Supporting information

Heterogeneous Photocatalytic Synthesis of Sulfenamide with Carbon Doped Potassium Poly(heptazine imide) through effective electron delocalization

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Fei Yuan and Leilei Zhang contributed equally to this work.

Chemicals

All chemicals were used without purification. All organic reactions were monitored by thin layer chromatography (TLC). Melamine (99%, Aladdin reagent Co.), 2,4,6-triaminopyrimidine (99.65%, Leyan reagent), potassium chloride (99.5%, 3Achem), 2-mercaptobenzothiazole (98%, Aladdin reagent Co.), 2-mercaptobenzoxazole (98%, Aladdin reagent Co.), tert-butylamine (99.5%, Aladdin reagent Co.), di-ethylamine (ACS, ≥99%, Aladdin reagent Co.), cyclohexylamine (98%, Aladdin reagent Co.), di-isopropylamine, (98%, Aladdin reagent Co.), pyrrolidine (99%, Aladdin reagent Co.), 3-methylpiperidine, (≥97%, Aladdin reagent Co.), morpholine (≥99.5%, Aladdin reagent Co.), thiomorpholine (98%, Aladdin reagent Co.), p-touidine (99.7%, Aladdin reagent Co.), 1-boc-piperazine (98%, Aladdin reagent Co.), 4-piperidone ethyleneketal (≥98%, Aladdin reagent Co.), 2,2-dithiobis(benzothiazole) (98%, Aladdin reagent Co.), butylamine (99%, Energy chemical), tetrabutylammonium perchlorate (98%, Energy chemical), chloroform-D, (D, 99.8% + 0.03% TMS, HEOWNS reagent), DMSO-d6 (D 99.8%, TMS 0.03%, Energy chemical), anhydrous acetonitrile (99.8%, H_2O: ≤0.005%), dichloromethane (AR ≥99.5%, Tianjin Fuyu Fine Chemical Co.), ethyl acetate (AR ≥99.5%, Tianjin Fuyu Fine Chemical Co.), petroleum ether (AR, Tianjin Fuyu Fine Chemical Co.), n-hexane (AR ≥99%, Tianjin Fuyu Fine Chemical Co.), deionized water, N,N-dimethylformamide (AR ≥99.5%, Kermel reagent), methanol (≥99.9%, Aladdin reagent Co.), ethanol (AR ≥99.7%, Tianjin Fuyu Fine Chemical Co.), 1,2-dichloroethane (AR ≥99.8%, Aladdin reagent Co.), dimethyl sulfoxide （AR, Kermel reagent).

Characterization methods

^{1}H and ^{13}C NMR spectra were recorded on a Bruker Avance III 400 MHz (at 400 MHz for Protons and 101 MHz for Carbon-13). NMR spectra were recorded in $CDCl_3$ or DMSO-d6. The chemical shifts are reported in ppm relative to the residual signal of $CHCl_3$ (7.26 ppm in ^{1}H NMR, 77.16 ppm for ^{13}C NMR) or DMSO (2.5 ppm in ^{1}H NMR, 39.52 ppm for ^{13}C NMR). The used abbreviations are as follows: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), br (broad).

Gas Chromatography and Mass Spectrometry (GC-MS) analyses of the organic products were carried out on a Thermo Fisher DSQ II with an EI ion source. Column (30 m* 0.25 mm*0.25 μm). Testing condition: high purity helium as the carrier gas, flow rate of 1.5 mL min^{-1}. The temperature program of the GC starts at 26 °C, then rises to 50 °C at a rate of 25 °C min^{-1}. MS program scan mass range of 13 m/z-50 m/z, the ion source temperature and injection port were set at 150 °C, the AUX temperature zone was set at 100 °C.

Liquid Chromatography and Mass Spectrometry (LC-MS) analyses of the organic products were carried out on Agilent 1260/6120B. Column-SDB C18 column (4.6 * 150 mm, 4.6 mm id). Mobile phase was composed of CH_3CN:CH_3OH = 70:30 and the flow speed was set at 1.0 mL min^{-1}.

High resolution mass spectra was obtained on Thermo Scientific LTQ Orbitrap XL instrument using the ESI technique.

Powder X-Ray diffraction patterns were measured on a Bruker D8 Advance diffractometer equipped with a scintillation counter detector with Cu-Kα radiation (40 kV and 40 mA) applying 2θ step size of 5° at a scan rate of 1° min^{-1}.

UV-Vis-NIR diffuse reflectance spectra was measured by using a UV-3600 Plus UV-Vis-NIR spectrometer (Shimadzu).

Photoluminescence (PL) spectra were recorded at room temperature on a F-4600 spectrofluorometer (370 nm excitation wavelength).

Transmission electron microscopy (TEM) and high-resolution TEM (HRTEM) measurements were obtained on Japan-JEOL-JEM 2100 F operated at 120 kV.

X-ray photoelectron spectroscopy (XPS) was performed using a Thermo ESCALAB 280 system with Al/K (photon energy = 1486.6 eV) anode mono-X-ray source. All binding energies were calibrated by using the contaminant carbon (C 1 s = 284.8 eV) as a reference.

Fourier transform infrared (FTIR) spectra were obtained on a Nicolet Nexus spectrometer.

Electron spin resonance (EPR) spectroscopy was performed on Bruker EMXnano.

Cyclic voltammetry electrochemical measurements were carried out with CHI 760E electrochemical testing station with the O_2 inlet and magnetic stir bar, and CHI 760e v. 18.4 electrochemical software for data logging. Glassy carbon was used as a WE, Ag wire in $AgNO_3$ with tetrabutylammonium perchlorate (0.1 M) in MeCN as a RE, Pt wire as a counter electrode. Measurements were performed at room temperature (20-25 °C). A solution of tetrabutylammonium perchlorate (0.1 M) in MeCN was used as electrolyte. The electrochemical cell was placed in the grounded Faraday's cage in

order to reduce noise.

The inductively coupled plasma optical emission spectroscopies (ICP-OES) were collected on Thermo Fisher (iCAP 7000 Series).

Elemental analysis (EA) was performed using a Elementar UNICUBE series CHNS, organic elemental analyzer.

Light sources

For light-promoted reactions, report the light source in detail (manufacturer and model, wavelength of peak intensity or broadband source, and available information about the spectral distribution and intensity); the material of the irradiation vessel if other than borosilicate glass; the distance from the light source to the irradiation vessel; and the use of filters if any.

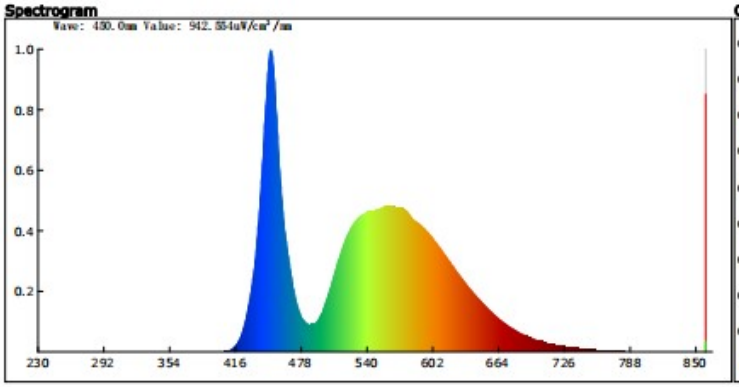
We use **real summer sunlight** in Zhengzhou, Henan, China.

We use **RLH-18 8-position Photo Reaction System**, which manufactured by Beijing Rogertech Co.ltd base in Beijing PRC. This Photo reactor we used have equipped 4 blue, 2 white, 2 green light 10 W LED, other LEDs could be selected and replaced each position. This blue light 10 W LED's energy peak wavelength is 456.7 nm, peak width at half-height is 23.7 nm, Iirradiance@sample position is 140 mW/cm^2. Irradiation vessel is borosilicate glass test tube, LED irradiate through a high-reflection channel to the test tube, path length is 2 cm. No filter between LED and test tube.
Spectrum as below:

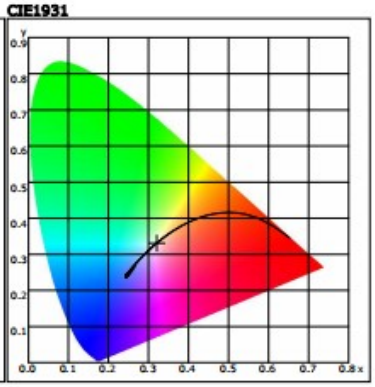
Parameter

Name	Value	Name	Value	Name	Value	Name	Value
ESuv(mW/cm²)	0.0000	SDCM	11.10	Peak Signal	55804		
Euvc(mW/cm²)	0.0000	Ra	73.4	Dark Signal	2294		
Euvb(mW/cm²)	0.0000	Ee(mW/cm²)	82.96883	Compensate level	2878		
Euva(mW/cm²)	0.0000	S/P	1.960				
Euv(mW/cm²)	0.00	Dominant(nm)	488.20				
Eb(mW/cm²)	26.22	Purity(%)	4.4				
Eg(mW/cm²)	39.04	HalfWidth(nm)	21.2				
Er(mW/cm²)	17.27	Peak(nm)	450.4				
Eir(mW/cm²)	1.13	Center(nm)	450.4				
E(lx)	268531.56	Centroid(nm)	541.0				
Candle E(fc)	24947.19	Color Ratio(RGB)	13.0,83.9,3.1				
CCT(K)	6060	CIE1931 X	382527.375				
Duv	-0.00045	CIE1931 Y	393164.813				
CIE x,y	0.3211,0.3300	CIE1931 Z	415774.031				
CIE u,v	0.2033,0.3134	TLCI-2012	75				
CIE u',v'	0.2033,0.4701	Integral Time(ms)	0.6				

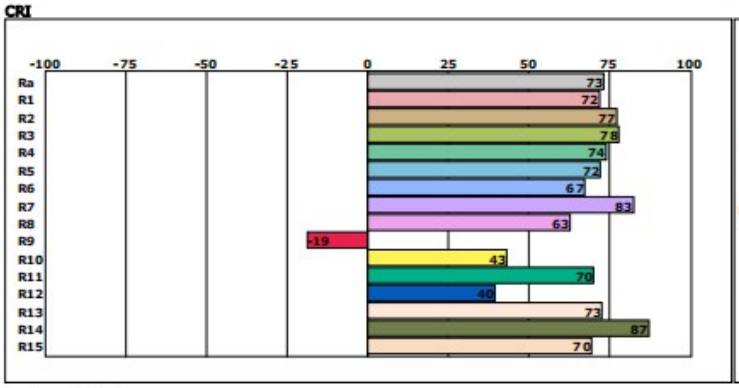
Spectrogram

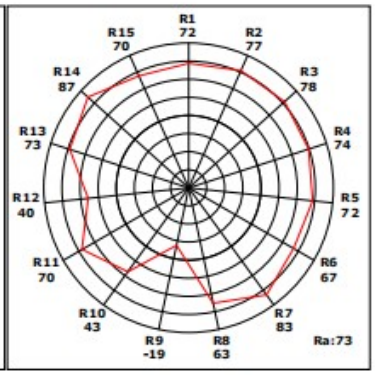


CIE1931



CRI



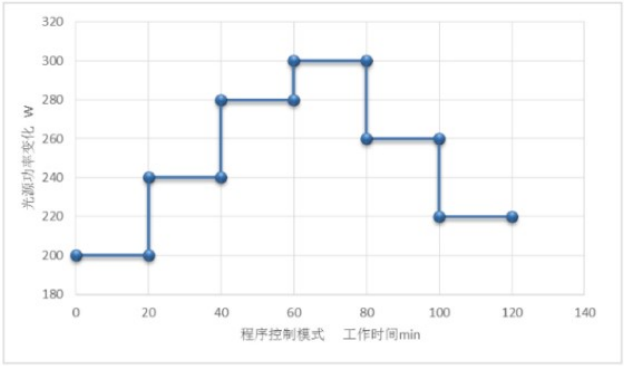


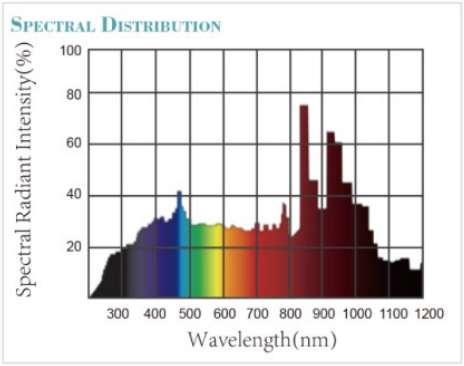
Instrument Status

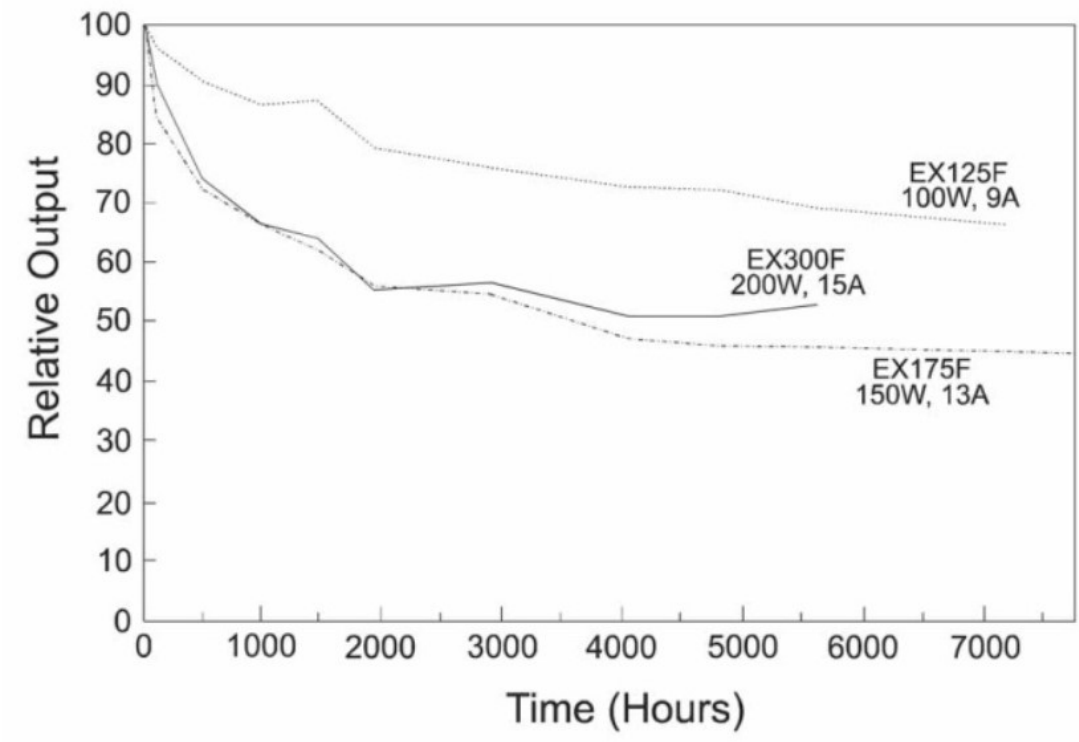
Type: OHSP-350UV SN: 0 Scan Range: 230-850nm

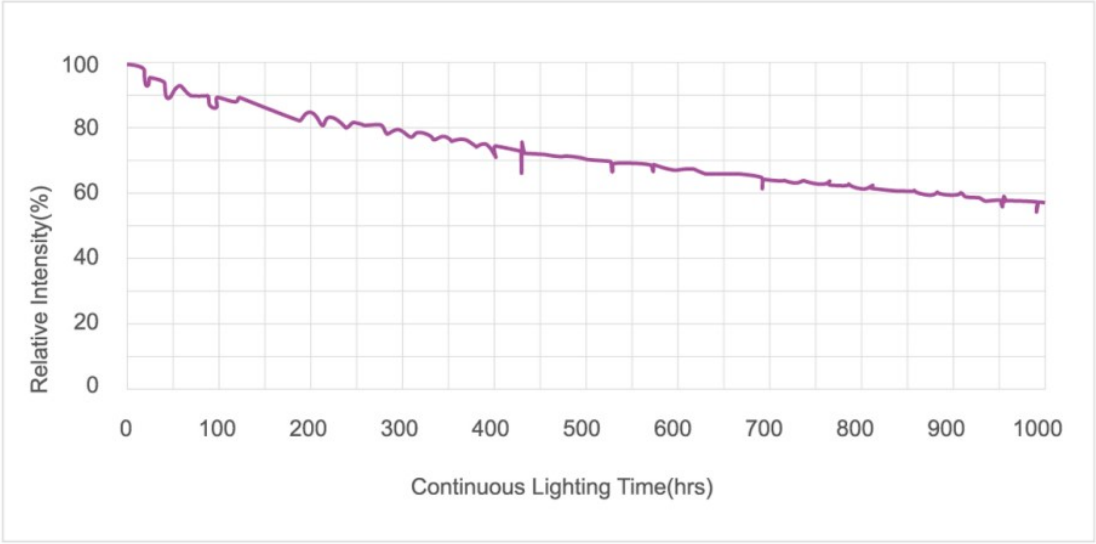
Integral Time: 0.573ms VPeak: 55804 VDark: 2294

We use **CEL-HXF300 Photocatalytic Xe Lamp Light Source**, which manufactured by Beijing CEAULIGHT Technology Co.ltd base in Beijing PRC. The light irradiation from a 300 W Xe lamp was used to simulate solar light, in which the outputting light density was about 100 mW cm^{-2}.
Spectrum as below:






Relative Output
100
90
80
70
60
50
40
30
20
10
0
0
1000
2000
3000
4000
5000
6000
7000
Time (Hours)
EX125F
100W, 9A
EX300F
200W, 15A
EX175F
150W, 13A


Relative Intensity(%)
100
80
60
40
20
0
0
100
200
300
400
500
600
700
800
900
1000
Continuous Lighting Time(hrs)

Computational methods

The first-principles calculations were carried out using the Spin-polarization density functional theory (DFT) as implemented in the Vienna Ab-initio Simulation Package (VASP), which has demonstrated good efficiency in explore the structure and property of materials.[1] The projector-augmented wave (PAW) pseudo-potential method[2] and plane-wave basis set were employed to describe the ionic cores and to take valence electrons into account, respectively. The configurations $2s^2 2p^2$ of C, $2s^2 2p^3$ of N, and $3s^2 3p^6 4s^1$ of K atoms were treated as valence electrons for the PAW pseudo-potentials. An energy cutoff of 500 eV was used for expansion of the plane-wave basis set. The generalized-gradient approximation (GGA) of Perdew-Burke-Ernzerhof (PBE) was used for the electronic exchange-correlation functional.[3] Van der Waals interactions have been considered using the PBE-based DFT-D2 correction method.[4] A vacuum of 15 Å perpendiculars to the sheets was applied to avoid the interaction between the periodic images. The 1×1×1 Gamma centered grid was used to sample the Brillouin zone. All structures investigated here are fully relaxed until the Hellmann-Feynman forces acting on all atoms are less than 0.05 eV/Å, and the total energy was smaller than 1×10^{-5} eV. For electronic structure and total energy calculation, the electronic self-consistent iteration were finished when it reach 1×10^{-6} eV.

Photocatalysts preparation

Synthesis of K-PHI-C_{doping}

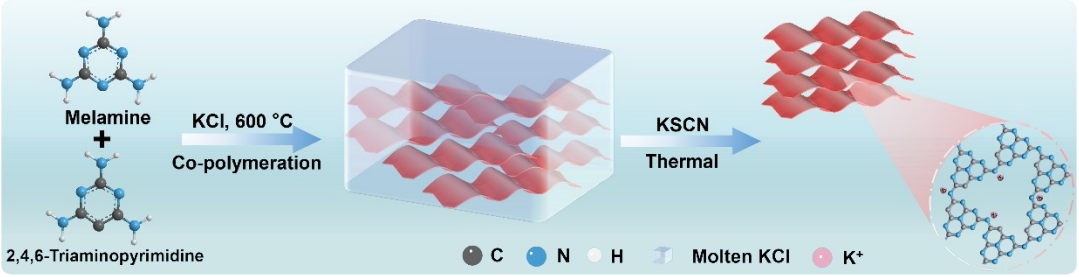
K-PHI-C_{doping} was prepared by a salt-template-induced in situ doping method.[5] A mixture of potassium chloride (4 g), melamine (2 g) and 2,4,6-triaminopyrimidine (TAP, 2 g) was grinded in a mortar for 20 min and dried in a vacuum oven at 60 °C for 3 h. Reaction mixtures were transferred into porcelain crucibles and covered with lids. Crucibles were placed in the oven and annealing at 600 °C for 3 h under constant atmospheric pressure. After completion of the heating program, the crucibles were allowed to cool slowly to room temperature. The crude products were washed with deionized water to remove the KCl salt and unreacted precursors, and dried in a vacuum oven at 60 °C overnight. Subsequently, the obtained products (2 g) and KSCN (4 g) were grinded in a mortar, and the mixed sample in a covered combustion boat was heated at 400 °C for 1 h and sequentially anneal at 500 °C for 30 min under Ar flow. The sample was cooled down to room temperature, washed with deionized water and dried in vacuum (60 °C, 20 mbar).

For control experiment, the pristine K-PHI and K-PHI-C_{doping}-X were prepared at the similar condition as K-PHI-C_{doping} by using only melamine or regulating the molar ratio of TAP and melamine precursor, respectively. for example, K-PHI-0.25 was prepared by copolymerization melamine (2.0 g) with TAP (0.5 g) under same procedure as K-PHI-C_{doping}.

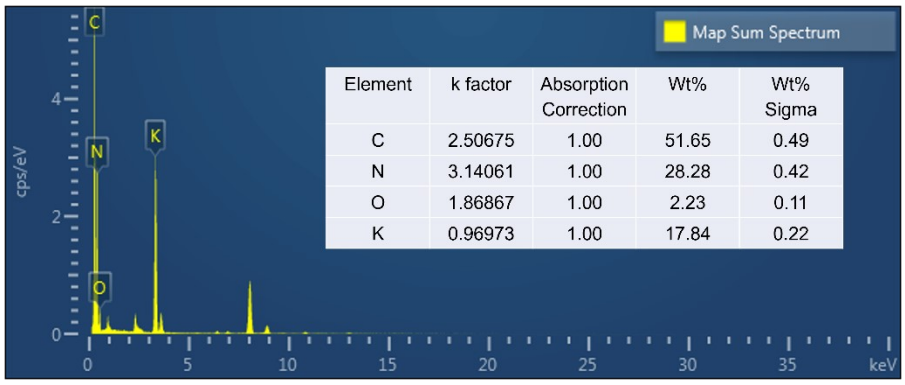
Synthesis of *g*-C_3N_4

g-C_3N_4 was prepared according to the following procedure. In brief, melamine (10.0 g) in a covered combustion boat was heated at 550 °C for 3 h using a heating rate of 10 °C min^{-1} in a muffle furnace. The resulting yellow product was grounded into power using an agate mortar for further use.

Figures of Supplementary Material Characterizations



Scheme S1. Schematic illustration of KCl salt-template-induced K-PHI-C_{doping}.



Element	k factor	Absorption Correction	Wt%	Wt% Sigma
C	2.50675	1.00	51.65	0.49
N	3.14061	1.00	28.28	0.42
O	1.86867	1.00	2.23	0.11
K	0.96973	1.00	17.84	0.22

Figure S1. Typical EDX spectrum obtained from K-PHI-C_{doping}.

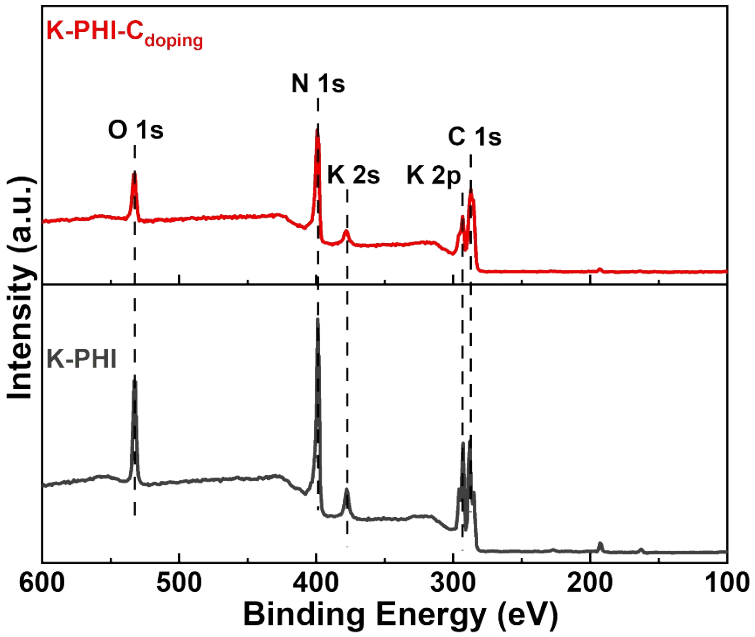


Figure S2. XPS survey spectra of K-PHI and K-PHI-C_{doping}.

