

Supporting Information

Transformation of thiols to disulfides via an oxidant-free radical pathway on the zeolite ETS-10

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Supporting Online Material

Content	Page no.
1. Chemicals and Methods	S2
2. Figures and Tables	S7
3. Analytical data	S18
4. References	S24
5. Spectra of these compounds	S25

1. Chemicals and Methods

Chemicals: Prior to reaction, the selected solvent cyclohexane was pre-deoxygenated to remove trace oxygen: Under a nitrogen stream, a round-bottomed flask (100 mL) containing cyclohexane (50 mL) was placed in ice-water bath for 60 min for solidification of the cyclohexane, and then it was re-placed in a room-temperature water bath for 30 min for dissolution of the solidified cyclohexane. The cyclohexane liquid was then pumped with mechanical pump for 3 h. Finally, the obtained cyclohexane was stored in nitrogen atmosphere, and used as solvent for activity experiments. Unless otherwise noted, all used chemicals in the ETS-10-catalyzed S-H/S-H self-coupling reaction were commercially available and were used as received without any further purification.

Methods

Prepare of KETS-10, RbETS-10 and CsETS-10 samples: The NaKETS-10 zeolite was synthesized according to our previous work.^{S1} The METS-10 (M = K, Rb, and Cs) samples were obtained by cation-exchanged treatment of the as-synthesized NaKETS-10. Typically, 2.0 g as-synthesized ETS-10 was added into an aqueous solution (20 mL, 0.25 mol/L) of the potassium nitrate, rubidium nitrate and cesium nitrate, respectively. The mixture was stirred at 50 °C for 16 h. Then, the suspension was filtrated; the obtained solid was thoroughly washed with deionized water to remove the residual nitrate. The final solid was dried at 100 °C for 8 h, and calcined at 200 °C for 2 h. The resulting materials were named KETS-10, RbETS-10 and CsETS-10, respectively.

Pre-deoxygenate of zeolite sample: To remove the oxygen molecules from the porous channels of zeolite catalyst, prior to reaction, the pre-weighed catalyst was degased for 3 h at 200 °C in vacuum and then backfilled with nitrogen. For the cycle test of CsETS-10 catalyst, the same deoxygenate treatment was conducted after each centrifugation to obtain the catalyst.

Analysis of products: The pure product was obtained by flash column chromatography on silica gel by using petroleum ether (60~90 °C) and ethyl acetate as eluents. Compounds described in the literature were characterized by comparing their ¹H and ¹³C NMR spectra with the reported data.

Nuclear Magnetic Resonance (NMR) spectra were recorded on a Bruker Advance III (300 MHz, 500 MHz, and 600 MHz) instruments at ambient temperature. All ^1H NMR spectra were measured in part per million (ppm) relative to the signals for tetramethylsilane (TMS) added into the deuterated chloroform (CDCl_3) (0 ppm) unless otherwise stated. Data for ^1H NMR were reported as follows: chemical shift (δ), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, qu = quintet, sex = sextet, m = multiplet, ovrlp = overlap), coupling constants (J , in Hz), and integration. All ^{13}C NMR spectra were reported in ppm relative to CDCl_3 (77.16 ppm) unless otherwise stated, and were obtained with complete ^1H decoupling. The ^1H and ^{13}C NMR spectra of **2t** were measured in part per million (ppm) relative to the signals for tetramethylsilane (TMS) added into the water- d_2 (D_2O). All GC analyses were performed on an Agilent Technologies 7890B GC system with a FID detector.

Calculation of the amount of produced H_2 : The precise yield of H_2 according to the yield of disulfide has been carefully calculated. Considering that the reaction is taking place in a nitrogen atmosphere, the relationship of the GC peak area of nitrogen (S_{N_2}) and hydrogen (S_{H_2}) with the injection volume (V_{N_2} and V_{H_2}) was established. As shown in Fig. S5, the S_{N_2} and S_{H_2} linearly increase with the increasing of V_{N_2} and V_{H_2} , and the following equations (1) and (2) were obtained by fitting the experimental data. Therefore, the V_{H_2} produced in the reaction can be calculated by Equation (3).

$$S_{\text{N}_2} = 8265.63V_{\text{N}_2} \quad (1)$$

$$S_{\text{H}_2} = 7180.77V_{\text{H}_2} \quad (2)$$

$$V_{\text{H}_2} = \frac{8265.63}{7180.77} \times \frac{S_{\text{H}_2}}{S_{\text{N}_2}} \times V_{\text{N}_2} \quad (3)$$

The self-coupling experiments of **1a** were performed in a reaction tube (10 mL) with the standard conditions. The cyclohexane (2 mL) was used as solvent; the V_{N_2} in the tube was thus 8 mL.

After the reaction was finished, the tail gas was analyzed by an Agilent 7890B chromatograph equipped with a TCD detector and packed column (TDX-01, 60-80 mesh) and the results were shown in Fig. S6. The S_{N_2} and S_{H_2} were also presented in this figure. The liquid phase was analyzed by an Agilent 7890B chromatograph equipped with a FID detector to obtain the yields of **2a** (Table S1).

The theoretical value and measured value of the V_{H_2} produced in the reaction were calculated by Equations (4) and (5), respectively, and the calculated values were showed in Table S1. It is shown that the measured value increased from 6.09 to 22.19 mL with the increasing of **2a** yield, and the theoretical value and measured value of the V_{H_2} according to the different yields of **2a** were almost always equal.

$$\text{theoretical value} = N \times \frac{y_{2a} \times n_{ini}}{2} \quad (4)$$

$$\text{measured value} = \frac{8265.63}{7180.77} \times \frac{S_{H_2}}{S_{N_2}} \times 8 \quad (5)$$

where N is the molar volume, ca 22.41 mL/mmol; y_{2a} is the yield of **2a**; n_{ini} is the initial molar of **1a** (2 mmol).

¹H NMR, EPR, and IR experiments

¹H NMR experiment: The ¹H magic angle spinning (MAS) NMR spectra of the pyrrole adsorbed catalyst samples were collected on Bruker AVANCE III 400-WB spectrometer. Pre-analyzed zeolite sample was outgassed at 400 °C for 15 h under dynamic vacuum up to a final pressure of 10⁻³ Pa. Then, the sample was cooling down to room temperature, and it was exposed to pyrrole vapor for 5 min and subsequently evacuated at 65 °C for 60 min to eliminate physisorbed pyrrole. The pyrrole chemisorbed samples were noted as NaK-ETS-10-P, KETS-10-P, RbETS-10-P and CsETS-10-P, respectively. The evacuated sample was immediately transferred into the rotors in a glove box. Then ¹H MAS NMR spectra were recorded at 399.9 MHz under room temperature, using a VT CP-MAS Varian probe with 5 mm silicon nitride rotors spinning at 13 kHz. The p/2 rad pulses of 6 ms

and a recycle delay of 5 s were used.

EPR experiment: EPR spectra were recorded on a JES FA200 spectrometer. The detailed experimental procedures are as follows: A dried sealed tube (10 mL) equipped with a stir bar was loaded with 0.5 mmol benzyl mercaptane **1a**, 60 μ L DMPO (5,5-dimethyl-1-pyrroline N-oxide), 20 mg catalyst and 1.5 mL deoxygenated cyclohexane. The reaction mixture was stirred under an N₂ atmosphere at 120 °C for 20 min. Then the mixture was taken out and transferred to a sample tube for EPR analysis. An EPR spectrum was recorded at room temperature on EPR spectrometer operated at 9.052 GHz. Typical spectrometer parameters were shown as follows, scan range: 50 mT; center field set: 322.611 mT; time constant: 30 ms; scan time: 60 s; modulation amplitude: 2.0 mT; modulation frequency: 100 kHz; receiver gain: 1.00×10^5 ; microwave power: 0.998 mW.

IR experiment: IR spectra of the BnSH (**1a**) chemisorbed CsETS-10 sample (CsETS-10-BnSH) were obtained on a Bruker TENSOR 27 infrared spectroscope equipped with a reactor cell. Prior to measurement, the CsETS-10 sample was evacuated to 10^{-2} Pa at 350 °C for 5 h, and then the temperature was decreased to 120 °C (reaction temperature). The BnSH was introduced into the reactor cell by He flow (20 mL/min) for 30 s. Immediately, the spectrum (CsETS-10-BnSH-0 min) was obtained in the absorbance mode and was shown after subtraction of a background spectrum for the CsETS-10 sample, which was also obtained at 120 °C. After the CsETS-10-BnSH sample was treated at 120 °C for 30 min, the spectrum of CsETS-10-BnSH-30 min was obtained. For comparison, the IR spectrum of pure benzyldisulfide (**2a**) was also recorded at 120 °C.

Density functional theory calculation

The reaction mechanism was explored by Gaussian 09 program (M. Frisch, G. Trucks, H.B. Schlegel, G. Scuseria, M. Robb, J. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. Petersson, Gaussian 09, revision D. 01, Gaussian, Inc., Wallingford CT, 2009). The model of NaKETS-10 was cut from the crystal structure reported by Anderson et al.^{S2} and a Ti-O-Ti unit was containing in this model based on Damin and coworker's model.^{S3} B3LYP hybrid exchange-correlation functional was used,^{S4} and the semiempirical Grimme's D3(BJ) correction was employed to

include van der Waals (vdW) interactions. ⁵⁵ H, O, Si, Al, and Ti were described by def2-SVP basis set.

Activity test

The typical experimental procedure for the S-H self-coupling reaction was as follows: Under N₂ stream, degassed catalyst (20 mg), benzyl mercaptane **1a** (0.5 mmol), heptane (as internal standard, 0.3 mmol) and cyclohexane (1.5 mL) were placed into a sealed tube (10 mL). The mixture was heated to 120 °C and kept for 3 h with stirring (500 rpm) by a stir bar. The reaction temperature and stirring rate in the sealed tube were controlled using an IKA stirrer (model of RTC BS025). When the reaction was finished and cooled to room temperature, the catalyst was separated by centrifugation and filtration to obtain the liquid phase. The liquid products were analyzed by an Agilent 7890B chromatograph. The thiols conversion and product selectivity were calculated as follows.

$$\text{Thiols conversion} = \frac{\text{Molar of reacted thiols}}{\text{Molar of initial thiols}} \times 100$$

$$\text{Product } i \text{ selectivity} = \frac{\text{Molar of product } i}{\text{Sum of product moles}} \times 100$$

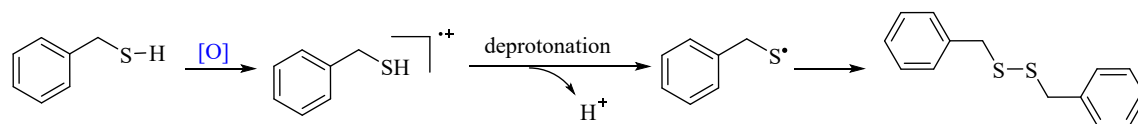
$$\text{Product } i \text{ yield} = \text{Thiols conversion} \times \text{Product } i \text{ selectivity} \times 100$$

Scale-up synthesis of 2a and catalyst recycle: The scale-up experiment was performed in the 300 mL Parr stainless autoclave with mechanical stirring, heating, and temperature control devices (model: 4566, controller: 4848; Fig. S8). 10 g **1a**, 130 mL cyclohexane and 3 g CsETS-10 were charged into autoclave. After the reactor was sealed, the air in the reactor was thoroughly replaced by filling of N₂ three times. The reaction mixture was heated to 120 °C for 10 h under a stirring rate of 300 rpm. The reaction products were analyzed with an Agilent 7890B GC installation. After the reaction completion, the catalyst was collected carefully from the reaction mixture by filtration and washed with cyclohexane, and then kept at 100 °C for 5 h. After that, the catalyst was deoxygenated prior to the next cycle.

2. Figures and Tables

Figures

(a) Oxidant-promoted the generation of sulfur radicals and dimerization of thiols



(b) Metal salts or metal oxide-catalyzed dimerization of thiols in the presence of oxidants

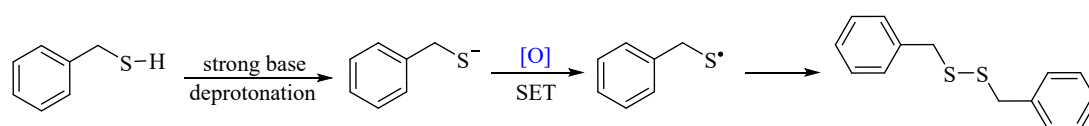


Fig. S1 Oxidation dimerization of thiols to disulfides.

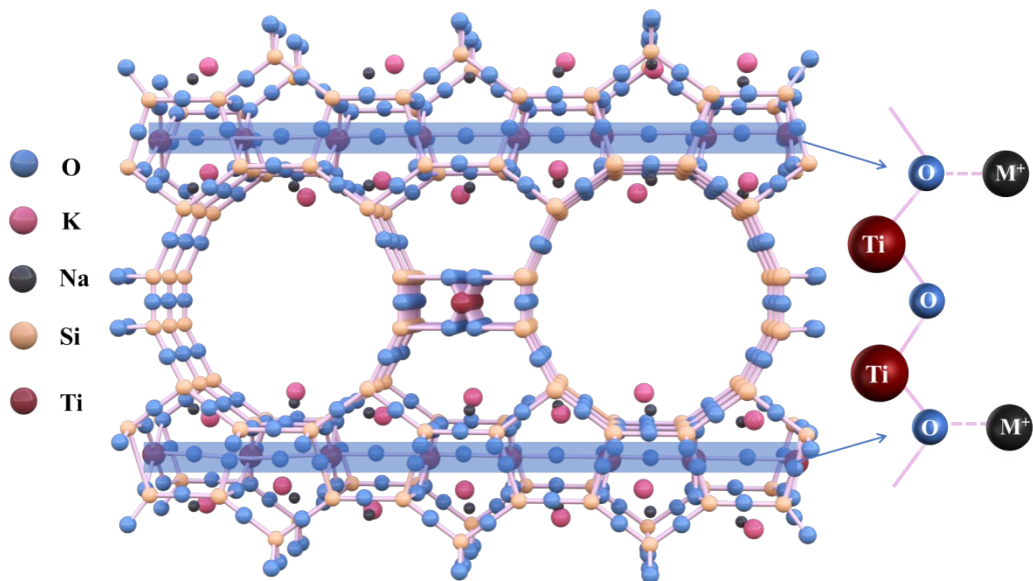


Fig. S2 The framework structure of NaKETS-10 zeolite.

Note: As shown in Fig. S2, the crystalline titanosilicate of ETS-10 zeolite is composed of corner-sharing tetrahedral silicon (SiO_4) and octahedral titanium (TiO_6)²⁻ linked through bridging oxygen atoms, generating a three dimensional 12-ring pore system ($0.76 \times 0.49 \text{ nm}$).^{S6} In this skeleton structure, each TiO_6 unit contributes two negative charges to the framework, which are balanced by exchangeable Na^+ and K^+ cations. Thus, in the ETS-10 crystal architecture, the existing one-dimensional linear chains of octahedral TiO_6 ($-\text{Ti}-\text{O}-\text{Ti}-$) as semiconductor wires have electron transport properties.^{S7} Meanwhile, charge transfer transition from the bridged oxygen to the Ti^{4+} in the two directions perpendicular to the $-\text{Ti}-\text{O}-\text{Ti}-$ chains can also occur.^{S8} Furthermore, the electron donating properties of the $-\text{Ti}-\text{O}-\text{Ti}-$ unit should be affected by the different electronegativity of compensating cations.

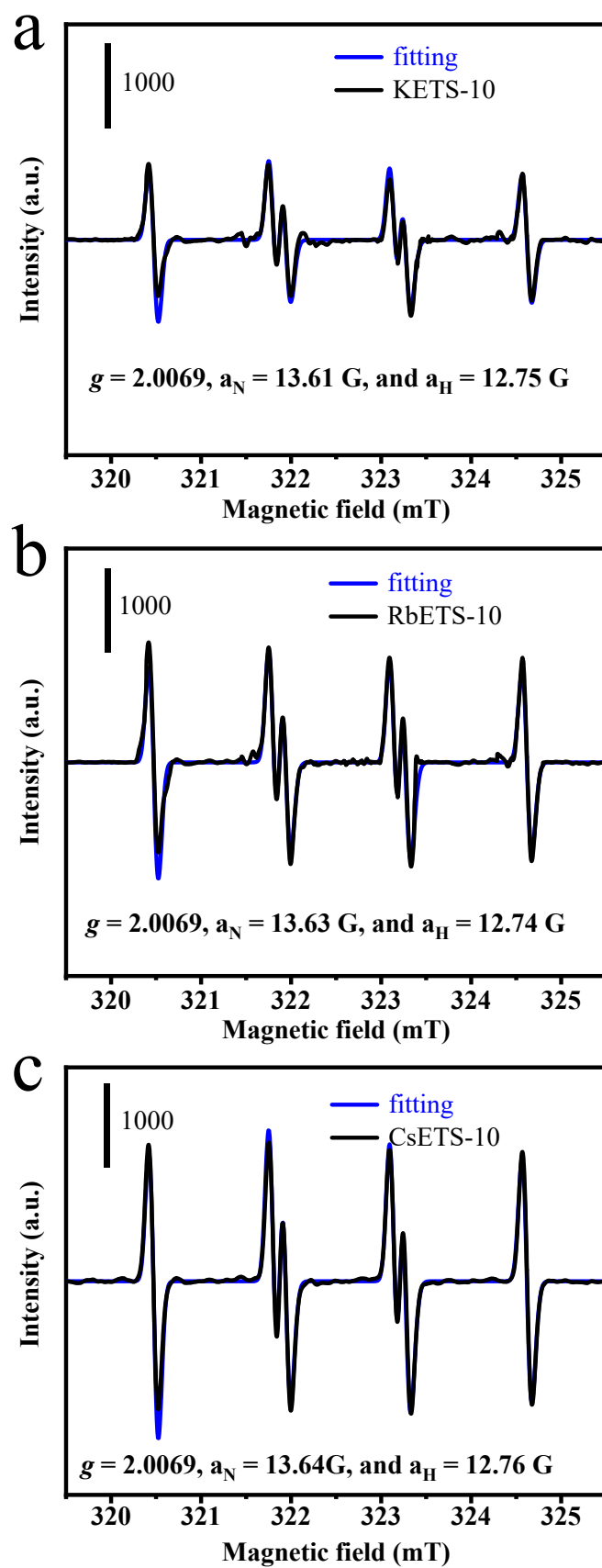


Fig. S3 Fitting the signals of EPR on (a) KETS-10, (b) RbETS-10, and (c) CsETS-10 catalysts.

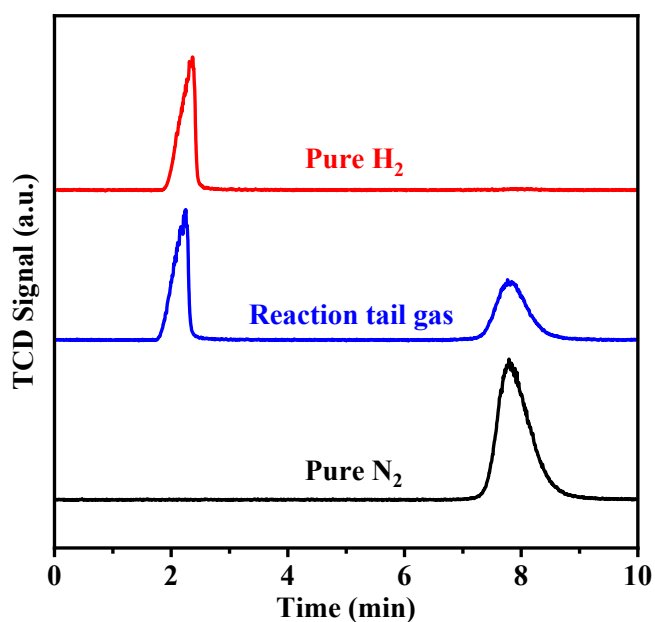


Fig. S4 The TCD signal of the tail gas. Reaction conditions: 2 mmol of **1a**, 100 mg of CsETS-10, 2 mL of cyclohexane, 120 °C, N₂ atmosphere, 5 h.

