Supporting information

Synthesis of Sulfinamides via Photocatalytic Alkylation or Arylation of Sulfinylamine

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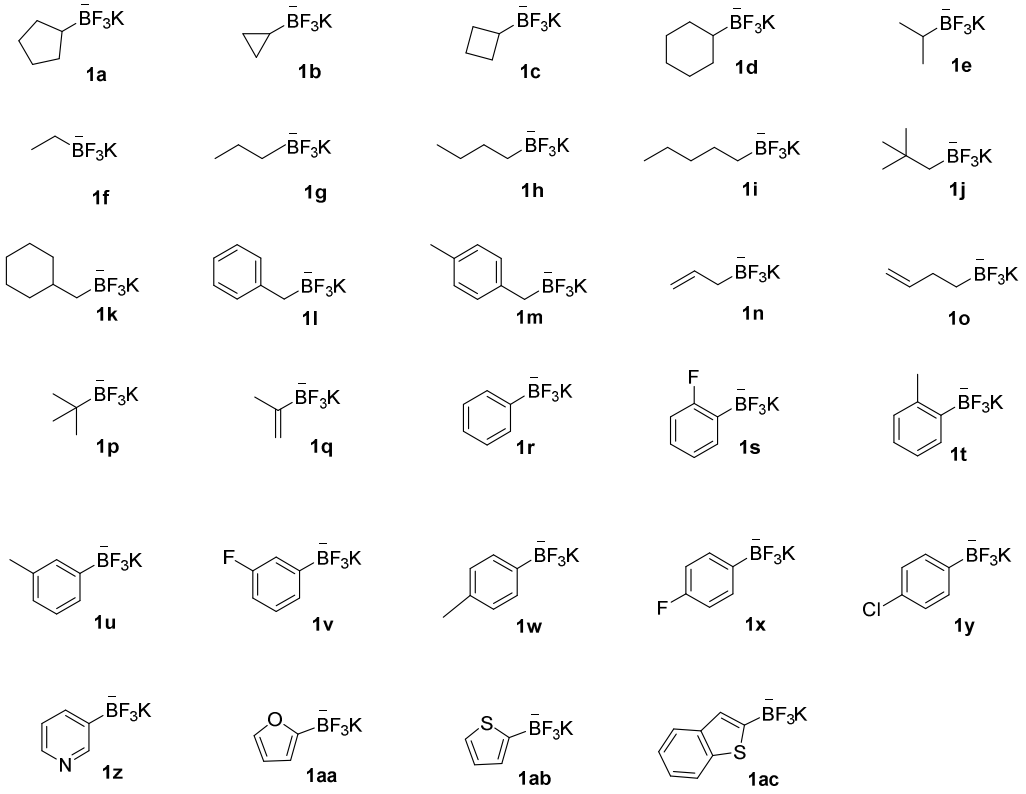
1. General experimental procedures

Unless otherwise stated, all reagents were purchased from commercial suppliers and used without further purification. All solvents employed in the reactions were distilled from appropriate drying agent prior to use. All reactions that required anhydrous or airless conditions were carried by standard procedures under an argon atmosphere. Organic solutions were concentrated under reduced pressure on a Büchi rotary evaporator. Reactions were monitored by thin-layer chromatography using 0.25 mm Merck silica gel precoated plates (60F-254). Visualization was accomplished by irradiation with UV light at 254 nm. Flash column chromatography was performed using Merck silica gel 60 (particle size 0.040–0.063 mm). Chemical yields refer to pure isolated substances.

NMR spectra were recorded at 25 °C on Bruker spectrometers at 400 MHz (^{1}H NMR), 101 MHz (^{13}C NMR) and 376 MHz (^{19}F NMR) respectively, using $CDCl_3$ or DMSO-d_6 as the solvent and TMS as the internal reference.Spectra were reported as follows: chemical shift (δ ppm), multiplicity (s =singlet, d = doublet, t = triplet, q = quartet, m = multiplet，br= broad), coupling constants (Hz), integration and assignment. Mass spectra were recorded on a Waters Vion IMS QTof system equipped with an ESI source.

2. Preparation of starting materials

(1) Potassium trifluoro(organo)borates are commercially available.



Figrue S1 Potassium trifluoro(organo)borates used in this experiment

(2) Synthesis of *N*-thionylaniline with the corresponding aniline.

N-thionylanilines were prepared according to the previous literature. [1-5] The spectral data were consistent with previously reported data.

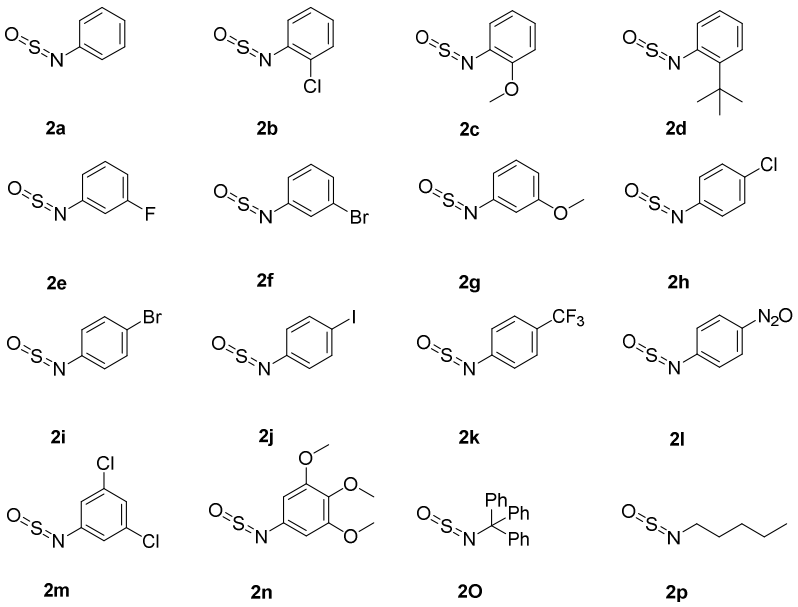
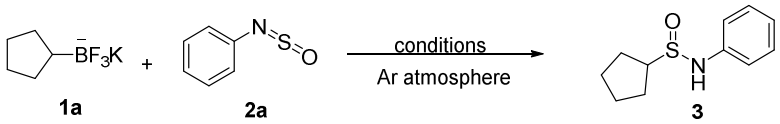


Figure S2 *N*-thionylaniline used in this experiment

3. Screening the reaction conditions

Table S1 Optimization of the reaction conditions[a]



Entry	PC	Solvent	Temp(°C)	Yield[b]
1	I	DCE[c]	RT	62
2	II	DCE	RT	<5
3	III	DCE	RT	85
4	IV	DCE	RT	51
5	V	DCE	RT	60
6	VI	DCE	RT	23
7	VII	DCE	RT	10
8	III	$CHCl_3$	RT	66
9	III	DCM	RT	80
10	III	1,4-dioxane	RT	63
11	III	DMF	RT	60
12	III	EA	RT	64
13	III	MeCN	RT	67
14	III	Acetone	RT	63
15	III	TMF	RT	67
16	III	DCE	40	83
17	III	DCE	20	66
18	III	DCE	0	53
19[d]	III	DCE	RT	85

20[e]	III	DCE	RT	61
21[f]	III	DCE	RT	67
22[g]	III	DCE	RT	41

[a]**1a** (0.2 mmol), **2a** (0.2 mmol), photocatalyst (0.002 mmol, 1 mol%) in solvent (2mL, 0.1 M) under white LED (12 W) irradiation for 12 h. [b]Isolated yield, [c]DCE= 1,2-Dichloroethane, [d]under white LED (24 W) irradiation, [e]under green LED, [f]irradiation for 6 h. [g]under air.

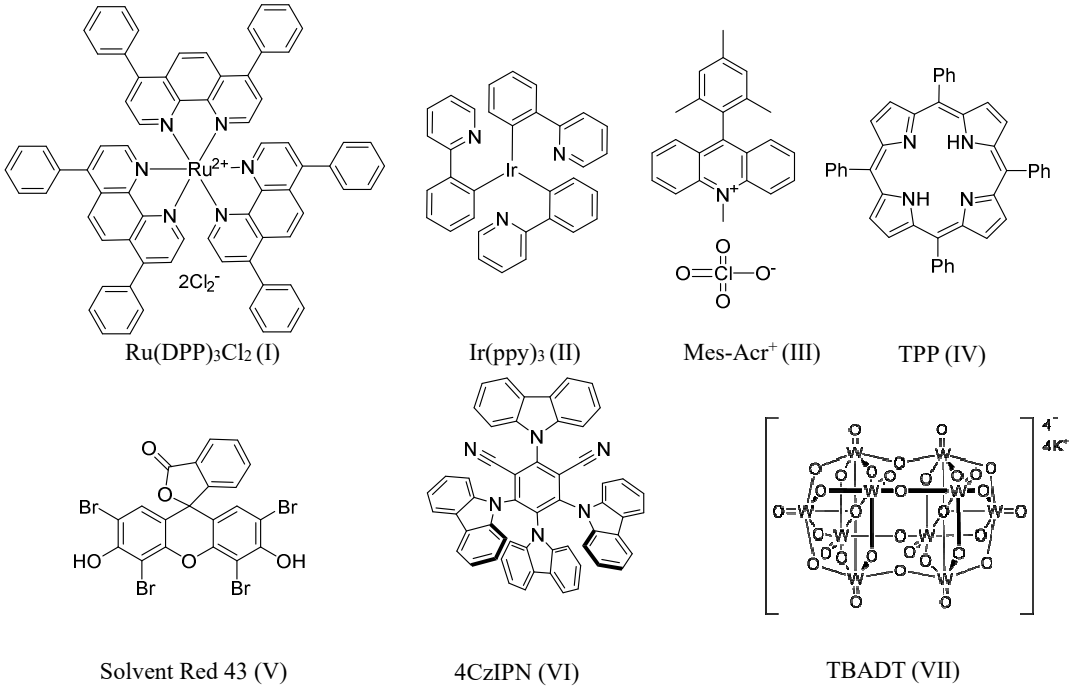
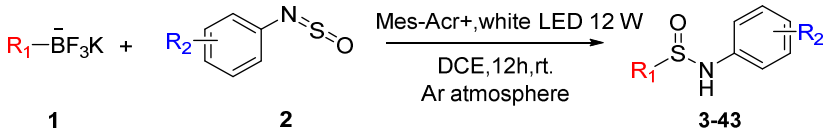


Figure S3 Structure of PC

4. General procedure for the preparation of products

4.1 General procedure for the preparation of products 3-43



1 2 3-43

General procedure for products **3-43**: A test tube equipped with a magnetic stirrer was charged with potassium trifluoro(organo)borates 1 (0.2 mmol, 1 equiv.) and *N*-thionylaniline (0.2 mmol,1 equiv.) followed by addition of Mes-Acr^{+} (0.002 mmol, 0.01 equiv.) and 1,2-dichloroethane (2 mL) under air, the tube was sealed and three vacuum/argon cycles were made. The mixture was then irradiated by a 12 W white LED tube and stirred at room temperature for 12 hours. Upon completion, the reaction mixture was concentrated under a vacuum and the residue was purified by column chromatography (petrol ether/EtOAc = 5:1) to give the desired products **3-43.**

We use LED tube (12 W white LED, the wavelength is 400-760 nm), which are manufactured by Guangdong Shenzhen Liangxi Optoelectronics Co. Ltd (see Figure S4). The irradiation vessel is an ordinary glass test tube. The distance from the light source to the irradiation vessel is about 5.0 cm. No filter between LED and test tube is used. The reaction vessel is cooled by using a small fan.

Figure S4 Reaction setup

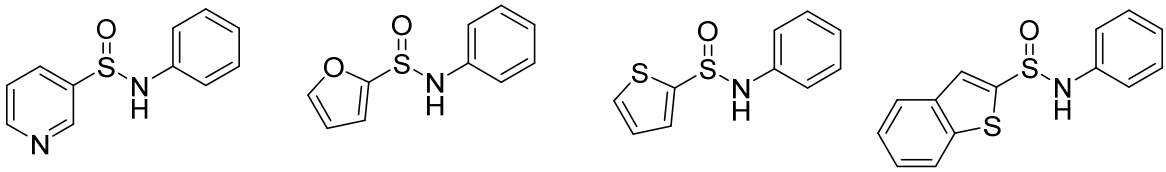
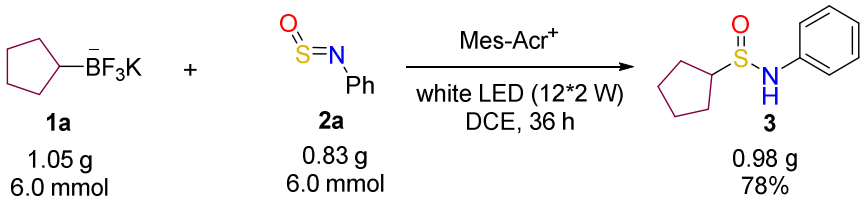


Figure S5 Unsuccessful examples under the standard reaction conditions

4.2 Gram-scale synthesis



Potassium cyclopentyltrifluoroborate (1.05g, 6.0mmol, 1.0 equiv.), *N*-thionylaniline (0.83 g, 6.0 mmol, 1.0 equiv.) were placed in a dry 100 mL Round-bottomed flask, followed by addition of Mes-Acr^{+} (24.65 mg, 0.06 mmol, 0.01 equiv.) and 1,2-dichloroethane (20 mL) under air. The flask was sealed and three vacuum/argon cycles were made. The reaction mixture was irradiated with 24 W (2 x 12 W) white LEDs at room temperature under Ar atmosphere for 36 h. After the completion of the reaction, the reaction mixture was taken out, filtered the resulting suspension and washed the precipitate with dichloromethane, the filtrate was collected and concentrated under reduced pressure, and the residue was purified by flash column chromatography (petroleum ether/EtOAc =10/1 to 5/1) afforded product.

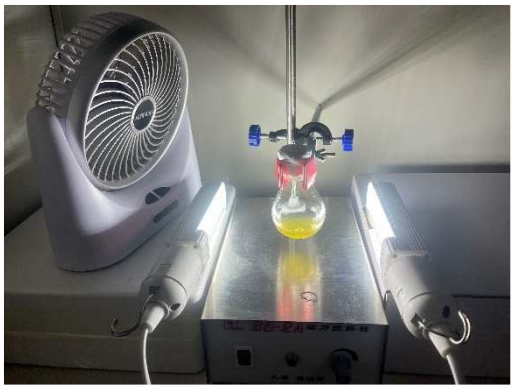
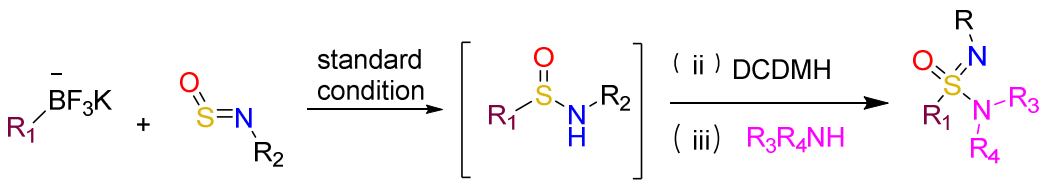


Figure S6 Reaction setup

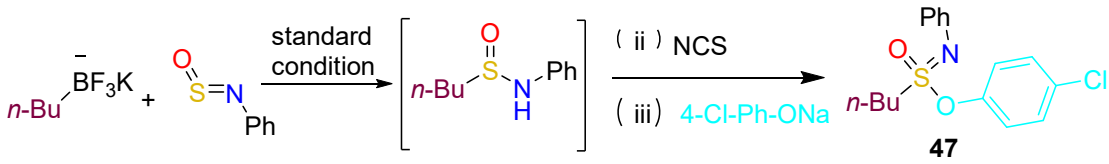
4.3 General procedure for the preparation of products 44-48.

General procedure for products 44-46:



A test tube equipped with a magnetic stirrer was charged with potassium trifluoro(organo)borates **1** (0.2mmol, 1.0 equiv.) and *N*-thionylaniline **2** (0.2 mmol, 1.0 equiv.) followed by the addition of Mes-Acr^{+}(0.002 mmol, 0.01 equiv.) and 1,2-dichloroethane (2 mL) under air, the tube was sealed and three vacuum/argon cycles were made. The mixture was then irradiated by a 12 W white LED strip and stirred at room temperature for 12 hours. Upon completion, the reaction mixture was directly carried out to the next step without separation and purification. After the reaction mixture was placed at -20°Cand stirred for 5 minutes, DCDMH (0.2 mmol, 1.0 equiv.) was directly added, and stirring was continued for 2 hours. The amines (0.4 mmol, 2.0 equiv.) were then added and stirring was continued at -20 °C for 10 hours. After the completion of the reaction, the reaction mixture was taken out, returned to room temperature, filtered the resulting suspension and washed the precipitate with dichloromethane, the filtrate was collected and concentrated under reduced pressure, and the residue was purified by flash column chromatography (petroleum ether/EtOAc =25/1 to 8/1) afforded products **44-46**.

General procedure for product 47

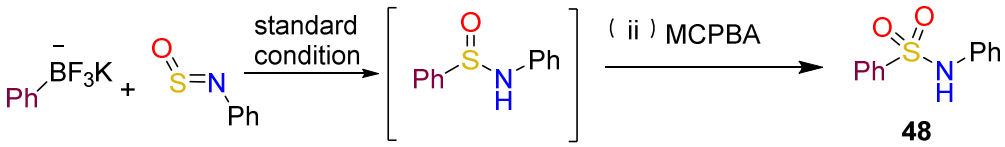


47

A test tube equipped with a magnetic stirrer was charged with potassium trifluoro(organo)borates **1** (0.2 mmol, 1.0 equiv.) and N-Thionylaniline **2** (0.2 mmol, 1.0 equiv.) followed by the addition of Mes-Acr^{+} (0.002 mmol, 0.01 equiv.) and 1,2-dichloroethane (2 mL) under air, the tube was sealed and three vacuum/argon cycles were made. The mixture was then irradiated by a 12 W white LED strip and stirred at room temperature for 12 hours. Upon completion, the reaction mixture was directly carried out to the next step without separation and purification. After the reaction mixture was placed at -20°C and stirred for 5 minutes, NCS (0.3 mmol, 1.5 equiv.) was directly added, and stirring was continued for 2 hours. The sodium 4-chlorophenolate (0.6 mmol, 3.0 equiv.) was then added and stirring was continued at -20 °C for 10 hours. After the completion of the reaction, the reaction mixture was taken out, returned to

room temperature, filtered the resulting suspension and washed the precipitate with dichloromethane, the filtrate was collected and concentrated under reduced pressure, and the residue was purified by flash column chromatography (petroleum ether/EtOAc = 15/1 to 10/1) afforded product **47**.

General procedure for the preparation of product 48.



A test tube equipped with a magnetic stirrer was charged with potassium trifluoro(organo)borates 1 (0.2mmol, 1.0 equiv.) and N-Thionylaniline 2 (0.2 mmol, 1.0 equiv.) followed by the addition of Mes-Acr^{+}(0.002 mmol, 0.01 equiv.) and 1, 2-dichloroethane (2 mL) under air, the tube was sealed and three vacuum/argon cycles were made. The mixture was then irradiated by a 12 W white LED strip and stirred at room temperature for 12 hours. MCPBA (0.3 mmol, 1.5 equiv.) was added, and stirring was continued for 10 minutes. After the completion of the reaction, the reaction mixture was taken out, filtered the resulting suspension and washed the precipitate with dichloromethane, the filtrate was collected and concentrated under reduced pressure, and the residue was purified by flash column chromatography (petroleum ether/EtOAc =10/1 to 5/1) afforded product **48**.

5. Mechanistic Investigations

5.1 Control experiments

To explore the reaction mechanism, some control experiments were first carried out (Table S2). The reaction did not proceed without white LED irradiation (entry 2). This result indicates that the reaction is not a simple polar reaction. In addition, almost no reaction occurred in the absence of the photocatalyst Mes-Acr$^+$ (entry 3), These facts suggest that the Mes-Acr$^+$ is the active species that absorbs white light for excitation. The results demonstrated that light, and photocatalyst, none of these can be excluded. The absence of anyone leads to the complete inhibition of this process.

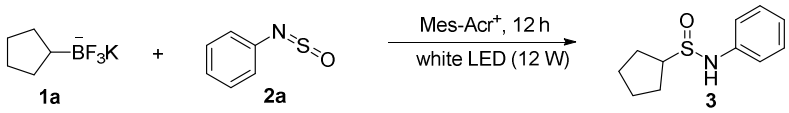
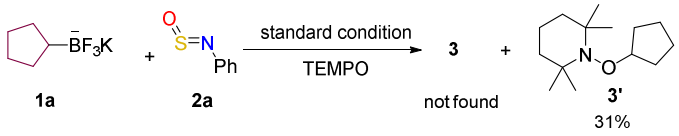


Table S2 Control experiments

Entry	Deviation from the standard conditions	Yield (%)
1	None	85
2	No light	trace
3	No Mes-Acr$^+$	trace

5.2 TEMPO trapping experiment



In the dark, a test tube equipped with a magnetic stirrer was charged with potassium cyclopentyltrifluoroborate **1a** (0.2 mmol), *N*-thionylaniline **2a** (0.2 mmol) and TEMPO (1.0 mmol, 5.0 equiv.) followed by addition of Mes-Acr$^+$ (0.002 mmol, 0.01 equiv.) and 1,2-dichloroethane (2 mL) under air, the tube was sealed and three vacuum/argon cycles were made. The mixture was then irradiated by a 12 W white LED strip and stirred at room temperature for 12 hours. Upon completion, the reaction mixture was concentrated under vacuum and the residue was purified by column chromatography (petrol ether/EtOAc = 30:1) to give the desired product **3'** (14.0 mg, yield: 31%). **3** was not found. This proves the generation of alkyl radical.

5.3 Investigation of the N-H bond via NMR experiments

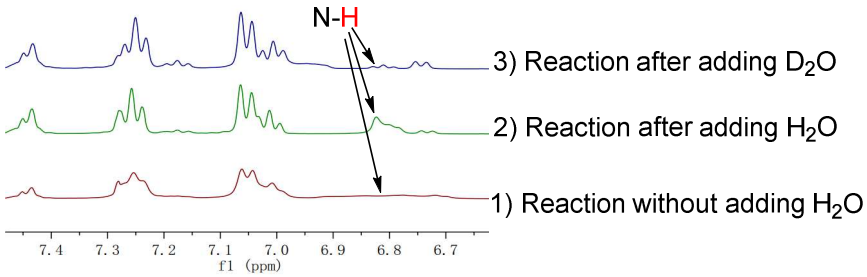


Figure S7 NMR experiment

5.4 UV-VIS spectroelectrochemistry experiments

The UV-vis experiments were performed on varioskan flash full wavelength scanning multi-function reader with a quartz cuvette (10 mm path length). According to figure S4, $[Mes\text{-}Acr^+]ClO_4^-$ has absorption at 362 nm and 424 nm regions.

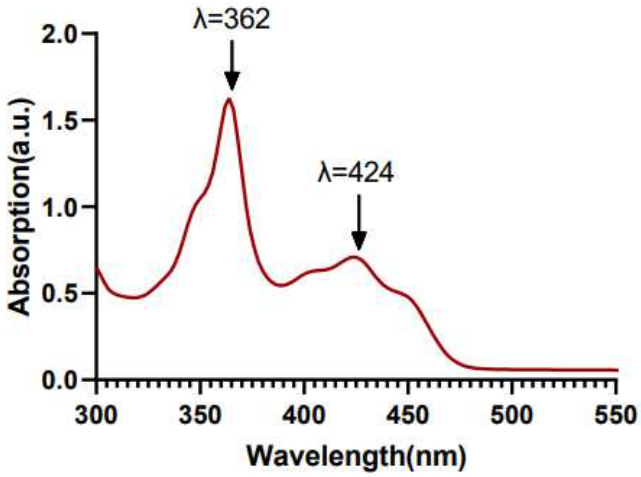


Figure S8 UV-Vis spectra of $[Mes\text{-}Acr^+]ClO_4^-$ (0.1 μmol/mL) in 1,2-dichloroethane

5.5 Stern-Volmer quenching experiments

Stern-Volmer quenching experiments were conducted on an F97Pro Fluorescence Spectrophotometer. Stern-Volmer luminescence quenching experiments were run with freshly prepared solutions of $[Mes\text{-}Acr^+]ClO_4^-$ (1.0×10^{-4} M) and quencher (2.5×10^{-3} M) in 1,2-Dichloroethane at room temperature. After degassing with argon for 5 min, the emission spectra of the samples were collected. In our experiments, white light is used to excite the reaction, and white light is a mixed light in the wavelength range of 400 nm to 760 nm, and the UV-Vis spectral data of $[Mes\text{-}Acr^+]ClO_4^-$ shows that it absorbs at both 362nm and 424 nm. Therefore, in the fluorescence quenching experiments, we chose 362 nm and 424 nm as the excitation wavelengths, respectively.

The preparation method of the sample solution is shown in Table S3. Other parameters are set as: wavelength scan range: 440 nm to 750 nm; scan speed: 1000 nm/min; scan interval: 1 nm; excitation bandwidth: 10 nm; transmit bandwidth: 10 nm.

Table S3. Sample solution preparation methods

Entry	Concentration of 1a (or 2a) (M)	Volume of Mes-Acr+	Volume of 1a (or 2a)	Volume of additional DCE	total volume
1	0	500ul	0μL	2500ul	3000μL
2	$0.83x10^{-4}$	500ul	100μl	2400ul	3000μL
3	$1.67x10^{-4}$	500ul	200μl	2300 ul	3000μL
4	$2.50x10^{-4}$	500ul	300μl	2200 ul	3000μL
5	3.33x10-^{4}	500ul	400μl	2100 ul	3000μL
6	$4.17x10^{-4}$	500ul	500μl	2000 ul	3000μL
7	$4.99x10^{-4}$	500ul	600μl	1900 ul	3000μL
8	$5.83x10^{-4}$	500ul	700μl	1800 ul	3000μL
9	$6.67x10^{-4}$	500ul	800μl	1700 ul	3000μL
10	$7.50x10^{-4}$	500ul	900μl	1600 ul	3000μL

Chose 362 nm as the excitation wavelengths

First, the emission spectrum of $[Mes\text{-}Acr^{+}]ClO_4^{-}$ under excitation at 362 nm was tested. We investigated the effect of adding different concentrations of 1a or 2a on the emission spectrum of $[Mes\text{-}Acr^{+}]ClO_4^{-}$ (Table S4 and Figure S9, Table S5 and Figure S10), Where I_0 being the luminescence intensity in the absence of any quencher, I being the luminescence intensity in the presence of a predefined quencher concentration.

Table S4. Stern-Vollmer quenching experiment of Mes-Acr+ with 1a in 1,2-dichloroethane.[a]

Concentration of 1a (M)	I_0	I	I_0/I
0	1284	1284	1.00
$0.83x10^{-4}$	1284	1264	1.02
$1.67x10^{-4}$	1284	1279	1.00
$2.50x10^{-4}$	1284	1341	0.96
$3.33x10^{-4}$	1284	1370	0.94
$4.17x10^{-4}$	1284	1302	0.99
4.99×10^{-4}	1284	1281	1.00
5.83×10^{-4}	1284	1327	0.97
6.67×10^{-4}	1284	1317	0.97
7.50×10^{-4}	1284	1400	0.92

[a](1×10^{-4} M $Mes\text{-}Acr^{+}$, 1,2-dichloroethane, 25 °C, λ_{ex} = 362 nm)

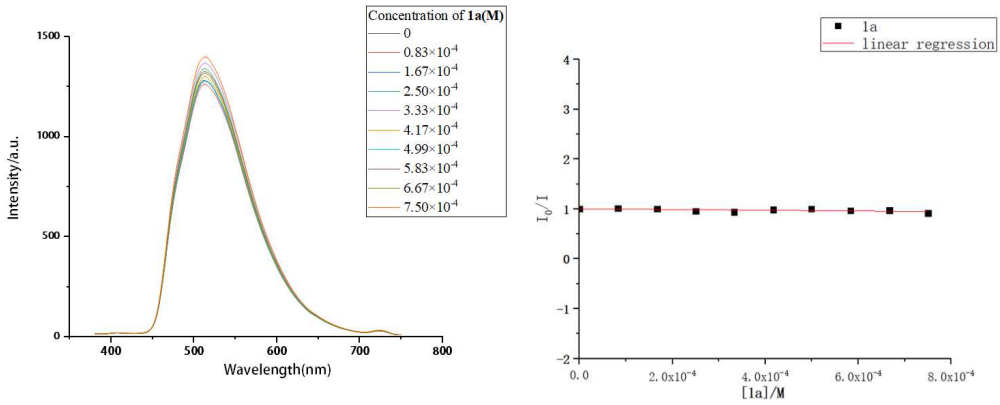


Figure S9. Stern-Vollmer quenching experiment of Mes-Acr$^+$ with **1a** in 1,2-dichloroethane. (1.0×10^{-4} M Mes-Acr$^+$, 1,2-dichloroethane, 25 °C, λ_{ex} = 362 nm)

Table S5. Stern-Vollmer quenching experiment of Mes-Acr$^+$ with **2a** in 1,2-Dichloroethane. [a]

Concentration of **2a** (M)	I_0	I	I_0/I
0	1284	1284	1.00
0.83 x 10-4	1284	1029	1.24
1.67 x 10-4	1284	847	1.51
2.50 x 10-4	1284	680	1.88
3.33 x 10-4	1284	483	2.65
4.17 x 10-4	1284	369	3.47
4.99 x 10-4	1284	294	4.36
5.83 x 10-4	1284	239	5.37
6.67 x 10-4	1284	187	6.86
7.50 x 10-4	1284	156	8.23

[a](1×10^{-4} M Mes-Acr$^+$1,2-dichloroethane, 25°C, λ_{ex} = 362 nm)

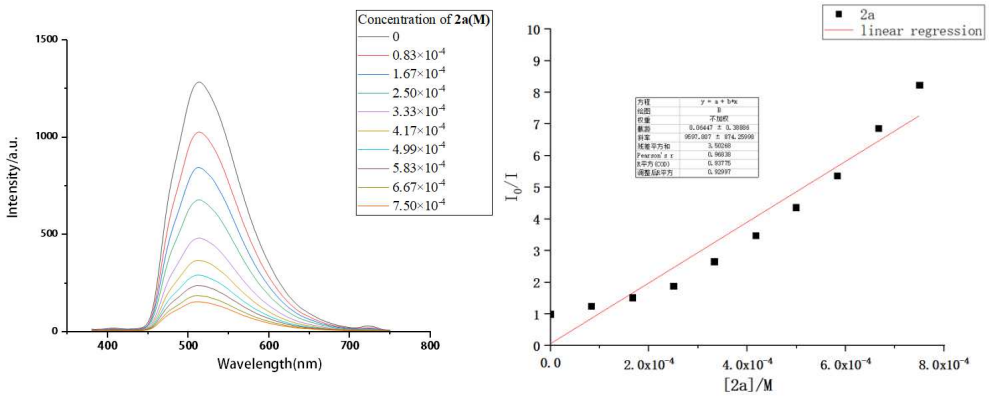


Figure S10. Stern-Vollmer quenching experiment of Mes-Acr$^+$ with **1a** in 1,2-dichloroethane. (1.0×10^{-4} M Mes-Acr$^+$, 1,2-dichloroethane, 25 °C, λ_{ex} = 362 nm)

Chose 424 nm as the excitation wavelengths

Subsequently, the emission spectrum of Mes-Acr$^+$ under excitation at 424 nm was tested. We investigated the effect of adding different concentrations of **1a** or **2a** on the emission spectrum of Mes-Acr$^+$ (Table S6 and Figure S11, Table S7 and Figure S12), Where I_0 being the luminescence intensity in the absence of any quencher, I being the luminescence intensity in the presence of a predefined quencher concentration.

Table S6. Stern-Vollmer quenching experiment of Mes-Acr$^+$ with **1a** in 1,2-dichloroethane[a].

Concentration of **1a** (M)	I_0	I	I_0/I
0	876	876	1.00
0.83 x 10^{-4}	876	870	1.00
1.67 x 10^{-4}	876	882	0.99
2.50 x 10^{-4}	876	915	0.95
3.33 x 10^{-4}	876	949	0.92
4.17 x 10^{-4}	876	888	0.98
4.99 x 10^{-4}	876	879	0.99
5.83 x 10^{-4}	876	917	0.95
6.67 x 10^{-4}	876	894	0.97
7.50 x 10^{-4}	876	969	0.90

[a](1.0×10^{-4} M Mes-Acr$^+$, 1,2-dichloroethane, 25 °C, λ_{ex} =424 nm)

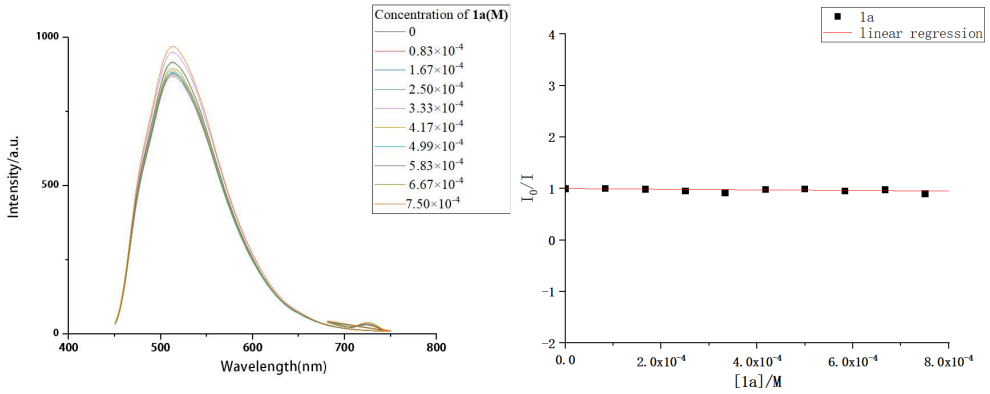


Figure S11. Stern-Vollmer quenching experiment of Mes-Acr$^+$ with 1a in 1,2-dichloroethane. (1.0×10^{-4} M Mes-Acr$^+$, 1,2-dichloroethane, 25 °C, λ_{ex} =424 nm)

Table S7. Stern-Vollmer quenching experiment of Mes-Acr$^+$ with **2a** in 1,2-Dichloroethane [a]

Concentration of **2a** (M)	I_0	I	I_0/I
0	1005	1005	1.00
0.83 x 10^{-4}	1005	904	1.11
1.67 x 10^{-4}	1005	935	1.07
2.50 x 10^{-4}	1005	938	1.07
3.33 x 10^{-4}	1005	919	1.09
4.17 x 10^{-4}	1005	916	1.09
4.99 x 10^{-4}	1005	889	1.13
5.83 x 10^{-4}	1005	900	1.12
6.67 x 10^{-4}	1005	897	1.12
7.50 x 10^{-4}	1005	925	1.09

[a](1.0×10^{-4} M Mes-Acr$^+$, 1,2-dichloroethane, 25 °C, λ_{ex} = 424 nm)

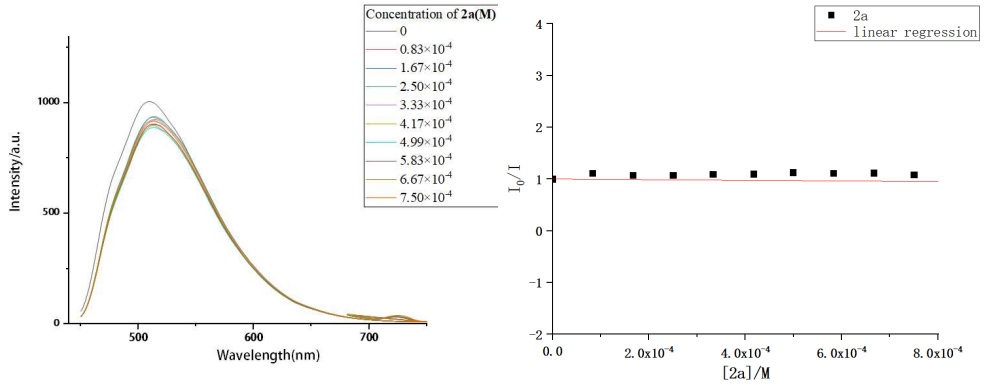


Figure S12. Stern-Vollmer quenching experiment of Mes-Acr^{+} with 2a in 1,2-dichloroethane. (1.0×10^{-4} M Mes-Acr^{+}, 1,2-Dichloroethane, 25 °C, λex =424 nm)

5.6 Cyclic voltammetry spectra of representative substrates

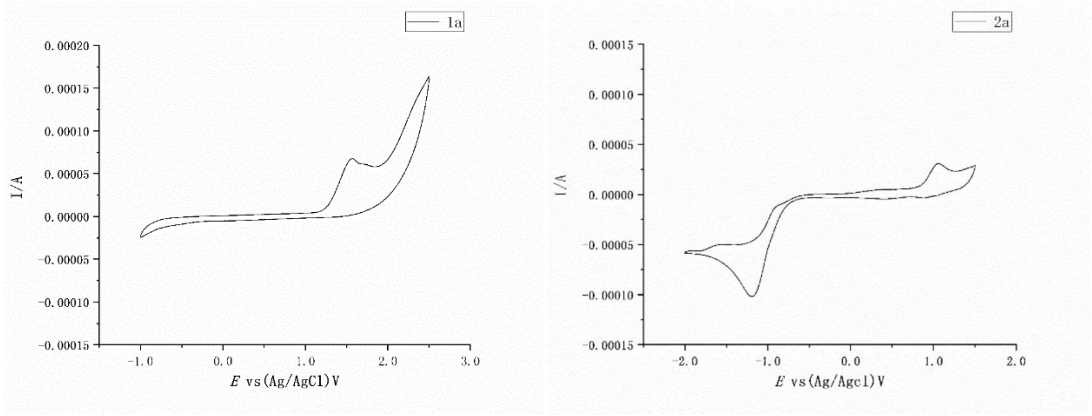
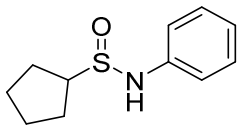


Figure S13 Cyclic voltammetry spectrum of **1a** and **2a**

6. Characterization of products

***N*-phenylcyclopentanesulfinamide (3)**



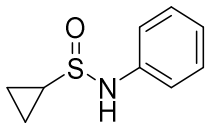
Yellow oil (35.5 mg, yield:85%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 – 7.19 (m, 2H), 7.07 – 6.95 (m, 3H), 6.90 (s, 1H), 3.48 – 3.40 (m, 1H), 2.22 – 2.05 (m, 1H), 2.02 – 1.84 (m, 2H), 1.84 – 1.51 (m, 5H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 141.8, 129.4, 122.7, 118.0, 64.1, 27.5, 27.1, 25.9, 25.8.

HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{11}H_{15}NOSNa^+$: 232.0772; found: 232.0776.

***N*-phenylcyclopropanesulfinamide (4)**



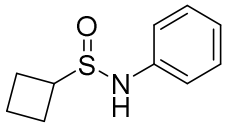
White solid (27.1 mg, yield: 75%), M.p.85-87℃.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 – 7.24 (m, 2H), 7.10 – 6.98(m, 3H), 6.04 (s, 1H), 2.46 – 2.29 (m, 1H), 1.40 – 1.32 (m, 1H), 0.99 – 0.83 (m, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 140.9, 129.5, 123.3, 118.5, 31.1, 3.5, -1.1.

HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_9H_{11}NOSNa^+$: 204.0459; found: 204.0462.

***N*-phenylcyclobutanesulfinamide (5)**



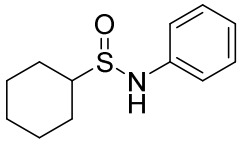
Yellow oil (26.9 mg, yield: 69%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.21 (t, J = 7.70 Hz, 2H), 7.15 (s, 1H), 7.04 (d, J = 7.90 Hz, 2H), 6.97 (t, J = 7.46 Hz, 1H), 3.84 – 3.68 (m, 1H), 2.66 – 2.45 (m, 1H), 2.30 – 2.11(m, 3H), 1.96 (t, J = 8.29 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 141.8, 129.3, 122.6, 117.9, 56.3, 22.9, 21.9, 17.5.

HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{10}H_{13}NOSNa^+$: 218.0616; found: 218.0618.

***N*-phenylcyclohexanesulfinamide (6)**



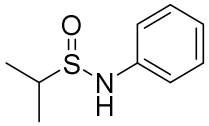
Yellow solid (34.8 mg, yield:78%), M.p.100-102℃.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.20 (t, *J* = 7.69 Hz, 2H), 7.11 (s, 1H), 7.04 – 6.89 (m, 3H), 3.04 – 2.86 (m, 1H), 2.14 (d, *J* = 13.26 Hz, 1H), 2.07 – 1.94 (m, 1H), 1.93 – 1.75 (m, 2H), 1.66 (s, 1H), 1.53 – 1.20 (m, 5H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 142.0, 129.3, 122.6, 117.9, 62.7, 26.6, 26.3, 25.5, 25.1, 25.0.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{12}H_{18}NOS^+$: 224.1109; found: 224.1102.

***N*-phenylpropane-2-sulfinamide (7)**



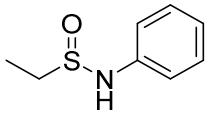
Yellow solid (28.5 mg, yield: 78%), M.p.68-70℃.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25 – 7.17 (m, 2H), 7.06 – 6.95 (m, 3H), 6.93 (s, 1H), 3.07 (p, *J* = 6.87 Hz, 1H), 1.31 (dd, *J* = 17.51, 6.91 Hz, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 141.9, 129.4, 122.7, 118.0, 54.5, 16.1, 15.7.

HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_9H_{13}NOSNa^+$: 206.0616; found: 206.0612.

***N*-phenylethanesulfinamide (8)**



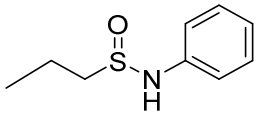
Yellow oil (24.7 mg, yield: 77%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24 (t, J = 7.49 Hz, 2H), 7.10 – 6.99 (m, 3H), 6.92 (s, 1H), 3.10 – 2.94(m, 2H), 1.33 (t, J = 7.44 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 141.3, 129.4, 123.1, 118.4, 49.6, 7.6.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_8H_{12}NOS^+$:170.0640; found: 170.0643.

***N*-phenylpropane-1-sulfinamide (9)**



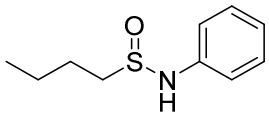
Yellow oil (25.6 mg, yield: 70%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 (d, J = 2.10 Hz, 1H), 7.24 (d, J = 1.92 Hz, 1H), 7.10 – 6.99(m, 4H), 3.02 – 2.93(m, 2H), 1.77 (q, J = 7.51 Hz, 2H), 1.05 (t, J = 7.43 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 141.3, 129.4, 123.0, 118.3, 57.7, 17.0, 13.2.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_9H_{14}NOS^+$: 184.0796; found: 184.0790.

***N*-phenylbutane-1-sulfinamide (10)**



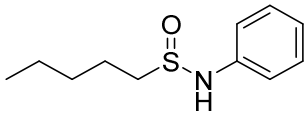
Yellow oil(31.5 mg, yield: 80%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25 (dd, *J* = 7.56, 6.19 Hz, 2H), 7.03 (dd, *J* = 7.97, 3.71 Hz, 3H), 6.81 (s, 1H), 3.01 – 2.94 (m, 2H), 1.77 – 1.65 (m, 2H), 1.52 – 1.37 (m, 2H), 0.94 (t, *J* = 7.34 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 141.3, 129.4, 123.1, 118.4, 55.8, 25.3, 21.8, 13.7.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{10}H_{16}NOS^+$:198.0953; found: 198.0950.

***N*-phenylpentane-1-sulfinamide (11)**



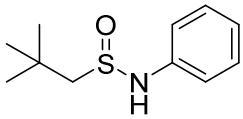
Yellow oil (31.7 mg, yield: 75%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 (s, 1H), 7.22 (t, *J* = 7.64 Hz, 2H), 7.00 (dd, *J* = 19.06, 7.62 Hz, 3H), 2.99 (t, *J* = 7.65 Hz, 2H), 1.78 – 1.63 (m, 2H), 1.45 – 1.22 (m, 4H), 0.89 (t, *J* = 6.68 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 141.5, 129.4, 122.8, 118.1, 55.8, 30.7, 23.1, 22.3, 13.8.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{11}H_{18}NOS^+$:212.1109; found: 212.1106.

2,2-dimethyl-*N*-phenylpropane-1-sulfinamide (12)



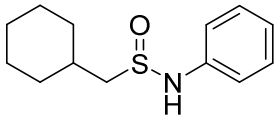
White solid (33.3 mg, yield: 79%), M.p.85-87℃.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 – 7.75 (m, 1H), 7.17 (t, J = 7.82 Hz, 2H), 7.00 (d, J = 7.95 Hz, 2H), 6.93 (t, J = 7.35 Hz, 1H), 3.09 (d, J = 13.15 Hz, 1H), 2.89 (d, J = 13.16 Hz, 1H), 1.08 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 141.6, 129.4, 122.5, 117.7, 70.0, 30.9, 29.7.

HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{11}H_{17}NOSNa^+$: 234.0929; found: 284.0921.

1-cyclohexyl-*N*-phenylmethanesulfinamide (13)



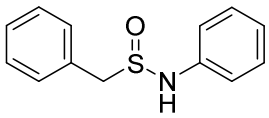
White solid (37.9 mg, yield: 80%), M.p.80-82℃.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 (s, 1H), 7.22 (t, J = 7.78 Hz, 2H), 7.08 – 6.93 (m, 3H), 2.99 – 2.89 (m, 1H), 2.86 – 2.78 (m, 1H), 1.93 (d, J = 12.66 Hz, 1H), 1.87 – 1.77 (m, 1H), 1.74 – 1.61 (m, 4H), 1.24 – 0.86 (m, 5H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 141.5, 129.4, 122.8, 118.0, 63.2, 33.4, 32.9, 32.3, 26.0, 25.9, 25.7.

HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{13}H_{19}NOSNa^+$: 260.1085; found: 260.1074.

***N*,1-diphenylmethanesulfinamide (14)**



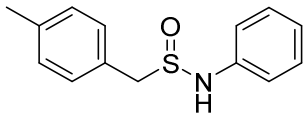
Yellow solid (32.8 mg, yield: 71%), M.p.107-109℃.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 – 7.32 (m, 5H), 7.21 (t, J = 7.89 Hz, 2H), 6.99 (t, J = 7.42 Hz, 1H), 6.93 (d, J = 7.64 Hz, 2H), 6.38 (s, 1H), 4.28 (d, J = 12.90 Hz, 1H), 4.12 (d, J = 12.91 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 140.9, 130.7, 129.4, 129.0, 128.7, 128.6, 123.3, 118.8, 61.3.

HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{13}H_{13}NOSNa^+$: 254.0610; found: 254.0613.

***N*-phenyl-1-(p-tolyl)methanesulfinamide (15)**



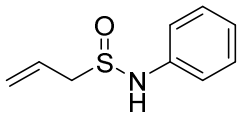
Yellow oil (35.6 mg, yield: 73%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.20 (d, *J* = 13.19 Hz, 6H),7.01 – 6.88(m, 3H), 6.60 – 6.34 (m, 1H), 4.25 (d, *J* = 12.92 Hz, 1H), 4.08 (d, *J* = 12.95 Hz, 1H), 2.34 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 141.1, 138.4, 130.6, 129.7, 129.4, 125.6, 123.2, 118.7, 61.0, 21.2.

HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{14}H_{15}NOSNa^+$: 268.0772; found: 268.0773.

***N*-phenylprop-2-ene-1-sulfinamide (16)**



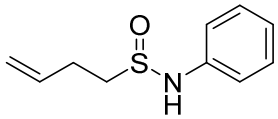
Yellow oil (24.6 mg, yield: 68%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.17 (m, 2H), 7.12 – 6.90 (m, 3H), 6.31 (s, 1H), 6.06 – 5.88 （m, 1H), 5.54 (d, J = 10.19 Hz, 1H), 5.45 (d, J = 17.20 Hz, 1H),, 3.79 (dd, J = 12.98, 6.37 Hz, 1H), 3.56 (dd, J = 12.95, 8.56 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 140.8, 129.5, 125.2, 124.4, 123.5, 118.9, 59.1.

HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_9H_{11}NOSNa^+$: 204.0459; found: 204.0451.

***N*-phenylbut-3-ene-1-sulfinamide (17)**



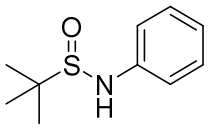
Yellow oil (30.4 mg, yield: 78%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (s, 1H), 7.23 – 7.16 (m, 2H), 7.04 – 6.92 (m, 3H), 5.89 – 5.70 (m, 1H), 5.18 – 5.01 (m, 2H), 3.08 (t, J = 7.53 Hz, 2H), 2.46 (q, J = 7.02 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 141.4, 134.7, 129.4, 122.9, 118.1, 117.1, 54.6, 27.6.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{10}H_{14}NOS^+$: 196.0796; found: 196.0784.

2-methyl-*N*-phenylpropane-2-sulfinamide (18)



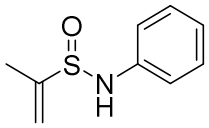
White solid (29.2 mg, yield: 74%), M.p.82-84℃.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 – 7.14 (m, 2H), 7.05 – 6.92 (m, 3H), 5.97 (s, 1H), 1.31 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 142.3, 129.3, 122.6, 118.1, 56.6, 22.5.

HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{10}H_{15}NOSNa^+$: 220.0772; found: 220.0776.

***N*-phenylprop-1-ene-2-sulfinamide (19)**



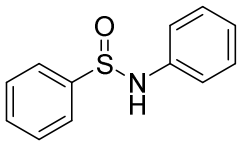
Yellow oil (25.3 mg, yield: 69%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 (d, *J* = 7.50 Hz, 2H), 7.07 (d, *J* = 8.09 Hz, 3H), 6.06 (s, 1H), 5.76 (s, 1H), 5.69 (s, 1H), 2.06 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 149.1, 140.9, 129.5, 123.6, 118.9, 118.8, 16.0.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_9H_{12}NOS^+$: 182.0640; found: 182.0644.

***N*-phenylbenzenesulfinamide (20)**



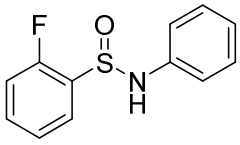
White solid (28.0 mg, yield: 65%), M.p.109-111℃.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 – 7.72(m, 2H), 7.63 – 7.46 (m, 3H), 7.29 (t, *J* = 7.74 Hz, 2H), 7.16 – 7.00 (m, 3H), 6.11 (s, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 144.6, 140.5, 131.5, 129.5, 129.1, 125.5, 123.8, 119.0.

HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{12}H_{11}NOSNa^+$: 240.0459; found: 240.0454.

2-fluoro-*N*-phenylbenzenesulfinamide (21)



Yellow oil (28.2 mg, yield: 62%).

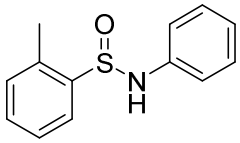
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (t, *J* = 7.34 Hz, 1H), 7.48 – 7.40 (m, 1H), 7.25 (t, *J* = 7.59 Hz, 1H), 7.19 (t, *J* = 7.81 Hz, 2H), 7.07 – 6.97 (m, 4H), 6.19 (s, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ158.6 (d, *J* =252.5Hz), 140.2, 133.6 (d, *J* =8.1 Hz), 131.7 (d, *J* =15.2 Hz), 129.4, 126.6, 124.7 (d, *J* =3.6 Hz), 124.1, 119.7, 116.2, (d, *J* =20.4 Hz).

^{19}F NMR (376 MHz, $CDCl_3$) δ -113.25.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{12}H_{11}FNOS^+$: 236.0545; found: 236.0592.

2-methyl-*N*-phenylbenzenesulfinamide (22)



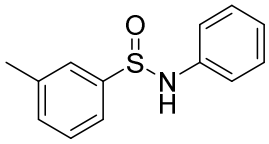
White solid (32.3 mg, yield: 70%), M.p.106-108℃.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17 – 7.88 (m, 1H), 7.47 – 7.38 (m, 2H), 7.33 – 7.20 (m, 3H), 7.13 – 7.00 (m, 3H), 5.93 (s, 1H), 2.46 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 142.5, 141.0, 135.9, 131.5, 131.1, 129.6, 126.8, 123.7, 123.5, 118.3, 18.5.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{13}H_{14}NOS^+$: 232.0796; found: 231.07867.

3-methyl-*N*-phenylbenzenesulfinamide (23)



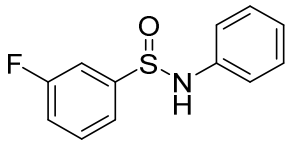
White solid (30.1 mg, yield: 67%), M.p.102-104℃.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (s, 1H), 7.58 (d, *J* = 7.79 Hz, 1H), 7.42 (t, *J* = 7.61 Hz, 1H), 7.37 – 7.24 (m, 3H), 7.14 – 7.02 (m, 3H), 6.08 (s, 1H), 2.44 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 144.5, 140.7, 139.4, 132.3, 129.5, 129.0, 125.7, 123.7, 122.5, 118.8, 21.4.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{13}H_{14}NOS^+$: 232.0796; found: 232.0784.

3-fluoro-*N*-phenylbenzenesulfinamide (24)



Yellow oil (30.1 mg, yield: 64%).

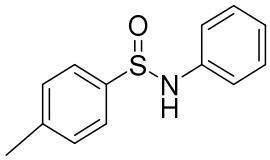
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 – 7.45 (m, 3H), 7.35 – 7.17 (m, 3H), 7.09 (d, *J* = 7.56 Hz, 3H), 6.30 (s, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 162.9(d, *J* =252.4Hz), 147.0, 140.2, 130.8(d, *J* = 7.62 Hz) ,129.6, 124.1, 121.4(d, *J* =3.23Hz), 119.3, 118.6 (d, *J* =21.5 Hz), 113.1(d, *J* =24.2Hz).

^{19}F NMR (376 MHz, $CDCl_3$) δ -109.88.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{12}H_{11}FNOS^+$: 236.0545; found: 236.0590.

4-methyl-*N*-phenylbenzenesulfinamide (25)



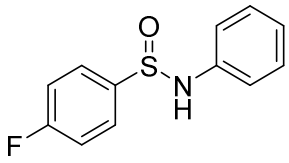
White solid (33.3 mg, yield: 72%), M.p.101-102℃.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (d, *J* = 8.27 Hz, 2H), 7.37 – 7.25 (m, 4H), 7.14 – 7.02 (m, 3H), 6.05 (s, 1H), 2.43 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 142.0, 141.6, 140.7, 129.8, 129.5, 125.4, 123.6, 118.9, 21.4.

HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{13}H_{13}NOSNa^+$: 254.0616; found: 254.0607.

4-fluoro-*N*-phenylbenzenesulfinamide (26)



White solid (30.7 mg, yield: 65%), M.p.115-116℃.

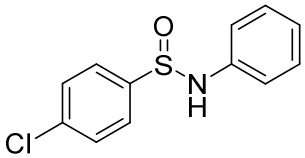
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 – 7.61 (m, 2H), 7.34 – 7.25 (m, 2H), 7.21 (t, *J* = 8.56 Hz, 2H), 7.13 – 6.99 (m, 3H), 6.23 (s, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 164.6 (d, *J* = 252.2 Hz), 140.2, 140.1, 129.5, 128.0 (d, *J* = 9.1 Hz), 124.0, 119.3, 116.3 (d, *J* = 22.5Hz).

^{19}F NMR (376 MHz, $CDCl_3$) δ -108.3.

HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{12}H_{10}FNOSNa^+$: 258.0365; found: 258.0361.

4-chloro-*N*-phenylbenzenesulfinamide (27)



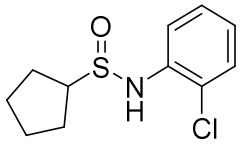
Yellow oil (33.7 mg, yield: 67%), M.p.144-145℃.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (d, *J* = 8.46 Hz, 2H), 7.49 (d, *J* = 8.53 Hz, 2H), 7.28 (t, *J* = 8.04 Hz, 2H), 7.08 (d, *J* = 8.06 Hz, 3H), 6.28 (s, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 143.0, 140.2, 137.8, 129.6, 129.4, 127.1, 124.1, 119.3.

HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{12}H_{10}ClNOSNa^+$: 274.0064; found:274.0061 .

***N*-(2-chlorophenyl)cyclopentanesulfinamide (28)**



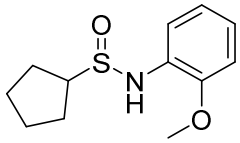
Yellow oil (36.0 mg, yield: 74%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 – 7.29 (m, 2H), 7.21 (t, *J* = 7.76 Hz, 1H), 6.94 (t, *J* = 7.70 Hz, 1H), 6.40 (s, 1H), 3.51 – 3.32 (m, 1H), 2.27 – 2.11 (m, 1H), 2.10 – 1.93 (m, 2H), 1.88 – 1.63 (m, 5H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 138.4, 129.7, 128.0, 123.3, 122.8, 117.8, 64.3, 27.4, 26.2, 26.0, 25.9.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{11}H_{15}ClNOS^+$: 244.0563; found: 244.0566.

***N*-(2-methoxyphenyl)cyclopentanesulfinamide (29)**



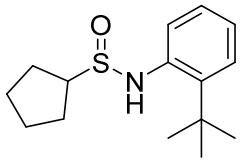
Yellow oil (35.8 mg, yield: 78%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 – 7.17 (m, 1H), 7.01 – 6.88 (m, 2H), 6.85 (d, *J* = 7.84 Hz, 1H), 6.29 (s, 1H), 3.83 (s, 3H), 3.42 – 3.25 (m, 1H), 2.25 – 2.11 (m, 1H), 2.09 – 1.92 (m, 2H), 1.84 – 1.62 (m, 5H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 148.6, 131.1, 122.8, 121.2, 116.8, 110.8, 64.2, 55.7, 27.5, 26.3, 26.0, 25.9.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{12}H_{18}NO_2S^+$: 240.1058; found: 240.1050.

***N*-(2-(tert-butyl)phenyl)cyclopentanesulfinamide (30)**



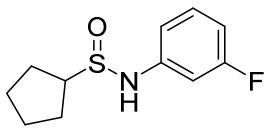
Yellow oil (38.7 mg, yield: 73%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 (d, *J* = 9.43 Hz, 1H), 7.34 (d, *J* = 9.54 Hz, 1H), 7.19 (t, *J* = 7.63 Hz, 1H), 7.02 (t, *J* = 7.63 Hz, 1H), 5.95 (s, 1H), 3.44 – 3.27 (m, 1H), 2.30 – 2.15 (m, 1H), 2.10 – 1.97 (m, 2H), 1.93 – 1.67 (m, 5H), 1.44 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 140.2, 138.9, 127.3, 126.9, 123.5, 120.9, 64.2, 34.4, 30.9, 27.7, 26.0, 25.8, 25.6.

HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{15}H_{23}NOSNa^+$: 288.1398; found: 288.1393.

***N*-(3-fluorophenyl)cyclopentanesulfinamide (31)**



Yellow oil (34.05 mg, yield: 75%).

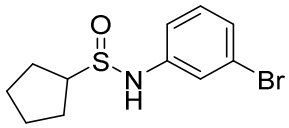
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (s, 1H), 7.18 – 7.06 (m, 1H), 6.83 – 6.71 (m, 2H), 6.63 (d, *J* = 2.37 Hz, 1H), 3.55 – 3.43 (m, 1H), 2.22 – 2.02 (m, 1H), 2.00 – 1.82 (m, 2H), 1.79 – 1.61 (m, 5H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 163.4 (d, *J* = 245.5 Hz), 144.0 (d, *J* = 10.2 Hz), 130.5 (d, *J* = 9.7 Hz), 112.8 (d, *J* = 2.8 Hz), 108.9 (d, *J* = 21.3 Hz), 104.5 (d, *J* = 25.4 Hz), 64.0, 27.4, 27.4, 25.9, 25.8.

^{19}F NMR (376 MHz, $CDCl_3$) δ -111.68.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{11}H_{15}FNOS^+$: 228.0858; found: 228.0853.

***N*-(3-bromophenyl)cyclopentanesulfinamide (32)**



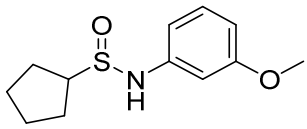
Yellow oil (41.3 mg, yield: 72%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (s, 1H), 7.19 (s, 1H), 7.13 – 6.98 (m, 2H), 6.96 – 6.89 (m, 1H), 3.78 – 2.99 (m, 1H), 2.18 – 2.01 (m, 1H), 2.00 – 1.80 (m, 2H), 1.77 – 1.50 (m, 5H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 143.7, 130.6, 125.2, 123.1, 120.1, 115.7, 64.0, 27.5, 27.4, 25.9, 25.8.

HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{11}H_{14}BrNOSNa^+$: 309.9877; found:309.9876.

***N*-(3-methoxyphenyl)cyclopentanesulfinamide (33)**



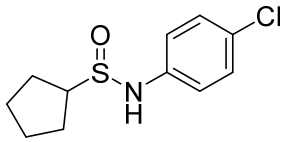
Yellow oil (36.0 mg, yield: 76%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 (s, 1H), 7.10 (t, *J* = 8.09 Hz, 1H), 6.66 – 6.55 (m, 2H), 6.53 – 6.47 (m, 1H), 3.71 (s, 3H), 3.55 – 3.36 m, 1H), 2.22 – 2.01 (m, 1H), 1.97 – 1.84 (m, 2H), 1.77 – 1.61 (m, 5H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 160.5, 143.4, 130.1, 109.9, 108.1, 103.4, 64.0, 55.2, 27.5, 27.3, 25.9, 25.8.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{12}H_{18}NO_2S^+$: 240.1058; found: 240.1051.

***N*-(4-chlorophenyl)cyclopentanesulfinamide(34)**



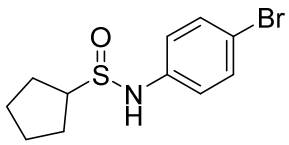
Yellow oil (38.4 mg, yield: 79%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.20 (d, J = 7.29 Hz, 2H), 6.96 (d, J = 7.88 Hz, 2H), 6.58 (s, 1H), 3.40 (d, J = 5.82 Hz, 1H), 2.19 – 2.08 (m, 1H), 1.97 (s, 2H), 1.81 – 1.63 (m, 5H).

^{13}C NMR (101 MHz, $CDCl_3$)) δ 140.3, 129.4, 128.1, 119.6, 64.2, 27.5, 26.8, 25.9, 25.8.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{11}H_{15}ClNOS^+$: 244.0563; found: 244.0565.

***N*-(4-bromophenyl)cyclopentanesulfinamide (35)**



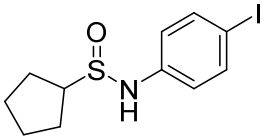
Yellow oil (45.7 mg, yield: 80%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 (s, 1H), 7.30 (d, *J* = 8.38 Hz, 2H), 6.94 – 6.82 (m, 2H), 3.51 – 3.40(m, 1H), 2.15 – 2.02 (m, 1H), 1.97 – 1.83 (m, 2H), 1.78 – 1.56 (m, 5H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 141.1, 132.2, 119.3, 115.0, 64.1, 27.4, 27.2, 25.9, 25.8.

HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{11}H_{14}BrNOSNa^+$: 309.9877; found:309.9870.

***N*-(4-iodophenyl)cyclopentanesulfinamide (36)**



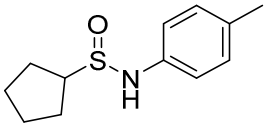
Yellow oil (51.4 mg, yield: 77%).

^{1}H NMR (400 MHz, DMSO-d_6) δ 8.81 (s, 1H), 7.58 (d, J = 8.43 Hz, 2H), 6.88 (d, J = 8.40 Hz, 2H), 3.51 – 3.40 (m, 1H), 2.02 – 1.81 (m, 3H), 1.66 – 1.54 (m, 5H).

^{13}C NMR (101 MHz, DMSO-d_6) δ 143.5, 138.3, 119.7, 84.6, 63.0, 27.4, 27.2, 26.0, 25.9.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{11}H_{15}INOS^+$: 335.9919 found:335.9913.

***N*-(*p*-tolyl)cyclopentanesulfinamide (37)**



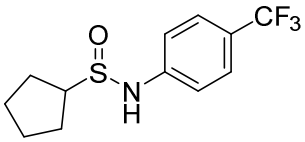
Yellow oil (32.6 mg, yield: 73%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.06 (d, J = 8.03 Hz, 2H), 6.94 (d, J = 8.34 Hz, 2H), 6.20 (s, 1H), 3.40 – 3.28 (m, 1H), 2.28 (s, 3H), 2.18 – 2.08 (m, 1H),2.02 – 1.90 (m, 2H), 1.83 – 1.60 (m, 5H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 138.9, 132.7, 129.9, 119.0, 64.1, 27.5, 26.7, 25.9, 25.9, 20.7.

HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{12}H_{17}NOSNa^+$: 246.0929; found: 246.0923.

***N*-(4-(trifluoromethyl)phenyl)cyclopentanesulfinamide (38)**



Yellow oil (39.3 mg, yield: 71%).

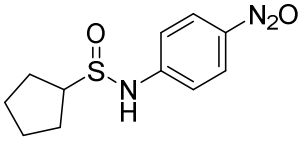
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (d, J = 4.44 Hz, 1H), 7.43 (d, J = 8.33 Hz, 2H), 7.05 (d, J = 8.36 Hz, 2H), 3.64 – 3.39 (m, 1H), 2.27 – 2.06 (m, 1H), 1.9 – 1.91 (m, 2H), 1.83 – 1.59 (m, 5H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 145.3, 126.6 (d, J = 3.85 Hz), 124.2(d, J = 272.70 Hz), 124.1 (d, J = 32.95 Hz), 116.5, 64.1, 27.4, 27.3, 25.9, 25.8.

^{19}F NMR (376 MHz, $CDCl_3$) δ -61.94.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{12}H_{15}F_3NOS^+$: 278.0826; found: 278.0822.

N-phenylcyclohexanesulfinamide (39)



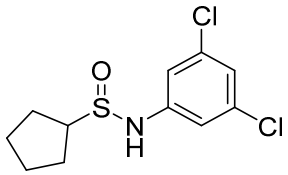
Yellow oil (35.8 mg, yield: 71%).

^{1}H NMR (400 MHz, DMSO-d_6) δ 9.72 (s, 1H), 8.18 (d, J = 9.10 Hz, 2H), 7.19 (d, J = 9.13 Hz, 2H), 3.59 – 3.51 (m, 1H), 2.04 – 1.87 (m, 3H), 1.74 – 1.50 (m, 5H).

^{13}C NMR (101 MHz, DMSO-d_6) δ 150.4, 141.2, 126.3, 115.9, 63.2, 27.3, 27.0, 25.9, 25.9.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{11}H_{14}N_3O_2S^+$: 253.0885; found: 253.0883.

***N*-(3, 5-dichlorophenyl)cyclopentanesulfinamide (40)**



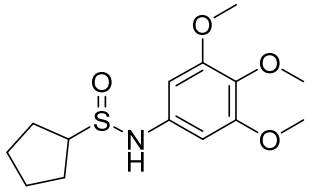
Yellow oil (41.0 mg, yield: 74%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (s, 1H), 6.91 (d, J = 2.82 Hz, 3H), 3.65 – 3.32 (m, 1H), 2.27 – 2.03 (m, 1H), 2.01 – 1.84 (m, 2H), 1.75 – 1.63 (m, 5H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 144.3, 135.7, 122.2, 115.3, 64.2, 27.4, 27.4, 25.9, 25.8.

HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{11}H_{13}Cl_2NOSNa^+$:299.9993; found: 299.9988.

***N*-(3,4,5-trimethoxyphenyl)cyclopentanesulfinamide (41)**



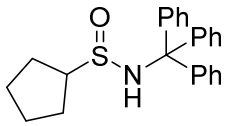
Yellow oil (47.8 mg, yield: 80%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.12 (s, 1H), 6.27 (s, 2H), 3.77 (d, J = 6.73 Hz, 9H), 3.57 – 3.43 (m, 1H), 2.23 – 2.04(m, 1H) 2.02 – 1.86 (m, 2H), 1.77 – 1.72 (m, 5H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 153.7, 138.1, 133.6, 95.7, 64.0, 60.9, 56.0, 27.5, 27.2, 25.9, 25.8.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{14}H_{22}NO_4S^+$:300.1270; found: 300.1269.

***N*-tritylcyclopentanesulfinamide (42)**



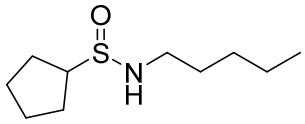
White solid (55.5 mg, yield: 74%), M.p.120-122℃.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 – 7.19 (m, 15H), 4.79 (s, 1H), 3.30 – 2.97 (m, 1H), 2.13 – 1.99 (m, 1H), 1.96 – 1.83 (m, 2H), 1.73 – 1.56 (m, 5H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 144.9, 129.4, 127.9, 127.4, 72.9, 65.1, 28.3, 25.9, 25.7, 25.5.

HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{24}H_{25}NOSNa^+$: 398.1555; found: 398.1557.

***N*-pentylcyclopentanesulfinamide (43)**



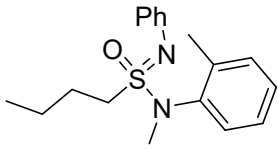
White solid (28.4 mg, yield: 70%), M.p.118-120℃.

^{1}H NMR (400 MHz, $CDCl_3$) δ 3.81 – 3.64 (m, 1H), 3.14 – 2.99, (m, 3H), 2.08 – 1.94 (m, 1H), 1.93 – 1.79 (m, 2H), 1.73 – 1.60 (m, 4H), 1.59 – 1.48 (m, 3H), 1.29 (s, 4H), 0.89 – 0.82 (m, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 63.3, 43.4, 30.5, 28.9, 27.6, 26.5, 25.8, 25.7, 22.3, 13.9.

HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{10}H_{21}NOSNa^+$:226.1242; found: 226.1243.

***N*-methyl-*N*'-phenyl-N-(*o*-tolyl)butane-1-sulfonimidamide (44)**



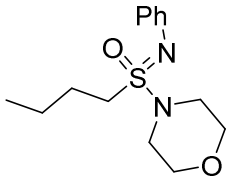
Brown oil (33.4 mg, yield: 53%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 – 7.04 (m, 8H), 7.01 – 6.91(m, 1H), 3.46 – 3.33 (m, 1H), 3.19 (s, 3H), 3.14 – 3.03 (m, 1H), 2.17 (s, 3H), 2.07 – 1.97 (m, 2H), 1.56 – 1.42(m, 2H), 0.98 (t, J = 7.36 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 144.3, 141.2, 131.6, 128.9, 128.0, 126.8, 124.1, 122.1, 39.7, 25.9, 21.8, 18.2, 13.8.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{18}H_{25}N_2OS^+$: 317.1688; found: 317.1684.

4-(*N*-phenylbutylsulfonimidoyl)morpholine (45)



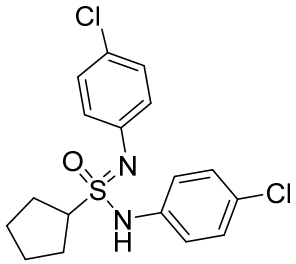
Yellow oil (34.9 mg, yield: 62%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.21 (t, *J* = 7.75 Hz, 2H), 7.11 (d, *J* = 8.28 Hz, 2H), 6.95 (t, *J* = 7.30 Hz, 1H), 3.70 – 3.61 (m, 2H), 3.61 – 3.50 (m, 2H), 3.36 – 3.24 (m, 4H), 3.23 – 3.10 (m, 1H), 3.06 – 2.87 (m, 1H), 2.02 – 1.78 (m, 2H), 1.55 – 1.40 (m, 2H), 0.98 (t, *J* = 7.37 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 143.9, 129.0, 123.4, 121.9, 66.6, 50.9, 46.6, 25.2, 21.7, 13.7.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{14}H_{23}N_2O_2S^+$: 283.1480; found: 283.1477.