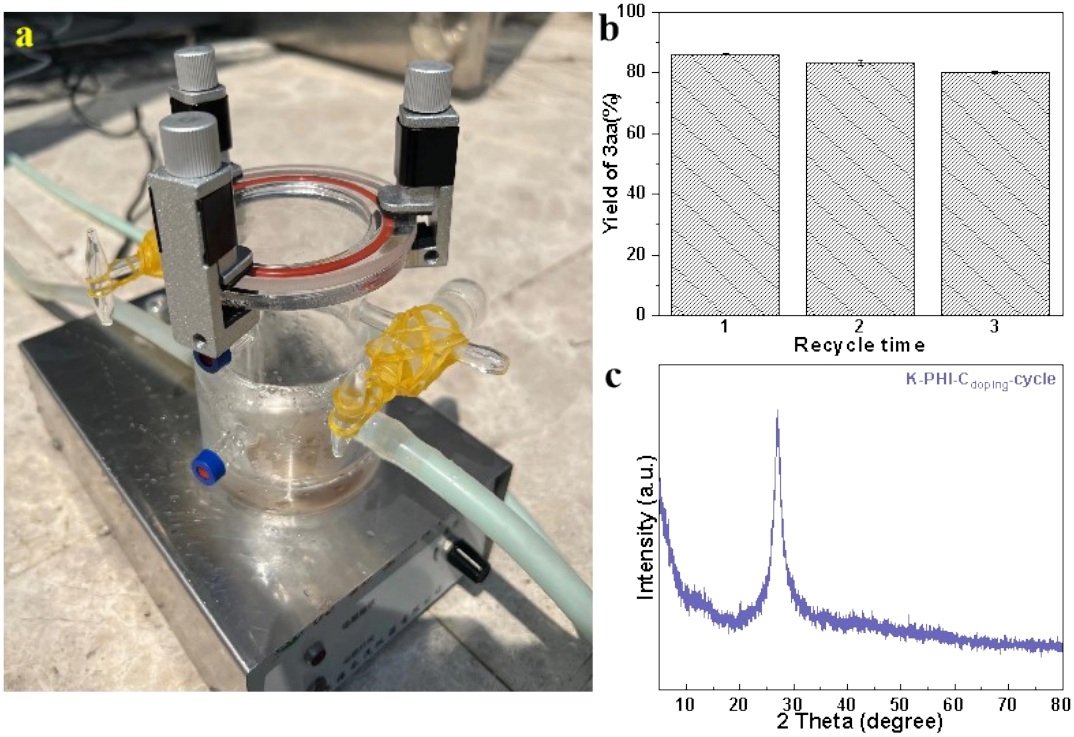


Figure S3. a The photograph of heterogeneous photocatalytic sulfenamide synthesis under real sunlight in summer. **b** Heterogeneous photocatalytic sulfenamide synthesis of 1a and 2a with recycled K-PHI-C_{doping} catalyst. Reaction conditions: 1a (0.1 mmol), 2a (1.0mmol), K-PHI-C_{doping} catalyst (10 mg), CH_3CN (2 mL), O_2, r.t., white LED, 24 h. Yields determined by GC. **c** The XRD pattern of K-PHI-C_{doping} after three recycles.

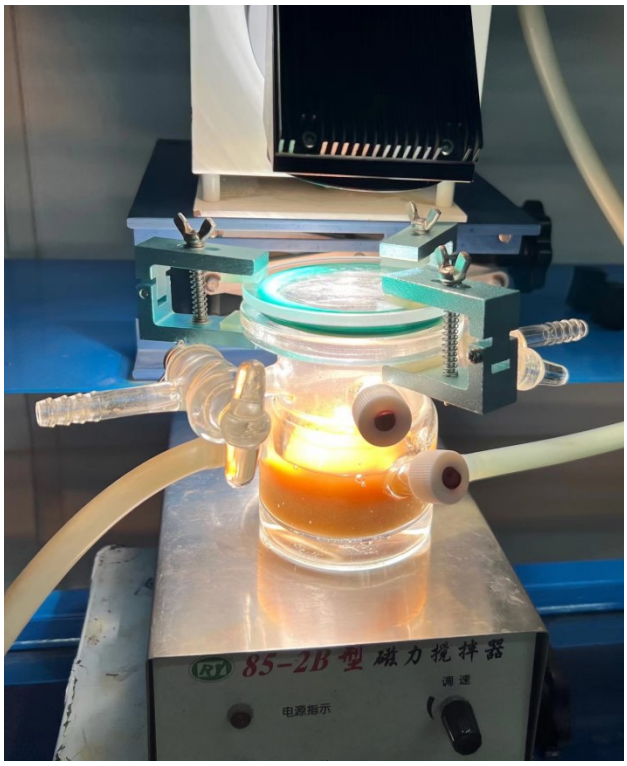


Figure S4. The photograph of heterogeneous photocatalytic sulfenamide synthesis under 300 W Xe lamp (100 mW·cm^{-2}).

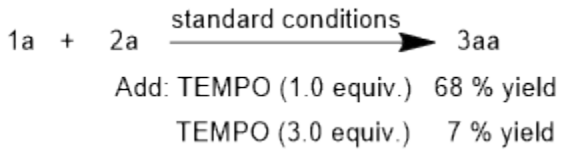


Figure S5. The yield of 3aa when TEMPO was added from 1.0 equiv. to 3.0 equiv. under the standard conditions.

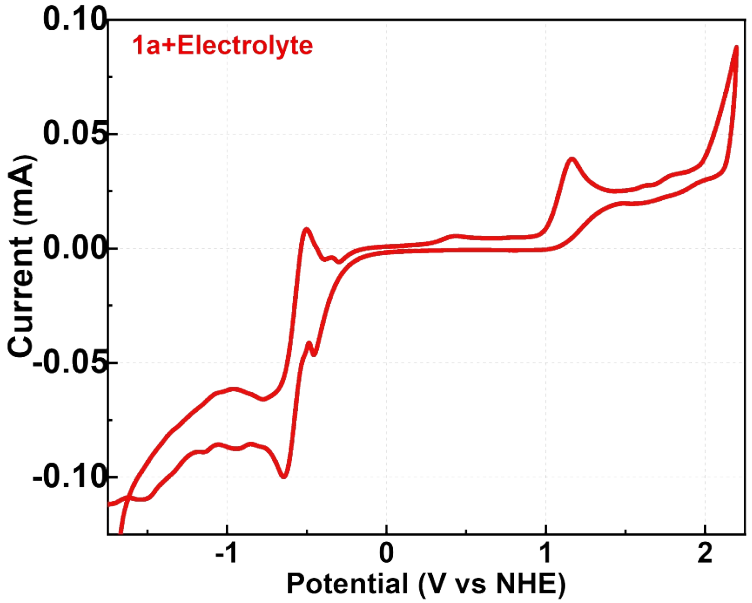


Figure S6. Cyclic voltammetry investigation of 2-mercaptobenzothiazole.

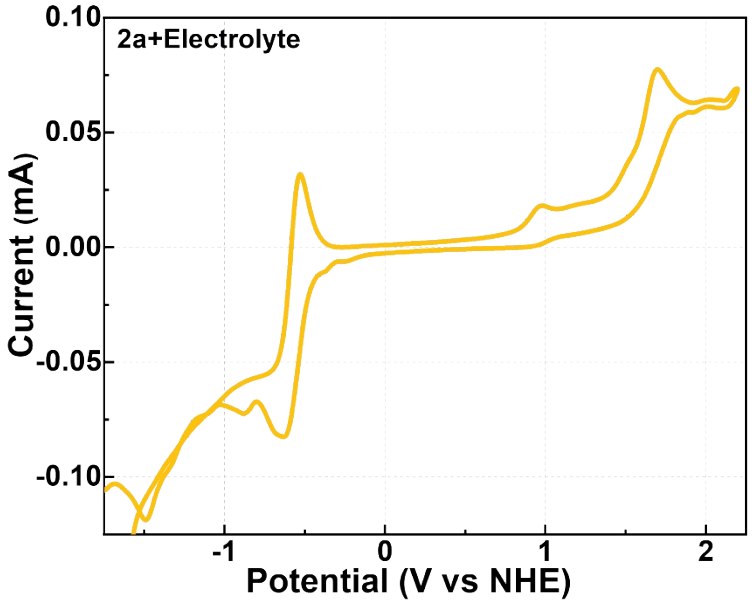


Figure S7. Cyclic voltammetry investigation of tert-butylamine.

Intermediate detection

The formation of thiyl radical and amine radical in the photocatalytic mechanism was confirmed by irradiating a mixture of DMPO, 2-mercaptobenzothiazole, tert-butylamine and K-PHI-C_{doping} in MeCN with white LED. LC-MS analysis of the reaction mixture revealed presence of several fragments with m/z 279.1, 185.2, and 114.1, which could be assigned to the of the $C_7H_4NS_2$-DMPO and $C_4H_{10}N$-DMPO adduct during the mass spectrum acquisition.

Reaction conditions: 2-mercaptobenzothiazole 0.1 mmol; tert-butylamine 0.1 mmol; DMPO 8.5 µl; K-PHI-C_{doping} 5 mg; MeCN 2 mL; T = 25 °C; O_2; irradiation with 10 W white LED.

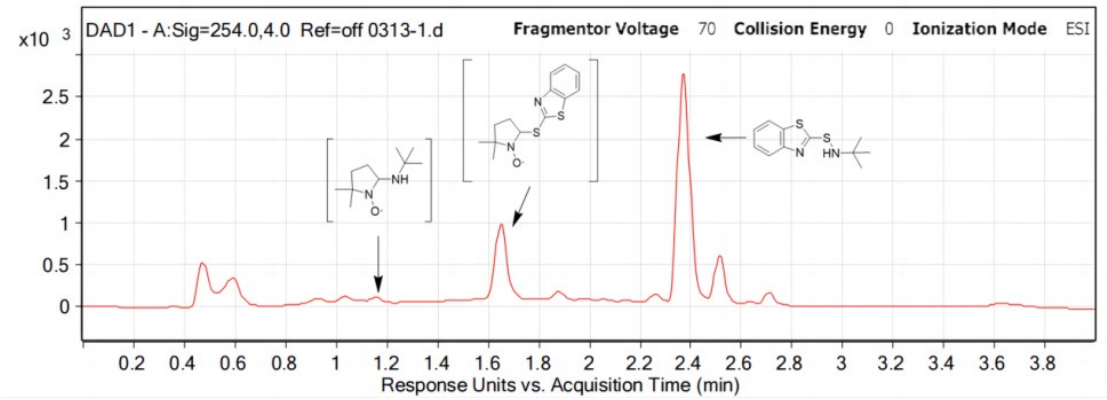


Figure S8. LC chromatogram of the reaction mixture after 20 h irradiation.

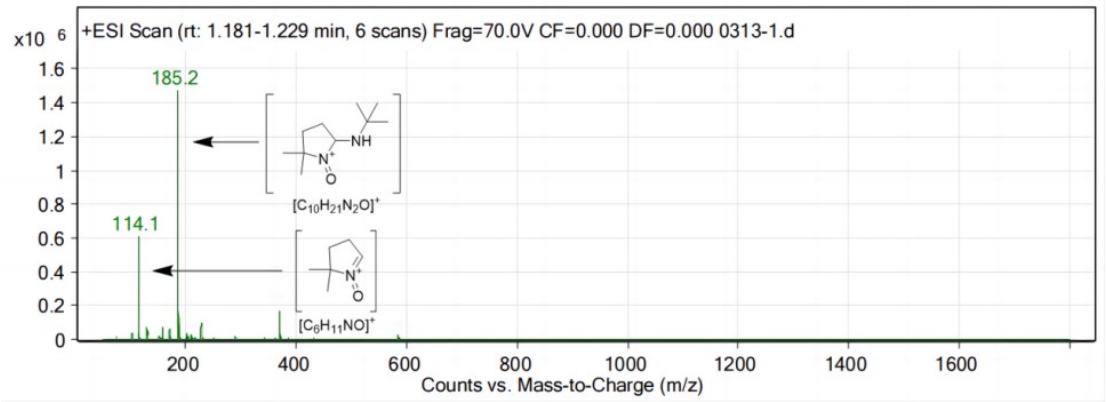


Figure S9. MS spectra of the DMPO-amine adduct (product with the retention time 1.210 min and M_z 185.2)

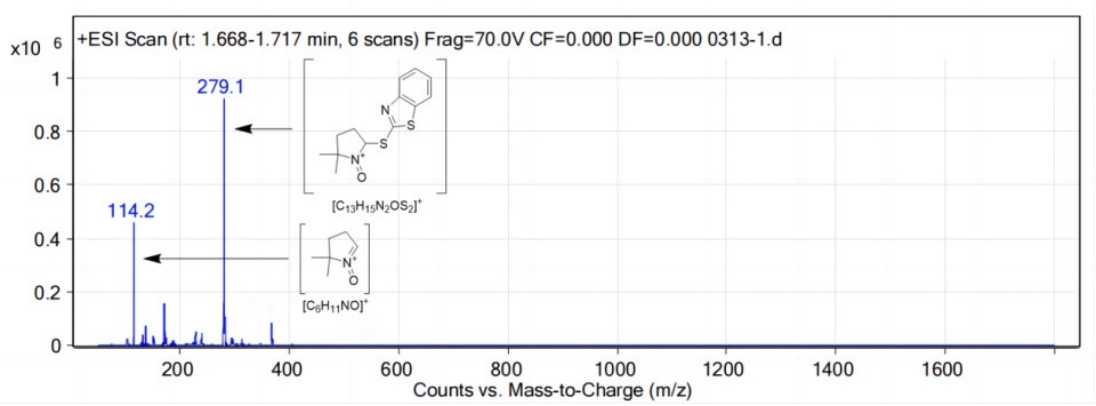


Figure S10. MS spectra of the DMPO-thiyl adduct (product with the retention time 1.688 min and M_z 279.1)

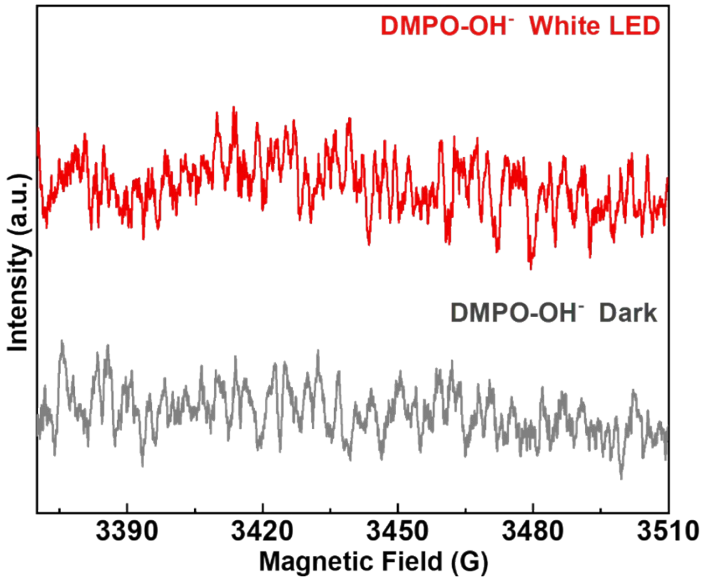


Figure S11. EPR spectra of DMPO-OH^- radical adduct under white LED irradiation and in dark with K-PHI-C_{doping} (5 mg), DMPO (0.0085 mL) in CH_3OH and CH_3CN (1:10).

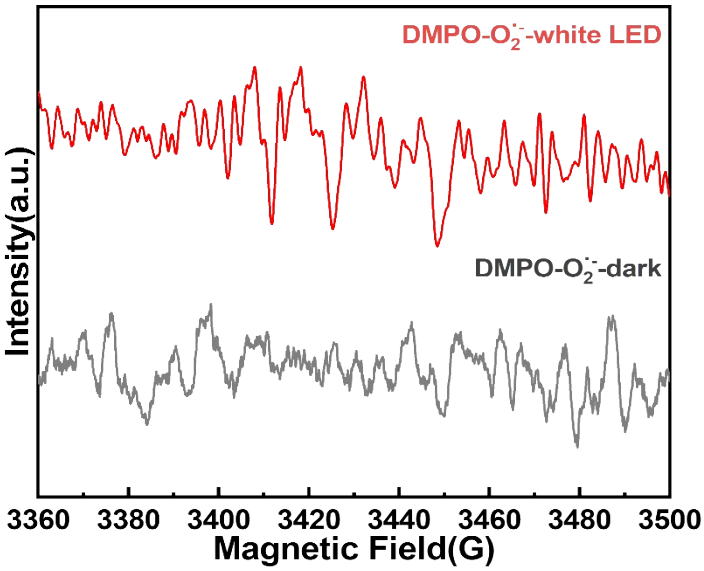


Figure S12. EPR spectra of DMPO-$O_2^{\cdot-}$ radical adduct under white LED irradiation and in dark with K-PHI-C_{doping} (5 mg), DMPO (0.0085 mL) in CH_3OH and CH_3CN (1:10).

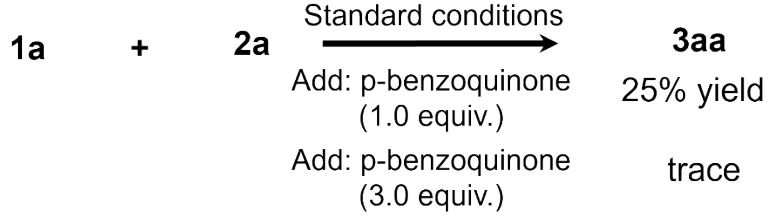


Figure S13. The yield of 3aa when p-benzoquinone was added from 1.0 to 3.0 equiv. under the standard conditions.

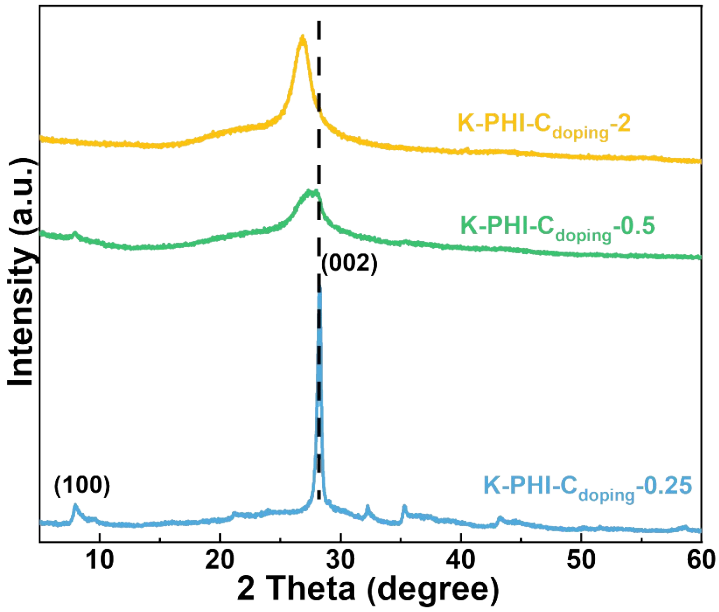


Figure S14. XRD pattern for K-PHI-C$_{doping}$-0.25, K-PHI-C$_{doping}$-0.5, K-PHI-C$_{doping}$-2.

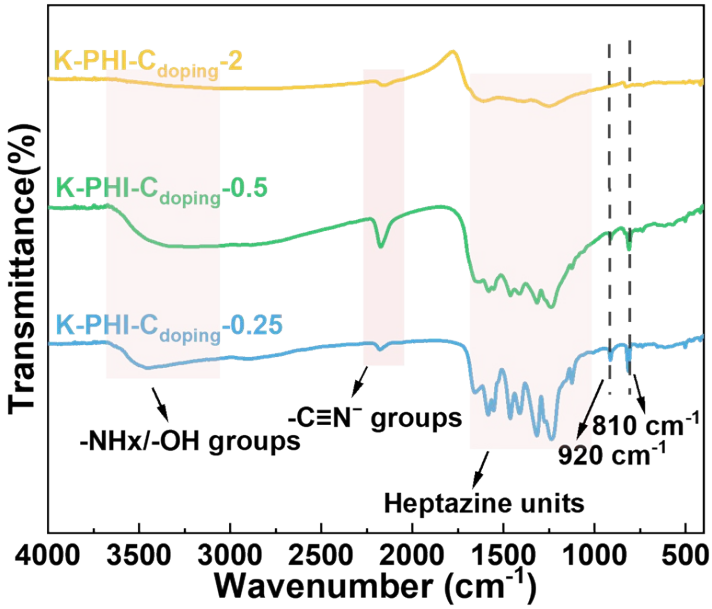


Figure S15. FTIR spectrum of K-PHI-C$_{doping}$-0.25, K-PHI-C$_{doping}$-0.5, K-PHI-C$_{doping}$-2.

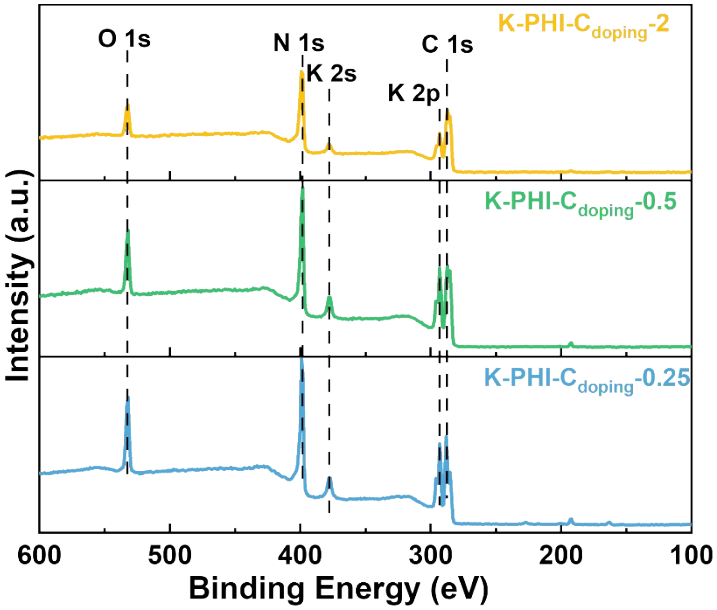


Figure S16. XPS survey spectra of K-PHI-C_{doping}-0.25, K-PHI-C_{doping}-0.5, K-PHI-C_{doping}-2.

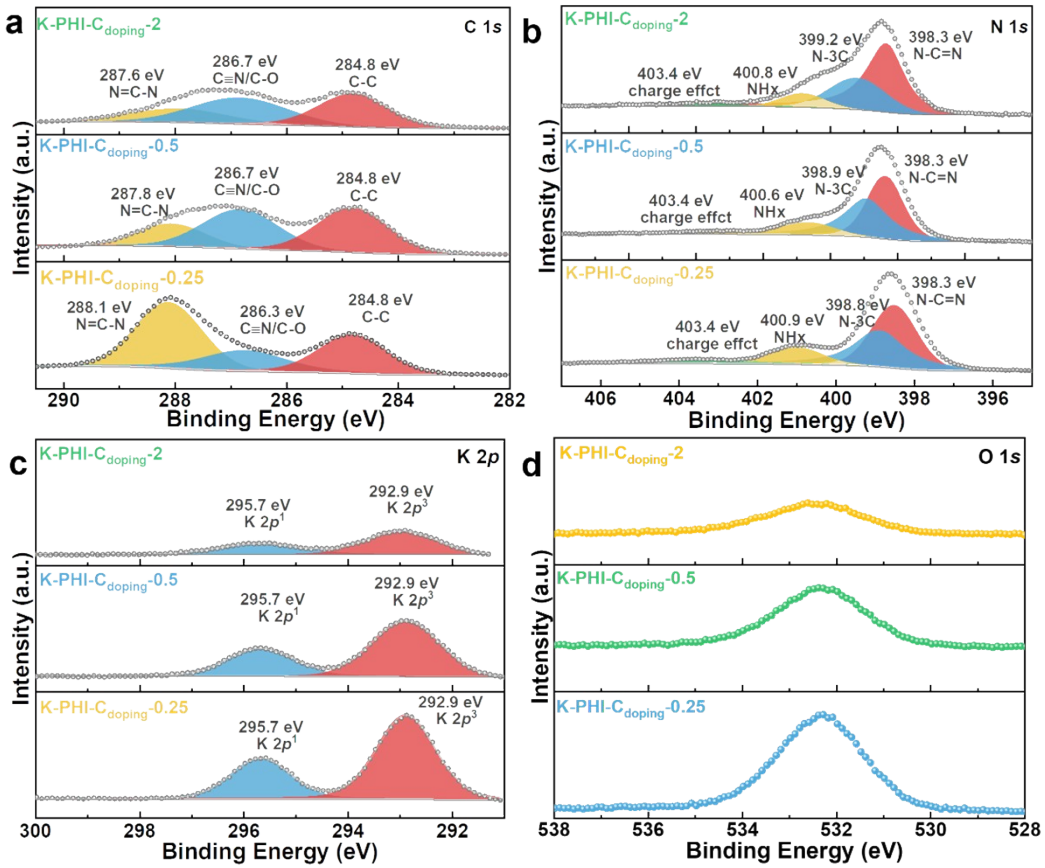


Figure S17. High-resolution XPS of (a) C 1*s*, (b) N 1 *s*, (c) K 2*p* and (d) O 1*s* for K-PHI-C_{doping}-0.25, K-PHI-C_{doping}-0.5, K-PHI-C_{doping}-2.

