Supporting Information

Generation and Precise Control of Sulfonyl Radicals: Visible-Light-Activated Redox-Neutral Formation of Sulfonates and Sulfonamides

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Contents

1. General Information

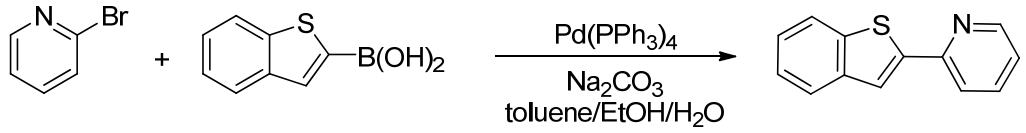
All commercially available reagents were used without further purification unless mentioned otherwise. ^{1}H and ^{13}C Nuclear Magnetic Resonance (NMR) spectra were recorded on Bruker Avance 400 Ultrashield NMR spectrometer. Chemical shifts (δ) were given in parts per million (ppm) and were measured downfield from internal tetramethylsilane. The melting points were determined on an X-4 microscope melting point apparatus and are uncorrected. Conversion was monitored by thin layer chromatography (TLC). Flash column chromatography was performed over silica gel (100-200 mesh). Blue LED (25 W, λmax = 480 nm), purchased from JIADENG (LS), was used for blue light irradiation. A fan attached to the apparatus was used to maintain the reaction temperature at room temperature.

2. Preparation of Photocatalyst and Substrate.

2.1 Preparation of photocatalysts $Ir(btp)_2Ala$, $Ir(btp)_2Gly$, $Ir(btp)_2Leu$ and $Ir(btp)_2$(*t*-Leu).

The photocatalysts were synthesized according to the following method. The other photocatalysts $Ir\{dF(CF_3)ppy\}_2(dtbbpy)PF_6$, $Ir(dtbbpy)(ppy)_2PF_6$, Eosin Y, $Ru(bpy)_3(PF_6)_2$, $Ir(ppy)_3$ and $Mes\text{-}Acr^+$ are commercially available.

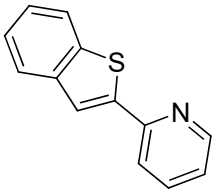
2.1.1 General Procedure 1 for Preparation of 2-(benzo[b]thiophen-2-yl)pyridine (L1).



L1

To a 50 mL round-bottom flask was added 2-bromopyridine (1.0 g, 6.25 mmol, 1.0 equiv), benzo[*b*]thiophene-2-boronic acid (1.2 g, 6.88 mmol, 1.1 equiv), Na_2CO_3 (1.99 g, 18.75 mmol, 3.0 equiv), (beta-4)-platinum (0.72 g, 0.62 mmol, 10 % mol), toluene (10 mL), EtOH (5 mL) and H_2O (5 mL) under argon atmosphere. The mixture was refluxed (100 ℃) with stirring for 12 h, then cooled to room temperature. The residue was taken into H_2O (20 mL), extracted with DCM (10 mL × 3). The combined organic phase was dried over anhydrous Na_2SO_4, filtered, and concentrated. The residue was purified by flash chromatography on a silica gel using petroleum ether and ethyl acetate (10:1, v/v) as the eluent to give 2-(benzo[*b*]thiophen-2-yl)pyridine (1.16 g, 5.5 mmol, 88 %).

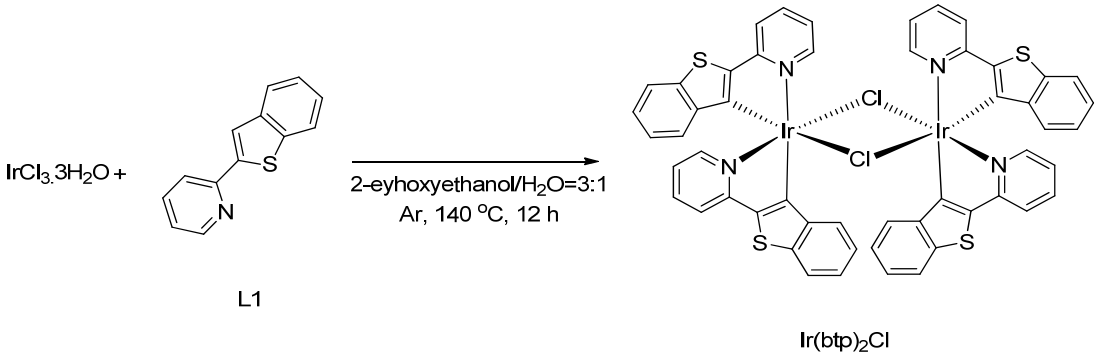
2-(Benzo[*b*]thiophen-2-yl)pyridine (L1).



General procedure 1 was followed to obtain **L1** (1.16 g, 5.5 mmol, 88 %) as a white solid.

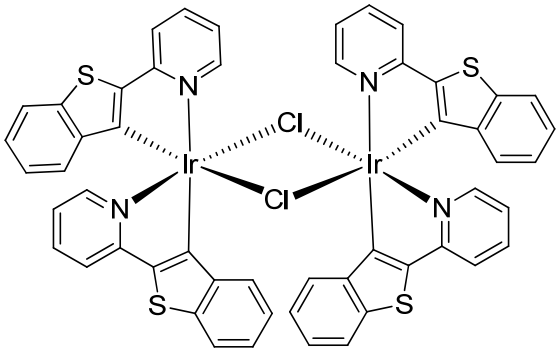
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.64 (d, J = 4.7 Hz, 1H, Ar-H), 7.90 – 7.86 (m, 1H, Ar-H), 7.85 (s, 1H, Ar-H), 7.83 – 7.79 (m, 2H, Ar-H), 7.76 – 7.72 (m, 1H, Ar-H), 7.38 – 7.33 (m, 2H, Ar-H), 7.23 – 7.20 (m, 1H, Ar-H).

2.1.2 General Procedure 2 for Preparation of $Ir(btp)_2Cl$ (L2).



To a 50 mL round-bottom flask was added 2-eyhoxyethanol (9 mL), H_2O (3 mL), $IrCl_3.3H_2O$ (1.0 g, 3.2 mmol, 1.0 equiv), and 2-(benzo[*b*]thiophen-2-yl)pyridine (1.5 g, 7.0 mmol, 2.2 equiv) under argon atmosphere. The mixture was refluxed (140 ℃) with stirring for 12 h, then cooled to room temperature. The mixture was filtered, washed with water (20 mL) and ethanol (20 mL), to get $Ir(btp)_2Cl$ (1.88 g, 0.15 mmol, 90%).

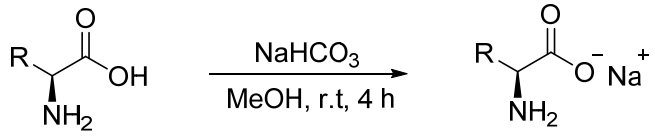
$Ir(btp)_2Cl$ (L2)



General procedure 2 was followed to obtain **L2** (1.46 g, 0.11 mmol, 70%) as a red solid. Mp > 300 °C.

^{1}H NMR (400 MHz, DMSO-d6) δ 9.93 (d, J = 5.4 Hz, 2H, Ar-H), 9.69 (d, J = 5.3 Hz, 2H, Ar-H), 8.17 (td, J = 8.0, 1.5 Hz, 2H, Ar-H), 8.09 (td, J = 7.8, 1.4 Hz, 2H, Ar-H), 7.92 (d, J = 7.6 Hz, 2H, Ar-H), 7.83 – 7.77 (m, 6H, Ar-H), 7.52 (ddd, J = 7.4, 5.9, 1.4 Hz, 2H, Ar-H), 7.45 (ddd, J = 7.4, 6.0, 1.5 Hz, 2H, Ar-H), 7.21 – 7.16 (m, 2H, Ar-H), 7.12 (m, 2H, Ar-H), 6.93 – 6.88 (m, 2H, Ar-H), 6.81 – 6.74 (m, 2H, Ar-H), 6.19 (d, J = 8.0 Hz, 2H, Ar-H), 5.55 (d, J = 8.2 Hz, 2H, Ar-H).**^{13}C NMR** (100 MHz, DMSO-*d6*) δ 164.7, 163.6, 153.0, 152.1, 146.7, 144.8, 144.3, 141.9, 141.8, 141.1, 140.7, 139.5, 136.5, 135.5, 125.7, 124.8, 124.6, 124.2, 123.9, 123.3, 123.1, 121.3, 121.0, 119.5, 119.4. **HRMS** (ESI) calcd for $C_{52}H_{33}Cl_2Ir_2N_4S_4$ $[M+H]^+$ 1297.0218, found 1297.0224.

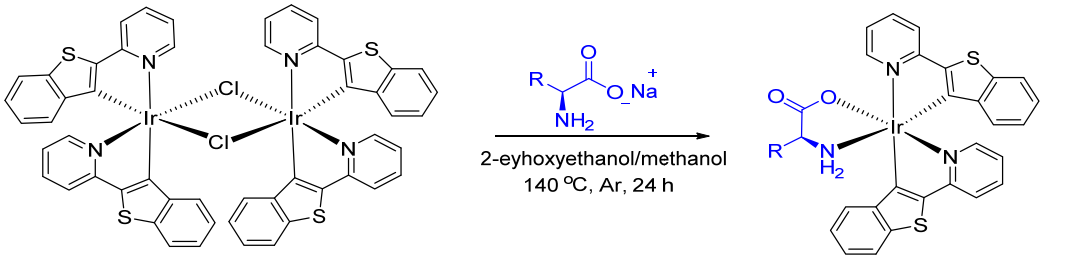
2.1.3 General Procedure 3 for Preparation of Ir(btp)$_2$Ala, Ir(btp)$_2$Gly, Ir(btp)$_2$Leu and Ir(btp)$_2$(*t*-Leu).



A1-A4 L2-L5

R=H, CH_3, $CH_2CH(CH_3)_2$, $C(CH_3)_3$

To a 50 mL round-bottom flask was added corresponding acids A1-A4 (0.85 mmol, 1.0 equiv), $NaHCO_3$ (0.07 g, 0.85 mmol, 1.0 equiv) and MeOH (10 mL). The mixture was stirred at room temperature for 3 h, concentrated to 3 ~5 mL under reduced pressure and got the corresponding concentrated methanol solution of L2-L5.

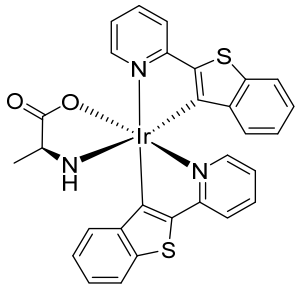


Ir(btp)$_2$Cl R=H, CH_3, $CH_2CH(CH_3)_2$, $C(CH_3)_3$

PC1-PC4

To a 50 mL round-bottom flask was added L2 (0.5 g, 0.39 mmol, 1.0 equiv), 2-eyhoxyethanol (10 mL), and the concentrated methanol solution of corresponding L2-L5 (0.85 mmol, 1.1 equiv) under argon atmosphere. The mixture was refluxed at 140 ℃ with stirring for 12~24 h and concentrated. The residue was purified by flash chromatography on a silica gel using DCM and methanol (50:1, v/v) as the eluent to give PC1-PC4.

