Supporting information

Highly efficient synthesis of 2-mercaptobenzothiazole derivatives in water: metal sulfide-disulfide dynamic interchange reaction

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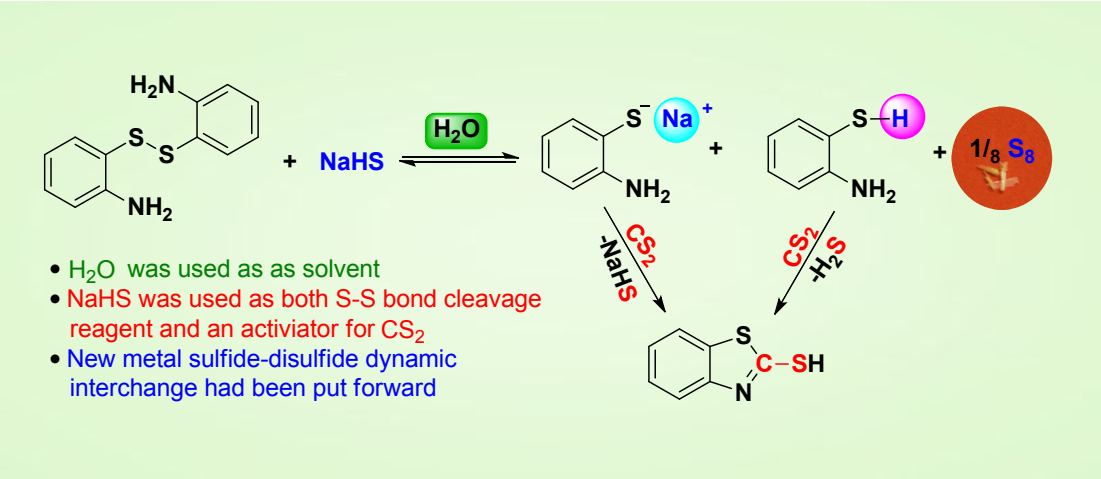

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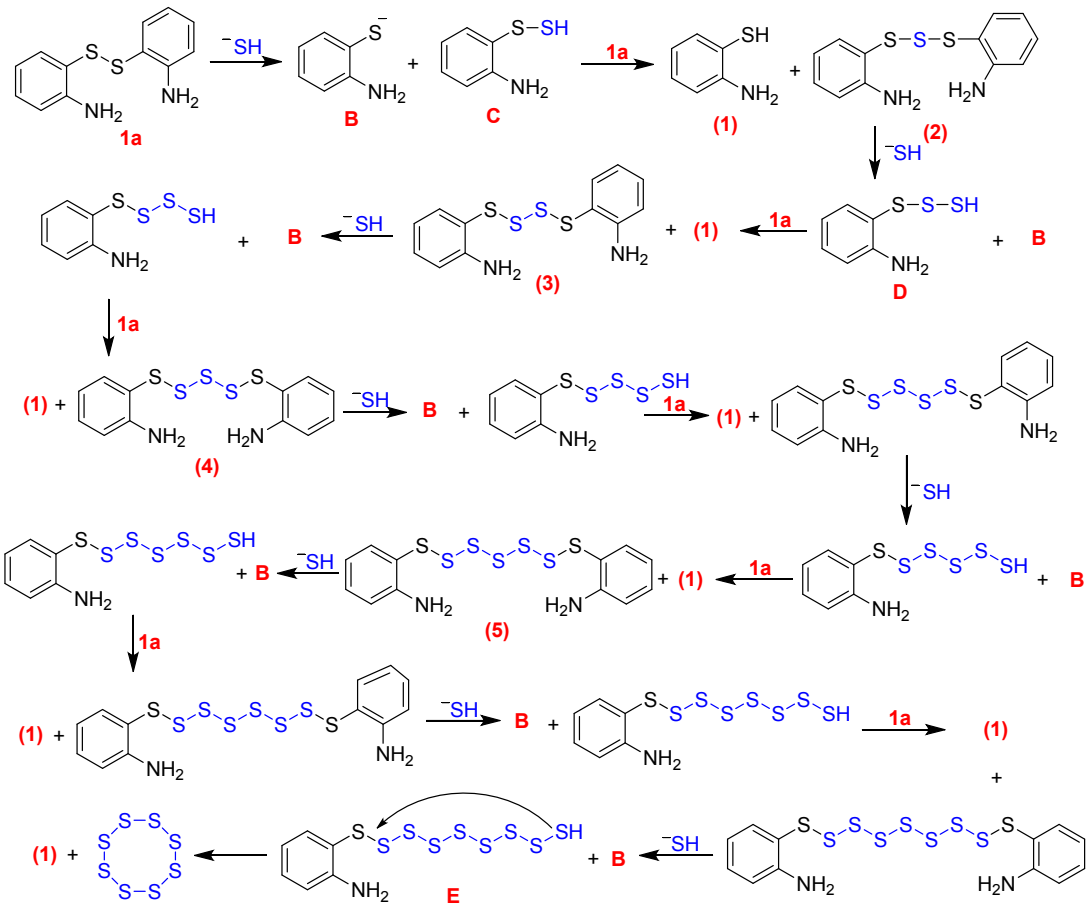
1. The detailed mechanism of metal sulfide-disulfide interchange reaction



Scheme S1 Proposed mechanism of metal sulfide-disulfide interchange reaction

2. LC-MS spectrometry of metal sulfide-disulfide interchange reaction

2,2'-disulfanediyldianiline **1a** (0.2 mmol), NaHS (0.4 mmol) in CH_3CH_2OH (2.5 mL) were put into a reaction tube of parallel reactor (Wattecs). The reaction mixture was stirred at room temperature for 20 min and tested by LCMS analysis.

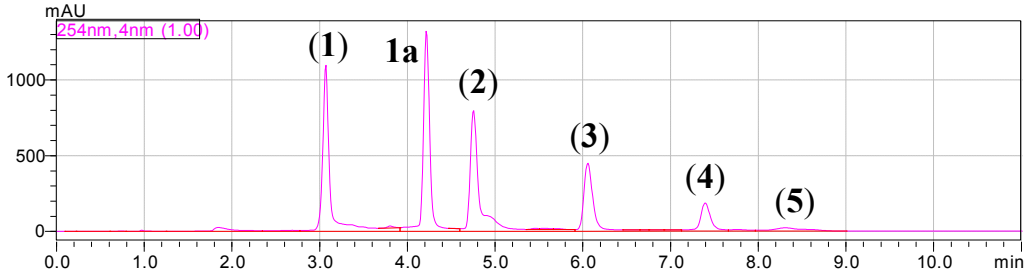
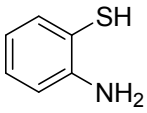


Fig. S1a The LC spectra of reaction mixture solution of NaHS and 1a

(1): Rt= 3.147 min



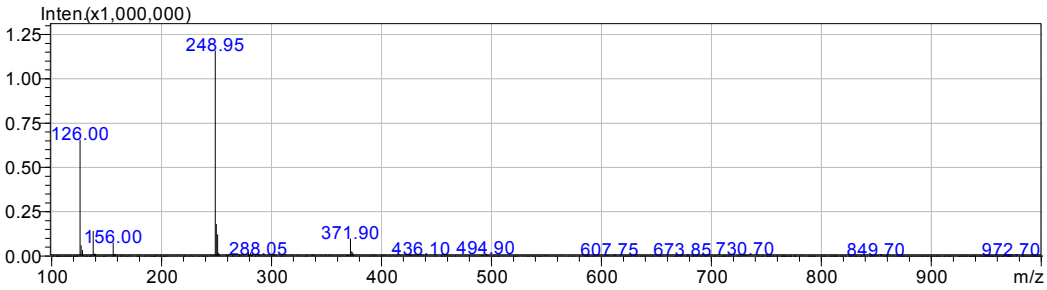
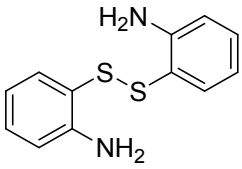


Fig. S1b The mass spectra of compound (1)

1a: Rt= 4.326 min



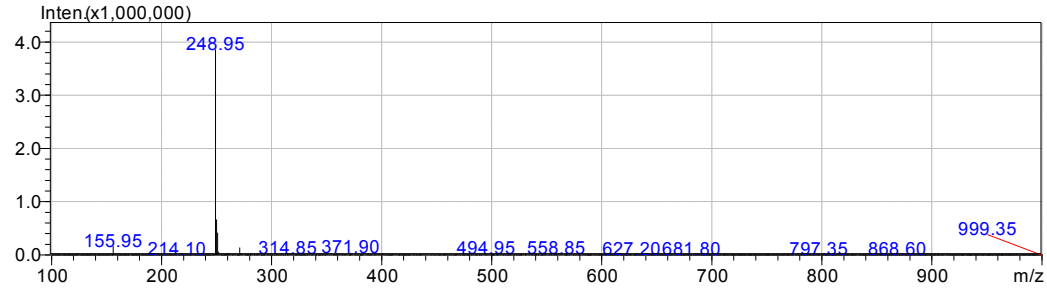
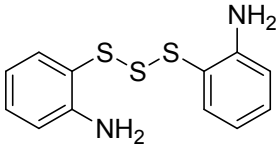