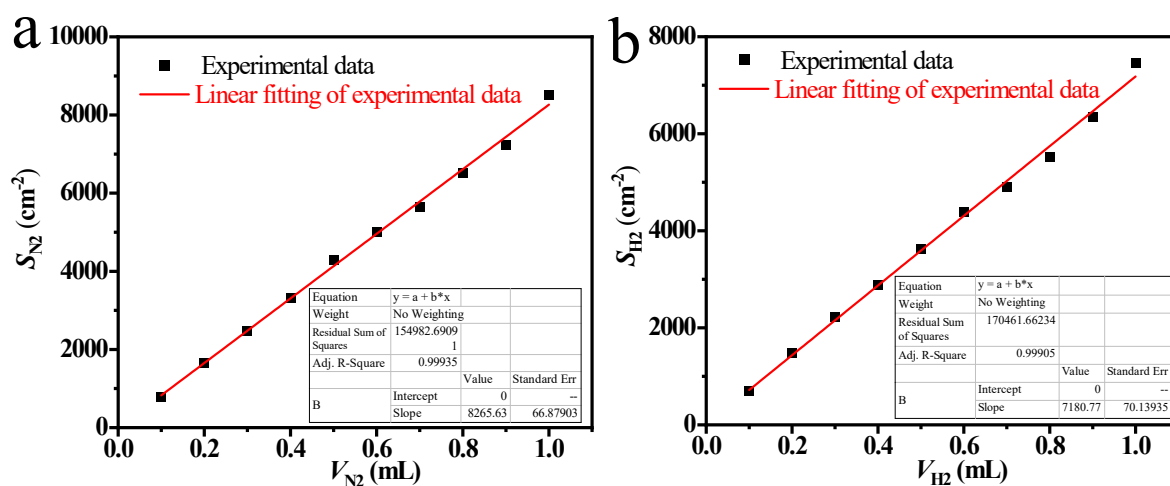


Fig. S5 The relationship between the GC peak area of (a) nitrogen, (b) hydrogen and the corresponding injection volume.

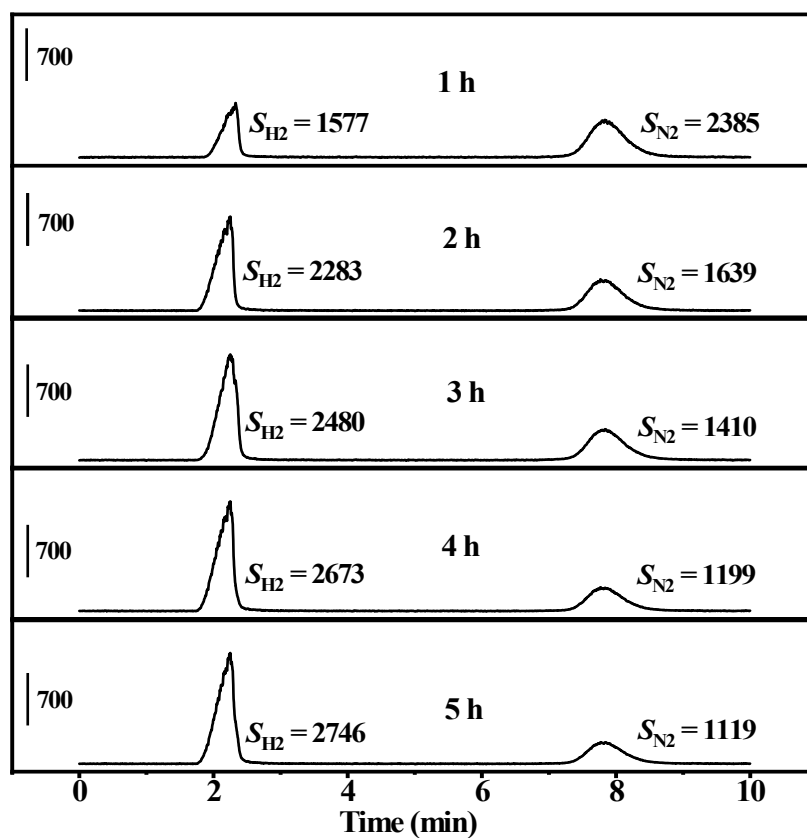


Fig. S6 The GC images for the collected tail gas.

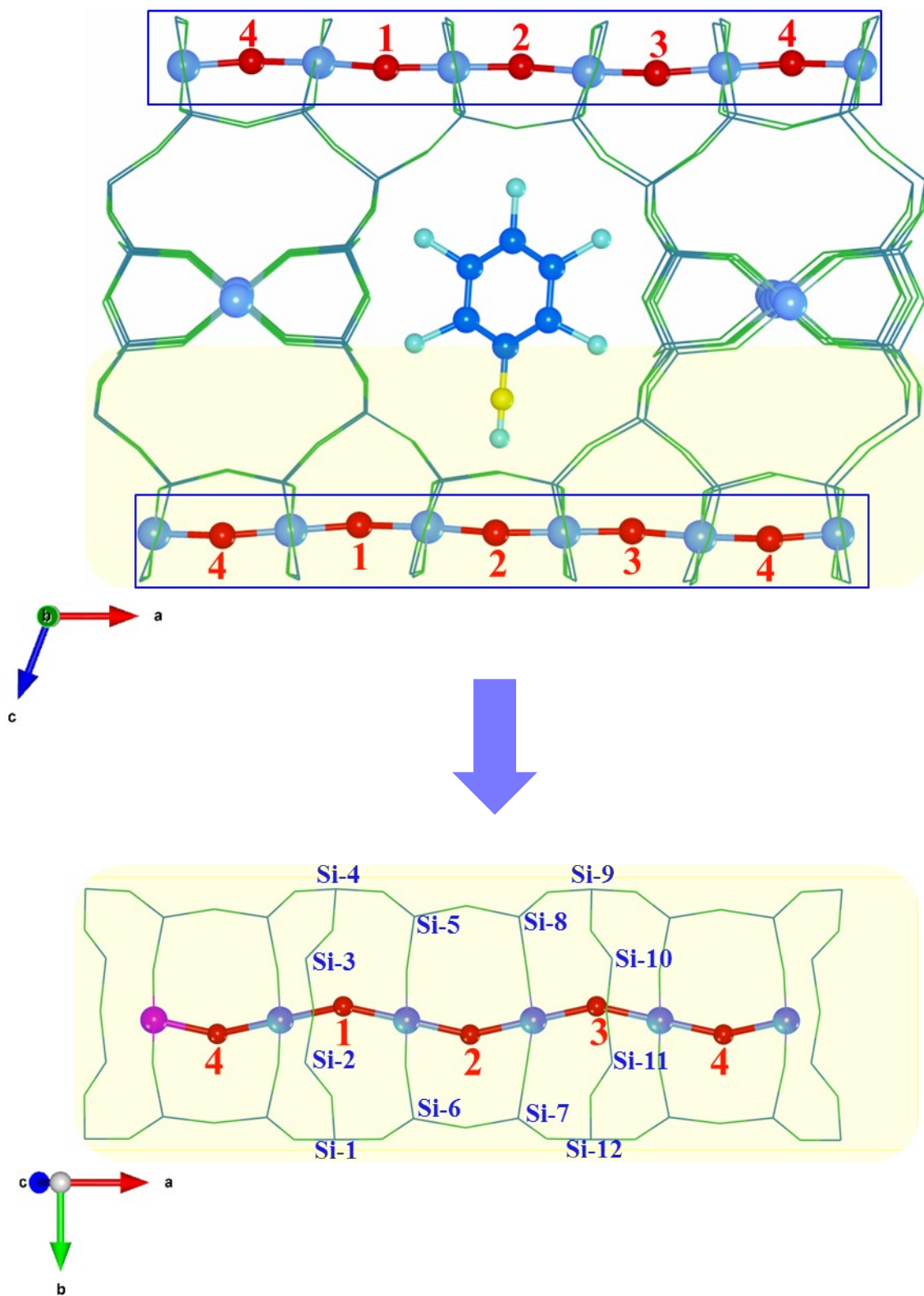


Fig. S7 Atomic labels on the walls of 12-ring pore in ETS-10 crystal. The labels shown here has been used to identify geometric parameters in Table S1.

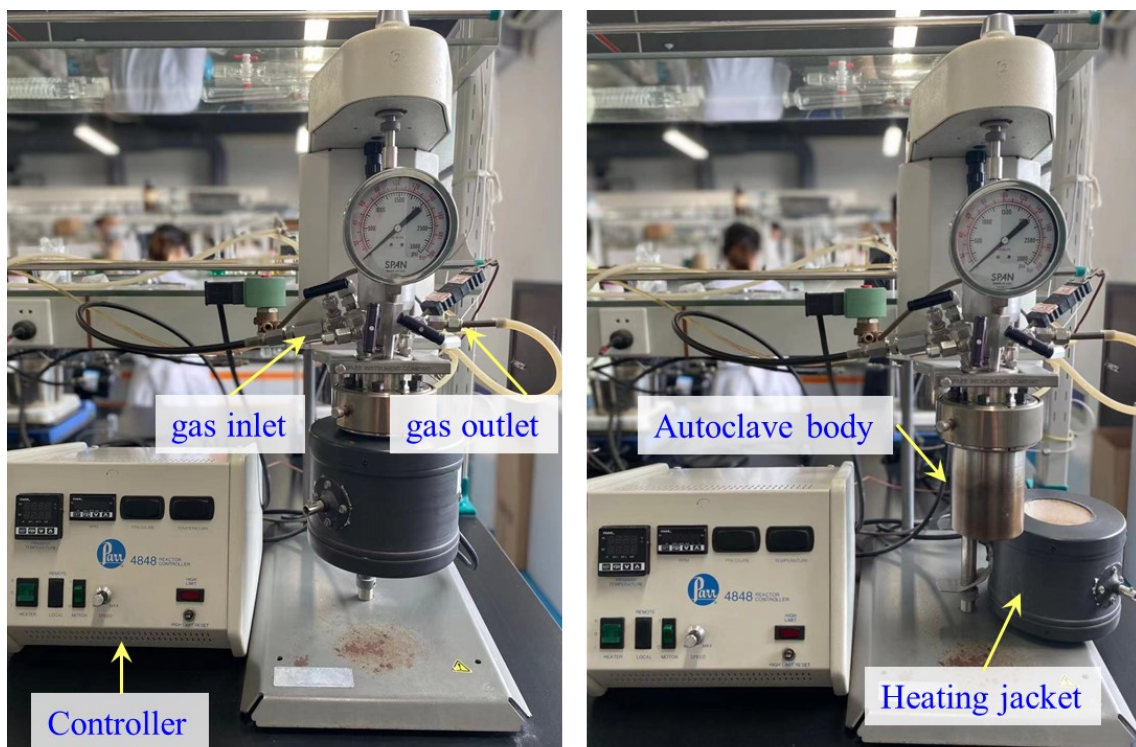
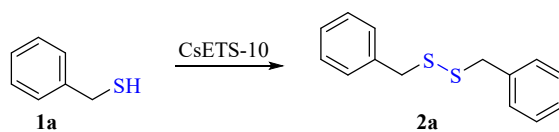


Fig. S8 Reaction instrument for the scale-up experiment.

Tables

Table S1 Self-coupling of benzyl mercaptane **1a**.^a



Time (h)	Yield of 2a (%) ^b	Volume of produced H ₂ (mL)	
		Theoretical value	Measured value
1	28	6.27	6.09
2	57	12.77	12.83
3	72	16.14	16.19
4	91	20.39	20.53
5	100	22.41	22.19

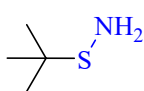
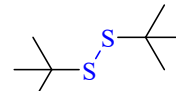
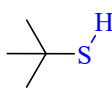
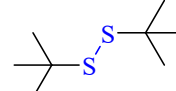
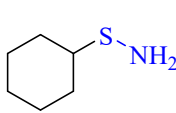
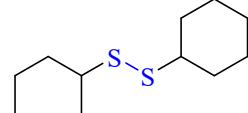
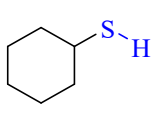
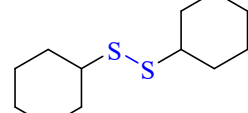
^a **1a** (2 mmol), CsETS-10 (100 mg), cyclohexane (2 mL), reaction tube (10 mL), N₂ atmosphere, temperature (120 °C). ^b GC yield.

Table S2 Geometric parameters for the selected region of ETS-10 crystal (The atom labels are defined in Figure S3).

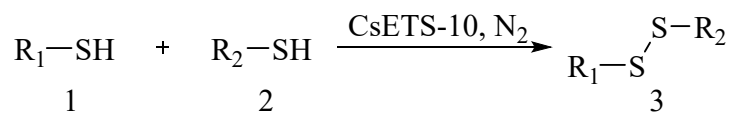
Atoms	Distances (Å) ^a	Pore size (Å)
Si1-Si4	5.6	
Si6-Si5	4.7	4.7 × 5.8
Si3-Si6	5.4	
Si5-Si1	5.8	
Si7-Si5	5.4	
Si6-Si10	6.8	
Si5-Si12	7.0	4.7 × 7.0
Si7-Si8	4.7	
Si7-Si10	5.4	
Si7-Si9	5.9	
Si7-Si10	5.4	
Si8-Si11	5.4	4.7 × 5.9
Si8-Si12	5.8	
Si7-Si8	4.7	



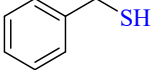
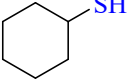


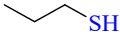
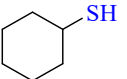
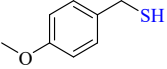
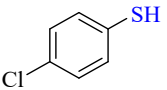
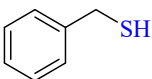
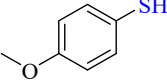
^a The distances between different labeled Si atoms were obtained in the VAST software (OpenGL version: 4.5.0).

Table S3 Self-coupling of thiols and corresponding thiolates on the CsETS-10 catalyst. ^a

Entry	Substrate	Product	Yield (%)
1 ^b			n.d.
2 ^c			100
3 ^b			n.d.
4 ^d			100

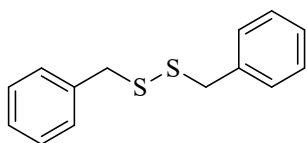
^a Reaction condition: substrate (0.5 mmol), cyclohexane (1.5 mL), CsETS-10 catalyst (20 mg), at 120 °C for 3 h. ^b reaction time (5 h). ^c reaction time (2 h). ^d reaction time (3 h).

Table S4 Cross-coupling of different thiols at the higher temperatures.^a

Entry	substrates		conversion (%) ^b		yield (%) ^b
	1	2	1	2	3
1			100,100 ^c ,100 ^d	100,100 ^c ,97 ^d	4,4 ^c ,3 ^d
2			100	100	trace
3			100	100	trace
4			100	100	n.d.
5			100	100	n.d.
6			100	100	n.d.
7			100	100	trace
8			100,100 ^c ,100 ^d	100,100 ^c ,100 ^d	3, 3 ^c , 4 ^d
9			100	100	n.d.

^a Reaction condition: **1** (0.5 mol), **2** (0.5 mmol), CsETS-10 (30 mg), cyclohexane (1.5 mL), at 120 °C for 5 h. ^b detected by GC. ^c reaction temperature (130 °C). ^d reaction temperature (140 °C).

3. Analytical data

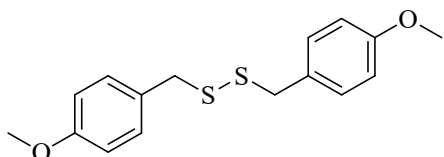


(2a) 1,2-dibenzyl disulfane^{S9}: colorless oil was obtained in 100% yield;

¹H NMR (500 MHz, CDCl₃) δ 7.25 – 7.12 (m, 10H), 3.50 (s, 4H);

¹³C NMR (125 MHz, CDCl₃) δ 136.30, 128.36, 127.43, 126.37, 42.20;

MS (70 eV) *m/z* (%): 91.15 (100), 78.52 (12), 124.05 (6).

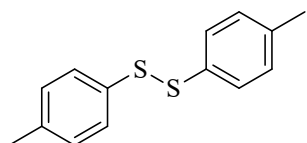


(2b) 1,2-bis(4-methoxybenzyl) disulfane^{S10}: pink crystal was obtained in 100%; m.p.: 75-77 °C;

¹H NMR (500 MHz, CDCl₃) δ 7.09 (d, *J* = 8.6 Hz, 4H), 6.77 (d, *J* = 8.6 Hz, 4H), 3.71 (s, 6H), 3.51 (s, 4H);

¹³C NMR (125 MHz, CDCl₃) δ 157.98, 129.49, 128.36, 112.85, 54.25, 41.72;

MS (70 eV) *m/z* (%): 121.06 (100), 77.04 (8), 91.04 (5).

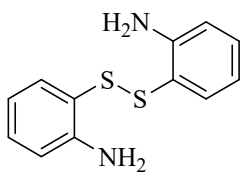


(2c) 1,2-di-p-tolyl disulfane^{S9}: white solid was obtained in 100% yield; m.p.: 47-49 °C;

¹H NMR (500 MHz, CDCl₃) δ 7.30 (d, *J* = 8.2 Hz, 4H), 7.02 (d, *J* = 7.9 Hz, 4H), 2.23 (s, 6H);

¹³C NMR (125 MHz, CDCl₃) δ 136.39, 132.84, 128.74, 127.48, 20.02;

MS (70 eV) *m/z* (%): 123.05 (100), 246.15 (87), 77.31 (22).

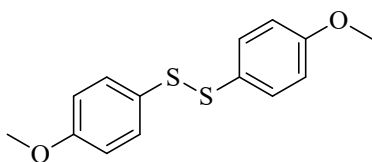


(2d) 2,2'-disulfanediyldianiline^{S9}: pale yellow solid was obtained in 98% yield; m.p.: 90.5 °C;

¹H NMR (500 MHz, CDCl₃) δ 7.11-7.05 (m, 4H), 6.66-6.62 (m, 2H), 6.54-6.49 (m, 2H), 4.26 (s, 4H);

¹³C NMR (125 MHz, CDCl₃) δ 147.59, 135.80, 130.58, 117.21, 114.20;

MS (70 eV) *m/z* (%): 124.35 (100), 79.89 (51), 248.33 (M⁺, 33).

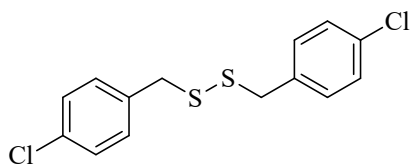


(2e) 1,2-bis(4-methoxyphenyl)disulfane^{S9}: colorless oil was obtained in 100% yield;

¹H NMR (500 MHz, CDCl₃) δ 7.32 (d, *J* = 8.8 Hz, 4H), 6.76 (d, *J* = 8.8 Hz, 4H), 3.72 (s, 6H);

¹³C NMR (125 MHz, CDCl₃) δ 159.06, 131.83, 127.58, 113.77, 54.52;

MS (70 eV) *m/z* (%): 139.15 (100), 140.15 (33), 96.48 (20).

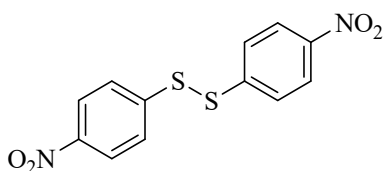


(2f) 1,2-bis(4-chlorobenzyl)disulfane^{S9}: colorless oil was obtained in 99% yield;

¹H NMR (500 MHz, CDCl₃) δ 7.26-7.19 (m, 4H), 7.11-7.01 (m, 4H), 3.49 (s, 4H);

¹³C NMR (125 MHz, CDCl₃) δ 134.78, 132.36, 129.63, 127.64;

MS (70 eV) *m/z* (%): 121.04 (100), 122.04 (11), 78.04 (10).

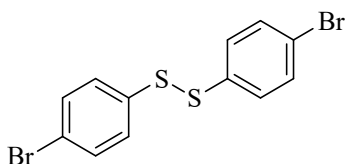


(2g) 1,2-bis(4-nitrophenyl)disulfane^{S10}: yellow solid was obtained in 97% yield; m.p.: 180-182 °C;

¹H NMR (500 MHz, CDCl₃) δ 8.31-8.05 (m, 4H), 7.72-7.53 (m, 4H);

¹³C NMR (125 MHz, CDCl₃) δ 147.01, 144.10, 126.41, 124.50;

MS (70 eV) *m/z* (%): 308.45 (M⁺, 100), 108.77 (32), 78.88 (24).