Ir(btp)$_2$Ala (PC1)

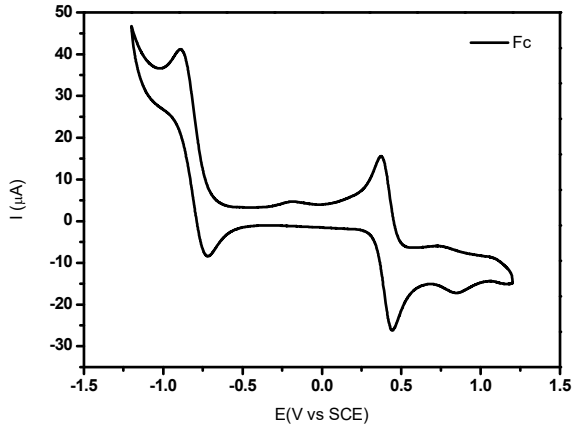


General procedure 3 was followed to obtain **PC1** (0.34 g, 0.49 mmol, 62%) as a red solid. **Mp** > 300 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.14 (d, J = 5.7 Hz, 1H, Ar-H), 8.66 (d, J = 5.7 Hz, 1H, Ar-H), 8.04 – 7.99 (m, 2H, Ar-H), 7.89 – 7.85 (m, 1H, Ar-H), 7.83 – 7.74 (m, 3H, Ar-H), 7.40 – 7.36 (m, 1H, Ar-H), 7.35 – 7.30 (m, 1H, Ar-H), 7.13 – 7.06 (m, 2H, Ar-H), 6.87 – 6.83 (m, 1H, Ar-H), 6.78 – 6.74 (m, 1H, Ar-H), 6.20 (d, J = 8.1 Hz, 1H, Ar-H), 5.82 (d, J = 8.2 Hz, 1H, Ar-H), 5.73 (dd, J = 11.9, 7.8 Hz, 1H, NH), 3.41 – 3.37 (m, 1H, CH), 1.18 (d, J = 7.0 Hz, 3H, CH_3). **^{13}C NMR** (100 MHz, DMSO-*d6*) δ 182.6, 165.5, 165.3, 152.0, 148.3, 146.7, 146.5, 145.6, 141.7, 141.6, 139.0, 135.2, 125.3, 124.9, 123.5, 123.5, 122.8, 120.1, 119.8, 118.7, 118.7, 62.8, 21.2. **HRMS** (ESI) calcd for $C_{29}H_{22}IrN_3O_2S_2$ $[M+H]^+$ 701.0777, found 701.0782.

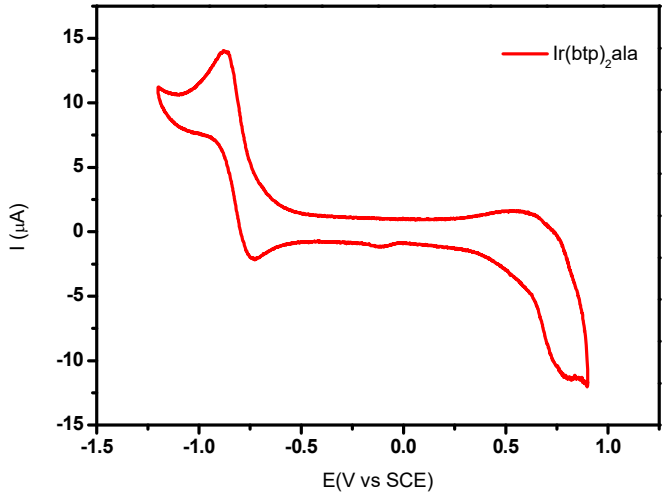
Cyclic Voltammetry and Determination of Excited State Potentials:

Cyclic voltammograms were acquired on a CH Instruments 700E potentiostat using a glassy carbon working electrode, a saturated calomel (SCE) reference electrode, and a Pt mesh counter electrode. The pH was not adjusted and voltammograms were obtained at room temperature in a 100 mM MeCN solution of tetrabutylammonium hexafluorophosphate containing 1 mM of the designated substances. The scan rate was 50 mV/s.

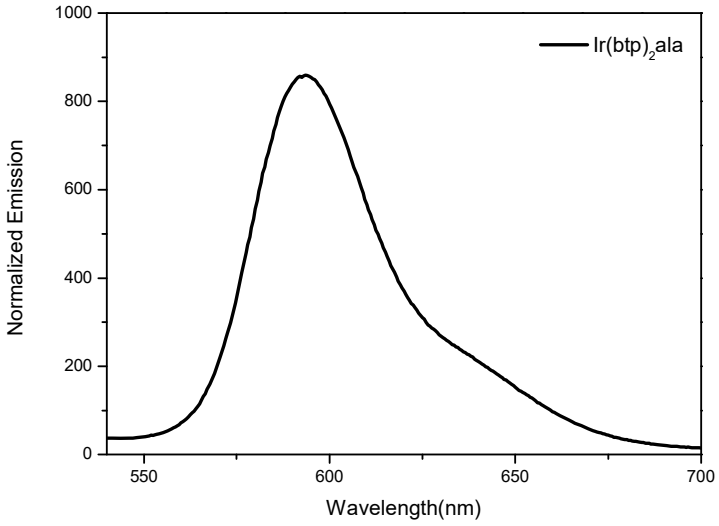


Cyclic voltammogram of ferrocence in acetonitrile solution (1.0×10^{-3} M) at room temperature. $E_{ox(Fc/Fc+)}$ = 0.372 V vs SCE in acetonitrile, the reported value is $E_{ox(Fc/Fc+)}$

= 0.38 V vs SCE in acetonitrile.[1]



Cyclic voltammogram of Ir(btp)$_2$ala in acetonitrile solution (1.0×10^{-3} M) at room temperature. Ir(III)/Ir(IV) E_{pc} = 0.573 V, E_{pa} = 0.802 V, Ir(II)/Ir(III) E_{pa} = -0.735 V, E_{pc} = -0.878 V. $E_{1/2}^{ox\ III/II}$ and $E_{1/2}^{red\ IV/III}$ values: −0.85 and +0.774 V (vs. SCE).



Normalized emission spectra of Ir(btp)$_2$ala in acetonitrile solution (1.0×10^{-5} M) at room temperature. The maxima was obtained at 595 nm; the intensity is 10% of the emission maxima at 530 nm.

Excited state potentials are estimated using the Rehm-Weller equations as given[2]:

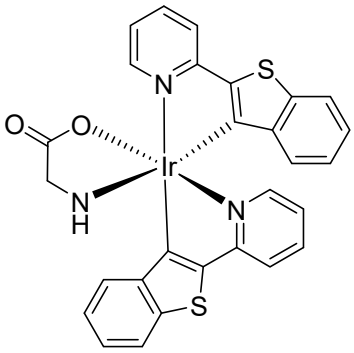
$$E^*_{ox} = E'_{ox} - E^{0\text{-}0}$$

$$E^*_{red} = E'_{red} - E^{0\text{-}0}$$

The E* means the excited state potential, E' means the ground state potential, $E^{0\text{-}0}$ represents the energy gap between the zeroeth level vibrational levels of the ground and excited state. E_{ox} is to mean the Ir(III)/Ir(IV) couples and E_{red} is to mean the

Ir(II)/(III) couples. Because of poor overlap between the absorbtion and emission spectra, $E^{0\text{-}0}$ is approximated as the high-energy onset of phosphorescence where the emission intensity is 10% of that obtained at the maximum emission wavelength, using the "10% rule"[3,1b]. Base on the above methods: $E_{1/2}^{*III/II}$, $E_{1/2}^{III/II}$, $E_{1/2}^{IV/*III}$, $E_p^{red\ IV/*III}$, and $E_{1/2}^{IV/III}$ values for Ir(btp)$_2$Ala: +1.50, −0.85, −1.58, −1.61, and +0.774 V (vs. SCE).

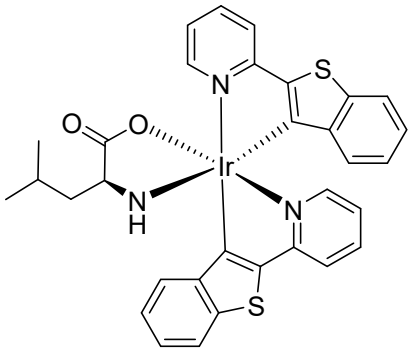
Ir(btp)$_2$Gly (PC2)



General procedure 3 was followed to obtain **PC2** (0.27 g, 0.40 mmol, 52%) as a red solid. **Mp** > 300 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.10 (d, J = 5.6 Hz, 1H, Ar-H), 8.70 (d, J = 5.6 Hz, 1H, Ar-H), 8.06 – 8.00 (m, 2H, Ar-H), 7.87 (d, J = 8.0 Hz, 1H, Ar-H), 7.81 – 7.76 (m, 3H, Ar-H), 7.41 – 7.38 (m, 1H, Ar-H), 7.35 – 7.32 (m, 1H, Ar-H), 7.13 – 7.07 (m, 2H, Ar-H), 6.87 – 6.83 (m, 1H, Ar-H), 6.79 – 6.74 (m, 1H, Ar-H), 6.20 (d, J = 8.1 Hz, 1H, Ar-H), 5.84 (d, J = 8.1 Hz, 1H, Ar-H), 5.49 – 5.16 (m, 1H, NH), 3.28 (dd, J = 13.2, 6.7 Hz, 2H, CH_2). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 182.4, 165.9, 165.5, 152.1, 151.7, 149.3, 147.98, 146.96, 145.9, 142.2, 142.1, 139.6, 135.8, 133.9, 125.7, 125.4, 124.1, 124.05, 123.4, 120.8, 120.4, 119.2, 63.3. **HRMS** (ESI) calcd for $C_{28}H_{20}IrN_3O_2S_2$ $[M+H]^+$ 687.0621, found 687.0623.

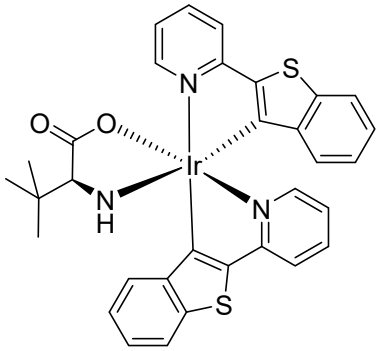
Ir(btp)$_2$Leu (PC3)



General procedure 3 was followed to obtain **PC3** (0.27 g, 0.37 mmol, 47 %) as a red solid. **Mp** > 300 °C.

