

# Supplementary Information

## Copper-catalyzed *N*-thioetherification of sulfoximines using disulfides

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## 1. General Considerations

Unless otherwise noted, all chemicals were purchased from commercial suppliers and used without further purification.  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra were recorded at ambient temperature on a 300 or 400 MHz NMR spectrometer (75 or 100 MHz for  $^{13}\text{C}$ ). NMR experiments are reported in  $\delta$  units, parts per million (ppm), and were referenced to  $\text{CDCl}_3$  as the internal standard. The coupling constants  $J$  are given in Hz. Column chromatography was performed using EM Silica gel 60 (300-400 mesh).

## 2. Experimental Procedures

### General procedure for the CuI-catalyzed *N*-thioetherification of sulfoximines using disulfides

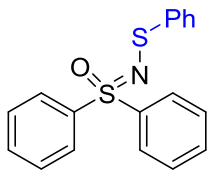
A 20 mL Schlenk tube equipped with a stir bar was charged with sulfoximine **1** (0.1 mmol), disulfide **2** (0.1 mmol, 1 equiv), CuI (3.8 mg, 0.02 mmol), sodium acetate (24.6 mg, 3 equiv), DMSO (2.0 mL). The tube was sealed with a Teflon cap. The reaction mixture was stirred at 60 °C for 15 h in oil bath. After the completion of the reaction, the reaction mixture was concentrated in vacuum and the residue was purified by flash column chromatography on silica gel with petroleum ether-EtOAc as the eluent to give the desired products.

### General procedure for the synthesis of sulfoximines<sup>1</sup>

To a 25 mL over-dried round bottom flask equipped with a magnetic stir bar and reflux condenser, sulfoxide (4.0 mmol), sodium azide (1.2 equiv) and  $\text{CHCl}_3$  (8.0 mL) were added at 0 °C. Then 1.6 mL conc.  $\text{H}_2\text{SO}_4$  was added dropwise over 10 min at 0 °C. The flask was placed into an oil bath and heated to 45 °C for overnight. After complete consumption of sulfoxide, the reaction flask was cooled to room temperature, quenched by water and extracted with  $\text{CHCl}_3$ . The combined organic extracts were washed with brine, dried over  $\text{Na}_2\text{SO}_4$  and concentrated under reduced pressure. The crude residue was purified using column chromatography on silica gel to afford the desired sulfoximine in good yield.

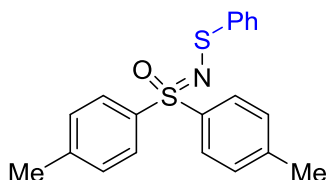
## 3. Characterization Data for the Products

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



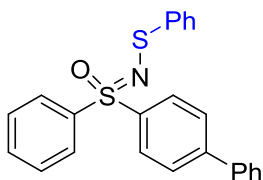
Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 10) give **3aa** (28.6 mg, 88% yield) as a white solid. Mp. 105-107 °C.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz):  $\delta$  8.10-8.00 (m, 4H), 7.60-7.45 (m, 8H), 7.28 (t,  $J$  = 7.8 Hz, 2H), 7.10 (t,  $J$  = 7.3 Hz, 1H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz):  $\delta$  142.1, 139.9, 133.2, 129.3, 128.5, 128.4, 125.0, 123.9; HRMS (ESI)  $m/z$  calcd for  $\text{C}_{18}\text{H}_{16}\text{NOS}_2(\text{M}+\text{H})^+$  326.0668, found 326.0666.

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



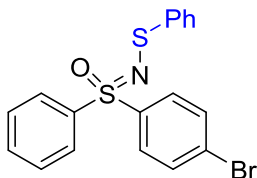
Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 10) give **3ba** (24.7 mg, 70% yield) as a white solid. Mp. 108-110 °C.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz):  $\delta$  7.94-7.87 (m, 4H), 7.46-7.44 (m, 2H), 7.32-7.25 (m, 6H), 7.10-7.07 (m, 1H), 2.41 (s, 6H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz):  $\delta$  144.0, 142.4, 137.2, 129.9, 128.4, 128.3, 124.8, 123.7, 21.5; HRMS (ESI)  $m/z$  calcd for  $\text{C}_{20}\text{H}_{20}\text{NOS}_2(\text{M}+\text{H})^+$  354.0981, found 354.0983.

### **S-phenyl-S-(1,1'-biphenyl)-N-phenylthiosulfoximine (3ca)**



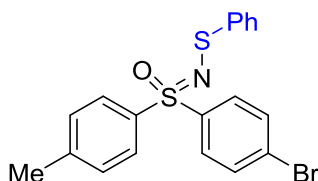
Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 10) give **3ca** (35.6mg, 89% yield) as a yellow solid. Mp. 122-124 °C.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz):  $\delta$  8.11-8.09 (m, 4H), 7.73 (d,  $J$  = 8.4 Hz, 2H), 7.62-7.41 (m, 10H), 7.30 (t,  $J$  = 7.9 Hz, 2H), 7.12 (t,  $J$  = 7.3 Hz, 1H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 75 MHz):  $\delta$  146.1, 142.1, 140.0, 139.0, 138.3, 133.2, 129.3, 129.1, 129.0, 128.5, 128.4, 128.3, 127.9, 127.3, 125.0, 123.9; HRMS (ESI)  $m/z$  calcd for  $\text{C}_{24}\text{H}_{20}\text{NOS}_2(\text{M}+\text{H})^+$  402.0981, found 402.0983.

**S-phenyl-S-(4-bromophenyl)-N-phenylthiosulfoximine (3da)**



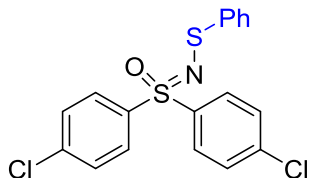
Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 10) give **3da** (28.2 mg, 70% yield) as a yellow oil.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz):  $\delta$  8.06-8.02 (m, 2H), 7.89-7.86 (m, 2H), 7.67-7.52 (m, 5H), 7.45-7.39 (m, 2H), 7.28 (t,  $J = 7.8$  Hz, 2H), 7.11 (t,  $J = 7.3$  Hz, 1H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 75 MHz):  $\delta$  141.7, 139.5, 139.0, 133.4, 132.6, 130.0, 129.4, 128.5, 128.4, 128.3, 125.2, 124.0; HRMS (ESI)  $m/z$  calcd for  $\text{C}_{18}\text{H}_{15}\text{BrNOS}_2(\text{M}+\text{H})^+$  403.9773, found 403.9771.

**S-(4-methylphenyl)-S-(4-bromophenyl)-N-phenylthiosulfoximine (3ea)**



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 10) give **3ea** (36.6 mg, 88% yield) as a yellow solid. Mp. 124-125  $^\circ\text{C}$ .  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz):  $\delta$  7.92-7.85 (m, 4H), 7.63 (d,  $J = 8.6$  Hz, 2H), 7.43 (d,  $J = 7.6$  Hz, 2H), 7.34-7.26 (m, 4H), 7.10 (t,  $J = 7.3$  Hz, 1H), 2.42 (s, 3H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz):  $\delta$  144.6, 141.9, 139.4, 136.3, 132.5, 130.1, 129.8, 128.5, 128.4, 128.3, 125.1, 123.9, 21.5; HRMS (ESI)  $m/z$  calcd for  $\text{C}_{19}\text{H}_{17}\text{BrNOS}_2(\text{M}+\text{H})^+$  417.9929, found 417.9932.

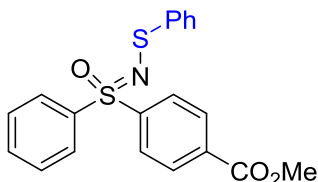
**S,S-di(4-chlorophenyl)-N-phenylthiosulfoximine (3fa)**



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 10) give **3fa** (31.8 mg, 81% yield) as a yellow solid. Mp. 120-122  $^\circ\text{C}$ .  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz):

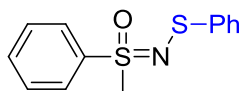
$\delta$  7.95-7.92 (m, 4H), 7.51-7.42 (m, 6H), 7.31-7.27 (m, 2H), 7.13 (t,  $J = 7.3$  Hz, 1H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz):  $\delta$  141.4, 140.2, 138.1, 129.9, 129.7, 128.5, 125.4, 124.2; HRMS (ESI)  $m/z$  calcd for  $\text{C}_{18}\text{H}_{14}\text{Cl}_2\text{NOS}_2(\text{M}+\text{H})^+$  393.9888, found 393.9891.

**S-phenyl-S-(4-methoxycarbonylphenyl)-N-phenylthiosulfoximine (3ga)**



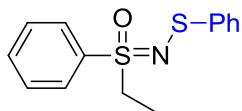
Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 5) give **3ga** (23.3 mg, 61% yield) as a yellow oil.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz):  $\delta$  8.17-8.04 (m, 6H), 7.64-7.53 (m, 3H), 7.43 (d,  $J = 7.7$  Hz, 2H), 7.28 (t,  $J = 7.8$  Hz, 2H), 7.11 (t,  $J = 7.3$  Hz, 1H), 3.95 (s, 3H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz):  $\delta$  165.5, 144.1, 141.7, 139.2, 134.2, 133.6, 130.4, 129.5, 128.6, 128.5, 128.4, 125.2, 124.1, 52.6; HRMS (ESI)  $m/z$  calcd for  $\text{C}_{20}\text{H}_{18}\text{NO}_3\text{S}_2(\text{M}+\text{H})^+$  384.0723, found 384.0725.

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



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 6) give **3ha** (13.4 mg, 51% yield) as a yellow oil.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz):  $\delta$  8.01-7.96 (m, 2H), 7.70-7.58 (m, 3H), 7.42-7.37 (m, 2H), 7.30-7.24 (m, 2H), 7.10 (t,  $J = 7.3$  Hz, 1H), 3.30 (s, 3H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz):  $\delta$  142.1, 133.7, 133.6, 129.5, 128.5, 128.4, 125.1, 123.8, 43.7; HRMS (ESI)  $m/z$  calcd for  $\text{C}_{13}\text{H}_{14}\text{NOS}_2(\text{M}+\text{H})^+$  264.0511, found 264.0515.

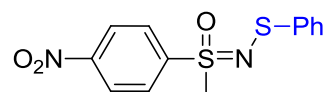
**S-ethyl-S-phenyl-N-phenylthiosulfoximine (3ia)**



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 10) give **3ia** (11.9 mg, 43% yield) as a yellow oil.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz):  $\delta$  7.98-7.88 (m,

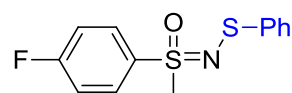
2H), 7.69-7.55 (m, 3H), 7.43-7.38 (m, 2H), 7.30-7.25 (m, 2H), 7.12-7.05 (m, 1H), 3.58-3.32(m, 2H), 1.33(t,  $J = 7.4$  Hz, 3H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz):  $\delta$  142.4, 136.8, 133.6, 129.4, 129.2, 128.4, 125.0, 123.9, 50.3, 7.8; HRMS (ESI)  $m/z$  calcd for  $\text{C}_{14}\text{H}_{16}\text{NOS}_2(\text{M}+\text{H})^+$  278.0668, found 278.0665.

### **S-methyl-S-(4-nitrophenyl)-N-phenylthiosulfoximine (3ja)**



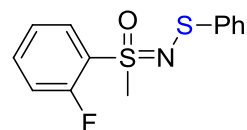
Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 4) give **3ja** (16.9 mg, 55% yield) as a yellow oil.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz):  $\delta$  8.33-8.29 (m, 2H), 8.07-8.02 (m, 2H), 7.30-7.17 (m, 4H), 7.07-7.02 (m, 1H), 3.27 (s, 3H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz):  $\delta$  150.8, 144.8, 141.0, 129.9, 128.6, 125.7, 124.5, 124.3, 43.6; HRMS (ESI)  $m/z$  calcd for  $\text{C}_{13}\text{H}_{12}\text{N}_2\text{NaO}_3\text{S}_2(\text{M}+\text{Na})^+$  331.0182, found 331.0182.

### **S-methyl-S-(4-fluorophenyl)-N-phenylthiosulfoximine (3ka)**



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 10) give **3ka** (22.2 mg, 79% yield) as a yellow oil.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz):  $\delta$  7.98-7.93 (m, 2H), 7.40-7.36 (m, 2H), 7.30-7.22 (m, 4H), 7.13-7.07 (m, 1H), 3.29 (s, 3H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 75 MHz):  $\delta$  165.8 (d,  $J_{\text{C-F}} = 255.0$  Hz), 141.8, 134.4 (d,  $J_{\text{C-F}} = 3.8$  Hz), 131.3 (d,  $J_{\text{C-F}} = 9.0$  Hz), 128.5, 125.2, 123.9, 116.8 (d,  $J_{\text{C-F}} = 22.5$  Hz), 43.9; HRMS (ESI)  $m/z$  calcd for  $\text{C}_{13}\text{H}_{13}\text{FNOS}_2(\text{M}+\text{H})^+$  282.0417, found 282.0420.

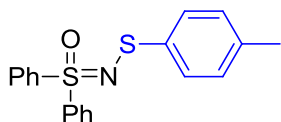
### **S-methyl-S-(2-fluorophenyl)-N-phenylthiosulfoximine (3la)**



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 10) give **3la** (23.8 mg, 85% yield) as a yellow oil.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz):  $\delta$  8.04-7.98 (m, 1H), 7.69-7.60 (m, 1H), 7.38-7.32 (m, 3H), 7.28-7.16 (m, 3H), 7.08(t,  $J = 7.3$  Hz, 1H),

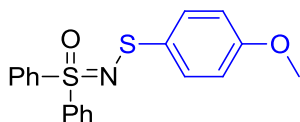
2.47 (s, 3H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz):  $\delta$  158.5 (d,  $J_{\text{C-F}} = 253.0$  Hz), 141.4, 136.1 (d,  $J_{\text{C-F}} = 9.0$  Hz), 131.6, 128.4, 125.2, 124.7 (d,  $J_{\text{C-F}} = 4.0$  Hz), 124.1, 117.1 (d,  $J_{\text{C-F}} = 22.0$  Hz), 42.8; HRMS (ESI)  $m/z$  calcd for  $\text{C}_{13}\text{H}_{13}\text{FNOS}_2(\text{M}+\text{H})^+$  282.0417, found 282.0414.

***S,S*-diphenyl-*N*-(4-methylphenylthio)sulfoximine (**3ab**)<sup>2</sup>**



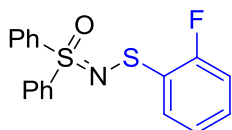
Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 10) give **3ab** (20.8 mg, 61% yield) as a yellow solid. Mp. 110-112 °C.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz):  $\delta$  8.06-8.00 (m, 4H), 7.58-7.48 (m, 6H), 7.35 (d,  $J = 8.2$  Hz, 2H), 7.07 (d,  $J = 8.0$  Hz, 2H), 2.29 (s, 3H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 75 MHz):  $\delta$  139.9, 138.2, 135.2, 133.1, 129.3, 129.2, 128.5, 125.1, 21.0.

***S,S*-diphenyl-*N*-(4-methoxyphenylthio)sulfoximine (**3ac**)**



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 10) give **3ac** (26.7mg, 75% yield) as a yellow oil.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz):  $\delta$  8.02-7.97 (m, 4H), 7.57-7.46 (m, 8H), 6.84-6.80 (m, 2H), 3.77 (m, 3H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz):  $\delta$  158.6, 140.1, 133.0, 129.5, 129.2, 128.5(2), 114.2, 55.3; HRMS (ESI)  $m/z$  calcd for  $\text{C}_{19}\text{H}_{18}\text{NO}_2\text{S}_2(\text{M}+\text{H})^+$  356.0773, found 356.0770.

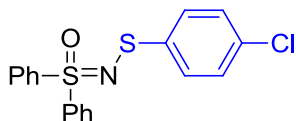
***S,S*-diphenyl-*N*-(2-fluorophenylthio)sulfoximine (**3ad**)**



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 15) give **3ad** (25.1 mg, 73% yield) as a white solid. Mp. 107-109 °C.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz):  $\delta$  8.03-7.98 (m, 4H), 7.76-7.70 (m, 1H), 7.59-7.50 (m, 6H), 7.14-7.03 (m, 2H), 6.90 (t,  $J = 9.6$  Hz, 1H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz):  $\delta$  157.0 (d,  $J_{\text{C-F}} = 241.0$  Hz), 139.7, 133.3,

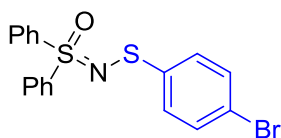
129.4, 128.4, 126.0 (d,  $J_{C-F} = 7.0$  Hz), 124.4 (d,  $J_{C-F} = 3.0$  Hz), 114.4 (d,  $J_{C-F} = 21.0$  Hz); HRMS (ESI)  $m/z$  calcd for  $C_{18}H_{15}FNOS_2(M+H)^+$  344.0574, found 344.0571.

