Supplementary Information

# Catalyst-free visible-light-initiated oxidative coupling of aryldiazo sulfones with thiols leading to unsymmetrical sulfoxides in air

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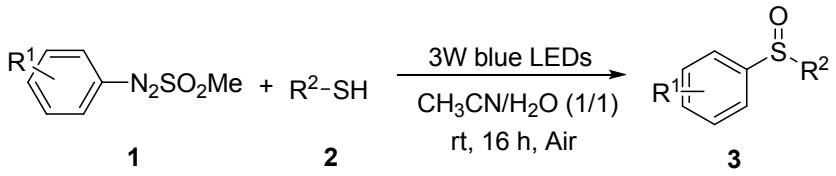
# Contents

## 1. General information

All commercially available reagent grade chemicals were purchased from Aldrich, Acros, Alfa Aesar and Energy Chemical Company and used as received without further purification unless otherwise stated. All solvents were dried according to standard procedures. $^{1}H$ NMR and $^{13}C$ NMR were recorded in $CDCl_3$ on a Bruker Avance III 400 spectrometer with TMS as internal standard (500 MHz $^{1}H$, 125 MHz $^{13}C$) at room temperature, the chemical shifts ($\delta$) were expressed in ppm and $J$ values were given in Hz. The following abbreviations are used to indicate the multiplicity: singlet (s), doublet (d), triplet (t), quartet (q), doublet of doublets (dd), doublet of triplets (dt), and multiplet (m). All first order splitting patterns were assigned on the basis of the appearance of the multiplet. Splitting patterns that could not be easily interpreted were designated as multiplet (m). Mass analyses and HRMS were obtained on a Finnigan-LCQDECA mass spectrometer and a Bruker Daltonics Bio-TOF-Q mass spectrometer by the ESI method, respectively. Column chromatography was performed on silica gel (200-300 mesh). There is 3.0 cm distance between the reactor and LEDs.

## 2. General procedure for the synthesis of sulfoxides from aryldiazo sulfones and various thiols in air.

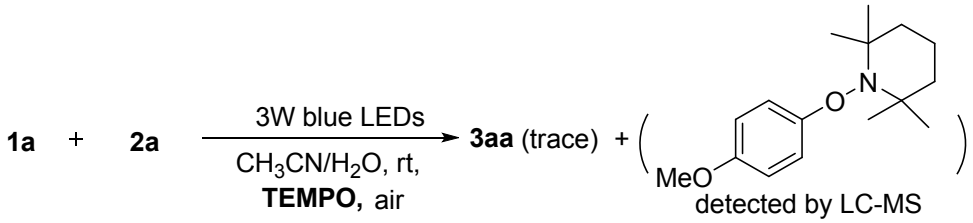



**1** **2** **3**

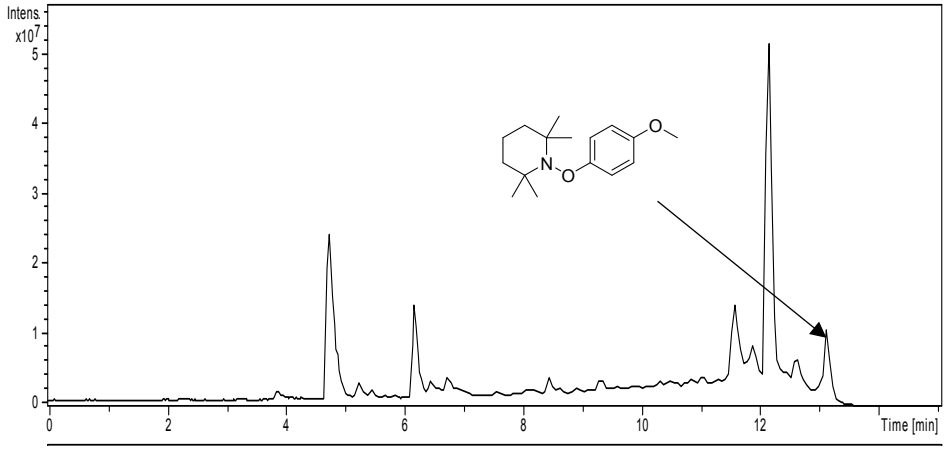
To a solution of aryldiazo sulfones **1** (0.3 mmol) in $CH_3CN/H_2O$ ($v_1/v_2$=1/1, 2 mL) was added thiol **2** (0.1 mmol). The reaction mixture was open to the air and stirred under the irradiation of 3W blue LEDs at room temperature for 16h. After completion of the reaction, the solution was concentrated in vacuum. The residue was purified by flash column chromatography using a mixture of petroleum ether and ethyl acetate as eluent to give the desired product **3**.

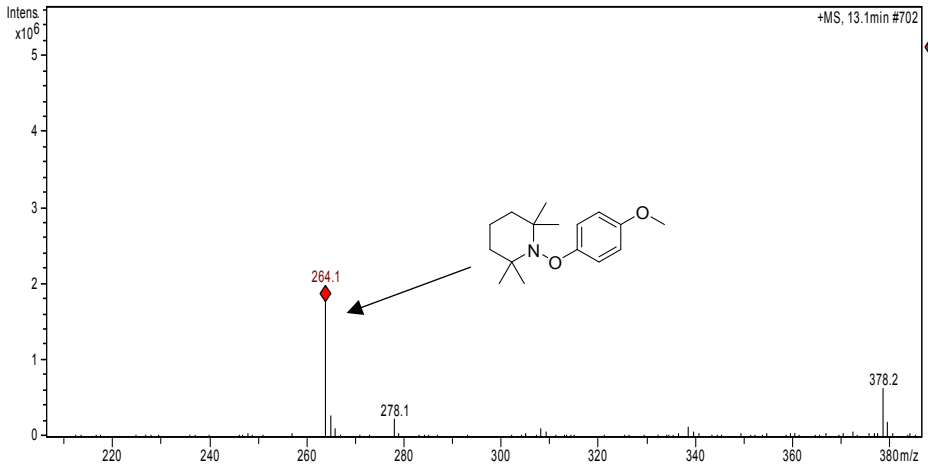
## 3. Preliminary mechanistic studies

### 3.1 The addition of TEMPO in the model reaction system.

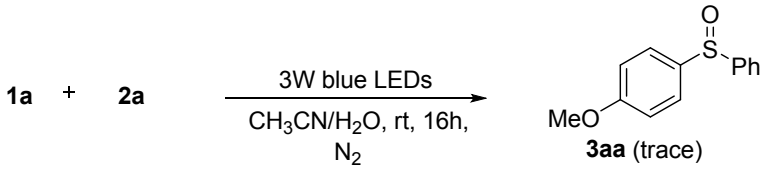



To a solution of 1-(4-methoxyphenyl)-2-(methylsulfonyl)diazene **1a** (0.3 mmol) and TEMPO (0.3 mmol) in $CH_3CN/H_2O$ ($v_1/v_2$=1/1, 2 mL) was added benzenethiol **2a**. The reaction mixture was open to the air and stirred under the irradiation of 3W blue LEDs at room temperature. After completion of the reaction, the solution was concentrated in vacuum, aryl-TEMPO adduct was detected LC-MS.



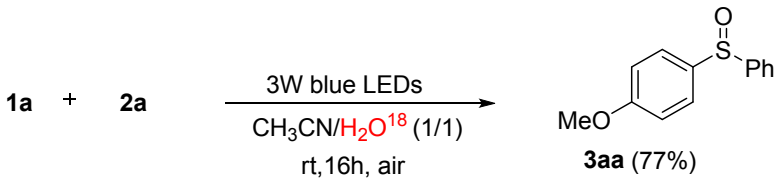




**3.2 The model reaction was carried out under $N_2$.**

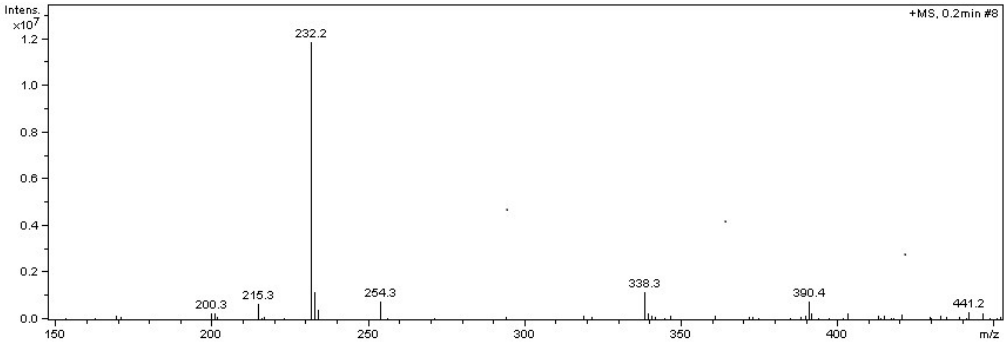



To the mixture of 1-(4-methoxyphenyl)-2-(methylsulfonyl)diazene **1a** (0.3 mmol) and benzenethiol **2a** (0.1 mmol) was added the solvent of $CH_3CN/H_2O$ ($v_1/v_2$=1/1, 2 mL) under $N_2$. The reaction mixture was stirred under the irradiation of 3W blue LEDs at room temperature. After completion of the reaction, the solution was concentrated in vacuum, only a trace amount of desired product was detected.

### 3.3 The model reaction was carried out under $H_2O^{18}$ ($^{18}O$-labeling experiment).




To a solution of 1-(4-methoxyphenyl)-2-(methylsulfonyl)diazene **1a** (0.3 mmol) in $CH_3CN/H_2O^{18}$ ($v_1/v_2$=1/1, 2 mL) was added benzenethiol **2a** (0.1 mmol). The reaction mixture was open to the air and stirred under the irradiation of 3W blue LEDs at room temperature. After completion of the reaction, the solution was concentrated in vacuum, The residue was purified by flash column chromatography using a mixture of petroleum ether and ethyl acetate as eluent to give the desired product **3aa** in 77% yield. The LC-MS spectrum of **3aa** is demonstrated as bellow

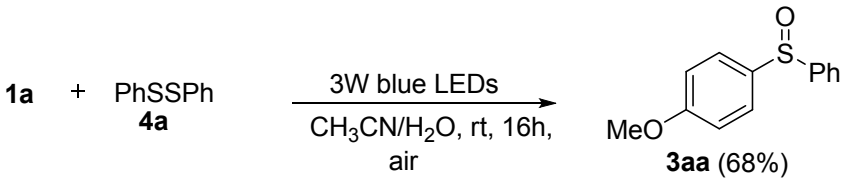



**MS spectra of 3aa**

### 3.4 The addition of DABCO in the model reaction system.

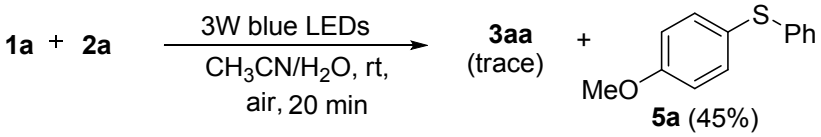

To a solution of 1-(4-methoxyphenyl)-2-(methylsulfonyl)diazene **1a** (0.3 mmol), and DABCO (0.2 mmol) in $CH_3CN/H_2O$ ($v_1/v_2$=1/1) 2 mL was added benzenethiol **2a** (0.1 mmol). The reaction mixture was open to the air and stirred under the irradiation of 3W blue LEDs at room temperature. After completion of the reaction, the solution was concentrated in vacuum, there is no desired product **3aa** was detected, which indicated that this transformation should involve $^1O_2$-mediated process.

### 3.5 The reaction of 1a with 4a.




$CH_3CN/H_2O$ ($v_1/v_2$=1/1) 2 mL was added to the mixture of 1,2-diphenyldisulfane **4a** and 1-(4-methoxyphenyl)-2-(methylsulfonyl)diazene **1a**. The reaction mixture was open to the air and stirred under the irradiation of 3W blue LEDs at room temperature. After completion of the reaction, the solution was concentrated in vacuum. The residue was purified by flash column chromatography using a mixture of petroleum ether and ethyl acetate as eluent to give the product **3aa** in 68% yield.

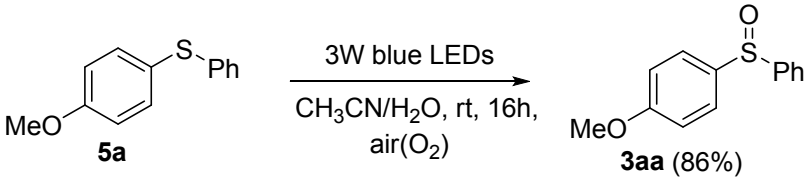
### 3.6 The model reaction was carried out for 20 min.




To a solution of 1-(4-methoxyphenyl)-2-(methylsulfonyl)diazene **1a** (0.3 mmol) in $CH_3CN/H_2O$ ($v_1/v_2$=1/1, 2 mL) was added benzenethiol **2a** (0.1 mmol). The reaction mixture was open to the air and stirred under the irradiation of 3W blue LEDs at room

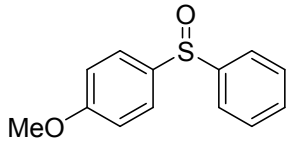
temperature for 20 min. The solution was concentrated in vacuum. The residue was purified by flash column chromatography using a mixture of petroleum ether and ethyl acetate as eluent to give the **5a** in 45%.

### 3.7 The transformation of 5a under the standard conditions.

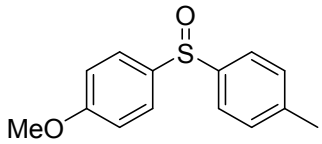



To a solution of $CH_3CN/H_2O$ ($v_1/v_2$=1/1, 2 mL) was added sulfide **5a** (0.1 mmol). The reaction mixture was open to the air and stirred under the irradiation of 3 W blue LEDs at room temperature for 16h. After completion of the reaction, the solution was concentrated in vacuum. The residue was purified by flash column chromatography using a mixture of petroleum ether and ethyl acetate as eluent to give the product **3aa** in 86% yield.

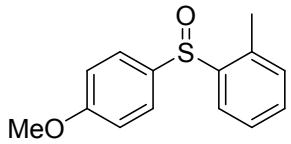
## 4. Characterization data of products 3aa-3ia



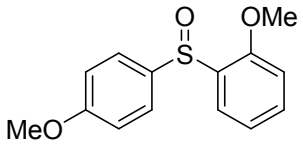

**1-Methoxy-4-(phenylsulfinyl)benzene**[1], Compound **3aa** was obtained in 79% yield according to the general procedure. $^1$H NMR ($CDCl_3$, 500 MHz, ppm): $\delta$ 7.62-7.60 (m, 2H), 7.58-7.56 (m, 2H), 7.47-7.43 (m, 3H), 6.96 (d, $J$ = 8.9 Hz, 2H), 3.82 (s, 3H); $^{13}$C NMR ($CDCl_3$, 125 MHz, ppm): $\delta$ 162.1, 145.7, 136.6, 130.8, 129.2, 127.3, 124.6, 114.9, 55.5; MS (EI); $[M+H]^+$: 233.2.



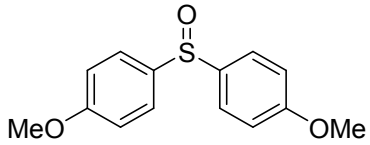
**1-Methoxy-4-(p-tolylsulfinyl)benzene**[1], Compound **3ab** was obtained in 82% yield according to the general procedure. $^1$H NMR ($CDCl_3$, 500 MHz, ppm): $\delta$ 7.55 (d, $J$ = 8.9 Hz, 2H), 7.49 (d, $J$ = 8.2 Hz, 2H), 7.25 (d, $J$ = 8.7 Hz, 2H), 6.95 (d, $J$ = 8.9 Hz, 2H), 3.81 (s, 3H), 2.37 (s, 3H); $^{13}$C NMR ($CDCl_3$, 125 MHz, ppm): $\delta$ 161.9, 142.7, 141.3, 137.0, 129.9, 127.1, 124.8, 114.8, 55.5, 21.4; MS (EI); $[M+H]^+$: 247.1.




**1-(4-Methoxyphenylsulfinyl)-2-methylbenzene**[1], Compound **3ac** was obtained in 80% yield according to the general procedure. $^1$H NMR ($CDCl_3$, 500 MHz, ppm): $\delta$ 8.03-8.01 (m, 1H), 7.52 (d, $J$ = 8.9 Hz, 2H), 7.44 (t, $J$ = 7.6 Hz, 1H), 7.38-7.35 (m, 1H), 7.15 (d, $J$ = 7.5 Hz, 1H), 6.93 (d, $J$ = 8.9 Hz, 2H), 3.81 (s, 3H), 2.26 (s, 3H); $^{13}$C NMR ($CDCl_3$, 125 MHz, ppm): $\delta$ 162.0, 142.8, 135.5, 135.3, 130.9, 130.8, 128.5, 127.0, 124.2, 114.8, 55.5, 18.5; MS (EI); $[M+H]^+$: 247.2.

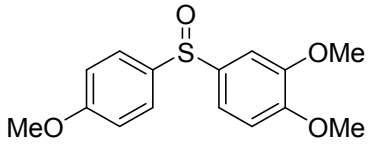



**1-Methoxy-2-(4-methoxyphenylsulfinyl)benzene**, Compound **3ad** was obtained in 82% yield according to the general procedure. $^1$H NMR ($CDCl_3$, 500 MHz, ppm): $\delta$ 7.94-7.92 (m, 1H), 7.61 (d, $J$ = 8.8 Hz, 2H), 7.42-7.38 (m, 1H), 7.16 (t, $J$ = 7.5 Hz, 1H), 6.91 (d, $J$ = 8.8 Hz, 2H), 6.84 (d, $J$ = 8.2 Hz, 1H), 3.80 (s, 3H), 3.77 (s, 3H); $^{13}$C NMR ($CDCl_3$, 125 MHz, ppm): $\delta$ 116.7, 115.5, 136.6, 133.3, 132.0, 127.5, 124.5, 121.5, 114.4, 111.0, 55.7, 55.4; HRMS calc. for $C_{14}H_{15}O_3S$ $(M+H)^+$, 263.0742; found, 263.0745.

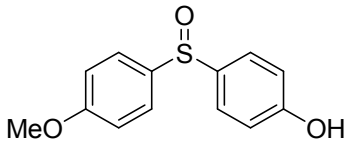



**4,4'-Sulfinylbis(methoxybenzene),** Compound **3ae** was obtained in 81% yield according to the general procedure. $^1$H NMR ($CDCl_3$, 500 MHz, ppm): $\delta$ 7.53 (d, $J$ = 8.8 Hz, 4H),

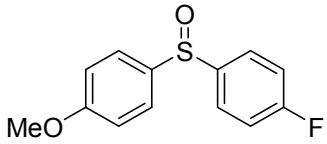
6.95 (d, $J$ = 8.8 Hz, 4H), 3.82 (s, 6H); $^{13}$C NMR ($CDCl_3$, 125 MHz, ppm): $\delta$ 161.8, 137.0, 126.9, 114.7, 55.5; HRMS calc. for $C_{14}H_{15}O_3S$ $(M+H)^+$, 263.0742; found, 263.0746.




**4,4'-Sulfinylbis(methoxybenzene),** Compound **3af** was obtained in 66% yield according to the general procedure. $^1$H NMR ($CDCl_3$, 500 MHz, ppm): $\delta$ 7.54 (d, $J$ = 8.8 Hz, 2H), 7.16 – 7.14 (m, 2H), 6.96 (d, $J$ = 8.8 Hz, 2H), 6.91 (d, $J$ = 8.8 Hz, 1H), 3.89 (s, 3H), 3.88 (s, 3H), 3.82 (s, 3H).; $^{13}$C NMR ($CDCl_3$, 125 MHz, ppm): $\delta$ 161.9, 151.3, 149.9, 137.1, 137.0, 126.9, 118.5, 114.7, 111.0, 107.0, 56.1, 56.1, 55.5; HRMS calc. for $C_{15}H_{17}O_4S$ $(M+H)^+$, 293.0848; found, 293.0849.




**4-(4-Methoxyphenylsulfinyl)phenol,** Compound **3ag** was obtained in 81% yield according to the general procedure. $^1$H NMR ($CDCl_3$, 500 MHz, ppm): $\delta$ 7.49 (d, $J$ = 8.8 Hz, 2H), 7.38 (d, $J$ = 8.6 Hz, 2H), 6.95 (d, $J$ = 8.8 Hz, 2H), 6.88 (d, $J$ = 8.7 Hz, 2H), 3.81 (s, 3H). $^{13}$C NMR ($CDCl_3$, 125 MHz, ppm): $\delta$ 162.0, 160.3, 135.2, 133.9, 127.7, 127.1, 116.7, 114.9, 55.5; HRMS calc. for $C_{13}H_{13}O_3S$ $(M+H)^+$, 249.0585; found, 249.0589.