^{1}H NMR (400 MHz, DMSO-*d6*) δ 9.16 (d, J = 4.4 Hz, 1H, Ar-H), 8.63 (d, J = 5.2 Hz, 1H, Ar-H), 8.02 (d, J = 7.0 Hz, 2H, Ar-H), 7.87 (t, J = 7.8 Hz, 1H, Ar-H), 7.80 – 7.76 (m, 3H, Ar-H), 7.36 (d, J = 5.2 Hz, 2H, Ar-H), 7.13 – 7.08 (m, 2H, Ar-H), 6.86 (t, J = 7.6 Hz, 1H, Ar-H), 6.76 (t, J = 7.8 Hz, 1H, Ar-H), 6.24 (d, J = 8.2 Hz, 1H, Ar-H), 5.93 – 5.81 (m, 1H, NH), 5.80 (d, J = 7.6 Hz, 1H, Ar-H), 3.51 – 3.47 (m, 1H, NH-CH), 1.26 – 1.24 (m, 2H, CH_2), 0.91 – 0.81 (m, 6H, CH_3), 0.77 – 0.76 (m, 1H, CH). **^{13}C NMR** (100 MHz, DMSO-*d6*) δ 182.7, 165.5, 151.9, 151.8, 148.3, 146.9, 146.5, 141.7, 141.6, 139.0, 135.2, 133.5, 125.5, 124.8, 123.5, 122.8, 122.78, 119.7, 118.7, 69.8, 52.8, 40.2, 40.0, 39.7, 39.5, 39.3, 39.1, 38.9, 23.5, 20.8. **HRMS** (ESI) calcd for $C_{32}H_{28}IrN_3O_2S_2$ $[M+H]^+$ 743.1247, found 743.1252.

Ir(btp)$_2$(*t*-Leu) (PC4)



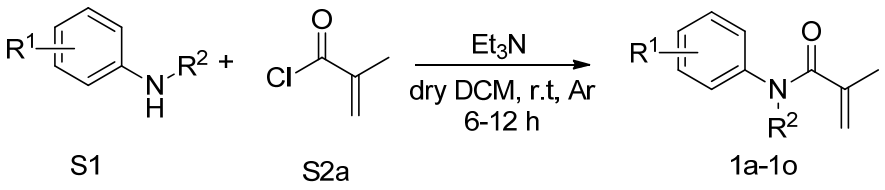
General procedure 3 was followed to obtain **PC4** (0.33 g, 0.45 mmol, 58%) as a red solid. **Mp** > 300 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.22 (d, J = 5.7 Hz, 1H, Ar-H), 8.65 (d, J = 5.7 Hz, 1H, Ar-H), 8.04 – 7.99 (m, 2H, Ar-H), 7.87 (d, J = 8.0 Hz, 1H, Ar-H), 7.79 – 7.75 (m, 3H, Ar-H), 7.36 – 7.31 (m, 2H, Ar-H), 7.12 – 7.07 (m, 2H, Ar-H), 6.87 – 6.83 (m, 1H, Ar-H), 6.78 – 6.74 (m, 1H, Ar-H), 6.22 (d, J = 8.1 Hz, 1H, Ar-H), 5.79 (d, J = 8.1 Hz, 1H, Ar-H), 5.75 (dd, J = 12.2, 8.0 Hz, 1H, NH), 2.99 (t, J = 8.9 Hz, 1H, CH), 0.96 (s, 9H, CH_3). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 180.8, 166.3, 165.9, 152.8, 151.8, 149.0, 147.4, 146.9, 142.2, 142.1, 139.4, 135.6, 134.1, 126.0, 125.5, 125.3, 125.2, 124.0, 123.9, 123.3, 123.26, 120.6, 119.8, 119.3, 119.1, 63.3, 35.5, 27.5. **HRMS** (ESI) calcd for $C_{32}H_{28}IrN_3O_2S_2$ $[M+H]^+$ 743.1247, found 743.1242.

2.2 Preparation of Substrates.

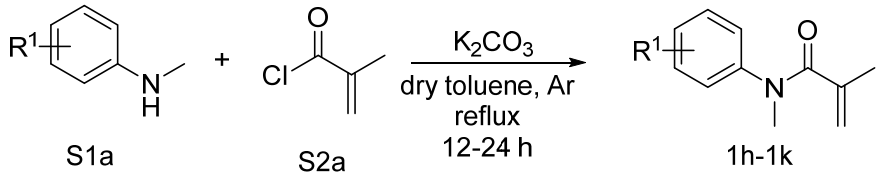
2.2.1 General Procedure 4 for Preparation of Substrates **1a**–**1o**, **1r**, **1s**, **1x** and **1z**.

Method A:



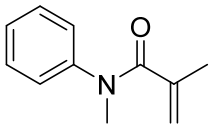
To a 50 mL round-bottom flask was added the solution of corresponding aniline S1 (2.0 mmol) in DCM (15 mL) and triethylamine (0.4 g, 4.0 mmol, 2.0 equiv). The mixture was stirred at 0℃, and added methacryloyl chloride S2a (0.31 g, 3.0 mmol, 1.5 equiv) slowly under argon atmosphere. The resulting solution was stirred at room temperature for 6~12 h, quenched with H_2O (50 mL), extracted with DCM (15 mL × 3). The combined organic layer was washed with brine (15 mL × 3), dried over Na_2SO_4, and concentrated. The residue was purified by flash chromatography on a silica gel using petroleum ether and ethyl acetate (15:1~10:1, v/v) as the eluent to give corresponding substrates **1a**–**1o**.

Method B:



To a 50 mL round-bottom flask was added the solution of corresponding *N*-methyl-4-nitroaniline S1a (2.0 mmol) in benzene (15 mL) and K_2CO_3 (0.42 g, 3.0 mmol, 1.5 equiv). The mixture was stirred and added slowly with acryloyl chloride S2a (0.31 g, 3.0 mmol, 1.5 equiv) under argon atmosphere. Then the reaction mixture was refluxed at 80 ℃ for 12~24 h, cooled to room temperature, and quenched with water (50 mL). The result solution was extracted with DCM (15 mL × 3). The combined organic layer was washed with brine (15 mL × 3), dried over Na_2SO_4 and concentrated. The residue was purified by flash chromatography on a silica gel using petroleum ether and ethyl acetate (15:1~10:1, v/v) as the eluent to give corresponding substrates **1h**–**1k**.

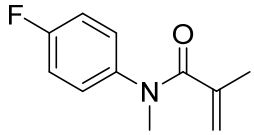
***N*-Methyl-*N*-phenylmethacrylamide (1a)**



General procedure 4 (A) was followed to obtain **1a** (0.31 g, 1.77 mmol, 95 %) as a white solid. **Mp** 60–61 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.33 (m, 2H, Ar-H), 7.28 – 7.25 (m, 1H, Ar-H), 7.15 (d, J = 1.4 Hz, 1H, Ar-H), 7.13 (d, J = 1.1 Hz, 1H, Ar-H), 5.04 (s, 1H, $=CH_2$), 4.99 (s, 1H, $=CH_2$), 3.35 (s, 3H, N-CH_3), 1.76 (s, 3H, CH_3). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 172.0, 144.7, 140.7, 129.2, 126.9, 126.5, 119.4, 37.7, 20.3.

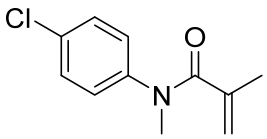
***N*-(4-Fluorophenyl)-*N*-methylmethacrylamide (1b)**



General procedure 4 (A) was followed to obtain **1b** (0.27 g, 1.41 mmol, 88%) as a dark brown oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.13 (d, J = 4.9 Hz, 1H, Ar-H), 7.10 (d, J = 4.9 Hz, 1H, Ar-H), 7.06 (d, J = 4.9 Hz, 1H, Ar-H), 7.02 (d, J = 4.9 Hz, 1H, Ar-H), 5.06 (s, 1H, $=CH_2$), 4.98 (s, 1H, $=CH_2$), 3.32 (s, 3H, N-CH_3), 1.77 (s, 3H, CH_3). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 171.9, 162.4, 159.9, 140.5, 128.3, 128.2, 119.4, 116.2, 116.0, 37.8, 20.3.

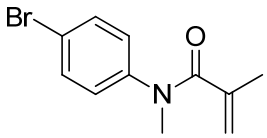
***N*-(4-Chlorophenyl)-N-methylmethacrylamide (1c)**



General procedure 4 (A) was followed to obtain **1c** (0.27 g, 1.29 mmol, 91%) as a white solid. **Mp** 60–61 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 (d, J = 8.7 Hz, 2H, Ar-H), 7.02 (d, J = 8.7 Hz, 2H, Ar-H), 5.11 – 5.04 (m, 1H, $=CH_2$), 5.01 – 4.96 (m, 1H, $=CH_2$), 3.33 (s, 3H, N-CH_3), 1.81 – 1.77 (m, 3H, CH_3). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 171.8, 143.2, 140.4, 132.5, 129.4, 127.7, 119.7, 37.6, 20.3.

***N*-(4-Bromophenyl)-*N*-methylmethacrylamide (1d)**

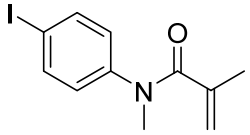


General procedure 4 (A) was followed to obtain **1c** (0.28 g, 1.10 mmol, 97%) as a purple solid. **Mp** 77–78 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 (d, J = 8.7 Hz, 2H, Ar-H), 7.02 (d, J = 8.7 Hz, 2H, Ar-H), 5.11 – 5.04 (m, 1H, $=CH_2$), 5.01 – 4.96 (m, 1H, $=CH_2$), 3.33 (s, 3H, N-CH_3),

1.81 – 1.77 (m, 3H, CH_3). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 171.8, 143.7, 140.4, 132.4, 128.1, 120.4, 119.8, 37.6, 20.3.

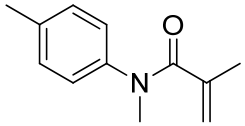
***N*-(4-Iodophenyl)-*N*-methylmethacrylamide (1e)**



General procedure 4 (A) was followed to obtain **1e** (0.24 g, 0.80 mmol, 91%) as a brown solid. **Mp** 107–108 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 (d, J = 8.4 Hz, 2H, Ar-H), 6.89 (d, J = 8.5 Hz, 2H, Ar-H), 5.08 (s, 1H, =CH_2), 4.99 (s, 1H, =CH_2), 3.32 (s, 3H, N-CH_3), 1.78 (s, 3H, CH_3). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 171.8, 144.4, 140.3, 138.4, 128.3, 119.9, 91.6, 77.4, 77.1, 76.7, 37.6, 21.5, 20.3.

