# SUPPORTING INFORMATION

**for**

# Use of Hypervalent Iodine Reagents in Visible Light-Promoted $\alpha$-Ketoacylations of Sulfoximines with Aryl Alkynes

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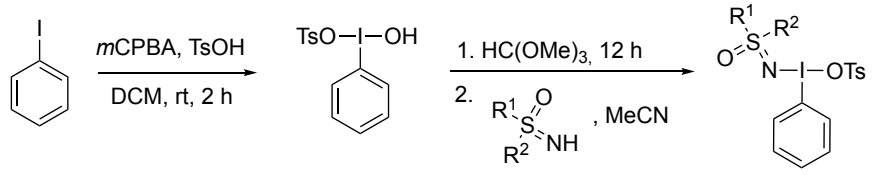
## 1. General information

Unless otherwise noted, the materials were purchased from commercial suppliers and used without further purification. All the solvents were treated according to general methods. The reactions were monitored by thin layer chromatography (TLC) with aluminium sheets silica gel 60 $F_{254}$ from Merck, and flash column chromatography purifications were performed using silica gel 60 (63-200 μm) from Merck. $^{1}H$ and $^{13}C$ NMR spectra were recorded with an Agilent VNMRS 600, Agilent VNMRS 400 or Varian Mercury 300 in deuterated solvents. Chemical shifts ($\delta$) are reported in parts per million (ppm) and spin-spin coupling constants ($J$) are given in Hz, while multiplicities are abbreviated by s (singlet), d (doublet), t (triplet), q (quartet), br (broad), m (multiplet). The IR spectra were recorded with a PerkinElmer Spectrum 100 spectrometer with an attached UATR device Diamond KRS-5. All IR data were collected by attenuated total reflectance (ATR) and wavenumbers $\nu$ are given in $cm^{-1}$. Mass spectra were recorded with a Finnigan SSQ Finnigan 7000 spectrometer (EI, 70 eV). High resolution mass spectra (HRMS) were recorded on a Thermo Scientific LTQ Orbitrap XL spectrometer. Melting points (mp) were determined on a Büchi B-540 melting point apparatus. Determination and separation of stereoisomers were performed by analytical high-performance liquid chromatography (HPLC) on an Agilent 1200-series with a Chiralpak AD-H column (250 mm • 4.6 mm) from Chiral Technologies Inc. as chiral stationary phase (CSP) and by preparative supercritical fluid chromatography (SFC) on a Thar SFC Prep 80 from Waters with a Chiralpak IA column (250 mm • 19 mm). *N*H-sulfoximines[S1] were prepared in accordance with previously published synthetic strategies. For the light-promoted reactions: Use of a blue-LEDs strip (24 W, 465–470 nm, manufacturer: ledxon modular GmbH). The distance from the light source to the irradiation vessel was about 3 cm, and the reaction vessel was cooled by using a small fan.

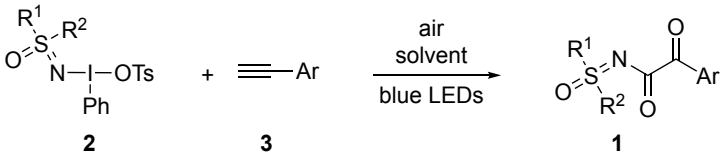
## 2. Experimental procedures

### 2.1. Experimental procedure for the preparation of hypervalent iodine reagents[S2]




Hydroxy(tosyloxy)iodobenzene[S2] was prepared starting from iodobenzene by sequential oxidation and ligand exchange. Hydroxy(tosyloxy)iodobenzene (784 mg, 2 mmol) was stirred in trimethyl orthoformate (2.0 mL) for 12 h. Then, the mixture was concentrated to dryness under vacuum. The residue was used in the next step without further purification. At room temperature, a solution of the residue in MeCN (3.0 mL) was treated with *S*-phenyl-*S*-methyl sulfoximine (310 mg, 2 mmol). Immediately, a white precipitate was formed, which was collected by filtration. The precipitate was washed with $Et_2O$ and dried *in vacuo* to afford the spectroscopically pure iodine(III) salt.

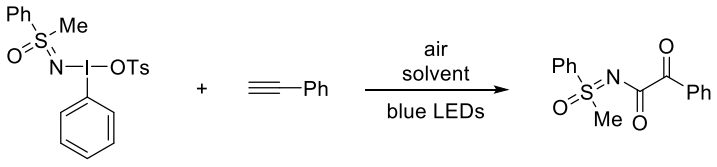
## 2.2. α-Ketoacylations of sulfoximines using iodine(III) reagents and aryl alkynes




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

In a 15 mL tube equipped with a magnetic stir bar, iodine(III) reagents **2** (0.3 mmol) and aryl alkynes **3** (0.2 mmol) were mixed with $CH_2Cl_2$ (3 mL), and the mixture was stirred under blue-LED (24 W) irradiation at room temperature for 24 h. After the reaction was complete, product **1** was purified by flash column chromatography (*n*-pentane/ethyl acetate = 4/1 to 1/1).

## 2.3. Reaction on a 2 mmol scale




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

In a 30 mL tube equipped with a magnetic stir bar, iodine(III) reagents **2a** (3.0 mmol, 1.6 g) and phenyl acetylene (**3a**, 2.0 mmol, 0.2 g) were mixed with $CH_2Cl_2$ (12 mL), and the mixture was stirred under blue-LED (24 W) irradiation at room temperature for 36 h. After the reaction was complete, product **1a** was purified by flash column chromatography (*n*-pentane/ethyl acetate = 2/1, 350 mg, 61%). *Note: the reaction tube was refilled the air several times.*

## 3. References

[S1] (a) Pandey, A.; Bolm, C. Metal-Free Synthesis of *N*-Cyano-Substituted Sulfilimines and Sulfoximines. *Synthesis* **2010**, 2922–2925. (b) Tota, A.; Zenzola, M.; Chawner, S. J.; John-Campbell, S. S.; Carlucci, C.; Romanazzi, G.; Degennaro, L.; Bull, J. A.; Luisi, R. Synthesis of *N*H-sulfoximines from sulfides by chemoselective one-pot N-and O-transfers. *Chem. Commun.* **2017**, *53*, 348–351.

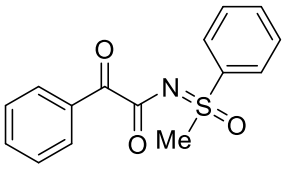
[S2] (a) Koser, G. F.; Wettach, R. H. [Hydroxy (tosyloxy) iodo] benzene, a versatile reagent for the mild oxidation of aryl iodides at the iodine atom by ligand transfer. *J. Org. Chem.* **1980**, *45*, 1542–1543. (b) Koser, G. F.; Wettach, R. H. New methodology in iodonium salt synthesis. Reactions of [hydroxy (tosyloxy) iodo] arenes with aryltrimethylsilanes. *J. Org. Chem.* **1980**, *45*, 4988–4989.

[S3] (a) Wang, L.; Priebbenow, D. L.; Zou, L.-H.; Bolm, C. The Copper-Catalyzed Oxidative N-Acylation of Sulfoximines. *Adv. Synth. Catal.* **2013**, *355*, 1490–1494. (b) Zou, Y.; Peng, Z.; Dong, W.; An, D. CuI-Mediated α-Ketoacylation of Sulfoximines under Solvent-Free Conditions. *Eur. J. Org. Chem.* **2015**, 4913–4921. (c) Cheng, H.; Bolm, C. Copper-Catalyzed Oxidative α-Ketoacylations of Sulfoximines with Aryl Methyl Ketones and Dioxygen as

Terminal Oxidant. *Synlett* **2016**, *27*, 769–772.

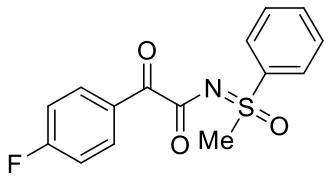
## 4. Characterization data

**_N_-[Methyl(oxo)(phenyl)-λ$^6$-sulfaneylidene]-2-oxo-2-phenylacetamide (1aa)**



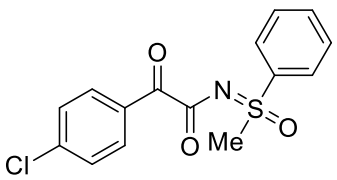
White solid (51 mg, 89% yield); isolation: *n*-pentane/ethyl acetate (2/1) as the eluent; m.p. 97–98 °C. $^1$H NMR (600 MHz, $CDCl_3$) δ 8.05 (ddt, *J* = 16.1, 7.0, 1.3 Hz, 4H), 7.73 – 7.70 (m, 1H), 7.65 – 7.62 (m, 2H), 7.59 (ddt, *J* = 8.7, 7.3, 1.3 Hz, 1H), 7.48 – 7.45 (m, 2H), 3.47 (s, 3H). $^{13}$C {$^1$H} NMR (151 MHz, $CDCl_3$) δ 190.1, 173.3, 137.7, 134.4, 134.2, 132.7, 130.2, 129.9, 128.7, 127.2, 127.1, 44.8. The spectroscopic data are in accordance with the previously reported data.[S3]

**2-(4-Fluorophenyl)-_N_-[methyl(oxo)(phenyl)-λ$^6$-sulfaneylidene]-2-oxoacetamide (1ab)**



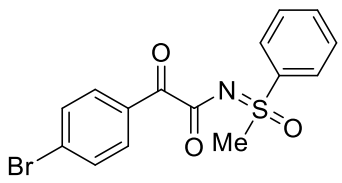
Light yellow solid (45 mg, 75% yield); isolation: *n*-pentane/ethyl acetate (2/1) as the eluent; m.p. 120–122 °C. $^1$H NMR (400 MHz, $CDCl_3$) δ 8.11 – 8.04 (m, 4H), 7.75 – 7.69 (m, 1H), 7.67 – 7.61 (m, 2H), 7.16 – 7.09 (m, 2H), 3.47 (s, 3H). $^{13}$C {$^1$H} NMR (101 MHz, $CDCl_3$) δ 188.4, 172.8, 166.5 ($J_{C\text{-}F}$ = 256.3 Hz), 137.6, 134.5, 132.9 ($J_{C\text{-}F}$ = 9.8 Hz), 129.9, 127.1, 115.9 ($J_{C\text{-}F}$ = 22.6 Hz), 44.8. The spectroscopic data are in accordance with the previously reported data.[S3b,c]

**2-(4-Chlorophenyl)-_N_-[methyl(oxo)(phenyl)-λ$^6$-sulfaneylidene]-2-oxoacetamide (1ac)**



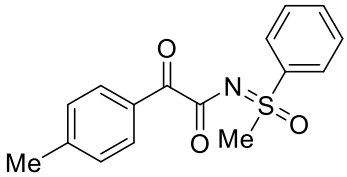
Light yellow solid (53 mg, 83% yield); isolation: *n*-pentane/ethyl acetate (3/1) as the eluent; m.p. 134–136 °C. $^1$H NMR (400 MHz, $CDCl_3$) δ 8.08 – 8.04 (m, 2H), 8.02 – 7.98 (m, 2H), 7.76 – 7.70 (m, 1H), 7.65 (dd, *J* = 8.3, 6.8 Hz, 2H), 7.46 – 7.42 (m, 2H), 3.48 (s, 3H). $^{13}$C {$^1$H} NMR (101 MHz, $CDCl_3$) δ 188.7, 172.6, 140.8, 134.5, 131.6, 129.9, 129.0, 127.1, 44.8. The spectroscopic data are in accordance with the previously reported data.[S3b,c]

**2-(4-Bromophenyl)-_N_-[methyl(oxo)(phenyl)-λ$^6$-sulfaneylidene]-2-oxoacetamide (1ad)**



White solid (59 mg, 81% yield); isolation: *n*-pentane/ethyl acetate (3/1) as the eluent; m.p. 125–126 °C. $^1$H NMR (400 MHz, $CDCl_3$) δ 8.07 – 8.03 (m, 2H), 7.93 – 7.89 (m, 2H), 7.75 – 7.70 (m, 1H), 7.67 – 7.58 (m, 4H), 3.47 (s, 3H). $^{13}$C {$^1$H} NMR (101 MHz, $CDCl_3$) δ 188.9, 172.5, 137.5, 134.5, 132.0, 131.6, 129.9, 129.6, 127.1, 44.8. The spectroscopic data are in accordance with the previously reported data.[S3b,c]

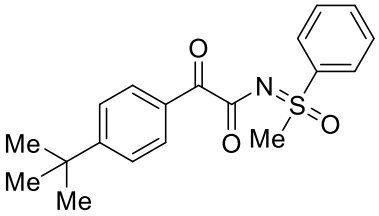
**_N_-[Methyl(oxo)(phenyl)-λ$^6$-sulfaneylidene]-2-oxo-2-(*p*-tolyl)acetamide (1ae)**



White solid (54 mg, 90% yield); isolation: *n*-pentane/ethyl acetate (2/1) as the eluent; m.p. 145–146 °C. $^1$H NMR (400 MHz, $CDCl_3$) δ 8.02 – 7.97 (m, 2H), 7.89 – 7.84 (m, 2H), 7.67 – 7.61 (m, 1H), 7.57 (dd, *J* = 8.4, 6.8 Hz, 2H), 7.21 – 7.16 (m, 2H), 3.40 (s, 3H), 2.34 (s, 3H). $^{13}$C {$^1$H} NMR (101 MHz, $CDCl_3$) δ

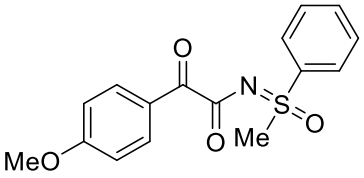
189.8, 173.5, 145.3, 137.7, 134.4, 130.3, 129.9, 129.4, 127.2, 44.8, 21.8. The spectroscopic data are in accordance with the previously reported data.[S3a,b]

**2-[4-(*Tert*-butyl)phenyl]-*N*-[methyl(oxo)(phenyl)- λ⁶-sulfaneylidene]-2-oxoacetamide (1af)**



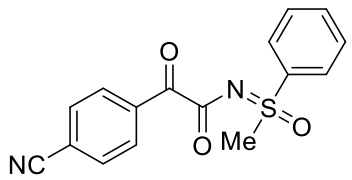
White solid (62 mg, 90% yield); isolation: *n*-pentane/ethyl acetate (2/1) as the eluent; m.p. 112–113 °C. $^1$H NMR (600 MHz, $CDCl_3$) δ 8.08 – 8.06 (m, 2H), 7.99 – 7.97 (m, 2H), 7.73 – 7.70 (m, 1H), 7.65 – 7.62 (m, 2H), 7.49 – 7.47 (m, 2H), 3.47 (s, 3H), 1.33 (s, 9H). $^{13}$C {$^1$H} NMR (151 MHz, $CDCl_3$) δ 189.8, 173.5, 158.2, 137.8, 134.4, 130.2, 130.1, 129.9, 127.2, 125.7, 44.8, 31.4, 31.0. MS (EI): *m/z* = 183 (10), 182 (100), 161 (9), 154 (3), 125 (5), 91 (5), 77 (5), 65 (3), 51 (2). IR (ATR): ν = 2960, 2927, 2869, 2164, 2022, 1678, 1633, 1604, 1449, 1407, 1366, 1330, 1268, 1218, 1180, 1096, 1009, 973, 820, 743, 683. HRMS *m/z*: $[M + H]^+$ calcd for $C_{19}H_{22}NO_3S$ 344.1315; Found 344.1316.

**2-(4-Methoxyphenyl)-*N*-[methyl(oxo)(phenyl)-λ⁶-sulfaneylidene]-2-oxoacetamide (1ag)**



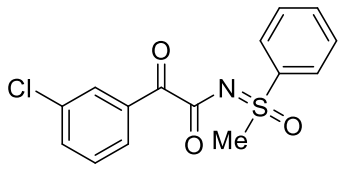
White solid (58 mg, 91% yield); isolation: *n*-pentane/ethyl acetate (1/1) as the eluent; m.p. 148–149 °C. $^1$H NMR (600 MHz, $CDCl_3$) δ 8.08 – 8.05 (m, 2H), 8.04 – 8.01 (m, 2H), 7.73 – 7.69 (m, 1H), 7.65 – 7.61 (m, 2H), 6.94 – 6.91 (m, 2H), 3.86 (s, 4H), 3.46 (s, 3H). $^{13}$C {$^1$H} NMR (151 MHz, $CDCl_3$) δ 188.8, 173.7, 164.5, 137.8, 134.4, 132.7, 129.9, 127.2, 125.7, 114.0, 55.5, 44.8. The spectroscopic data are in accordance with the previously reported data.[S3b,c]

**2-(4-Cyanophenyl)-*N*-[methyl(oxo)(phenyl)-λ⁶-sulfaneylidene]-2-oxoacetamide (1ah)**



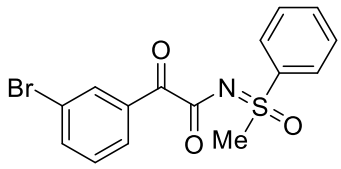
Brown solid (37 mg, 60% yield); isolation: *n*-pentane/ethyl acetate (2/1) as the eluent; m.p. 95–96 °C. $^1$H NMR (600 MHz, $CDCl_3$) δ 8.17 – 8.14 (m, 2H), 8.07 – 8.05 (m, 2H), 7.77 – 7.73 (m, 3H), 7.68 – 7.64 (m, 2H), 3.49 (s, 3H). $^{13}$C {$^1$H} NMR (151 MHz, $CDCl_3$) δ 188.2, 171.7, 137.4, 136.0, 134.6, 132.4, 130.5, 130.0, 127.1, 117.8, 117.2, 44.8. MS (EI): *m/z* = 313 (1), 280 (5), 183 (10), 182 (100), 130 (5), 125 (8), 102 (7), 93 (3), 77 (9), 51 (5). IR (ATR): ν = 3091, 3024, 2922, 2853, 2231, 2171, 1692, 1632, 1448, 1408, 1325, 1024, 1088, 1012, 978, 857, 824, 753, 679. HRMS *m/z*: $[M + H]^+$ calcd for $C_{16}H_{13}N_2O_3S$ 313.0641; Found 313.0644.

**2-(3-Chlorophenyl)-*N*-[methyl(oxo)(phenyl)-λ⁶-sulfaneylidene]-2-oxoacetamide (1ai)**



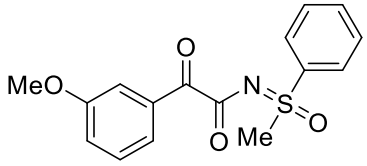
White solid (52 mg, 81% yield); isolation: *n*-pentane/ethyl acetate (3/1) as the eluent; m.p. 92–93 °C. $^1$H NMR (600 MHz, $CDCl_3$) δ 8.08 – 8.05 (m, 2H), 8.02 (t, *J* = 1.9 Hz, 1H), 7.93 (dt, *J* = 7.8, 1.4 Hz, 1H), 7.76 – 7.72 (m, 1H), 7.68 – 7.64 (m, 2H), 7.56 (ddd, *J* = 7.9, 2.2, 1.1 Hz, 1H), 7.41 (t, *J* = 7.9 Hz, 1H), 3.48 (s, 3H). $^{13}$C {$^1$H} NMR (151 MHz, $CDCl_3$) δ 188.6, 172.3, 137.5, 134.9, 134.5, 134.4, 134.1, 130.0, 129.9, 128.4, 127.1, 44.8. MS (EI): *m/z* = 185 (7), 184 (11), 182 (100), 111 (9), 93 (4), 77 (9), 65 (5), 51 (5). IR (ATR): ν = 3067, 3019, 2927, 2162, 1687, 1631, 1573, 1447, 1410, 1324, 1195, 1092, 1026,

973, 895, 831, 739, 680. HRMS *m/z*: $[M + H]^+$ calcd for $C_{15}H_{13}NO_3SCl$ 322.0299; Found 322.0300.



**2-(3-Bromophenyl)-*N*-[methyl(oxo)(phenyl)-λ$^6$-sulfaneylidene]-2-oxoacetamide (1aj)**

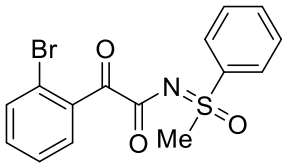
White solid (57 mg, 79% yield); isolation: *n*-pentane/ethyl acetate (3/1) as the eluent; m.p. 88–89 °C. $^1$H NMR (600 MHz, $CDCl_3$) δ 8.17 (t, *J* = 1.8 Hz, 1H), 8.08 – 8.05 (m, 2H), 7.98 (dt, *J* = 7.8, 1.3 Hz, 1H), 7.76 – 7.70 (m, 2H), 7.68 – 7.64 (m, 2H), 7.35 (t, *J* = 7.9 Hz, 1H), 3.48 (s, 3H). $^{13}$C {$^1$H} NMR (151 MHz, $CDCl_3$) δ 188.5, 172.3, 137.5, 137.0, 134.6, 134.5, 132.8, 130.2, 130.0, 128.9, 127.1, 122.9, 77.2, 77.0, 76.8, 44.8. MS (EI): *m/z* = 184 (6), 183 (13), 182 (100), 157 (5), 156 (5), 124 (7), 97 (2), 77 (7), 51 (3). IR (ATR): ν = 3308, 2926, 2163, 1732, 1689, 1632, 1449, 1328, 1058, 969, 796, 741, 681. HRMS *m/z*: $[M + H]^+$ calcd for $C_{15}H_{13}NO_3SBr$ 365.9794; Found 365.9794.



**2-(3-Methoxyphenyl)-*N*-[methyl(oxo)(phenyl)-λ$^6$-sulfaneylidene]-2-oxoacetamide (1ak)**

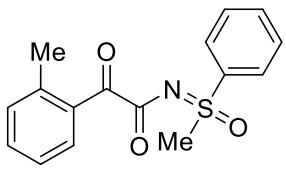
White solid (42 mg, 67% yield); isolation: *n*-pentane/ethyl acetate (1/1) as the eluent; m.p. 67–69 °C. $^1$H NMR (600 MHz, $CDCl_3$) δ 8.09 – 8.06 (m, 2H), 7.75 – 7.71 (m, 1H), 7.67 – 7.61 (m, 3H), 7.56 (dd, *J* = 2.7, 1.5 Hz, 1H), 7.37 (t, *J* = 7.9 Hz, 1H), 7.17 – 7.13 (m, 1H), 3.84 (s, 3H), 3.48 (s, 3H). $^{13}$C {$^1$H} NMR (151 MHz, $CDCl_3$) δ 190.0, 173.2, 159.8, 137.7, 134.4, 134.0, 129.9, 129.7, 127.2, 123.4, 121.4, 113.2, 55.5, 44.8. The spectroscopic data are in accordance with the previously reported data.[S3c]

**2-(2-Bromophenyl)-*N*-[methyl(oxo)(phenyl)-λ$^6$-sulfaneylidene]-2-oxoacetamide (1al)**



White solid (57 mg, 78% yield); isolation: *n*-pentane/ethyl acetate (3/1) as the eluent; m.p. 105–107 °C. $^1$H NMR (600 MHz, $CDCl_3$) δ 8.04 (ddp, *J* = 6.1, 2.6, 1.4 Hz, 2H), 7.69 (dddt, *J* = 19.1, 7.6, 3.3, 1.6 Hz, 2H), 7.64 – 7.58 (m, 3H), 7.39 (tdd, *J* = 7.5, 2.6, 1.2 Hz, 1H), 7.35 (tt, *J* = 7.6, 1.9 Hz, 1H), 3.50 (s, 3H). $^{13}$C {$^1$H} NMR (151 MHz, $CDCl_3$) δ 190.9, 170.6, 137.6, 136.5, 134.4, 133.5, 133.1, 131.8, 129.8, 127.4, 127.2, 121.2, 77.2, 77.0, 76.8, 44.2. MS (EI): *m/z* = 185 (3), 184 (7), 182 (100), 159 (3), 155 (2), 125 (7), 97 (4), 77 (17), 65 (7), 51 (7). IR (ATR): ν = 3448, 3014, 2924, 2163, 1692, 1630, 1584, 1470, 1444, 1406, 1314, 1275, 1218, 1090, 977, 864, 829, 803, 740, 684. HRMS *m/z*: $[M + H]^+$ calcd for $C_{15}H_{13}NO_3BrS$ 365.9794; Found 365.9798.