Fig. S1c The mass spectra of compound 1a

(2): Rt= 4.855 min



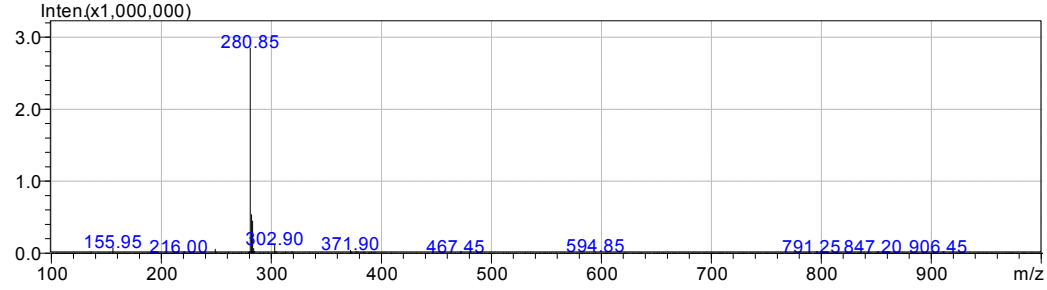
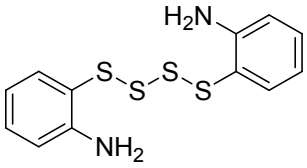


Fig. S1d The mass spectra of compound (2)

(3): Rt= 6.164 min



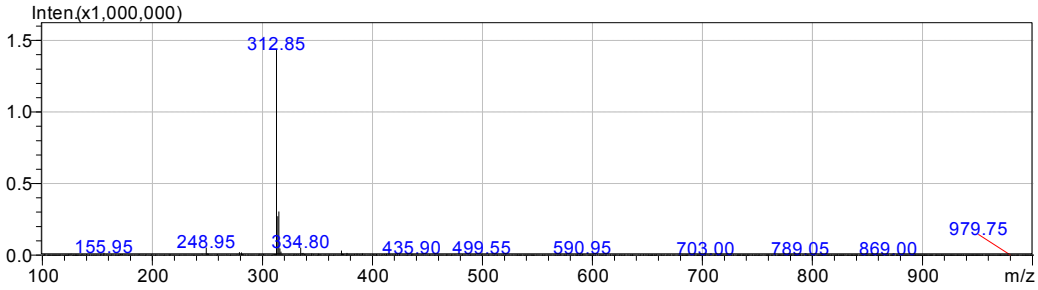
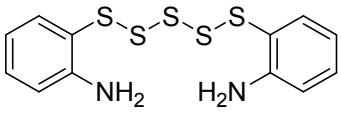


Fig. S1e The mass spectra of compound (3)

(4): Rt= 7.417 min



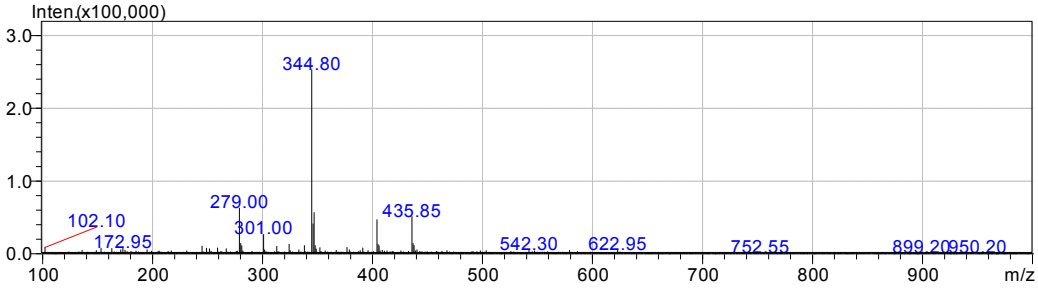
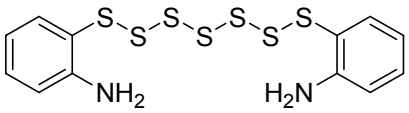


Fig. S1f The mass spectra of compound (4)

(5): Rt= 8.283 min



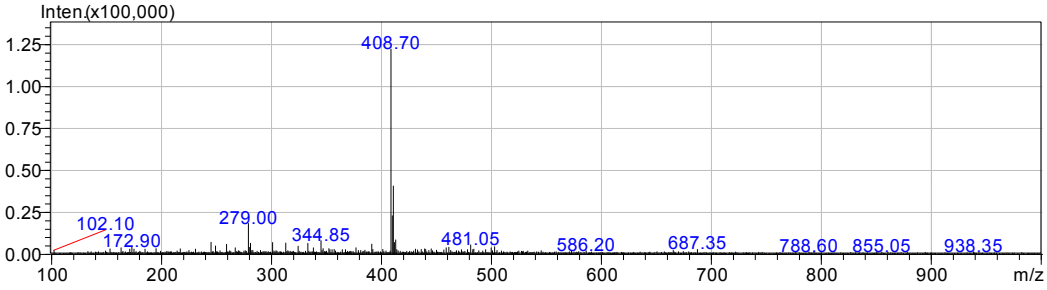


Fig. S1g The mass spectra of compound (5)

3. Crystallographic details of S_8

X-ray data was collected on Bruker D8 VENTURE diffractometer with graphite monochromated Mo-Kα (λ = 0.71073 Å) radiation. All data were collected using the φ- and ω-scan techniques. The molecular configurations were solved by direct methods and refined by full-matrix least squares on F2 using SHELXL-97. All non-hydrogen atoms were refined anisotropically.

The crystal structures have been determined by X-ray single crystal diffraction analysis. Crystal data and relevant structural parameters are listed in Table 1. The selected bond lengths and angles are listed in Table 2.

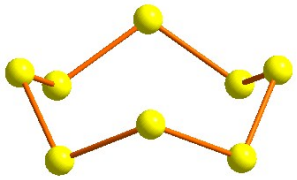


Fig. S2 Crystallographic details for sulfur S_8.

Table S1. Crystal data and structure parameters for S_8.

Empirical formula	S_8
Formula weight	256.56
Temperature / K	293(2)
Crystal system	Monoclinic
Space group	P2/c
a [Å]	8.2208(6)
b [Å]	13.0693(11)
c [Å]	9.2715(6)
α [deg]	90
β[deg]	122.462(5)
γ [deg]	90
Volume [Å^3]	840.48(11)
Z	4
ρ_{calc} [g cm^{-3}]	2.028
μ [mm^{-1}]	2.026
F(000)	512
*θ*range[deg]	3.03-28.34
Reflections collected	16944
Completeness to*θ*	99.5
*T*max. and *T*min.	0.746 and 0.593

Final*R*indices [I>2sigma(I)]	R1 = 0.0373, wR2 = 0.0883
Goodness-of-fit on F^2	1.067
FinalRindices[$I>2\sigma(I)$]	R1 = 0.0373, wR2 = 0.0883
R indices (all data)	R1 = 0.0436, wR2 = 0.0921

Table S2. Bond lengths [Å] and angles [deg] for S_8.

S_8			
S(6)-S(6)#1	2.0366(14)	S(8)-S(8)#1	2.059(2)
S(6)-S(5)	2.0461(10)	S(6)#1-S(6)-S(5)	108.50(5)
S(4)-S(3)	2.0359(12)	S(3)-S(4)-S(4)#2	107.46(5)
S(4)-S(4)#2	2.0404(17)	S(4)-S(3)-S(2)	107.98(5)
S(3)-S(2)	2.0474(16)	S(1)-S(2)-S(3)	107.39(5)
S(2)-S(1)	2.0398(14)	S(7)-S(5)-S(6)	107.87(4)
S(5)-S(7)	2.0443(11)	S(2)-S(1)-S(1)#2	108.05(6)
S(1)-S(1)#2	2.068(2)	S(5)-S(7)-S(8)	107.77(5)
S(7)-S(8)	2.0449(12)	S(7)-S(8)-S(8)#1	107.74(6)

4. ^{13}CNMR spectra of the NaHS and CS_2

Procedure for the reaction of NaHS and CS_2 in a NMR tube. The CS_2 (30μL) was dissolved in 0.5 mL of deuterated DMF in an NMR tube, and the ^{13}CNMR spectra were acquired. Then NaHS (15 mg) was added into the NMR tube, and the ^{13}CNMR spectra of mixing NaHS and CS_2 were acquired, which were shown in Figure S3.