**S,S-diphenyl-N-(4-chlorophenylthio)sulfoximine (3ae)**



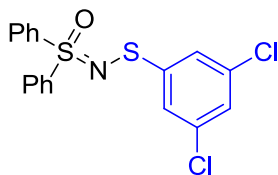
Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 10) give **3ae** (31.4mg, 87% yield) as a white solid. Mp. 121-123 °C.  $^1H$  NMR ( $CDCl_3$ , 300 MHz):  $\delta$  8.03-7.99 (m, 4H), 7.61-7.49 (m, 6H), 7.39-7.33 (m, 2H), 7.23-7.19 (m, 2H);  $^{13}C$  NMR ( $CDCl_3$ , 75 MHz):  $\delta$  140.9, 139.7, 133.3, 130.5, 129.4, 128.5, 128.4, 125.2; HRMS (ESI)  $m/z$  calcd for  $C_{18}H_{15}ClNOS_2(M+H)^+$  360.0278, found 360.0283.

**S,S-diphenyl-N-(4-bromophenylthio)sulfoximine (3af)**



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 10) give **3af** (33.9 mg, 84% yield) as a white solid. Mp. 122-123 °C.  $^1H$  NMR ( $CDCl_3$ , 300 MHz):  $\delta$  7.95-7.91 (m, 4H), 7.52-7.40 (m, 6H), 7.29-7.18 (m, 4H);  $^{13}C$  NMR ( $CDCl_3$ , 75 MHz):  $\delta$  141.6, 139.6, 133.3, 131.3, 129.4, 128.4, 125.3, 118.2; HRMS (ESI)  $m/z$  calcd for  $C_{18}H_{15}BrNOS_2(M+H)^+$  403.9773, found 403.9775.

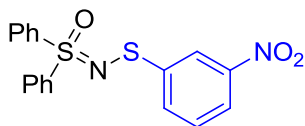
**S,S-diphenyl-N-(3,5-dichlorophenylthio)sulfoximine (3ag)**



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 15) give **3ag** (27.8 mg, 71% yield) as a yellow solid. Mp. 111-113 °C.  $^1H$  NMR ( $CDCl_3$ , 400 MHz):  $\delta$  8.03 (d,  $J = 7.5$  Hz, 4H), 7.64-7.54 (m, 6H), 7.28-7.23 (m, 2H), 7.04 (s, 1H);  $^{13}C$

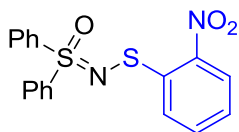
NMR (CDCl<sub>3</sub>, 100 MHz):  $\delta$  146.7, 139.5, 134.9, 133.5, 129.5, 128.4, 124.6, 121.0;  
 HRMS (ESI)  $m/z$  calcd for C<sub>18</sub>H<sub>14</sub>Cl<sub>2</sub>NOS<sub>2</sub>(M+H)<sup>+</sup> 393.9888, found 393.9888.

***S,S*-diphenyl-*N*-(3-nitrophenylthio)sulfoximine (3ah)**



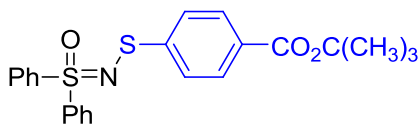
Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 10) give **3ah** (22.9 mg, 62% yield) as a yellow solid. Mp. 156-157 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz):  $\delta$  8.28-8.22 (m, 1H), 8.05-8.01 (m, 4H), 7.90-7.85 (m, 1H), 7.70-7.67 (m, 1H), 7.61-7.53 (m, 6H), 7.41-7.35 (m, 1H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz):  $\delta$  148.5, 145.9, 139.4, 133.5, 129.5, 129.0, 128.7, 128.4, 119.5, 117.8; HRMS (ESI): Calcd. for C<sub>18</sub>H<sub>15</sub>N<sub>2</sub>O<sub>3</sub>S<sub>2</sub>(M+H)<sup>+</sup> 371.0519, found 371.0515.

***S,S*-diphenyl-*N*-(2-nitrophenylthio)sulfoximine (3ai)<sup>2</sup>**



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 10) give **3ai** (32.8 mg, 89% yield) as a yellow solid. Mp. 161-162 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz):  $\delta$  8.31-8.22 (m, 2H), 8.05 (d,  $J$  = 7.2 Hz, 4H), 7.62-7.53 (m, 7H), 7.19 (t,  $J$  = 8.1 Hz, 1H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz):  $\delta$  146.4, 141.9, 139.8, 133.8, 133.4, 129.5, 128.2, 125.5, 125.3, 124.1.

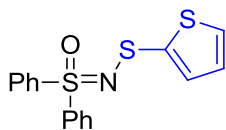
***S,S*-diphenyl-*N*-(pivalatephenylthio)sulfoximine (3aj)**



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 10) give **3aj** (31.8 mg, 75% yield) as a yellow solid. Mp. 127-128 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz):  $\delta$  8.05-7.98 (m, 4H), 7.58-7.41 (m, 8H), 6.95 (d,  $J$  = 8.6 Hz, 2H), 1.33 (s, 9H); <sup>13</sup>C NMR

(CDCl<sub>3</sub>, 100 MHz):  $\delta$  177.0, 148.9, 139.8, 138.9, 133.2, 129.3, 128.4, 125.7, 121.5, 39.0, 27.1; HRMS (ESI): Calcd. for C<sub>23</sub>H<sub>24</sub>NO<sub>3</sub>S<sub>2</sub>(M+H)<sup>+</sup> 426.1192, found 426.1195.

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



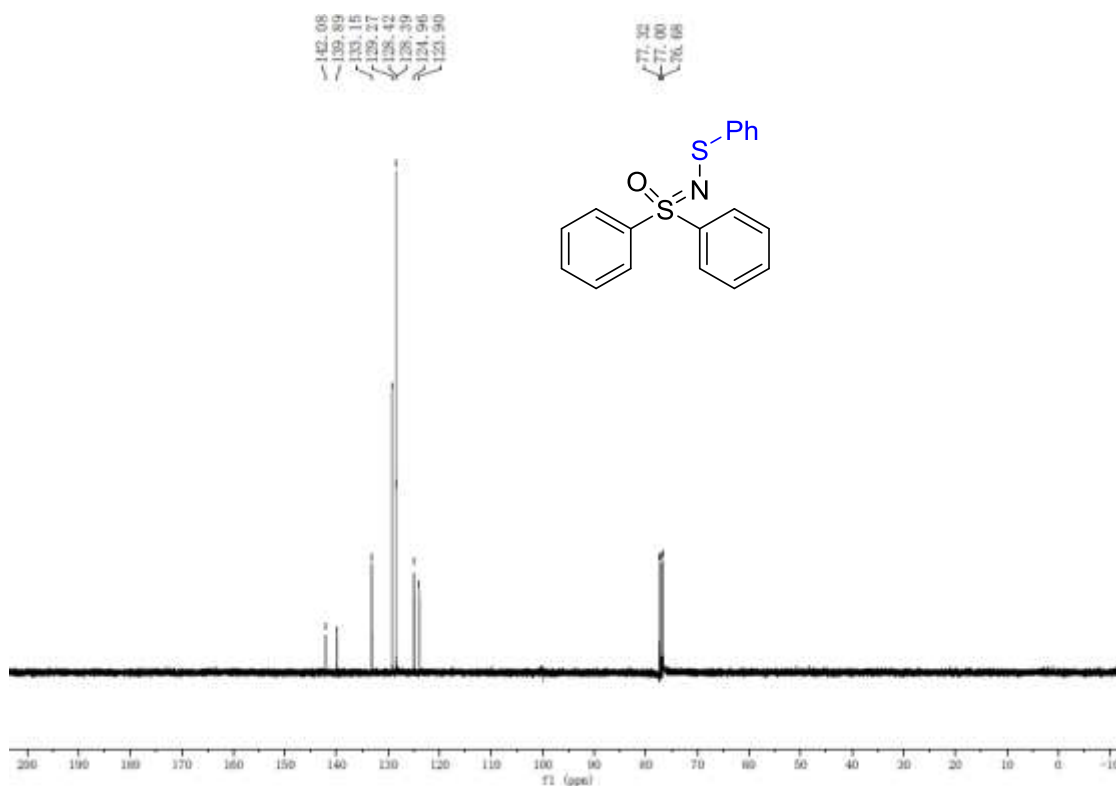
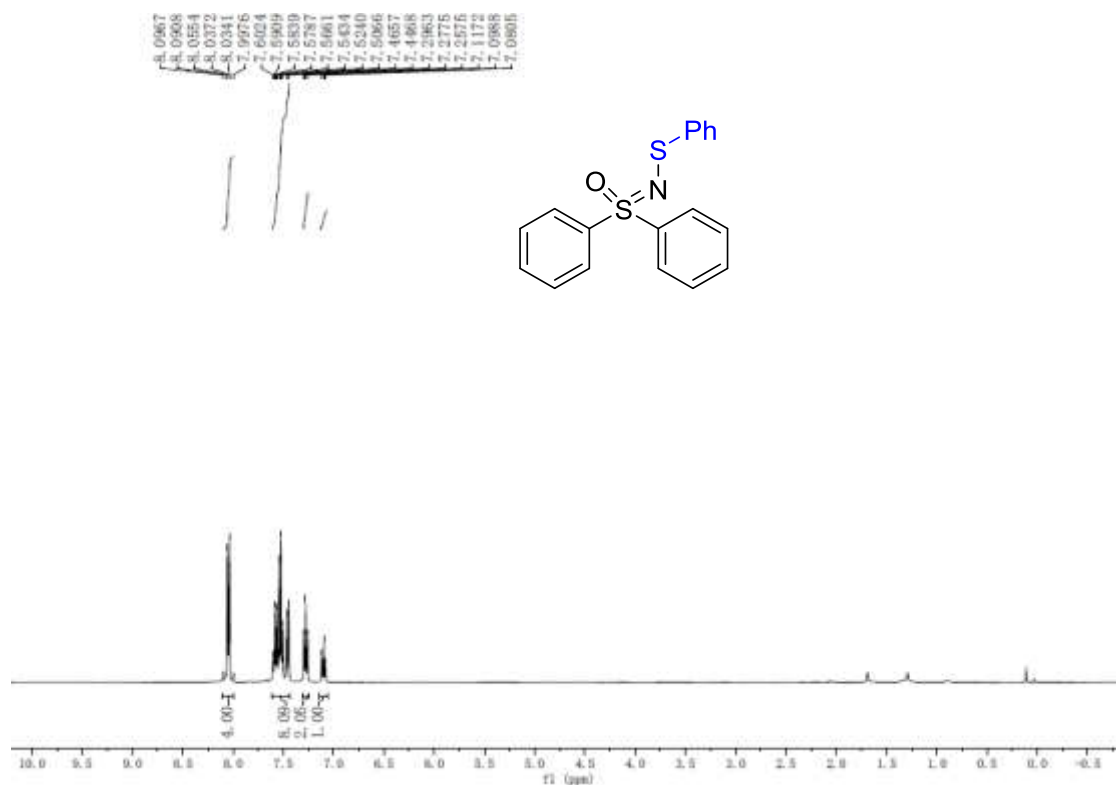
Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 10) give **3ak** (24.6 mg, 74% yield) as a yellow oil. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz):  $\delta$  8.09-8.02 (m, 4H), 7.69-7.58 (m, 7H), 7.54-7.48 (m, 1H), 7.06-6.98 (m, 1H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz):  $\delta$  139.8, 133.7, 133.0, 130.9, 129.2, 128.4, 127.8, 127.1; HRMS (ESI): Calcd. for C<sub>16</sub>H<sub>14</sub>NOS<sub>3</sub>(M+H)<sup>+</sup> 332.0232, found 332.0230.

## **4. References**

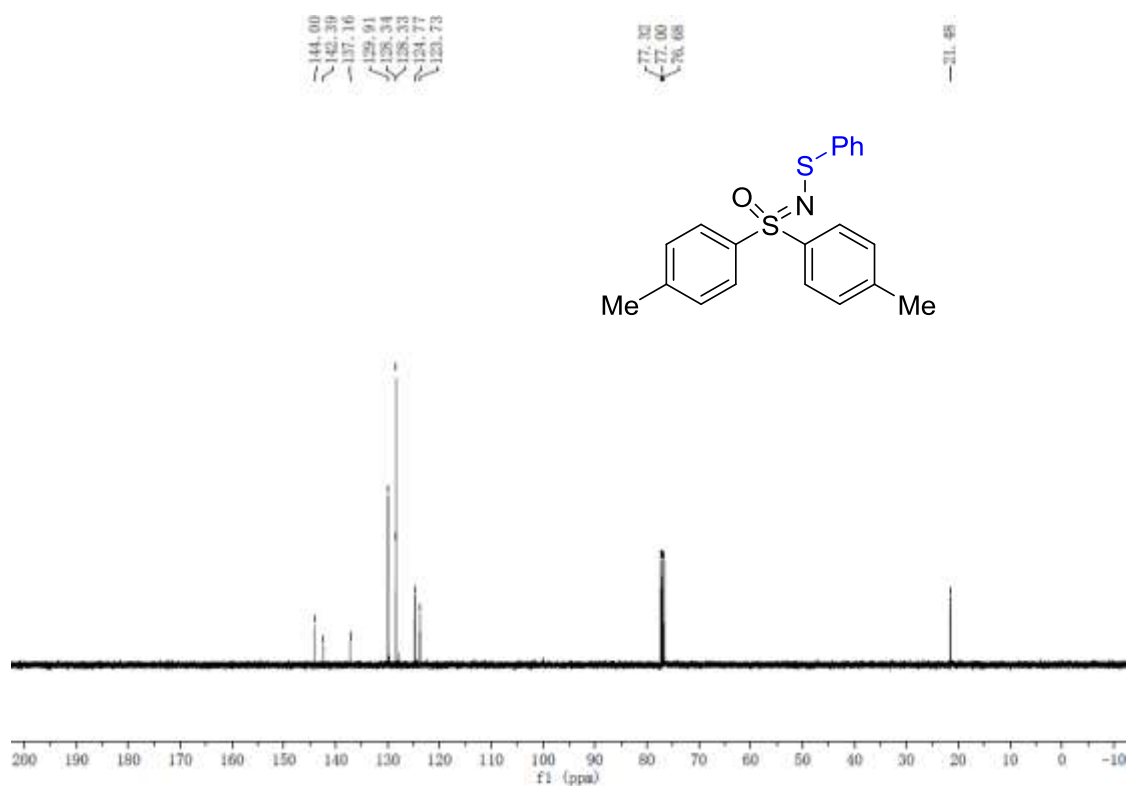
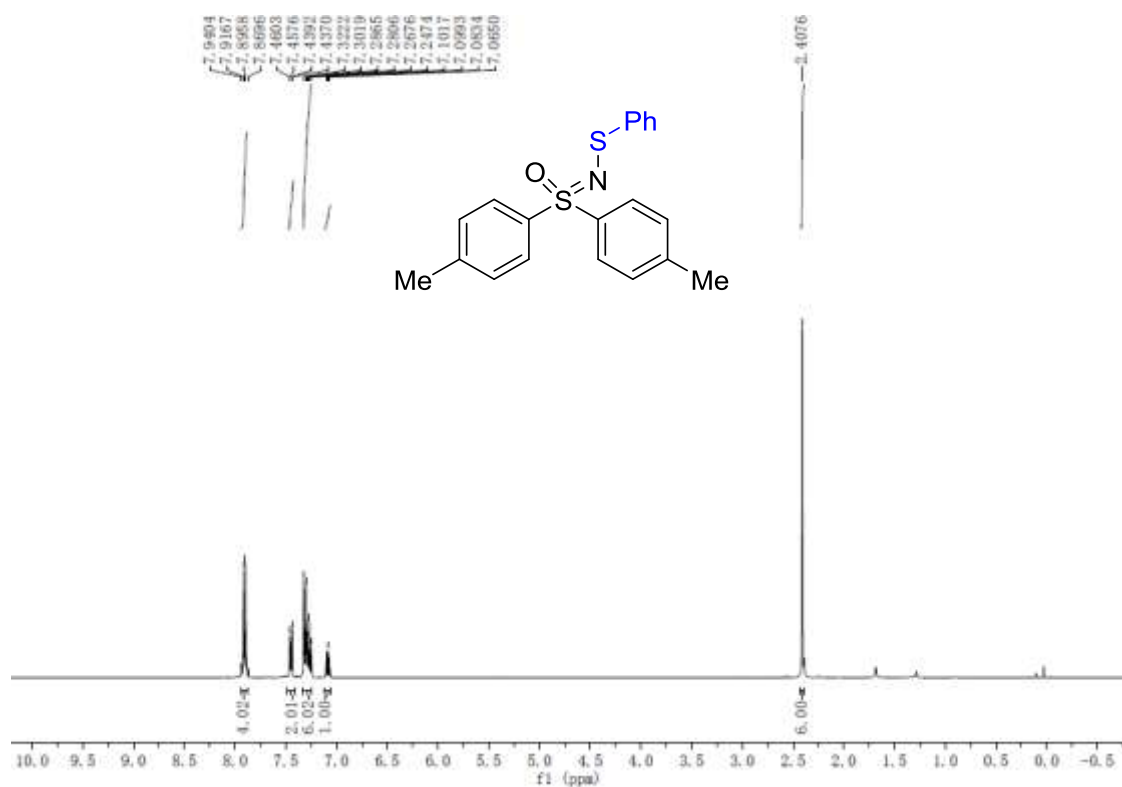
1. M. R. Yadav, R. K. Rit and A. K. Sahoo, *Chem. Eur. J.*, 2012, **18**, 5541.
2. K. Akutagawa, N. Furukawa and S. Oae, *Bull. Chem. Soc. Jpn.*, 1984, **57**, 518.

