Electronic Supplementary Information

For

Synthesis of *N*-sulfenylsulfoximines and sulfenamides through metal-free N-H/S-H dehydrocoupling reaction

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1 General information

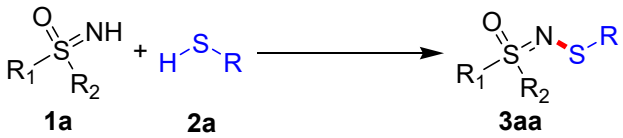
Unless otherwise indicated, solvents and reagents were purchased from Alfa Aesar, Sigma-Aldrich, TCI and J&K chemical companies and used without further purification. The sulfoximines were synthesized according to the procedure reported in the literature.[1] The products were purified by column chromatography in gradient elution (petroleum ether and ethyl acetate) of the Still protocol.[2] ^{1}H NMR, ^{13}C NMR were recorded on a Bruker Avance 400 spectrometer at ambient temperature. All signals were recorded in δ units, parts per million (ppm) with the internal reference of 7.26 ppm or 77.0 ppm for deuteron-chloroform as the reference, Data were reported as follows: br = broad, m = multiplet, q = quartet, t = triplet, d = doublet, s = singlet. Coupling constants (*J*) were given in Hertz (Hz). HRMS (High-resolution mass spectra) were performed on a Bruker Daltonics Bio-TOF-Q mass spectrometer by the ESI method. Melting points were obtained with a WRS-100 melting point apparatus.

2 General procedure for synthesis of *N*- sulfenylation of sulfoximines and anilines

To a 25 mL round-bottom flask equipped with a stir bar were added sulfoximine or aniline (0.1 mmol), thiol (0.2 mmol), and PEG_{400} (1.5 mL). Then the flask was immersed in a pre-heated oil bath set at 50 °C. Iodine (0.01 mmol) and hydrogen peroxide (0.25 mmol) were then added to the flask. After the flask was stirring for a set time, a saturated solution of $Na_2S_2O_3$ (5 mL) and ethyl acetate (15 mL) was added to the reaction mixture. The mixture was extracted with ethyl acetate (3×15 mL). The combined organic layers were washed with saturated solution of Na_2CO_3, and then dried over anhydrous $MgSO_4$. The solution was condensed at a rotary evaporator and the residue was subject to flash chromatography (silica gel) with a mixture of petroleum ether and ethyl acetate as eluent to provide the desired product.

3 Reaction condition optimization

Table 1 Screening of Reaction Conditions [a]



1a **2a** **3aa**

entry	catalyst (mol %)	oxidant (equiv)	**2a** (equiv)	solvent	*t* (°C)	time (h)	**3aa** (%) [b]
1	I_2 (10)	DMSO (3)	1.1	PEG_{400}	80	12	31
2	I_2 (10)	H_2O_2 (1)	1.1	PEG_{400}	80	12	40
3	I_2 (10)	TBHP (1)	1.1	PEG_{400}	80	12	5
4	I_2 (10)	DTBP (1)	1.1	PEG_{400}	80	12	0
5	I_2 (10)	O_2	1.1	PEG_{400}	80	12	0
6	I_2 (10)	Air	1.1	PEG_{400}	80	12	0
7	I_2 (10)	H_2O_2 (2)	1.1	PEG_{400}	80	12	50
8	I_2 (10)	H_2O_2 (2.5)	1.1	PEG_{400}	80	4	52
9	I_2 (10)	H_2O_2 (2.5)	1.1	PEG_{400}	50	4	54
10	I_2 (10)	H_2O_2 (2.5)	1.5	PEG_{400}	50	4	87
11	**I_2 (10)**	**H_2O_2 (2.5)**	**2**	**PEG_{400}**	**50**	**4**	**91**
12	I_2 (10)	H_2O_2 (2.5)	2.5	PEG_{400}	50	4	90
13	I_2 (10)	H_2O_2 (3)	2	PEG_{400}	50	4	86
14	I_2 (5)	H_2O_2 (2.5)	2	PEG_{400}	50	4	69
15	I_2 (15)	H_2O_2 (2.5)	2	PEG_{400}	50	4	89
16	KI (10)	H_2O_2 (2.5)	2	PEG_{400}	50	4	21

17	TBAI (10)	H_2O_2 (2.5)	2	PEG_{400}	50	4	trace
18	NH_4I (10)	H_2O_2 (2.5)	2	PEG_{400}	50	4	61
19	NH_4I (20)	H_2O_2 (2.5)	2	PEG_{400}	50	4	88
20	I_2 (10)	H_2O_2 (2.5)	2	PEG_{200}	50	4	90
21	I_2 (10)	H_2O_2 (2.5)	2	PEG_{300}	50	4	63
22	I_2 (10)	H_2O_2 (2.5)	2	PEG_{600}	50	4	72
23	I_2 (10)	H_2O_2 (2.5)	2	PE_{1000}	50	4	35
24	I_2 (10)	H_2O_2 (2.5)	2	MeCN	50	4	38
25	I_2 (10)	H_2O_2 (2.5)	2	EtOH	50	4	45
26	I_2 (10)	H_2O_2 (2.5)	2	H_2O	50	12	63
27	I_2 (10)	H_2O_2 (2.5)	2	DMSO	50	4	28
28	I_2 (10)	H_2O_2 (2.5)	2	DMF	50	4	31
29	I_2 (10)	H_2O_2 (2.5)	2	THF	50	4	32
30	I_2 (10)	H_2O_2 (2.5)	2	Toluene	50	4	15
31	I_2 (10)	H_2O_2 (2.5)	2	DCE	50	4	17
32	-	H_2O_2 (2.5)	2	PEG_{400}	50	4	0 [c]

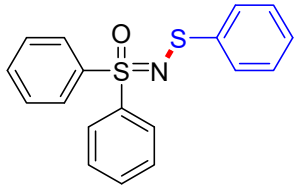
[a] Reaction conditions: A mixture of **1a** (0.1 mmol, 1 equiv), **2a** (1.1-2.5 equiv) in the solvent (1.5 mL), catalysts and oxidants were then added, stirred for 4 or 12 h. [b] Isolated yields. [c] Byproduct diphenyl disulfide with 98% yield was obtained and **1a** was almost fully recovered.

Our study was initiated with diphenylsulfoximine (**1a**) and thiophenol (**2a**) as model substrates, and I_2 as catalyst for reaction condition optimization. Different oxidants including dimethyl sulfoxide (DMSO), *tert*-butyl hydroperoxide (TBHP), *tert*-butyl peroxide (DTBP), oxygen (air), and hydrogen peroxide (H_2O_2) were evaluated (entries 1-6), and H_2O_2 was found to be the best choice (entry 2). Increasing the amount of the oxidant, lowering the temperature, and shortening the reaction time gave higher yields (entries 7-9). It was found that the ratio of starting materials was crucial in this transformation, and the highest yield was achieved when the ratio of **1a**: **2a** was 1:2 (entries 10-12). And the best amount of the catalyst was 10 mol % (entries 11, 14-15). By further screening of the catalysts, it turned out that both KI and tetrabutylammonium Iodide (TBAI) were not as effective as I_2 (entries 16-17). However, NH_4I exhibited excellent efficiency and 88% yield was reached when its dosage was increased to 20 mol % (entries 18-19).

To confirm the influence of various solvents on this reaction, other common solvents were used, including different type of PEGs, protic organic solvents, aprotic polar solvents, and water. The reaction proceeded smoothly in PEG_{200}, PEG_{300}, PEG_{600} (entries 20-22), but only 35% yield of product obtained when PEG_{1000} was used (entry 23), probably because of the poorer solubility. Most of other solvents could not give the desired product in good yields (entries 24-25, 27-31). To our delight, the reaction was performed well in water, 63% yield was obtained in a prolonged reaction time (entry 26). When the experiment was performed in the absence of catalyst, 98% diphenyl disulfide as by product was formed and **1a** was almost totally recovered (entry 32). Therefore, the standard condition was set as **1a** (1 equiv), **2a** (2 equiv), I_2 (10 mol %), H_2O_2 (2.5 equiv) in PEG_{400} at 50 °C.

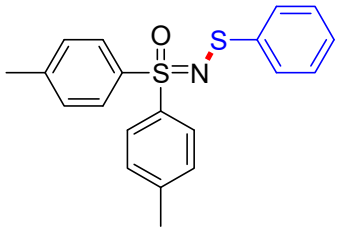
4 Characterization data for the products

_S,S_-diphenyl-_N_-phenylthiosulfoximine (3aa):[3]



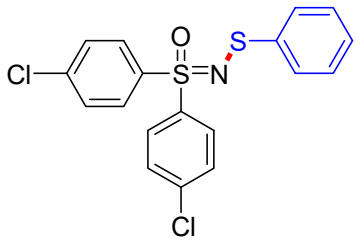
Flash column chromatography on a silica gel (petroleum ether: ethyl acetate, 10: 1) give **3aa** (29.6 mg, 91% yield) as a white solid; Mp. 105-107 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 – 8.01 (m, 4H), 7.62 – 7.43 (m, 8H), 7.32 – 7.24 (m, 2H), 7.10 (t, *J* = 7.4 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 142.1, 139.9, 133.2, 129.4, 128.5, 128.5, 125.0, 124.0; HRMS (ESI) *m/z* calcd for $C_{18}H_{16}NOS_2$ $(M+H)^+$ 326.0668, found 326.0666.

_S,S_-di(4-methylphenyl)-_N_-phenylthiosulfoximine (3ba):[4]



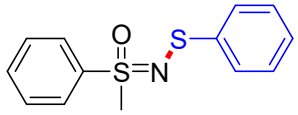
Flash column chromatography on a silica gel (petroleum ether: ethyl acetate, 10: 1) give **3ba** (32.5 mg, 92% yield) as a white solid; Mp. 108-110 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (d, *J* = 8.3 Hz, 4H), 7.45 (d, *J* = 7.4 Hz, 2H), 7.32 (d, *J* = 8.2 Hz, 4H), 7.28 (dd, *J* = 10.2, 5.4 Hz, 2H), 7.09 (t, *J* = 7.4 Hz, 1H), 2.42 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.1, 142.4, 137.2, 130.0, 128.4, 128.4, 124.9, 123.8, 21.6; HRMS (ESI) *m/z* calcd for $C_{20}H_{20}NOS_2$ $(M+H)^+$ 354.0981, found 354.0983.

_S,S_-di(4-chlorophenyl)-_N_-phenylthiosulfoximine (3ca):[3]



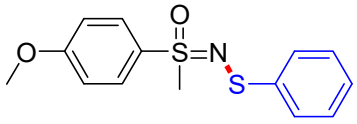
Flash column chromatography on a silica gel (petroleum ether: ethyl acetate, 10: 1) give **3ca** (38.3 mg, 97% yield) as a white solid; Mp. 120-122 ºC; ^{1}H NMR (400 MHz, CDCl3) δ 7.97 – 7.91 (m, 4H), 7.54 – 7.48 (m, 4H), 7.42 (dd, *J* = 8.4, 1.0 Hz, 2H), 7.29 (dd, *J* = 9.5, 6.1 Hz, 2H), 7.14 (d, *J* = 7.3 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.5, 140.3, 138.1, 129.9, 129.8, 128.6, 125.4, 124.2; HRMS (ESI) m/z calcd for $C_{18}H_{13}Cl_2NNaOS_2$ $(M+Na)^+$ 415.9708, found 415.9713.

_S_-methyl-_S_-phenyl-_N_-phenylthiosulfoximine (3da):[3]



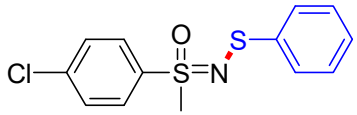
Flash column chromatography on a silica gel (petroleum ether: ethyl acetate, 5: 1) give **3da** (24.2 mg, 92% yield) as a yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 – 7.95 (m, 2H), 7.69 (t, *J* = 7.4 Hz, 1H), 7.60 (t, *J* = 7.6 Hz, 2H), 7.42 (d, *J* = 7.5 Hz, 2H), 7.29 (t, *J* = 7.8 Hz, 2H), 7.11 (t, *J* = 7.3 Hz, 1H), 3.30 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 142.2, 138.7, 133.8 129.5, 128.5, 128.4, 125.1, 123.9, 43.8; HRMS (ESI) *m/z* calcd for $C_{13}H_{13}NNaOS_2$ $(M+Na)^+$ 286.0331, found 286.0334.

S-methyl-S-(4-methoxyphenyl)-N-phenylthiosulfoximine (3ea):



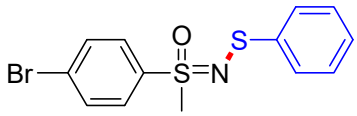
Flash column chromatography on a silica gel (petroleum ether: ethyl acetate, 5: 1) give **3ea** (27.9 mg, 95% yield) as a yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 – 7.86 (m, 2H), 7.42 (d, *J* = 7.9 Hz, 2H), 7.29 (t, *J* = 7.8 Hz, 2H), 7.10 (t, *J* = 7.4 Hz, 1H), 7.07 – 7.03 (m, 2H), 3.91 (s, 3H), 3.28 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.9, 142.4, 130.6, 129.7, 128.5, 125.0, 123.7, 114.8, 55.8, 44.1; HRMS (ESI) *m/z* calcd for $C_{14}H_{16}NO_2S_2$ $(M+H)^+$ 294.0617, found 294.0605.

S-methyl-S-(4-chlorophenyl)-N-phenylthiosulfoximine (3fa):



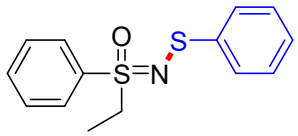
Flash column chromatography on a silica gel (petroleum ether: ethyl acetate, 10: 1) give **3fa** (28.9 mg, 97% yield) as a colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (d, *J* = 8.4 Hz, 2H), 7.57 (d, *J* = 8.4 Hz, 2H), 7.40 (d, *J* = 8.2 Hz, 2H), 7.30 (t, *J* = 7.6 Hz, 2H), 7.13 (t, *J* = 7.3 Hz, 1H), 3.30 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.8, 140.6, 137.2, 130.0, 129.8, 128.6, 125.3, 124.0, 43.9; HRMS (ESI) *m/z* calcd for $C_{13}H_{12}ClNNaOS_2$ $(M+Na)^+$ 319.9941, found 319.9940.

S-methyl-S-(4-bromophenyl)-N-phenylthiosulfoximine (3ga):



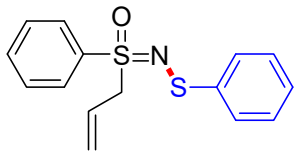
Flash column chromatography on a silica gel (petroleum ether: ethyl acetate, 10: 1) give **3ga** (24.3 mg, 71% yield) as a colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (d, *J* = 8.5 Hz, 2H), 7.68 (d, *J* = 8.5 Hz, 2H), 7.35 (d, *J* = 7.7 Hz, 2H), 7.28 – 7.21 (m, 2H), 7.10 – 7.05 (m, 1H), 3.25 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.7, 137.8, 132.8, 130.0, 129.2, 128.6, 125.3, 124.1, 43.9; HRMS (ESI) *m/z* calcd for $C_{13}H_{12}BrNNaOS_2$ $(M+Na)^+$ 363.9436, found 363.9429.

S-ethyl-S-phenyl-N-phenylthiosulfoximine (3ha):[3]



Flash column chromatography on a silica gel (petroleum ether: ethyl acetate, 10: 1) give **3ha** (26.6 mg, 96% yield) as a yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (dd, *J* = 5.3, 3.3 Hz, 2H), 7.68 – 7.57 (m, 3H), 7.44 – 7.39 (m, 2H), 7.28 (t, *J* = 7.8 Hz, 2H), 7.10 (t, *J* = 7.3 Hz, 1H), 3.52 – 3.39 (m, 2H), 1.33 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 142.5, 136.7, 133.7, 129.4, 129.3, 128.5, 125.0, 123.8, 50.3, 7.8; HRMS (ESI) *m/z* calcd for $C_{14}H_{15}NNaOS_2$ $(M+Na)^+$ 300.0493, found 300.0487.

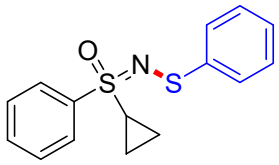
S-ethenyl-S-phenyl-N-phenylthiosulfoximine (3ia):



Flash column chromatography on a silica gel (petroleum ether: ethyl acetate, 10: 1) give **3ia** (24.0 mg, 83%

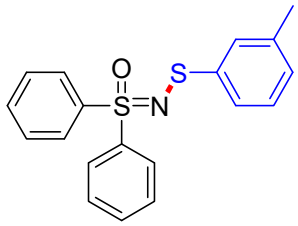
yield) as a colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 – 7.89 (m, 2H), 7.68 (t, *J* = 7.4 Hz, 1H), 7.58 (dd, *J* = 11.6, 4.2 Hz, 2H), 7.47 – 7.40 (m, 2H), 7.29 (m, 2H), 7.11 (t, *J* = 7.3 Hz, 1H), 5.88 – 5.74 (m, 1H), 5.35 (d, *J* = 10.1 Hz, 1H), 5.14 (d, *J* = 17.1 Hz, 1H), 4.20 (dd, *J* = 13.9, 7.2 Hz, 1H), 4.09 (dd, *J* = 13.9, 7.7 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 142.4, 136.4, 133.8, 129.5, 129.2, 128.5, 125.2, 125.1, 124.7, 123.8, 59.8; HRMS (ESI) *m/z* calcd for $C_{15}H_{16}NOS_2$ $(M+H)^+$ 290.0668, found 290.0669.

_S_-cyclopropyl-_S_-phenyl-_N_-phenylthiosulfoximine (3ja):



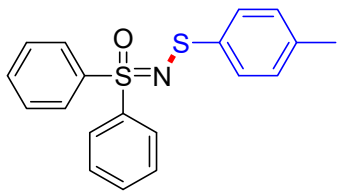
Flash column chromatography on a silica gel (petroleum ether: ethyl acetate, 5: 1) give **3ja** (26.0 mg, 90% yield) as a colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 – 7.89 (m, 2H), 7.66 (t, *J* = 7.4 Hz, 1H), 7.58 (t, *J* = 7.5 Hz, 2H), 7.39 (d, *J* = 8.2 Hz, 2H), 7.28 (m, 2H), 7.09 (t, *J* = 7.3 Hz, 1H), 2.74 – 2.67 (m, 1H), 1.75 – 1.67 (m, 1H), 1.32 – 1.14 (m, 2H), 1.00 – 0.91 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 142.6, 139.1, 133.3, 129.4, 128.5, 128.4, 124.9, 123.7, 33.0, 6.7, 5.6; HRMS (ESI) *m/z* calcd for $C_{15}H_{16}NOS_2$ $(M+H)^+$ 290.0668, found 290.0657.

_S, S_-diphenyl-_N_-(3-methylphenylthio)sulfoximine (3ab):



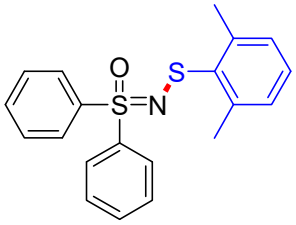
Flash column chromatography on a silica gel (petroleum ether: ethyl acetate, 10: 1) give **3ab** (27.8 mg, 82% yield) as a white solid; Mp. 106-108 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 – 8.01 (m, 4H), 7.63 – 7.57 (m, 2H), 7.57 – 7.49 (m, 4H), 7.30 – 7.23 (m, 2H), 7.18 (t, *J* = 7.6 Hz, 1H), 6.92 (d, *J* = 7.5 Hz, 1H), 2.32 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.8, 140.0, 138.2, 133.2, 129.3, 128.5, 128.4, 126.1, 124.6, 121.3, 21.5; HRMS (ESI) *m/z* calcd for $C_{19}H_{17}NNaOS_2$ $(M+Na)^+$ 362.0644, found 362.0642.

_S, S_-diphenyl-_N_-(4-methylphenylthio)sulfoximine (3ac):[3k]



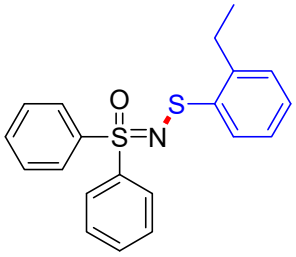
Flash column chromatography on a silica gel (petroleum ether: ethyl acetate, 10: 1) give **3ac** (26.5 mg, 78% yield) as a white solid; Mp. 110-112 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (d, *J* = 7.5 Hz, 4H), 7.58 (d, *J* = 7.2 Hz, 2H), 7.53 (t, *J* = 7.5 Hz, 4H), 7.38 (d, *J* = 8.2 Hz, 2H), 7.10 (d, *J* = 8.1 Hz, 2H), 2.32 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 140.1, 138.3, 135.2, 133.1, 129.3, 129.3, 128.5, 125.2, 21.0; HRMS (ESI) *m/z* calcd for $C_{19}H_{17}NNaOS_2$ $(M+Na)^+$ 362.0644, found 362.0649.

_S, S_-diphenyl-_N_-(2,6-dimethylphenylthio)sulfoximine (3ad):



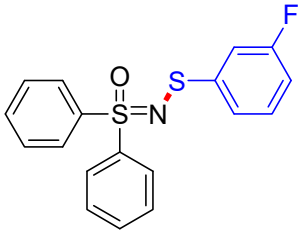
Flash column chromatography on a silica gel (petroleum ether: ethyl acetate, 10: 1) give **3ad** (26.3 mg, 70% yield) as a white solid; Mp. 108-110 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (dd, *J* = 5.2, 3.4 Hz, 4H), 7.54 – 7.47 (m, 2H), 7.40 (dd, *J* = 10.6, 4.8 Hz, 4H), 7.07 (d, *J* = 6.9 Hz, 1H), 6.98 (d, *J* = 7.5 Hz, 2H), 2.45 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.9, 140.4, 137.7, 132.7, 129.0, 128.6, 128.5, 127.8, 21.6; HRMS (ESI) *m/z* calcd for $C_{20}H_{19}NNaOS_2$ $(M+H)^+$ 376.0800, found 376.0796.

***S, S*-diphenyl-*N*-(2-ethylphenylthio)sulfoximine (3ae):**



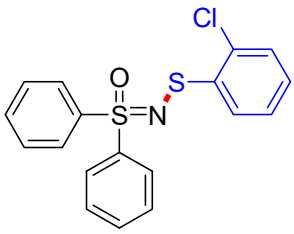
Flash column chromatography on a silica gel (petroleum ether: ethyl acetate, 10: 1) give **3ae** (27.6 mg, 78% yield) as a white solid; Mp. 111-113 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (dd, *J* = 5.3, 3.5 Hz, 4H), 7.80 (d, *J* = 7.9 Hz, 1H), 7.62 – 7.56 (m, 2H), 7.55 – 7.50 (m, 4H), 7.23 (dt, *J* = 8.2, 4.2 Hz, 1H), 7.07 (d, *J* = 4.0 Hz, 2H), 2.51 (q, *J* = 7.5 Hz, 2H), 1.14 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 140.3, 140.1, 138.4, 133.1, 129.3, 128.5, 127.4, 126.3, 124.8, 124.2, 25.7, 13.9; HRMS (ESI) *m/z* calcd for $C_{20}H_{19}NNaOS_2$ $(M+Na)^+$ 376.0800, found 376.0802.

***S, S*-diphenyl-*N*-(3-fluorophenylthio)sulfoximine (3af):**



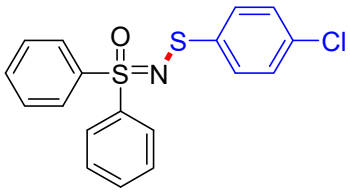
Flash column chromatography on a silica gel (petroleum ether: ethyl acetate, 10: 1) give **3af** (33.0 mg, 96% yield) as a white solid; Mp. 100-102 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 – 8.03 (m, 4H), 7.65 – 7.58 (m, 2H), 7.55 (dd, *J* = 10.2, 4.7 Hz, 4H), 7.25 – 7.18 (m, 2H), 7.14 (d, *J* = 8.0 Hz, 1H), 6.77 (d, *J* = 2.3 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.1 (d, *J* = 247.0 Hz), 145.2 (d, *J* = 7.5 Hz), 139.8, 133.4, 129.7 (d, *J* = 8.5 Hz), 129.4, 128.5, 118.7 (d, *J* = 2.9 Hz), 111.6 (d, *J* = 21.7 Hz), 110.5 (d, *J* = 24.6 Hz); HRMS (ESI) *m/z* calcd for $C_{18}H_{14}FNNaOS_2$ $(M+Na)^+$ 366.0393, found 366.0397.

***S, S*-diphenyl-*N*-(2-chlorophenylthio)sulfoximine (3ag):**



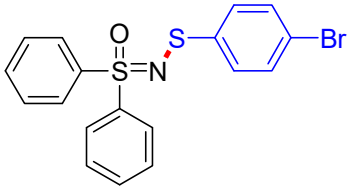
Flash column chromatography on a silica gel (petroleum ether: ethyl acetate, 10: 1) give **3ag** (34.9mg, 97% yield) as a white solid; Mp. 117-119 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (d, *J* = 7.4 Hz, 4H), 7.78 (dd, *J* = 8.0, 1.3 Hz, 1H), 7.62 (dd, *J* = 8.3, 6.2 Hz, 2H), 7.56 (t, *J* = 7.4 Hz, 4H), 7.28 (dd, *J* = 9.2, 6.1 Hz, 1H), 7.21 (d, *J* = 7.3 Hz, 1H), 7.04 (dd, *J* = 7.6, 1.1 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.5, 139.9, 133.39, 129.5, 128.6, 128.5, 127.0, 125.1, 124.3; HRMS (ESI) *m/z* calcd for $C_{18}H_{15}ClNOS_2$ $(M+H)^+$ 360.0278, found 360.0278.

***S, S*-diphenyl-*N*-(4-chlorophenylthio)sulfoximine (3ah):[3]**



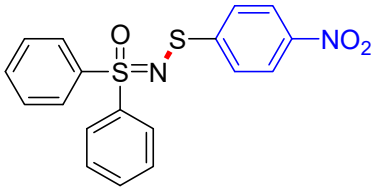
Flash column chromatography on a silica gel (petroleum ether: ethyl acetate, 10: 1) give **3ah** (33.8mg, 94% yield) as a white solid; Mp. 121-123 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (d, *J* = 7.5 Hz, 4H), 7.61 (t, *J* = 7.3 Hz, 2H), 7.55 (t, *J* = 7.4 Hz, 4H), 7.38 (d, *J* = 8.6 Hz, 2H), 7.24 (d, *J* = 8.6 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.0, 139.8, 133.4, 130.6, 129.4, 128.6, 128.5, 125.3; HRMS (ESI) *m/z* calcd for $C_{18}H_{15}ClNOS_2$ $(M+H)^+$ 360.0278, found 360.0273.

***S, S*-diphenyl-*N*-(4-bromophenylthio)sulfoximine (3ai):[3]**



Flash column chromatography on a silica gel (petroleum ether: ethyl acetate, 10: 1) give **3ai** (37.2 mg, 92% yield) as a white solid; Mp. 122-124 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 – 8.00 (m, 4H), 7.64 – 7.58 (m, 2H), 7.58 – 7.51 (m, 4H), 7.40 – 7.28 (m, 4H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.7, 139.8, 133.4, 131.4, 129.5, 128.5, 125.4, 118.4; HRMS (ESI) *m/z* calcd for $C_{18}H_{14}BrNNaOS_2$ $(M+Na)^+$ 425.9592, found 425.9603.