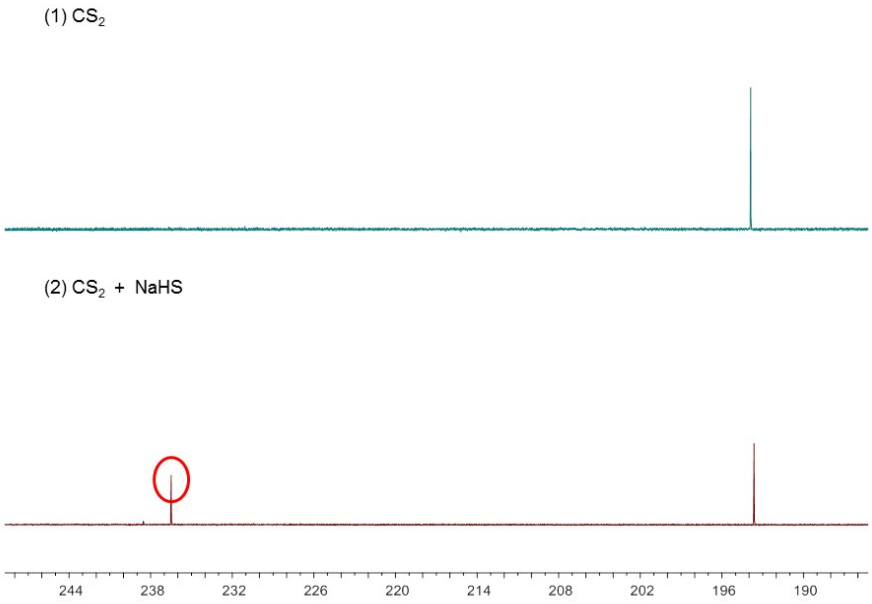
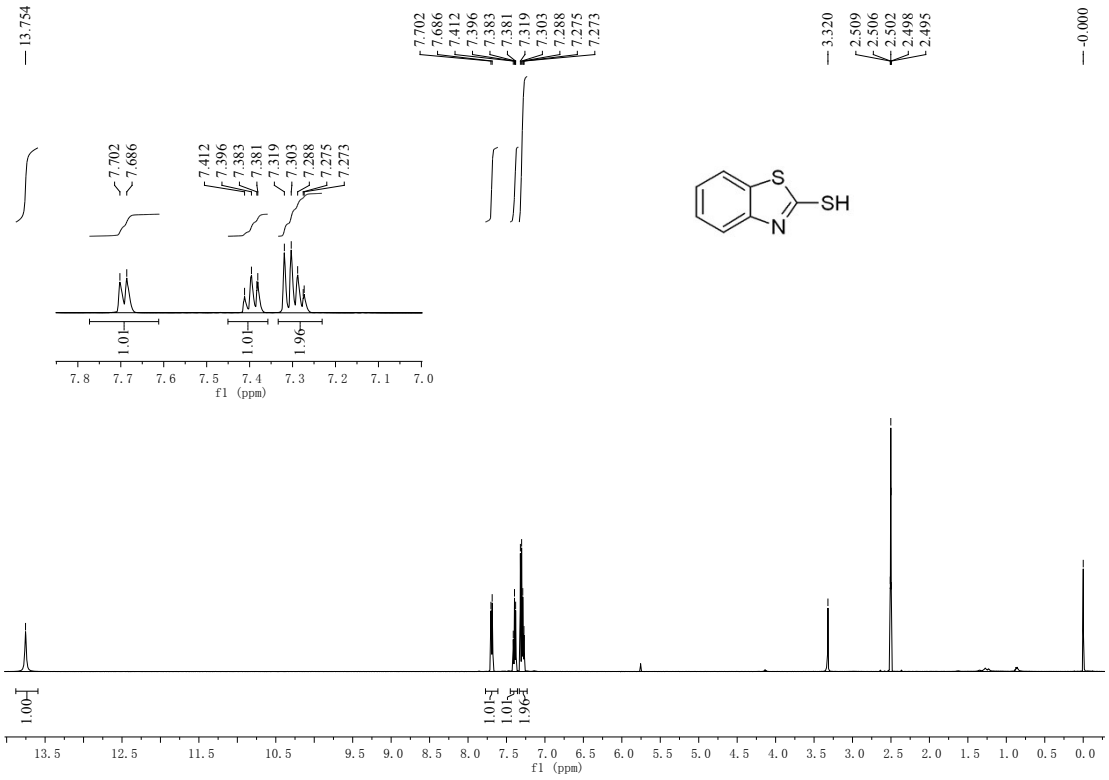


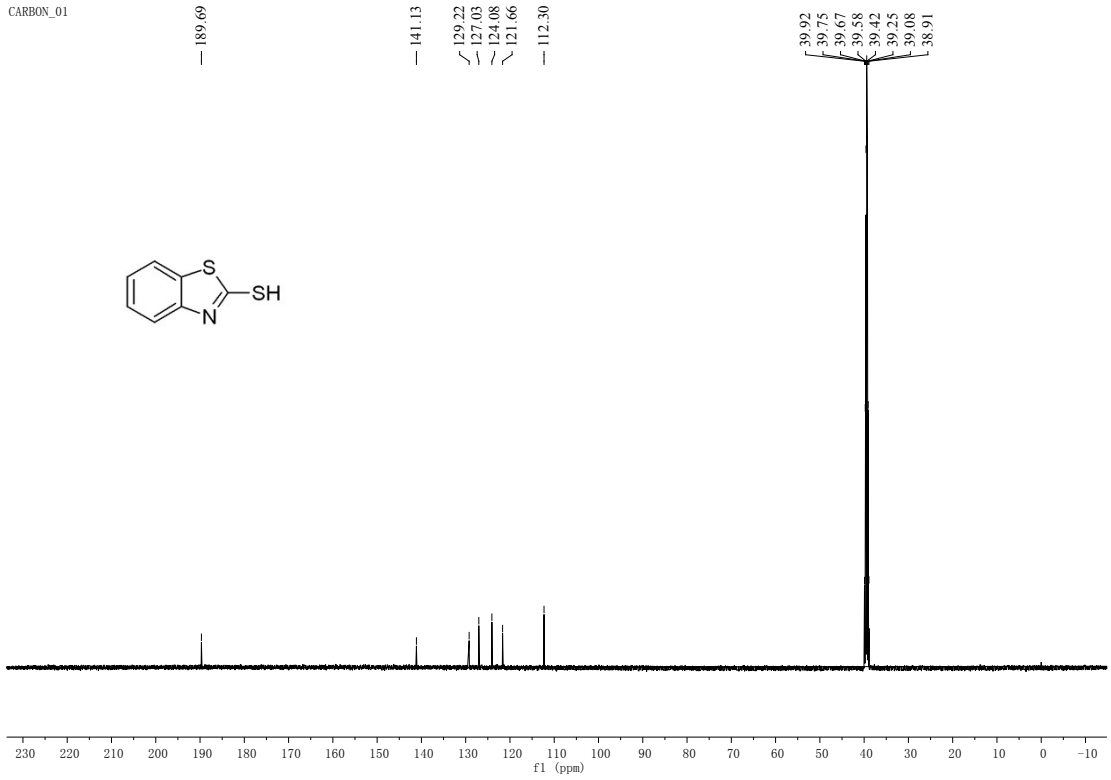
Fig. S3 The ^{13}CNMR spectra of the NaHS and CS_2

