

*Supplementary information for*

***t*BuOK-Triggered Bond Formation Reactions**

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## General Information

Glassware was pre-dried in an oven at 150 °C for several hours and cooled prior to use. All solvents were purchased as super dry standard solvent and used as received. Aromatic thiols and alkyl disulfides were purchased from Energy Chemical, Aladdin Chemical or Macklin Biochemical. Hydrazobenzene were prepared according to literature report.<sup>1</sup> *t*BuOK was obtained from Sigma-Aldrich and used after sublimation. <sup>1</sup>H NMR, <sup>13</sup>C NMR spectra were recorded on Zhongke-Niujin 400 at room temperature using tetramethylsilane as an internal reference and CDCl<sub>3</sub> as a solvent. Chemical shifts (δ) are given in parts per million (ppm). Coupling constants (*J*) are given in Hertz (Hz) and are referenced to tetramethylsilane (δ 0.00). Chemical shifts for carbons are reported in parts per million (ppm, δ scale) downfield from tetramethylsilane and are referenced to the carbon resonance of CDCl<sub>3</sub> (δ 77.0). High-resolution mass spectroscopy data were obtained on Agilent 6530, Agilent 6224 TOF LC/MS spectrometer. Thin layer chromatography (TLC) employed glass 0.25 mm silica gel plates. Flash chromatography columns were packed with 100-200 mesh silica gel in petroleum ether (bp. 60-90 °C). Gas chromatographic analyses were performed on GC-2010 Plus gas chromatography instrument with a FID detector and isooctane was used as an internal standard. GC-MS spectra were recorded on a GCMS-QP2010 SE. High-Resolution MS analyses were performed on Agilent 6530 Accurate – Mass Q-TOF LC/MS with ESI mode or Waters Micro Mass GCT Premier with EI mode.

### **General procedure for the *t*BuOK-triggered disulfide metathesis**

Under ambient condition, a pressure tube was charged with 0.2 mmol of aromatic thiols or 0.1 mmol of aromatic disulfides and 0.2 mmol of alkyl disulfides, then 1.0 mL of 0.01 M *t*BuOK THF solution was added to the pressure tube. The tube was sealed with air and heat at 60 °C for the time shown and analyzed by gas chromatographic analyses using isooctane as internal standard. Isolated products were obtained after flash chromatography using petroleum ether as eluent.

### **General procedure for the *t*BuOK- triggered synthesis of symmetrical disulfides**

Under ambient condition, a sample vial was charged with 0.2 mmol of thiols, then 1.0 mL of 0.01 M *t*BuOK THF solution was added. The vial was sealed at room temperature and stirred for the time shown and analyzed by gas chromatographic analyses using isooctane as internal standard. Isolated products were obtained after flash chromatography using petroleum ether as eluent.

### **General procedure for the *t*BuOK- triggered synthesis of unsymmetrical disulfides**

Under ambient condition, a pressure tube was charged with 0.2 mmol of aromatic thiols and 0.4 mmol of alkyl thiols, then 1.0 mL of 0.01 M *t*BuOK THF solution was added. The tube was sealed and heated at 100 °C for the time shown and analyzed by gas chromatographic analyses using isooctane as internal standard. Isolated products were obtained after flash chromatography using petroleum ether as eluent.

### **General procedure for the preparation of symmetrical hydrazobenzene**

In a 100 mL pressure tube was added amine (1.0 g), toluene (60 mL), activated MnO<sub>2</sub> (10 equiv). The mixture was heated at reflux and monitored by TLC. Then, the reaction mixture was filtered through Celite pad and washed with toluene for three times. The filtrate was subjected to vacuum to afford the crude azobenzene which was directly dissolved in EtOH (50 mL) with 5 weight % of Pd/C and 10 mol% pyridine. The solution was reduced with hydrogen balloon and monitored using TLC. After all the azobenzene was converted the reaction mixture was quickly filtered, and the solvent was removed to get the desired hydrazobenzene in quantitative yield.

### **General procedure for the preparation of unsymmetrical hydrazobenzene**

To a solution of nitrosobenzene (0.5 g, 4.7 mmol) in glacial acetic acid (12 mL) and EtOH (3 mL), the amine (1.0 equiv) was added. The reaction mixture was stirred at 40 °C for overnight. Then, the mixture was poured into ice water and filtered to afford azobenzene crude product which was directly used for the next step without purification. The crude product was dissolved in EtOH (50 mL) with 5 weight % of Pd/C and 10 mol% pyridine. The solution was reduced with hydrogen balloon and monitored using TLC. After all the azobenzene was converted the reaction mixture was quickly filtered, and the solvent was removed to get the desired hydrazobenzene in quantitative yield.

### **General procedure for the *t*BuOK-triggered synthesis of azobenzene from hydrazobenzene**

Under ambient condition, a pressure tube was charged with 0.2 mmol of hydrazobenzene, 1.0 mL of 0.01 M *t*BuOK THF solution, then sealed and heated at 60 °C for the time shown and analyzed by gas chromatographic analyses using isooctane as internal standard. Isolated products were obtained after flash chromatography using petroleum ether:ethyl acetate (20:1) as eluent.

### **General procedure for the *t*BuOK-mediated synthesis of azobenzene from aniline**

In an autoclave, a 4 mL glass vial with a needle gas inlet was charged with 0.2 mmol of aniline, 1.0 mL of 0.2 M *t*BuOK THF solution, then the autoclave was filled with 1 bar O<sub>2</sub>, sealed and heated at 100 °C for the time shown and analyzed by gas chromatographic analyses using isooctane as internal standard. Isolated products were obtained after flash chromatography using petroleum ether: ethyl acetate (20:1) as eluent.

### **General procedure for the *t*BuOK-mediated synthesis of imine from *N*-benzylaniline**

In an autoclave, a 4 mL glass vial with a needle gas inlet was charged with 0.2 mmol of *N*-benzylaniline, 1.0 mL of 0.2 M *t*BuOK THF solution, then the autoclave was filled with 1 bar O<sub>2</sub>, sealed and heated at 130 °C for the time shown and analyzed by gas chromatographic analyses using isooctane as internal standard. Isolated products were obtained after flash chromatography using petroleum ether: ethyl acetate (20:1) as eluent.

## Supplementary Tables

**Table S1.** Condition optimization for *t*BuOK-triggered unsymmetrical disulfides production<sup>a</sup>

Cc1ccc(SSc2ccc(C)cc2)cc1 **1a** or Cc1ccc(S)cc1 **1a'** + CC(C)(C)SSC(C)(C)C **2a**  $\xrightarrow[\text{T, air, THF, 8 h}]{t\text{BuOK (5 mol\%)}}$  Cc1ccc(SCC(C)(C)C)cc1 **3a**

entries	reactant	T [°C]	<b>3a</b> yields [%] <sup>b</sup>
1	<b>1a</b>	100	96
2	<b>1a</b>	60	95
3	<b>1a'</b>	60	92
4 <sup>c</sup>	<b>1a</b>	60	0

<sup>a</sup>*p*-Tolyl disulfide (0.1 mmol, 24.6 mg) or *p*-thiocresol (0.2 mmol, 24.8 mg), *t*BuOK (0.01 mmol), THF (1.0 mL) in 38 mL pressure tube and heat for 8 h at temperature shown in the table; <sup>b</sup>yields were determined by GC using isooctane as internal standard; <sup>c</sup>reaction was performed without *t*BuOK. There were no other side products from thiols or disulfide detected.

**Table S2.** Base effect on the oxidative dehydrogenation of *p*-thiocresol **1a'** to *p*-tolyl disulfide **1a**.<sup>a</sup>

$2 \times$  Cc1ccc(S)cc1 **1a'**  $\xrightarrow[\text{THF, air, 25 °C, 2 - 4h}]{\text{bases (5 mol\%)}}$  Cc1ccc(SSc2ccc(C)cc2)cc1 **1a**

entries	bases	yields [%] <sup>b</sup>
1	<i>t</i> BuOK	95
2	<i>t</i> BuOLi	77
3	<i>t</i> BuONa	84
4	CS <sub>2</sub> CO <sub>3</sub>	61
5	MeONa	74
6	EtONa	80
7	NaHCO <sub>3</sub>	15
8	-	3

<sup>a</sup>*p*-thiocresol (0.2 mmol, 24.8 mg), bases (0.01 mmol), THF 1.0 mL in 20 mL sample vial, 25 °C, 2 h; <sup>b</sup>yields were determined by GC using isooctane as internal standard.

**Table S3.** Temperature optimization for the *t*BuOK-triggered oxidative coupling of *p*-thiocresol with *tert*-butylthiol<sup>a</sup>

Cc1ccc(S)cc1 (1a') + CC(C)(C)S  $\xrightarrow[\text{THF, air, T, 8 h}]{t\text{BuOK (5 mol\%)}}$  Cc1ccc(SSC(C)(C)C)cc1 (3a)

entries	T [°C]	yields [%] <sup>b</sup>
1	25	5
2	60	54
3	100	75

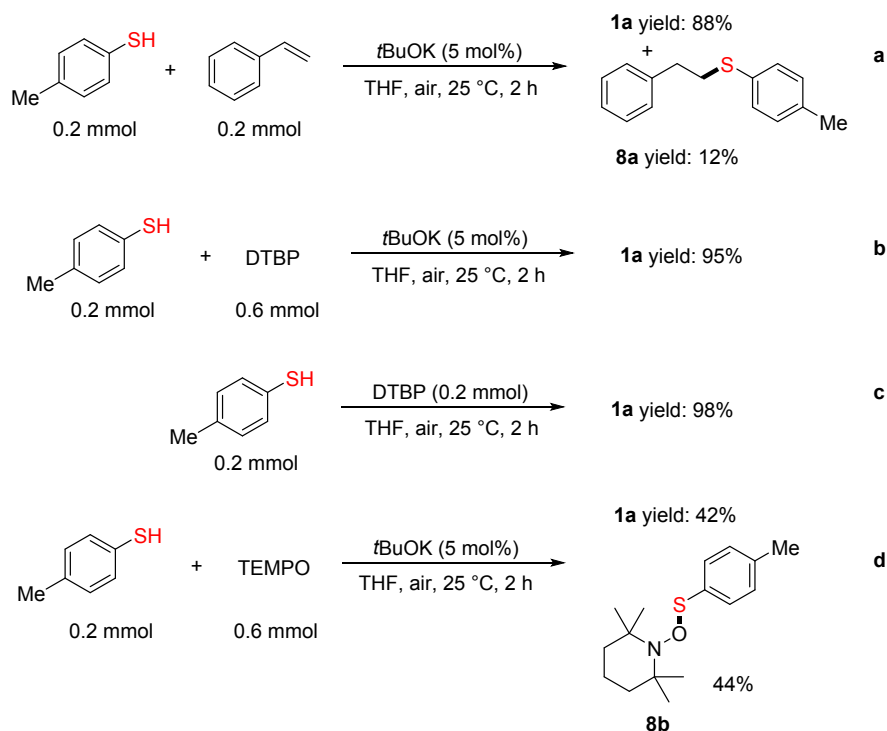
<sup>a</sup>*p*-thiocresol (0.2 mmol, 24.8 mg), *tert*-butylthiol (0.4 mmol, 45  $\mu$ l), *t*BuOK (0.01 mmol), THF (1.0 mL) in 38 mL pressure tube and heat for 8 h at temperature shown in the table; <sup>b</sup>yields were determined by GC using isooctane as internal standard. There were no other side products from thiols or disulfide detected.

**Table S4.** Comparison of our results with other developed system for oxidative dehydrogenation of thiols.

Entries	Catalysts	Loading [mol%]	Temperature [°C]	Yields [%]	Ref.
1	<i>t</i> BuOK	5	25	67-99	this study
2	FeCl <sub>3</sub> /NaI	10	25	96-99	2
3	cobalt(II) phthalocyanines	1	25	83-96	3
4	CsF/Celite	150	25	75-92	4
5	VOCl <sub>3</sub>	5	25	53-98	5
6	K <sub>3</sub> PO <sub>4</sub>	50	25	85-91	6
7	Et <sub>3</sub> N	100	25 and sonication	49-98	7

From the table we can see that compared to metal-catalyzed reaction our methods use cheaper and transition-metal free base *t*BuOK as catalyst. On the other hand, when compared to other base system, we have advantages of lower catalyst loading, other base system had to use at least 0.5 equiv. of base. We have inserted this table as Table S4 in the supporting information.

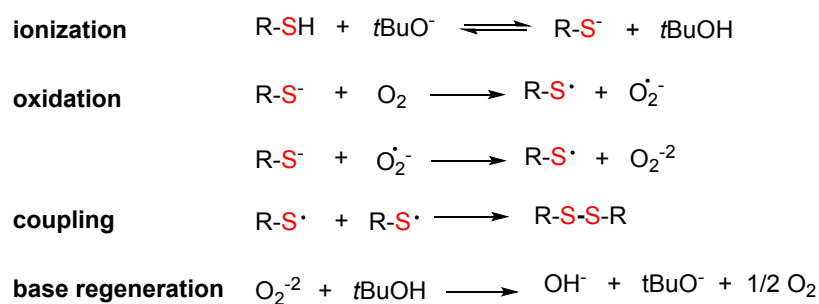
## Mechanism Investigation



**Scheme S1.** Control experiments with different radical scavengers.

In order to gain more information about the reaction mechanism, control experiments were performed (Scheme S1). Initially, styrene was added into the reaction solution, after 2 h, 12% of the linear addition product **8a** was formed with dehydrocoupling product **1a** in 88% yield (Scheme S1a). The formation of linear adduct **8a** suggested that a radical intermediate might involve in the reaction process. Addition of radical initiator DTBP did not affect the reaction results, **1a** with 95% yield was observed (Scheme S1b). This probably because DTBP itself can also mediate the S-S bond formation (Scheme S1c) or a fast reaction rate of sulfur radical self-couplings. Eventually, the addition of TEMPO successfully captured the sulfur radical and gave the adduct **8b** in 44% yield (Scheme S1d).

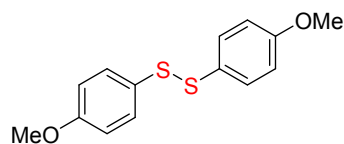




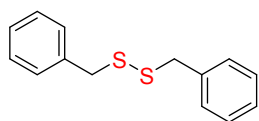
**Scheme S2.** Proposed reaction pathway.

Based on the mechanism studies and literature reports,<sup>8</sup> we proposed the following reaction mechanism (Scheme S2): Firstly, thiol was deprotonated to form thiolate anion, which was oxidized subsequently by oxygen to form sulfur radical species and superoxide anion, the superoxide anion could also oxidize thiolate anion to form peroxide. Coupling of sulfur radical gave disulfide product. Finally, the reaction of peroxide with *t*BuOH regenerated *t*BuO<sup>•</sup>.

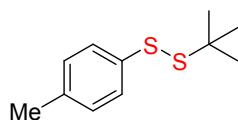
## Products Characterization



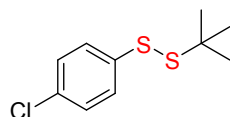
**1,2-bis(4-methoxyphenyl)disulfide 1b:** light yellow solid was obtained in 93% yield, melting point: 44 - 46 °C.  $^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  7.39 (d,  $J$  = 8.1 Hz, 4H), 6.82 (d,  $J$  = 8.2 Hz, 4H), 3.78 (s, 6H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  159.9, 132.6, 128.4, 114.6, 55.3.