***N*, *N*'-bis(4-chlorophenyl)cyclopentanesulfonimidamide (46)**



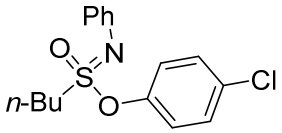
Brown oil (46.3 mg, yield: 63%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.20 (d, J = 8.35 Hz, 4H), 7.10 (d, J = 8.34 Hz, 4H), 3.82 – 3.66 (m, 1H), 2.24 – 2.10 (m, 2H), 2.06 – 1.95 (m, 2H), 1.89 – 1.76 (m, 2H), 1.70 – 1.56 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 129.3, 128.8, 123.0, 62.7, 28.0, 25.8.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{17}H_{19}Cl_2N_2OS^+$:369.0595; found: 369.0590.

4-chlorophenyl N-phenylbutane-1-sulfonimidate (47)



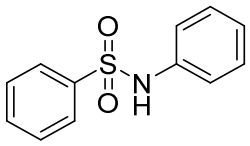
Yellow oil (42.6 mg, yield: 66%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 (d, J = 8.57 Hz, 2H), 7.23 (d, J = 7.51 Hz, 2H), 7.09 (t, J = 7.59 Hz, 4H), 7.03 (t, J = 7.34 Hz, 1H) ， 3.48 – 3.26 (m, 2H), 2.12 – 1.99 (m, 2H), 1.57 – 1.47 (m, 2H), 1.02 (t, *J* = 7.36 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 129.9, 129.8, 129.2, 129.1, 124.8, 123.9, 123.9, 123.6, 52.6, 25.6, 21.4, 13.6.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{16}H_{18}ClNO_2S^+$:348.0644; found:348.0648

***N*-phenylbenzenesulfonamide(48)**



White solid (31.0 mg, yield: 67%), M.p.108-110℃.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (d, J = 7.62 Hz, 2H), 7.52 (t, J = 7.44 Hz, 1H), 7.43 (t, J = 7.69 Hz, 2H), 7.30 – 7.19 (m, 2H), 7.19 – 7.02 (m, 4H).

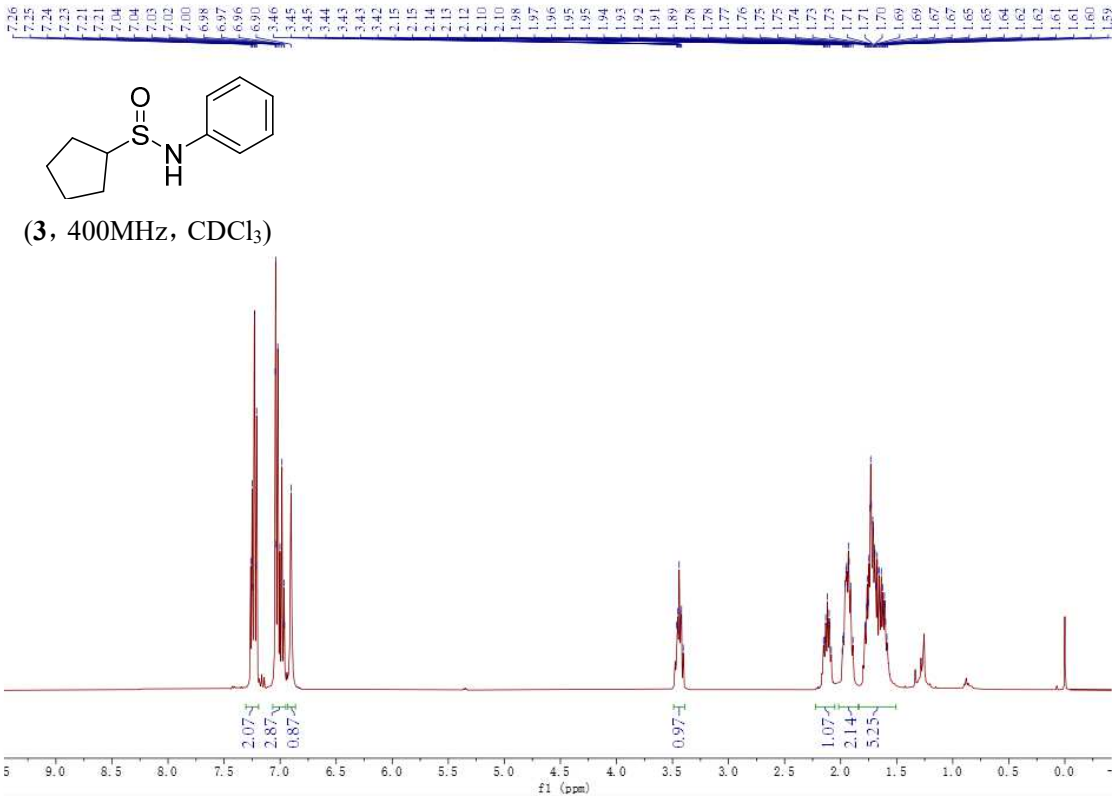
^{13}C NMR (101 MHz, $CDCl_3$) δ 139.0, 136.4, 133.1, 129.3, 129.1, 127.3, 125.5, 121.7.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{12}H_{12}NO_2S^+$: 234.0589; found: 234.0583.

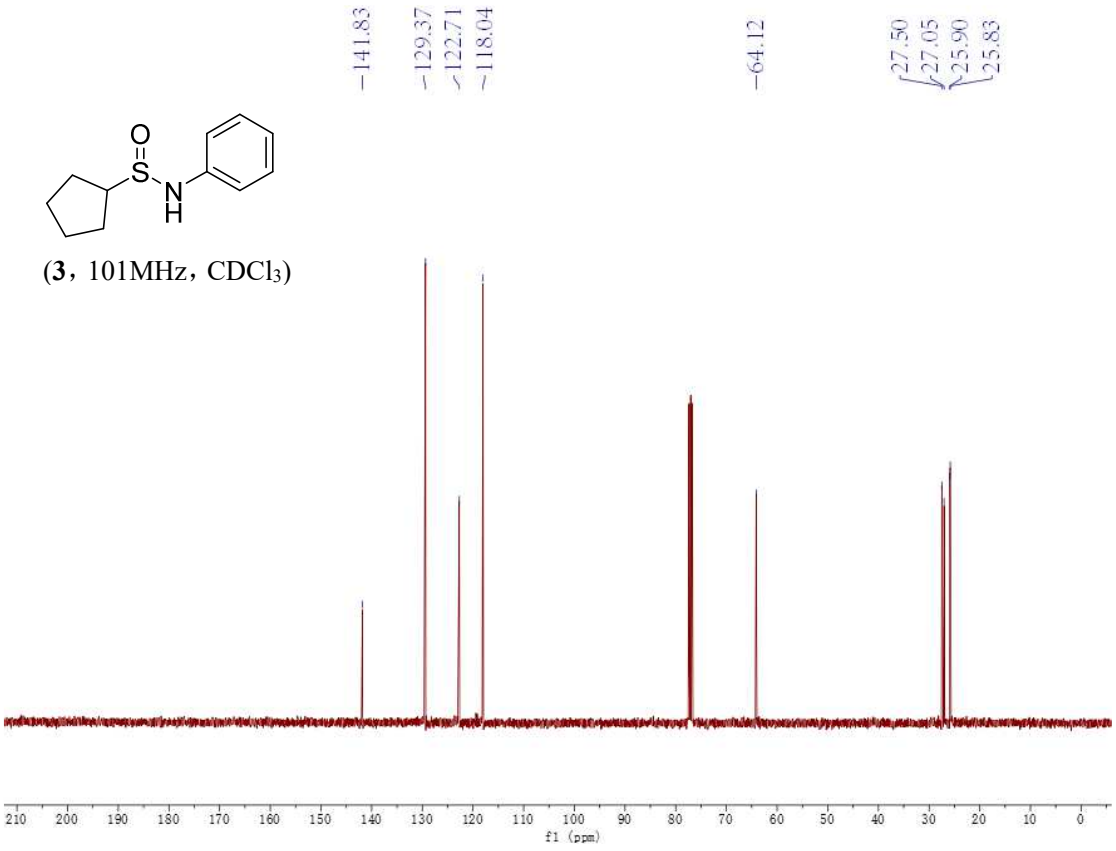
References

1. Chemes, D. M.; Alonso de Armiño, D. J.; Cutin, E. H.; Oberhammer, H.; Robles, N. L., Synthesis, characterization and vibrational studies of p-chlorosulfinylaniline. *Journal of Molecular Structure* **2017,** *1127*, 191-198.
2. Endeshaw, M. M.; Hansen, L. K.; Gautun, O. R., Preparation and evaluation of N-sulfinyl dienophiles for asymmetric hetero-diels-alder reactions. *Journal of Heterocyclic Chemistry* **2008,** *45*, 149-154.
3. Fan, M.; Chen, G.; Xiang, Y.; Li, J.; Yu, X.; Zhang, W.; Long, X.; Xu, L.; Wu, J.; Xu, Z.; Zhang, Q., Anthrathiadiazole Derivatives: Synthesis, Physical Properties and Two-photon Absorption. *Chemistry – A European Journal* **2021,** *27*, 10898-10902.
4. Li, L.; Zhang, S.-q.; Chen, Y.; Cui, X.; Zhao, G.; Tang, Z.; Li, G.-x., Photoredox Alkylation of Sulfinylamine Enables the Synthesis of Highly Functionalized Sulfinamides and S(VI) Derivatives. *ACS Catalysis* **2022,** *12*, 15334-15340.
5. Longobardi, L. E.; Wolter, V.; Stephan, D. W., Frustrated Lewis Pair Activation of an N-Sulfinylamine: A Source of Sulfur Monoxide. *Angewandte Chemie International Edition* **2015,** *54*, 809-812.

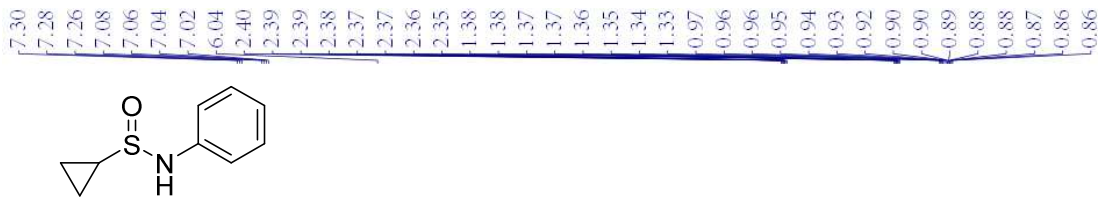
7. NMR Spectra



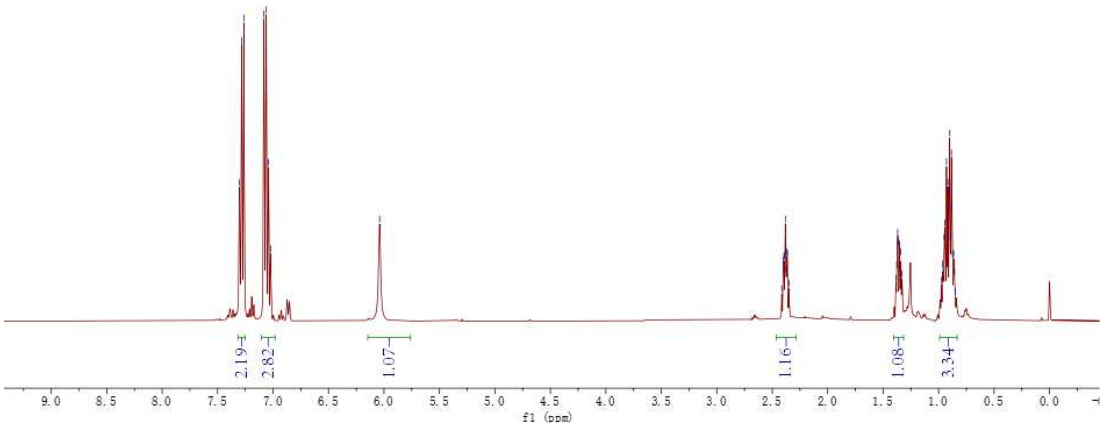
(**3**，400MHz，$CDCl_3$)

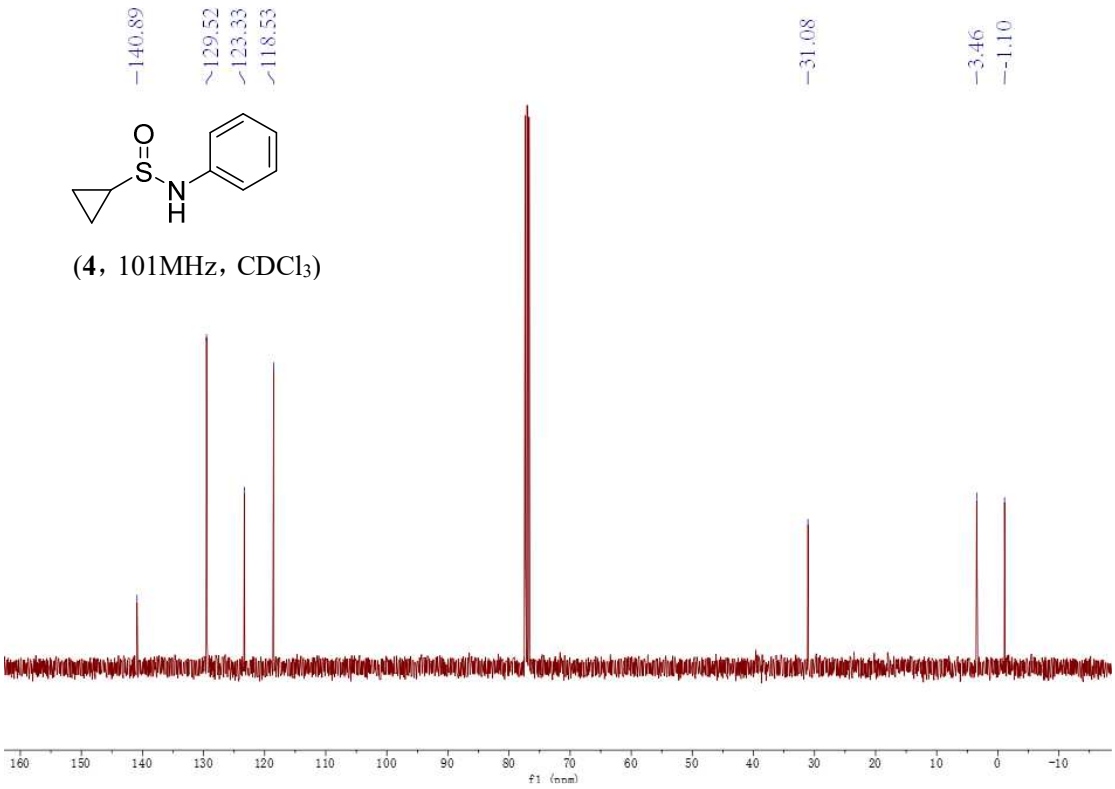


(**3**，101MHz，$CDCl_3$)

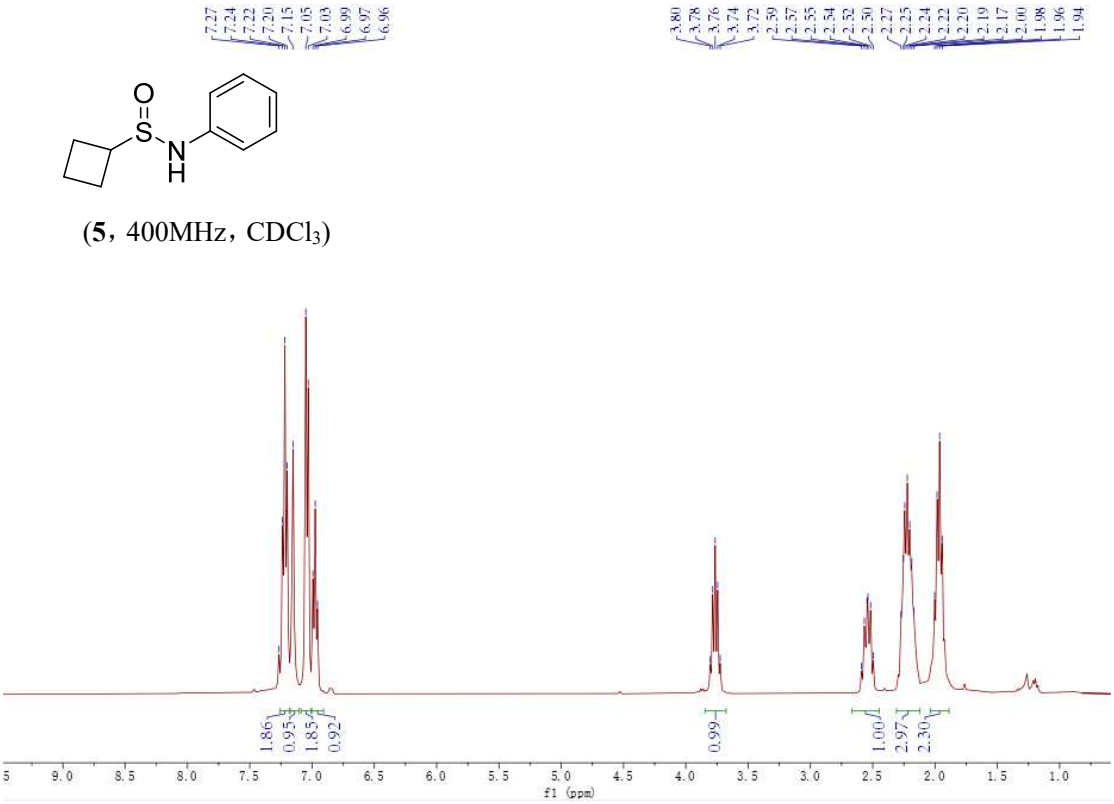


(**4**，400MHz，$CDCl_3$)

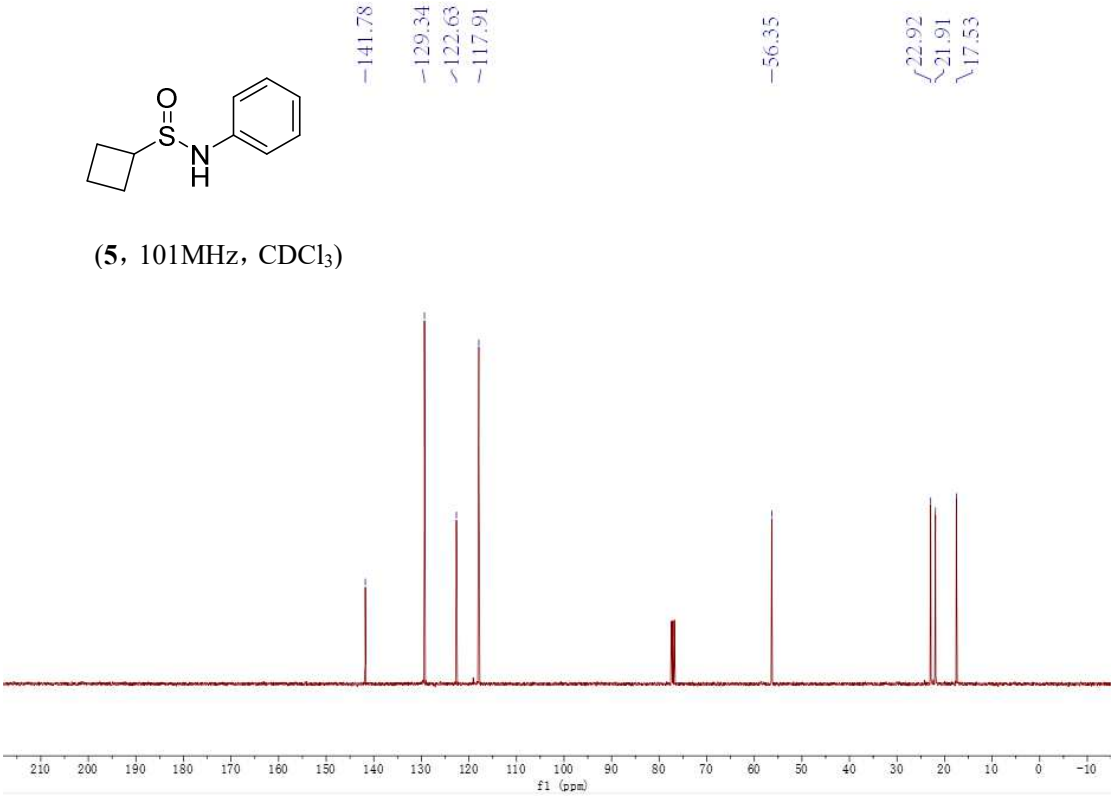




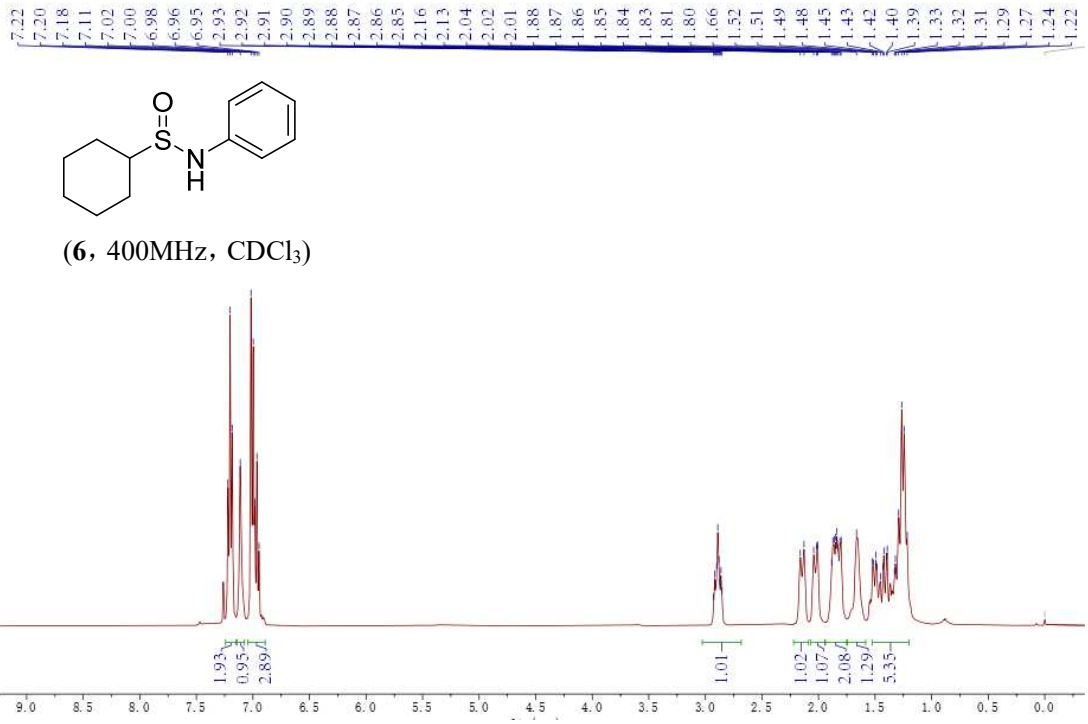
(**4**，101MHz，$CDCl_3$)



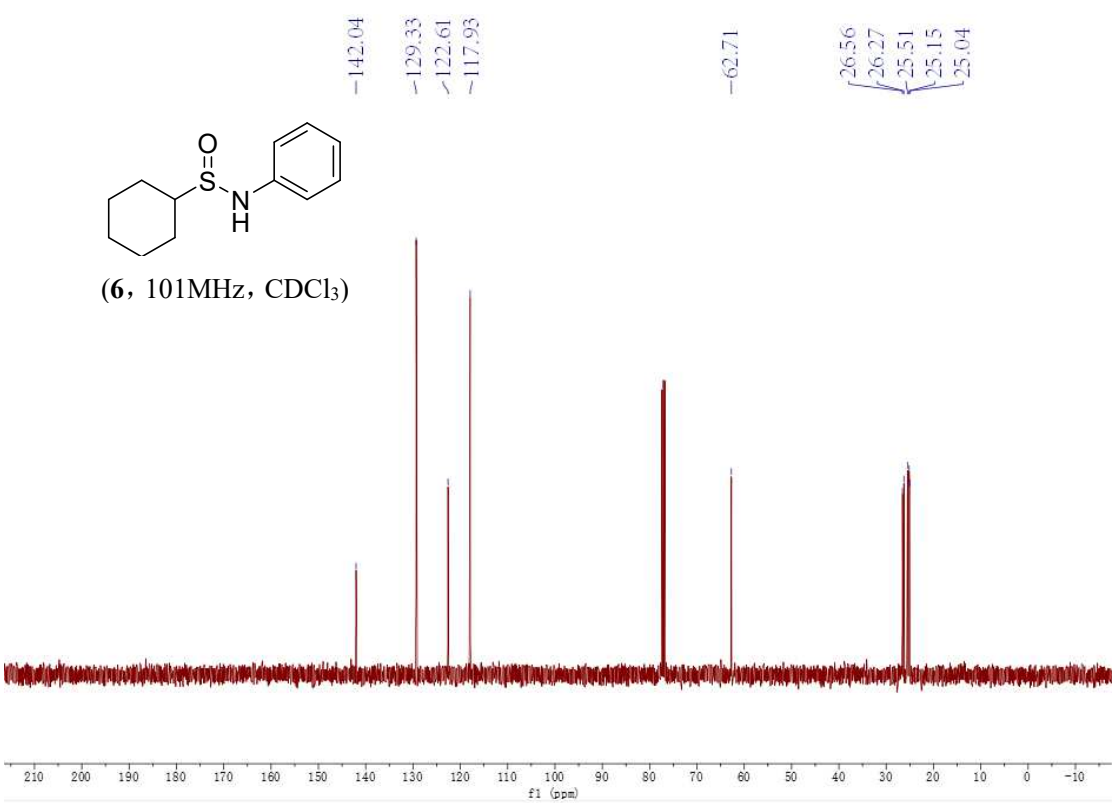
(**5**，400MHz，$CDCl_3$)



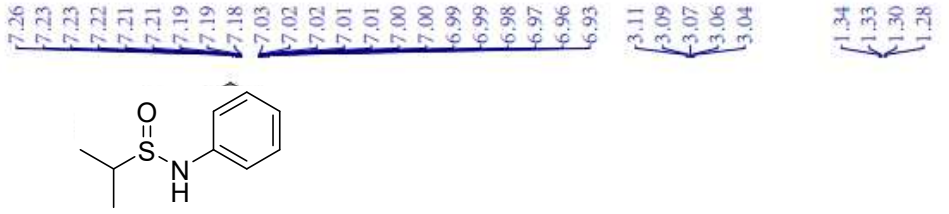
(**5**，101MHz，$CDCl_3$)



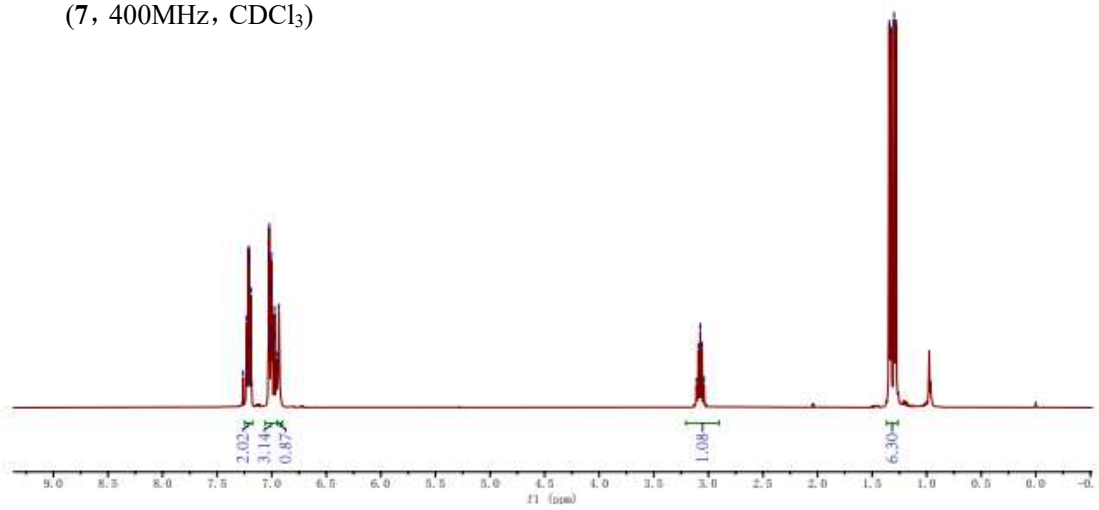
(**6**，400MHz，$CDCl_3$)

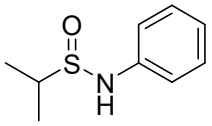


(**6**，101MHz，$CDCl_3$)

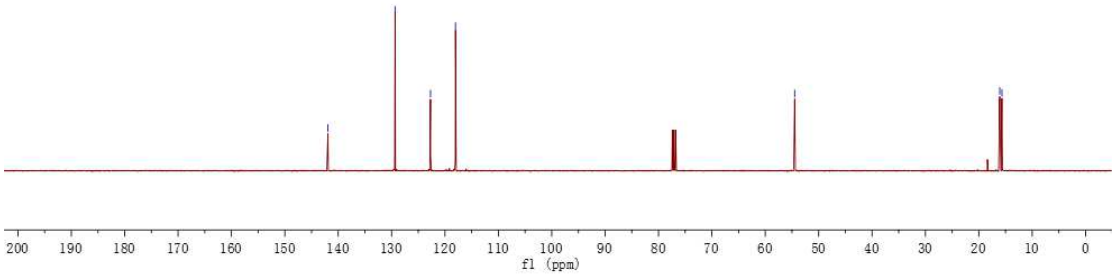


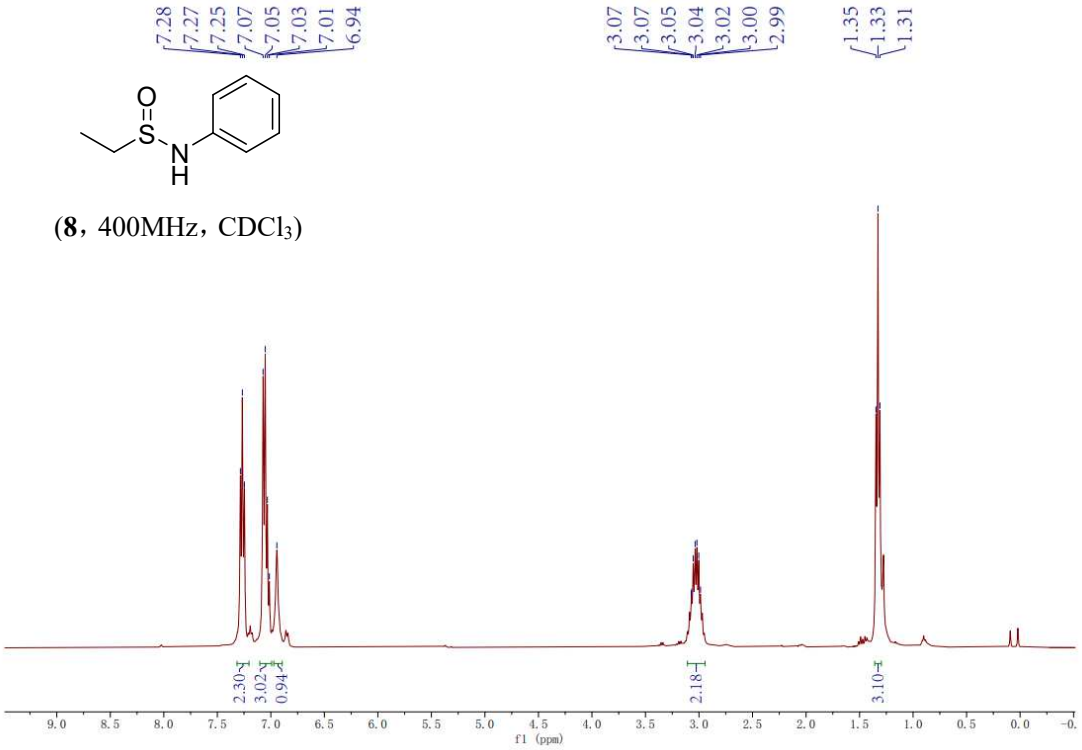
(**7**，400MHz，$CDCl_3$)



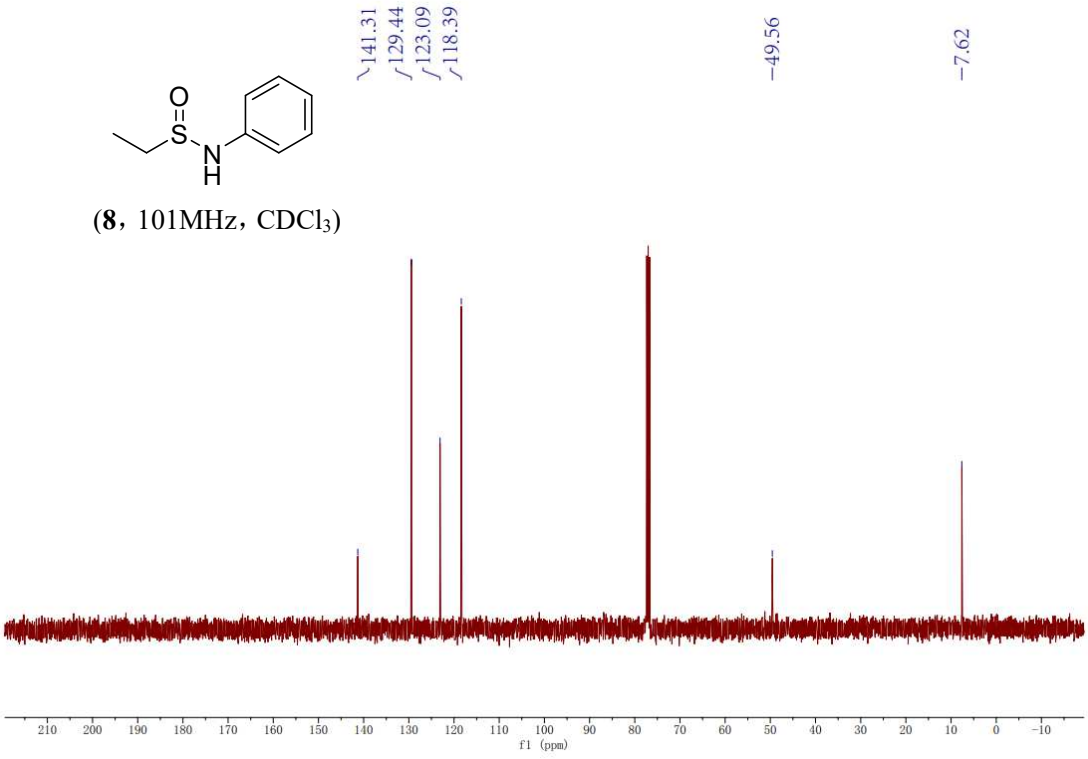


(**7**，101MHz，$CDCl_3$)

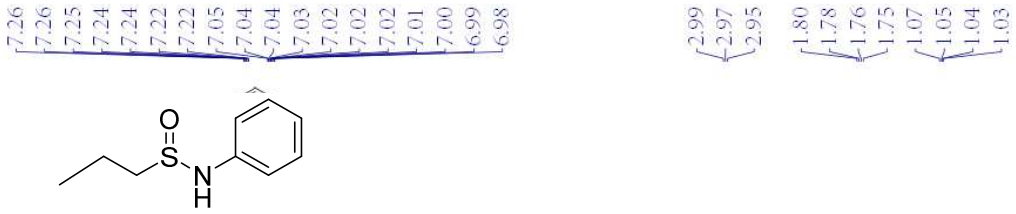




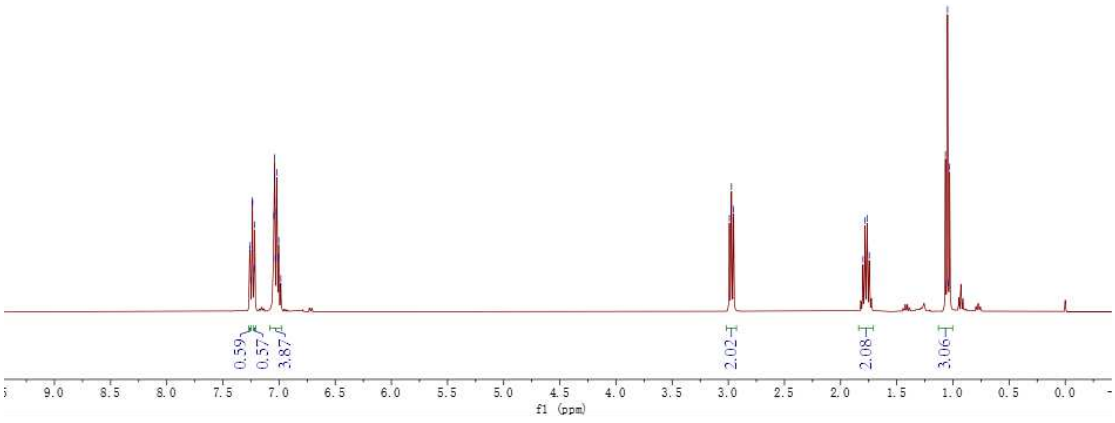
(**8**，400MHz，$CDCl_3$)

