Supporting Information

Multicomponent reactions access to S-Aryl dithiocarbamates via electron donor-acceptor under open-to air condition

YiSong Tang,[a,b] Yougen Cai,[b] Zhiwei Xie,[b] XiaoYun Chen,*[a] Jun Yi*[b]

[a]*School of Environmental and Chemical Engineering, Jiangsu University of Science and Technology, Zhenjiang, 212003, P. R. China.*

[b]*School of Materials Engineering, Changshu Institute of Technology, Changshu, Jiangsu, 215500, P. R. China.*

[b]*E-mail: yijun08@mail.ustc.edu.cn

[a]*E-mail: chenxy@just.edu.cn

Table of Contents

I. General Information and Materials

A. General Information

All commercially available starting materials were purchased from Titan and Energy Chemical Company and were used without further purification unless otherwise stated. All reaction vessels were dried in an oven at 110°C and cooled in an air atmosphere before use. Unless otherwise indicated, the solvents used were all common solvents, no further drying was required, reactions were performed under an air atmosphere and 40 W white LEDs (4000k) irradiation at room temperature. All the reactions were monitored by TLC using precoated sheets of silica gel G/UV-254 of 0.25 mm thickness (Merck 60F254) using UV light for observation. Using 200-300 mesh silica gel for column chromatography. Yields generally referred to chromatographically isolated yields, unless otherwise noted. **^{1}H NMR** (400MHz), **^{13}C NMR** (100 MHz) spectra were recorded on BRUKER DRX-400 spectrometer in chloroform-D1 and TMS as an internal standard. For **^{1}H NMR** (400MHz), chloroform-D1 (δ= 7.26 ppm) serverd as internal standard and the following abbreviations were used to indicate the multiplicity, for **^{13}C NMR** (100MHz), chloroform-D1 (δ= 77.16 ppm): singlet (s), doublet (d), triplet (t), quartet (q), doublet of doublets (dd), doublet of triplets (dt), and multiplet (m). The data of HRMS was carried out on Agilent 6210TOF LC/MS mass spectrometer. X-ray crystallographic data were collected by using a Bruker D8 QUEST X-ray single crystal diffractometer at Changshu Institute of Technology, China. UV-visible spectroscopy was recorded on a SHIMADZU UV 3600 UV-visible spectrophotometer.

B. Materials

B.1 Photochemical Reaction Set-up

All reactions have been studied in the oven-dried glass round bottom flask (commercial supplier: Synthware). The light source used for illuminating the quartz reaction tube consists of white LEDs (4000 k) and adapter (manufacturer: Xuzhou Facai Lighting Co. Ltd. of China), and the radiator purchased from Taobao (https://gpiled.taobao.com). The reactor was 3.0 cm from 40 W white LEDs and magnetic stirrer maintains a speed of 800 RPM.

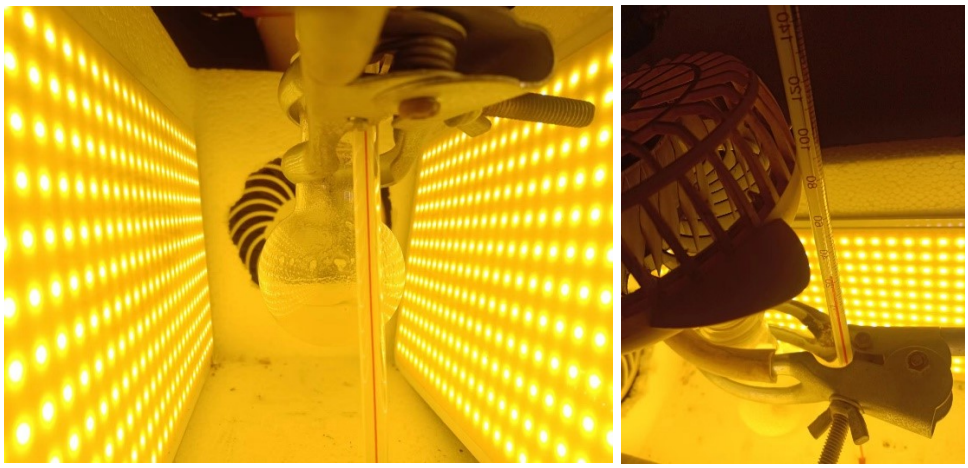
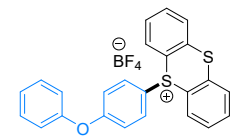


Figure S1. Photograph of the reaction setup.

B.2 Table S1. thianthrenium salt used in this study

The tetrafluoroborate thianthrenium salts **1** were synthesized from the corresponding commercially available compounds, according to the literature procedure.[1]



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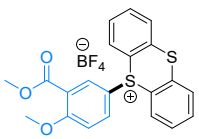

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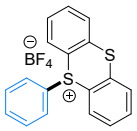

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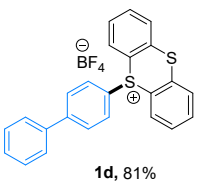

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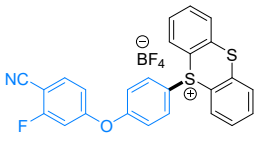

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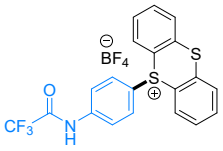

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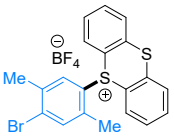

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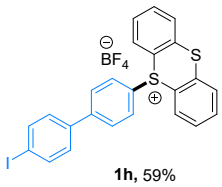

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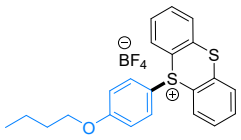

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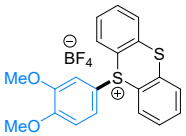

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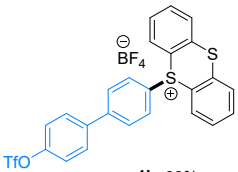

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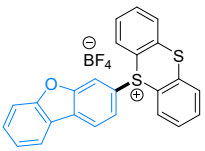

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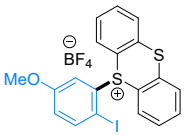

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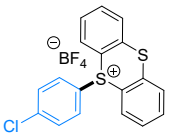

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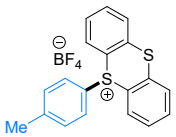

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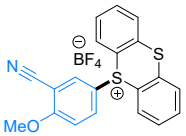

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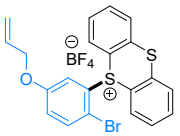

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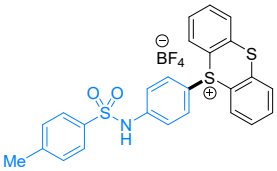

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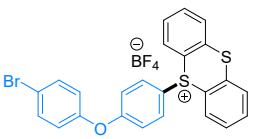

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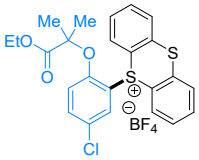

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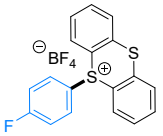

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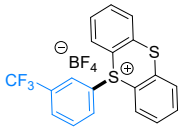

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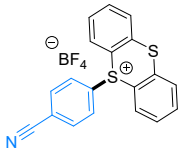

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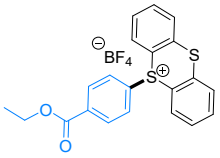

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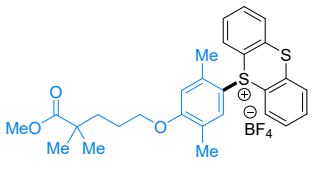

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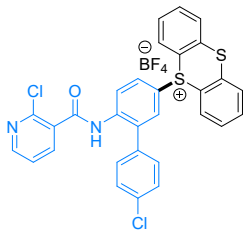

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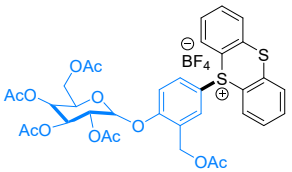

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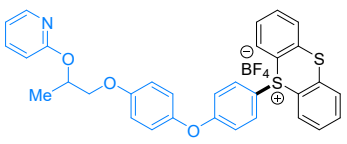

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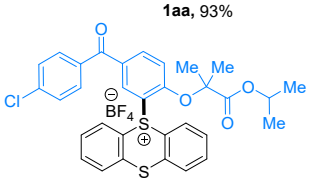
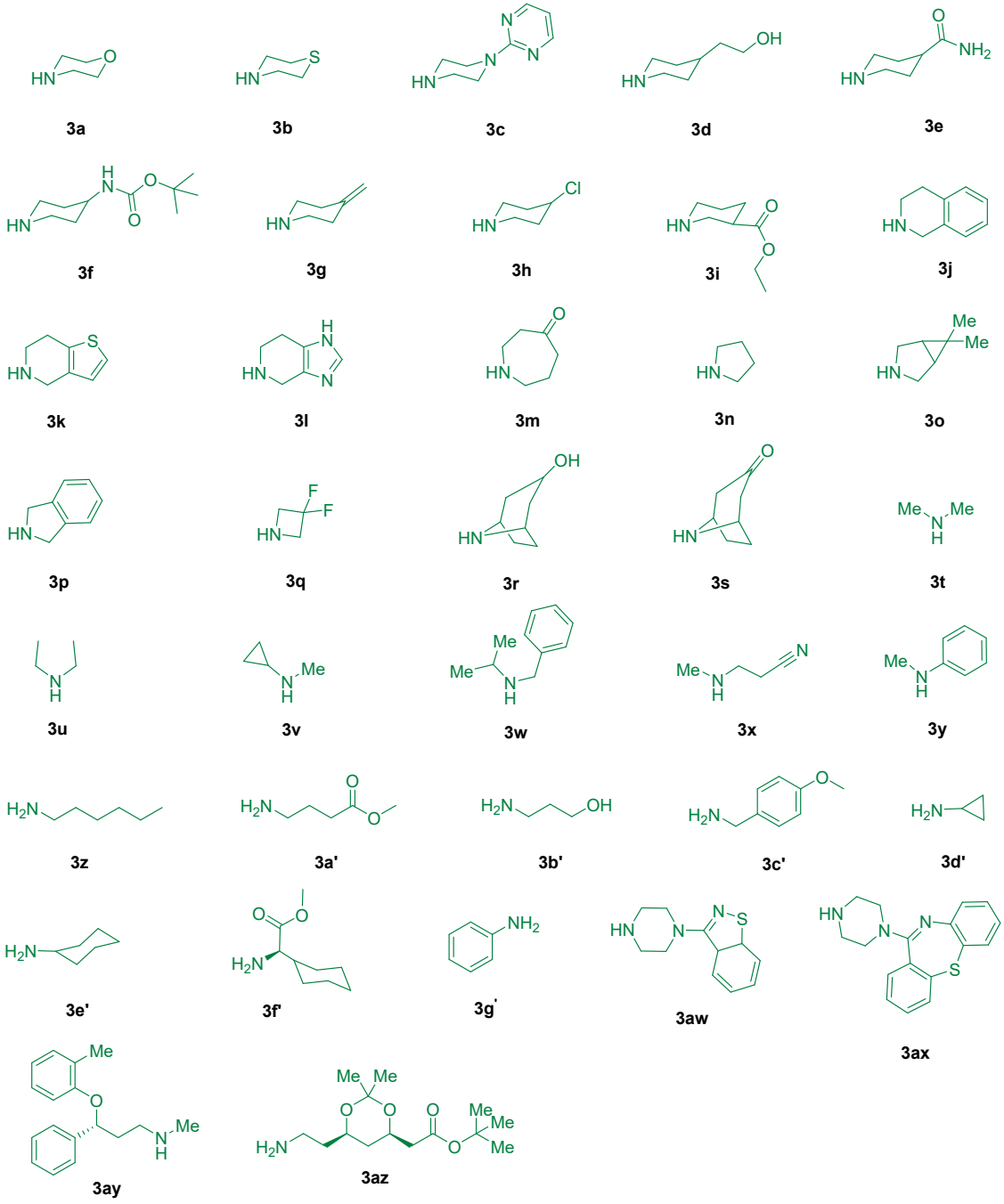


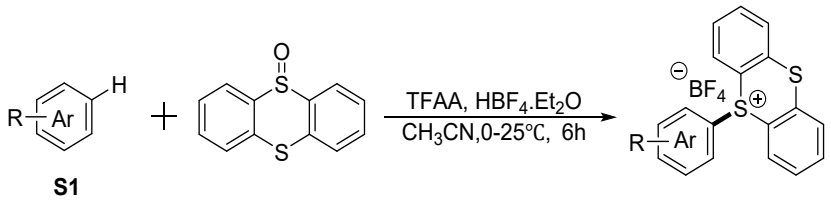
1ac, 69%

B.3 Table S2. Amine used in this study.

All the amine are commercially available.

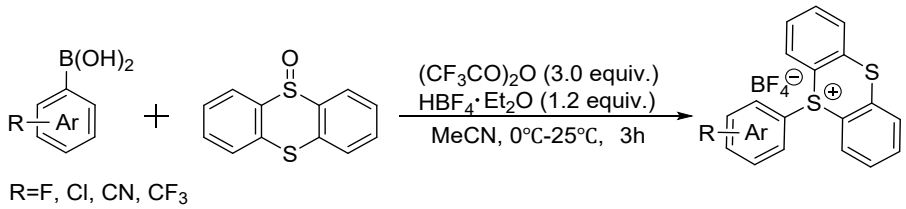


Procedure A[1]:



Under ambient atmosphere, a 100.0 mL round-bottom flask equipped with a magnetic stir bar was charged with **S1** (10.0 mmol, 1.0 equiv.) and MeCN (22.7 mL, C= 0.44 M). Trifluoroacetic anhydride (2780 μL, 20.0 mmol, 2.0 equiv.) was added at ambient temperature while stirring. After cooling to 0°C, thianthrene S-oxide (2320 mg, 10.0 mmol, 1.0 equiv.) was added in one portion, followed by the addition of $HBF_4{\cdot}OEt_2$ (2993 μL, 22 mmol, 2.2 equiv.) in one portion. The mixture was stirred at 0 °C for 1 h, then at ambient temperature for 5 h. The reaction mixture was concentrated under reduced pressure, and subsequently diluted with DCM (50.0 mL). The solution was poured onto a saturated aqueous $NaHCO_3$ solution (100.0 mL), and the layers were separated. The organic phase was washed with aqueous $NaBF_4$ solution (3×50.0 mL, 10%), and with water (2×100.0 mL). The organic phase was dried over Na_2SO_4, filtered, and the solvent was removed under reduced pressure. The residue was purified by chromatography on silica gel eluting with DCM/MeOH (v/v) to afford products**1**.

Procedure B[2]:



Under ambient atmosphere, a 100.0 mL borosilicate vial was charged with arylboronic acid (10.0 mmol, 1.00 equiv.), thianthrene-S-oxide (2320 mg, 10.0 mmol, 1.00 equiv.) and dry MeCN (40.0 mL, C= 0.25 M). After cooling to 0 °C, trifluoroacetic anhydride (4170 μL, 30.0 mmol, 3.0 equiv.) addition at 0 °C in one portion, followed by $HBF_4{\cdot}OEt_2$ (1632 μL, 12.0 mmol, 1.2 equiv.) was added in one portion at 0 C. The vial was sealed with a screw-cap, and the deep purple mixture was allowed to stand at 0 °C for 1 h, followed by warming the reaction mixture to 25 °C over a period of 1 h. After stirring at 25 °C for 1 h further, the reaction mixture was concentrated under reduced pressure, and the residue was diluted with 50.0 mL CH_2Cl_2. The CH_2Cl_2 solution was poured onto a saturated aqueous $NaHCO_3$ solution (100.0 mL). The mixture was poured into a separatory funnel, and the layers were separated. The CH_2Cl_2 layer was collected, and the aqueous layer was further extracted with CH_2Cl_2 (2×20 mL). The combined CH_2Cl_2 solution was washed with aqueous $NaBF_4$ solution (3×50.0 mL, 5 % w/w). The organic layer was dried over Na_2SO_4, filtered, and the solvent was removed under reduced pressure. The residue was purified by chromatography on silica gel eluting with CH_2Cl_2/MeOH (v/v). The desired products were collected and dried in vacuo to afford **1n, 1u-1x.**

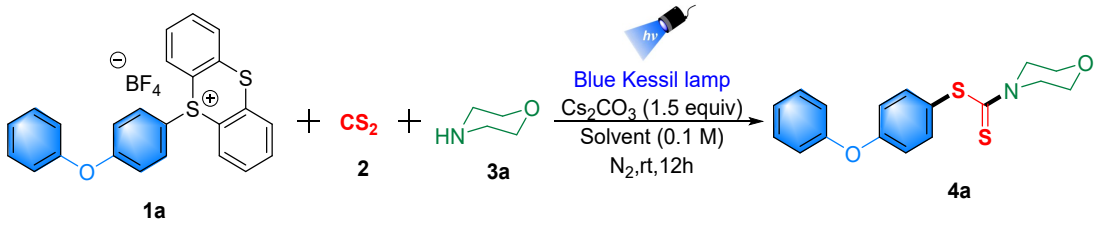
Reference

1 (a) E. M. Alvarez, T. Karl, F. Berger, L. Torkowski and T. Ritter, *Angew. Chem. Int. Ed.*, 2021, **60**, 13609-13613; (b) F. Berger, M. B. Plutschack, J. Riegger, W. Yu, S. Speicher, M. Ho, N. Frank and T. Ritter, *Nature.*, 2019, **567**, 223-228; (c) P. S. Engl, A. P. Haring, F. Berger, G. Berger, A. Perez-Bitrian and T. Ritter, *J. Am. Chem. Soc.*, 2019, **141**, 13346-13351; (d) J. Li, J. Chen, R. Sang, W. S. Ham, M. B. Plutschack, F. Berger, S. Chabbra, A. Schnegg, C. Genicot and T. Ritter, *Nat. Chem.*, 2020, **12**, 56-62; (e) R. Sang, S. E. Korkis, W. Su, F. Ye, P. S. Engl, F. Berger and T. Ritter, *Angew. Chem. Int. Ed.*, 2019, **58**, 16161-16166; (f) A. Selmani and F. Schoenebeck, *Org. Lett.*, 2021, **23**, 4779-4784; (g) F. Ye, F. Berger, H. Jia, J. Ford, A. Wortman, J. Borgel, C. Genicot and T. Ritter, *Angew. Chem. Int. Ed.*, 2019, **58**, 14615-14619; (h) Y.-L. Zhang, G.-H. Wang, Y. Wu, C.-Y. Zhu and P. Wang, *Org. Lett.*, 2021, **23**, 8522-8526; (i) Y. Zhao, C. Yu, W. Liang and F. W. Patureau, *Org. Lett.*, 2021, **23**, 6232-6236.3.

2 (a) J. Li, J. Chen, R. Sang, W. S. Ham, M. B. Plutschack, F. Berger, S. Chabbra, A. Schnegg, C. Genicot and T. Ritter, *Nat. Chem.*, 2020, **12**, 56-62. (b) X.-Y. Chen, Y.-N. Li, Y. Wu, J. Bai, Y. Guo and P. Wang, *J. Am. Chem. Soc.*, 2023, **145**, 10431-10440.

II. Optimization of reaction conditions

Table 1. Effect of solvent on the reaction[a]

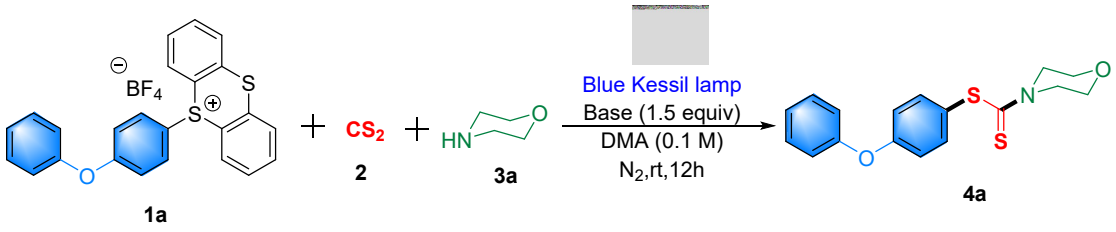


Entry	Solvent	Yield of 4a (%)[b]
1	DMSO	23
2	DMF	38
3	CH_3CN	29
4	AcOEt	13
5	DCM	22
6	DCE	16
7	THF	18
8	DMA	46
9	1,4-oxidant	26
10	NMP	37
11	Acetone	24
12	Et_2O	14
13	DMC	28
14	MeOH	21
15	Toluene	trace
16	tBuOH	16
17[c]	DMA	48

18	**DMA/H_2O (v/v=3:1)**	**42**

[a]Reaction procedure:under an N_2 atmosphere, 0.2 mmol scale utilizing **1a** (1 equiv), **2** (1.5 equiv), **3a** (3 equiv) and Cs_2CO_3 (1.5 equiv) in dry solvent (2ml, 0.1 M) under blue Kessil irradiation (λ_{max}=465 nm) for 12h at rt. [b]Isolated yield. [c] DMA was not degassed and dried.

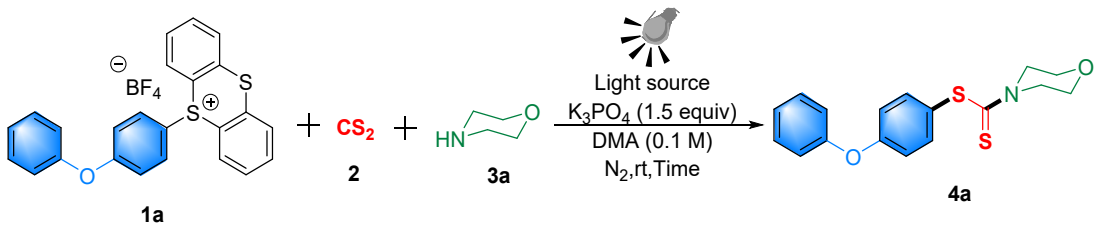
Table 2. Effect of base on the reaction[a]



Entry	Base	Yield of 4a (%)[b]
1	**Na_2CO_3**	**56**
2	**K_2CO_3**	**27**
3	**tBuOK**	**35**
4	**KOH**	**39**
5	**NaOH**	**32**
6	**$NaHCO_3$**	**40**
7	**K_3PO_4**	**67**
8	**K_2HPO_4**	**56**
9	**KH_2PO_4**	**48**
10	**Na_2HPO_4**	**34**
11	**Na_3PO_4•$12H_2O$**	**47**
12	**$NaHSO_4$**	**25**
13	**Na_2SO_4**	**32**
14	**NaOAc**	**19**
15	**DIPEA**	**60**
16	**DABCO**	**25**
17	**DMAP**	**35**
18	**DBU**	**50**
19	**TEA**	**36**
20	**Py**	**29**

[a]Reaction procedure:under an N_2 atmosphere, 0.2 mmol scale utilizing **1a** (1 equiv), **2** (1.5 equiv), **3a** (3 equiv) and base (1.5 equiv) in DMA (2ml, 0.1 M) under blue Kessil irradiation (λ_{max}=465 nm) for 12h at rt. [b]Isolated yield.

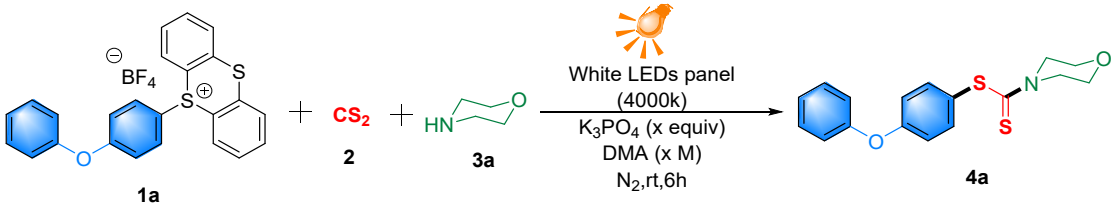
Table 3. Effect of Light source and reaction time on the reaction[a]



Entry	Light source	Time	Yield of 4a (%)[b]
1	Blue Kessil (λ_{max}= 456 nm)	12	67
2	White Kessil (7000k)	12	70
3	Purple Kessil (λ_{max}= 370 nm)	12	traces
4	Purple Kessil (λ_{max}= 390 nm)	12	traces
5	Blue LEDs panel (λ_{max} = 455 nm)	12	65
6	White LEDs panel (6000k)	12	76
7	**White LEDs panel (4000k)**	**12**	**86**
8	Purple LEDs panel (λ_{max} = 395 nm)	12	traces
9	White LEDs panel (4000k)	10	78
10	White LEDs panel (4000k)	14	84

[a]Reaction procedure:under an N_2 atmosphere, 0.2 mmol scale utilizing **1a** (1 equiv), **2** (1.5 equiv), **3a** (3 equiv) and base (1.5 equiv) in DMA (2ml, 0.1 M) under light irradiation for 12h at rt. [b]Isolated yield.

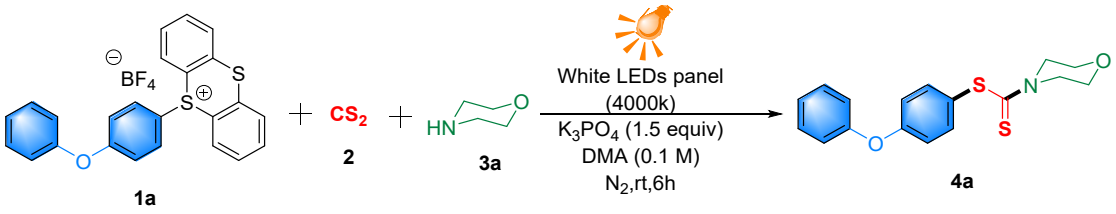
Table 4. Effect of the concentration and loading of CS_2/base/amine on the reaction[a]



Entry	2(equiv)	3a(equiv)	K_3PO_4(equiv)	[solvent]	Yield of 4a(%)[b]
1	**3**	**1.5**	**1.5**	**0.1 M**	**86**
2	**3**	**1.5**	**2**	**0.1 M**	**75**
3	**3**	**1.5**	**1**	**0.1 M**	**47**
4	**3**	**2**	**1.5**	**0.1 M**	**83**
5	**3**	**3**	**1.5**	**0.1 M**	**77**
6	**3**	**1**	**1.5**	**0.1 M**	**66**
7	**2**	**1.5**	**1.5**	**0.1 M**	**79**
8	**4**	**1.5**	**1.5**	**0.1 M**	**84**
9	**3**	**1.5**	**1.5**	**0.2 M**	**88**
10	**3**	**1.5**	**1.5**	**0.06 M**	**83**
11	**3**	**1.5**	**1.5**	**0.05 M**	**64**

[a]Reaction procedure:under an N_2 atmosphere, 0.2 mmol scale utilizing **1a** (1 equiv), **2**, **3a** and base in DMA under White LEDs panel (4000k) irradiation for 12h at rt. [b]Isolated yield.

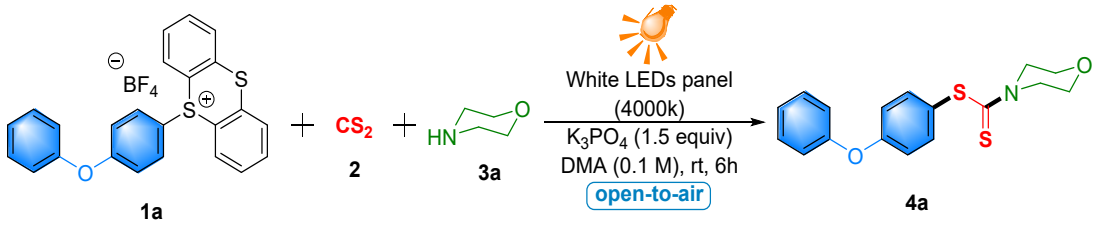
Table 5. Control experiment[a]



Entry	Variation	Yield of 4a (%)[b]
1	No Light	n.r.
2[c]	No Light	n.r.
3	No K_3PO_4	traces

[a]Reaction procedure:under an N_2 atmosphere, 0.2 mmol scale utilizing **1a** (1 equiv), **2** (1.5 equiv), **3a** (3 equiv) and K_3PO_4 (1.5 equiv) in DMA (2ml, 0.1 M) under White LEDs panel (4000k) irradiation for 12h at rt. [b]Isolated yield. [c] 60℃ instead of rt. n.r. = No reaction.

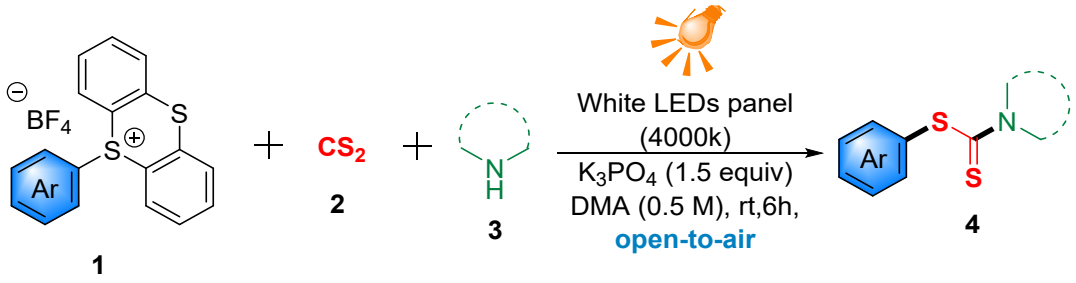
Open-to-air



Under an air atmosphere, to a 10-ml glass tube quipped with a magnetic stirring bar was charged with thianthrenium salt **1a** (0.2 mmol, 1.0 equiv), K_3PO_4 (0.3 mmol, 1.5 equiv) and DMA (Dimethylacetamide, 1.0 ml, c=0.2 M), After uniform mixing, **3a** (0.3 mmol, 1.5 equiv) and carbon disulfide (0.6 mmol, 3.0 equiv) were added to the tube and closed with a cap. Subsequently, the reaction mixture was stirred at room temperature with the irradiation of a 40 W white LEDs panel (4000k) for 12h. Upon completion, the reaction mixture was quenched with H_2O (2.0 ml), poured into a separatory funnel and extracted with EtOAc (3x20 mL). The combined organic layers were washed with saturated aqueous NaCl solution (2x30 mL). The EtOAc layer was dried over Na_2SO_4, filtered, and the solvent was removed under reduced pressure. The residue was purified by flash column chromatography on silica gel eluting with PE/EA (20:1(v/v)), then the solvent was removed in vacuo to provide the desired product **4a** (86%, 56.9 mg) as a amorphous yellow solid.

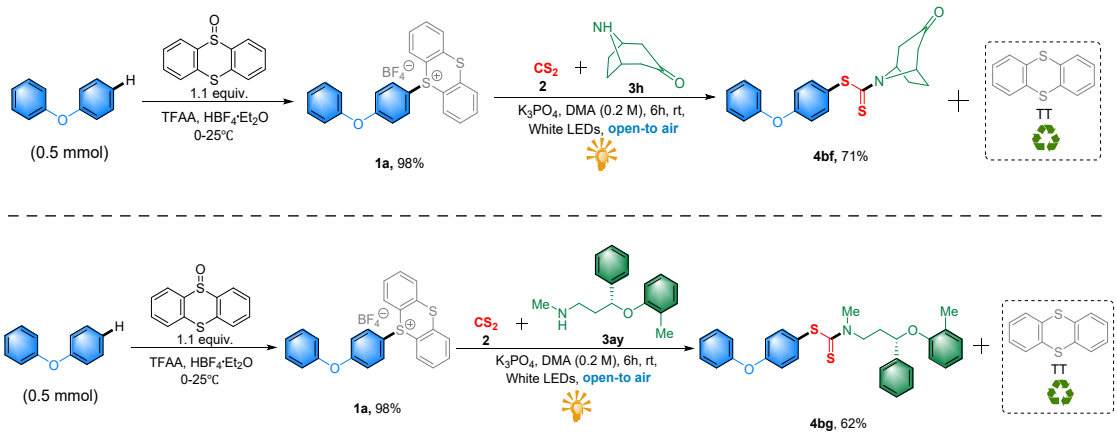
III. Synthesis synthesis of S-Aryl dithiocarbamates and synthetic applications

A. General procedure for the synthesis of S-Aryl dithiocarbamates



Under an air atmosphere, to a 10-ml glass tube quipped with a magnetic stirring bar was charged with thianthrenium salt **1** (0.2 mmol, 1.0 equiv), K_3PO_4 (0.3 mmol, 1.5 equiv) and DMA (Dimethylacetamide, 1.0 ml, c=0.2 M), After uniform mixing, **3a** (0.3 mmol, 1.5 equiv) and carbon disulfide (0.6 mmol, 3.0 equiv) were added to the tube and closed with a cap. Subsequently, the reaction mixture was stirred at room temperature with the irradiation of a 40 W white LEDs panel (4000k) for 12h. Upon completion, the reaction mixture was quenched with H_2O (10.0 ml), poured into a separatory funnel and extracted with EtOAc (3x20 mL). The combined organic layers were washed with saturated aqueous NaCl solution (2x20 mL). The EtOAc layer was dried over Na_2SO_4, filtered, and the solvent was removed under reduced pressure. The residue was purified by flash column chromatography on silica gel eluting with PE/EA, then the solvent was removed in vacuo to provide the desired products **4**.

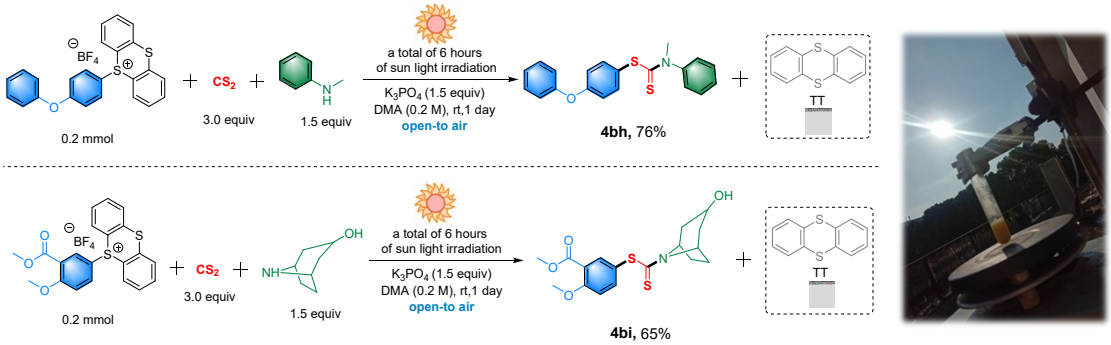
B. Two-step One-pot reactions for S-Aryl dithiocarbamates



In the air, diphenyl ether (0.5 mmol, 1.0 equiv.) and dry CH_3CN (1.0 mL) were added to a 25.0 mL round-bottom flask, and trifluoroacetic anhydride (139 μL, 1.0 mmol, 2.0 equiv.) was added at once while stirring, and the reaction solution was cooled to 0 °C. Subsequently, thianthrene S-oxide (116.0 mg, 0.5 mmol, 1.0 equiv.) and $HBF_4{\cdot}OEt_2$ (150 μL, 1.1 mmol, 2.2 equiv.) were added sequentially in one portion while stirring, and the reaction mixture was stirred at 0 °C for 1h, then warmed to room temperature and continued to stir for 5 hours. The reaction mixture was concentrated under reduced pressure, and then DMA (2.5 mL), K_3PO_4 (159.2 mg, 0.75 mmol, 1.5 equiv) **3h** (87 μL, 0.75 mmol, 1.5 equiv)/**3ay** (187 μL, 0.75 mmol, 1.5 equiv.), **CS_2** (90 μL, 1.5 mmol, 3.0 equiv) were added. The vial was sealed with PTFE cap, and the reaction was stirred and irradiated with a White LEDs (approximately 3 cm away from the light source) at room temperature (the actual reaction temperature is about 33~40 °C) for 6 h. The reaction mixture was diluted with

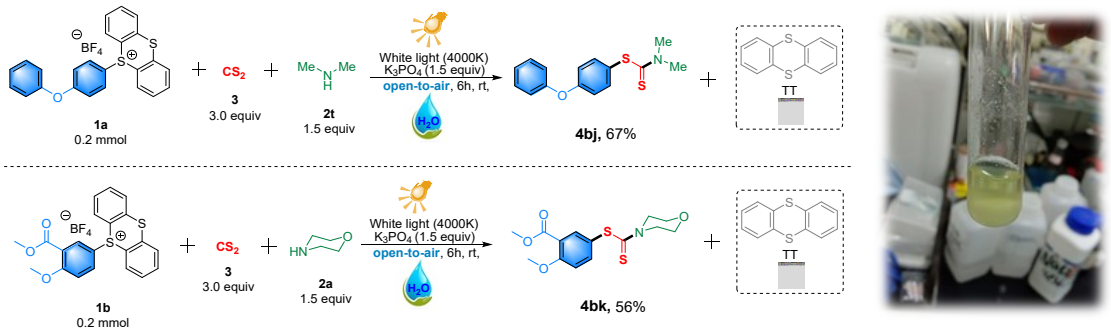
50.0 mL of ethyl acetate, followed by washing with saturated aqueous NaCl solution (3x15 mL). The ethyl acetate layer was dried over Na_2SO_4, filtered, and the solvent was removed under reduced pressure. The resulting crude product was purified by column chromatography, (eluent: PE/AcOEt) as eluent, to provide the products **4bf** and **4bg** in 71% and 62% yields, respectively.

C. Irradiation with natural sunlight



In the air, to a 10.0 mL glass tube quipped with a magnetic stirring bar was charged with thianthrenium salt **1a** (94.4 mg, 0.2 mmol)/**1b** (93.6 mg, 0.2 mmol), then 2.0 mL DMA, **CS_2** (36 μL, 0.6 mmol, 3.0 equiv.), *N*-Methylaniline **3y** (33 μL, 0.3 mmol, 1.5 equiv.)/ Nortropine **3r** (35 μL, 0.3 mmol, 1.5 equiv.), and K_3PO_4 (0.3 mmol, 1.5 equiv) were added to the tube and followed closed with a cap. Subsequently, the reaction mixture was stirred under solar light at room temperature for one day (A total of 6 hours of sunlight irradiation, Location: 31° 36′ 44″ N, 120° 44′ 06″ E). Upon completion, the reaction mixture was diluted with 20.0 mL of ethyl acetate, followed by washing with saturated aqueous NaCl solution (3x10 mL). The ethyl acetate layer was dried over Na_2SO_4, filtered, and the solvent was removed under reduced pressure. The resulting crude product was purified by column chromatography, (eluent: PE/AcOEt) as eluent, to provide the products **4bh** and **4bi** in 76% and 65% yields, respectively.

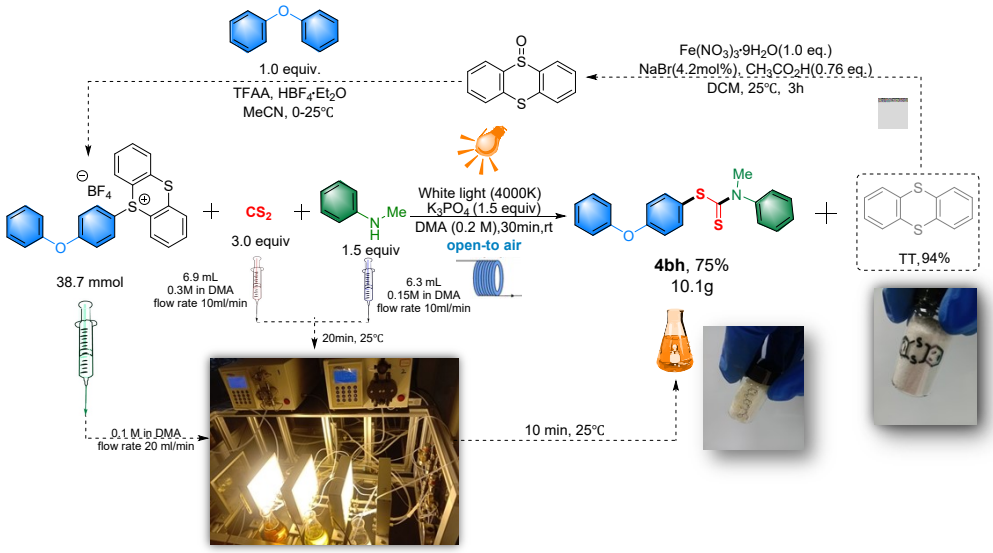
D. H_2O as the green solvent



In the air, to a 10.0 mL glass tube quipped with a magnetic stirring bar was charged with thianthrenium salt **1a** (94.4 mg, 0.2 mmol)/**1b** (93.6 mg, 0.2 mmol), then 2.0 mL H_2O, **CS_2** (36 μL, 0.6 mmol, 3.0 equiv.), dimethylamine **3t** (15 μL, 0.3 mmol, 1.5 equiv.)/Morpholine **3a** (26 μL, 0.3 mmol, 1.5 equiv.), and K_3PO_4 (63.7 mg, 0.3 mmol, 1.5 equiv) were added to the tube and followed closed with a cap. Subsequently, the reaction was stirred and irradiated with a White LEDs

(approximately 3 cm away from the light source) at room temperature (the actual reaction temperature is about 33~40 °C) for 6 h. The reaction mixture was diluted with 20.0 mL of ethyl acetate, followed by washing with saturated aqueous NaCl solution (3x10 mL). The ethyl acetate layer was dried over Na_2SO_4, filtered, and the solvent was removed under reduced pressure. The resulting crude product was purified by column chromatography, (eluent: PE/AcOEt) as eluent, to provide the products **4bj** and **4bk** in 67% and 56% yields, respectively.

E. Flow-gram scale reaction



Under an air atmosphere, the flow system adopted a two-feed microreactor consisted of a 4 mL piece of PFA tube with an internal diameter of 0.8 mm (1/16" outer diameter) and a length of 600 cm. thianthrenium salt **1a** (18.3 g, 38.7 mmol, 1.0 equiv.) was dissolved in DMA (194.0 mL) and pumped into the microreactor through the feed **2** (flow rate: 9700 μL/min), while the mixture containing **CS_2** (7.0 mL, 116.1 mmol, 3.0 equiv.) and *N*-methylaniline (8.4 mL, 77.4 mmol, 2.0 equiv.) in DMA (387.0 mL) was introduced into the microreactor through the feed **1** (flow rate: 12900 μL/min), the back pressure regulator was attached to the output line to maintain a stable system pressure of 5.0 bar. The reaction temperature was maintained at 35°C by adjusting the heat sink system, and the reaction mixture was pumped at a total flow rate of 22600 μL/min with a dwell time of 10 min at the 40W White LEDs irradiation. The reaction mixture was collected in a separate 1000.0 mL output conical flask. H_2O (120.0 mL) and EtOAc (120.0 mL) were added to the reaction mixture and stirred 5 min open-to-air, then poured at once into a 1500 mL separatory funnel and the organic phase was collected. The aqueous phase was extracted with EtOAc (2×100.0 mL). The combined organic phases were washed with brine (2×100.0 mL), dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by silica gel flash column chromatography (petroleum ether/EtOAc = 10:1) to afford compound **4bh** (10.1g, 75%) as light yellow solid.

IV. Mechanistic Investigations

A1. UV/vis studies:

UV/vis absorption spectra were measured in a 1 cm quartz cuvette using a SHIMADZU UV-3600

UV-visible spectrophotometer. Absorption spectra of individual reaction components and mixtures thereof were recorded. A bathochromic shift was observed for a mixture of thianthrenium tetrafluoroborate salt **1a**, carbon disulfide **3**, and K_3PO_4 in DMA (0.2 M), which was a visibly intense yellow in color (Figure S3**, bottle 6**). This indicates the formation of an electron donor-acceptor (EDA) complex (Figure S4, **dark grey band**).

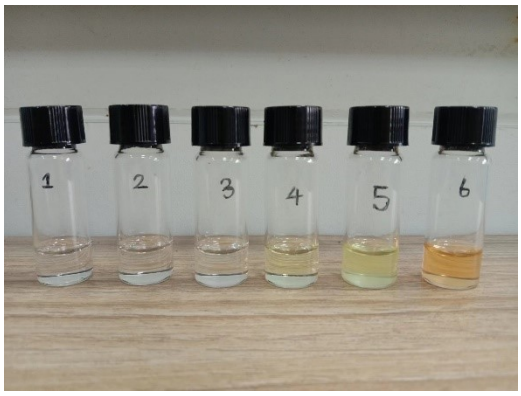


Figure S3. Visual appearance of reaction components and mixtures thereof.

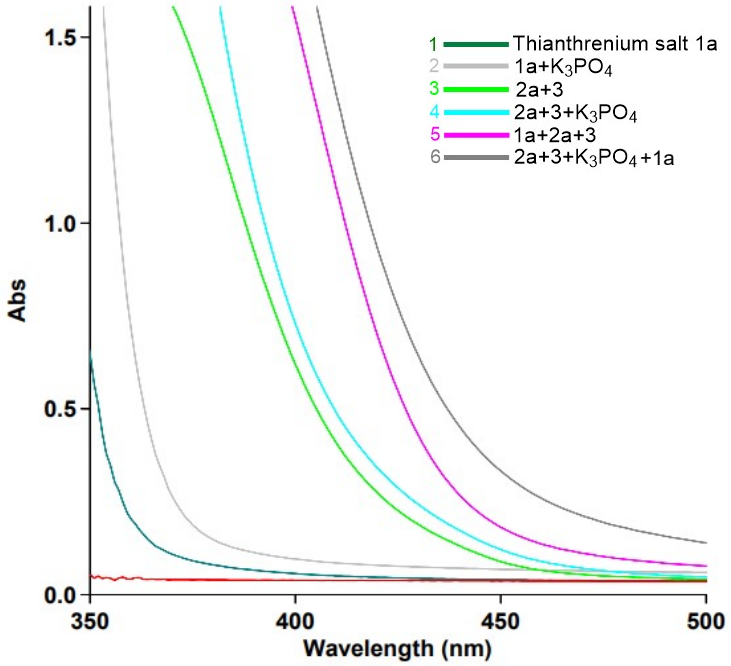


Figure S4. UV/vis absorption spectra of individual reaction components and a combination thereof. All spectra were measured in DMA and with a concentration of 0.1 M thianthrenium salt **1a**, 0.15M morpholine **2a**, 0.3M carbon disulfide **3a**, and 0.15M K_3PO_4. The stoichiometry and concentration of samples reflects the used reaction conditions.

A2. Job Plot

A Job's plot was drawn to evaluate the stoichiometry of the EDA complex (A) with thianthrenium salt **1a** and thiolate **5** (where **5** was generated through the reaction of carbon disulfide **2** and

morpholine **3a** in the presence of K_3PO_4). First, the absorption spectrum of the EDA complex was recorded using a SHIMADZU UV-3600 UV-Vis spectrophotometer in a 1 mm path quartz cuvette to find its maximum absorption wavelength at 380 nm **(Figure S5)**. Next, we measured the absorption at 380 nm of DMA solution with different donor/acceptor ratios in a constant concentration (0.10 M) of the two components. All absorbances were recorded in 96-well plates by using a Infinite M 200 PRO (TECAN, Switzerland). The absorbance values were plotted against the molar fraction (%) of thianthrenium salt **1a** and thiolate **5**. The maximum absorbance was obtained with a 1:1 mixture, indicating that it is the stoichiometry of the EDA complex in solution **(Figure S6)**, plotted as a function of molar fraction of the potassium dithiocarbamate of **5**. A parabolic curve with a maximum absorbance value at 50% mol fraction of thianthrenium salt **1a** was obtained, indicating a 1:1 EDA complex between **1a** and the conjugated base of **5**.

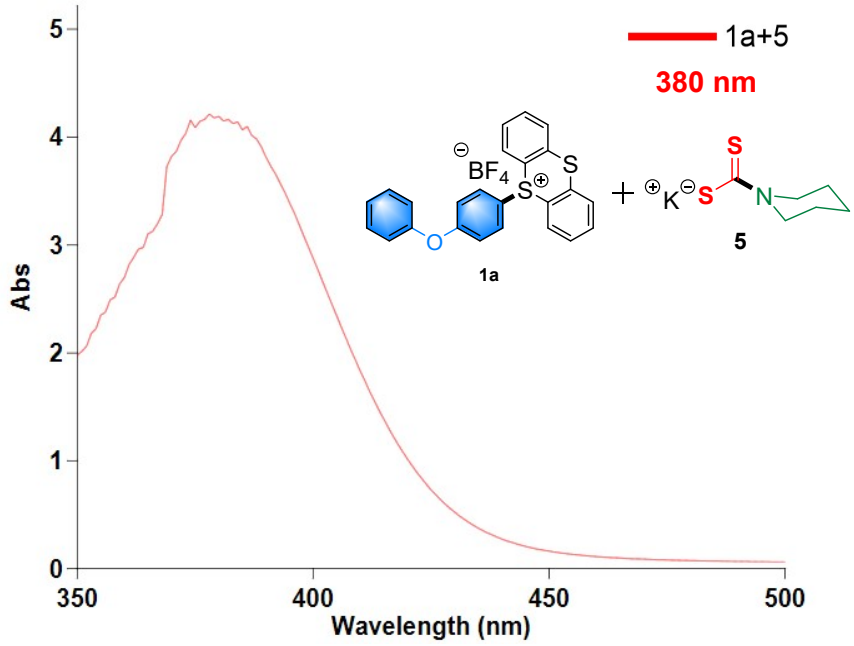


Figure S5. UV-vis Absorption Spectra of 5.

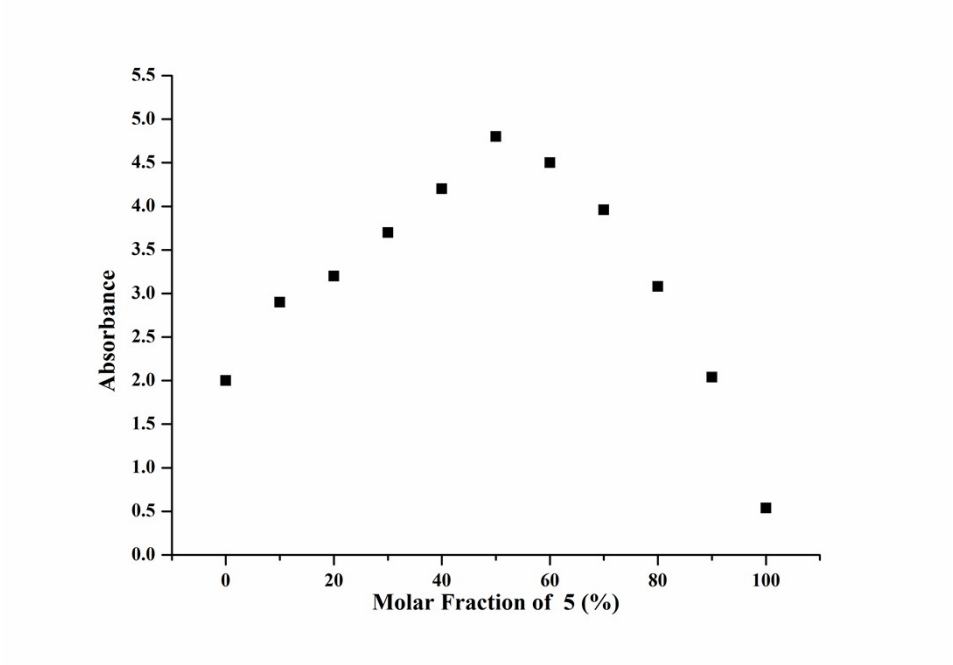


Figure S6. Job Plot of the EDA complex system between 1a and 5 at 380 nm.

A3. Benesi–Hildebrand Plot

The association constant of the EDA complex formed between thianthrenium salt **1a** and thiolate **5** were determined spectrophotometrically in DMA, by using the Hildebrand-Benesi method, and the absorbance values of five solutions containing a constant value of 0.01 M of thianthrenium salt **1a** and increasing amounts of the thiolate of **5** from 0.01 M to 0.05 M were recorded in 1mm path quartz cuvettes at 380 nm by using a SHIMADZU UV-3600 UV-visible spectrophotometer. According to the methodology, 1/ΔAbsorbance versus 1/[thiolate of **5**] were plotted and a linear relationship (**Figures S7**) was observed. The following association constants (K_{EDA}), calculated dividing the intercept by the slope, were found to be 13.6 M^{-1} for the **1a** /**5** complex.

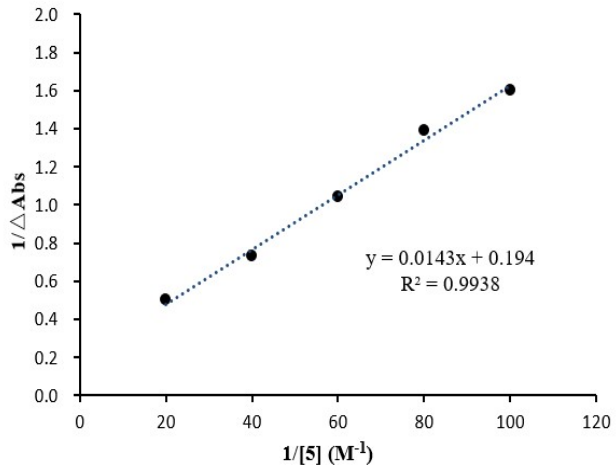


Figure S7. Benesi-Hildebrand Plot of the EDA complex system between **1a** and **5** at 380 nm

A4. Light on/off experiment

In the air, to six 10.0 mL glass tube equipped with a magnetic stirring bar were charged with thianthrenium salt **1a** (94.4 mg, 0.2 mmol), then 2.0 mL DMA, $\mathbf{CS_2}$ (36 μL, 0.6 mmol, 3.0 equiv.), morpholine **3a** (26 μL, 0.3 mmol, 1.5 equiv.), and K_3PO_4 (63.7 mg, 0.3 mmol, 1.5 equiv) were added to the tube and followed closed with a cap. Subsequently, the reaction was stirred and irradiated with a white LEDs (approximately 3 cm away from the light source) at room temperature (the actual reaction temperature is about 33~40 °C). After 2 h, the white LEDs was turned off, and one tube was removed from the irradiation setup for analysis. The remaining five tubes were stirred in the absence of light for an additional 2 h. Then, one tube was removed for analysis, and the white LEDs was turned back on to irradiate the remaining four reaction mixtures. After an additional 2h of irradiation, the white LEDs was turned off, and one tube was removed for analysis. The remaining three tubes were stirred in the absence of light for an additional 2 h. Then, a tube was removed for analysis, and the white LEDs was turned back on to irradiate the remaining two reaction mixtures. After 2 h, the white LEDs was turned off, and one tube was removed for analysis. The last tube was stirred in the absence of light for an additional 2 h, and then it was analyzed. The yields were determined by HRMS (**Figure S8**).

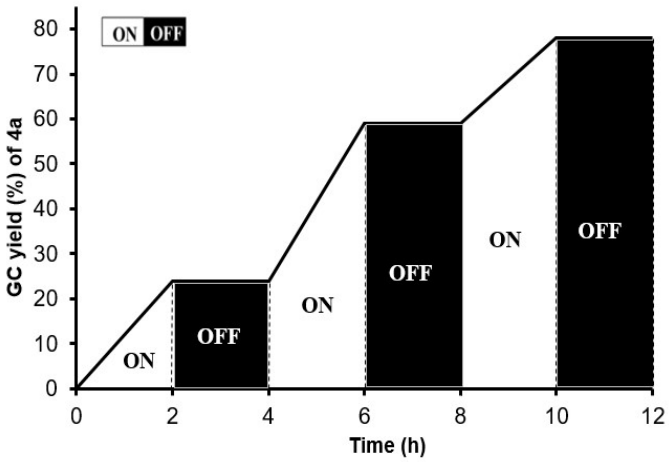
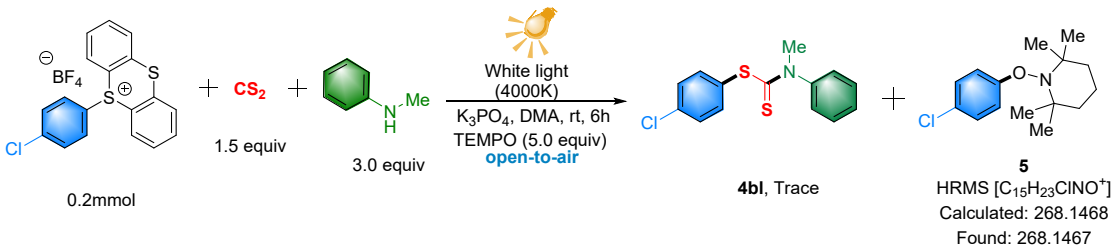


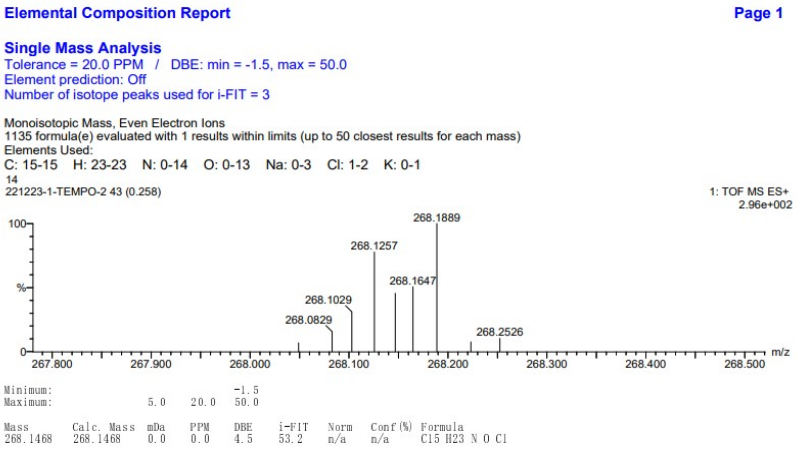
Figure S8. Light on/off experiment

B. Control Reactions

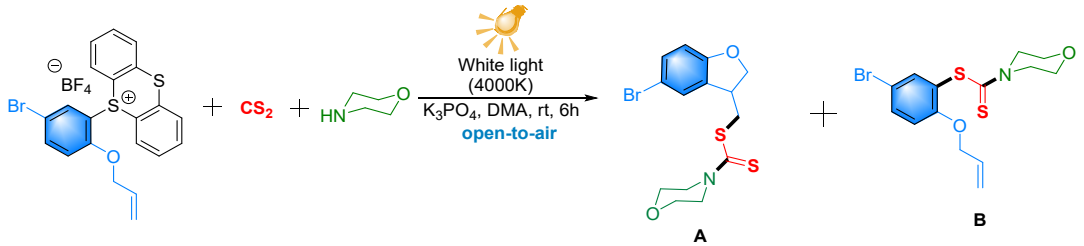
B.1 Radial inhibitors (TEMPO)



Under an air atmosphere, to a 10-ml glass tube quipped with a magnetic stirring bar was charged with thianthrenium salt **1n** (0.2 mmol, 1.0 equiv), TEMPO (156.3 mg, 1.0 mmol, 5.0 equiv), K_3PO_4 (52.3 mg, 0.6 mmol, 1.5 equiv) and DMA (Dimethylacetamide, 1.0 mL, C=0.2 M), After uniform mixing, **3a** (33 μL, 0.3 mmol, 1.5 equiv) and **CS_2** (36 μL, 0.6 mmol, 3.0 equiv) were added to the tube and closed with a cap. Subsequently, the reaction mixture was stirred at room temperature with the irradiation of a 40 W White LEDs panel (4000k) for 6 h, only trace amounts of **4bl** was observed and the radical trapping product **5** was detected by HRMS.



B.2 Radical clock experiment



In the air, to a 10.0 mL glass tube quipped with a magnetic stirring bar was charged with thianthrenium salt **1q** (102.8 mg, 0.2 mmol) and K_3PO_4 (63.7 mg, 0.3 mmol, 1.5 equiv), then 2.0 mL DMA, **CS_2** (36 µL, 0.6 mmol, 3.0 equiv.), and morpholine **3a** (26 µL, 0.3 mmol, 1.5 equiv.) were added to the tube and followed closed with a cap. Subsequently, the reaction was stirred and irradiated with a White LEDs (approximately 3 cm away from the light source) at room temperature (the actual reaction temperature is about 33~40 °C) for 6 h. The reaction mixture was diluted with

20.0 mL of ethyl acetate, followed by washing with saturated aqueous NaCl solution (3x10 mL). The ethyl acetate layer was dried over Na_2SO_4, filtered, and the solvent was removed under reduced pressure. The resulting crude product was purified by column chromatography, (eluent: PE/AcOEt=8:1) as eluent, to provide the mixture products of **A** and **B** in 67% yield, and the ratio of **B** to **A** was found to be 2:1 from the **^{1}HNMR** spectra. In addition, the cyclized product **A** was observed by HRMS.

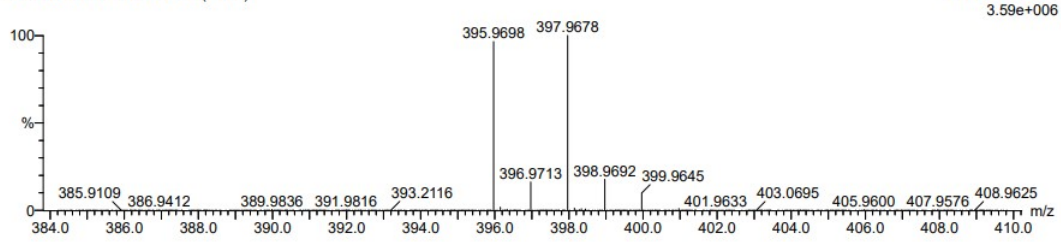
Elemental Composition Report **Page 1**

Single Mass Analysis
Tolerance = 20.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

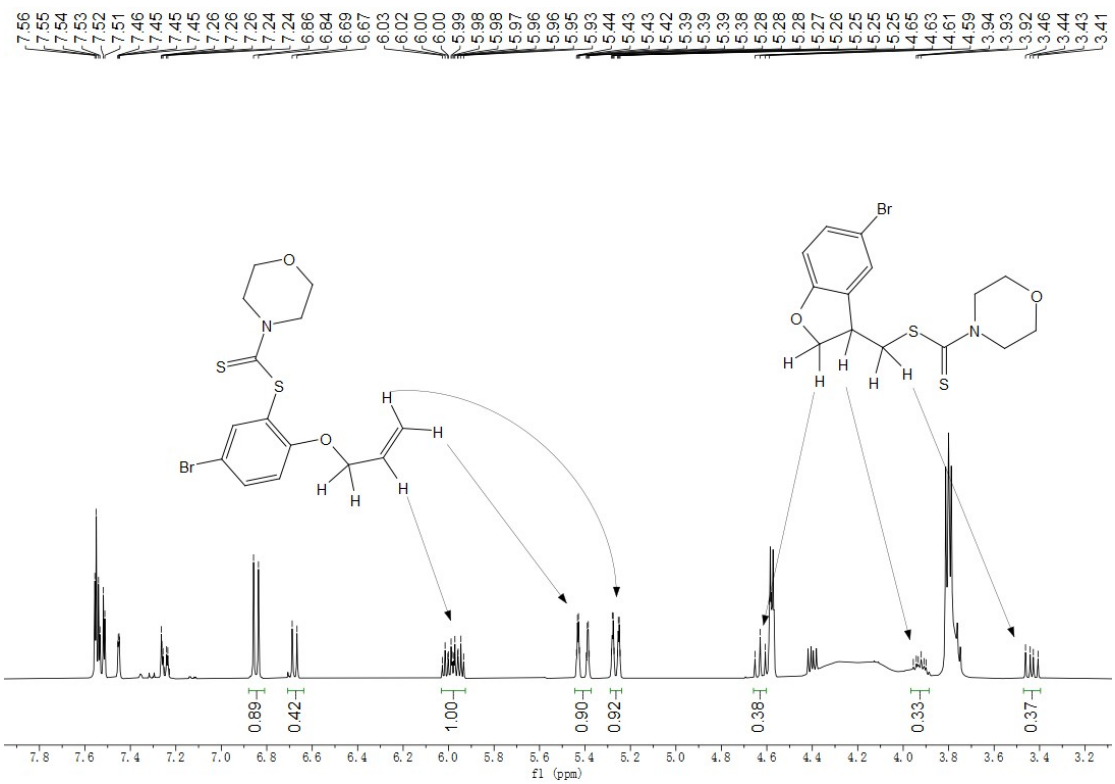
Monoisotopic Mass, Even Electron Ions
2020 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)
Elements Used:
C: 14-14 H: 16-16 N: 0-14 O: 0-13 Na: 0-3 S: 2-3 K: 0-1 Br: 1-5

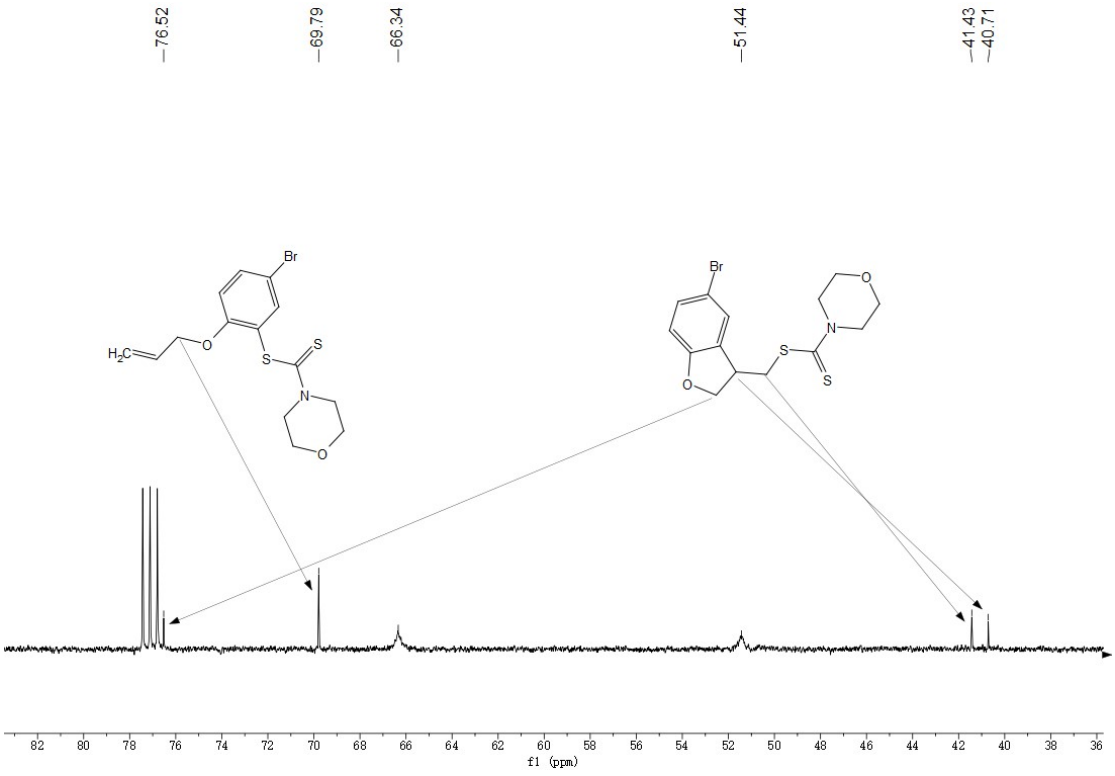
14
221223-1-hunhuachanwu 14 (0.098)

1: TOF MS ES+
3.59e+006

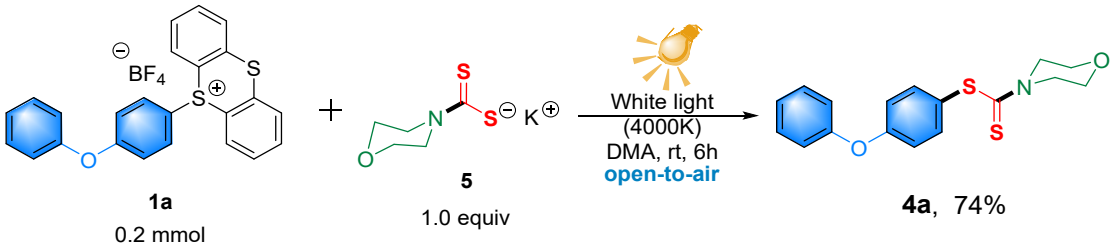


Minimum:				-1.5				
Maximum:		5.0	20.0	50.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
395.9698	395.9704	-0.6	-1.5	6.5	626.4	n/a	n/a	C14 H16 N 02 Na S2 Br



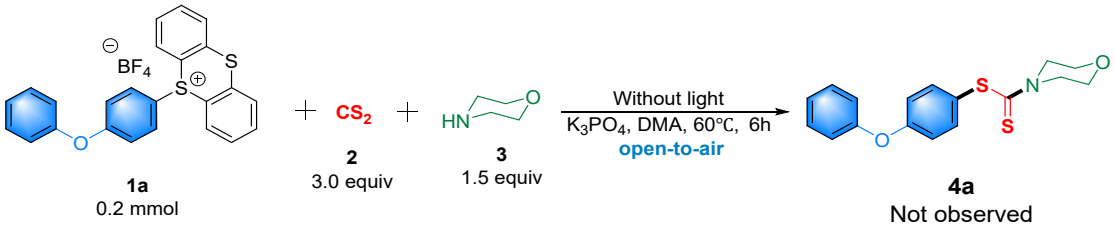


B.3 7 was chosen as the coupling partner with thianthrenium salt 1a.



In the air, to a 10.0 mL glass tube quipped with a magnetic stirring bar was charged with thianthrenium salt **1a** (94.4 mg, 0.2 mmol) and DMA (2.0 mL), then **5** (40.2 mg, 0.2 mmol, 1.0 equiv.) was added to the tube and followed closed with a cap. Subsequently, the reaction was stirred and irradiated with a 40 W white LEDs (approximately 3 cm away from the light source) at room temperature (the actual reaction temperature is about 33~40 °C) for 6 h. The reaction mixture was diluted with 20.0 mL of ethyl acetate, followed by washing with saturated aqueous NaCl solution (3x10 mL). The ethyl acetate layer was dried over Na_2SO_4, filtered, and the solvent was removed under reduced pressure. The resulting crude product was purified by column chromatography, (eluent: PE/AcOEt=8:1) as eluent, to to afford compound **4a** in 74% yield as light yellow oil.

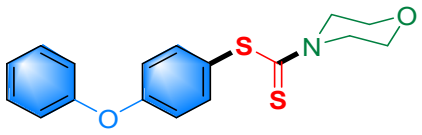
B.4 Without light and 60 ℃ conditions.



In the air, to a 10.0 mL glass tube quipped with a magnetic stirring bar was charged with thianthrenium salt **1a** (94.4 mg, 0.2 mmol) and K_3PO_4 (63.7 mg, 0.3 mmol, 1.5 equiv), then 2.0 mL DMA, **CS_2** (36 μL, 0.6 mmol, 3.0 equiv.), and morpholine **3a** (26 μL, 0.3 mmol, 1.5 equiv.) were added to the tube and followed closed with a cap. Subsequently, the reaction was stirred and irradiated under dark at 60℃ for 6 h and monitored by TLC. The reaction failed to provide the desired product **4a**.

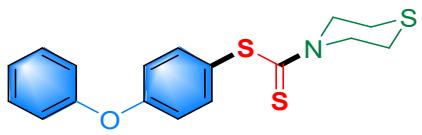
V. Characterization of the Target Products

4-phenoxyphenyl morpholine-4-carbodithioate (4a)



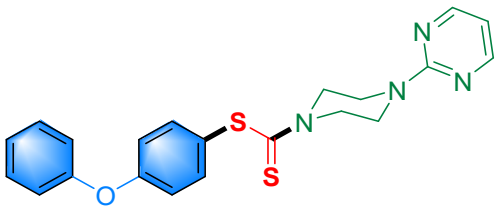
Following general procedure, thianthrenium salt **1a** (95.0 mg, 0.2 mmol), **CS_2** (36 μL, 0.6 mmol, 3.0 equiv.) and morpholine **3a** (27 μL, 0.3 mmol, 1.5 equiv.) were used to afford the desired product **4a**.
56.9 mg, yield 86%. Light yellow oil.
R_f=0.32 (eluent petroleum ether/ ethyl acetate =8:1, v/v).
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.43 – 7.38 (m, 4H), 7.16 (t, *J* = 2.0 Hz, 1H), 7.14 – 7.09 (d, *J* = 2.0 Hz, 2H), 7.07 – 7.03 (m, 2H), 4.34 – 3.96 (m, 4H), 3.83 (t, *J* = 7.4 Hz, 4H).
^{13}C NMR (101 MHz, Chloroform-*d*) δ 198.5, 159.6, 155.8, 138.7, 129.9, 124.2, 124.0, 120.0, 118.5, 66.3, 51.2 (d, *J* = 74.7 Hz).
HRMS-ESI (m/z) [M+H] $^+$ calculated for $C_{17}H_{18}NO_2S_2^+$ 332.0779, found 332.0786.