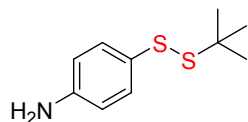
**1,2-dibenzyl disulfide 2d:** white solid was obtained in 75% yield, melting point: 70 - 73 °C.  $^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  7.40 – 7.35 (m, 5H), 7.34 – 7.28 (m, 5H), 3.67 (s, 4H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  137.4, 129.4, 128.5, 127.4, 43.3.



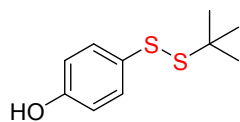
**1-(tert-butyl)-2-(p-tolyl)disulfide 3a:** colorless liquid was obtained in 75% yield.  $^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  7.49 (d,  $J$  = 8.2 Hz, 2H), 7.14 (d,  $J$  = 8.4 Hz, 2H), 2.36 (s, 3H), 1.34 (s, 9H).  $^{13}\text{C}$  NMR (101 MHz, Chloroform-*d*)  $\delta$  136.3, 135.4, 129.5, 127.5, 49.0, 29.9, 21.0.



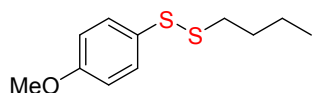
**1-(tert-butyl)-2-(4-chlorophenyl)disulfide 3d:** colorless liquid was obtained in 82% yield.  $^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  7.54 (d,  $J$  = 8.6 Hz, 2H), 7.31 (d,  $J$  = 8.6 Hz, 2H), 1.35 (s, 9H).  $^{13}\text{C}$  NMR (101 MHz, Chloroform-*d*)  $\delta$  137.5, 132.2, 128.8, 128.2, 49.5, 29.8.



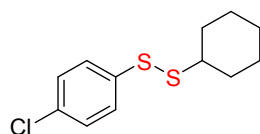
**4-(tert-butyl disulfide)aniline 3e:** colorless liquid was obtained in 88% yield.  $^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  7.38 (d,  $J$  = 7.6 Hz, 2H), 6.73 – 6.62 (m, 2H), 4.41 (s, 2H), 1.29 (s, 9H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  144.3, 131.0, 128.4, 116.3, 48.8, 30.0. HRMS calcd for  $\text{C}_{10}\text{H}_{16}\text{NS}_2$ : 214.0724  $[\text{M}+\text{H}]^+$ , found: 214.0718.



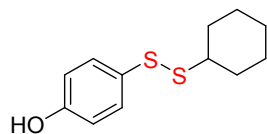
**4-(tert-butylidisulfideyl)phenol 3j:** colorless liquid was obtained in 48% yield.  $^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  7.45 (d,  $J$  = 8.5 Hz, 2H), 6.79 (s, 2H), 5.02 (s, 1H), 1.30 (s, 9H).  $^{13}\text{C}$  NMR (101 MHz, Chloroform-*d*)  $\delta$  154.7, 130.4, 130.1, 115.9, 49.0, 29.9. HRMS calcd for  $\text{C}_{10}\text{H}_{15}\text{OS}_2$ : 215.0564  $[\text{M}+\text{H}]^+$ , found: 215.0563.



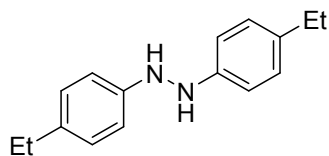
**1-butyl-2-(4-methoxyphenyl)disulfide 3k:** colorless liquid was obtained in 48% yield.  $^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  7.48 (d,  $J$  = 8.5 Hz, 2H), 6.86 (d,  $J$  = 8.8 Hz, 2H), 3.81 (s, 3H), 2.73 (t,  $J$  = 7.3 Hz, 2H), 1.69 – 1.63 (m, 2H), 1.40 (dd,  $J$  = 14.8, 7.4 Hz, 2H), 0.89 (t,  $J$  = 7.4 Hz, 3H).  $^{13}\text{C}$  NMR (101 MHz, Chloroform-*d*)  $\delta$  159.5, 131.6, 128.6, 114.6, 107.1, 55.4, 38.6, 30.8, 21.6, 13.6. HRMS calcd for  $\text{C}_{11}\text{H}_{16}\text{OS}_2$ : 229.0721  $[\text{M}+\text{H}]^+$ , found: 229.0716.



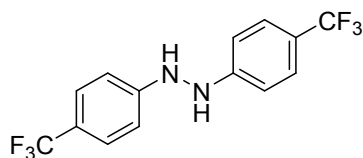
**1-(4-chlorophenyl)-2-cyclohexyldisulfide 3h:** colorless liquid was obtained in 87% yield.  $^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  7.51 (d,  $J$  = 8.6 Hz, 2H), 7.31 (d,  $J$  = 8.6 Hz, 2H), 2.87 – 2.80 (m, 1H), 2.05 – 2.02 (m, 2H), 1.82 – 1.79 (m, 2H), 1.65 – 1.62 (m, 1H), 1.42 – 1.21 (m, 5H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  137.2, 132.3, 128.9, 128.2, 50.0, 32.6, 26.0, 25.5.



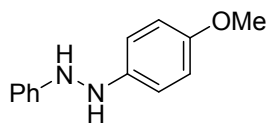
**4-(cyclohexyldisulfideyl)phenol 3o:** colorless liquid was obtained in 61% yield.  $^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  7.47 (d,  $J$  = 8.8 Hz, 2H), 6.83 (d,  $J$  = 8.8 Hz, 2H), 5.09 (s, 1H), 2.89 – 2.81 (m, 1H), 2.06 – 2.03 (m, 2H), 1.82 – 1.77 (m, 2H), 1.66 – 1.61 (m, 1H), 1.28 – 1.43 (m, 5H).  $^{13}\text{C}$  NMR (101 MHz, Chloroform-*d*)  $\delta$  155.0, 130.9, 129.6, 116.0, 49.7, 32.5, 25.9, 25.6. HRMS calcd for  $\text{C}_{12}\text{H}_{17}\text{OS}_2$ : 241.0721  $[\text{M}+\text{H}]^+$ , found: 241.0716.



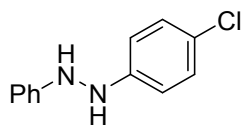
**1,2-bis(4-ethylphenyl)hydrazine 4b:** yellow solid was obtained in 57% yield in two steps, melting point: 110 - 113 °C.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  6.98 (d,  $J$  = 8.4 Hz, 2H), 6.62 (d,  $J$  = 8.2 Hz, 2H), 3.52 (s, 2H), 2.54 (q,  $J$  = 7.6 Hz, 2H), 1.18 (t,  $J$  = 7.6 Hz, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  144.0, 134.4, 128.5, 115.2, 27.9, 15.9.



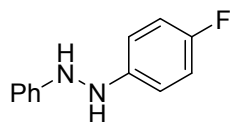
**1,2-bis(4-(trifluoromethyl)phenyl)hydrazine 4c:** brown solid was obtained in 60% yield in two steps, melting point: 88 - 90 °C.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.47 (d,  $J$  = 8.3 Hz, 4H), 6.88 (d,  $J$  = 8.3 Hz, 4H), 5.95 (s, 2H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  150.8, 126.9 (d,  $J$  = 3.9 Hz), 124.6 (q,  $J$  = 270.8 Hz), 122.2 (q,  $J$  = 37.0, 34.6 Hz), 111.7.



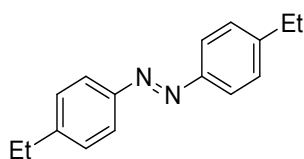
**1-(4-methoxyphenyl)-2-phenylhydrazine 4d:** pale yellow solid was obtained in 55% yield in two steps, melting point: 78 - 81 °C.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.21 (t,  $J$  = 7.9 Hz, 2H), 6.88 – 6.82 (m, 3H), 6.80 (s, 4H), 5.59 (s, 1H), 5.45 (s, 1H), 3.75 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  142.8, 129.3, 119.8, 114.9, 113.7, 112.4, 55.7.



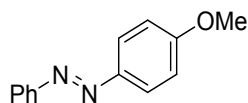
**1-(4-chlorophenyl)-2-phenylhydrazine 4e:** pale yellow solid was obtained in 69% yield in two steps, melting point: 83 - 85 °C.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.30 – 7.19 (m, 4H), 6.95 – 6.81 (m, 5H), 5.70 (s, 2H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  147.5, 129.4, 129.3, 129.2, 120.1, 119.9, 113.5, 112.3.



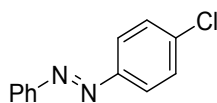
**1-(4-fluorophenyl)-2-phenylhydrazine 4f:** yellow solid was obtained in 67% yield in two steps, melting point: 58 - 60 °C.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.32 – 7.23 (m, 2H), 6.96 (t,  $J$  = 8.6 Hz, 2H), 6.88 (d,  $J$  = 8.4 Hz, 5H), 5.67 (s, 1H), 5.59 (s, 1 H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $^{13}\text{C}$  NMR (101 MHz, Chloroform- $d$ )  $\delta$  158.4, 148.7, 145.1, 129.4, 120.1, 115.8 (d,  $J$  = 22.6 Hz), 113.4 (d,  $J$  = 7.6 Hz), 112.4.



**(E)-1,2-bis(4-ethylphenyl)diazene 5b:** Yellow solid was obtained in 97% yield, melting point: 130 - 132 °C.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.90 (d,  $J$  = 8.3 Hz, 4H), 7.40 (d,  $J$  = 8.3 Hz, 4H), 2.79 (q,  $J$  = 7.6 Hz, 4H), 1.35 (t,  $J$  = 7.6 Hz, 6H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$   $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  151.1, 147.5, 128.5, 122.8, 28.8, 15.4.

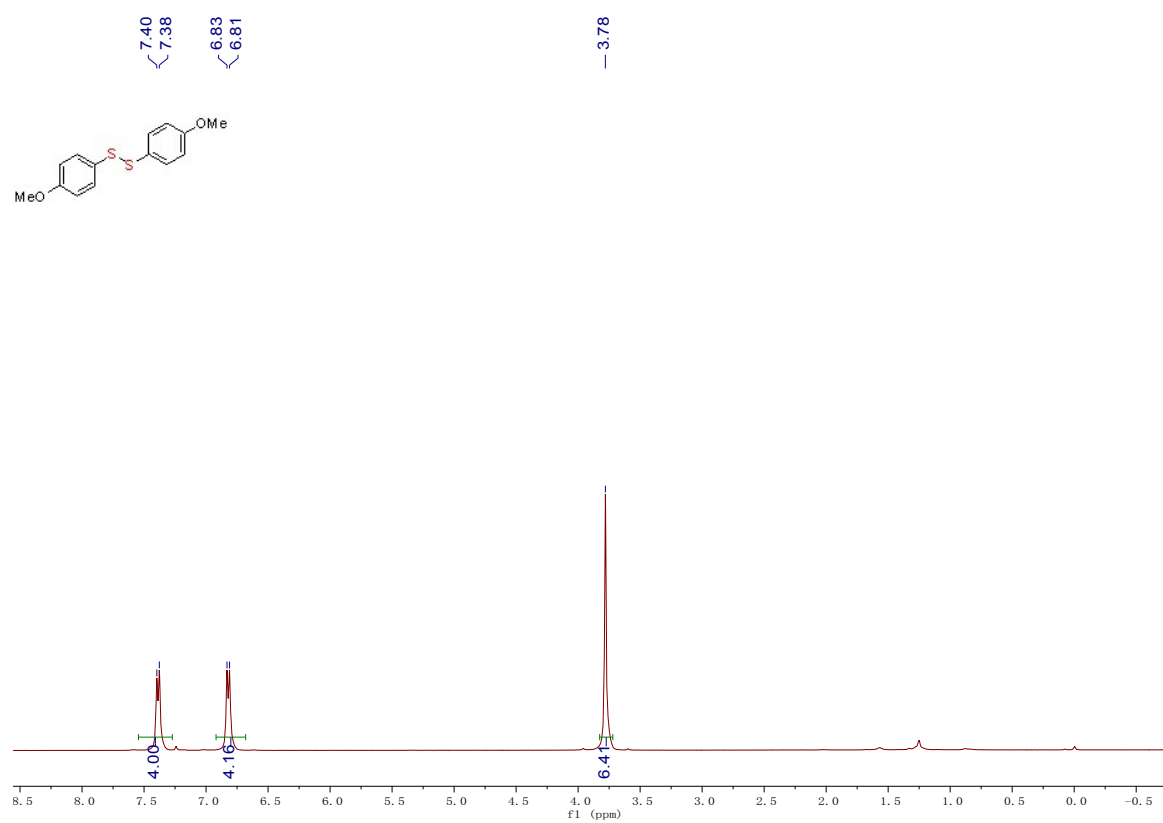


**(E)-1-(4-methoxyphenyl)-2-phenyldiazene 5d:** Pale yellow solid was obtained in 93% yield, melting point: 53 - 55 °C.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.98 (d,  $J$  = 8.7 Hz, 2H), 7.93 (d,  $J$  = 7.6 Hz, 2H), 7.52 (dt,  $J$  = 26.3, 7.1 Hz, 3H), 7.07 (d,  $J$  = 8.8 Hz, 2H), 3.95 (s, 3H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  166.4, 162.1, 152.8, 147.1, 130.3, 129.0, 124.7, 122.6, 114.2, 55.6.

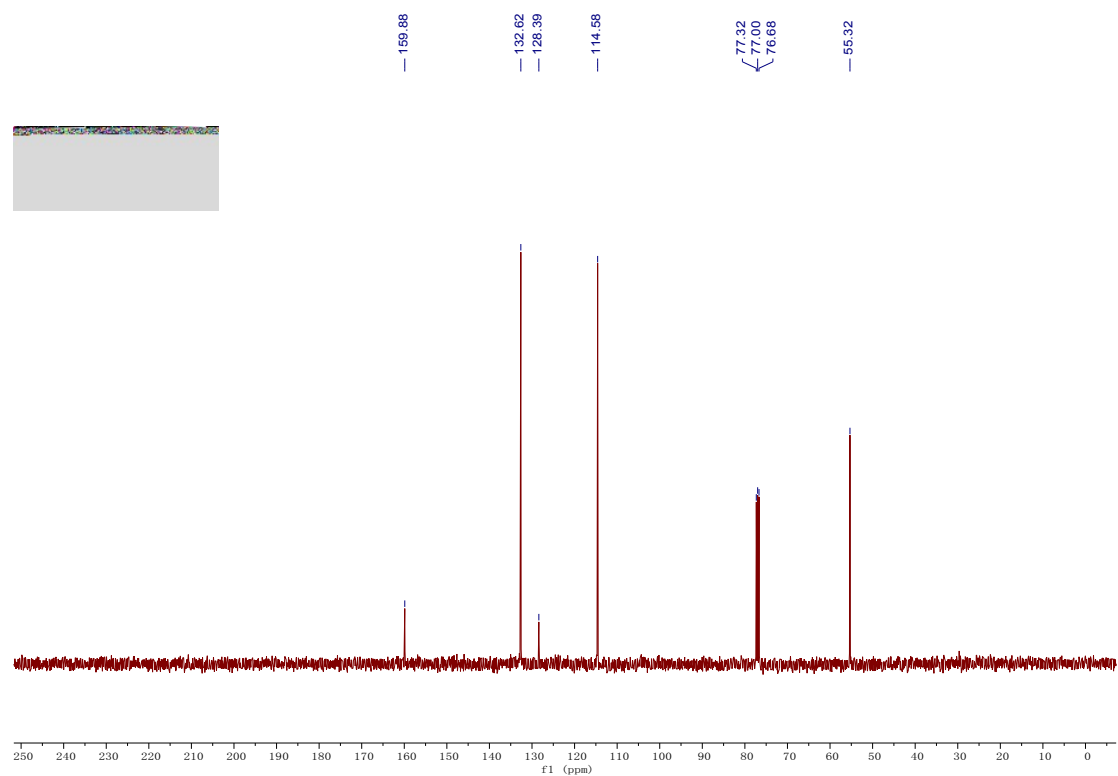


**(E)-1-(4-chlorophenyl)-2-phenyldiazene 5e:** Yellow solid was obtained in 93% yield, melting point: 83 - 85 °C.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.92 – 7.87 (dd,  $J$  = 14.5, 8.0 Hz, 4H), 7.54 – 7.48 (t,  $J$  = 9.3 Hz, 5H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$   $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  152.5, 151.0, 136.9, 131.3, 129.3, 129.1, 124.1, 122.9.