## 5. Copies of the $^1\text{H}$ NMR and $^{13}\text{C}$ NMR spectra

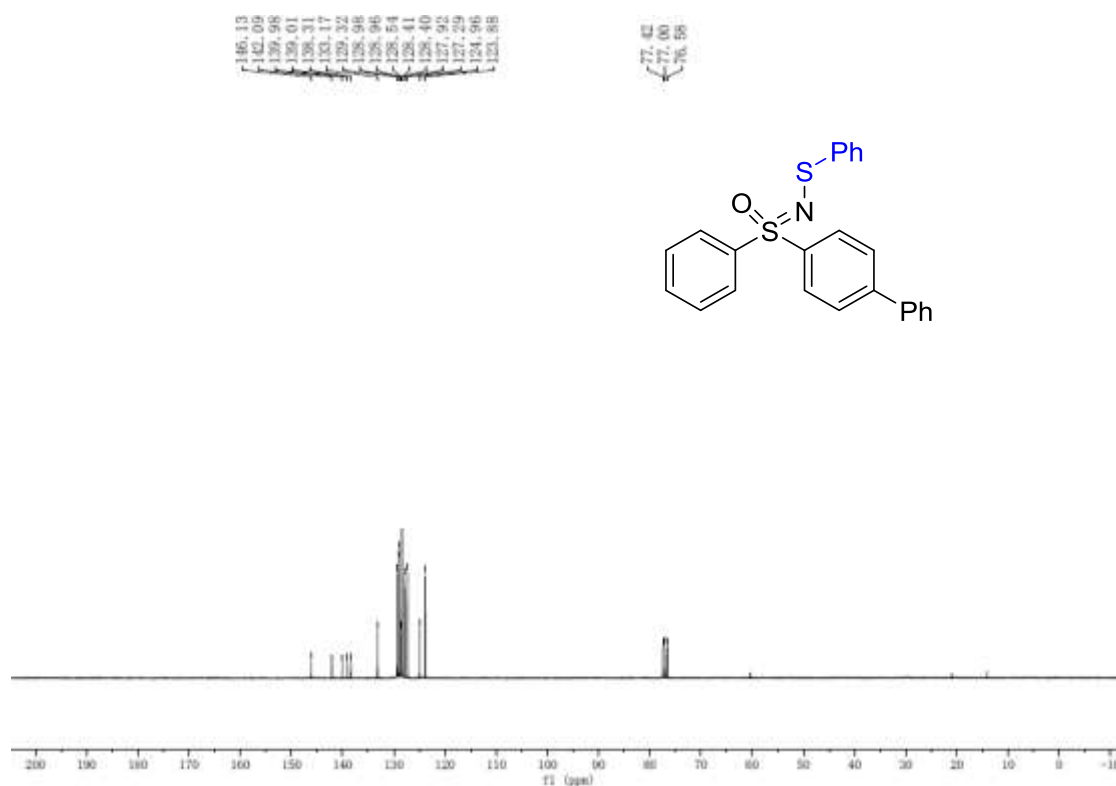
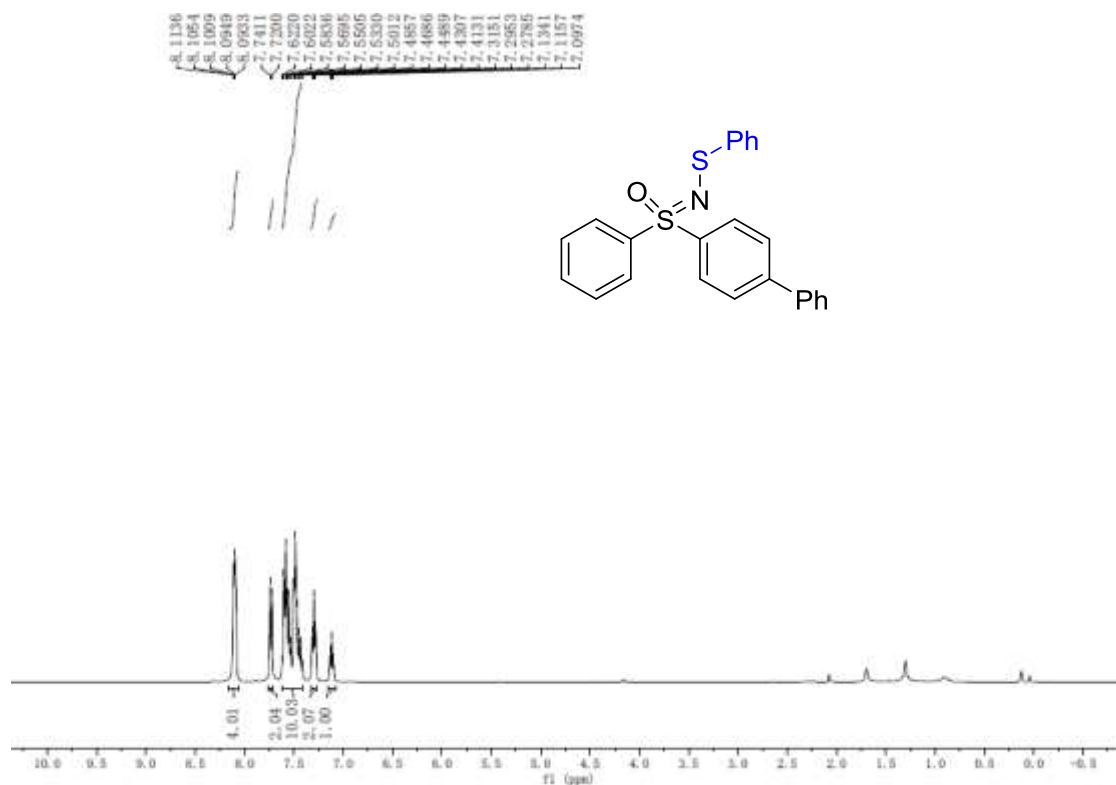
### *S,S*-diphenyl-*N*-phenylthiosulfoximine (3aa)



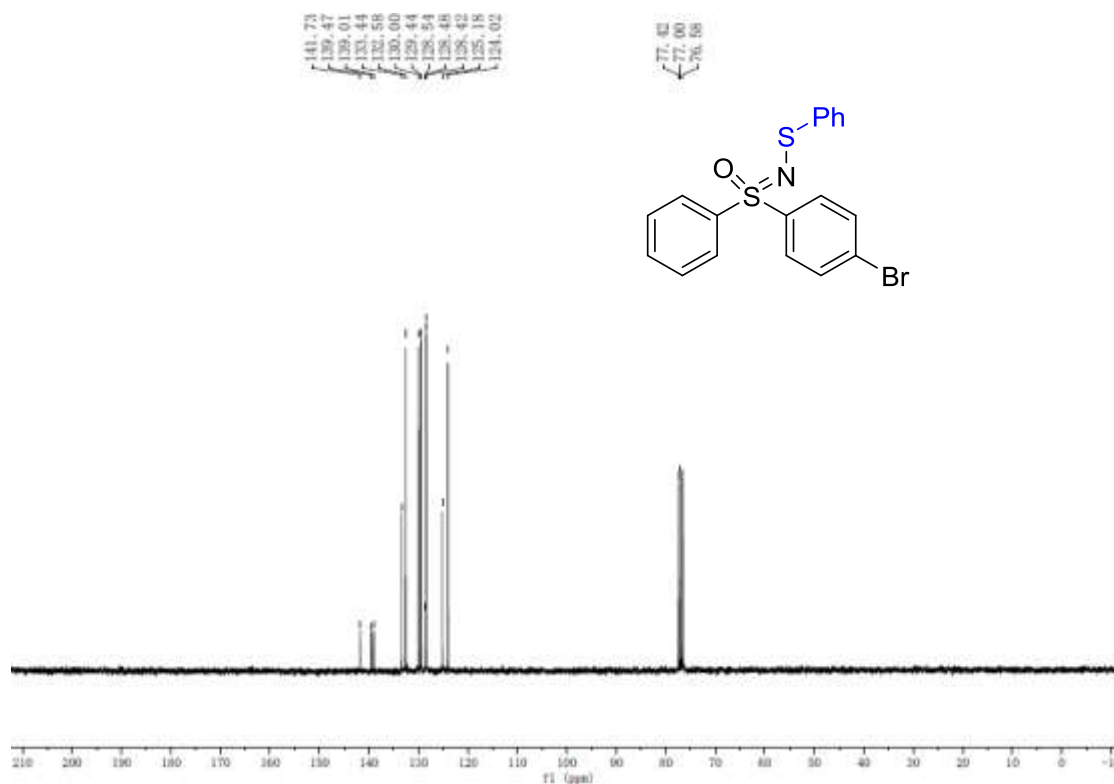
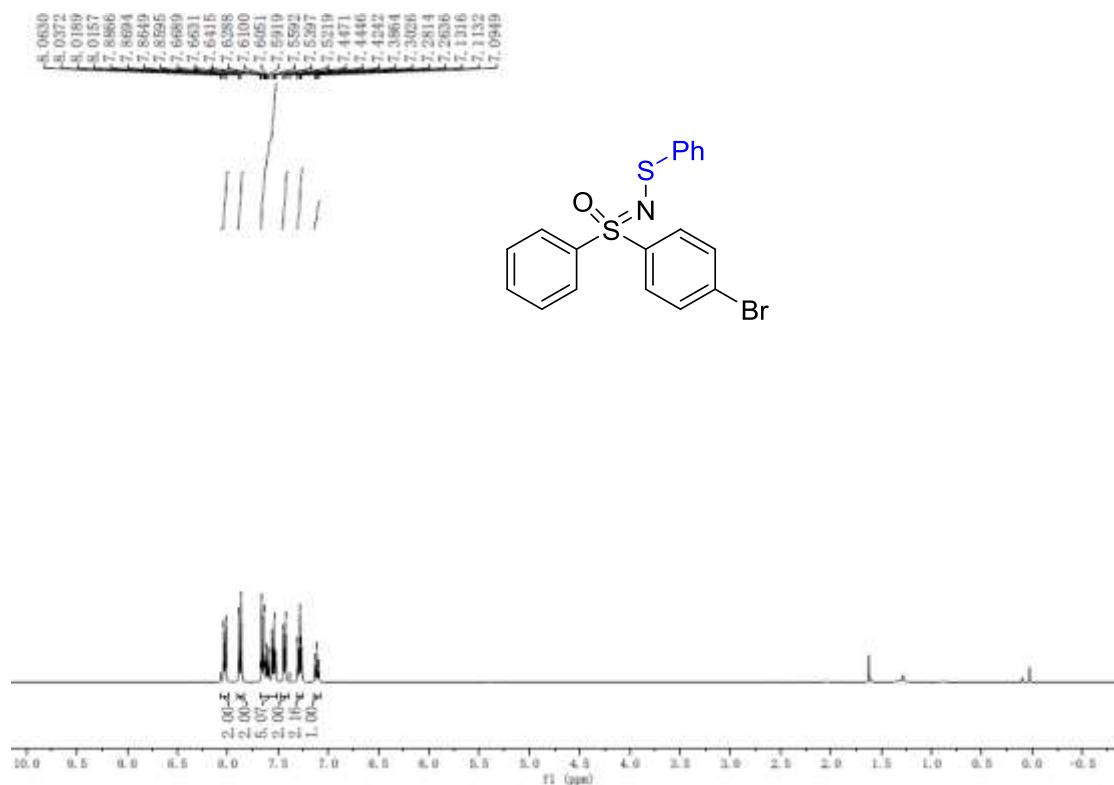
***S,S*-di(4-methylphenyl)-*N*-phenylthiosulfoximine (3ba)**



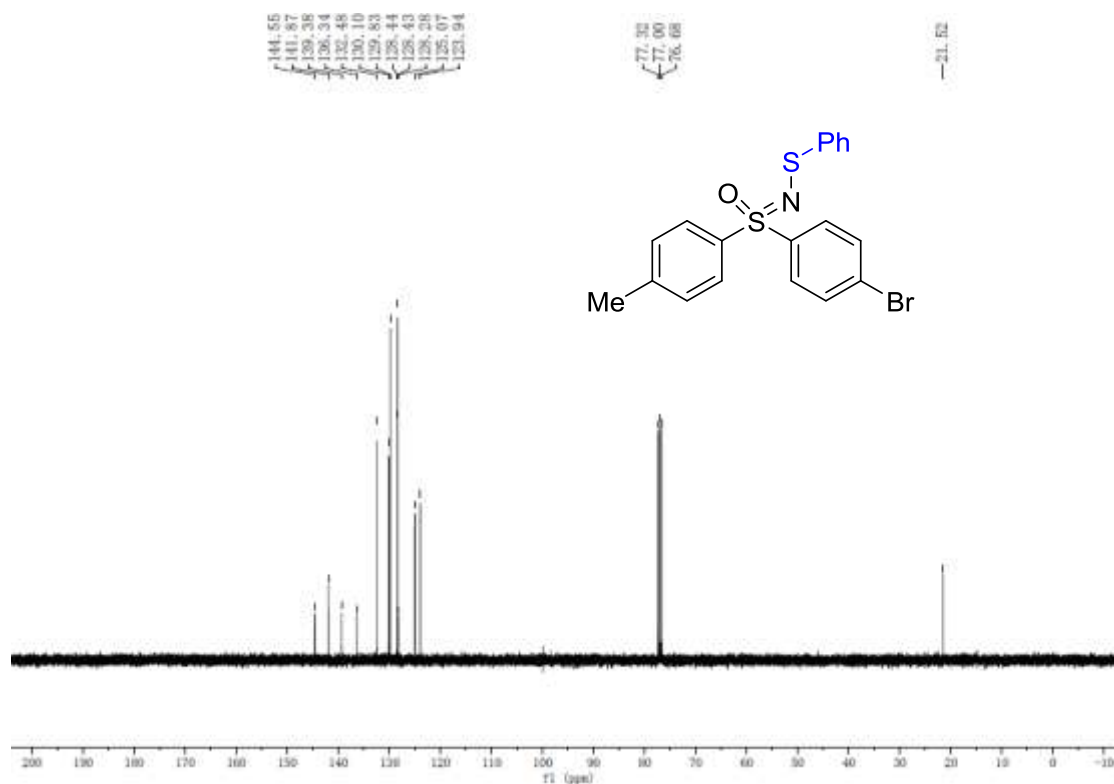
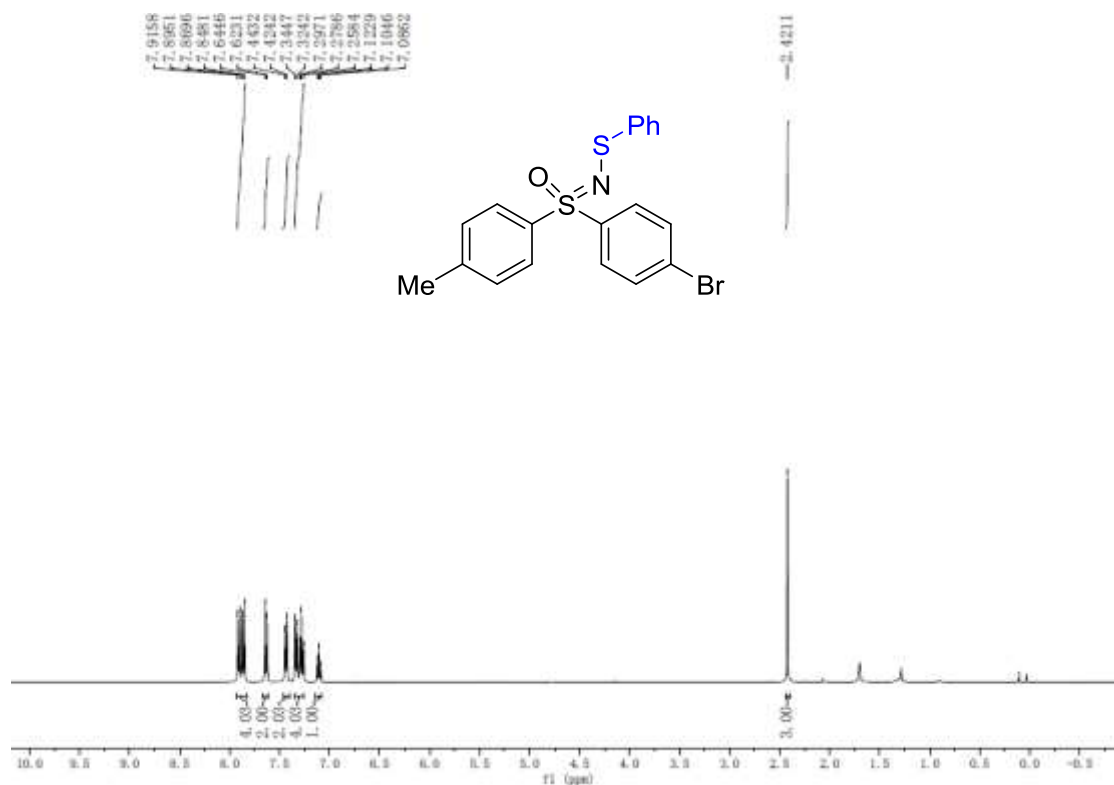
**S-phenyl-S-(1,1'-biphenyl)-N-phenylthiosulfoximine (3ca)**