5. ^{1}H and ^{13}C-NMR spectra of compounds 2a-j

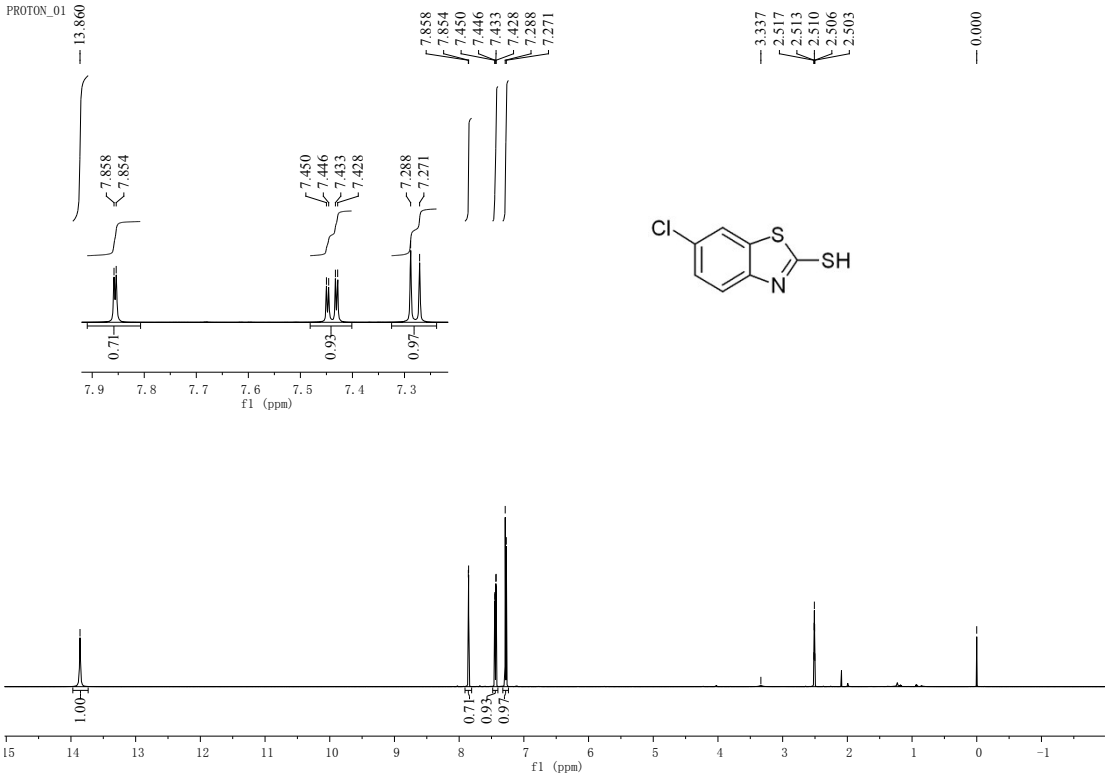
^{1}H NMR spectrum of compound **2a**



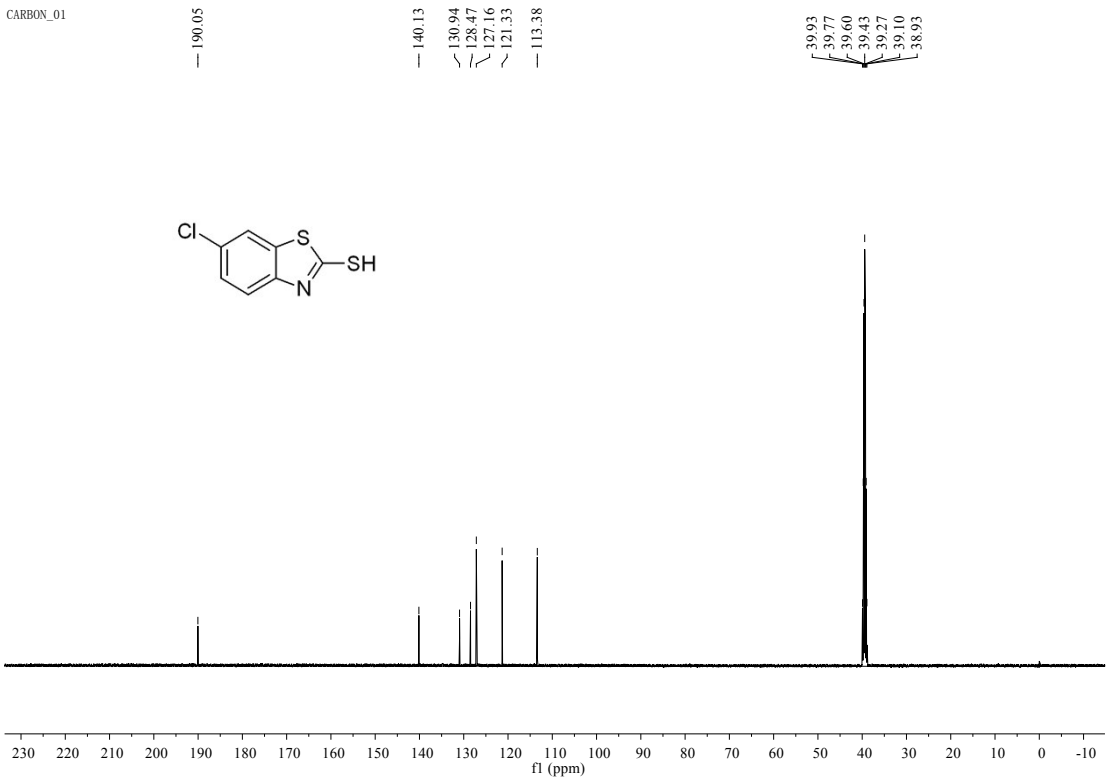
^{13}C NMR spectrum of compound **2a**



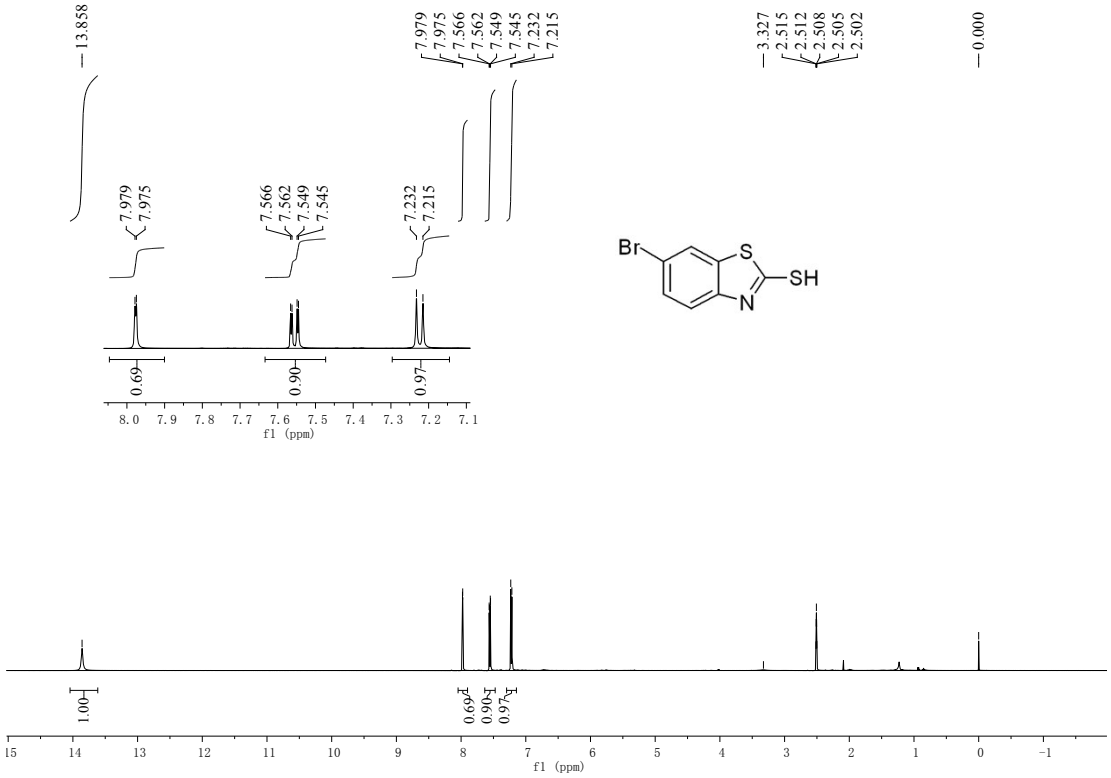
^{1}H NMR spectrum of compound **2b**