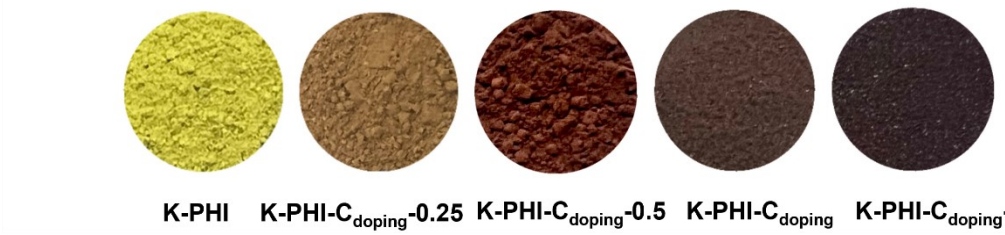


Figure S18. The appearance colors of K-PHI, K-PHI-C_{doping}-0.25, K-PHI-C_{doping}-0.5, K-PHI-C_{doping} and K-PHI-C_{doping}-2.

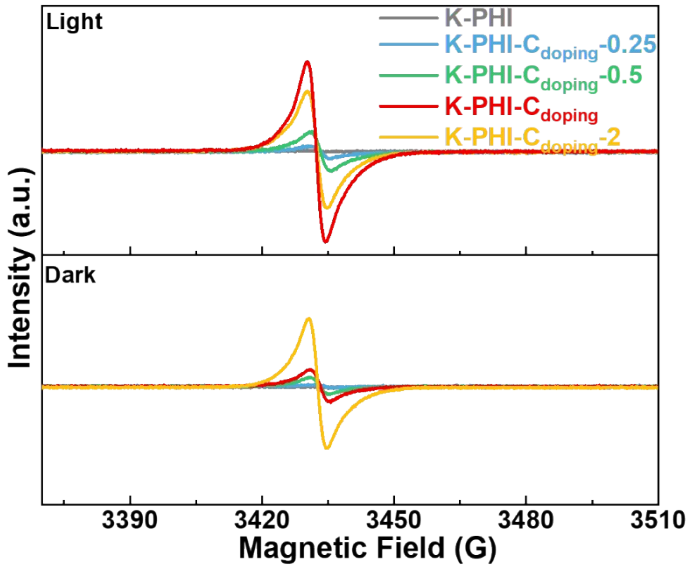


Figure S19. EPR spectra of K-PHI and K-PHI-C_{doping}-X in dark and under 300 W Xe irradiation.

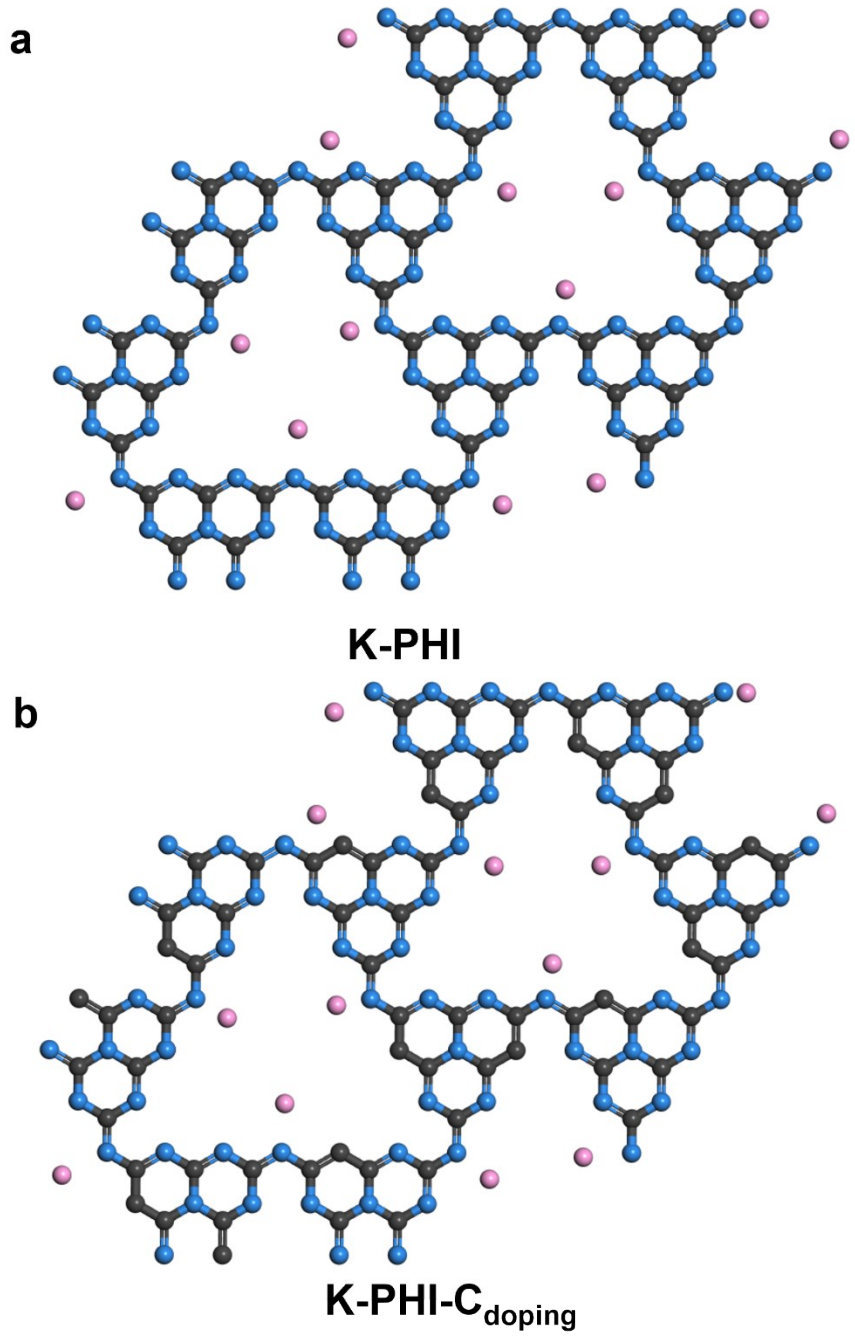


Figure S20. The structure of (a) K-PHI and (b) K-PHI-C_{doping} before structural optimization.

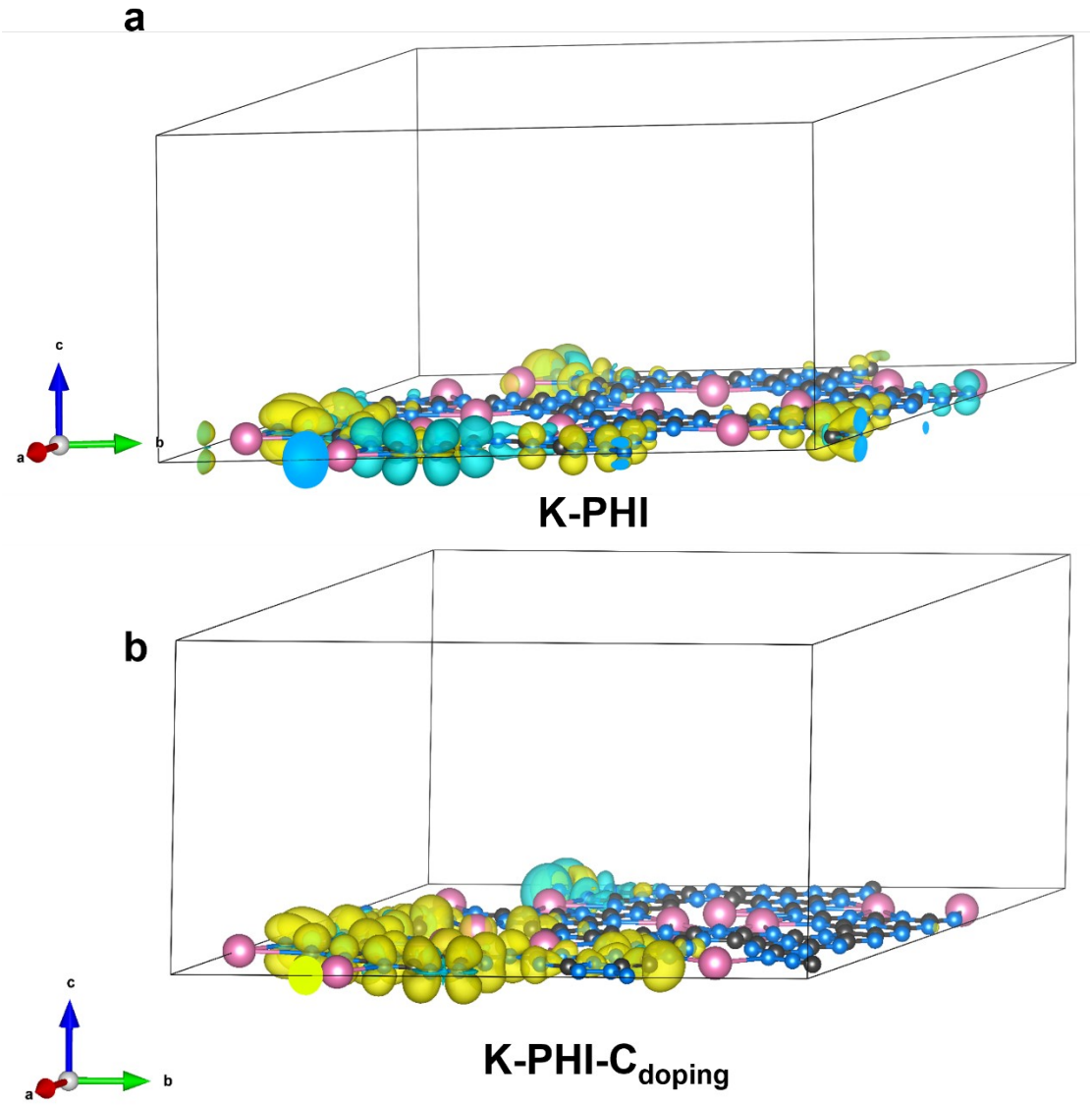


Figure S21. The corresponding side-view of charge density isosurface of (a) K-PHI and (b) K-PHI-C_{doping}, the yellow represents the electron accumulation area, and the cyan represents the electron depletion area. The isosurface value is 0.0005 eV Å^{-3}.

Table S1. Surface elemental compositions of the K-PHI, K-PHI-C_{doping}-0.25, K-PHI-C_{doping}-0.5, K-PHI-C_{doping} and K-PHI-C_{doping}-2 obtained from the XPS analysis.

	C 1s	N 1s	O 1s	C:N ratio	K 2s
K-PHI	23.57	36.56	21.41	0.64	18.46
K-PHI-C_{doping}-0.25	25.50	36.53	19.83	0.70	18.13
K-PHI-C_{doping}-0.5	30.06	34.06	17.24	0.88	18.63
K-PHI-C_{doping}	33.65	37.02	16.88	0.91	12.45
K-PHI-C_{doping}-2	35.53	37.37	14.88	0.95	12.21

Table S2. Composition of the reference K-PHI, K-PHI-C_{doping}-0.25, K-PHI-C_{doping}-0.5, K-PHI-C_{doping} and K-PHI-C_{doping}-2 according to XPS analysis.

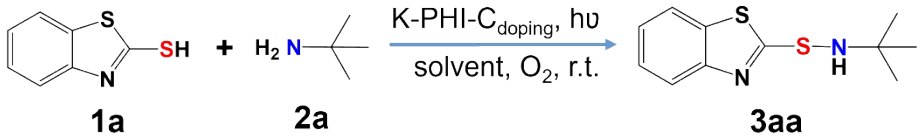
	C-C	C≡N/C-O	N=C-N	C-C/N=C-N ratio
K-PHI	28.41	11.17	60.42	0.47
K-PHI-C_{doping}-0.25	29.38	25.46	51.60	0.57
K-PHI-C_{doping}-0.5	44.55	21.32	37.14	1.20
K-PHI-C_{doping}	42.27	21.54	36.19	1.17
K-PHI-C_{doping}-2	37.67	32.86	29.47	1.28

Table S3. Elemental analysis of K-PHI, K-PHI-C_{doping}-0.25, K-PHI-C_{doping}-0.5, K-PHI-C_{doping} and K-PHI-C_{doping}-2.

	C (%)	N (%)	H (%)	C/N (wt/wt)
K-PHI	26.064	42.482	1.291	0.614
K-PHI-C_{doping}-0.25	27.119	41.366	1.394	0.655
K-PHI-C_{doping}-0.5	29.252	38.846	1.547	0.753
K-PHI-C_{doping}	34.710	44.112	1.506	0.787
K-PHI-C_{doping}-2	35.682	42.036	1.322	0.849

Reaction conditions optimization

Table S4. Sulfenamide synthesis at different solvents[a].



1a 2a 3aa

Entry	Solvent	Photocatalyst	λ_{max} (nm)	Yield[b] (%)
1	Acetonitrile	K-PHI-C_{doping}	White LED	92
2	DMSO	K-PHI-C_{doping}	White LED	37
3	DMF	K-PHI-C_{doping}	White LED	56
4	DCE	K-PHI-C_{doping}	White LED	75
5	Ethanol	K-PHI-C_{doping}	White LED	42
6	Deionize water	K-PHI-C_{doping}	White LED	0
7	Methanol	K-PHI-C_{doping}	White LED	34
8	Ethyl acetate	K-PHI-C_{doping}	White LED	77
9	Dichloromethane	K-PHI-C_{doping}	White LED	71

a Reaction conditions: 0.1 mmol 1a, 1.0 mmol 2a, 10 mg catalyst, 2 mL solvent, O_2 flow, White LED, 24 h, r.t.

b Yield is determined by GC.

Table S5. Sulfenamide synthesis at different temperature[a].

Entry	Temperature	Photocatalyst	λ_{max} (nm)	Yield[b] (%)
1	10	K-PHI-C_{doping}	White LED	78
2	25	K-PHI-C_{doping}	White LED	92
3	35	K-PHI-C_{doping}	White LED	81
4	45	K-PHI-C_{doping}	White LED	74

a Reaction conditions: 0.1 mmol 1a, 1.0 mmol 2a,10 mg catalyst, 2 mL CH_3CN, O_2 flow, White LED, 24 h.

b Yield is determined by GC.

Table S6. Sulfeniamide synthesis at different material ratio[a].

Entry	Solvent	2a(eq.)	Yield[b] (%)
1	**CH_3CN**	**1.0**	**65**
2	**CH_3CN**	**2.0**	**73**
3	**CH_3CN**	**4.0**	**80**
4	**CH_3CN**	**6.0**	**82**
5	**CH_3CN**	**8.0**	**85**
6	**CH_3CN**	**10.0**	**92**

a Reaction conditions: 1.0 eq.1a, 10 mg catalyst, 2 mL CH_3CN, O_2 flow, White LED, 24 h, r.t.

b Yield were determined by GC.

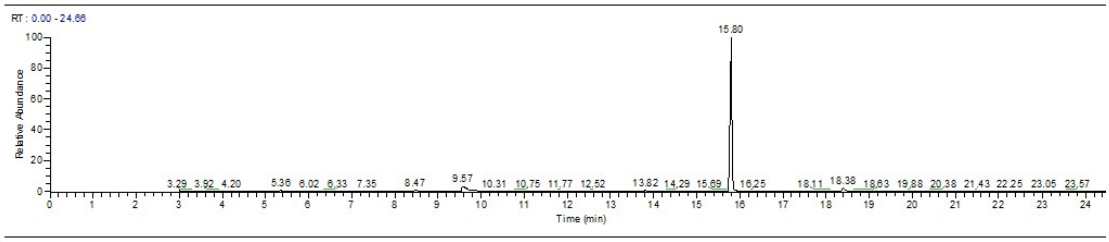
Synthesis methods

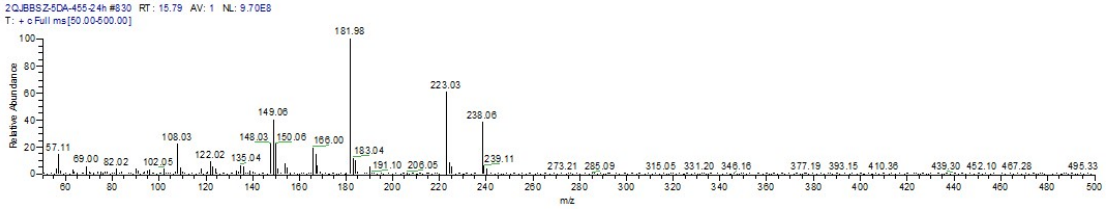
Preparation of Sulfenamides

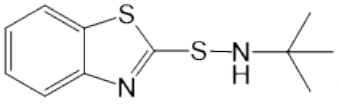
A substrate (0.1 mmol) and K-PHI-C_{doping} (10 mg) was added into a 10 mL screw-cap glass tube. The tube was fitted with the gas and placed into a metal block on a parallel reactor with a reflux condenser. The reactor was evacuated, refilled with O_2 flow for three times and closed with valve. Then amine (10 mmol) and acetonitrile (2 ml) were added into the reaction tube using syringes through a silicone pad on the cap. The reaction mixture was stirred under white LED irradiation at room temperature for 24 h. At the end of the reaction, the solid was filtered off and washed thoroughly with ethyl acetate. Then saturated sodium chloride solution (10 mL) was added to the filtrate. The products were extracted by ethyl acetate (3×15 mL). The combined organic extract was dried by Na_2SO_4 overnight and concentrated, then purified by column chromatography. Residue was analyzed by NMR and GC-MS.

Preparation of 3aa. To a reactor (10 mL) was added 2-mercaptobenzothiazole (0.1 mmol), K-PHI-C_{doping} (10 mg), tert-butylamine (1 mmol), 2 mL acetonitrile. The reactor was stirred under O_2 flow at room temperature for 24 h under white LED (82 mW·cm^{-2}) irradiation. The filtrate was extracted with ethyl acetate and the resulting residue was purified by flash chromatography on silica gel to give the isolated product with ethylacetate/hexane (1/15) as eluent. Residue was analyzed by NMR and GC-MS.

GC-MS of the reaction mixture prepared with 2-mercaptobenzothiazole (0.1 mmol) and tert-butylamine (1 mmol):



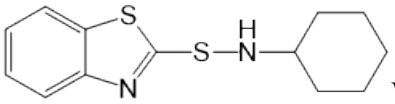




White solid, isolated yield 92%. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ 7.81 (d, *J* = 8.1 Hz, 1H), 7.79 (d, *J* = 7.9 Hz, 1H), 7.42 – 7.37 (m, 1H), 7.26 – 7.23 (m, 1H), 3.45 (s, 1H), 1.28 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 181.27, 155.22,

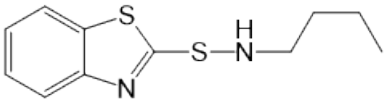
135.03, 125.87, 123.53, 121.56, 121.02, 55.62, 29.12. HRMS (ESI) m/z calcd. for $C_{11}H_{14}N_2S_2$ $[M+H]^+$:239.0671, found 239.0675. LRMS (EI) m/z calcd. for $C_{11}H_{14}N_2S_2M^+$: 238, found 238.

Preparation of 3ab. To a reactor (10 mL) was added 2-mercaptobenzothiazole (0.1 mmol), K-PHI-C_{doping} (10 mg), cyclohexylamine (1 mmol), 2 mL acetonitrile. The reactor was stirred under O_2 flow at room temperature for 24 h under white LED (82 $mW \cdot cm^{-2}$) irradiation. The filtrate was extracted with ethyl acetate and the resulting residue was purified by flash chromatography on silica gel to give the isolated product with ethylacetate/hexane (1/15) as eluent. Residue was analyzed by NMR and GC-MS.



White solid, isolated yield 88%. ^1H NMR (400 MHz, $CDCl_3$, 298 K) δ 7.81 (d, J = 7.9 Hz, 1H), 7.78 (d, J = 8.1 Hz, 1H), 7.42 – 7.36 (m, 1H), 7.26 (dd, J = 15.3, 1.2 Hz, 1H), 3.26 (br, 1H), 2.95 – 2.86 (m, 1H), 2.09 (d, J = 9.3 Hz, 2H), 1.77 (dd, J = 8.8, 3.5 Hz, 2H), 1.62 – 1.60 (m 1H), 1.32 – 1.18 (m, 5H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 180.31, 155.54, 135.44, 126.25, 123.96, 121.97, 121.42, 60.72, 34.17, 26.08, 25.32. HRMS m/z (ESI) calcd for $C_{13}H_{16}N_2S_2$ $[M+H]^+$: 265.0828, found 265.0830. LRMS (EI) m/z calcd. for $C_{13}H_{16}N_2S_2M^+$: 264, found 264.

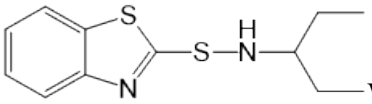
Preparation of 3ac. To a reactor (10 mL) was added 2-mercaptobenzothiazole (0.1 mmol), K-PHI-C_{doping} (10 mg), n-butylamine (1 mmol), 2 mL acetonitrile. The reactor was stirred under O_2 flow at room temperature for 24 h under white LED (82 $mW \cdot cm^{-2}$) irradiation. The filtrate was extracted with ethyl acetate and the resulting residue was purified by flash chromatography on silica gel to give the isolated product with ethylacetate/hexane (1/10) as eluent. Residue was analyzed by NMR and GC-MS.



Light yellow oil, isolated yield 84%. ^1H NMR (400 MHz, $CDCl_3$, 298 K) δ 7.85 (d, J = 8.2 Hz, 1H), 7.79 (d, J = 7.8 Hz, 1H), 7.43 – 7.37 (m, 1H), 7.26 (dd, J = 15.2, 1.2 Hz, 1H), 3.41 (d, J = 5.9 Hz, 1H), 3.15 – 3.07 (m, 2H), 1.59 (p, J = 7.2 Hz, 2H), 1.40 (dq, J = 14.4, 7.3 Hz, 2H), 0.95 (t, J = 7.4 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 178.41, 154.75, 134.83, 125.66, 123.42, 121.37, 120.86, 52.62, 32.47, 19.72, 13.67. HRMS (ESI) m/z calcd. for $C_{10}H_{12}N_2S_2$ $[M+H]^+$: 225.0515, found 225.0515. LRMS (EI) m/z calcd. for $C_{10}H_{12}N_2S_2M^+$: 224, found 224.

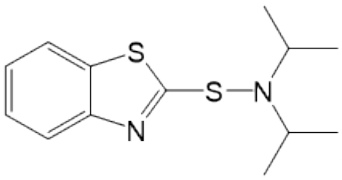
Preparation of 3ad. To a reactor (10 mL) was added 2-mercaptobenzothiazole (0.1 mmol), K-PHI-C_{doping} (10 mg), diethylamine (1 mmol), 2 mL acetonitrile. The reactor was stirred under O_2 flow at room temperature for 24 h under white LED (82 $mW \cdot cm^{-2}$) irradiation. The filtrate was extracted with ethyl acetate and the resulting residue

was purified by flash chromatography on silica gel to give the isolated product with ethylacetate/hexane (1/15) as eluent. Residue was analyzed by NMR and GC-MS.



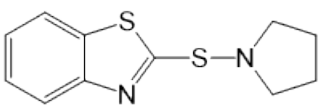
White solid, isolated yield 75%. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ 7.81 (d, *J* = 8.2 Hz, 1H), 7.78 (d, *J* = 7.8 Hz, 1H), 7.39 (t, *J* = 7.8 Hz, 1H), 7.29 – 7.25 (m, 1H), 3.18 (q, *J* = 7.1 Hz, 4H), 1.27 (t, *J* = 7.1 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 178.99, 155.02, 134.84, 125.59, 123.29, 121.32, 120.72, 52.31, 13.31. HRMS (ESI) m/z calcd for $C_{11}H_{14}N_2S_2$ $[M+H]^+$: 239.0671, found 239.0676. LRMS (EI) m/z calcd. for $C_{11}H_{14}N_2S_2M^+$: 224, found 224.

Preparation of 3ae. To a reactor (10 mL) was added 2-mercaptobenzothiazole (0.1 mmol), K-PHI-C_{doping} (10 mg), diisopropylamine (1 mmol), 2 mL acetonitrile. The reactor was stirred under O_2 flow at room temperature for 24 h under white LED (82 $mW \cdot cm^{-2}$) irradiation. The filtrate was extracted with ethyl acetate and the resulting residue was purified by flash chromatography on silica gel to give the isolated product with ethylacetate/hexane (1/20) as eluent. Residue was analyzed by NMR and GC-MS.



White solid, isolated yield 31%. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ 7.79 (d, *J* = 8.1 Hz, 1H), 7.75 (d, *J* = 7.3 Hz, 1H), 7.38 (ddd, *J* = 8.3, 7.3, 1.3 Hz, 1H), 7.27 – 7.22 (m, 1H), 3.48 (hept, *J* = 6.5 Hz, 2H), 1.26 (d, *J* = 6.5 Hz, 12H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 182.43, 134.78, 125.81, 123.44, 121.40, 120.91, 55.75, 22.55, 21.74. HRMS (ESI) m/z calcd. for $C_{13}H_{18}N_2S_2$ $[M+H]^+$: 267.0984, found 267.0986. LRMS (EI) m/z calcd. for $C_{13}H_{18}N_2S_2M^+$: 266, found 266.

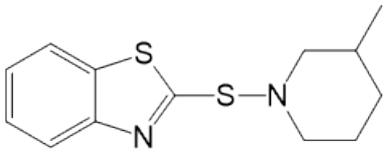
Preparation of 3af. To a reactor (10 mL) was added 2-mercaptobenzothiazole (0.1 mmol), K-PHI-C_{doping} (10 mg), pyrrolidine (1 mmol), 2 mL acetonitrile. The reactor was stirred under O_2 flow at room temperature for 24 h under white LED (82 $mW \cdot cm^{-2}$) irradiation. The filtrate was extracted with ethyl acetate and the resulting residue was purified by flash chromatography on silica gel to give the isolated product with ethylacetate/hexane (1/12) as eluent. Residue was analyzed by NMR and GC-MS.