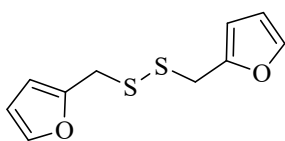


(2h) 1,2-bis(4-bromophenyl)disulfane^{S11}: yellow solid was obtained in 96% yield; m.p.: 93.5 °C;

¹H NMR (500 MHz, CDCl₃) δ 7.35 (d, *J* = 8.6 Hz, 4H), 7.25 (d, *J* = 8.6 Hz, 4H);

¹³C NMR (125 MHz, CDCl₃) δ 134.68, 131.18, 128.34, 120.50;

MS (70 eV) *m/z* (%): 108.49 (100), 109.22 (76), 189.05 (43).

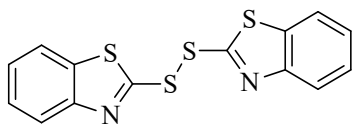


(2i) 1,2-bis(furan-2-ylmethyl)disulfane^{S9}: yellow oil was obtained in 98% yield;

¹H NMR (500 MHz, CDCl₃) δ 7.31 (dd, *J* = 1.7, 0.7 Hz, 2H), 6.26 (dd, *J* = 3.1, 1.9 Hz, 2H), 6.15 (d, *J* = 3.0 Hz, 2H), 3.61 (s, 4H);

¹³C NMR (125 MHz, CDCl₃) δ 148.90, 141.20, 109.50, 107.70, 34.36;

MS (70 eV) *m/z* (%): 81.85 (100), 161.52 (12), 226.77 (M⁺, 9).

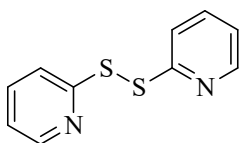


(2j) 1,2-bis(benzo[d]thiazol-2-yl)disulfane^{S9}: white solid was obtained in 98% yield; m.p.: 179-180 °C;

¹H NMR (300 MHz, CDCl₃) δ 7.87 (d, *J* = 8.2 Hz, 2H), 7.70 (d, *J* = 7.9 Hz, 2H), 7.45 – 7.33 (m, 2H), 7.33 – 7.23 (m, 2H).

¹³C NMR (75 MHz, CDCl₃) δ 167.90, 154.56, 136.15, 126.62, 125.33, 122.70, 121.34;

MS (70 eV) *m/z* (%): 332.15 (M⁺, 100), 167.55 (92), 108.11 (87).

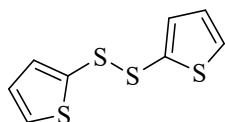


(2k) 1,2-di(pyridin-2-yl)disulfane^{S9}: yellow solid was obtained in 100% yield; m.p.: 53 °C;

¹H NMR (300 MHz, CDCl₃) δ 8.38 (d, *J* = 4.7 Hz, 2H), 7.62 – 7.38 (m, 4H), 7.02 (td, *J* = 5.1, 3.1 Hz, 2H).

¹³C NMR (75 MHz, CDCl₃) δ 158.88, 149.57, 137.45, 121.16, 119.68;

MS (70 eV) *m/z* (%): 78.29 (100), 220.12 (M⁺, 95), 156.45 (67).

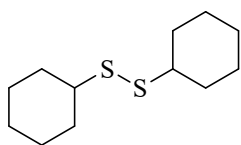


(2l) 1,2-di(thiophen-2-yl)disulfane^{S9}: yellow solid was obtained in 99% yield; m.p.: 56 °C;

¹H NMR (500 MHz, CDCl₃) δ 7.41 (dd, *J* = 5.3, 1.3 Hz, 2H), 7.07 (dd, *J* = 3.6, 1.3 Hz, 2H), 6.93 (dd, *J* = 5.3, 3.6 Hz, 2H);

¹³C NMR (125 MHz, CDCl₃) δ 134.65, 134.61, 131.25, 126.72;

MS (70 eV) *m/z* (%): 71.09 (100), 115.52 (96), 230.05 (M⁺, 35).

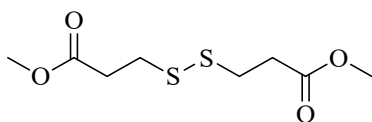


(2m) 1,2-dicyclohexyldisulfane^{S12}: colorless oil was obtained in 100% yield;

¹H NMR (500 MHz, CDCl₃) δ 2.65-2.58 (m, 2H), 2.02-1.95 (m, 4H), 1.74-1.68 (m, 4H), 1.58-1.51 (m, 2H), 1.27-1.18 (m, 10H);

¹³C NMR (125 MHz, CDCl₃) δ 48.95, 31.84, 25.07, 24.68;

MS (70 eV) *m/z* (%): 83.59 (100), 146.15 (95), 230.11 (M⁺, 67).

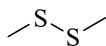


(2n) dimethyl 3,3'-disulfanediyldipropanoate^{S10}: colorless oil was obtained in 100% yield;

¹H NMR (300 MHz, CDCl₃) δ 3.64 (s, 6H), 2.87 (dd, *J* = 10.8, 3.7 Hz, 4H), 2.68 (dd, *J* = 8.6, 5.4 Hz, 4H).

¹³C NMR (75 MHz, CDCl₃) δ 171.10, 50.87, 32.86, 32.06;

MS (70 eV) *m/z* (%): 118.25 (100), 238.12 (M⁺, 79), 87.45 (67).

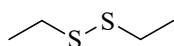


(2o) 1,2-dimethyldisulfane: yellow liquid was obtained in 100% yield;

¹H NMR (500 MHz, CDCl₃) δ 2.43 (s, 6H);

¹³C NMR (125 MHz, CDCl₃) δ 22.15;

MS (70 eV) *m/z* (%): 94.19 (M⁺, 100), 79.55 (75), 616.45 (27).

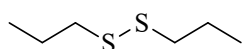


(2p) 1,2-diethyldisulfane: colorless oil was obtained in 100% yield;

¹H NMR (500 MHz, CDCl₃) δ 2.64 (q, *J* = 7.3 Hz, 4H), 1.26 (t, *J* = 7.3 Hz, 6H);

¹³C NMR (125 MHz, CDCl₃) δ 31.85, 13.40;

MS (70 eV) *m/z* (%): 66.42 (100), 122.09 (M⁺, 65), 94.45 (49).

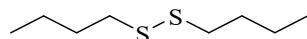


(2q) 1,2-dipropyldisulfane^{S13}: pale yellow liquid was obtained in 100% yield;

¹H NMR (500 MHz, CDCl₃) δ 2.60 (t, *J* = 7.2 Hz, 4H), 1.71-1.57 (m, 4H), 0.93 (t, *J* = 7.3 Hz, 6H);

¹³C NMR (125 MHz, CDCl₃) δ 40.09, 21.43, 12.04;

MS (70 eV) *m/z* (%): 150.21 (M⁺, 100), 108.59 (95), 76.08 (67).

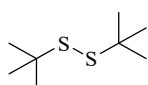


(2r) 1,2-dibutyldisulfane^{S11}: slightly brown liquid was obtained in 100% yield;

¹H NMR (500 MHz, CDCl₃) δ 2.62 (t, *J* = 7.4 Hz, 4H), 1.68-1.53 (m, 4H), 1.42-1.27 (m, 4H), 0.86 (t, *J* = 7.4 Hz, 6H);

¹³C NMR (125 MHz, CDCl₃) δ 37.87, 30.29, 20.64, 12.68;

MS (70 eV) *m/z* (%): 122.29 (100), 178.19 (M⁺, 95), 90.45 (17).

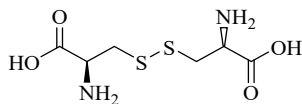


(2s) 1,2-di-tert-butyl disulfane^{S13}: yellow liquid was obtained in 100% yield;

¹H NMR (500 MHz, CDCl₃) δ 1.24 (s, 18H);

¹³C NMR (125 MHz, CDCl₃) δ 45.14, 29.55;

MS (70 eV) *m/z* (%): 178.23 (M⁺, 100), 122.09 (85), 57.88 (67).

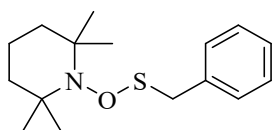


(2t) cystine: white solid was obtained in 100% yield; m.p.: 260-262 °C;

¹H NMR (600 MHz, D₂O) δ 3.52 (dd, *J* = 7.7, 4.6 Hz, 2H), 3.03 (dd, *J* = 13.8, 4.6 Hz, 2H), 2.82 (dd, *J* = 13.8, 7.7 Hz, 2H);

¹³C NMR (150 MHz, D₂O) δ 180.11, 54.71, 42.90;

MS (70 eV) *m/z* (%): 59.31 (100), 60.11 (95), 58.01 (67).



(2u) 1-((benzylthio)oxy)-2,2,6,6-tetramethylpiperidine: yellow solid; m.p.: 79-81 °C;

¹H NMR (600 MHz, CDCl₃) δ 7.31-7.27 (m, 5H), 4.20 (s, 2H), 1.47 (s, 12H), 1.19 (s, 6H);

¹³C NMR (101 MHz, CDCl₃) δ 130.09, 129.14, 127.46, 127.34, 64.17, 59.44, 43.38, 28.68, 15.54;

MS (70 eV) *m/z* (%): 91.02 (100), 216.16 (55), 280.12 (M⁺, 19).

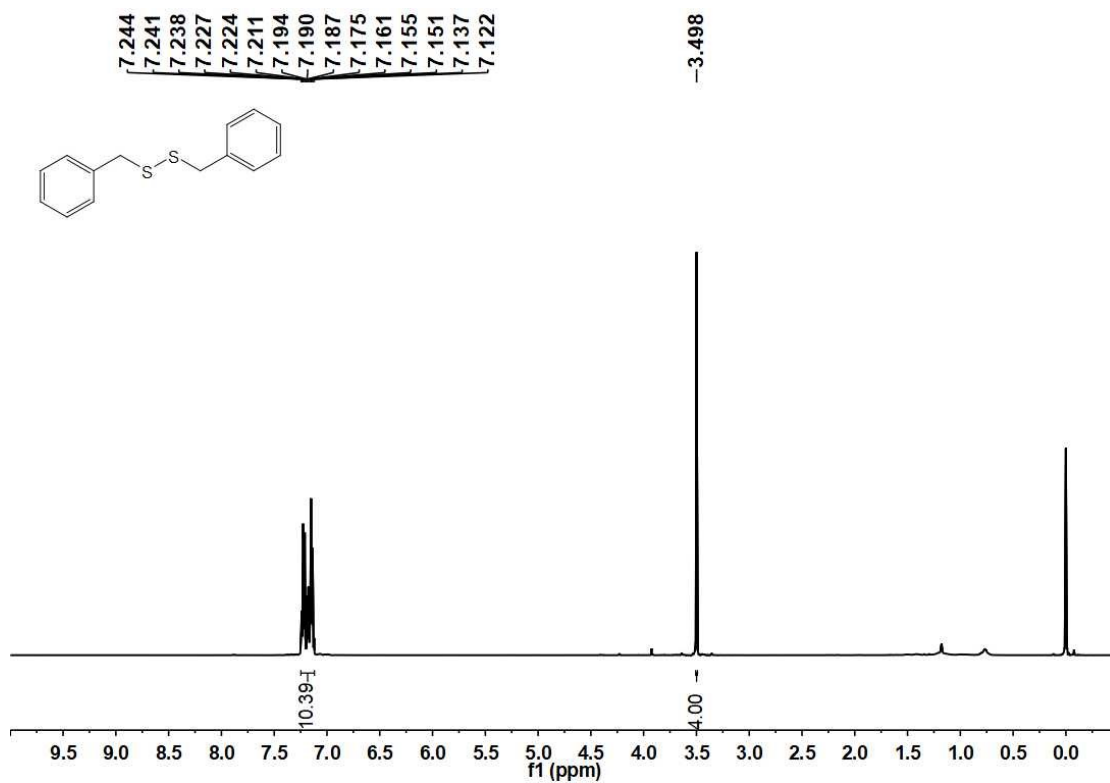
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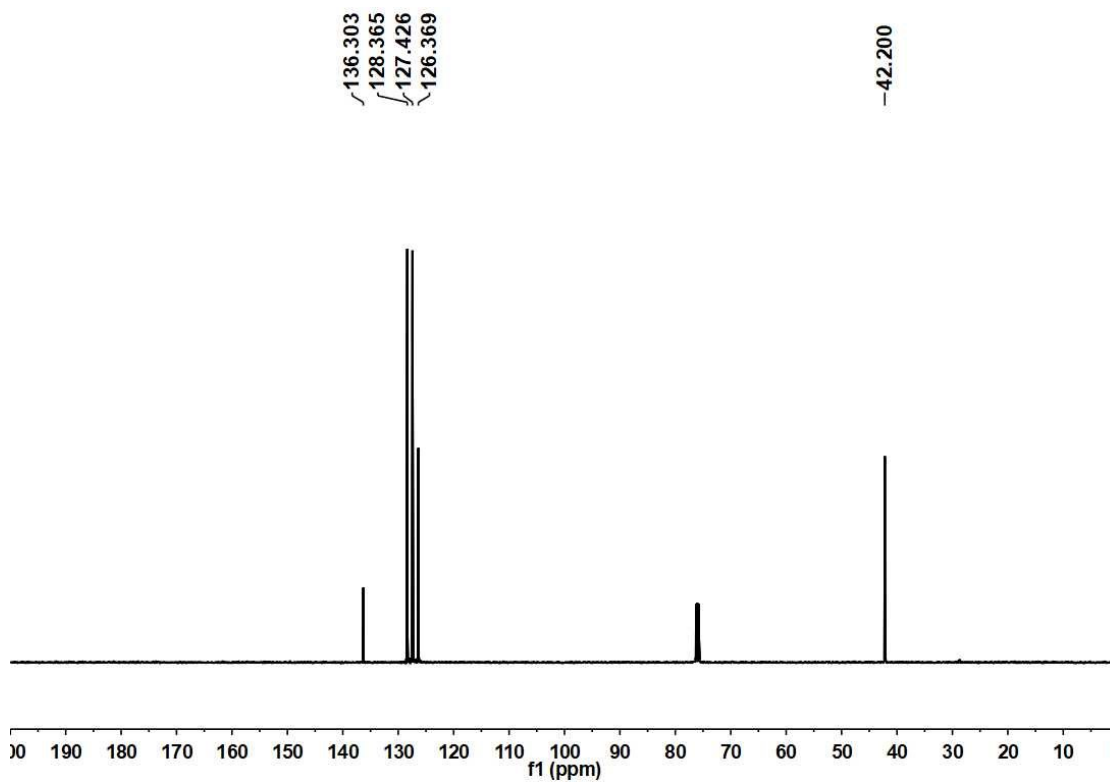
5. Spectra of these compounds

