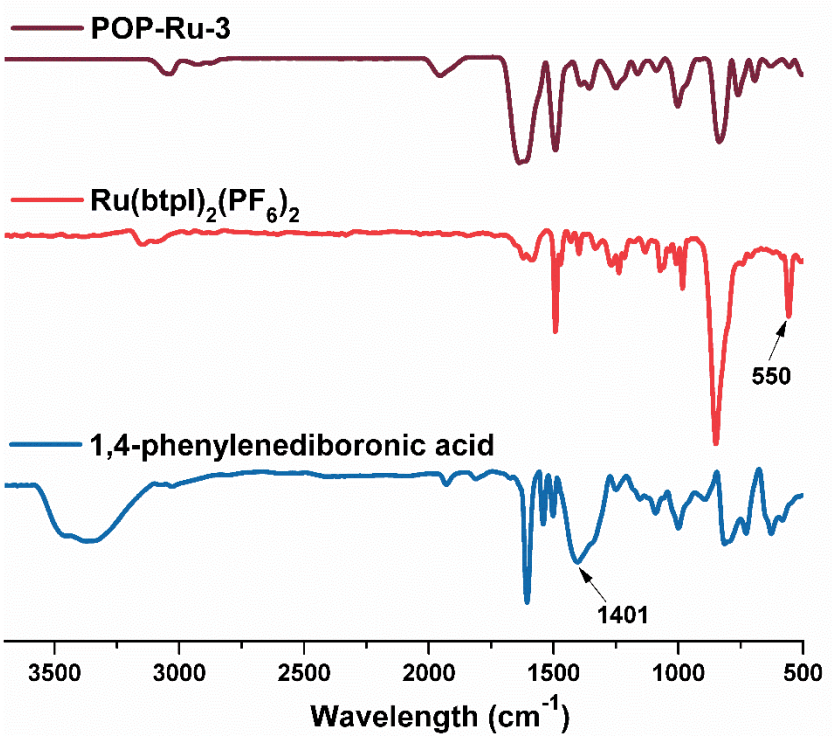


Fig. S6. FT-IR spectra of POP-Ru-3 and corresponding monomers.

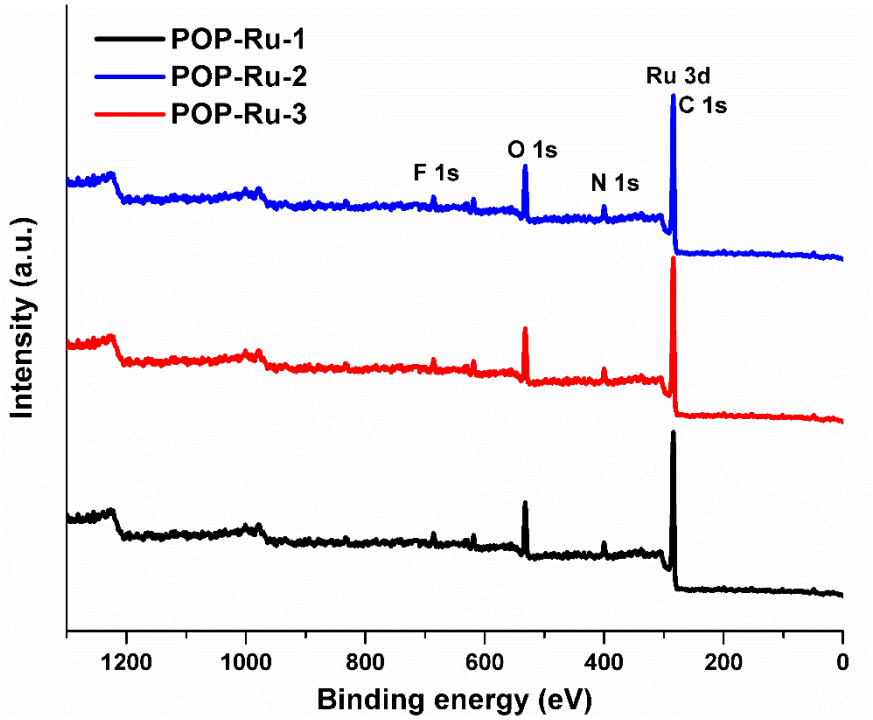


Fig. S7. XPS survey spectra of POP-Ru.

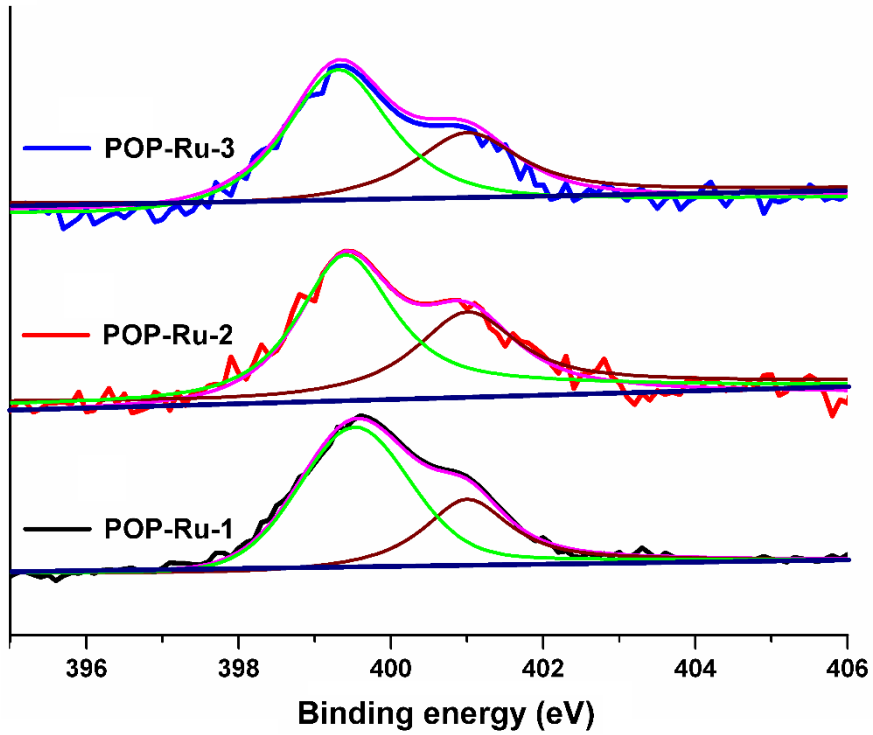


Fig. S8. XPS survey spectra of POP-Ru.

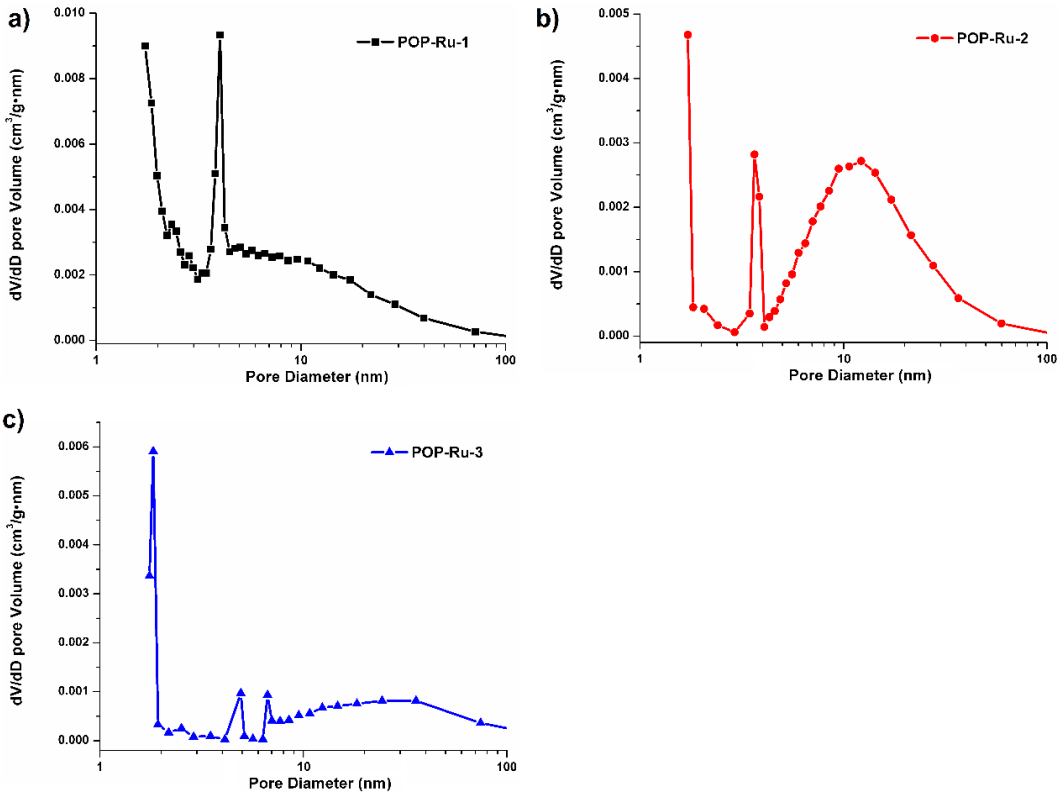


Fig. S9. Pore size distribution of POP-Ru.

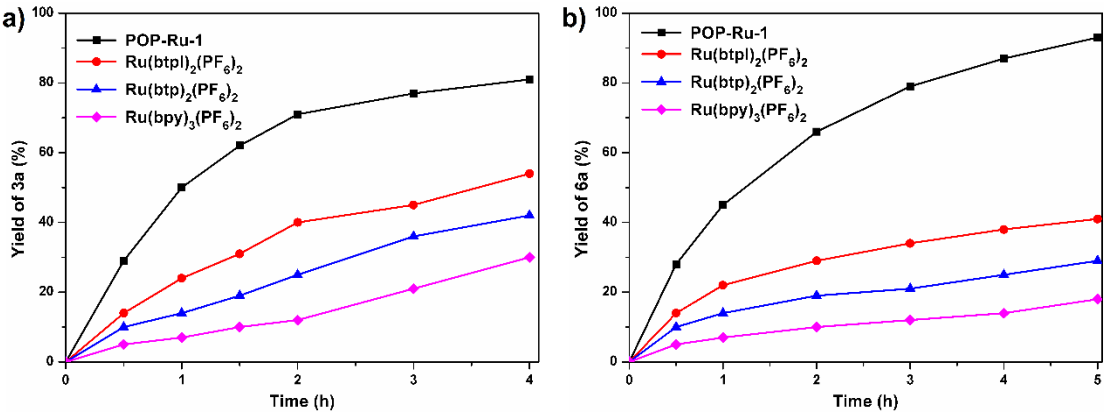


Fig. S10. (a) Visible light induced photosynthesis of thiocarbomates (yield versus reaction time) and (b) Coupling of thiols (yield versus reaction time) catalyzed by POP-Ru-1, $Ru(btpI)_2(PF_6)_2$, $Ru(btp)_2(PF_6)_2$ and $Ru(bpy)_3(PF_6)_2$.

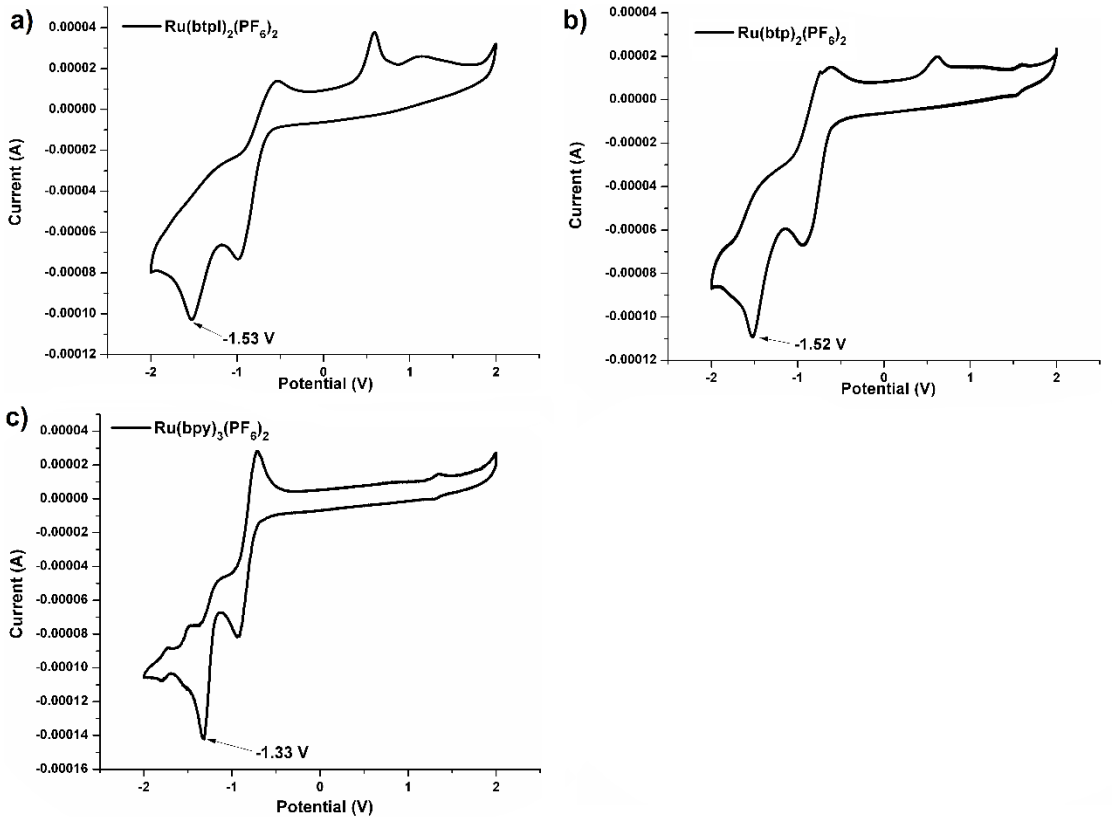


Fig. S11. Cyclic voltammetry (CV) curve of (a) $Ru(btpI)_2(PF_6)_2$, (b) $Ru(btp)_2(PF_6)_2$ and (c) $Ru(bpy)_3(PF_6)_2$.

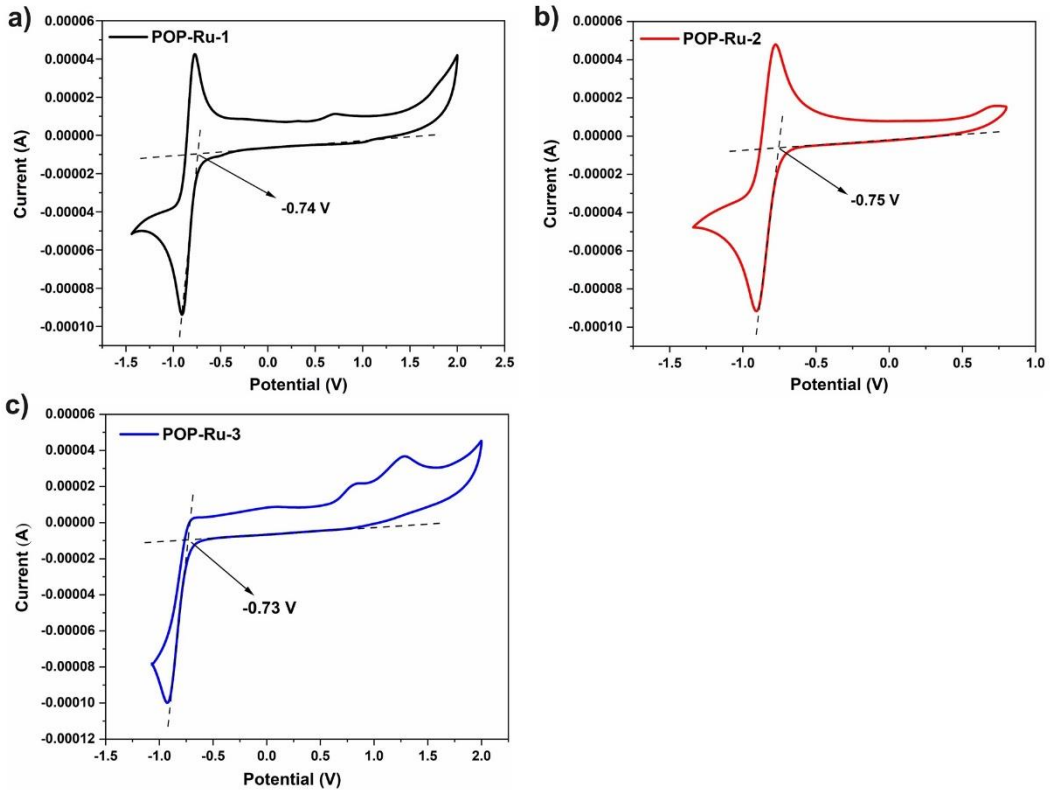
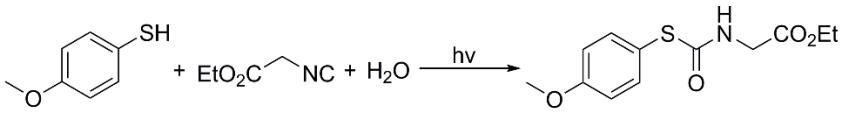


Fig. S12. Cyclic voltammetry (CV) curve of (a) POP-Ru-1, (b) POP-Ru-2 and (c) POP-Ru-3.

Table S1 Photocatalytic reaction of under various conditions[a].



Entry	Catalyst	Atmosphere	Additive	Yield (%)[b]
1	No catalyst	O_2	-	0
2	POP-Ru-1	Dark	-	0
3	POP-Ru-1	N_2	-	Trace
4	POP-Ru-1	Dry	-	Trace
5[c]	POP-Ru-1	O_2	benzoquinone	12
6[d]	POP-Ru-1	O_2	NaN_3	94
7[e]	POP-Ru-1	O_2	TEMPO	10

[a] Reaction conditions: 4-methylthiophenol (0.2 mmol), ethyl isocyanoacetate (0.4 mmol), H_2O (0.1 mL), photocatalyst (1.0 mol%), EtOAc (3 mL), O_2 balloon, blue light LED (6 W), room temperature, 4 h. [b] Isolated yield. [c] benzoquinone as a superoxide scavenger. [d] NaN_3 as a singlet oxygen scavenger. [e] TEMPO as a free radical scavenger.

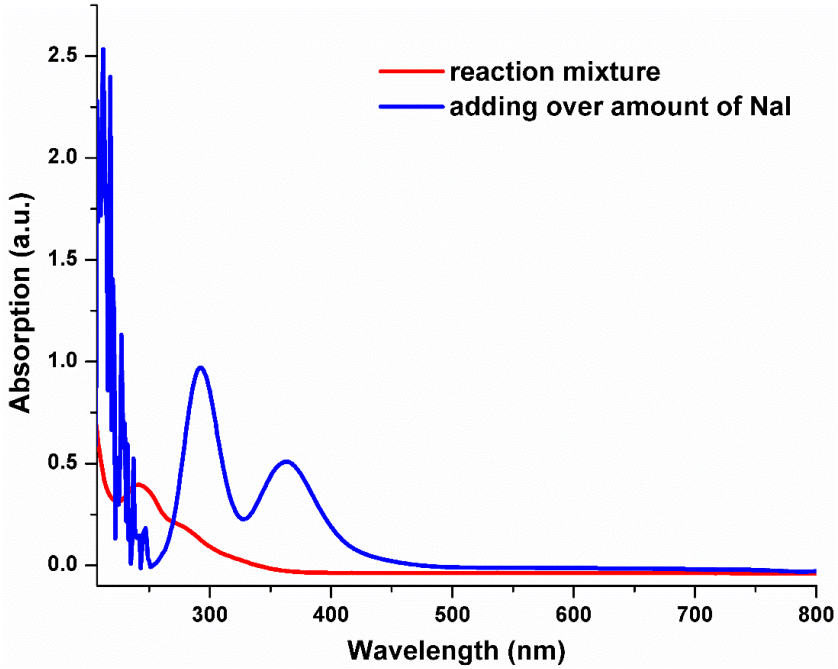


Fig. S13. UV/Vis absorption spectra of the reaction mixture before and after the addition of NaI.

Note: The formed H_2O_2 can oxidize I^- to I_2, which further react with another I^- to form I_3^-. I_3^- shows two characteristic peaks at ~295 and ~360 nm in UV/Vis spectra.

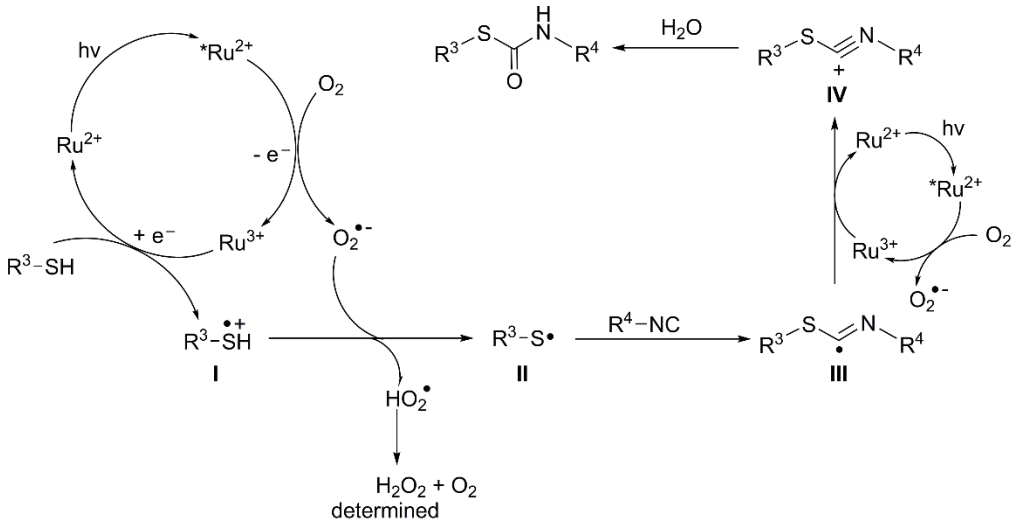


Fig. S14. Proposed reaction mechanism for photosynthesis of thiocarbomates.

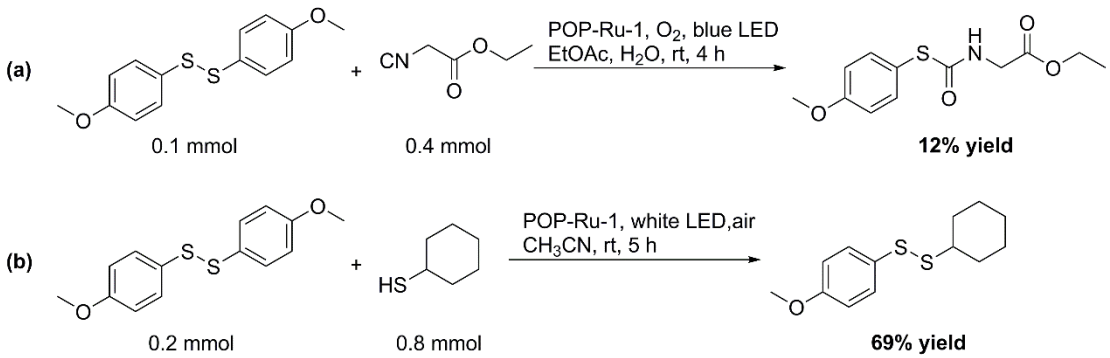
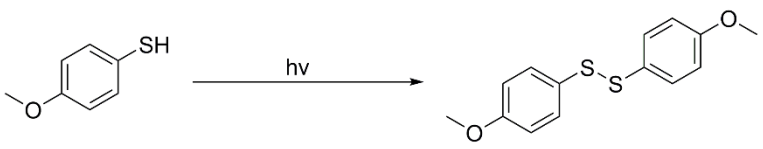


Fig. S15. Control experiments.

Table S2 Visible light driven oxidative alkylation of styrene under various conditions[a].



Entry	Catalyst	Atmosphere	Additive	Yield (%)[b]
1	POP-Ru-1	Dark	-	Trace
2	No catalyst	Air	-	Trace
3	POP-Ru-1	N_2	-	89
4[c]	POP-Ru-1	Air	TEMPO	13

[a] Reaction conditions: 4-methoxythiophenol (0.4 mmol), photocatalyst (0.5 mol%), white LED (6 W), solvent (3 mL), air, room temperature, 5 h. [b] Isolated yield. [c] TEMPO as a free radical scavenger.

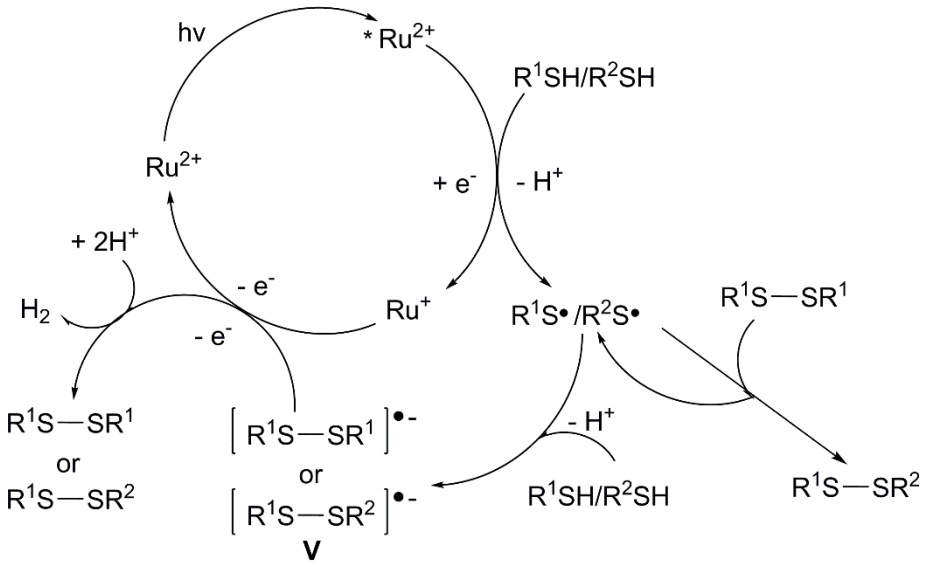


Fig. S16. Proposed reaction mechanism for coupling of thiols.

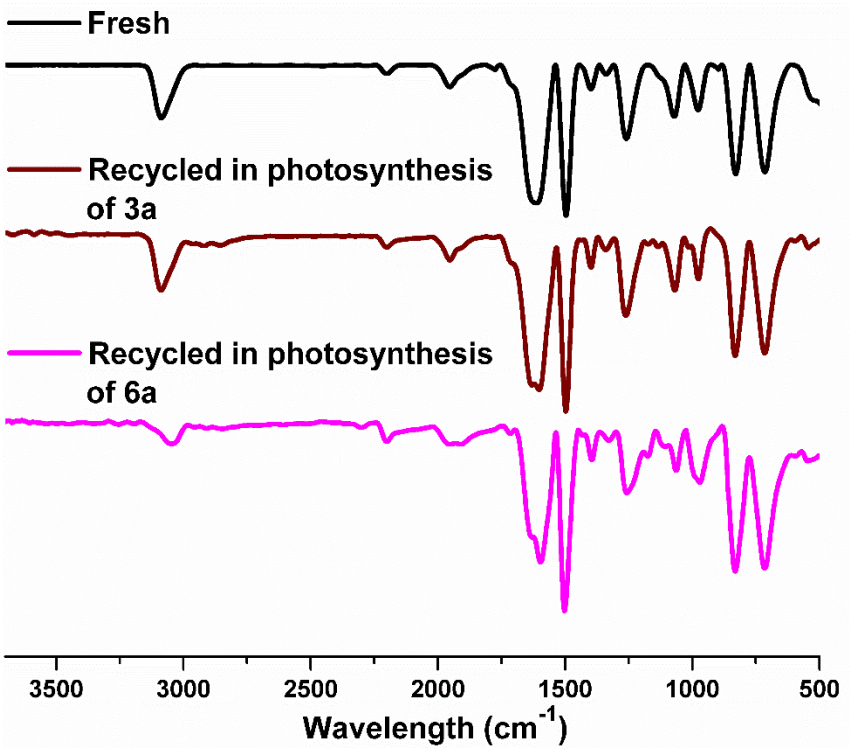


Fig. S17. FT-IR spectra of fresh and recycled POP-Ru-1.

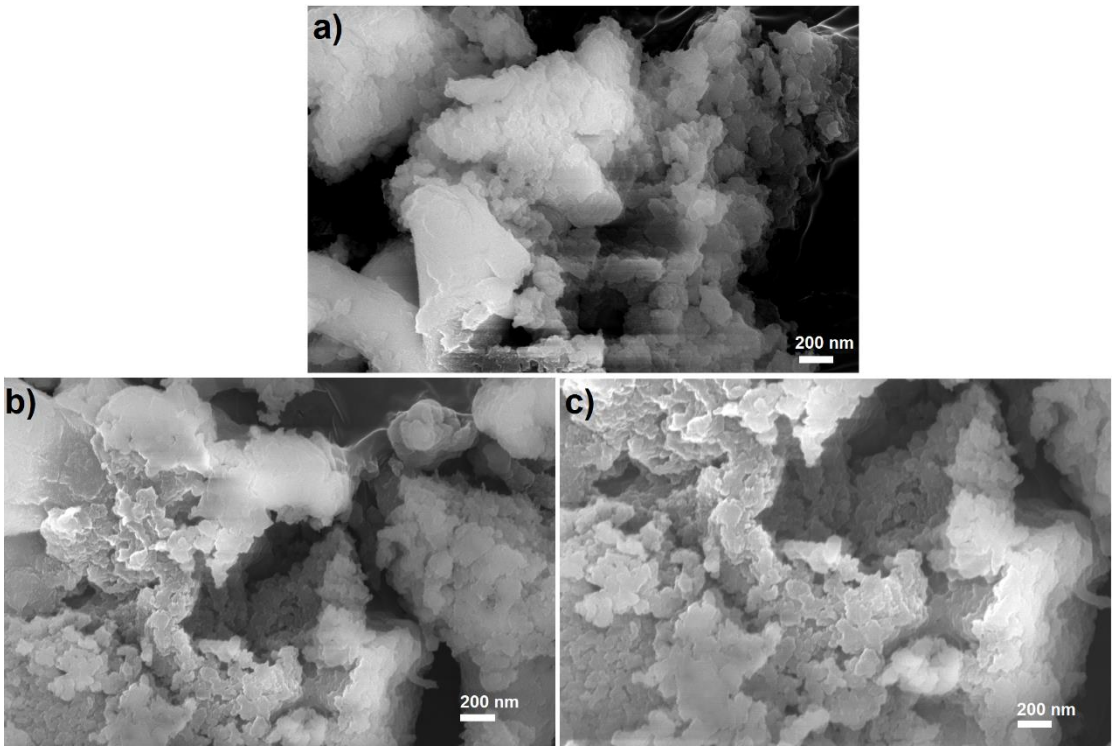


Fig. S18. SEM images of (a) fresh POP-Ru-1, (b) 10th recycled POP-Ru-1 in photosynthesis of 3a, and (c) 10th recycled POP-Ru-1 in photosynthesis of 6a.

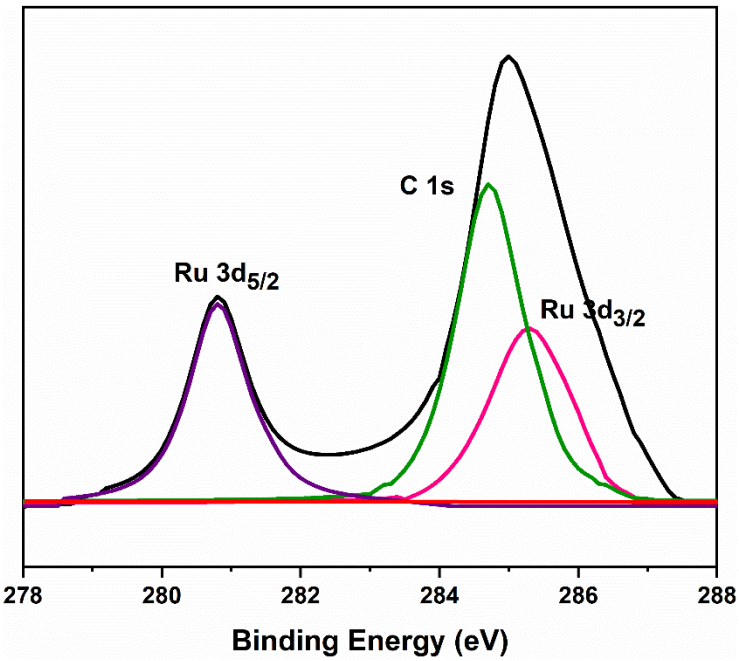
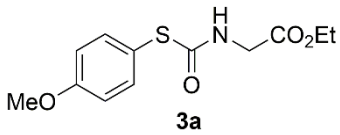


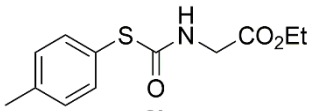
Fig. S18. Ru 3d spectra of recycled POP-Ru-1 in photosynthesis of 3a.