Yellow oil, isolated yield 60%. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ 7.82 (d, *J* = 8.1 Hz, 1H), 7.78 (d, *J* = 8.2 Hz, 1H), 7.38 (td, *J* = 7.7, 1.3 Hz, 1H), 7.26 (ddd, *J* = 8.3, 7.3, 1.2 Hz, 1H), 3.56 – 3.49 (m, 4H), 2.81 – 2.74 (m, 4H).

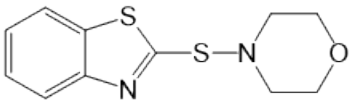
HRMS (ESI) m/z calcd for $C_{11}H_{12}N_2S_2$ $[M+H]^+$: 237.0515, found 237.0519. LRMS (EI) m/z calcd. for $C_{11}H_{12}N_2S_2M^+$: 236, found 236.

Preparation of 3ag. To a reactor (10 mL) was added 2-mercaptobenzothiazole (0.1 mmol), K-PHI-C_{doping} (10 mg), 3-methylpiperidine (1 mmol), 2 mL acetonitrile. The reactor was stirred under O_2 flow at room temperature for 24 h under white LED (82 $mW \cdot cm^{-2}$) irradiation. The filtrate was extracted with ethyl acetate and the resulting residue was purified by flash chromatography on silica gel to give the isolated product with ethylacetate/hexane (1/15) as eluent. Residue was analyzed by NMR and GC-MS.



Light yellow oil, isolated yield 75%, ^{1}H NMR (400 MHz, $CDCl_3$,298 K) δ 7.82 (d, *J* = 8.1 Hz, 1H), 7.79 (d, *J* = 7.9 Hz, 1H), 7.43 – 7.34 (m, 1H), 7.26 (dd, *J* = 15.1, 1.1 Hz, 1H), 3.27 (dt, *J* = 10.4, 5.1 Hz, 2H), 3.06 (t, *J* = 11.0 Hz, 1H), 2.76 (t, *J* = 11.0 Hz, 1H), 1.88 (dtd, *J* = 10.4, 6.8, 3.5 Hz, 1H), 1.80 – 1.71 (m, 3H), 1.06 – 0.92 (m, 1H), 0.91 (d, *J* = 6.7 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 177.61, 155.41, 135.33, 125.88, 123.67, 121.78, 121.43, 121.09, 65.02, 57.58, 32.79, 31.78, 26.80, 19.33. HRMS (ESI) m/z calcd. for $C_{13}H_{16}N_2S_2$ $[M+H]^+$: 265.0828, found 265.0831. LRMS (EI) m/z calcd. for $C_{13}H_{16}N_2S_2M^+$: 264, found 264.

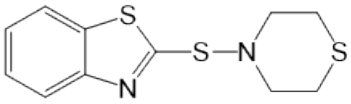
Preparation of 3ah. To a reactor (10 mL) was added 2-mercaptobenzothiazole (0.1 mmol), K-PHI-C_{doping} (10 mg), morpholine (1 mmol), 2 mL acetonitrile. The reactor was stirred under O_2 flow at room temperature for 24 h under white LED (82 $mW \cdot cm^{-2}$) irradiation. The filtrate was extracted with ethyl acetate and the resulting residue was purified by flash chromatography on silica gel to give the isolated product with ethylacetate/hexane (1/15) as eluent. Residue was analyzed by NMR and GC-MS.



White solid, isolated yield 87%. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ 7.82 (d, *J* = 8.1 Hz, 1H), 7.78 (d, *J* = 7.9 Hz, 1H), 7.38 (t, *J* = 7.1 Hz, 1H), 7.26 (d, *J* = 14.1 Hz, 1H), 3.82 – 3.78 (m, 4H), 3.29 – 3.23 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.90, 155.15, 135.13, 126.11, 124.05, 122.00, 121.15, 67.99, 56.69. HRMS (ESI) m/z calcd for $C_{11}H_{12}N_2OS_2$ $[M+H]^+$: 253.0464, found 253.0467.LRMS (EI) m/z calcd. for $C_{11}H_{12}N_2OS_2M^+$: 252, found 252.

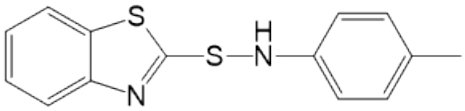
Preparation of 3ai. To a reactor (10 mL) was added 2-mercaptobenzothiazole (0.1 mmol), K-PHI-C_{doping} (10 mg), thiomorpholine (1 mmol), 2 mL acetonitrile. The reactor was stirred under O_2 flow at room temperature for 24 h under white LED (82 $mW \cdot cm^{-2}$) irradiation. The filtrate was extracted with ethyl acetate and the resulting residue was

purified by flash chromatography on silica gel to give the isolated product with ethylacetate/hexane (1/20) as eluent. Residue was analyzed by NMR and GC-MS.



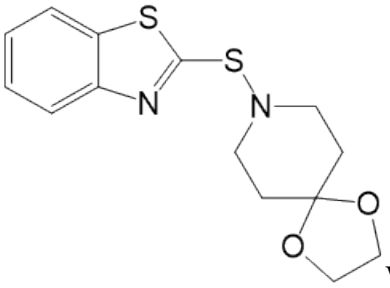
Yellow solid, isolated yield 90%. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ 7.82 (d, *J* = 8.1 Hz, 1H), 7.78 (d, *J* = 7.9 Hz, 1H), 7.39 (ddd, *J* = 8.3, 7.3, 1.3 Hz, 1H), 7.26 (d, *J* = 1.5 Hz, 1H), 3.38 – 3.30 (m, 4H), 2.01 – 1.93 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 178.22, 155.30, 135.19, 125.91, 123.69, 121.73, 121.12, 55.85, 26.34. HRMS (ESI) m/z calcd. for $C_{11}H_{12}N_2S_3$ $[M+H]^+$: 269.0235, found 269.0237. LRMS (EI) m/z calcd. for $C_{11}H_{12}N_2S_3M^+$:268, found 268.

Preparation of 3aj. To a reactor (10 mL) was added 2-mercaptobenzothiazole (0.1 mmol), K-PHI-C_{doping} (10 mg), paratoluidine (1 mmol), 2 mL acetonitrile. The reactor was stirred under O_2 flow at room temperature for 24 h under white LED (82 mW·cm^{-2}) irradiation. The filtrate was extracted with ethyl acetate and the resulting residue was purified by flash chromatography on silica gel to give the isolated product with ethylacetate/hexane (1/25) as eluent. Residue was analyzed by NMR and GC-MS.



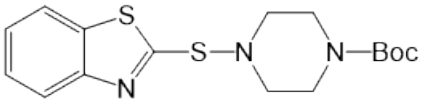
Light yellow solid, isolated yield 27%. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ 7.86 (d, *J* = 8.1 Hz, 1H), 7.72 (d, *J* = 7.9 Hz, 1H), 7.41 (t, *J* = 8.4 Hz, 1H), 7.28 (d, *J* = 7.3 Hz, 2H), 7.08 (d, *J* = 8.2 Hz, 2H), 7.02 (d, *J* = 8.7 Hz, 2H), 5.40 (s, 1H), 2.28 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 176.68, 154.85, 142.55, 134.97, 131.39, 130.00, 126.13, 124.02, 121.85, 121.16, 115.27, 20.59. HRMS (ESI) m/z calcd. for $C_{14}H_{12}N_2S_2$ $[M+H]^+$: 273.0515, found 273.0521. LRMS (EI) m/z calcd. for $C_{14}H_{12}N_2S_2M^+$: 272, found 272.

Preparation of 3ak. To a reactor (10 mL) was added 2-mercaptobenzothiazole (0.1 mmol), K-PHI-C_{doping} (10 mg), 4-piperidone ethyleneketal (1 mmol), 2 mL acetonitrile. The reactor was stirred under O_2 flow at room temperature for 24 h under white LED (82 mW·cm^{-2}) irradiation. The filtrate was extracted with ethyl acetate and the resulting residue was purified by flash chromatography on silica gel to give the isolated product with ethylacetate/hexane (1/15) as eluent. Residue was analyzed by NMR and GC-MS.



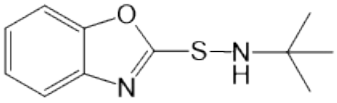
White solid, isolated yield 76%. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ 7.82 (d, J = 8.1 Hz, 1H), 7.79 (d, J = 7.8 Hz, 1H), 7.42 – 7.36 (m, 1H), 7.26 (dd, J = 15.2, 1.2 Hz, 1H), 3.97 (s, 4H), 3.38 (t, J = 5.7 Hz, 4H), 1.89 (t, J = 5.8 Hz, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 176.92, 155.39, 135.31, 125.96, 123.78, 121.86, 121.13, 105.94, 64.52, 55.32, 36.23. HRMS (ESI) m/z calcd for $C_{14}H_{16}N_2O_2S_2$ $[M+H]^+$: 309.0726, found 309.0732. LRMS (EI) m/z calcd for $C_{14}H_{16}N_2O_2S_2M^+$: 308, found 308.

Preparation of 3al. To a reactor (10 mL) was added 2-mercaptobenzothiazole (0.1 mmol), K-PHI-C_{doping} (10 mg), 1-boc-piperazine (1 mmol), 2 mL acetonitrile. The reactor was stirred under O_2 flow at room temperature for 24 h under white LED (82 $mW \cdot cm^{-2}$) irradiation. The filtrate was extracted with ethyl acetate and the resulting residue was purified by flash chromatography on silica gel to give the isolated product with ethylacetate/hexane (1/15) as eluent. Residue was analyzed by NMR and GC-MS.



White solid, isolated yield 75%. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ 7.81 (d, J = 8.2 Hz, 1H), 7.77 (d, J = 7.8 Hz, 1H), 7.42 – 7.34 (m, 1H), 7.28 – 7.23 (m, 1H), 3.58 – 3.51 (m, 4H), 3.21 (t, J = 5.0 Hz, 4H), 1.45 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.83, 155.14, 154.69, 135.16, 126.12, 124.08, 122.02, 121.16, 80.32, 56.34, 28.52. HRMS (ESI) m/z calcd. for $C_{16}H_{21}N_3O_2S_2$ $[M+H]^+$: 352.1148, found 352.1150.

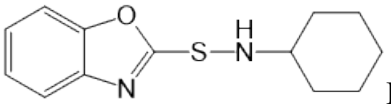
Preparation of 3ba. To a reactor (10 mL) was added 2-mercaptobenzoxazole (0.1 mmol), K-PHI-C_{doping} (10 mg), tert-butylamine (1 mmol), 2 mL acetonitrile. The reactor was stirred under O_2 flow at room temperature for 24 h under white LED (82 $mW \cdot cm^{-2}$) irradiation. The filtrate was extracted with ethyl acetate and the resulting residue was purified by flash chromatography on silica gel to give the isolated product with ethylacetate/hexane (1/15) as eluent. Residue was analyzed by NMR and GC-MS.



White solid, isolated yield 73%. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ 7.61 (d, J = 7.9 Hz, 1H), 7.45 (d, J = 8.0 Hz, 1H), 7.29 – 7.20 (m, 2H), 3.17 (s, 1H), 1.22 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.19, 152.08, 142.47, 124.66,

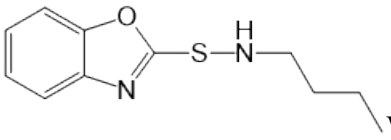
124.26, 119.25, 110.39, 55.84, 29.37. HRMS (ESI) m/z calcd for $C_{11}H_{14}N_2OS$ $[M+H]^+$:223.0900, found 223.0904.

Preparation of 3bb. To a reactor (10 mL) was added 2-mercaptobenzoxazole (0.1 mmol), K-PHI-C_{doping} (10 mg), cyclohexylamine (1 mmol), 2 mL acetonitrile. The reactor was stirred under O_2 flow at room temperature for 24 h under white LED (82 $mWcm^{-2}$) irradiation. The filtrate was extracted with ethyl acetate and the resulting residue was purified by flash chromatography on silica gel to give the isolated product with ethylacetate/hexane (1/15) as eluent. Residue was analyzed by NMR and GC-MS.



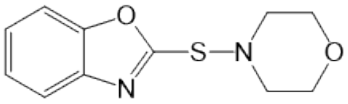
Light yellow solid, isolated yield 66%. ^1H NMR (400 MHz, $CDCl_3$, 298 K) δ 7.66 – 7.59 (m, 1H), 7.47 – 7.44 (m, 1H), 7.31 – 7.22 (m, 2H), 3.27 (s, 1H), 2.09 – 2.00 (m, 2H), 1.74 (s, 2H), 1.31 – 1.18 (m, 5H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.98, 151.60, 141.75, 124.05, 123.60, 118.49, 109.85, 58.07, 32.50, 25.57, 24.14. HRMS (ESI) m/z calcd for $C_{13}H_{16}N_2OS$ $[M+H]^+$: 249.1056, found 249.1061.

Preparation of 3bc. To a reactor (10 mL) was added 2-mercaptobenzoxazole (0.1 mmol), K-PHI-C_{doping} (10 mg), n-butylamine (1 mmol), 2 mL acetonitrile. The reactor was stirred under O_2 flow at room temperature for 24 h under white LED (82 $mW \cdot cm^{-2}$) irradiation. The filtrate was extracted with ethyl acetate and the resulting residue was purified by flash chromatography on silica gel to give the isolated product with ethylacetate/hexane (1/15) as eluent. Residue was analyzed by NMR.



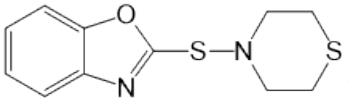
White oil, isolated yield 71%. ^1H NMR (400 MHz, $CDCl_3$, 298 K) δ 7.63 (d, J = 5.7 Hz, 1H), 7.48 – 7.43 (m, 1H), 7.34 – 7.26 (m, 2H), 3.23 (d, J = 5.3 Hz, 1H), 3.20 – 3.12 (m, 2H), 1.61 – 1.55 (m, 2H), 1.41 – 1.36 (m, 2H), 0.92 (d, J = 7.3 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.12, 152.03, 142.08, 124.47, 124.04, 118.83, 110.24, 52.58, 32.08, 20.03, 13.99.

Preparation of 3bd. To a reactor (10 mL) was added 2-mercaptobenzoxazole (0.1 mmol), K-PHI-C_{doping} (10 mg), morpholine (1 mmol), 2 mL acetonitrile. The reactor was stirred under O_2 flow at room temperature for 24 h under white LED (82 $mW \cdot cm^{-2}$) irradiation. The filtrate was extracted with ethyl acetate and the resulting residue was purified by flash chromatography on silica gel to give the isolated product with ethylacetate/hexane (1/15) as eluent. Residue was analyzed by NMR and GC-MS.



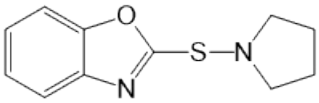
White solid, isolated yield 56%. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ 7.65 (dd, *J* = 6.5, 1.8 Hz, 1H), 7.49 (dd, *J* = 7.1, 2.2 Hz, 1H), 7.36 – 7.26 (m, 2H), 3.80 – 3.73 (m, 4H), 3.50 – 3.38 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.28, 151.51, 141.80, 124.56, 124.46, 119.31, 110.30, 67.86, 55.93. HRMS (ESI) m/z calcd for $C_{11}H_{12}N_2O_2S$ $[M+H]^+$: 237.0692, found 237.0696.

Preparation of 3be. To a reactor (10 mL) was added 2-mercaptobenzoxazole (0.1 mmol), K-PHI-C_{doping} (10 mg), thiomorpholine (1 mmol), 2 mL acetonitrile. The reactor was stirred under O_2 flow at room temperature for 24 h under white LED (82 mW·cm^{-2}) irradiation. The filtrate was extracted with ethyl acetate and the resulting residue was purified by flash chromatography on silica gel to give the isolated product with ethylacetate/hexane (1/15) as eluent. Residue was analyzed by NMR and GC-MS.



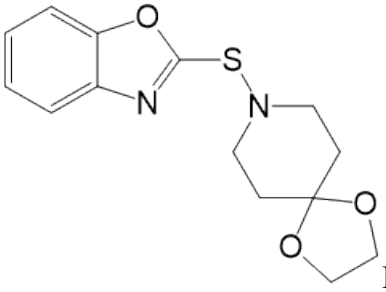
White solid, isolated yield 59%. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ 7.38 (d, *J* = 8.7 Hz, 1H), 7.27 (d, *J* = 8.2 Hz, 1H), 7.19 (td, *J* = 7.7, 1.2 Hz, 1H), 7.04 (td, *J* = 7.7, 1.2 Hz, 1H), 4.02 – 3.99 (m, 4H), 2.76 – 2.72 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.76, 148.72, 142.98, 124.15, 120.84, 116.36, 108.85, 48.12, 26.75. HRMS (ESI) m/z calcd for $C_{11}H_{12}N_2OS$ $[M+H]^+$: 253.0464, found 253.0468.

Preparation of 3bf. To a reactor (10 mL) was added 2-mercaptobenzoxazole (0.1 mmol), K-PHI-C_{doping} (10 mg), pyrrolidine (1 mmol), 2 mL acetonitrile. The reactor was stirred under O_2 flow at room temperature for 24 h under white LED (82 mW·cm^{-2}) irradiation. The filtrate was extracted with ethyl acetate and the resulting residue was purified by flash chromatography on silica gel to give the isolated product with ethylacetate/hexane (1/15) as eluent. Residue was analyzed by NMR.



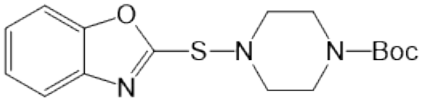
White oil, isolated yield 57%. ^{1}H NMR (400 MHz, DMSO, 298 K) δ 7.68 (dd, *J* = 6.2, 2.5 Hz, 2H), 7.38 – 7.29 (m, 2H), 3.31 (d, *J* = 6.7 Hz, 4H), 1.96 – 1.88 (m, 4H). ^{13}C NMR (101 MHz, DMSO) δ 165.30, 150.91, 141.13, 124.60, 124.31, 118.59, 110.41, 54.76, 25.66.

Preparation of 3bg. To a reactor (10 mL) was added 2-mercaptobenzoxazole (0.1 mmol), K-PHI-C_{doping} (10 mg), 4-piperidone ethyleneketal (1 mmol), 2 mL acetonitrile. The reactor was stirred under O_2 flow at room temperature for 24 h under white LED (82 mW·cm^{-2}) irradiation. The filtrate was extracted with ethyl acetate and the resulting residue was purified by flash chromatography on silica gel to give the isolated product with ethylacetate/hexane (1/15) as eluent. Residue was analyzed by NMR.



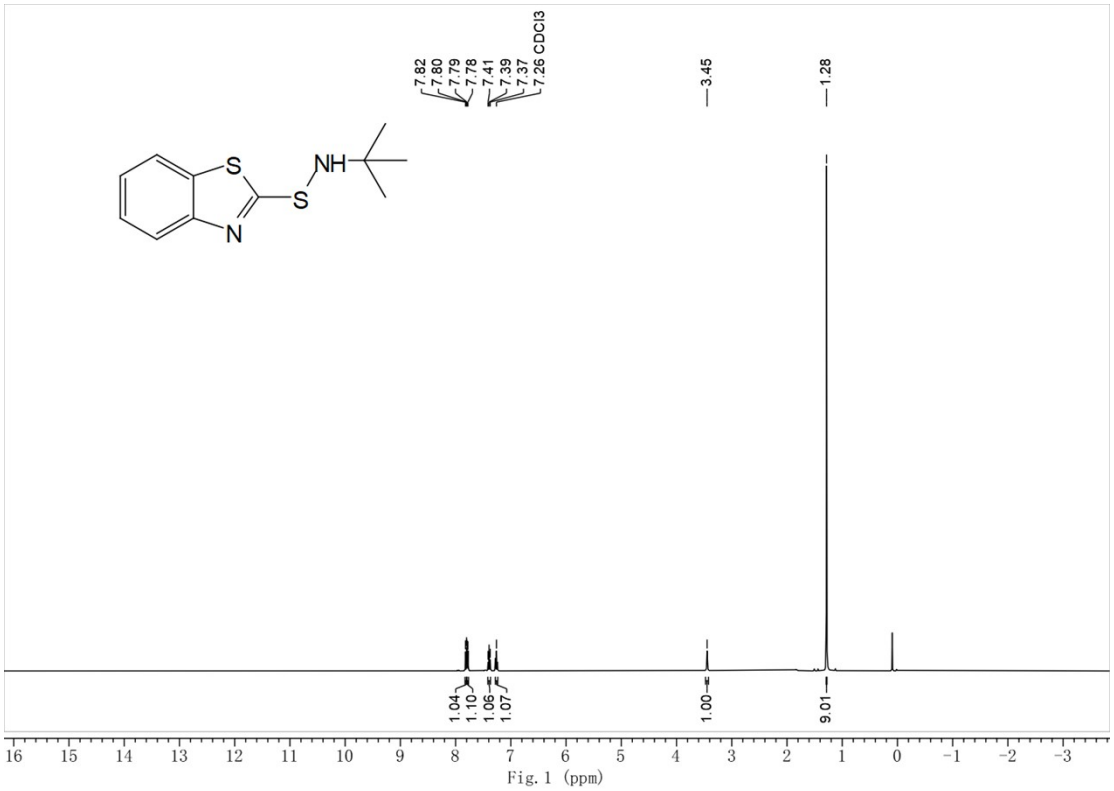
Light yellow oil, isolated yield 72%. ^{1}H NMR (400 MHz, DMSO, 298 K) δ 7.81 – 7.65 (m, 1H), 7.48 – 7.31 (m, 1H), 3.89 (s, 1H), 3.44 (t, J = 5.7 Hz, 1H), 1.74 (t, J = 5.8 Hz, 1H). ^{13}C NMR (101 MHz, DMSO) δ 164.61, 150.71, 141.07, 124.73, 124.69, 118.83, 110.48, 104.79, 63.74, 54.14, 35.71.

Preparation of 3bh. To a reactor (10 mL) was added 2-mercaptobenzoxazole (0.1 mmol), K-PHI-C_{doping} (10 mg), 1-boc-piperazine (1 mmol), 2 mL acetonitrile. The reactor was stirred under O_2 flow at room temperature for 24 h under white LED (82 mW·cm^{-2}) irradiation. The filtrate was extracted with ethyl acetate and the resulting residue was purified by flash chromatography on silica gel to give the isolated product with ethylacetate/hexane (1/15) as eluent. Residue was analyzed by NMR.



White solid, isolated yield 67%. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ 7.81 (d, J = 7.8 Hz, 1H), 7.78 (d, J = 7.9 Hz, 1H), 7.41 – 7.35 (m, 1H), 7.26 (d, J = 15.8 Hz, 1H), 3.58 – 3.51 (m, 4H), 3.21 (t, J = 5.0 Hz, 4H), 1.45 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.81, 155.13, 154.68, 135.15, 126.11, 124.07, 122.01, 121.15, 80.31, 56.34, 28.51, 1.14.

