Supporting information

Photocatalytic synthesis of carbamo(dithioperoxo)thioates via Z-scheme $H_2WO_4/CsPbBr_3$ heterojunction

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1. General

All commercial reagents were used directly without further purification, unless otherwise stated. CH_3CN was purchased from J & K chemical, stored over 4 Å molecular sieves and handled under N_2. DMSO-*d6* and $CDCl_3$ were purchased from Shanghai aladdin Biochemical Technology Co. The following abbreviations were used to describe NMR signals: s = singlet, d = doublet, t = triplet, m = mulitplet, dd = doublet of doublets, q = quartet.

Characterization. The scanning electron microscope (SEM) images were obtained on a ZEISS Gemini SEM 300 microscope with an accelerating voltage of 3 kV. Transmission electron microscopy (TEM) images were obtained on a FEI-Talos F200S microscopy with an accelerating voltage of 200 kV. The energy dispersive X-ray (EDX) composition analysis was carried out using an accessory attached on TEM. Powder X-ray diffraction (XRD) patterns were collected on a Rigaku SmartLab diffractometer using a Cu Kα radiation at a scan rate of 10^o min^{-1}. X-ray photoelectron spectroscopy (XPS) measurements were carried out using an electron spectrometer (Thermo Scientific K-Alpha, USA). The steady-state photoluminescence (PL) spectra were recorded on a FLS1000 fluorescence spectrometer with an excitation wavelength of 370nm. UV-vis diffuse reflectance spectra (DRS) of the samples were obtained on a Lambda 1050 spectrometer (TU-1901, CN).

2. Experimental sections

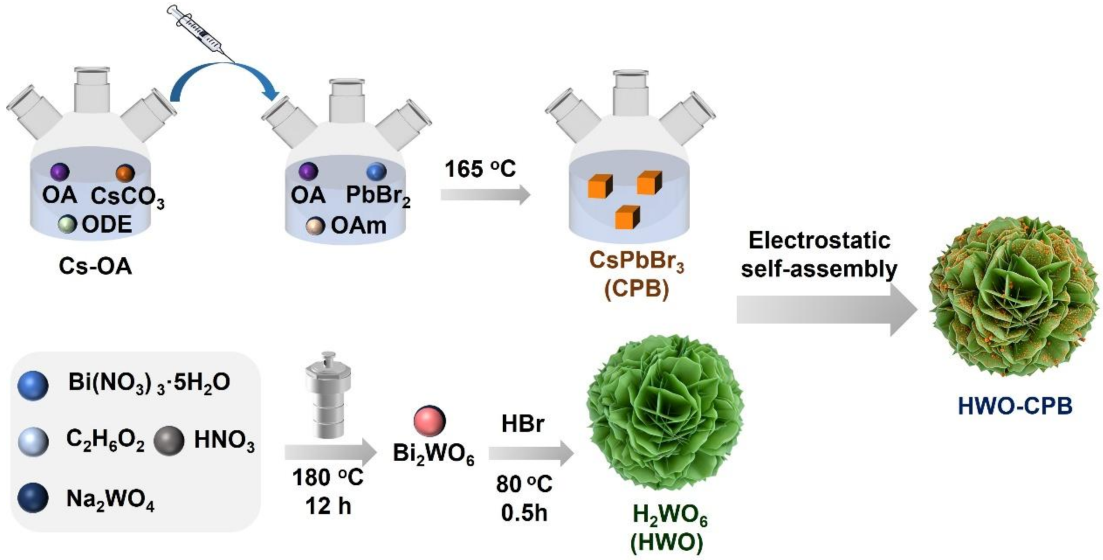


Fig. S1 Schematic image of the synthesis of HWO-CPB

2.1 Preparation of Bi_2WO_6 (BWO)

1 mmol of $Bi(NO_3)_3 \cdot 5H_2O$ was dissolved in 40 mL of ethylene glycol with stirring, and the pH of the system was adjusted to 1.4 with the addition of 0.04 mol/L nitric acid. In the meantime, 0.5 mmol of $Na_2WO_4 \cdot 2H_2O$ was added and sonicated for 60 min. The obtained mixture was transferred to a Teflon-lined autoclave and treated at 180 °C for 12 h. Ultimately, the resultant was collected by centrifugation, followed by repeated washing with water several times and drying at 80 °C for 12 h. The obtained gray solid Bi_2WO_6 was polished and collected.

2.2 Preparation of H_2WO_4 (HWO)

The HWO was prepared by acid etching of Bi_2WO_6 nanosheets (BWO). Briefly, 100 mg of BWO were dispersed in 100 mL of absolute ethanol by sonication for 30 min to form a homogeneous suspension. The Bi_2WO_6 dispersion was then transferred to an oil bath (80 ℃) and maintained at this temperature for 1 h under continuous stirring. Next, 500 μL of the 48 wt.% HBr solution was added dropwise, and the stirring continued for 30 min at 80 ℃. The light-yellow solid product was collected by centrifugation, then washed twice with ethyl acetate and absolute ethanol to remove any organic residues. Finally, the product was vacuum-dried at 80 °C for 12 h.

2.3 Preparation of $CsPbBr_3$ (CPB)

The synthesis process of $CsPbBr_3$ was adopted from the literature. Briefly, 0.207 g $PbBr_2$ and 15 mL ODE were loaded into a 25 mL three-necked round bottom flask. Under Ar flow, the mixture was heated at 120 °C with magnetic stirring for 30 min. At the same time, the Cs-OA stock solution was prepared by mixing 0.203 g Cs_2CO_3, 10 mL ODE, and 0.65 mL OA at 150 °C for 1 h under Ar flow. Subsequently, 3 mL OA and 1.65 mL OAm were added into the $PbBr_2$ precursor. The mixture was heated to 165 °C. When a yellow homogeneous solution appeared ($PbBr_2$ precursor), 1.2 mL Cs-OA stock solution was swiftly injected into $PbBr_2$. After 5 s, the mixture was cooled down using an ice-water bath. The yellow precipitate was centrifuged and washed using 5 mL EA to remove the organic residue. The collected $CsPbBr_3$ were dispersed into 10 mL hexane and centrifuged at 6000 rpm for 5 min to remove the aggregated particles.

2.4 Preparation of HWO-CPB Photocatalyst

In a typical procedure, 250 μL $CsPbBr_3$ solution (8 mg/mL) was mixed with 10 mg H_2WO_4 powder in EA, and the final total volume was maintained at 10 mL in EA. The suspension was ultrasonicated for 10 min and stirred for 30 min under dark conditions. Finally, the HWO-CPB composites were centrifuged at 6000 rpm for 5 min, then the precipitate was washed with EA followed by drying at 50 °C for 2 h under vacuum. The mass ratios of $CsPbBr_3$ with respect to H_2WO_4 were 1:5, which are labeled as HWO-CPB respectively.

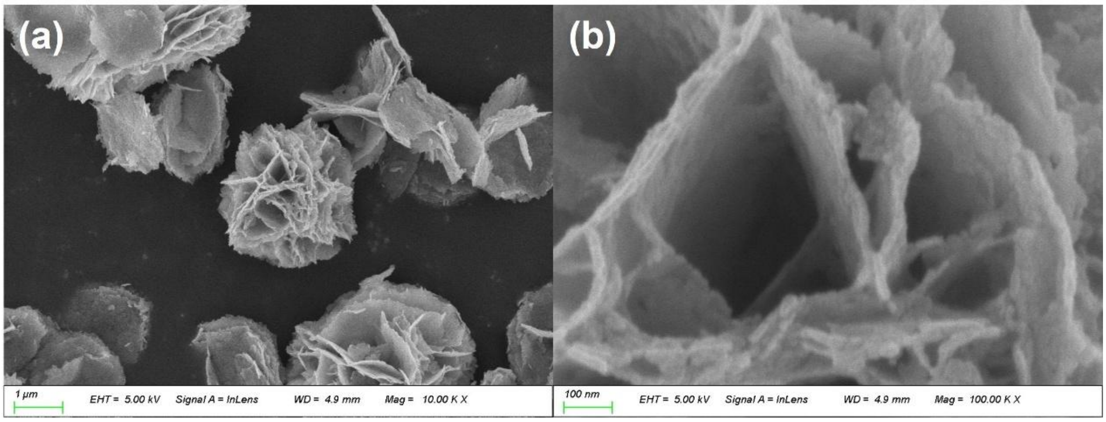


Fig. S2 SEM images of HWO-CPB composites

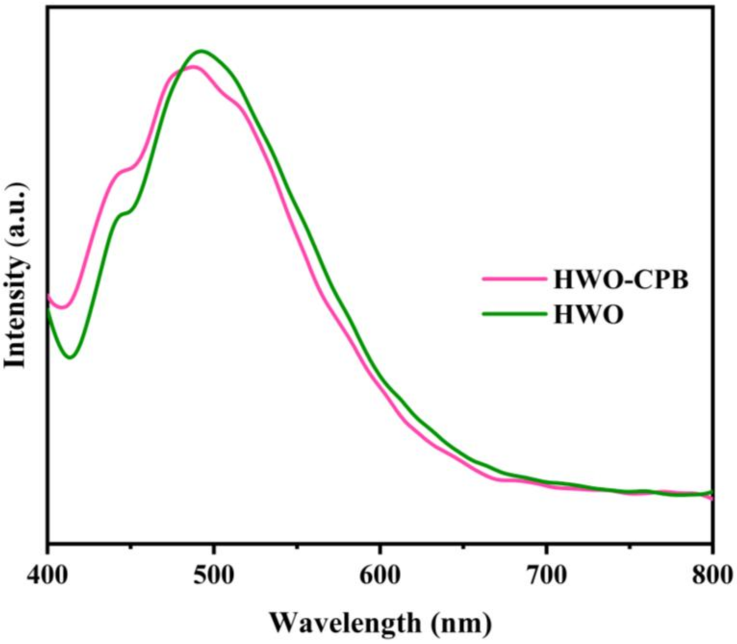
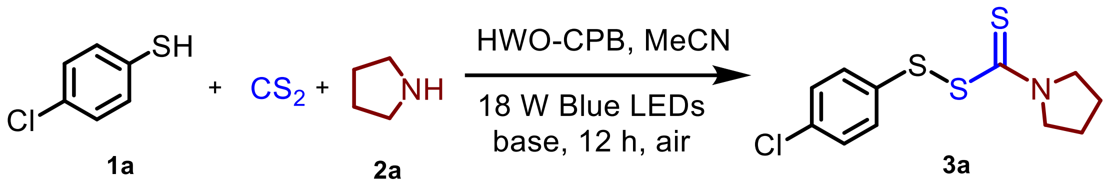


Fig. S3 Photoluminescence (PL) emission spectra of HWO and HWO-CPB

2.5 Optimization of reaction conditions

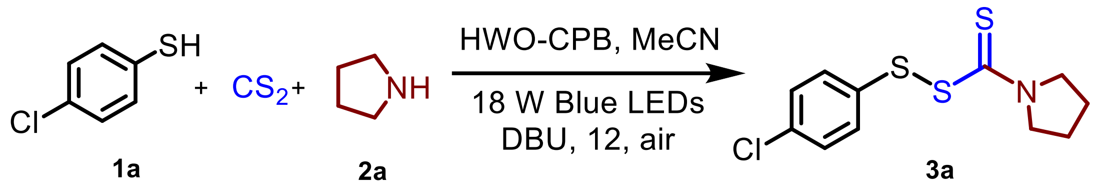
Table S1. Optimization of bases[a]



Entry	Base (1.0 equiv.)	Yield (%)[b]
1	K_2CO_3	60
2	Na_2CO_3	22
3	DIPEA	27
4	$NaHCO_3$	29
5	DABCO	32
6	*t*BuOK	65
7	NaOH	52
8	DBU	72
9	/	trace

[a]Reaction condition：**1a** (0.1 mmol), CS_2 (0.3 mmol), **2a** (0.3 mmol), HWO-CPB (10 mg), MeCN (2 mL), base (0.1 mmol), 12 W blue LEDs irradiation, room temperature, 12 h, under air atmosphere. [b]Isolated yield.