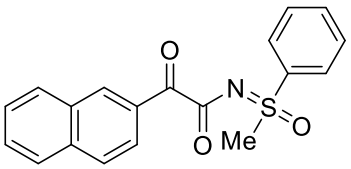
***N*-[Methyl(oxo)(phenyl)-λ$^6$-sulfaneylidene]-2-oxo-2-(*o*-tolyl)acetamide (1am)**



White solid (48 mg, 80% yield); isolation: *n*-pentane/ethyl acetate (2/1) as the eluent; m.p. 140–142 °C. $^1$H NMR (600 MHz, $CDCl_3$) δ 8.06 (dt, *J* = 8.4, 1.1 Hz, 2H), 7.82 (dd, *J* = 7.7, 1.4 Hz, 1H), 7.73 – 7.69 (m, 1H), 7.63 (ddt, *J* = 8.9, 7.5, 1.7 Hz, 2H), 7.43 (td, *J* = 7.5, 1.4 Hz, 1H), 7.28 – 7.24 (m, 2H), 3.46 (s, 3H), 2.62 (s, 3H). $^{13}$C {$^1$H} NMR (151 MHz, $CDCl_3$) δ 192.6, 173.9, 141.1, 137.7, 134.4, 133.1, 132.7, 132.1, 131.6, 129.9, 127.2, 125.7,

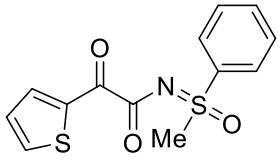
44.8, 21.6. MS (EI): *m/z* = 183 (11), 182 (100), 140 (3), 119 (10), 91 (12), 65 (9), 51 (4). IR (ATR): ν = 3341, 3056, 3016, 2919, 2311, 2171, 1676, 1628, 1570, 1451, 1411, 1320, 1286, 1221, 1197, 1131, 1090, 981, 893, 830, 780, 680, 665. HRMS *m/z*: $[M + Na]^+$ calcd for $C_{16}H_{15}NO_3SNa$ 324.0665; Found 324.0665. The spectroscopic data are in accordance with the previously reported data.[S3b]

**_N_-[Methyl(oxo)(phenyl)-λ⁶-sulfaneylidene]-2-(naphthalen-2-yl)-2-oxoacetamide (1an)**



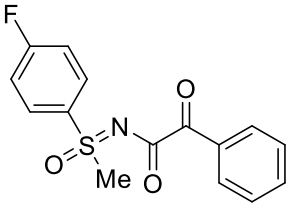
White solid (64 mg, 95% yield); isolation: *n*-pentane/ethyl acetate (3/1) as the eluent; m.p. 133–135 °C. $^1$H NMR (600 MHz, $CDCl_3$) δ 8.60 (s, 1H), 8.11 (dt, *J* = 8.4, 1.4 Hz, 2H), 8.08 (dt, *J* = 8.6, 1.4 Hz, 1H), 7.94 (d, *J* = 8.2 Hz, 1H), 7.90 (d, *J* = 8.6 Hz, 1H), 7.86 (d, *J* = 8.2 Hz, 1H), 7.76 – 7.71 (m, 1H), 7.66 (td, *J* = 8.0, 7.5, 1.8 Hz, 2H), 7.61 (ddd, *J* = 8.1, 6.9, 1.4 Hz, 1H), 7.54 (ddd, *J* = 8.1, 6.9, 1.3 Hz, 1H), 3.50 (s, 3H). $^{13}$C {$^1$H} NMR (151 MHz, $CDCl_3$) δ 190.1, 173.4, 137.7, 136.1, 134.5, 133.5, 132.4, 130.0, 130.0, 129.9, 129.1, 128.6, 127.8, 127.2, 126.8, 124.4, 44.9. The spectroscopic data are in accordance with the previously reported data.[S3b,c]

**_N_-[Methyl(oxo)(phenyl)-λ⁶-sulfaneylidene]-2-oxo-2-(thiophen-2-yl)acetamide (1ao)**



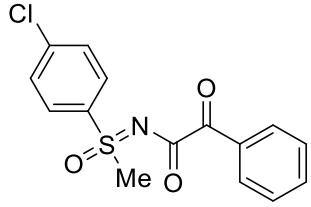
Light yellow solid (48 mg, 83% yield); isolation: *n*-pentane/ethyl acetate (2/1) as the eluent; m.p. 105–107 °C. $^1$H NMR (400 MHz, $CDCl_3$) δ 8.10 – 8.04 (m, 3H), 7.75 – 7.70 (m, 2H), 7.67 – 7.62 (m, 2H), 7.14 (dd, *J* = 4.9, 3.9 Hz, 1H), 3.47 (s, 3H). $^{13}$C {$^1$H} NMR (101 MHz, $CDCl_3$) δ 180.8, 170.7, 139.1, 137.6, 136.8, 136.5, 134.4, 129.9, 128.3, 127.2, 44.7. The spectroscopic data are in accordance with the previously reported data.[S3b,c]

**_N_-[(4-Fluorophenyl)(methyl)(oxo)-λ⁶-sulfaneylidene]-2-oxo-2-phenylacetamide (1ba)**



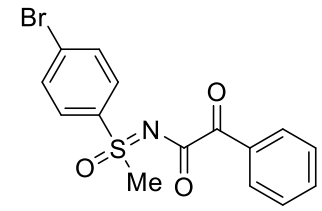
Light yellow solid (51 mg, 73% yield); isolation: *n*-pentane/ethyl acetate (3/1) as the eluent; m.p. 91–93 °C. $^1$H NMR (400 MHz, $CDCl_3$) δ 8.11 – 8.02 (m, 4H), 7.60 (t, *J* = 7.5 Hz, 1H), 7.47 (t, *J* = 7.6 Hz, 2H), 7.31 (t, *J* = 8.4 Hz, 2H), 3.48 (s, 3H). $^{13}$C {$^1$H} NMR (101 MHz, $CDCl_3$) δ 190.0, 173.2, 166.2 ($J_{C\text{-}H}$ = 256.8 Hz), 134.3, 133.5 ($J_{C\text{-}H}$ = 3.8 Hz), 132.6, 130.2, 130.1, 128.7, 117.3 ($J_{C\text{-}H}$ = 22.8 Hz), 45.0. The spectroscopic data are in accordance with the previously reported data.[S3b]

**_N_-[(4-Chlorophenyl)(methyl)(oxo)-λ⁶-sulfaneylidene]-2-oxo-2-phenylacetamide (1ca)**



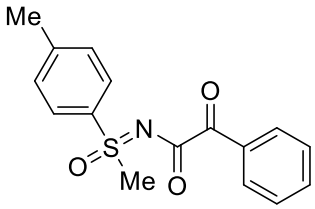
White solid (54 mg, 85% yield); isolation: *n*-pentane/ethyl acetate (3/1) as the eluent; m.p. 135–136 °C. $^1$H NMR (400 MHz, $CDCl_3$) δ 8.07 – 8.03 (m, 2H), 7.96 – 7.92 (m, 2H), 7.62 – 7.56 (m, 1H), 7.49 – 7.40 (m, 5H), 3.46 (s, 3H), 2.47 (s, 3H). $^{13}$C {$^1$H} NMR (101 MHz, $CDCl_3$) δ 189.9, 173.1, 141.4, 136.1, 134.3, 132.6, 130.2, 130.1, 128.7, 128.7, 44.8. The spectroscopic data are in accordance with the previously reported data.[S3b,c]

***N*-[(4-Bromophenyl)(methyl)(oxo)-λ$^6$-sulfaneylidene]-2-oxo-2-phenylacetamide (1da)**



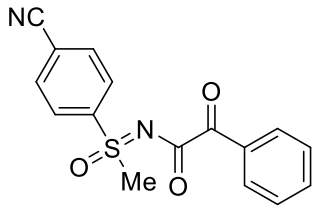
White solid (60 mg, 83% yield); isolation: *n*-pentane/ethyl acetate (3/1) as the eluent; m.p. 107–109 °C. $^1$H NMR (400 MHz, $CDCl_3$) δ 8.05 – 8.01 (m, 2H), 7.95 – 7.91 (m, 2H), 7.80 – 7.76 (m, 2H), 7.63 – 7.58 (m, 1H), 7.50 – 7.44 (m, 2H), 3.47 (s, 3H). $^{13}$C {$^1$H} NMR (101 MHz, $CDCl_3$) δ 189.9, 173.1, 136.7, 134.3, 133.2, 132.6, 132.6, 130.2, 130.0, 128.7, 128.7, 44.8. The spectroscopic data are in accordance with the previously reported data.[S3b,c]

***N*-[Methyl(oxo)(*p*-tolyl)-λ$^6$-sulfaneylidene]-2-oxo-2-phenylacetamide (1ea)**



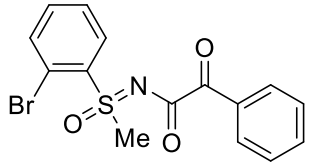
White solid (53 mg, 89% yield); isolation: *n*-pentane/ethyl acetate (2/1) as the eluent; m.p. 110–112 °C. $^1$H NMR (400 MHz, $CDCl_3$) δ 8.08 – 8.01 (m, 2H), 7.97 – 7.91 (m, 2H), 7.62 – 7.56 (m, 1H), 7.49 – 7.40 (m, 4H), 3.46 (s, 3H), 2.47 (s, 3H). $^{13}$C {$^1$H} NMR (101 MHz, $CDCl_3$) δ 190.2, 173.2, 145.7, 134.6, 134.1, 132.8, 130.5, 130.2, 128.6, 127.2, 45.0, 21.6. The spectroscopic data are in accordance with the previously reported data.[S3b,c]

***N*-[(4-Cyanophenyl)(methyl)(oxo)-λ$^6$-sulfaneylidene]-2-oxo-2-phenylacetamide (1fa)**



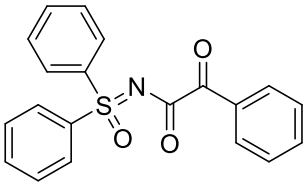
White solid (53 mg, 85% yield); isolation: *n*-pentane/ethyl acetate (2/1) as the eluent; m.p. 105–107 °C. $^1$H NMR (400 MHz, $CDCl_3$) δ 8.20 (d, $J$ = 8.0 Hz, 2H), 7.98 (dd, $J$ = 31.2, 7.8 Hz, 4H), 7.62 (t, $J$ = 7.5 Hz, 1H), 7.48 (t, $J$ = 7.7 Hz, 2H), 3.49 (s, 3H). $^{13}$C {$^1$H} NMR (101 MHz, $CDCl_3$) δ 189.6, 173.0, 142.1, 134.5, 133.6, 132.4, 130.1, 128.7, 128.0, 118.2, 116.7, 44.5. MS (EI): *m/z* = 209 (5), 208 (11), 207 (100), 150 (5), 105 (8), 77 (6), 51 (3). IR (ATR): ν = 3094, 3024, 2925, 2854, 2236, 1679, 1633, 1593, 1448, 1397, 1326, 1212, 1171, 1084, 1020, 973, 845, 818, 794, 739, 707, 668. HRMS *m/z*: $[M + H]^+$ calcd for $C_{16}H_{13}N_2O_3S$ 313.0641; Found 313.0644.

***N*-[(2-Bromophenyl)(methyl)(oxo)-λ$^6$-sulfaneylidene]-2-oxo-2-phenylacetamide (1ga)**



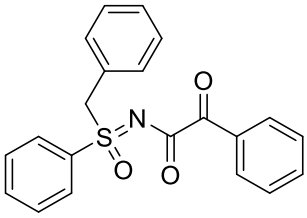
Light yellow solid (57 mg, 78% yield); isolation: *n*-pentane/ethyl acetate (3/1) as the eluent; m.p. 100–102 °C. $^1$H NMR (400 MHz, $CDCl_3$) δ 8.34 (dd, J = 8.0, 1.7 Hz, 1H), 8.05 – 8.00 (m, 2H), 7.80 (dd, J = 7.8, 1.3 Hz, 1H), 7.65 – 7.50 (m, 3H), 7.45 (t, J = 7.7 Hz, 2H), 3.63 (s, 3H). $^{13}$C {$^1$H} NMR (101 MHz, $CDCl_3$) δ 189.5, 172.1, 136.9, 135.9, 135.3, 134.1, 132.7, 131.8, 130.1, 128.6, 128.5, 119.4, 42.3, 29.6. MS (EI): *m/z* = 263 (6), 262 (10), 261 (100), 260 (98), 218 (4), 205 (9), 203 (8), 155 (4), 105 (20), 77 (25), 51 (10). IR (ATR): ν = 3007, 2924, 2323, 2095, 1673, 1640, 1593, 1448, 1426, 1324, 1301, 1206, 1172, 1019, 971, 897, 818, 789, 753, 715, 675. HRMS *m/z*: $[M + H]^+$ calcd for $C_{15}H_{13}NO_3SBr$ 365.9794; Found 365.9794.

**2-Oxo-*N*-(oxodiphenyl-λ$^6$-sulfaneylidene)-2-phenylacetamide (1ha)**



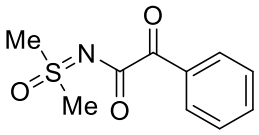
White solid (64 mg, 92% yield); isolation: *n*-pentane/ethyl acetate (4/1) as the eluent; m.p. 79–80 °C. $^1$H NMR (400 MHz, $CDCl_3$) δ 8.04 – 7.94 (m, 6H), 7.57 – 7.45 (m, 6H), 7.44 – 7.35 (m, 3H). $^{13}$C {$^1$H} NMR (101 MHz, $CDCl_3$) δ 190.1, 173.1, 143.2, 138.8, 134.1, 133.8, 132.8, 132.6, 130.2, 129.7, 129.1, 128.6, 127.9, 127.6. The spectroscopic data are in accordance with the previously reported data.[S3b,c]

***N*-[Benzyl(oxo)(phenyl)-λ$^6$-sulfaneylidene]-2-oxo-2-phenylacetamide (1ia)**



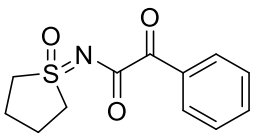
White solid (53 mg, 73% yield); isolation: *n*-pentane/ethyl acetate (3/1) as the eluent; m.p. 88–90 °C. $^1$H NMR (400 MHz, $CDCl_3$) δ 8.00 (d, $J$ = 7.6 Hz, 2H), 7.65 (d, $J$ = 7.9 Hz, 2H), 7.56 (dt, $J$ = 16.1, 7.4 Hz, 2H), 7.41 (td, $J$ = 7.6, 4.0 Hz, 4H), 7.28 (t, $J$ = 7.4 Hz, 1H), 7.18 (t, $J$ = 7.5 Hz, 2H), 6.97 (d, $J$ = 7.5 Hz, 2H), 4.92 – 4.75 (m, 2H). $^{13}$C {$^1$H} NMR (101 MHz, $CDCl_3$) δ 190.3, 173.6, 134.3, 134.3, 134.1, 132.8, 131.3, 130.1, 129.5, 129.3, 128.7, 128.6, 128.4, 126.2, 62.8. MS (EI): *m/z* = 260 (5), 259 (12), 258 (75), 125 (54), 105 (29), 92 (8), 91 (100), 77 (22), 65 (9), 51 (11). IR (ATR): ν = 3065, 2981, 2923, 2329, 1680, 1618, 1495, 1449, 1334, 1301, 1212, 1168, 1132, 1089, 1004, 922, 886, 837, 757, 687. HRMS *m/z*: $[M + H]^+$ calcd for $C_{21}H_{18}NO_3S$ 386.0821; Found 386.0825.

***N*-[Dimethyl(oxo)-λ$^6$-sulfaneylidene]-2-oxo-2-phenylacetamide (1ja)**



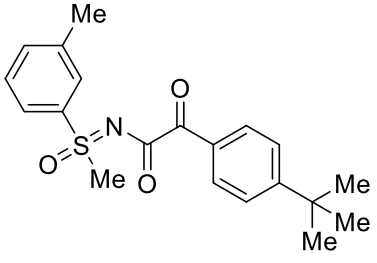
White solid (33 mg, 73% yield); isolation: *n*-pentane/ethyl acetate (2/1) as the eluent; m.p. 77–78 °C. $^1$H NMR (400 MHz, $CDCl_3$) δ 8.06 – 8.01 (m, 2H), 7.64 – 7.58 (m, 1H), 7.51 – 7.45 (m, 2H), 3.44 (s, 6H). $^{13}$C {$^1$H} NMR (101 MHz, $CDCl_3$) δ 190.1, 173.2, 134.3, 132.7, 130.1, 128.7, 42.2. The spectroscopic data are in accordance with the previously reported data.[S3b,c]

***N*-(1-Oxidotetrahydro-1λ$^6$-thiophen-1-ylidene)-2-oxo-2-phenylacetamide (1ka)**



White solid (43 mg, 86% yield); isolation: *n*-pentane/ethyl acetate (2/1) as the eluent; m.p. 145–146 °C. $^1$H NMR (600 MHz, $CDCl_3$) δ 8.08 – 8.04 (m, 2H), 7.61 (tt, $J$ = 7.3, 1.3 Hz, 1H), 7.51 – 7.46 (m, 2H), 3.78 – 3.69 (m, 2H), 3.45 – 3.39 (m, 2H), 2.46 – 2.29 (m, 4H). $^{13}$C {$^1$H} NMR (151 MHz, $CDCl_3$) δ 190.3, 173.7, 134.3, 132.8, 130.2, 128.7, 53.2, 23.7. The spectroscopic data are in accordance with the previously reported data.[S3b,c]

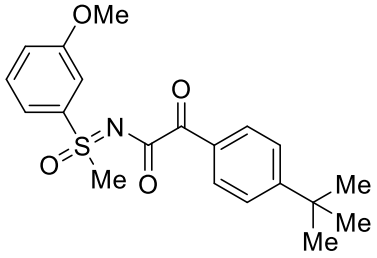
**2-[4-(*Tert*-butyl)phenyl]-*N*-[(3-methyl(oxo)(*p*-tolyl)-λ$^6$-sulfaneylidene]-2-oxoacetamide (1lf)**



Light yellow solid (60 mg, 85% yield); isolation: *n*-pentane/ethyl acetate (2/1) as the eluent; m.p. 105–107 °C. $^1$H NMR (600 MHz, $CDCl_3$) δ 8.00 – 7.97 (m, 2H), 7.95 – 7.93 (m, 2H), 7.49 – 7.46 (m, 3H), 7.43 – 7.41 (m, 2H), 3.45 (s, 3H), 2.47 (s, 3H), 1.32 (s, 9H). $^{13}$C {$^1$H} NMR (151 MHz, $CDCl_3$) δ 190.0, 173.5, 158.1, 145.6, 134.7, 130.5, 127.2, 125.6, 45.0, 35.3, 31.0, 21.7. MS (EI): *m/z* = 294 (2), 180 (6), 197 (12), 196 (100), 161 (6), 139 (6), 91 (8), 65 (2). IR (ATR): ν = 3020, 2961, 2870, 2164, 1678,

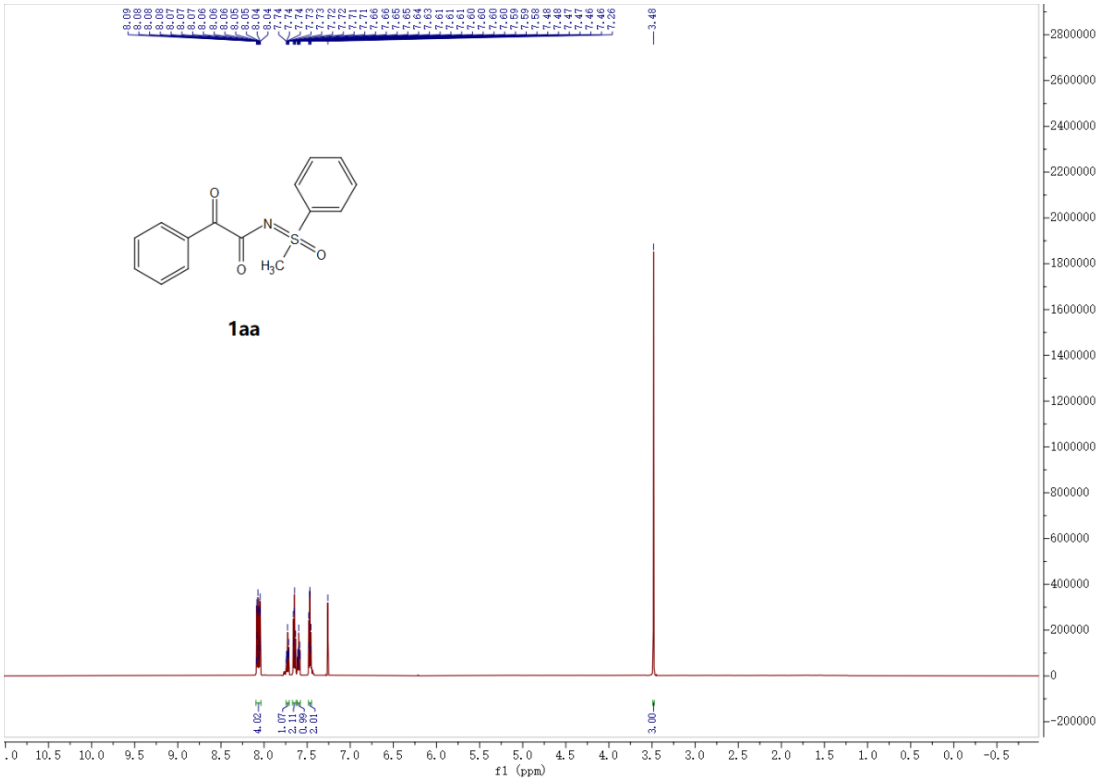
1633, 1603, 1473, 1407, 1329, 1264, 1217, 1180, 1098, 1026, 974, 816, 783, 718, 680. HRMS *m/z*: $[M + Na]^+$ calcd for $C_{20}H_{23}NO_3SNa$ 386.0821; Found 386.0825.

**2-[4-(*Tert*-butyl)phenyl]-*N*-[(3-methoxyphenyl)(methyl)(oxo)-λ$^6$-sulfaneylidene]-2-oxoacetamide (1mf)**

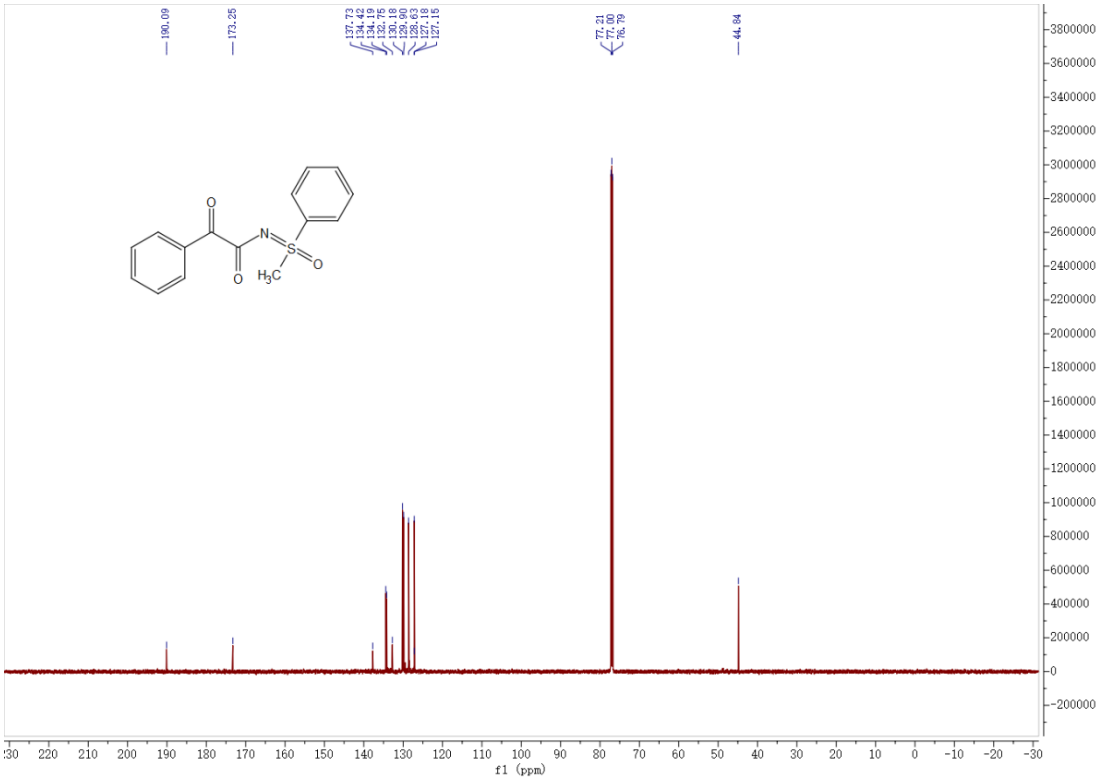



Light yellow solid (66 mg, 89% yield); isolation: *n*-pentane/ethyl acetate (2/1) as the eluent; m.p. 105–107 °C. $^1$H NMR (400 MHz, $CDCl_3$) δ 8.00 – 7.96 (m, 2H), 7.63 (ddd, J = 7.8, 1.8, 1.0 Hz, 1H), 7.57 – 7.46 (m, 4H), 7.22 (ddd, J = 8.3, 2.6, 1.0 Hz, 1H), 3.89 (s, 3H), 3.45 (s, 3H), 1.33 (s, 9H). $^{13}$C {$^1$H} NMR (101 MHz, $CDCl_3$) δ 189.9, 173.5, 160.5, 158.2, 138.9, 131.0, 130.2, 125.7, 121.0, 119.2, 111.6, 55.9, 44.9, 35.3, 31.0. MS (EI): *m/z* = 310 (2), 214 (7), 213 (12), 161 (7), 155 (11), 124 (2), 118 (2), 95 (5), 77 (4). IR (ATR): ν = 3015, 2961, 2870, 2163, 1678, 1633, 1599, 1480, 1428, 1327, 1290, 1218, 1180, 1101, 1026, 974, 849, 816, 782, 715, 678. HRMS *m/z*: $[M + Na]^+$ calcd for $C_{20}H_{23}NO_4SNa$ 380.1291; Found 380.1293.