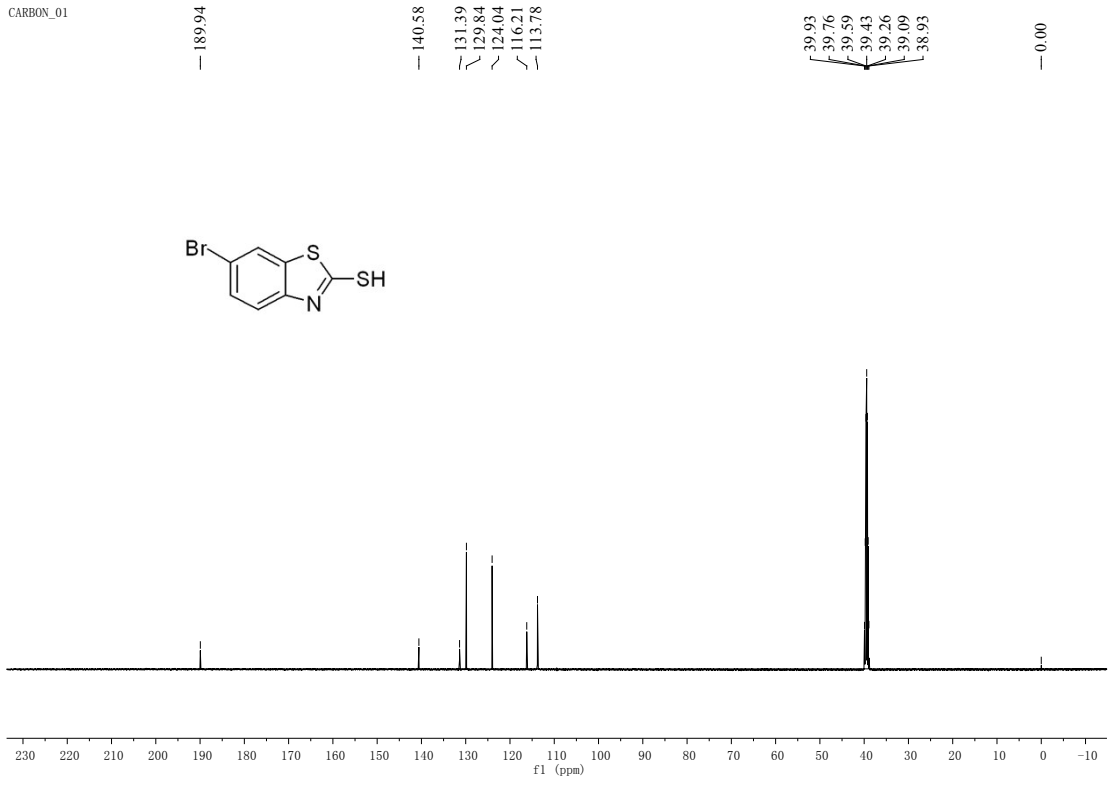
^{13}C NMR spectrum of compound **2b**



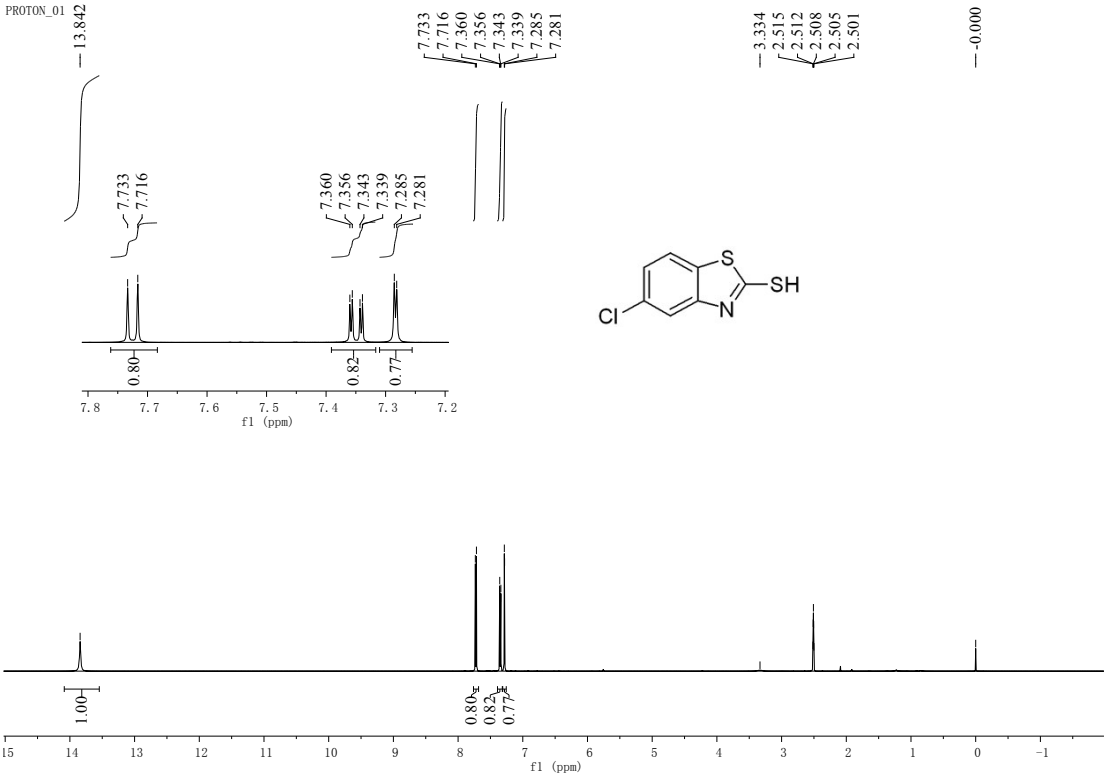
^{1}H NMR spectrum of compound **2c**



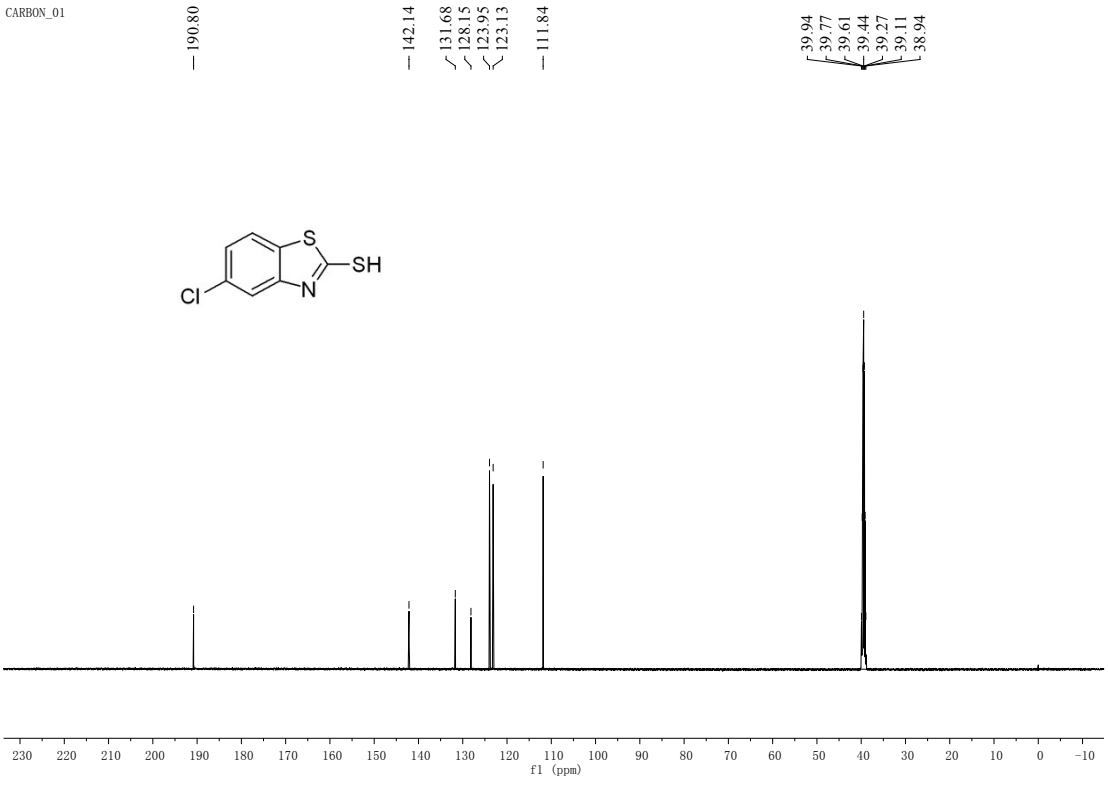
^{13}C NMR spectrum of compound **2c**



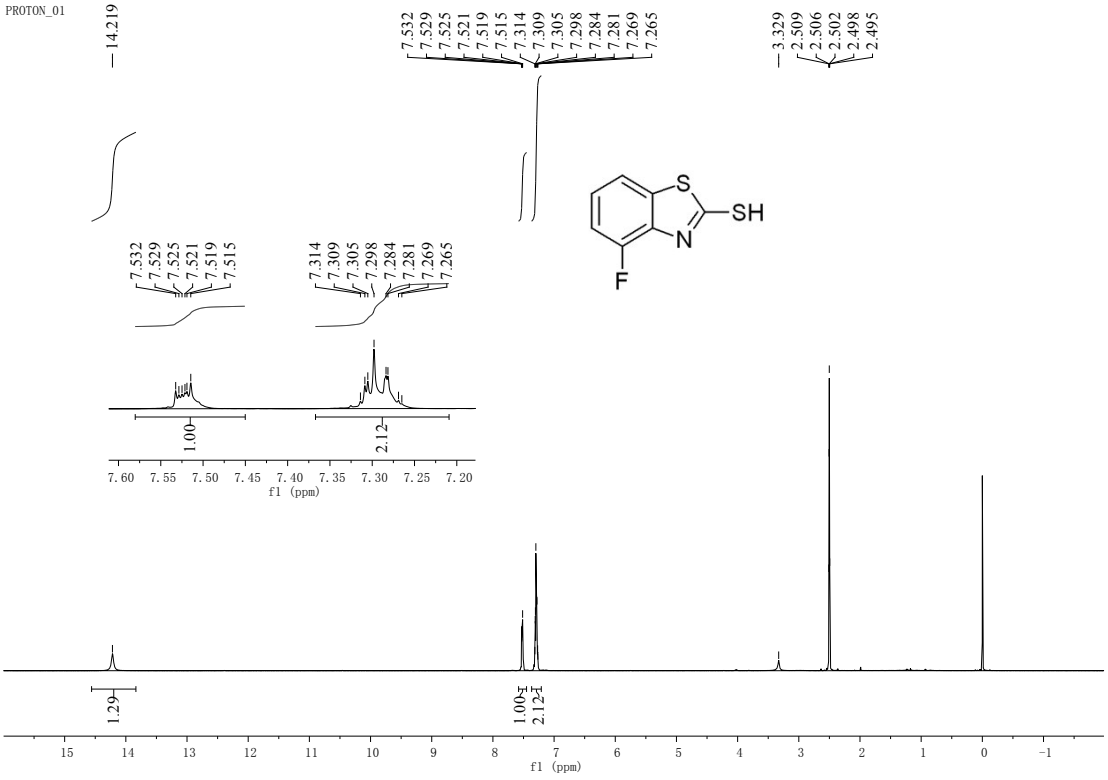
1H NMR spectrum of compound **2d**