Table S2. Optimization of the amount of bases[a]

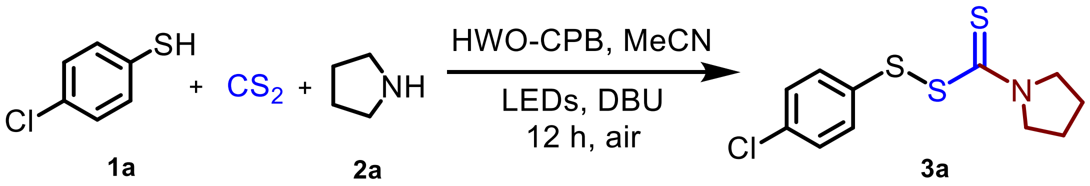


Entry	Deviation from standard conditions	Yield (%)[b]
1	0.5 equiv. of DBU	60
2	1 equiv. of DBU	77
3	1.5 equiv. of DBU	76
4	2 equiv. of DBU	61

5	5 mg catalyst (HWO-CPB)	77

[a]Reaction condition: **1a** (0.1 mmol), CS_2 (0.3 mmol), **2a** (0.3 mmol), HWO-CPB (10 mg), MeCN (2 mL), DBU (0.1 mmol), 12 W blue LEDs irradiation, room temperature, 12 h, under air atmosphere. [b]Isolated yield.

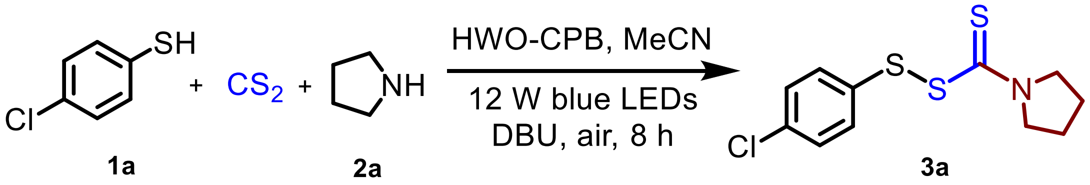
Table S3. Optimization of light source[a]



Entry	Deviation from standard conditions	Yield (%)[b]
1	12 W blue LEDs	77
2	18 W white LEDs	63
3	18 W green LEDs	N.R.
4	50 W blue LEDs	29

[a]Reaction condition: **1a** (0.1 mmol), CS_2 (0.3 mmol), **2a** (0.3 mmol), HWO-CPB (5 mg), MeCN (2 mL), DBU (0.1 mmol), LEDs irradiation, room temperature, 12 h, under air atmosphere. [b]Isolated yield.

Table S4. Optimization of reaction times, catalyst and gas atmosphere[a]



Entry	Deviation from standard conditions	Yield (%)[b]
1	6 h	70
2	8 h	87
3	10 h	72
4	14 h	64
5	BWO as catalyst	26
6	CPB as catalyst	44

7	Without catalyst	N.R.
8	dark	N.R.
9	HWO-CPB (1:5)	43
10	HWO-CPB (1:1)	55
11	N_2	trace
12	O_2	18
13	TEMPO (5 equiv.)	66
14	BHT (5 equiv.)	52

[a]Reaction condition: **1a** (0.1 mmol), CS_2 (0.3 mmol), **2a** (0.3 mmol), HWO-CPB (5 mg), MeCN (2 mL), DBU (0.1 mmol), 12 W blue LEDs irradiation, room temperature, 12 h, under air atmosphere. [b]Isolated yield.

2.6 General experimental procedure

A 10 mL glass tube was charged with the amine **2** (0.3 mmol), CS_2 (0.3 mmol), DBU (0.1 mmol), and acetonitrile (0.5 mL). The mixture was irradiated with a 12 W blue LED (λmax ≈ 455 nm) in air at room temperature for 0.5 h. Subsequently, the thiol compound **1** (0.1 mmol), the photocatalyst (2 mg), and additional acetonitrile (1.5 mL) were added. The reaction vessel was placed approximately 8 cm from the light source (no optical filter used) and irradiation was continued under an air atmosphere for 8 h at room temperature. The reaction progress was monitored by thin-layer chromatography (TLC). Upon completion, the crude mixture was purified by flash chromatography on silica gel (eluent: ethyl acetate/petroleum ether = 1:20) to afford the desired product.

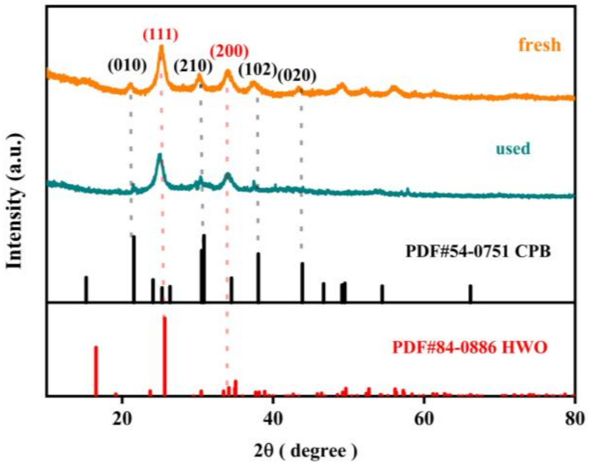


Fig. S4 XRD patterns of HWO-CPB composites

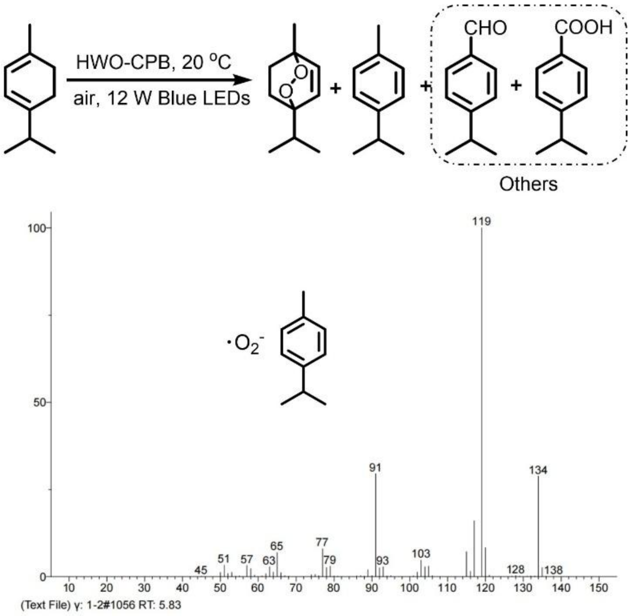


Fig. S5 Photocatalytic oxidation of α-terpinene in O_2 atmosphere under visible light irradiation

