Supplementary Information

Single Atom Copper Catalyst for S-arylation Reaction to Produce Diaryl Disulfides

Yiming Zhao,[a] Yan Zhou,[a] Shanshan Lv,[a] Han Li,[a] Qikang Wu,[a] Shaohuan Liu,[a] Wanying Li,[a] Taiyu Chen,[a] Zheng Chen*[a]

[a]Key Laboratory of Functional Molecular Solids, Ministry of Education, Anhui Laboratory of Molecule-Based Materials, College of Chemistry and Materials Science, Anhui Normal University, Wuhu, Anhui 241000, China

Experiment Methods

Chemicals

Copper(II) Chloride Dihydrate [$CuCl_2 \cdot 2H_2O$], Cerium(III) Nitrate Hexahydrate and Sodium Hydroxide were purchased from Sinopharm Chemical Reagent Co. Ltd. (Shanghai, China). Ar/H_2 (5%) was purchased from Linde Gas. The water used in all experiments was ultrapure (18.2 MΩ). All chemicals were used as received without further purification.

Synthesis of CeO_x Nanorods

5 mL 0.8 M $Ce(NO_3)_4$ and 75 mL 6.4 M NaOH put together into a 200 mL Beaker, then dissolved in r.t. for 0.5 h and then transferred into a Teflon bottle. The Teflon bottle was tightly sealed and hydrothermally treated in a stainless-steel autoclave at 100 °C for 24 h. The separated solid was heated under air at 2 ^{o}C min^{-1} (2.5 h) up to 300 ^{o}C and then treated at 300 ^{o}C for 2h. The yellow and fluffy powder is obtained after the temperature dropped.

Synthesis of Cu_1/CeO_x nanorods

5 mL $CuCl_2$ (0.01g mL^{-1}) was added into the CeO_x aqueous dispersion (500 mg CeO_x dispersed in 50 mL of distilled water) and keeping stirring at 50 ^{o}C for 12 h. The resulting product was washed with distilled water several times, and was then dried in vacuum at 50 ^{o}C overnight to give $CuCl_2/CeO_2$ sample, followed by annealing at 150 ^{o}C in H_2/Ar (5%) atmosphere for 2 h to give Cu_1/CeO_x sample.

Synthesis of Cu_{1+x}/CeO_x nanorods (1% Cu species)

10 mL $CuCl_2$ (0.01g mL^{-1}) was added into the CeO_x aqueous dispersion (500 mg CeO_x dispersed in 45 mL of distilled water) and keeping stirring at 50 ^{o}C for 12 h. The resulting product evaporated under vacuum, and was then dried in vacuum at 50 ^{o}C overnight to give $CuCl_2/CeO_2$ sample, followed by annealing at 150 ^{o}C in H_2/Ar (5%) atmosphere for 2 h to give Cu_1/CeO_x sample.

Synthesis of Cu_{1+x}/CeO_x nanorods (2% Cu species)

20 mL $CuCl_2$ (0.01 g mL^{-1}) was added into the CeO_x aqueous dispersion (500 mg CeO_x dispersed in 35 mL of distilled water) and keeping stirring at 50 °C for 12 h. The resulting product evaporated under vacuum, and was then dried in vacuum at 50 °C overnight to give $CuCl_2/CeO_2$ sample, followed by annealing at 150 °C in H_2/Ar (5%) atmosphere for 2 h to give Cu_1/CeO_x sample.

Procedure for dithiolation of aryl iodides

In a typical reaction, a 10 mL Schlenk tube was charged with iodobenzene (102.0 mg, 0.5 mmol), 0.75 mmol elemental sulfur (24.0 mg, 1.5 equiv., 0.75 mmol), NaOH (80.0 mg, 4.0 equiv., 2 mmol) and 20 mg Cu_1/CeO_x catalyst and 2 mL DMF under nitrogen atmosphere. After stirring the result mixture under specific temperature and time, the catalyst was removed through centrifugation. GC-FID (SP-6890) and GC-MS was used to determine the conversion and selectivity. Then the mixture was cooled and then poured into 5 mL saturated NH_4Cl solution, extracted with ethyl acetate (3 x 10 mL), and washed with water (3 x 10 mL). The combined organic layers were dried over anhydrous Na_2SO_4. The residue was purified by flash column chromatography on silica gel use petroleum ether to afford the desired product **2a**.

Recycling studies

In a typical reaction, a 10 mL Schlenk tube was charged with iodobenzene (102.0 mg, 0.5 mmol), 0.75 mmol elemental sulfur (24.0 mg, 1.5 equiv., 0.75 mmol), NaOH (80.0 mg, 4.0 equiv., 2 mmol) and 60 mg Cu/CeO_x catalyst and 2 mL DMF under nitrogen atmosphere. After stirring the result mixture under specific temperature and time, the catalyst was removed through centrifugation. GC-FID (SP-6890) and GC-MS was used to determine the conversion and selectivity. After reaction, the catalyst was separated through centrifugation and the catalyst was washed with ethyl acetate, methanol, 0.1 mol/L HCl, DDI water successively. And then dried in a vacuum oven at 60 ºC for 3 hours, and reused in a next run.

Characterization

The crystalline structure and phase purity were determined by Rigaku RU-200b X-ray powder diffractometer with Cu Ka radiation (l = 1.5418 Å). The size and morphology of as-synthesized samples were determined by using Hitachi-7700 transmission electron microscope working at 100 kV. The high-angle annular dark-field scanning TEM (HAADF-STEM) were operated at 200 kV by a JEOL-ARM200F. The composition of the product was measured by the inductively coupled plasma-atomic emission spectrometry and energy dispersive X-ray spectrometer. Inductively Coupled Plasma Optical Emission Spectrometer (ICP-OES) results were obtained in Agilent 720ES.

Photoemission spectroscopy experiments (XPS) were performed on a ULVAC PHI Quantera microprobe in Beijing, China. The end station is comprised of four ultrahigh vacuum (UHV) chambers including analysis chamber, preparation chamber, molecular beam epitaxy (MBE) chamber, and a radial distribution chamber (RDC). The base pressures are 7×10^{-11}, 1×10^{-10}, 5×10^{-10} and 2×10^{-11} mbar, respectively. In addition, a quick sample load-lock system is attached to the RDC. The analysis chamber is equipped with a VG Scienta R4000 analyzer and a monochromatic Al Ka X-ray source. The sample was annealed at the preparation chamber and then transferred to the analysis chamber for characterization. The core-level spectra were measured using a monochromatic Al Ka X-ray source. For the core-level spectra, the binding energies were calibrated using the C 1s feature located at 284.6 eV as the reference.

X-ray absorption data collection and analysis

The Cu K-edge X-ray absorption spectra were collected at room temperature in fluorescence mode at beamline 1W1B of Beijing Synchrotron Radiation Facility (BSRF) using a Si (111) double-crystal monochromator. The storage rings of BSRF were operated at 2.5 GeV with a maximum current of 250 mA in decay mode. The energy was calibrated using Cu foil, while the incident and fluorescence x-ray intensities were monitored by using standard 25% Ar and 75% N_2-filled ion chamber and Ar-filled Lytle-type detector, respectively. A detuning of about 20% by misaligning the silicon crystals was also performed to suppress the high harmonic content. The samples were pelletized as disks of 13 mm diameter with 1mm thickness before measurements.

The XAFS raw data were background-subtracted, normalized, and Fourier transformed by the standard procedures with the ATHENA program. To obtain the quantitative structural parameters around the absorbing Cu atoms, least-squares curve fitting analysis of the EXAFS $\chi(k)$ data was performed using the ARTEMIS package, with the theoretical scattering amplitudes, phase shifts and the photoelectron mean free path for all paths calculated by FEFF6.

The following EXAFS equation was used:

$$\chi(k) = \sum_j \frac{N_j S_o^2 F_j(k)}{k R_j^2} \exp[-2 k^2 \sigma_j^2] \exp[\frac{-2 R_j}{\lambda(k)}] \sin[2k R_j + \phi_j(k)]$$

where S_0^2 is the amplitude reduction factor, $F_j(k)$ is the effective curved-wave backscattering amplitude, N_j is the number of neighbors in the j^{th} atomic shell, R_j is the distance between the X-ray absorbing central atom and the atoms in the j^{th} atomic shell (backscatterer), λ is the mean free path in Å, $\phi_j(k)$ is the phase shift (including the phase shift for each shell and the total central atom phase shift), σ_j is the Debye-Waller parameter of the j^{th} atomic shell (variation of distances around the average R_j). In present work, the variable parameters that are determined by using the EXAFS equation to fit the experimental data include N, R, and the EXAFS Debye-Waller factor (σ^2). S_0^2 was determined in the fit of Cu standard to be 0.85, and used as fixed value in the rest of the EXAFS models. All fits were performed in the R space with k-weight of 3. The EXAFS R-factor (R_f) that measures the percentage misfit of the theory to the data was used to evaluate the goodness of the fit.

N_2O titration tests

The dispersion test of copper was carried out on the TP 5080 adsorption-desorption instrument (Xianquan Industrial and Trading Co. Ltd., China) with a thermal conductivity cell by the N_2O titration method. The catalyst is loaded into a customized quartz reaction tube, and then the catalyst is preheated from 20 °C to 230 °C at 10 °C/min under 10% hydrogen/nitrogen (30 ml/min) atmosphere, then purged with argon (30 ml/min) at 230 °C for 30 min to remove excess hydrogen. Then use 10% CO_2/Ar to oxidize the Ce^{3+} obtained from pretreatment reduction at 40 °C to Ce^{4+} for 15 min. After the sample is cooled and kept at 50 °C, pure N_2O was pulsed into the reaction tube through a six-way valve with 50 μL or 100 μL. The amount of N_2O consumed can be obtained, and the final exposed metal copper can be calculated based on $n_{Cu0}/n_{N2O} = 2$.

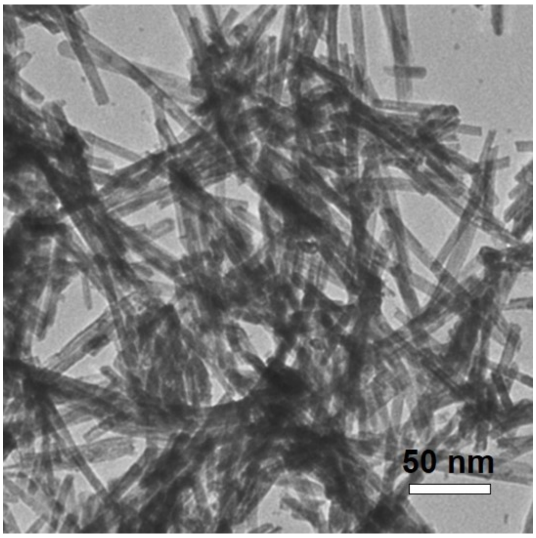


Figure S1. The representative TEM image of CeO_x nanorods.

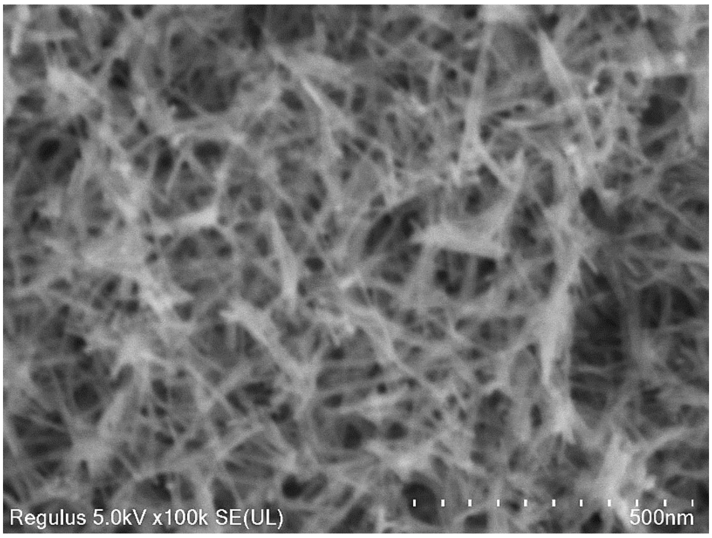


Figure S2. The representative SEM image of Cu_1/CeO_x nanorods.

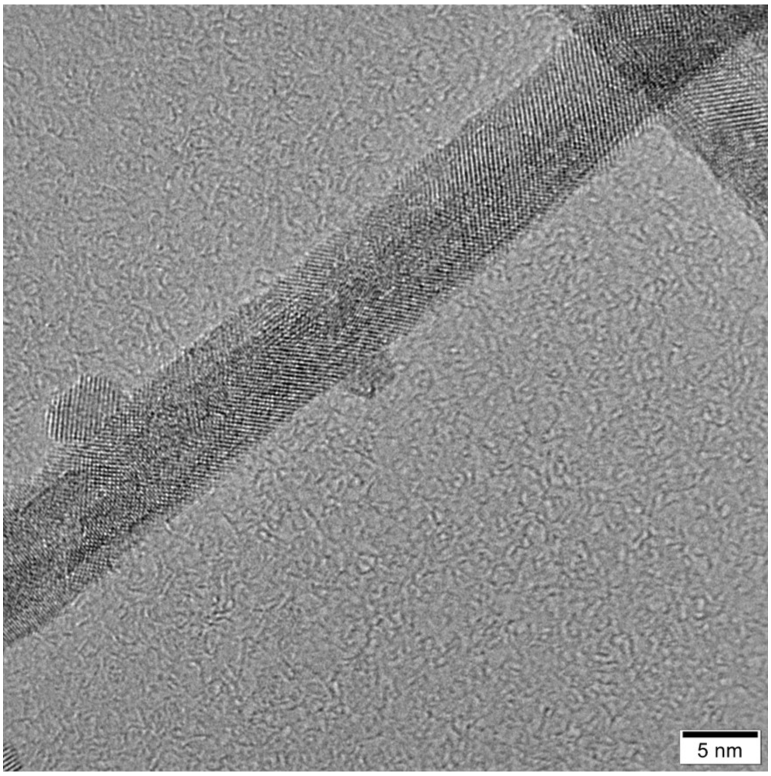


Figure S3. The representative TEM image of 1% Cu/CeO$_x$.

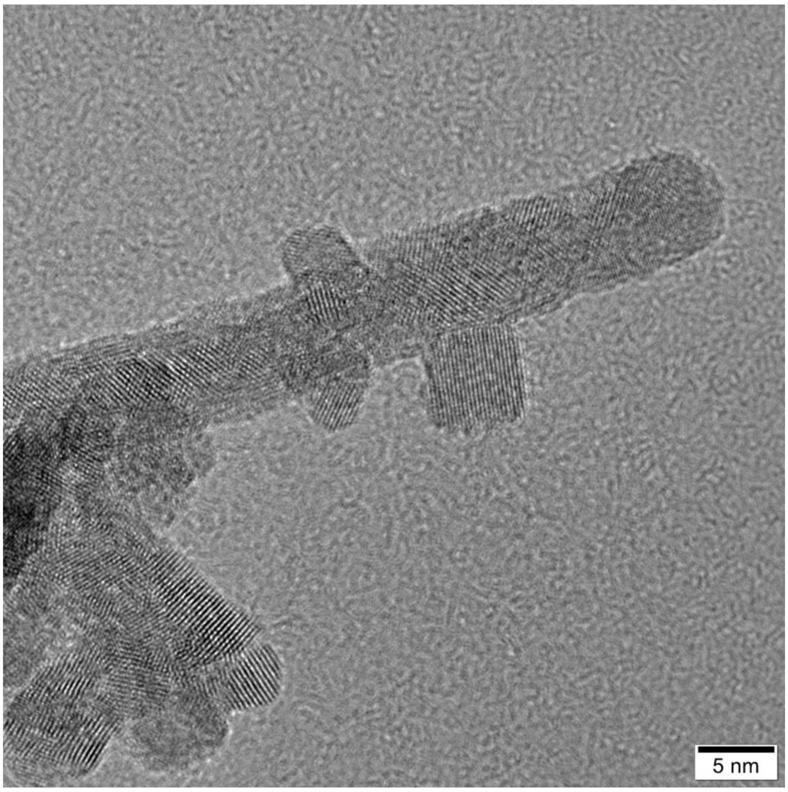


Figure S4. The representative TEM image of 2% Cu/CeO_x .

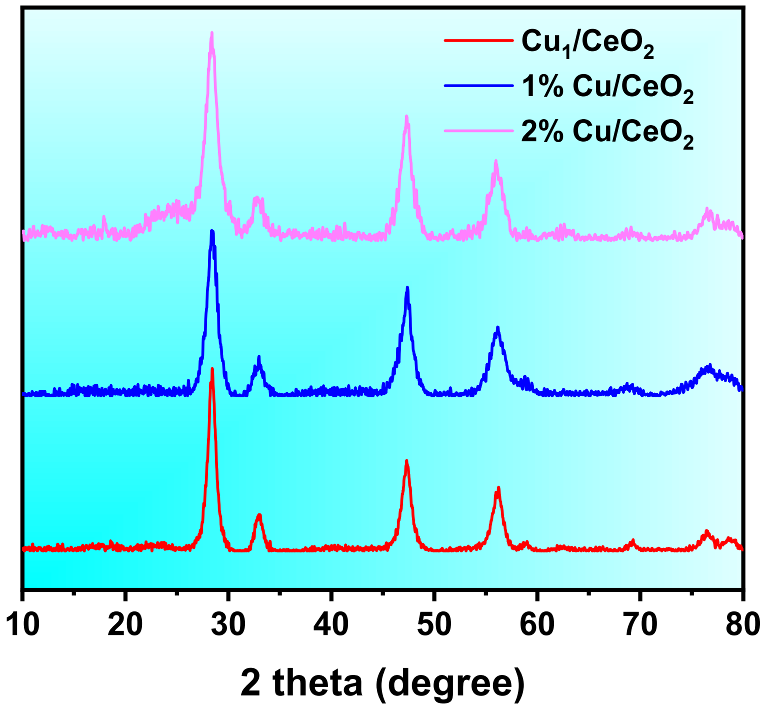


Figure S5. The Comparison between the XRD patterns for original Cu$_1$/CeO$_x$, 1% Cu/CeO$_x$ and 2% Cu/CeO$_x$ catalysts.

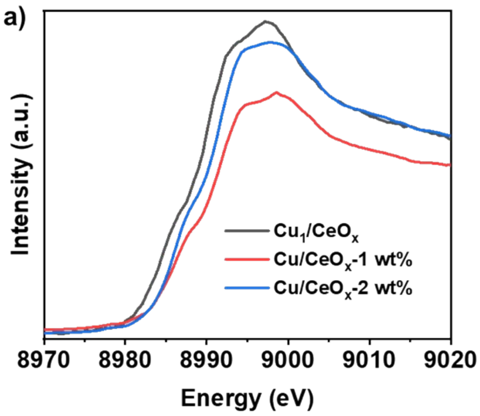


Figure S6. a) XANES spectra at the Cu K-edge of Cu_1/CeO_x, Cu/CeO_x-1 wt% and Cu/CeO_x-2 wt%; b) FT EXAFS spectra of Cu/CeO_x-1 wt% and Cu/CeO_x-2 wt%.

Table S1. N_2O titration test results for Cu species.

Sample	ICP-OES results for Cu species	Calculated Isolated Cu species	Dispersion of Cu species (%)
Cu_1/CeOx	0.138 mg	0.160 mg	>99%
1% Cu/CeOx	0.205 mg	0.196 mg	95.6%
2% Cu/CeOx	0.413 mg	0.372 mg	90.1%

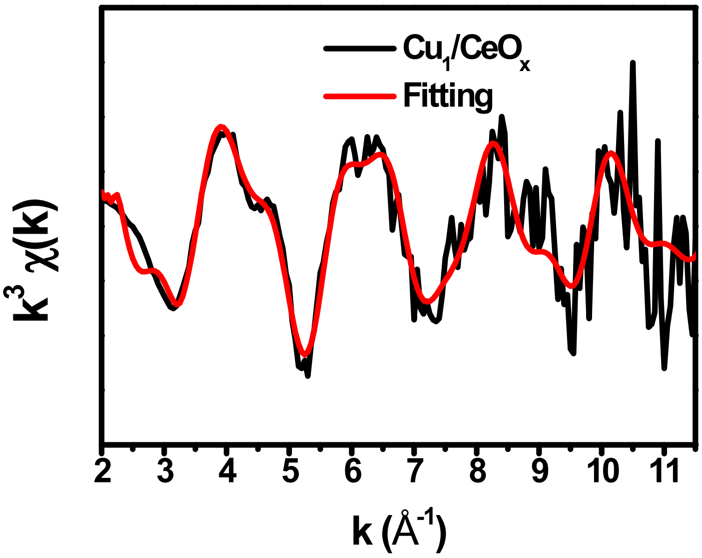


Figure S7. EXAFS fitting curves of the Cu_1/CeO_x in *k* space.

Table S2. Structural parameters extracted from the EXAFS fitting. ($S_0^2 = 0.85$)

Sample	Scattering pair	CN	R(Å)	$\sigma^2(10^{-3}Å^2)$	$\Delta E_0(eV)$	R factor
Cu_1/CeO_x	Cu-O	4.1	1.80	0.0046	-2.5	0.0033
	Cu-O	1.1	2.54	0.0002	-3.4	0.026
	Cu-Ce	3.9	3.17	0.0139	-4.7	0.031

S_0^2 is the amplitude reduction factor; CN is the coordination number; R is interatomic distance (the bond length between Fu central atoms and surrounding coordination atoms); σ^2 is Debye-Waller factor (a measure of thermal and static disorder in absorber-scatterer distances); ΔE_0 is edge-energy shift (the difference between the zero kinetic energy value of the sample and that of the theoretical model). R factor is used to value the goodness of the fitting.

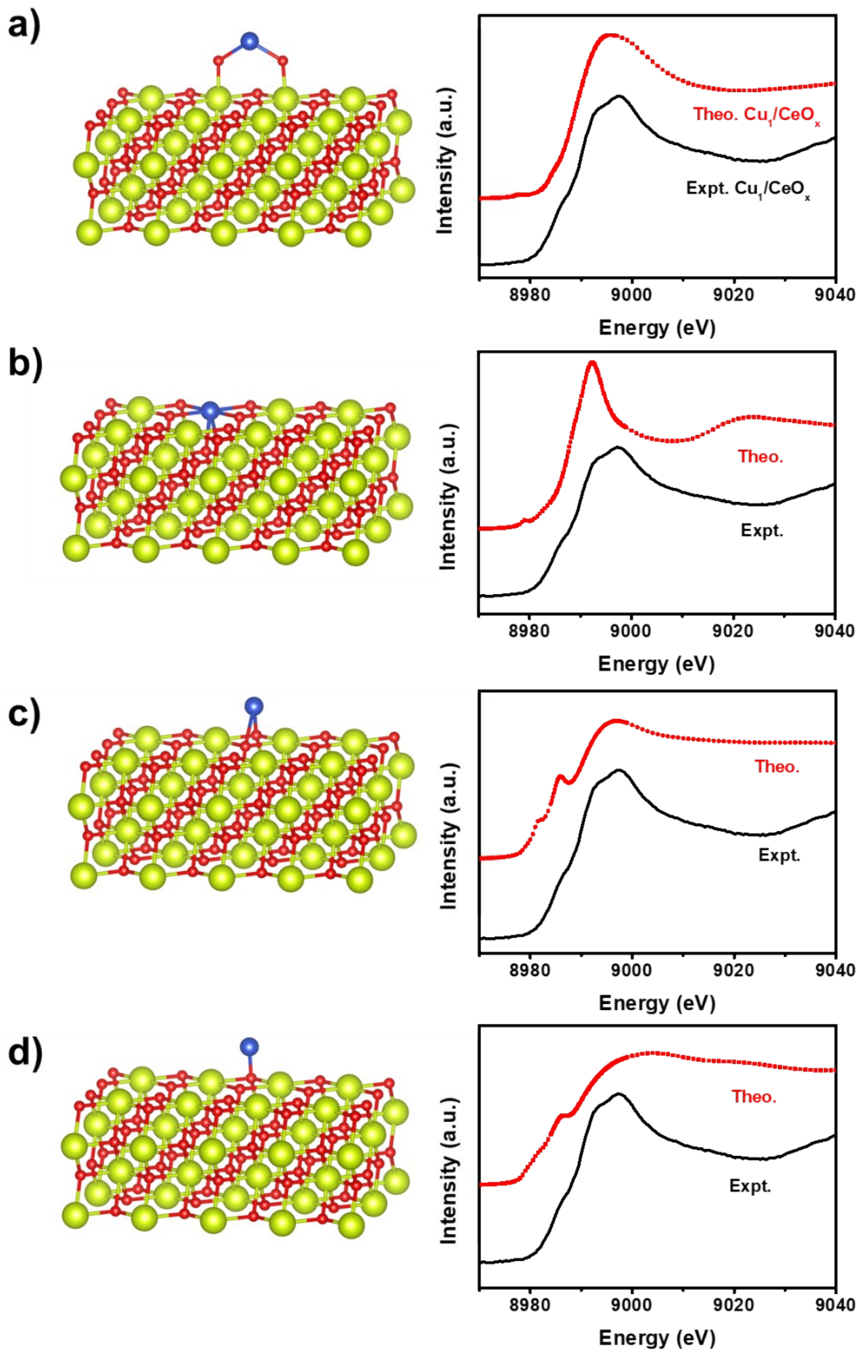


Figure S8. Comparison between the experimental Cu K-edge XANES spectra of Cu_1/CeO_x and the theoretical spectra of four different structures. The red, yellow and blue balls refer to O, Ce, and Cu atoms, respectively.