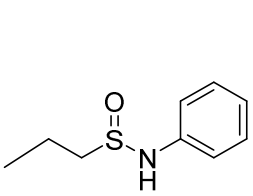


(**8**，101MHz，$CDCl_3$)

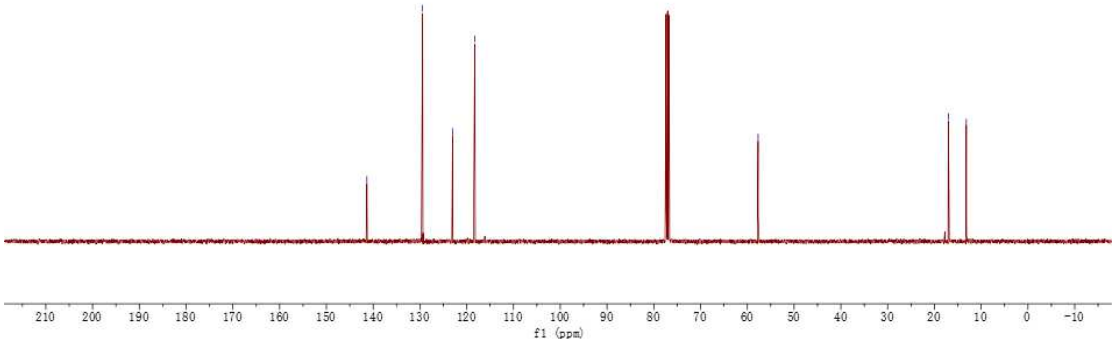


(**9**，400MHz，$CDCl_3$)





(**9**，101MHz，$CDCl_3$)



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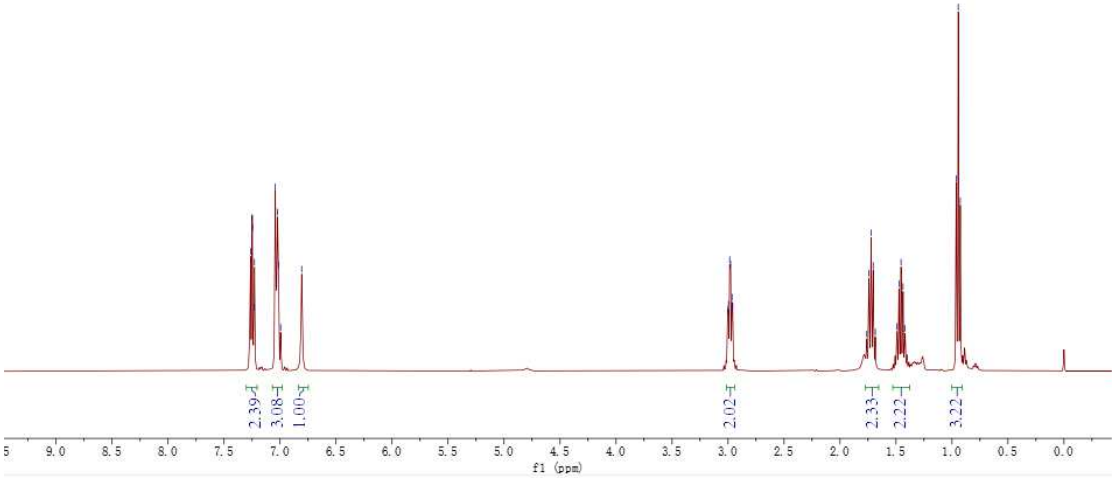
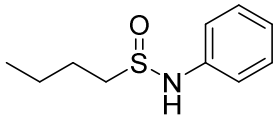
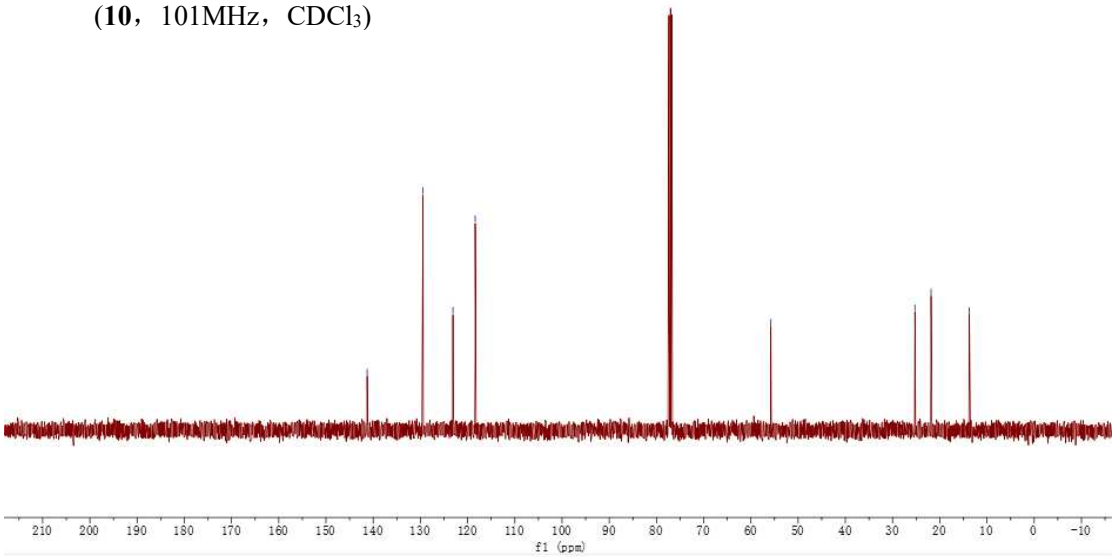
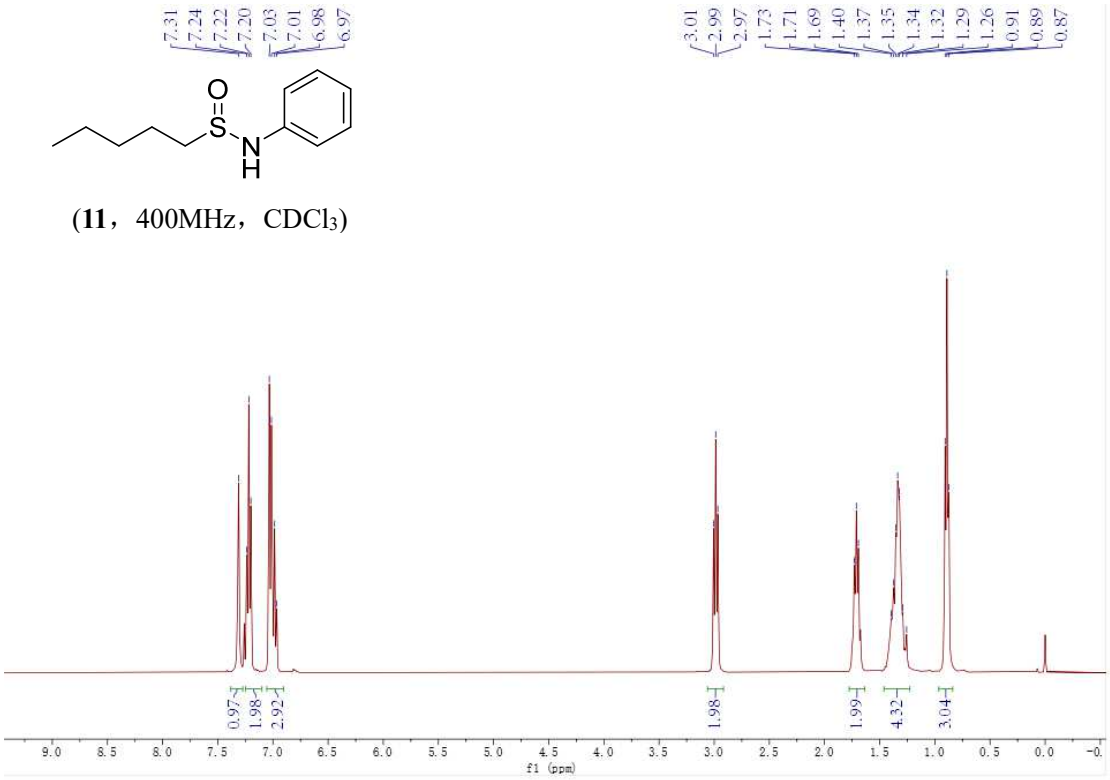




(**10**，101MHz，$CDCl_3$)





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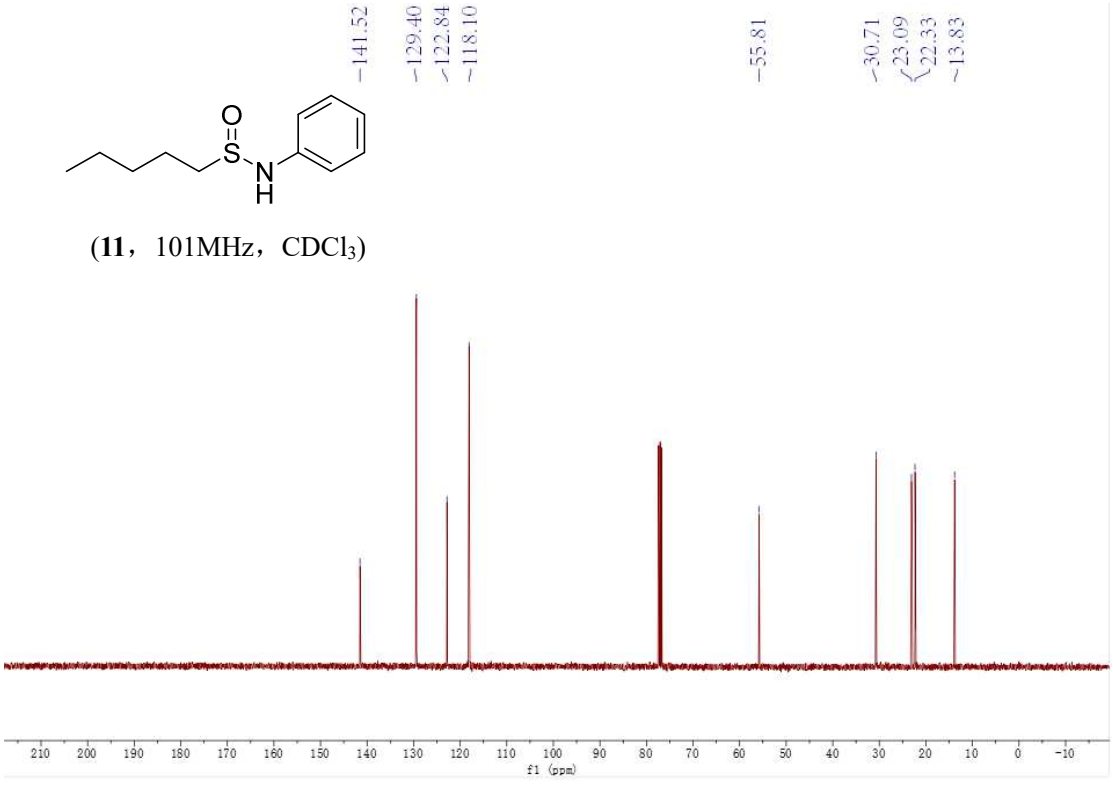
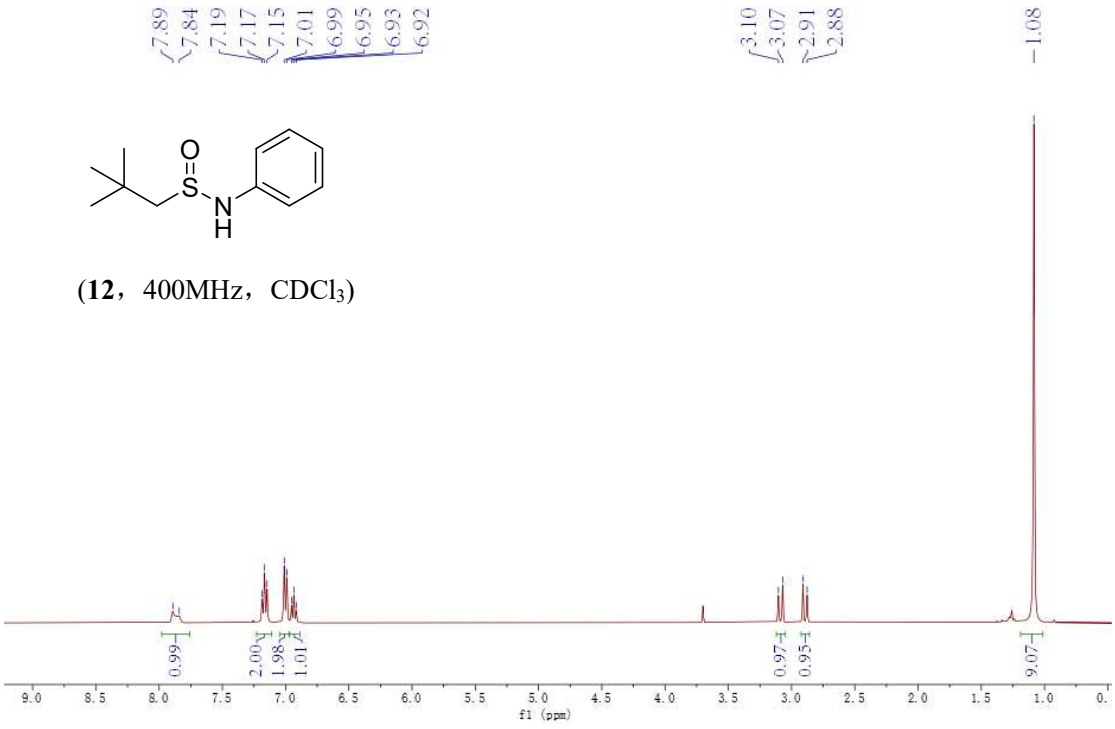


(**11**，101MHz，$CDCl_3$)



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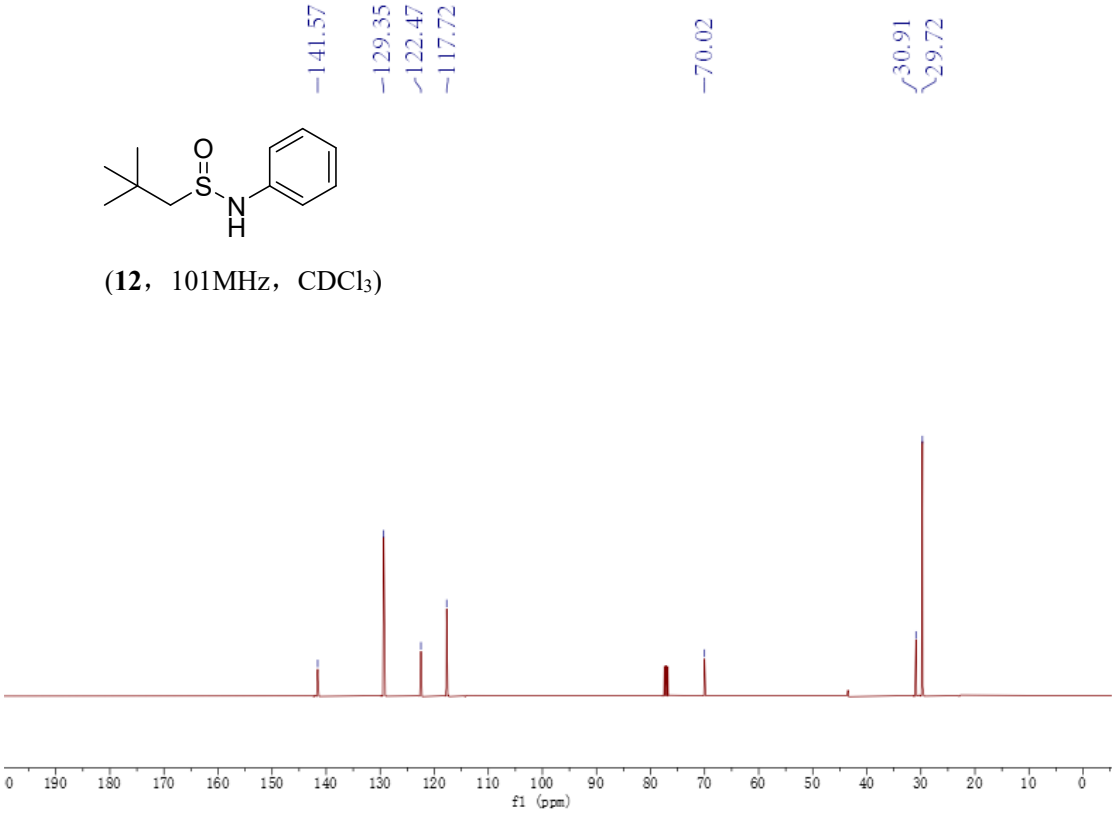

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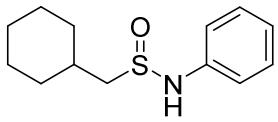

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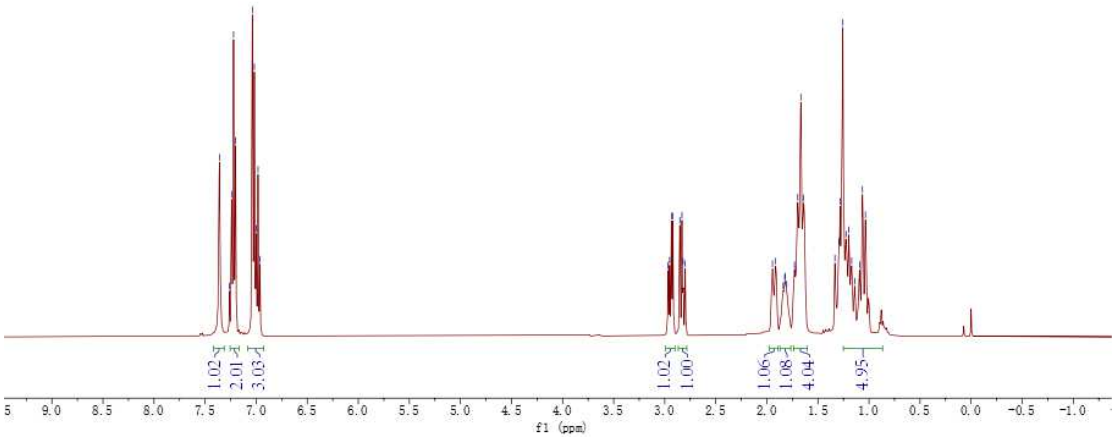

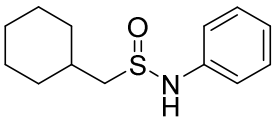

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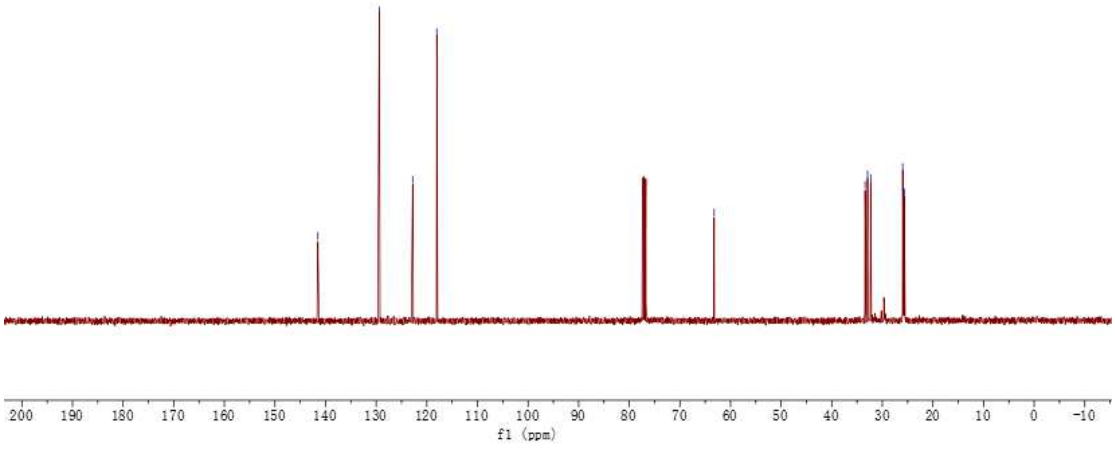

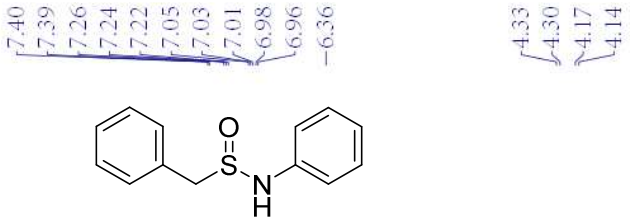

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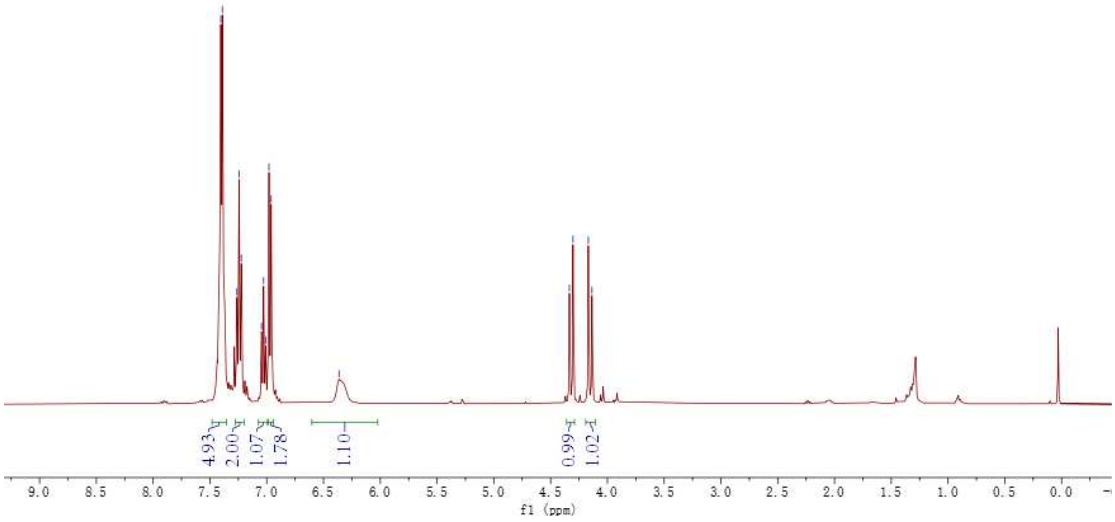

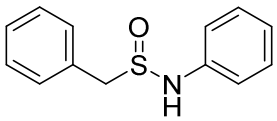

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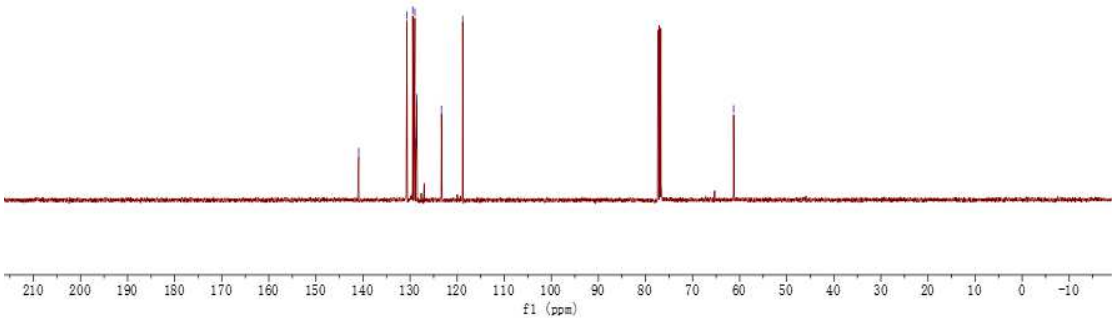

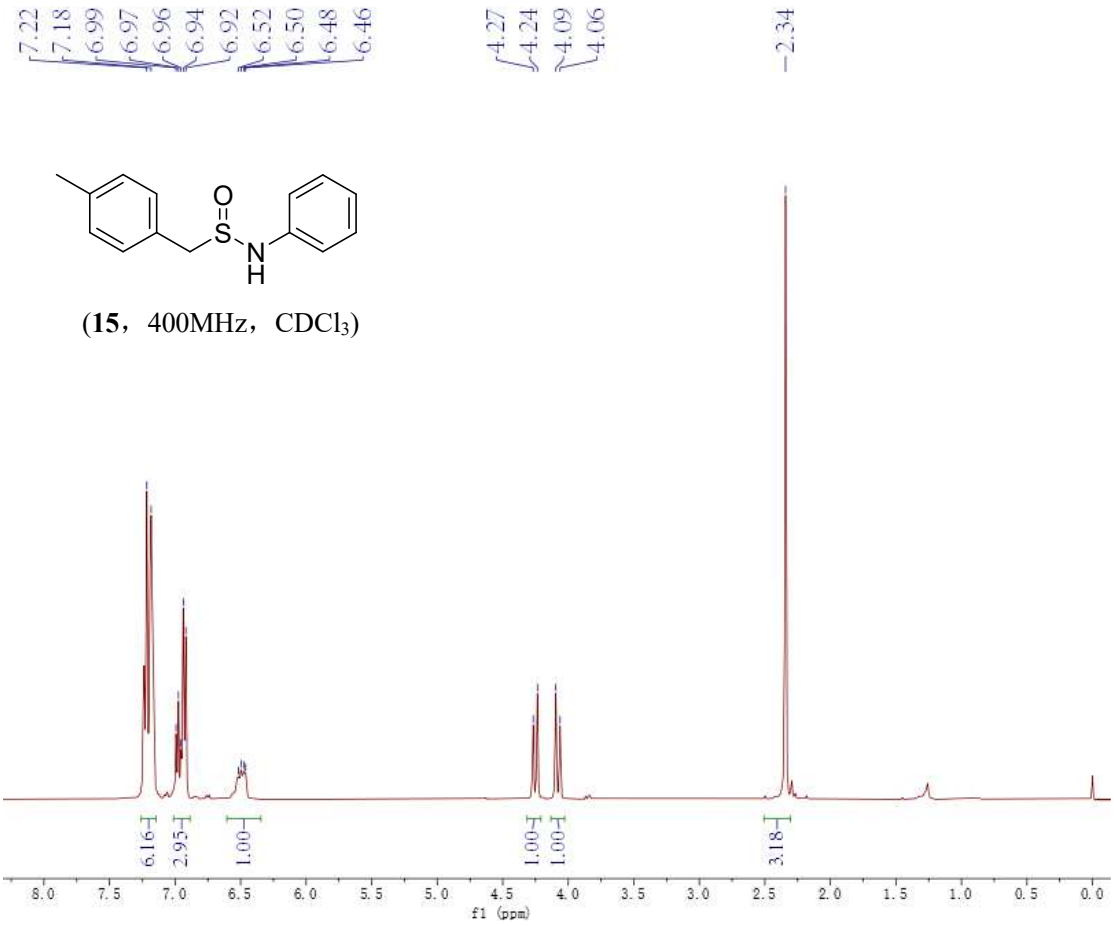

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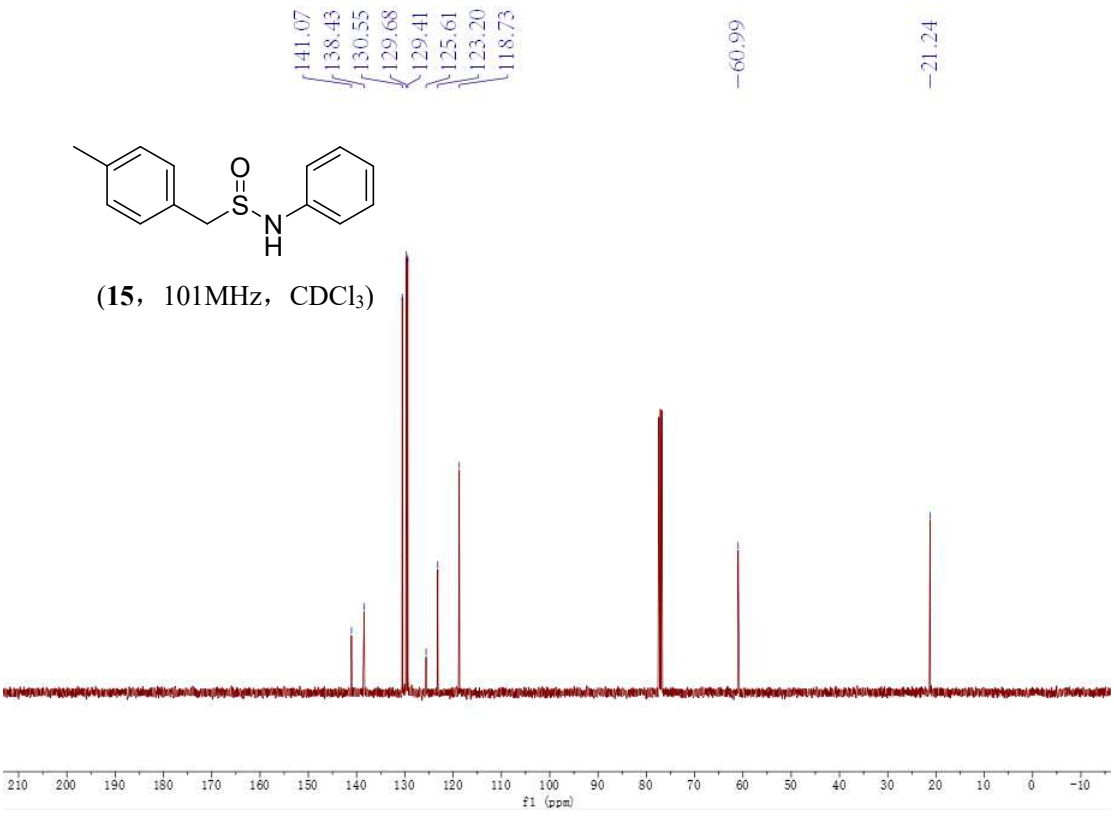

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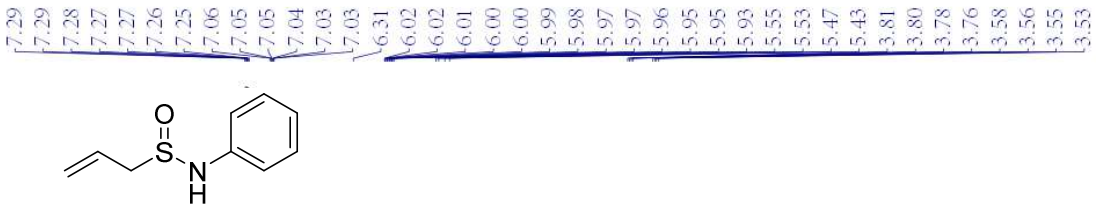

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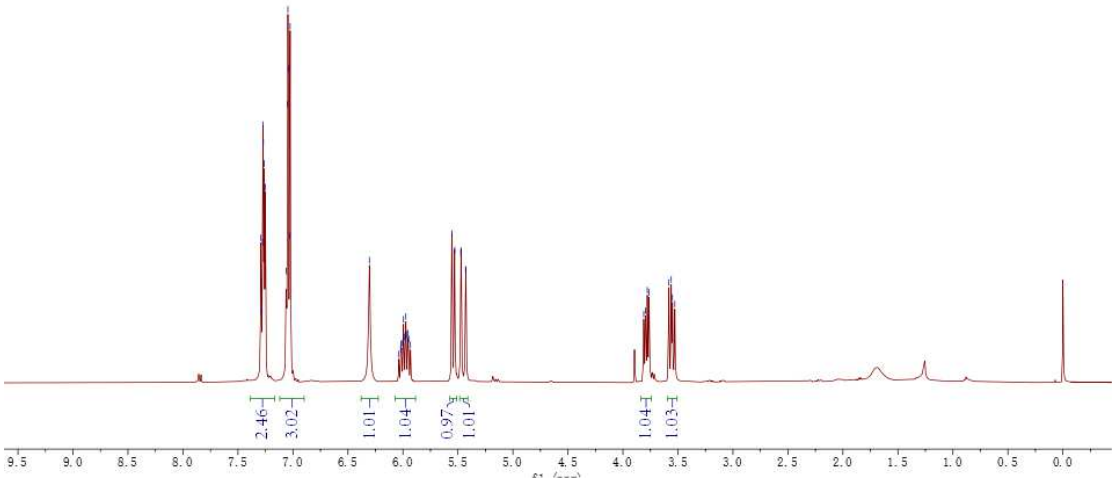

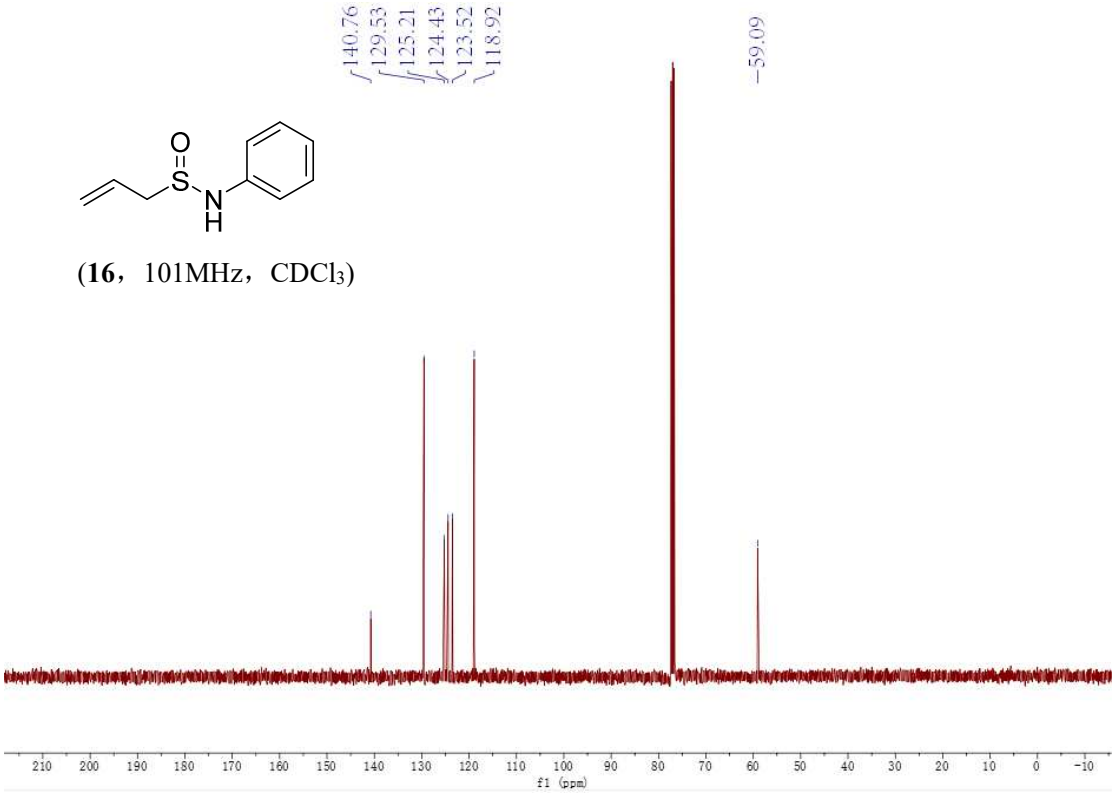

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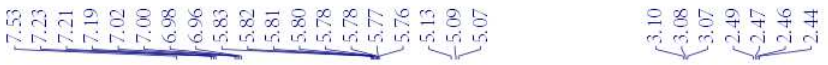
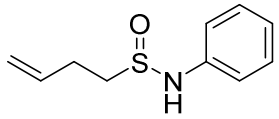
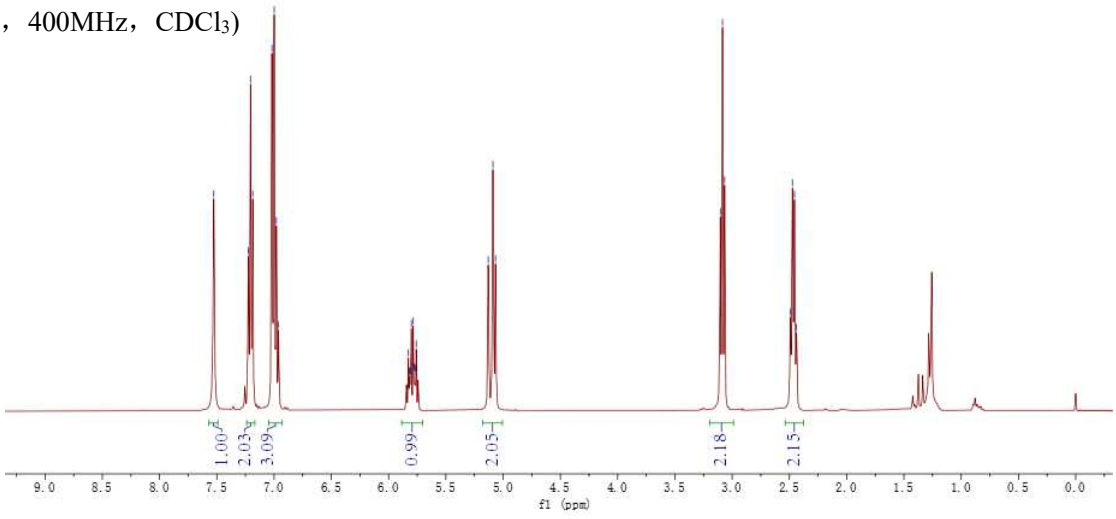
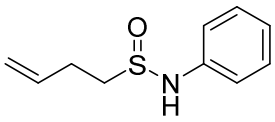