Products characterization



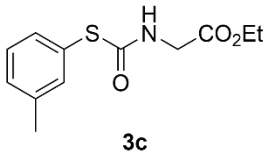
3a

Prepared according to general catalytic procedure and obtained as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.53-7.45 (m, 2H), 6.98-6.91 (m, 2H), 5.89 (s, 1H), 4.18 (q, *J* = 7.2 Hz, 2H), 4.01 (d, *J* = 5.2 Hz, 2H), 3.83 (s, 3H), 1.26 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 169.33, 167.81, 161.14, 137.37, 118.59, 115.25, 61.70, 55.43, 42.64, 14.12.



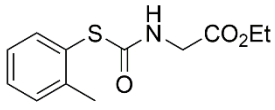
3b

Prepared according to general catalytic procedure and obtained as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.46 (d, *J* = 8.0 Hz, 2H), 7.23 (d, *J* = 8.0 Hz, 2H), 5.92 (s, 1H), 4.18 (q, *J* = 7.2 Hz, 2H), 4.01 (d, *J* = 5.1 Hz, 2H), 2.38 (s, 3H), 1.26 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 168.28, 166.34, 139.38, 134.57, 129.42, 123.47, 60.66, 41.64, 20.33, 13.08.



3c

Prepared according to general catalytic procedure and obtained as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.43-7.35 (m, 2H), 7.32 (t, *J* = 7.5 Hz, 1H), 7.25 (d, *J* = 7.5 Hz, 1H), 5.92 (s, 1H), 4.20 (q, *J* = 7.2 Hz, 2H), 4.02 (d, *J* = 5.1 Hz, 2H), 2.37 (s, 3H), 1.26 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 169.27, 167.11, 139.59, 136.16, 132.60, 130.84, 129.44, 127.66, 61.71, 42.69, 21.26, 14.12.



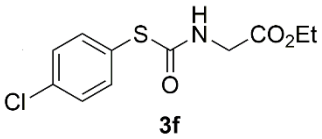
3d

Prepared according to general catalytic procedure and obtained as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.59 (d, *J* = 7.6 Hz, 1H), 7.43-7.30 (m, 2H), 7.28-7.22 (m, 1H), 5.79 (s, 1H), 4.19 (q, *J* = 7.2 Hz, 2H), 4.01 (d, *J* = 5.2 Hz, 2H), 2.49 (s, 3H), 1.26 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 169.28, 166.70, 143.12, 137.10, 131.20, 130.78, 127.46, 127.13, 61.70, 42.62, 21.09, 14.12.

3e

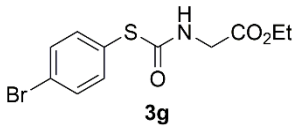
Prepared according to general catalytic procedure and obtained as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.58-7.49 (m, 2H), 7.15-7.05 (m, 2H), 6.02 (s, 1H), 4.20 (q, *J* = 7.2 Hz, 2H), 4.03 (d, *J* = 5.1 Hz, 2H), 1.27 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (1

01 MHz, $CDCl_3$): δ 169.30, 166.56, 164.98, 162.49, 137.74, 137.65, 123.27, 123.24, 116.79, 116.57, 61.80, 42.76, 14.11.



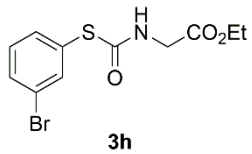
3f

Prepared according to general catalytic procedure and obtained as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.53-7.46 (m, 2H), 7.42-7.36 (m, 2H), 5.92 (s, 1H), 4.22 (q, *J* = 7.2 Hz, 2H), 4.05 (d, *J* = 5.1 Hz, 2H), 1.28 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 169.23, 166.02, 136.71, 136.30, 129.67, 126.34, 61.86, 42.79, 14.13.



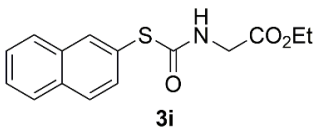
3g

Prepared according to general catalytic procedure and obtained as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.60-7.50 (m, 2H), 7.49-7.35 (m, 2H), 5.93 (s, 1H), 4.21 (q, *J* = 7.2 Hz, 2H), 4.03 (d, *J* = 5.2 Hz, 2H), 1.27 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 169.21, 165.84, 136.89, 132.61, 126.99, 124.54, 61.86, 42.80, 14.13.



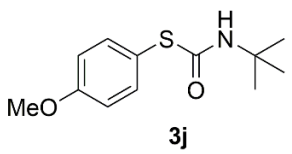
3h

Prepared according to general catalytic procedure and obtained as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.72 (t, *J* = 1.7 Hz, 1H), 7.58-7.46 (m, 2H), 7.29 (t, *J* = 7.7 Hz, 1H), 5.95 (s, 1H), 4.23 (q, *J* = 7.2 Hz, 2H), 4.06 (d, *J* = 5.1 Hz, 2H), 1.28 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.18, 165.65, 137.85, 133.96, 132.83, 130.64, 129.87, 122.82, 61.89, 42.83, 14.14.



3i

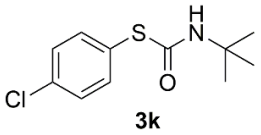
Prepared according to general catalytic procedure and obtained as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.12 (s, 1H), 7.93-7.82 (m, 3H), 7.64-7.50 (m, 3H), 5.95 (s, 1H), 4.18 (q, *J* = 7.2 Hz, 2H), 4.04 (d, *J* = 5.1 Hz, 2H), 1.25 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 169.23, 166.95, 135.66, 133.62, 133.51, 131.65, 129.32, 128.09, 127.84, 127.51, 126.86, 125.18, 61.74, 42.72, 14.10.



3j

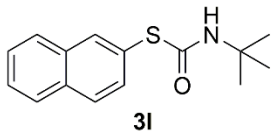
Prepared according to general catalytic procedure and obtained as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.47-7.42 (m, 2H), 6.95-6.90 (m, 2H), 5.17 (s, 1H), 3.82 (s, 3H), 1.31 (s, 9H). ^{13}C NMR (101

MHz, $CDCl_3$): δ 164.98, 160.71, 137.20, 119.86, 114.93, 55.40, 53.37, 28.85.



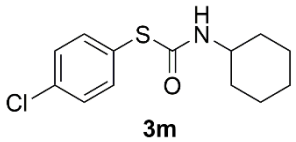
3k

Prepared according to general catalytic procedure and obtained as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.46-7.40 (m, 2H), 7.36-7.32 (m, 2H), 5.22 (s, 1H), 1.34 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 163.18, 136.56, 135.66, 129.34, 127.42, 53.73, 28.88.



3l

Prepared according to general catalytic procedure and obtained as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.06 (s, 1H), 7.89-7.80 (m, 3H), 7.58 (dd, J_1 = 8.5, J_2 = 1.8 Hz, 1H), 7.55-7.48 (m, 2H), 5.24 (s, 1H), 1.33 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 164.06, 135.16, 133.56, 133.28, 131.76, 128.88, 128.03, 127.77, 127.16, 126.60, 126.35, 53.60, 28.87.

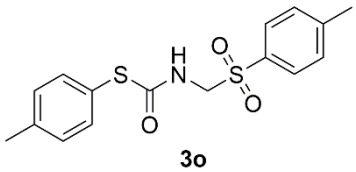


3m

Prepared according to general catalytic procedure and obtained as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.48-7.42 (m, 2H), 7.39-7.34 (m, 2H), 5.21 (s, 1H), 3.72 (s, 1H), 1.98-1.86 (d, J = 9.3 Hz, 2H), 1.68 (d, J = 12.4 Hz, 2H), 1.39-1.09 (m, 6H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 164.03, 136.52, 135.82, 129.44, 127.21, 50.85, 32.96, 25.34, 24.65.

3n

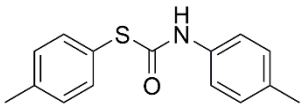
Prepared according to general catalytic procedure and obtained as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.43 (d, J = 8.1 Hz, 2H), 7.21 (d, J = 8.1 Hz, 2H), 5.21 (d, J = 7.9 Hz, 1H), 3.72 (d, J = 7.9 Hz, 1H), 2.37 (s, 3H), 1.96-1.79 (m, 2H), 1.66-1.48 (m, 3H), 1.40-1.00 (m, 5H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 165.47, 139.97, 135.46, 130.27, 125.41, 50.43, 32.87, 25.37, 24.59, 21.34.



3o

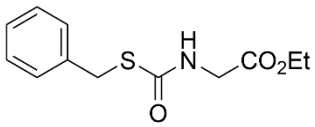
Prepared according to general catalytic procedure and obtained as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.77 (d, J = 8.2 Hz, 2H), 7.37 (d, J = 8.2 Hz, 2H), 7.30 (d, J = 7.9 Hz, 2H), 7.22 (d, J = 7.9 Hz, 2H), 6.14 (t, J = 6.7 Hz, 1H), 4.60 (d, J = 6.7 Hz, 2H), 2.46 (s, 3H), 2.38 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 167.06, 145.67, 140.95, 135.48, 133.50, 130.62, 130.08, 128.99, 123.33,

61.16, 21.81, 21.39.



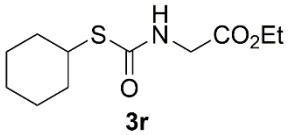
3p

Prepared according to general catalytic procedure and obtained as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 (d, *J* = 8.1 Hz, 2H), 7.17-7.13 (m, 4H), 7.07 (s, 1H), 6.99 (d, *J* = 8.4 Hz, 2H), 2.30 (s, 3H), 2.20 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 163.74, 139.31, 134.60, 134.03, 133.19, 129.34, 128.51, 123.65, 118.65, 20.33, 19.81.



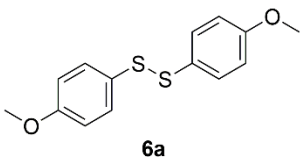
3q

Prepared according to general catalytic procedure and obtained as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36-7.27 (m, 4H), 7.26-7.21 (m, 1H), 5.85 (s, 1H), 4.23 (q, *J* = 7.1 Hz, 2H), 4.17 (s, 2H), 4.08 (d, *J* = 4.9 Hz, 2H), 1.29 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 168.35, 166.35, 136.96, 127.80, 127.56, 126.24, 60.74, 41.77, 33.20, 13.11.



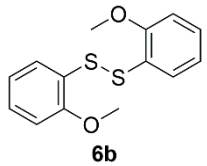
3r

Prepared according to general catalytic procedure and obtained as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.84 (s, 1H), 4.21 (q, *J* = 7.1 Hz, 2H), 4.04 (d, *J* = 5.1 Hz, 2H), 3.56-3.37 (m, 1H), 2.03-1.91 (m, 2H), 1.75-1.65 (m, 2H), 1.61-1.53 (m, 1H), 1.49-1.36 (m, 4H), 1.28 (t, *J* = 7.1 Hz, 3H), 1.25-1.20 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 169.55, 167.93, 61.68, 43.77, 42.56, 33.71, 26.01, 25.53, 14.15.



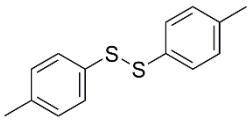
6a

Prepared according to general catalytic procedure and obtained as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.40 (d, *J* = 8.8 Hz, 4H), 6.84 (d, *J* = 8.8 Hz, 4H), 3.80 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 159.94, 132.73, 128.44, 114.65, 55.40.



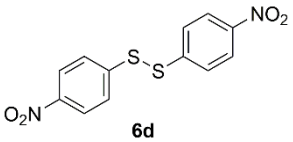
6b

Prepared according to general catalytic procedure and obtained as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.58-7.50 (m, 2H), 7.22-7.16 (m, 2H), 6.94-6.84 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 156.61, 127.80, 127.55, 124.55, 121.39, 110.51, 55.93.



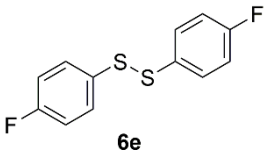
6c

Prepared according to general catalytic procedure and obtained as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.41 (d, J = 8.2 Hz, 4H), 7.12 (d, J = 8.2 Hz, 4H), 2.34 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 137.50, 133.94, 129.86, 128.56, 21.13.



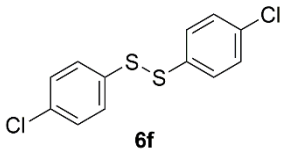
6d

Prepared according to general catalytic procedure and obtained as a yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.20 (d, J = 8.9 Hz, 4H), 7.62 (d, J = 8.9 Hz, 4H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 146.96, 144.09, 126.37, 124.49.



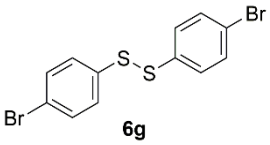
6e

Prepared according to general catalytic procedure and obtained as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.49-7.39 (m, 4H), 7.05-6.95 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 163.87, 161.41, 132.21, 132.18, 131.34, 131.26, 116.44, 116.22.



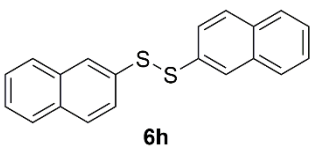
6f

Prepared according to general catalytic procedure and obtained as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.44-7.36 (m, 4H), 7.29-7.27 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 133.17, 131.68, 127.37, 127.36.



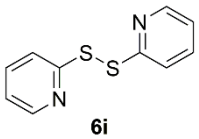
6g

Prepared according to general catalytic procedure and obtained as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.48-7.38 (m, 4H), 7.37-7.28 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 135.77, 132.26, 129.43, 121.58.



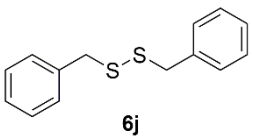
6h

Prepared according to general catalytic procedure and obtained as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.00 (s, 2H), 7.83-7.71 (m, 6H), 7.68-7.60 (m, 2H), 7.51-7.41 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 134.32, 133.52, 132.55, 129.03, 127.82, 127.52, 126.79, 126.60, 126.29, 125.71.



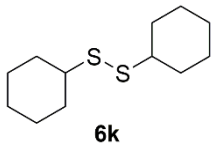
6i

Prepared according to general catalytic procedure and obtained as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.48-8.43 (m, 2H), 7.63-7.56 (m, 4H), 7.12-7.07 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 158.94, 149.61, 137.46, 121.15, 119.67.



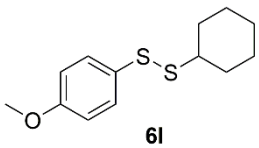
6j

Prepared according to general catalytic procedure and obtained as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.36-7.21 (m, 10H), 3.59 (s, 4H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 137.40, 129.47, 128.53, 127.48, 43.27.



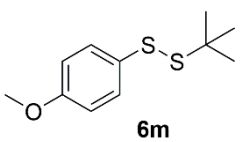
6k

Prepared according to general catalytic procedure and obtained as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.77-2.60 (m, 2H), 2.09-2.00 (m, 4H), 1.83-1.73 (m, 4H), 1.65-1.58 (m, 2H), 1.35-1.21 (m, 10H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 49.99, 32.87, 26.11, 25.71.



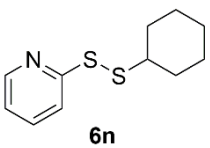
6l

Prepared according to general catalytic procedure and obtained as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.58-7.36 (m, 2H), 6.90-6.78 (m, 2H), 3.79 (s, 3H), 2.92-2.65 (m, 1H), 2.05-1.96 (m, 2H), 1.80-1.70 (m, 2H), 1.64-1.57 (m, 1H), 1.38-1.21 (m, 5H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 159.16, 131.18, 129.39, 114.56, 55.40, 49.68, 32.60, 26.02, 25.66.



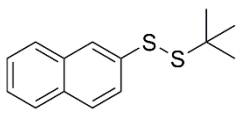
6m

Prepared according to general catalytic procedure and obtained as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.52-7.46 (m, 2H), 6.85-6.81 (m, 2H), 3.79 (s, 3H), 1.29 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 158.92, 130.30, 129.77, 114.44, 55.38, 48.97, 29.92.



6n

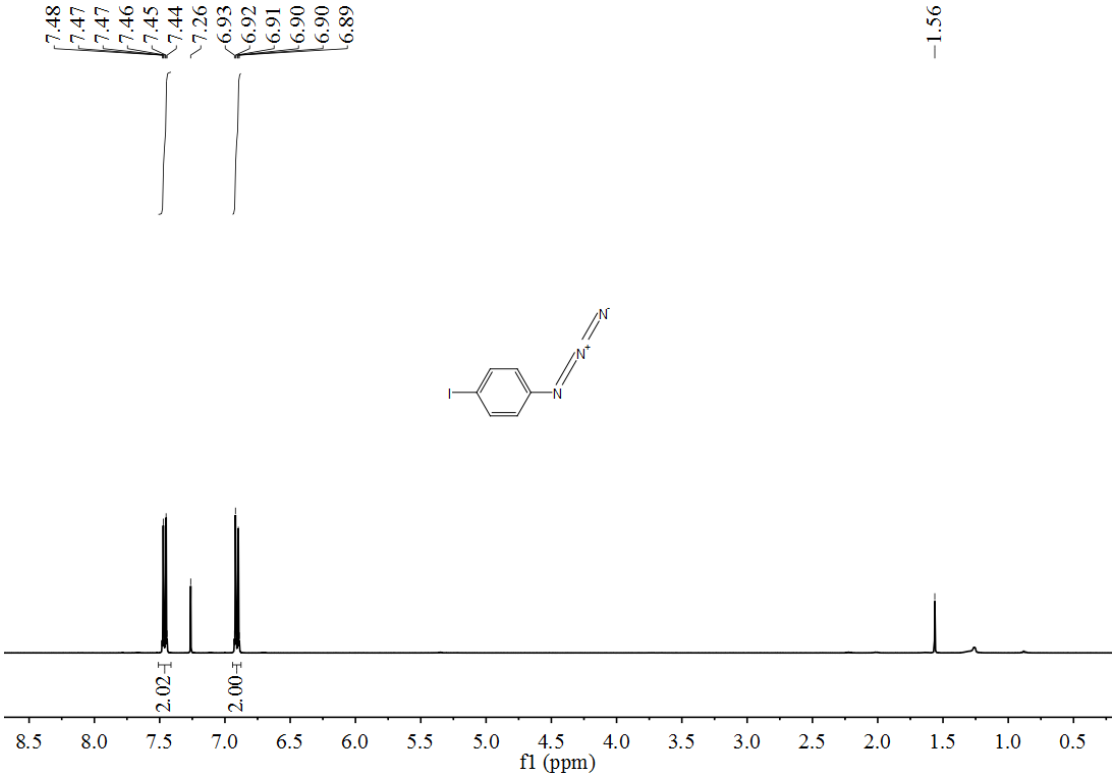
Prepared according to general catalytic procedure and obtained as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.50-8.29 (m, 1H), 7.78-7.71 (m, 1H), 7.66-7.53 (m, 1H), 7.08-7.97 (m, 1H), 2.87-2.75 (m, 1H), 2.04-1.97 (m, 2H), 1.76-1.68 (m, 2H), 1.58-1.50 (m, 1H), 1.39-1.15 (m, 5H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 168.28, 166.34, 139.38, 134.57, 129.42, 123.47, 60.66, 41.64, 20.33, 13.08.



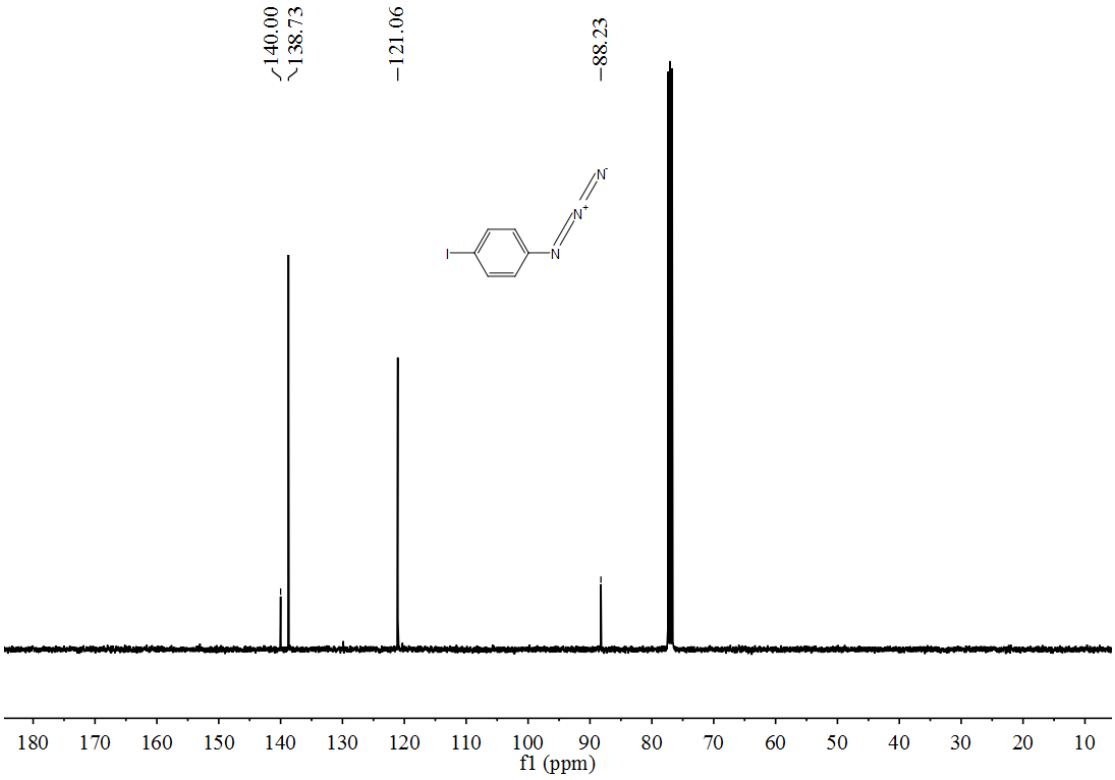
6o

Prepared according to general catalytic procedure and obtained as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.00 (s, 1H), 7.82-7.75 (m, 3H), 7.69-7.64 (m, 1H), 7.50-7.41 (m, 2H), 1.33 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 168.28, 166.34, 139.38, 134.57, 129.42, 123.47, 60.66, 41.64, 20.33, 13.08.

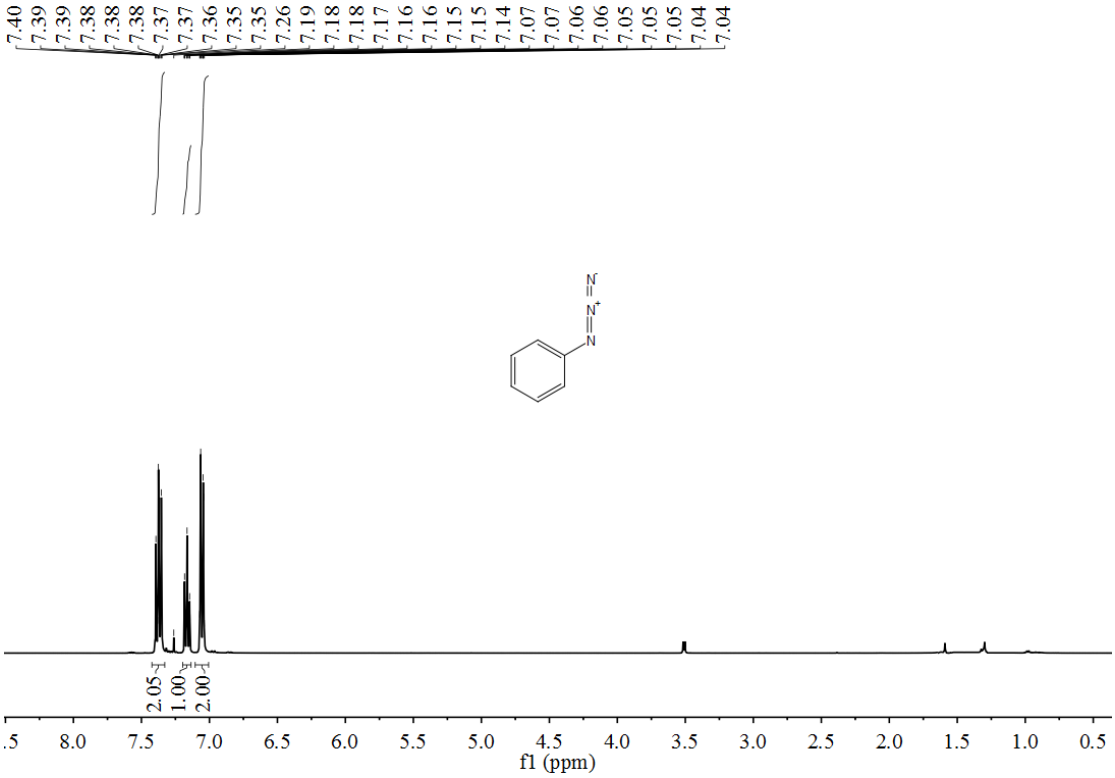
Copies of NMR spectra of building blocks