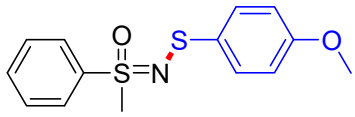
***S, S*-diphenyl-*N*-(4-nitrophenylthio)sulfoximine (3aj):**



Flash column chromatography on a silica gel (petroleum ether: ethyl acetate, 10: 1) give **3aj** (24.8mg, 67% yield) as a yellow solid; Mp. 164-165 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 (d, *J* = 8.9 Hz, 2H), 8.05 (d, *J* = 7.4 Hz, 4H), 7.65 (t, *J* = 7.3 Hz, 2H), 7.59 (t, *J* = 7.5 Hz, 4H), 7.51 (d, *J* = 8.9 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.5, 144.7, 139.4, 133.7, 129.6, 128.4, 123.7, 122.1; HRMS (ESI) *m/z* calcd for

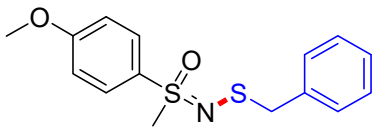
$C_{18}H_{14}N_2NaO_3S_2$ $(M+Na)^+$ 393.0338, found 393.0328.

_S_-methyl-_S_-phenyl-_N_-(4-methoxyphenylthio)sulfoximine (3ak):



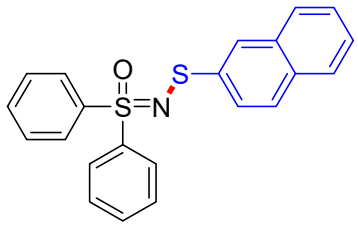
Flash column chromatography on a silica gel (petroleum ether: ethyl acetate, 3: 1) give **3ak** (21.0 mg, 59% yield) as a colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (d, J = 7.5 Hz, 2H), 7.67 (d, J = 7.3 Hz, 1H), 7.59 (t, J = 7.6 Hz, 2H), 7.47 – 7.42 (m, 2H), 6.88 – 6.82 (m, 2H), 3.81 (s, 3H), 3.25 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.7, 139.0, 133.6, 131.9, 129.5, 129.4, 128.5, 114.3, 55.4, 43.9; HRMS (ESI) *m/z* calcd for $C_{14}H_{15}NNaO_2S_2$ $(M+Na)^+$ 316.0442, found 316.0444.

_S_-methyl-_S_-(4-methoxyphenyl)-_N_-benzylthiosulfoximine (3al):



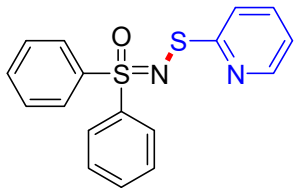
Flash column chromatography on a silica gel (petroleum ether: ethyl acetate, 10: 1) give **3al** (19.1 mg, 62% yield) as a yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (d, J = 8.9 Hz, 2H), 7.38 (d, J = 7.3 Hz, 2H), 7.32 (d, J = 7.2 Hz, 2H), 7.27 – 7.21 (m, 1H), 7.05 (d, J = 8.9 Hz, 2H), 4.18 – 4.05 (m, 2H), 3.91 (s, 3H), 3.10 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.7, 136.9, 130.6, 130.2, 129.6, 128.3, 127.0, 114.7, 55.7, 46.0, 43.8; HRMS (ESI) *m/z* calcd for $C_{15}H_{17}NNaO_2S_2$ $(M+H)^+$ 330.0593, found 330.0596.

_S, S_-diphenyl-_N_-(naphthalene-1-thio)sulfoximine (3am):



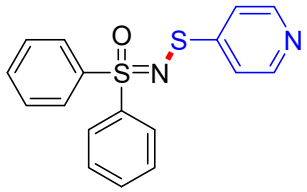
Flash column chromatography on a silica gel (petroleum ether: ethyl acetate, 10: 1) give **3am** (26.7 mg, 71% yield) as a white solid; Mp. 129-130 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (d, J = 7.3 Hz, 4H), 7.89 (s, 1H), 7.75 (d, J = 9.2 Hz, 3H), 7.60 (d, J = 7.1 Hz, 2H), 7.57 – 7.49 (m, 5H), 7.47 – 7.36 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 139.9, 139.7, 133.7, 133.3, 131.7, 129.4, 128.5, 128.0, 127.7, 127.2, 126.2, 124.7, 122.8, 121.5; HRMS (ESI) *m/z* calcd for $C_{22}H_{18}NOS_2$$(M+H)^+$ 376.0824, found 376.0823.

_S, S_-diphenyl-_N_-(2-pyridinethio)sulfoximine (3an):



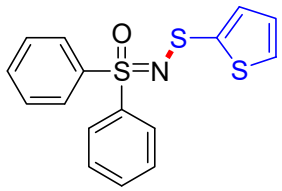
Flash column chromatography on a silica gel (petroleum ether: ethyl acetate, 5: 1) give **3an** (29.4 mg, 90% yield) as a white solid; Mp. 105-106. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.32 (dd, J = 4.8, 0.7 Hz, 1H), 8.07 – 8.00 (m, 4H), 7.71 (d, J = 8.2 Hz, 1H), 7.62 – 7.49 (m, 7H), 6.94 – 6.88 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.2, 148.5, 139.7, 136.6, 133.4, 129.5, 128.5, 119.0, 117.9; HRMS (ESI) *m/z* calcd for $C_{17}H_{14}N_2NaOS_2$ $(M+Na)^+$ 349.0440, found 349.0445.

***S, S*-diphenyl-*N*-(4-pyridinethio)sulfoximine (3ao):**



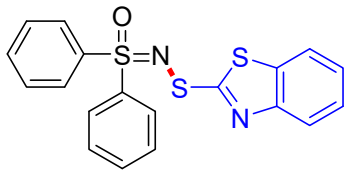
Flash column chromatography on a silica gel (petroleum ether: ethyl acetate, 1: 1) give **3ao** (31.0 mg, 95% yield) as a white solid; Mp. 102-104 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.37 (d, *J* = 5.1 Hz, 2H), 8.07 – 8.01 (m, 4H), 7.65 – 7.59 (m, 2H), 7.56 (t, *J* = 7.7 Hz, 4H), 7.32 – 7.29 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.6, 148.8, 139.5, 133.6, 129.6, 128.4, 116.9; HRMS (ESI) *m/z* calcd for $C_{17}H_{14}N_2NaOS_2$ $(M+Na)^+$ 327.0620, found 327.0625.

***S, S*-diphenyl-*N*-(2-thiophenethio)sulfoximine (3ap):[3]**



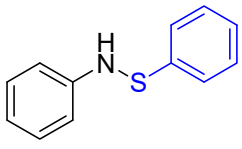
Flash column chromatography on a silica gel (petroleum ether: ethyl acetate, 10: 1) give **3ap** (21.5mg, 65% yield) as a yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 – 7.96 (m, 4H), 7.57 (d, *J* = 7.3 Hz, 2H), 7.51 (t, *J* = 7.5 Hz, 4H), 7.43 – 7.39 (m, 1H), 7.17 – 7.15 (m, 1H), 6.94 – 6.90 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 139.9, 133.8, 133.1, 131.0, 129.2, 128.5, 127.9, 127.2; HRMS (ESI) *m/z* calcd for $C_{16}H_{13}NNaOS_3$ $(M+H)^+$ 354.0051, found 354.0040

***S, S*-diphenyl-*N*-(2-benzothiazolethio)sulfoximine (3aq):**



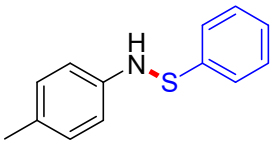
Flash column chromatography on a silica gel (petroleum ether: ethyl acetate, 10: 1) give **3aq** (28.3 mg, 74% yield) as a white solid; Mp. 138-140 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (d, *J* = 7.5 Hz, 4H), 7.80 (d, *J* = 7.5 Hz, 2H), 7.64 (t, *J* = 7.3 Hz, 2H), 7.58 (t, *J* = 7.5 Hz, 4H), 7.40 (t, *J* = 7.6 Hz, 1H), 7.30 – 7.24 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 177.3, 154.6, 139.0, 135.0, 133.8, 129.6, 128.5, 125.9, 123.4, 121.4, 120.9; HRMS (ESI) *m/z* calcd for $C_{19}H_{15}N_2OS_3$ $(M+H)^+$ 383.0341, found 383.0346.

***N*-(phenylthio)benzenamine (5aa):[5]**



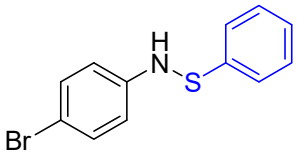
Flash column chromatography on a silica gel (petroleum ether: ethyl acetate, 100: 1) give **3ca** (12.7 mg, 63% yield) as a white solid; Mp. 53-55 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 – 7.22 (m, 6H), 7.17 (d, *J* = 7.2 Hz, 1H), 7.07 (d, *J* = 7.9 Hz, 2H), 6.92 (t, *J* = 7.3 Hz, 1H), 5.20 (s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 146.7, 141.5, 129.3, 128.9, 125.5, 122.4, 120.6, 114.7; HRMS (ESI) *m/z* calcd for $C_{12}H_{12}NS$ $(M+H)^+$ 202.0685, found 202.0682.

4-methyl-*N*-(phenylthio)benzenamine (5ab):[5]



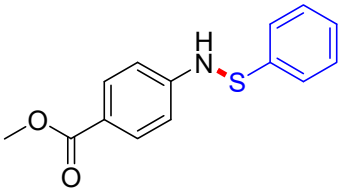
Flash column chromatography on a silica gel (petroleum ether: ethyl acetate, 100: 1) give **5ab** (13.1mg, 61% yield) as a white solid; Mp. 52-53 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 (d, *J* = 7.0 Hz, 2H), 7.24 (d, *J* = 7.3 Hz, 2H), 7.16 (d, *J* = 7.2 Hz, 1H), 7.06 (d, *J* = 8.3 Hz, 2H), 6.97 (d, *J* = 8.4 Hz, 2H), 5.11 (s, 1H), 2.30 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.25, 141.78, 129.87, 129.80, 128.88, 125.39, 122.39, 114.65, 20.49; HRMS (ESI) *m/z* calcd for $C_{13}H_{14}NS$ $(M+H)^+$ 216.0841, found 216.0838.

4-bromo-*N*-(phenylthio)benzenamine (5ac):[5]



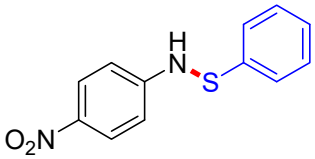
Flash column chromatography on a silica gel (petroleum ether: ethyl acetate, 80: 1) give **5ac** (13.1 mg, 61% yield) as a white solid; Mp. 104-105 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 (dd, *J* = 7.7, 5.5 Hz, 3H), 7.29 (m, 1H), 7.19 (dd, *J* = 10.1, 7.8 Hz, 3H), 6.95 (d, *J* = 8.9 Hz, 2H), 5.21 (s, 1H).^{13}C NMR (101 MHz, $CDCl_3$) δ 145.9, 140.8, 132.1, 129.0, 125.8, 122.6, 116.4, 112.5; HRMS (ESI) *m/z* calcd for $C_{12}H_{11}BrNS$ $(M+H)^+$ 279.9790, found 279.9788.

methyl 4-(phenylthioamino)benzoate (5ad):



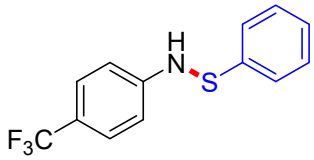
Flash column chromatography on a silica gel (petroleum ether: ethyl acetate, 20: 1) give **5ad** (18.2 mg, 70% yield) as a white solid; Mp. 115-116 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, *J* = 8.7 Hz, 2H), 7.31 (t, *J* = 7.7 Hz, 2H), 7.24 – 7.14 (m, 3H), 7.08 (d, *J* = 8.8 Hz, 2H), 5.61 (s, 1H), 3.89 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.0, 151.2, 140.3, 131.4, 129.1, 126.0, 122.8, 122.2, 114.1, 51.8; HRMS (ESI) *m/z* calcd for $C_{14}H_{14}NO_2S$ $(M+H)^+$ 260.0745, found 260.0743.

4-nitro-*N*-(phenylthio)benzenamine (5ae):[5]



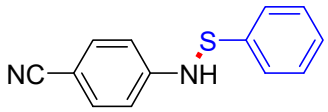
Flash column chromatography on a silica gel (petroleum ether: ethyl acetate, 10: 1) give **5ae** (11.6 mg, 51% yield) as a yellow solid; Mp. 102-103 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19 – 8.14 (m, 2H), 7.37 – 7.31 (m, 2H), 7.24 – 7.18 (m, 3H), 7.15 – 7.09 (m, 2H), 5.81 (s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 152.9, 141.3, 139.2, 129.3, 126.5, 125.9, 123.1, 114.2; HRMS (ESI) *m/z* calcd for $C_{12}H_{11}N_2O_2S$ $(M+H)^+$ 247.0536, found 247.0533.

***N*-(phenylthio)-4-(trifluoromethyl)benzenamine (5af):**



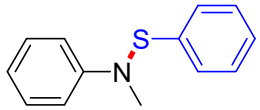
Flash column chromatography on a silica gel (petroleum ether: ethyl acetate, 40: 1) give **5af** (16.4 mg, 61% yield) as a yellow solid; Mp. 82-83 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 (d, *J* = 8.5 Hz, 2H), 7.33 (t, *J* = 7.7 Hz, 2H), 7.20 (dd, *J* = 15.7, 7.6 Hz, 3H), 7.13 (d, *J* = 8.5 Hz, 2H), 5.45 (s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 149.7, 140.3, 129.1, 127.4 (q, *J* = 33.5 Hz), 126.7 (q, *J* = 3.7 Hz), 126.0, 122.7, 121.9 (q, *J* = 271.7 Hz), 114.4; HRMS (ESI) *m/z* calcd for $C_{13}H_{11}F_3NS$ $(M+H)^+$ 270.0559, found 270.0550.

4-(phenylthioamino)benzonitrile (5ag):[5]



Flash column chromatography on a silica gel (petroleum ether: ethyl acetate, 10: 1) give **5ag** (14.0 mg, 62% yield) as a white solid; Mp. 105-106 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 (d, *J* = 8.7 Hz, 2H), 7.37 – 7.30 (m, 2H), 7.23 – 7.17 (m, 3H), 7.11 (d, *J* = 8.7 Hz, 2H), 5.68 (s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.9, 139.6, 133.7, 129.2, 126.3, 122.9, 119.6, 115.0, 103.1; HRMS (ESI) *m/z* calcd for $C_{13}H_{11}N_2S$ $(M+H)^+$ 227.0637, found 227.0641.

***N*-methyl-*N*-(phenylthio)benzenamine (5ah):**[6]



Flash column chromatography on a silica gel (petroleum ether: ethyl acetate, 100: 1) give **5ah** (13.3 mg, 62% yield) as a white solid; Mp. 54-56 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 – 7.27 (m, 4H), 7.23 (d, *J* = 7.9 Hz, 2H), 7.19 – 7.10 (m, 3H), 6.91 (t, *J* = 7.2 Hz, 1H), 3.52 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 149.8, 140.6, 129.1, 129.0, 125.5, 122.6, 119.6, 115.0, 44.5; HRMS (ESI) *m/z* calcd for $C_{13}H_{14}NS$ $(M+H)^+$ 216.0841, found 216.0837.

5 References

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2 W. C. Still, M. Kahn, A. Mitra, *J. Org. Chem.*, 1978, **43**, 2923.

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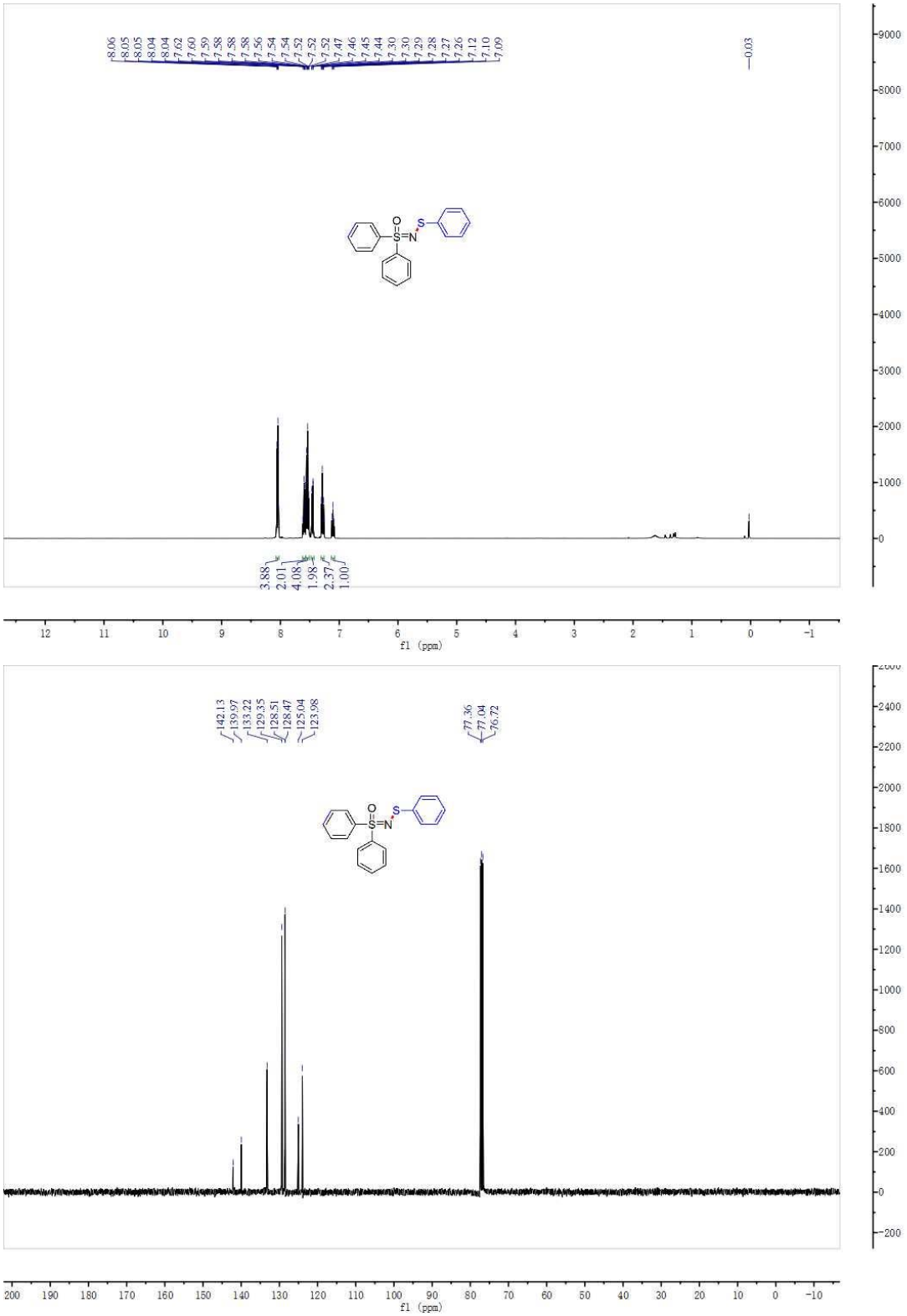
5 P. K. Claus; W. Silbernagel; W. Franek; W. Rieder, *Monatsh. Chem.* **1985**, *116*, 841.

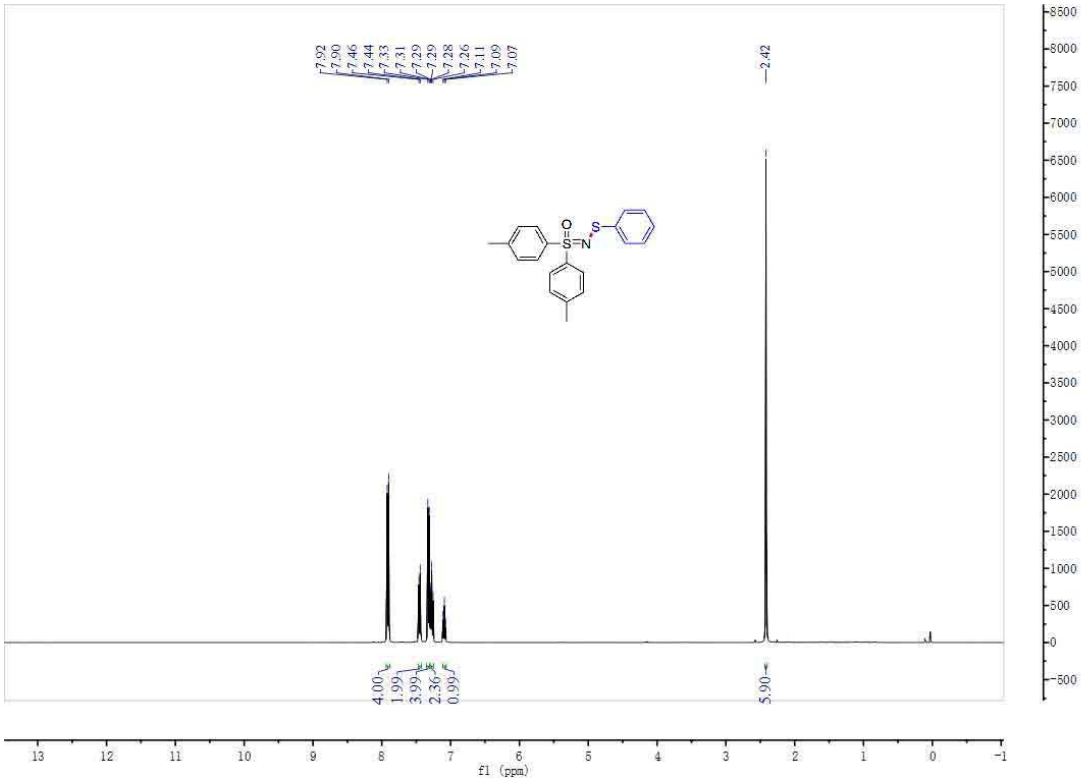
6 F. A. Davis; C. J. Horner; E. R. Fretz; J. F. Stackhouse, *J. Org. Chem.* **1973**, *38*, 695.

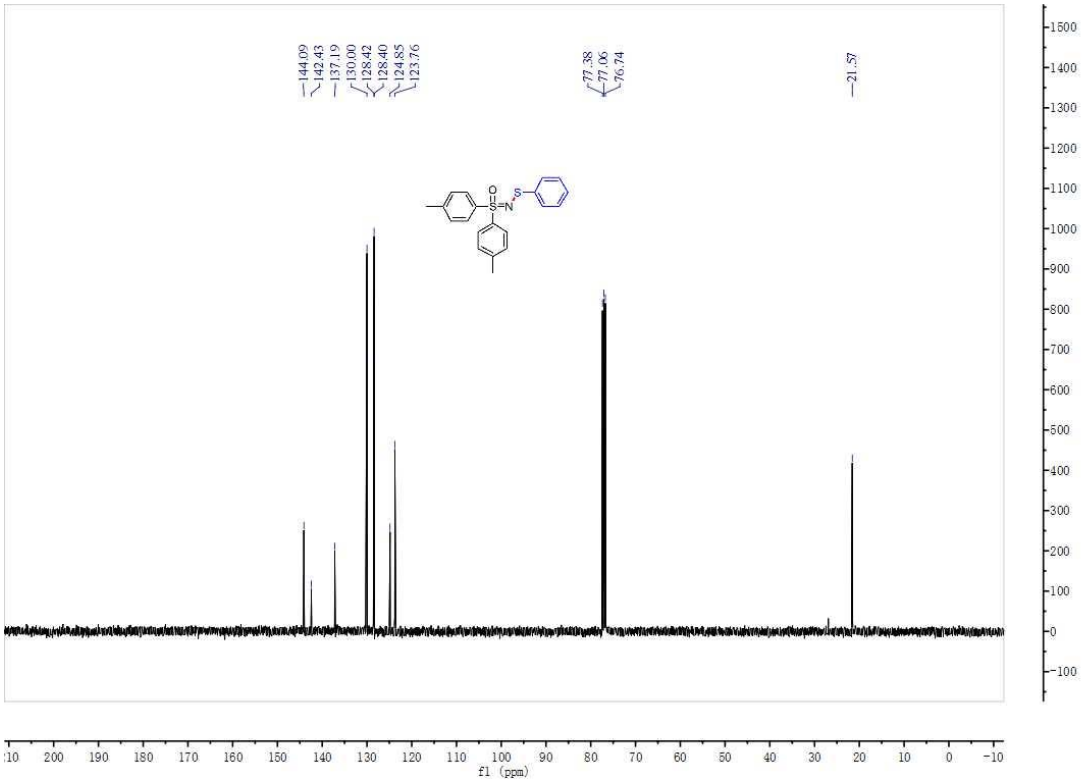
6 Copies of the ^{1}H NMR and ^{13}C NMR Spectra

S, S-diphenyl-*N*-phenylthiosulfoximine (3aa)