**1-Fluoro-4-(4-methoxyphenylsulfinyl)benzene[1],** Compound **3ah** was obtained in 77% yield according to the general procedure. $^1$H NMR ($CDCl_3$, 500 MHz, ppm): $\delta$ 7.62 – 7.58 (m, 2H), 7.55 (d, $J$ = 8.9 Hz, 2H), 7.15 (t, $J$ = 8.6 Hz, 2H), 6.97 (d, $J$ = 8.8 Hz, 2H), 3.82 (s, 3H). $^{13}$C NMR ($CDCl_3$, 125 MHz, ppm): $\delta$ 164.2 (d, $J_{CF}$ = 250.0 Hz), 162.2, 141.3 (d, $J_{CF}$ = 2.9 Hz), 136.4, 127.2, 127.0 (d, $J_{CF}$ = 8.9 Hz), 116.5 (d, $J_{CF}$ = 22.4 Hz), 114.9, 55.5; MS (EI); $[M+H]^+$: 251.1.

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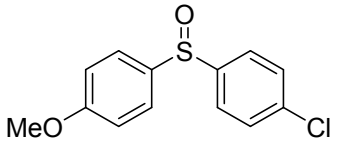
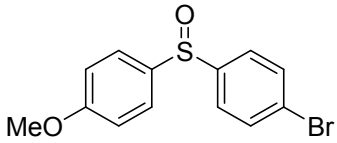
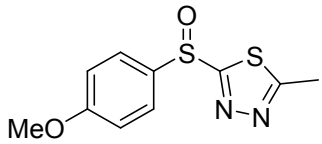


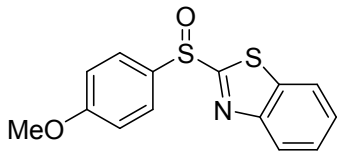

**1-Chloro-4-(4-methoxyphenylsulfinyl)benzene**[1]**,** Compound **3ai** was obtained in 68% yield according to the general procedure. $^1$H NMR ($CDCl_3$, 500 MHz, ppm): $\delta$ 7.58 – 7.52 (m, 4H), 7.43 (d, $J$ = 8.6 Hz, 2H), 6.97 (d, $J$ = 8.8 Hz, 2H), 3.83 (s, 3H); $^{13}$C NMR ($CDCl_3$, 125 MHz, ppm): $\delta$ 162.3, 144.3, 137.0, 136.2, 129.5, 127.3, 126.0, 115. 0, 55.6; MS (EI); $[M+H]^+$: 267.2.



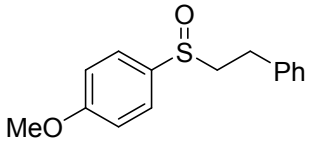

**1-Bromo-4-(4-methoxyphenylsulfinyl)benzene,** Compound **3aj** was obtained in 58% yield according to the general procedure. $^1$H NMR ($CDCl_3$, 500 MHz, ppm): $\delta$ 7.59 (d, $J$ = 8.6 Hz, 2H), 7.55 (d, $J$ = 8.9 Hz, 2H), 7.47 (d, $J$ = 8.6 Hz, 2H), 6.96 (d, $J$ = 8.9 Hz, 2H), 3.82 (s, 3H).; $^{13}$C NMR ($CDCl_3$, 125 MHz, ppm): $\delta$ 162.3, 145.0, 136.2, 132.4, 127.3, 126.1, 125.2, 115.0, 55.6; HRMS calc. for $C_{13}H_{12}BrO_2S$ $(M+H)^+$, 310.9741; found, 310.9743.



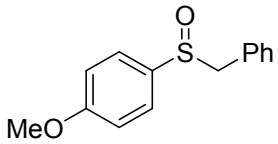

**2-(4-Methoxyphenylsulfinyl)-5-methyl-1,3,4-thiadiazole,** Compound **3ak** was obtained in 46% yield according to the general procedure. $^1$H NMR ($CDCl_3$, 500 MHz, ppm): $\delta$ 7.74 (d, $J$ = 8.8 Hz, 2H), 7.04 (d, $J$ = 8.8 Hz, 2H), 3.85 (s, 3H), 2.79 (s, 3H); $^{13}$C NMR ($CDCl_3$, 125 MHz, ppm): $\delta$ 162.9, 133.7, 126.9, 126.5, 115.3, 114.7, 55.6, 16.1; HRMS calc. for $C_{10}H_{11}N_2O_2S_2$ $(M+H)^+$, 255.0262; found, 255.0265.



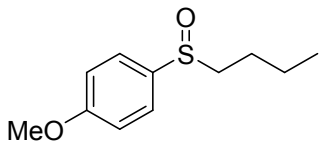
**2-(4-Methoxyphenylsulfinyl)benzo[d]thiazole,** Compound **3al** was obtained in 47% yield according to the general procedure. $^1$H NMR ($CDCl_3$, 500 MHz, ppm): $\delta$ 8.02 (d, $J$ = 7.9 Hz, 1H), 7.93 (d, $J$ = 8.1 Hz, 1H), 7.81 (d, $J$ = 8.9 Hz, 2H), 7.53 – 7.48 (m, 1H), 7.46 – 7.41 (m, 1H), 7.01 (d, $J$ = 8.9 Hz, 2H), 3.82 (s, 3H); $^{13}$C NMR ($CDCl_3$, 125 MHz, ppm): $\delta$ 178.7, 162.9, 153.8, 135.9, 134.0, 127.1, 126.8, 126.3, 124.2, 122.3, 115.2, 55.6; HRMS calc. for $C_{14}H_{12}NO_2S_2$ $(M+H)^+$, 290.0309; found, 290.0308.




**1-Methoxy-4-(phenethylsulfinyl)benzene,** Compound **3am** was obtained in 73% yield according to the general procedure. $^1$H NMR ($CDCl_3$, 500 MHz, ppm): $\delta$ 7.58 (d, $J$ = 8.8 Hz, 2H), 7.29 (t, $J$ = 7.4 Hz, 2H), 7.21 (t, $J$ = 7.4 Hz, 1H), 7.17 (d, $J$ = 7.1 Hz, 2H), 7.03 (d, $J$ = 8.7 Hz, 2H), 3.86 (s, 3H), 3.06 – 3.02 (m, 3H), 2.92-2.88 (m, 1H); $^{13}$C NMR ($CDCl_3$, 125 MHz, ppm): $\delta$ 162.0, 138.9, 134.5, 128.7, 128.5, 126.7, 126.0, 114.8, 58.5, 55.6, 28.3; HRMS calc. for $C_{15}H_{17}O_2S$ $(M+H)^+$, 261.0949; found, 261.0951.

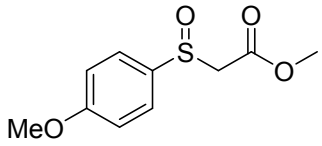



**1-(Benzylsulfinyl)-4-methoxybenzene,** Compound **3an** was obtained in 73% yield according to the general procedure. $^1$H NMR ($CDCl_3$, 500 MHz, ppm): $\delta$ 7.31 (d, $J$ = 8.8 Hz, 2H), 7.28 - 7.26 (m, 1H), 7.25 – 7.23 (m, 2H), 6.98 (d, $J$ = 6.5 Hz, 2H), 6.92 (d, $J$ = 8.8 Hz, 2H), 4.12 (d, $J$ = 12.5 Hz, 1H), 3.96 (d, $J$ = 12.5 Hz, 1H), 3.84 (s, 3H); $^{13}$C NMR ($CDCl_3$, 125 MHz, ppm): $\delta$ 162.1, 133.6, 130.4, 129.3, 128.5, 128.2, 126.4, 114.4, 63.8, 55.5; HRMS calc. for $C_{14}H_{15}O_2S$ $(M+H)^+$, 247.0793; found, 247.0791.

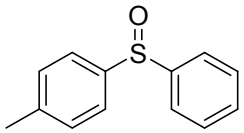



**1-(Butylsulfinyl)-4-methoxybenzene,** Compound **3ao** was obtained in 80% yield according to the general procedure. $^1$H NMR ($CDCl_3$, 500 MHz, ppm): $\delta$ 7.57 (d, $J$ = 8.7

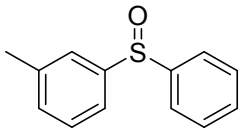
Hz, 2H), 7.03 (d, *J* = 8.7 Hz, 2H), 3.86 (s, 3H), 2.86 – 2.72 (m, 2H), 1.68 – 1.57 (m, 2H), 1.48 – 1.40 (m, 2H), 0.92 (t, J = 7.3 Hz, 3H); $^{13}$C NMR ($CDCl_3$, 125 MHz, ppm): $\delta$ 161.9, 134.9, 126.0, 114.7, 57.2, 55.5, 24.3, 21.9, 13.7; HRMS calc. for $C_{11}H_{17}O_2S$ $(M+H)^+$, 213.0949; found, 213.0951.



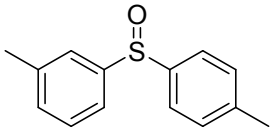

**2-(4-Methoxyphenylsulfinyl)acetate,** Compound **3ap** was obtained in 70% yield according to the general procedure. $^1$H NMR ($CDCl_3$, 500 MHz, ppm): $\delta$ 7.55 (d, *J* = 8.8 Hz, 2H), 6.96 (d, *J* = 8.8 Hz, 2H), 3.80 (d, *J* = 13.6 Hz, 1H), 3.79 (s, 3H), 3.63 (s, 3H), 3.57 (d, *J* = 13.6 Hz, 1H); $^{13}$C NMR ($CDCl_3$, 125 MHz, ppm): $\delta$ 164.2, 161.5, 132.8, 125.2, 113.9, 60.6, 54.6, 51.7; HRMS calc. for $C_{10}H_{13}O_4S$ $(M+H)^+$, 229.0535; found, 229.0537.



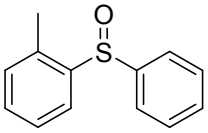

**1-Methyl-4-(phenylsulfinyl)benzene[2],** Compound **3ba** was obtained in 74% yield according to the general procedure. $^1$H NMR ($CDCl_3$, 500 MHz, ppm): $\delta$ 7.57 – 7.55(m, 2H), 7.46 (d, *J* = 8.2 Hz, 2H), 7.40 – 7.35 (m, 3H), 7.19 (d, *J* = 7.9 Hz, 2H), 2.29 (s, 3H); $^{13}$C NMR ($CDCl_3$, 125 MHz, ppm): $\delta$ 145.8, 142.5, 141.7, 130.9, 130.1, 129.3, 125.0, 124.7, 21.4; MS (EI); $[M+H]^+$: 217.2.



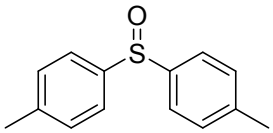

**1-Methyl-3-(phenylsulfinyl)benzene[3],** Compound **3ca** was obtained in 72% yield according to the general procedure. $^1$H NMR ($CDCl_3$, 500 MHz, ppm): $\delta$ 7.67 – 7.62 (m, 2H), 7.49 – 7.43 (m, 4H), 7.42 (d, *J* = 7.7 Hz, 1H), 7.33 (t, *J* = 7.6 Hz, 1H), 7.24 (d, *J* = 7.5 Hz, 1H), 2.38 (s, 3H); $^{13}$C NMR ($CDCl_3$, 125 MHz, ppm): $\delta$ 145.7, 145.4, 139.6, 132.0, 131.0, 129.3, 129.1, 125.0, 124.8, 122.0, 21.4; MS (EI); $[M+H]^+$: 217.2.



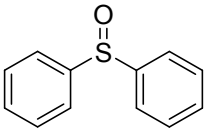
**1-Methyl-3-(p-tolylsulfinyl)benzene,** Compound **3cb** was obtained in 66% yield according to the general procedure. $^1$H NMR ($CDCl_3$, 500 MHz, ppm): $\delta$ 7.53 (d, $J$ = 8.2 Hz, 2H), 7.47 (s, 1H), 7.39 (d, $J$ = 7.8 Hz, 1H), 7.32 (t, $J$ = 7.6 Hz, 1H), 7.25 (d, $J$ = 6.5 Hz, 2H), 7.23 (d, $J$ = 7.5 Hz, 1H), 2.37 (s, 3H), 2.37 (s, 3H); $^{13}$C NMR ($CDCl_3$, 125 MHz, ppm): $\delta$ 145.6, 142.6, 141.5, 139.5, 131.8, 130.0, 129.1, 125.0, 124.9, 121.9, 21.4, 21.4; HRMS calc. for $C_{14}H_{15}OS$ $(M+H)^+$, 231.0844; found, 231.0845.



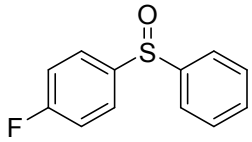
**1-Methyl-2-(phenylsulfinyl)benzene,**[5] Compound **3da** was obtained in 68% yield according to the general procedure. $^1$H NMR ($CDCl_3$, 500 MHz, ppm): $\delta$ 7.95 – 7.94 (m, 1H), 7.61 – 7.59 (m, 2H), 7.46 – 7.43 (m, 3H), 7.41 (d, $J$ = 7.5 Hz, 1H), 7.37 – 7.35 (m, 1H), 7.17 (d, $J$ = 7.3 Hz, 1H), 2.36 (s, 3H); $^{13}$C NMR ($CDCl_3$, 125 MHz, ppm): $\delta$ 144.6, 142.9, 135.8, 131.1, 131.0, 131.0, 129.3, 127.2, 125.9, 124.8, 18.6; MS (EI); $[M+H]^+$: 217.1.



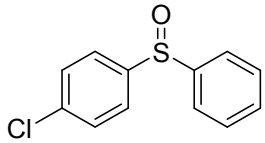
**4,4'-Sulfinylbis(methylbenzene)**[3]**,** Compound **3bb** was obtained in 70% yield according to the general procedure. $^1$H NMR ($CDCl_3$, 500 MHz, ppm): $\delta$ 7.51 (d, $J$ = 8.2 Hz, 4H), 7.25 (d, $J$ = 8.0 Hz, 4H), 2.36 (s, 6H); $^{13}$C NMR ($CDCl_3$, 125 MHz, ppm): $\delta$ 142.6, 141.5, 130.0, 124.9, 21.4; MS (EI); $[M+H]^+$: 231.1.



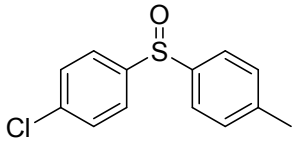
**Sulfinyldibenzene[4],** Compound **3ea** was obtained in 68% yield according to the general procedure. $^1$H NMR ($CDCl_3$, 500 MHz, ppm): $\delta$ 7.66 – 7.64 (m, 4H), 7.48 – 7.43 (m, 6H); $^{13}$C NMR ($CDCl_3$, 125 MHz, ppm): $\delta$ 145.2, 131.1, 129.3, 124.8; MS (EI); $[M+H]^+$: 203.1.



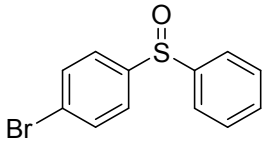

**1-Fluoro-4-(phenylsulfinyl)benzene[4],** Compound **3fa** was obtained in 68% yield according to the general procedure. $^1$H NMR ($CDCl_3$, 500 MHz, ppm): $\delta$ 7.70 – 7.59 (m, 4H), 7.50 – 7.44 (m, 3H), 7.15 (t, $J$ = 8.6 Hz, 2H); $^{13}$C NMR ($CDCl_3$, 125 MHz, ppm): $\delta$ 164.3 (d, $J$ = 250.4Hz), 145.4, 141.2, 131.2, 129.4, 127.2 (d, $J$ = 8.9Hz), 124.7, 116.8, 116.7 (d, $J$ = 22.4Hz); MS (EI); $[M+H]^+$: 221.1.



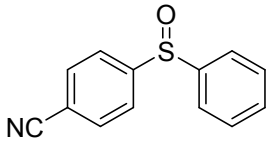

**1-Chloro-4-(phenylsulfinyl)benzene[2],** Compound **3ga** was obtained in 72% yield according to the general procedure. $^1$H NMR ($CDCl_3$, 500 MHz, ppm): $\delta$ 7.64 – 7.62 (m, 2H), 7.58 (d, $J$ = 8.5 Hz, 2H), 7.49 – 7.46 (m, 3H), 7.43 (d, $J$ = 8.5 Hz, 2H); $^{13}$C NMR ($CDCl_3$, 125 MHz, ppm): $\delta$ 145.4, 144.3, 137.3, 131.4, 129.6, 129.5, 126.1, 124.7; MS (EI); $[M+H]^+$: 237.0.




**1-Chloro-4-(p-tolylsulfinyl)benzene[2],** Compound **3gb** was obtained in 67% yield according to the general procedure. $^1$H NMR ($CDCl_3$, 500 MHz, ppm): $\delta$ 7.57 – 7.55 (m, 2H), 7.51 (d, $J$ = 8.2 Hz, 2H), 7.43 – 7.42 (m, 2H), 2.37 (s, 3H); $^{13}$C NMR ($CDCl_3$, 125 MHz, ppm): $\delta$ 144.4, 142.1, 142.1, 137.1, 130.2, 129.6, 126.0, 125.0, 21.4; MS (EI); $[M+H]^+$: 251.0.




**1-Bromo-4-(phenylsulfinyl)benzene[5],** Compound **3ha** was obtained in 55% yield according to the general procedure. $^{1}$H NMR ($CDCl_3$, 500 MHz, ppm): $\delta$ 7.64 – 7.62 (m, 2H), 7.59 (d, $J$ = 8.6 Hz, 2H), 7.51 (d, $J$ = 8.6 Hz, 2H), 7.48 – 7.46 (m, 3H); $^{13}$C NMR ($CDCl_3$, 125 MHz, ppm): $\delta$ 145.2, 144.8, 132.6, 131.4, 129.5, 126.3, 125.6, 124.7; MS (EI); $[M+H]^+$: 281.2.




**4-(Phenylsulfinyl)benzonitrile[6],** Compound **3ia** was obtained in 62% yield according to the general procedure. $^{1}$H NMR ($CDCl_3$, 500 MHz, ppm): $\delta$ 7.79 – 7.73 (m, 4H), 7.68 – 7.64 (m, 2H), 7.51 – 7.49 (m, 3H); $^{13}$C NMR ($CDCl_3$, 125 MHz, ppm): $\delta$ 151.2, 144.5, 133.0, 132.0, 129.8, 125.0, 124.9, 117.7, 114.7; MS (EI); $[M+H]^+$: 228.1.

**References：**

[1] Dong Hyuk Kim, Juyoung Lee, and Anna Lee, *Org. Lett*. **2018**, 20, 764−767

[2] Yiming Li, Ming Wang, and Xuefeng Jiang , *ACS Catal* , **2017**, *7*, 7587–7592.