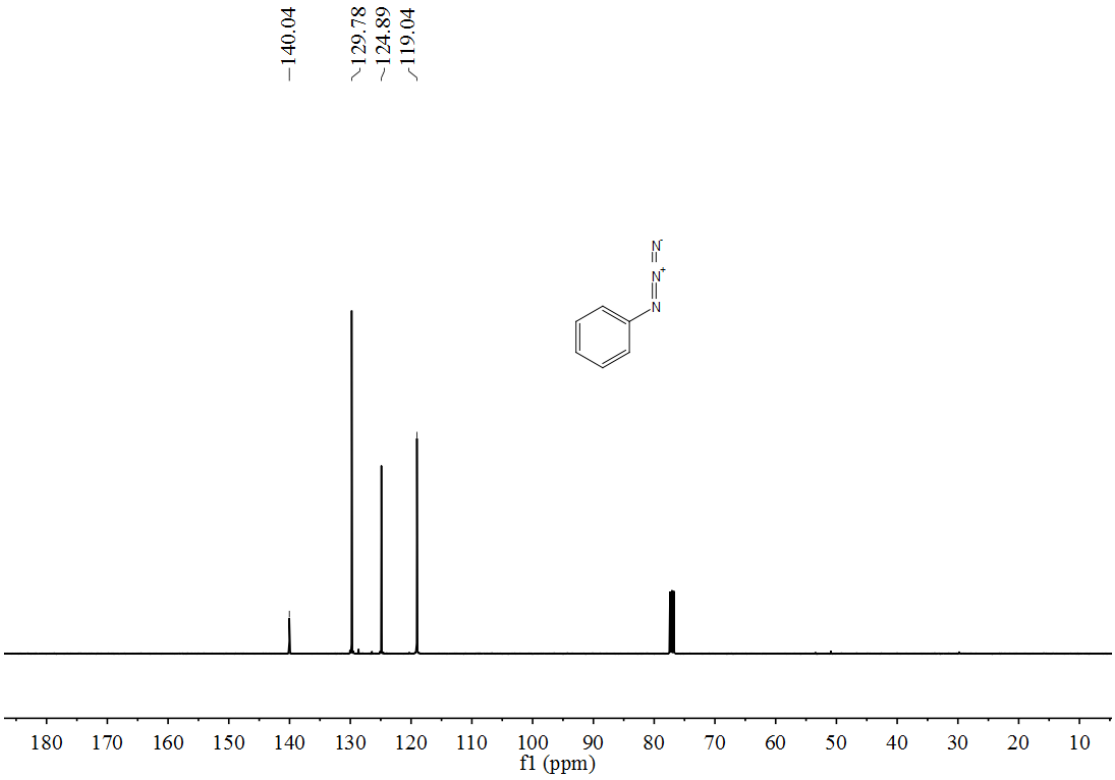
^{1}H NMR spectrum of **B1**



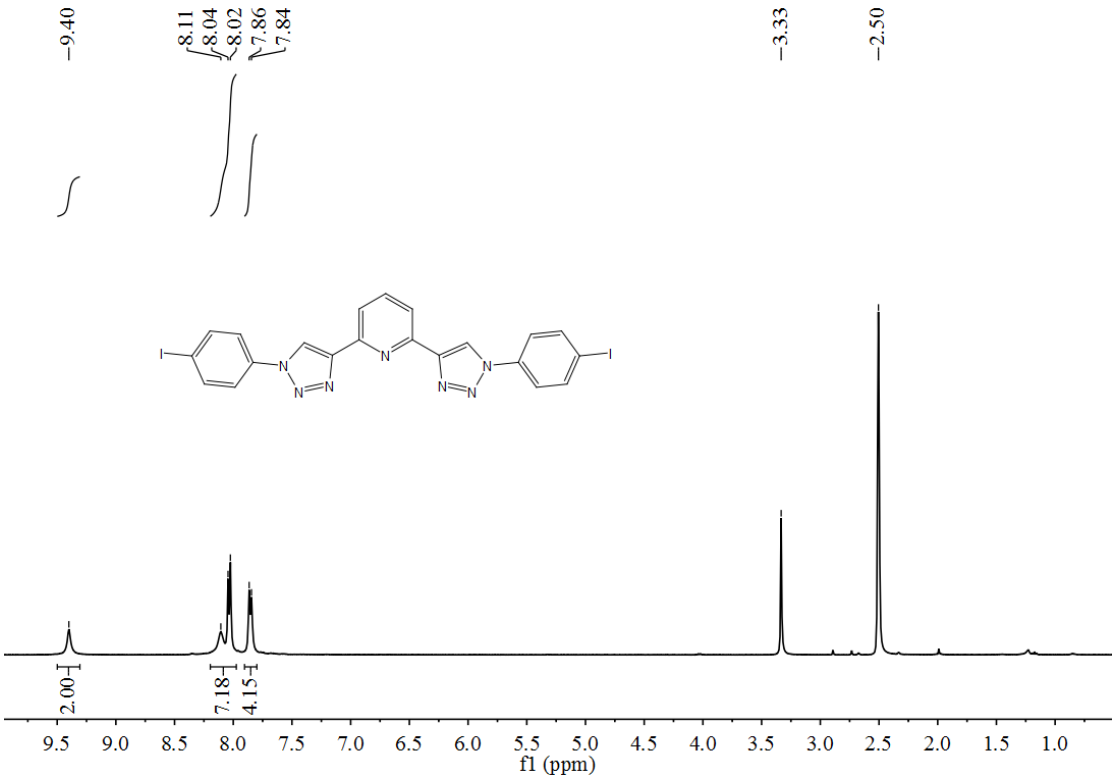
^{13}C NMR spectrum of **B1**



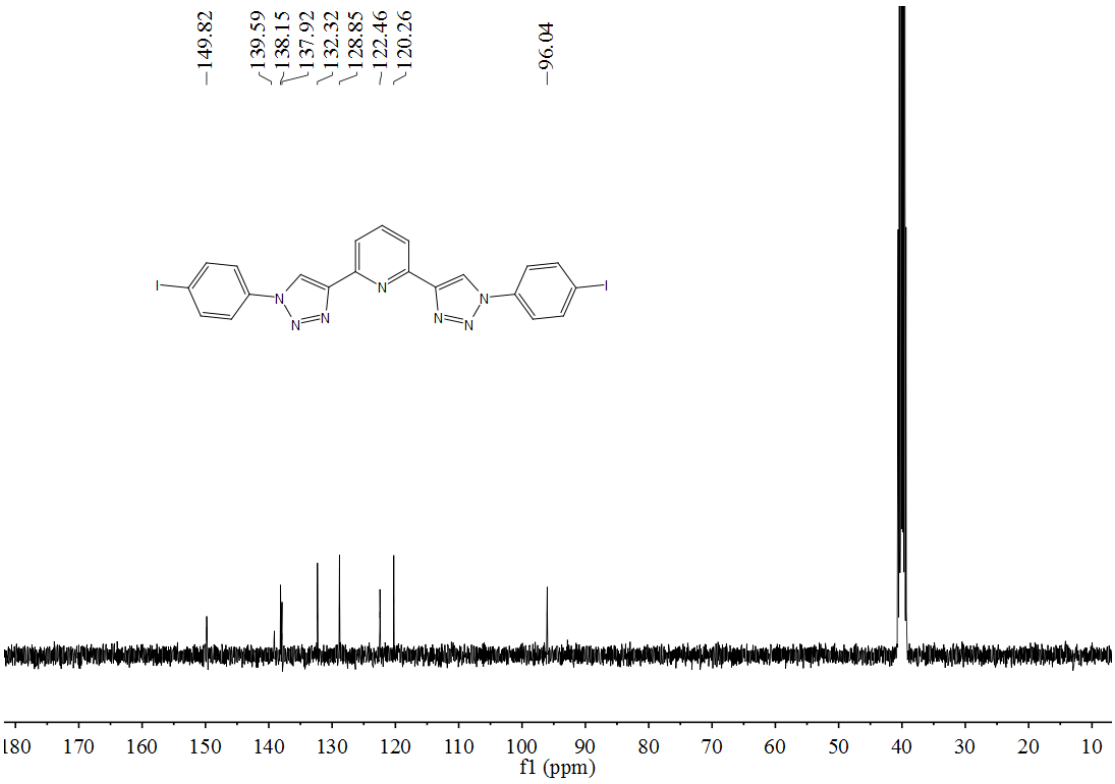
^{1}H NMR spectrum of **B2**



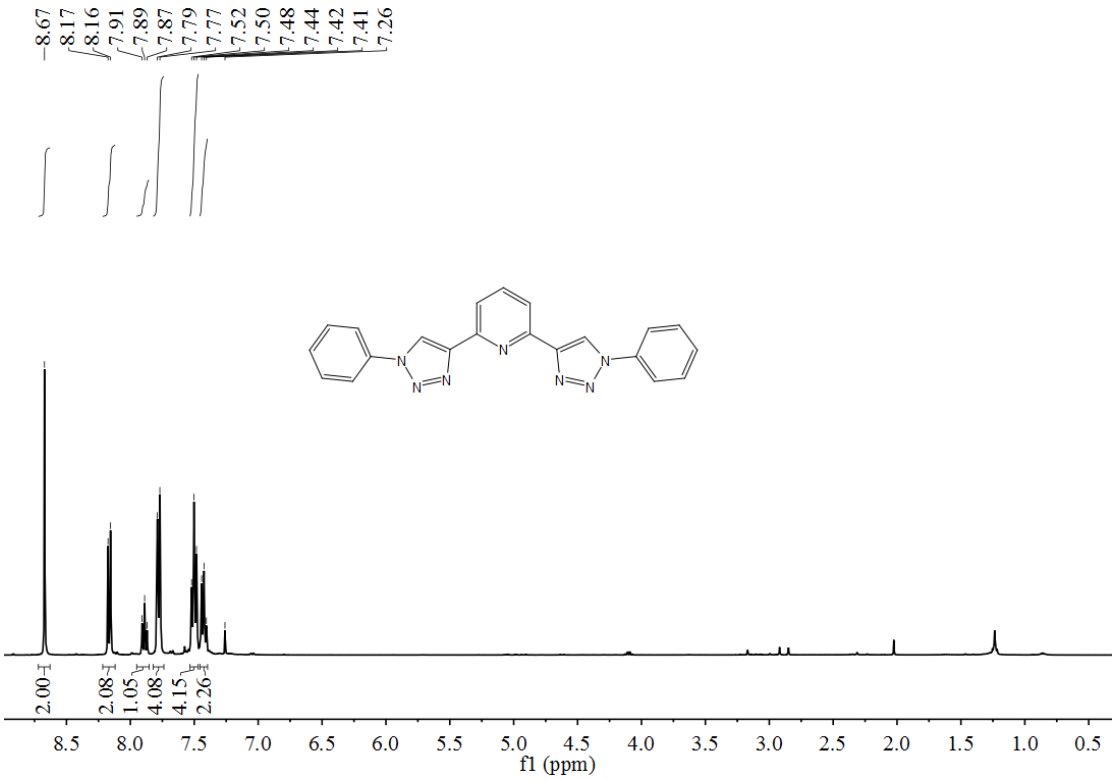
^{13}C NMR spectrum of **B2**



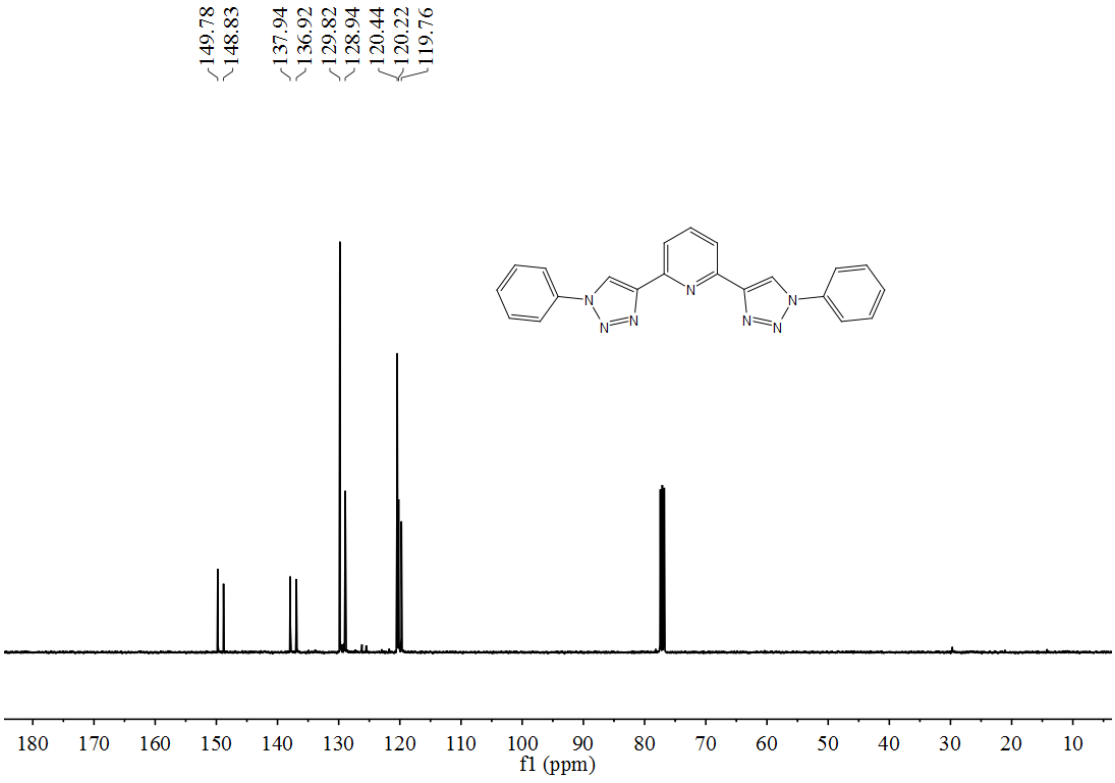
^{1}H NMR spectrum of **btpI**



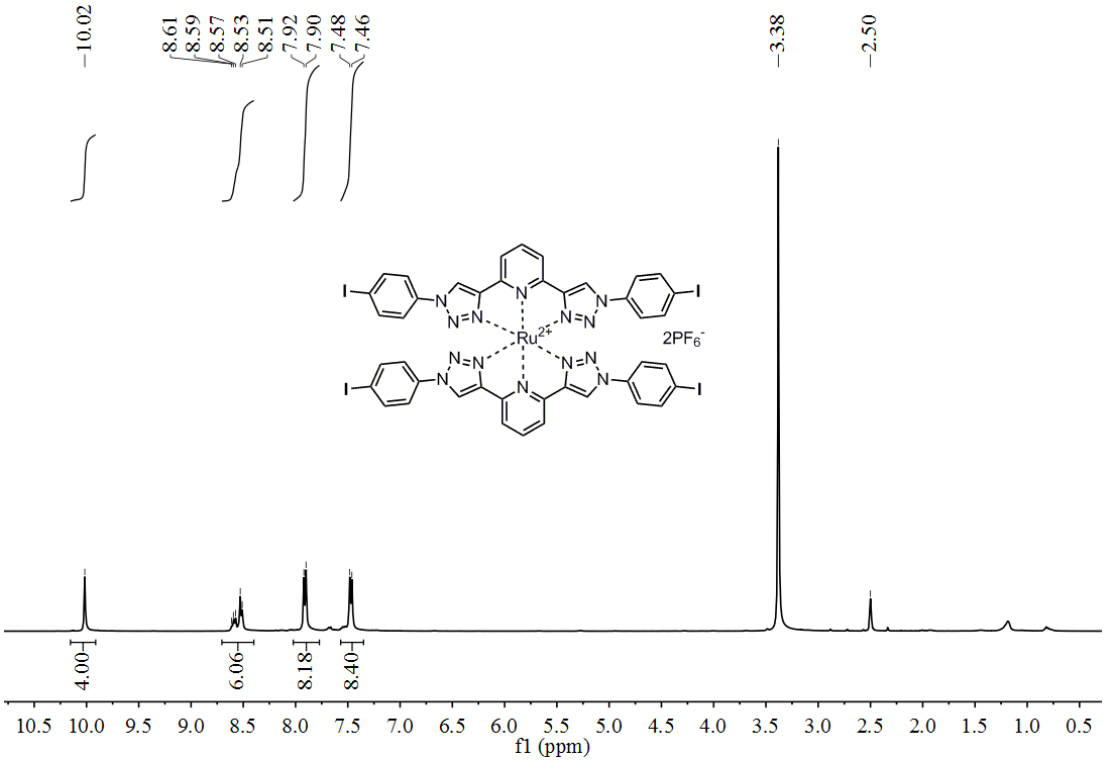
^{13}C NMR spectrum of **btpI**



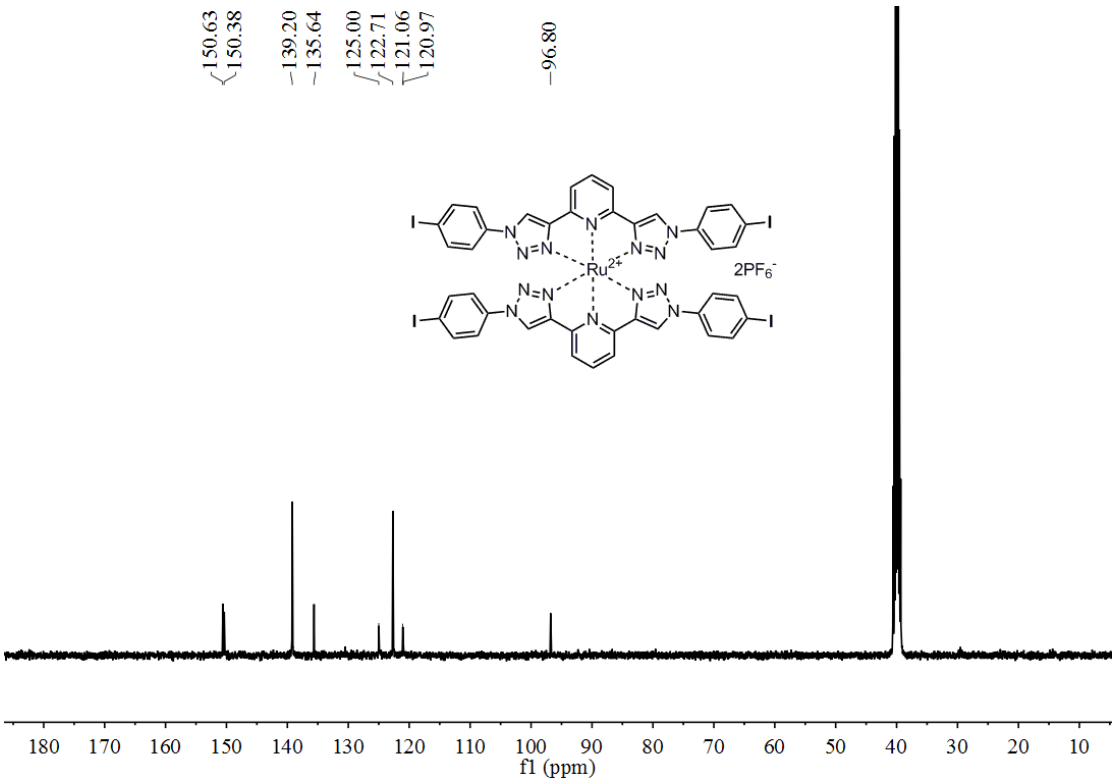
^{1}H NMR spectrum of **btp**



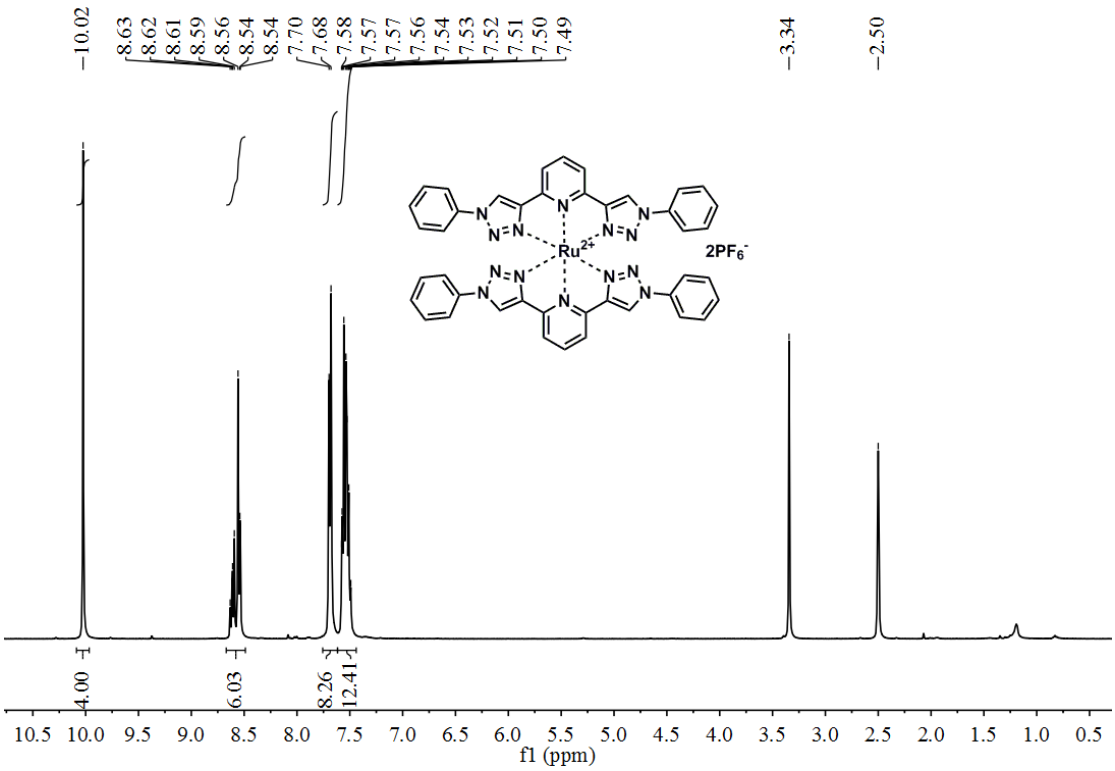
^{13}C NMR spectrum of **btp**



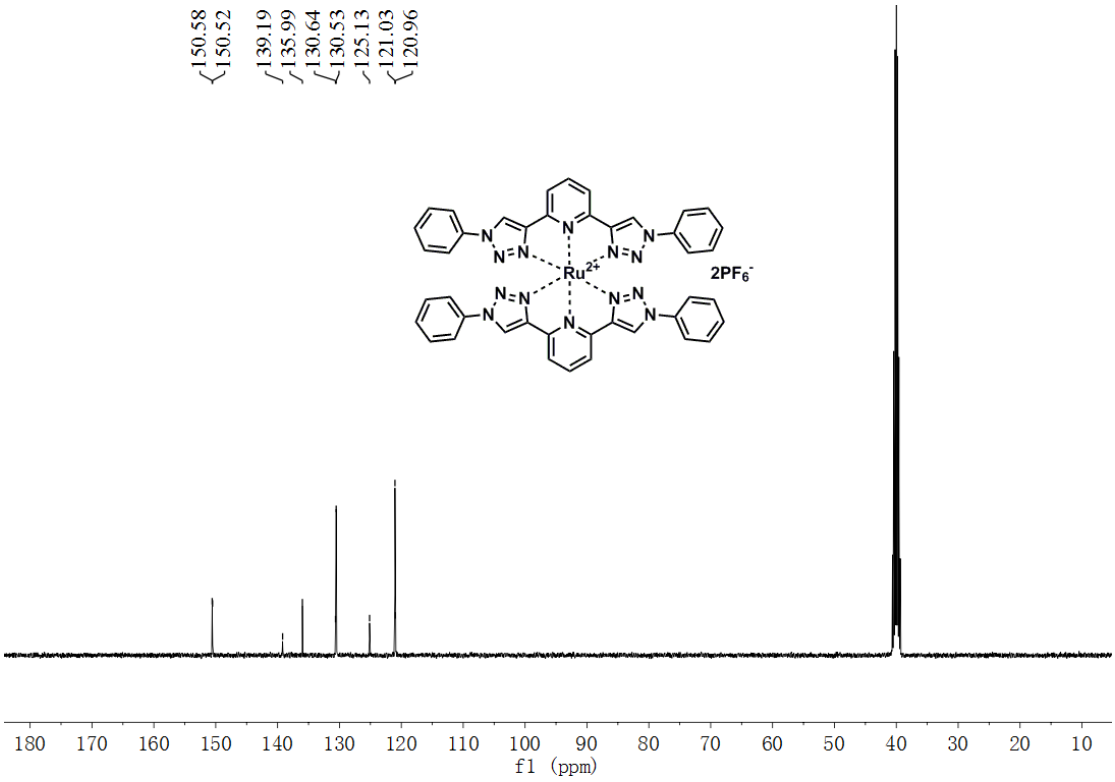
^{1}H NMR spectrum of $Ru(btpI)_2(PF_6)_2$