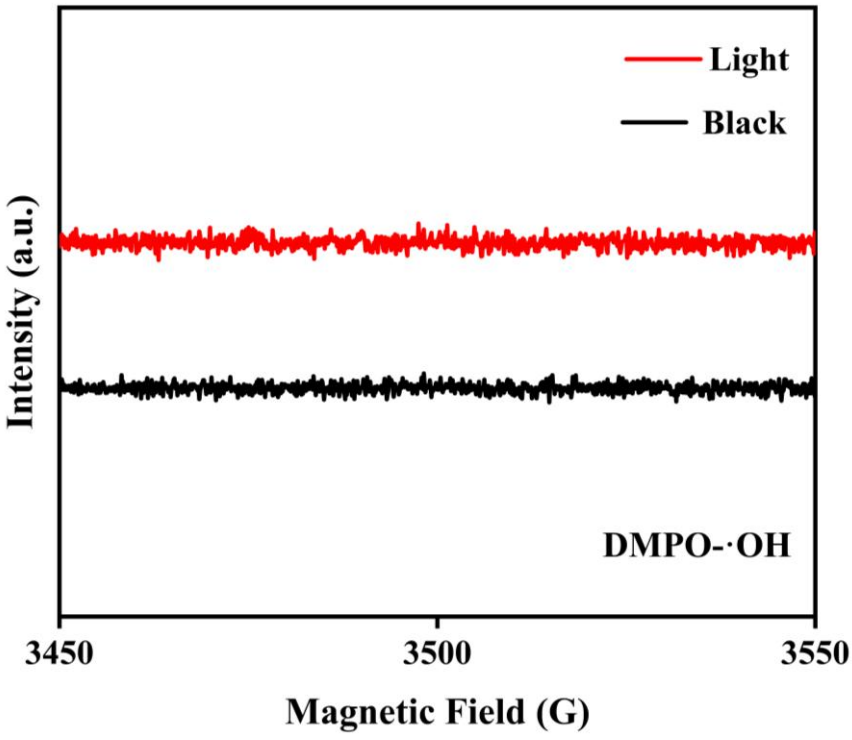


Fig. S6 EPR spectra of the DMPO-trapped ·OH

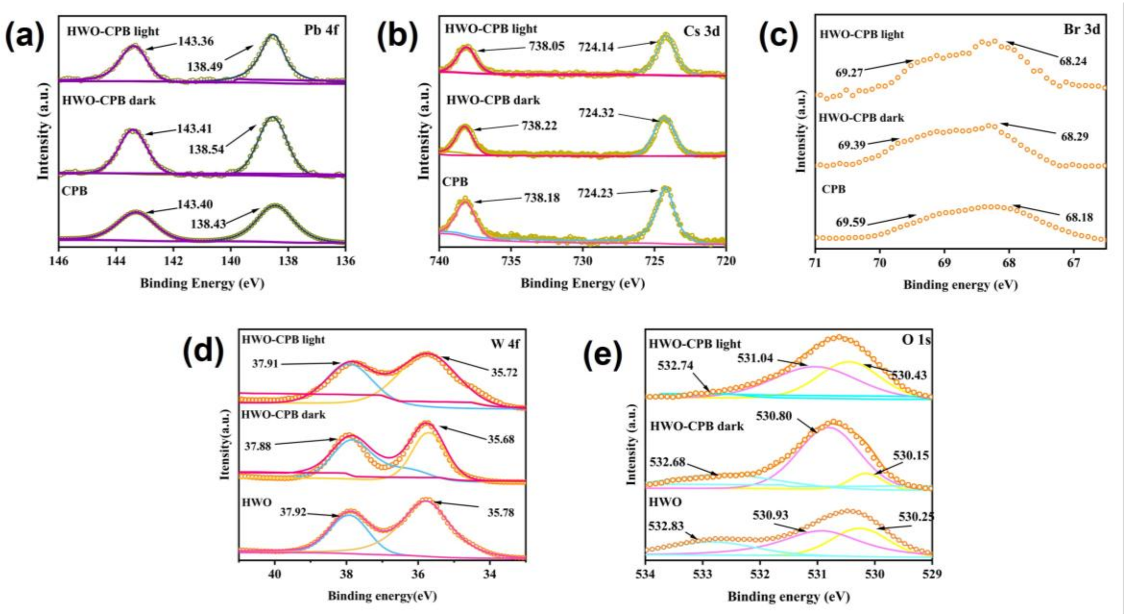
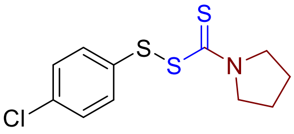


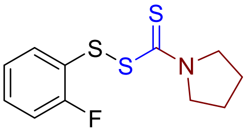
Fig. S7 In situ XPS survey spectra of (a) Pb 4f, (b) Cs 3d, (c) Br 3d, (d) W 4f and (f) O 1s of HWO-CPB

3. Data for the products.



4-chlorophenyl pyrrolidine-1-carbo(dithioperoxo)thioate

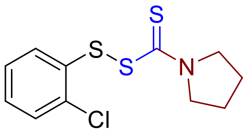
Thin-layer chromatography (petroleum ether/ethyl acetate 20:1) afforded the titled compound as a yellow oil. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.54 (d, *J* = 8.7 Hz, 2H), 7.26 (d, *J* = 8.6 Hz, 2H), 3.97 (t, *J* = 7.0 Hz, 2H), 3.76 (t, *J* = 6.9 Hz, 2H), 2.13 (p, *J* = 6.8 Hz, 2H), 2.01 (p, *J* = 6.9 Hz, 2H).



2-fluorophenyl pyrrolidine-1-carbo(dithioperoxo)thioate

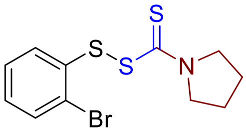
Thin-layer chromatography (petroleum ether/ethyl acetate 20:1) afforded the titled compound as a yellow oil. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.72 (td, *J* = 7.7, 1.8

Hz, 1H), 7.26 (d, J = 5.9 Hz, 1H), 7.19 – 7.02 (m, 2H), 3.96 (t, J = 7.2 Hz, 2H), 3.77 (t, J = 6.9 Hz, 2H), 2.17 – 2.09 (m, 2H), 2.00 (p, J = 6.9 Hz, 2H).



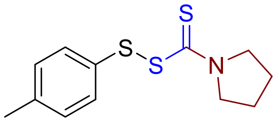
2-chlorophenyl pyrrolidine-1-carbo(dithioperoxo)thioate

Thin-layer chromatography (petroleum ether/ethyl acetate 30:1) afforded the titled compound as a yellow oil. ^{1}H NMR (500 MHz, Chloroform-d) δ 8.23 – 8.16 (m, 1H), 8.16 – 8.13 (m, 1H), 7.64 – 7.59 (m, 2H), 3.98 (t, J = 7.0 Hz, 2H), 3.85 (t, J = 7.0 Hz, 2H), 2.19 (p, J = 6.9 Hz, 2H), 2.06 (q, J = 7.0 Hz, 2H).



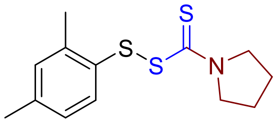
2-bromophenyl pyrrolidine-1-carbo(dithioperoxo)thioate

Thin-layer chromatography (petroleum ether/ethyl acetate 20:1) afforded the titled compound as a yellow oil. ^{1}H NMR (500 MHz, Chloroform-d) δ 7.46 (dd, J = 13.0, 8.6 Hz, 2H), 7.23 – 7.15 (m, 1H), 7.06 – 6.92 (m, 1H), 3.90 (t, J = 7.0 Hz, 2H), 3.77 (t, J = 6.9 Hz, 2H), 2.09 (p, J = 6.9 Hz, 2H), 1.96 (p, J = 7.2 Hz, 2H).



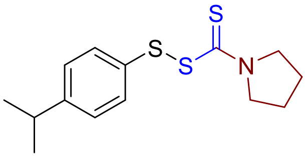
***p*-tolyl pyrrolidine-1-carbo(dithioperoxo)thioate**

Thin-layer chromatography (petroleum ether/ethyl acetate 30:1) afforded the titled compound as a yellow oil. ^{1}H NMR (500 MHz, Chloroform-d) δ 7.53 (d, J = 8.0 Hz, 2H), 7.10 (d, J = 7.9 Hz, 2H), 3.97 (t, J = 7.0 Hz, 2H), 3.75 (t, J = 6.9 Hz, 2H), 2.31 (s, 3H), 2.11 (p, J = 6.8 Hz, 2H), 1.99 (p, J = 7.0 Hz, 2H).



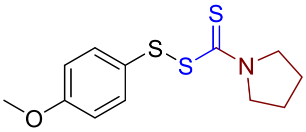
2,4-dimethylphenyl pyrrolidine-1-carbo(dithioperoxo)thioate

Thin-layer chromatography (petroleum ether/ethyl acetate 30:1) afforded the titled compound as a yellow oil. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.62 (d, *J* = 8.0 Hz, 1H), 7.10 – 6.87 (m, 2H), 3.96 (q, *J* = 7.3 Hz, 2H), 3.74 (t, *J* = 6.9 Hz, 2H), 2.49 (d, *J* = 25.4 Hz, 3H), 2.30 (d, *J* = 22.4 Hz, 3H), 2.13 – 2.05 (m, 2H), 1.98 (h, *J* = 6.6 Hz, 2H).



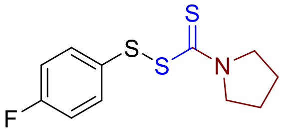
4-isopropylphenyl pyrrolidine-1-carbo(dithioperoxo)thioate

Thin-layer chromatography (petroleum ether/ethyl acetate 30:1) afforded the titled compound as a yellow oil. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.48 (d, *J* = 8.1 Hz, 2H), 7.08 (d, *J* = 8.0 Hz, 2H), 3.89 (t, *J* = 7.0 Hz, 2H), 3.68 (t, *J* = 6.9 Hz, 2H), 2.79 (p, *J* = 6.9 Hz, 1H), 2.03 (p, *J* = 7.0 Hz, 2H), 1.91 (p, *J* = 6.9 Hz, 2H), 1.17 – 1.12 (m, 6H).



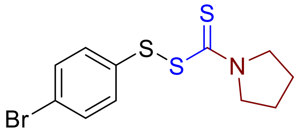
4-methoxyphenyl pyrrolidine-1-carbo(dithioperoxo)thioate

Thin-layer chromatography (petroleum ether/ethyl acetate 30:1) afforded the titled compound as a yellow oil. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.60 (d, *J* = 8.7 Hz, 2H), 6.75 (d, *J* = 8.4 Hz, 2H), 3.89 (t, *J* = 7.0 Hz, 2H), 3.71 (s, 3H), 3.64 (t, *J* = 6.9 Hz, 2H), 2.02 (p, *J* = 6.9 Hz, 2H), 1.90 (p, *J* = 6.9 Hz, 2H).



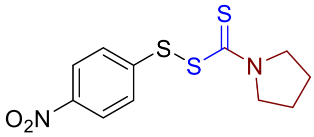
4-fluorophenyl pyrrolidine-1-carbo(dithioperoxo)thioate

Thin-layer chromatography (petroleum ether/ethyl acetate 30:1) afforded the titled compound as a yellow oil. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.62 (d, *J* = 8.2 Hz, 2H), 7.54 (d, *J* = 8.3 Hz, 2H), 3.98 (t, *J* = 7.0 Hz, 2H), 3.82 (t, *J* = 6.9 Hz, 2H), 2.15 (q, *J* = 6.9 Hz, 2H), 2.02 (q, *J* = 6.1, 5.3 Hz, 2H).



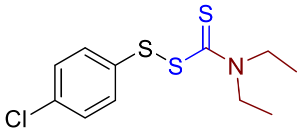
4-bromophenyl pyrrolidine-1-carbo(dithioperoxo)thioate

Thin-layer chromatography (petroleum ether/ethyl acetate 30:1) afforded the titled compound as a yellow oil. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.47 (d, *J* = 8.7 Hz, 2H), 7.41 (d, *J* = 8.6 Hz, 2H), 3.96 (t, *J* = 7.1 Hz, 2H), 3.76 (t, *J* = 6.9 Hz, 2H), 2.13 (p, *J* = 6.9 Hz, 2H), 2.01 (p, *J* = 6.9 Hz, 2H).



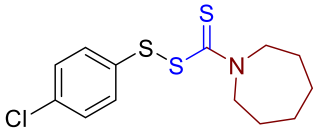
4-nitrophenyl pyrrolidine-1-carbo(dithioperoxo)thioate

Thin-layer chromatography (petroleum ether/ethyl acetate 30:1) afforded the titled compound as a yellow oil. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.20 (d, *J* = 9.0 Hz, 1H), 8.15 (d, *J* = 6.8 Hz, 1H), 7.61 (t, *J* = 7.9 Hz, 2H), 3.98 (t, *J* = 6.8 Hz, 2H), 3.85 (t, *J* = 6.9 Hz, 2H), 2.19 (dq, *J* = 11.7, 5.9, 4.9 Hz, 2H), 2.06 (p, *J* = 8.1, 7.6 Hz, 2H).