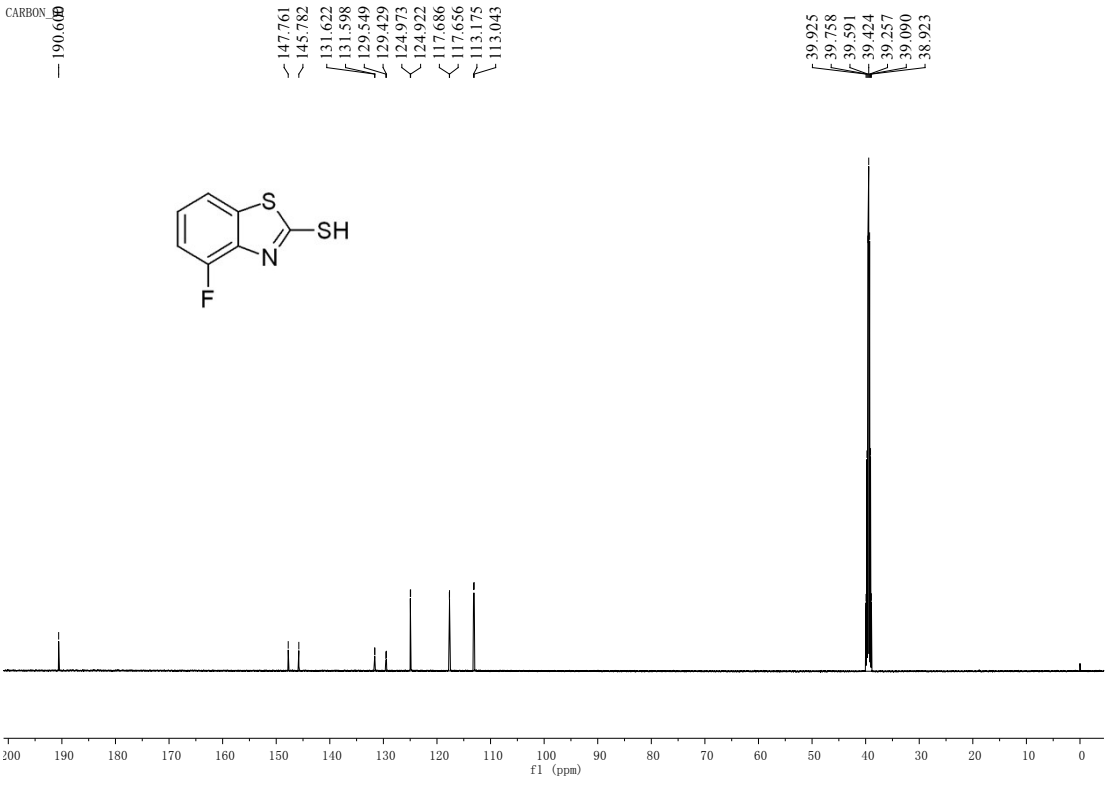
^{13}C NMR spectrum of compound **2d**



^{1}H NMR spectrum of compound **2e**

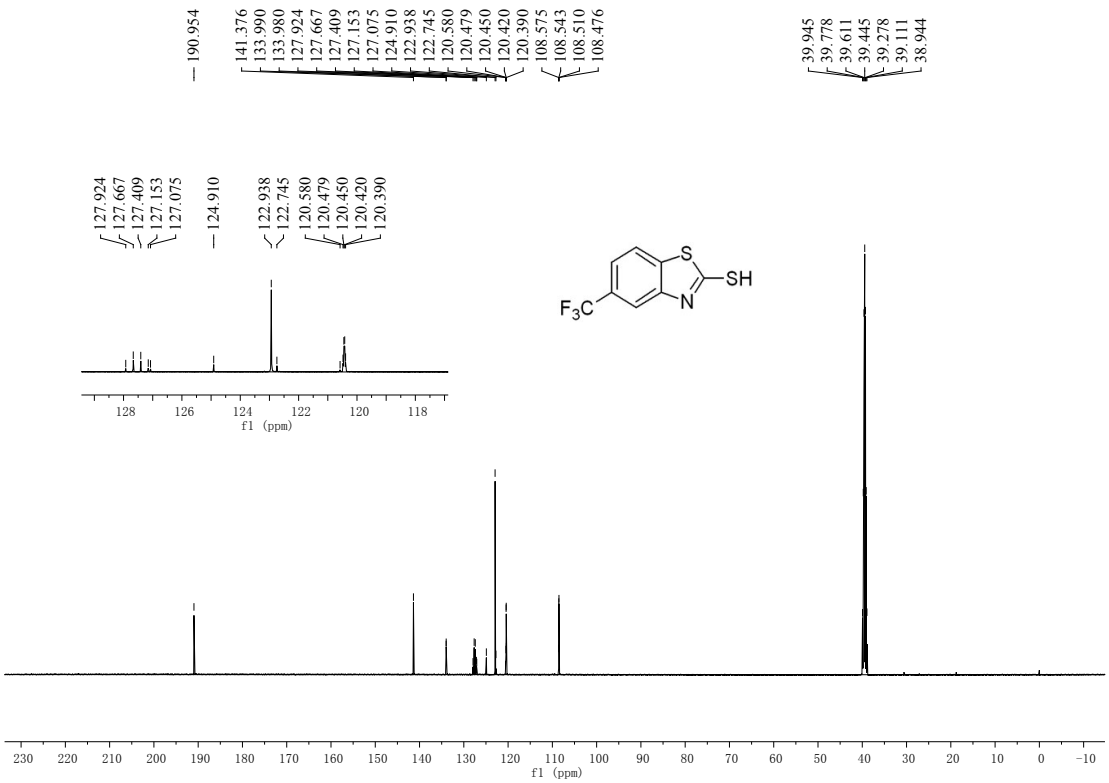


^{13}C NMR spectrum of compound **2e**

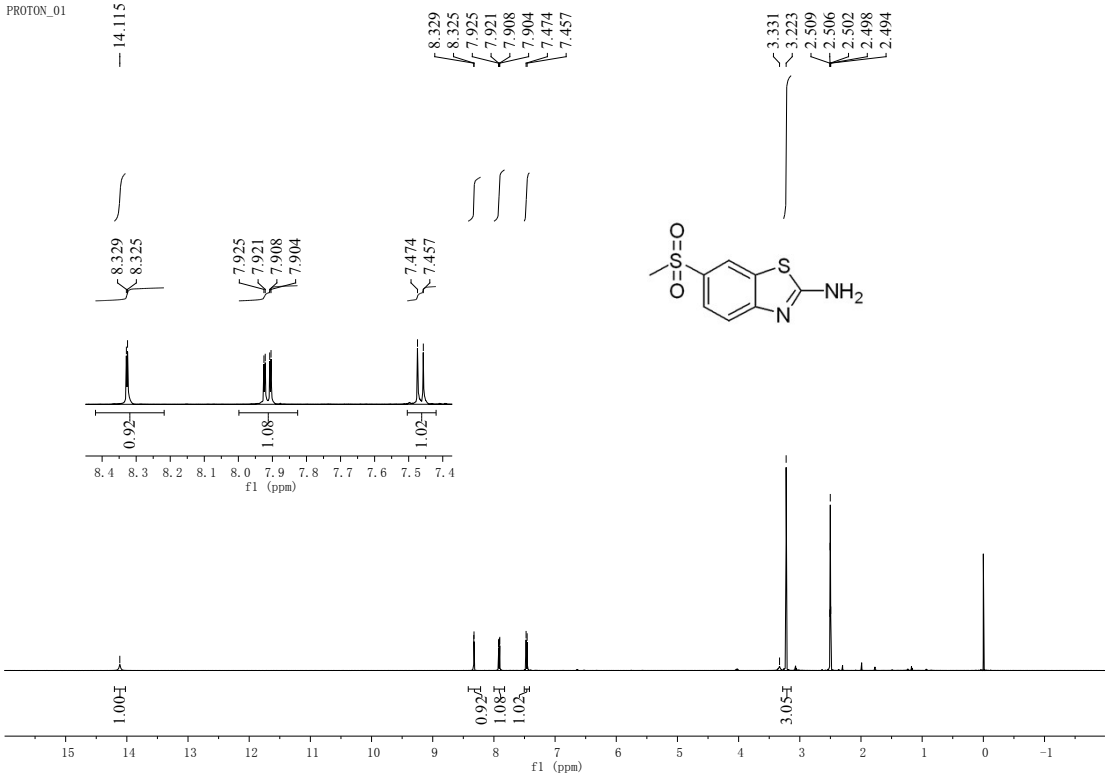


^{1}H NMR spectrum of compound **2f**