^{13}C NMR spectrum of $Ru(btpI)_2(PF_6)_2$

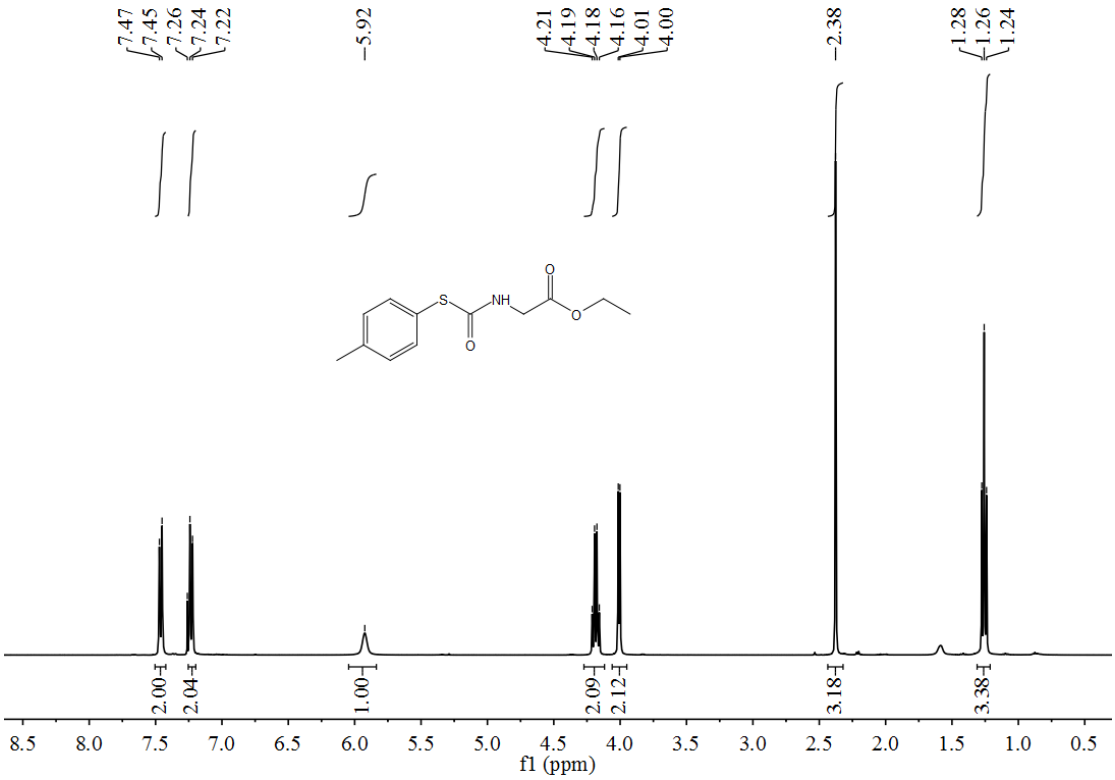


^{1}H NMR spectrum of $Ru(btp)_2(PF_6)_2$

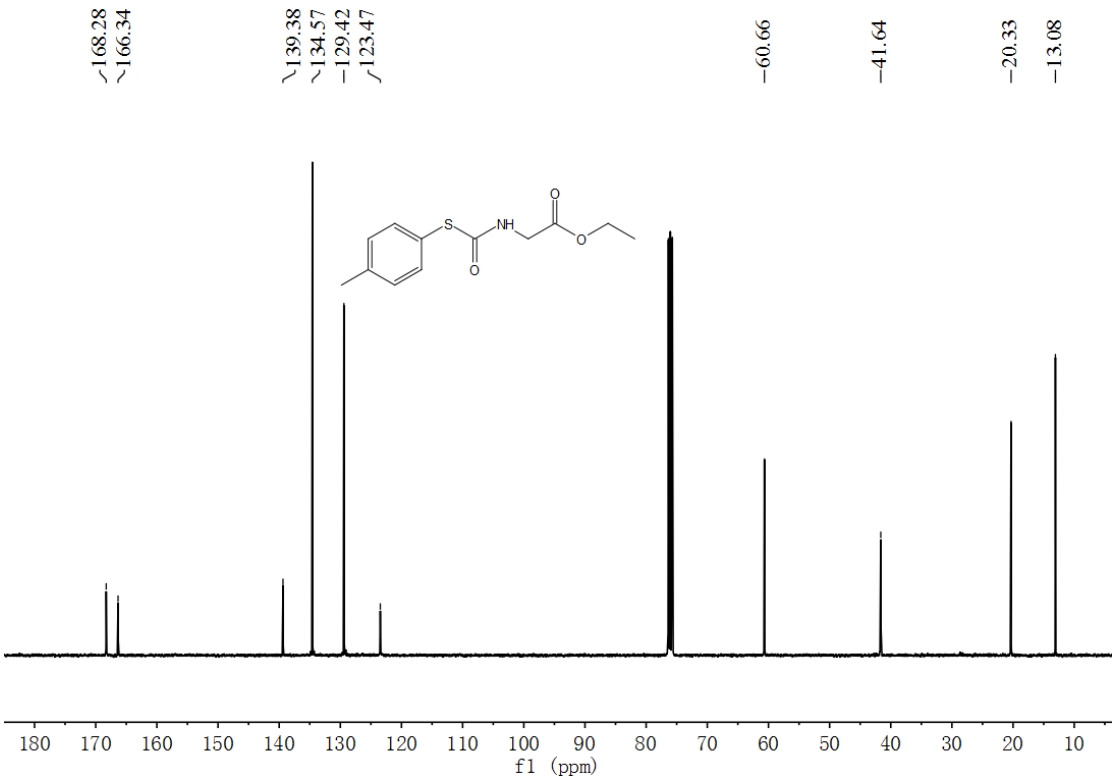


^{13}C NMR spectrum of $Ru(btp)_2(PF_6)_2$

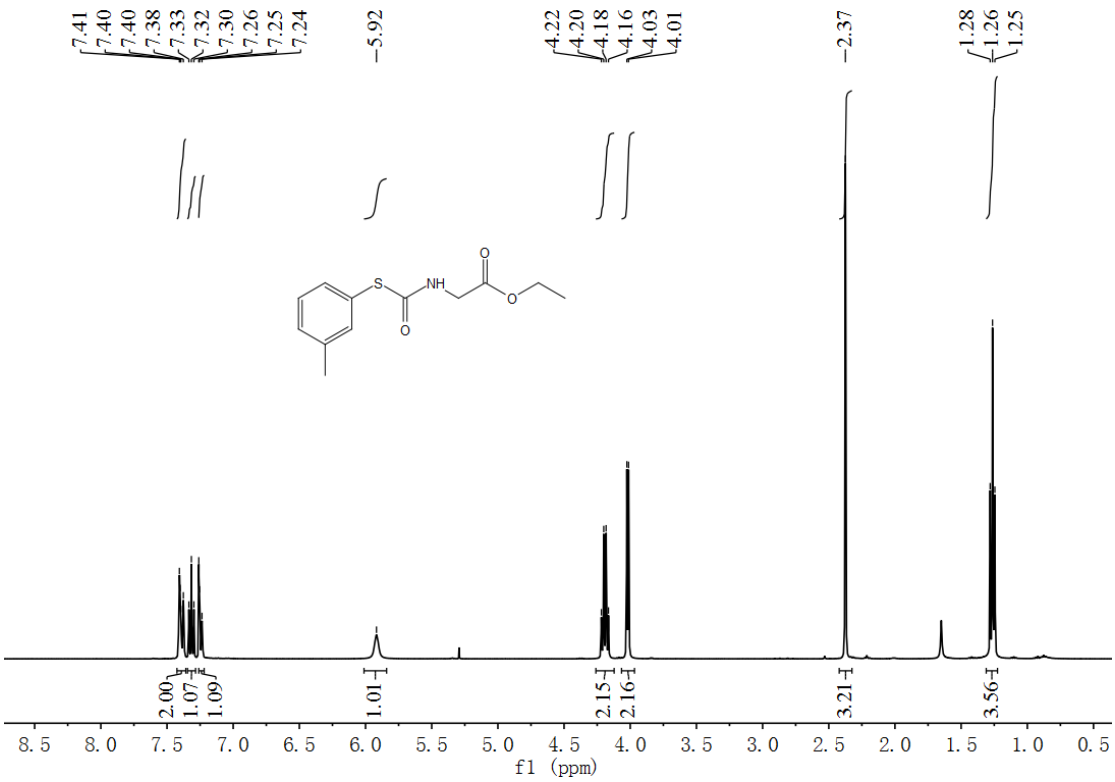
Copies of NMR spectra of products



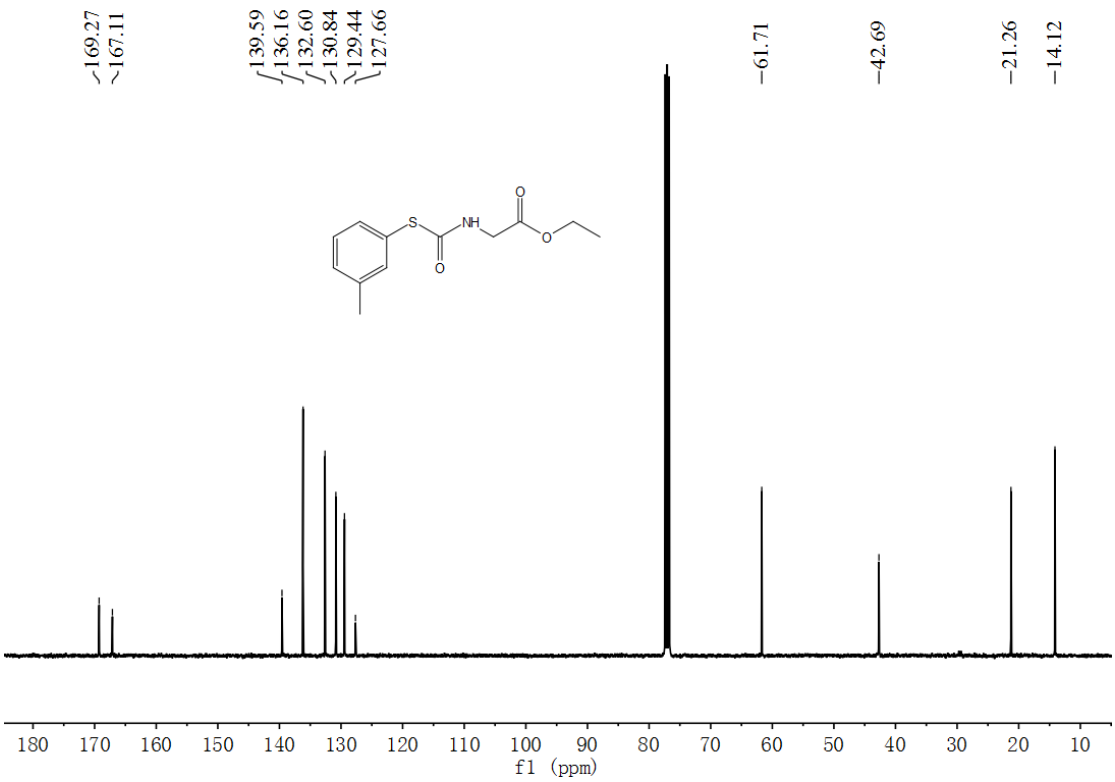
^{1}H NMR spectrum of **3a**



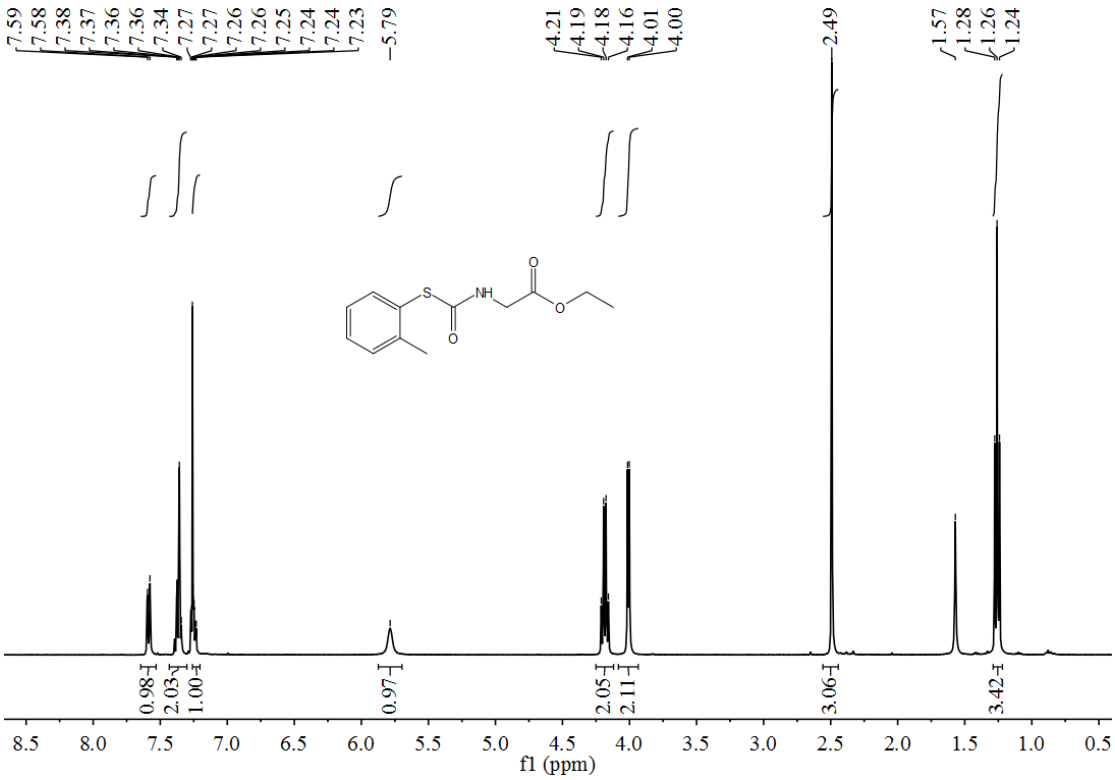
^{13}C NMR spectrum of **3a**



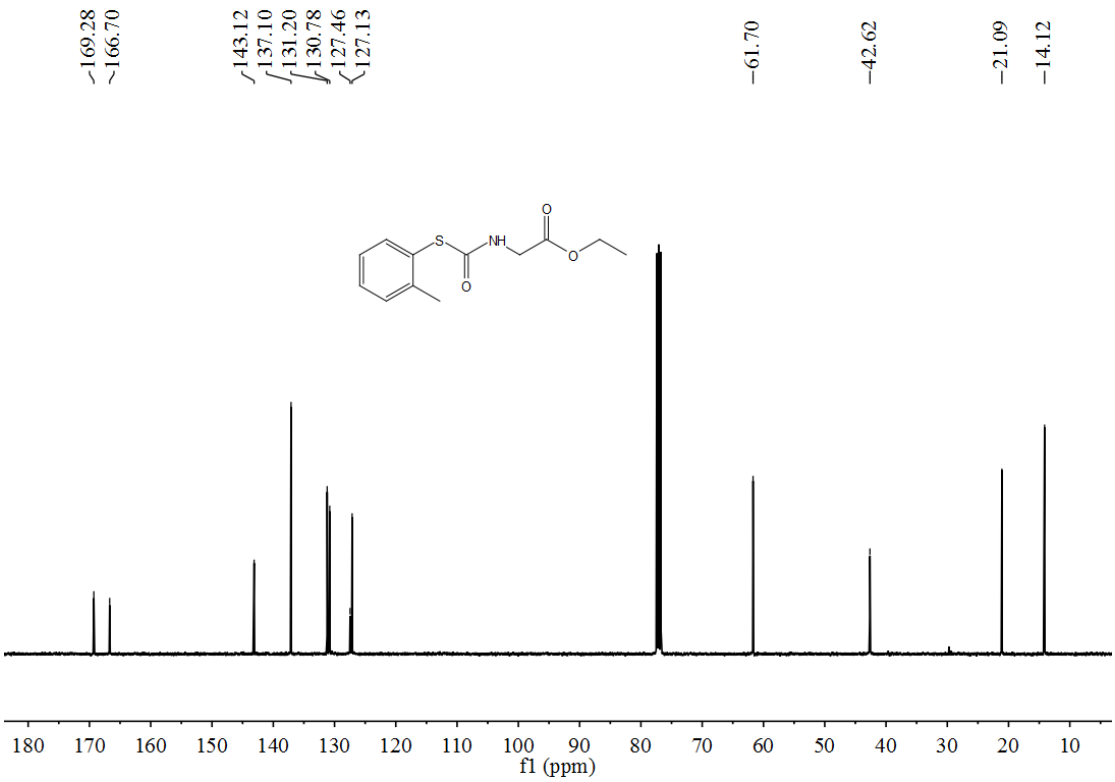
^{1}H NMR spectrum of **3b**



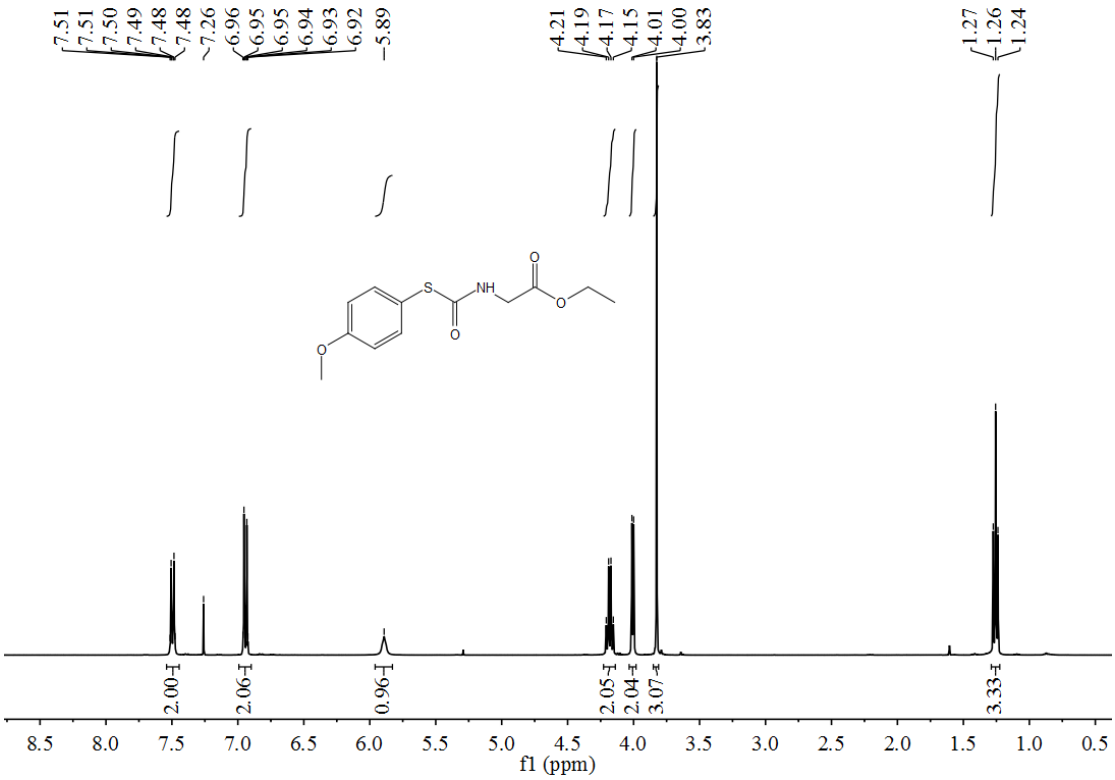
^{13}C NMR spectrum of **3b**



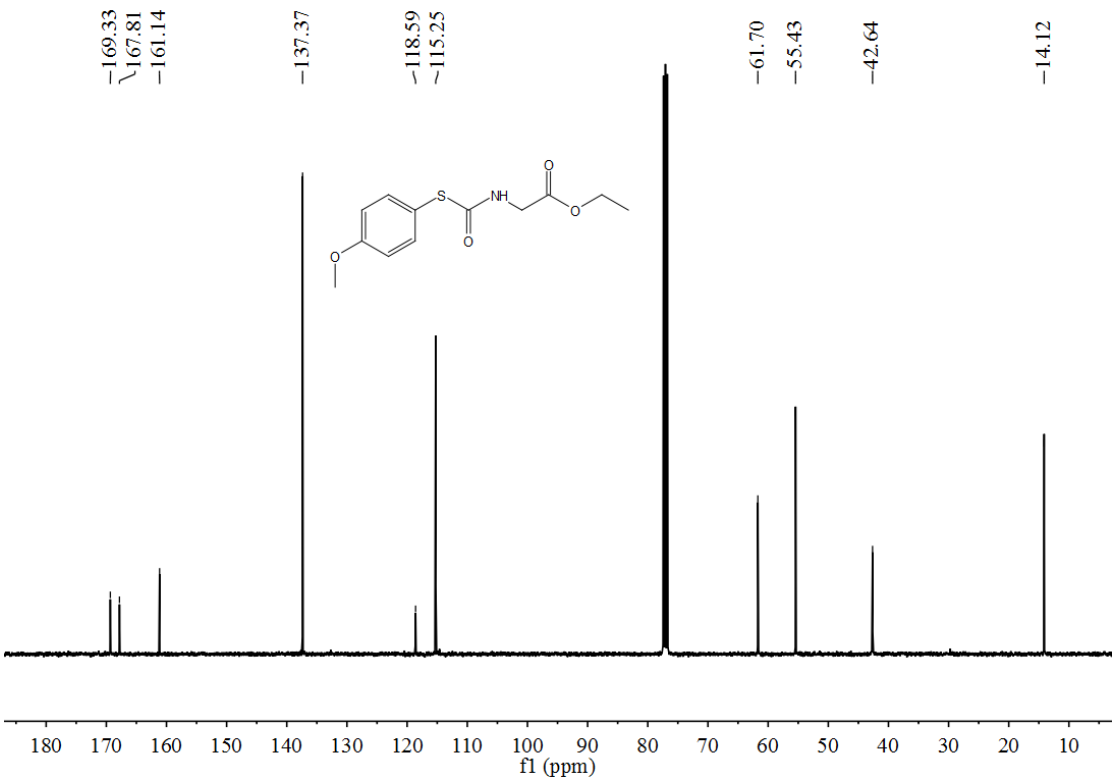
^{1}H NMR spectrum of **3c**



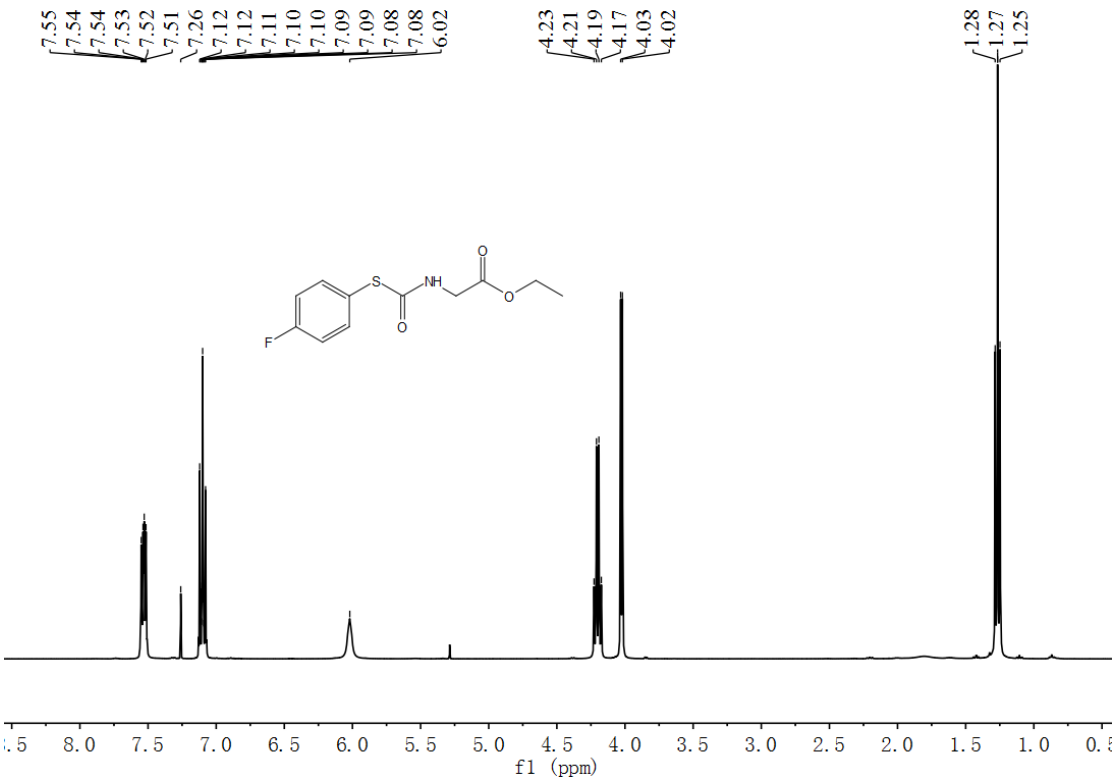
^{13}C NMR spectrum of **3c**



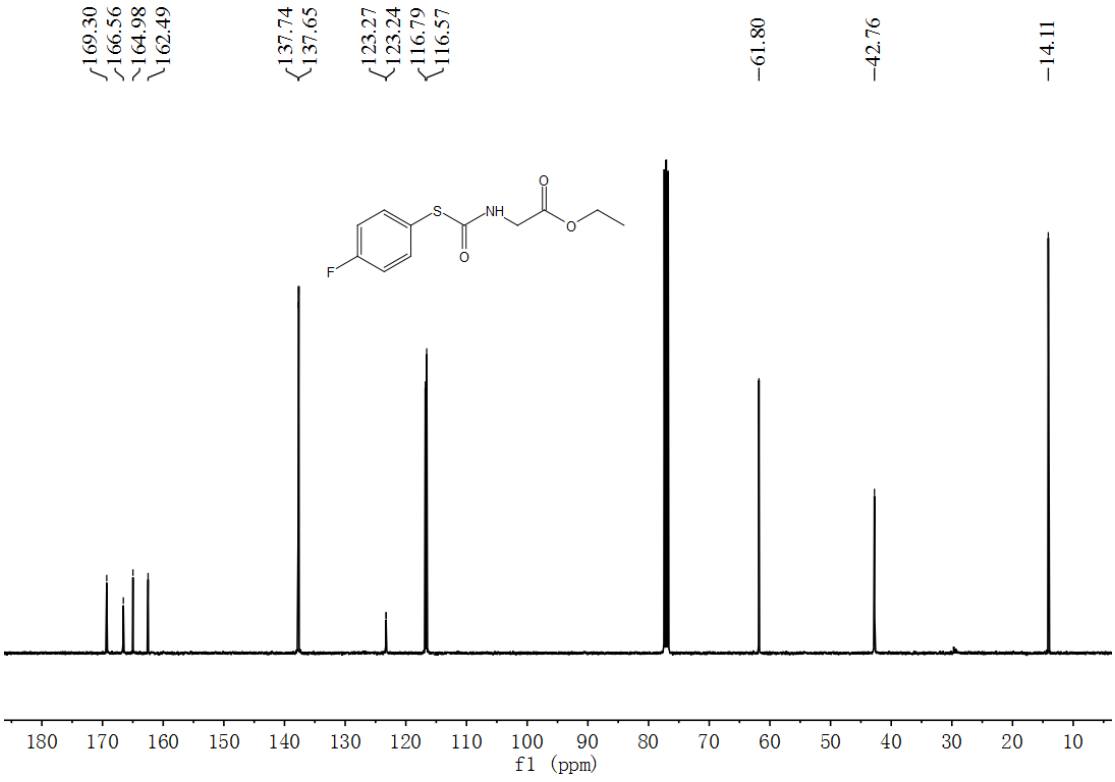
^{1}H NMR spectrum of **3d**



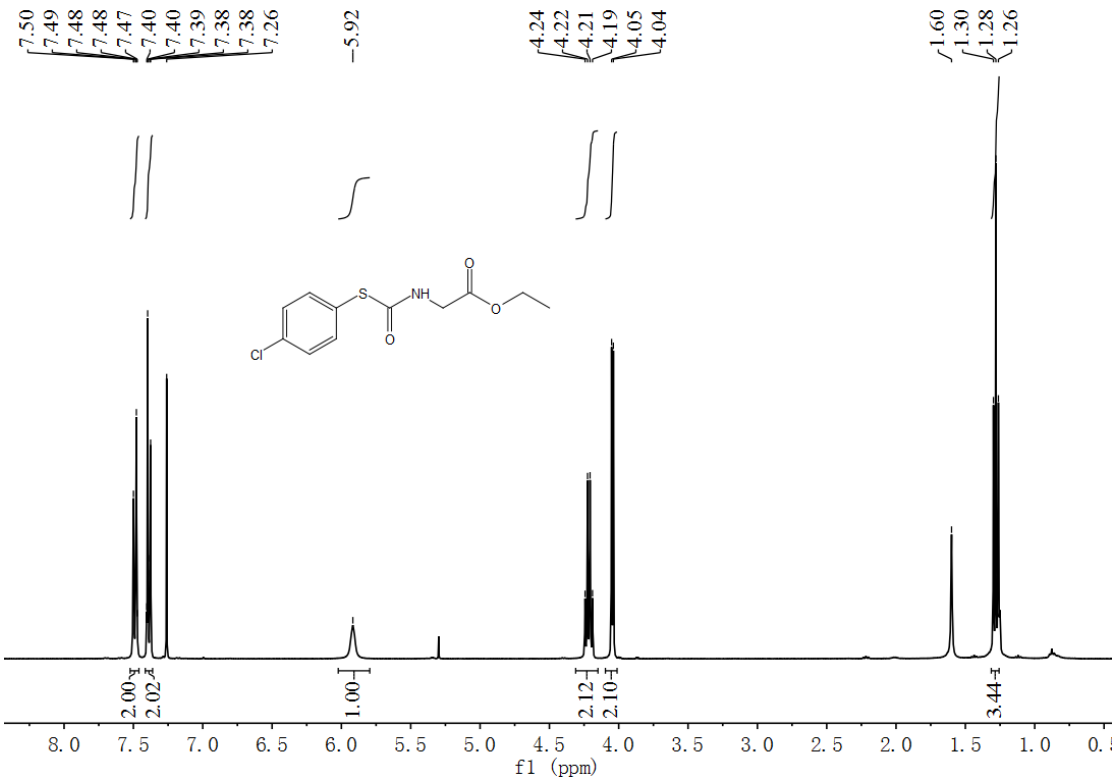
^{13}C NMR spectrum of **3d**



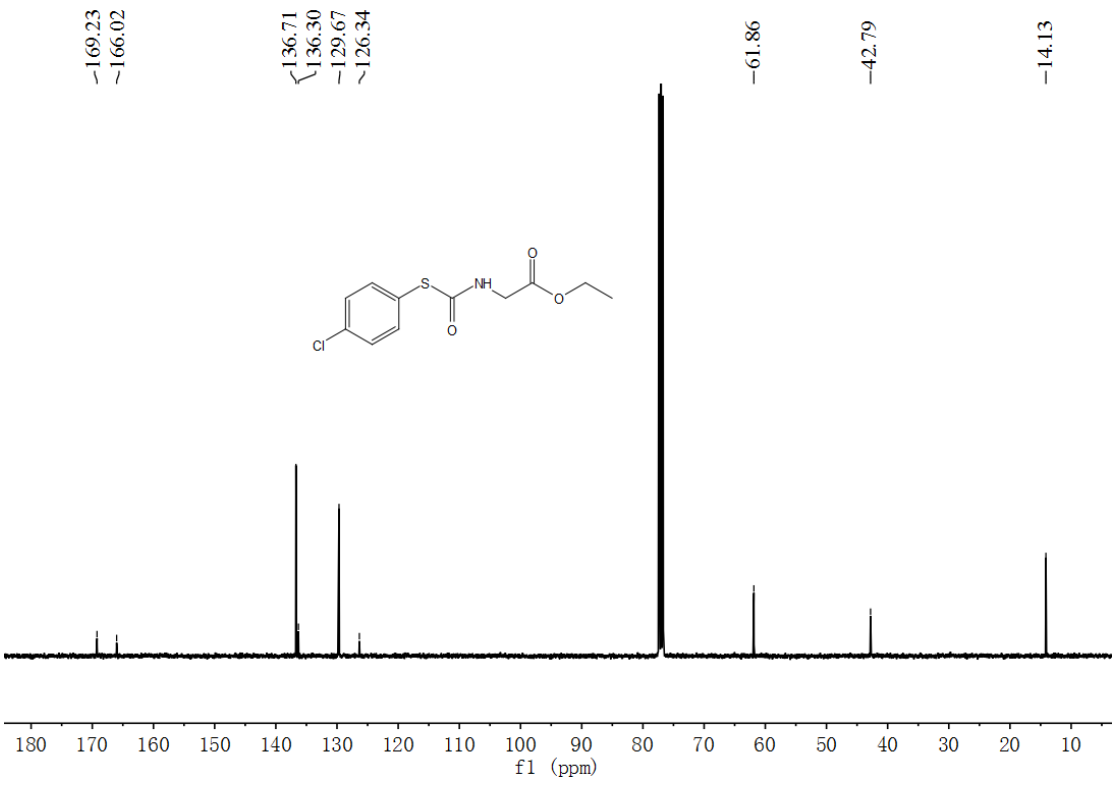
^{1}H NMR spectrum of **3e**



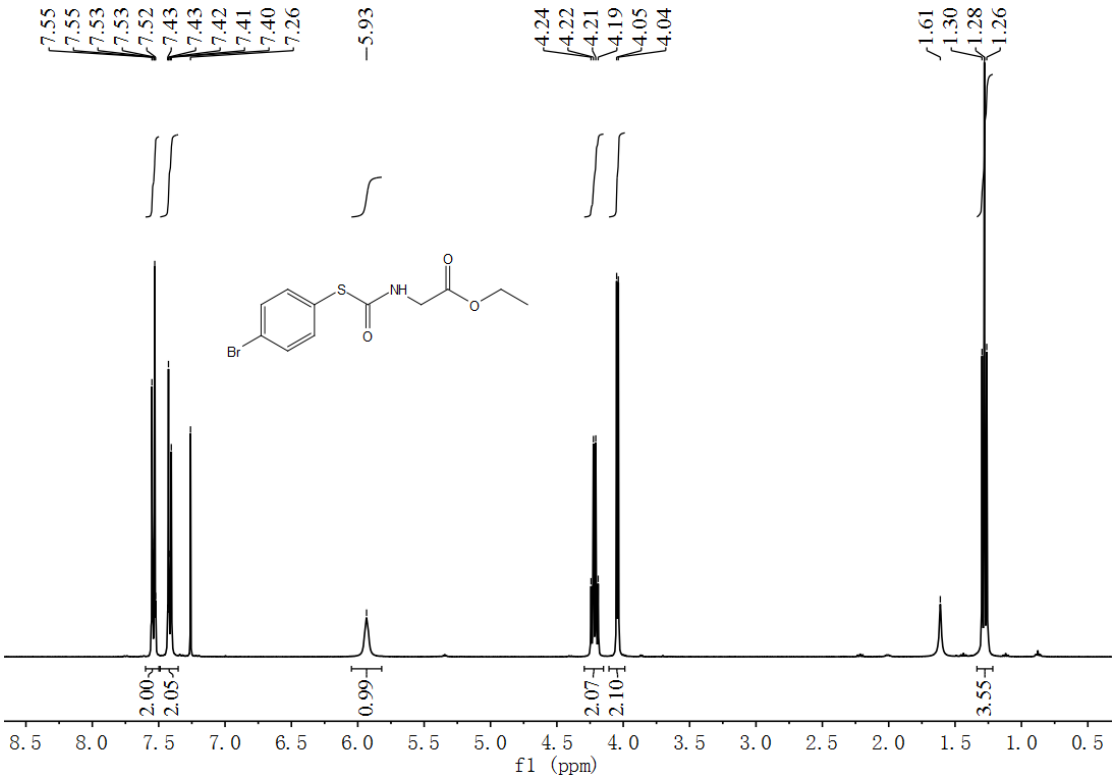