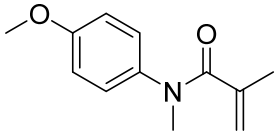
***N*-Methyl-*N*-(*p*-tolyl)methacrylamide (1f)**



General procedure 4 (A) was followed to obtain **1f** (0.30 g, 1.59 mmol, 96%) as a yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.14 (d, J = 8.1 Hz, 2H, Ar-H), 7.02 (d, J = 8.3 Hz, 2H, Ar-H), 5.02 (s, 1H, =CH_2), 4.99 (s, 1H, =CH_2), 3.32 (s, 3H, N-CH_3), 2.35 (s, 3H, Ar-CH_3), 1.76 (s, 3H, CH_3). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 172.0, 142.1, 140.8, 136.8, 129.8, 126.3, 119.1, 37.7, 21.0, 20.4.

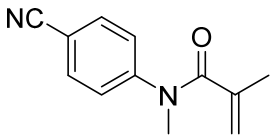
***N*-(4-Methoxyphenyl)-*N*-methylmethacrylamide (1g)**



General procedure 4 (A) was followed to obtain **1g** (0.32 g, 1,53 mmol, 92%) as a purple oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.05 (d, J = 8.9 Hz, 2H, Ar-H), 6.86 (d, J = 8.9 Hz, 2H, Ar-H), 5.03 (s, 1H, =CH_2), 4.99 (s, 1H, =CH_2), 3.81 (s, 3H, O-CH_3), 3.31 (s, 3H, N-CH_3), 1.74 (s, 3H, CH_3). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 172.3, 158.3, 140.8, 127.7, 114.4, 77.5, 77.1, 76.8, 55.4, 20.4.

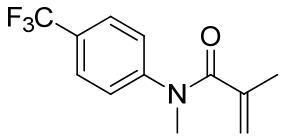
***N*-(4-Cyanophenyl)-*N*-methylmethacrylamide (1h)**



General procedure 4 (B) was followed to obtain **1h** (0.24 g, 1.20 mmol, 79%) as a white solid. **Mp** 80–81 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (d, J = 8.7 Hz, 2H, Ar-H), 7.26 (d, J = 6.3 Hz, 2H, Ar-H), 5.15 (m, 1H, $=CH_2$), 5.00 – 4.99 (m, 1H, $=CH_2$), 3.39 (s, 3H, N-CH_3), 1.88 – 1.79 (m, 3H, CH_3). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 171.7, 148.7, 140.1, 133.2, 126.5, 120.5, 118.2, 110.1, 37.4, 20.1.

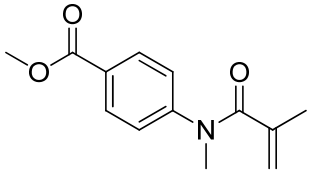
***N*-Methyl-*N*-(4-(trifluoromethyl)phenyl)methacrylamide (1i)**



General procedure 4 (B) was followed to obtain **1i** (0.26 g, 1.06 mmol, 93%) as a yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (d, J = 8.4 Hz, 2H, Ar-H), 7.27 (d, J = 3.4 Hz, 2H, Ar-H), 5.15 – 5.07 (m, 1H, $=CH_2$), 5.04 – 4.95 (m, 1H, $=CH_2$), 3.38 (s, 3H, N-CH_3), 1.87 – 1.77 (m, 3H, CH_3). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 171.8, 147.8, 140.2, 128.6 (q, J = 432.9 Hz), 126.4, 126.3 (q, J = 3.7 Hz), 120.2, 37.5, 20.2.

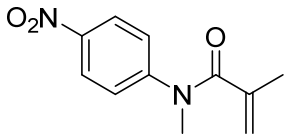
***N*-Methyl 4-(*N*-methylmethacrylamido)benzoate (1j)**



General procedure 4 (B) was followed to obtain **1j** (0.23 mg, 1.0 mmol, 83%) as a white solid. **Mp** 58–59 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (d, J = 8.6 Hz, 2H, Ar-H), 7.21 (d, J = 8.6 Hz, 2H, Ar-H), 5.10 – 5.07 (m, 1H, $=CH_2$), 5.02 – 4.97 (m, 1H, $=CH_2$), 3.92 (s, 3H, -OCH_3), 3.39 (s, 3H, N-CH_3), 1.84 – 1.78 (m, 3H, CH_3). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 171.8, 166.2, 148.8, 140.4, 130.7, 128.3, 125.9, 120.1, 52.2, 37.4, 20.1.

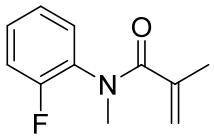
***N*-Methyl-*N*-(4-nitrophenyl)methacrylamide (1k)**



General procedure 4 (B) was followed to obtain **1k** (0.22 g, 0.10 mmol, 83%) as a yellow solid. **Mp** 76–77 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.23 (d, J = 9.1 Hz, 2H, Ar-H), 7.31 (d, J = 9.1 Hz, 2H, Ar-H), 5.19– 5.15 (m, 1H, =CH_2), 5.04 – 4.99 (m, 1H, =CH_2), 3.42 (s, 3H, N-CH_3), 1.90 – 1.85 (m, 3H, CH_3). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 171.72, 150.40, 145.50, 140.02, 126.14, 124.69, 120.70, 37.44, 20.07.

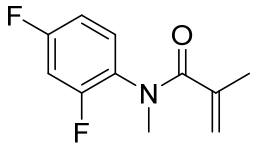
***N*-(2-Fluorophenyl)-*N*-methylmethacrylamide (1l)**



General procedure 4 (A) was followed to obtain **1l** (0.30 g, 1.55 mmol, 97 %) as a yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 – 7.26 (m, 1H, Ar-H), 7.20 – 7.08 (m, 3H, Ar-H), 5.01 (s, 1H, =CH_2), 4.94 (s, 1H, =CH_2), 3.30 (s, 3H, N-CH_3), 1.83 (s, 3H, CH_3). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 171.9, 143.5, 141.2, 129.1, 127.2, 126.5, 120.9, 29.7, 19.9.

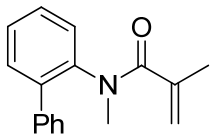
***N*-(2,4-Difluorophenyl)-*N*-methylmethacrylamide (1m)**



General procedure 4 (A) was followed to obtain **1m** (0.26 g, 1.23 mmol, 88 %) as a yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.75 (d, J = 1.8 Hz, 1H, Ar-H), 6.72 (d, J = 1.8 Hz, 1H, Ar-H), 6.70 (s, 1H, Ar-H), 5.15 (s, 1H, =CH_2), 5.05 (s, 1H, =CH_2), 3.34 (s, 3H, N-CH_3), 1.84 (s, 3H, CH_3). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 171.7, 164.3, 164.2, 161.8, 161.7, 146.9, 140.2, 127.1, 120.0, 37.5, 20.1.

***N*-([1,1'-Biphenyl]-2-yl)-*N*-methylmethacrylamide (1n)**

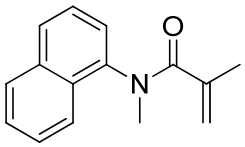


General procedure 4 (A) was followed to obtain **1n** (0.25 g, 1.0 mmol, 92 %) as a white solid. **Mp** 105–106 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.28 (m, 8H, Ar-H), 4.93 (s, 1H, =CH_2), 4.67 (s, 1H, =CH_2), 3.27 (s, 3H, N-CH_3), 1.30 (s, 3H, CH_3). **^{13}C NMR** (100 MHz, $CDCl_3$) δ

170.9, 142.3, 140.0, 138.8, 131.3, 128.9, 128.7, 128.4, 128.1, 127.6, 127.5, 119.6, 38.4, 19.7.

***N*-Methyl-*N*-(naphthalen-1-yl)methacrylamide (1o)**

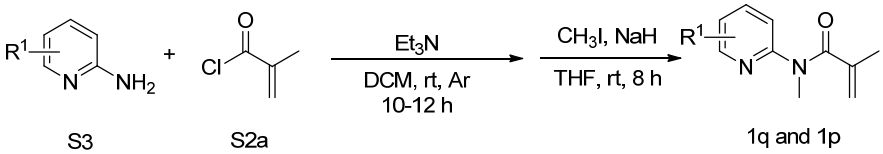


General procedure 4 (A) was followed to obtain **1o** (0.28 g, 1.24 mmol, 98 %) as a brown solid. **Mp** 103–104 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 – 7.79 (m, 2H, Ar-H), 7.38 – 7.34 (m, 1H, Ar-H), 7.53 – 7.45 (m, 2H, Ar-H), 7.36 (d, J = 7.8 Hz, 1H, Ar-H), 7.19 (d, , J = 8.0 Hz, 1H, Ar-H), 4.83 (s, 1H, =CH_2), 4.69 (s, 1H, =CH_2), 3.34 (s, 3H, N-CH_3), 1.62 (s, 3H, CH_3).

^{13}C NMR (100 MHz, $CDCl_3$) δ 173.0, 141.0, 140.5, 134.6, 130.2, 128.7, 128.3, 127.2, 126.5, 125.6, 125.4, 122.8, 117.9, 37.6, 20.4.

2.2.2 General Procedure 5 for Preparation of Substrates 1p and 1q.

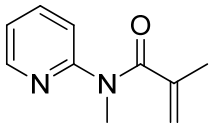


To a 50 mL round-bottom flask was added the solution of corresponding aniline S3 (2.0 mmol) in DCM (15 mL) and triethylamine (0.4 g, 4.0 mmol, 2.0 equiv). The mixture was stirred at 0 ℃, and added slowly methacryloyl chloride S2a (0.25 g, 2.4 mmol, 1.2 equiv) under argon atmosphere. The resulting solution was stirred at room temperature for 6 h, quenched with H_2O (50 mL), and extracted with DCM (15 mL × 3). The combined organic layer was washed with brine (15 mL × 3), dried over Na_2SO_4, and concentrated. The residue was purified by flash chromatography on a silica gel using petroleum ether and ethyl acetate (5:1, v/v) as the eluent to give corresponding intermediates, which were directly used for the next step.

To a 50 mL round-bottom flask was added the solution of corresponding intermediates (2.0 mmol) in THF (10 mL). The mixture was stirred at 0 ℃, and added slowly NaH (0.07 g, 3.0 mmol, 1.5 equiv). Then the reaction mixture was stirred at 0 ℃ for 30 min, and added MeI (0.43 g, 3.0 mmol, 1.5 equiv). The resulting solution was stirred at room temperature for 8 h, quenched with H_2O (50 mL), and extracted with DCM (15 mL × 3). The combined organic layer was washed with brine (15 mL × 3), dried over Na_2SO_4, and concentrated. The residue was purified by flash

chromatography on a silica gel using petroleum ether and ethyl acetate (10:1, v/v) as the eluent to give corresponding compounds **1p** and **1q**.