4-phenoxyphenyl thiomorpholine-4-carbodithioate (4b)



Following general procedure, thianthrenium salts **1a** (94.4 mg, 0.2 mmol), **CS_2** (36 *uL*, 0.6 mmol, 3.0 equiv.) and thiomorpholine **3b** (30 *uL*, 3.0 mmol, 1.5 equiv.) were used to afford the desired product **4b.**
51.4 mg, yield 74%. Yellow solid.
R_f= 0.36 (eluent petroleum ether/ethyl acetate =8:1, v/v).
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.40 -7.35 (m, 4H), 7.17 (t, *J* = 7.4 Hz, 1H), 7.10 (d, *J* = 8.0 Hz, 2H), 7.03 (d, *J* = 8.4 Hz, 2H), 4.49 (d, *J* = 80.3 Hz, 4H), 2.81 (t, *J* = 5.1 Hz, 4H).
^{13}C NMR (101 MHz, Chloroform-*d*) δ 197.9, 159.7, 155.9, 138.8, 130.0 124.3, 124.2, 120.1, 118.5, 54.3 (d, *J* = 129.3 Hz), 27.3 (d, *J* = 28.3 Hz).
HRMS-ESI (m/z) [M+Na] $^+$ calculated for $C_{17}H_{17}NNaOS_3^+$ 370.0370, found 370.0372.

4-phenoxyphenyl 4-(pyrimidin-2-yl)piperazine-1-carbodithioate (4c)



Following general procedure, thianthrenium salt **1a** (94.4 mg, 0.2 mmol), **CS_2** (36 μL, 0.6 mmol, 3.0 equiv.) and 2-(piperazin-1-yl)pyrimidine **3** (43 μL, 0.3 mmol, 1.5 equiv.) were used to afford the desired product **4c**.

68.6 mg, yield 84%. Yellow solid.

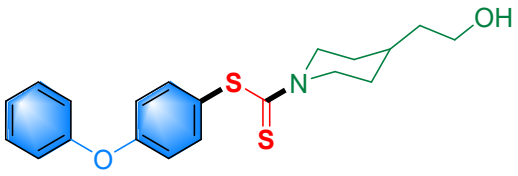
R_f=0.30 (eluent petroleum ether/ ethyl acetate =8:1, v/v).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.28 (d, *J* = 4.8 Hz, 2H), 7.38 – 7.24 (m, 4H), 7.09 (t, *J* = 7.4 Hz, 1H), 7.02 (d, *J* = 8.0 Hz, 2H), 6.95 (d, *J* = 8.7 Hz, 2H), 6.51 (t, *J* = 4.8 Hz, 1H), 4.22 (d, *J* = 97.3 Hz, 4H), 3.93 (s, 4H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 198.3, 161.2, 159.6, 157.9, 155.9, 138.7, 130.0, 124.3, 124.2, 120.1, 118.5, 110.8, 43.0.

HRMS-ESI (m/z) $[M+H]^+$ calculated for $C_{21}H_{21}N_4OS_2^+$ 409.1157, found 409.1162.

4-phenoxyphenyl 4-(2-hydroxyethyl)piperidine-1-carbodithioate (4d)



Following general procedure, thianthrenium salt **1a** (95.0 mg, 0.2 mmol), **CS_2** (36 μL, 0.6 mmol, 3.0 equiv.) and 2-(piperidin-4-yl)ethan-1-ol **3** (39 μL, 0.3 mmol, 1.5 equiv.) were used to afford the desired product **4d**.

43.3 mg, yield 58%. Light yellow solid.

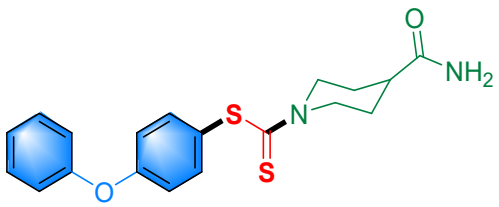
R_f=0.32 (eluent petroleum ether/ ethyl acetate =8:1, v/v).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.41 – 7.36 (m, 4H), 7.16 (t, *J* = 7.3 Hz, 1H), 7.09 (d, *J* = 8.0 Hz, 2H), 7.02 (d, *J* = 8.6 Hz, 2H), 5.55 (s, 1H), 4.76 (s, 1H), 3.55 (d, *J* = 5.8 Hz, 2H), 3.22 (d, *J* = 72.2 Hz, 2H), 1.95 – 1.86 (m, 3H), 1.65 (s, 2H), 1.47 – 1.37 (m, 2H), 1.25 (s, 1H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 197.0, 159.5, 156.0, 138.8, 130.0, 124.8, 124.2, 120.0, 118.5, 66.9, 51.4 (d, *J* = 156.6 Hz), 38.5, 29.7, 28.5(d, *J* = 79.8 Hz).

HRMS-ESI (m/z) $[M+H]^+$ calculated for $C_{20}H_{24}NO_2S_2^+$ 374.1248, found 374.1241.

4-phenoxyphenyl 4-carbamoylpiperidine-1-carbodithioate (4e)



Following general procedure, thianthrenium salt **1a** (94.4 mg, 0.2 mmol), carbon disulfide (36 μL, 0.6

mmol, 3.0 equiv.) and piperidine-4-carboxamide (38.5mg, 0.3 mmol, 1.5 equiv.) were used to afford the desired product **4e**.

69.9 mg, 74%. Yellow solid.

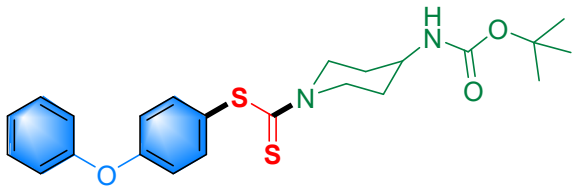
R_f=0.28 (petroleum ether/ethyl acetate =1:1 (v:v))

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.38 (t, *J* = 7.8 Hz, 4H), 7.17 (t, *J* = 7.4 Hz, 1H), 7.09 (d, *J* = 8.0 Hz, 2H), 7.02 (d, *J* = 8.4 Hz, 2H), 5.77 (d, *J* = 93.2 Hz, 2H), 5.03 (d, *J* = 263.3 Hz, 2H), 3.42 (s, 2H), 2.59 – 2.52 (m, 1H), 2.04 – 1.89 (m, 4H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 197.6, 176.0, 159.5, 155.9, 138.8, 130.0, 124.5, 124.3, 120.1, 118.5, 50.6 (d, *J* = 143.4 Hz), 41.7, 28.43.

HRMS-ESI (m/z) $[M+Na]^+$ calculated for $C_{19}H_{20}N_2NaO_2S_2^+$ 395.0864, found 395.0859.

4-phenoxyphenyl 4-((tert-butoxycarbonyl)amino)piperidine-1-carbodithioate (4f)



Following general procedure, thianthrenium salts **1a** (94.4 mg, 0.2 mmol), CS_2 (36 *uL*, 0.6 mmol, 3.0 equiv.) and tert-butyl piperidin-4-ylcarbamate (60.1mg, 3.0 mmol, 1.5 equiv.) were used to afford the desired product **4f.**

72.8 mg, yield 82%. Yellow solid.

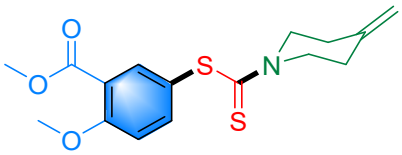
R_f= 0.32 (eluent petroleum ether/ethyl acetate =3:1, v/v).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.40 – 7.35 (m, 4H), 7.17 (t, *J* = 8.0 Hz, 1H), 7.09 (d, *J* = 7.5 Hz, 2H), 7.02 (d, *J* = 8.7 Hz, 2H), 5.36 (s, 1H), 4.56 (d, *J* = 54.0 Hz, 2H), 3.82 (s, 1H), 3.39 (s, 2H), 2.10 (s, 2H), 1.61 – 1.49 (m, 2H), 1.46 (s, 9H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 197.6, 159.5, 155.9, 155.1, 138.7, 129.9, 124.6, 124.2, 120.0, 118.4, 79.8, 50.0 (d, *J* = 54.0 Hz), 47.5, 32.1 (d, *J* = 67.7 Hz), 28.4.

HRMS-ESI (m/z) $[M+Na]^+$ calculated for $C_{23}H_{28}N_2NaO_3S_2^+$ 467.1439, found 467.1434.

Methyl 2-methoxy-5-((4-methylenepiperidine-1-carbonothioyl)thio)benzoate (4g)



Following general procedure, thianthrenium salt **1b** (90.4 mg, 0.2 mmol), **CS_2** (36 *μL*, 0.6 mmol, 3.0 equiv.) and 4-methylenepiperidine **3** (34 *μL*, 0.3 mmol, 1.5 equiv.) were used to afford the desired product **4g**.

46.5 mg, yield 69%. Yellow solid.

R_f=0.34 (eluent petroleum ether/ ethyl acetate =10:1, v/v).

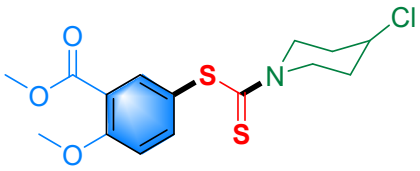
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.85 (d, *J* = 2.4 Hz, 1H), 7.49 (dd, *J* = 8.7, 2.4 Hz, 1H), 6.98 (d, *J*

= 8.7 Hz, 1H), 4.81 (s, 2H), 4.11 (d, *J* = 113.1 Hz, 4H), 3.89 (s, 3H), 3.80 (s, 3H), 2.34 (s, 4H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 196.9, 165.6, 160.7, 143.0, 142.6, 140.6, 122.3, 120.5, 112.7, 110.8, 56.7, 52.8 (d, *J* = 189.9 Hz), 52.1, 34.0 (d, *J* = 73.7 Hz).

HRMS-ESI (m/z) [M+Na] $^{+}$ calculated for $C_{16}H_{19}NNaO_3S_2^{+}$ 360.0704, found 360.0706.

Methyl 5-((4-chloropiperidine-1-carbonothioyl)thio)-2-methoxybenzoate (4h)



Following general procedure, thianthrenium salt **1b** (93.6 mg, 0.2 mmol), **CS_2** (36 *μL*, 0.6 mmol, 3.0 equiv.) and 4-chloropiperidine **3** (33 *μL*, 0.3 mmol, 1.5 equiv.) were used to afford the desired product **4h**.

53.9 mg, yield 75%. Yellow solid.

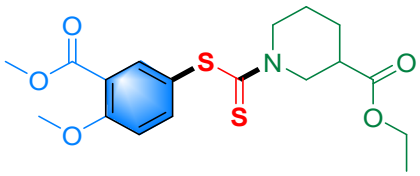
R_f=0.32 (eluent petroleum ether/ ethyl acetate =10:1, v/v).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.90 (d, *J* = 2.4 Hz, 1H), 7.55 (dd, *J* = 8.7, 2.4 Hz, 1H), 7.05 (d, *J* = 8.7 Hz, 1H), 4.85 – 4.50 (m, 1H), 4.44 – 4.39 (m, 1H), 4.34 – 4.11 (m, 3H), 3.96 (s, 3H), 3.88 (s, 3H), 2.23 (s, 2H), 2.04 (s, 2H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 197.4, 165.6, 160.8, 142.6, 140.6, 122.1, 120.6, 112.7, 56.2, 55.7, 52.1.

HRMS-ESI (m/z) [M+Na]$^{+}$ calculated for $C_{15}H_{18}ClNNaO_3S_2^{+}$ 382.0314, found 382.0309.

Ethyl-1-(((4-methoxy-3-(methoxycarbonyl)phenyl)thio)carbonothioyl)piperidine-3-carboxylate (4i)



Following general procedure, thianthrenium salt **1b** (93.6 mg, 0.2 mmol), **CS_2** (36 *μL*, 0.6 mmol) and ethyl piperidine-3-carboxylate (47 *μL*, 0.3 mmol) were used to afford the desired product **4i**.

54.0 mg, yield 68%. Yellow solid.

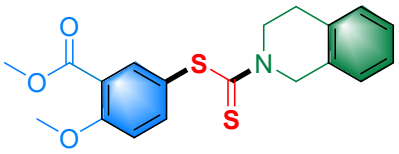
R_f=0.32 (petroleum ether/ethyl acetate =6:1 (v:v))

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.90 (d, *J* = 2.3 Hz, 1H), 7.55 (dd, *J* = 8.7, 2.4 Hz, 1H), 7.05 (d, *J* = 8.7 Hz, 1H), 5.37 (d, *J* = 122.8 Hz, 1H), 4.67 (d, *J* = 53.4 Hz, 1H), 4.18 (s, 2H), 3.96 (s, 3H), 3.87 (s, 3H), 3.46 (d, *J* = 83.5 Hz, 2H), 2.72 – 2.65 (m, 1H), 2.19 (dd, *J* = 13.1, 3.8 Hz, 1H), 1.90 – 1.67 (m, 3H), 1.28 (t, *J* = 8.0 Hz, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 197.5, 172.5, 165.6, 160.8, 142.6, 140.6, 122.2, 120.6, 112.7, 61.0, 56.2, 52.3, 52.1, 41.1, 29.7, 27.4, 24.2, 14.2.

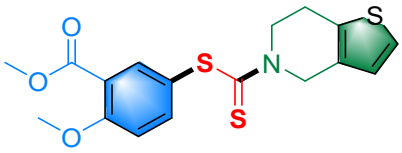
HRMS-ESI (m/z) $[M+Na]^+$ calculated for $C_{18}H_{23}NNaO_5S_2^+$ 420.0915, found 420.0918.

Methyl-2-methoxy-5-((1,2,3,4-tetrahydroisoquinoline-2- carbonothioyl)thio) Benzoate (4j)



Following general procedure, thianthrenium salt **1b** (93.6 mg, 0.2 mmol), carbon disulfide (36 uL, 0.6 mmol) and 1,2,3,4-tetrahydroisoquinoline (38 uL, 0.3 mmol) were used to afford the desired product **4j**.
59.8 mg, yield 83%. Yellow solid.
R_f=0.46 (petroleum ether/ethyl acetate =5:1 (v:v))
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.93 (d, *J* = 2.4 Hz, 1H), 7.57 (dd, *J* = 8.7, 2.4 Hz, 1H), 7.22 (dd, *J* = 9.0, 3.9 Hz, 4H), 7.06 (d, *J* = 8.7 Hz, 1H), 5.22 (d, *J* = 72.9 Hz, 2H), 4.31 (dt, *J* = 99.4, 5.8 Hz, 2H), 3.96 (s, 3H), 3.87 (s, 3H), 3.08 – 3.01 (m, 2H).
^{13}C NMR (101 MHz, Chloroform-*d*) δ 197.1, 165.5, 160.8, 142.6, 140.7, 134.7 (d, *J* = 96.0 Hz), 132.2 (d, *J* = 123.2 Hz), 128.1 (d, *J* = 60.1 Hz), 127.4 (d, *J* = 33.3 Hz), 126.9 (d, *J* = 16.2 Hz), 126.5 (d, *J* = 47.5 Hz), 121.8, 120.6, 112.7, 56.2, 52.1, 51.4 (d, *J* = 588.8 Hz), 51.2 (d, *J* = 134.3 Hz), 28.9 (d, *J* = 71.7 Hz).
HRMS-ESI (m/z) $[M+Na]^+$ calculated for $C_{19}H_{19}NNaO_3S_2^+$ 396.0704, found 396.0706.

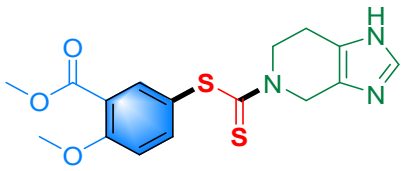
Methyl-2-methoxy-5-((4,5,6,7-tetrahydrothieno[3,2-c]pyridine-5-carbonothioyl)thio)benzoate (4k)



Following general procedure, thianthrenium salt **1b** (93.6 mg, 0.2 mmol), carbon disulfide (36 uL, 0.6 mmol) and 4,5,6,7-tetrahydrothieno[3,2-c]pyridine (52.7 mg, 0.3 mmol) were used to afford the desired product **4k**.
50.0 mg, yield 66%. Yellow solid.
R_f=0.40 (petroleum ether/ethyl acetate =5:1 (v:v))
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.93 (d, *J* = 2.4 Hz, 1H), 7.57 (dd, *J* = 8.7, 2.4 Hz, 1H), 7.19 (s, 1H), 7.06 (d, *J* = 8.7 Hz, 1H), 6.83 (s, 1H), 5.21 (d, *J* = 85.7 Hz, 2H), 4.49 (d, *J* = 123.3 Hz, 2H), 3.96 (s, 3H), 3.87 (s, 3H), 3.06 (d, *J* = 26.7 Hz, 2H).
^{13}C NMR (101 MHz, Chloroform-*d*) δ 198.9, 166.6, 161.9, 143.7, 141.7, 133.0, 131.2, 126.0, 125.4, 122.8, 121.6, 113.8, 57.2, 53.2, 51.3 (d, *J* = 26.3 Hz), 49.9, 25.9 (d, *J* = 88.9 Hz).
HRMS-ESI (m/z) $[M+Na]^+$ calculated for $C_{17}H_{17}NNaO_3S_3$ 402.0268, found 402.0266.

Methyl-2-methoxy-5-((4,5,6,7-tetrahydro-1H-imidazo[4,5-c]pyridine-5-

carbonothioyl)thio)benzoate (4l)



Following general procedure, thianthrenium salt **1b** (93.6 mg, 0.2 mmol), carbon disulfide (36 uL, 0.6 mmol, 3.0 equiv.) and 4,5,6,7-tetrahydro-1H-imidazo[4,5-c]pyridine (47.9 mg, 0.3 mmol, 1.5 equiv) were used to afford the desired product **4l**.

40.7 mg, yield 56%. Yellow solid.

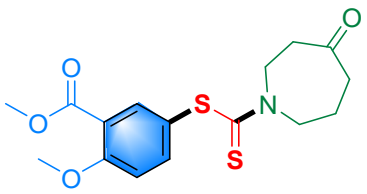
R_f=0.38 (dichloromethane/ methanol =30:1 (v:v))

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.90 (d, *J* = 2.4 Hz, 1H), 7.61 (s, 1H), 7.57 – 7.49 (m, 2H), 7.04 (d, *J* = 8.8 Hz, 1H), 5.20 (d, *J* = 91.3 Hz, 2H), 4.48 (d, *J* = 119.8 Hz, 2H), 3.94 (s, 3H), 3.86 (s, 3H), 2.91 (d, *J* = 36.2 Hz, 2H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 198.9 (d, *J* = 53.5 Hz), 165.7, 160.7, 142.6, 140.6, 137.5, 135.6, 134.7, 121.9, 120.4, 112.8, 56.2, 52.2, 49.8 (d, *J* = 76.8 Hz), 29.9 (d, *J* = 49.5 Hz), 22.1 (d, *J* = 167.0 Hz).

HRMS-ESI (m/z) $[M+Na]^+$ calculated for $C_{20}H_{17}N_3NaO_3S_2$ 386.0609, found 386.0611.

Methyl 2-methoxy-5-((4-oxoazepane-1-carbonothioyl)thio)benzoate (4m)



Following general procedure, thianthrenium salts **1b** (93.6 mg, 0.2 mmol), **CS_2** (36 *uL*, 0.6 mmol, 3.0 equiv.) and azepan-4-one (35 *uL*, 0.3 mmol, 1.5 equiv.) were used to afford the desired product **4m.**

50.8 mg, yield 72%. Yellow solid.

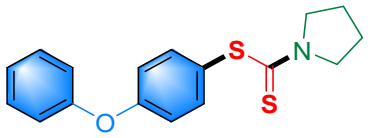
R_f= 0.34 (eluent petroleum ether/ethyl acetate =6:1, v/v).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.82 (d, *J* = 2.5 Hz, 1H), 7.47 (dd, *J* = 8.7, 2.4 Hz, 1H), 6.98 (d, *J* = 8.8 Hz, 1H), 4.34 – 4.31 (m, 2H), 4.20 – 4.11 (m, 2H), 3.89 (s, 3H), 3.81 (s, 3H), 2.85 – 2.78 (m, 2H), 2.74 – 2.67 (m, 2H), 2.03 – 1.86 (m, 2H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 210.1, 197.3, 165.5, 160.9, 142.6, 140.6, 121.7, 120.6, 112.8, 56.2, 55.4, 52.2, 51.6, 43.1, 40.5, 25.1.

HRMS-ESI (m/z) $[M+Na]^+$ calculated for $C_{16}H_{19}NNaO_4S_2^+$ 376.0653, found 376.0648.

4-phenoxyphenyl pyrrolidine-1-carbodithioate (4n)



Following general procedure, thianthrenium salts **1a** (94.4 mg, 0.2 mmol), **CS_2** (36 *uL*, 0.6 mmol, 3.0 equiv.) and thiomorpholine (25 *uL*, 0.3 mmol, 1.5 equiv.) were used to afford the desired product **4n.**

52.9 mg, yield 84%. Yellow solid.

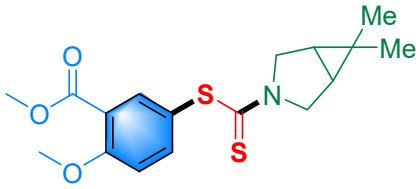
R_f= 0.36 (eluent petroleum ether/ethyl acetate =8:1, v/v).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.44 – 7.33 (m, 4H), 7.16 (t, *J* = 7.4 Hz, 1H), 7.09 (d, *J* = 7.9 Hz, 2H), 7.04 – 6.99 (m, 2H), 3.94 (t, *J* = 1.5 Hz, 2H), 3.79 (t, *J* = 2.0 Hz, 2H), 2.17 – 2.10 (m, 2H), 2.04 – 1.97 (m, 2H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 193.5, 159.4, 155.9, 138.5, 129.9, 124.4, 124.2, 120.0, 118.4, 55.4, 51.0, 26.3, 24.4.

HRMS-ESI (m/z) $[M+Na]^+$ calculated for $C_{17}H_{17}NNaOS_2^+$ 338.0649, found 338.0651.

Methyl 5-((6,6-dimethyl-3-azabicyclo[3.1.0]hexane-3-carbonothioyl)thio)-2-methoxybenzoate (4o)



Following general procedure, thianthrenium salts **1b** (93.6 mg, 0.2 mmol), **CS_2** (36 *uL*, 0.6 mmol, 3.0 equiv.) and 6,6-dimethyl-3-azabicyclo[3.1.0]hexane (37 *uL*, 0.3 mmol, 1.5 equiv.) were used to afford the desired product **4o.**

54.8 mg, yield 78%. Yellow solid.

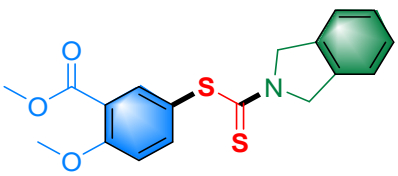
R_f= 0.34 (eluent petroleum ether/ethyl acetate =8:1, v/v).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.83 (d, *J* = 2.4 Hz, 1H), 7.48 (dd, *J* = 8.7, 2.4 Hz, 1H), 6.96 (d, *J* = 8.7 Hz, 1H), 3.88 – 3.93 (m, 2H), 3.87 (s, 3H), 3.79 (s, 3H), 3.83 – 3.75 (m, 2H), 1.56-1.52 (m,1H), 1.48-1.42 (m, 1H), 1.02 (s, 3H), 0.88 (s, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 192.3, 165.6, 160.7, 142.4, 140.4, 121.9, 120.5, 112.6, 56.2, 55.6, 52.1, 50.8, 28.3, 26.5, 26.0, 19.6, 12.7.

HRMS-ESI (m/z) $[M+Na]^+$ calculated for $C_{17}H_{21}NNaO_3S_2^+$ 374.0861, found 374.0859.

Methyl 5-((isoindoline-2-carbonothioyl)thio)-2-methoxybenzoate (4p)



Following general procedure, thianthrenium salts **1b** (93.6 mg, 0.2 mmol), **CS_2** (36 *uL*, 0.6 mmol, 3.0 equiv.) and isoindoline (34 *uL*, 0.3 mmol, 1.5 equiv.) were used to afford the desired product **4p**.

54.6 mg, 76%. Yellow solid.

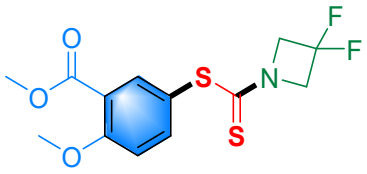
R_f=0.34 (petroleum ether/ethyl acetate =9:1 (v:v))

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.98 (d, *J* = 2.4 Hz, 1H), 7.63 (d, *J* = 8.9 Hz, 1H), 7.34 (d, *J* = 3.5 Hz, 4H), 7.08 (d, *J* = 8.7 Hz, 1H), 5.22 (s, 2H), 5.14 (s, 2H), 3.98 (s, 3H), 3.88 (s, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 194.3, 165.5, 160.9, 142.4, 140.4, 135.3, 135.1, 128.2, 128.0, 122.8, 122.8, 121.7, 120.7, 112.8, 60.9, 56.2, 56.1, 52.1.

HRMS-ESI (m/z) $[M+H]^+$ calculated for $C_{18}H_{18}NO_3S_2^+$ 360.0728, found 360.0735.

Methyl 5-((3,3-difluoroazetidine-1-carbonothioyl)thio)-2-methoxybenzoate (4q)



Following general procedure, thianthrenium salt **1b** (93.6 mg, 0.2 mmol), **CS_2** (36 *uL*, 0.6 mmol, 3.0 equiv.) and 3,3-difluoroacridine (25 *uL*, 0.3 mmol, 1.5 equiv.) were used to afford the desired product **4q**.

38.0 mg, 57%. Yellow solid.

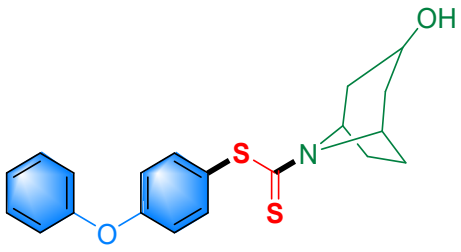
R_f=0.36 (petroleum ether/ethyl acetate =10:1 (v:v))

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.85 (d, *J* = 2.4 Hz, 1H), 7.50 (dd, *J* = 8.7, 2.4 Hz, 1H), 7.00 (d, *J* = 8.7 Hz, 1H), 4.54 (t, *J* = 11.3 Hz, 4H), 3.89 (s, 3H), 3.81 (s, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 196.3, 165.4, 161.0, 142.0, 140.1, 120.9, 120.3, 114.4 (t, *J* = 273.7 Hz), 113.0, 66.2, 64.4, 56.2, 52.2.

HRMS-ESI (m/z) $[M+Na]^+$ calculated for $C_{13}H_{13}F_2NNaO_3S_2^+$ 356.0203, found 356.0193.

4-phenoxyphenyl 3-hydroxy-8-azabicyclo[3.2.1]octane-8-carbodithioate (4r)



Following general procedure, thianthrenium salt **1a** (94.4 mg, 0.2 mmol), **CS_2** (36 *uL*, 0.6 mmol, 3.0 equiv.) and 8-azabicyclo[3.2.1]octan-3-ol (35 *uL*, 0.3 mmol, 1.5 equiv.) were used to afford the

desired product **4r**.

54.2 mg, 73%. Yellow solid.

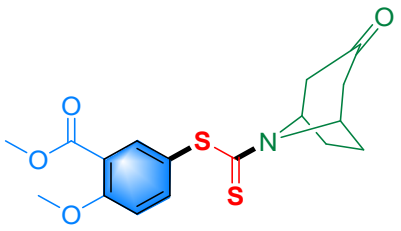
R_f=0.32 (petroleum ether/ethyl acetate =4:1 (v:v))

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.43 – 7.31 (m, 4H), 7.16 (t, *J* = 7.4 Hz, 1H), 7.09 (d, *J* = 7.7 Hz, 2H), 7.02 (d, *J* = 8.7 Hz, 2H), 5.32 – 5.29 (m, 1H), 4.87 – 4.82 (m, 1H), 4.19 – 4.13 (m, 1H), 2.51 – 2.40 (m, 2H), 2.38 – 2.28 (m, 2H), 2.22 – 2.13 (m, 1H), 2.11 – 2.02 (m, 1H), 1.96 – 1.91 (m, 1H), 1.84 – 1.79 (m, 1H), 1.71 (s, 1H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 190.3, 159.5, 155.9, 138.7, 130.0, 124.2, 124.0, 120.0, 118.4, 64.8, 60.4, 58.2, 39.4, 37.9, 28.2, 26.2.

HRMS-ESI (m/z) $[M+Na]^+$ calculated for $C_{20}H_{21}NNaO_2S_2^+$ 394.0911, found 394.0902.

Methyl-2-methoxy-5-((3-oxo-8-azabicyclo[3.2.1]octane-8-carbonothioyl)thio)benzoate (4s)



Following general procedure, thianthrenium salt **1b** (93.6 mg, 0.2 mmol), **CS_2** (36 *μL*, 0.6 mmol, 3.0 equiv.) and 8-azabicyclo[3.2.1]octan-3-one **3** (38 *μL*, 0.3 mmol, 1.5 equiv.) were used to afford the desired product **4s**.

66.4 mg, yield 91%. Yellow solid.

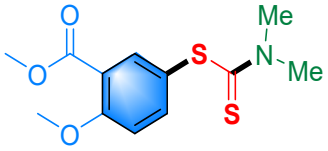
R_f=0.32 (eluent petroleum ether/ ethyl acetate =9:1, v/v).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.95 (d, *J* = 2.4 Hz, 1H), 7.60 (dd, *J* = 8.7, 2.4 Hz, 1H), 7.08 (d, *J* = 8.7 Hz, 1H), 5.53 (t, *J* = 6.0 Hz, 1H), 5.12 (t, *J* = 6.0 Hz, 1H), 3.97 (s, 3H), 3.88 (s, 3H), 3.13 – 3.07 (m, 1H), 2.96 – 2.90 (m, 1H), 2.58 – 2.33 (m, 3H), 2.29 – 2.20 (m, 1H), 2.00 – 1.93 (m, 1H), 1.88 – 1.81 (m, 1H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 206.3, 193.3, 165.5, 160.9, 142.5, 140.5, 121.0, 120.7, 112.8, 59.8, 57.0, 56.2, 52.2, 48.4, 47.4, 29.4, 27.0.

HRMS-ESI (m/z) $[M+Na]^+$ calculated for $C_{14}H_{17}NNaO_3S_2^+$ 334.0548, found 334.0543.

Methyl 5-((dimethylcarbamothioyl)thio)-2-methoxybenzoate (4t)



Following general procedure, thianthrenium salt **1b** (93.6 mg, 0.2 mmol), **CS_2** (36 *μL*, 0.6 mmol, 3.0 equiv.) and dimethylamine **3** (10 *μL*, 0.3 mmol, 1.5 equiv.) were used to afford the desired product **4t**.

50.7 mg, yield 89%. Light yellow solid.

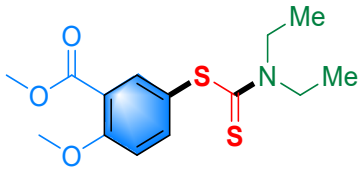
R_f=0.34 (eluent petroleum ether/ ethyl acetate =10:1, v/v).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.91 (d, *J* = 2.3 Hz, 1H), 7.55 (dd, *J* = 8.7, 2.4 Hz, 1H), 7.05 (d, *J* = 8.7 Hz, 1H), 3.96 (s, 3H), 3.87 (s, 3H), 3.56 (s, 3H), 3.49 (s, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 197.8, 165.6, 160.7, 142.5, 140.5, 122.6, 120.5, 112.7, 56.2, 52.1, 45.9, 42.0.

HRMS-ESI (m/z) $[M+Na]^+$ calculated for $C_{12}H_{15}NNaO_3S_2^+$ 308.0391, found 308.0390.

Methyl 5-((diethylcarbamothioyl)thio)-2-methoxybenzoate (4u)



Following general procedure, thianthrenium salt **1b** (93.6 mg, 0.2 mmol), **CS_2** (36 *μL*, 0.6 mmol, 3.0 equiv.) and diethylamine (31 uL, 0.3 mmol, 1.5 equiv.) were used to afford the desired product **4u**.

53.2 mg, 85%. Yellow solid.

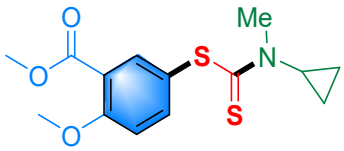
R_f=0.36 (petroleum ether/ethyl acetate =16:1 (v:v))

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.92 (d, *J* = 2.4 Hz, 1H), 7.56 (dd, *J* = 8.7, 2.4 Hz, 1H), 7.05 (d, *J* = 8.7 Hz, 1H), 4.02 (q, *J* = 7.2 Hz, 2H), 3.96 (s, 3H), 3.87 (s, 3H), 3.84 (t, *J* = 7.1 Hz, 2H), 1.40 (t, *J* = 7.1 Hz, 3H), 1.28 (q, *J* = 6.5, 6.0 Hz, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 196.1, 165.6, 160.7, 142.7, 140.7, 122.4, 120.5, 112.6, 56.2, 52.1, 50.1, 47.2, 12.8, 11.6.

HRMS-ESI (m/z) $[M+Na]^+$ calculated for $C_{14}H_{19}NNaO_3S_2^+$ 336.0704, found 336.0711.

Methyl 5-((cyclopropyl(methyl)carbamothioyl)thio)-2-methoxybenzoate (4v)



Following general procedure, thianthrenium salt **1b** (93.6 mg, 0.2 mmol), **CS_2** (36 *μL*, 0.6 mmol, 3.0 equiv.) and *N*-methylcyclopropanamine **3** (25 *μL*, 0.3 mmol, 1.5 equiv.) were used to afford the desired product **4v**.

47.9 mg, yield 77%. Yellow solid.

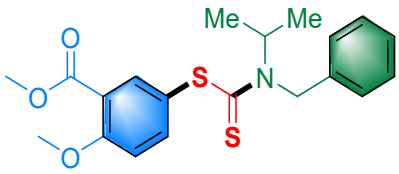
R_f=0.34 (eluent petroleum ether/ ethyl acetate =10:1, v/v).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.91 (d, *J* = 2.4 Hz, 1H), 7.55 (dd, *J* = 8.6, 2.4 Hz, 1H), 7.04 (d, *J* = 8.7 Hz, 1H), 3.95 (s, 3H), 3.86 (s, 3H), 3.49 (s, 3H), 3.03 (s, 1H), 1.10 (s, 4H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 201.9, 165.6, 160.6, 142.4, 140.5, 123.1, 120.5, 112.6, 56.2, 52.1, 44.2, 35.7, 10.9.

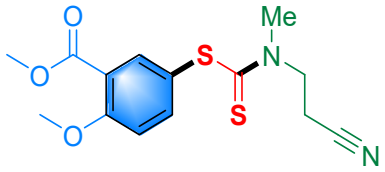
HRMS-ESI (m/z) $[M+Na]^+$ calculated for $C_{14}H_{17}NNaO_3S_2^+$ 334.0548, found 334.0543.

Methyl 5-((benzyl(isopropyl)carbamothioyl)thio)-2-methoxybenzoate (4w)



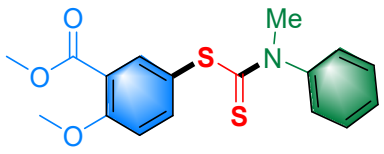
Following general procedure, thianthrenium salt **1b** (93.6 mg, 0.2 mmol), **CS_2** (36 μL, 0.6 mmol) and *N*-benzylpropan-2-amine (50 μL, 0.3 mmol) were used to afford the desired product **4w**.
56.8 mg, 73%. Yellow solid.
R_f=0.34 (petroleum ether/ethyl acetate =6:1 (v:v))
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.92 (d, *J* = 37.3 Hz, 1H), 7.57 (dd, *J* = 35.5, 8.7 Hz, 1H), 7.41 – 7.19 (m, 5H), 7.04 (dd, *J* = 13.2, 8.5 Hz, 1H), 5.97 – 5.90 (m, 1H), 5.31 (s, 1H), 5.04 (s, 1H), 3.95 (s, 3H), 3.88 (s, 3H), 1.30 (d, *J* = 8.0, 3H), 1.21 (d, *J* = 8.0, 3H).
^{13}C NMR (101 MHz, Chloroform-*d*) δ 199.4 (d, *J* = 18.2 Hz), 165.6, 160.7, 142.7 (d, *J* = 15.2 Hz), 140.6, 136.8 (d, *J* = 82.8 Hz), 128.5 (d, *J* = 32.3 Hz), 127.1 (d, *J* = 50.5 Hz), 126.4 (d, *J* = 39.4 Hz), 122.4, 120.5, 112.6 (d, *J* = 8.1 Hz), 56.2, 55.3 (d, *J* = 106.1 Hz), 52.1, 51.7 (d, *J* = 210.8 Hz), 20.9, 19.8.
HRMS-ESI (m/z) $[M+Na]^+$ calculated for $C_{20}H_{23}NNaO_3S_2$ 412.1017, found 412.1016.

Methyl 5-(((2-cyanoethyl)(methyl)carbamothioyl)thio)-2-methoxybenzoate (4x)



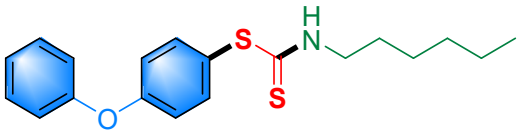
Following general procedure, thianthrenium salts **1b** (93.6 mg, 0.2 mmol), **CS_2** (36 *uL*, 0.6 mmol, 3.0 equiv.) and 3-(methylamino)propanenitrile (23 *uL*, 0.3 mmol, 1.5 equiv.) were used to afford the desired product **4x.**
43.4 mg, yield 67%. Yellow solid.
R_f= 0.34 (eluent petroleum ether/ethyl acetate =7:1, v/v).
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.83 (d, *J* = 2.3 Hz, 1H), 7.47 (dd, *J* = 8.7, 2.4 Hz, 1H), 6.99 (d, *J* = 8.7 Hz, 1H), 4.18 (t, *J* = 6.4 Hz, 2H), 3.89 (s, 3H), 3.81 (s, 3H), 3.55 (s, 3H), 2.84 (t, *J* = 6.4 Hz, 2H).
^{13}C NMR (101 MHz, Chloroform-*d*) δ 192.6, 166.7, 159.1, 133.6, 131.6, 120.1, 120.0, 118.5, 112.0, 56.0, 52.6, 52.0, 41.1, 16.5.
HRMS-ESI (m/z) $[M+Na]^+$ calculated for $C_{14}H_{16}N_2NaO_3S_2^+$ 347.0500, found 347.0498.

Methyl 2-methoxy-5-((methyl(phenyl)carbamothioyl)thio)benzoate (4y)



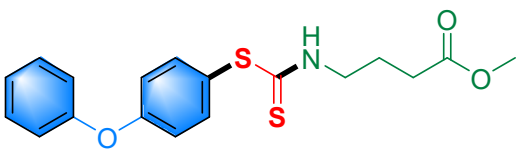
Following Procedure X, thianthrenium salt **1b** (93.6 mg, 0.2 mmol), **CS_2** (36 *uL*, 0.6 mmol, 3.0 equiv.) and *N*-methylaniline (33 *uL*, 0.3 mmol, 1.5 equiv.) were used to afford the desired product **4y**.
61.8 mg, 89%. Yellow solid.
R_f=0.36 (petroleum ether/ethyl acetate =8:1 (v:v))
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.85 (d, *J* = 2.4 Hz, 1H), 7.54 – 7.44 (m, 4H), 7.36 (d, *J* = 7.0 Hz, 2H), 7.01 (d, *J* = 8.7 Hz, 1H), 3.94 (s, 3H), 3.86 (s, 3H), 3.78 (s, 3H).
^{13}C NMR (101 MHz, Chloroform-*d*) δ 199.7, 165.6, 160.6, 144.8, 142.3, 140.4, 129.9, 129.3, 126.9, 123.4, 120.4, 112.6, 56.1, 52.1, 46.7.
HRMS-ESI (m/z) $[M+Na]^+$ calculated for $C_{17}H_{17}NNaO_3S_2^+$ 370.0548, found 370.0540.

4-phenoxyphenyl hexylcarbamodithioate (4z)



Following general procedure, thianthrenium salts **1a** (94.4 mg, 0.2 mmol), **CS_2** (36 *uL*, 0.6 mmol, 3.0 equiv.) and thiomorpholine (40 *uL*, 3.0 mmol, 1.5 equiv.) were used to afford the desired product **4z.**
53.8 mg, yield 78%. Yellow solid.
R_f= 0.38 (eluent petroleum ether/ethyl acetate =9:1, v/v).
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.51 (d, *J* = 8.7 Hz, 2H), 7.41 (t, *J* = 8.0 Hz, 1H), 7.22 (t, *J* = 7.4 Hz, 1H), 7.10 – 7.05 (m, 4H), 6.64 (s, 1H), 3.65 – 3.60 (m, 2H), 1.54 – 1.47 (m, 2H), 1.30 – 1.15 (m, 8H), 0.87 (t, *J* = 8.0 Hz, 3H).
^{13}C NMR (101 MHz, Chloroform-*d*) δ 195.2, 160.5, 155.2, 137.5, 130.2, 124.9, 121.6, 120.2, 119.3, 46.4, 31.3, 28.0, 26.4, 22.5, 14.0.
HRMS-ESI (m/z) $[M+Na]^+$ calculated for $C_{19}H_{23}NNaOS_2^+$ 368.1119, found 368.1122.

Methyl 4-((((4-phenoxyphenyl)thio)carbonothioyl)amino)butanoate (4a')



Following general procedure, thianthrenium salt **1a** (94.4 mg, 0.2 mmol), carbon disulfide (36 *uL*, 0.6 mmol, 3.0 equiv.) and methyl 4-aminobutanoate (31 *uL*, 0.3 mmol, 1.5 equiv.) were used to afford the desired product **4a'**.

51.3 mg, 71%. Yellow solid.

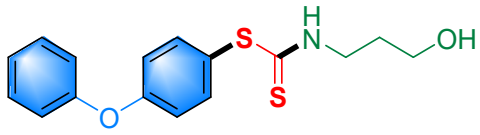
R_f=0.36 (petroleum ether/ethyl acetate =8:1 (v:v))

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.51 (d, *J* = 8.7 Hz, 2H), 7.41 (t, *J* = 7.9 Hz, 2H), 7.21 (t, *J* = 7.4 Hz, 1H), 7.08 -7.05 (m, 5H), 3.73 -3.68 (m, 2H), 3.64 (s, 3H), 2.33 (t, *J* = 7.0 Hz, 2H), 1.91 - 1.84 (m, 2H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 196.0, 173.6, 160.5, 155.3, 137.6, 130.2, 124.8, 121.5, 120.2, 119.3, 51.9, 45.9, 31.3, 23.1.

HRMS-ESI (m/z) $[M+Na]^+$ calculated for $C_{18}H_{19}NNaO_3S_2^+$ 384.0704, found 384.0699.

4-phenoxyphenyl (3-hydroxypropyl)carbamodithioate (4b')



Following general procedure, thianthrenium salts **1a** (94.4 mg, 0.2 mmol), **CS_2** (36 *uL*, 0.6 mmol, 3.0 equiv.) and 3-aminopropan-1-ol (23 *uL*, 3.0 mmol, 1.5 equiv.) were used to afford the desired product **4b'.**

42.1 mg, yield 66%. Light yellow oil.

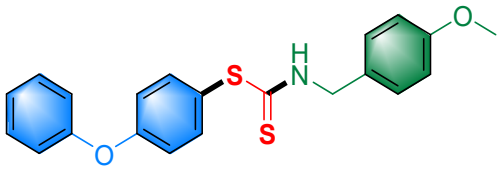
R_f= 0.32 (eluent petroleum ether/ethyl acetate =4:1, v/v).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.61 (s, 1H), 7.51 (d, *J* = 8.7 Hz, 2H), 7.40 (t, *J* = 8.0 Hz, 2H), 7.21 (t, *J* = 7.5 Hz, 1H), 7.08 – 7.03 (m, 4H), 3.82 (q, *J* = 5.6 Hz, 2H), 3.67 (t, *J* = 5.4 Hz, 2H), 2.07 – 1.66 (m, 1H), 1.77 – 1.71 (m, 2H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 196.0, 160.4, 155.4, 137.7, 130.2, 124.7, 121.6, 120.1, 119.3, 61.2, 45.4, 30.1.

HRMS-ESI (m/z) $[M+Na]^+$ calculated for $C_{16}H_{17}NNaO_2S_2^+$ 342.0598, found 342.0599.

4-phenoxyphenyl (4-methoxybenzyl)carbamodithioate (4c')



Following general procedure, thianthrenium salt **1a** (94.4 mg, 0.2 mmol), **CS_2** (36 *uL*, 0.6 mmol, 3.0 equiv.) and 4-methoxybenzylamine (39 *uL*, 0.3 mmol, 1.5 equiv.) were used to afford the desired product **4c'**.

61.0 mg, 80%. Yellow solid.

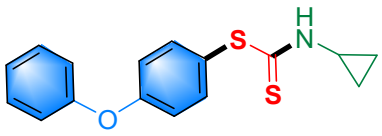
R_f=0.36 (petroleum ether/ethyl acetate =8:1 (v:v))

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.49 (d, *J* = 8.6 Hz, 2H), 7.38 (t, *J* = 7.9 Hz, 2H), 7.20 (t, *J* = 7.4 Hz, 1H), 7.11 (d, *J* = 8.6 Hz, 2H), 7.04 – 6.97 (m, 4H), 6.84 (d, *J* = 8.6 Hz, 2H), 6.79 (s, 1H), 4.76 (d, *J* = 5.2 Hz, 2H), 3.79 (s, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 195.5, 160.4, 159.4, 155.3, 137.4, 130.2, 129.1, 127.8, 124.8, 121.5, 120.1, 119.4, 114.3, 55.3, 49.9.

HRMS-ESI (m/z) $[M+Na]^+$ calculated for $C_{21}H_{19}NNaO_2S_2$ 404.0755, found 404.0749.

4-phenoxyphenyl cyclopropylcarbamodithioate (4d')



Following general procedure, thianthrenium salt **1a** (94.4 mg, 0.2 mmol), **CS_2** (36 *uL*, 0.6 mmol, 3.0 equiv.) and cyclohexylamine (21 *uL*, 0.3 mmol, 1.5 equiv.) were used to afford the desired product **4d'**.

37.3 mg, 62%. Light yellow oil.

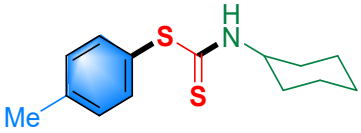
R_f=0.36 (petroleum ether/ethyl acetate =6:1 (v:v))

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.47 (d, *J* = 8.6 Hz, 2H), 7.42 (t, *J* = 8.0 Hz, 2H), 7.22 (t, *J* = 7.4 Hz, 1H), 7.08 (d, *J* = 7.7 Hz, 2H), 7.05 (d, *J* = 8.7 Hz, 2H), 6.66 (s, 1H), 3.13 (m, 1H), 0.90 – 0.85 (m, 2H), 0.55 – 0.51 (m, 2H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 197.2, 160.5, 155.2, 137.3, 130.2, 124.9, 121.8, 120.3, 120.1, 119.2, 29.2, 7.5.

HRMS-ESI (m/z) $[M+Na]^+$ calculated for $C_{16}H_{15}NNaOS_2^+$ 324.0493, found 324.0492.

p-tolyl cyclohexylcarbamodithioate (4e')



Following general procedure, thianthrenium salt **1o** (78.8 mg, 0.2 mmol), **CS_2** (36 *uL*, 0.6 mmol, 3.0 equiv.) and cyclohexylamine (34 *uL*, 0.3 mmol, 1.5 equiv.) were used to afford the desired product **4e'**.

35.5 mg, 67%. Light yellow oil.

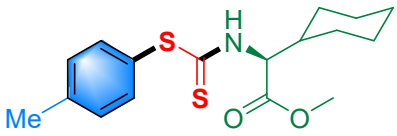
R_f=0.34 (petroleum ether/ethyl acetate =8:1 (v:v))

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.45 (d, *J* = 8.1 Hz, 2H), 7.32 (d, *J* = 7.9 Hz, 2H), 6.50 (d, *J* = 8.1 Hz, 1H), 4.40 – 4.31 (m, 1H), 2.43 (s, 3H), 1.92 – 1.88 (m, 2H), 1.56 – 1.48 (m, 3H), 1.42 – 1.25 (m, 2H), 1.18 – 1.01 (m, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 193.8, 141.8, 135.4, 131.2, 125.3, 54.4, 31.3, 25.2, 24.2, 21.5.

HRMS-ESI (m/z) $[M+Na]^+$ calculated for $C_{14}H_{19}NNaS_2^+$ 288.0857, found 288.0861.

Methyl (S)-2-cyclohexyl-2-(((p-tolylthio)carbonothioyl)amino)acetate (4f')



Following general procedure, thianthrenium salt **1o** (78.8 mg, 0.2 mmol), **CS_2** (36 *uL*, 0.6 mmol, 3.0 equiv.) and methyl (S)-2-amino-2-cyclohexylacetate (51.4 mg, 0.3 mmol, 1.5 equiv.) were used to afford the desired product **4f'**.

47.2 mg, 70%. Yellow solid.

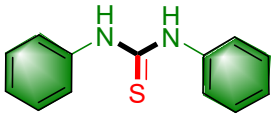
R_f=0.44 (petroleum ether/ethyl acetate =9:1 (v:v))

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.50 (d, *J* = 8.1 Hz, 2H), 7.36 (d, *J* = 7.8 Hz, 2H), 7.12 (d, *J* = 8.3 Hz, 1H), 5.07 (dd, *J* = 8.3, 4.7 Hz, 1H), 3.70 (s, 3H), 2.44 (s, 3H), 1.90 – 1.81 (m, 1H), 1.72 – 1.60 (m, 3H), 1.57 – 1.42 (m, 2H), 1.33 – 1.10 (m, 2H), 1.04 – 0.74 (m, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 196.0, 170.8, 142.0, 135.6, 131.2, 124.9, 62.3, 52.4, 40.8, 29.2, 28.4, 25.9, 21.5.

HRMS-ESI (m/z) $[M+Na]^+$ calculated for $C_{17}H_{23}NNaO_2S_2^+$ 360.1068, found 360.1074.

1,3-diphenylthiourea (4g')



Following general procedure, thianthrenium salt **1a** (93.6 mg, 0.2 mmol), carbon disulfide (36 *uL*, 0.6 mmol) and aniline (27.3 *uL*, 0.3 mmol, 1.5 equiv.) were used to afford the desired product **4g'**.

37.4 mg, 87%. Light yellow solid.

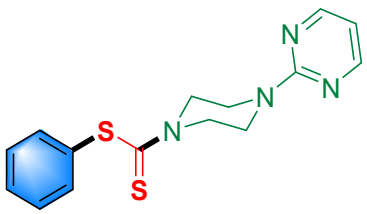
R_f=0.36 (petroleum ether/ethyl acetate =9:1 (v:v))

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.21 (s, 2H), 7.42 – 7.36 (m, 8H), 7.29 – 7.23 (m, 2H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 179.7, 137.1, 129.5, 127.0, 125.3.

HRMS-ESI (m/z) $[M+Na]^+$ calculated for $C_{13}H_{12}N_2NaS$ 251.0619, found 251.0616.

Phenyl 4-(pyrimidin-2-yl)piperazine-1-carbodithioate (4aa)



Following general procedure, thianthrenium salt **1c** (76.0 mg, 0.2 mmol), **CS_2** (36 *uL*, 0.6 mmol, 3.0 equiv.) and 2-(piperazin-1-yl)pyrimidine (49.3mg, 0.3 mmol, 1.5 equiv.) were used to afford the desired product **4aa**.

45.5 mg, 72%. Light yellow solid.

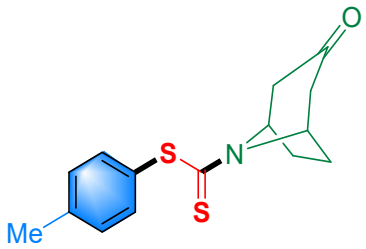
R_f=0.39 (petroleum ether/ethyl acetate =8:1 (v:v))

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.37 (d, *J* = 4.8 Hz, 2H), 7.51-7.43 (m, 5H), 6.59 (t, *J* = 4.8 Hz, 1H), 4.30 (d, *J* = 84.1 Hz, 4H), 4.02 (s, 4H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 197.9, 161.1, 157.8, 137.1, 131.0, 130.2, 129.2, 110.7, 50.7 (d, *J* = 84.8 Hz), 43.1.

HRMS-ESI (m/z) $[M+H]^+$ calculated for $C_{15}H_{17}N_4S_2^+$ 317.0895, found 317.0890.

p-tolyl 3-oxo-8-azabicyclo[3.2.1]octane-8-carbodithioate (4ab)



Following general procedure, thianthrenium salt **1o** (76.0 mg, 0.2 mmol), **CS_2** (36 *uL*, 0.6 mmol, 3.0 equiv.) and 8-azabicyclo[3.2.1]octan-3-one (35 *uL*, 0.3 mmol, 1.5 equiv.) were used to afford the desired product **4ab**.

44.2 mg, 76%. Light yellow solid.

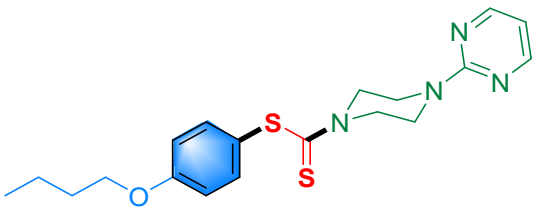
R_f=0.36 (petroleum ether/ethyl acetate =9:1 (v:v))

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.40 (d, *J* = 7.8 Hz, 2H), 7.28 (t, *J* = 8.0 Hz, 2H), 5.55 (t, *J* = 6.2 Hz, 1H), 5.13 (t, *J* = 6.0 Hz, 1H), 3.11 (dd, *J* = 15.5, 4.1 Hz, 1H), 2.97 – 2.92 (m, 1H), 2.54 – 2.33 (m, 6H), 2.25 (t, *J* = 4.0 Hz, 1H), 1.99 – 1.93 (m, 1H), 1.88 – 1.81 (m, 1H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 206.6, 193.7, 140.9, 136.8, 130.2, 126.8, 59.7, 57.0, 48.4, 47.4, 29.4, 27.0, 21.6.

HRMS-ESI (m/z) $[M+Na]^+$ calculated for $C_{15}H_{17}NNaOS_2^+$ 314.0649, found 314.0644.

4-butoxyphenyl 4-(pyrimidin-2-yl)piperazine-1-carbodithioate (4ac)



Following general procedure, thianthrenium salt **1i** (90.4 mg, 0.2 mmol), **CS_2** (36 *uL*, 0.6 mmol, 3.0 equiv.) and 2-(piperazin-1-yl)pyrimidine (49.3 mg, 0.3 mmol, 1.5 equiv.) were used to afford the desired product **4ac**.

52.8 mg, 68%. Yellow solid.

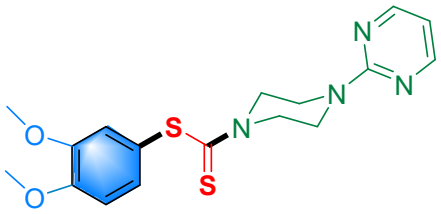
R_f=0.36 (petroleum ether/ethyl acetate =6:1 (v:v))

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.37 (d, *J* = 4.8 Hz, 2H), 7.38 (d, *J* = 8.7 Hz, 2H), 6.96 (d, *J* = 8.7 Hz, 2H), 6.59 (t, *J* = 4.7 Hz, 1H), 4.30 (d, *J* = 95.3 Hz, 4H), 4.03 – 3.98 (m, 6H), 1.82 – 1.72 (m, 2H), 1.55 – 1.42 (m, 2H), 0.98 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 199.2, 160.9, 157.8, 138.5, 121.3, 134.2, 115.3, 110.7, 67.8, 50.6 (d, *J* = 143.4 Hz), 43.1, 31.3, 19.3, 13.9.

HRMS-ESI (m/z) $[M+H]^+$ calculated for $C_{19}H_{25}N_4OS_2^+$ 389.1470, found 389.1467.

3,4-dimethoxyphenyl 4-(pyrimidin-2-yl)piperazine-1-carbodithioate (4ad)



Following general procedure, thianthrenium salt **1j** (88.1 mg, 0.2 mmol), **CS_2** (36 *uL*, 0.6 mmol, 3.0 equiv.) and 2-(piperazin-1-yl)pyrimidine (49.3mg, 0.3 mmol, 1.5 equiv.) were used to afford the desired product **4ad**.

52.7 mg, 70%. Light yellow solid.

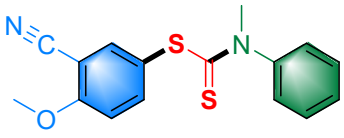
R_f=0.46 (petroleum ether/ethyl acetate =6:1 (v:v))

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.37 (d, *J* = 4.8 Hz, 2H), 7.09 (dd, *J* = 8.3, 2.1 Hz, 1H), 6.99 (d, *J* = 2.0 Hz, 1H), 6.94 (d, *J* = 8.3 Hz, 1H), 6.59 (t, *J* = 4.8 Hz, 1H), 4.29 (d, *J* = 108.6 Hz, 4H), 4.02 (s, 4H), 3.93 (s, 3H), 3.90 (s, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 198.7, 161.2, 157.9, 150.9, 149.1, 130.2, 121.7, 119.6, 111.3, 110.7, 56.1, 55.9, 50.6 (d, *J* = 142.4 Hz), 43.1.

HRMS-ESI (m/z) $[M+Na]^+$ calculated for $C_{17}H_{20}N_4NaO_2S_2^+$ 399.0925, found 399.0927.

3-cyano-4-methoxyphenyl methyl(phenyl)carbamodithioate (4ae)



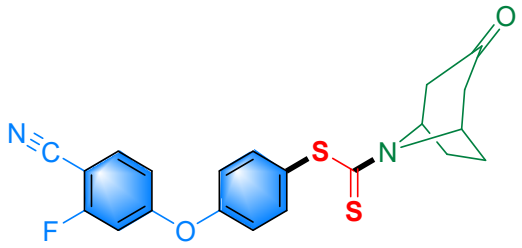
Following general procedure, thianthrenium salt **1p** (69.6 mg, 0.2 mmol), **CS_2** (36 *uL*, 0.6 mmol, 3.0 equiv.) and *N*-methylaniline (33 *uL*, 0.3 mmol, 1.5 equiv.) were used to afford the desired product **4ae**.

42.8 mg, 68%. Yellow oil.

R_f=0.38 (petroleum ether/ethyl acetate =5:1 (v:v))

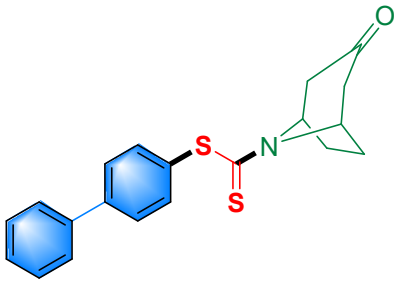
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.57 – 7.46 (m, 5H), 7.36 (d, *J* = 6.9 Hz, 2H), 7.00 (d, *J* = 8.7 Hz, 1H), 3.97 (s, 3H), 3.78 (s, 3H).
^{13}C NMR (101 MHz, Chloroform-*d*) δ 198.6, 162.3, 144.5, 143.2, 142.0, 130.0, 129.5, 126.9, 124.6, 115.6, 111.8, 102.7, 56.3, 46.8.
HRMS-ESI (m/z) $[M+H]^+$ calculated for $C_{16}H_{15}N_2OS_2^+$ 315.0626, found 315.0632.

4-(4-cyano-3-fluorophenoxy)phenyl-3-oxo-8-azabicyclo[3.2.1]octane-8-carbodithioate (4af)



Following general procedure, thianthrenium salt **1e** (85.7 mg, 0.2 mmol), **CS_2** (36 *uL*, 0.6 mmol, 3.0 equiv.) and 8-azabicyclo[3.2.1]octan-3-one (35 *uL*, 0.3 mmol, 1.5 equiv.) were used to afford the desired product **4af**.
70.9 mg, 86%. Light yellow solid.
R_f=0.36 (petroleum ether/ethyl acetate =5:1 (v:v))
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.57 – 7.48 (m, 3H), 7.19 (d, *J* = 8.0 Hz, 1H), 6.96 (t, *J* = 8.4 Hz, 1H), 6.78 (d, *J* = 8.5 Hz, 1H), 5.55 (q, *J* = 6.0 Hz, 1H), 5.14 (q, *J* = 6.0 Hz, 1H), 3.10 (dd, *J* = 16.3, 4.9 Hz, 1H), 2.94 (dd, *J* = 16.2, 4.9 Hz, 1H), 2.57 – 2.35 (m, 3H), 2.32 – 2.21 (m, 1H), 2.02 – 1.95 (m, 1H), 1.90 – 1.87 (m, 1H).
^{13}C NMR (101 MHz, Chloroform-*d*) δ 206.3, 192.7, 164.1 (d, *J* = 261.6 Hz), 160.0 (d, *J* = 4.0 Hz), 156.4, 139.2, 135.1, 127.0, 120.6, 112.9 (d, *J* = 3.0 Hz), 111.0, 110.5 (d, *J* = 19.2 Hz), 94.3 (d, *J* = 18.2 Hz), 59.8, 57.2, 48.4, 47.4, 29.5, 27.0.
HRMS-ESI (m/z) $[M+Na]^+$ calculated for $C_{21}H_{17}FN_2NaO_2S_2$ 435.0613, found 435.0617.

4-fluorobenzyl (*E*)-3-(dipropylamino)-2-(trifluoromethyl)acrylate (4ag)



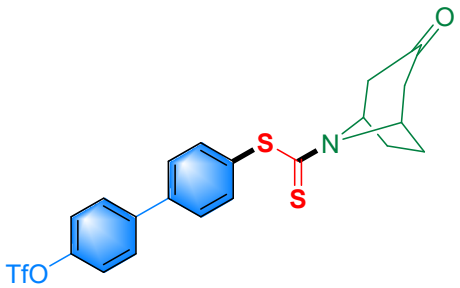
Following general procedure, thianthrenium salt **1d** (73.8 mg, 0.2 mmol), **CS_2** (36 *μL*, 0.6 mmol, 3.0 equiv.) and 8-azabicyclo[3.2.1]octan-3-one **3** (35 *uL*, 0.3 mmol, 1.5 equiv.) were used to afford the desired product **4ag**.
56.5 mg, yield 80%. Yellow solid.
R_f=0.32 (eluent petroleum ether/ ethyl acetate =9:1, v/v).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.69 (d, *J* = 8.0 Hz, 2H), 7.64 (d, *J* = 7.6 Hz, 2H), 7.58 (d, *J* = 8.0 Hz, 2H), 7.46 (t, *J* = 7.5 Hz, 2H), 7.38 (t, *J* = 7.3 Hz, 1H), 5.56 (t, *J* = 6.2 Hz, 1H), 5.15 (t, *J* = 6.0 Hz, 1H), 3.15 – 3.10 (m, 1H), 2.99 – 2.93 (m, 1H), 2.55 – 2.35 (m, 3H), 2.30 – 2.25 (m, 1H), 2.00 – 1.93 (m, 1H), 1.89 – 1.82 (m, 1H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 206.3, 193.0, 143.1, 140.0, 137.2, 128.90, 128.9, 127.9, 127.9, 127.3, 59.6, 57.1, 48.4, 47.4, 29.4, 27.0.

HRMS-ESI (m/z) $[M+H]^+$ calculated for $C_{20}H_{20}NOS_2^+$ 354.0986, found 354.0996.

4'-(((trifluoromethyl)sulfonyl)oxy)-[1,1'-biphenyl]-4-yl-3-oxo-8-azabicyclo[3.2.1] octane-8-carbodithioate (4ah)



Following general procedure, thianthrenium salt **1k** (120.8 mg, 0.2 mmol), **CS_2** (36 *μL*, 0.6 mmol, 3.0 equiv.) and 8-azabicyclo[3.2.1]octan-3-one **3** (35 *μL*, 0.3 mmol, 1.5 equiv.) were used to afford the desired product **4ah**.

74.2 mg, yield 74%. Yellow solid.

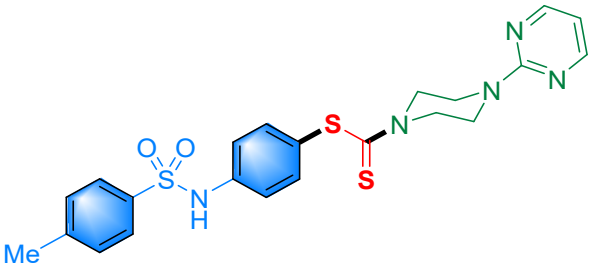
R_f=0.32 (eluent petroleum ether/ ethyl acetate = 9:1, v/v).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.71 – 7.59 (m, 6H), 7.37 (d, *J* = 8.0 Hz, 2H), 5.56 (t, *J* = 6.1 Hz, 1H), 5.15 (t, *J* = 6.1 Hz, 1H), 3.15 – 3.09 (m, 1H), 2.99 – 2.93 (m, 1H), 2.57 – 2.36 (m, 3H), 2.32 – 2.22 (m, 1H), 2.02 – 1.95 (m, 1H), 1.90– 1.83 (m, 1H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 206.3, 192.6, 149.3, 141.1, 140.5, 137.5, 130.1, 129.1, 128.0, 121.82, 118.8 (q, *J* = 322.2 Hz), 59.7, 57.2, 48.4, 47.4, 29.5, 27.1.

HRMS-ESI (m/z) $[M+Na]^+$ calculated for $C_{21}H_{18}F_3NNaO_4S_3^+$ 524.0248, found 524.0241.

4-((4-methylphenyl)sulfonamido)phenyl-4-(pyrimidin-2-yl)piperazine-1-carbod ithioate (4ai)



Following general procedure, thianthrenium salts **1r** (109.8 mg, 0.2 mmol), **CS_2** (36 *μL*, 0.6 mmol, 3.0 equiv.) and 2-(piperazin-1-yl)pyrimidine (43 *μL*, 3.0 mmol, 1.5 equiv.) were used to afford the desired product **4ai.**

80.5 mg, yield 83%. Yellow solid.

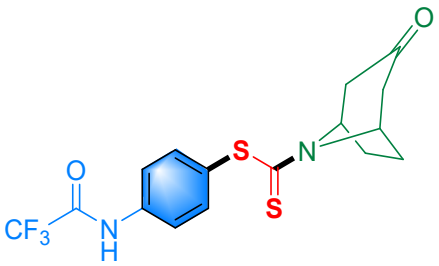
R_f= 0.34 (eluent petroleum ether/ethyl acetate =4:1, v/v).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.36 (d, *J* = 4.8 Hz, 2H), 7.70 (d, *J* = 7.9 Hz, 2H), 7.34 (d, *J* = 8.1 Hz, 2H), 7.25 (d, *J* = 8.7 Hz, 3H), 7.13 (d, *J* = 8.2 Hz, 2H), 6.99 (s, 1H), 6.59 (t, *J* = 4.8 Hz, 1H), 4.27 (d, *J* = 110.2 Hz, 4H), 4.00 (s, 4H), 2.38 (s, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 197.6, 161.2, 157.9, 144.2, 138.6, 138.2, 135.9, 129.8, 127.3, 126.9, 121.0, 110.8, 43.0, 21.6.

HRMS-ESI (m/z) $[M+Na]^+$ calculated for $C_{22}H_{23}N_5NaO_2S_3^+$ 508.0912, found 508.0905.

4-(2,2,2-trifluoroacetamido)phenyl-3-oxo-8-azabicyclo[3.2.1]octane-8-carbodithioate (4aj)



Following general procedure, thianthrenium salt **1f** (98.2 mg, 0.2 mmol), **CS_2** (36 *μL*, 0.6 mmol, 3.0 equiv.) and 8-azabicyclo[3.2.1]octan-3-one (35 *μL*, 0.3 mmol, 1.5 equiv.) were used to afford the desired product **4aj**.

57.4 mg, 74%. Yellow solid.

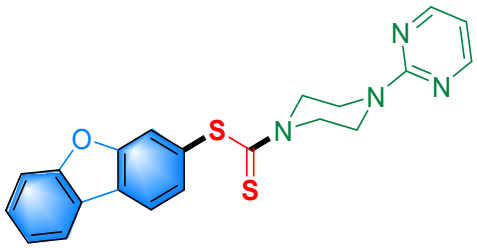
R_f=0.36 (petroleum ether/ethyl acetate =6:1 (v:v))

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.11 (s, 1H), 7.71 (d, *J* = 8.4 Hz, 2H), 7.54 (d, *J* = 8.3 Hz, 2H), 5.53 (t, *J* = 6.2 Hz, 1H), 5.12 (t, *J* = 5.9 Hz, 1H), 3.12 – 3.07 (m, 1H), 2.96 – 2.91 (m, 1H), 2.56 – 2.36 (m, 3H), 2.30 – 2.21 (m, 1H), 2.01 – 1.94 (m, 1H), 1.89 – 1.82 (m, 1H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 206.3, 192.6, 154.8 (d, *J* = 37.4 Hz), 138.2, 137.1, 127.7, 120.8,115.4 (t, *J* = 267.7 Hz), 59.8, 57.2, 48.4, 47.4, 29.4, 27.0.

HRMS-ESI (m/z) $[M+Na]^+$ calculated for $C_{16}H_{15}F_3N_2NaO_2S_2^+$ 411.0425, found 411.0433.

Dibenzo[b,d]furan-3-yl 4-(pyrimidin-2-yl)piperazine-1-carbodithioate (4ak)



Following general procedure, thianthrenium salt **1l** (94.1 mg, 0.2 mmol), **CS_2** (36 *μL*, 0.6 mmol, 3.0 equiv.) and 2-(piperazin-1-yl)pyrimidine (49.3mg, 0.3 mmol, 1.5 equiv.) were used to afford the desired product **4ak**.

65.0 mg, 80%. Yellow solid.

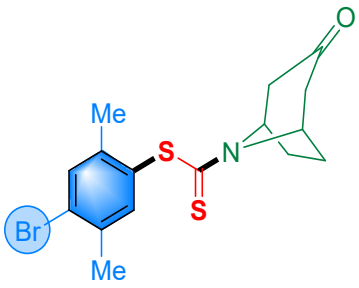
R_f=0.38 (petroleum ether/ethyl acetate =8:1 (v:v))

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.37 (d, *J* = 4.6 Hz, 2H), 8.09 (s, 1H), 7.94 (d, *J* = 7.7 Hz, 1H), 7.65 (d, *J* = 8.5 Hz, 1H), 7.61 – 7.55 (m, 2H), 7.49 (t, *J* = 8.0 Hz, 1H), 7.36 (t, *J* = 7.5 Hz, 1H), 6.60 (t, *J* = 4.7 Hz, 1H), 4.33 (d, *J* = 88.4 Hz, 4H), 4.04 (s, 4H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 198.6, 161.0, 157.8, 157.2, 156.6, 136.1, 129.9, 127.7, 125.4, 124.7, 123.6, 123.1, 121.0, 112.6, 111.8, 110.7, 50.7 (d, *J* = 122.2 Hz), 43.1.

HRMS-ESI (m/z) $[M+H]^+$ calculated for $C_{21}H_{19}N_4OS_2^+$ 407.1000, found 407.0991.

4-bromo-2,5-dimethylphenyl-3-oxo-8-azabicyclo[3.2.1]octane-8-carbodithioate (4al)



Following general procedure, thianthrenium salt **1g** (79.8 mg, 0.2 mmol), **CS_2** (36 *μL*, 0.6 mmol, 3.0 equiv.) and 8-azabicyclo[3.2.1]octan-3-one **3** (35 *μL*, 0.3 mmol, 1.5 equiv.) were used to afford the desired product **4al**.

54.4 mg, yield 71%. Yellow solid.

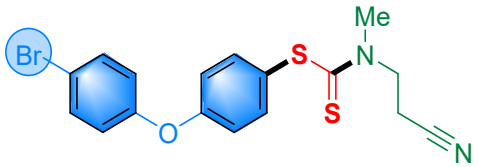
R_f=0.32 (eluent petroleum ether/ ethyl acetate =9:1, v/v).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.55 (s, 1H), 7.32 (s, 1H), 5.52 (t, *J* = 6.3 Hz, 1H), 5.12 (t, *J* = 6.1 Hz, 1H), 3.114 – 3.08 (m, 1H), 2.97 – 2.91 (m, 1H), 2.55 – 2.50 (m, 1H), 2.43 (d, *J* = 16.0 Hz, 1H), 2.39 (s, 3H), 2.36 (s, 3H), 2.33 – 2.20 (m, 2H), 2.00 – 1.93 (m, 1H), 1.89 – 1.82 (m, 1H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 206.3, 191.4, 142.8, 139.4, 136.5, 134.4, 128.6, 128.1, 59.6, 57.2, 48.4, 47.3, 29.5, 27.1, 22.3, 20.3.