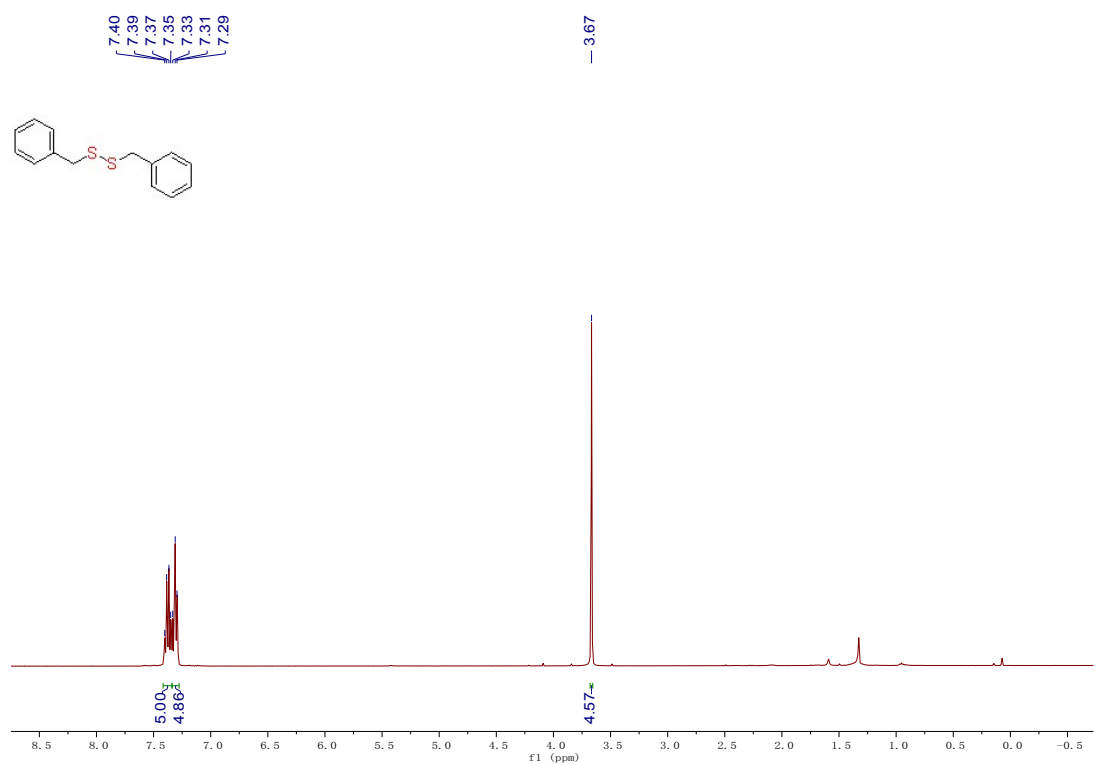
## NMR Spectra



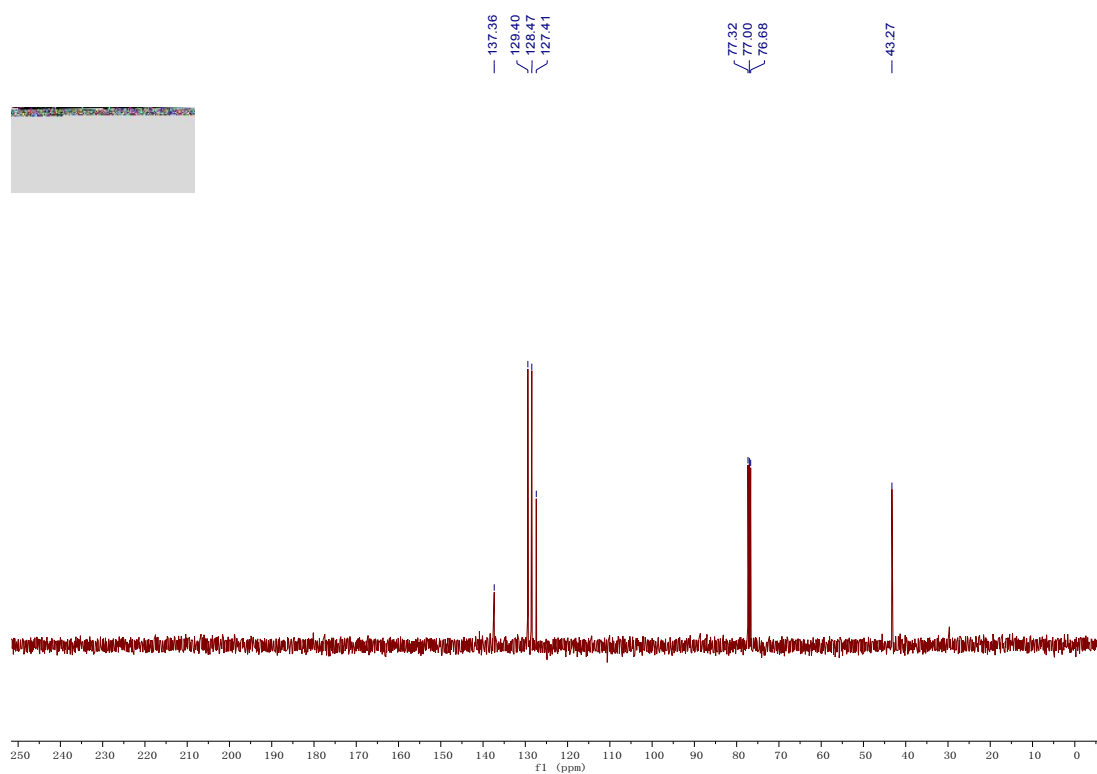
<sup>1</sup>H NMR spectrum of **1b** (Chloroform-*d*)



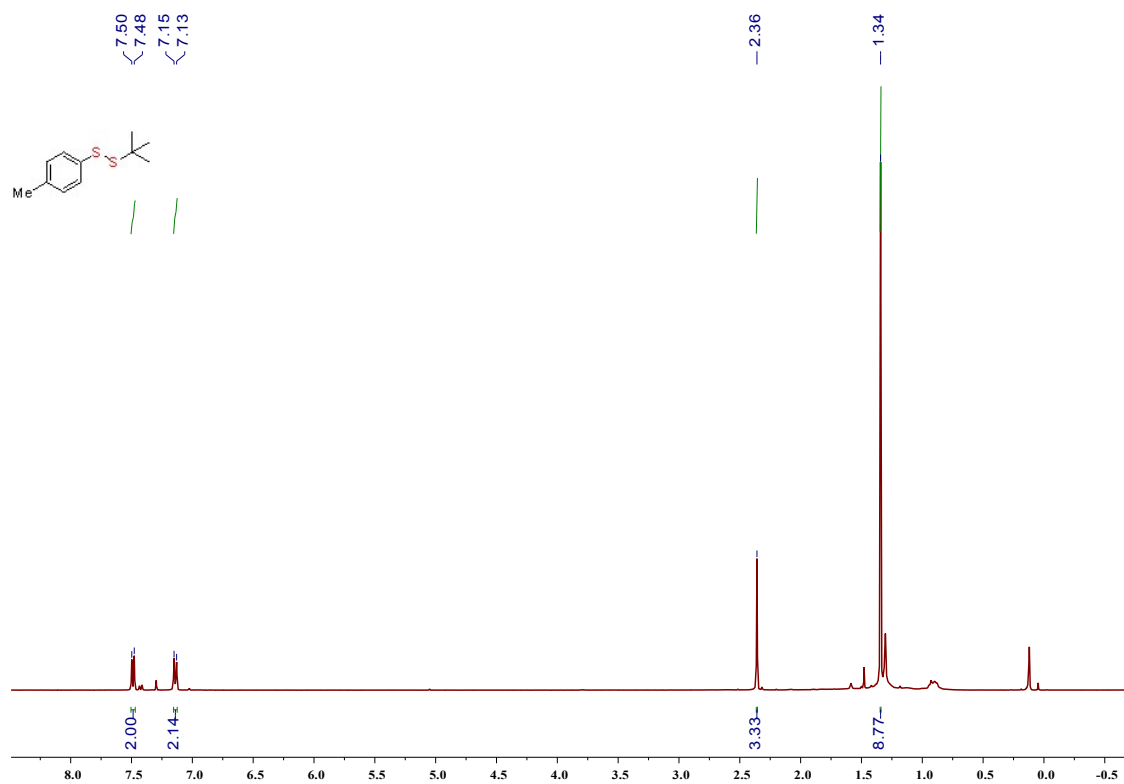
$^{13}\text{C}$  NMR spectrum of **1b** (Chloroform-*d*)



$^1\text{H}$  NMR spectrum of **2d** (Chloroform-*d*)

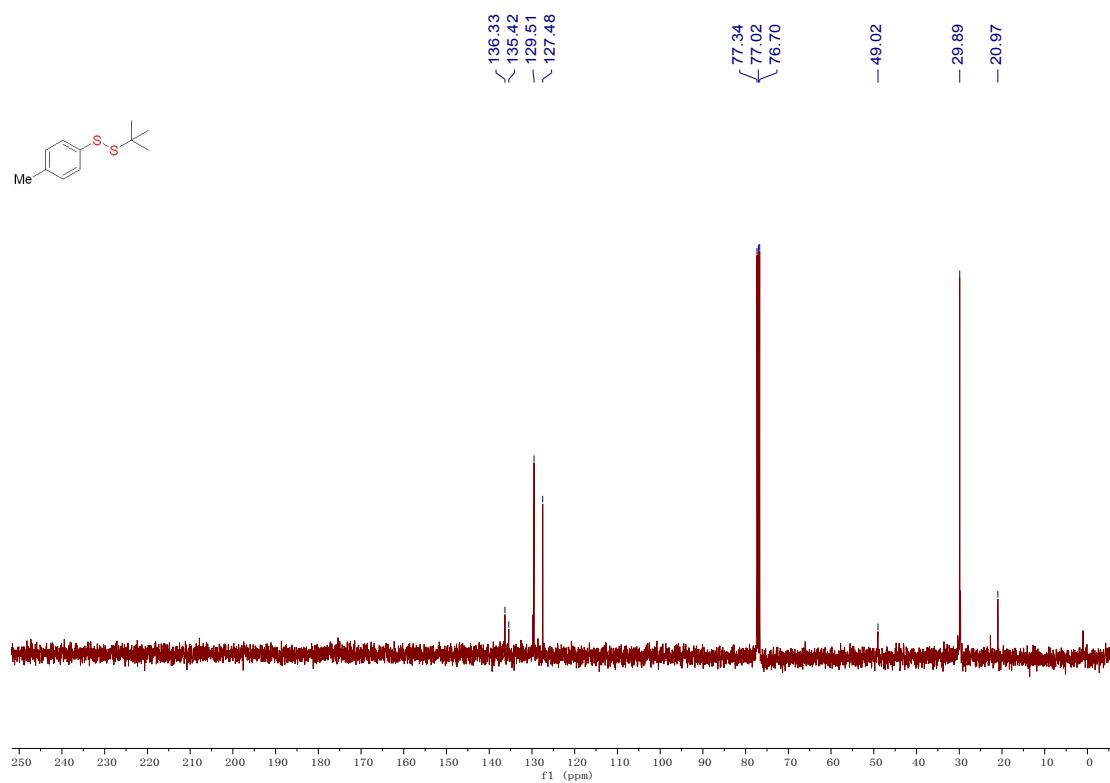


$^{13}\text{C}$  NMR spectrum of **2d** (Chloroform-*d*)

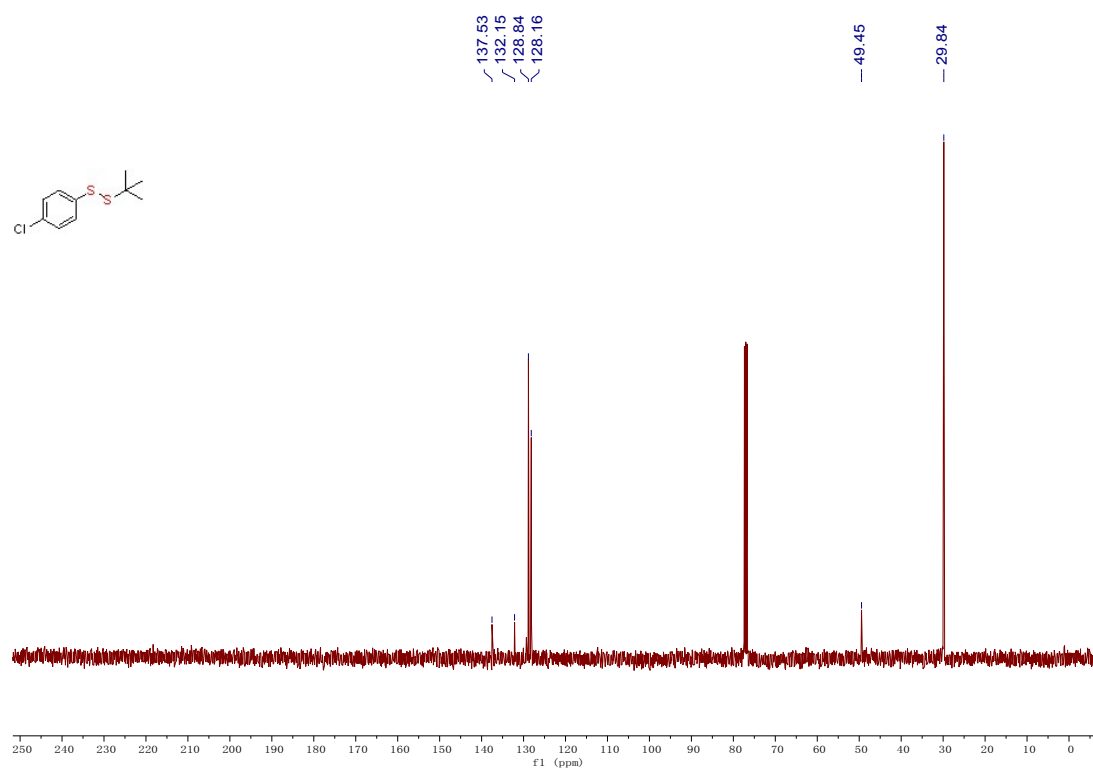
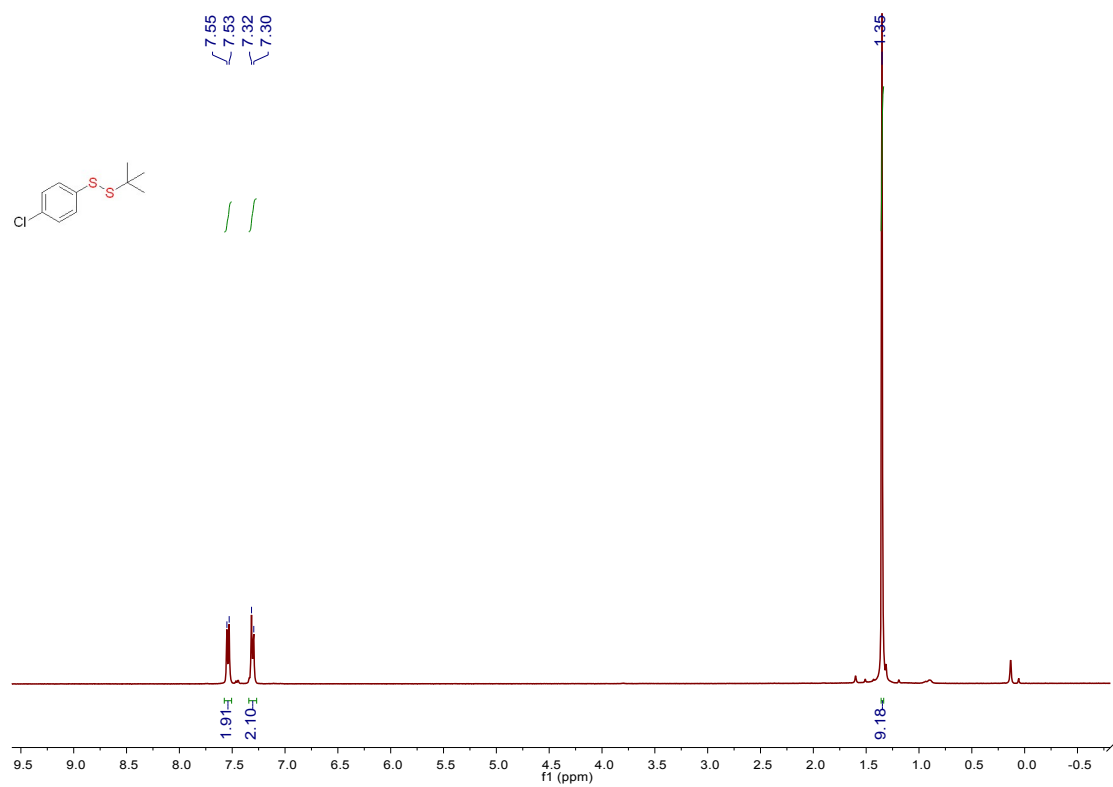