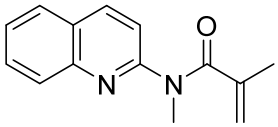
***N*-Methyl-*N*-(pyridin-2-yl)methacrylamide (1p)**



General procedure 5 was followed to obtain **1p** (0.14 g, 0.79 mmol, 42 %) as a brown solid. **Mp** 77–78 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.46 (d, J = 4.8 Hz, 1H, Ar-H), 7.68 – 7.64 (m, 1H, Ar-H), 7.15 (d, J = 7.7 Hz, 1H, Ar-H), 7.14 – 7.10 (m, 1H, Ar-H), 5.08 (s, 1H, $=CH_2$), 5.00 (s, 1H, $=CH_2$), 3.45 (s, 3H, N-CH_3), 1.90 (s, 3H, CH_3). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 172.3, 156.7, 148.7, 141.1, 137.6, 121.2, 120.3, 119.1, 35.4, 20.0.

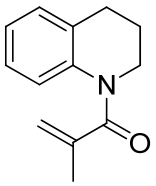
***N*-Methyl-*N*-(quinolin-2-yl)methacrylamide (1q)**



General procedure 5 was followed to obtain **1q** (0.18 g, 0.80 mmol, 46 %) as a brown solid. Mp 140–141 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (d, J = 8.7 Hz, 1H, Ar-H), 7.96 (d, J = 8.5 Hz, 1H, Ar-H), 7.79 (d, J = 8.1 Hz, 1H, Ar-H), 7.73 – 7.69 (m, 1H, Ar-H), 7.54 – 7.50 (m, 1H, Ar-H), 7.27 (d, J = 8.3 Hz, 1H, Ar-H), 5.09 (s, 1H, $=CH_2$), 5.04 (s, 1H, $=CH_2$), 3.58 (s, 3H, N-CH_3), 2.00 (s, 3H, CH_3). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 172.8, 155.7, 146.9, 141.4, 137.5, 130.0, 128.6, 127.4, 126.3, 126.2, 119.4, 119.0, 35.4, 20.0. **HRMS** (ESI) calcd for $C_{14}H_{15}N_2O$ $[M+H]^+$ 227.1179, found 227.1186.

1-(3,4-Dihydroquinolin-1(2*H*)-yl)-2-methylprop-2-en-1-one (1r)

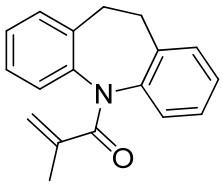


General procedure 4 (A) was followed to obtain **1r** (0.28 g, 1.38 mmol, 92 %) as a yellow solid. **Mp** 57–58 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.20 (d, J = 7.5 Hz, 1H, Ar-H), 7.13 (d, J = 7.1 Hz, 1H, Ar-H), 7.12 – 7.04 (m, 2H, Ar-H), 5.20 – 5.17 (m, 1H, $=CH_2$), 5.16 – 5.12 (m, 1H, $=CH_2$), 3.85 – 3.77 (t, J = 6.0 Hz, 2H), 2.77 (t, J = 6.7 Hz, 2H), 2.02 – 1.96 (m, 2H),

1.87 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 171.5, 141.4, 139.0, 131.4, 128.4, 125.9, 124.8, 124.2, 119.0, 44.0, 26.8, 24.0, 19.9.

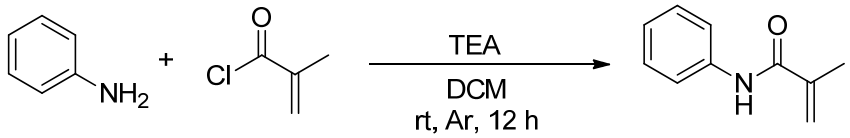
1-(10,11-Dihydro-5*H*-dibenzo[*b*,*f*]azepin-5-yl)-2-methylprop-2-en-1-one (1s)



General procedure 4 (A) was followed to obtain **1s** (0.25 g, 0.95 mmol, 93 %) as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 – 7.14 (m, 8H, Ar-H), 5.14 (s, 1H, $=CH_2$), 5.09 (s, 1H, $=CH_2$), 3.45 (t, J = 8.0 Hz, 2H, CH_2), 2.88 (t, J = 8.0 Hz, 2H, CH_2), 1.84 (s, 3H, CH_3). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 171.0, 140.7, 135.7, 130.1, 128.1, 127.8, 126.8, 118.9, 77.4, 77.1, 76.8, 30.8, 20.4.

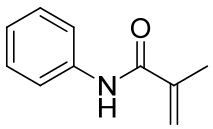
2.2.3 General Procedure 6 for Preparation of S4a.



S3a S2a S4a

To a 50 mL round-bottom flask was added the solution of aniline S3a (5.0 g, 0.054 mol, 1.0 equiv) in DCM (30 mL) and triethylamine (10.87 g, 0.11 mol, 2.0 equiv). The mixture was stirred at 0℃, and added slowly chloride S2a (11.63 g, 0.081 mol, 1.5 equiv) under argon atmosphere. The resulting solution was stirred at room temperature for 12 h, followed by the addition of H_2O (50 mL) to quench excess acyl chloride, extracted with DCM (20 mL × 3). The combined organic layer was washed with brine (15 mL × 3), dried over Na_2SO_4, and concentrated. The residue was purified by flash chromatography on a silica gel using petroleum ether and ethyl acetate (10:1, v/v) as the eluent to give **S4a**.

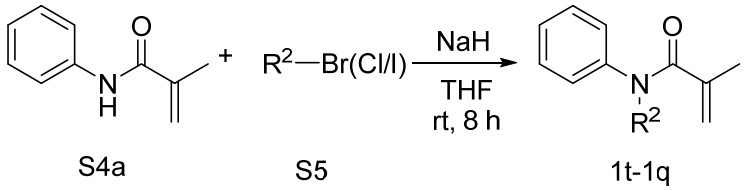
***N*-Phenylmethacrylamide (S4a)**



General procedure 6 was followed to obtain **S4a** (8.2 g, 0.051 mol, 95 %) as a white solid. **Mp** 83–84 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (dr, 1H, NH), 7.56 (d, J = 8.0 Hz, 2H, Ar-H), 7.33 (t, J = 7.9 Hz, 2H, Ar-H), 7.12 (t, J = 7.4 Hz, 1H, Ar-H), 5.79 (s, 1H, =CH_2), 5.50 – 5.42 (m, 1H, =CH_2), 2.06 (s, 3H, CH_3).

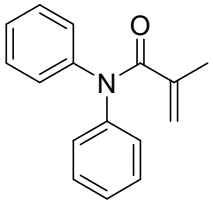
2.2.4 General Procedure 7 for Preparation of Substrates **1t**–**1q**.



S4a S5 1t-1q

To a 50 mL round-bottom flask was added the solution of S4a (2.0 mmol) in THF (10 mL). The mixture was stirred at 0 ℃, and added slowly NaH (3.0 mmol). Then S5 (2.4 mmol, l.2 equiv) was added to the mixture. The resulting solution was stirred at room temperature for 2–8 h, followed by the addition of H_2O (50 mL) to quench excess NaH, and extracted with DCM (15 mL × 3). The combined organic layer was washed with brine (15 mL × 3), dried over Na_2SO_4, and concentrated. The solvent was removed under reduced pressure to get products **1t**–**1q**.

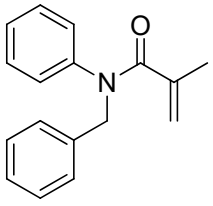
***N,N*-Diphenylmethacrylamide (1t)**



General procedure 7 was followed to obtain **1t** (0.28 g, 1.17 mmol, 94 %) as a white solid. **Mp** 105–106 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 – 7.23 (m, 4H, Ar-H), 7.24 – 7.21 (m, 2H, Ar-H), 7.17 (d, J = 7.3 Hz, 4H, Ar-H), 5.23 (s, 1H, =CH_2), 5.17 (s, 1H, =CH_2), 1.84 (s, 3H, CH_3). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 171.9, 143.5, 141.2, 129.1, 127.2, 126.5, 121.0, 77.4, 77.0, 76.7, 20.0.

***N*-Benzyl-*N*-phenylmethacrylamide (1u)**

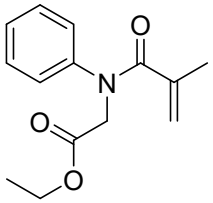


General procedure 7 was followed to obtain **1u** (0.29 g, 1.14 mmol, 92 %) as a yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 – 7.27 (m, 1H, Ar-H), 7.26 – 7.25 (m, 3H, Ar-H), 7.24 – 7.20 (m, 4H, Ar-H), 7.00 – 6.95 (m, 2H, Ar-H), 5.05 – 5.02 (m, 1H, =CH_2),

5.02 – 5.01 (m, 1H, =CH_2), 4.97 (s, 2H, CH_2), 1.81 – 1.74 (m, 3H, CH_3). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 171.9, 143.2, 140.8, 137.6, 129.0, 128.8, 128.4, 127.5, 127.3, 127.1, 119.4, 53.2, 20.4.

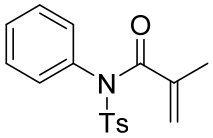
Ethyl *N*-methacryloyl-*N*-phenylglycinate (1v)



General procedure 7 was followed to obtain **1a** (0.29 g, 1.18 mmol, 95 %) as a yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 (d, J = 10.1, 2H, Ar-H), 7.30 – 7.27 (m, 1H, Ar-H), 7.26 – 7.23 (m, 2H, Ar-H), 5.08 (d, J = 4.0, 2H, =CH_2), 4.44 (s, 2H, CH_2), 4.20 (q, J = 7.1 Hz, 2H, O-CH_2), 1.78 (s, 3H, CH_3), 1.28 (t, J = 7.1 Hz, 3H, OCH_2-CH_3). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 172.0, 169.0, 143.6, 140.0, 129.2, 127.3, 127.1, 120.2, 61.3, 51.7, 20.1, 14.1.

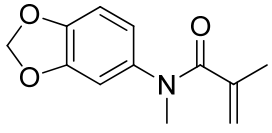
***N*-Phenyl-*N*-tosylmethacrylamide (1w)**



General procedure 7 was followed to obtain **1w** (0.36 g, 1.14 mmol, 92 %) as a white solid. **Mp** 128–129 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (d, J = 8.4 Hz, 2H, Ar-H), 7.42 – 7.34 (m, 3H, Ar-H), 7.30 (d, J = 8.0 Hz, 2H, Ar-H), 7.16 – 7.14 (m, 1H, Ar-H), 7.14 – 7.12 (m, 1H, Ar-H), 5.37 – 5.36 (m, 1H, =CH_2), 5.30 – 5.20 (m, 1H, =CH_2), 2.44 (s, 3H, N-CH_3), 1.68 – 1.65 (m, 3H, CH_3). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 170.9, 144.8, 139.4, 137.2, 135.3, 130.0, 129.4, 129.2, 129.19, 124.3, 21.7, 19.2.