Copies of ^{1}H-NMR and ^{13}C-NMR spectrum



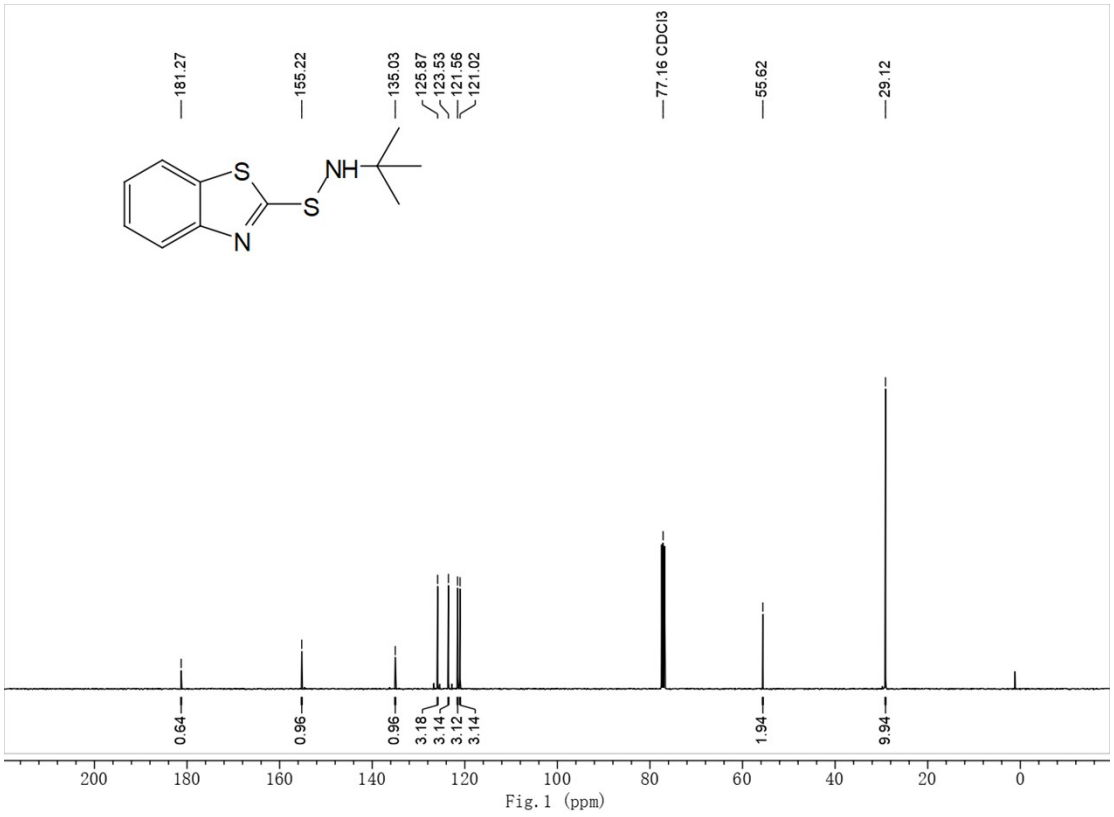


Figure S22. ^{1}H-NMR and ^{13}C-NMR spectrum of

S-(benzo[d]thiazol-2-yl)-*N*-(tert-butyl)thiohydroxylamine

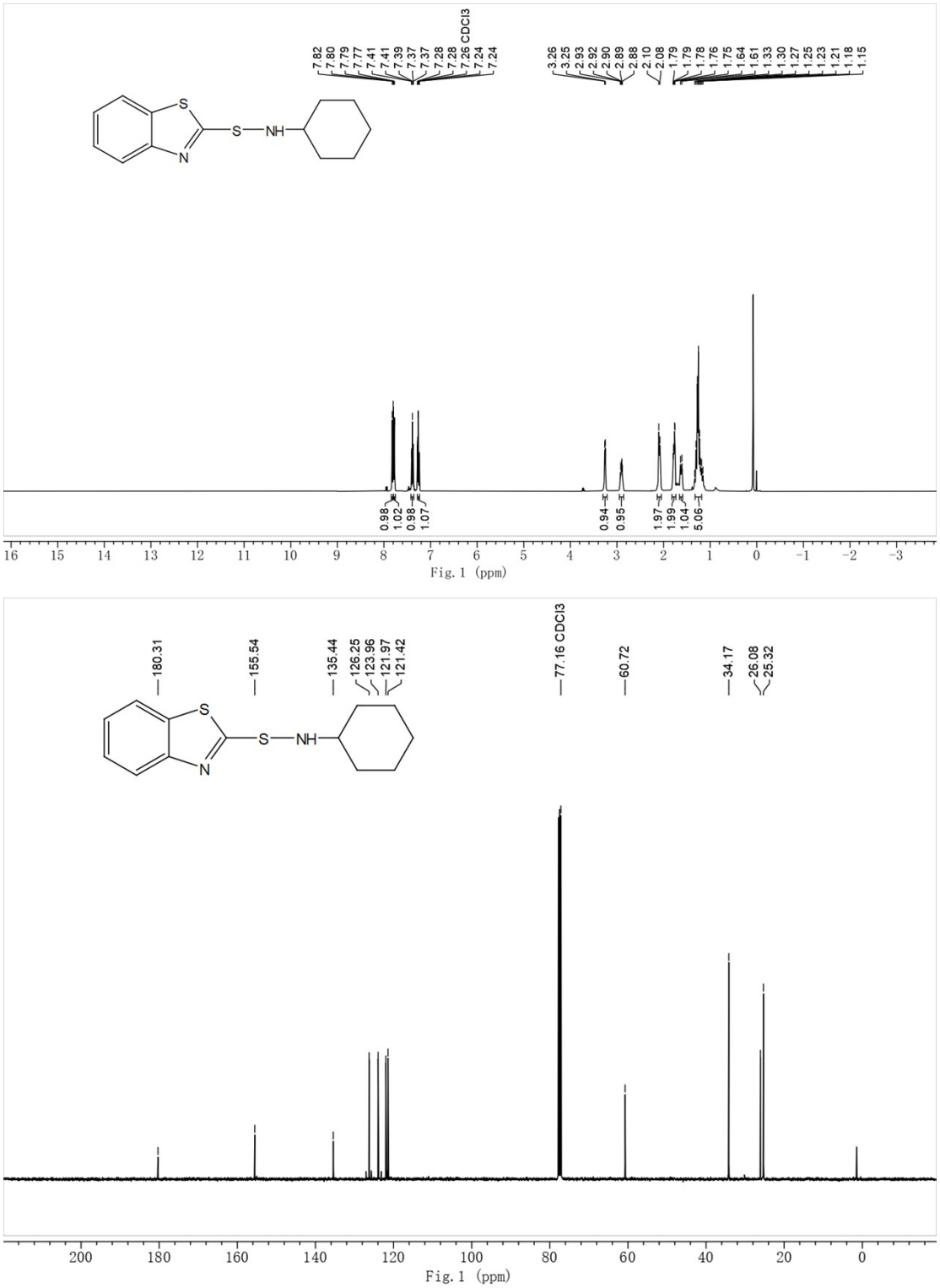
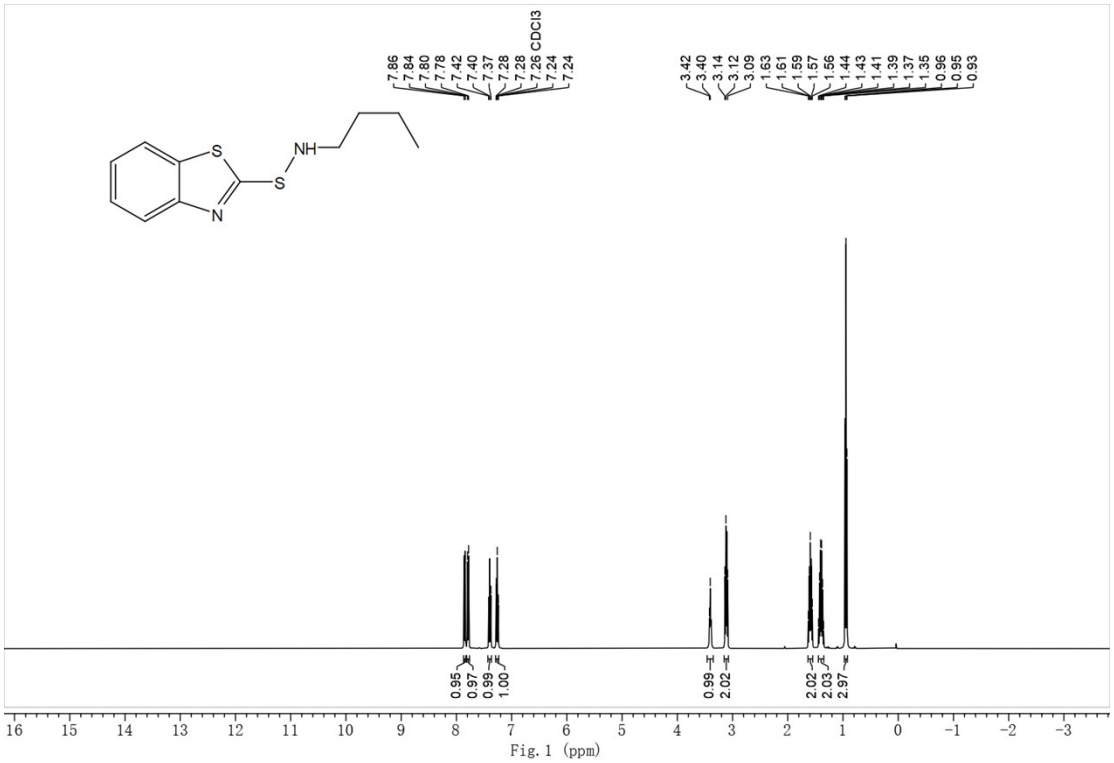


Figure S23. ^{1}H-NMR and ^{13}C-NMR spectrum of

S-(benzo[d]thiazol-2-yl)-*N*-cyclohexylthiohydroxylamine



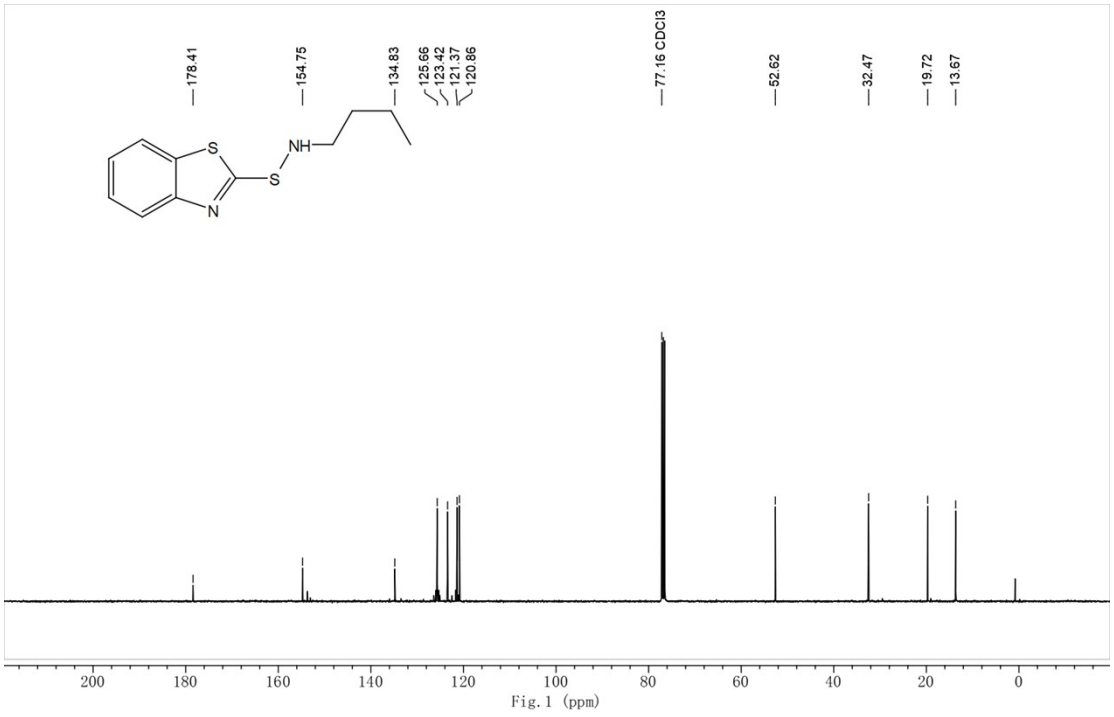


Figure S24. ^{1}H-NMR and ^{13}C-NMR spectrum of *S*-(benzo[*d*]thiazol-2-yl)-*N*-butylthiohydroxylamine

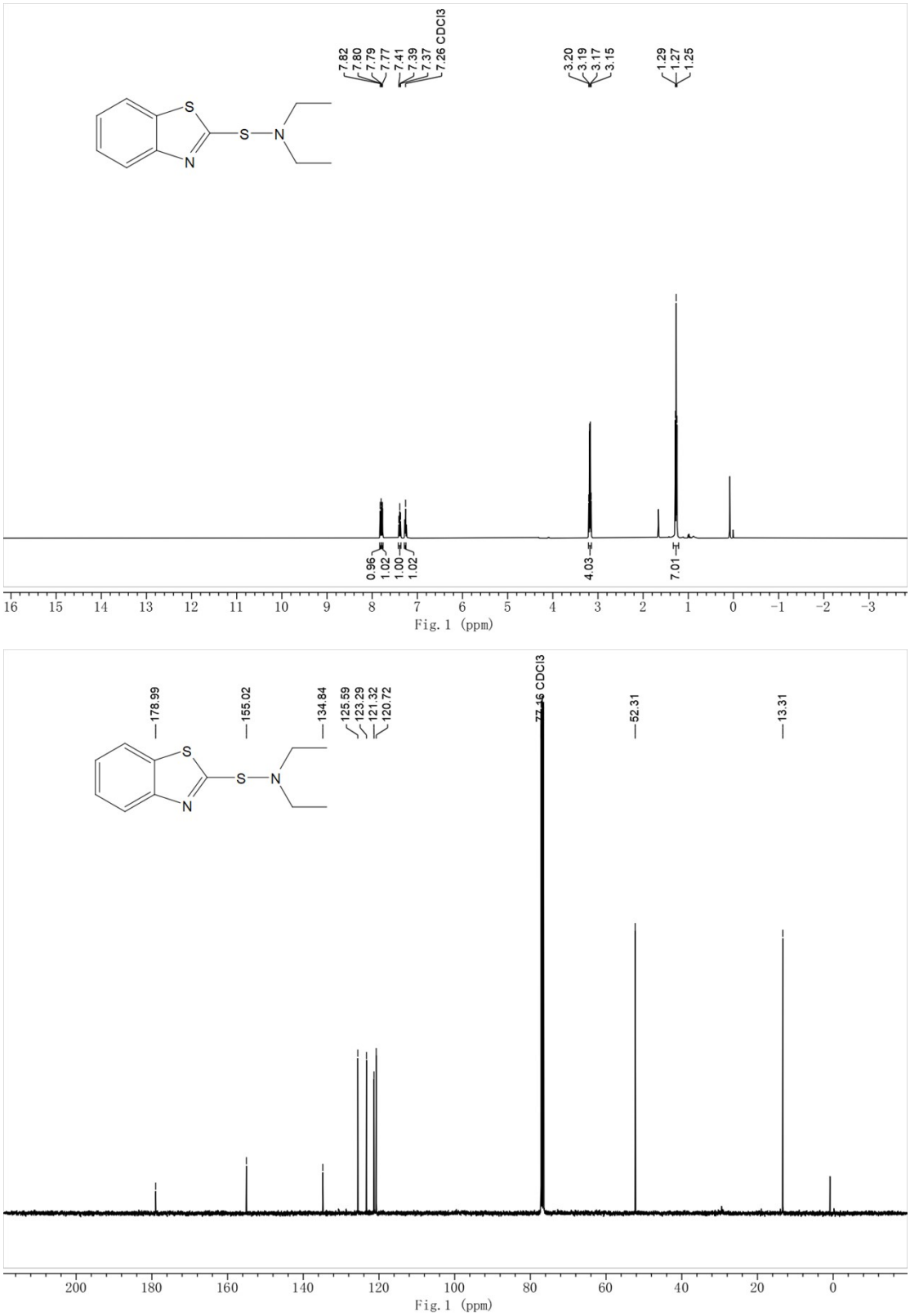
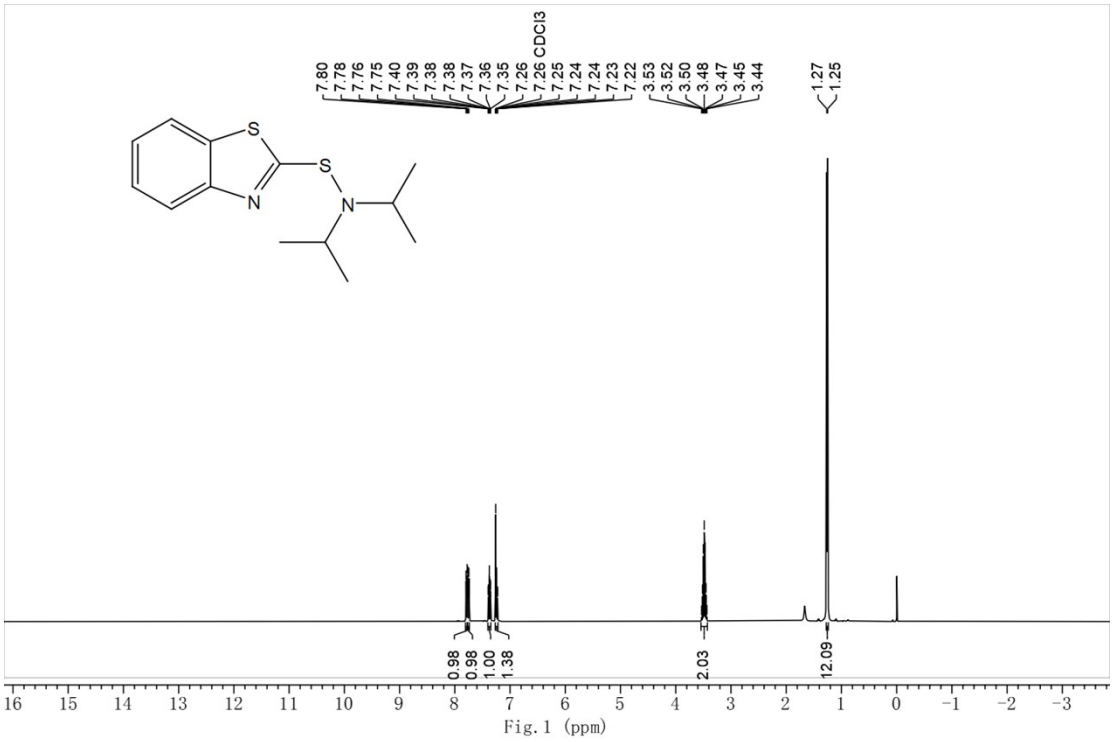


Figure S25. ^{1}H-NMR and ^{13}C-NMR spectrum of

S-(benzo[d]thiazol-2-yl)-*N*-(pentan-3-yl)thiohydroxylamine



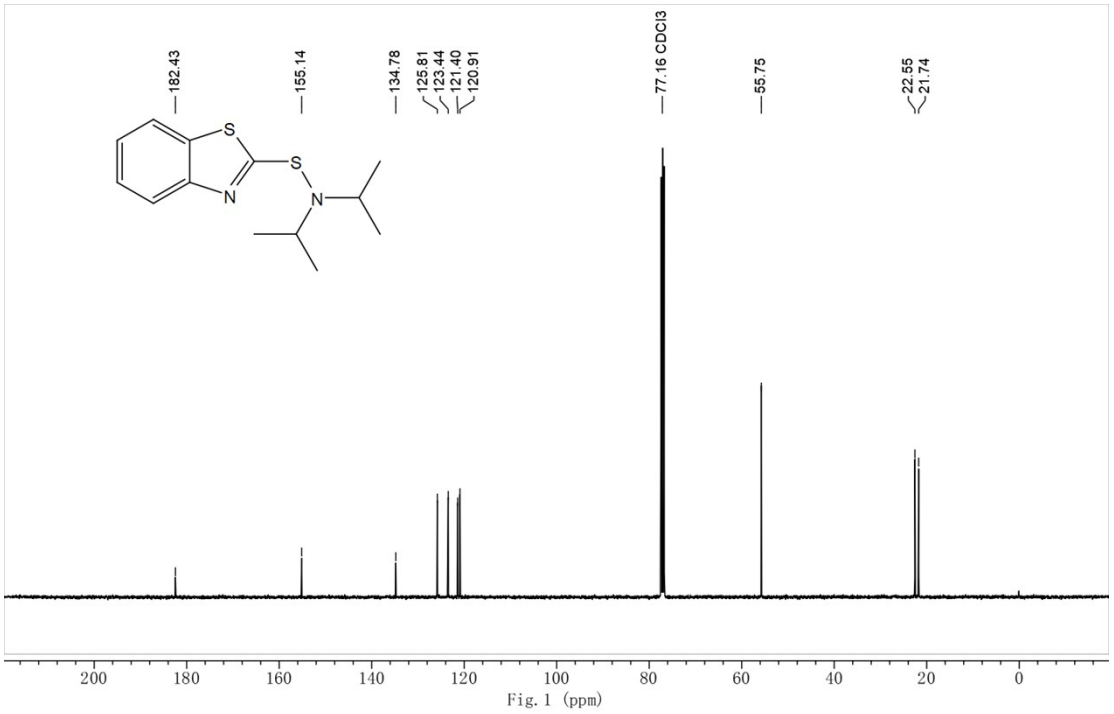
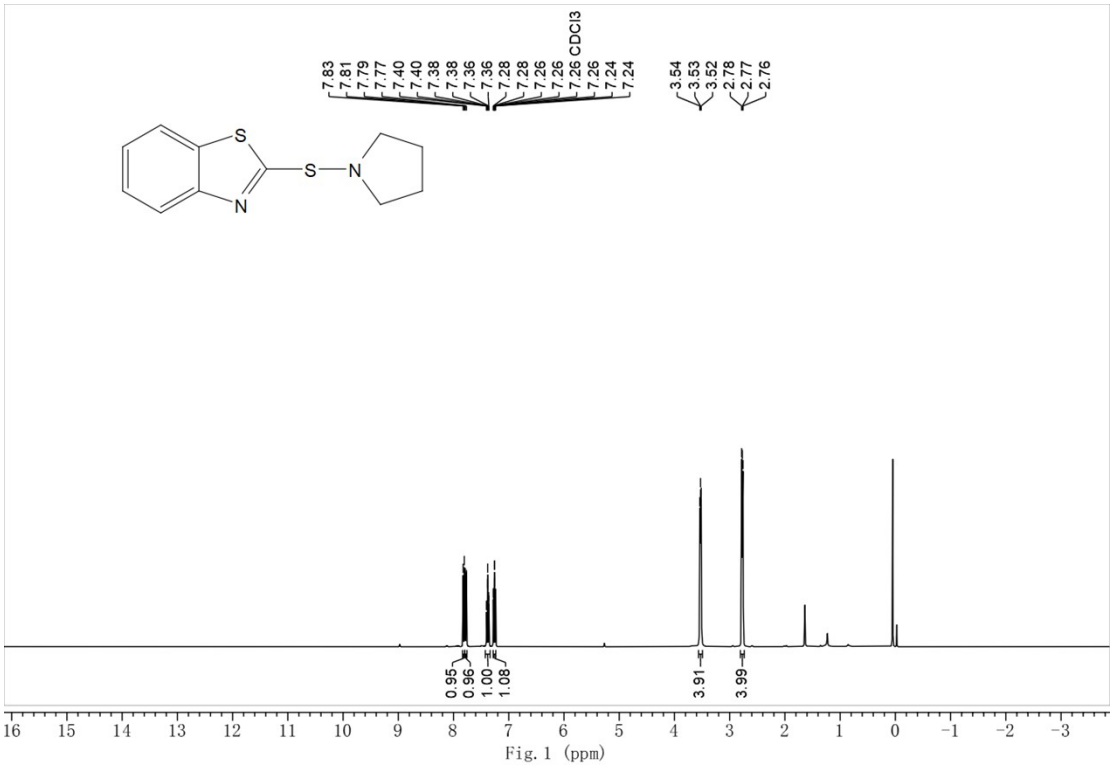


Figure S26. ^{1}H-NMR and ^{13}C-NMR spectrum of

S-(benzo[*d*]thiazol-2-yl)-*N,N*-diisopropylthiohydroxylamine



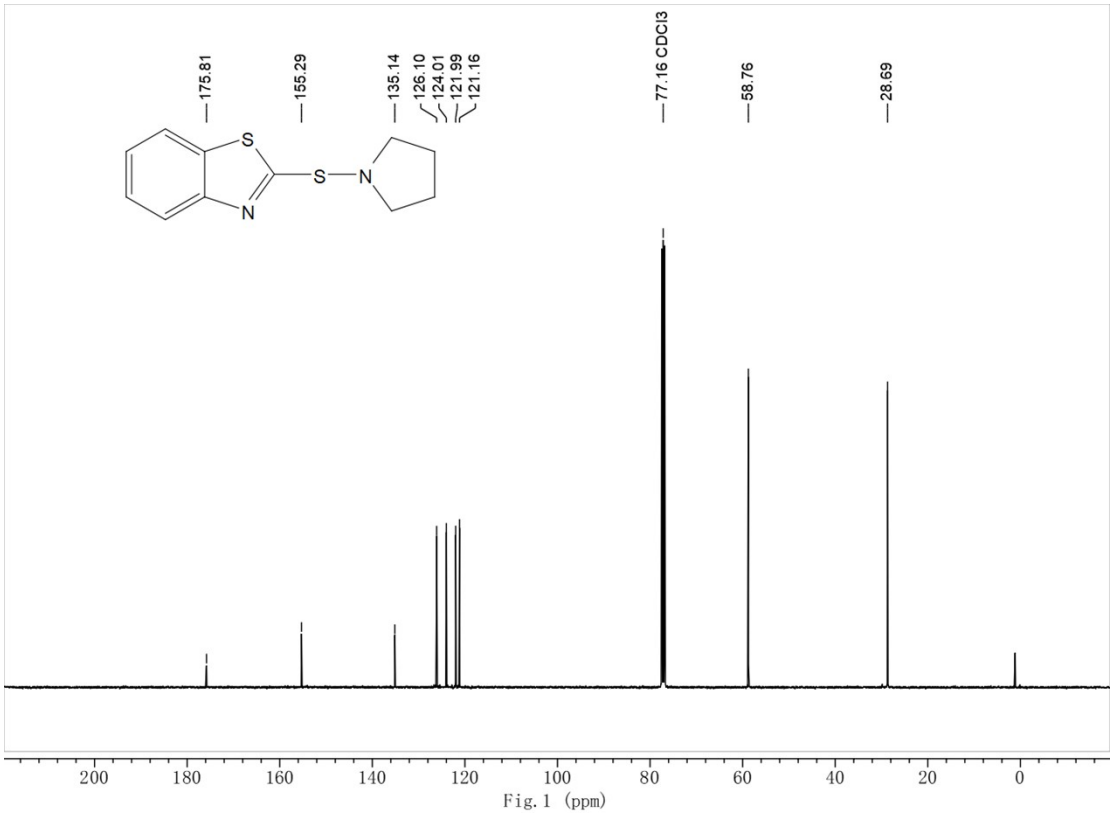


Figure S27. ^{1}H-NMR and ^{13}C-NMR spectrum of

2-(pyrrolidin-1-ylthio)benzo[*d*]thiazole

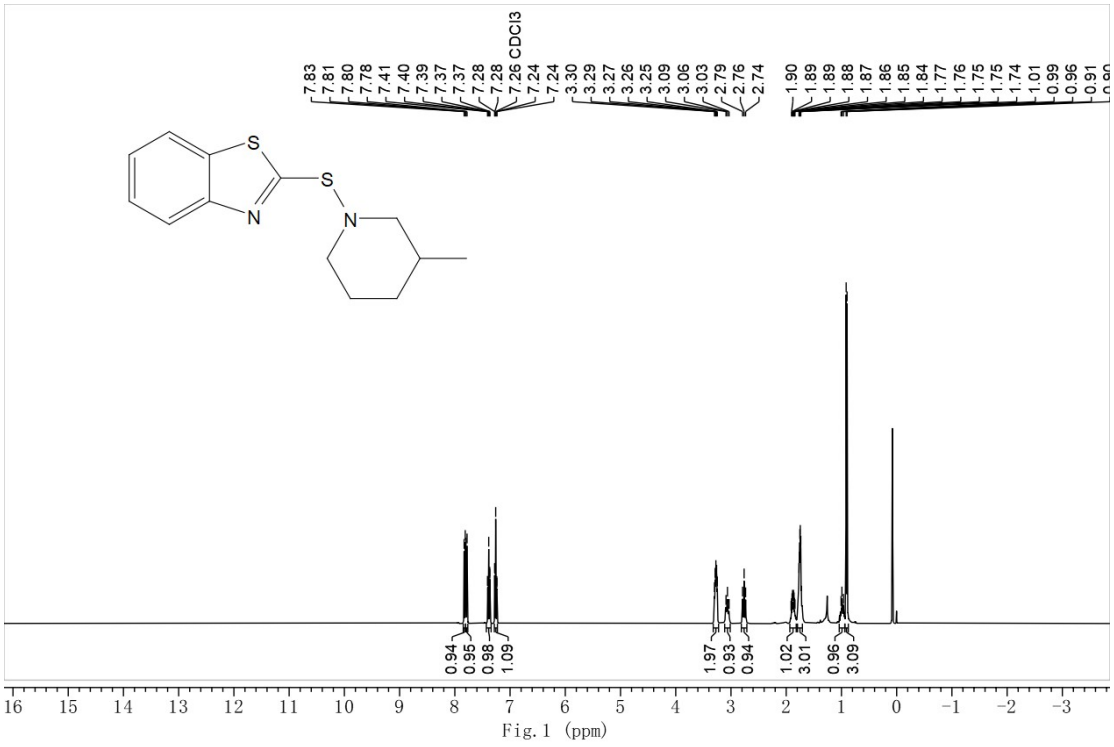


Fig. 1 (ppm)