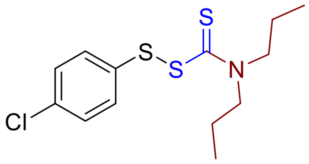
azepan-1-yl (4-chlorophenyl) carbonotrithioate

Thin-layer chromatography (petroleum ether/ethyl acetate 40:1) afforded the titled compound as a yellow oil. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.43 (d, *J* = 8.3 Hz, 2H), 7.18 (d, *J* = 8.1 Hz, 2H), 4.14 (d, *J* = 6.1 Hz, 2H), 3.91 (t, *J* = 6.1 Hz, 2H), 1.85 – 1.80 (m, 4H), 1.54 – 1.51 (m, 4H).



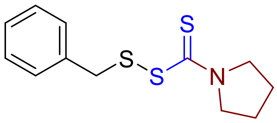
4-chlorophenyl azepane-1-carbo(dithioperoxo)thioate

Thin-layer chromatography (petroleum ether/ethyl acetate 30:1) afforded the titled compound as a yellow oil. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.50 (d, *J* = 8.5 Hz, 2H), 7.26 (d, *J* = 8.0 Hz, 2H), 4.04 (t, *J* = 7.2 Hz, 2H), 3.83 (q, *J* = 7.5 Hz, 2H), 1.31 (dd, *J* = 14.1, 7.0 Hz, 6H).



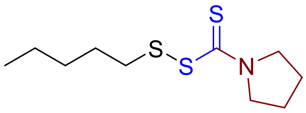
benzyl pyrrolidine-1-carbo(dithioperoxo)thioate

Thin-layer chromatography (petroleum ether/ethyl acetate 30:1) afforded the titled compound as a yellow oil. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.30 (d, *J* = 7.1 Hz, 2H), 7.24 (t, *J* = 7.4 Hz, 2H), 7.19 (dd, *J* = 8.9, 5.8 Hz, 1H), 4.03 (s, 2H), 3.89 (t, *J* = 7.0 Hz, 2H), 3.62 (t, *J* = 6.9 Hz, 2H), 2.01 (p, *J* = 6.8 Hz, 2H), 1.91 (p, *J* = 6.9 Hz, 2H).



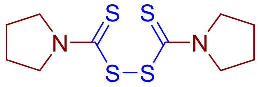
pentyl pyrrolidine-1-carbo(dithioperoxo)thioate

Thin-layer chromatography (petroleum ether/ethyl acetate 30:1) afforded the titled compound as a yellow oil. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 3.96 (t, *J* = 7.0 Hz, 2H), 3.75 (t, *J* = 7.0 Hz, 2H), 2.98 – 2.81 (m, 2H), 2.12 (p, *J* = 6.8 Hz, 2H), 2.00 (p, *J* = 6.8 Hz, 2H), 1.67 (p, *J* = 7.4 Hz, 2H), 1.41 – 1.30 (m, 4H), 0.90 (t, *J* = 7.1 Hz, 3H).



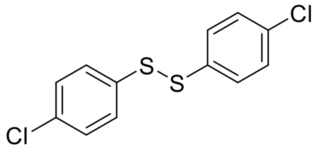
pentyl pyrrolidine-1-carbo(dithioperoxo)thioate

Thin-layer chromatography (petroleum ether/ethyl acetate 20:1) afforded the titled compound as a yellow oil. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 3.96 (t, *J* = 7.0 Hz, 2H), 3.75 (t, *J* = 7.0 Hz, 2H), 2.98 – 2.81 (m, 2H), 2.12 (p, *J* = 6.8 Hz, 2H), 2.00 (p, *J* = 6.8 Hz, 2H), 1.67 (p, *J* = 7.4 Hz, 2H), 1.41 – 1.30 (m, 4H), 0.90 (t, *J* = 7.1 Hz, 3H).



pyrrolidine-1-carbothioic dithioperoxyanhydride

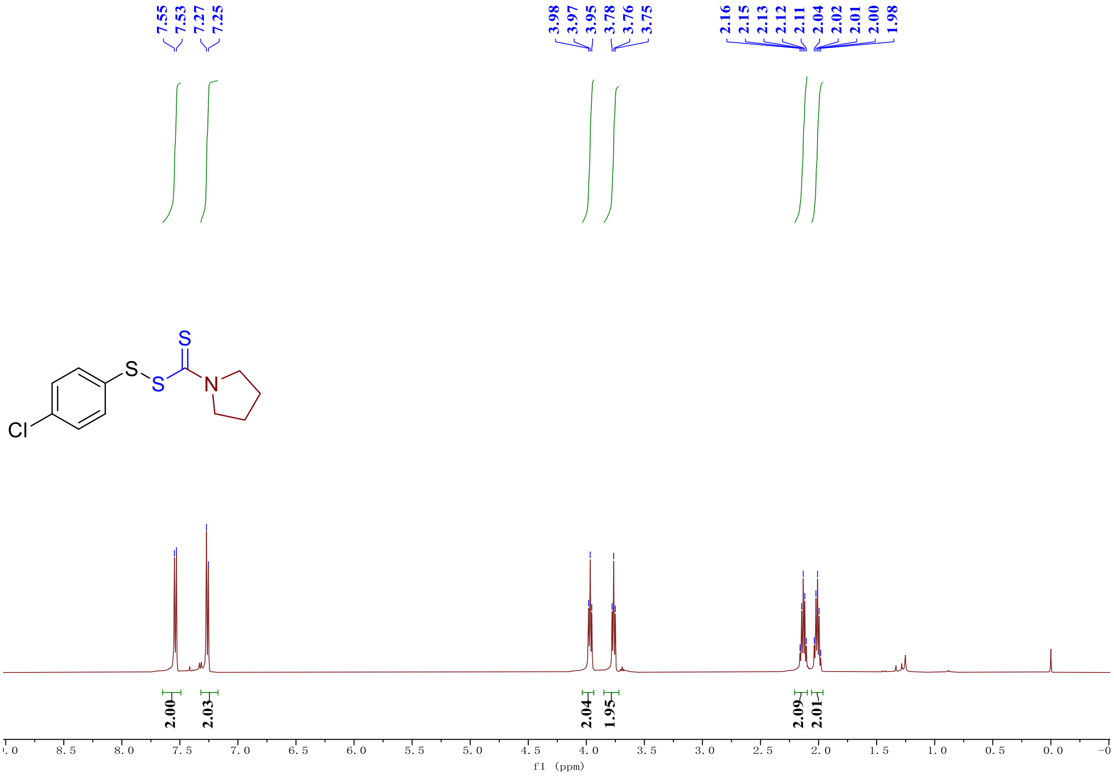
Thin-layer chromatography (petroleum ether/ethyl acetate 20:1) afforded the titled compound as a yellow solid. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 3.97 (q, *J* = 7.6 Hz, 8H), 2.22 – 2.12 (m, 4H), 2.03 (q, *J* = 6.9 Hz, 4H).

