

## Supporting Information

### Access to 1-aryl-pyrazolin-5-ones via photoinduced chemoselective cyclization of N-methacrylo aldehyde hydrazones

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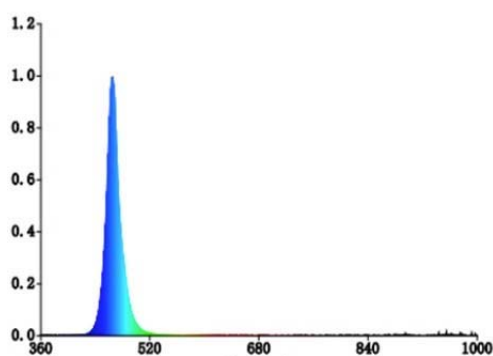
## 1. General Considerations

**General Information:** Unless otherwise noted, all chemicals were purchased and used without further purification.  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra were recorded at ambient temperature on a 400 MHz NMR spectrometer (101 MHz for  $^{13}\text{C}$ ). NMR experiments are reported in  $\delta$  units, parts per million (ppm). The coupling constants  $J$  are given in Hz. Column chromatography was performed using EM Silica gel 60 (300-400 mesh). HRMS were recorded on a TOF LC/MS equipped with electrospray ionization (ESI) probe operating in positive ion mode. Emission intensities were recorded using a FS5 spectrophotometer. Cyclic voltammetry was performed on the CHI-660E electrochemical workstation (Shanghai Chenhua Instrument Co., Ltd., China).



**Figure S1.** Photoreactor used in this work (20 W blue LEDs,  $\lambda_{\text{max}} = 465$  nm).

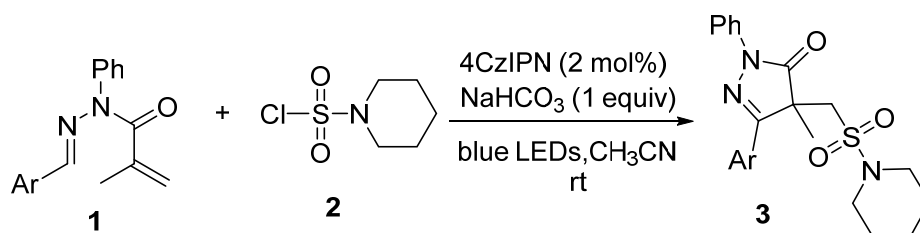
The photochemical reaction was carried out under visible light irradiation by a 20W 460-465 nm blue LED at room temperature. This blue LED was purchased from taobao (link: [https://shop358870690.taobao.com/?spm=pc\\_detail.27183998.202202.3.6d807dd6mNb2jH](https://shop358870690.taobao.com/?spm=pc_detail.27183998.202202.3.6d807dd6mNb2jH)). The blue LED's energy peak wavelength is 465 nm, the peak width at half-height is 18.6 nm, and irradiance@20 W is 26.92 mW/cm<sup>2</sup>. The reaction vessel is a borosilicate glass tube. The distance between the tube and lamp is about 1.5 cm, and no filter is applied.



**Figure S2.** The spectral distribution of 20 W 460-465 nm blue LED

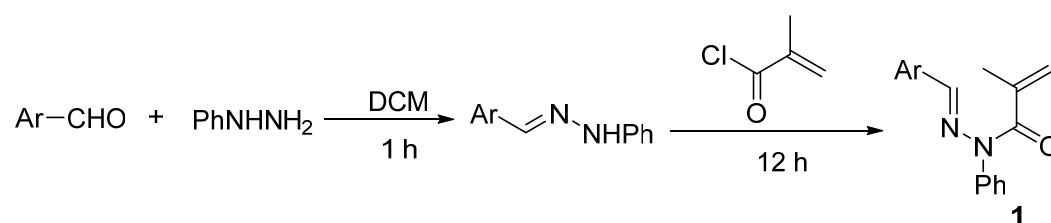
## 2. General Synthetic Procedures

### General procedure for the synthesis of compounds 3



To an over-dried Schlenk tube equipped with a magnetic stir bar, (*E*)-*N'*-benzylidene-*N*-phenylmethacrylohydrazide **1** (0.10 mmol, 1.0 equiv), piperidine-1-sulfonyl chloride **2** (0.2 mmol, 2 equiv), 4CzIPN (2 mol%, 1.6 mg) and CH<sub>3</sub>CN (1.0 mL) was added. The tube was evacuated and backfilled with nitrogen (repeated for five times). The mixture was stirred at room temperature under 460-465 nm blue LEDs for 16 hours. Then, the solvent was evaporated under reduced pressure, and the residue was purified by silica gel flash column chromatography (eluent: petroleum ether/ethyl acetate) to obtain the product **3**.

### General procedure for the synthesis of compounds 1



**Step 1:** To a round-bottom flask, 10 mmol hydrazine, 10 mmol aldehyde and 20 mL of dry dichloromethane was added and stirred at room temperature for 1 hour until dissolved. Afterwards, the solvent was removed under vacuum. The precipitation was washed with petroleum ether and dried in vacuum to afford corresponding *N*-substituted hydrazones, which was directly used in the next step without further purification.

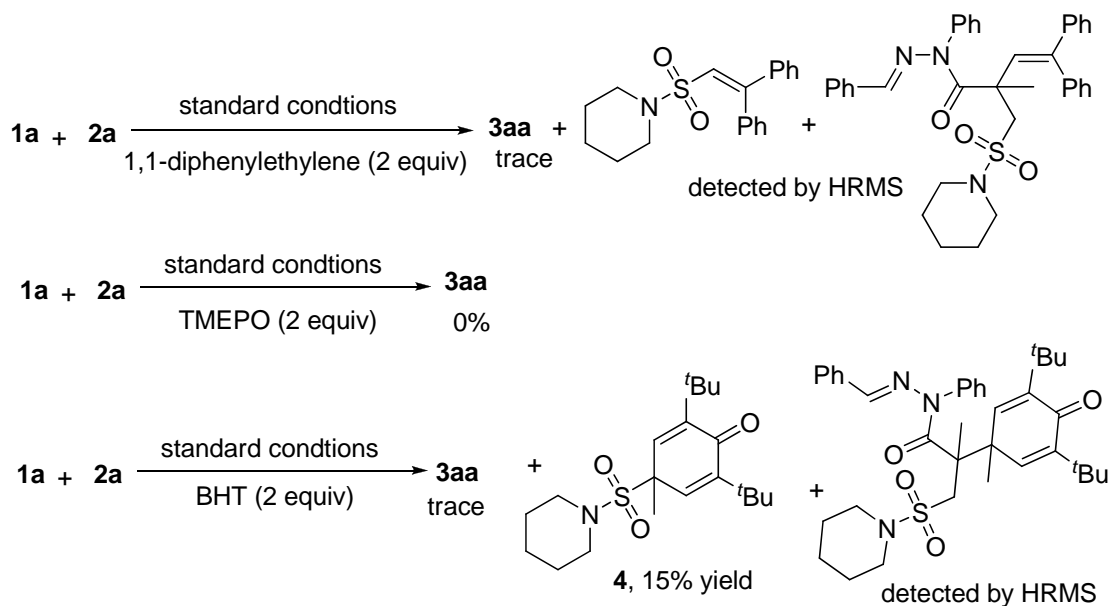
**Step 2:** A mixture of *N*-substituted hydrazones (5 mmol) and triethylamine (1.5 equiv) in DCM (10 mL) was added to a round-bottom flask and cooled to 0 °C. Methacryloyl chloride (1.2 equiv) was added dropwise at 0 °C. The resulting solution was allowed to warm to room temperature and continuously stirred for 12 h till the completion of the reaction (monitored by TLC). Afterwards, the solvent was evaporated and the crude mixture was purified via silica gel column chromatography (eluent: petroleum ether/ethyl acetate) to afford **1**.

### 1 mmol Scale Reaction for 3aa

To an over-dried Schlenk bottle equipped with a magnetic stir bar, (*E*)-*N'*-benzylidene-*N*-phenylmethacrylohydrazide **1a** (1 mmol), piperidine-1-sulfonyl chloride **2a** (2 mmol, 2 equiv), 4CzIPN (2 mol%, 16 mg) and CH<sub>3</sub>CN (10 mL) was added. The bottle was evacuated and backfilled with nitrogen (repeated for five times). The mixture was stirred at room temperature under 460-465 nm blue LEDs for 16 hours. Then, the solvent was evaporated under reduced pressure, and the residue was purified by silica gel flash column chromatography (eluent: petroleum ether/ethyl acetate) to obtain the product **3aa** (295 mg, 72% yield).

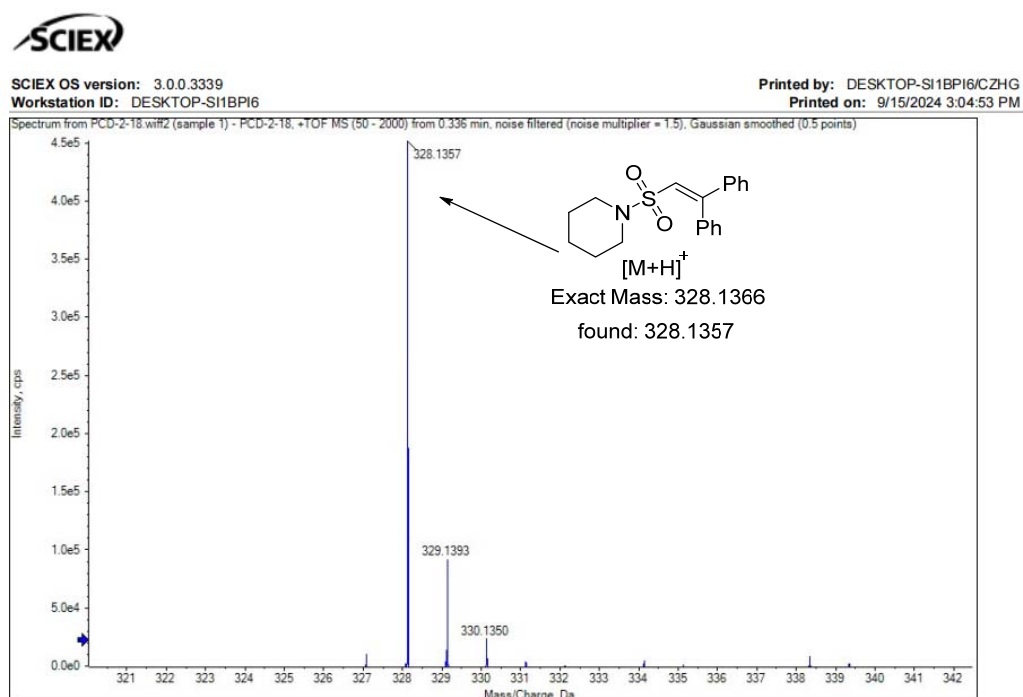
### 3. Mechanism Studies

#### 3.1 Radical inhibiting experiments



Under standard conditions, radical inhibitor BHT (0.2 mmol, 88.1 mg, 2 equiv) TEMPO (0.2 mmol, 31.2 mg, 2 equiv) or 1,1-diphenylethylene (0.4 mmol, 72.0 mg, 2 equiv) was added, the mixture was stirred at room temperature under 460-465 nm blue LEDs for 16 hours. Then, the mixture was detected by HRMS. Compound **4** was isolated in 15% yield via silica gel column chromatography (eluent: petroleum ether/ethyl acetate).

**2,6-Di-tert-butyl-4-methyl-4-(piperidin-1-ylsulfonyl)cyclohexa-2,5-dienone 4:**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  6.63 (s, 2H), 3.10 (s, 4H), 1.70 (s, 3H), 1.49 (s, 6H), 1.26 (s, 18H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  185.6, 150.6, 136.1, 66.4, 49.1, 35.3, 29.3, 26.4, 23.6, 22.4. HRMS (ESI)  $m/z$  calcd for  $\text{C}_{20}\text{H}_{33}\text{NNaO}_3\text{S}^+$   $[\text{M}+\text{Na}]^+$  390.2073, found 390.2077.



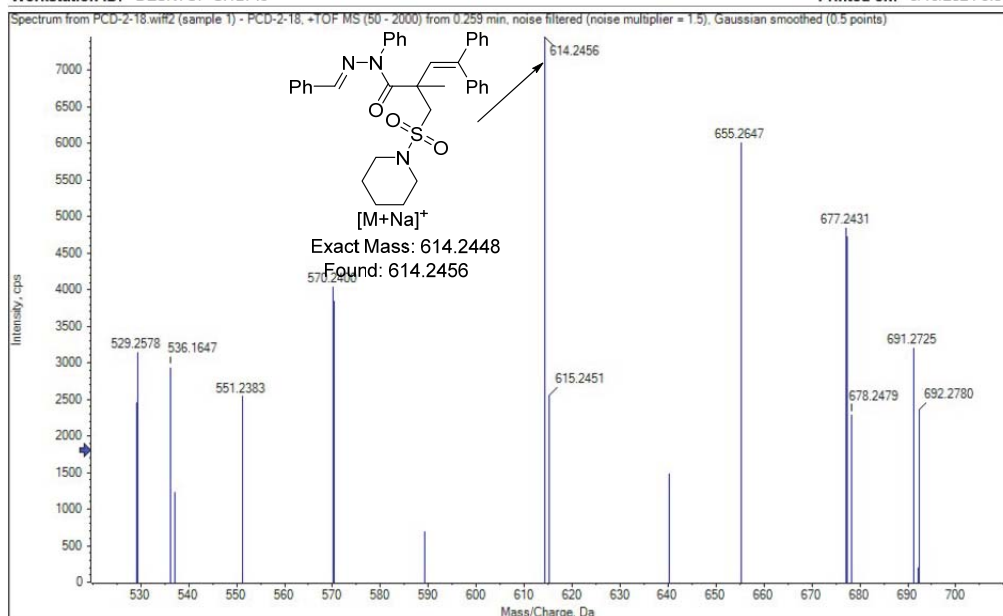
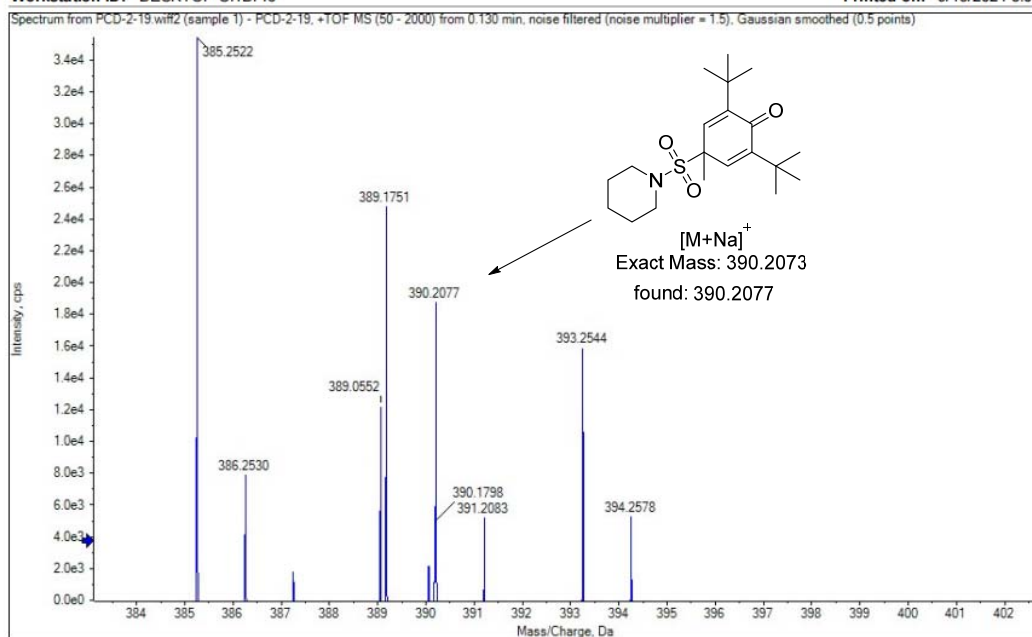
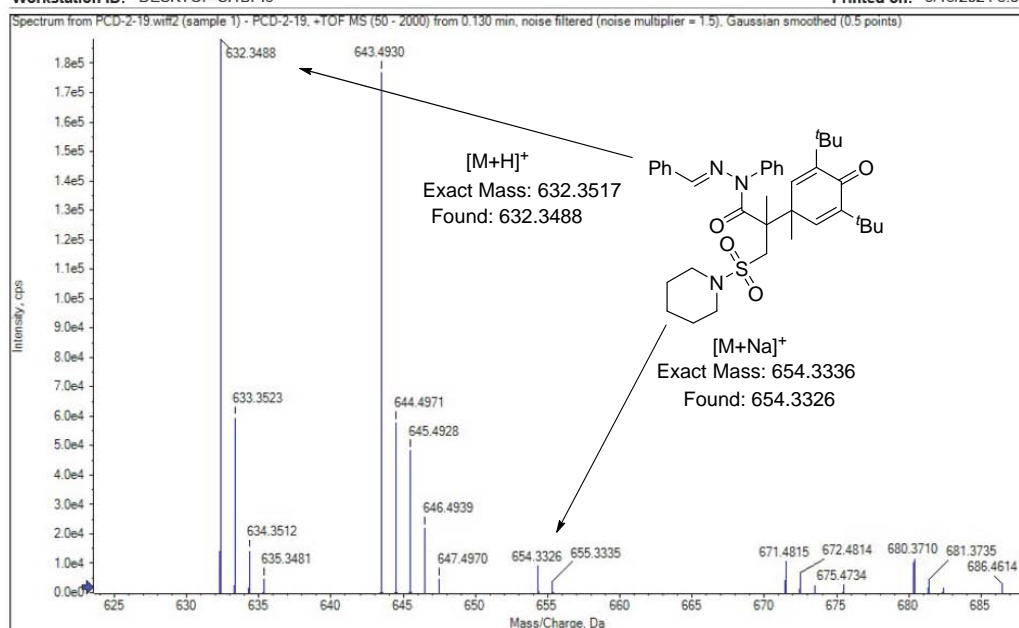
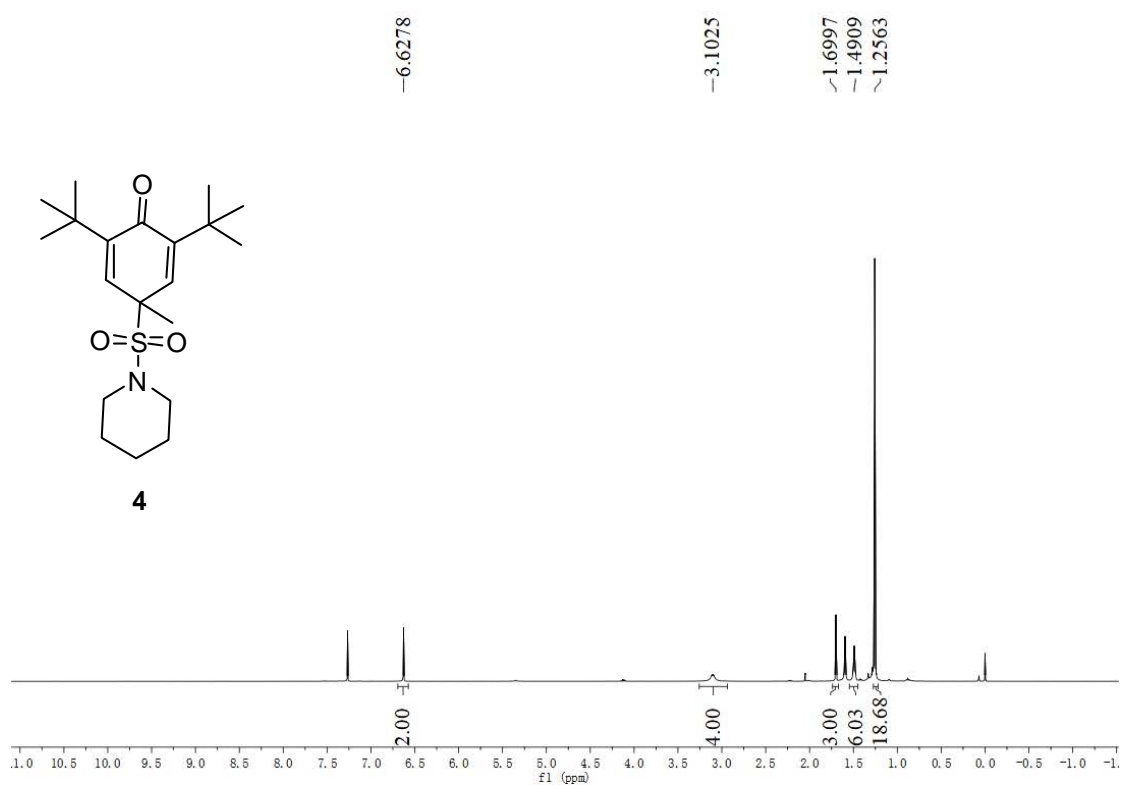


Figure S3. The HRMS spectra for the radical-trapping experiment with 1,1-diphenylethylene.





**Figure S4.** The HRMS spectra for the radical-trapping experiment with BHT.



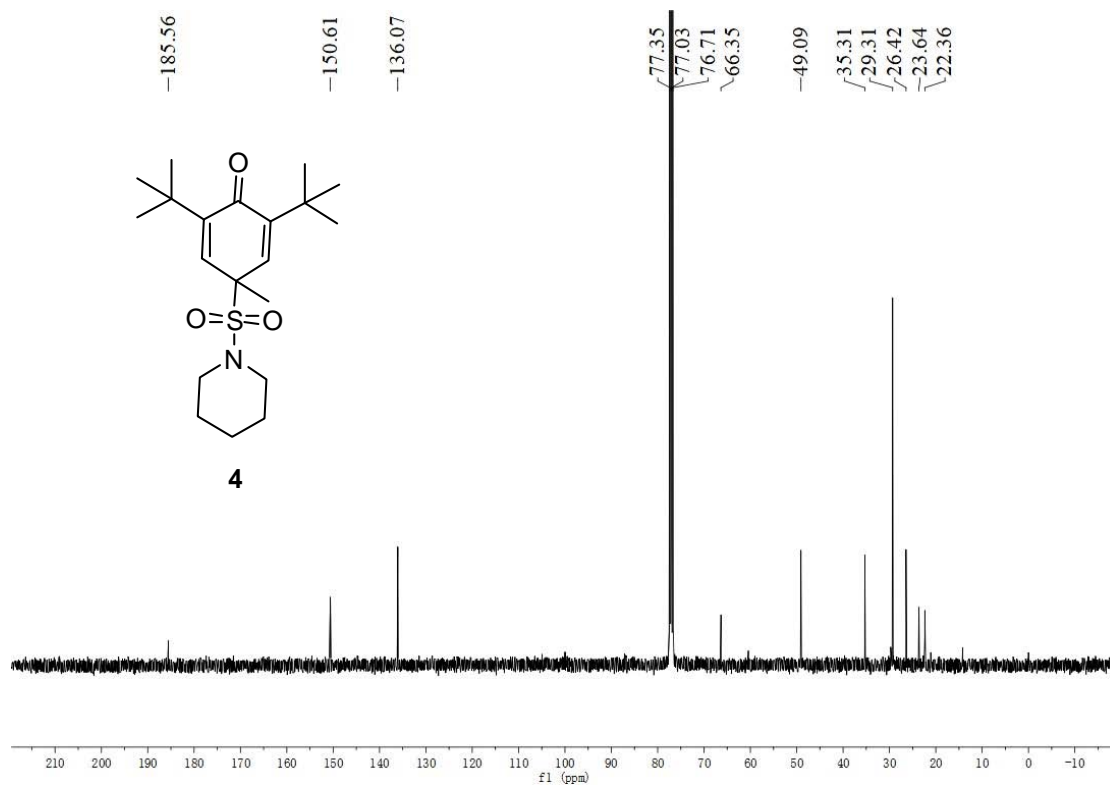


Figure S5.  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra of compound **4**.

### 3.2 Fluorescence quenching experiments

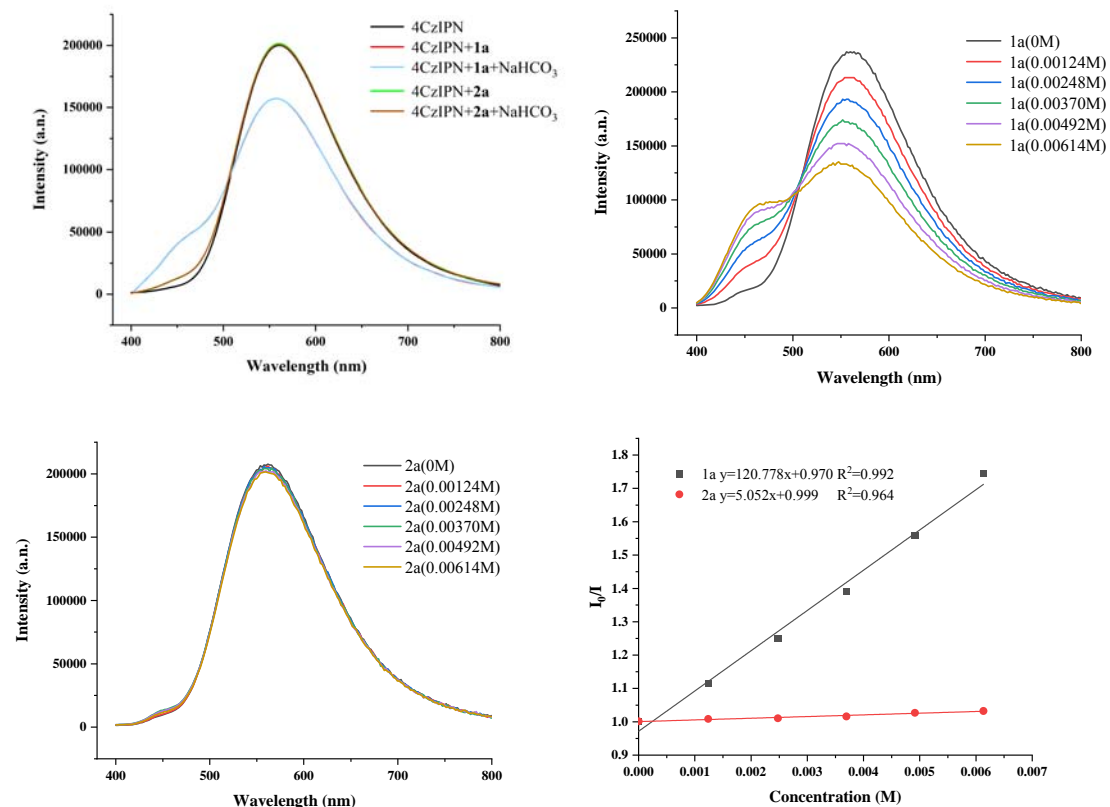


Figure S6. Luminescence quenching of 4CzIPN by **1a** or **2a** and the Stern-Volmer plots.

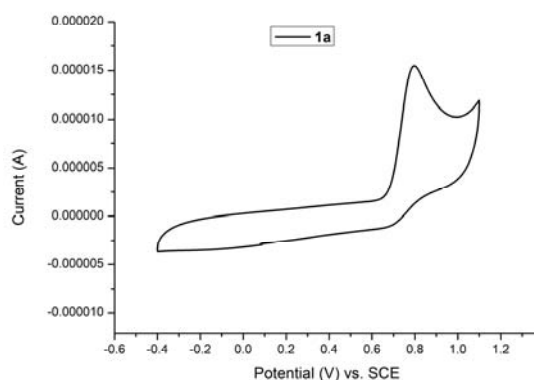
### 3.3 Cyclic voltammetry study

Cyclic voltammetric investigations were performed on the ChenhuaCHI400C electrochemical workstation with the conventional three-electrode system. The measurements were conducted in 0.1 M tetrabutylammonium hexafluorophosphate (TBAPF<sub>6</sub>) in CH<sub>3</sub>CN. The solutions were kept under positive pressure of nitrogen. Cyclic voltammetry (CV) with the following settings: Scan Rates = 0.1 V/s, Sweep Segments = 10, Sample Interval = 0.001 V, Quiet Time = 2 sec. CV recording is based on the traditional IUPAC (positive anode current and negative cathode current).

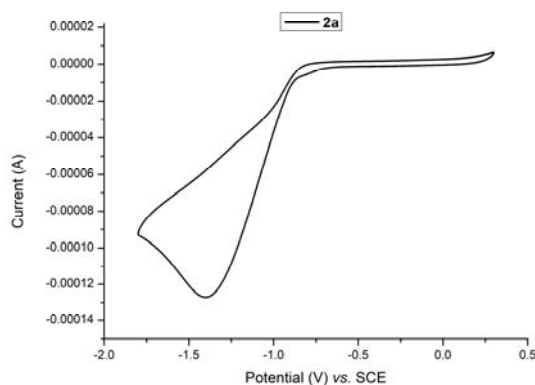
**Supporting electrolyte:** TBAPF<sub>6</sub> was purchased from Energy Chemical and used without further purification. The concentration of electrolyte is 0.1 M.

**Solvent:** Anhydrous CH<sub>3</sub>CN was purchased from Energy Chemical and exhausted via a nitrogen blast for 30 min before using.

**Electrodes:** The working electrode is a glassy carbon electrode (Φ3 mm, 7x10<sup>-6</sup> cm<sup>2</sup>). It was first polished with sandpaper in steps (3000 mesh–2000 mesh–1000 mesh); then with 1.0 μm, 0.3 μm, and 0.05 μm alumina powder until the surface of the electrode is mirror-like, then, the electrodes are washed with distilled water and acetone before air drying. Saturated calomel electrode (SCE) was used as the reference electrode. Pt column (Φ1 mm x 5 mm) was used as the counter electrode.



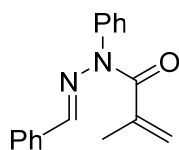
**Figure S7.** The CV experiment of **1a** ( $1.0 \times 10^{-3}$  M) and NBu<sub>4</sub>PF<sub>6</sub> (0.1 M) in degassed CH<sub>3</sub>CN, plotting based on IUPAC.  $E_{1/2}^{\text{ox}} = +0.73$  V vs SCE for **1a**.



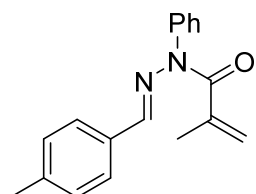
**Figure S8.** The CV experiment of **2a** ( $1.0 \times 10^{-3}$  M) and NBu<sub>4</sub>PF<sub>6</sub> (0.1 M) in degassed CH<sub>3</sub>CN, plotting based on IUPAC.  $E_{1/2}^{\text{red}} = -0.99$  V vs SCE for **2a**.



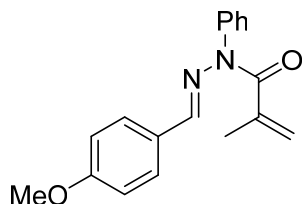
#### 4. Characterization Data for the Substrates and Products



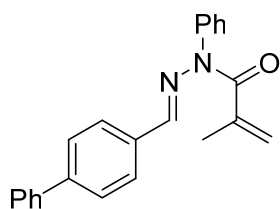
**(E)-N'-(benzylidene)-N-phenylmethacrylohydrazide (1a)**, yellow solid,  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.59-7.54 (m, 4H), 7.51-7.46 (m, 1H), 7.36-7.33 (m, 3H), 7.29-7.22 (m, 3H), 5.52 (s, 1H), 5.41 (t,  $J = 1.4$  Hz, 1H), 2.21 (s, 3H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  172.7, 142.2, 141.7, 135.9, 134.3, 130.3, 129.9, 129.4, 129.2, 128.7, 127.3, 118.9, 20.7. HRMS (ESI)  $m/z$  calcd for  $\text{C}_{17}\text{H}_{17}\text{N}_2\text{O}^+$   $[\text{M}+\text{H}]^+$  265.1335, found 265.1332.



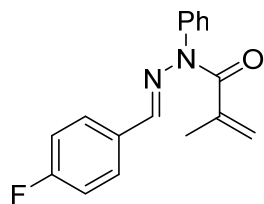
**(E)-N'-(4-methylbenzylidene)-N-phenylmethacrylohydrazide (1b)**, yellow solid,  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.58-7.54 (m, 2H), 7.50-7.46 (m, 1H), 7.44 (d,  $J = 8.1$  Hz, 2H), 7.27-7.21 (m, 3H), 7.16 (d,  $J = 8.0$  Hz, 2H), 5.51 (t,  $J = 0.9$  Hz, 1H), 5.40 (d,  $J = 1.4$  Hz, 1H), 2.35 (s, 3H), 2.20 (t,  $J = 1.2$  Hz, 3H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  172.3, 142.4, 141.8, 140.2, 136.0, 131.6, 130.2, 129.5, 129.3, 129.2, 129.2, 127.3, 118.9, 21.5, 20.8, 18.8. HRMS (ESI)  $m/z$  calcd for  $\text{C}_{18}\text{H}_{19}\text{N}_2\text{O}^+$   $[\text{M}+\text{H}]^+$  278.1492, found 278.1503.



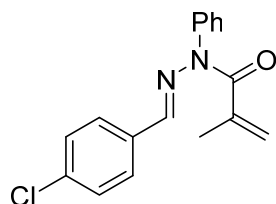
**(E)-N'-(4-methoxybenzylidene)-N-phenylmethacrylohydrazide (1c)**, yellow oil,  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.58-7.54 (m, 2H), 7.52-7.46 (m, 3H), 7.26-7.22 (m, 3H), 6.90-6.86 (m, 2H), 5.51 (t,  $J = 1.0$  Hz, 1H), 5.39 (t,  $J = 1.5$  Hz, 1H), 3.81 (s, 3H), 2.21 (t,  $J = 1.2$  Hz, 3H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  172.5, 161.1, 142.2, 141.9, 136.1, 130.2, 129.31, 129.27, 128.8, 127.0, 118.7, 114.2, 55.4, 20.8. HRMS (ESI)  $m/z$  calcd for  $\text{C}_{18}\text{H}_{19}\text{N}_2\text{O}_2^+$   $[\text{M}+\text{H}]^+$  295.1441, found 295.1440.



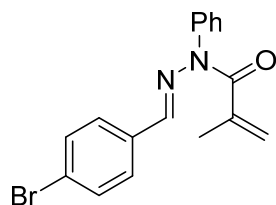
**(E)-N'-([1,1'-biphenyl]-4-ylmethylene)-N-phenylmethacrylohydrazide (1d)**, yellow solid,  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.57-7.50 (m, 9H), 7.44-7.36 (m, 3H), 7.32-7.29 (m, 1H), 7.20-7.17 (m, 2H), 5.47 (t,  $J = 1.0$  Hz, 1H), 5.37 (t,  $J = 1.5$  Hz, 1H), 2.17 (t,  $J = 1.2$  Hz, 3H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  172.7, 142.6, 141.8, 141.7, 140.3, 136.0, 133.3, 130.3, 129.4, 129.2, 129.1, 128.9, 127.8, 127.4, 127.0, 119.0, 20.8. HRMS (ESI)  $m/z$  calcd for  $\text{C}_{23}\text{H}_{21}\text{N}_2\text{O}^+$   $[\text{M}+\text{H}]^+$  341.1648, found 341.1655.



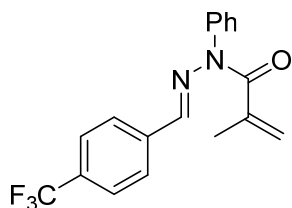
**(E)-N'-(4-fluorobenzylidene)-N-phenylmethacrylohydrazide (1e)**, yellow solid,  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.60-7.55 (m, 2H), 7.52-7.48 (m, 1H), 7.33-7.30 (m, 2H), 7.26-7.21 (m, 4H), 7.06-7.01 (m, 1H), 5.51 (t,  $J = 1.0$  Hz, 1H), 5.43 (t,  $J = 1.4$  Hz, 1H), 2.20 (t,  $J = 1.3$  Hz, 3H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  172.1, 163.0 (d,  $J_{\text{C-F}} = 247.5$  Hz), 141.4, 140.6 (d,  $J_{\text{C-F}} = 3.0$  Hz), 136.6 (d,  $J_{\text{C-F}} = 7.1$  Hz), 135.8, 130.3 (d,  $J_{\text{C-F}} = 4.0$  Hz), 130.2, 129.6, 129.1, 123.5 (d,  $J_{\text{C-F}} = 2.8$  Hz), 119.1, 116.8 (d,  $J_{\text{C-F}} = 21.7$  Hz), 113.3 (d,  $J_{\text{C-F}} = 22.7$  Hz), 20.7. HRMS (ESI)  $m/z$  calcd for  $\text{C}_{17}\text{H}_{16}\text{FN}_2\text{O}^+ [\text{M}+\text{H}]^+$  283.1241, found 283.1237.



**(E)-N'-(3-chlorobenzylidene)-N-phenylmethacrylohydrazide (1f)**, yellow solid,  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.58 (t,  $J = 7.4$  Hz, 2H), 7.53-7.48 (m, 2H), 7.41 (d,  $J = 7.0$  Hz, 1H), 7.32-7.28 (m, 2H), 7.22 (t,  $J = 3.2$  Hz, 3H), 5.52 (s, 1H), 5.44 (s, 1H), 2.20 (s, 3H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  172.6, 141.3, 140.5, 136.1, 135.8, 134.8, 130.3, 129.9, 129.8, 129.6, 129.1, 127.1, 125.4, 119.3, 20.7. HRMS (ESI)  $m/z$  calcd for  $\text{C}_{17}\text{H}_{16}\text{ClN}_2\text{O}^+ [\text{M}+\text{H}]^+$  299.0946, found 299.0941.

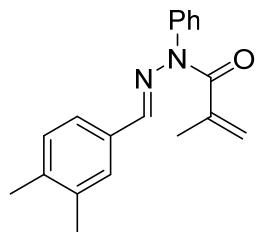


**(E)-N'-(2-bromobenzylidene)-N-phenylmethacrylohydrazide (1g)**, yellow solid,  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.96-7.93 (m, 1H), 7.71 (s, 1H), 7.62-7.58 (m, 2H), 7.53-7.49 (m, 2H), 7.34 (t,  $J = 7.5$  Hz, 1H), 7.27 (t,  $J = 0.8$  Hz, 1H), 7.25-7.18 (m, 2H), 5.52 (t,  $J = 1.0$  Hz, 1H), 5.43 (t,  $J = 1.4$  Hz, 1H), 2.21 (t,  $J = 1.2$  Hz, 3H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  172.1, 141.6, 141.5, 135.8, 133.2, 133.1, 130.4, 129.6, 129.0, 127.7, 127.4, 124.6, 119.1, 20.7. HRMS (ESI)  $m/z$  calcd for  $\text{C}_{17}\text{H}_{16}\text{BrN}_2\text{O}^+ [\text{M}+\text{H}]^+$  343.0441, found 343.0450.

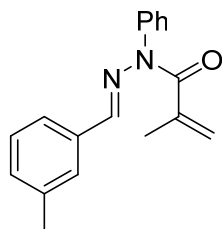


**(E)-N-phenyl-N'-(4-(trifluoromethyl)benzylidene)methacrylohydrazide (1h)**, yellow oil,  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.57-7.54 (m, 2H), 7.50-7.46 (m, 1H), 7.31-7.27 (m, 2H), 7.24-7.19 (m, 4H), 7.04-6.99 (m, 1H), 5.50 (t,  $J = 0.9$  Hz, 1H), 5.41 (t,  $J = 1.4$  Hz, 1H), 2.19 (t,  $J = 1.2$  Hz, 3H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  172.7, 141.3, 140.1, 137.7, 135.7, 131.7 (q,  $J_{\text{C-F}} = 32.4$  Hz),

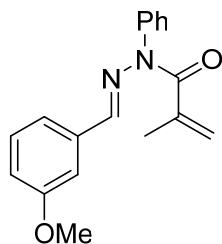
130.6, 130.4, 130.0, 129.1, 127.4, 125.7 (q,  $J_{C-F} = 3.81$  Hz), 123.9 (q,  $J_{C-F} = 273.2$  Hz), 119.3, 20.7. HRMS (ESI)  $m/z$  calcd for  $C_{18}H_{16}F_3N_2O^+$   $[M+H]^+$  333.1209, found 333.1208.



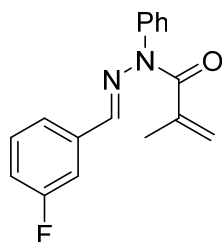
**(E)-N'-(3,4-dimethylbenzylidene)-N-phenylmethacrylohydrazide (1i)**, yellow solid,  $^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta$  7.59-7.54 (m, 2H), 7.50-7.46 (m, 1H), 7.30 (d,  $J = 7.0$  Hz, 2H), 7.25-7.21 (m, 3H), 7.12 (d,  $J = 8.0$  Hz, 1H), 5.52 (t,  $J = 1.0$  Hz, 1H), 5.41 (t,  $J = 1.4$  Hz, 1H), 2.26 (d,  $J = 4.3$  Hz, 6H), 2.21 (t,  $J = 1.3$  Hz, 3H);  $^{13}C$  NMR (101 MHz,  $CDCl_3$ )  $\delta$  172.6, 142.8, 141.8, 138.9, 137.0, 136.1, 131.9, 130.2, 130.0, 129.30, 129.26, 128.5, 124.8, 119.0, 20.8, 19.84, 19.77. HRMS (ESI)  $m/z$  calcd for  $C_{19}H_{21}N_2O^+$   $[M+H]^+$  293.1648, found 293.1640.



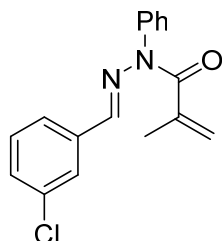
**(E)-N'-(3-methylbenzylidene)-N-phenylmethacrylohydrazide (1j)**, yellow solid,  $^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta$  7.58-7.54 (m, 2H), 7.50-7.46 (m, 1H), 7.36 (t,  $J = 7.6$  Hz, 2H), 7.26-7.21 (m, 4H), 7.16 (d,  $J = 7.5$  Hz, 1H), 5.52 (s, 1H), 5.41 (t,  $J = 1.4$  Hz, 1H), 2.34 (s, 3H), 2.21 (s, 3H);  $^{13}C$  NMR (101 MHz,  $CDCl_3$ )  $\delta$  172.6, 142.6, 141.7, 138.4, 136.1, 134.2, 130.8, 130.2, 129.4, 129.2, 128.6, 128.0, 124.4, 119.0, 21.4, 20.8. HRMS (ESI)  $m/z$  calcd for  $C_{18}H_{19}N_2O^+$   $[M+H]^+$  278.1492, found 278.1494.



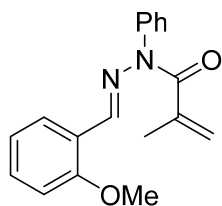
**(E)-N'-(3-methoxybenzylidene)-N-phenylmethacrylohydrazide (1k)**, yellow oil,  $^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta$  7.60-7.55 (m, 2H), 7.52-7.47 (m, 1H), 7.27 (d,  $J = 8.3$  Hz, 1H), 7.25-7.22 (m, 3H), 7.16-7.15 (m, 1H), 7.08 (d,  $J = 7.6$  Hz, 1H), 6.92-6.89 (m, 1H), 5.52 (t,  $J = 1.0$  Hz, 1H), 5.42-5.40 (m, 1H), 3.81 (s, 3H), 2.21 (t,  $J = 1.1$  Hz, 3H);  $^{13}C$  NMR (101 MHz,  $CDCl_3$ )  $\delta$  172.7, 159.9, 142.0, 141.6, 135.9, 135.7, 130.3, 129.7, 129.4, 129.2, 120.3, 119.0, 116.0, 111.6, 55.3, 20.7. HRMS (ESI)  $m/z$  calcd for  $C_{18}H_{19}N_2O_2^+$   $[M+H]^+$  295.1441, found 295.1443.



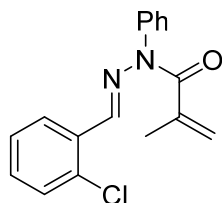
**(E)-N'-(3-fluorobenzylidene)-N-phenylmethacrylohydrazide (1l)**, yellow oil,  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.58-7.55 (m, 2H), 7.51-7.46 (m, 1H), 7.33-7.28 (m, 2H), 7.25-7.21 (m, 4H), 7.04-6.99 (m, 1H), 5.52 (t,  $J = 0.9$  Hz, 1H), 5.43 (t,  $J = 1.4$  Hz, 1H), 2.20 (t,  $J = 1.0$  Hz, 3H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  172.7, 163.0 (d,  $J_{\text{C-F}} = 247.1$  Hz), 141.1, 140.6 (d,  $J_{\text{C-F}} = 3.0$  Hz), 136.7 (d,  $J_{\text{C-F}} = 7.9$  Hz), 135.8, 130.4, 130.3, 129.6, 129.1, 123.5 (d,  $J_{\text{C-F}} = 2.7$  Hz), 119.1, 116.8 (d,  $J_{\text{C-F}} = 21.7$  Hz), 113.3 (d,  $J_{\text{C-F}} = 22.7$  Hz), 20.7. HRMS (ESI)  $m/z$  calcd for  $\text{C}_{17}\text{H}_{16}\text{FN}_2\text{O}^+$   $[\text{M}+\text{H}]^+$  283.1241, found 283.123.



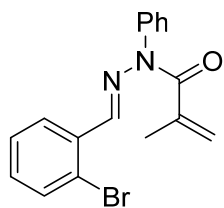
**(E)-N'-(3-chlorobenzylidene)-N-phenylmethacrylohydrazide (1m)**, yellow solid,  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.58 (t,  $J = 7.4$  Hz, 2H), 7.53-7.48 (m, 2H), 7.41 (d,  $J = 7.0$  Hz, 1H), 7.32-7.28 (m, 2H), 7.22 (t,  $J = 3.2$  Hz, 3H), 5.52 (s, 1H), 5.44 (s, 1H), 2.20 (s, 3H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  172.6, 141.3, 140.5, 136.1, 135.8, 134.8, 130.3, 129.9, 129.8, 129.6, 129.1, 127.1, 125.4, 119.3, 20.7. HRMS (ESI)  $m/z$  calcd for  $\text{C}_{17}\text{H}_{16}\text{ClN}_2\text{O}^+$   $[\text{M}+\text{H}]^+$  299.0946, found 299.0948.



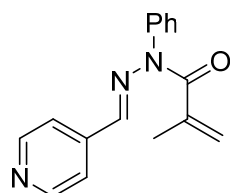
**(E)-N'-(2-methoxybenzylidene)-N-phenylmethacrylohydrazide (1n)**, yellow oil,  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.59-7.55 (m, 2H), 7.52-7.47 (m, 1H), 7.26-7.22 (m, 4H), 7.16-7.15 (m, 1H), 7.08 (d,  $J = 7.6$  Hz, 1H), 6.92-6.89 (m, 1H), 5.52 (t,  $J = 1.0$  Hz, 1H), 5.42-5.41 (m, 1H), 3.81 (s, 3H), 2.21 (t,  $J = 1.1$  Hz, 3H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  172.7, 159.9, 142.0, 141.6, 135.9, 135.7, 130.3, 129.7, 129.4, 129.2, 120.3, 119.0, 116.0, 111.6, 55.3, 20.7. HRMS (ESI)  $m/z$  calcd for  $\text{C}_{18}\text{H}_{19}\text{N}_2\text{O}_2^+$   $[\text{M}+\text{H}]^+$  295.1441, found 295.1441.



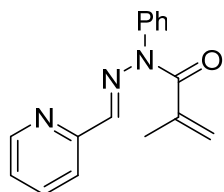
**(E)-N'-(2-chlorobenzylidene)-N-phenylmethacrylohydrazide (1o)**, yellow solid,  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.97-7.94 (m, 1H), 7.73 (s, 1H), 7.60-7.56 (m, 2H), 7.52-7.48 (m, 1H), 7.31-7.27 (m, 3H), 7.25-7.22 (m, 2H), 5.51 (t,  $J = 1.0$  Hz, 1H), 5.41 (t,  $J = 1.4$  Hz, 1H), 2.20 (t,  $J = 1.4$  Hz, 3H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  172.7, 141.5, 139.0, 135.8, 134.4, 131.8, 130.7, 130.4, 129.8, 129.58, 128.96, 127.09, 127.07, 119.0, 20.7. HRMS (ESI)  $m/z$  calcd for  $\text{C}_{17}\text{H}_{16}\text{ClN}_2\text{O}^+$   $[\text{M}+\text{H}]^+$  299.0946, found 299.0945.



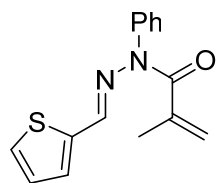
**(E)-N'-(2-bromobenzylidene)-N-phenylmethacrylohydrazide (1p)**, yellow solid,  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.96-7.93 (m, 1H), 7.71 (s, 1H), 7.62-7.58 (m, 2H), 7.53-7.49 (m, 2H), 7.34 (t,  $J$  = 7.5 Hz, 1H), 7.27 (t,  $J$  = 0.8 Hz, 1H), 7.25-7.18 (m, 2H), 5.52 (t,  $J$  = 1.0 Hz, 1H), 5.43 (t,  $J$  = 1.4 Hz, 1H), 2.21 (t,  $J$  = 1.2 Hz, 3H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  172.1, 141.6, 141.5, 135.8, 133.2, 133.1, 130.4, 129.6, 129.0, 127.7, 127.4, 124.6, 119.1, 20.7. HRMS (ESI)  $m/z$  calcd for  $\text{C}_{17}\text{H}_{16}\text{BrN}_2\text{O}^+$   $[\text{M}+\text{H}]^+$  343.0441, found 343.0450.



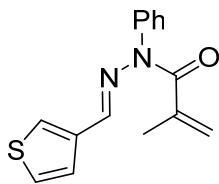
**(E)-N-phenyl-N'-(pyridin-4-ylmethylene)methacrylohydrazide (1q)**, yellow oil,  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.57-8.56 (m, 2H), 7.57-7.53 (m, 2H), 7.50-7.46 (m, 1H), 7.38-7.37 (m, 2H), 7.20-7.17 (m, 3H), 5.50 (t,  $J$  = 0.9 Hz, 1H), 5.43 (t,  $J$  = 1.4 Hz, 1H), 2.17 (t,  $J$  = 1.2 Hz, 3H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  172.7, 150.3, 141.6, 141.0, 139.0, 135.4, 130.4, 130.0, 128.9, 121.1, 119.6, 20.7. HRMS (ESI)  $m/z$  calcd for  $\text{C}_{16}\text{H}_{16}\text{N}_2\text{O}^+$   $[\text{M}+\text{H}]^+$  266.1288, found 266.1289.



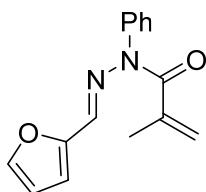
**(E)-N-phenyl-N'-(pyridin-2-ylmethylene)methacrylohydrazide (1r)**, yellow solid,  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.49 (d,  $J$  = 4.8 Hz, 1H), 7.95 (d,  $J$  = 8.0 Hz, 1H), 7.73-7.69 (m, 1H), 7.56-7.52 (m, 2H), 7.48-7.44 (m, 1H), 7.42 (s, 1H), 7.25-7.18 (m, 3H), 5.52 (s, 1H), 5.42 (t,  $J$  = 1.4 Hz, 1H), 2.19 (s, 3H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  172.7, 153.6, 149.3, 142.7, 141.3, 136.6, 135.5, 130.4, 129.6, 129.0, 124.0, 120.1, 119.3, 20.7. HRMS (ESI)  $m/z$  calcd for  $\text{C}_{16}\text{H}_{16}\text{N}_2\text{O}^+$   $[\text{M}+\text{H}]^+$  266.1288, found 266.1288.



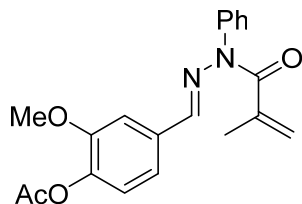
**(E)-N-phenyl-N'-(thiophen-2-ylmethylene)methacrylohydrazide (1s)**, yellow solid,  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.58 (t,  $J$  = 7.3 Hz, 2H), 7.50-7.44 (m, 2H), 7.33-7.30 (m, 3H), 7.22 (d,  $J$  = 7.4 Hz, 2H), 5.50 (s, 1H), 5.38 (d,  $J$  = 1.3 Hz, 1H), 2.19 (s, 3H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  172.5, 141.7, 137.6, 137.5, 135.9, 130.3, 129.4, 129.2, 126.8, 126.7, 125.1, 118.9, 20.7. HRMS (ESI)  $m/z$  calcd for  $\text{C}_{15}\text{H}_{15}\text{N}_2\text{OS}^+$   $[\text{M}+\text{H}]^+$  271.0900, found 271.0889.



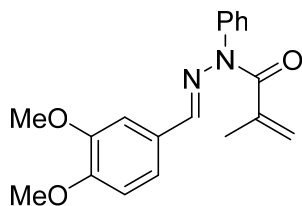
**(E)-N-phenyl-N'-(thiophen-3-ylmethylene)methacrylohydrazide (1t)**, yellow solid,  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.56 (t,  $J = 7.3$  Hz, 2H), 7.50-7.44 (m, 2H), 7.33-7.30 (m, 3H), 7.22 (d,  $J = 7.5$  Hz, 2H), 5.50 (s, 1H), 5.38 (d,  $J = 1.2$  Hz, 1H), 2.19 (s, 3H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  172.5, 141.7, 137.6, 137.5, 135.9, 130.3, 129.4, 129.2, 126.8, 126.7, 125.1, 119.0, 20.7. HRMS (ESI)  $m/z$  calcd for  $\text{C}_{15}\text{H}_{15}\text{N}_2\text{OS}^+$   $[\text{M}+\text{H}]^+$  271.0900, found 271.0899.



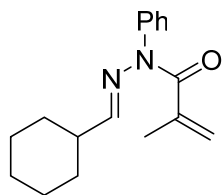
**(E)-N'-(furan-2-ylmethylene)-N-phenylmethacrylohydrazide (1u)**, yellow solid,  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.56 (t,  $J = 7.3$  Hz, 2H), 7.48 (t,  $J = 7.5$  Hz, 2H), 7.21 (d,  $J = 7.4$  Hz, 2H), 7.17 (s, 1H), 6.57 (d,  $J = 3.4$  Hz, 1H), 6.43-6.42 (m, 1H), 5.57 (s, 1H), 5.42 (s, 1H), 2.18 (s, 3H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  172.2, 149.8, 144.3, 141.3, 135.8, 132.4, 130.4, 129.5, 129.2, 120.0, 112.6, 111.8, 20.7. HRMS (ESI)  $m/z$  calcd for  $\text{C}_{15}\text{H}_{15}\text{N}_2\text{O}_2^+$   $[\text{M}+\text{H}]^+$  255.1128, found 255.1125.



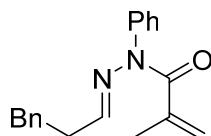
**(E)-4-((2-methacryloyl-2-phenylhydrazineylidene)methyl)-2-methoxyphenyl acetate (1v)**, yellow oil,  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.60-7.55 (m, 2H), 7.52-7.47 (m, 1H), 7.28 (d,  $J = 1.6$  Hz, 1H), 7.24-7.21 (m, 3H), 7.06-6.99 (m, 2H), 5.51 (t,  $J = 1.0$  Hz, 1H), 5.40 (t,  $J = 1.4$  Hz, 1H), 3.84 (s, 3H), 2.31 (s, 3H), 2.19 (t,  $J = 1.2$  Hz, 3H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  172.5, 168.9, 151.4, 141.6, 141.3, 141.1, 135.9, 133.3, 130.3, 129.5, 129.1, 123.0, 120.7, 119.1, 110.0, 55.8, 20.70, 20.68. HRMS (ESI)  $m/z$  calcd for  $\text{C}_{19}\text{H}_{21}\text{N}_2\text{O}_3^+$   $[\text{M}+\text{H}]^+$  352.1496, found 352.1491.



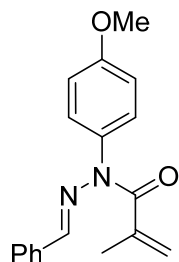
**(E)-N'-(3,4-dimethoxybenzylidene)-N-phenylmethacrylohydrazide (1w)**, yellow solid,  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.57 (t,  $J = 7.2$  Hz, 2H), 7.49 (t,  $J = 7.3$  Hz, 1H), 7.26-7.23 (m, 4H), 6.98 (d,  $J = 8.3$  Hz, 1H), 6.82 (d,  $J = 8.3$  Hz, 1H), 5.51 (s, 1H), 5.39 (s, 1H), 3.90 (d,  $J = 5.8$  Hz, 6H), 2.20 (s, 3H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  177.7, 172.5, 150.8, 149.3, 142.6, 141.6, 136.1, 130.2, 129.4, 129.2, 127.3, 121.9, 119.0, 110.7, 108.4, 56.0, 55.8, 51.6, 27.2, 20.7. HRMS (ESI)  $m/z$  calcd for  $\text{C}_{19}\text{H}_{21}\text{N}_2\text{O}_3^+$   $[\text{M}+\text{H}]^+$  325.1547, found 325.1556.



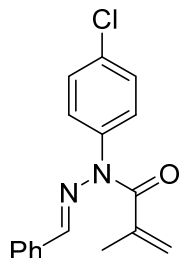
**(E)-N'-(cyclohexylmethylene)-N-phenylmethacrylohydrazide (1x)**, yellow solid,  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.50 (t,  $J = 7.6$  Hz, 2H), 7.41 (t,  $J = 7.2$  Hz, 1H), 7.26 (s, 1H), 7.12 (d,  $J = 7.7$  Hz, 2H), 5.40 (s, 1H), 5.28 (s, 1H), 2.25-2.19 (m, 1H), 2.09 (s, 3H), 1.76-1.69 (m, 4H), 1.33-1.10 (m, 6H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  172.2, 151.0, 142.0, 136.5, 130.0, 129.2, 128.9, 118.4, 40.8, 30.0, 25.9, 25.5, 20.6. HRMS (ESI)  $m/z$  calcd for  $\text{C}_{17}\text{H}_{23}\text{N}_2\text{O}^+$   $[\text{M}+\text{H}]^+$  299.0946, found 299.0945.



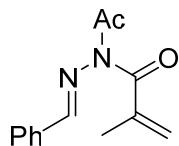
**(E)-N-phenyl-N'-(3-phenylpropylidene)methacrylohydrazide (1y)**, yellow solid,  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.52-7.47 (m, 2H), 7.44-7.40 (m, 1H), 7.29-7.25 (m, 3H), 7.21-7.17 (m, 1H), 7.13-7.09 (m, 3H), 6.72 (t,  $J = 5.0$  Hz, 1H), 5.35 (d,  $J = 1.0$  Hz, 1H), 5.27 (t,  $J = 1.5$  Hz, 1H), 2.81 (t,  $J = 7.4$  Hz, 2H), 2.59-2.54 (m, 2H), 2.03 (t,  $J = 1.2$  Hz, 3H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  172.1, 146.2, 141.8, 140.7, 136.4, 130.1, 129.2, 129.1, 128.46, 128.45, 126.2, 118.6, 34.2, 32.5, 20.5. HRMS (ESI)  $m/z$  calcd for  $\text{C}_{19}\text{H}_{21}\text{N}_2\text{O}^+$   $[\text{M}+\text{H}]^+$  293.1648, found 293.1657.



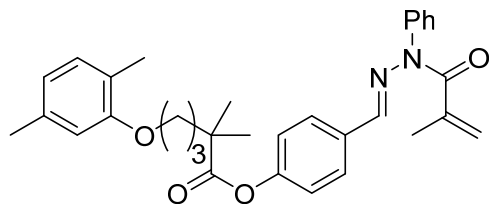
**(E)-N'-benzylidene-N-(4-methoxyphenyl)methacrylohydrazide (1z)**, yellow oil,  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.57-7.54 (m, 2H), 7.36-7.34 (m, 3H), 7.32 (s, 1H), 7.16-7.12 (m, 2H), 7.08-7.04 (m, 2H), 5.49 (s, 1H), 5.38 (t,  $J = 1.5$  Hz, 1H), 3.86 (s, 3H), 2.20 (s, 3H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  173.0, 160.0, 142.0, 141.9, 134.4, 130.3, 129.9, 128.7, 128.2, 127.3, 118.6, 115.5, 55.6, 20.8. HRMS (ESI)  $m/z$  calcd for  $\text{C}_{18}\text{H}_{19}\text{N}_2\text{O}_2^+$   $[\text{M}+\text{H}]^+$  295.1441, found 295.1442.



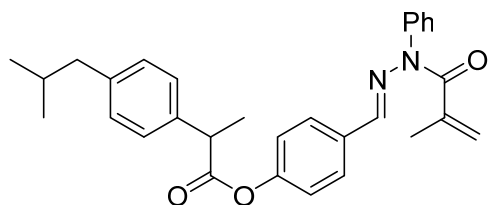
**(E)-N'-benzylidene-N-(4-chlorophenyl)methacrylohydrazide (1aa)**, yellow oil,  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.57-7.53 (m, 4H), 7.38-7.36 (m, 3H), 7.29 (s, 1H), 7.20-7.17 (m, 2H), 5.53 (t,  $J = 1.0$  Hz, 1H), 5.43 (t,  $J = 1.4$  Hz, 1H), 2.20 (t,  $J = 1.4$  Hz, 3H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  167.9, 137.5, 136.6, 130.6, 129.7, 129.3, 125.9, 125.8, 125.4, 124.1, 122.6, 114.6, 16.0. HRMS (ESI)  $m/z$  calcd for  $\text{C}_{17}\text{H}_{16}\text{ClN}_2\text{O}^+$   $[\text{M}+\text{H}]^+$  299.0946, found 299.0945.



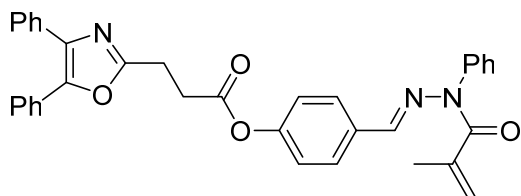
**(E)-N-acetyl-N'-benzylidenemethacrylohydrazide (1ab)**, white solid,  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.07 (s, 1H), 7.69 (d,  $J = 7.6$  Hz, 2H), 7.41 (d,  $J = 5.8$  Hz, 3H), 5.73 (s, 1H), 5.68 (s, 1H), 2.47 (s, 3H), 2.06 (s, 3H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  174.3, 173.2, 150.4, 141.3, 133.6, 131.0, 128.8, 127.7, 125.2, 23.22, 17.8. HRMS (ESI)  $m/z$  calcd for  $\text{C}_{13}\text{H}_{15}\text{N}_2\text{O}_2^+$   $[\text{M}+\text{H}]^+$  231.1128, found 231.1126.



**(E)-4-((2-methacryloyl-2-phenylhydrazineylidene)methyl)phenyl 5-(2,5-dimethylphenoxy)-2,2-dimethylpentanoate (1a')**, yellow oil,  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.54-7.53 (m, 4H), 7.48-7.44 (m, 1H), 7.26 (s, 1H), 7.22-7.20 (m, 2H), 7.03-6.97 (m, 3H), 6.65 (t,  $J = 7.5$  Hz, 2H), 5.51 (t,  $J = 1.0$  Hz, 1H), 5.40 (t,  $J = 1.4$  Hz, 1H), 3.96 (t,  $J = 5.3$  Hz, 2H), 2.29 (s, 3H), 2.20 (m, 6H), 1.89-1.82 (m, 4H), 1.36 (s, 6H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  176.2, 172.7, 156.9, 141.7, 141.2, 136.5, 132.0, 130.44, 130.35, 129.5, 129.2, 128.4, 123.6, 122.1, 120.9, 119.0, 112.0, 67.7, 42.6, 37.2, 25.3, 25.2, 21.5, 20.8, 15.9. HRMS (ESI)  $m/z$  calcd for  $\text{C}_{32}\text{H}_{37}\text{N}_2\text{O}_4^+$   $[\text{M}+\text{H}]^+$  513.2748, found 513.2756.



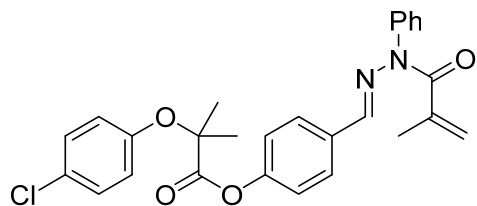
**(E)-4-((2-methacryloyl-2-phenylhydrazineylidene)methyl)phenyl 2-(4-isobutylphenyl)propanoate (1b')**, yellow oil,  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.56 (t,  $J = 7.6$  Hz, 2H), 7.52-7.46 (m, 3H), 7.29-7.20 (m, 3H), 7.21 (d,  $J = 7.5$  Hz, 2H), 7.14 (d,  $J = 7.9$  Hz, 2H), 6.99 (d,  $J = 8.5$  Hz, 2H), 5.49 (s, 1H), 5.39 (s, 1H), 3.95-3.90 (m, 1H), 2.47 (d,  $J = 7.2$  Hz, 2H), 2.18 (s, 3H), 1.91-1.81 (m, 1H), 1.59 (d,  $J = 7.1$  Hz, 3H), 0.90 (d,  $J = 6.6$  Hz, 6H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  173.0, 172.6, 152.0, 141.6, 141.1, 140.9, 137.0, 135.9, 131.9, 130.3, 129.6, 129.4, 129.2, 128.3, 127.2, 121.8, 118.9, 45.3, 45.1, 30.2, 22.4, 20.7, 18.5. HRMS (ESI)  $m/z$  calcd for  $\text{C}_{30}\text{H}_{33}\text{N}_2\text{O}_3^+$   $[\text{M}+\text{H}]^+$  469.2486, found 462.2478.



**(E)-4-((2-methacryloyl-2-phenylhydrazineylidene)methyl)phenyl 3-(4,5-diphenyloxazol-2-yl)propanoate (1c')**, yellow oil,  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.65 (d,  $J = 6.8$  Hz, 2H), 7.58-7.55 (m, 6H), 7.46 (t,  $J = 7.3$  Hz, 1H), 7.37-7.29 (m, 7H), 7.21 (d,  $J = 7.4$  Hz, 2H), 7.10 (d,  $J = 8.6$  Hz, 2H), 5.50 (s, 1H), 5.40 (s, 1H), 3.28 (t,  $J = 7.2$  Hz, 2H), 3.15 (t,  $J =$

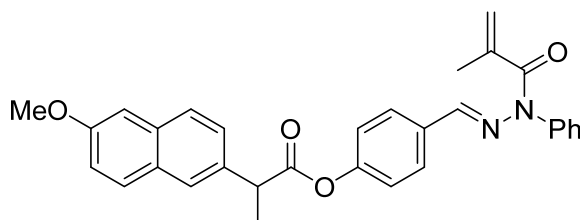


7.0 Hz, 2H), 2.19 (s, 3H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  172.7, 170.5, 161.4, 151.8, 145.7, 141.6, 141.2, 135.9, 135.2, 132.4, 132.1, 130.3, 129.5, 129.2, 129.0, 128.9, 128.7, 128.6, 128.4, 128.2, 127.9, 126.6, 122.0, 119.0, 31.3, 23.5, 20.8. HRMS (ESI)  $m/z$  calcd for  $\text{C}_{35}\text{H}_{30}\text{N}_3\text{O}_4^+$   $[\text{M}+\text{H}]^+$  556.2231, found 556.222.



**(E)-4-((2-methacryloyl-2-phenylhydrazineylidene)methyl)phenyl**

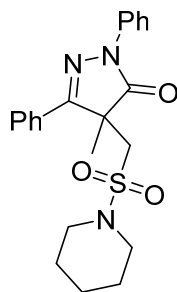
**2-(4-chlorophenoxy)-2-methylpropanoate (1d')**, yellow oil,  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.58-7.54 (m, 4H), 7.48 (t,  $J = 7.3$  Hz, 1H), 7.25-7.21 (m, 5H), 7.00 (d,  $J = 8.6$  Hz, 2H), 6.91-6.87 (m, 2H), 5.50 (s, 1H), 5.40 (s, 1H), 2.19 (s, 3H), 1.72 (s, 6H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  172.7, 172.5, 153.9, 151.6, 141.5, 140.9, 135.9, 132.5, 130.3, 129.5, 129.3, 129.2, 128.5, 121.7, 120.5, 119.0, 25.3, 20.7. HRMS (ESI)  $m/z$  calcd for  $\text{C}_{27}\text{H}_{26}\text{ClN}_2\text{O}_4^+$   $[\text{M}+\text{H}]^+$  477.1576, found 477.1574.



**(E)-4-((2-methacryloyl-2-phenylhydrazineylidene)methyl)phenyl**

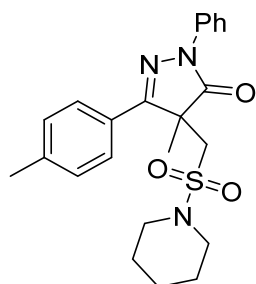
**2-(6-methoxynaphthalen-2-yl)propanoate (1e')**, yellow oil,  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.74 (t,  $J = 7.7$  Hz, 3H), 7.57-7.47 (m, 5H), 7.25-7.13 (m, 6H), 6.98 (d,  $J = 8.6$  Hz, 2H), 5.48 (s, 1H), 5.38 (s, 1H), 4.11-4.06 (m, 1H), 3.91 (s, 3H), 2.17 (s, 3H), 1.68 (d,  $J = 7.0$  Hz, 3H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  173.0, 172.7, 130.3, 129.5, 129.4, 129.2, 128.3, 127.5, 126.2, 126.1, 121.9, 119.2, 105.6, 55.4, 45.6, 20.8, 18.5. HRMS (ESI)  $m/z$  calcd for  $\text{C}_{31}\text{H}_{29}\text{N}_2\text{O}_4^+$   $[\text{M}+\text{H}]^+$  493.2122, found 493.2114.

### Characterization Data for the Products

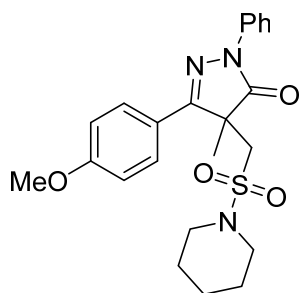


**4-Methyl-2,5-diphenyl-4-((piperidin-1-ylsulfonyl)methyl)-2,4-dihydro-3H-pyrazol-3-one (3aa)**, 32 mg, 79% yield), colorless oil;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.04 (d,  $J = 8.2$  Hz, 2H), 7.91 (t,  $J = 2.2$  Hz, 2H), 7.44 (t,  $J = 5.9$  Hz, 5H), 7.23 (t,  $J = 7.7$  Hz, 1H), 3.81 (d,  $J = 14.7$  Hz, 1H), 3.69 (d,  $J = 14.7$  Hz, 1H), 2.98 (d,  $J = 5.2$  Hz, 4H), 1.59 (s, 3H), 1.53-1.35 (m, 6H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  174.3, 158.9, 138.1, 130.8, 130.5, 129.0, 128.8, 126.6, 125.5, 119.2, 55.7, 50.8, 46.4,

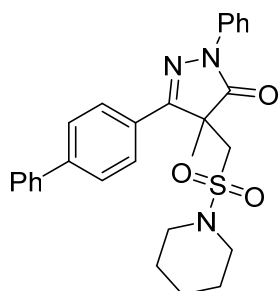
25.4, 24.0. HRMS (ESI)  $m/z$  calcd for  $C_{22}H_{26}N_3O_3S^+$   $[M+H]^+$  412.1689, found 412.1681.