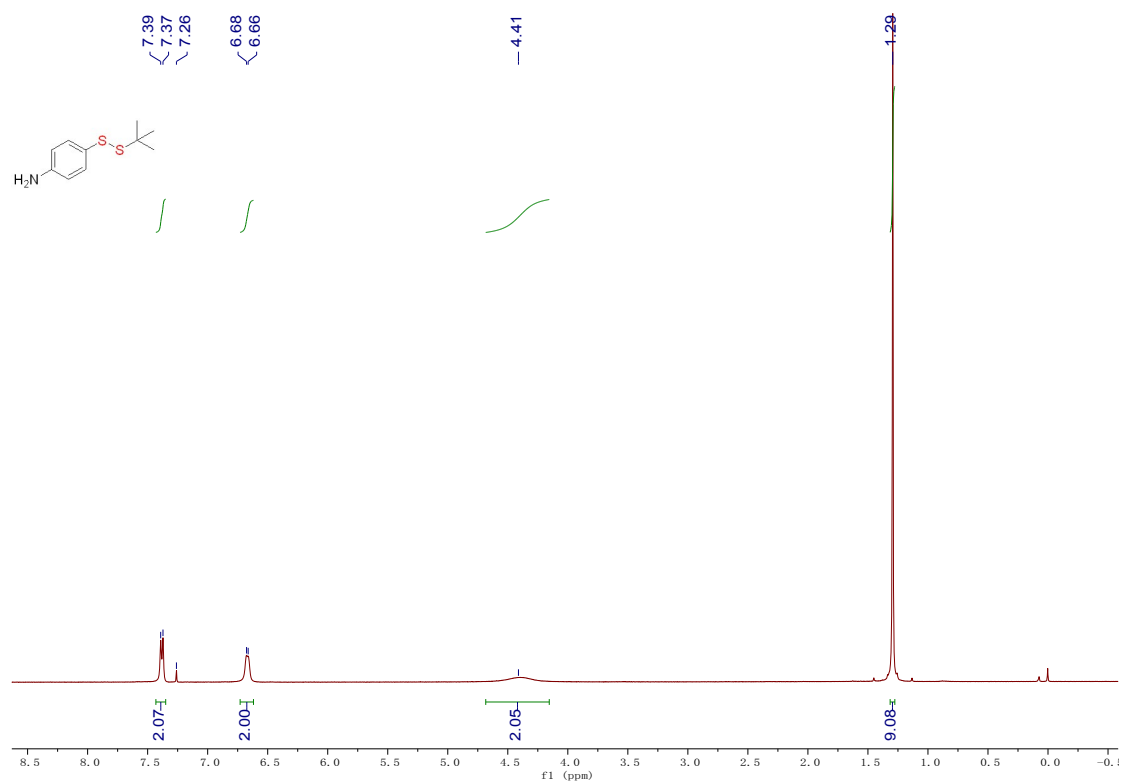


$^1\text{H}$  NMR spectrum of **3a** (Chloroform-*d*)

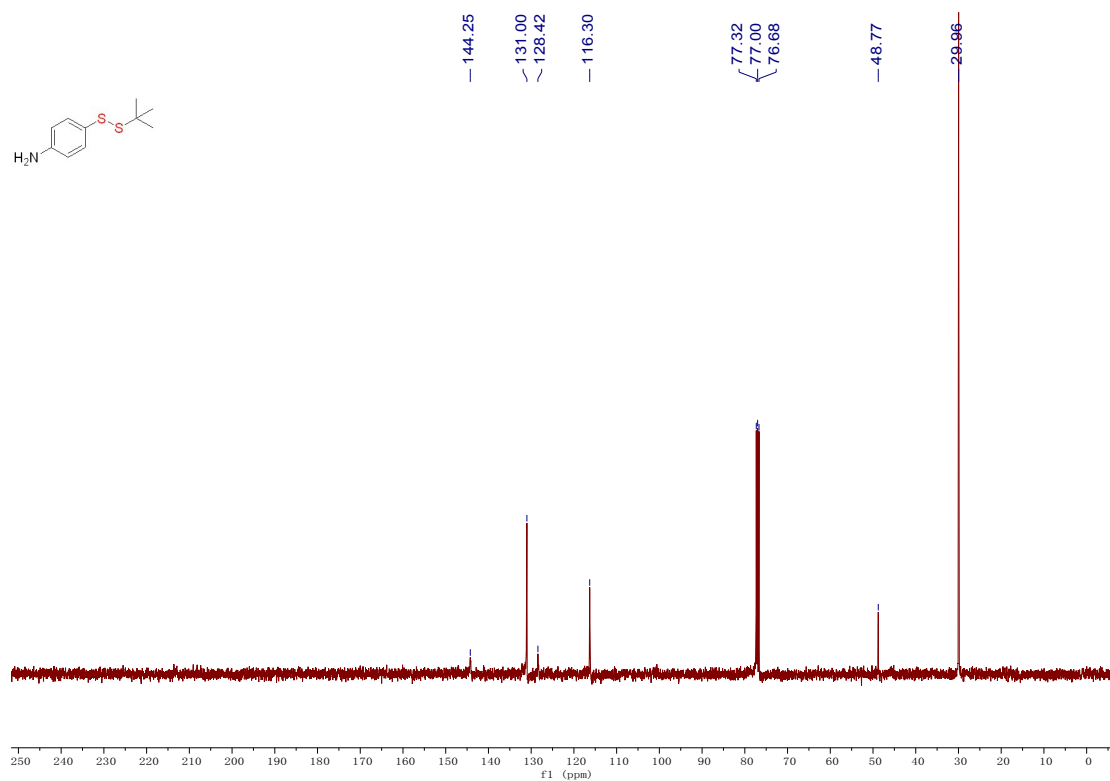


$^{13}\text{C}$  NMR spectrum of **3a** (Chloroform-*d*)

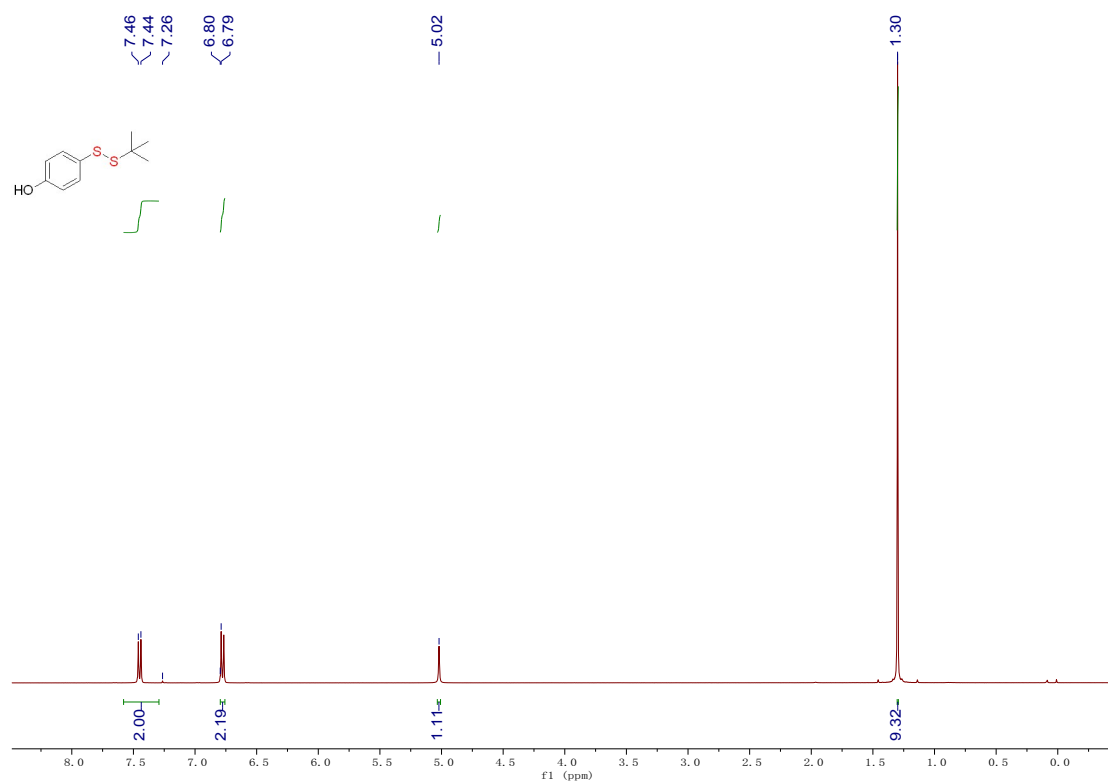




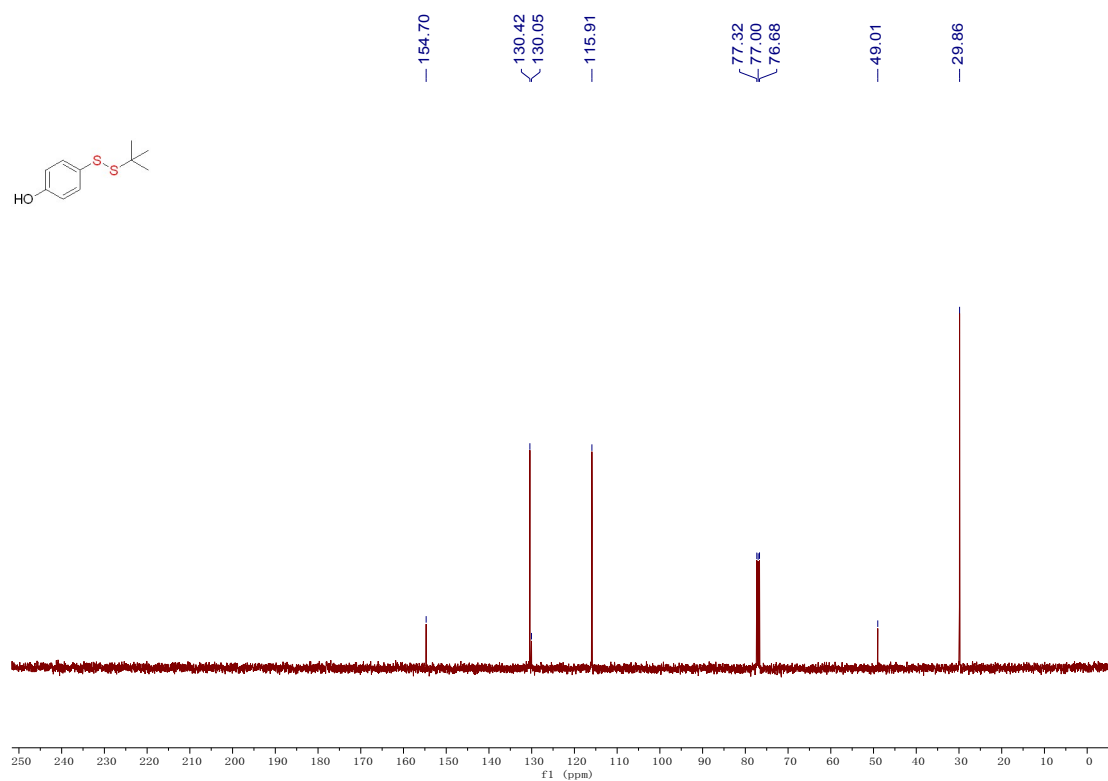
<sup>1</sup>H NMR spectrum of **3e** (Chloroform-*d*)