HRMS-ESI (m/z) $[M+H]^+$ calculated for $C_{16}H_{19}BrNOS_2^+$ 384.0091, found 384.0091.

4-(4-bromophenoxy)phenyl (2-cyanoethyl)(methyl)carbamodithioate (4am)



Following general procedure, thianthrenium salt **1s** (109.9 mg, 0.2 mmol), **CS_2** (36 *μL*, 0.6 mmol, 3.0 equiv.) and 3-(methylamino)propanenitrile (76 *μL*, 0.3 mmol, 1.5 equiv.) were used to afford the desired product **4am**.

60.9 mg, 75%. Yellow solid.

R_f=0.42 (petroleum ether/ethyl acetate =16:1 (v:v))

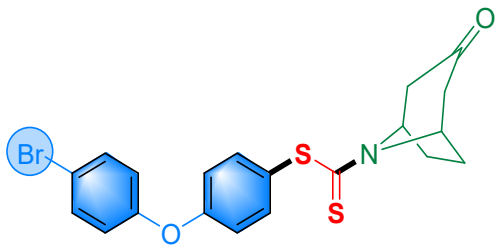
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.48 (d, *J* = 8.6 Hz, 2H), 7.40 (d, *J* = 8.4 Hz, 2H), 7.03 (d, *J*

= 8.3 Hz, 2H), 6.98 (d, *J* = 8.6 Hz, 2H), 4.26 (t, *J* = 6.4 Hz, 2H), 3.63 (s, 3H), 2.91 (t, *J* = 6.4 Hz, 2H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 199.9, 159.2, 155.1, 138.7, 133.0, 124.8, 121.6, 118.7, 118.1, 116.9, 53.3, 41.8, 15.1.

HRMS-ESI (m/z) $[M+Na]^+$ calculated for $C_{17}H_{15}BrN_2NaOS_2$ 428.9707, found 428.9710.

4-(4-bromophenoxy)phenyl-3-oxo-8-azabicyclo[3.2.1]octane-8-carbodithioate (4an)



Following general procedure, thianthrenium salt **1s** (110.0 mg, 0.2 mmol), **CS_2** (36 *μL*, 0.6 mmol, 3.0 equiv.) and 8-azabicyclo[3.2.1]octan-3-one (35 *μL*, 0.3 mmol, 1.5 equiv.) were used to afford the desired product **4an**.

75.1mg, 84%. Yellow solid.

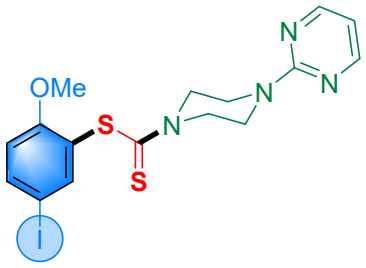
R_f=0.36 (petroleum ether/ethyl acetate =8:1 (v:v))

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.49 (d, *J* = 8.8 Hz, 2H), 7.45 (d, *J* = 8.7 Hz, 2H), 7.04 (d, *J* = 8.7 Hz, 2H), 6.98 (d, *J* = 8.8 Hz, 2H), 5.54 (t, *J* = 6.2 Hz, 1H), 5.12 (t, *J* = 6.1 Hz, 1H), 3.13 – 3.07 (m, 1H), 2.96 – 2.91 (m, 1H), 2.55 – 2.33 (m, 3H), 2.30 – 2.20 (m, 1H), 2.00 – 1.91 (m, 1H), 1.88 – 1.81 (m, 1H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 206.3, 193.4, 159.2, 155.1, 138.8, 133.0, 124.0, 121.7, 118.6, 116.9, 59.7, 57.0, 48.5, 47.4, 29.4, 27.0.

HRMS-ESI (m/z) $[M+Na]^+$ calculated for $C_{20}H_{18}BrNNaO_2S_2^+$ 469.9860, found 469.9869.

5-iodo-2-methoxyphenyl 4-(pyrimidin-2-yl)piperazine-1-carbodithioate (4ao)



Following general procedure, thianthrenium salt **1m** (107.2 mg, 0.2 mmol), **CS_2** (36 *μL*, 0.6 mmol, 3.0 equiv.) and 2-(piperazin-1-yl)pyrimidine (49.3 mg, 0.3 mmol, 1.5 equiv.) were used to afford the desired product **4ao**.

58.5 mg, 62%. Yellow solid.

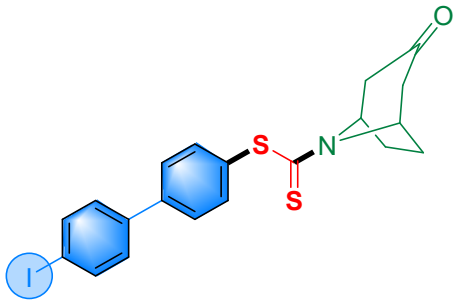
R_f=0.42 (petroleum ether/ethyl acetate =8:1 (v:v))

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.37 (d, *J* = 4.8 Hz, 2H), 7.87 (d, *J* = 2.2 Hz, 1H), 7.44 (dd, *J* = 8.5, 2.2 Hz, 1H), 6.89 (d, *J* = 8.5 Hz, 1H), 6.60 (t, *J* = 4.8 Hz, 1H), 4.42 (s, 4H), 4.01 (s, 4H), 3.93 (s, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 198.0, 161.1, 159.7, 157.9, 147.3, 138.7, 123.5, 111.0, 110.8, 85.9, 56.5, 50.6 (d, *J* = 145.4 Hz), 43.1.

HRMS-ESI (m/z) $[M+Na]^+$ calculated for $C_{16}H_{17}IN_4NaOS_2^+$ 494.9786, found 494.9786.

4'-iodo-[1,1'-biphenyl]-4-yl 3-oxo-8-azabicyclo[3.2.1]octane-8-carbodithioate (4ap)



Following general procedure, thianthrenium salt **1h** (116.4 mg, 0.2 mmol), **CS_2** (36 *μL*, 0.6 mmol, 3.0 equiv.) and 8-azabicyclo[3.2.1]octan-3-one (35 *μL*, 0.3 mmol, 1.5 equiv.) were used to afford the desired product **4ap**.

73.8 mg, 77%. Yellow solid.

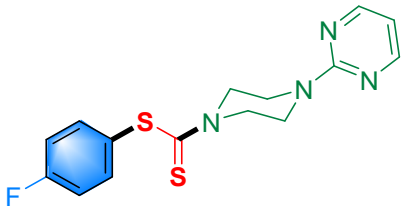
R_f=0.42 (petroleum ether/ethyl acetate =5:1 (v:v))

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.79 (d, *J* = 8.0 Hz, 2H), 7.65 (d, *J* = 8.4 Hz, 2H), 7.58 (d, *J* = 8.3 Hz, 2H), 7.38 (q, *J* = 6.0 Hz, 2H), 5.55 (q, *J* = 6.1 Hz, 1H), 5.14 (q, *J* = 6.1 Hz, 1H), 3.12 (dd, *J* = 12.1, 8.0 Hz, 1H), 2.96 (dd, *J* = 12.1, 8.0 Hz, 1H), 2.58 – 2.36 (m, 3H), 2.31 – 2.22 (m, 1H), 2.00 – 1.94 (m, 1H), 1.89 – 1.82 (m, 1H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 206.3, 192.8, 142.0, 139.5, 138.0, 137.4, 129.5, 129.1, 127.7, 94.0, 59.7, 57.2, 48.4, 47.4, 29.5, 27.1.

HRMS-ESI (m/z) $[M+H]^+$ calculated for $C_{20}H_{19}INOS_2^+$ 479.9953, found 479.9956.

4-fluorophenyl 4-(pyrimidin-2-yl)piperazine-1-carbodithioate (4aq)



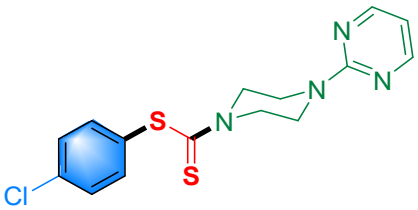
Following general procedure, thianthrenium salt **1u** (80.0 mg, 0.2 mmol), **CS_2** (36 *μL*, 0.6 mmol, 3.0 equiv.) and 2-(piperazin-1-yl)pyrimidine (49.3 mg, 0.3 mmol, 1.5 equiv.) were used to afford the desired product **4aq**.

50.8 mg, 76%. Yellow solid.

R_f=0.42 (petroleum ether/ethyl acetate =5:1 (v:v))

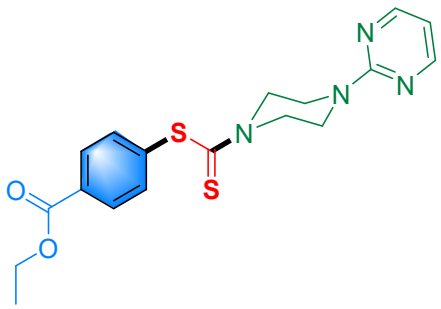
^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.36 (d, *J* = 4.8 Hz, 2H), 7.46 (dd, *J* = 8.6, 5.4 Hz, 2H), 7.14 (t, *J* = 8.6 Hz, 2H), 6.60 (t, *J* = 4.8 Hz, 1H), 4.29 (d, *J* = 100.7 Hz, 4H), 4.02 (s, 4H).
^{13}C NMR (101 MHz, Chloroform-*d*) δ 197.6 (d, *J* = 2.0 Hz), 163.2 (t, *J* = 211.1 Hz), 157.9, 139.2 (d, *J* = 9.1 Hz), 126.4 (d, *J* = 4.0 Hz), 116.6, 116.4, 110.8, 50.7 (d, *J* = 134.3 Hz), 43.0.
HRMS-ESI (m/z) $[M+H]^+$ calculated for $C_{15}H_{16}FN_4S_2^+$ 335.0800, found 335.0797.

4-chlorophenyl 4-(pyrimidin-2-yl)piperazine-1-carbodithioate (4ar)



Following general procedure, thianthrenium salt **1n** (82.8 mg, 0.2 mmol), **CS_2** (36 *μL*, 0.6 mmol, 3.0 equiv.) and 2-(piperazin-1-yl)pyrimidine (49.3 mg, 0.3 mmol, 1.5 equiv.) were used to afford the desired product **4ar**.
51.8 mg, 74%. Yellow solid.
R_f=0.38 (petroleum ether/ethyl acetate =10:1 (v:v))
^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.36 (d, *J* = 4.8 Hz, 2H), 7.42 (s, 4H), 6.59 (t, *J* = 4.8 Hz, 1H), 4.28 (d, *J* = 105.6 Hz, 4H), 4.02 (s, 4H).
^{13}C NMR (101 MHz, Chloroform-*d*) δ 196.9, 161.2, 157.9, 138.3, 136.8, 129.5, 129.4, 110.8, 50.7 (d, *J* = 112.1 Hz), 43.03.
HRMS-ESI (m/z) $[M+H]^+$ calculated for $C_{15}H_{16}ClN_4S_2^+$ 351.0505, found 351.0503.

Ethyl 4-((4-(pyrimidin-2-yl)piperazine-1-carbonothioyl)thio)benzoate (4as)



Following general procedure, thianthrenium salt **1x** (90.5 mg, 0.2 mmol), **CS_2** (36 *μL*, 0.6 mmol, 3.0 equiv.) and 2-(piperazin-1-yl)pyrimidine (49.3 mg, 0.3 mmol, 1.5 equiv.) were used to afford the desired product **4as.**
53.6 mg, 69%. Yellow solid.

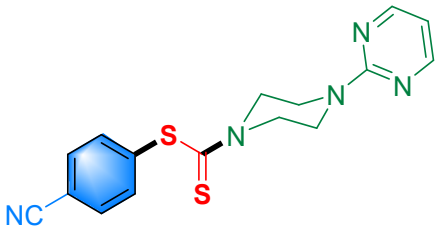
R_f=0.36 (petroleum ether/ethyl acetate =6:1 (v:v))

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.37 (d, *J* = 4.8 Hz, 2H), 8.11 (d, *J* = 8.0 Hz, 2H), 7.58 (d, *J* = 8.0 Hz, 2H), 6.60 (t, *J* = 4.8 Hz, 1H), 4.40 (q, *J* = 7.1 Hz, 2H), 4.35 – 4.09 (m, 4H), 4.03 (s, 4H), 1.40 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 196.2, 165.9, 161.1, 157.9, 136.9, 136.2, 131.8, 130.1, 110.8, 61.3, 50.7, 43.1, 14.4.

HRMS-ESI (m/z) $[M+H]^+$ calculated for $C_{18}H_{21}N_4O_2S_2$ 389.1106, found 389.1096.

4-cyanophenyl 4-(pyrimidin-2-yl)piperazine-1-carbodithioate (4at)



Following general procedure, thianthrenium salt **1w** (81.0 mg, 0.2 mmol), **CS_2** (36 *μL*, 0.6 mmol, 3.0 equiv.) and 2-(piperazin-1-yl)pyrimidine (49.3mg, 0.3 mmol, 1.5 equiv.) were used to afford the desired product **4at**.

39.6 mg, 58%. Yellow solid.

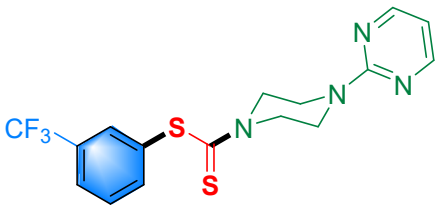
R_f=0.38 (petroleum ether/ethyl acetate =6:1 (v:v))

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.37 (d, *J* = 8.0 Hz, 2H), 7.72 (d, *J* = 8.0 Hz, 2H), 7.61 (d, *J* = 8.0 Hz, 2H), 6.61 (t, *J* = 4.0 Hz, 1H), 4.28 (d, *J* = 104.3 Hz, 4H), 4.03 (s, 4H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 195.0, 161.0, 157.9, 137.6, 136.9, 132.5, 118.3, 113.8, 110.9, 50.8 (d, *J* = 85.9 Hz), 43.0.

HRMS-ESI (m/z) $[M+Na]^+$ calculated for $C_{16}H_{15}N_5NaS_2$ 364.0667, found 364.0673.

4-cyanophenyl 4-(pyrimidin-2-yl)piperazine-1-carbodithioate (4au)



Following general procedure, thianthrenium salt **1v** (89.6 mg, 0.2 mmol), **CS_2** (36 *μL*, 0.6 mmol, 3.0 equiv.) and 2-(piperazin-1-yl)pyrimidine (49.3mg, 0.3 mmol, 1.5 equiv.) were used to afford the desired product **4au**.

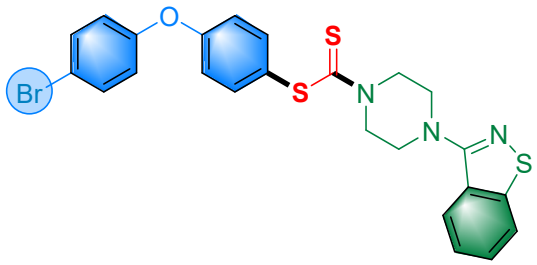
41.5 mg, 54%. Yellow solid.

R_f=0.42 (petroleum ether/ethyl acetate =9:1 (v:v))

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.37 (d, *J* = 4.8 Hz, 2H), 7.76 – 7.72 (m, 2H), 7.68 (d, *J* = 7.8

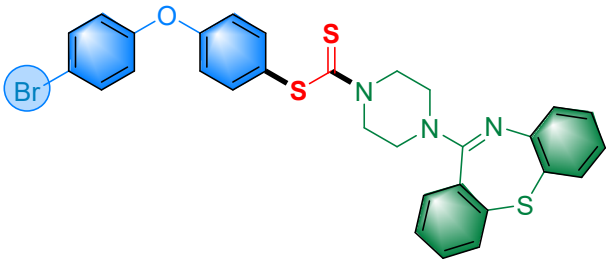
Hz, 1H), 7.58 (t, J = 7.8 Hz, 1H), 6.60 (t, J = 4.8 Hz, 1H), 4.29 (d, J = 97.0 Hz, 4H), 4.03 (s, 4H).
^{13}C NMR (101 MHz, Chloroform-*d*) δ 196.1, 161.1, 157.9, 140.5, 133.8 (q, J = 4.4 Hz), 132.2, 131.4 (q, J = 33.3 Hz), 129.5, 126.9 (q, J = 3.0 Hz), 123.6(q, J = 273.7 Hz), 110.8, 50.8 (d, J = 106.1 Hz), 43.0.
HRMS-ESI (m/z) $[M+Na]^+$ calculated for $C_{16}H_{15}F_3N_4NaS_2$ 407.0588, found 407.0594.

4-(4-bromophenoxy)phenyl-4-(benzo[d]isothiazol-3-yl)piperazine-1-carbodithioate (4av)



Following general procedure, thianthrenium salt **1s** (109.9 mg, 0.2 mmol), **CS_2** (36 μL, 0.6 mmol, 3.0 equiv.) and 3-(piperazin-1-yl)benzo[d]isothiazole (65.8 mg, 0.3 mmol, 1.5 equiv.) were used to afford the desired product **4av**.
74.7 mg, 69%. Yellow solid.
R_f=0.42 (petroleum ether/ethyl acetate =16:1 (v:v))
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.93 (d, J = 8.2 Hz, 1H), 7.85 (d, J = 8.1 Hz, 1H), 7.53-7.39 (m, 6H), 7.03 (d, J = 8.3 Hz, 2H), 6.98 (d, J = 8.4 Hz, 2H), 4.43 (d, J = 93.1 Hz, 4H), 3.74 (s, 4H).
^{13}C NMR (101 MHz, Chloroform-*d*) δ 198.3, 162.6, 159.0, 155.1, 152.9, 138.9, 132.9, 127.9, 127.6, 124.8, 124.3, 123.6, 121.6, 120.8, 118.7, 116.8, 51.1, 49.4.
HRMS-ESI (m/z) $[M+Na]^+$ calculated for $C_{24}H_{20}BrN_3NaOS_3^+$ 563.9850, found 563.9854.

4-(4-bromophenoxy)phenyl-4-(dibenzo[b,f][1,4]thiazepin-11-yl)piperazine-1-carbodithioate (4aw)



Following general procedure, thianthrenium salt **1s** (109.9 mg, 0.2 mmol), **CS_2** (36 μL, 0.6 mmol, 3.0 equiv.) and 11-(piperazin-1-yl)dibenzo[b,f][1,4]thiazepine (110.5 mg, 0.3 mmol, 1.5 equiv.) were used to afford the desired product **4aw**.
65.4 mg, 53%. Yellow solid.

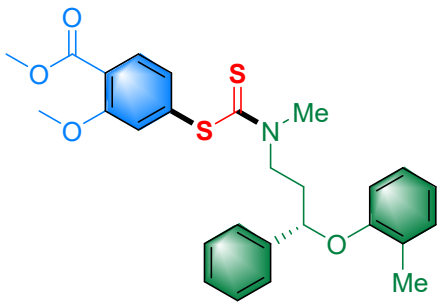
R_f=0.36 (petroleum ether/ethyl acetate =20:1 (v:v))

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.55 – 7.31 (m, 9H), 7.21 (t, *J* = 7.5 Hz, 1H), 7.13 (d, *J* = 7.9 Hz, 1H), 7.02 – 6.92 (m, 5H), 4.53 – 3.48 (m, 8H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 198.1, 160.5, 159.0, 155.2, 148.1, 140.2, 138.9, 133.6, 133.0, 132.4, 132.4, 131.4, 129.3, 128.9, 128.6, 128.1, 125.4, 124.9, 123.6, 121.6, 118.7, 116.8, 48.6 (d, *J* = 397.9 Hz).

HRMS-ESI (m/z) $[M+H]^+$ calculated for $C_{30}H_{25}BrN_3OS_3$ 618.0343, found 618.0346.

Methyl(S)-2-methoxy-4-((methyl(3-phenyl-3-(o-tolyloxy)propyl)carbamothioyl) thio)benzoate (4ax)



Following general procedure, thianthrenium salt **1b** (93.6 mg, 0.2 mmol), **CS_2** (36 *μL*, 0.6 mmol, 3.0 equiv.) and (S)-N-methyl-3-phenyl-3-(o-tolyloxy)propan-1-amine (87.5mg, 0.3 mmol, 1.5 equiv.) were used to afford the desired product **4ax**.

74.3 mg, 75%. Yellow solid.

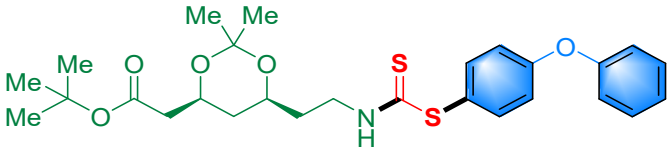
R_f=0.36 (petroleum ether/ethyl acetate =5:1 (v:v))

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.85 (dd, *J* = 23.1, 2.3 Hz, 1H), 7.51 – 7.21 (m, 6H), 7.12 (dd, *J* = 7.5, 3.6 Hz, 1H), 7.03 – 6.87 (m, 2H), 6.78 (q, *J* = 7.4 Hz, 1H), 6.58 (dd, *J* = 8.3, 3.1 Hz, 1H), 5.28 – 5.18 (m, 1H), 4.32 – 4.01 (m, 2H), 3.93 (s, 3H), 3.86 (s, 3H), 3.44 (d, *J* = 30.0 Hz, 3H), 2.37 (d, *J* = 11.4 Hz, 5H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 197.6 (d, *J* = 21.2 Hz), 165.6, 160.7 (d, *J* = 4.0 Hz), 155.6 (d, *J* = 13.1 Hz), 142.6, 141.0 (d, *J* = 49.5 Hz), 140.5, 136.4 (d, *J* = 177.8 Hz), 130.8 (d, *J* = 11.1 Hz), 128.8 (d, *J* = 21.2 Hz), 127.9 (d, *J* = 25.3 Hz), 126.9, 126.7, 125.6 (d, *J* = 6.1 Hz), 122.4 (d, *J* = 13.1 Hz), 120.5 (d, *J* = 17.2 Hz, 2C), 112.7, 76.6, 56.2, 53.5 (d, *J* = 318.2 Hz), 52.1, 42.3 (d, *J* = 370.7 Hz), 35.9 (d, *J* = 119.2 Hz), 16.7 (d, *J* = 6.1 Hz).

HRMS-ESI (m/z) $[M+Na]^+$ calculated for $C_{27}H_{29}NNaO_4S_2$ 518.1436, found 518.1437.

Tert-butyl 2-((4S,6S)-2,2-dimethyl-6-(2-((((4-phenoxyphenyl)thio)carbonothioyl) amino)ethyl)-1,3-dioxan-4-yl)acetate (4ay)



Following general procedure, thianthrenium salt **1a** (94.4 mg, 0.2 mmol), **CS_2** (36 μL, 0.6 mmol, 3.0 equiv.) and tert-butyl 2-((4S,6S)-6-(2-aminoethyl)-2,2-dimethyl-1,3-dioxan-4-yl)acetate (55 μL, 0.3 mmol, 1.5 equiv.) were used to afford the desired product **4ay**.

72.4 mg, 70%. Light yellow oil.

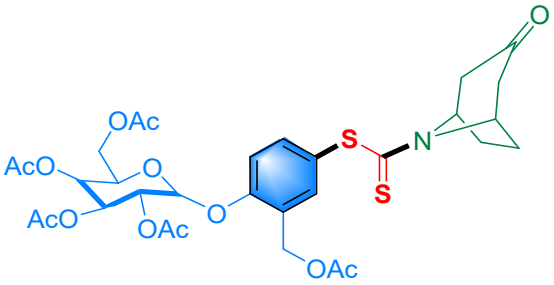
R_f=0.38 (petroleum ether/ethyl acetate =6:1 (v:v))

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.48 (d, *J* = 8.7 Hz, 2H), 7.41 (t, *J* = 8.0 Hz, 2H), 7.22 (t, *J* = 7.5 Hz, 2H), 7.08 (d, *J* = 8.2 Hz, 2H), 7.03 (d, *J* = 8.7 Hz, 2H), 4.23 – 4.16 (m, 2H), 3.93 – 3.84 (m, 2H), 3.74 – 3.64 (m, 1H), 2.47 – 2.38 (m, 1H), 2.34 – 2.26 (m, 1H), 1.88 – 1.80 (m, 1H), 1.62 – 1.51 (m, 2H), 1.44 (s, 9H), 1.36 (s, 3H), 1.22 (s, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 195.4, 170.1, 160.4, 155.2, 137.3, 130.2, 124.9, 121.9, 120.3, 119.0, 98.8, 80.7, 67.9, 66.1, 43.9, 42.5, 36.1, 34.1, 30.0, 28.1, 19.7.

HRMS-ESI (m/z) $[M+Na]^+$ calculated for $C_{27}H_{35}NNaO_5S_2$ 540.1854, found 540.1853.

(2R,4S,5R)-2-(acetoxymethyl)-6-(2-(acetoxymethyl)-4-((3-oxo-8-azabicyclo[3.2.1]octane-8-carbonothioyl)thio)phenoxy)tetrahydro-2H-pyran-3,4,5-triyl triacetate (4az)



Following general procedure, thianthrenium salt **1aa** (159.6 mg, 0.2 mmol), **CS_2** (36 μL, 0.6 mmol, 3.0 equiv.) and 8-azabicyclo[3.2.1]octan-3-one (35 μL, 0.3 mmol, 1.5 equiv.) were used to afford the desired product **4az**.

84.8 mg, 61%. Light yellow solid.

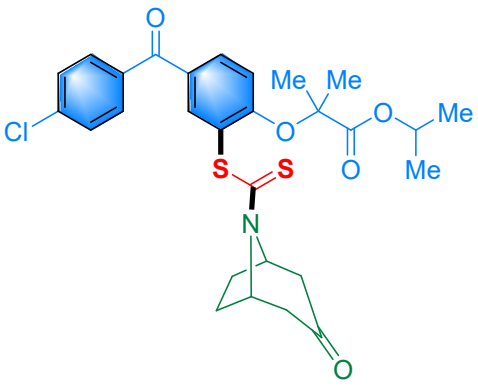
R_f=0.32 (petroleum ether/ethyl acetate =2:1 (v:v))

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.49 (d, *J* = 2.0 Hz, 1H), 7.43 (dd, *J* = 8.5, 2.2 Hz, 1H), 7.15 (d, *J* = 8.6 Hz, 1H), 5.53 (t, *J* = 6.1 Hz, 1H), 5.37 – 5.30 (m, 2H), 5.22 – 5.17 (m, 2H), 5.14 – 5.05 (m, 3H), 4.29 (dd, *J* = 12.3, 5.4 Hz, 1H), 4.20 (dd, *J* = 12.3, 2.4 Hz, 1H), 3.95 – 3.90 (m, 1H), 3.10 (dd, *J* = 16.2, 4.8 Hz, 1H), 2.94 (dd, *J* = 16.2, 4.8 Hz, 1H), 2.55 – 2.34 (m, 3H), 2.27 – 2.21 (m, 1H), 2.11 (s, 6H), 2.08 (s, 3H), 2.06 (d, *J* = 3.3 Hz, 6H), 2.02 – 1.94 (m, 1H), 1.89 – 1.82 (m, 1H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 206.2, 192.9, 170.6, 170.6, 170.2, 169.4, 169.3, 155.9, 138.3, 137.8, 127.0, 124.3, 115.6, 98.7, 72.5, 72.2, 70.8, 68.2, 61.8, 60.6, 59.7, 57.0, 48.4, 47.4, 29.4, 27.0, 21.0, 20.7, 20.6 (3C).

HRMS-ESI (m/z) $[M+Na]^+$ calculated for $C_{31}H_{37}NNaO_{13}S_2$ 718.1604, found 718.1613.

Isopropyl-2-(4-(4-chlorobenzoyl)-2-(((1R,5S)-3-oxo-8-azabicyclo[3.2.1]octane-8-carbonothioyl)thio)phenoxy)-2-methylpropanoate (4ba)



Following general procedure, thianthrenium salt **1ac** (132.4 mg, 0.2 mmol), **CS_2** (36 μL, 0.6 mmol, 3.0 equiv.) and 8-azabicyclo[3.2.1]octan-3-one (35 μL, 0.3 mmol, 1.5 equiv.) were used to afford the desired product **4ba**.

63.7 mg, 57%. Yellow solid.

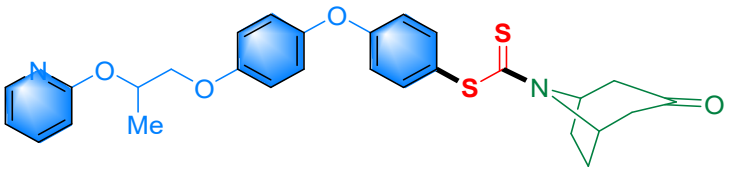
R_f=0.38 (petroleum ether/ethyl acetate =6:1 (v:v))

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.91 (d, *J* = 8.2 Hz, 2H), 7.79 – 7.77 (m, 2H), 7.48 – 7.45 (m, 2H), 6.82 (d, *J* = 8.4 Hz, 1H), 5.50 (t, *J* = 5.9 Hz, 1H), 5.16 – 5.12 (m, 1H), 5.11 – 5.06 (m, 1H), 3.15 – 3.09 (m, 1H), 3.03 – 2.97 (m, 1H), 2.55 – 2.22 (m, 3H), 2.00 – 1.94 (m, 1H), 1.89 – 1.82 (m, 1H), 1.64 (d, *J* = 12.1 Hz, 7H), 1.22 (dd, *J* = 6.3, 4.2 Hz, 6H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 206.5, 193.4, 191.6, 172.7, 160.2, 141.5, 138.7, 135.9, 133.8, 131.4, 130.3, 128.7, 120.8, 115.7, 69.6, 59.6, 57.5, 48.3, 47.3, 29.5, 27.2, 25.3, 24.8, 21.6 (d, *J* = 2.0 Hz).

HRMS-ESI (m/z) $[M+Na]^+$ calculated for $C_{28}H_{30}ClNNaO_5S_2^+$ 582.1152, found 582.1158.

4-(4-(2-(pyridin-2-yloxy)propoxy)phenoxy)phenyl-3-oxo-8-azabicyclo[3.2.1] octane-8-carbodithioate (4bb)



Following general procedure, thianthrenium salt **1ab** (107.2 mg, 0.2 mmol), **CS_2** (36 μL, 0.6 mmol, 3.0 equiv.) and 8-azabicyclo[3.2.1]octan-3-one (35 μL, 0.3 mmol, 1.5 equiv.) were used to afford the desired product **4bb**.

56.2 mg, 54%. Light yellow solid.

R_f=0.32 (petroleum ether/ethyl acetate =6:1 (v:v))

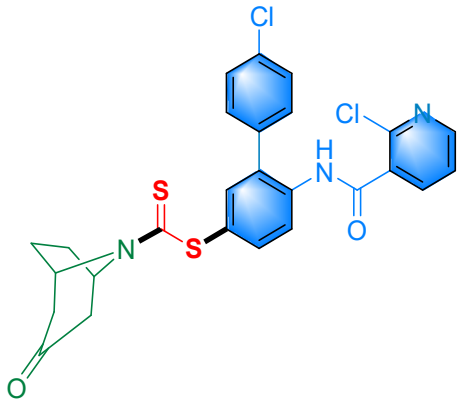
^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.16 (d, *J* = 5.0 Hz, 1H), 7.58 (t, *J* = 8.0 Hz, 1H), 7.40 (d, *J* = 8.4 Hz, 2H), 7.03 (d, *J* = 8.8 Hz, 2H), 6.97 (t, *J* = 8.0 Hz, 4H), 6.87 (t, *J* = 6.1 Hz, 1H), 6.76 (d, *J* = 8.3 Hz, 1H), 5.64 – 5.58 (m, 1H), 5.54 (t, *J* = 6.0 Hz, 1H), 5.12 (t, *J* = 5.9 Hz, 1H), 4.20 (dd, *J* = 9.9, 5.4 Hz, 1H), 4.09 (dd, *J* = 9.9, 4.8 Hz, 1H), 3.10 (dd, *J* = 16.2, 4.6 Hz, 1H), 2.93 (dd, *J* = 16.2, 4.0 Hz, 1H), 2.53 – 2.33 (m, 3H), 2.28 – 2.19 (m, 1H), 1.98 – 1.92 (m, 1H), 1.87 – 1.80 (m, 1H),

1.49 (d, *J* = 6.4 Hz, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 206.4, 193.9, 163.1, 160.8, 155.9, 148.9, 146.7, 138.9, 138.6, 122.6, 121.7, 117.5, 116.8, 115.9, 111.7, 71.0, 69.4, 59.7, 57.0, 48.4, 47.4, 29.4, 27.0, 17.0.

HRMS-ESI (m/z) $[M+Na]^+$ calculated for $C_{28}H_{28}N_2NaO_4S_2^+$ 543.1388, found 543.1381.

4'-chloro-6-(2-chloronicotinamido)-[1,1'-biphenyl]-3-yl(1R,5S)-3-oxo-8-azabicyclo[3.2.1]octane-8-carbodithioate (4bc)



Following general procedure, thianthrenium salt **1z** (128.8 mg, 0.2 mmol), **CS_2** (36 *μL*, 0.6 mmol, 3.0 equiv.) and 8-azabicyclo[3.2.1]octan-3-one (35 *μL*, 0.3 mmol, 1.5 equiv.) were used to afford the desired product **4bc**.

80.1 mg, 74%. Yellow solid.

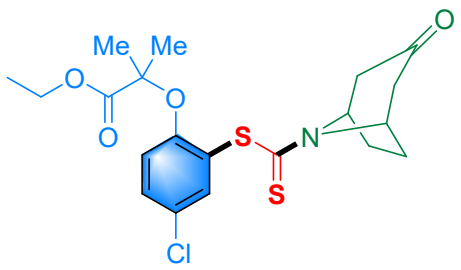
R_f=0.32 (petroleum ether/ethyl acetate =3:1 (v:v))

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.67 (d, *J* = 8.6 Hz, 1H), 8.47 (dd, *J* = 4.8, 2.0 Hz, 1H), 8.37 (s, 1H), 8.16 (dd, *J* = 7.8, 2.0 Hz, 1H), 7.59 (dd, *J* = 8.7, 2.2 Hz, 1H), 7.47 – 7.37 (m, 6H), 5.55 (t, *J* = 6.2 Hz, 1H), 5.14 (t, *J* = 5.9 Hz, 1H), 3.11 (dd, *J* = 12.1, 4.0 Hz, 1H), 2.94 (dd, *J* = 16.1, 4.0 Hz, 1H), 2.58 – 2.35 (m, 3H), 2.31 – 2.22 (m, 1H), 2.01 – 1.94 (m, 1H), 1.90 – 1.83 (m, 1H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 206.2, 192.7, 162.5, 151.5, 146.5, 140.3, 138.7, 137.3, 136.4, 135.0, 134.9, 132.2, 130.9, 130.8, 129.5, 126.1, 123.0, 121.8, 59.7, 57.1, 48.4, 47.4, 29.4, 27.0.

HRMS-ESI (m/z) $[M+Na]^+$ calculated for $C_{26}H_{21}Cl_2N_3NaO_2S_2^+$ 564.0350, found 564.0343.

Ethyl-2-(4-chloro-2-((3-oxo-8-azabicyclo[3.2.1]octane-8-carbonothioyl)thio)phenoxy)-2-methylpropanoate (4bd)



Following general procedure, thianthrenium salt **1t** (91.4 mg, 0.2 mmol), **CS_2** (36 *μL*, 0.6 mmol, 3.0

equiv.) and 8-azabicyclo[3.2.1]octan-3-one (35 μL, 0.3 mmol, 1.5 equiv.) were used to afford the desired product **4bd**.

58.2 mg, 66%. Light yellow solid.

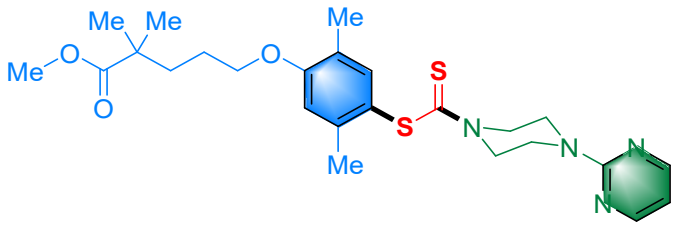
R_f=0.40 (petroleum ether/ethyl acetate =9:1 (v:v))

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.48 (d, *J* = 2.7 Hz, 1H), 7.33 (dd, *J* = 8.8, 2.7 Hz, 1H), 6.72 (d, *J* = 8.9 Hz, 1H), 5.50 (t, *J* = 6.1 Hz, 1H), 5.12 (t, *J* = 6.0 Hz, 1H), 4.23 (q, *J* = 7.1 Hz, 2H), 3.15 – 3.09 (m, 1H), 3.01 – 2.95 (m, 1H), 2.54 – 2.30 (m, 3H), 2.27 – 2.21 (m, 1H), 1.99 – 1.93 (m, 1H), 1.89 – 1.82 (m, 1H), 1.58 (d, *J* = 12.8 Hz, 6H), 1.25 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 206.5, 191.5, 173.7, 155.2, 138.1, 131.5, 126.3, 122.7, 117.8, 80.0, 61.7, 59.6, 57.5, 48.4, 47.3, 29.5, 27.2, 25.3, 24.7, 14.1.

HRMS-ESI (m/z) $[M+Na]^+$ calculated for $C_{20}H_{24}ClNNaO_4S_2^+$ 464.0733, found 464.0735.

Methyl-5-(2,5-dimethyl-4-((4-(pyrimidin-2-yl)piperazine-1-carbonothioyl) thio)phenoxy)-2,2-dimethylpentanoate (4be)



Following general procedure, thianthrenium salt **1y** (95.8 mg, 0.2 mmol), **CS_2** (36 μL, 0.6 mmol, 3.0 equiv.) and 2-(piperazin-1-yl)pyrimidine (49.3mg, 0.3 mmol, 1.5 equiv.) were used to afford the desired product **4be**.

69.3 mg, 69%. Light yellow solid.

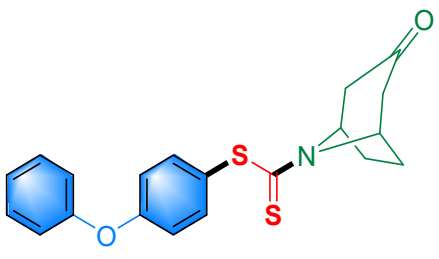
R_f=0.38 (petroleum ether/ethyl acetate =5:1 (v:v))

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.37 (d, *J* = 4.8 Hz, 2H), 7.27 (s, 1H), 6.76 (s, 1H), 6.60 (t, *J* = 4.8 Hz, 1H), 4.31 (d, *J* = 79.6 Hz, 4H), 4.02 (s, 4H), 3.97 (t, *J* = 5.5 Hz, 2H), 3.67 (s, 3H), 2.36 (s, 3H), 2.19 (s, 3H), 1.73 (dd, *J* = 4.5, 1.9 Hz, 4H), 1.23 (s, 6H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 198.2, 178.3, 160.9, 159.1, 157.8, 143.0, 139.4, 125.3, 120.1, 112.9, 110.7, 67.9, 51.8, 50.5, 43.2, 42.1, 37.1, 25.2, 25.1, 21.1, 15.7.

HRMS-ESI (m/z) $[M+Na]^+$ calculated for $C_{25}H_{34}N_4NaO_3S_2^+$ 525.1970, found 525.1971.

4-phenoxyphenyl 3-oxo-8-azabicyclo[3.2.1]octane-8-carbodithioate (4bf)



Following general procedure, thianthrenium salt **1a** (94.5 mg, 0.2 mmol), **CS_2** (36 μL, 0.6 mmol, 3.0 equiv.) and 8-azabicyclo[3.2.1]octan-3-one (38 μL, 0.3 mmol, 1.5 equiv.) were used to afford the desired product **4bf**.

52.4 mg, 71%. Yellow solid.

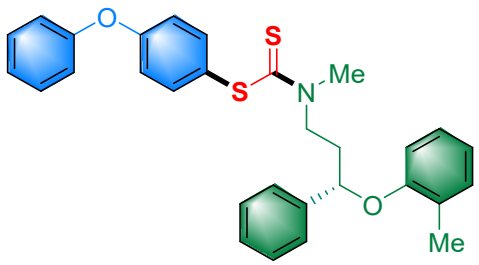
R_f=0.42 (petroleum ether/ethyl acetate =8:1 (v:v))

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.45 – 7.36 (m, 4H), 7.17 (t, *J* = 7.4 Hz, 1H), 7.10 (d, *J* = 7.8 Hz, 2H), 7.04 (d, *J* = 8.7 Hz, 2H), 5.53 (t, *J* = 6.2 Hz, 1H), 5.12 (t, *J* = 6.0 Hz, 1H), 3.13 – 3.07 (m, 1H), 2.96 – 2.90 (m, 1H), 2.53 – 2.32 (m, 3H), 2.28 – 2.19 (m, 1H), 1.98 – 1.91 (m, 1H), 1.87 – 1.80 (m, 1H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 206.4, 193.6, 159.8, 155.8, 138.7, 130.0, 124.4, 123.4, 120.1, 118.5, 59.7, 57.0, 48.4, 47.4, 29.5, 27.0.

HRMS-ESI (m/z) $[M+Na]^+$ calculated for $C_{20}H_{19}NNaO_2S_2^+$ 392.0755, found 392.0764.

4-phenoxyphenyl(S)-methyl(3-phenyl-3-(o-tolyloxy)propyl)carbamodithioate (4bg)



Following general procedure, thianthrenium salt **1a** (94.4 mg, 0.2 mmol), **CS_2** (36 μL, 0.6 mmol, 3.0 equiv.) and (S)-*N*-methyl-3-phenyl-3-(o-tolyloxy)propan-1-amine (76.6 mg, 0.3 mmol, 1.5 equiv.) were used to afford the desired product **4bg**.

61.9 mg, 62%. Yellow solid.

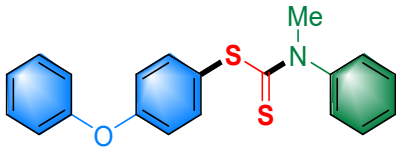
R_f=0.38 (petroleum ether/ethyl acetate =10:1 (v:v))

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.38 – 7.21 (m, 9H), 7.17 – 7.07 (m, 4H), 7.02 – 6.93 (m, 3H), 6.78 (q, *J* = 7.2 Hz, 1H), 6.58 (d, *J* = 8.2 Hz, 1H), 5.27 – 5.22 (m, 1H), 4.33 – 4.03 (m, 2H), 3.44 (d, *J* = 30.7 Hz, 3H), 2.47 – 2.33 (m, 5H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 198.0 (d, *J* = 18.2 Hz), 159.5, 156.0, 155.6 (d, *J* = 14.1 Hz), 141.1 (d, *J* = 49.5 Hz), 138.7 (d, *J* = 4.0 Hz), 130.8 (d, *J* = 12.1 Hz), 130.0, 128.8 (d, *J* = 20.2 Hz), 127.9 (d, *J* = 26.3 Hz), 126.9 (d, *J* = 4.0 Hz), 126.7, 125.6 (d, *J* = 6.1 Hz), 124.9 (d, *J* = 15.2 Hz), 124.2, 120.6 (d, *J* = 18.2 Hz), 120.0, 118.5 (d, *J* = 11.1 Hz), 112.6 (d, *J* = 17.2 Hz), 77.0 (d, *J* = 67.7 Hz), 53.5 (d, *J* = 315.1 Hz), 42.3 (d, *J* = 362.6 Hz), 35.9 (d, *J* = 117.2 Hz), 16.7 (d, *J* = 5.1 Hz).

HRMS-ESI (m/z) $[M+K]^+$ calculated for $C_{30}H_{29}KNO_2S_2^+$ 538.1277, found 538.1279.

4-phenoxyphenyl methyl(phenyl)carbamodithioate (4bh)



Following general procedure, thianthrenium salt **1a** (94.5 mg, 0.2 mmol), **CS_2** (36 μL, 0.6 mmol, 3.0 equiv.) and *N*-methylaniline (38 μL, 0.3 mmol, 1.5 equiv.) were used to afford the desired product **4bh**.

53.4 mg, 76%. Yellow solid.

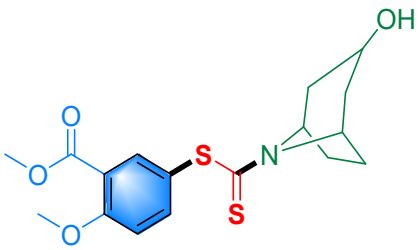
R_f=0.44 (petroleum ether/ethyl acetate =8:1 (v:v))

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.54 – 7.43 (m, 3H), 7.39 – 7.30 (m, 6H), 7.15 (t, *J* = 7.4 Hz, 1H), 7.08 (d, *J* = 7.9 Hz, 2H), 6.98 (d, *J* = 8.7 Hz, 2H), 3.79 (s, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 200.1, 159.3, 155.9, 144.9, 138.4, 129.9, 129.9, 129.2, 127.0, 125.9, 124.2, 120.1, 118.4, 46.7.

HRMS-ESI (m/z) $[M+Na]^+$ calculated for $C_{20}H_{17}NNaOS_2^+$ 374.0649, found 374.0646.

Methyl-5-((3-hydroxy-8-azabicyclo[3.2.1]octane-8-carbonothioyl)thio)-2-methoxy benzoate (4bi)



Following general procedure, thianthrenium salt **1b** (93.6 mg, 0.2 mmol), **CS_2** (36 μL, 0.6 mmol, 3.0 equiv.) and 8-azabicyclo[3.2.1]octan-3-ol (35 μL, 0.3 mmol, 1.5 equiv.) were used to afford the desired product **4bi**.

47.7 mg, 65%. Yellow solid.

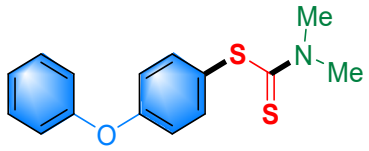
R_f=0.32 (petroleum ether/ethyl acetate =5:1 (v:v))

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.94 (d, *J* = 2.4 Hz, 1H), 7.59 (dd, *J* = 8.7, 2.4 Hz, 1H), 7.05 (d, *J* = 8.7 Hz, 1H), 5.31 – 5.28 (m, 1H), 4.86 – 4.83 (m, 1H), 4.20 (t, *J* = 4.8 Hz, 1H), 3.96 (s, 3H), 3.87 (s, 3H), 2.49 – 2.43 (m, 2H), 2.39 – 2.30 (m, 2H), 2.23 – 2.14 (m, 1H), 2.11 – 2.02 (m, 1H), 1.98 – 1.93 (m, 1H), 1.85 – 1.80 (m, 1H), 1.72 (s, 1H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 189.9, 165.6, 160.7, 142.6, 140.6, 121.6, 120.4, 112.6, 64.8, 60.4, 58.3, 56.2, 52.1, 39.4, 37.9, 28.2, 26.2.

HRMS-ESI (m/z) $[M+Na]^+$ calculated for $C_{17}H_{21}NNaO_4S_2^+$ 390.0810, found 390.0805.

4-phenoxyphenyl dimethylcarbamodithioate (4bj)



Following general procedure, thianthrenium salt **1a** (94.4 mg, 0.2 mmol), **CS_2** (36 μL, 0.6 mmol, 3.0 equiv.) and dimethylamine (10 μL, 0.3 mmol, 1.5 equiv.) were used to afford the desired product **4bj**.

38.7 mg, yield 67%. Yellow solid.

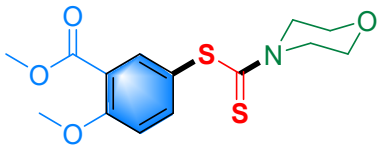
R_f=0.36 (eluent petroleum ether/ ethyl acetate =10:1, v/v).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.40 – 7.35 (m, 4H), 7.16 (t, *J* = 7.4 Hz, 1H), 7.09 (d, *J* = 7.6 Hz, 2H), 7.02 (d, *J* = 8.7 Hz, 2H), 3.55 (s, 3H), 3.48 (s, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 198.1, 159.5, 156.0, 138.7, 130.0, 125.0, 124.2, 120.0, 118.5, 45.8, 42.0.

HRMS-ESI (m/z) $[M+Na]^+$ calculated for $C_{15}H_{15}NNaOS_2^+$ 312.0493, found 312.0487.

Methyl 2-methoxy-5-((morpholine-4-carbonothioyl)thio)benzoate (4bk)



Following general procedure, thianthrenium salt **1b** (234.0 mg, 0.5 mmol), **CS_2** (90 μL, 1.5 mmol, 3.0 equiv.) and morpholine (66.3 μL, 0.75 mmol, 1.5 equiv.) were used to afford the desired product **4bk**.

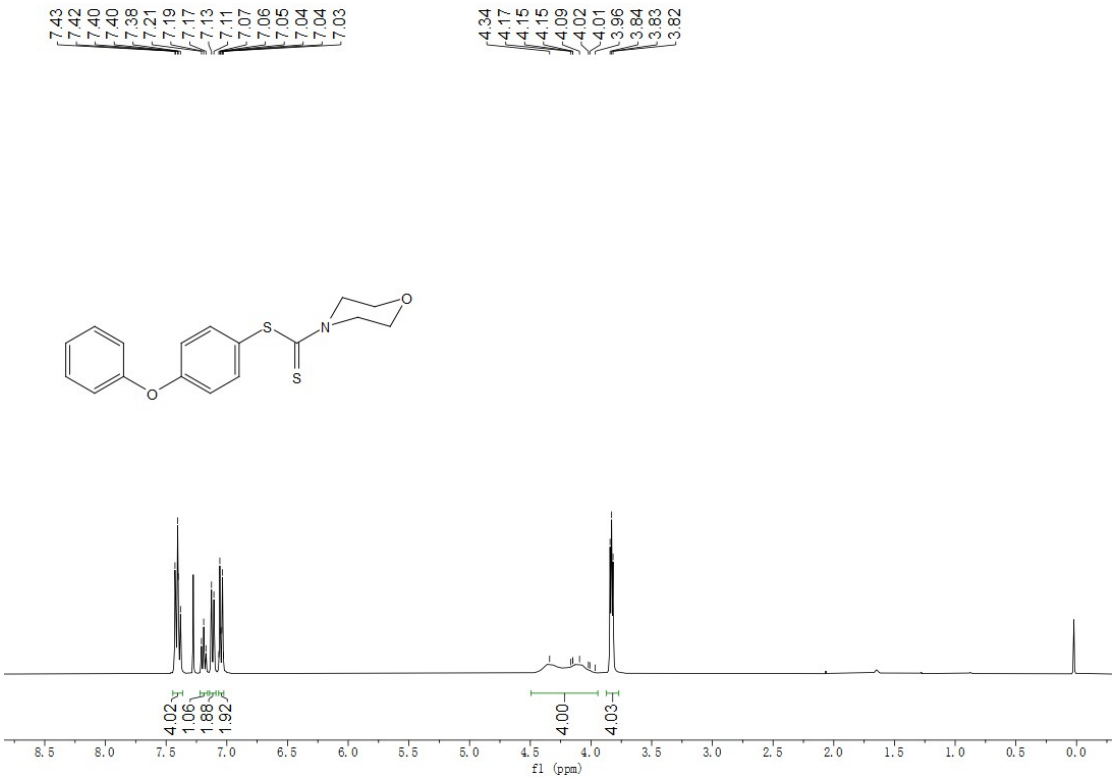
36.6 mg, 56%. Light yellow solid.

R_f=0.36 (petroleum ether/ethyl acetate =9:1 (v:v))

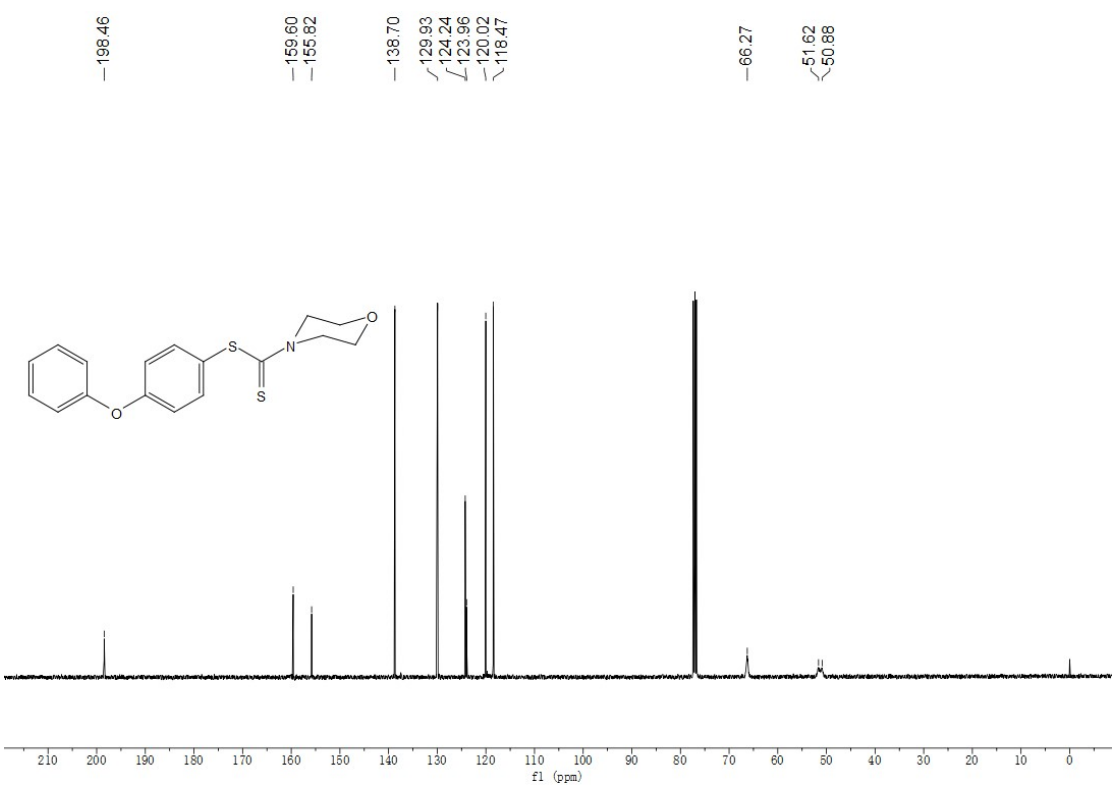
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.91 (d, *J* = 2.4 Hz, 1H), 7.56 (dd, *J* = 8.7, 2.4 Hz, 1H), 7.06 (d, *J* = 8.7 Hz, 1H), 4.35 – 4.06 (m, 4H), 3.96 (s, 3H), 3.88 (s, 3H), 3.82 (t, *J* = 6.0 Hz, 4H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 198.1, 165.5, 160.8, 142.6, 140.6, 121.6, 120.6, 112.7, 66.3, 56.2, 52.2, 51.4 (d, *J* = 86.9 Hz).

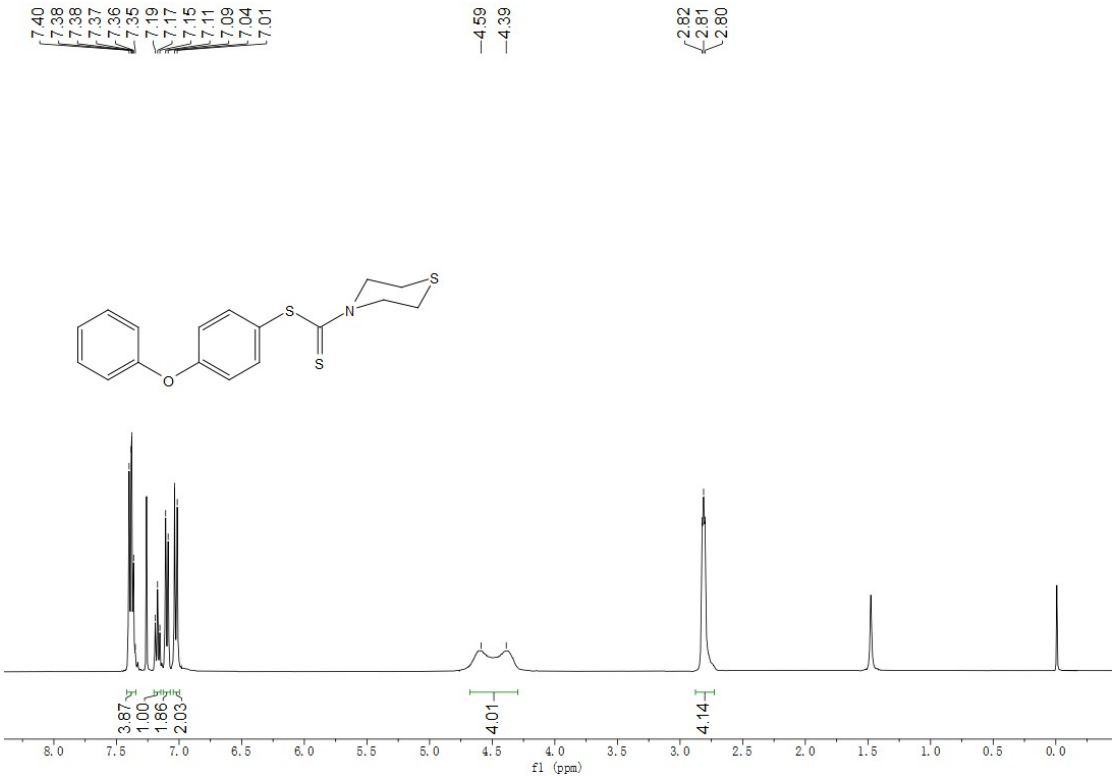
HRMS-ESI (m/z) $[M+Na]^+$ calculated for $C_{14}H_{17}NNaO_4S_2$ 350.0497, found 350.0490.



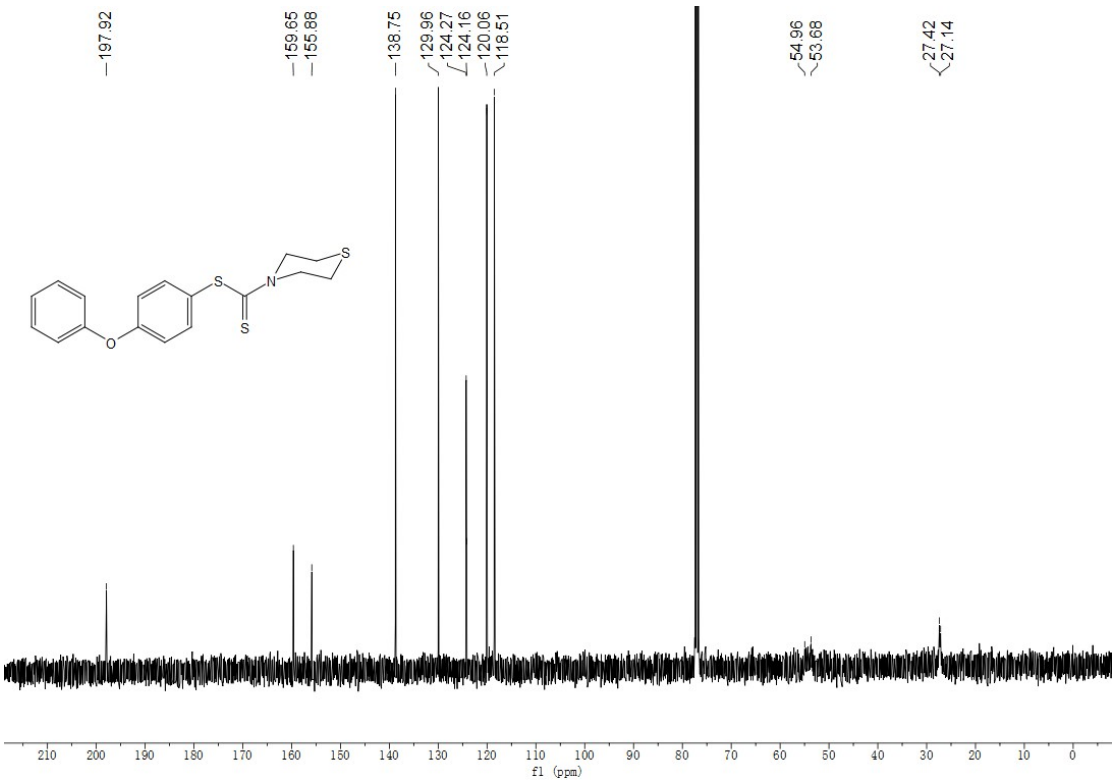
^{1}H NMR (400 MHz, Chloroform-*d*) of compound **4a.**



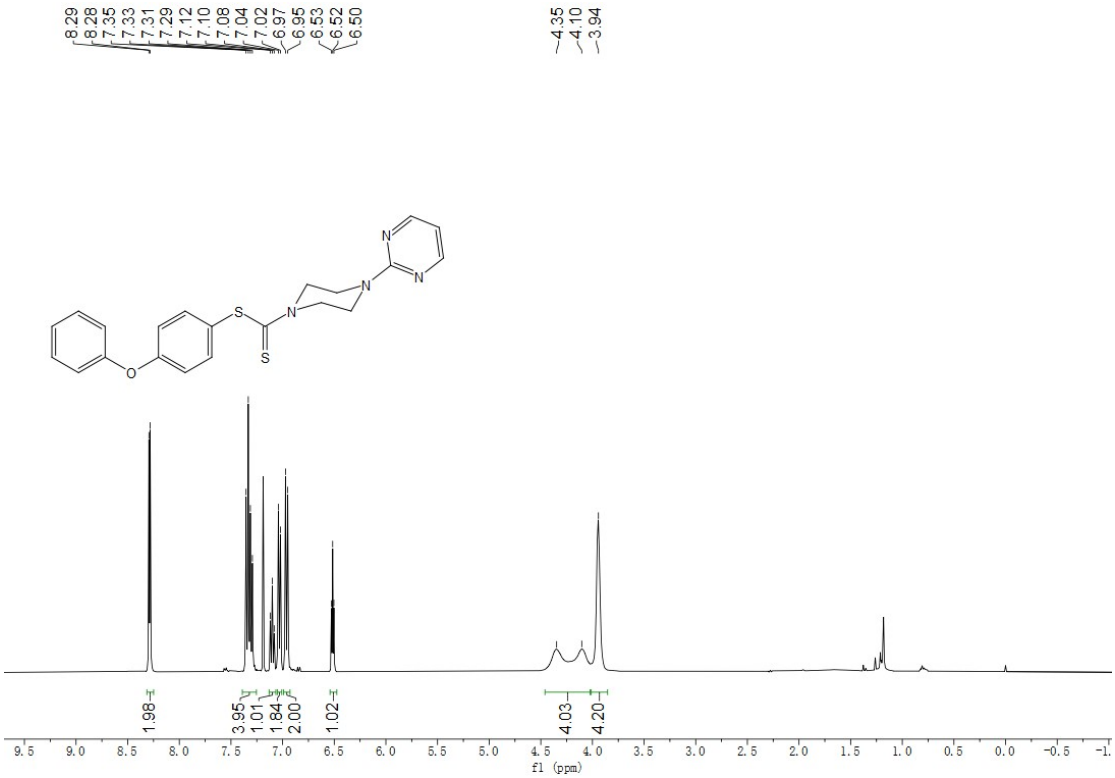
^{13}C NMR (400 MHz, Chloroform-*d*) of compound **4a.**



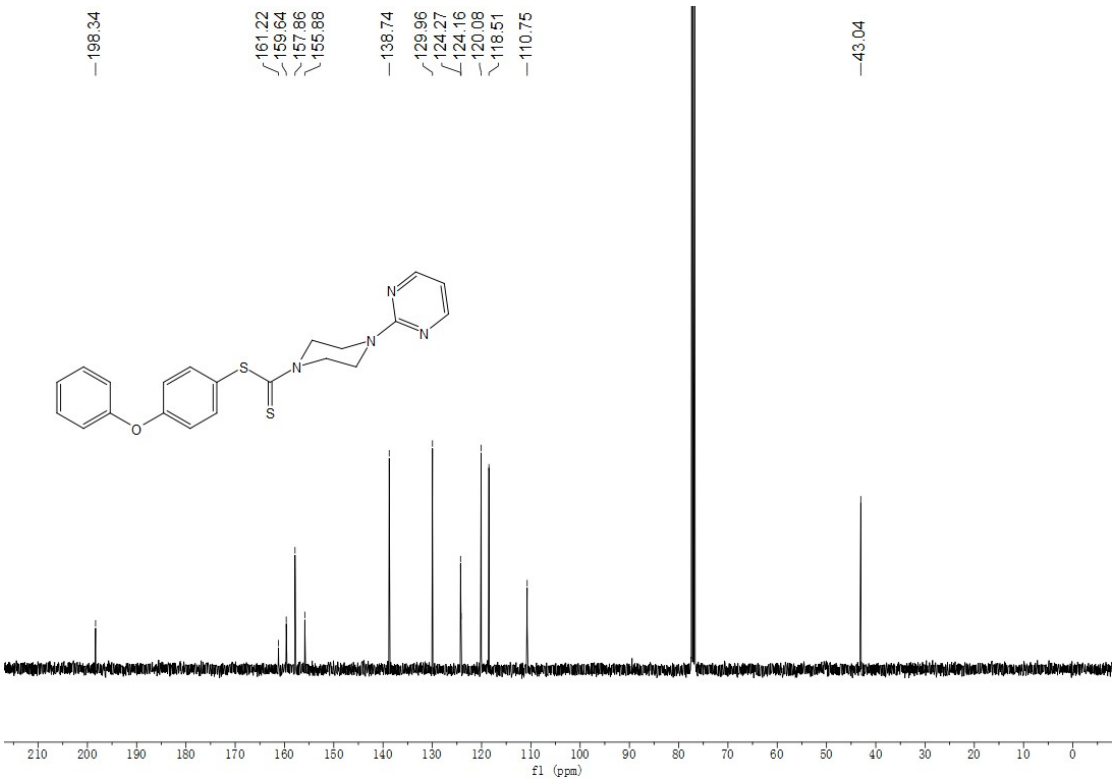
^{1}H NMR (400 MHz, Chloroform-*d*) of compound **4b.**



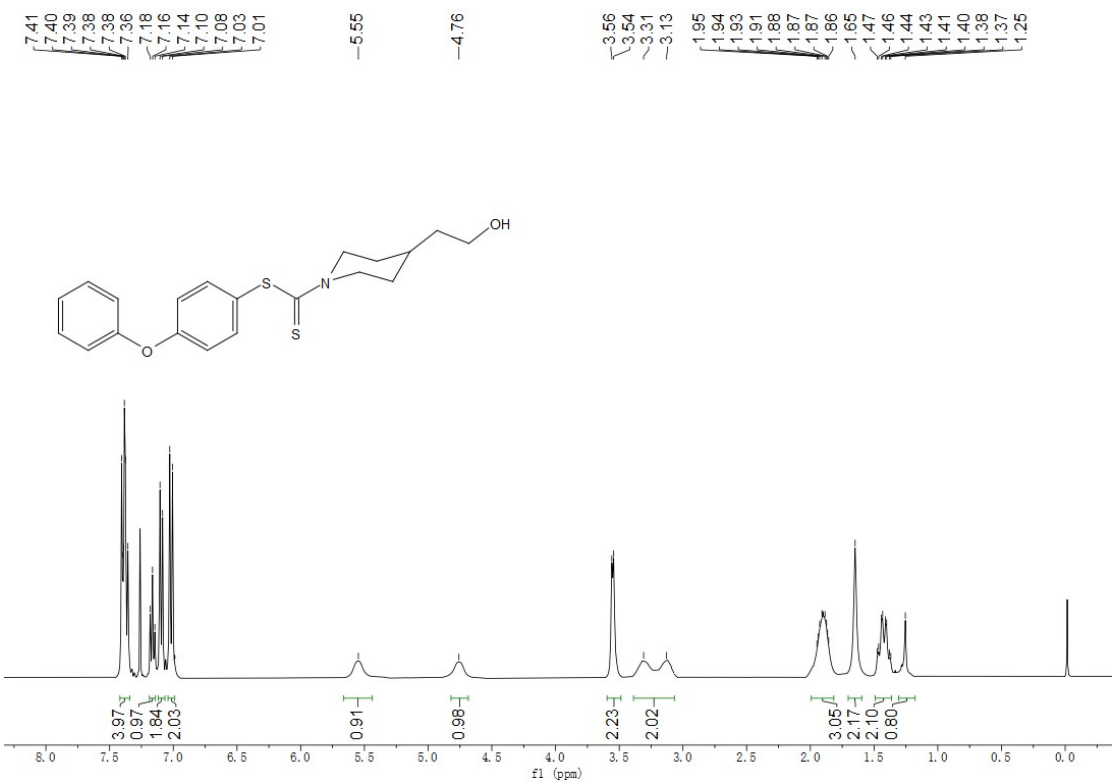
^{13}C NMR (400 MHz, Chloroform-*d*) of compound **4b.**



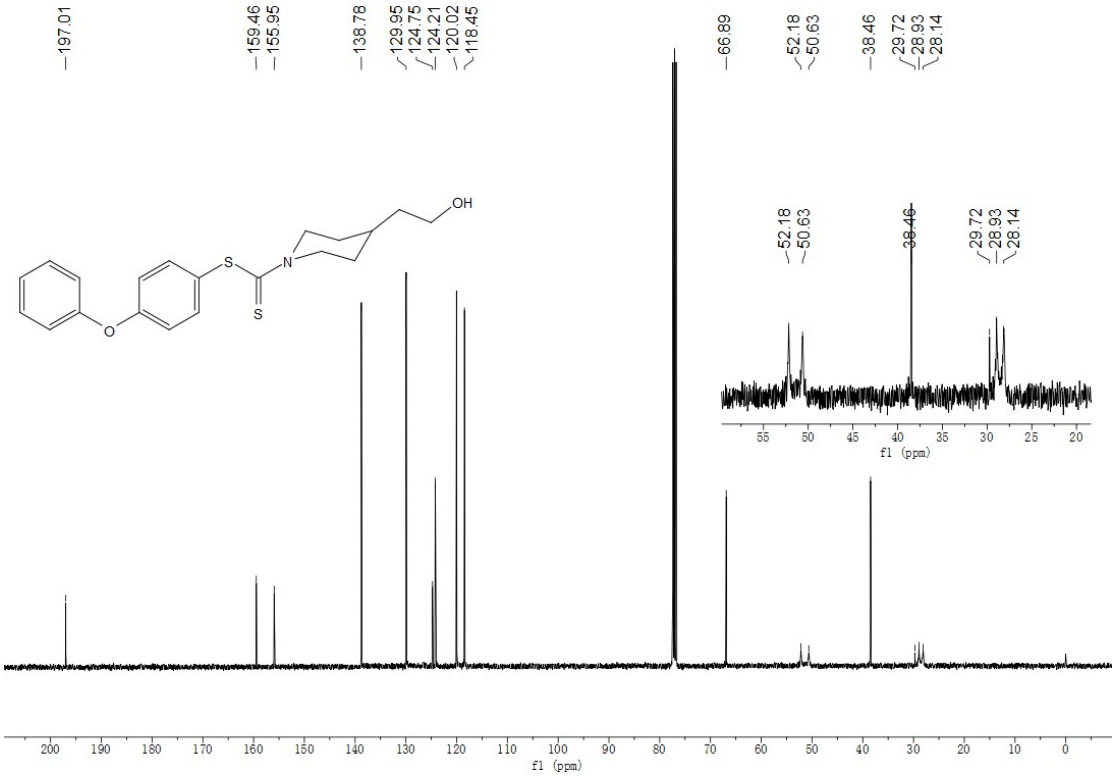
^{1}H NMR (400 MHz, Chloroform-*d*) of compound **4c.**