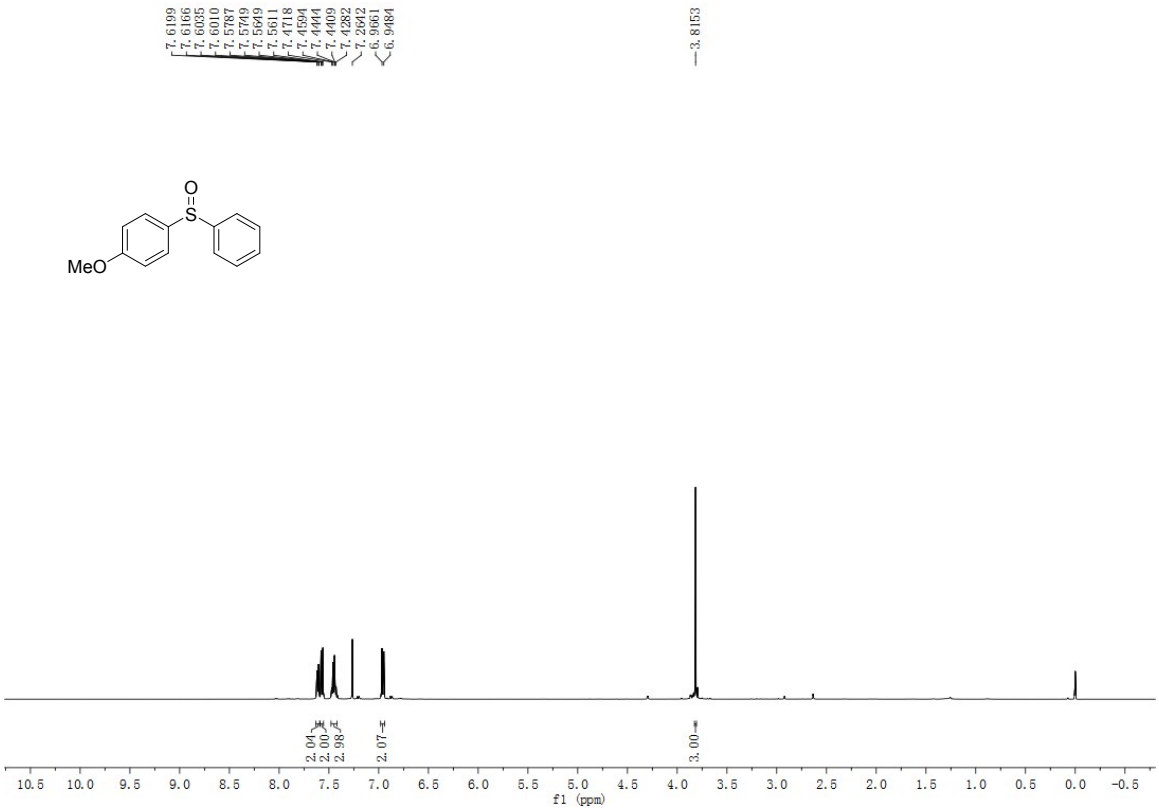
[3] Frédéric Izquierdo, Anthony Chartoire and Steven P. Nolan, *ACS Catal.* **2013**, 3, 2190–2193

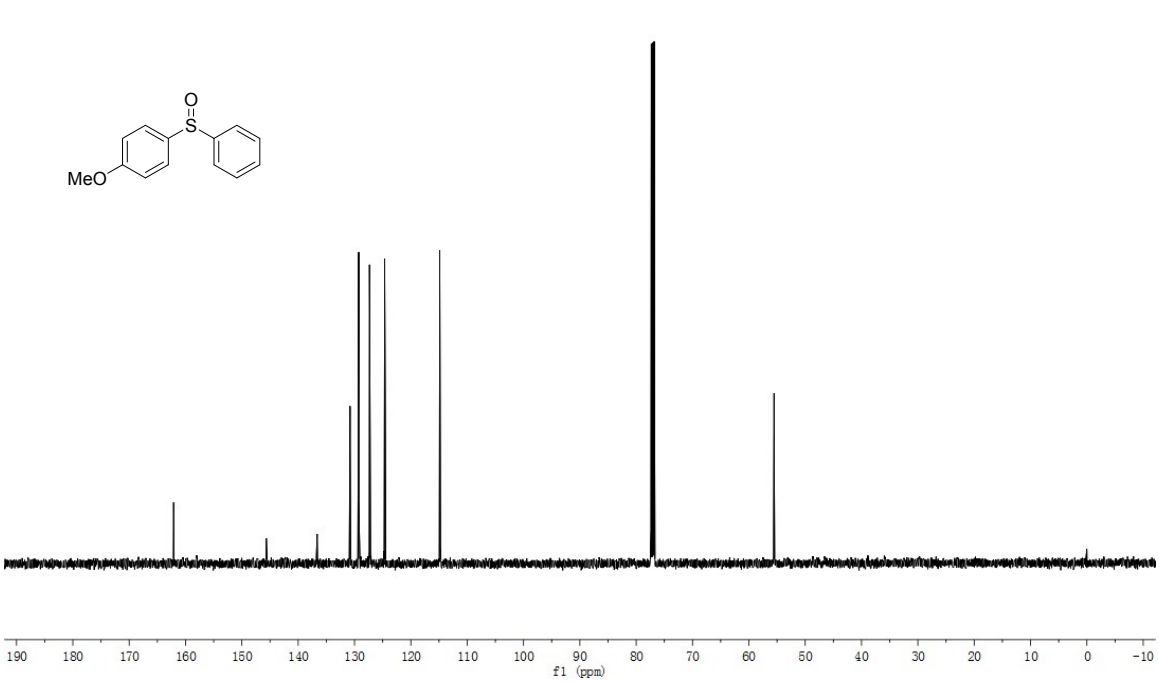
[4]Tiezheng Jia, Mengnan Zhang, Irina K. Sagamanova, Carol Y. Wang, and Patrick J. Walsh**,** *Org. Lett.* **2015**,*17*, 1168–1171.

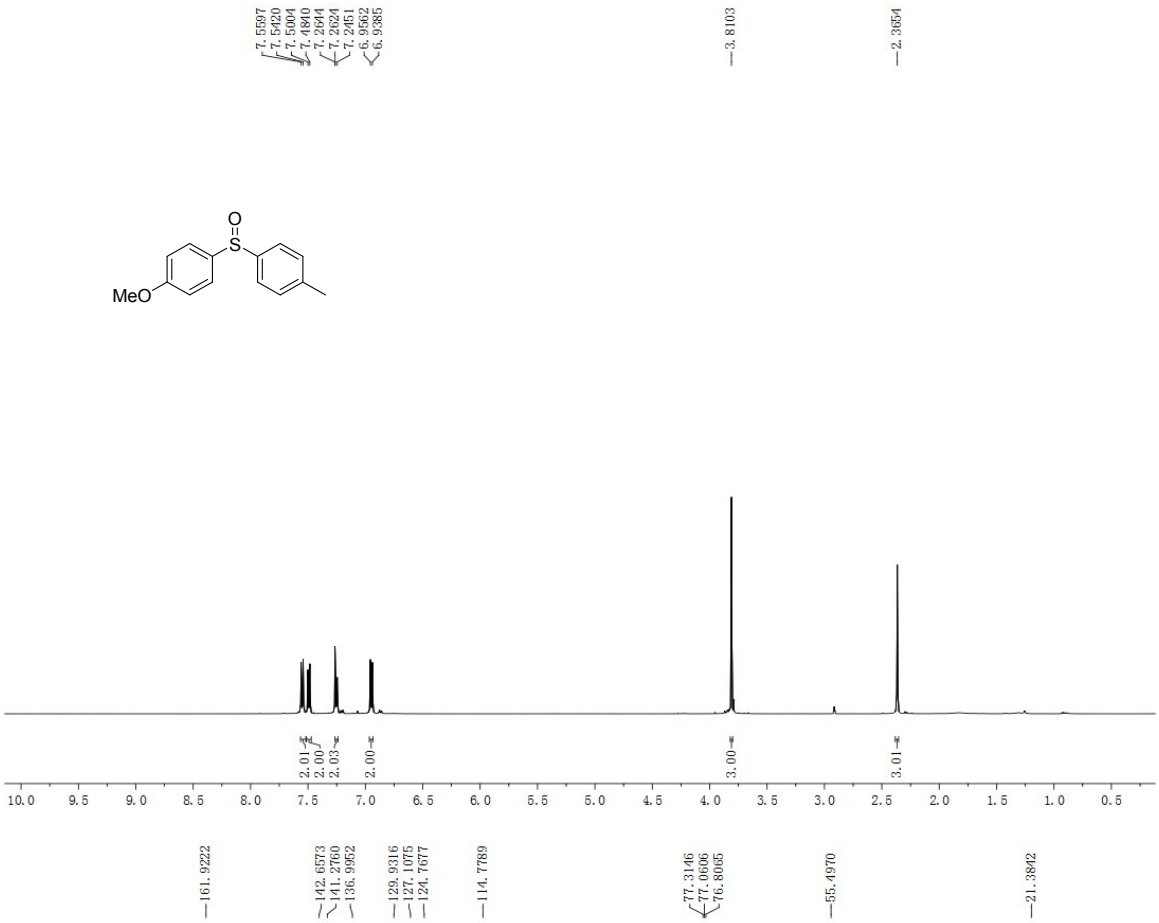
[5] Hao Yu, Zhen Li, and Carsten Bolm, *Org. Lett.* **2018**, 20, 7104−7106.

[6] Tiezheng Jia, Mengnan Zhang, Irina K. Sagamanova, Carol Y. Wang, and Patrick J. Walsh, *Org. Lett*, **2015**, *17*, 1168 - 1171.