***N*-(Benzo[*d*][1,3]dioxol-5-yl)-*N*-methylmethacrylamide (1x)**

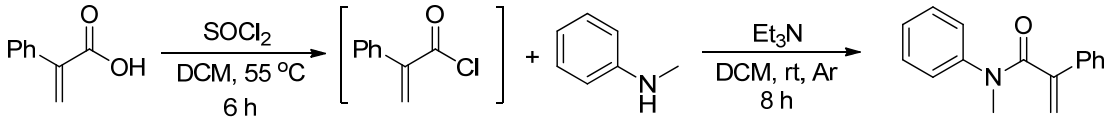


General procedure 4 (A) was followed to obtain **1x** (0.27 g, 1.23 mmol, 92 %) as a brown solid. **Mp** 94–95 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.75 (d, J = 8.1 Hz, 1H, Ar-H), 6.63 (d, J = 2.0 Hz, 1H, Ar-H), 6.59 (dd, J = 8.1, 2.1 Hz, 1H, Ar-H), 6.00 (s, 2H, CH_2), 5.05 (s, 1H, =CH_2),

5.02 (s, 1H, =CH_2), 3.29 (s, 3H, N-CH_3), 1.78 (s, 3H, CH_3). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 172.1, 148.1, 146.5, 140.8, 138.6, 120.1, 118.9, 108.2, 107.8, 101.7, 37.9, 20.4.

2.2.5 General Procedure 8 for Preparation of Substrates **1y**.

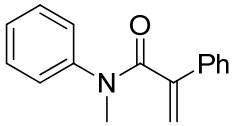


S6a S2b S1a 1y

S6a (2.0 mmol) and DCM (10 mL) were added to a 50 mL round-bottom flask. The mixture was stirred at 0 ℃, and added slowly thionylchloride (3.0 mmol), then refluxed at 55 ℃ for 6 h. The solvent was removed under reduced pressure to get product **S2b**, which was used directly to the next step.

To a 50 mL round-bottom flask was added the solution of aniline **S1a** (2.0 mmol) in DCM (15 mL) and triethylamine (0.4 g, 4.0 mmol, 2.0 equiv). The mixture was stirred at 0 ℃, and added slowly the solution of **S2b** (0.31 g, 3.0 mmol, 1.5 equiv) in DCM (5 mL) under argon atmosphere. The resulting solution was stirred at room temperature for 8 h, followed by the addition of H_2O (50 mL) to quench excess acyl chloride, and extracted with DCM (15 mL × 3). The combined organic layer was washed with brine (15 mL × 3), dried over Na_2SO_4, and concentrated. The residue was purified by flash chromatography on a silica gel using petroleum ether and ethyl acetate (10:1, v/v) as the eluent to give product **1y**.

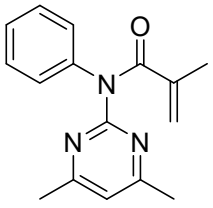
***N*-Methyl-N,2-diphenylacrylamide (1y)**



General procedure 8 was followed to obtain **1y** (0.26 g, 1.22 mmol, 66%) as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24 – 6.87 (m, 9H, Ar-H), 5.47 (s, 1H, =CH_2), 5.37 (s, 1H, =CH_2), 3.40 (s, 3H, N-CH_3). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 170.6, 145.8, 128.9, 128.3, 128.0, 127.9, 127.0, 126.95, 126.93, 126.91, 126.86, 126.1, 37.5.

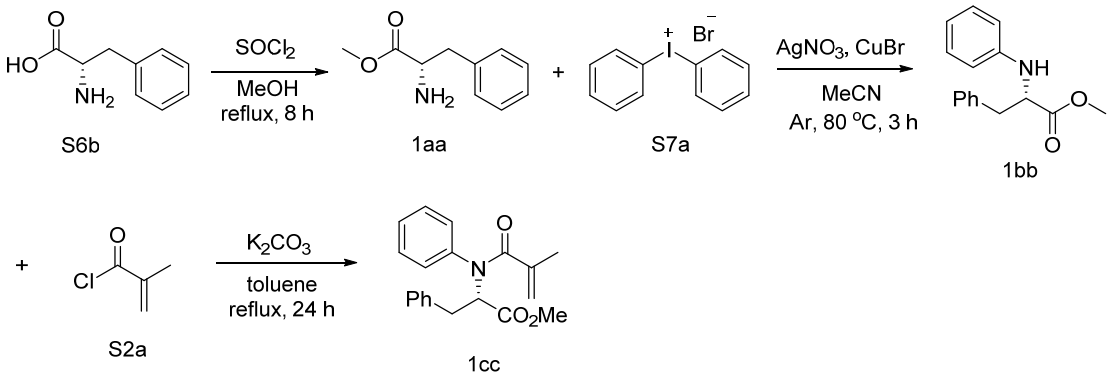
***N*-(4,6-Dimethylpyrimidin-2-yl)-*N*-phenylmethacrylamide (1z)**



General procedure 4 (A) was followed to obtain **1z** (0.31g,1.16 mmol, 58%) as a yellow solid. **Mp** 152–153 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.35 (m, 2H, Ar-H), 7.28 – 7.24 (m, 1H, Ar-H), 7.18 (d, J = 7.6 Hz, 2H, Ar-H), 6.80 (s, 1H, Ar-H), 5.19 (s, 1H, $=CH_2$), 5.05 (s, 1H, $=CH_2$), 2.39 (s, 6H, Ar-H), 2.04 (s, 3H, CH_3). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 173.6, 168.3, 162.1, 143.3, 141.2, 129.0, 127.2, 126.7, 117.7, 117.0, 77.4, 77.1, 76.7, 23.8, 19.7. **HRMS** (ESI) calcd for $C_{16}H_{18}N_3O$ $[M+H]^+$ 268.1444, found 268.1449.

2.2.6 General Procedure 9 for Preparation of Substrates **1cc**.



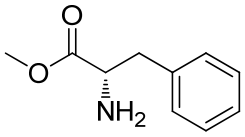
To a 50 mL round-bottom flask was added the solution of **S6b** (0.5 g, 3.0 mmol, 1.0 equiv) in MeOH (25 mL). The mixture was stirred at 0 ℃, and added slowly thionylchloride (0.71 g, 6.0 mol, 5.0 equiv), refluxed under stirring for 4 h. The solvent was removed under reduced pressure to get the product **1aa** (0.52 g).

To a 20 mL Schlenk tube was added **1aa** (0.36 g, 2.0 mmol, 1.0 equiv), diphenyliodonium bromide **S7a** (0.79 g, 2.2 mmol, 1.1 equiv), silver nitrate (0.37 g, 2.2 mmol, 1.1 equiv) and CuBr (2.87 mg, 0.02 mmol, 1.0 %mol) and MeCN (10 mL) under argon atmosphere. The mixture was refluxed under stirring for 3 h, followed by the addition of H_2O (50 mL), and extracted with DCM (15 mL × 3). The combined organic layer was washed with brine (15 mL × 3), dried over Na_2SO_4, and concentrated. The residue was purified by flash chromatography on a silica gel using petroleum ether and ethyl acetate (8:1, v/v) as the eluent to give product **1bb**.

To a 50 mL round-bottom flask was added the solution of **1bb** (0.51 g, 2.0 mmol, 1.0 equiv) in benzene (15 mL) and K_2CO_3 (0.42 g, 3.0 mmol, 1.5 equiv). Then the reaction mixture was added slowly with acryloyl chloride **S2a** (0.31 g, 3.0 mmol, 1.5 equiv) under argon atmosphere, refluxed under stirring for 24 h. After cooling to room temperature, the reaction mixture was quenched with water (50 mL) and extracted with DCM (15 mL × 3). The combined organic layer was washed with brine

(15 mL × 3), dried over Na_2SO_4, and concentrated. The residue was purified by flash chromatography on a silica gel using petroleum ether and ethyl acetate (5:1, v/v) as the eluent to give product **1cc**.

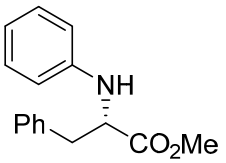
(*S*)-Methyl 2-amino-3-phenylpropanoate (1aa)



General procedure 9 was followed to obtain **1aa** (0.52 g, 2.88 mmol, 96 %) as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 – 7.18 (m, 5H, Ar-H), 3.76 – 3.73 (m, 1H, CO-CH), 3.72 (s, 3H, O-CH_3), 3.09 (dd, J = 13.5, 5.2 Hz, 1H, Ar-CH_2), 2.86 (dd, J = 13.5, 7.9 Hz, 1H, Ar-CH_2), 1.48 (s, 2H, NH_2).

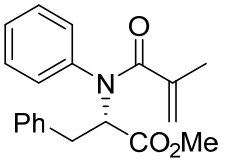
(*S*)-Methyl 3-phenyl-2-(phenylamino)propanoate (1bb)



General procedure 9 was followed to obtain **1bb** (0.42 g, 1.66 mmol, 83 %) as a yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 – 7.24 (m, 3H, Ar-H), 7.22 – 7.13 (m, 4H, Ar-H), 6.76 – 6.72 (m, 1H, Ar-H), 6.60 (d, J = 8.4 Hz, 2H, Ar-H), 4.37 (t, J = 6.2 Hz, 1H, CH), 4.17 (dr, 1H, NH), 3.66 (s, 3H, O-CH_3), 3.13 (qd, J = 13.6, 6.2 Hz, 2H, CH_2).

(*S*)-Methyl 3-phenyl-2-(*N*-phenylmethacrylamido)propanoate (1cc)

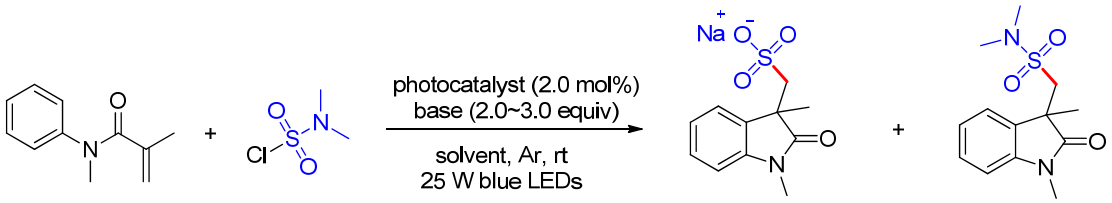


General procedure 9 was followed to obtain **1bb** (0.60 g, 1.84 mmol, 92 %) as a yellow solid. **Mp** 79–80 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 – 7.27 (m, 3H, Ar-H), 7.21 – 7.12 (m, 5H, Ar-H), 6.61 – 6.57 (m, 2H, Ar-H), 5.00 – 4.95 (s, 1H, =CH_2), 4.89 (s, 1H, =CH_2), 4.56 (dd, J = 10.5, 5.3 Hz, 1H, CH), 3.80 (s, 3H, O-CH_3), 3.52 – 3.39 (m, 2H, CH_2), 1.67 (s, 3H, CH_3). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 172.0, 171.0, 140.4, 138.3, 129.6, 128.9, 128.6, 127.6, 127.3, 126.8, 119.9, 65.4, 52.5, 34.8, 19.9. **HRMS** (ESI) calcd for $C_{20}H_{22}NO_3$ $[M+H]^+$ 324.1594, found 324.1598.