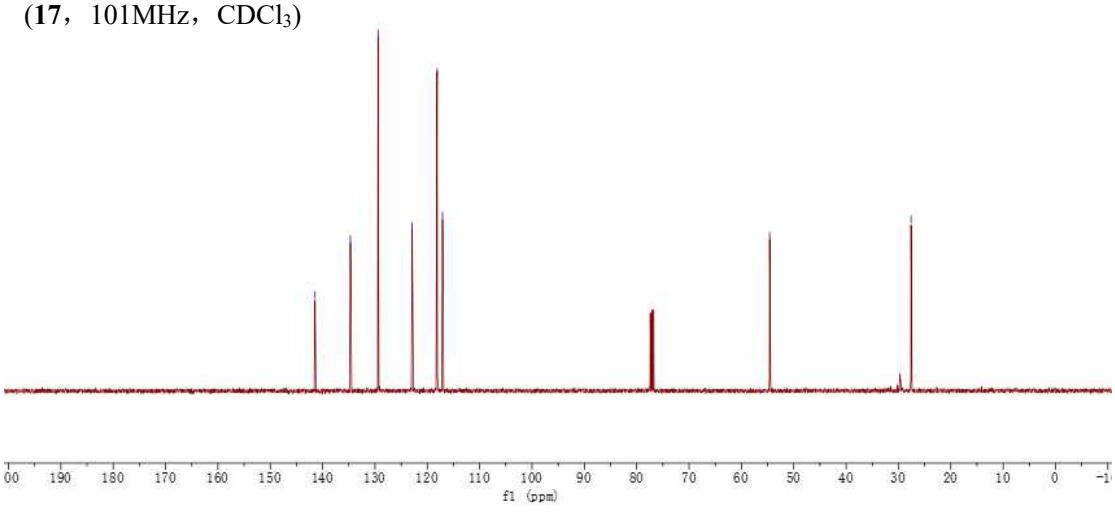


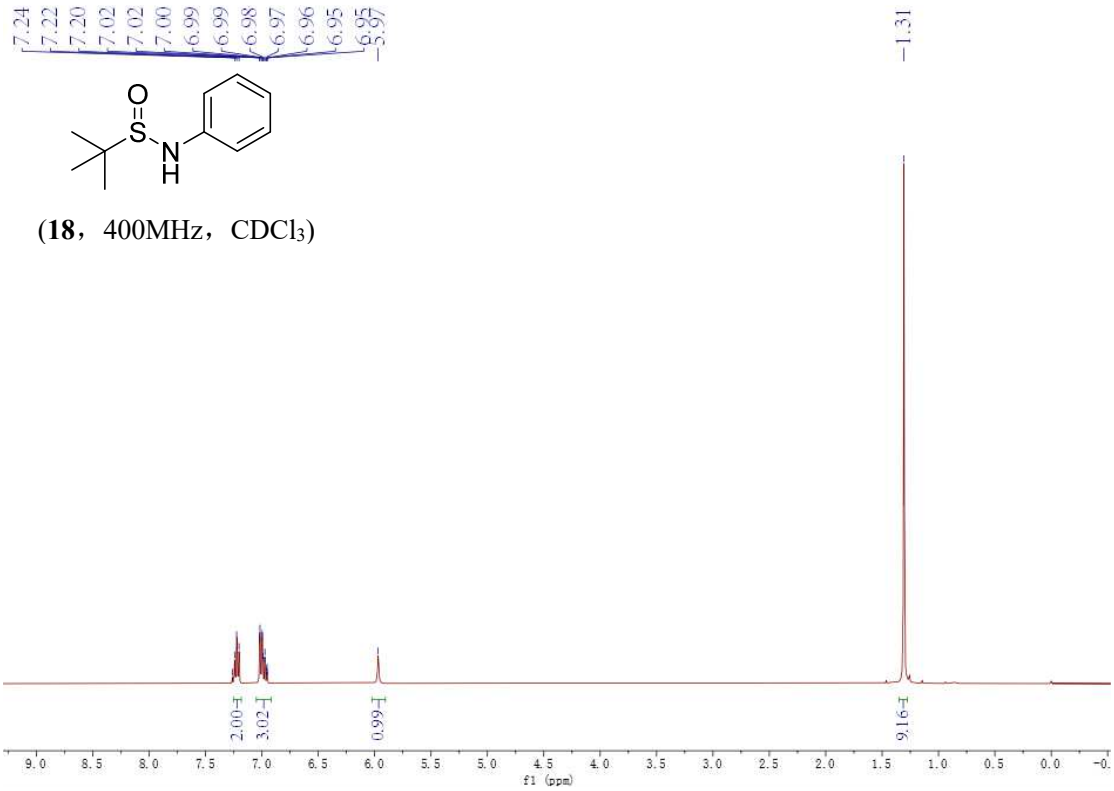
(**17**，400MHz，$CDCl_3$)



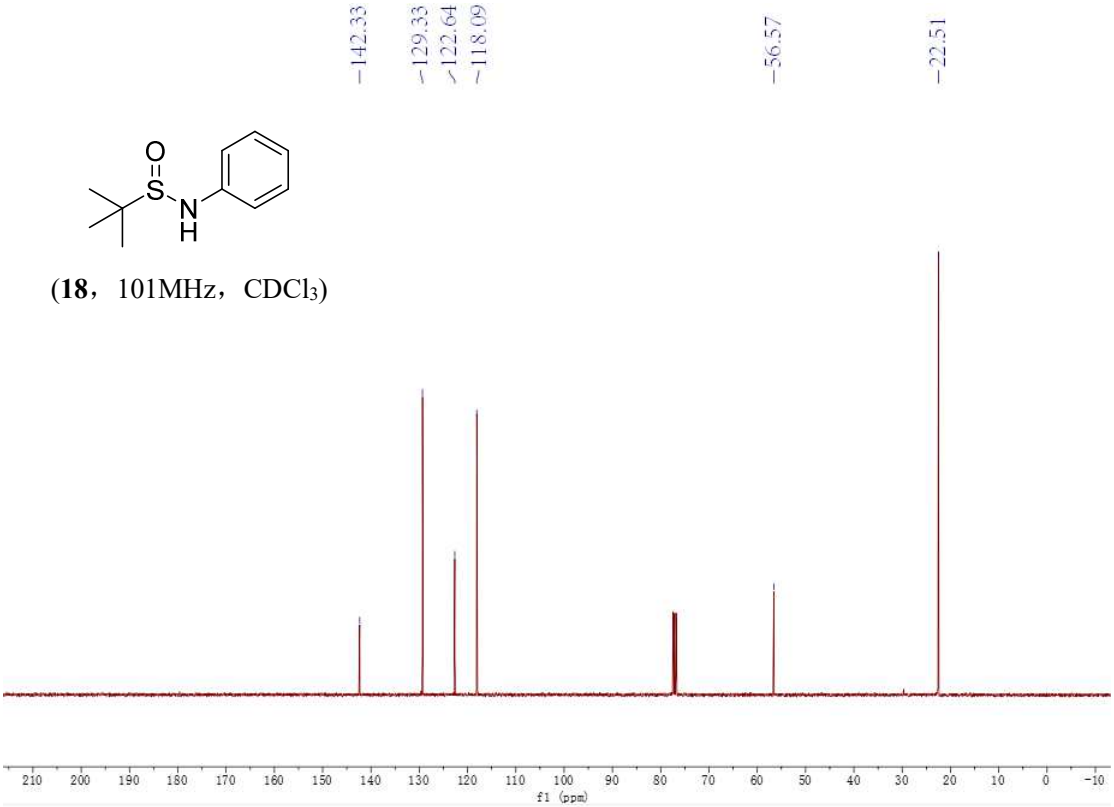


(**17**，101MHz，$CDCl_3$)

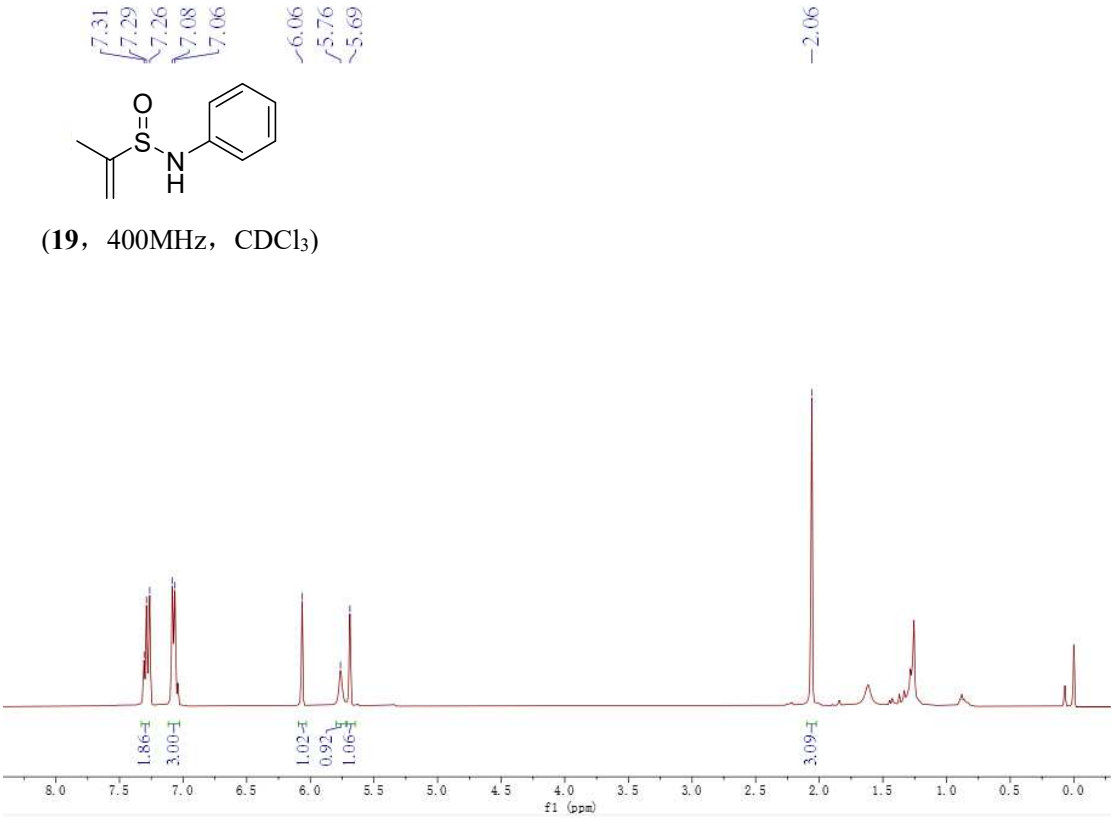




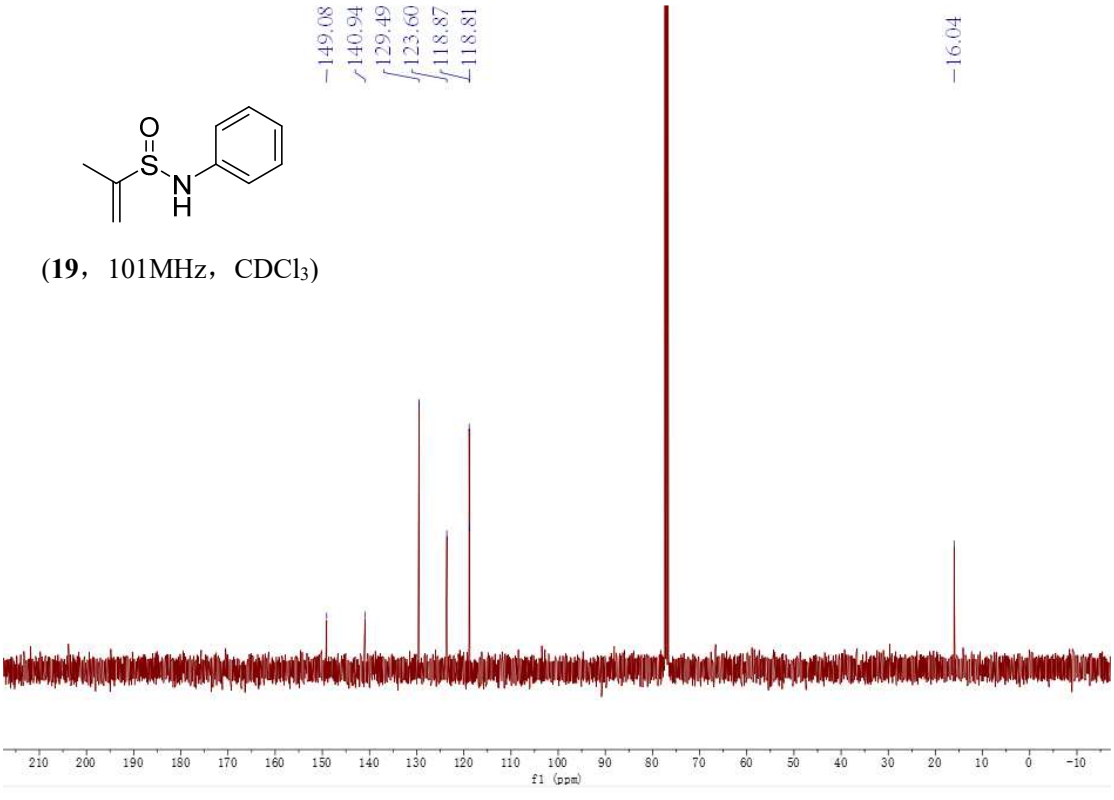
(**18**，400MHz，$CDCl_3$)



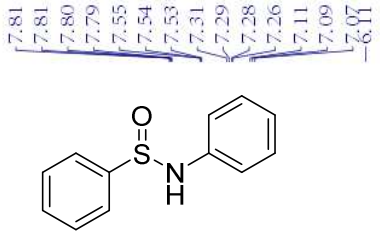
(**18**，101MHz，$CDCl_3$)



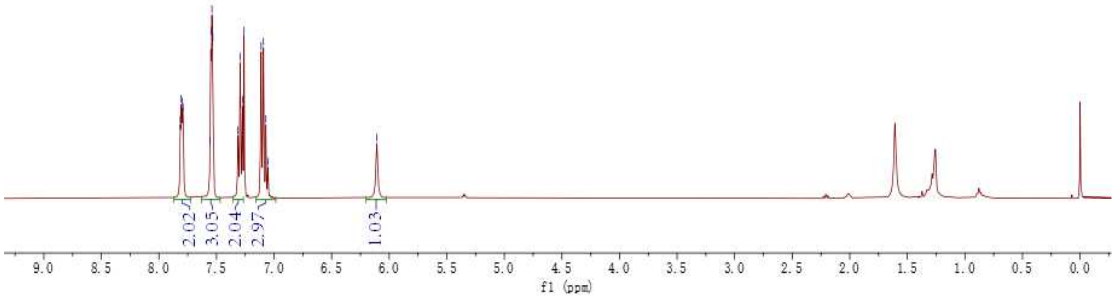
(**19**，400MHz，$CDCl_3$)

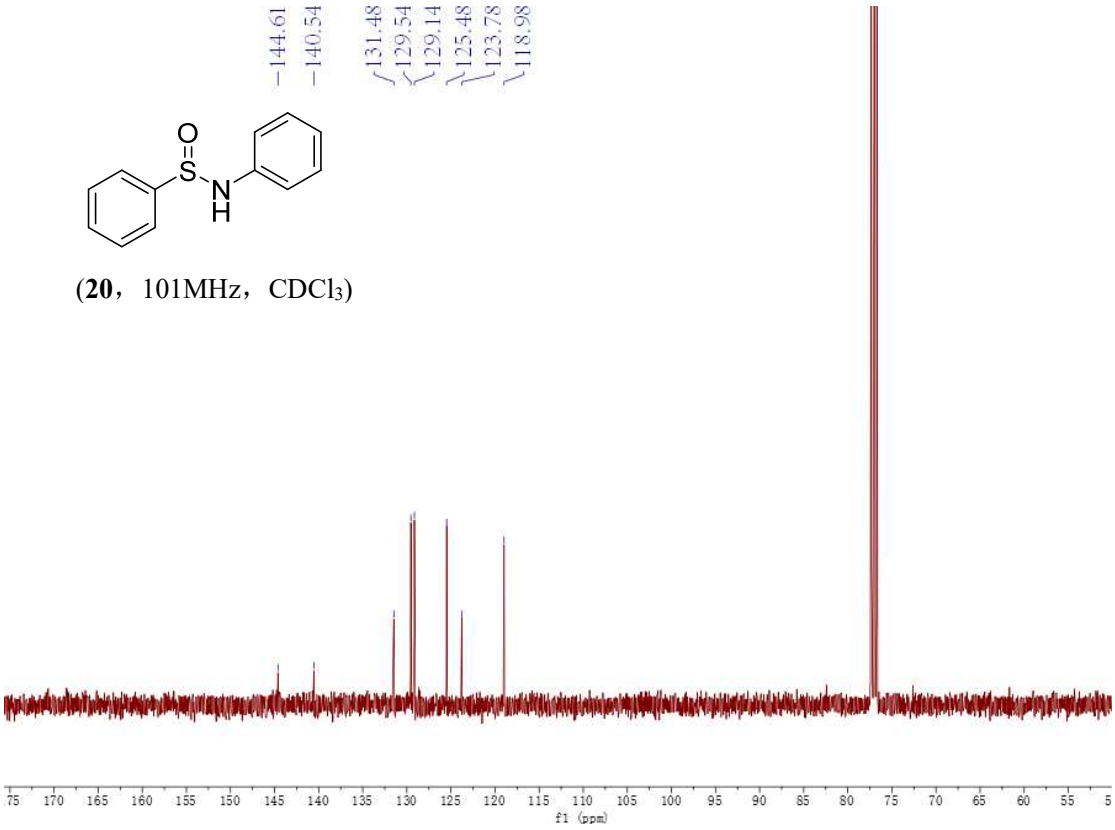


(**19**，101MHz，$CDCl_3$)

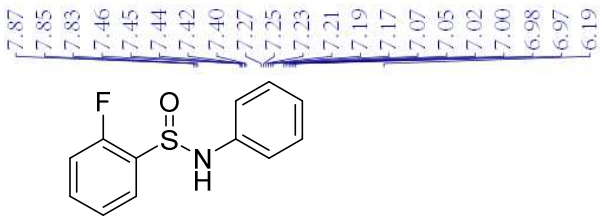


(**20**，400MHz，$CDCl_3$)

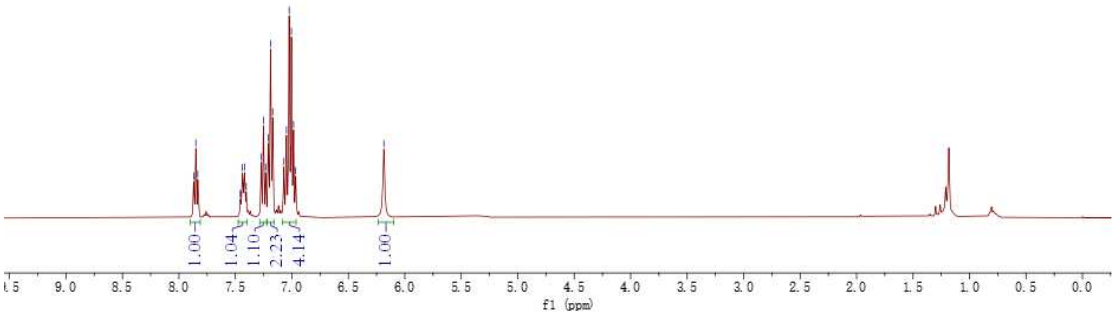


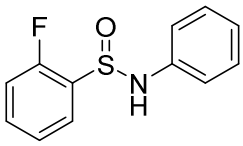


(**20**，101MHz，$CDCl_3$)

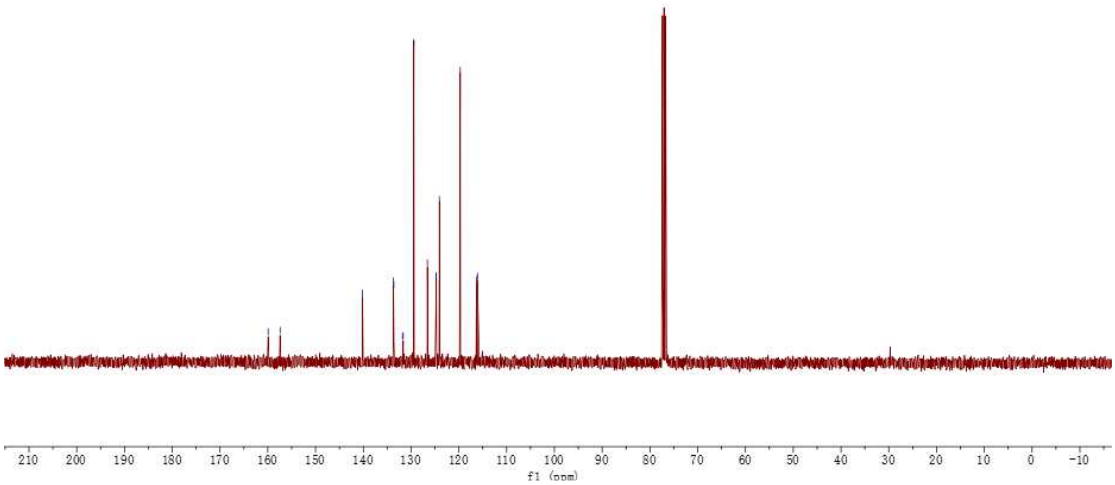


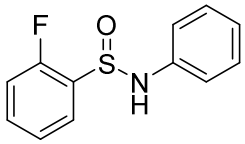
(**21**，400MHz，$CDCl_3$)



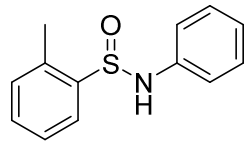


(**21**，101MHz，$CDCl_3$)

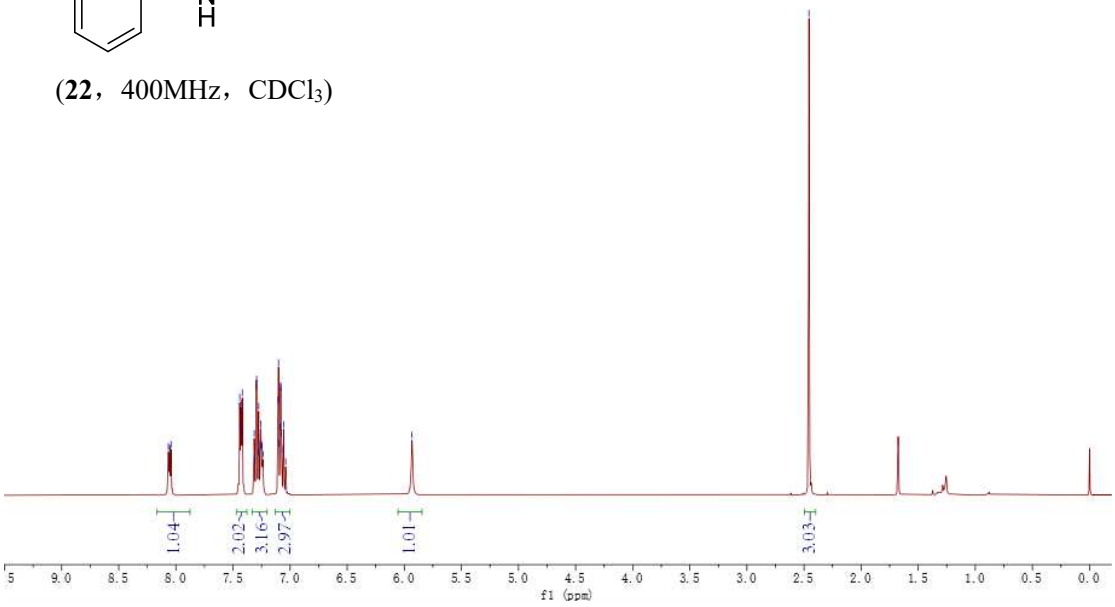


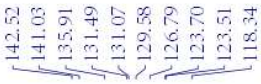


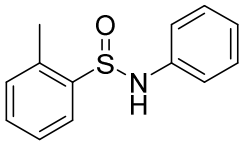
(**21**，376MHz，$CDCl_3$)



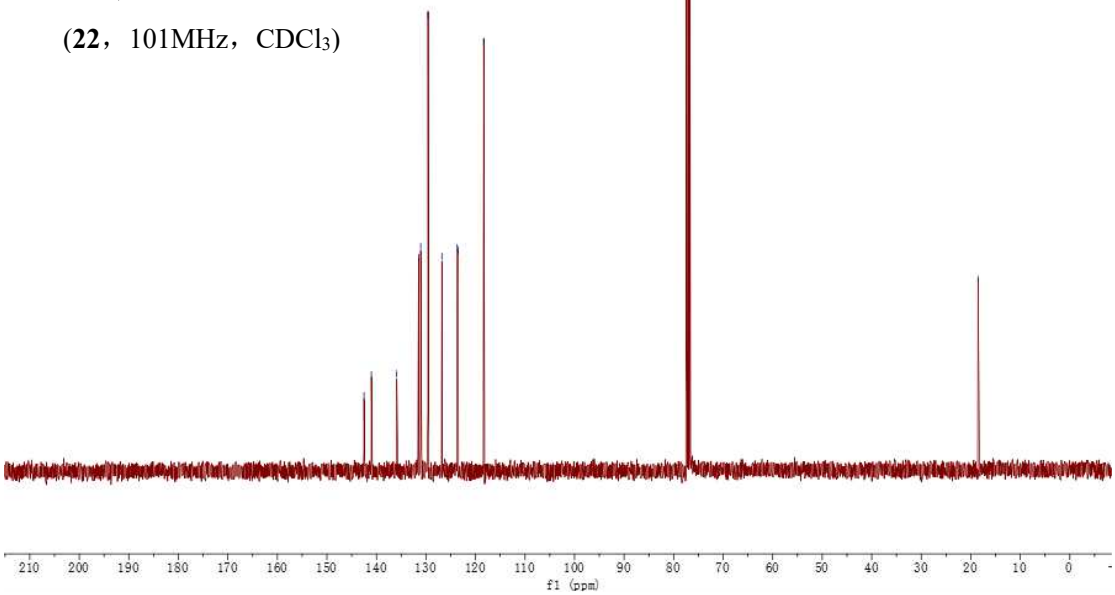
(**22**，400MHz，$CDCl_3$)

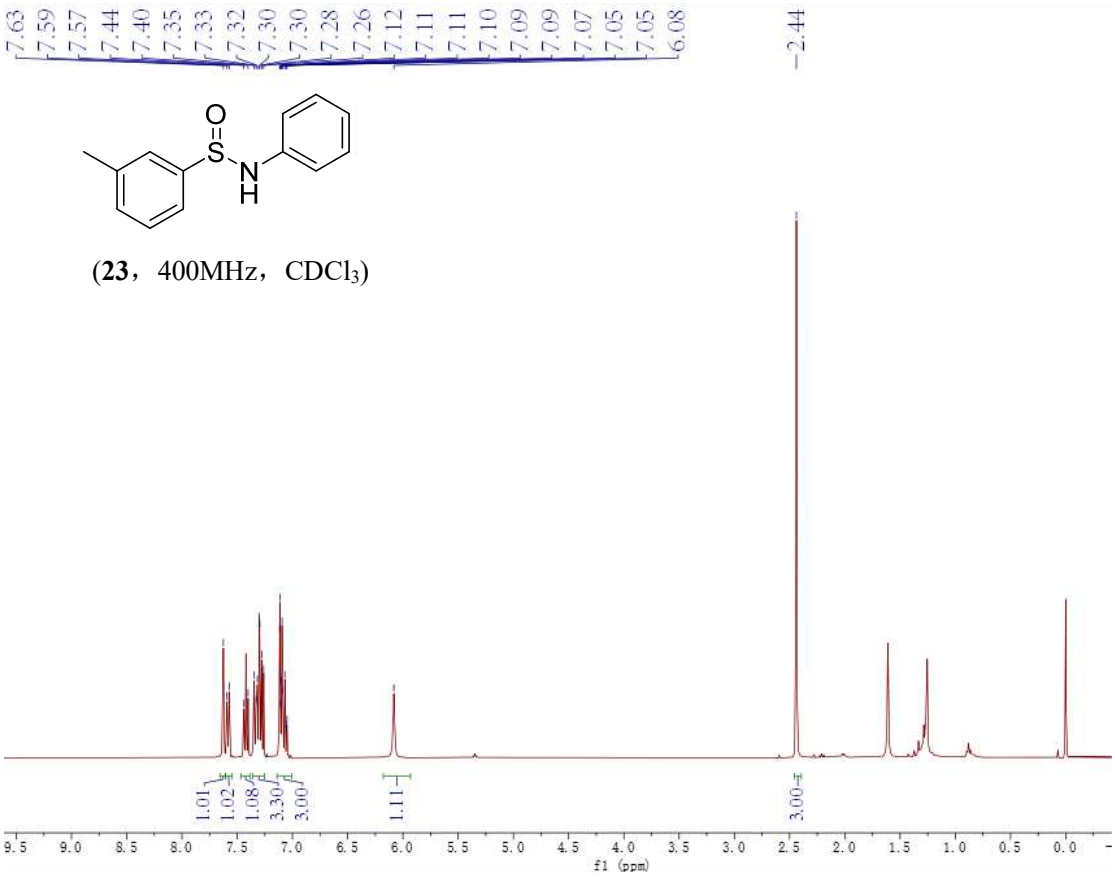




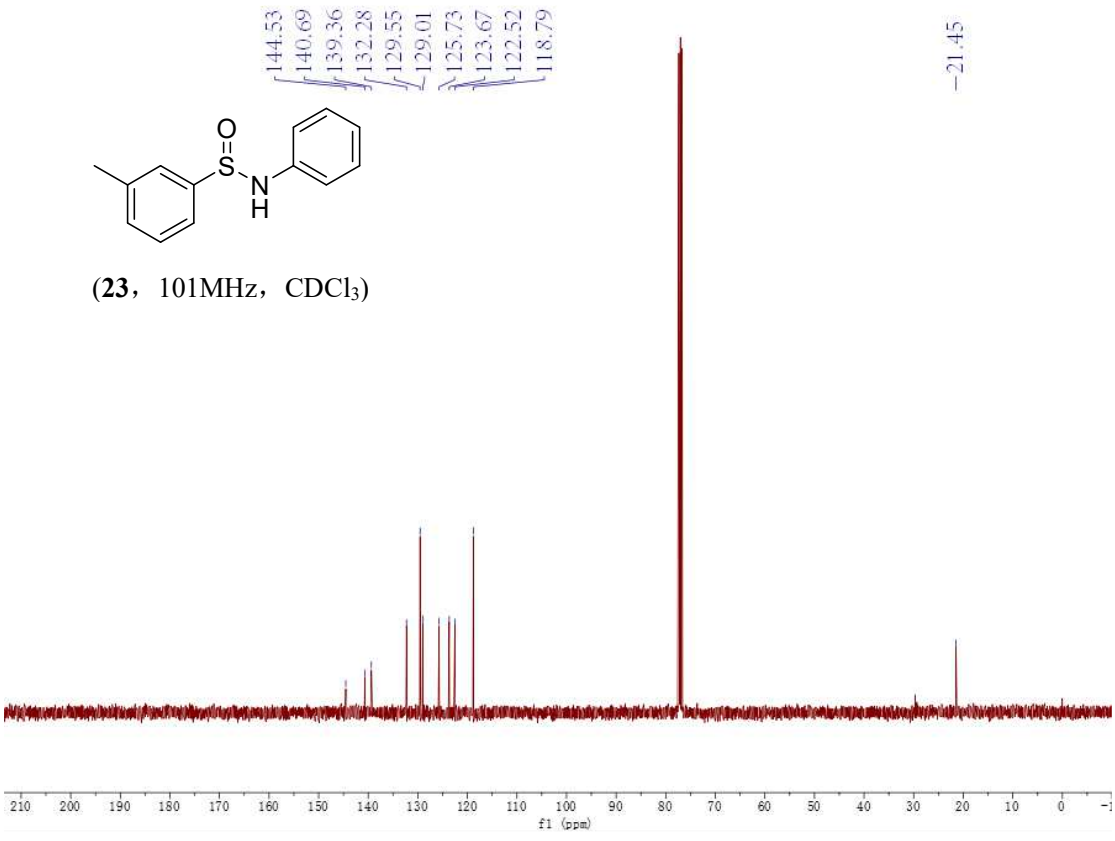


(**22**，101MHz，$CDCl_3$)



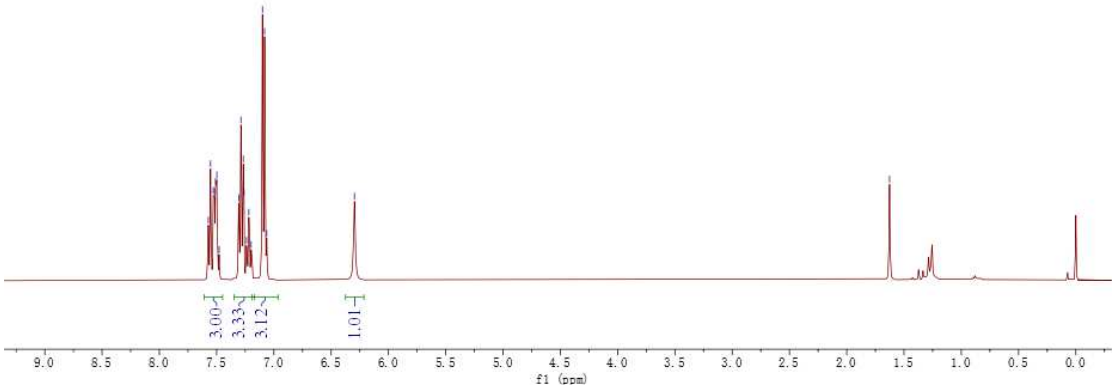


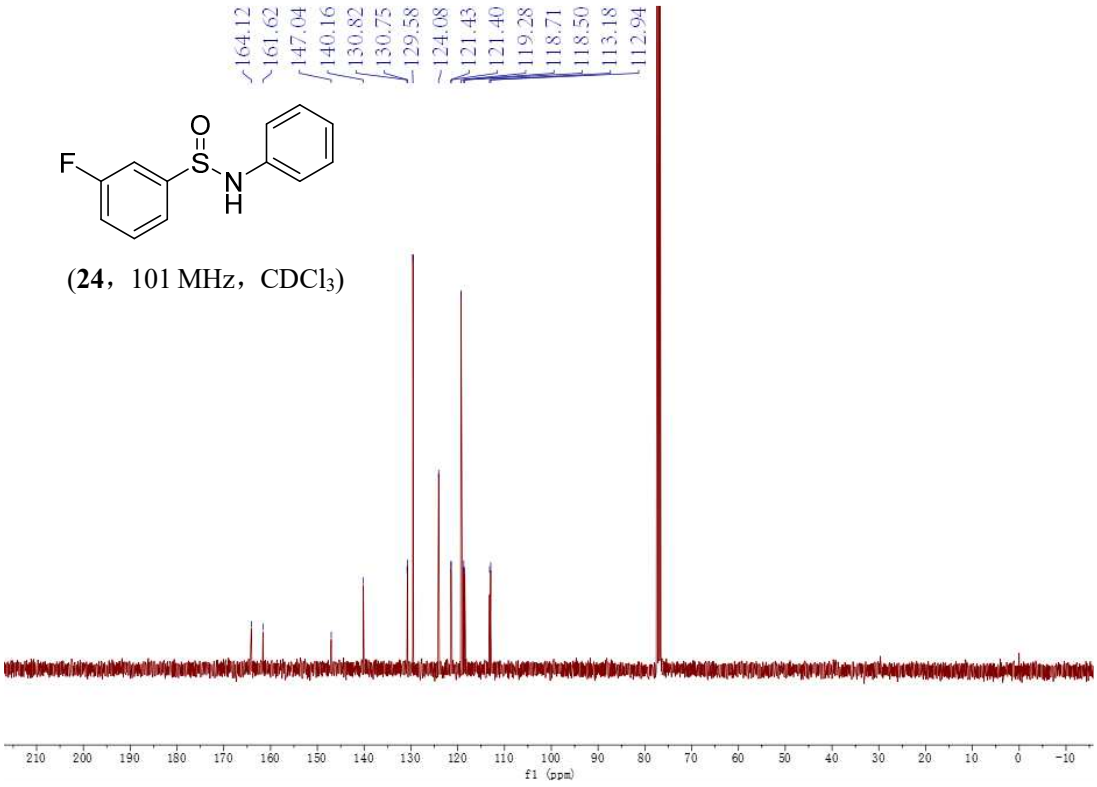
(**23**，400MHz，$CDCl_3$)