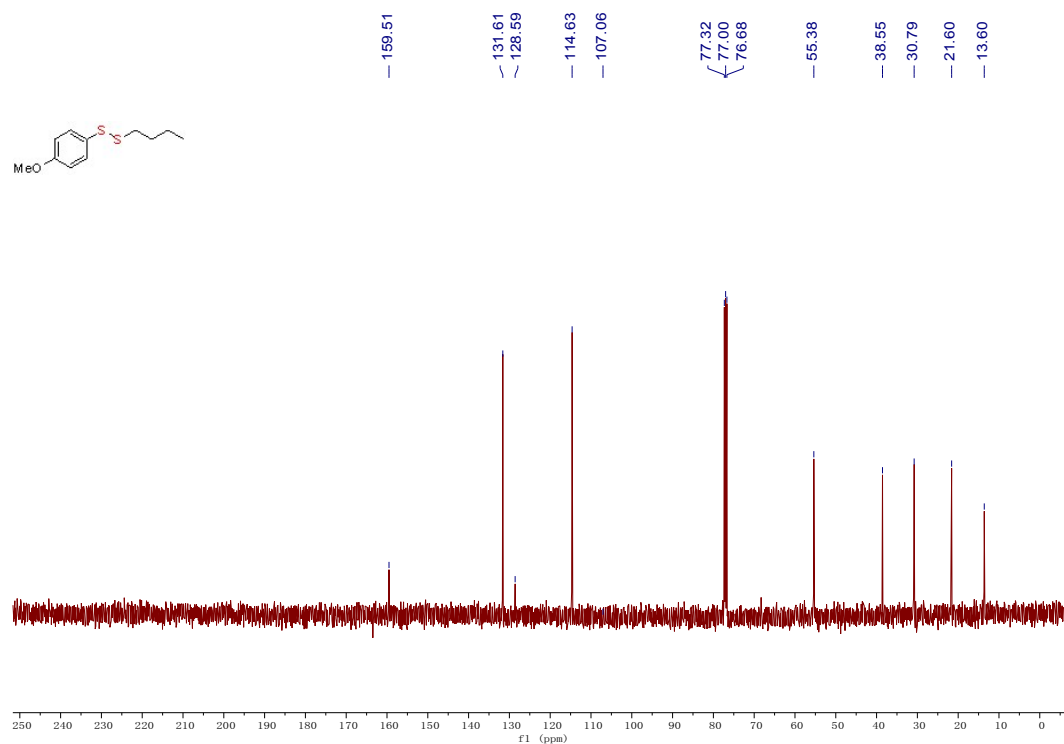
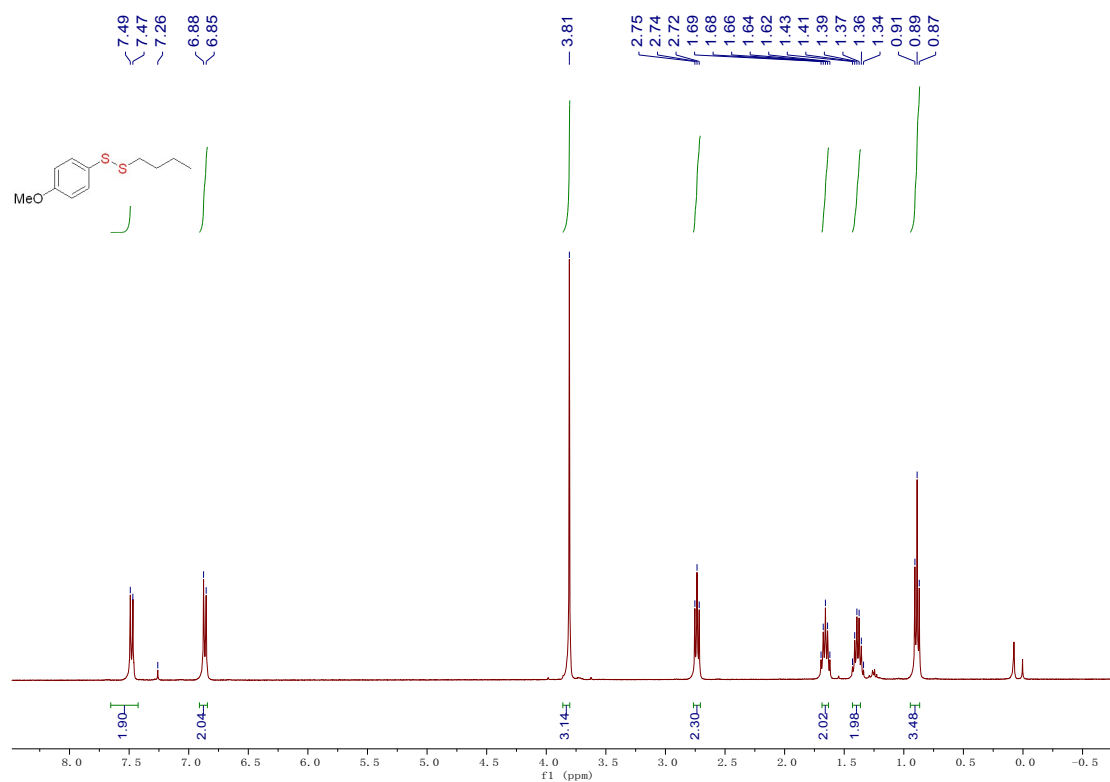
<sup>13</sup>C NMR spectrum of **3e** (Chloroform-*d*)

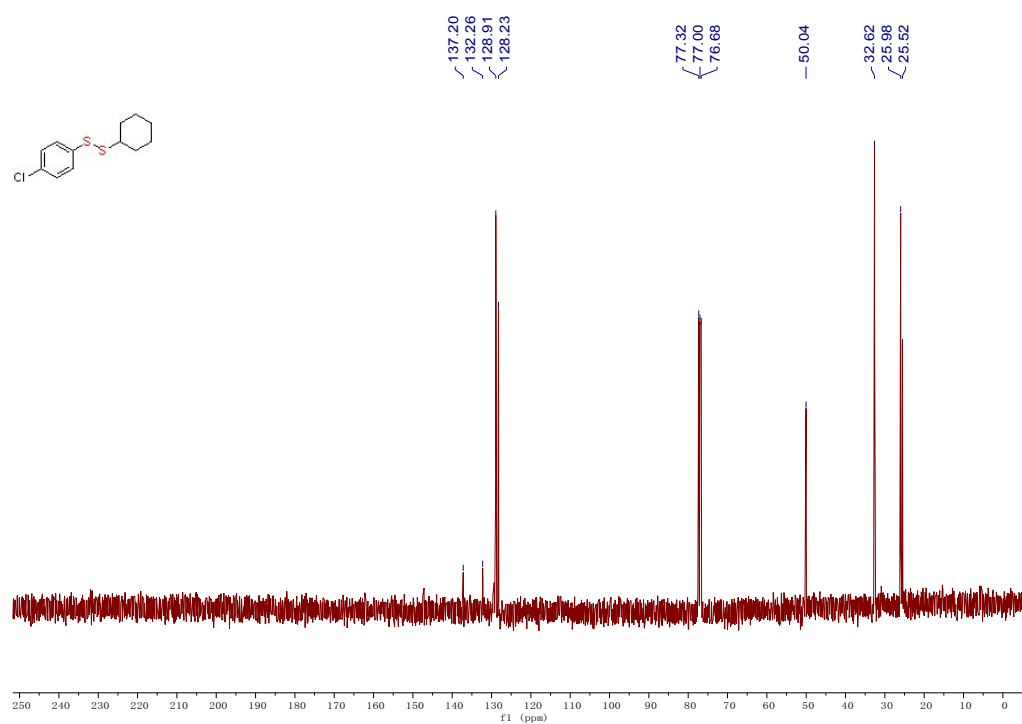
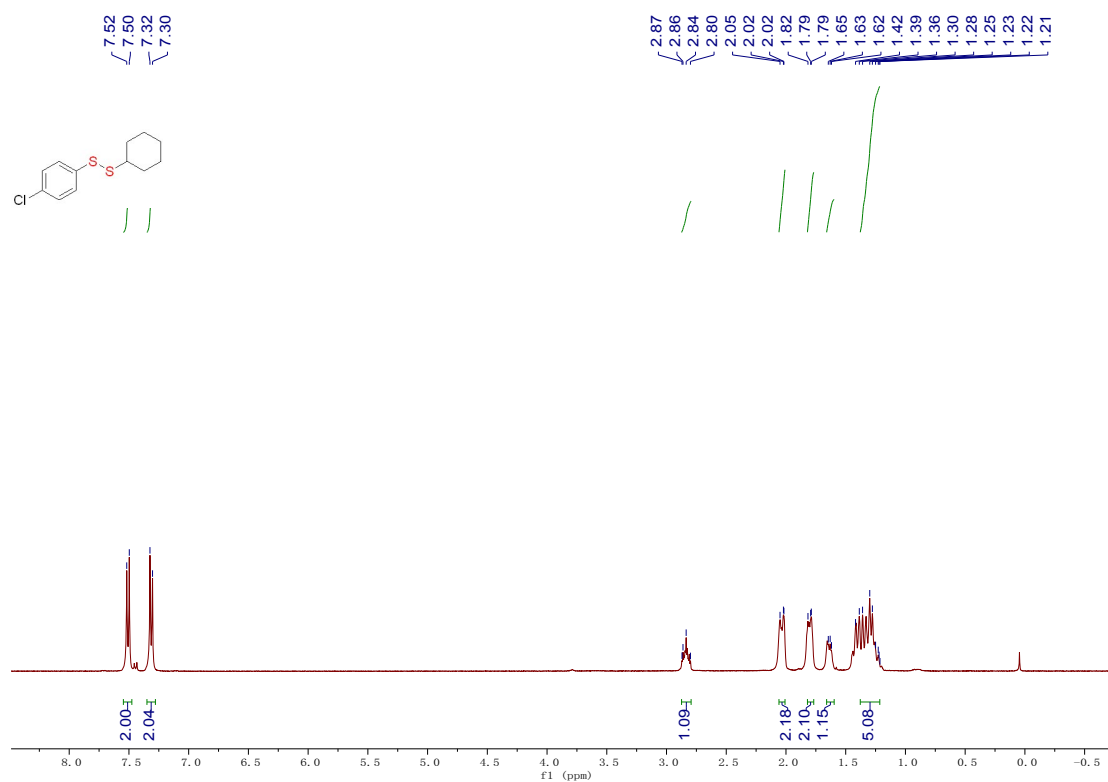


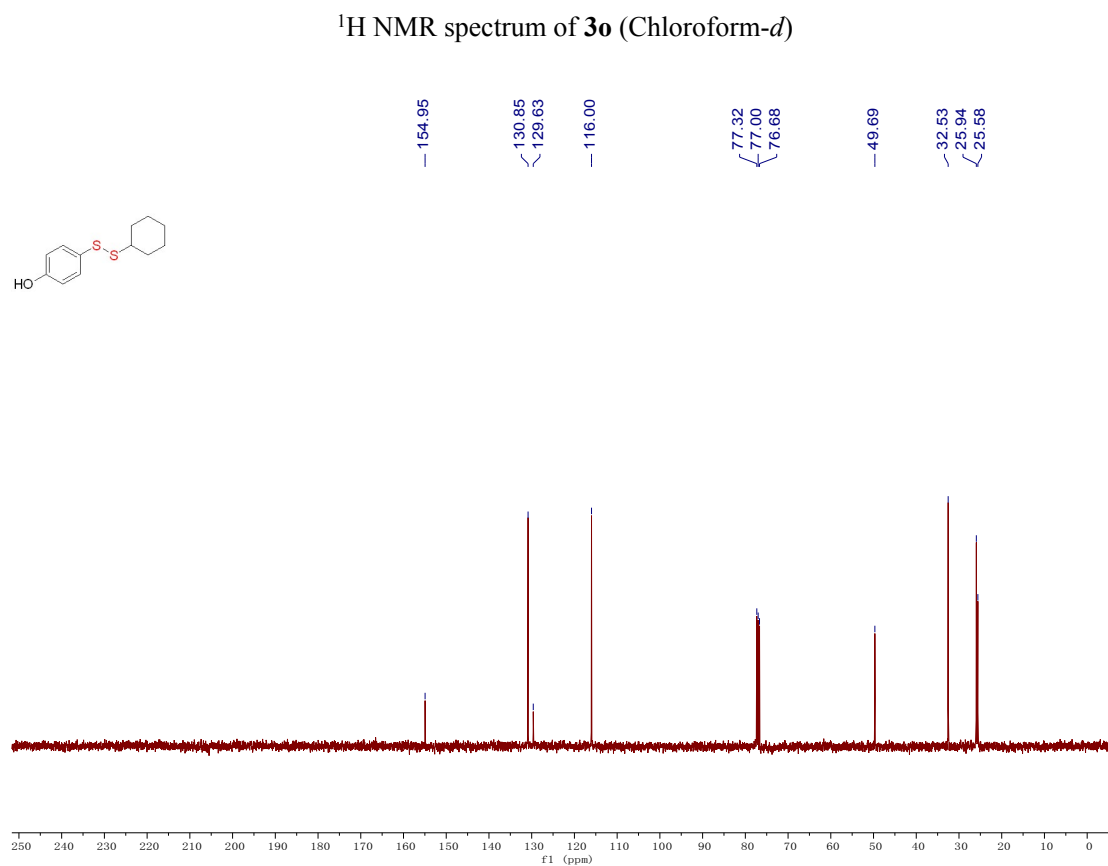
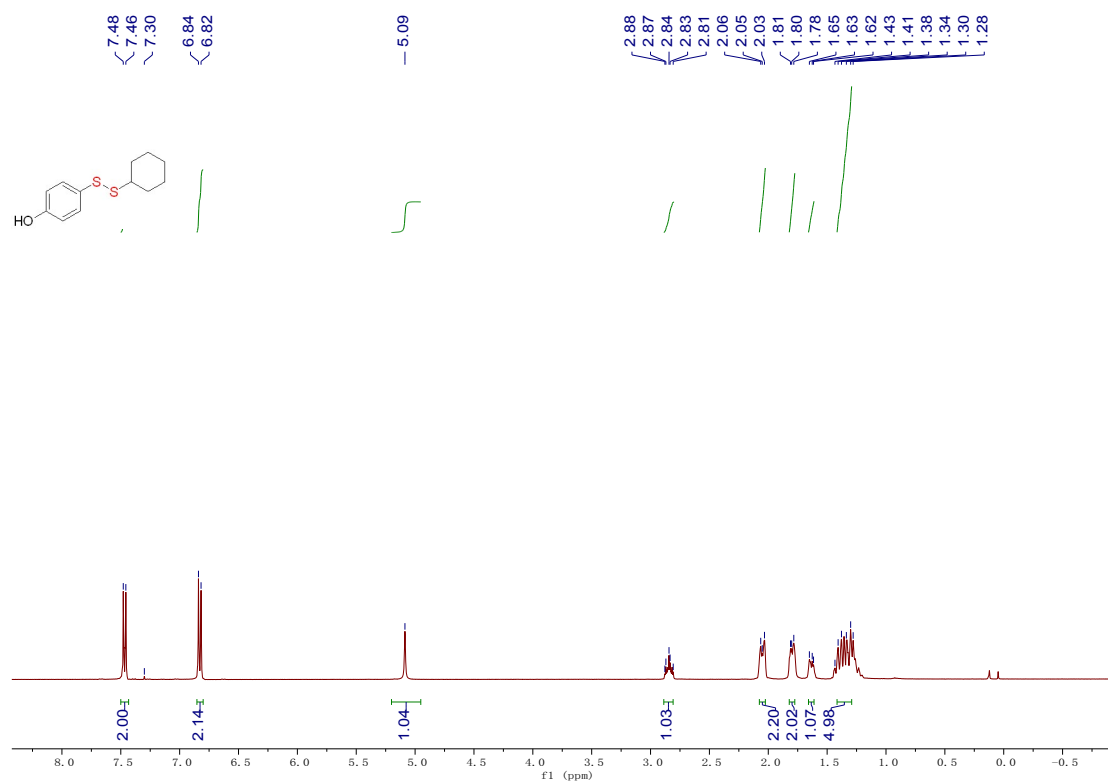
$^1\text{H}$  NMR spectrum of **3j** (Chloroform-*d*)