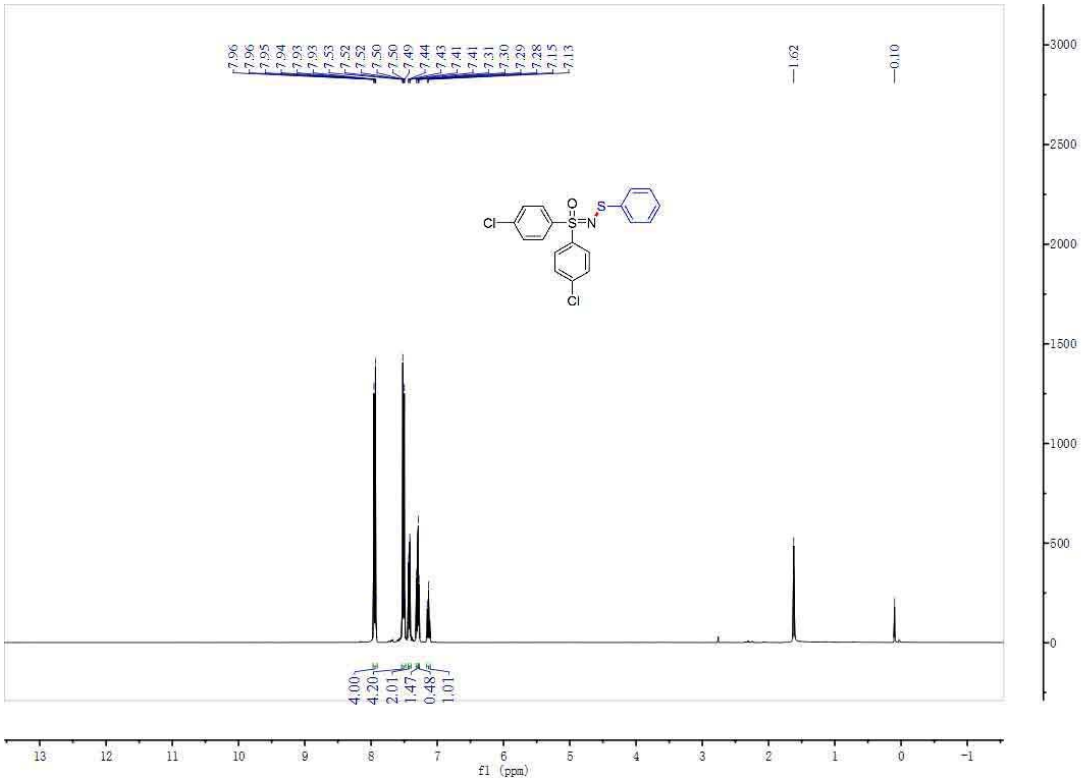


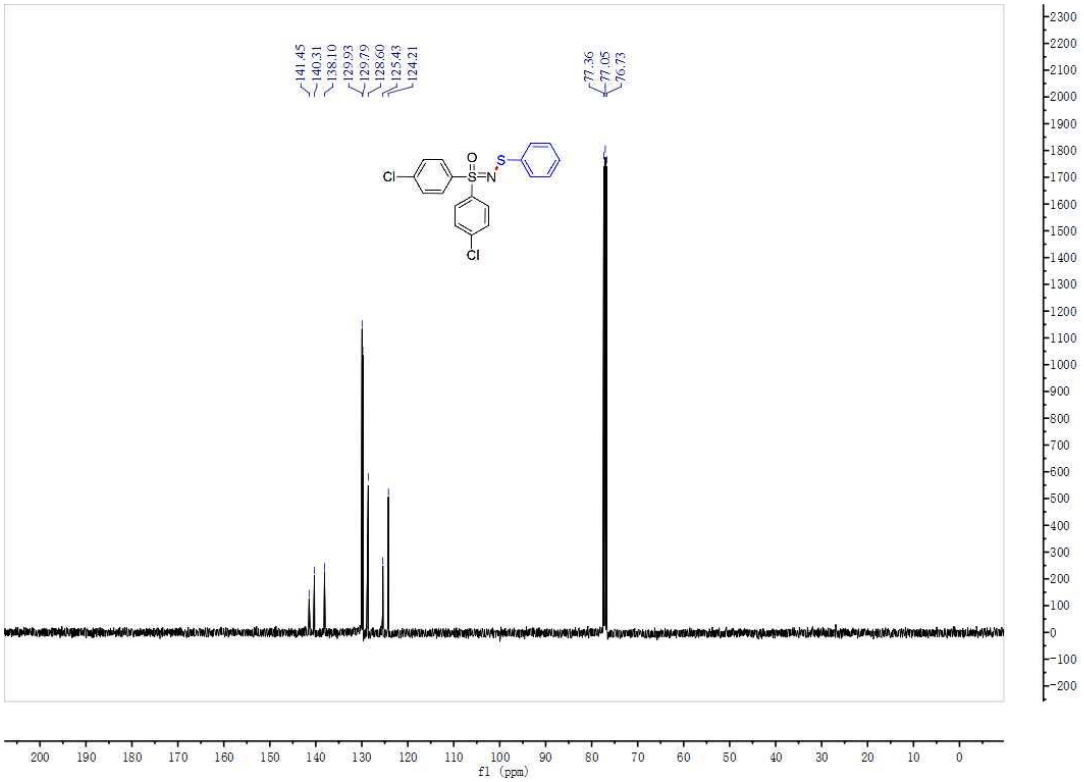
***S, S*-di(4-methylphenyl)-*N*-phenylthiosulfoximine (3ba)**



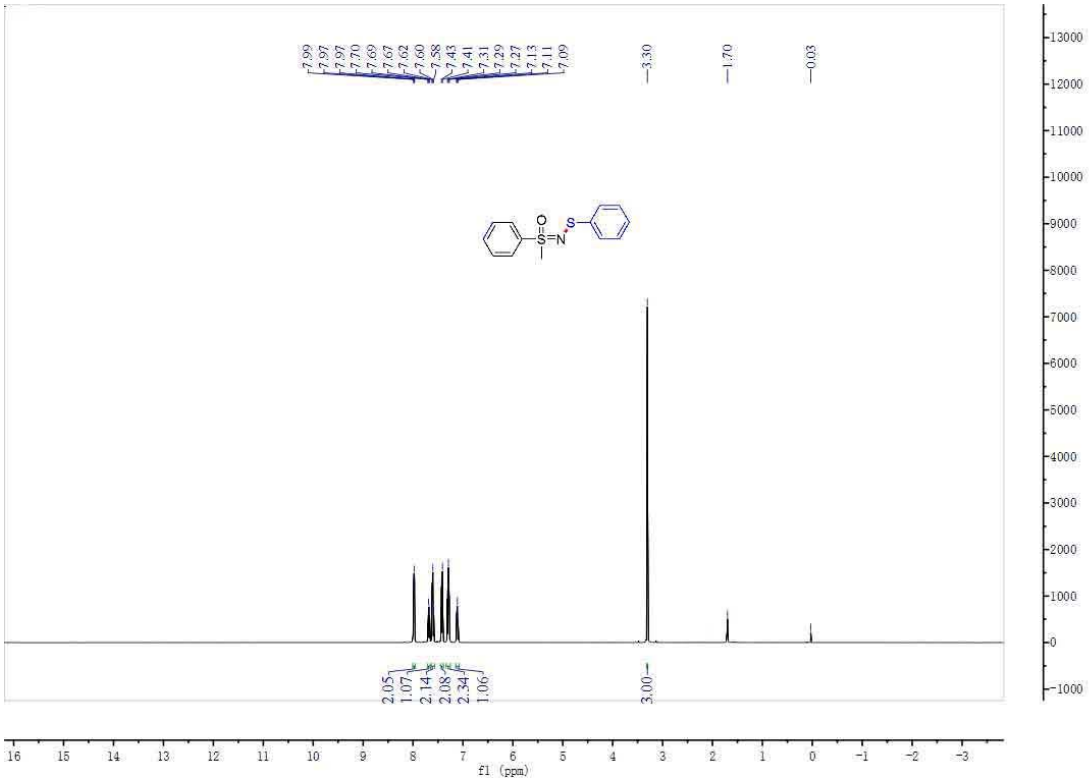


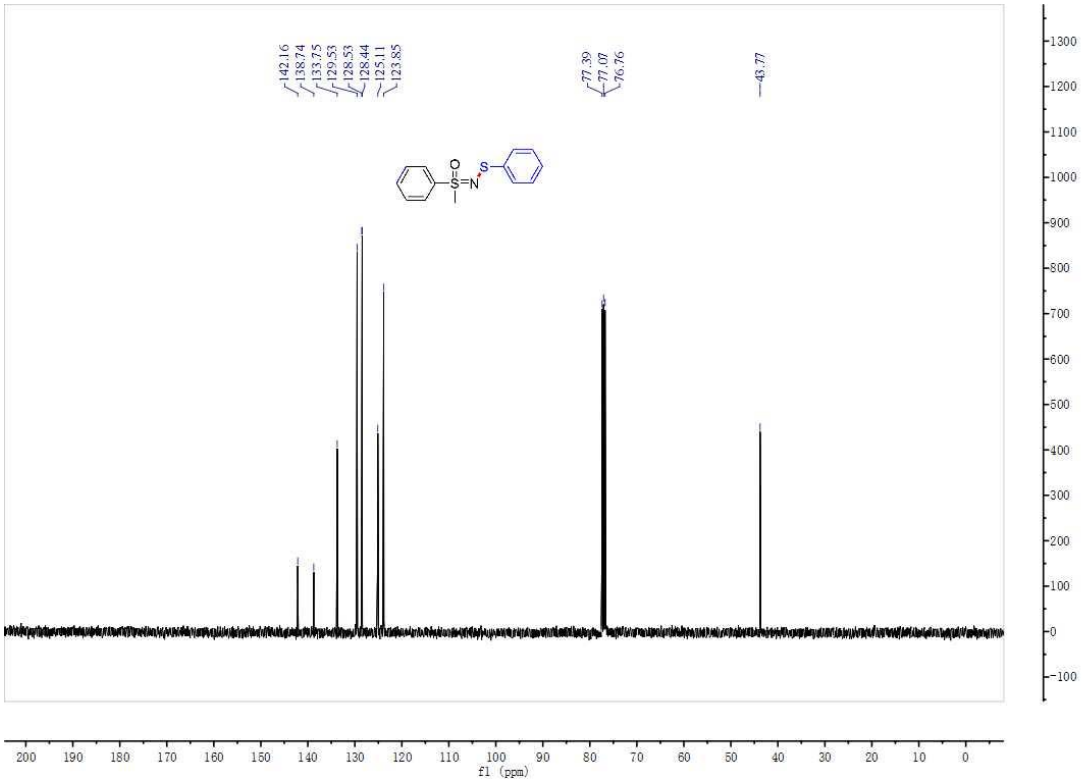
***S, S*-di(4-chlorophenyl)-*N*-phenylthiosulfoximine (3ca)**





***S*-methyl-*S*-phenyl-*N*-phenylthiosulfoximine (3da)**





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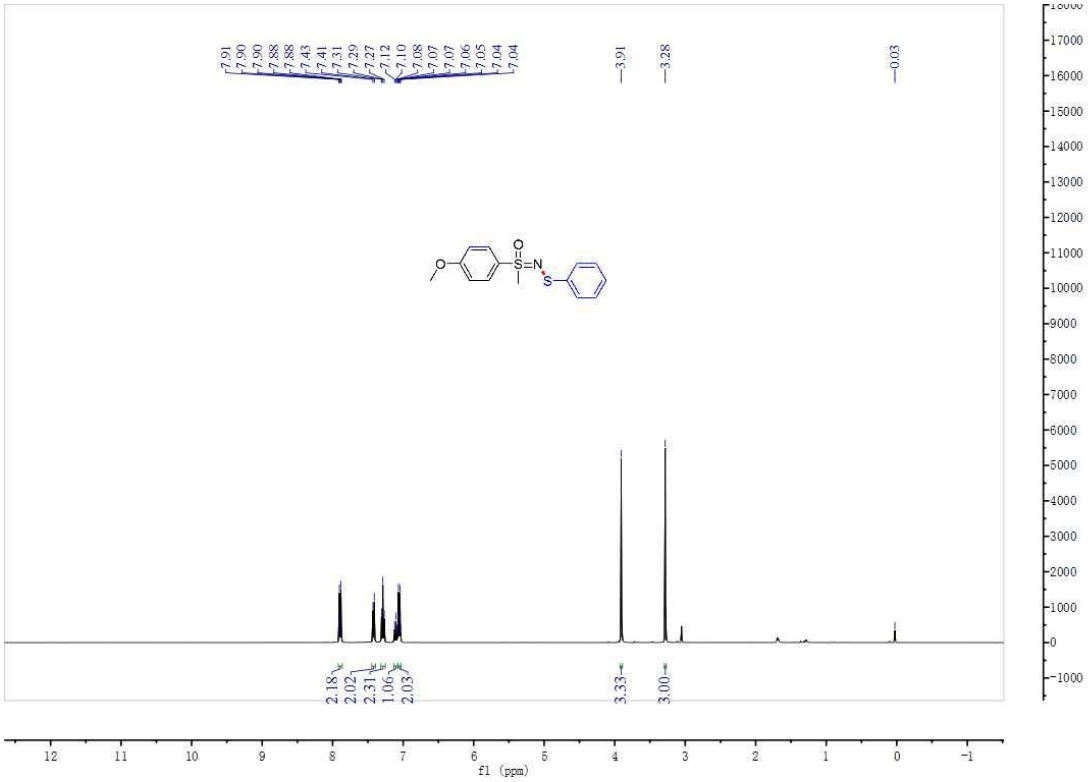

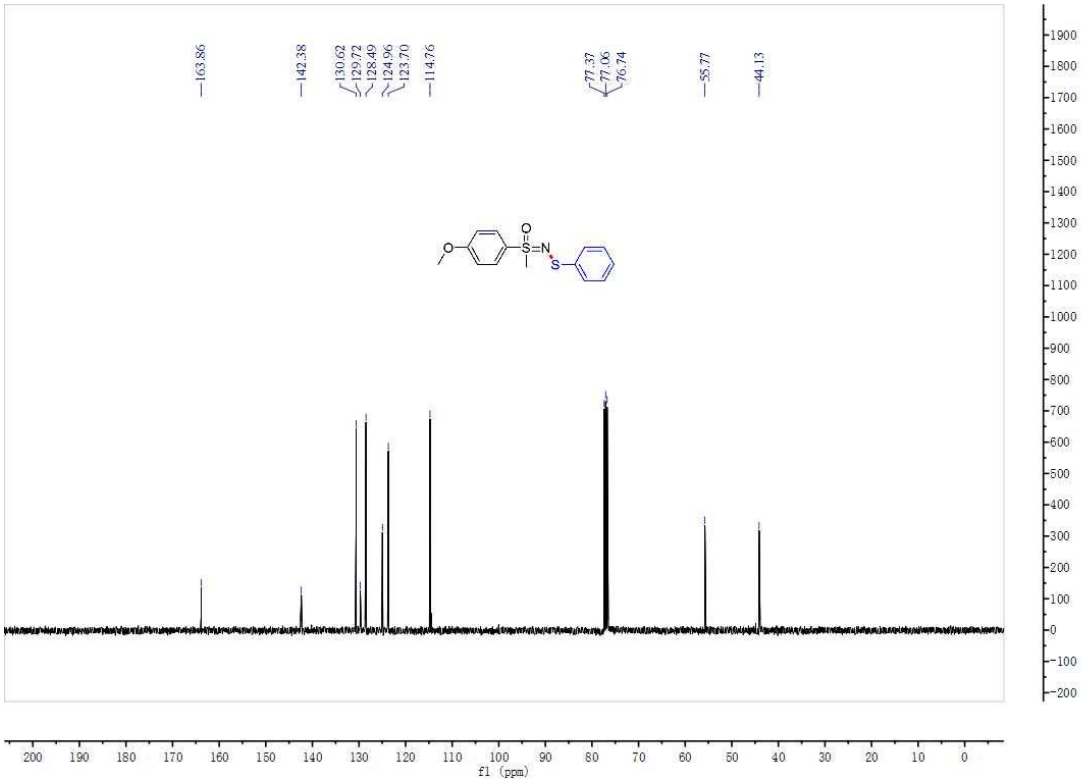

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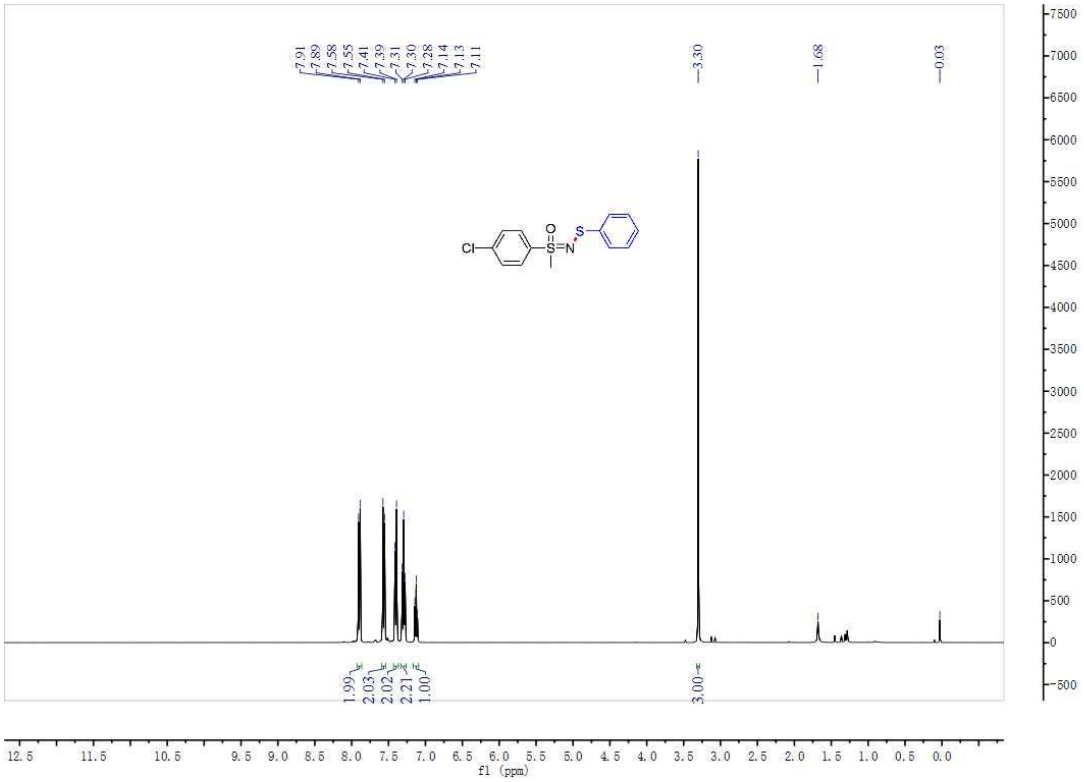
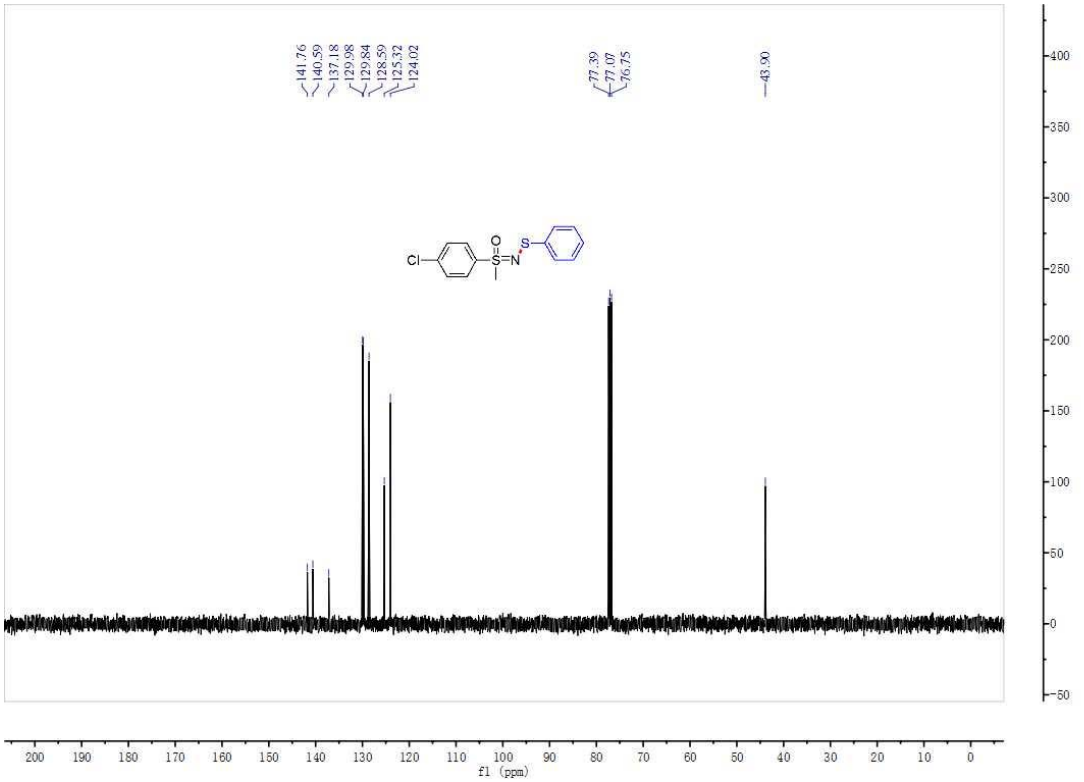
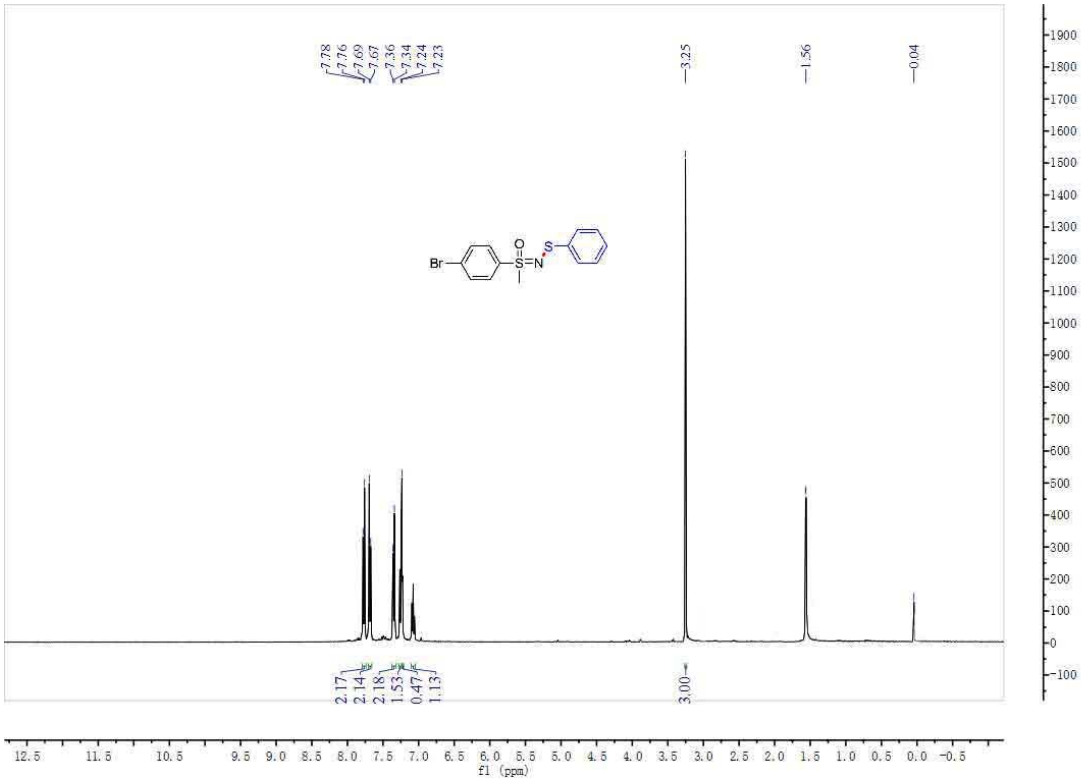
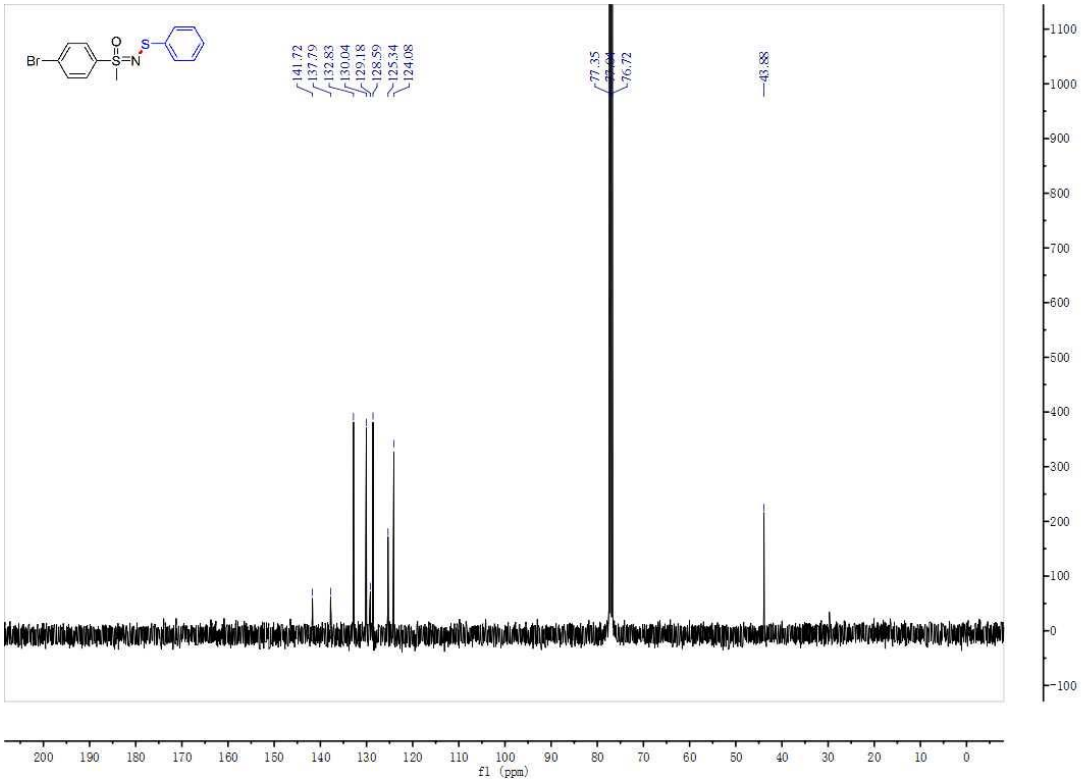


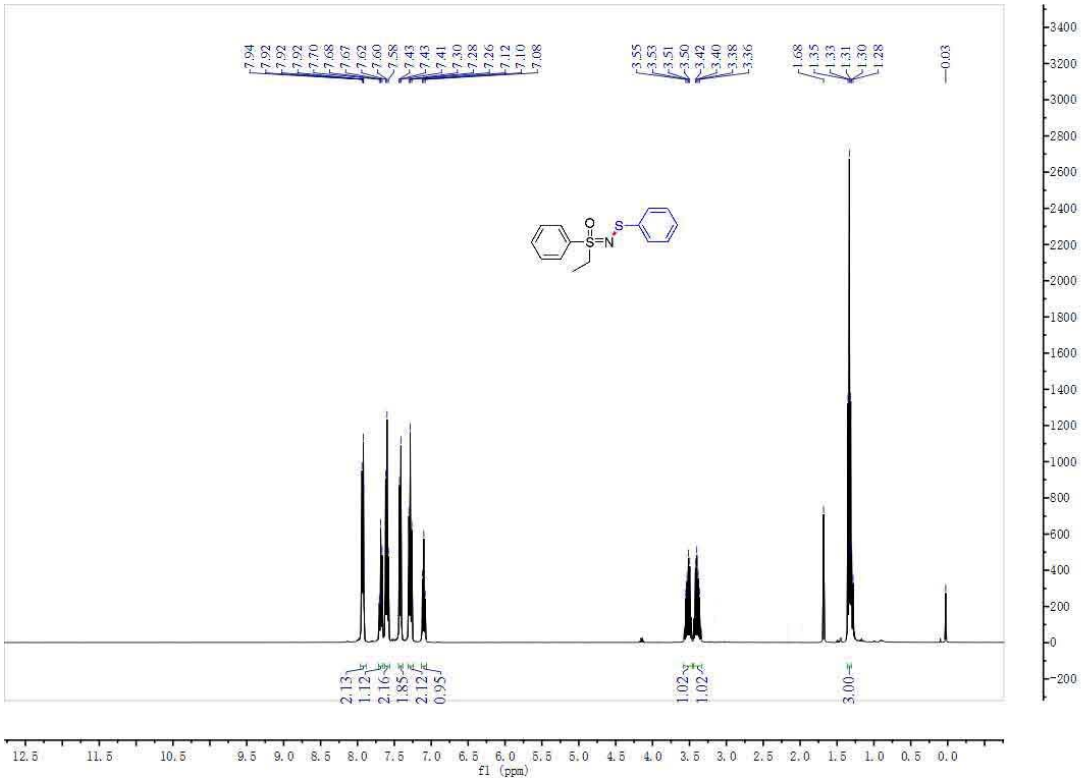


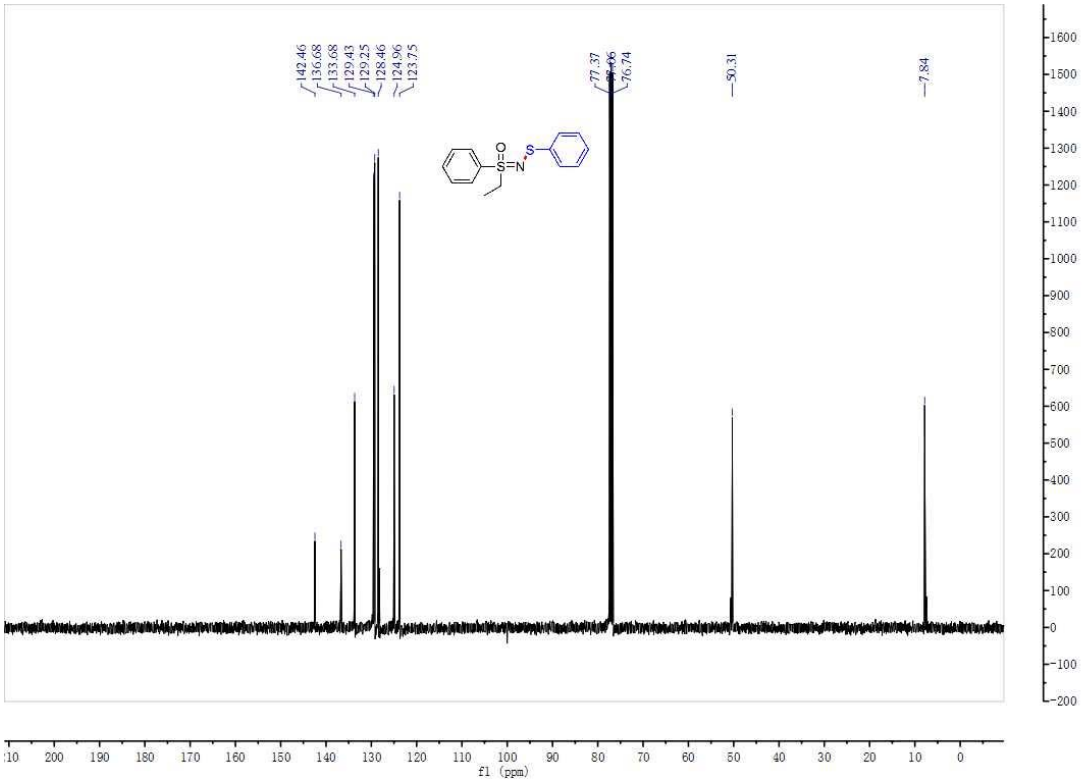
***S*-methyl-*S*-(4-bromophenyl)-*N*-phenylthiosulfoximine (3ga)**