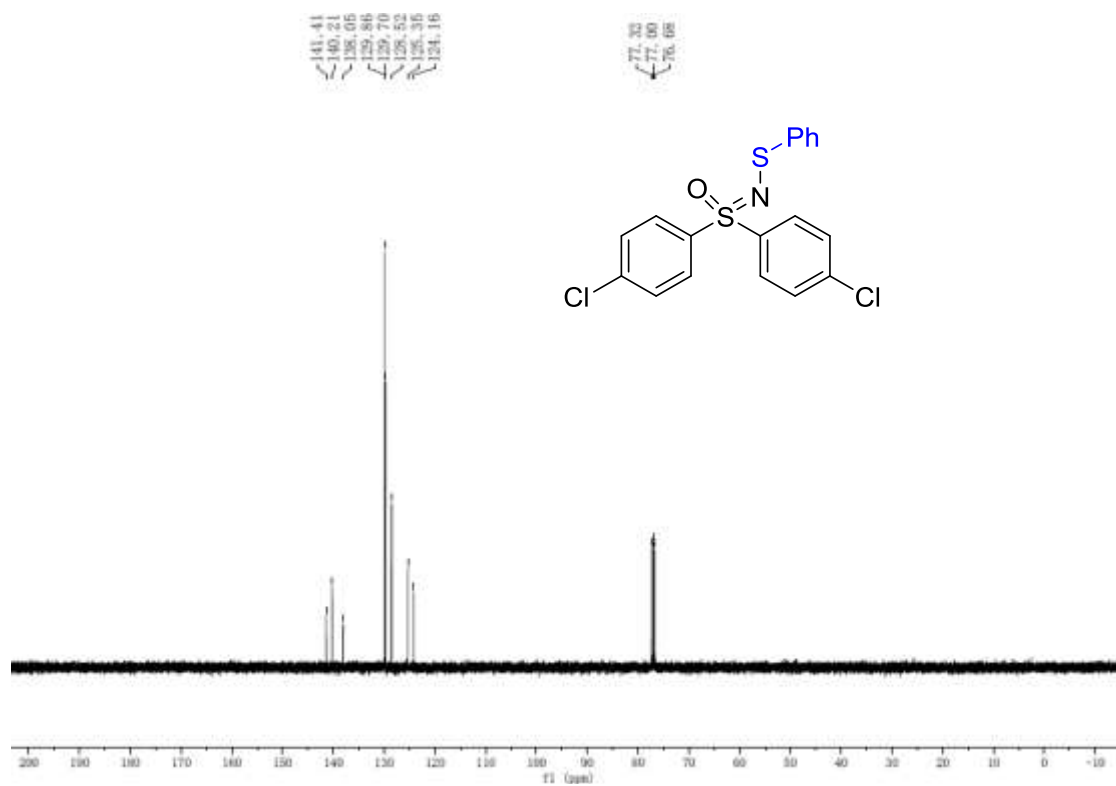
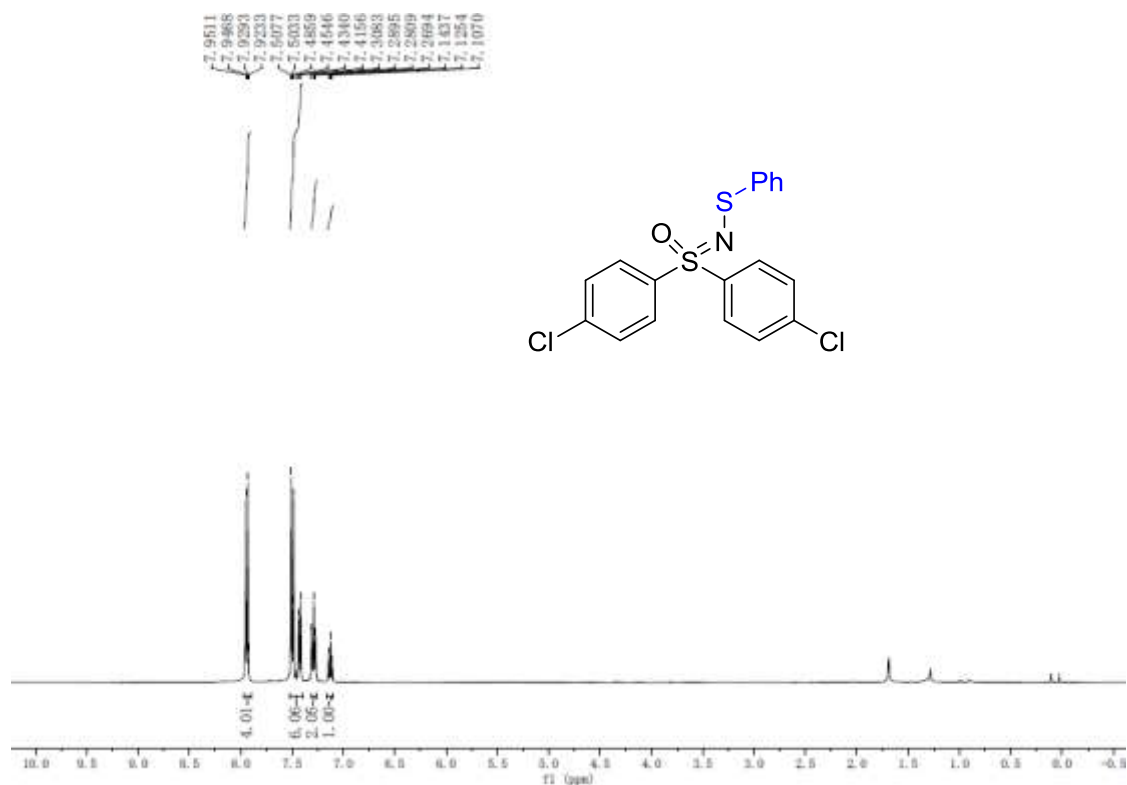
**S-phenyl-S-(4-bromophenyl)-N-phenylthiosulfoximine (3da)**



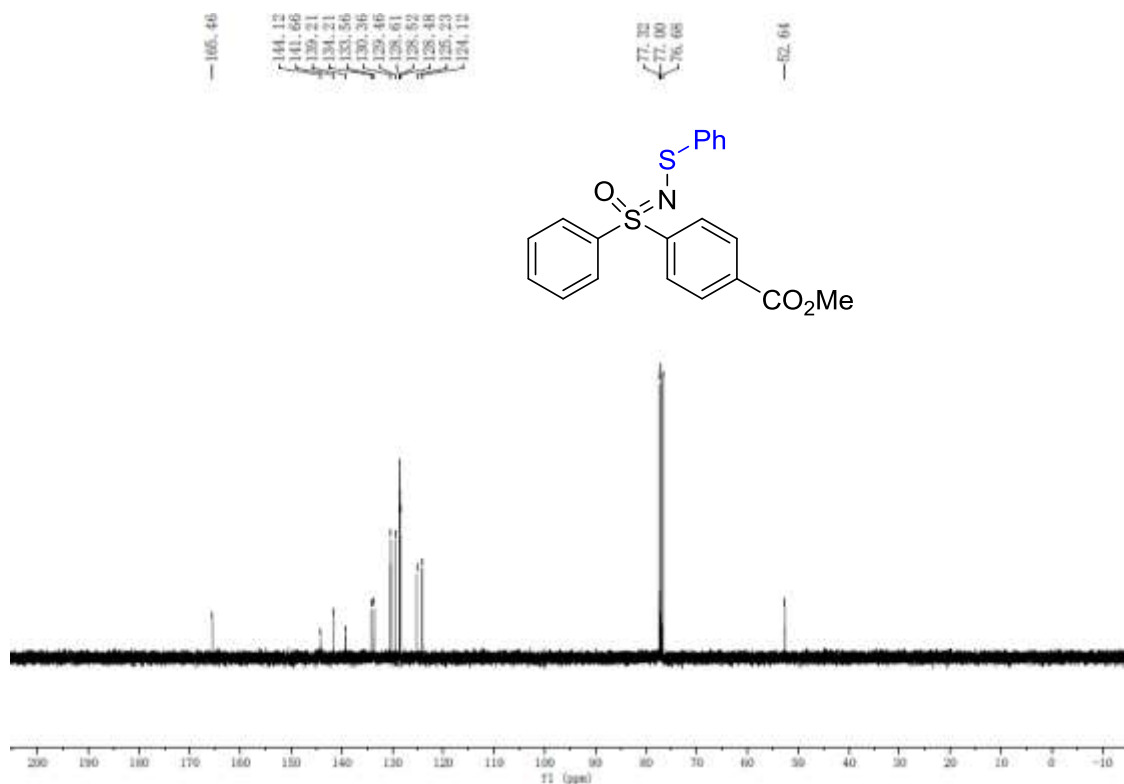
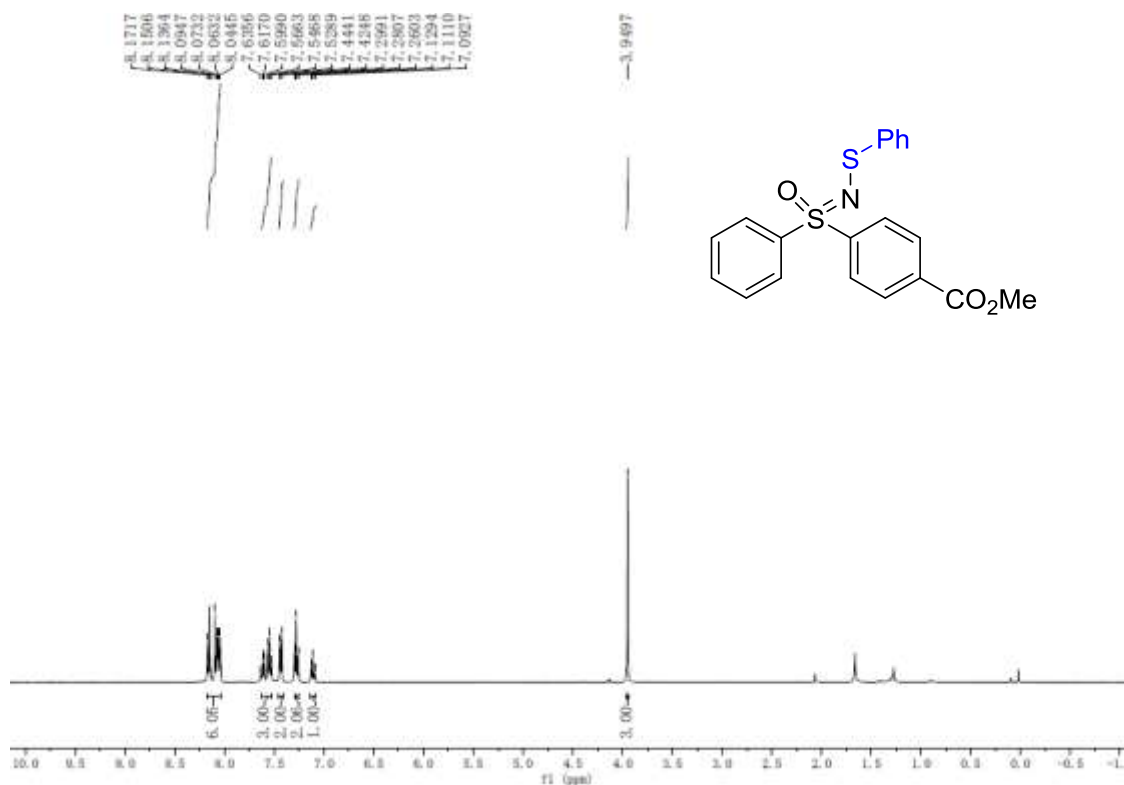
**S-(4-methylphenyl)-S-(4-bromophenyl)-N-phenylthiosulfoximine (3ea)**



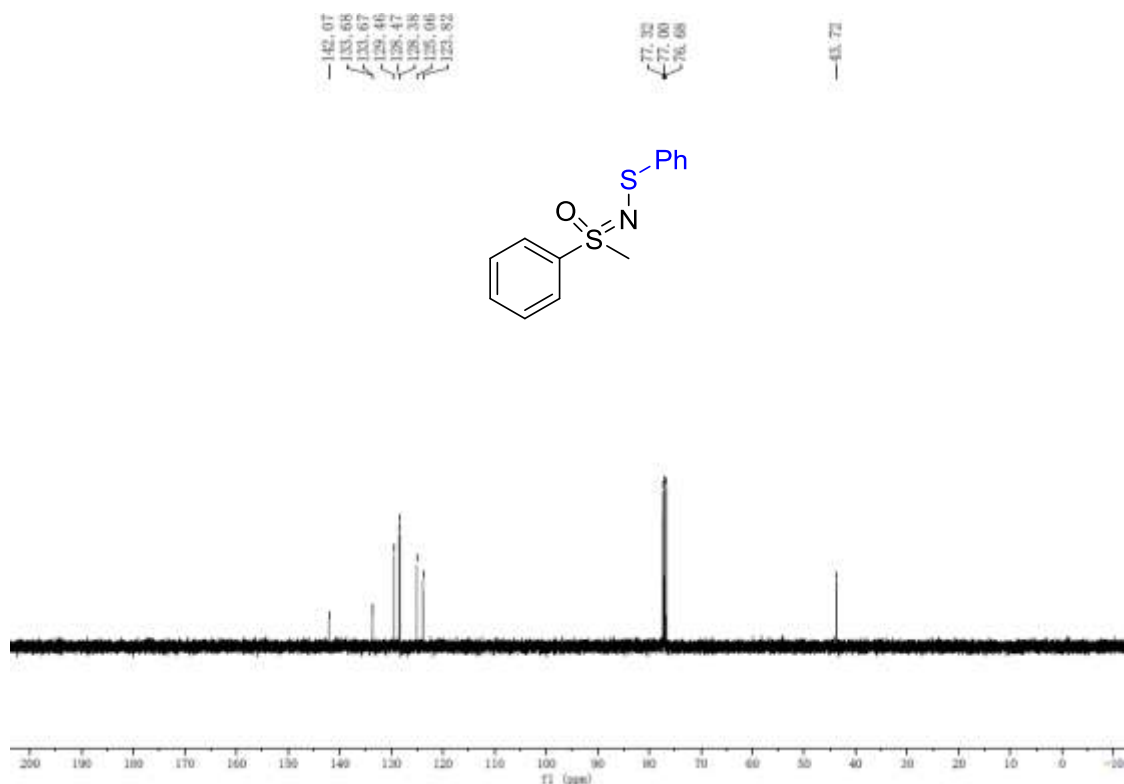
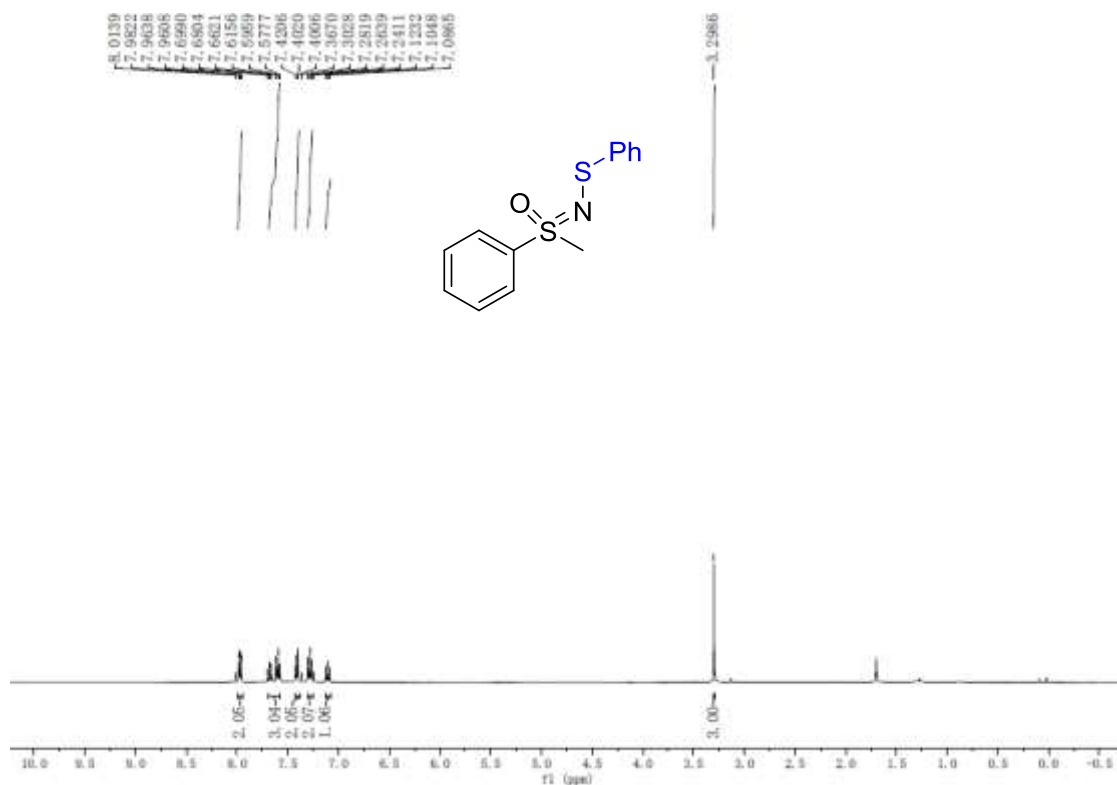
***S,S*-di(4-chlorophenyl)-*N*-phenylthiosulfoximine (3fa)**