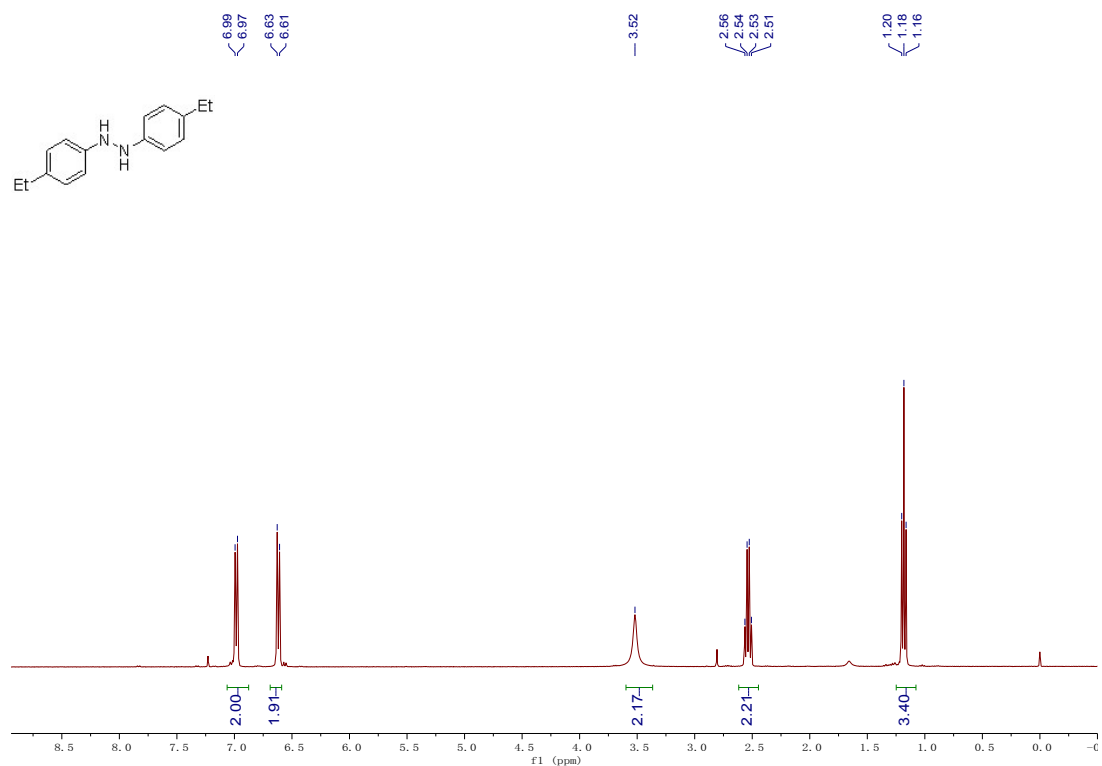


$^{13}\text{C}$  NMR spectrum of **3j** (Chloroform-*d*)

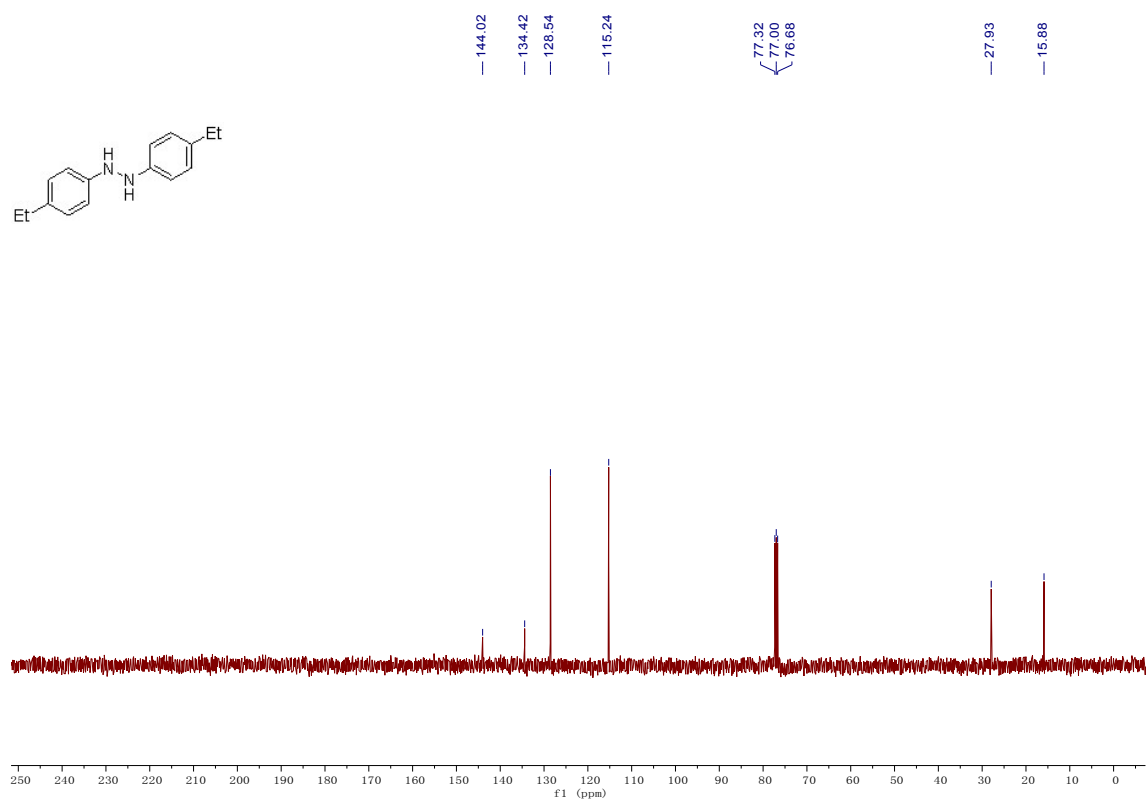






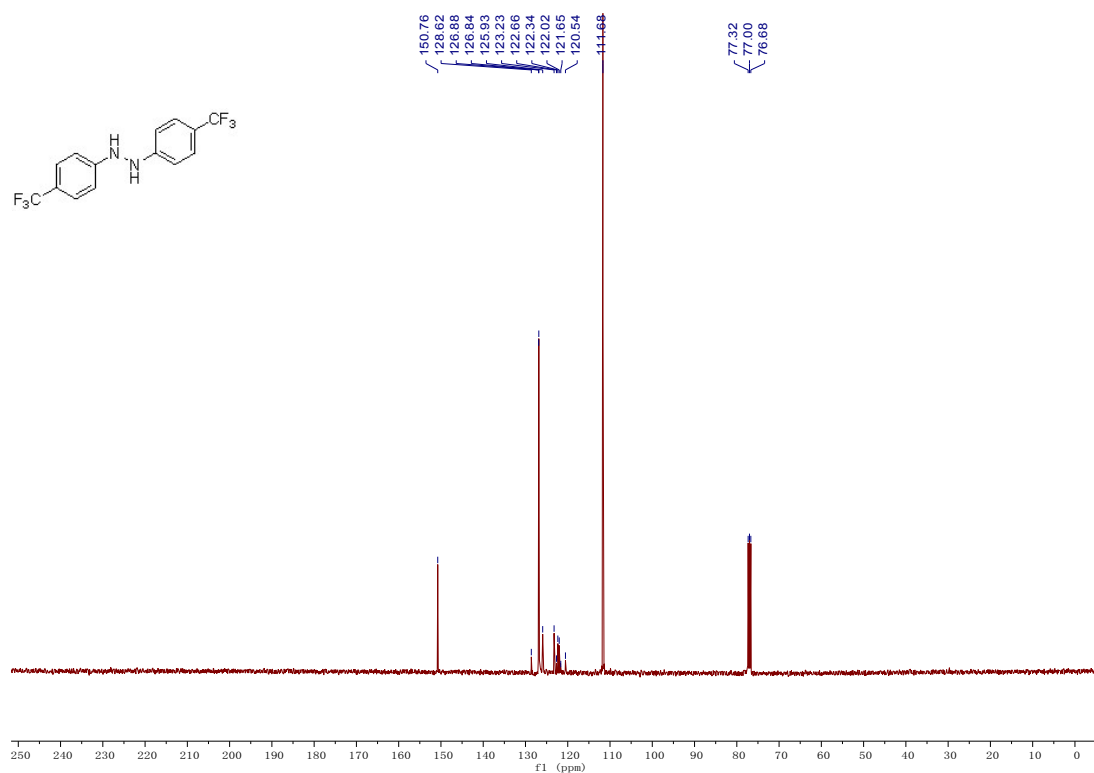
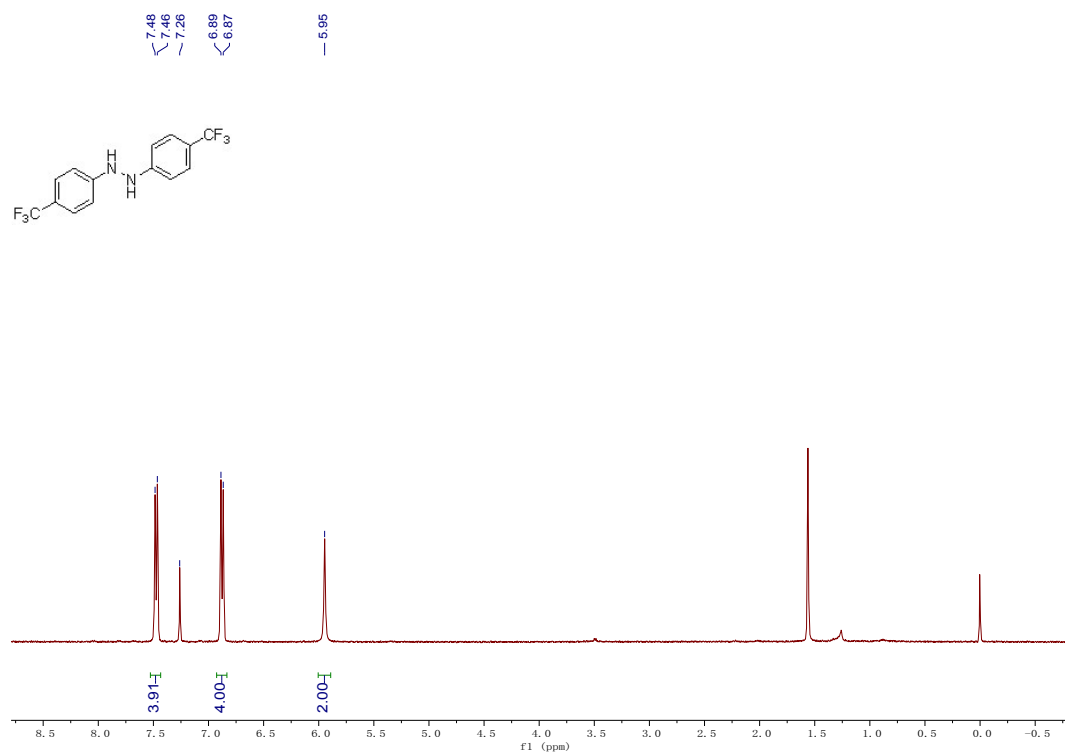


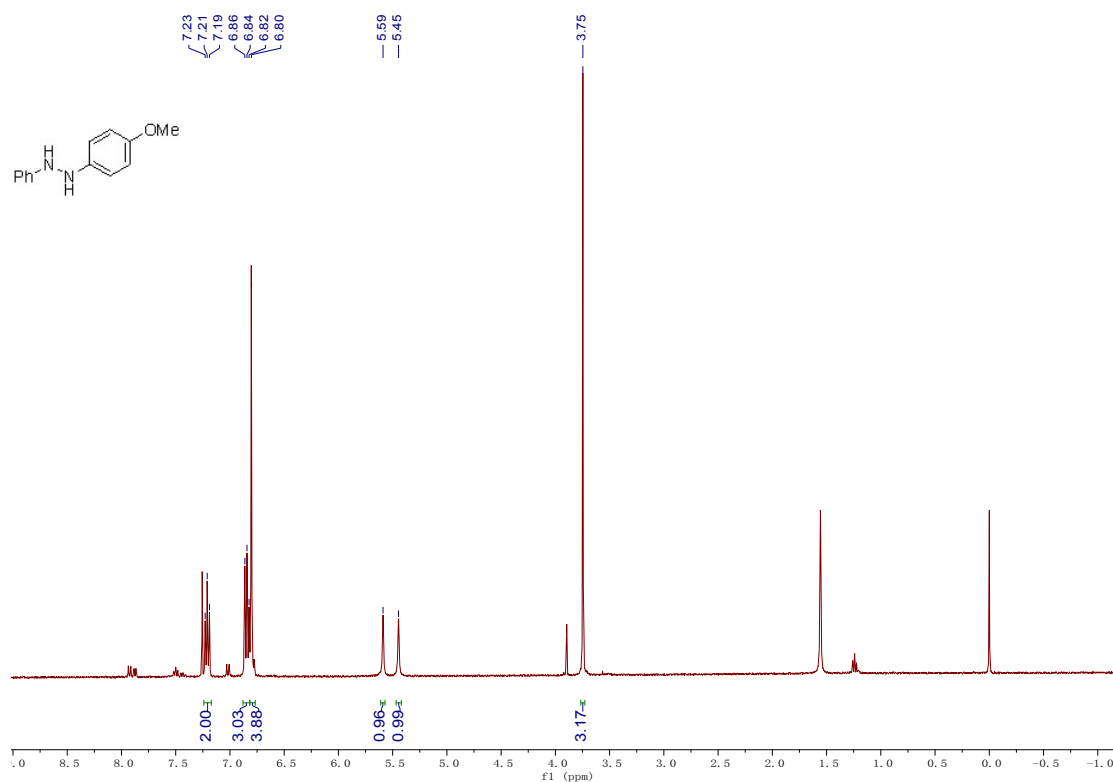
<sup>1</sup>H NMR spectrum of **4b** (Chloroform-*d*)



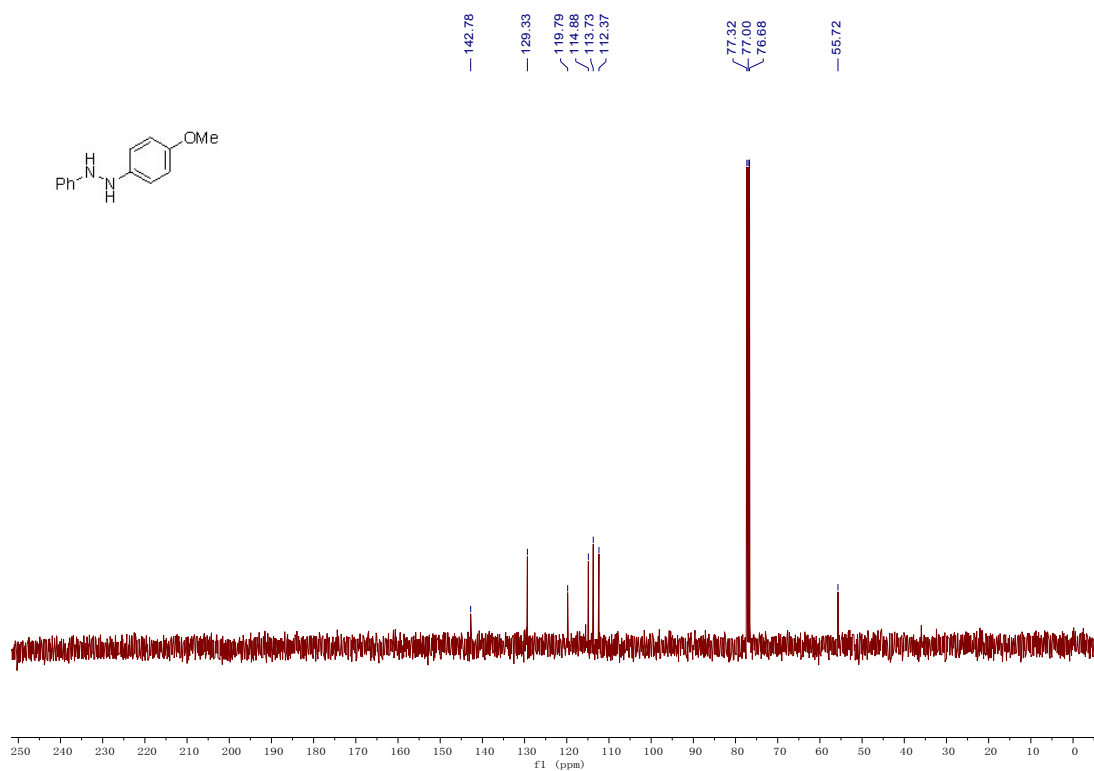
<sup>13</sup>C NMR spectrum of **4b** (Chloroform-*d*)