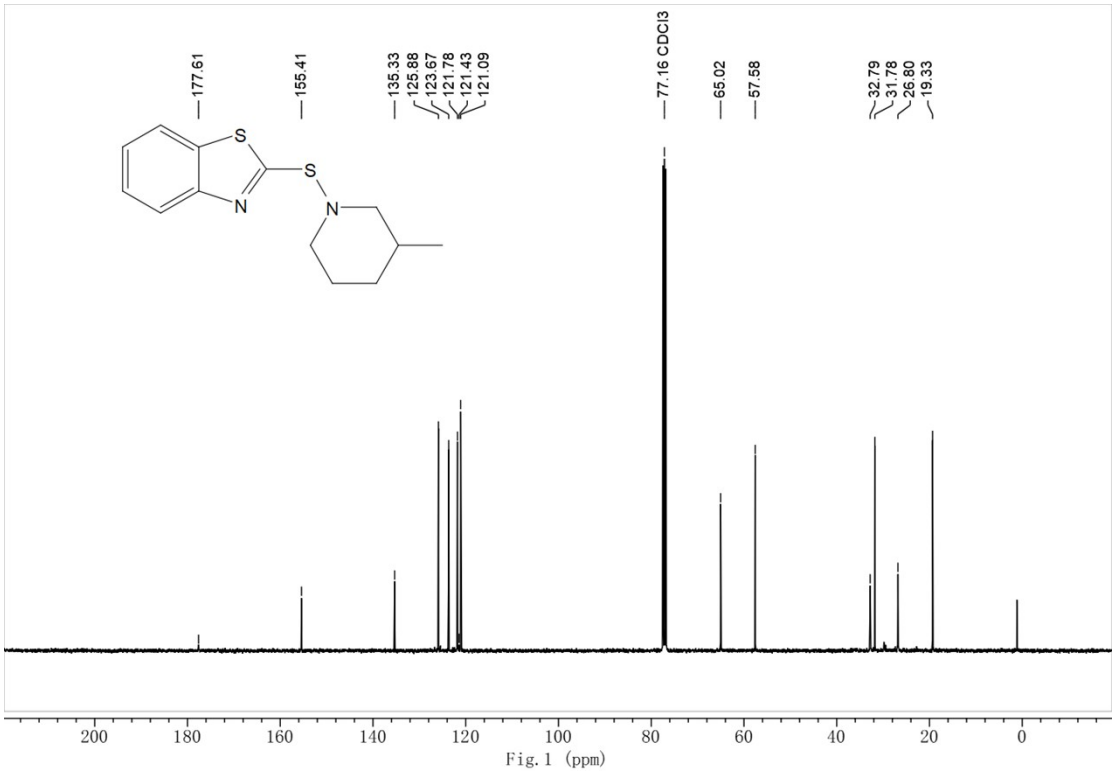
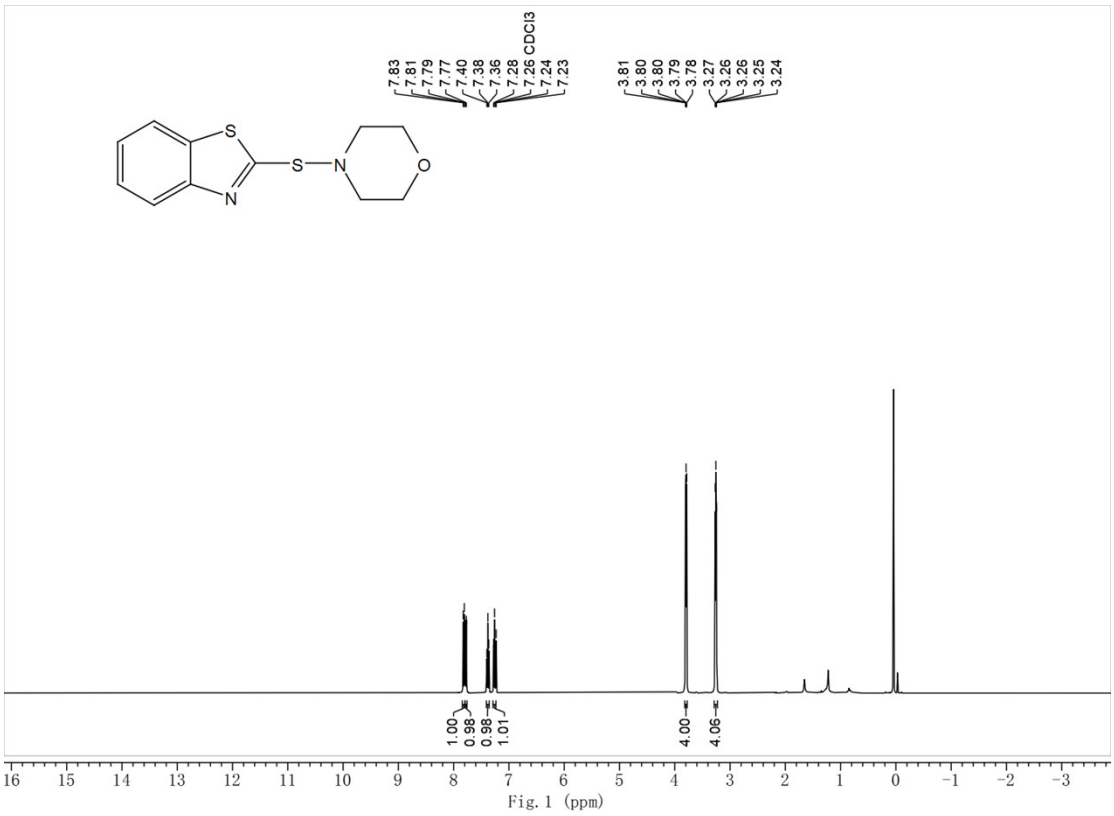


Fig. 1 (ppm)

Figure S28. ^{1}H-NMR and ^{13}C-NMR spectrum of 2-((3-methylpiperidin-1-yl)thio)benzo[*d*]thiazole



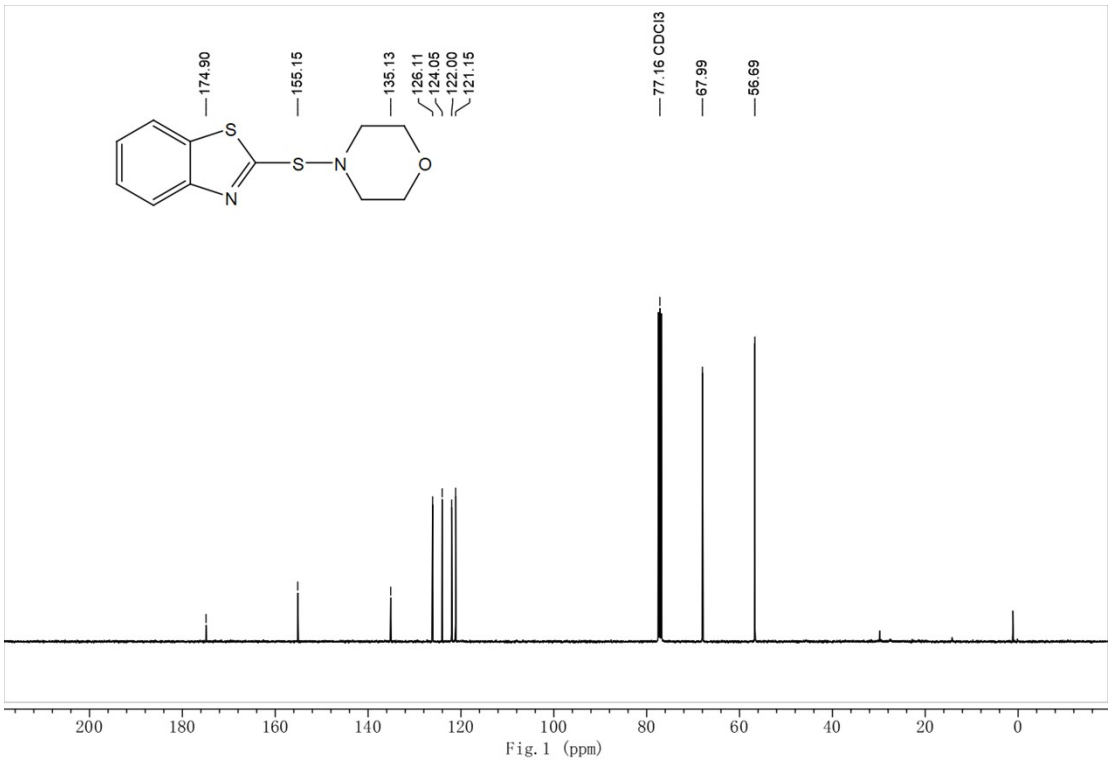


Figure S29. ^{1}H-NMR and ^{13}C-NMR spectrum of
4-(benzo[*d*]thiazol-2-ylthio)morpholine

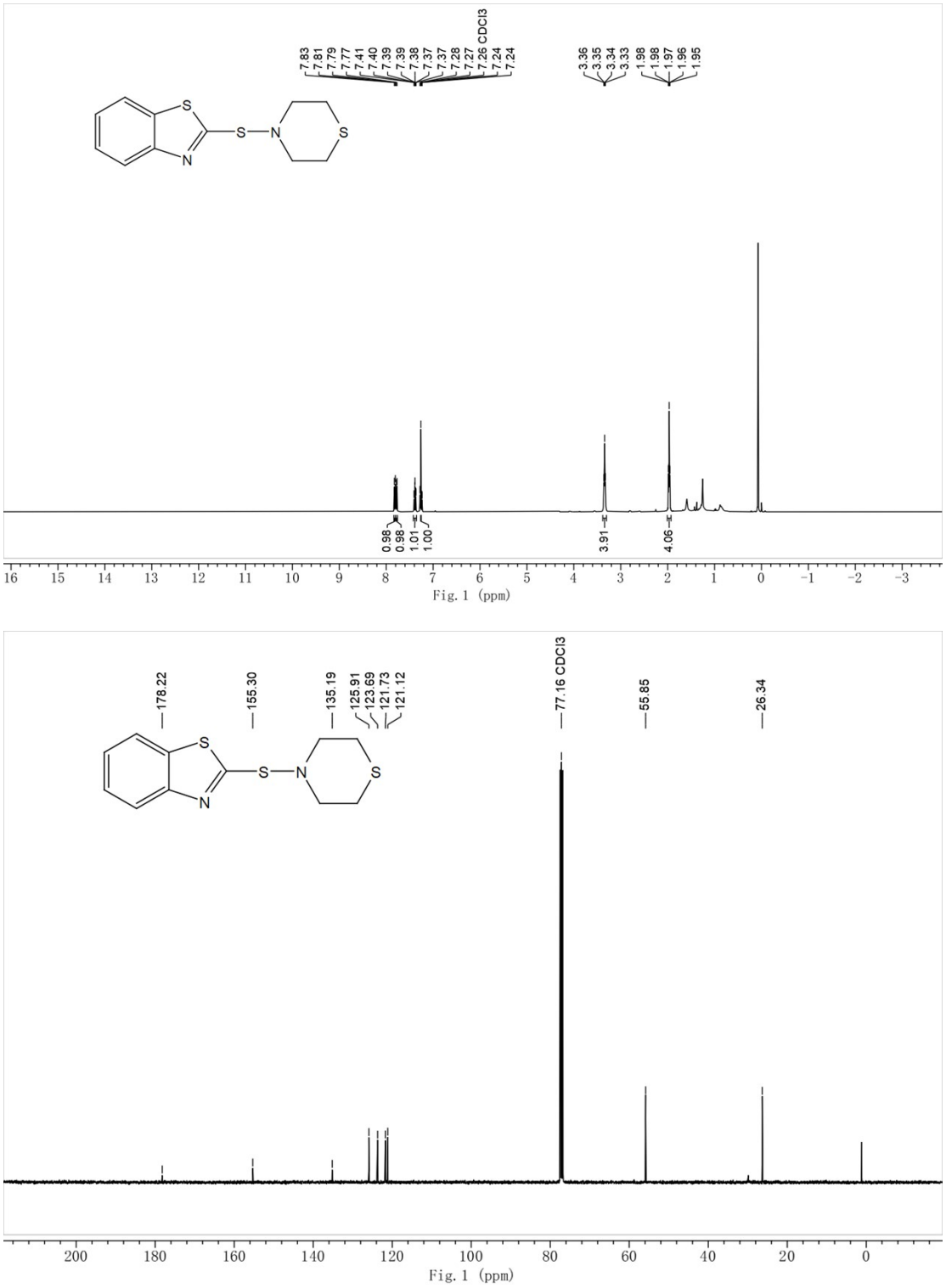
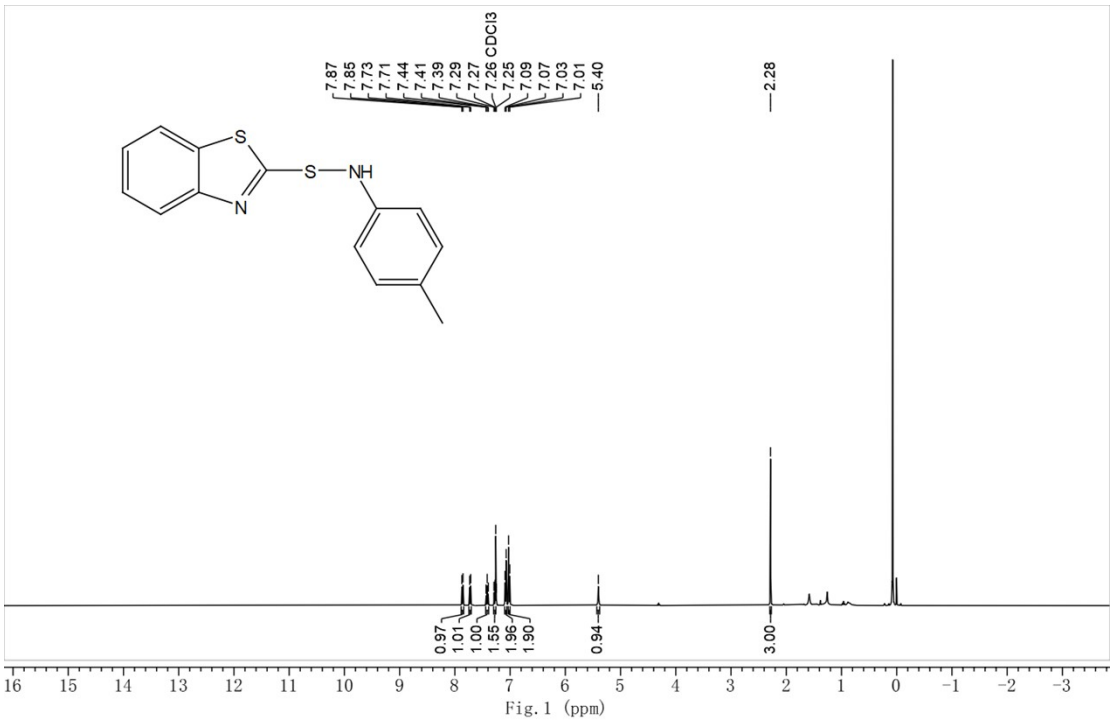


Figure S30. ^{1}H-NMR and ^{13}C-NMR spectrum of

2-(thiomorpholinothio)benzo[*d*]thiazole



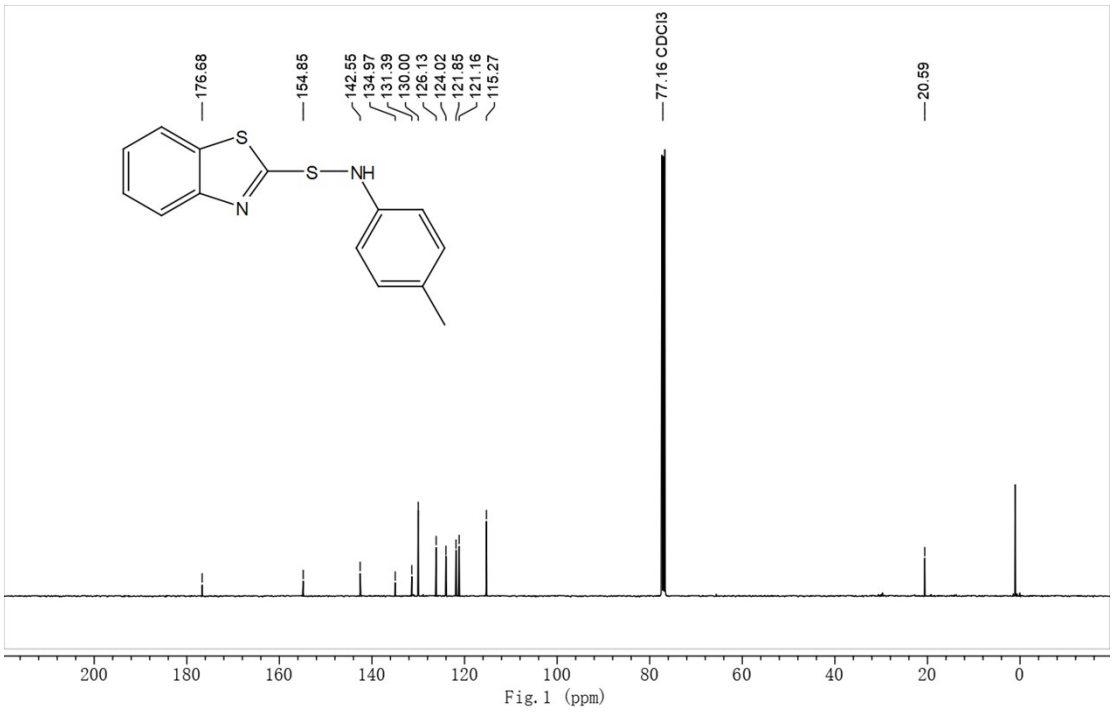
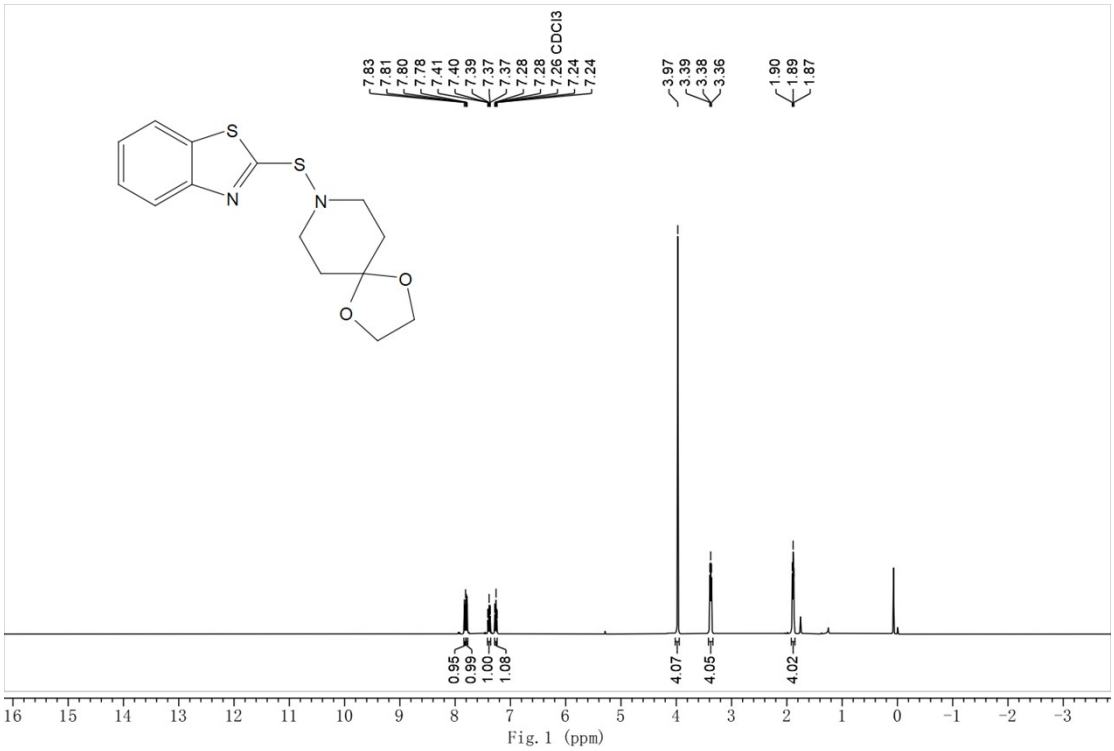