***S*-ethyl-*S*-phenyl-*N*-phenylthiosulfoximine (3ha)**





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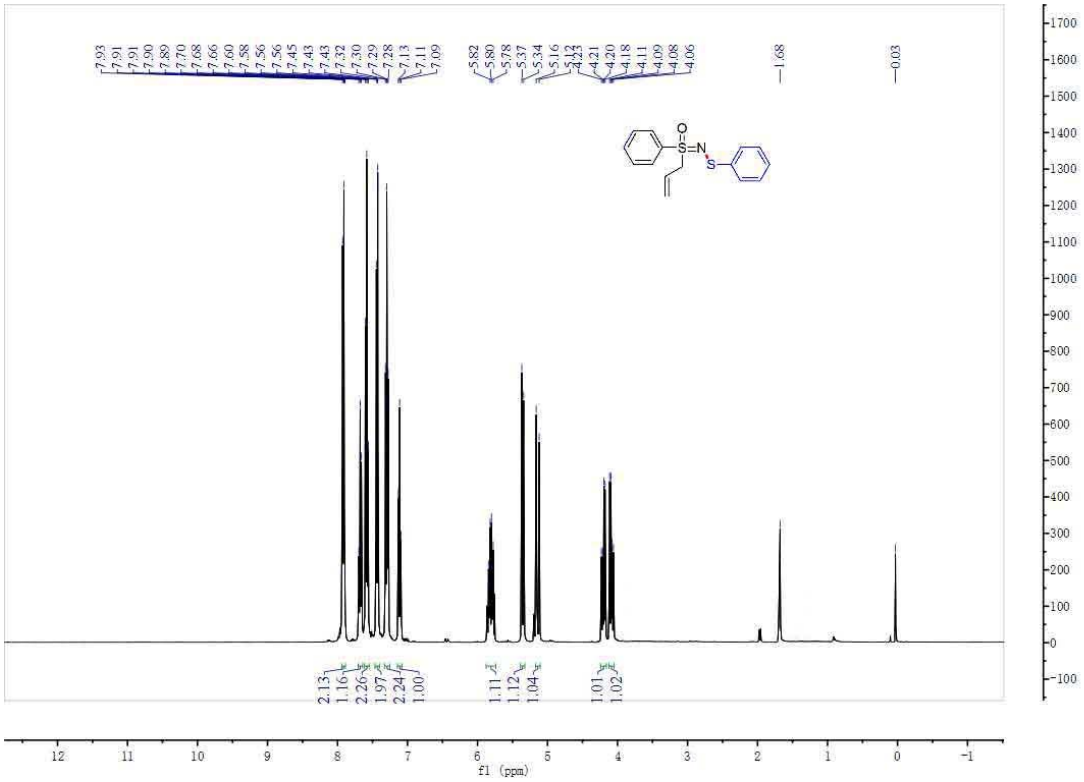
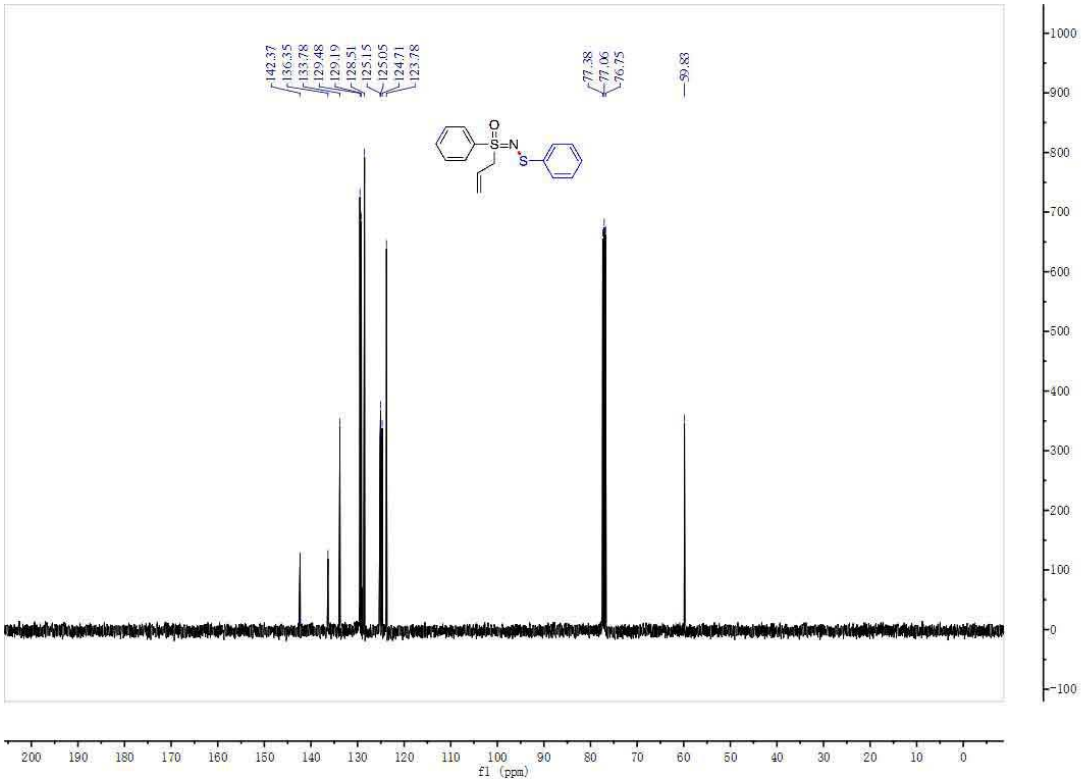
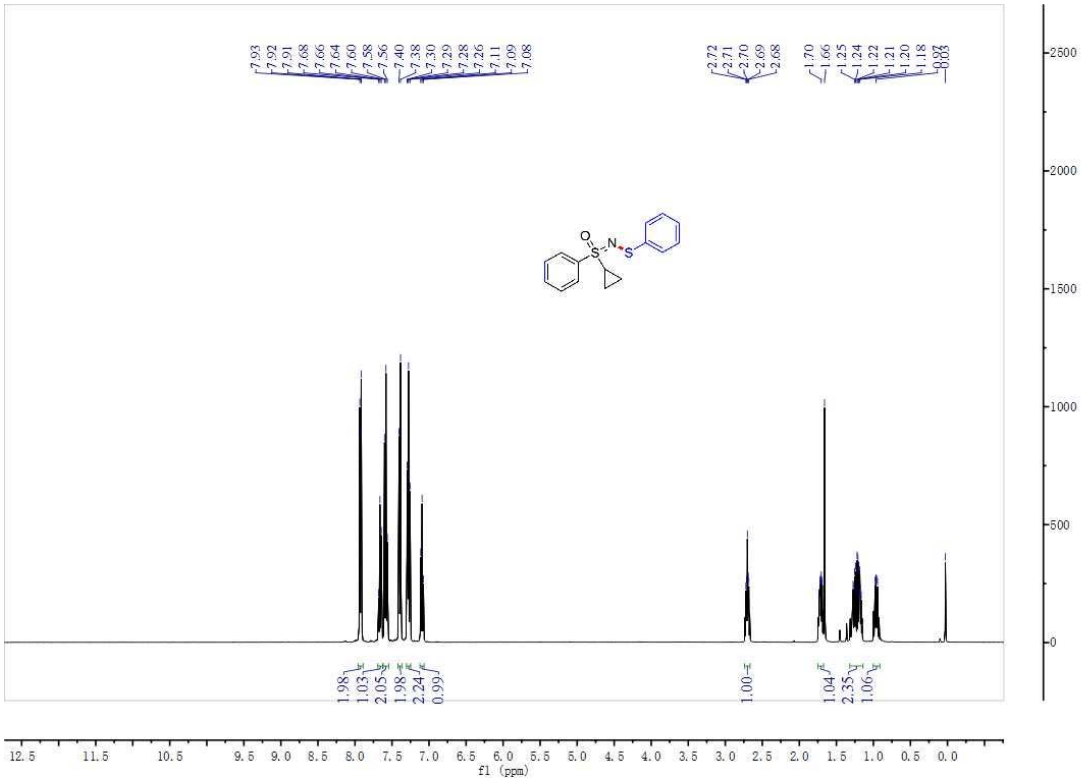
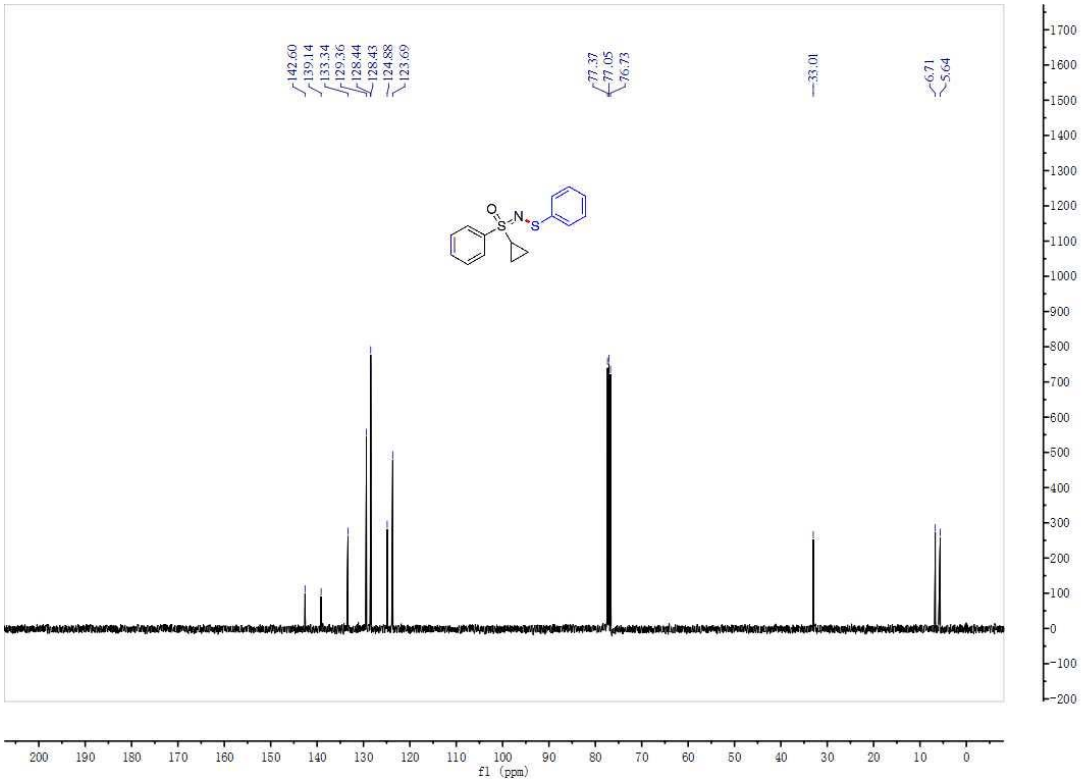


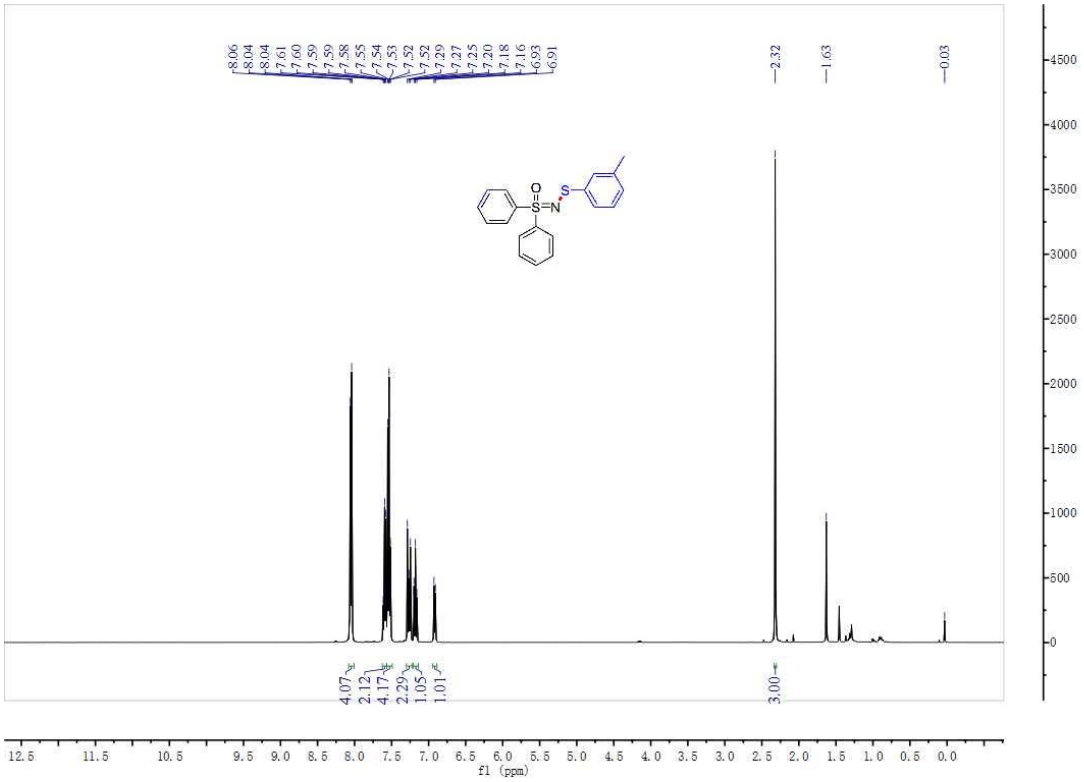


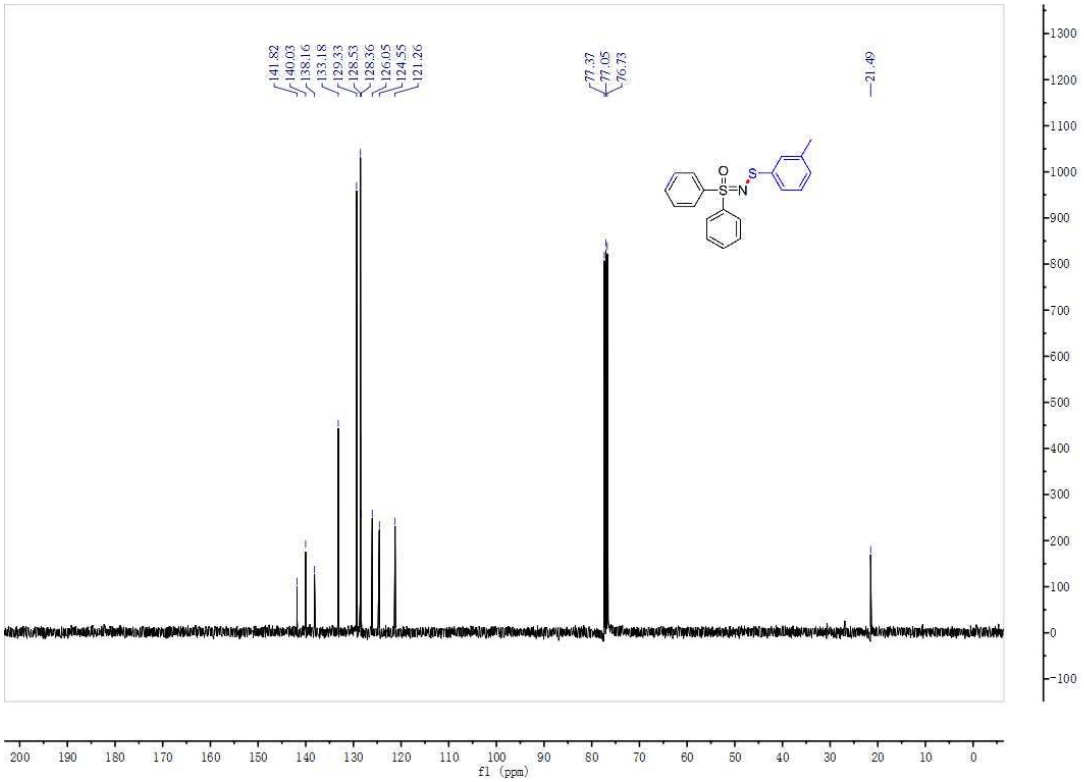
***S*-cyclopropyl-*S*-phenyl-*N*-phenylthiosulfoximine (3ja)**





***S, S*-diphenyl-*N*-(3-methylphenylthio)sulfoximine (3ab)**





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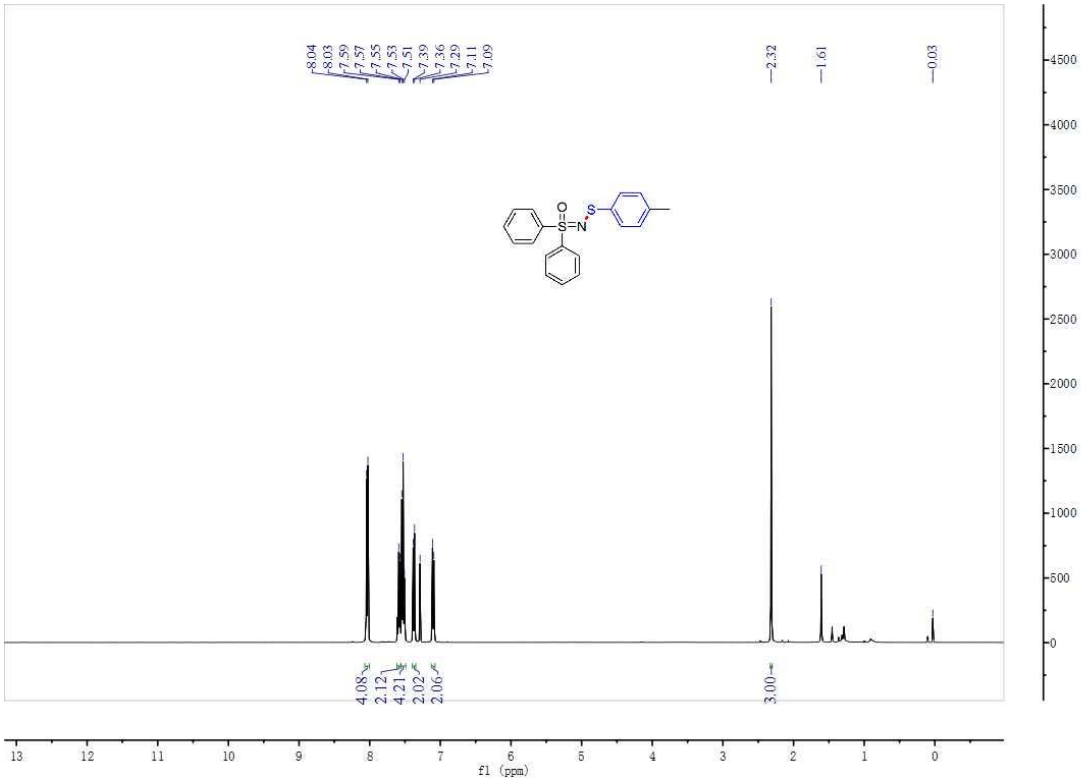
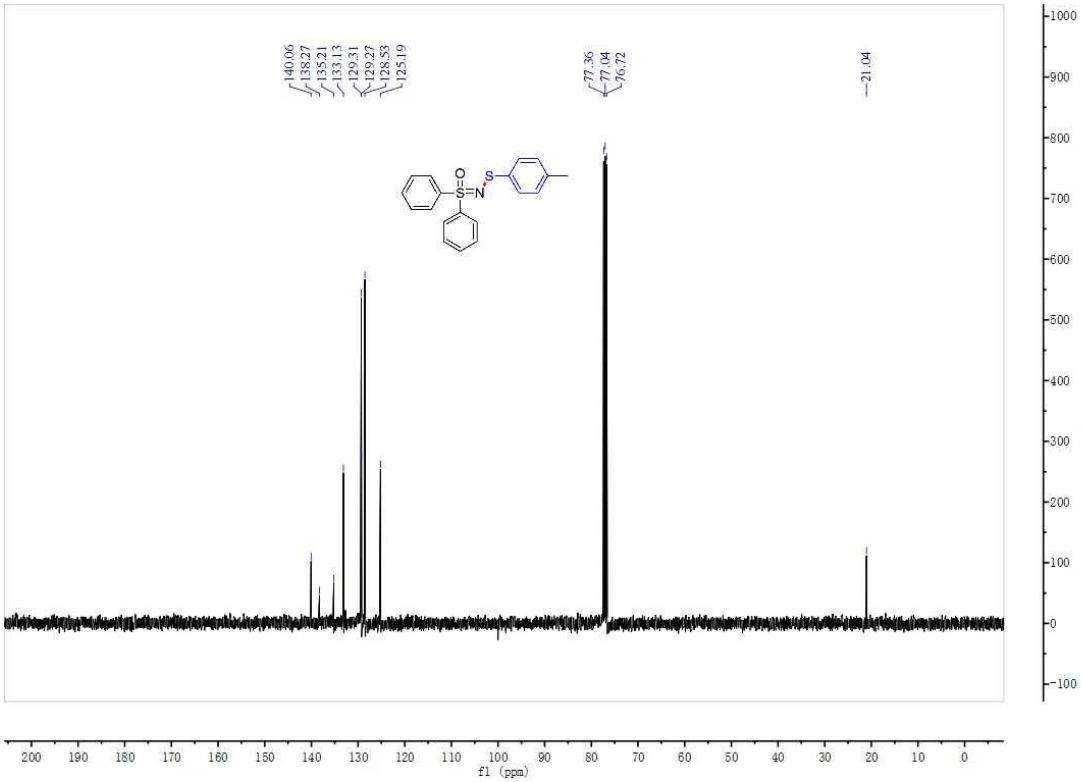
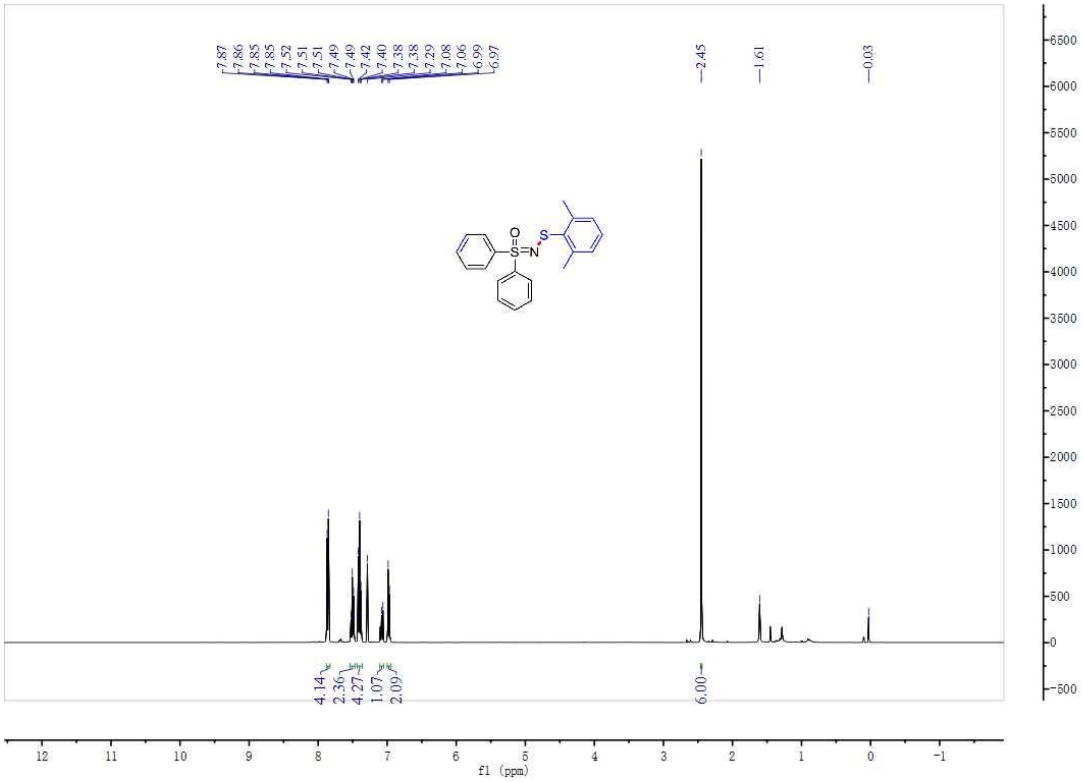
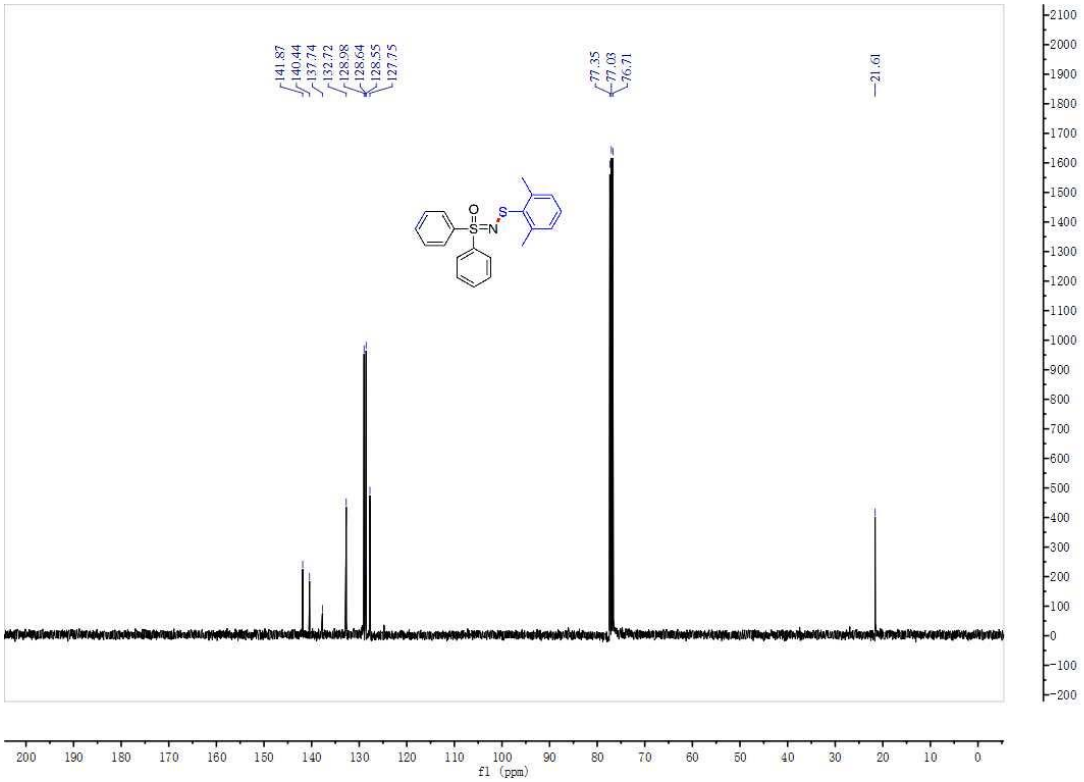