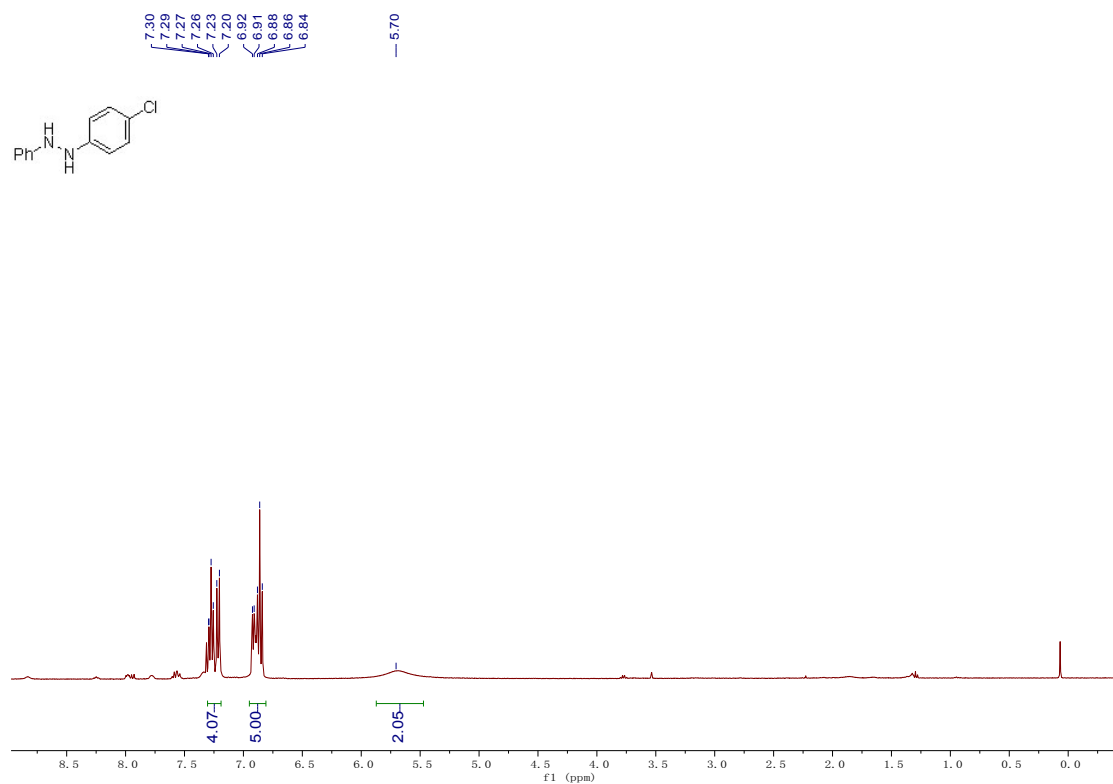




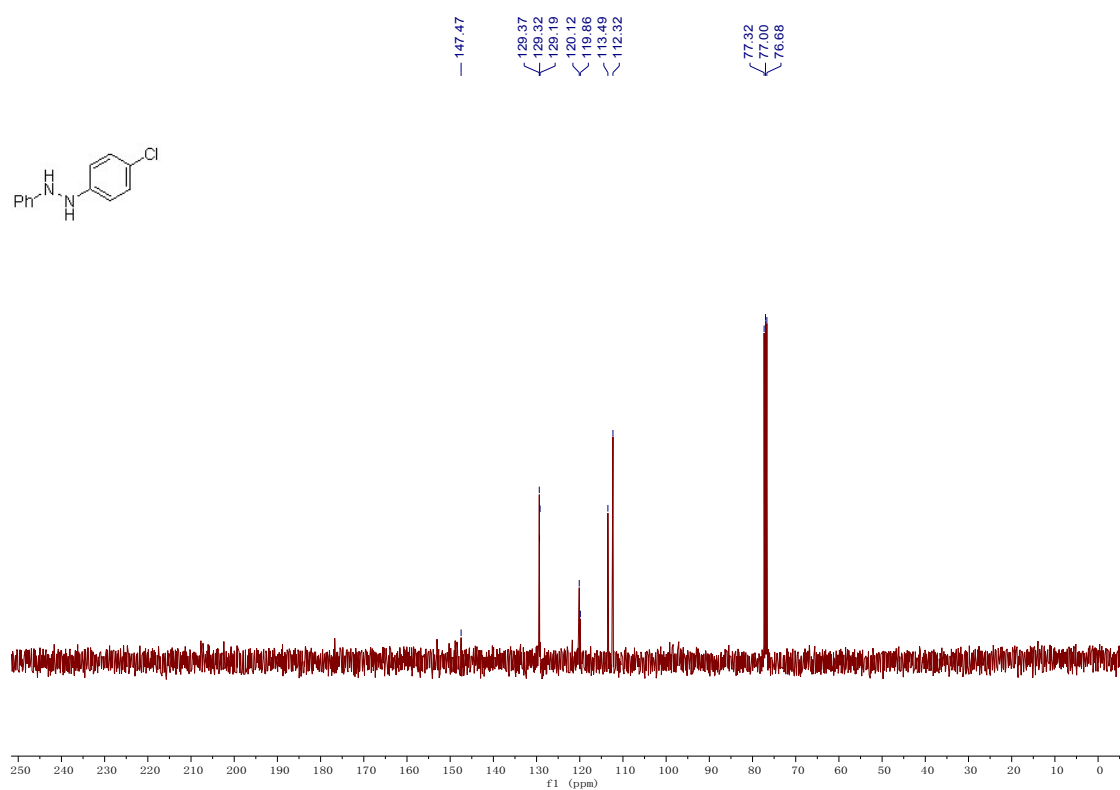
<sup>1</sup>H NMR spectrum of **4d** (Chloroform-*d*)



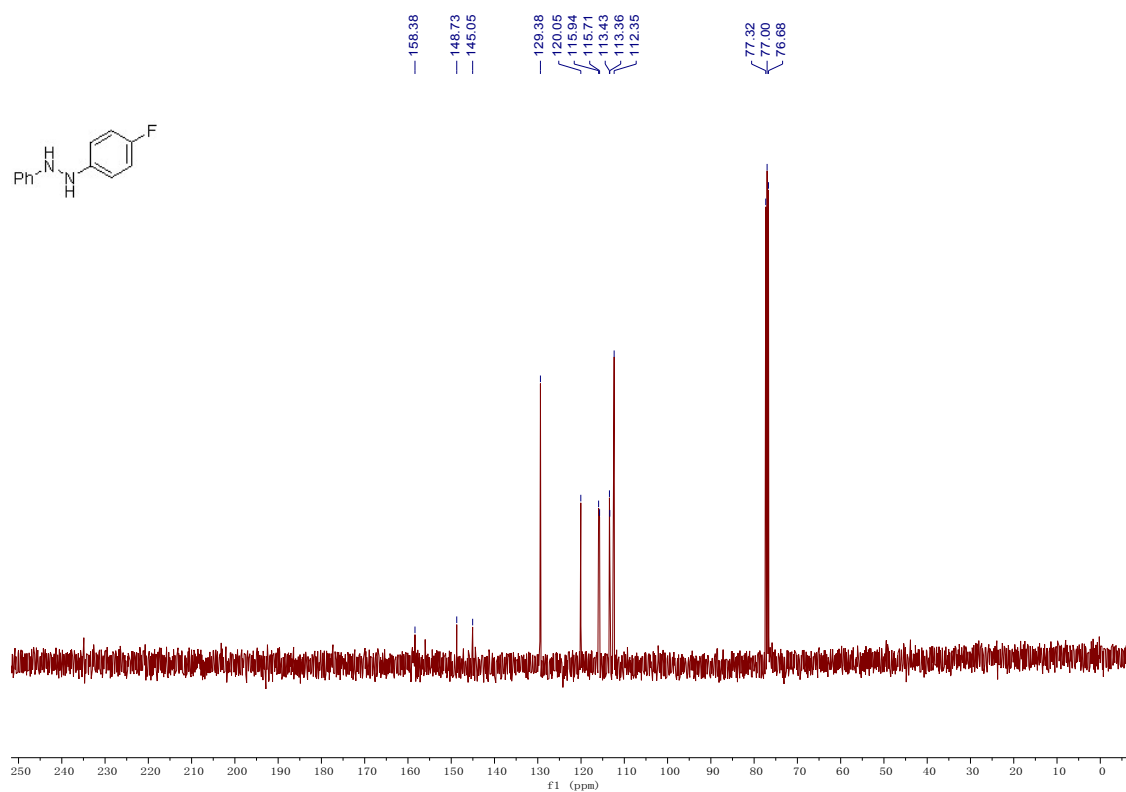
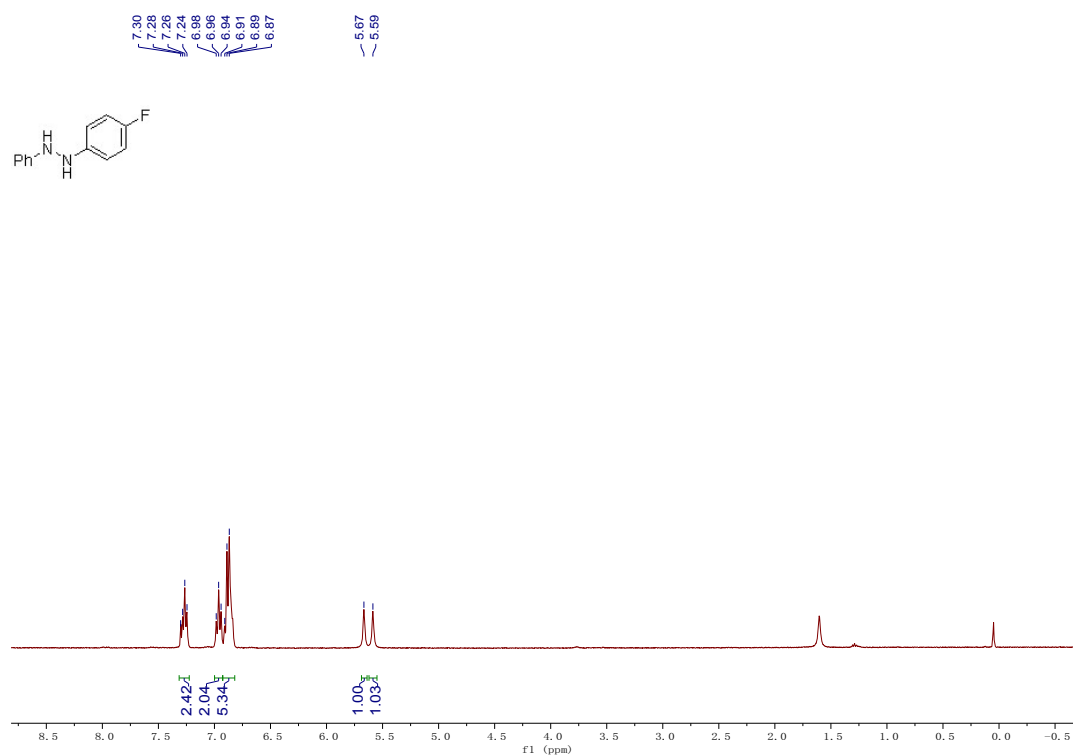
<sup>13</sup>C NMR spectrum of **4d** (Chloroform-*d*)



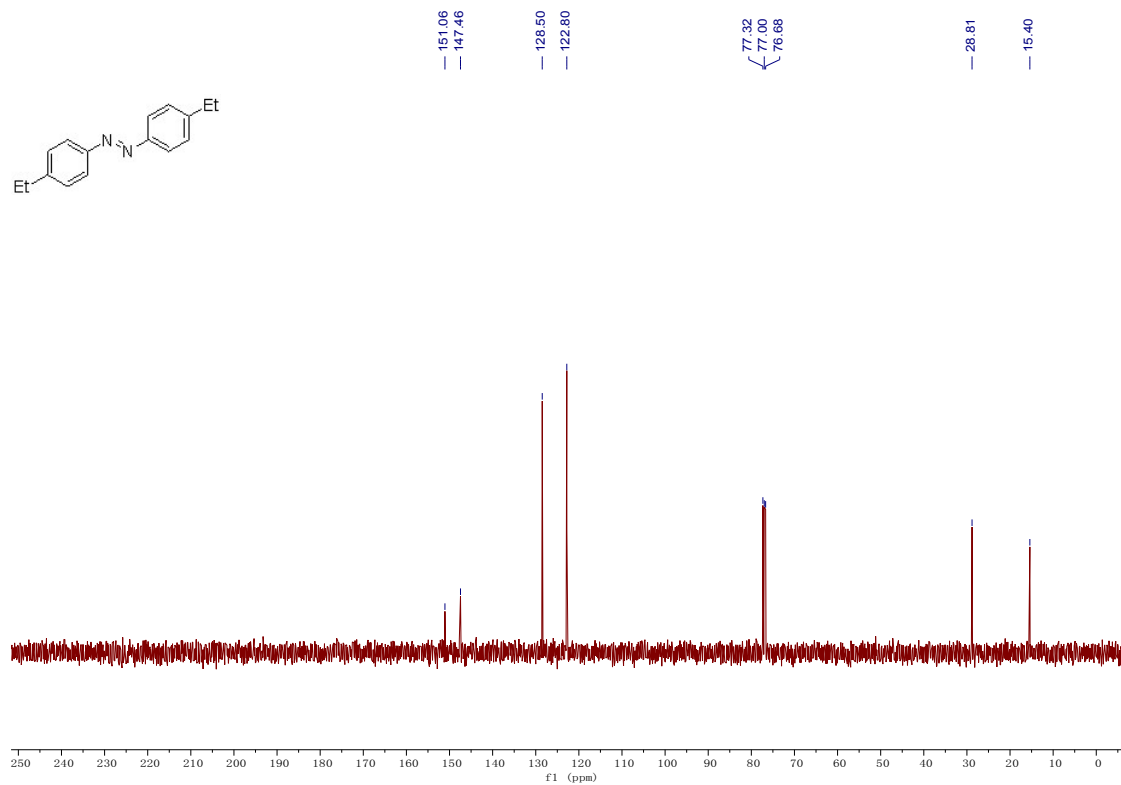
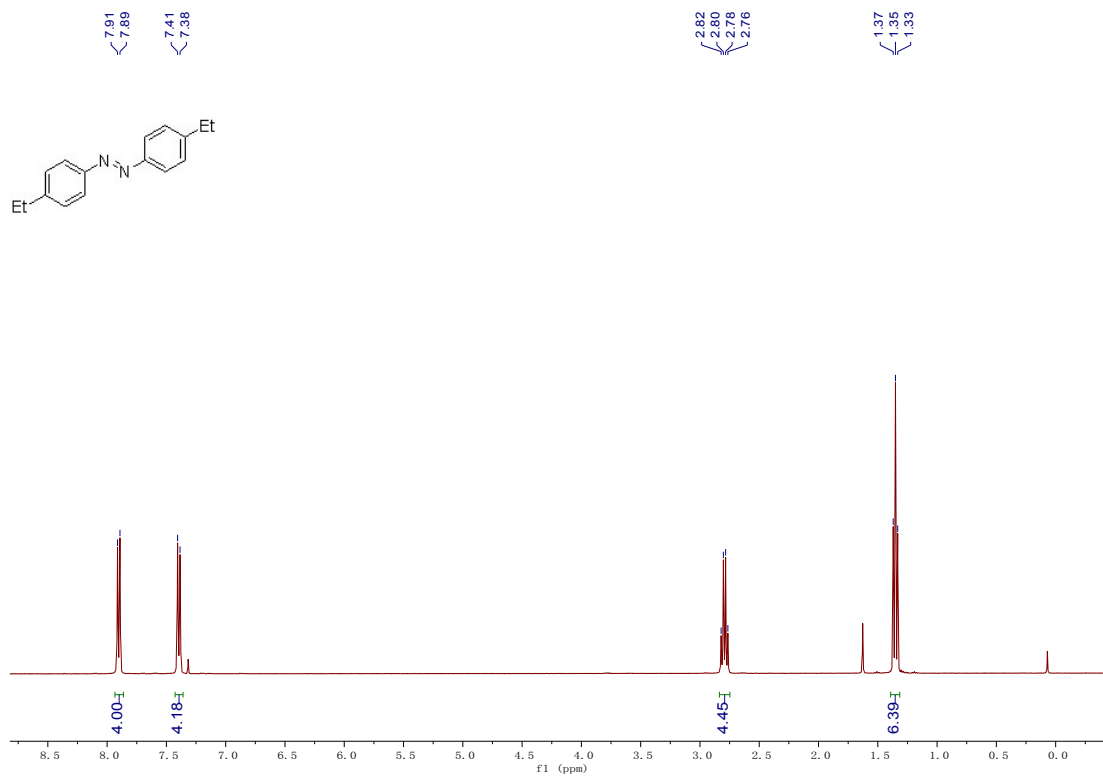
<sup>1</sup>H NMR spectrum of **4e** (Chloroform-*d*)