2a

^1H NMR

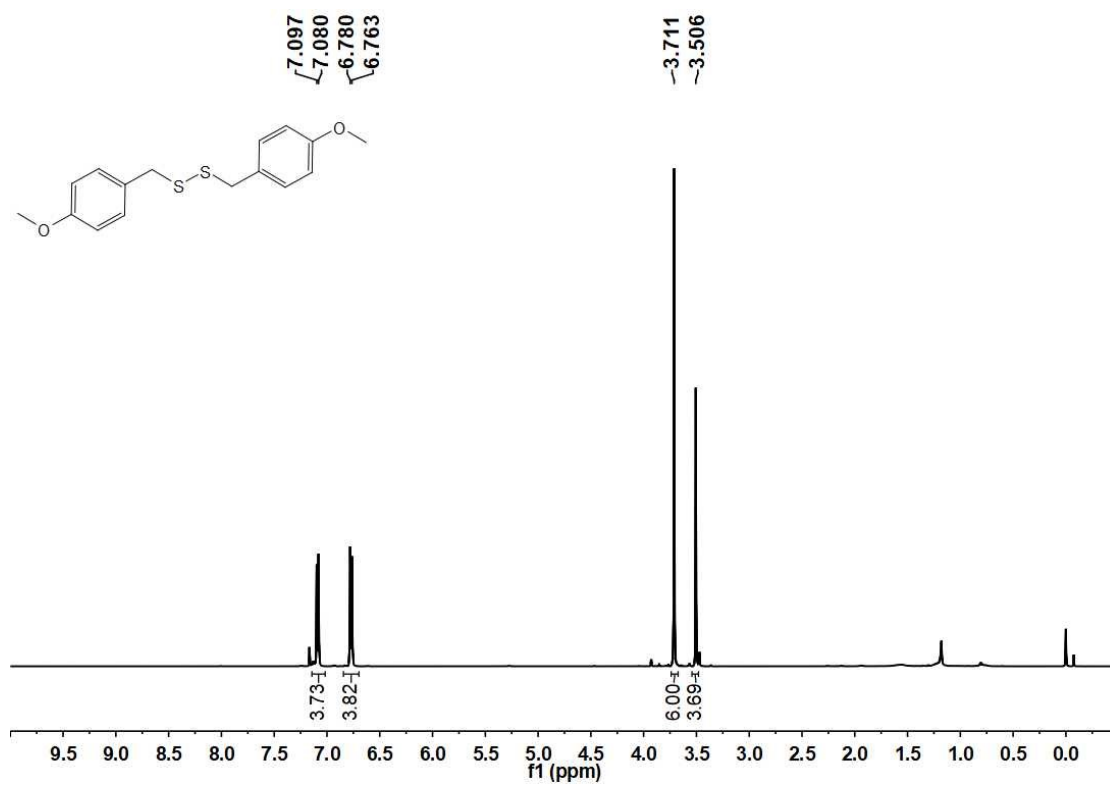


^{13}C NMR

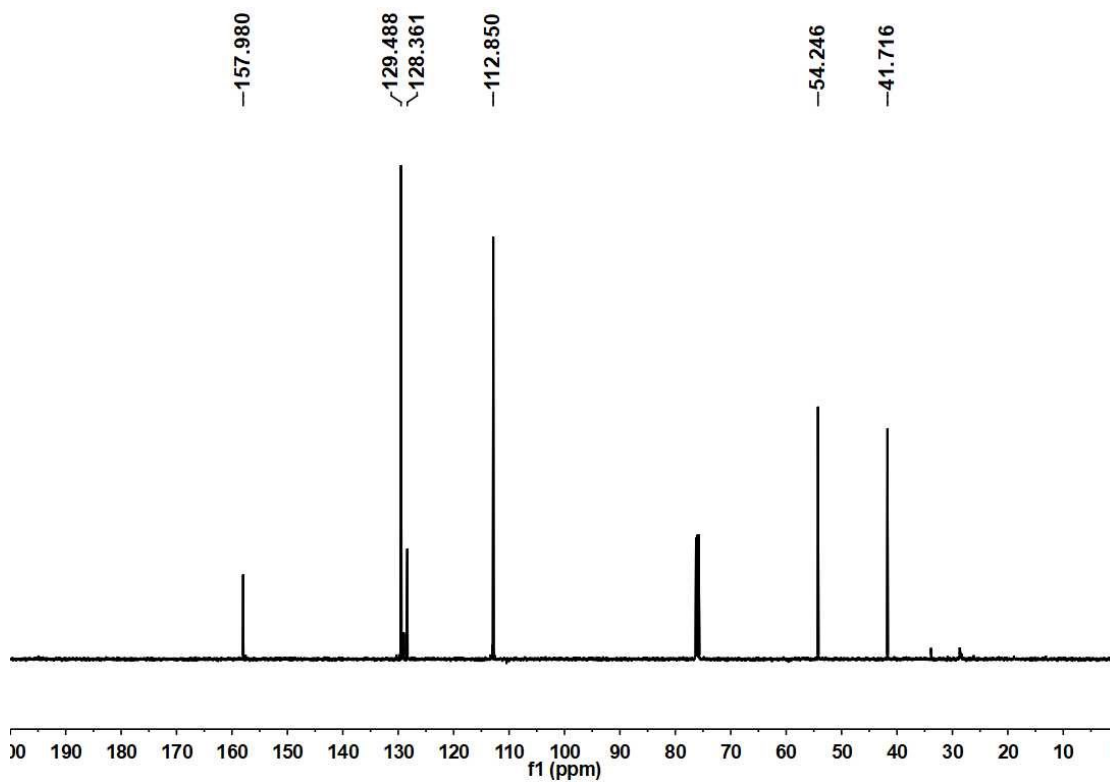


2b

¹H NMR

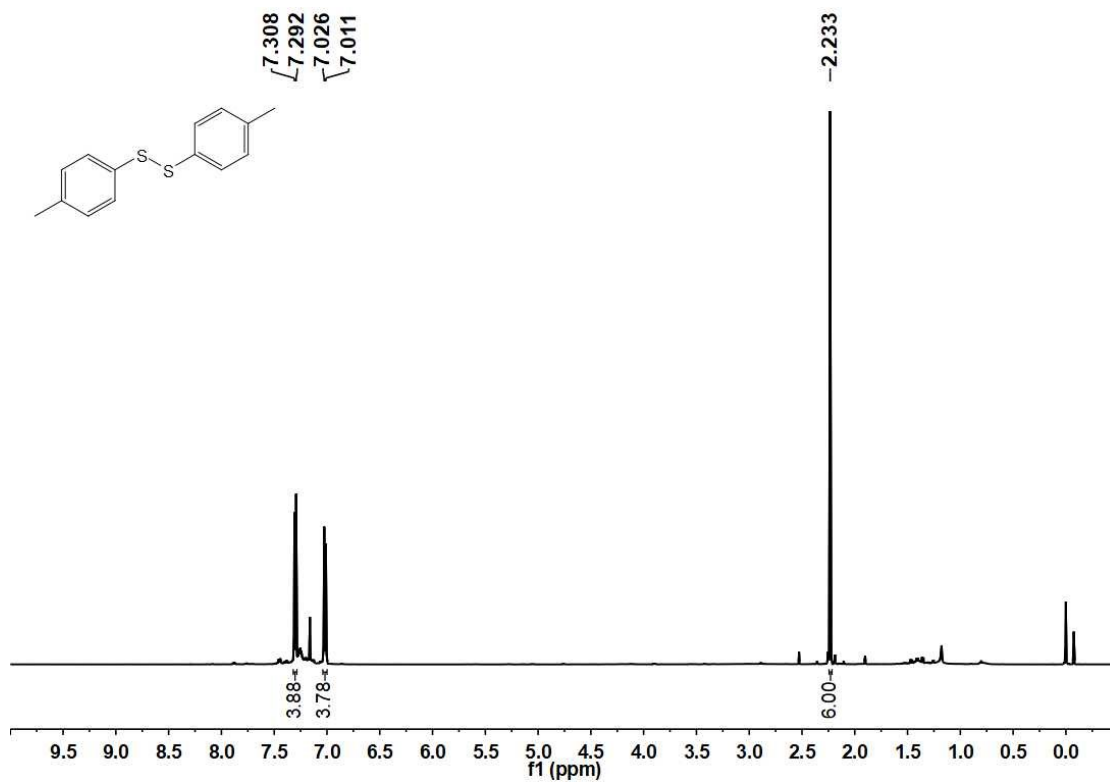


¹³C NMR

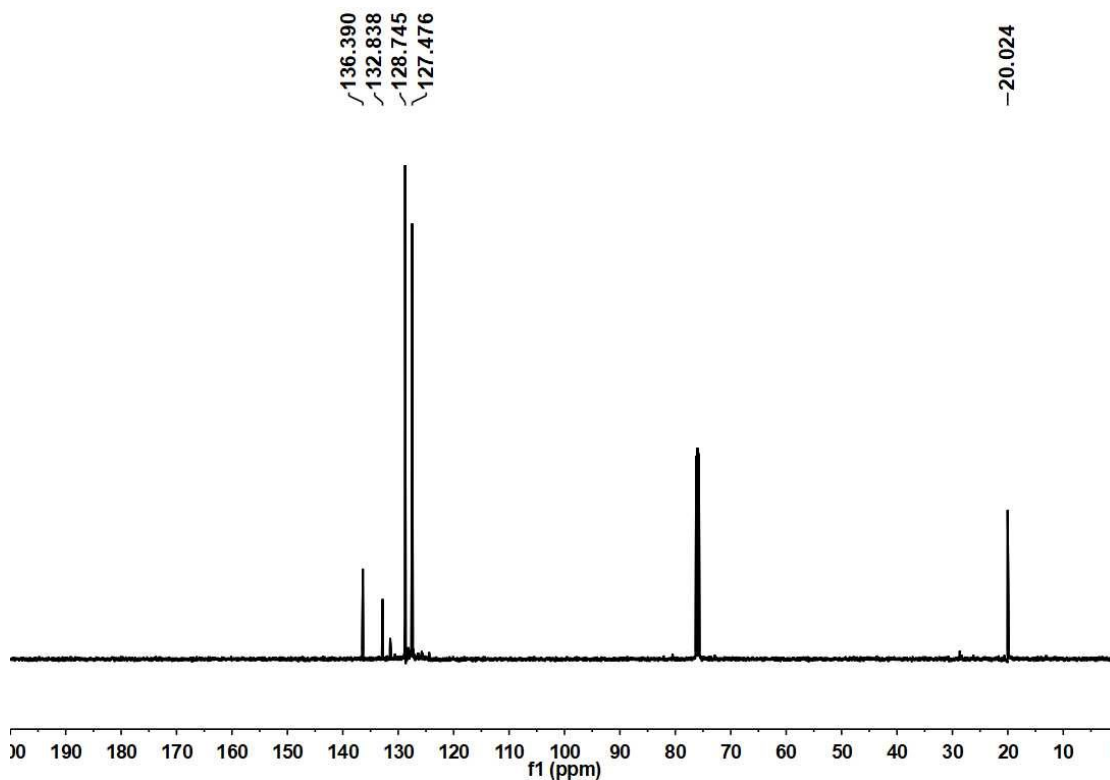


2c

¹H NMR

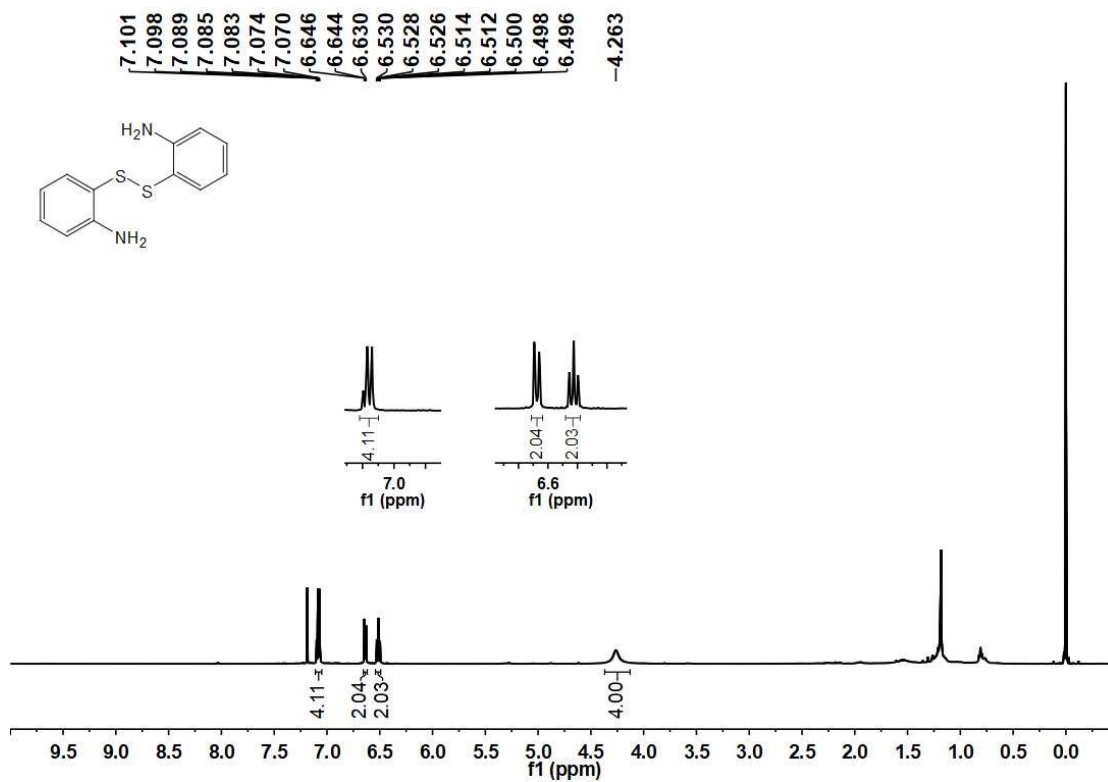


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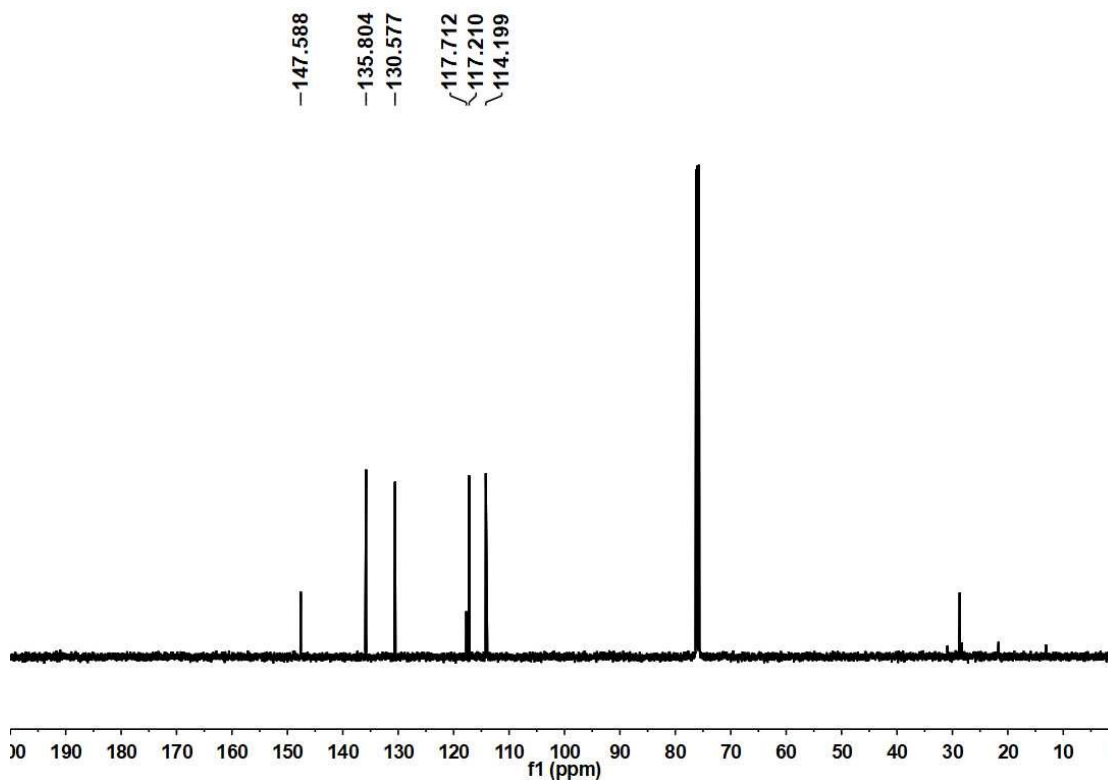


2d

¹H NMR

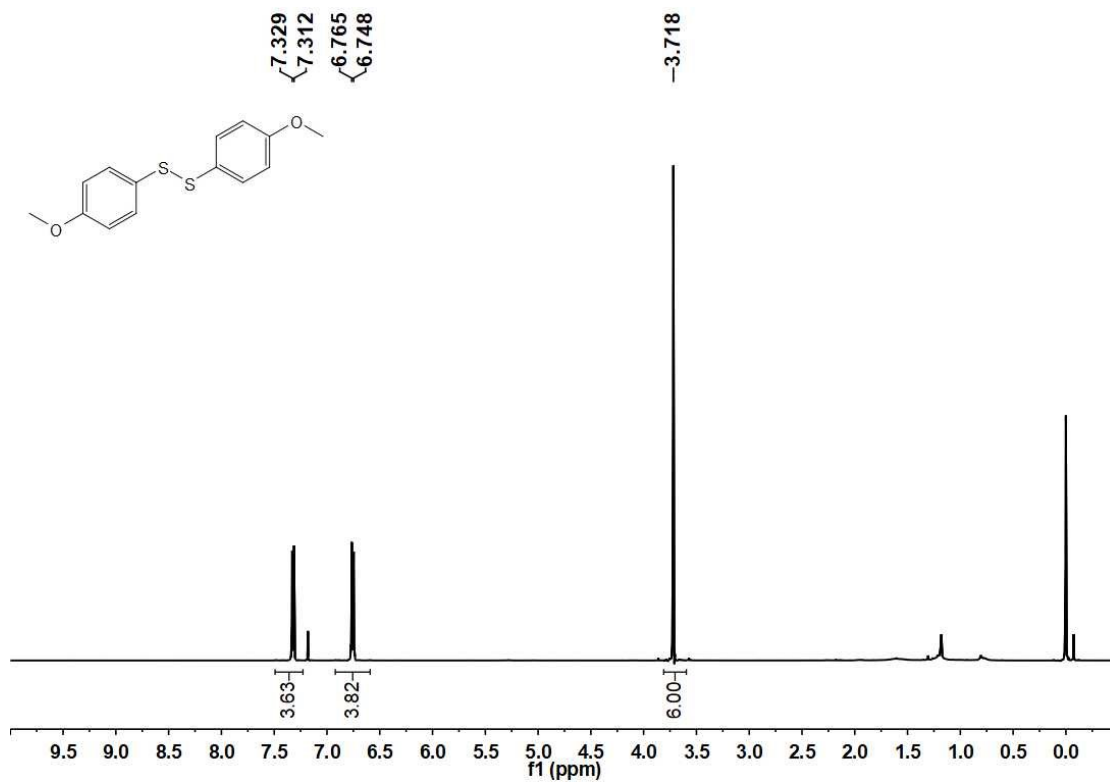


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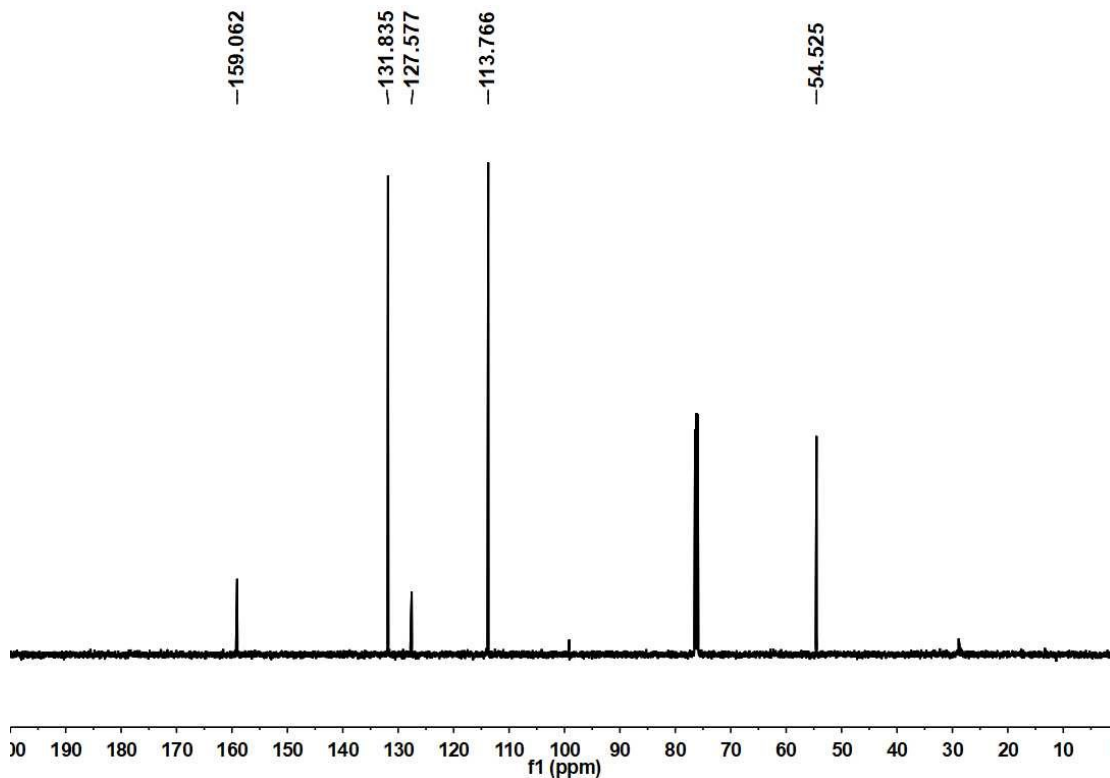


2e

¹H NMR

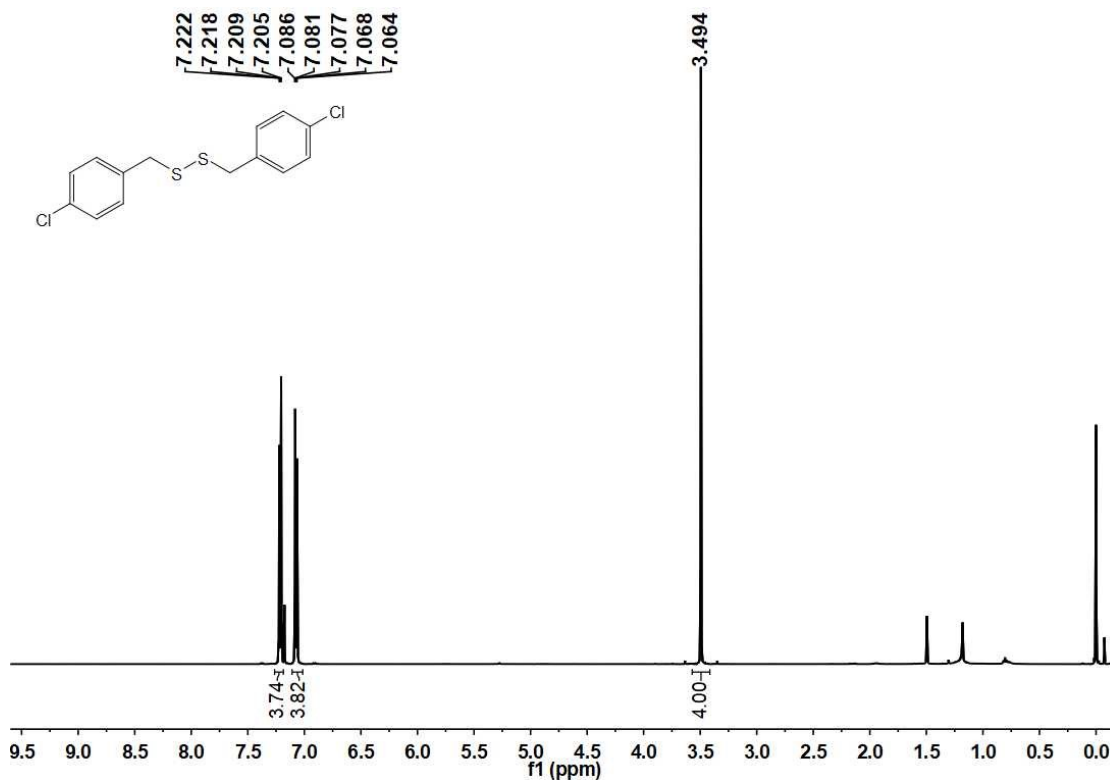


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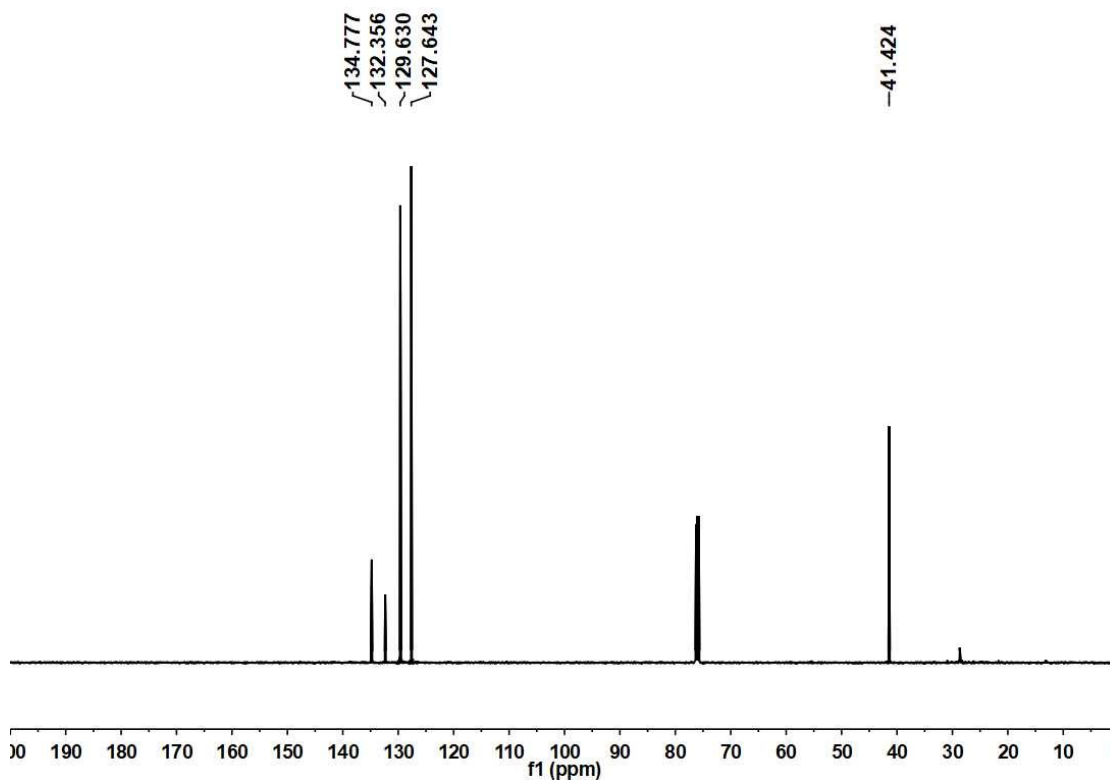