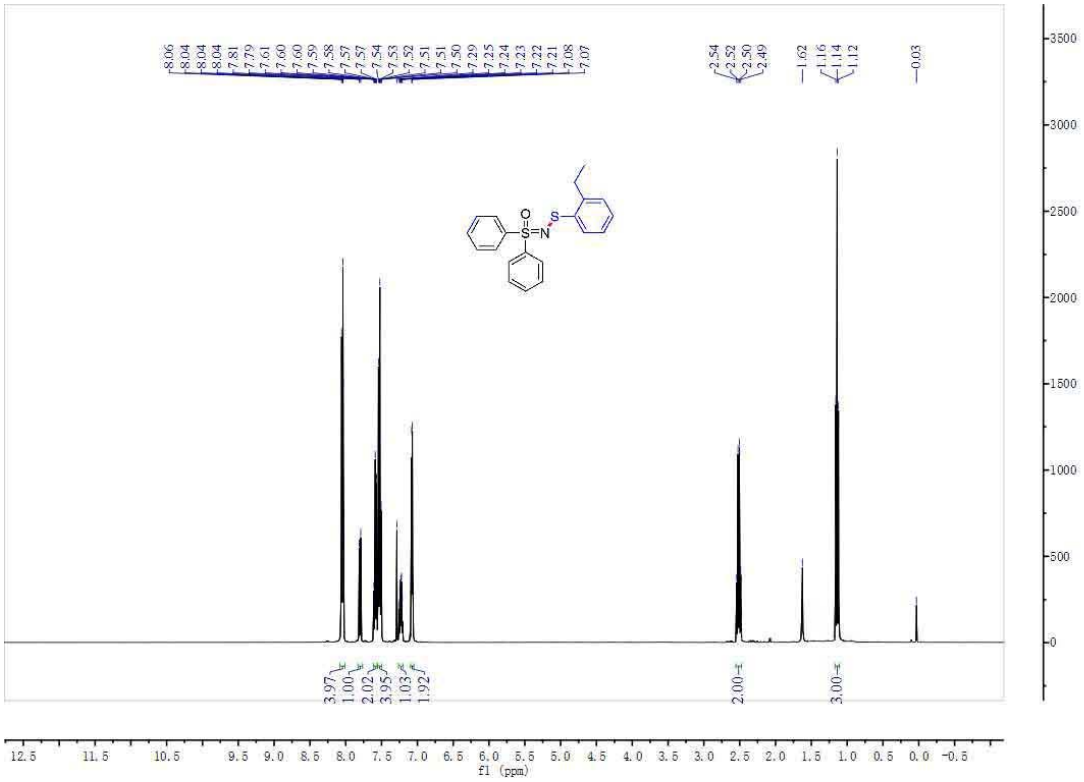


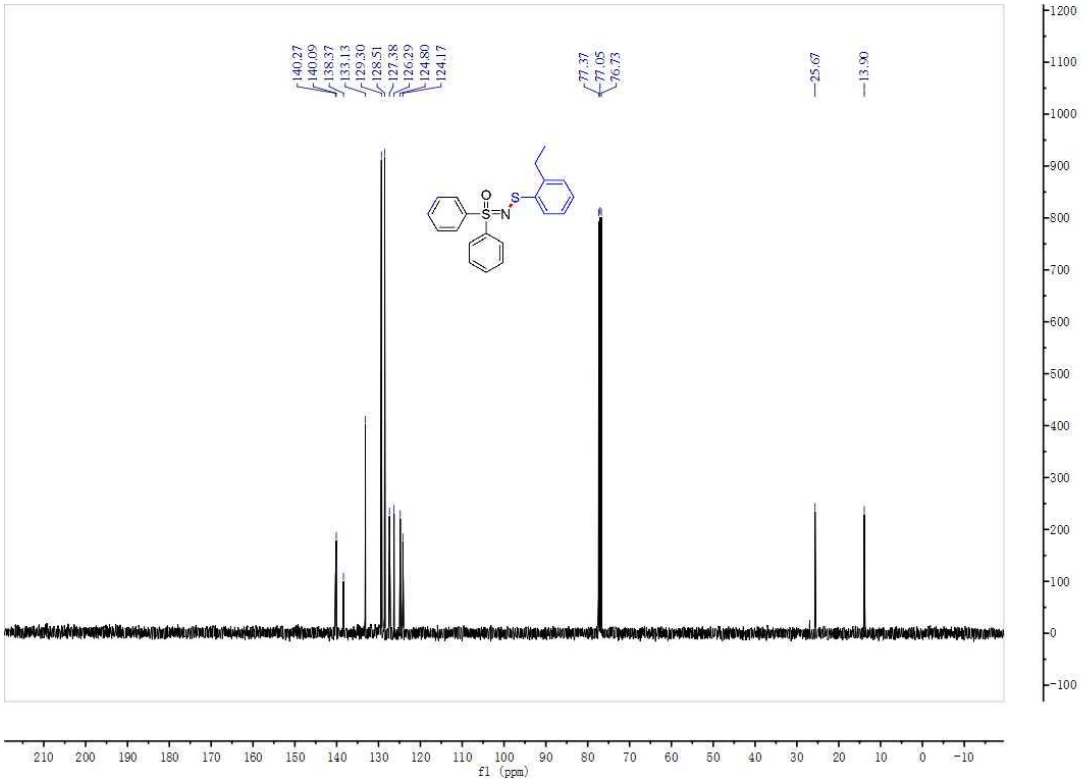
***S, S*-diphenyl-*N*-(2,6-dimethylphenylthio)sulf-oximine (3ad)**





***S, S*-diphenyl-*N*-(2-ethylphenylthio)sulfoximine (3ae)**





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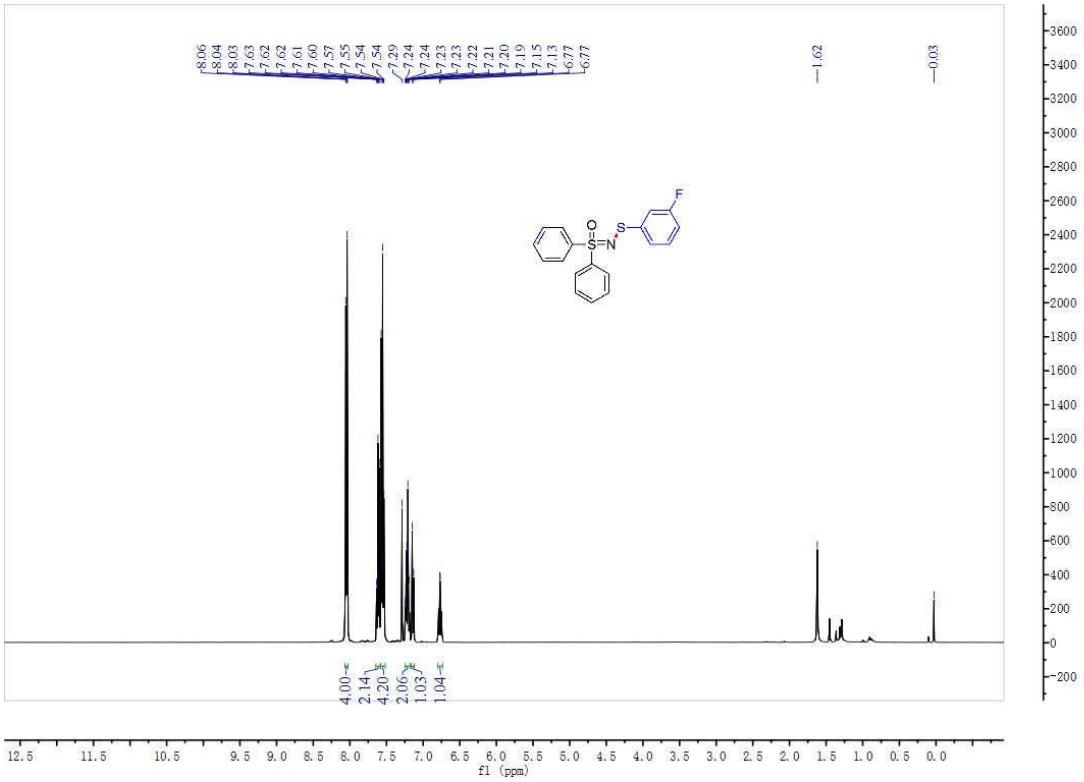
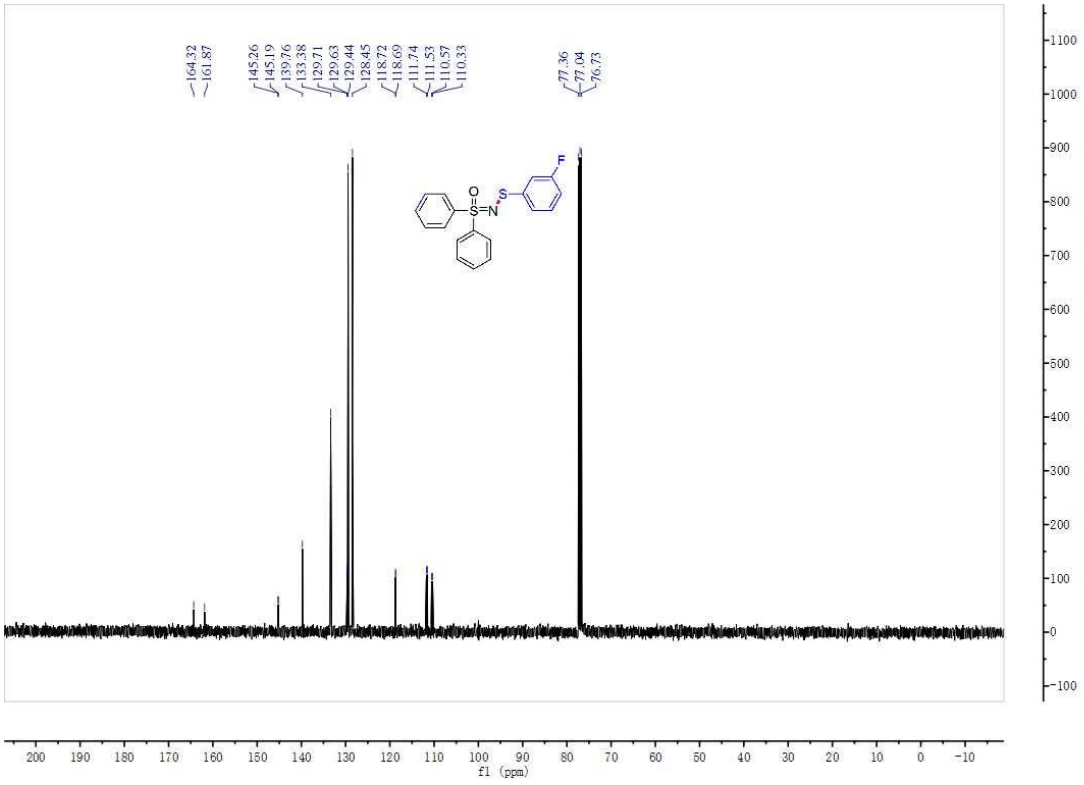
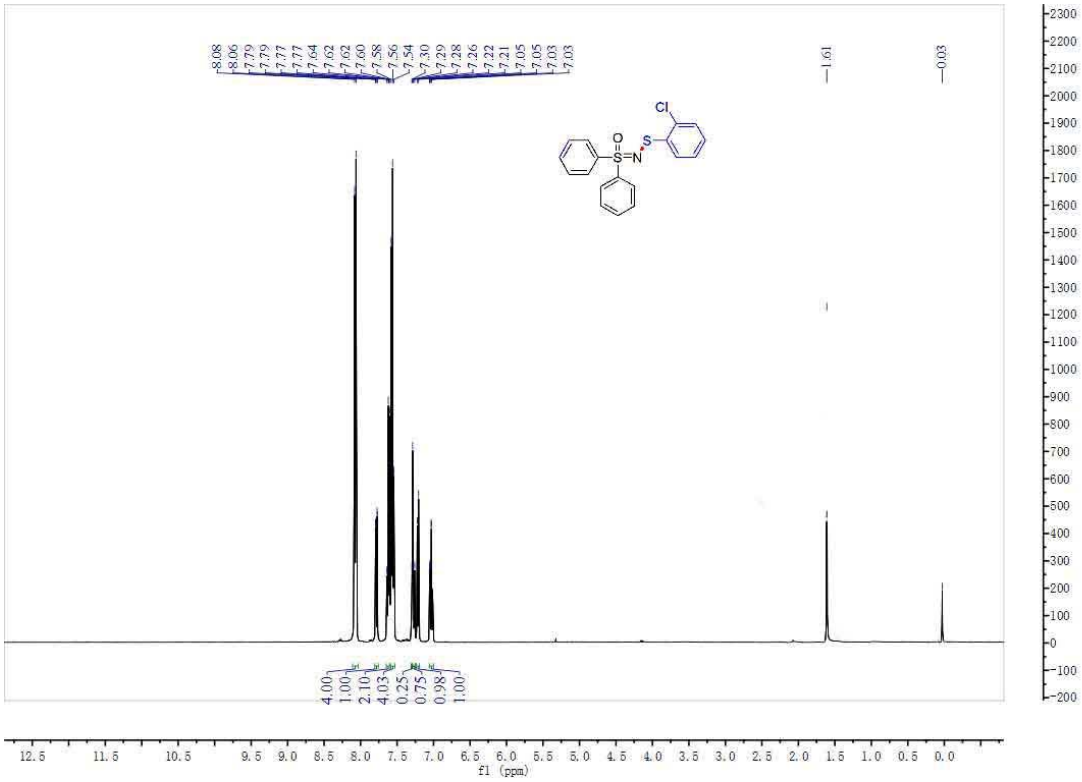
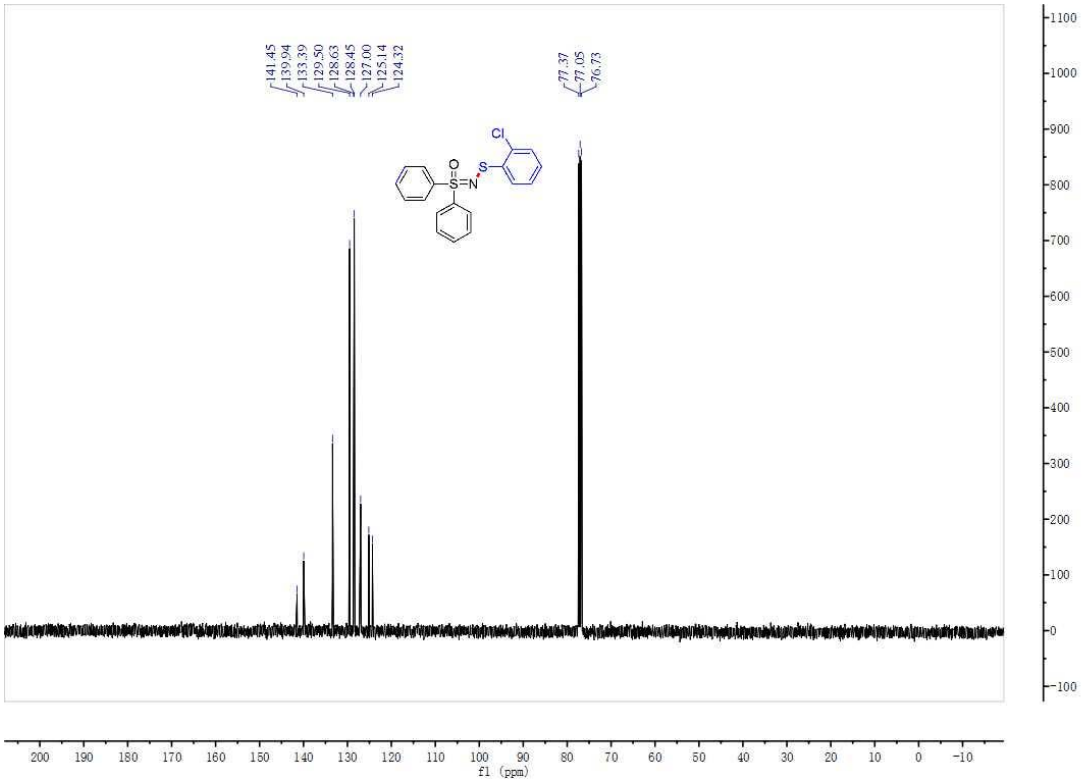




***S, S*-diphenyl-*N*-(2-chlorophenylthio)sulfoximine (3ag)**





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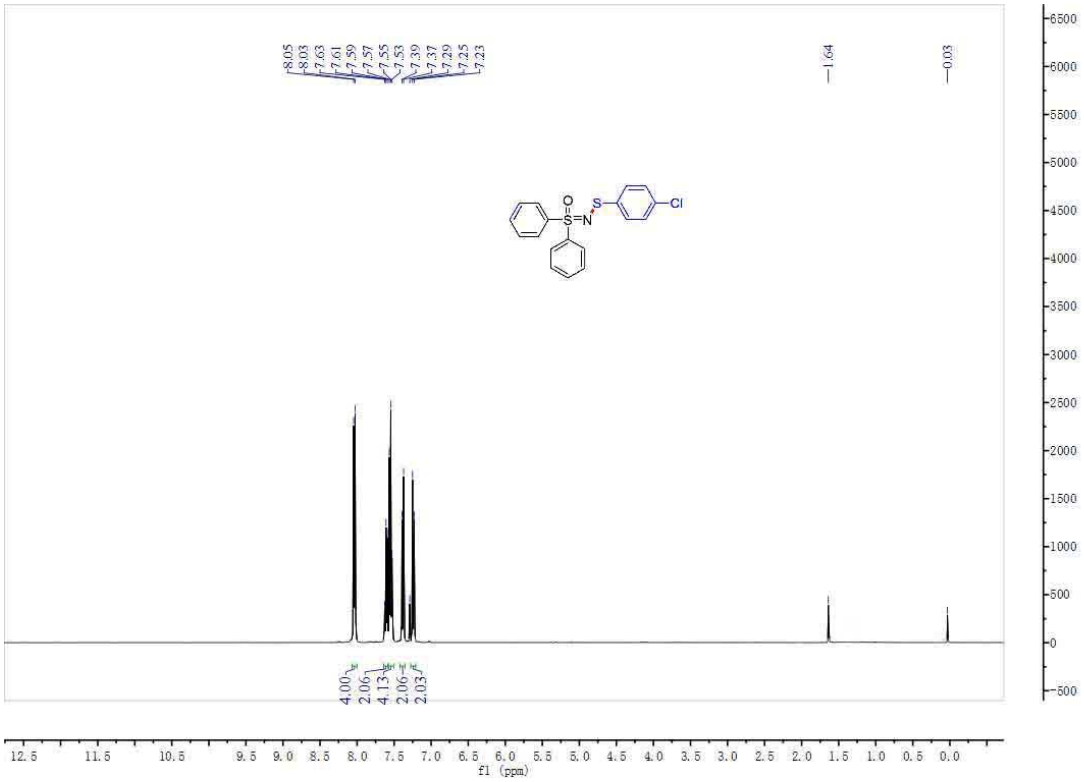