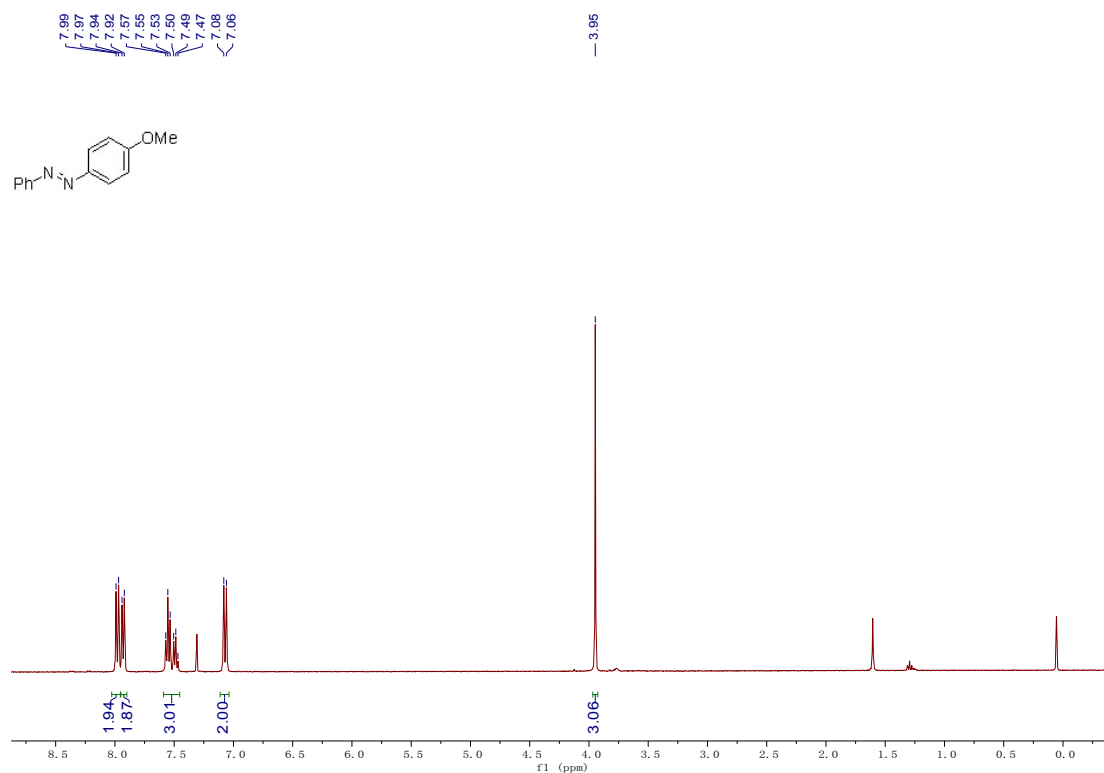
<sup>13</sup>C NMR spectrum of **4e** (Chloroform-*d*)



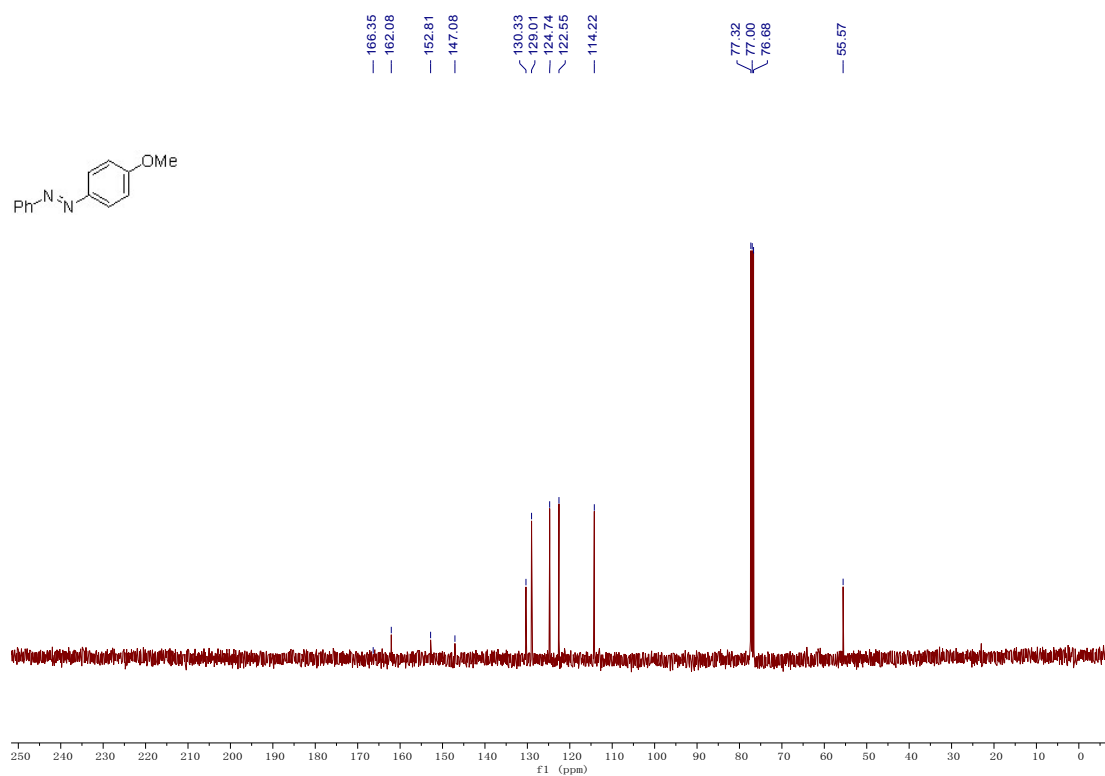
<sup>13</sup>C NMR spectrum of **4f** (Chloroform-*d*)



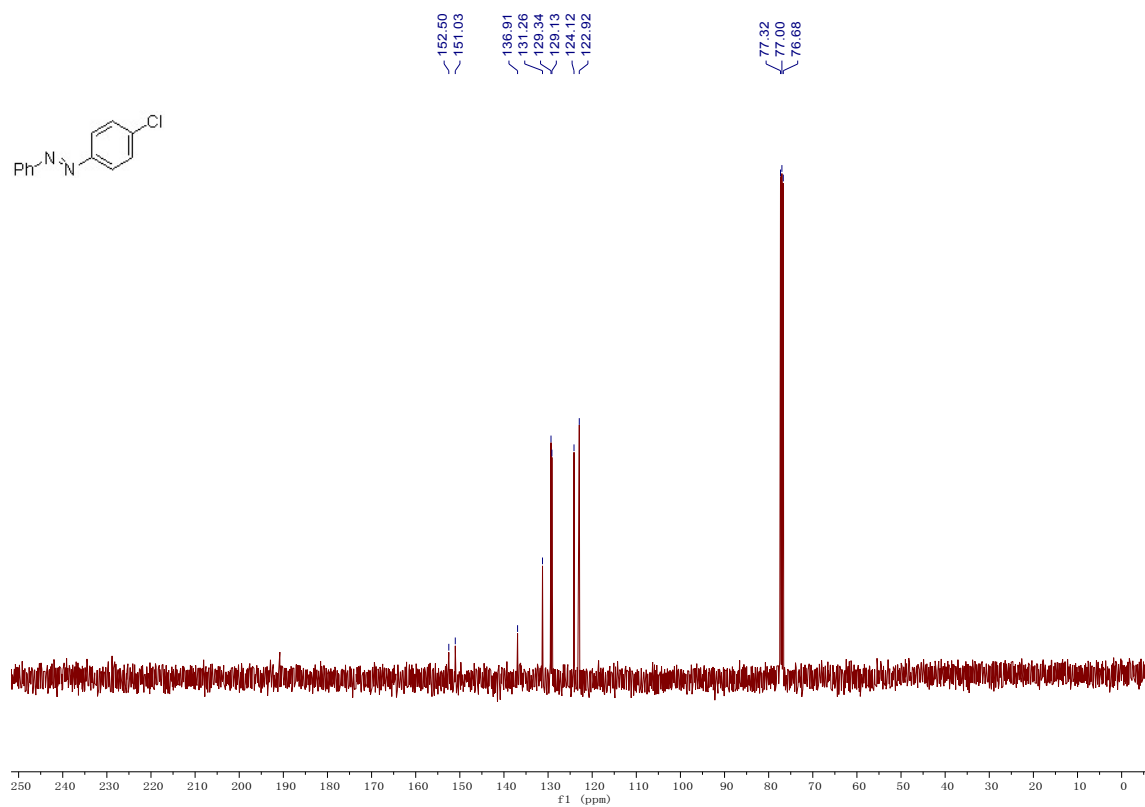
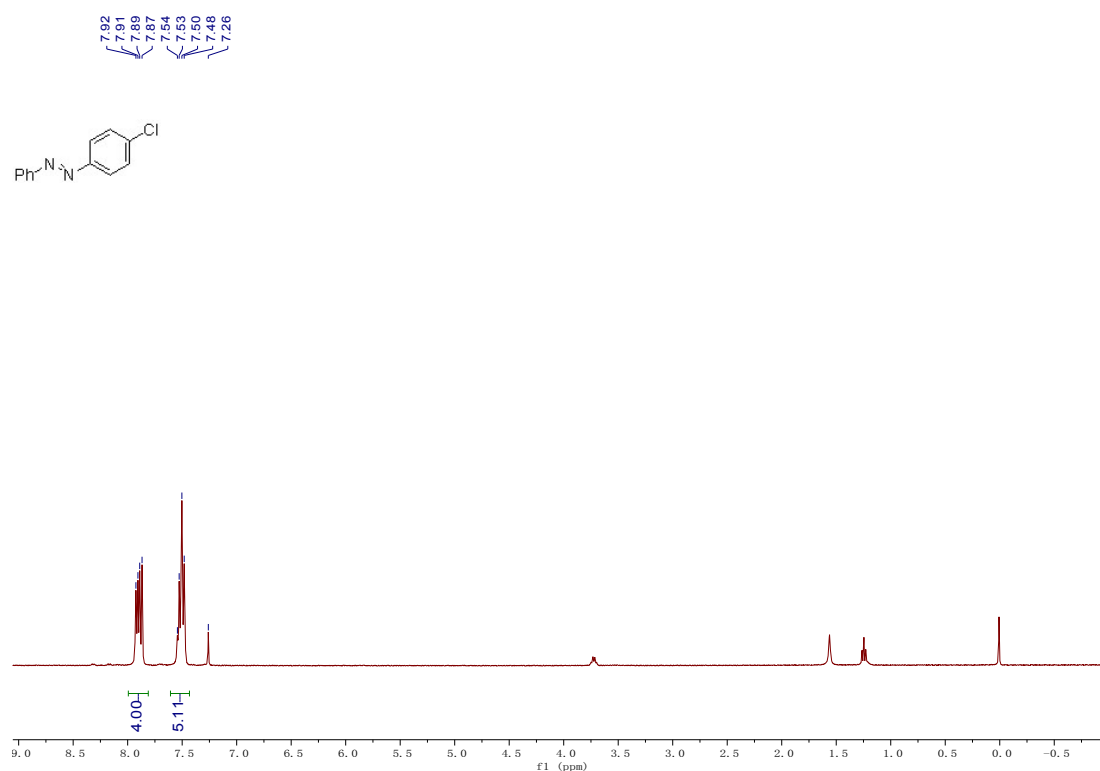
<sup>13</sup>C NMR spectrum of **5b** (Chloroform-*d*)



<sup>1</sup>H NMR spectrum of **5d** (Chloroform-*d*)



<sup>13</sup>C NMR spectrum of **5d** (Chloroform-*d*)



<sup>13</sup>C NMR spectrum of **5e** (Chloroform-*d*)





## References

1. Wang, L.; Ishida, A.; Hashidoko, Y.; Hashimoto, M., Dehydrogenation of the NH-NH Bond Triggered by Potassium tert-Butoxide in Liquid Ammonia. *Angew. Chem. Int. Ed.* **2017**, *56*, 870-873.
2. Iranpoor, N.; Zeynizadeh, B., Air Oxidative Coupling of Thiols to Disulfides Catalyzed by Fe(III)/NaI. *Synthesis* **1999**, 49-50.
3. Chauhan, S. M. S.; Kumar, A.; Srinivas, K. A., Oxidation of thiols with molecular oxygen catalyzed by cobalt(ii) phthalocyanines in ionic liquid. *Chem. Commun.* **2003**, 2348-2349.
4. Shah, S. T. A.; Khan, K. M.; Fecker, M.; Voelter, W., A novel method for the syntheses of symmetrical disulfides using CsF–Celite as a solid base. *Tetrahedron Lett.* **2003**, *44*, 6789-6791.
5. Kirihaara, M.; Okubo, K.; Uchiyama, T.; Kato, Y.; Ochiai, Y.; Matsushita, S.; Hatano, A.; Kanamori, K., Aerobic Oxidation of Thiols to Disulfides Catalyzed by Trichlorooxyvanadium. *Chem. Pharm. Bull.* **2004**, *52*, 625-627.
6. Joshi, A. V.; Bhusare, S.; Baidossi, M.; Qafisheh, N.; Sasson, Y., Oxidative coupling of thiols to disulfides using a solid anhydrous potassium phosphate catalyst. *Tetrahedron Lett.* **2005**, *46*, 3583-3585.
7. Garcia Ruano, J. L.; Parra, A.; Aleman, J., Efficient synthesis of disulfides by air oxidation of thiols under sonication. *Green Chem.* **2008**, *10*, 706-711.
8. Wallace, T. J.; Schriesheim, A., Solvent Effects in the Base-Catalyzed Oxidation of Mercaptans with Molecular Oxygen. *J. Org. Chem.* **1962**, *27*, 1514-1516.