**4-Methyl-2-phenyl-4-((piperidin-1-ylsulfonyl)methyl)-5-(p-tolyl)-2,4-dihydro-3H-pyrazol-3-one (3ba**, 30 mg, 70% yield), colorless oil;  $^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta$  8.04 (d,  $J = 8.3$  Hz, 2H), 7.79 (d,  $J = 8.0$  Hz, 2H), 7.44 (t,  $J = 7.6$  Hz, 2H), 7.27 (d,  $J = 8.1$  Hz, 2H), 7.22 (t,  $J = 7.4$  Hz, 1H), 3.81 (d,  $J = 14.7$  Hz, 1H), 3.67 (d,  $J = 14.7$  Hz, 1H), 3.03-2.94 (m, 4H), 2.40 (s, 3H), 1.58 (s, 3H), 1.52-1.36 (m, 6H);  $^{13}C$  NMR (101 MHz,  $CDCl_3$ )  $\delta$  174.3, 159.0, 140.8, 138.2, 129.6, 129.0, 128.1, 126.5, 125.4, 119.2, 55.8, 50.8, 46.5, 25.4, 24.0, 23.7, 21.6. HRMS (ESI)  $m/z$  calcd for  $C_{23}H_{28}N_3O_3S^+$   $[M+H]^+$  426.1846, found 426.1844.

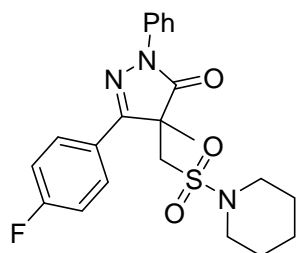


**5-(4-Methoxyphenyl)-4-methyl-2-phenyl-4-((piperidin-1-ylsulfonyl)methyl)-2,4-dihydro-3H-pyrazol-3-one (3ca**, 39 mg, 89% yield), yellow oil;  $^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta$  8.05 (d,  $J = 8.5$  Hz, 2H), 7.85 (d,  $J = 8.8$  Hz, 2H), 7.43 (t,  $J = 7.5$  Hz, 2H), 7.21 (t,  $J = 7.4$  Hz, 1H), 6.98 (d,  $J = 8.6$  Hz, 2H), 3.84 (s, 3H), 3.80 (d,  $J = 14.8$  Hz, 1H), 3.66 (d,  $J = 14.8$  Hz, 1H), 3.03-2.94 (m, 4H), 1.56 (s, 3H), 1.52-1.34 (m, 6H);  $^{13}C$  NMR (101 MHz,  $CDCl_3$ )  $\delta$  174.2, 161.3, 158.7, 138.2, 130.0, 128.2, 125.3, 123.5, 119.1, 114.3, 55.7, 55.4, 50.8, 46.5, 25.4, 24.0, 23.7. HRMS (ESI)  $m/z$  calcd for  $C_{23}H_{28}N_3O_4S^+$   $[M+H]^+$  442.1795, found 442.1796.

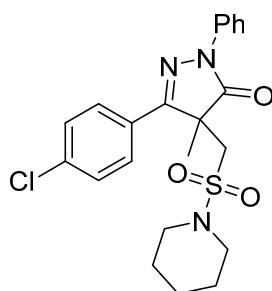


**5-([1,1'-Biphenyl]-4-yl)-4-methyl-2-phenyl-4-((piperidin-1-ylsulfonyl)methyl)-2,4-dihydro-3H-pyrazol-3-one (3da**, 34 mg, 70% yield), colorless oil;  $^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta$  8.07 (d,  $J = 8.4$  Hz, 2H), 7.97 (d,  $J = 8.2$  Hz, 2H), 7.69 (d,  $J = 8.1$  Hz, 2H), 7.63 (d,  $J = 8.0$  Hz, 2H), 7.47-7.43 (m, 4H), 7.38 (t,  $J = 7.2$  Hz, 1H), 7.23 (t,  $J = 6.6$  Hz, 1H), 3.84 (d,  $J = 14.7$  Hz, 1H), 3.72 (d,  $J = 14.8$  Hz, 1H), 3.05-2.92 (m, 4H), 1.60 (s, 3H), 1.53-1.34 (m, 6H);  $^{13}C$  NMR (101 MHz,  $CDCl_3$ )  $\delta$  174.4, 158.7, 143.1, 140.1, 138.2, 129.7, 129.04, 128.99, 128.0, 127.5, 127.13,

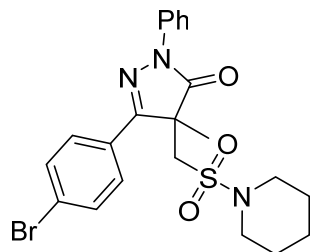
127.05, 125.6, 119.2, 55.8, 50.8, 46.5, 25.4, 24.0, 23.7. HRMS (ESI)  $m/z$  calcd for  $C_{28}H_{30}N_3O_3S^+$   $[M+H]^+$  488.2002, found 488.1998.



**5-(4-Fluorophenyl)-4-methyl-2-phenyl-4-((piperidin-1-ylsulfonyl)methyl)-2,4-dihydro-3H-pyrazol-3-one (3ea)**, 29 mg, 66% yield), colorless oil;  $^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta$  8.02 (d,  $J = 7.8$  Hz, 2H), 7.67-7.60 (m, 2H), 7.47-7.41 (m, 3H), 7.24 (t,  $J = 7.2$  Hz, 1H), 7.15 (t,  $J = 8.2$  Hz, 1H), 3.80 (d,  $J = 14.7$  Hz, 1H), 3.64 (d,  $J = 14.7$  Hz, 1H), 3.05-2.96 (m, 4H), 1.58 (s, 3H), 1.47-1.43 (m, 6H);  $^{13}C$  NMR (101 MHz,  $CDCl_3$ )  $\delta$  174.2, 162.9 (d,  $J_{C-F} = 247.3$  Hz), 157.8 (d,  $J_{C-F} = 3.0$  Hz), 137.9, 132.9 (d,  $J_{C-F} = 7.9$  Hz), 130.4 (d,  $J_{C-F} = 8.2$  Hz), 129.0, 125.7, 122.3 (d,  $J_{C-F} = 3.0$  Hz), 119.2, 117.4 (d,  $J_{C-F} = 21.0$  Hz), 113.4 (d,  $J_{C-F} = 23.4$  Hz), 55.5, 50.7, 46.5, 25.4, 23.8, 23.6. HRMS (ESI)  $m/z$  calcd for  $C_{25}H_{25}FN_3O_3S^+$   $[M+H]^+$  430.1959, found 430.1953.

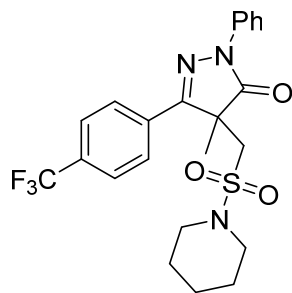


**5-(4-Chlorophenyl)-4-methyl-2-phenyl-4-((piperidin-1-ylsulfonyl)methyl)-2,4-dihydro-3H-pyrazol-3-one (3fa)**, 29 mg, 66% yield), colorless oil;  $^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta$  8.02 (d,  $J = 8.4$  Hz, 2H), 7.83 (d,  $J = 8.5$  Hz, 2H), 7.45 (t,  $J = 6.0$  Hz, 4H), 7.24 (t,  $J = 8.6$  Hz, 1H), 3.80 (d,  $J = 14.7$  Hz, 1H), 3.61 (d,  $J = 14.7$  Hz, 1H), 3.06-2.97 (m, 4H), 1.56 (s, 3H), 1.53-1.37 (m, 6H);  $^{13}C$  NMR (101 MHz,  $CDCl_3$ )  $\delta$  174.2, 158.0, 138.0, 136.5, 129.3, 129.1, 129.0, 127.9, 126.7, 119.2, 55.5, 50.7, 46.5, 25.4, 23.8, 23.6. HRMS (ESI)  $m/z$  calcd for  $C_{22}H_{25}ClN_3O_3S^+$   $[M+H]^+$  446.1300, found 446.1302.

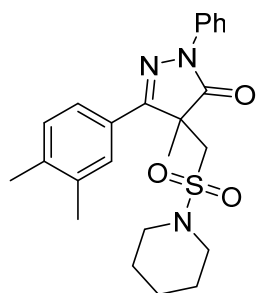


**5-(4-Bromophenyl)-4-methyl-2-phenyl-4-((piperidin-1-ylsulfonyl)methyl)-2,4-dihydro-3H-pyrazol-3-one (3ga)**, 26 mg, 53% yield), yellow oil;  $^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta$  8.01 (d,  $J = 7.8$  Hz, 2H), 7.76 (d,  $J = 8.6$  Hz, 2H), 7.60 (d,  $J = 8.5$  Hz, 2H), 7.45 (t,  $J = 8.3$  Hz, 2H), 7.24 (t,  $J = 8.6$  Hz, 1H), 3.80 (d,  $J = 14.7$  Hz, 1H), 3.61 (d,  $J = 14.7$  Hz, 1H), 3.05-2.97 (m, 4H), 1.56 (s, 3H), 1.53-1.38 (m, 6H);  $^{13}C$  NMR (101 MHz,  $CDCl_3$ )  $\delta$  174.2, 158.1, 137.9, 132.1, 129.8, 129.0, 128.0,

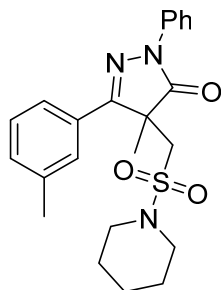
125.7, 124.9, 119.2, 55.5, 50.6, 46.5, 25.4, 23.8, 23.6. HRMS (ESI)  $m/z$  calcd for  $C_{22}H_{25}BrN_3O_3S^+$   $[M+H]^+$  490.0795, found 490.0801.



**4-Methyl-2-phenyl-4-((piperidin-1-ylsulfonyl)methyl)-5-(4-(trifluoromethyl)phenyl)-2,4-dihydro-3H-pyrazol-3-one (3ha)**, 21 mg, 43% yield), colorless oil;  $^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta$  8.02 (d,  $J = 8.3$  Hz, 4H), 7.73 (d,  $J = 8.2$  Hz, 2H), 7.46 (t,  $J = 7.6$  Hz, 2H), 7.26 (s, 1H), 3.84 (d,  $J = 14.7$  Hz, 1H), 3.63 (d,  $J = 14.7$  Hz, 1H), 3.08-2.99 (m, 4H), 1.61 (s, 3H), 1.53-1.40 (m, 6H);  $^{13}C$  NMR (101 MHz,  $CDCl_3$ )  $\delta$  174.2, 157.7, 137.8, 134.1, 132.0 (q,  $J_{C-F} = 42.3$  Hz), 129.1, 128.8, 126.9, 125.8 (q,  $J_{C-F} = 42$  Hz), 123.8 (q,  $J_{C-F} = 273.4$  Hz), 119.2, 55.4, 50.6, 46.5, 25.3, 23.7, 23.6. HRMS (ESI)  $m/z$  calcd for  $C_{23}H_{25}N_3O_3S^+$   $[M+H]^+$  480.1563, found 480.1574.

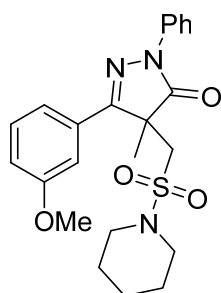


**5-(3,4-Dimethylphenyl)-4-methyl-2-phenyl-4-((piperidin-1-ylsulfonyl)methyl)-2,4-dihydro-3H-pyrazol-3-one (3ia)**, 35 mg, 80% yield), colorless oil;  $^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta$  8.05 (d,  $J = 8.4$  Hz, 2H), 7.75 (s, 1H), 7.55 (d,  $J = 7.8$  Hz, 1H), 7.44 (t,  $J = 7.5$  Hz, 2H), 7.22 (t,  $J = 6.2$  Hz, 2H), 3.81 (d,  $J = 14.7$  Hz, 1H), 3.69 (d,  $J = 14.7$  Hz, 1H), 3.04-2.94 (m, 4H), 2.32 (d,  $J = 11.4$  Hz, 6H), 1.58 (s, 3H), 1.52-1.40 (m, 6H);  $^{13}C$  NMR (101 MHz,  $CDCl_3$ )  $\delta$  174.3, 159.2, 139.7, 138.2, 137.2, 130.0, 129.0, 128.4, 127.6, 125.4, 124.1, 119.2, 55.8, 50.9, 46.5, 25.4, 24.2, 23.7, 20.1, 19.9. HRMS (ESI)  $m/z$  calcd for  $C_{24}H_{30}N_3O_3S^+$   $[M+H]^+$  440.2002, found 440.1995.

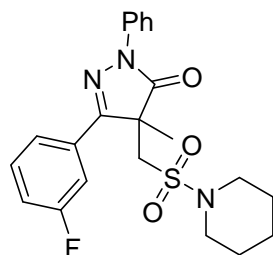


**4-Methyl-2-phenyl-4-((piperidin-1-ylsulfonyl)methyl)-5-(m-tolyl)-2,4-dihydro-3H-pyrazol-3-one (3ja)**, 25 mg, 58% yield), colorless oil;  $^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta$  8.05 (d,  $J = 8.6$  Hz, 2H), 7.78 (s, 1H), 7.63 (d,  $J = 7.7$  Hz, 1H), 7.45 (t,  $J = 7.9$  Hz, 1H), 7.36 (t,  $J = 7.6$  Hz, 1H), 7.28 (s, 1H), 7.22 (d,  $J = 7.4$  Hz, 1H), 3.82 (d,  $J = 14.7$  Hz, 1H), 3.69 (d,  $J = 14.7$  Hz, 1H), 3.03-3.01 (m,

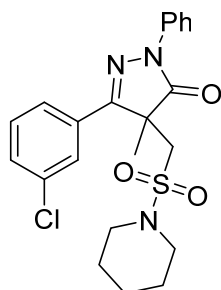
4H), 2.43 (s, 3H), 1.60 (s, 3H), 1.53-1.37 (m, 6H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  174.3, 159.1, 138.6, 138.1, 131.4, 130.7, 129.0, 128.6, 127.1, 125.5, 123.7, 119.2, 55.8, 50.8, 46.4, 25.4, 24.1, 23.7, 21.7. HRMS (ESI)  $m/z$  calcd for  $\text{C}_{23}\text{H}_{28}\text{N}_3\text{O}_3\text{S}^+$   $[\text{M}+\text{H}]^+$  426.1846, found 426.1843.



**5-(2-Methoxyphenyl)-4-methyl-2-phenyl-4-((piperidin-1-ylsulfonyl)methyl)-2,4-dihydro-3H-pyrazol-3-one (3ka)**, 31 mg, 70% yield), colorless oil;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.03 (d,  $J$  = 7.7 Hz, 2H), 7.51 (s, 1H), 7.51-7.35 (m, 4H), 7.23 (t,  $J$  = 7.4 Hz, 1H), 3.87 (s, 3H), 3.79 (d,  $J$  = 14.7 Hz, 1H), 3.68 (d,  $J$  = 14.7 Hz, 1H), 3.04-2.95 (m, 4H), 1.59 (s, 3H), 1.52-1.35 (m, 6H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  174.3, 159.8, 158.7, 138.0, 132.0, 129.8, 129.0, 125.5, 119.2, 119.1, 116.1, 112.0, 55.6, 55.4, 50.8, 46.4, 25.4, 24.0, 23.6. HRMS (ESI)  $m/z$  calcd for  $\text{C}_{23}\text{H}_{28}\text{N}_3\text{O}_4\text{S}^+$   $[\text{M}+\text{H}]^+$  442.1795, found 442.1797.

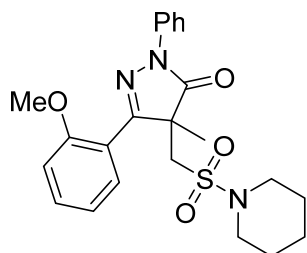


**5-(3-Fluorophenyl)-4-methyl-2-phenyl-4-((piperidin-1-ylsulfonyl)methyl)-2,4-dihydro-3H-pyrazol-3-one (3la)**, 33 mg, 77% yield), colorless oil;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.02 (d,  $J$  = 8.6 Hz, 2H), 7.67-7.60 (m, 2H), 7.47-7.41 (m, 3H), 7.24 (t,  $J$  = 7.2 Hz, 1H), 7.16 (t,  $J$  = 8.2 Hz, 1H), 3.80 (d,  $J$  = 14.7 Hz, 1H), 3.64 (d,  $J$  = 14.7 Hz, 1H), 3.05-2.96 (m, 4H), 1.58 (s, 3H), 1.54-1.37 (m, 6H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  174.2, 162.9 (d,  $J_{\text{C-F}}$  = 247.2 Hz), 157.8 (d,  $J_{\text{C-F}}$  = 2.9 Hz), 137.4, 132.9 (d,  $J_{\text{C-F}}$  = 8.0 Hz), 130.4 (d,  $J_{\text{C-F}}$  = 8.2 Hz), 129.0, 125.7, 122.3 (d,  $J_{\text{C-F}}$  = 2.9 Hz), 119.2, 117.5 (d,  $J_{\text{C-F}}$  = 21.4 Hz), 113.4 (d,  $J_{\text{C-F}}$  = 23.4 Hz), 55.5, 50.7, 46.5, 25.4, 23.8, 23.6. HRMS (ESI)  $m/z$  calcd for  $\text{C}_{25}\text{H}_{25}\text{FN}_3\text{O}_3\text{S}^+$   $[\text{M}+\text{H}]^+$  430.1595, found 430.1601.

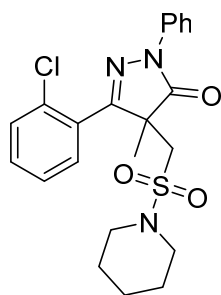


**5-(3-Chlorophenyl)-4-methyl-2-phenyl-4-((piperidin-1-ylsulfonyl)methyl)-2,4-dihydro-3H-pyrazol-3-one (3ma)**, 22 mg, 50% yield), colorless oil;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.02 (d,  $J$  = 8.4 Hz, 2H), 7.93 (s, 1H), 7.72 (d,  $J$  = 6.7 Hz, 1H), 7.50-7.39 (m, 4H), 7.24 (d,  $J$  = 7.0 Hz, 1H),

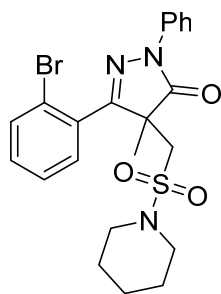
3.82 (d,  $J = 14.7$  Hz, 1H), 3.64 (d,  $J = 14.7$  Hz, 1H), 3.06-2.97 (m, 4H), 1.59 (s, 3H), 1.52-1.38 (m, 6H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  174.2, 157.7, 137.9, 135.0, 132.6, 130.4, 130.1, 139.1, 126.5, 125.7, 124.7, 119.2, 55.5, 50.7, 46.5, 25.4, 23.8, 23.6. HRMS (ESI)  $m/z$  calcd for  $\text{C}_{22}\text{H}_{25}\text{ClN}_3\text{O}_3\text{S}^+$   $[\text{M}+\text{H}]^+$  446.1300, found 446.1311.



**5-(2-Methoxyphenyl)-4-methyl-2-phenyl-4-((piperidin-1-ylsulfonyl)methyl)-2,4-dihydro-3H-pyrazol-3-one (3na, 35 mg, 80% yield)**, colorless oil;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.03 (d,  $J = 7.7$  Hz, 2H), 7.51 (s, 1H), 7.51-7.35 (m, 4H), 7.23 (t,  $J = 7.4$  Hz, 1H), 7.00 (t,  $J = 7.6$  Hz, 1H), 3.87 (s, 3H), 3.79 (d,  $J = 14.7$  Hz, 1H), 3.68 (d,  $J = 14.7$  Hz, 1H), 3.04-2.95 (m, 4H), 1.59 (s, 3H), 1.53-1.36 (m, 6H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  174.3, 159.8, 158.7, 138.0, 132.0, 129.8, 129.0, 125.5, 119.2, 119.1, 116.1, 112.0, 55.6, 55.4, 50.8, 46.4, 25.4, 24.0, 23.6. HRMS (ESI)  $m/z$  calcd for  $\text{C}_{23}\text{H}_{28}\text{N}_3\text{O}_4\text{S}^+$   $[\text{M}+\text{H}]^+$  442.1795, found 442.1783.

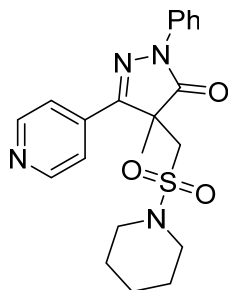


**5-(2-Chlorophenyl)-4-methyl-2-phenyl-4-((piperidin-1-ylsulfonyl)methyl)-2,4-dihydro-3H-pyrazol-3-one (3oa, 32 mg, 72% yield)**, colorless oil;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.98 (d,  $J = 7.4$  Hz, 3H), 7.54 (t,  $J = 4.0$  Hz, 1H), 7.45-7.38 (m, 4H), 7.22 (t,  $J = 7.4$  Hz, 1H), 3.60 (d,  $J = 14.8$  Hz, 1H), 3.42 (d,  $J = 14.8$  Hz, 1H), 3.17-3.10 (m, 4H), 1.53-1.51 (m, 6H), 1.46 (s, 3H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  173.3, 157.9, 138.0, 134.2, 130.97, 130.95, 130.87, 129.5, 129.0, 127.0, 125.6, 119.3, 54.1, 52.9, 46.5, 25.5, 23.7, 22.3. HRMS (ESI)  $m/z$  calcd for  $\text{C}_{22}\text{H}_{25}\text{ClN}_3\text{O}_3\text{S}^+$   $[\text{M}+\text{H}]^+$  446.1300, found 446.1295.

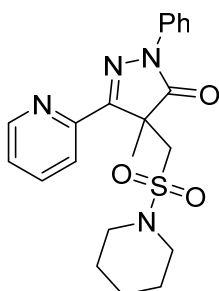


**5-(2-Bromophenyl)-4-methyl-2-phenyl-4-((piperidin-1-ylsulfonyl)methyl)-2,4-dihydro-3H-pyrazol-3-one (3pa, 34 mg, 69% yield)**, colorless oil;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.98 (t,  $J = 8.1$  Hz, 3H), 7.75 (d,  $J = 8.0$  Hz, 1H), 7.46-7.41 (m, 3H), 7.32 (t,  $J = 7.9$  Hz, 1H), 7.23 (t,  $J = 7.4$  Hz,

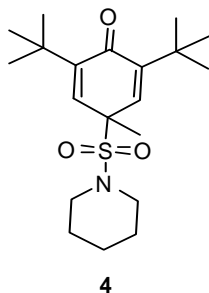
1H), 3.60 (d,  $J = 14.8$  Hz, 1H), 3.42 (d,  $J = 14.8$  Hz, 1H), 3.15 (d,  $J = 4.6$  Hz, 4H), 1.56-1.52 (m, 6H), 1.45 (s, 3H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  173.0, 158.6, 138.0, 134.3, 131.3, 131.2, 130.9, 129.0, 127.6, 125.6, 123.9, 119.4, 54.1, 52.8, 46.5, 25.5, 23.7, 21.9. HRMS (ESI)  $m/z$  calcd for  $\text{C}_{22}\text{H}_{25}\text{BrN}_3\text{O}_3\text{S}^+$   $[\text{M}+\text{H}]^+$  490.0795, found 490.0808.



**4-Methyl-2-phenyl-4-((piperidin-1-ylsulfonyl)methyl)-5-(pyridin-4-yl)-2,4-dihydro-3H-pyrazol-3-one (3qa)**, 15 mg, 37% yield), colorless oil;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.72 (s, 2H), 7.97 (d,  $J = 8.5$  Hz, 2H), 7.71 (d,  $J = 4.5$  Hz, 2H), 7.44 (t,  $J = 7.5$  Hz, 2H), 7.23 (d,  $J = 7.6$  Hz, 1H), 3.79 (d,  $J = 14.6$  Hz, 1H), 3.60 (d,  $J = 14.7$  Hz, 1H), 3.04-2.96 (m, 4H), 1.57 (s, 3H), 1.52-1.35 (m, 6H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  174.3, 156.8, 150.5, 137.8, 137.7, 129.1, 126.0, 120.3, 119.3, 55.3, 50.4, 46.5, 25.3, 23.6, 23.5. HRMS (ESI)  $m/z$  calcd for  $\text{C}_{21}\text{H}_{25}\text{N}_4\text{O}_3\text{S}^+$   $[\text{M}+\text{H}]^+$  413.1642, found 413.1645.

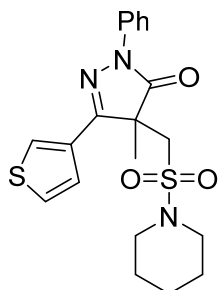


**4-Methyl-2-phenyl-4-((piperidin-1-ylsulfonyl)methyl)-5-(pyridin-2-yl)-2,4-dihydro-3H-pyrazol-3-one (3ra)**, 29 mg, 70% yield), colorless oil;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.61-8.60 (m, 1H), 8.22-8.20 (m, 1H), 8.03-8.01 (m, 2H), 7.80-7.76 (m, 1H), 7.46-7.42 (m, 2H), 7.33-7.29 (m, 1H), 7.25-7.21 (m, 1H), 4.40 (d,  $J = 14.0$  Hz, 1H), 3.65 (d,  $J = 14.0$  Hz, 1H), 3.01-2.97 (m, 2H), 2.92-2.87 (m, 2H), 1.71 (s, 3H), 1.46-1.40 (m, 6H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  174.9, 159.2, 150.5, 148.9, 138.1, 136.5, 129.02, 128.97, 125.5, 124.4, 120.9, 119.3, 54.9, 50.8, 46.3, 25.3, 23.7, 23.5. HRMS (ESI)  $m/z$  calcd for  $\text{C}_{21}\text{H}_{25}\text{N}_4\text{O}_3\text{S}^+$   $[\text{M}+\text{H}]^+$  413.1642, found 413.1638.

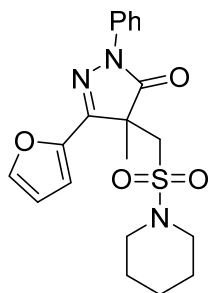


**4-Methyl-2-phenyl-4-((piperidin-1-ylsulfonyl)methyl)-5-(thiophen-2-yl)-2,4-dihydro-3H-pyrazol-3-one (3sa)**, 14.9 mg, 34% yield), colorless oil;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.00 (d,  $J = 7.8$

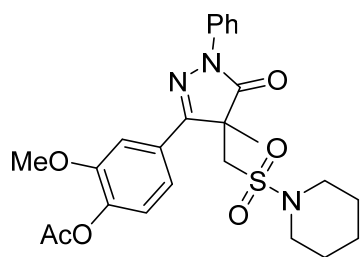
Hz, 2H), 7.47-7.42 (m, 4H), 7.23 (t,  $J = 7.4$  Hz, 1H), 7.16-7.14 (m, 1H), 3.79 (d,  $J = 14.7$  Hz, 1H), 3.63 (d,  $J = 14.7$  Hz, 1H), 3.07-3.02 (m, 2H), 2.99-2.94 (m, 2H), 1.60 (s, 3H), 1.49-1.44 (m, 6H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  173.5, 155.2, 137.9, 134.2, 130.0, 128.3, 127.7, 127.2, 125.5, 119.2, 55.6, 50.9, 46.5, 25.4, 24.2, 23.7. HRMS (ESI)  $m/z$  calcd for  $\text{C}_{20}\text{H}_{24}\text{N}_3\text{O}_3\text{S}_2^+$   $[\text{M}+\text{Na}]^+$  440.1073, found 440.1096.



**4-Methyl-2-phenyl-4-((piperidin-1-ylsulfonyl)methyl)-5-(thiophen-3-yl)-2,4-dihydro-3H-pyrazol-3-one (3ta**, 30 mg, 72% yield), colorless oil;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.01 (d,  $J = 7.7$  Hz, 2H), 7.69-7.67 (m, 2H), 7.46-7.41 (m, 3H), 7.23 (t,  $J = 7.4$  Hz, 1H), 3.78 (d,  $J = 14.7$  Hz, 1H), 3.60 (d,  $J = 14.7$  Hz, 1H), 3.08-3.0 (m, 2H), 2.98-2.93 (m, 2H), 1.56 (s, 3H), 1.48-1.44 (m, 6H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  173.8, 155.9, 138.0, 132.6, 129.0, 126.4, 126.0, 125.5, 125.0, 119.2, 55.5, 50.7, 46.4, 25.4, 24.0, 23.7. HRMS (ESI)  $m/z$  calcd for  $\text{C}_{20}\text{H}_{24}\text{N}_3\text{O}_3\text{S}_2^+$   $[\text{M}+\text{H}]^+$  418.1254, found 418.1256.



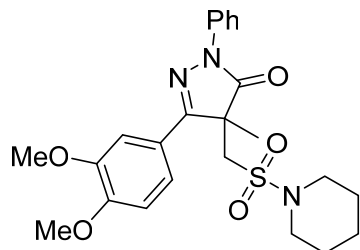
**5-(Furan-2-yl)-4-methyl-2-phenyl-4-((piperidin-1-ylsulfonyl)methyl)-2,4-dihydro-3H-pyrazol-3-one (3ua**, 18.1 mg, 45% yield), colorless oil;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.98 (d,  $J = 8.1$  Hz, 2H), 7.59 (s, 1H), 7.43 (t,  $J = 7.7$  Hz, 2H), 7.22 (t,  $J = 7.4$  Hz, 1H), 7.07 (d,  $J = 3.5$  Hz, 1H), 6.59 (t,  $J = 1.5$  Hz, 1H), 3.79 (d,  $J = 14.5$  Hz, 1H), 3.71 (d,  $J = 14.5$  Hz, 1H), 3.10-3.03 (m, 2H), 2.98-2.93 (m, 2H), 1.59 (s, 3H), 1.50-1.38 (m, 6H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  173.1, 152.0, 147.2, 144.1, 138.0, 129.0, 125.5, 119.3, 112.2, 110.8, 55.1, 50.4, 46.4, 25.4, 23.7, 23.3. HRMS (ESI)  $m/z$  calcd for  $\text{C}_{20}\text{H}_{24}\text{N}_3\text{O}_4\text{S}^+$   $[\text{M}+\text{H}]^+$  402.1482, found 402.1470.



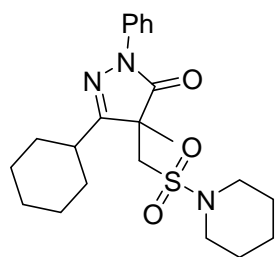
**2-Methoxy-4-(4-methyl-5-oxo-1-phenyl-4-((piperidin-1-ylsulfonyl)methyl)-4,5-dihydro-1H-pyrazol-3-yl)phenyl acetate (3va**, 36 mg, 72% yield), colorless oil;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$



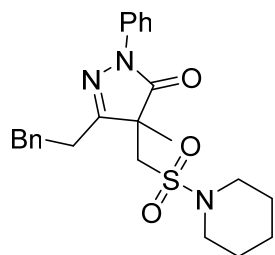
8.02-8.00 (m, 2H), 7.70 (d,  $J = 1.8$  Hz, 1H), 7.47-7.42 (m, 2H), 7.29-7.27 (m, 1H), 7.47-7.42 (m, 2H), 3.92 (s, 3H), 3.79 (d,  $J = 14.7$  Hz, 1H), 3.65 (d,  $J = 14.7$  Hz, 1H), 3.04-2.95 (m, 4H), 2.33 (s, 3H), 1.56 (s, 3H), 1.51-1.44 (m, 6H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  174.2, 168.8, 158.3, 151.6, 141.7, 138.0, 129.6, 129.0, 125.6, 122.9, 119.4, 119.3, 110.4, 56.1, 55.5, 50.8, 46.4, 25.4, 24.0, 23.6, 20.7. HRMS (ESI)  $m/z$  calcd for  $\text{C}_{25}\text{H}_{30}\text{N}_3\text{O}_6\text{S}^+$   $[\text{M}+\text{H}]^+$  500.1850, found 500.1852.



**5-(3,4-Dimethoxyphenyl)-4-methyl-2-phenyl-4-((piperidin-1-ylsulfonyl)methyl)-2,4-dihydro-3H-pyrazol-3-one (3wa)**, 38 mg, 81% yield), colorless oil;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.04 (d,  $J = 8.1$  Hz, 2H), 7.65 (s, 1H), 7.45 (t,  $J = 7.6$  Hz, 2H), 7.25 (m, 2H), 6.91 (d,  $J = 8.4$  Hz, 1H), 3.98 (s, 3H), 3.93 (s, 3H), 3.81 (d,  $J = 14.7$  Hz, 1H), 3.67 (d,  $J = 14.7$  Hz, 1H), 3.06-3.01 (m, 4H), 1.58 (s, 3H), 1.54-1.37 (m, 6H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  174.2, 158.7, 151.2, 149.4, 138.1, 128.9, 125.4, 123.7, 120.0, 119.3, 110.5, 109.0, 56.03, 55.95, 55.7, 50.8, 46.5, 25.4, 24.3, 23.6. HRMS (ESI)  $m/z$  calcd for  $\text{C}_{24}\text{H}_{30}\text{N}_3\text{O}_5\text{S}^+$   $[\text{M}+\text{H}]^+$  472.1901, found 472.1902.

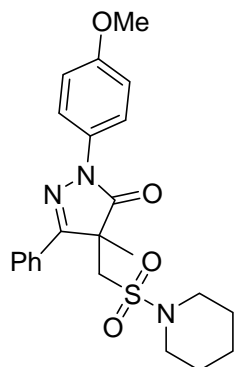


**5-Cyclohexyl-4-methyl-2-phenyl-4-((piperidin-1-ylsulfonyl)methyl)-2,4-dihydro-3H-pyrazol-3-one (3xa)**, 25 mg, 60% yield), colorless oil;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.93 (d,  $J = 7.8$  Hz, 2H), 7.39 (t,  $J = 7.6$  Hz, 2H), 7.17 (t,  $J = 7.4$  Hz, 1H), 3.54 (d,  $J = 14.6$  Hz, 1H), 3.28 (d,  $J = 14.6$  Hz, 1H), 3.12-3.01 (m, 4H), 2.55 (t,  $J = 11.2$  Hz, 1H), 2.19 (d,  $J = 13.1$  Hz, 1H), 2.02 (t,  $J = 6.2$  Hz, 1H), 1.90-1.71 (m, 5H), 1.49-1.43 (m, 5H), 1.40 (s, 3H), 1.35-1.25 (m, 4H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  173.7, 168.2, 138.3, 128.7, 125.0, 118.9, 54.2, 52.1, 46.5, 38.7, 33.6, 29.8, 26.4, 26.2, 25.9, 25.4, 23.7, 23.2. HRMS (ESI)  $m/z$  calcd for  $\text{C}_{22}\text{H}_{32}\text{N}_3\text{O}_3\text{S}^+$   $[\text{M}+\text{H}]^+$  418.2159, found 418.2157.

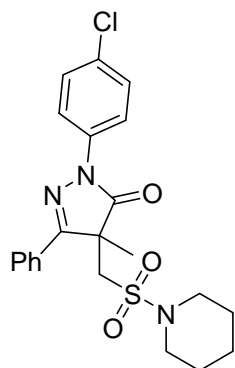


**4-Methyl-5-phenethyl-2-phenyl-4-((piperidin-1-ylsulfonyl)methyl)-2,4-dihydro-3H-pyrazol-3-one (3ya)**, 20 mg, 47% yield), colorless oil;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.98-7.96 (m, 2H), 7.44-7.40 (m, 2H), 7.31 (d,  $J = 4.4$  Hz, 4H), 7.24-7.18 (m, 2H), 3.58 (d,  $J = 14.6$  Hz, 1H),

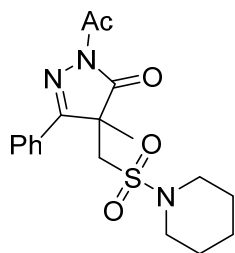
3.21-3.16 (m, 3H), 3.13-3.06 (m, 5H), 2.66-2.58 (m, 1H), 1.52-1.46 (m, 6H), 1.27 (s, 3H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  173.7, 164.0, 141.4, 138.2, 128.9, 128.6, 128.5, 126.2, 125.1, 118.8, 54.0, 51.5, 46.5, 31.0, 30.5, 25.4, 23.7, 22.3. HRMS (ESI)  $m/z$  calcd for  $\text{C}_{24}\text{H}_{30}\text{N}_3\text{O}_3\text{S}^+$   $[\text{M}+\text{H}]^+$  440.2002, found 440.2002.



**2-(4-Methoxyphenyl)-4-methyl-5-phenyl-4-((piperidin-1-ylsulfonyl)methyl)-2,4-dihydro-3H-pyrazol-3-one (3za**, 19 mg, 43% yield), colorless oil;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.92-7.87 (m, 4H), 7.48-7.44 (m, 3H), 6.99-6.95 (m, 2H), 3.83 (s, 3H), 3.80 (d,  $J = 14.7$  Hz, 1H), 3.68 (d,  $J = 14.7$  Hz, 1H), 3.03-2.92 (m, 4H), 1.59 (s, 3H), 1.47-1.43 (m, 6H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  174.0, 158.7, 157.3, 131.4, 130.9, 130.4, 128.8, 126.5, 121.1, 114.1, 55.7, 55.5, 50.6, 46.4, 25.4, 23.9, 23.7. HRMS (ESI)  $m/z$  calcd for  $\text{C}_{23}\text{H}_{28}\text{N}_3\text{O}_4\text{S}^+$   $[\text{M}+\text{H}]^+$  442.1795, found 442.1798.

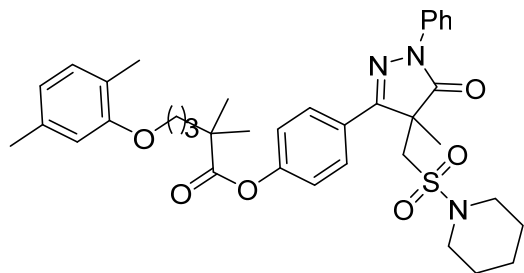


**2-(4-Chlorophenyl)-4-methyl-5-phenyl-4-((piperidin-1-ylsulfonyl)methyl)-2,4-dihydro-3H-pyrazol-3-one (3aaa**, 17 mg, 38% yield), colorless oil;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.03-8.00 (m, 2H), 7.90-7.87 (m, 2H), 7.49-7.46 (m, 3H), 7.42-7.38 (m, 2H), 3.79 (d,  $J = 14.7$  Hz, 1H), 3.68 (d,  $J = 14.7$  Hz, 1H), 3.02-2.91 (m, 4H), 1.60 (s, 3H), 1.47-1.38 (m, 6H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  174.3, 159.2, 136.7, 130.6, 130.6, 130.6, 129.0, 128.9, 126.6, 120.3, 55.7, 50.8, 46.4, 25.4, 23.9, 23.6. HRMS (ESI)  $m/z$  calcd for  $\text{C}_{22}\text{H}_{25}\text{ClN}_3\text{O}_3\text{S}^+$   $[\text{M}+\text{H}]^+$  446.1300, found 446.1299.

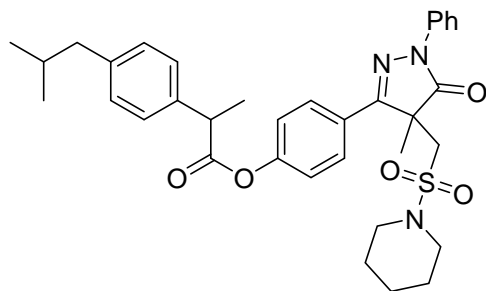


**2-Acetyl-4-methyl-5-phenyl-4-((piperidin-1-ylsulfonyl)methyl)-2,4-dihydro-3H-pyrazol-3-one (3aba**, 26 mg, 70% yield), colorless oil;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.87 (d,  $J = 6.0$  Hz, 2H), 7.47 (d,  $J = 6.0$  Hz, 3H), 3.73 (d,  $J = 14.6$  Hz, 1H), 3.67 (d,  $J = 14.8$  Hz, 1H), 3.00 (d,  $J = 16.9$  Hz,

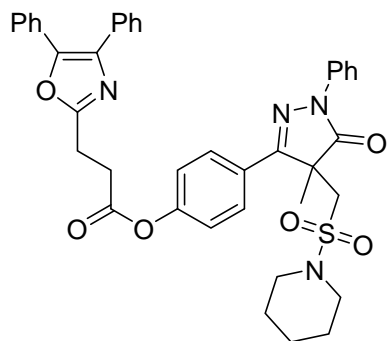
4H), 2.62 (s, 3H), 1.58 (s, 3H), 1.52-1.42 (m, 6H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  175.2, 167.6, 159.6, 131.2, 130.0, 128.9, 127.0, 55.6, 50.8, 46.4, 25.4, 24.3, 23.6, 23.5. HRMS (ESI)  $m/z$  calcd for  $\text{C}_{18}\text{H}_{24}\text{N}_3\text{O}_4\text{S}^+$   $[\text{M}+\text{H}]^+$  378.1482, found 378.1488.



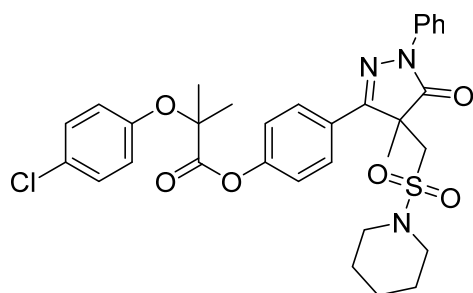
**4-(4-Methyl-5-oxo-1-phenyl-4-((piperidin-1-ylsulfonyl)methyl)-4,5-dihydro-1H-pyrazol-3-yl)phenyl 3-(2,5-dimethylphenoxy)-2,2-dimethylpropanoate (3a'a**, 26 mg, 41% yield), colorless oil;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.04-8.01 (m, 2H), 7.92-7.88 (m, 2H), 7.46-7.42 (m, 2H), 7.25 (t,  $J = 1.2$  Hz, 1H), 7.18-7.14 (m, 2H), 7.01 (d,  $J = 7.4$  Hz, 1H), 6.67 (t,  $J = 7.5$  Hz, 2H), 3.99 (t,  $J = 5.2$  Hz, 2H), 3.81 (d,  $J = 14.7$  Hz, 1H), 3.64 (d,  $J = 14.7$  Hz, 1H), 3.03-2.94 (m, 4H), 2.31 (s, 3H), 2.19 (s, 3H), 1.89 (d,  $J = 3.2$  Hz, 4H), 1.57 (s, 3H), 1.45 (d,  $J = 3.7$  Hz, 6H), 1.52-1.44 (m, 6H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  176.0, 174.2, 158.2, 156.9, 152.6, 138.0, 136.5, 130.4, 129.0, 127.8, 125.6, 123.6, 122.1, 120.8, 119.2, 112.0, 67.7, 55.6, 50.7, 46.5, 42.6, 37.1, 25.4, 25.3, 25.2, 23.9, 23.6, 21.5, 15.9. HRMS (ESI)  $m/z$  calcd for  $\text{C}_{37}\text{H}_{46}\text{N}_3\text{O}_6\text{S}^+$   $[\text{M}+\text{H}]^+$  660.3102, found 660.3103.



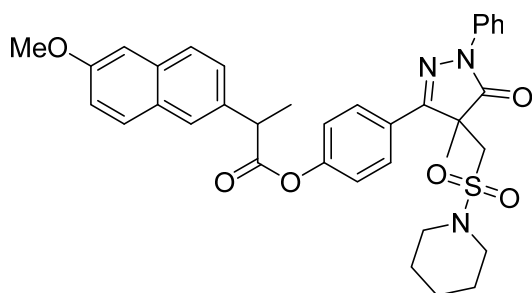
**4-(4-Methyl-5-oxo-1-phenyl-4-((piperidin-1-ylsulfonyl)methyl)-4,5-dihydro-1H-pyrazol-3-yl)phenyl 2-(4-isobutylphenyl)propanoate (3b'a**, 35 mg, 57% yield), colorless oil;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.03 (d,  $J = 7.8$  Hz, 2H), 7.89 (t,  $J = 2.4$  Hz, 2H), 7.46-7.42 (m, 2H), 7.31 (d,  $J = 8.1$  Hz, 2H), 7.25-7.21 (m, 1H), 7.17-7.12 (m, 4H), 3.99-3.94 (m, 1H), 3.80 (d,  $J = 14.6$  Hz, 1H), 3.65-3.60 (m, 1H), 3.03-2.93 (m, 4H), 2.48 (d,  $J = 7.2$  Hz, 2H), 1.91-1.84 (m, 1H), 1.63-1.61 (m, 3H), 1.56 (s, 3H), 1.44-1.43 (m, 6H), 0.92 (d,  $J = 6.6$  Hz, 6H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  174.2, 172.9, 158.1, 152.4, 141.0, 138.0, 137.0, 129.6, 129.0, 128.3, 127.7, 127.2, 125.5, 121.9, 119.2, 55.6, 50.7, 46.5, 45.3, 45.1, 30.2, 25.4, 23.8, 23.6, 22.4, 18.5. HRMS (ESI)  $m/z$  calcd for  $\text{C}_{35}\text{H}_{42}\text{N}_3\text{O}_5\text{S}^+$   $[\text{M}+\text{H}]^+$  616.2840, found 616.2818.



**4-(4-Methyl-5-oxo-1-phenyl-4-((piperidin-1-ylsulfonyl)methyl)-4,5-dihydro-1H-pyrazol-3-yl)phenyl 3-(4,5-diphenyloxazol-2-yl)propanoate (3c'a, 33 mg, 48% yield), colorless oil; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.04-8.02 (m, 2H), 7.93-7.89 (m, 2H), 7.68-7.66 (m, 2H), 7.61-7.59 (m, 2H), 7.47-7.43 (m, 2H), 7.39-7.33 (m, 6H), 7.25-7.22 (m, 3H), 3.81 (d, *J* = 14.8 Hz, 1H), 3.64 (d, *J* = 14.7 Hz, 1H), 3.34-3.30 (m, 2H), 3.22-3.18 (m, 2H), 3.06-2.94 (m, 4H), 1.56 (s, 3H), 1.46-1.42 (m, 6H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 174.2, 170.4, 161.4, 158.1, 152.1, 145.7, 138.0, 135.2, 132.4, 129.0, 128.9, 128.7, 128.64, 128.61, 128.56, 128.2, 127.90, 127.85, 126.6, 125.6, 122.1, 119.2, 55.6, 50.7, 46.5, 31.3, 25.4, 23.8, 23.6, 23.5. HRMS (ESI) *m/z* calcd for C<sub>40</sub>H<sub>39</sub>N<sub>4</sub>O<sub>6</sub>S<sup>+</sup> [M+H]<sup>+</sup> 703.2585, found 703.2610.**

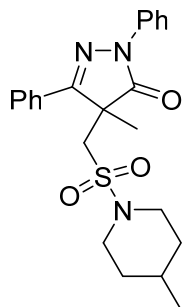


**4-(4-Methyl-5-oxo-1-phenyl-4-((piperidin-1-ylsulfonyl)methyl)-4,5-dihydro-1H-pyrazol-3-yl)phenyl 2-(4-chlorophenoxy)-2-methylpropanoate (3d'a, 44 mg, 71% yield), colorless oil; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.03-8.0 (m, 2H), 7.94-7.89 (m, 2H), 7.46-7.42 (m, 2H), 7.27 (t, *J* = 3.4 Hz, 1H), 7.25-7.22 (m, 2H), 7.15-7.12 (m, 2H), 6.93-6.89 (m, 2H), 3.81 (d, *J* = 14.8 Hz, 1H), 3.63 (d, *J* = 14.7 Hz, 1H), 3.04-2.94 (m, 4H), 1.75 (s, 6H), 1.57 (s, 3H), 1.46-1.43 (m, 6H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 174.2, 172.3, 158.0, 153.9, 151.9, 138.0, 129.4, 129.0, 128.9, 127.9, 127.7, 125.6, 121.7, 120.5, 119.2, 79.6, 55.4, 50.7, 46.5, 25.38, 25.37, 25.3, 23.8, 23.6. HRMS (ESI) *m/z* calcd for C<sub>32</sub>H<sub>35</sub>ClN<sub>3</sub>O<sub>6</sub>S<sup>+</sup> [M+H]<sup>+</sup> 624.1930, found 624.1299.**

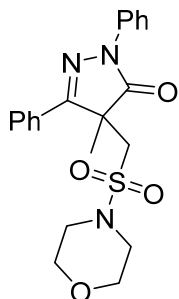


**(4-Methyl-5-oxo-1-phenyl-4-((piperidin-1-ylsulfonyl)methyl)-4,5-dihydro-1H-pyrazol-3-yl)ph**

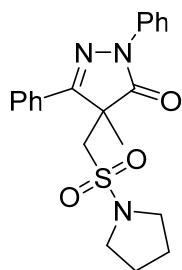
enyl 2-(6-methoxynaphthalen-2-yl)propanoate (**3e'a**, 36 mg, 56% yield), colorless oil;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.01 (d,  $J = 8.6$  Hz, 2H), 7.86-7.84 (m, 2H), 7.75 (t,  $J = 8.8$  Hz, 3H), 7.51-7.48 (m, 1H), 7.42 (t,  $J = 7.8$  Hz, 2H), 7.23-7.10 (m, 5H), 4.14-4.08 (m, 1H), 3.91 (s, 3H), 3.79-3.75 (m, 1H), 3.62-3.57 (m, 1H), 3.0-2.91 (m, 4H), 1.70 (d,  $J = 7.1$  Hz, 3H), 1.52 (s, 3H), 1.43-1.40 (m, 6H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  174.2, 172.8, 158.1, 157.8, 152.4, 129.4, 129.0, 127.8, 127.5, 121.9, 119.23, 119.21, 55.62, 55.60, 55.4, 50.7, 46.4, 45.6, 25.4, 23.8, 23.6, 18.5. HRMS (ESI)  $m/z$  calcd for  $\text{C}_{36}\text{H}_{38}\text{N}_3\text{O}_6\text{S}^+$   $[\text{M}+\text{H}]^+$  640.2476, found 640.2470..



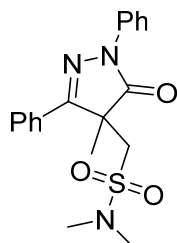
**4-Methyl-4-(((4-methylpiperidin-1-yl)sulfonyl)methyl)-2,5-diphenyl-2,4-dihydro-3H-pyrazol-3-one (3ab**, 35 mg, 81% yield), colorless oil;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.05 (d,  $J = 8.4$  Hz, 2H), 7.91 (t,  $J = 2.3$  Hz, 2H), 7.45 (t,  $J = 6.2$  Hz, 5H), 7.23 (t,  $J = 8.1$  Hz, 1H), 3.84 (d,  $J = 14.8$  Hz, 1H), 3.70 (d,  $J = 14.8$  Hz, 1H), 3.49 (t,  $J = 10.7$  Hz, 2H), 2.53 (t,  $J = 12.2$  Hz, 1H), 2.40 (t,  $J = 12.2$  Hz, 1H), 1.59 (s, 3H), 1.48 (d,  $J = 13.2$  Hz, 2H), 1.34-1.26 (m, 1H), 1.04-0.93 (m, 2H), 0.78 (d,  $J = 6.5$  Hz, 3H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  174.3, 158.9, 138.1, 130.8, 130.5, 129.0, 128.8, 126.6, 125.5, 119.1, 55.9, 50.8, 46.0, 45.8, 33.44, 33.39, 30.2, 24.0, 21.5. HRMS (ESI)  $m/z$  calcd for  $\text{C}_{23}\text{H}_{28}\text{N}_3\text{O}_3\text{S}^+$   $[\text{M}+\text{H}]^+$  426.1846, found 426.1848.



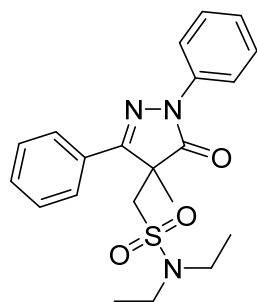
**4-Methyl-4-((morpholin)sulfonyl)methyl)-2,5-diphenyl-2,4-dihydro-3H-pyrazol-3-one (3ac**, 22 mg, 54% yield), colorless oil;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.04 (d,  $J = 7.8$  Hz, 2H), 7.90-7.85 (t,  $J = 3.3$  Hz, 2H), 7.48-7.44 (m, 5H), 7.24 (d,  $J = 7.4$  Hz, 1H), 3.86 (d,  $J = 14.8$  Hz, 1H), 3.73 (d,  $J = 14.9$  Hz, 1H), 3.56-3.45 (m, 4H), 3.08-3.0 (m, 4H), 1.63 (s, 3H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  174.2, 158.8, 138.0, 130.7, 129.1, 129.0, 126.5, 125.7, 119.1, 66.2, 55.5, 50.8, 45.5, 29.3, 24.0. HRMS (ESI)  $m/z$  calcd for  $\text{C}_{21}\text{H}_{24}\text{N}_3\text{O}_4\text{S}^+$   $[\text{M}+\text{H}]^+$  414.1482, found 414.1475.



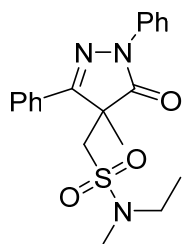
**4-Methyl-2,5-diphenyl-4-((pyrrolidin-1-ylsulfonyl)methyl)-2,4-dihydro-3H-pyrazol-3-one (3ad)**, 25 mg, 62% yield), colorless oil;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.06-8.04 (m, 2H), 7.93-7.91 (m, 2H), 7.48-7.42 (m, 5H), 7.25-7.21 (m, 1H), 3.89 (d,  $J = 15.0$  Hz, 1H), 3.81 (d,  $J = 15.0$  Hz, 1H), 3.17-3.12 (m, 2H), 3.07-3.01 (m, 2H), 1.61 (s, 3H), 1.58-1.43 (m, 4H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  174.3, 159.1, 138.1, 130.8, 130.5, 129.0, 128.9, 126.5, 125.5, 119.0, 57.1, 50.9, 47.4, 25.5, 23.9. HRMS (ESI)  $m/z$  calcd for  $\text{C}_{21}\text{H}_{24}\text{N}_3\text{O}_3\text{S}^+$   $[\text{M}+\text{H}]^+$  398.1533, found 398.1534.



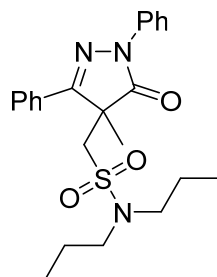
**N,N-dimethyl-1-(4-methyl-5-oxo-1,3-diphenyl-4,5-dihydro-1H-pyrazol-4-yl)methanesulfonamide (3ae)**, 12 mg, 32% yield), brown oil;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.04 (d,  $J = 7.8$  Hz, 2H), 7.91 (t,  $J = 2.9$  Hz, 2H), 7.49-7.43 (m, 5H), 7.23 (t,  $J = 7.4$  Hz, 1H), 3.85 (d,  $J = 14.8$  Hz, 1H), 3.74 (d,  $J = 14.8$  Hz, 1H), 2.59 (s, 6H), 1.62 (s, 3H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  174.2, 159.0, 138.0, 130.8, 130.6, 129.0, 128.9, 126.5, 125.6, 119.1, 55.5, 50.8, 36.9, 24.0. HRMS (ESI)  $m/z$  calcd for  $\text{C}_{19}\text{H}_{22}\text{N}_3\text{O}_3\text{S}^+$   $[\text{M}+\text{H}]^+$  372.1376, found 372.1367.



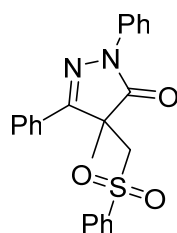
**N,N-diethyl-1-(4-methyl-5-oxo-1,3-diphenyl-4,5-dihydro-1H-pyrazol-4-yl)methanesulfonamide (3af)**, 22 mg, 55% yield), colorless oil;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.04-8.02 (m, 2H), 7.93-7.90 (m, 2H), 7.49-7.42 (m, 5H), 7.25-7.21 (m, 1H), 3.79 (d,  $J = 14.5$  Hz, 1H), 3.69 (d,  $J = 14.5$  Hz, 1H), 3.20-3.11 (m, 2H), 3.11-3.01 (m, 2H), 1.60 (s, 3H), 1.08 (t,  $J = 7.1$  Hz, 6H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  174.4, 159.1, 138.1, 130.9, 130.5, 128.9, 128.8, 126.7, 125.5, 119.4, 57.5, 51.0, 41.7, 24.0, 14.4. HRMS (ESI)  $m/z$  calcd for  $\text{C}_{21}\text{H}_{25}\text{N}_3\text{NaO}_3\text{S}^+$   $[\text{M}+\text{Na}]^+$  422.1509, found 422.1507.



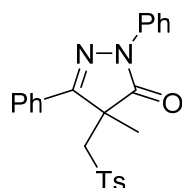
**N-ethyl-N-methyl-1-(4-methyl-5-oxo-1,3-diphenyl-4,5-dihydro-1H-pyrazol-4-yl)methanesulfonamide (3ag**, 25 mg, 66% yield), colorless oil;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.05 (d,  $J = 8.5$  Hz, 2H), 7.92 (t,  $J = 2.6$  Hz, 2H), 7.45 (t,  $J = 7.0$  Hz, 5H), 7.24 (t,  $J = 8.5$  Hz, 1H), 3.84 (d,  $J = 14.8$  Hz, 1H), 3.74 (d,  $J = 14.9$  Hz, 1H), 3.06-2.97 (m, 1H), 2.92-2.84 (m, 1H), 2.60 (s, 3H), 1.60 (s, 3H), 1.03 (t,  $J = 7.1$  Hz, 3H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  174.3, 159.1, 138.1, 130.8, 130.5, 129.0, 128.9, 126.5, 125.5, 119.2, 56.2, 50.9, 44.7, 33.3, 24.0, 13.2. HRMS (ESI)  $m/z$  calcd for  $\text{C}_{20}\text{H}_{24}\text{N}_3\text{O}_3\text{S}^+$   $[\text{M}+\text{H}]^+$  386.1533, found 386.1527.



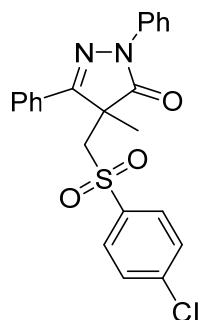
**1-(4-Methyl-5-oxo-1,3-diphenyl-4,5-dihydro-1H-pyrazol-4-yl)-N,N-dipropylmethanesulfonamide (3ah**, 27 mg, 64% yield), colorless oil;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.04-8.01 (m, 2H), 7.92-7.89 (m, 2H), 7.48-7.46 (m, 3H), 7.44-7.42 (m, 2H), 7.25-7.21 (m, 1H), 3.78 (d,  $J = 14.4$  Hz, 1H), 3.68 (d,  $J = 14.4$  Hz, 1H), 3.06-2.98 (m, 2H), 2.96-2.88 (m, 2H), 1.61 (s, 3H), 1.53-1.47 (m, 4H), 0.81 (t,  $J = 7.3$  Hz, 6H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  174.4, 159.2, 138.1, 130.9, 130.4, 128.9, 128.8, 126.7, 125.5, 119.5, 57.1, 51.1, 49.5, 24.0, 22.1, 11.1. HRMS (ESI)  $m/z$  calcd for  $\text{C}_{23}\text{H}_{30}\text{N}_3\text{O}_3\text{S}^+$   $[\text{M}+\text{H}]^+$  428.2002, found 428.2000.



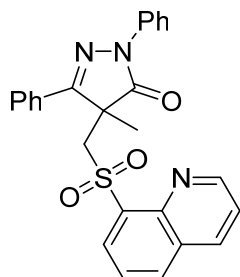
**4-Methyl-2,5-diphenyl-4-((phenylsulfonyl)methyl)-2,4-dihydro-3H-pyrazol-3-one (3ai**, 33 mg, 83% yield), yellow oil;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.94 (d,  $J = 8.2$  Hz, 2H), 7.76 (d,  $J = 6.1$  Hz, 2H), 7.68 (d,  $J = 7.8$  Hz, 2H), 7.45-7.38 (m, 6H), 7.24 (t,  $J = 7.7$  Hz, 3H), 4.01 (d,  $J = 14.9$  Hz, 1H), 3.94 (d,  $J = 15.0$  Hz, 1H), 1.56 (s, 3H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  173.5, 158.2, 138.4, 137.9, 134.0, 130.6, 130.4, 129.1, 128.9, 128.8, 128.2, 126.4, 125.6, 119.3, 61.4, 50.6, 24.3. HRMS (ESI)  $m/z$  calcd for  $\text{C}_{23}\text{H}_{21}\text{N}_2\text{O}_3\text{S}^+$   $[\text{M}+\text{H}]^+$  405.1267, found 405.1262.



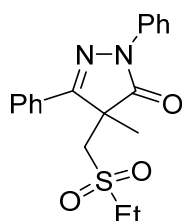
**4-Methyl-2,5-diphenyl-4-(tosylmethyl)-2,4-dihydro-3H-pyrazol-3-one (3aj, 36 mg, 90% yield),** yellow oil;  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.92 (d,  $J = 8.4$  Hz, 2H), 7.75 (d,  $J = 6.6$  Hz, 2H), 7.53 (d,  $J = 8.1$  Hz, 2H), 7.43 (t,  $J = 7.6$  Hz, 2H), 7.39-7.34 (m, 3H), 7.23 (t,  $J = 8.3$  Hz, 1H), 6.98 (d,  $J = 8.0$  Hz, 2H), 4.00 (d,  $J = 14.9$  Hz, 1H), 3.93 (d,  $J = 15.0$  Hz, 1H), 2.20 (s, 3H), 1.54 (s, 3H);  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  173.4, 158.2, 145.2, 138.0, 135.1, 130.5, 130.3, 129.6, 128.9, 128.7, 128.4, 126.4, 125.5, 119.2, 61.5, 50.6, 24.4, 21.5. HRMS (ESI)  $m/z$  calcd for  $\text{C}_{24}\text{H}_{23}\text{N}_2\text{O}_3\text{S}^+$   $[\text{M}+\text{Na}]^+$  441.1243, found 446.1239.



**4-(((4-Chlorophenyl)sulfonyl)methyl)-4-methyl-2,5-diphenyl-2,4-dihydro-3H-pyrazol-3-one (3ak, 40 mg, 93% yield),** yellow oil;  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.93–7.90 (m, 2H), 7.71-7.68 (m, 2H), 7.56-7.53 (m, 2H), 7.46-7.39 (m, 2H), 7.36-7.32 (m, 3H), 7.26-7.22 (m, 1H), 7.14-7.11 (m, 2H), 4.00 (d,  $J = 15.1$  Hz, 1H), 3.95 (d,  $J = 15.1$  Hz, 1H), 1.55 (s, 3H);  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  173.3, 157.9, 140.9, 137.8, 136.5, 130.5, 130.3, 129.8, 129.3, 129.0, 128.8, 126.2, 125.7, 119.2, 61.4, 50.6. HRMS (ESI)  $m/z$  calcd for  $\text{C}_{23}\text{H}_{20}\text{ClN}_2\text{O}_3\text{S}^+$   $[\text{M}+\text{H}]^+$  439.0878, found 439.0872.



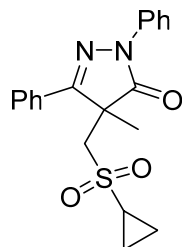
**4-Methyl-2,5-diphenyl-4-((quinolin-8-ylsulfonyl)methyl)-2,4-dihydro-3H-pyrazol-3-one (3al, 20 mg, 44% yield),** colorless oil;  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  9.09-9.07 (m, 1H), 8.14-8.11 (m, 1H), 8.01-7.99 (m, 1H), 7.95-7.92 (m, 2H), 7.72-7.70 (m, 1H), 7.48-7.46 (m, 1H), 7.45-7.41 (m, 2H), 7.33-7.29 (m, 3H), 7.25-7.22 (m, 1H), 6.97 (t,  $J = 7.4$  Hz, 1H), 6.83 (t,  $J = 7.9$  Hz, 2H), 5.17 (d,  $J = 15.3$  Hz, 1H), 4.43 (d,  $J = 15.3$  Hz, 1H), 1.59 (s, 3H);  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  174.1, 151.2, 136.8, 134.9, 134.8, 132.7, 129.7, 129.5, 128.9, 128.6, 127.7, 125.6, 125.33, 125.27, 122.1, 119.6, 60.0, 50.7, 23.9. HRMS (ESI)  $m/z$  calcd for  $\text{C}_{26}\text{H}_{22}\text{N}_3\text{O}_3\text{S}^+$   $[\text{M}+\text{H}]^+$  456.1376, found 456.1378.



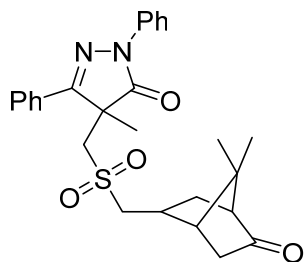
**4-((Ethylsulfonyl)methyl)-4-methyl-2,5-diphenyl-2,4-dihydro-3H-pyrazol-3-one (3am, 26 mg, 74% yield),** colorless oil;  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.01 (d,  $J = 8.4$  Hz, 2H), 7.88 (d,  $J = 4.0$



Hz, 2H), 7.44 (t,  $J = 8.5$  Hz, 5H), 7.24 (t,  $J = 7.0$  Hz, 1H), 3.81 (d,  $J = 14.8$  Hz, 1H), 3.72 (d,  $J = 14.8$  Hz, 1H), 2.91-2.76 (m, 2H), 1.64 (s, 3H), 1.23 (t,  $J = 7.5$  Hz, 3H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  174.2, 158.8, 137.9, 130.7, 130.6, 129.1, 129.0, 126.6, 125.8, 119.6, 57.0, 50.5, 49.4, 24.2, 6.3. HRMS (ESI)  $m/z$  calcd for  $\text{C}_{19}\text{H}_{21}\text{N}_2\text{O}_3\text{S}^+$   $[\text{M}+\text{H}]^+$  357.1267, found 357.1255.