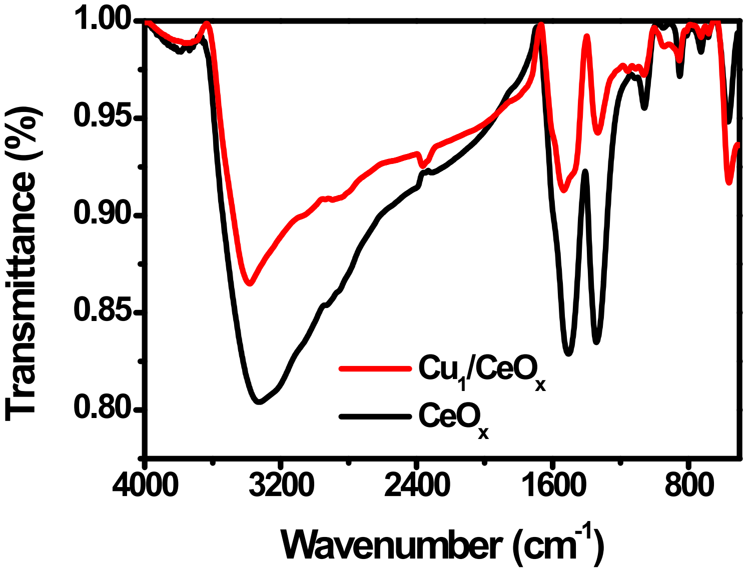


Figure S9. Infrared spectrum of CeO$_x$ and Cu$_1$/CeO$_x$ samples.

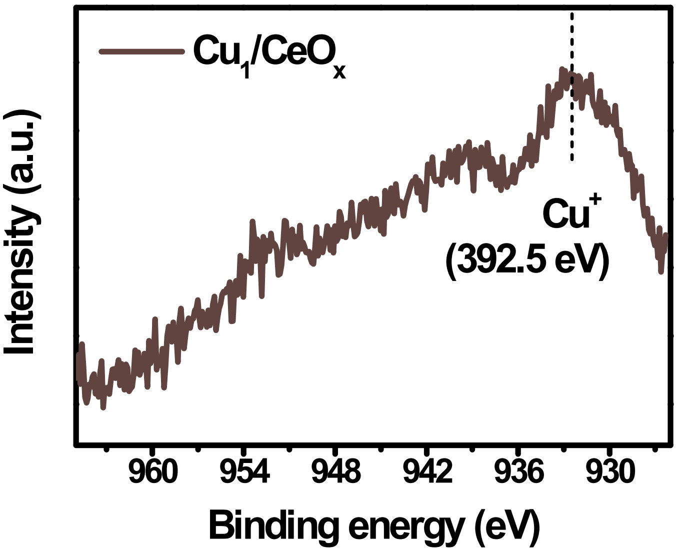


Figure S10. High-resolution spectra of Cu 2p in Cu_1/CeO_x sample.

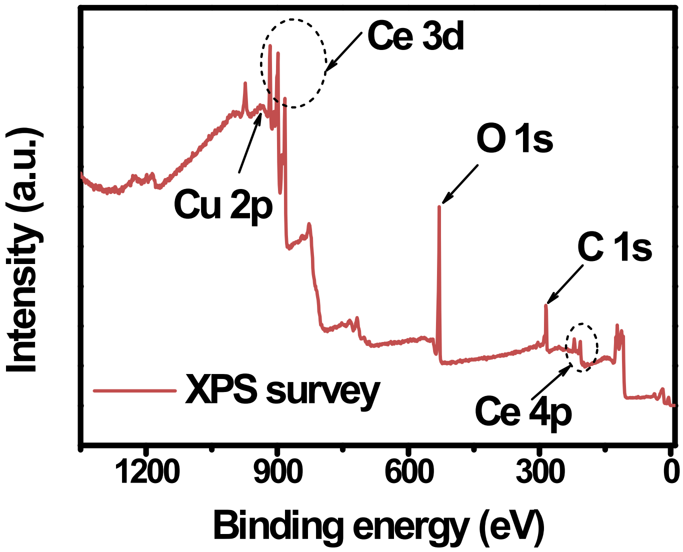


Figure S11. XPS spectra of Cu_1/CeO_x sample.

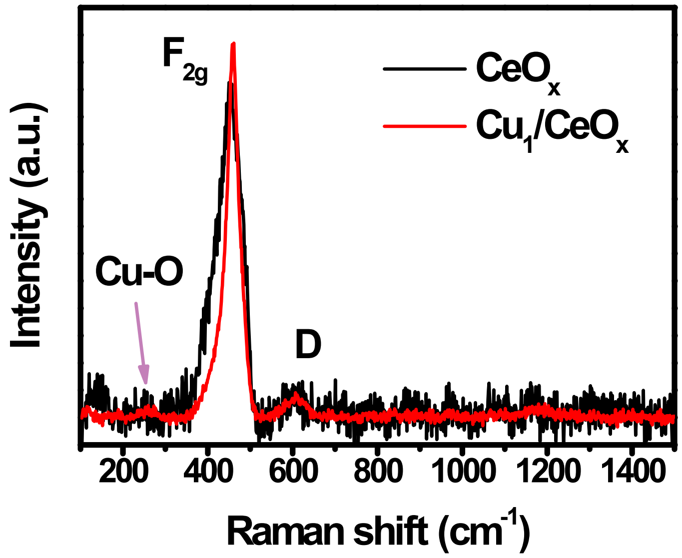
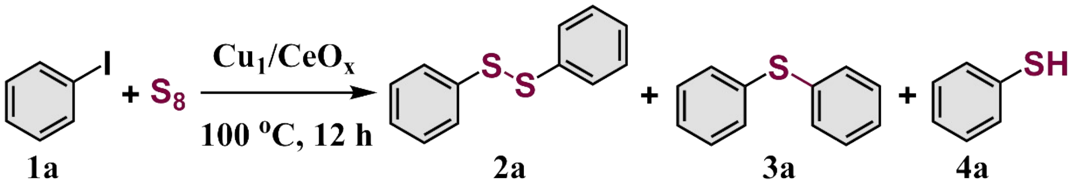


Figure S12. Raman spectra (lex = 532 nm) of CeO_x and Cu_1/CeO_x samples.

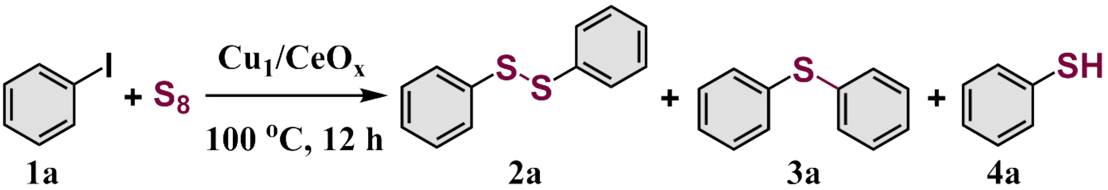
Table S3. The solvents optimization for dithiolation reaction of Iodobenzene.[a]



Entry	Solvent	Con. (%)	Sel. (%)		
			2a	3a	4a
1	MeCN	-	-	-	-
2	Toluene	-	-	-	-
3	NMP	-	-	-	-
4	DMAc	24.5	11.1	50.3	38.6
5	HMPA	-	-	-	-
6	n-butanol	-	-	-	-
7	DMF	68.8	85.4	0	14.6
9	DMF + 0.02 mL H_2O	81.2	90.7	0	9.3
10	DMF + 0.067 mL H_2O	82.6	97.4	2.1	0.52
11	DMF + 0.2 mL H_2O	81.5	90.0	0	10.0
12	DMF + 0.67 mL H_2O	41.6	93.7	0	3.3
13	DMF + 2 mL H_2O	-	-	-	-

[a] Reaction conditions: iodobenzene (0.5 mmol), S_8 (24 mg), NaOH (80 mg), Cu_1/CeO_x (20 mg), in Ar for 12 h.

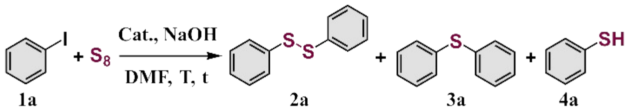
Table S4. The bases optimization for dithiolation reaction of Iodobenzene.[a]



Entry	Base	Con. (%)	Sel. (%)		
			2a	**3a**	**4a**
1	NaOH	82.6	97.4		
2	KOH	83.3	95.7	2.1	2.2
3	CsOH	66.1	86.9	0	13.1
4	t-BuOK	10.4	67.3	9.8	22.9
5	K_2CO_3	57.2	90.3	0.8	8.9
6	Na_2CO_3	46.8	86.1	0.9	13.0
7	Cs_2CO_3	12.4	78.9	0	21.1
8	$NaHCO_3$	51.3	92.0	0	8.0
9	$KHCO_3$	65.1	91.3	0.3	8.4
10	Pyrrolidine	-	-	-	-
11	Et_3N	-	-	-	-
12	DABCO	35.9	83.4	0	16.6
13	DBU	60.7	66.7	0	33.3

[a] Reaction conditions: iodobenzene (0.5 mmol), S_8 (24 mg), Cu_1/CeO_x (20 mg), DMF (2 mL) and H_2O (67 uL) as solvent, in Ar for 12 h.

Table S5. Catalyst Comparisons



Entry [a]	Cat.	T (°C)	t (h)	Con. (%)[b]	Sel. (%)[b]		
					2a	3a	4a
1	Cu_1/CeO_x	80	12	28.9	92.6	0	7.4
2	Cu_1/CeO_x	90	12	50.2	88.6	0	11.4
3	Cu_1/CeO_x	100	12	82.6	97.4	2.1	0.5
4	Cu_1/CeO_x	110	12	97.7	88.3	0.5	11.2
5	Cu_1/CeO_x	120	12	99.7	87.3	2.3	10.4
6	Cu_1/CeO_x	130	12	97.7	84.6	5.4	10.0
7	Cu_1/CeO_x	110	14	97.8	87.1	0.8	12.1
8	Cu_1/CeO_x	110	8	89.6	95.2	1.1	3.7
9	Cu_1/CeO_x	110	10	97.1	94.8	1.1	4.1
10	$CuCl_2$	110	10	43.8	79.3	17.8	2.9
11	CuCl	110	10	50.4	85.8	13.7	0.5
12	CuO	110	10	28.6	73.4	0	26.6
13	Cu_2O	110	10	58.0	89.6	5.2	5.2
14	$CuCl_2$	110	8	14.3	85.4	14.6	0
15	CuCl	110	8	35.2	86.2	13.8	0
16	CuO	110	8	5.41	91.7	8.3	0
17	Cu_2O	110	8	36.2	69.5	18.34	12.2
18	$Cu_{1+x}(1\%)/CeO_x$	110	10	14.5	58.5	37.9	3.6
19[c]	$Cu_{1+x}(1\%)/CeO_x$	110	10	27.3	61.6	38.4	0
20	$Cu_{1+x}(2\%)/CeO_x$	110	10	18.5	70.3	29.7	0
21[d]	$Cu_{1+x}(2\%)/CeO_x$	110	10	39.6	43.8	56.5	0
22[e]	$CuCl_2$	110	10	51.7	85.8	14.2	0

[a] Reaction Conditions: Iodobenzene (0.5 mmol), S_8 (0.75 mmol), catalyst (0.4 mol% based on Cu to iodobenzene), NaOH (2.0 mmol), DMF (2 mL) and H_2O (67 uL), Ar. [b] conversion and selectivity are determined by GC and GC-MS. [c] 20 mg catalysts was used. [d] 20 mg catalysts were used. [e] 1.2 mol% based on Cu to iodobenzene.

Table S6. Recycled for the catalyst. ICP-OES shows that 0.638% Cu species in recycled Cu_1/CeO_x catalysts.

Recycled times[a]	**Con. (%)**[b]	**Sel. (%)**[b]		
		2a	**3a**	**4a**
1	96.6	99.3	0.7	0
2	94.6	98.7	1.3	0
3	93.6	97.8	1.4	0.8
4	93.5	98.2	0.6	1.2

[a] Reaction Conditions: Iodobenzene (0.5 mmol), S_8 (0.75 mmol), Cu_1/CeO_x (1.2% mol based on Cu to iodobenzene), NaOH (2.0 mmol), DMF (2 mL) and H_2O (67 μL), Ar. [b] conversion and selectivity are determined by GC and GC-MS.

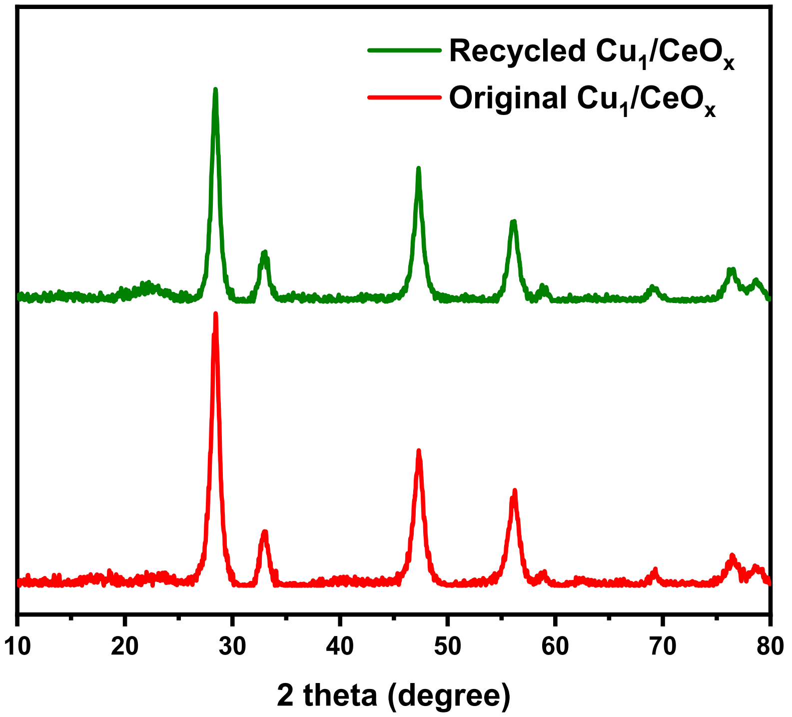


Figure S13. The XRD comparison between original Cu_1/CeO_x and recycled Cu_1/CeO_x catalysts.

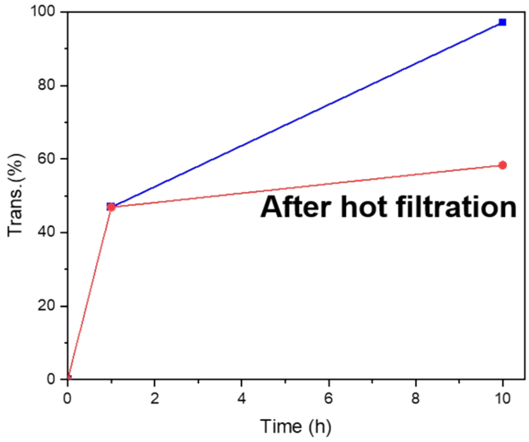


Figure S14. Hot filtration reaction. ICP-OES shows that just 0.0022% Cu species in reaction tube.

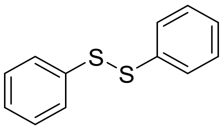
NMR data for compound 2

General information

^{1}H NMR, ^{13}C NMR and ^{19}F NMR spectra were recorded on a BRUKER AVANCE-400 in $CDCl_3$ with TMS as an internal standard at room temperature. All diaryl disulfide are known compounds, and analytical data are consistent with literature values[2-14].

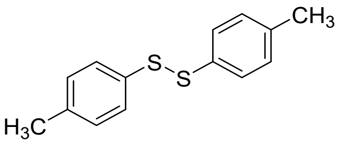
Procedure and NMR data for 2a-2z

1,2-diphenyldisulfane (2a)[4,6]



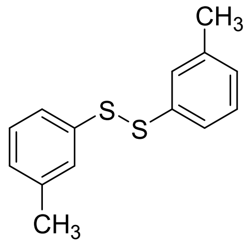
A 10 mL Schlenk tube was charged with iodobenzene (102.0 mg, 0.5 mmol), 0.75 mmol elemental sulfur (24.0 mg, 1.5 equiv., 0.75 mmol), NaOH (80.0 mg, 4.0 equiv., 2 mmol) and Cu_1/CeO_x catalyst (20 mg, 0.434 mol%, 2.17 x 10^{-3} mmol) and 2 mL DMF under nitrogen atmosphere. After stirring the result mixture under specific temperature and time, the catalyst was removed through centrifugation. Then the mixture was cooled and then poured into 5 mL saturated NH_4Cl solution, extracted with ethyl acetate (3 x 10 mL), and washed with water (3 x 10 mL). The combined organic layers were dried over anhydrous Na_2SO_4. The residue was purified by flash column chromatography on silica gel use petroleum ether to afford the desired product **2a** as White solid (87% yield, 47.4 mg); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.57-7.50 (m, 4H), 7.38-7.29 (m, 4H), 7.29-7.22 (m, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 137.1, 129.1, 127.5, 127.2.

1,2-di-*p*-tolyldisulfane (2b)[3]



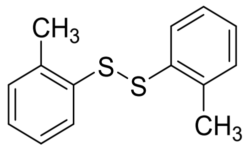
A 10 mL Schlenk tube was charged with 1-iodo-4-methylbenzene (108.9 mg, 0.5 mmol), 0.75 mmol elemental sulfur (24.0 mg, 1.5 equiv., 0.75 mmol), NaOH (80.0 mg, 4.0 equiv., 2 mmol) and Cu_1/CeO_x catalyst (20 mg, 0.434 mol%, 2.17 x 10^{-3} mmol) and 2 mL DMF under nitrogen atmosphere. After stirring the result mixture under specific temperature and time, the catalyst was removed through centrifugation. Then the mixture was cooled and then poured into 5 mL saturated NH_4Cl solution, extracted with ethyl acetate (3 x 10 mL), and washed with water (3 x 10 mL). The combined organic layers were dried over anhydrous Na_2SO_4. The residue was purified by flash column chromatography on silica gel use petroleum ether to afford the desired product **2b** as white solid (93% yield, 57.2 mg); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.54-7.37 (m, 4H), 7.27-7.07 (m, 4H), 2.35 (s, 6H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 137.5, 134.0, 129.9, 128.6, 21.1.

1,2-di-m-tolyldisulfane (2c)[8]



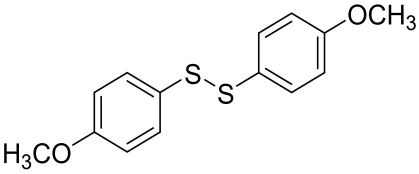
A 10 mL Schlenk tube was charged with 1-iodo-3-methylbenzene (108.9 mg, 0.5 mmol), 0.75 mmol elemental sulfur (24.0 mg, 1.5 equiv., 0.75 mmol), NaOH (80.0 mg, 4.0 equiv., 2 mmol) and Cu_1/CeO_x catalyst (20 mg, 0.434 mol%, 2.17 x 10^{-3} mmol) and 2 mL DMF under nitrogen atmosphere. After stirring the result mixture under specific temperature and time, the catalyst was removed through centrifugation. Then the mixture was cooled and then poured into 5 mL saturated NH_4Cl solution, extracted with ethyl acetate (3 x 10 mL), and washed with water (3 x 10 mL). The combined organic layers were dried over anhydrous Na_2SO_4. The residue was purified by flash column chromatography on silica gel use petroleum ether to afford the desired product **2c** as yellow solid (84% yield, 51.7 mg); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.35-7.29 (m, 4H), 7.24-7.17 (m, 2H), 7.09-7.00 (m, 2H), 2.33 (s, 6H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 139.0, 136.9, 128.9, 128.1, 128.0, 124.6, 21.4.

1,2-di-o-tolyldisulfane (2d)[8]



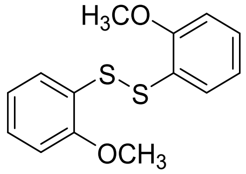
A 10 mL Schlenk tube was charged with 1-iodo-2-methylbenzene (108.9 mg, 0.5 mmol), 0.75 mmol elemental sulfur (24.0 mg, 1.5 equiv., 0.75 mmol), NaOH (80.0 mg, 4.0 equiv., 2 mmol) and Cu_1/CeO_x catalyst (20 mg, 0.434 mol%, 2.17 x 10^{-3} mmol) and 2 mL DMF under nitrogen atmosphere. After stirring the result mixture under specific temperature and time, the catalyst was removed through centrifugation. Then the mixture was cooled and then poured into 5 mL saturated NH_4Cl solution, extracted with ethyl acetate (3 x 10 mL), and washed with water (3 x 10 mL). The combined organic layers were dried over anhydrous Na_2SO_4. The residue was purified by flash column chromatography on silica gel use petroleum ether to afford the desired product **2d** as yellow solid (81% yield, 49.8 mg); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.60-7.44 (m, 2H), 7.23-7.07 (m, 6H), 2.44 (s, 6H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 137.4, 135.4, 130.4, 128.6, 127.3, 126.7, 20.0.

1,2-bis(4-methoxyphenyl)disulfane (2e)[3,5]



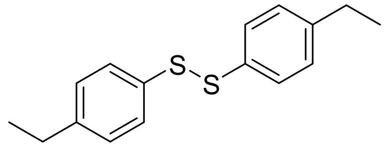
A 10 mL Schlenk tube was charged with 1-iodo-4-methoxybenzene (117.0 mg, 0.5 mmol), 0.75 mmol elemental sulfur (24.0 mg, 1.5 equiv., 0.75 mmol), NaOH (80.0 mg, 4.0 equiv., 2 mmol) and Cu_1/CeO_x catalyst (20 mg, 0.434 mol%, 2.17 x 10^{-3} mmol) and 2 mL DMF under nitrogen atmosphere. After stirring the result mixture under specific temperature and time, the catalyst was removed through centrifugation. Then the mixture was cooled and then poured into 5 mL saturated NH_4Cl solution, extracted with ethyl acetate (3 x 10 mL), and washed with water (3 x 10 mL). The combined organic layers were dried over anhydrous Na_2SO_4. The residue was purified by flash column chromatography on silica gel use petroleum ether to afford the desired product **2e** as yellow oil (85% yield, 59.1 mg); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.42-7.38 (m, 4H), 6.88-6.81 (m, 4H), 3.80 (s, 6H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 159.9, 132.7, 128.5, 114.6, 55.4.

1,2-bis(2-methoxyphenyl)disulfane (2f)[3]



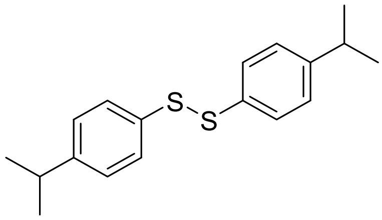
A 10 mL Schlenk tube was charged with 1-iodo-2-methoxybenzene (117.0 mg, 0.5 mmol), 0.75 mmol elemental sulfur (24.0 mg, 1.5 equiv., 0.75 mmol), NaOH (80.0 mg, 4.0 equiv., 2 mmol) and Cu_1/CeO_x catalyst (20 mg, 0.434 mol%, 2.17 x 10^{-3} mmol) and 2 mL DMF under nitrogen atmosphere. After stirring the result mixture under specific temperature and time, the catalyst was removed through centrifugation. Then the mixture was cooled and then poured into 5 mL saturated NH_4Cl solution, extracted with ethyl acetate (3 x 10 mL), and washed with water (3 x 10 mL). The combined organic layers were dried over anhydrous Na_2SO_4. The residue was purified by flash column chromatography on silica gel use petroleum ether to afford the desired product **2f** as colorless Oil (78% yield, 54.2 mg); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.55-7.50 (m, 2H), 7.24-7.15 (m, 2H), 6.98-6.82 (m, 4H), 3.90 (s, 6H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 156.6, 127.8, 127.6, 124.6, 121.4, 110.5, 55.9.

1,2-bis(4-ethylphenyl)disulfane (2g)[9]



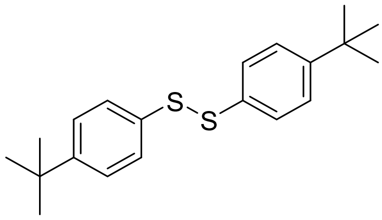
A 10 mL Schlenk tube was charged with 1-ethyl-4-iodobenzene (116.0 mg, 0.5 mmol), 0.75 mmol elemental sulfur (24.0 mg, 1.5 equiv., 0.75 mmol), NaOH (80.0 mg, 4.0 equiv., 2 mmol) and Cu_1/CeO_x catalyst (20 mg, 0.434 mol%, 2.17 x 10^{-3} mmol) and 2 mL DMF under nitrogen atmosphere. After stirring the result mixture under specific temperature and time, the catalyst was removed through centrifugation. Then the mixture was cooled and then poured into 5 mL saturated NH_4Cl solution, extracted with ethyl acetate (3 x 10 mL), and washed with water (3 x 10 mL). The combined organic layers were dried over anhydrous Na_2SO_4. The residue was purified by flash column chromatography on silica gel use petroleum ether to afford the desired product **2g** as colorless oil (79% yield, 54.1 mg); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.47-7.40 (m, 4H), 7.18-7.11 (m, 4H), 2.63 (q, *J* = 7.6 Hz, 4H), 1.22 (t, *J* = 7.6 Hz, 6H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 143.8, 134.2, 128.7, 128.4, 28.5, 15.5.