Figure S31. ^{1}H-NMR and ^{13}C-NMR spectrum of

S-(benzo[*d*]thiazol-2-yl)-*N*-(*p*-tolyl)thiohydroxylamine



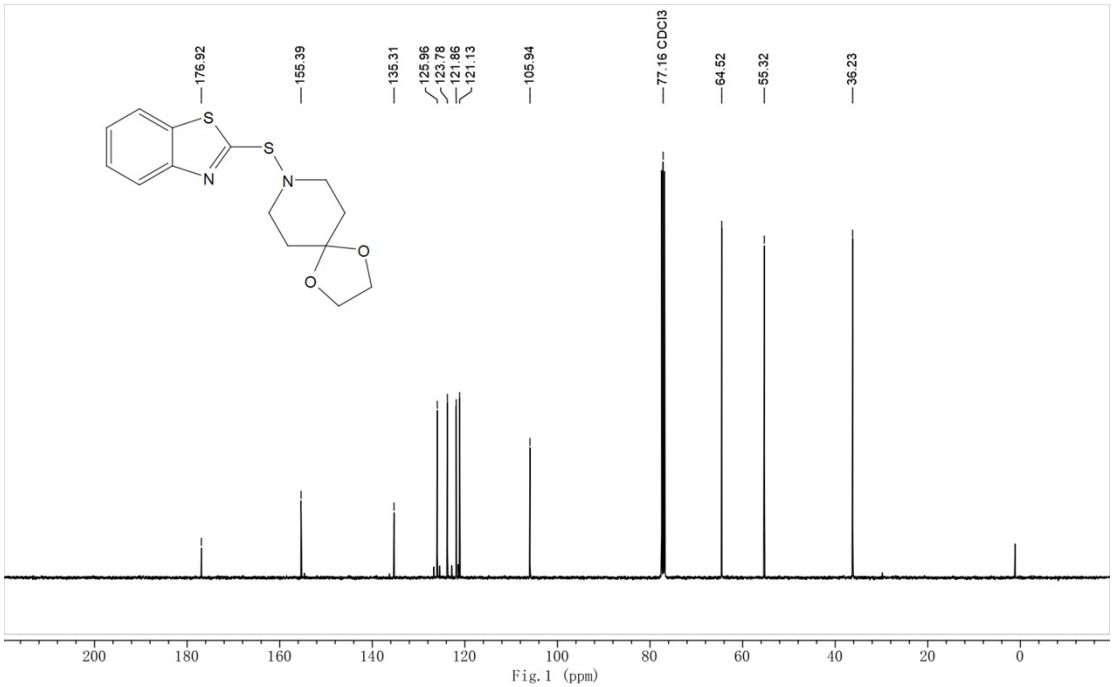
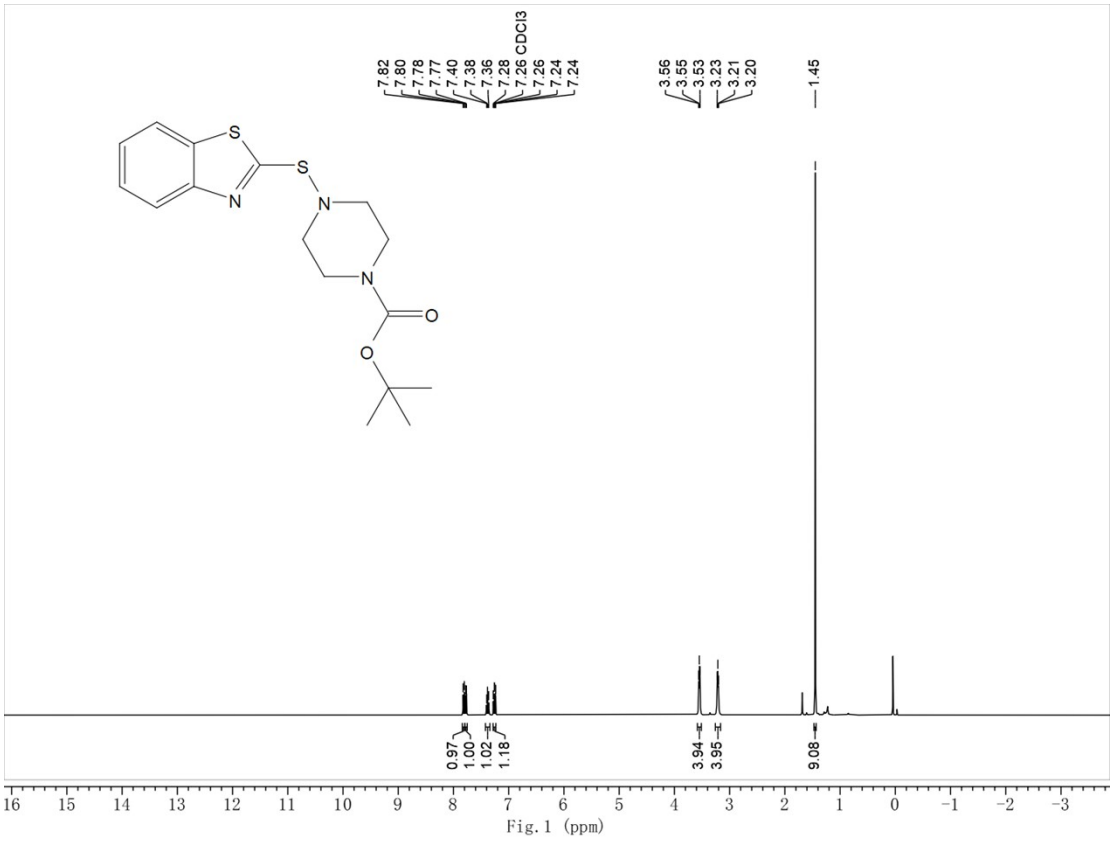


Figure S32. ^{1}H-NMR and ^{13}C-NMR spectrum of
8-(benzo[*d*]thiazol-2-ylthio)-1,4-dioxa-8-azaspiro[4.5]decane



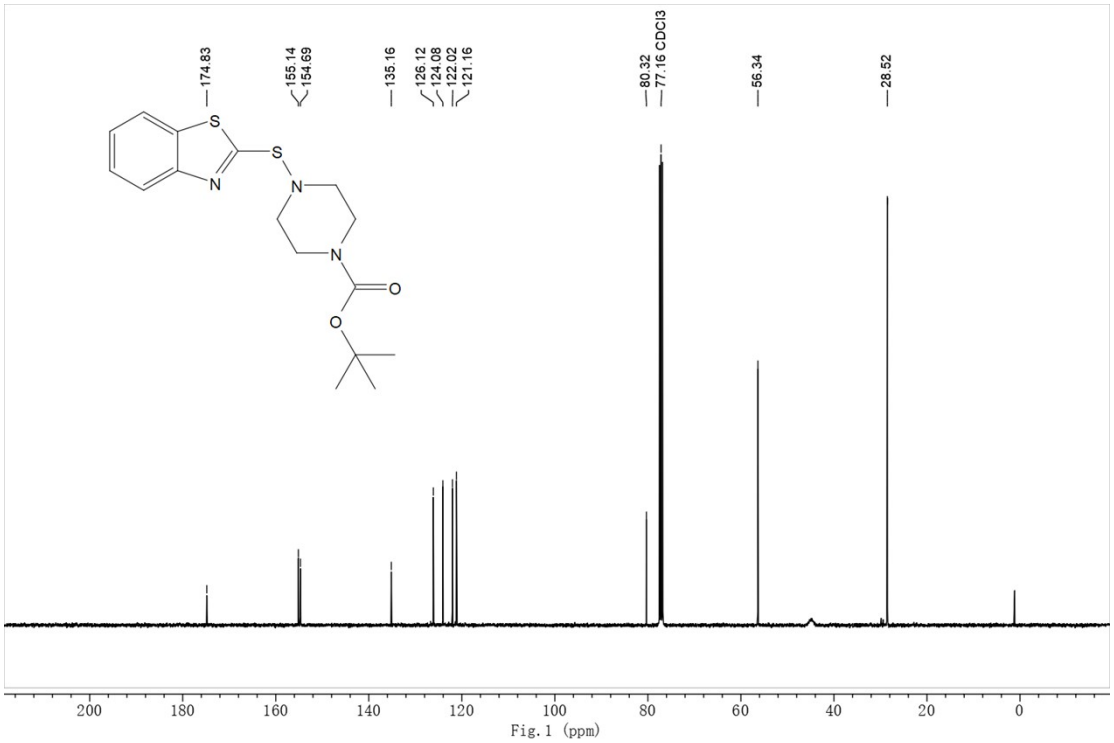
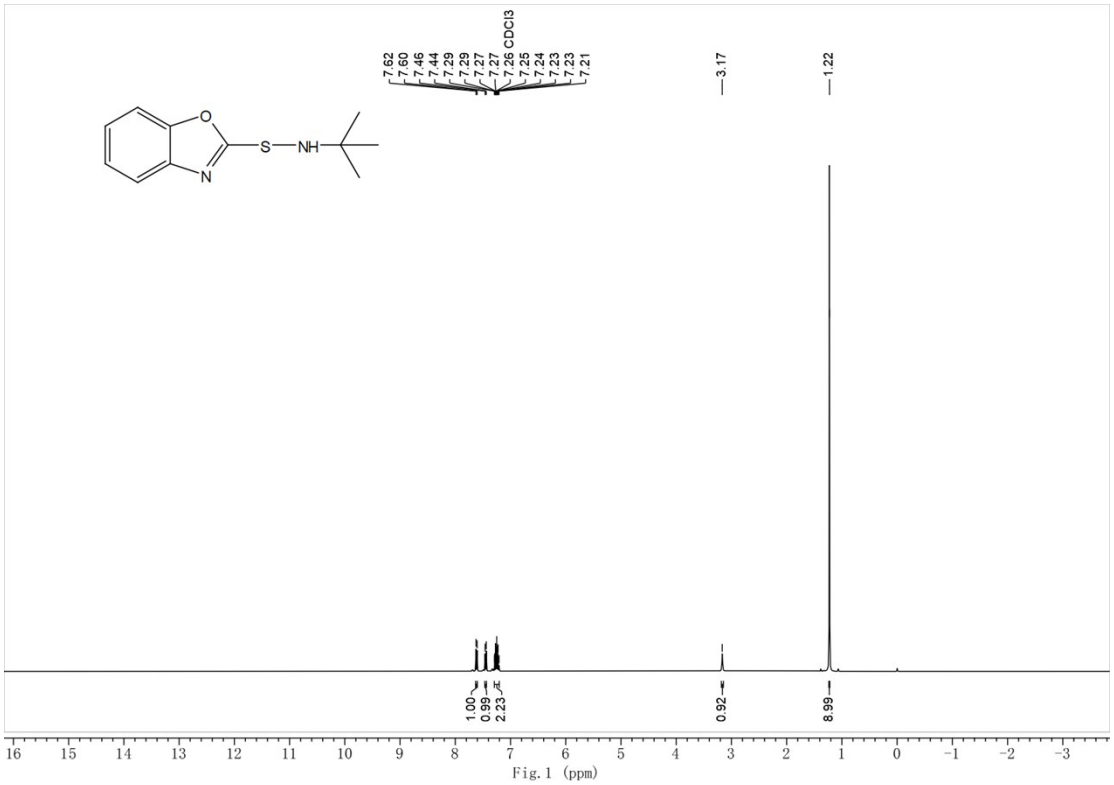


Figure S33. ^{1}H-NMR and ^{13}C-NMR spectrum of
tert-butyl 4-(benzo[d]thiazol-2-ylthio)piperazine-1-carboxylate



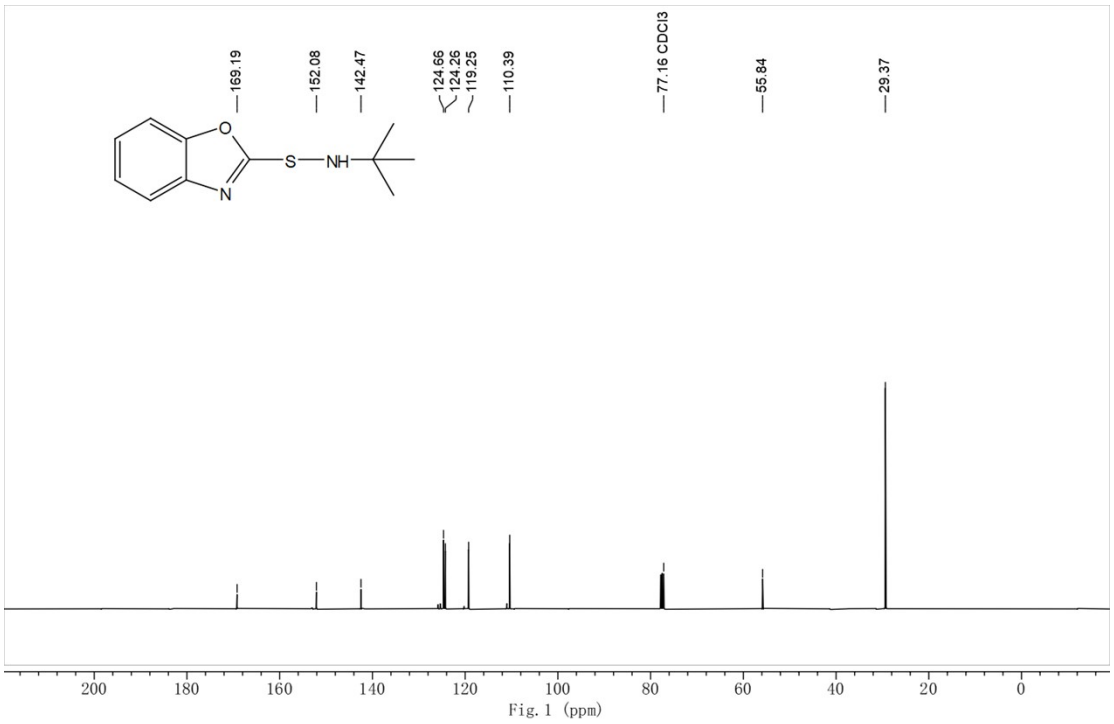
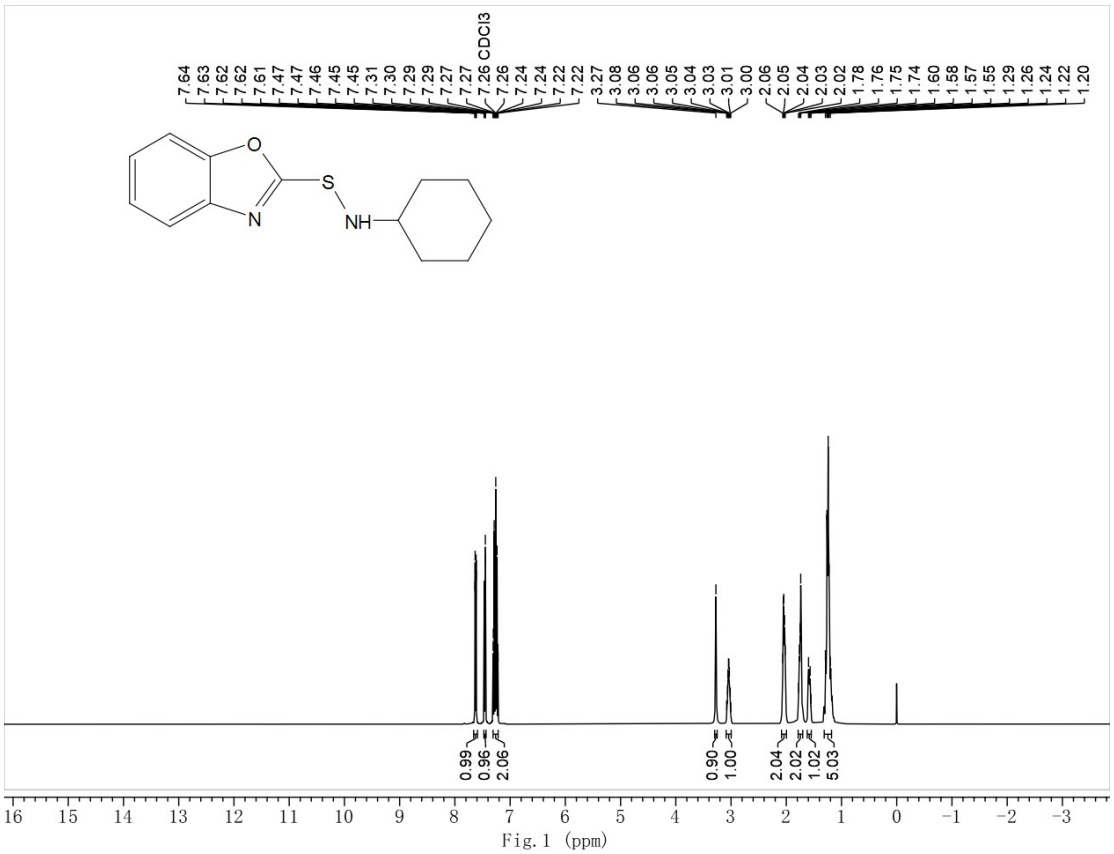


Figure S34. ^{1}H-NMR and ^{13}C-NMR spectrum of *S*-(benzo[*d*]oxazol-2-yl)-*N*-(tert-butyl)thiohydroxylamine



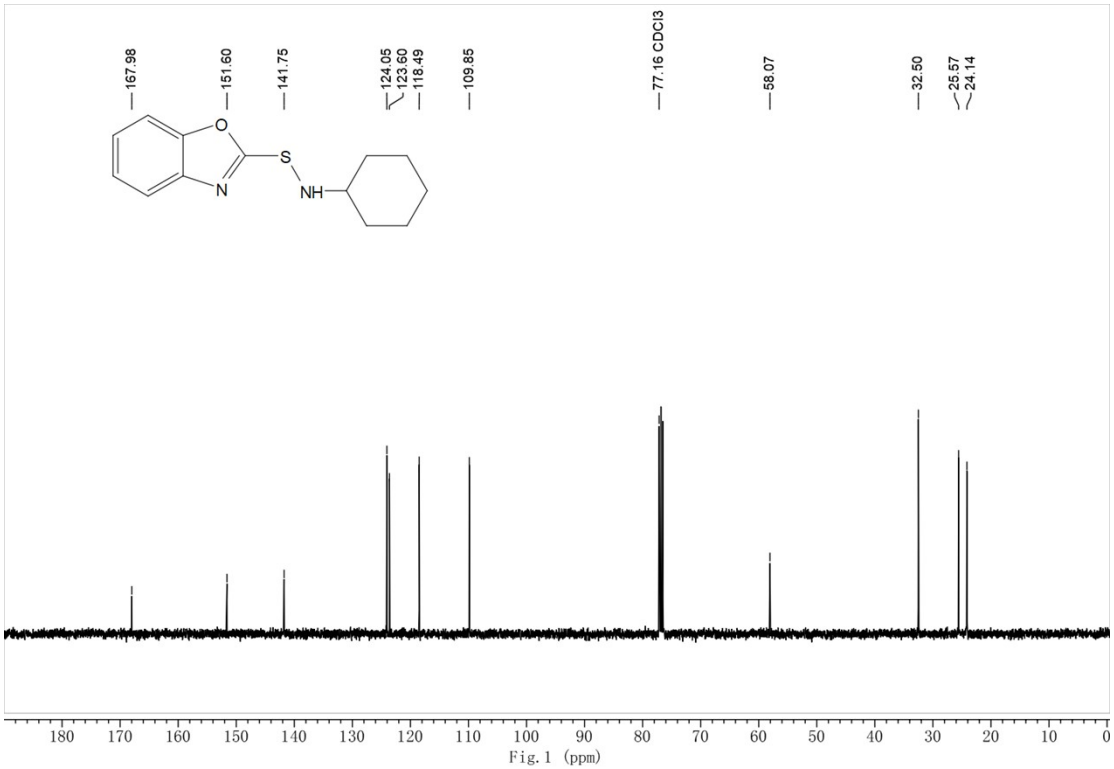


Figure S35. ^{1}H-NMR and ^{13}C-NMR spectrum of

S-(benzo[*d*]oxazol-2-yl)-*N*-cyclohexylthiohydroxylamine

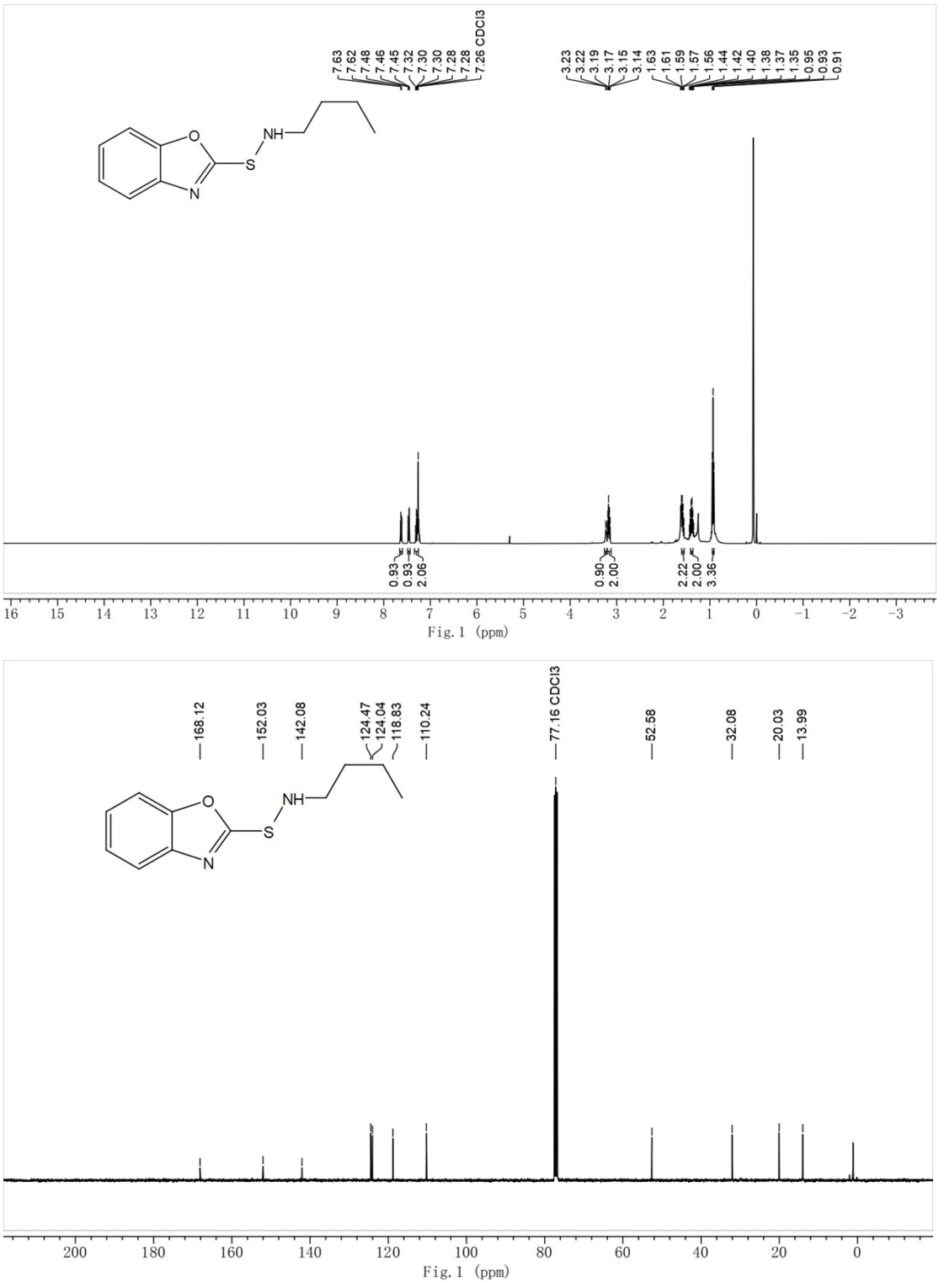
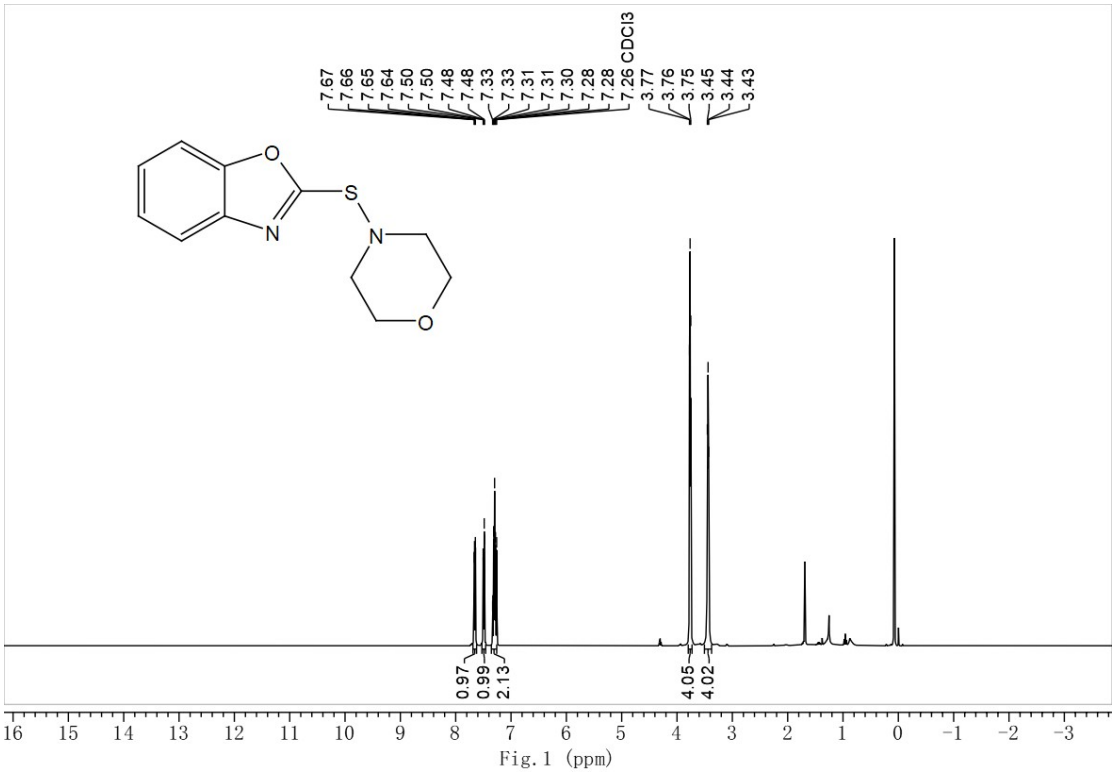


Figure S36. ^{1}H-NMR and ^{13}C-NMR spectrum of S-(benzo[d]oxazol-2-yl)-N-butylthiohydroxylamine