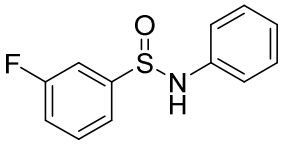
(**23**，101MHz，$CDCl_3$)

(**24**，400MHz，$CDCl_3$)

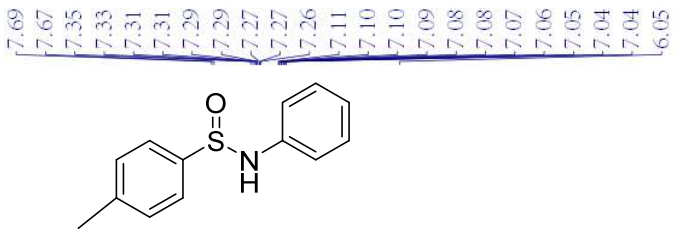




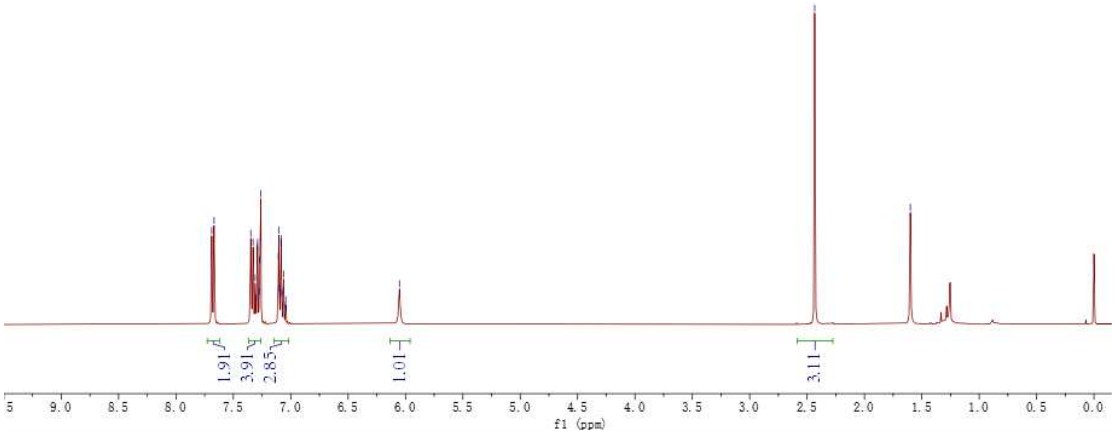
(**24**，101 MHz，$CDCl_3$)

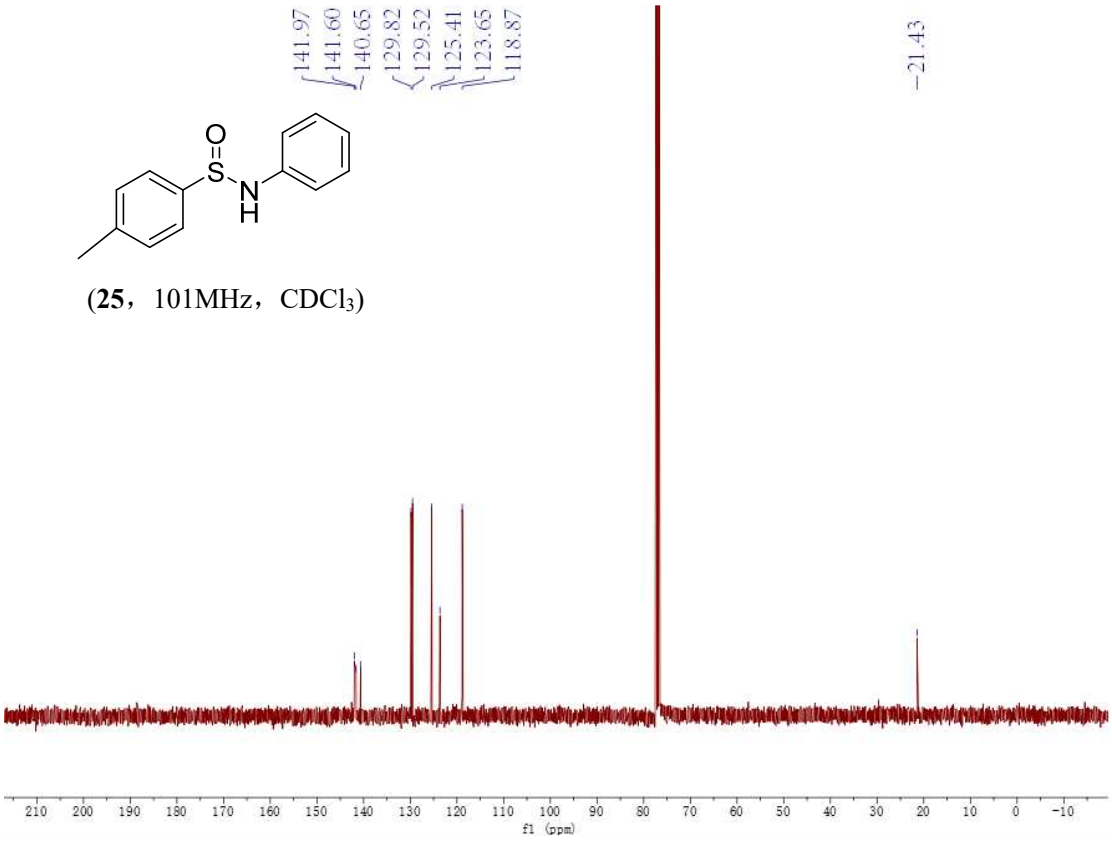


(**24**，376MHz，$CDCl_3$)

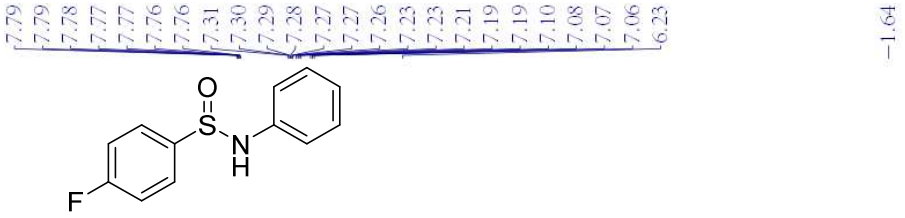


(**25**，400MHz，$CDCl_3$)

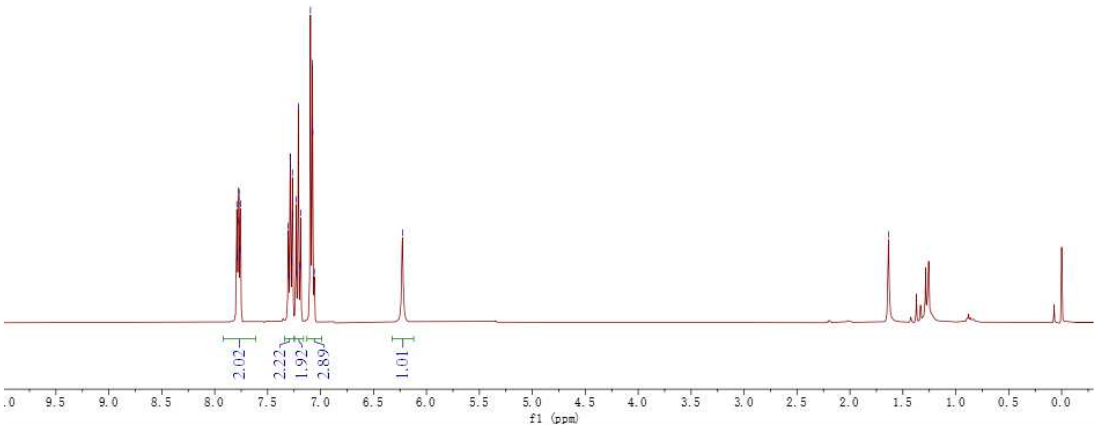


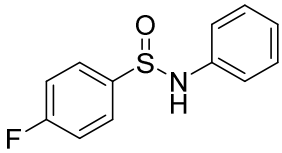


(**25**，101MHz，$CDCl_3$)

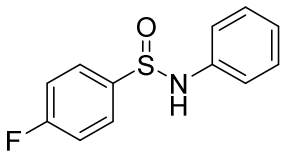


(**26**，400MHz，$CDCl_3$)



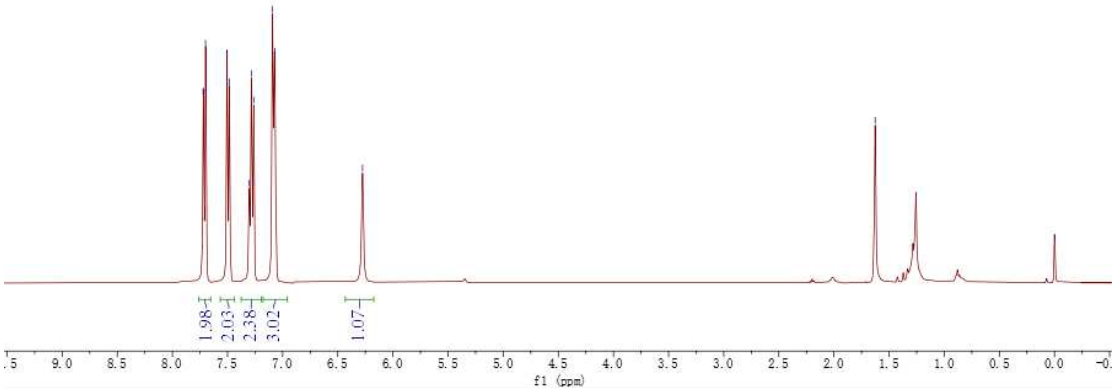


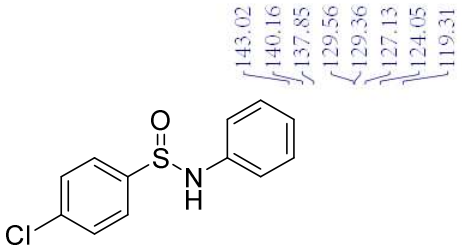
(**26**，101MHz，$CDCl_3$)



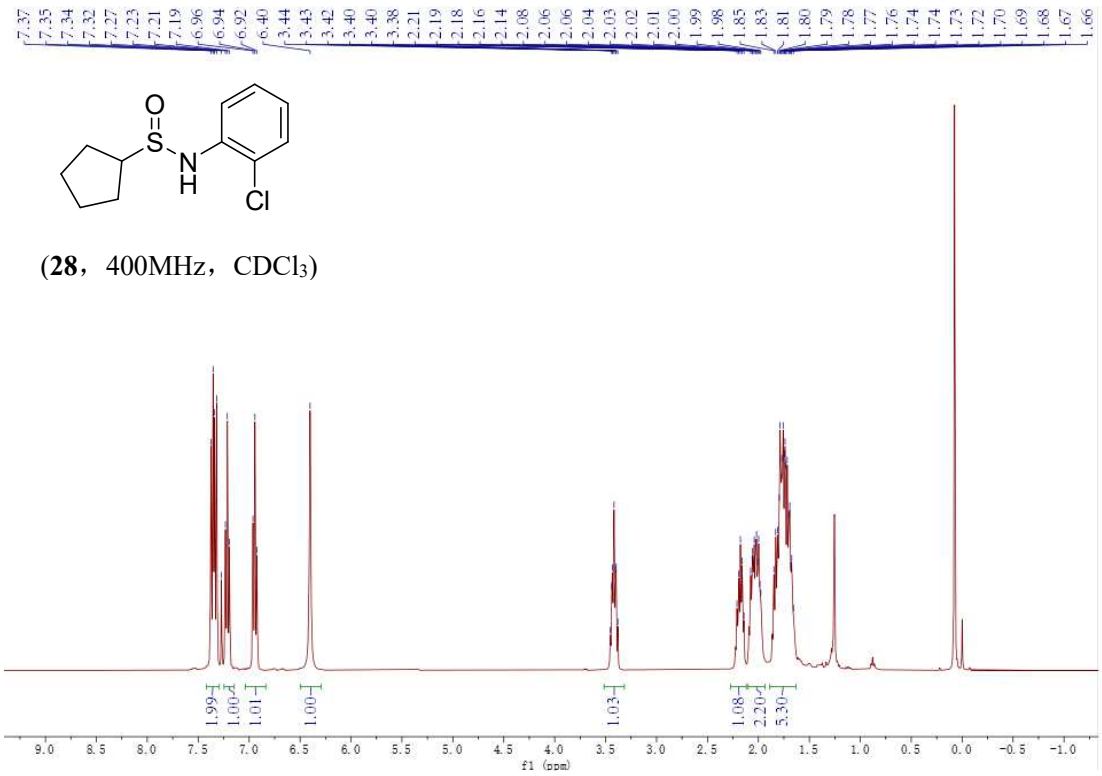
(**26**，376MHz，$CDCl_3$)

(**27**，400MHz，$CDCl_3$)

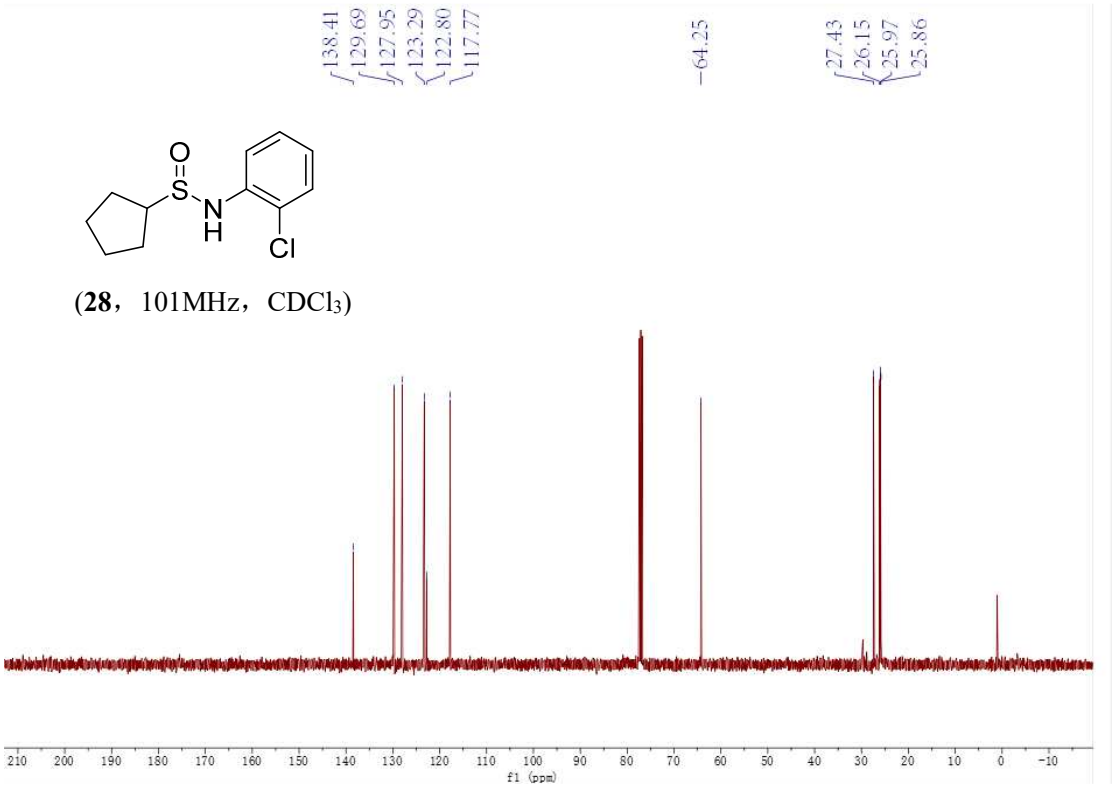




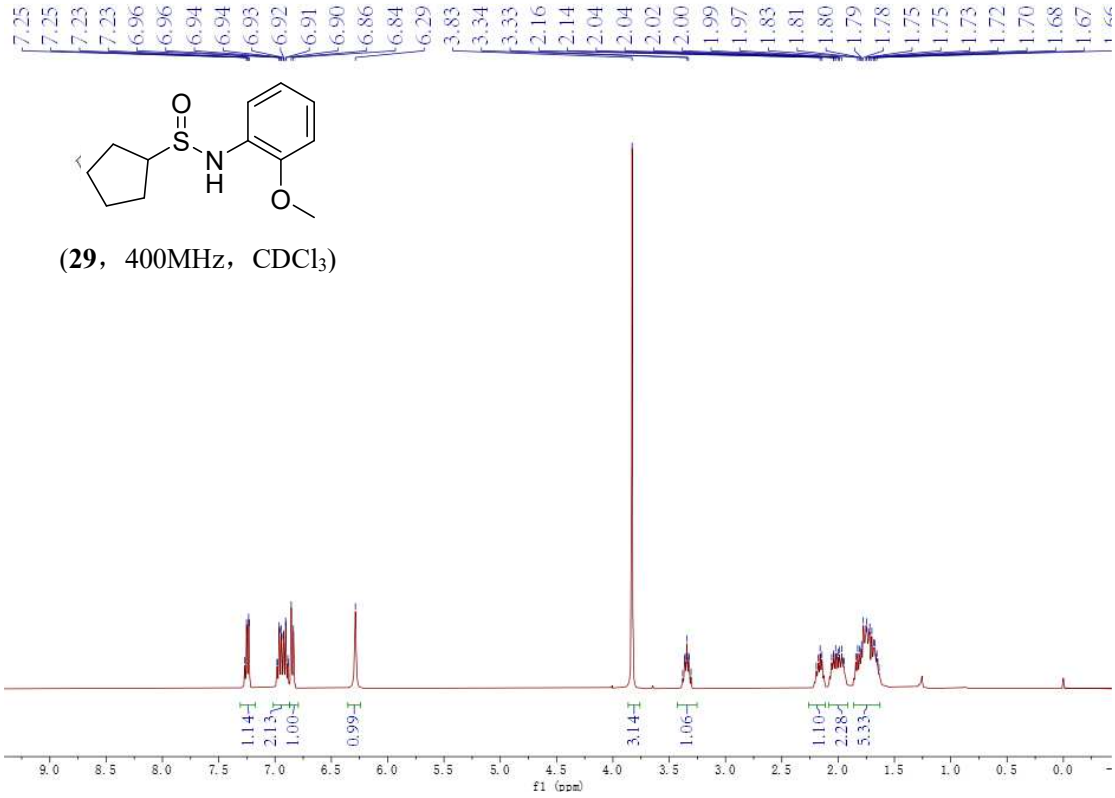
(**27**，101MHz，$CDCl_3$)



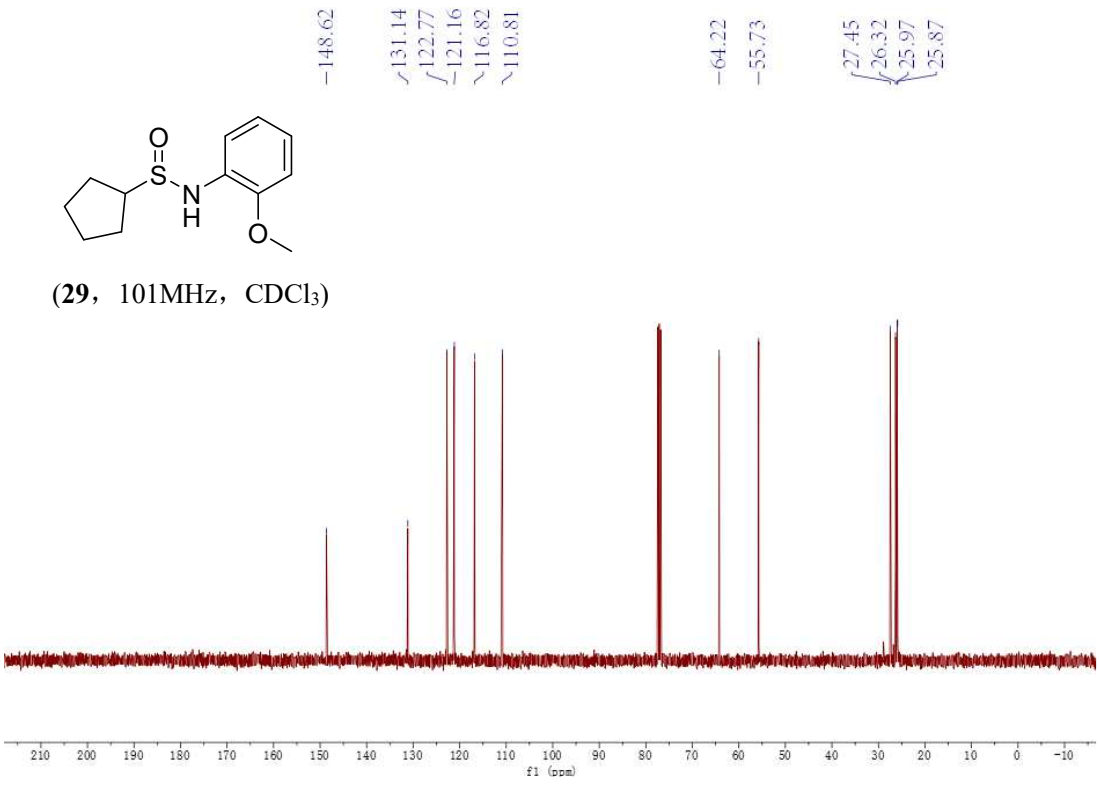
(**28**，400MHz，$CDCl_3$)



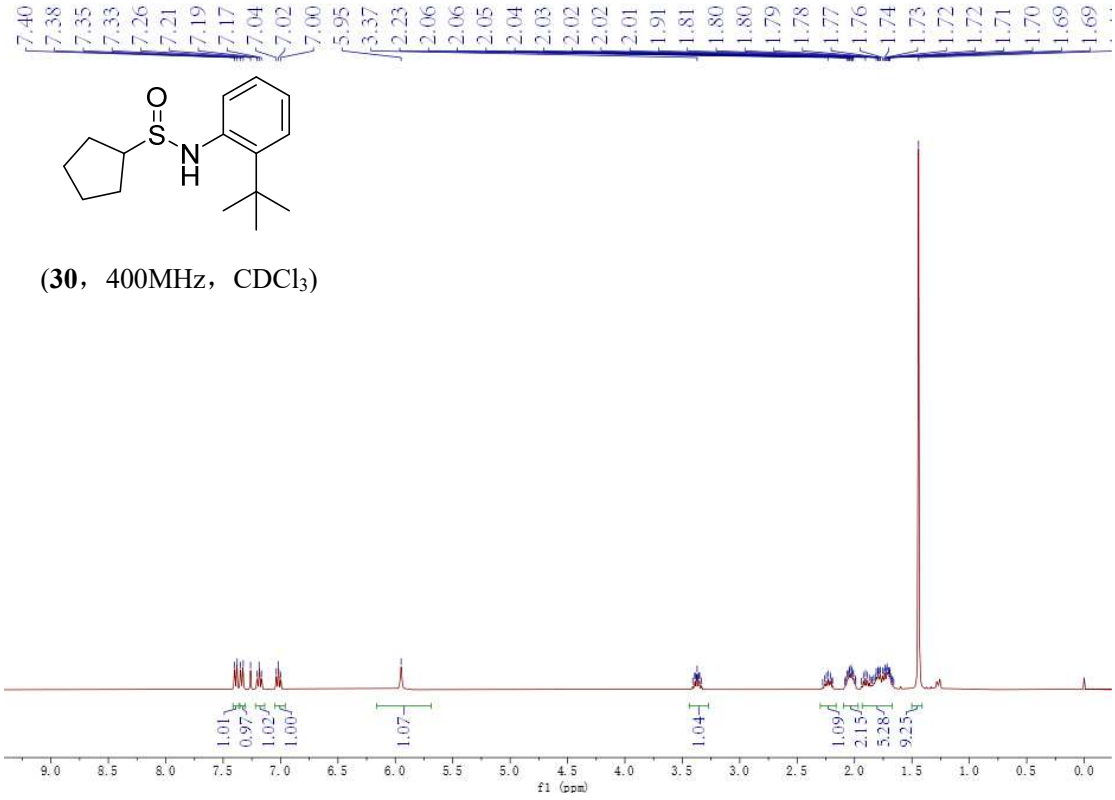
(**28**，101MHz，$CDCl_3$)



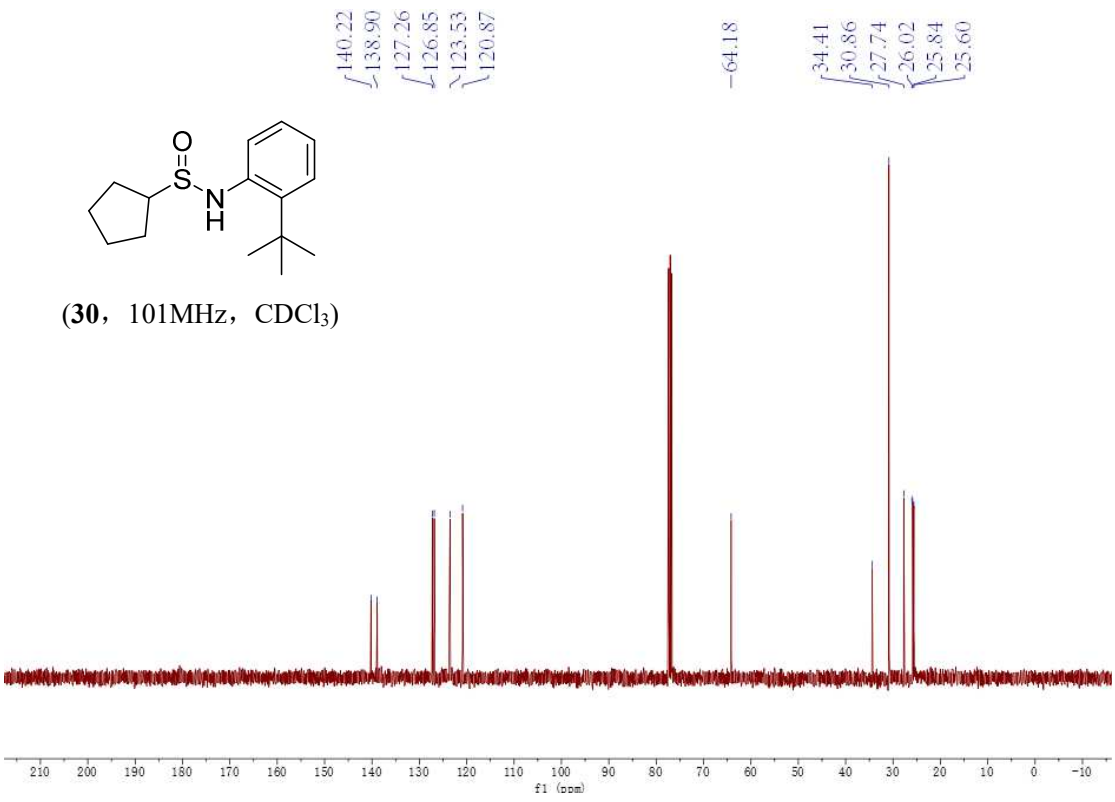
(**29**，400MHz，$CDCl_3$)



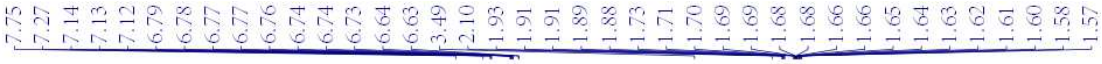
(**29**，101MHz，$CDCl_3$)

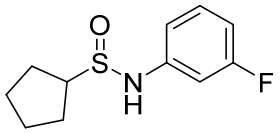


(**30**，400MHz，$CDCl_3$)

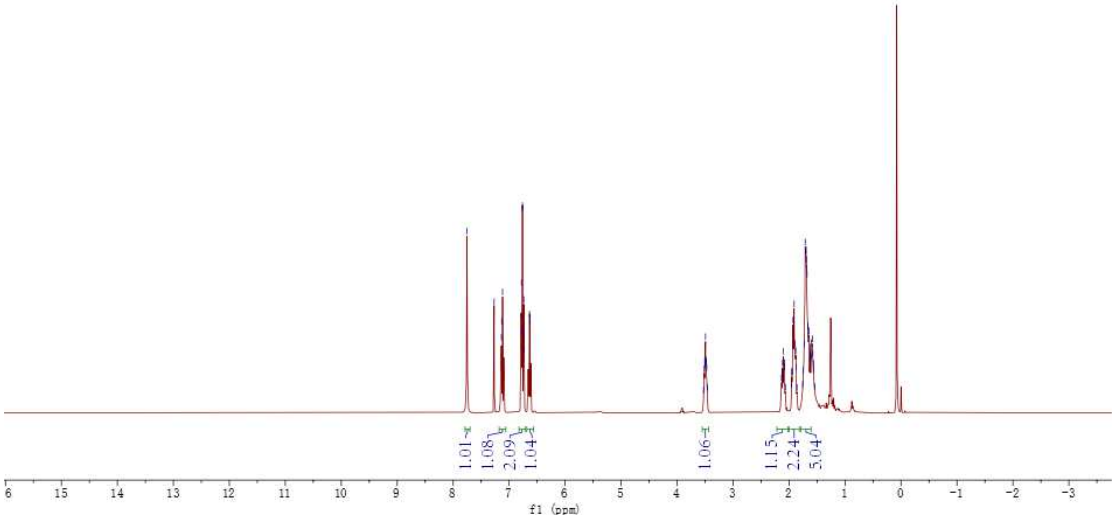


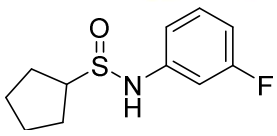
(**30**，101MHz，$CDCl_3$)



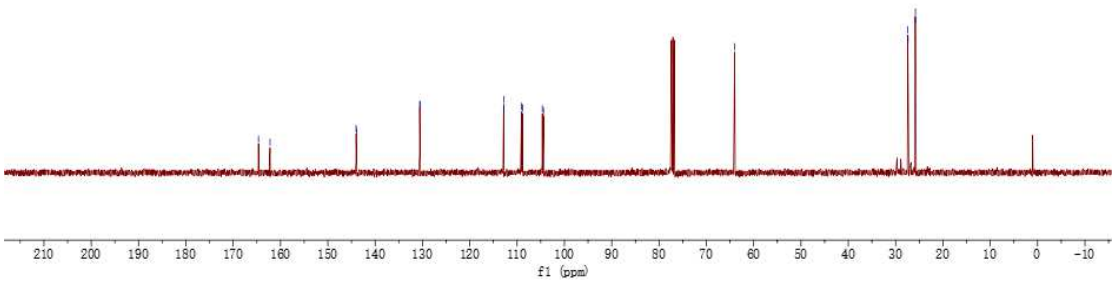


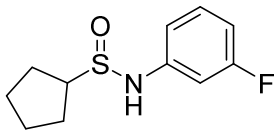
(**31**，400MHz，$CDCl_3$)



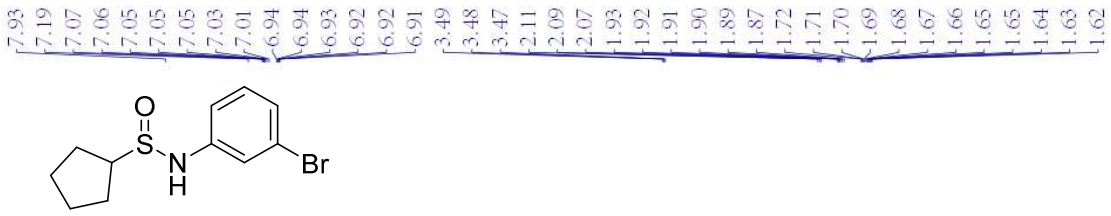


(**31**，101MHz，$CDCl_3$)

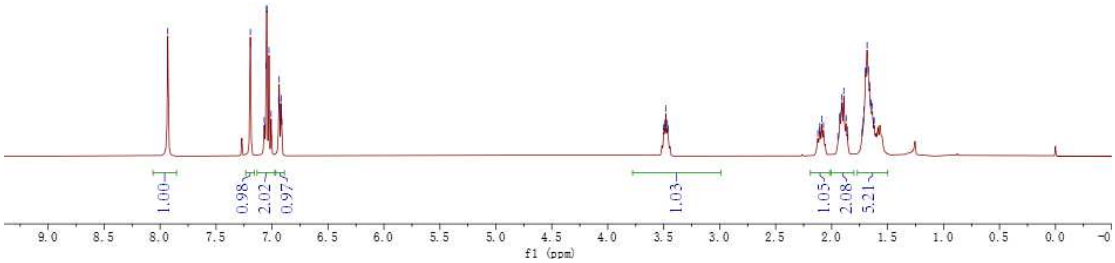


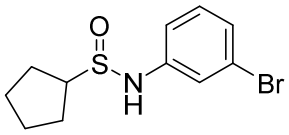


(**31**，376MHz，$CDCl_3$)