1,2-bis(4-isopropylphenyl)disulfane (2h)[7]



A 10 mL Schlenk tube was charged with 1-iodo-4-isopropylbenzene (123.0 mg, 0.5 mmol), 0.75 mmol elemental sulfur (24.0 mg, 1.5 equiv., 0.75 mmol), NaOH (80.0 mg, 4.0 equiv., 2 mmol) and Cu_1/CeO_x catalyst (20 mg, 0.434 mol%, 2.17 x 10^{-3} mmol) and 2 mL DMF under nitrogen atmosphere. After stirring the result mixture under specific temperature and time, the catalyst was removed through centrifugation. Then the mixture was cooled and then poured into 5 mL saturated NH_4Cl solution, extracted with ethyl acetate (3 x 10 mL), and washed with water (3 x 10 mL). The combined organic layers were dried over anhydrous Na_2SO_4. The residue was purified by flash column chromatography on silica gel use petroleum ether to afford the desired product **2h** as yellow oil (85% yield, 64.2 mg); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.49-7.42 (m, 4H), 7.24-7.13 (m, 4H), 2.94-2.85 (m, 2H), 1.24 (d, *J* = 6.9 Hz, 12H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 148.3, 131.1, 128.2, 127.3, 33.8, 23.9.

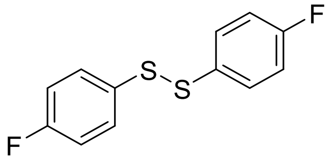
1,2-bis(4-(*tert*-butyl)phenyl)disulfane (2i)[5]



A 10 mL Schlenk tube was charged with 1-(*tert*-butyl)-4-iodobenzene (130.0 mg, 0.5 mmol), 0.75 mmol elemental sulfur (24.0 mg, 1.5 equiv., 0.75 mmol), NaOH (80.0 mg, 4.0 equiv., 2 mmol) and Cu_1/CeO_x catalyst (20 mg, 0.434 mol%, 2.17 x 10^{-3} mmol) and

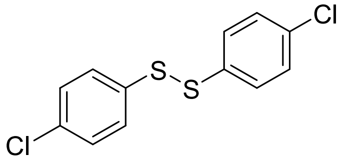
2 mL DMF under nitrogen atmosphere. After stirring the result mixture under specific temperature and time, the catalyst was removed through centrifugation. Then the mixture was cooled and then poured into 5 mL saturated NH_4Cl solution, extracted with ethyl acetate (3 x 10 mL), and washed with water (3 x 10 mL). The combined organic layers were dried over anhydrous Na_2SO_4. The residue was purified by flash column chromatography on silica gel use petroleum ether to afford the desired product **2i** as white solid (66% yield, 54.5 mg); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.44 (d, *J* = 8.5 Hz, 4H), 7.33 (d, *J* = 8.5 Hz, 4H), 1.29 (s, 18H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 150.5, 134.0, 127.8, 126.2, 34.6, 31.3.

1,2-bis(4-fluorophenyl)disulfane (2j)[3,4,5]



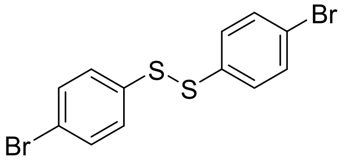
A 10 mL Schlenk tube was charged with 1-fluoro-4-iodobenzene (111.0 mg, 0.5 mmol), 0.75 mmol elemental sulfur (24.0 mg, 1.5 equiv., 0.75 mmol), NaOH (80.0 mg, 4.0 equiv., 2 mmol) and Cu_1/CeO_x catalyst (20 mg, 0.434 mol%, 2.17 x 10^{-3} mmol) and 2 mL DMF under nitrogen atmosphere. After stirring the result mixture under specific temperature and time, the catalyst was removed through centrifugation. Then the mixture was cooled and then poured into 5 mL saturated NH_4Cl solution, extracted with ethyl acetate (3 x 10 mL), and washed with water (3 x 10 mL). The combined organic layers were dried over anhydrous Na_2SO_4. The residue was purified by flash column chromatography on silica gel use petroleum ether to afford the desired product **2j** as white solid (81% yield, 51.4 mg); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.61-7.41 (m, 4H), 7.12-6.85 (m, 4H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 162.6 (d, *J* = 248.0 Hz), 132.2 (d, *J* = 3.0 Hz), 131.3 (d, *J* = 8.1 Hz), 116.3 (d, *J* = 21.9 Hz). ^{19}F NMR (377 MHz, Chloroform-*d*) δ -113.6.

1,2-bis(4-chlorophenyl)disulfane (2k)[3,6]



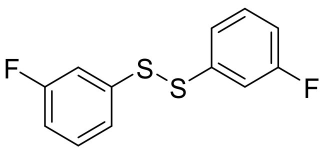
A 10 mL Schlenk tube was charged with 1-chloro-4-iodobenzene (119.0 mg, 0.5 mmol), 0.75 mmol elemental sulfur (24.0 mg, 1.5 equiv., 0.75 mmol), NaOH (80.0 mg, 4.0 equiv., 2 mmol) and Cu_1/CeO_x catalyst (20 mg, 0.434 mol%, 2.17 x 10^{-3} mmol) and 2 mL DMF under nitrogen atmosphere. After stirring the result mixture under specific temperature and time, the catalyst was removed through centrifugation. Then the mixture was cooled and then poured into 5 mL saturated NH_4Cl solution, extracted with ethyl acetate (3 x 10 mL), and washed with water (3 x 10 mL). The combined organic layers were dried over anhydrous Na_2SO_4. The residue was purified by flash column chromatography on silica gel use petroleum ether to afford the desired product **2k** as white solid (72% yield, 51.5 mg); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.44-7.38 (m, 4H), 7.32-7.25 (m, 4H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 135.2, 133.7, 129.5, 129.4.

1,2-bis(4-bromophenyl)disulfane (2l)[2,4,6]



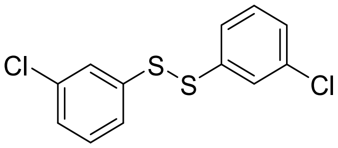
A 10 mL Schlenk tube was charged with 1-bromo-4-iodobenzene (140.9 mg, 0.5 mmol), 0.75 mmol elemental sulfur (24.0 mg, 1.5 equiv., 0.75 mmol), NaOH (80.0 mg, 4.0 equiv., 2 mmol) and Cu_1/CeO_x catalyst (20 mg, 0.434 mol%, 2.17 x 10^{-3} mmol) and 2 mL DMF under nitrogen atmosphere. After stirring the result mixture under specific temperature and time, the catalyst was removed through centrifugation. Then the mixture was cooled and then poured into 5 mL saturated NH_4Cl solution, extracted with ethyl acetate (3 x 10 mL), and washed with water (3 x 10 mL). The combined organic layers were dried over anhydrous Na_2SO_4. The residue was purified by flash column chromatography on silica gel use petroleum ether to afford the desired product **2l** as yellow solid (66% yield, 61.7 mg); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.44– 7.42 (m, 4H), 7.35 – 7.32 (m, 4H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 135.8, 132.2, 129.4, 121.6.

1,2-bis(3-fluorophenyl)disulfane (2m)[10]



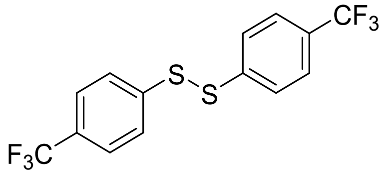
A 10 mL Schlenk tube was charged with 1-fluoro-3-iodobenzene (111.0 mg, 0.5 mmol), 0.75 mmol elemental sulfur (24.0 mg, 1.5 equiv., 0.75 mmol), NaOH (80.0 mg, 4.0 equiv., 2 mmol) and Cu_1/CeO_x catalyst (20 mg, 0.434 mol%, 2.17 x 10^{-3} mmol) and 2 mL DMF under nitrogen atmosphere. After stirring the result mixture under specific temperature and time, the catalyst was removed through centrifugation. Then the mixture was cooled and then poured into 5 mL saturated NH_4Cl solution, extracted with ethyl acetate (3 x 10 mL), and washed with water (3 x 10 mL). The combined organic layers were dried over anhydrous Na_2SO_4. The residue was purified by flash column chromatography on silica gel use petroleum ether to afford the desired product **2m** as colorless oil (67% yield, 42.5 mg); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.43-7.12 (m, 3H), 7.02-6.83 (m, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 163.1 (d, *J* = 249.2 Hz), 130.5 (d, *J* = 8.2 Hz), 122.7 (d, *J* = 2.9 Hz), 117.0 (d, *J* = 23.4 Hz), 114.4 (d, *J* = 21.6 Hz), 114.0 (d, *J* = 24.1 Hz). ^{19}F NMR (377 MHz, Chloroform-*d*) δ -111.2.

1,2-bis(3-chlorophenyl)disulfane (2n)[3]



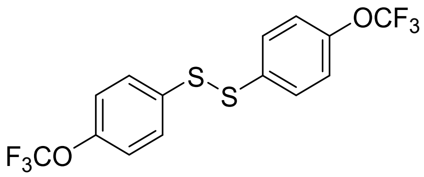
A 10 mL Schlenk tube was charged with 1-chloro-3-iodobenzene (119.0 mg, 0.5 mmol), 0.75 mmol elemental sulfur (24.0 mg, 1.5 equiv., 0.75 mmol), NaOH (80.0 mg, 4.0 equiv., 2 mmol) and Cu_1/CeO_x catalyst (20 mg, 0.434 mol%, 2.17 x 10^{-3} mmol) and 2 mL DMF under nitrogen atmosphere. After stirring the result mixture under specific temperature and time, the catalyst was removed through centrifugation. Then the mixture was cooled and then poured into 5 mL saturated NH_4Cl solution, extracted with ethyl acetate (3 x 10 mL), and washed with water (3 x 10 mL). The combined organic layers were dried over anhydrous Na_2SO_4. The residue was purified by flash column chromatography on silica gel use petroleum ether to afford the desired product **2n** as colorless oil (62% yield, 44.3 mg); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.53 -7.49 (m, 2H), 7.41-7.33 (m, 2H), 7.32-7.21 (m, 4H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 138.4, 135.2, 130.3, 127.6, 127.0, 125.4.

1,2-bis(4-(trifluoromethyl)phenyl)disulfane (2o)[3]



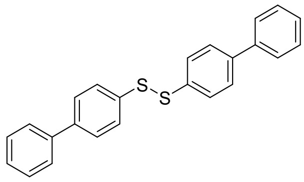
A 10 mL Schlenk tube was charged with 1-iodo-4-(trifluoromethyl)benzene (136.0 mg, 0.5 mmol), 0.75 mmol elemental sulfur (24.0 mg, 1.5 equiv., 0.75 mmol), NaOH (80.0 mg, 4.0 equiv., 2 mmol) and Cu_1/CeO_x catalyst (20 mg, 0.434 mol%, 2.17 x 10^{-3} mmol) and 2 mL DMF under nitrogen atmosphere. After stirring the result mixture under specific temperature and time, the catalyst was removed through centrifugation. Then the mixture was cooled and then poured into 5 mL saturated NH_4Cl solution, extracted with ethyl acetate (3 x 10 mL), and washed with water (3 x 10 mL). The combined organic layers were dried over anhydrous Na_2SO_4. The residue was purified by flash column chromatography on silica gel use petroleum ether to afford the desired product **2o** as colorless oil (60% yield, 53.1 mg); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.58 (s, 8H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 140.8, 129.4 (q, *J* = 32.7 Hz), 126.6, 126.2 (q, *J* = 3.8 Hz), 123.9 (q, *J* = 272.3 Hz). ^{19}F NMR (377 MHz, Chloroform-*d*) δ -62.6.

1,2-bis(4-(trifluoromethoxy)phenyl)disulfane (2p)[5]



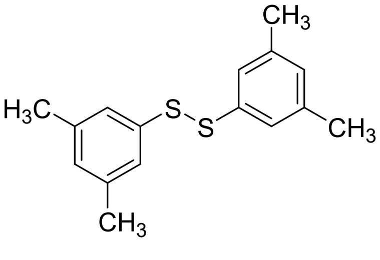
A 10 mL Schlenk tube was charged with 1-iodo-4-(trifluoromethoxy)benzene (144.0 mg, 0.5 mmol), 0.75 mmol elemental sulfur (24.0 mg, 1.5 equiv., 0.75 mmol), NaOH (80.0 mg, 4.0 equiv., 2 mmol) and Cu_1/CeO_x catalyst (20 mg, 0.434 mol%, 2.17 x 10^{-3} mmol) and 2 mL DMF under nitrogen atmosphere. After stirring the result mixture under specific temperature and time, the catalyst was removed through centrifugation. Then the mixture was cooled and then poured into 5 mL saturated NH_4Cl solution, extracted with ethyl acetate (3 x 10 mL), and washed with water (3 x 10 mL). The combined organic layers were dried over anhydrous Na_2SO_4. The residue was purified by flash column chromatography on silica gel use petroleum ether to afford the desired product **2p** as colorless oil (71% yield, 67.6 mg); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.54-7.51 (m, 4H), 7.20-7.18 (m, 4H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 148.7, 135.2, 129.3, 121.7, 120.5 (q, J = 257.7 Hz). ^{19}F NMR (376 MHz, Chloroform-*d*) δ -58.07.

1,2-di([1,1'-biphenyl]-4-yl)disulfane (2q)[11]



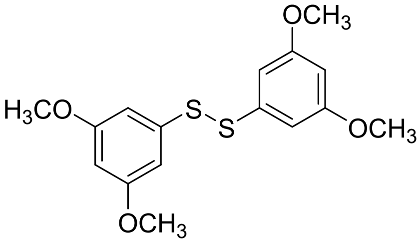
A 10 mL Schlenk tube was charged with 4-iodo-1,1'-biphenyl (140.0 mg, 0.5 mmol), 0.75 mmol elemental sulfur (24.0 mg, 1.5 equiv., 0.75 mmol), NaOH (80.0 mg, 4.0 equiv., 2 mmol) and Cu_1/CeO_x catalyst (20 mg, 0.434 mol%, 2.17 x 10^{-3} mmol) and 2 mL DMF under nitrogen atmosphere. After stirring the result mixture under specific temperature and time, the catalyst was removed through centrifugation. Then the mixture was cooled and then poured into 5 mL saturated NH_4Cl solution, extracted with ethyl acetate (3 x 10 mL), and washed with water (3 x 10 mL). The combined organic layers were dried over anhydrous Na_2SO_4. The residue was purified by flash column chromatography on silica gel use petroleum ether to afford the desired product **2q** as white solid (75% yield, 69.4 mg); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.67-7.55 (m, 12H), 7.51-7.42 (m, 4H), 7.41-7.33 (m, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 140.4, 140.2, 136.1, 128.9, 128.2, 127.8, 127.6, 127.0.

1,2-bis(3,5-dimethylphenyl)disulfane (2r)[5]



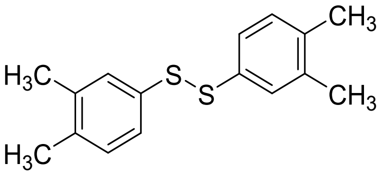
A 10 mL Schlenk tube was charged with 1-iodo-3,5-dimethylbenzene (116.0 mg, 0.5 mmol), 0.75 mmol elemental sulfur (24.0 mg, 1.5 equiv., 0.75 mmol), NaOH (80.0 mg, 4.0 equiv., 2 mmol) and Cu_1/CeO_x catalyst (20 mg, 0.434 mol%, 2.17 x 10^{-3} mmol) and 2 mL DMF under nitrogen atmosphere. After stirring the result mixture under specific temperature and time, the catalyst was removed through centrifugation. Then the mixture was cooled and then poured into 5 mL saturated NH_4Cl solution, extracted with ethyl acetate (3 x 10 mL), and washed with water (3 x 10 mL). The combined organic layers were dried over anhydrous Na_2SO_4. The residue was purified by flash column chromatography on silica gel use petroleum ether to afford the desired product **2r** as white solid (83% yield, 56.9 mg); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.11 (s, 4H), 6.85 (s, 2H), 2.28 (s, 12H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 138.8, 136.8, 129.0, 125.1, 21.3.

1,2-bis(3,5-dimethoxyphenyl)disulfane (2s)[12]



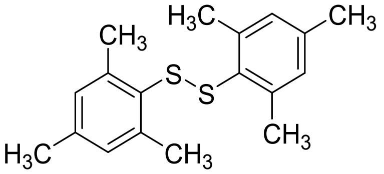
A 10 mL Schlenk tube was charged with 1-iodo-3,5-dimethoxybenzene (132.0 mg, 0.5 mmol), 0.75 mmol elemental sulfur (24.0 mg, 1.5 equiv., 0.75 mmol), NaOH (80.0 mg, 4.0 equiv., 2 mmol) and Cu_1/CeO_x catalyst (20 mg, 0.434 mol%, 2.17 x 10^{-3} mmol) and 2 mL DMF under nitrogen atmosphere. After stirring the result mixture under specific temperature and time, the catalyst was removed through centrifugation. Then the mixture was cooled and then poured into 5 mL saturated NH_4Cl solution, extracted with ethyl acetate (3 x 10 mL), and washed with water (3 x 10 mL). The combined organic layers were dried over anhydrous Na_2SO_4. The residue was purified by flash column chromatography on silica gel use petroleum ether to afford the desired product **2s** as colorless oil (77% yield, 65.1 mg); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 6.67 (s, 4H), 6.30 (s, 2H), 3.75 (s, 12H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 161.1, 139.0, 105.0, 99.7, 55.5.

1,2-bis(3,4-dimethylphenyl)disulfane (2t)[13]



A 10 mL Schlenk tube was charged with 1-iodo-3,5-dimethylbenzene (116.0 mg, 0.5 mmol), 0.75 mmol elemental sulfur (24.0 mg, 1.5 equiv., 0.75 mmol), NaOH (80.0 mg, 4.0 equiv., 2 mmol) and Cu_1/CeO_x catalyst (20 mg, 0.434 mol%, 2.17 x 10^{-3} mmol) and 2 mL DMF under nitrogen atmosphere. After stirring the result mixture under specific temperature and time, the catalyst was removed through centrifugation. Then the mixture was cooled and then poured into 5 mL saturated NH_4Cl solution, extracted with ethyl acetate (3 x 10 mL), and washed with water (3 x 10 mL). The combined organic layers were dried over anhydrous Na_2SO_4. The residue was purified by flash column chromatography on silica gel use petroleum ether to afford the desired product **2t** as yellow oil (72% yield, 49.3 mg); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.26-7.22 (m, 4H), 7.09-7.03 (m, 2H), 2.22 (s, 12H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 137.5, 136.1, 134.2, 130.3, 129.6, 126.0, 19.8, 19.4.

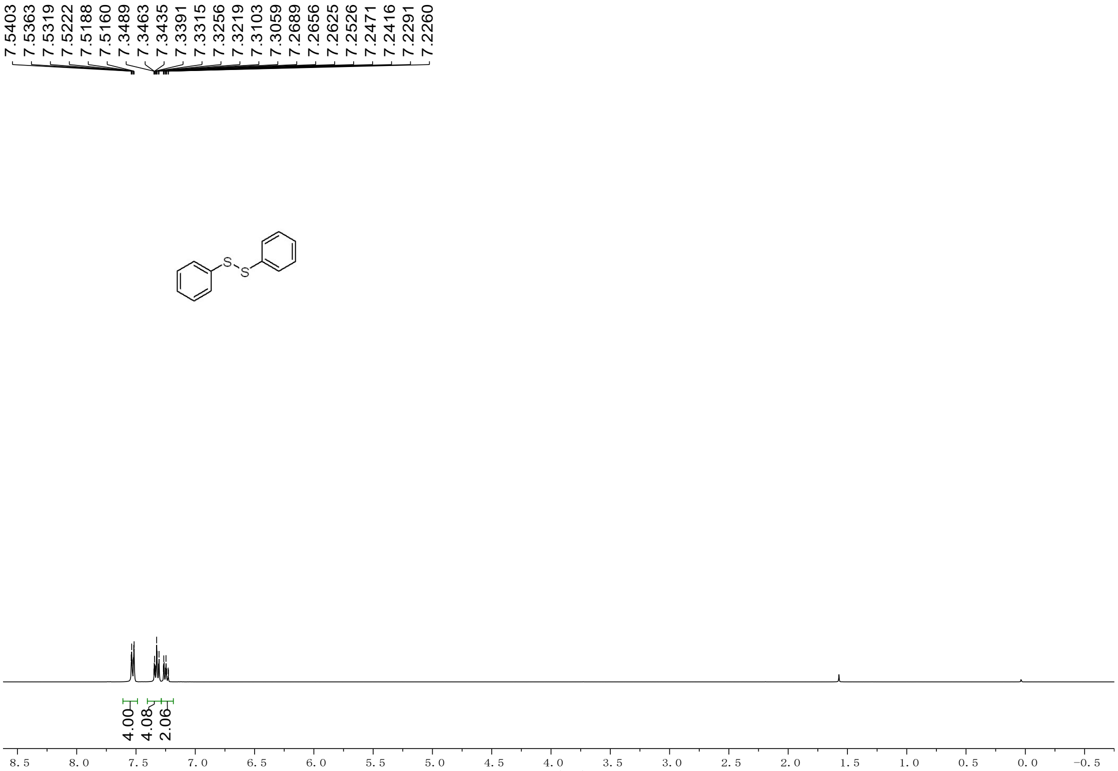
1,2-dimesityldisulfane (2u)[14]

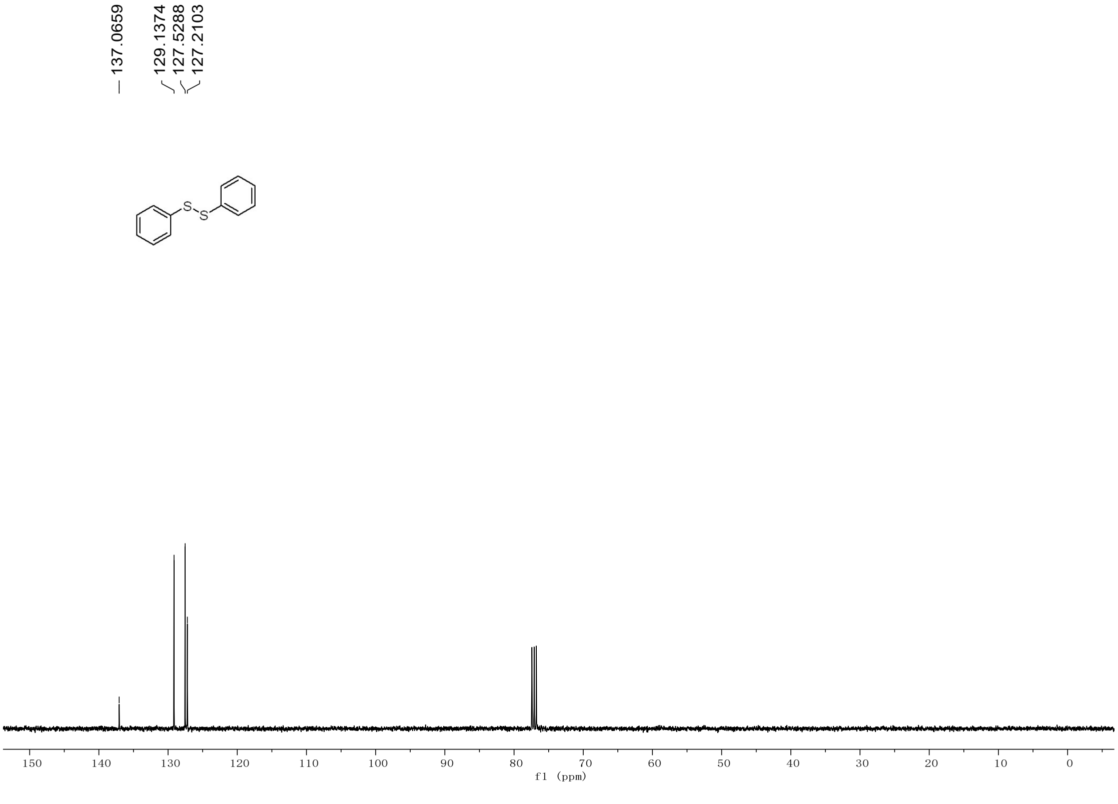


A 10 mL Schlenk tube was charged with 2-iodo-1,3,5-trimethylbenzene (123.0 mg, 0.5 mmol), 0.75 mmol elemental sulfur (24.0 mg, 1.5 equiv., 0.75 mmol), NaOH (80.0 mg, 4.0 equiv., 2 mmol) and Cu_1/CeO_x catalyst (20 mg, 0.434 mol%, 2.17 x 10^{-3} mmol) and 2 mL DMF under nitrogen atmosphere. After stirring the result mixture under specific temperature and time, the catalyst was removed through centrifugation. Then the mixture was cooled and then poured into 5 mL saturated NH_4Cl solution, extracted with ethyl acetate (3 x 10 mL), and washed with water (3 x 10 mL). The combined organic layers were dried over anhydrous Na_2SO_4. The residue was purified by flash column chromatography on silica gel use petroleum ether to afford the desired product **2u** as white solid (75% yield, 56.6 mg); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 6.83 (s, 4H), 2.25 (s, 6H), 2.20 (s, 12H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 143.3, 139.3, 131.6, 128.9, 21.4, 21.1.