^{13}C NMR spectrum of **3e**



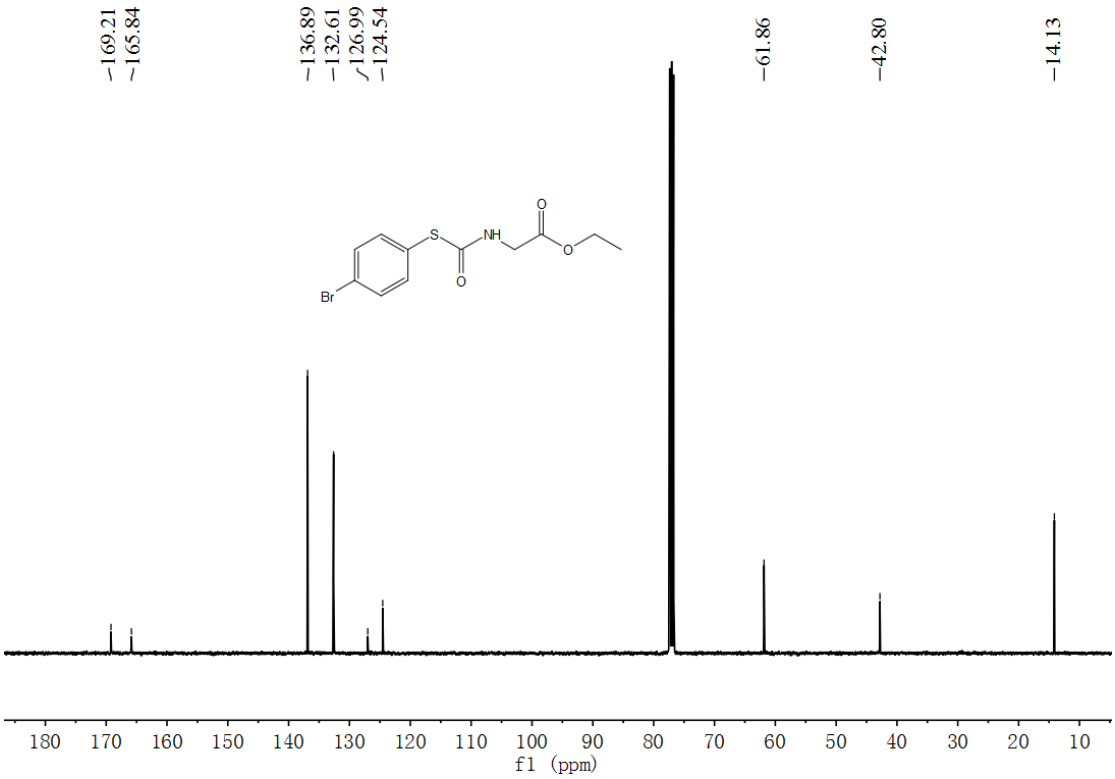
^{1}H NMR spectrum of **3f**



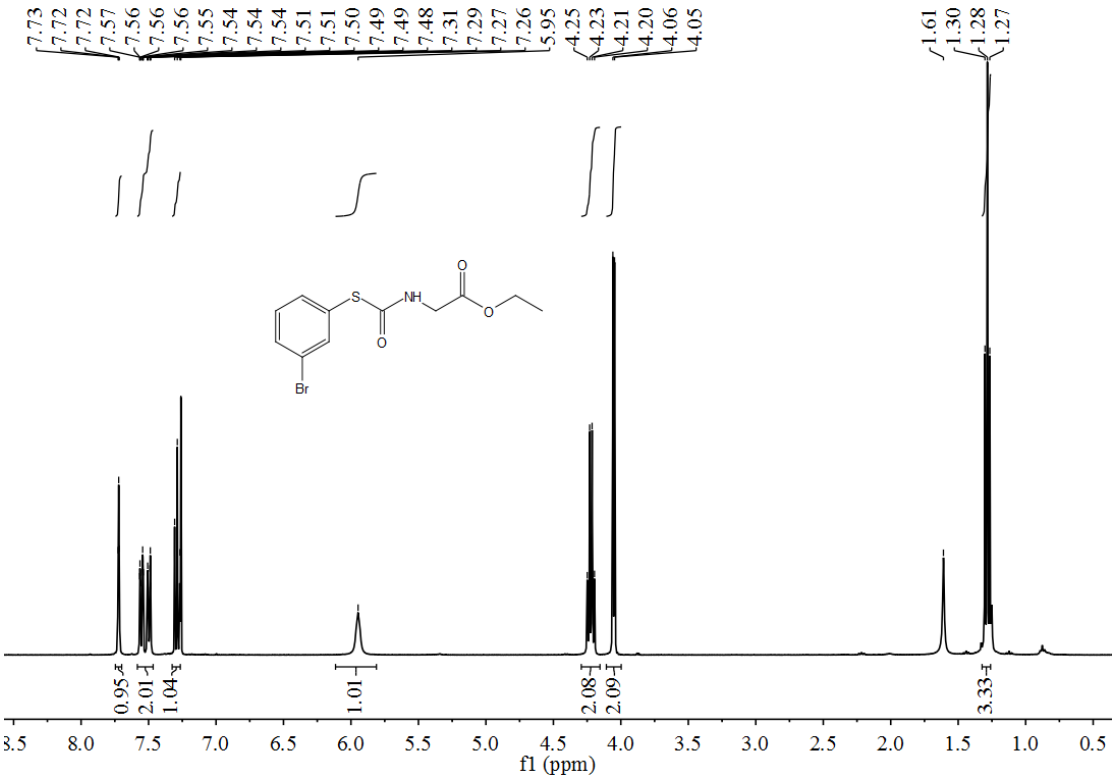
^{13}C NMR spectrum of **3f**



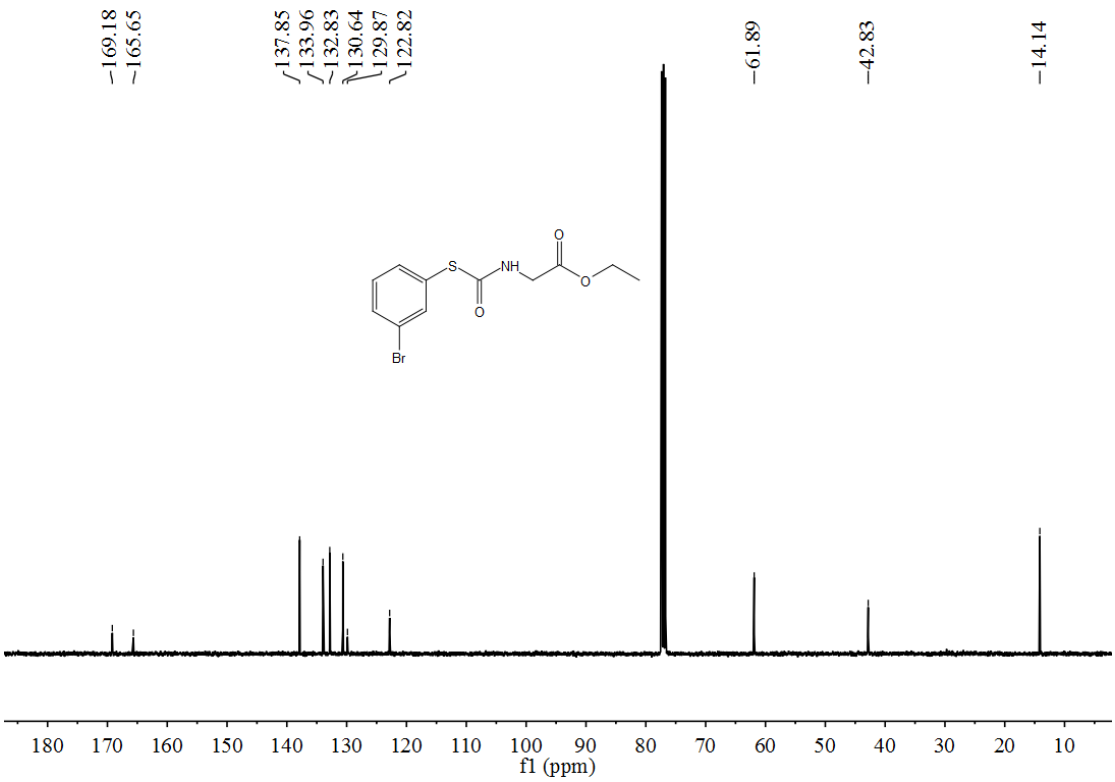
^{1}H NMR spectrum of **3g**



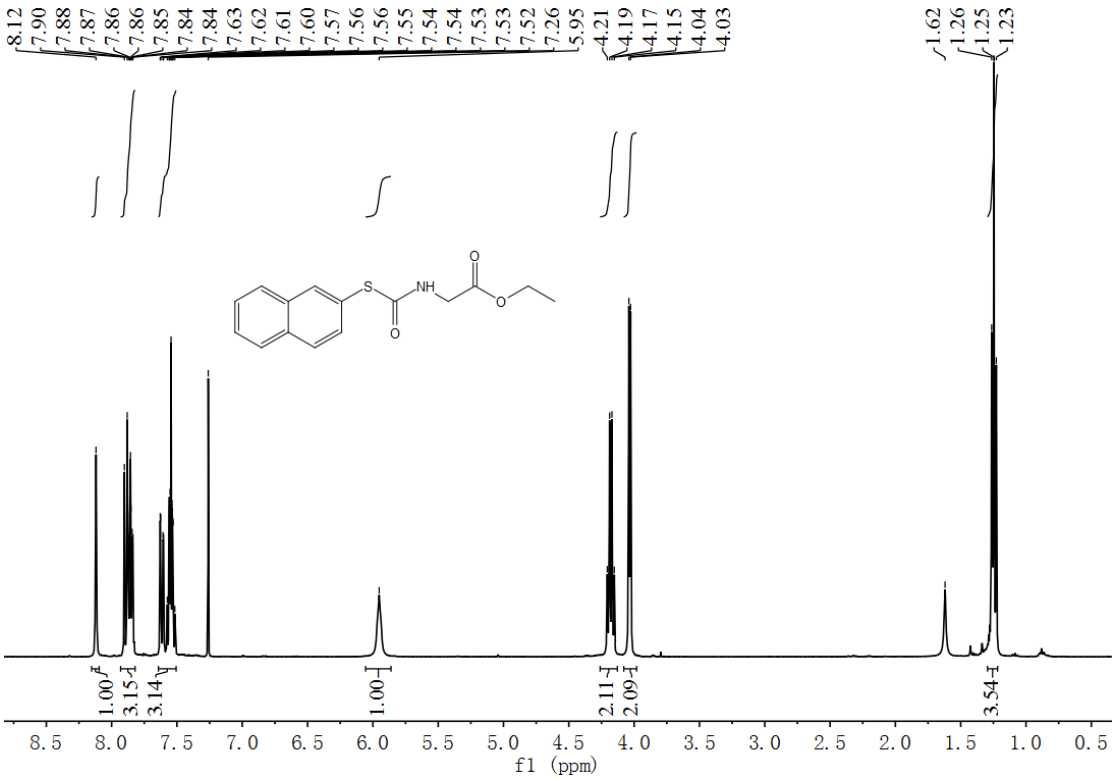
^{13}C NMR spectrum of **3g**



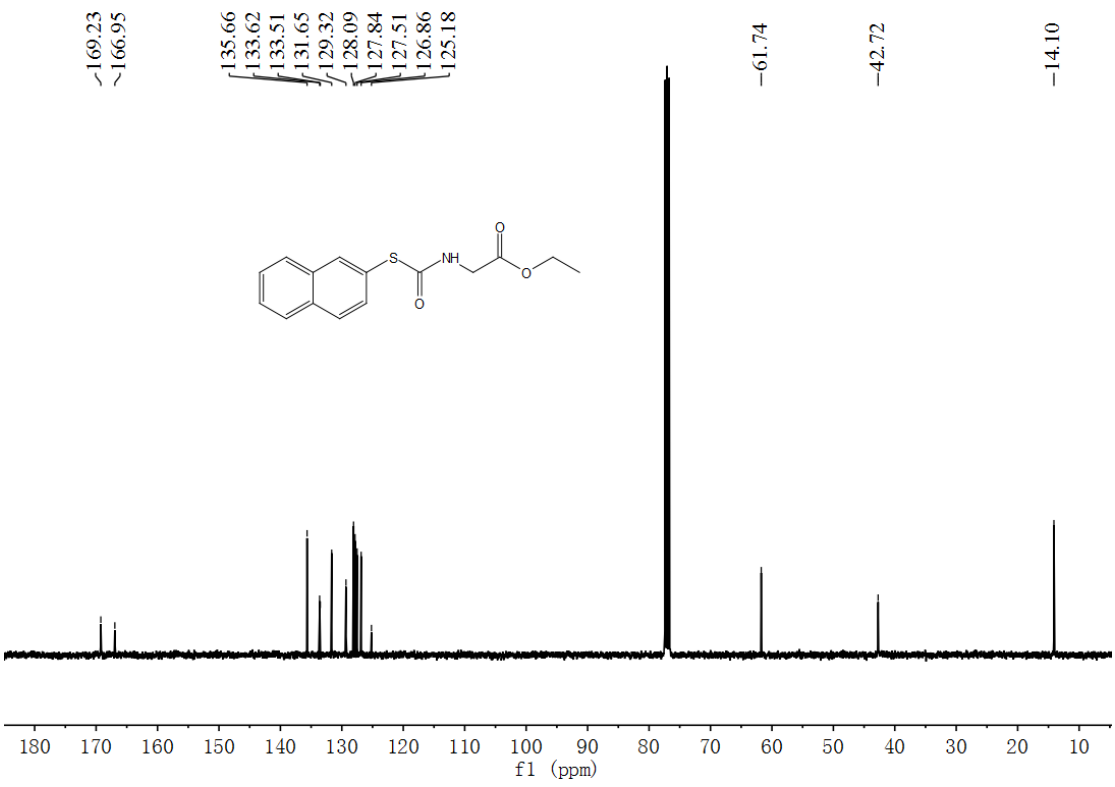
^{1}H NMR spectrum of **3h**



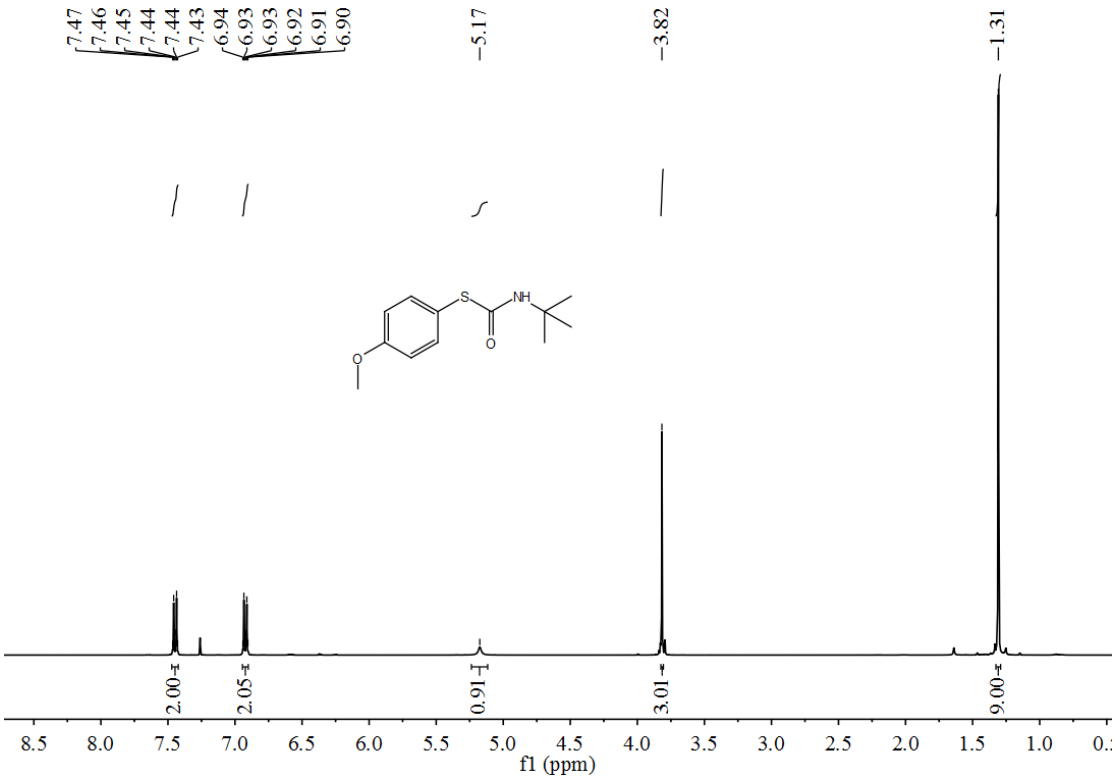
^{13}C NMR spectrum of **3h**



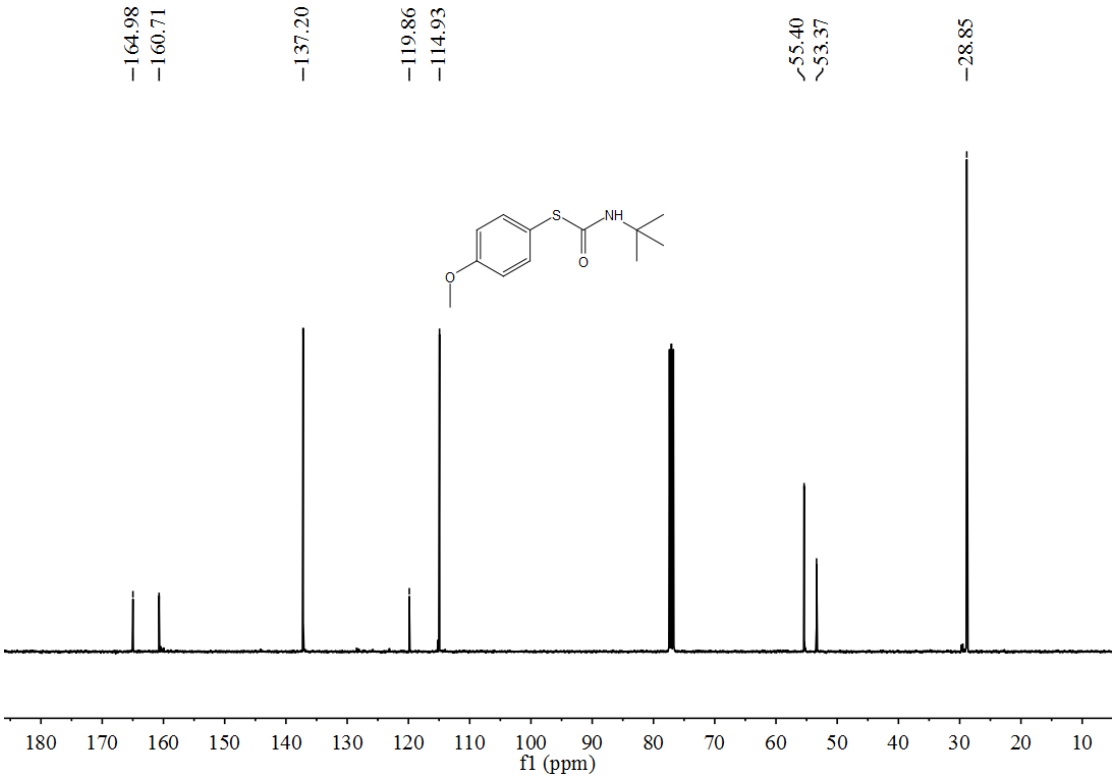
^{1}H NMR spectrum of **3i**



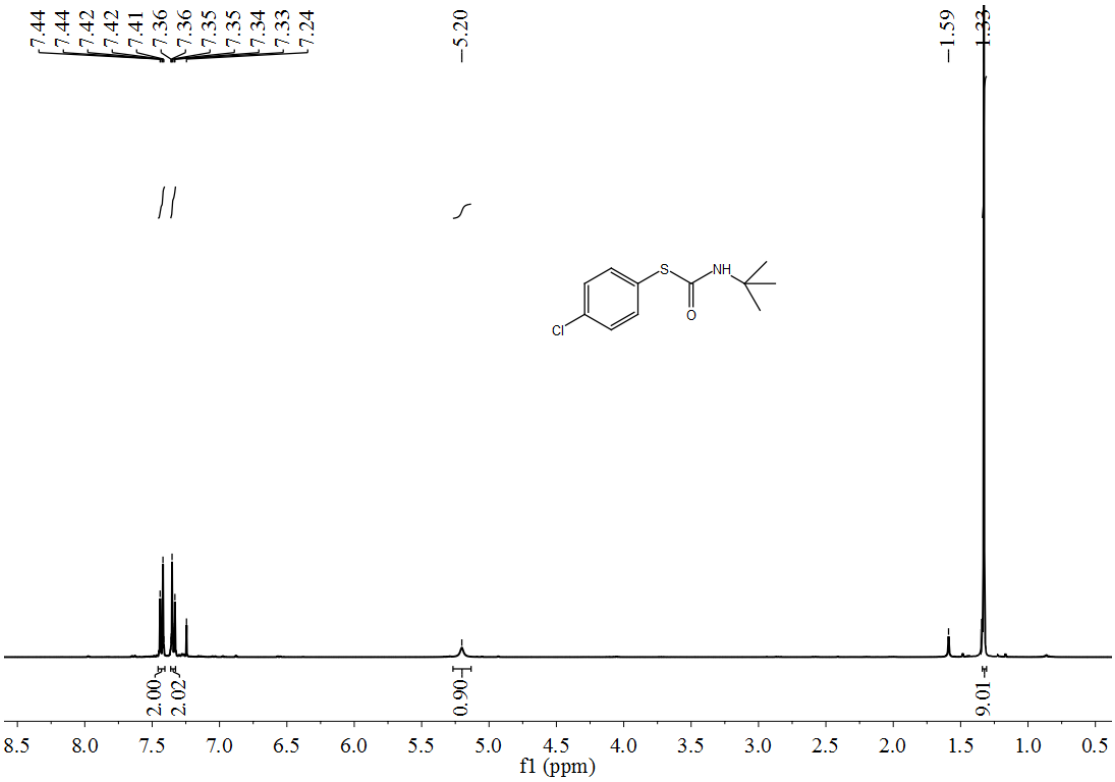
^{13}C NMR spectrum of **3i**



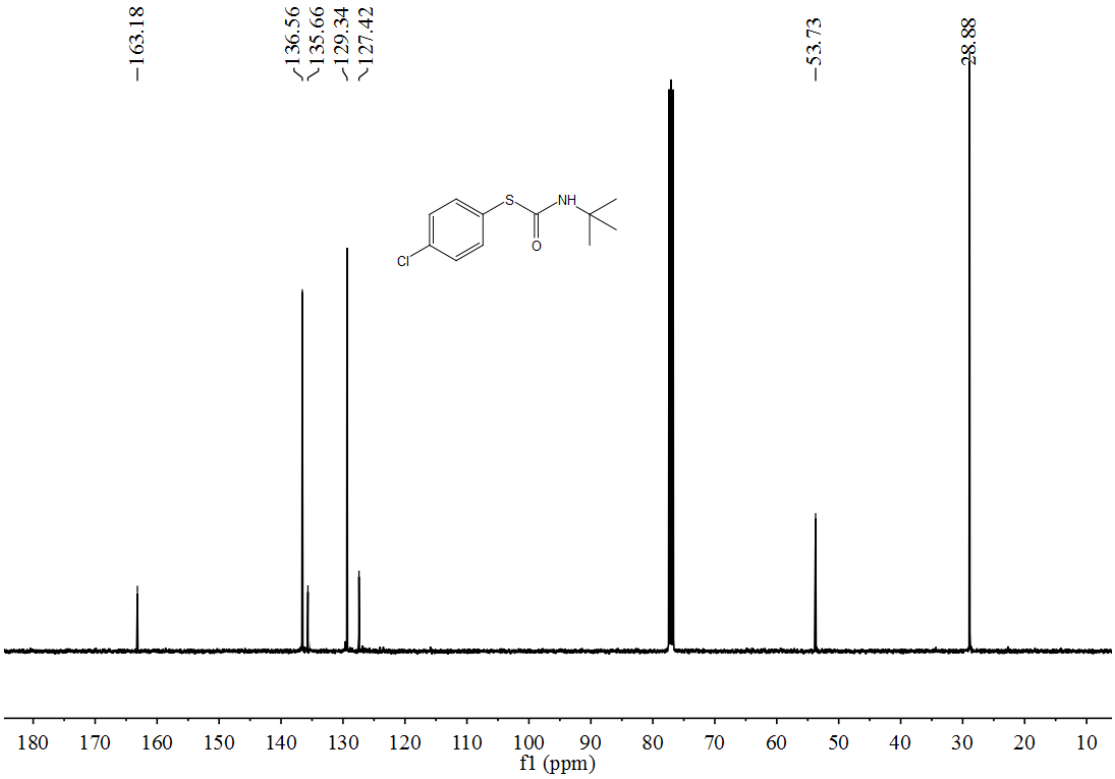
^{1}H NMR spectrum of **3j**



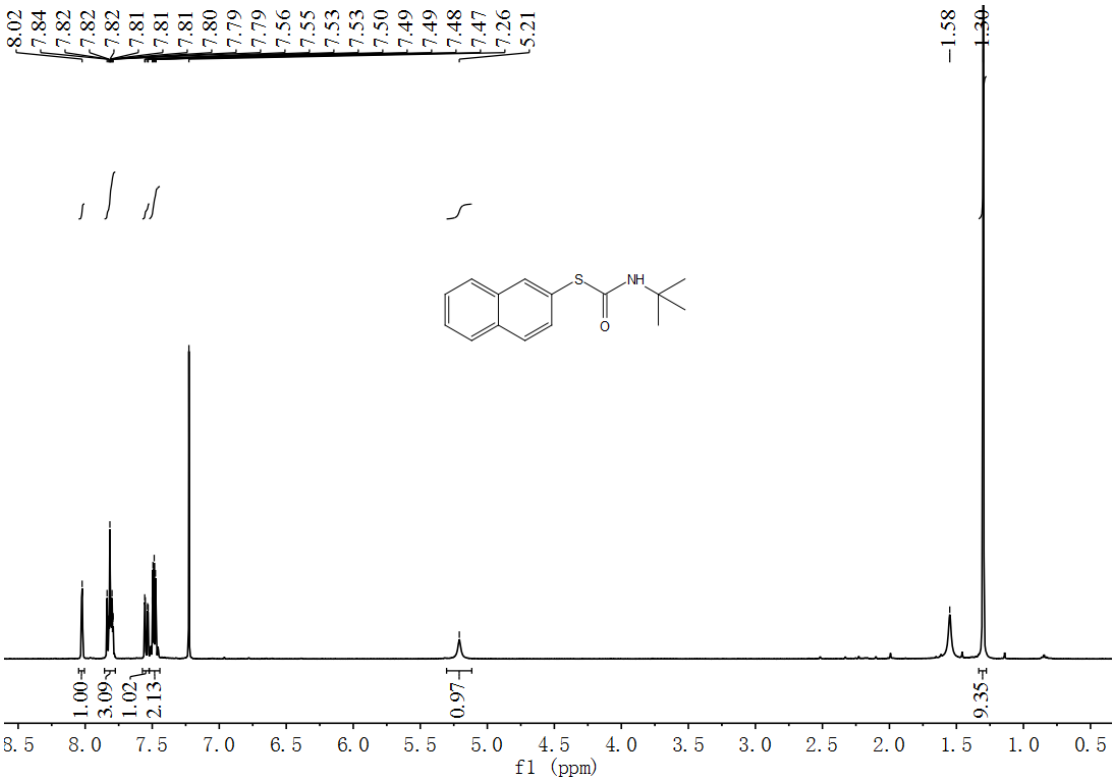
^{13}C NMR spectrum of **3j**



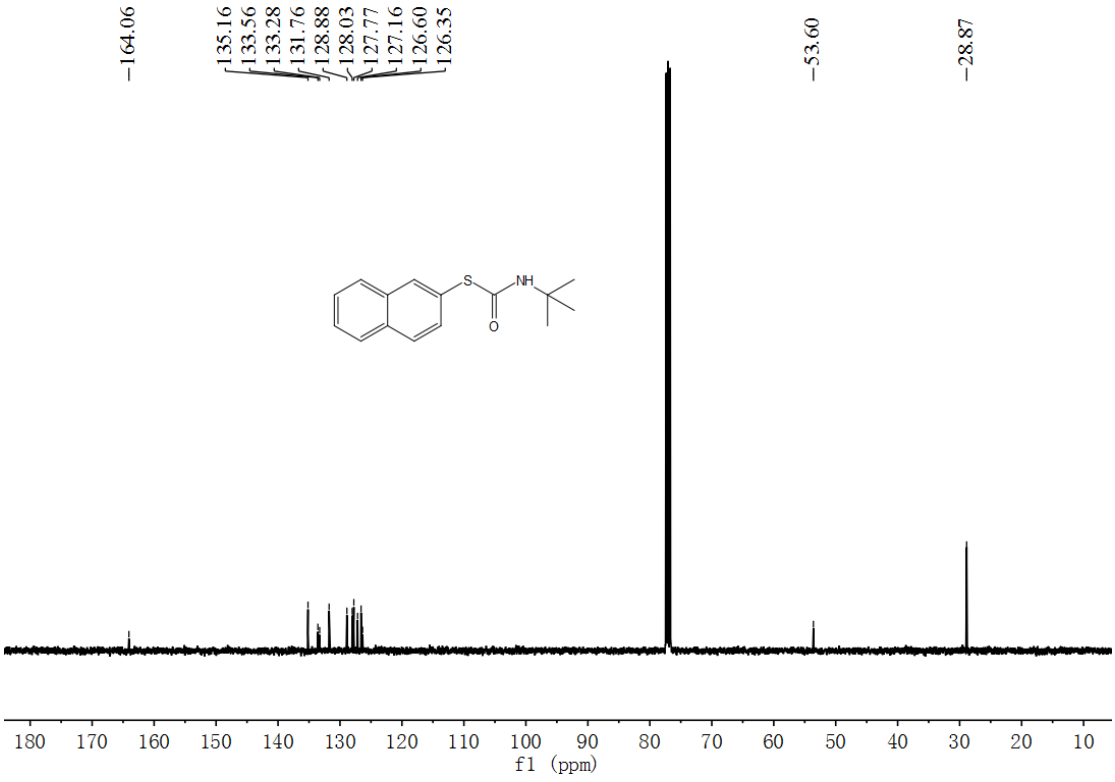
^{1}H NMR spectrum of **3k**



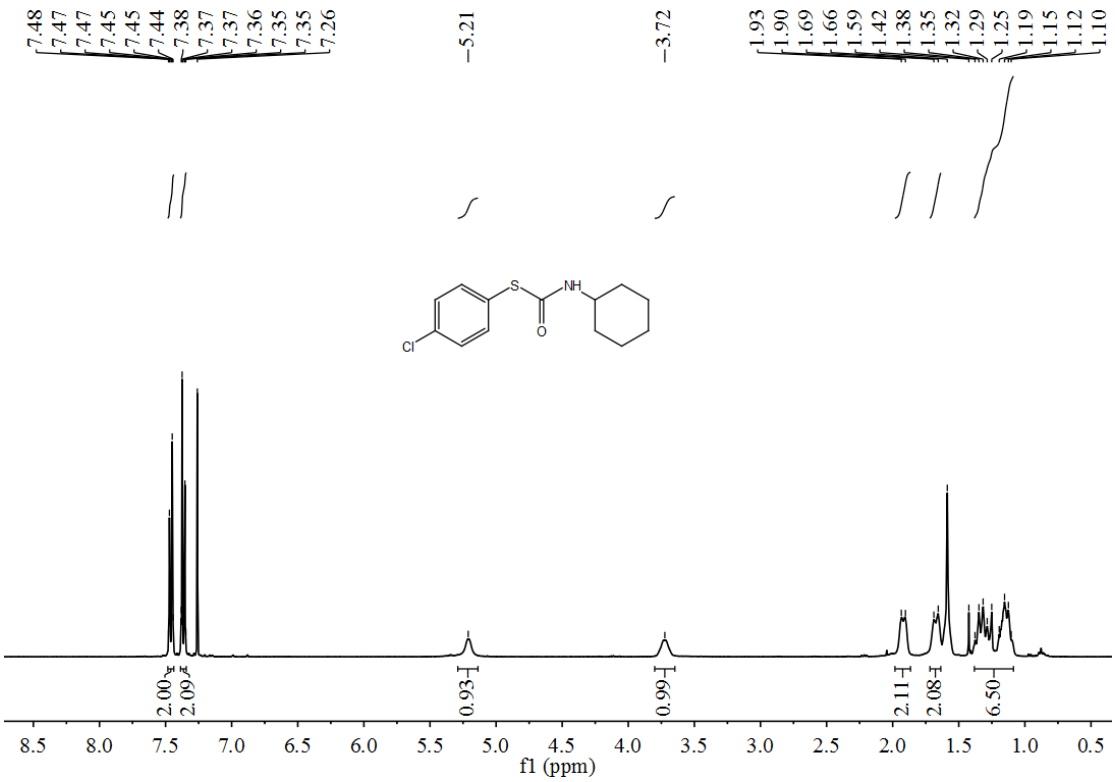
^{13}C NMR spectrum of **3k**



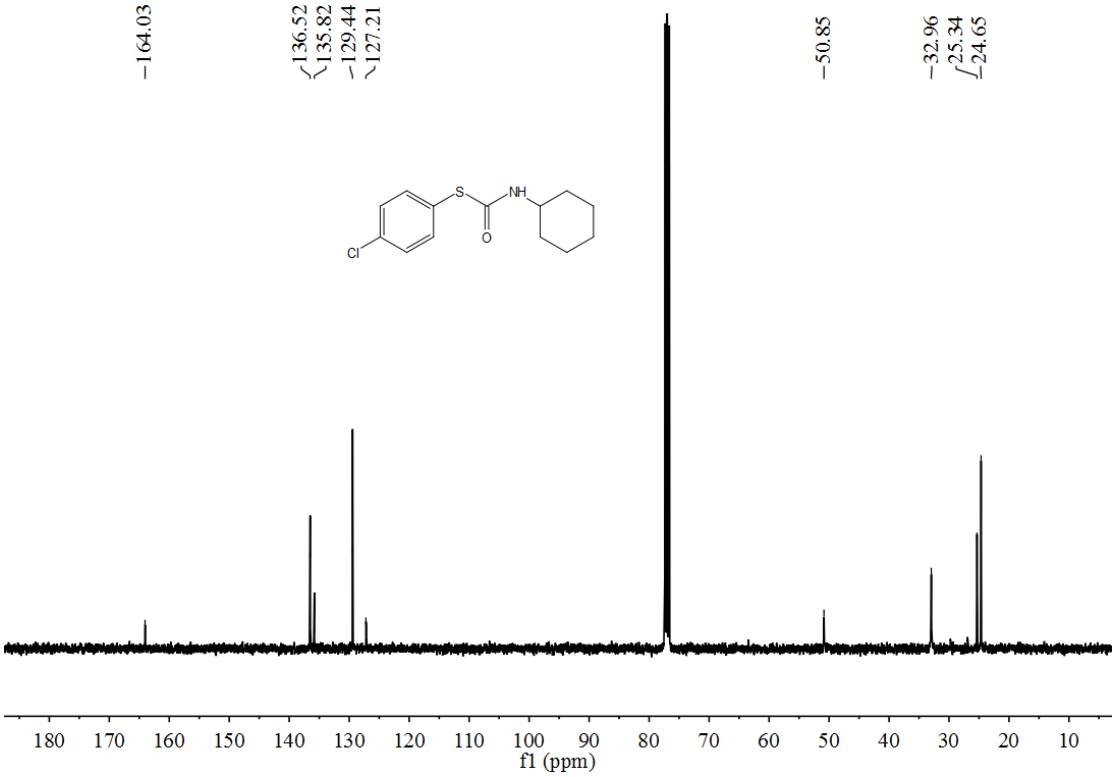
^{1}H NMR spectrum of **3l**



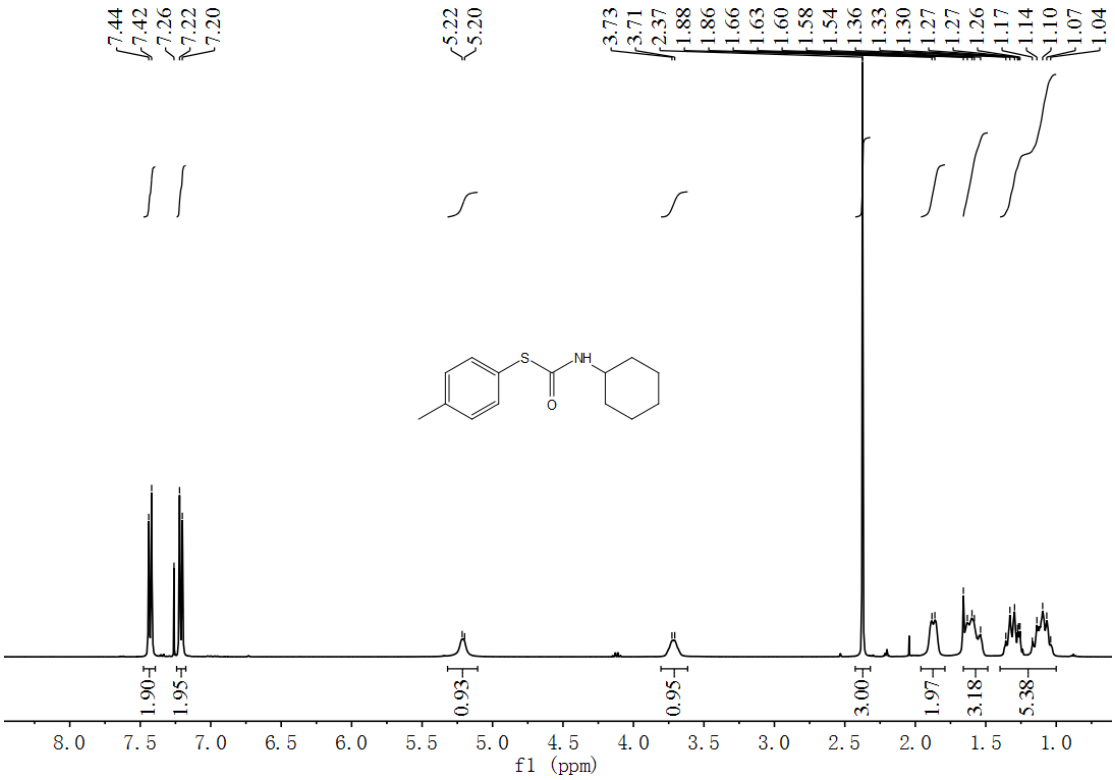