2f

¹H NMR

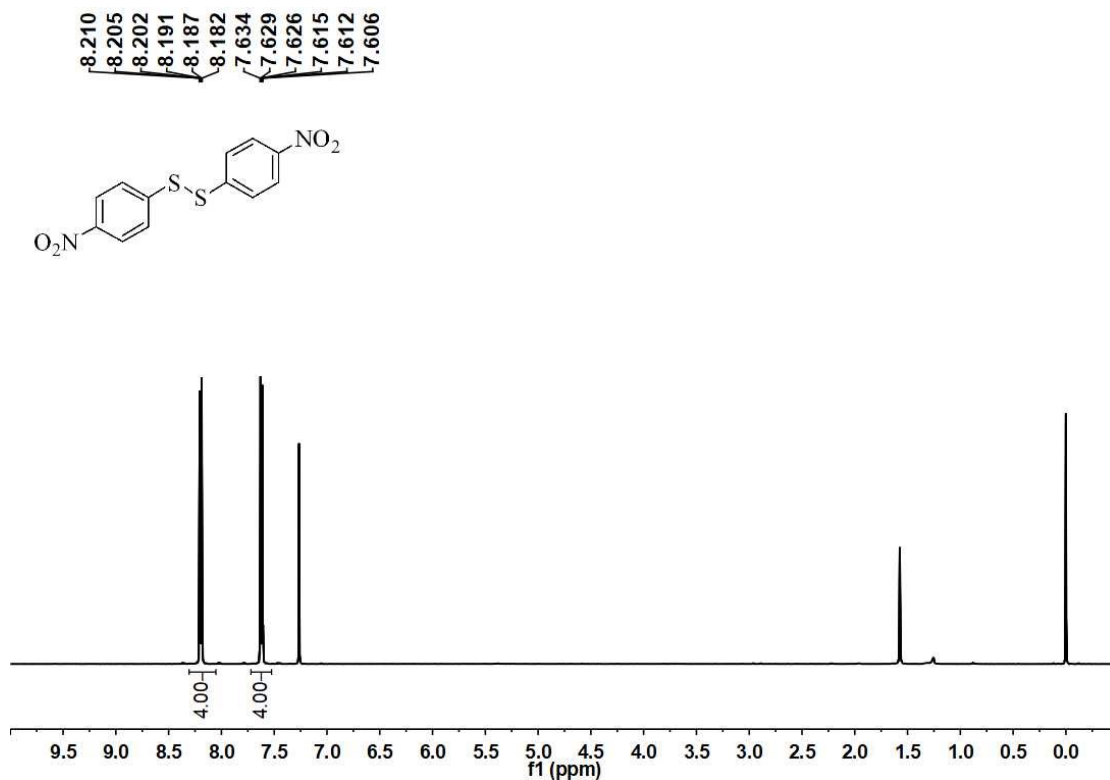


¹³C NMR

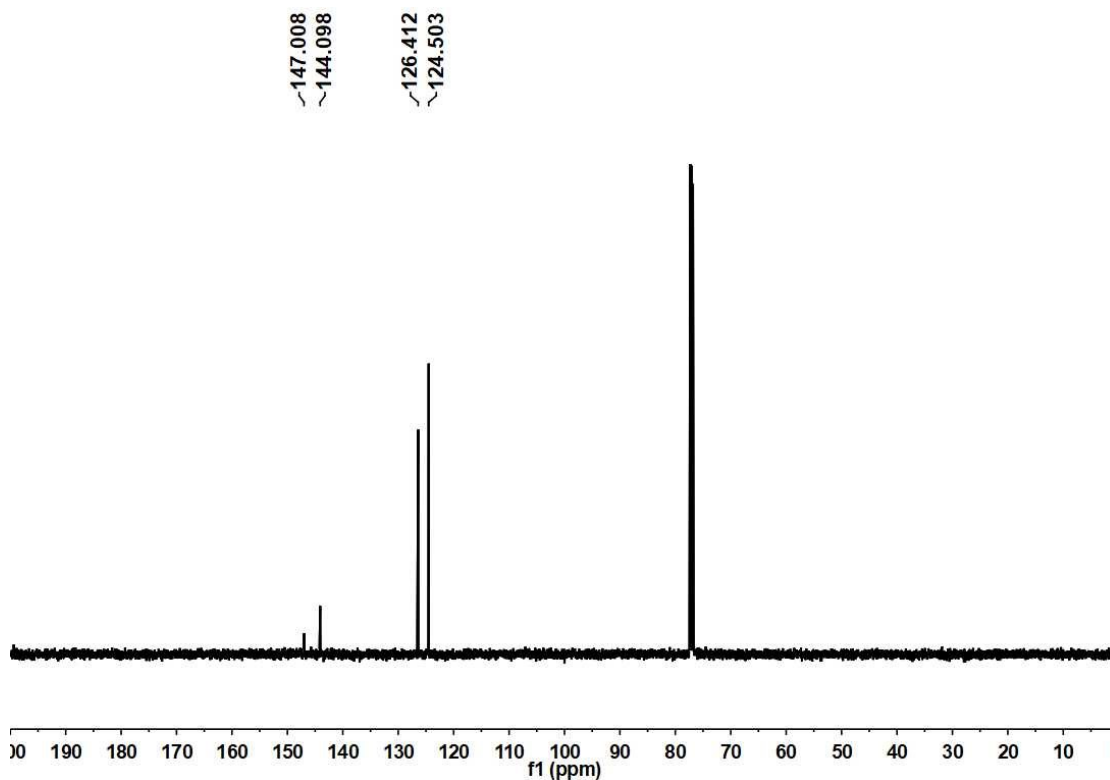


2g

¹H NMR

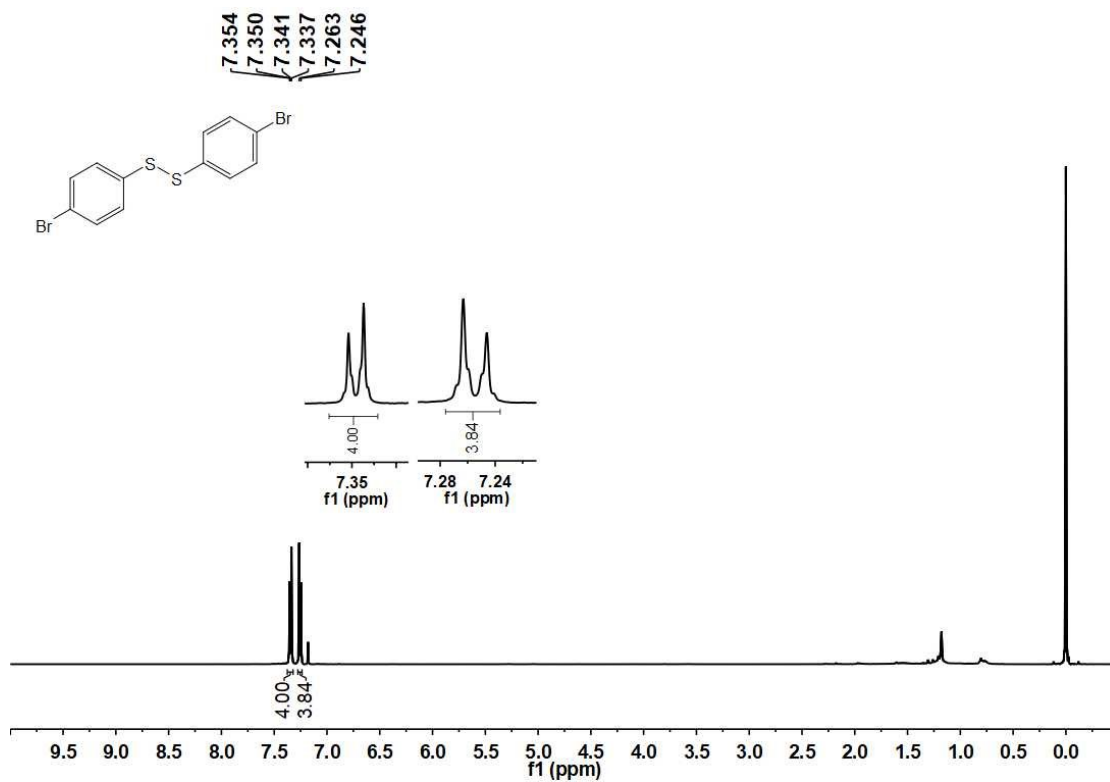


¹³C NMR

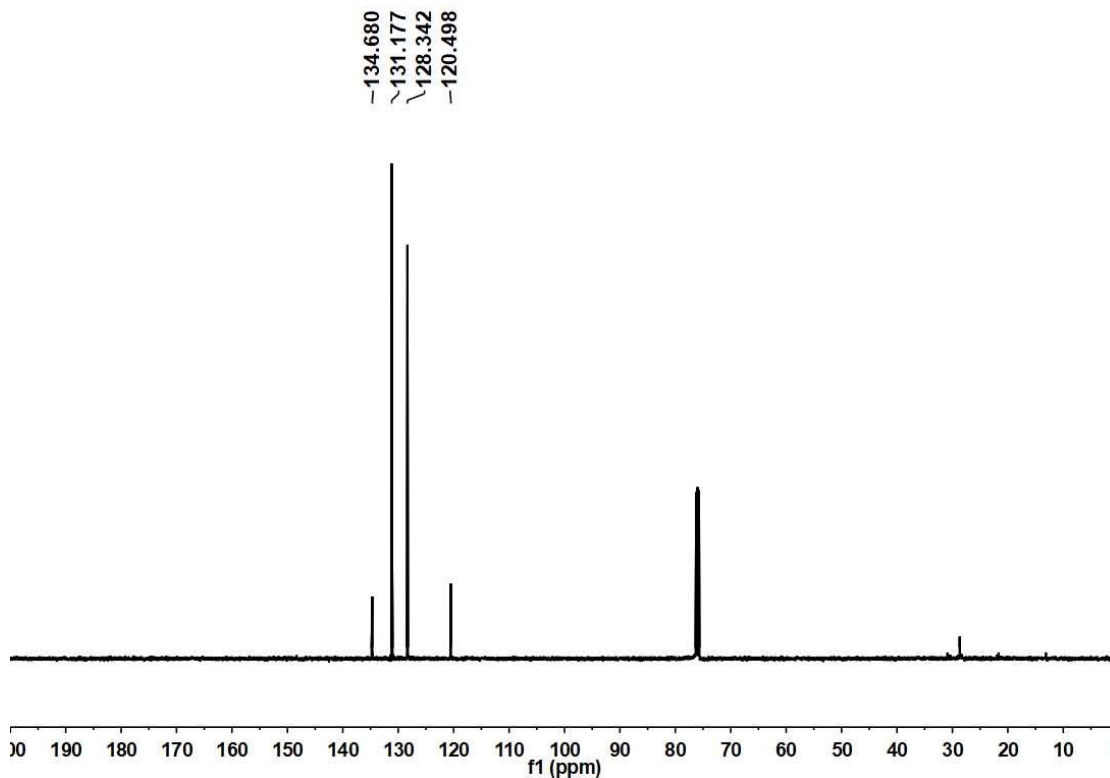


2h

¹H NMR

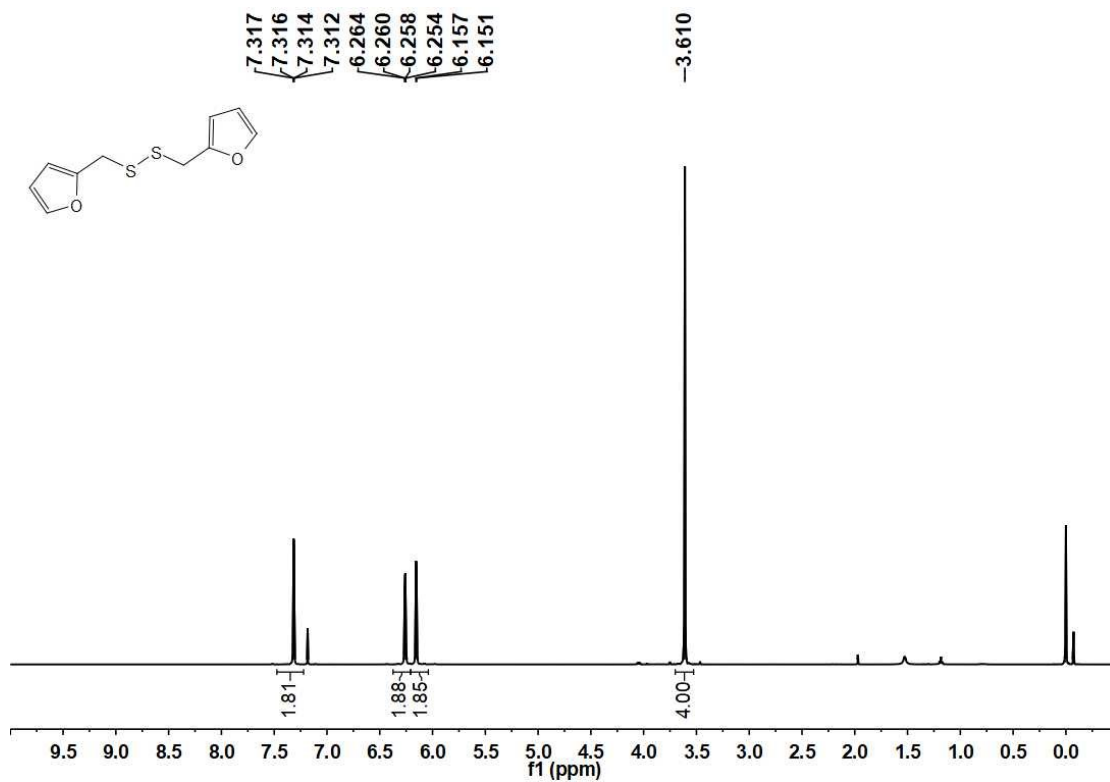


¹³C NMR

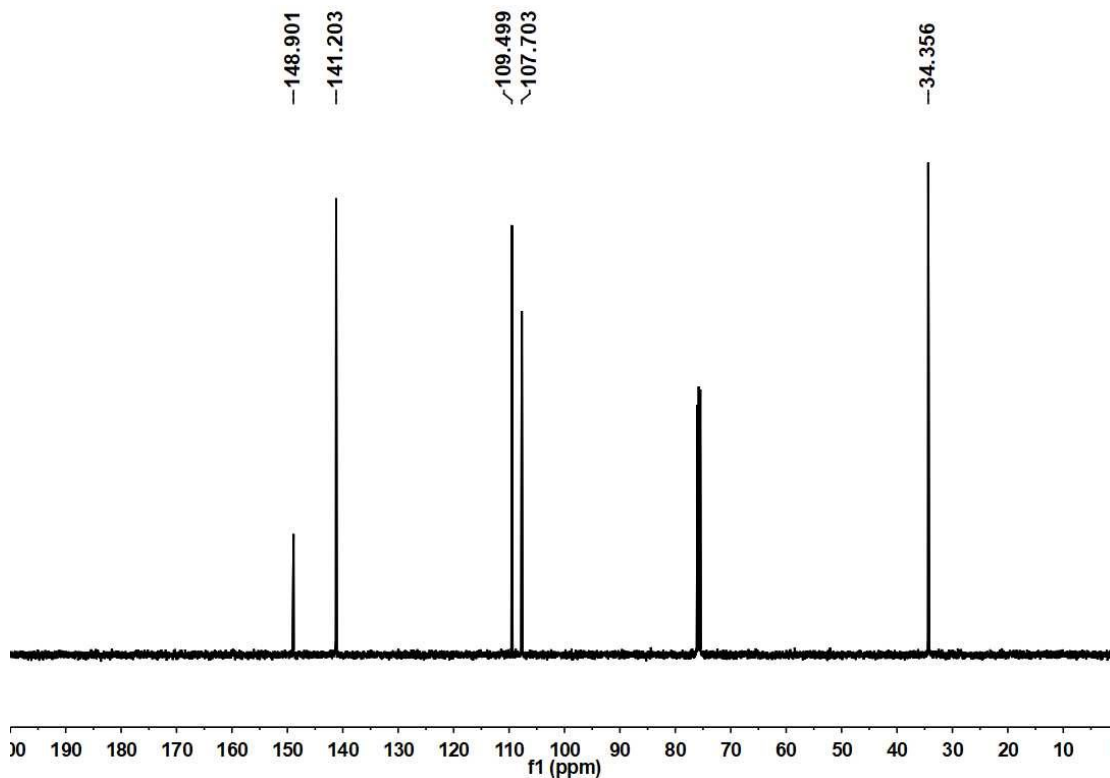