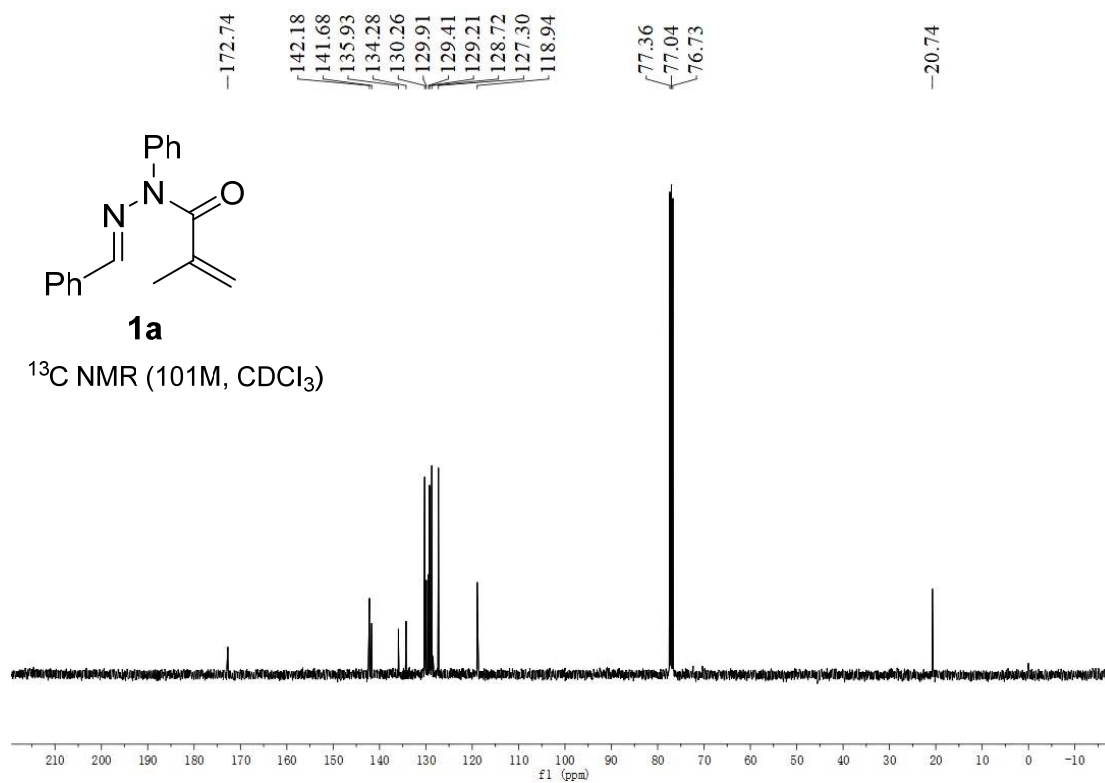
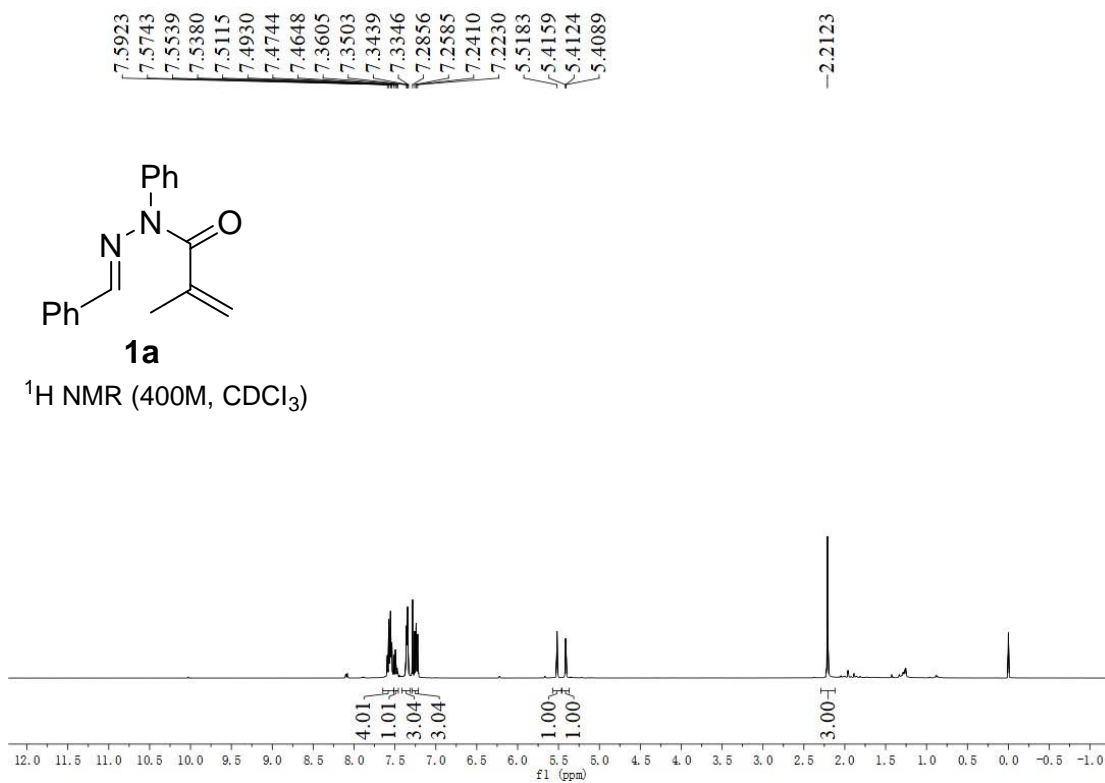


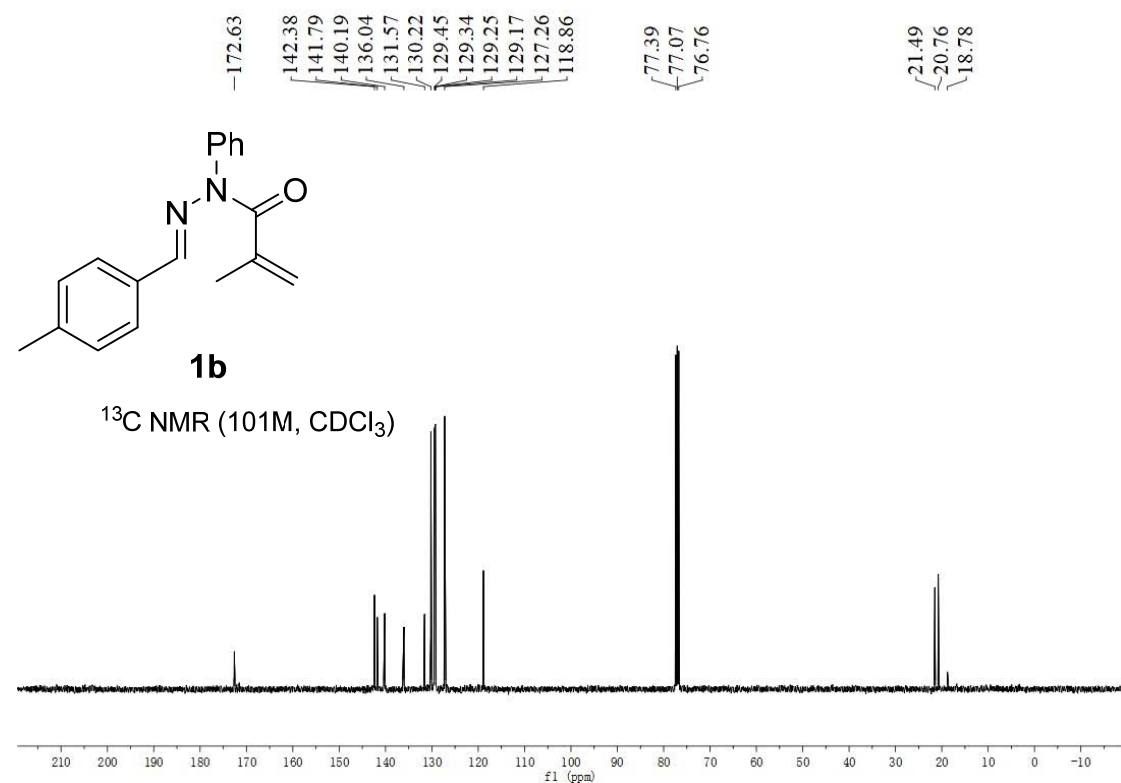
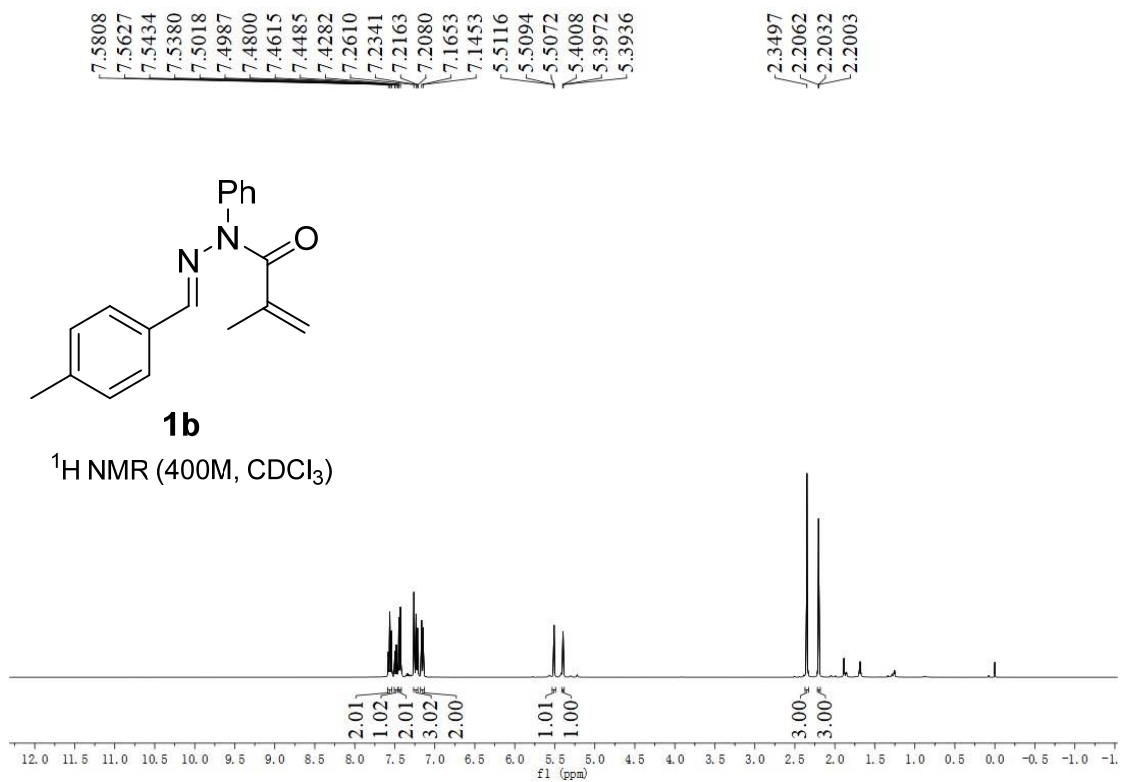
**4-((Cyclopropylsulfonyl)methyl)-4-methyl-2,5-diphenyl-2,4-dihydro-3H-pyrazol-3-one (3an,** 29 mg, 80% yield), colorless oil;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.04-8.01 (m, 2H), 7.92-7.89 (m, 2H), 7.50-7.42 (m, 5H), 7.26-7.22 (m, 1H), 3.95 (d,  $J = 14.9$  Hz, 1H), 3.85 (d,  $J = 14.9$  Hz, 1H), 2.23-2.17 (m, 1H), 1.65 (s, 3H), 1.15-1.08 (m, 1H), 1.06-1.0 (m, 1H), 0.88-0.81 (m, 1H), 0.76-0.69 (m, 1H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  174.2, 158.8, 137.9, 130.7, 130.6, 129.0, 126.6, 125.7, 119.4, 59.4, 50.6, 31.2, 24.2, 5.7, 5.4. HRMS (ESI)  $m/z$  calcd for  $\text{C}_{20}\text{H}_{21}\text{N}_2\text{O}_3\text{S}^+$   $[\text{M}+\text{H}]^+$  369.1267, found 369.1263.

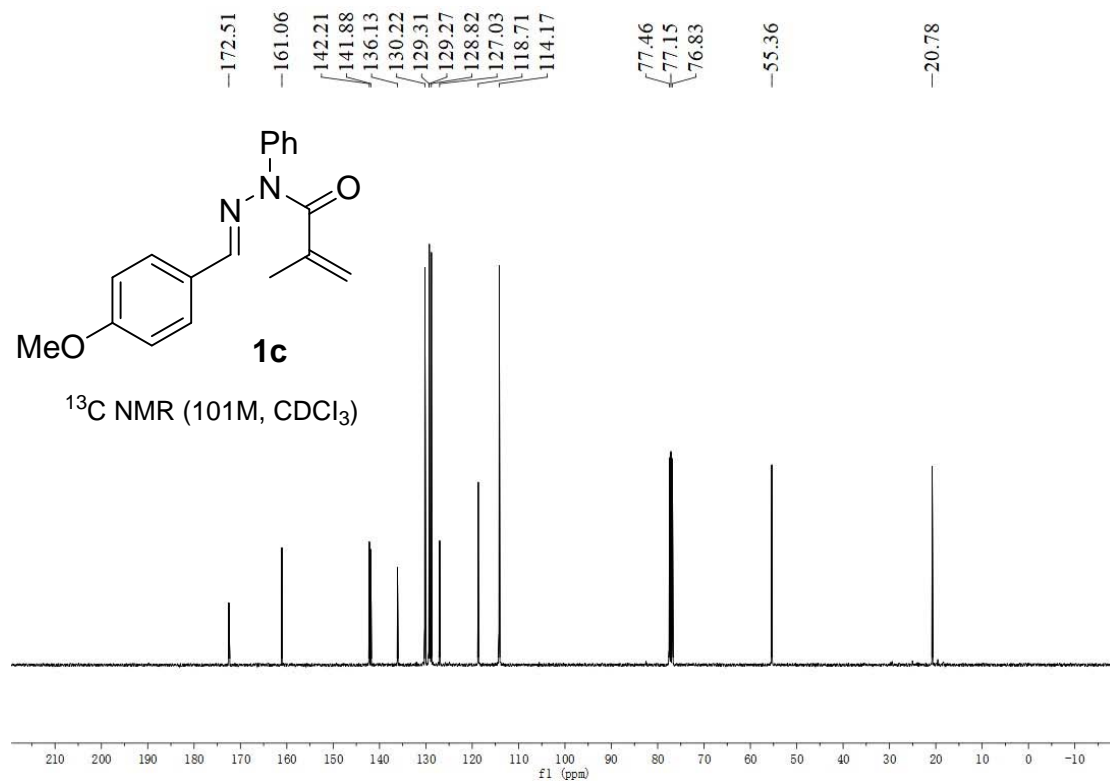
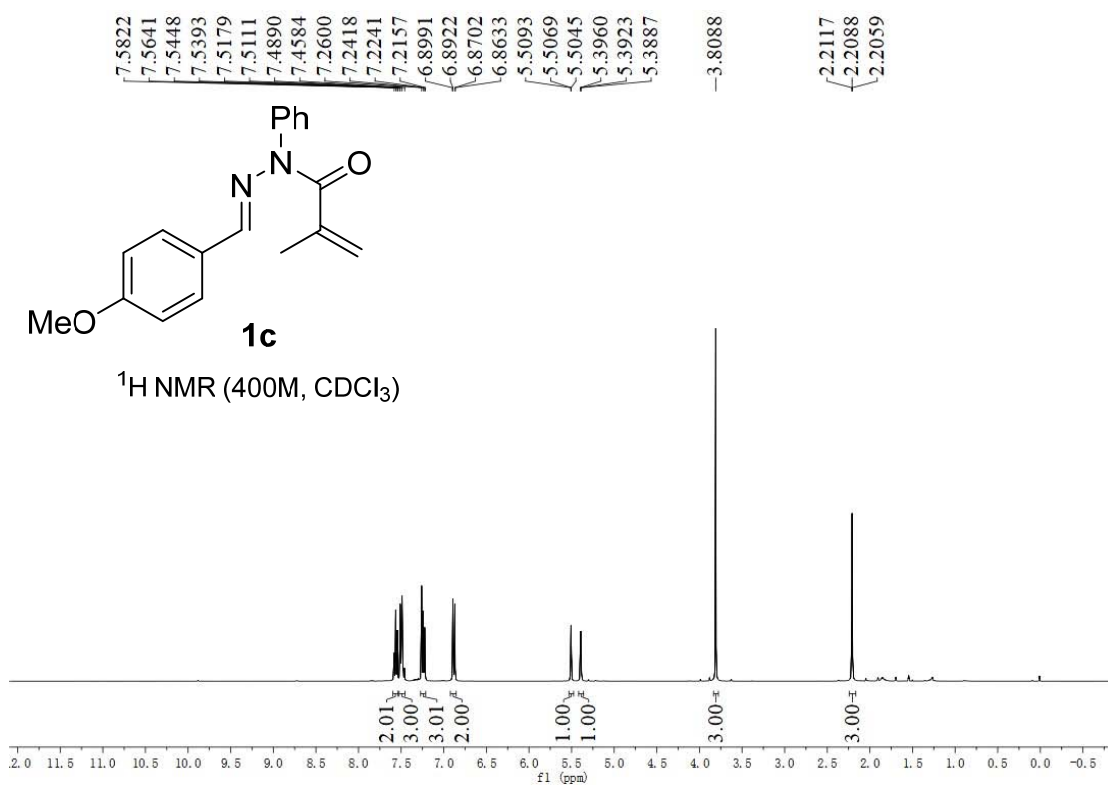


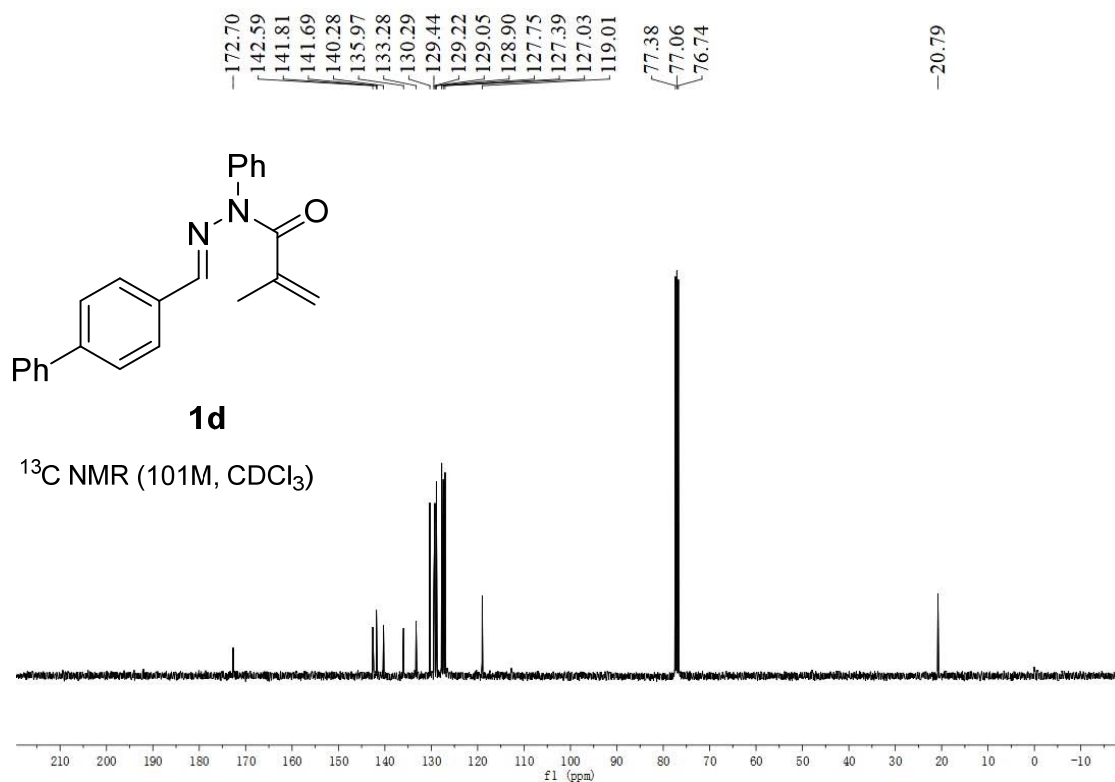
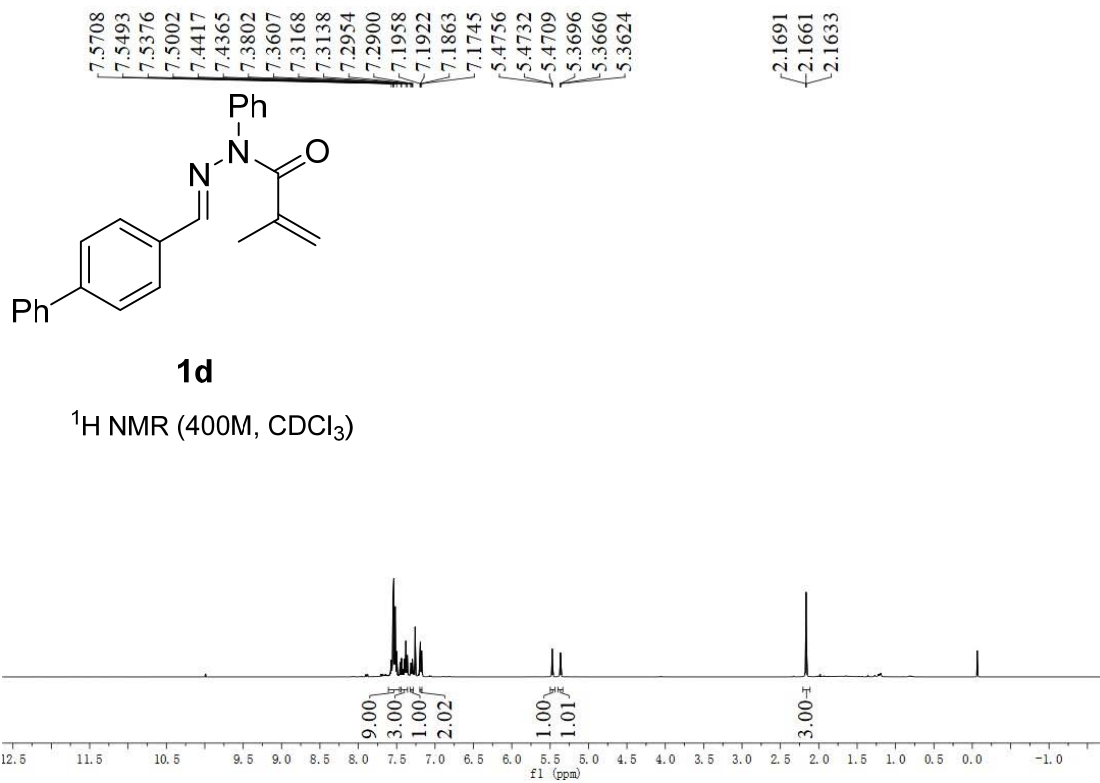
**4-(((1R,4S)-7,7-dimethyl-5-oxobicyclo[2.2.1]heptan-2-yl)methyl)sulfonyl)methyl)-4-methyl-2,5-diphenyl-2,4-dihydro-3H-pyrazol-3-one (3ao,** 39 mg, 82% yield), colorless oil;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.04-7.95 (m, 3H), 7.90-7.88 (m, 1H), 7.49-7.41 (m, 5H), 7.25-7.21 (m, 1H), 4.48 (d,  $J = 15.1$  Hz, 0.5H), 4.25 (d,  $J = 14.9$  Hz, 0.5H), 4.10 (d,  $J = 14.9$  Hz, 0.5H), 3.98 (d,  $J = 15.0$  Hz, 0.5H), 3.43 (d,  $J = 15.0$  Hz, 0.5H), 3.17 (d,  $J = 15.1$  Hz, 0.5H), 2.75 (d,  $J = 15.0$  Hz, 0.5H), 2.51 (d,  $J = 15.1$  Hz, 0.5H), 2.40-2.26 (m, 1H), 2.21-2.09 (m, 1H), 2.06-2.02 (m, 1H), 1.92-1.86 (m, 2H), 1.76-1.70 (m, 1H), 1.67 (d,  $J = 12.0$  Hz, 3H), 1.44-1.33 (m, 1H), 0.86 (s, 1.5H), 0.82 (s, 1.5H), 0.80 (s, 1.5H), 0.50 (s, 1.5H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  215.9, 215.4, 174.4, 157.7, 138.1, 138.0, 130.7, 130.6, 130.5, 130.4, 129.1, 128.9, 126.8, 126.5, 125.59, 125.58, 119.7, 119.5, 61.1, 61.0, 59.2, 59.1, 53.8, 53.1, 50.8, 50.4, 48.9, 48.8, 42.7, 42.6, 42.43, 42.41, 27.1, 25.4, 25.1, 24.2, 24.0, 19.7, 19.4, 19.34, 19.32. HRMS (ESI)  $m/z$  calcd for  $\text{C}_{27}\text{H}_{31}\text{N}_2\text{O}_4\text{S}^+$   $[\text{M}+\text{H}]^+$  479.1999, found 479.1993.

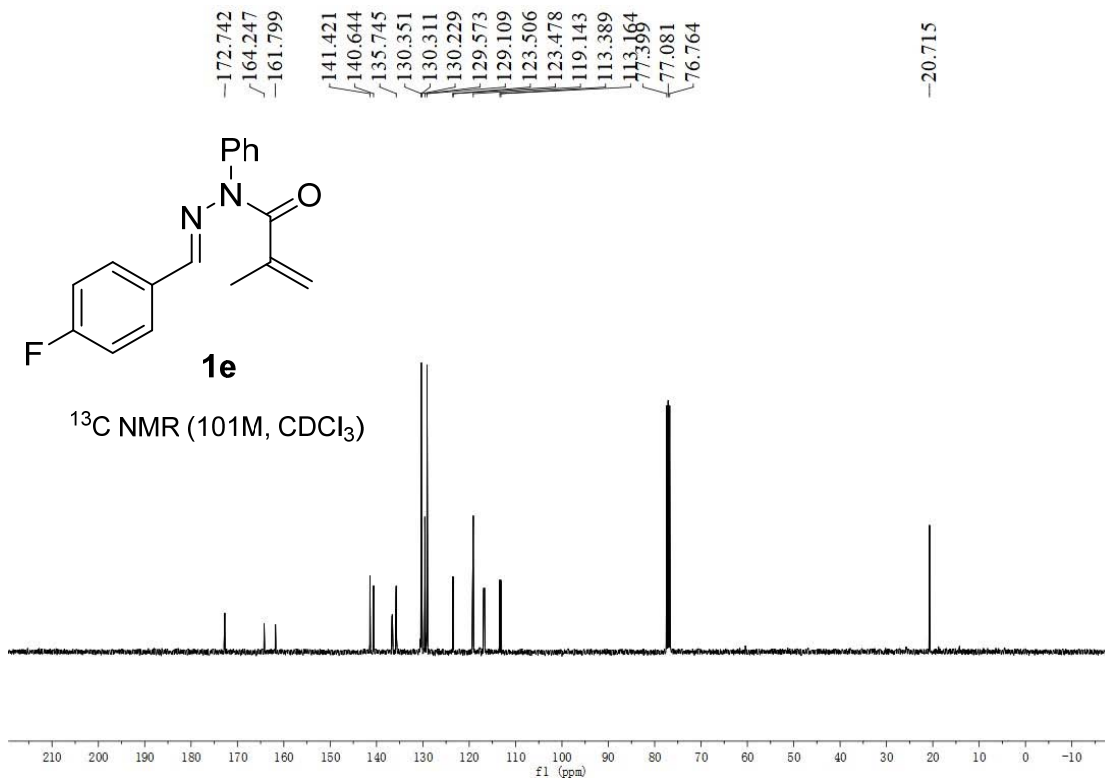
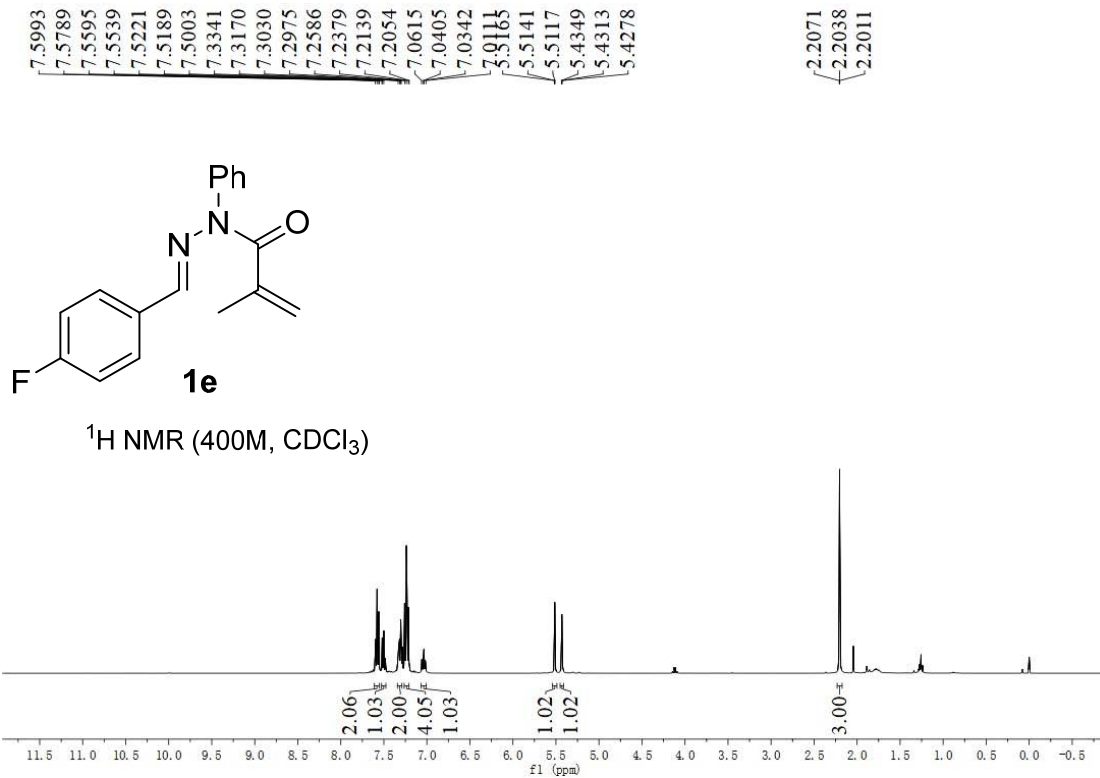
## 6. Copies of $^1\text{H}$ NMR and $^{13}\text{C}$ NMR Spectra

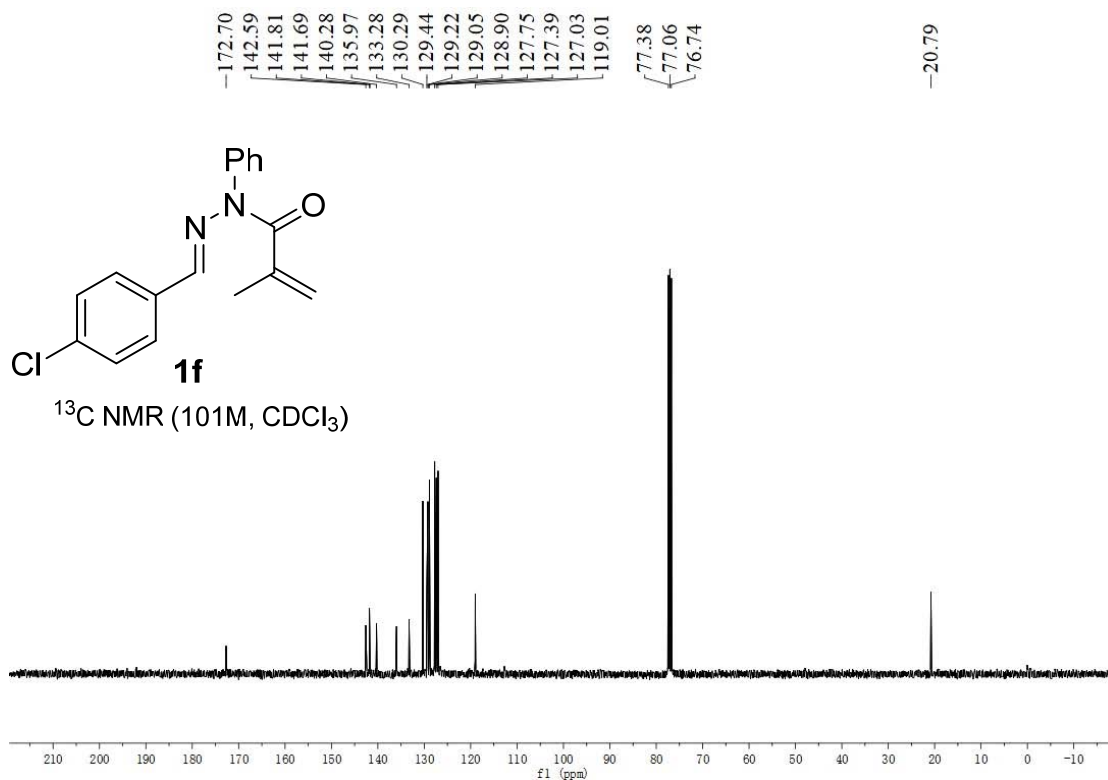
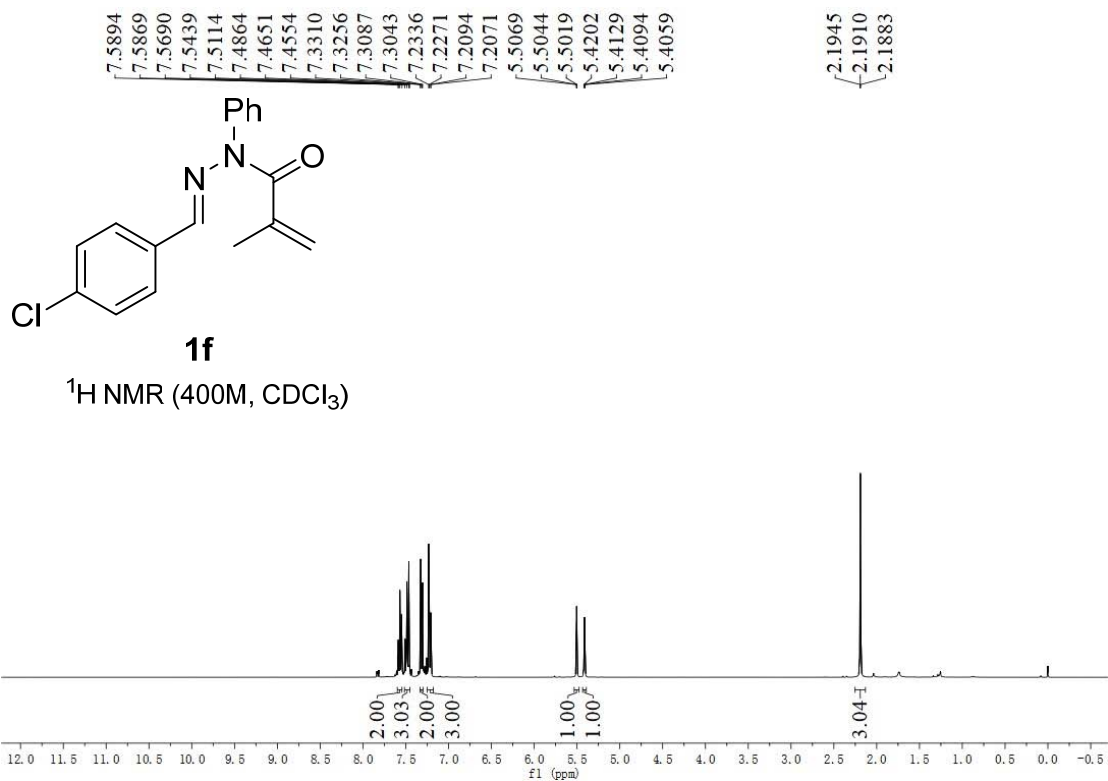


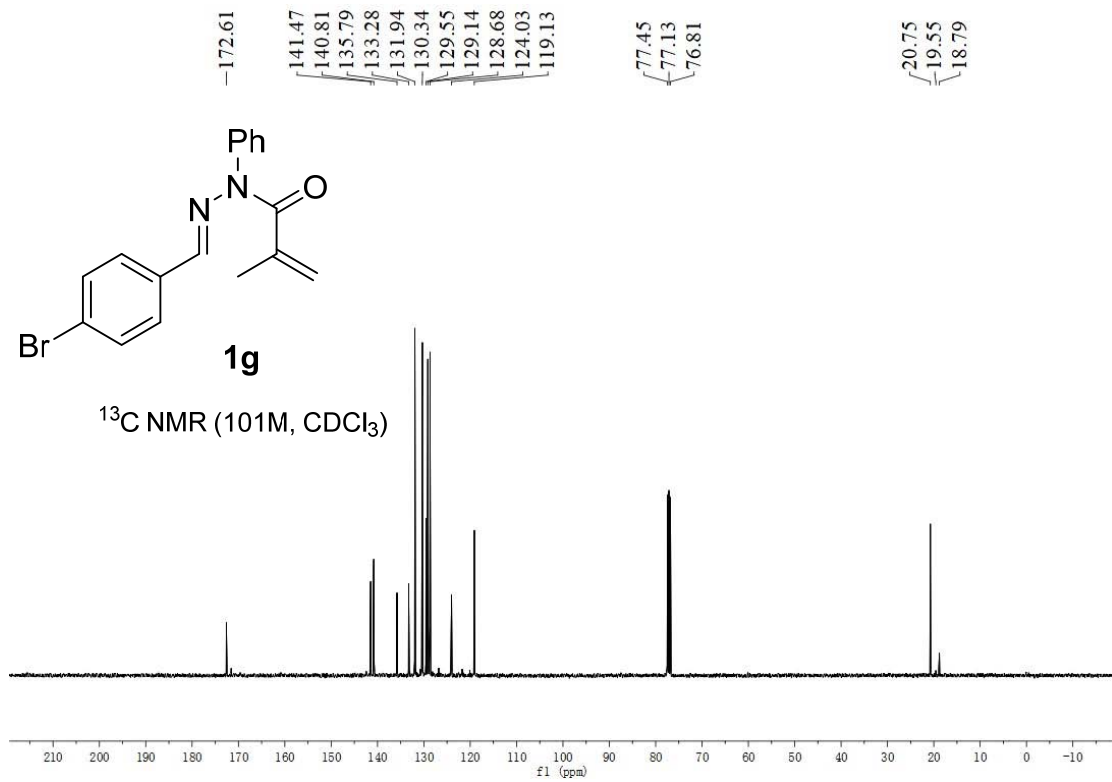
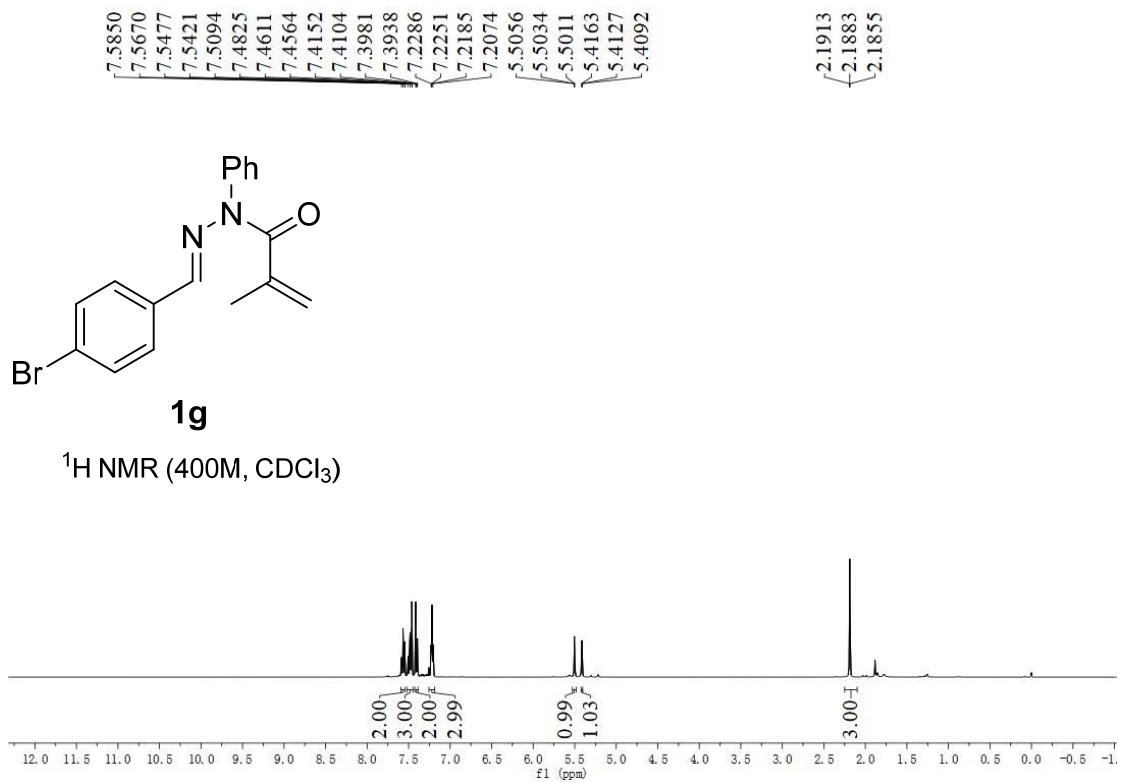








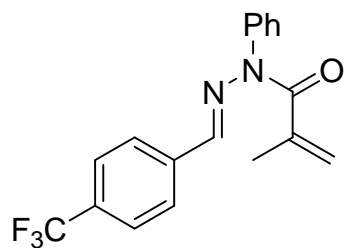






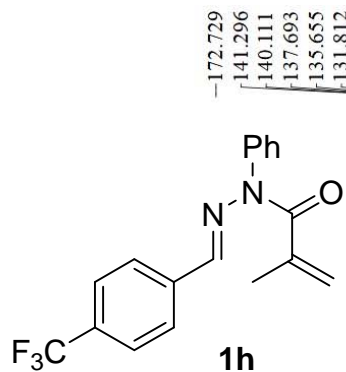
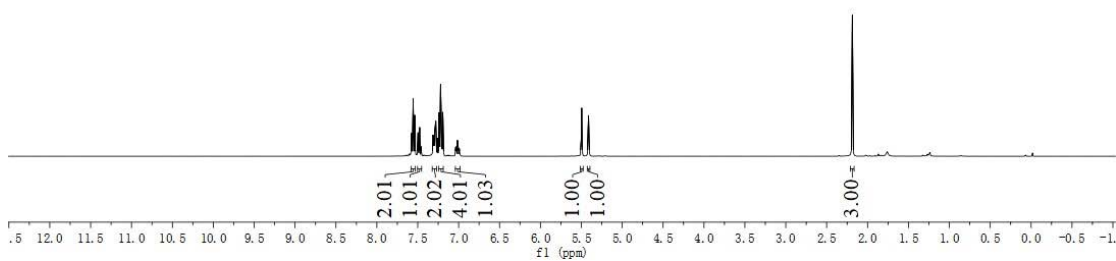
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5.4116  
5.4082

2.1884  
2.1855  
2.1827



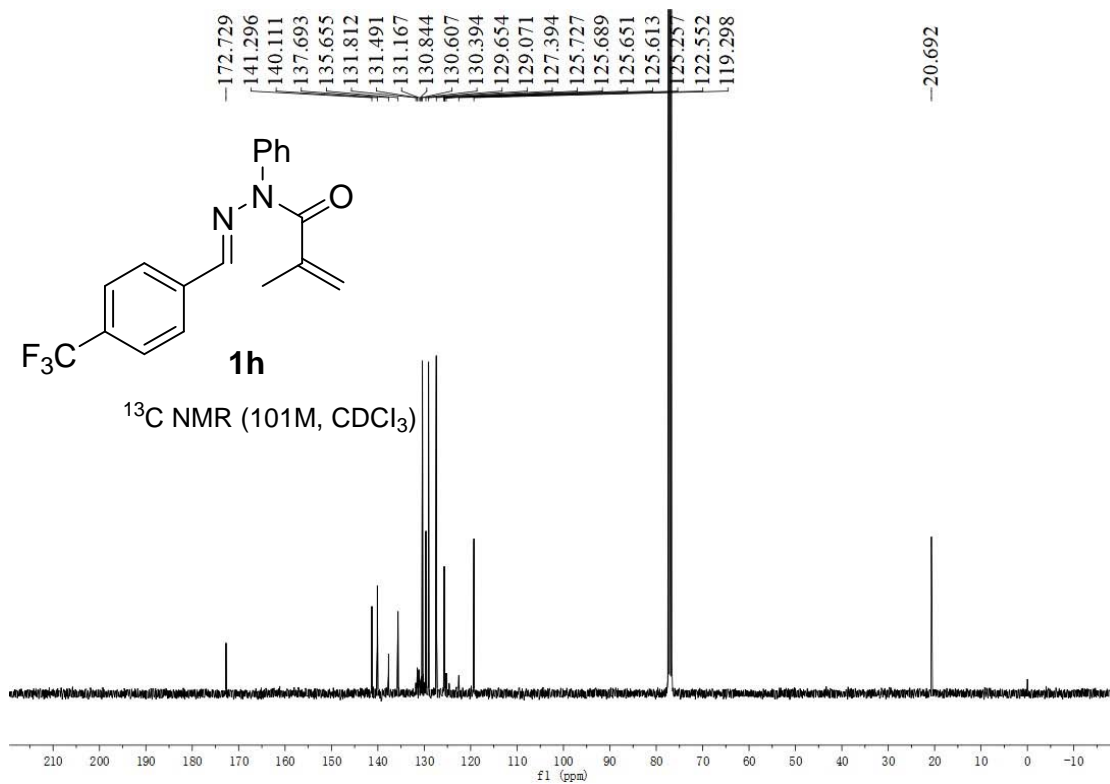
**1h**

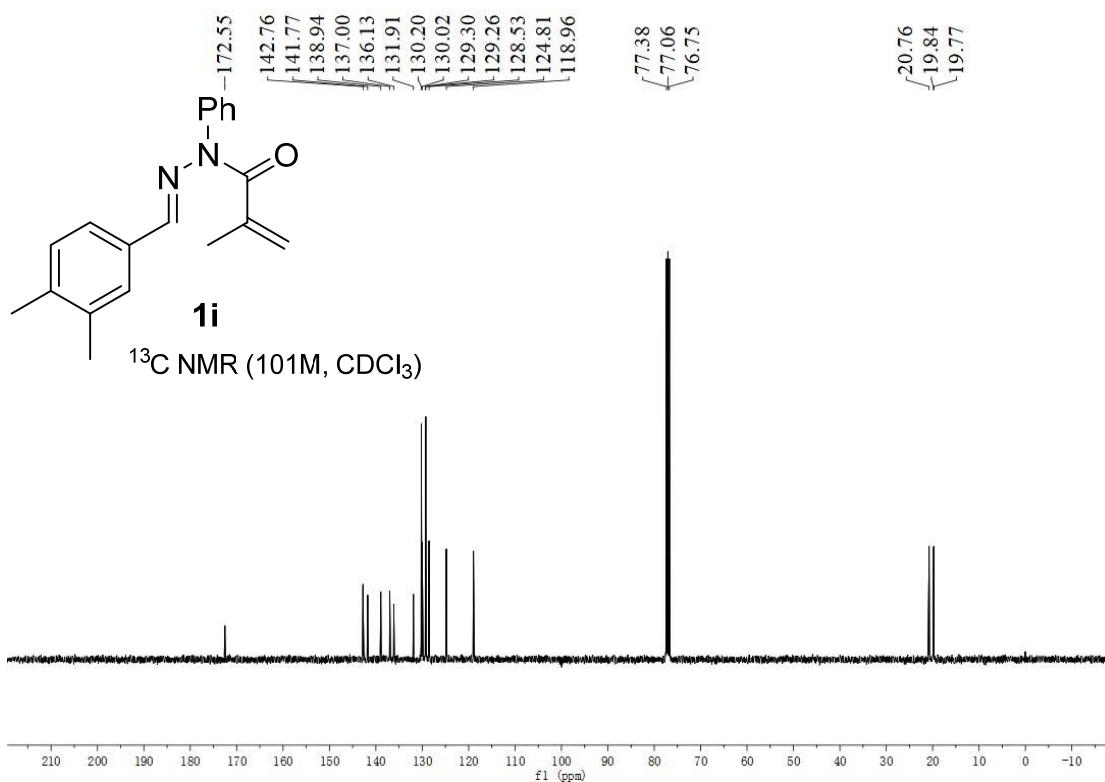
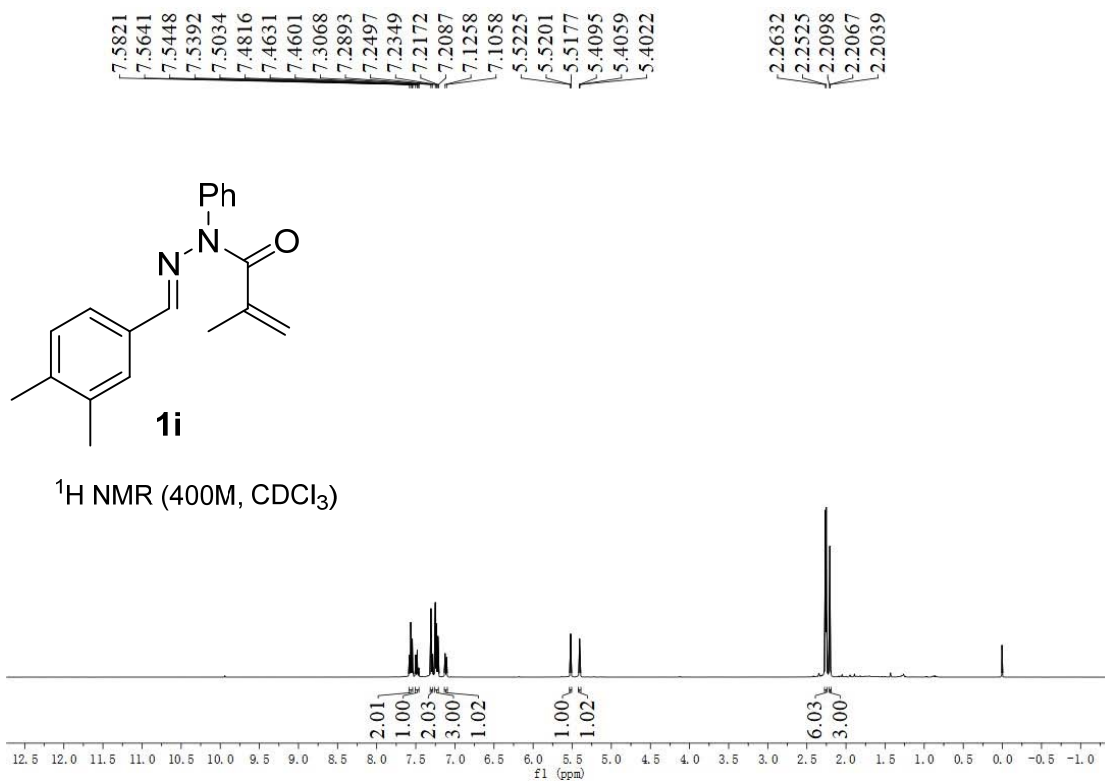
<sup>1</sup>H NMR (400M, CDCl<sub>3</sub>)

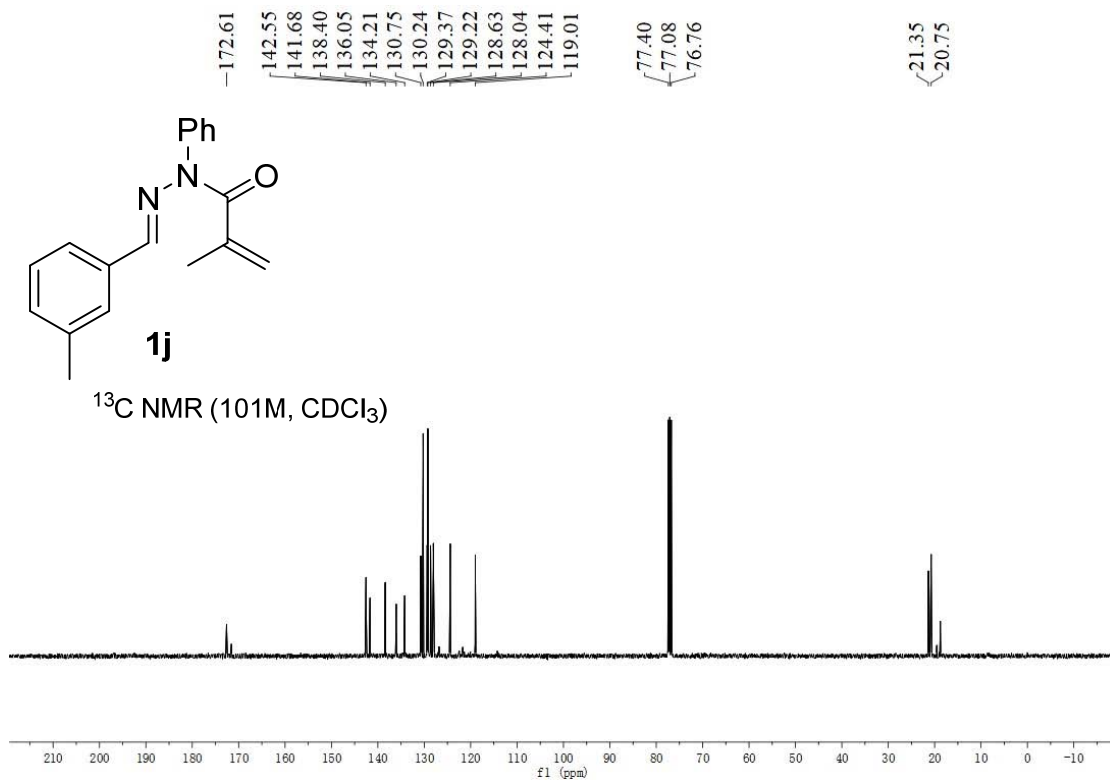
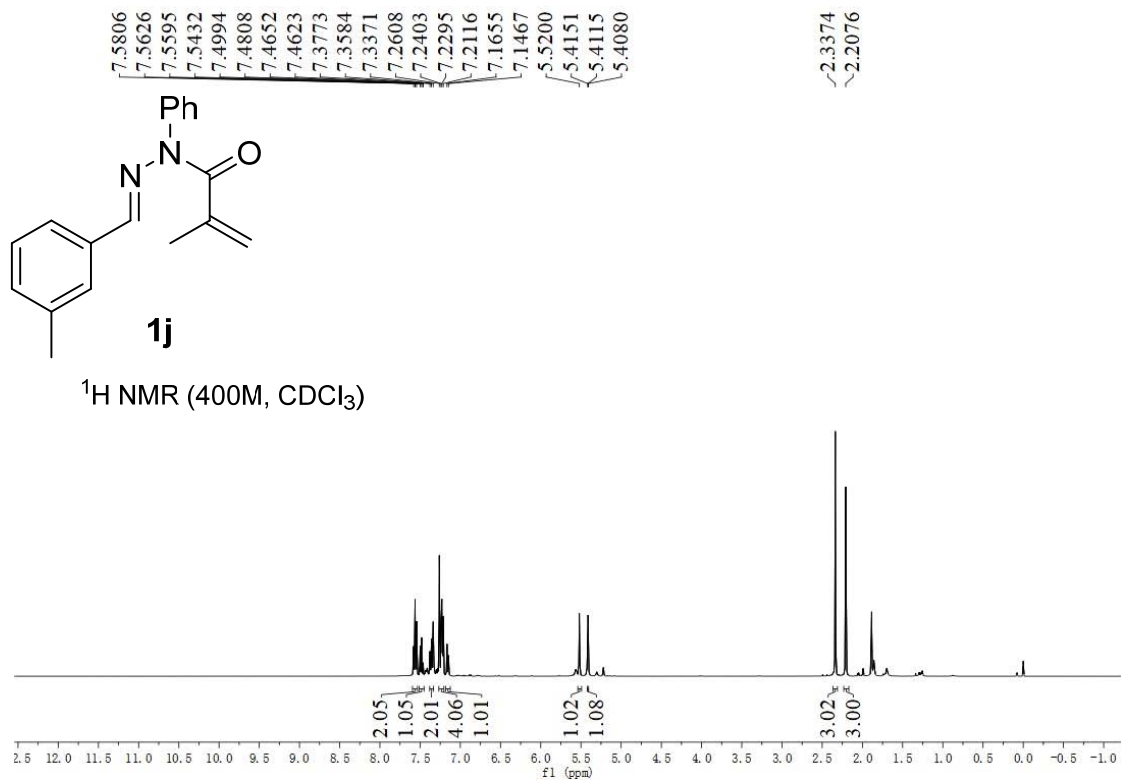


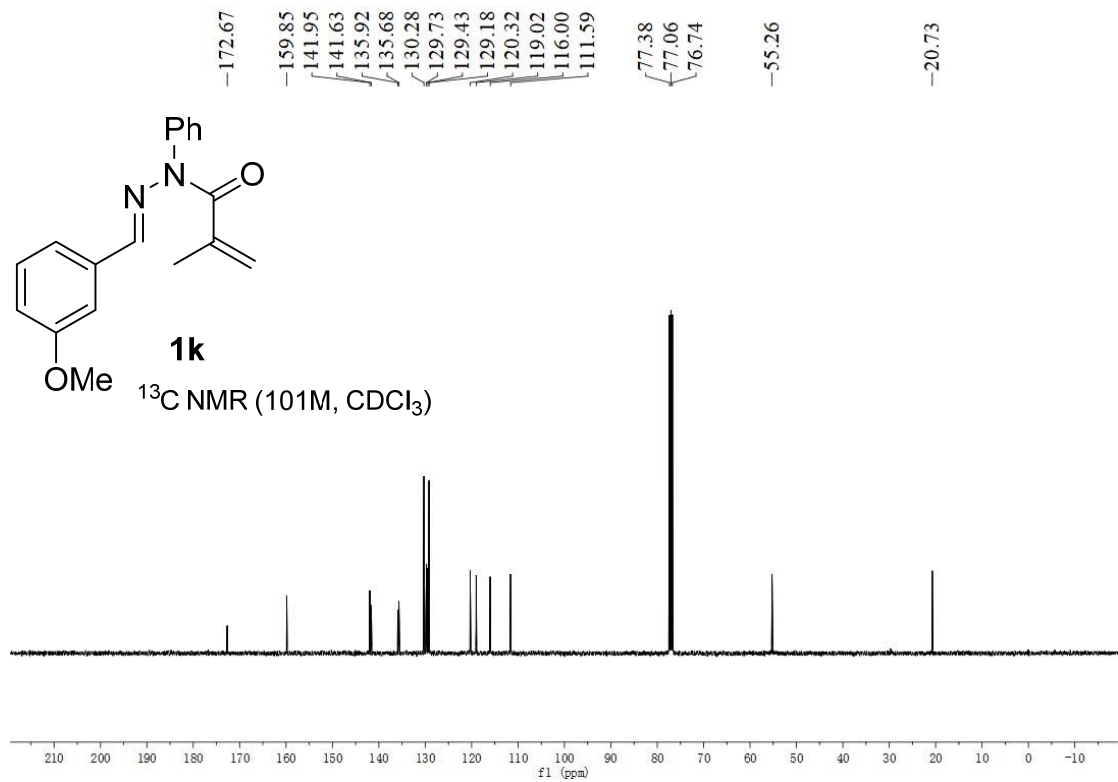
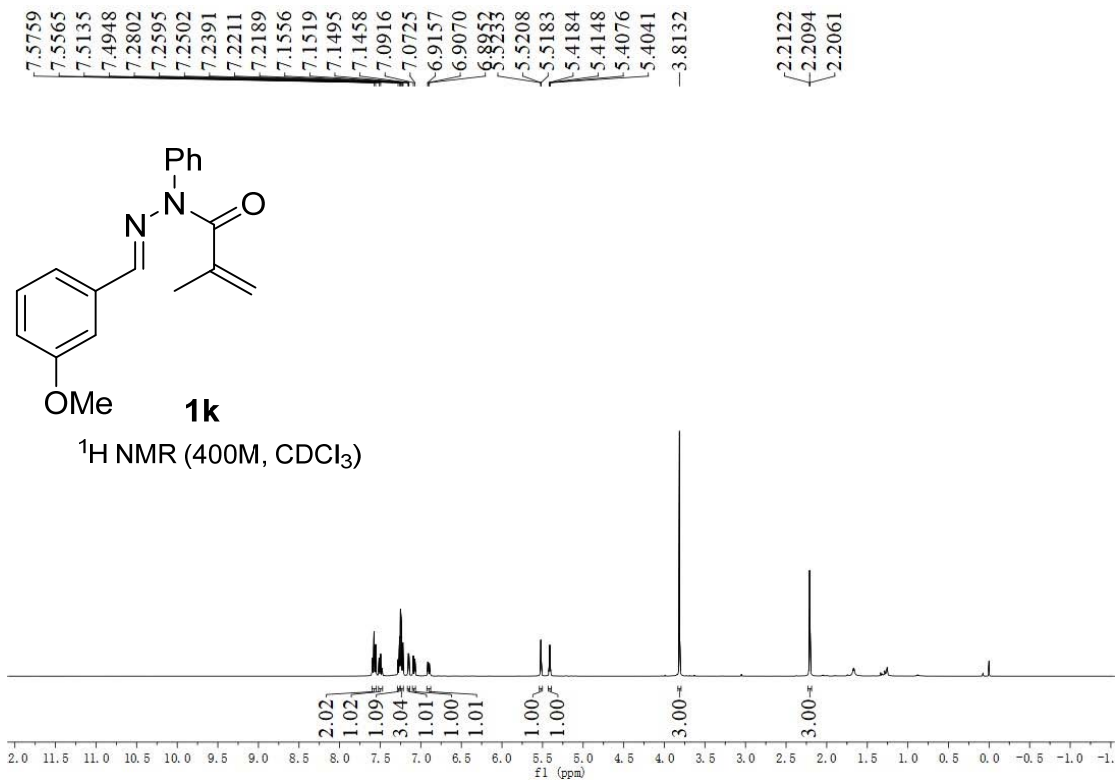
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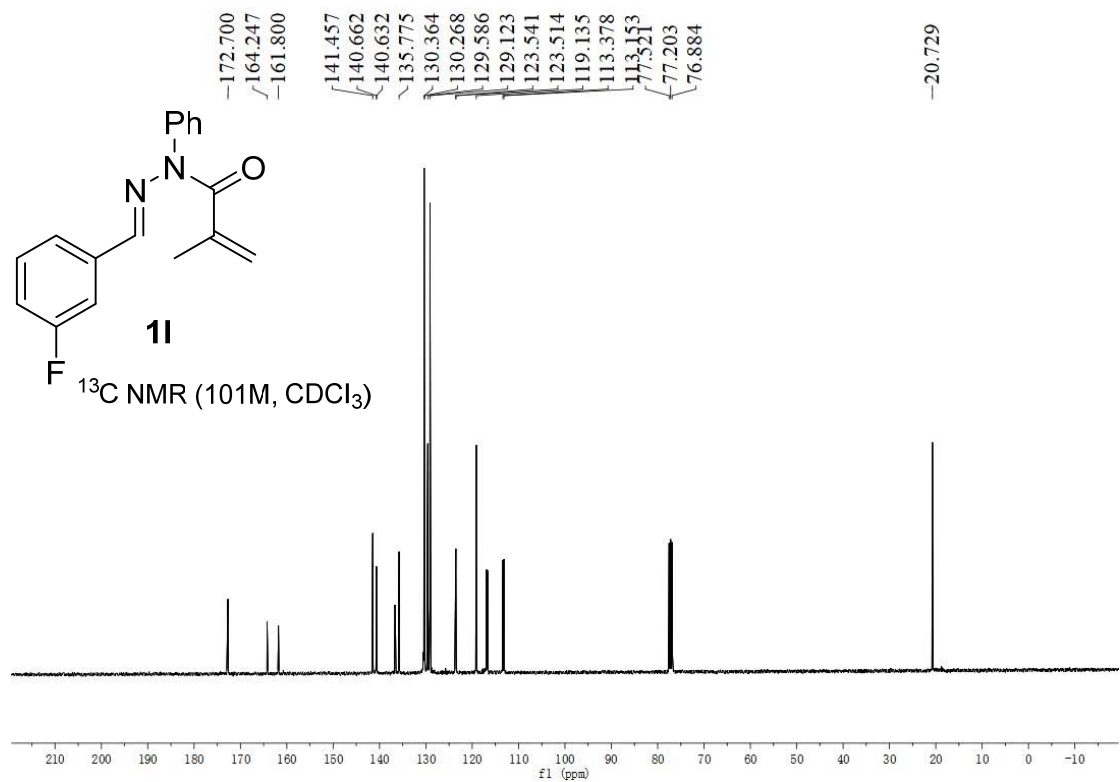
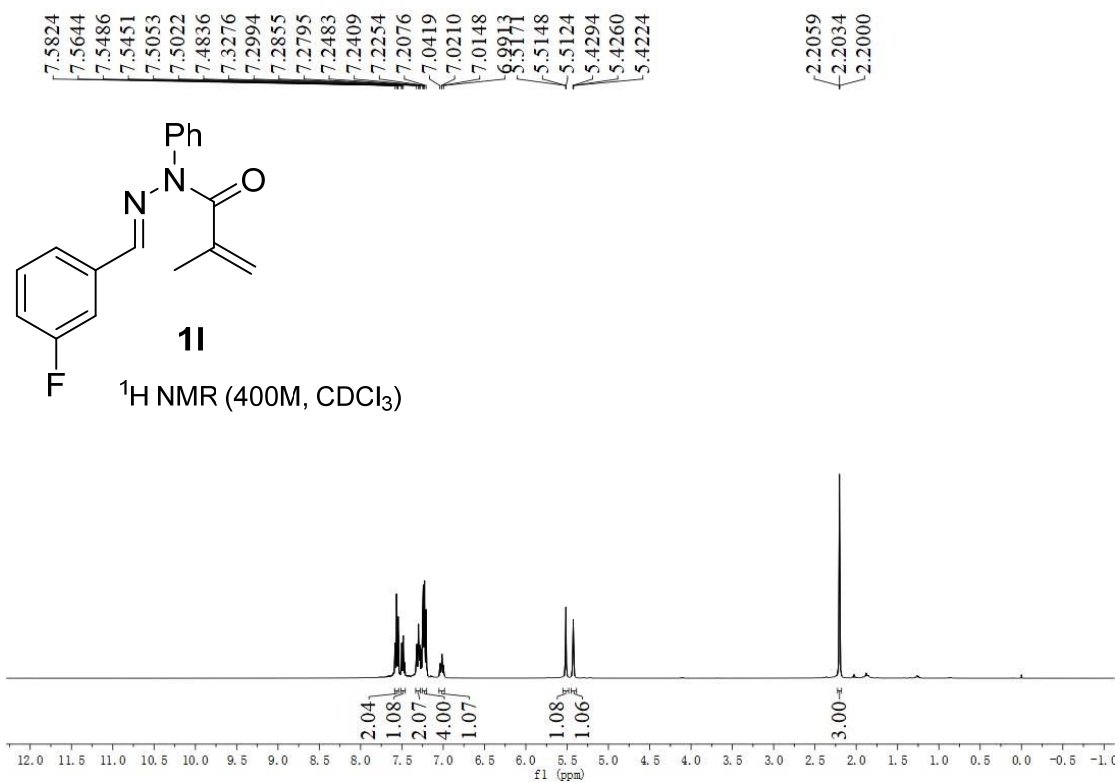
<sup>13</sup>C NMR (101M, CDCl<sub>3</sub>)

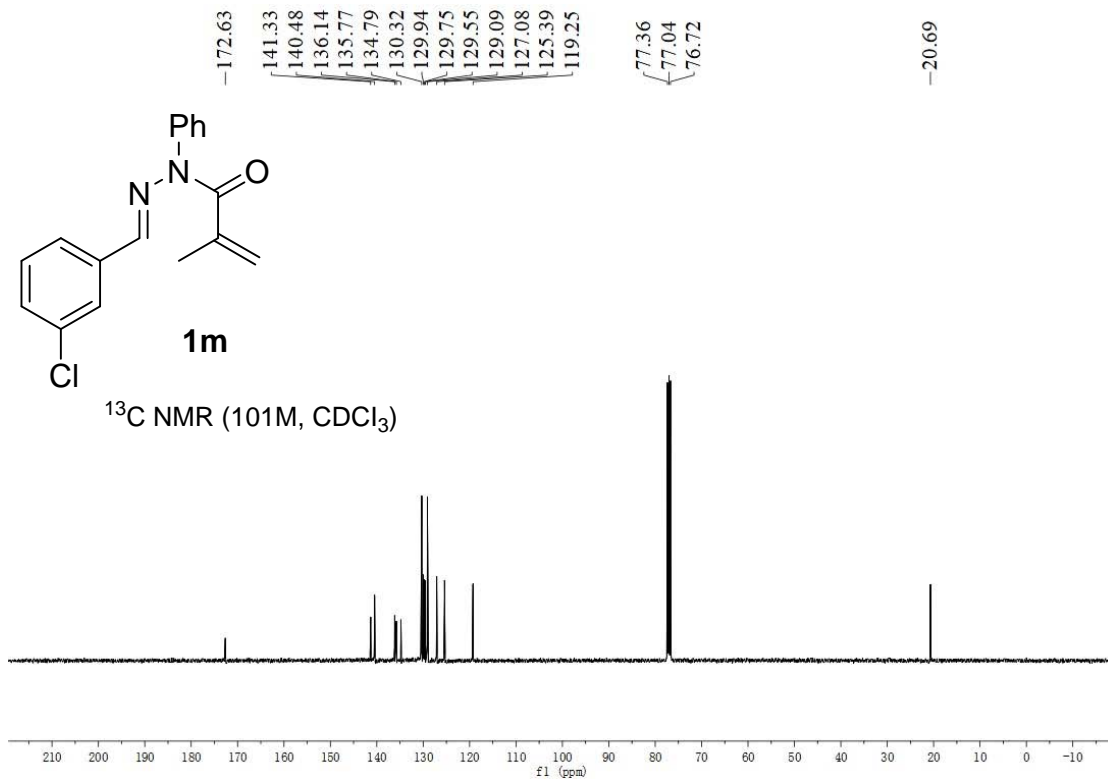
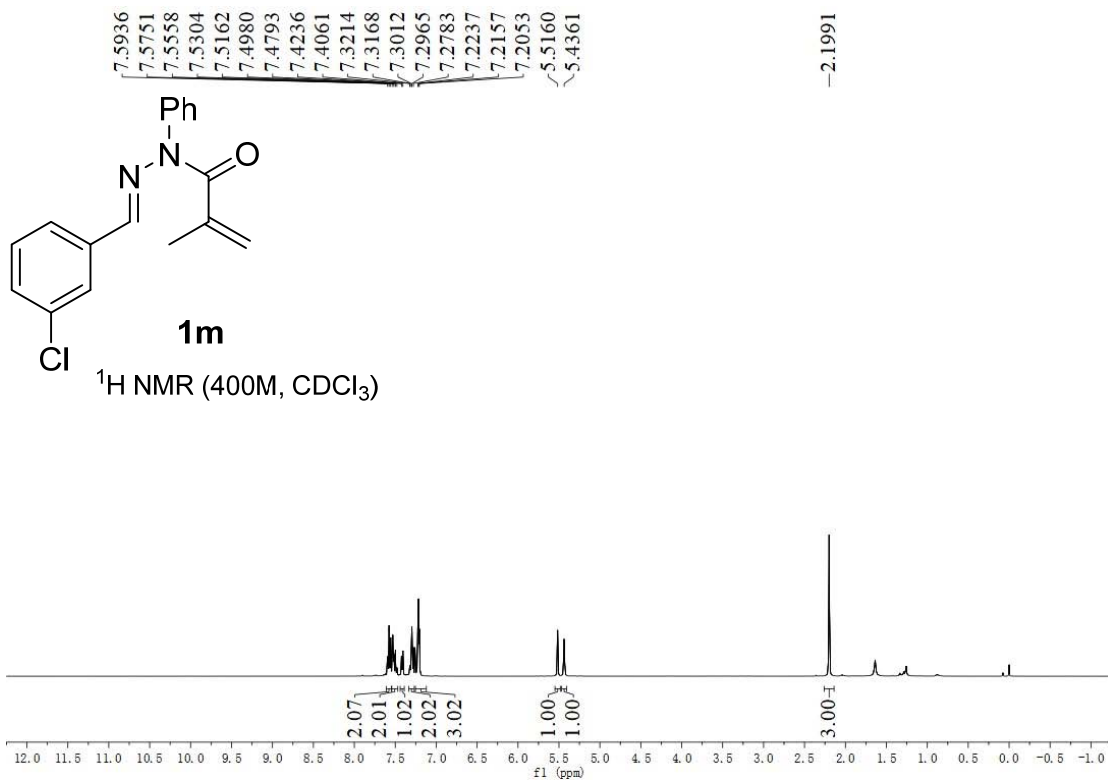