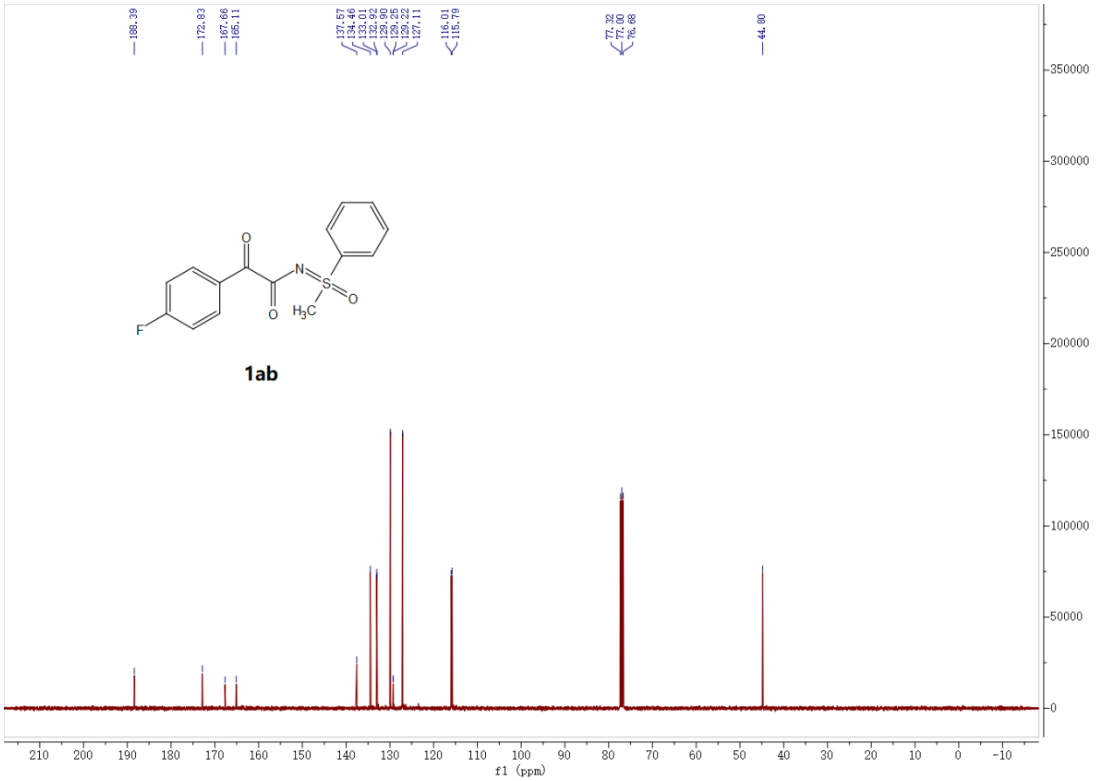
## 5. $^{1}$H and $^{13}$C NMR spectra



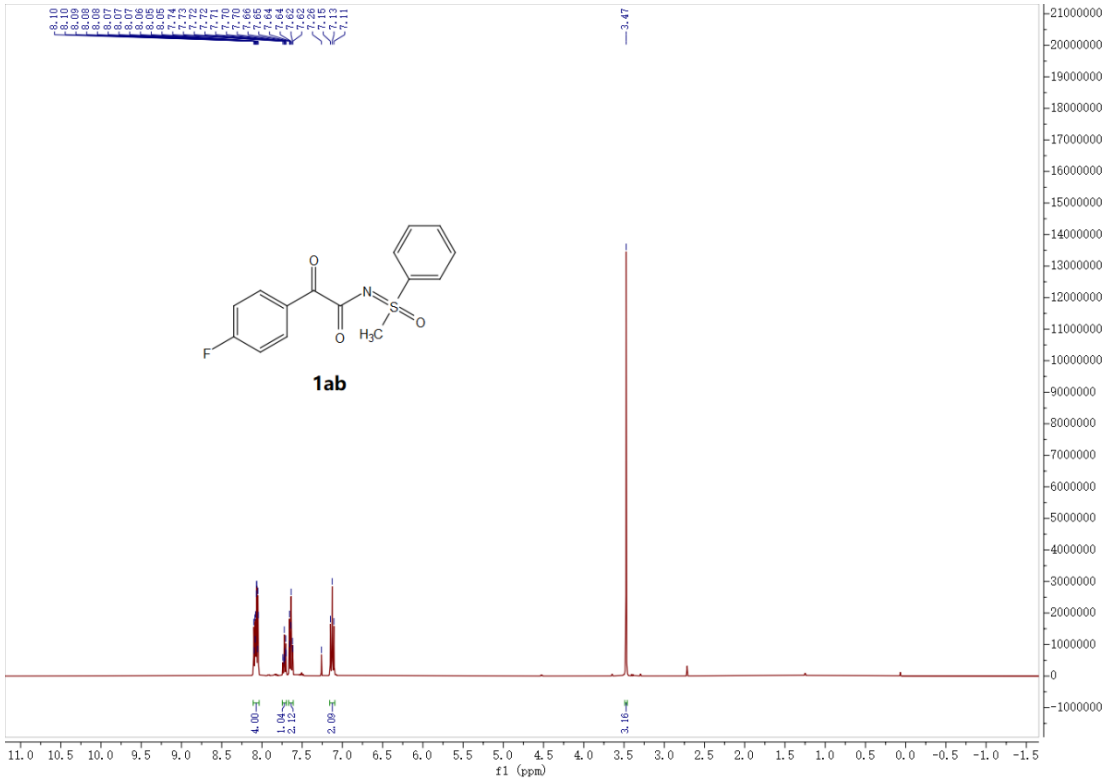

$^{1}$H NMR spectrum of compound **1aa** (600 MHz, $CDCl_3$)



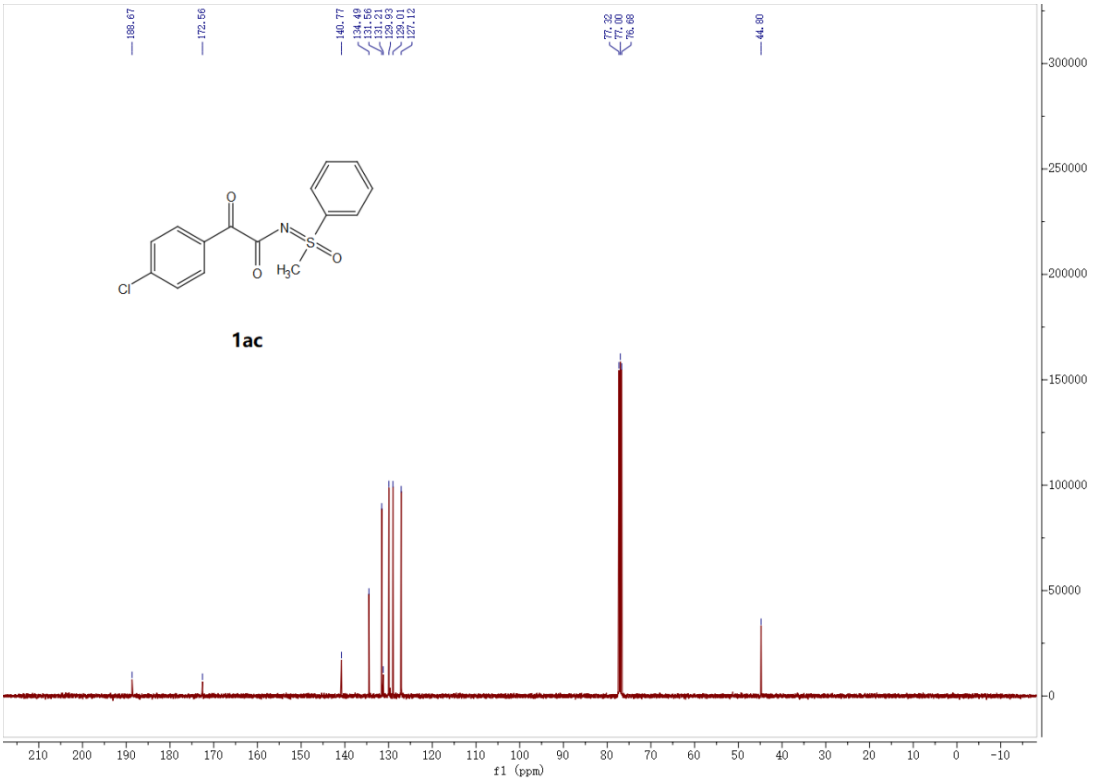

$^{13}C\{^{1}H\}$ NMR spectrum of compound **1aa** (151 MHz, $CDCl_3$)



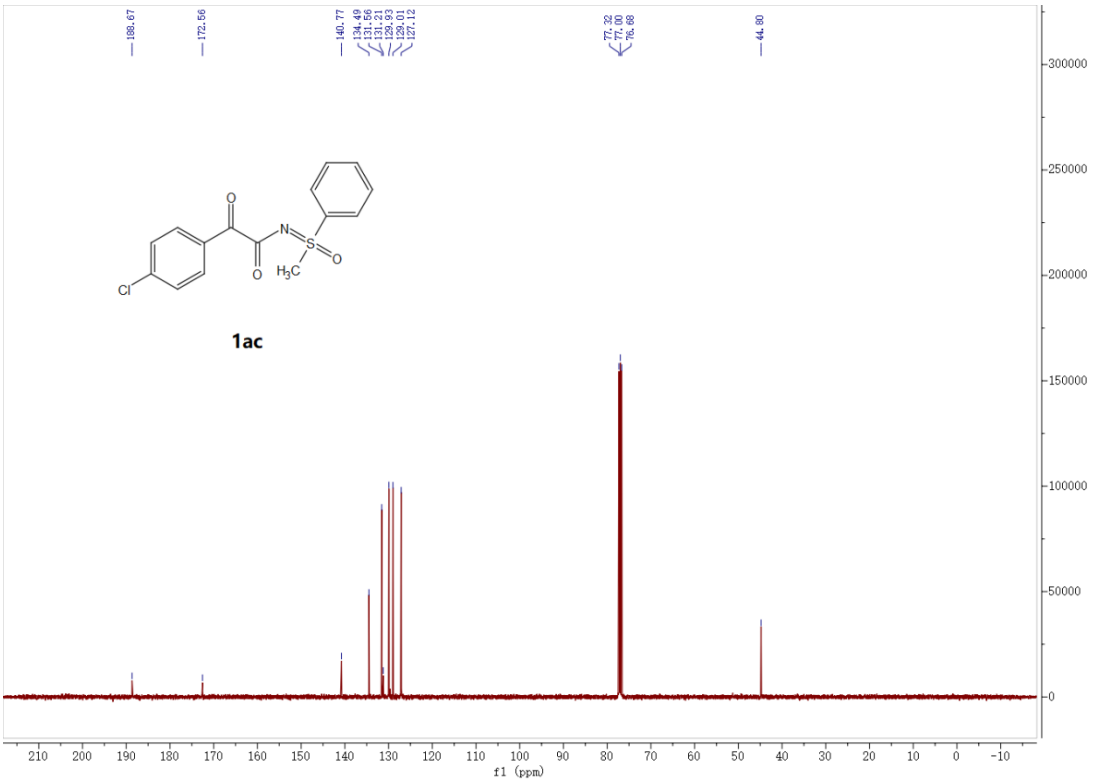

$^{1}$H NMR spectrum of compound **1ab** (400 MHz, $CDCl_3$)



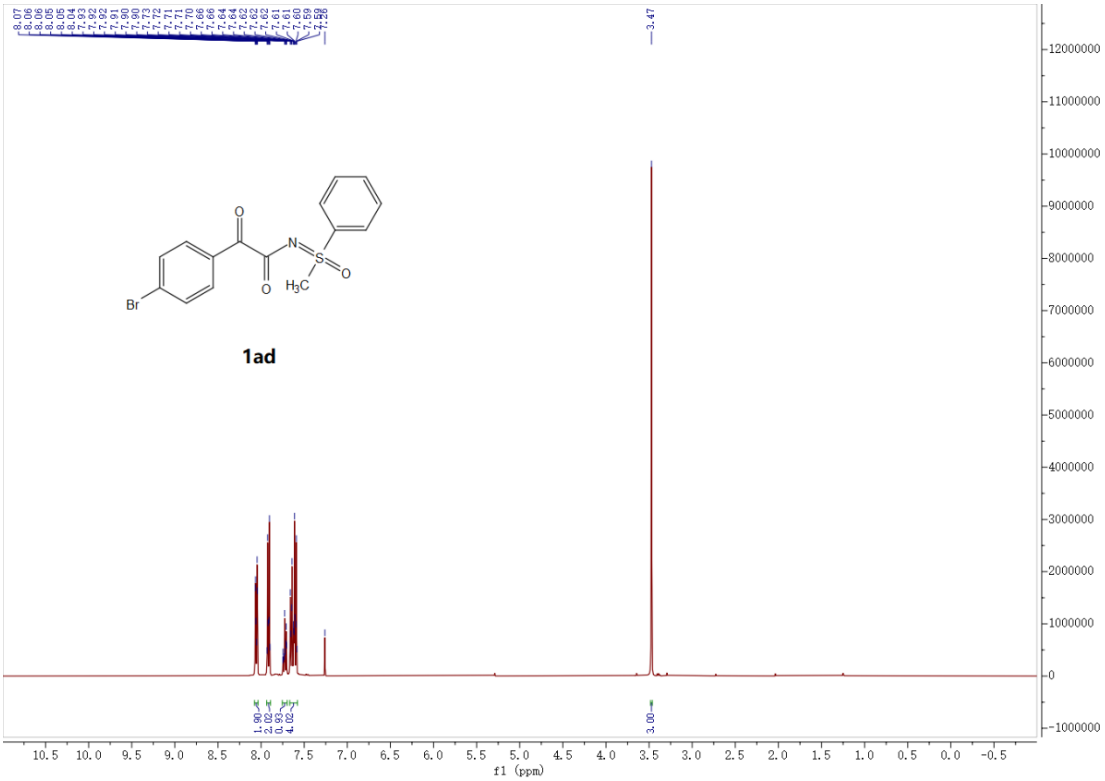

$^{13}C\{^{1}H\}$ NMR spectrum of compound **1ab** (101 MHz, $CDCl_3$)



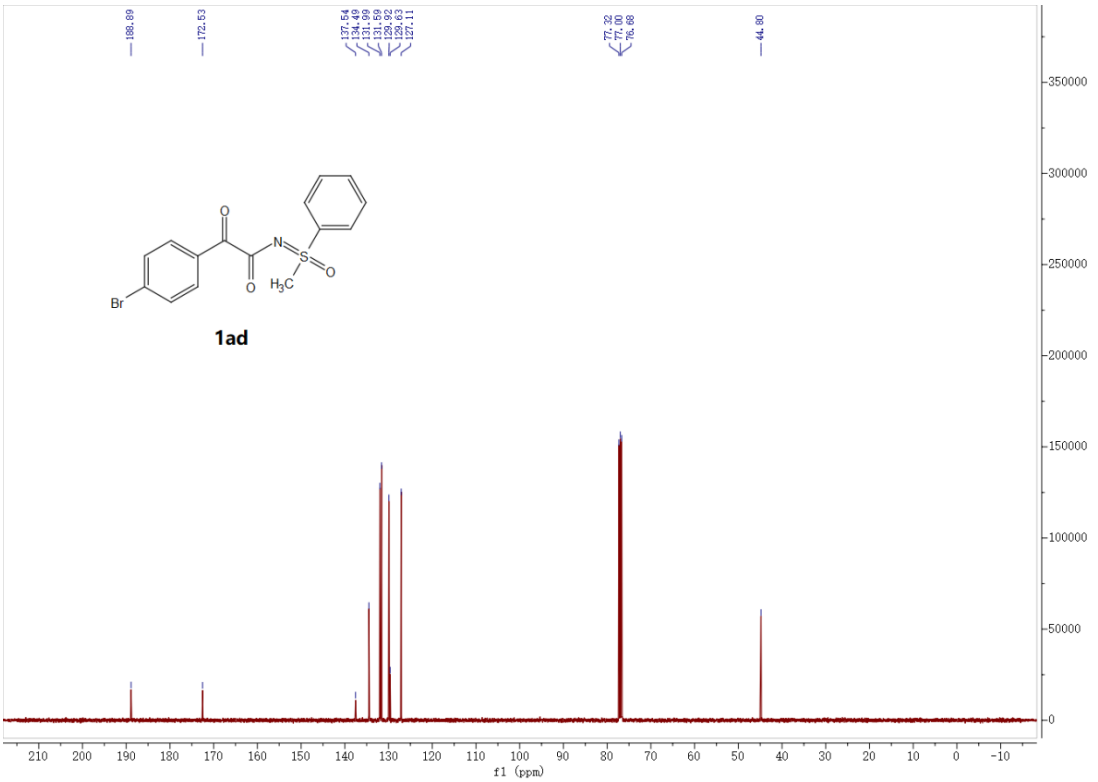

$^{1}$H NMR spectrum of compound **1ac** (400 MHz, $CDCl_3$)



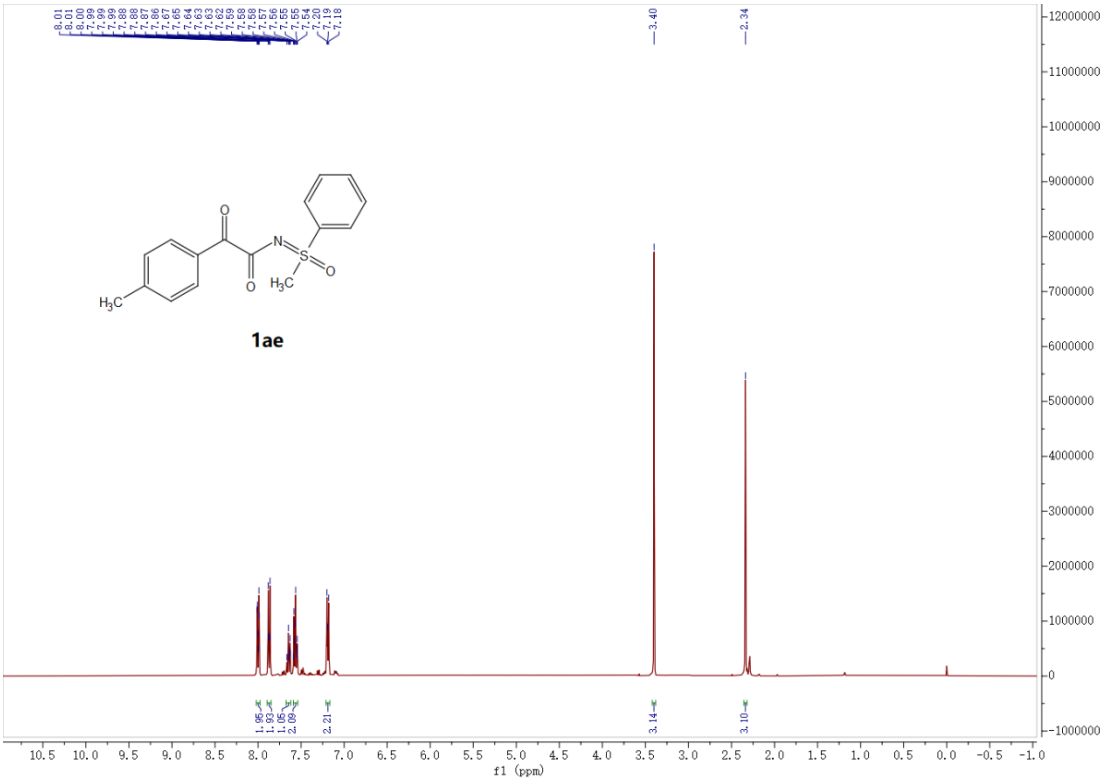

$^{13}$C{$^{1}$H} NMR spectrum of compound **1ac** (101 MHz, $CDCl_3$)



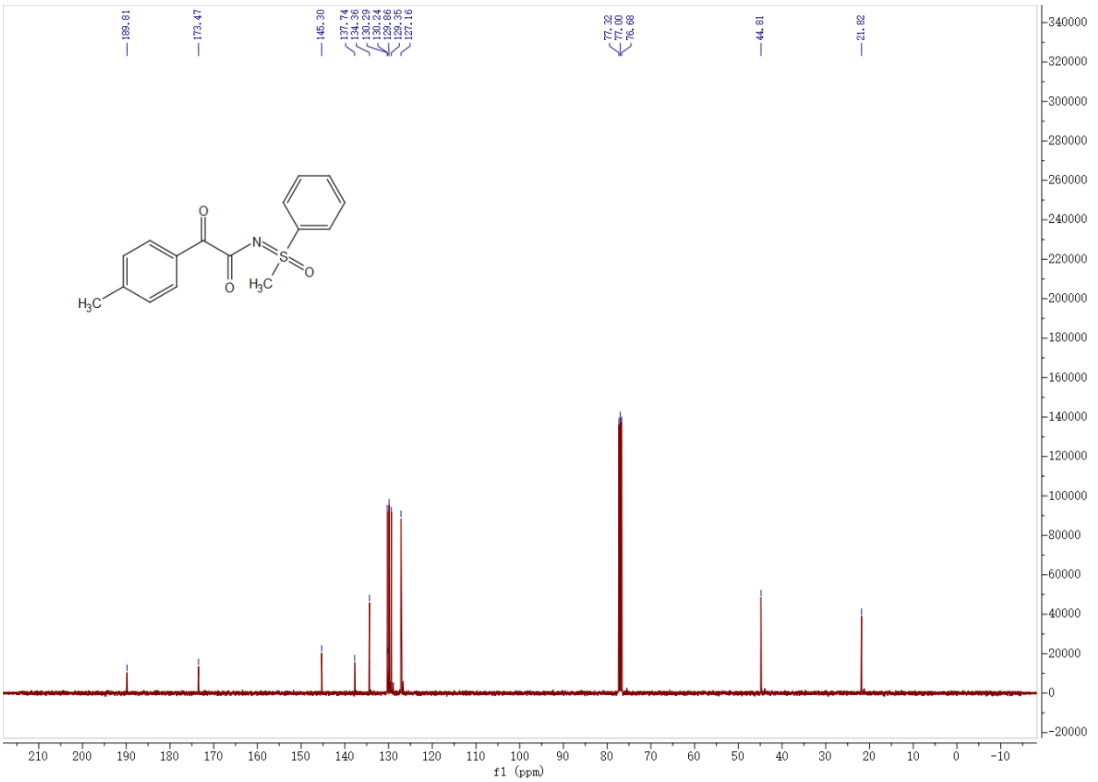

$^{1}$H NMR spectrum of compound **1ad** (400 MHz, $CDCl_3$)