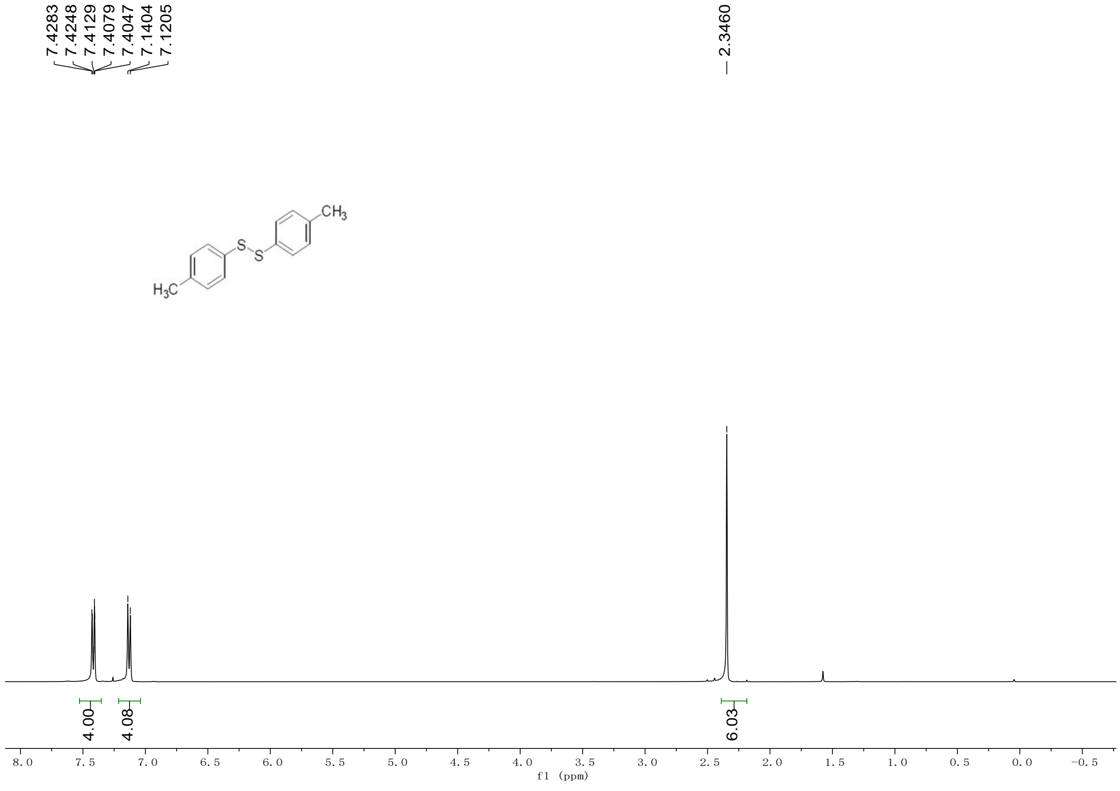
Copies of NMR spectra of compounds 2

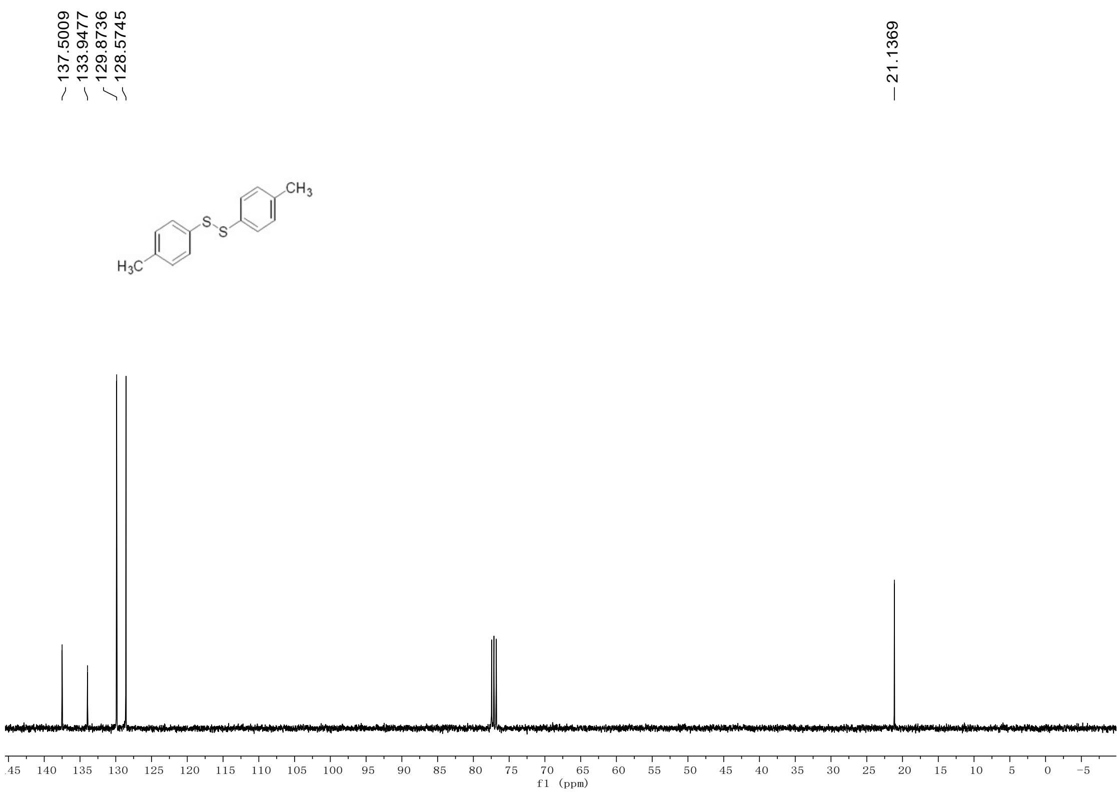
1,2-diphenyldisulfane (2a)



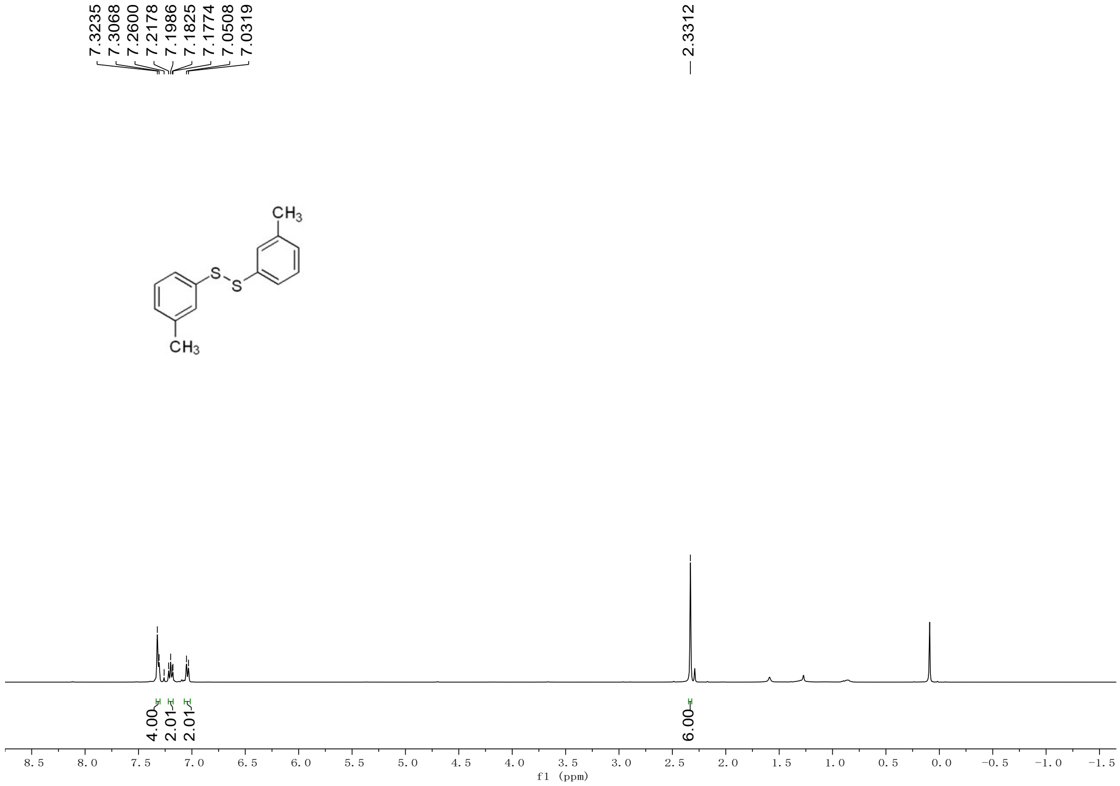


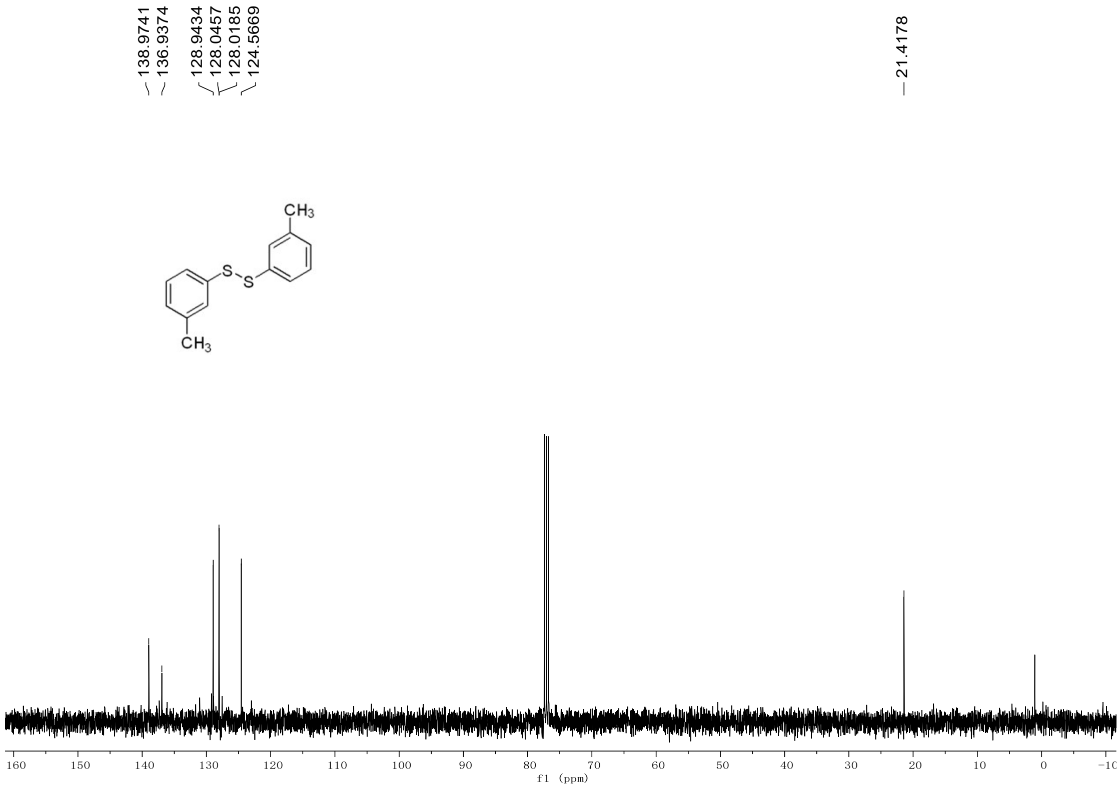
1,2-di-p-tolyldisulfane (2b)



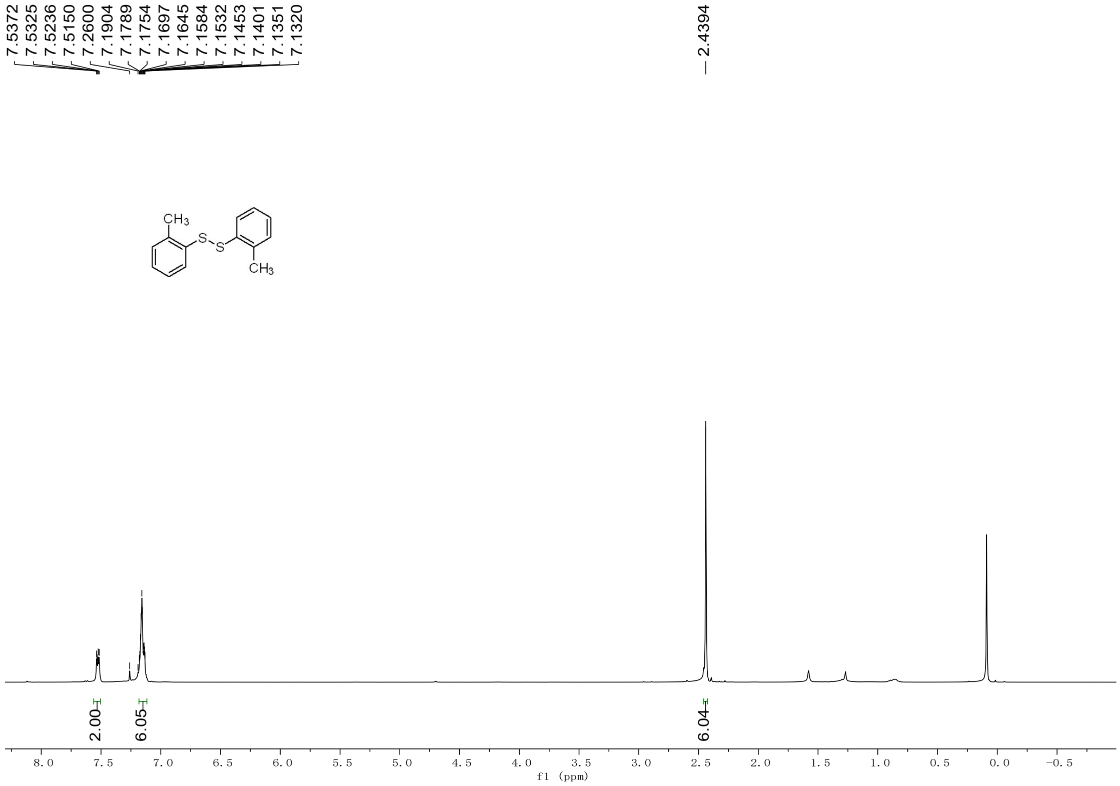


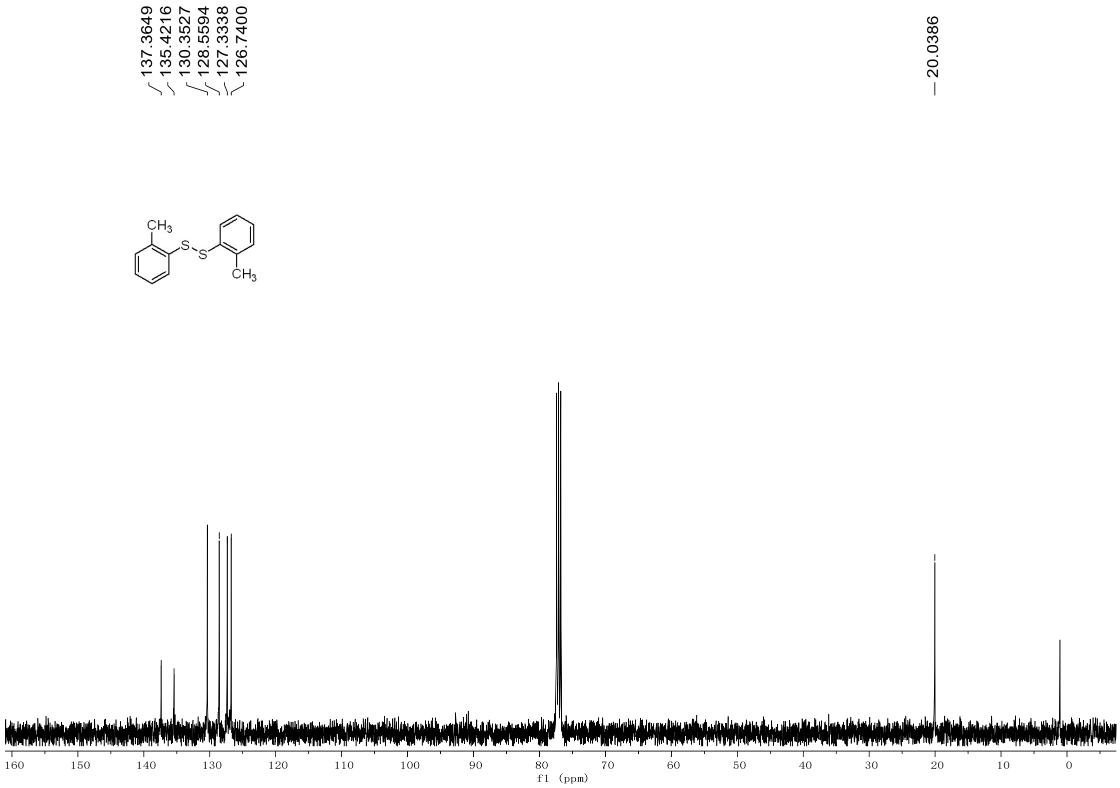
1,2-di-m-tolyldisulfane (2c)



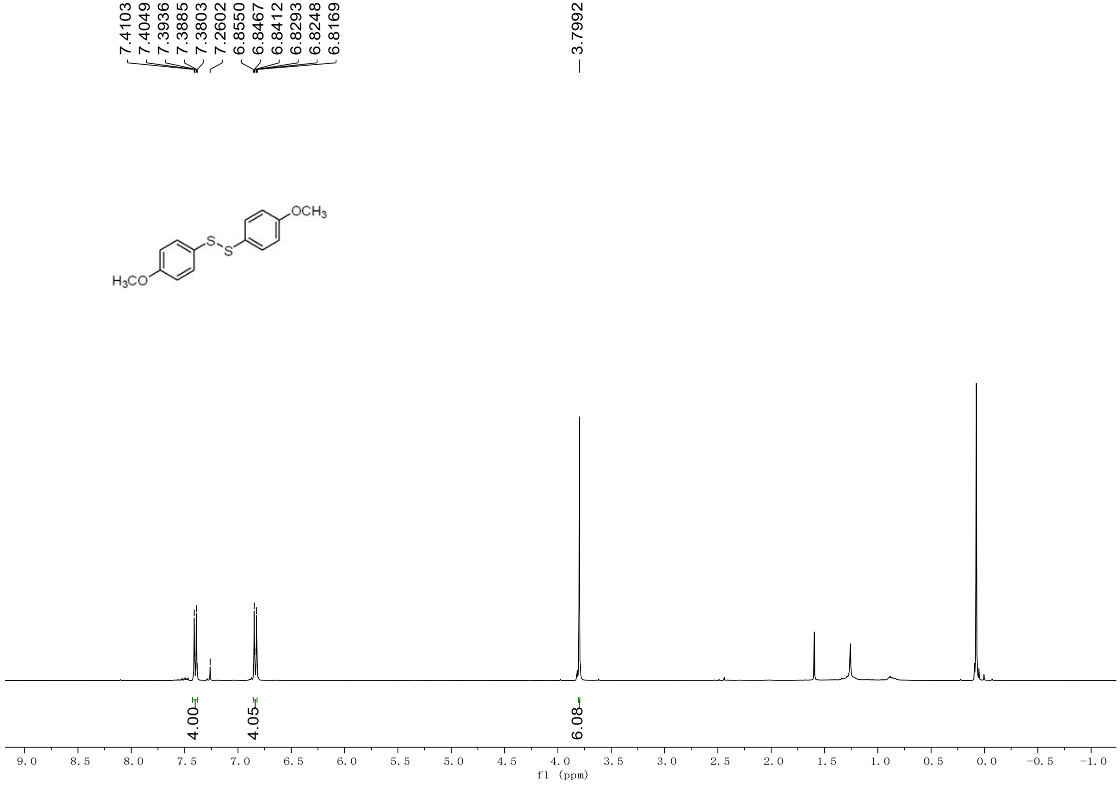


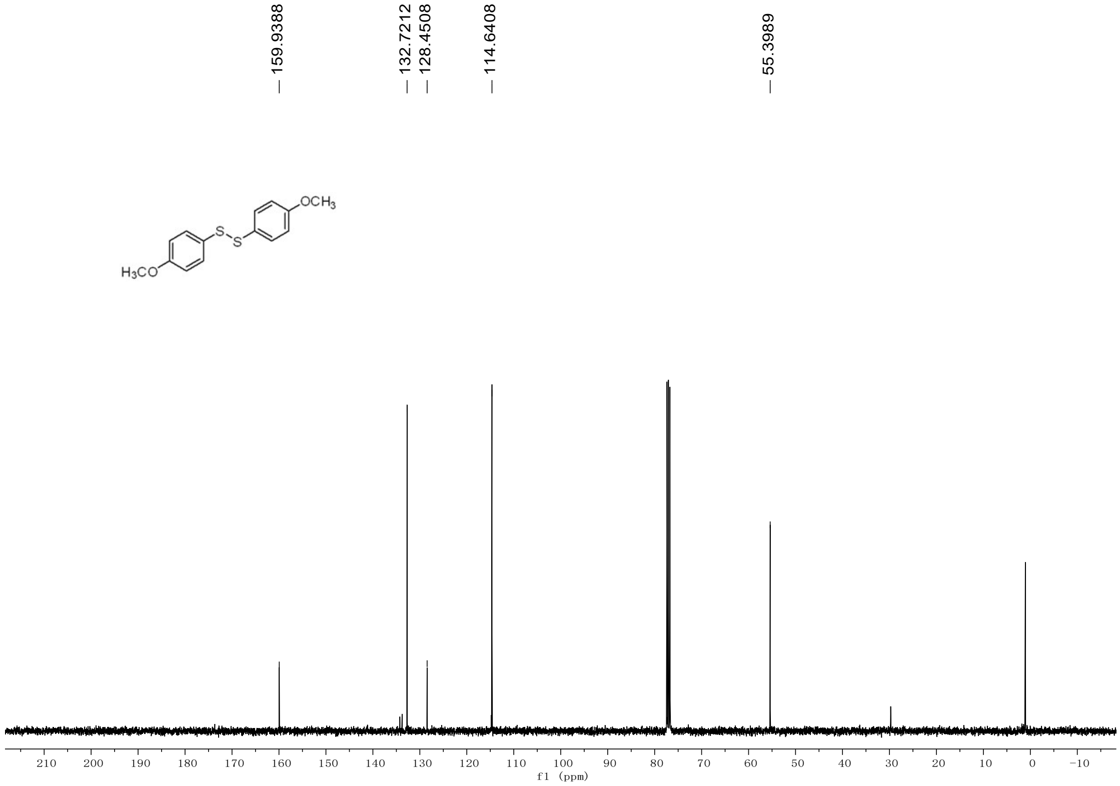
1,2-di-o-tolyldisulfane (2d)



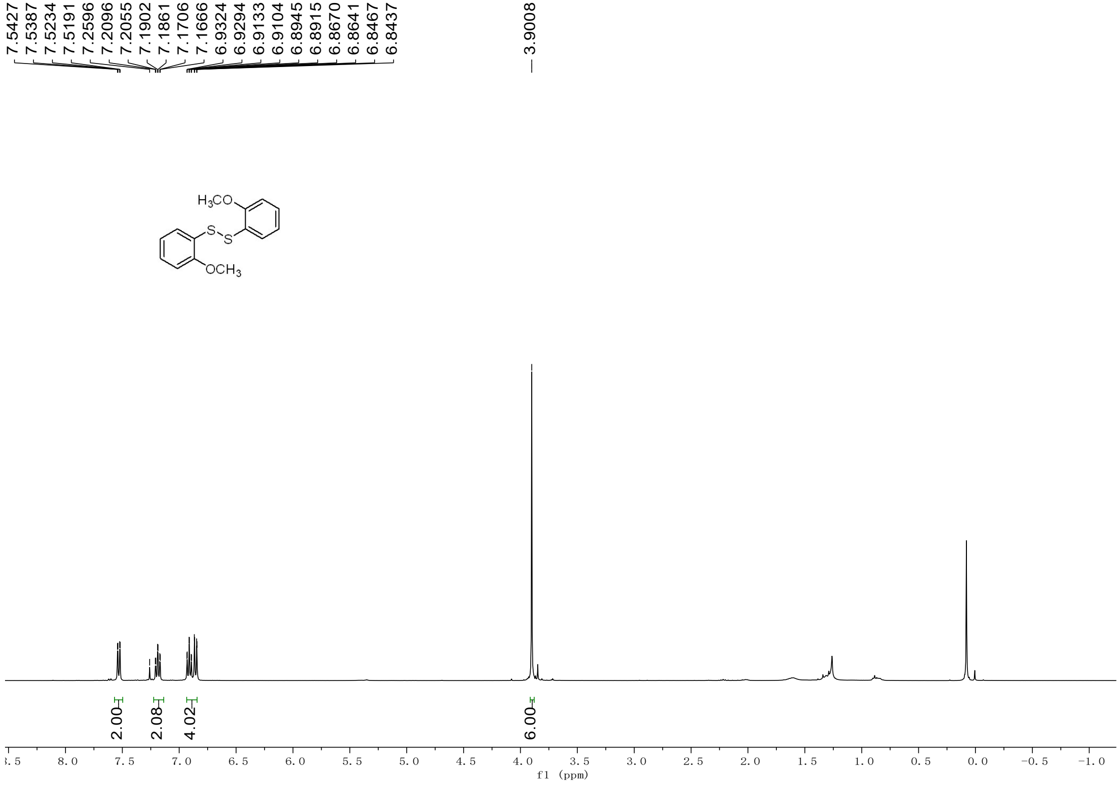


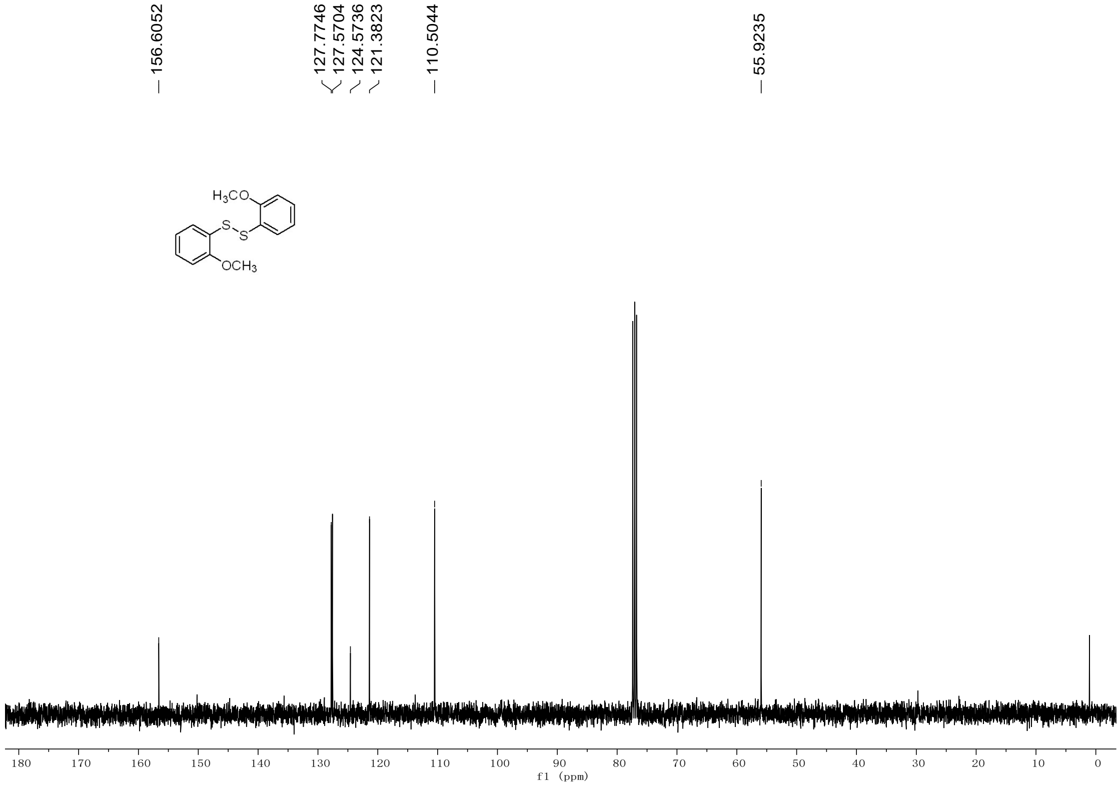
1,2-bis(4-methoxyphenyl)disulfane (2e)