**S-phenyl-S-(4-methoxycarbonylphenyl)-N-phenylthiosulfoximine (3ga)**

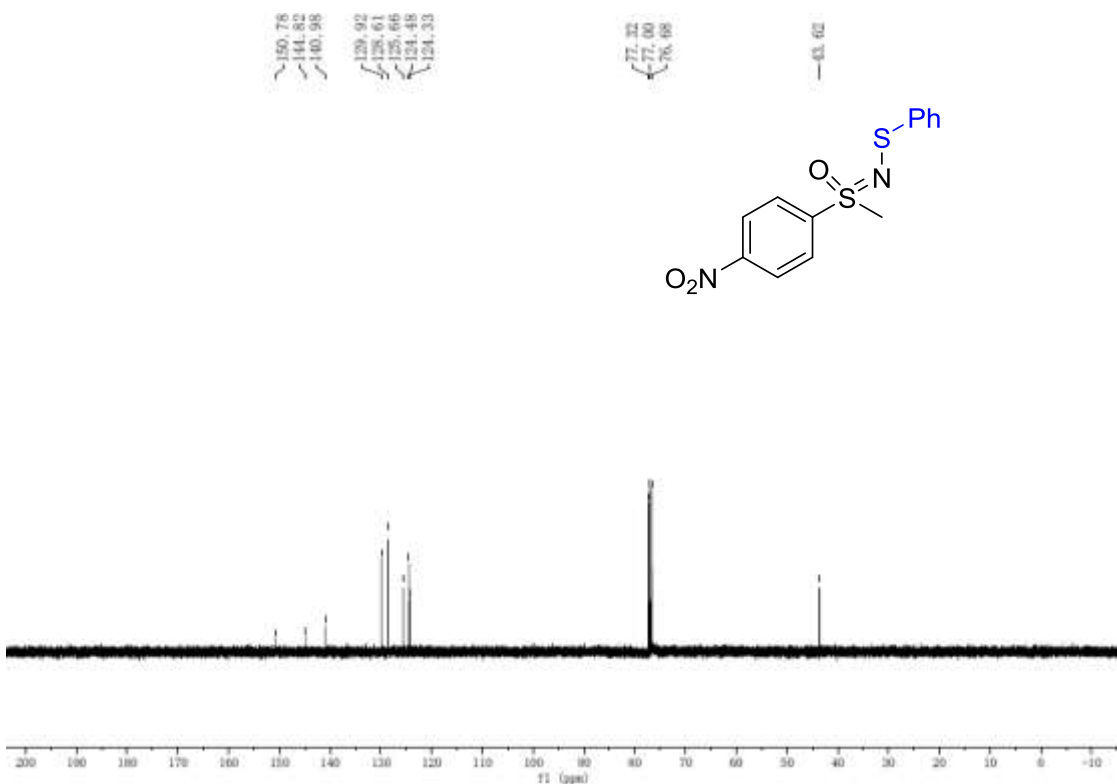
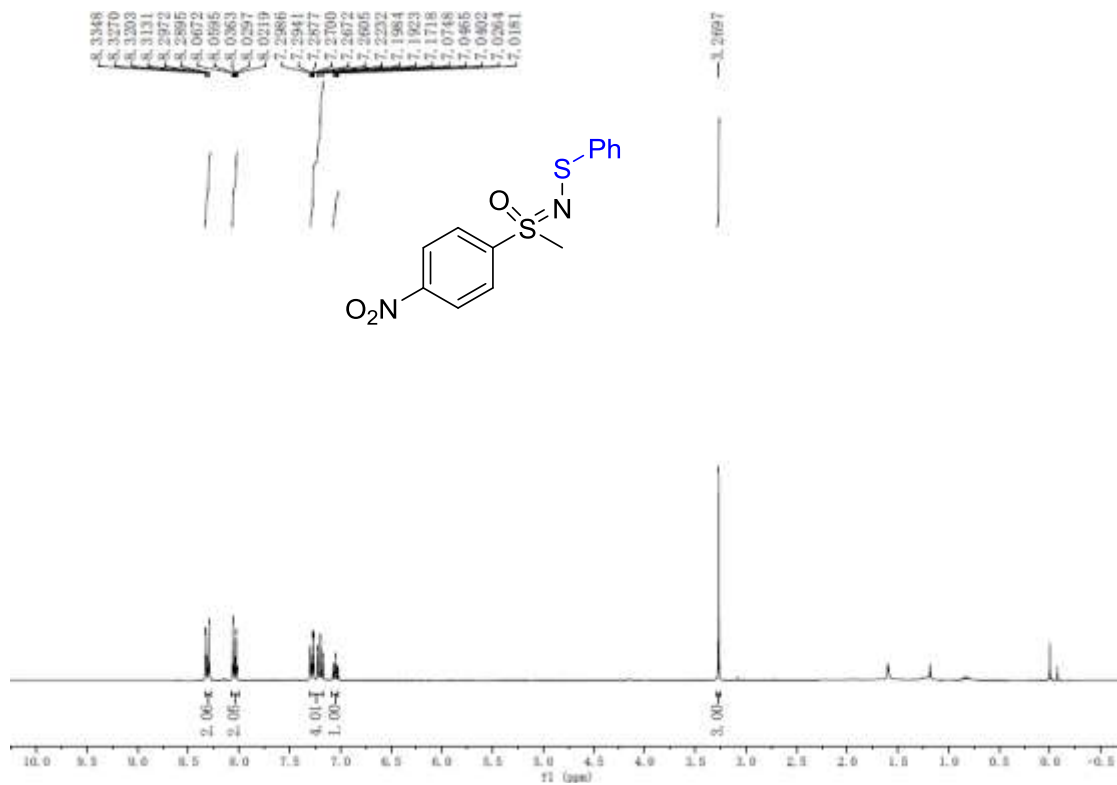


**S-methyl-S-phenyl-N-phenylthiosulfoximine (3ha)**

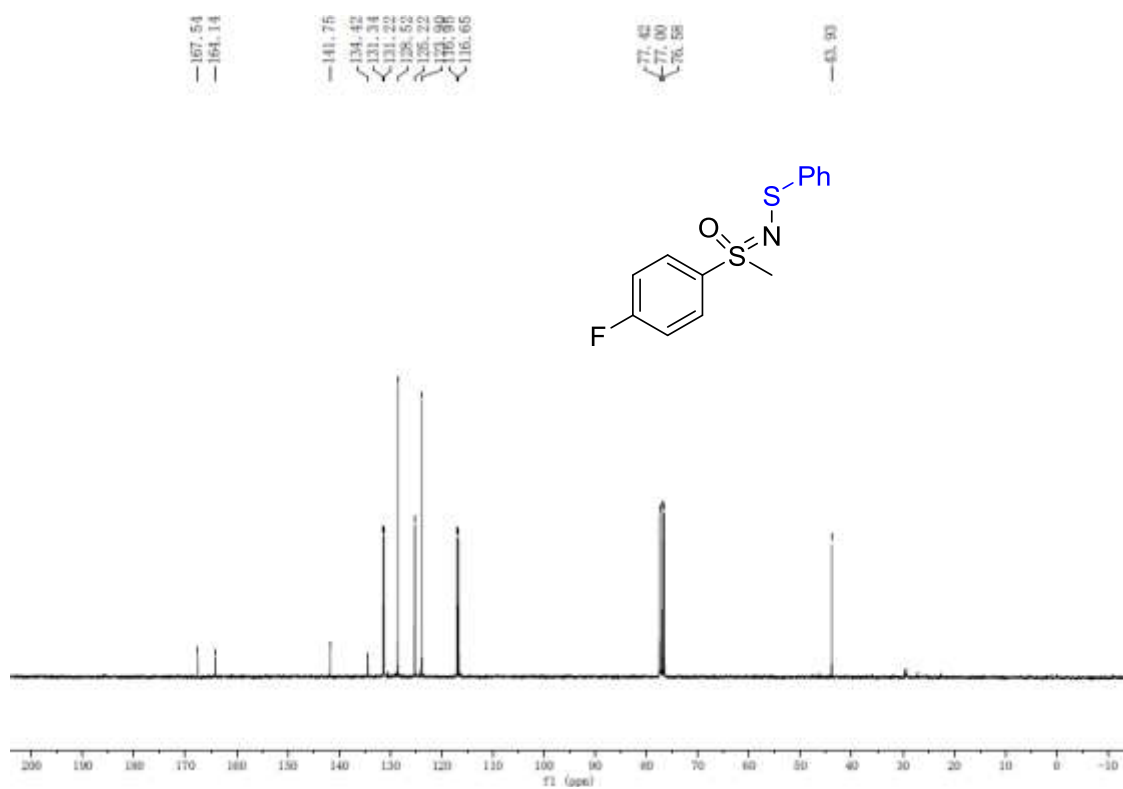
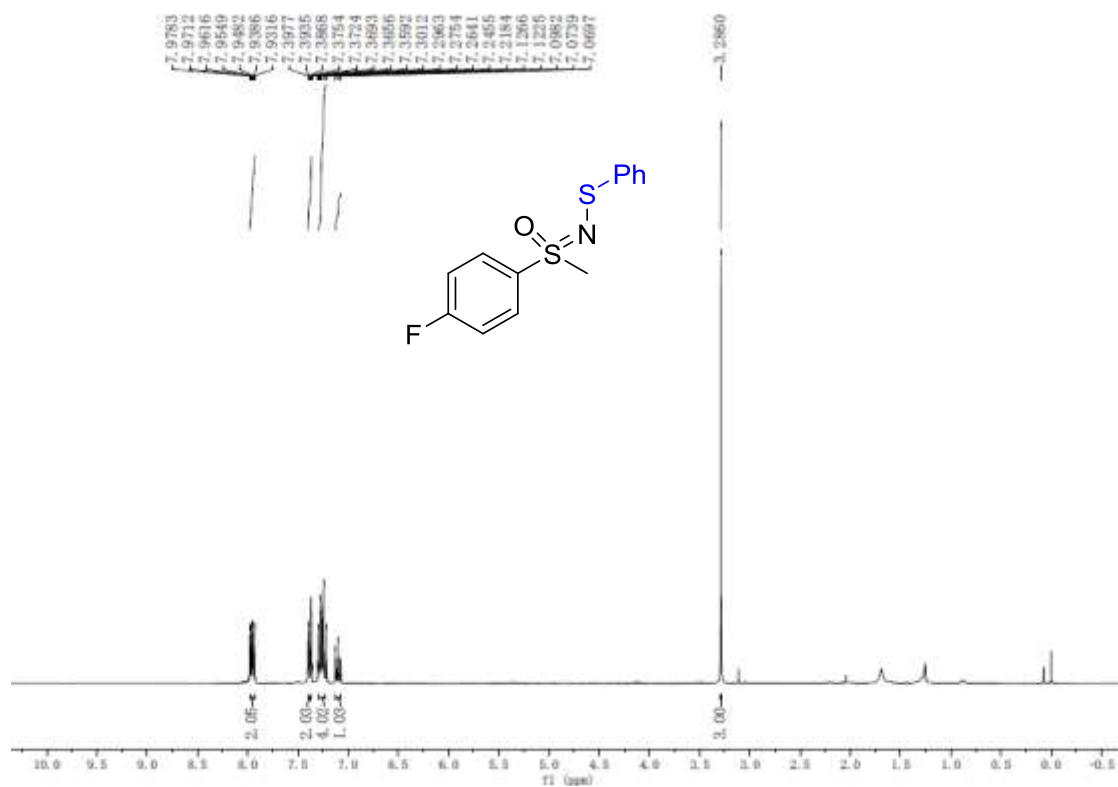




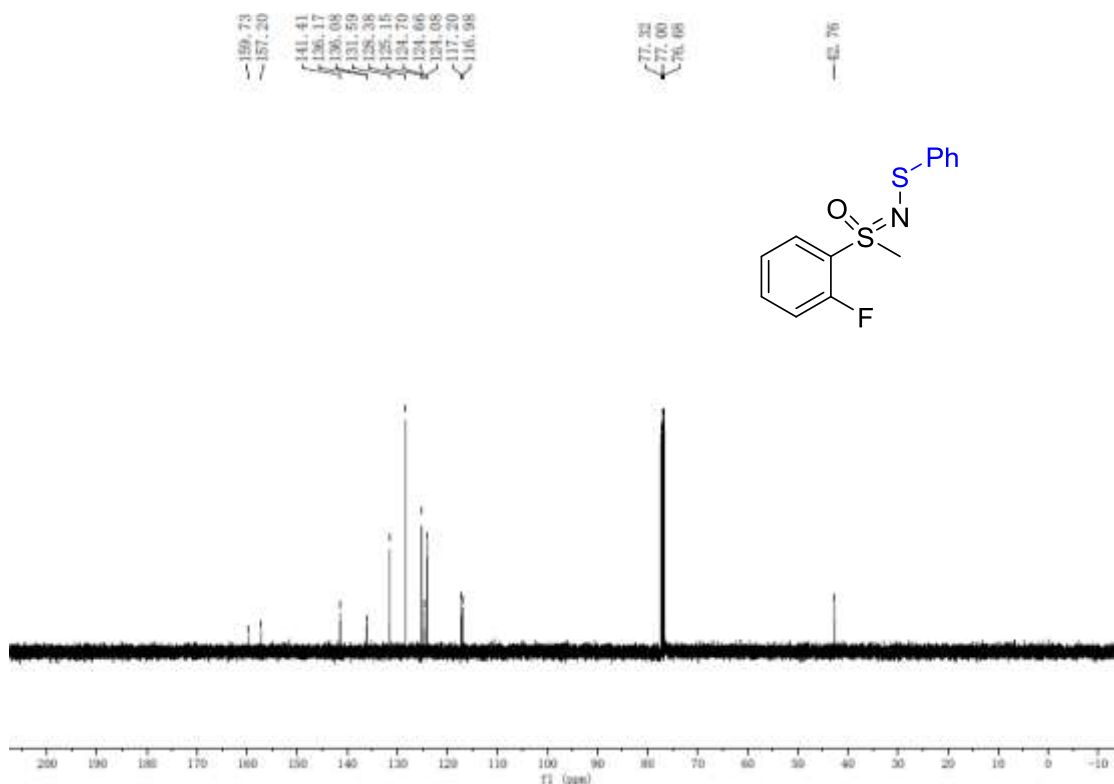
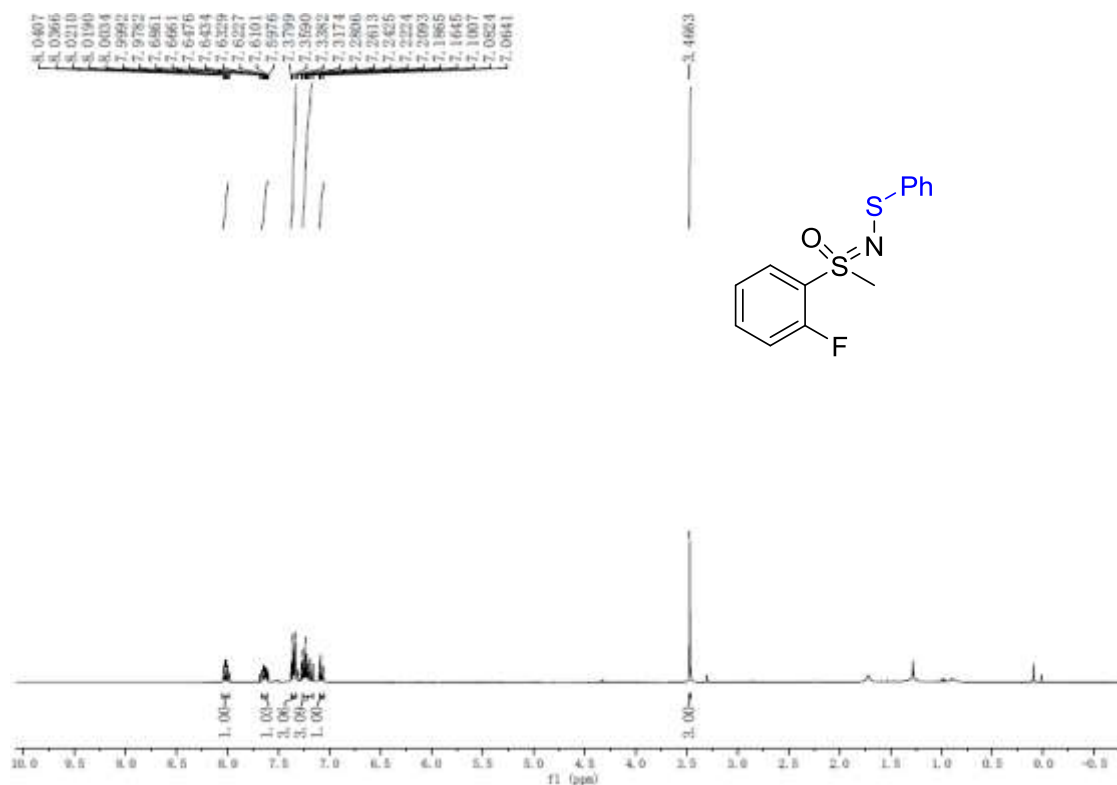
**S-methyl-S-(4-nitrophenyl)-N-phenylthiosulfoximine (3ja)**