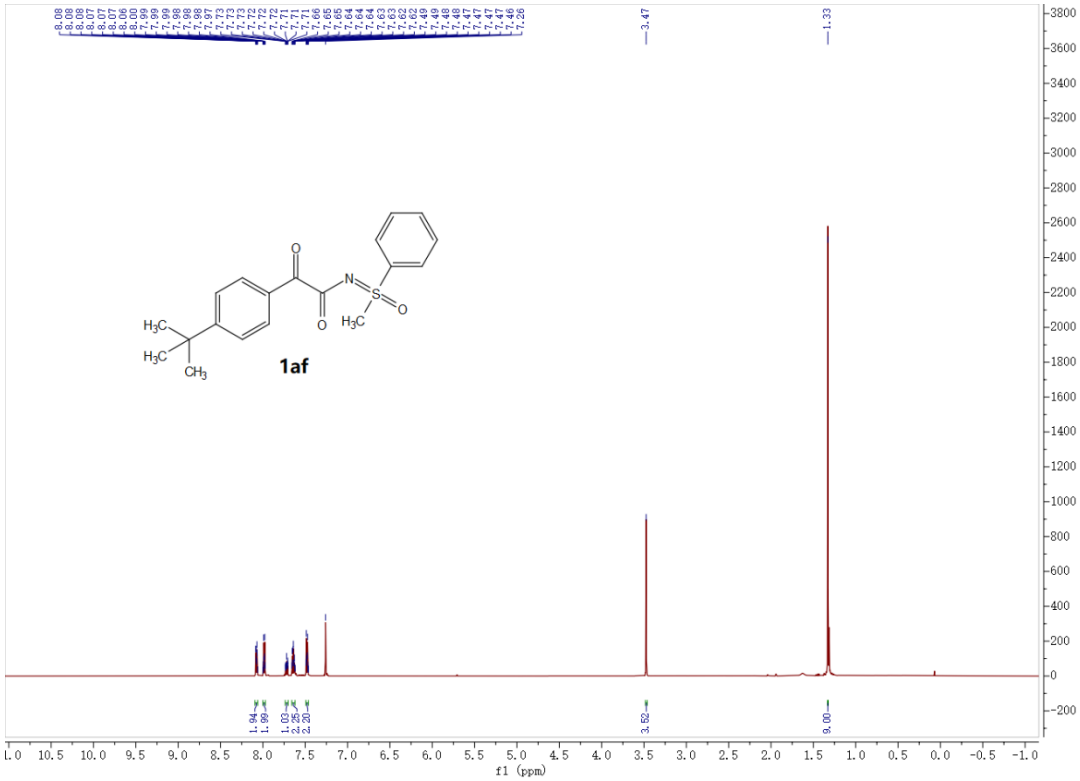

$^{13}C\{^{1}H\}$ NMR spectrum of compound **1ad** (101 MHz, $CDCl_3$)



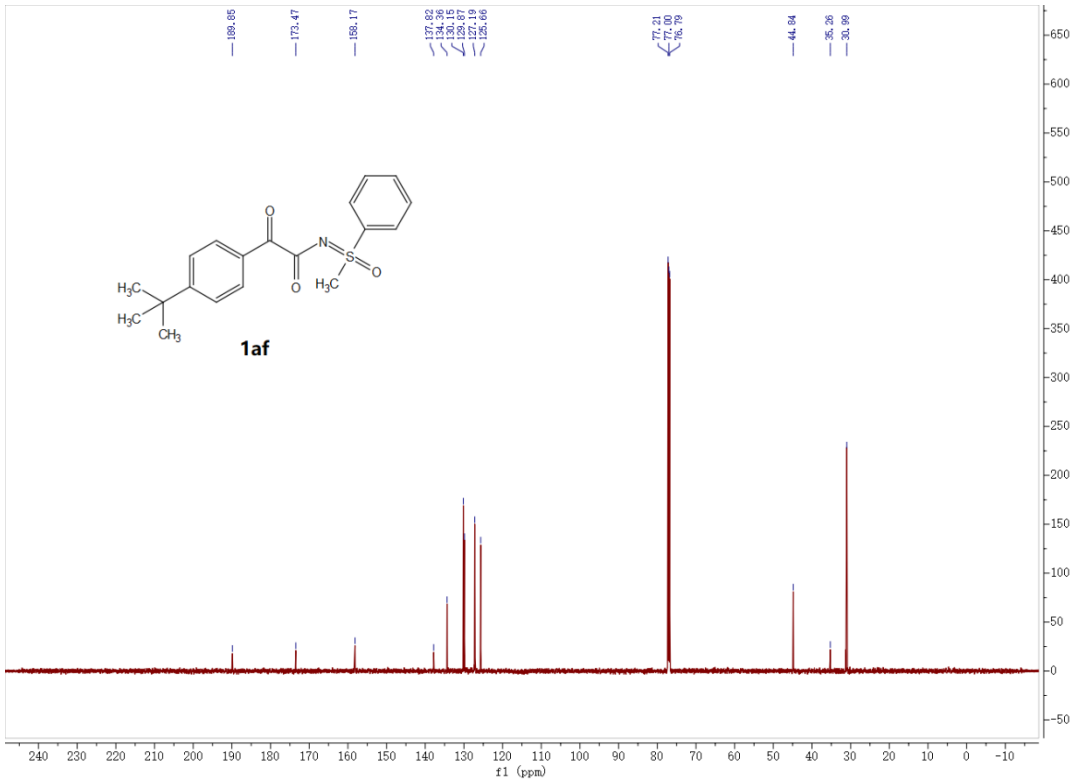

$^{1}$H NMR spectrum of compound **1ae** (400 MHz, $CDCl_3$)



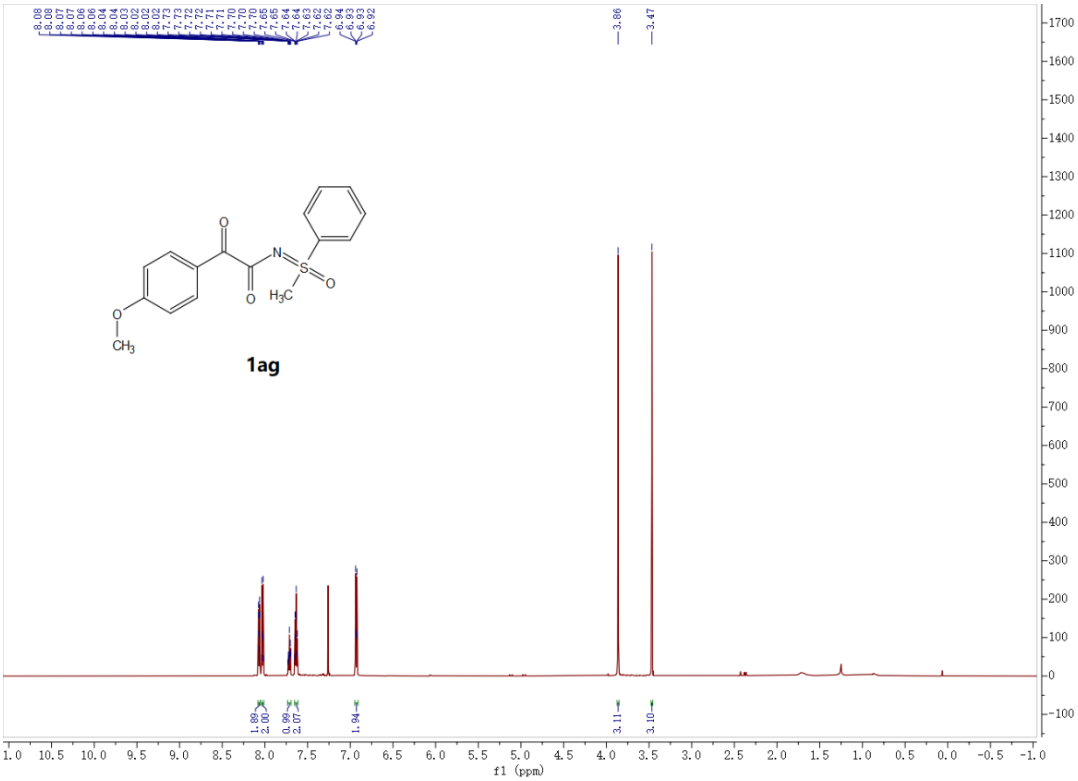

$^{13}C\{^{1}H\}$ NMR spectrum of compound **1ae** (101 MHz, $CDCl_3$)



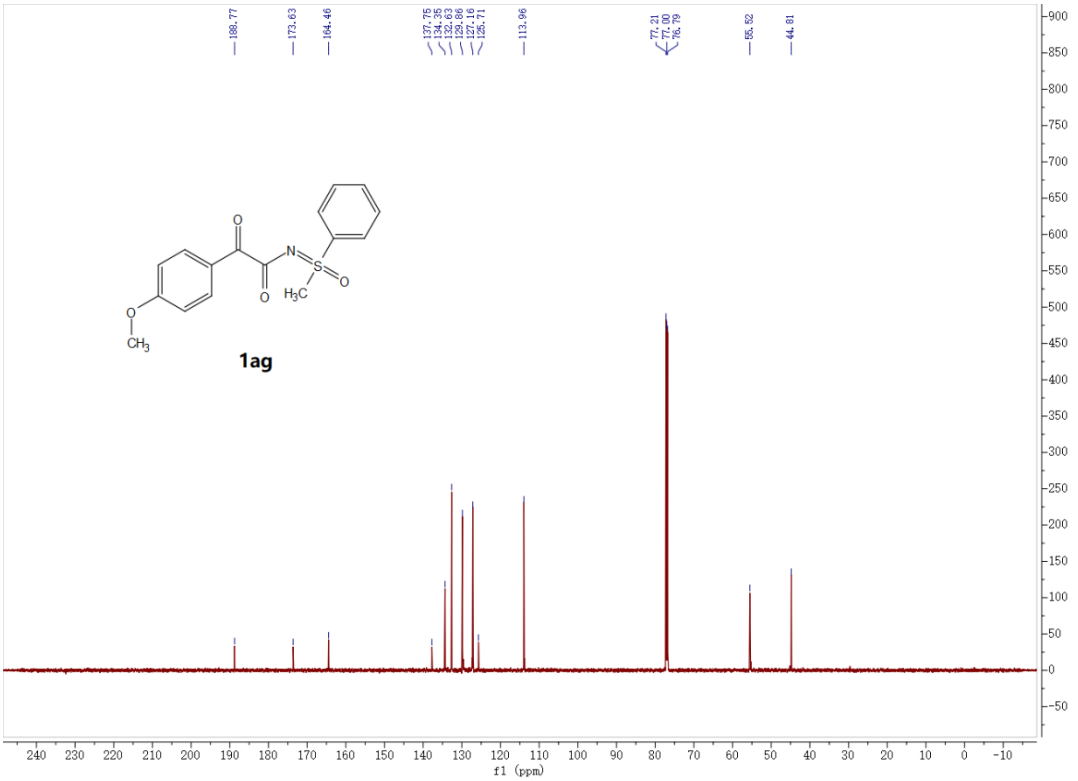

$^{1}$H NMR spectrum of compound **1af** (600 MHz, $CDCl_3$)



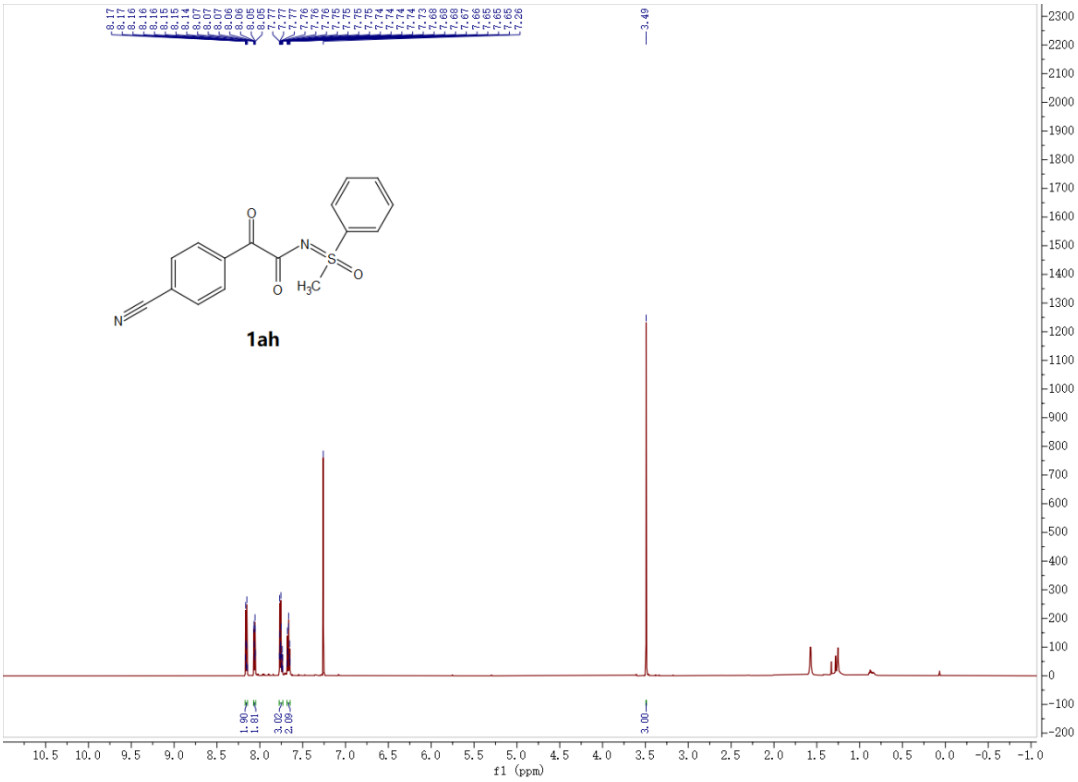

$^{13}$C{$^{1}$H} NMR spectrum of compound **1af** (151 MHz, $CDCl_3$)



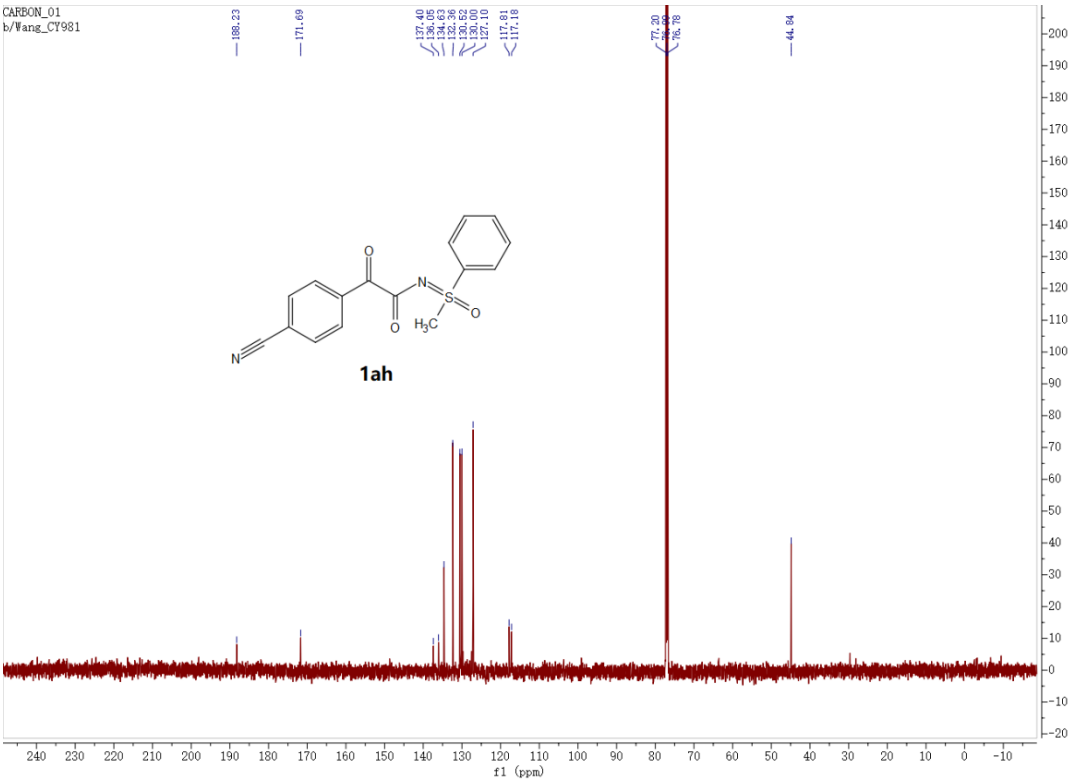

$^{1}$H NMR spectrum of compound **1ag** (600 MHz, $CDCl_3$)



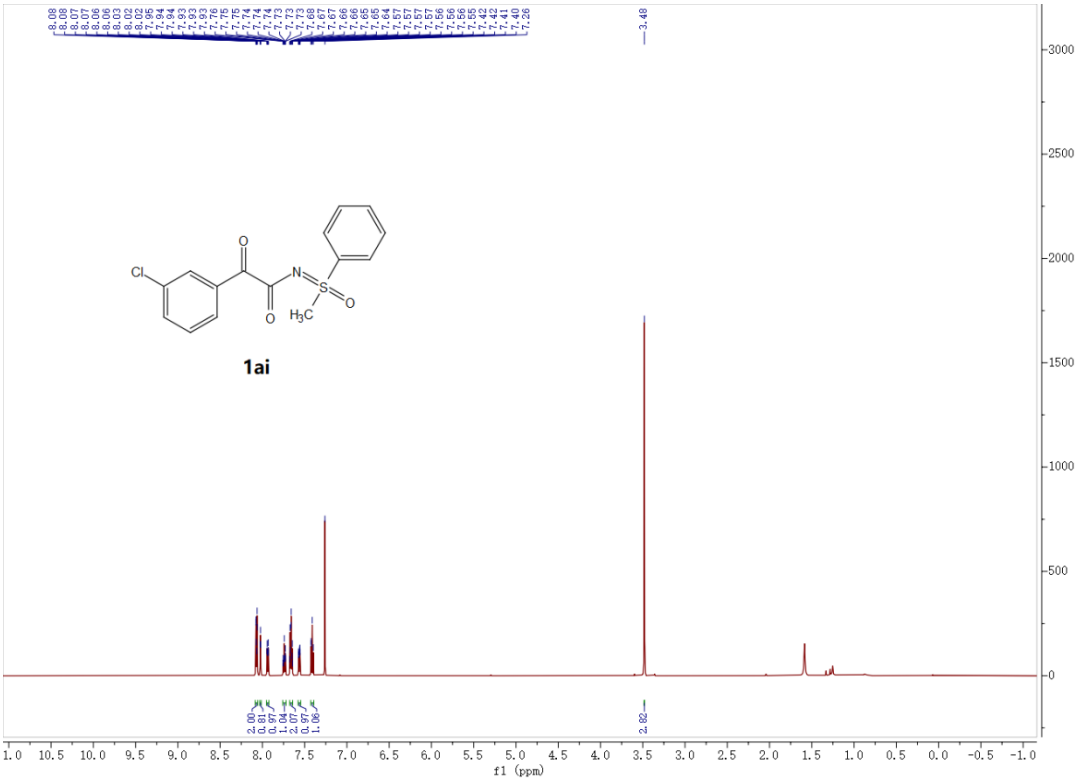

$^{13}$C{$^{1}$H} NMR spectrum of compound **1ag** (151 MHz, $CDCl_3$)



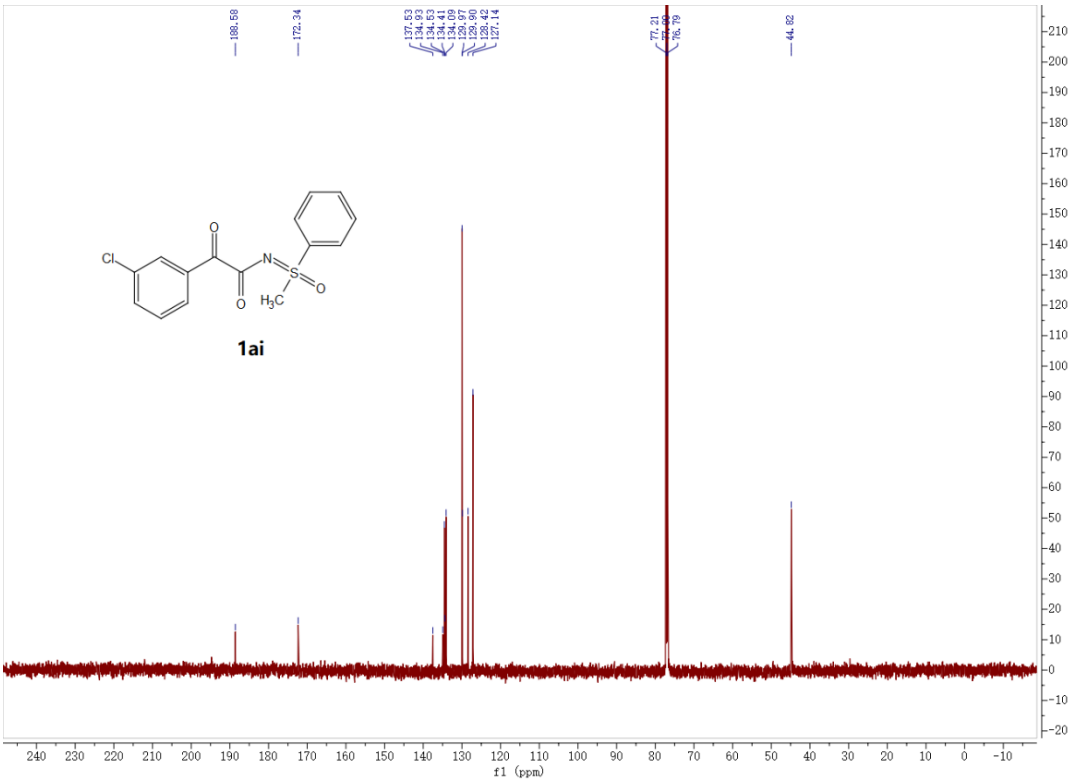

$^{1}$H NMR spectrum of compound **1ah** (600 MHz, $CDCl_3$)



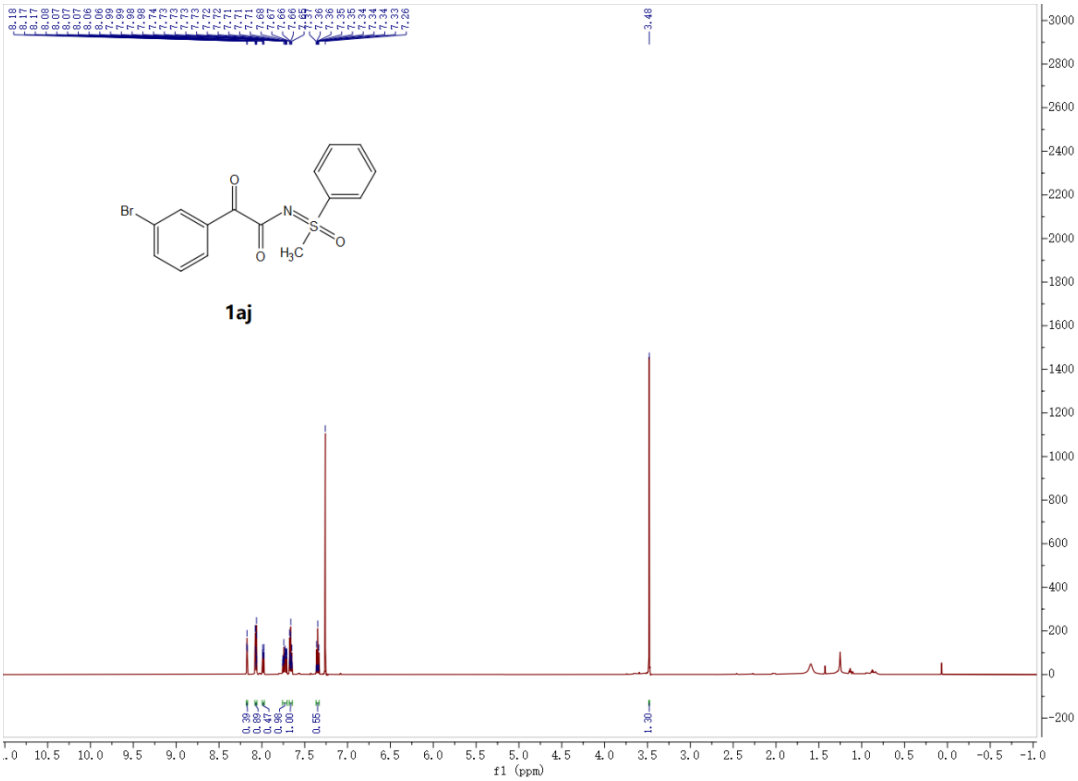

$^{13}$C{$^{1}$H} NMR spectrum of compound **1ah** (151 MHz, $CDCl_3$)