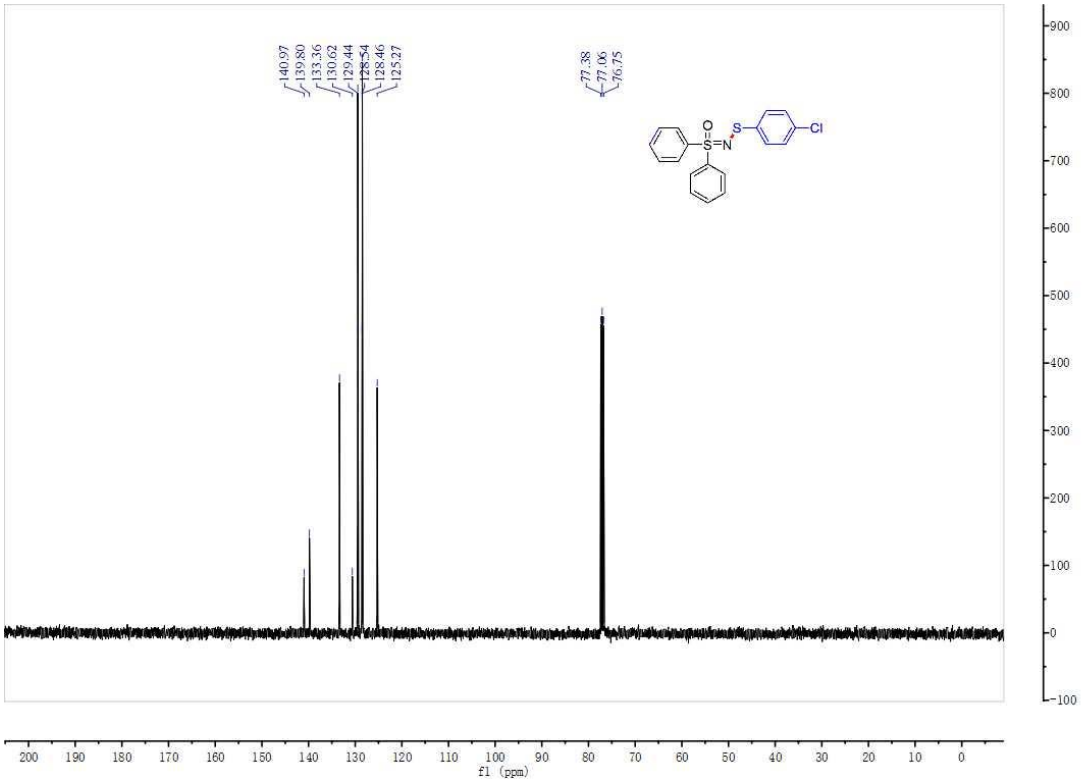

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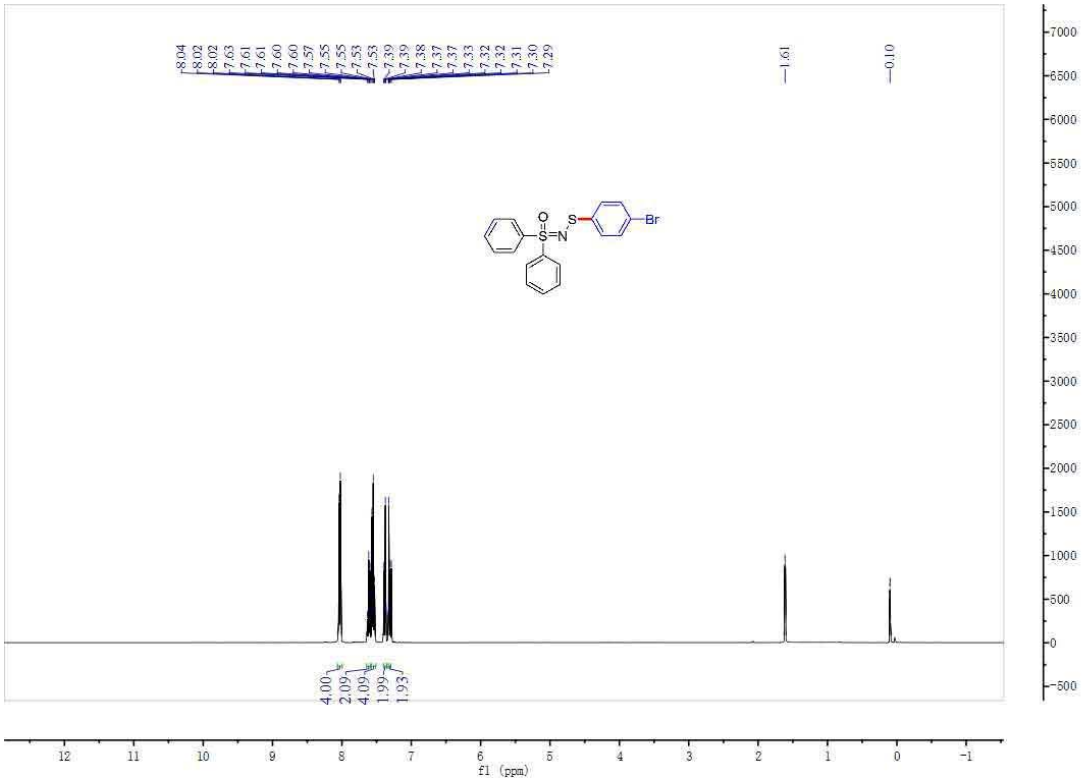
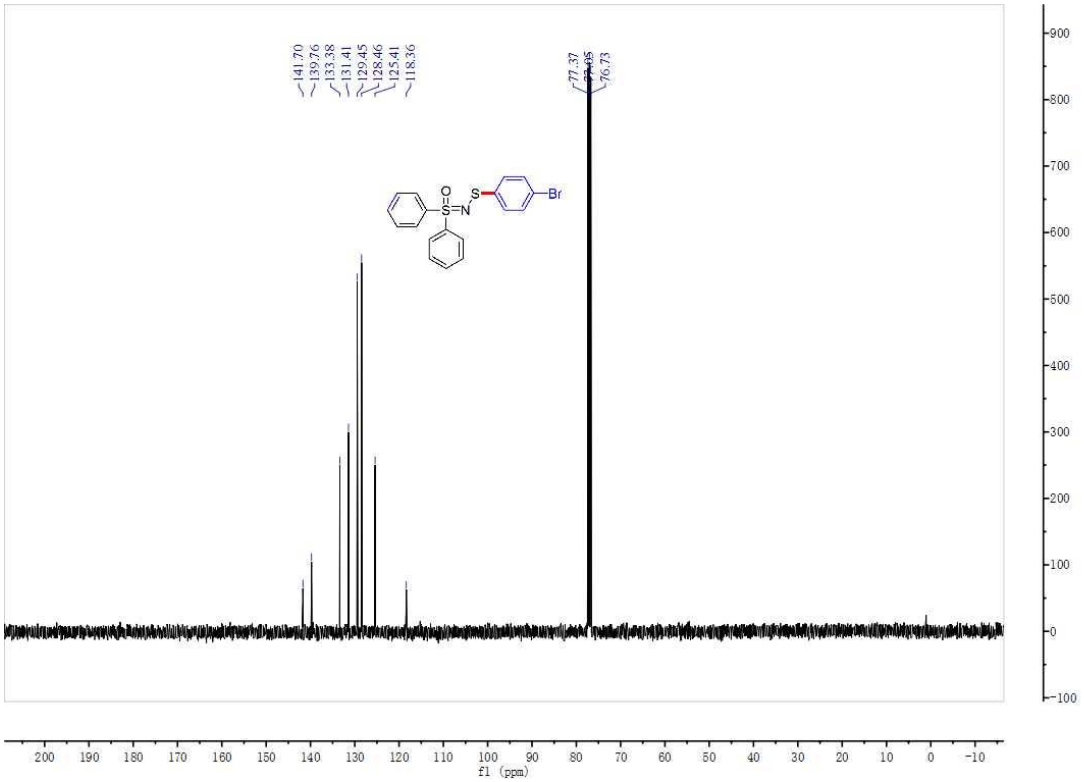
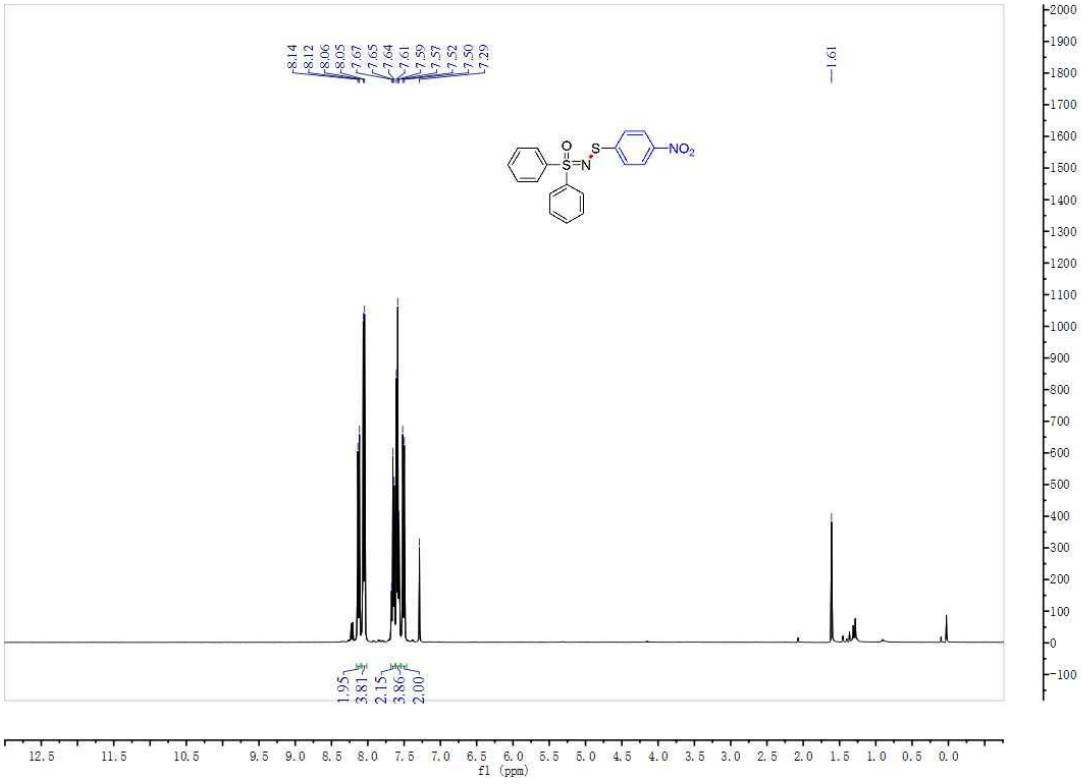
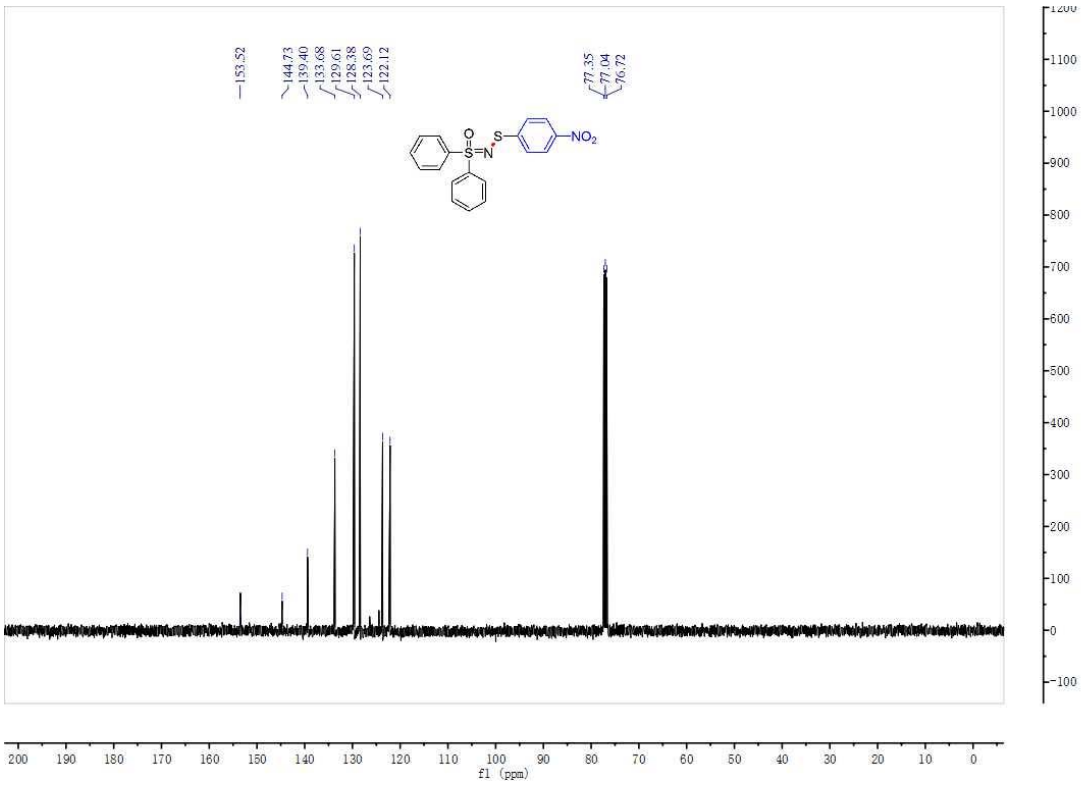


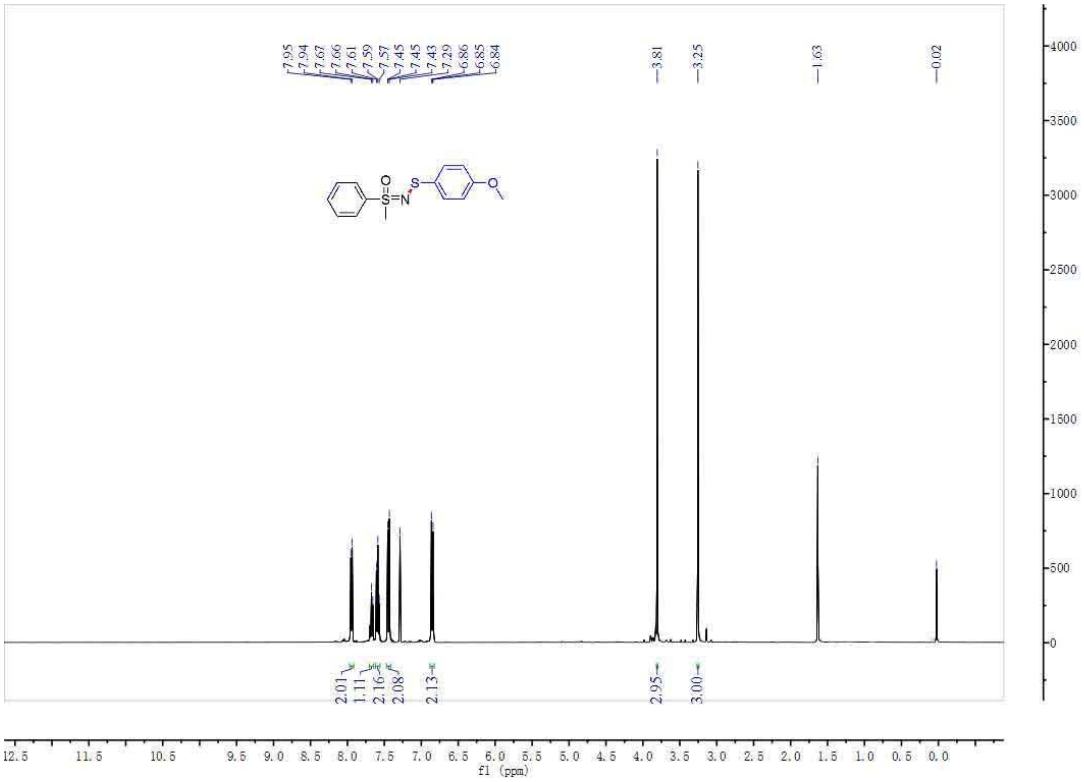


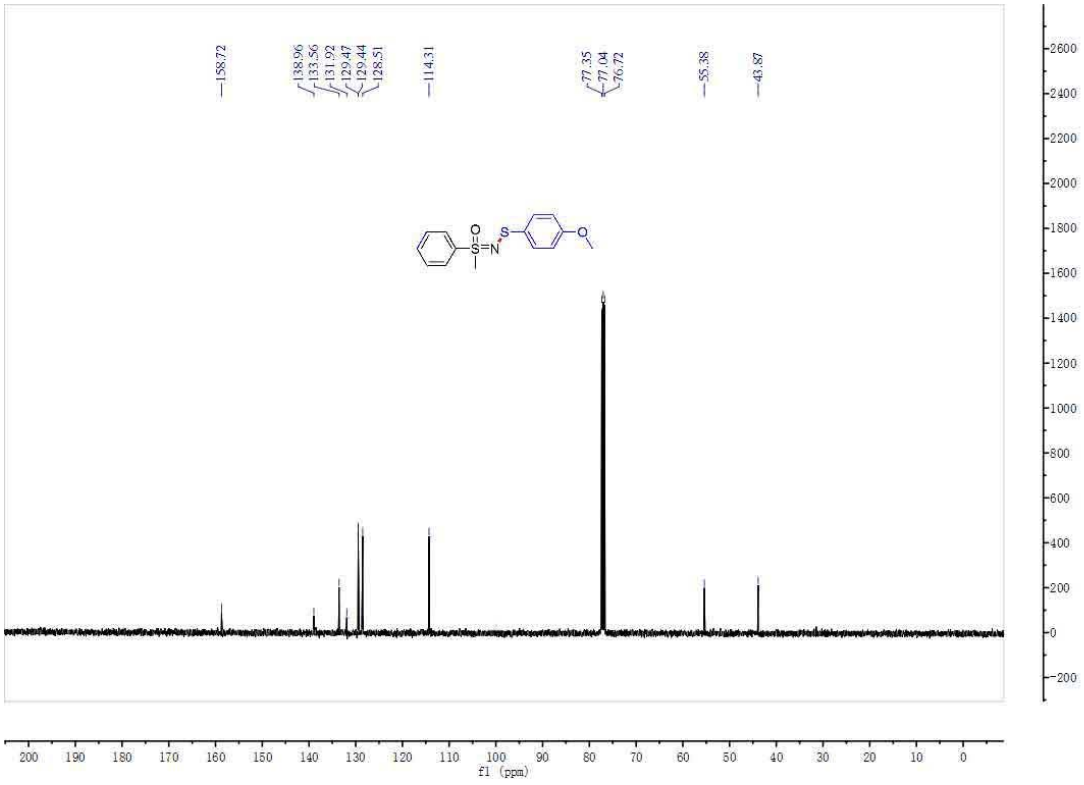
***S, S*-diphenyl-*N*-(4-nitrophenylthio)sulfoximine (3aj)**



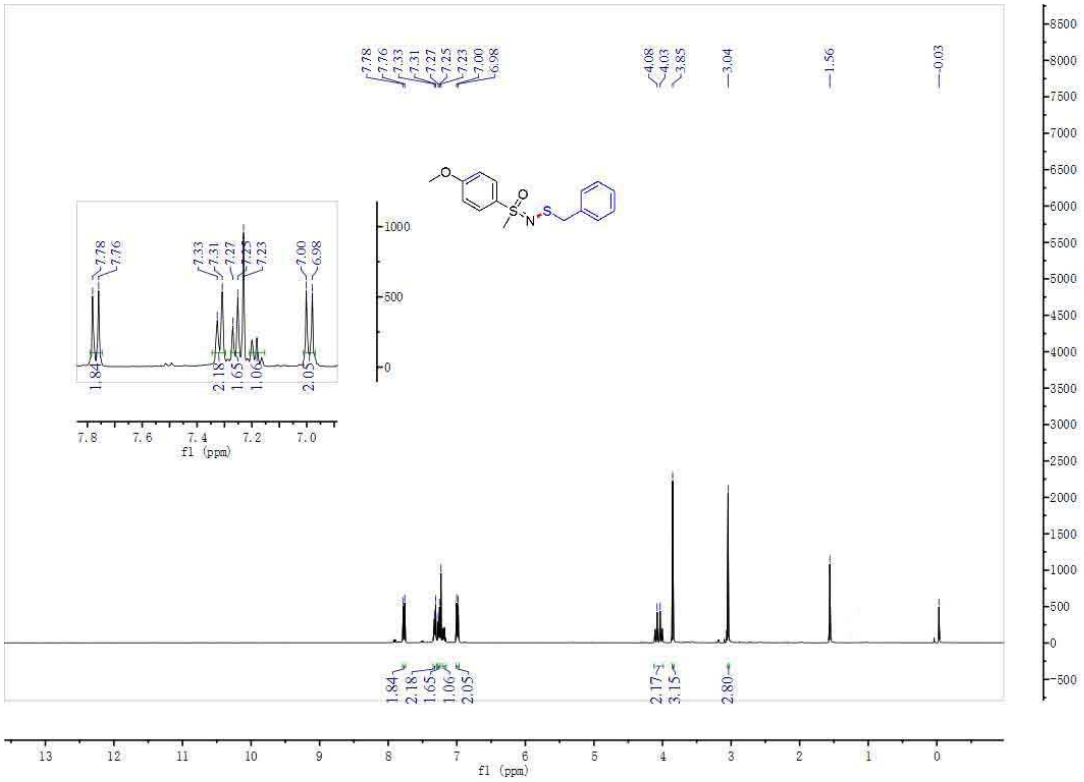


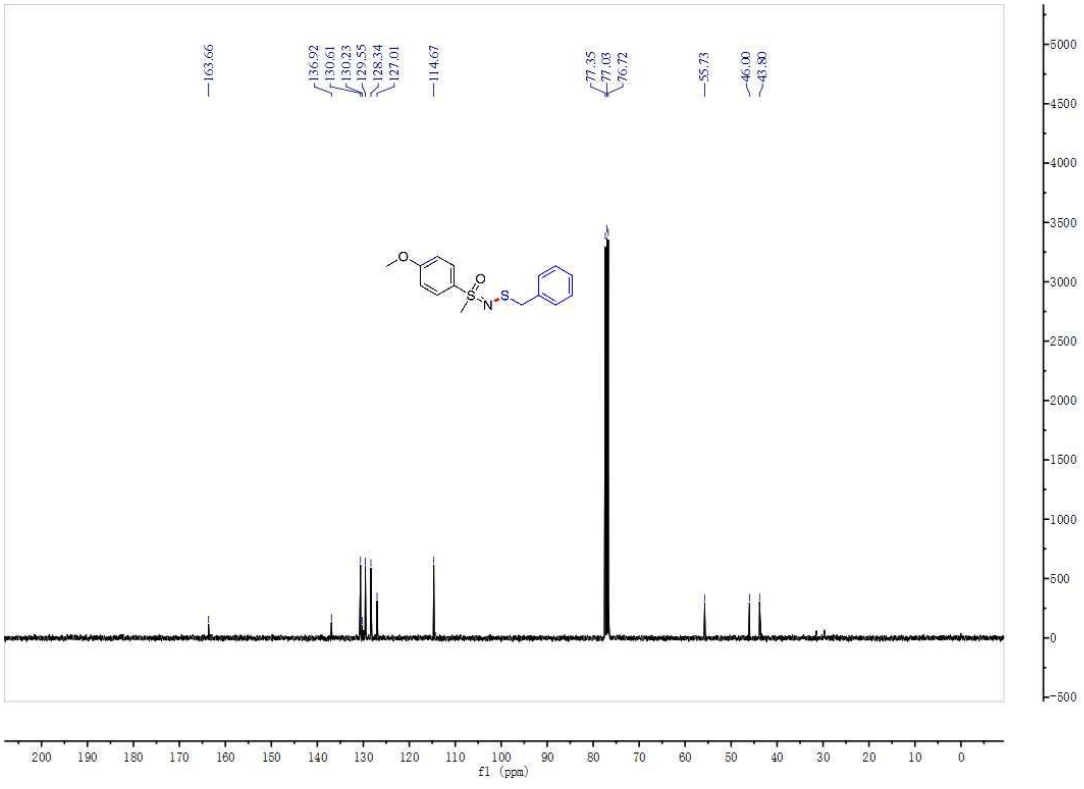
***S*-methyl-*S*-phenyl-*N*-(4-methoxyphenylthio)sulfoximine (3ak)**