2i

¹H NMR

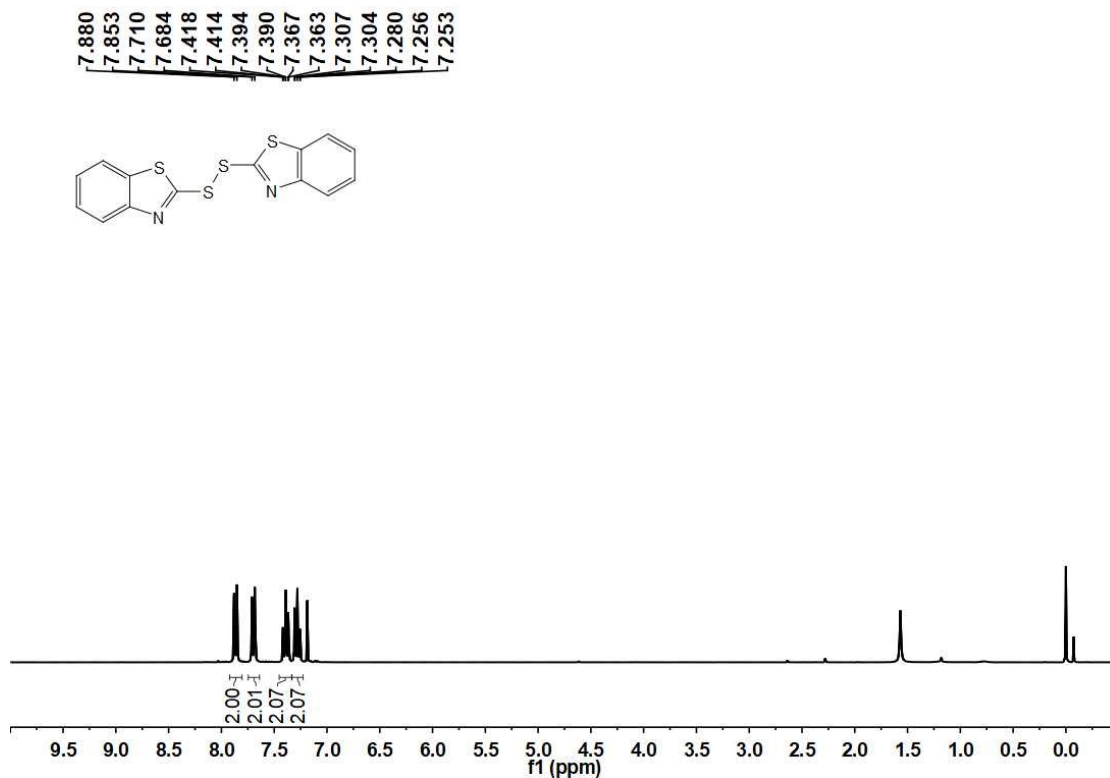


¹³C NMR

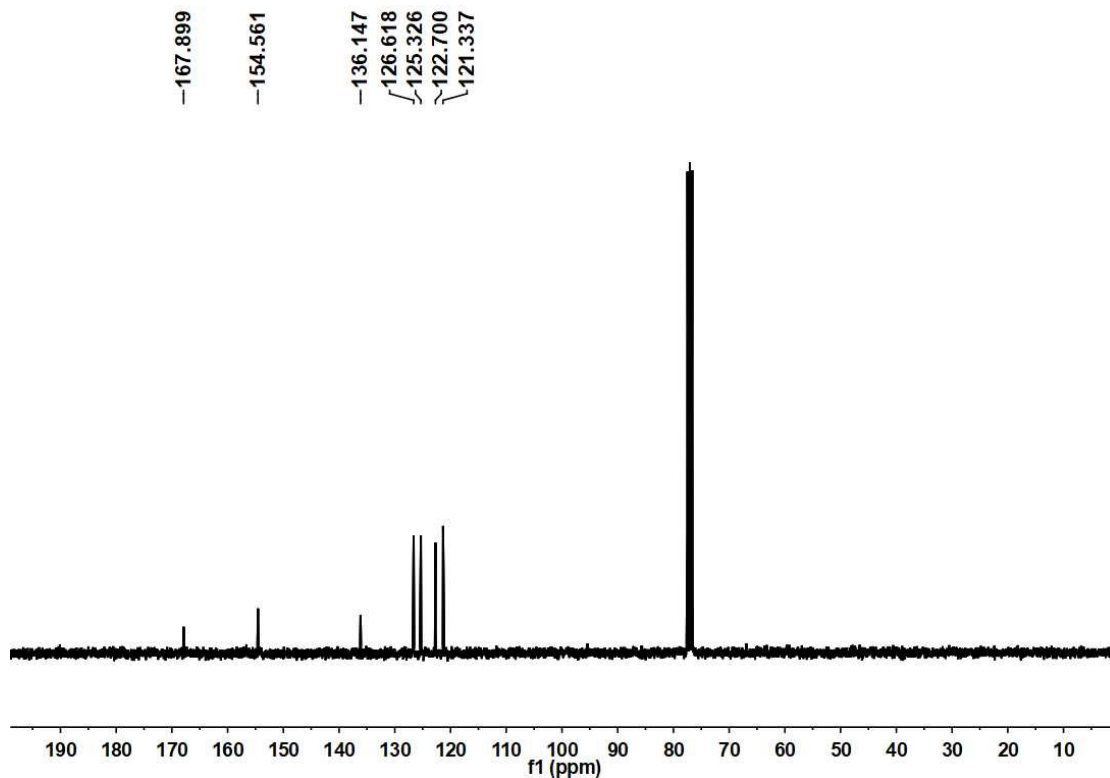


2j

¹H NMR

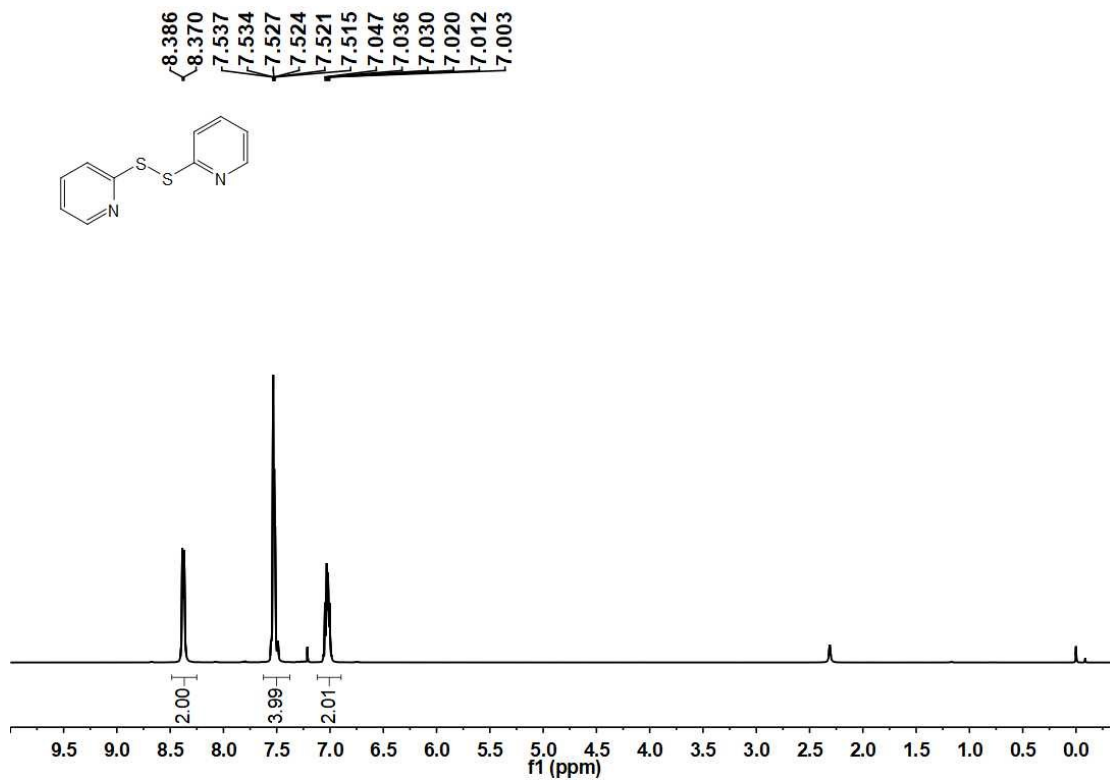


¹³C NMR

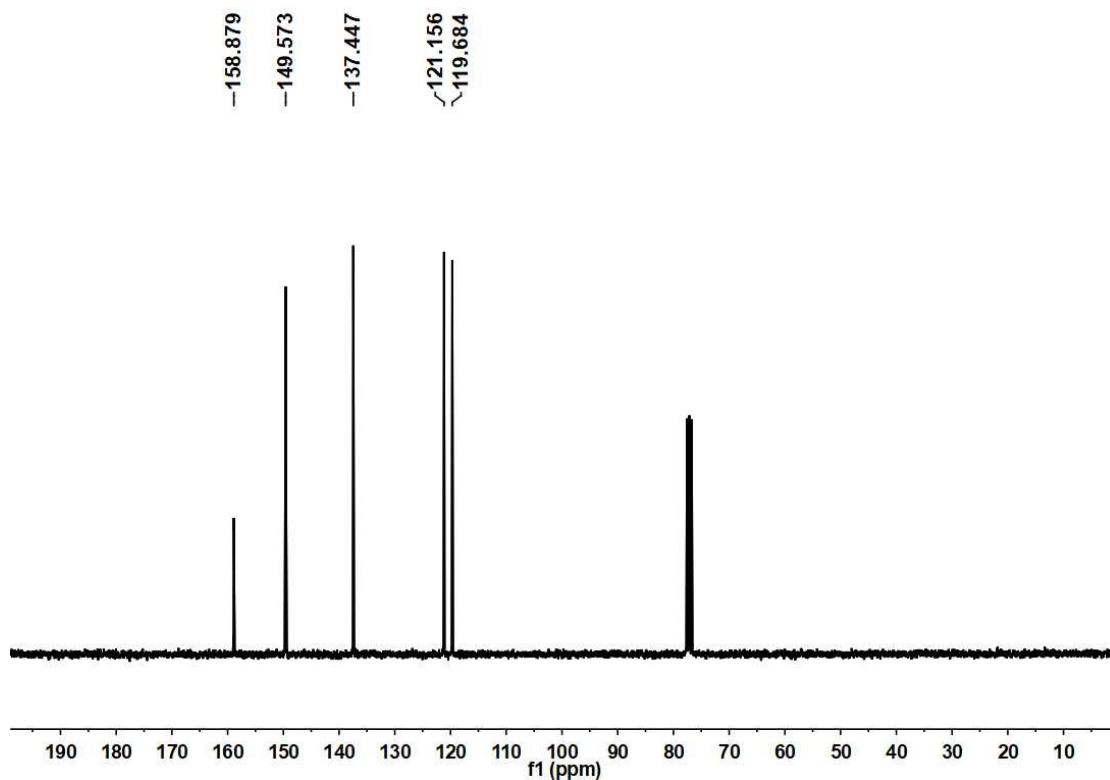


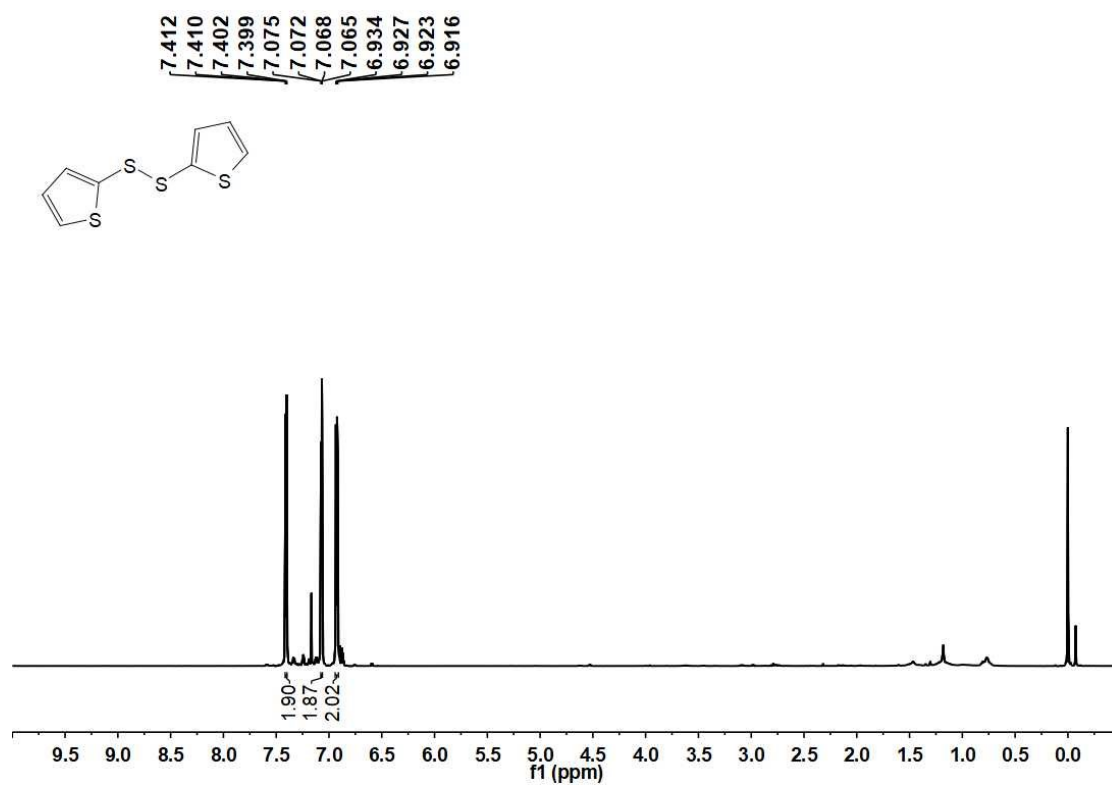
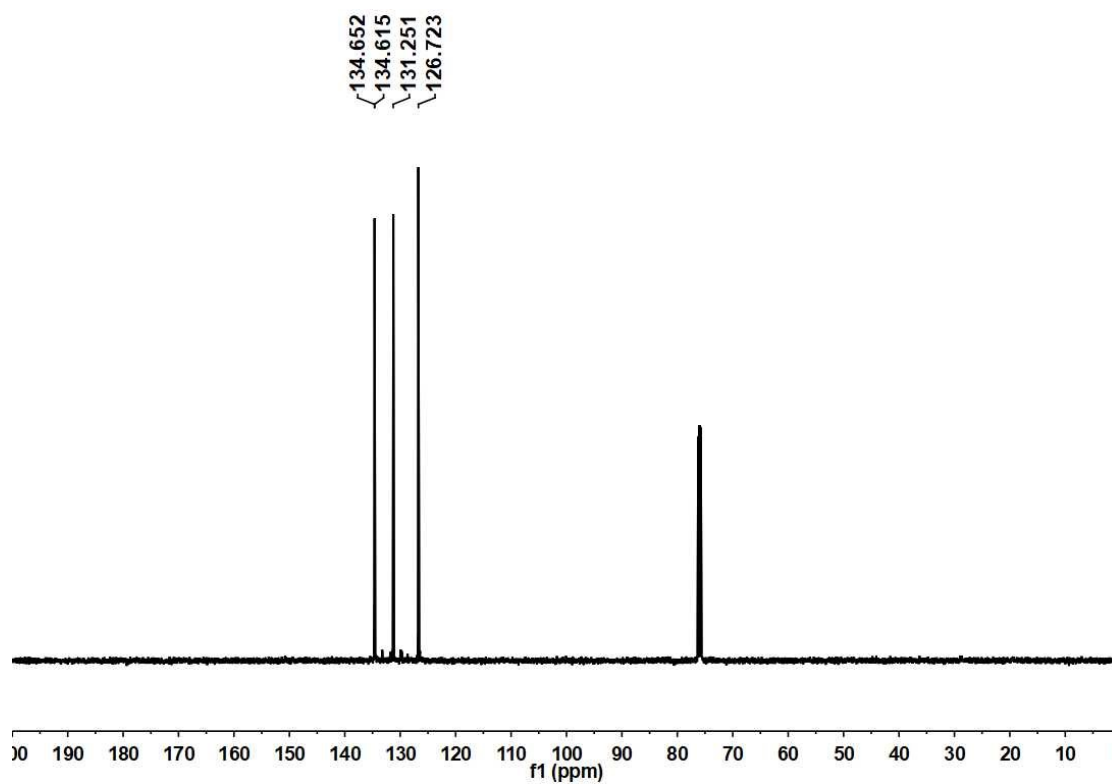
2k