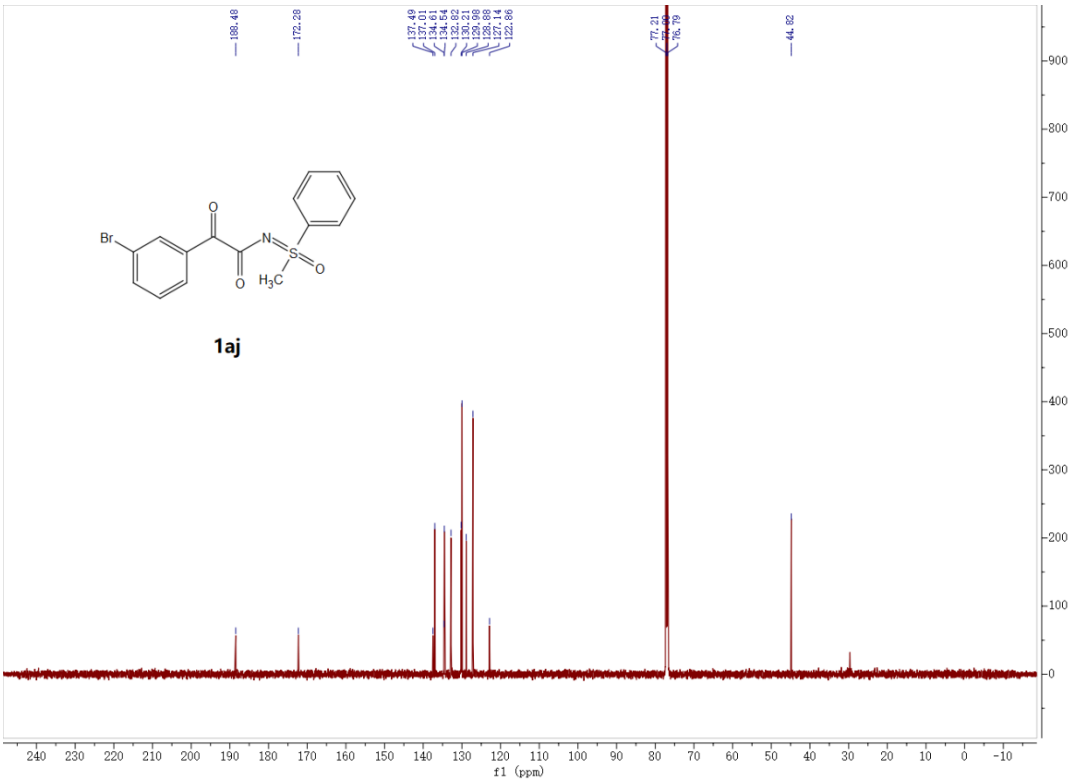

$^{1}$H NMR spectrum of compound **1ai** (600 MHz, $CDCl_3$)



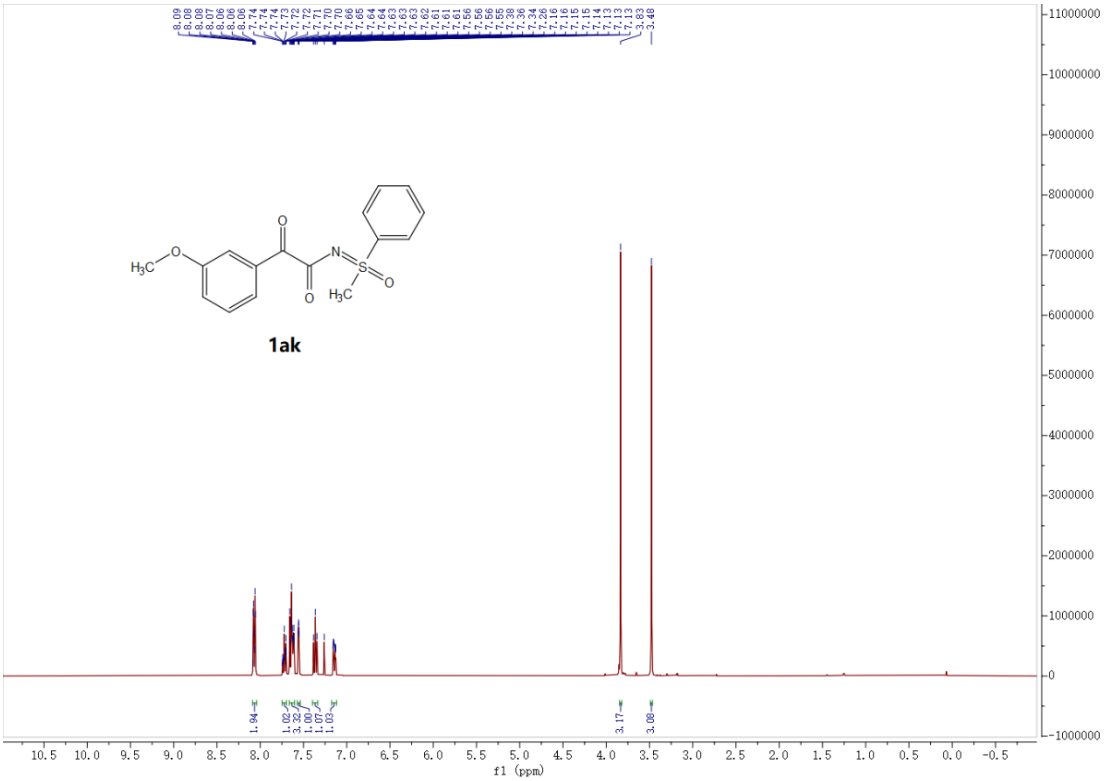

$^{13}$C{$^{1}$H} NMR spectrum of compound **1ai** (151 MHz, $CDCl_3$)



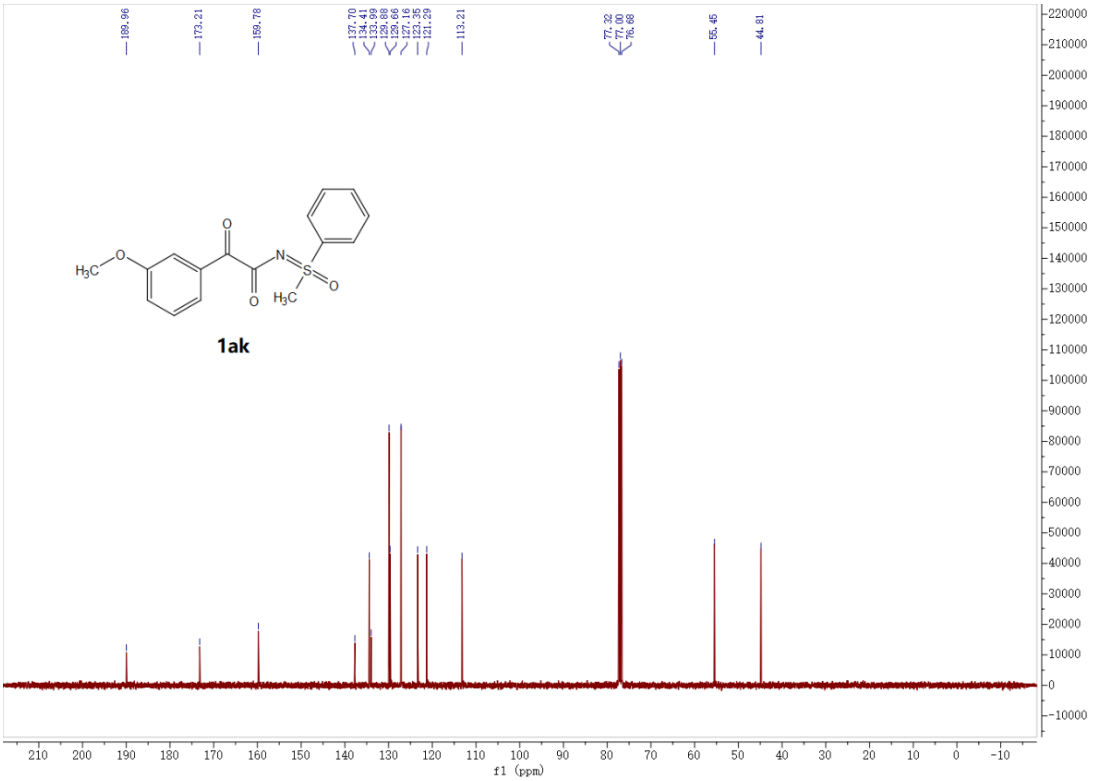

$^{1}$H NMR spectrum of compound **1aj** (600 MHz, $CDCl_3$)



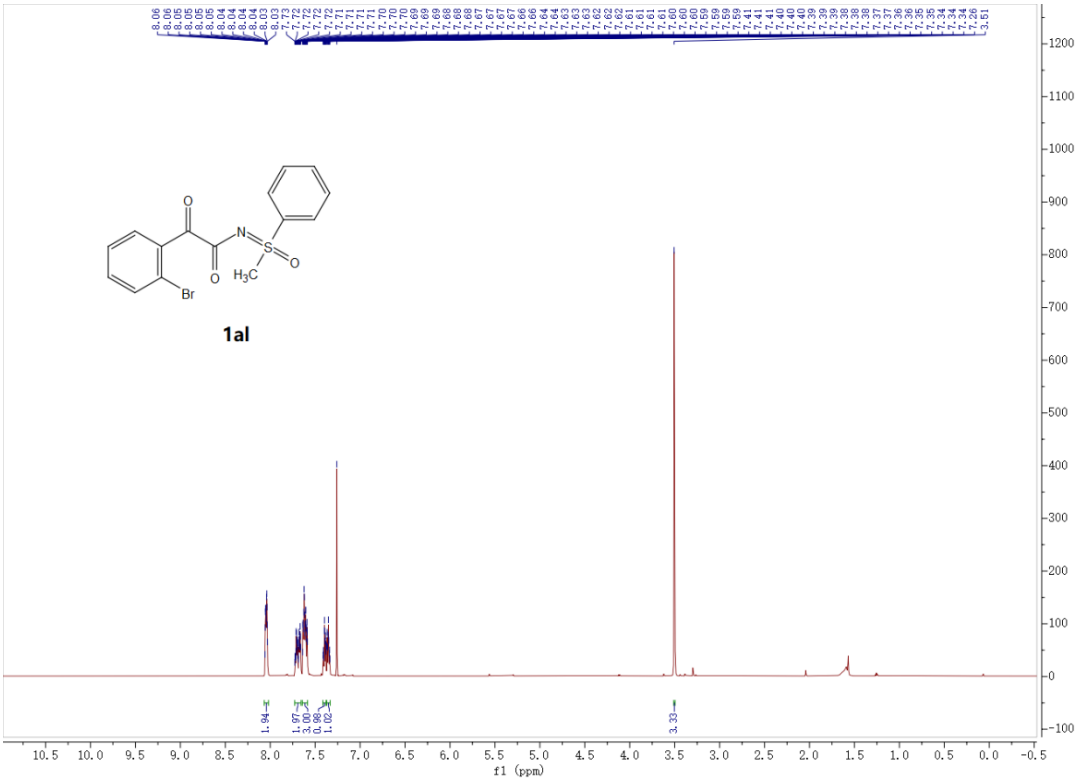

$^{13}C\{^{1}H\}$ NMR spectrum of compound **1aj** (151 MHz, $CDCl_3$)



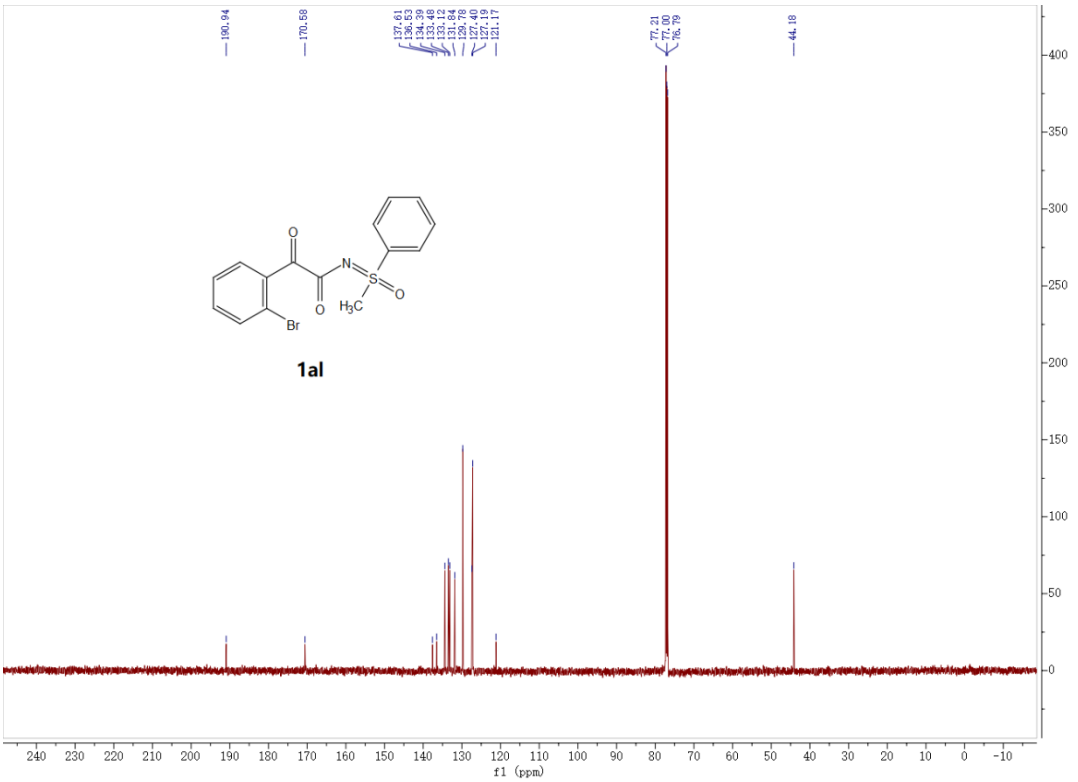

$^{1}$H NMR spectrum of compound **1ak** (600 MHz, $CDCl_3$)



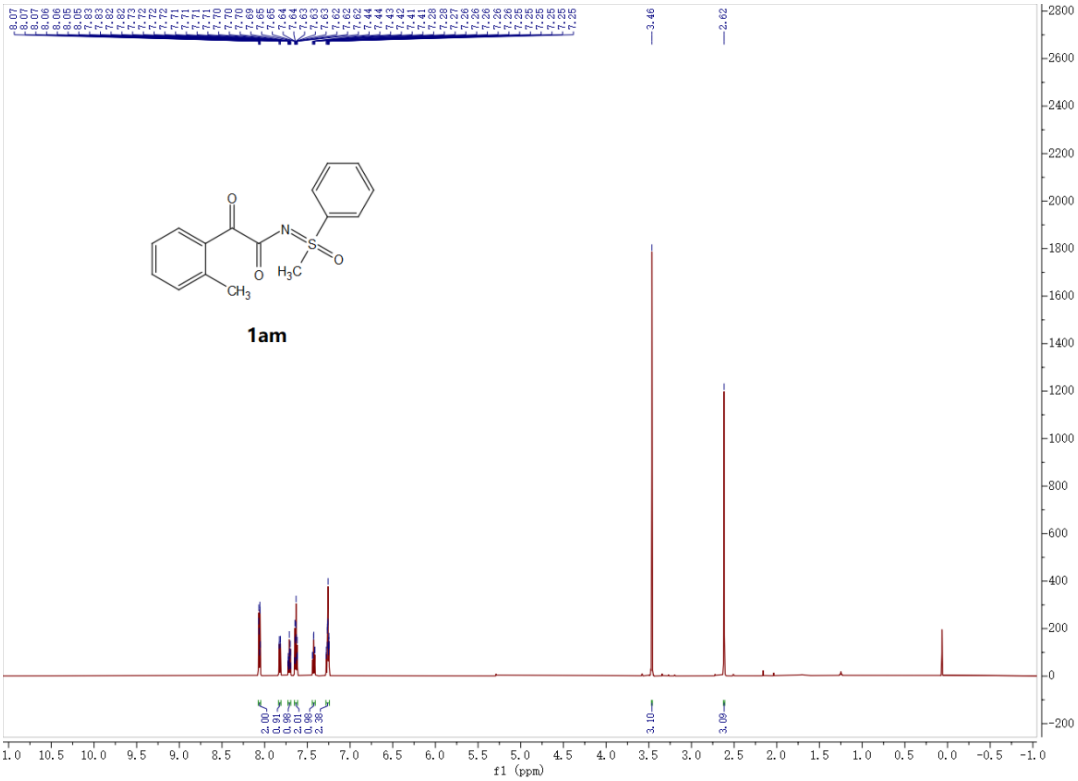

$^{13}C\{^{1}H\}$ NMR spectrum of compound **1ak** (151 MHz, $CDCl_3$)



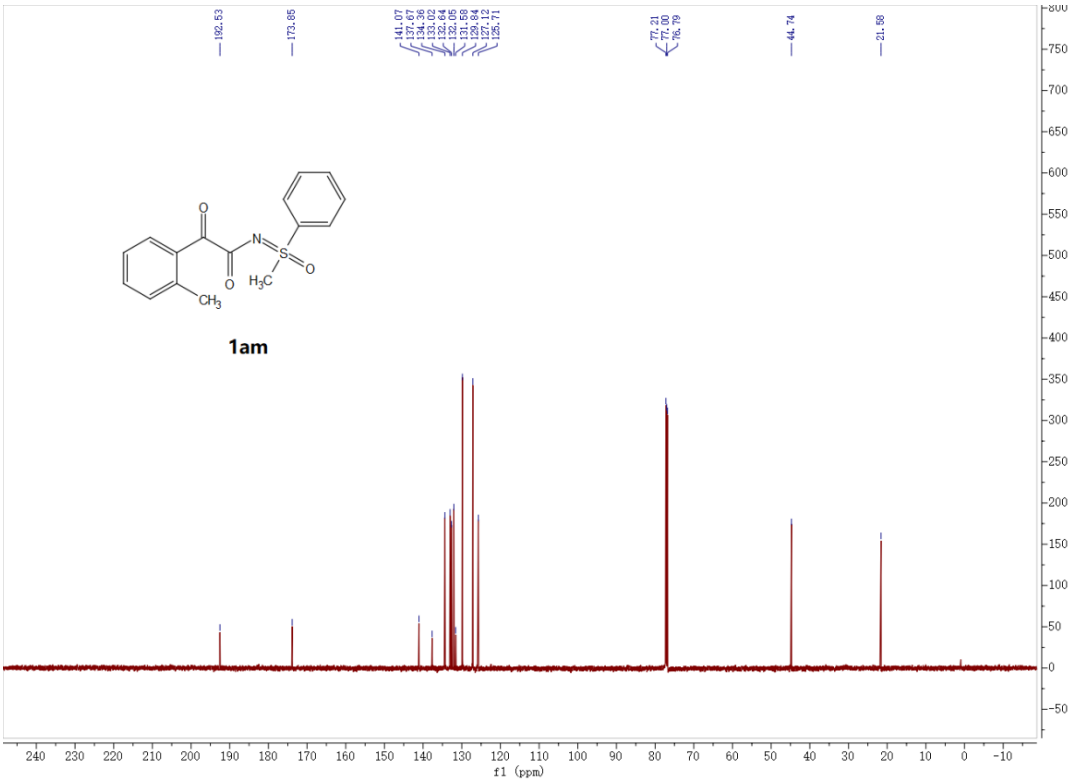

$^{1}$H NMR spectrum of compound **1al** (600 MHz, $CDCl_3$)



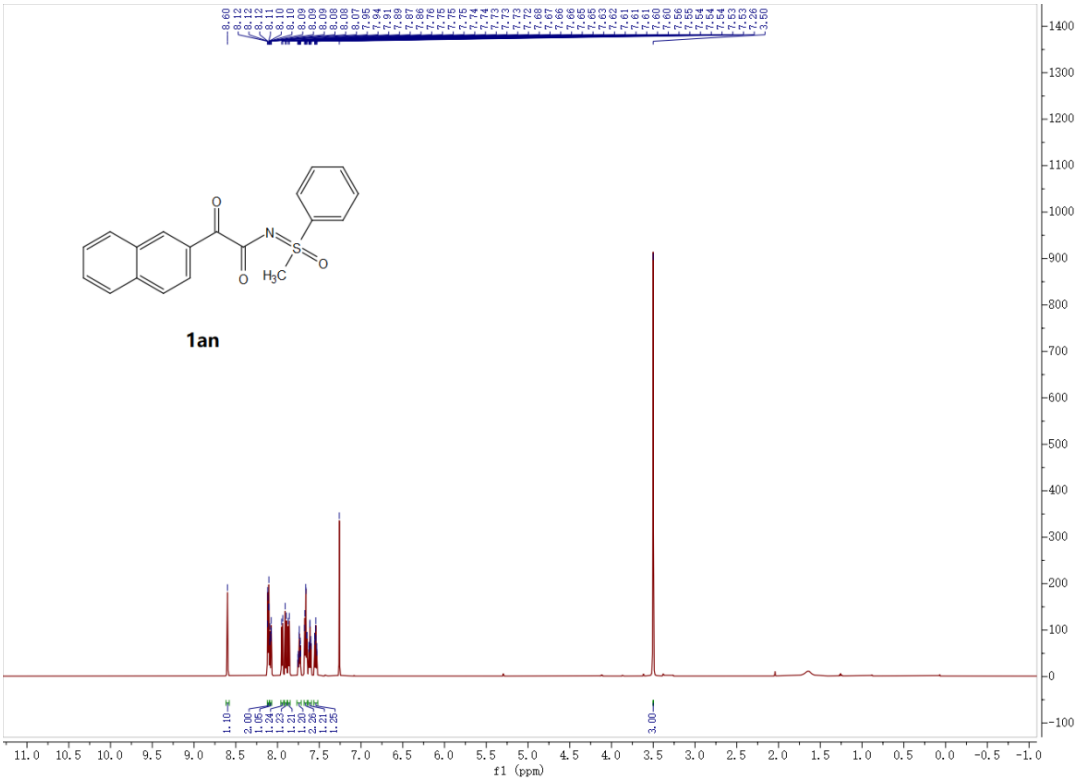

$^{13}C\{^{1}H\}$ NMR spectrum of compound **1al** (151 MHz, $CDCl_3$)



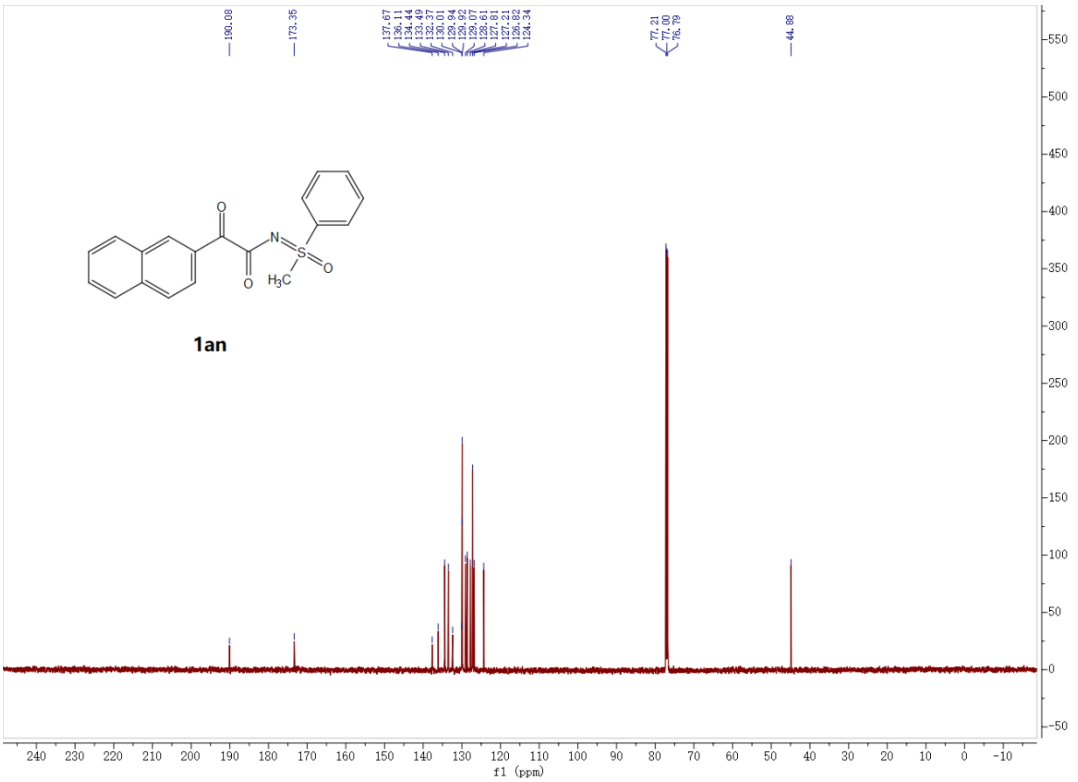

$^{1}$H NMR spectrum of compound **1am** (600 MHz, $CDCl_3$)