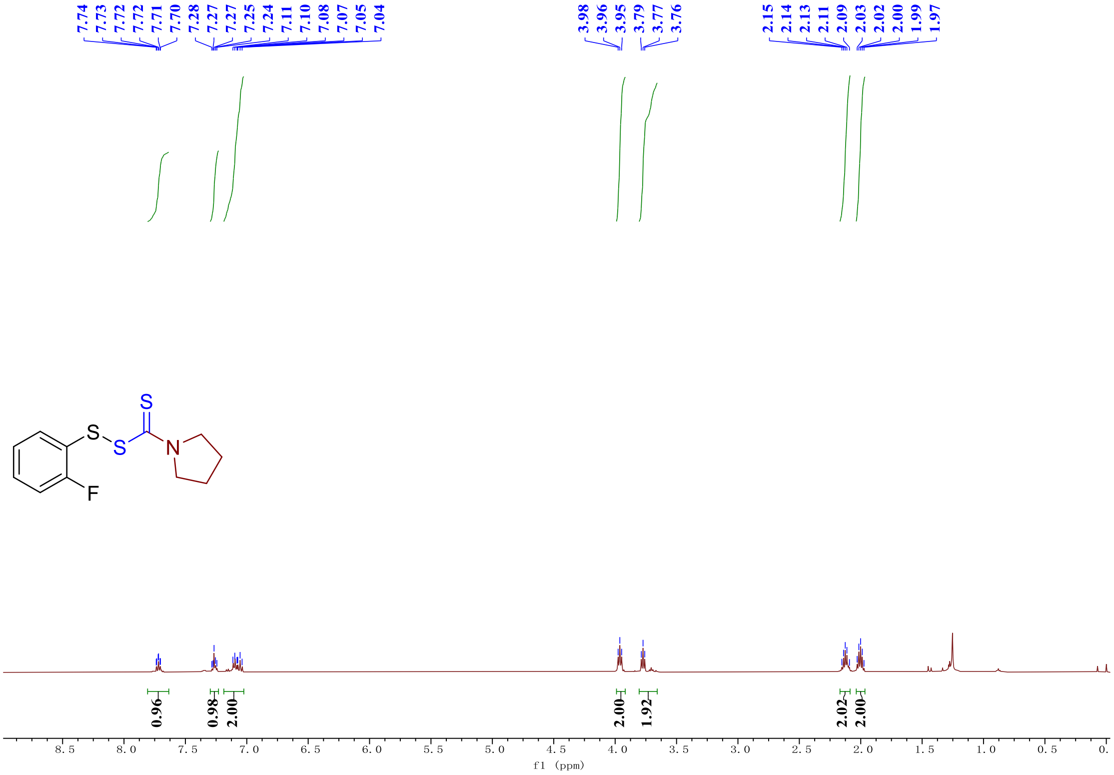


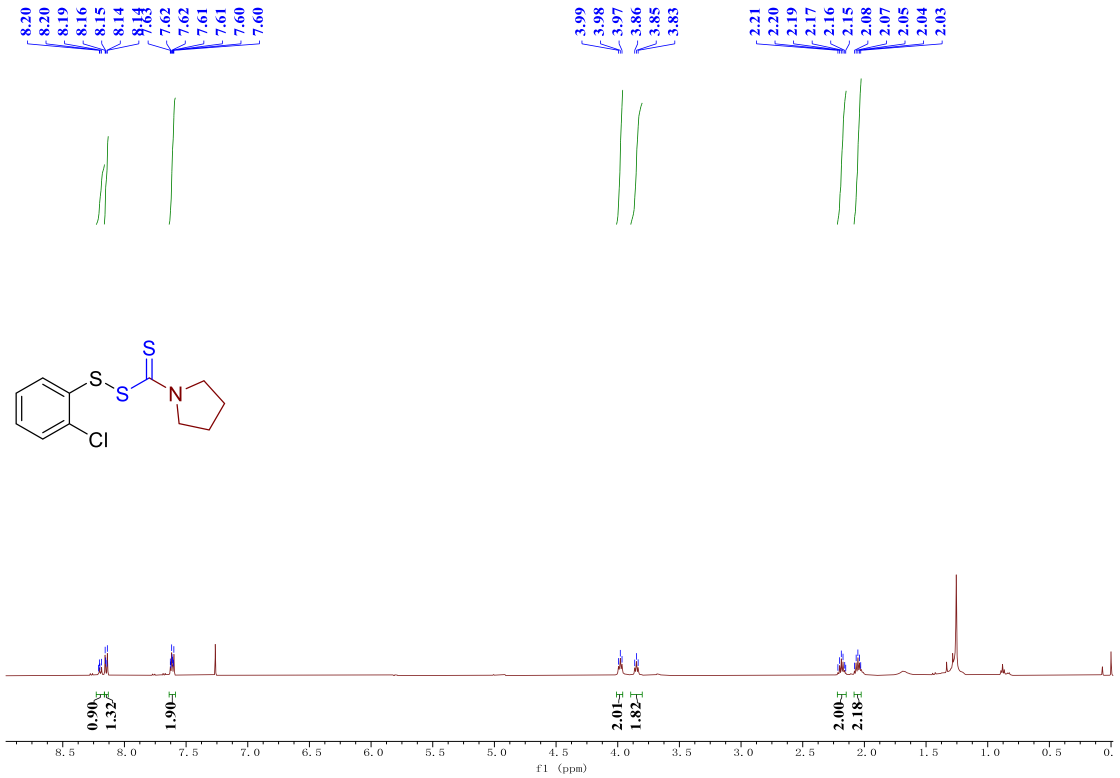
1,2-bis(4-chlorophenyl)disulfane

Thin-layer chromatography (petroleum ether/ethyl acetate 20:1) afforded the titled compound as a yellow solid. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.42 – 7.38 (m, 4H), 7.30 – 7.26 (m, 4H).