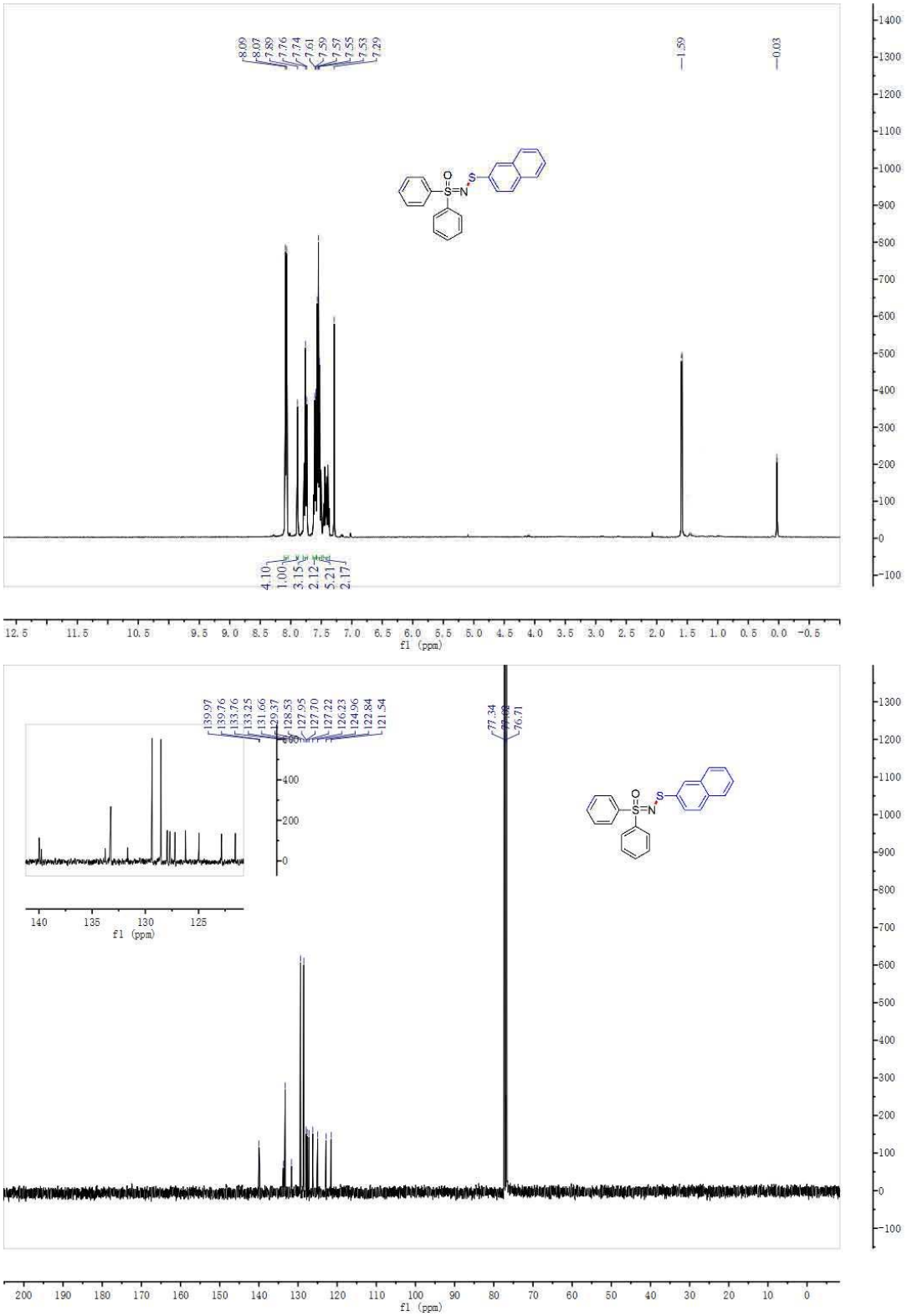


***S*-methyl-*S*-(4-methoxyphenyl)-*N*-benzylthio-sulfoximine (3al)**

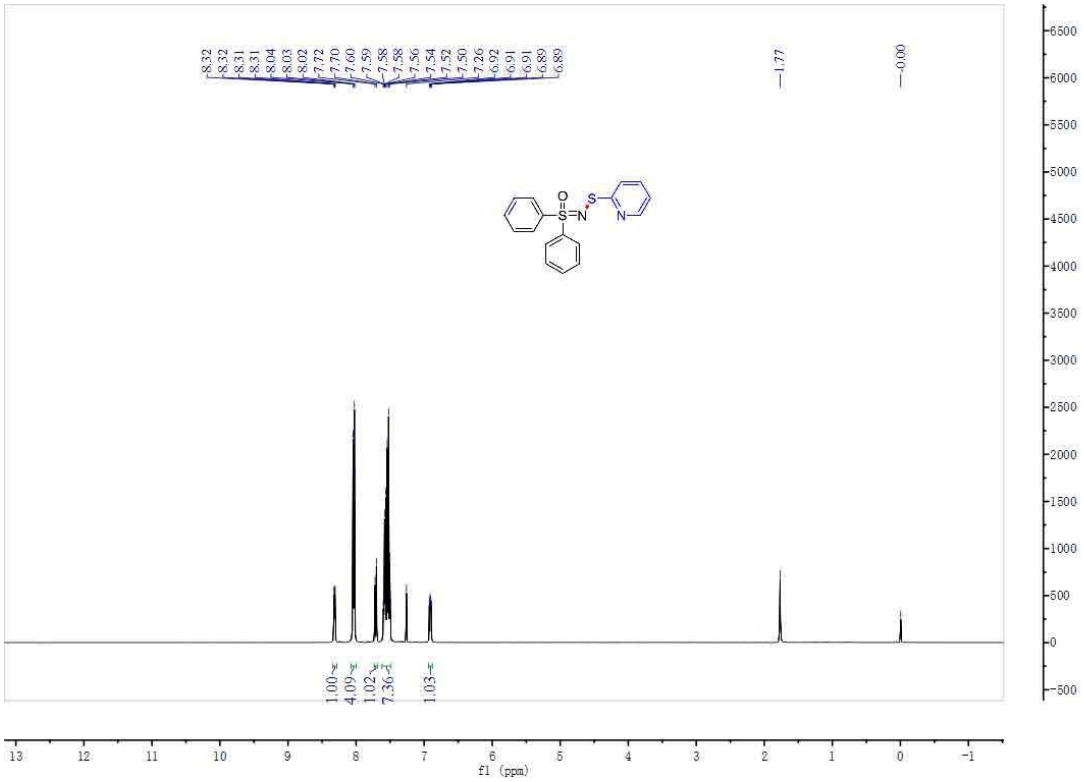


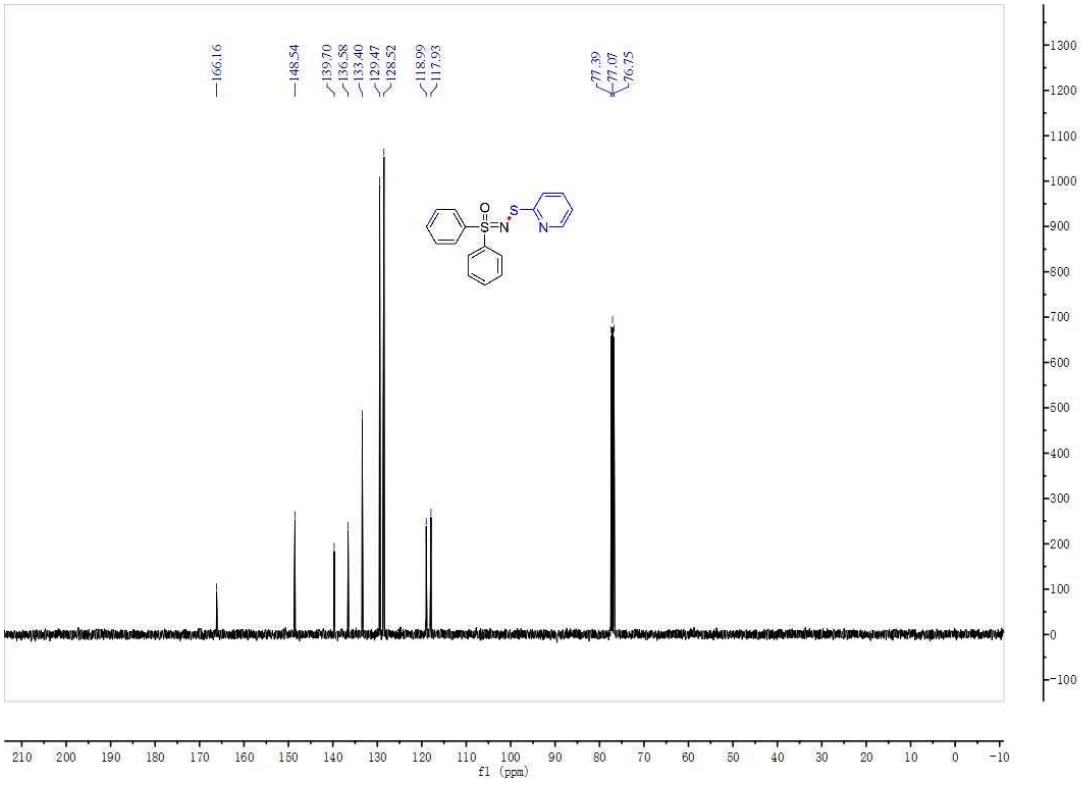


***S, S*-diphenyl-*N*-(naphthalene-1-thio)sulfoximine (3am)**

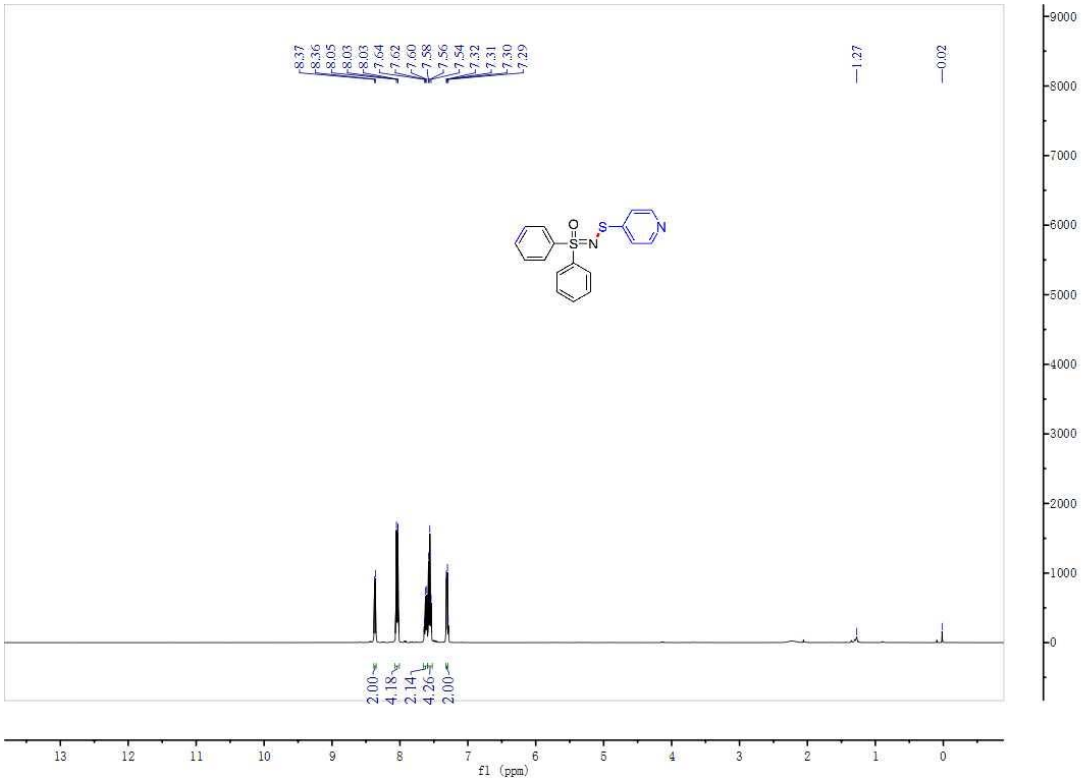


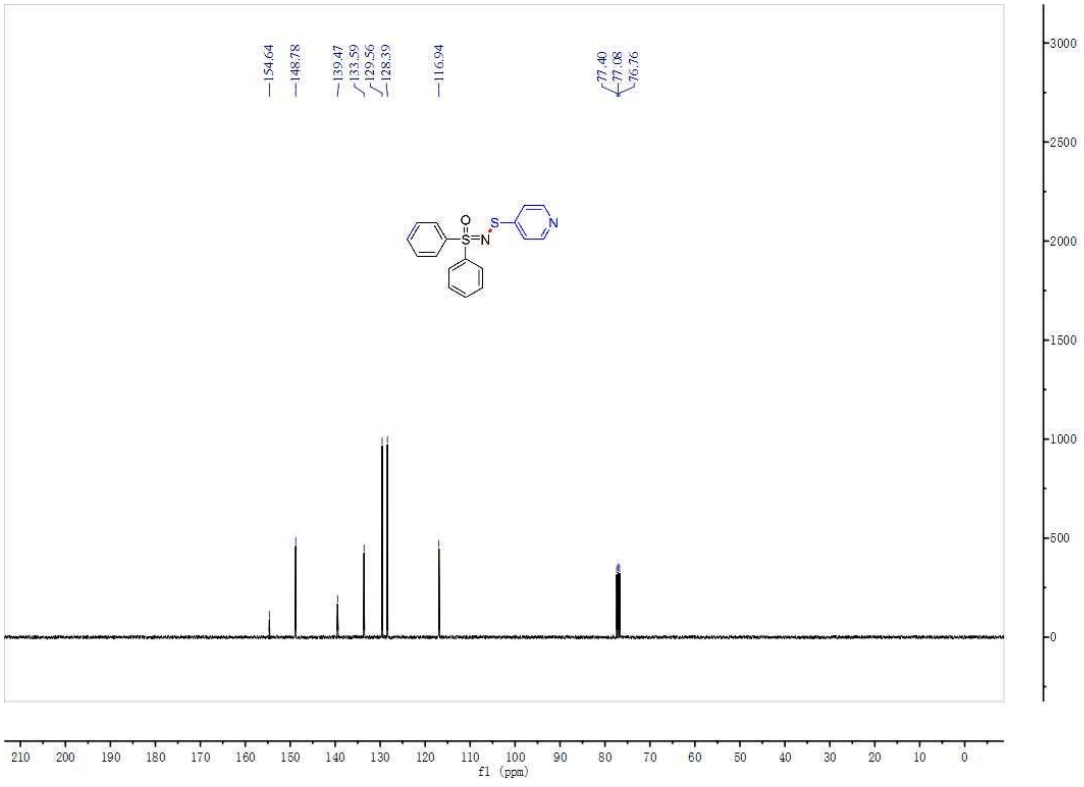
***S, S*-diphenyl-*N*-(2-pyridinethio)sulfoximine (3an)**



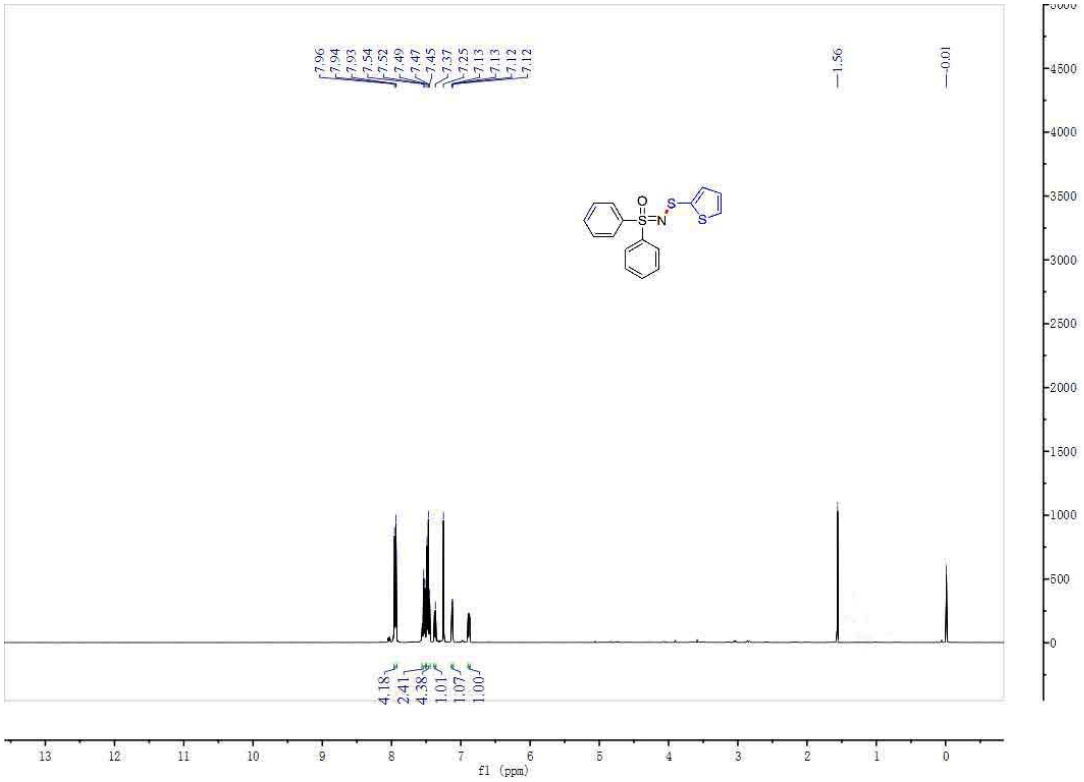


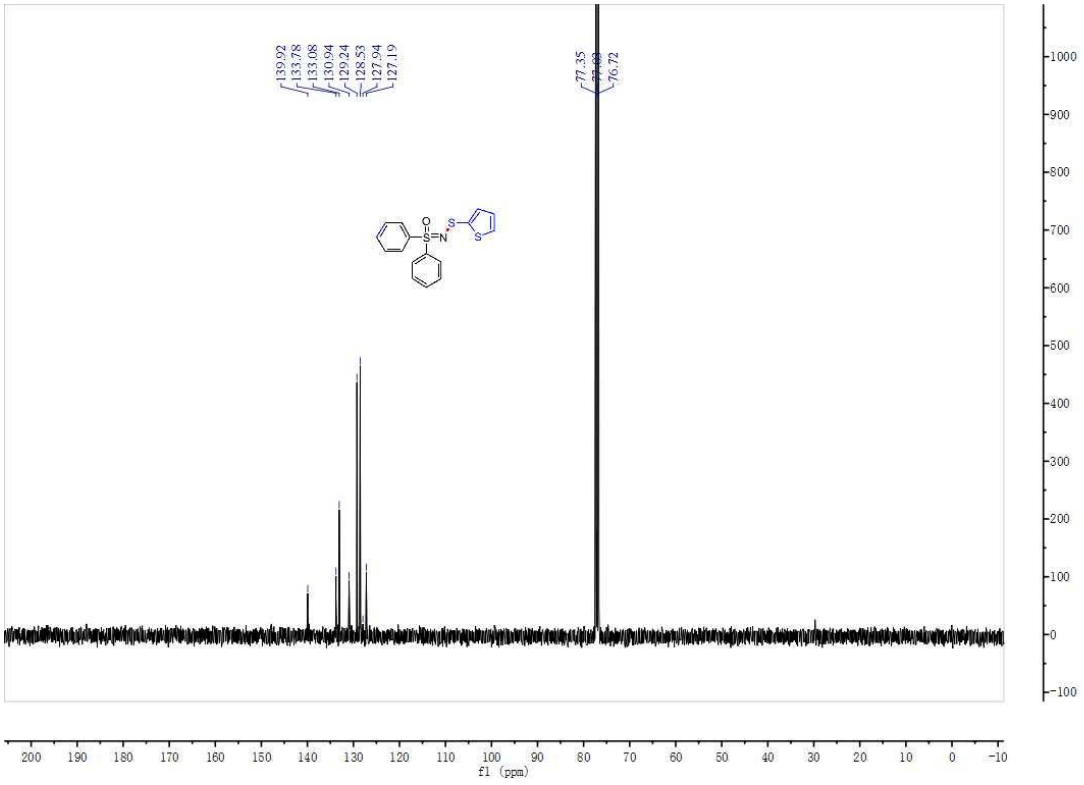
***S, S*-diphenyl-*N*-(4-pyridinethio)sulfoximine (3ao)**



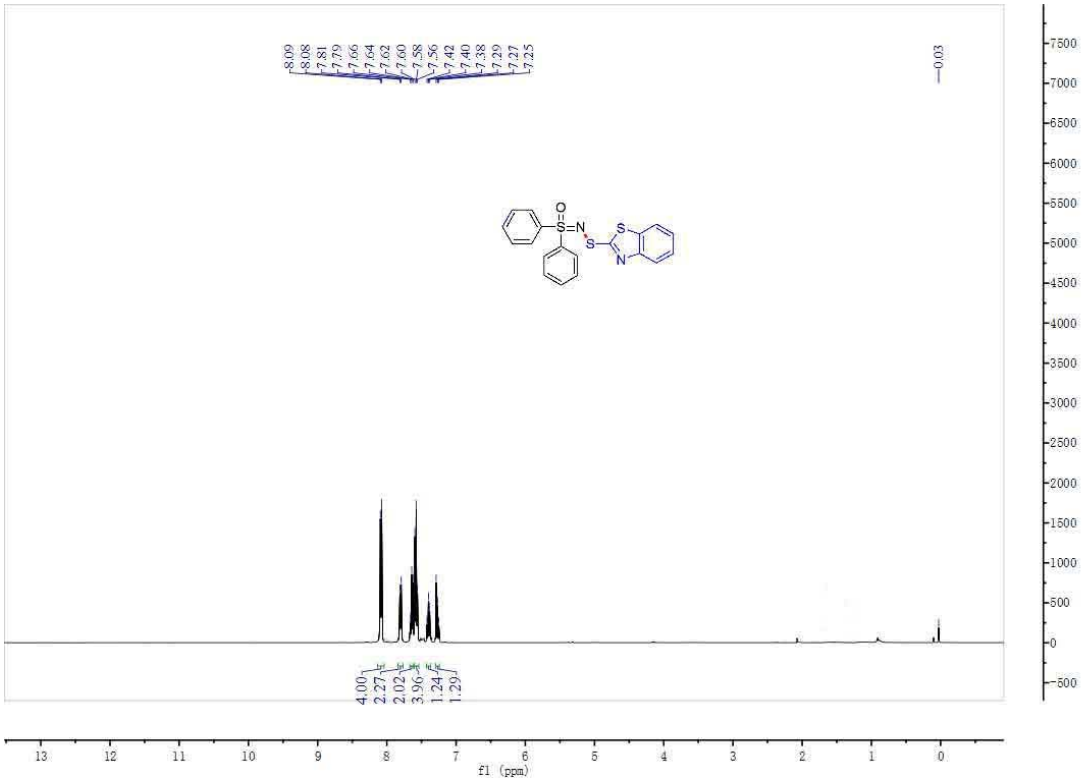


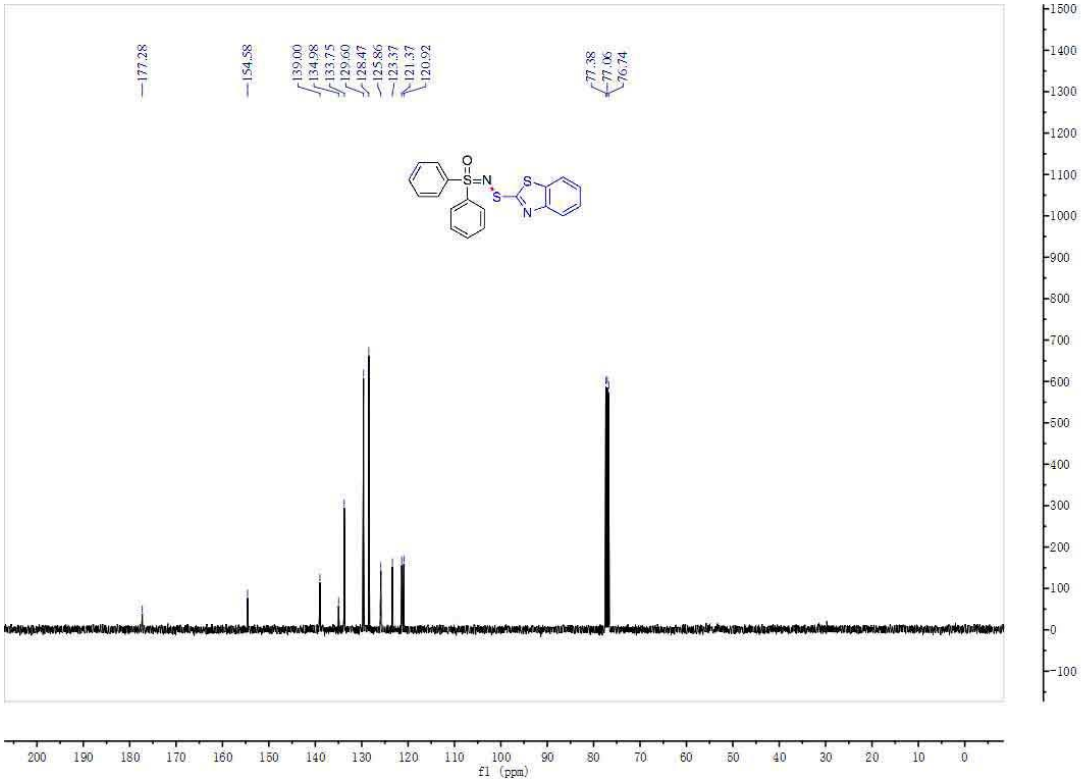
***S, S*-diphenyl-*N*-(2-thiophenethio)sulfoximine (3ap)**



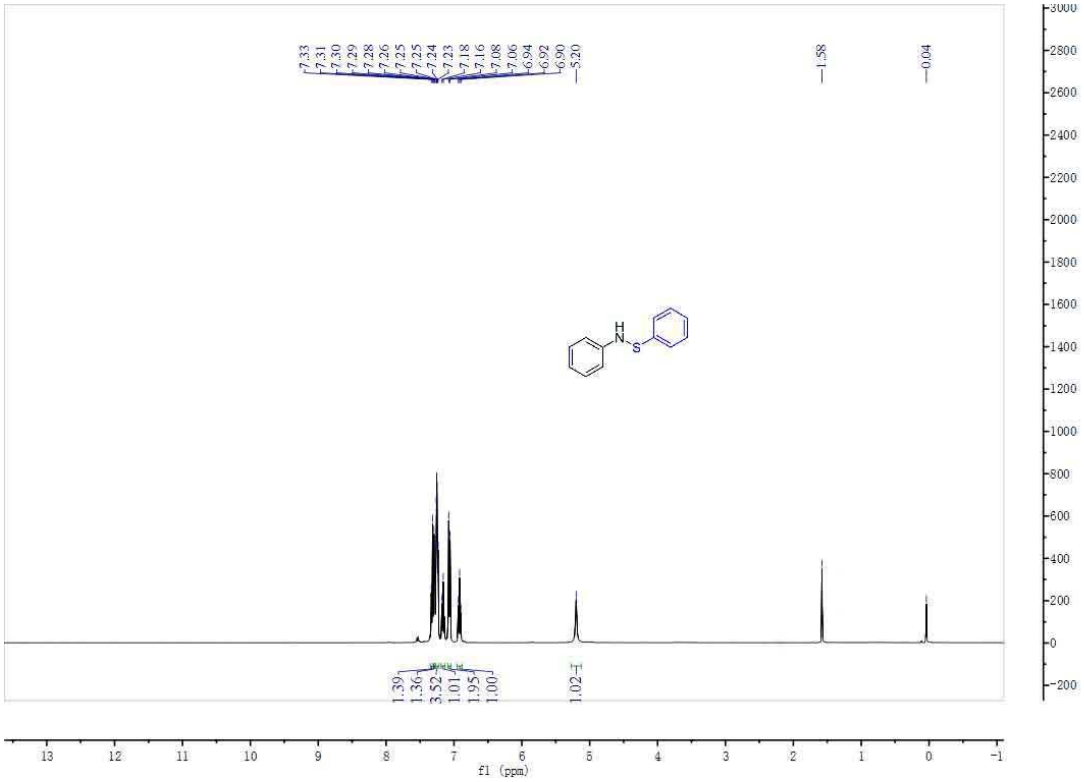


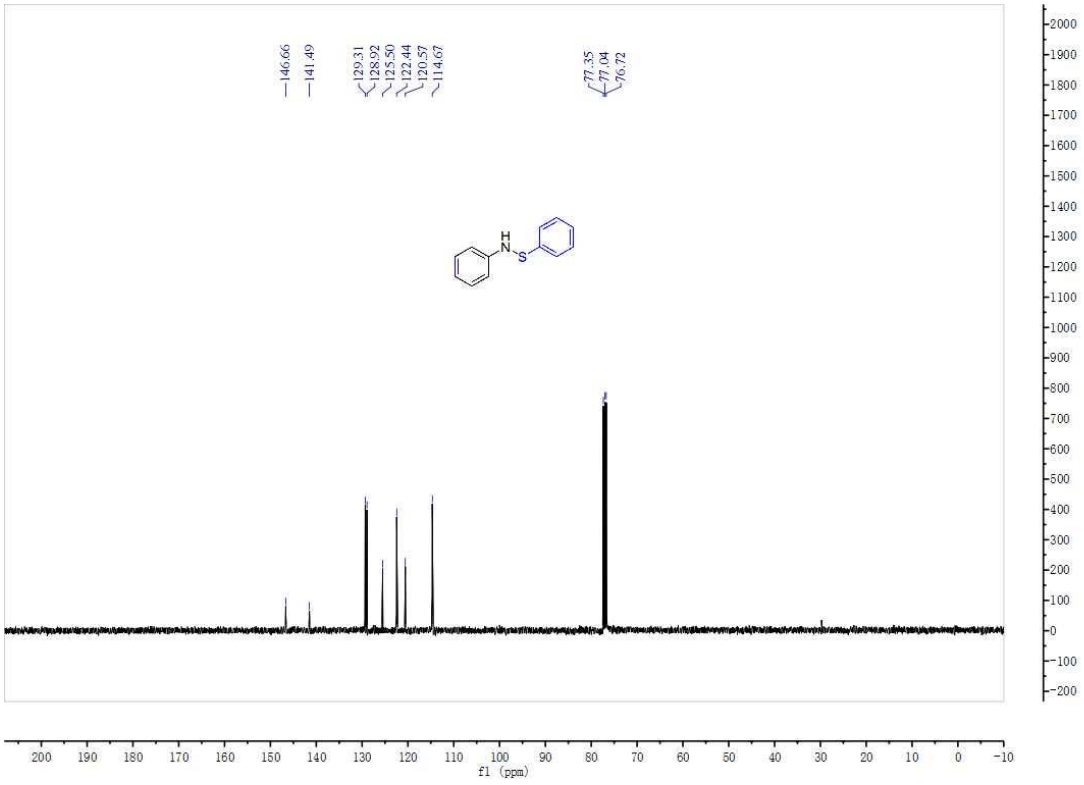
***S,S*-diphenyl-*N*-(2-benzothiazolethio)sulfoximine (3aq)**