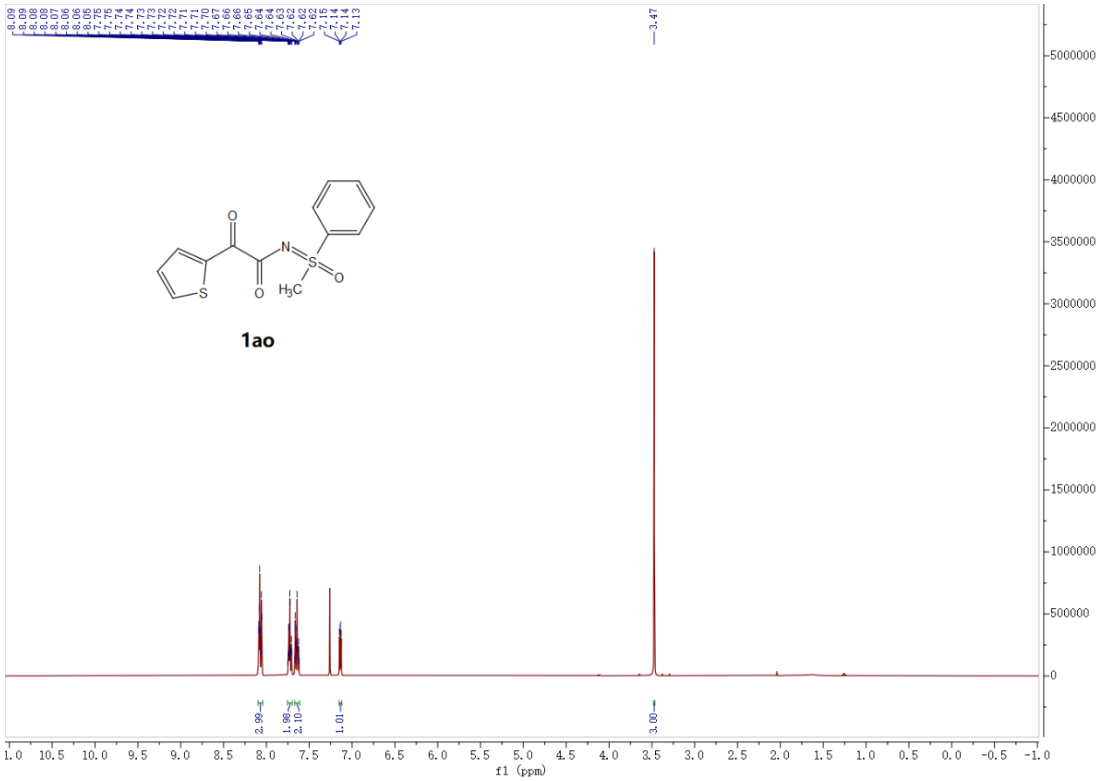

$^{13}C\{^{1}H\}$ NMR spectrum of compound **1am** (151 MHz, $CDCl_3$)



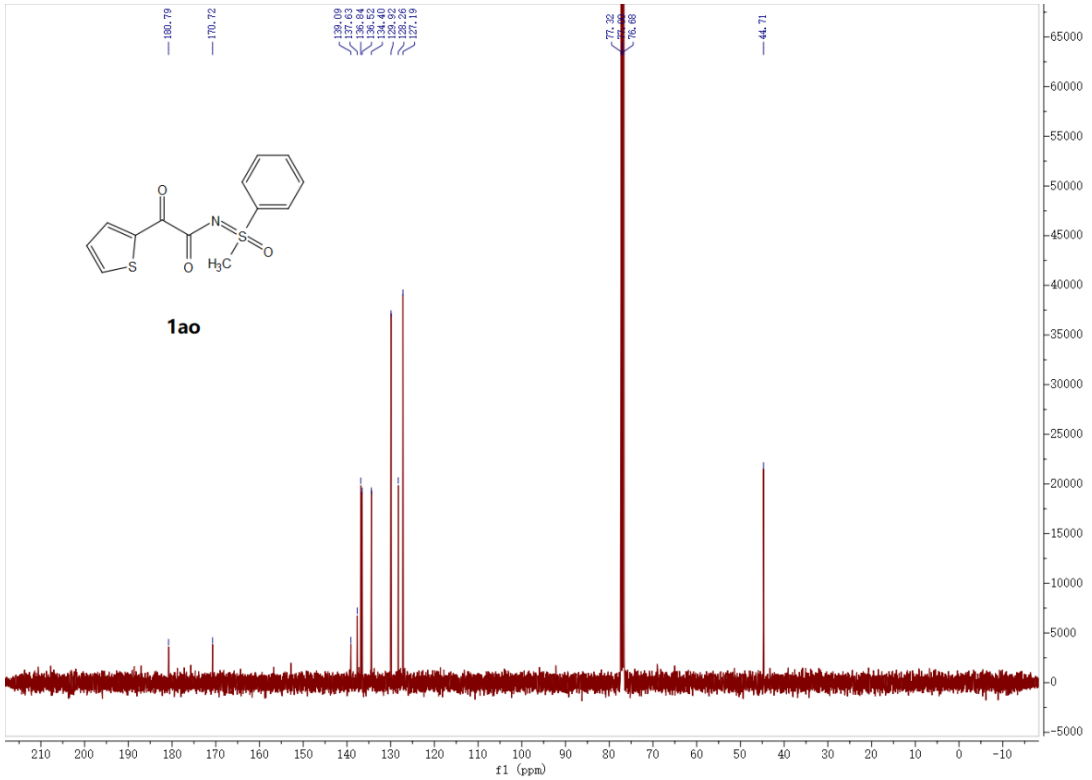

$^{1}$H NMR spectrum of compound **1an** (600 MHz, $CDCl_3$)



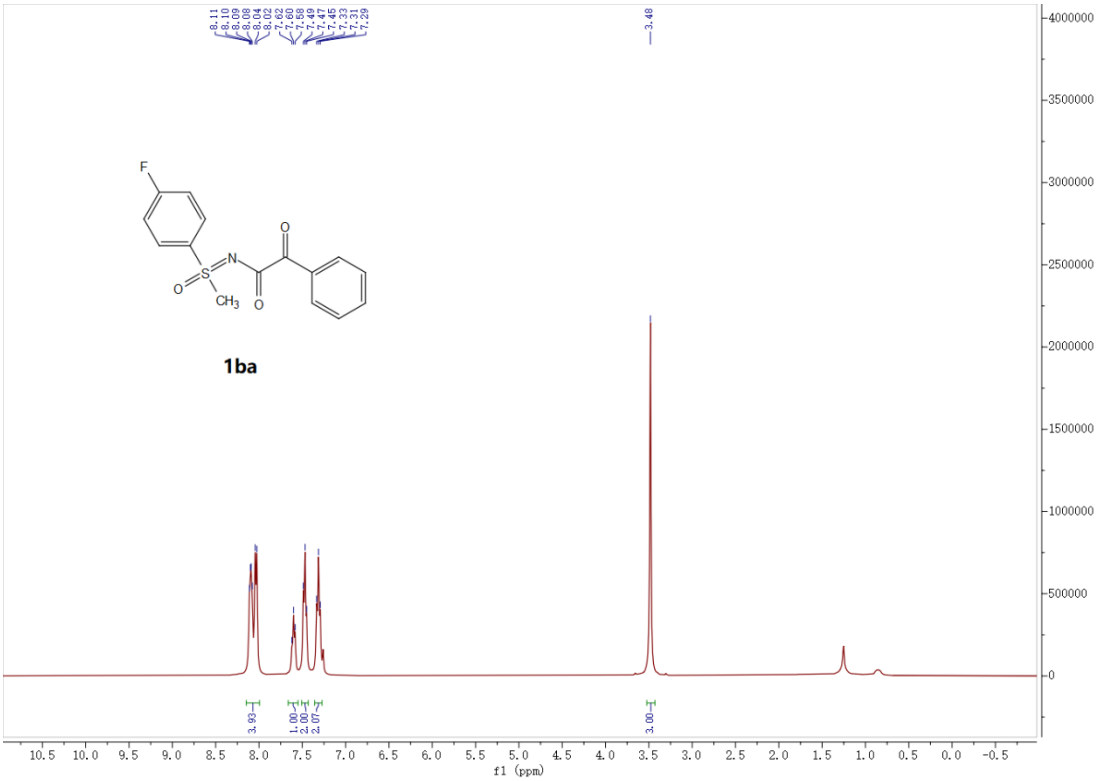

$^{13}C\{^{1}H\}$ NMR spectrum of compound **1an** (151 MHz, $CDCl_3$)



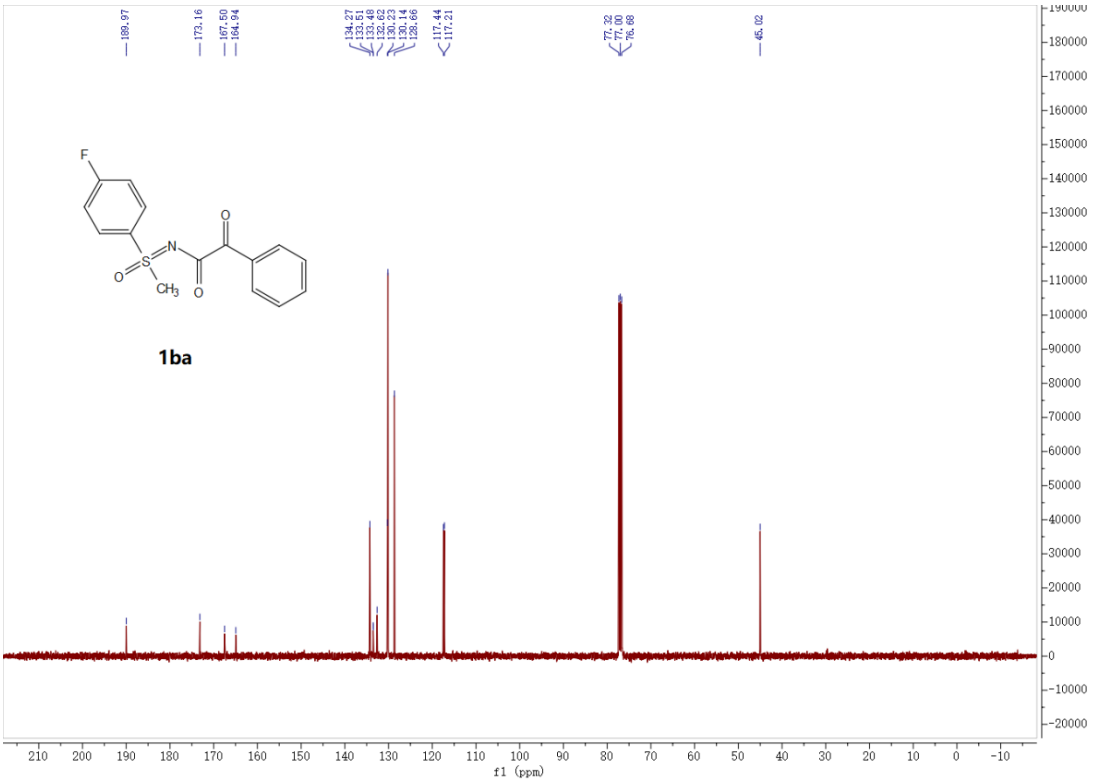

$^{1}$H NMR spectrum of compound **1ao** (400 MHz, $CDCl_3$)



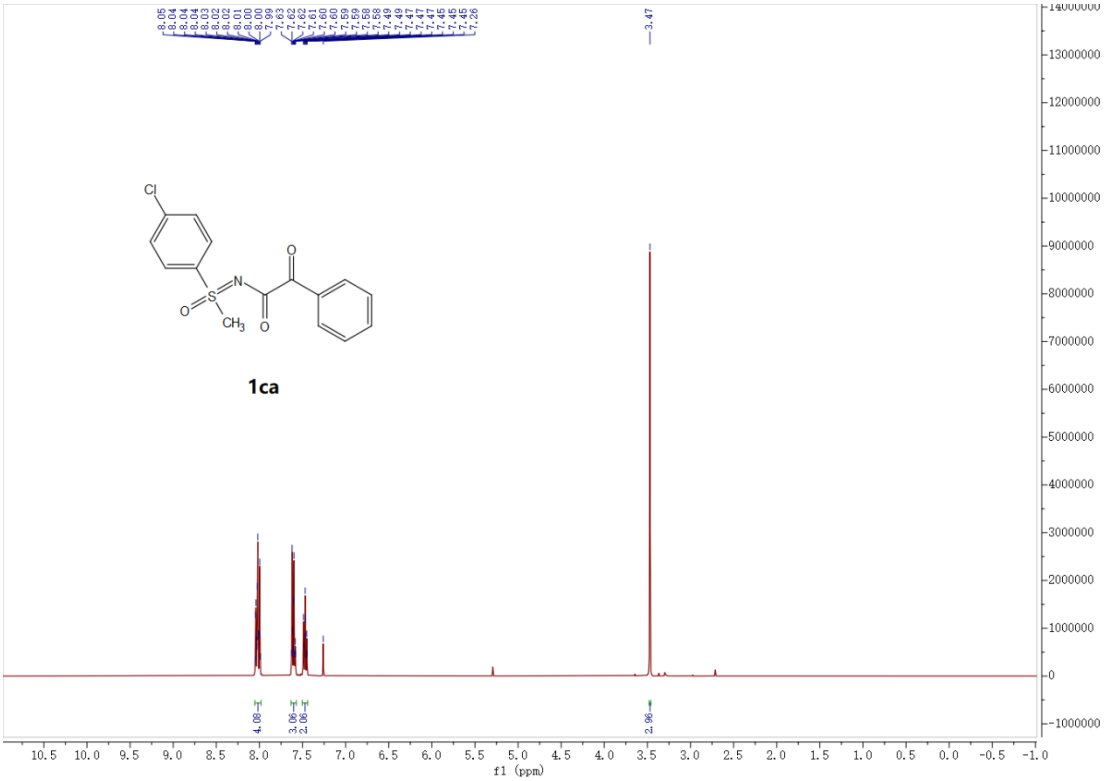

$^{13}C\{^{1}H\}$ NMR spectrum of compound **1ao** (101 MHz, $CDCl_3$)



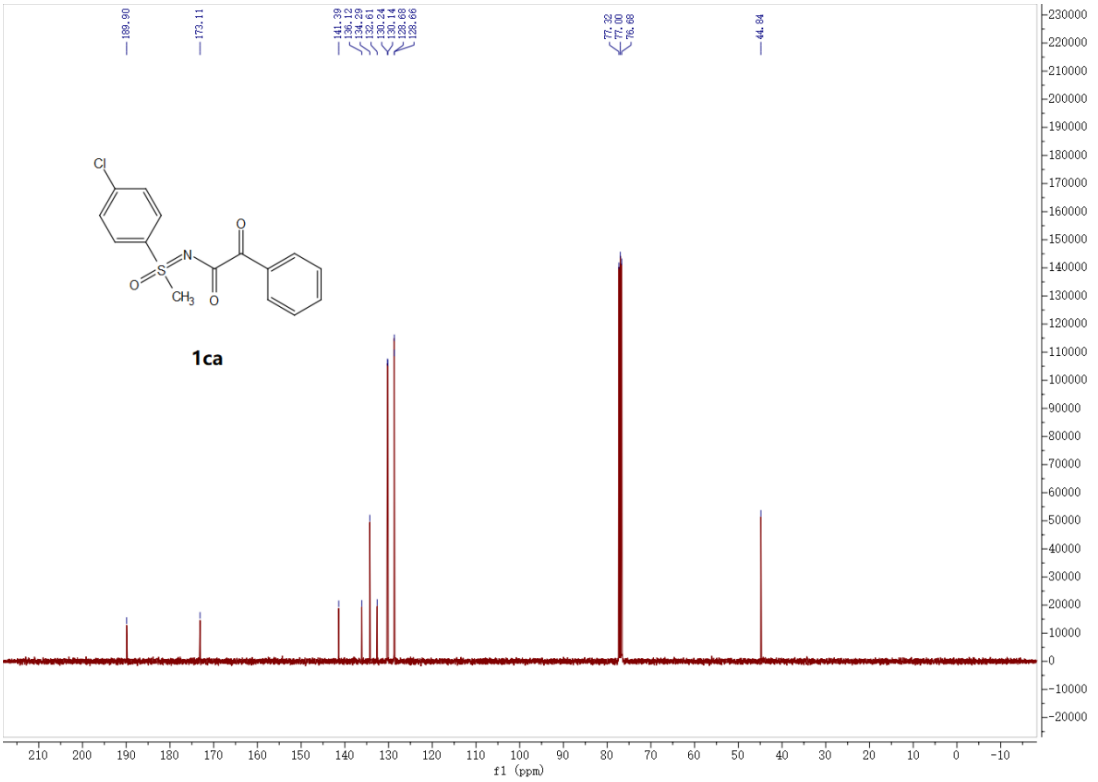

$^{1}$H NMR spectrum of compound **1ba** (400 MHz, $CDCl_3$)



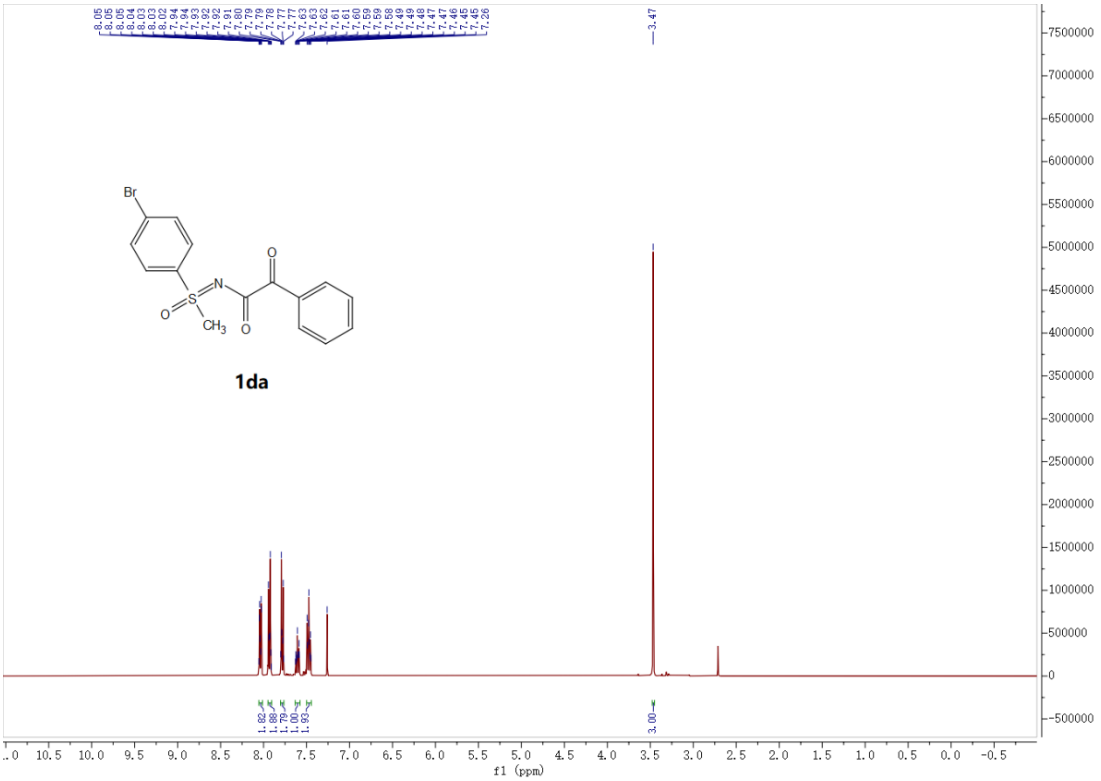

$^{13}$C{$^{1}$H} NMR spectrum of compound **1ba** (101 MHz, $CDCl_3$)



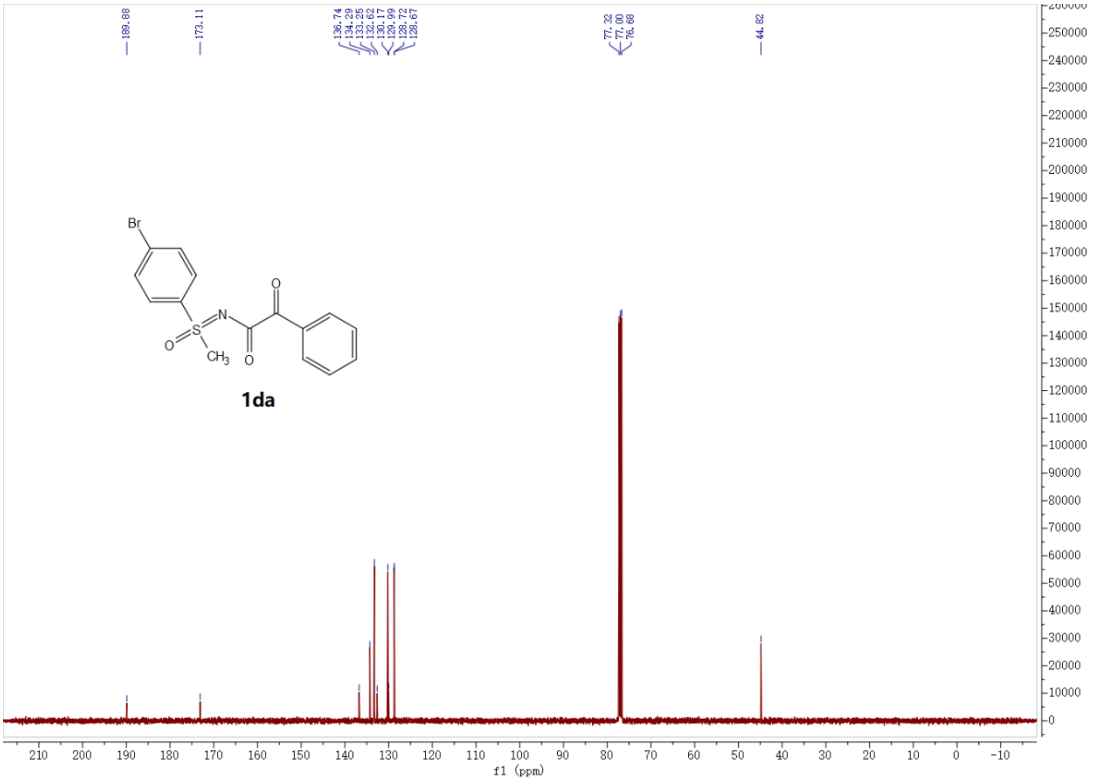

$^{1}$H NMR spectrum of compound **1ca** (400 MHz, $CDCl_3$)



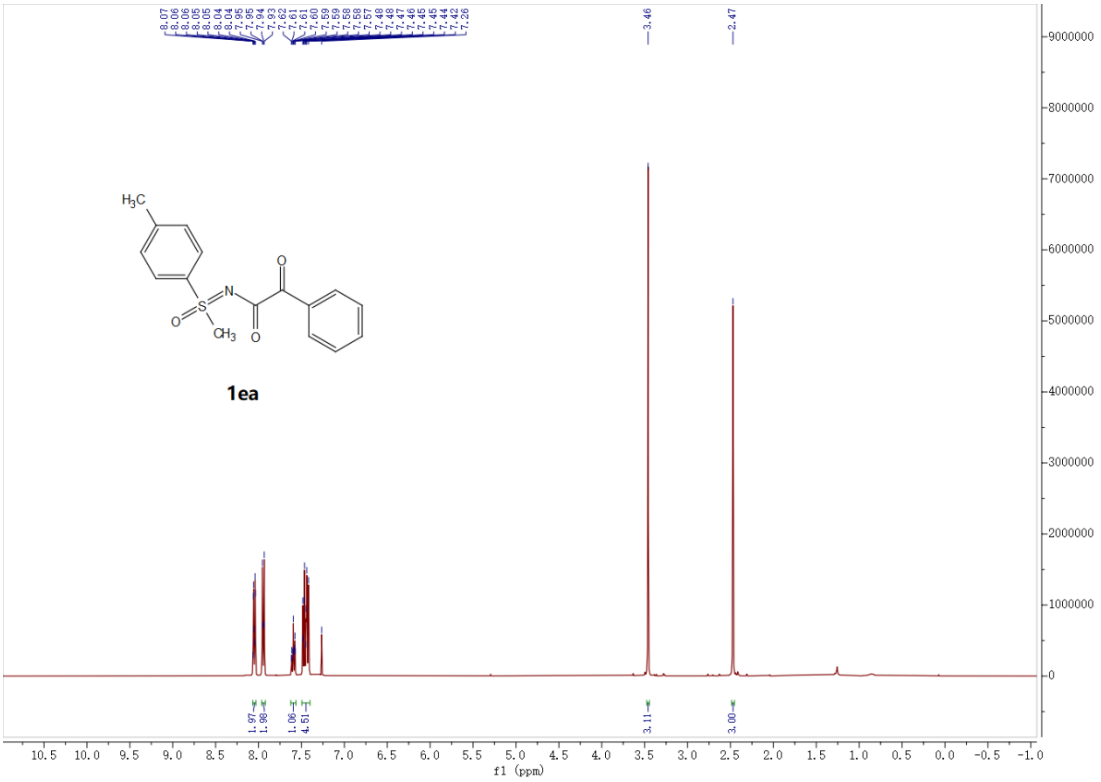

$^{13}C\{^{1}H\}$ NMR spectrum of compound **1ca** (101 MHz, $CDCl_3$)