4. ^{1}H NHR spectra for compounds



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2.04
2.03
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S
S
N
Cl
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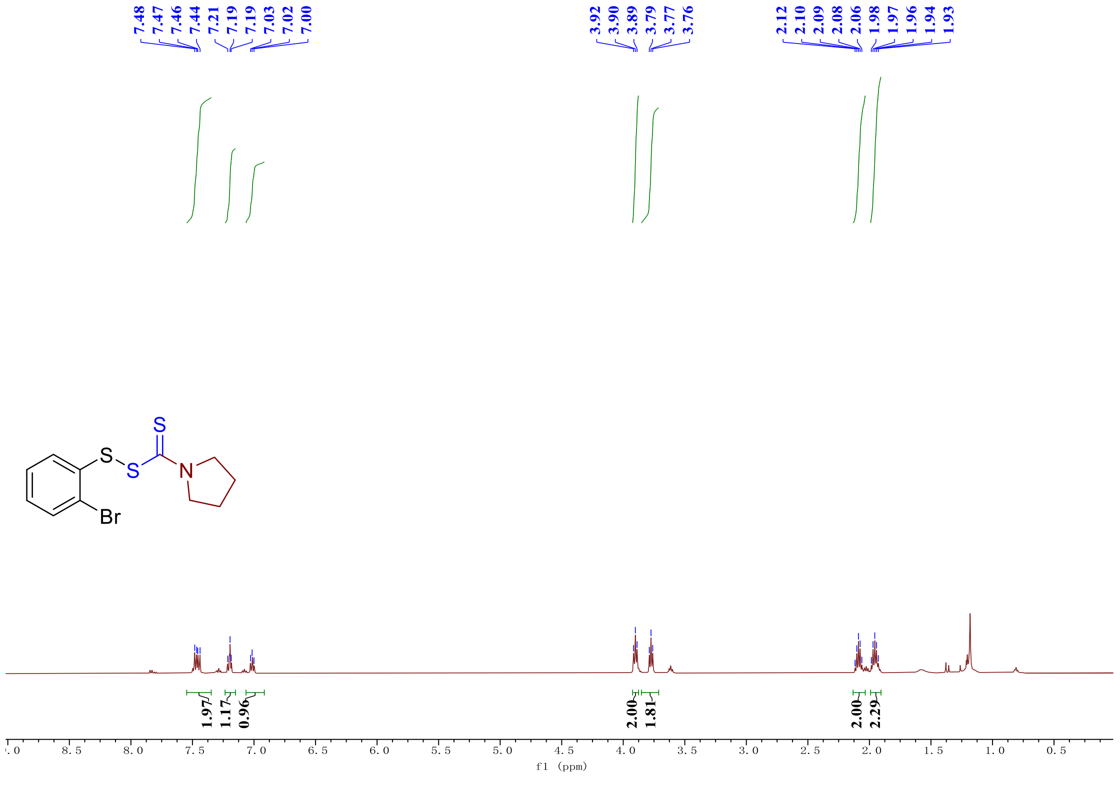
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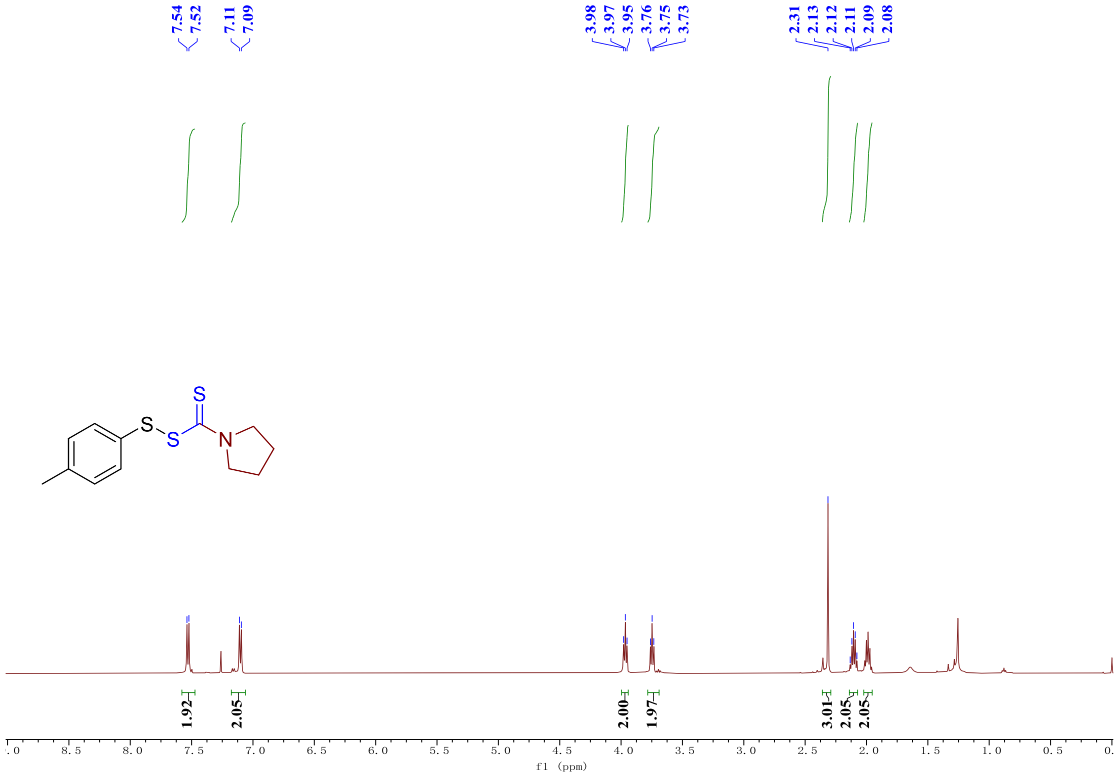
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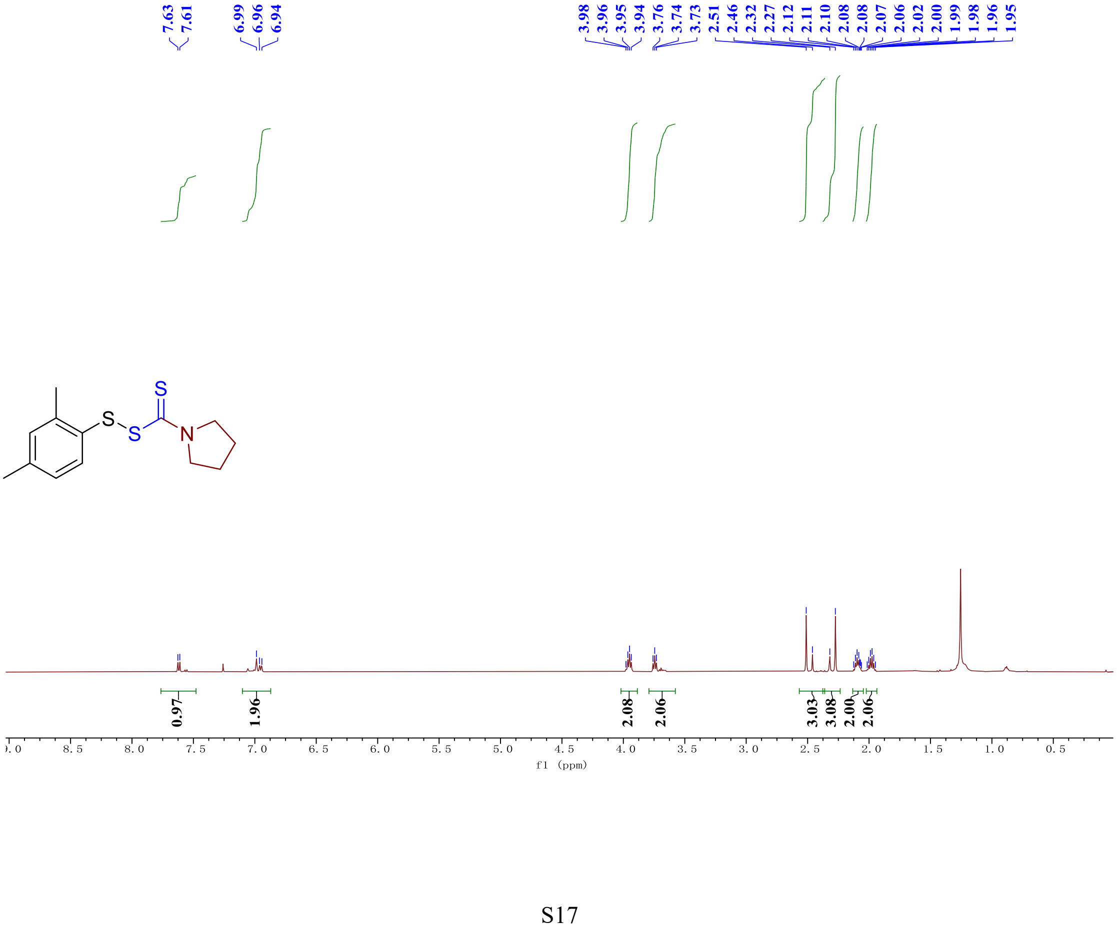
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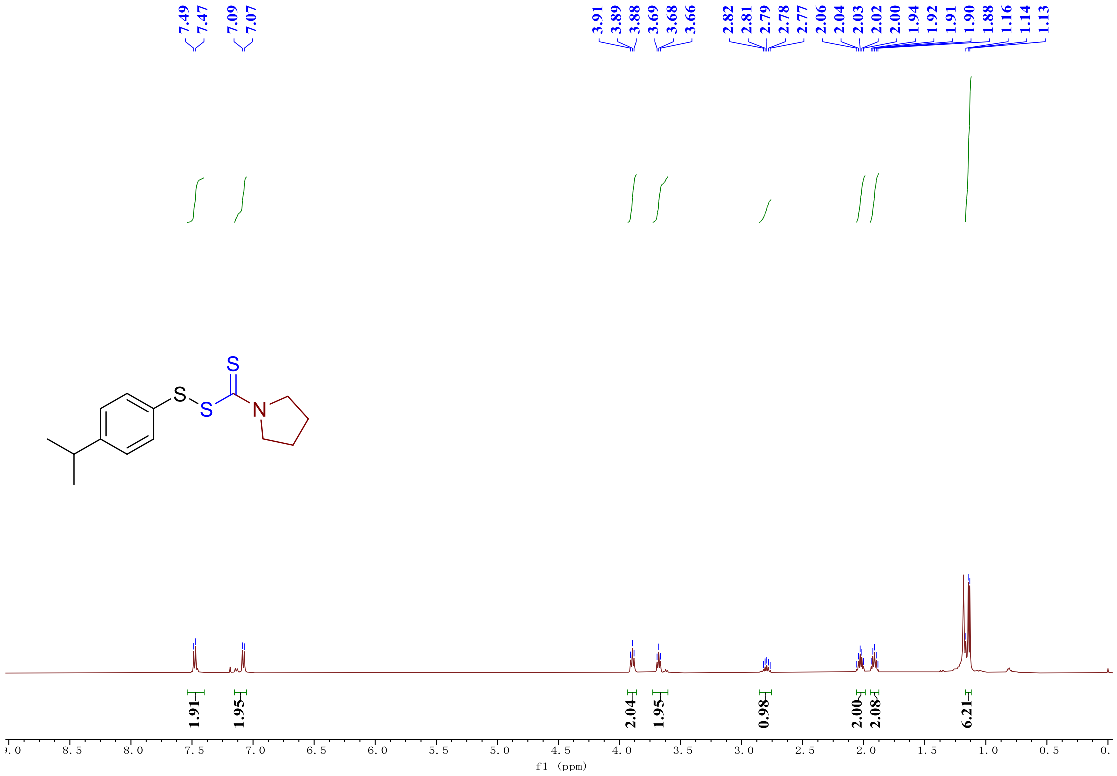