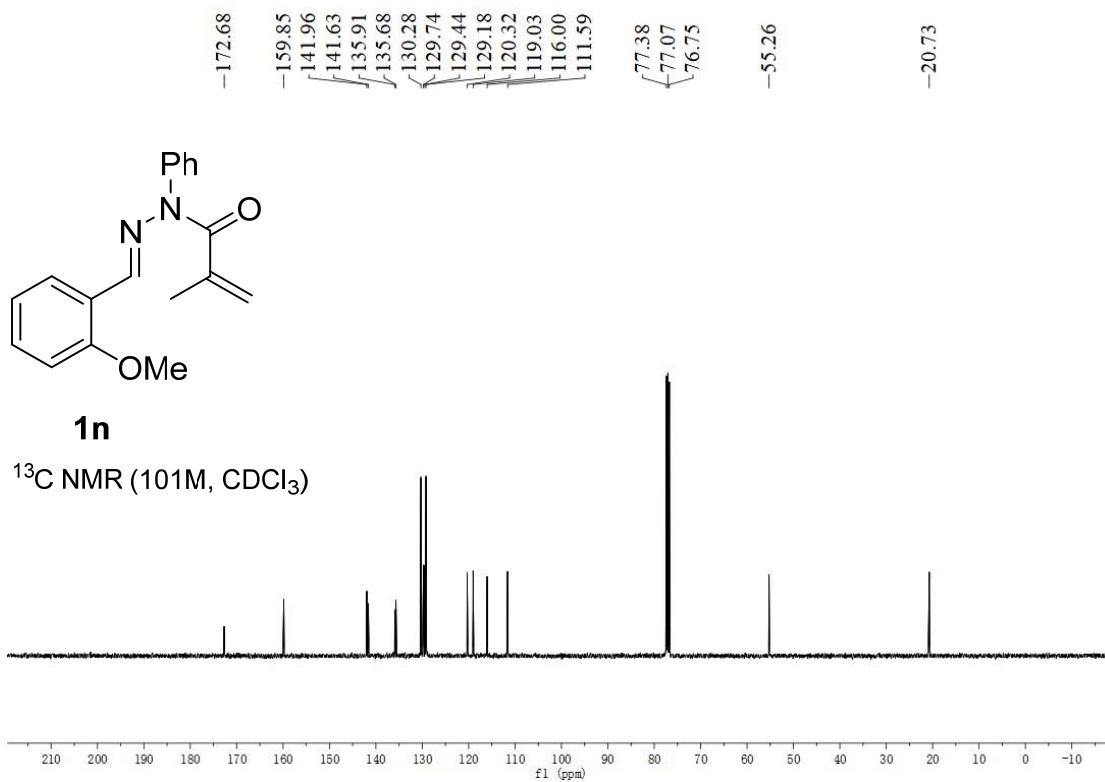
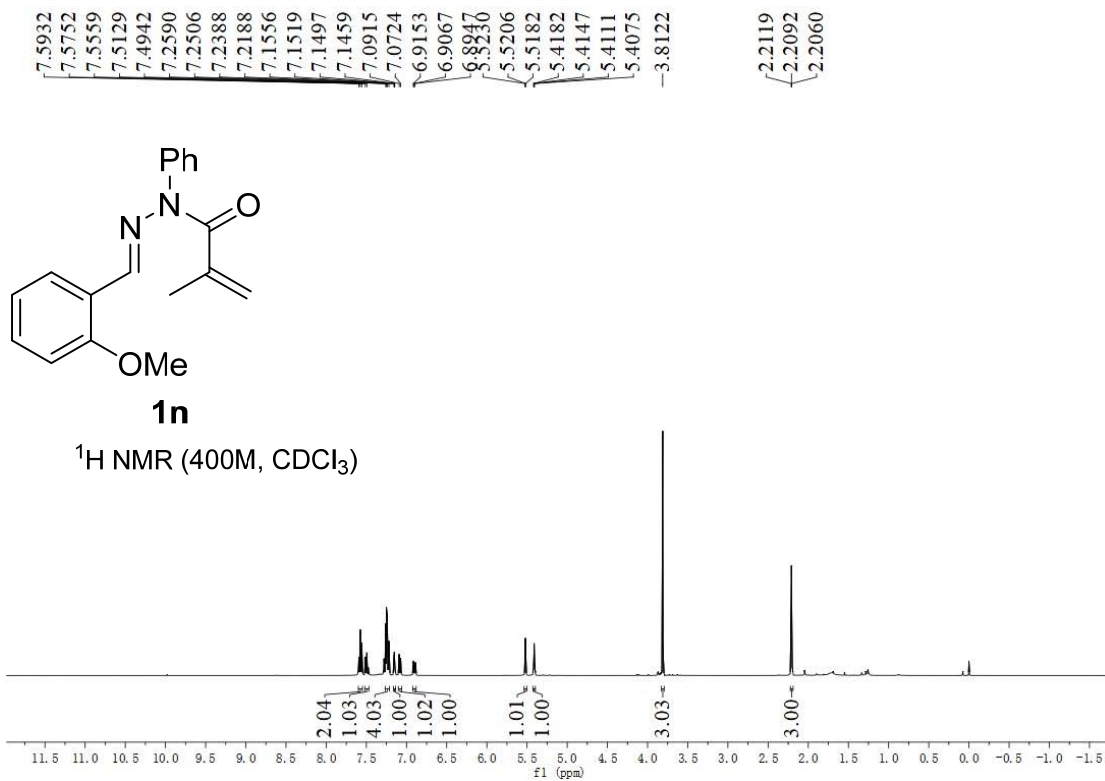


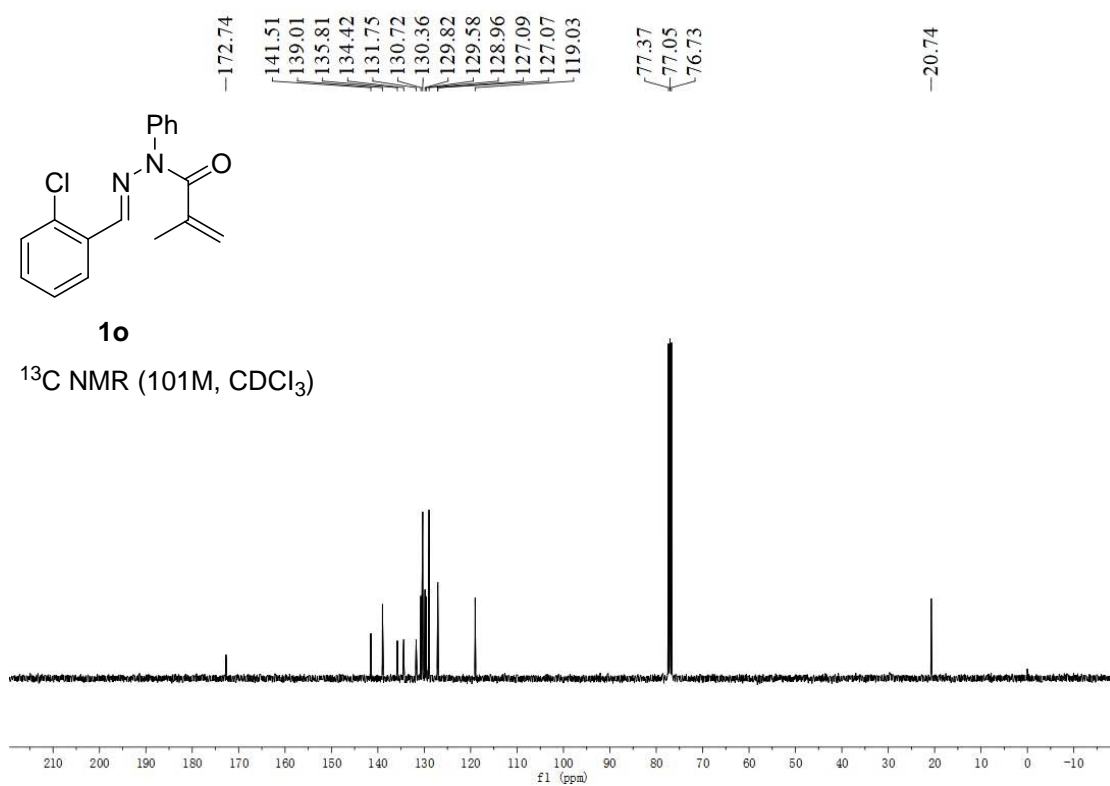
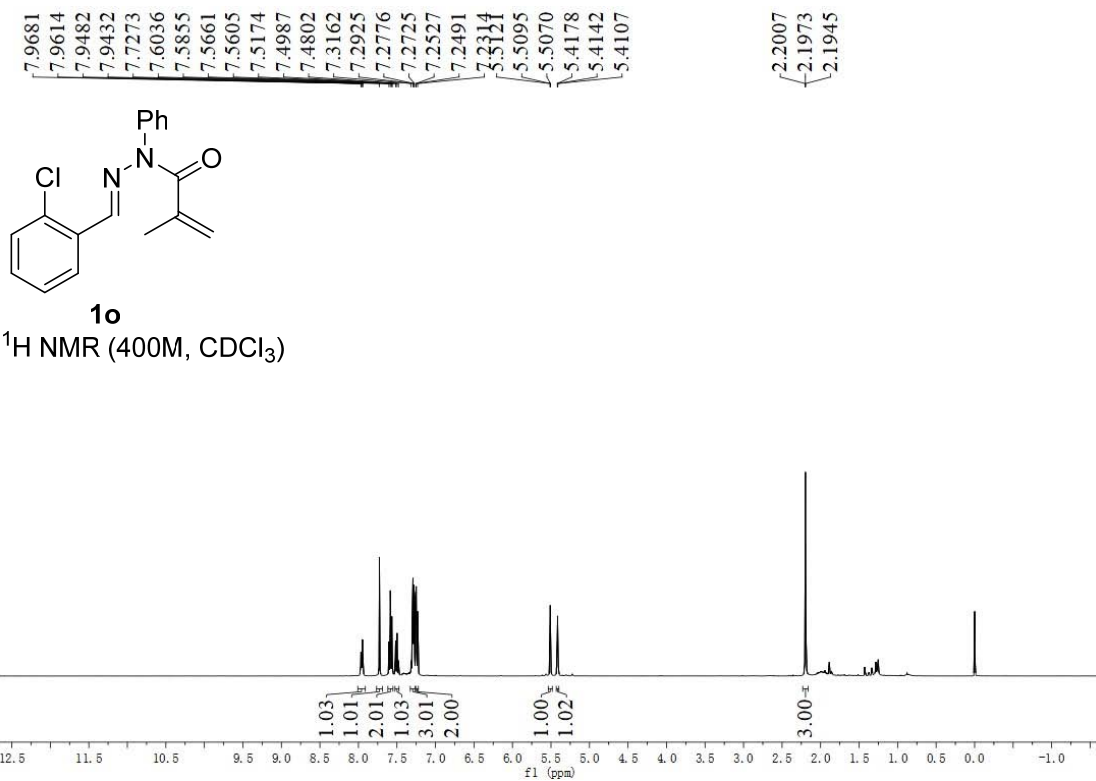




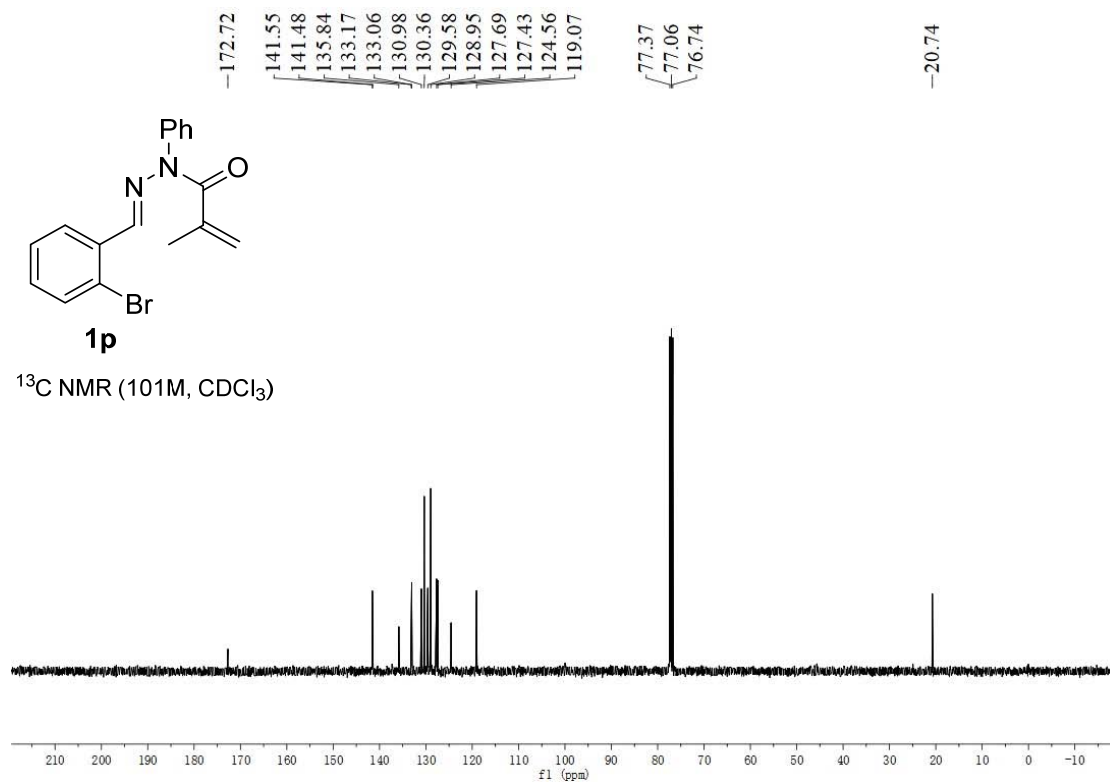
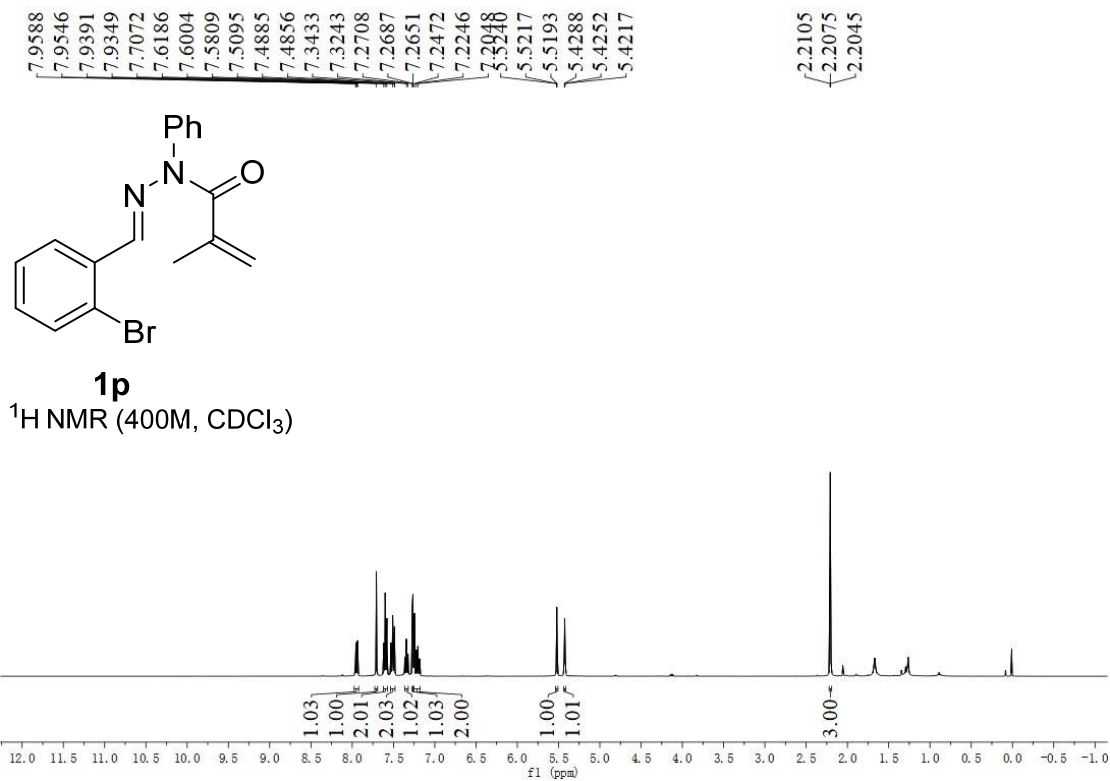


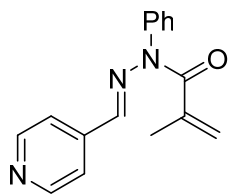






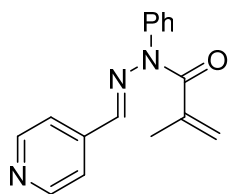
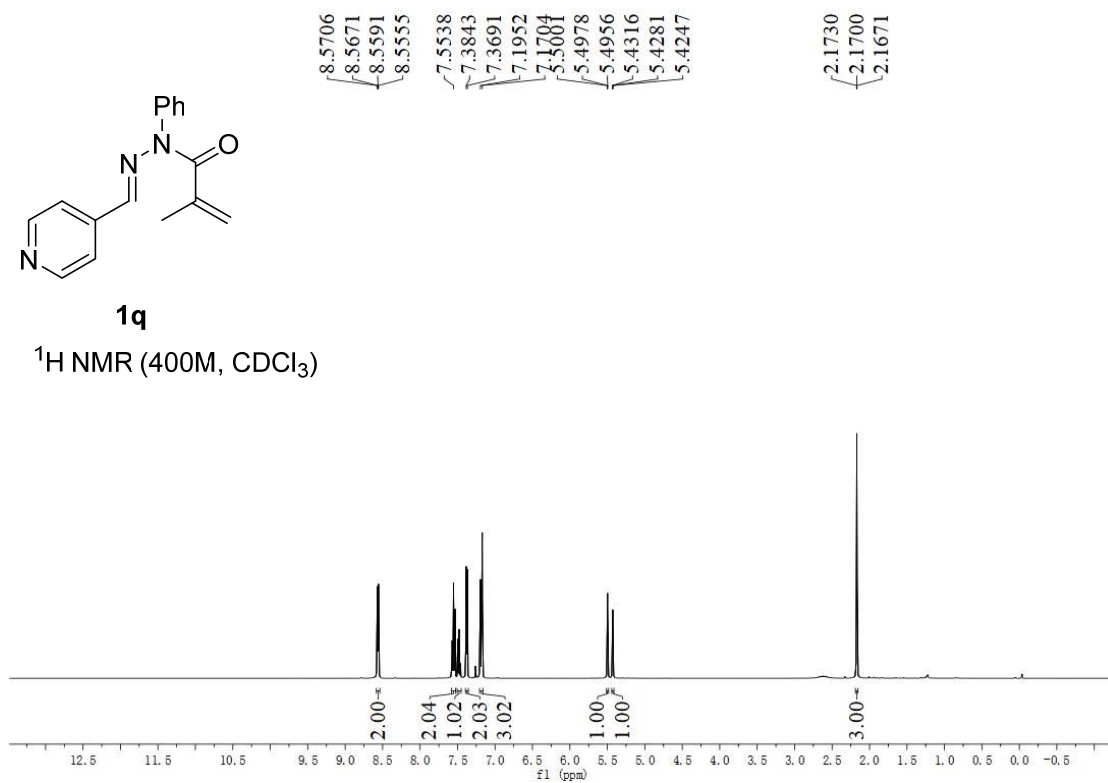






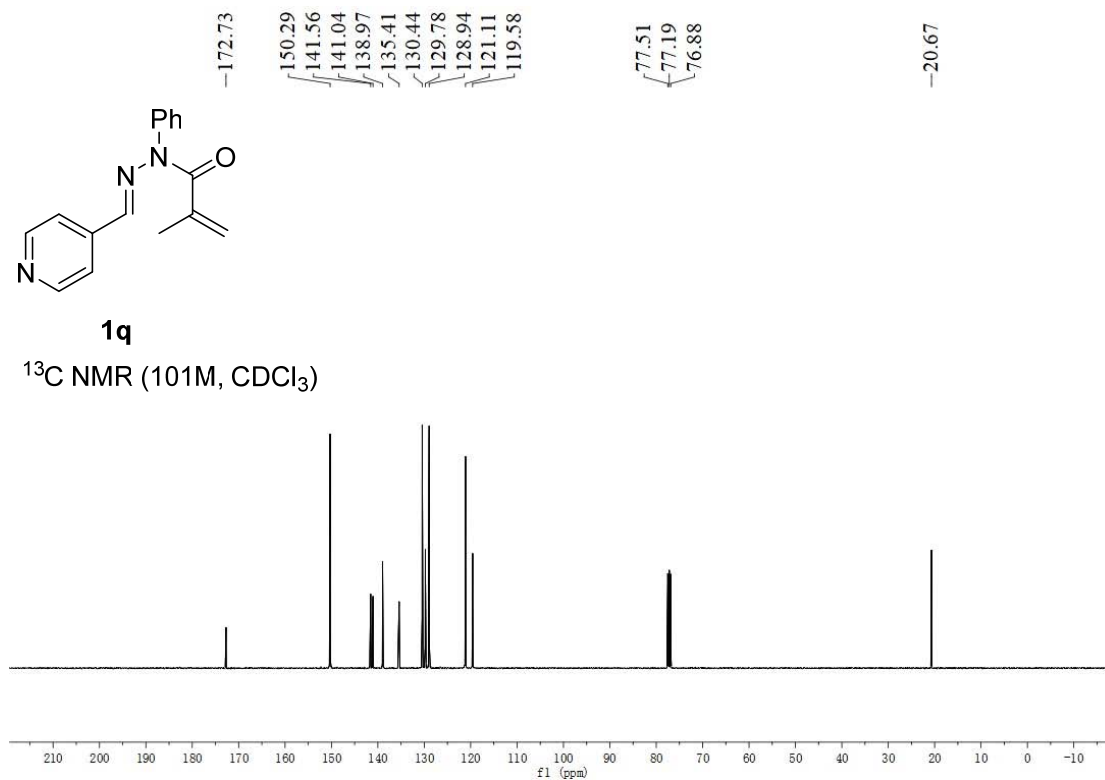
**1q**

<sup>1</sup>H NMR (400M, CDCl<sub>3</sub>)



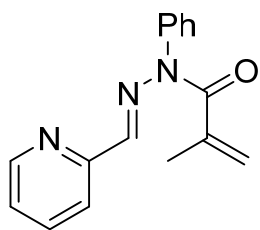
**1q**

<sup>13</sup>C NMR (101M, CDCl<sub>3</sub>)



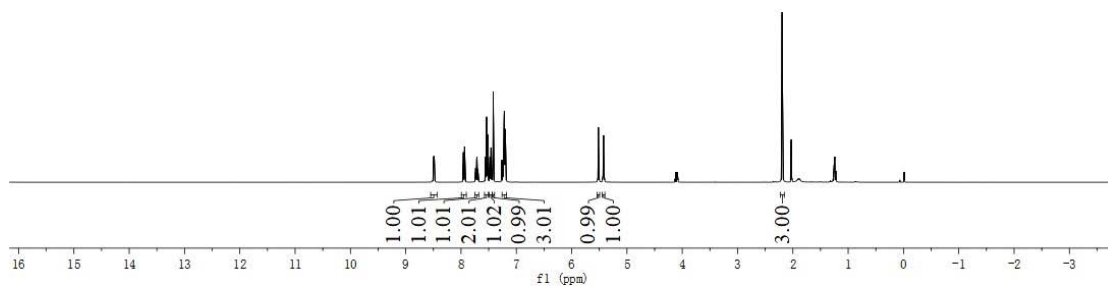
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7.5544  
7.5404  
7.5207  
7.4771  
7.4584  
7.4531  
7.4399  
7.4189  
7.2420  
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7.1994  
5.5165  
5.4272  
5.4237  
5.4203

-2.1943



**1r**

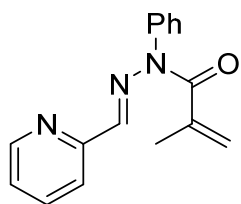
<sup>1</sup>H NMR (400M, CDCl<sub>3</sub>)



172.73  
150.29  
141.56  
141.04  
138.97  
135.41  
130.44  
129.78  
128.94  
121.11  
119.58

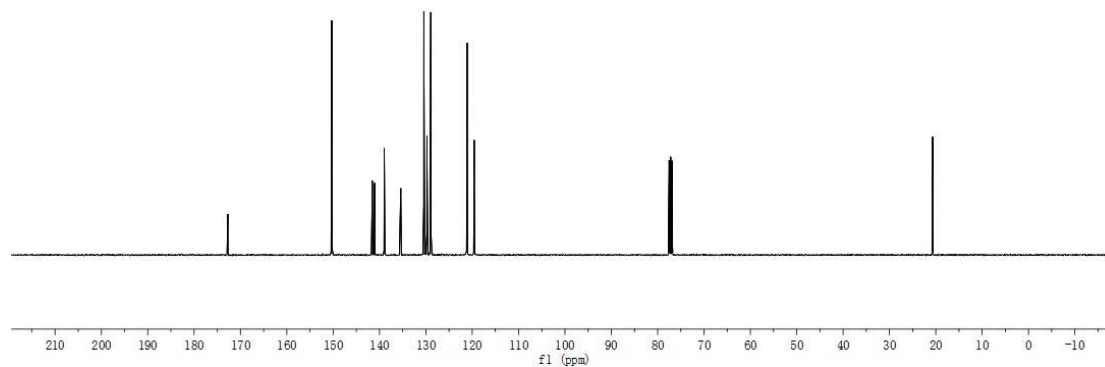
77.51  
77.19  
76.88

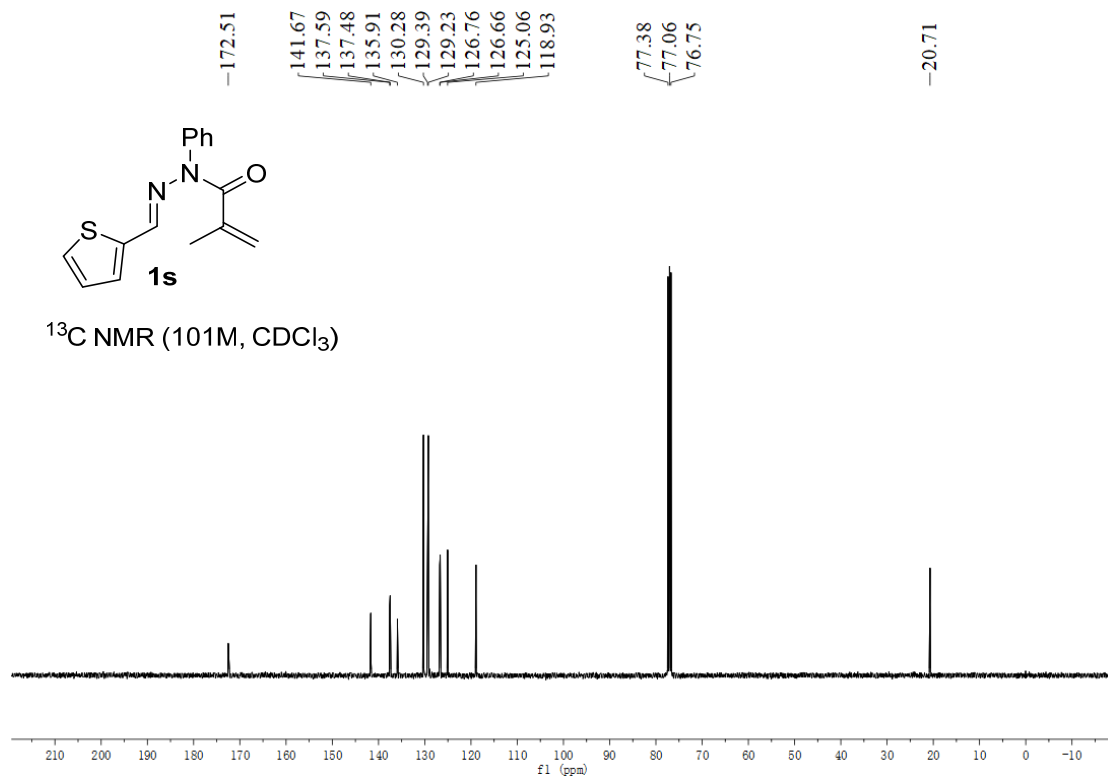
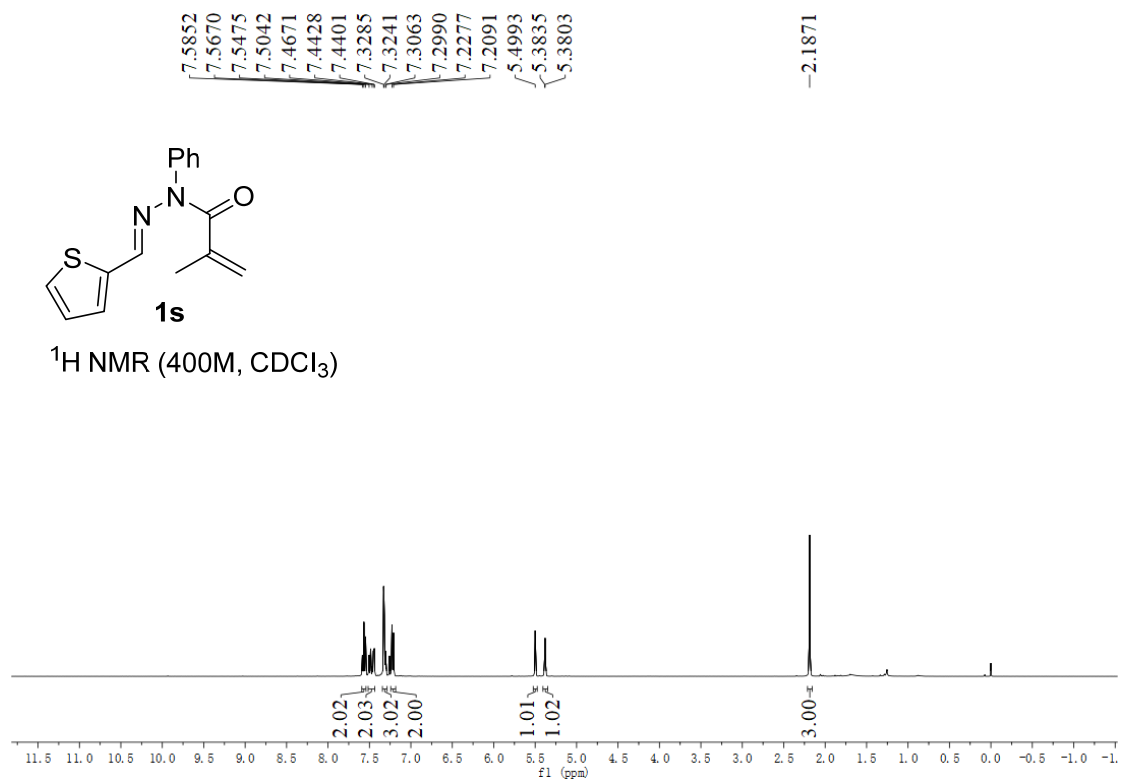
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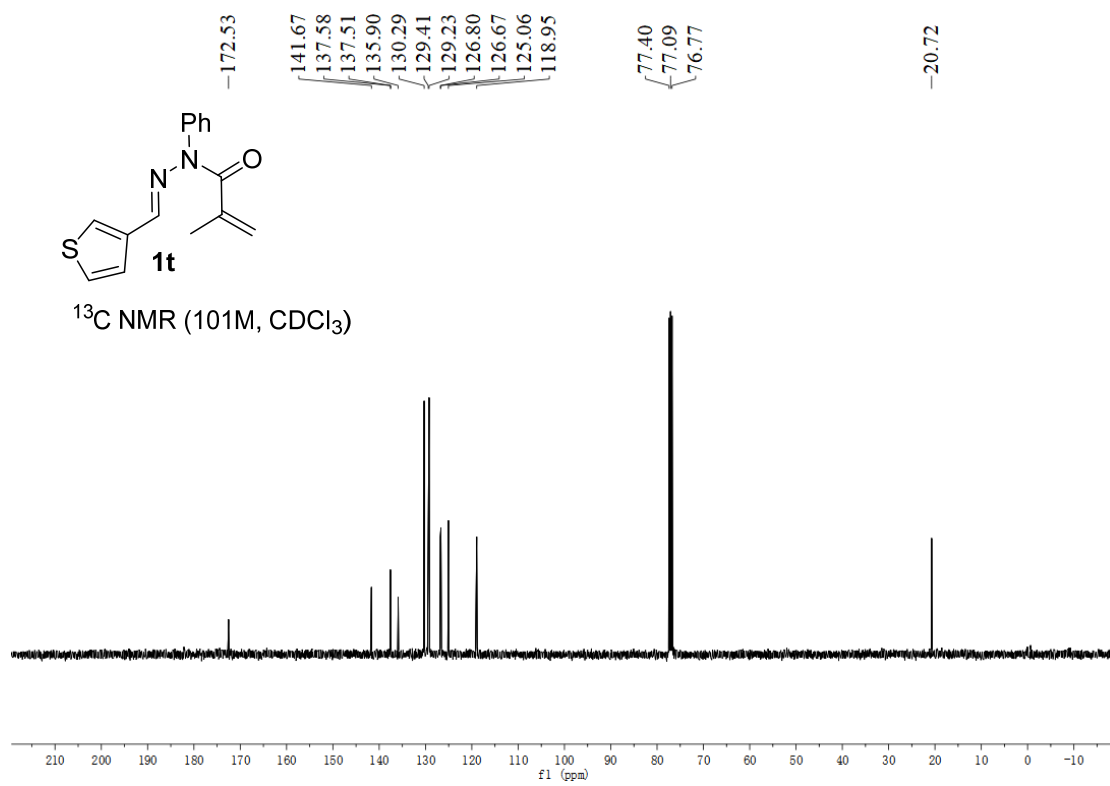
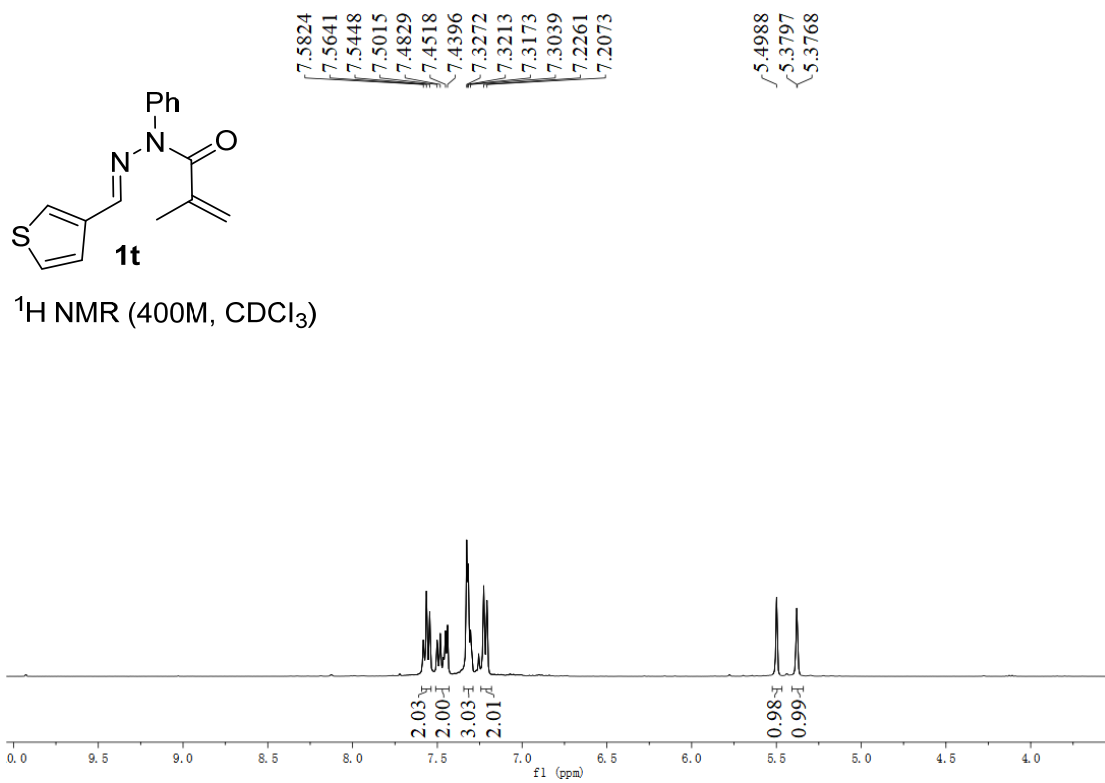


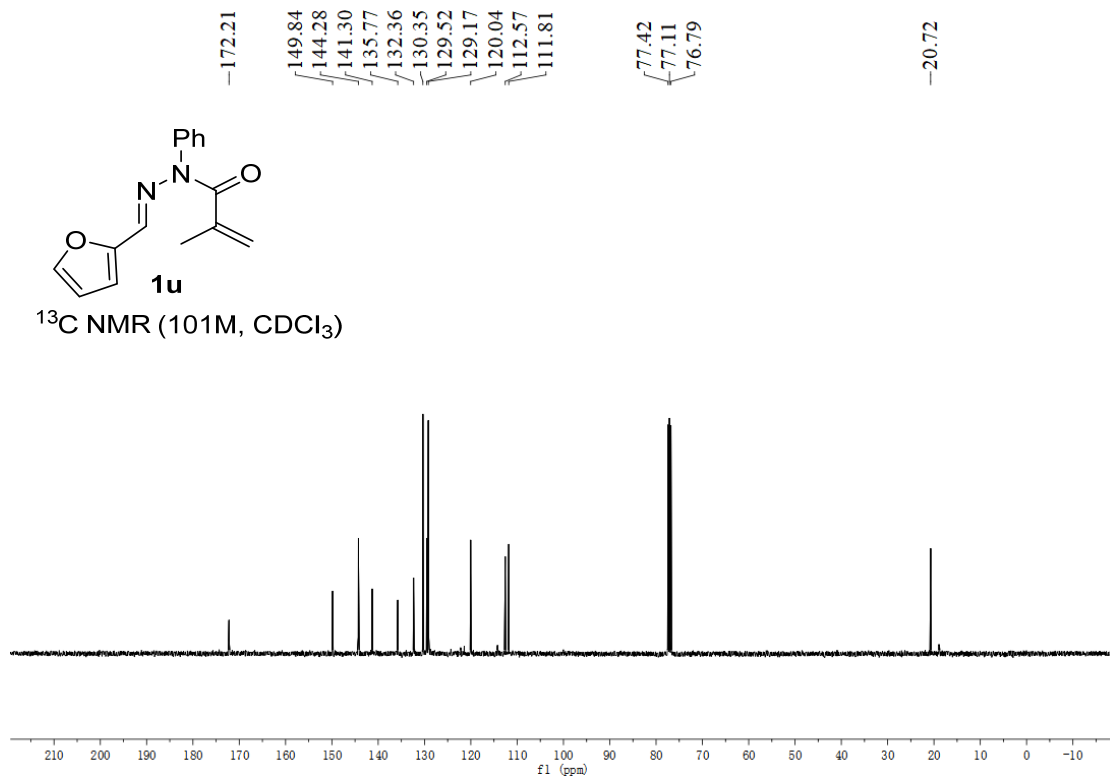
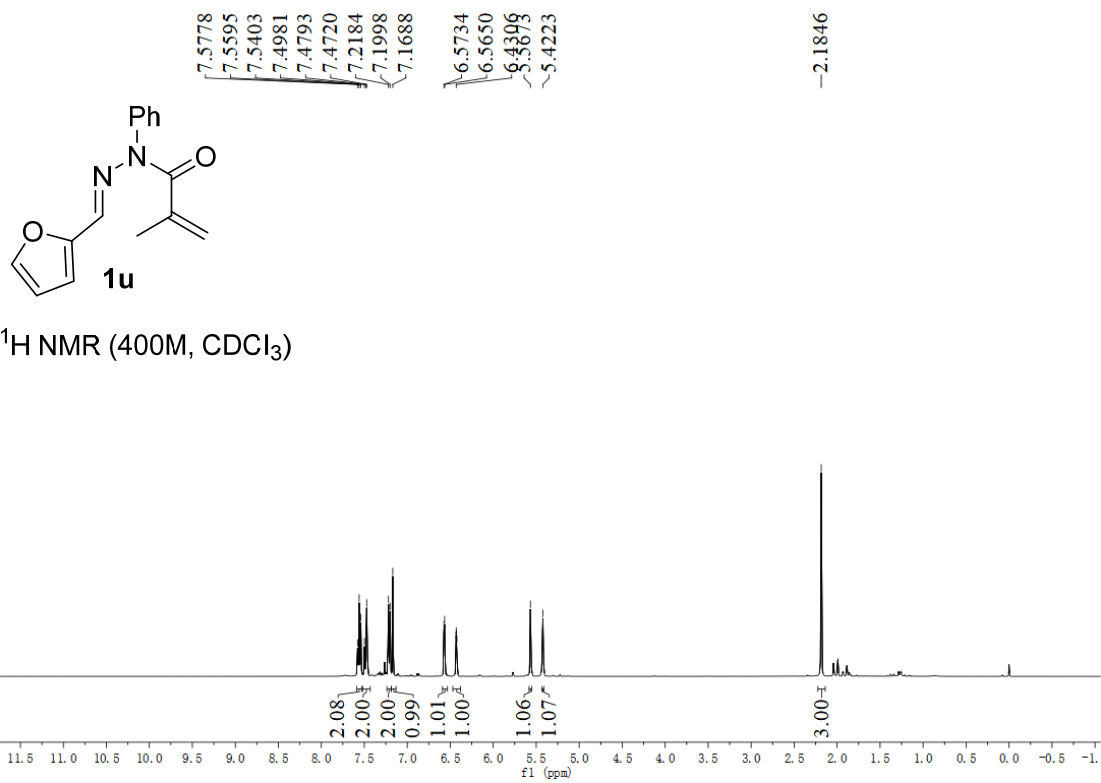
**1r**

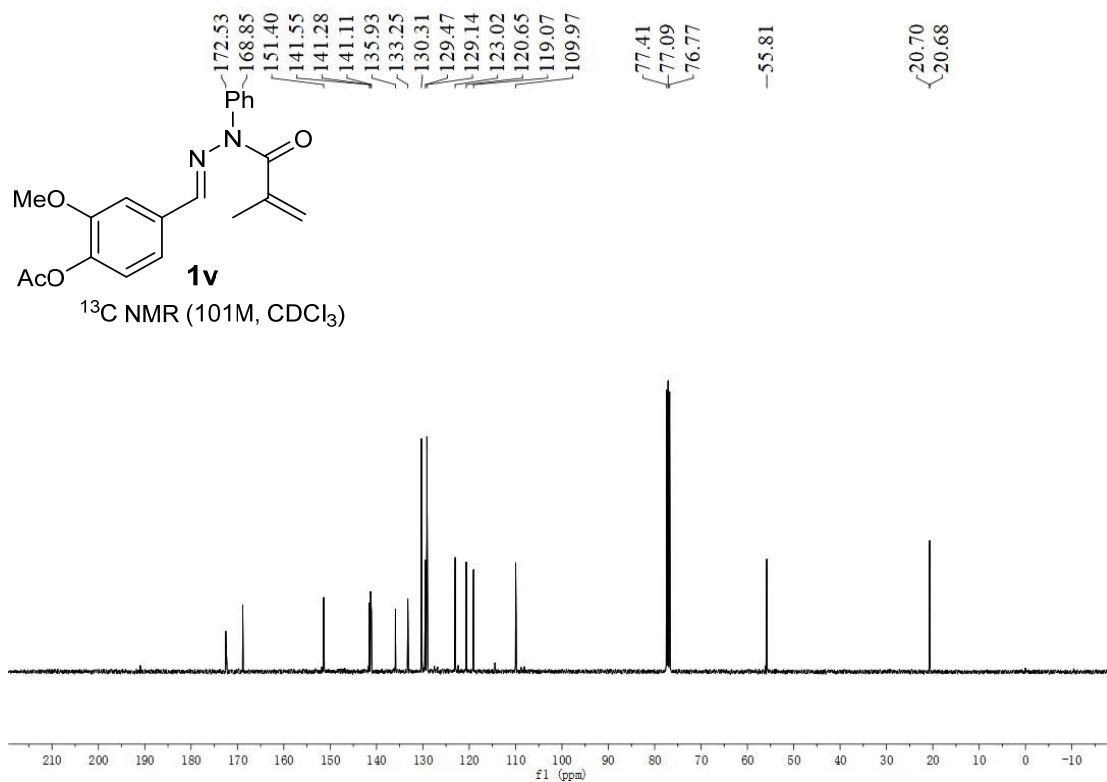
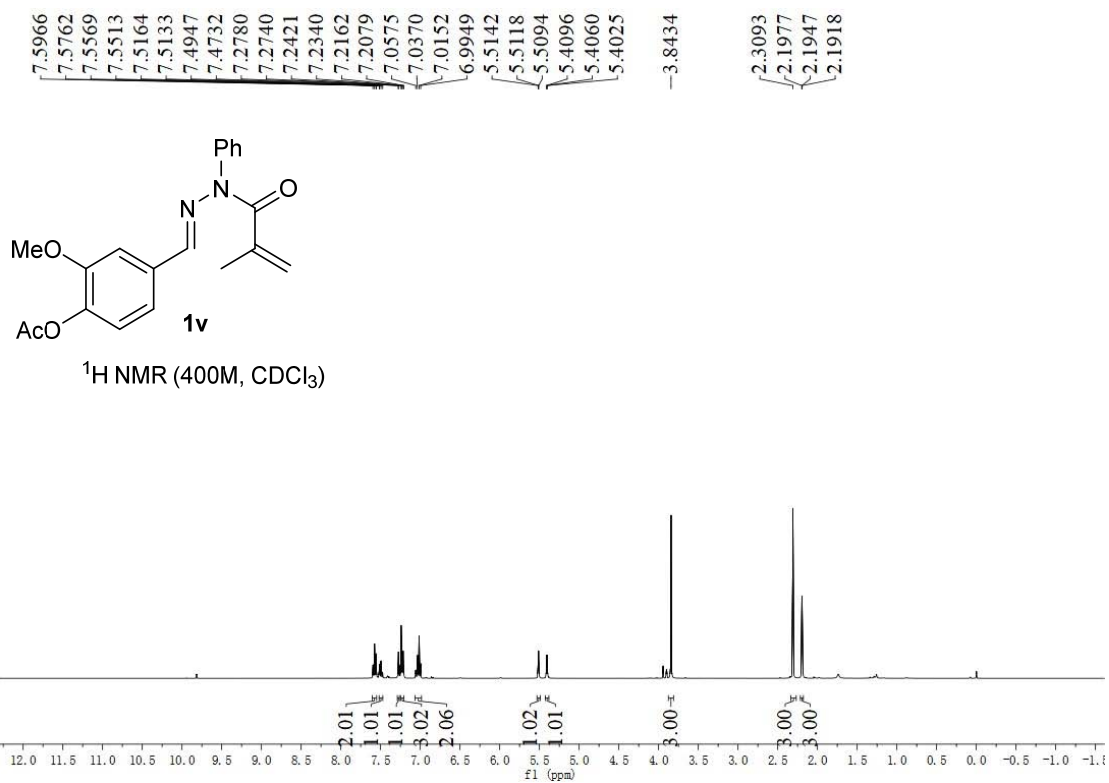
<sup>13</sup>C NMR (101M, CDCl<sub>3</sub>)

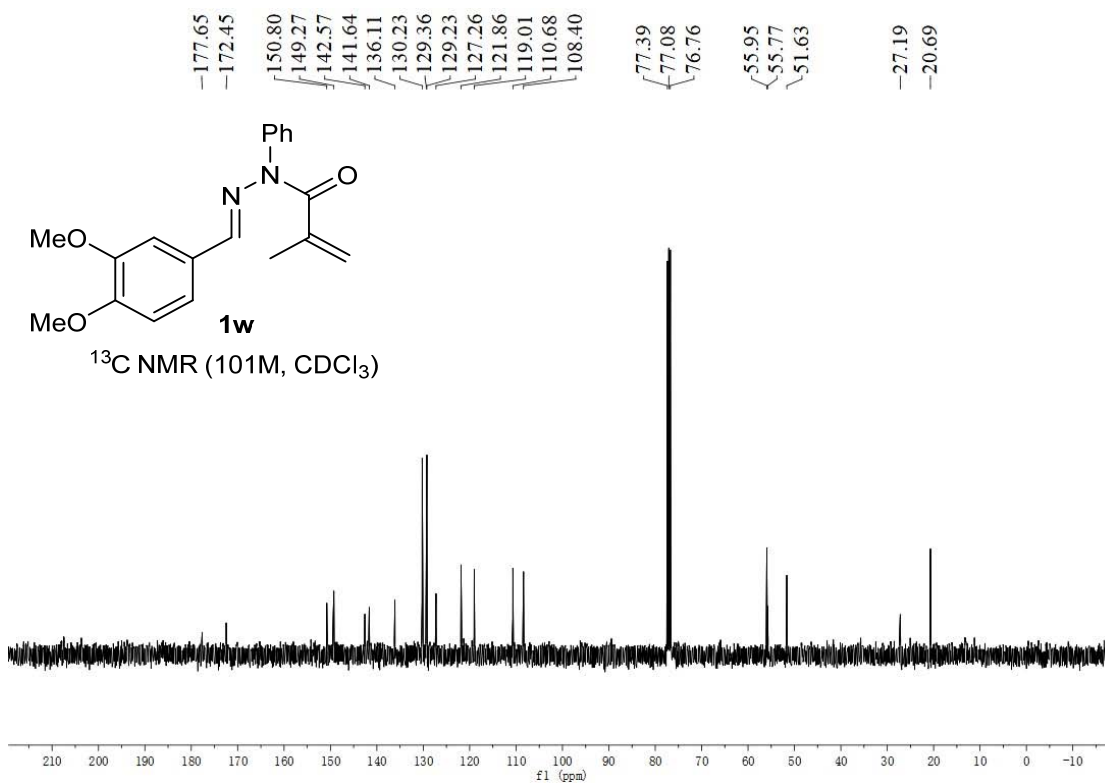
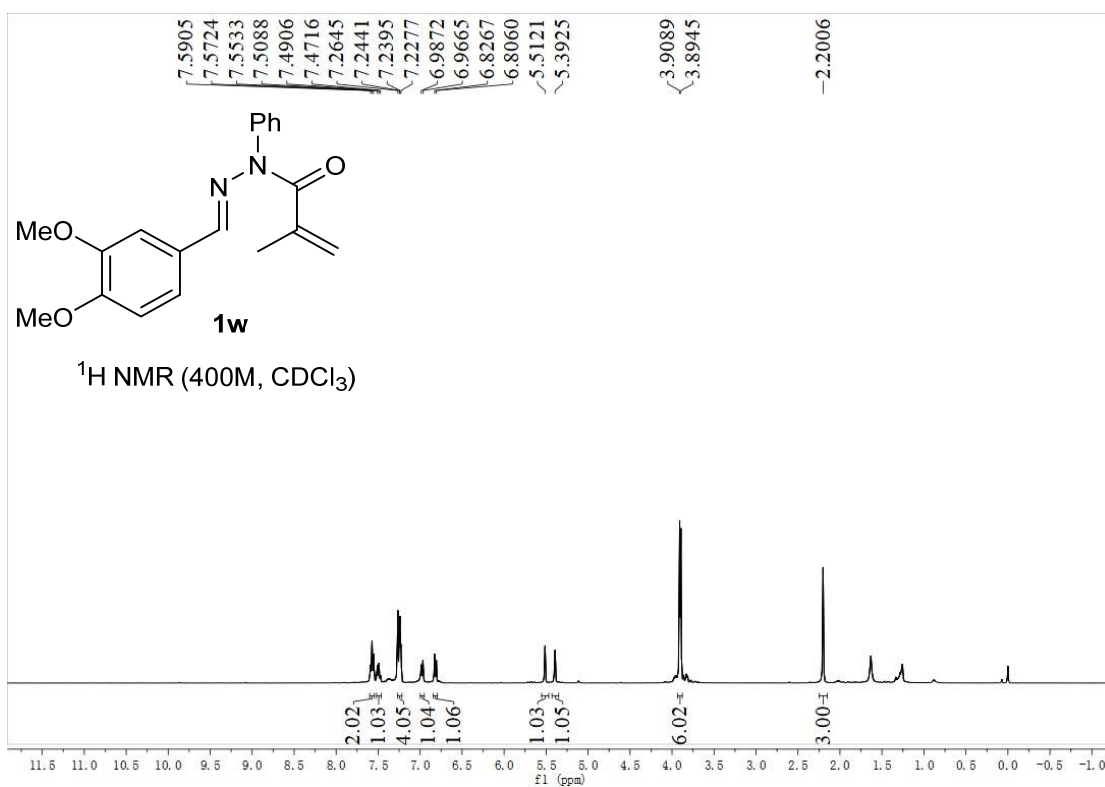




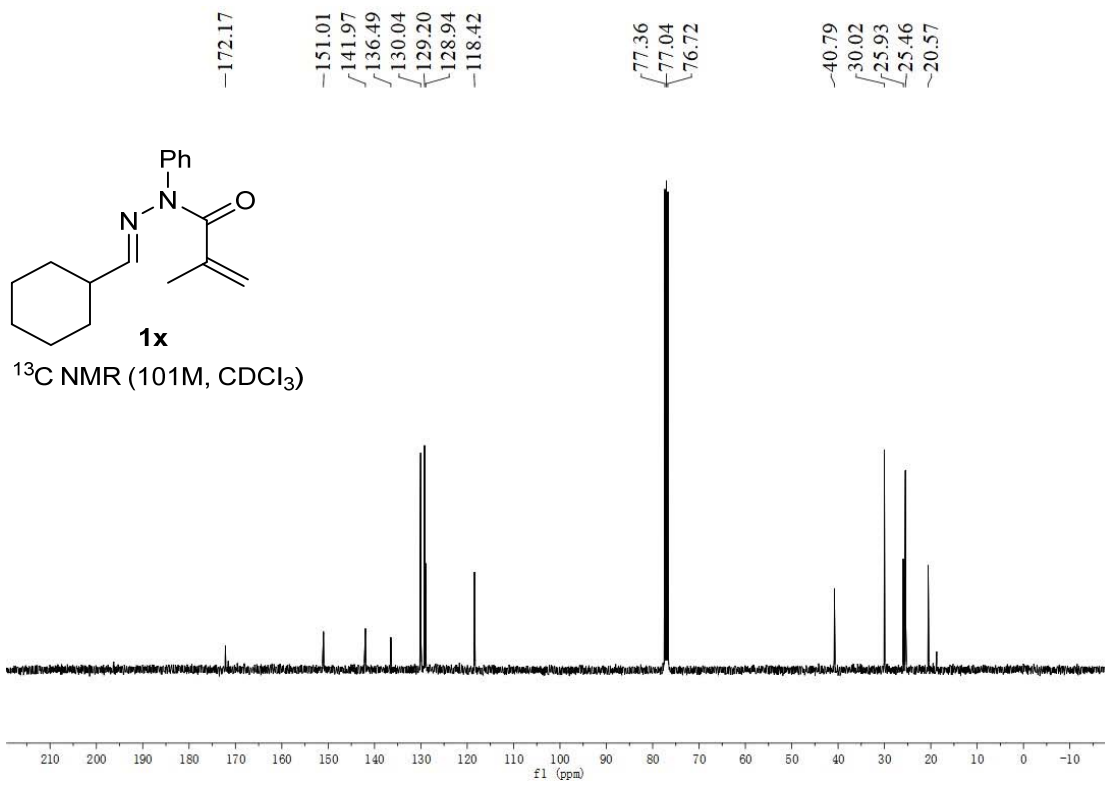
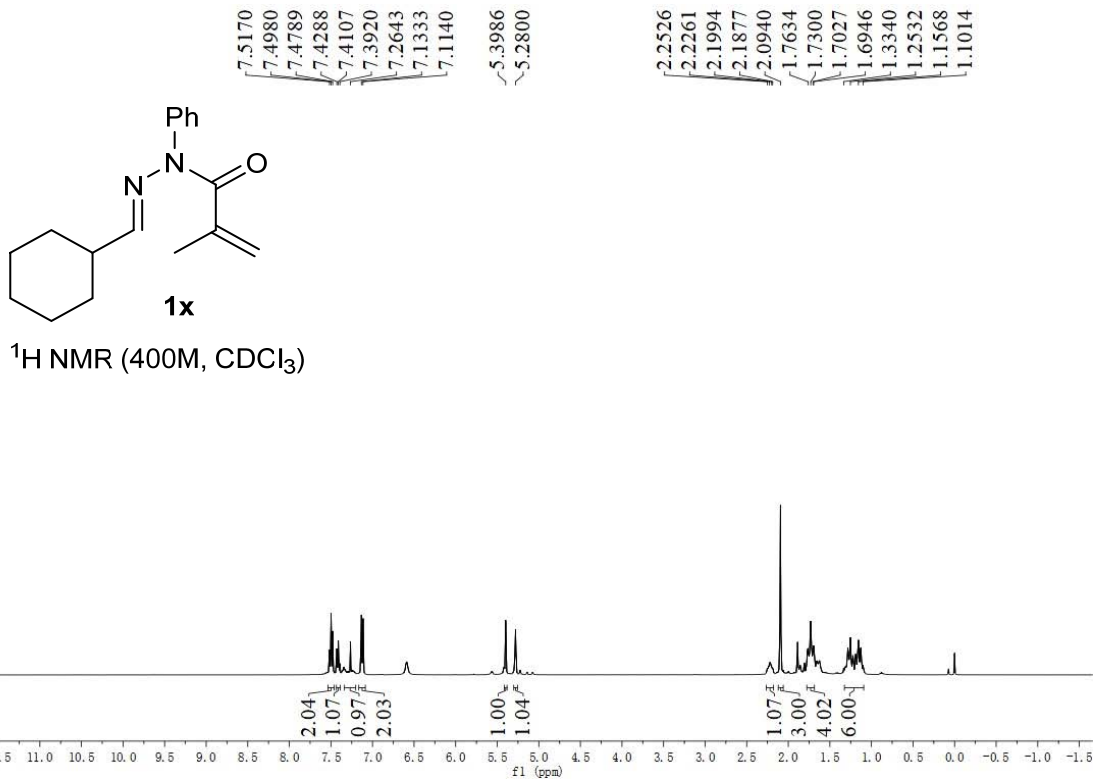




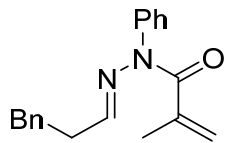






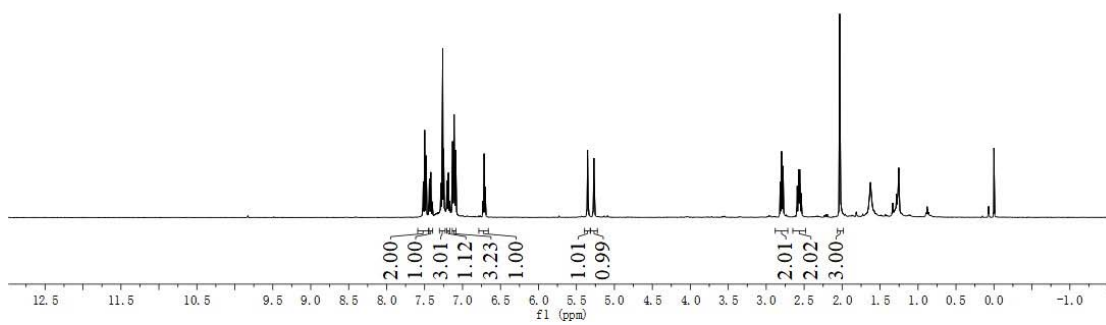


7.5199  
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7.4801  
7.4404  
7.4372  
7.4186  
7.2852  
7.2677  
7.2610  
7.2488  
7.2051  
7.1868  
7.1685  
7.1347  
7.1111  
7.1073  
7.0896  
7.0873  
6.7281  
6.7155  
6.3028  
6.3526  
5.3502  
5.2737  
5.2700  
5.2664  
2.8163  
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2.0297

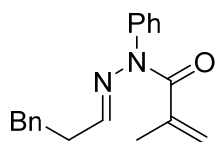


**1y**

<sup>1</sup>H NMR (400M, CDCl<sub>3</sub>)

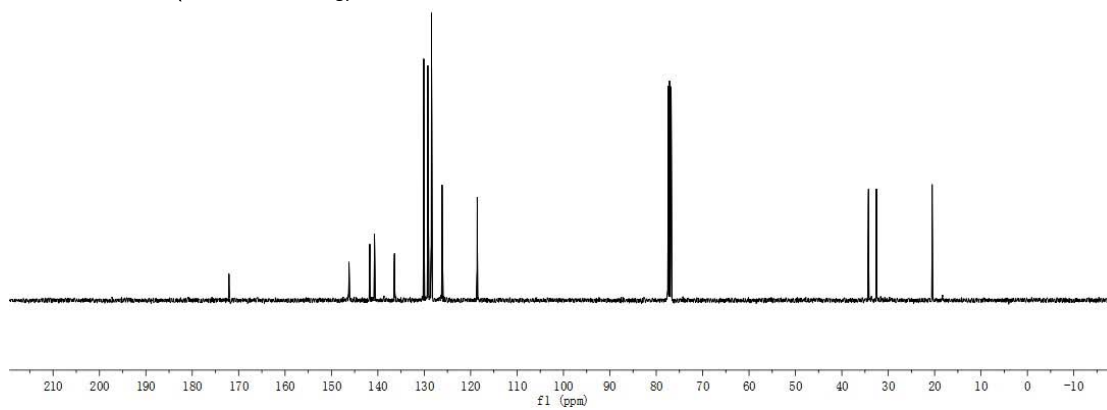


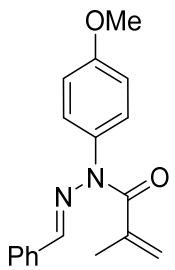
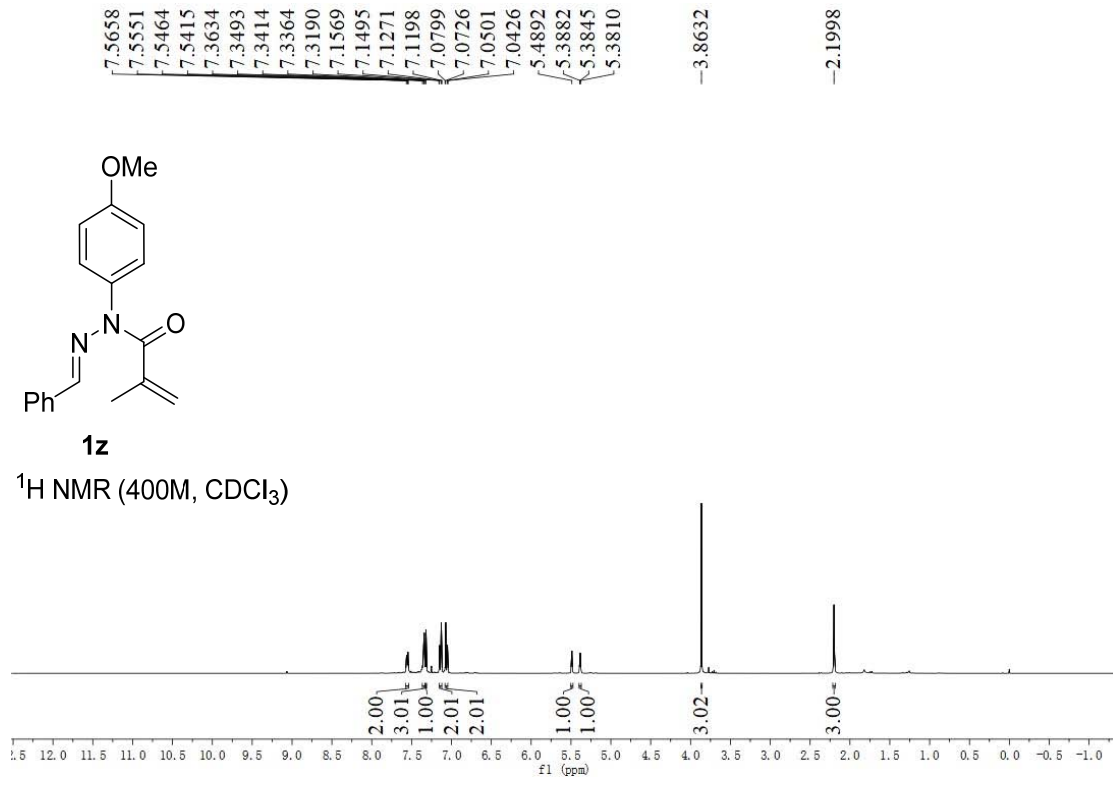
172.10  
146.22  
141.75  
140.73  
136.40  
130.12  
129.24  
129.13  
128.46  
128.45  
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118.58  
77.43  
77.11  
76.79  
34.24  
32.54  
20.54



**1y**

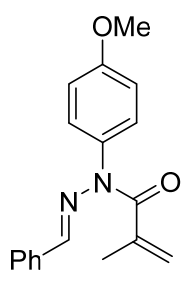
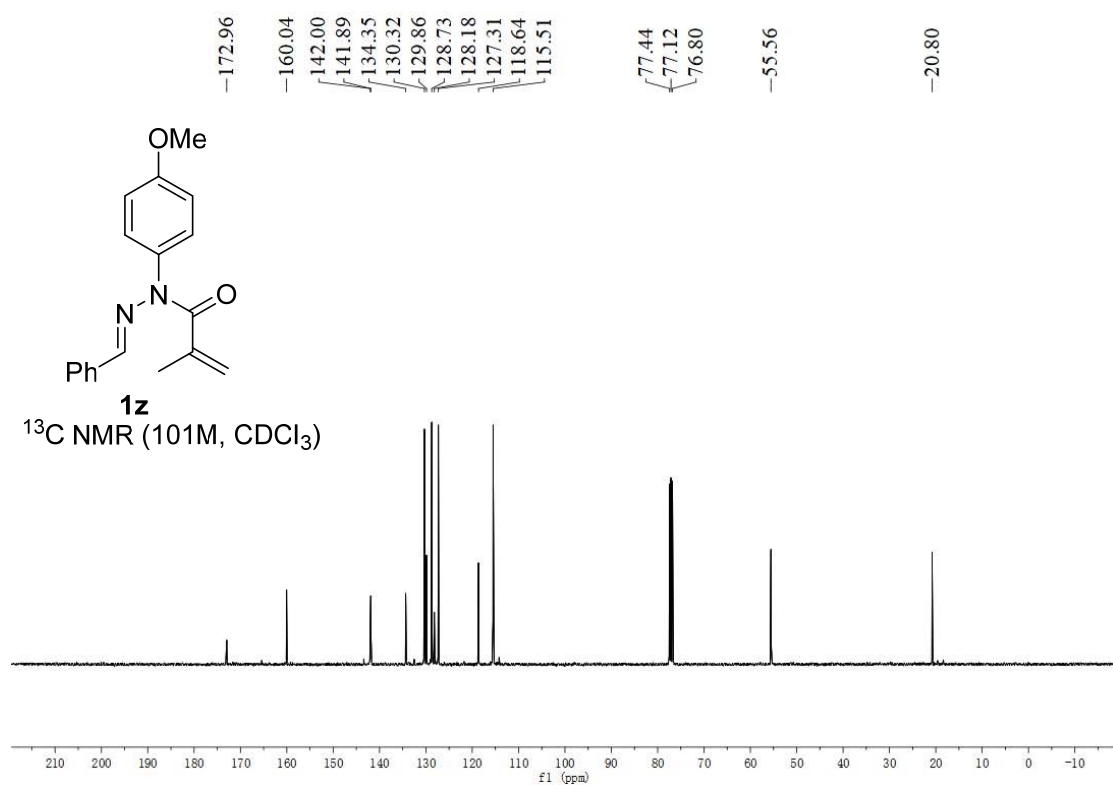
<sup>13</sup>C NMR (101M, CDCl<sub>3</sub>)





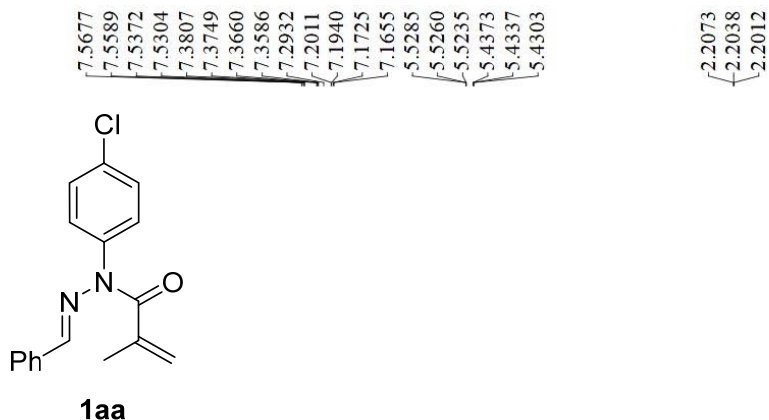
**1z**

<sup>1</sup>H NMR (400M, CDCl<sub>3</sub>)

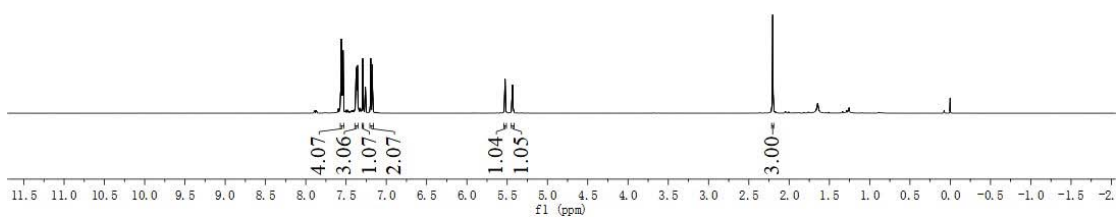


**1z**

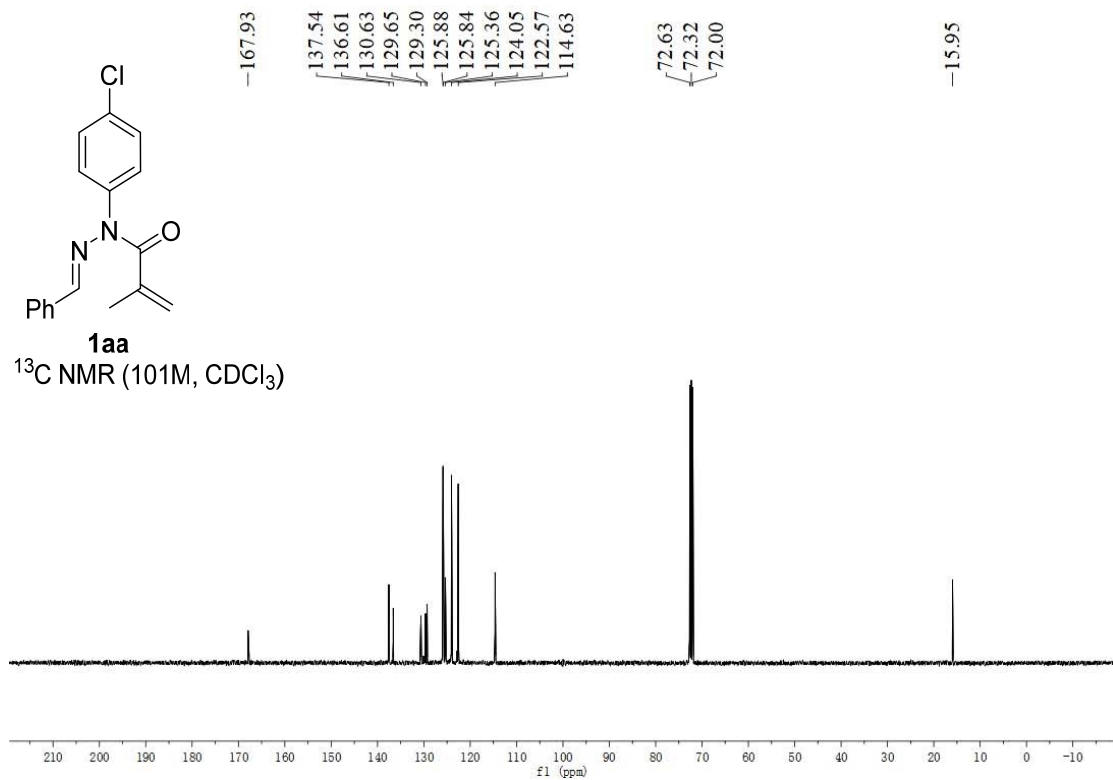
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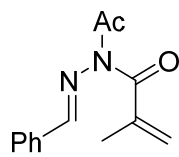