## 6. Copies of NMR Spectra for 3aa−3ia

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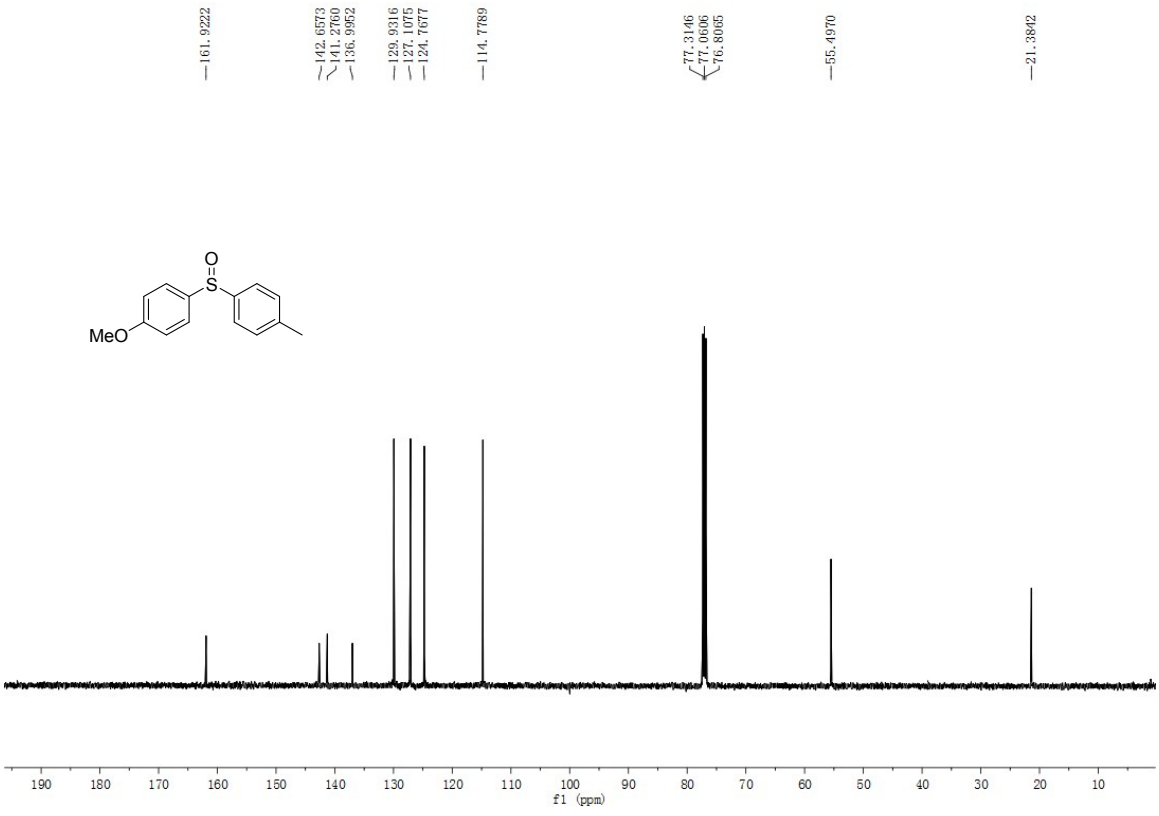
MeO
2.01
2.00
2.03
2.00
3.00
3.01
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5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141.2760
136.9952
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124.7677
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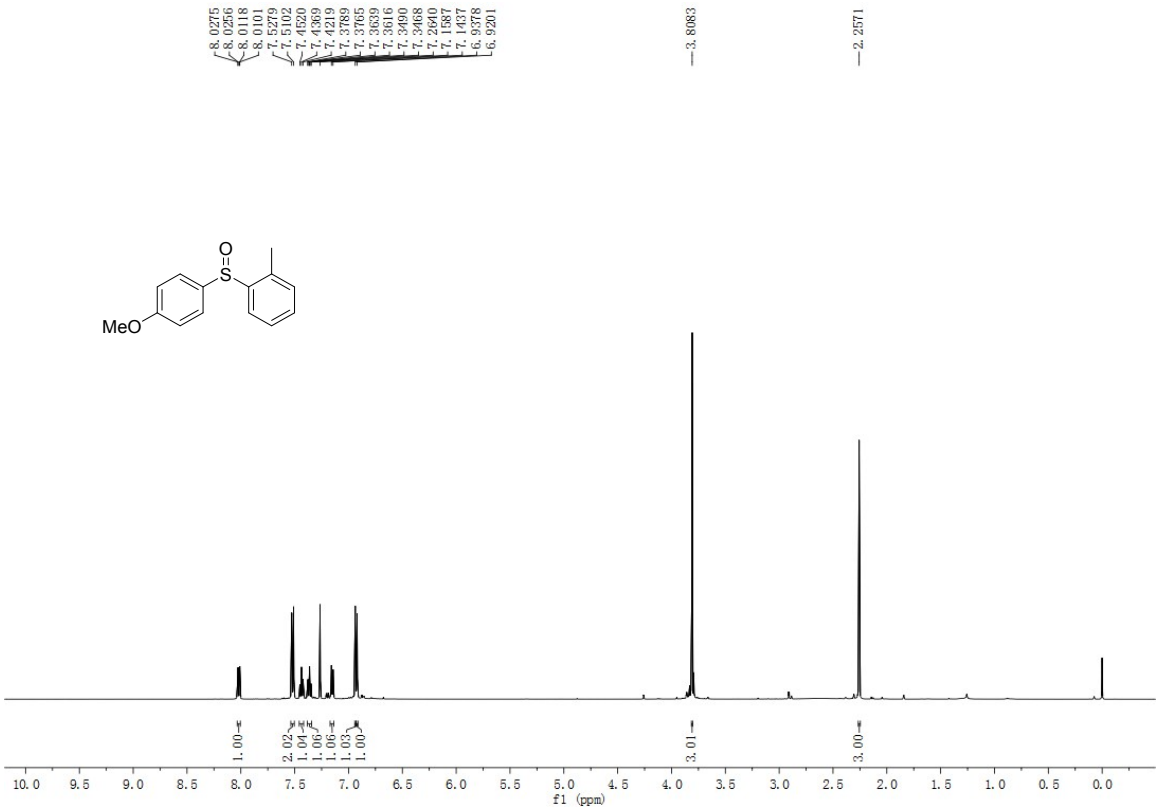
76.8065
55.4970
21.3842
MeO
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)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8.0118
8.0101
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7.5102
7.4520
7.4369
7.4219
7.3789
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7.3639
7.3616
7.3490
7.3468
7.2690
7.1587
7.1437
6.9378
6.9201
3.8083
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MeO
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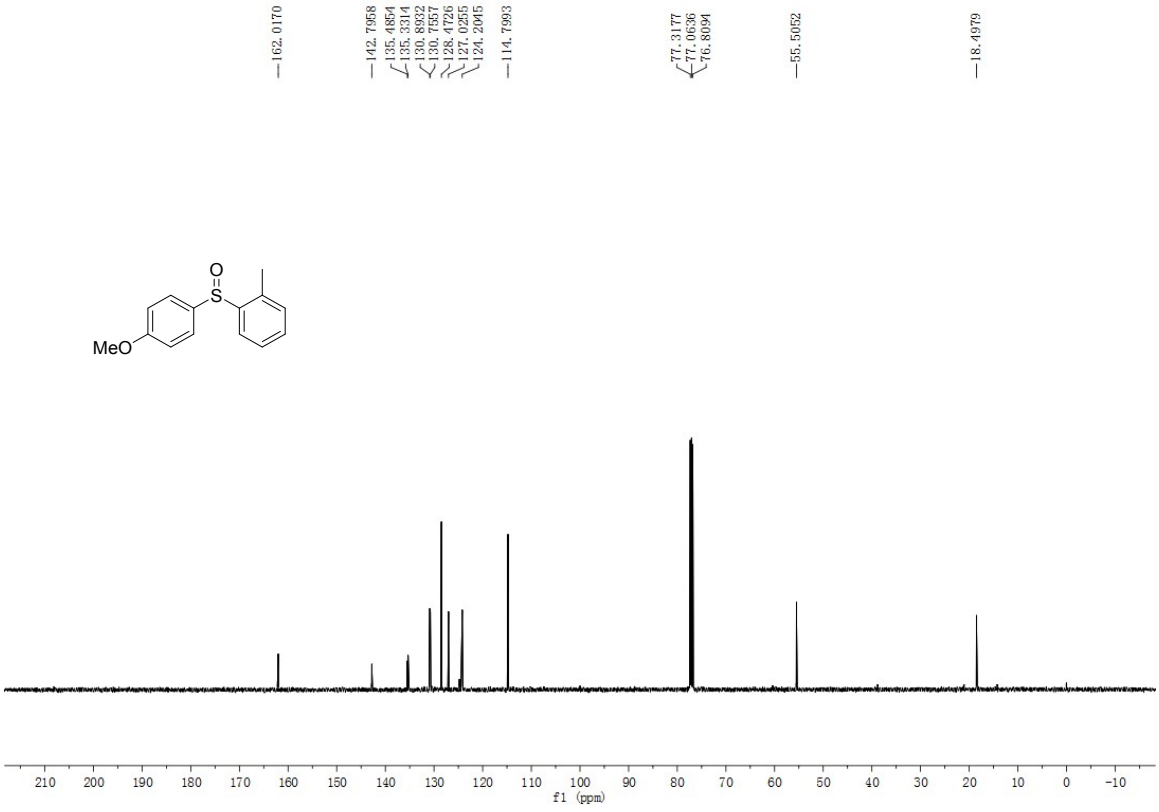
1.06
1.06
1.03
1.00
3.01
3.00
f1 (ppm)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55.5052
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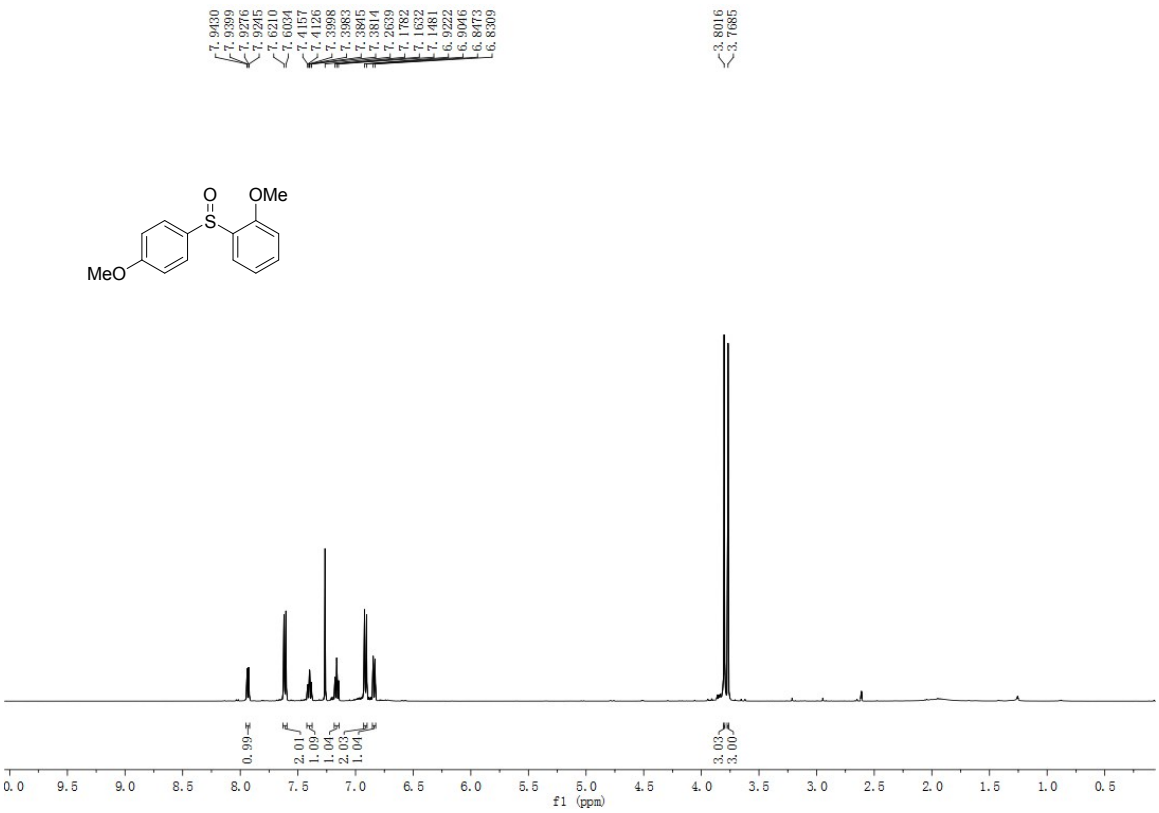
f1 (ppm)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7.3814
7.2639
7.1782
7.1632
7.1481
6.9222
6.9046
6.8473
6.8309
3.8016
3.7685
O
S
OMe
MeO
0.99
2.01
1.09
1.04
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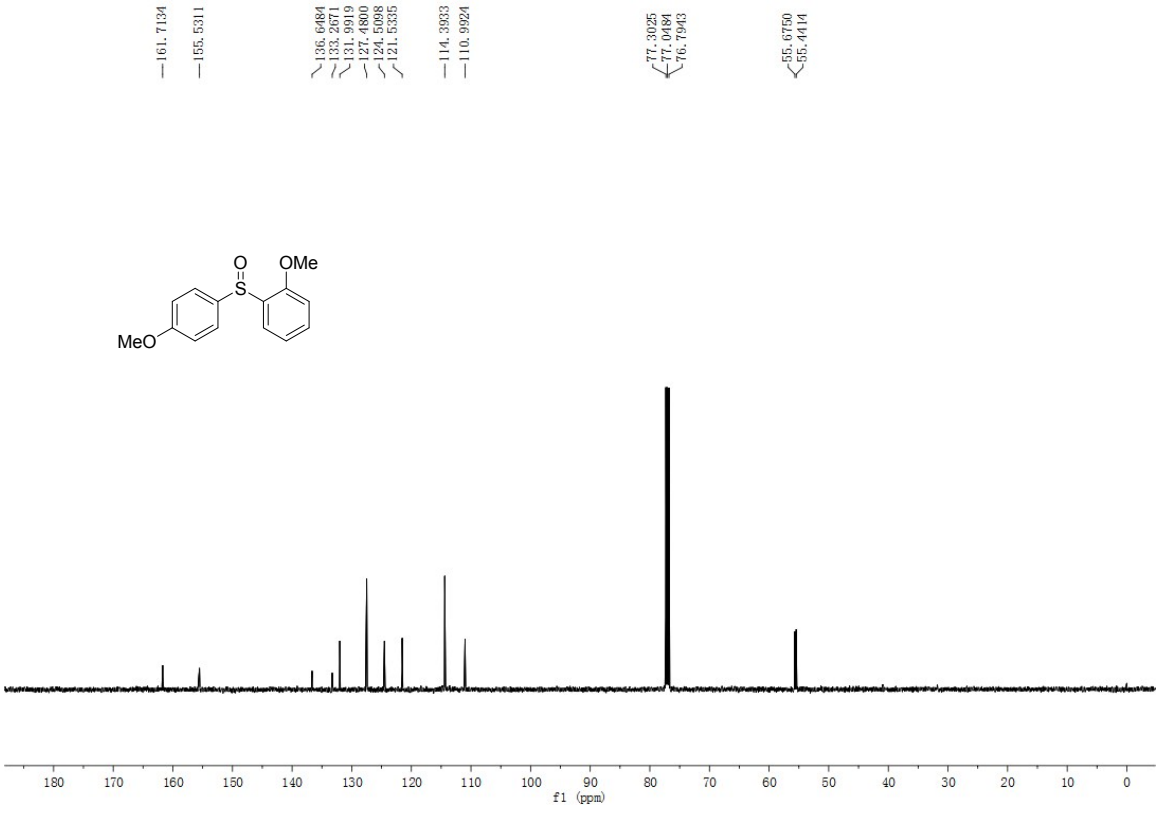
1.04
3.03
3.00
f1 (ppm)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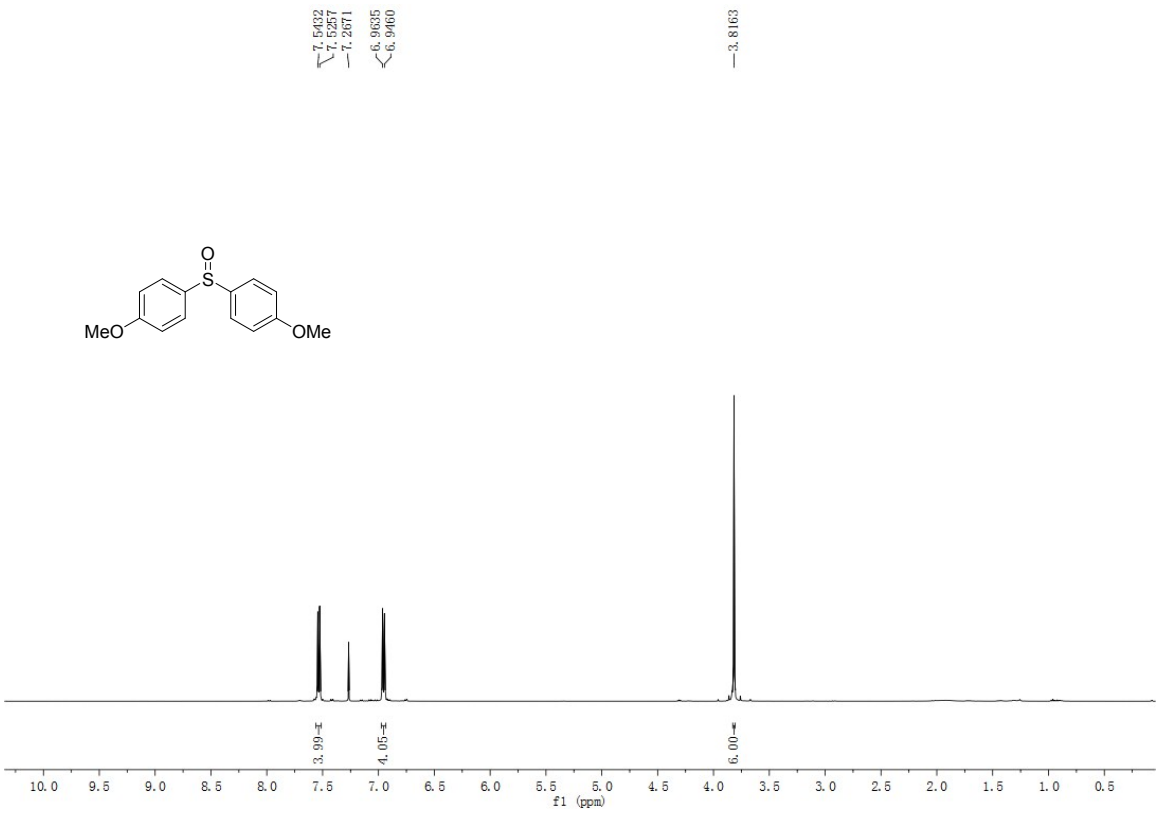
O
S
OMe
MeO
f1 (ppm)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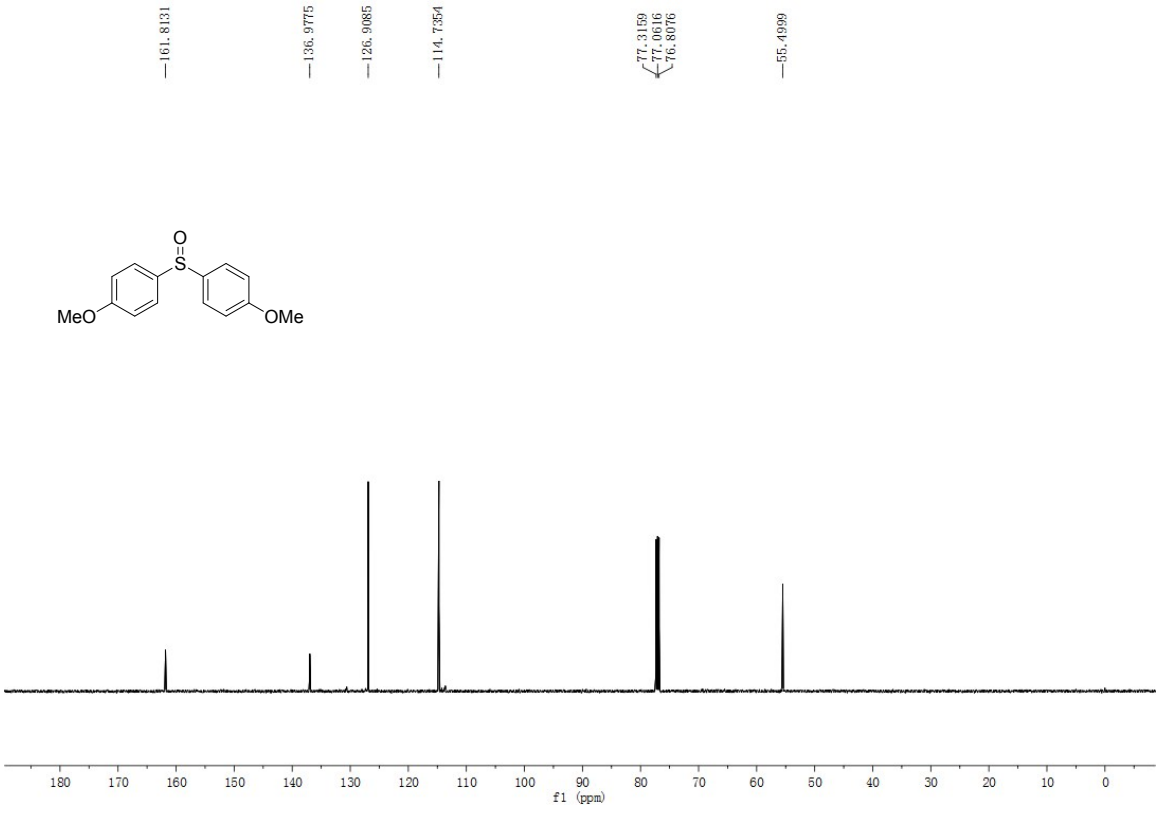
4.05
6.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)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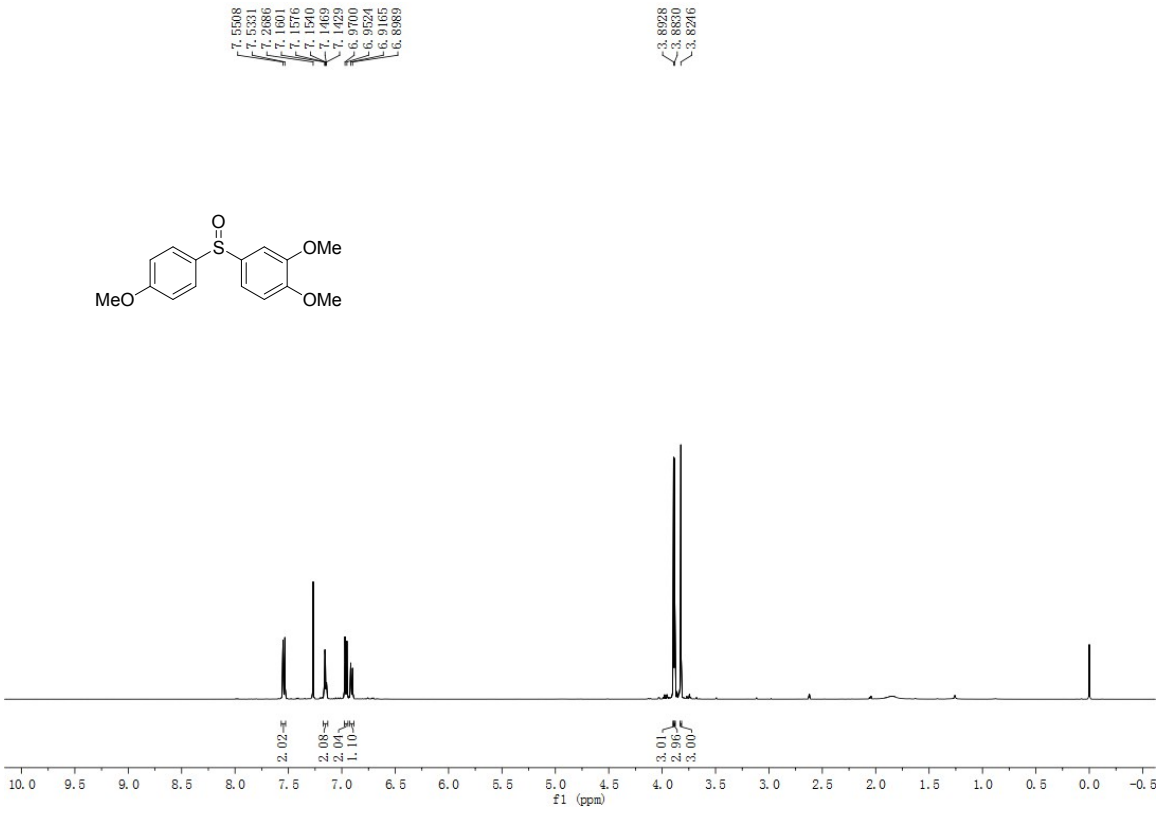
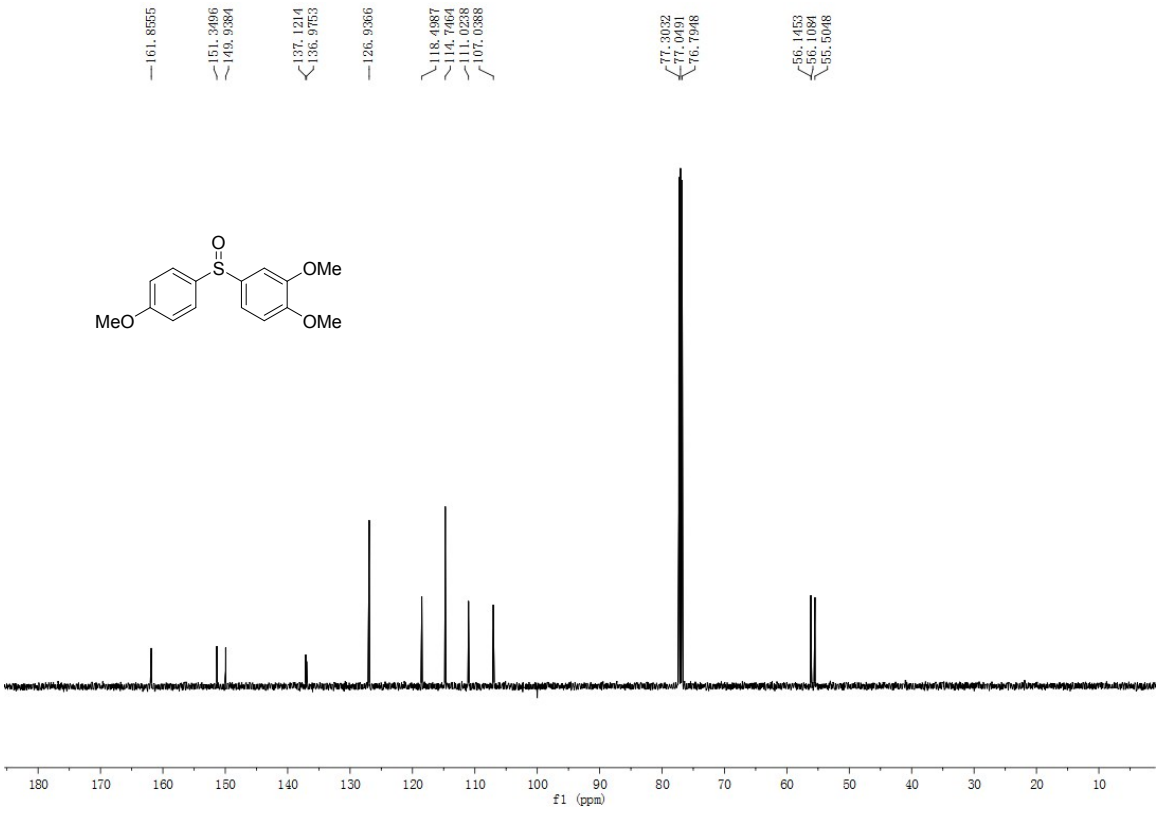
136.9775
126.9085
114.7354
77.3159
77.0616
76.8076
55.4999
MeO
OMe
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


7.5508
7.5331
7.2686
7.1601
7.1576
7.1540
7.1469
7.1429
6.9700
6.9524
6.9165
6.8989
3.8928
3.8830
3.8246
O
S
OMe
MeO
OMe
2.02
2.08
2.04
1.10
3.01
2.96
3.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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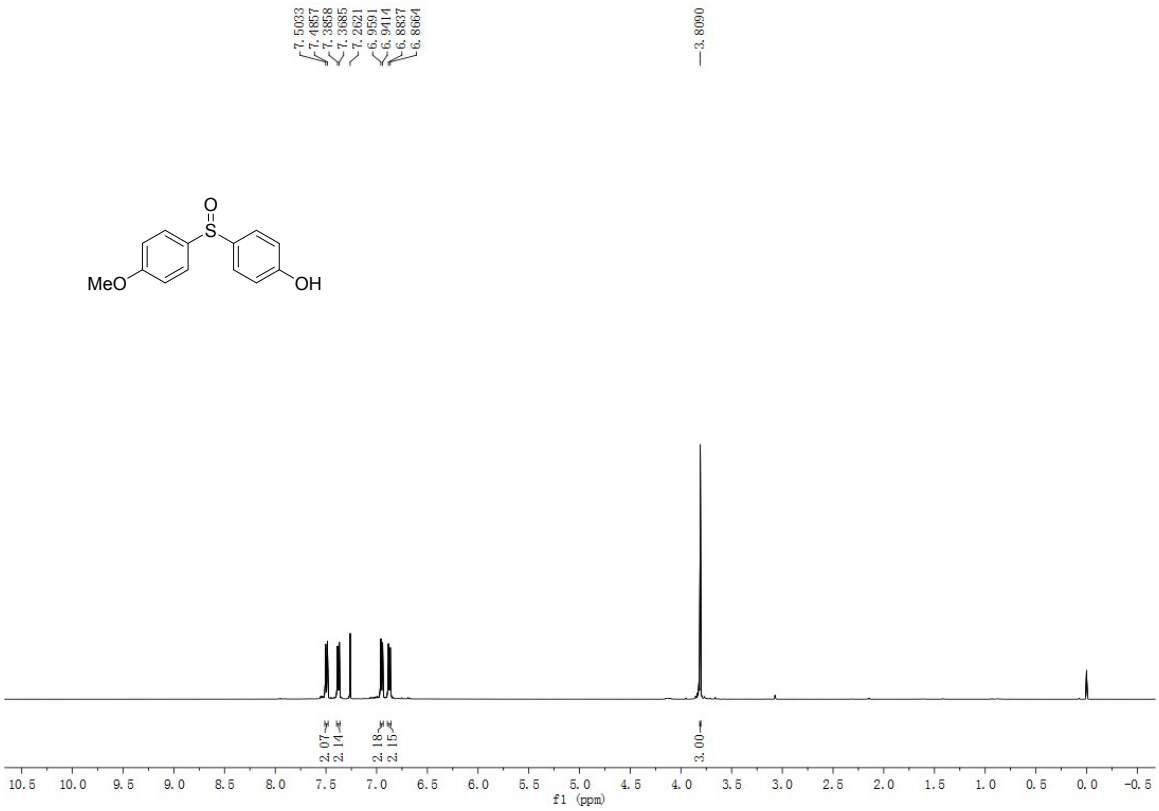
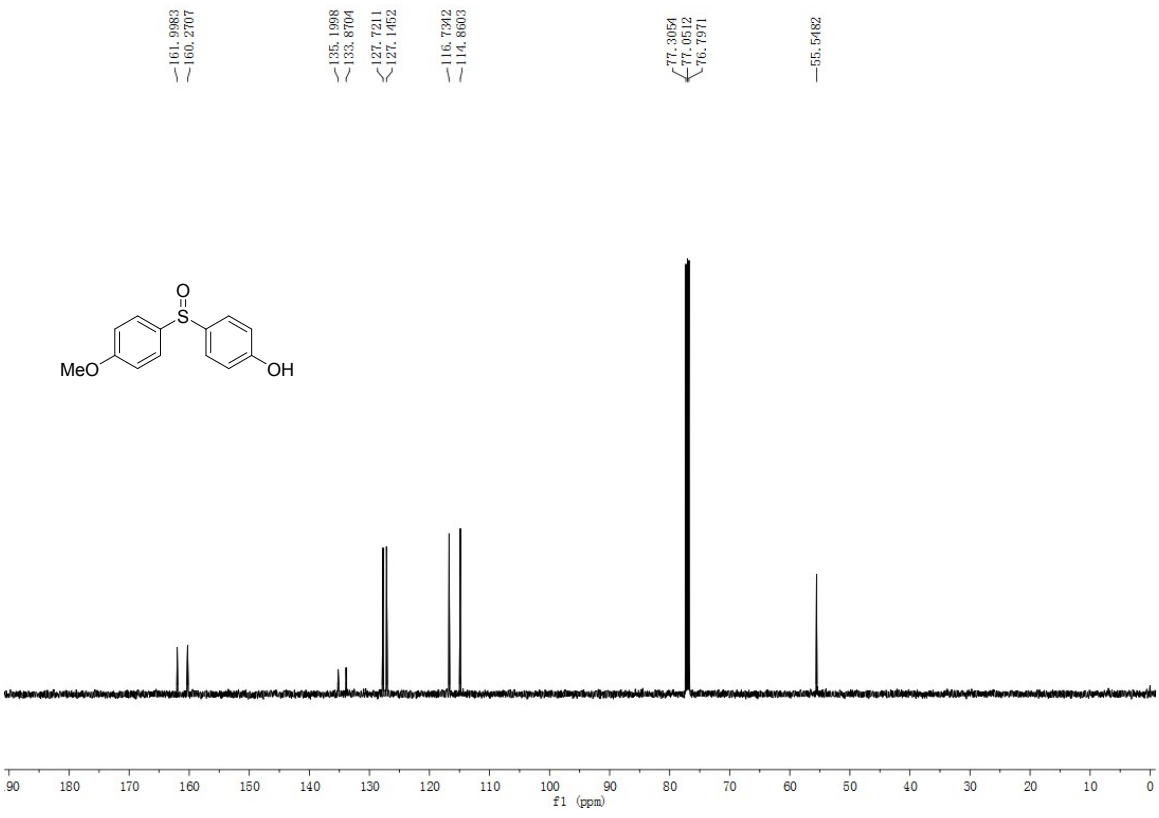
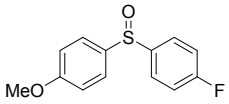
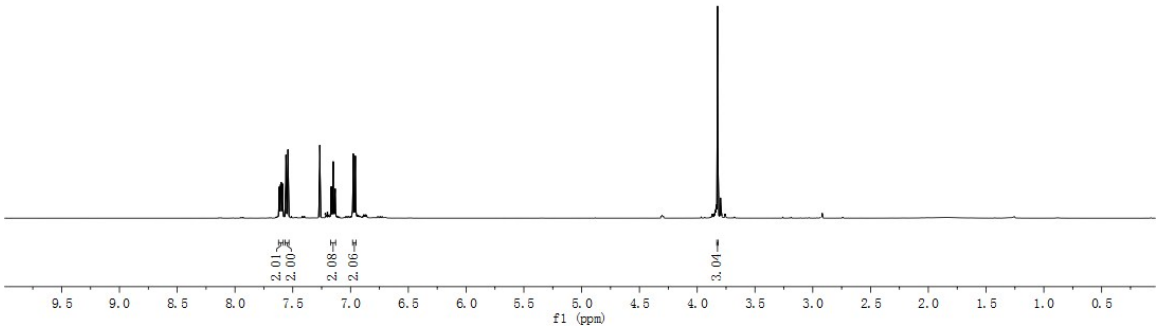
151.3496
149.9384
137.1214
136.9753
126.9366
118.4987
114.7464
111.0238
107.0368
77.3032
77.0491
76.7948
56.1453
56.1084
55.5048
O
S
OMe
MeO
OMe
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