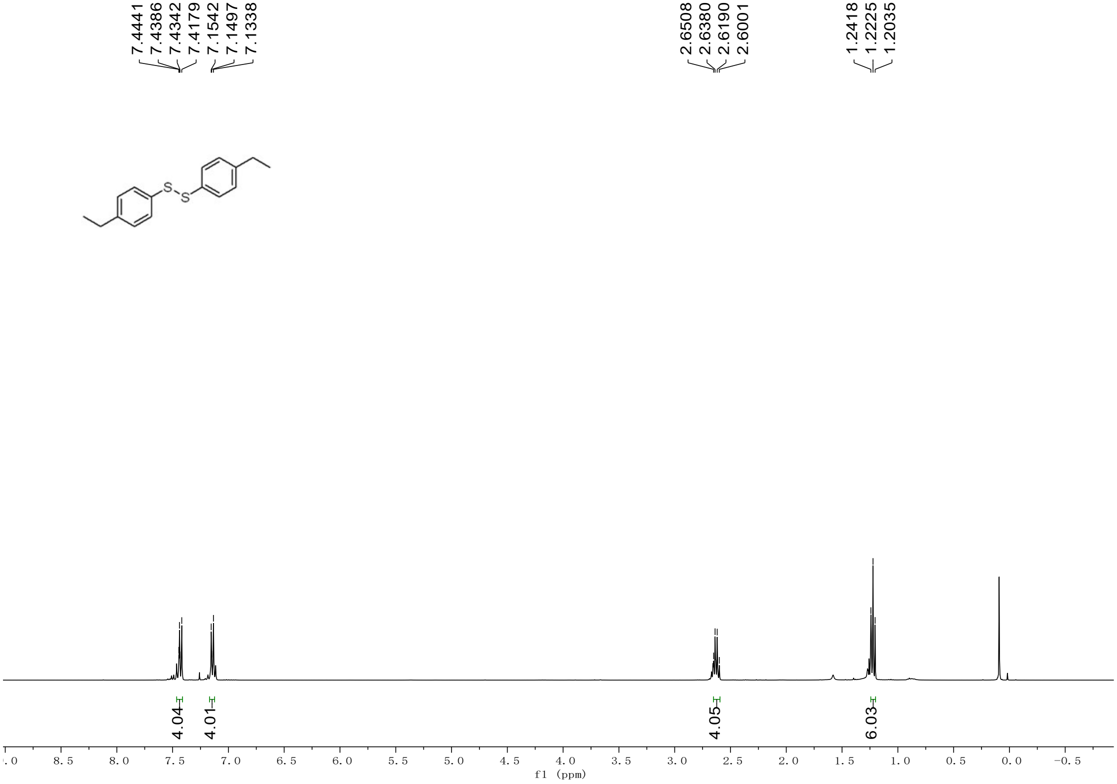


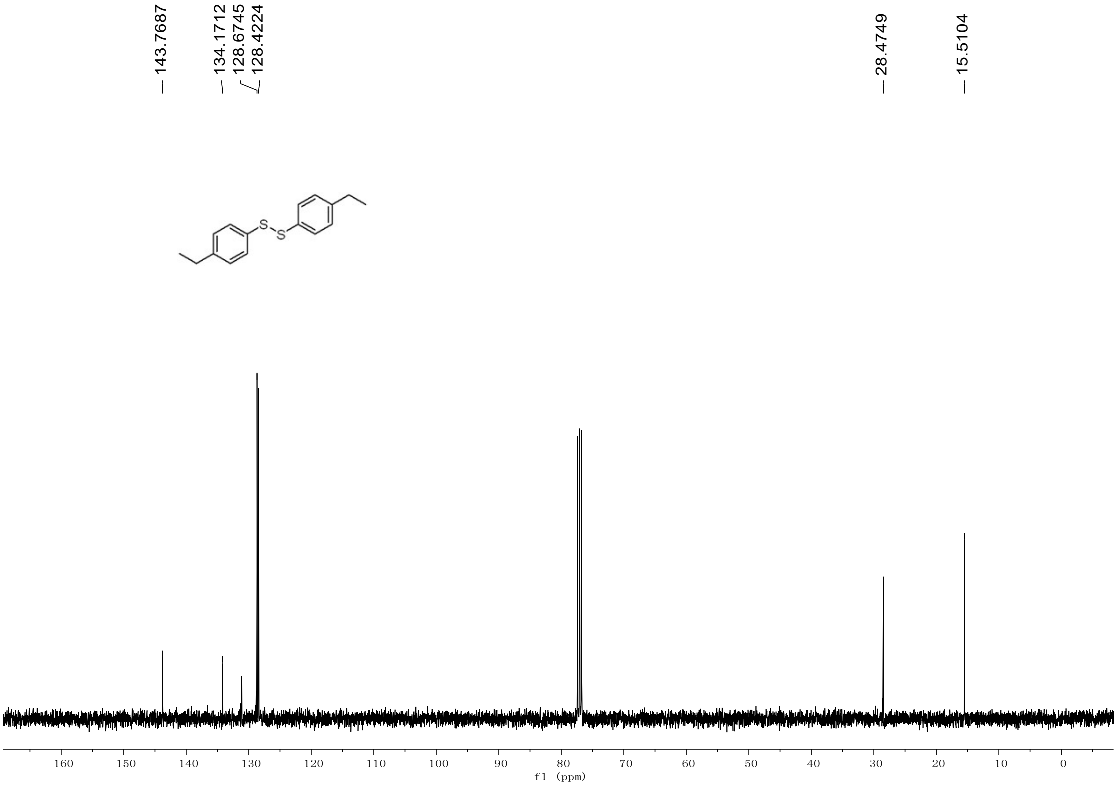
1,2-bis(2-methoxyphenyl)disulfane (2f)



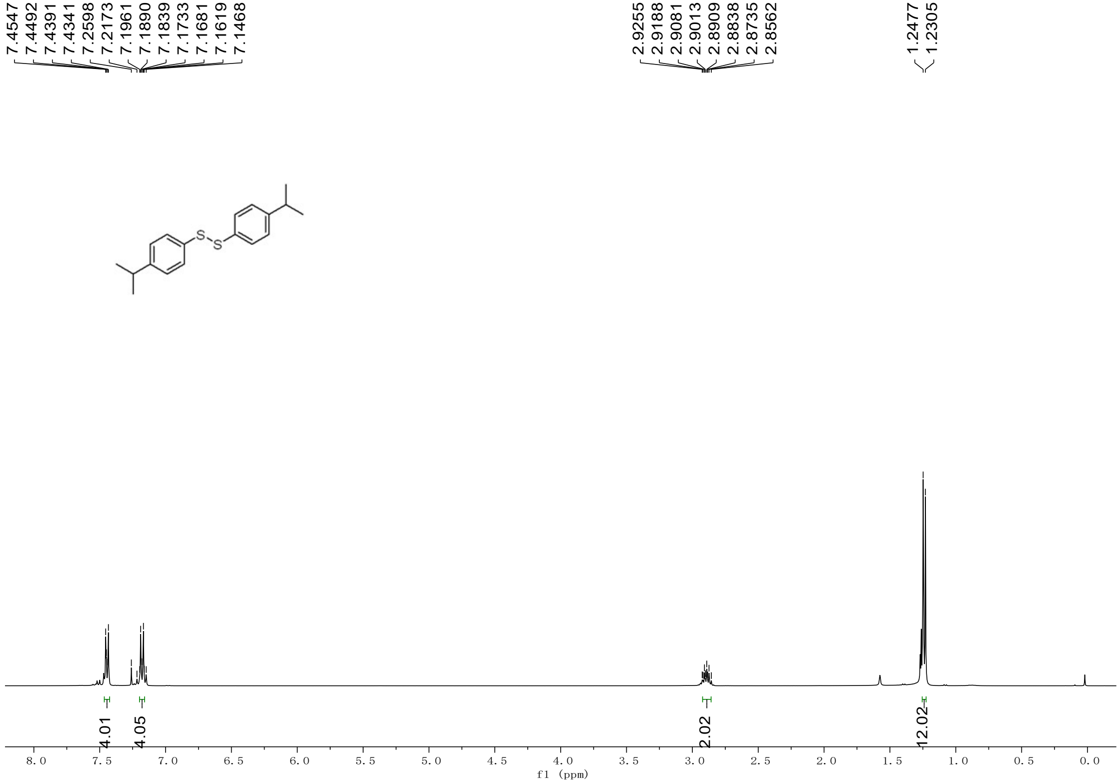


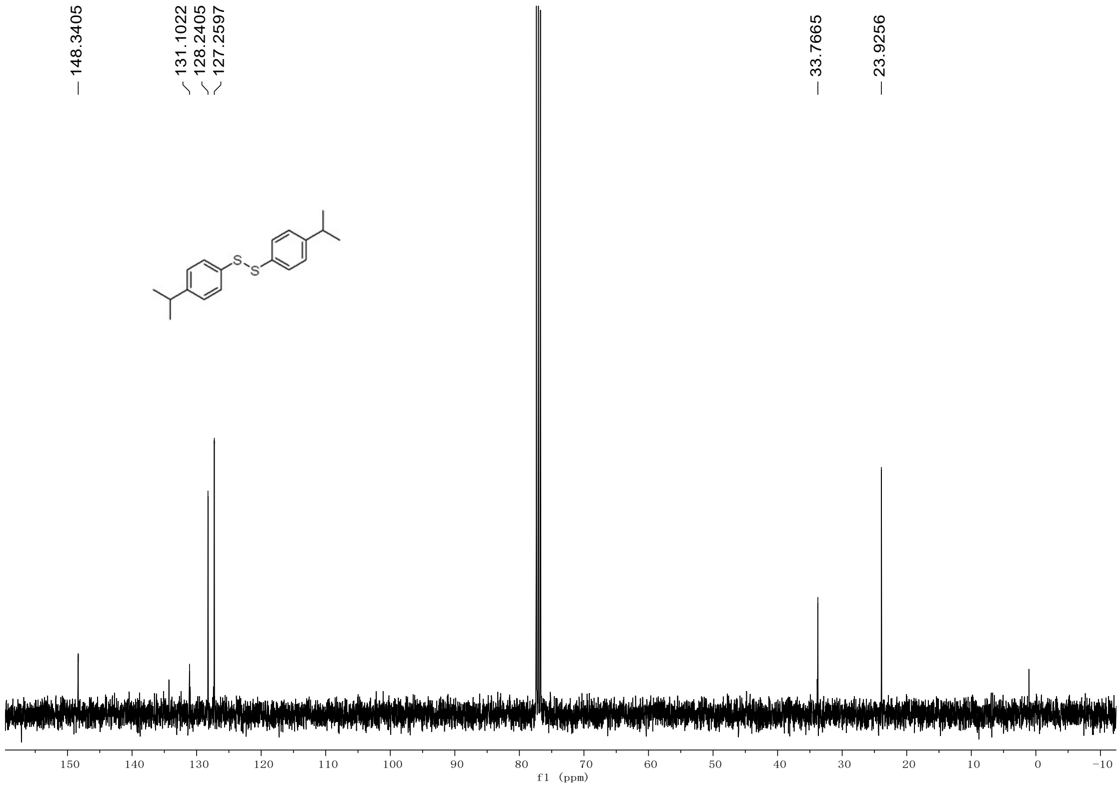
1,2-bis(4-ethylphenyl)disulfane (2g)



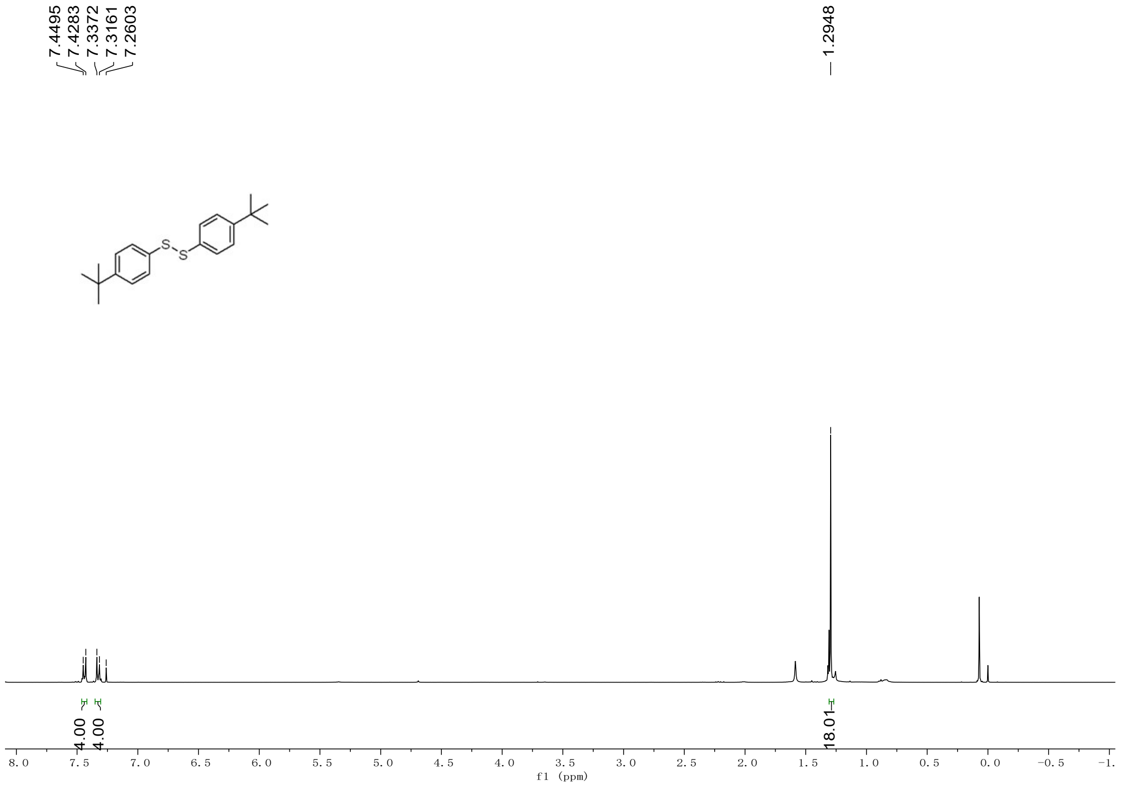


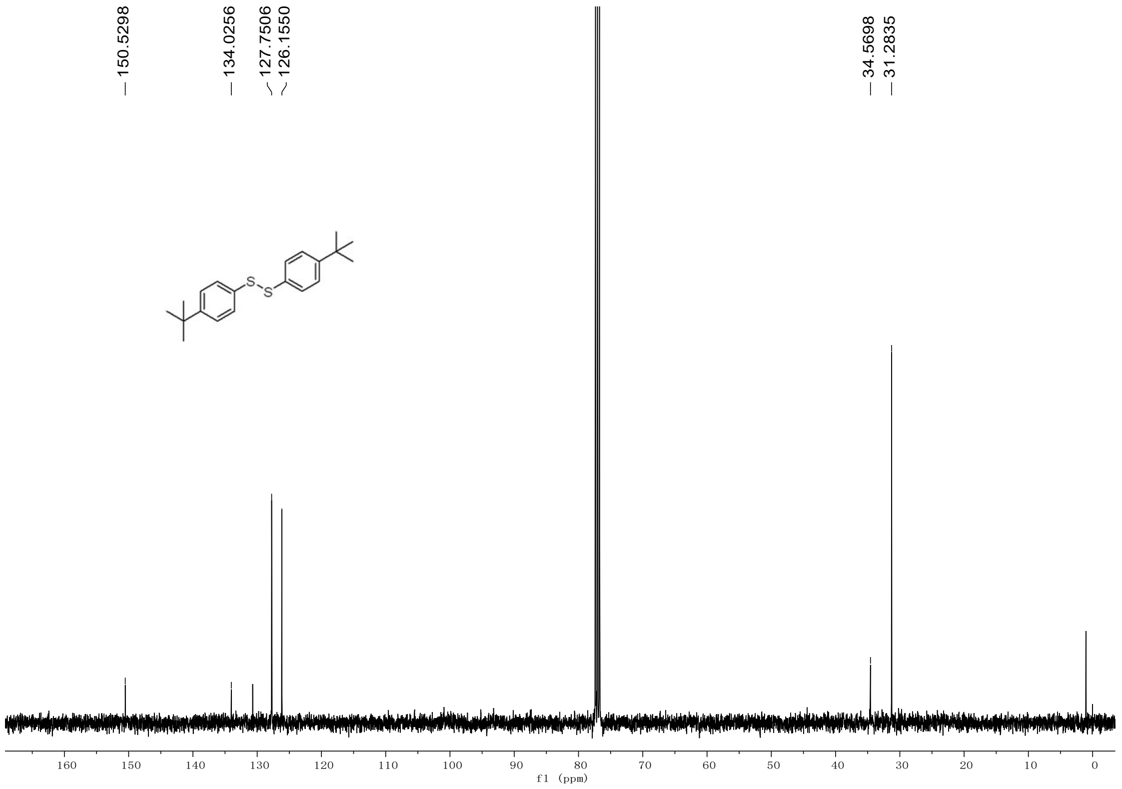
1,2-bis(4-isopropylphenyl)disulfane (2h)



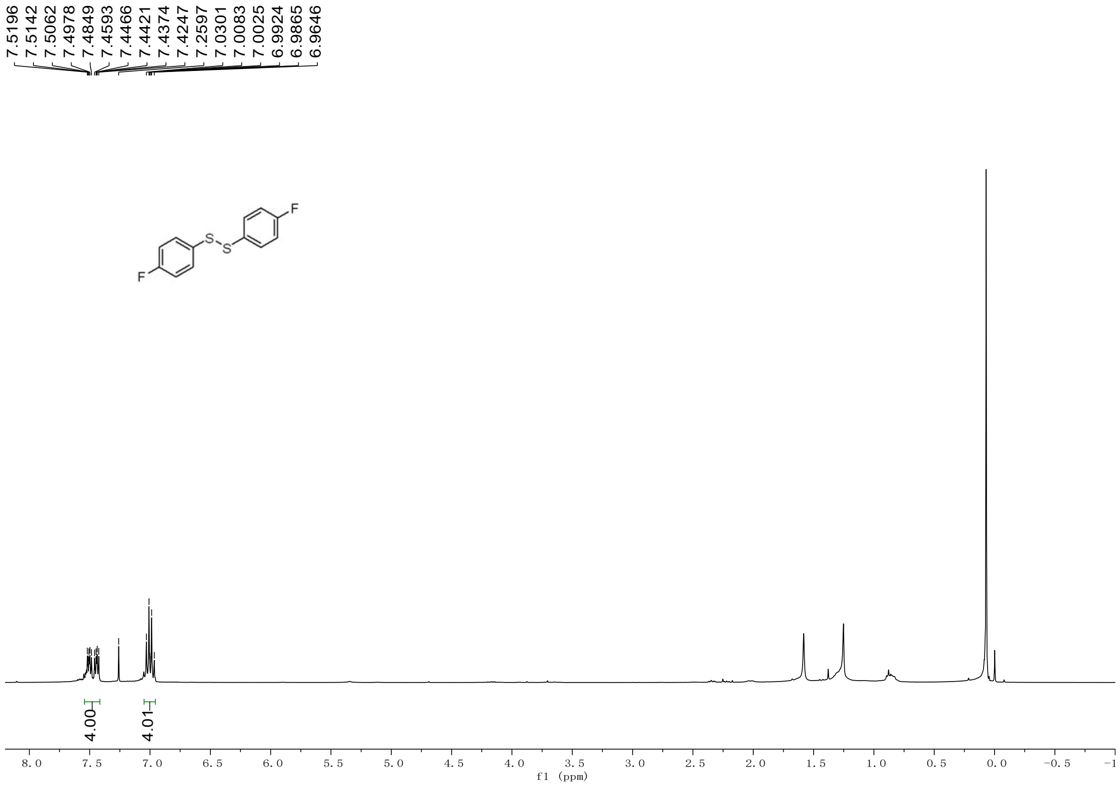


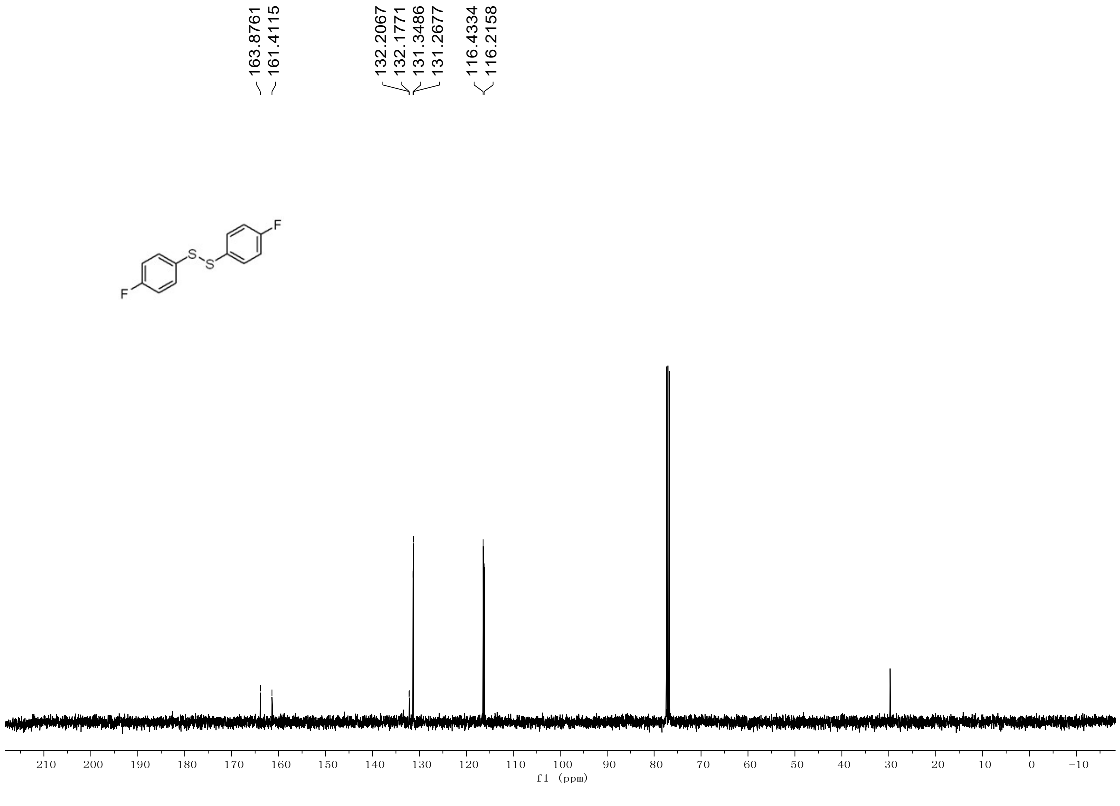
1,2-bis(4-(*tert*-butyl)phenyl)disulfane (2i)