^{13}C NMR spectrum of **3l**



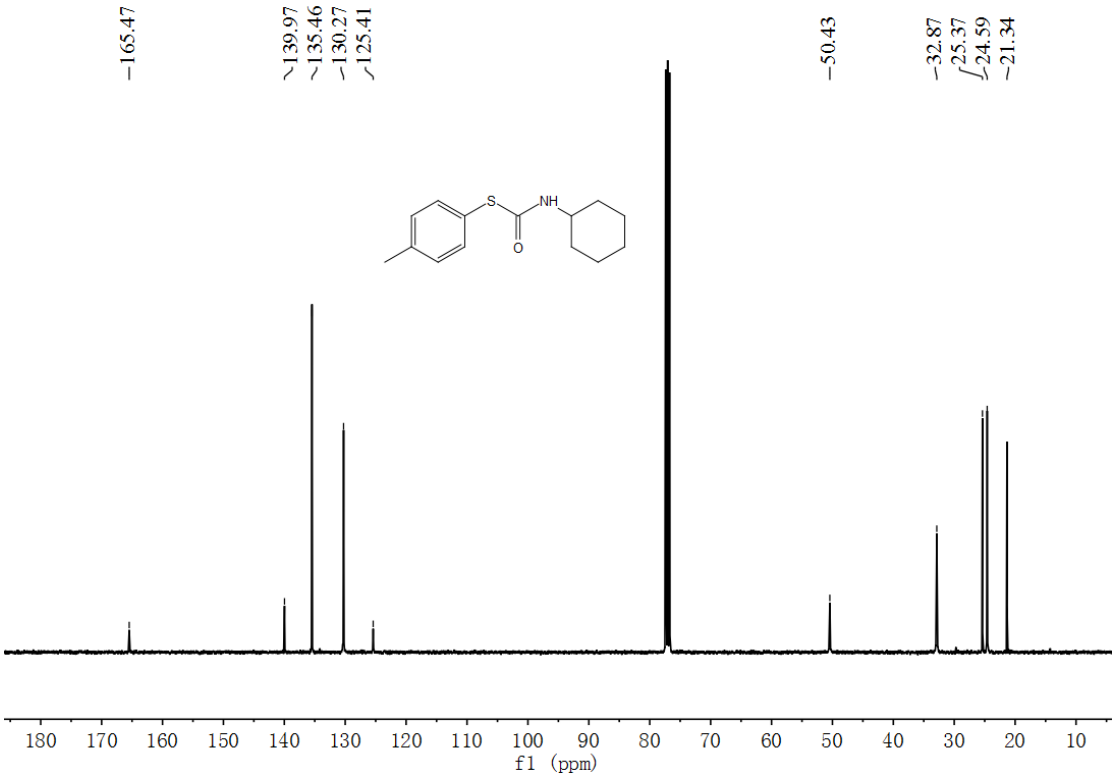
^{1}H NMR spectrum of **3m**



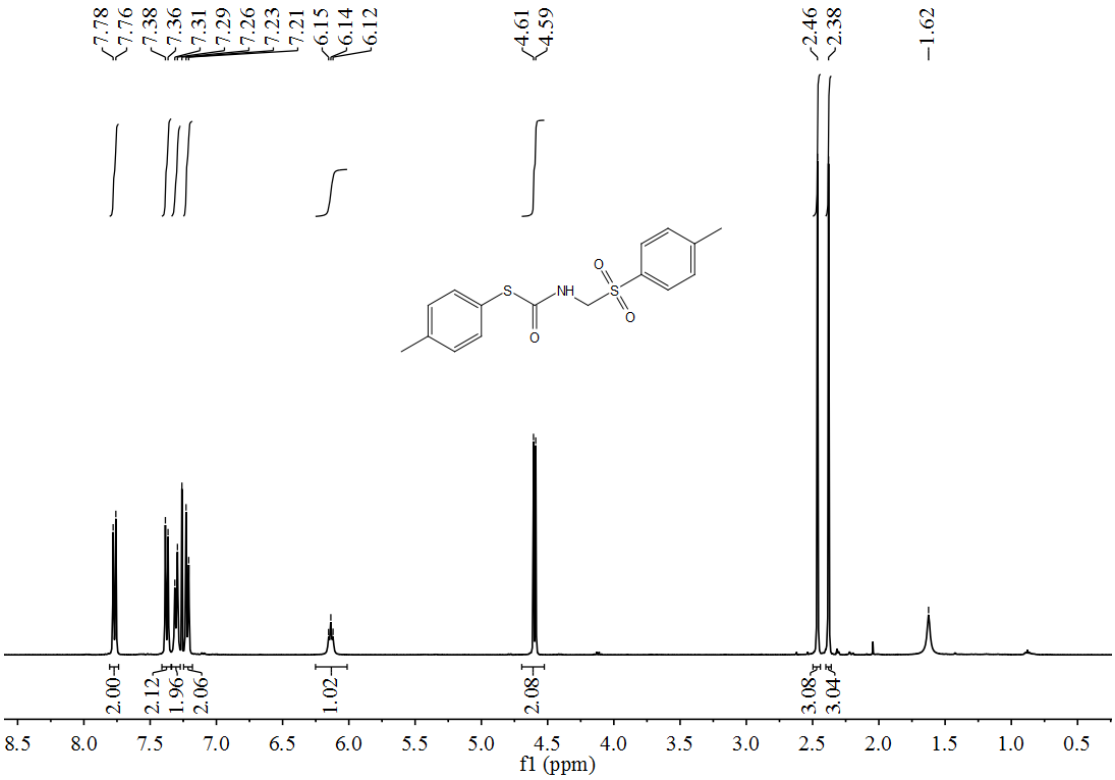
^{13}C NMR spectrum of **3m**



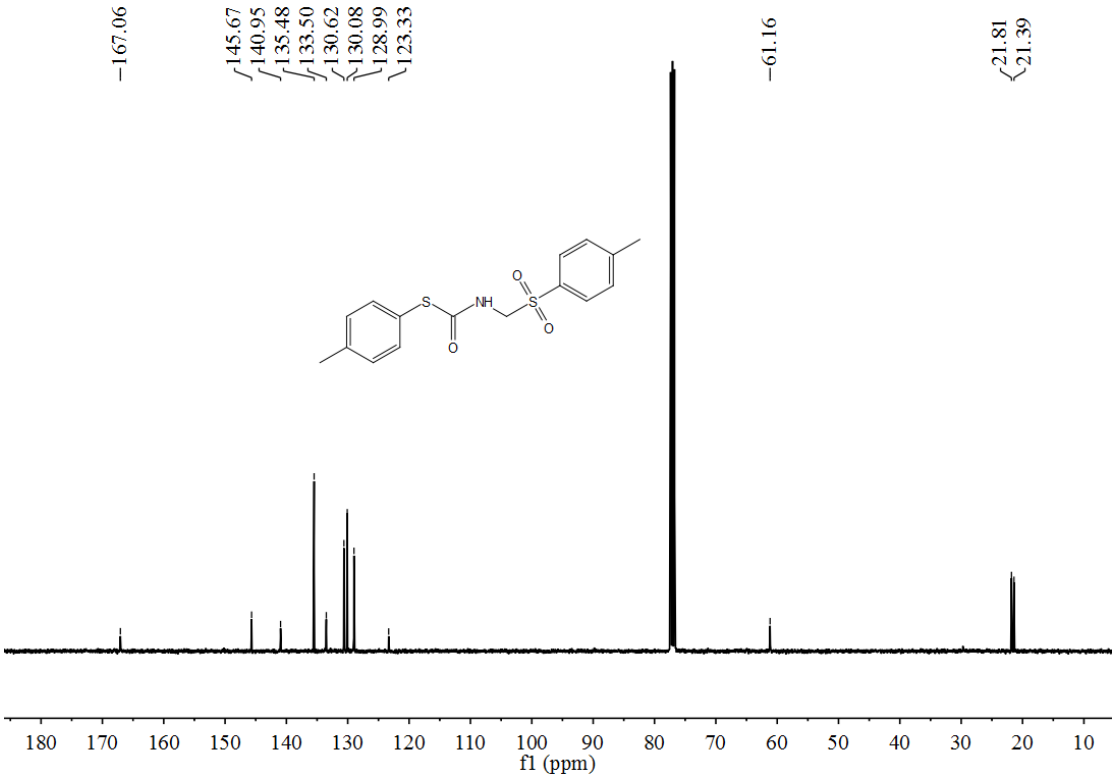
^{1}H NMR spectrum of **3n**



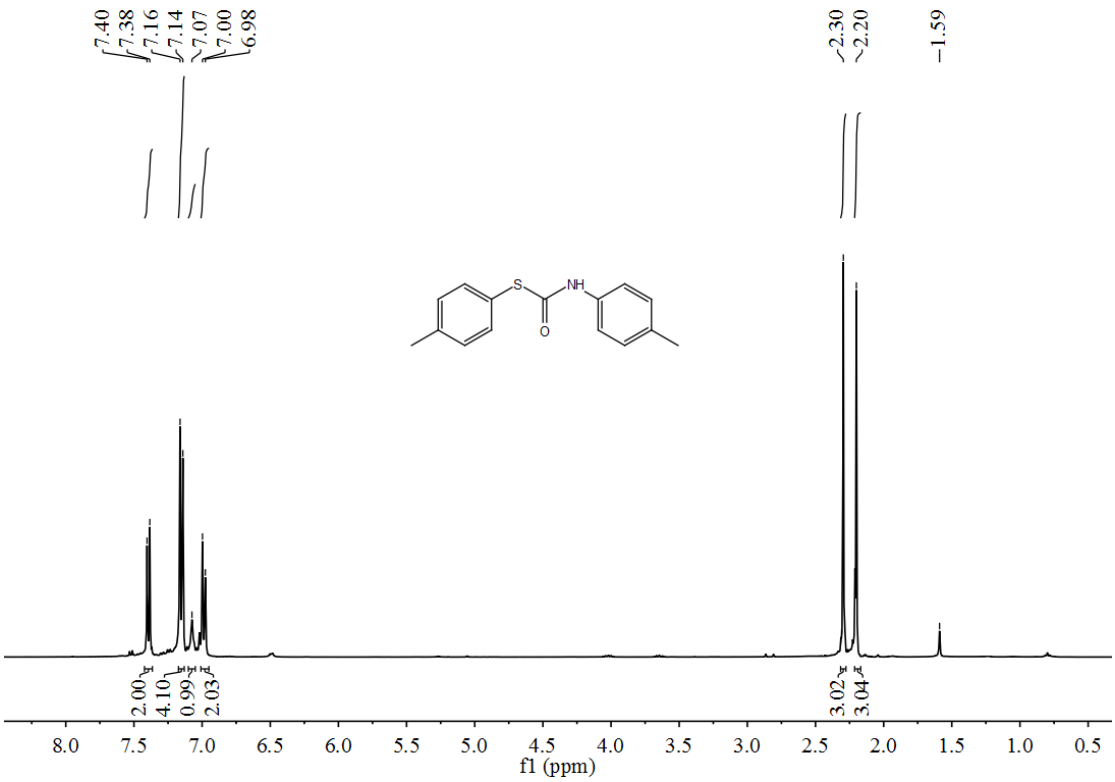
^{13}C NMR spectrum of **3n**



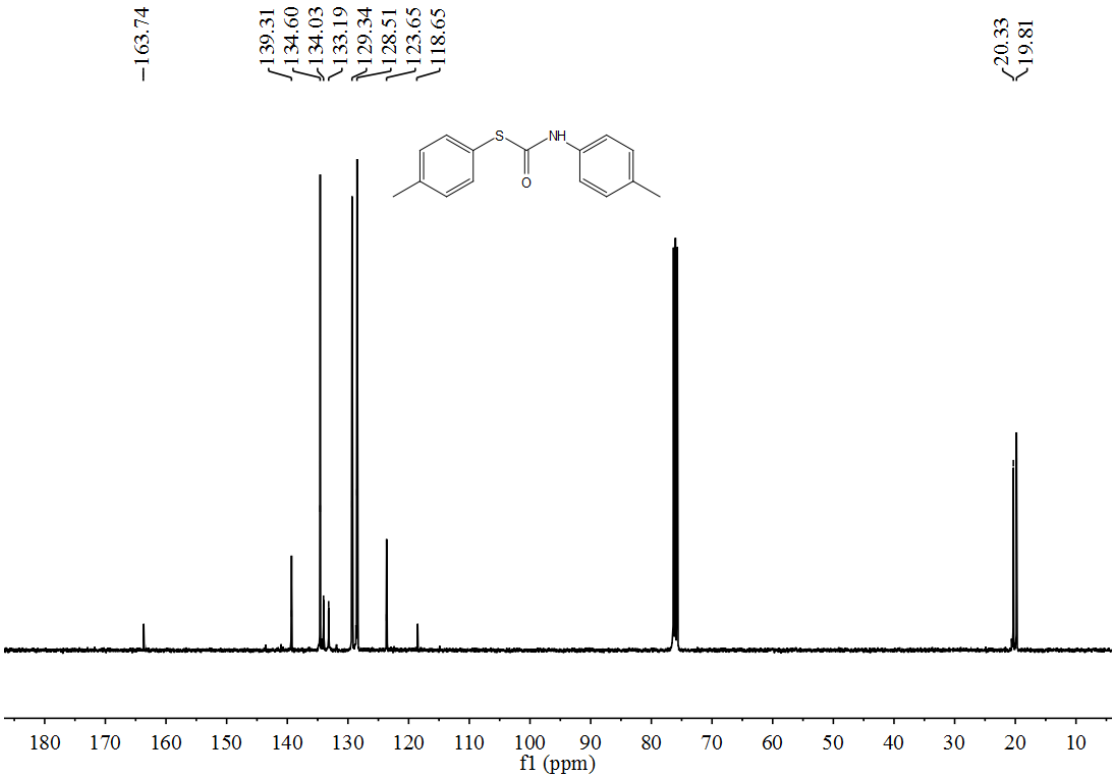
^{1}H NMR spectrum of **3o**



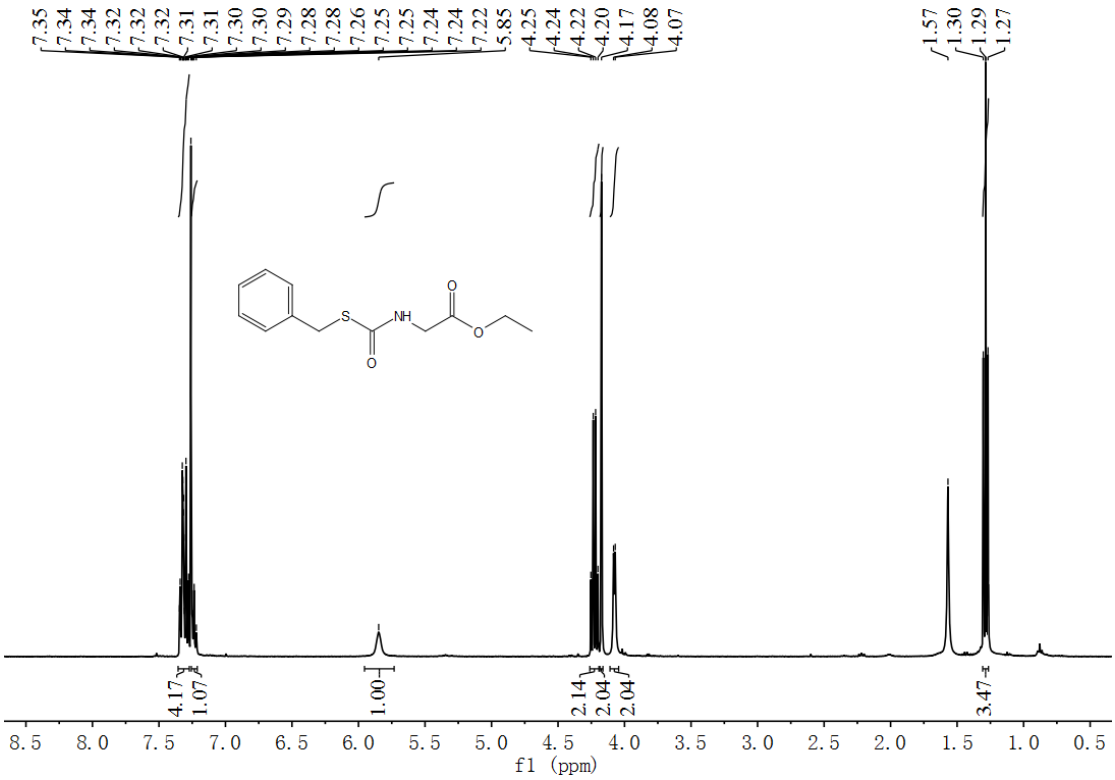
^{13}C NMR spectrum of **3o**



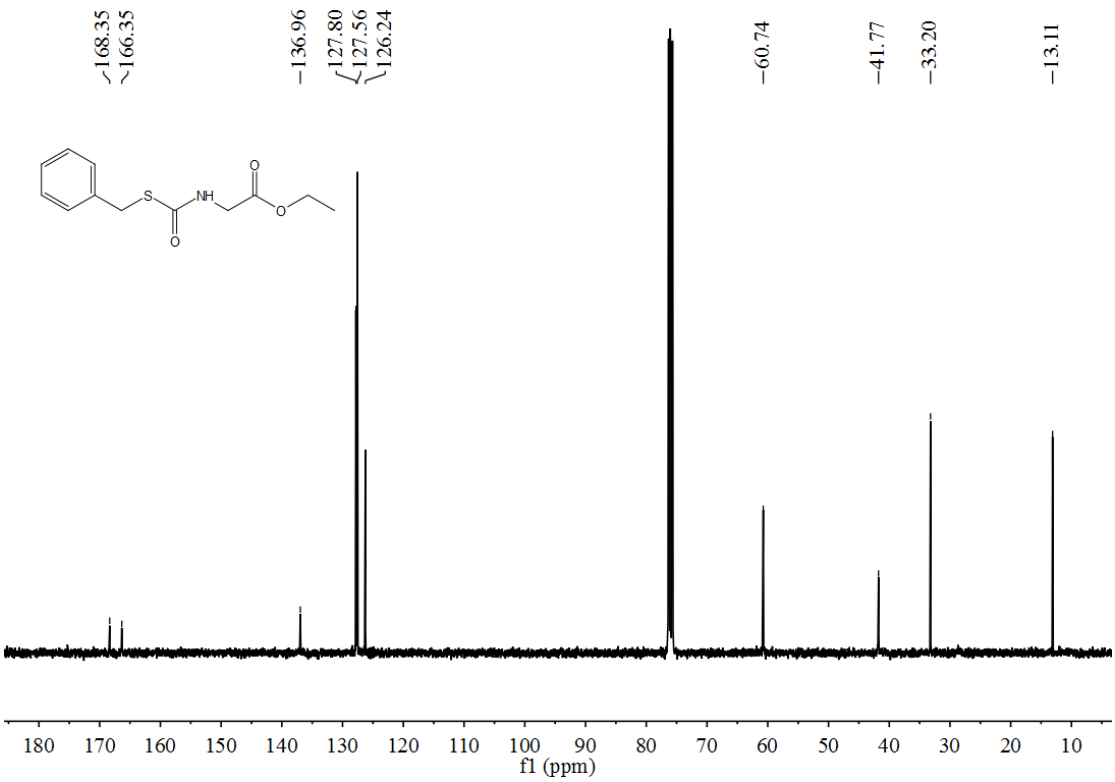
^{1}H NMR spectrum of **3p**



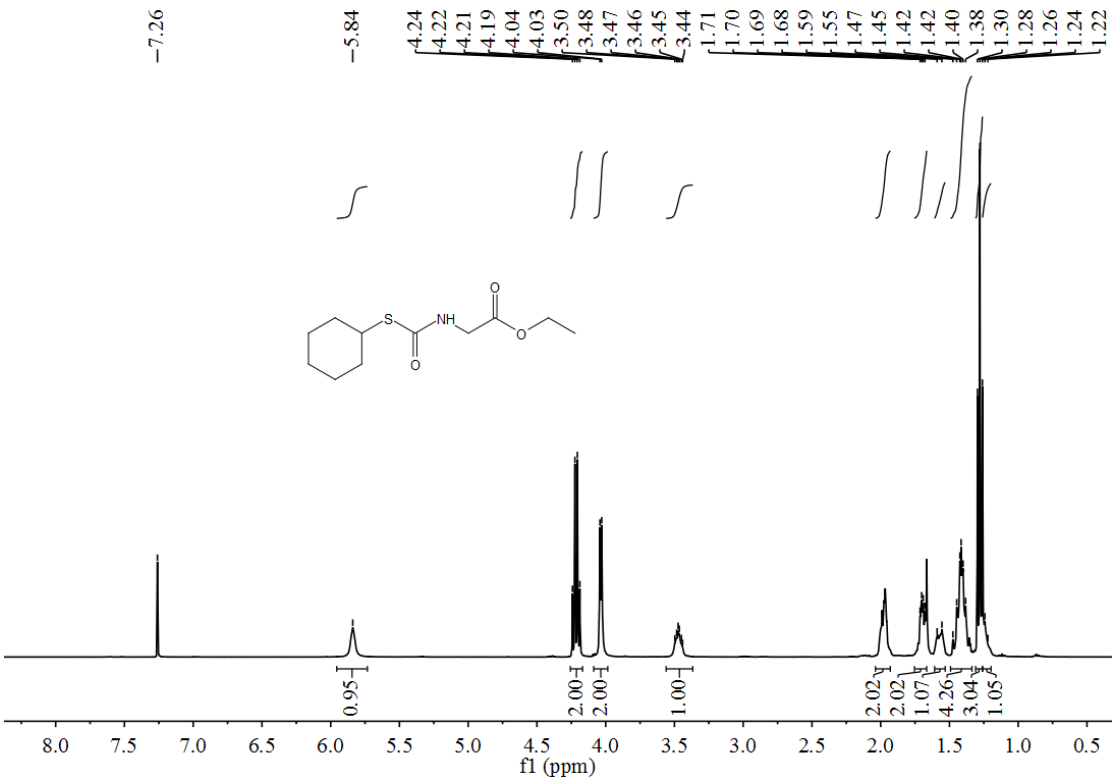
^{13}C NMR spectrum of **3p**



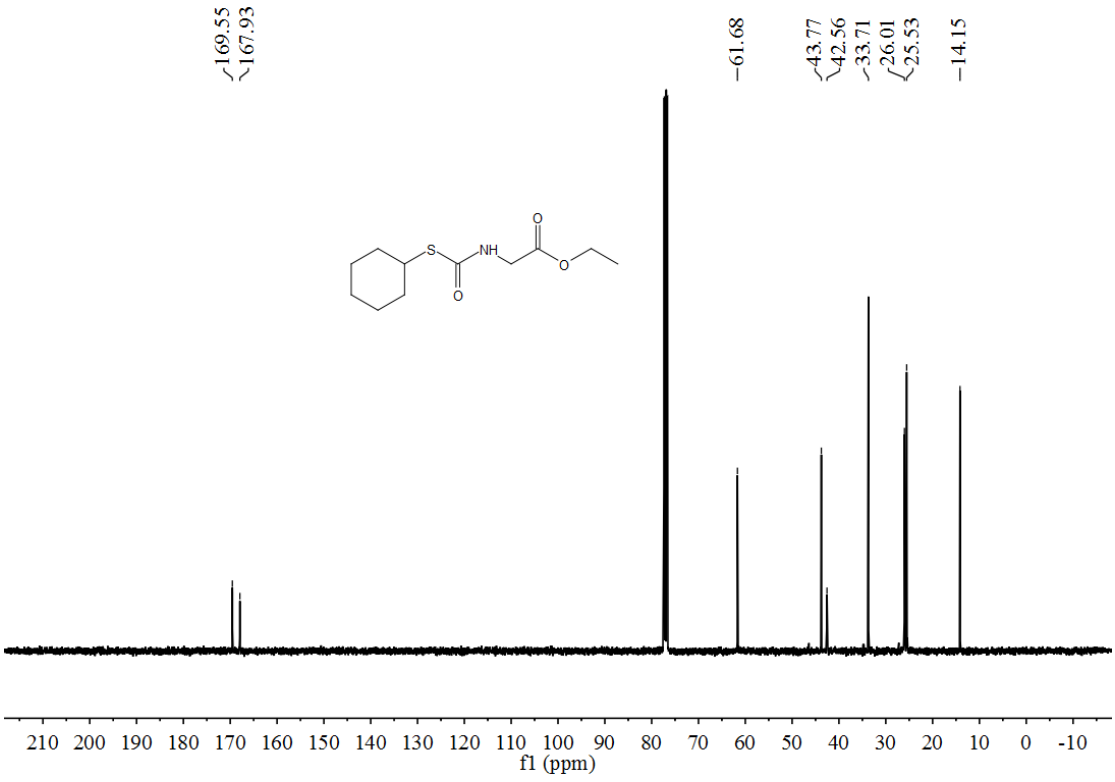
^{1}H NMR spectrum of **3q**



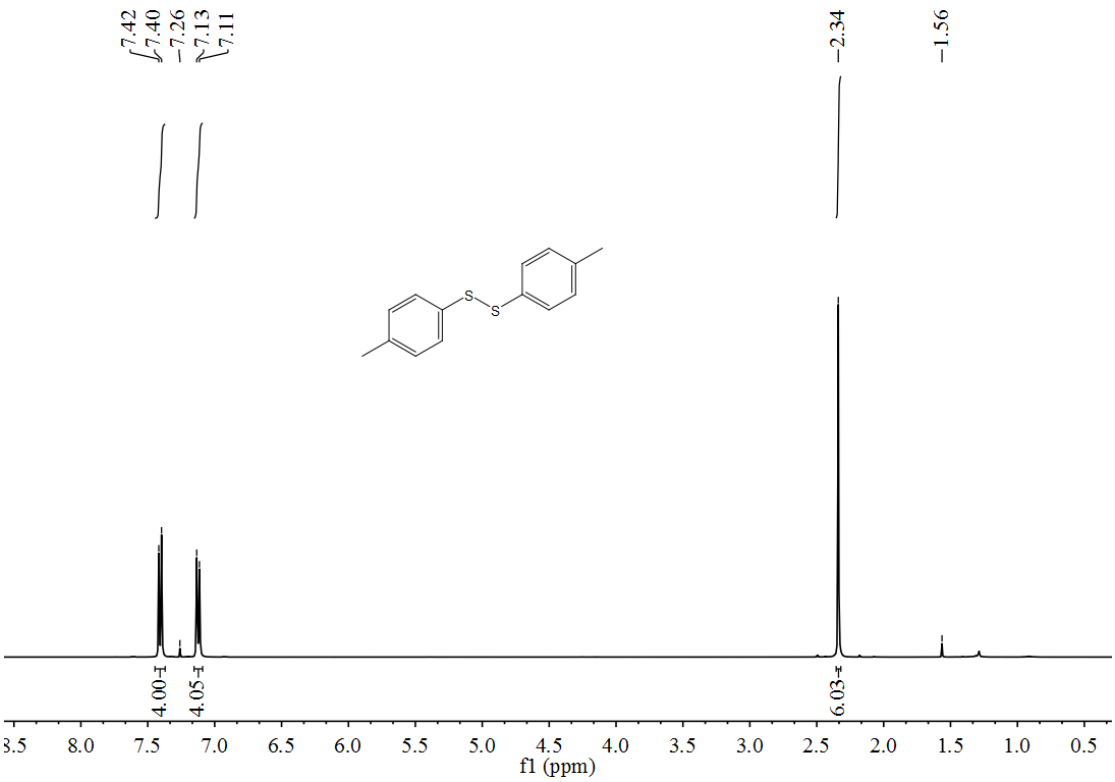
^{13}C NMR spectrum of **3q**



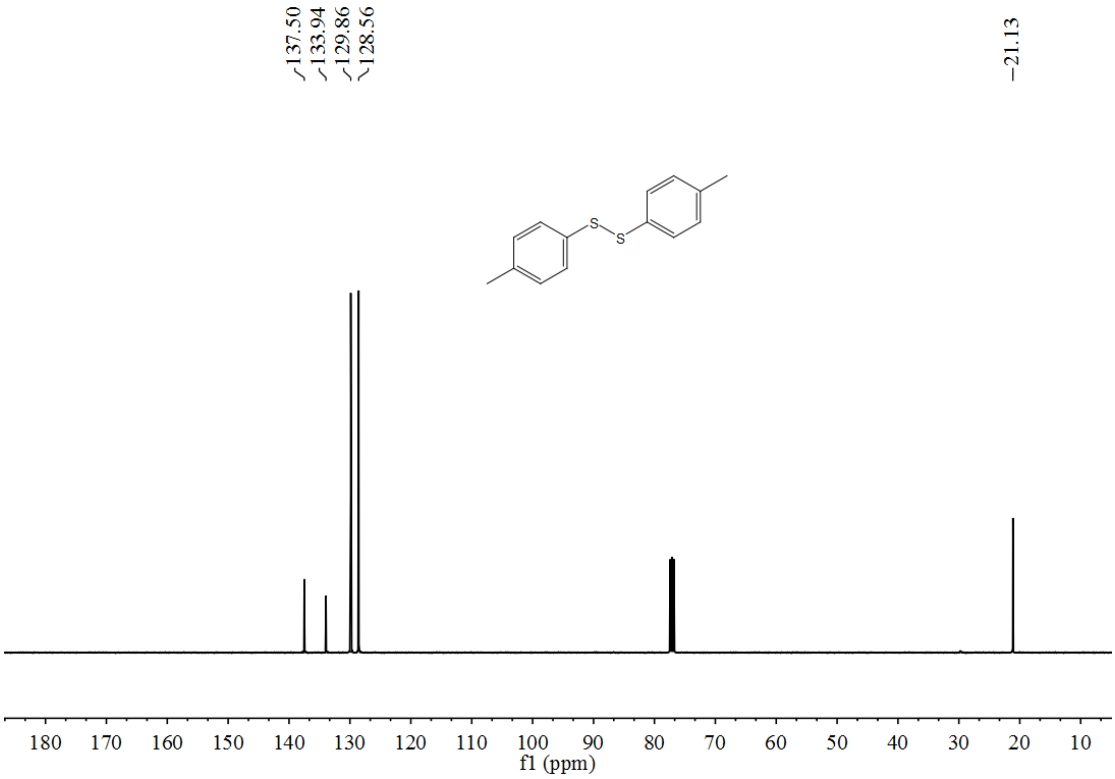
^{1}H NMR spectrum of **3r**



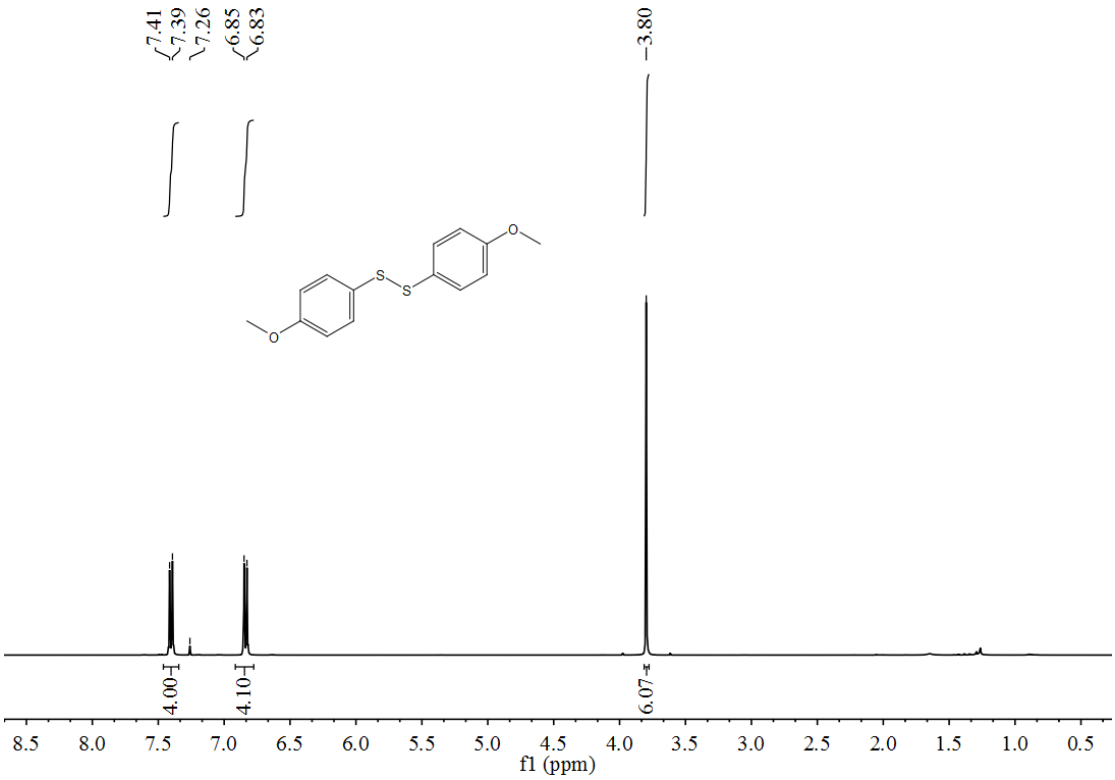
^{13}C NMR spectrum of **3r**



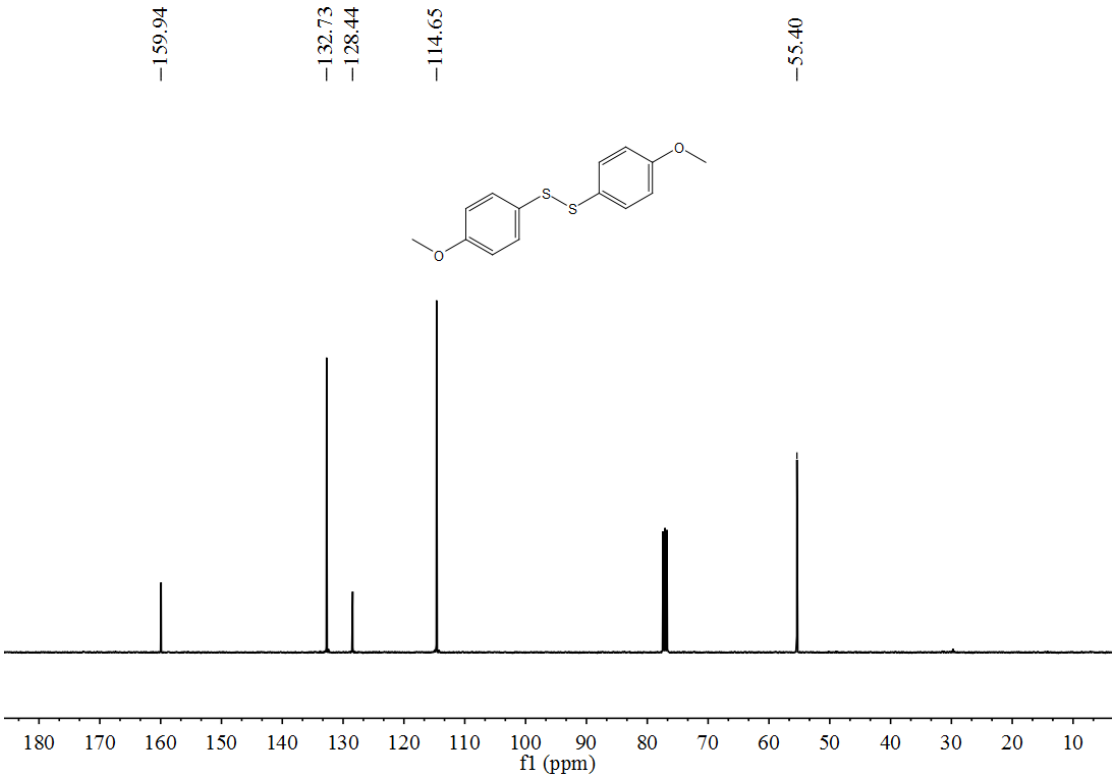
^{1}H NMR spectrum of **6a**