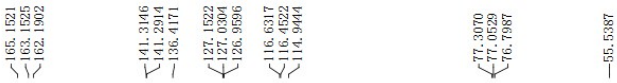

7.5033
7.4857
7.3858
7.3685
7.2621
6.9591
6.9414
6.8837
6.8664
3.8090
O
S
MeO
OH
2.07
2.14
2.18
2.15
3.00
f1 (ppm)

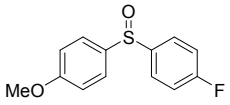

161.9983
160.2707
135.1998
133.8704
127.7211
127.1452
116.7342
114.8603
77.3054
77.0512
76.7971
55.5482
O
S
MeO
OH
f1 (ppm)


7.6167
7.6127
7.6065
7.6027
7.5991
7.5931
7.5889
7.5591
7.5414
7.2663
7.1671
7.1499
7.1328
6.9763
6.9687
3.8243

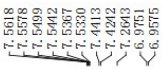

O
S
MeO
F


2.01
2.00
2.08
2.06
3.04
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

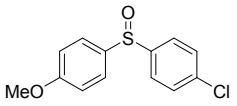

165.1521
163.1525
162.1902
141.3146
141.2914
136.4171
127.1522
127.0304
126.9596
116.6317
116.4522
114.9444
77.3970
77.0529
76.7987
55.5387

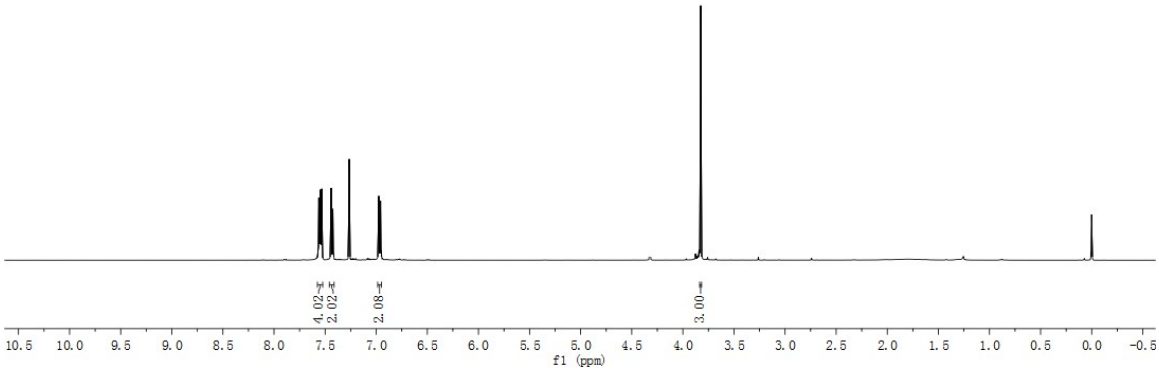

O
S
MeO
F


210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

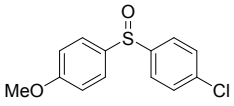

7.5618
7.5578
7.5499
7.5442
7.5367
7.5330
7.4413
7.4242
7.2643
6.9751
6.9575

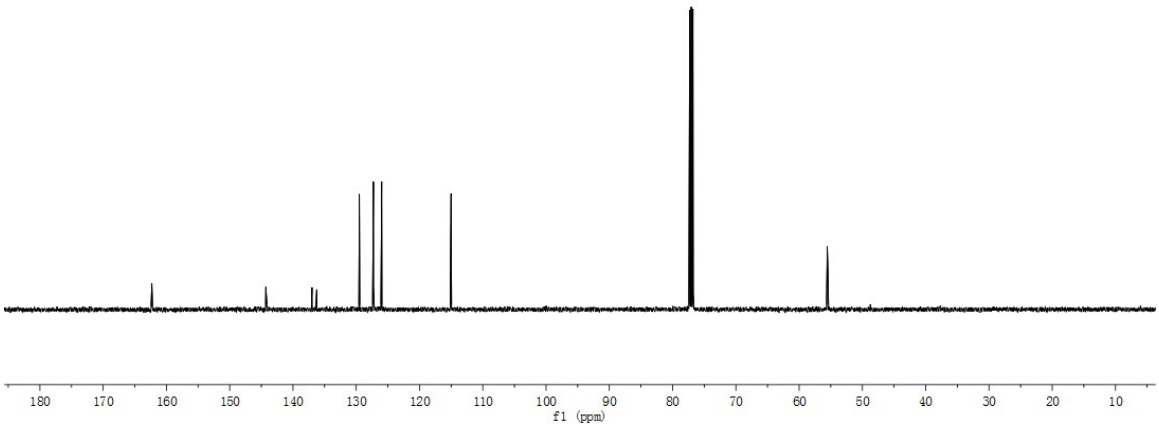

3.8250

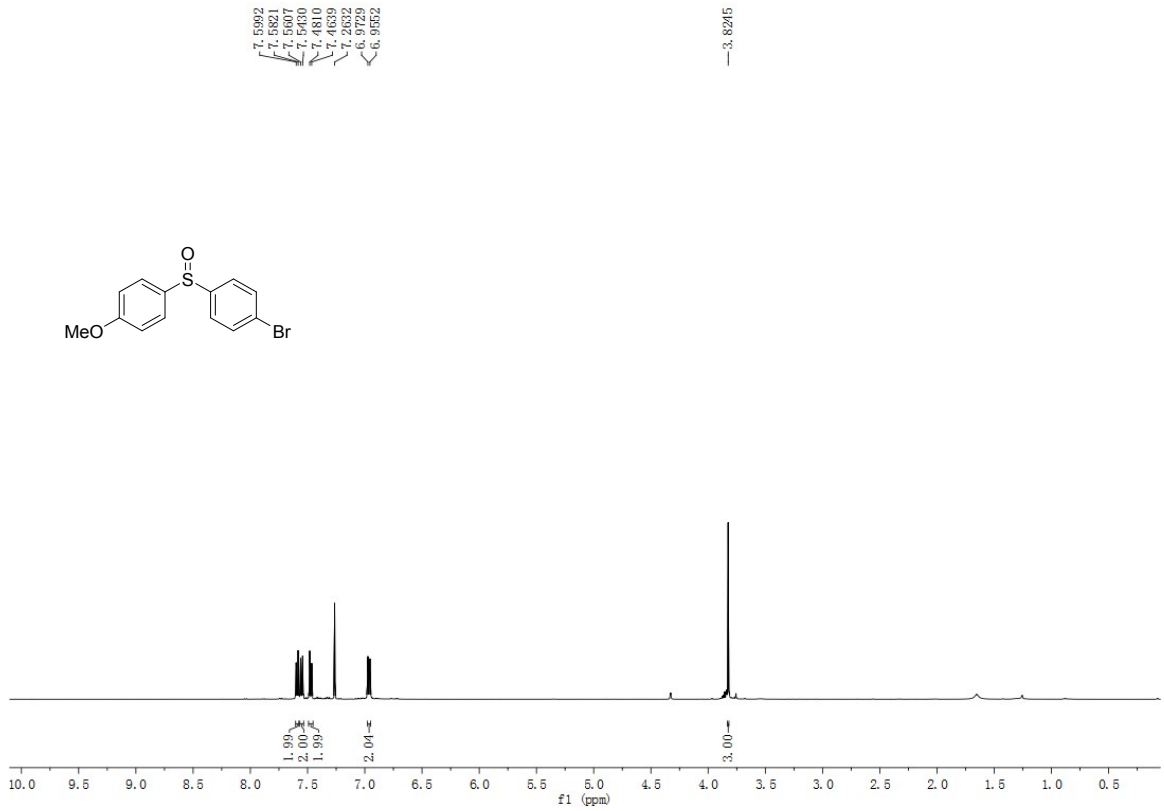

O
S
MeO
Cl

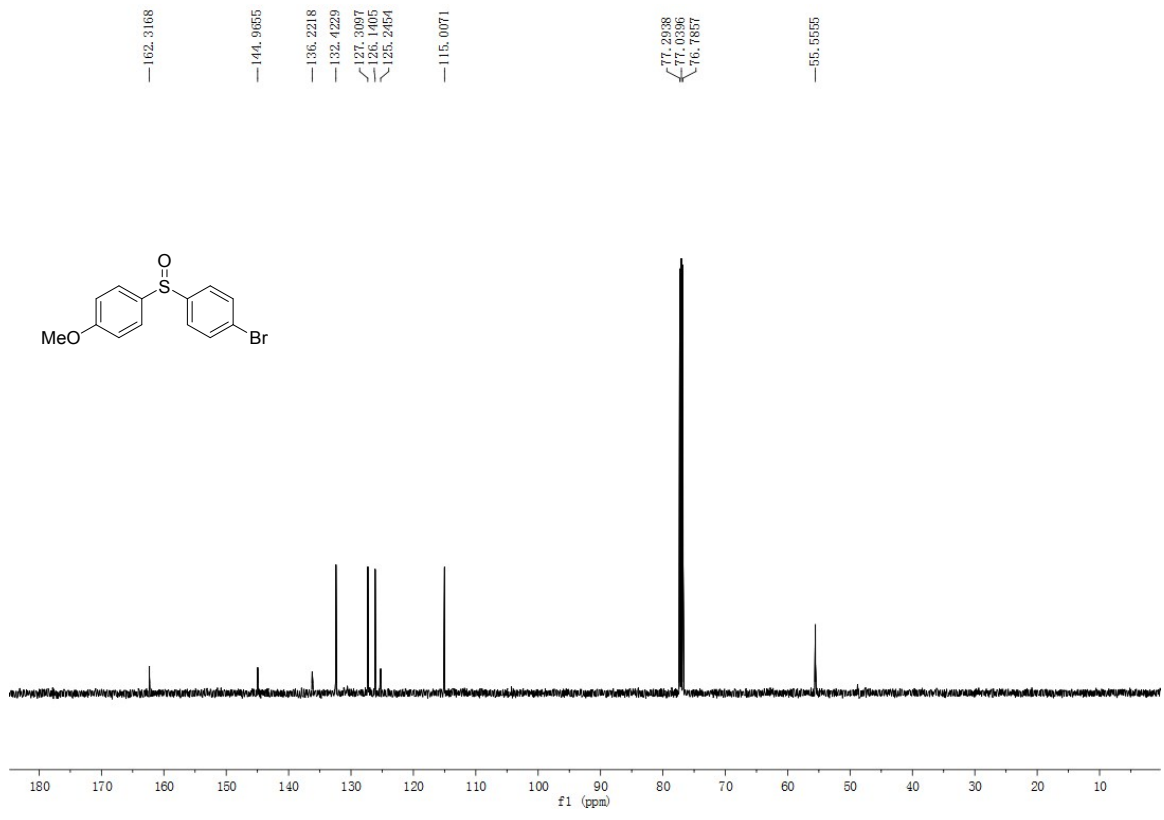

4.02
2.02
2.08
3.00
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

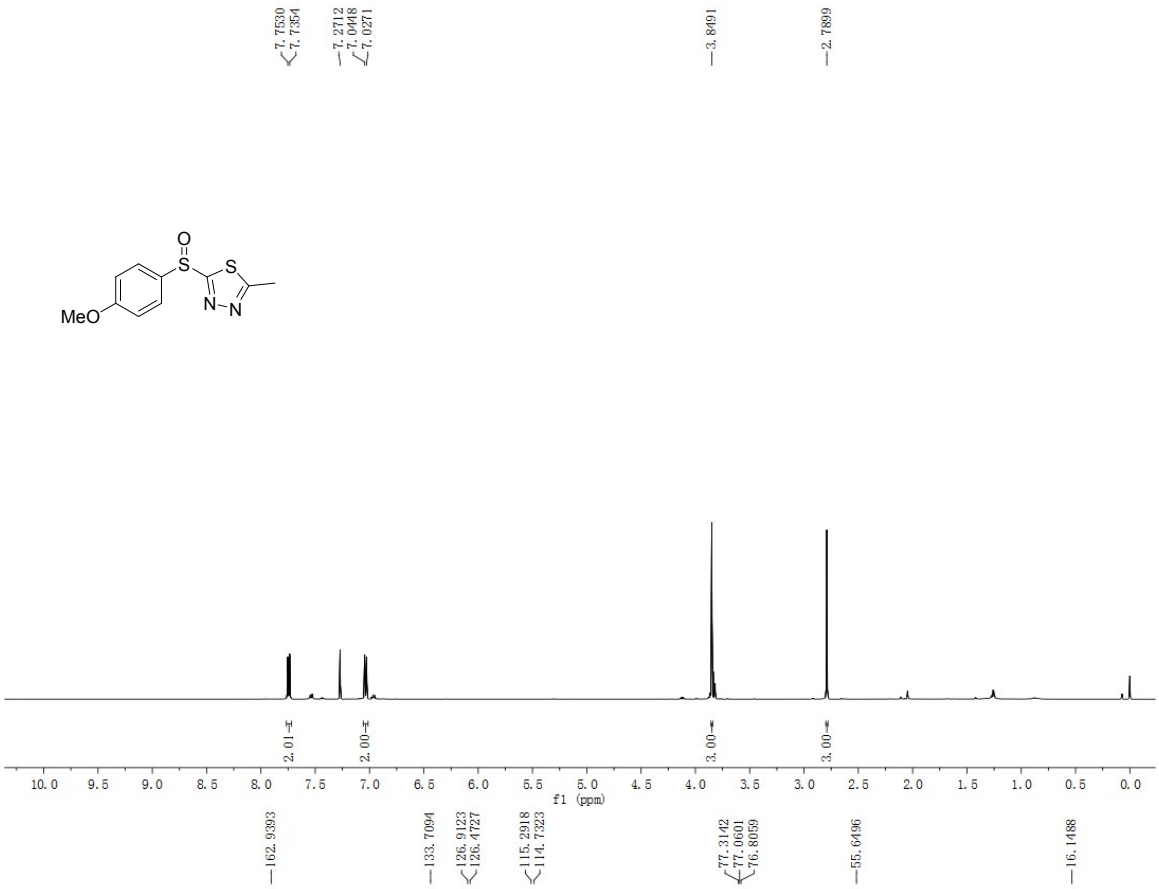

162.3094
144.2852
137.0095
136.2426
129.5110
127.2991
125.9845
115.0049
77.2982
77.0439
76.7899
55.5540


O
S
MeO
Cl

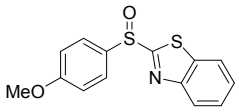

180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

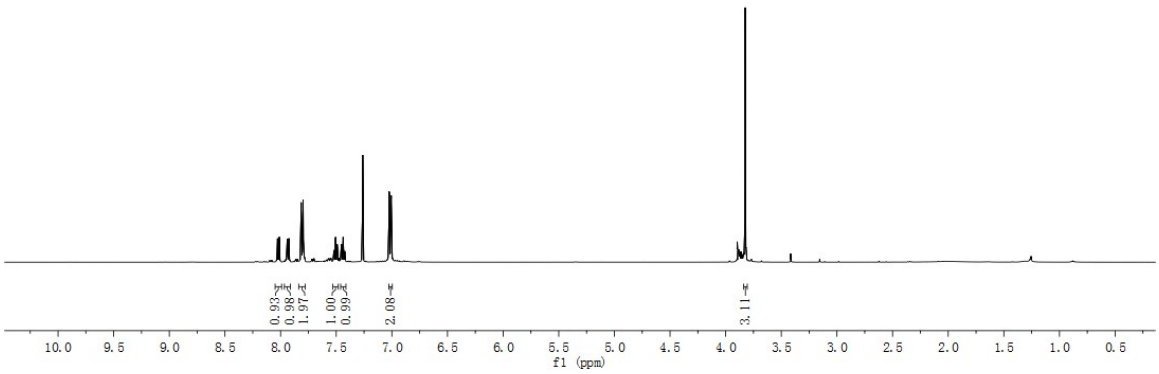

7.5992
7.5821
7.5607
7.5450
7.4810
7.4639
7.2632
6.9729
6.9552
3.8245
O
S
MeO
Br
1.99
2.00
1.99
2.04
3.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

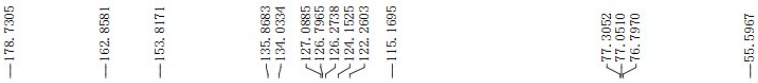

162.3168
144.9655
136.2218
132.4229
127.3097
126.1405
125.2454
115.0071
77.2938
77.0396
76.7857
55.5555
O
S
MeO
Br
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

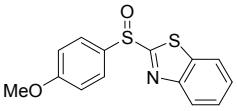

7.7530
7.7354
7.2712
7.0448
7.0271
3.8491
2.7899
MeO
2.01
2.00
3.00
3.00
f1 (ppm)
162.9393
133.7094
126.9123
126.4727
115.2918
114.7323
77.3142
77.0601
76.8059
55.6496
16.1488
MeO
f1 (ppm)


8.0277
8.0118
7.9403
7.9250
7.8147
7.7968
7.5228
7.5205
7.5082
7.5062
7.4919
7.4897
7.4542
7.4519
7.4378
7.4236
7.4214
7.2617
7.0238
7.0060
3.8245

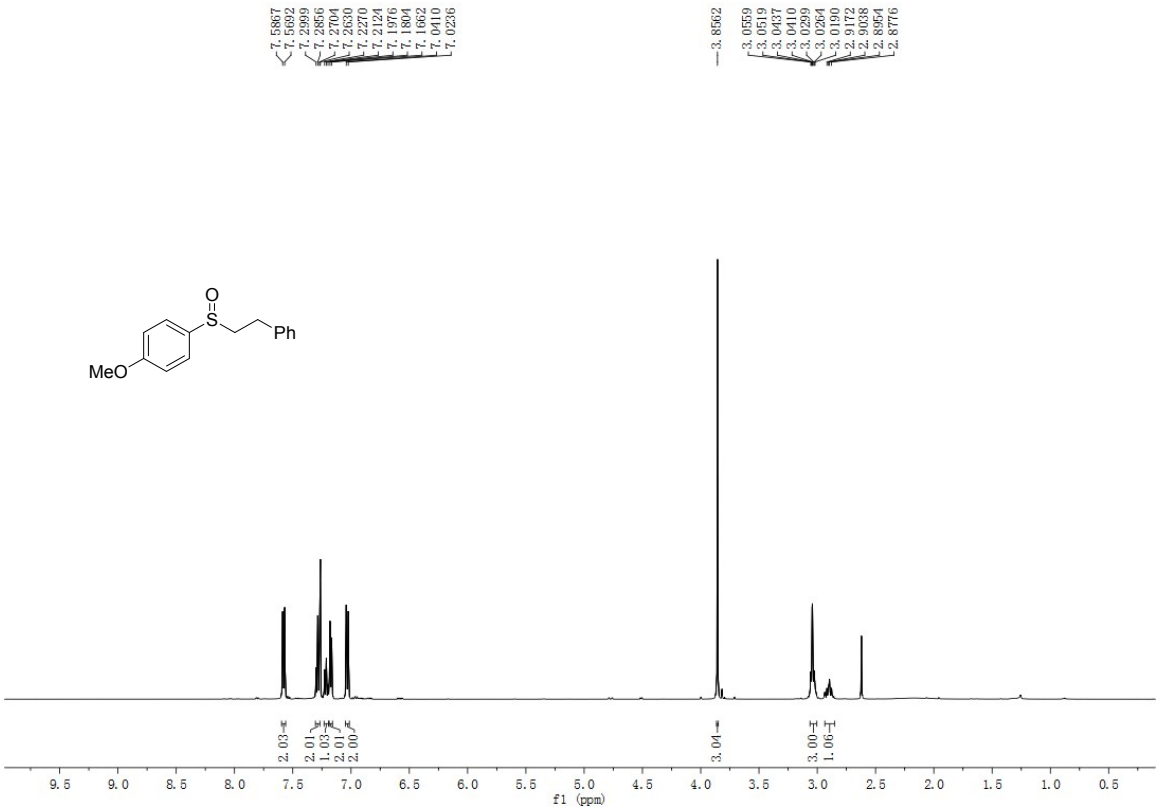

O
S
S
N
MeO


0.93
0.98
1.97
1.00
0.99
2.08
3.11
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)