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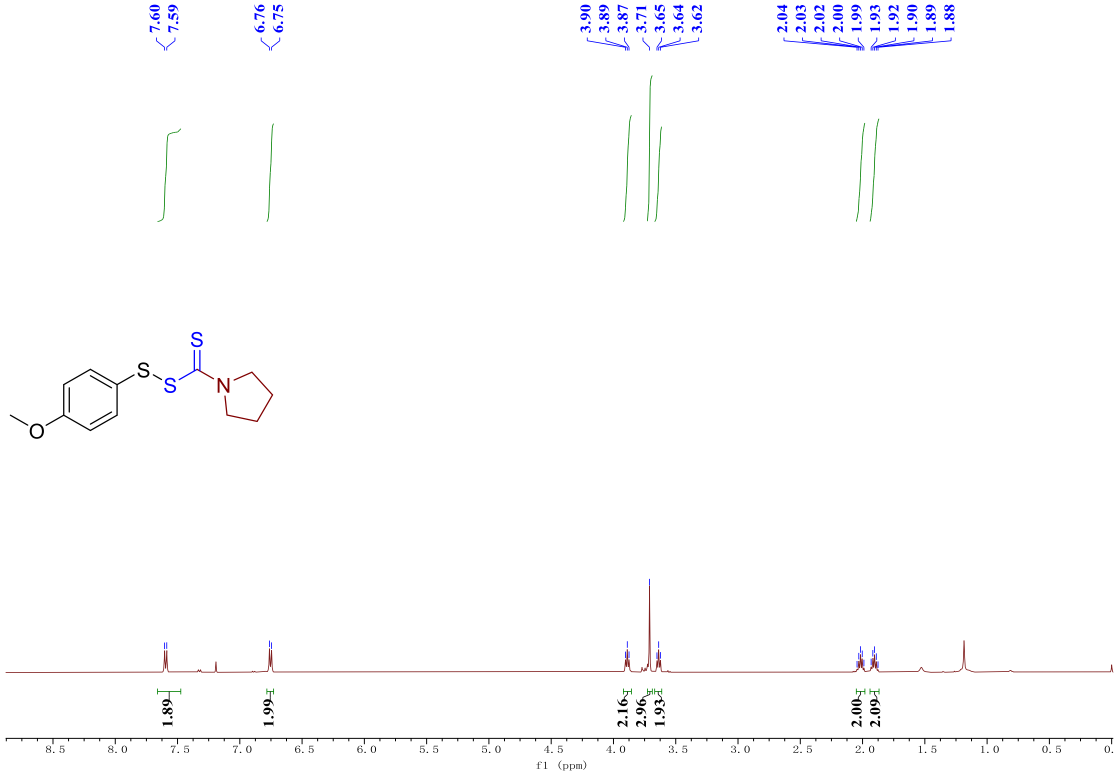
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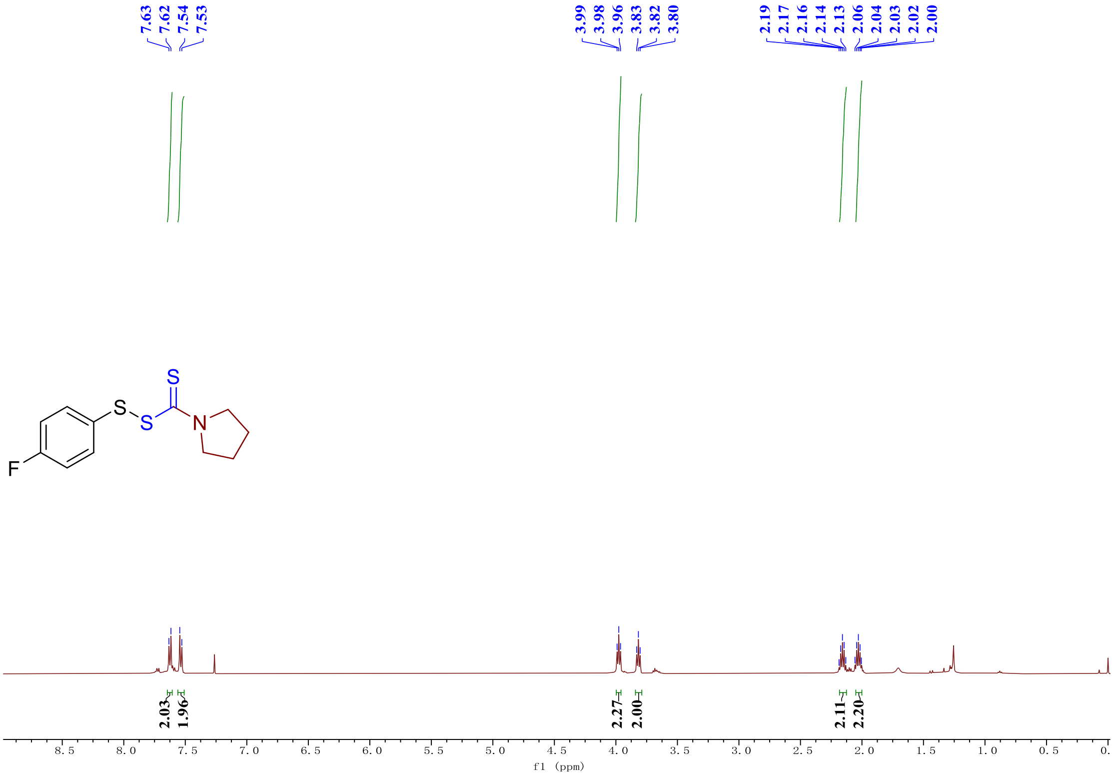
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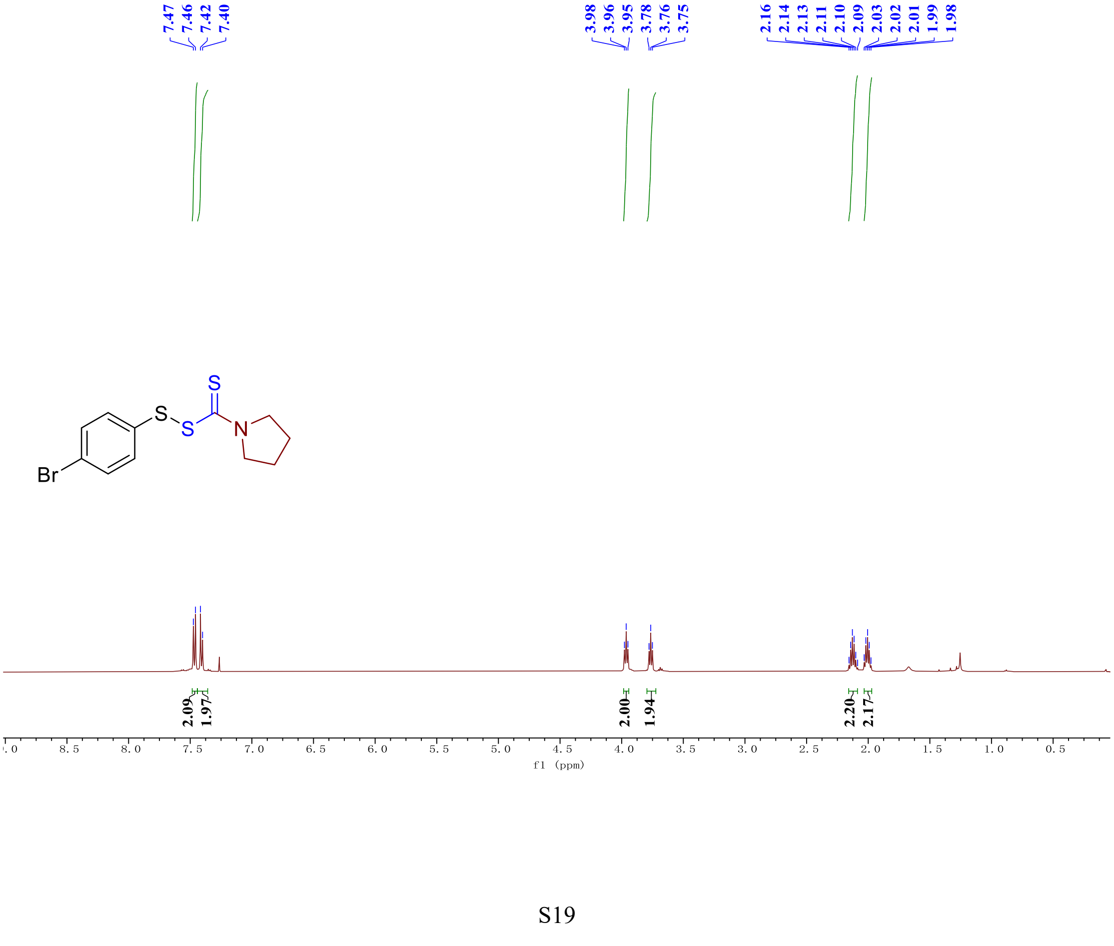
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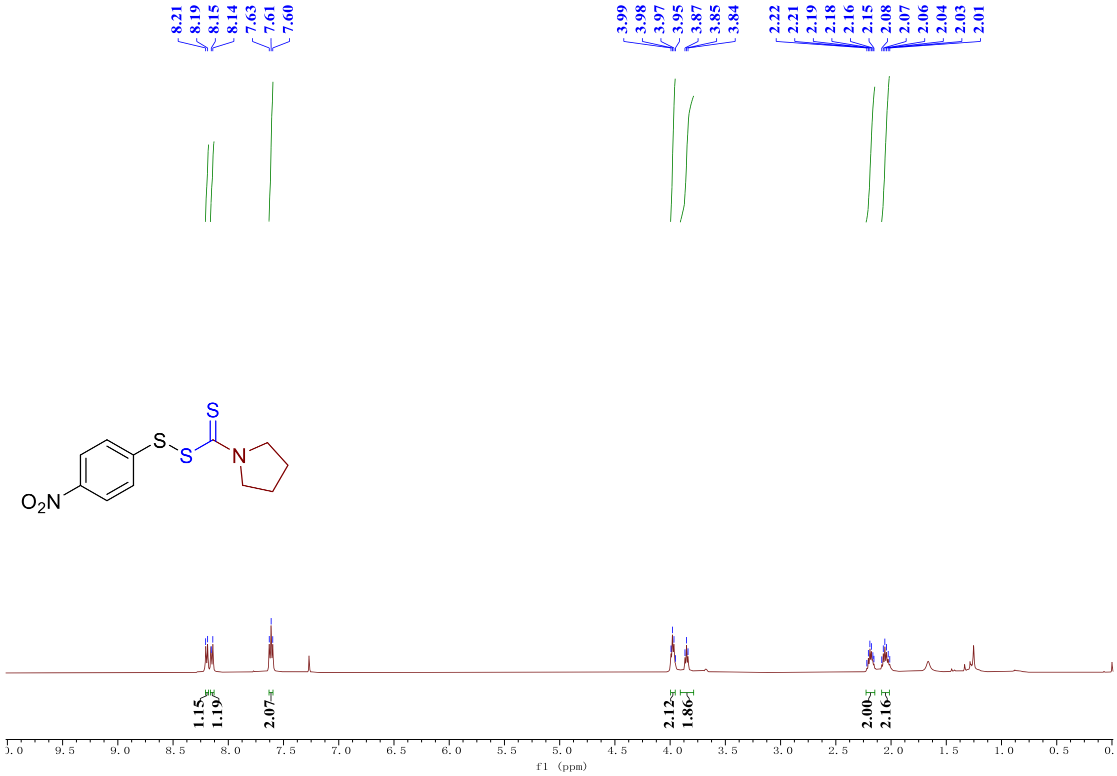
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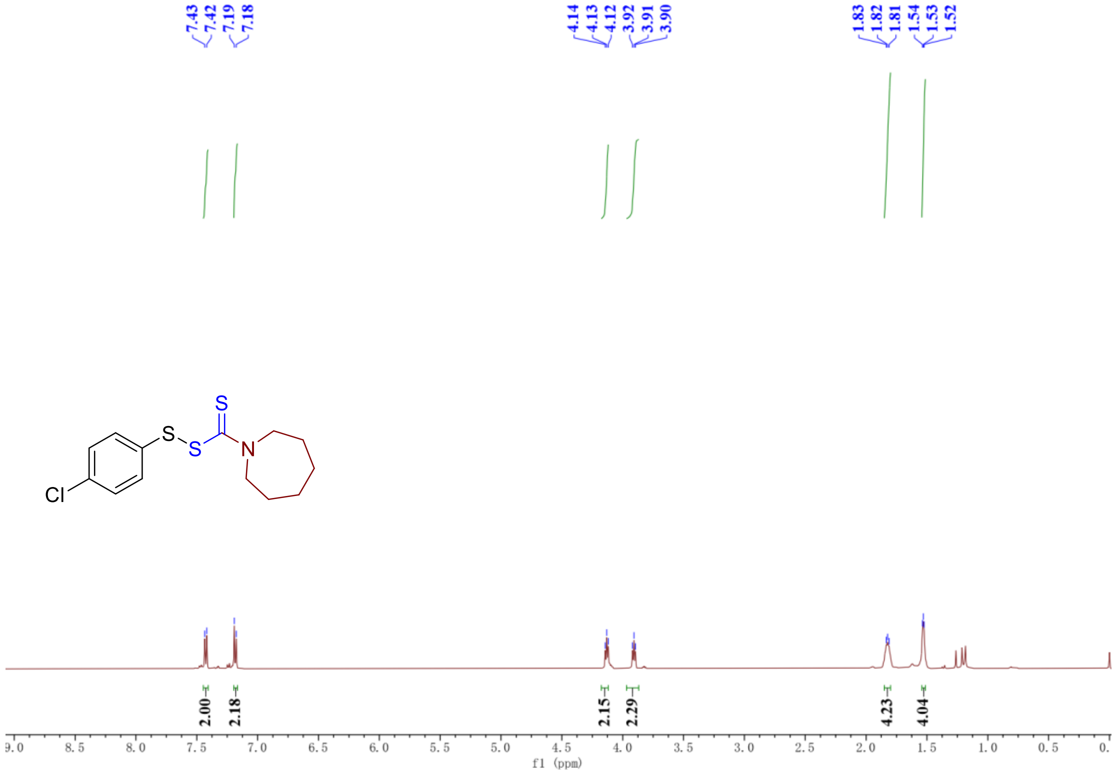