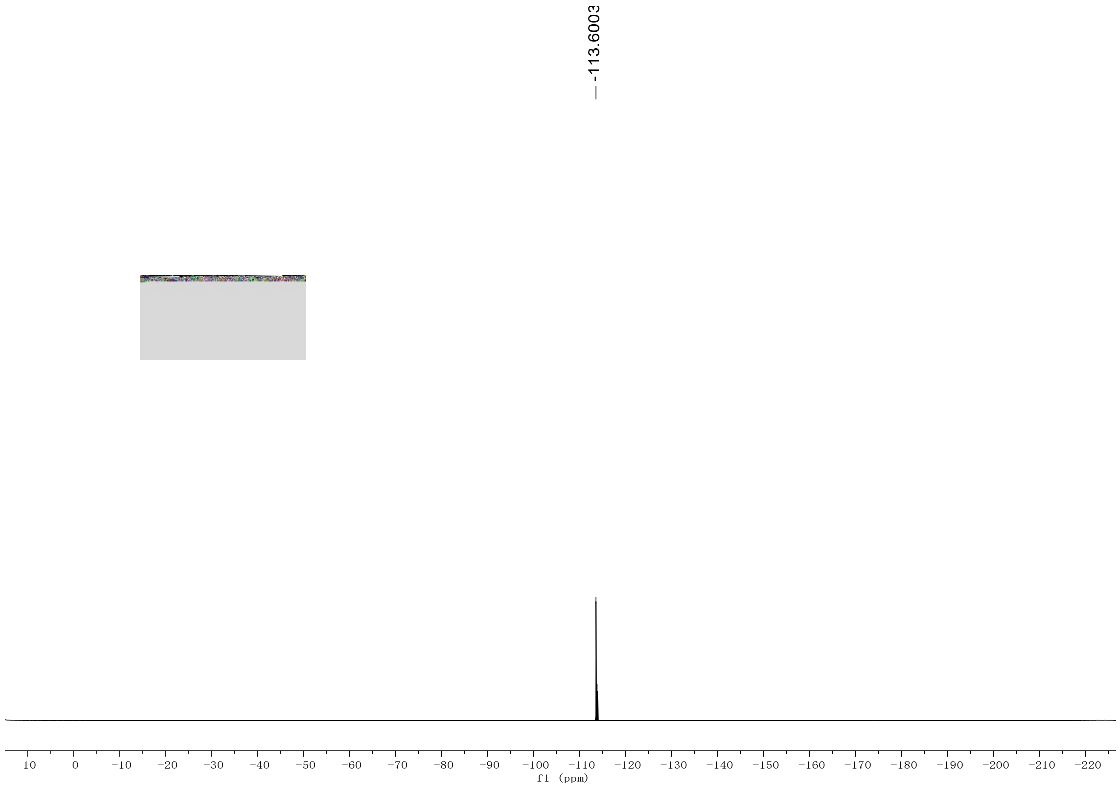




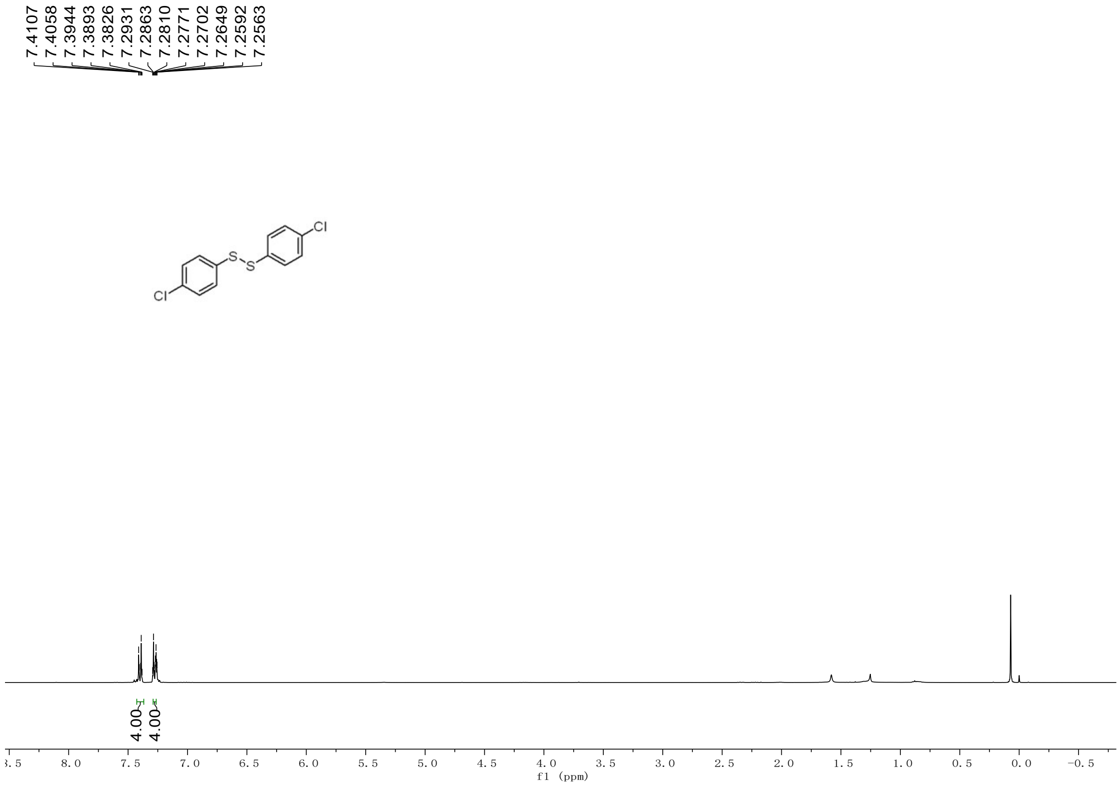
1,2-bis(4-fluorophenyl)disulfane (2j)

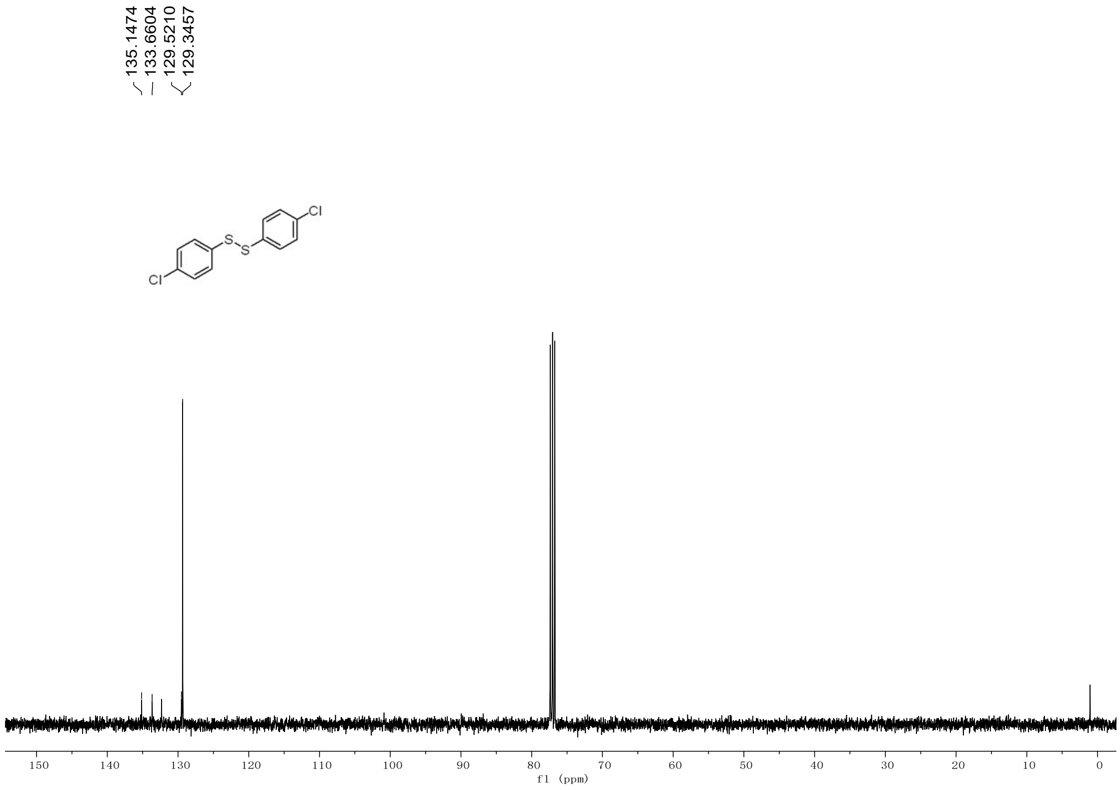




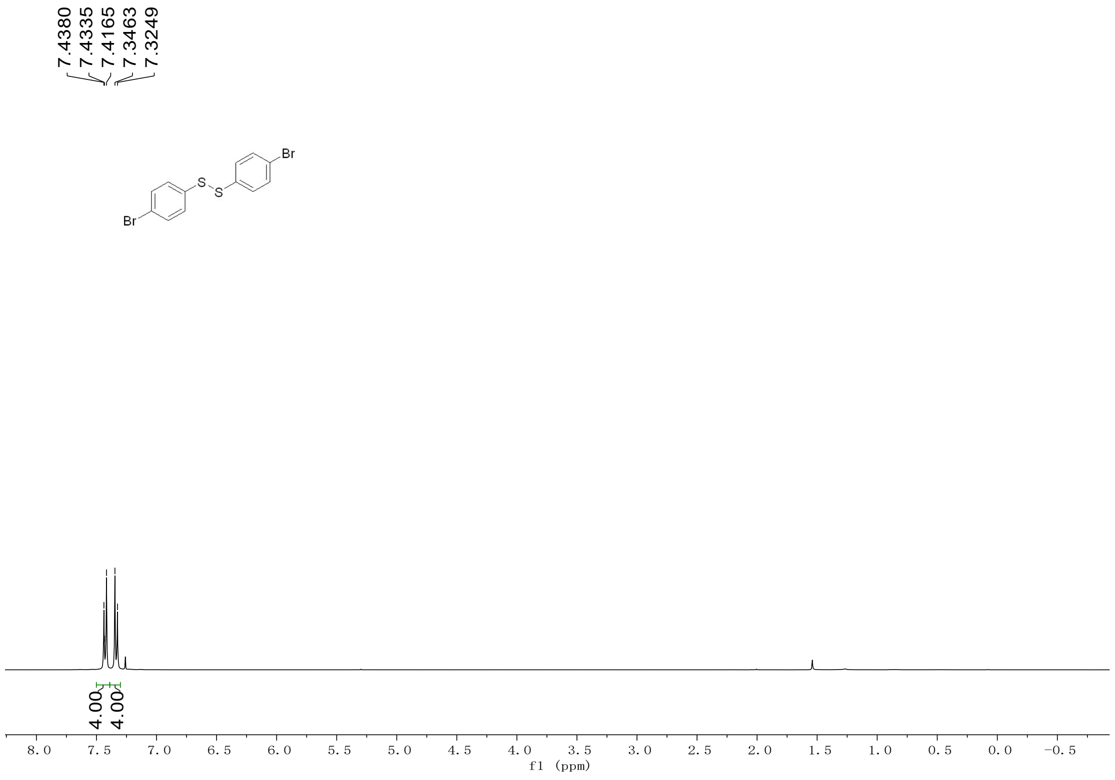

-113.6003
10
0
−10
−20
−30
−40
−50
−60
−70
−80
−90
−100
−110
−120
−130
−140
−150
−160
−170
−180
−190
−200
−210
−220
f1 (ppm)

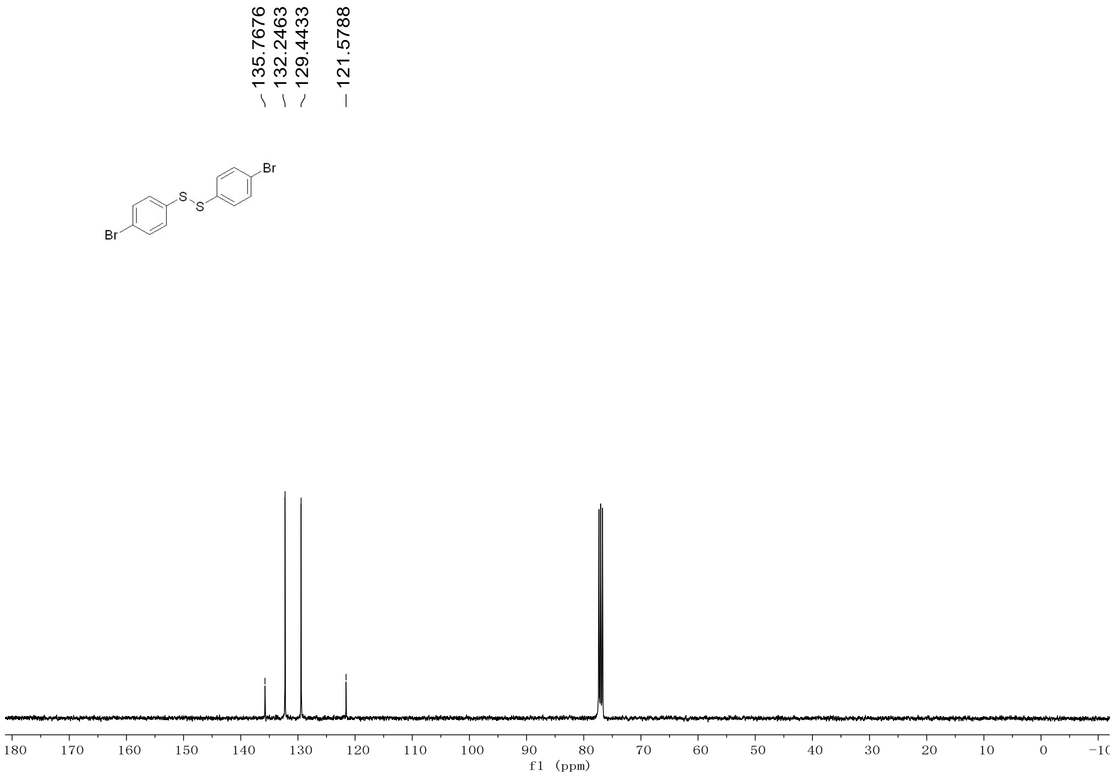
1,2-bis(4-chlorophenyl)disulfane (2k)



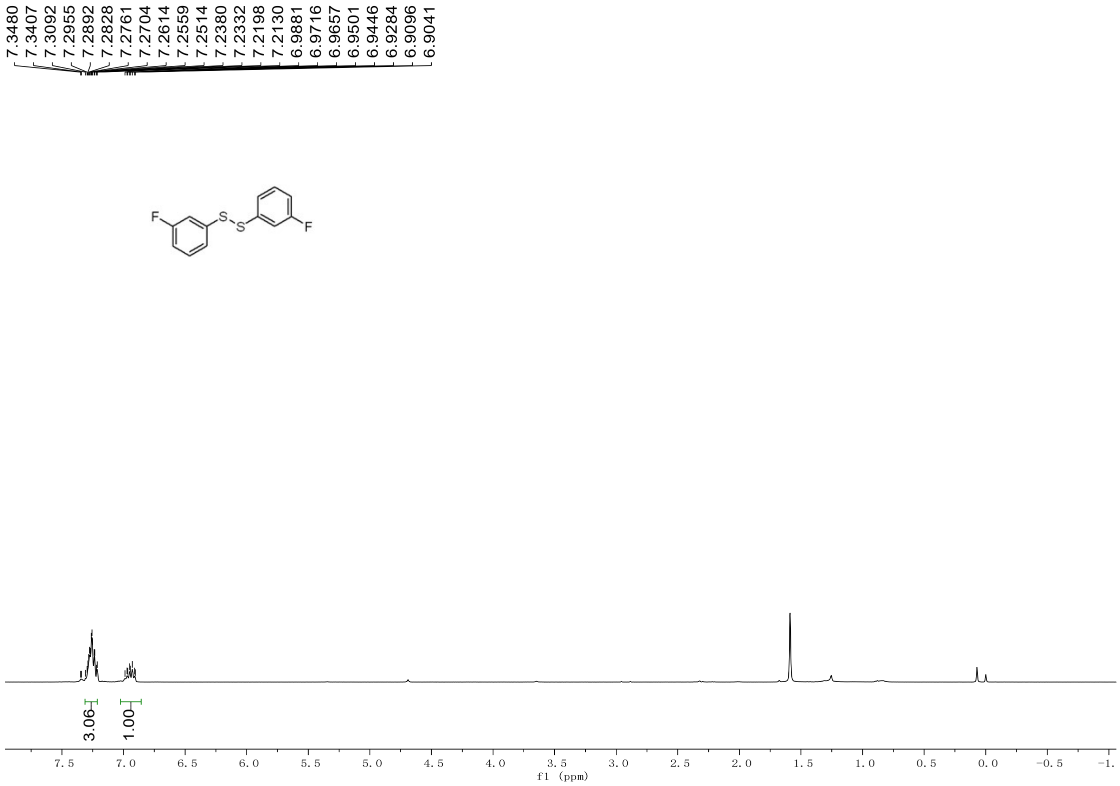


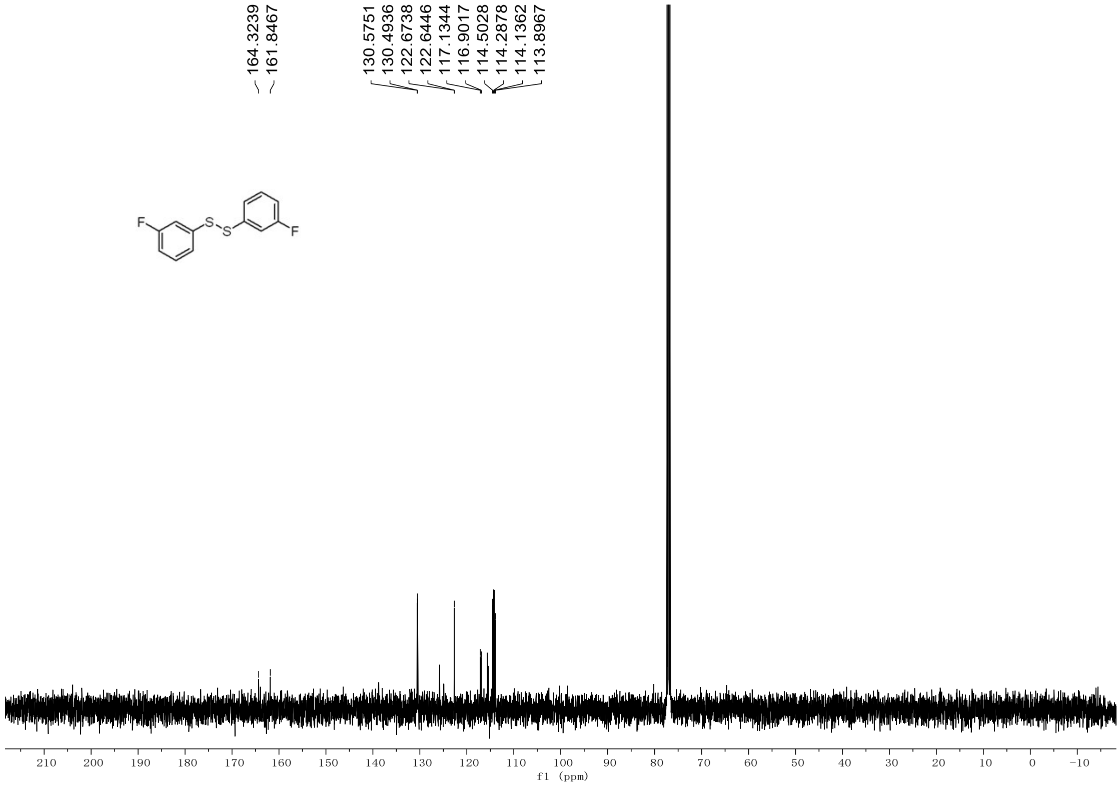
1,2-bis(4-bromophenyl)disulfane (2l)

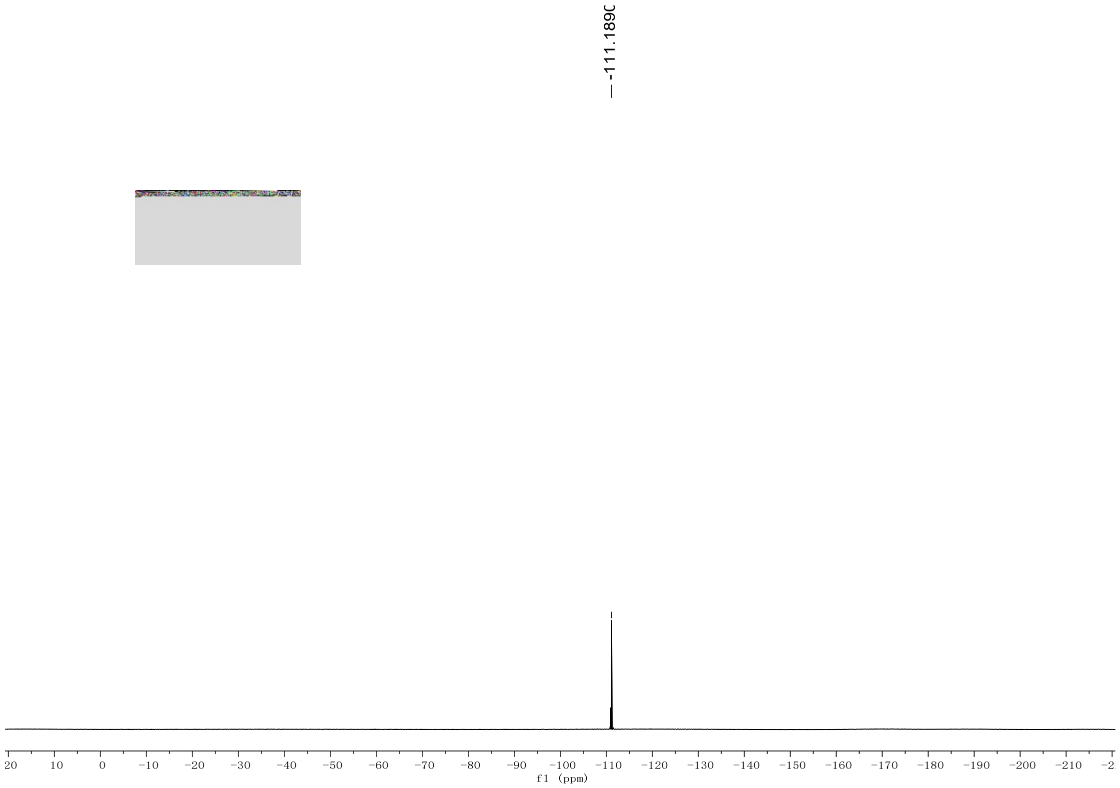




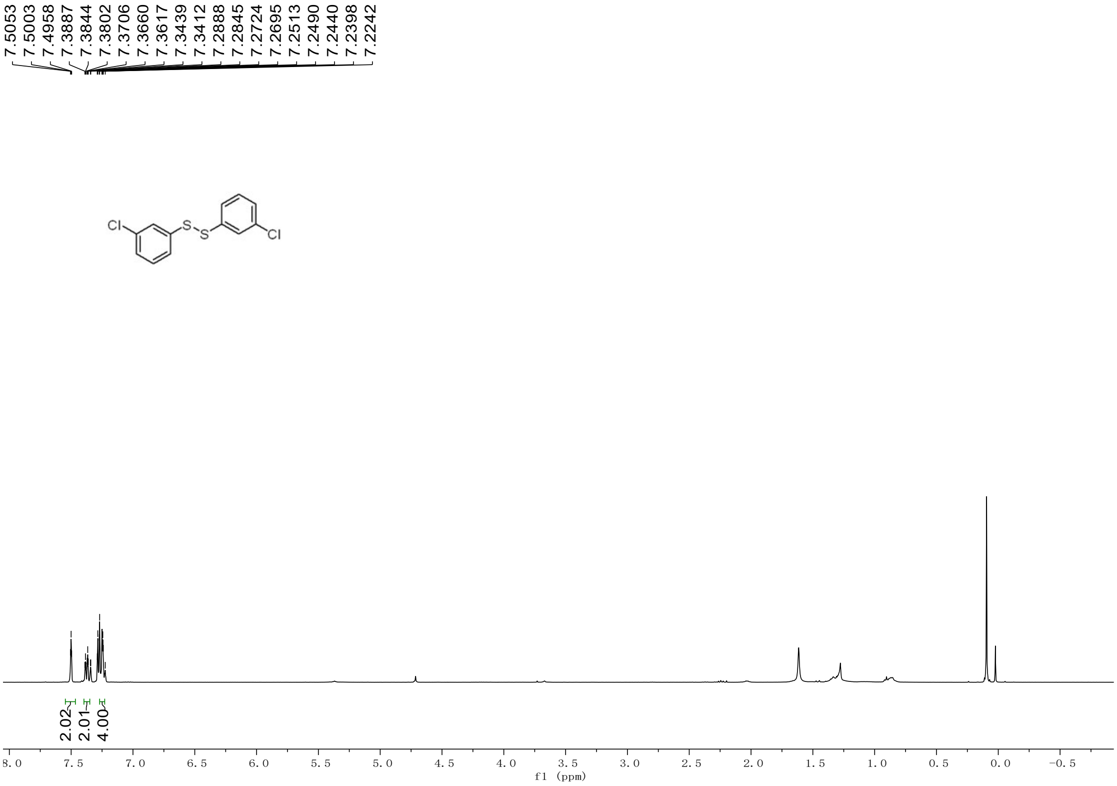
1,2-bis(3-fluorophenyl)disulfane (2m)