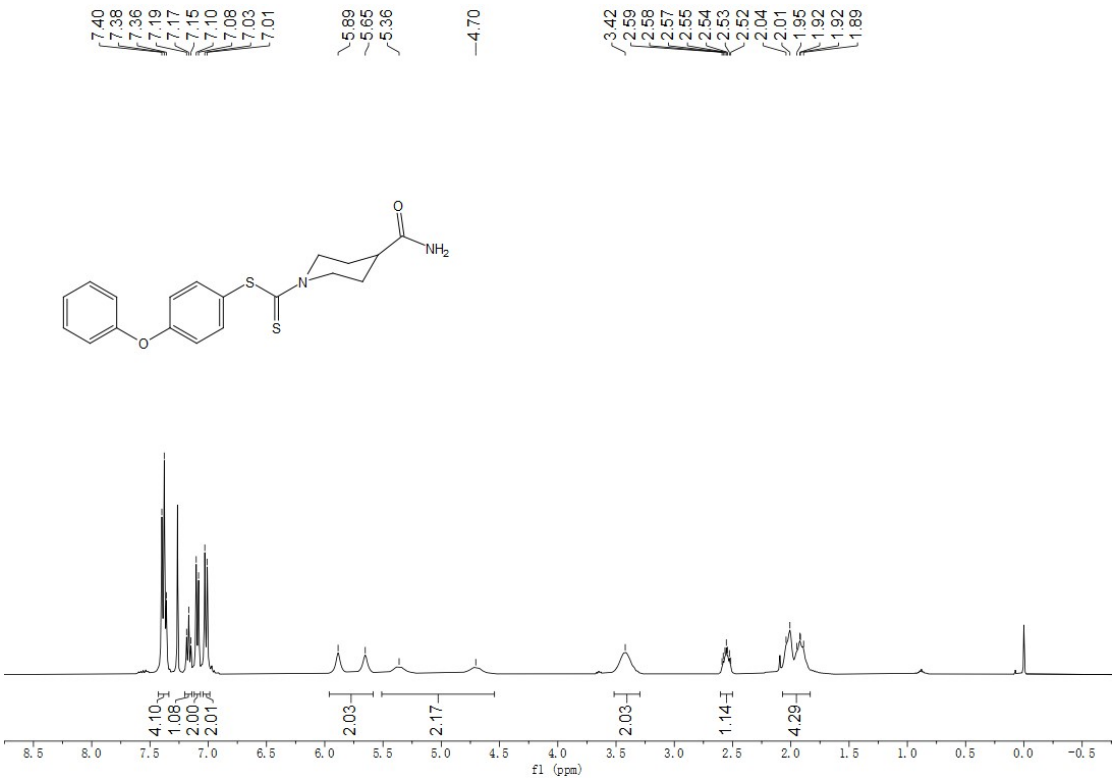
^{13}C NMR (400 MHz, Chloroform-*d*) of compound **4c.**



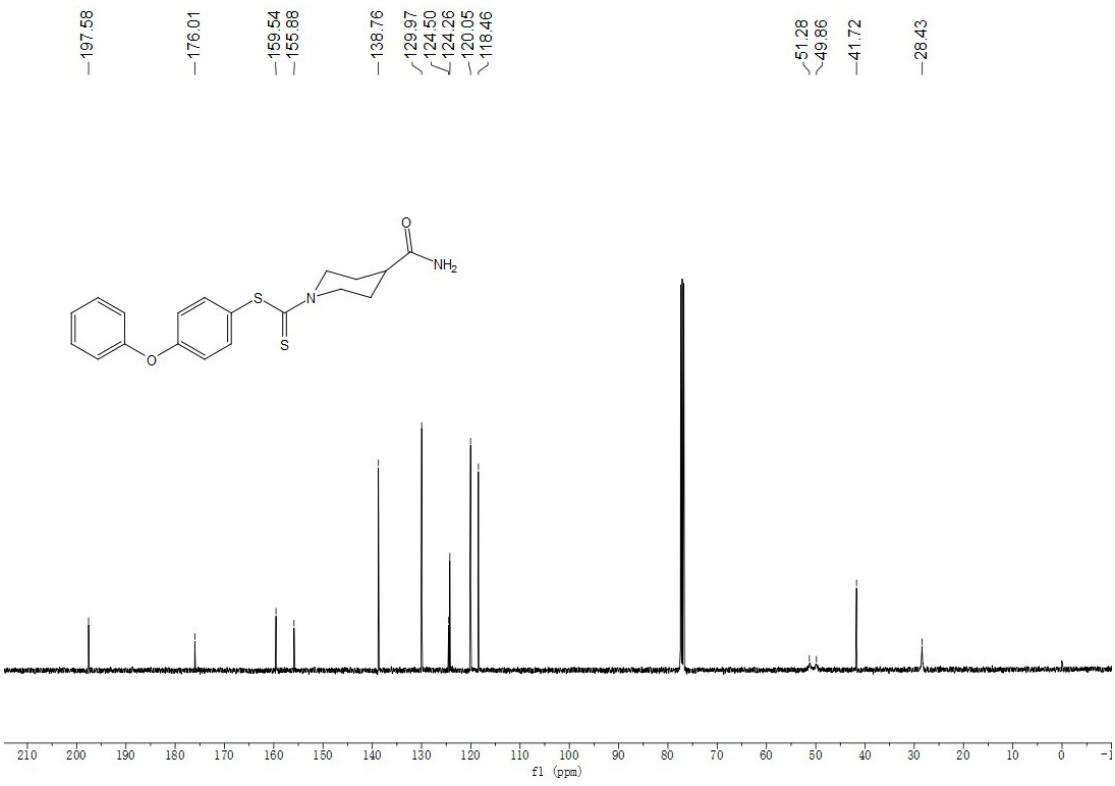
^{1}H NMR (400 MHz, Chloroform-*d*) of compound **4d.**



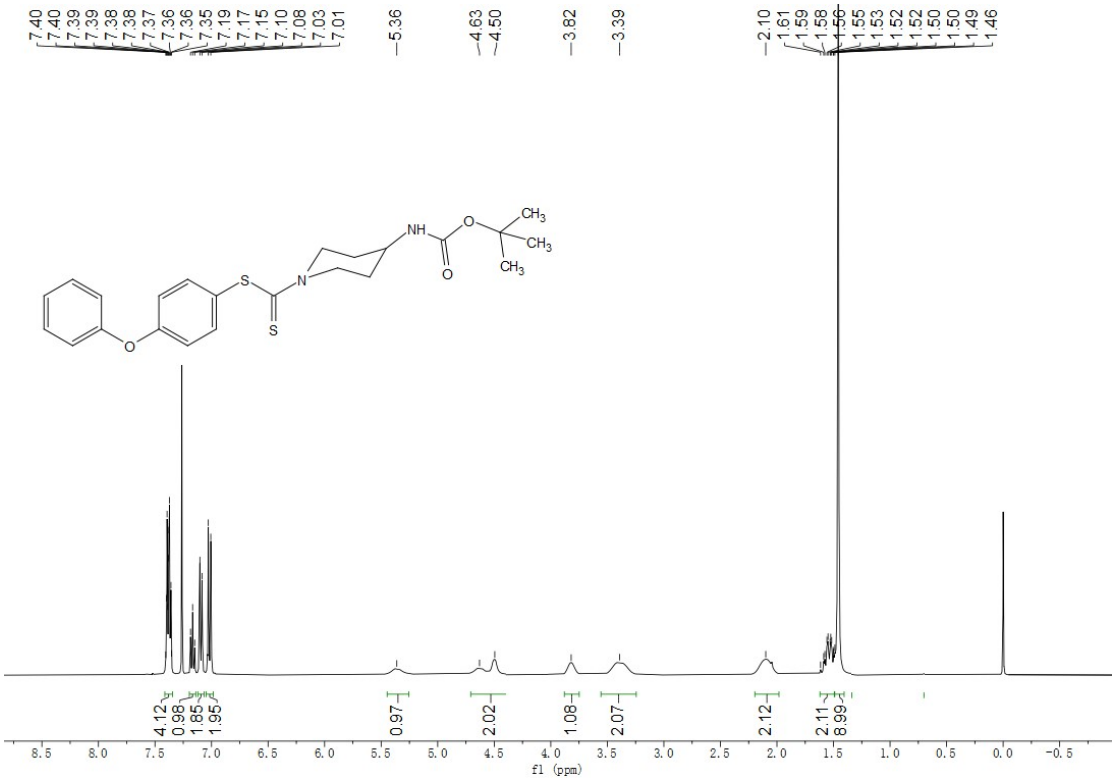
^{13}C NMR (400 MHz, Chloroform-*d*) of compound **4d.**



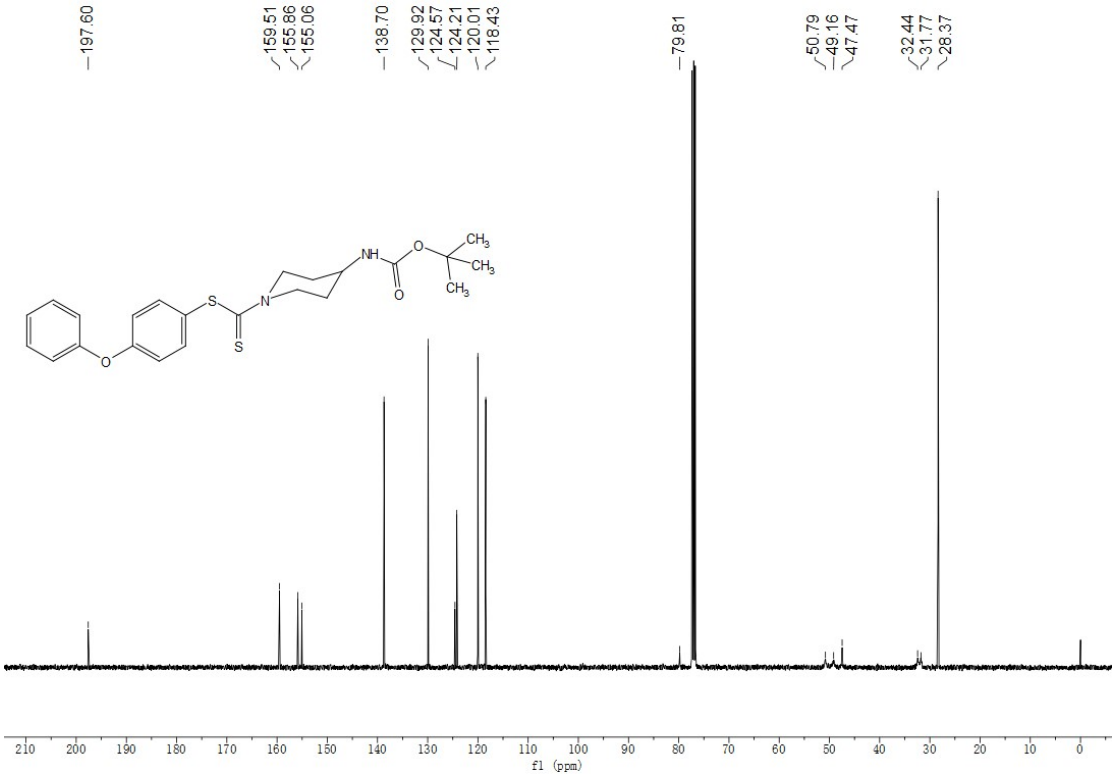
^{1}H NMR (400 MHz, Chloroform-*d*) of compound **4e.**



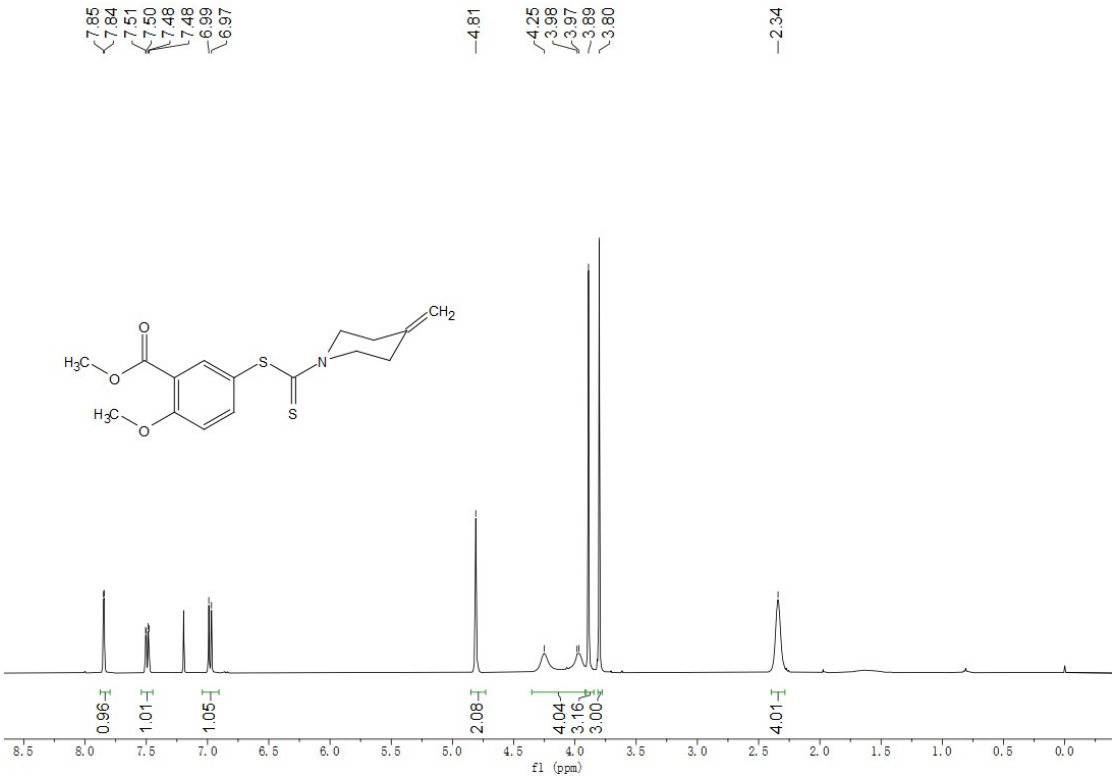
^{13}C NMR (400 MHz, Chloroform-*d*) of compound **4e.**



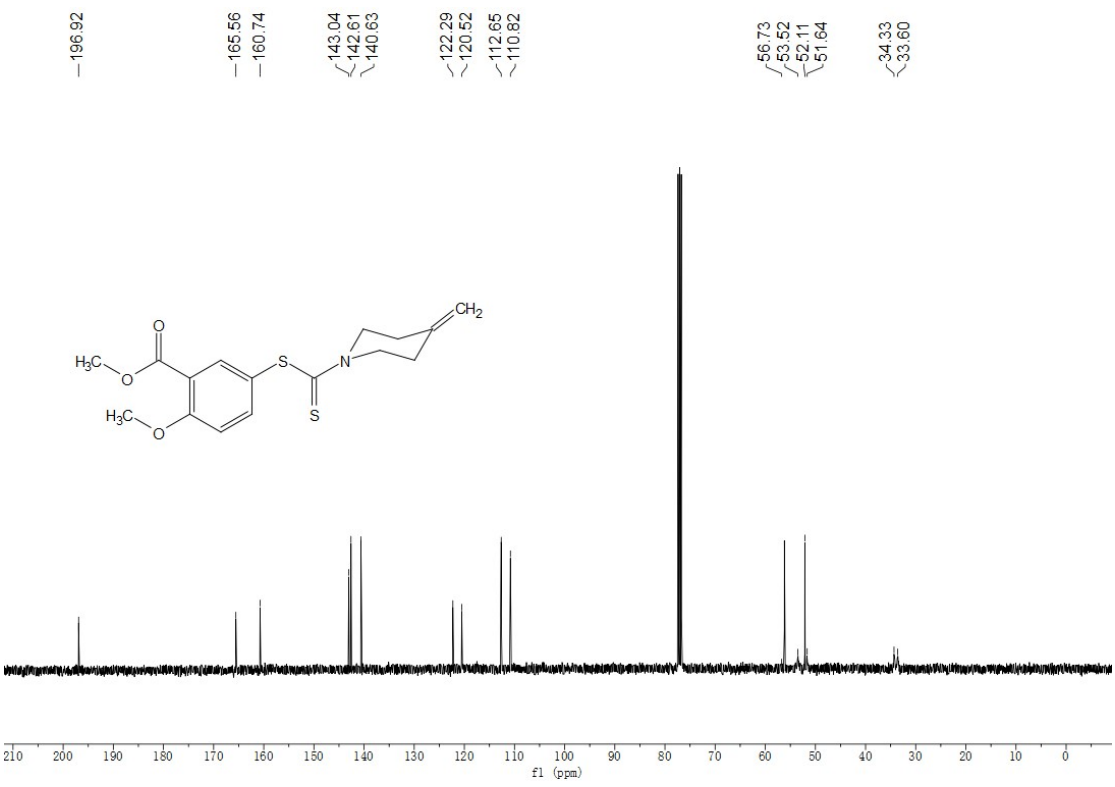
^{1}H NMR (400 MHz, Chloroform-*d*) of compound **4f.**



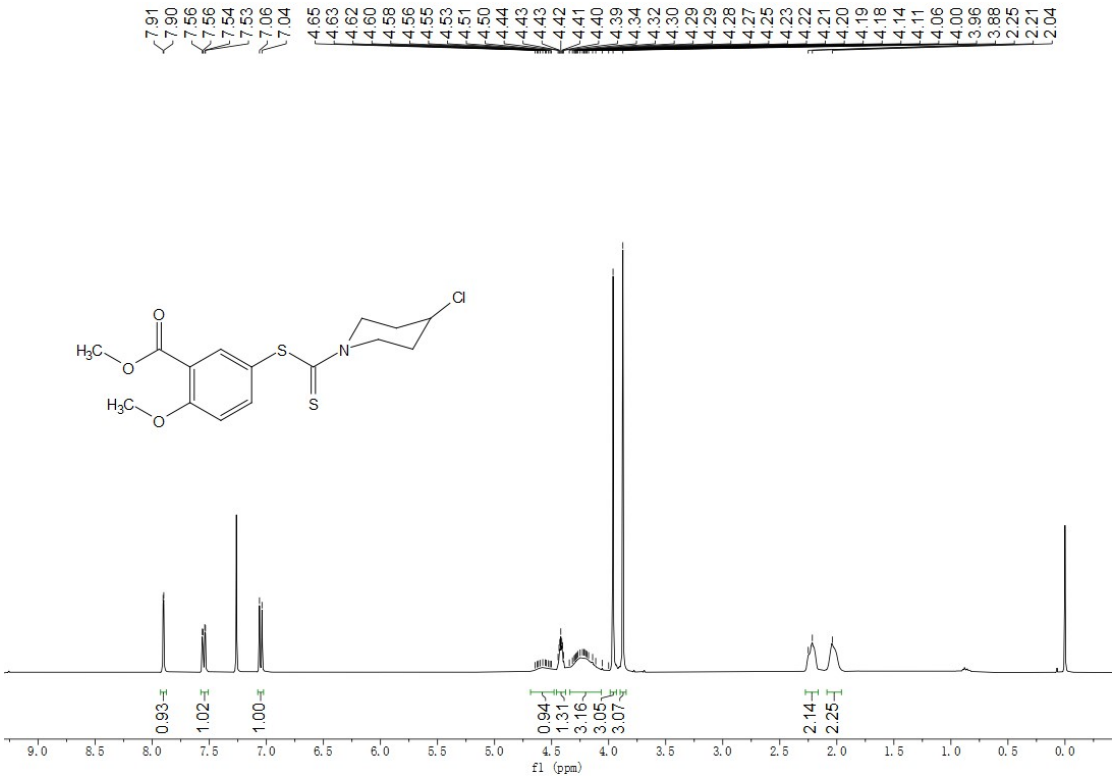
^{13}C NMR (400 MHz, Chloroform-*d*) of compound **4f.**



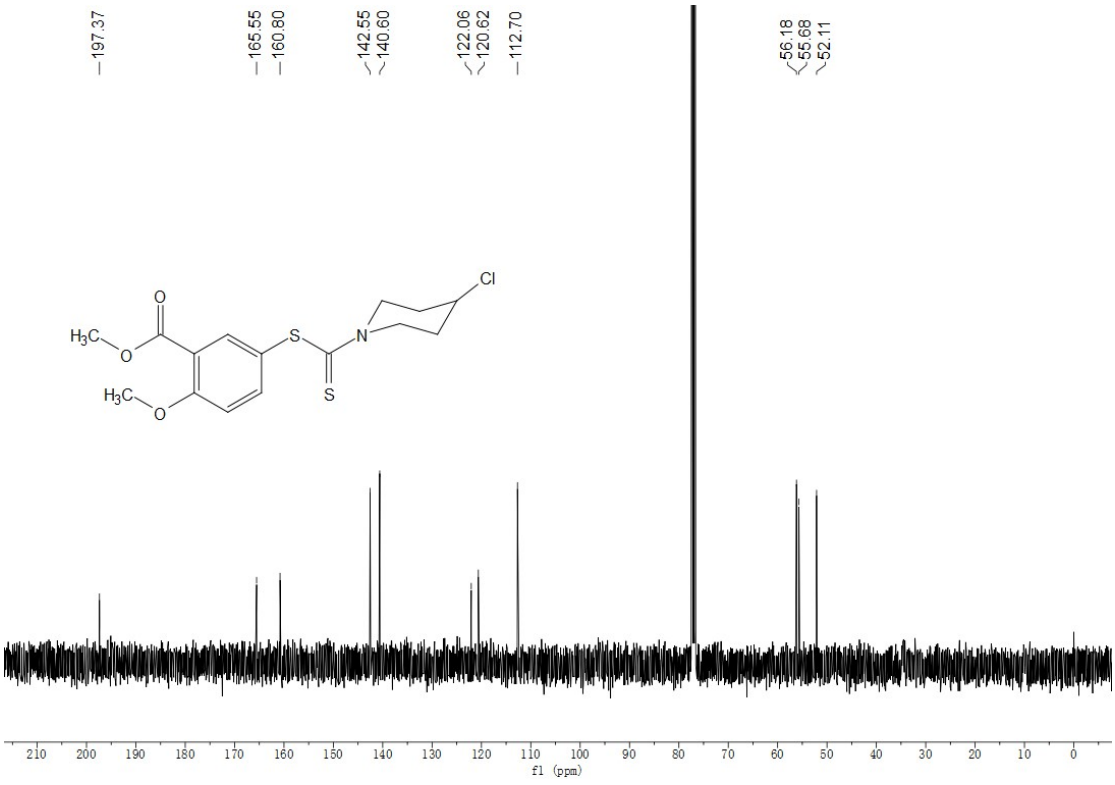
^{1}H NMR (400 MHz, Chloroform-*d*) of compound **4g.**



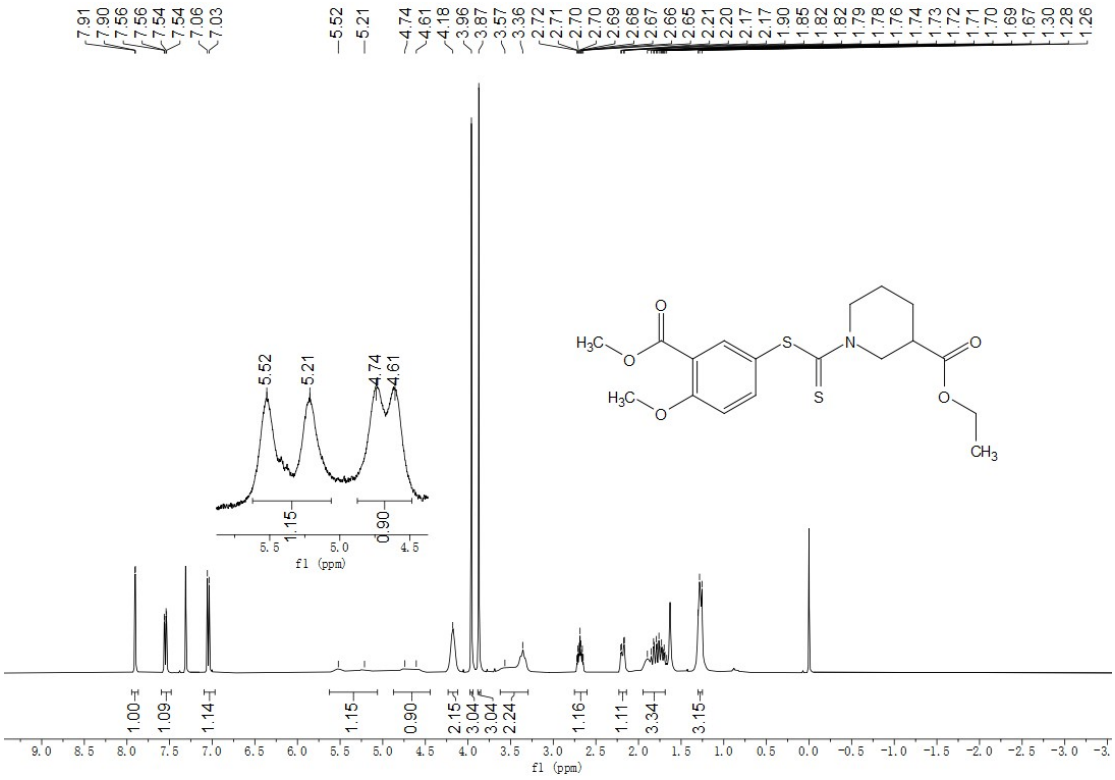
^{13}C NMR (400 MHz, Chloroform-*d*) of compound **4g.**



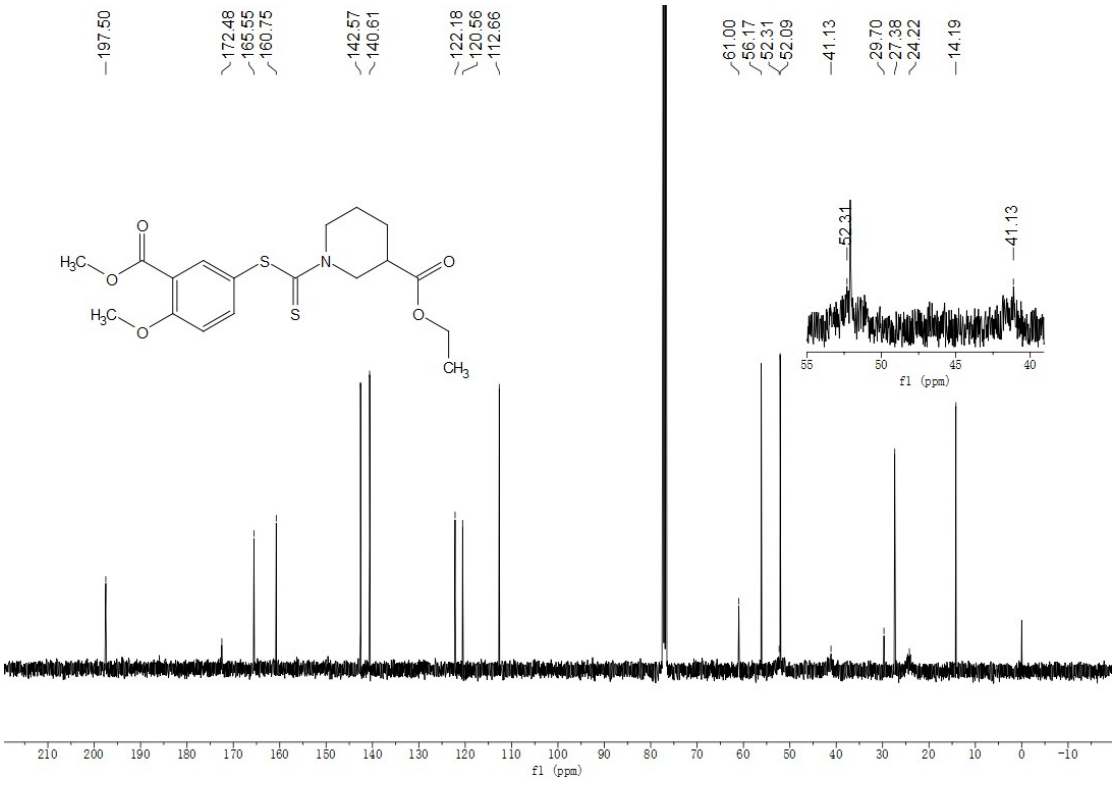
^{1}H NMR (400 MHz, Chloroform-*d*) of compound **4h.**



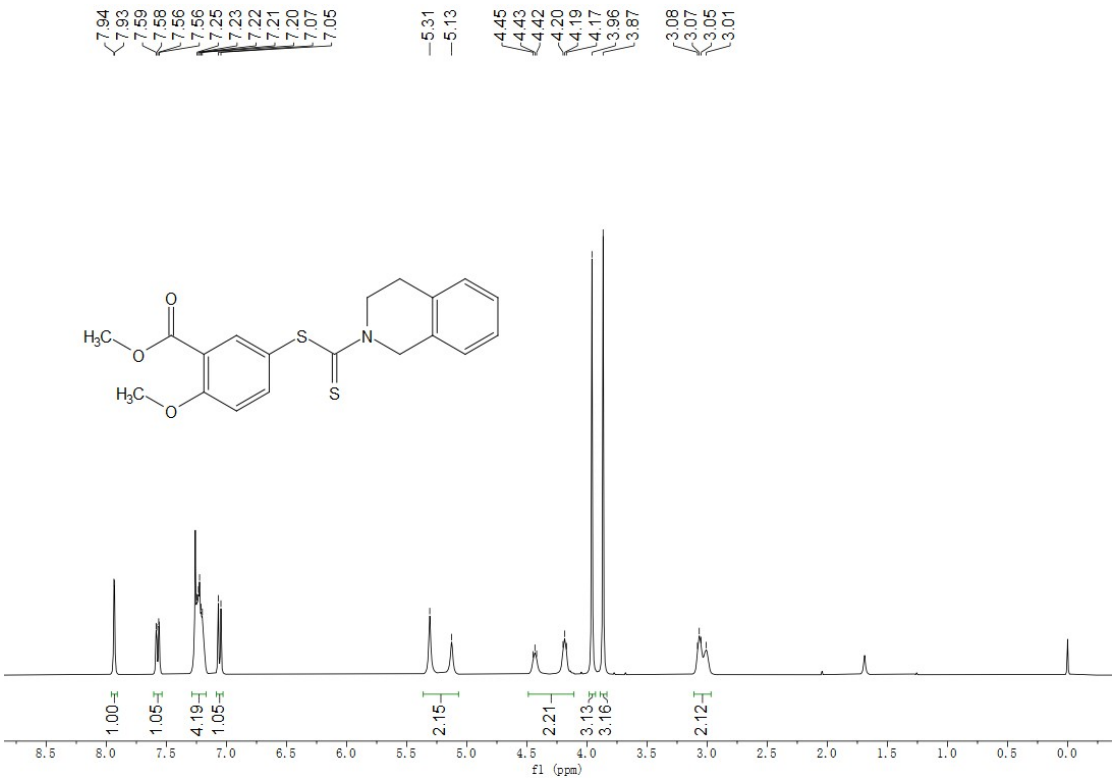
^{13}C NMR (400 MHz, Chloroform-*d*) of compound **4h.**



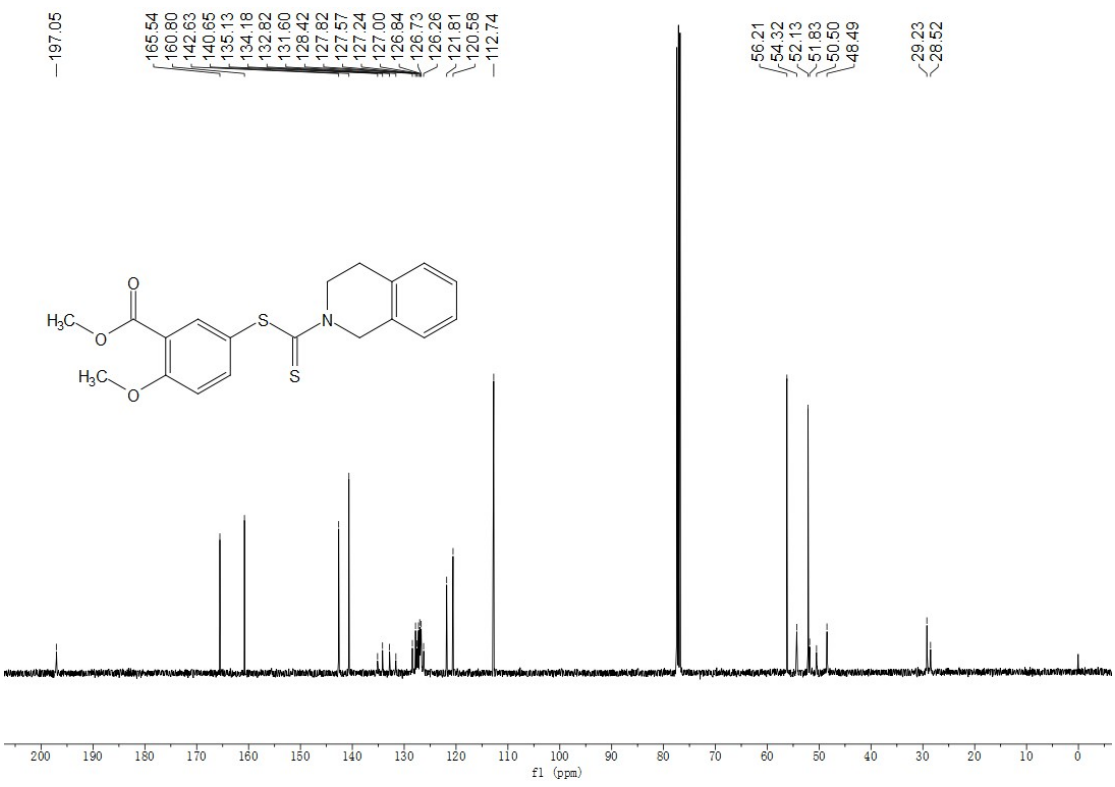
^{1}H NMR (400 MHz, Chloroform-*d*) of compound **4i.**



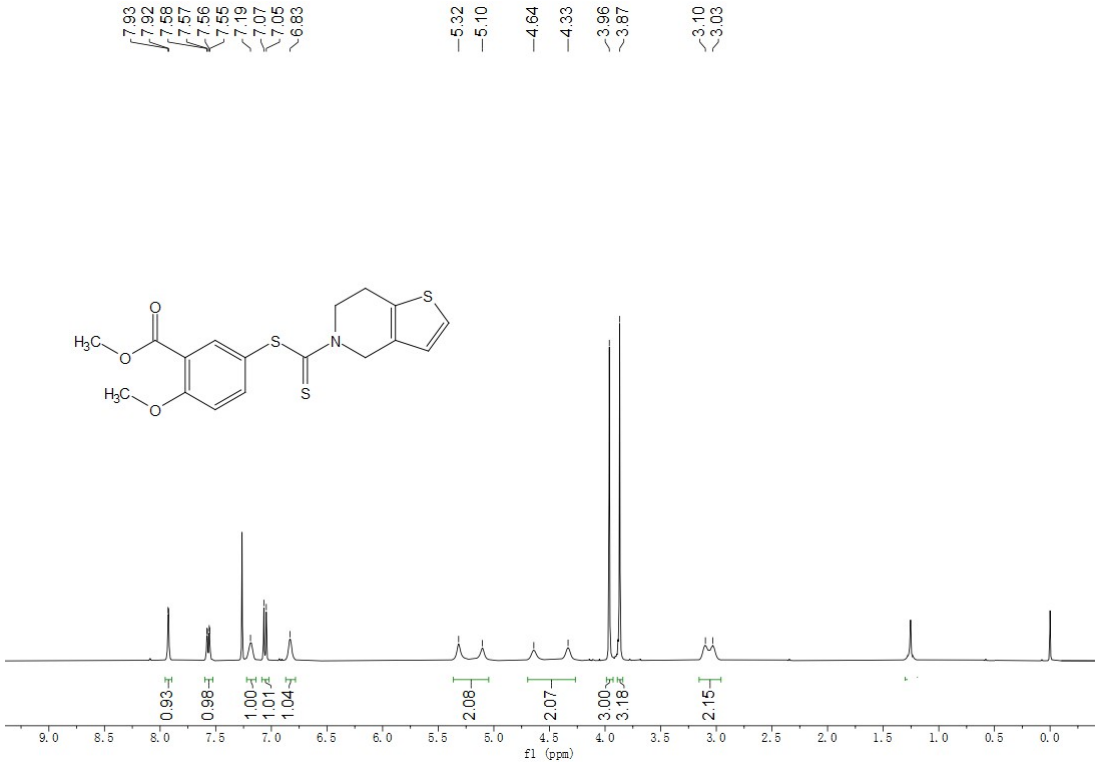
^{13}C NMR (400 MHz, Chloroform-*d*) of compound **4i.**



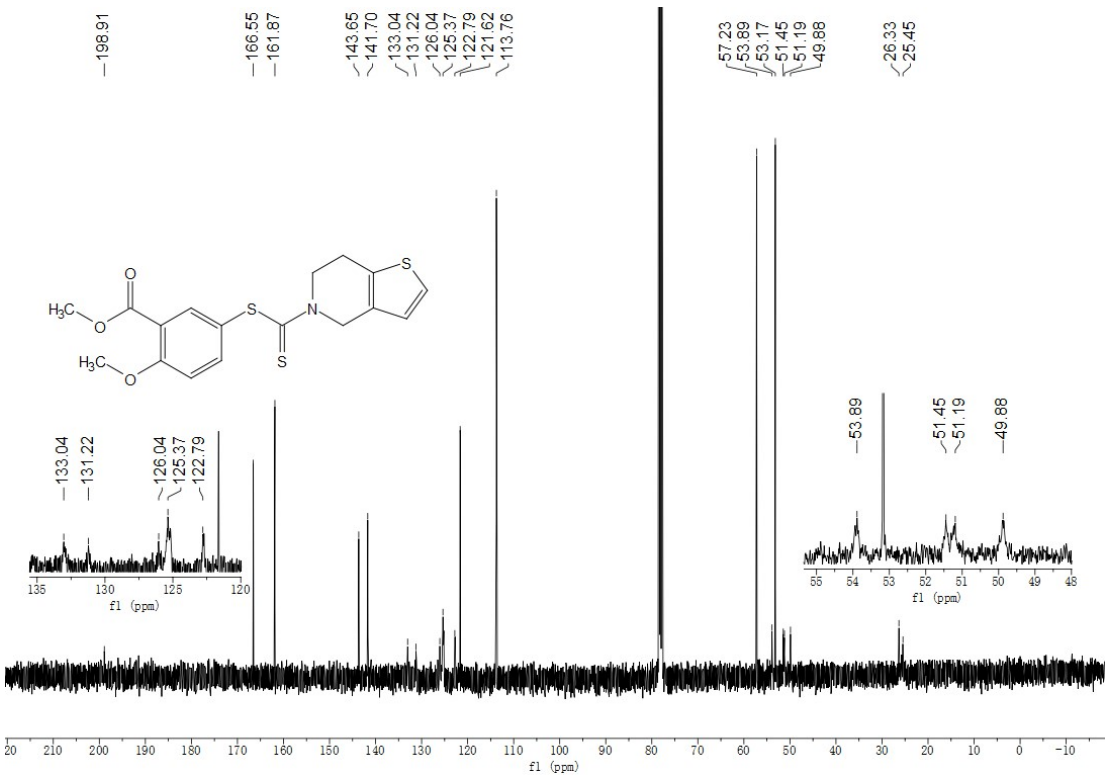
^{1}H NMR (400 MHz, Chloroform-*d*) of compound **4j.**



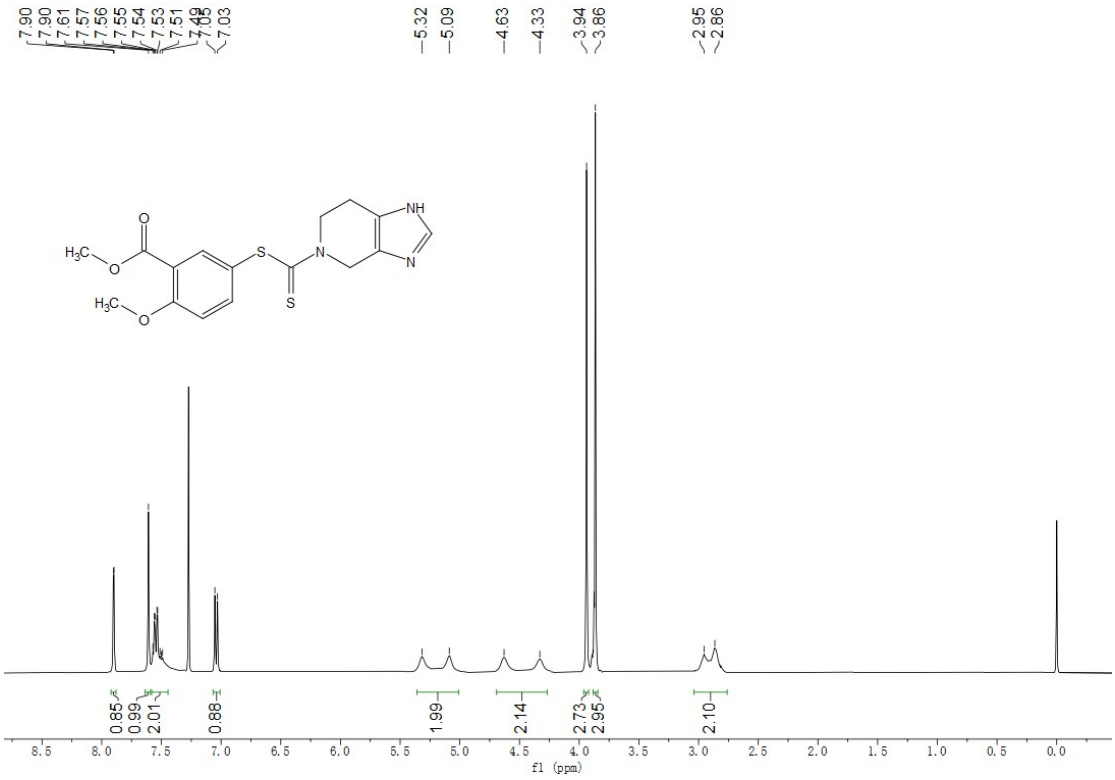
^{13}C NMR (400 MHz, Chloroform-*d*) of compound **4j.**



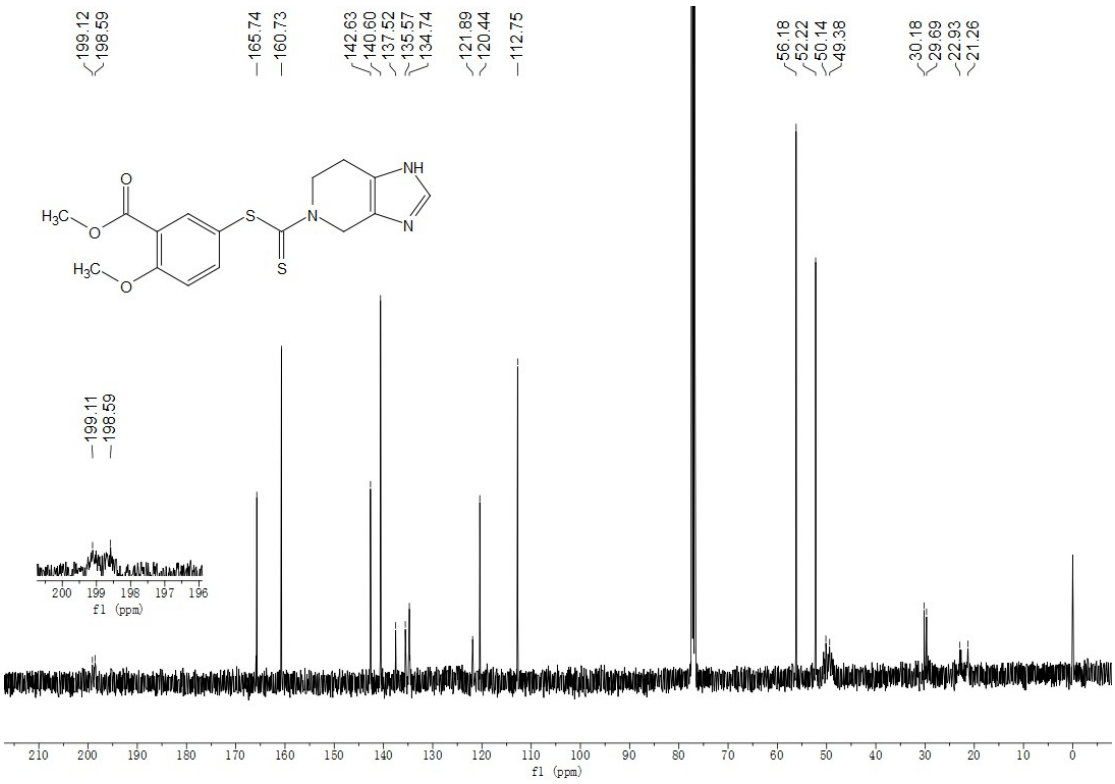
^{1}H NMR (400 MHz, Chloroform-*d*) of compound **4k.**



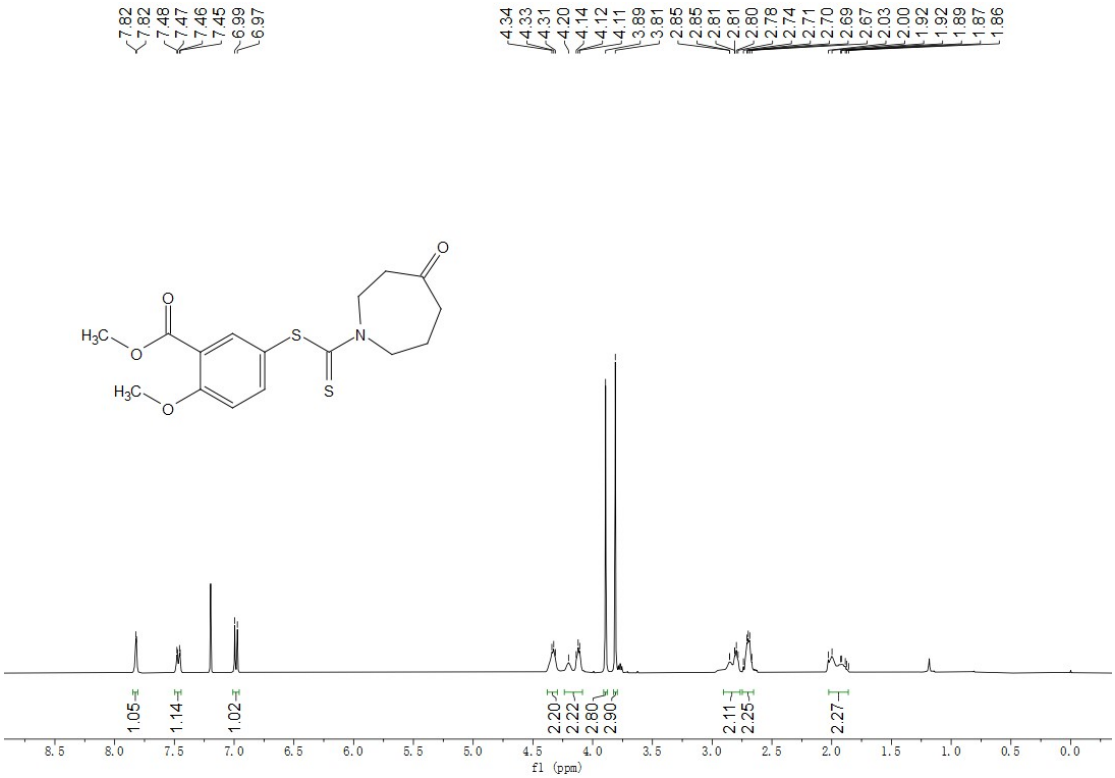
^{13}C NMR (400 MHz, Chloroform-*d*) of compound **4k.**



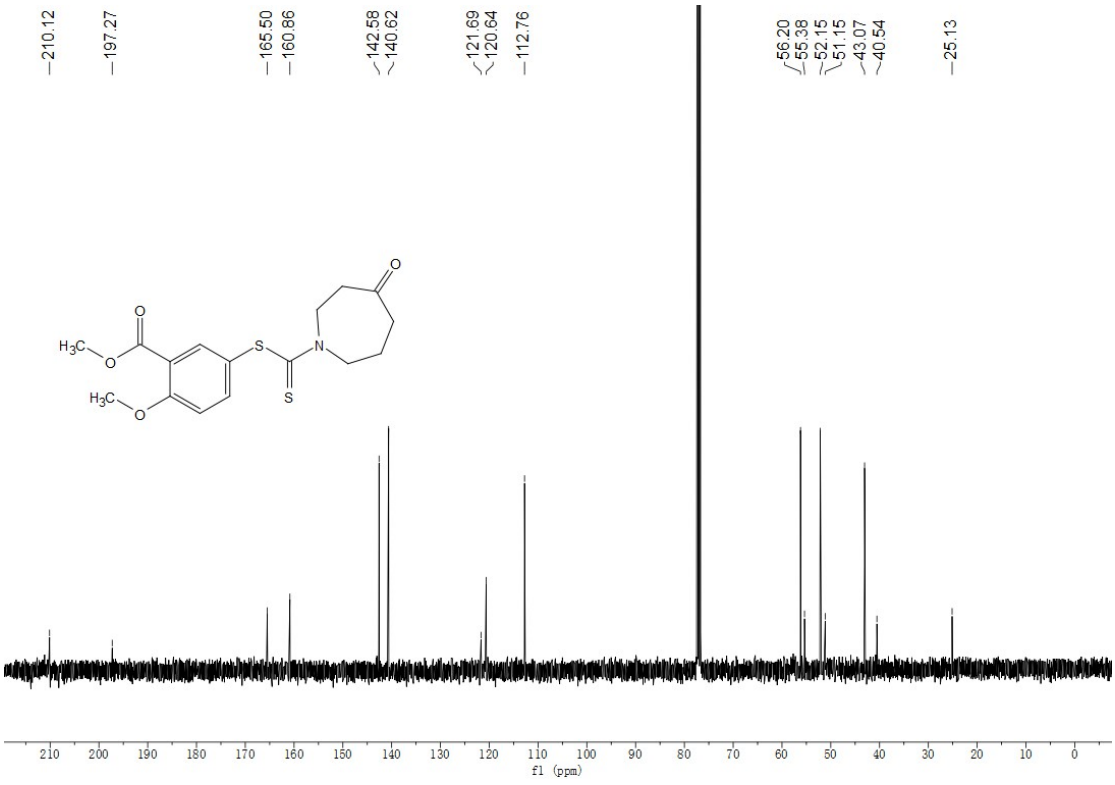
^{1}H NMR (400 MHz, Chloroform-*d*) of compound **4l.**



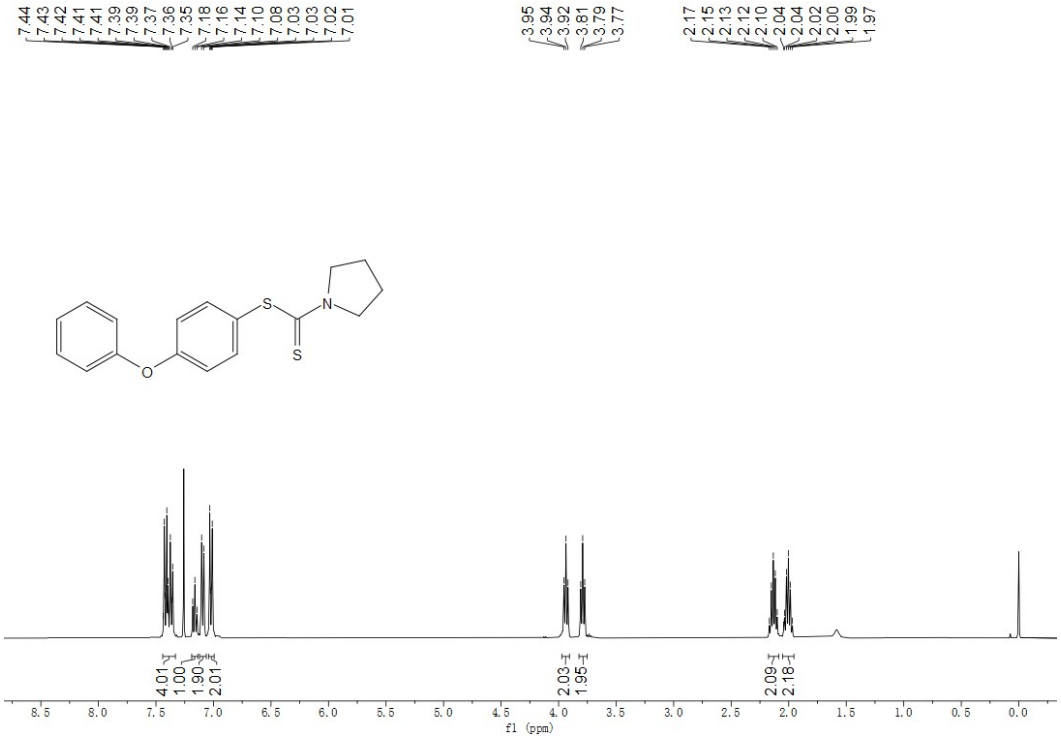
^{13}C NMR (400 MHz, Chloroform-*d*) of compound **4l.**



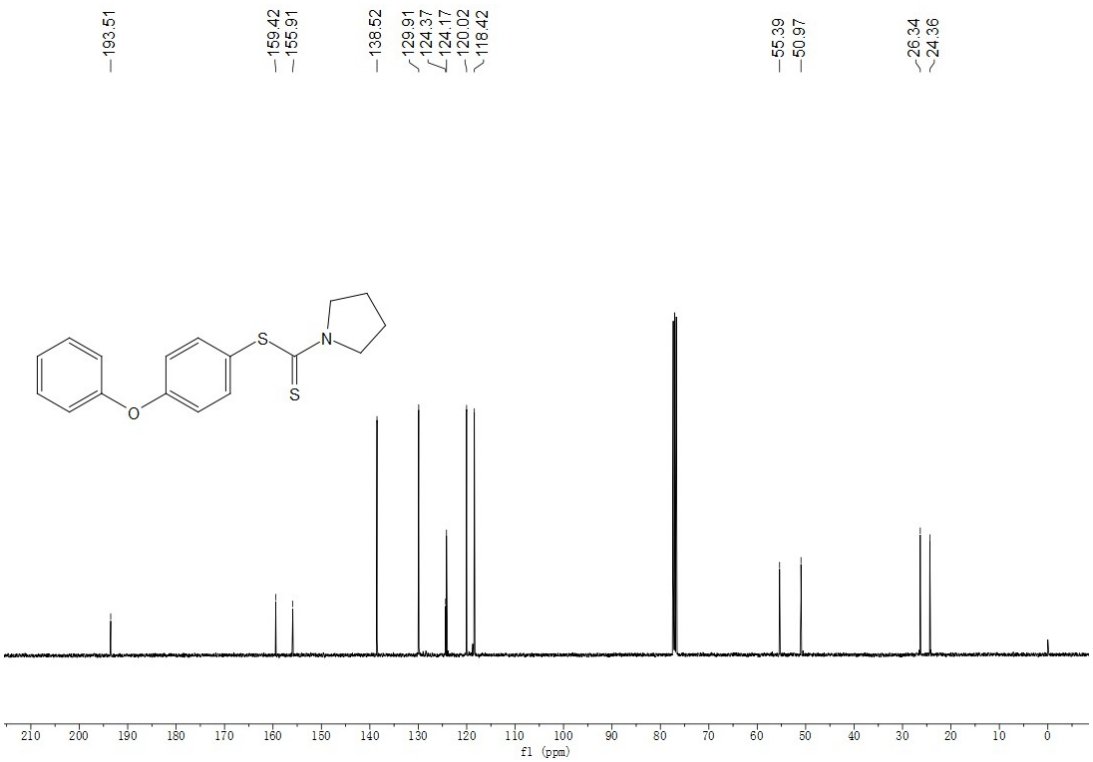
^{1}H NMR (400 MHz, Chloroform-*d*) of compound **4m.**



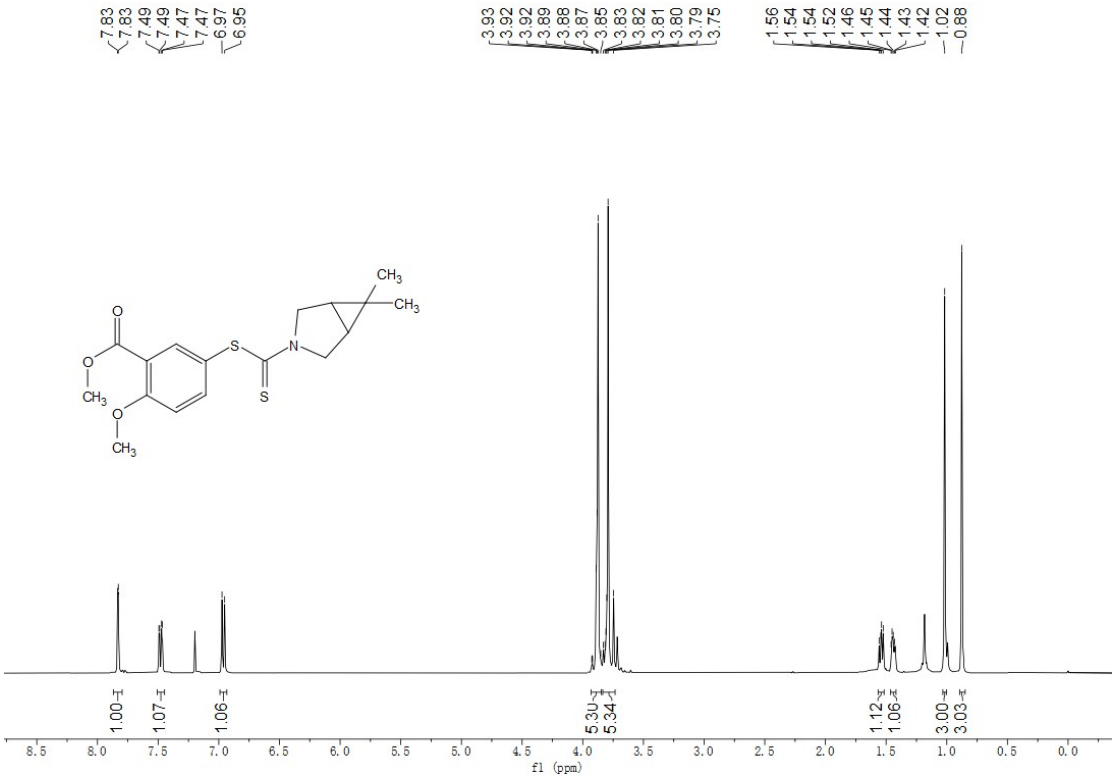
^{13}C NMR (400 MHz, Chloroform-*d*) of compound **4m.**



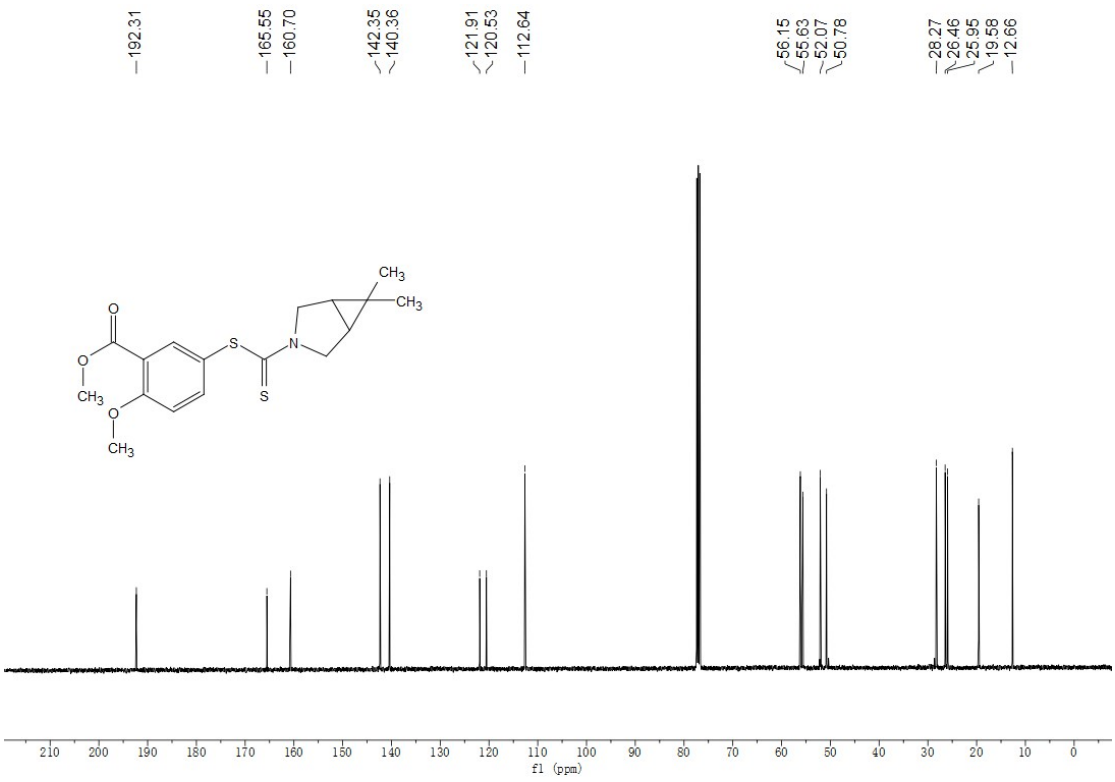
[1]H NMR (400 MHz, Chloroform-*d*) of compound **4n.**



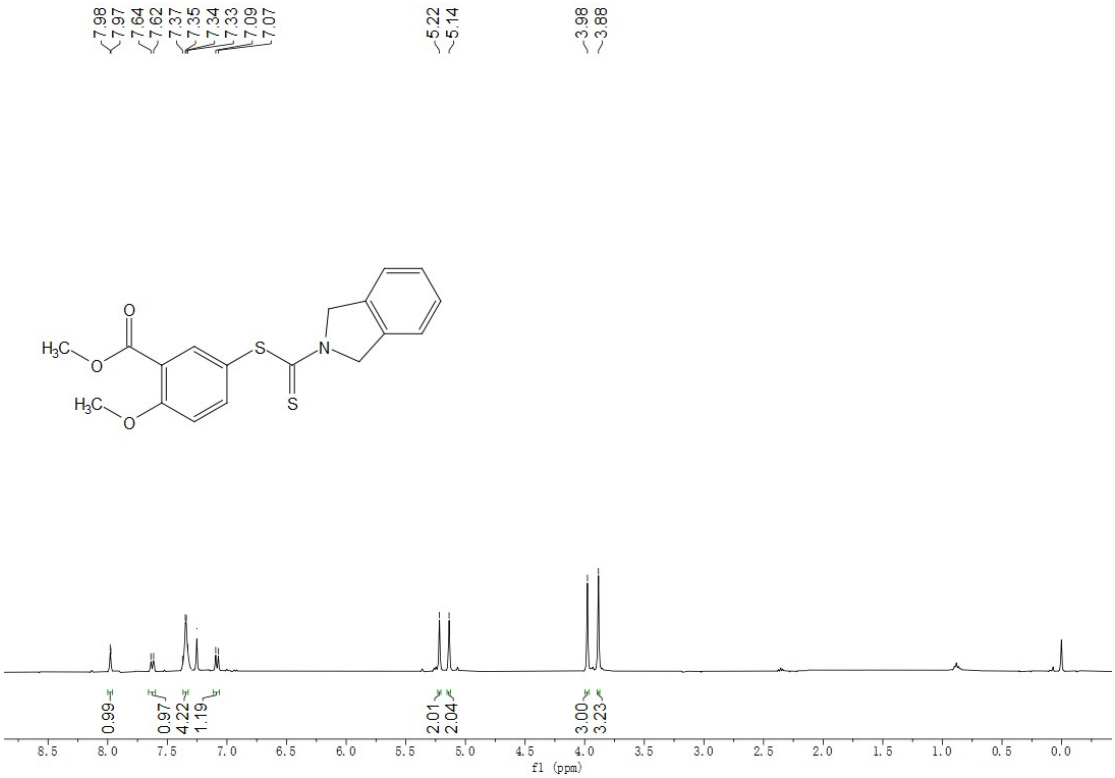
[13]C NMR (400 MHz, Chloroform-*d*) of compound **4n.**



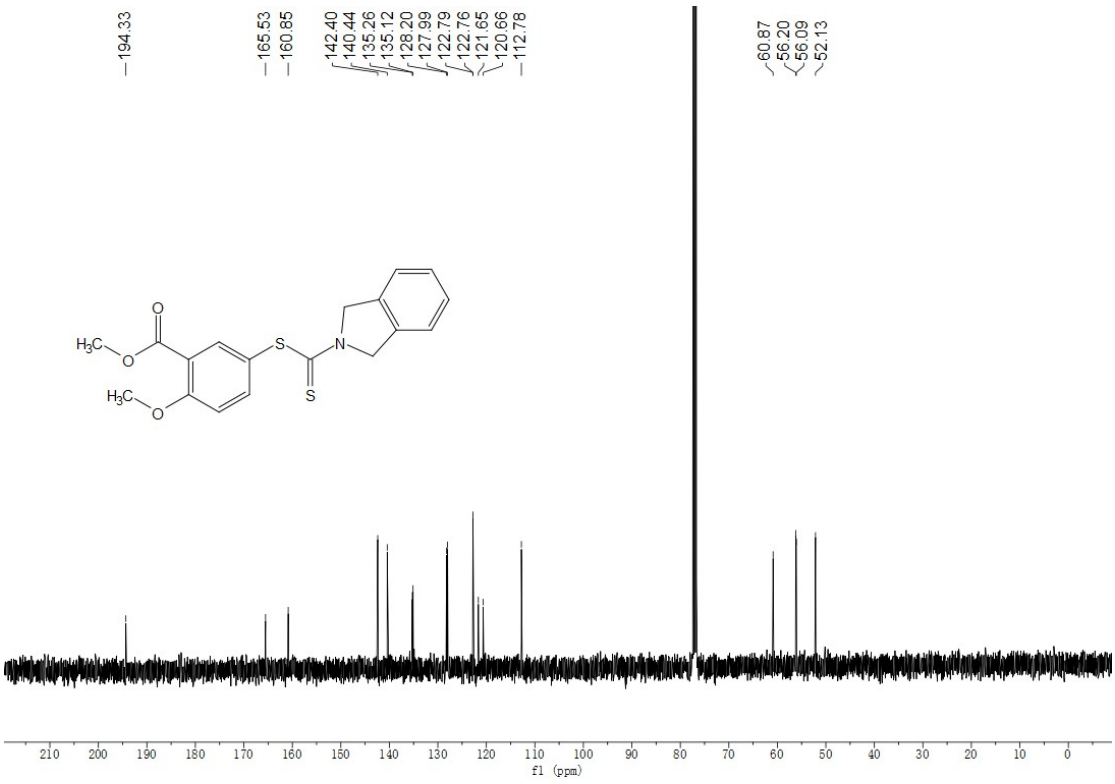
[1]H NMR (400 MHz, Chloroform-*d*) of compound **4o.**



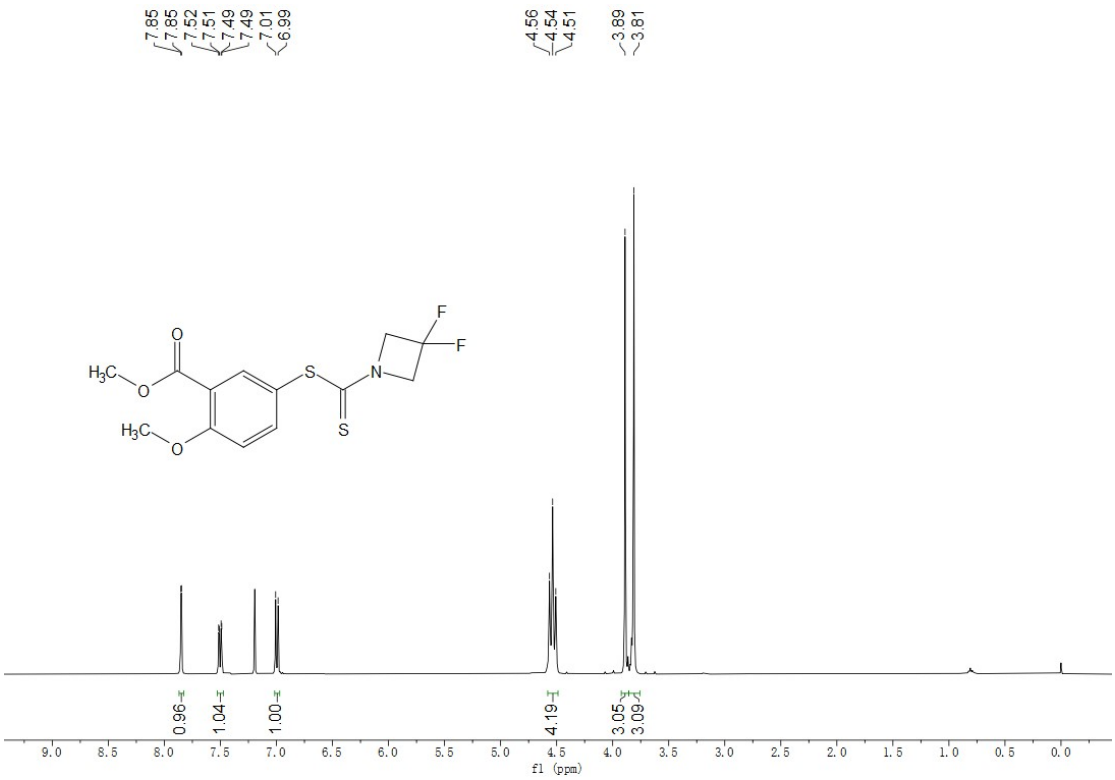
[13]C NMR (400 MHz, Chloroform-*d*) of compound **4o.**



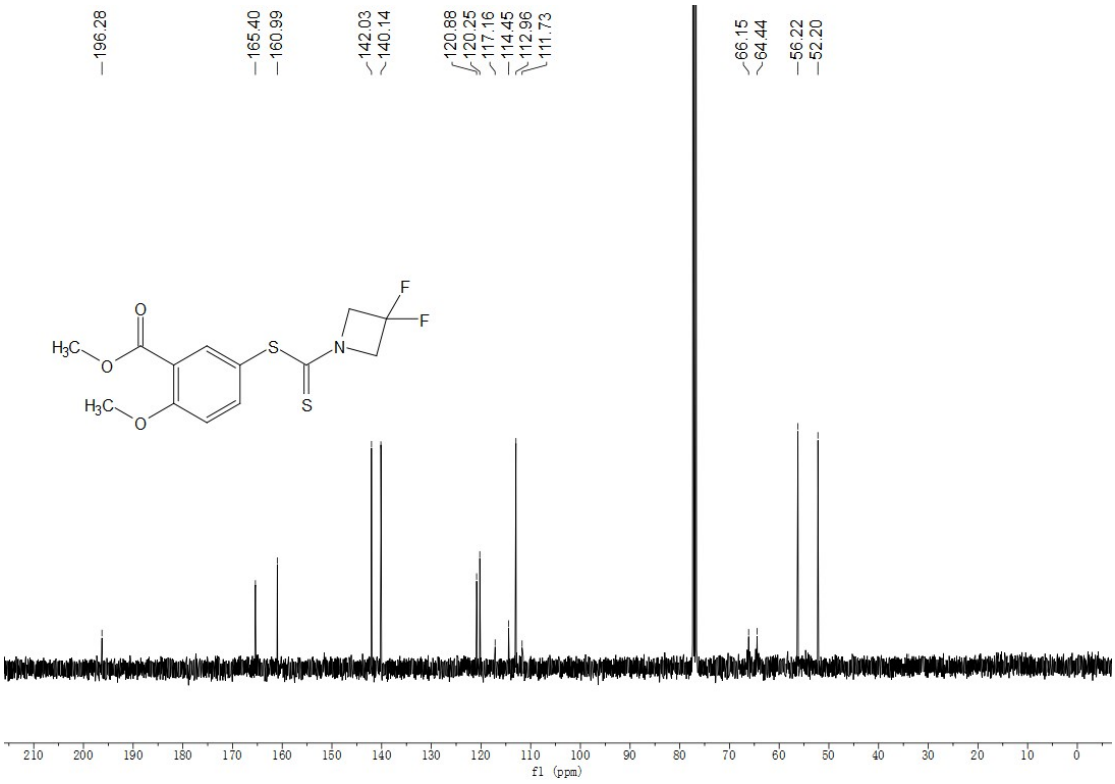
^{1}H NMR (400 MHz, Chloroform-*d*) of compound **4p.**