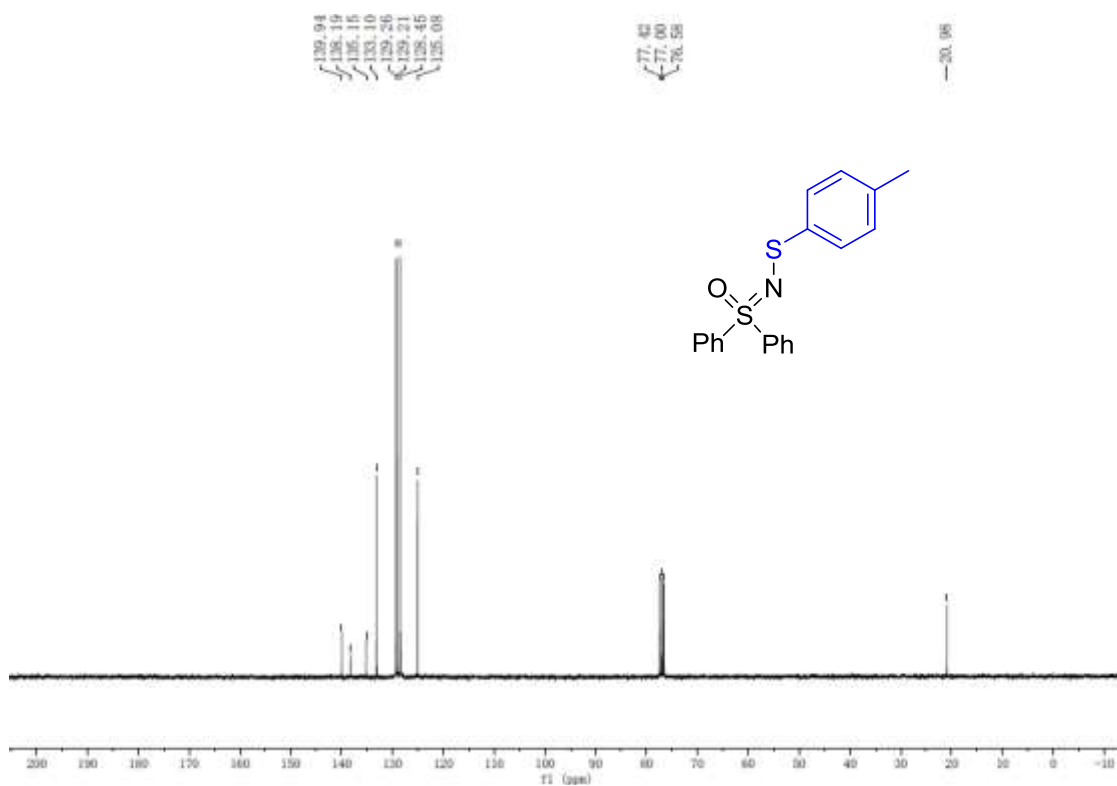
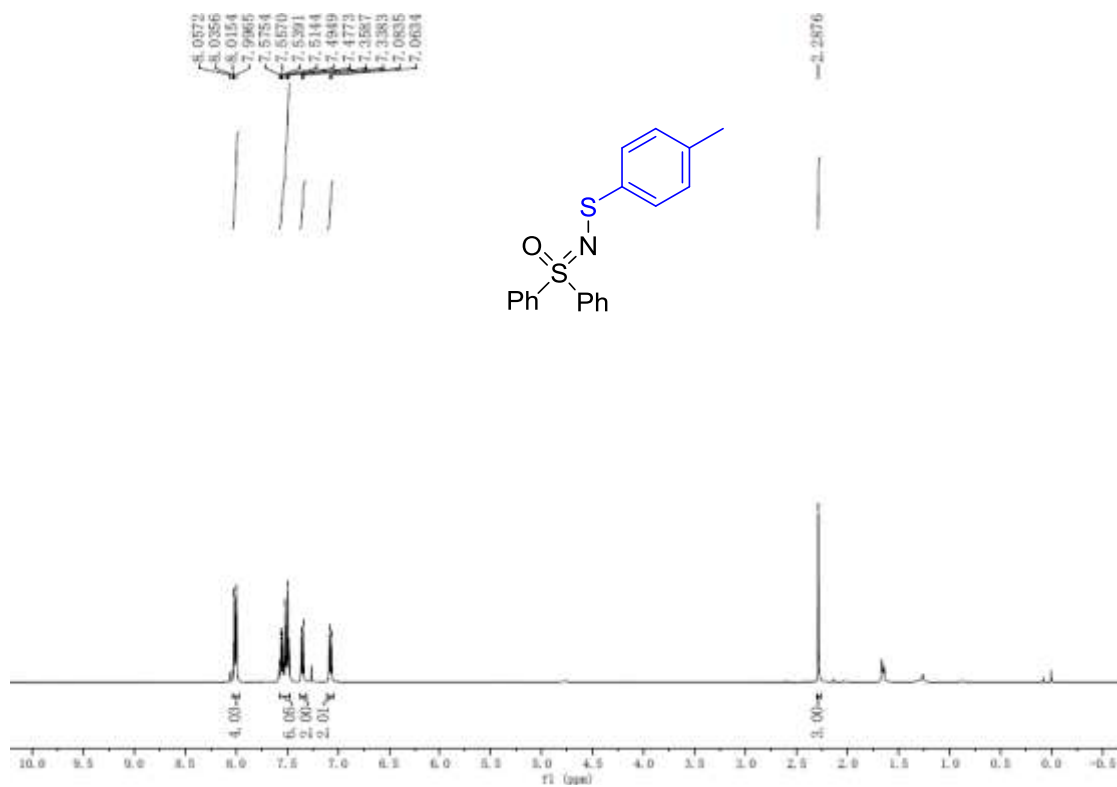
**S-methyl-S-(4-fluorophenyl)-N-phenylthiosulfoximine (3ka)**



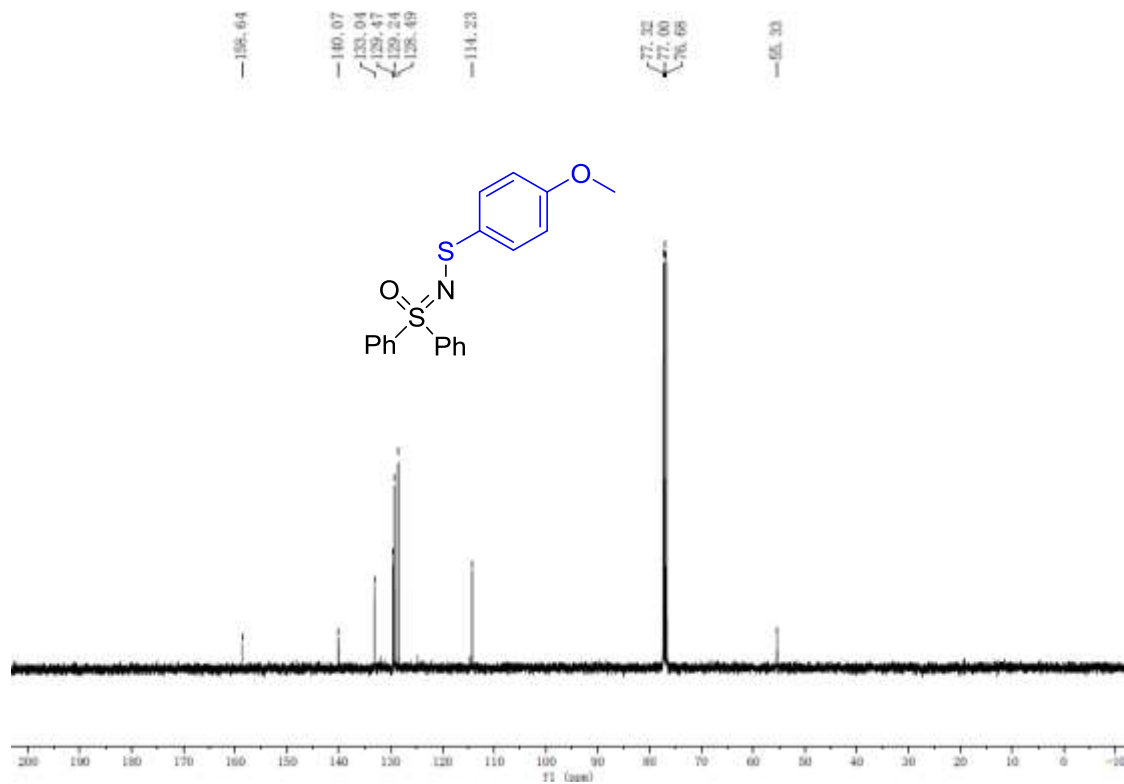
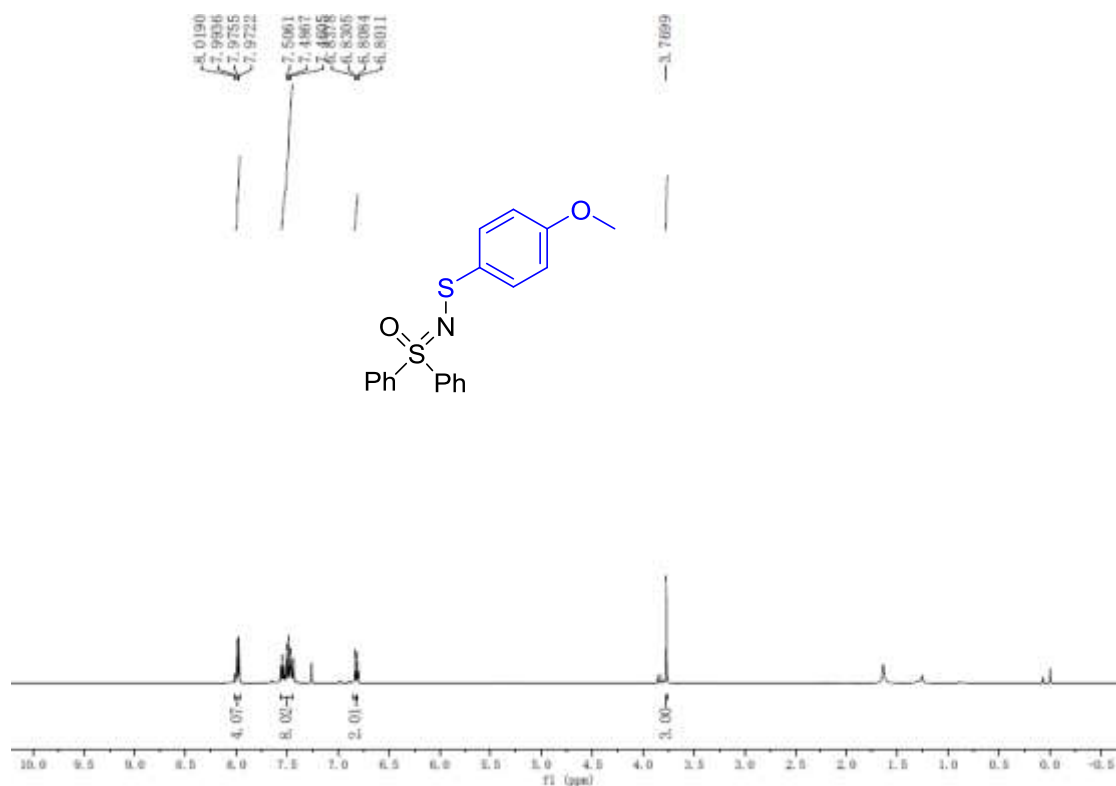
**S-methyl-S-(2-fluorophenyl)-N-phenylthiosulfoximine (3la)**



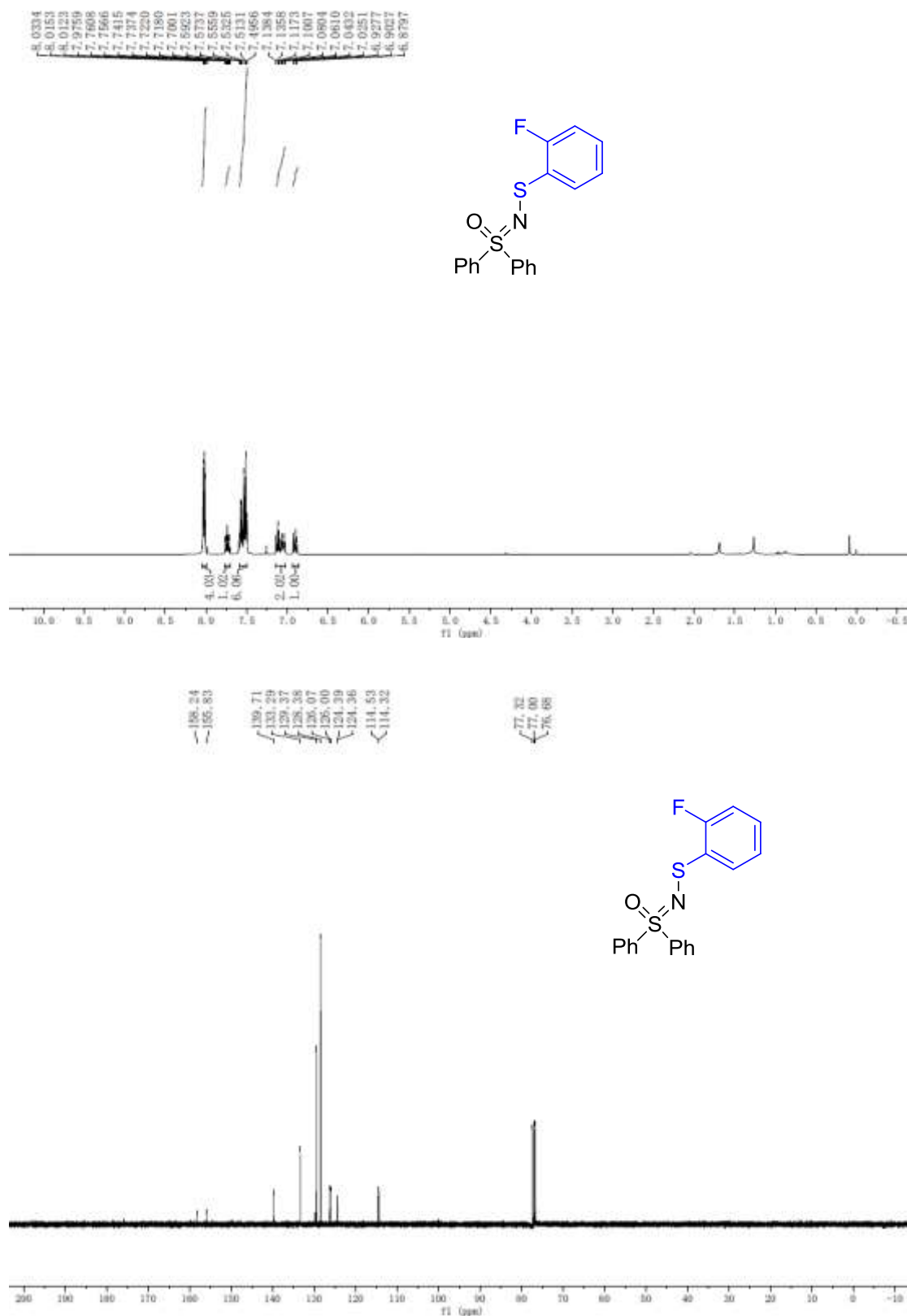
***S,S*-diphenyl-*N*-(4-methylphenylthio)sulfoximine (3ab)**