¹H NMR



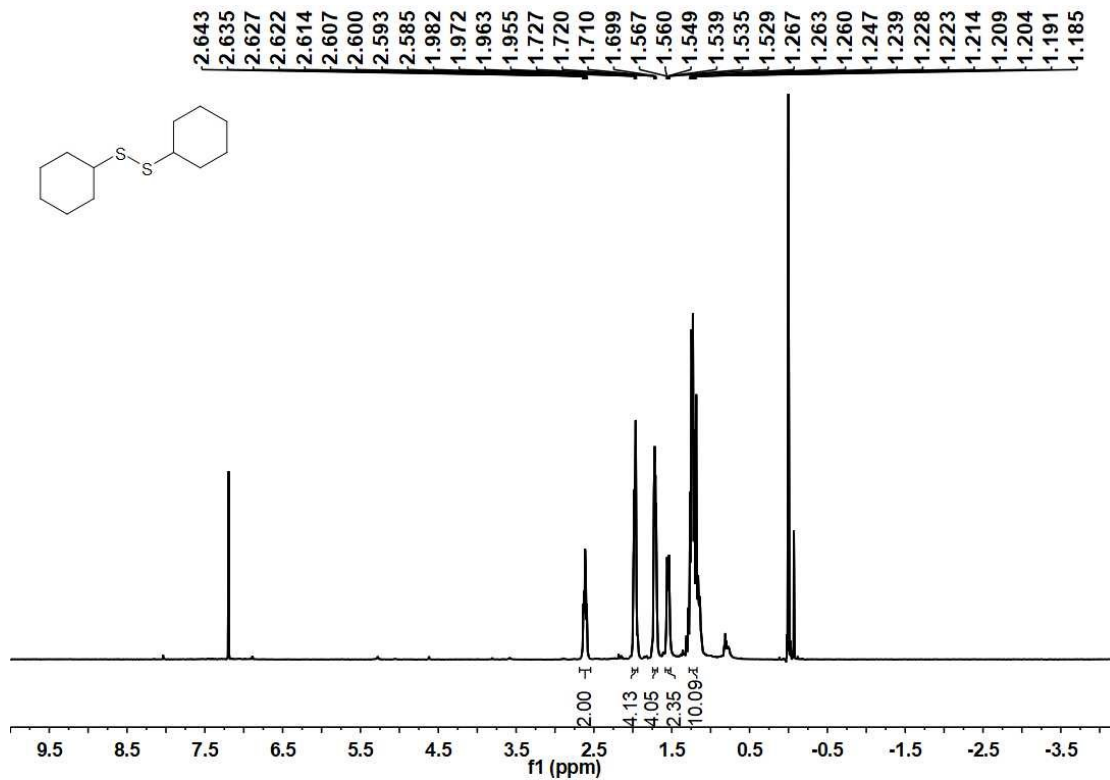
¹³C NMR



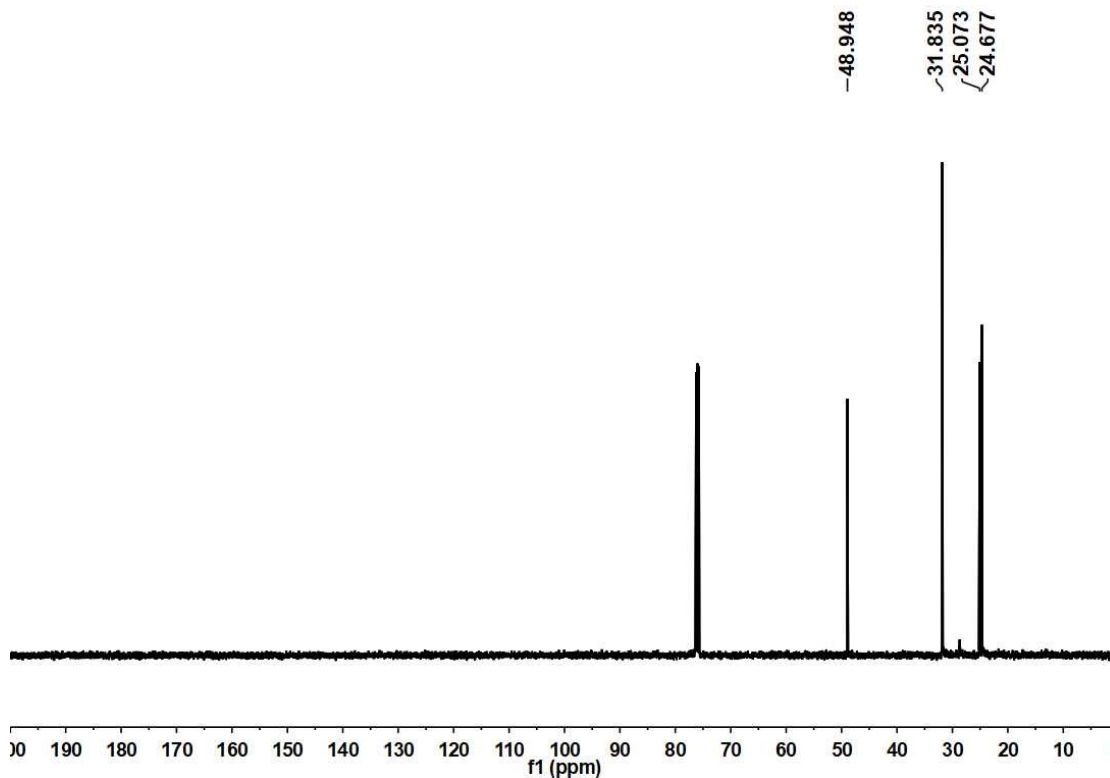
¹H NMR¹³C NMR

2m

¹H NMR

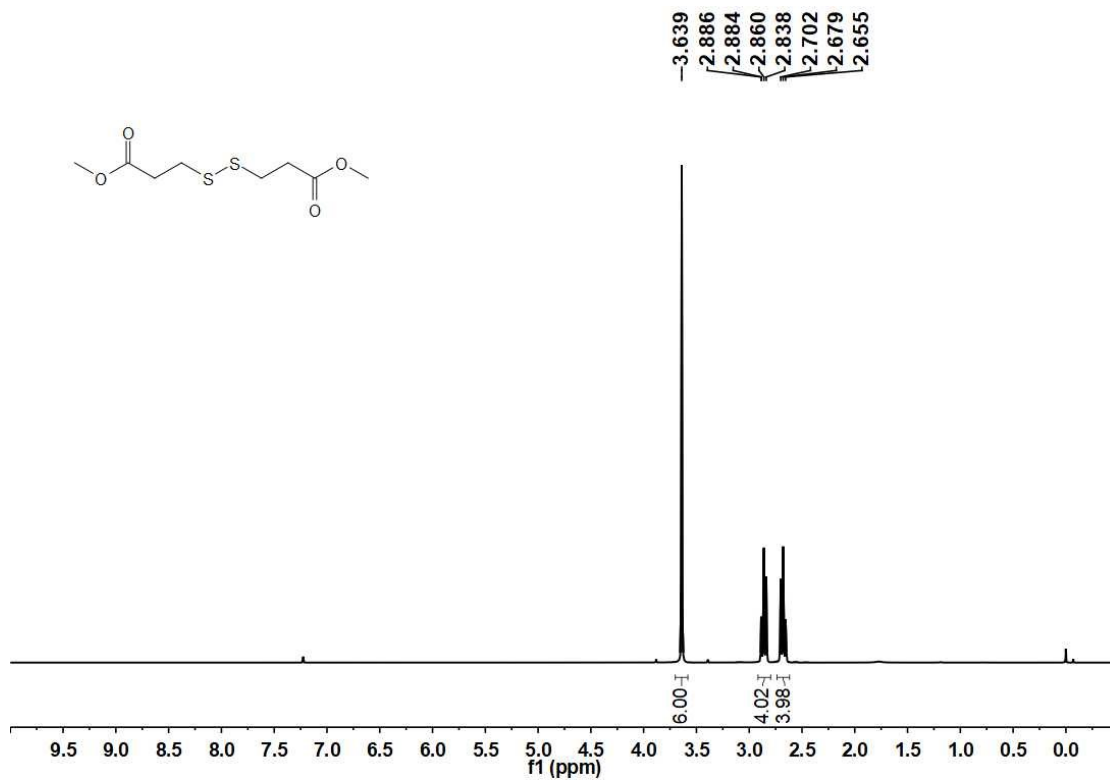


¹³C NMR

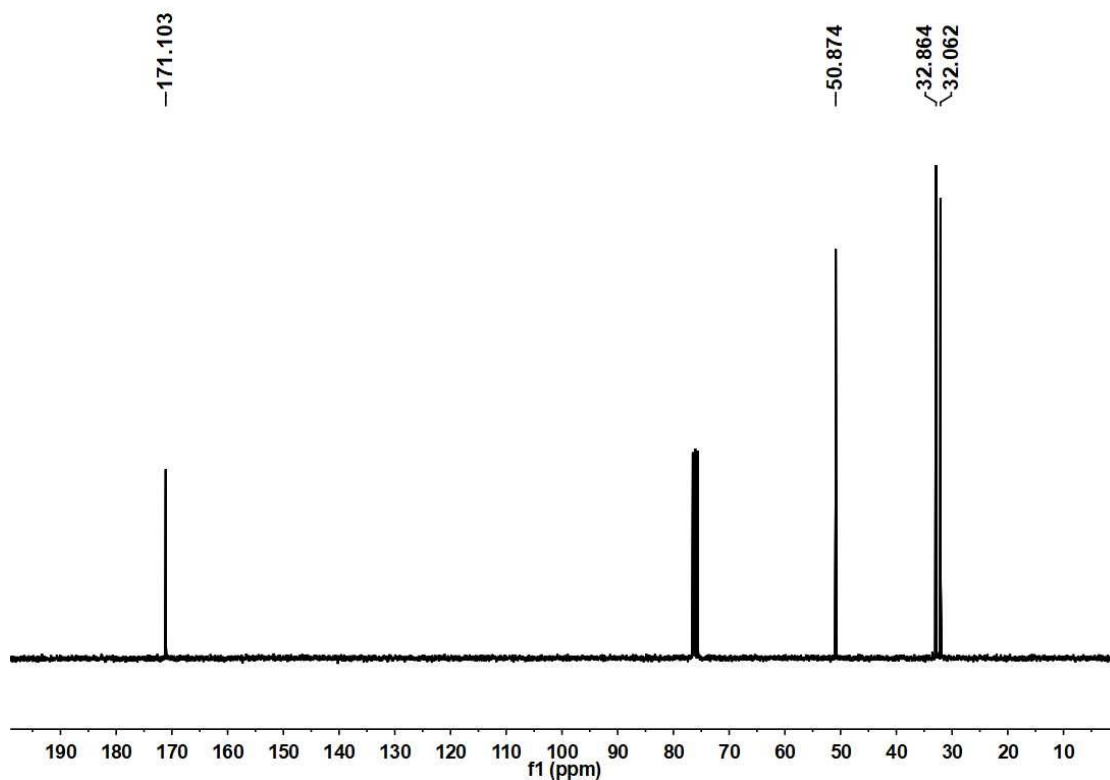


2n

¹H NMR

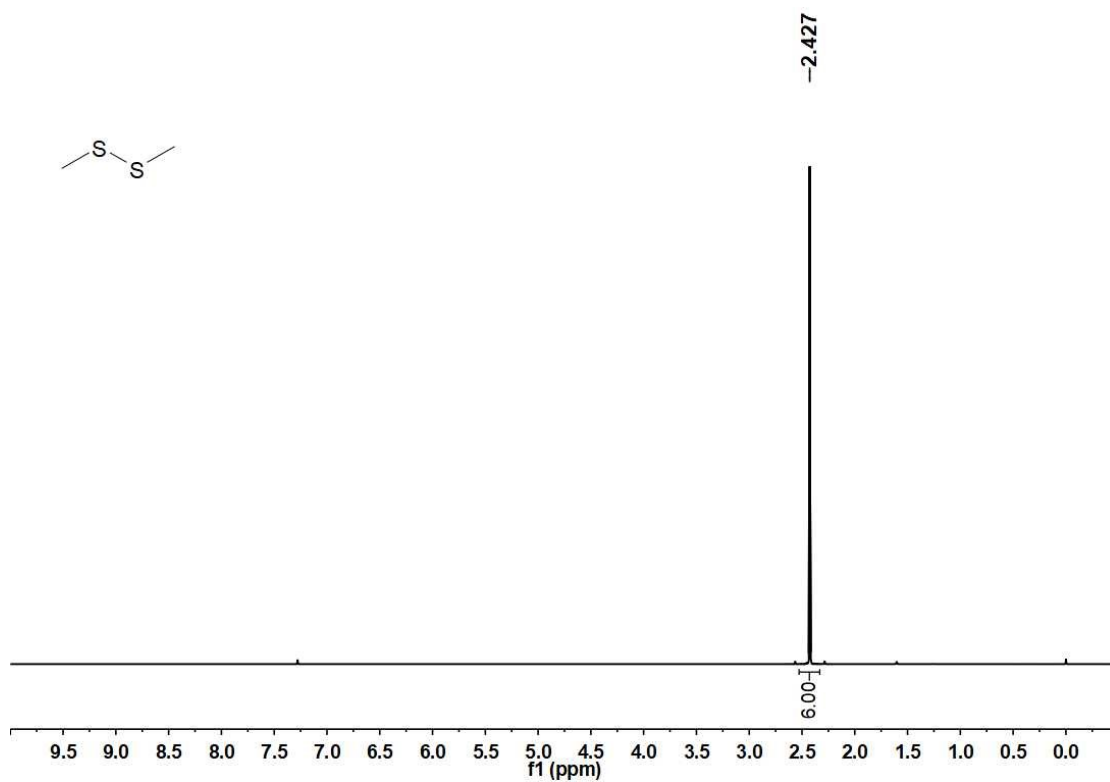


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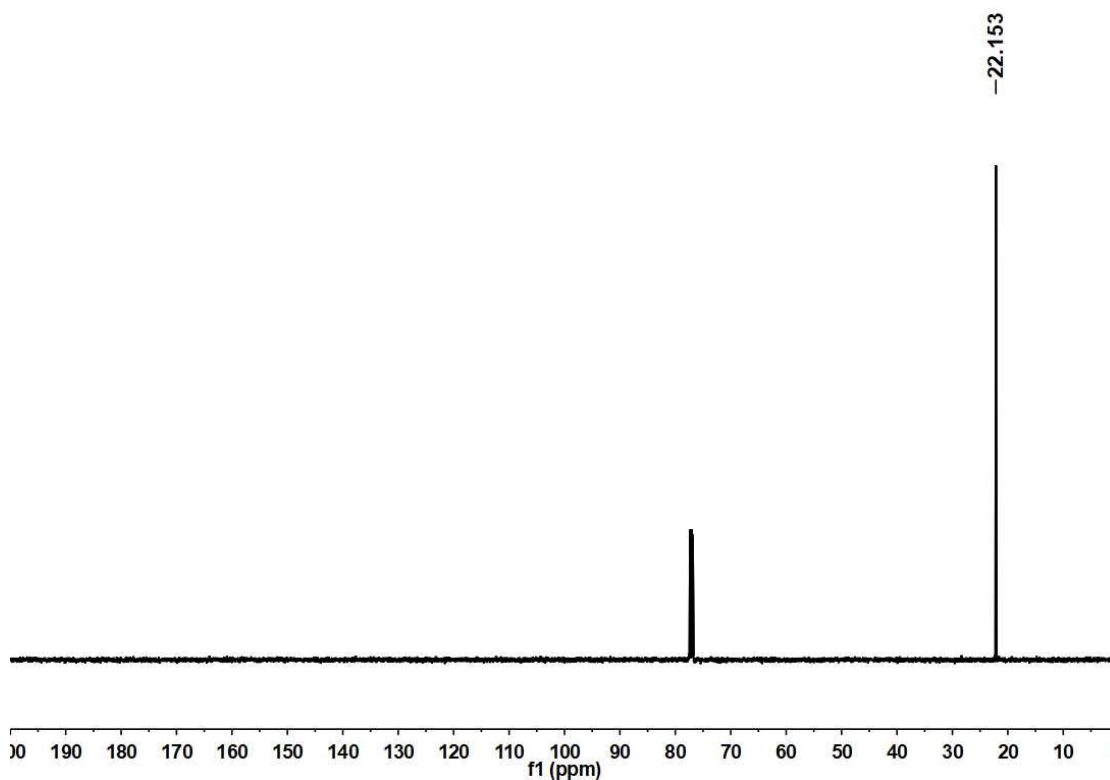