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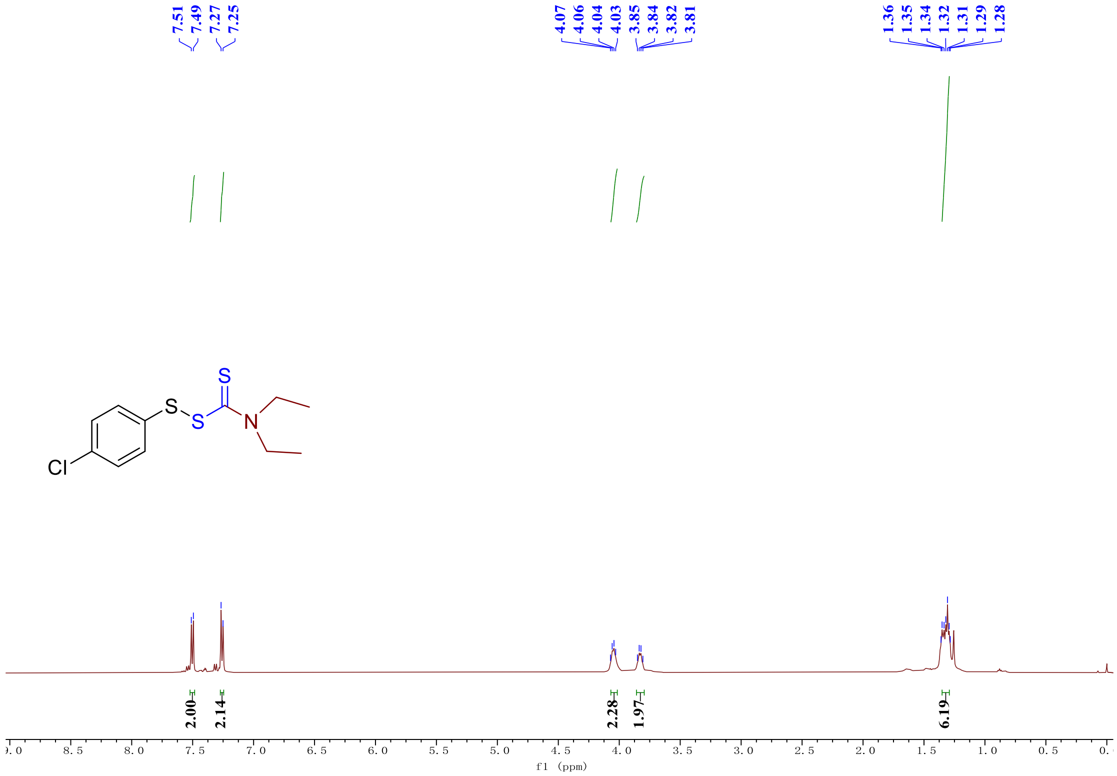
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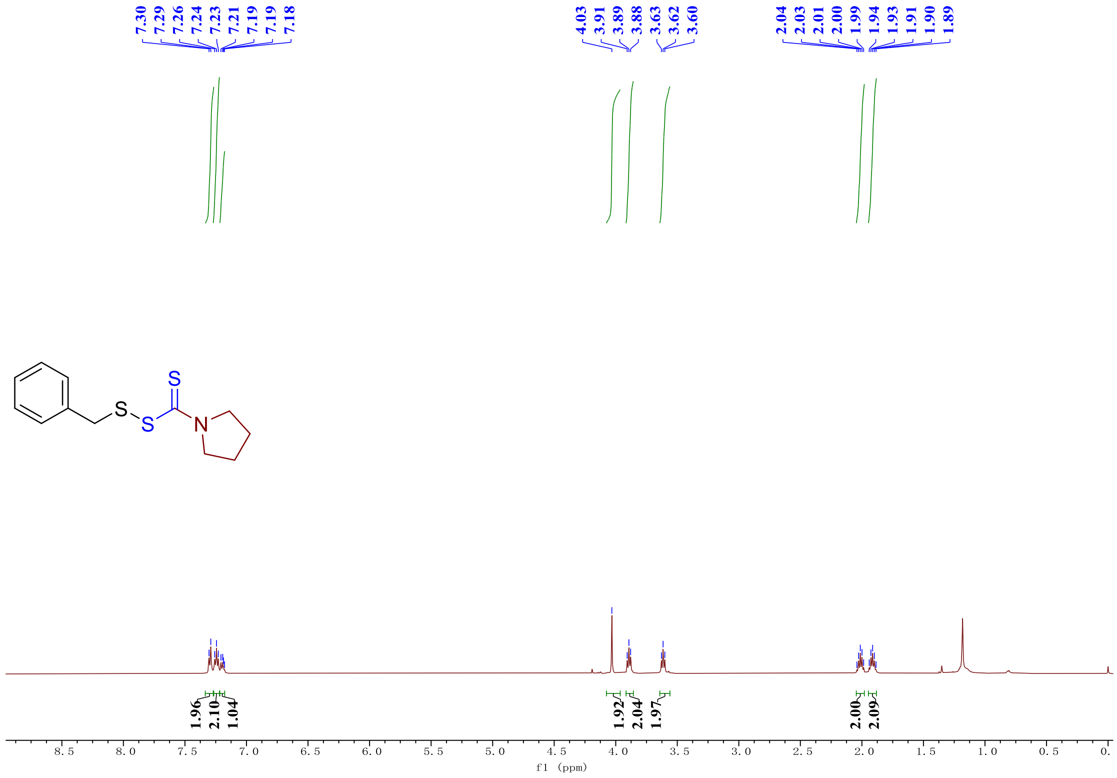
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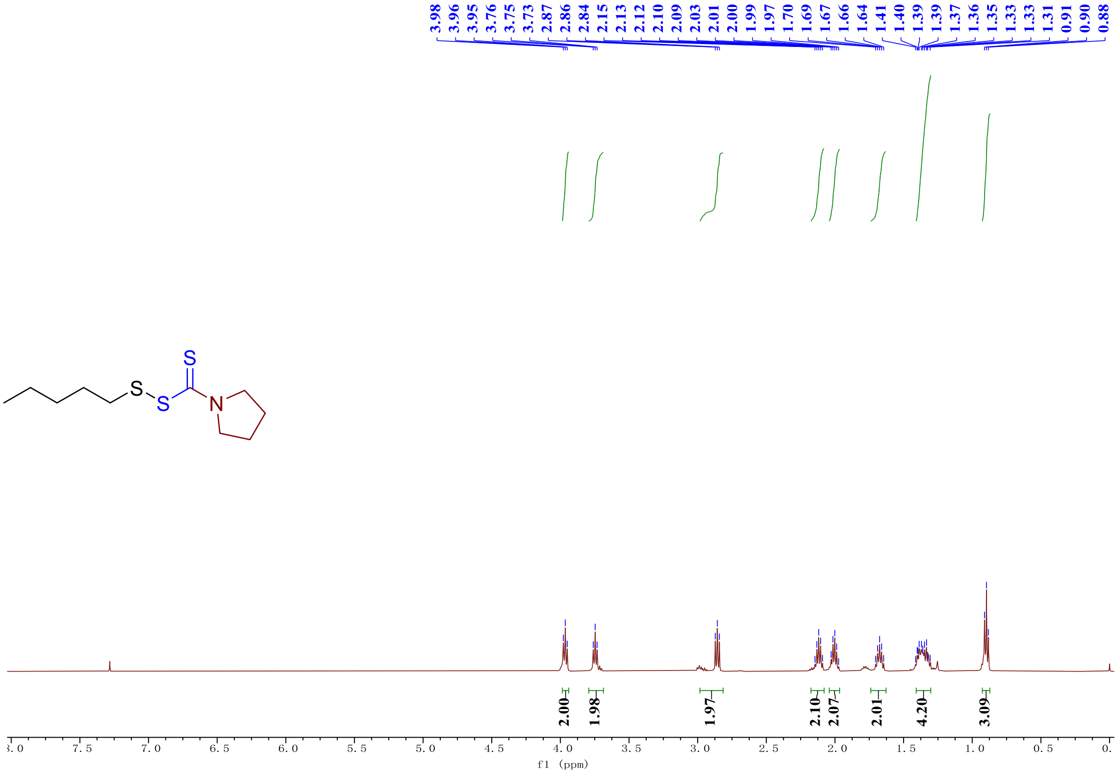
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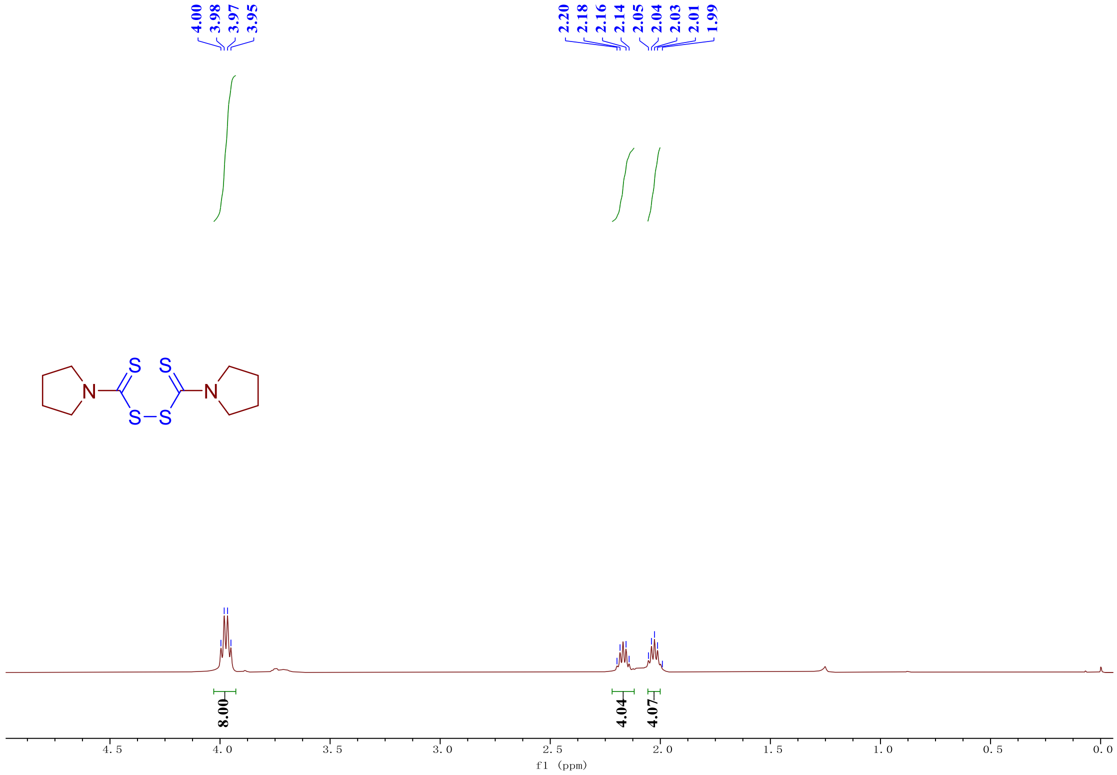
中间体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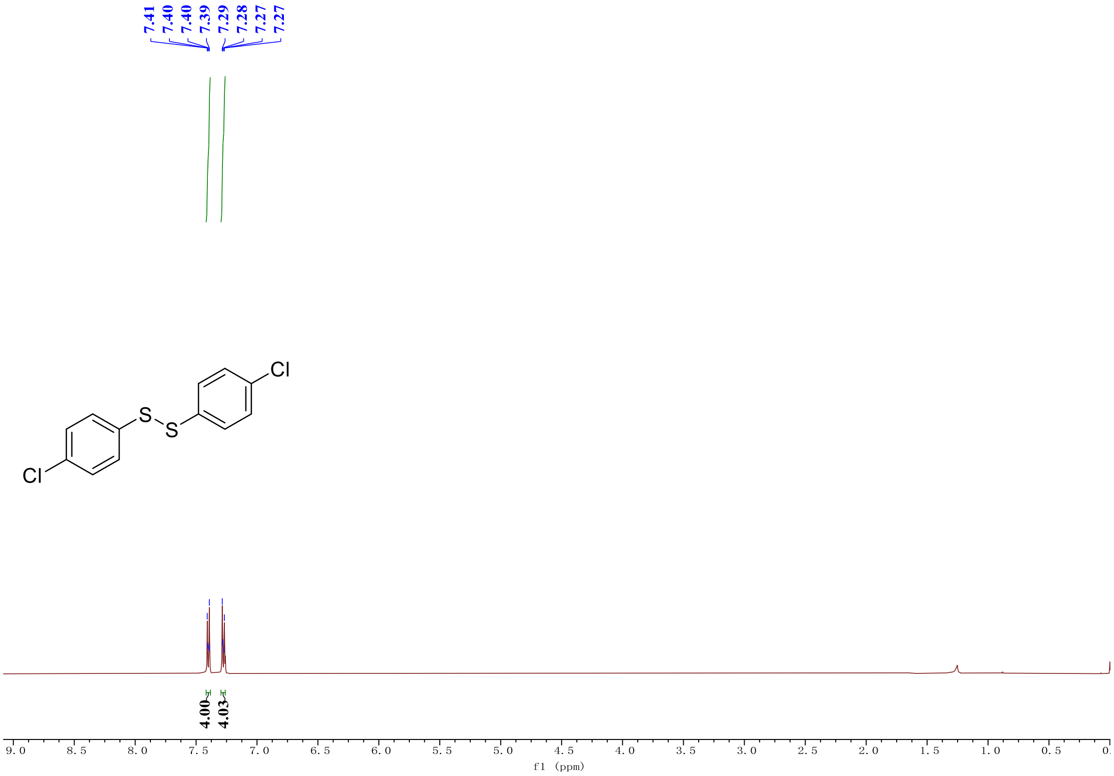
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