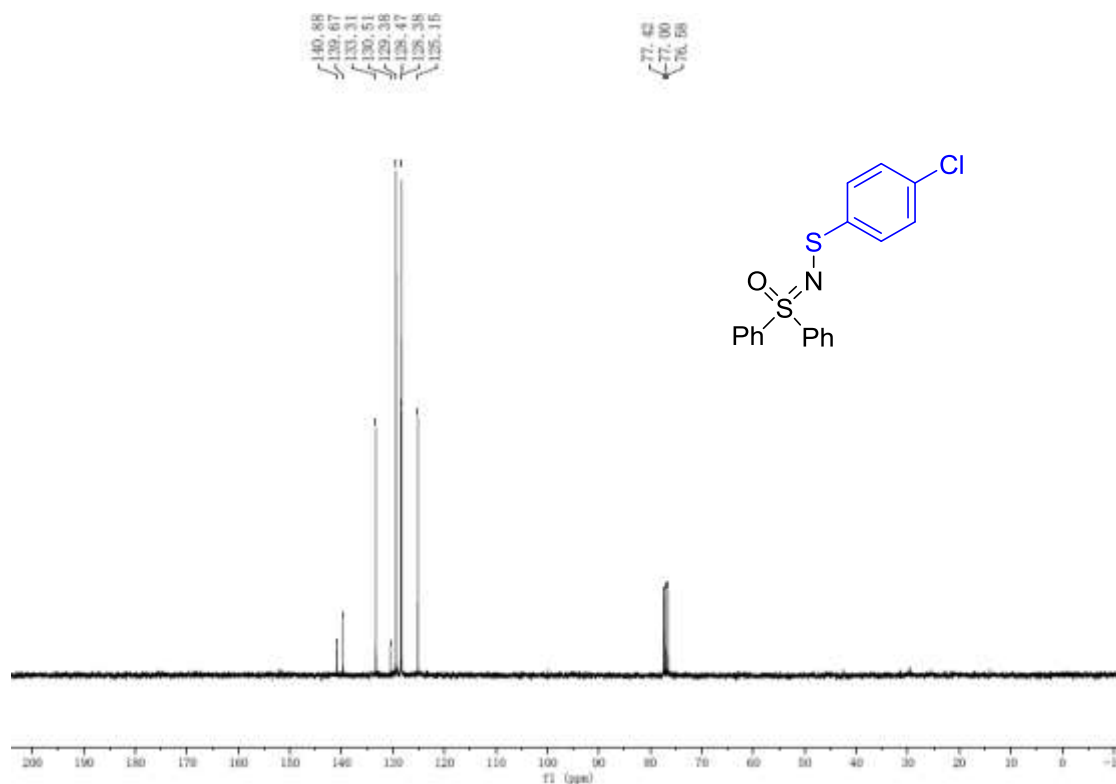
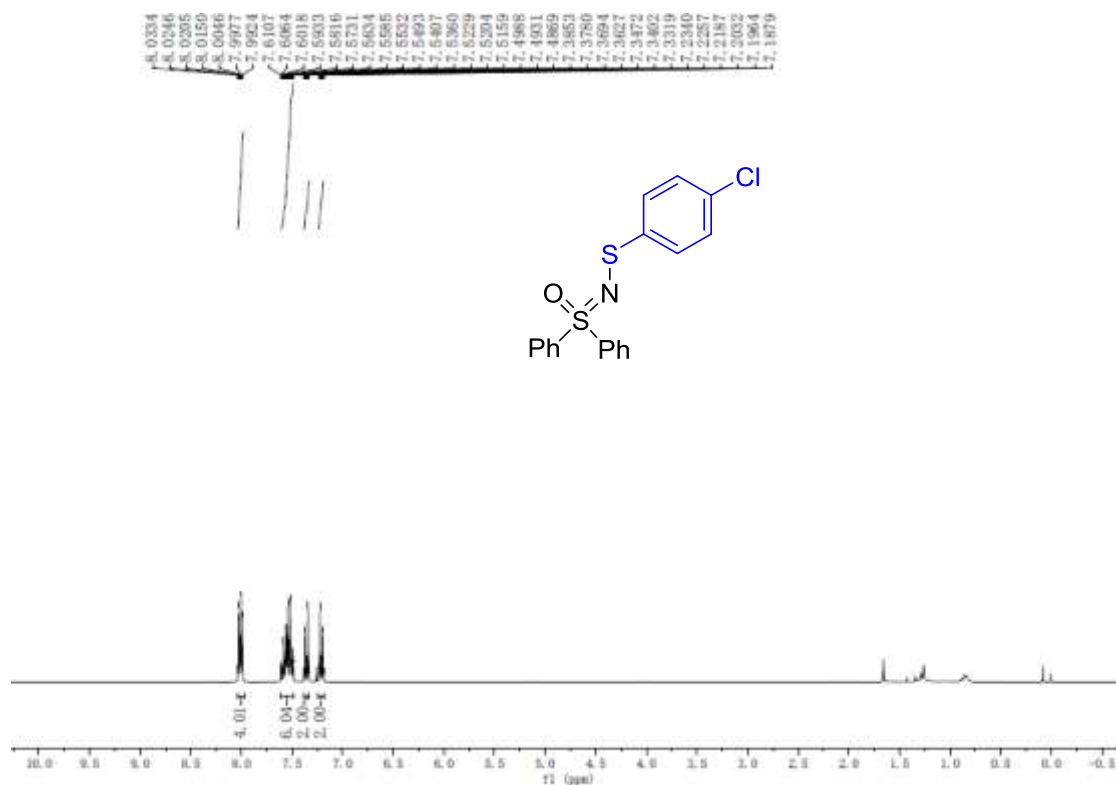
***S,S*-diphenyl-*N*-(4-methoxyphenylthio)sulfoximine (3ac)**



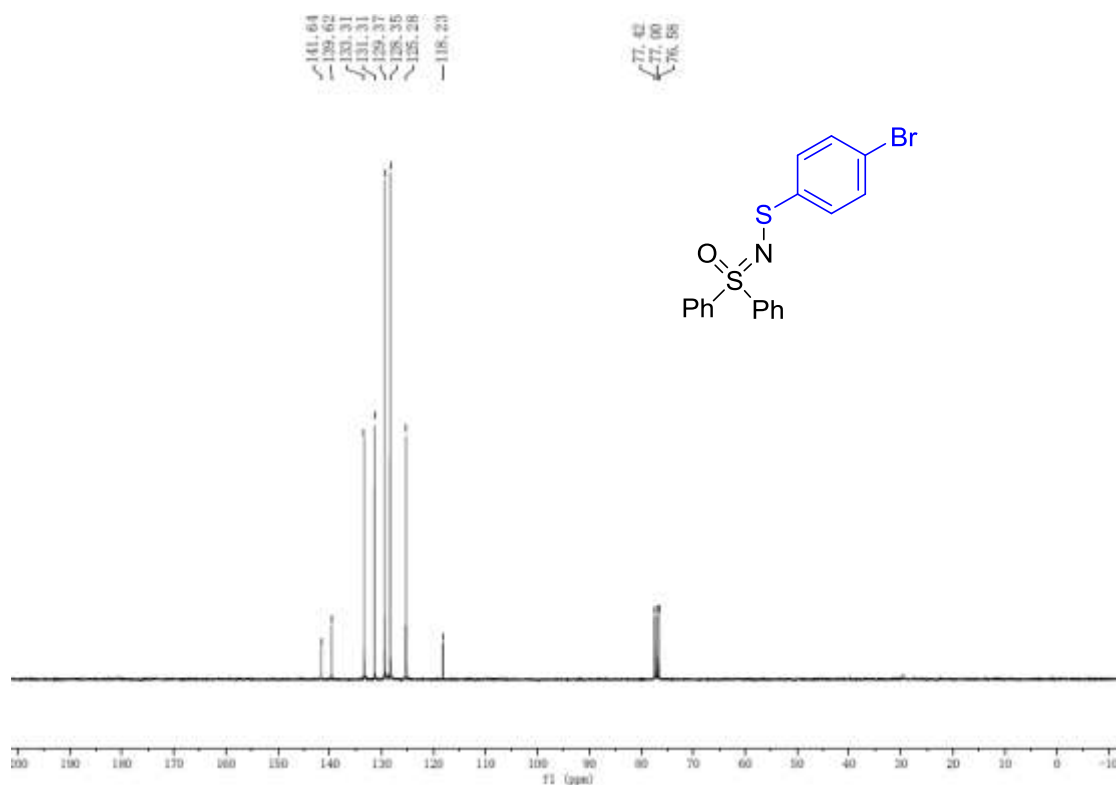
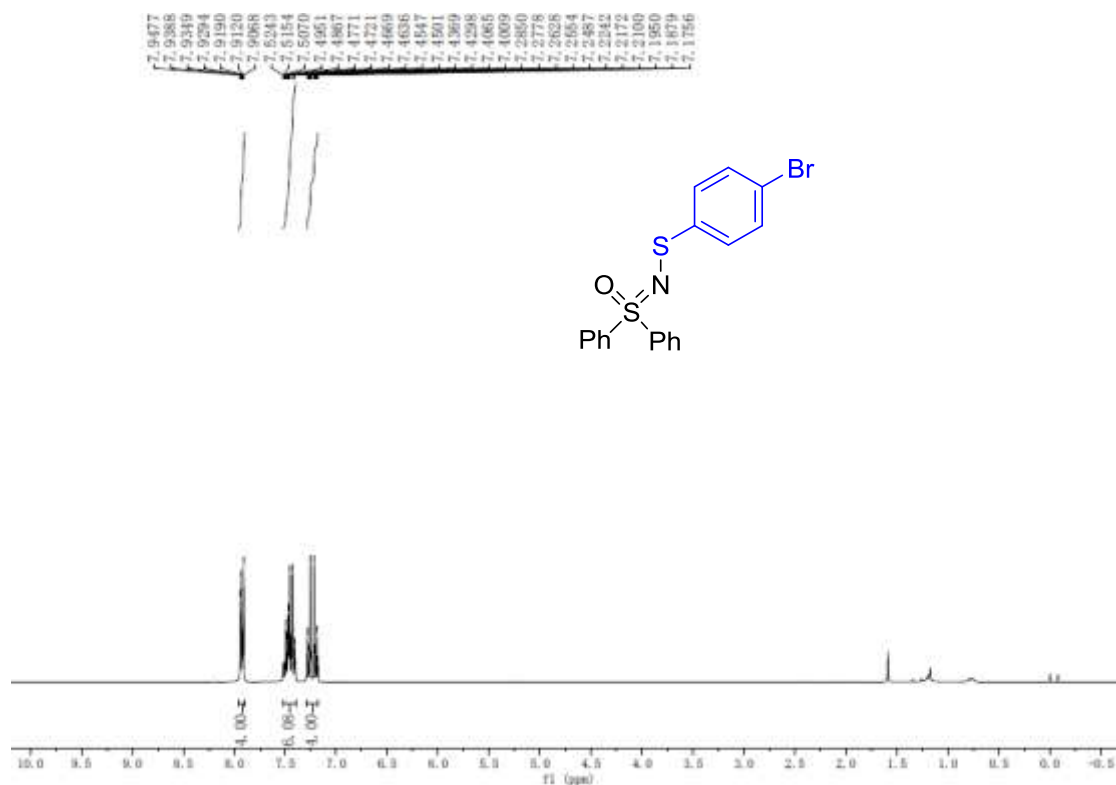
***S,S*-diphenyl-*N*-(2-fluorophenylthio)sulfoximine (3ad)**



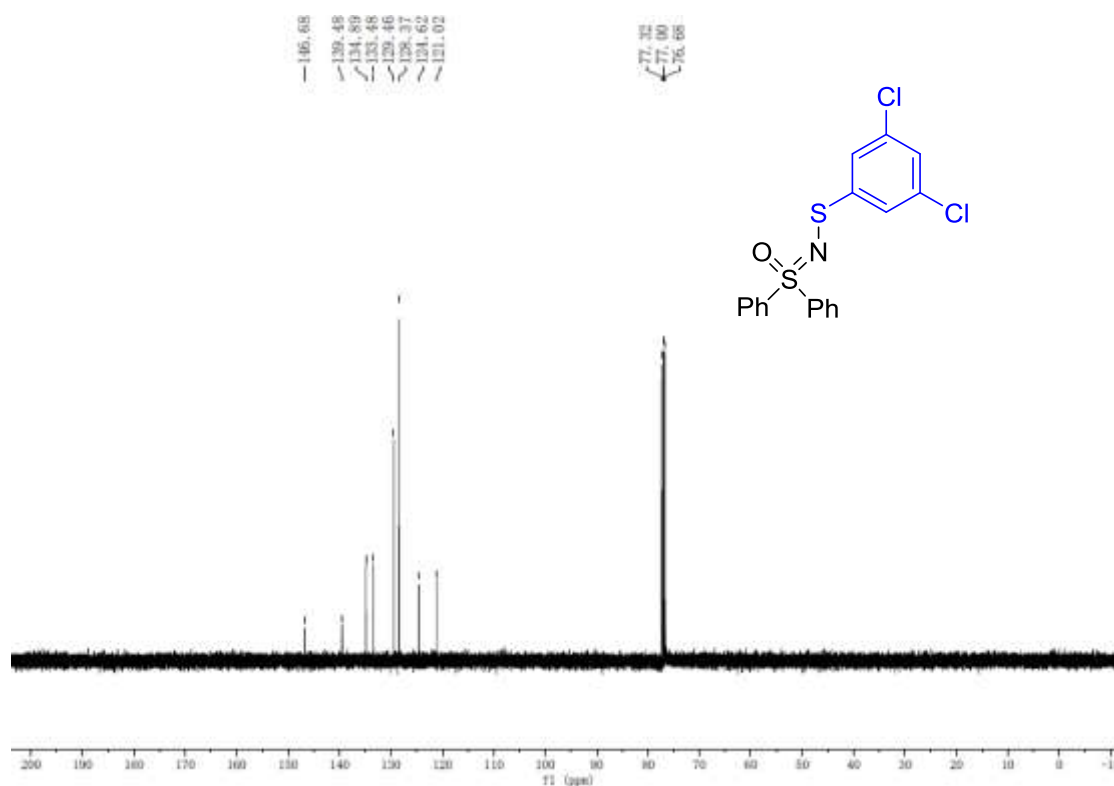
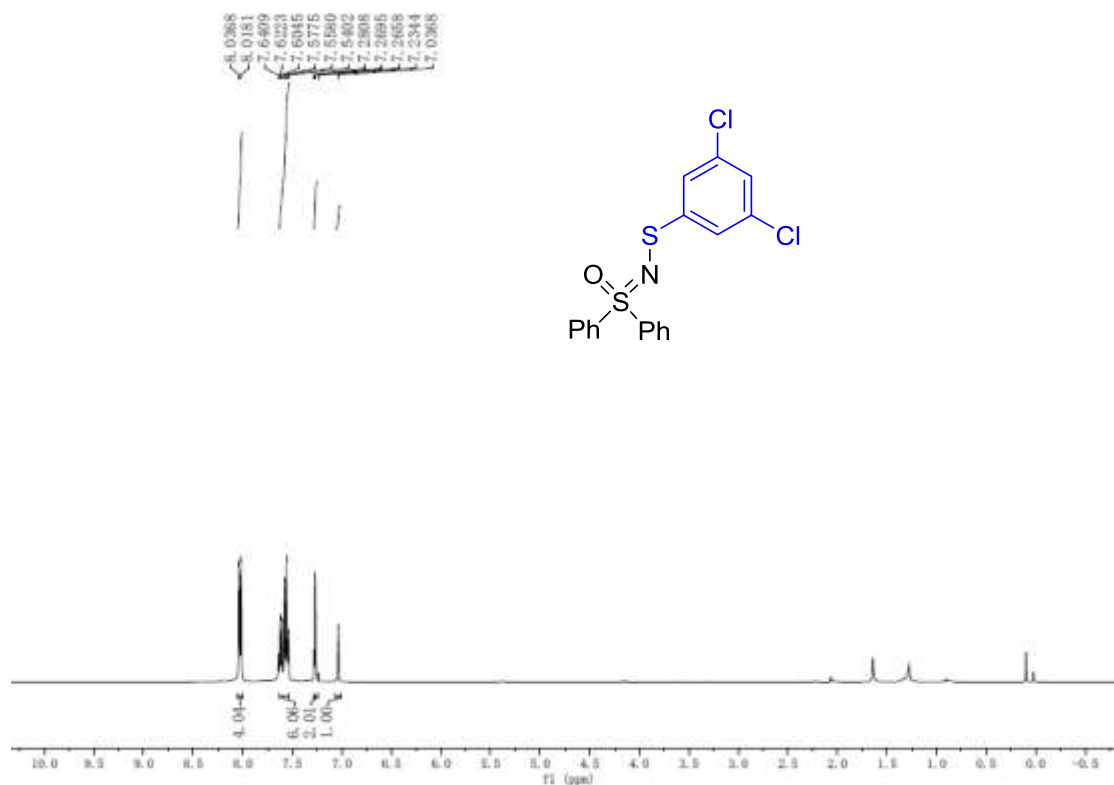
***S,S*-diphenyl-*N*-(4-chlorophenylthio)sulfoximine (3ae)**