178.7305
162.8581
153.8171
135.8683
134.0334
127.0885
126.7965
126.2738
124.1525
122.2603
115.1695
77.3052
77.0510
76.7970
55.5967


O
S
S
N
MeO


190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)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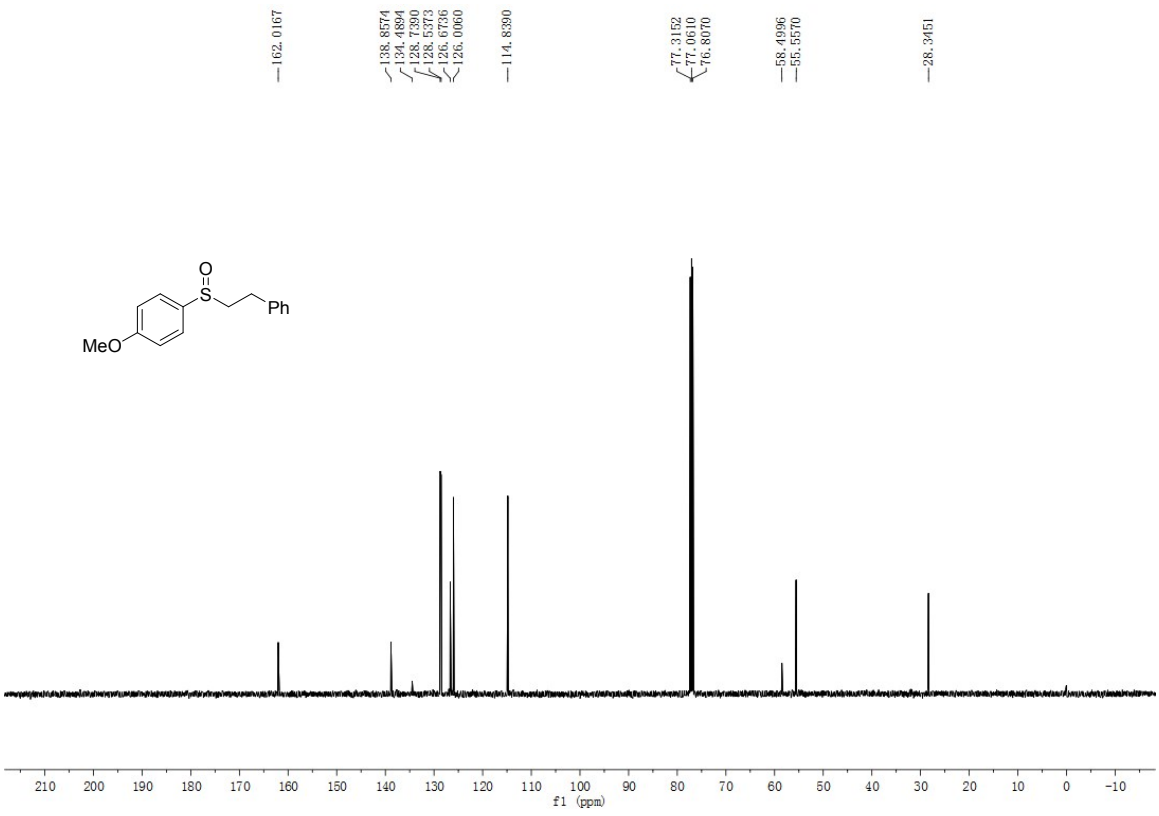
7.5692
7.2999
7.2856
7.2704
7.2630
7.2270
7.2124
7.1976
7.1804
7.1662
7.0410
7.0236
3.8562
3.0559
3.0519
3.0437
3.0410
3.0299
3.0264
3.0190
2.9172
2.9038
2.8954
2.8776
O
S
Ph
MeO
2.03
2.01
1.03
2.01
2.00
3.04
3.00
1.06
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)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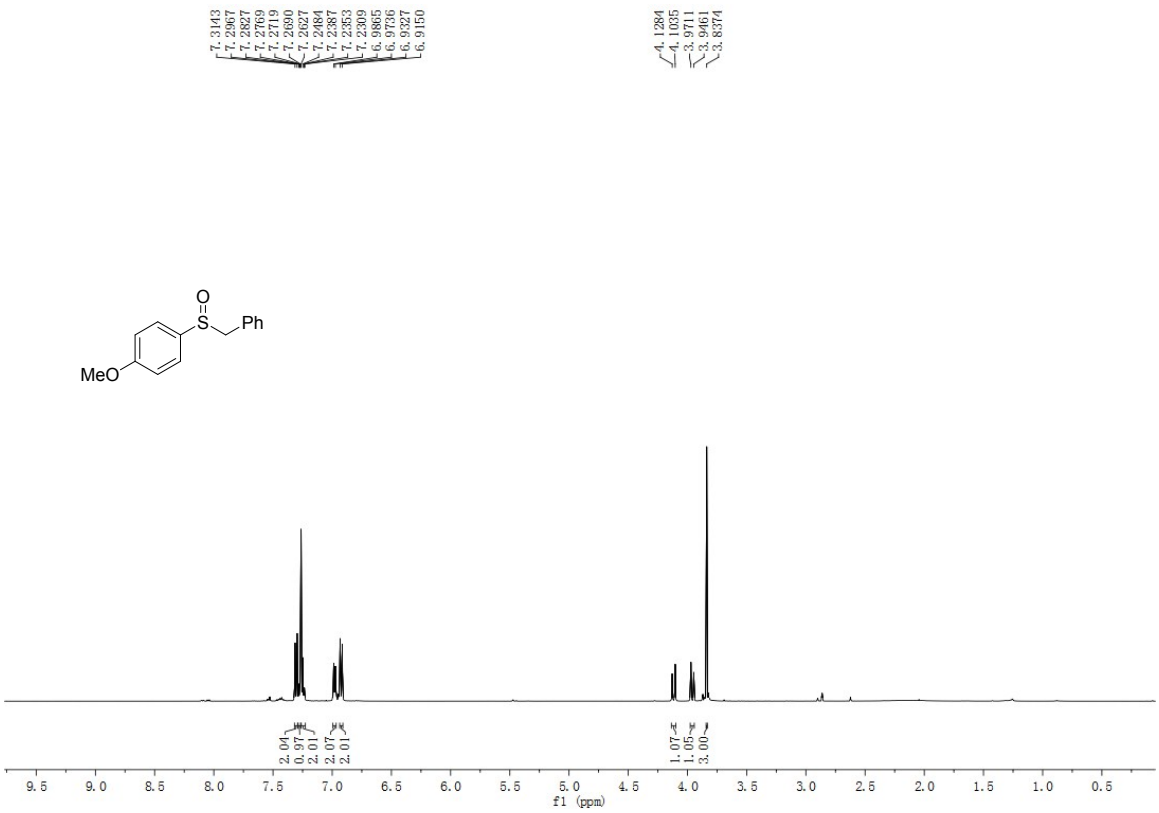
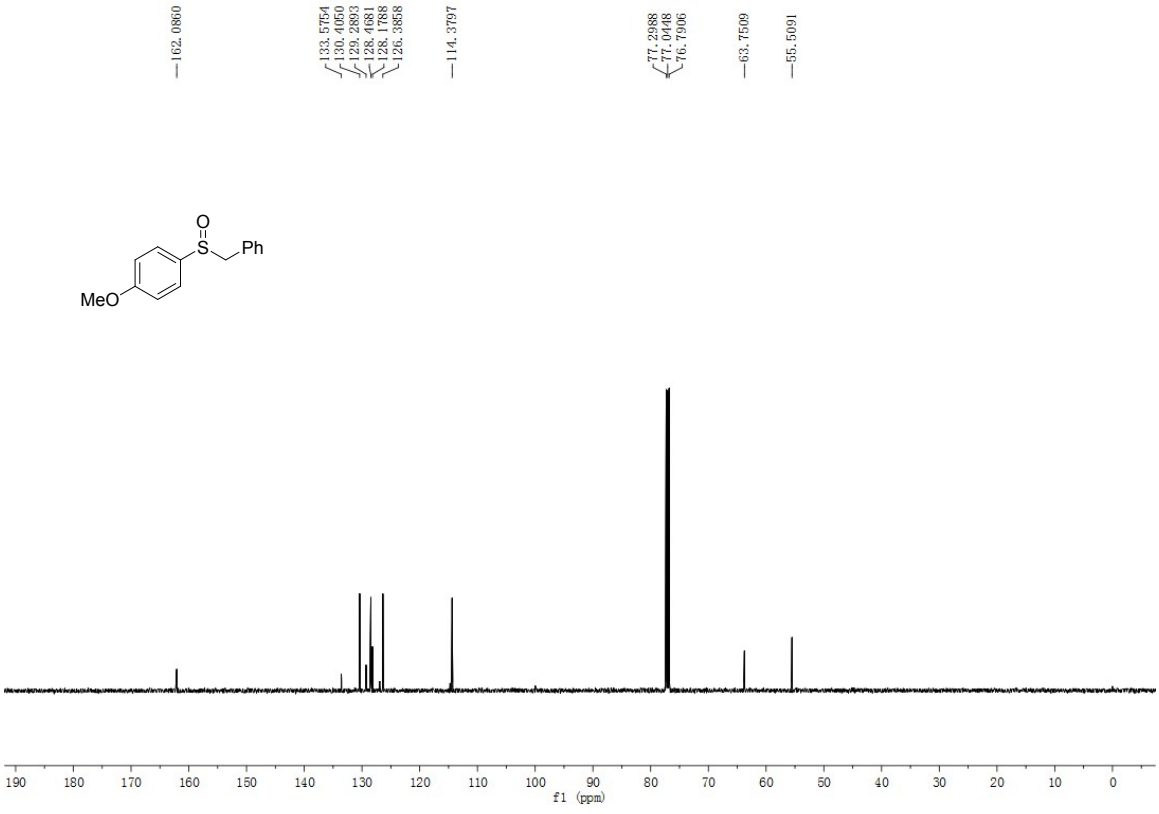
138.8574
134.4894
128.7390
128.5373
126.6736
126.0060
114.8390
77.3152
77.0610
76.8070
58.4996
55.5570
28.3451
O
S
Ph
MeO
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


7.3143
7.2967
7.2827
7.2769
7.2719
7.2690
7.2627
7.2484
7.2387
7.2353
7.2309
6.9865
6.9736
6.9327
6.9150
4.1284
4.1035
3.9711
3.9461
3.8374
O
S
Ph
MeO
2.04
0.97
2.01
2.07
2.01
1.07
1.05
3.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)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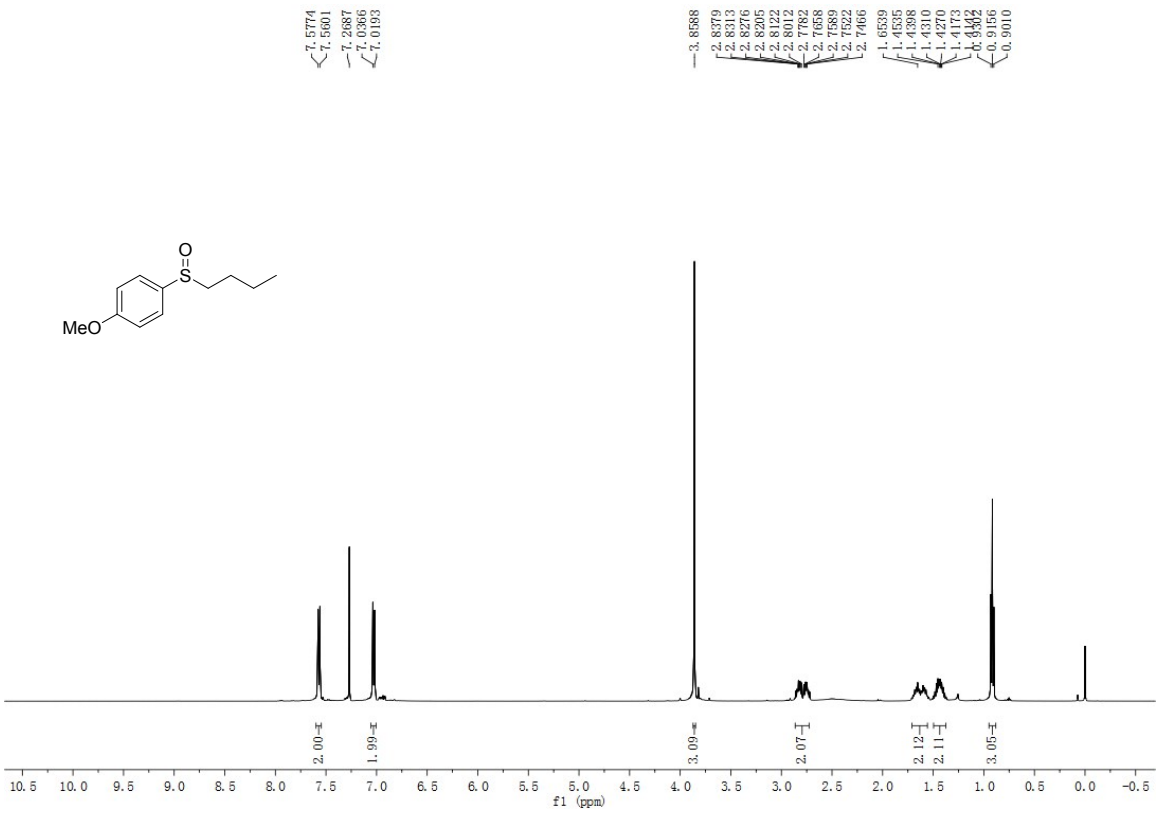
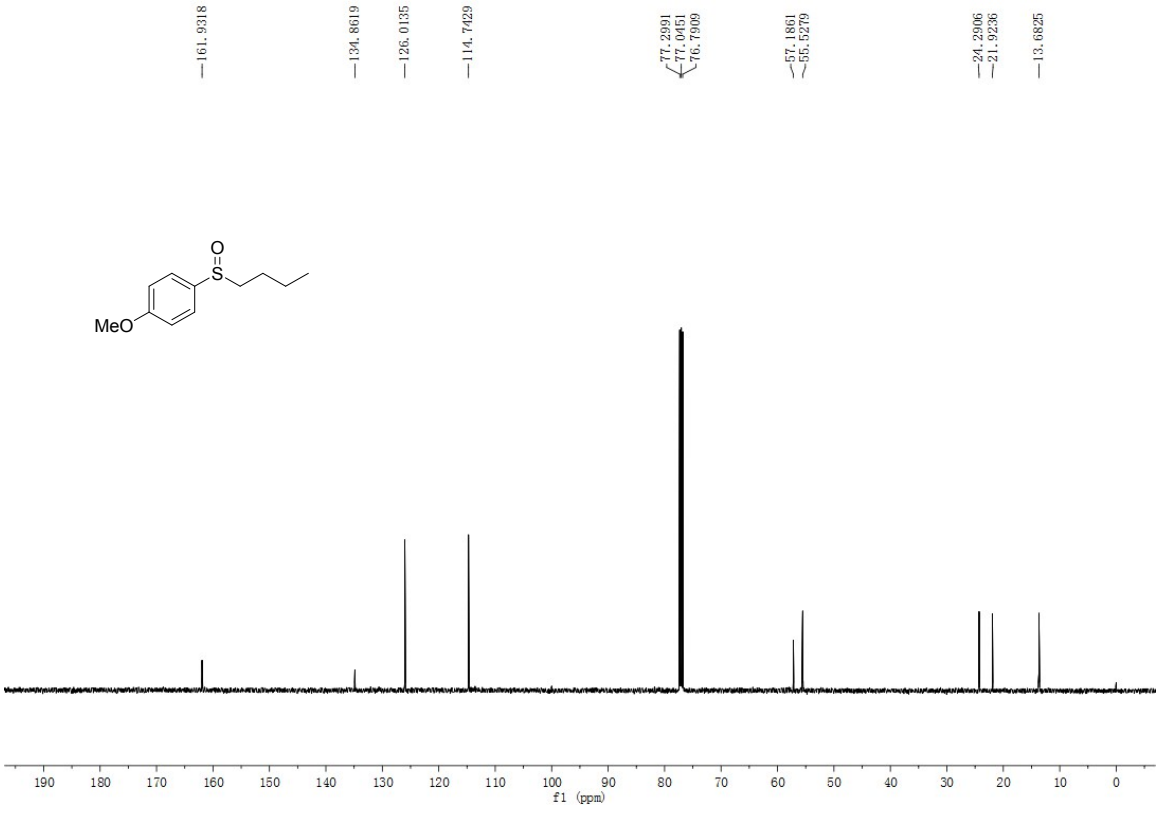
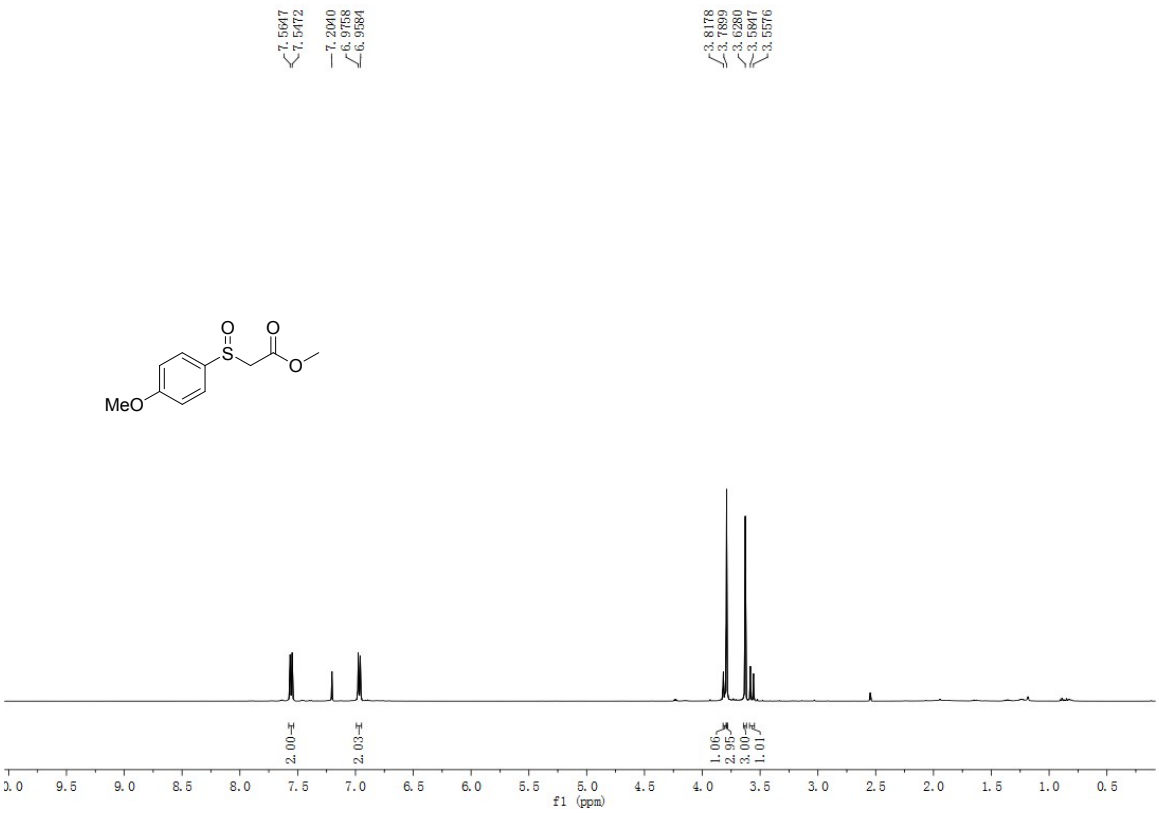
130.4050
129.2893
128.4681
128.1788
126.3858
114.3797
77.2988
77.0448
76.7906
63.7509
55.5091
O
S
Ph
MeO
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