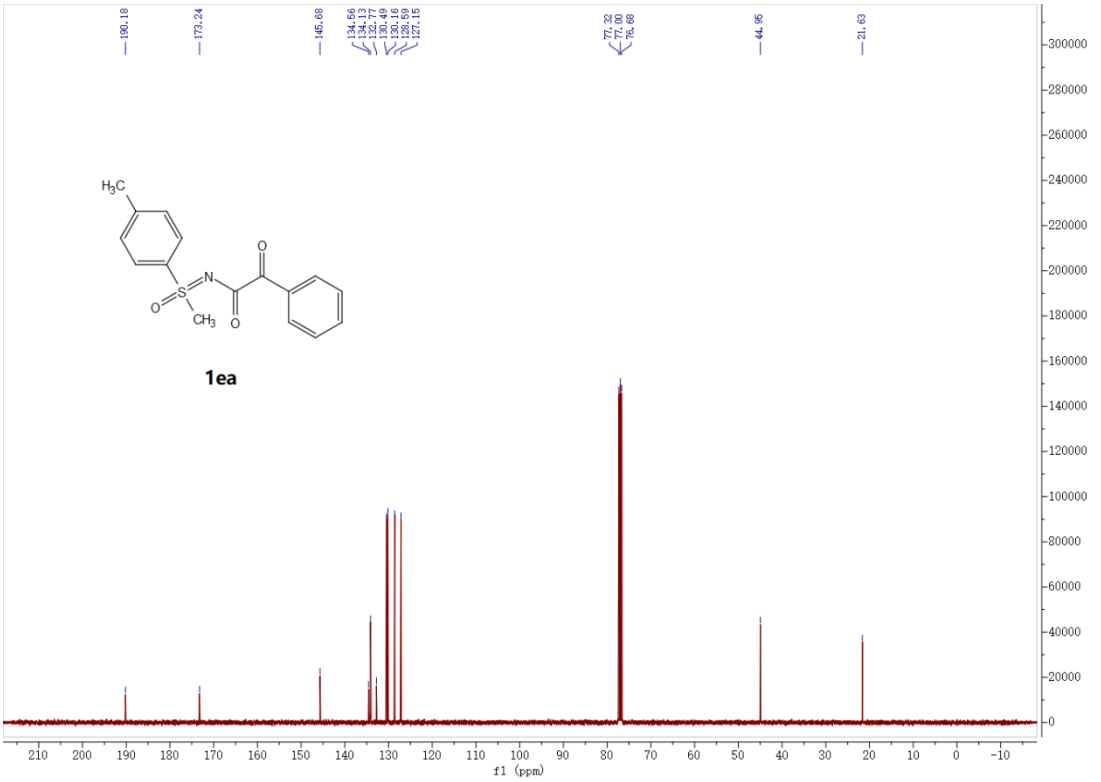

$^{1}$H NMR spectrum of compound **1da** (400 MHz, $CDCl_3$)



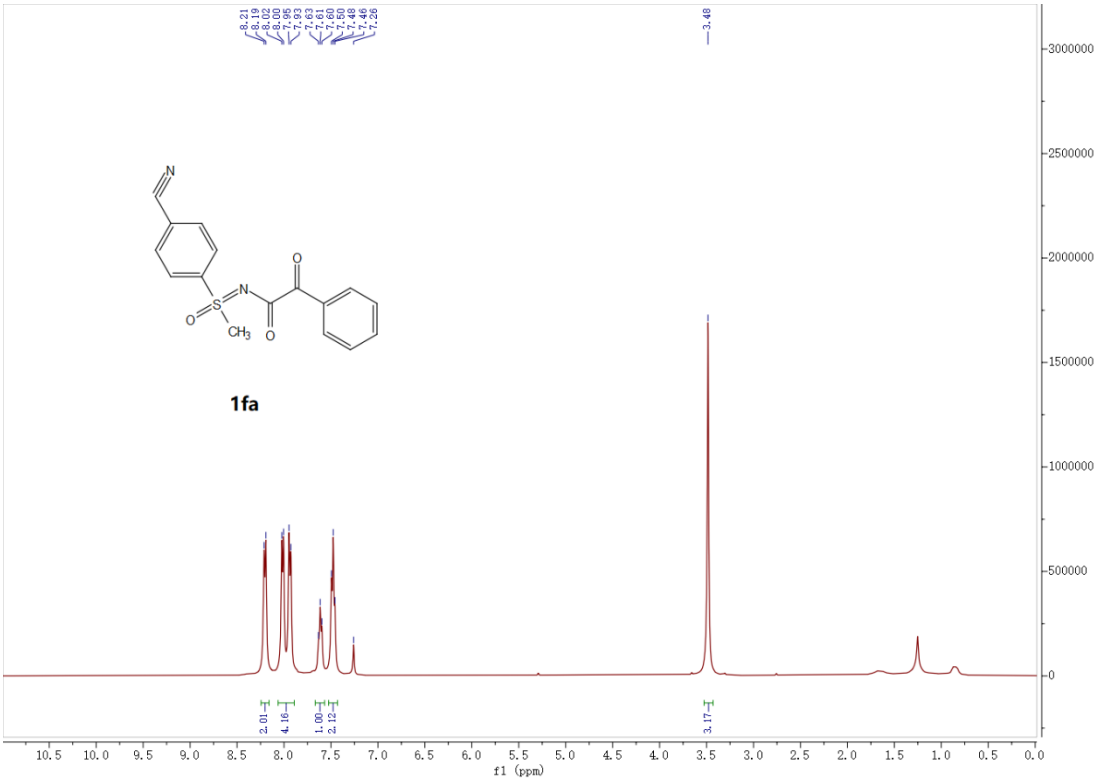

$^{13}C\{^{1}H\}$ NMR spectrum of compound **1da** (101 MHz, $CDCl_3$)



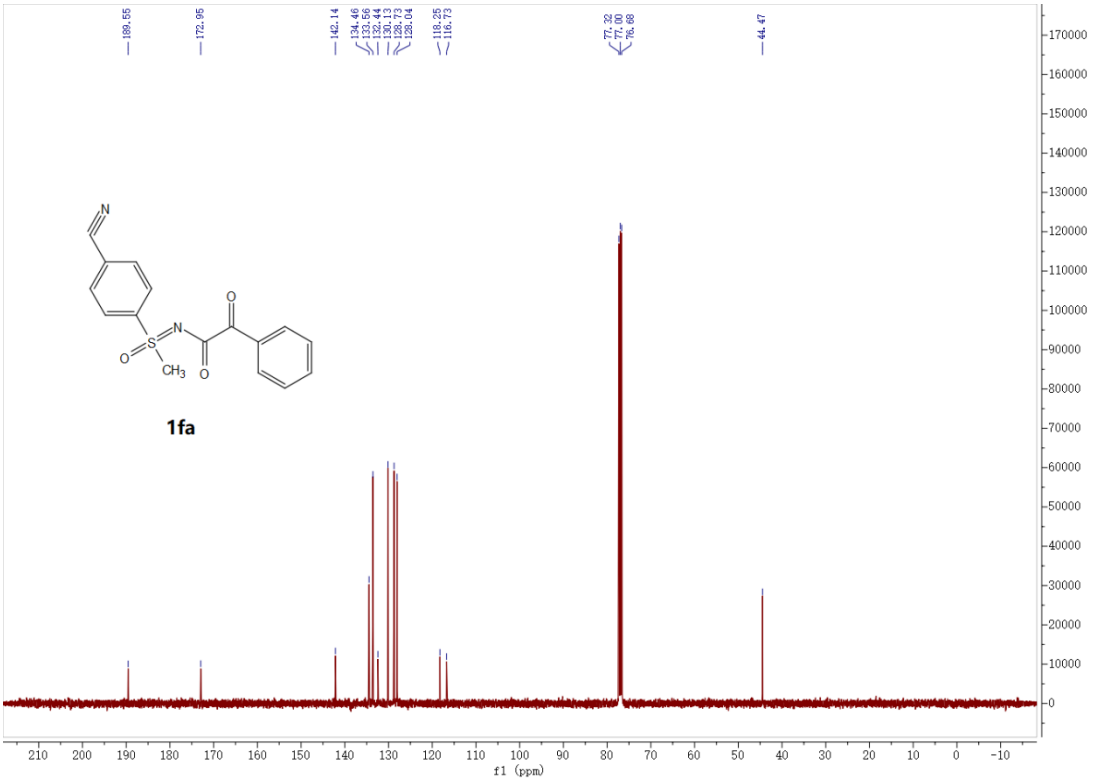

$^{1}$H NMR spectrum of compound **1ea** (400 MHz, $CDCl_3$)



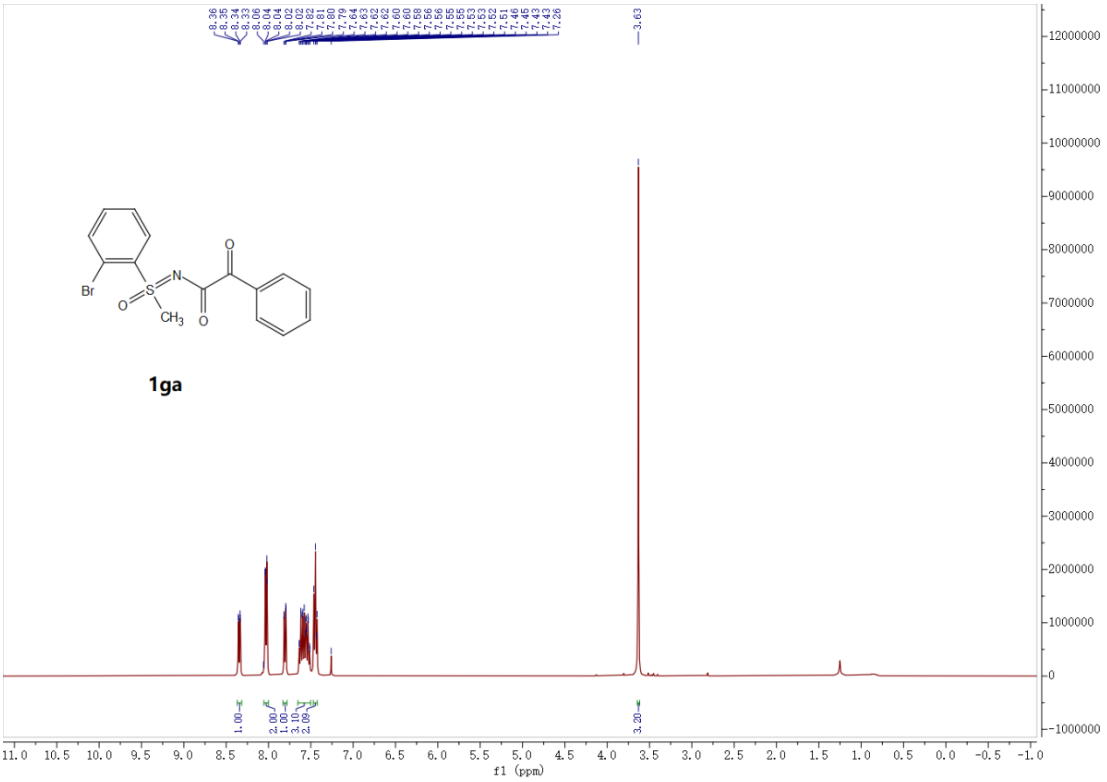

$^{13}C\{^{1}H\}$ NMR spectrum of compound **1ea**(101 MHz, $CDCl_3$)



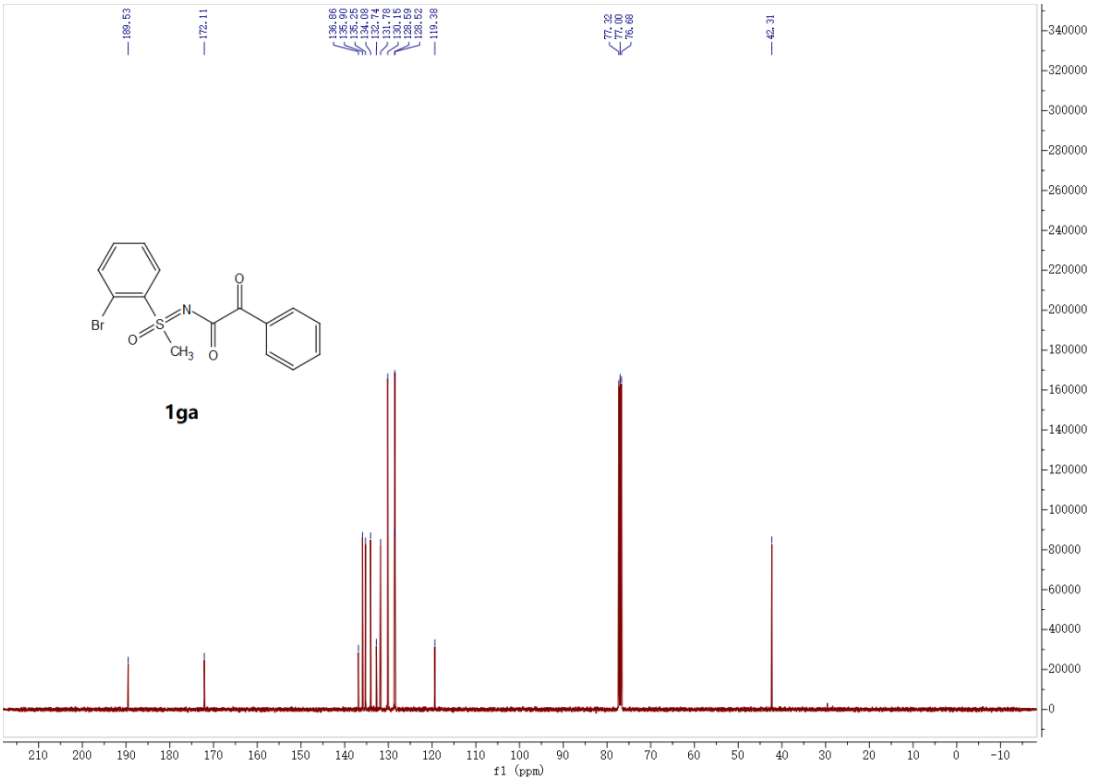

$^{1}$H NMR spectrum of compound **1fa** (400 MHz, $CDCl_3$)



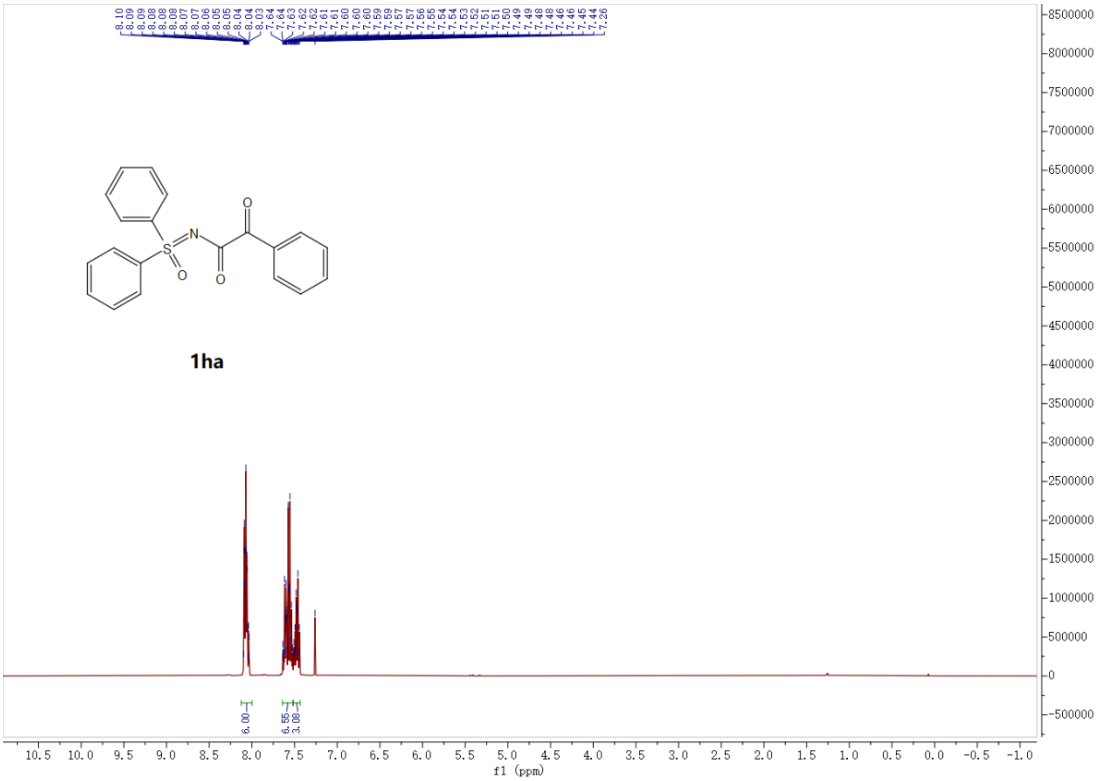

$^{13}$C{$^{1}$H} NMR spectrum of compound **1fa** (101 MHz, $CDCl_3$)



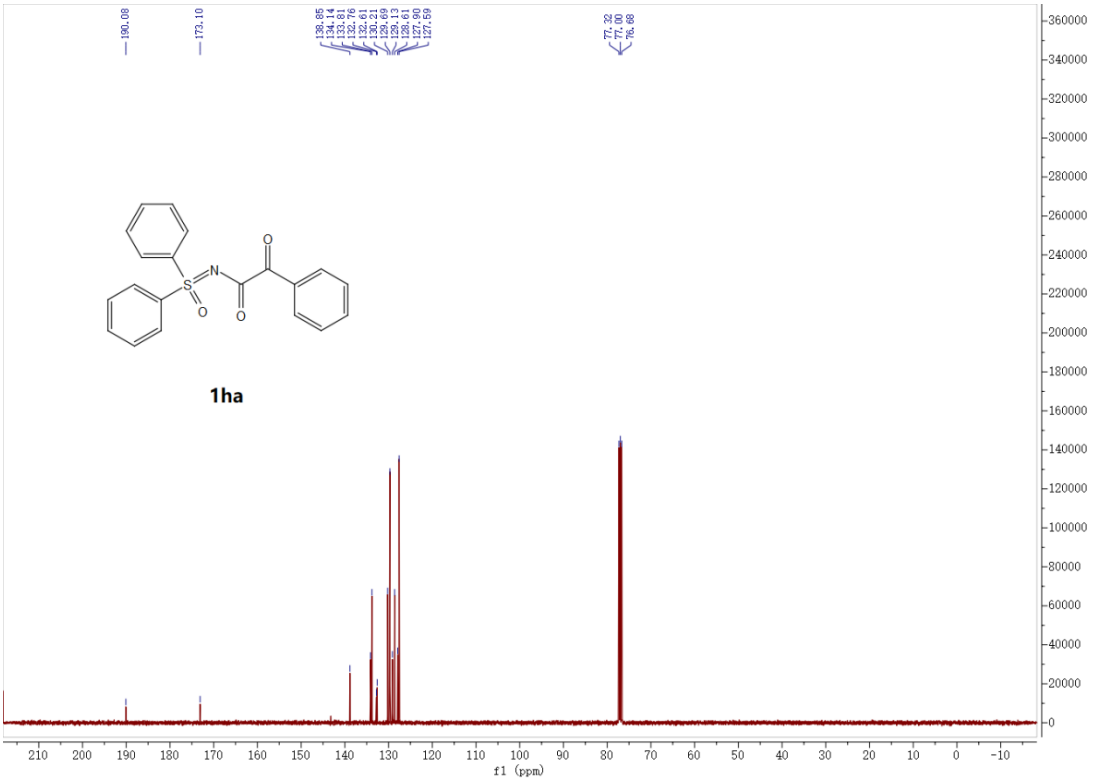

$^{1}$H NMR spectrum of compound **1ga** (400 MHz, $CDCl_3$)



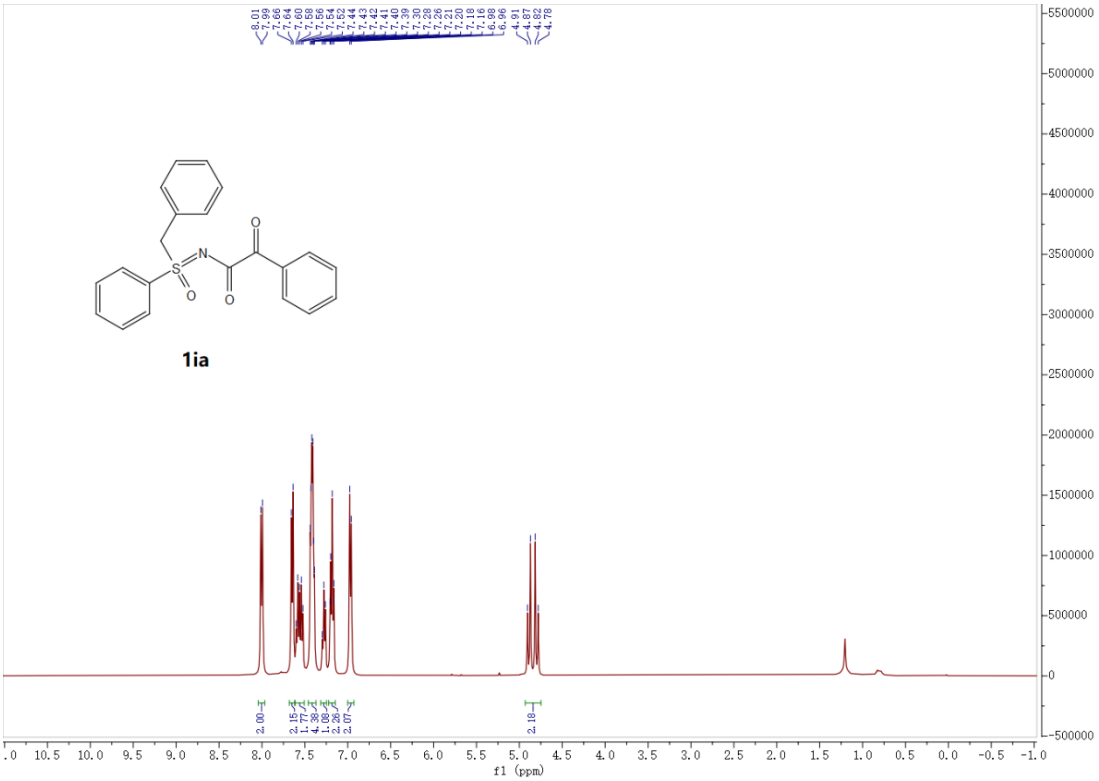

$^{13}C\{^{1}H\}$ NMR spectrum of compound **1ga** (101 MHz, $CDCl_3$)