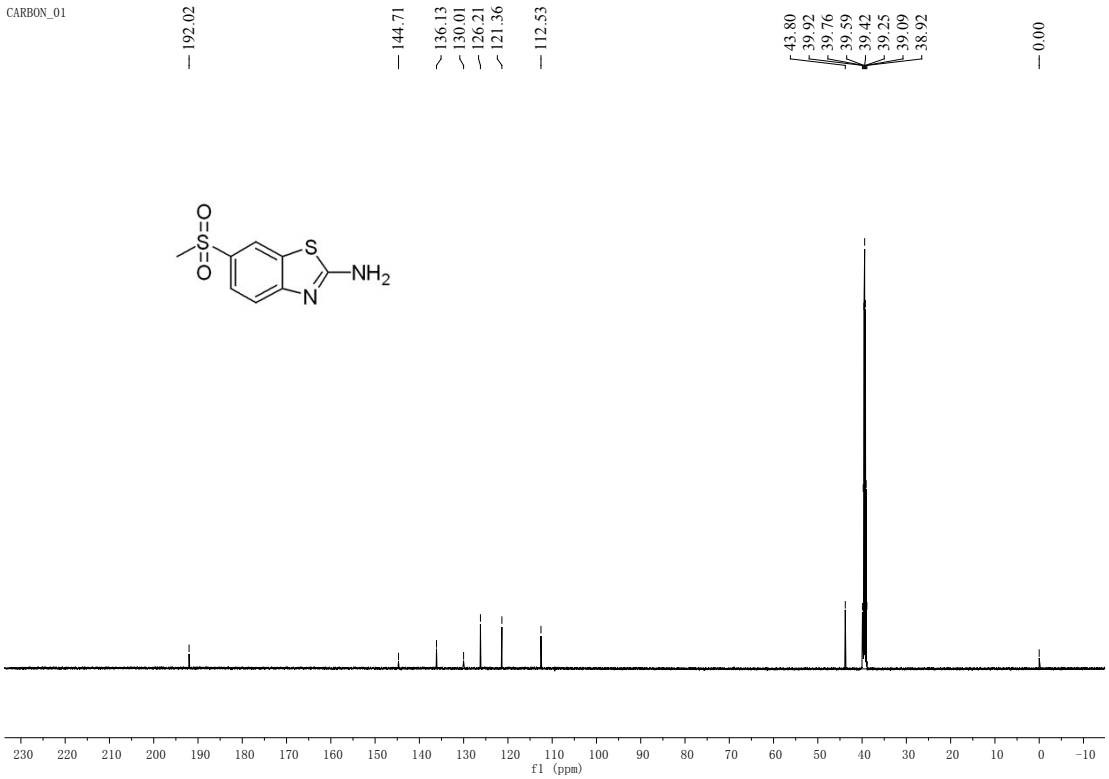
^{13}C NMR spectrum of compound **2f**



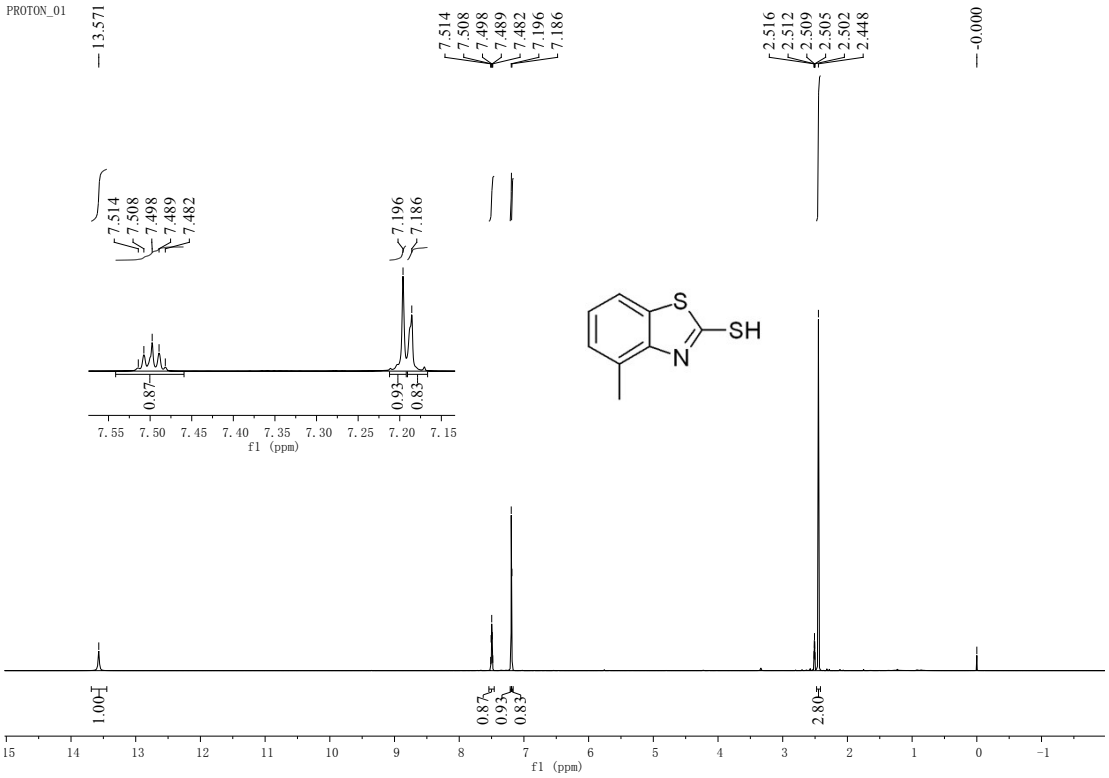
^{1}H NMR spectrum of compound **2g**



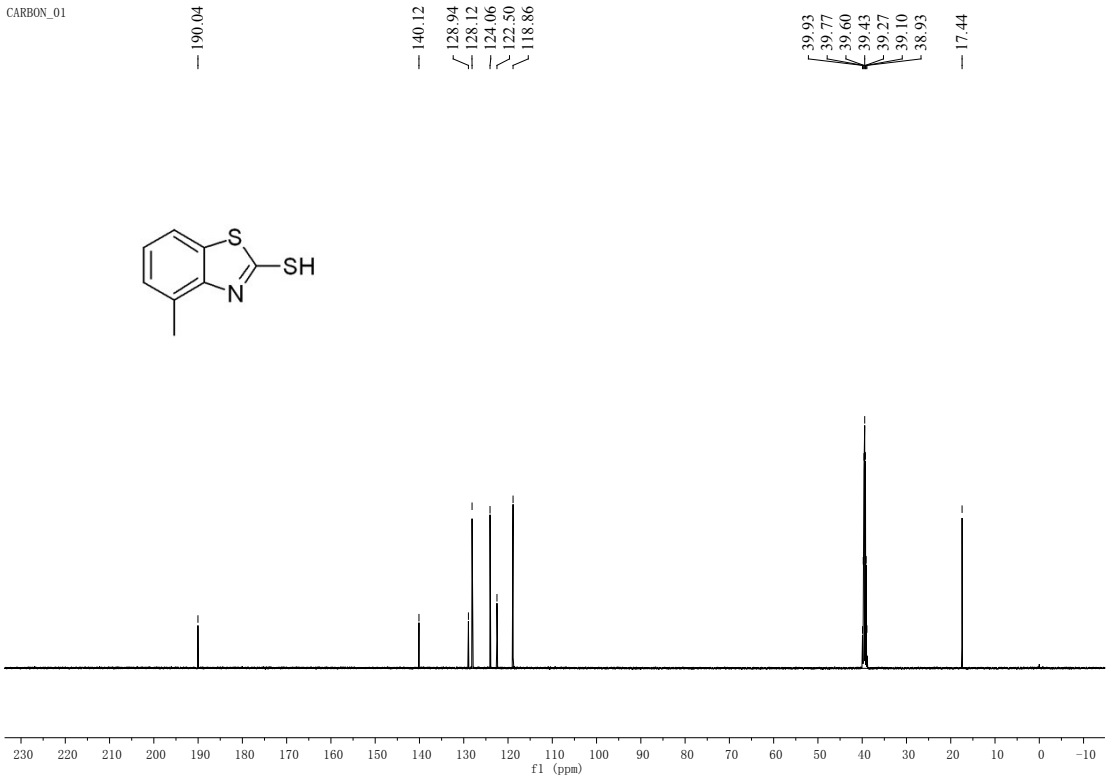
^{13}C NMR spectrum of compound **2g**



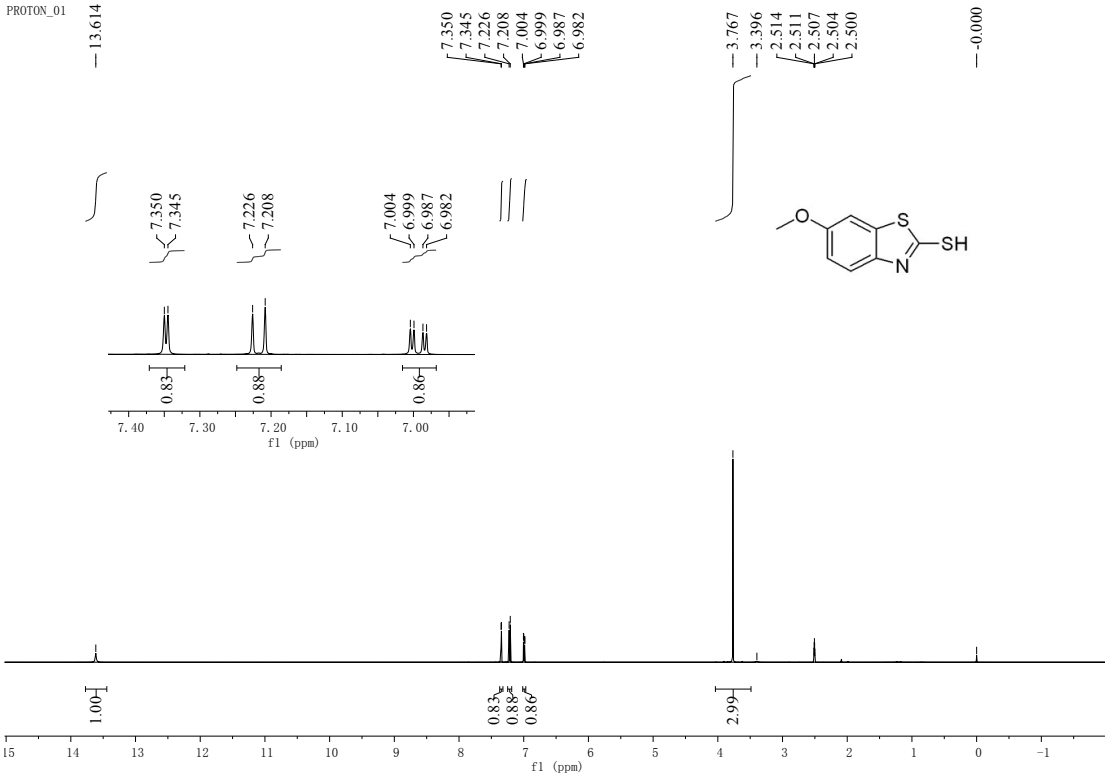
^{1}H NMR spectrum of compound **2h**