MeO
f1 (ppm)


MeO
f1 (ppm)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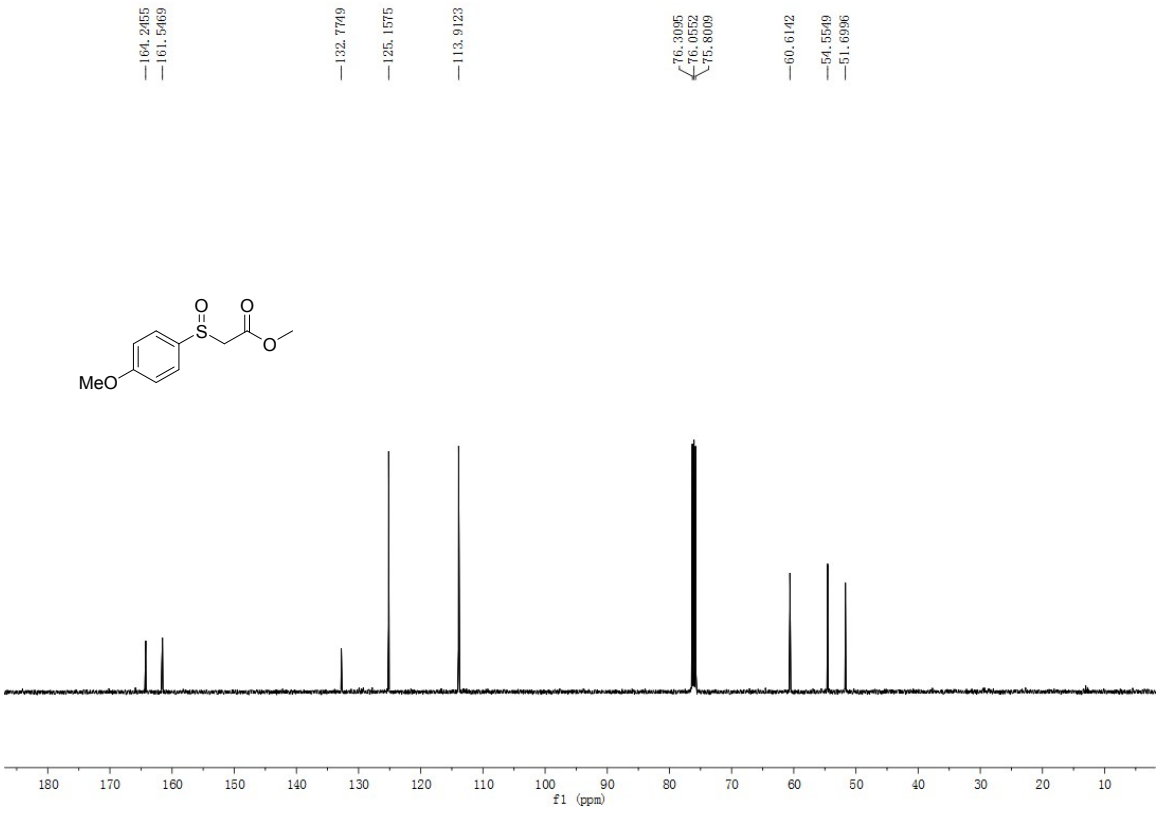
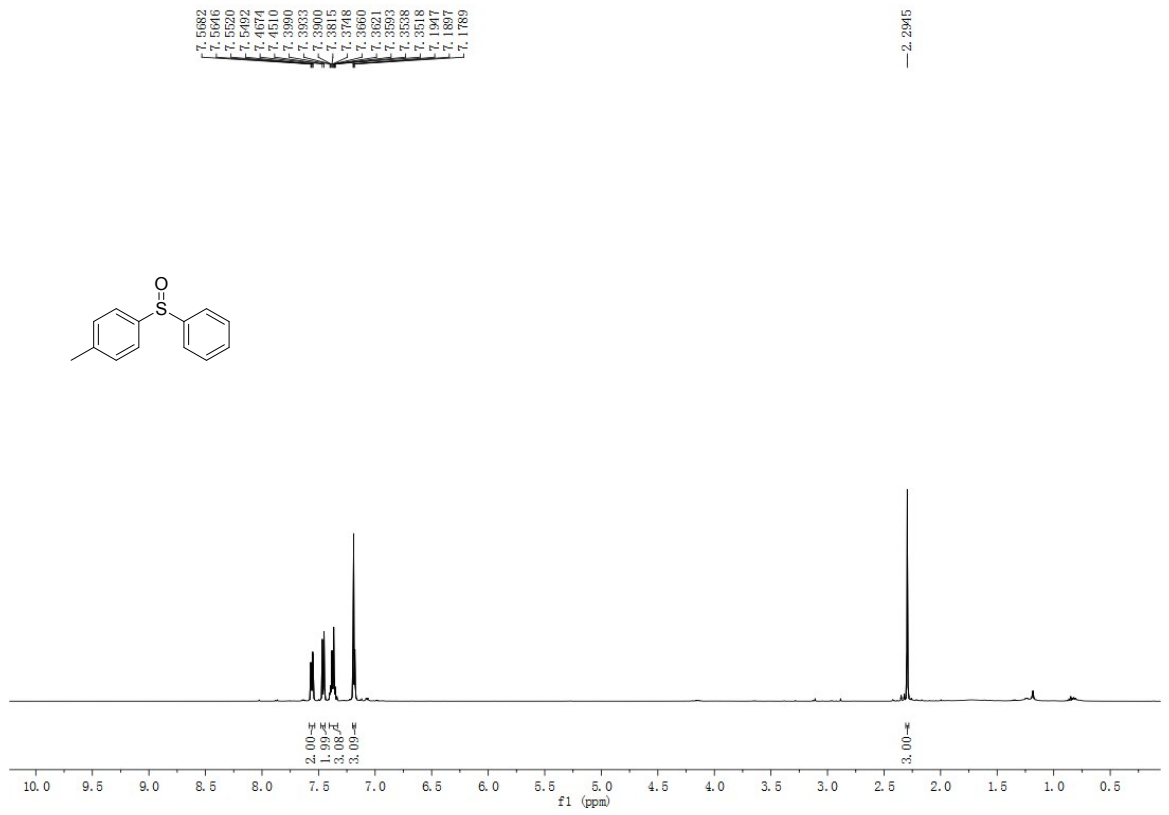
7.5472
7.2040
6.9758
6.9584
3.8178
3.7899
3.6280
3.5847
3.5576
MeO
2.00
2.03
1.06
2.95
3.00
1.01
f1 (ppm)


164.2455
161.5469
132.7749
125.1575
113.9123
76.3095
76.0552
75.8009
60.6142
54.5549
51.6996
MeO
f1 (ppm)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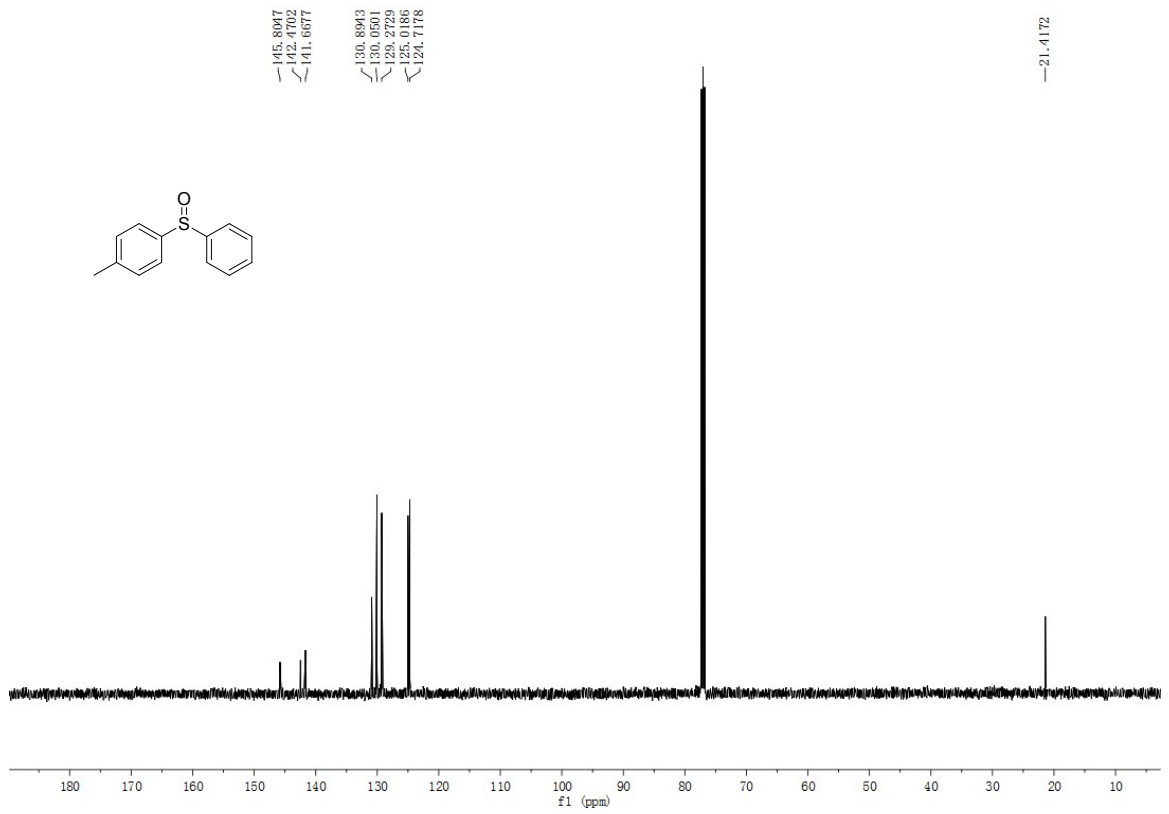
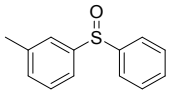
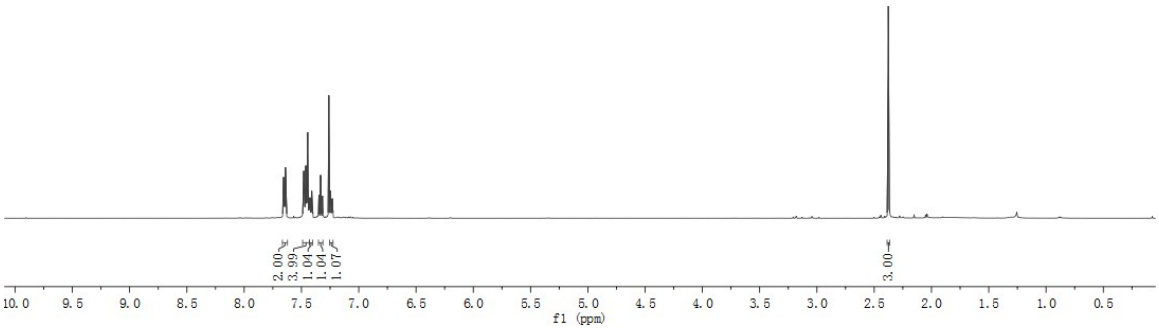
7.5646
7.5520
7.5492
7.4674
7.4510
7.3990
7.3933
7.3900
7.3815
7.3748
7.3660
7.3621
7.3593
7.3538
7.3518
7.1947
7.1897
7.1789
2.2945
2.00
1.99
3.08
3.09
3.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)


145.8947
142.4702
141.6677
130.8943
130.0501
129.2729
125.0186
124.7178
21.4172
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

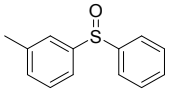

7.6565
7.6528
7.6492
7.6403
7.6375
7.4792
7.4728
7.4693
7.4611
7.4539
7.4495
7.4459
7.4424
7.4343
7.4320
7.4254
7.4100
7.3476
7.3324
7.3170
7.2615
7.2472
7.2322


2.3761

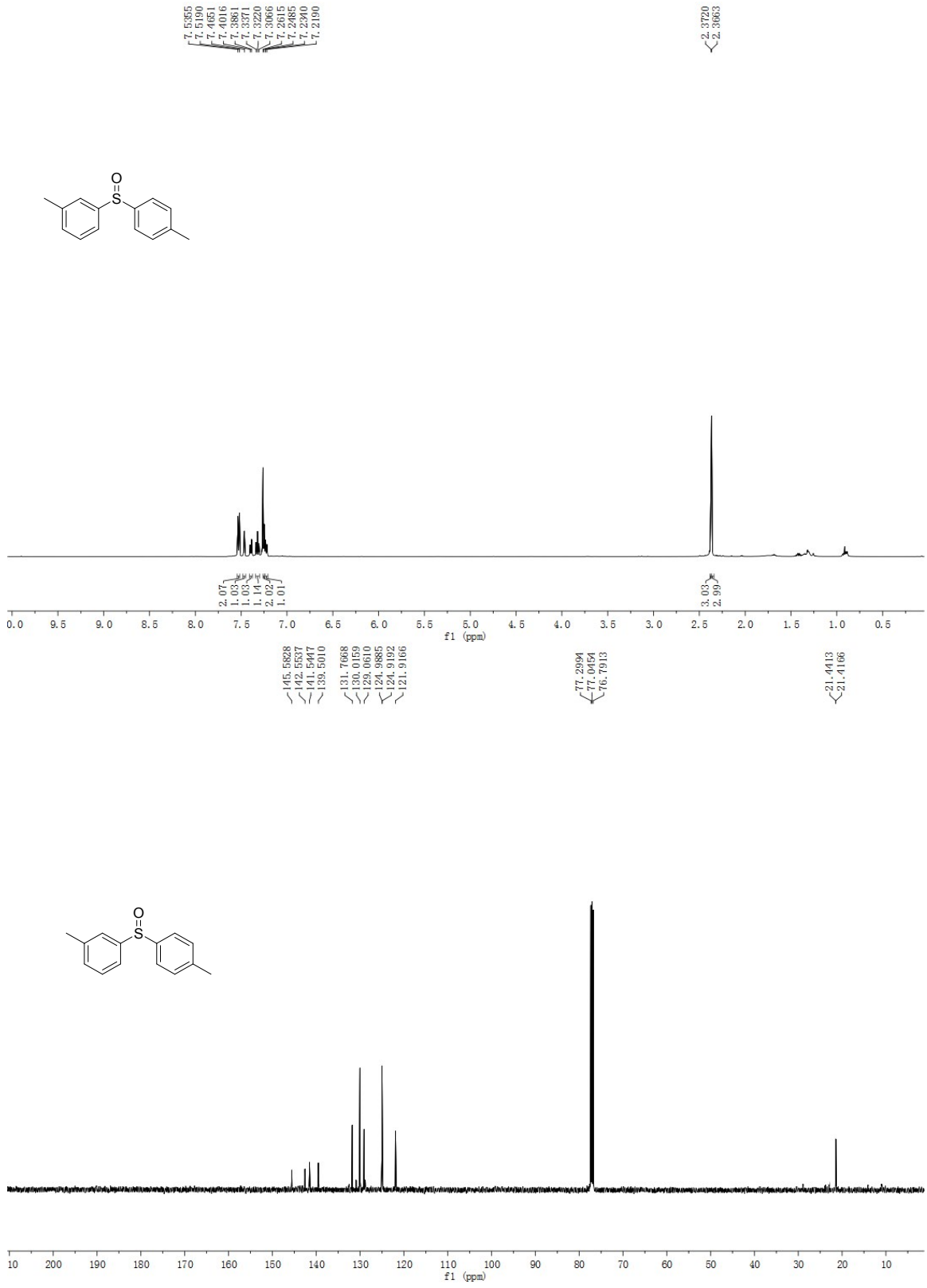

O
S

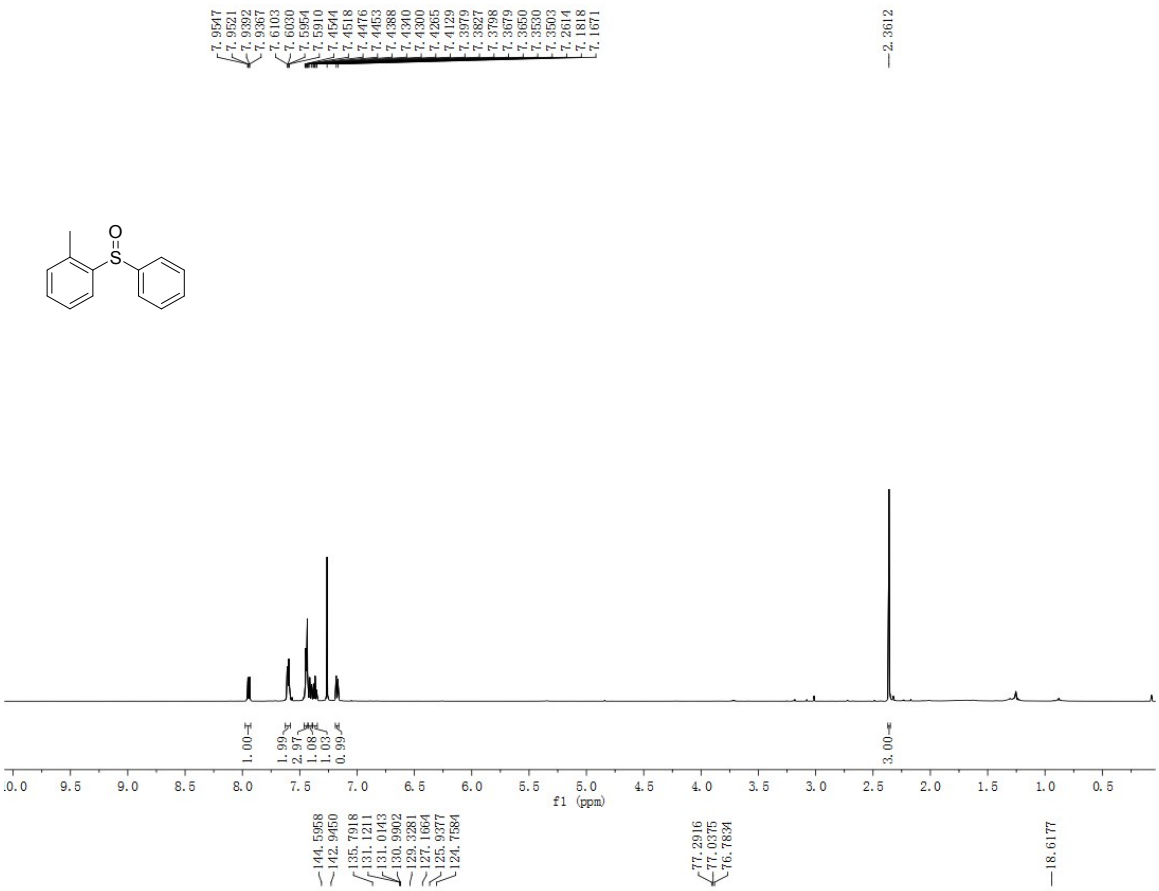

2.00
3.99
1.04
1.04
1.07
3.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)


145.6885
145.3876
139.5995
131.9541
130.9839
129.3114
129.1330
125.0126
124.7985
122.0259
77.2997
77.0458
76.7916
21.4437

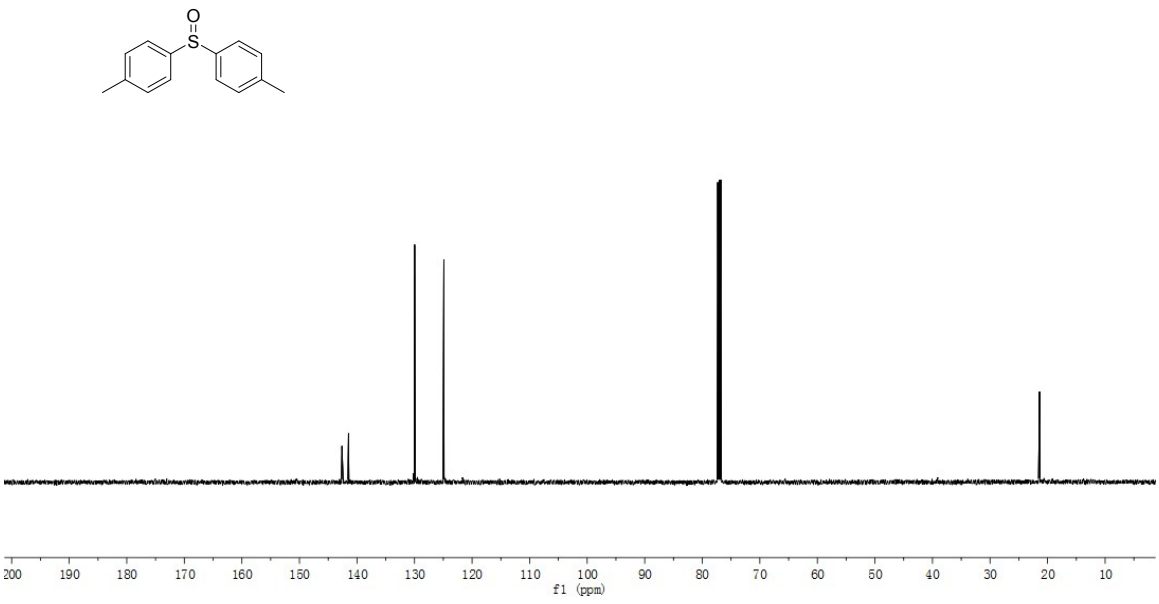

O
S

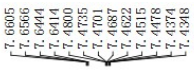

90
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

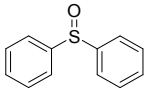

7.5355
7.5190
7.4651
7.4016
7.3861
7.3371
7.3220
7.3066
7.2615
7.2485
7.2340
7.2190
2.3720
2.3663
O
S
2.07
1.03
1.03
1.14
2.02
1.01
3.03
2.99
f1 (ppm)
145.5828
142.5537
141.5447
139.5010
131.7668
130.0159
129.0610
124.9885
124.9192
121.9166
77.2994
77.0459
76.7913
21.4413
21.4166
f1 (ppm)