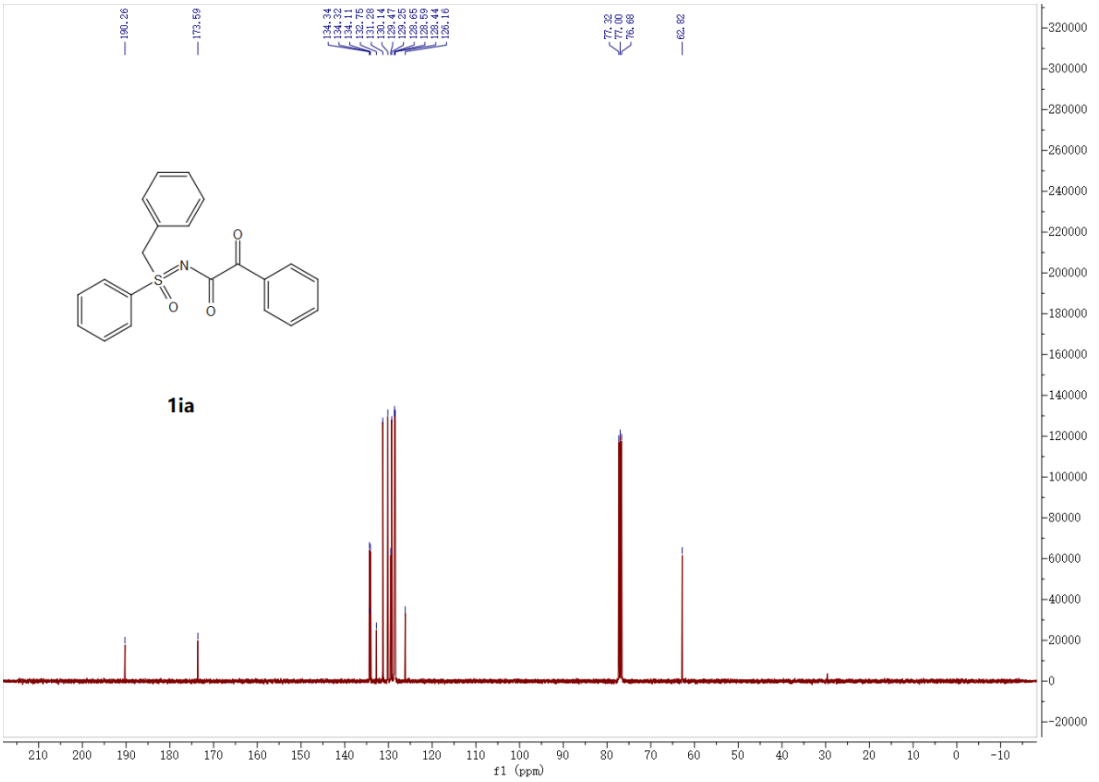

$^{1}$H NMR spectrum of compound **1ha** (400 MHz, $CDCl_3$)



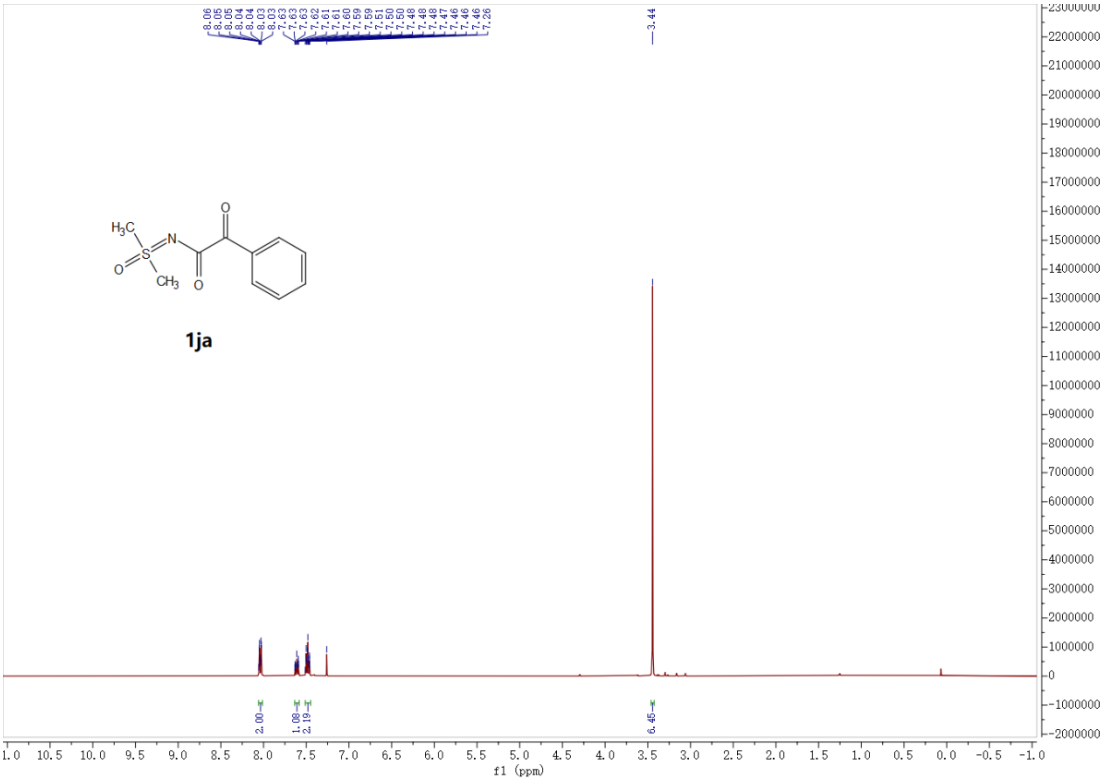

$^{13}C\{^{1}H\}$ NMR spectrum of compound **1ha** (101 MHz, $CDCl_3$)



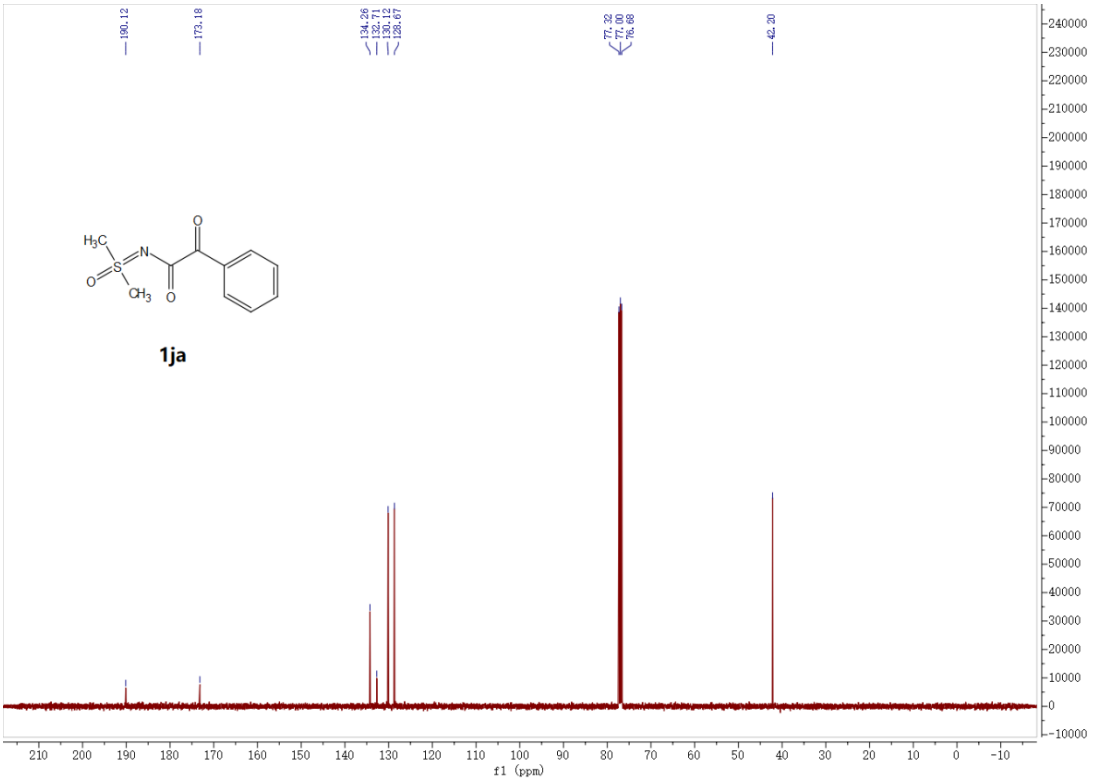

$^{1}$H NMR spectrum of compound **1ia** (400 MHz, $CDCl_3$)



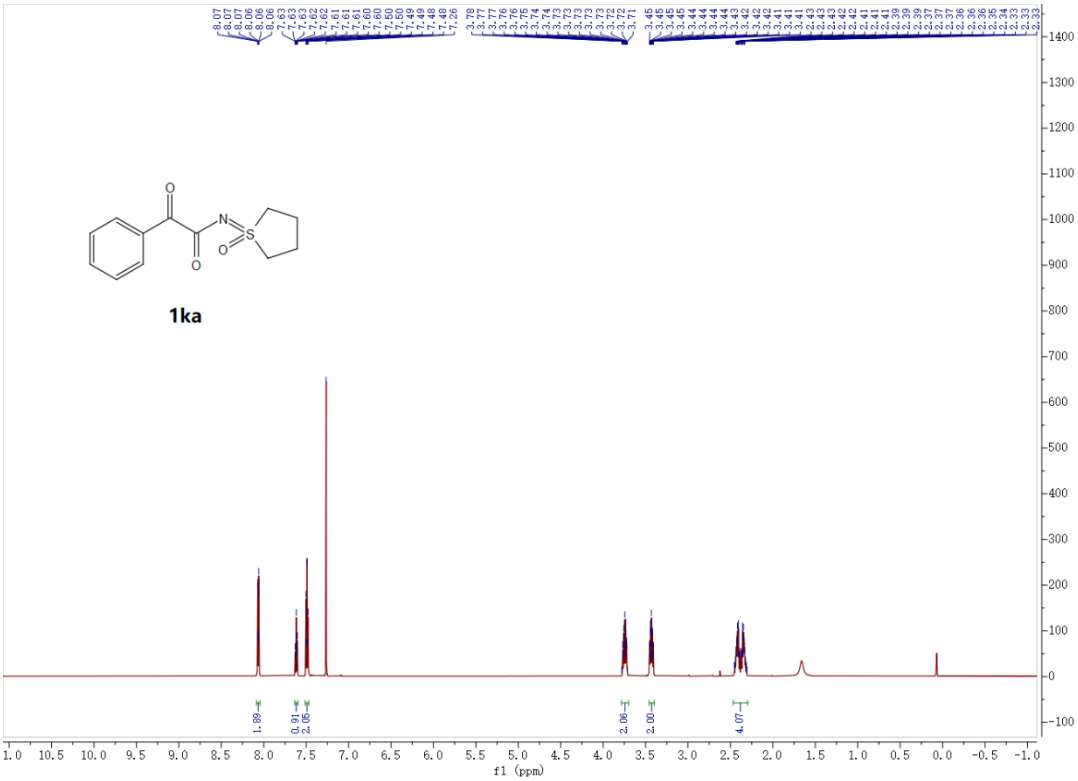

$^{13}C\{^{1}H\}$ NMR spectrum of compound **1ia** (101 MHz, $CDCl_3$)



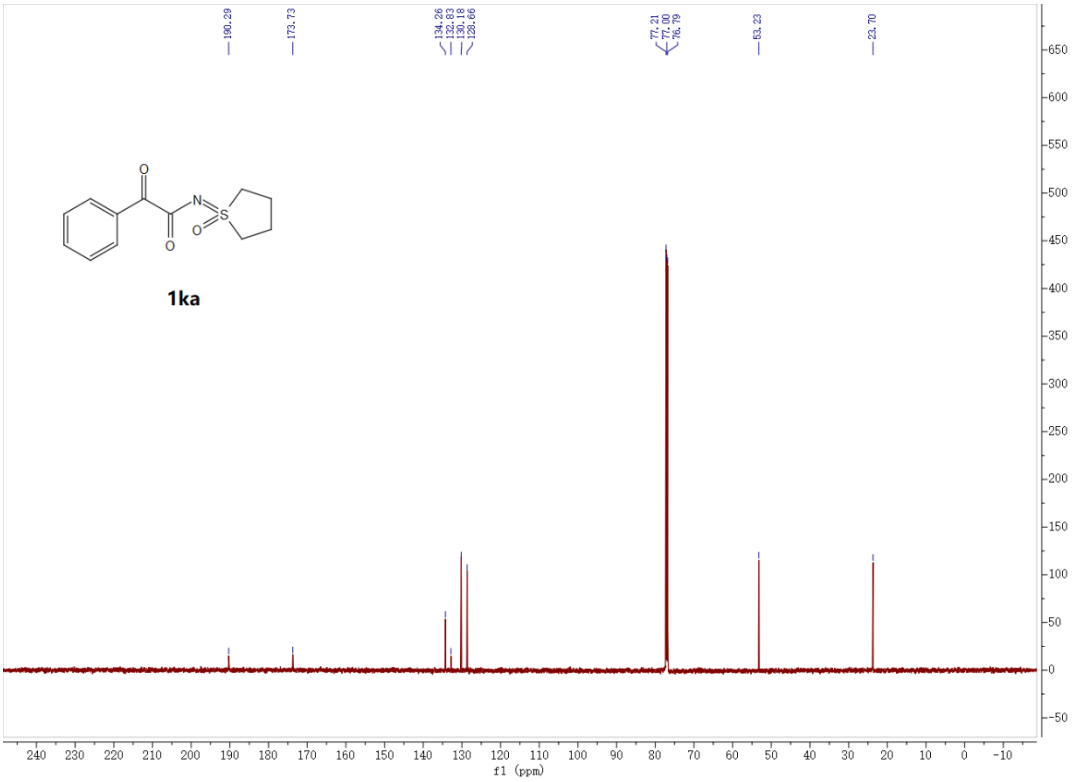

$^{1}$H NMR spectrum of compound **1ja** (400 MHz, $CDCl_3$)



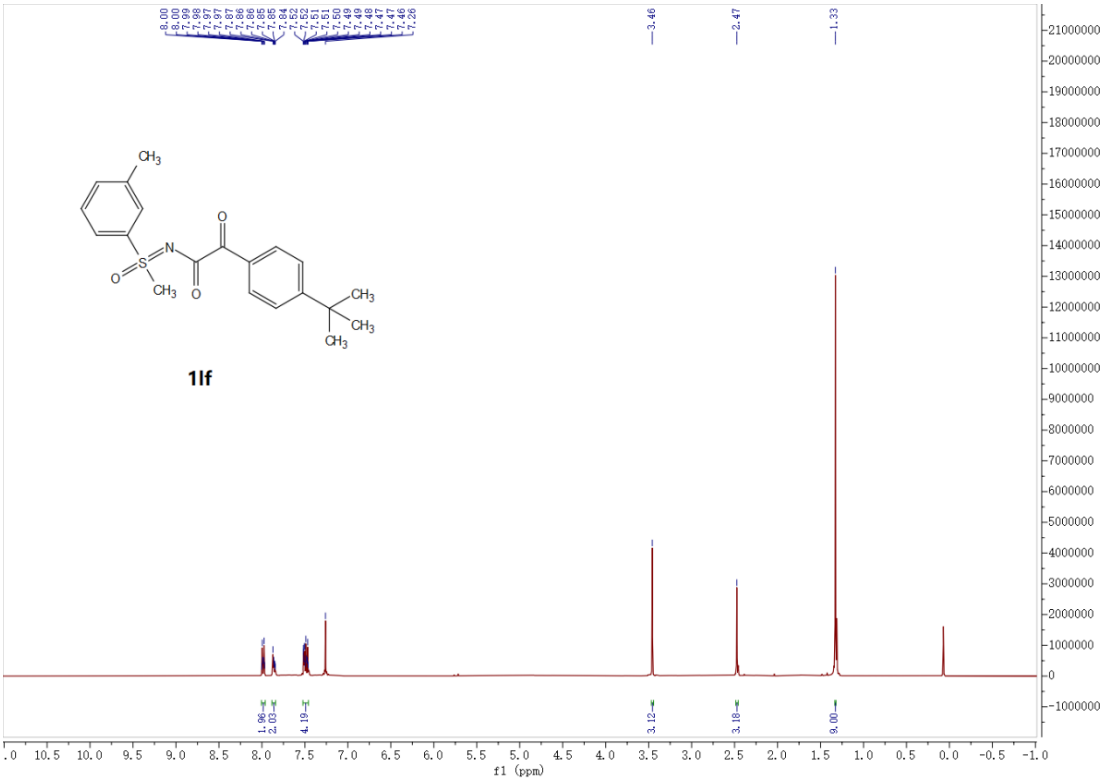

$^{13}C\{^{1}H\}$ NMR spectrum of compound **1ja** (101 MHz, $CDCl_3$)



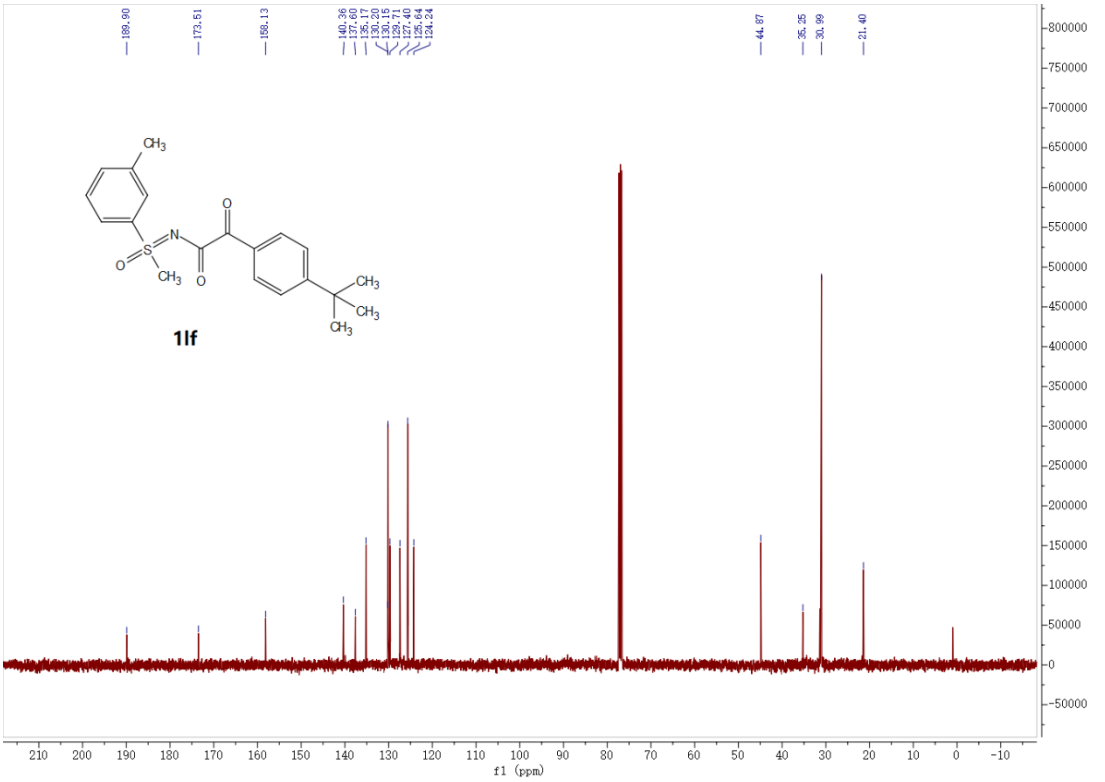

$^{1}$H NMR spectrum of compound **1ka** (600 MHz, $CDCl_3$)



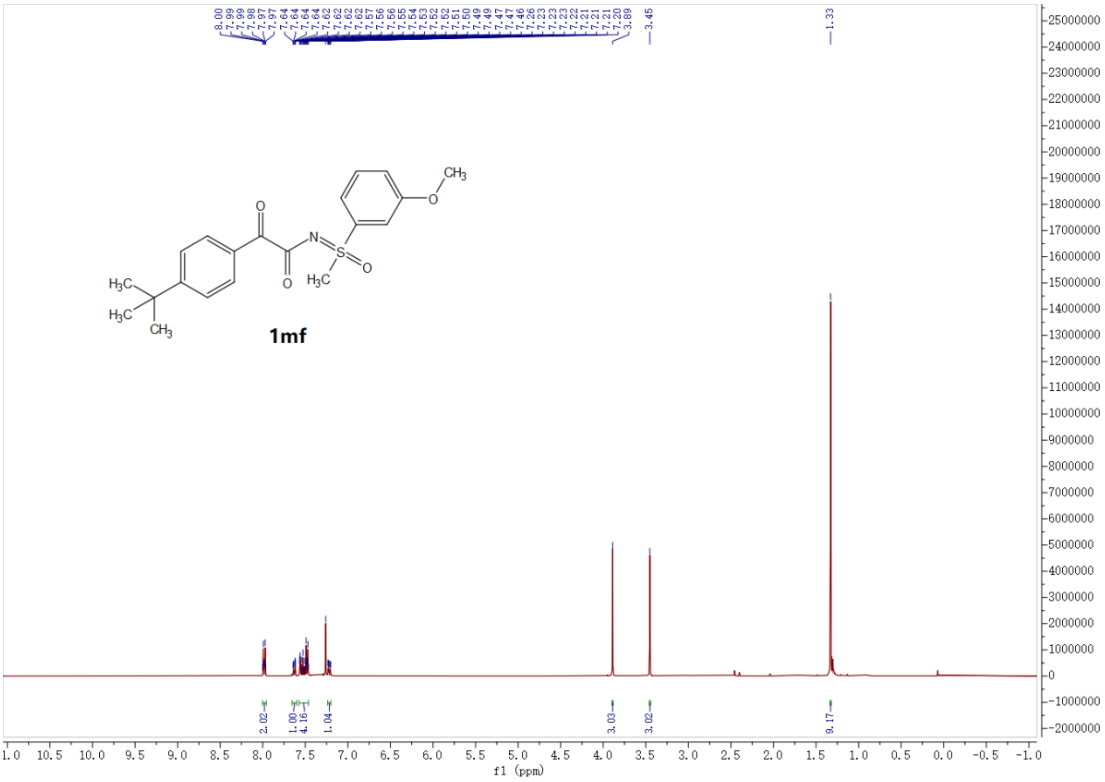

$^{13}C\{^{1}H\}$ NMR spectrum of compound **1ka** (151 MHz, $CDCl_3$)



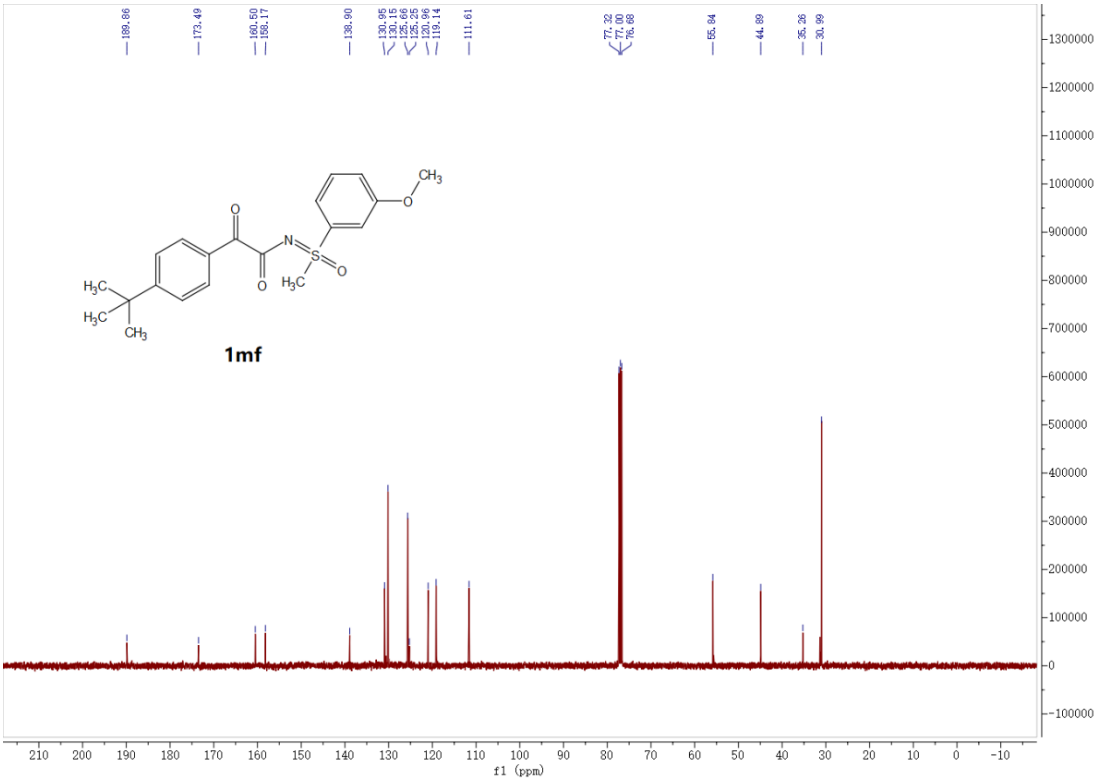

$^{1}$H NMR spectrum of compound **1lf** (600 MHz, $CDCl_3$)




$^{13}C\{^{1}H\}$ NMR spectrum of compound **1lf** (151 MHz, $CDCl_3$)




$^{1}$H NMR spectrum of compound **1mf** (600 MHz, $CDCl_3$)




$^{13}C\{^{1}H\}$ NMR spectrum of compound **1mf** (151 MHz, $CDCl_3$)