<sup>1</sup>H NMR (400M, CDCl<sub>3</sub>)



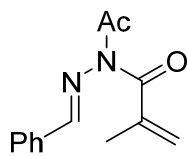
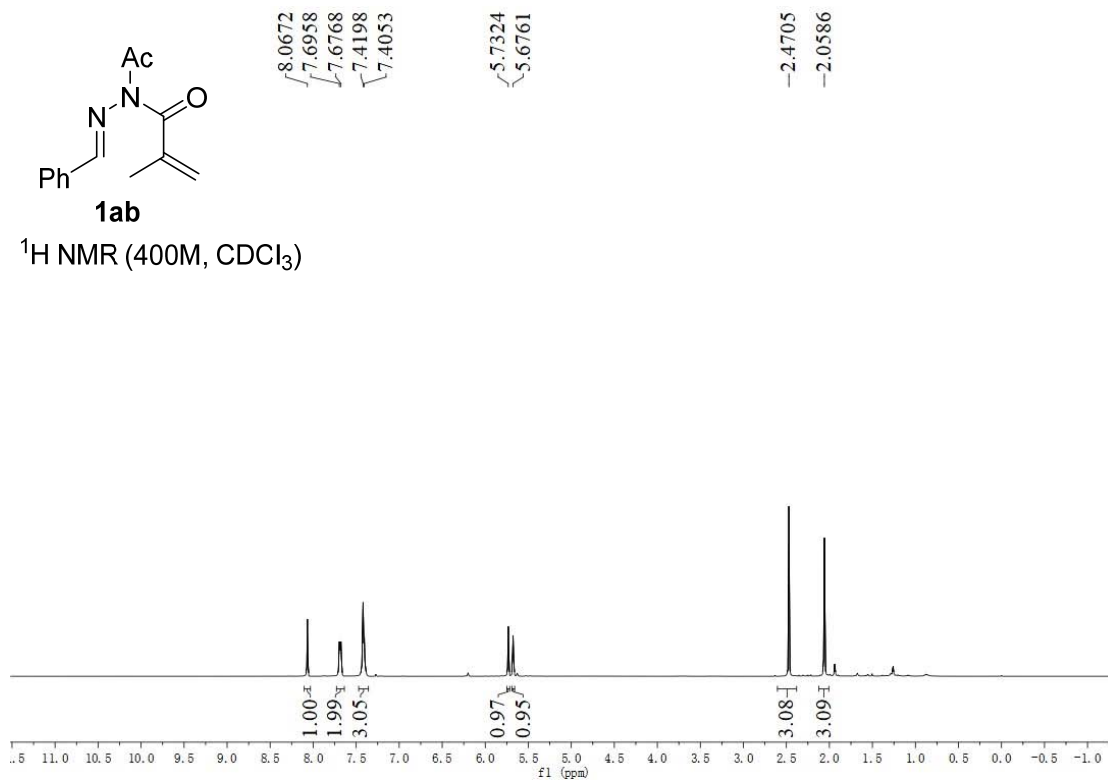
<sup>13</sup>C NMR (101M, CDCl<sub>3</sub>)





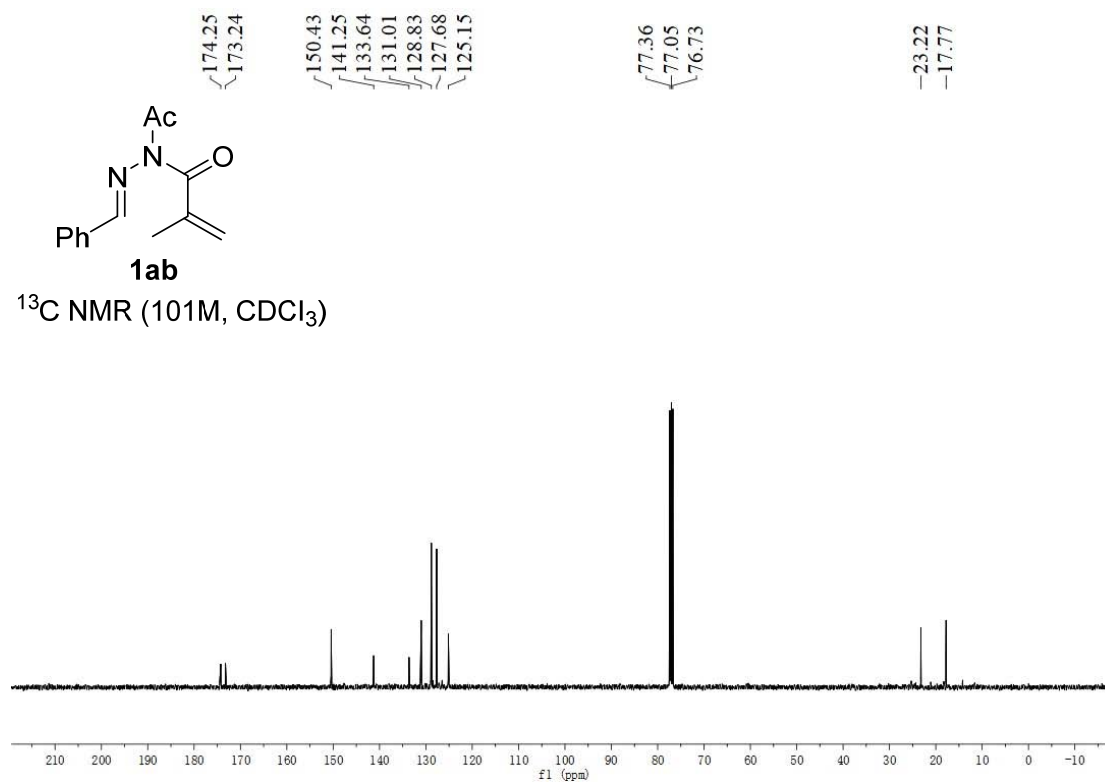
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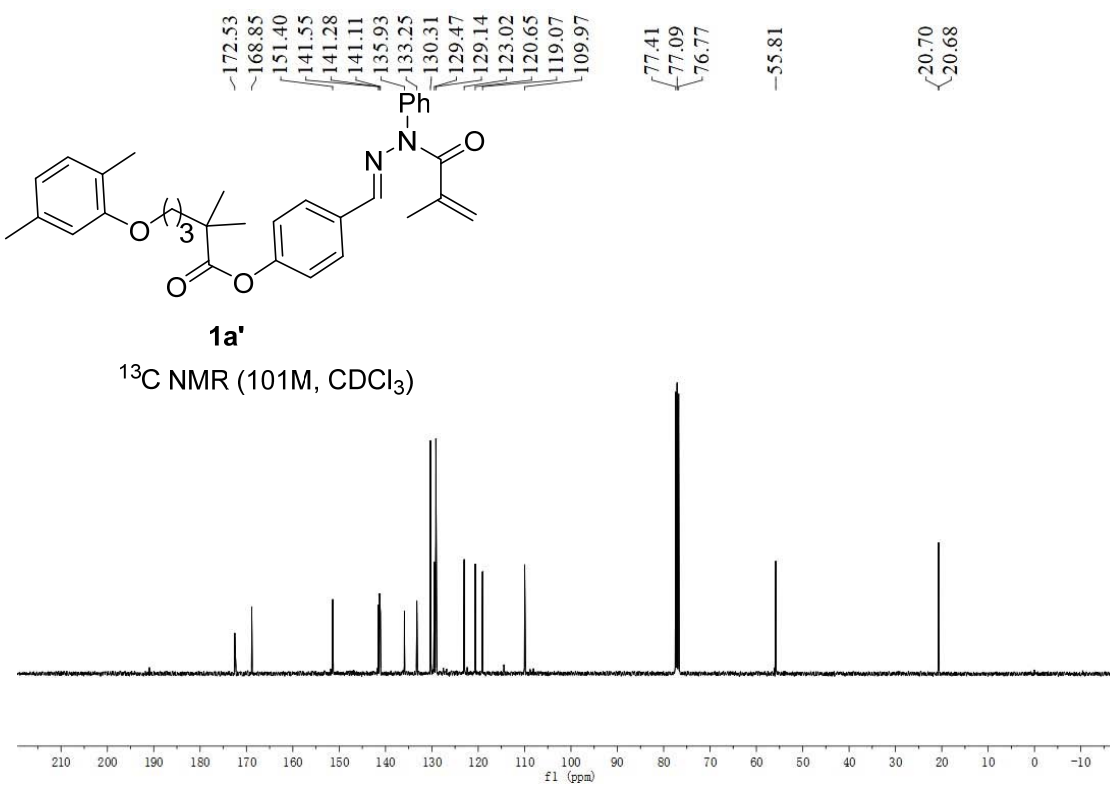
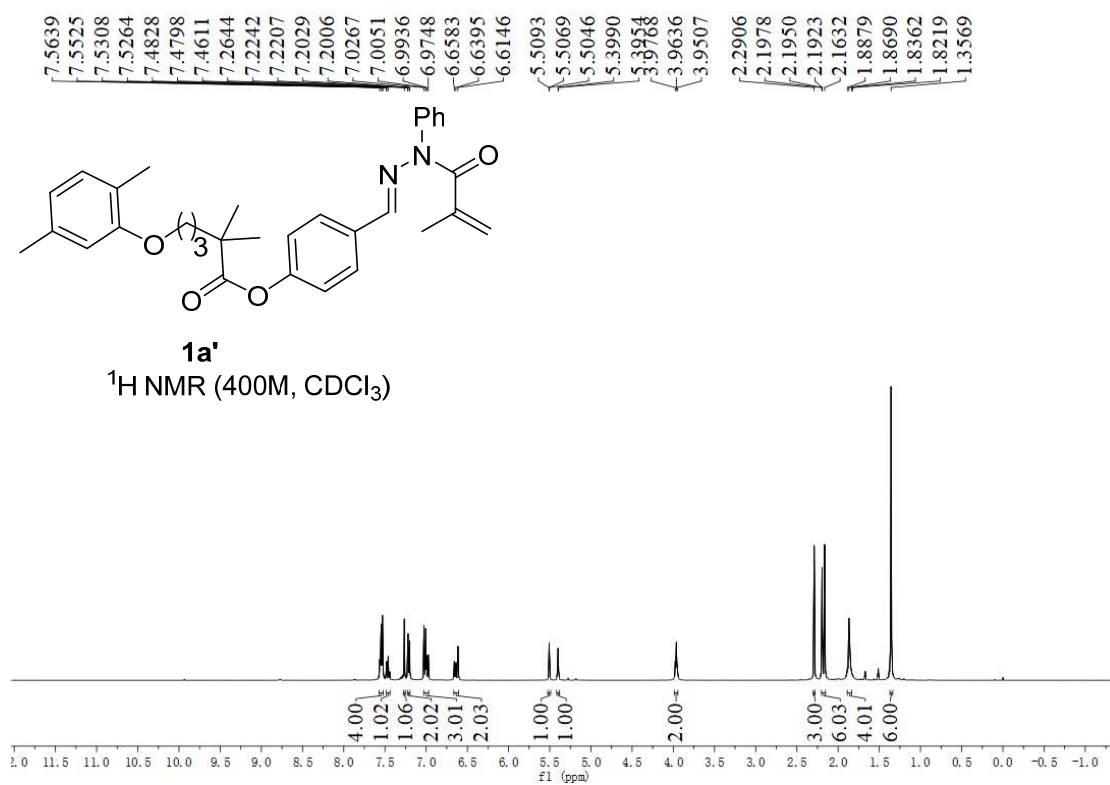
<sup>1</sup>H NMR (400M, CDCl<sub>3</sub>)

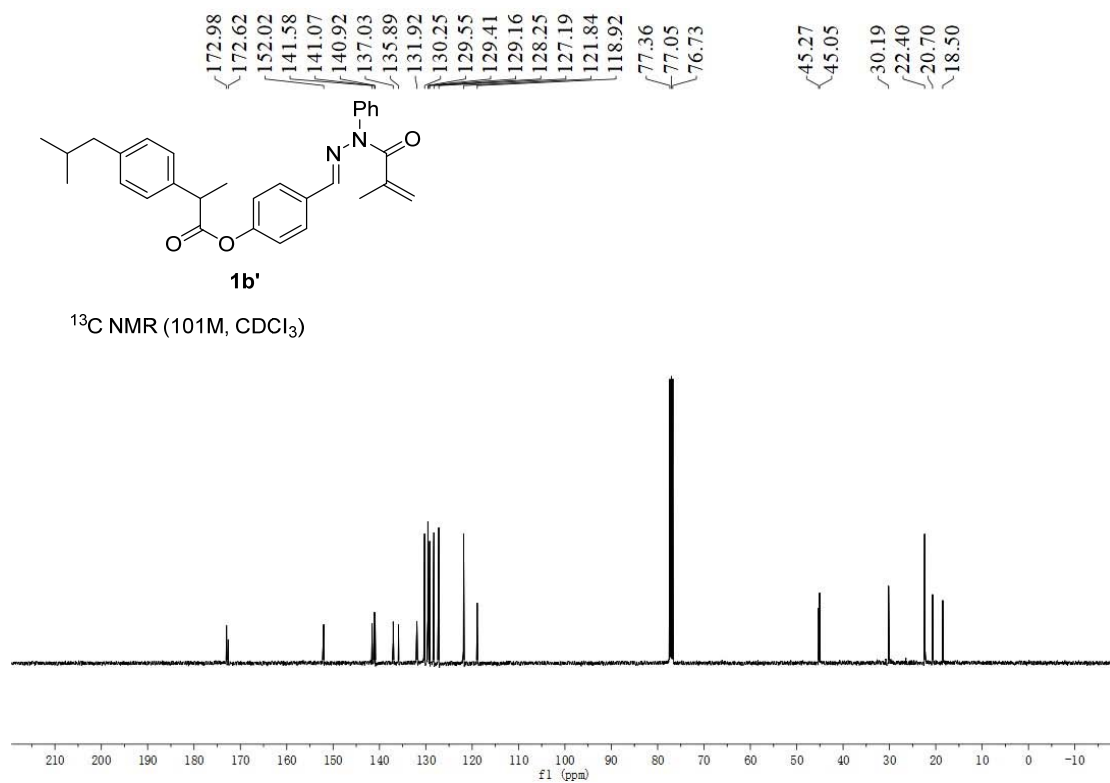
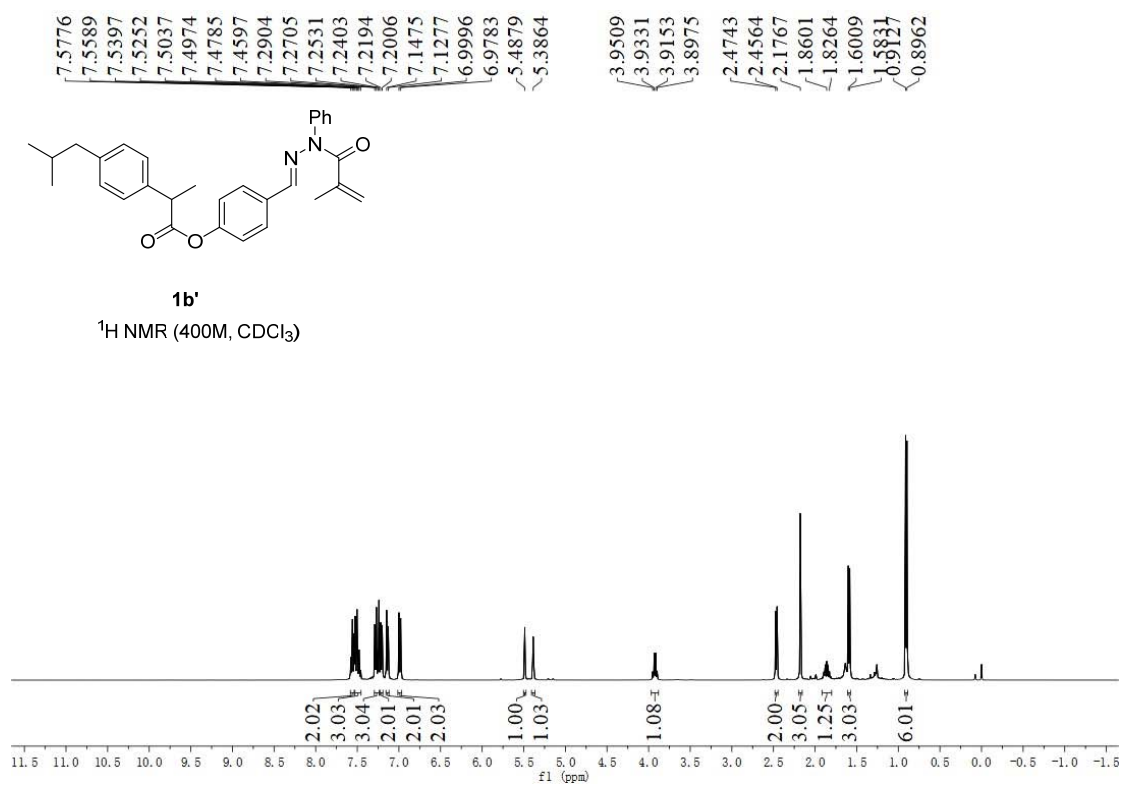


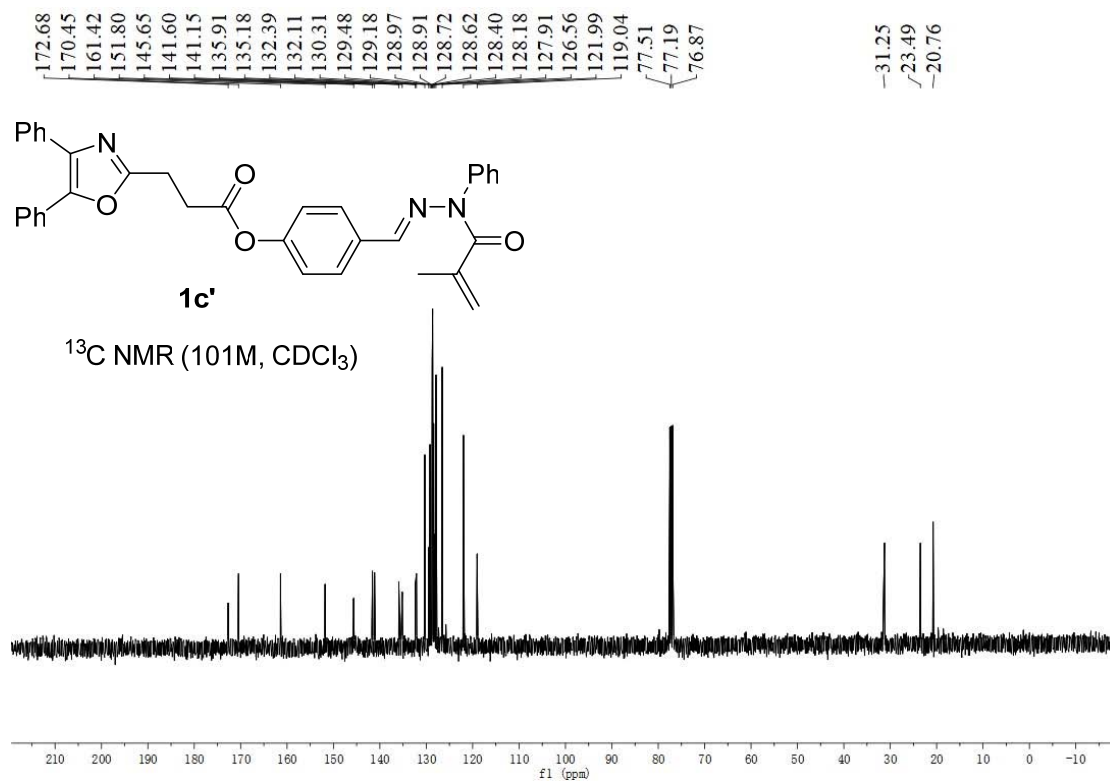
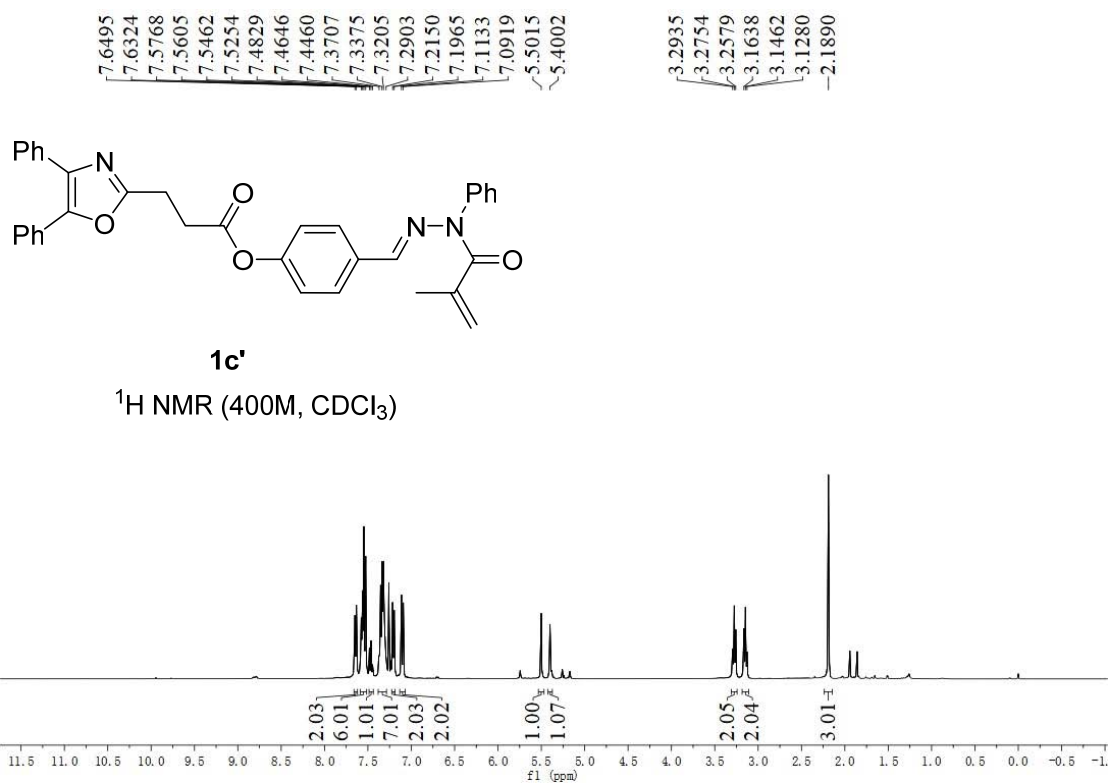
**1ab**

<sup>13</sup>C NMR (101M, CDCl<sub>3</sub>)

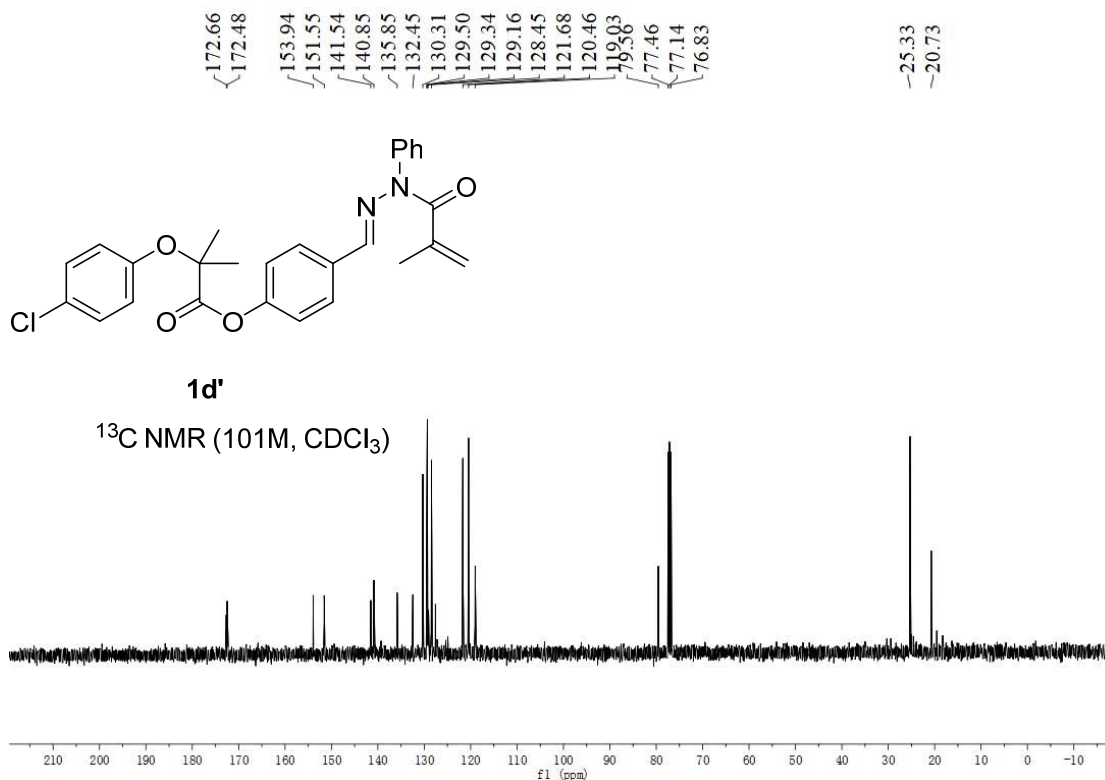
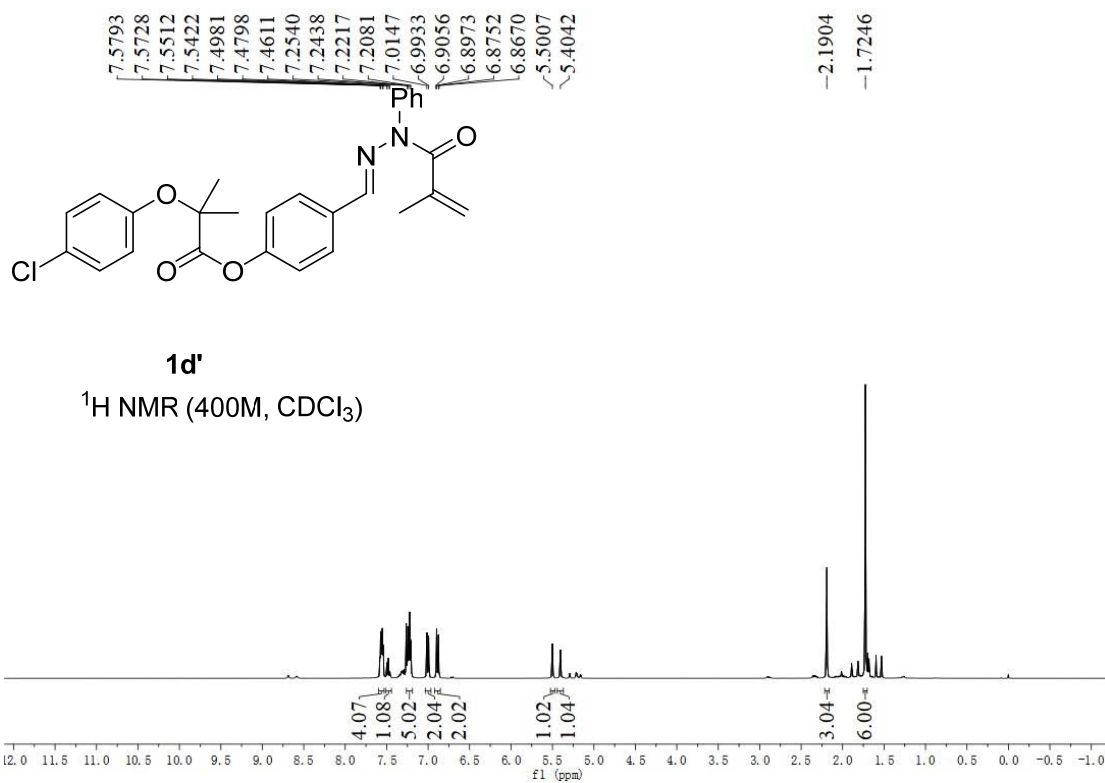


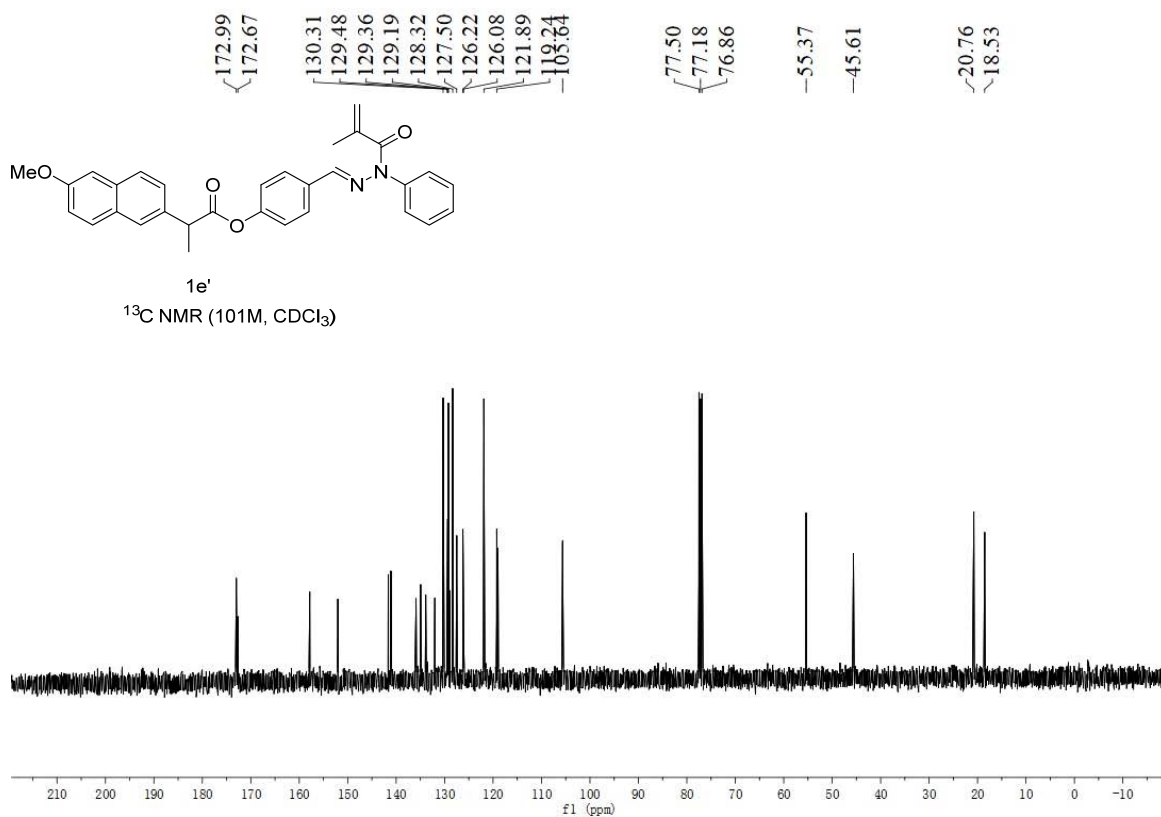
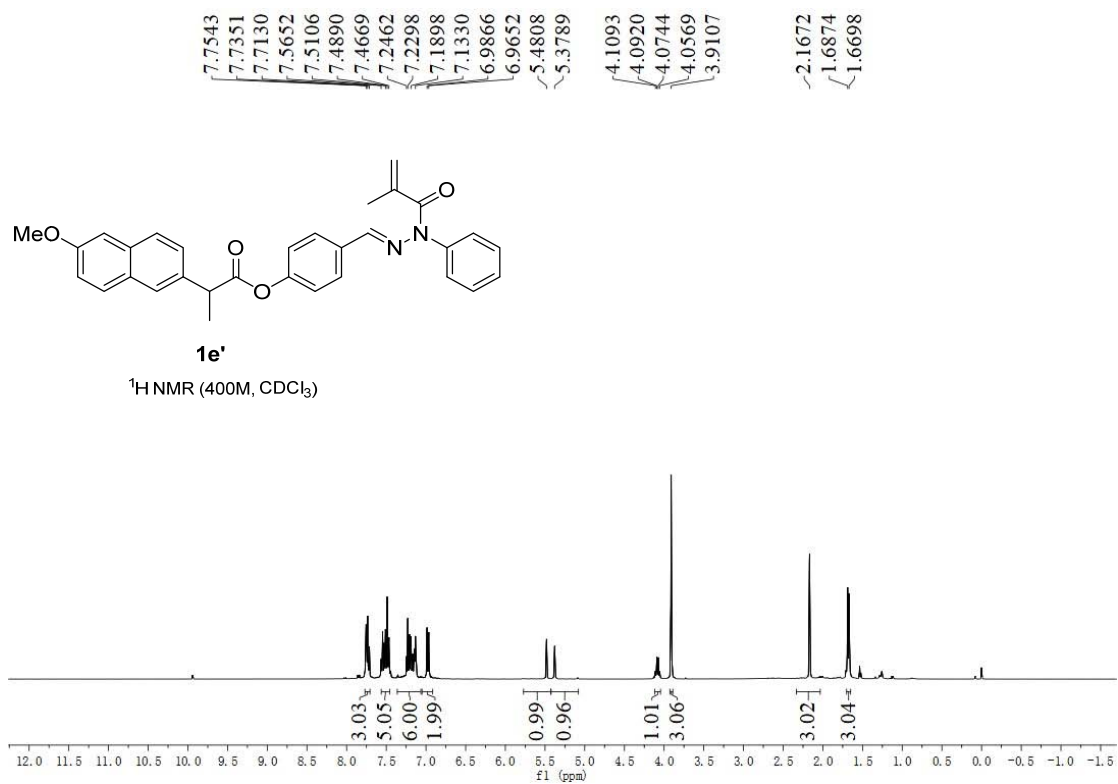


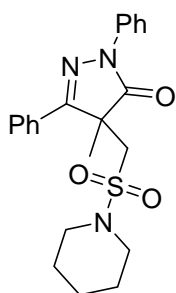






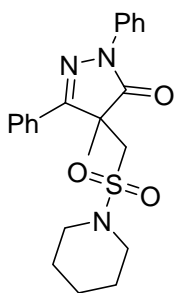
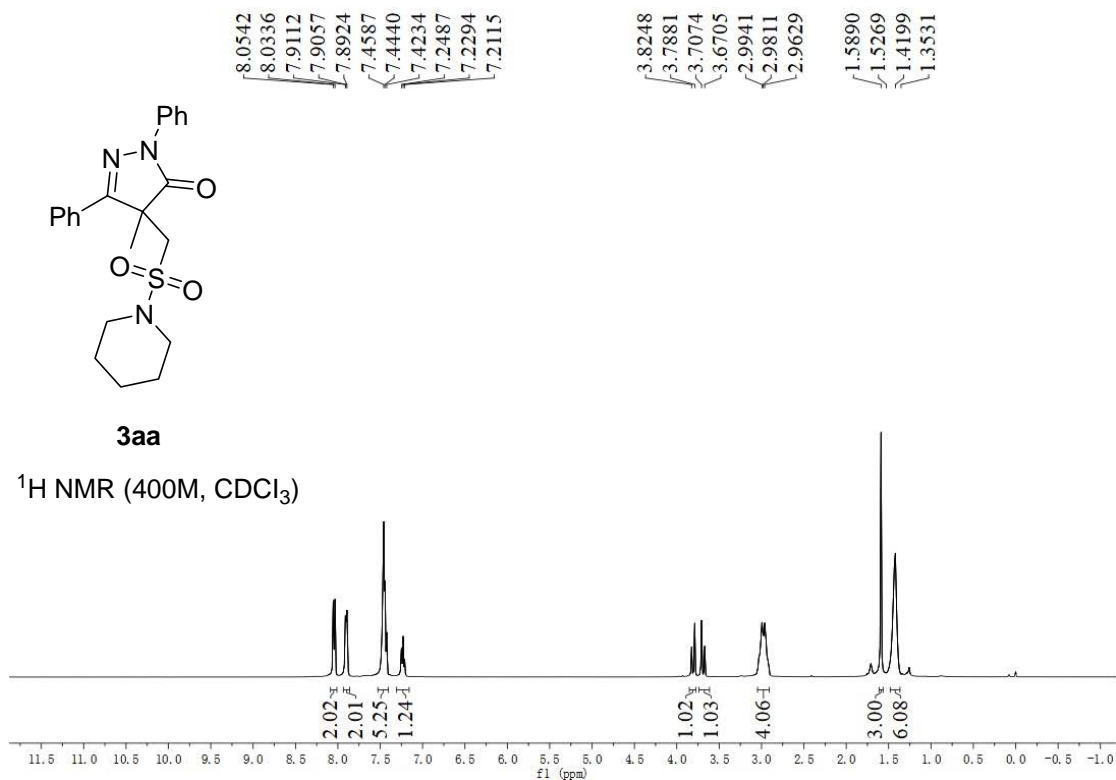






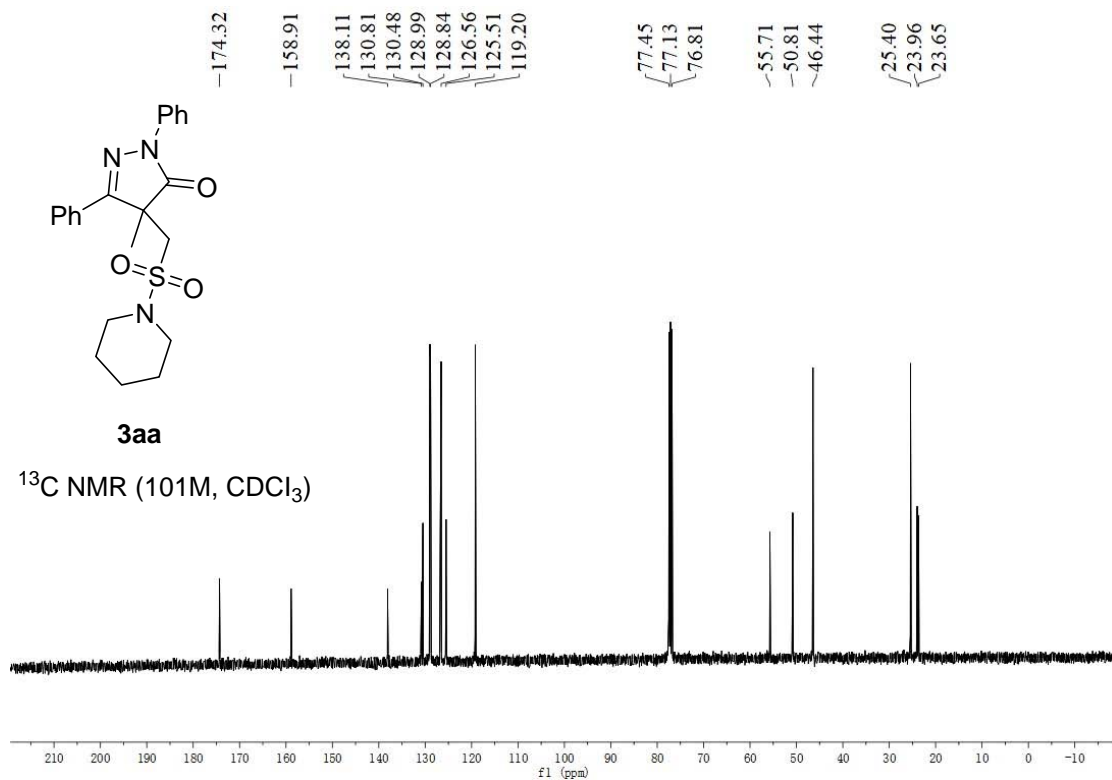
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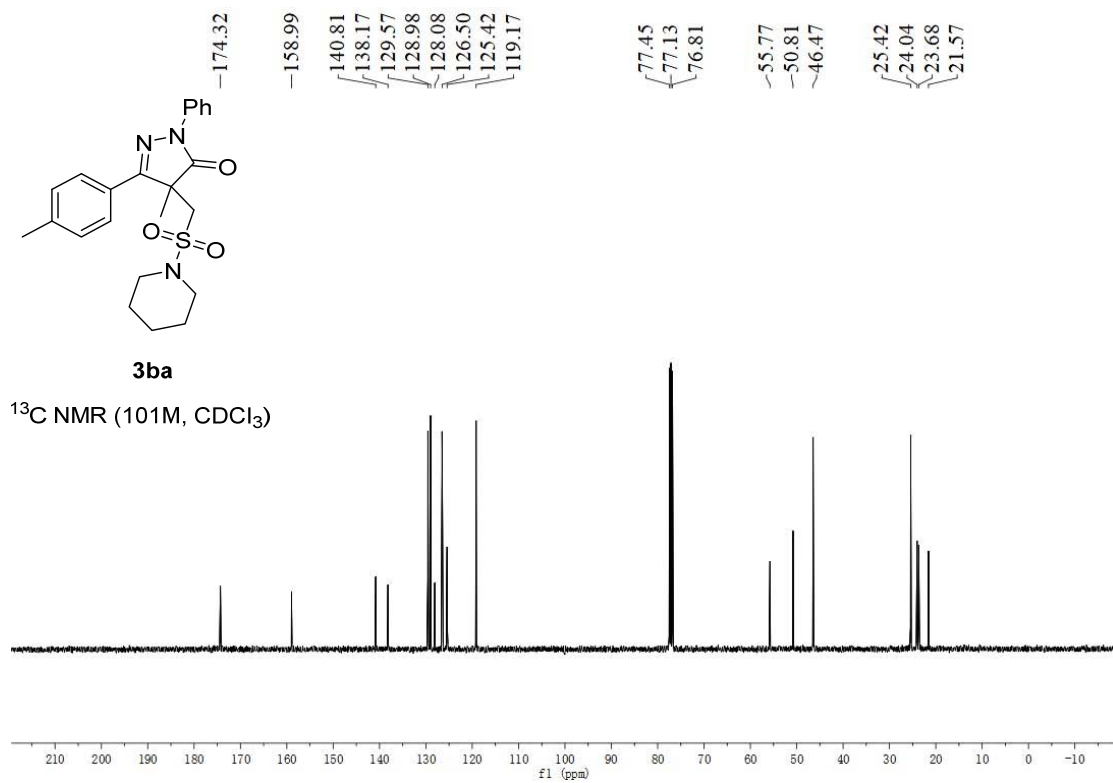
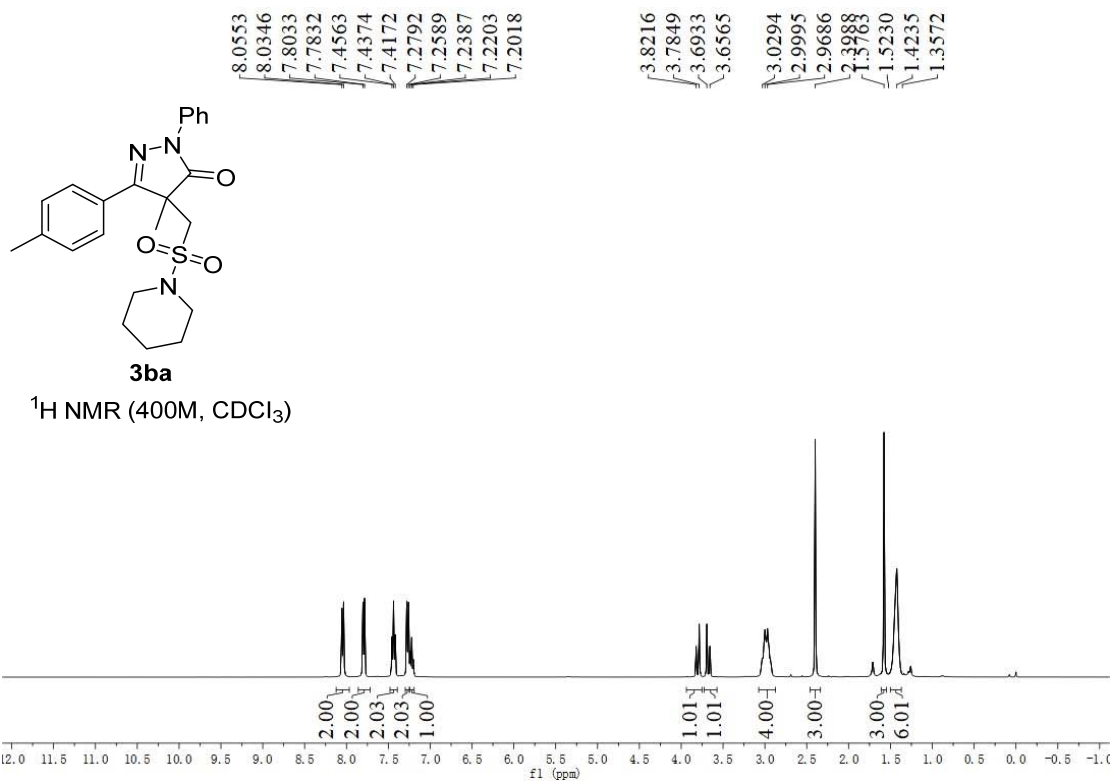
<sup>1</sup>H NMR (400M, CDCl<sub>3</sub>)

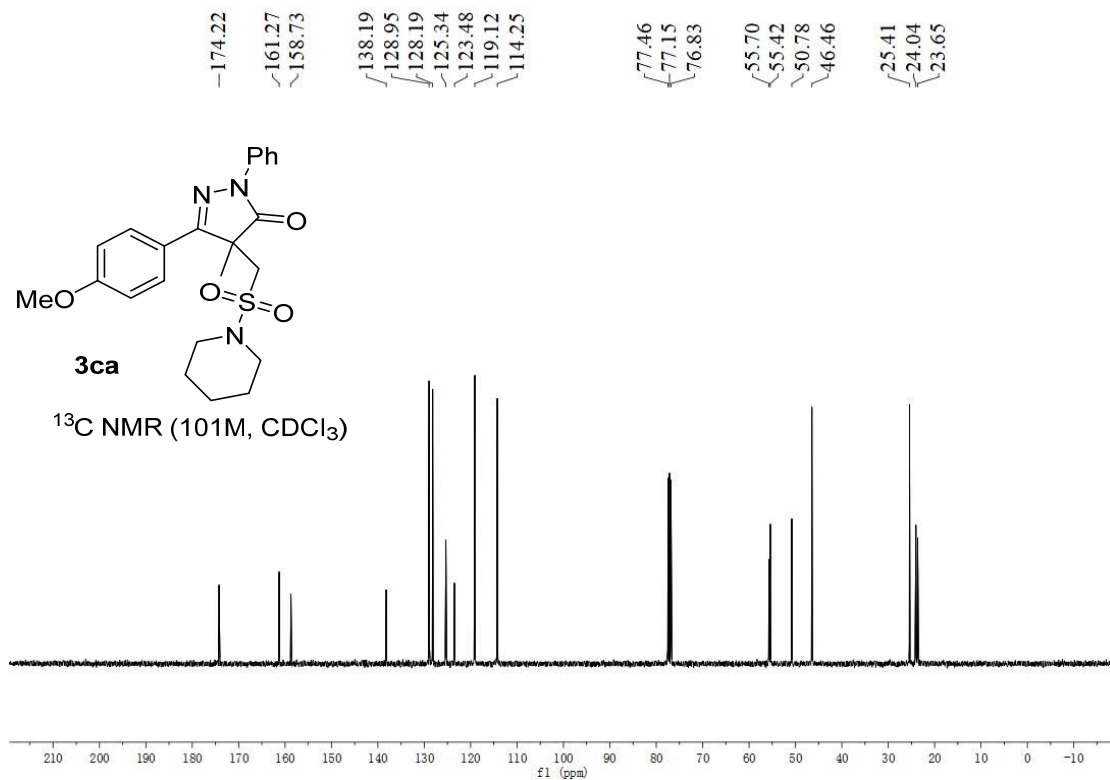
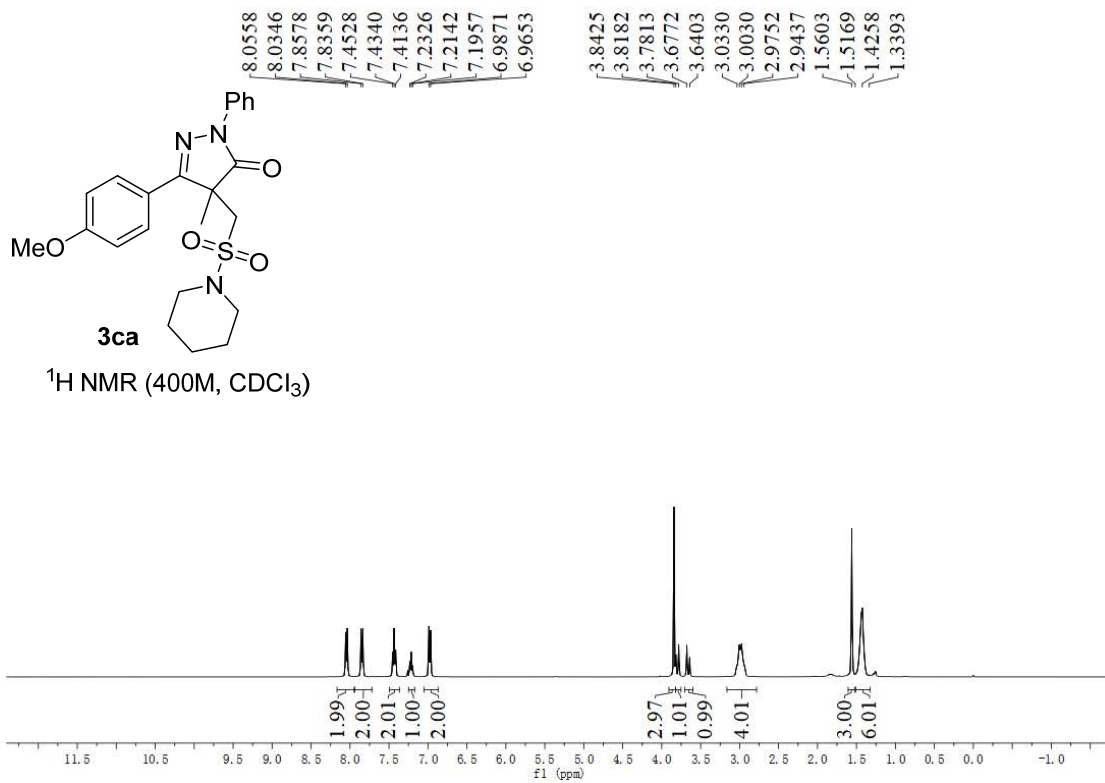


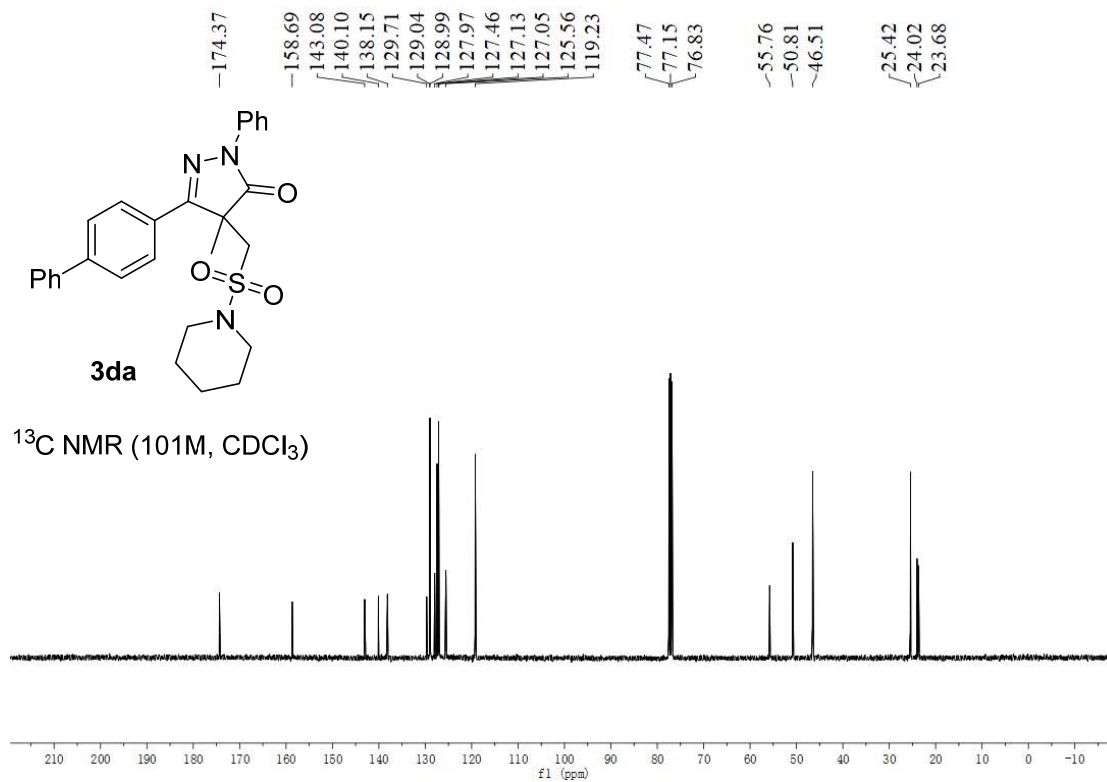
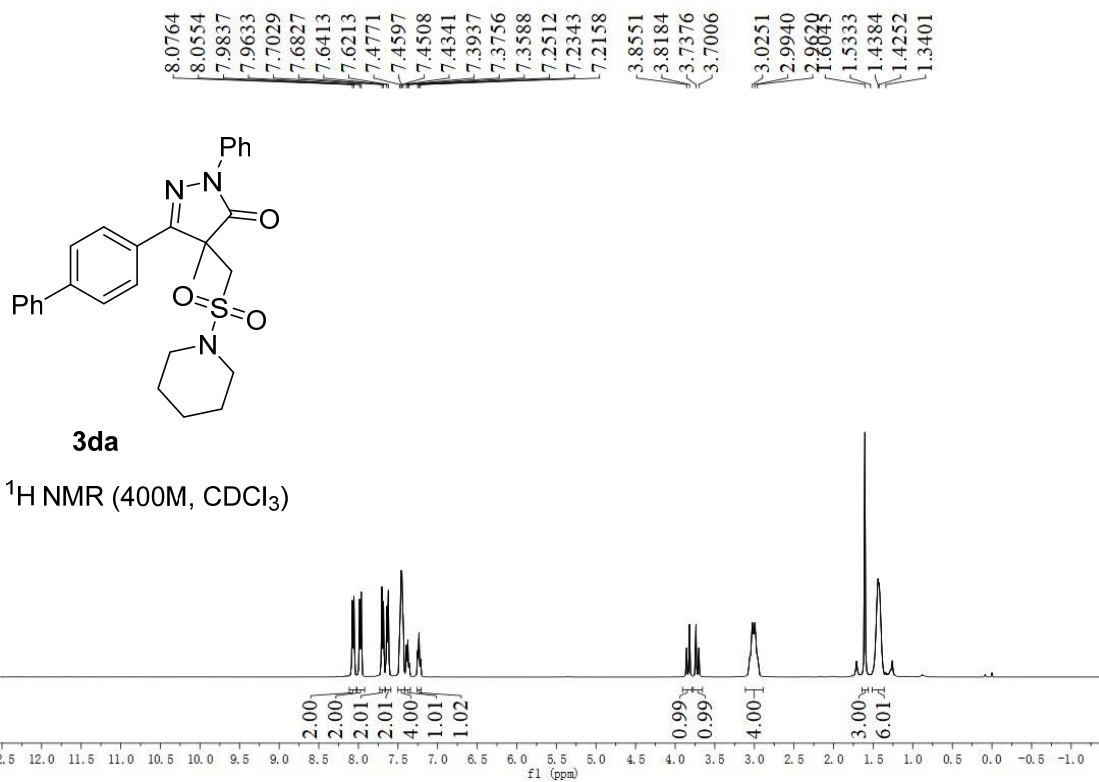
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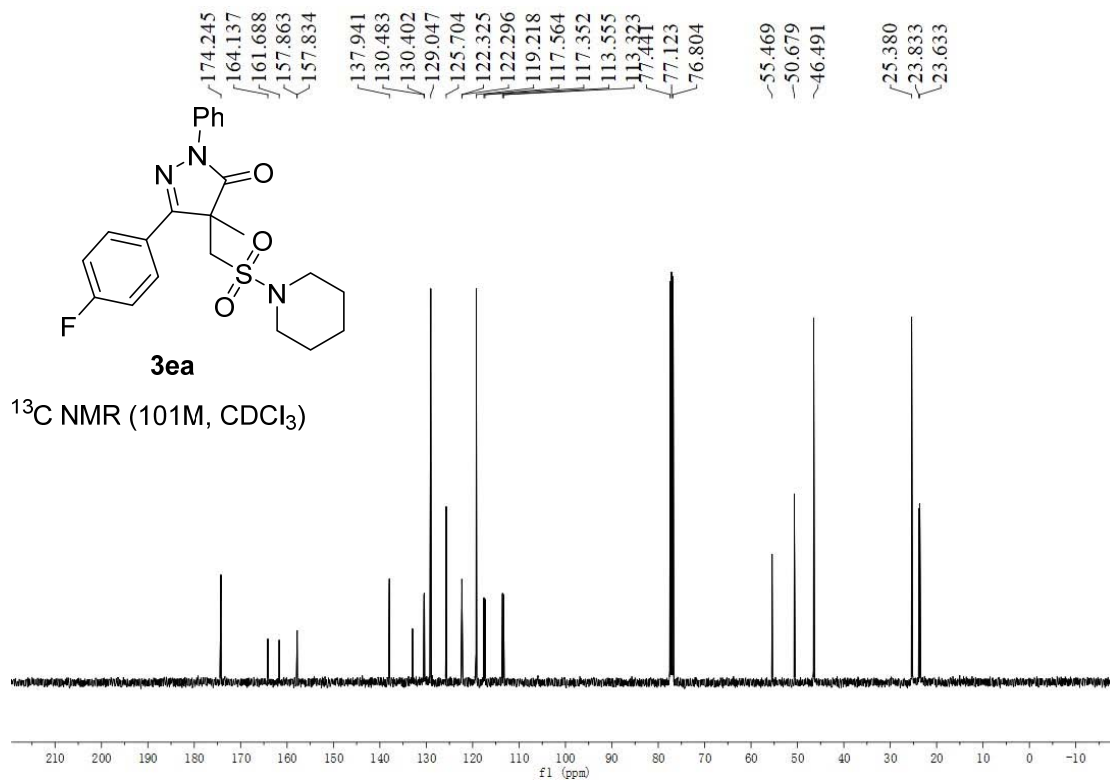
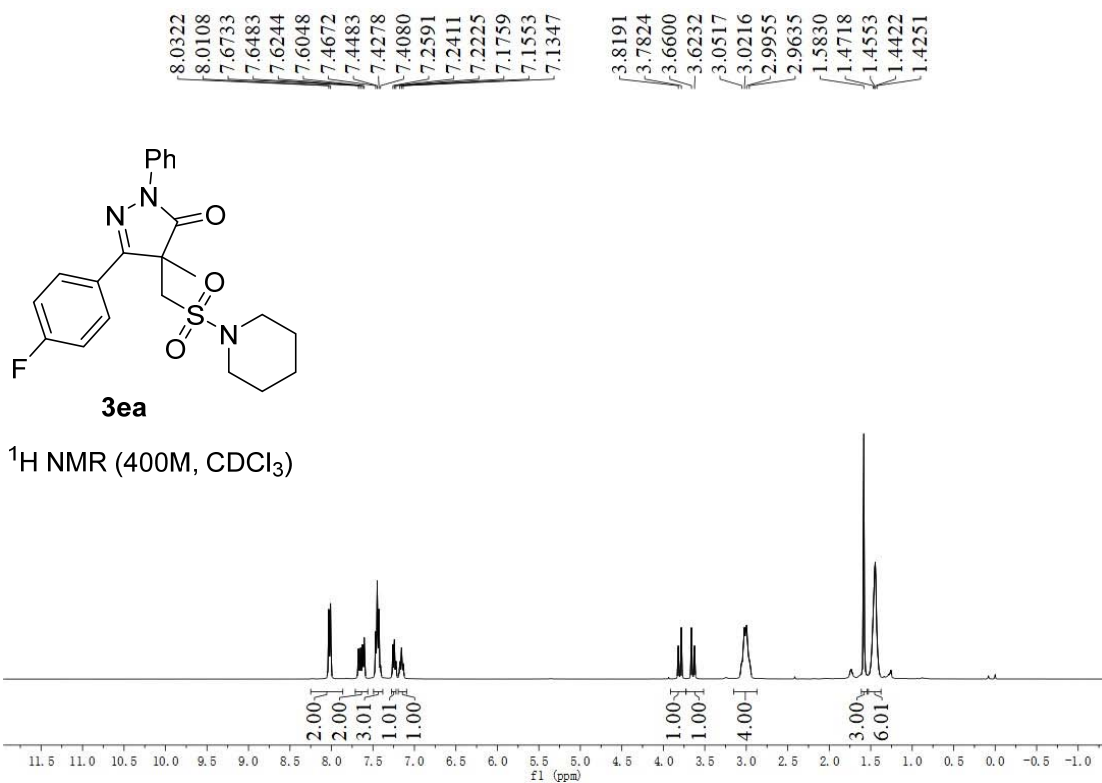
<sup>13</sup>C NMR (101M, CDCl<sub>3</sub>)

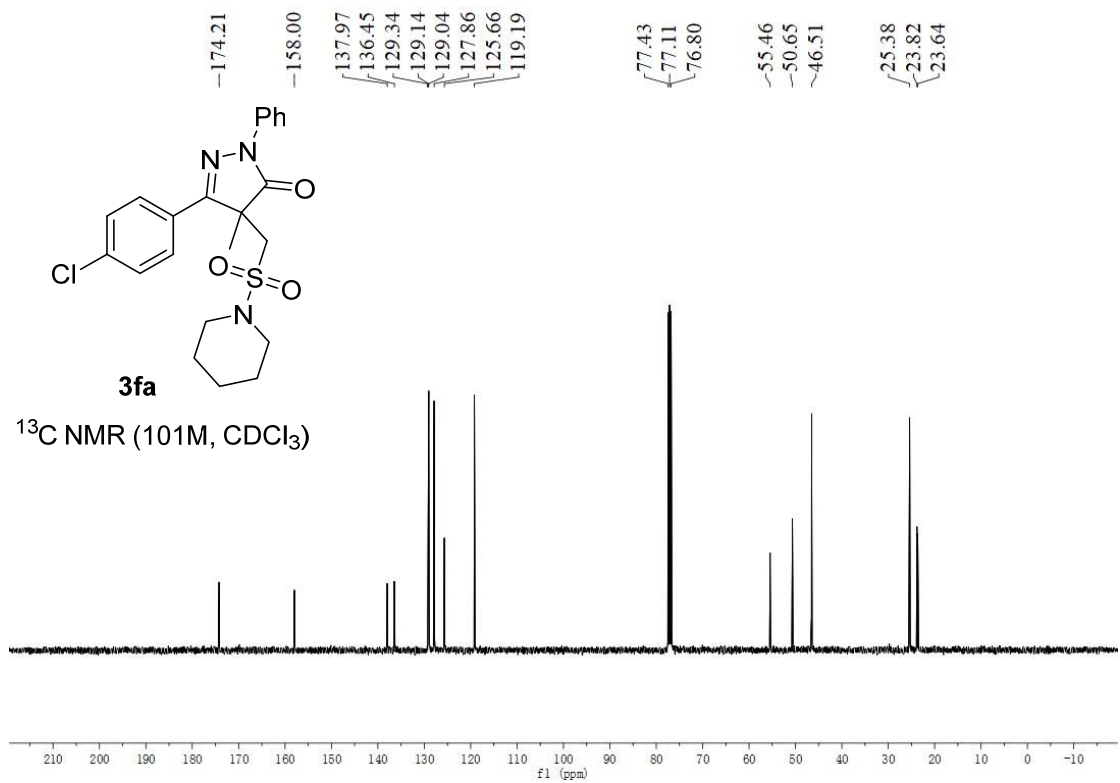
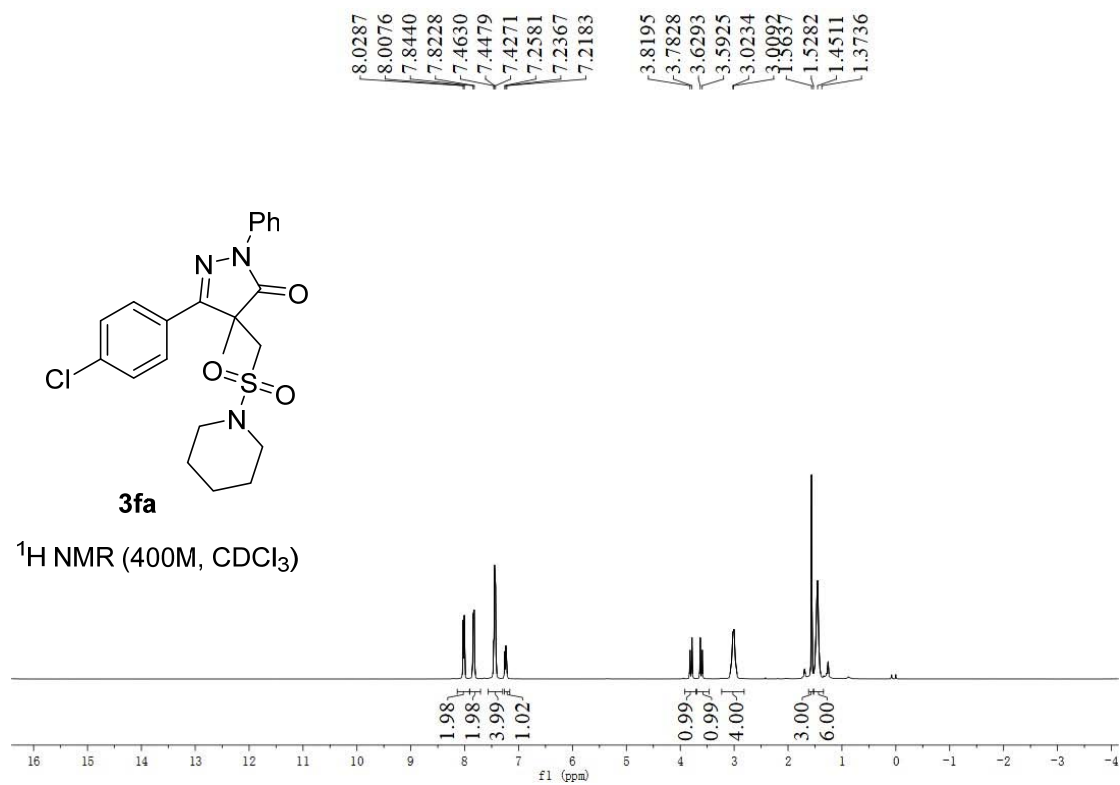




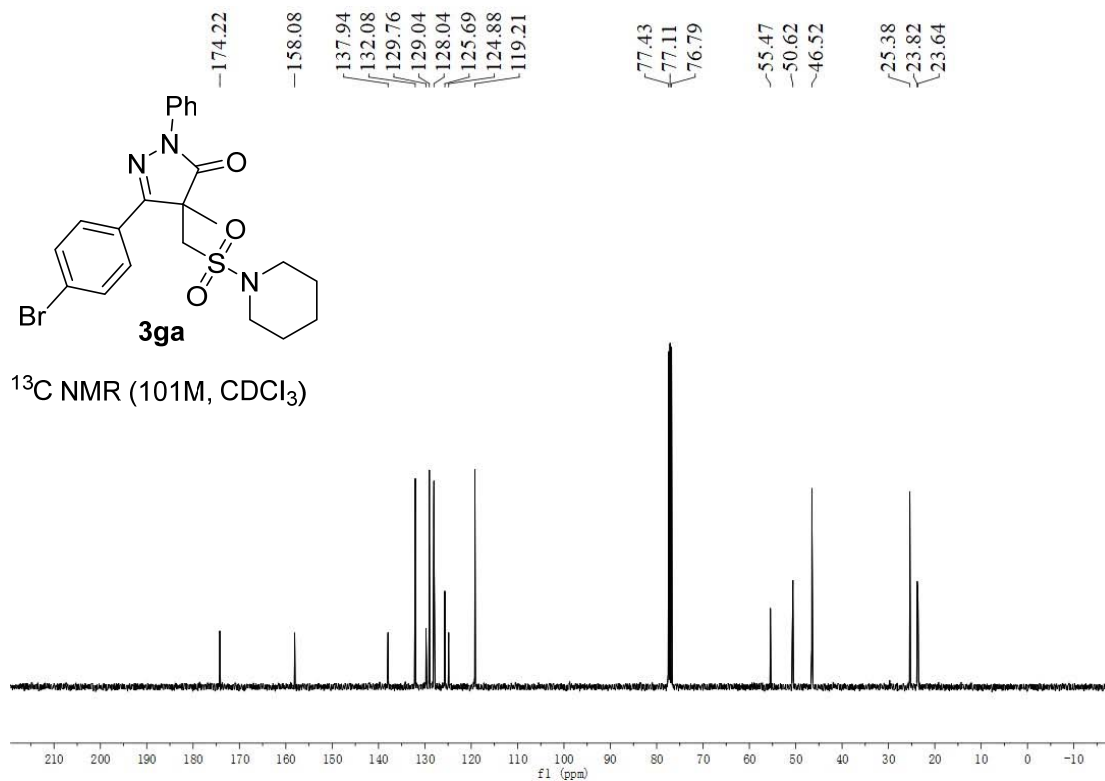
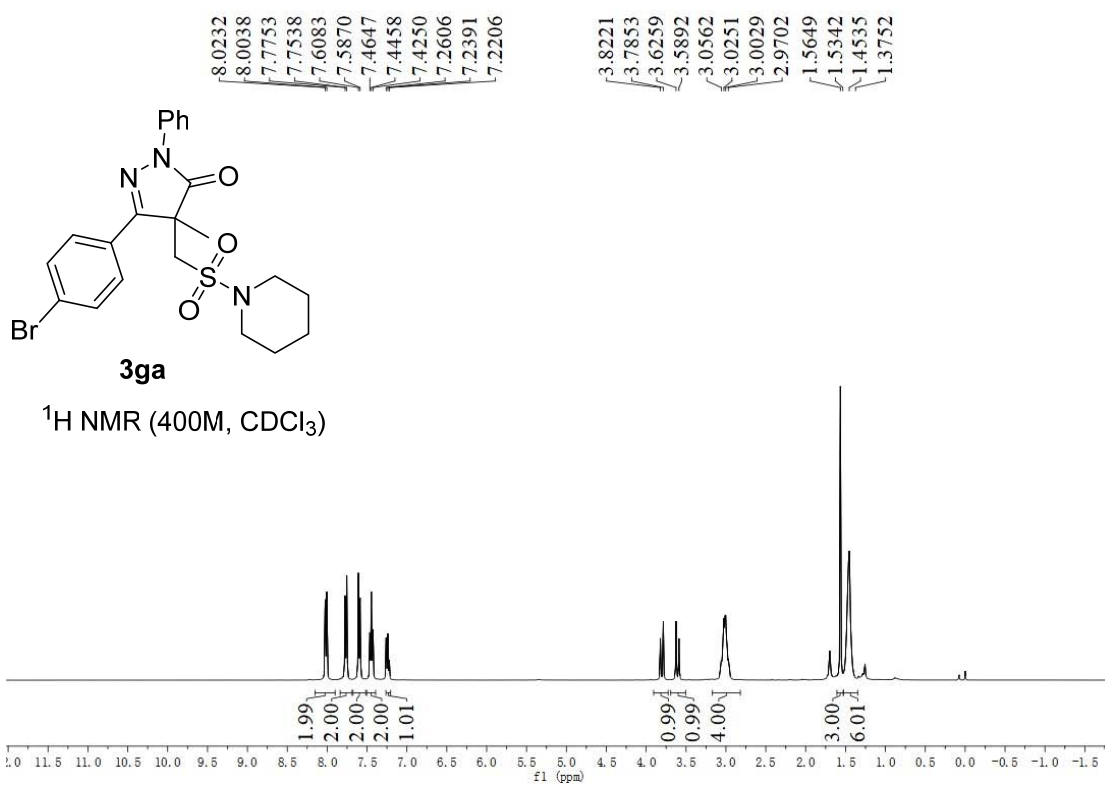