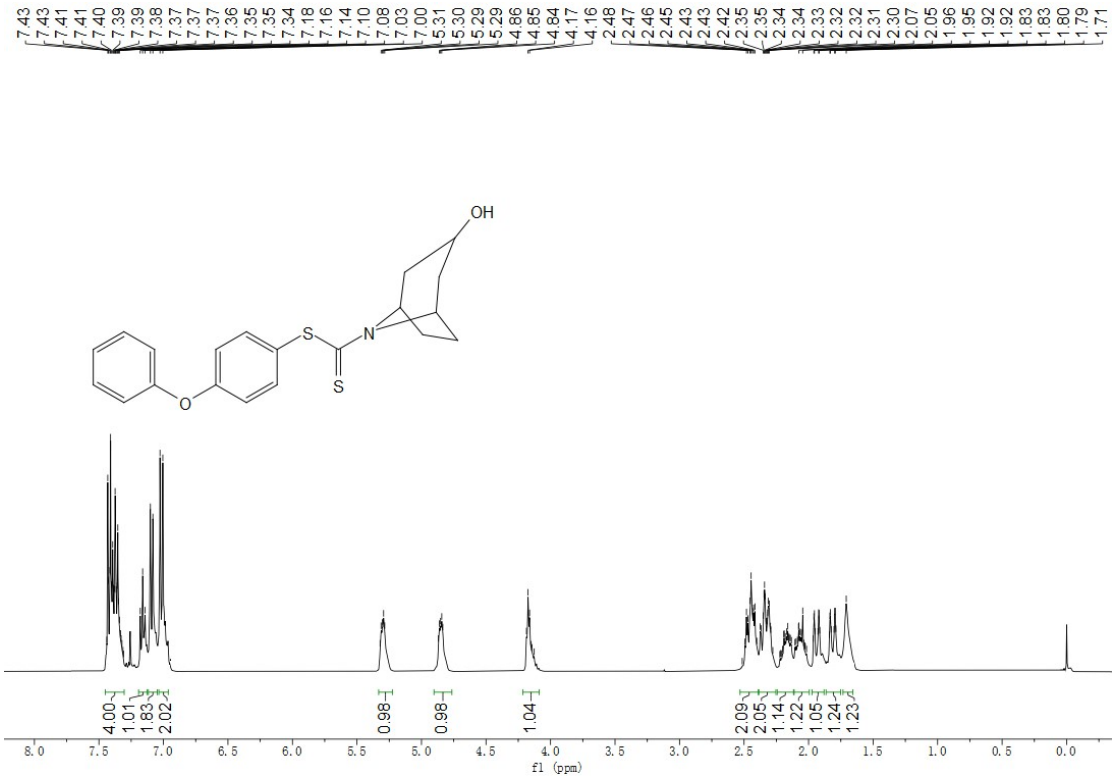
^{13}C NMR (400 MHz, Chloroform-*d*) of compound **4p.**



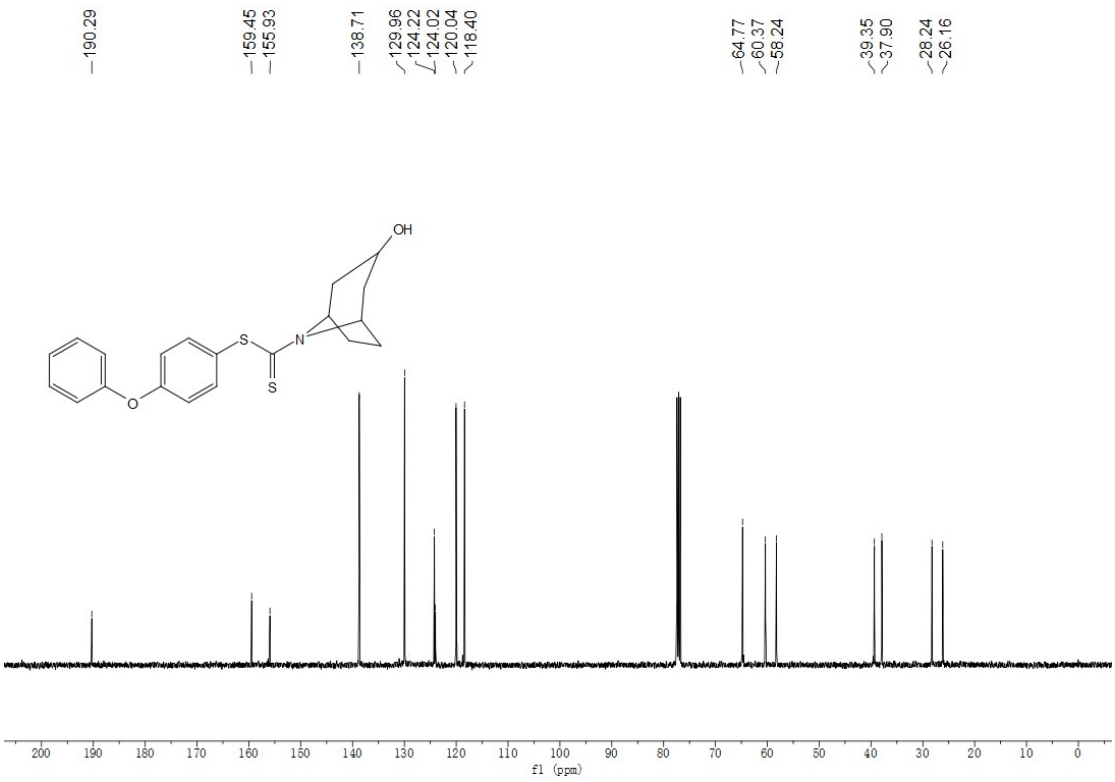
^{1}H NMR (400 MHz, Chloroform-*d*) of compound **4q.**



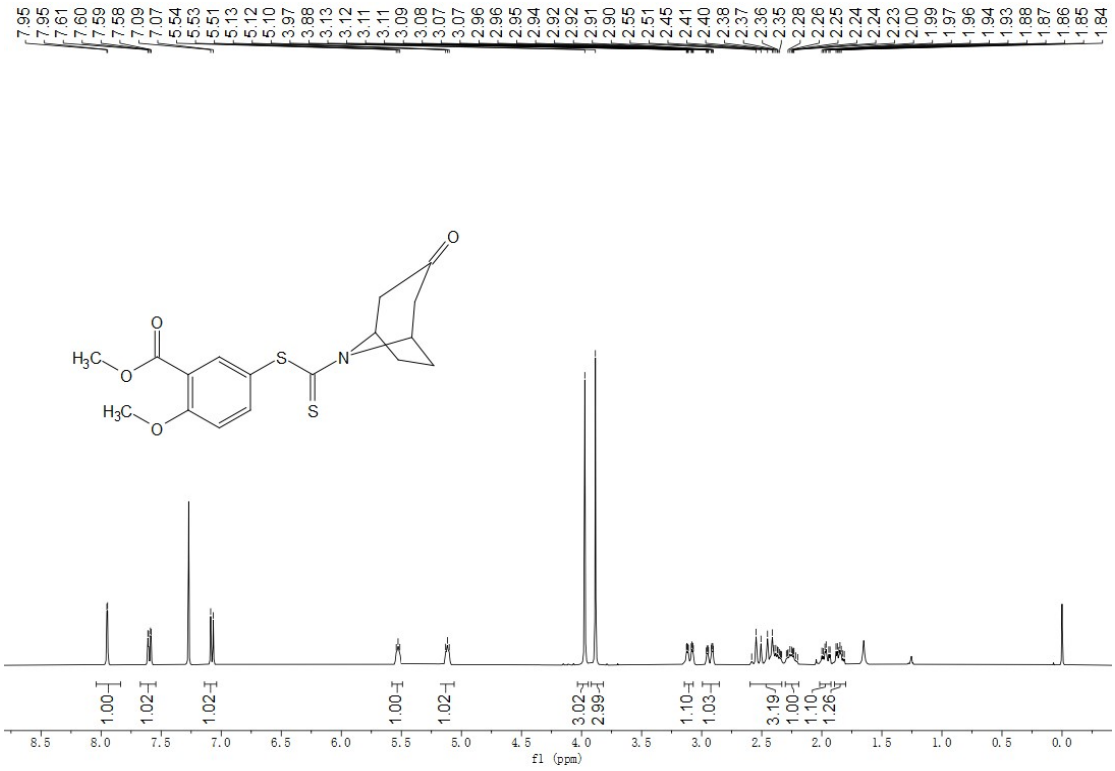
^{13}C NMR (400 MHz, Chloroform-*d*) of compound **4q.**



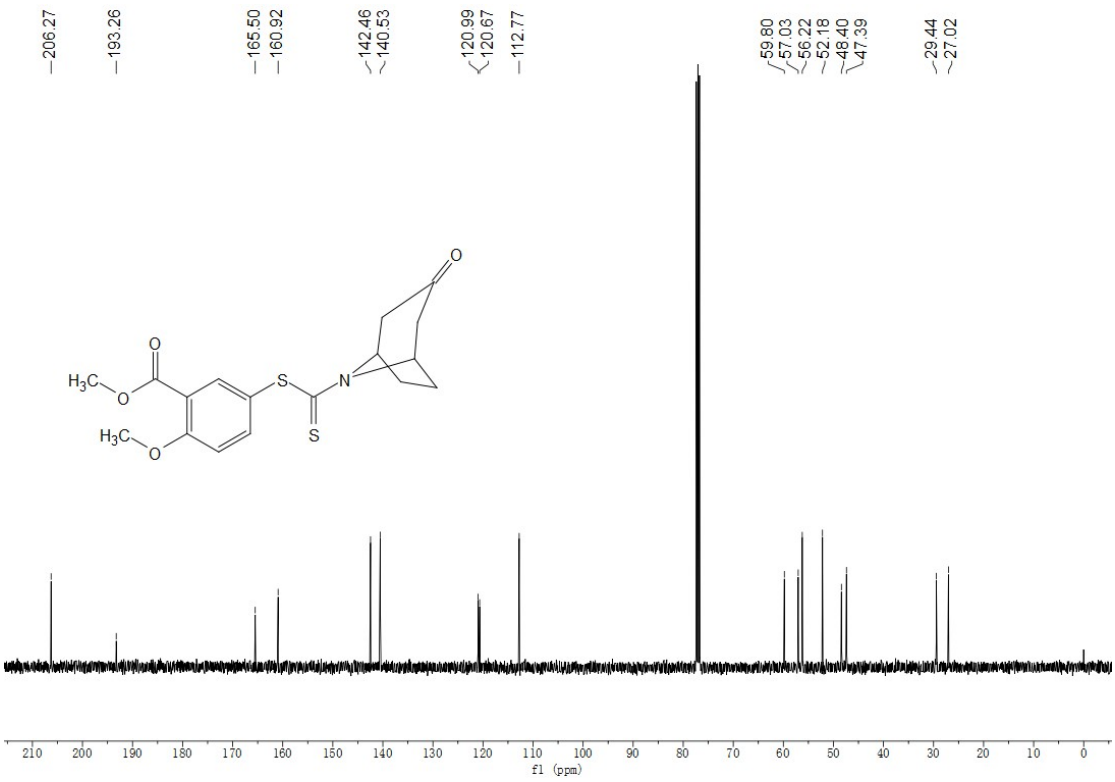
^{1}H NMR (400 MHz, Chloroform-*d*) of compound **4r.**



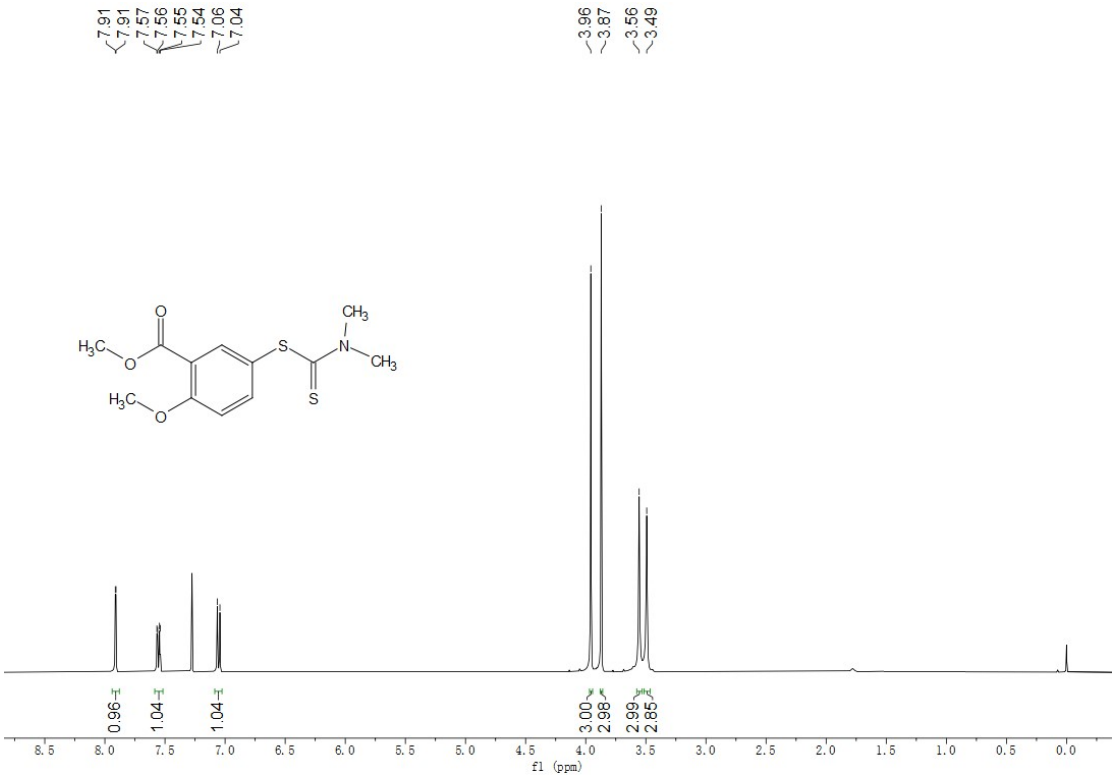
^{13}C NMR (400 MHz, Chloroform-*d*) of compound **4r.**



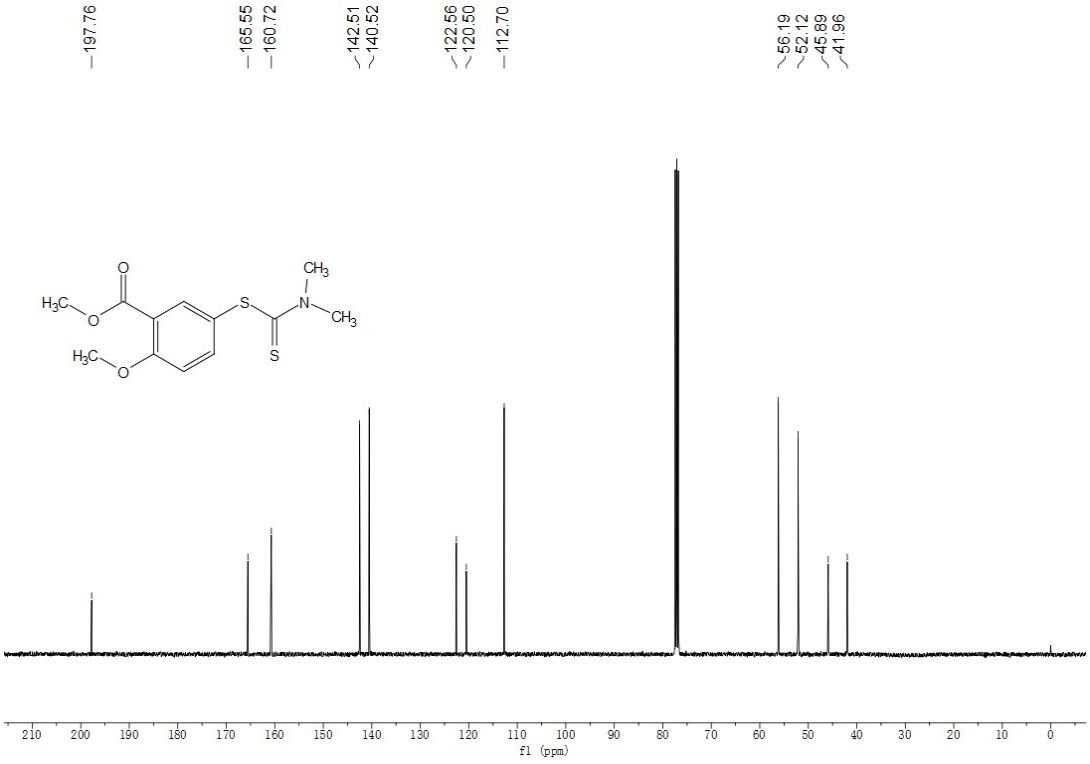
^{1}H NMR (400 MHz, Chloroform-*d*) of compound **4s.**



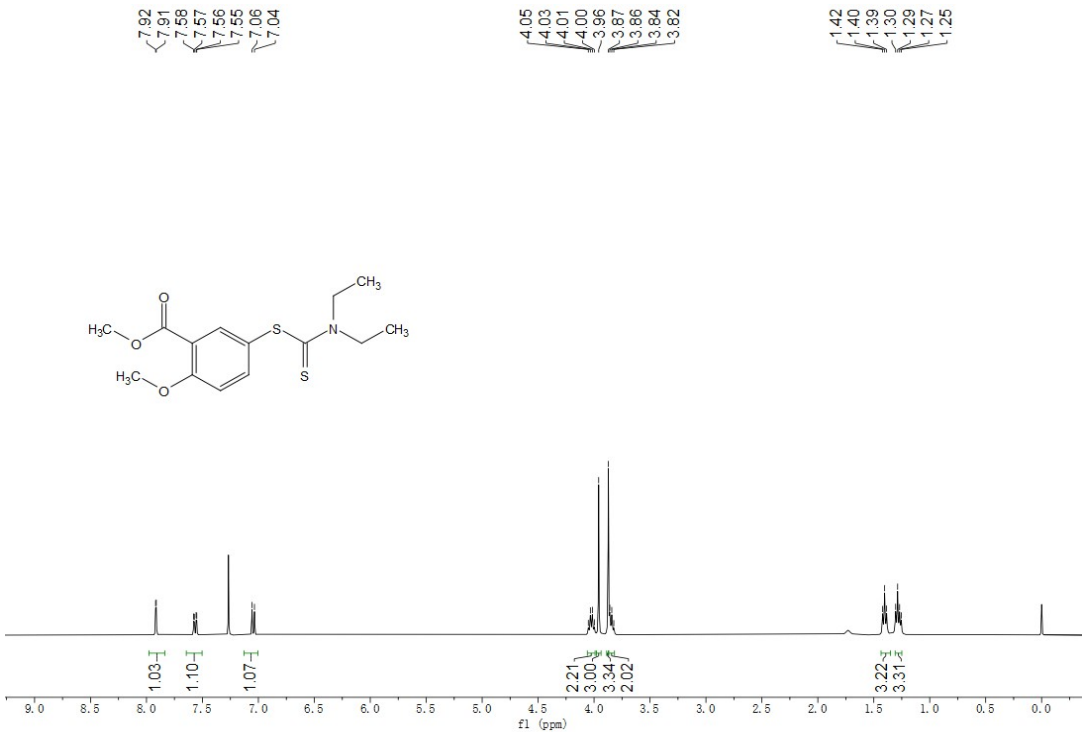
^{13}C NMR (400 MHz, Chloroform-*d*) of compound **4s.**



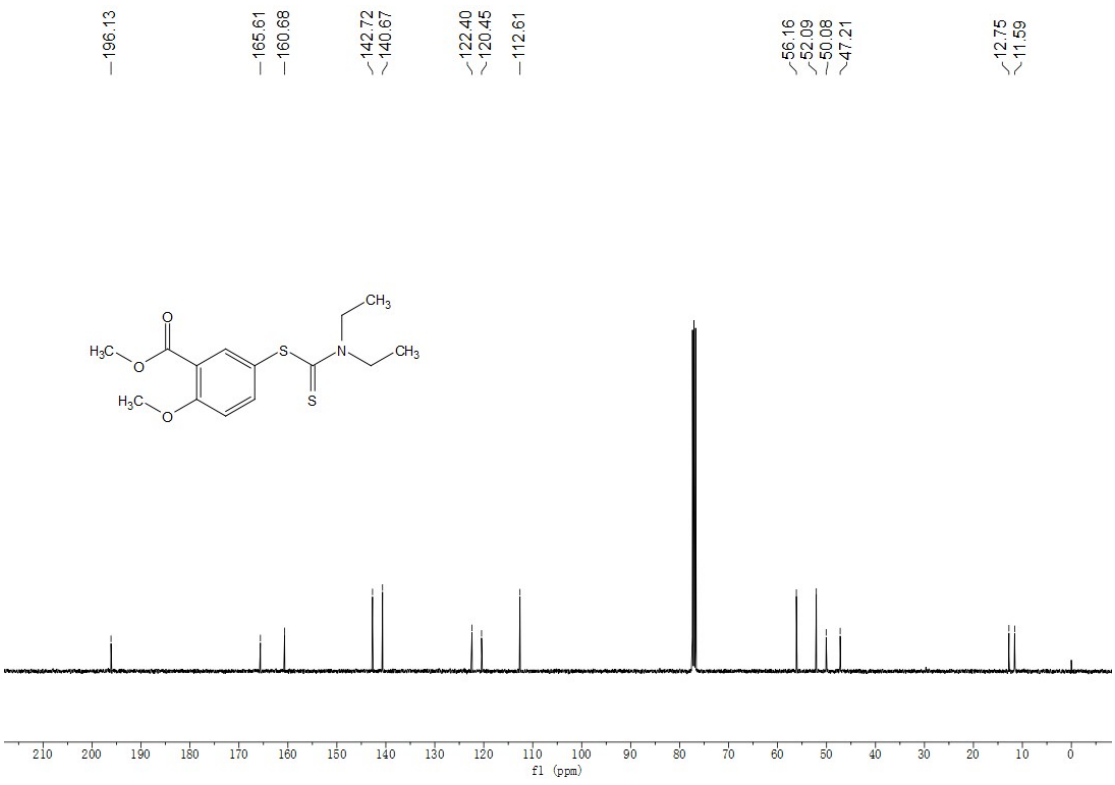
^{1}H NMR (400 MHz, Chloroform-*d*) of compound **4t.**



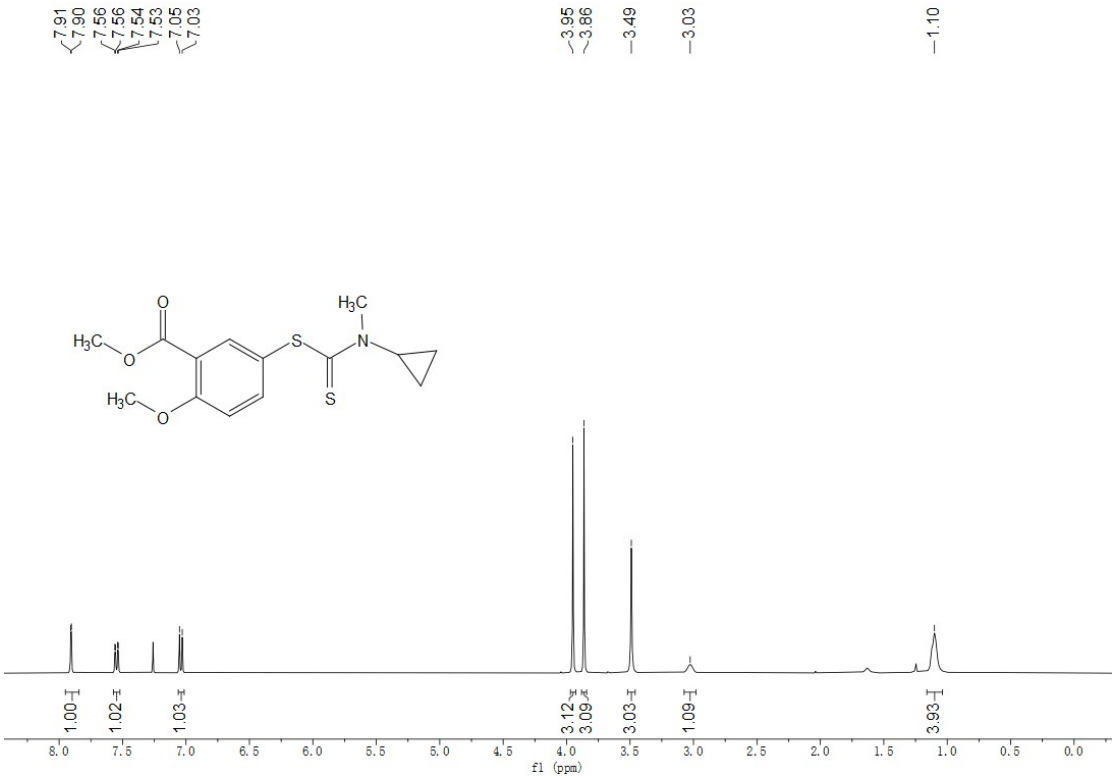
^{13}C NMR (400 MHz, Chloroform-*d*) of compound **4t.**



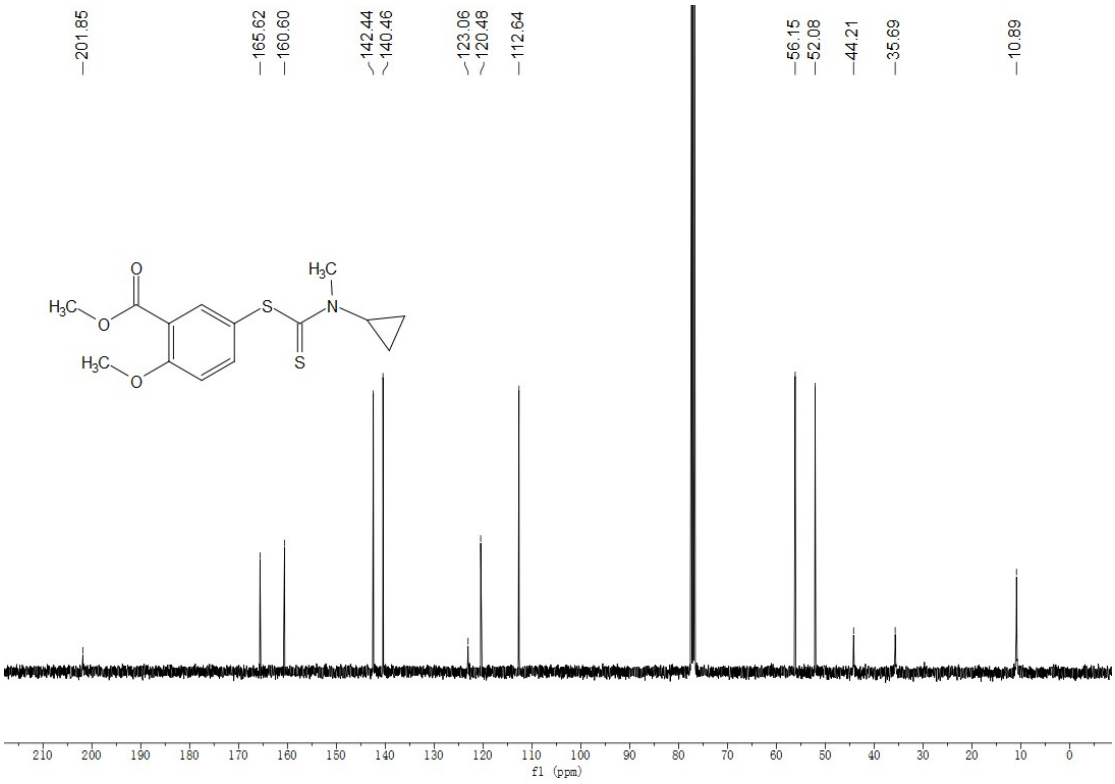
^{1}H NMR (400 MHz, Chloroform-*d*) of compound **4u.**



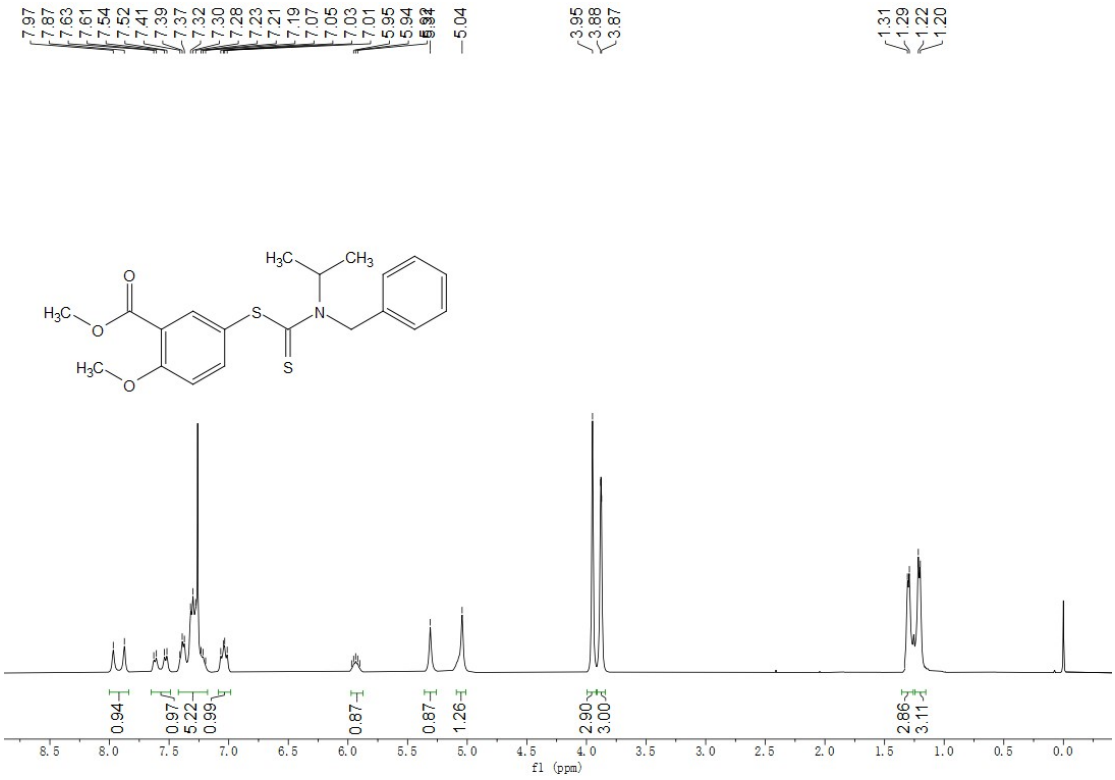
^{13}C NMR (400 MHz, Chloroform-*d*) of compound **4u.**



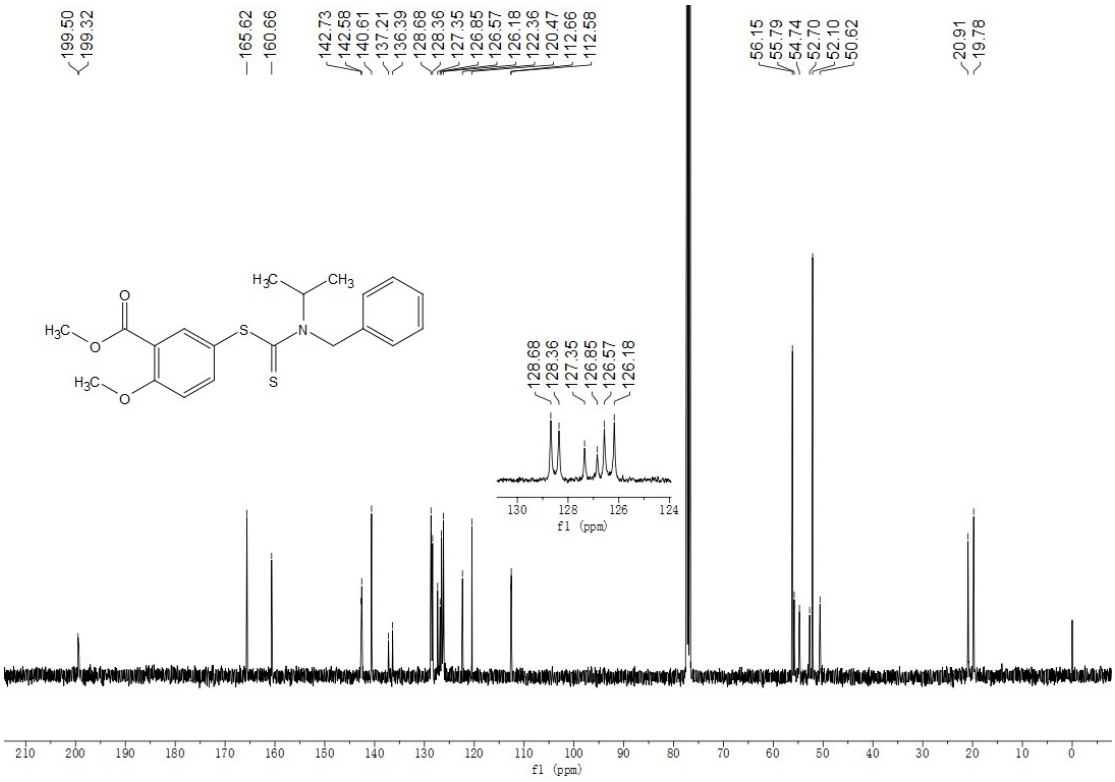
^{1}H NMR (400 MHz, Chloroform-*d*) of compound **4v.**



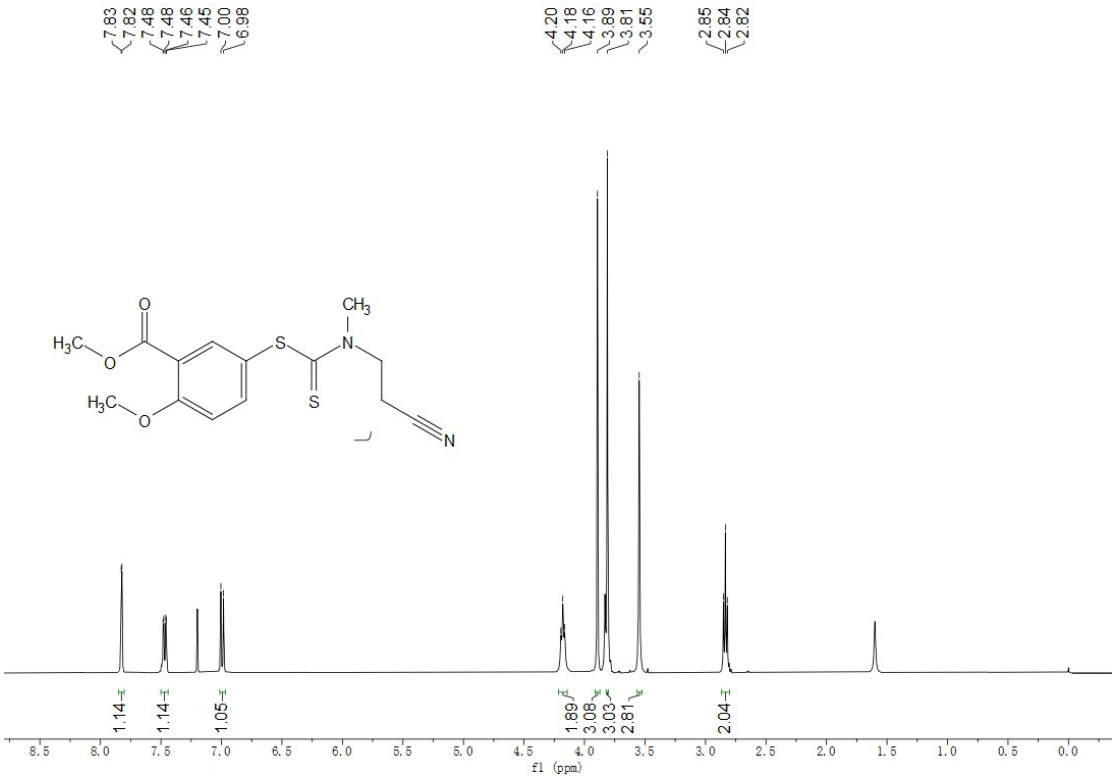
^{13}C NMR (400 MHz, Chloroform-*d*) of compound **4v.**



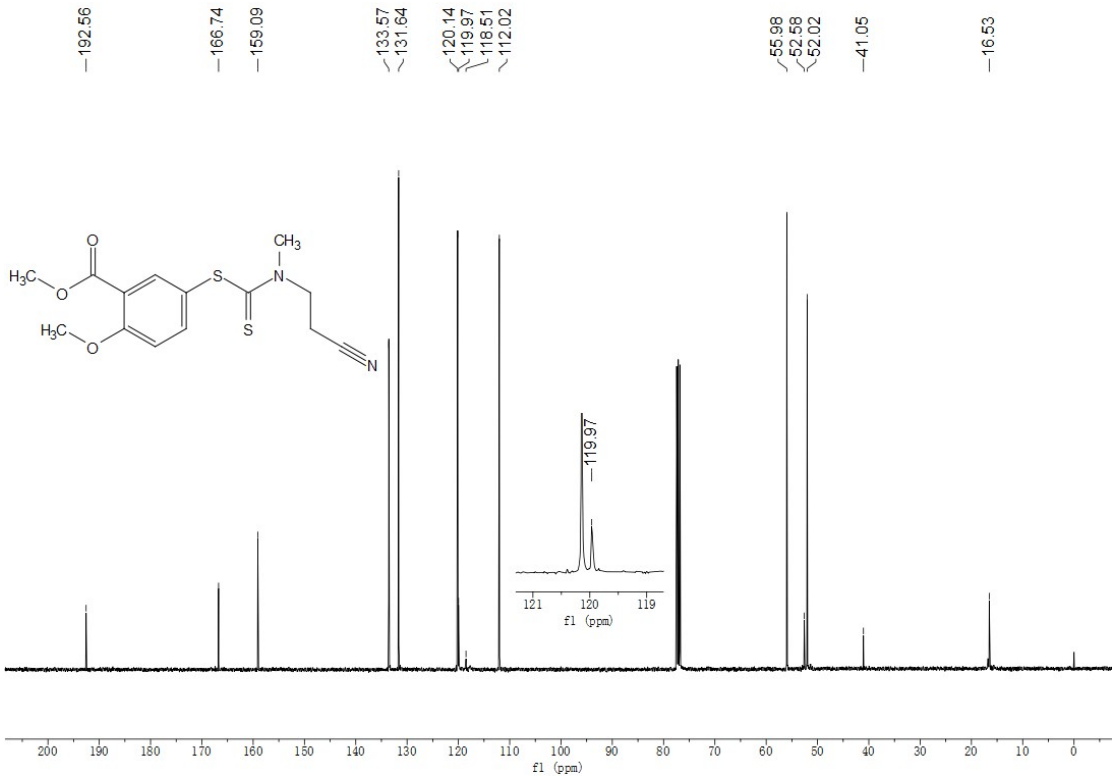
^{1}H NMR (400 MHz, Chloroform-*d*) of compound **4w.**



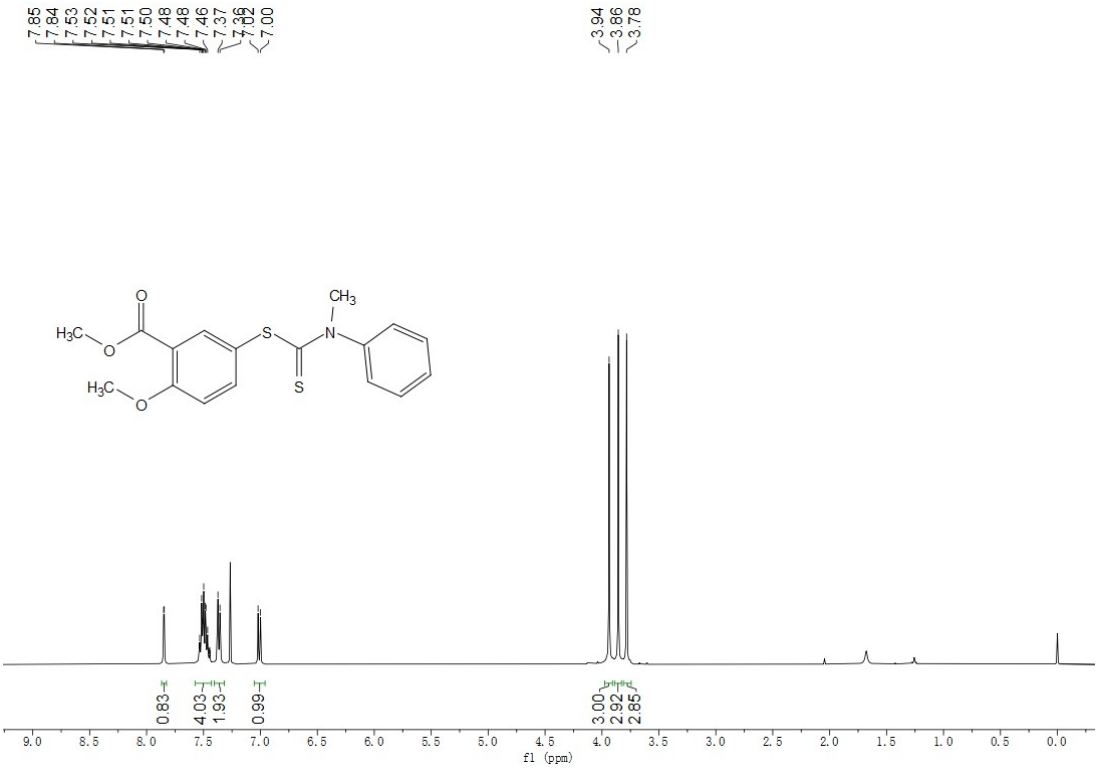
^{13}C NMR (400 MHz, Chloroform-*d*) of compound **4w.**



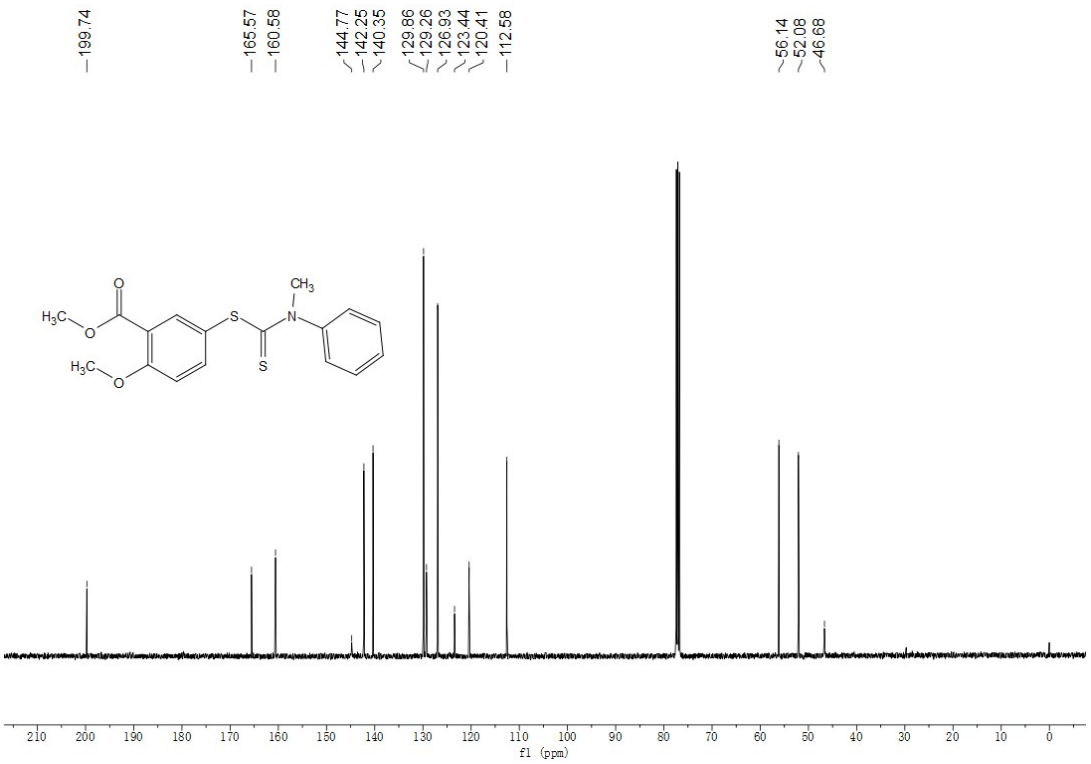
^{1}H NMR (400 MHz, Chloroform-*d*) of compound **4x.**



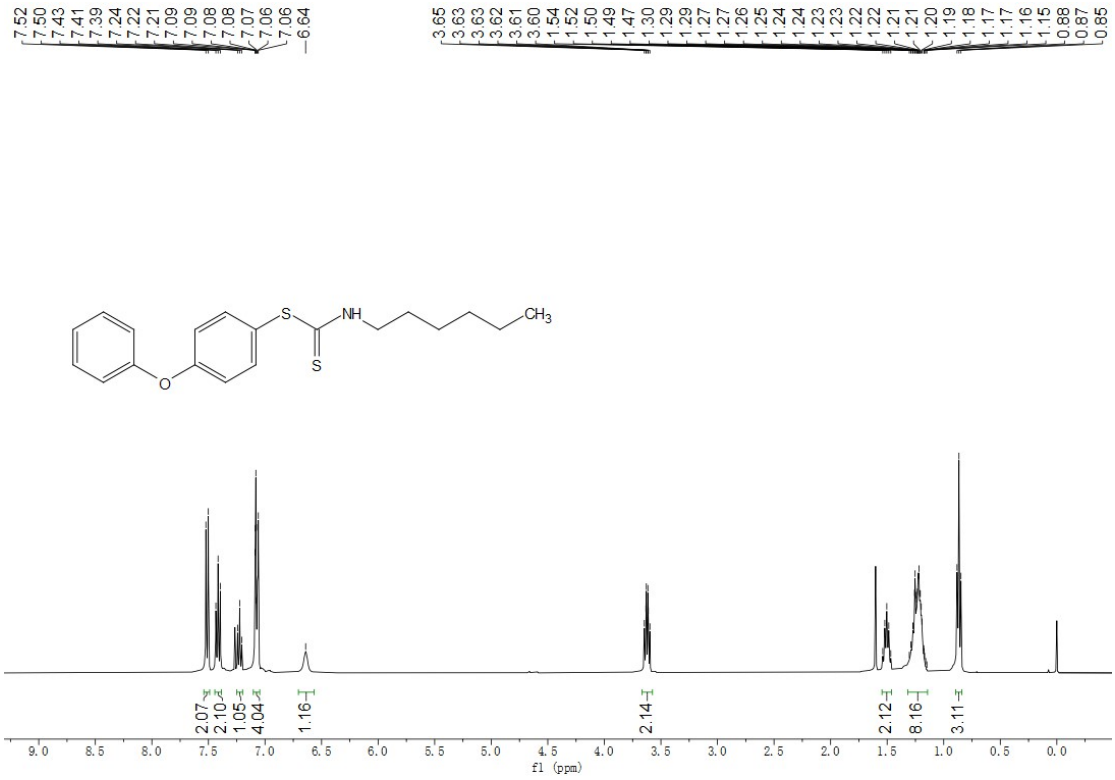
^{13}C NMR (400 MHz, Chloroform-*d*) of compound **4x.**



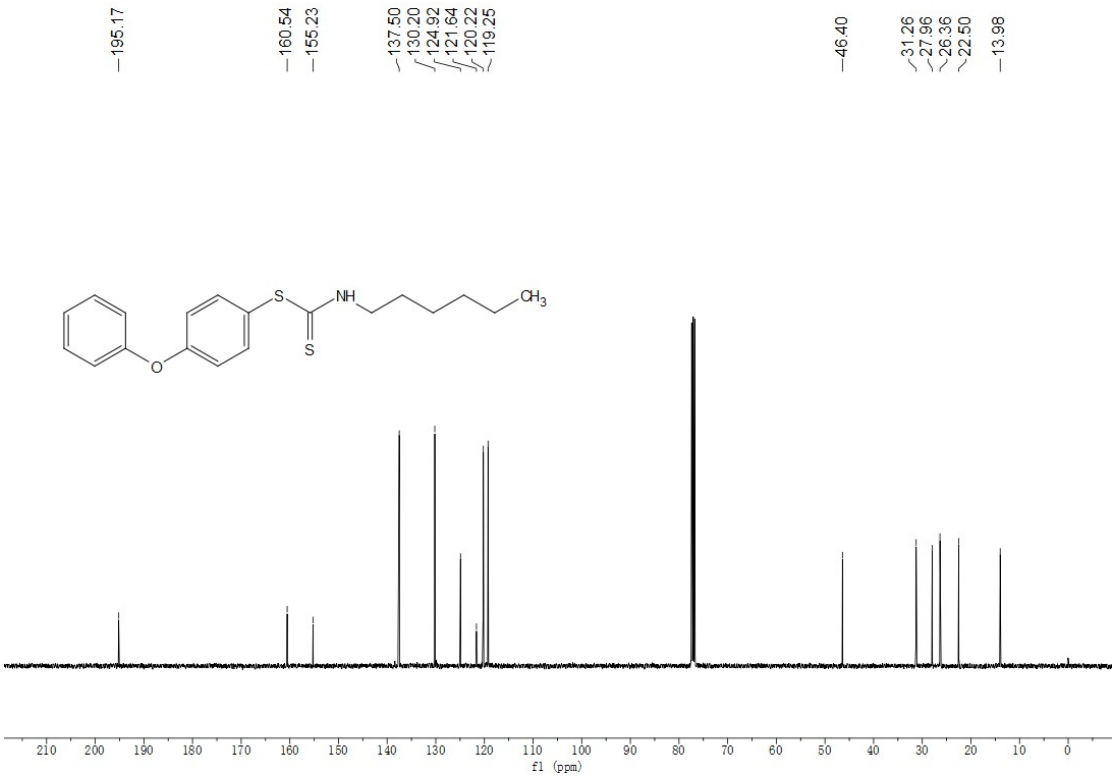
[1]H NMR (400 MHz, Chloroform-*d*) of compound **4y.**



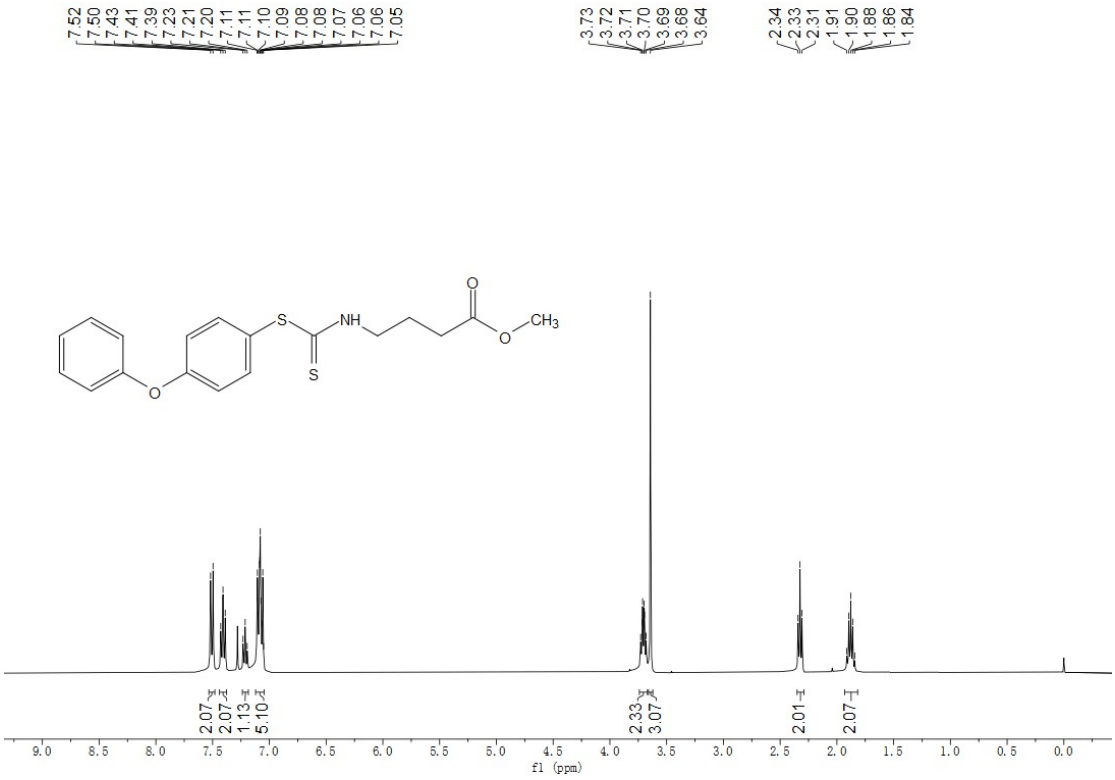
[13]C NMR (400 MHz, Chloroform-*d*) of compound **4y.**



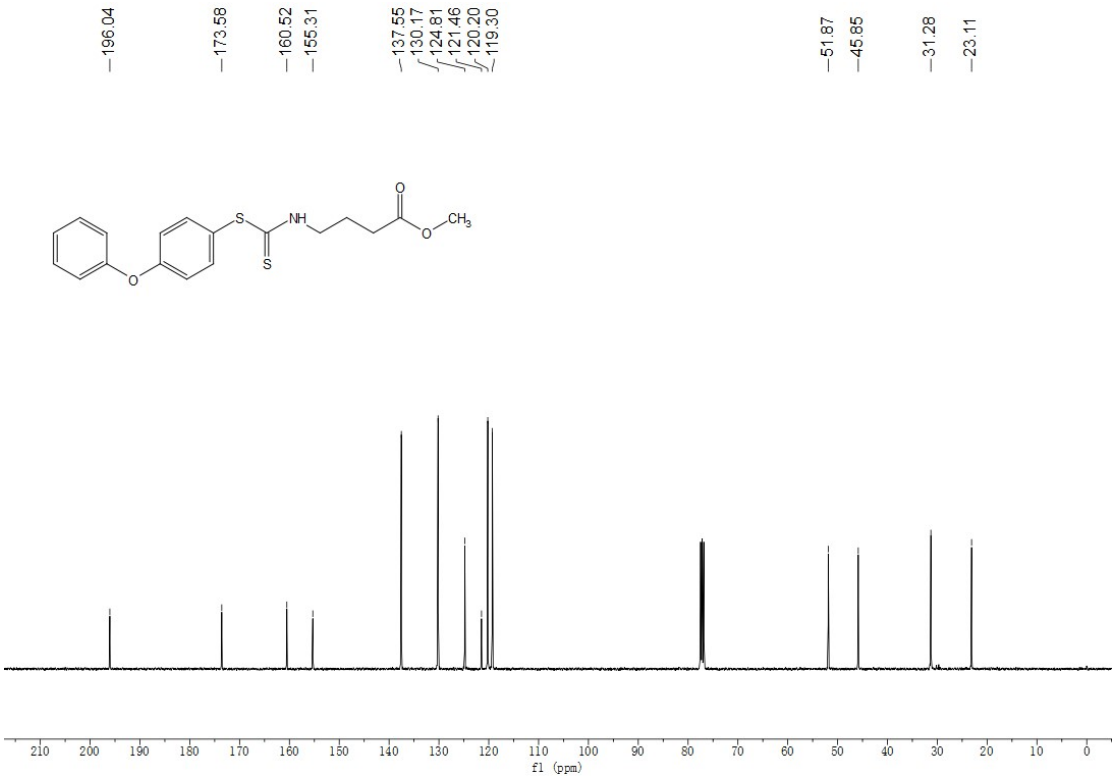
^{1}H NMR (400 MHz, Chloroform-*d*) of compound **4z.**



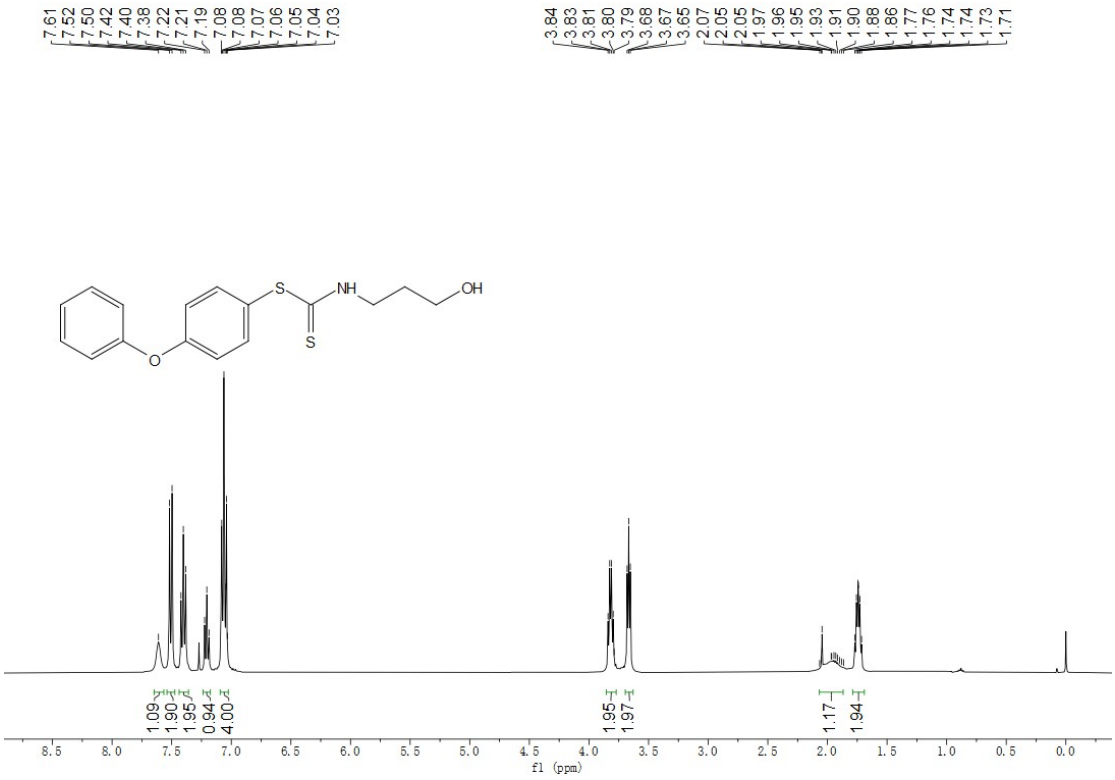
^{13}C NMR (400 MHz, Chloroform-*d*) of compound **4z.**



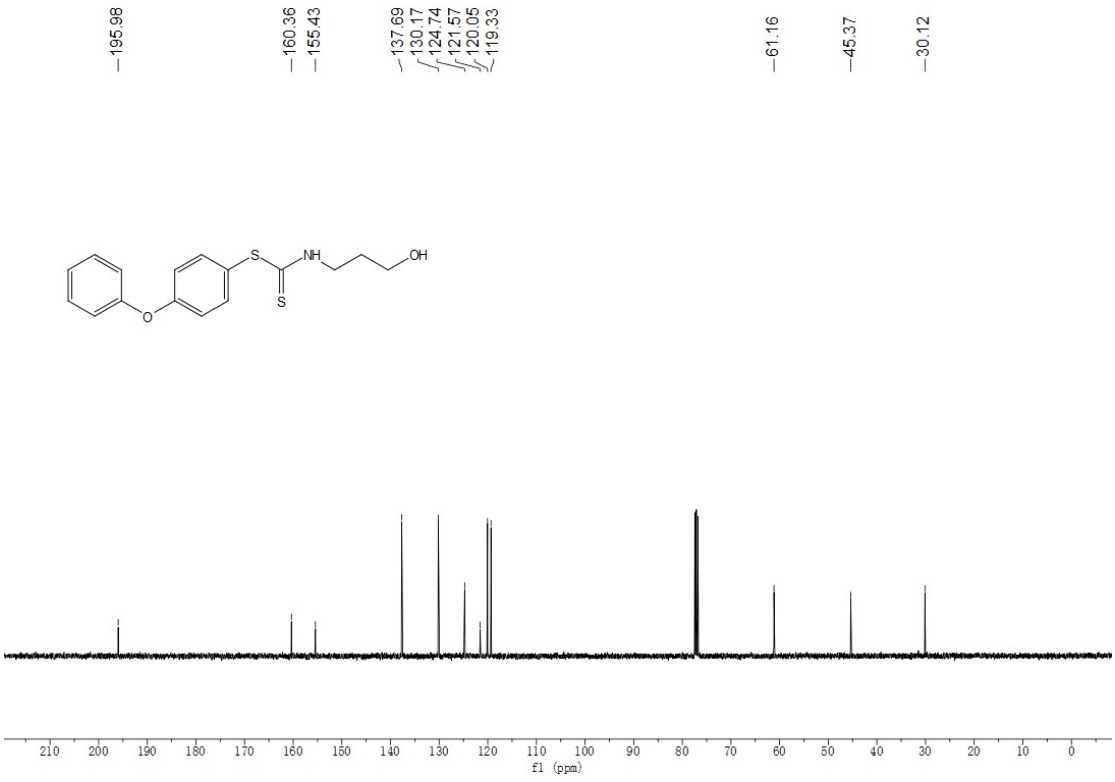
^{1}H NMR (400 MHz, Chloroform-*d*) of compound **4a'.**



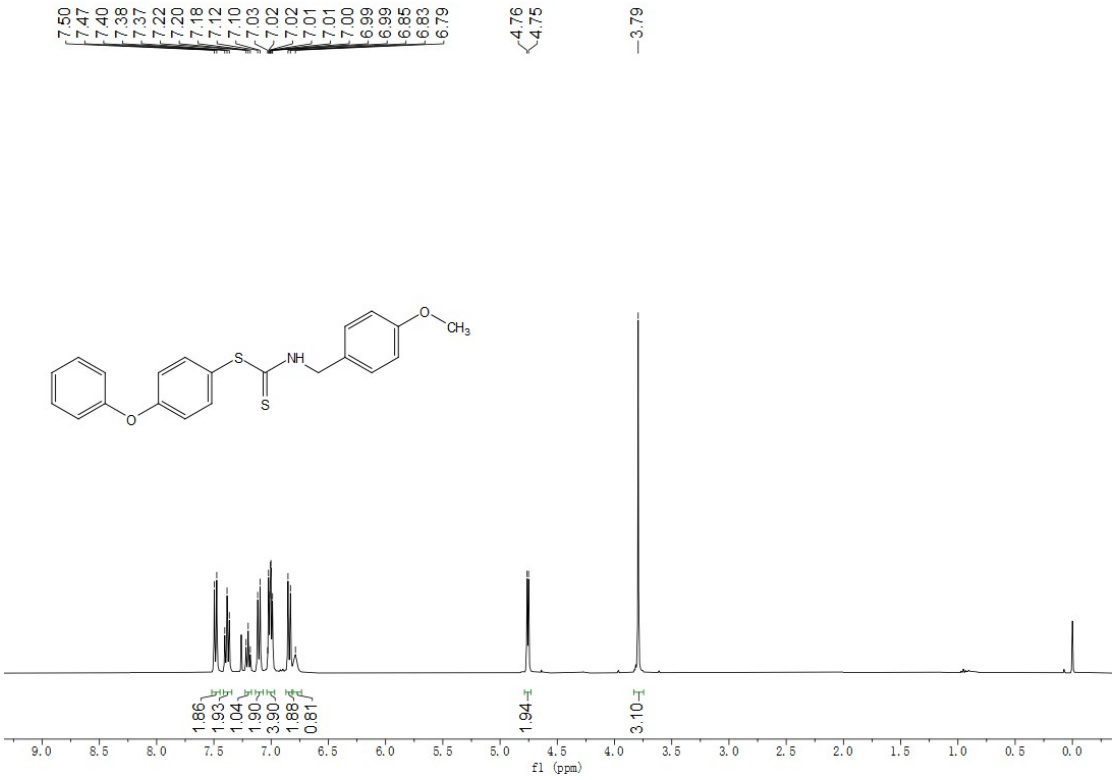
^{13}C NMR (400 MHz, Chloroform-*d*) of compound **4a'.**



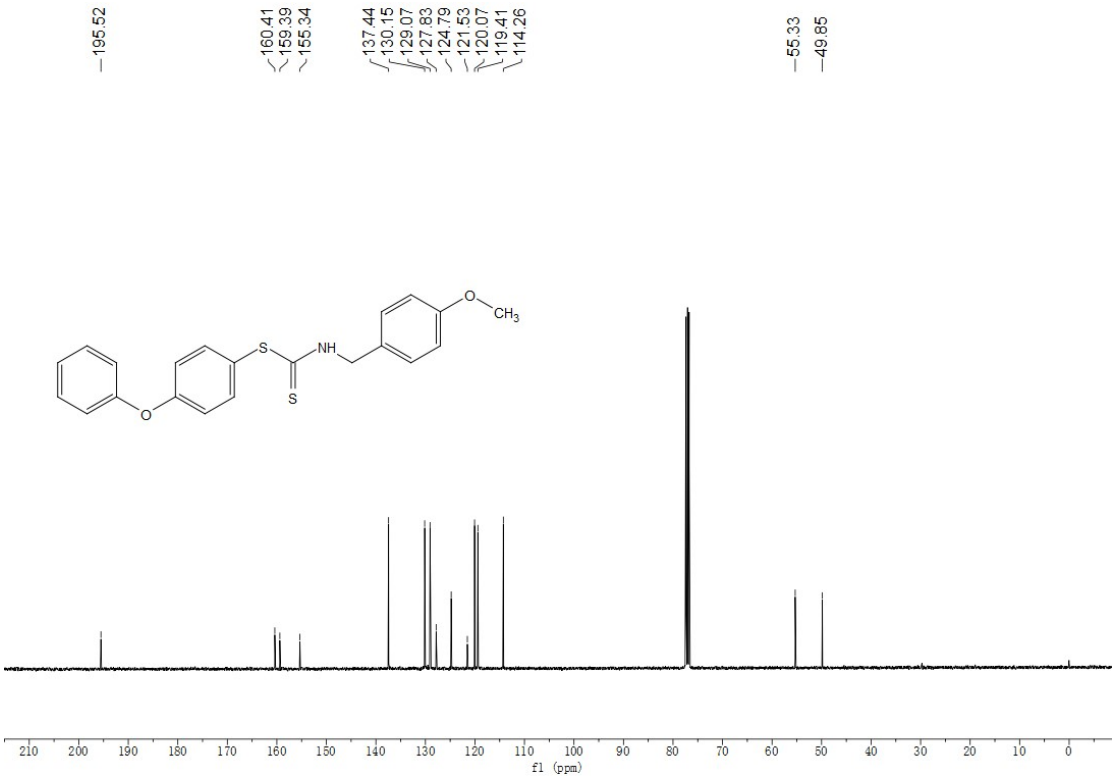
^{1}H NMR (400 MHz, Chloroform-*d*) of compound **4b'.**



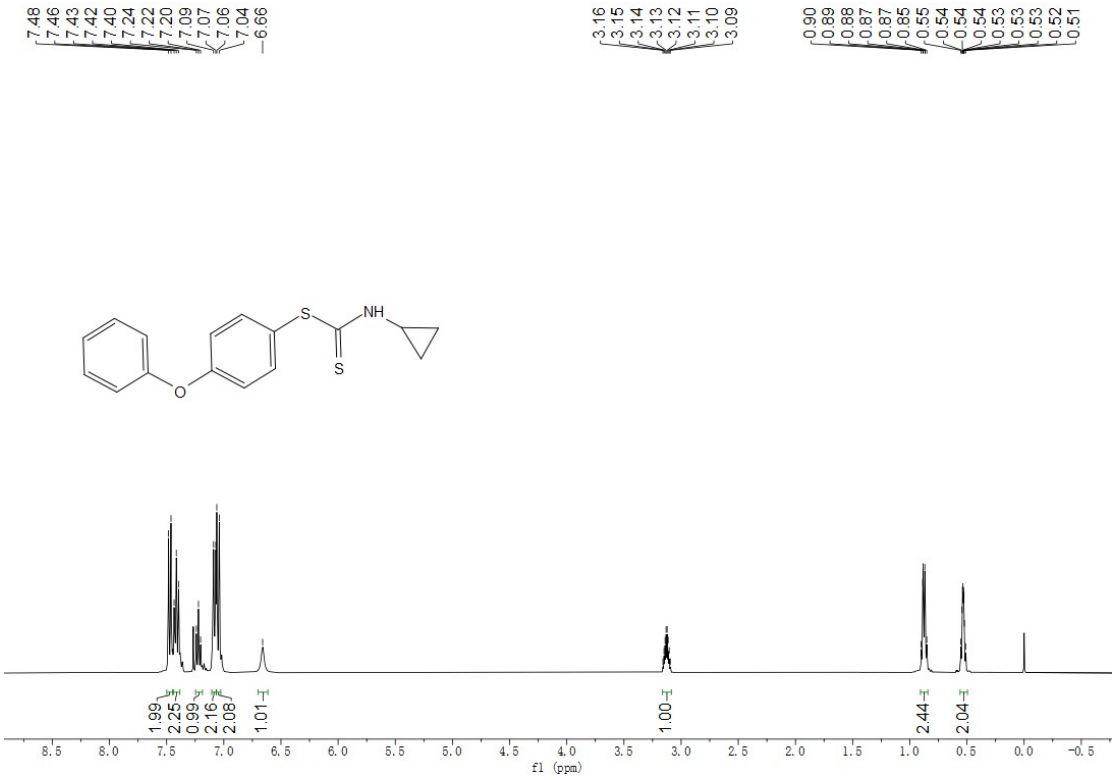
^{13}C NMR (400 MHz, Chloroform-*d*) of compound **4b'.**



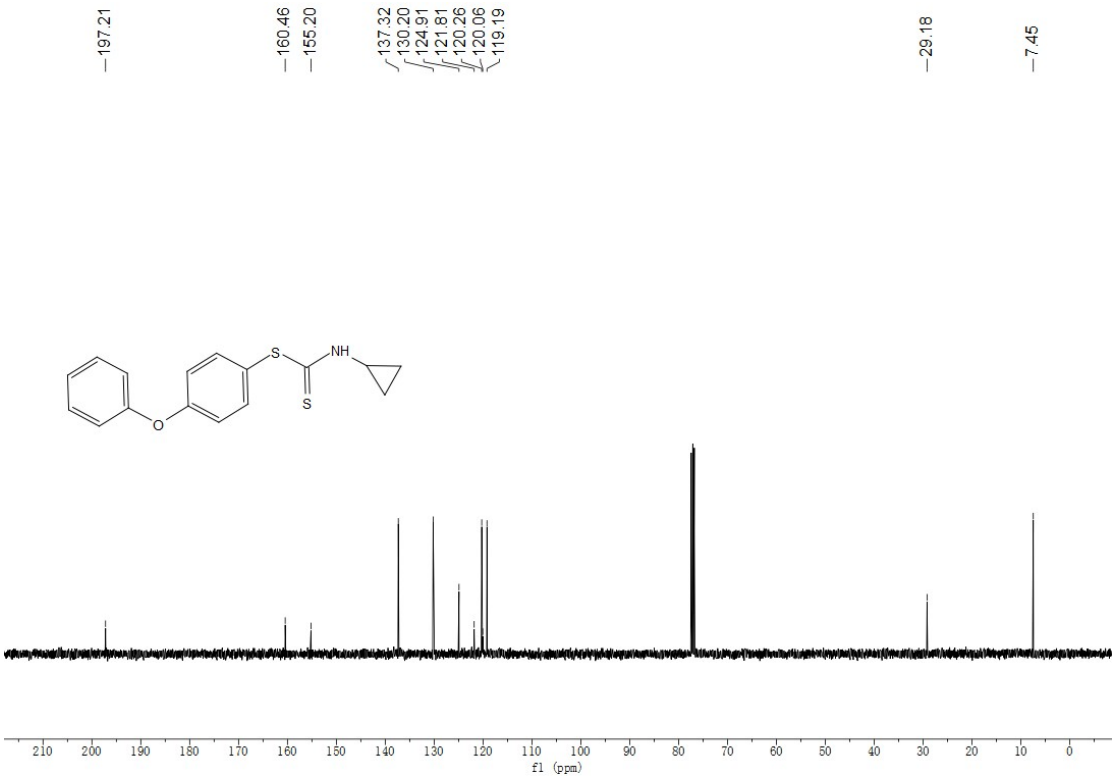
^{1}H NMR (400 MHz, Chloroform-*d*) of compound **4c'.**



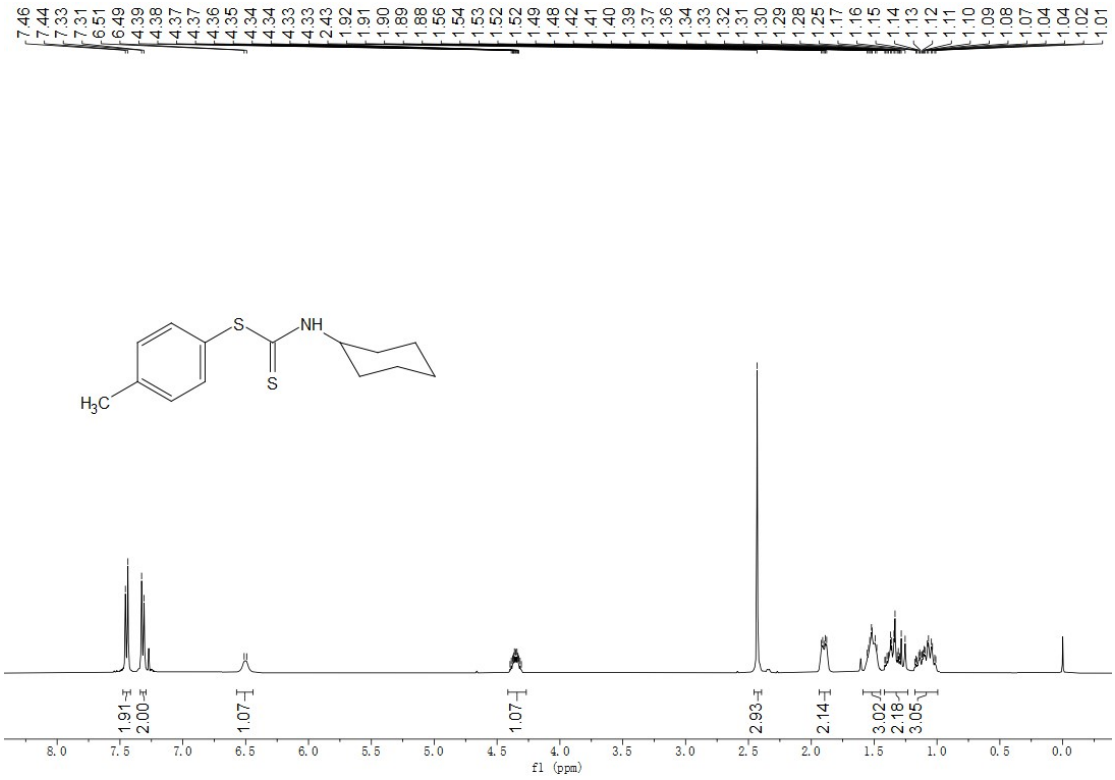
^{13}C NMR (400 MHz, Chloroform-*d*) of compound **4c'.**