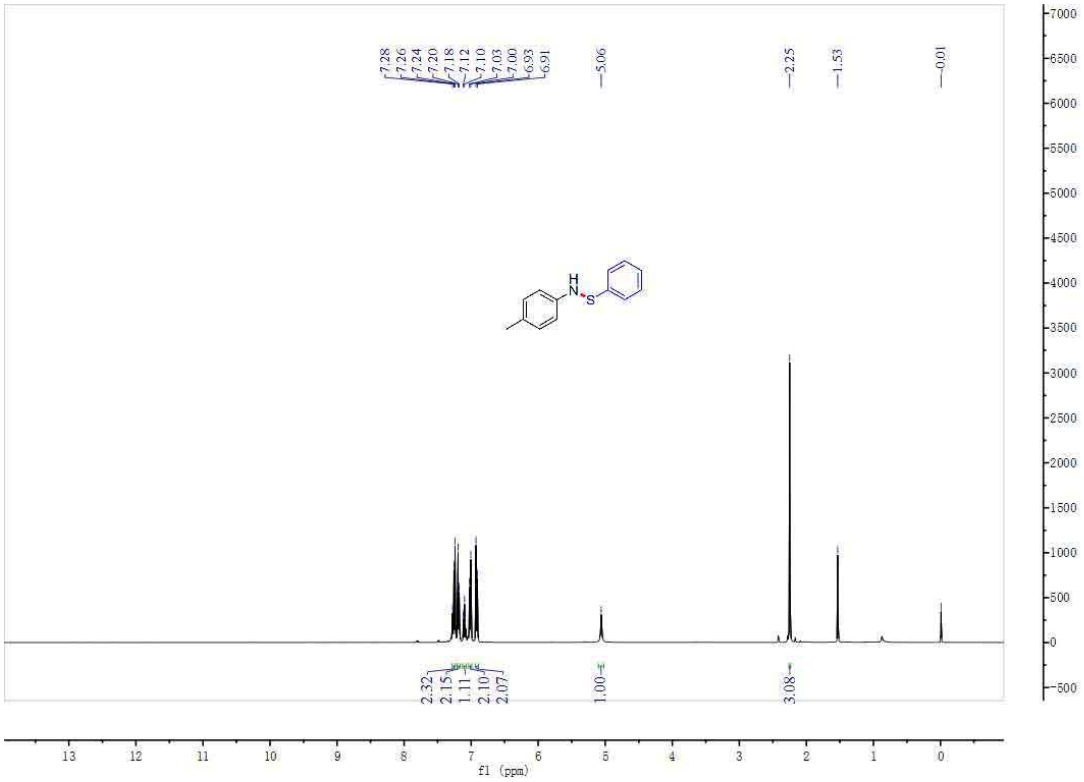


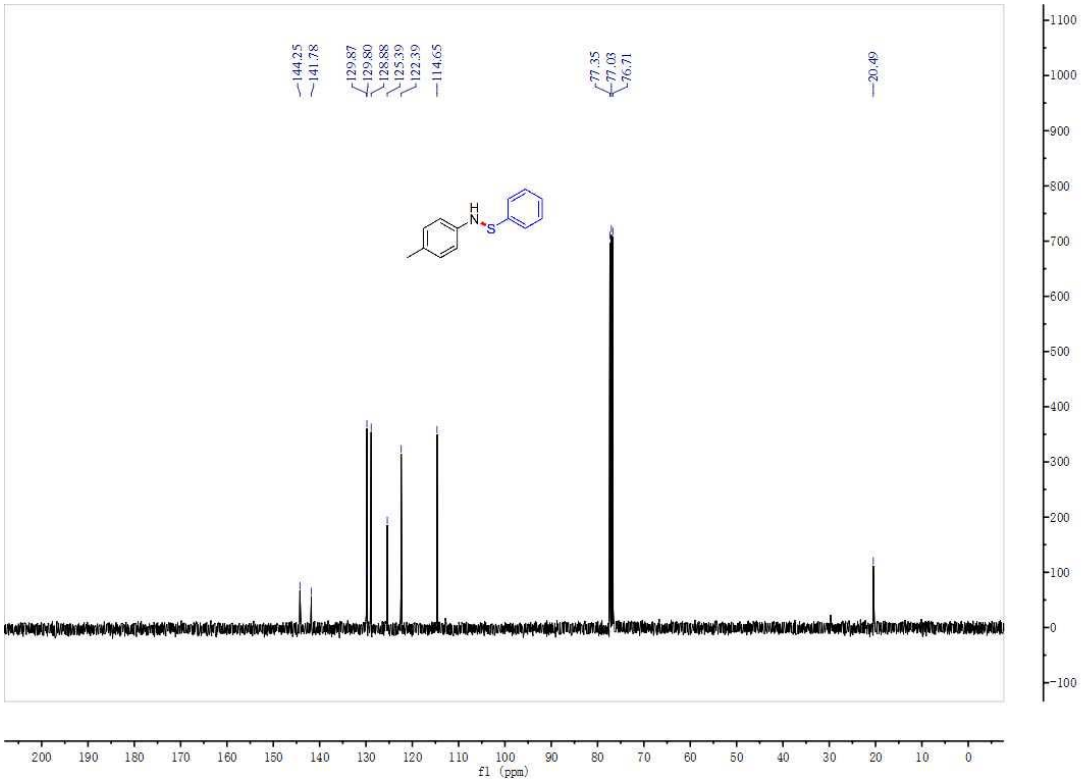
***N*-(phenylthio)benzenamine (5aa)**



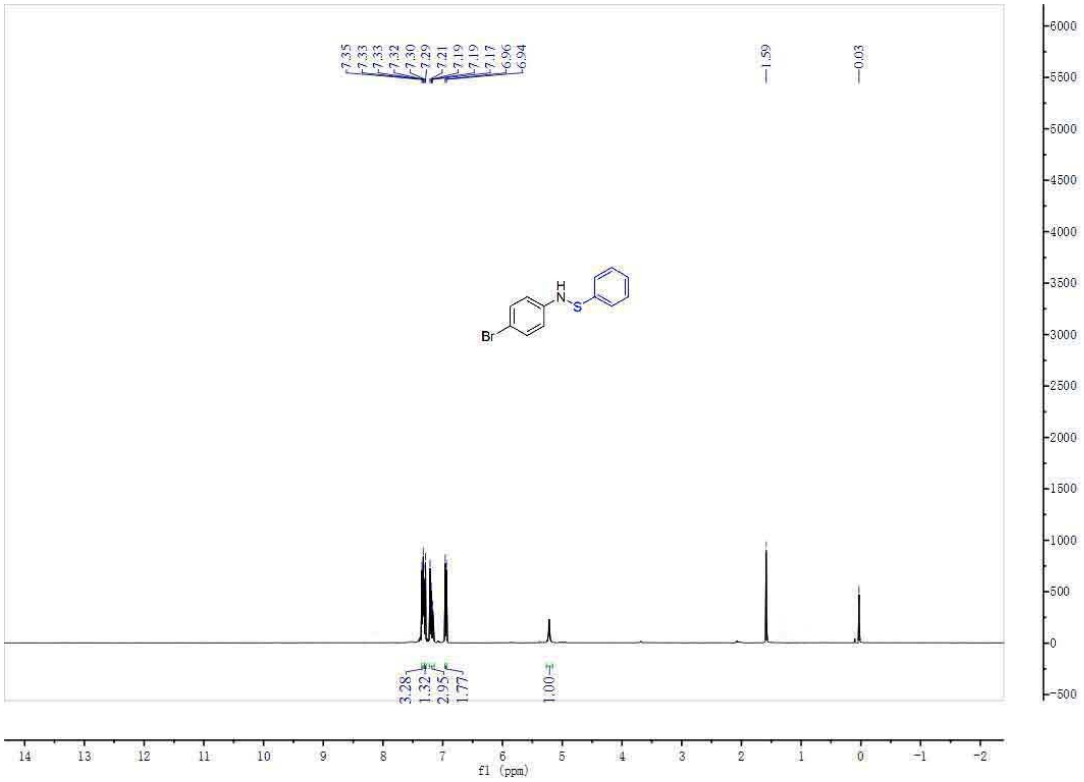


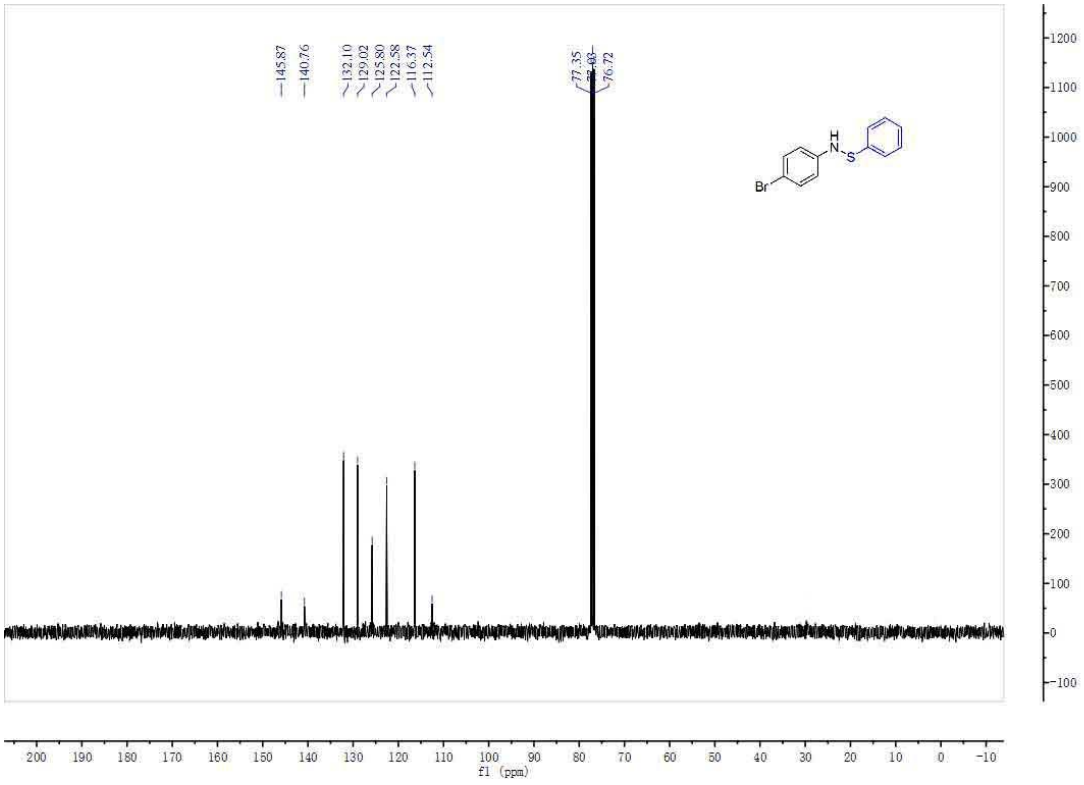
4-methyl-*N*-(phenylthio)benzenamine (5ab)



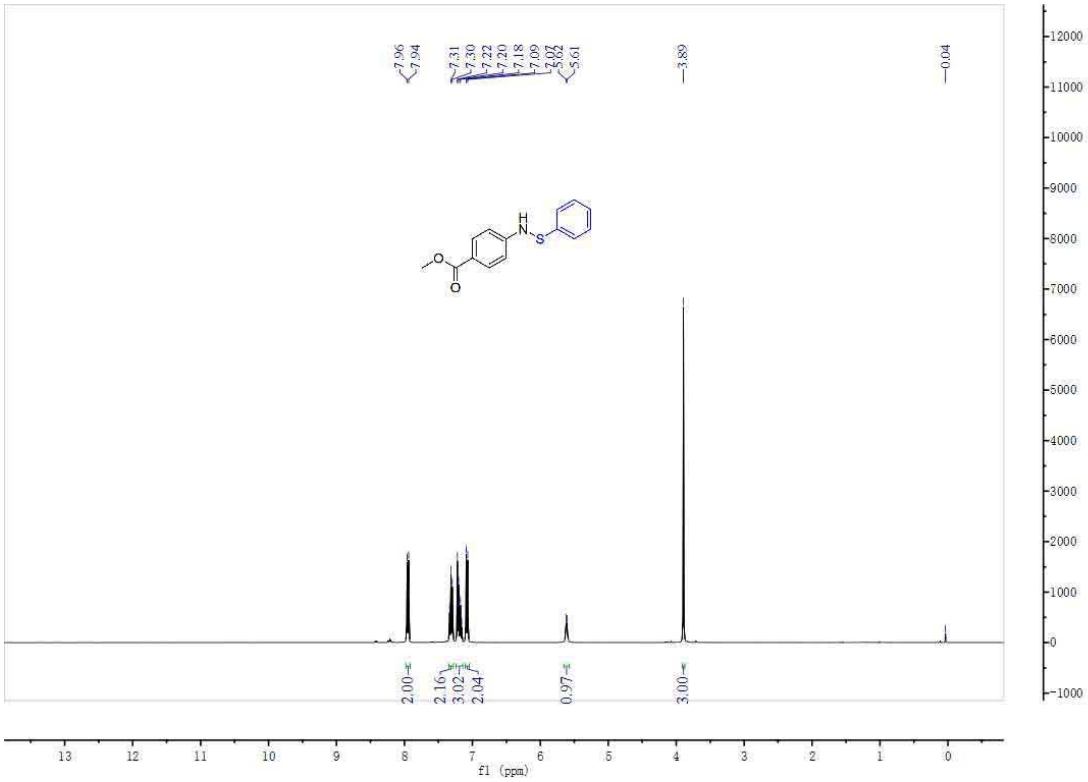


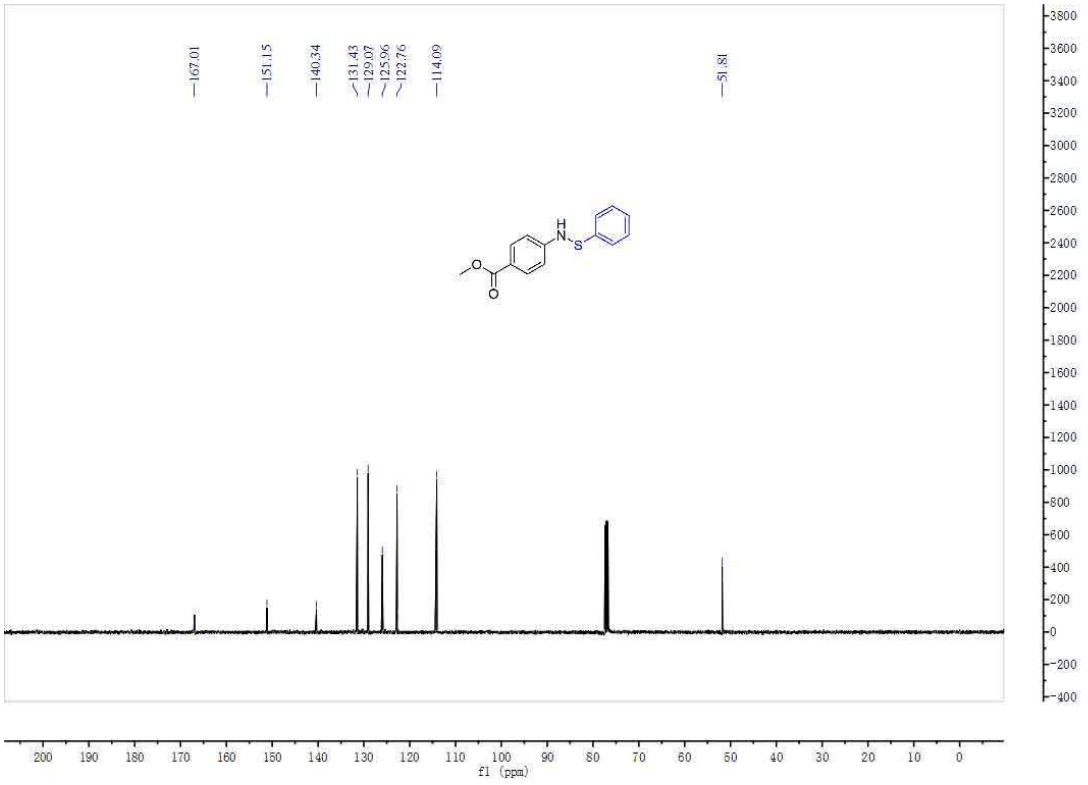
4-bromo-*N*-(phenylthio)benzenamine (5ac)



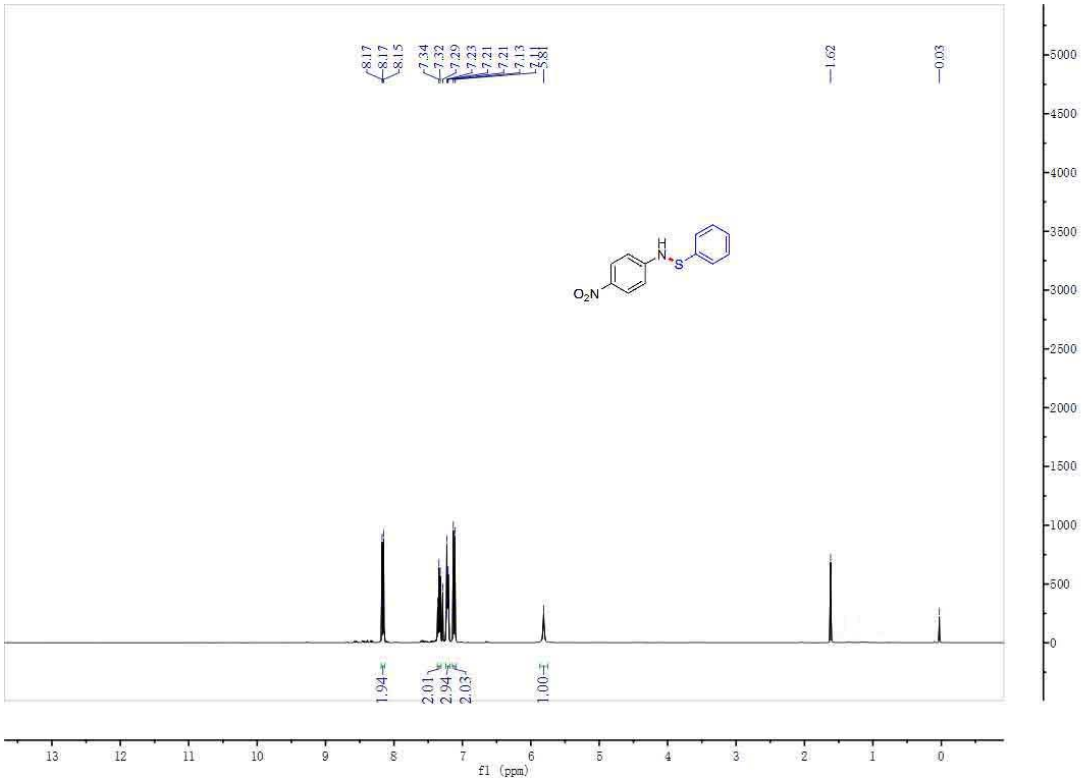


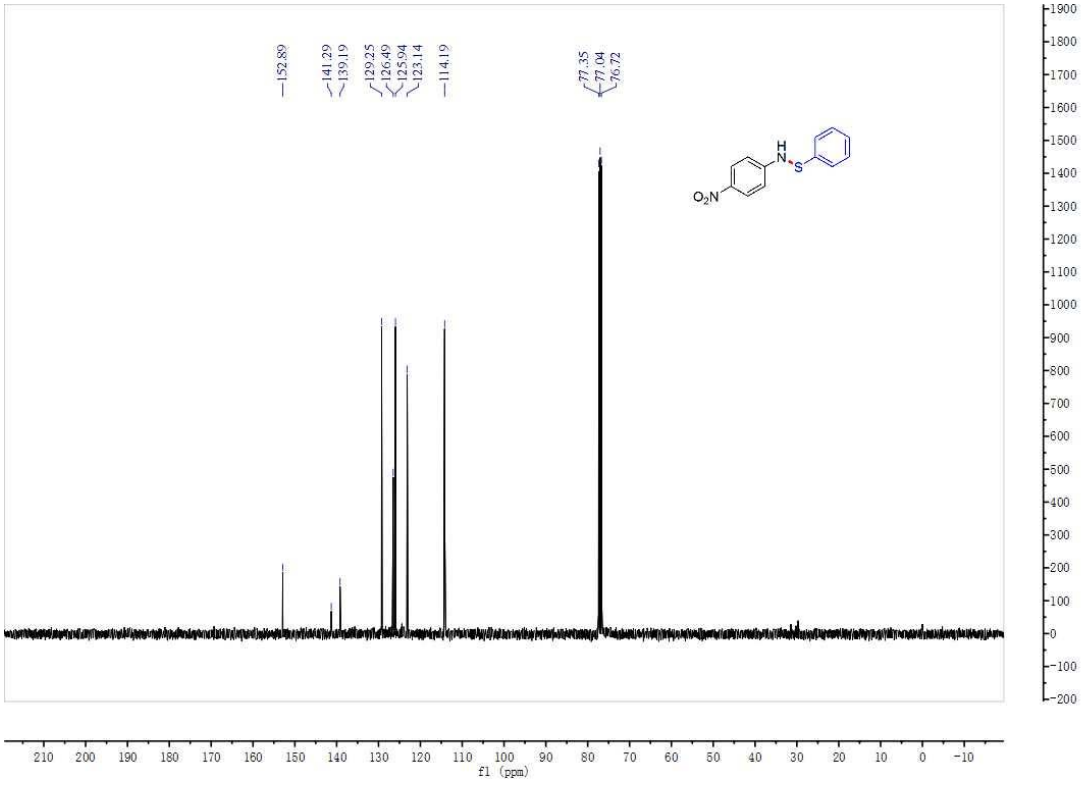
methyl 4-(phenylthioamino)benzoate (5ad)



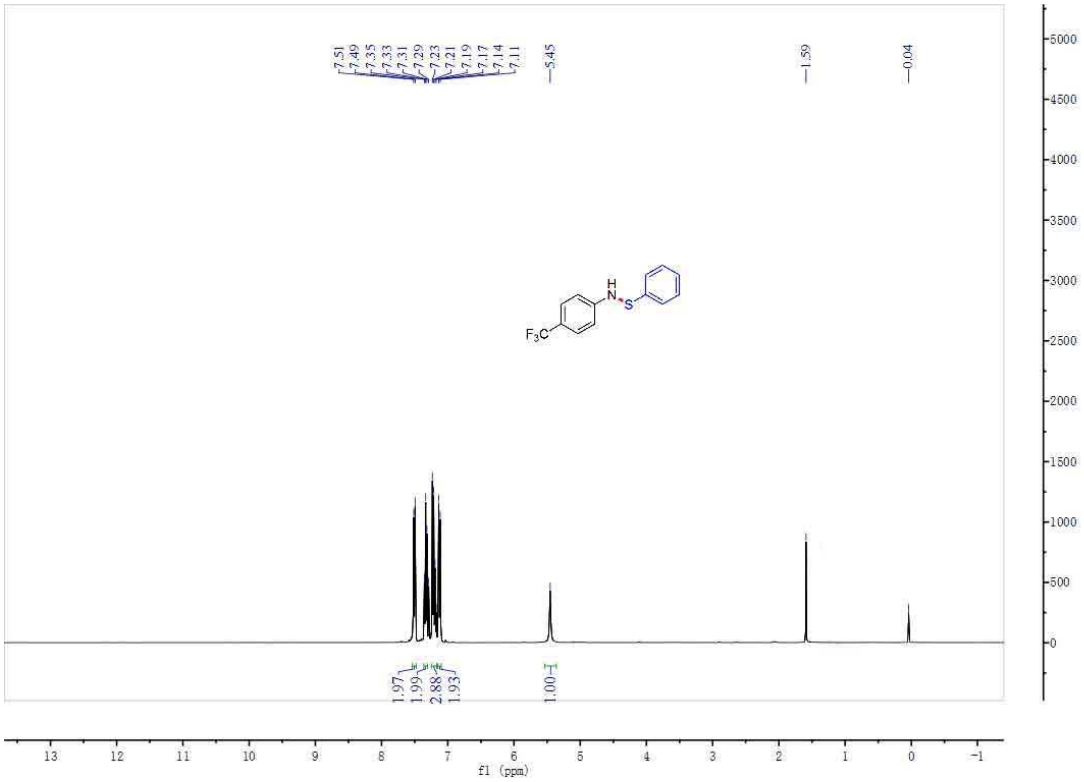


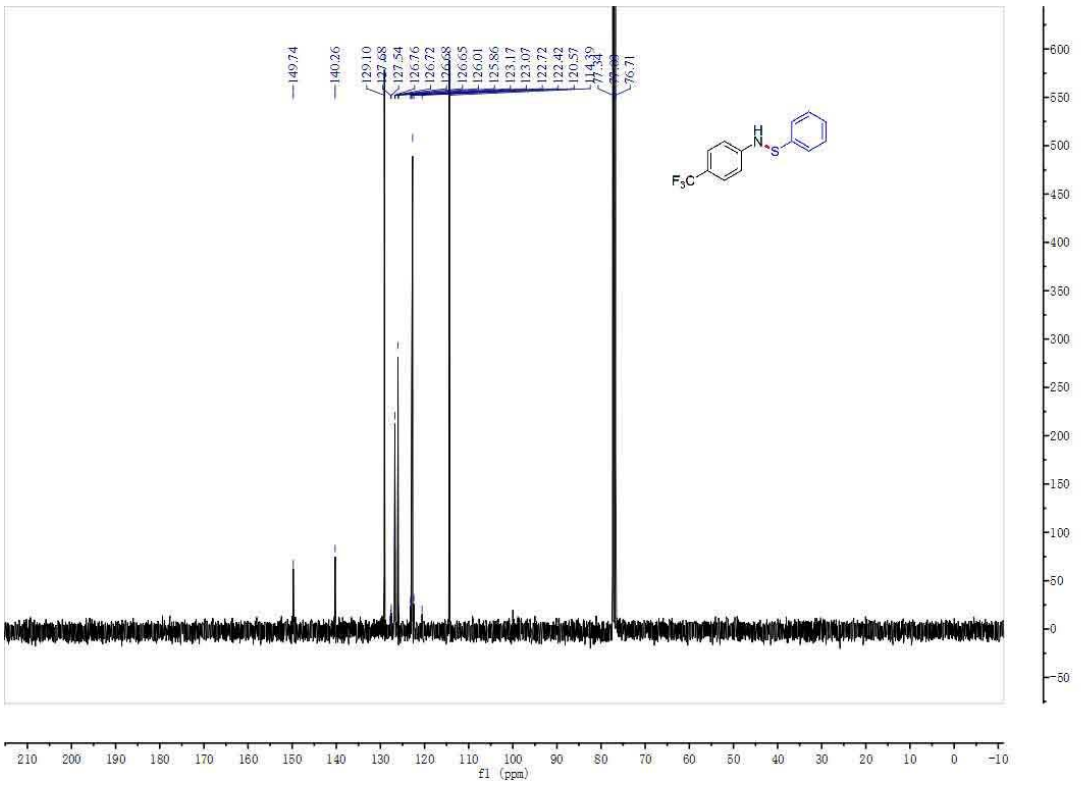
4-nitro-*N*-(phenylthio)benzenamine (5ae)



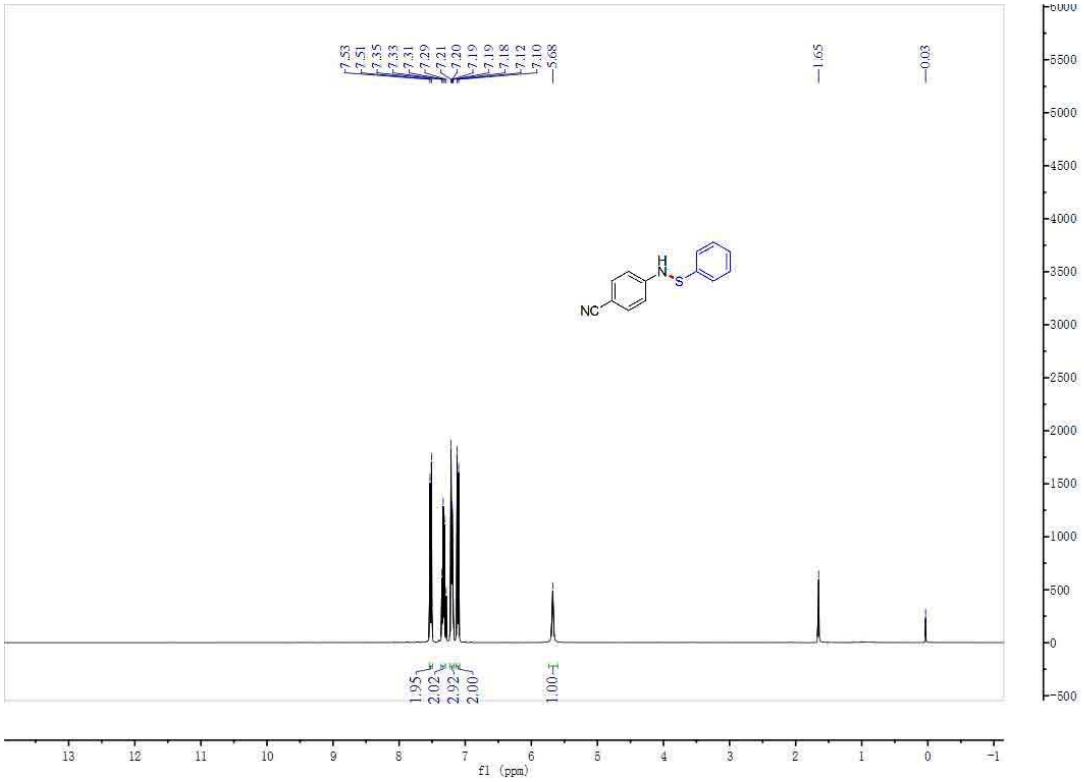


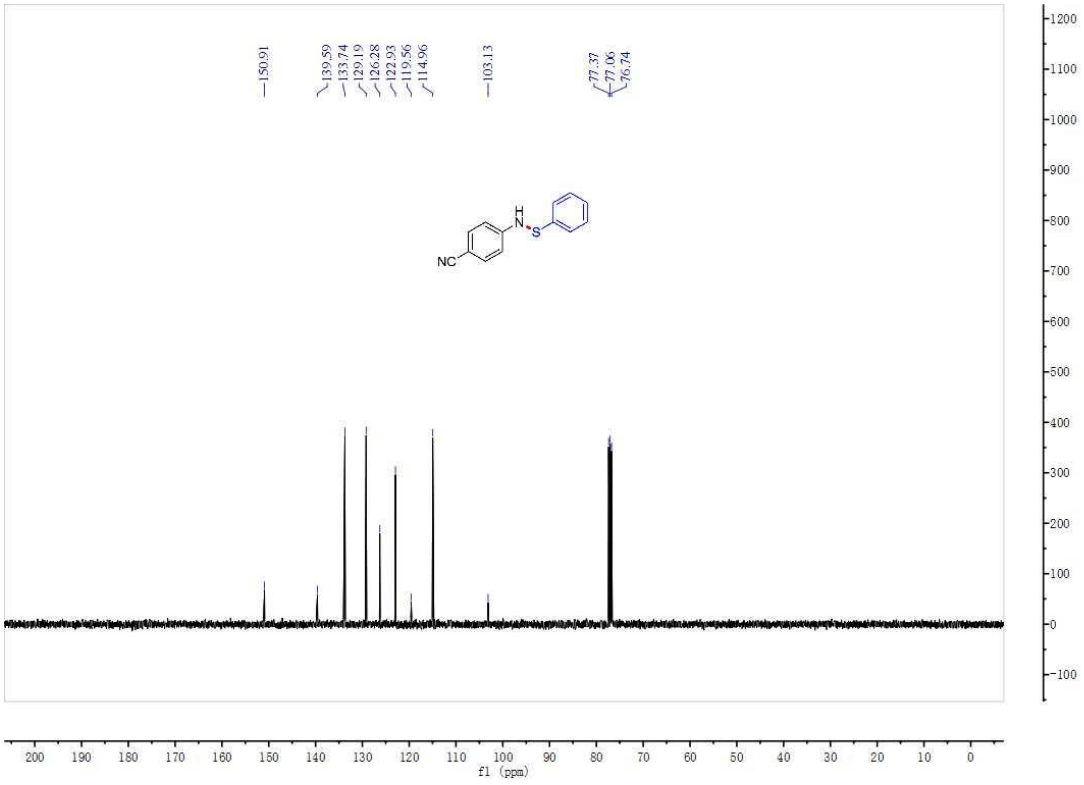
***N*-(phenylthio)-4-(trifluoromethyl)benzenamine (5af)**





4-(phenylthioamino)benzonitrile (5ag)





***N*-methyl-*N*-(phenylthio)benzenamine (5ah)**