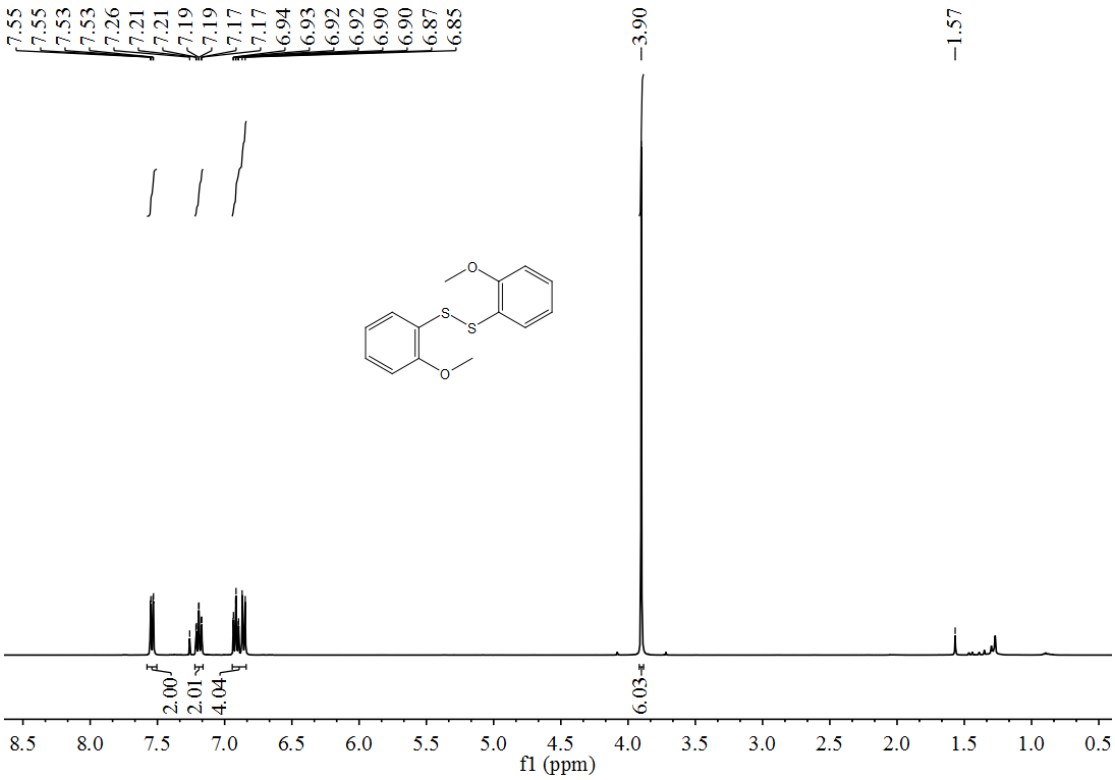
^{13}C NMR spectrum of **6a**



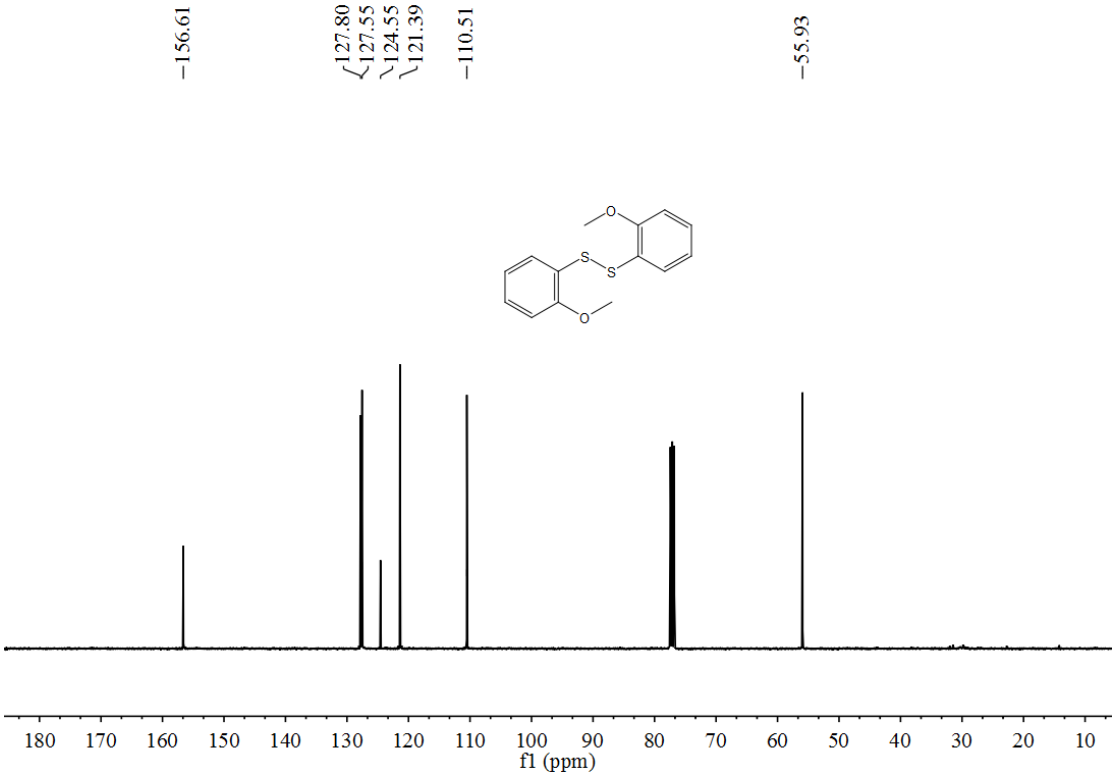
^{1}H NMR spectrum of **6b**



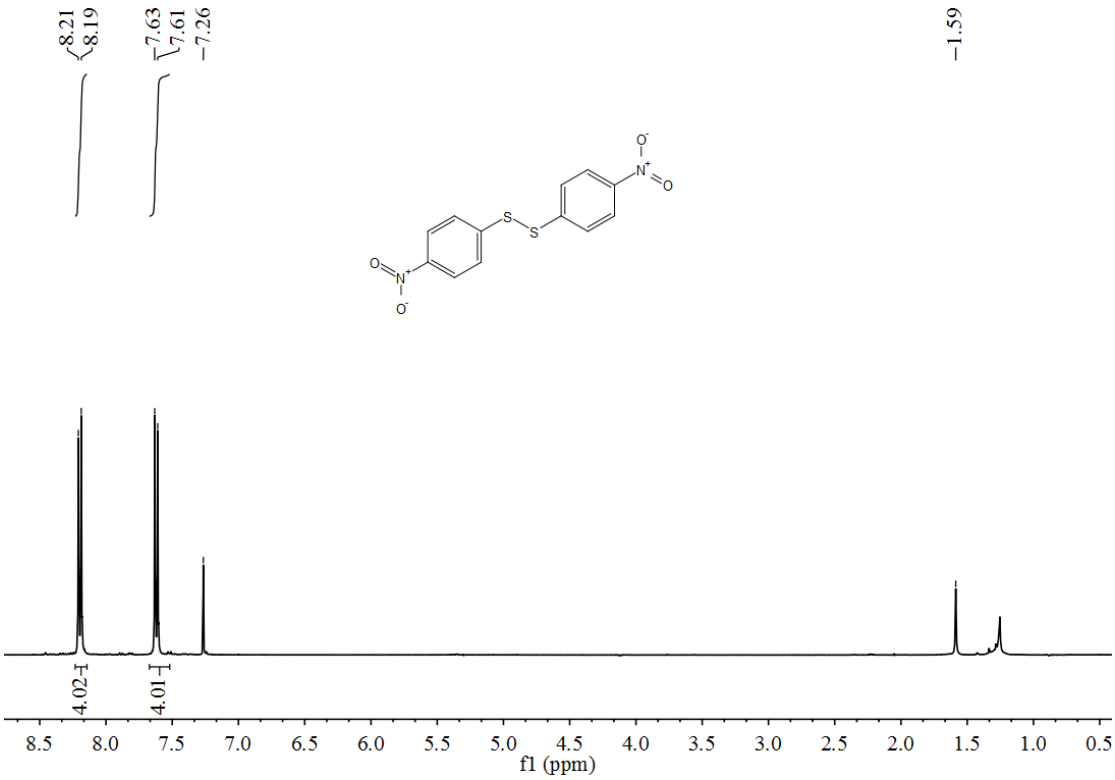
^{13}C NMR spectrum of **6b**



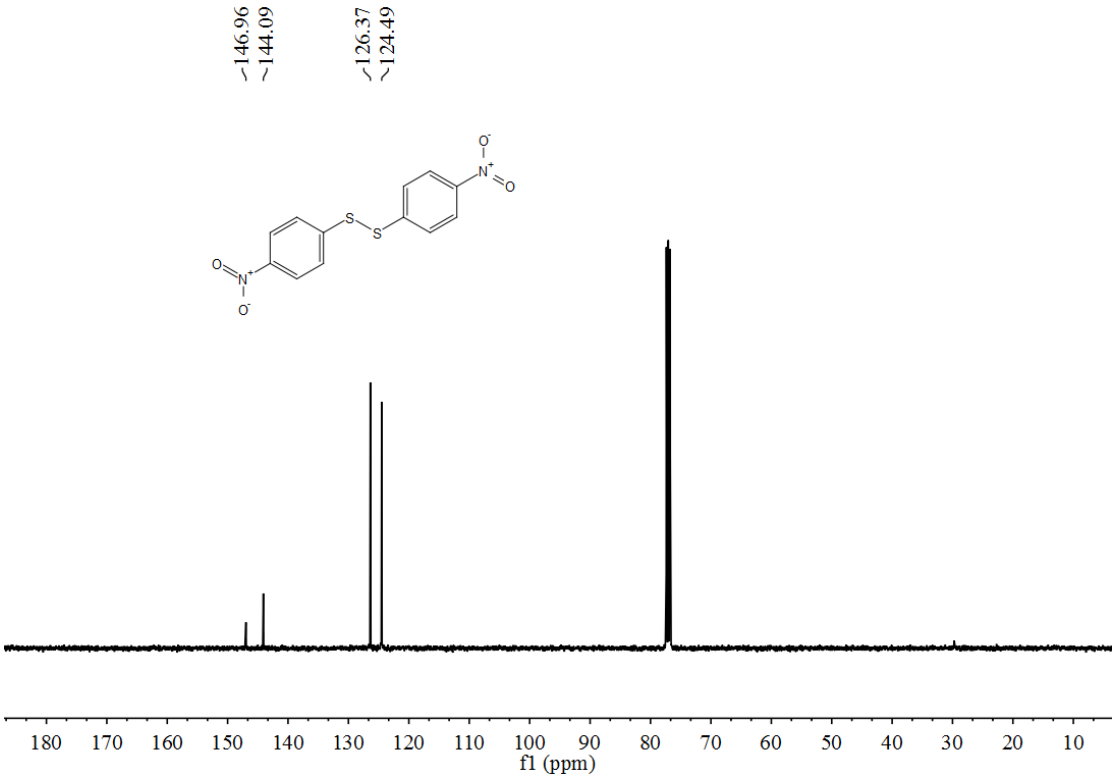
^{1}H NMR spectrum of **6c**



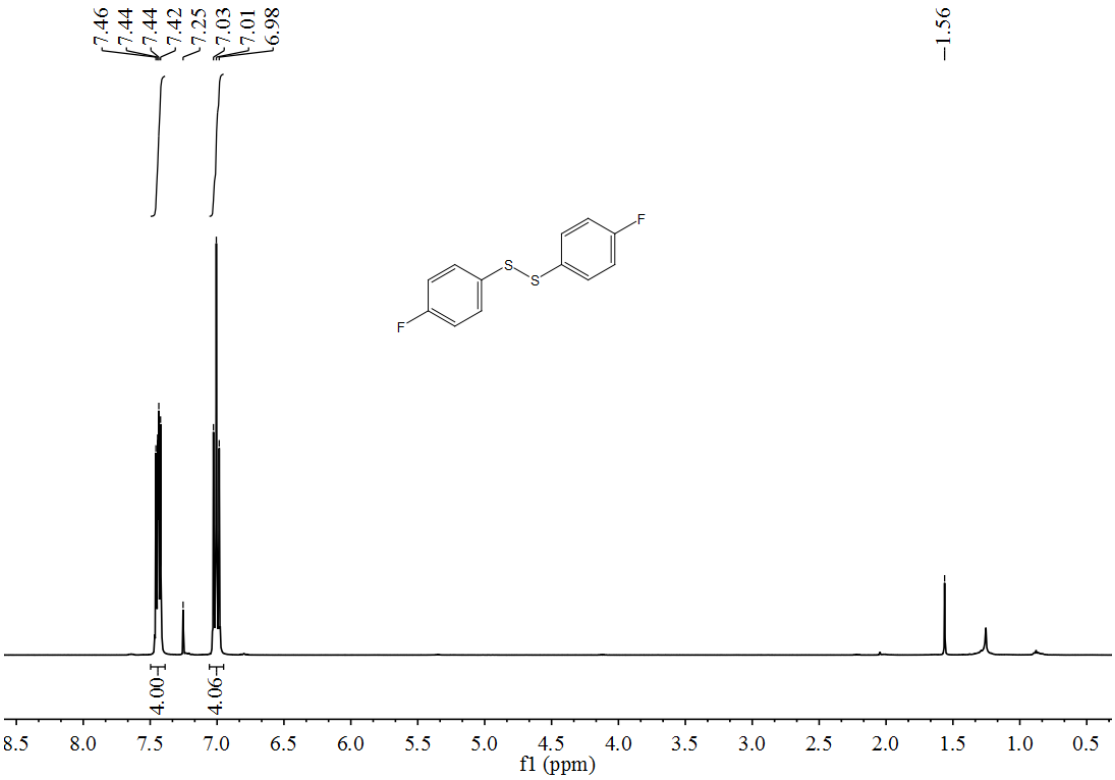
^{13}C NMR spectrum of **6c**



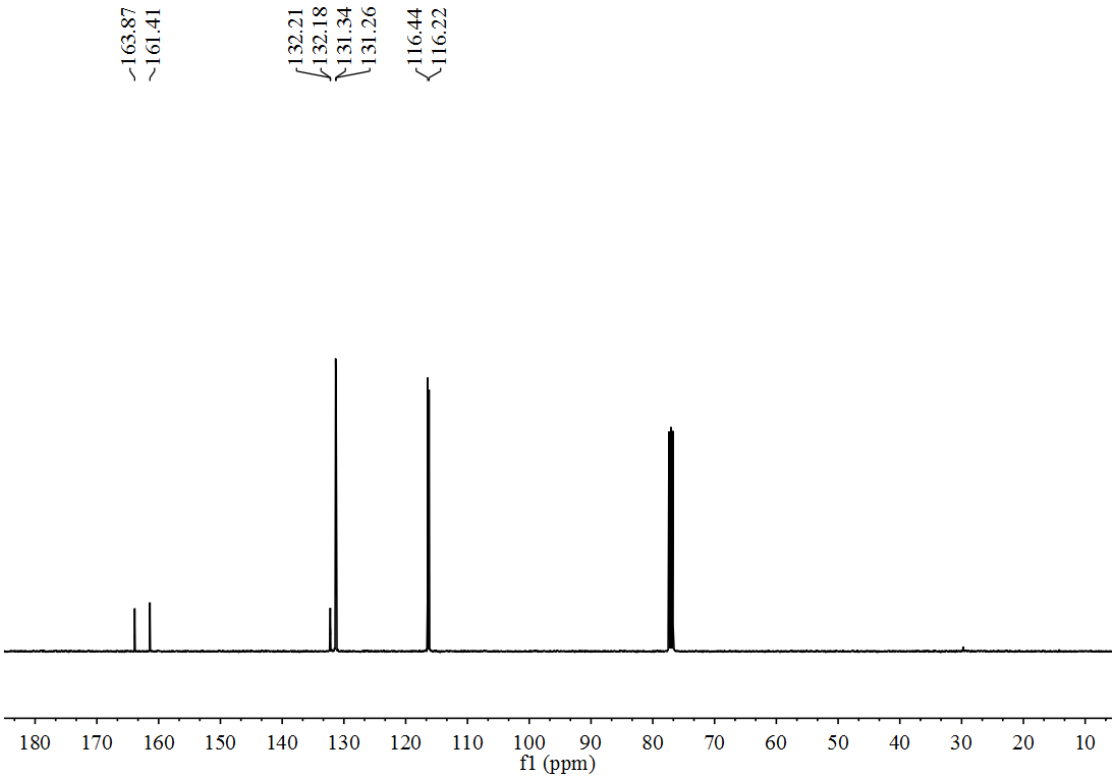
^{1}H NMR spectrum of **6d**



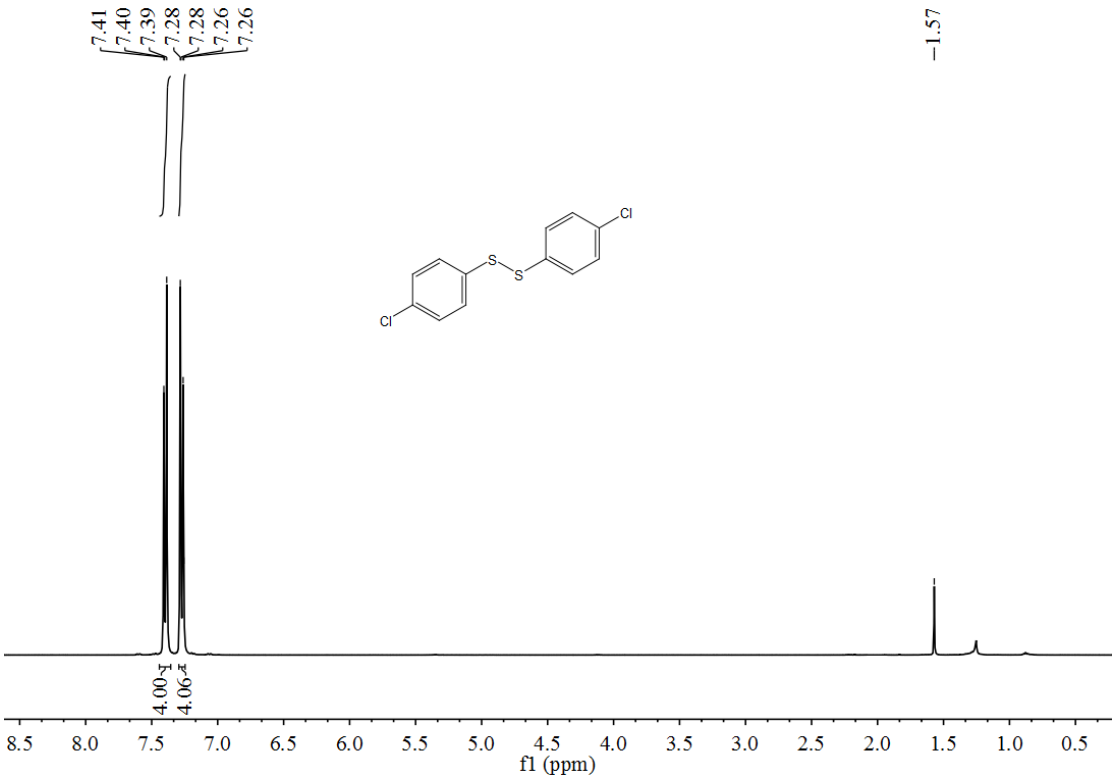
^{13}C NMR spectrum of **6d**



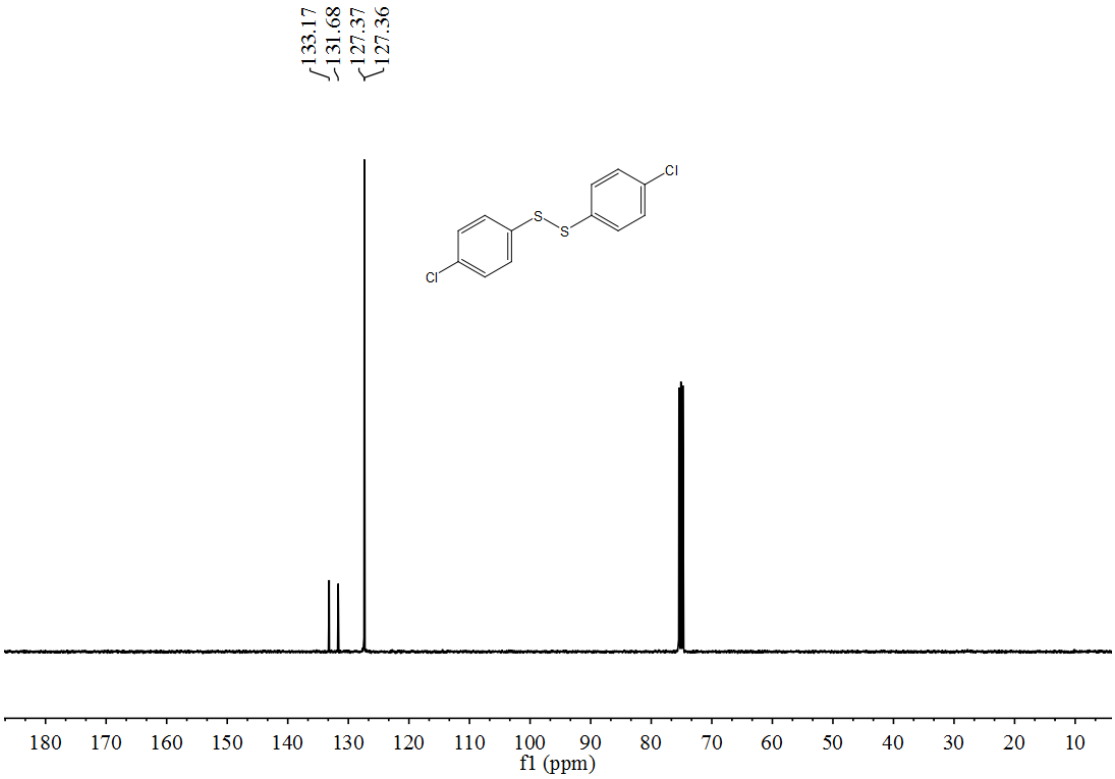
^{1}H NMR spectrum of **6e**



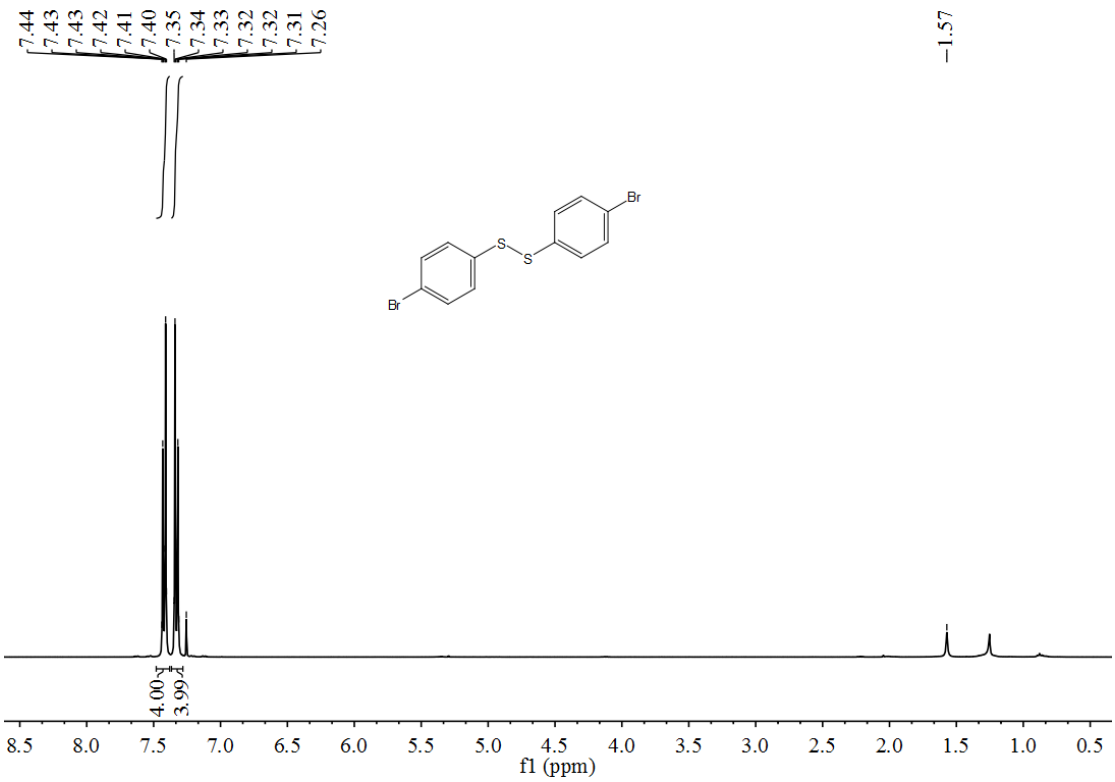
^{13}C NMR spectrum of **6e**



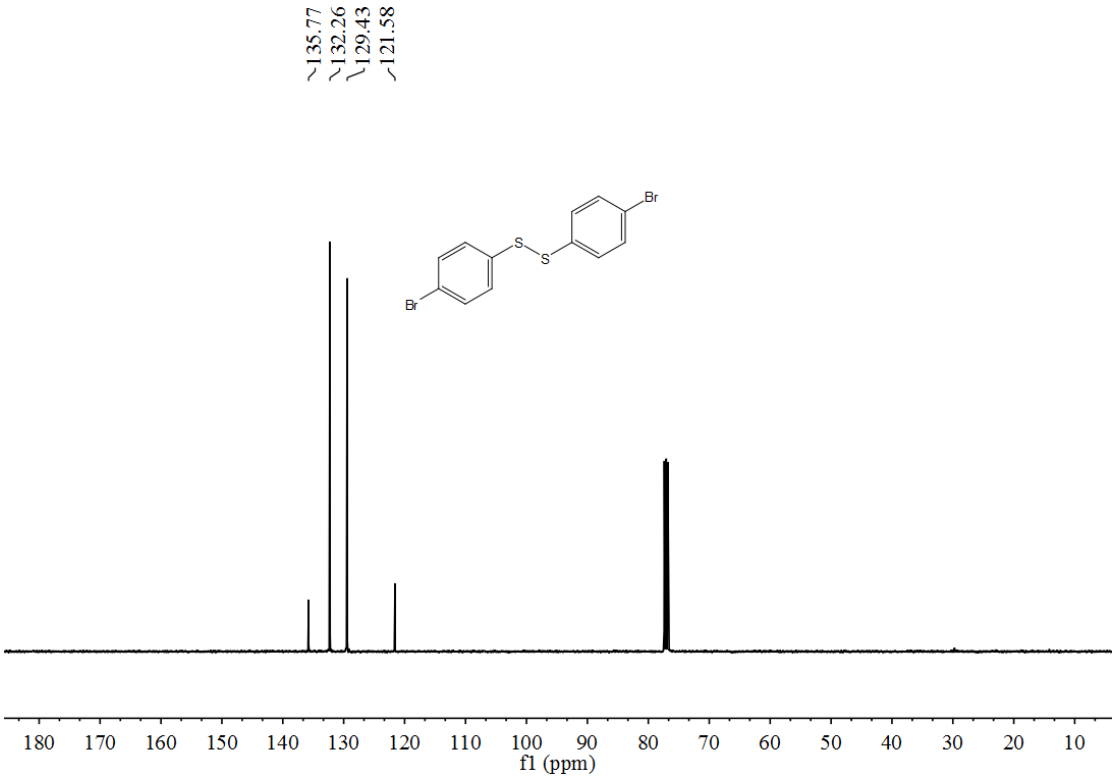
^{1}H NMR spectrum of **6f**



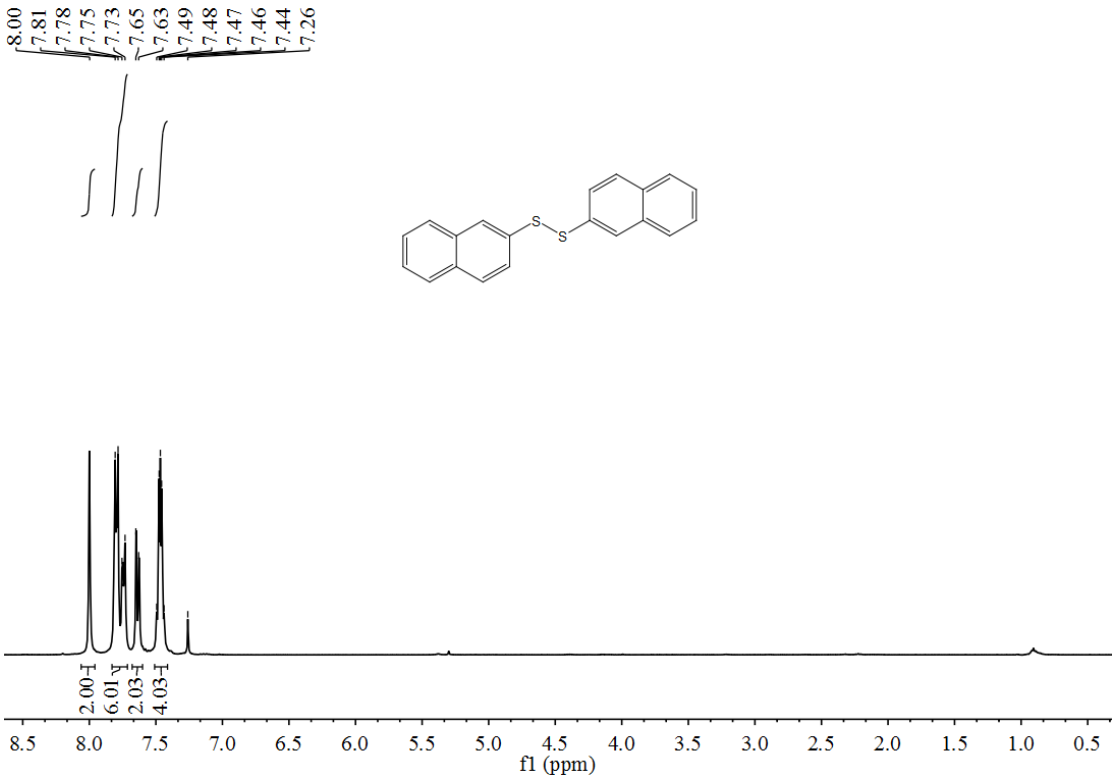
^{13}C NMR spectrum of **6f**



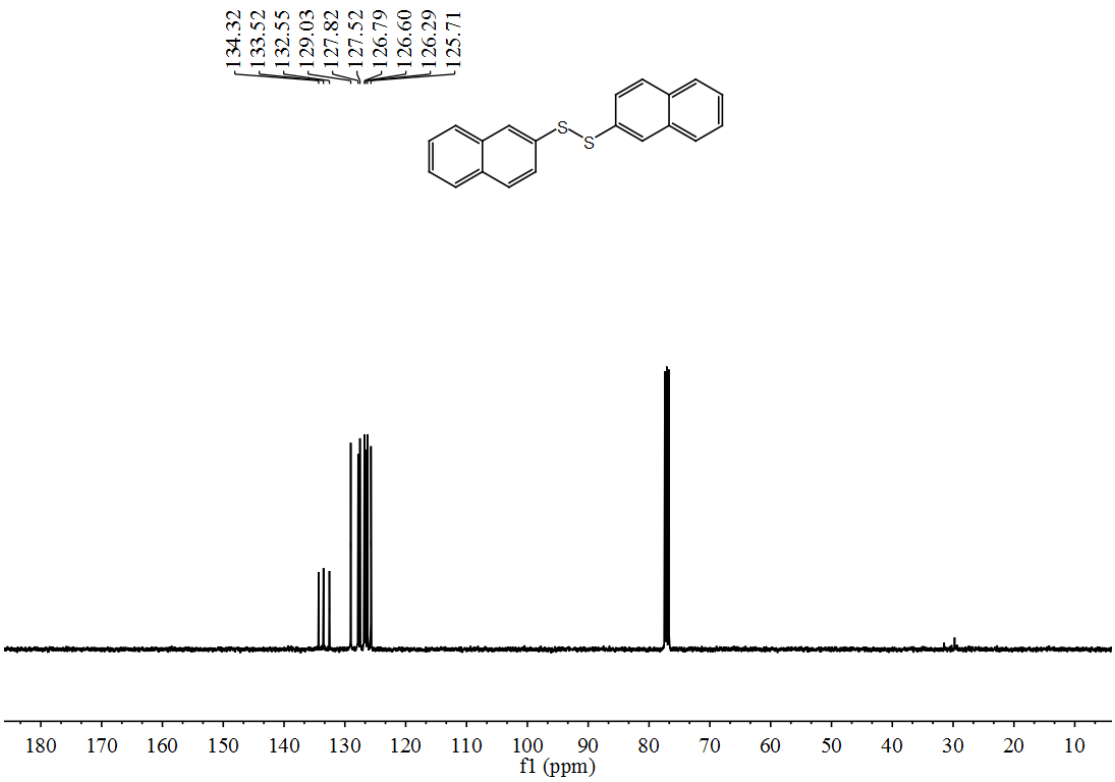
^{1}H NMR spectrum of **6g**



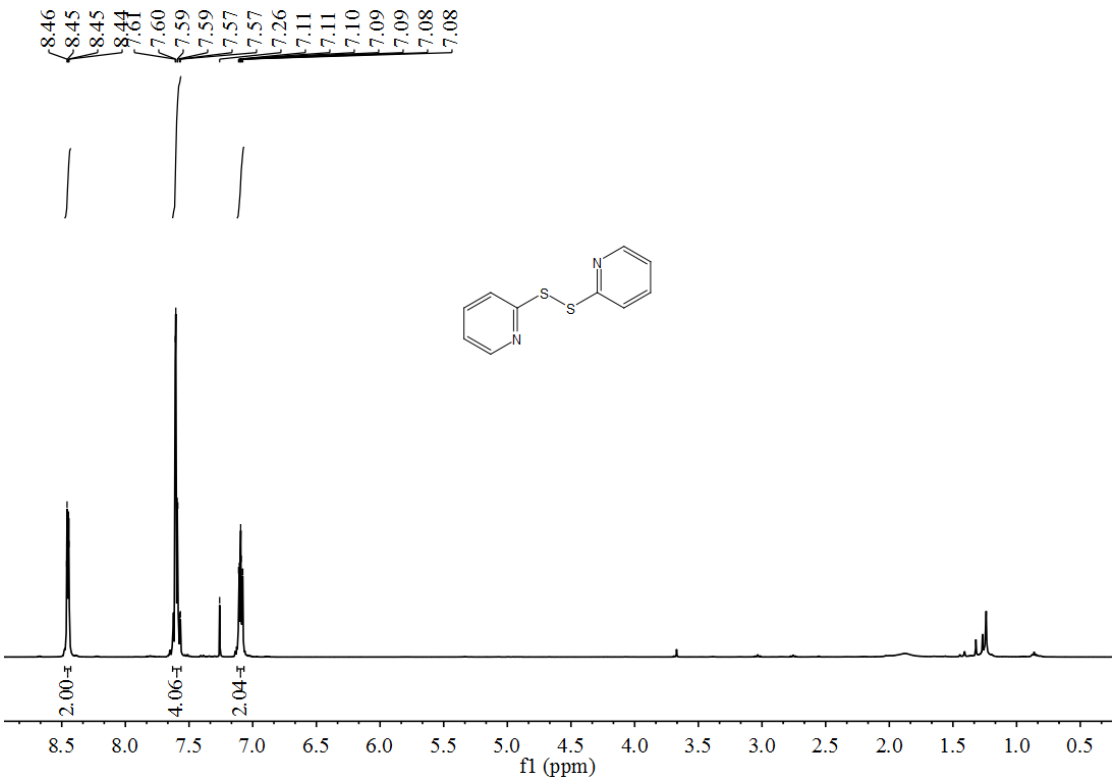
^{13}C NMR spectrum of **6g**



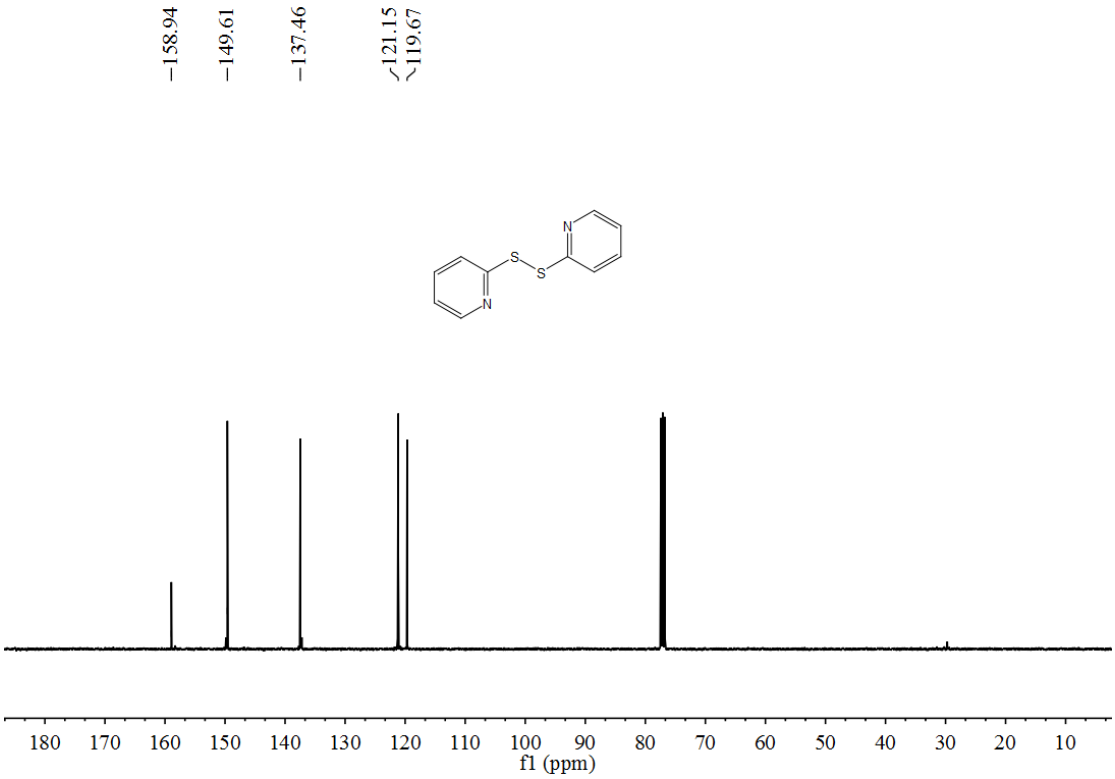