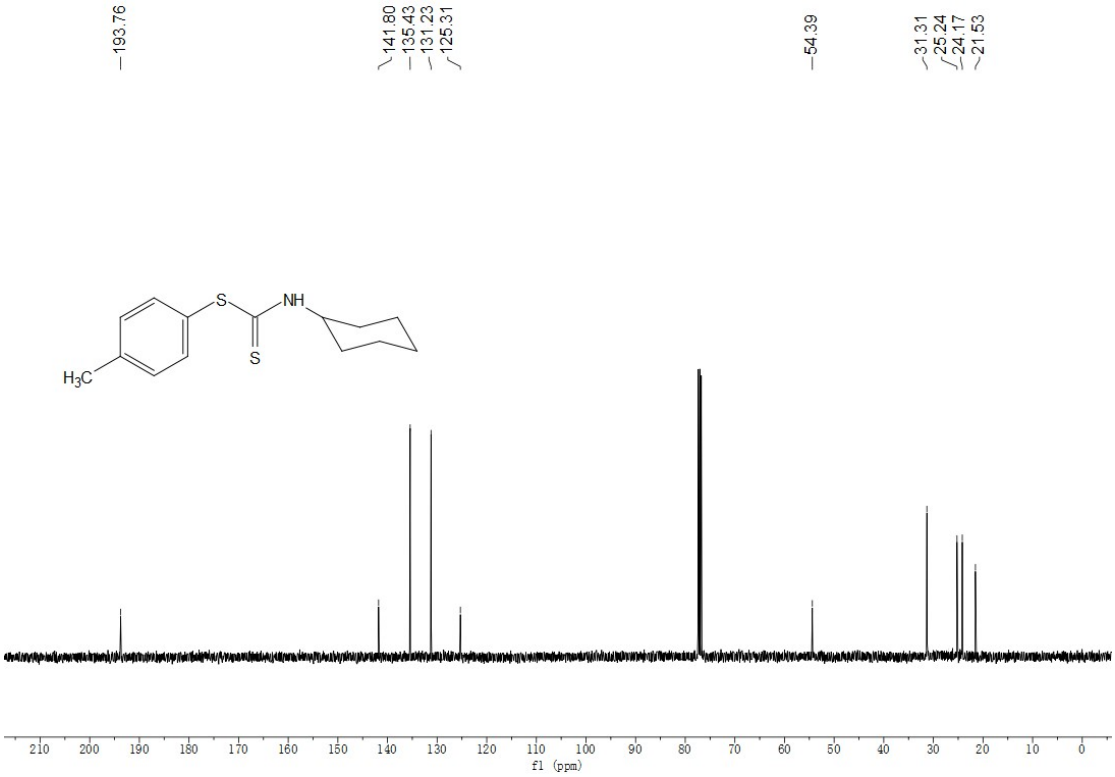
^{1}H NMR (400 MHz, Chloroform-*d*) of compound **4d'.**



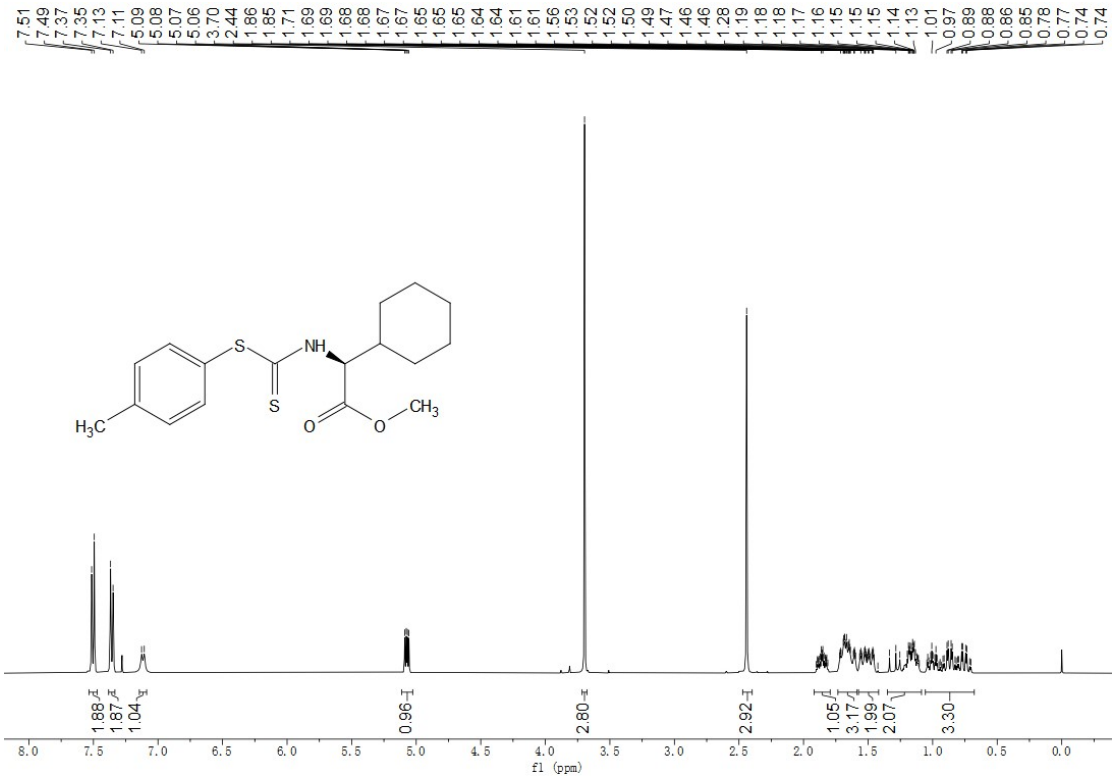
^{13}C NMR (400 MHz, Chloroform-*d*) of compound **4d'.**



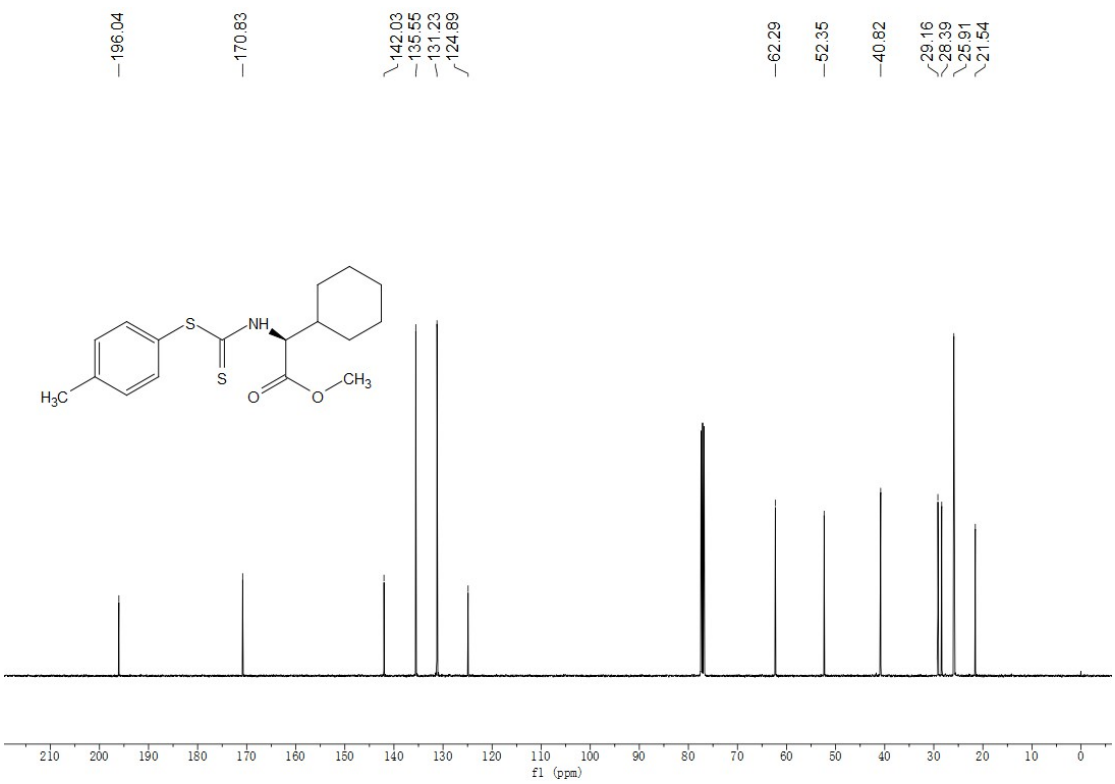
^{1}H NMR (400 MHz, Chloroform-*d*) of compound **4e'.**



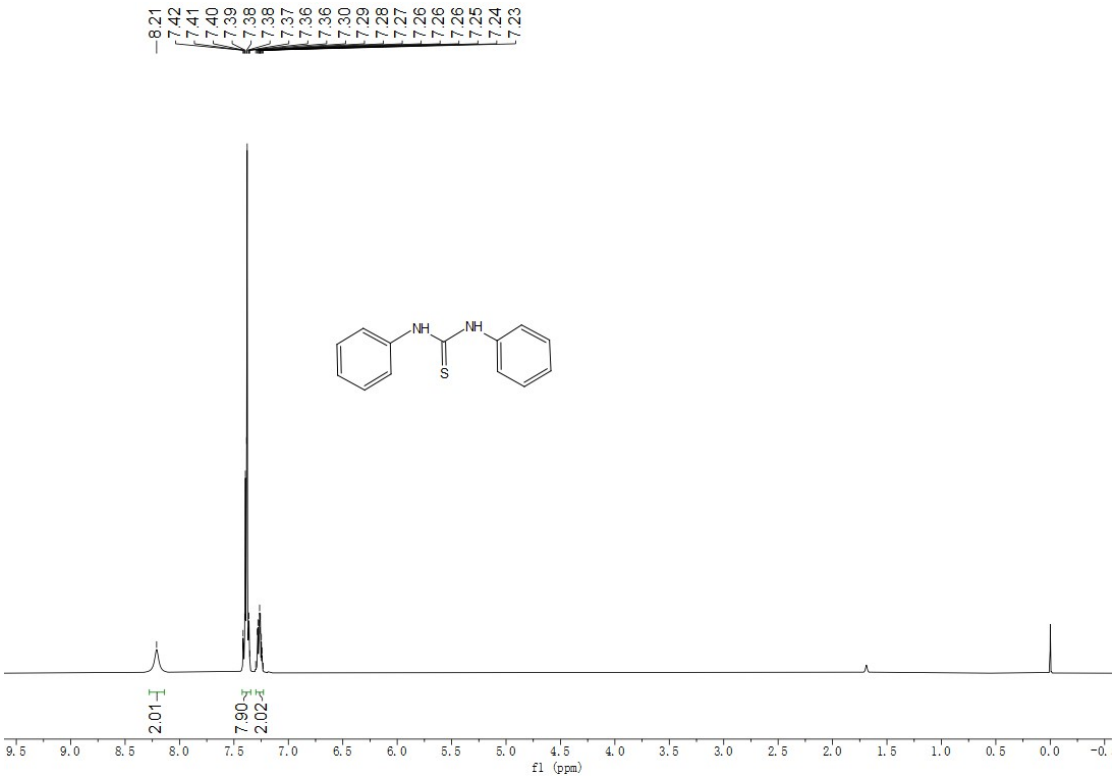
^{13}C NMR (400 MHz, Chloroform-*d*) of compound **4e'.**



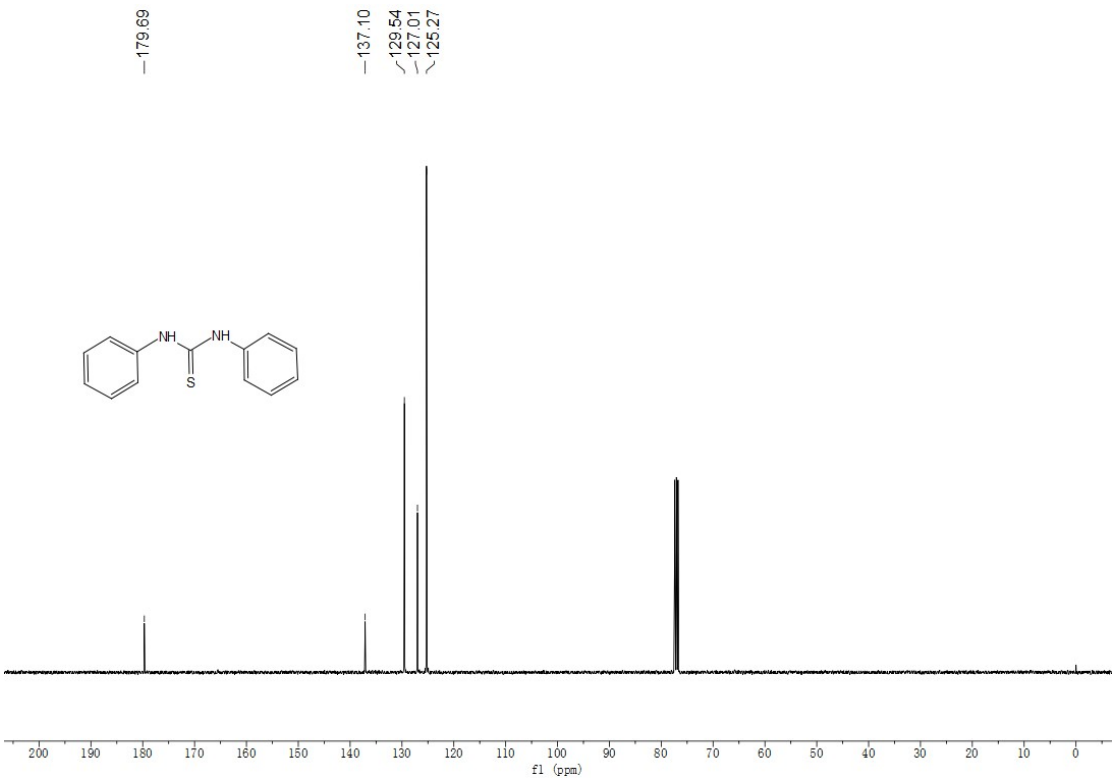
^{1}H NMR (400 MHz, Chloroform-*d*) of compound **4f'.**



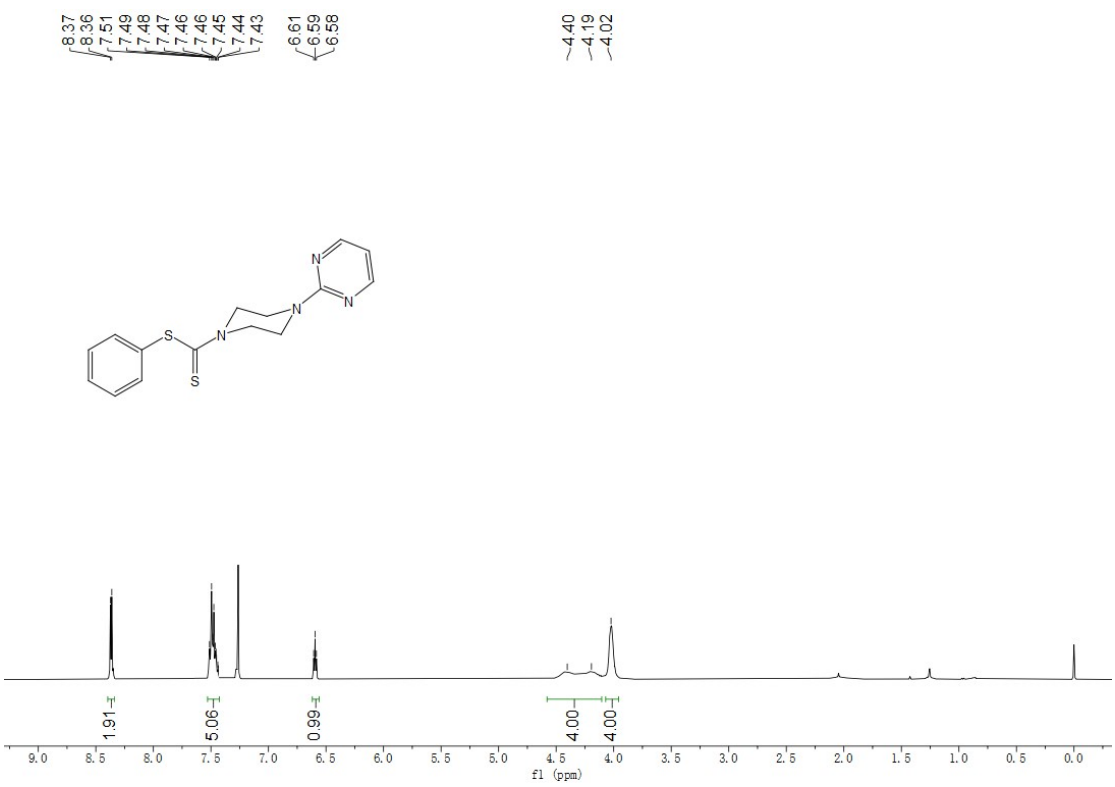
^{13}C NMR (400 MHz, Chloroform-*d*) of compound **4f'.**



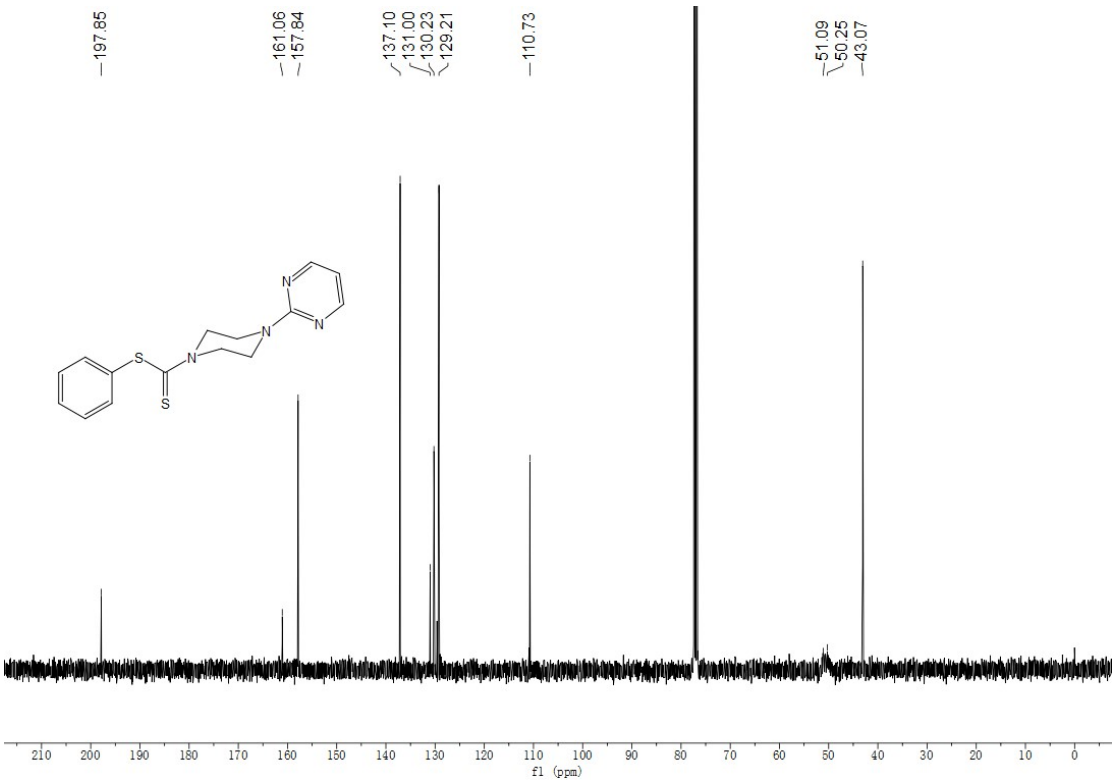
^{1}H NMR (400 MHz, Chloroform-*d*) of compound **4g'.**



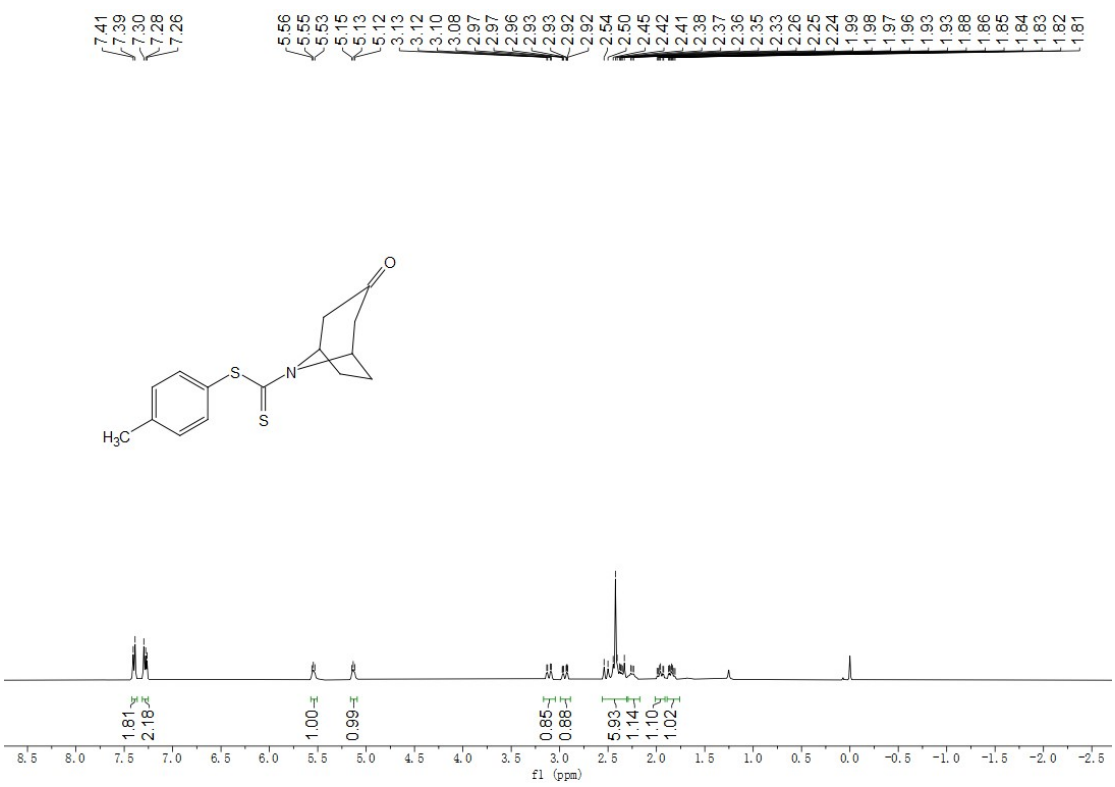
^{13}C NMR (400 MHz, Chloroform-*d*) of compound **4g'.**



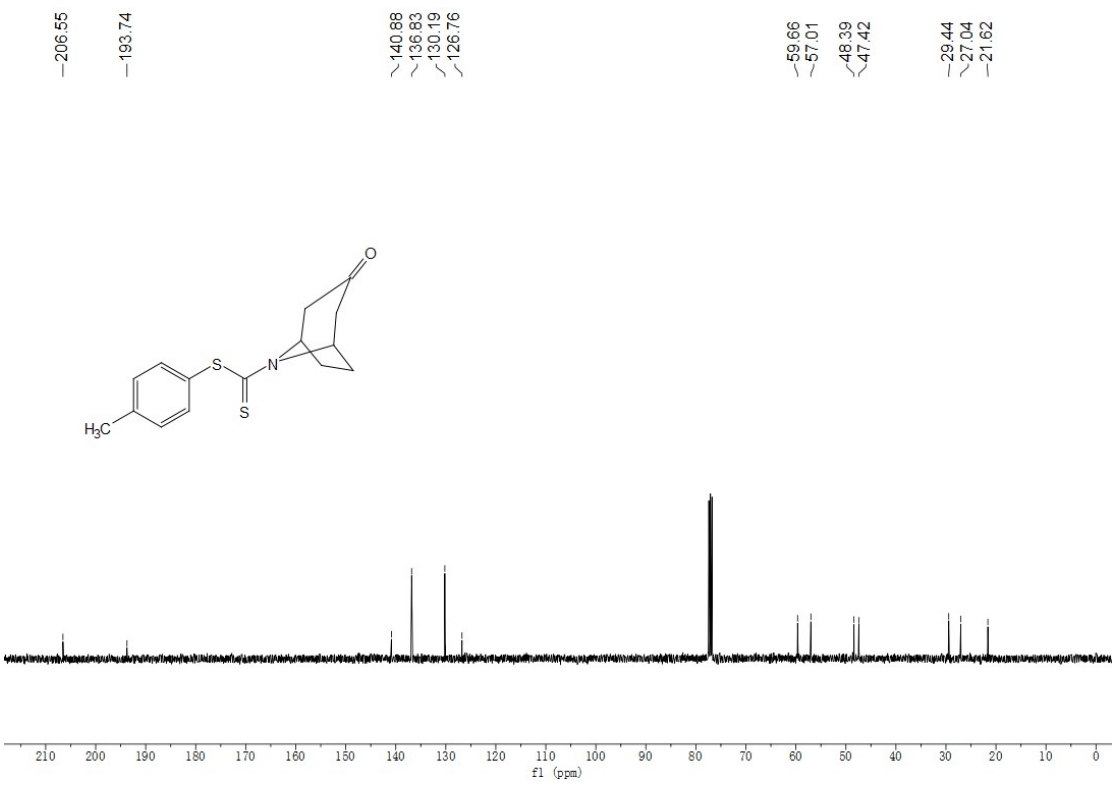
^{1}H NMR (400 MHz, Chloroform-*d*) of compound **4aa.**



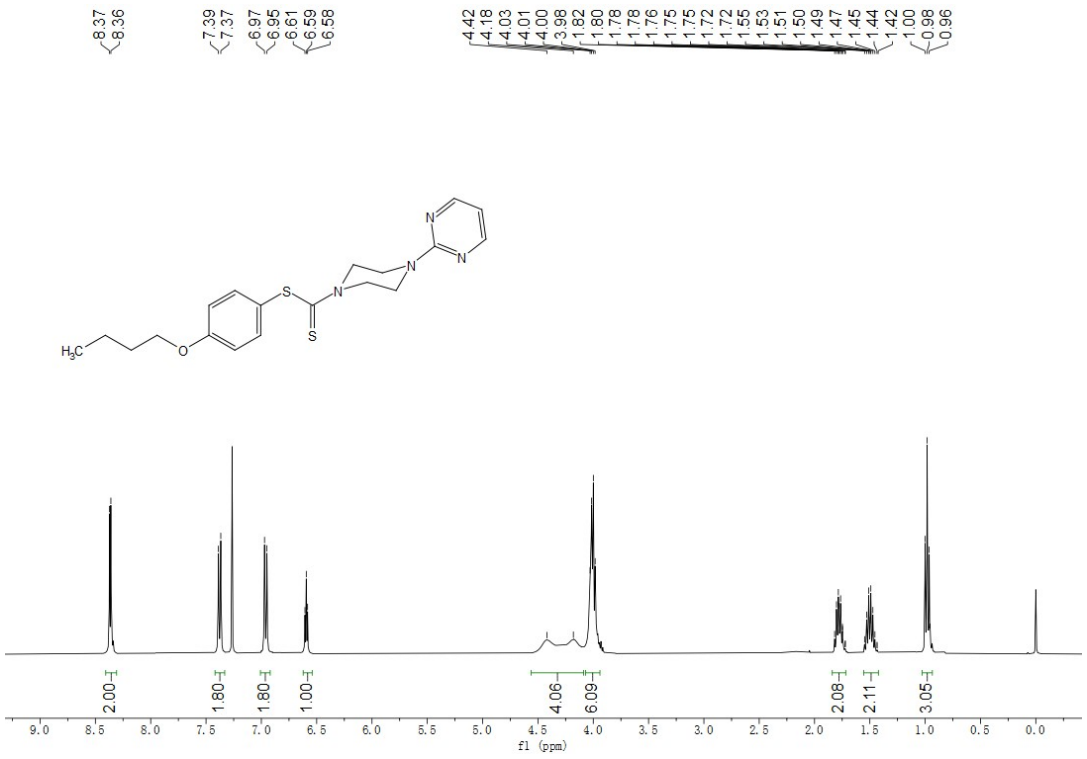
^{13}C NMR (400 MHz, Chloroform-*d*) of compound **4aa.**



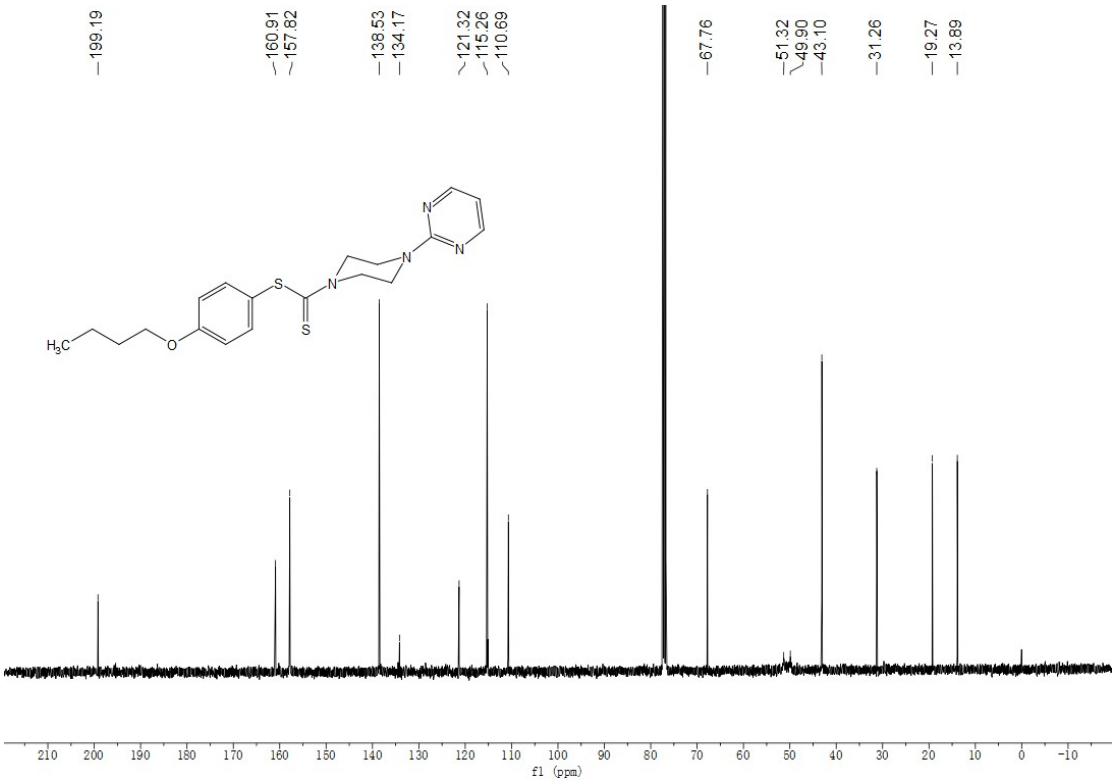
^{1}H NMR (400 MHz, Chloroform-*d*) of compound **4ab.**



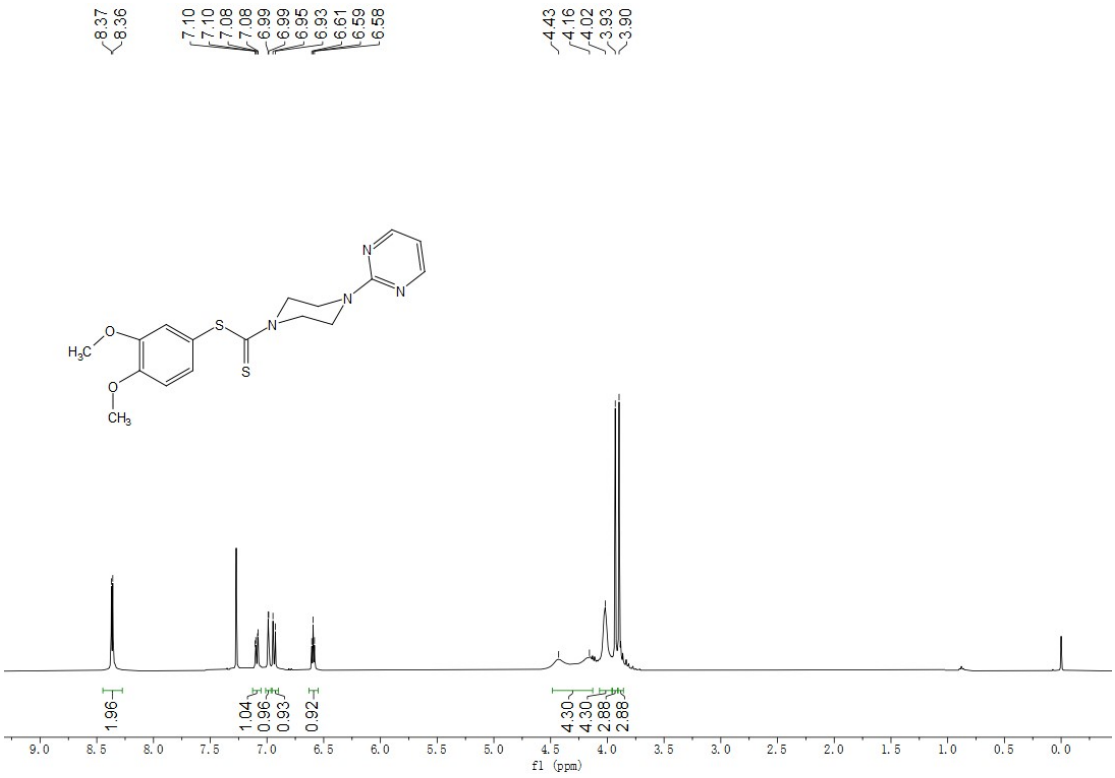
^{13}C NMR (400 MHz, Chloroform-*d*) of compound **4ab.**



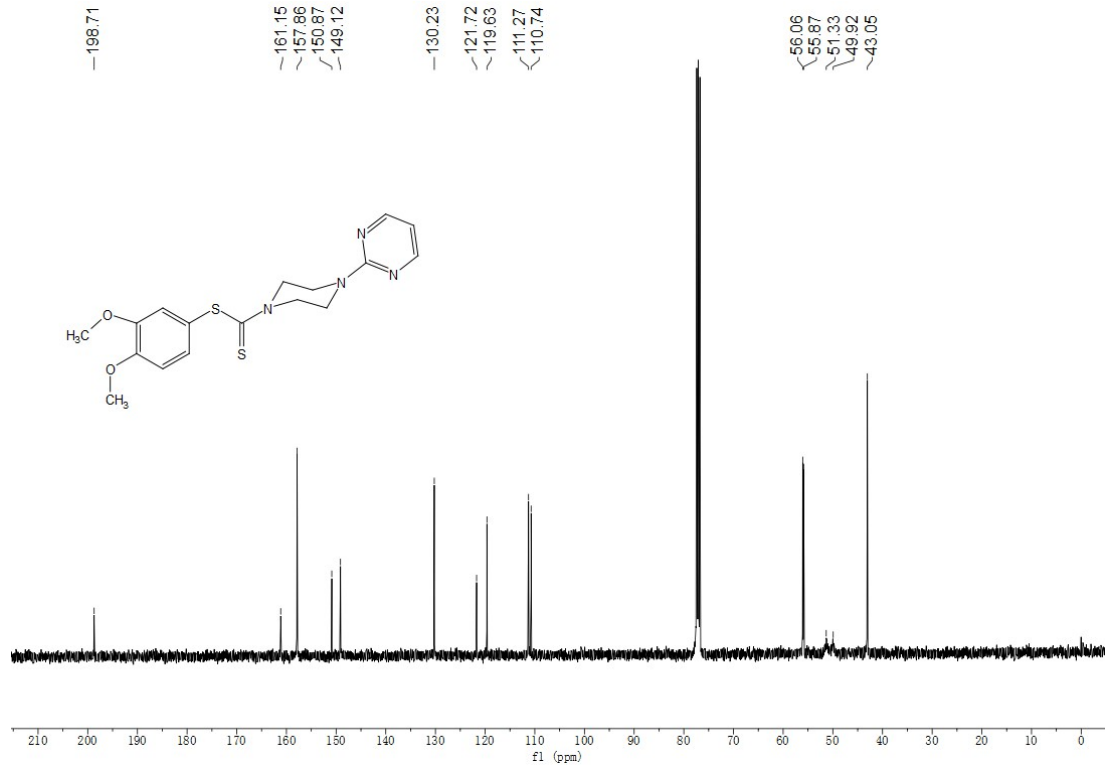
^{1}H NMR (400 MHz, Chloroform-*d*) of compound **4ac.**



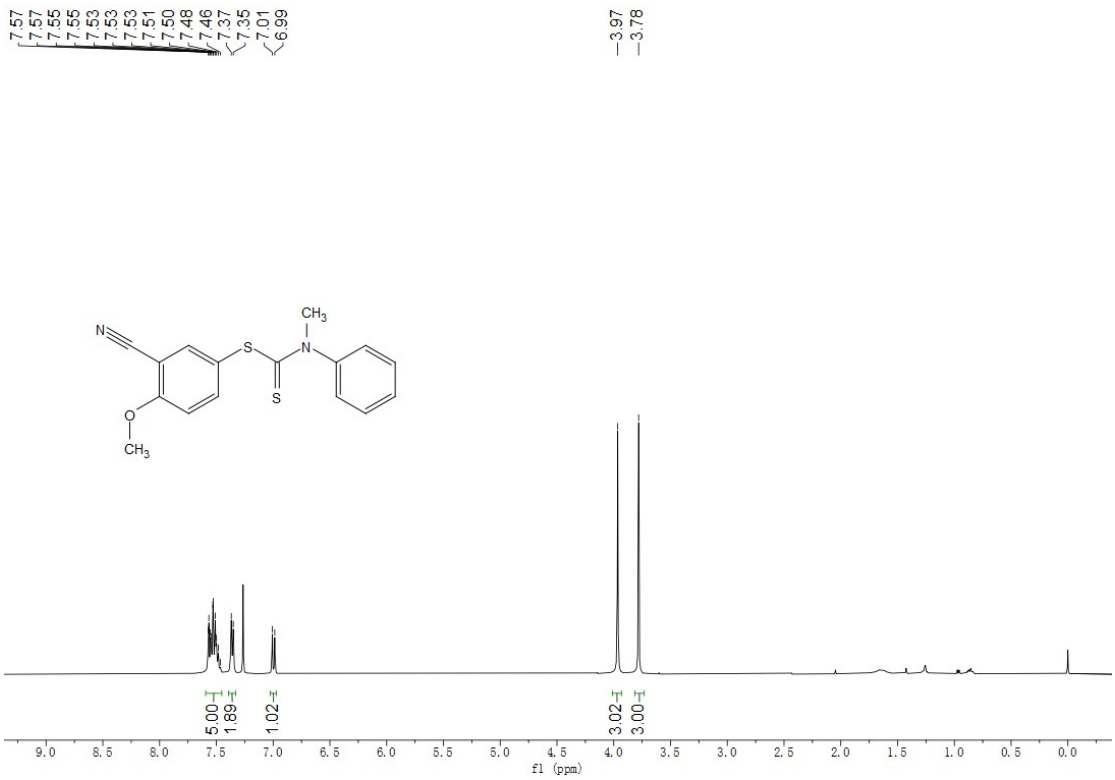
^{13}C NMR (400 MHz, Chloroform-*d*) of compound **4ac.**



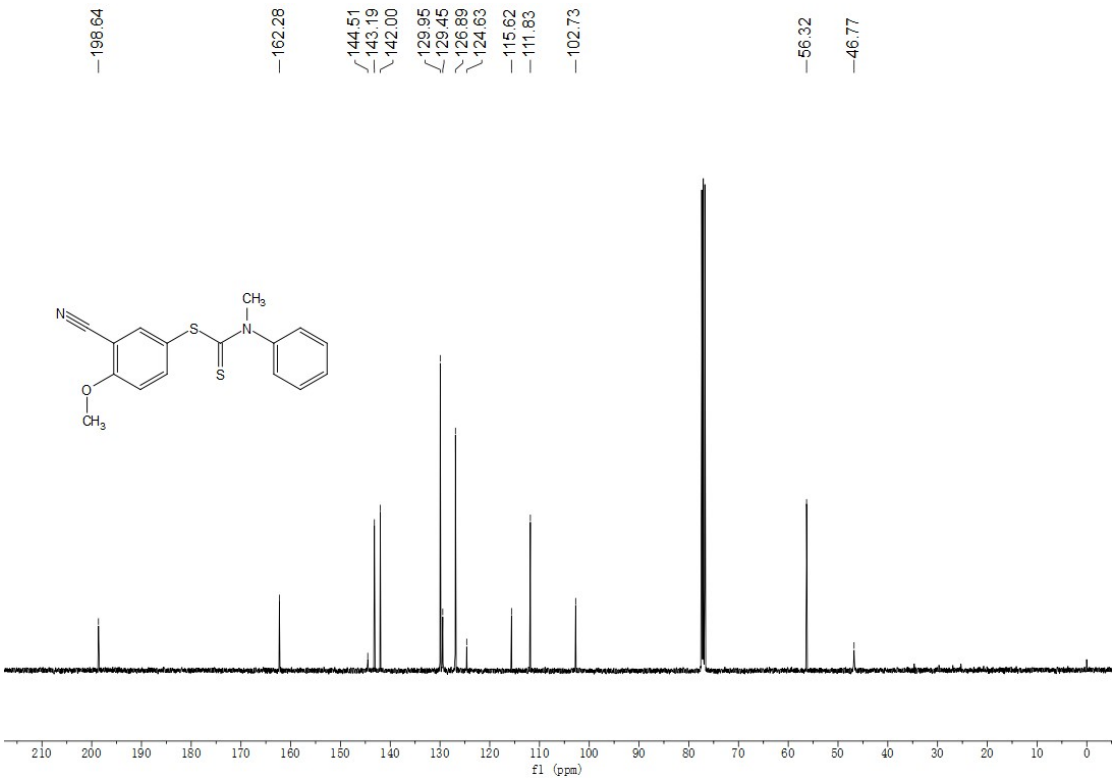
^{1}H NMR (400 MHz, Chloroform-*d*) of compound **4ad.**



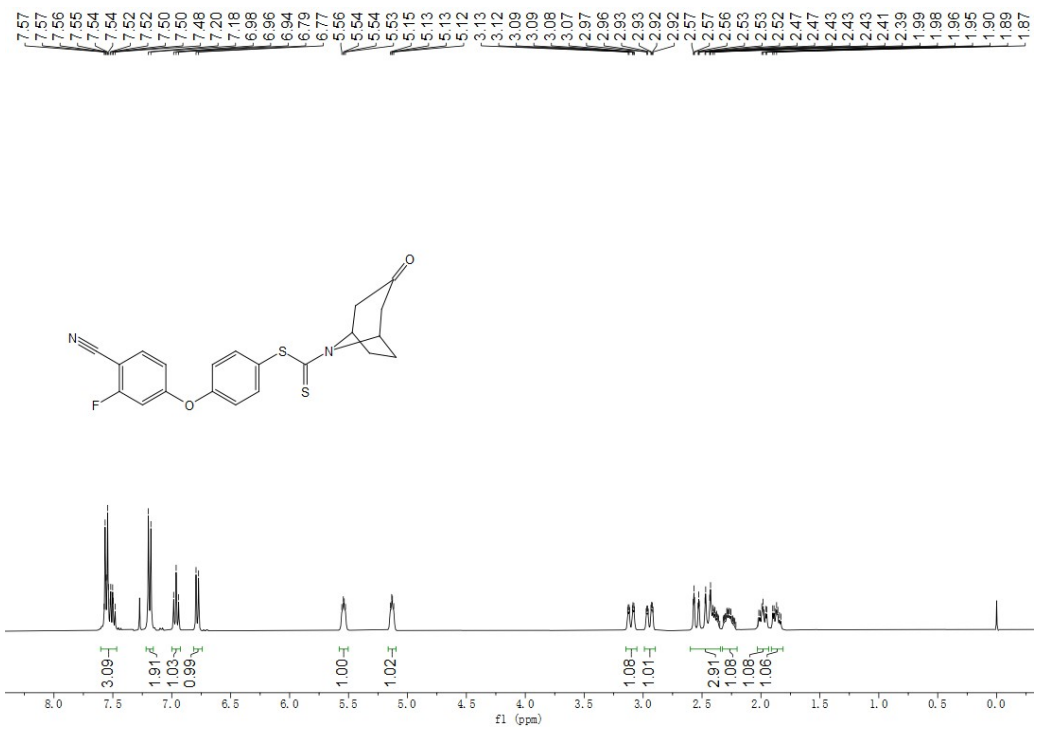
^{13}C NMR (400 MHz, Chloroform-*d*) of compound **4ad.**



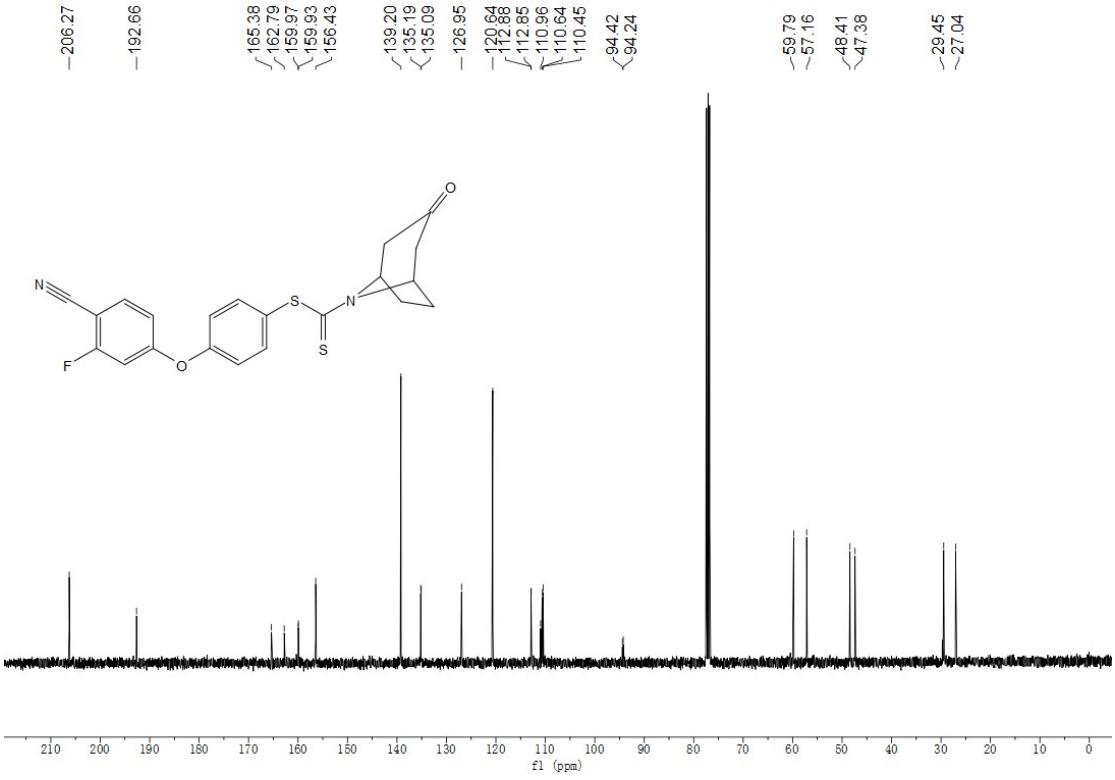
^{1}H NMR (400 MHz, Chloroform-*d*) of compound **4ae.**



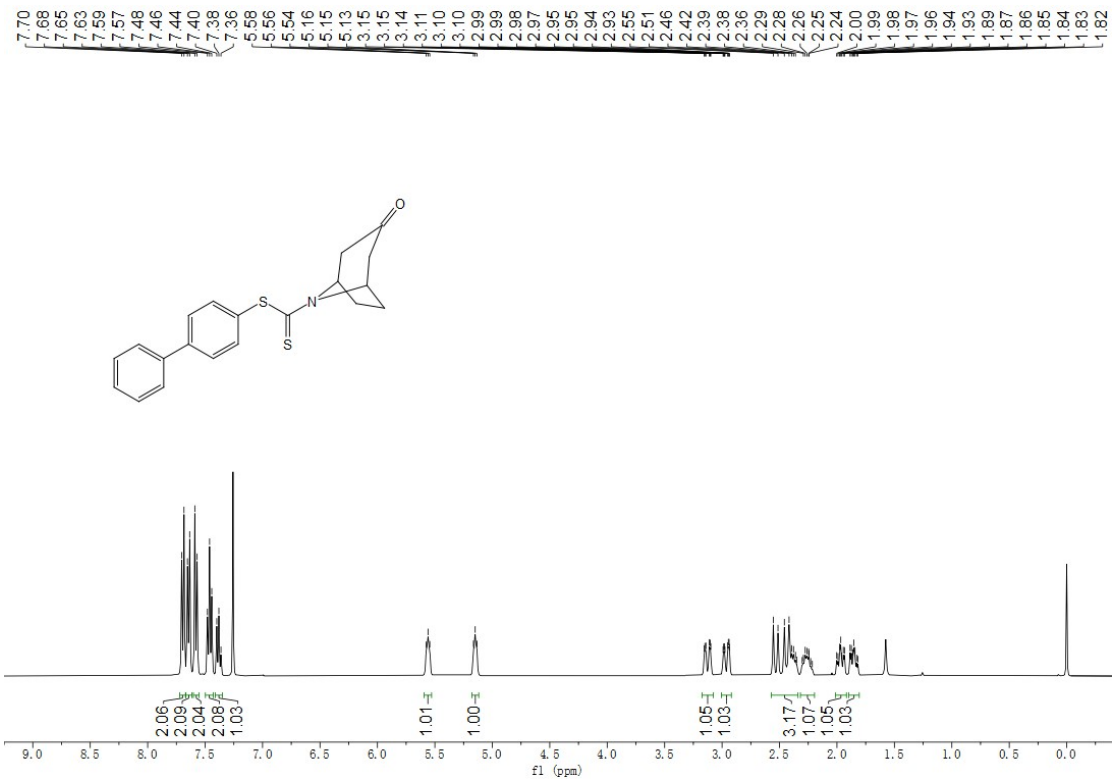
^{13}C NMR (400 MHz, Chloroform-*d*) of compound **4ae.**



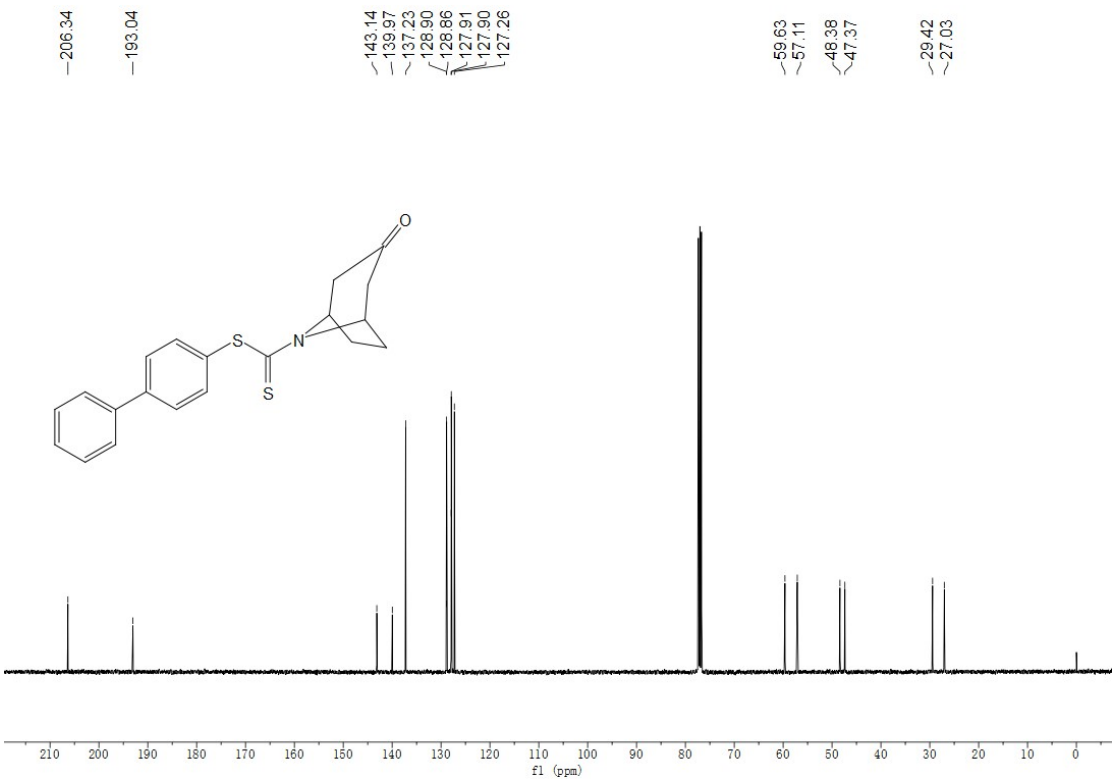
^{1}H NMR (400 MHz, Chloroform-*d*) of compound **4af.**



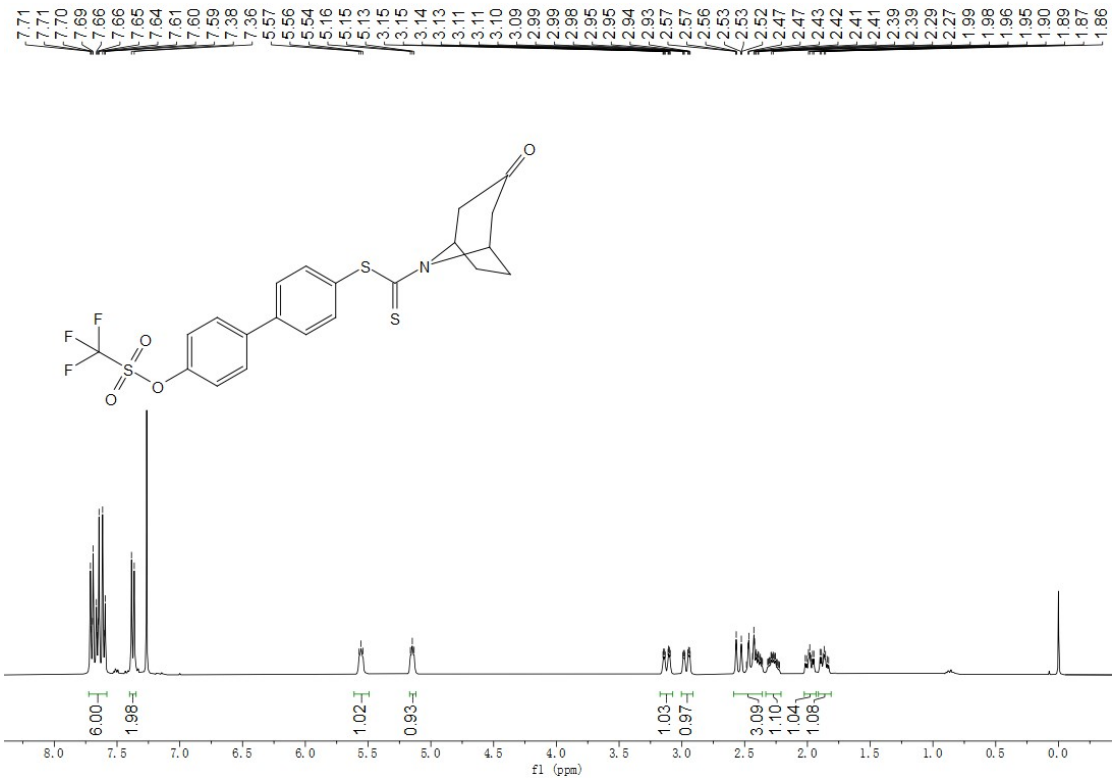
^{13}C NMR (400 MHz, Chloroform-*d*) of compound **4af.**



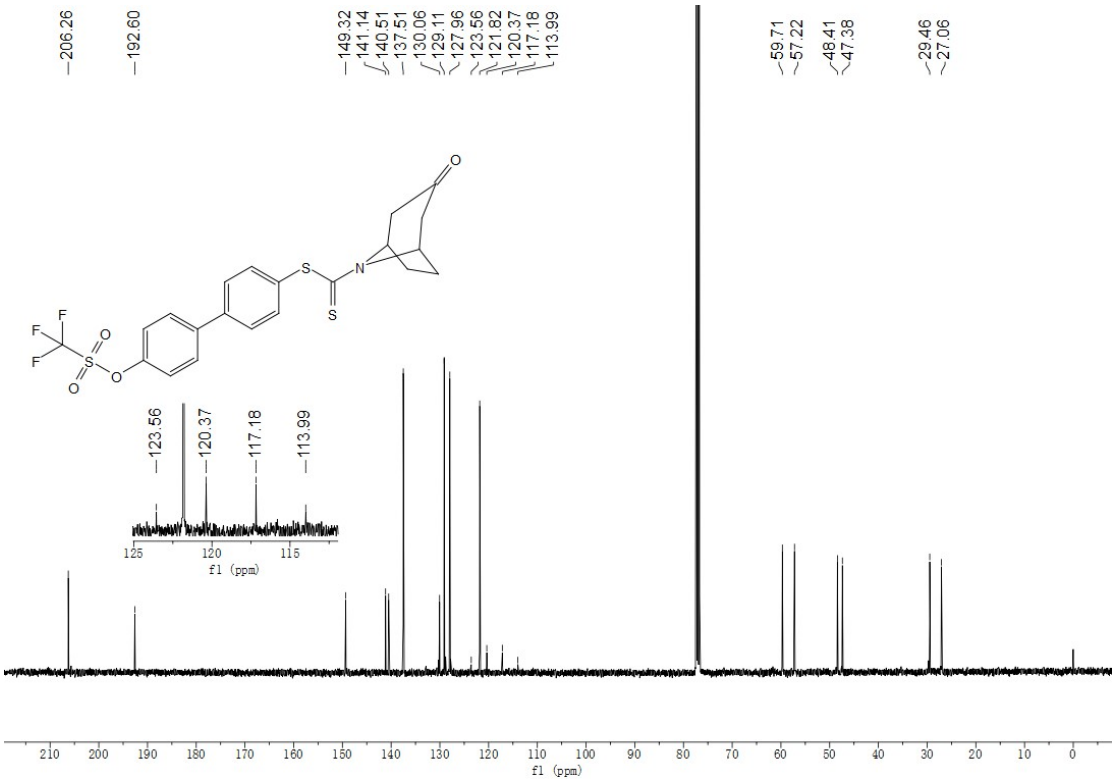
^{1}H NMR (400 MHz, Chloroform-*d*) of compound **4ag.**



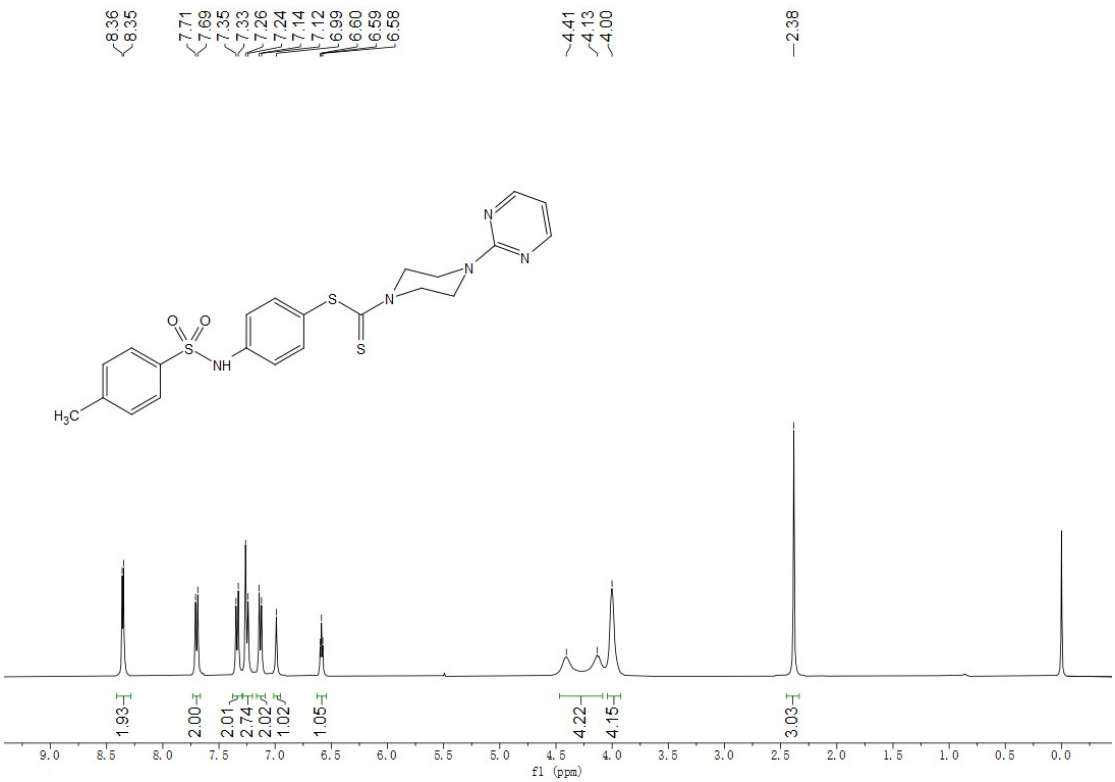
^{13}C NMR (400 MHz, Chloroform-*d*) of compound **4ag.**



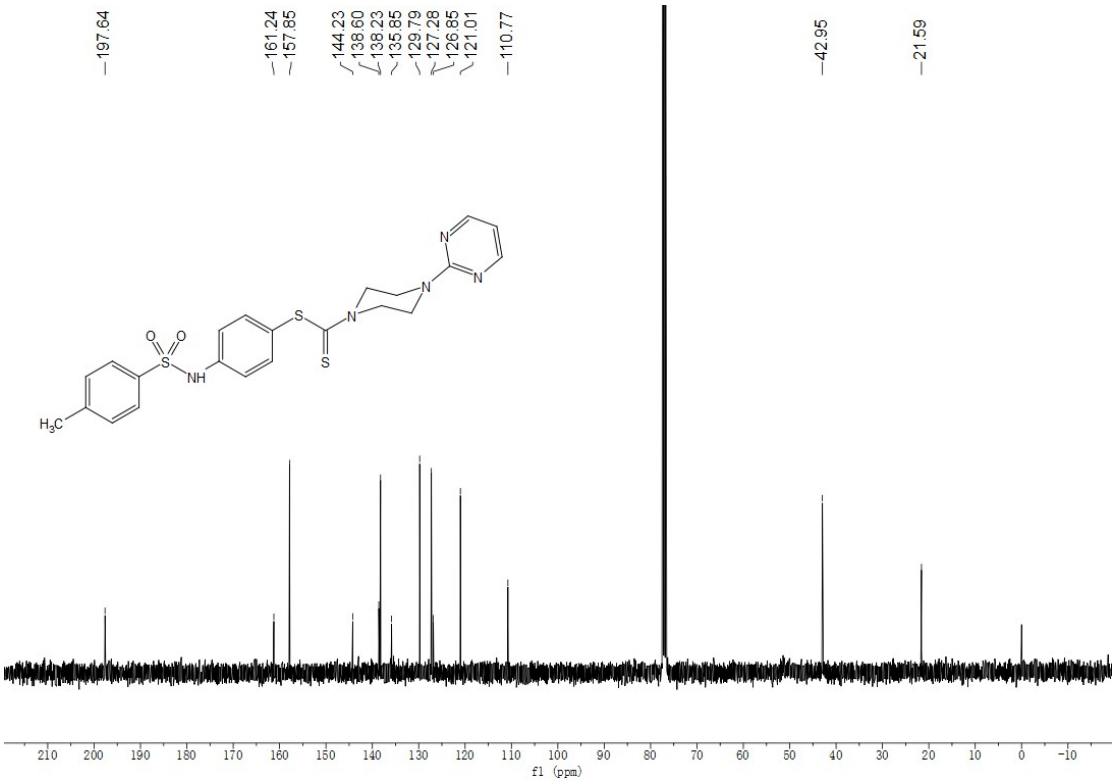
^{1}H NMR (400 MHz, Chloroform-*d*) of compound **4ah.**



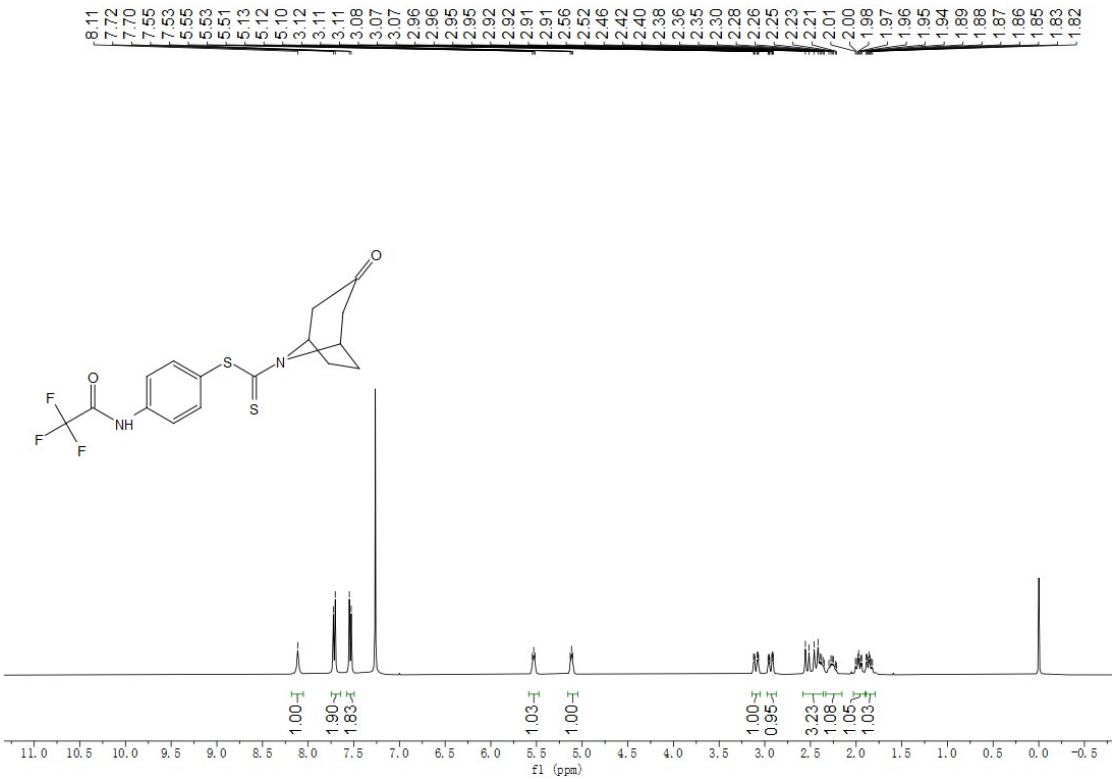
^{13}C NMR (400 MHz, Chloroform-*d*) of compound **4ah.**



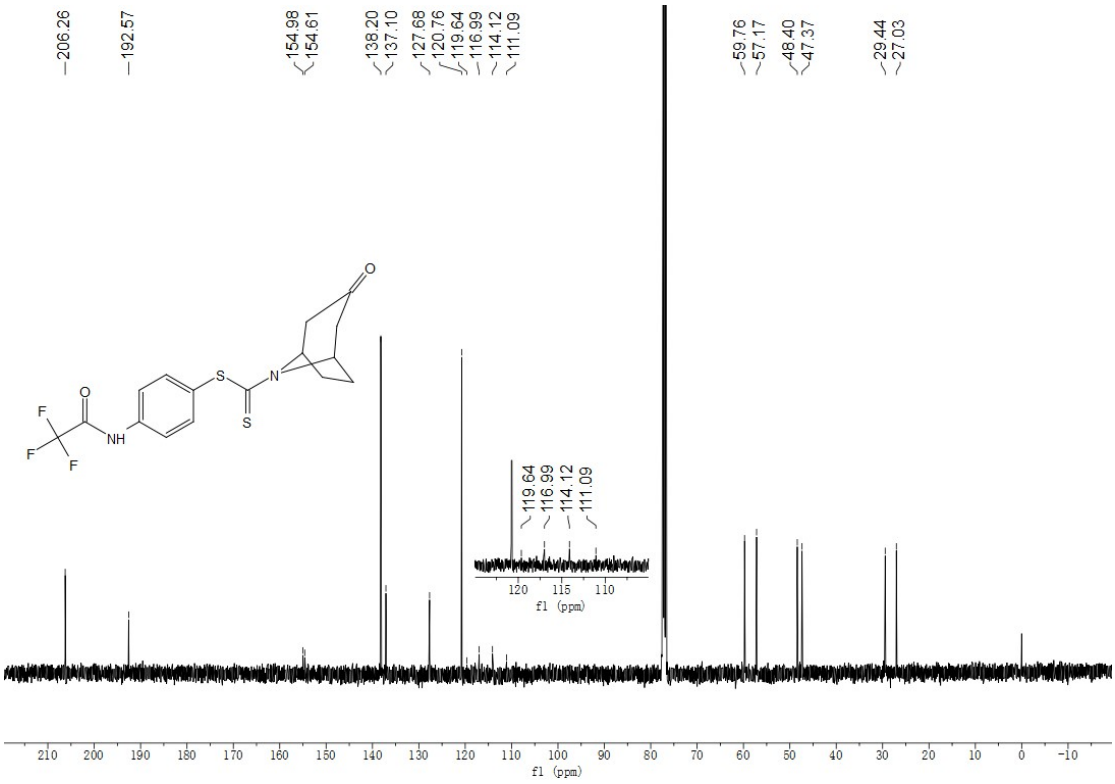
[1]H NMR (400 MHz, Chloroform-*d*) of compound **4ai.**



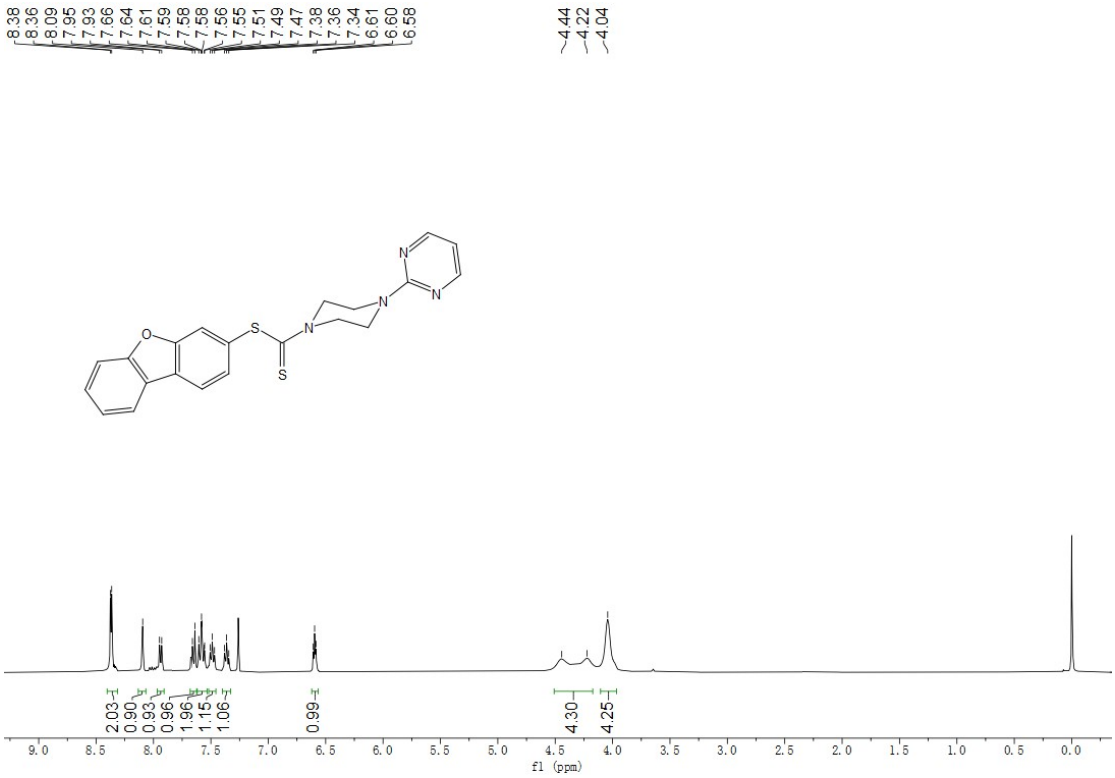
[13]C NMR (400 MHz, Chloroform-*d*) of compound **4ai.**