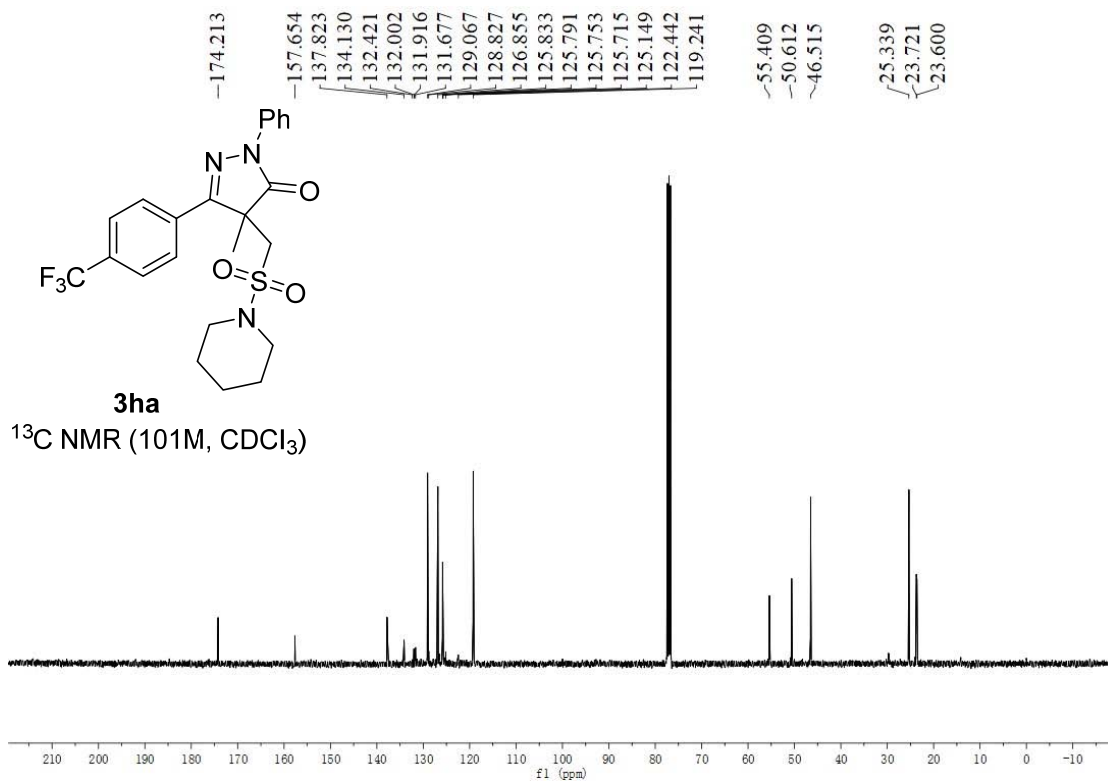
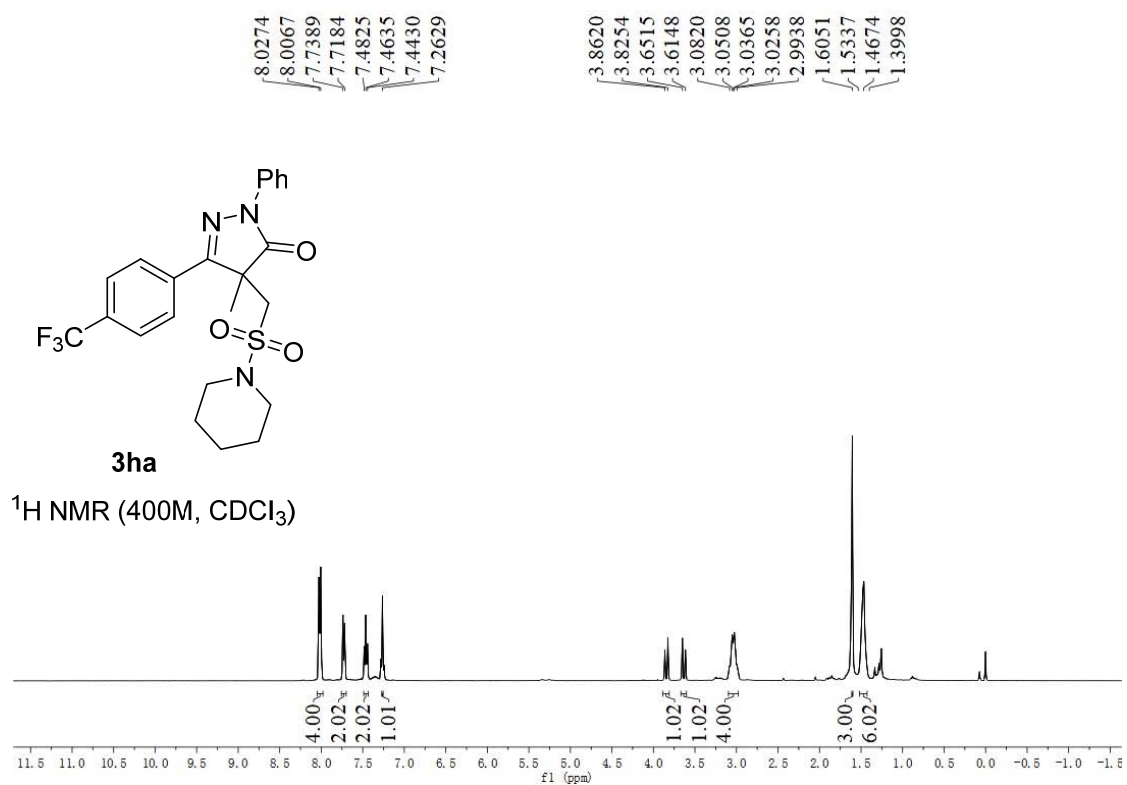


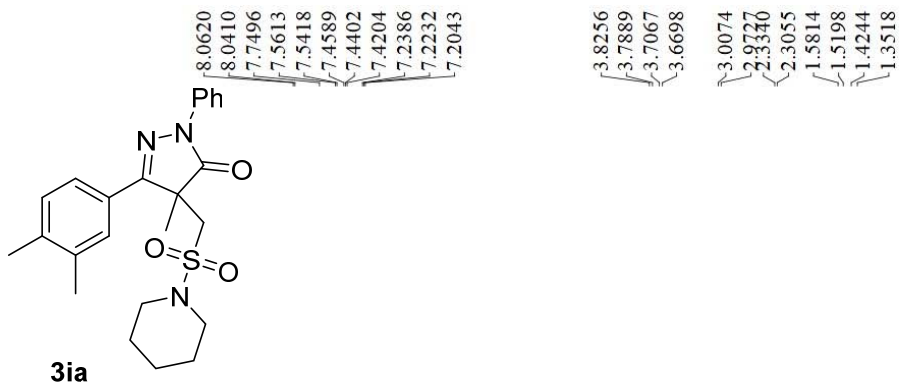




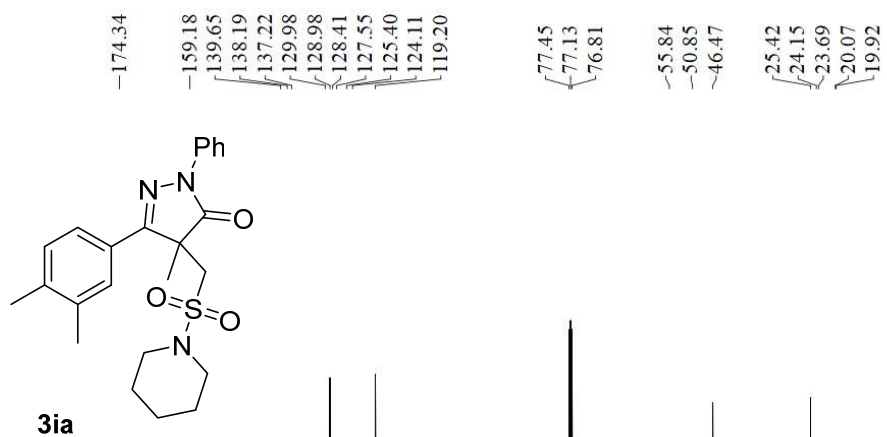
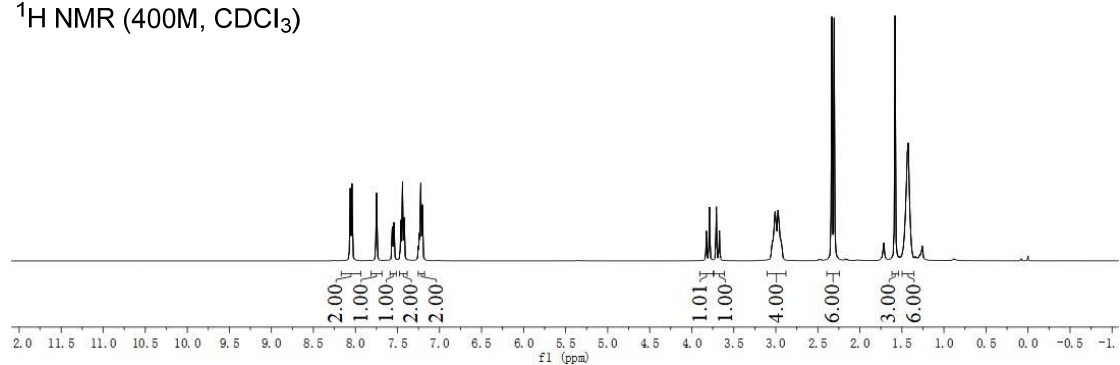




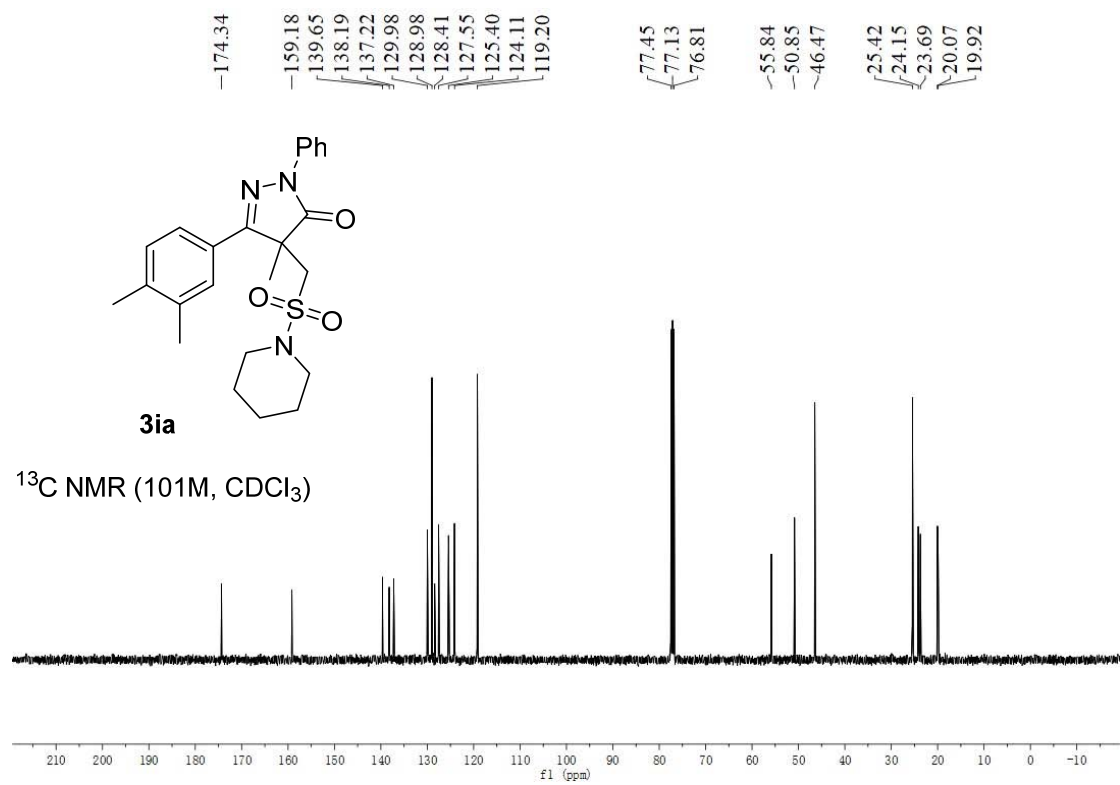


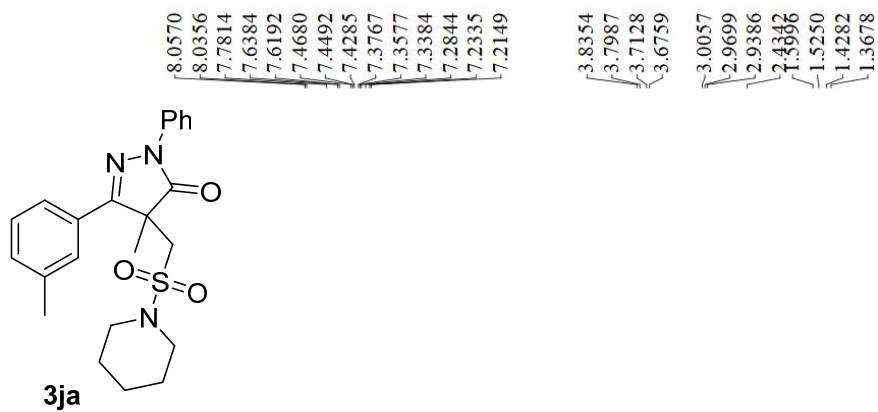


<sup>1</sup>H NMR (400M, CDCl<sub>3</sub>)

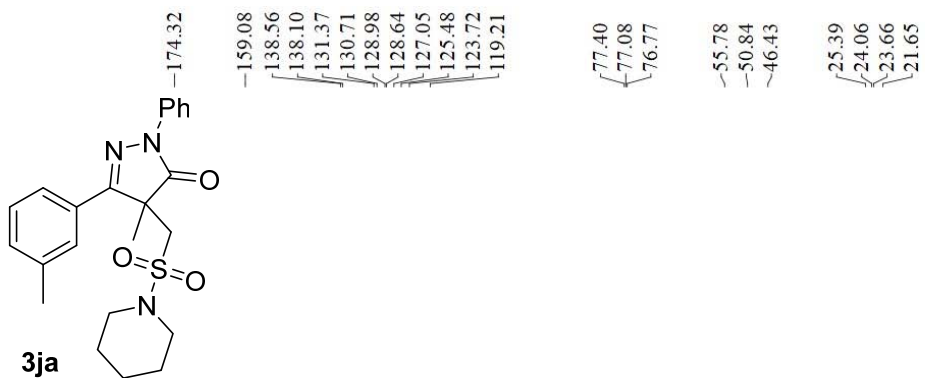
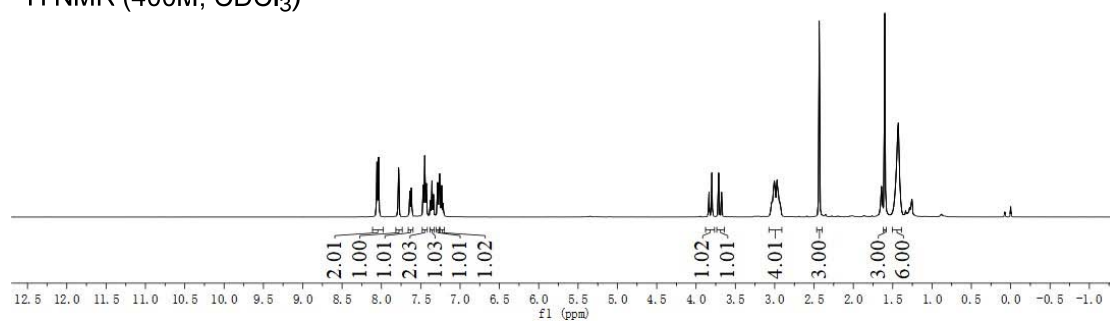


<sup>13</sup>C NMR (101M, CDCl<sub>3</sub>)

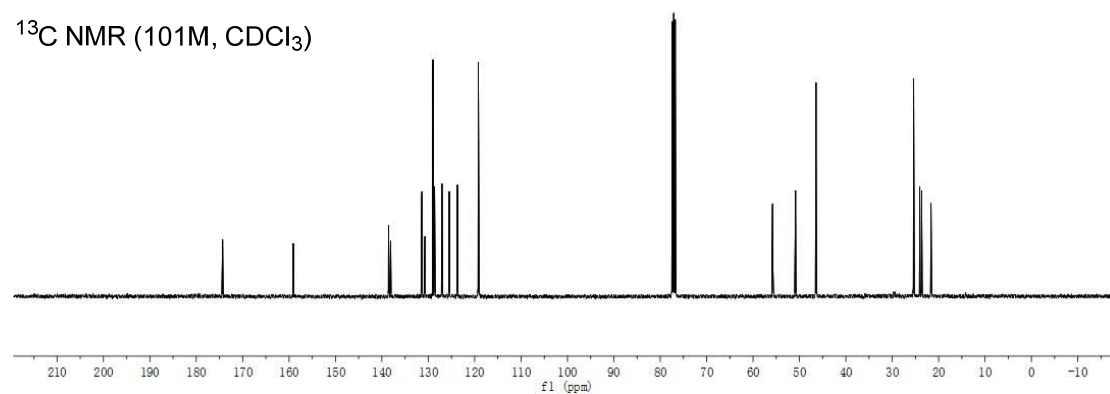


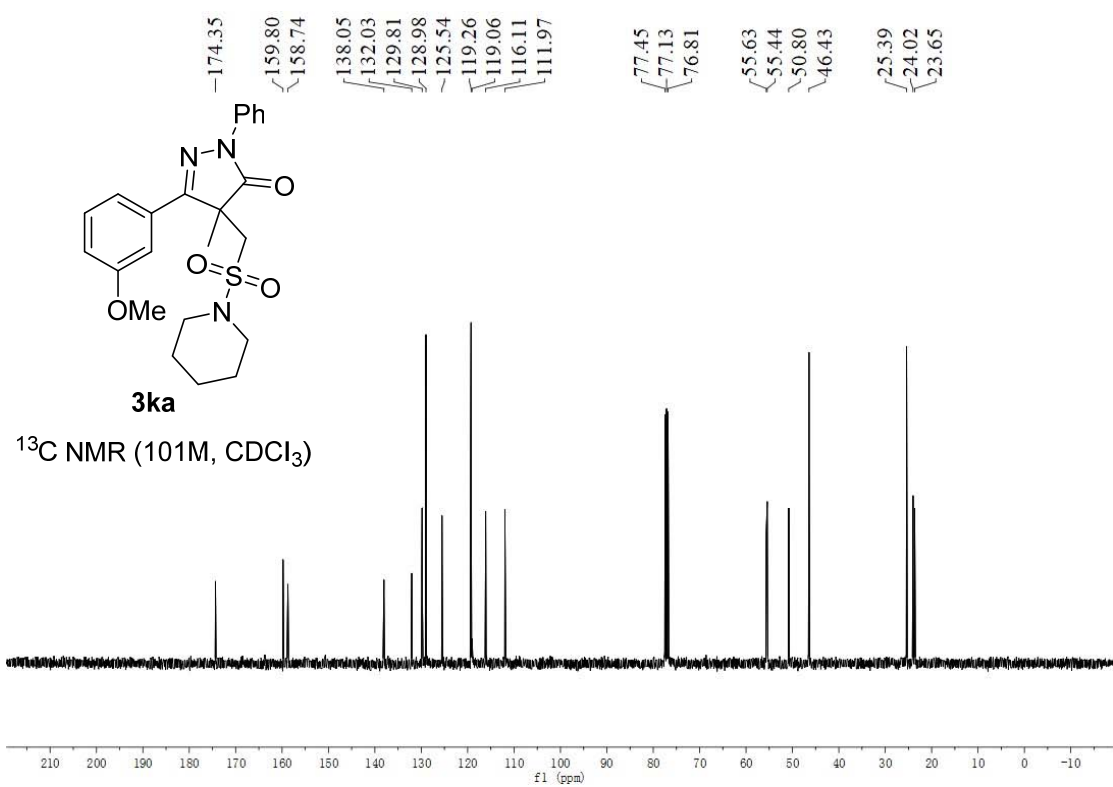
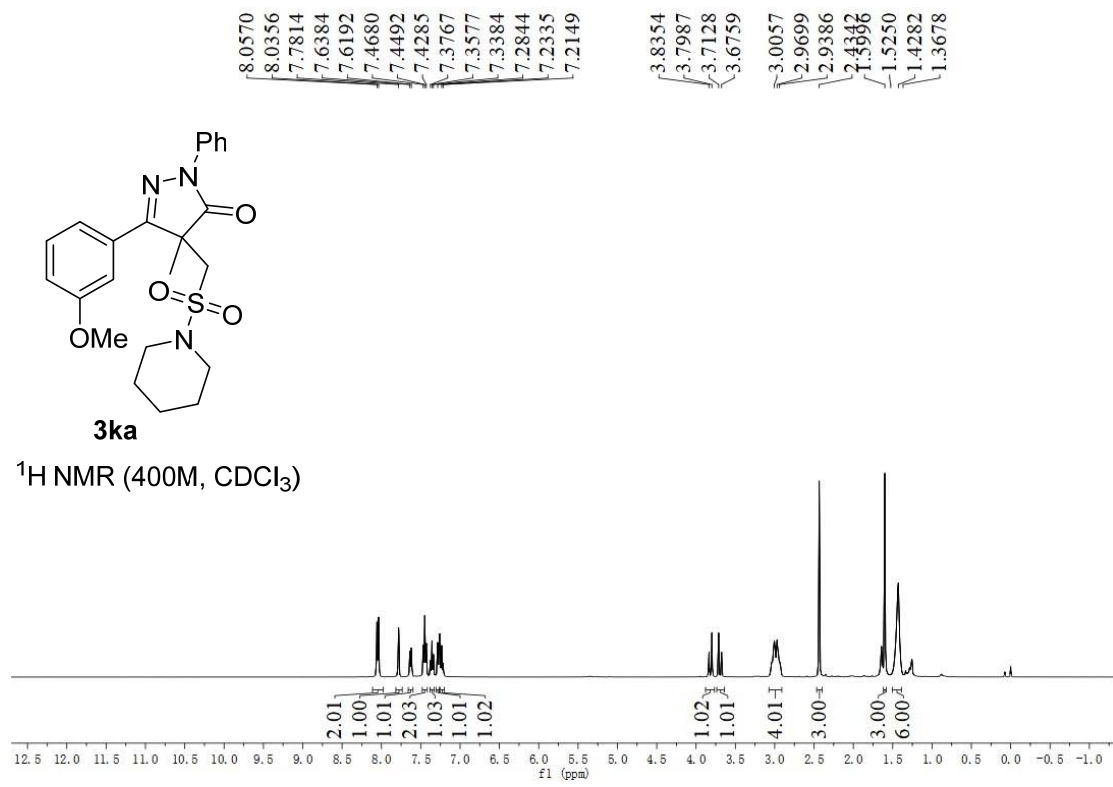


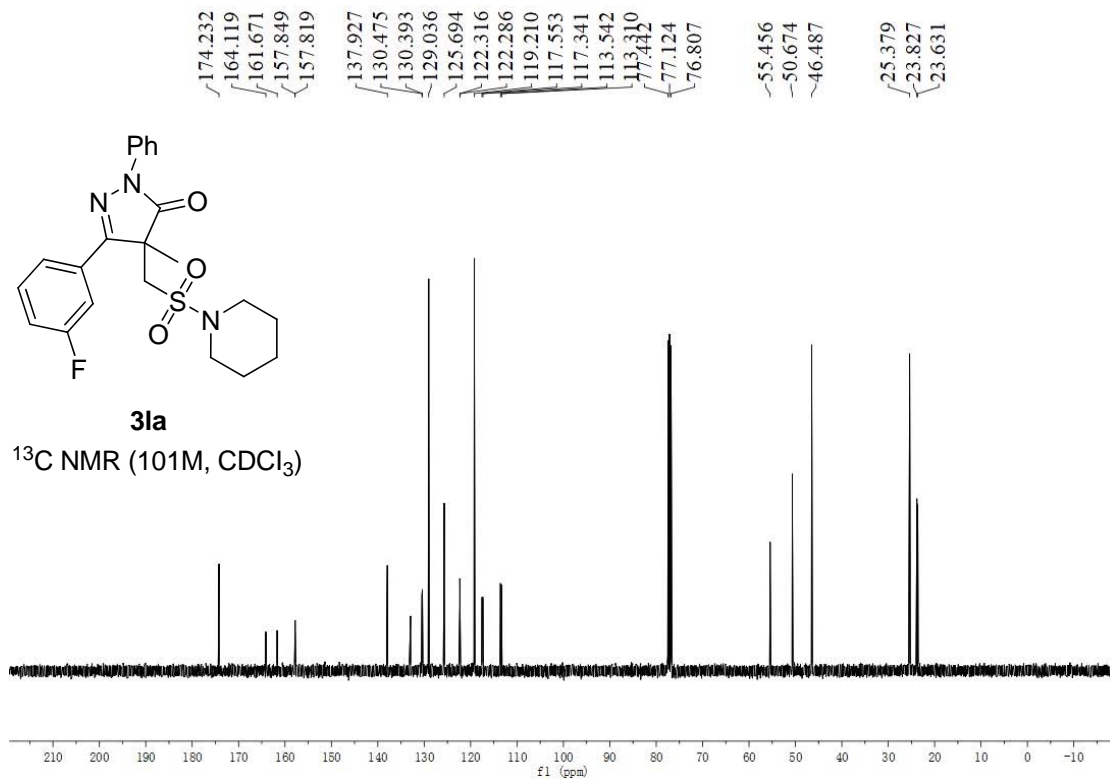
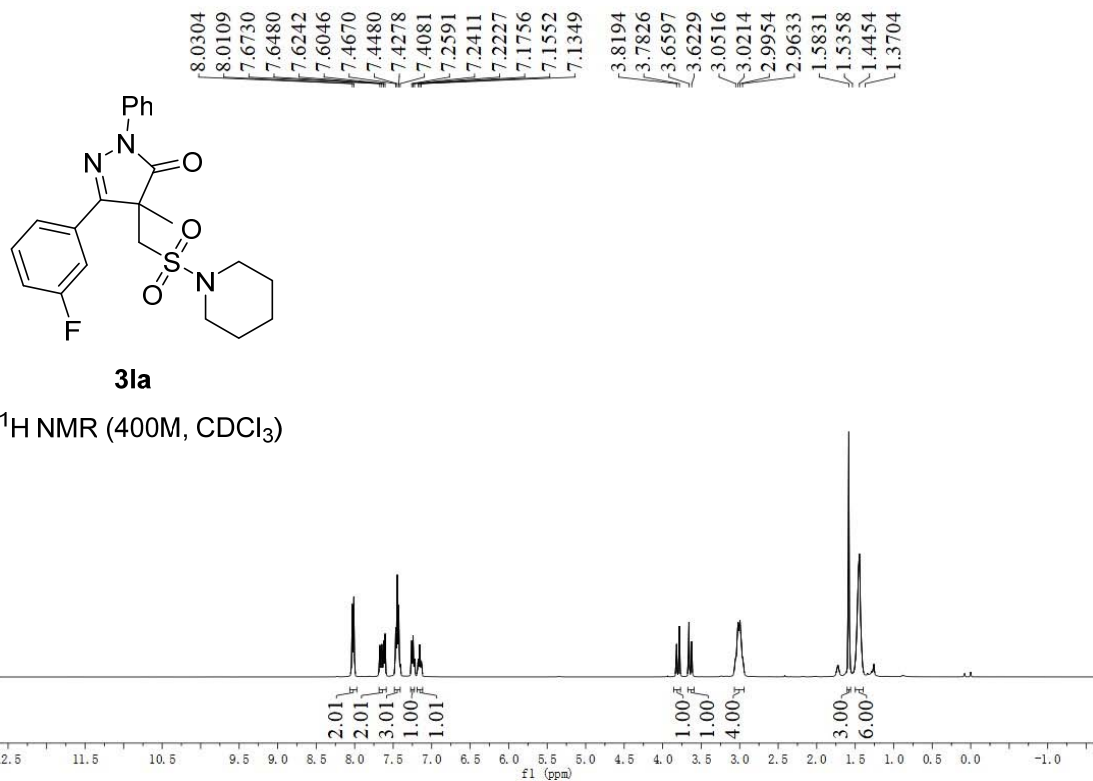
<sup>1</sup>H NMR (400M, CDCl<sub>3</sub>)

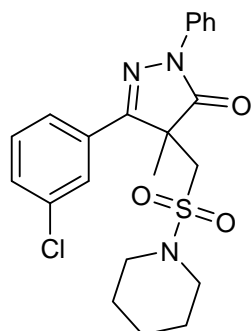


<sup>13</sup>C NMR (101M, CDCl<sub>3</sub>)



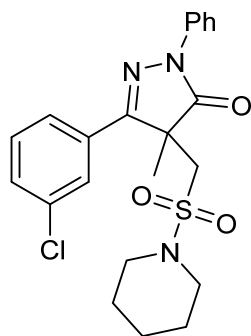
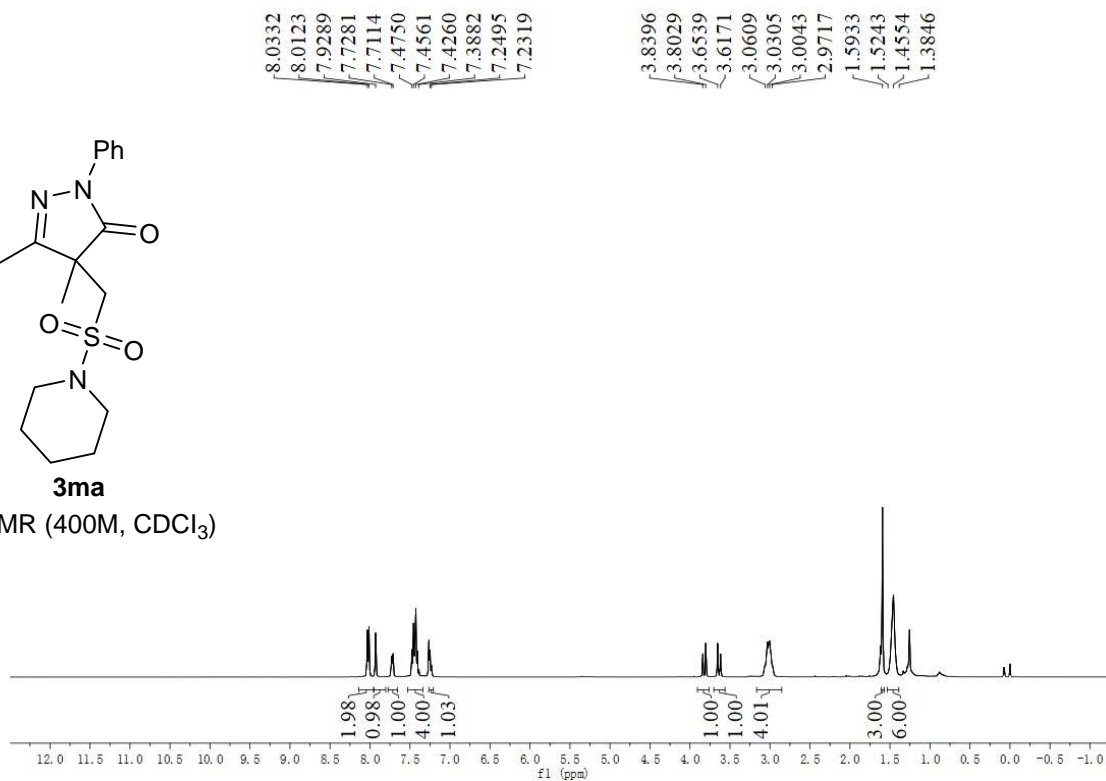






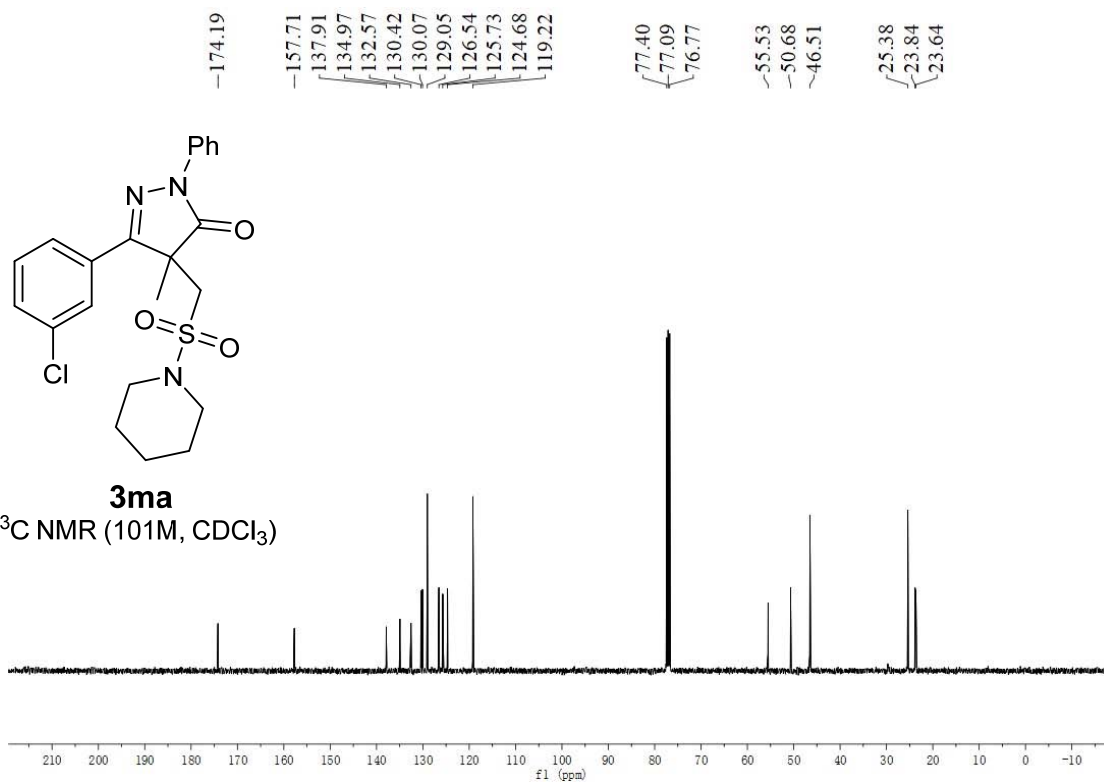
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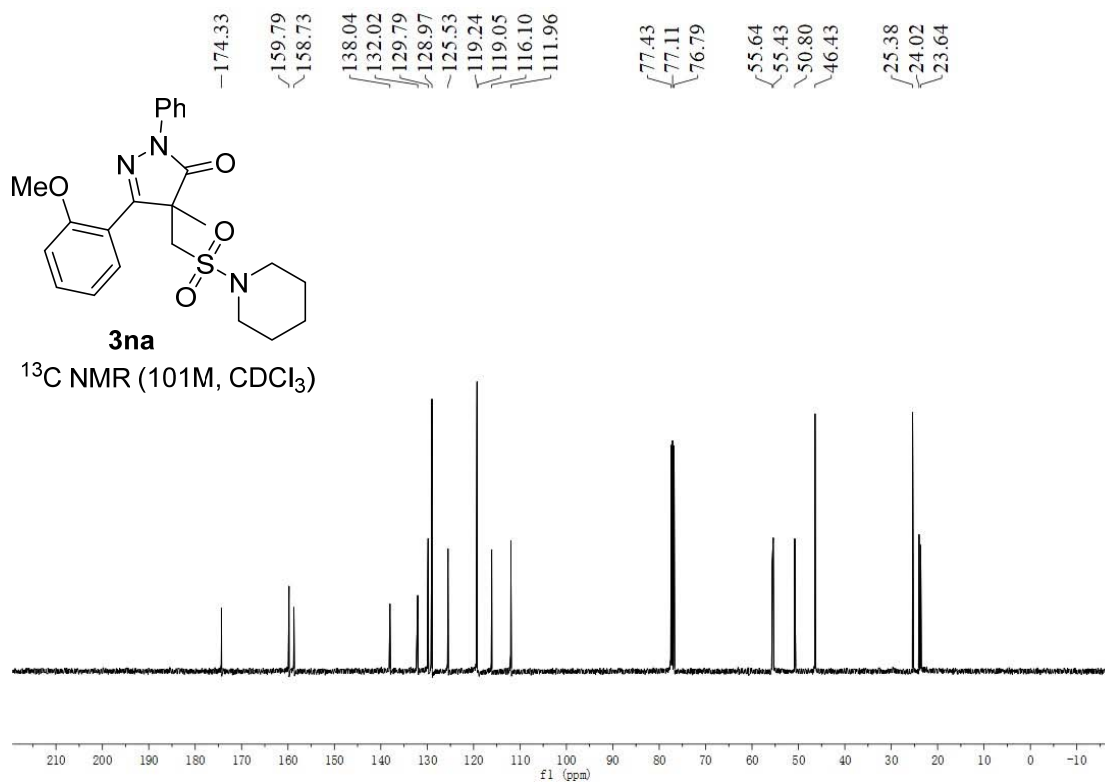
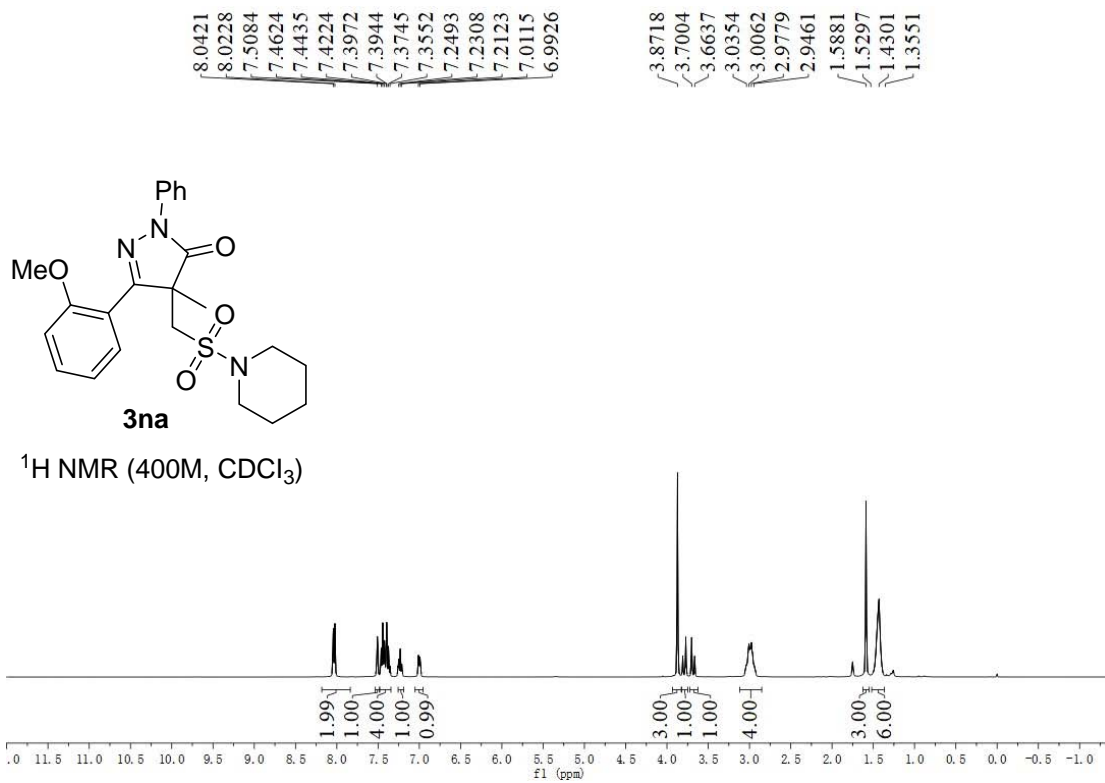
$^1\text{H NMR}$  (400M,  $\text{CDCl}_3$ )



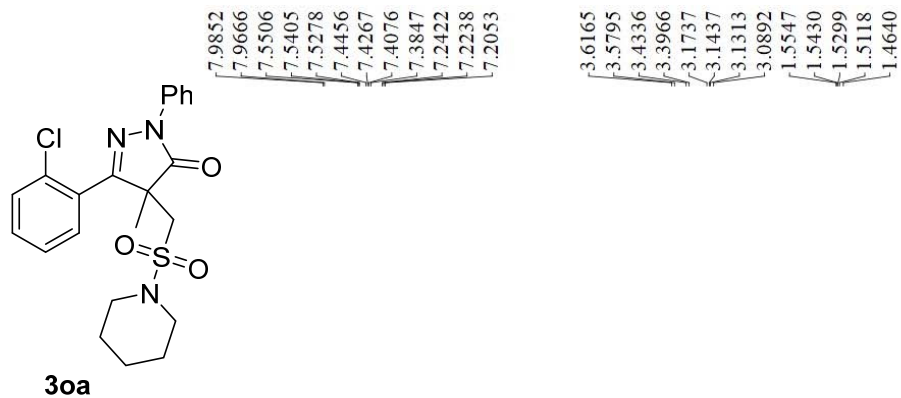
**3ma**

$^{13}\text{C NMR}$  (101M,  $\text{CDCl}_3$ )

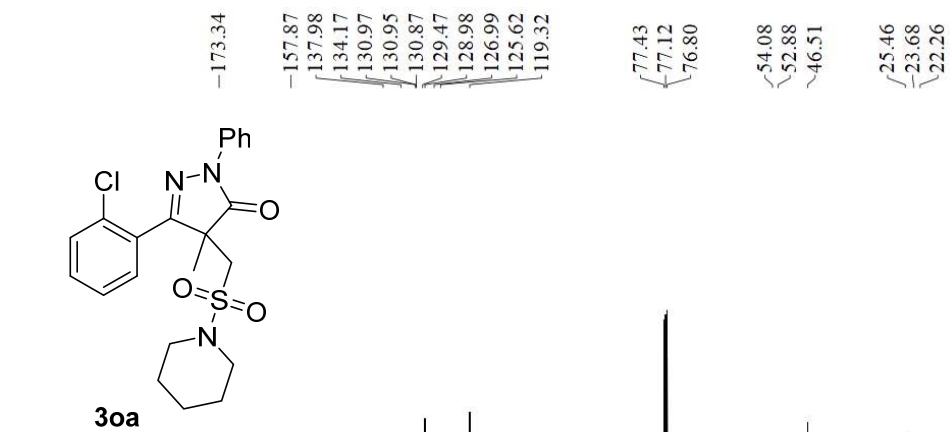
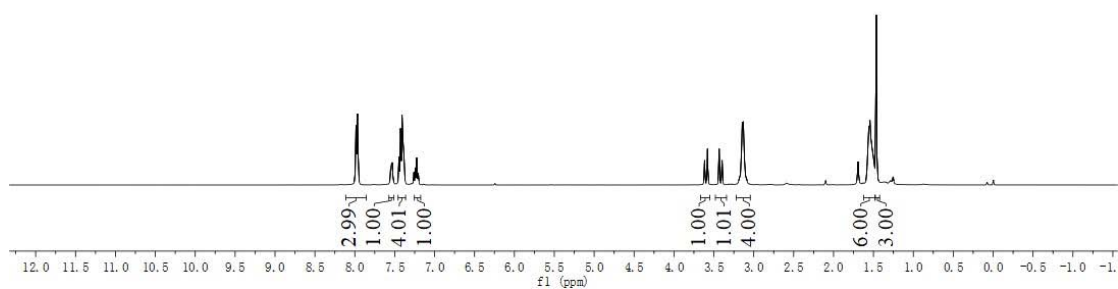




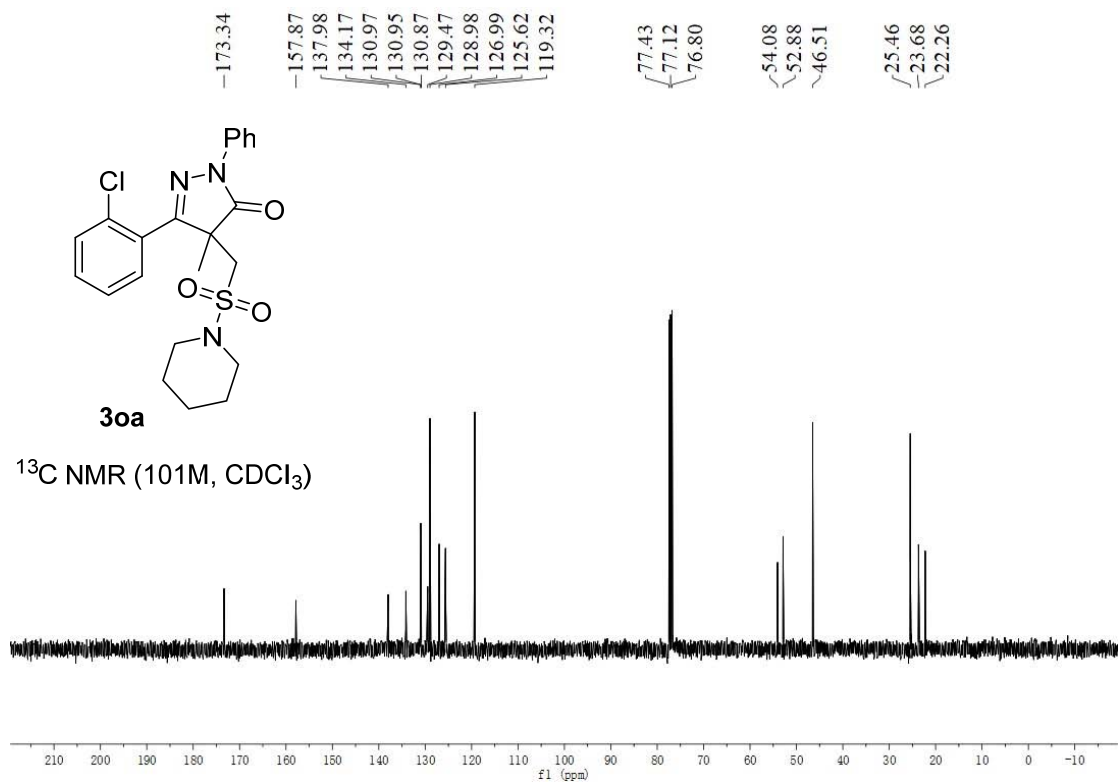


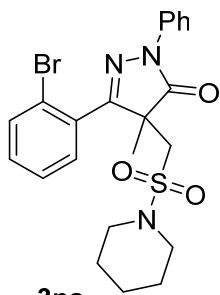


$^1\text{H}$  NMR (400M,  $\text{CDCl}_3$ )



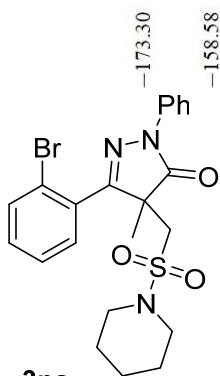
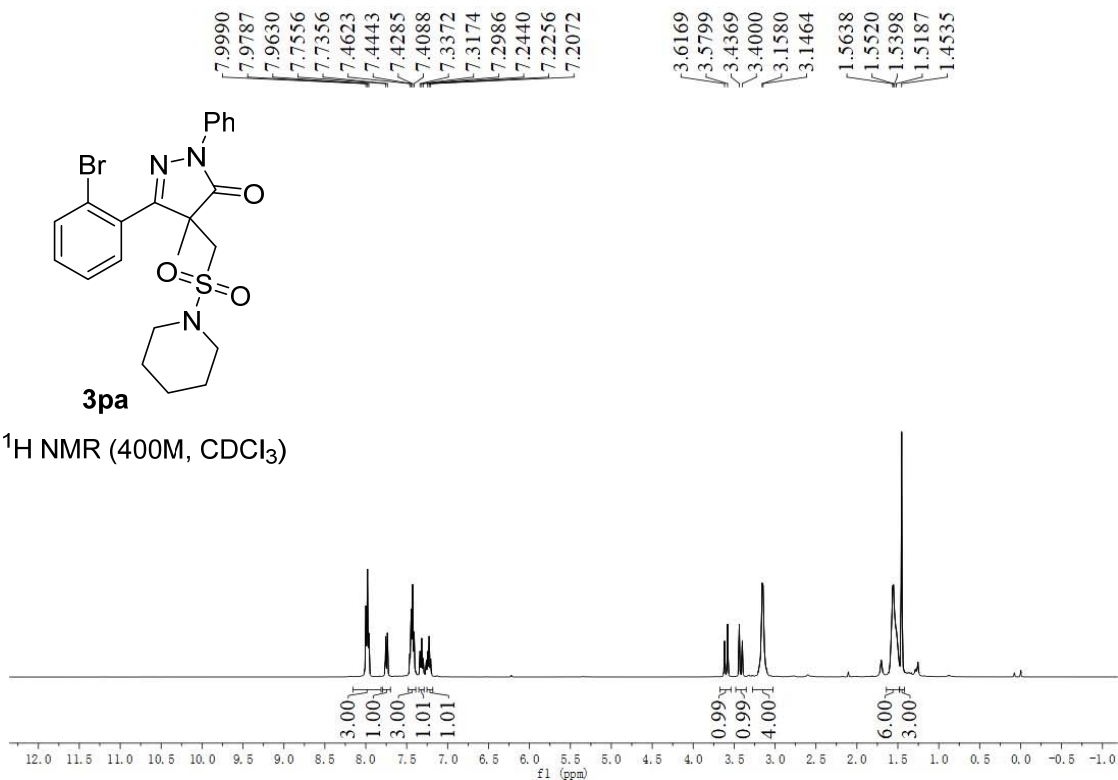
$^{13}\text{C}$  NMR (101M,  $\text{CDCl}_3$ )





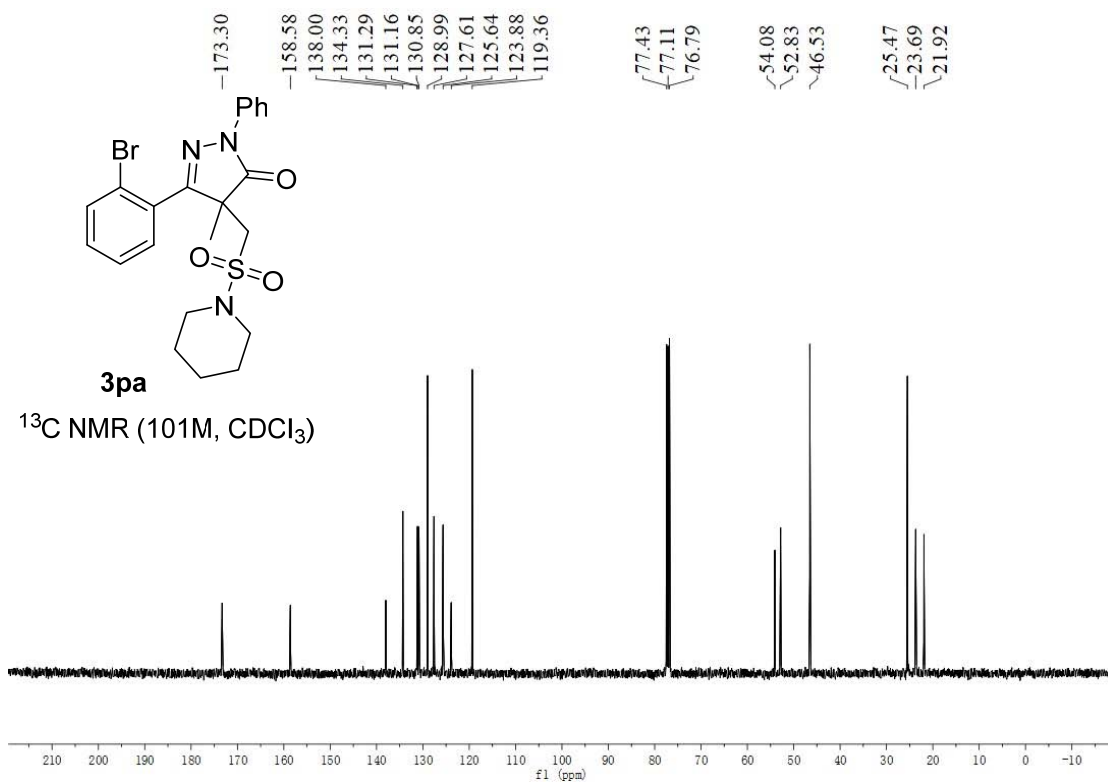
**3pa**

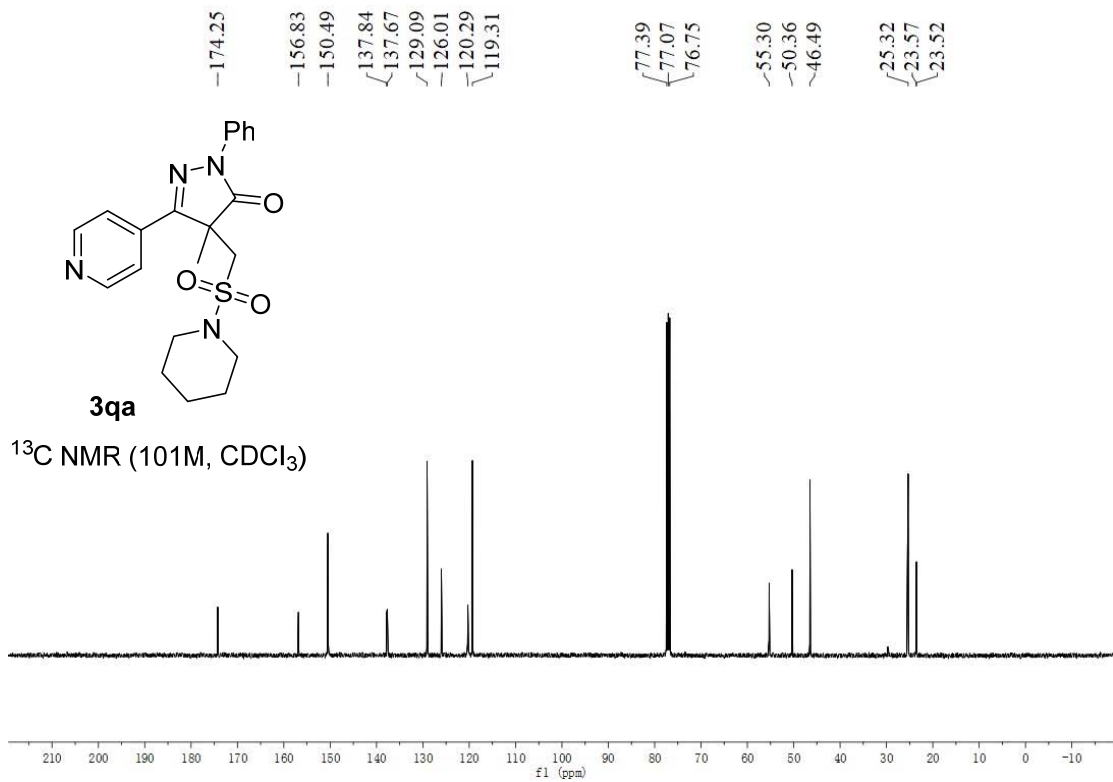
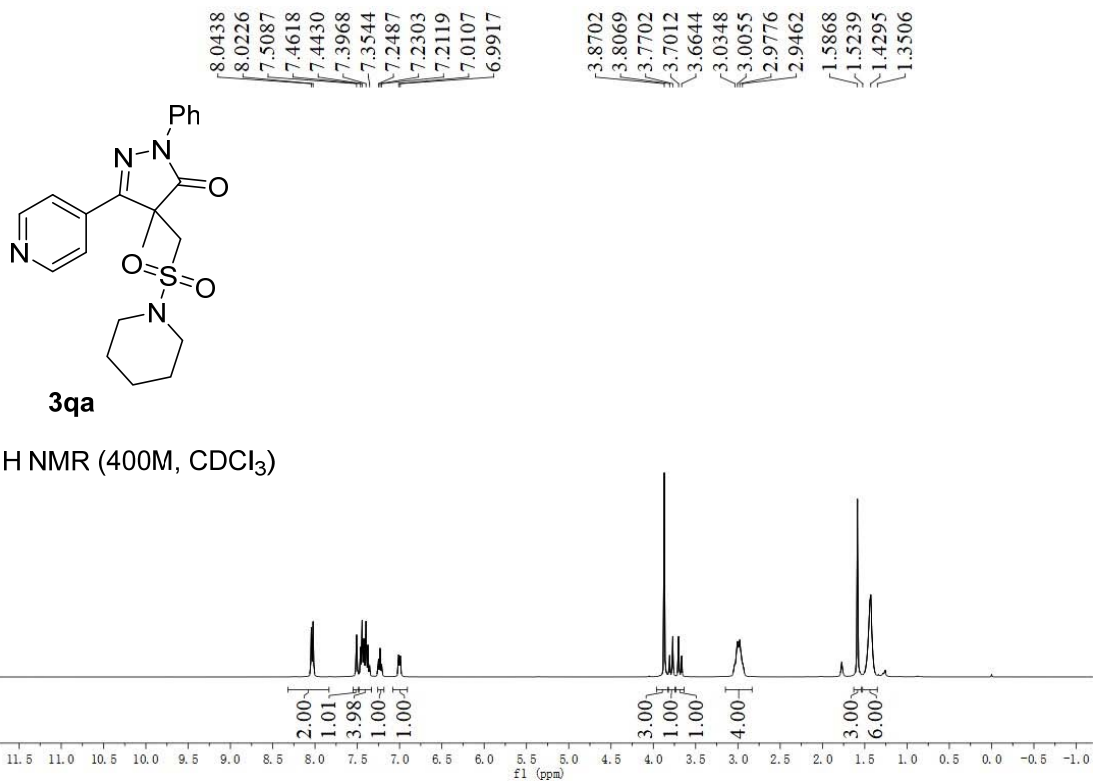
$^1\text{H}$  NMR (400M,  $\text{CDCl}_3$ )

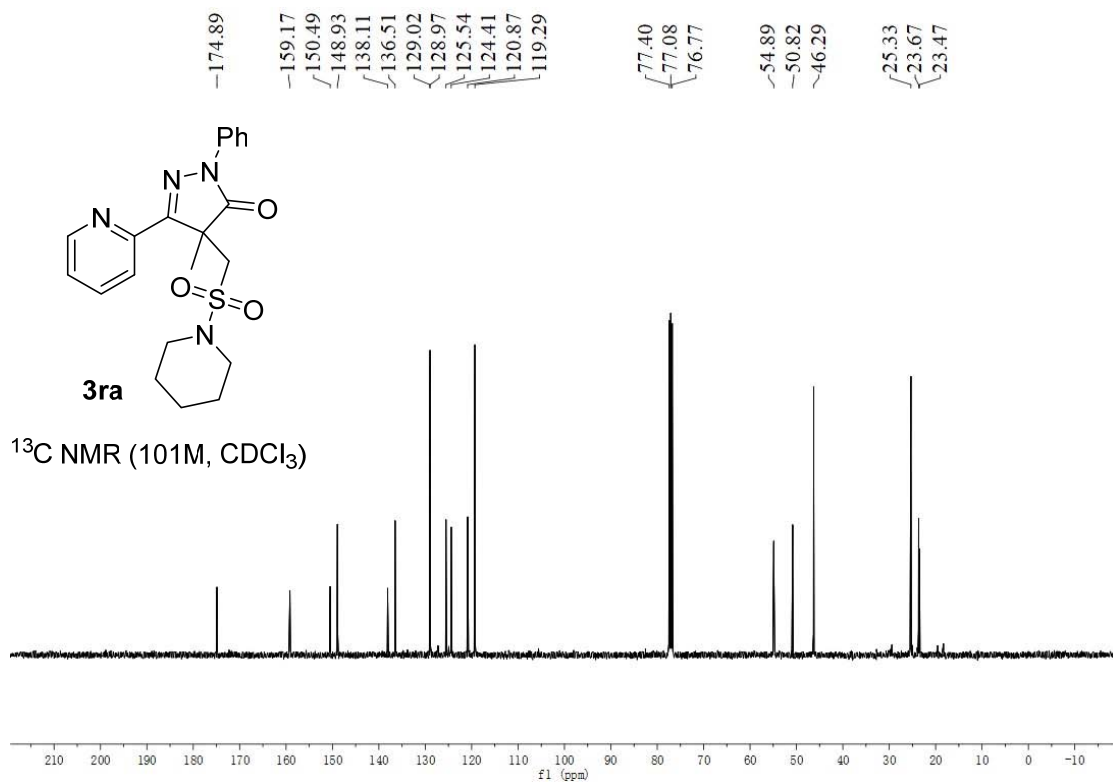
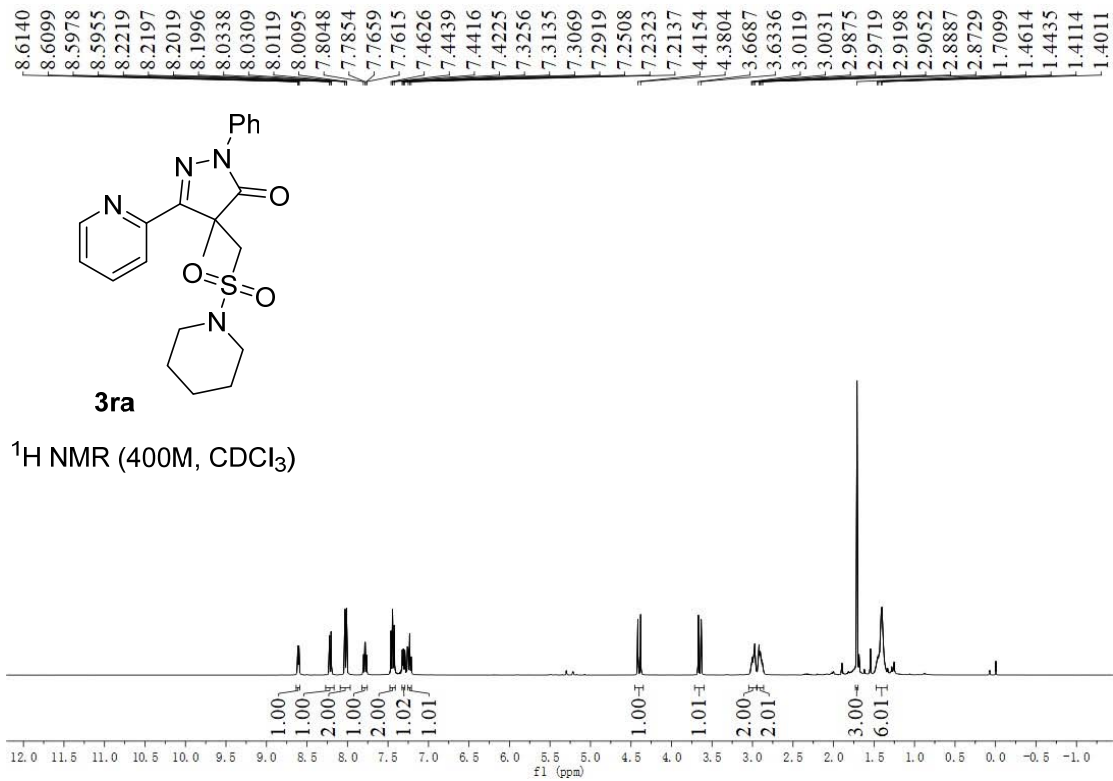


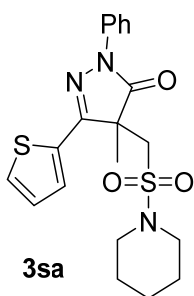
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$^{13}\text{C}$  NMR (101M,  $\text{CDCl}_3$ )

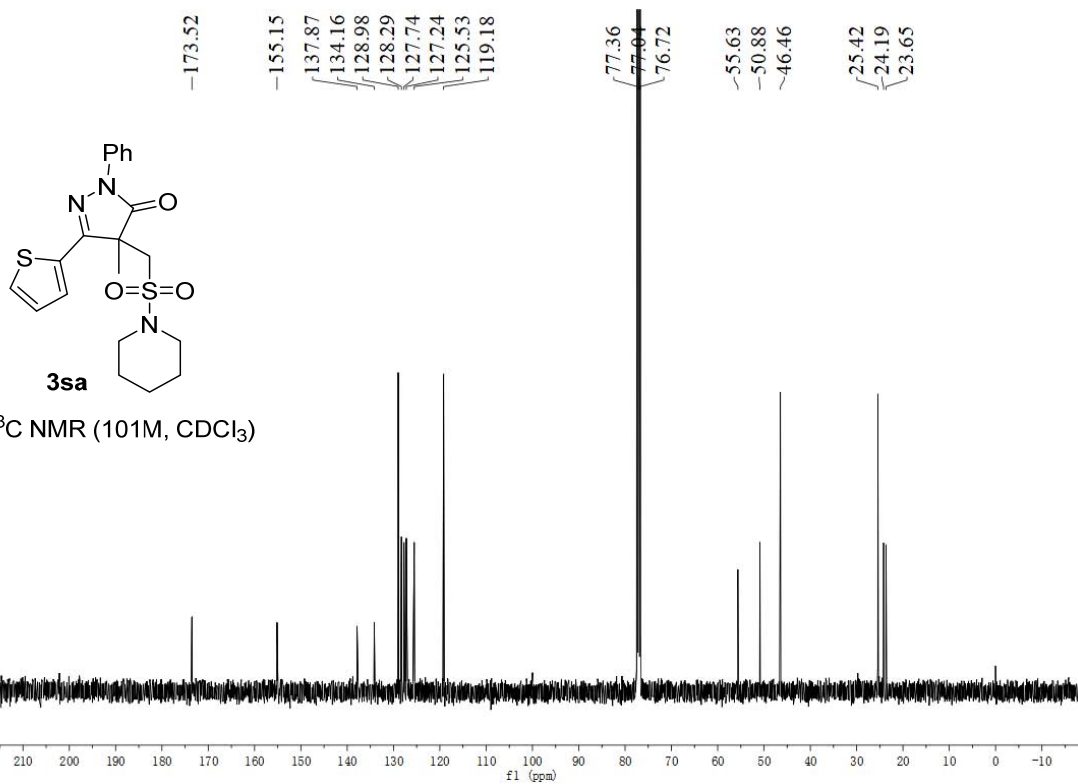
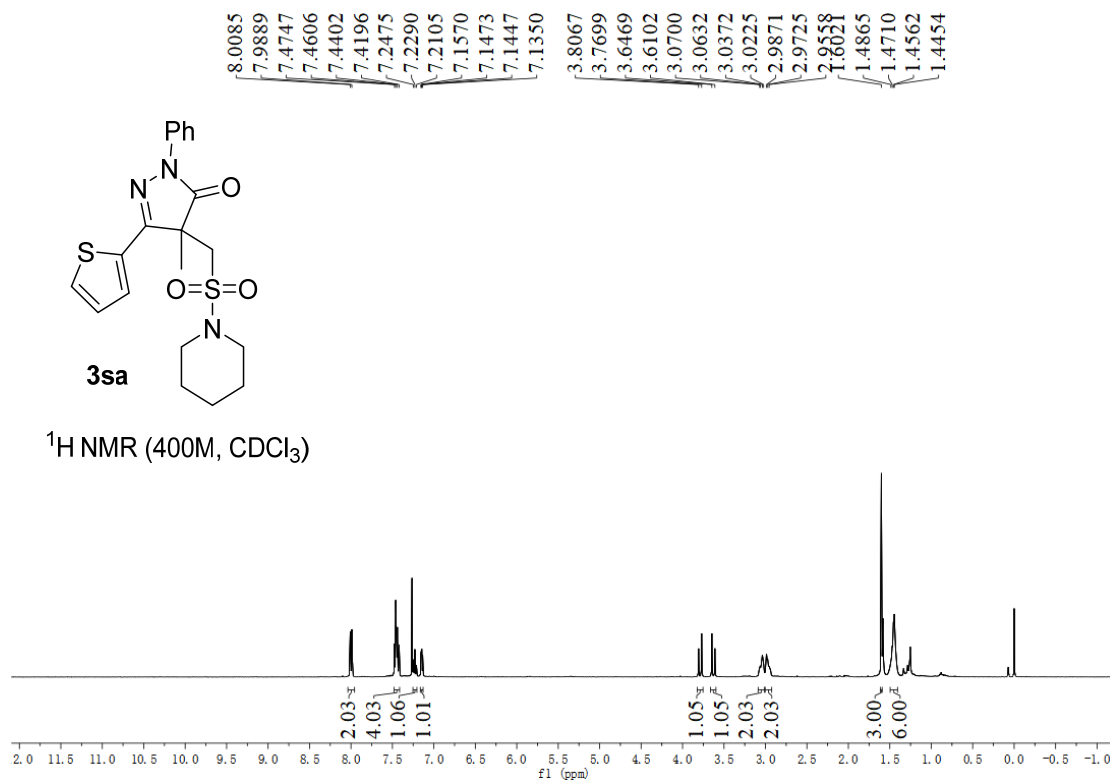