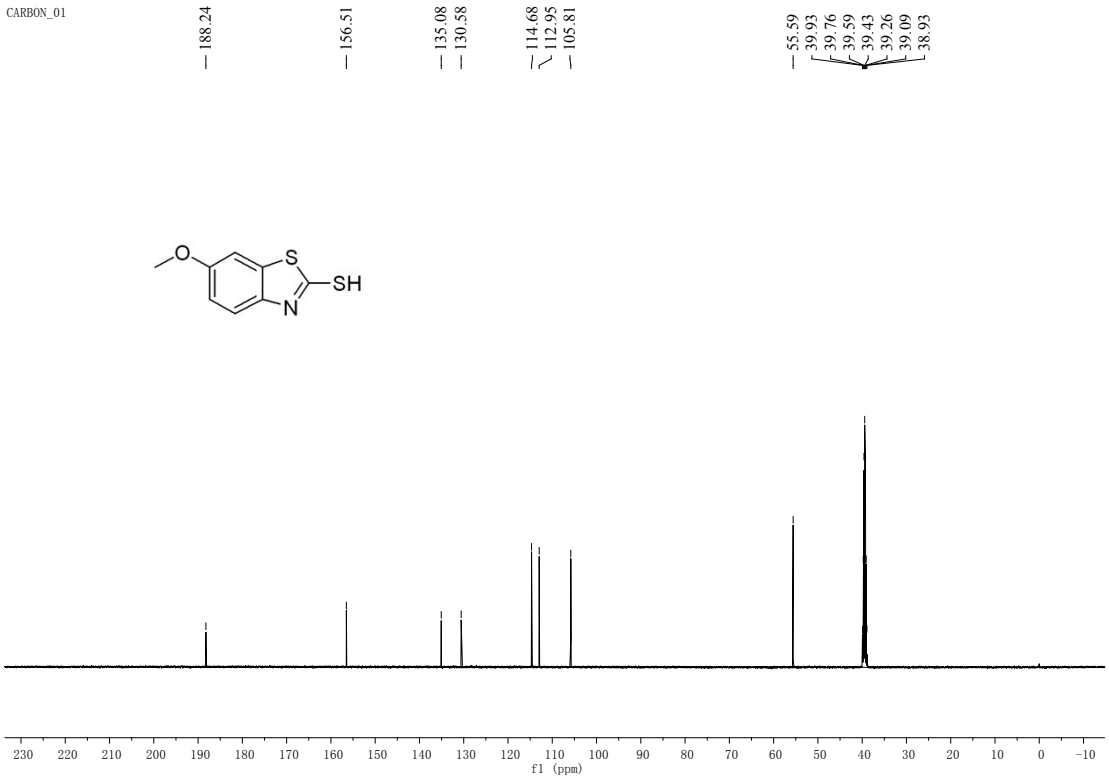
^{13}C NMR spectrum of compound **2h**



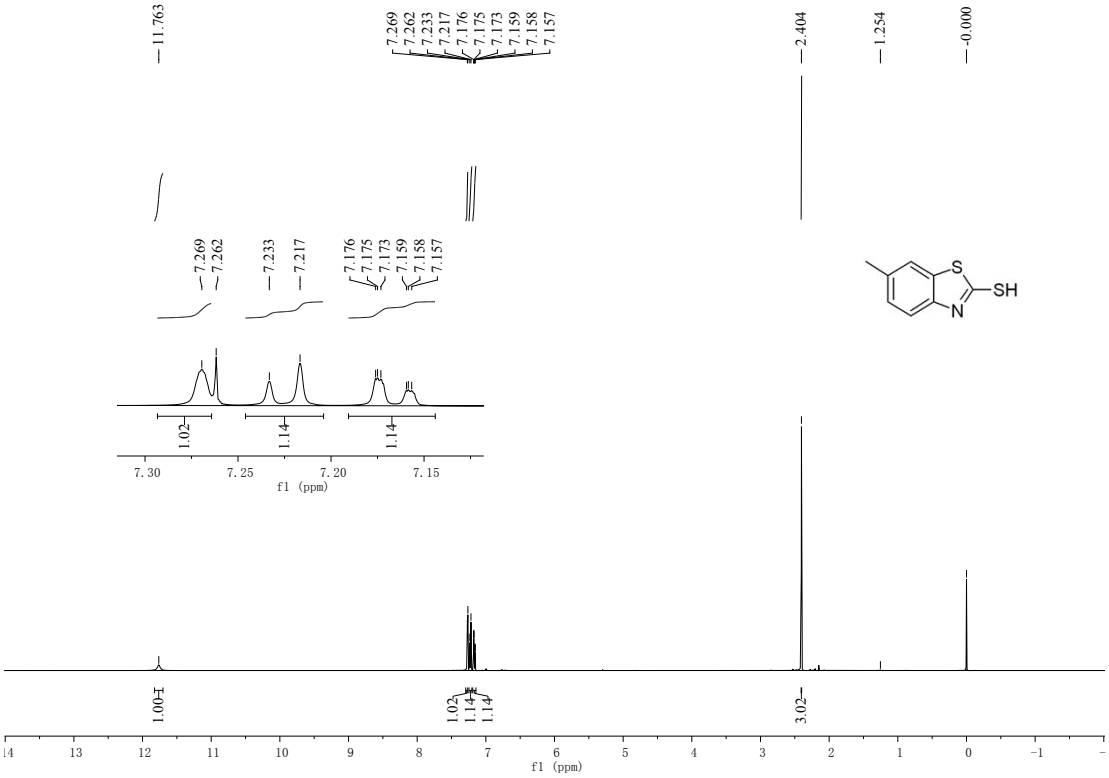
^{1}H NMR spectrum of compound **2i**



^{13}C NMR spectrum of compound **2i**



^{1}H NMR spectrum of compound **2j**



^{13}C NMR spectrum of compound **2j**