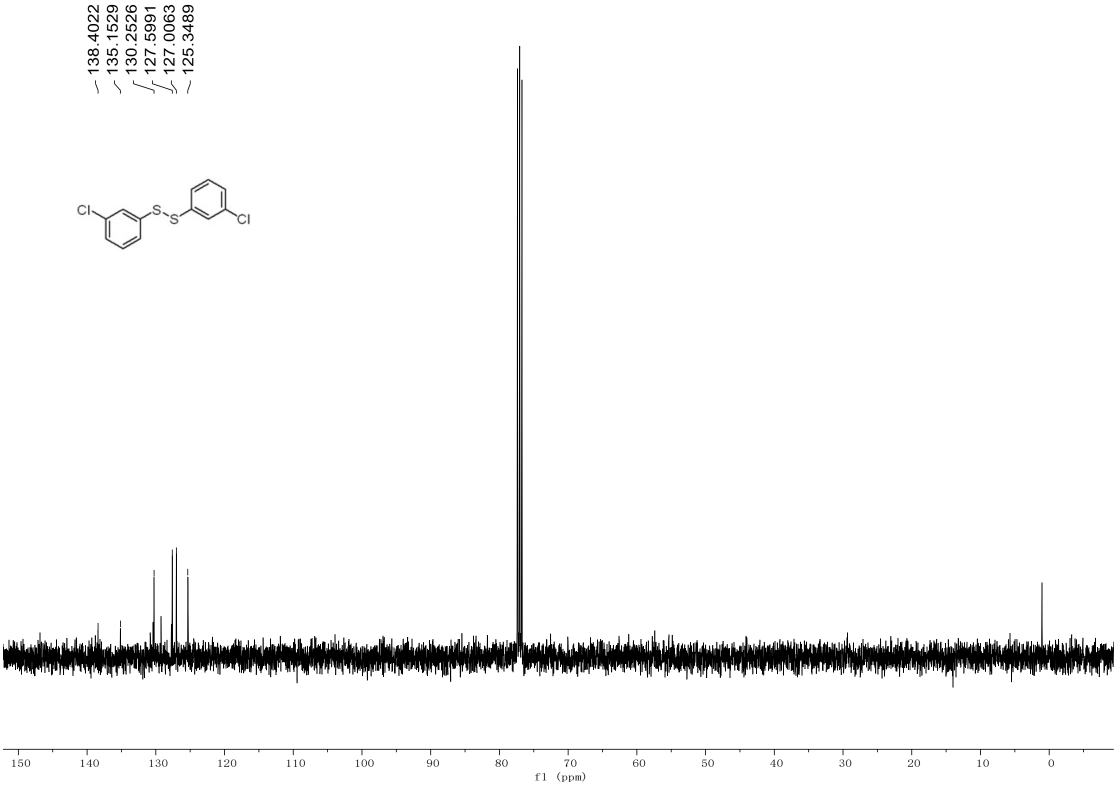




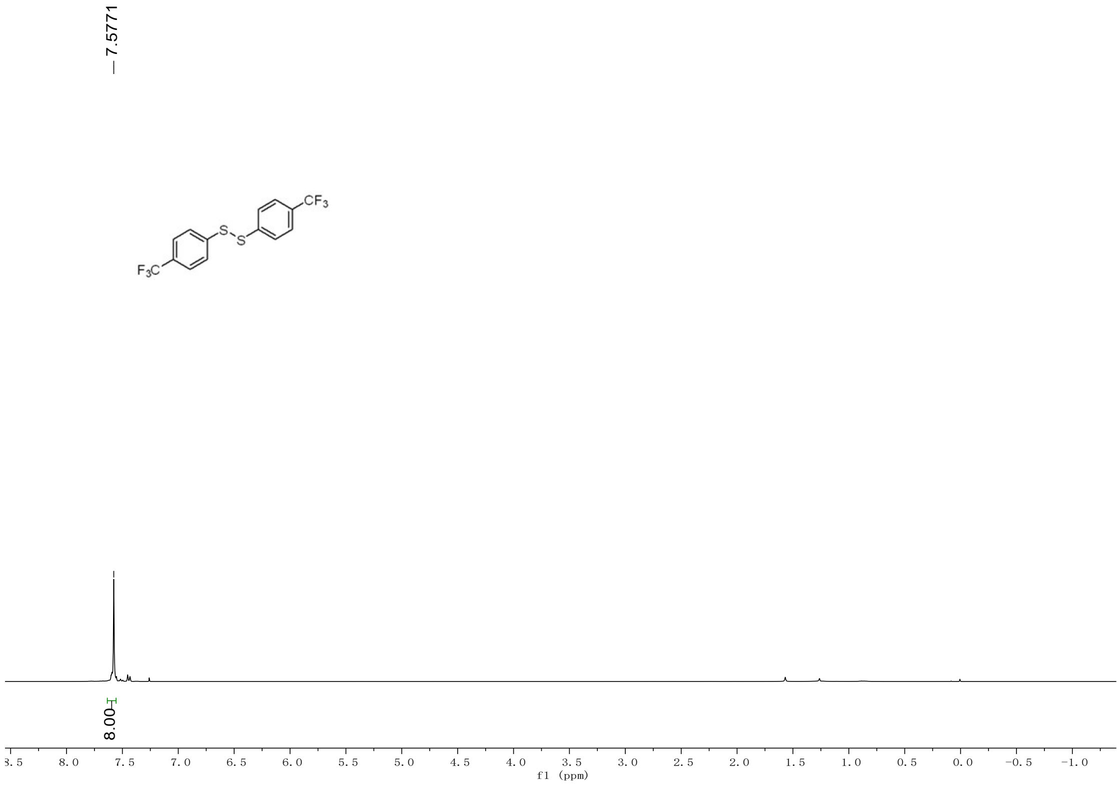

-111.1890
20
10
0
−10
−20
−30
−40
−50
−60
−70
−80
−90
−100
−110
−120
−130
−140
−150
−160
−170
−180
−190
−200
−210
−2
f1 (ppm)

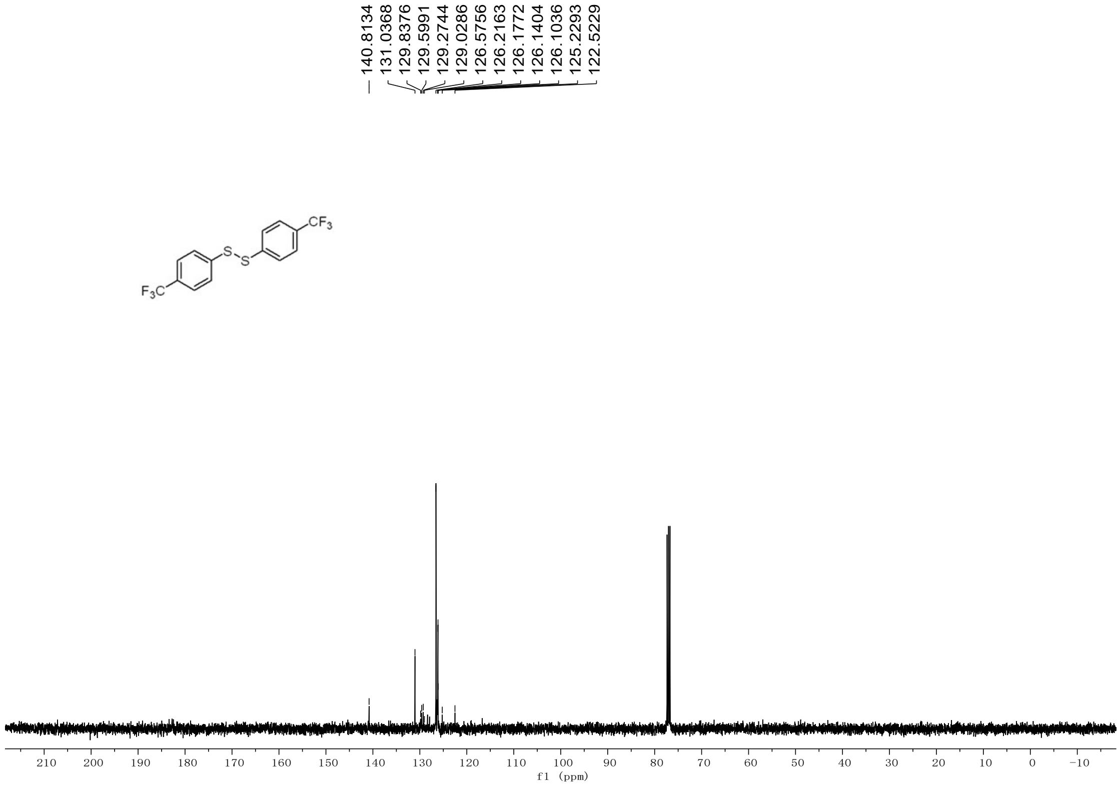
1,2-bis(3-chlorophenyl)disulfane (2n)

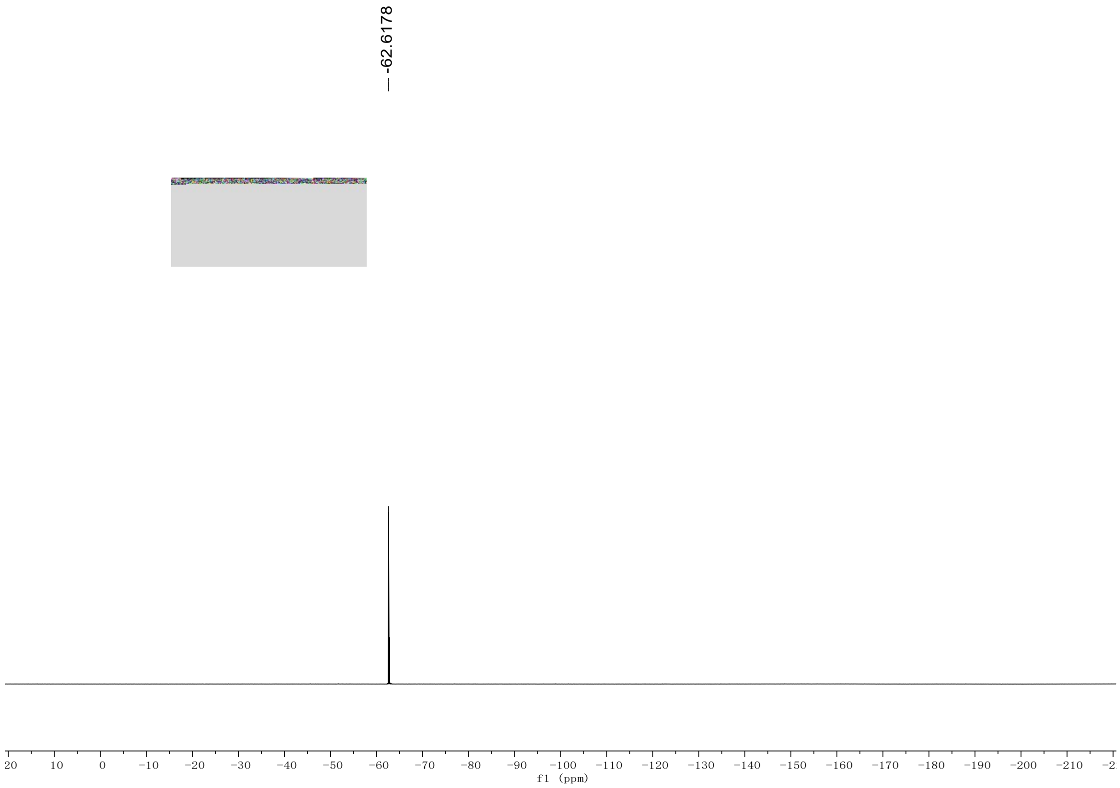




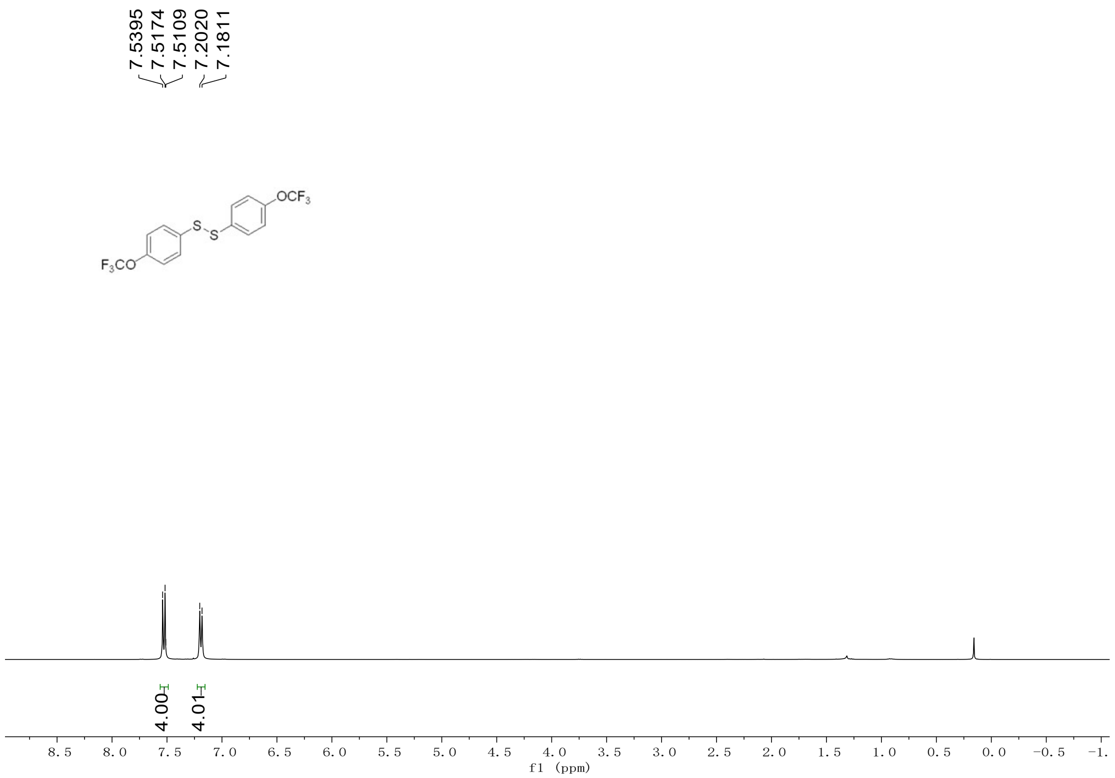
1,2-bis(4-(trifluoromethyl)phenyl)disulfane (2o)

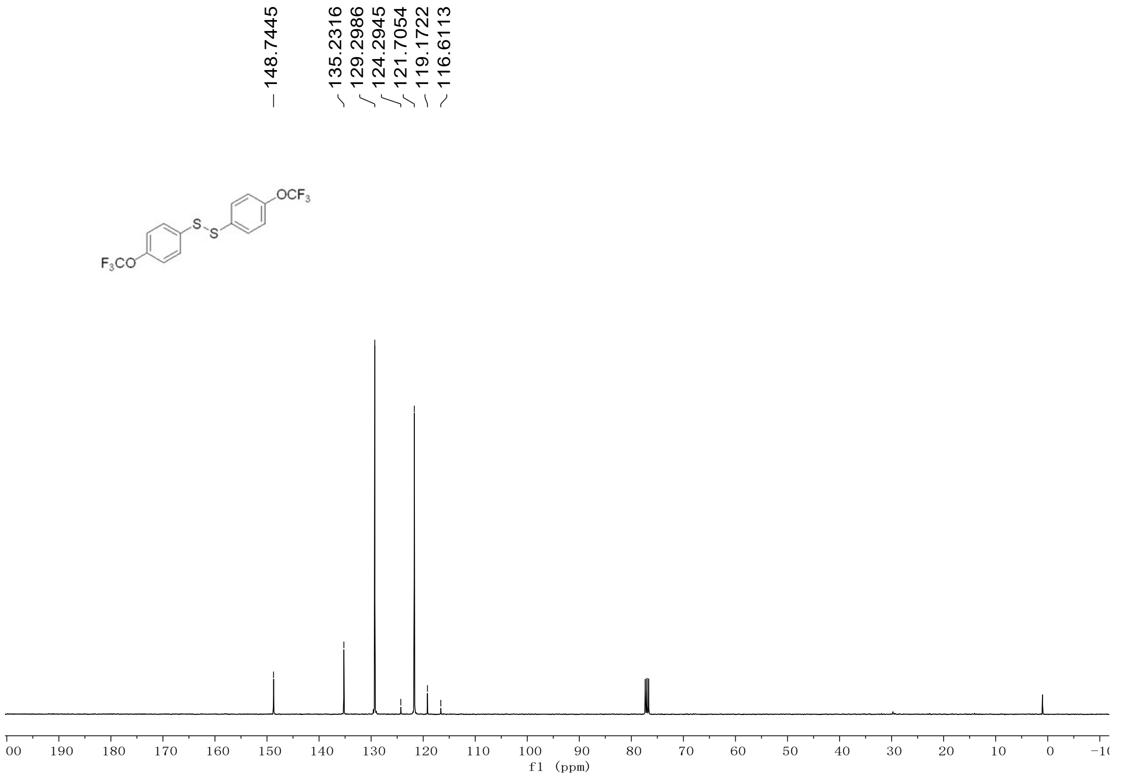


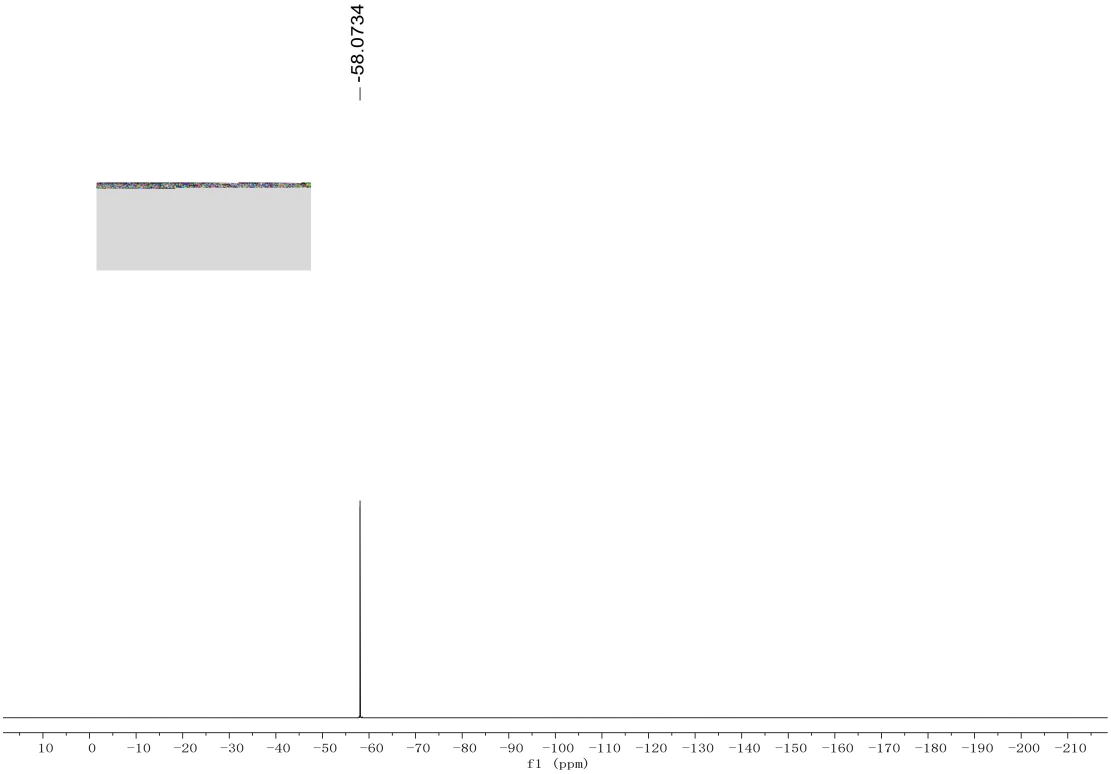



-62.6178
20
10
0
−10
−20
−30
−40
−50
−60
−70
−80
−90
−100
−110
−120
−130
−140
−150
−160
−170
−180
−190
−200
−210
−2
f1 (ppm)

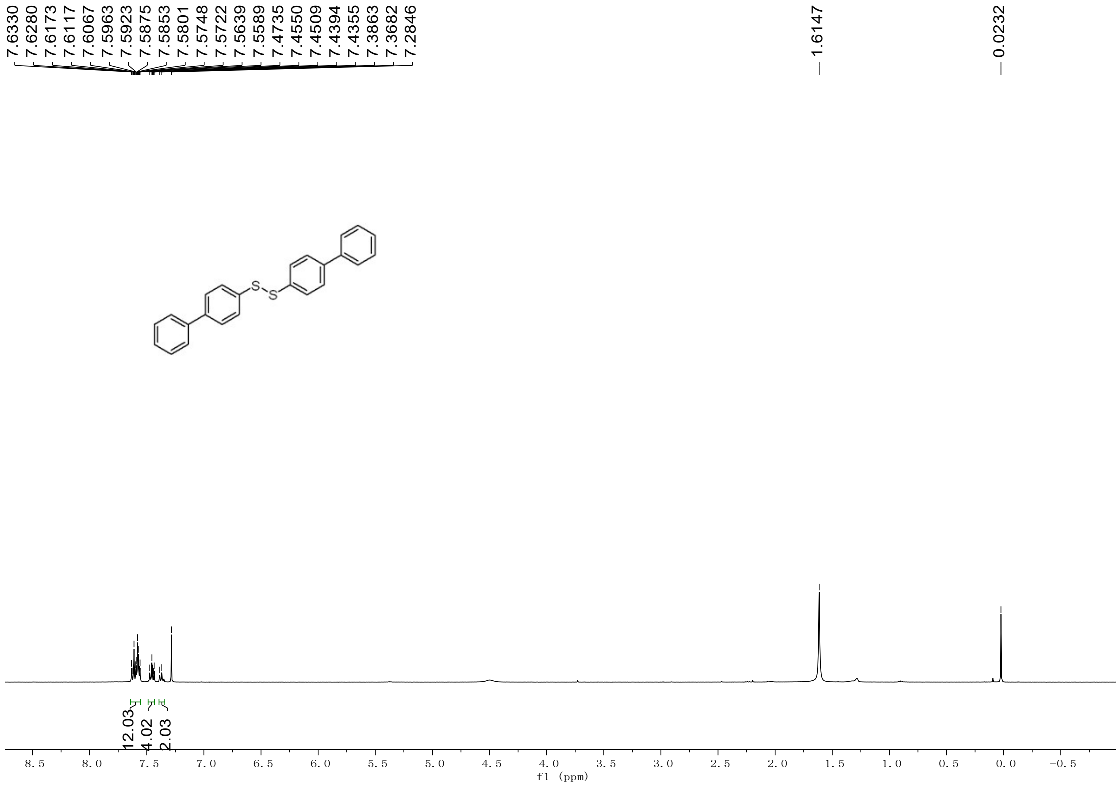
1,2-bis(4-(trifluoromethoxy)phenyl)disulfane (2p)