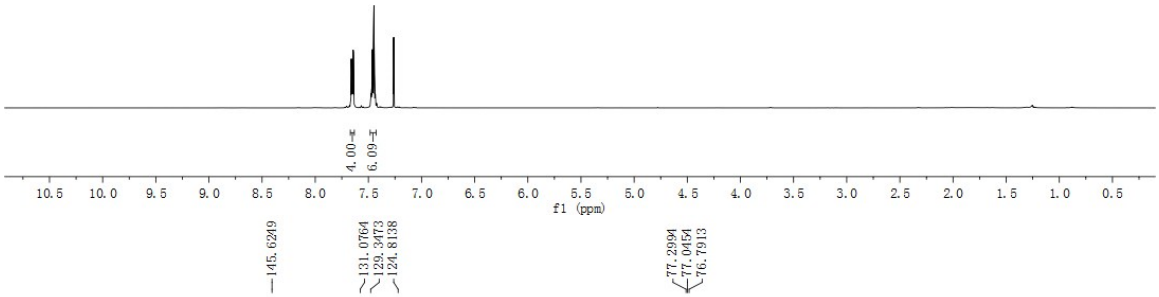

7.9547
7.9521
7.9392
7.9367
7.6103
7.6030
7.5954
7.5910
7.4544
7.4518
7.4476
7.4453
7.4388
7.4340
7.4300
7.4265
7.4129
7.3979
7.3827
7.3798
7.3679
7.3650
7.3530
7.3503
7.2614
7.1818
7.1671
2.3612
1.00
1.99
2.97
1.08
1.03
0.99
3.00
f1 (ppm)
144.5958
142.9450
135.7918
131.1211
131.0143
130.9902
129.3281
127.1664
125.9377
124.7584
77.2916
77.0375
76.7834
18.6177
f1 (ppm)


7.5186
7.5023
7.2616
7.2570
7.2409
2.3610
4.03
4.01
6.00
f1 (ppm)

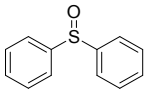

142.6039
141.4709
129.9865
124.9071
77.3018
77.0477
76.7936
21.3995
f1 (ppm)

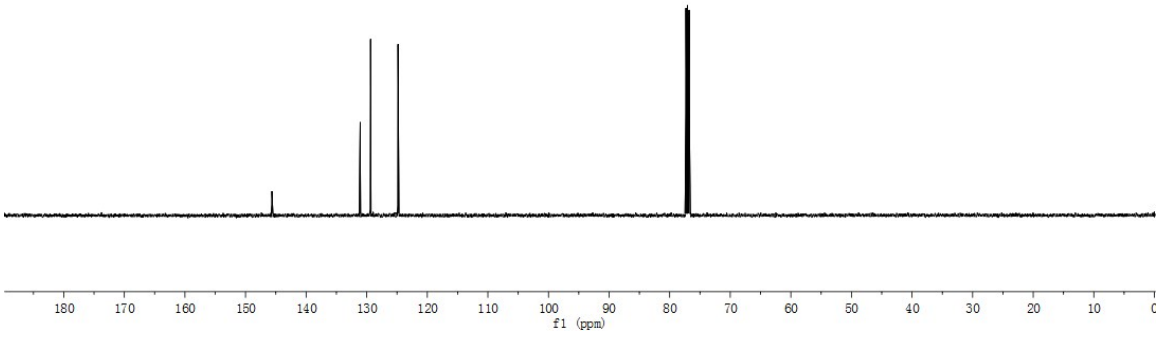

7.6605
7.6566
7.6444
7.6414
7.4800
7.4735
7.4701
7.4687
7.4622
7.4515
7.4478
7.4374
7.4348



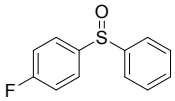

4.00
6.09
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

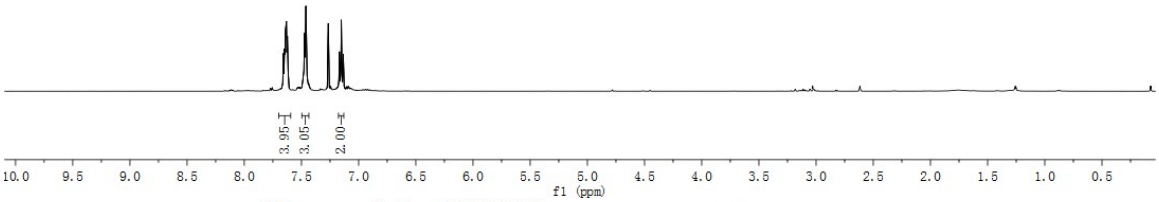

145.6249
131.0764
129.3473
124.8138
77.2994
77.0454
76.7913



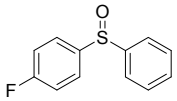

180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

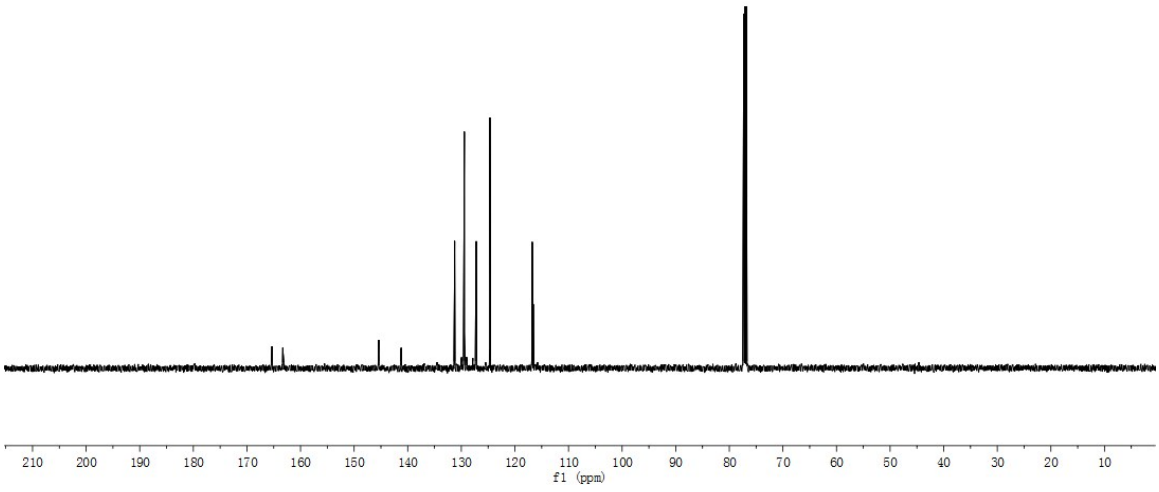

7.6589
7.6486
7.6396
7.6316
7.6228
7.4920
7.4848
7.4817
7.4745
7.4622
7.4608
7.4537
7.4443
7.4379
7.2651
7.1684
7.1512
7.1342

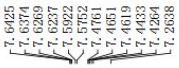

O
S
F

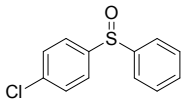

3.95
3.05
2.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

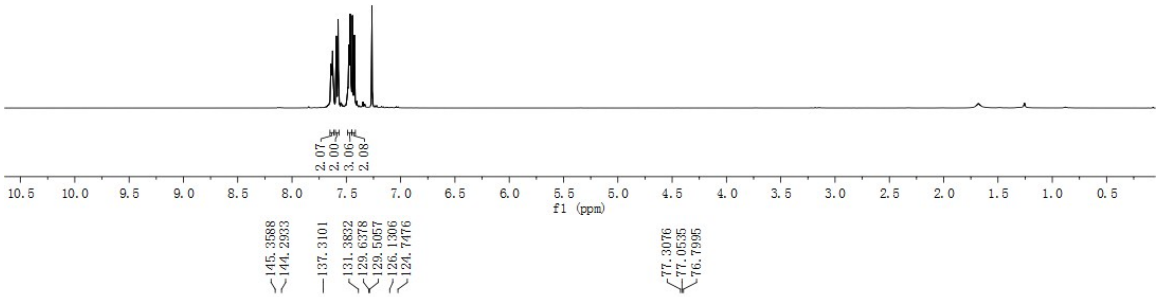

165.3160
163.3130
145.4014
141.2163
131.2390
129.4389
127.2696
127.1983
124.6664
116.7694
116.5899
77.3124
77.0581
76.8041


O
S
F

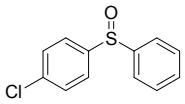

210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)


7.6425
7.6374
7.6269
7.6237
7.5922
7.5752
7.4761
7.4651
7.4619
7.4433
7.4264
7.2638

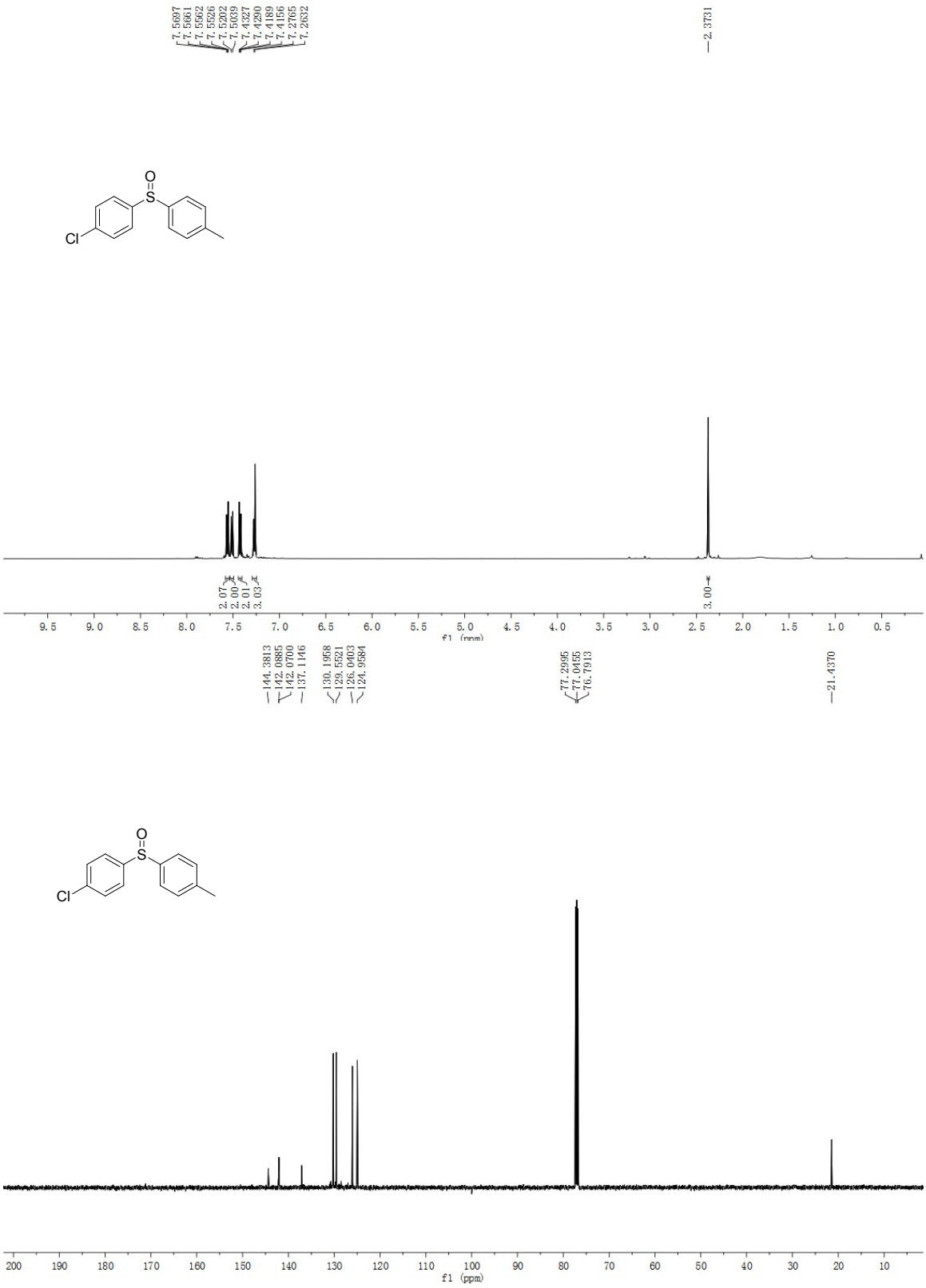

O
S
Cl

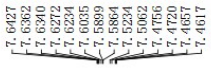

2.07
2.00
3.06
2.08
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

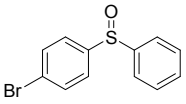

145.3588
144.2933
137.3101
131.3832
129.6378
129.5057
126.1306
124.7476
77.3076
77.0535
76.7995

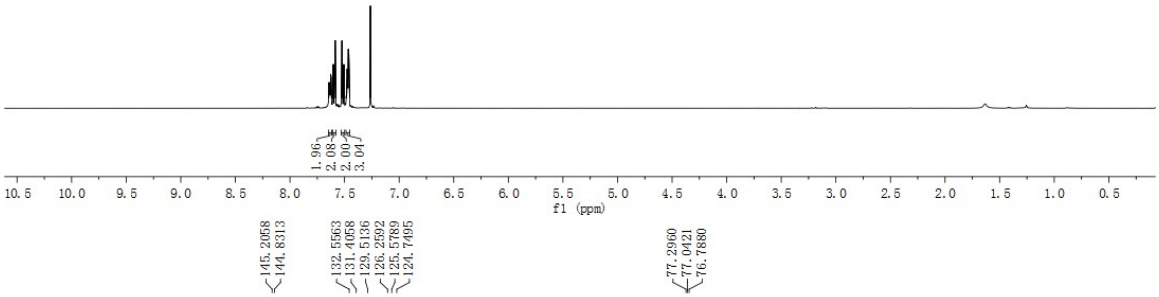

O
S
Cl


190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

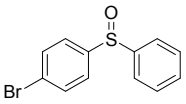

7.5697
7.5661
7.5562
7.5526
7.5202
7.5039
7.4327
7.4290
7.4189
7.4156
7.2765
7.2632
2.3731
O
S
Cl
2.07
2.00
2.01
3.03
3.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)
144.3813
142.0885
142.0700
137.1146
130.1958
129.5521
126.0403
124.9584
77.2995
77.0455
76.7913
21.4370
O
S
Cl
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

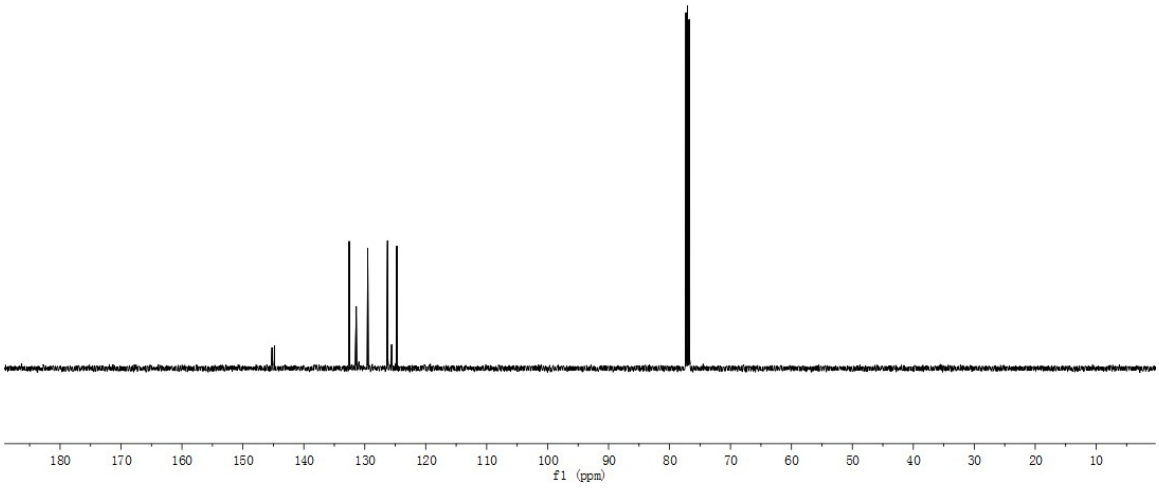

7.6427
7.6362
7.6340
7.6272
7.6234
7.6035
7.5899
7.5864
7.5234
7.5062
7.4756
7.4720
7.4657
7.4617

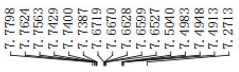

O
S
Br

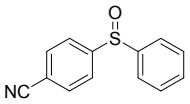

1.96
2.08
2.00
3.04
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

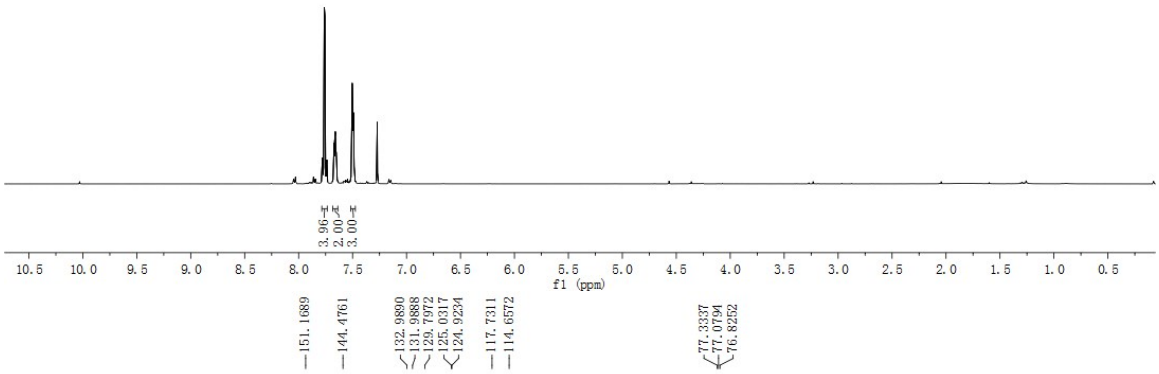

145.2058
144.8313
132.5563
131.4068
129.5136
126.2592
125.5789
124.7495
77.2960
77.0421
76.7880


O
S
Br

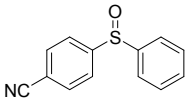

180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

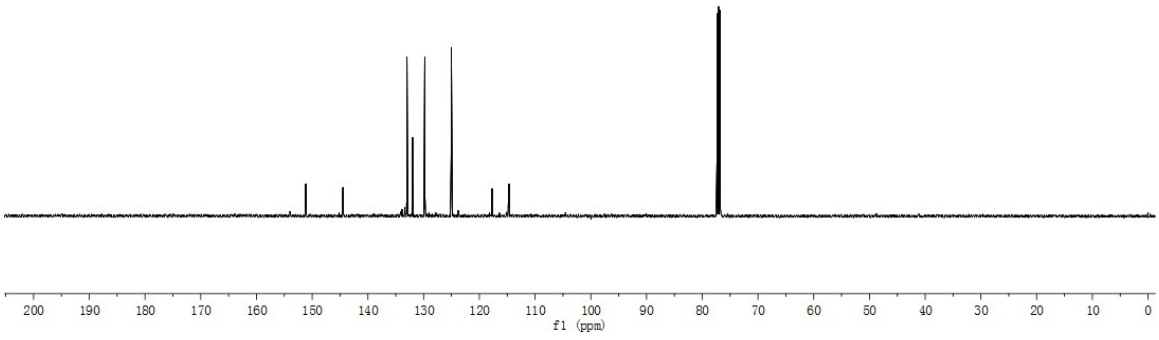

7.7798
7.7624
7.7563
7.7429
7.7400
7.7387
7.6719
7.6670
7.6628
7.6599
7.6527
7.5040
7.4983
7.4948
7.4913
7.2713


O
S
NC


3.96
2.00
3.00
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)


151.1689
144.4761
132.9890
131.9888
129.7972
125.0317
124.9234
117.7311
114.6572
77.3337
77.0794
76.8252


O
S
NC


200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)