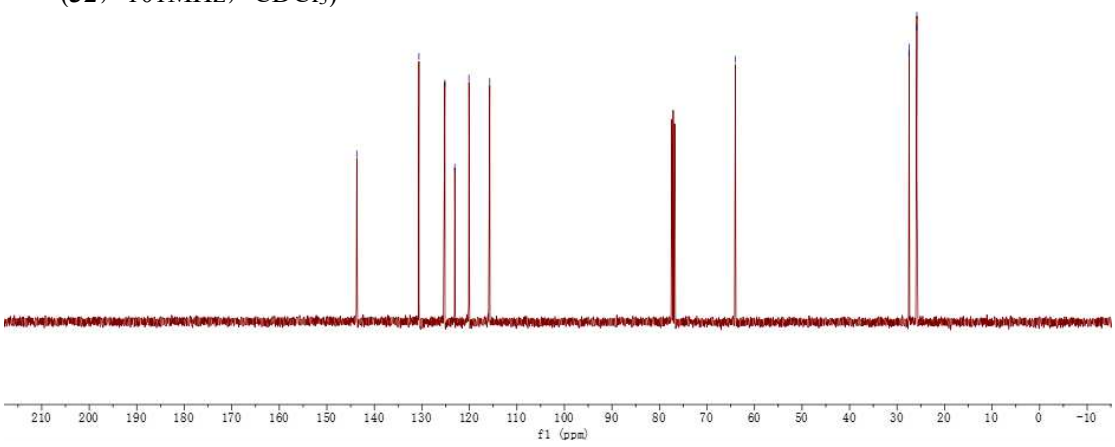


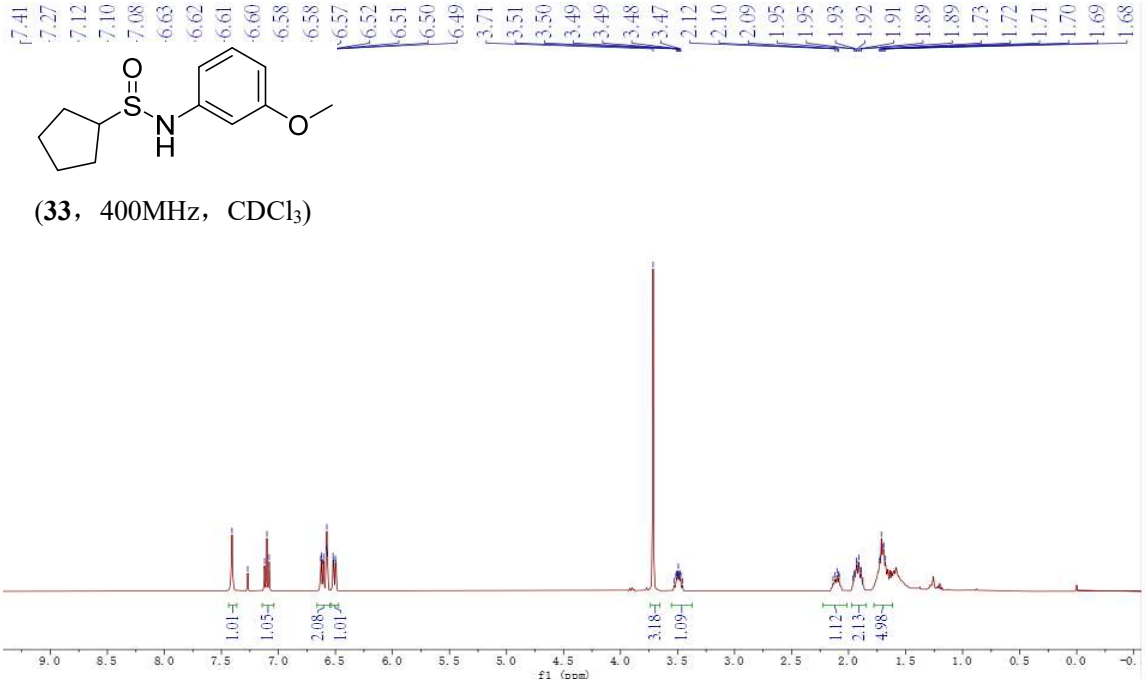
(**32**，400MHz，$CDCl_3$)



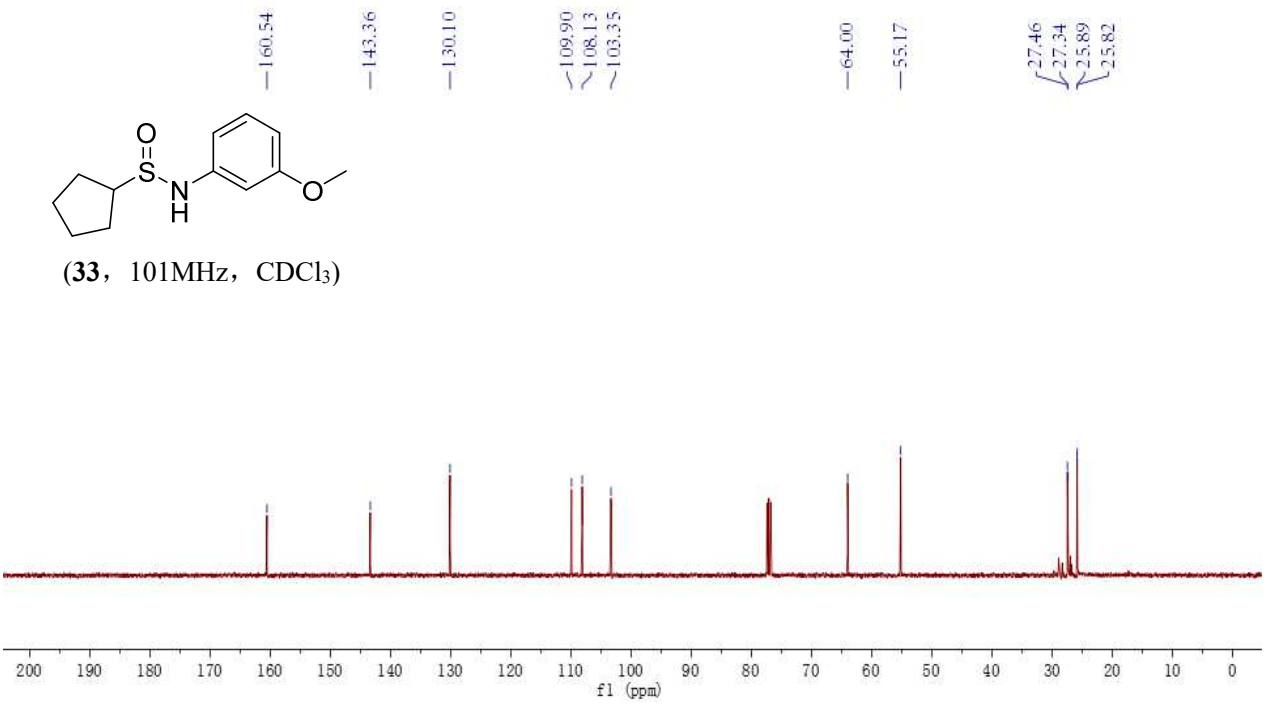


(**32**，101MHz，$CDCl_3$)

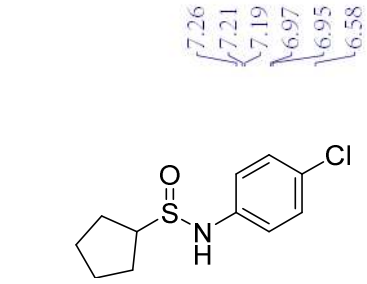




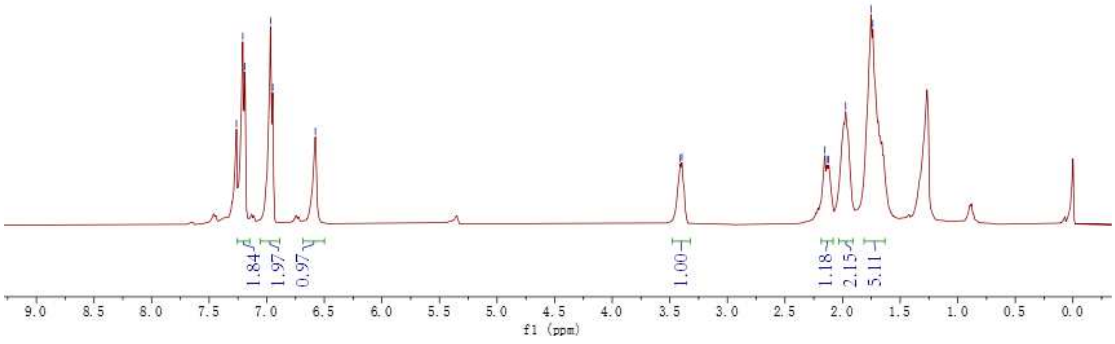
(**33**，400MHz，$CDCl_3$)

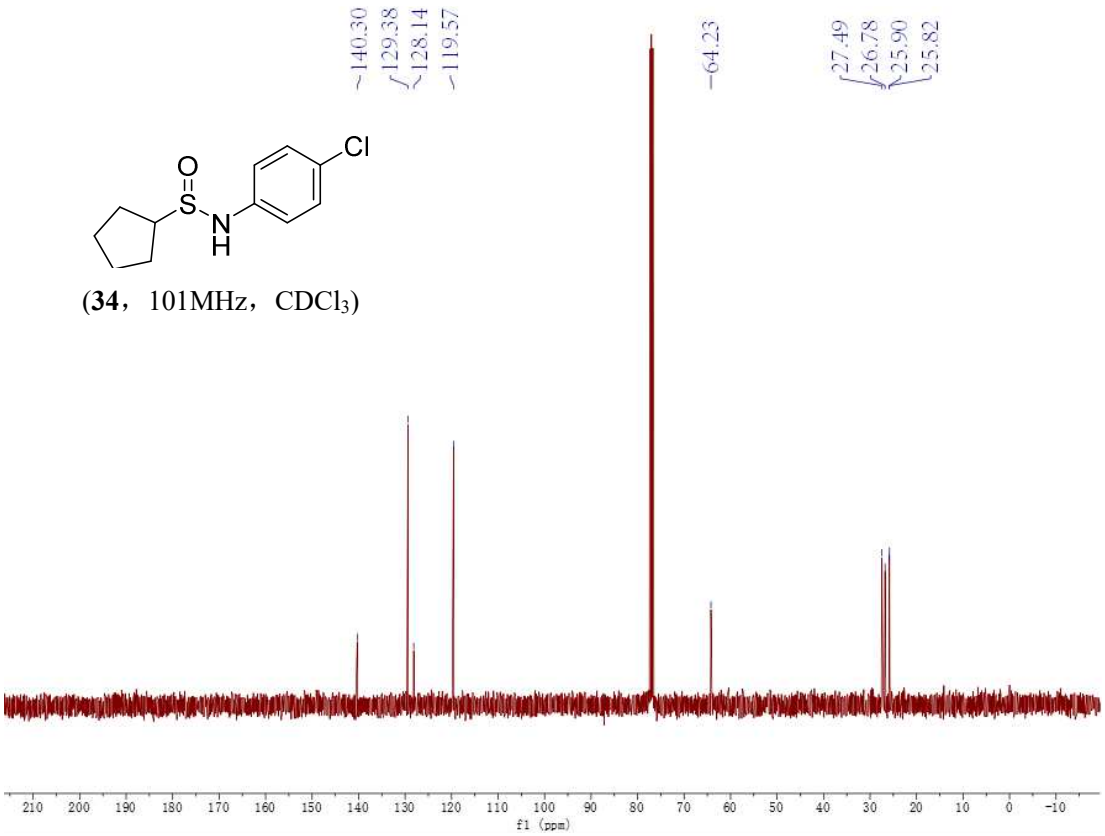


(**33**，101MHz，$CDCl_3$)

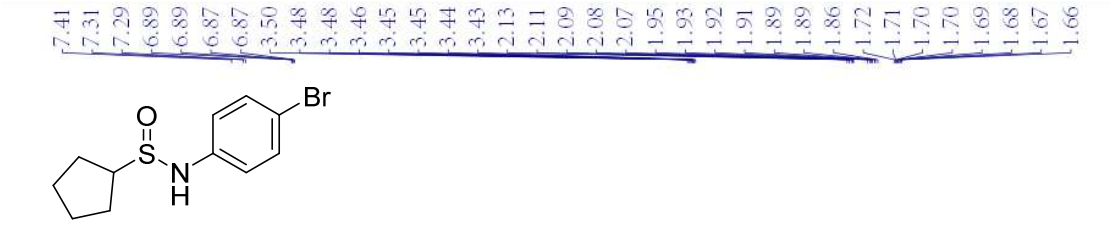


(**34**，400MHz，$CDCl_3$)

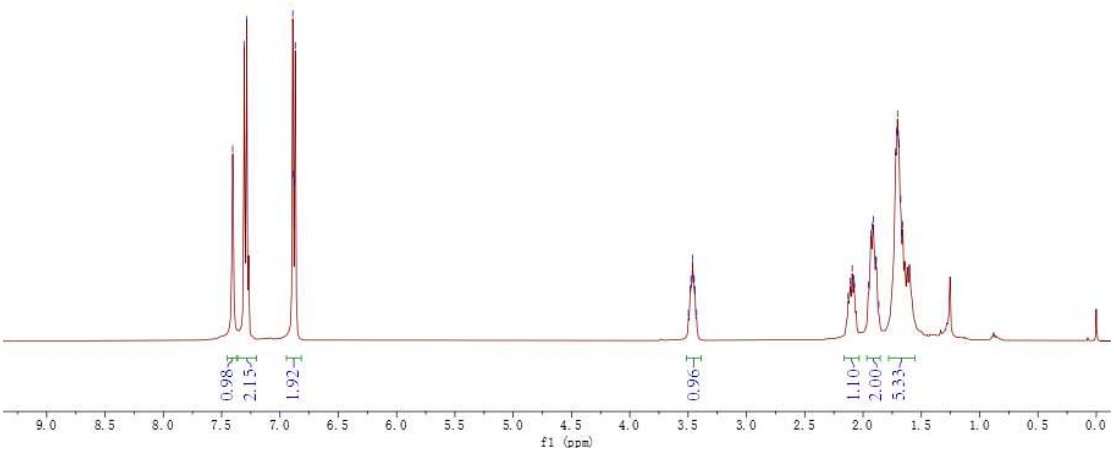




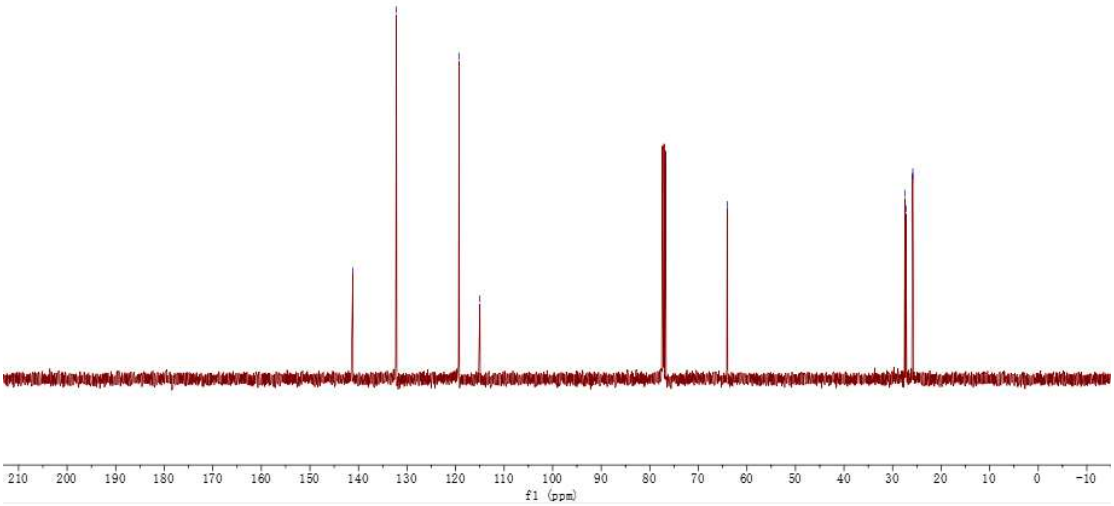
(**34**，101MHz，$CDCl_3$)

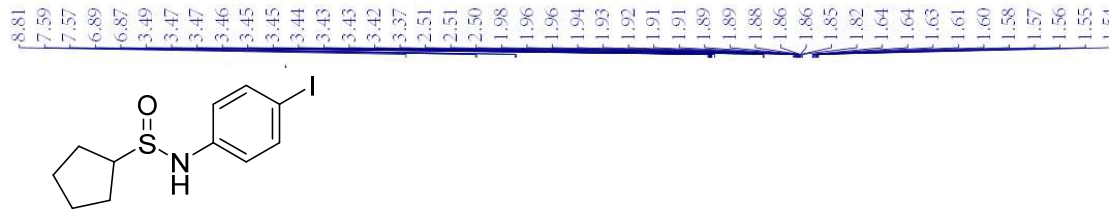


(**35**，400MHz，$CDCl_3$)

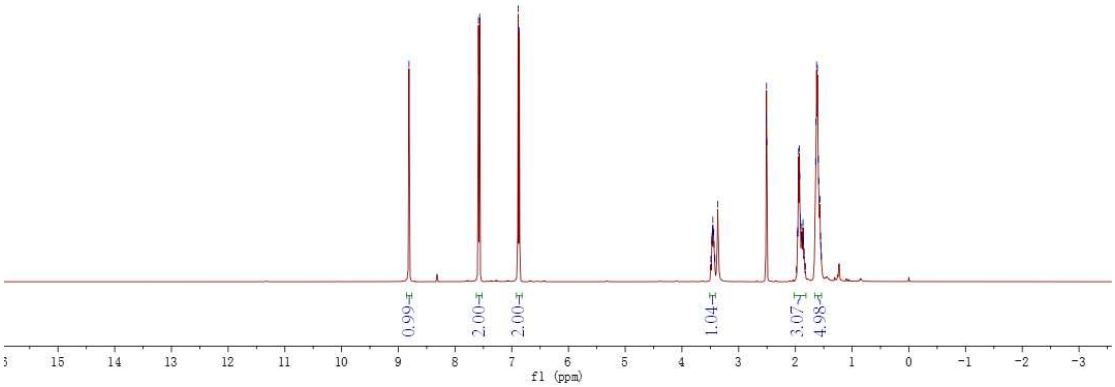


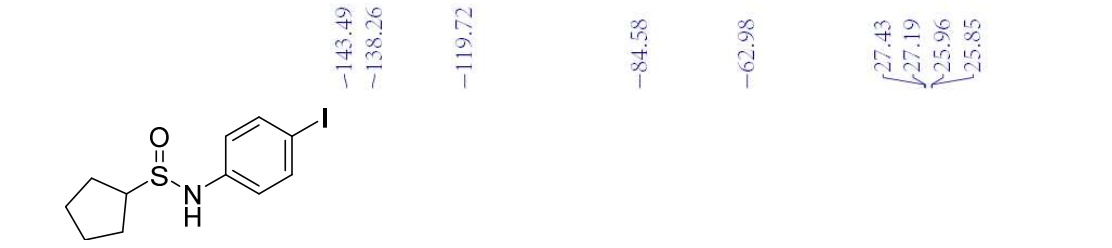
(**35**，101MHz，$CDCl_3$)



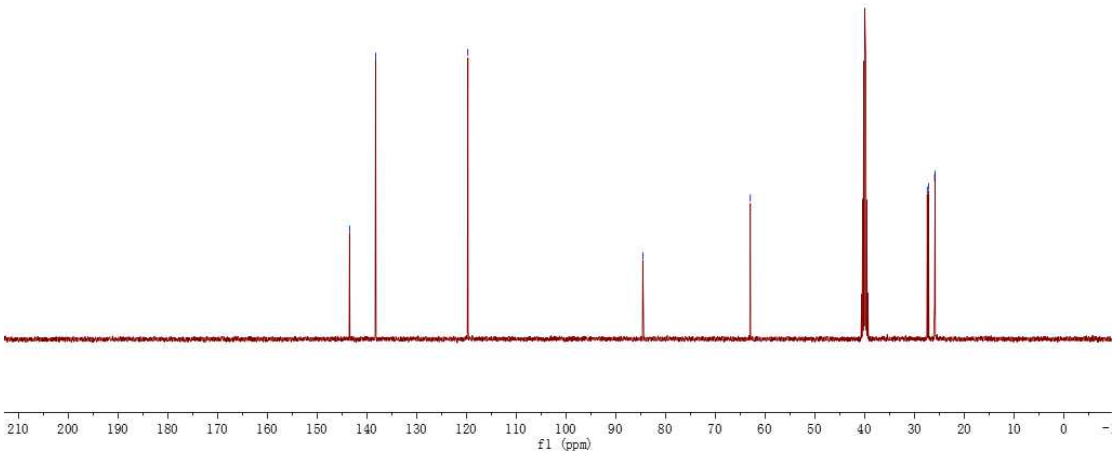


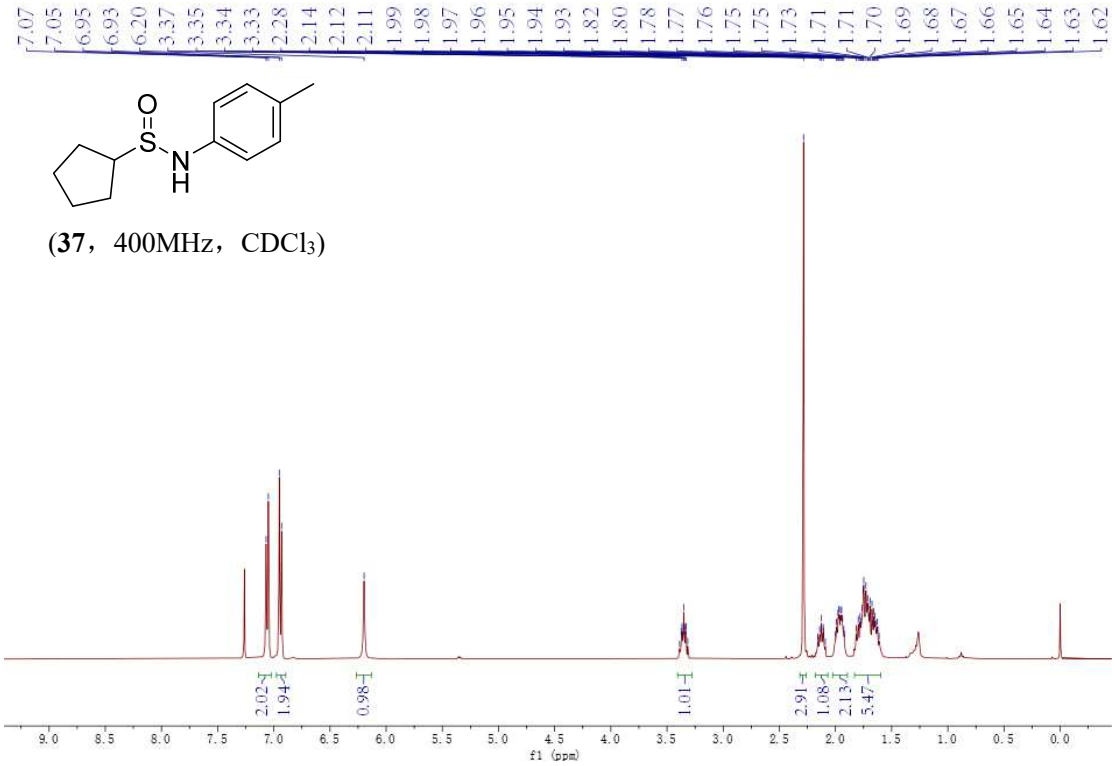
(**36**，400MHz，DMSO)



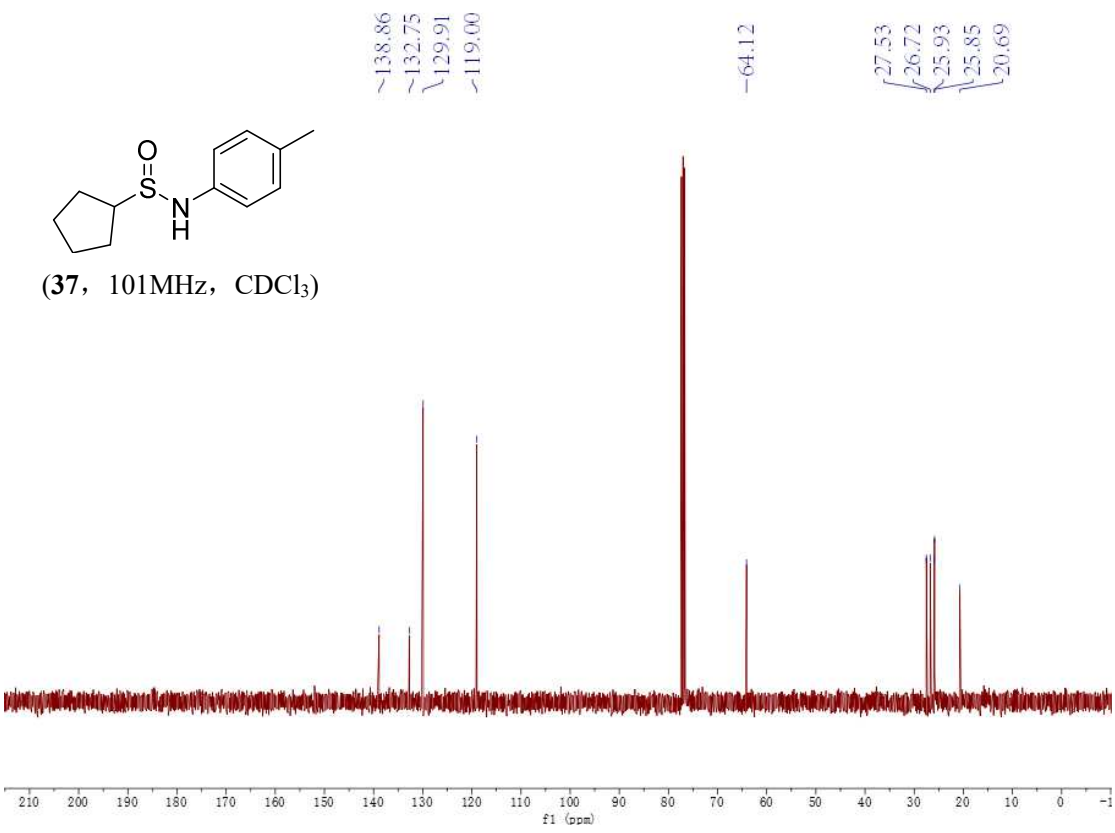


(**36**，101MHz，DMSO)

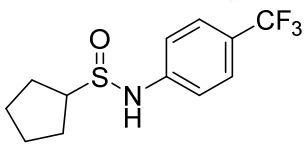




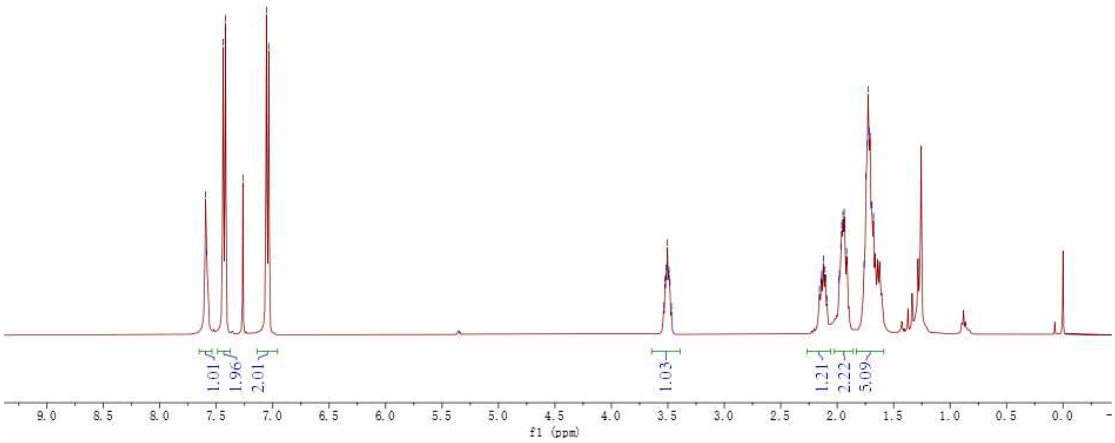
(**37**，400MHz，$CDCl_3$)

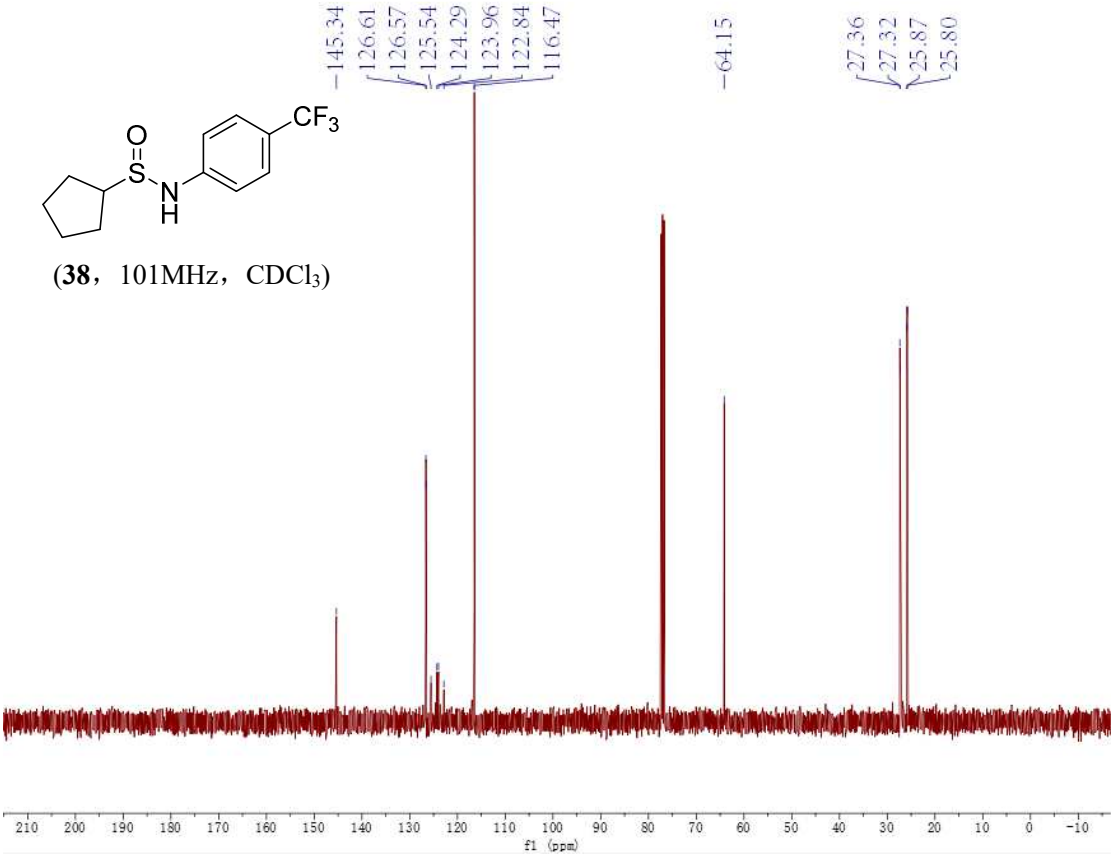


(**37**，101MHz，$CDCl_3$)

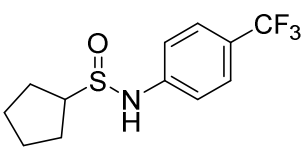


(**38**，400MHz，$CDCl_3$)

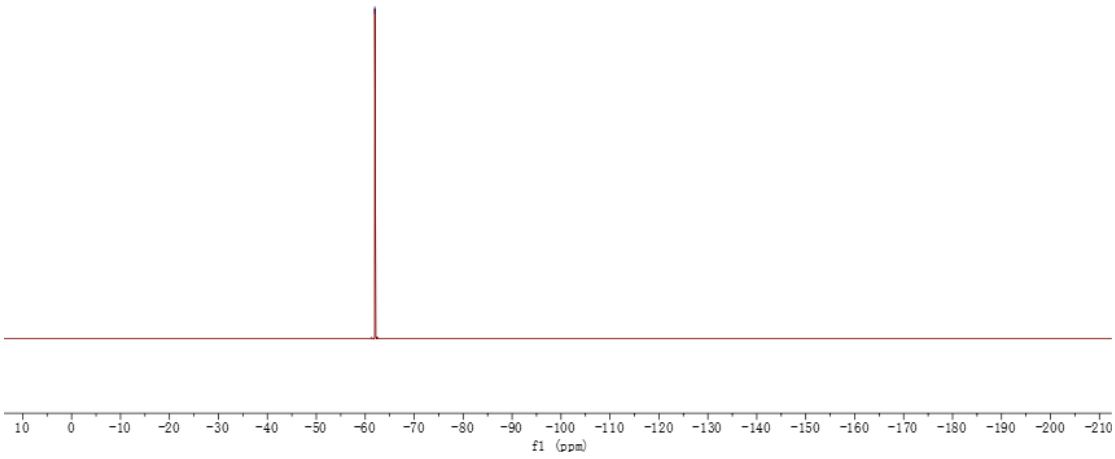


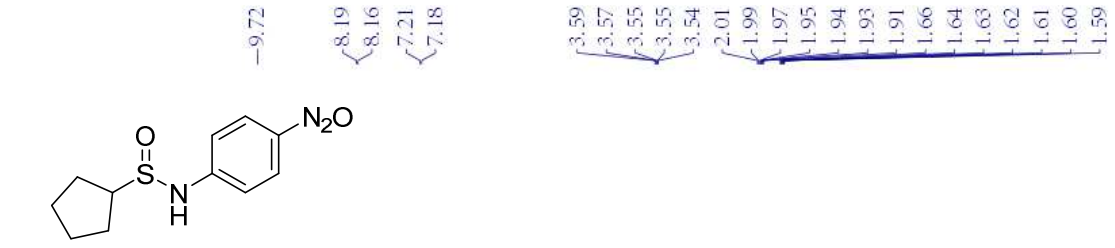


(**38**，101MHz，$CDCl_3$)

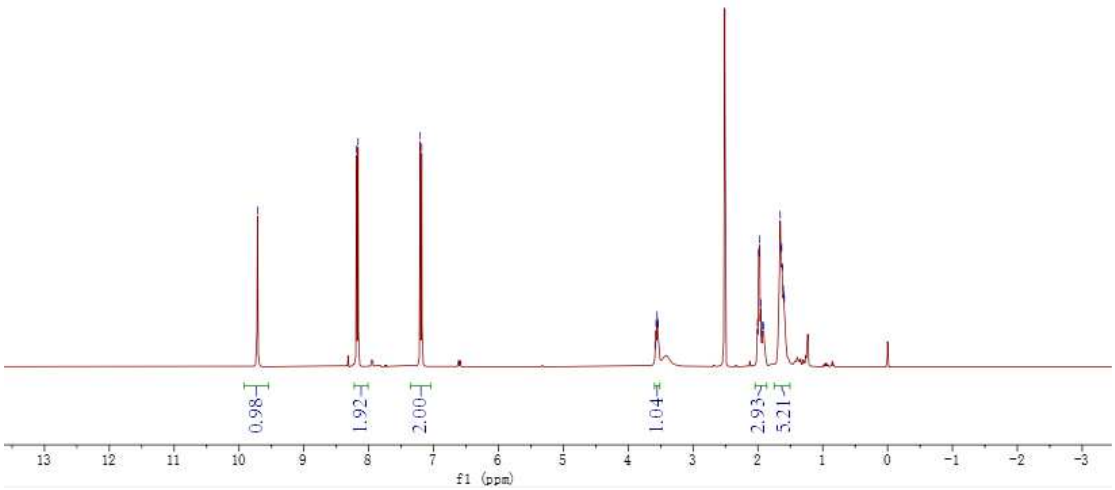


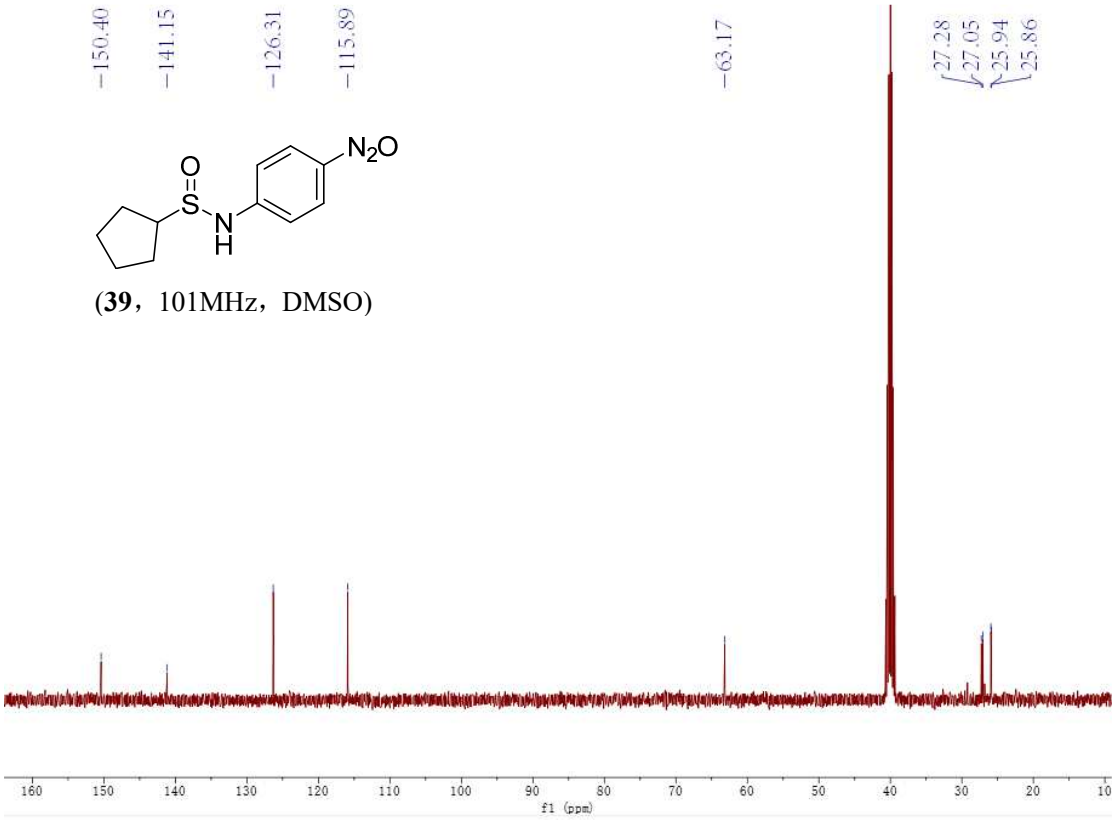
(**38**，376MHz，$CDCl_3$)