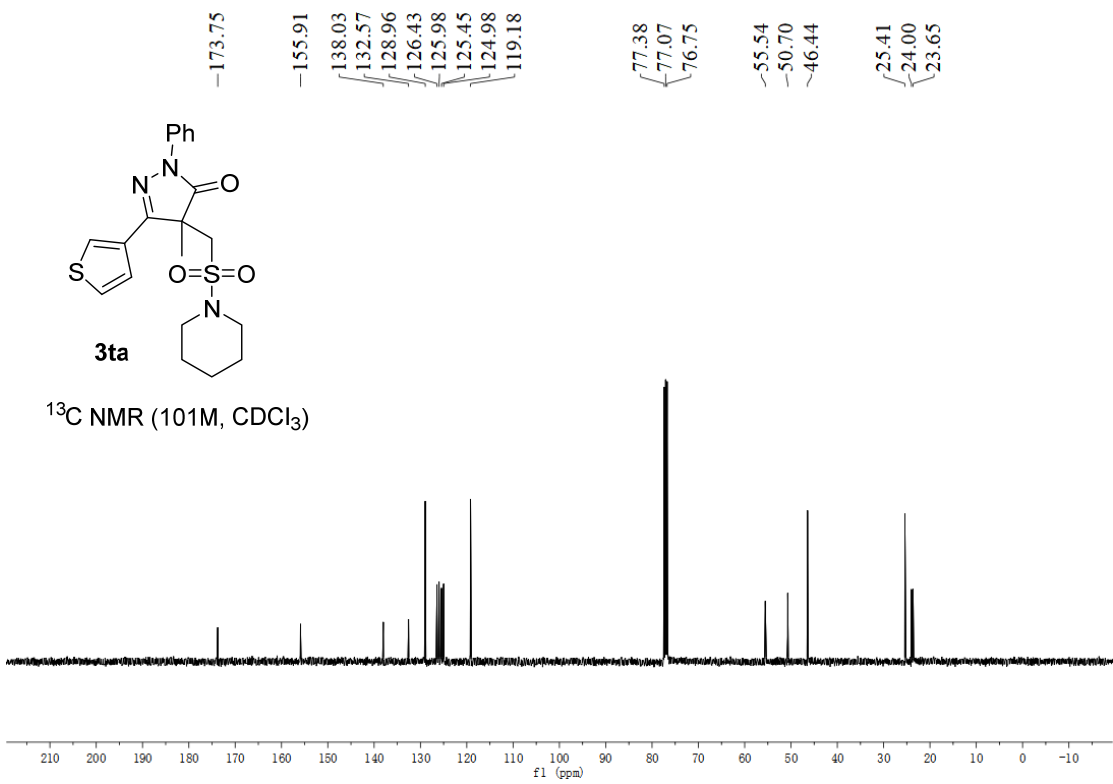
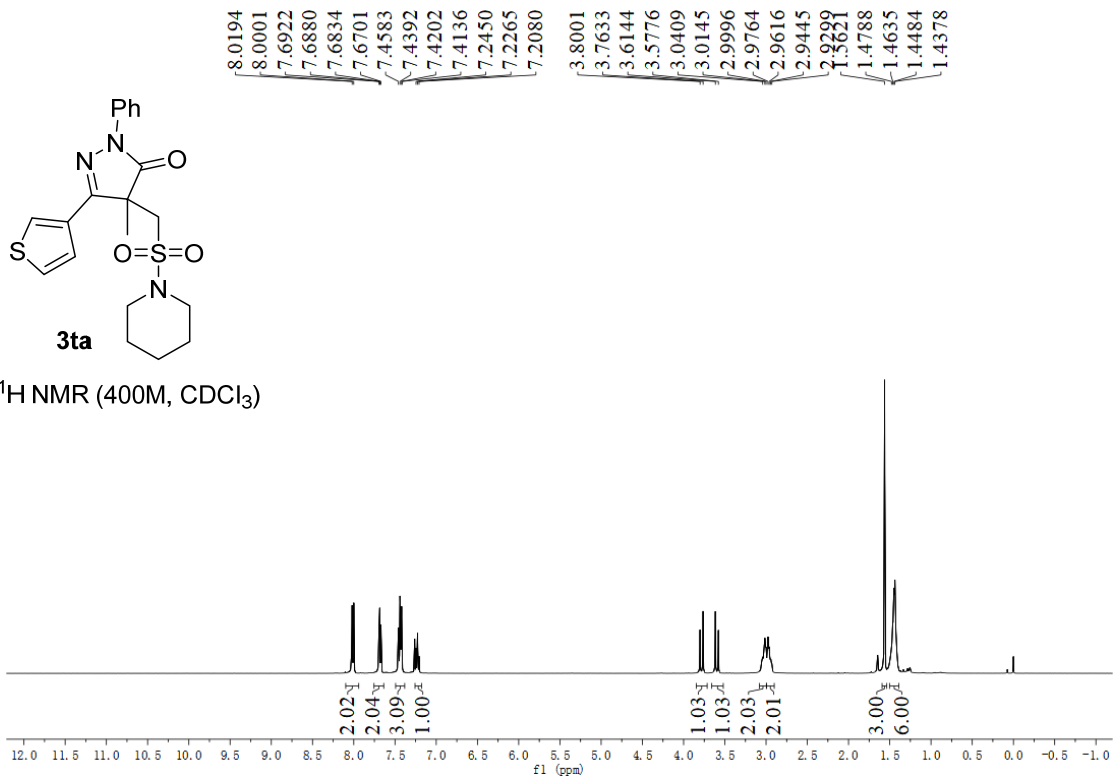


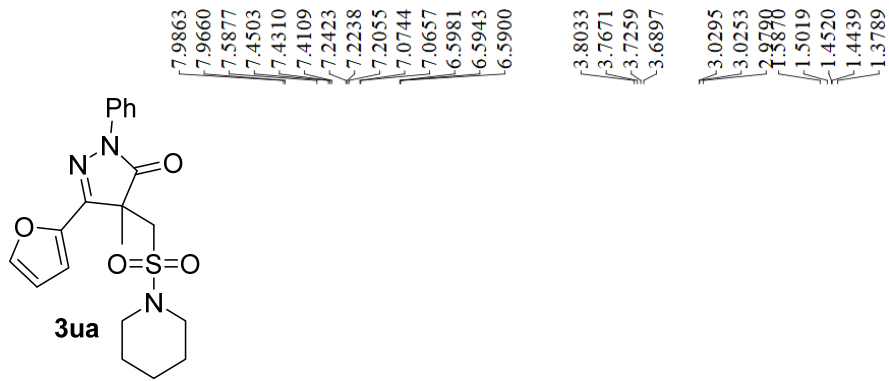




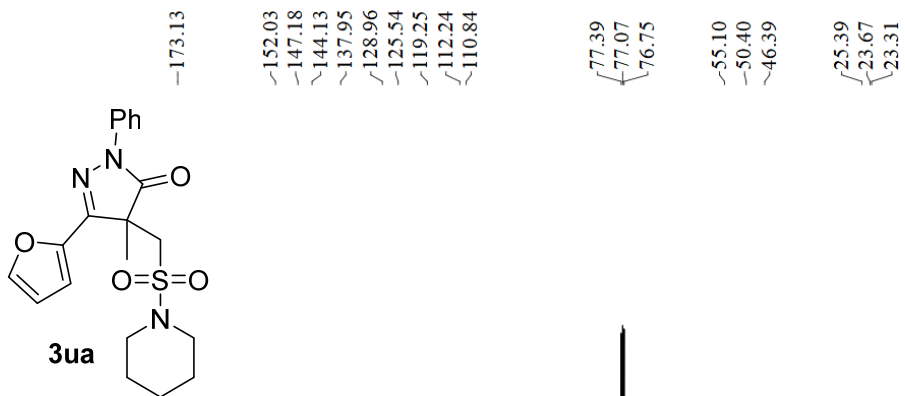
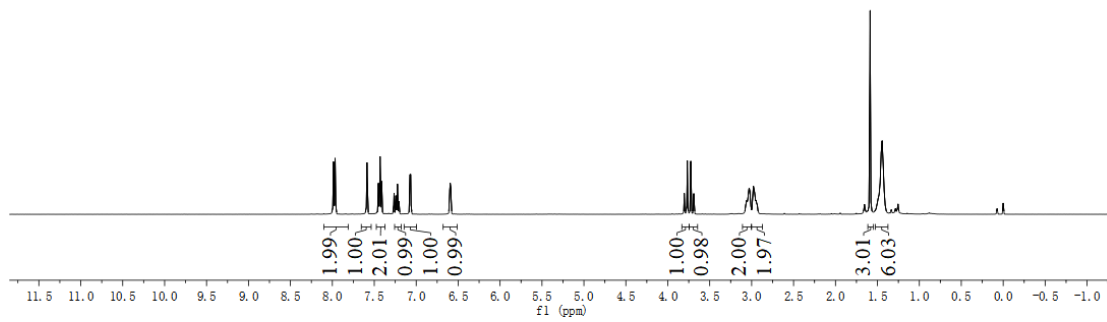
<sup>1</sup>H NMR (400M, CDCl<sub>3</sub>)



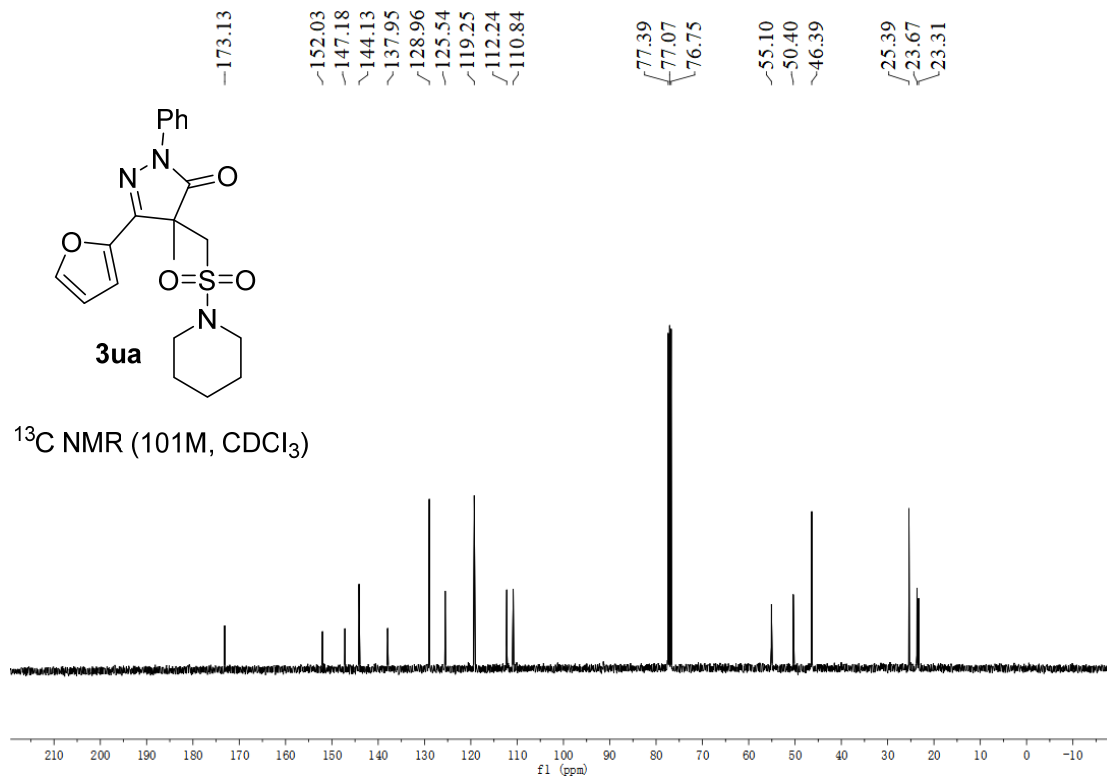




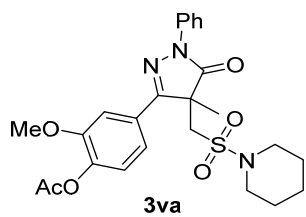
<sup>1</sup>H NMR (400M, CDCl<sub>3</sub>)



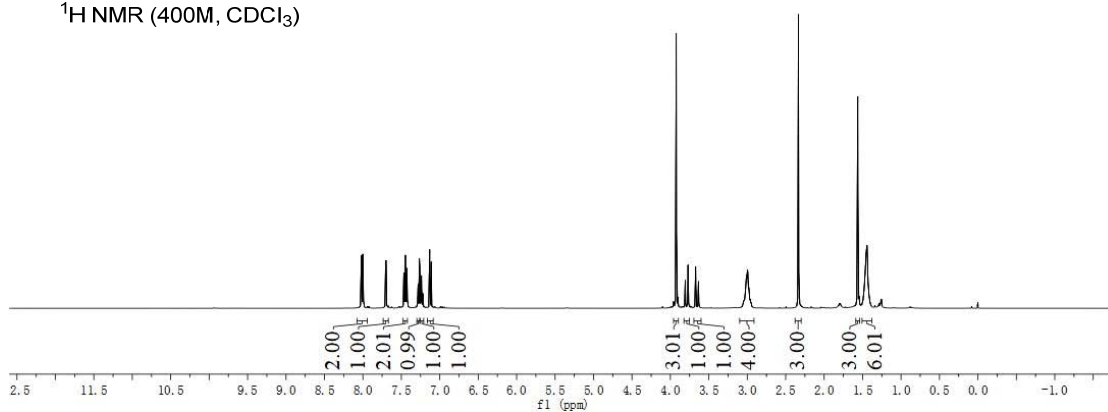
<sup>13</sup>C NMR (101M, CDCl<sub>3</sub>)



8.0226  
8.0197  
8.0007  
7.9983  
7.7036  
7.6990  
7.4669  
7.4482  
7.4269  
7.4220  
7.2857  
7.2808  
7.2650  
7.2570  
7.2383  
7.2198  
7.2172  
7.1314  
7.1108  
3.9240  
3.8069  
3.7700  
3.6716  
3.6348  
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1.4524  
1.4437

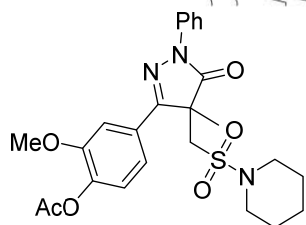


<sup>1</sup>H NMR (400M, CDCl<sub>3</sub>)

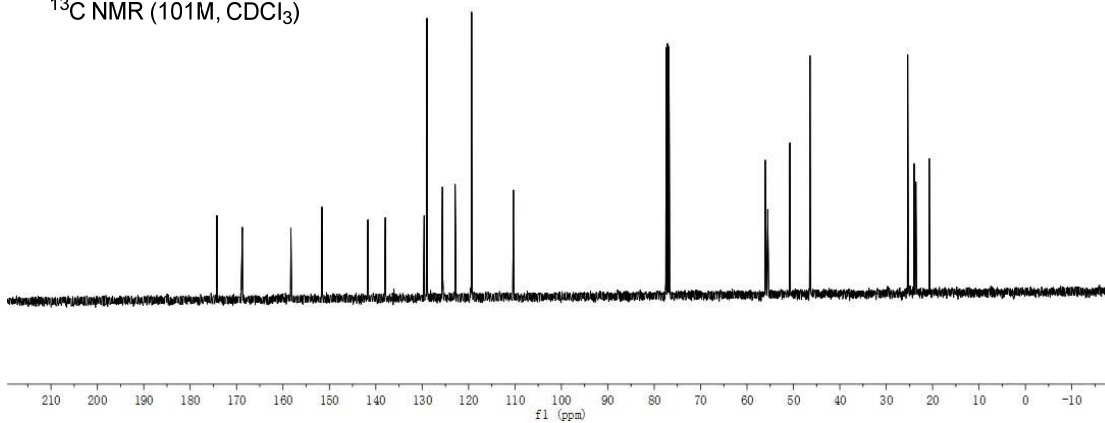


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168.77  
158.29  
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141.69  
137.94  
129.57  
128.97  
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119.36  
119.31  
110.35

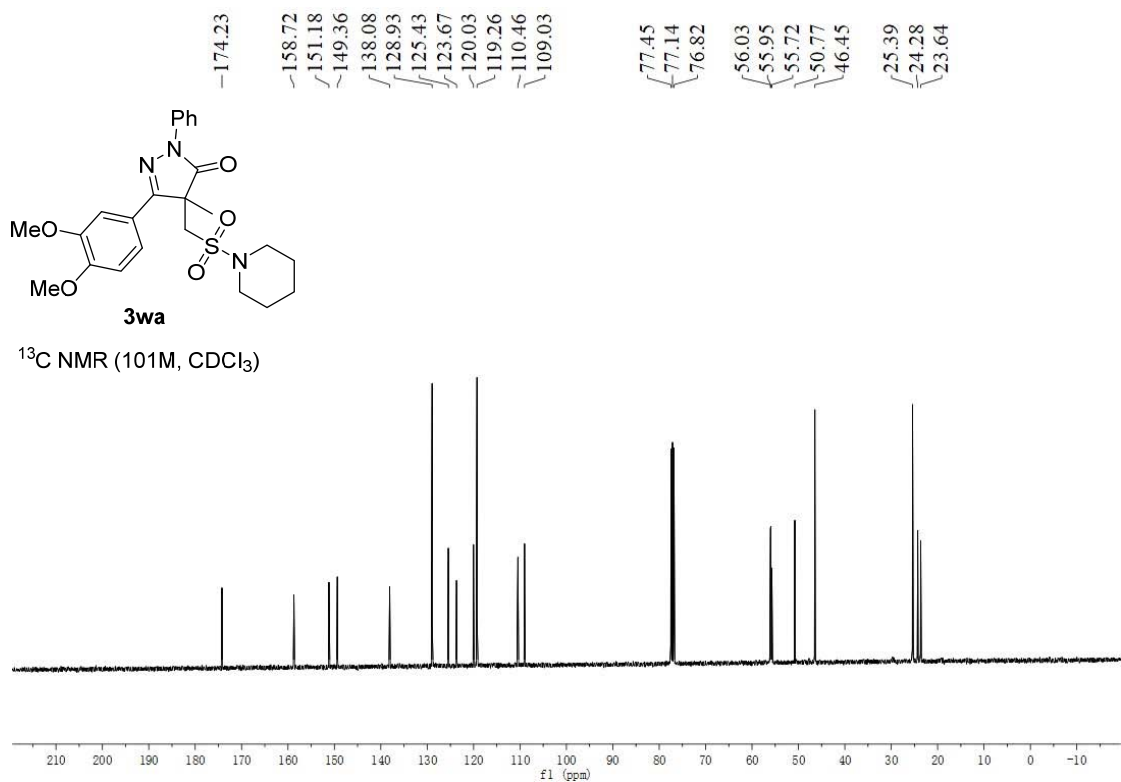
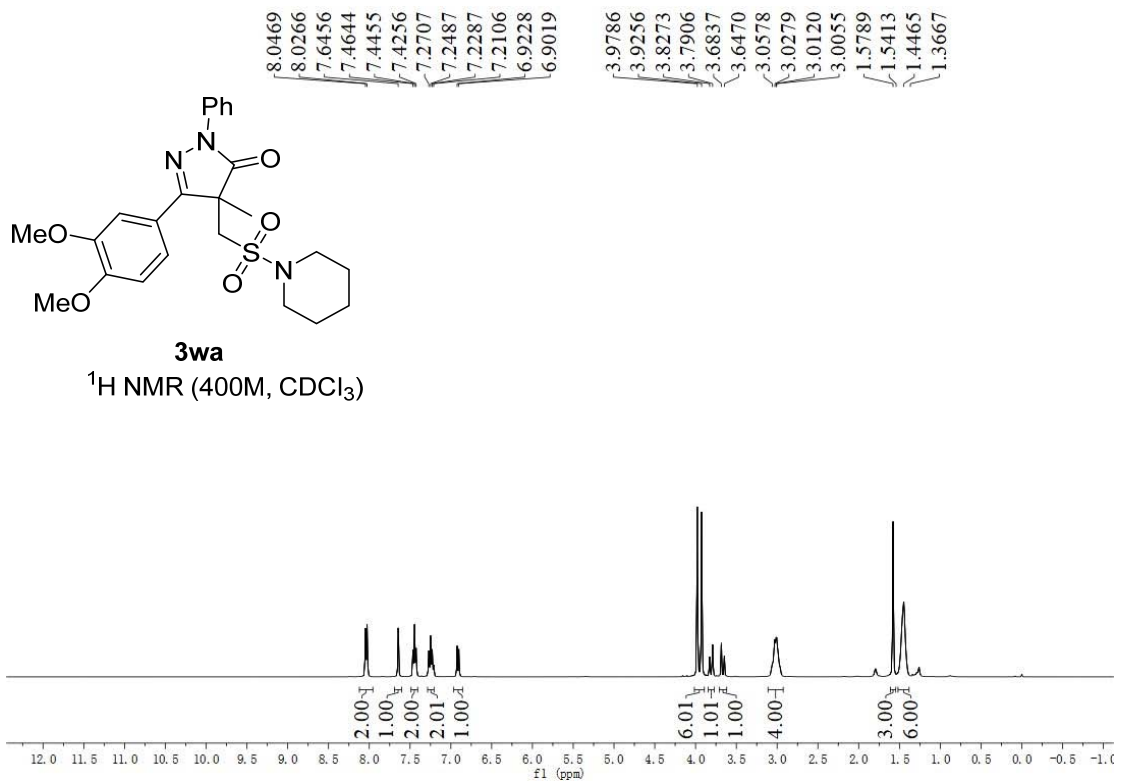
77.45  
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56.09  
55.53  
50.75  
46.43  
25.37  
24.00  
23.61  
20.73

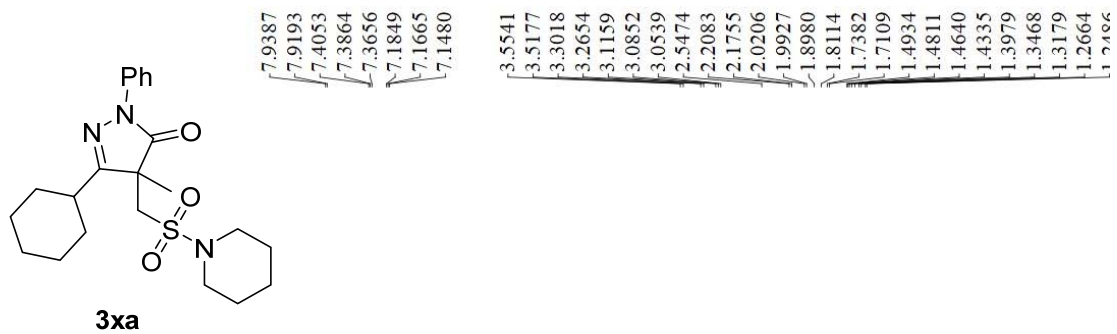


<sup>13</sup>C NMR (101M, CDCl<sub>3</sub>)

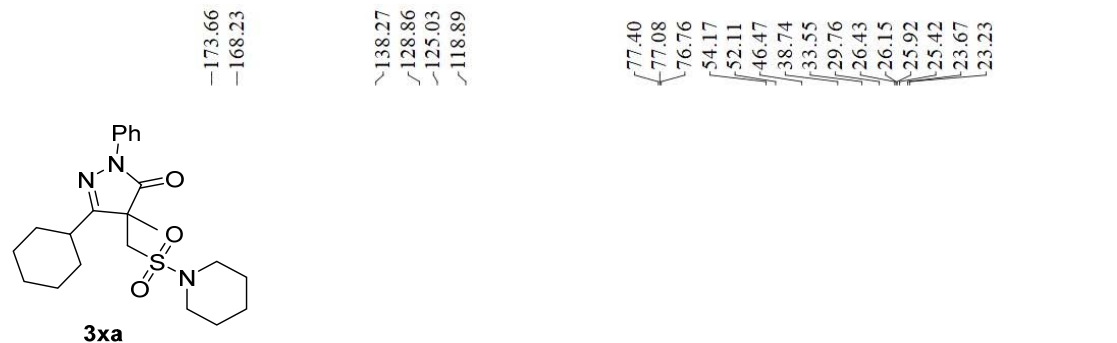
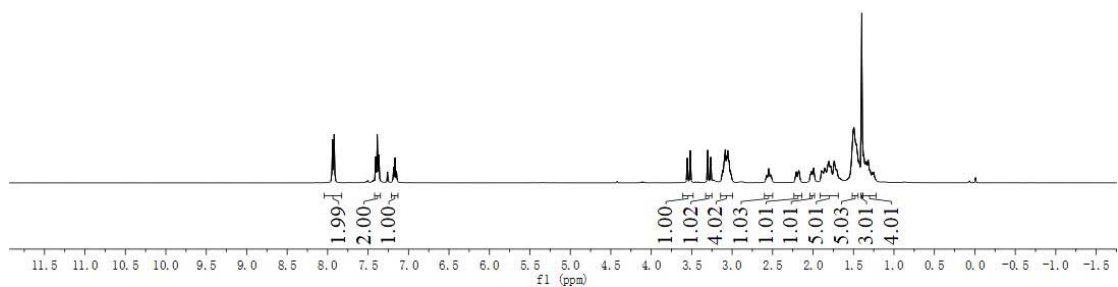




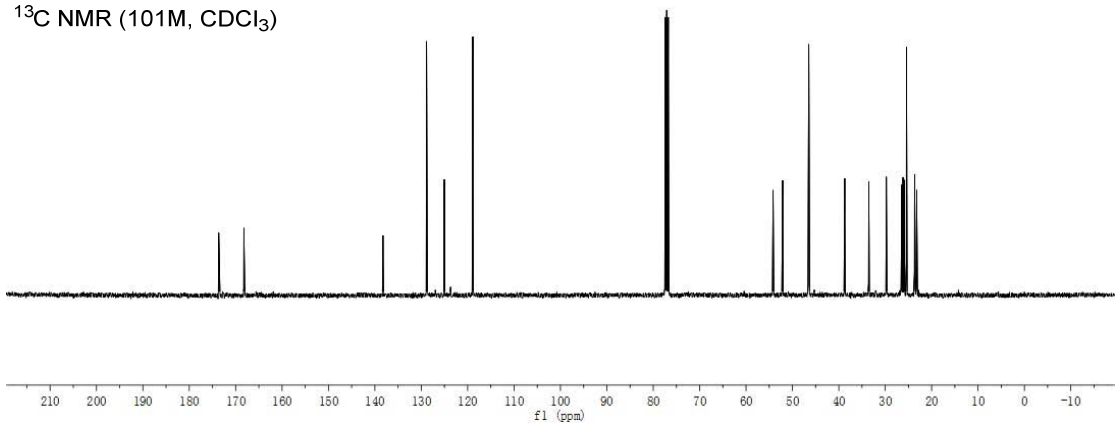


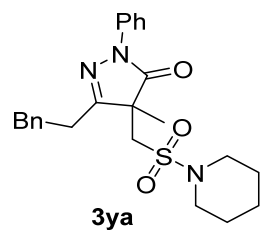


<sup>1</sup>H NMR (400M, CDCl<sub>3</sub>)

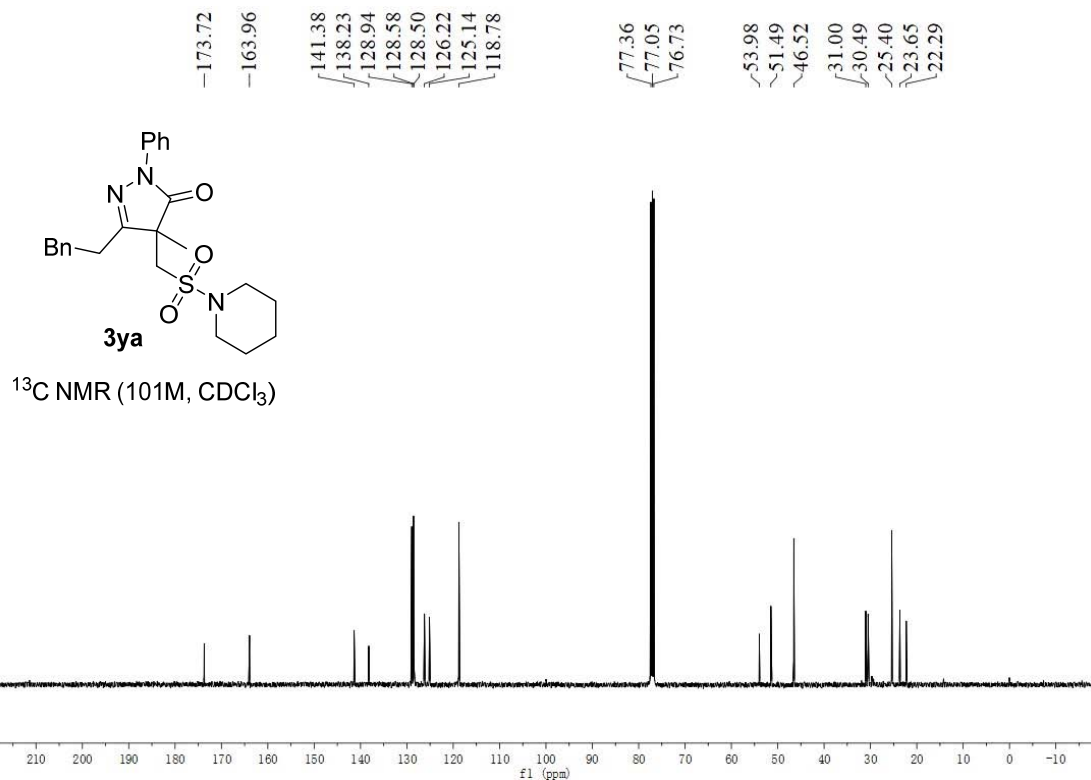
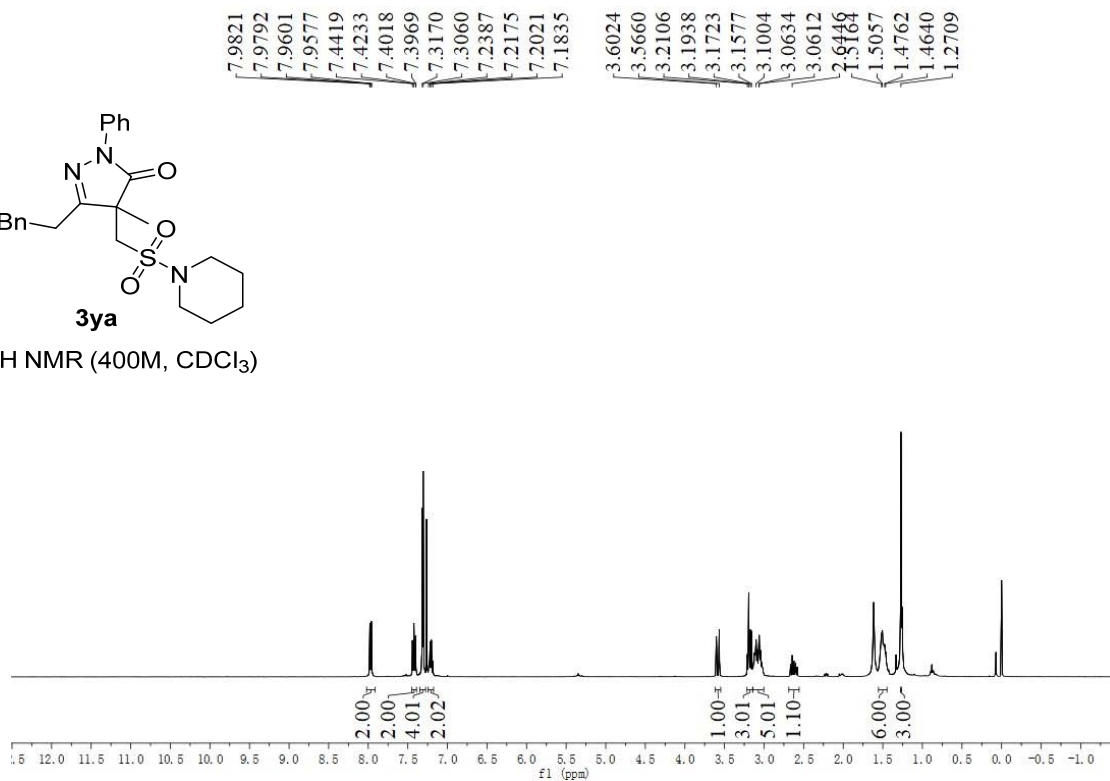


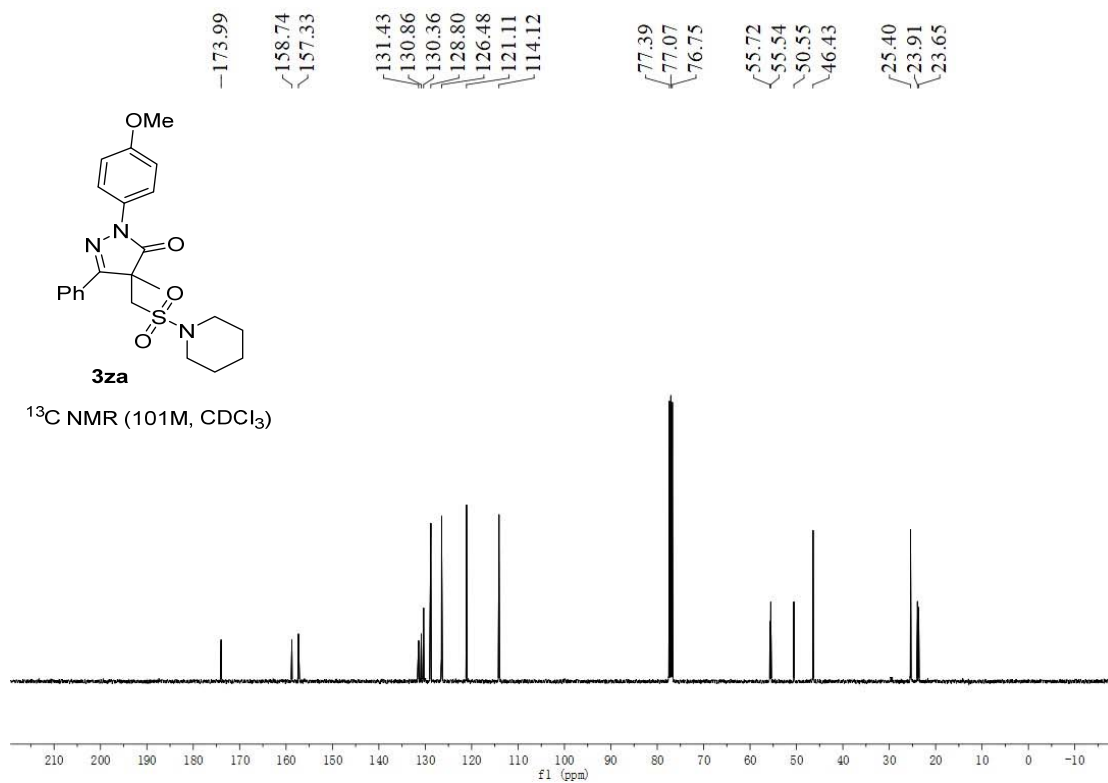
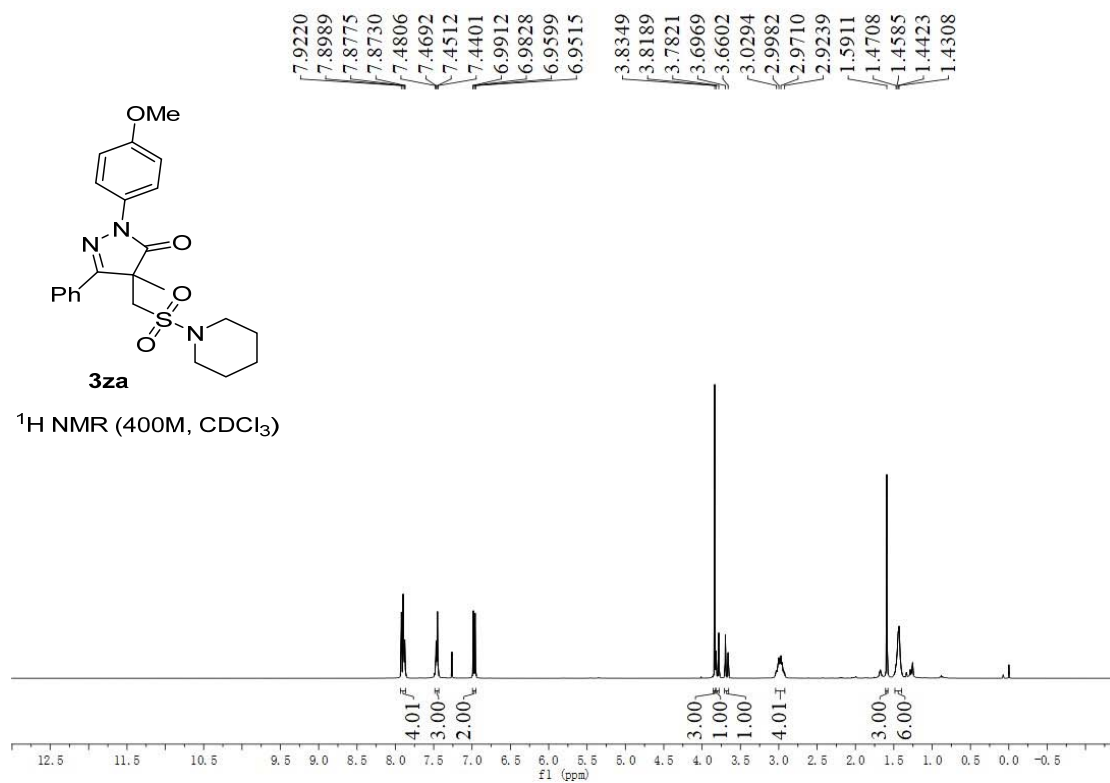
<sup>13</sup>C NMR (101M, CDCl<sub>3</sub>)

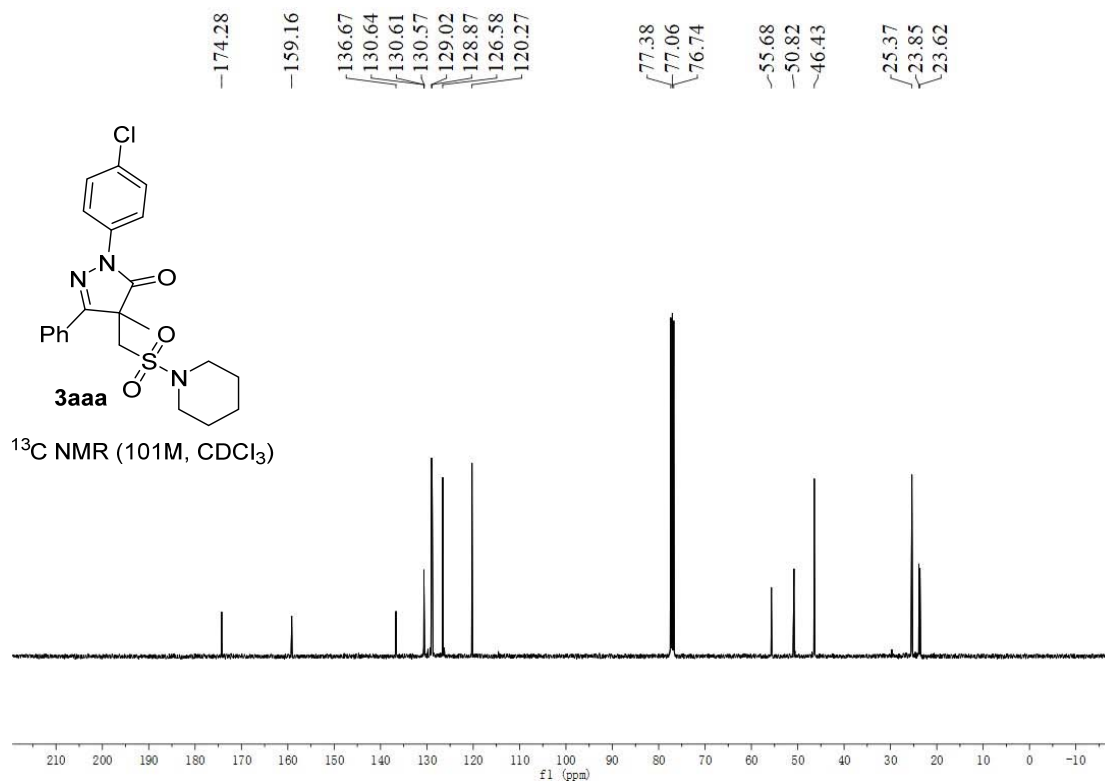
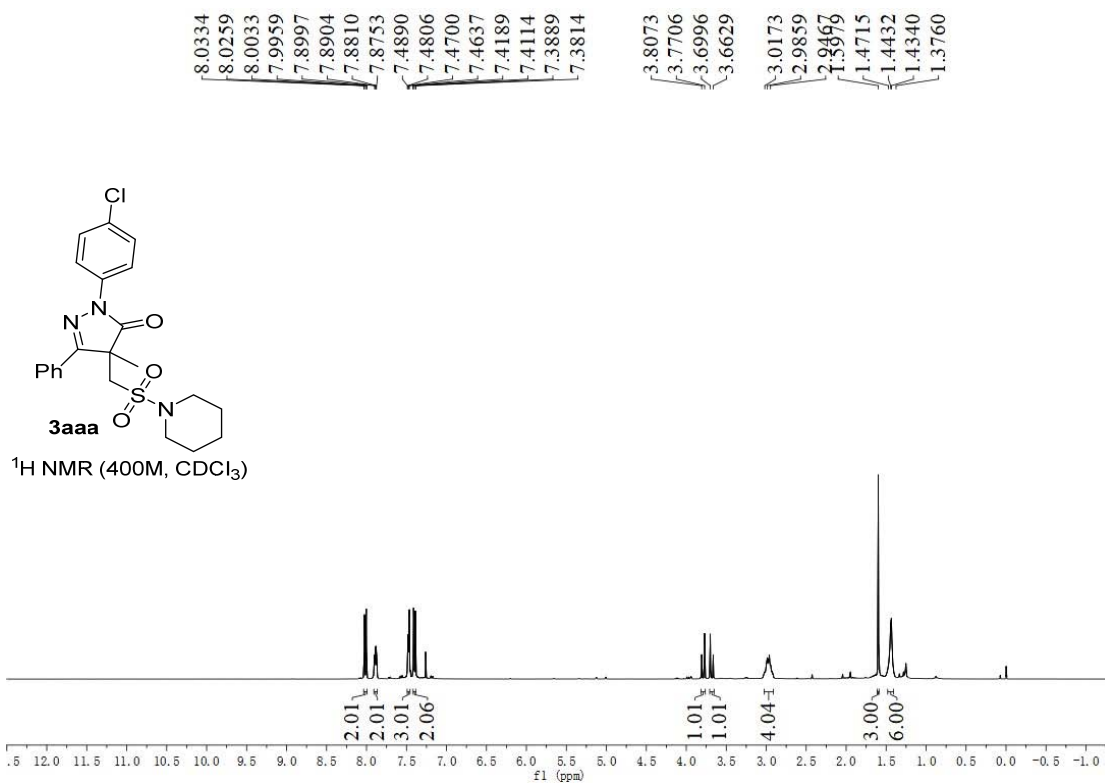


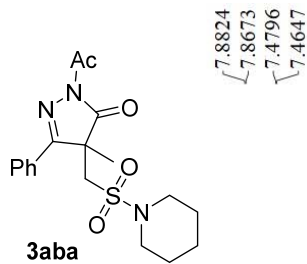


<sup>1</sup>H NMR (400M, CDCl<sub>3</sub>)

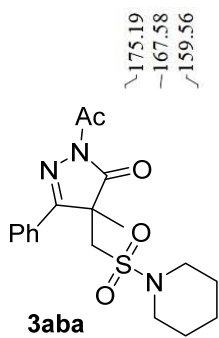
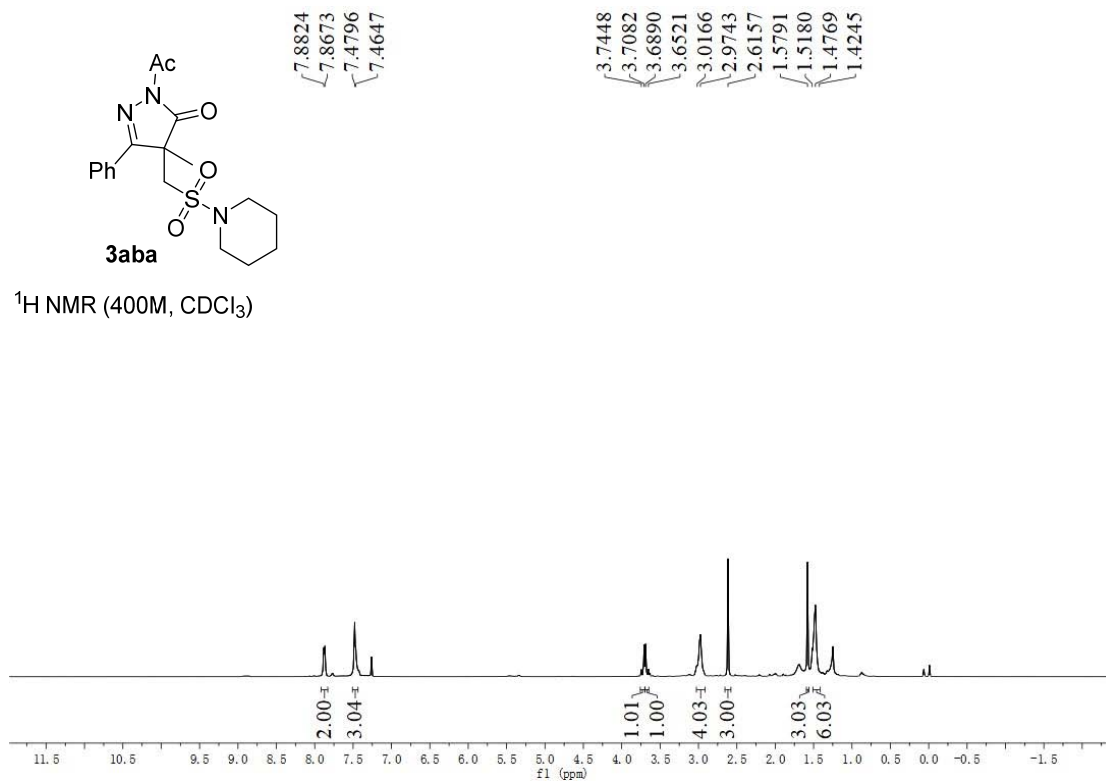




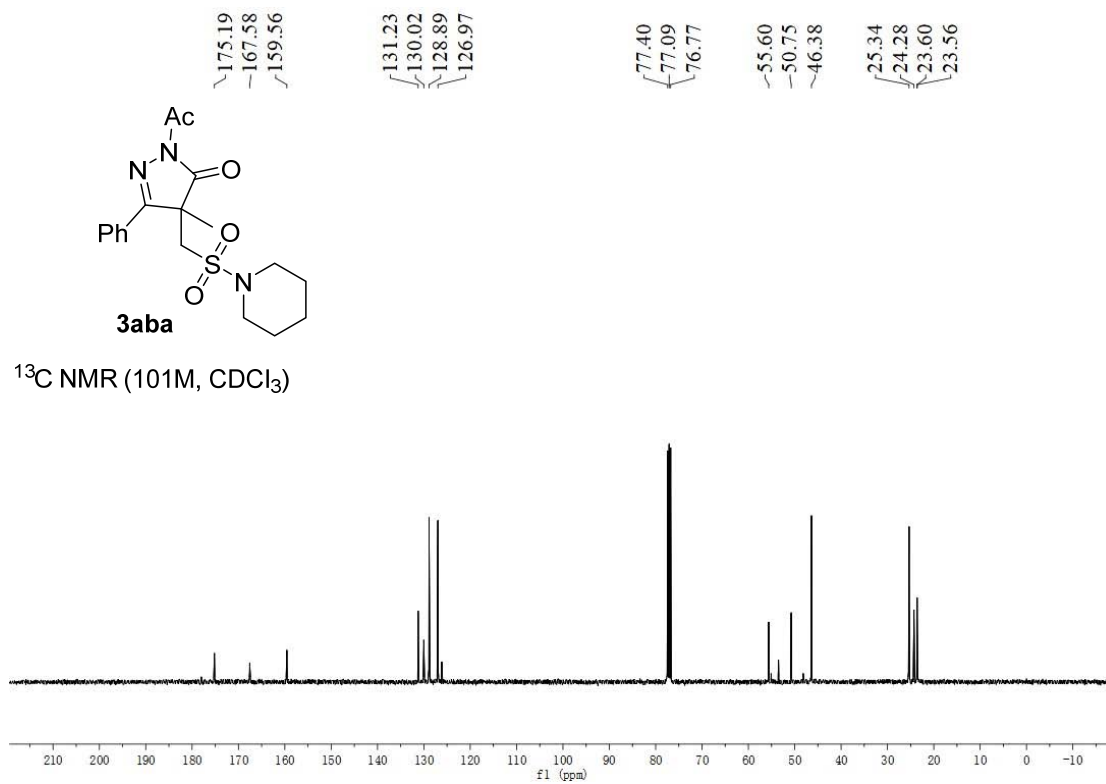


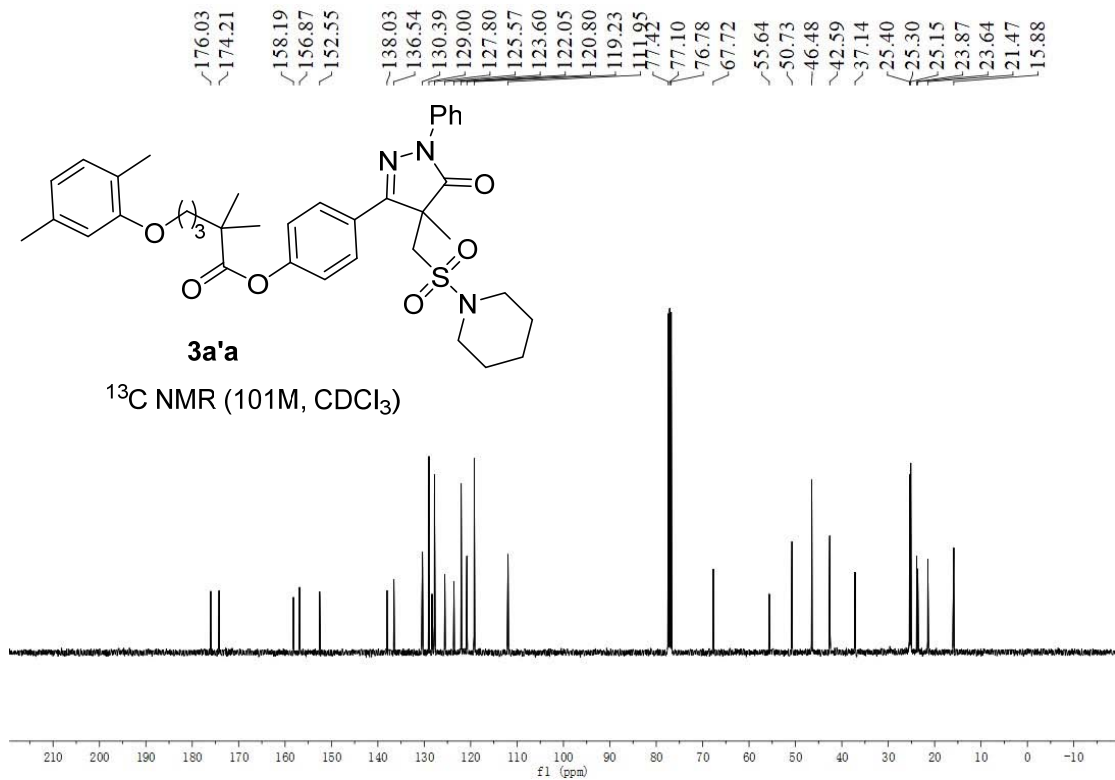
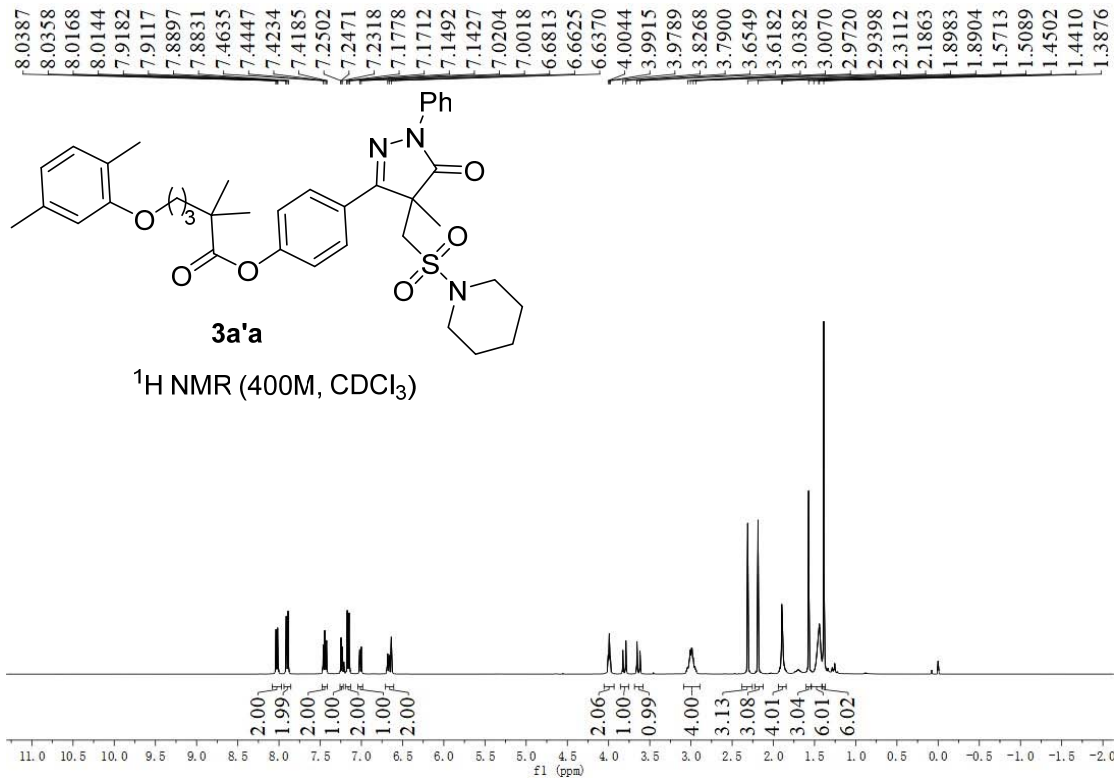


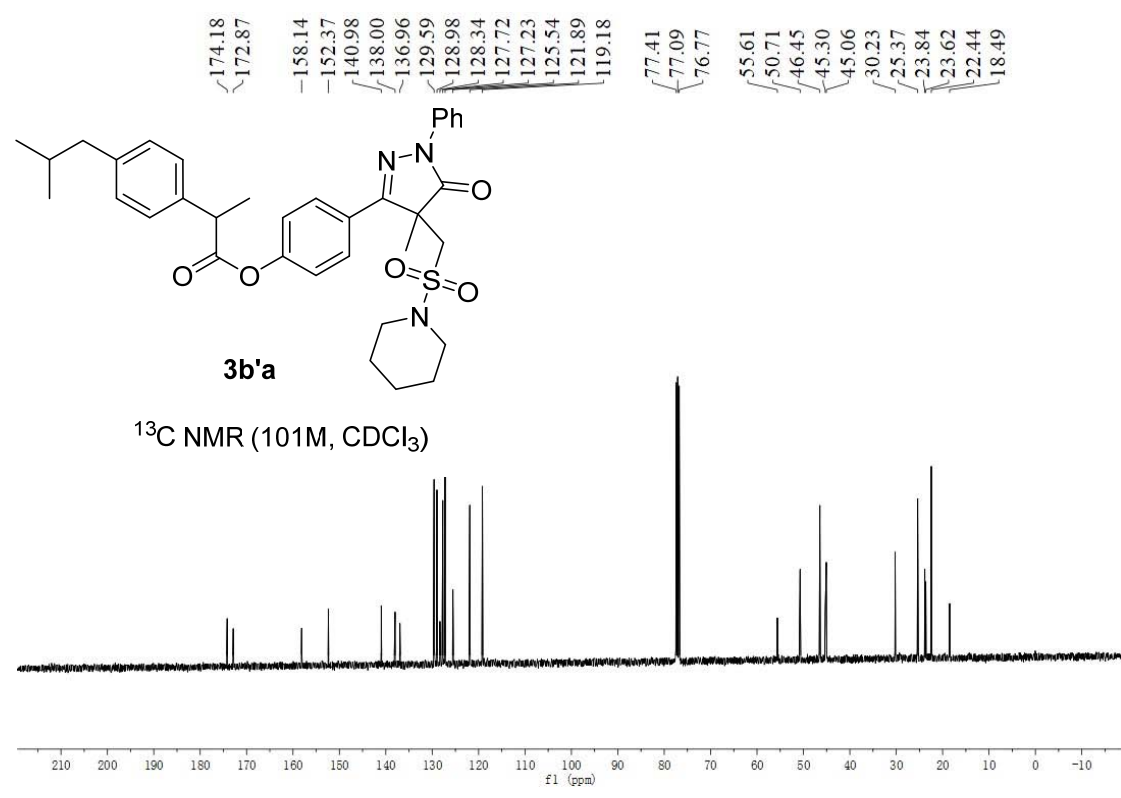
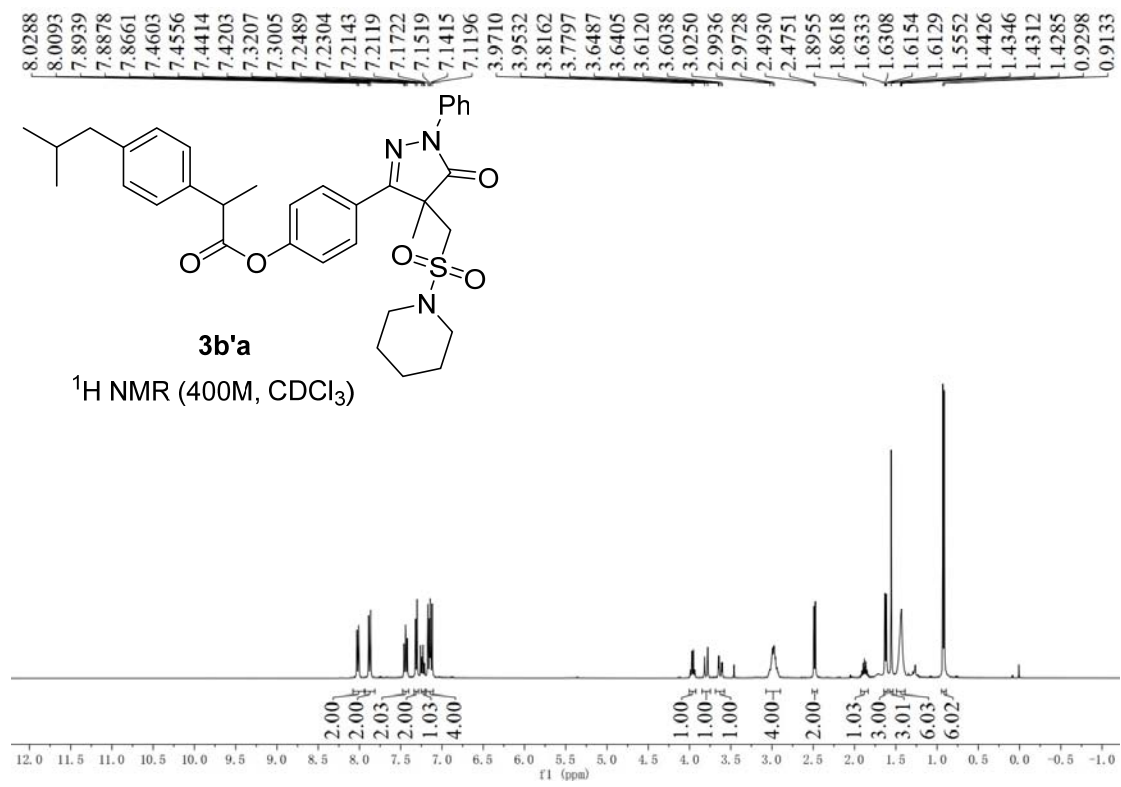
<sup>1</sup>H NMR (400M, CDCl<sub>3</sub>)



<sup>13</sup>C NMR (101M, CDCl<sub>3</sub>)

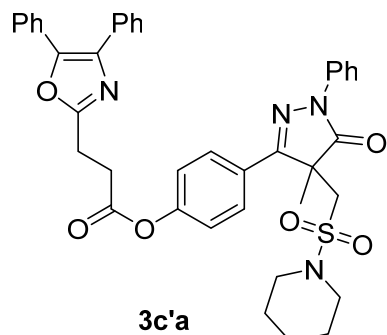




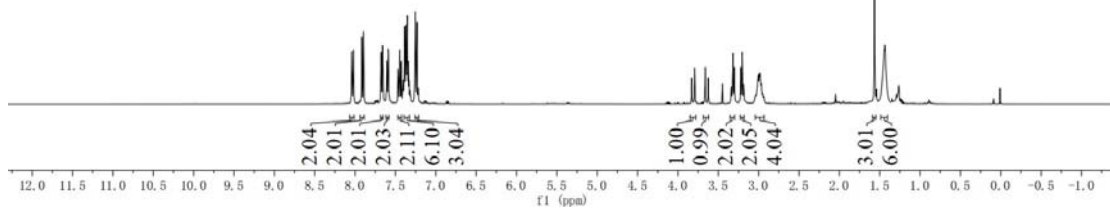




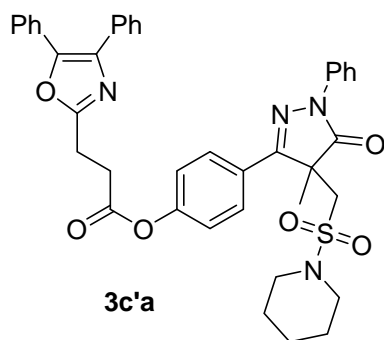
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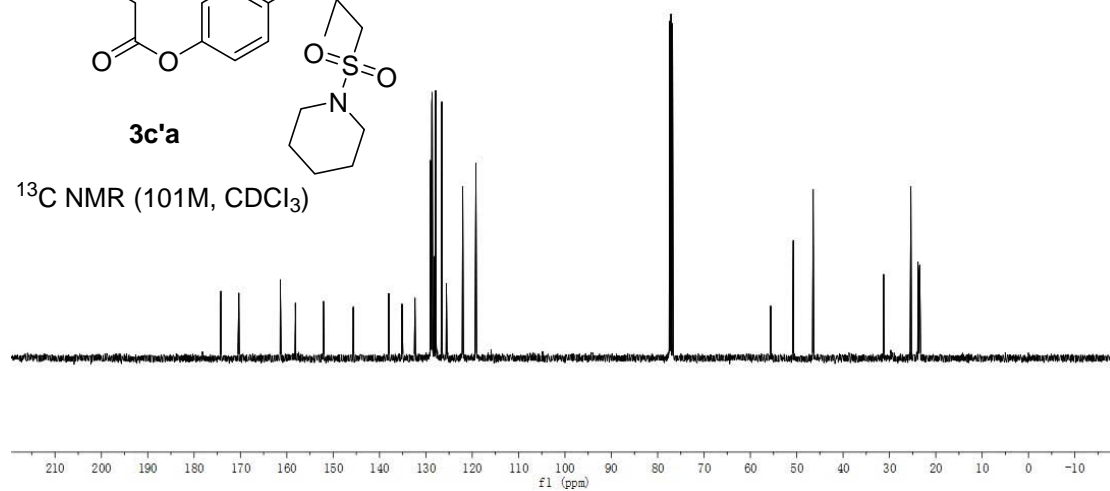
$^1\text{H NMR}$  (400M,  $\text{CDCl}_3$ )

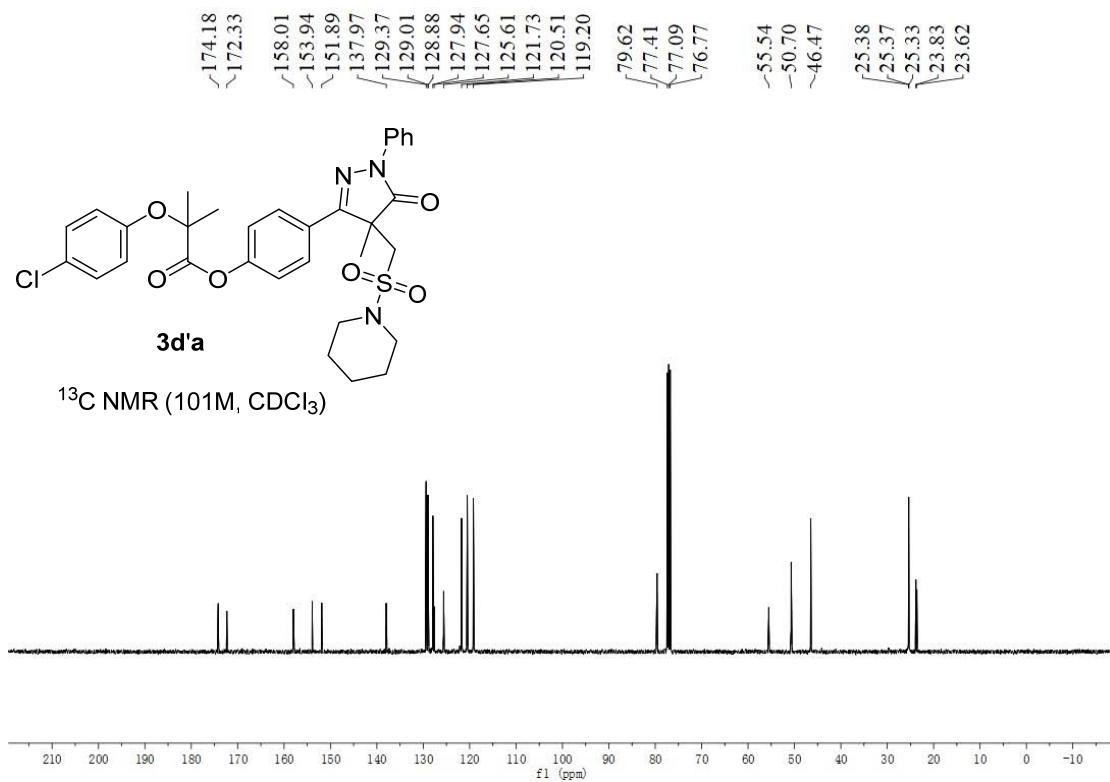
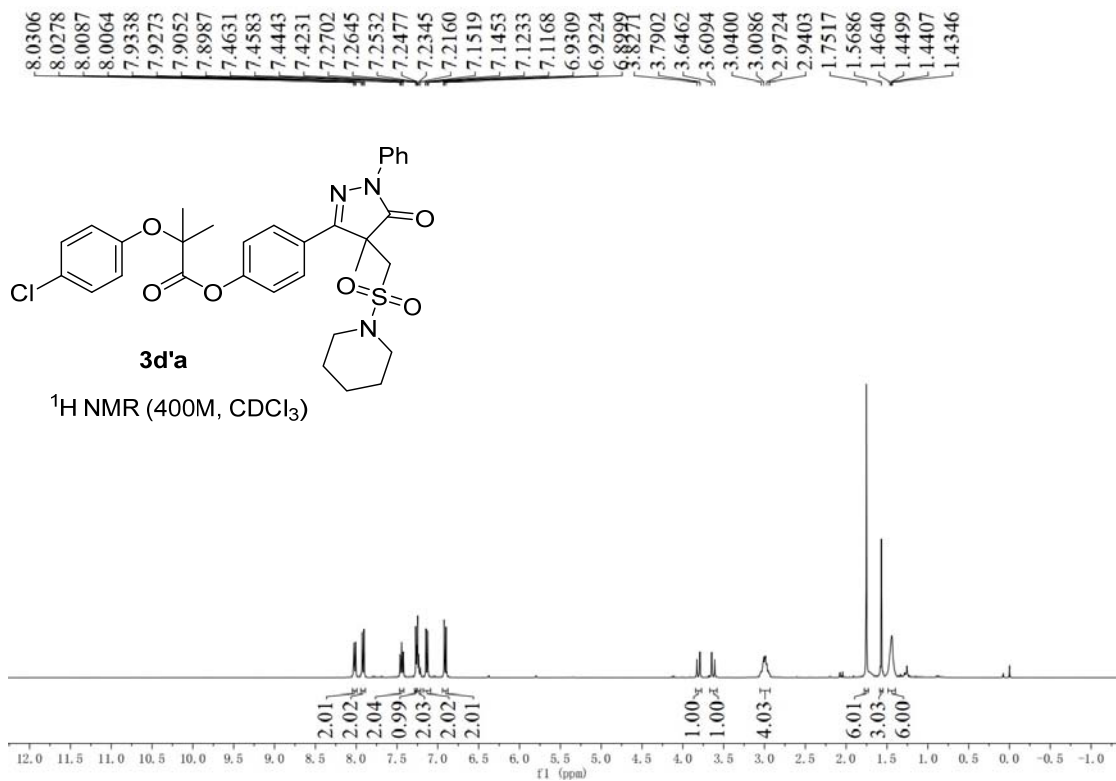