3. Investigation of the Key Reaction Parameters.

Table S1. Screening of photocatalysts and base.



1a 2b 3a 4a

entry	photocatalysts	base	3a yield (%)	4a yield (%)
1[a]	Ir{dF(CF$_3$)ppy}$_2$(dtbbpy)PF$_6$	K$_2$HPO$_4$	32	20
2[a]	Ir{dF(CF$_3$)ppy}$_2$(dtbbpy)PF$_6$	Na$_2$HPO$_4$	44	22
3[a]	Ir{dF(CF$_3$)ppy}$_2$(dtbbpy)PF$_6$	NaOAc	34	≤5
4[a]	Ir{dF(CF$_3$)ppy}$_2$(dtbbpy)PF$_6$	K$_2$CO$_3$	87	0
5[a]	Ir{dF(CF$_3$)ppy}$_2$(dtbbpy)PF$_6$	Na$_2$CO$_3$	92	0
6[a]	Ir{dF(CF$_3$)ppy}$_2$(dtbbpy)PF$_6$	NaOH	89	0
7[a]	Ir{dF(CF$_3$)ppy}$_2$(dtbbpy)PF$_6$	Na$_2$CO$_3$	21	0
8[a]	Ir(dtbbpy)(ppy)$_2$PF$_6$	Na$_2$CO$_3$	62	28
9[a]	Ir(ppy)$_3$	Na$_2$CO$_3$	23	0
10[a]	Ru(bpy)$_3$Cl$_2$.6H$_2$O	Na$_2$CO$_3$	16	0
11[a]	Eosin Y	Na$_2$CO$_3$	0	0
12[b]	Ir(btp)$_2$Ala	Na$_2$CO$_3$	0	0
13[b]	Ir(btp)$_2$Ala	K$_2$HPO$_4$	0	0
14[b]	Ir(btp)$_2$Ala	NaOAc	0	94
15[b]	Ir(btp)$_2$Gly	NaOAc	0	74
16[b]	Ir(btp)$_2$Leu	NaOAc	0	81
17[b]	Ir(btp)$_2$(*t*-Leu)	NaOAc	0	70

[a] Reaction conditions: alkene 1a (0.3 mmol), 2a (0.9 mmol), base (0.9 mmol), photocatalyst (2.0 mol%), MeCN (2.0 mL) under 25 W blue LED irradiation (λ max = 480 nm) for 36 h. Yields of isolated products. [b] Reaction conditions: alkene 1a (0.3 mmol), 2a (0.75 mmol), base (0.75 mmol), photocatalyst (2.0 mol%), MeCN (2.0 mL) under 25 W blue LED irradiation (λ max = 480 nm) for 24 h. Yields of isolated products.

Table S2. Screening of solvent

entry	solvent	3a yield (%)	4a yield (%)
1[a]	MeCN	92	0
2[a]	toluene	≤5	0
3[a]	DMF	56	0
4[a]	DCM	32	0
5[a]	THF	≤5	0
6[b]	MeCN	0	94

[a] Reaction conditions: alkene 1a (0.3 mmol), 2a (0.9 mmol), Na$_2$CO$_3$ (0.9 mmol), Ir{dF(CF$_3$)ppy}$_2$(dtbbpy)PF$_6$ (2.0 mol%), solvent (2.0 mL) under 25W blue LED irradiation (λ max = 480 nm) for 36 h. Yields of isolated products. [b] Reaction conditions: alkene 1a (0.3 mmol), 2a (0.75 mmol), NaOAc (0.75 mmol), Ir(btp)$_2$Ala (2.0 mol%), solvent (2.0 mL) under 25W blue LED irradiation (λ max = 480 nm) for 36 h. Yields of isolated products.

Table S3. Screening of ratio of 1a and 2a/base

entry	ratio of 1a and 2a	base	3a yield (%)	4a yield (%)
1[a]	1:1.5	1.5 equiv	61	0
2[a]	1:2.0	2.0 equiv	74	0
3[a]	1:2.5	2.5 equiv	84	0
4[a]	1:3.0	3.0 equiv	92	0
5[b]	1:1.5	1.5 equiv	0	50
6[b]	1:2.0	2.0 equiv	0	77
7[b]	1:2.5	2.5 equiv	0	94

[a] Reaction conditions: alkene 1a (0.3 mmol), 2a, Na_2CO_3, Ir{dF(CF_3)ppy}$_2$(dtbbpy)PF_6 (2.0 mol%), MeCN (2.0 mL) under 25W blue LED irradiation (λ max = 480 nm) for 36 h. Yields of isolated products. [b] Reaction conditions: alkene 1a (0.3 mmol), 2a (0.75 mmol), NaOAc, Ir(btp)$_2$Ala (2.0 mol%), MeCN (2.0 mL) under 25W blue LED irradiation (λ max = 480 nm) for 36 h. Yields of isolated products.

Table S4. Screening of time

entry	time	3a yield (%)	4a yield (%)
1[a]	12 h	46	0
2[a]	24 h	70	0
3[a]	36 h	92	0
4[a]	48 h	89	0
5[b]	12 h	0	87
6[b]	24 h	0	94
7[b]	36 h	0	94

[a] Reaction conditions: alkene 1a (0.3 mmol), 2a (0.9 mmol), Na_2CO_3 (0.9 mmol), Ir{dF(CF_3)ppy}$_2$(dtbbpy)PF_6 (2.0 mol%), MeCN (2.0 mL) under 25W blue LED irradiation (λ max = 480 nm). Yields of isolated products. [b] Reaction conditions: alkene 1a (0.3 mmol), 2a (0.75 mmol), NaOAc (0.75 mmol), Ir(btp)$_2$Ala (2.0 mol%), MeCN (2.0 mL) under 25W blue LED irradiation (λ max = 480 nm). Yields of isolated products.

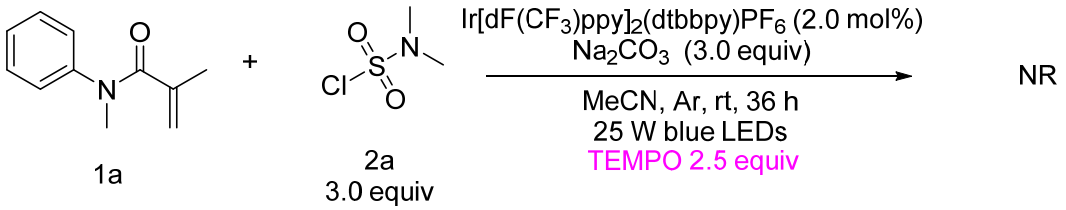
Table S4. Screening of Light Source

entry	light source	3a yield (%)	4a yield (%)
1[a]	5 W blue	44	0
2[a]	10 W blue	48	0
3[a]	25 W blue	92	0
4[b]	25 W blue	0	94

[a] Reaction conditions: alkene 1a (0.3 mmol), 2a (0.9 mmol), Na_2CO_3 (0.9 mmol), Ir{dF(CF_3)ppy}$_2$(dtbbpy)PF_6 (2.0 mol%), MeCN (2.0 mL) under blue LED irradiation (λ max = 480 nm) for 36 h. Yields of isolated products. [b] Reaction conditions: alkene 1a (0.3 mmol), 2a (0.75 mmol), NaOAc (0.75 mmol), Ir(btp)$_2$Ala (2.0 mol%), MeCN (2.0 mL) under 25W blue LED irradiation (λ max = 480 nm) for 24 h. Yields of isolated products.

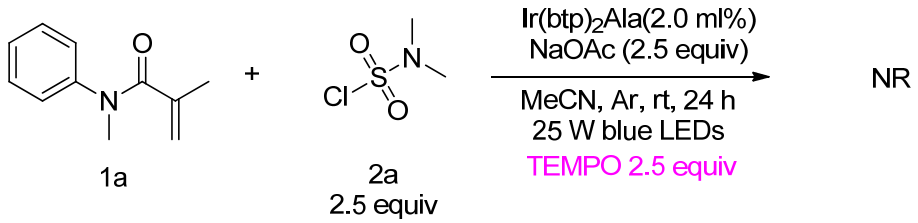
4. Investigation of the mechamism.

4.1 General Procedure 10 for Mechanistic Study (a)



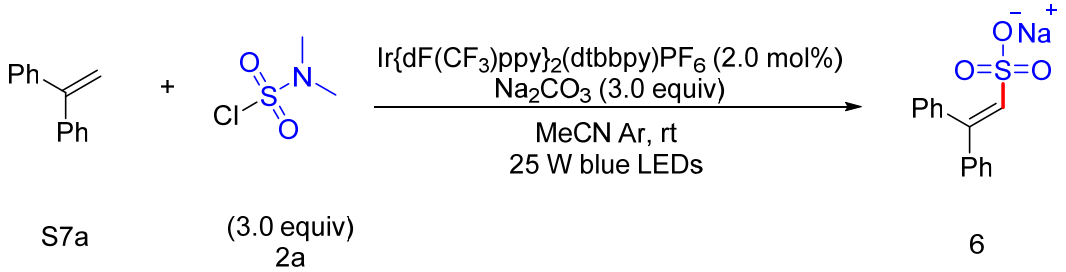
Under argon atmosphere, to a 10 mL Schlenk tube was added **1a** (52.6 mg, 0.3 mmol, 1.0 equiv), dimethylsulfamoyl chloride (129.2 mg, 0.9 mmol, 3.0 equiv), Na_2CO_3 (95.4 mg, 0.9 mmol, 3.0 equiv), TEMPO (117.18 mg, 0.75 mmol, 2.5 equiv), Ir{dF(CF_3)ppy}$_2$(dtbbpy)PF_6 (6.7 mg, 0.06mmol, 2.0 mol%) and 2 mL MeCN. The reaction mixture was stirred at room temperature under 25 W blue LED irradiation for 36 hours.

4.2 General Procedure 11 for Mechanistic Study (b)



Under argon atmosphere, to a 10 mL Schlenk tube was added **1a** (52.6 mg, 0.3 mmol, 1.0 equiv), NaOAc (61.5 mg, 0.75 mmol, 2.5 equiv), dimethylsulfamoyl chloride (0.75 mmol, 2.5 equiv), TEMPO (117.18 mg, 0.75 mmol, 2.5 equiv), Ir(btp)$_2$Ala (4.5 mg, 0.06mmol, 2.0 mol%) and 2 mL MeCN. The reaction mixture was stirred at room temperature under 25 W blue LED irradiation for 24 hours.