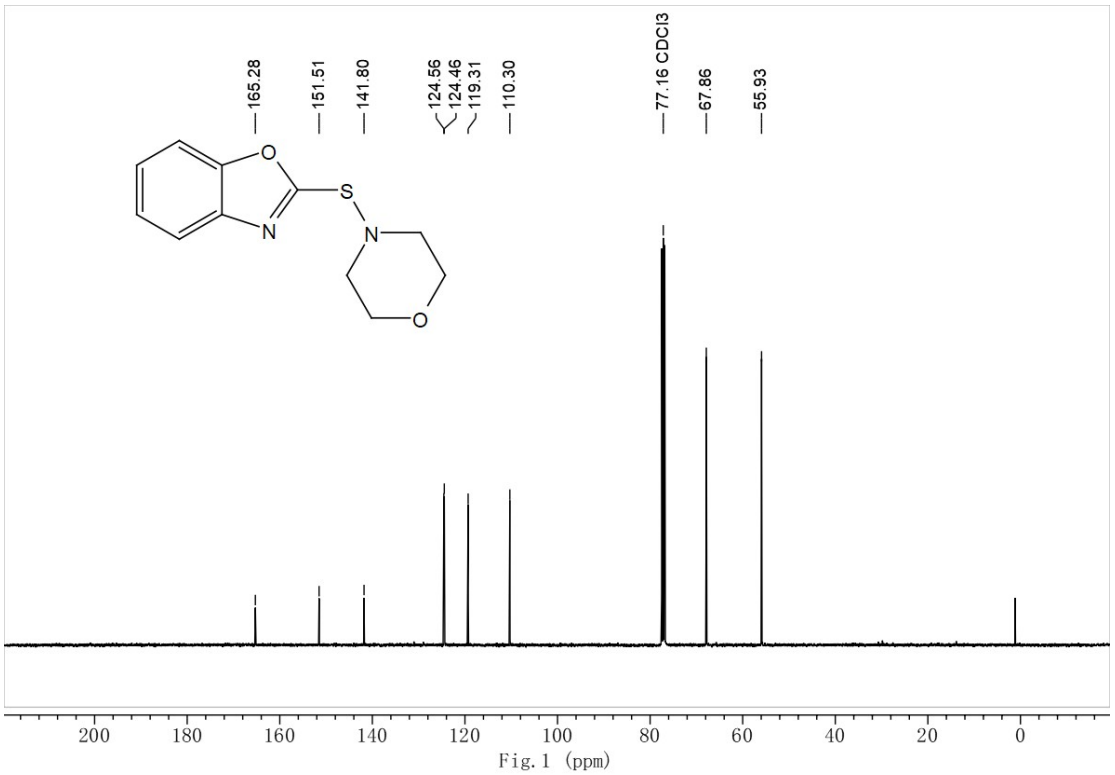


Figure S37. ^{1}H-NMR and ^{13}C-NMR spectrum of
2-(morpholinothio)benzo[*d*]oxazole

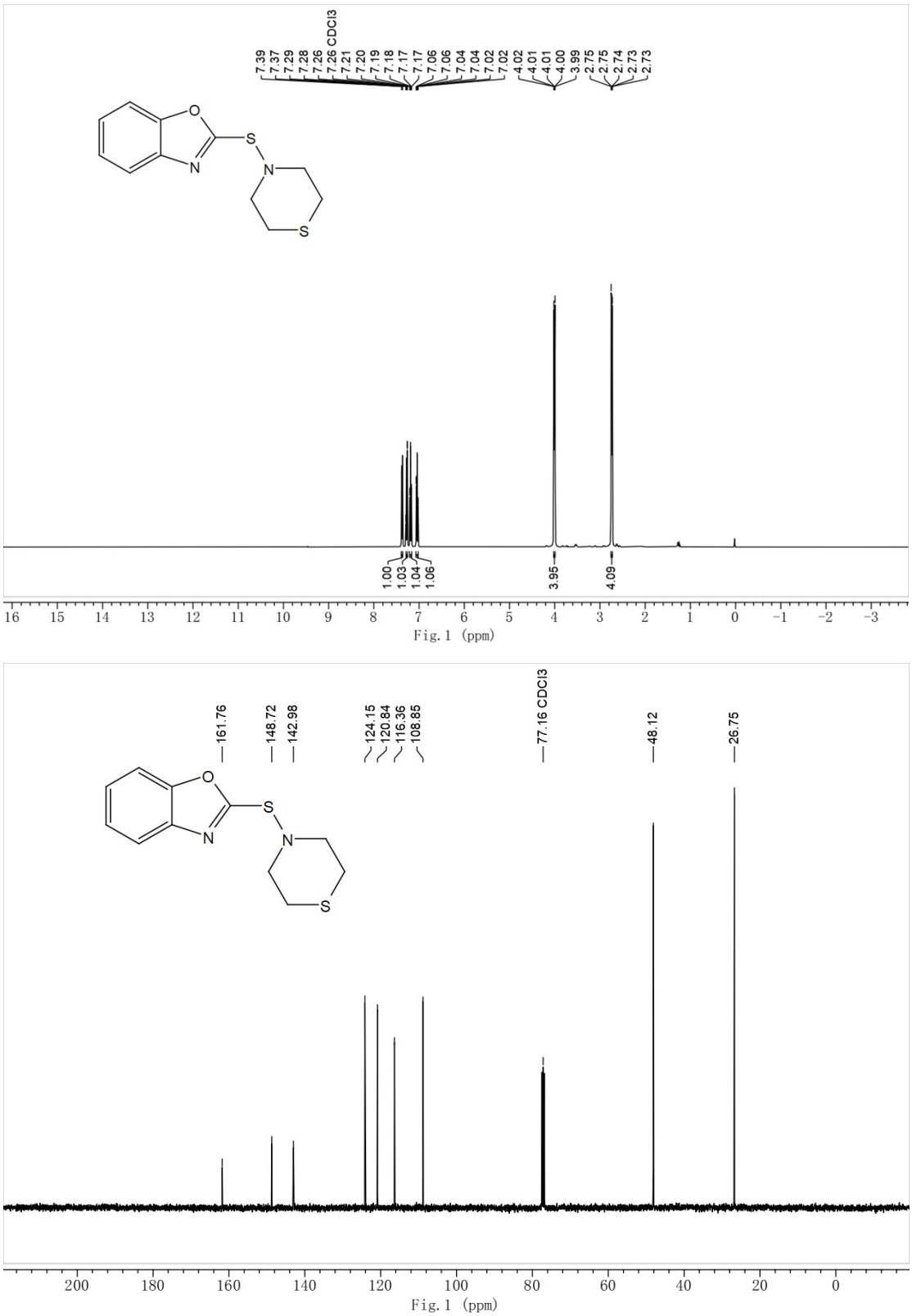
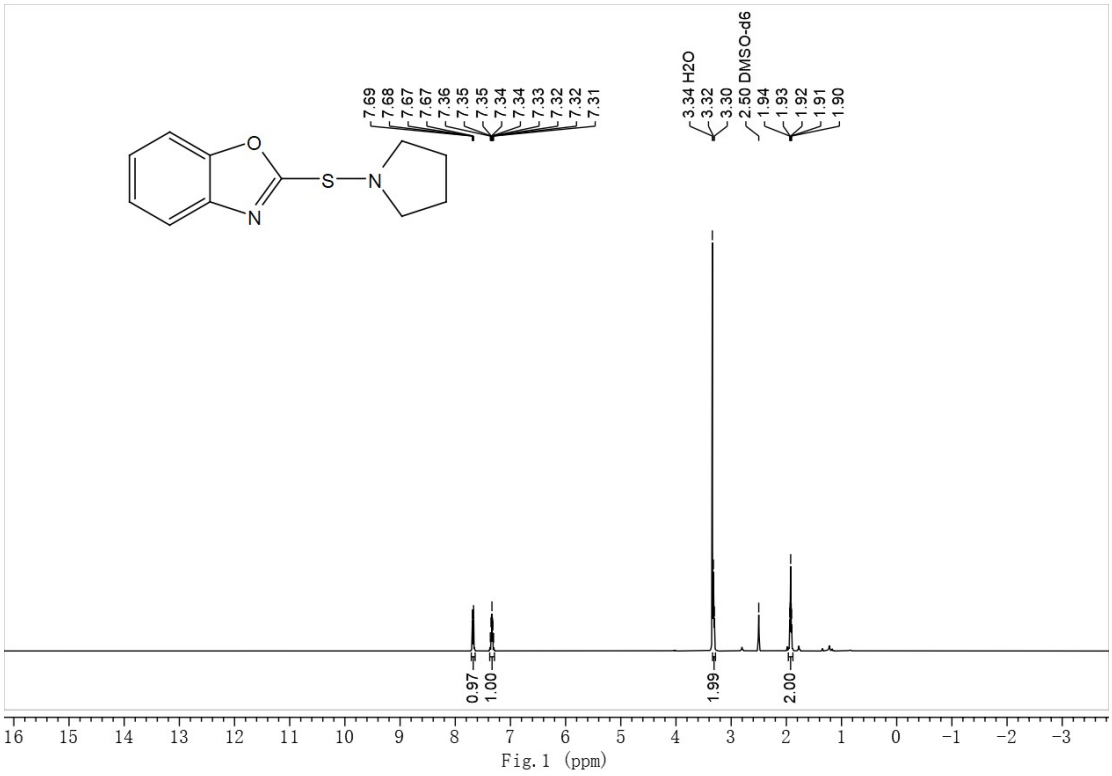


Figure S38. ^{1}H-NMR and ^{13}C-NMR spectrum of

2-(thiomorpholinothio)benzo[*d*]oxazole



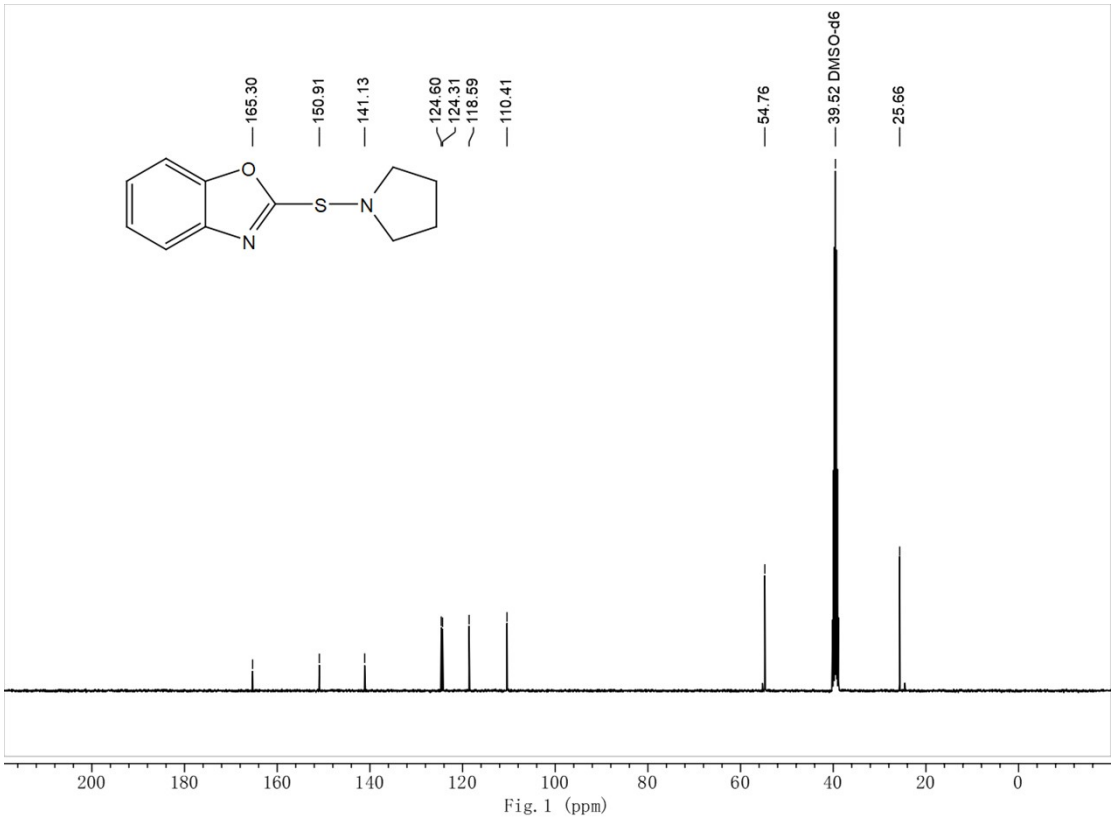
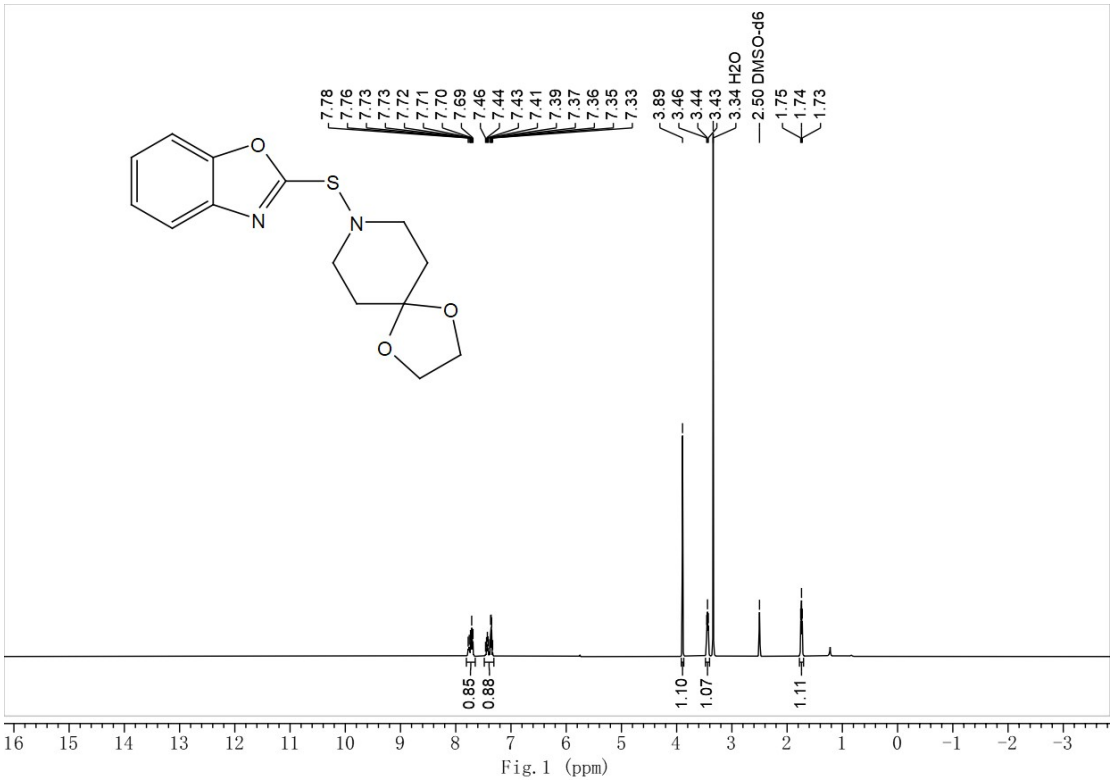


Figure S39. ^{1}H-NMR and ^{13}C-NMR spectrum of (pyrrolidin-1-ylthio)benzo[d]oxazole



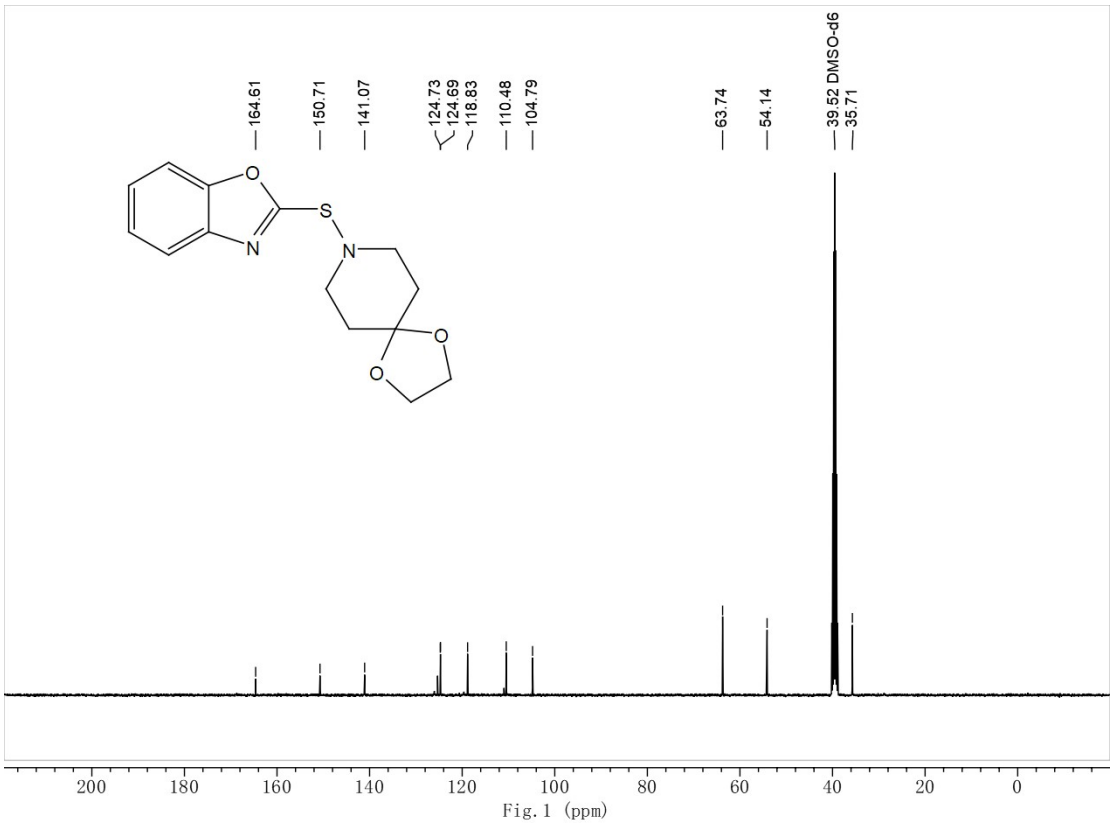
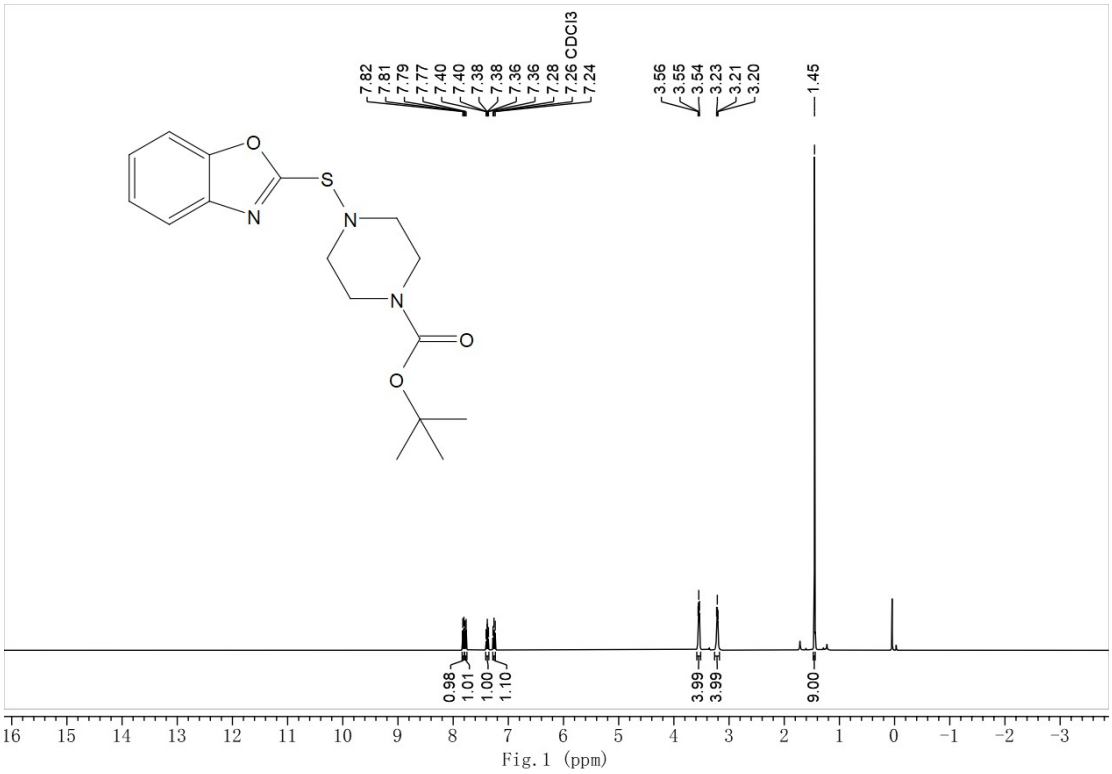


Figure S40. ^{1}H-NMR and ^{13}C-NMR spectrum of 8-(benzo[d]oxazol-2-ylthio)-1,4-dioxa-8-azaspiro[4.5]decane



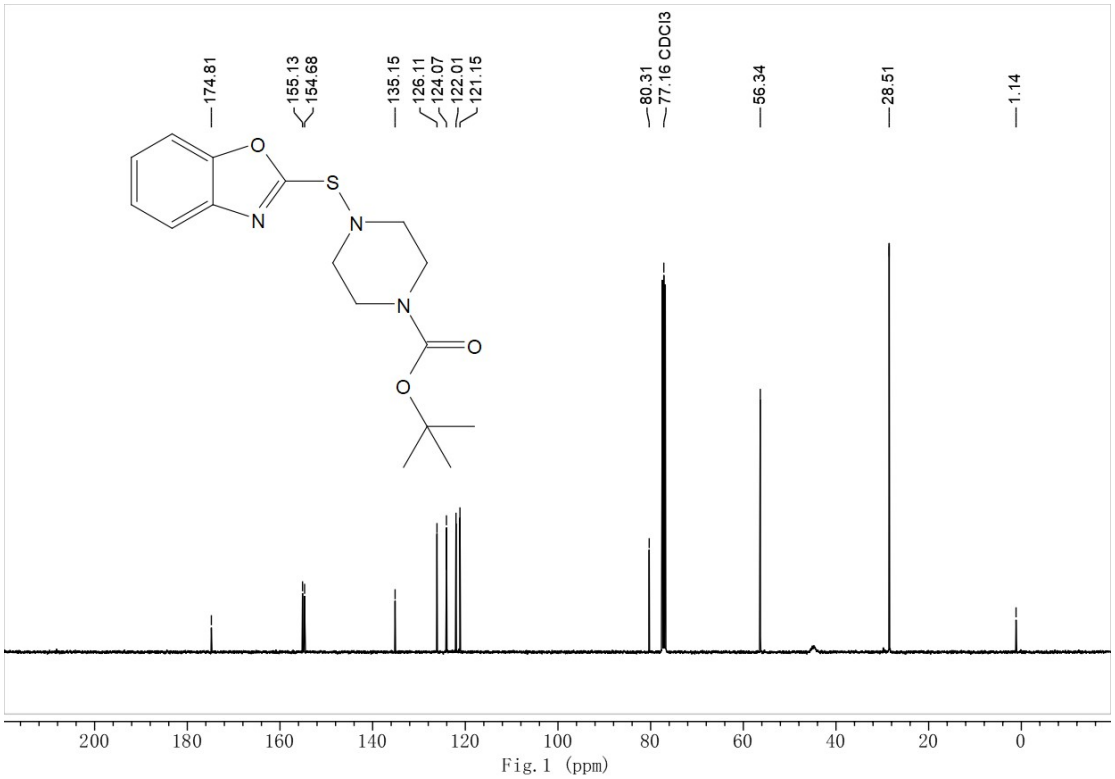


Figure S41. ^{1}H-NMR and ^{13}C-NMR spectrum of tert-butyl 4-(benzo[d]oxazol-2-ylthio)piperazine-1-carboxylate

References:

1 (a) P. Hohenberg and W. Kohn, *Phys. Rev.*, 1964, **136**, B864; (b) W. Kohn and L. J. Sham, *Phys. Rev.*, 1965, **137**, A1697; (c) G. Kresse and J. Furthmüller, *Phys. Rev. B.*, 1996, **54**, 11169; (d) G. Kresse and J. Furthmüller, *Comput. Mater. Sci.*, 1996, **6**, 15-50; (e) G. Kresse and D. Joubert, *Phys. Rev. B.*, 1999, **59**, 1758.

2 (a) J. A. Hernandez and R. Caracas, *Phys. Rev. Lett.*, 2016, **117**, 135503; (b) L. Zhang, Q. Wu, S. Li, Y. Sun, X. Yan, Y. Chen and H. Y. Geng, *ACS Appl. Mater. Int.*, 2021, **13**, 6130-6139; (c) L. Zhang, H. Y. Geng and Q. Wu, *Matter. Radiat. Extremes*, 2021, **6**; (d) H. Luo, Q. Gao, H. Liu, Y. Gu, D. Wu, C. Yi, J. Jia, S. Wu, X. Luo, Q. Gao, Y. Xu, Z. Lin, Q. Wang, H. Mao, G. Liu, Z. Zhu, Y. Shi, K. Jiang, J. Hu, Z. Xu and X. J. Zhou, *Nat. Commun.*, 2022, **13**, 273; (e) J. Yin, J. Jin, Z. Yin, L. Zhu, X. Du, Y. Peng, P. Xi, C. H. Yan and S. Sun, *Nat. Commun.*, 2023, **14**, 1724; (f) P E. Blöchl, *Phys. Rev. B.*, 1994, **50**, 17953.

3 J. P. Perdew and K. Burke, *Phys. Rev. Lett.*, 1996, **77**, 3865.

4 S. Grimme, *J. Comput. Chem.*, 2006, **27**, 1787-1799.

5 Y. Xu, M. Fan, W. Yang, Y. Xiao, L. Zeng, X. Wu, Q. Xu, C. Su and Q. He, *Adv. Mater.*, 2021, **33**, 2101455.