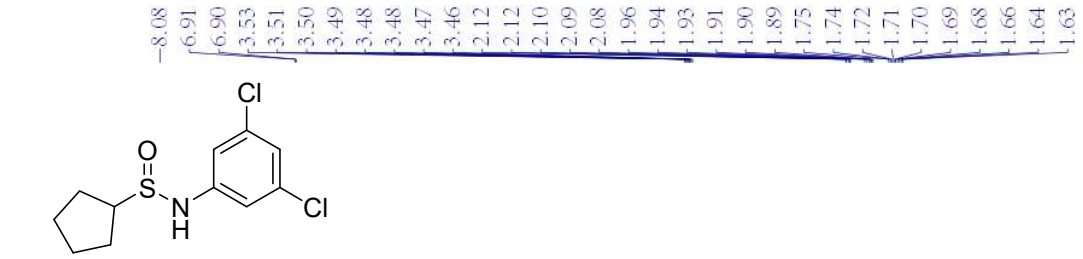


(**39**，400MHz，DMSO)

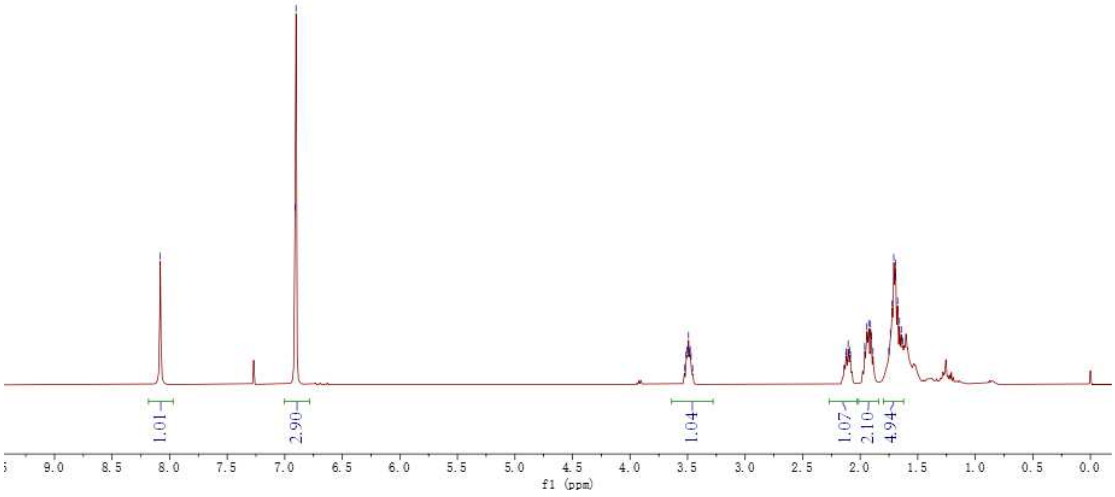


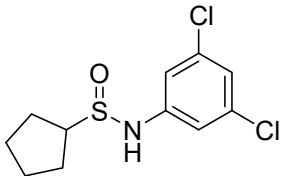


(**39**，101MHz，DMSO)

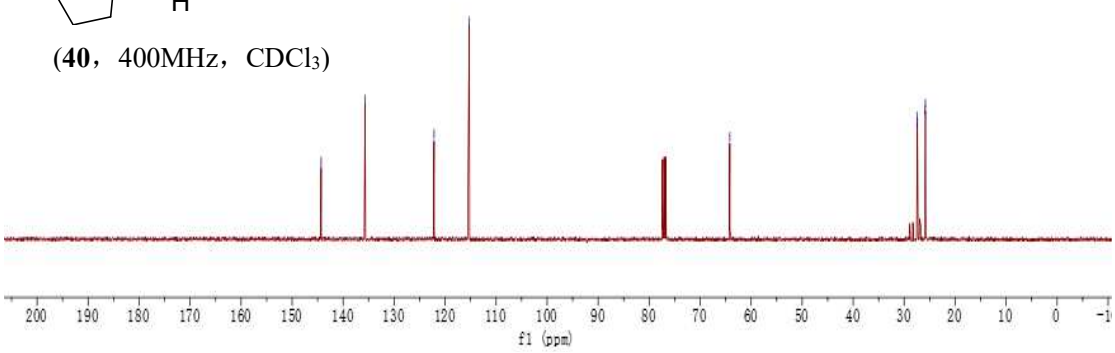


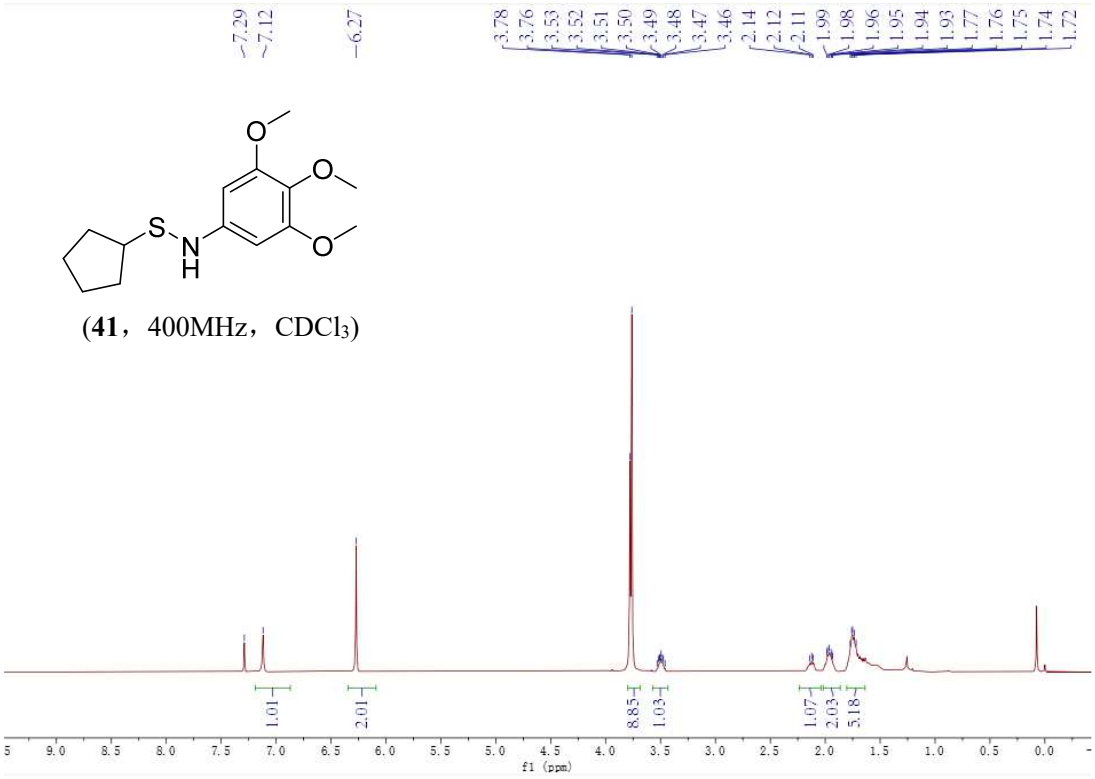
(**40**，400MHz，$CDCl_3$)



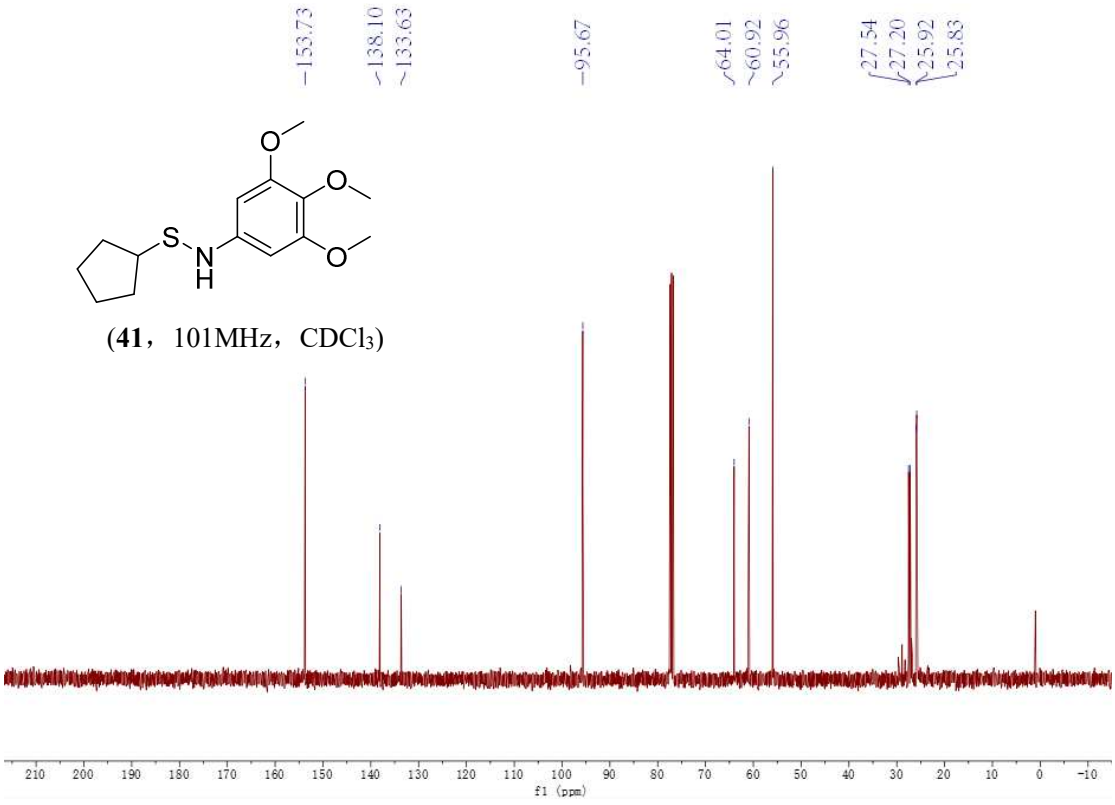


(**40**，400MHz，$CDCl_3$)

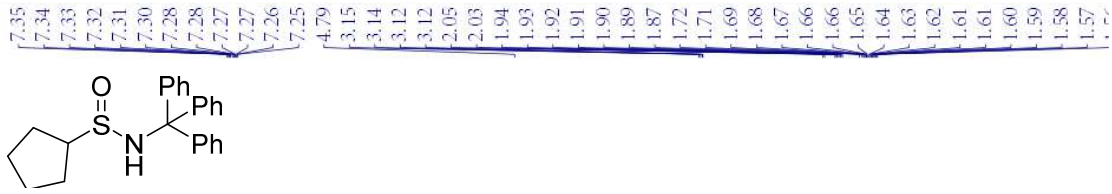




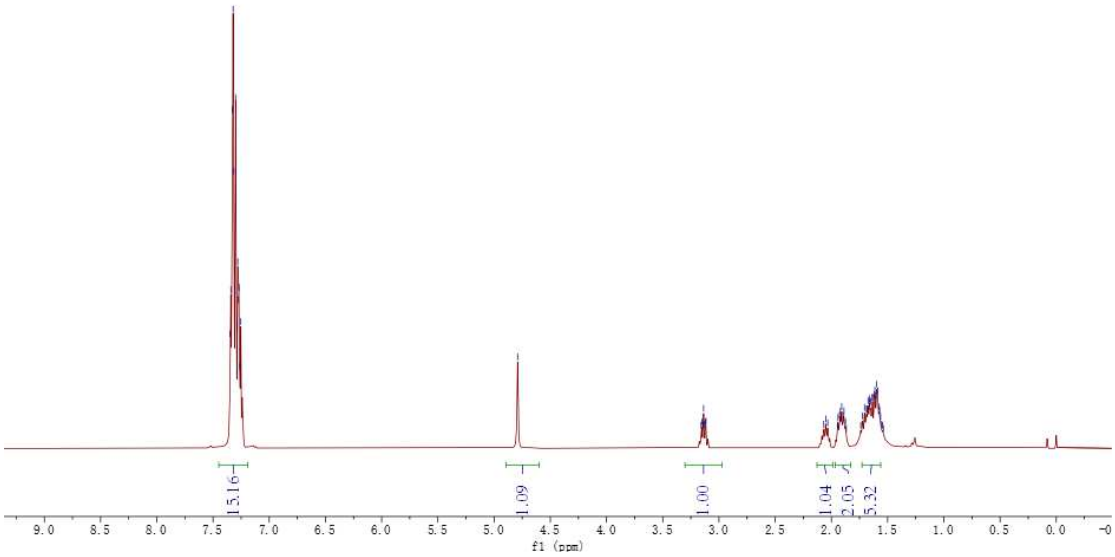
(**41**，400MHz，$CDCl_3$)

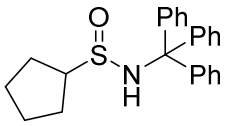


(**41**，101MHz，$CDCl_3$)

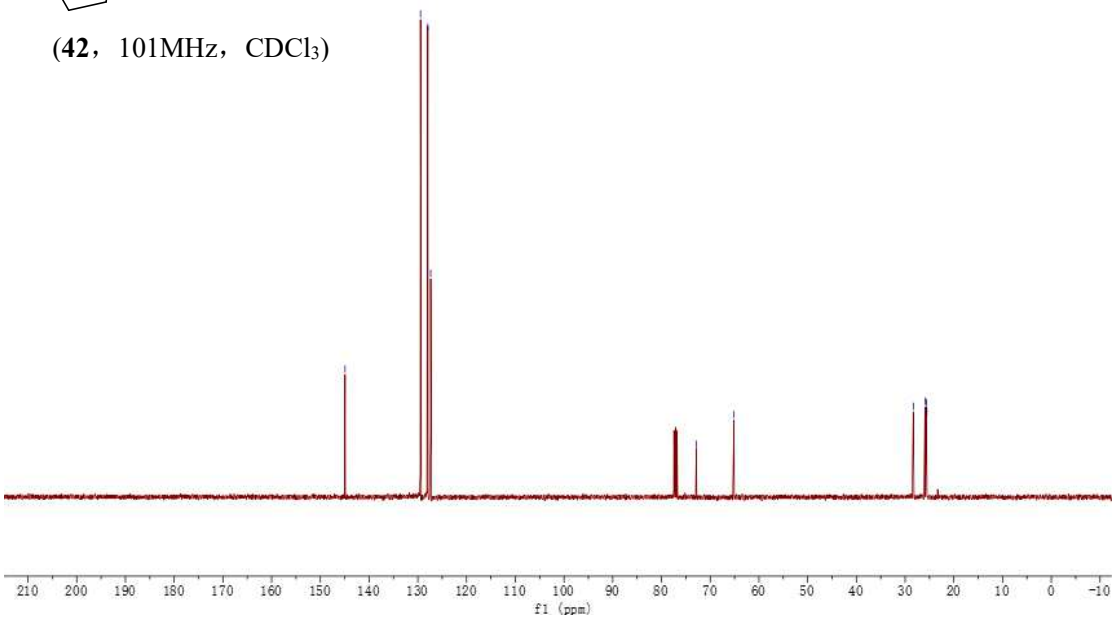


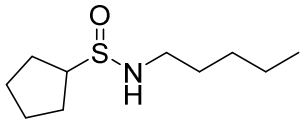
(**42**，400MHz，$CDCl_3$)



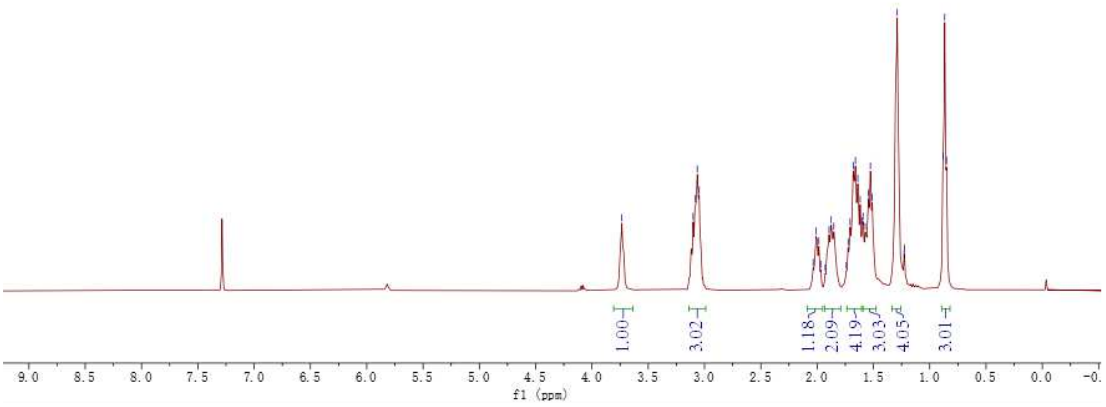


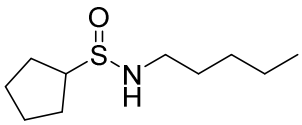
(**42**，101MHz，$CDCl_3$)



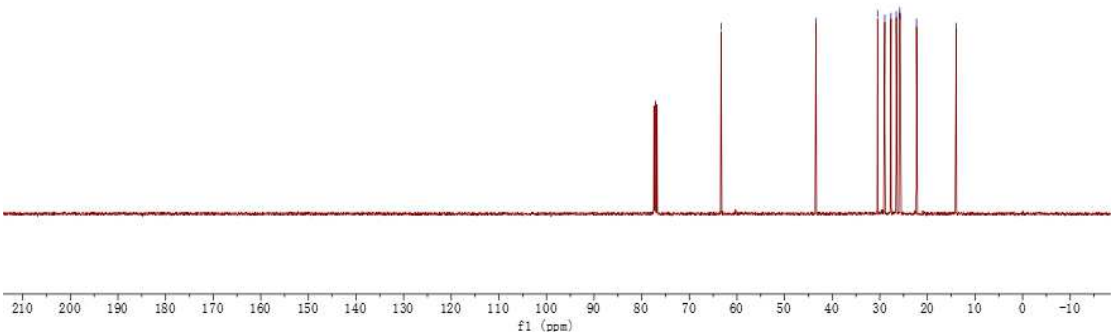


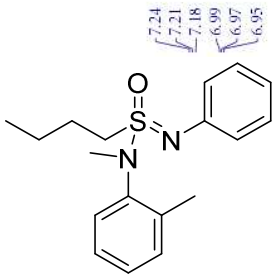
(**43**，400MHz，$CDCl_3$)



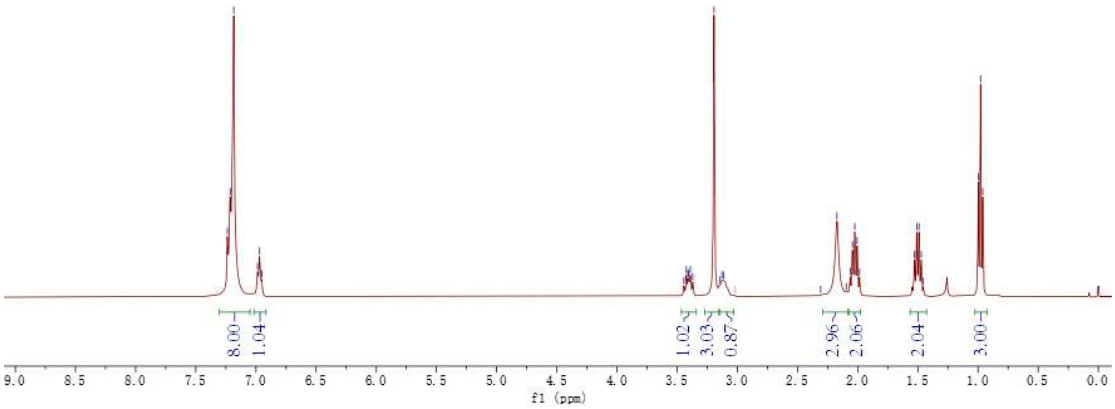


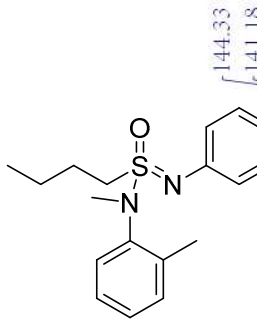
(**43**，101 MHz，$CDCl_3$)



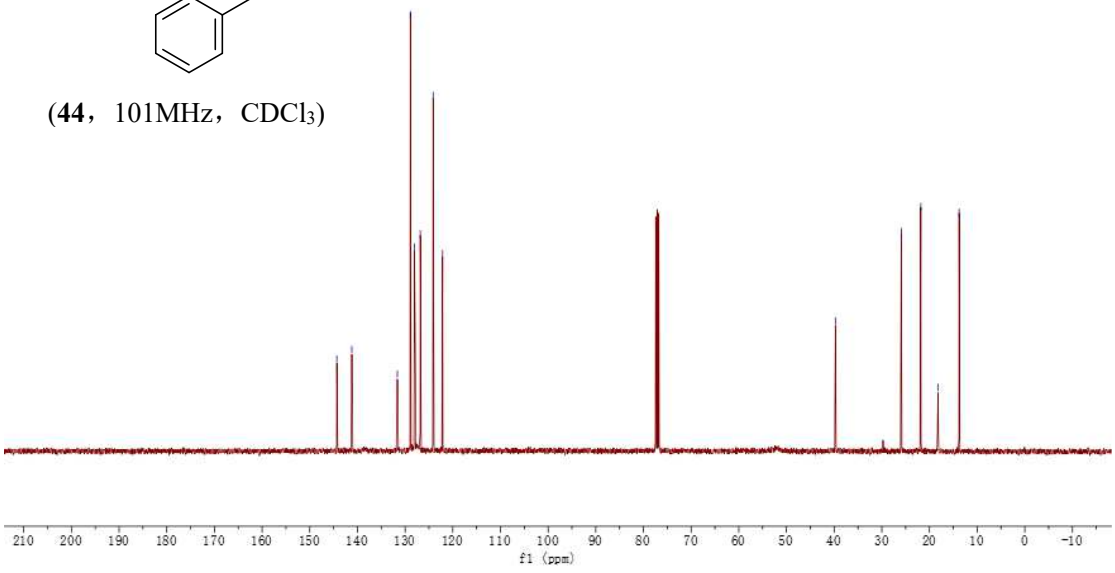


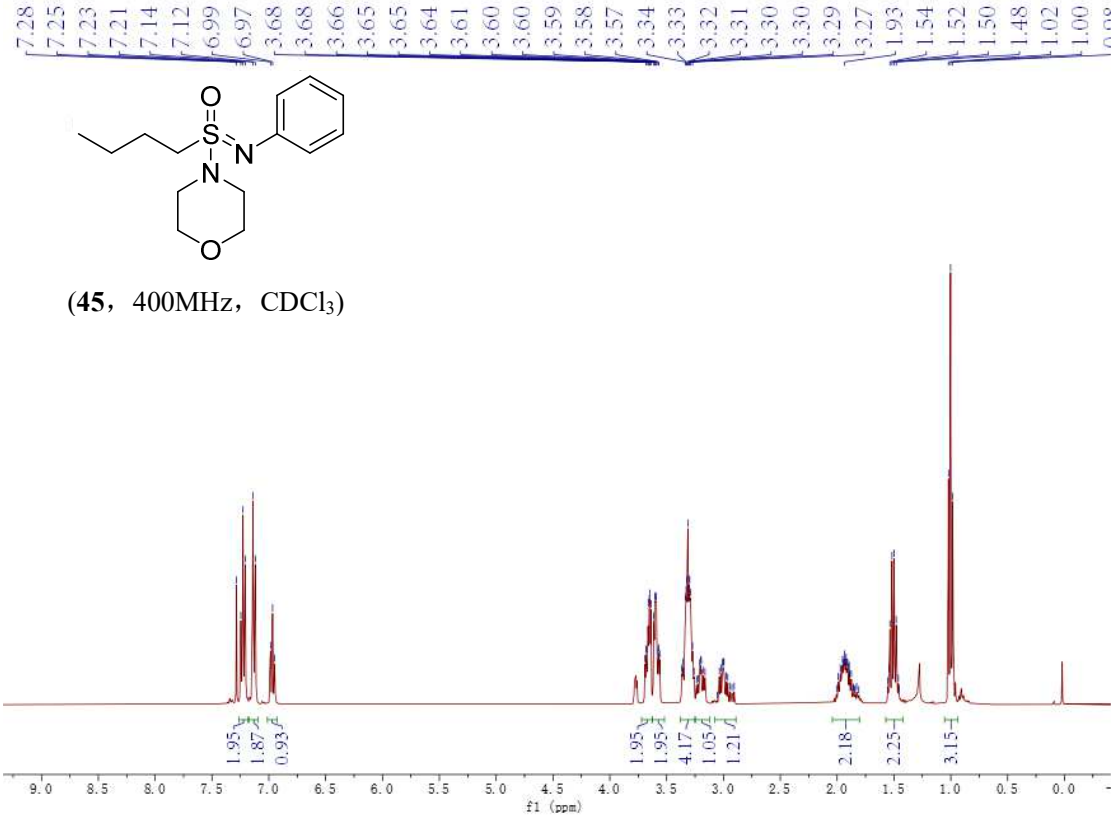
(**44**，400MHz，$CDCl_3$)





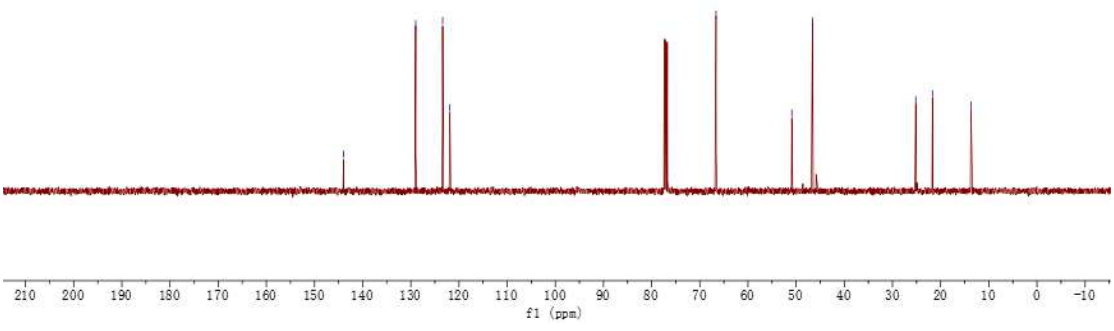
(**44**，101MHz，$CDCl_3$)

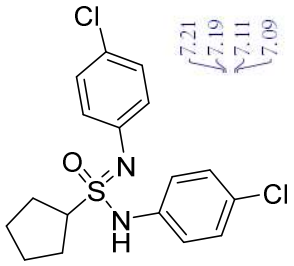




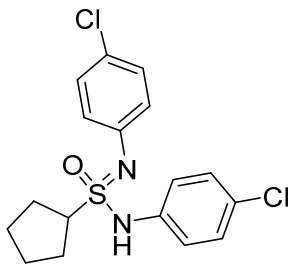
(**45**，400MHz，$CDCl_3$)

(**45**，101MHz，$CDCl_3$)

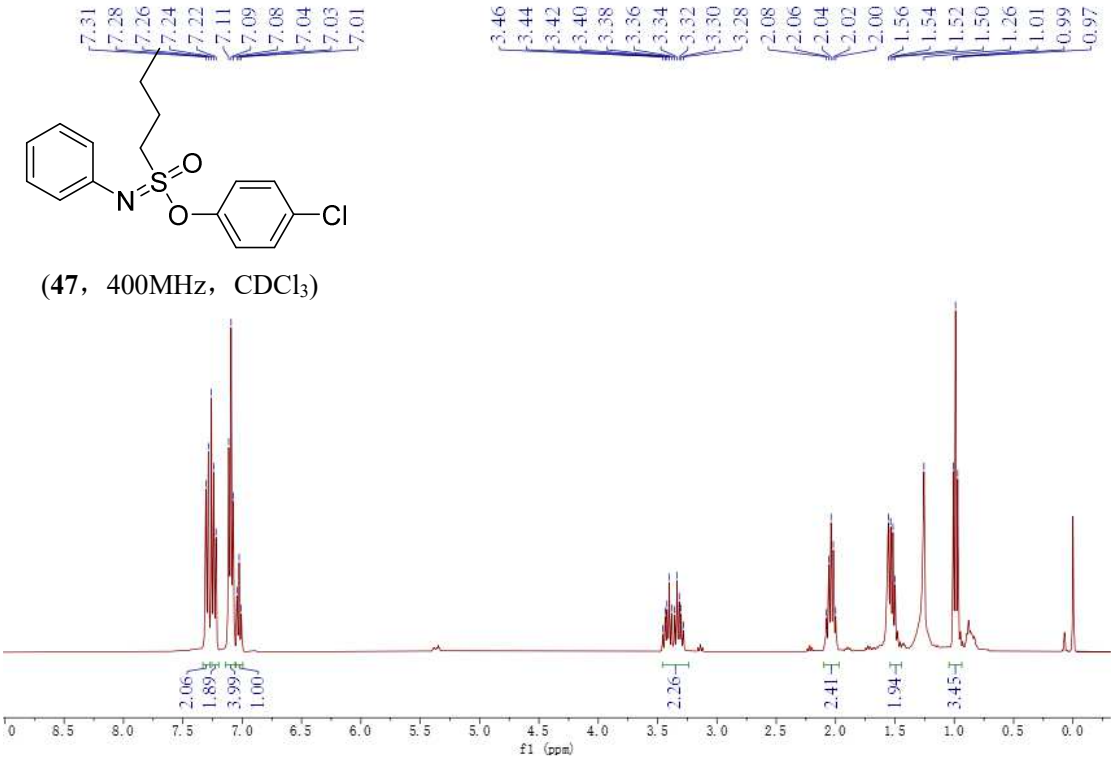




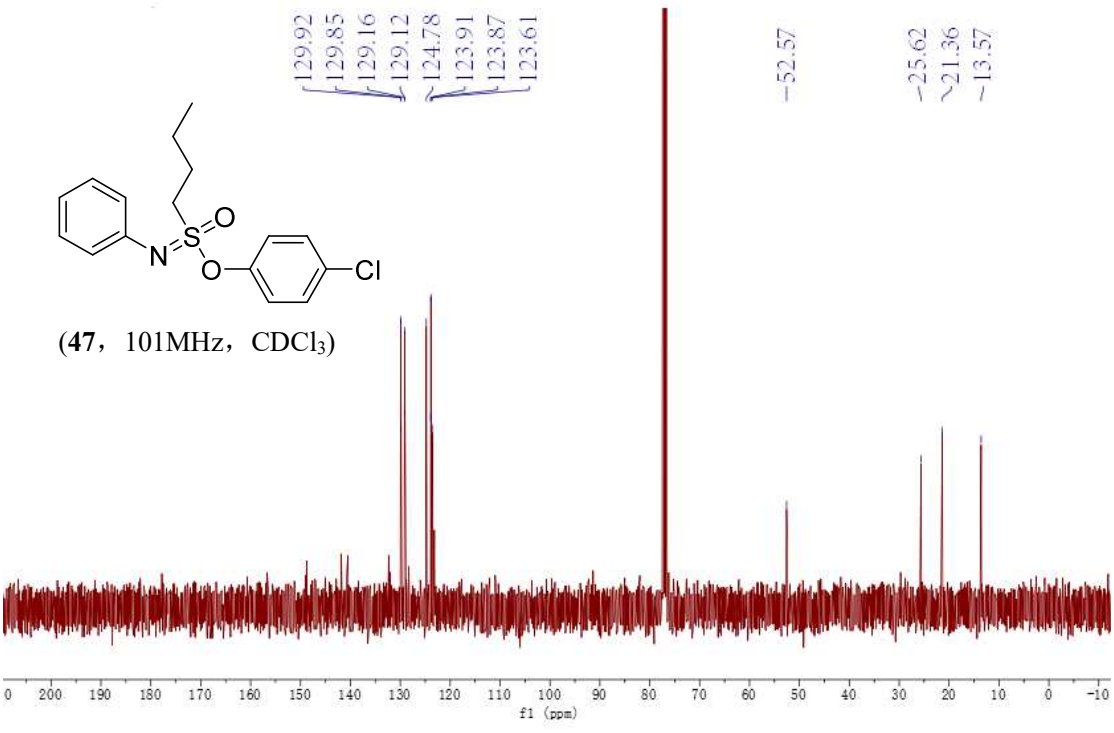
(**46**，400MHz，$CDCl_3$)



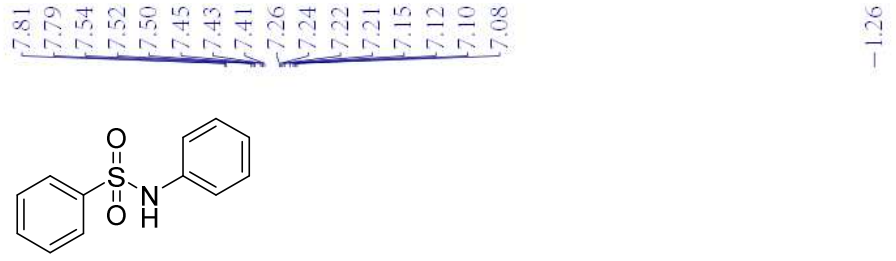
(**46**，101MHz，$CDCl_3$)



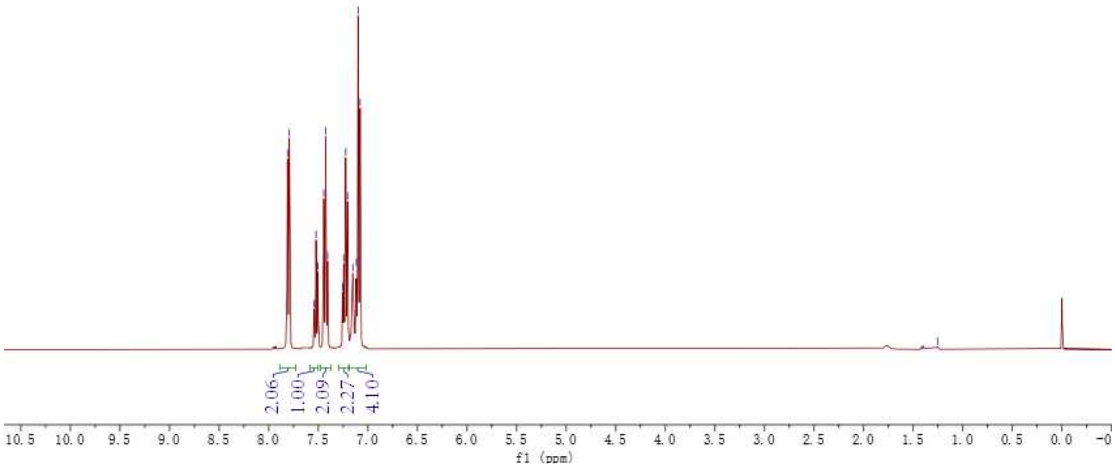
(**47**，400MHz，$CDCl_3$)

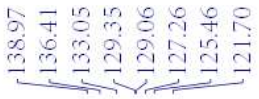


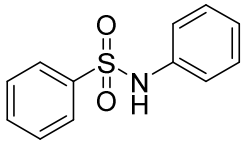
(**47**，101MHz，$CDCl_3$)



(**48**，400MHz，$CDCl_3$)







(**48**，101MHz，$CDCl_3$)