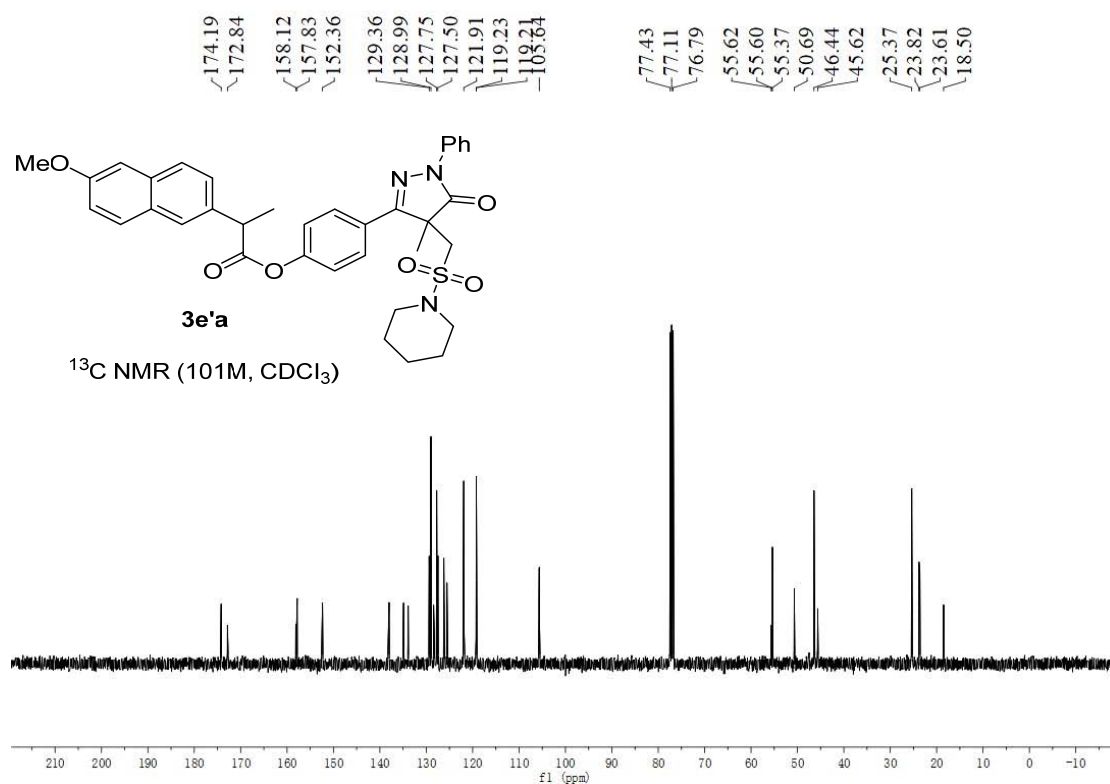
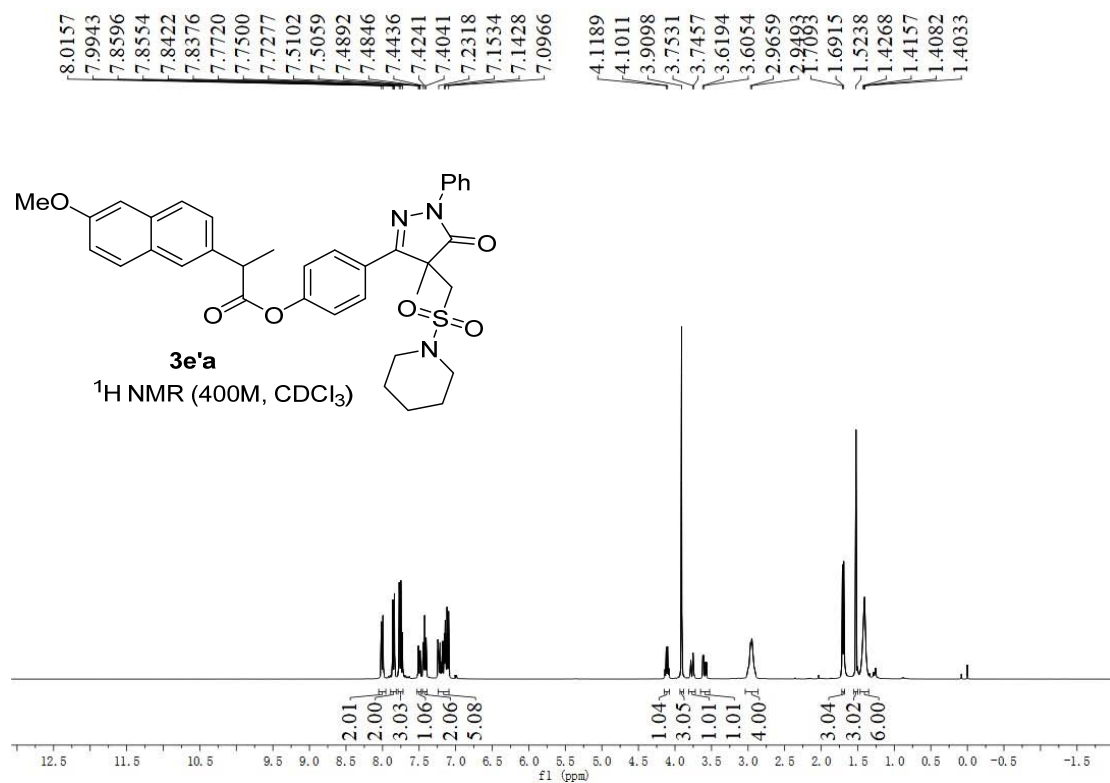
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126.55  
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119.21  
77.43  
77.11  
76.80  
55.62  
50.73  
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23.47



$^{13}\text{C NMR}$  (101M,  $\text{CDCl}_3$ )

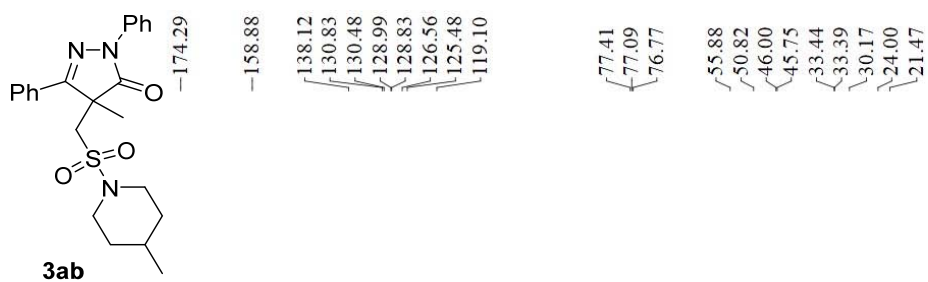
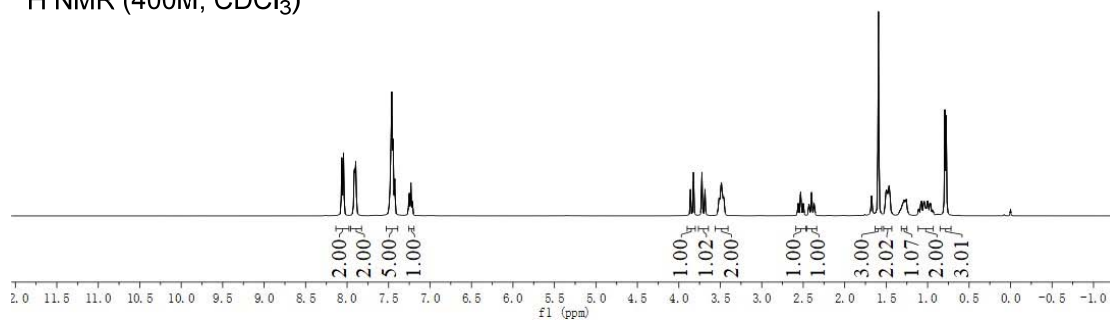




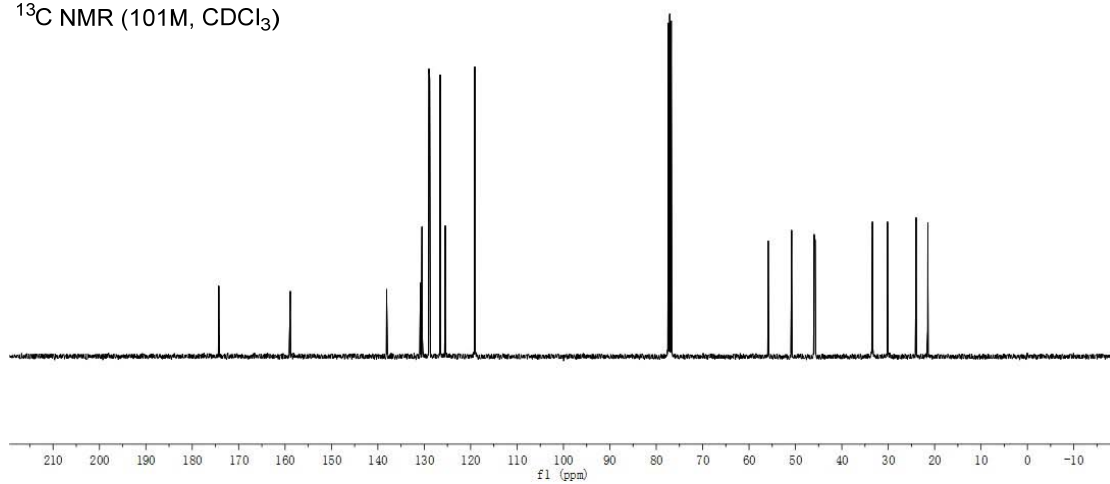


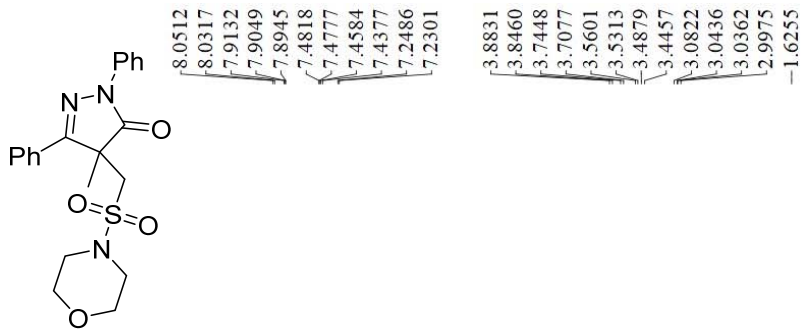


<sup>1</sup>H NMR (400M, CDCl<sub>3</sub>)



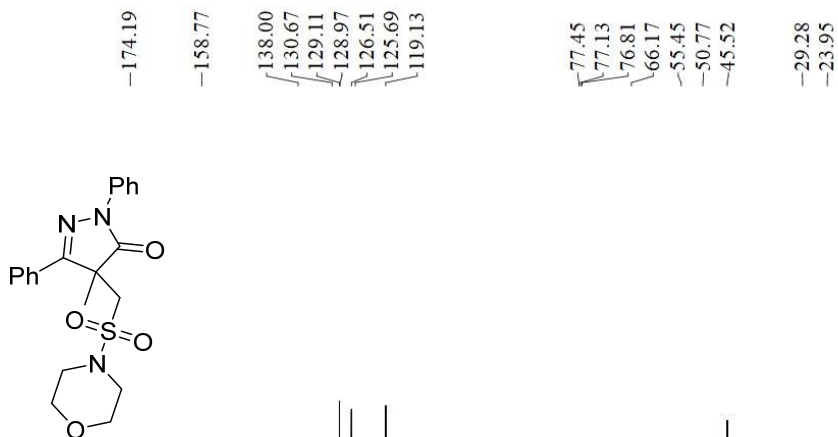
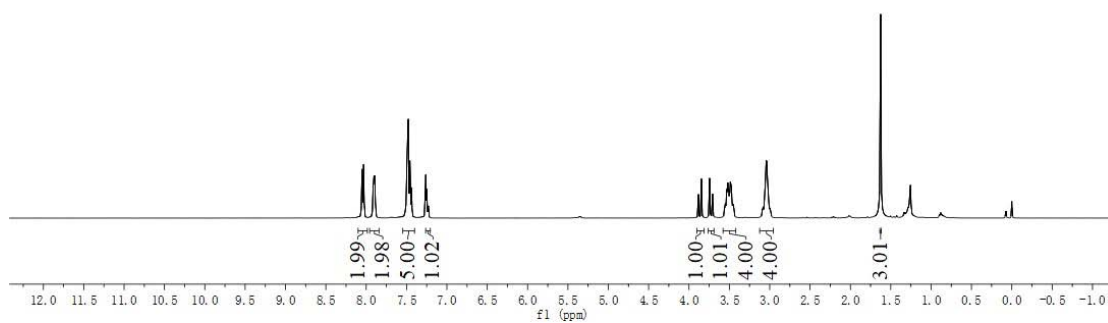
<sup>13</sup>C NMR (101M, CDCl<sub>3</sub>)





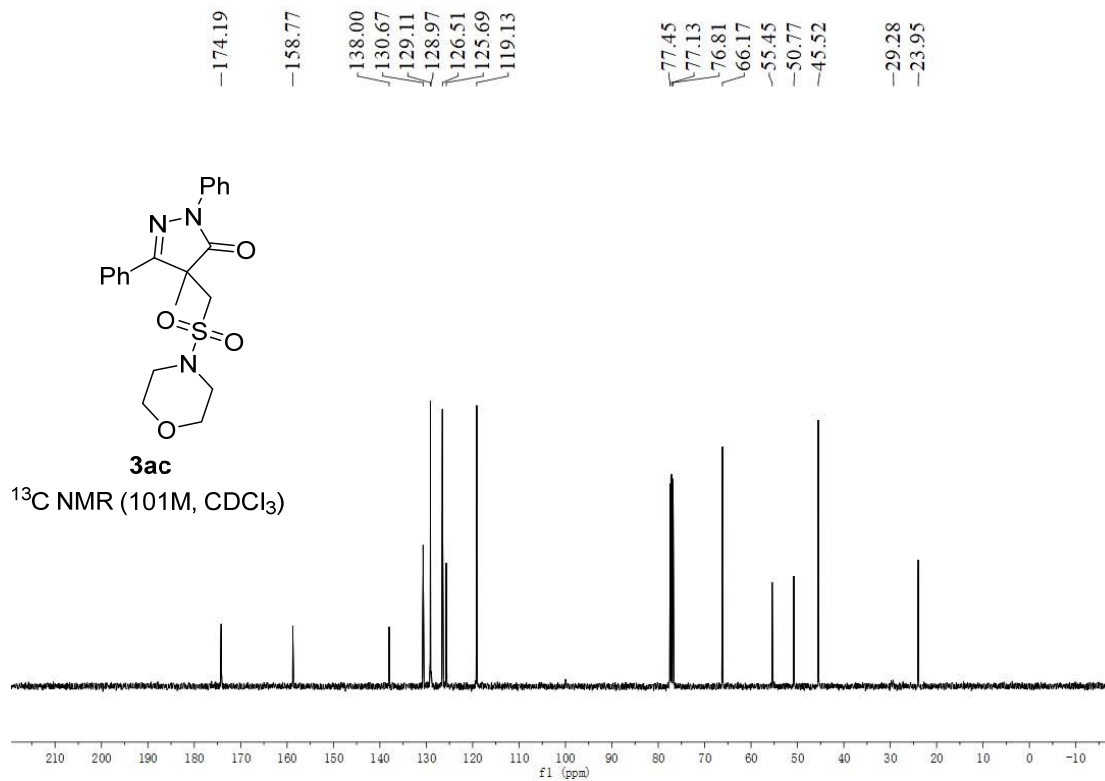
**3ac**

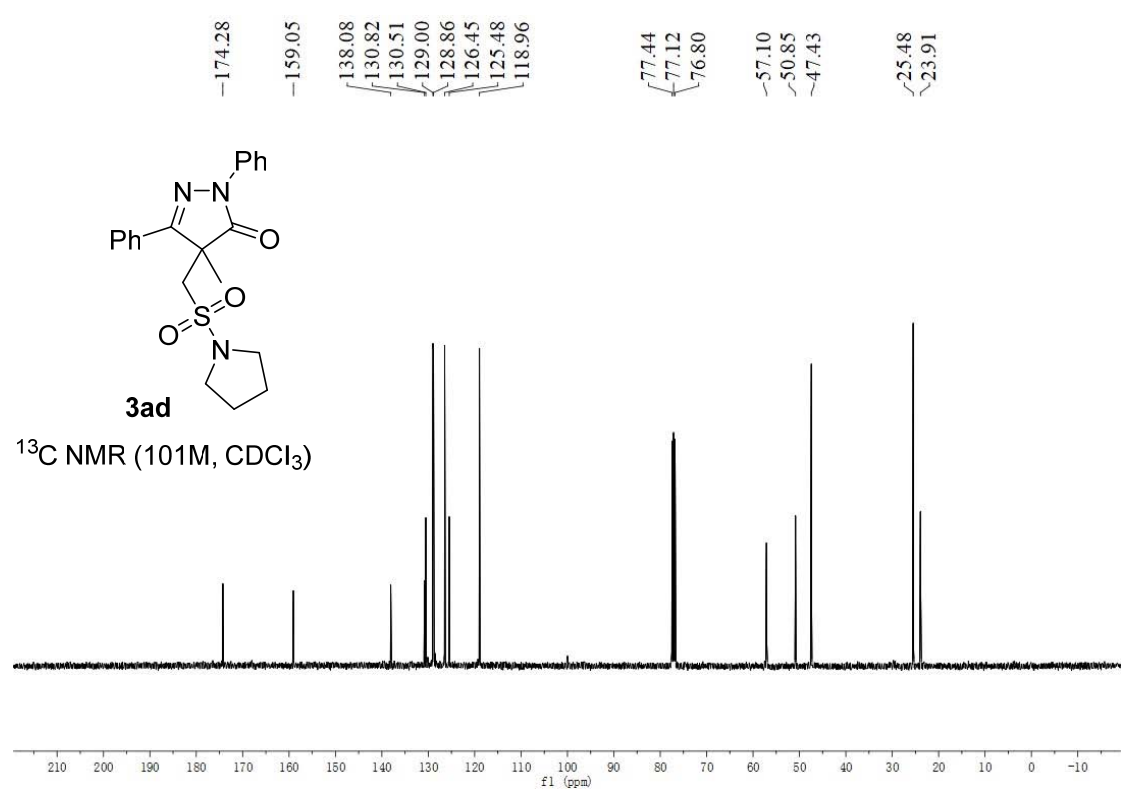
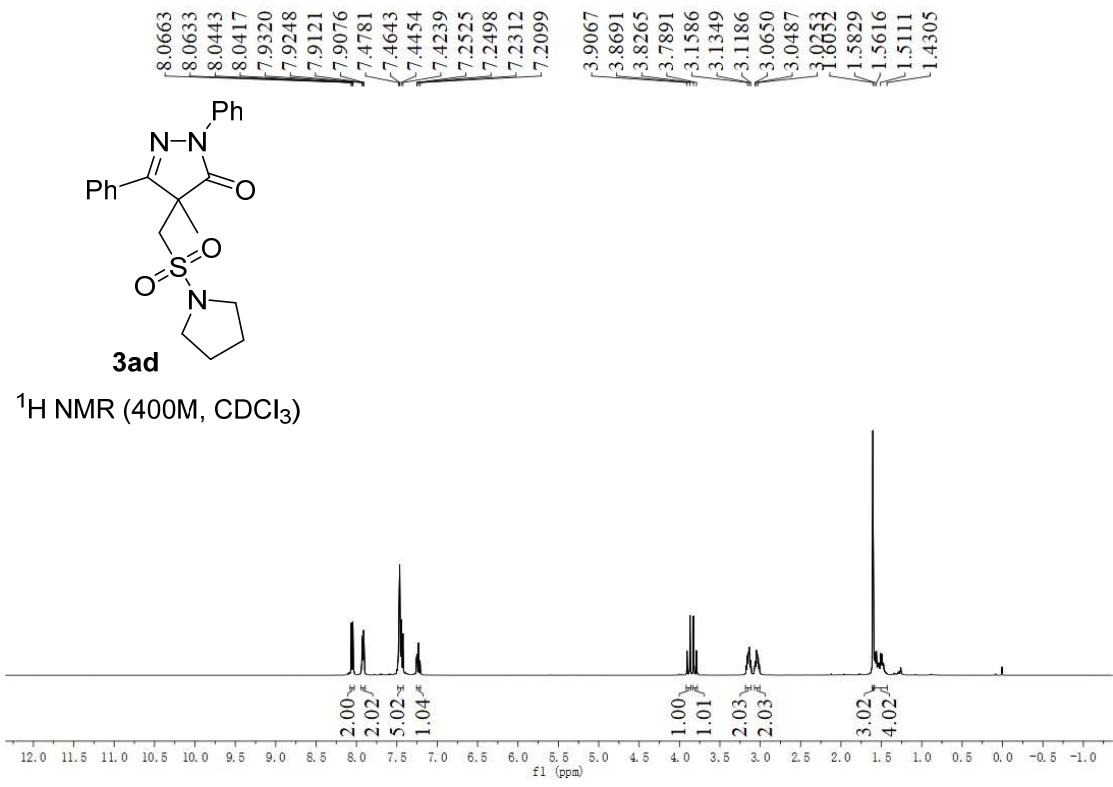
$^1\text{H}$  NMR (400M,  $\text{CDCl}_3$ )

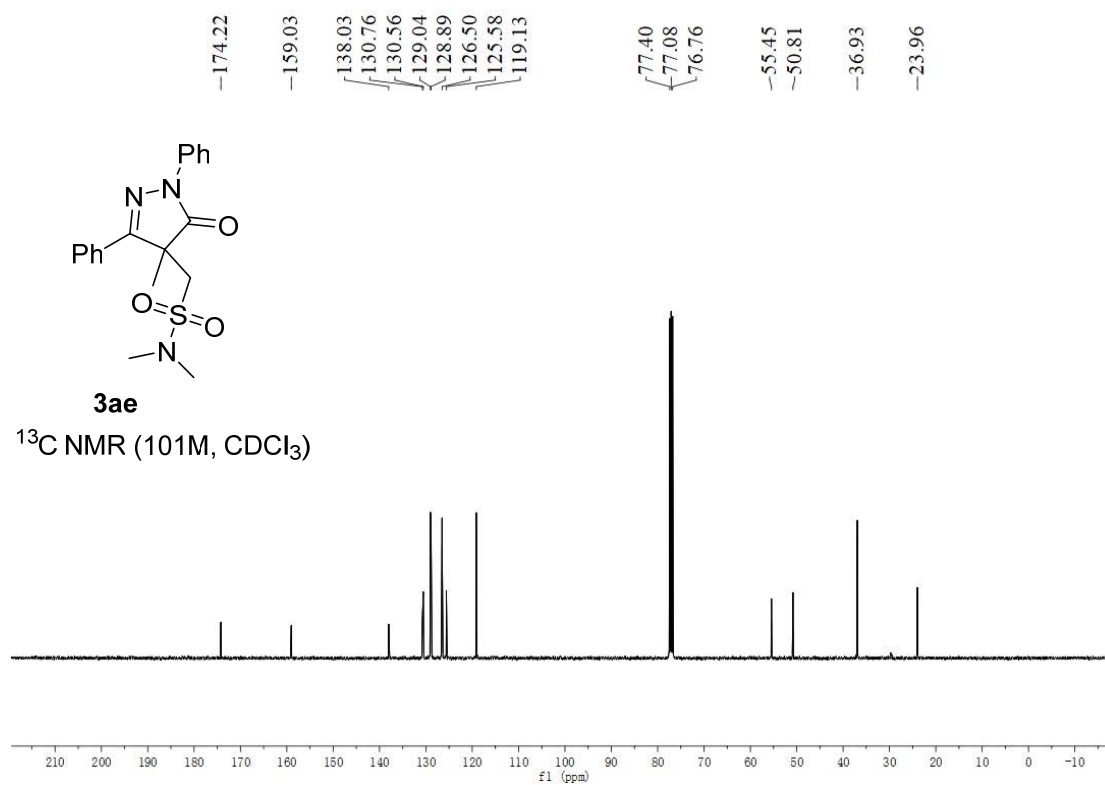
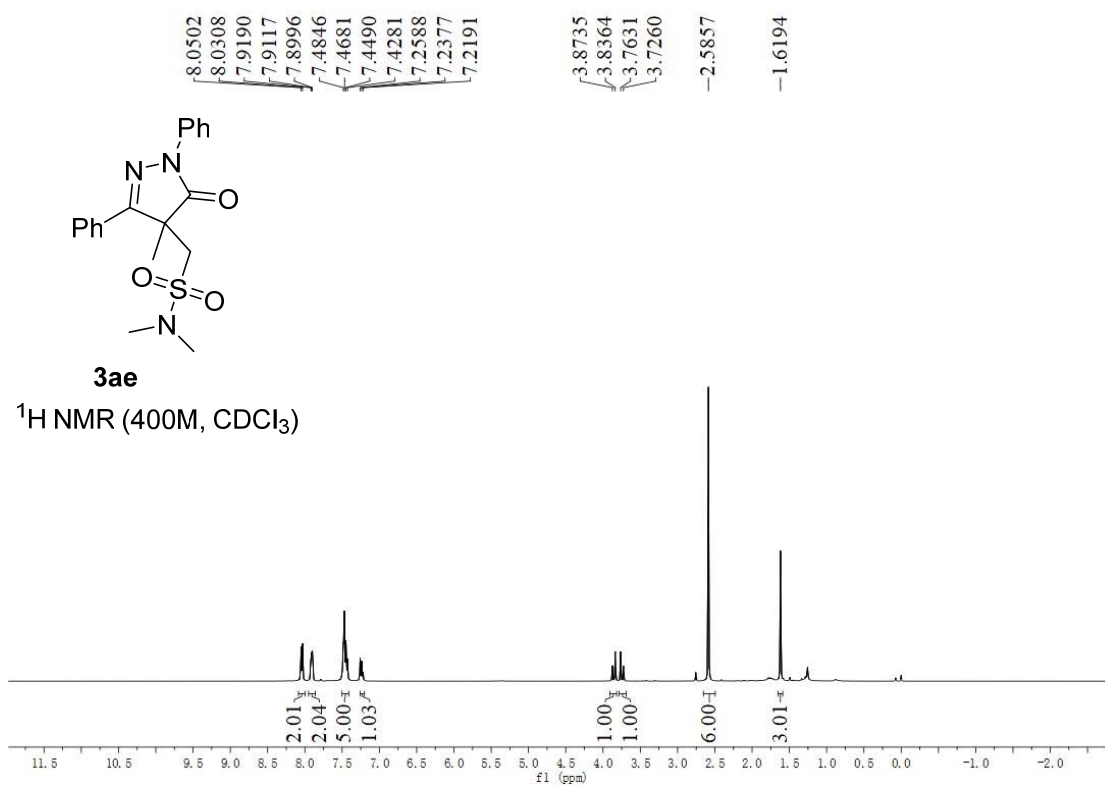


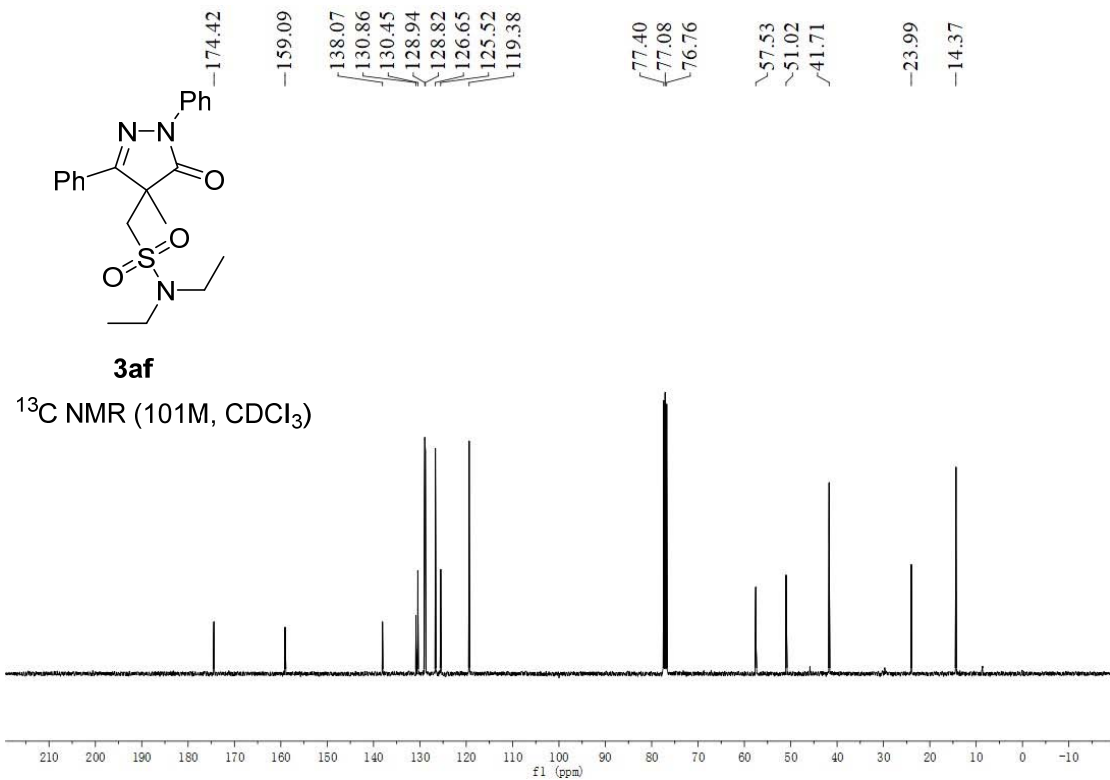
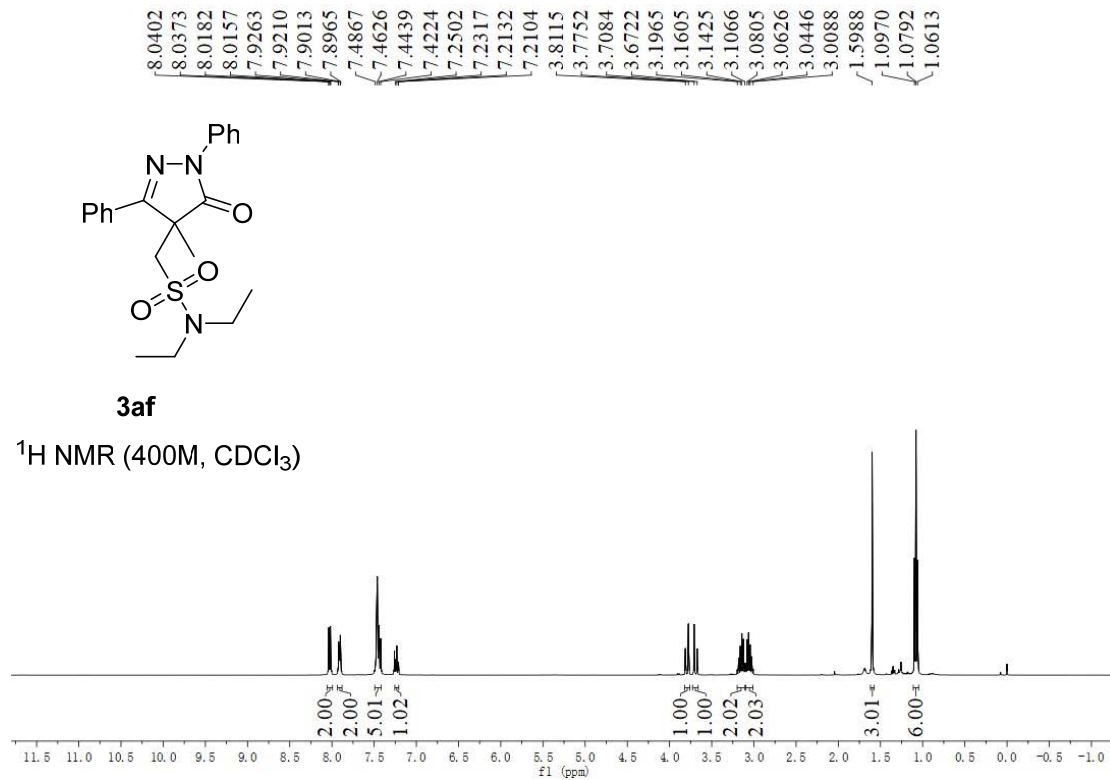
**3ac**

$^{13}\text{C}$  NMR (101M,  $\text{CDCl}_3$ )

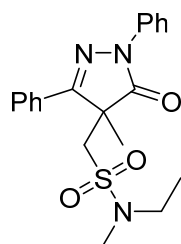






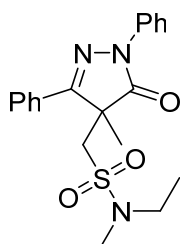
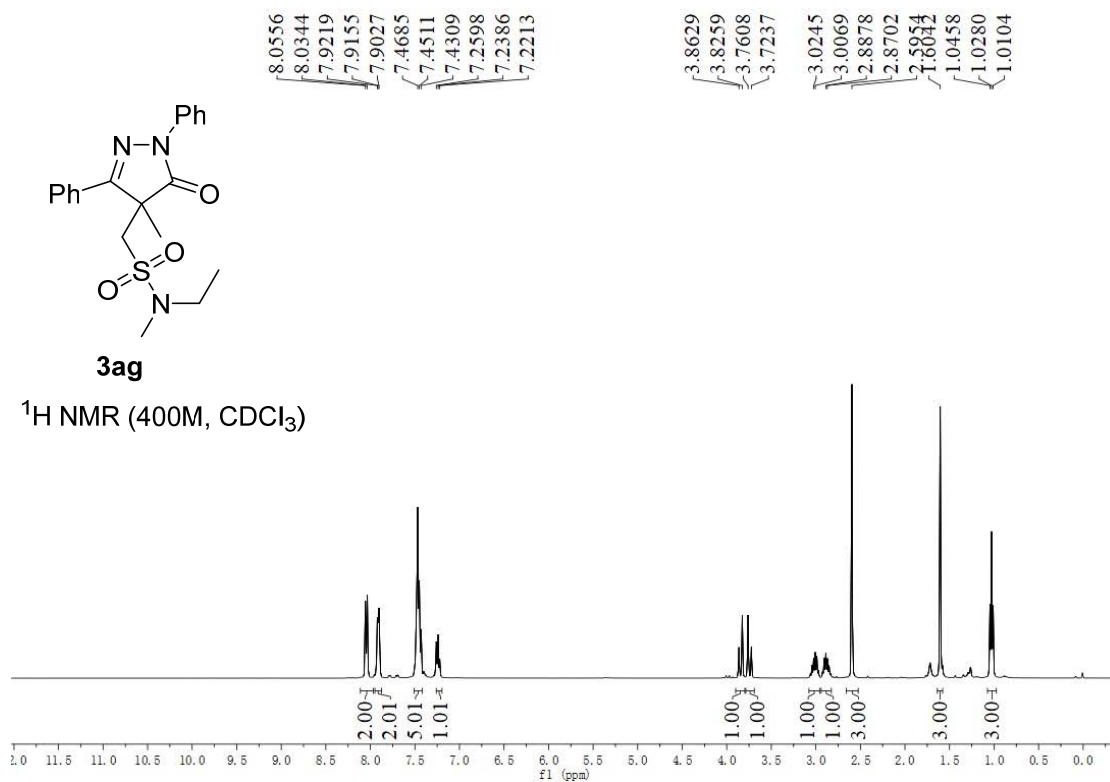






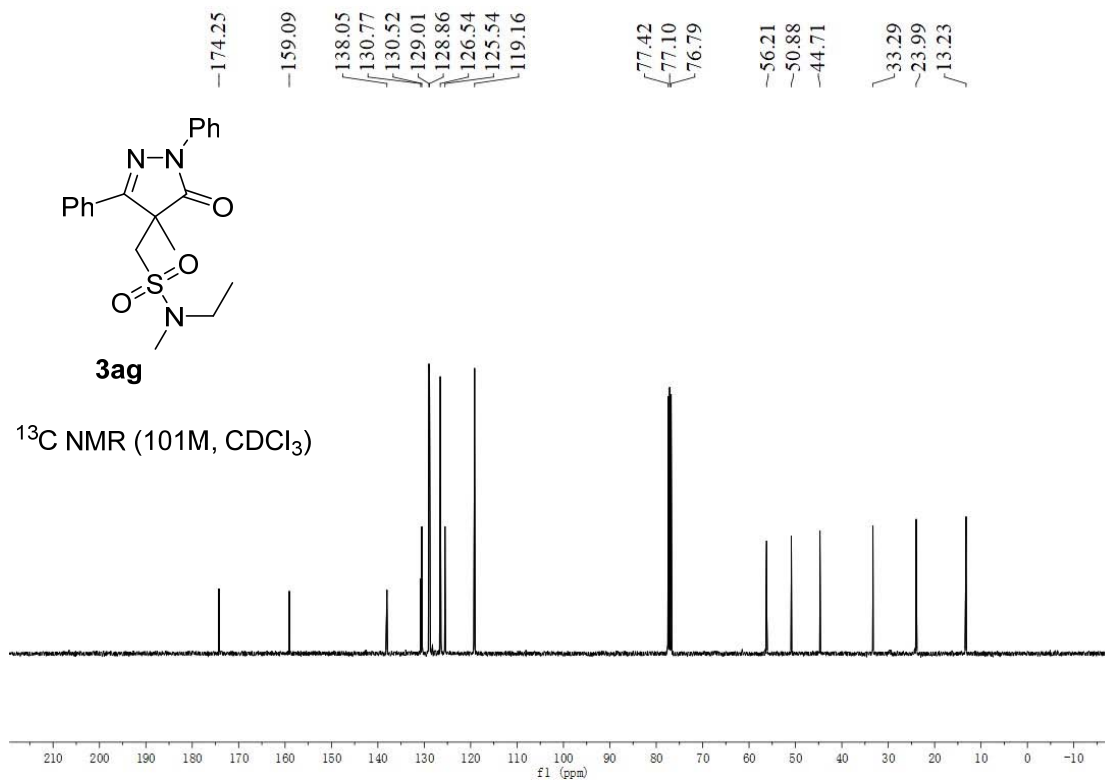
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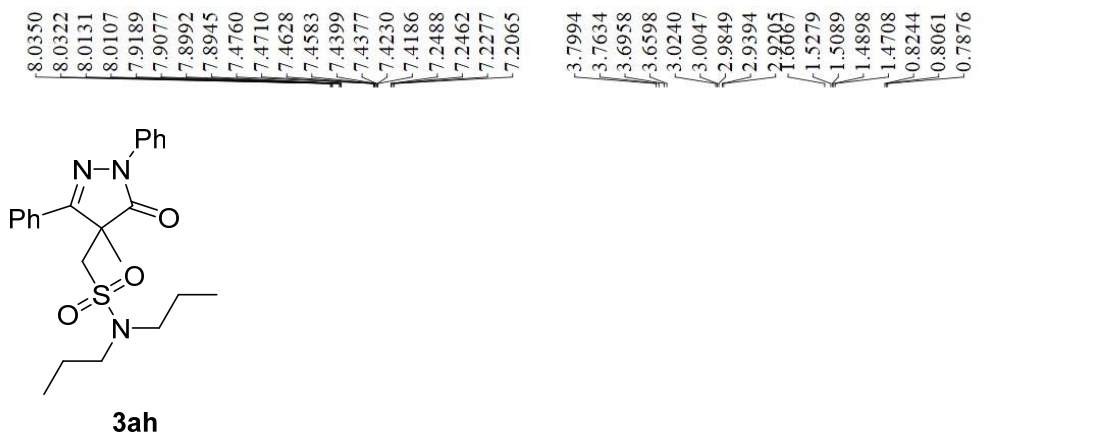
$^1\text{H}$  NMR (400M,  $\text{CDCl}_3$ )



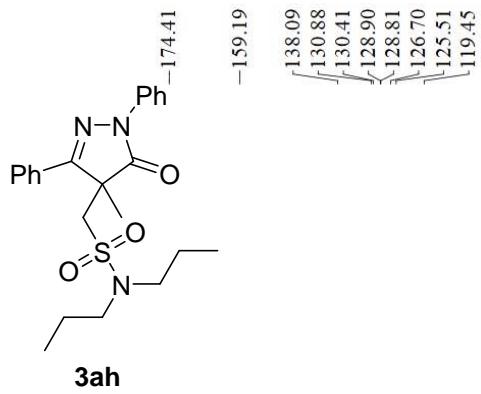
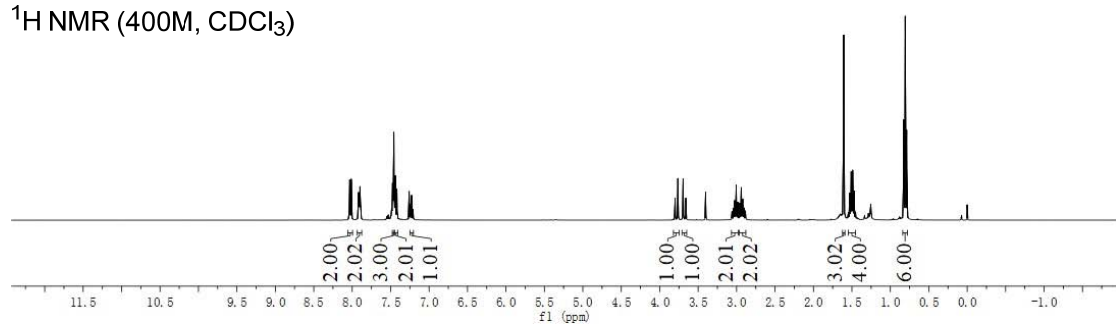
**3ag**

$^{13}\text{C}$  NMR (101M,  $\text{CDCl}_3$ )

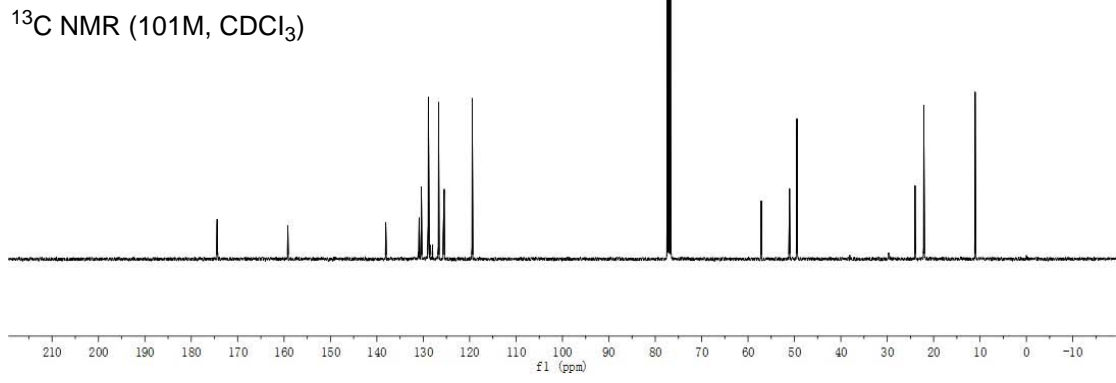


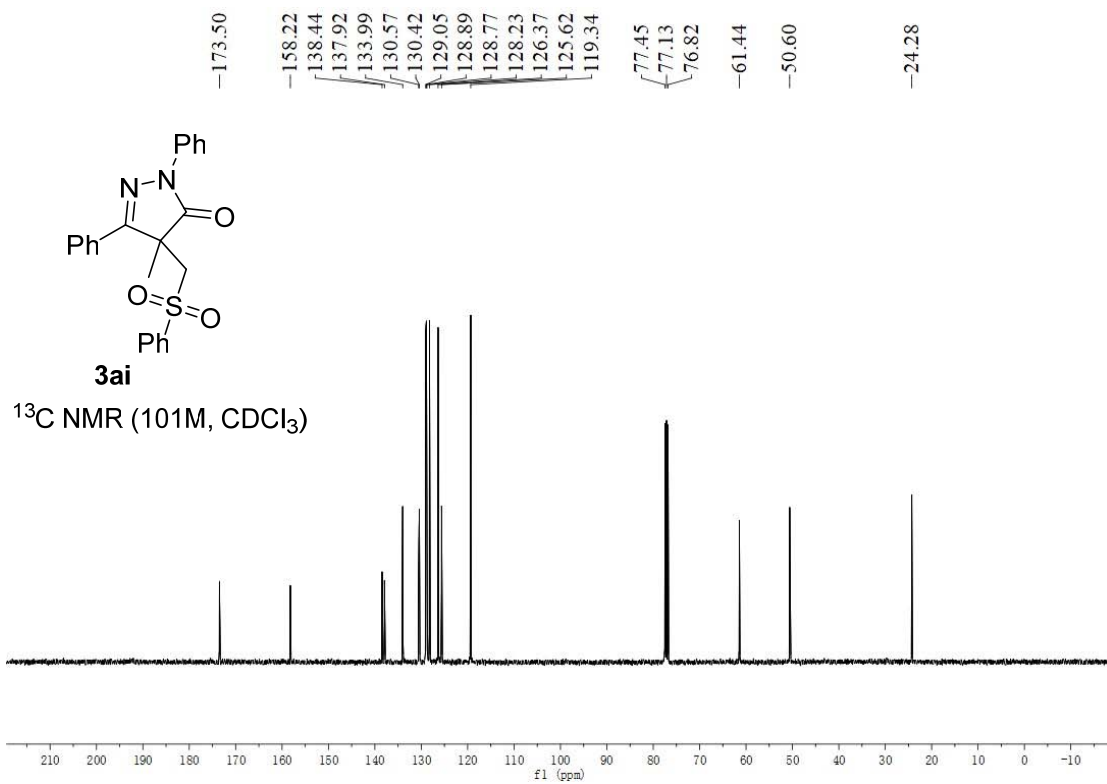
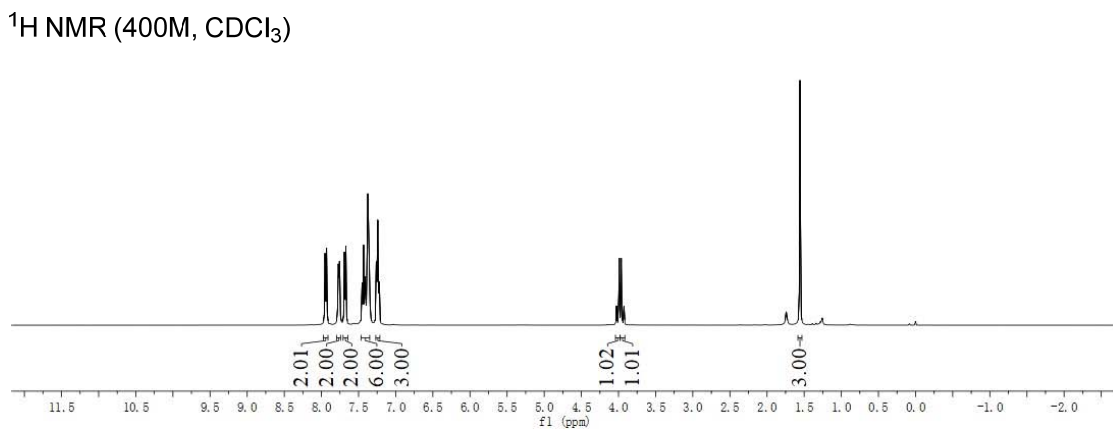
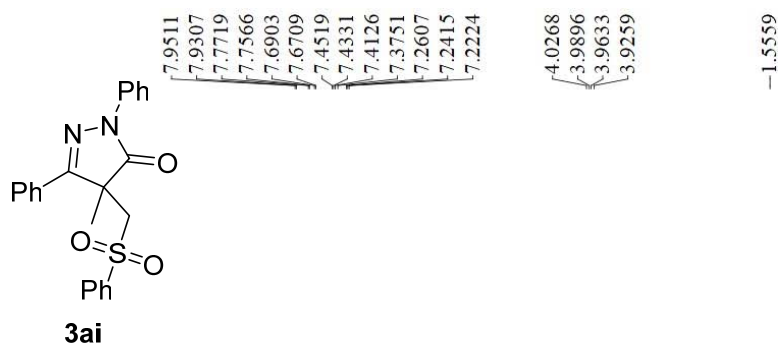


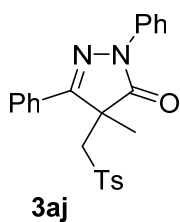
<sup>1</sup>H NMR (400M, CDCl<sub>3</sub>)



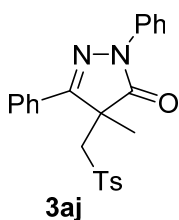
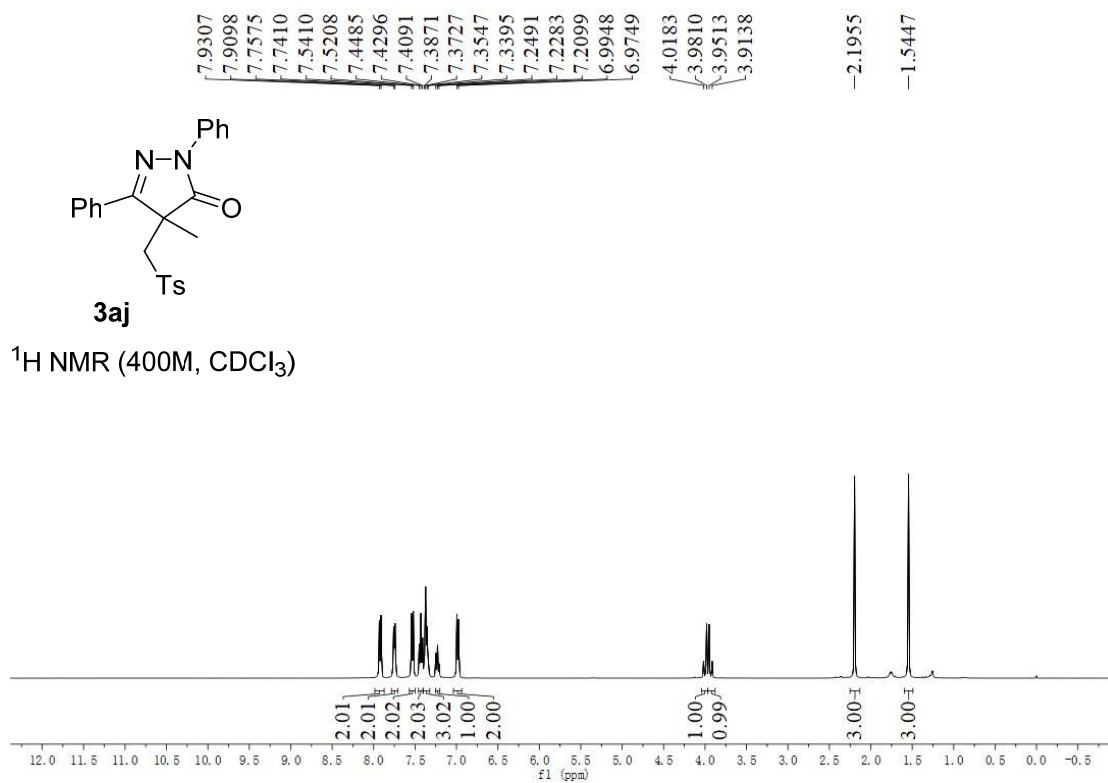
<sup>13</sup>C NMR (101M, CDCl<sub>3</sub>)



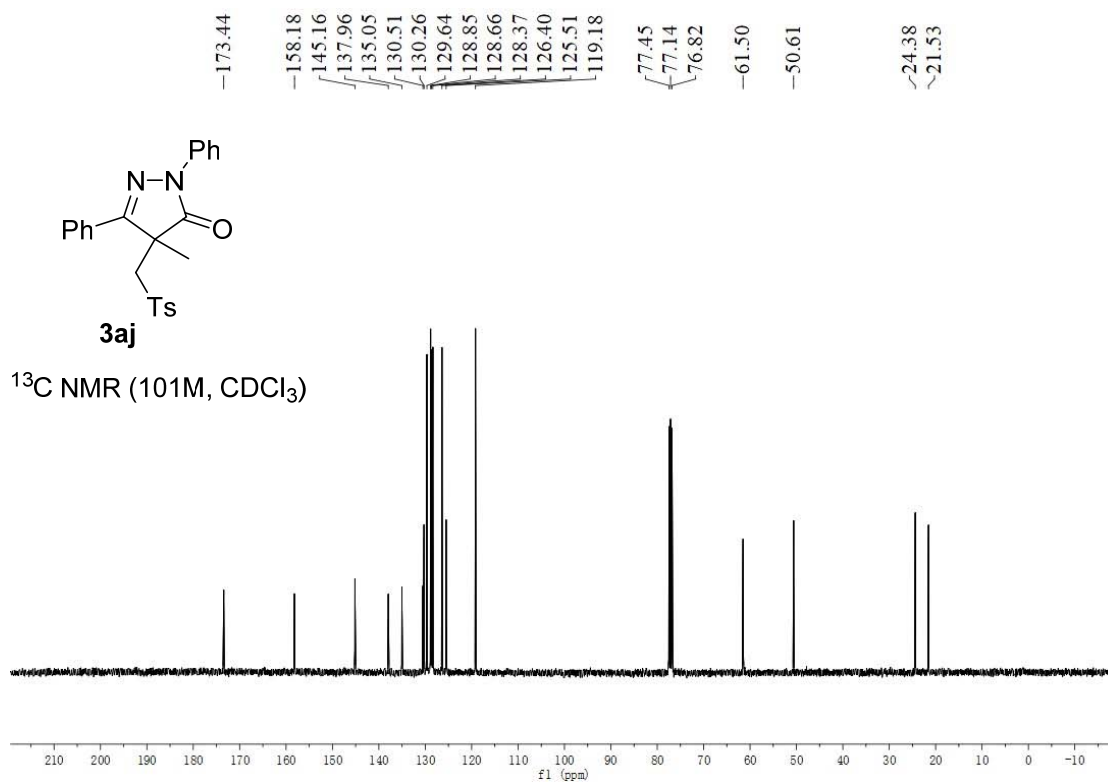


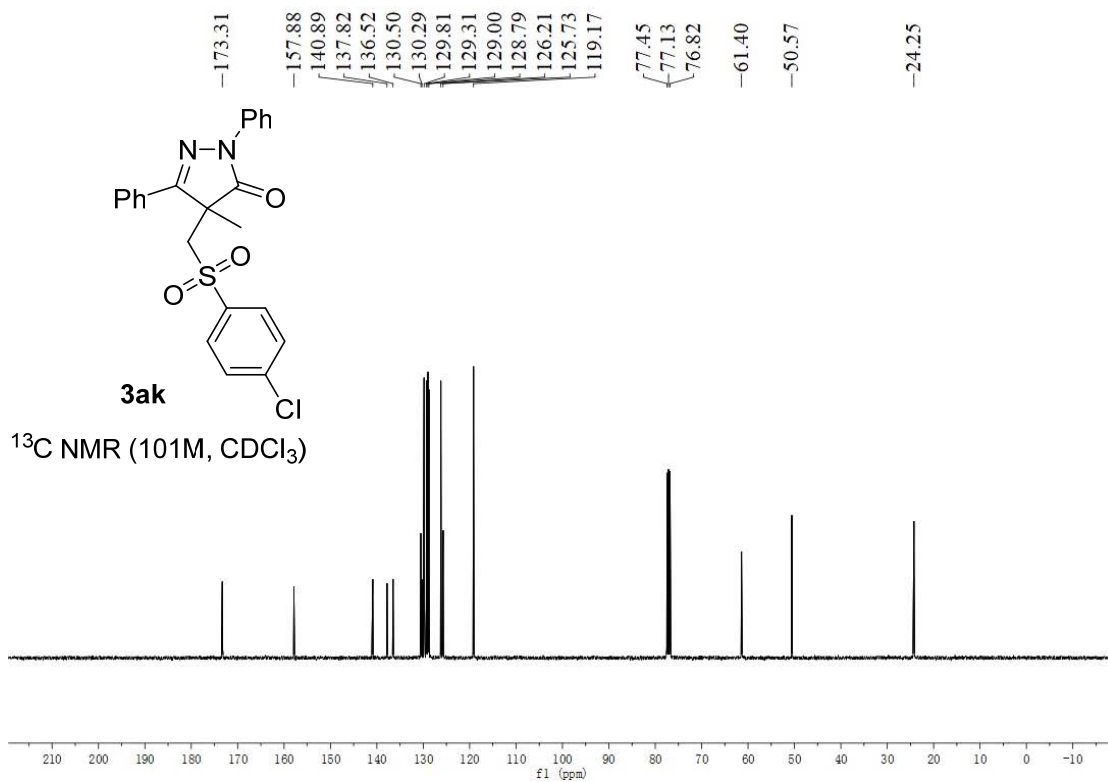
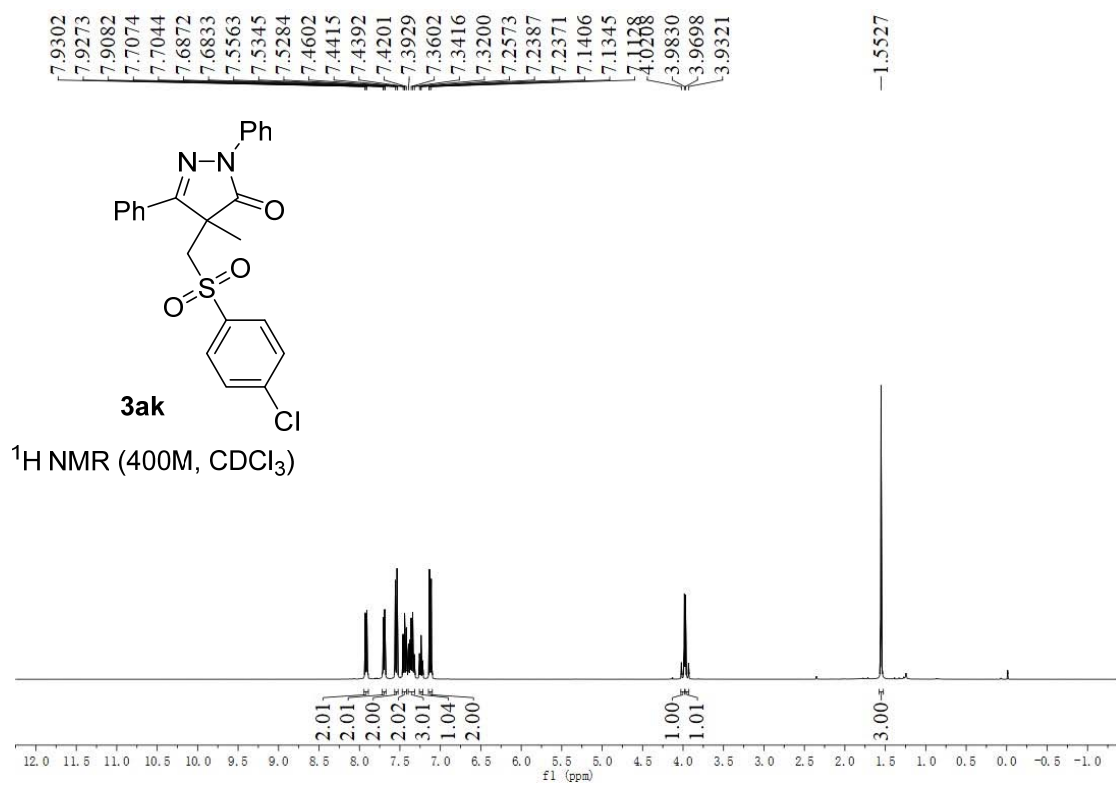


<sup>1</sup>H NMR (400M, CDCl<sub>3</sub>)

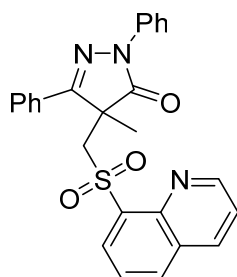


<sup>13</sup>C NMR (101M, CDCl<sub>3</sub>)



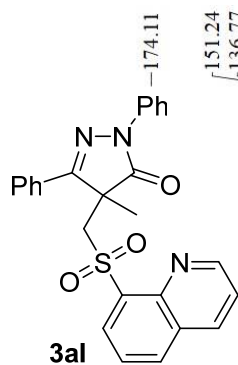
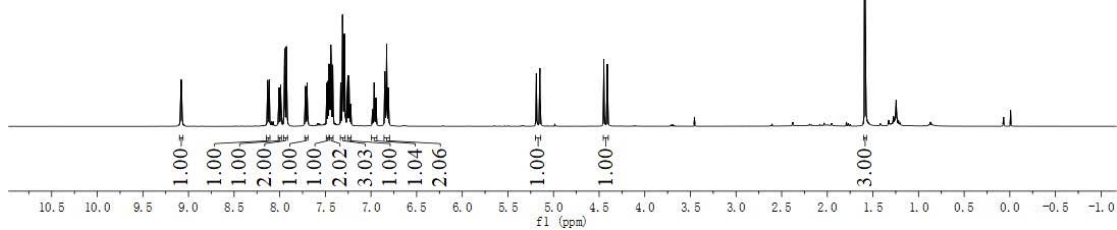


9.0870  
9.0826  
9.0763  
9.0720  
8.1362  
8.1327  
8.1178  
8.1142  
8.0119  
8.0076  
7.9911  
7.9868  
7.9490  
7.9461  
7.9271  
7.9248  
7.7214  
7.7180  
7.7009  
7.6975  
7.4832  
7.4725  
7.4624  
7.4593  
7.4519  
7.4405  
7.4384  
7.4193  
7.3320  
7.3117  
7.2914  
7.2880  
7.2532  
7.2412  
6.9651  
6.9466  
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5.1883  
5.1500  
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4.4104  
1.5874



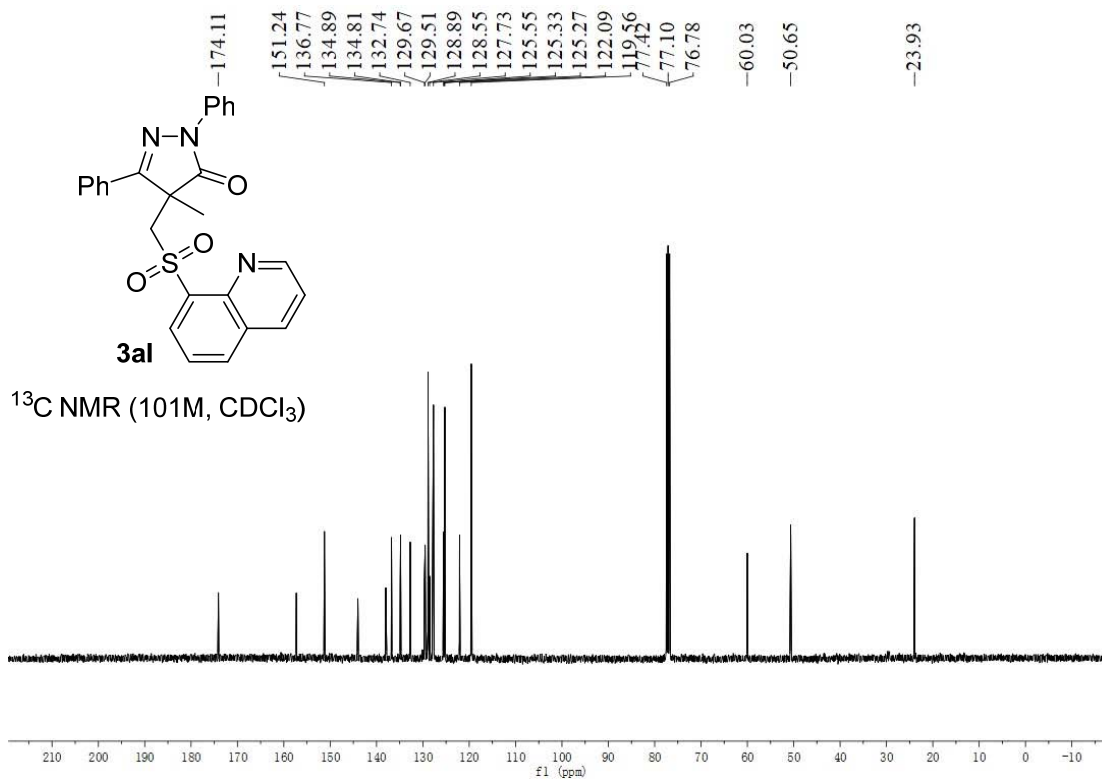
**3al**

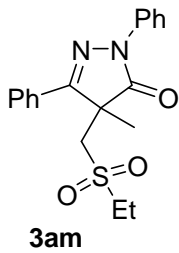
<sup>1</sup>H NMR (400M, CDCl<sub>3</sub>)



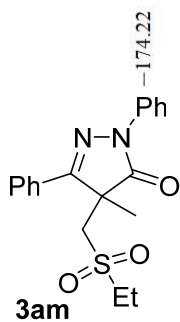
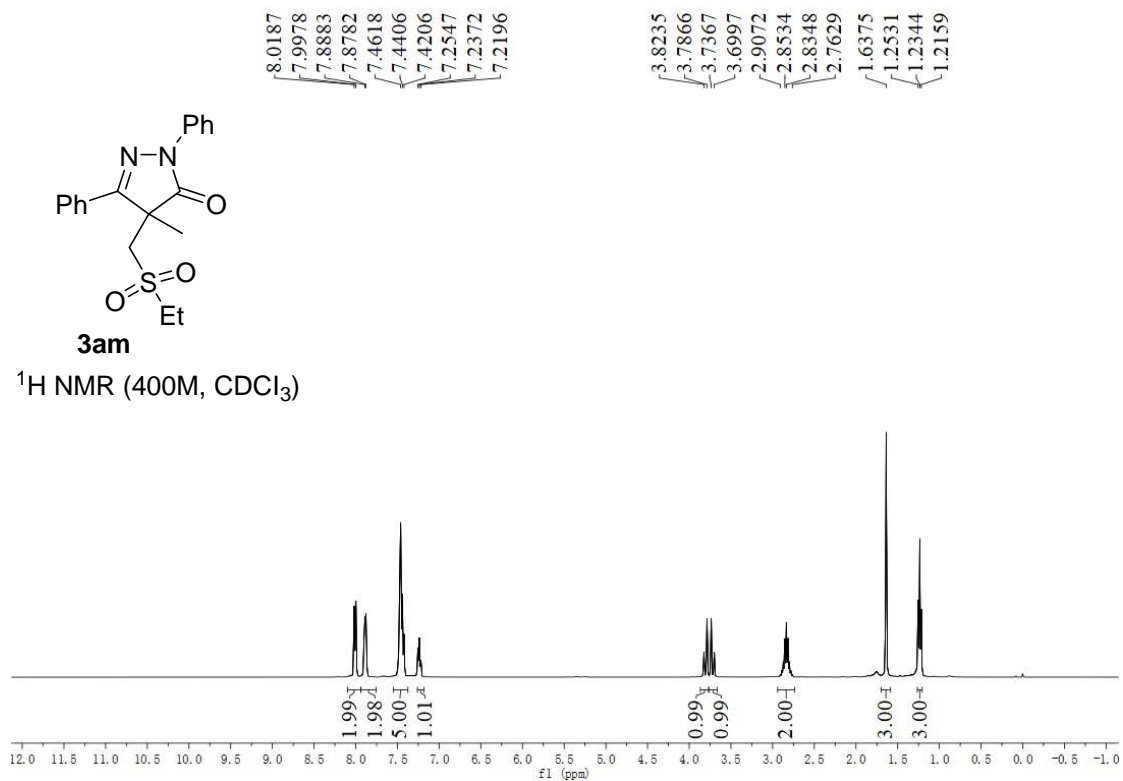
**3al**

<sup>13</sup>C NMR (101M, CDCl<sub>3</sub>)

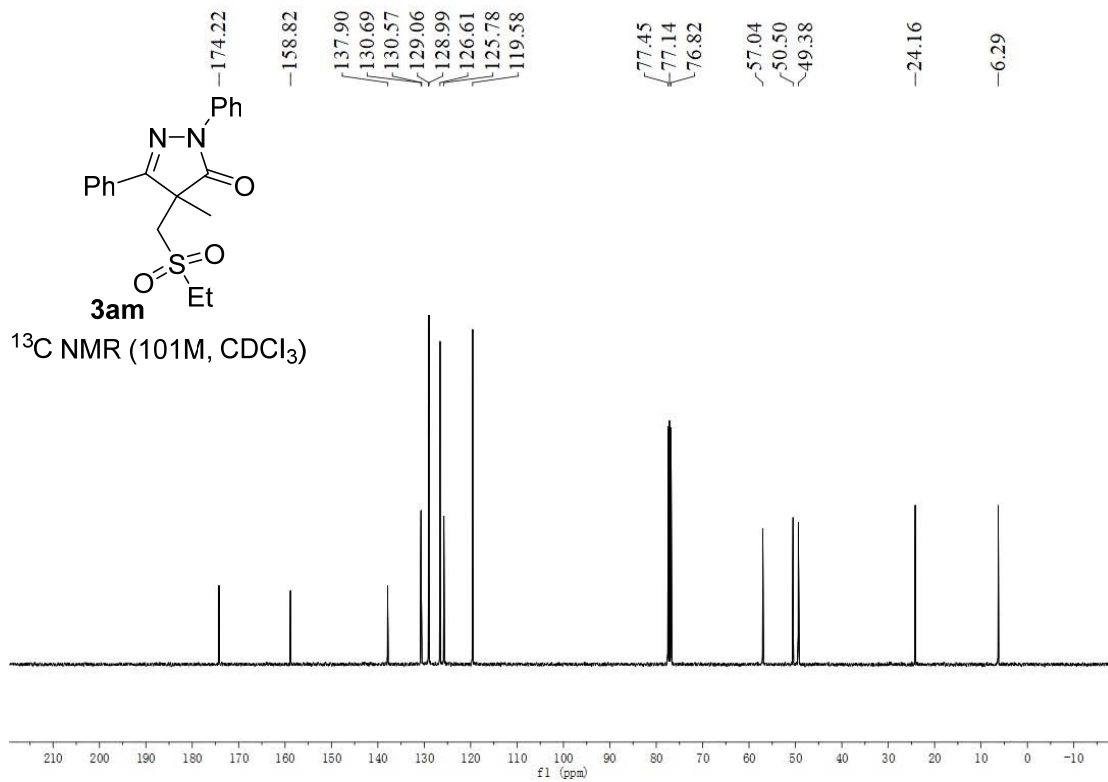




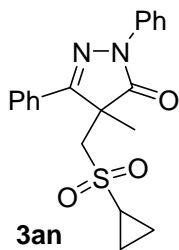
<sup>1</sup>H NMR (400M, CDCl<sub>3</sub>)



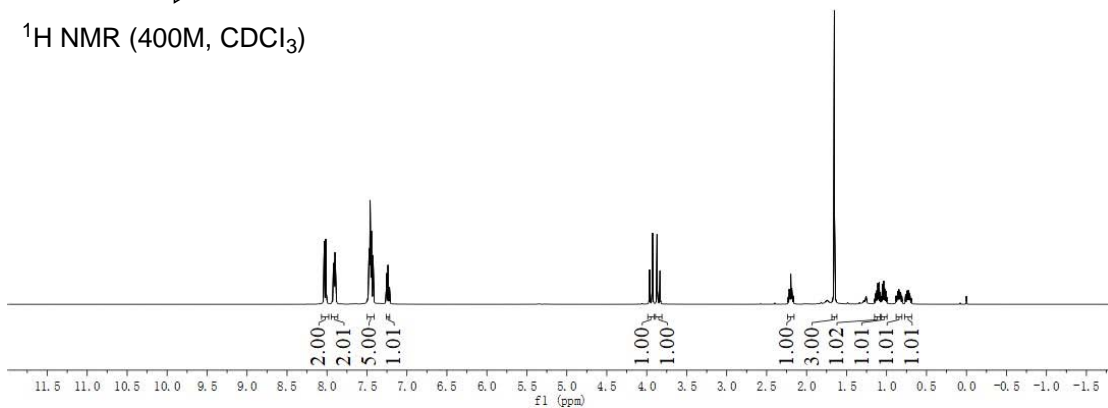
<sup>13</sup>C NMR (101M, CDCl<sub>3</sub>)



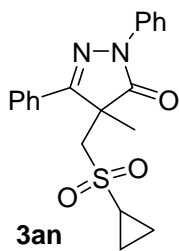
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7.9075  
7.9031  
7.8991  
7.8940  
7.8853  
7.4598  
7.4546  
7.4174  
7.2579  
7.2552  
7.2367  
7.2154  
3.9651  
3.9279  
3.8707  
3.8336  
2.2299  
2.2179  
2.1981  
2.1662  
1.6534  
1.1093  
1.0924  
1.0806  
1.0639  
1.0355  
1.0095  
0.9973  
0.8808  
0.8517  
0.8213  
0.8097  
0.7610  
0.7493  
0.7249



$^1\text{H NMR}$  (400M,  $\text{CDCl}_3$ )



-174.17  
-158.75  
137.94  
130.65  
130.63  
129.00  
126.55  
125.71  
119.40  
77.44  
77.12  
76.80  
-59.41  
-50.60  
-31.24  
-24.24  
5.70  
5.42



$^{13}\text{C NMR}$  (101M,  $\text{CDCl}_3$ )