^{1}H NMR spectrum of **6h**



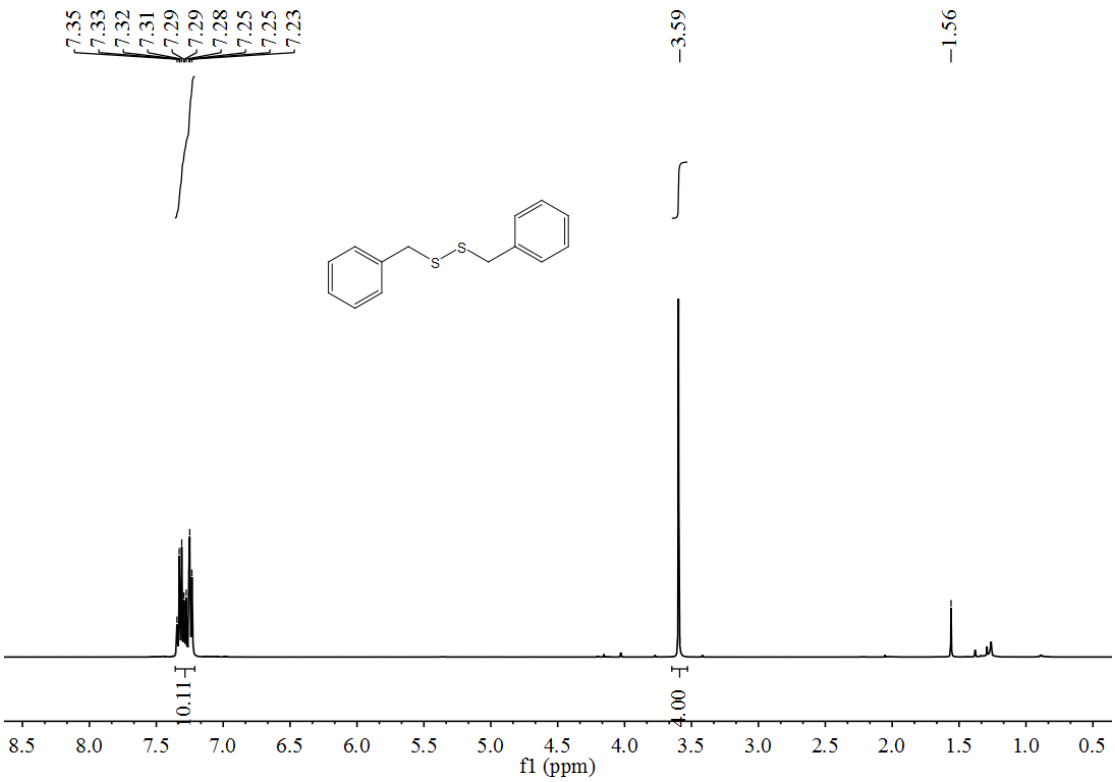
^{13}C NMR spectrum of **6h**



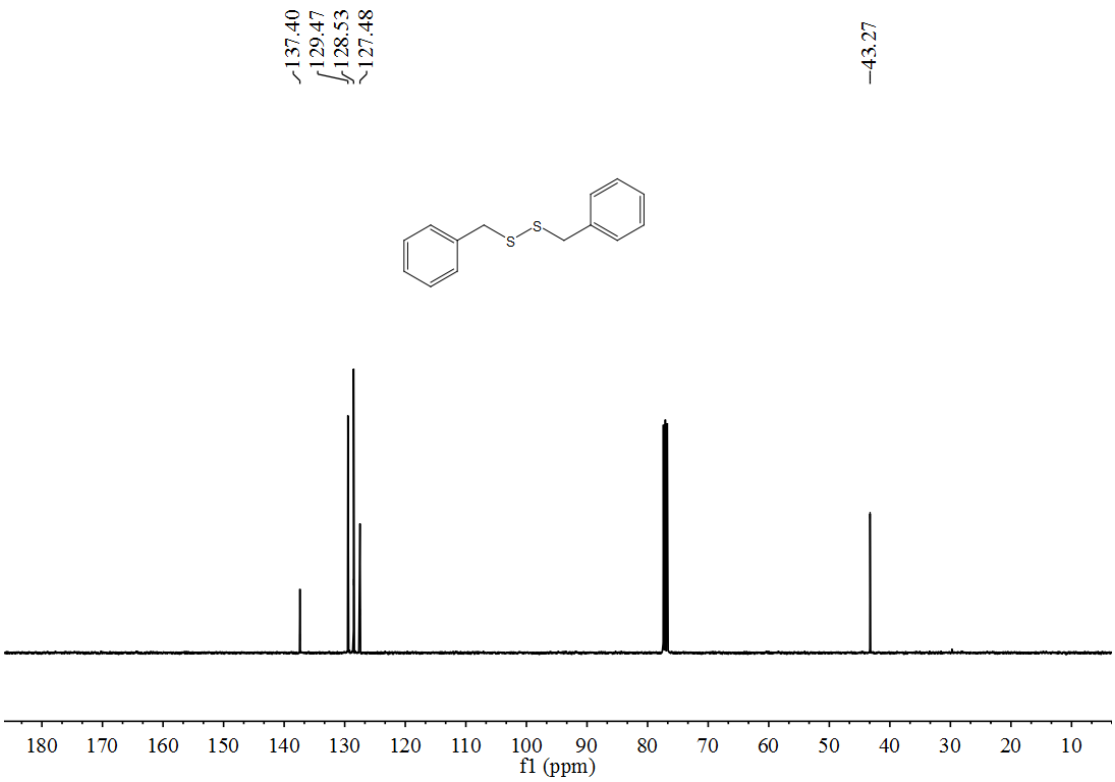
^{1}H NMR spectrum of **6i**



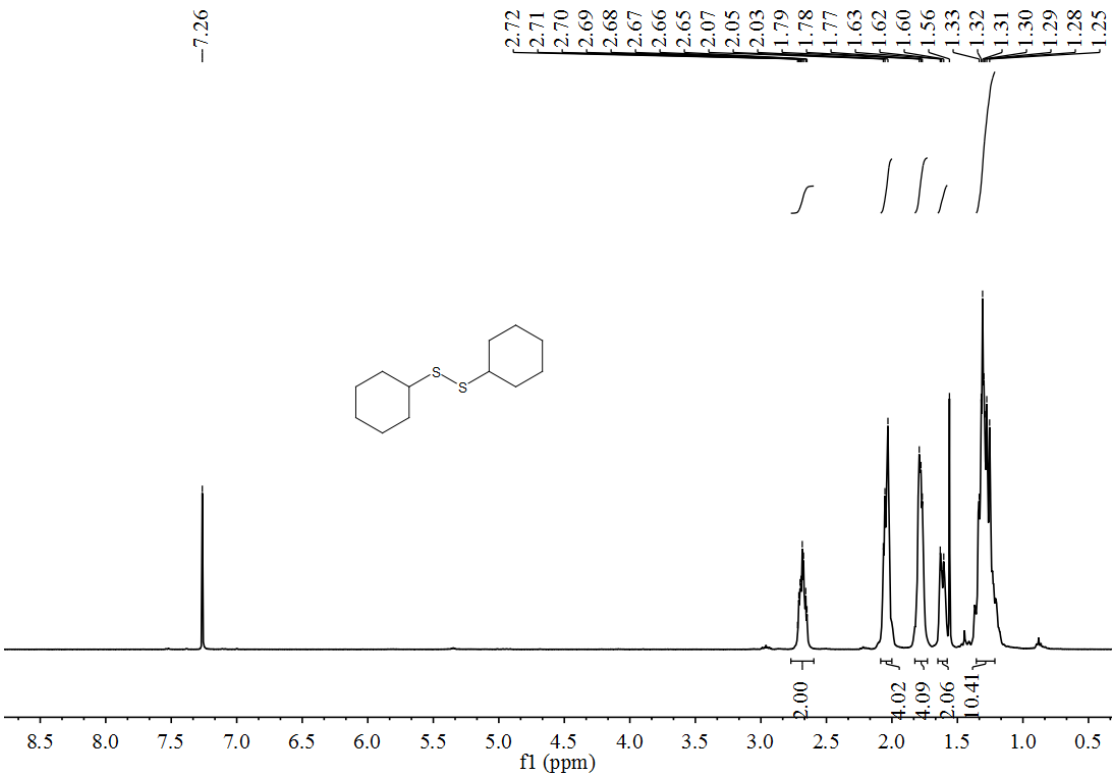
^{13}C NMR spectrum of **6i**



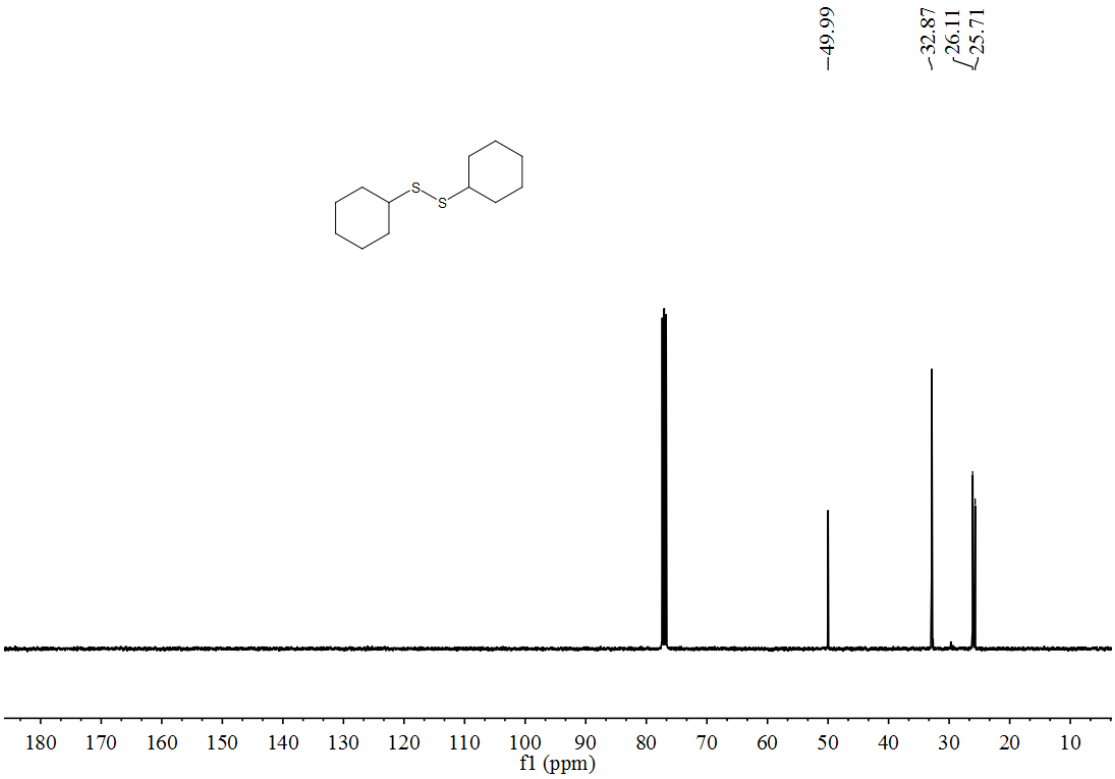
^{1}H NMR spectrum of **6j**



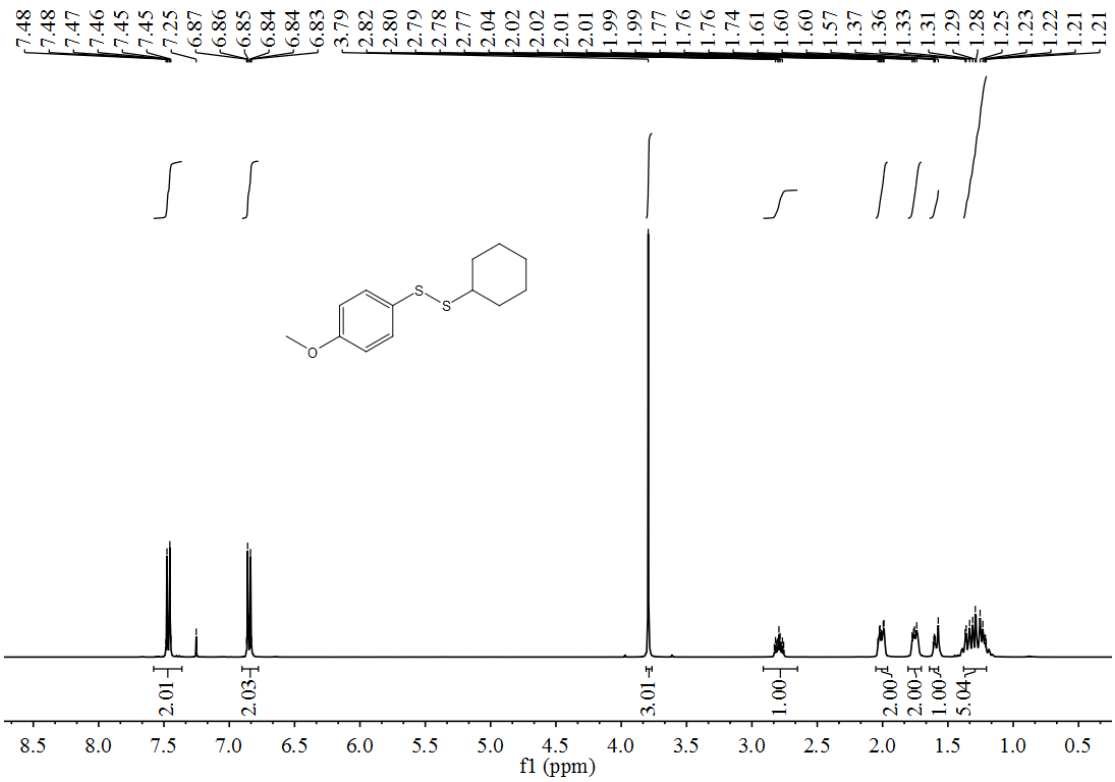
^{13}C NMR spectrum of **6j**



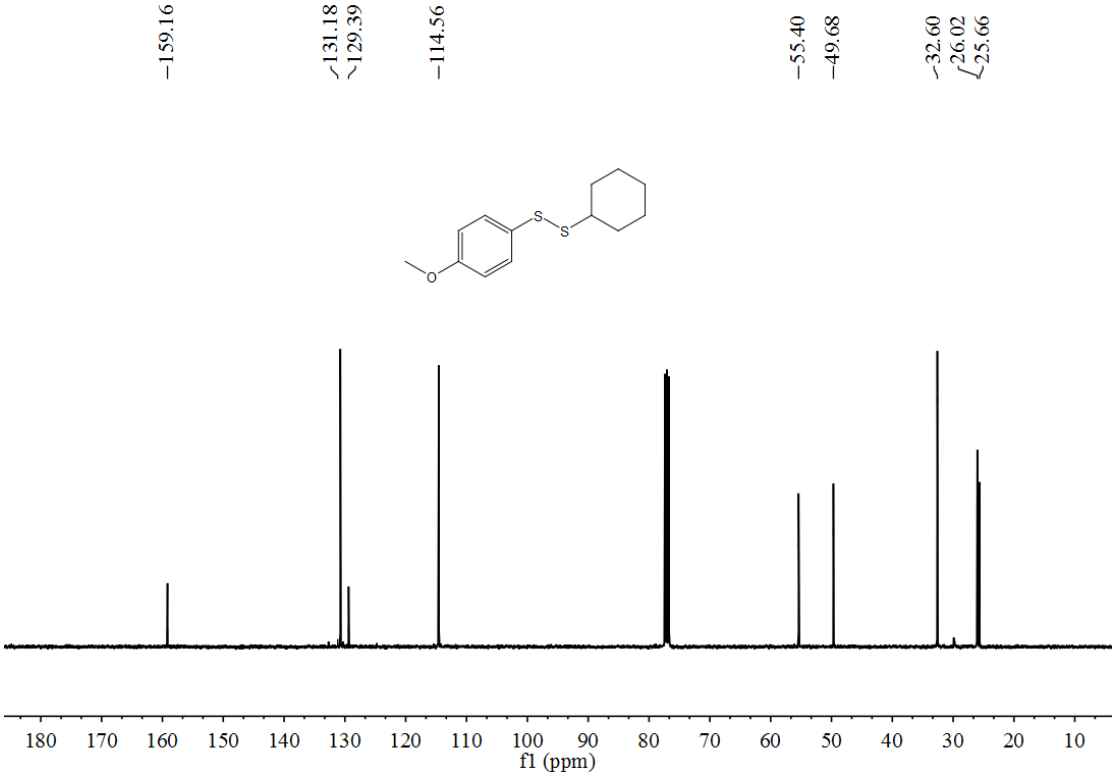
^{1}H NMR spectrum of **6k**



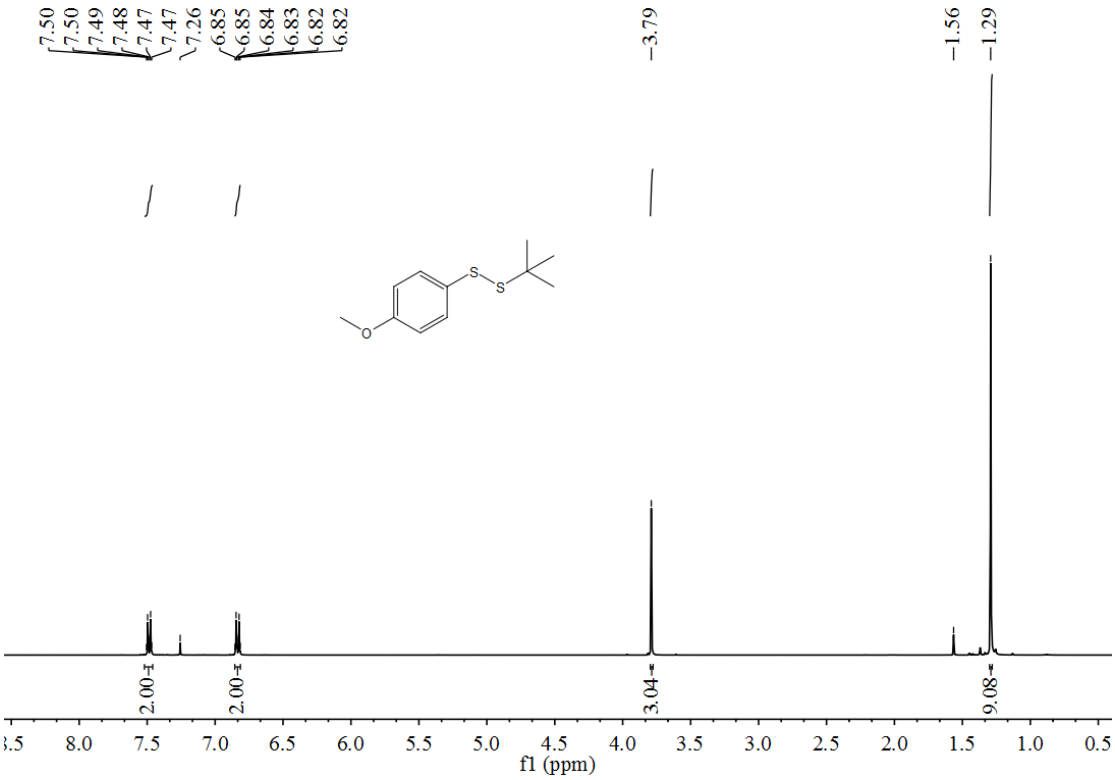
^{13}C NMR spectrum of **6k**



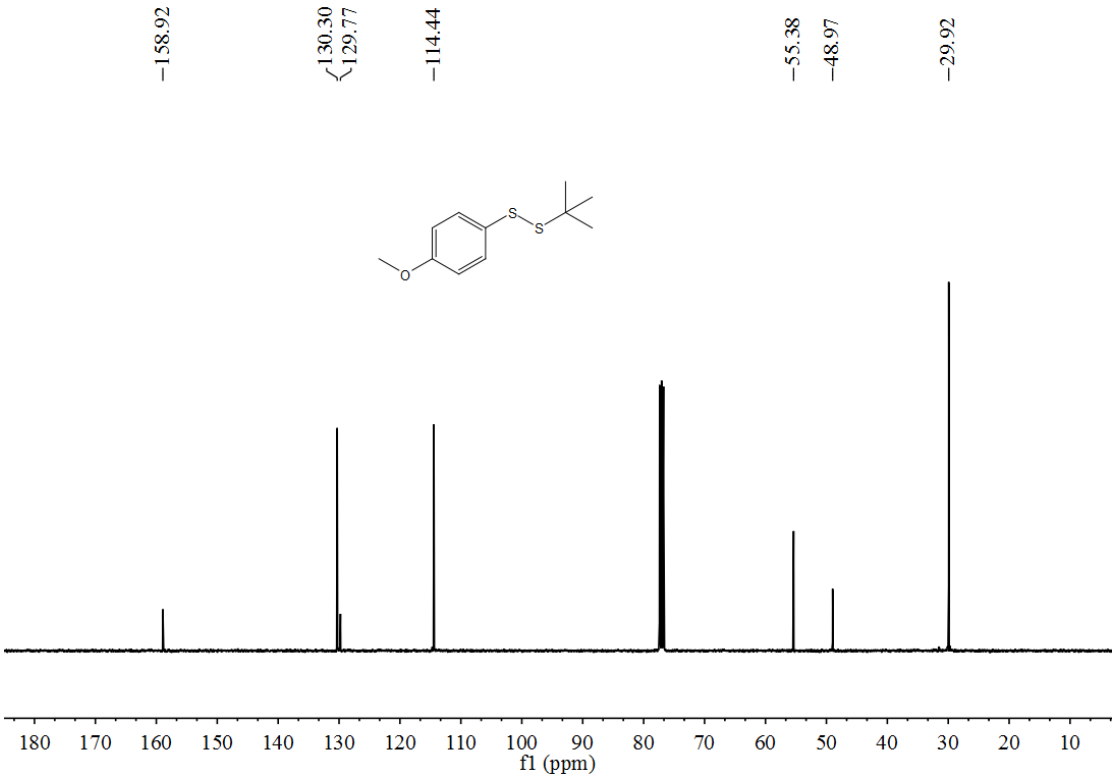
^{1}H NMR spectrum of **6l**



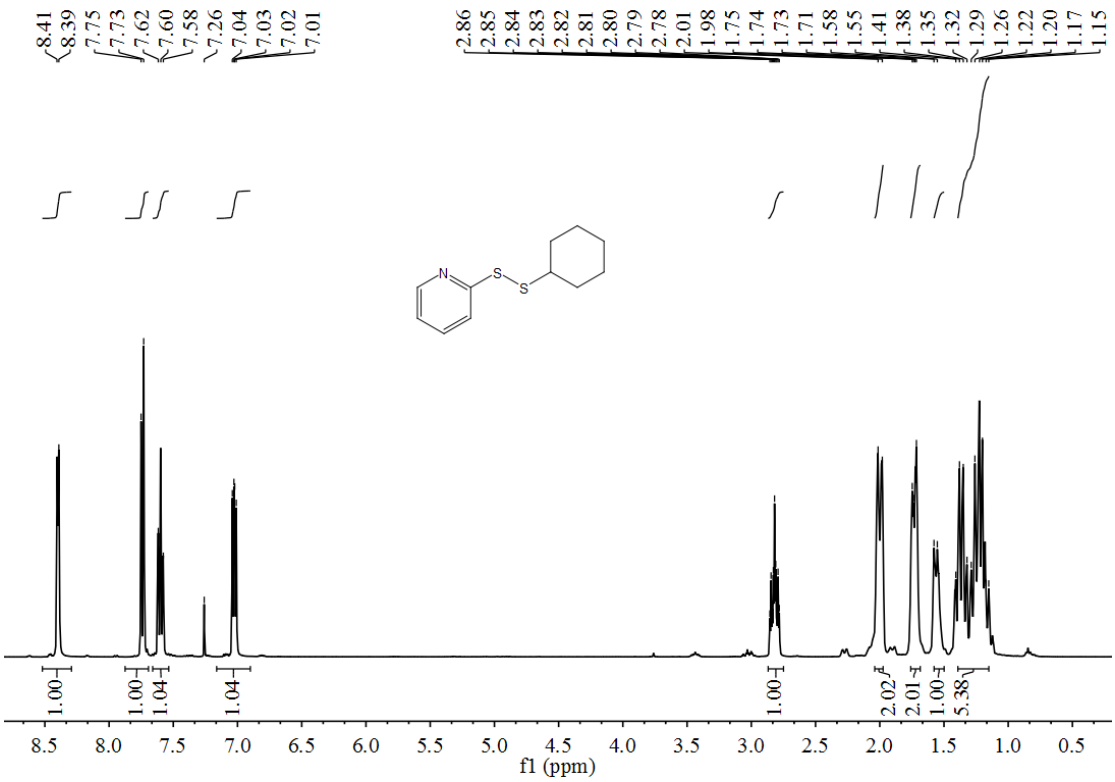
^{13}C NMR spectrum of **6l**



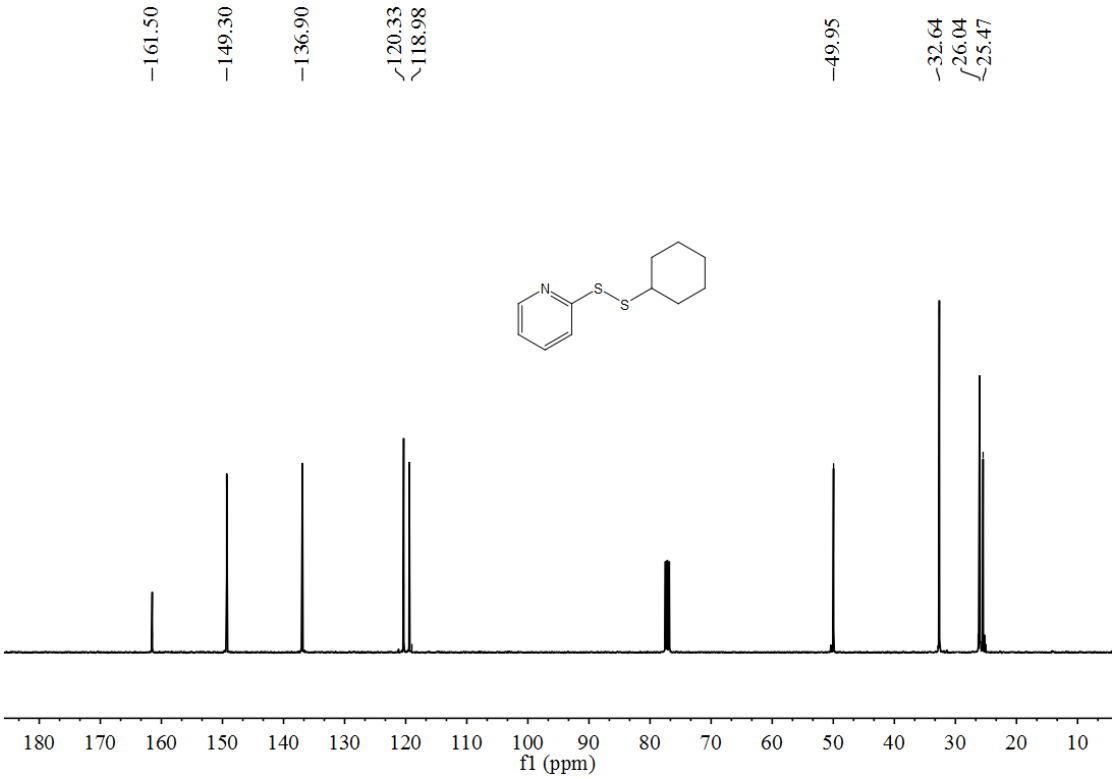
^{1}H NMR spectrum of **6m**



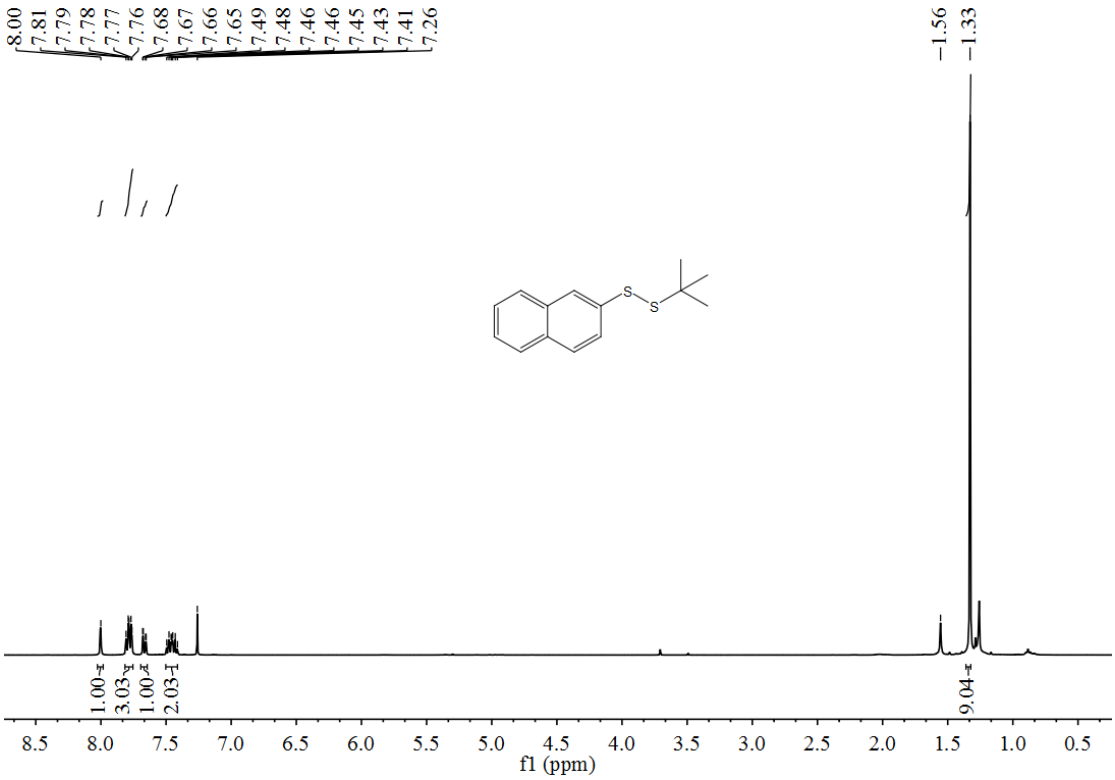
^{13}C NMR spectrum of **6m**



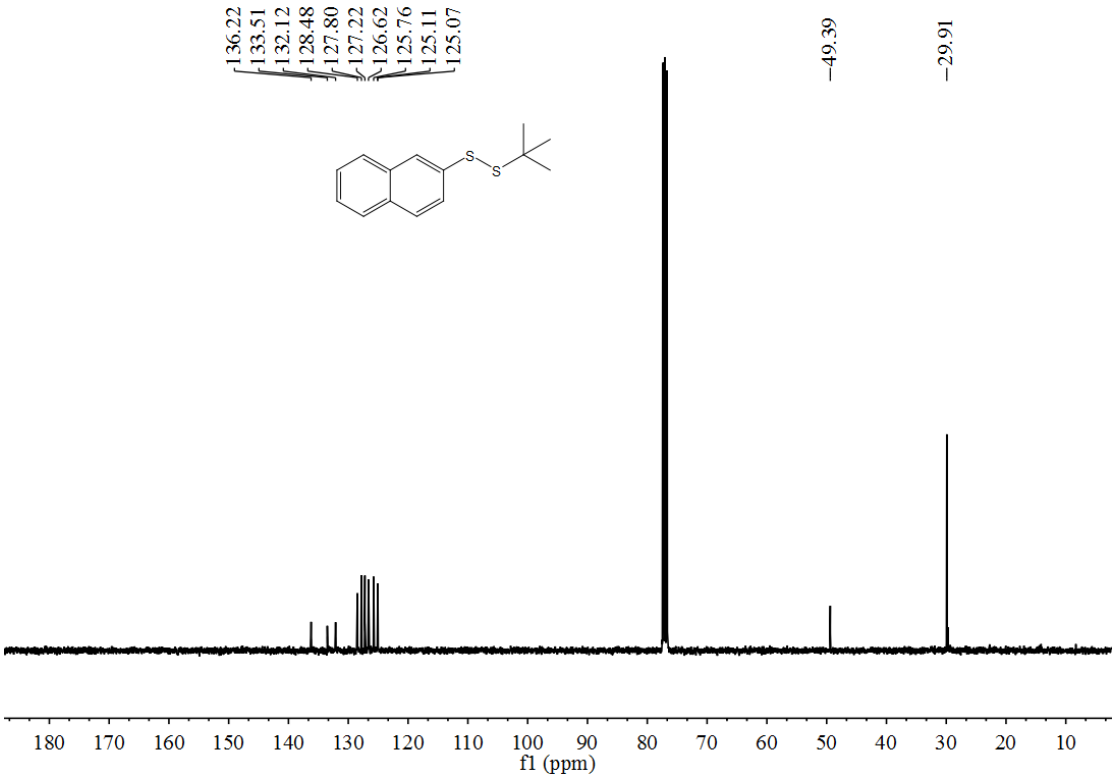
^{1}H NMR spectrum of **6n**



^{13}C NMR spectrum of **6n**



^{1}H NMR spectrum of **6o**



^{13}C NMR spectrum of **6o**