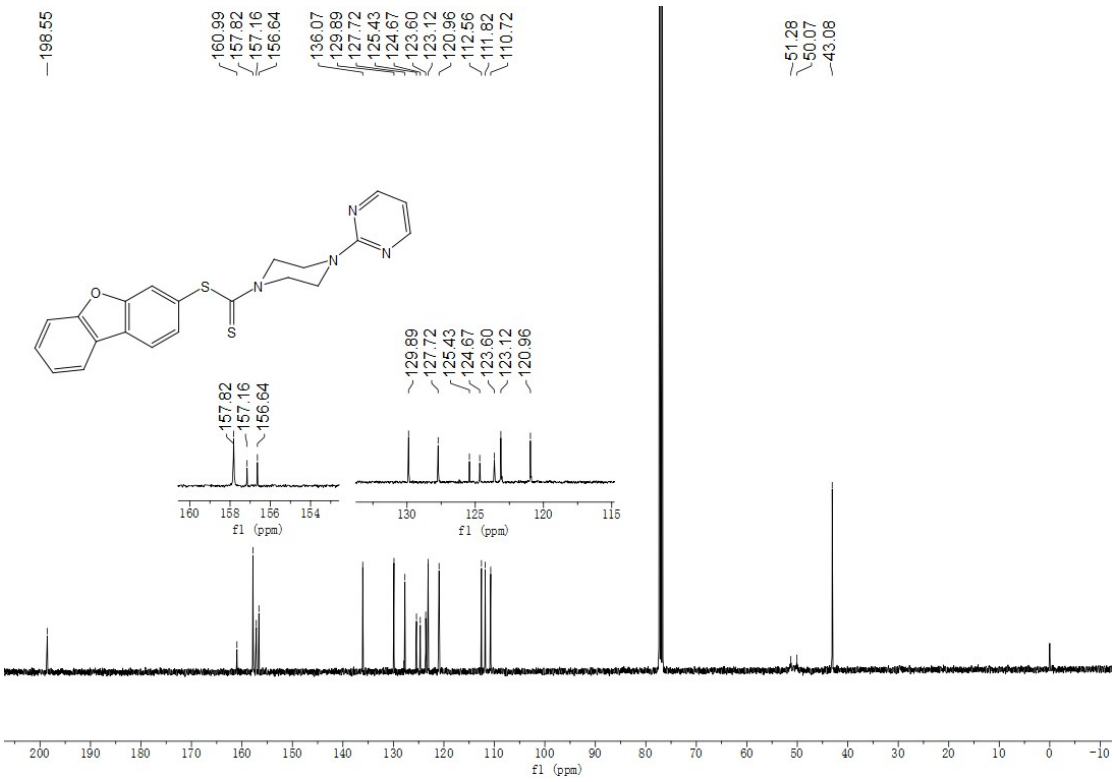
^{1}H NMR (400 MHz, Chloroform-*d*) of compound **4aj.**



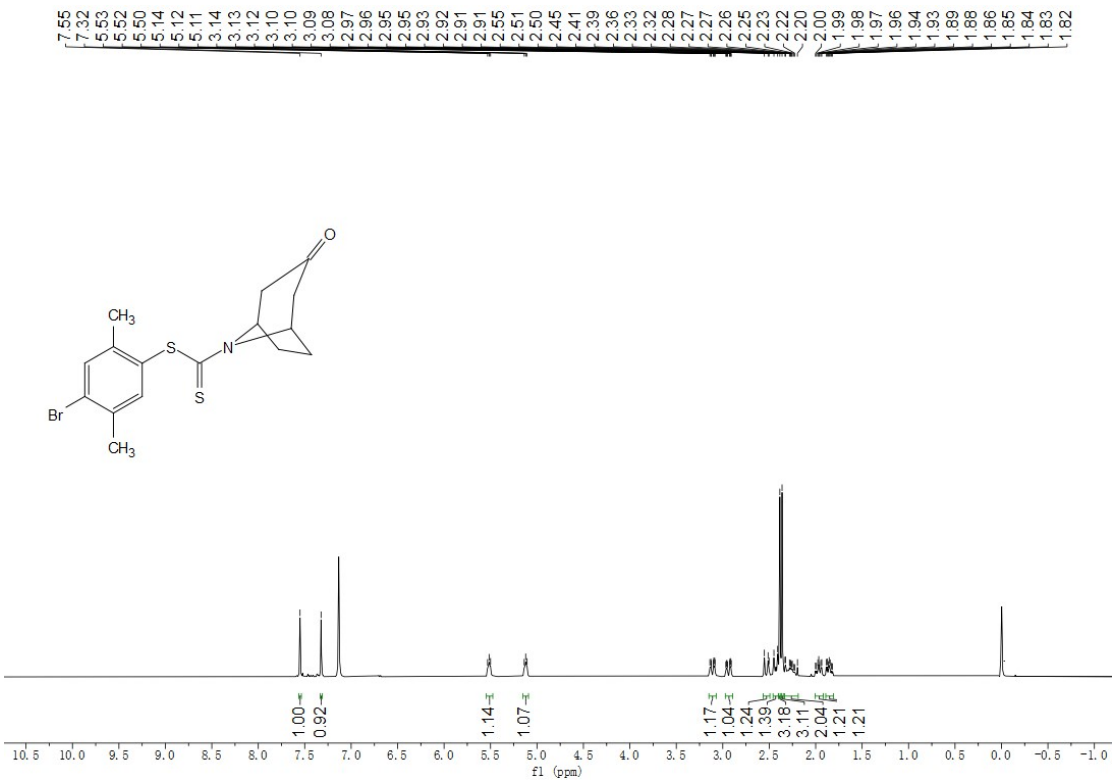
^{13}C NMR (400 MHz, Chloroform-*d*) of compound **4aj.**



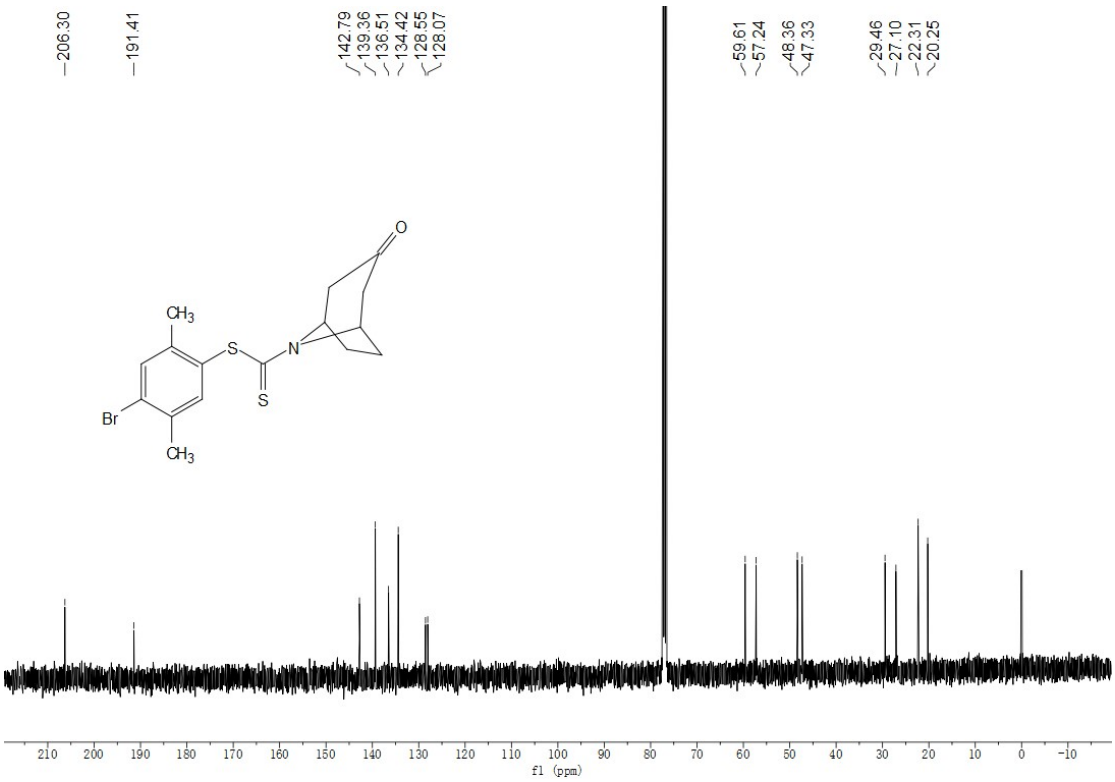
^{1}H NMR (400 MHz, Chloroform-*d*) of compound **4ak.**



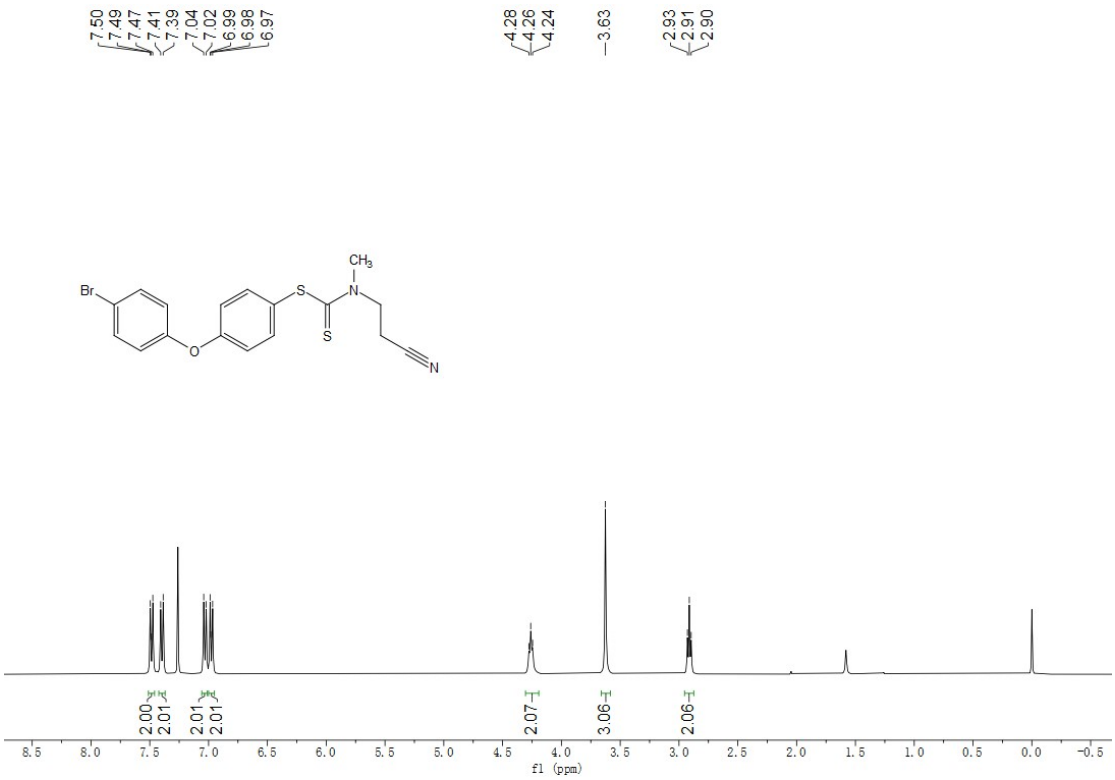
^{13}C NMR (400 MHz, Chloroform-*d*) of compound **4ak.**



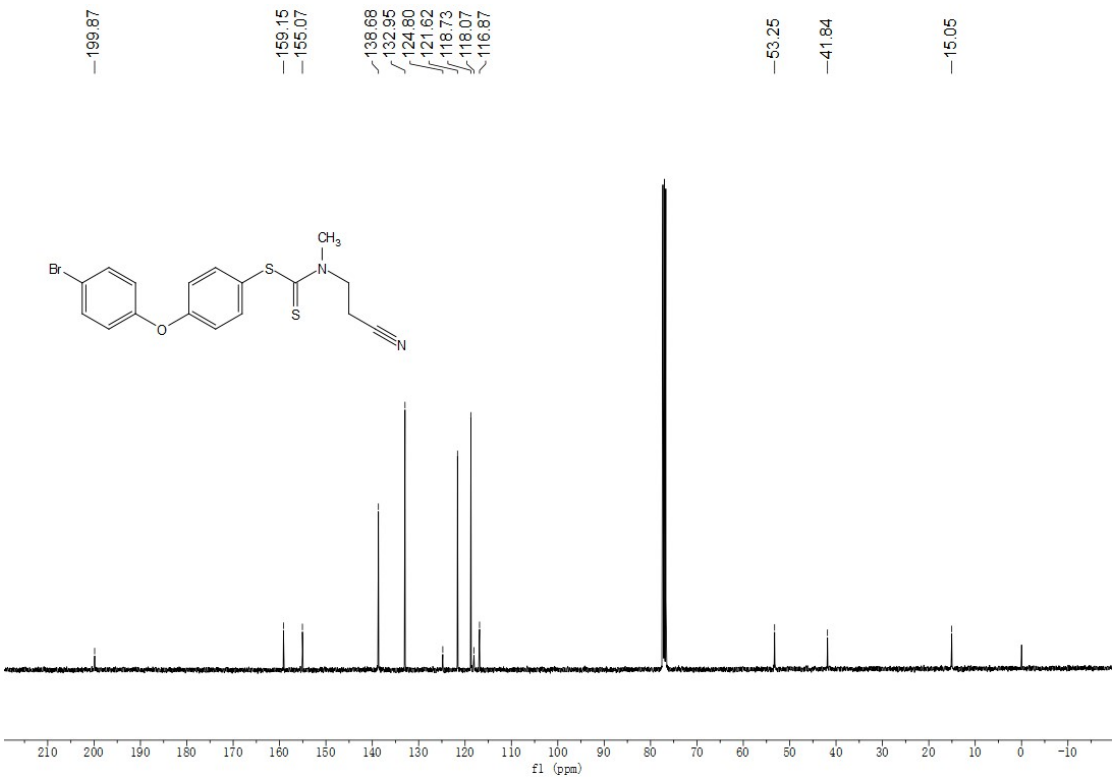
^{1}H NMR (400 MHz, Chloroform-*d*) of compound **4al.**



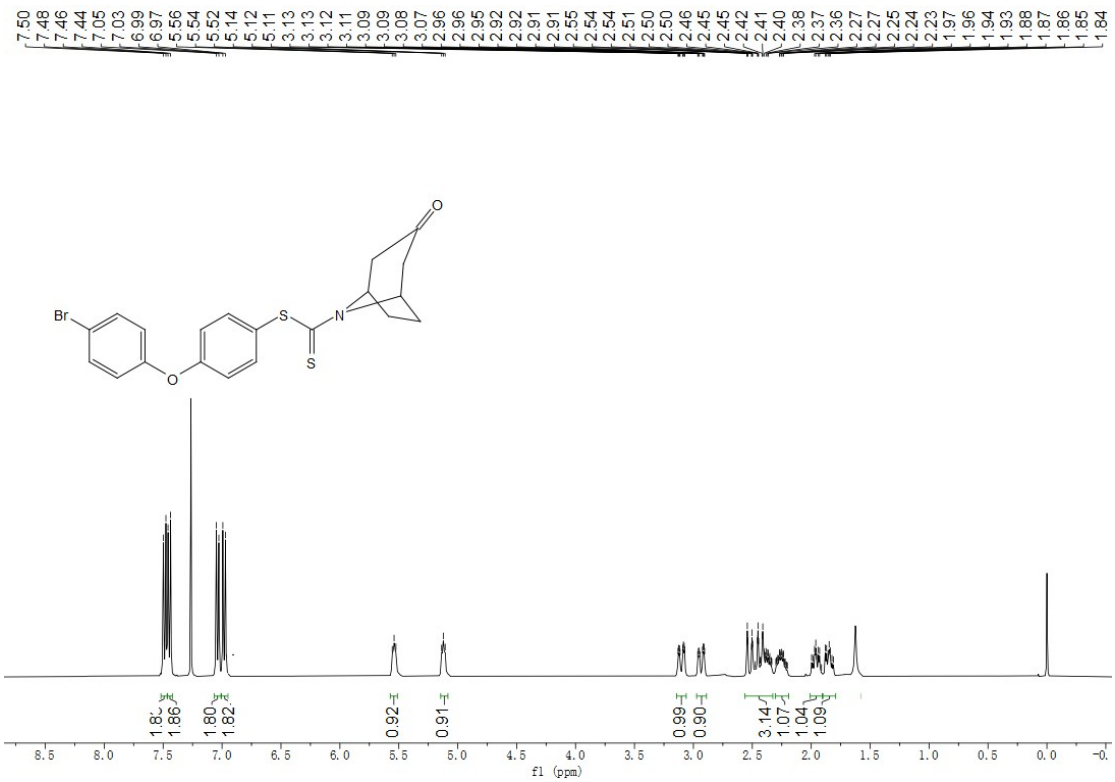
^{13}C NMR (400 MHz, Chloroform-*d*) of compound **4al.**



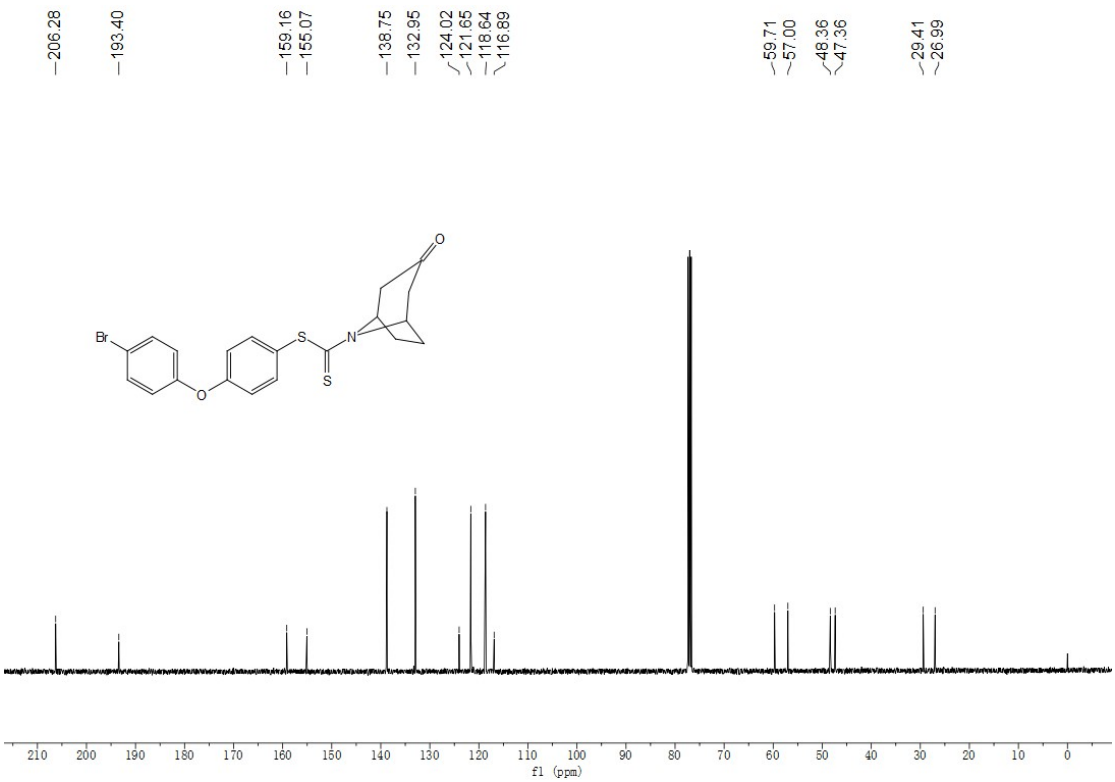
^{1}H NMR (400 MHz, Chloroform-*d*) of compound **4am.**



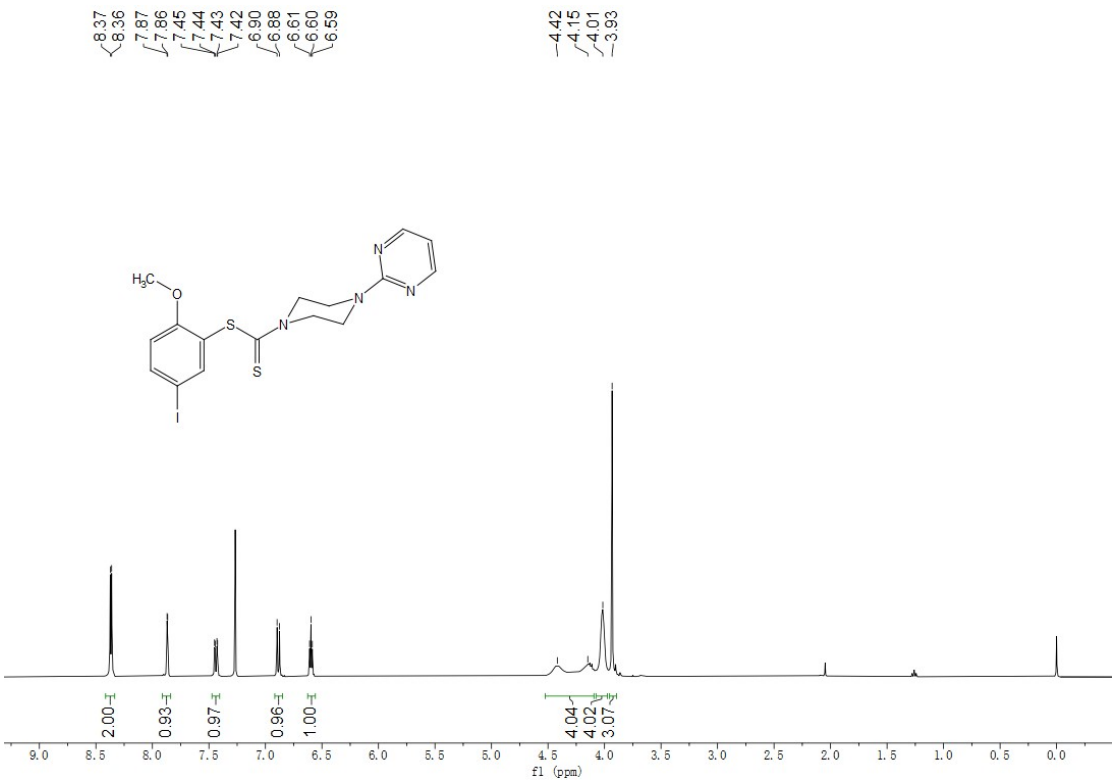
^{13}C NMR (400 MHz, Chloroform-*d*) of compound **4am.**



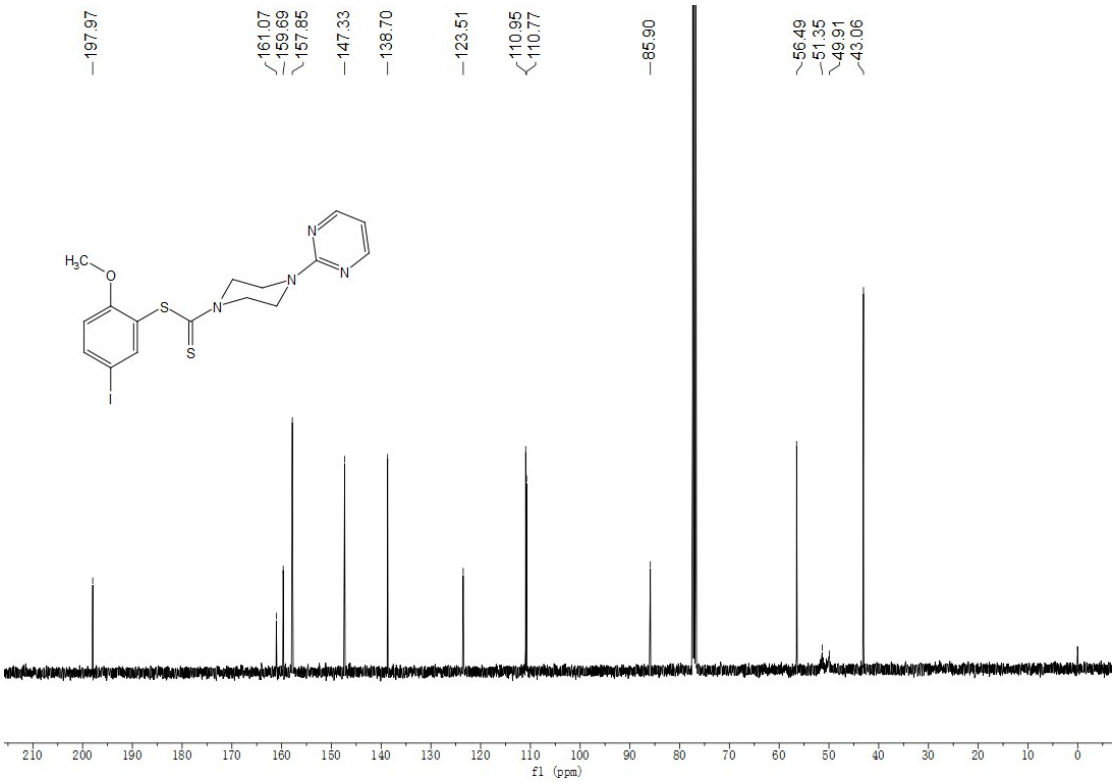
^{1}H NMR (400 MHz, Chloroform-*d*) of compound **4an.**



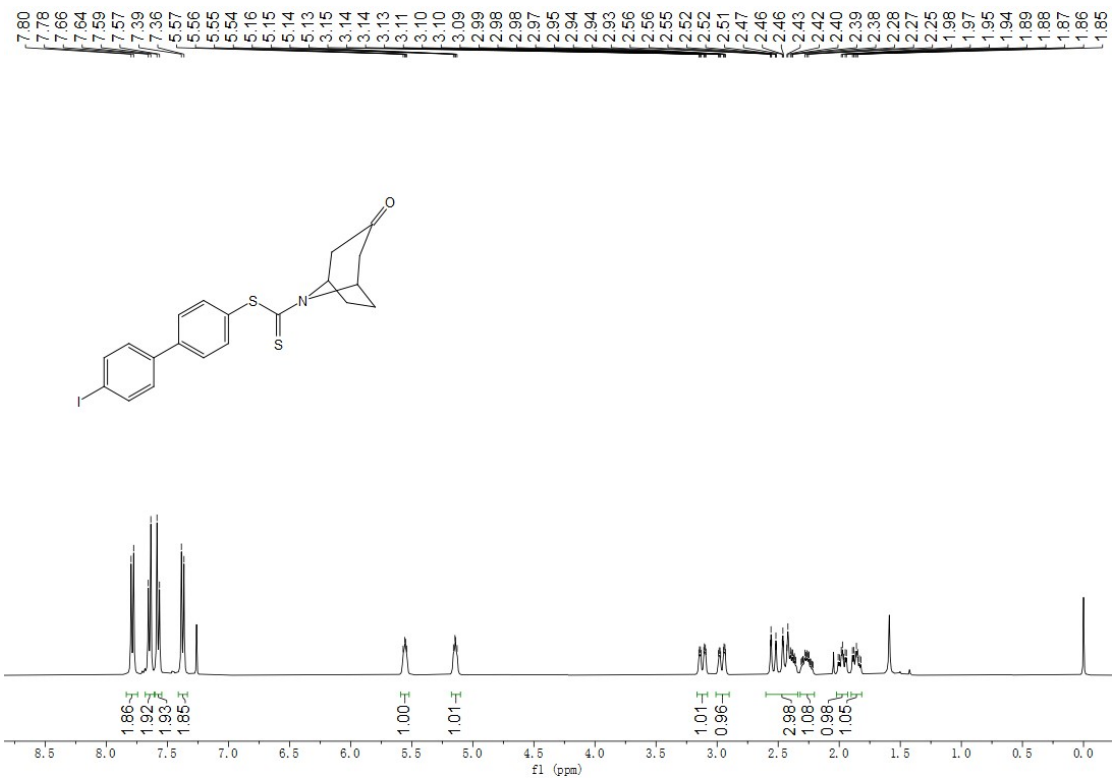
^{13}C NMR (400 MHz, Chloroform-*d*) of compound **4an.**



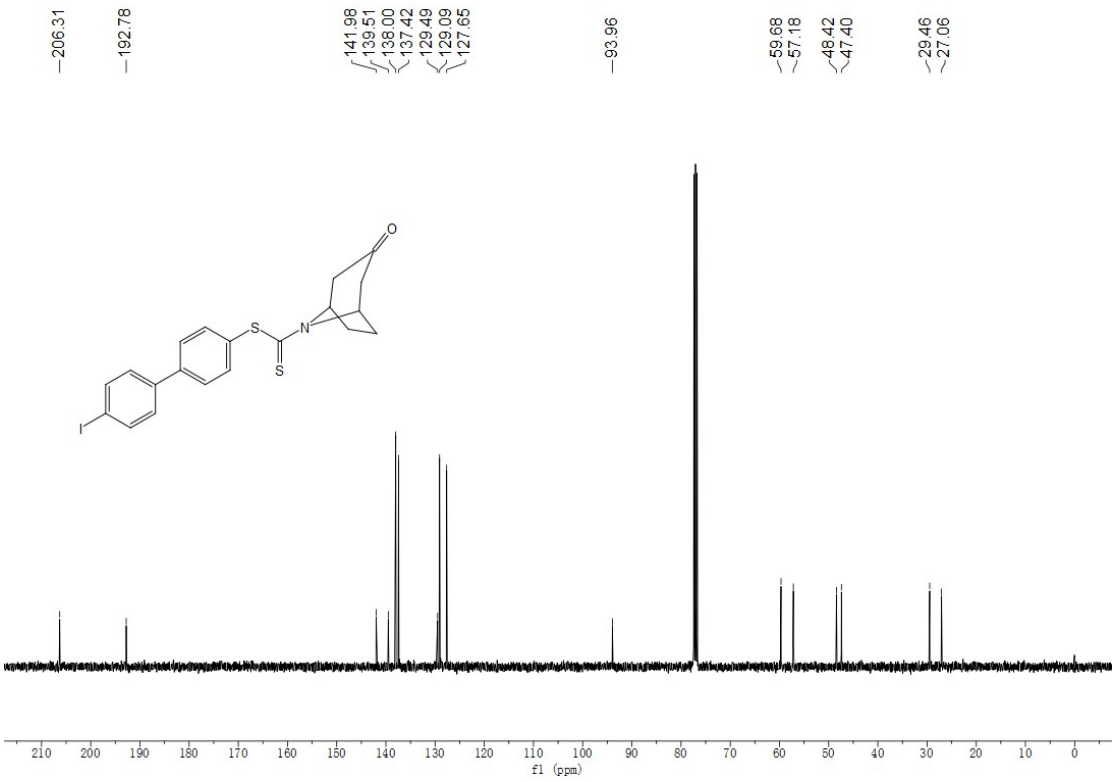
^{1}H NMR (400 MHz, Chloroform-*d*) of compound **4ao.**



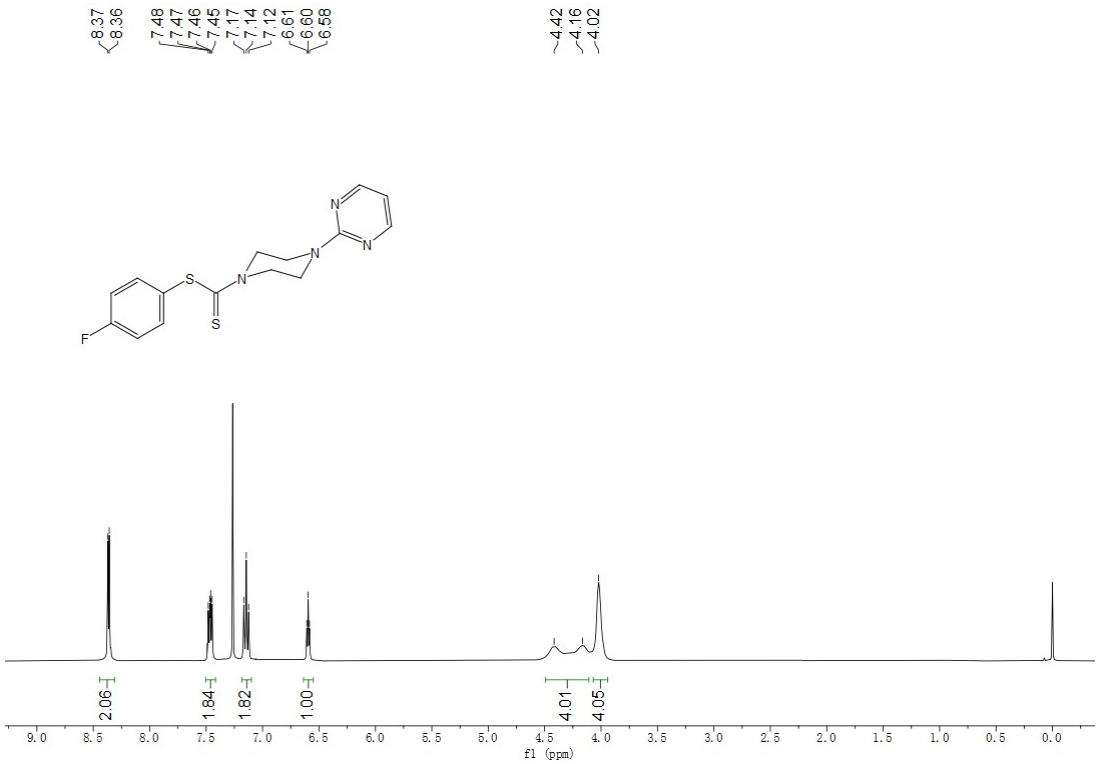
^{13}C NMR (400 MHz, Chloroform-*d*) of compound **4ao.**



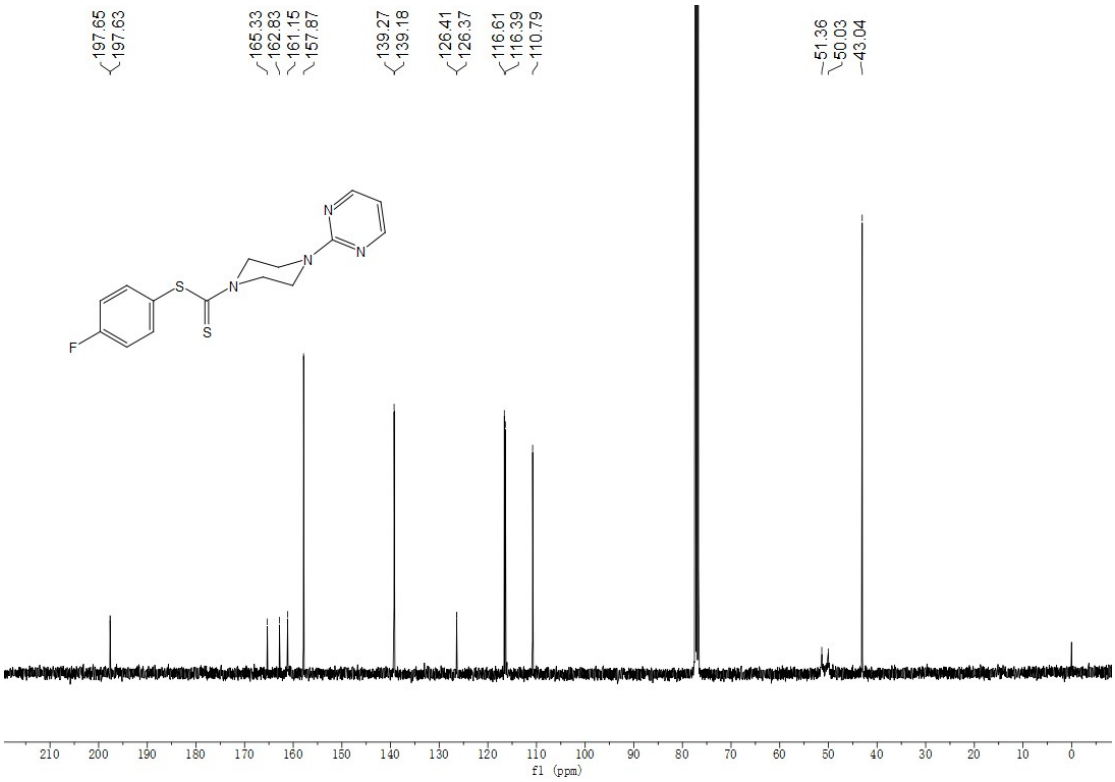
^{1}H NMR (400 MHz, Chloroform-*d*) of compound **4ap.**



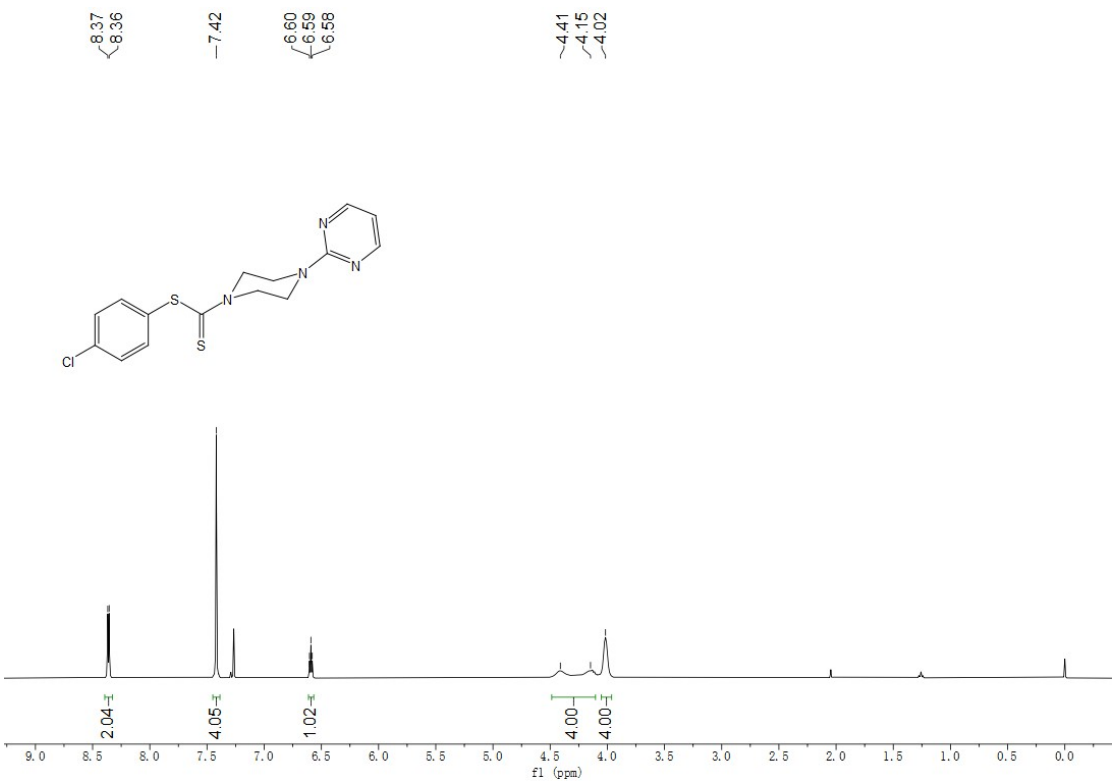
^{13}C NMR (400 MHz, Chloroform-*d*) of compound **4ap.**



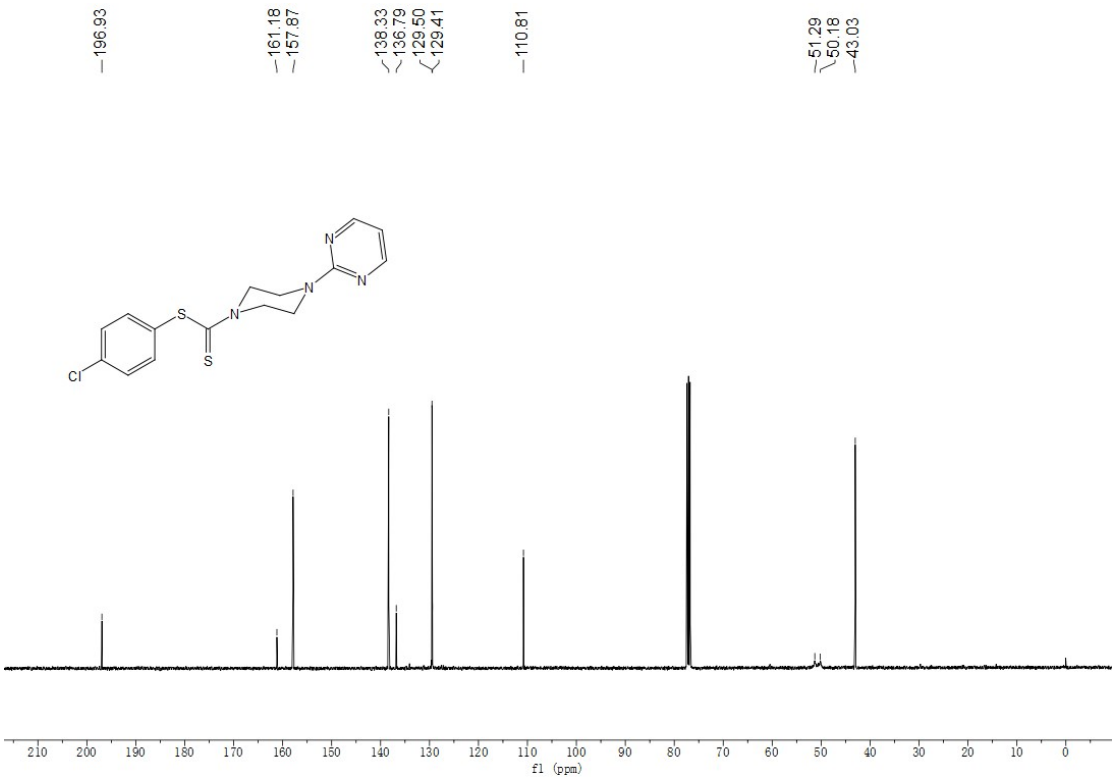
^{1}H NMR (400 MHz, Chloroform-*d*) of compound **4aq.**



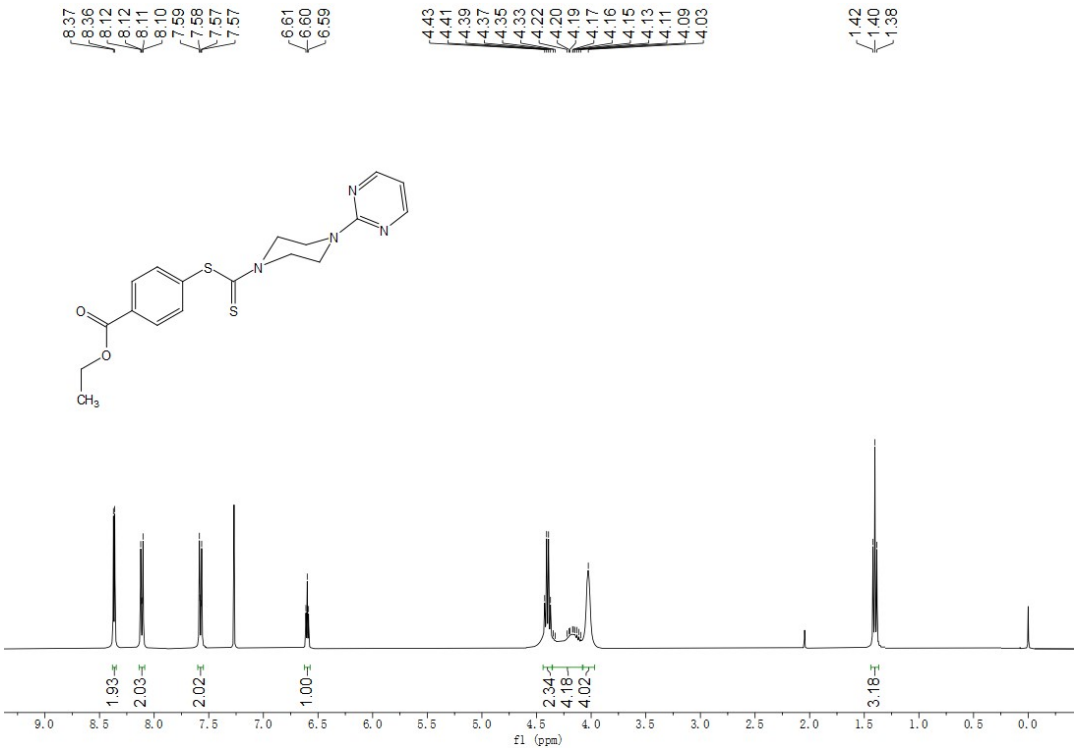
^{13}C NMR (400 MHz, Chloroform-*d*) of compound **4aq.**



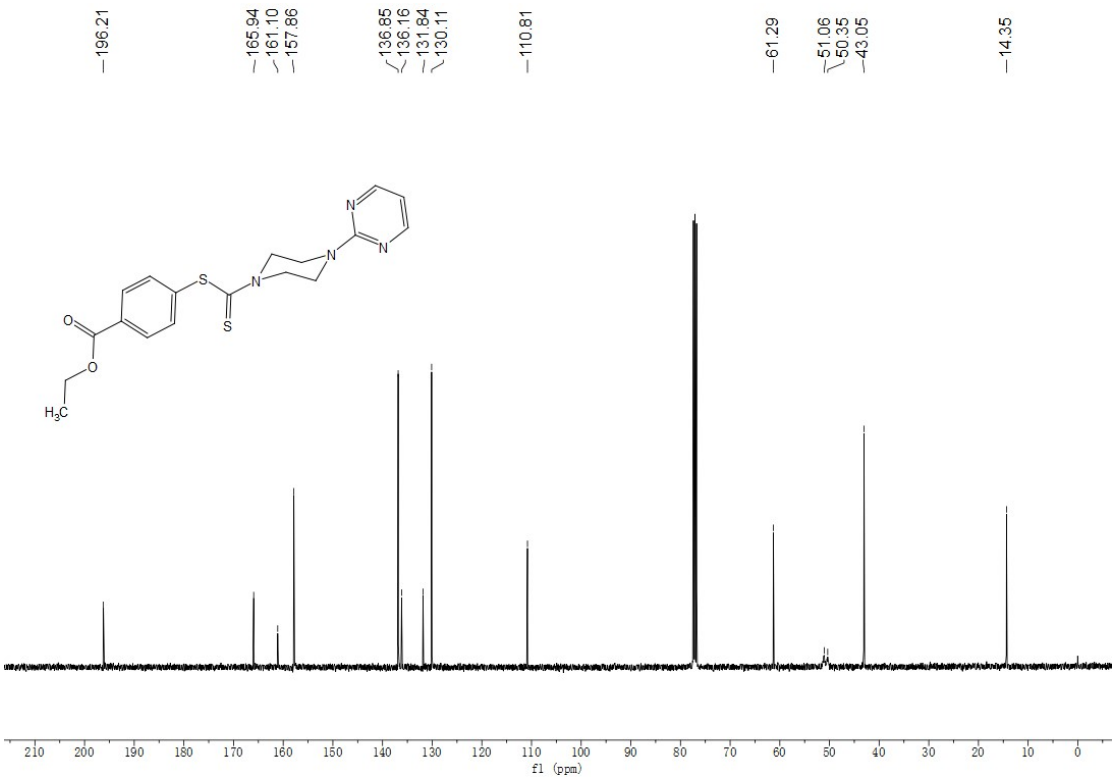
^{1}H NMR (400 MHz, Chloroform-*d*) of compound **4ar.**



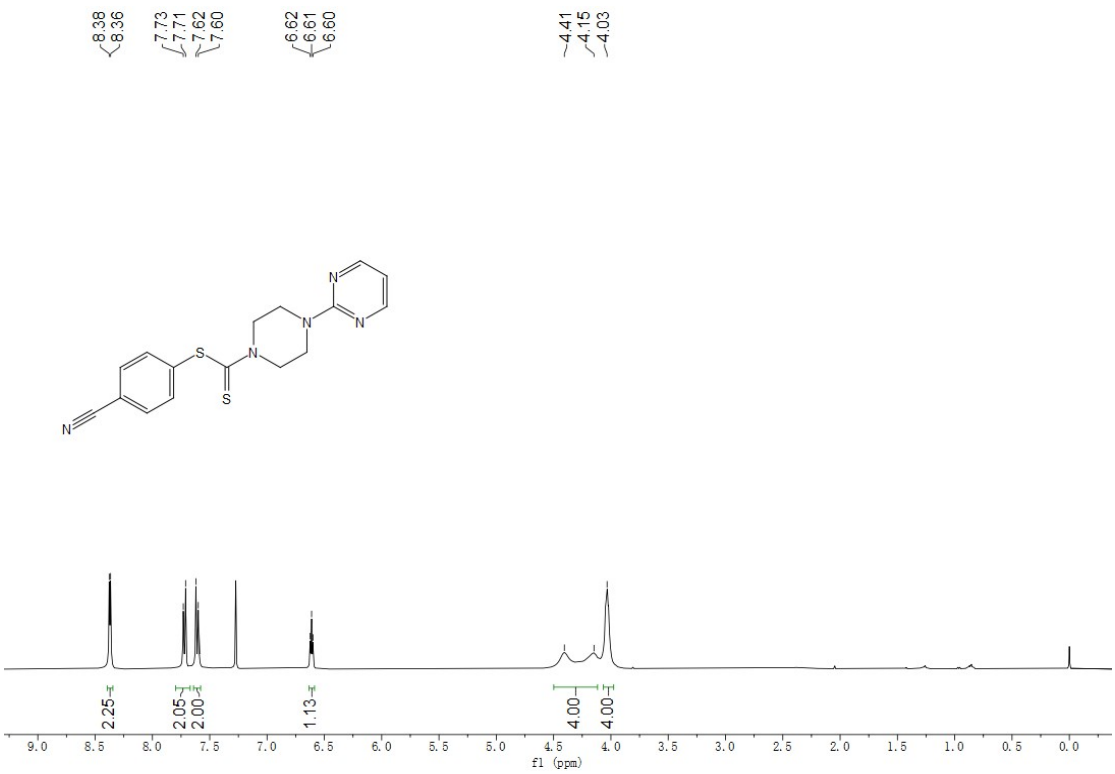
^{13}C NMR (400 MHz, Chloroform-*d*) of compound **4ar.**



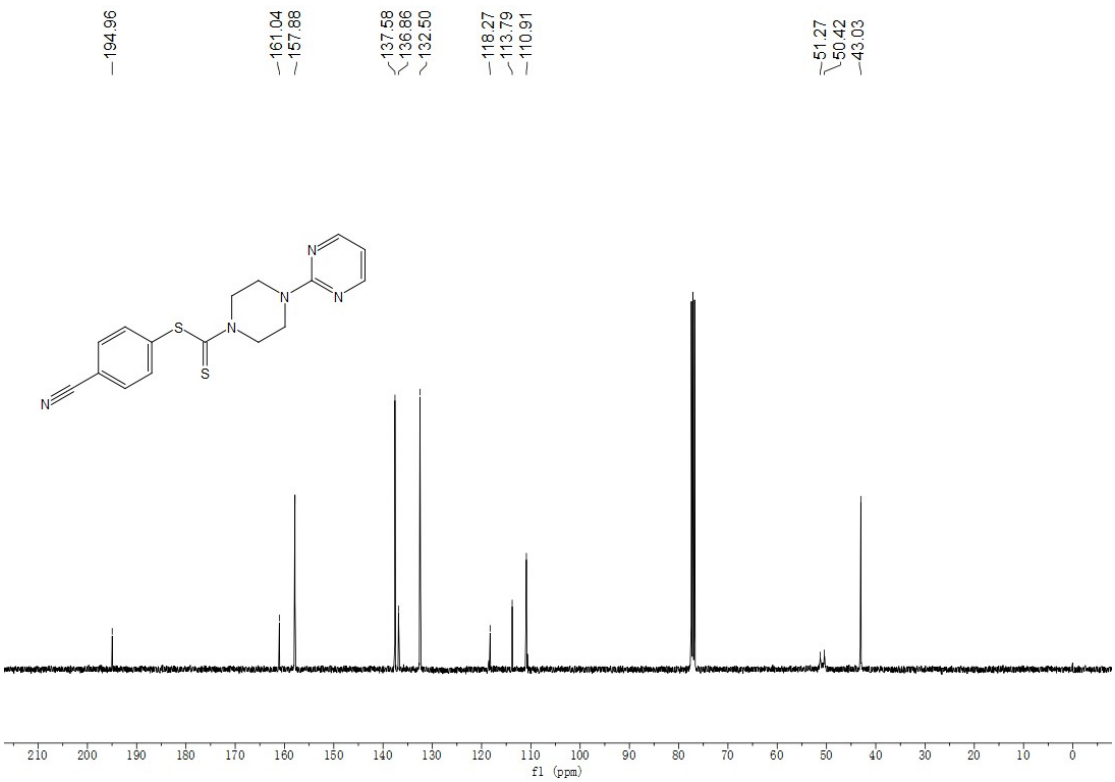
^{1}H NMR (400 MHz, Chloroform-*d*) of compound **4as.**



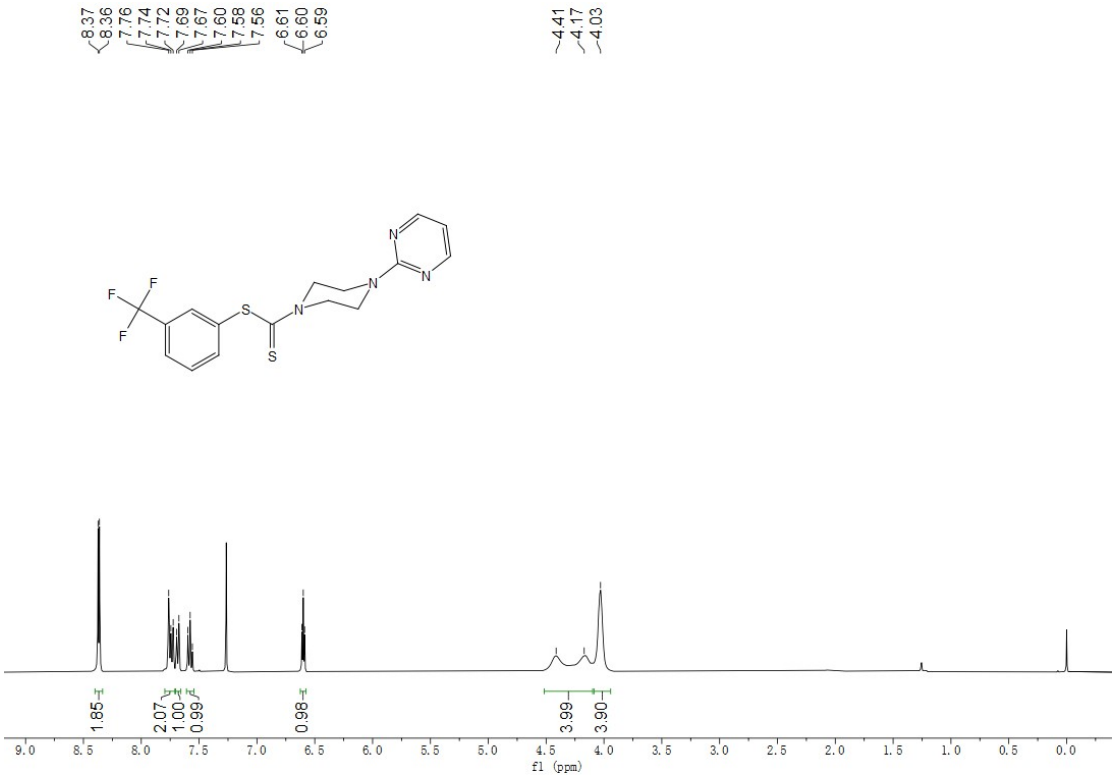
^{13}C NMR (400 MHz, Chloroform-*d*) of compound **4as.**



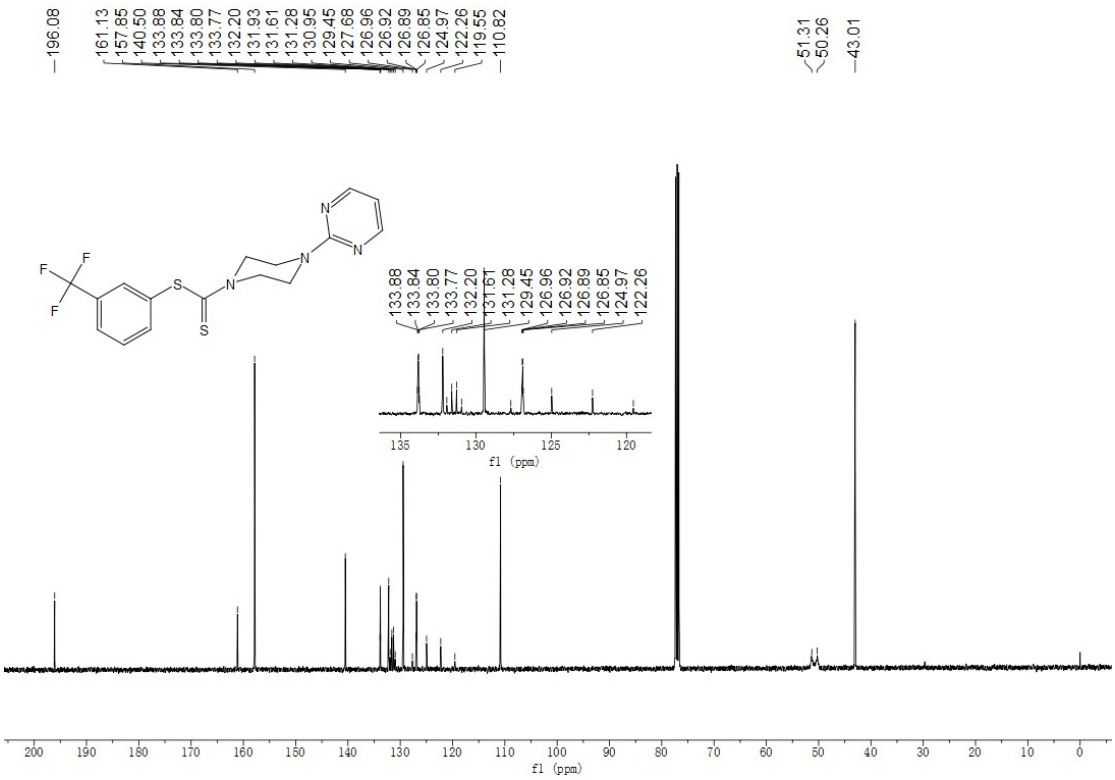
^{1}H NMR (400 MHz, Chloroform-*d*) of compound **4at.**



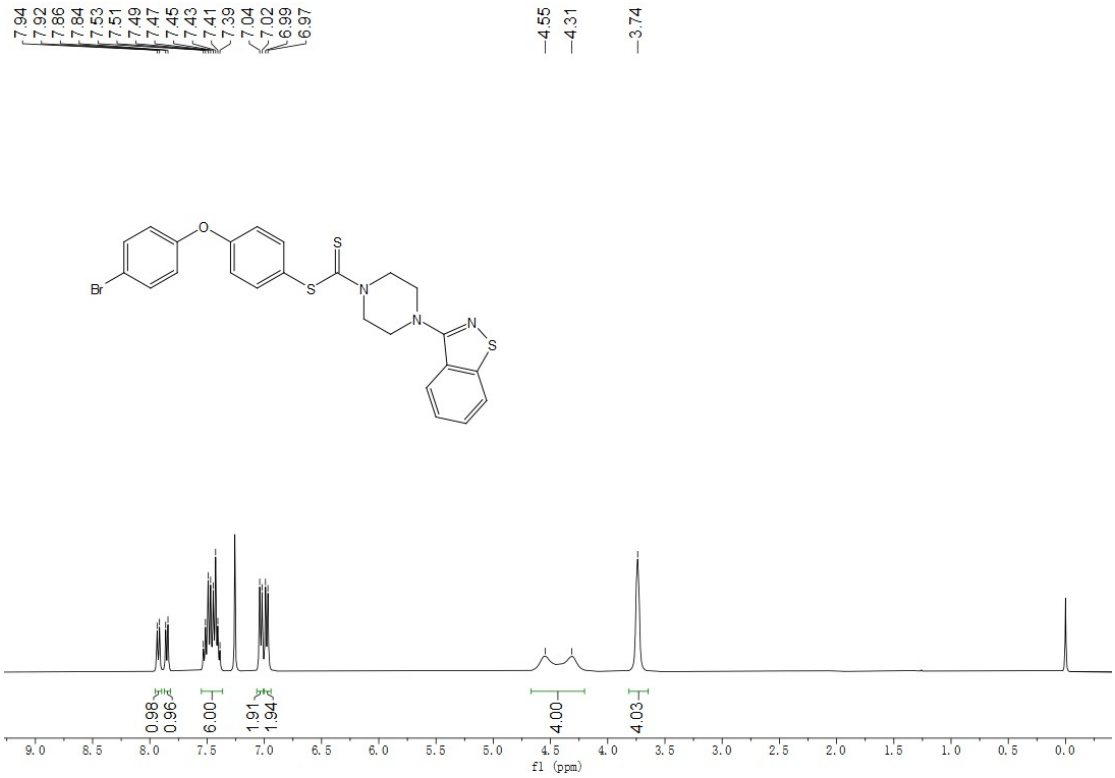
^{13}C NMR (400 MHz, Chloroform-*d*) of compound **4at.**



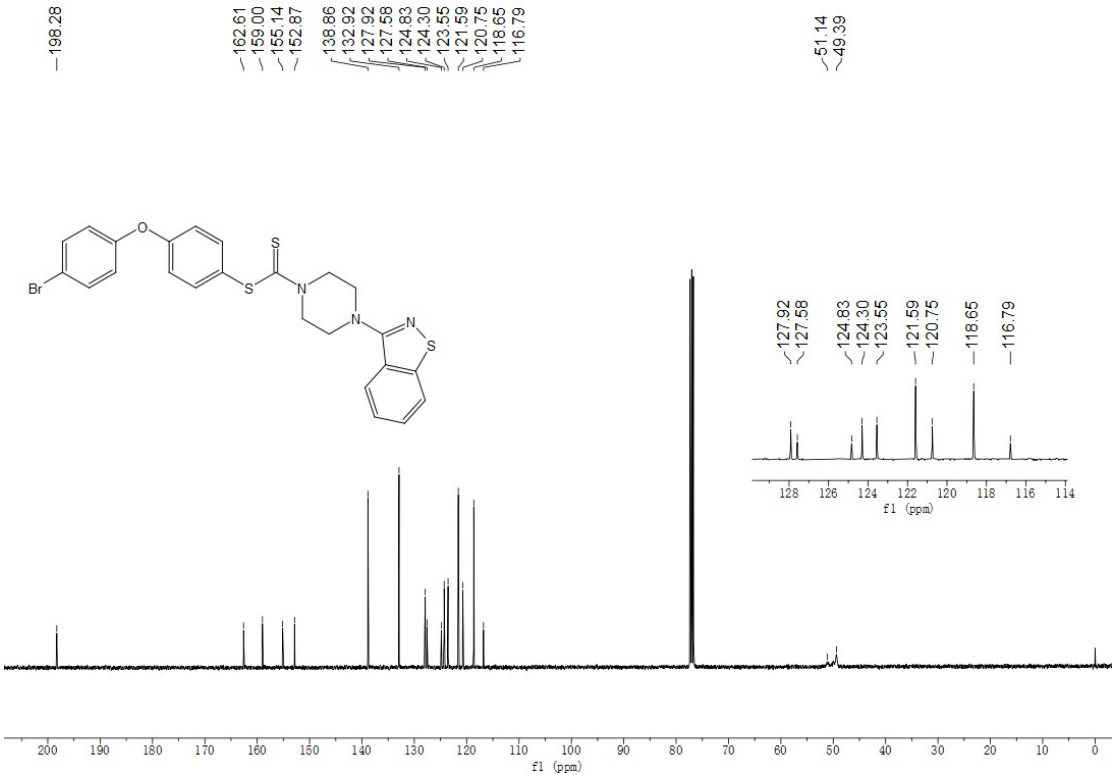
^{1}H NMR (400 MHz, Chloroform-*d*) of compound **4au.**



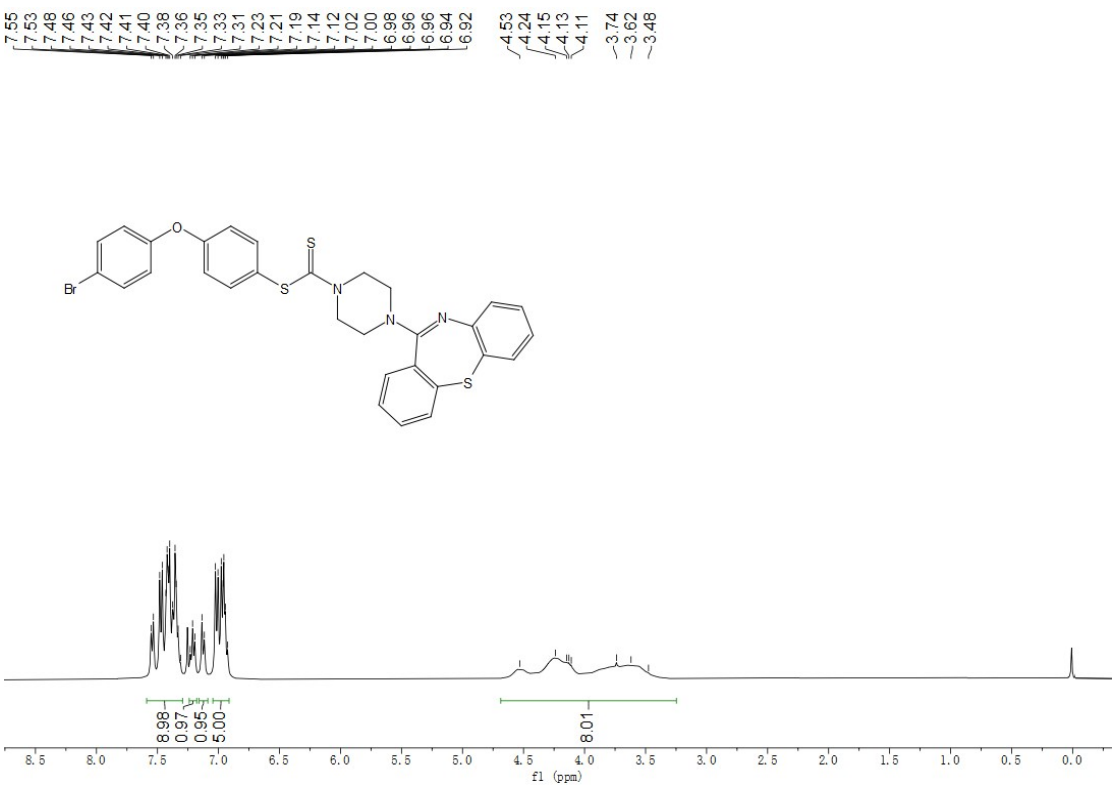
^{13}C NMR (400 MHz, Chloroform-*d*) of compound **4au.**



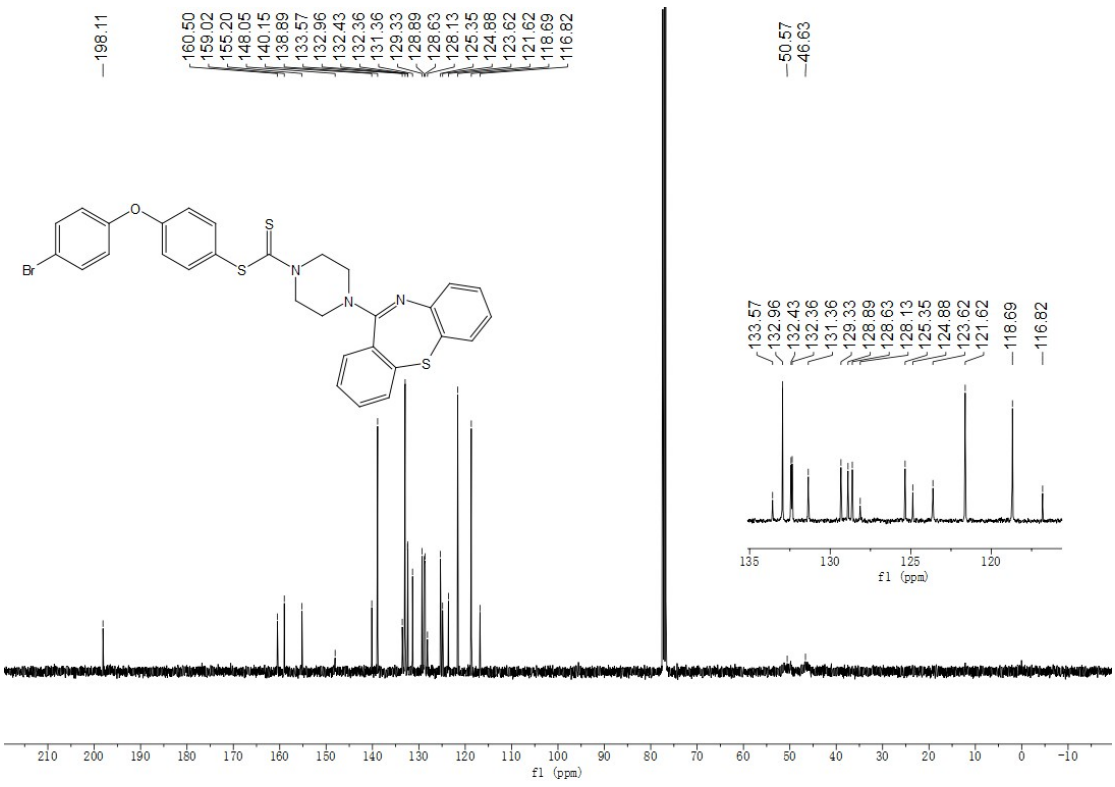
^{1}H NMR (400 MHz, Chloroform-*d*) of compound **4av.**



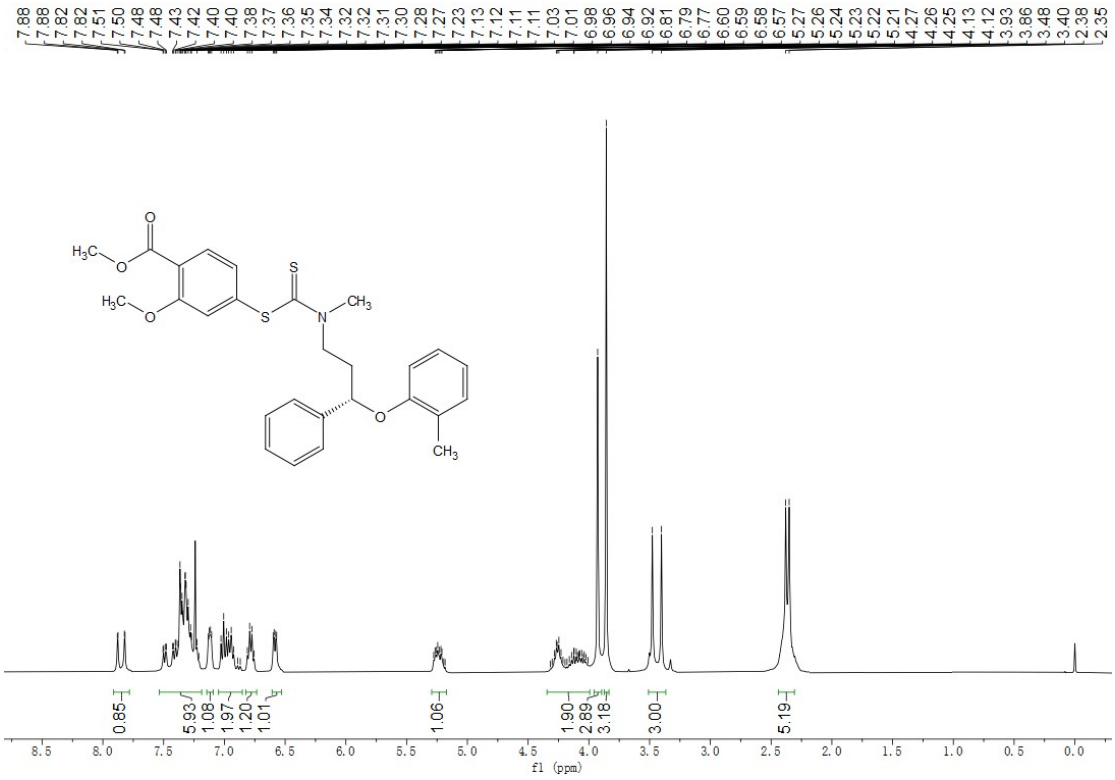
^{13}C NMR (400 MHz, Chloroform-*d*) of compound **4av.**