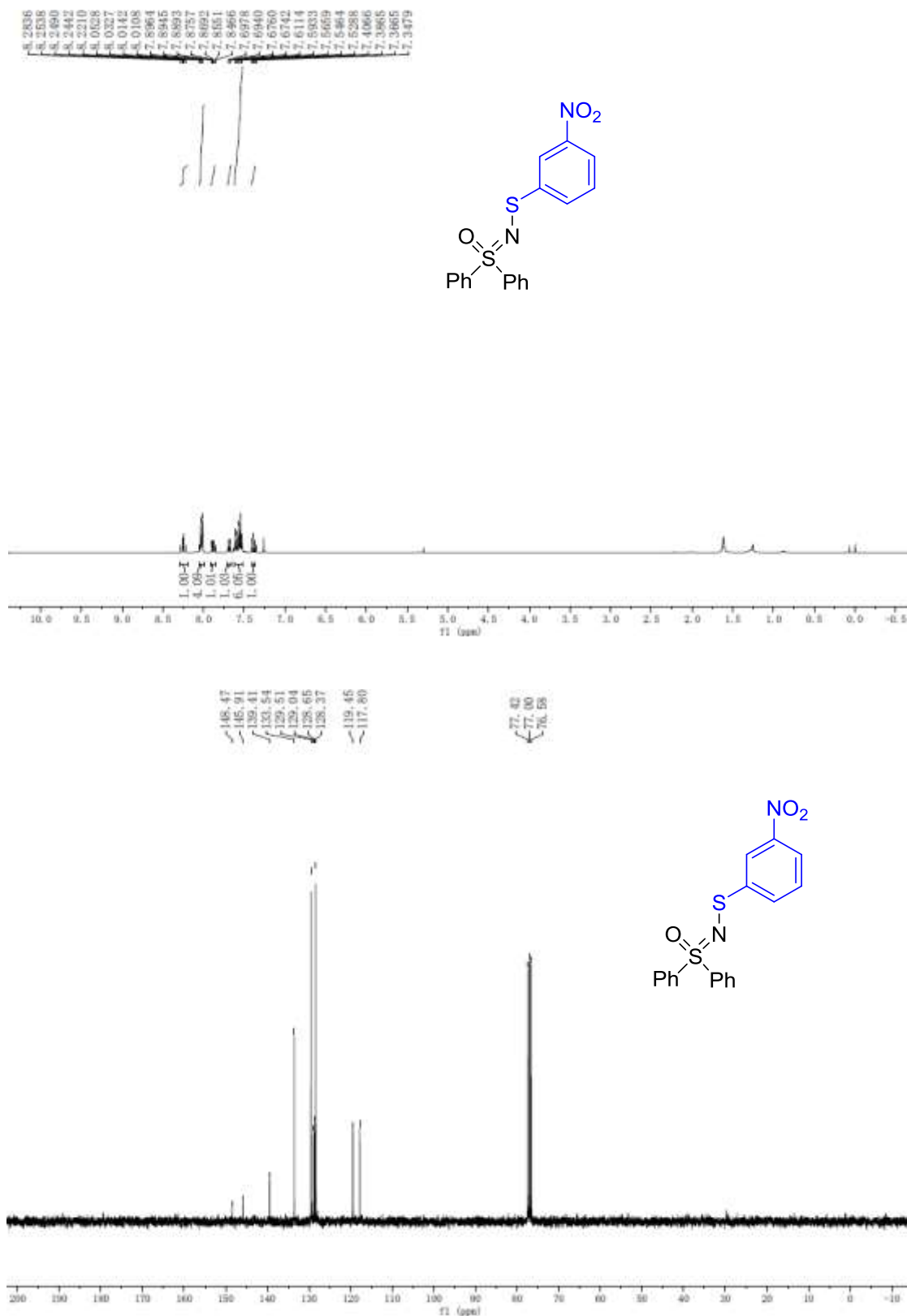
***S,S*-diphenyl-*N*-(4-bromophenylthio)sulfoximine (3af)**



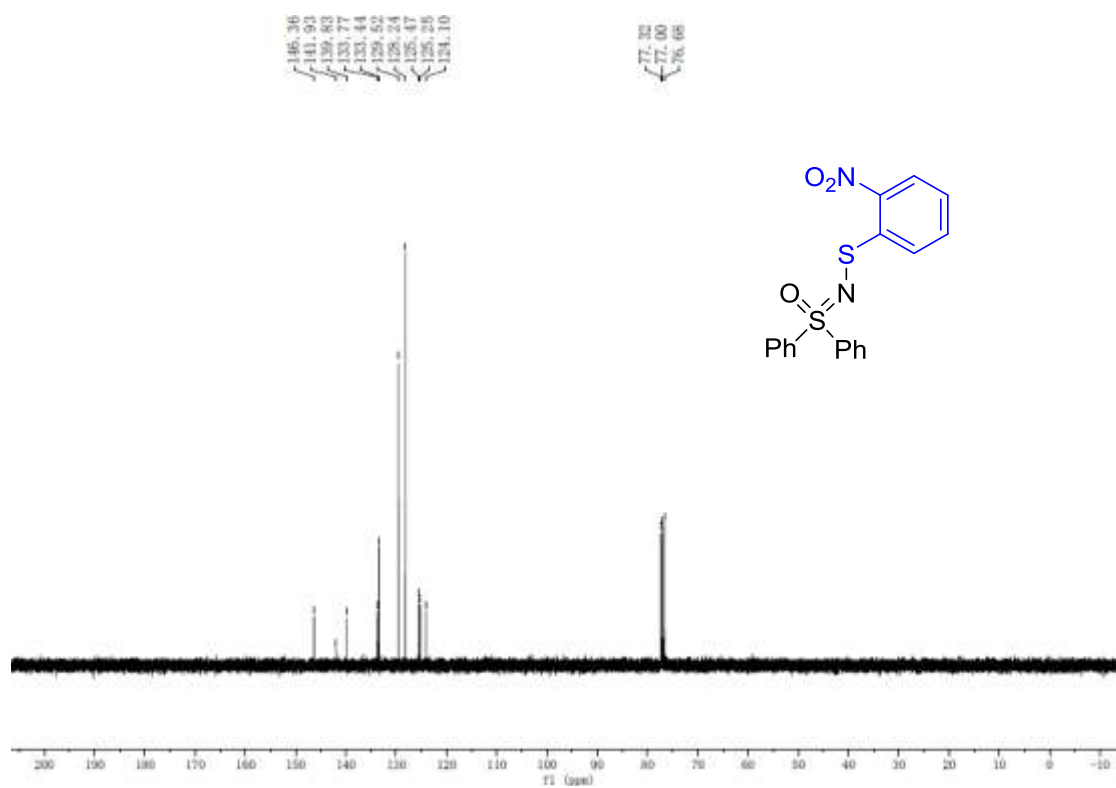
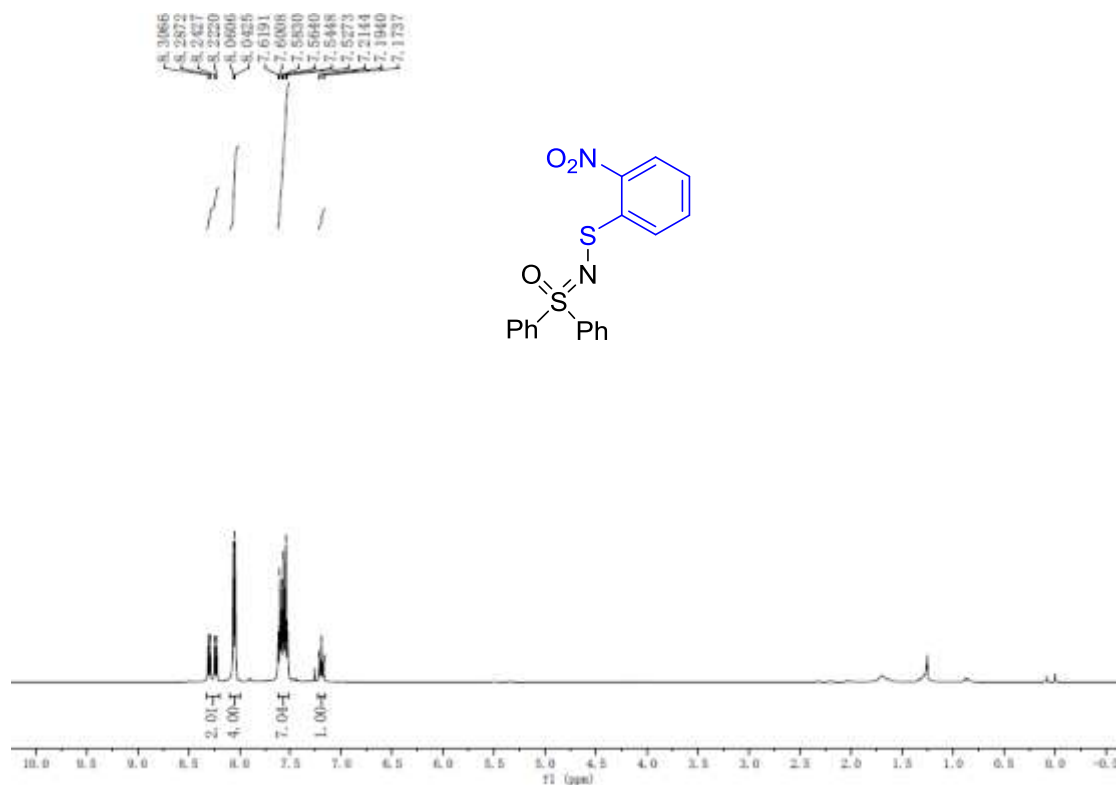
***S,S*-diphenyl-*N*-(3,5-dichlorophenylthio)sulfoximine (3ag)**



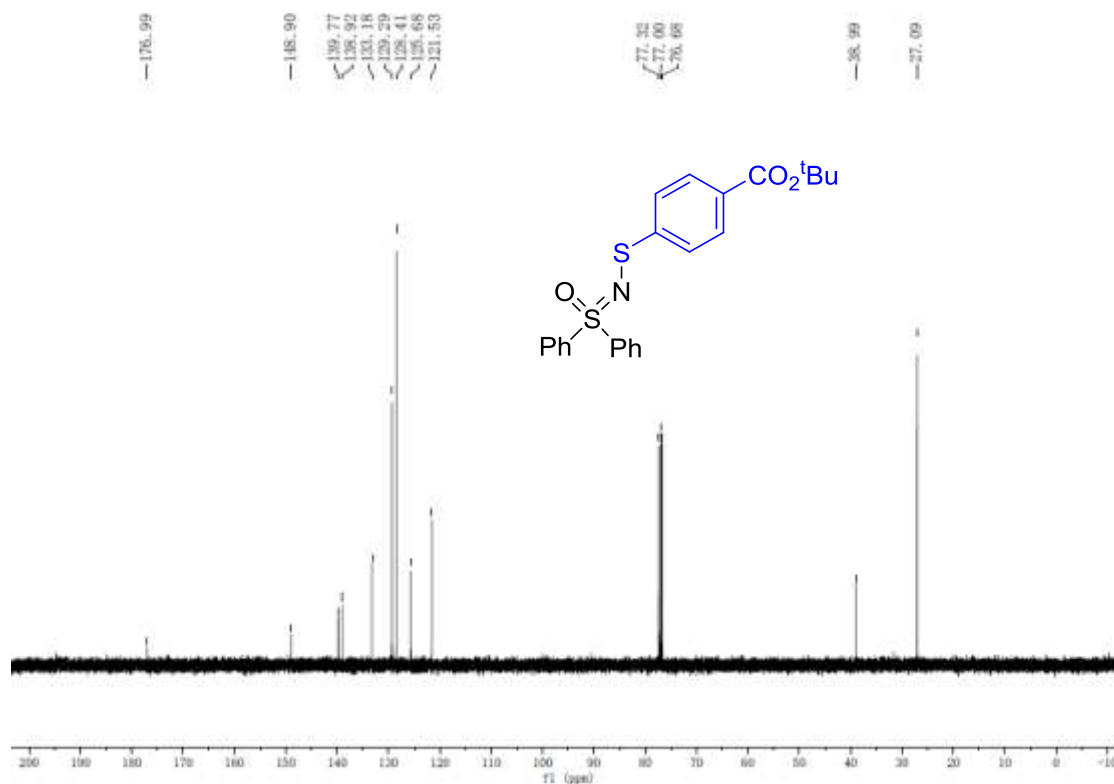
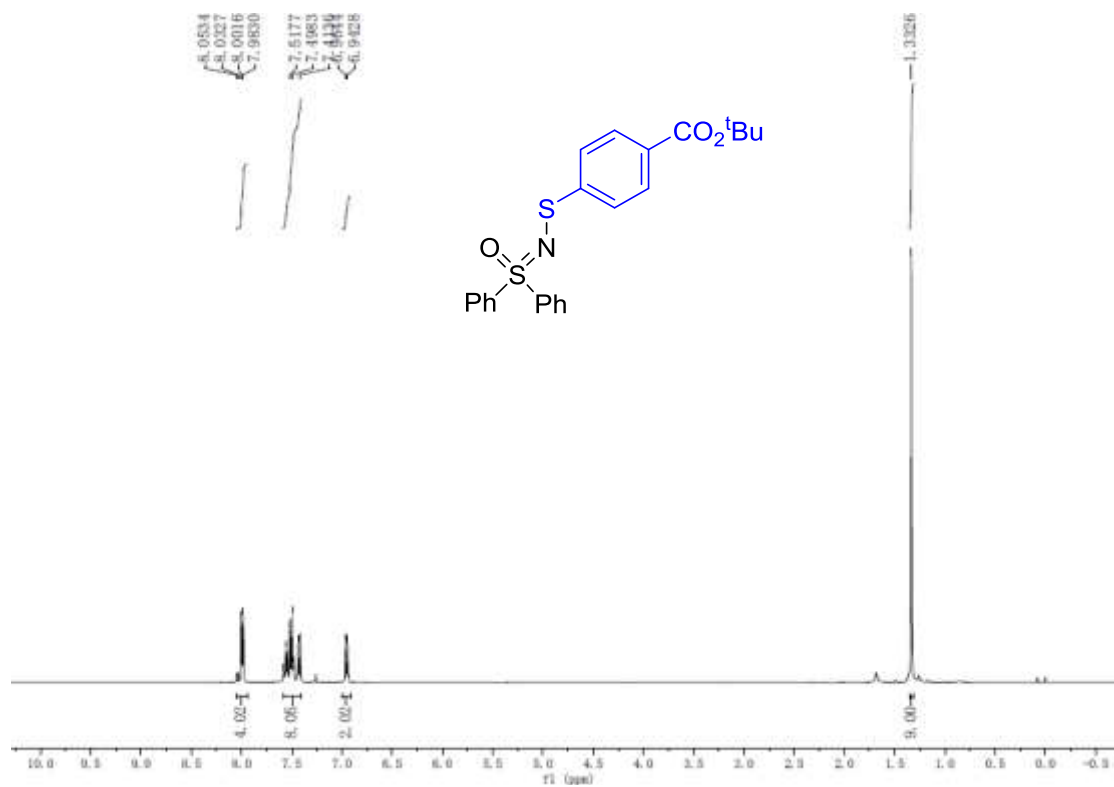
***S,S*-diphenyl-*N*-(3-nitrophenylthio)sulfoximine (3ah)**



***S,S*-diphenyl-*N*-(2-nitrophenylthio)sulfoximine (3ai)**



***S,S*-diphenyl-*N*-(pivalatephenylthio)sulfoximine (3aj)**



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