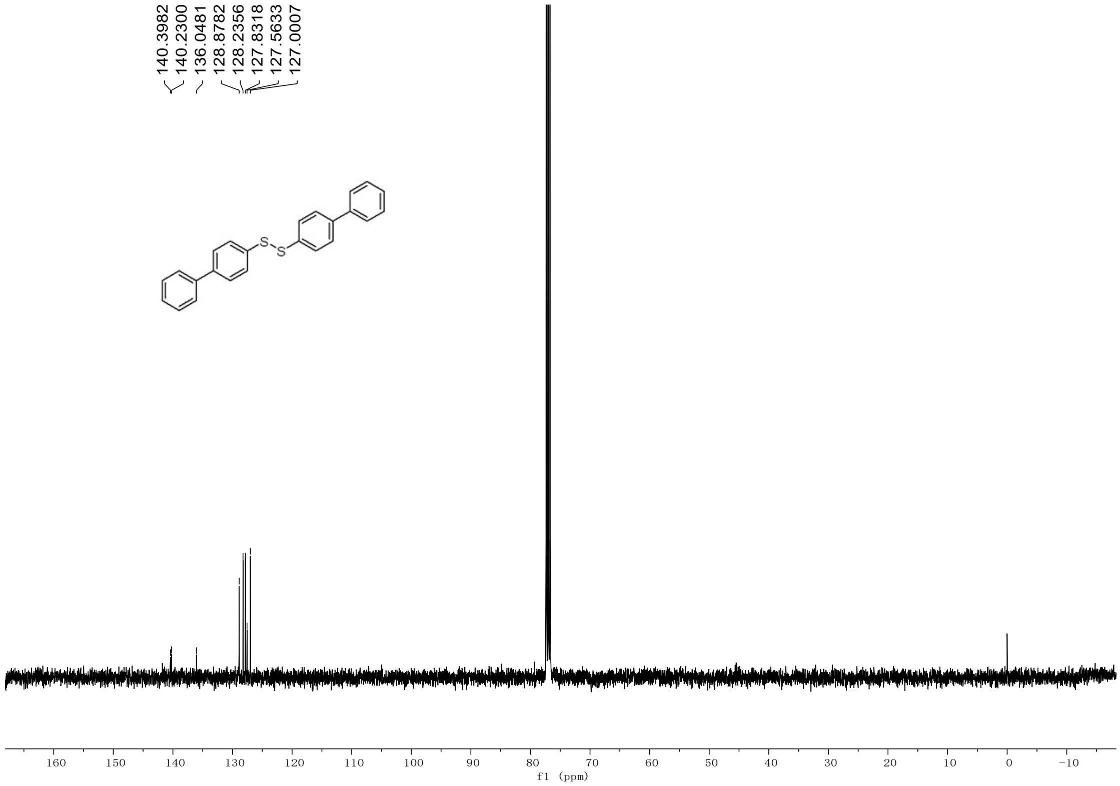




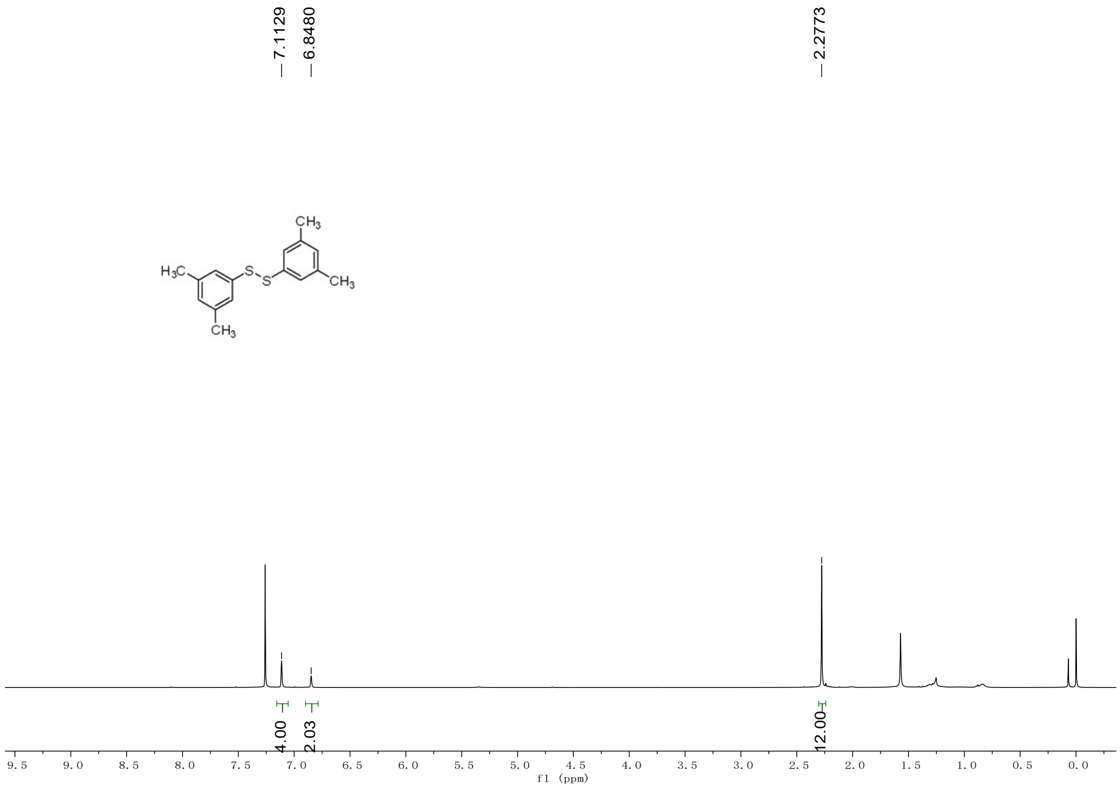

-58.0734
10
0
−10
−20
−30
−40
−50
−60
−70
−80
−90
−100
−110
−120
−130
−140
−150
−160
−170
−180
−190
−200
−210
f1 (ppm)

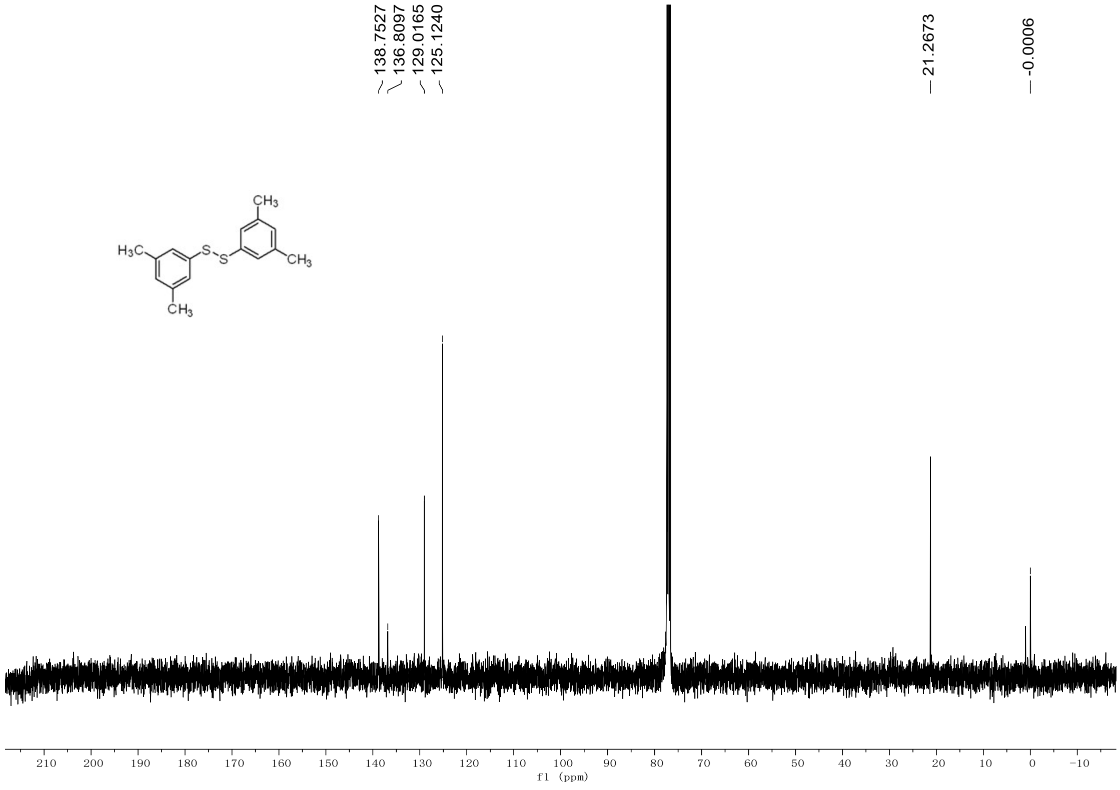
1,2-di([1,1'-biphenyl]-4-yl)disulfane (2q)



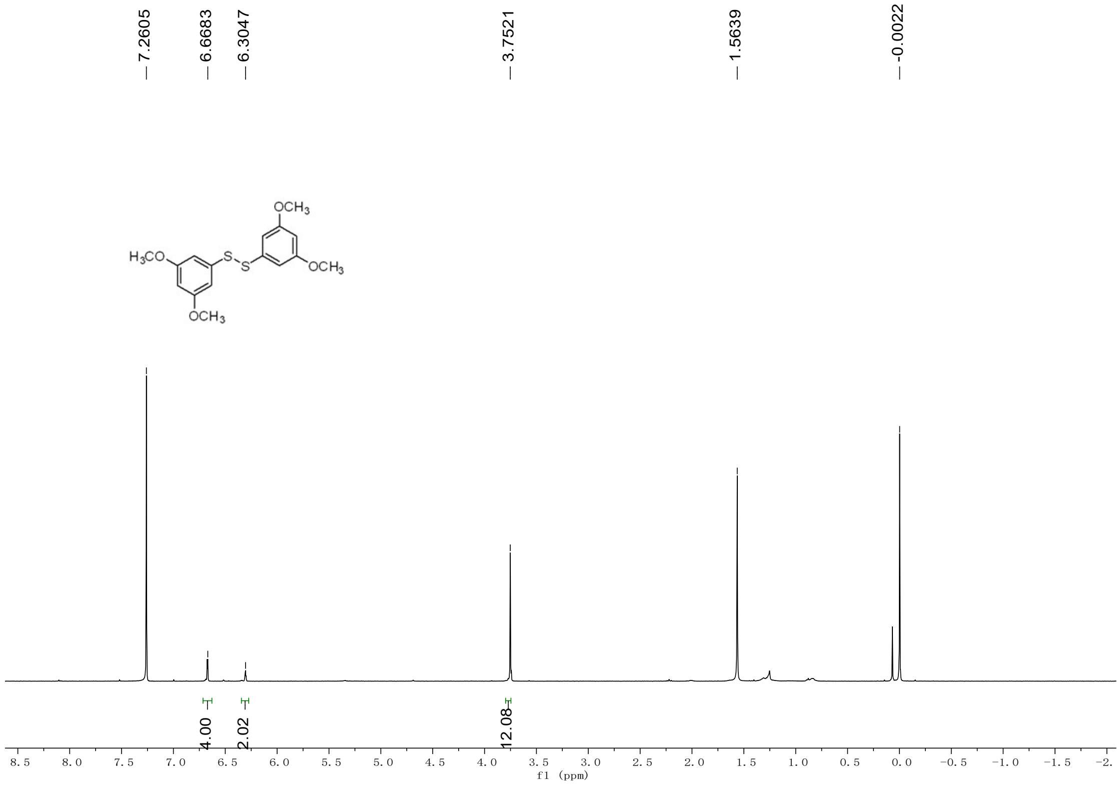


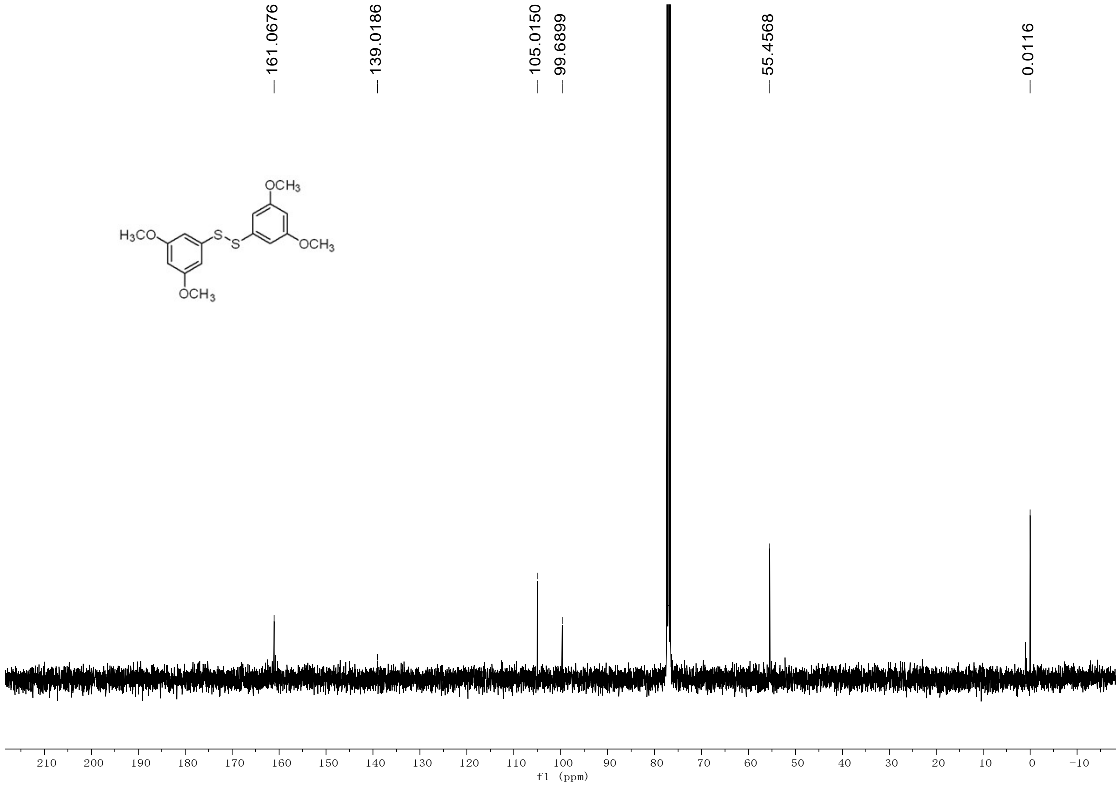
1,2-bis(3,5-dimethylphenyl)disulfane (2r)



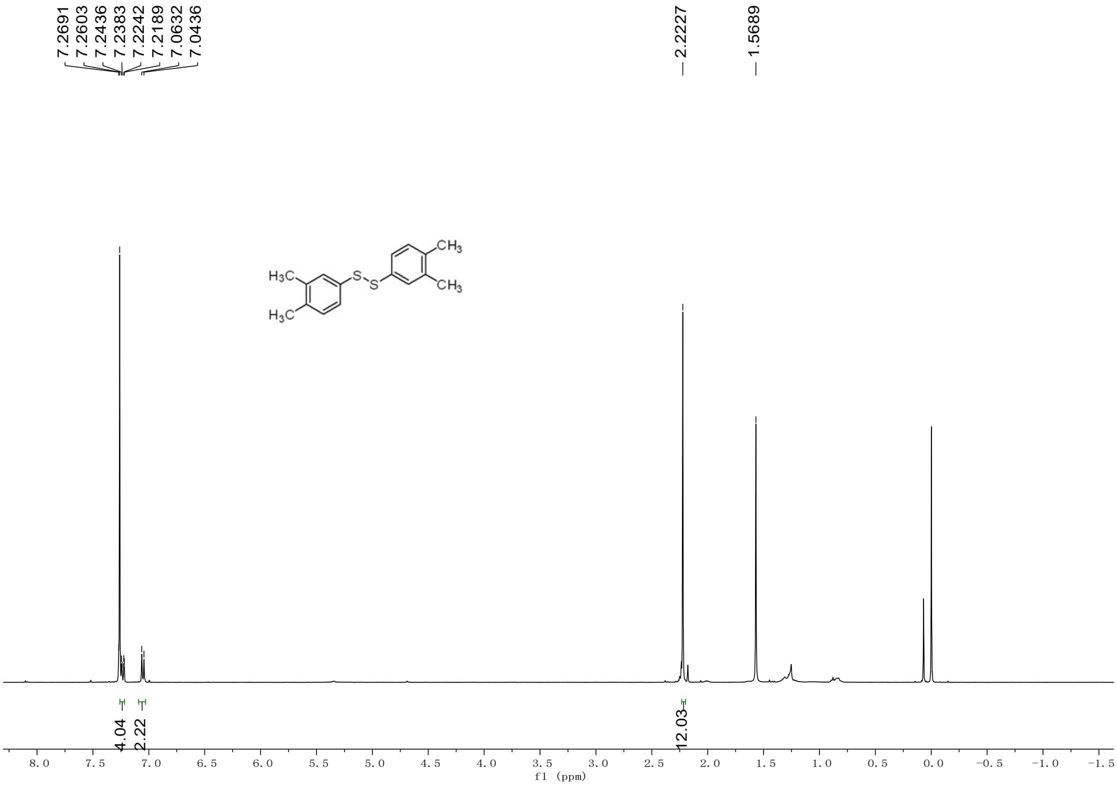


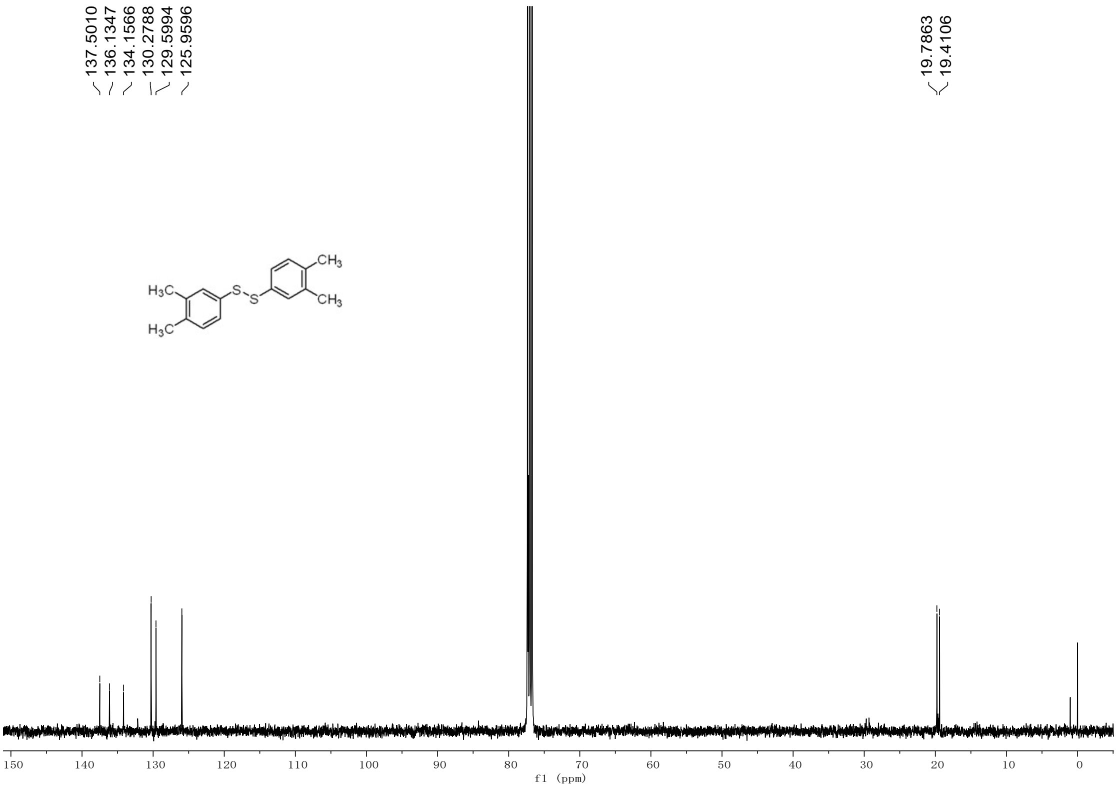
1,2-bis(3,5-dimethoxyphenyl)disulfane (2s)



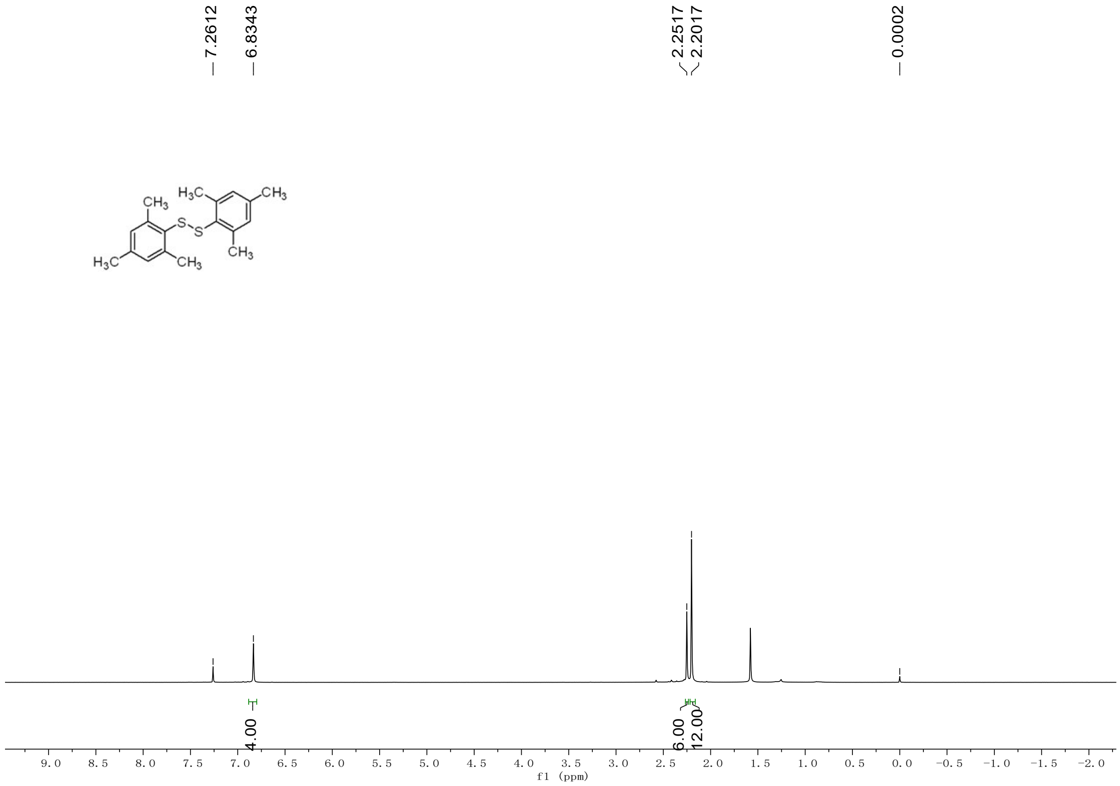


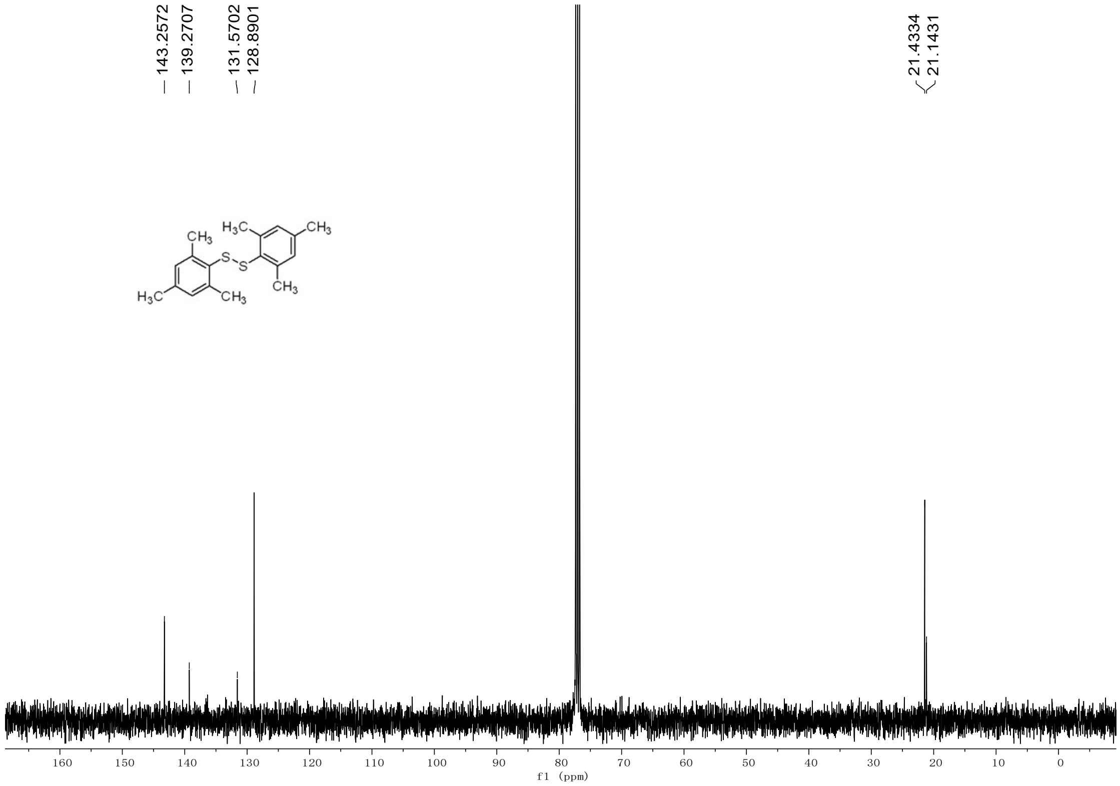
1,2-bis(3,4-dimethylphenyl)disulfane (2t)





1,2-dimesityldisulfane (2u)





References

(1) K.M. Rajesha, B. Ajithaa, Ashok Kumar Reddyb, Y., Suneethac, Y., Sreedhara Reddy, P. *Materials Today: Proceedings* **2016**, *3*, 1985

(2) A. M. Sipyagin, V. S. Enshov, S. A. Kashtanov, V. A. Potemkin, J. S. Thrasher, A. Waterfeld. *Russian Chemical Bulletin, International Edition,* 2004, *53,* 420-434.

(3) X. Qiu, X. Yang, Y. Zhang, S. Song, N. Jiao. *Org. Chem. Front.*, **2019,** *6,* 2220–2225.

(4) C. Bottecchia, N. Erdmann, P. M. A. Tijssen, L. Milroy, L. Brunsveld, V. Hessel, T. NoÚl. *ChemSusChem,* **2016**, *9*, 1781 – 1785.

(5) F. Zhu, E. Miller, S. Zhang, D. Yi, S, O'Neill, X. Hong, M. A. Walczak. *J. Am. Chem. Soc.* **2018**, *140*, 18140−18150.

(6) S. C. Banfield, A. T. Omori, H. Leisch, T. Hudlicky. *J. Org. Chem.* **2007**, *72*, 4989-4992.

(7) M. Hayashi, K. Okunaga, S. Nishida, K. Kawamura, K. Eda. *Tetrahedron Letters* **2010,** *51,* 6734 – 6736.

(8) L. Song, W. Li, W. Duan, J. An, S. Tang, L. Li, G. Yang. *Green Chem.,* **2019,** *21,* 1432–1438.

(9) K. Nishino, S. Tsukahara, Y. Ogiwara, N. Sakai. *Eur. J. Org. Chem.* **2019,** 1588-1593.

(10) J. Howard, C. Schotten, S. Alston, D. Browne. *Chem. Commun.*, **2016,** *52,* 8448-8451.

(11) J. Leng, S. Wang, H. Qin. *Beilstein J. Org. Chem.* **2017,** *13,* 903–909.\

(12) G. Martino, M. Edler, G. Regina, A. Coluccia, M. Barbera, D. Barrow, R. Nicholson, G. Chiosis, A. Brancale, E. Hamel, M. Artico, R. Silvestri. *J. Med. Chem.* **2006**, *49,* 947-954.

(13) S. Dharmarathna, C. King'ondu, L. Pahalagedara, C. Kuo, Y. Zhang, S. L. Suib. *Applied Catalysis B: Environmental*, **2014,** *147,* 124-131.

(14) R. Tata, C. Hampton, M. Harmata. *Adv. Synth. Catal.* **2017**, *359*, 1232-1241.