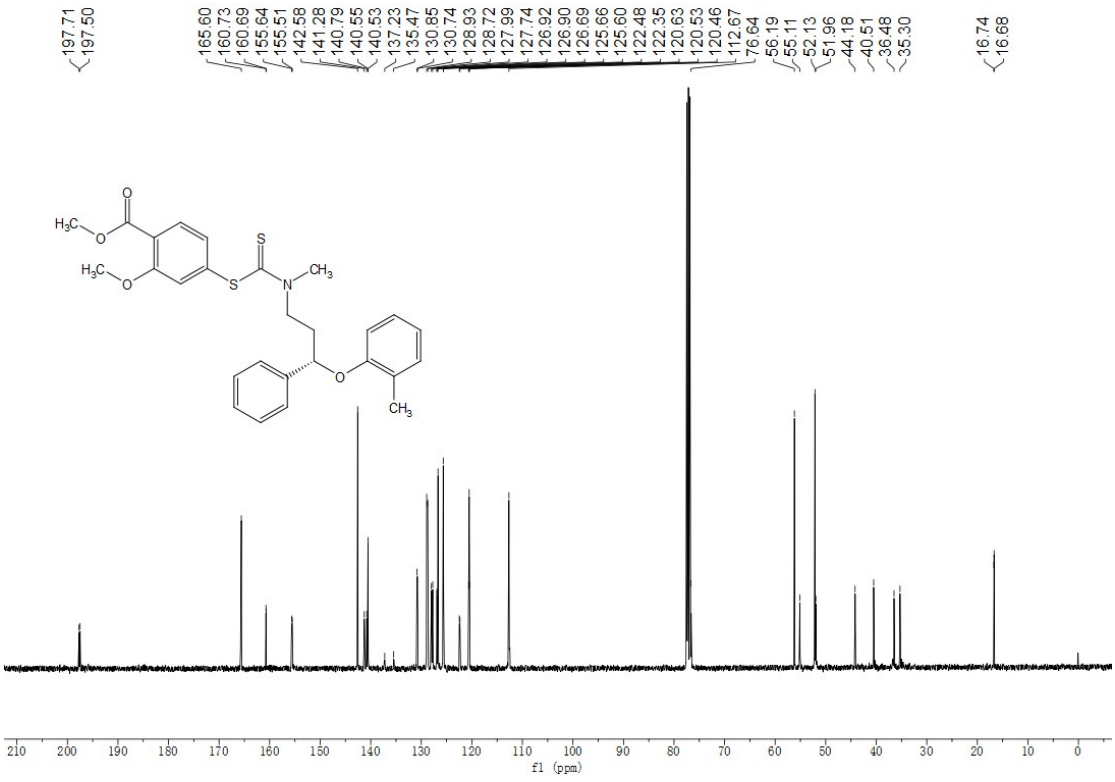
^{1}H NMR (400 MHz, Chloroform-*d*) of compound **4aw.**



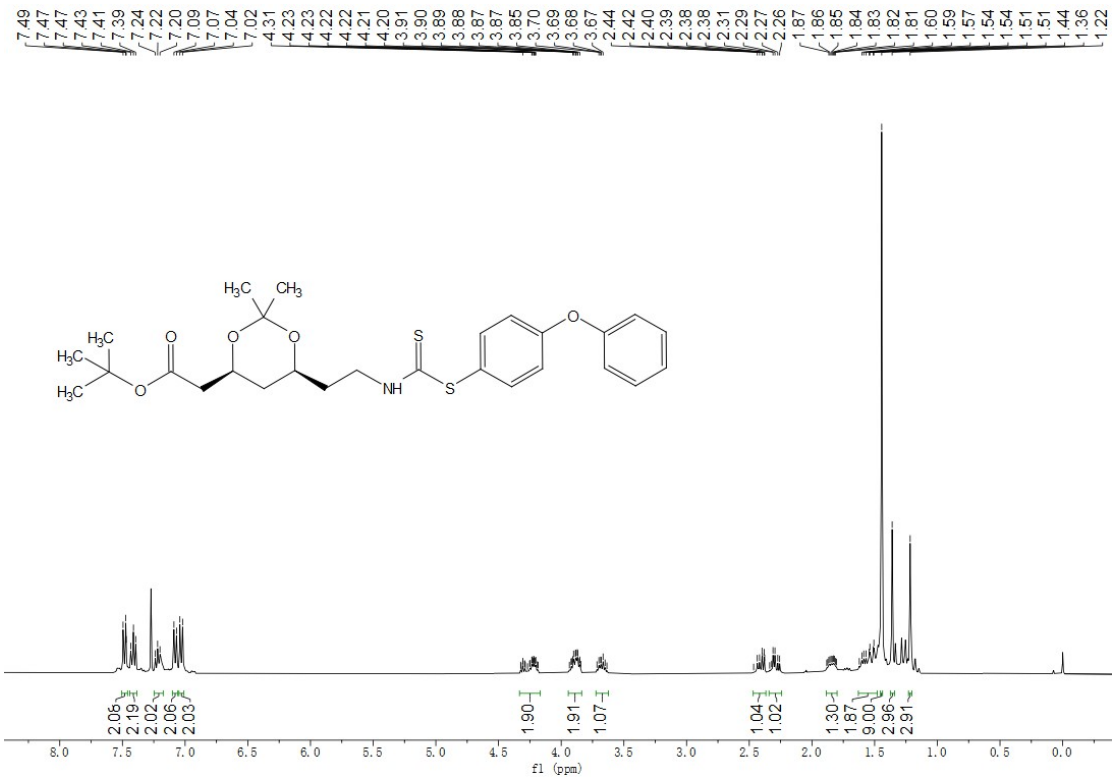
^{13}C NMR (400 MHz, Chloroform-*d*) of compound **4aw.**



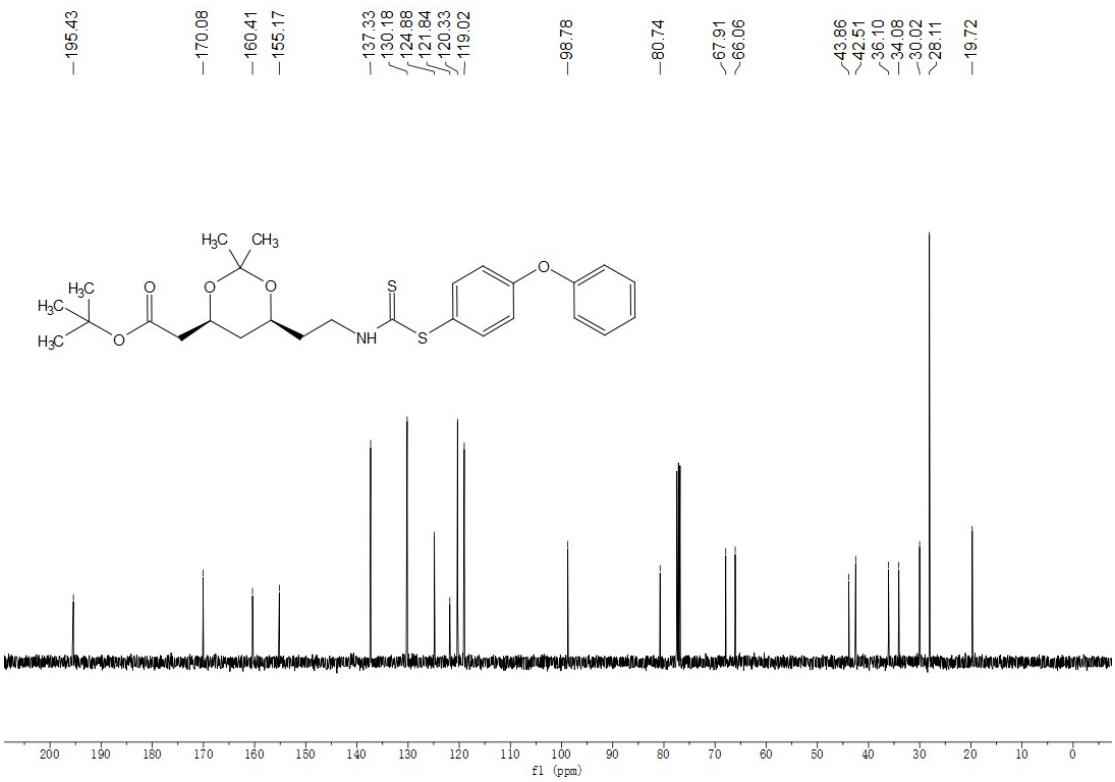
^{1}H NMR (400 MHz, Chloroform-*d*) of compound **4ax.**



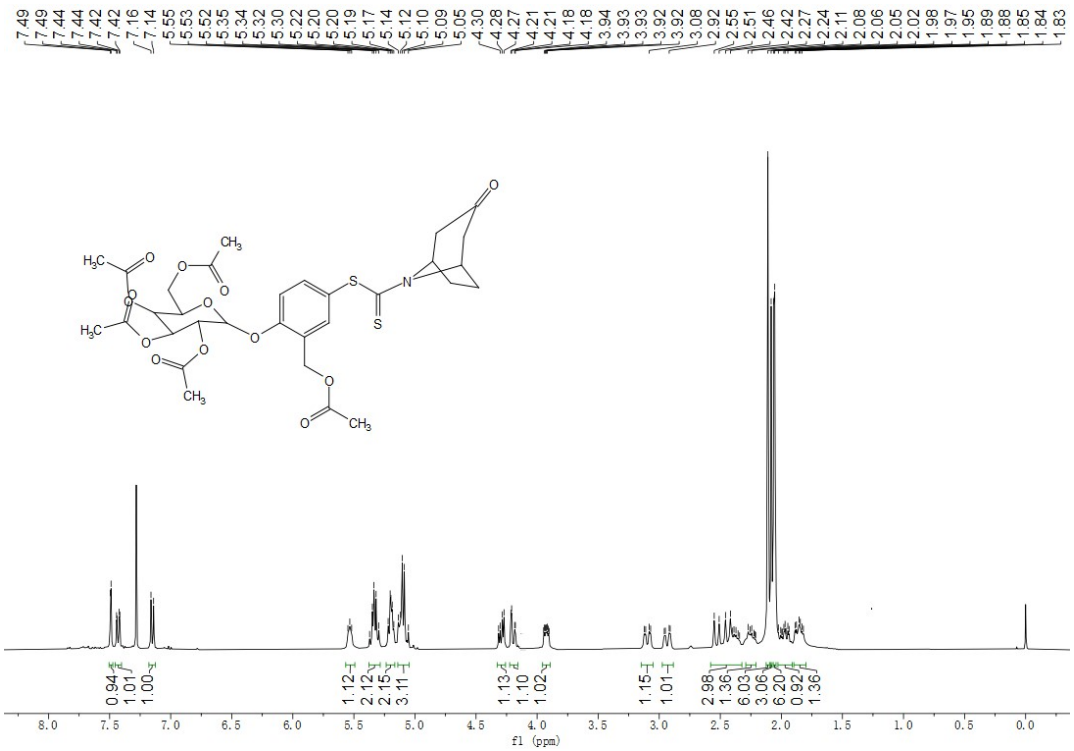
^{13}C NMR (400 MHz, Chloroform-*d*) of compound **4ax.**



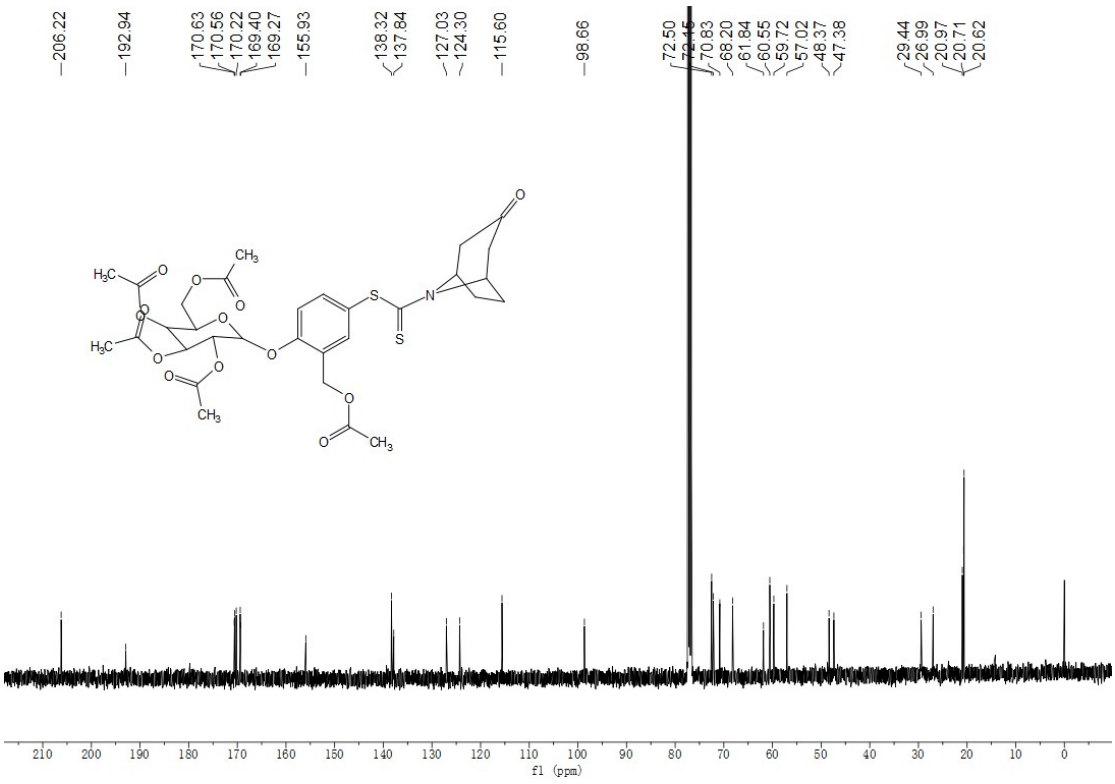
^{1}H NMR (400 MHz, Chloroform-*d*) of compound **4ay.**



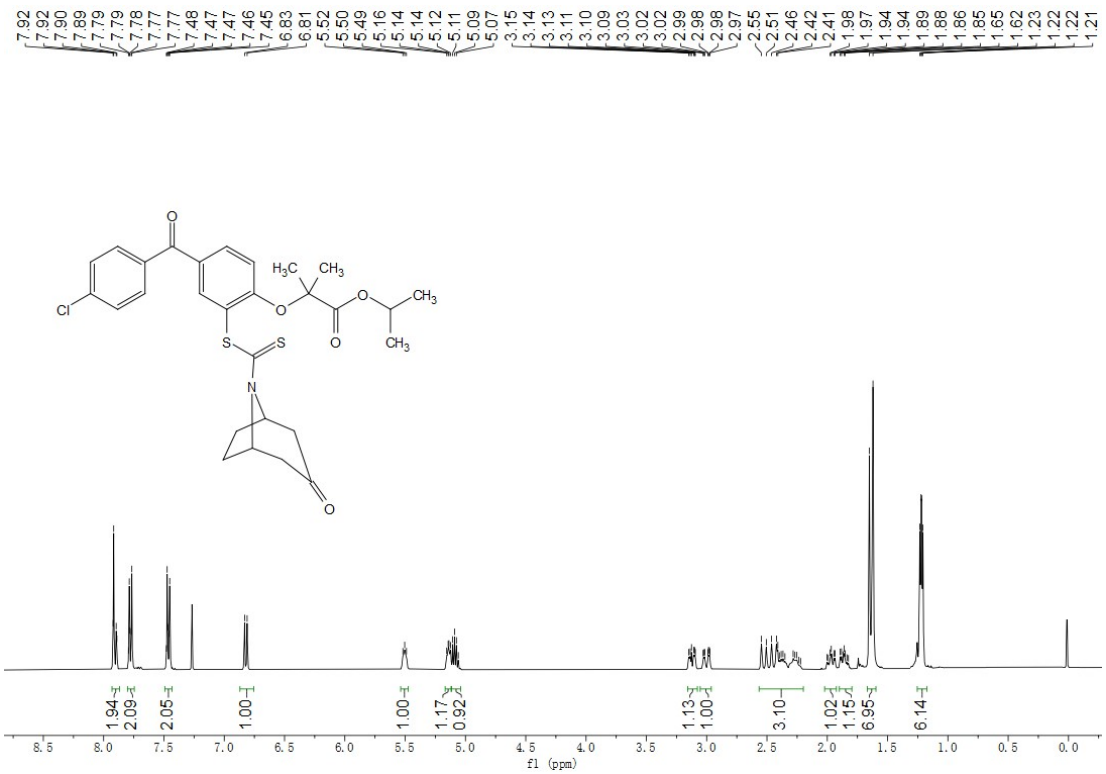
^{13}C NMR (400 MHz, Chloroform-*d*) of compound **4ay.**



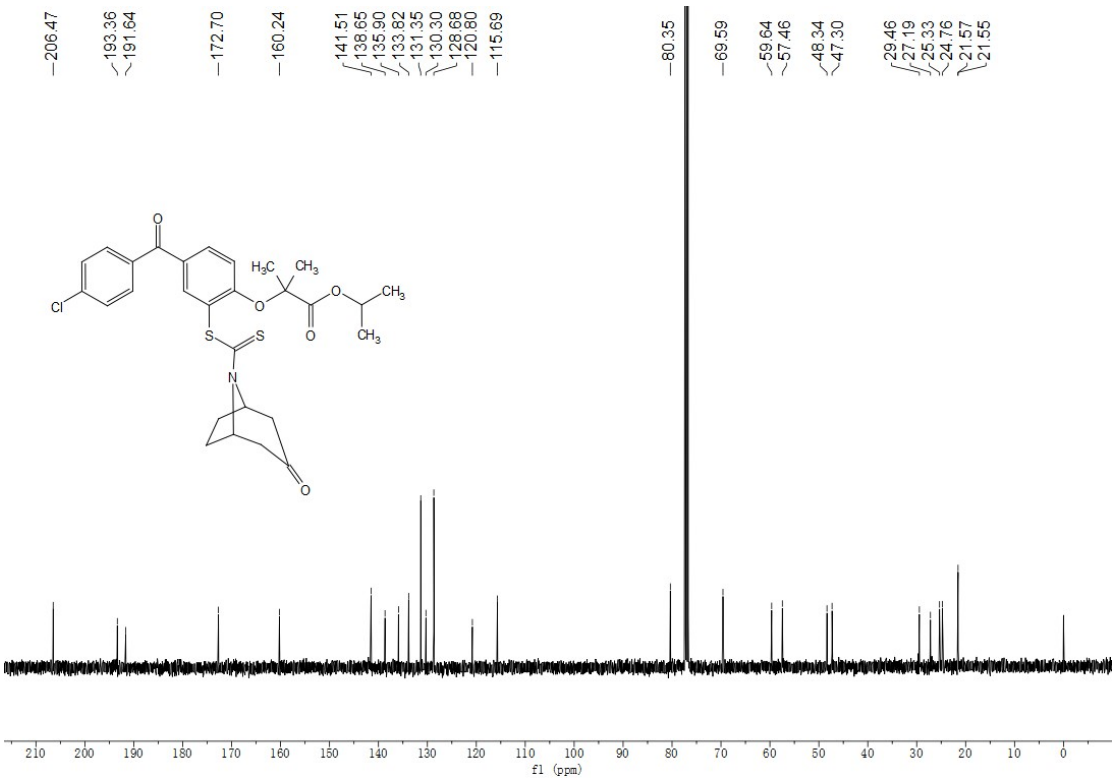
^{1}H NMR (400 MHz, Chloroform-*d*) of compound **4az.**



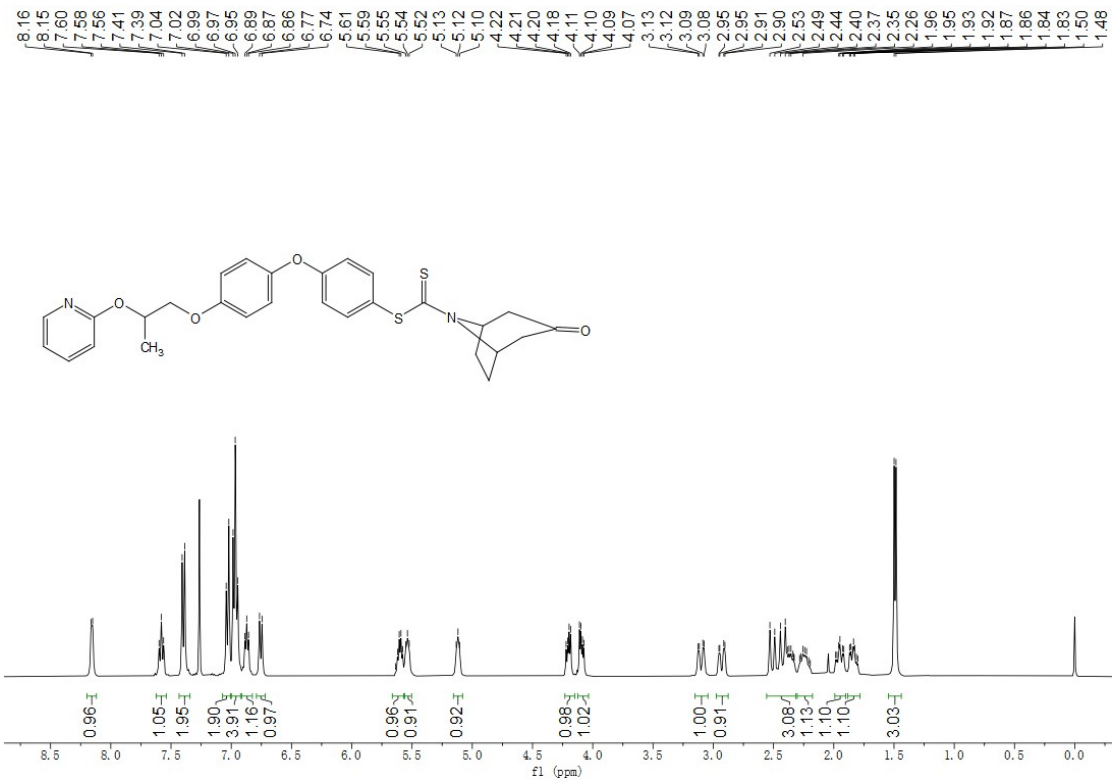
^{13}C NMR (400 MHz, Chloroform-*d*) of compound **4az.**



^{1}H NMR (400 MHz, Chloroform-*d*) of compound **4ba.**

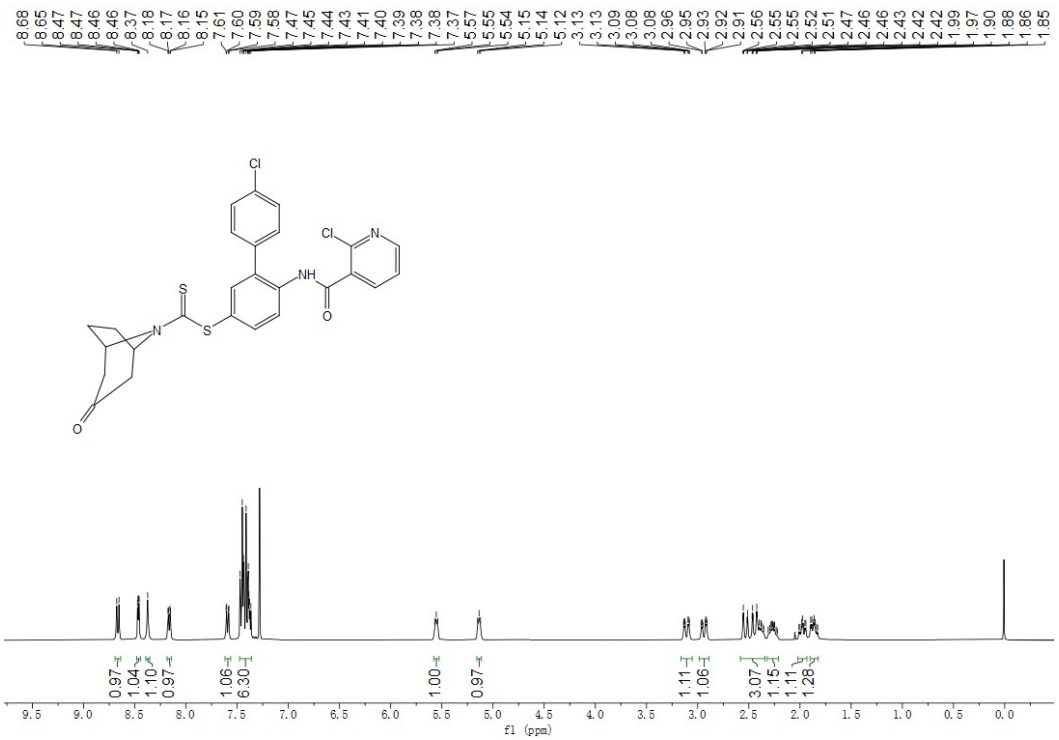


^{13}C NMR (400 MHz, Chloroform-*d*) of compound **4ba.**

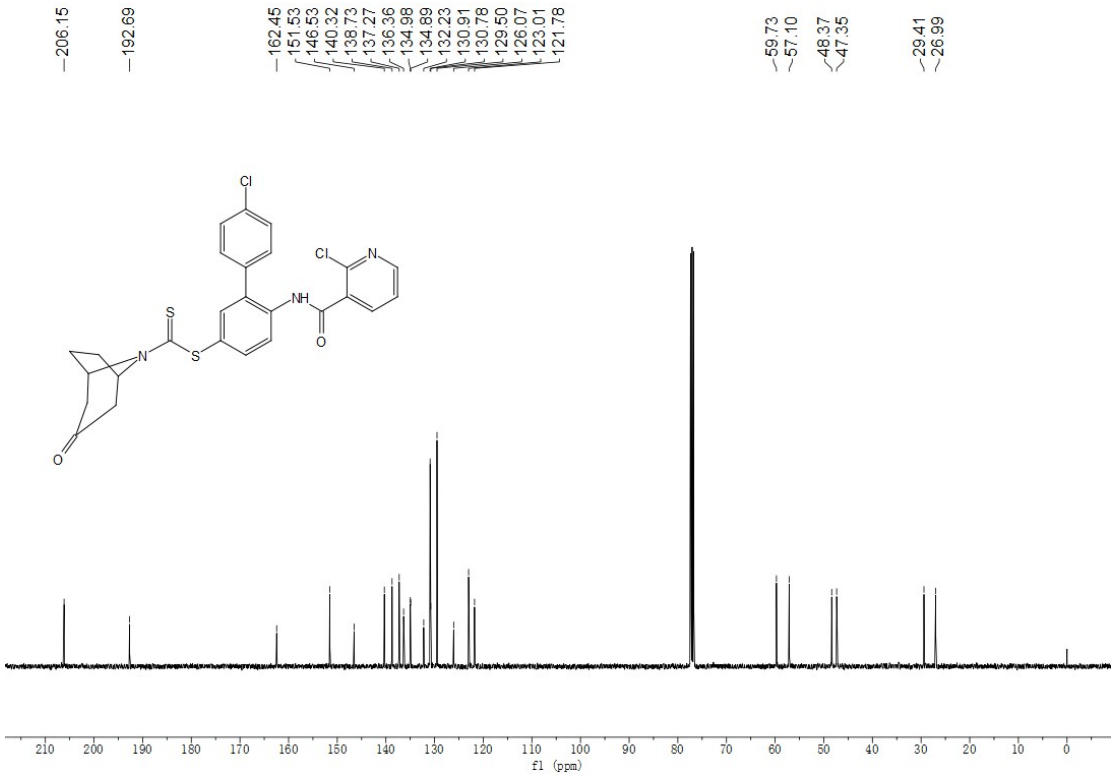


^{1}H NMR (400 MHz, Chloroform-*d*) of compound **4bb.**

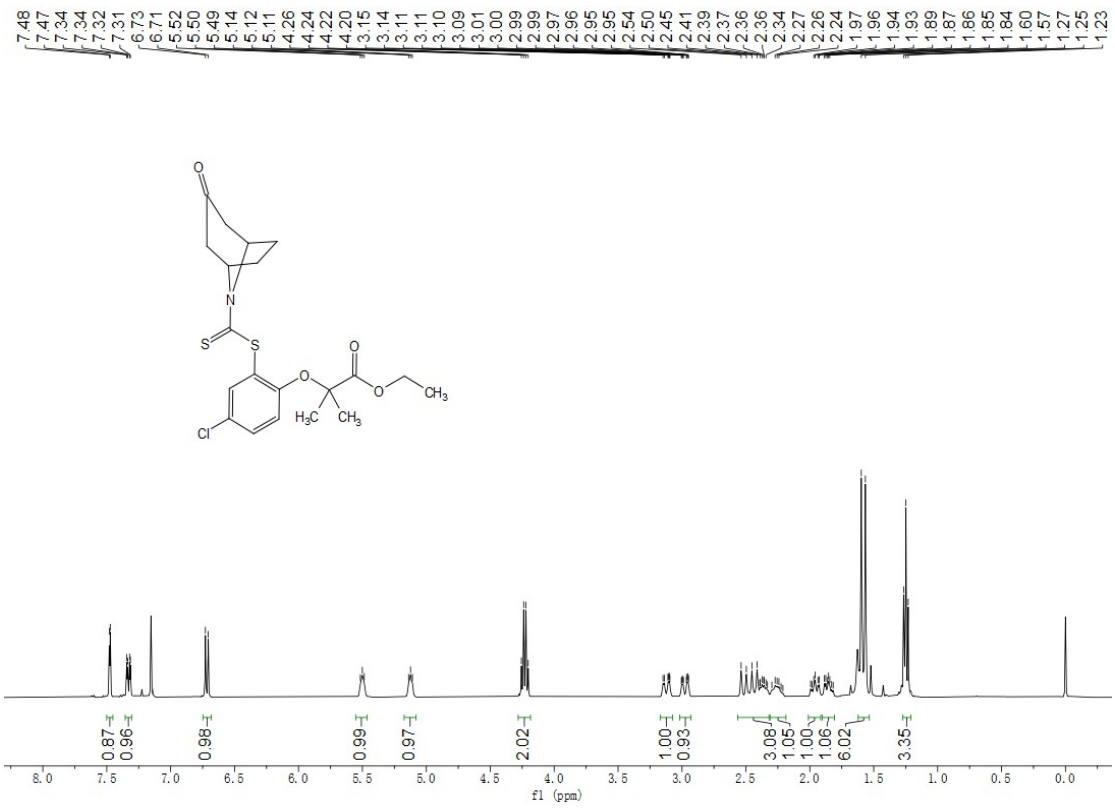
^{13}C NMR (400 MHz, Chloroform-*d*) of compound **4bb.**



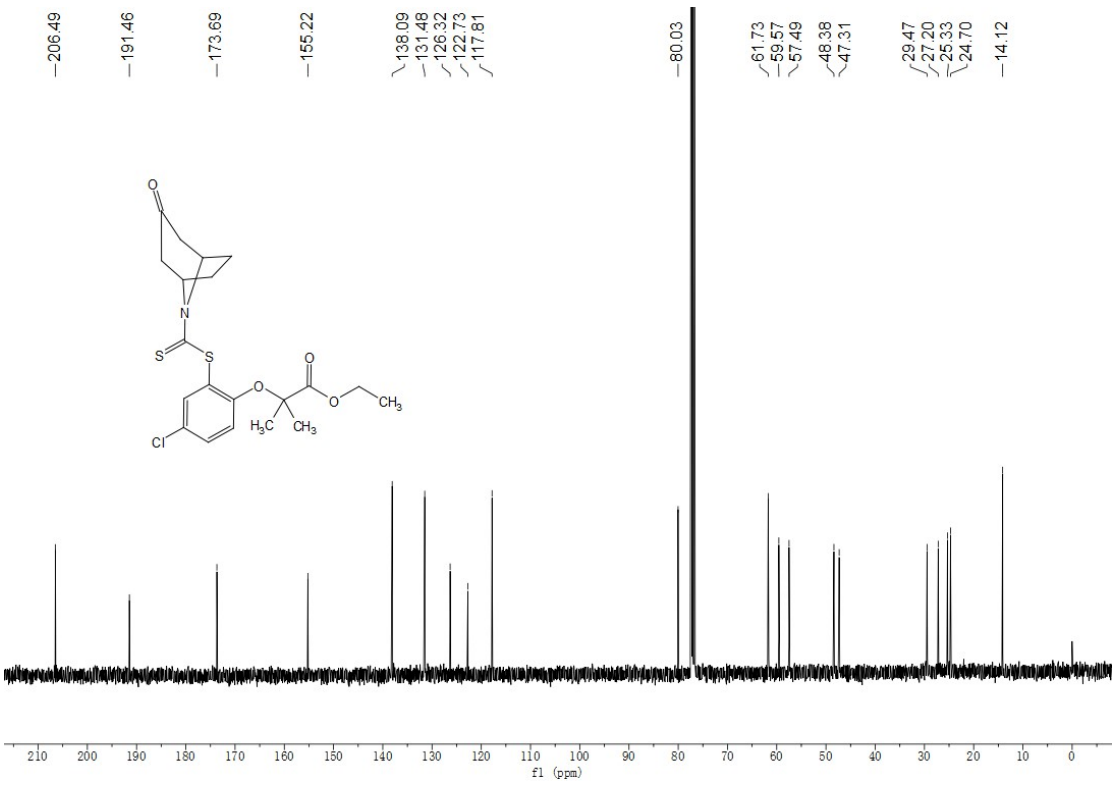
^{1}H NMR (400 MHz, Chloroform-*d*) of compound **4bc.**



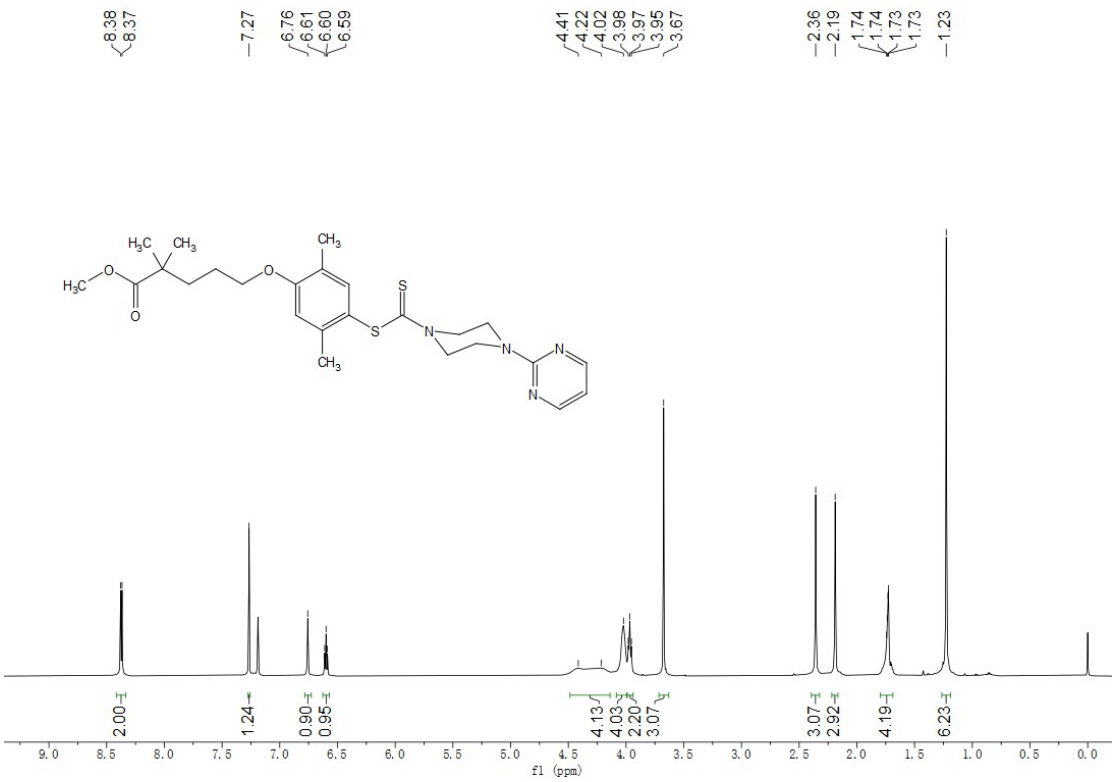
^{13}C NMR (400 MHz, Chloroform-*d*) of compound **4bc.**



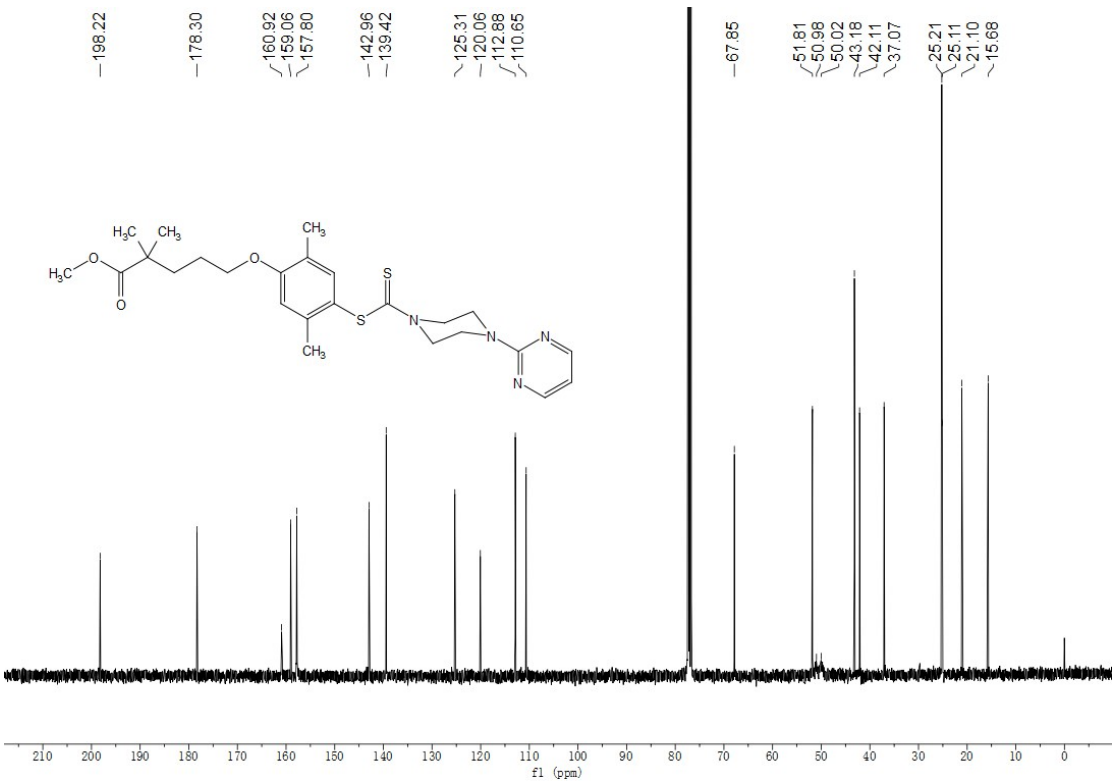
^{1}H NMR (400 MHz, Chloroform-*d*) of compound **4bd.**



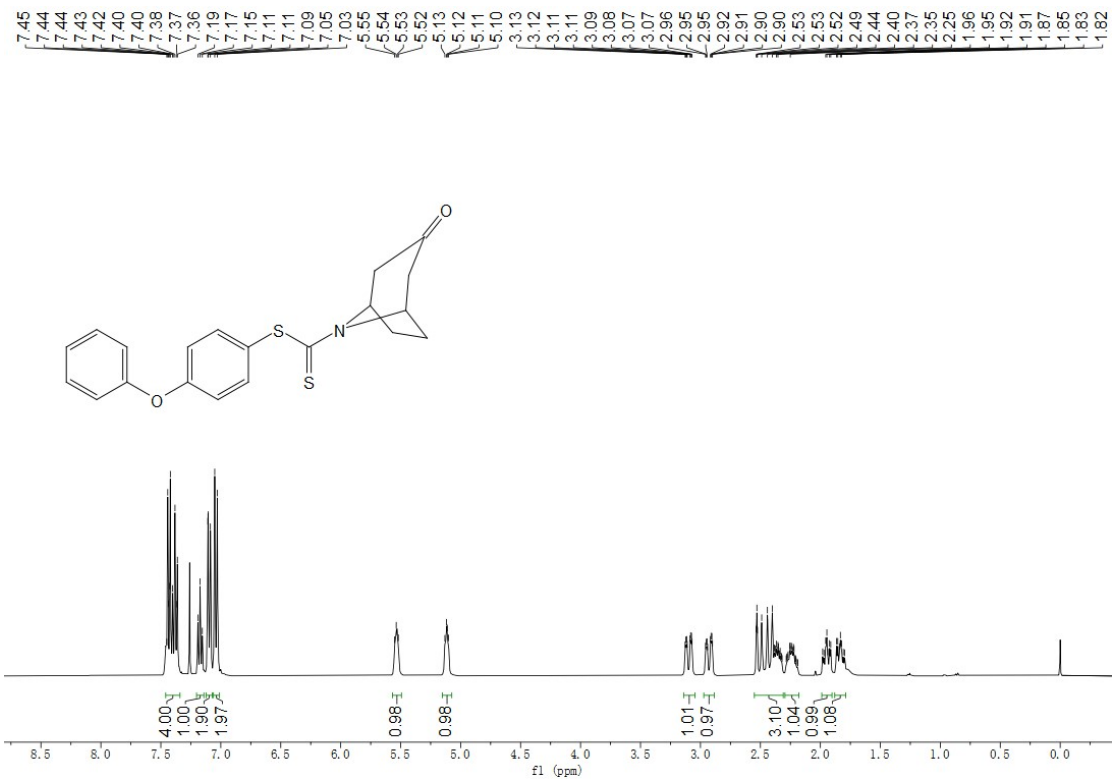
^{13}C NMR (400 MHz, Chloroform-*d*) of compound **4bd.**



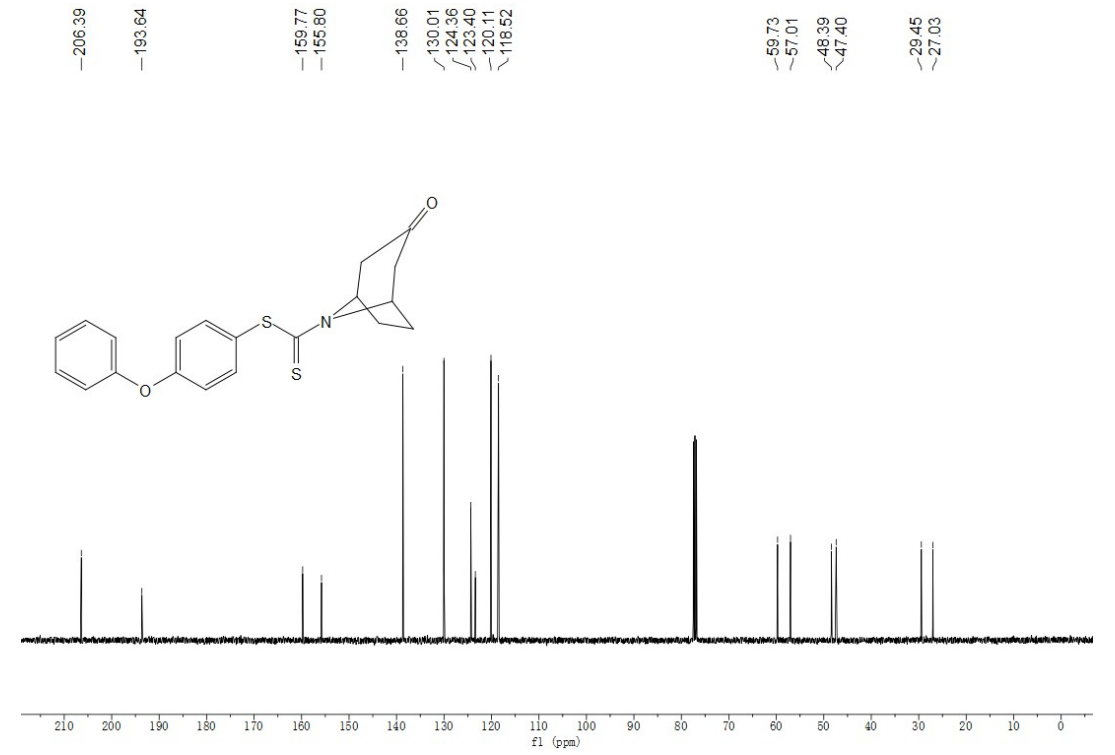
[1]H NMR (400 MHz, Chloroform-*d*) of compound **4be.**



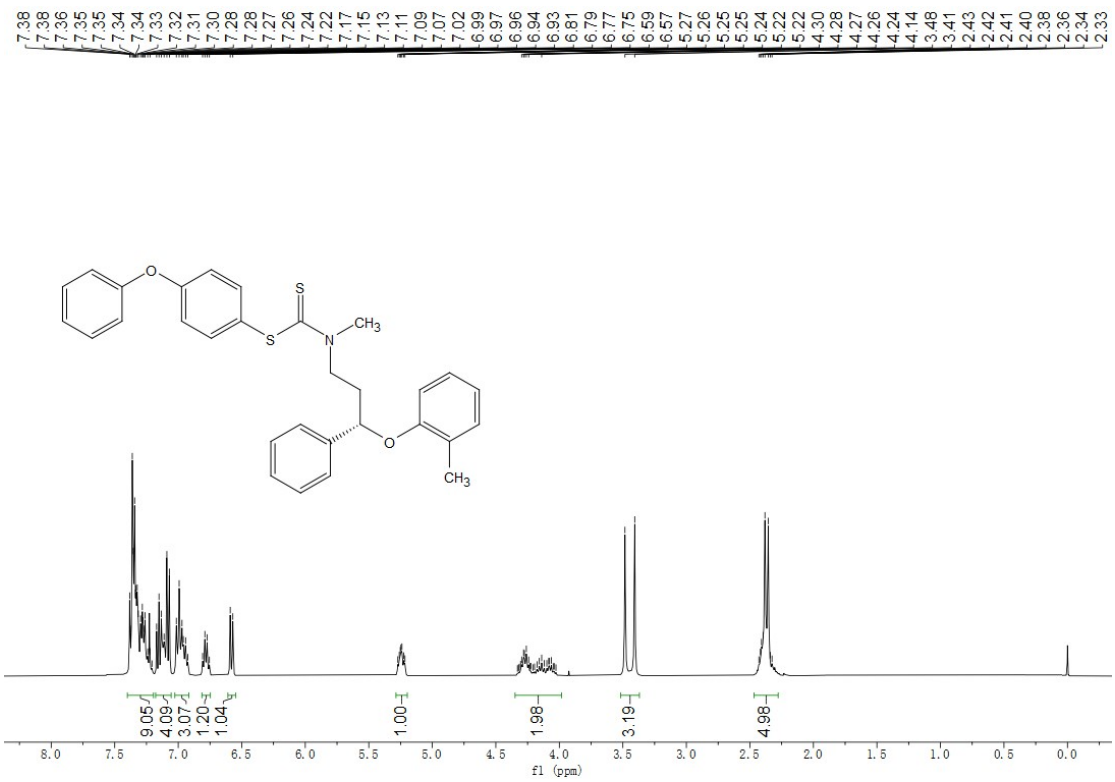
[13]C NMR (400 MHz, Chloroform-*d*) of compound **4be.**



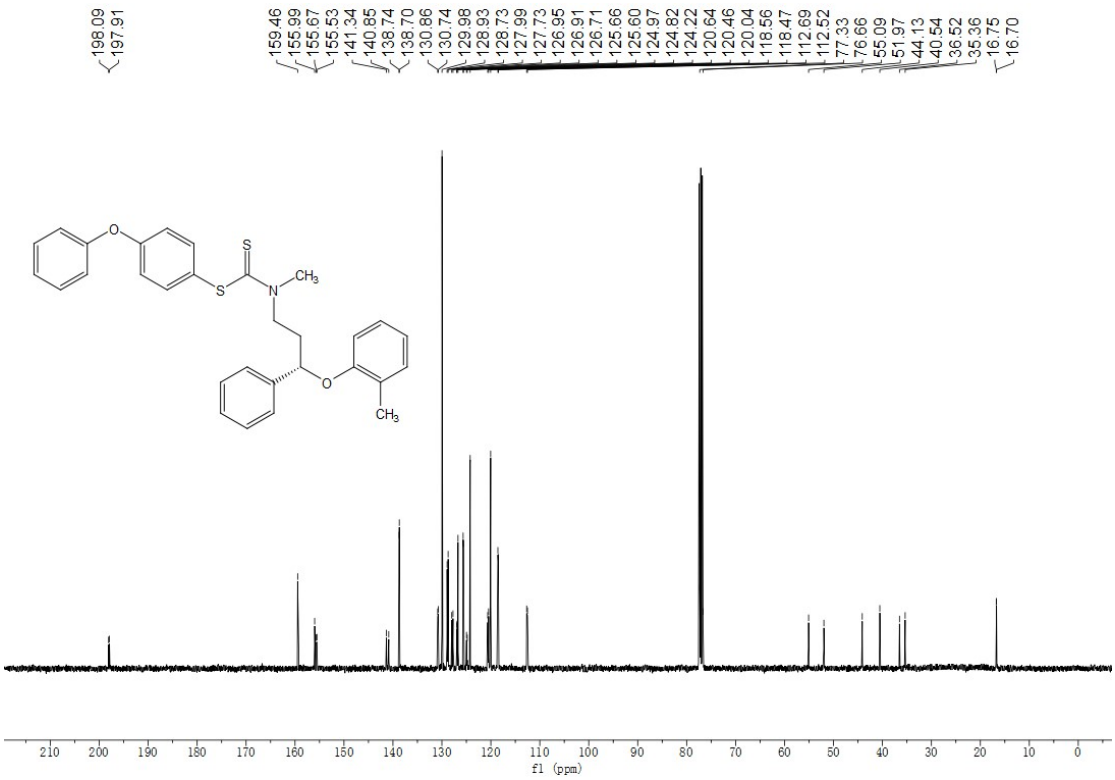
^{1}H NMR (400 MHz, Chloroform-*d*) of compound **4bf.**



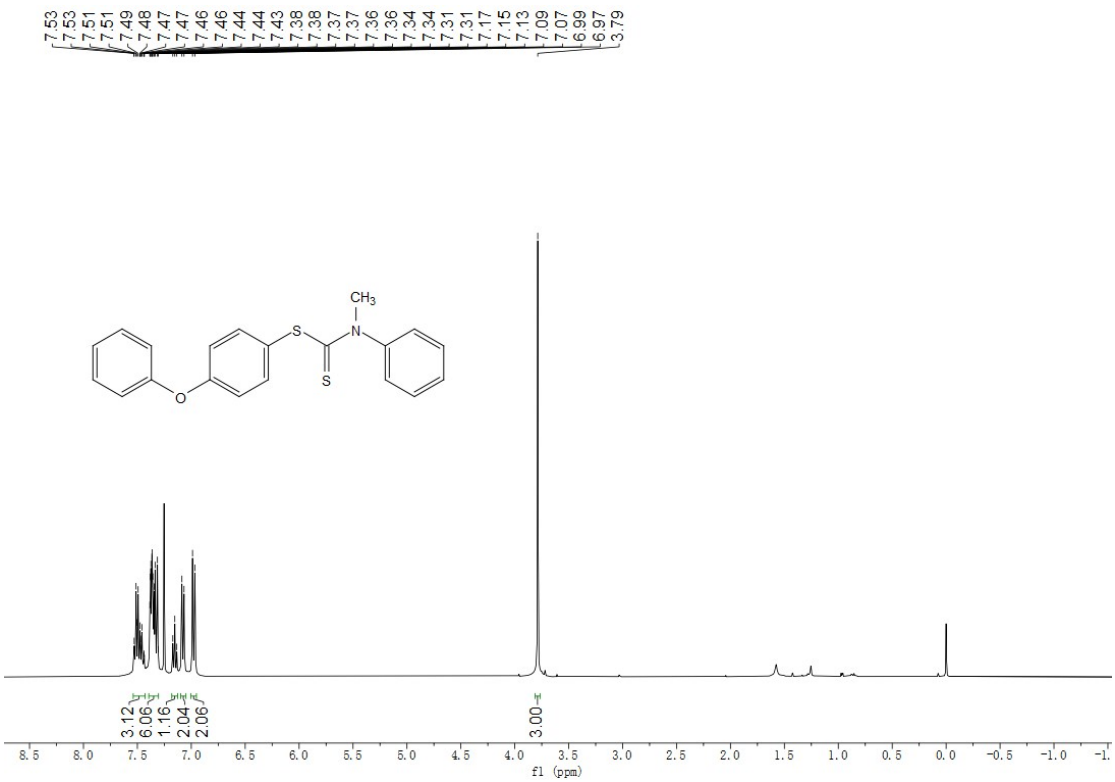
^{13}C NMR (400 MHz, Chloroform-*d*) of compound **4bf.**



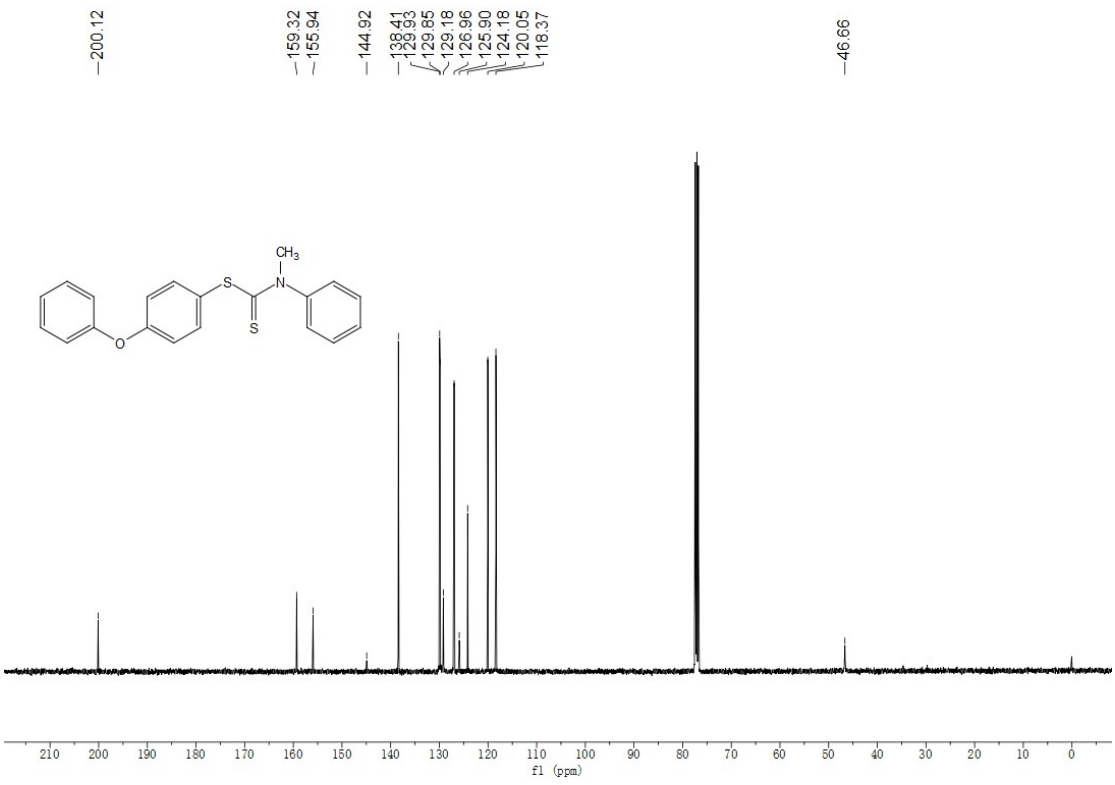
^{1}H NMR (400 MHz, Chloroform-*d*) of compound **4bg.**



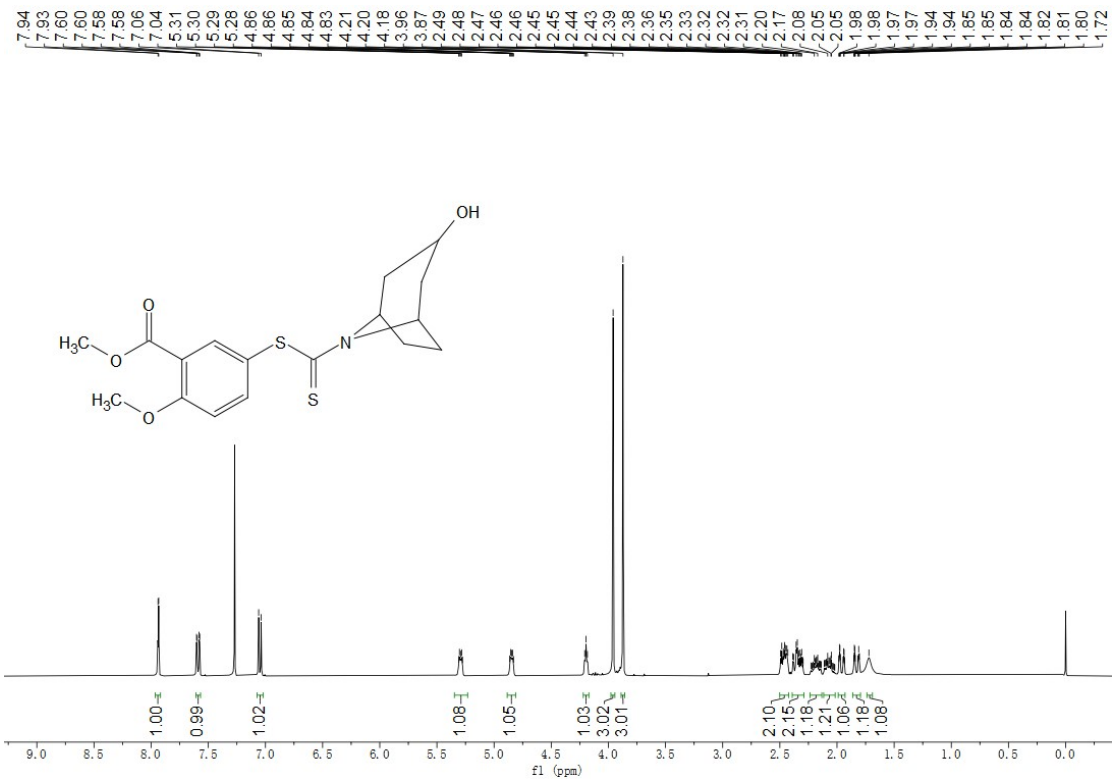
^{13}C NMR (400 MHz, Chloroform-*d*) of compound **4bg.**



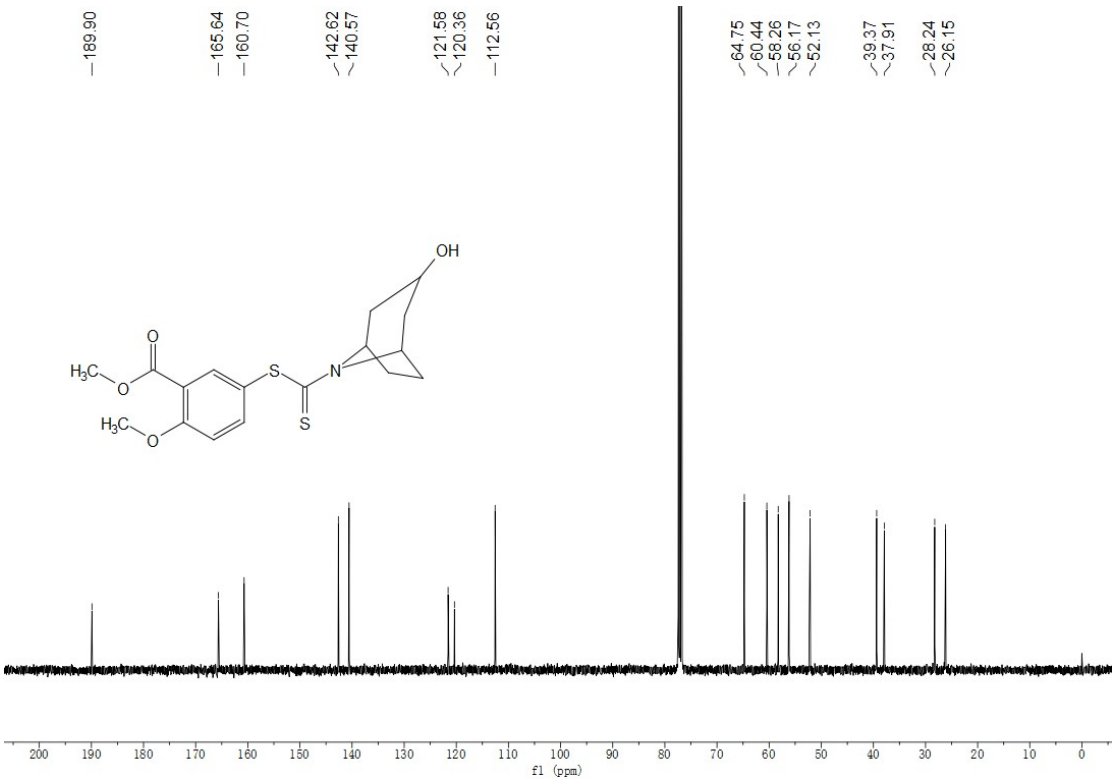
^{1}H NMR (400 MHz, Chloroform-*d*) of compound **4bh.**



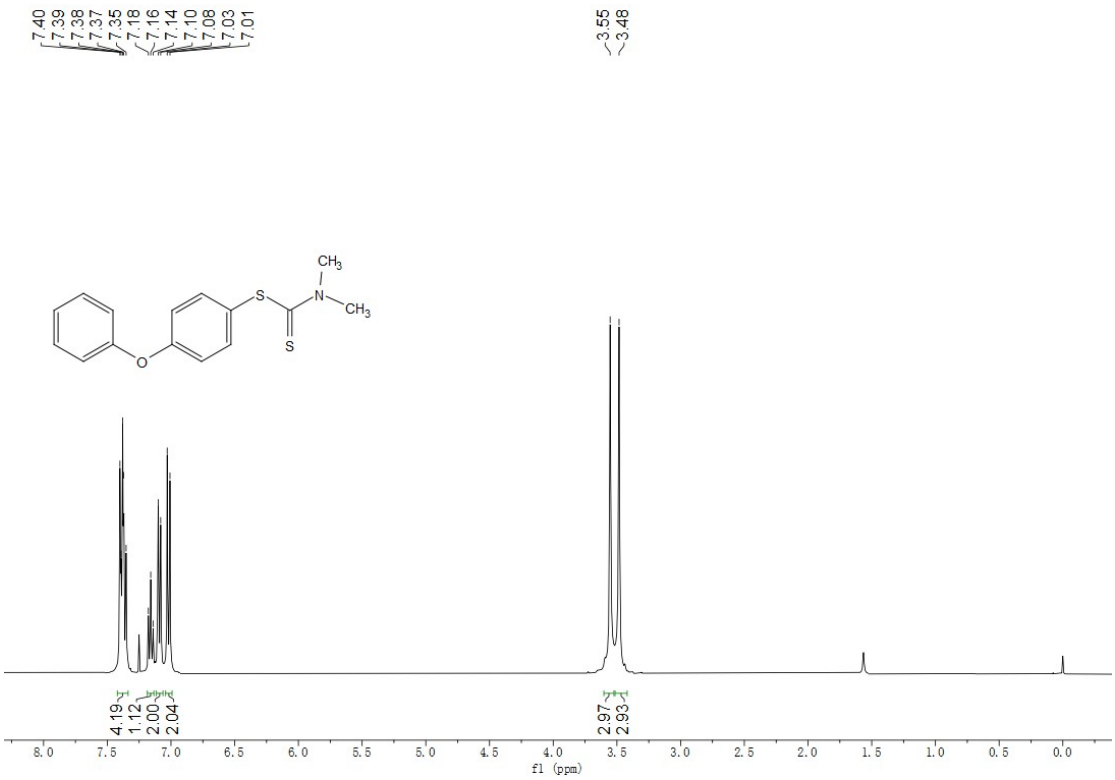
^{13}C NMR (400 MHz, Chloroform-*d*) of compound **4bh.**



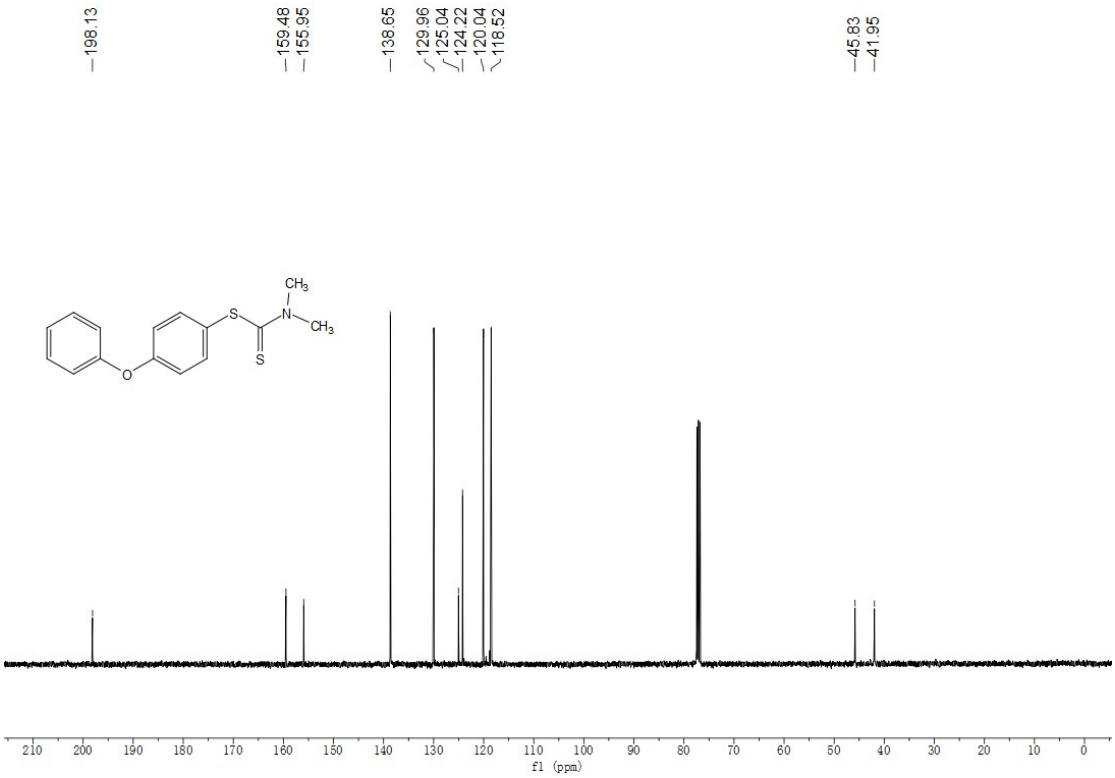
^{1}H NMR (400 MHz, Chloroform-*d*) of compound **4bi.**



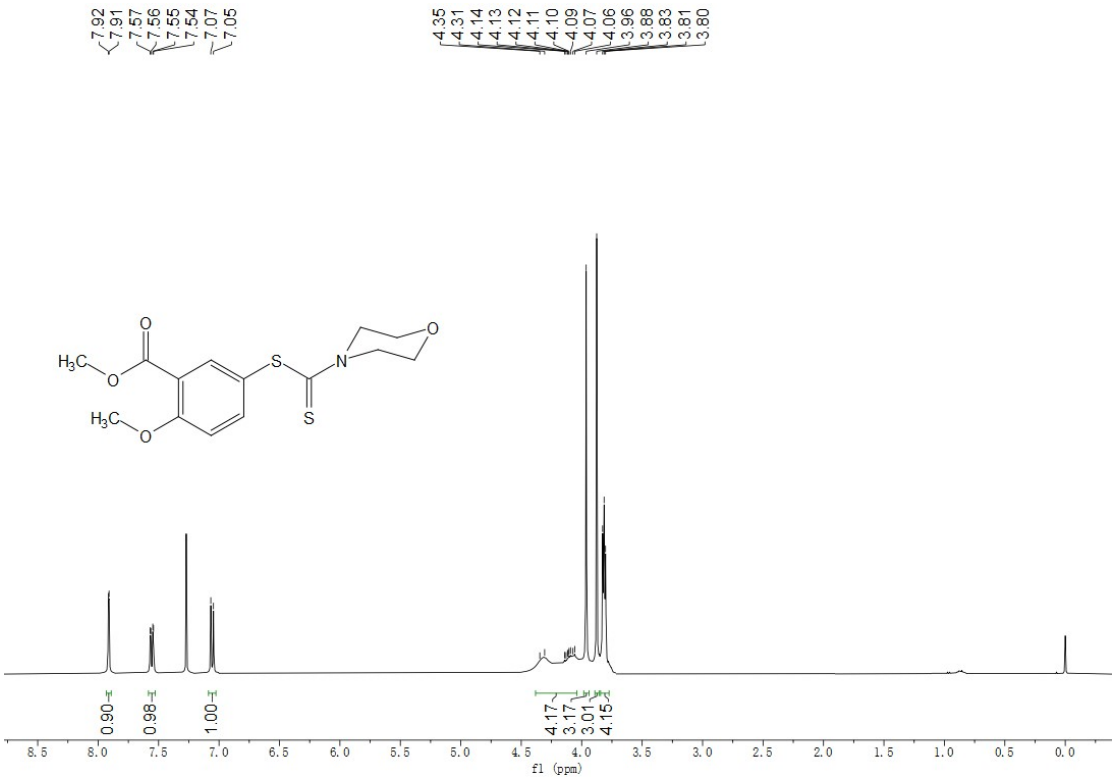
^{13}C NMR (400 MHz, Chloroform-*d*) of compound **4bi.**



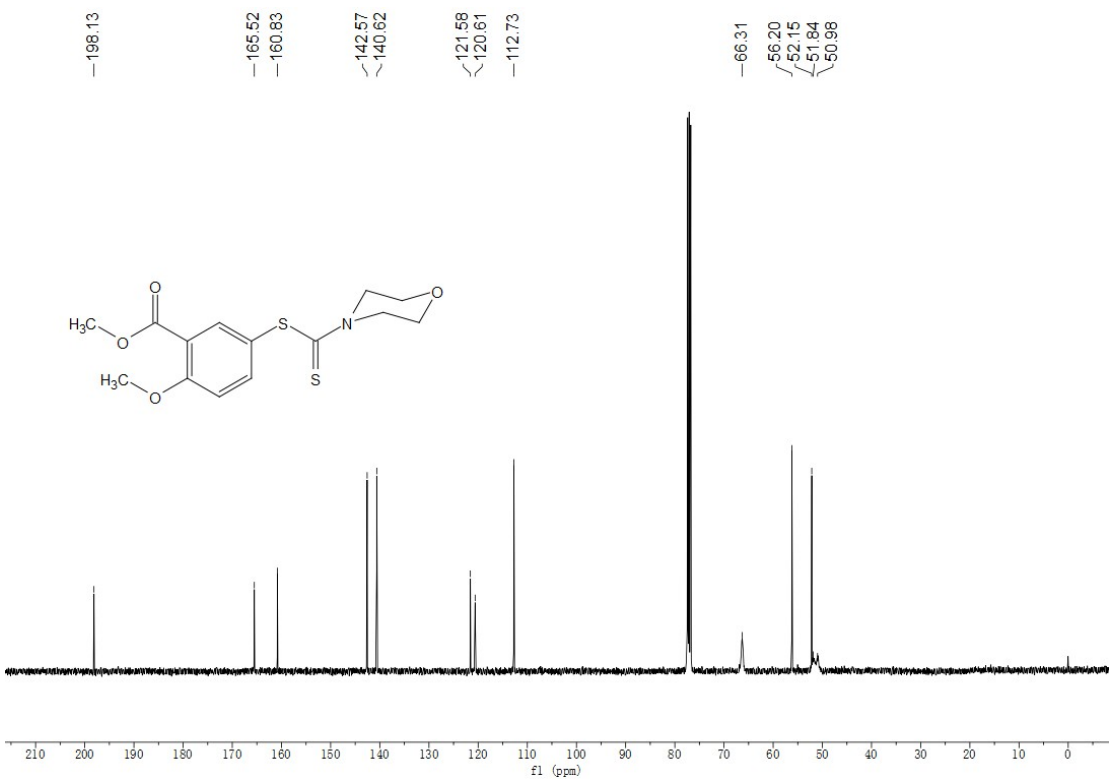
^{1}H NMR (400 MHz, Chloroform-*d*) of compound **4bj.**



^{13}C NMR (400 MHz, Chloroform-*d*) of compound **4bj.**



^{1}H NMR (400 MHz, Chloroform-*d*) of compound **4bk.**



^{13}C NMR (400 MHz, Chloroform-*d*) of compound **4bk.**