20

¹H NMR



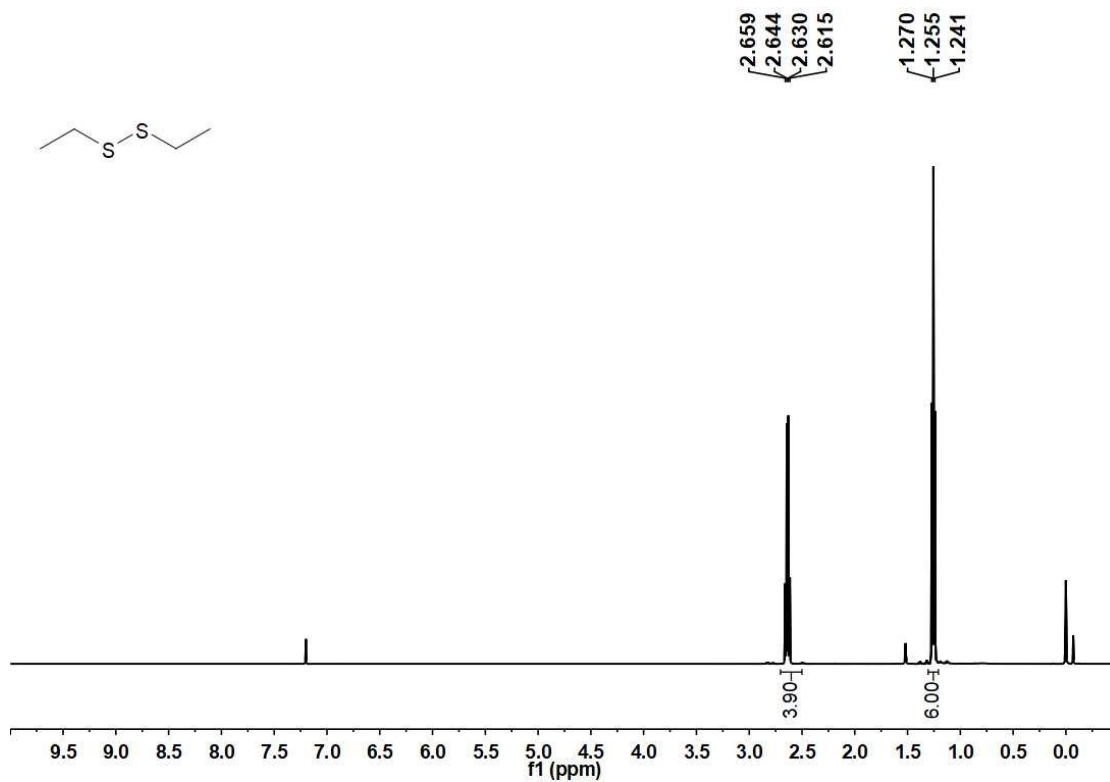
¹³C NMR



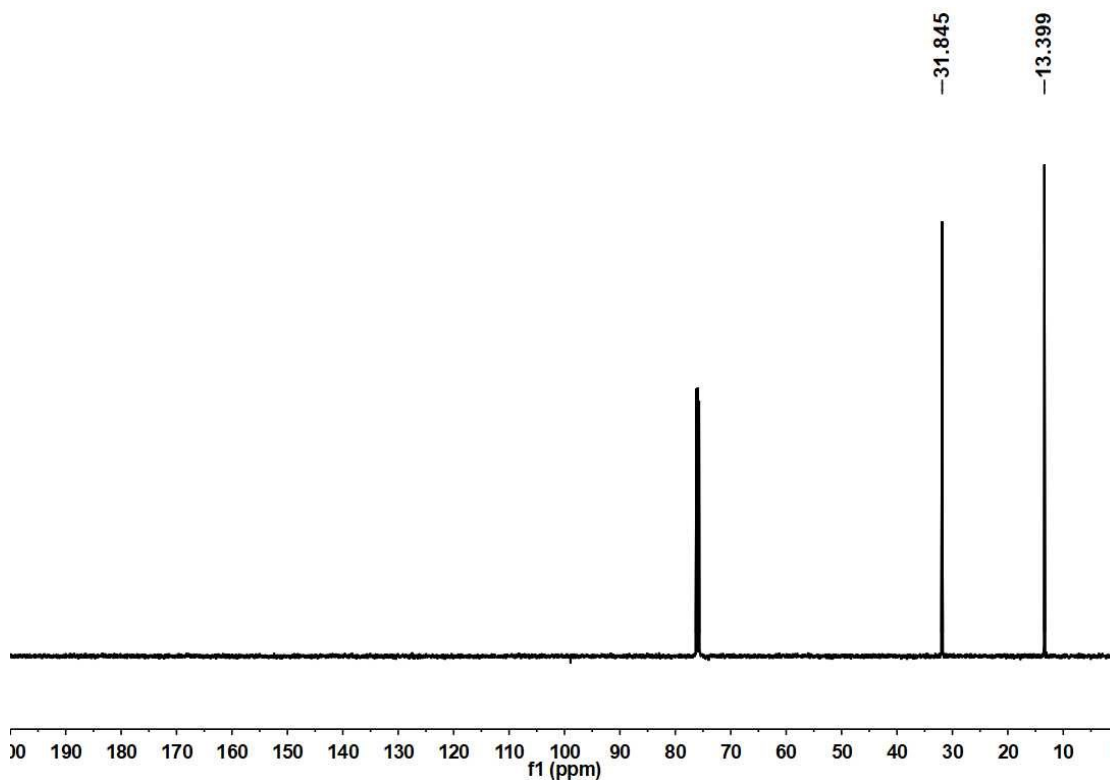
S40

2p

¹H NMR

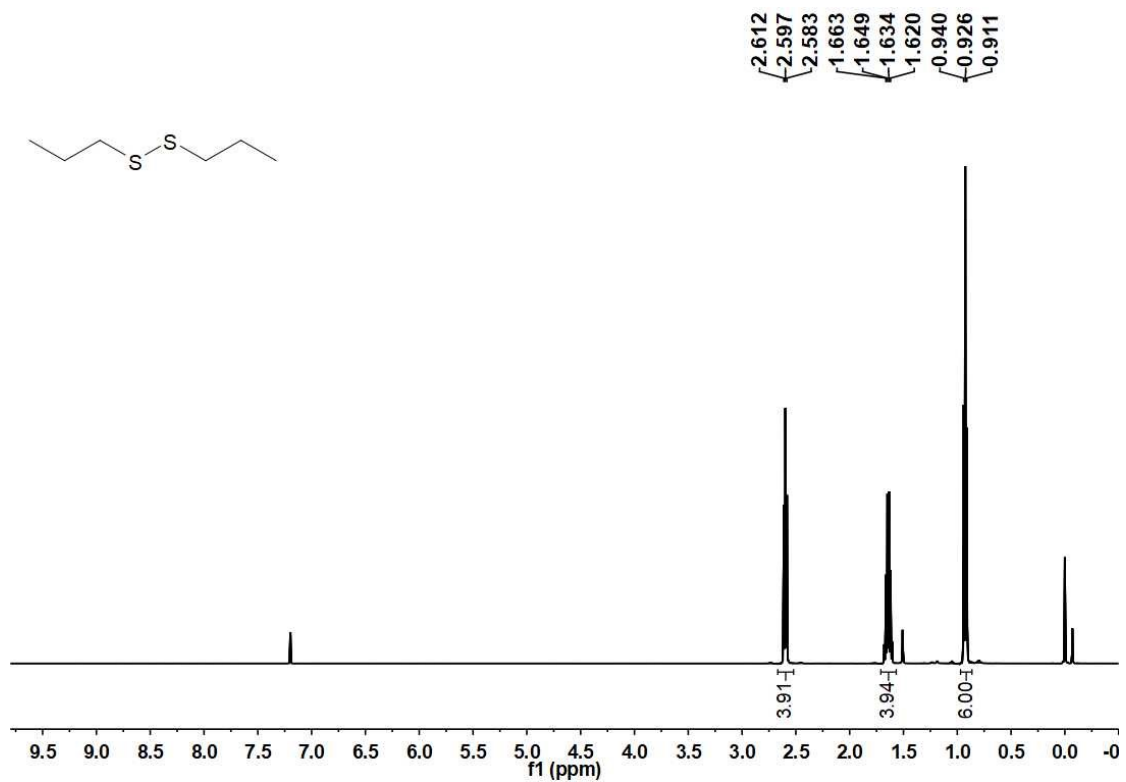


¹³C NMR

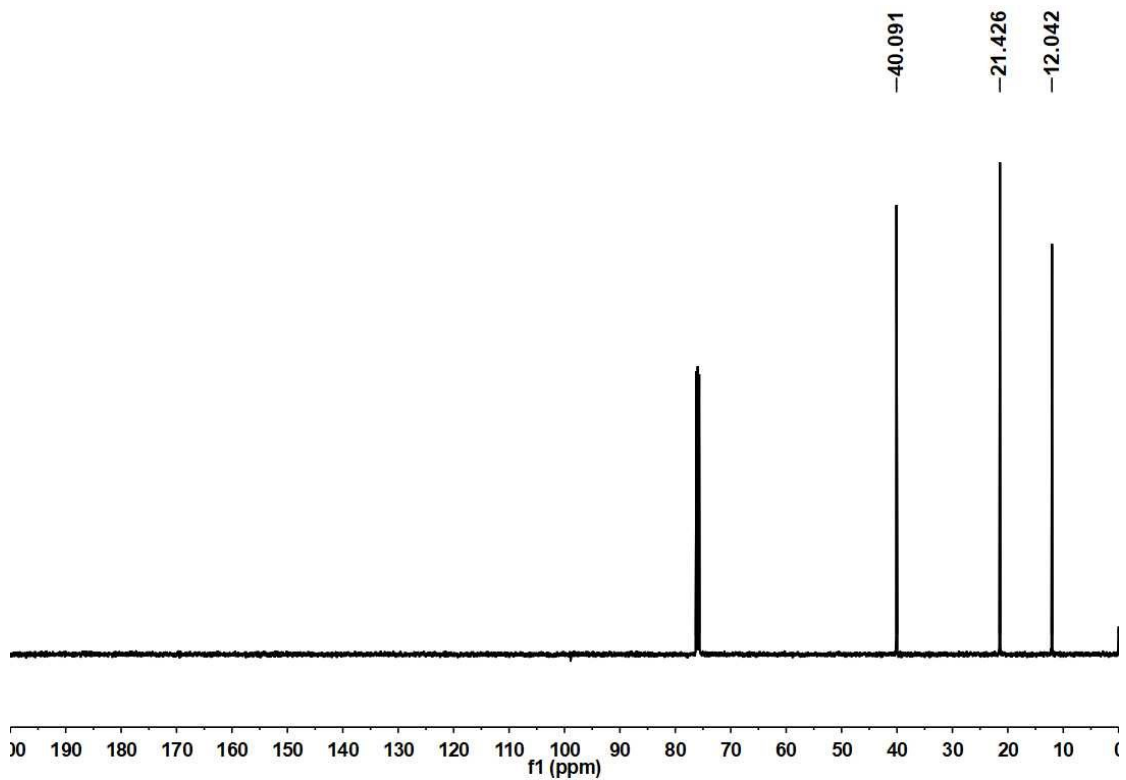


2q

¹H NMR

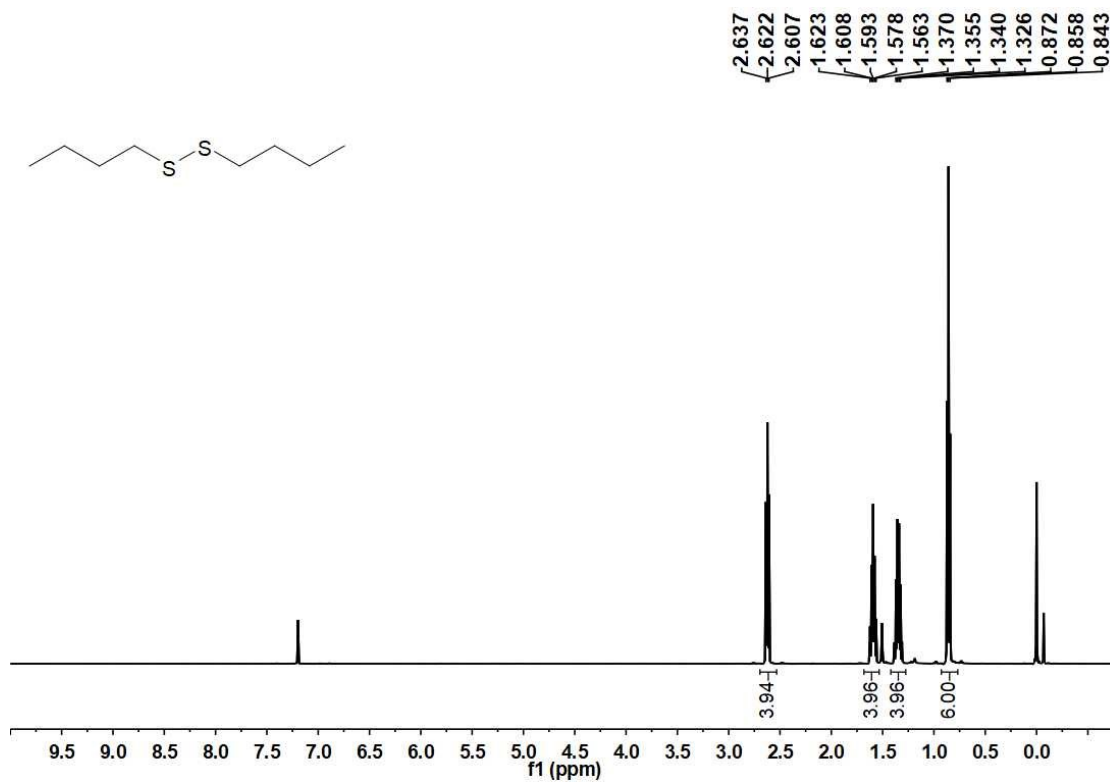


¹³C NMR

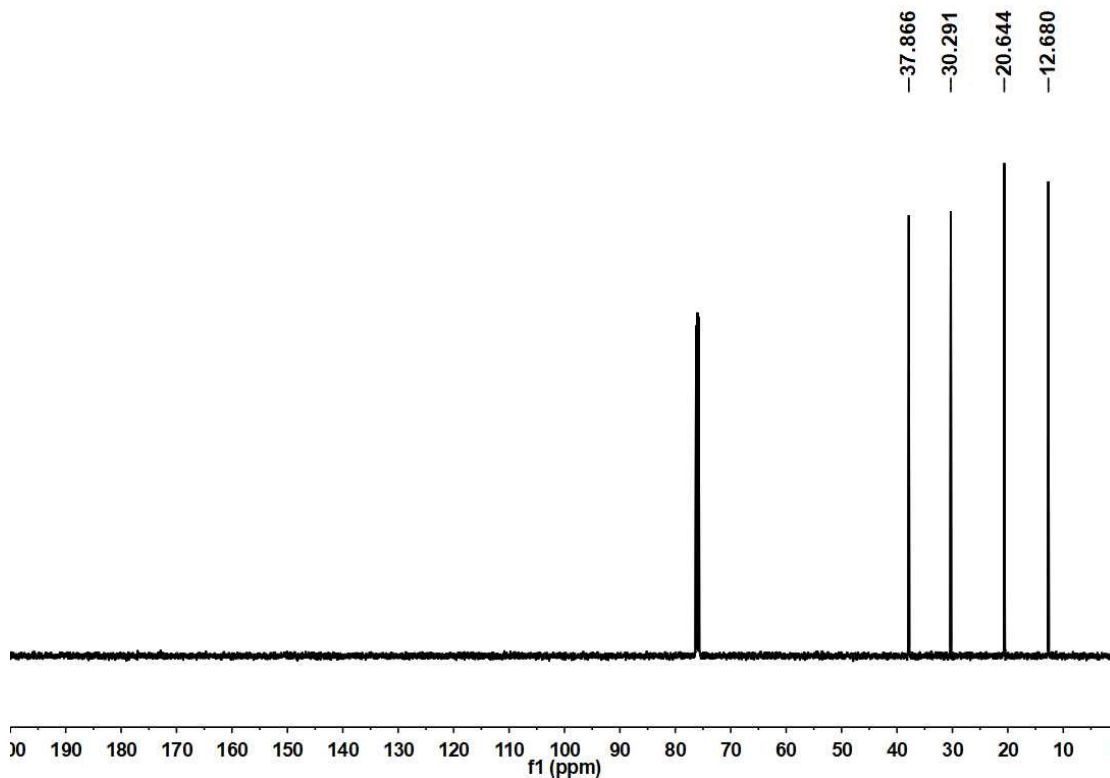


2r

¹H NMR

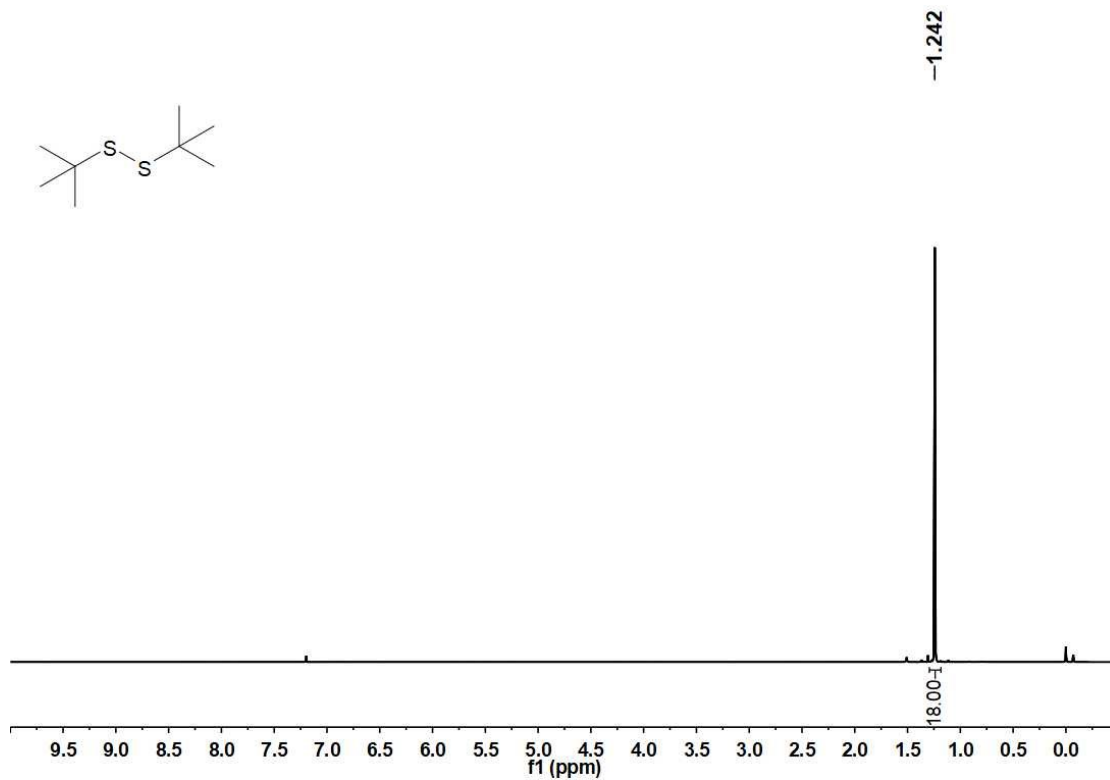


¹³C NMR

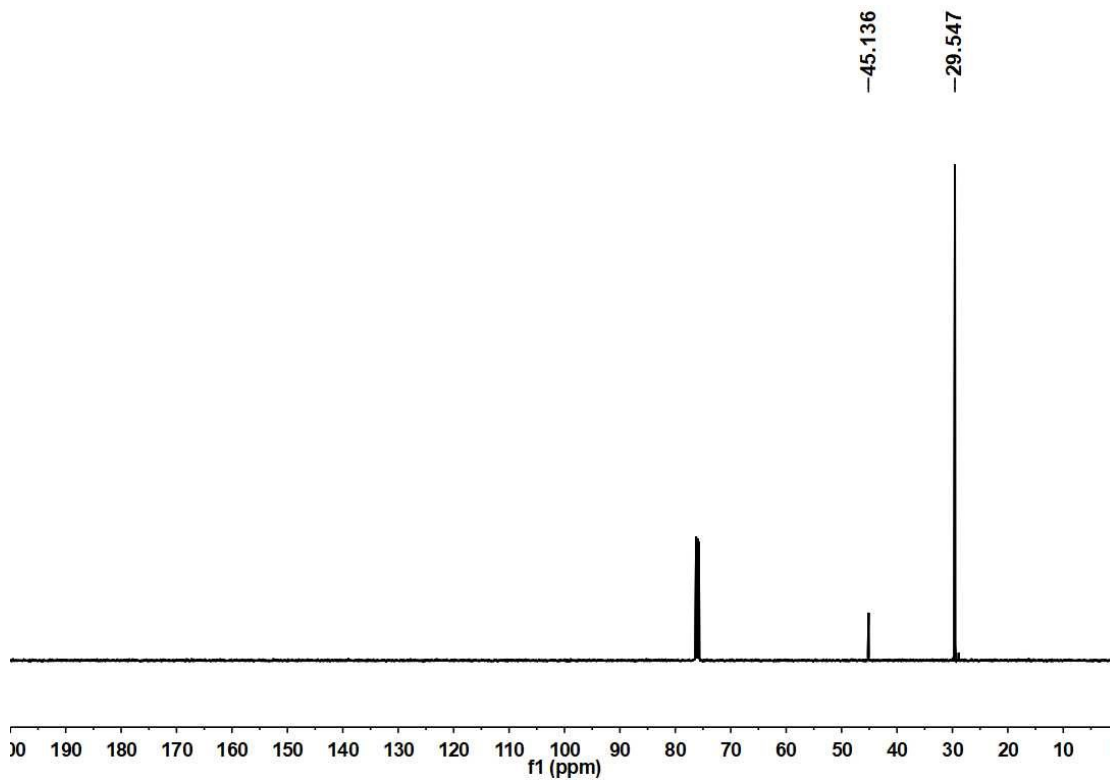


2s

¹H NMR

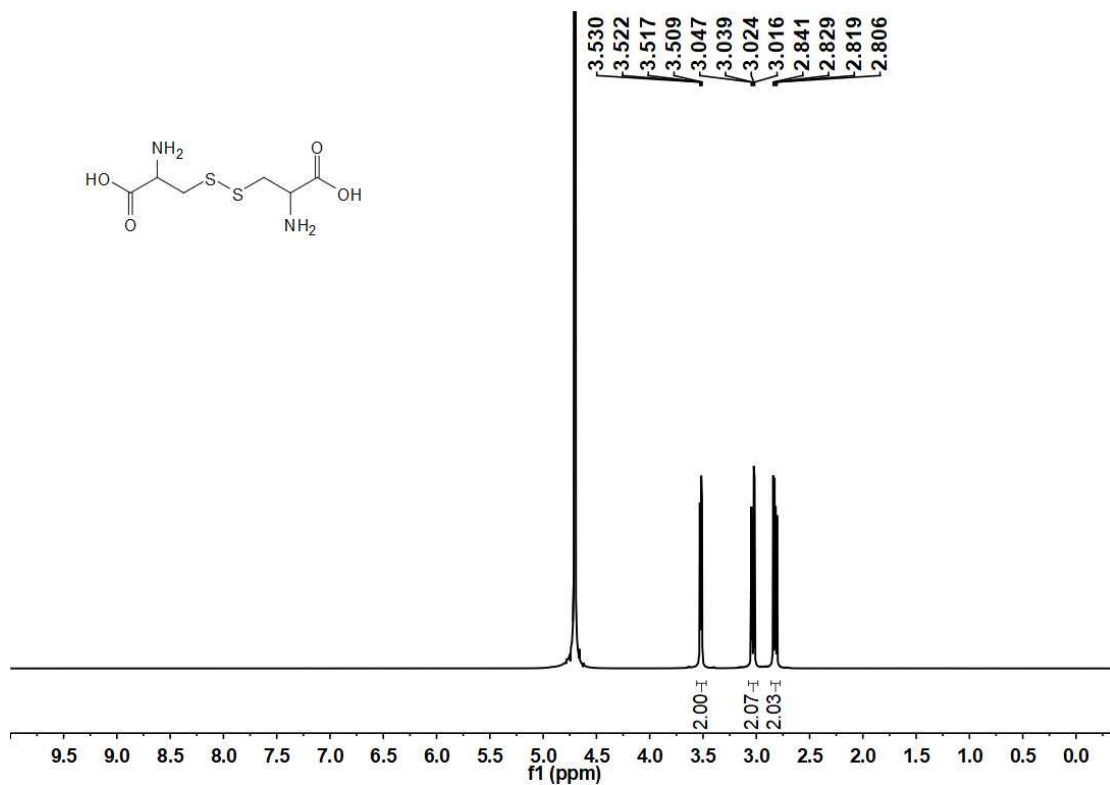


¹³C NMR

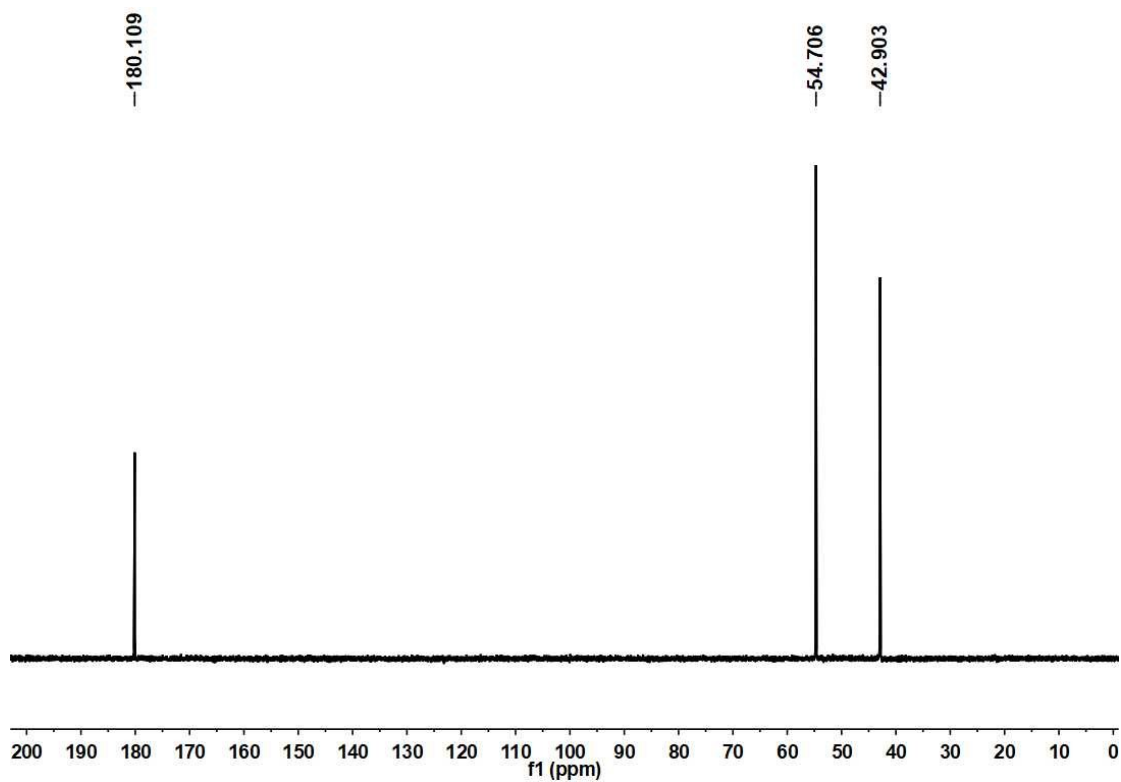


2t

¹H NMR

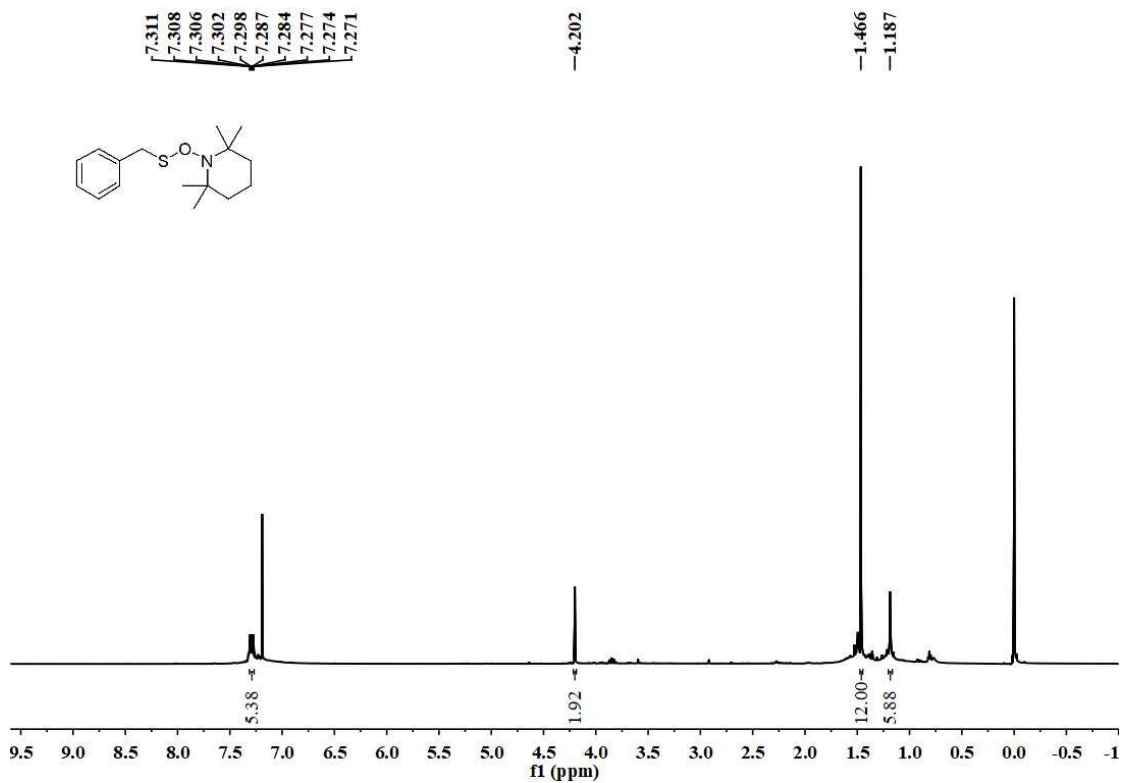


¹³C NMR



2u

¹H NMR



¹³C NMR