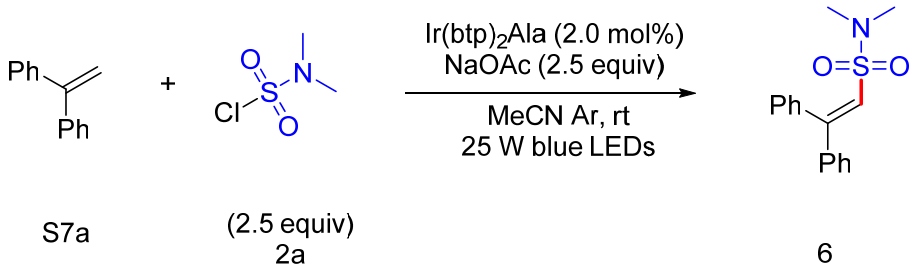
4.3 General Procedure 12 for Mechanistic Study (c)



Under argon atmosphere, to a 10 mL Schlenk tube was added **S7a** (54.1 mmol, 0.3 mmol, 1.0 equiv), dimethylsulfamoyl chloride (129.2 mg, 0.9 mmol, 3.0 equiv), Na_2CO_3 (95.4 mg, 0.9 mmol, 3.0 equiv), Ir{dF(CF_3)ppy}$_2$(dtbbpy)PF_6 (6.7 mg, 0.06mmol, 2.0 mol%) and 2 mL MeCN. The reaction mixture was stirred at room temperature under 25 W blue LED irradiation for 36 hours. The solution was concentrated in vacuo. The product was determined by HRMS (ESI) calcd for

$C_{14}H_{11}O_3S$ $[M\text{-}Na]^-$ 259.0434, found 259.0433.

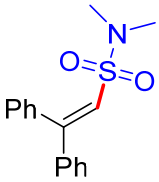
4.4 General Procedure 13 for Mechanistic Study (d)



S7a (2.5 equiv) 2a 6

Under argon atmosphere, to a 10 mL Schlenk tube was added **S7a** (54.1 mg, 0.3 mmol, 1.0 equiv), dimethylsulfamoyl chloride (107.7 mg, 0.75 mmol, 2,5 equiv), NaOAc (61.5 mg, 0.75 mmol, 2.5 equiv), $Ir(btp)_2Ala$ (4.5 mg, 0.06mmol, 2.0 mol%) and 2 mL MeCN. The reaction mixture was stirred at room temperature under 25 W blue LED irradiation for 24 hours, followed by the addition of H_2O (20 mL), and extracted with DCM (10 mL × 3). The combined organic layer was washed with brine (10 mL × 3), dried over Na_2SO_4, and concentrated. The residue was purified by flash chromatography on a silica gel using petroleum ether and ethyl acetate (8:1, v/v) as the eluent to give product **6**.

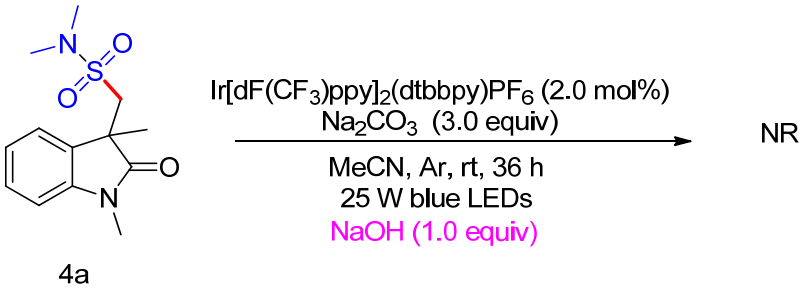
***N,N*-Dimethyl-2,2-diphenylethene-1-sulfonamide (7)**



General procedure 13 was followed to obtain **7** (49.1 mg, 0.17 mmol, 57 %) as a white solid. **Mp** 141–142 °C.

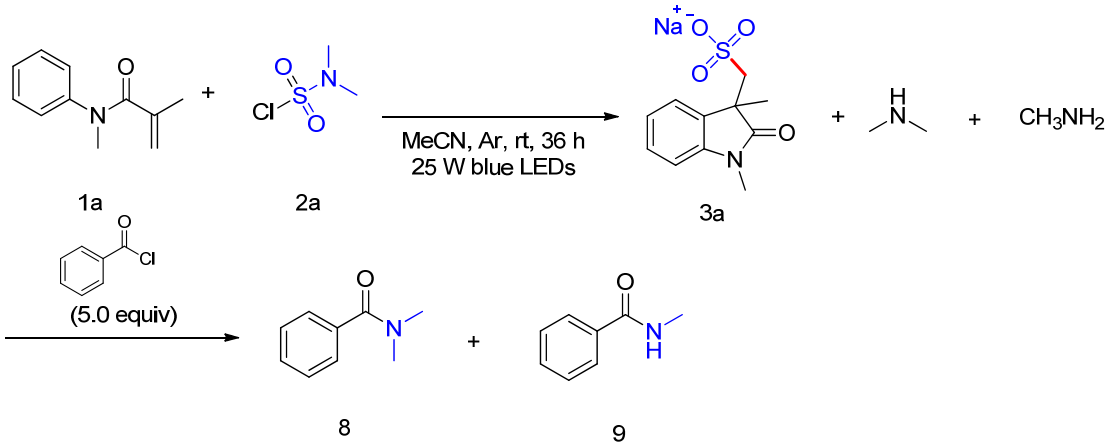
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 – 7.38 (m, 4H, Ar-H), 7.38 – 7.30 (m, 5H, Ar-H), 7.26– 7.24 (m, 1H, Ar-H), 6.66 (s, 1H, CH), 2.67 (s, 6H, N-CH_3). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 154.5, 139.8, 136.6, 130.0, 129.7, 128.9, 128.6, 128.2, 128.0, 122.3, 37.1. HRMS (ESI) calcd for $C_{16}H_{18}NO_2S$ $[M+H]^+$ 288.1053, found 288.1059.

4.5 General Procedure 14 for Mechanistic Study (e)



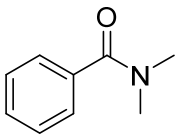
Under argon atmosphere, to a 10 mL Schlenk tube was added **4a** (84.7 mg, 0.3 mmol, 1.0 equiv), Na_2CO_3 (95.4 mg, 0.9 mmol, 3.0 equiv), NaOH (36.0 mg, 0.9 mmol, 3.0 equiv), Ir{dF(CF_3)ppy}$_2$(dtbbpy)PF_6 (6.7 mg, 0.06 mmol, 2.0 mol%) and 2 mL MeCN. The reaction mixture was stirred at room temperature under 25 W blue LED irradiation for 36 hours.

4.6 General Procedure 15 for Mechanistic Study (f)



Under argon atmosphere, to a 10 mL Schlenk tube was added **1** (52.6 mg, 0.3 mmol, 1.0 equiv), dimethylsulfamoyl chloride (129.2 mg, 0.9 mmol, 3.0 equiv), Na_2CO_3 (95.4 mg, 0.9 mmol, 3.0 equiv), Ir{dF(CF_3)ppy}$_2$(dtbbpy)PF_6 (6.7 mg, 0.06 mmol, 2.0 mol%) and 2 mL MeCN. The reaction mixture was stirred at room temperature under 25 W blue LED irradiation for 36 hours. Benzoyl chloride (210.84 mg, 1.5 mmol, 5.0 equiv) was added to the reaction mixture. The resulting solution was stirred at room temperature for 12 h. The solvent was removed under reduced pressure and the residue was purified by flash chromatography on a silica gel using petroleum ether and ethyl acetate (20:1, v/v) as the eluent to give **8** and **9**.

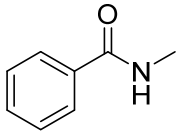
***N,N*-Dimethylbenzamide (8)**



General procedure 15 was followed to obtain **8** (20.6 mg, 0.14 mmol, 46 %) as a white solid. **Mp** 41–43 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 – 7.36 (m, 5H, Ar-H), 3.11 (s, 3H, N-CH_3), 2.97 (s, 3H, N-CH_3).

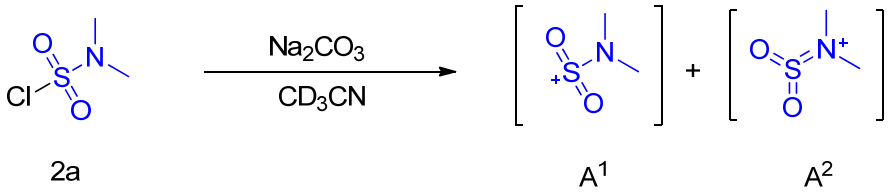
***N*-Methylbenzamide (9)**



General procedure 15 was followed to obtain **8** (10.9 mg, 0.08 mmol, 27 %) as a white solid. **Mp** 78–79 °C.

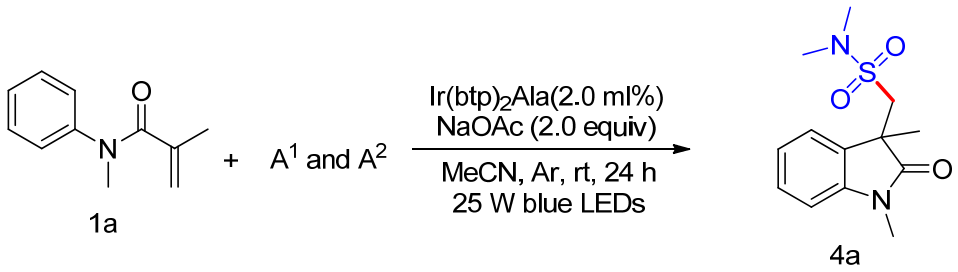
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 – 7.75 (m, 2H, Ar-H), 7.51 – 7.47 (m, 1H, Ar-H), 7.45 – 7.39 (m, 2H, Ar-H), 3.02 (d, J = 4.9 Hz, 3H, N-CH_3).

4.7 General Procedure 16 for Mechanistic Study (g)



Under argon atmosphere, to a 10 mL Schlenk tube was added dimethylsulfamoyl chloride (129.2 mg, 0.9 mmol, 3.0 equiv), Na_2CO_3 (95.4 mg, 0.9 mmol, 3.0 equiv) and 2 mL CD_3CN. The reaction mixture was stirred at room temperature for 12 hours. The product was determined by ^{1}H NMR spectrum, ^{13}C NMR spectrum and **HRMS** (ESI) calcd for $C_2H_6NO_2S$ $[M]^+$ 108.0114, found 108.0111.

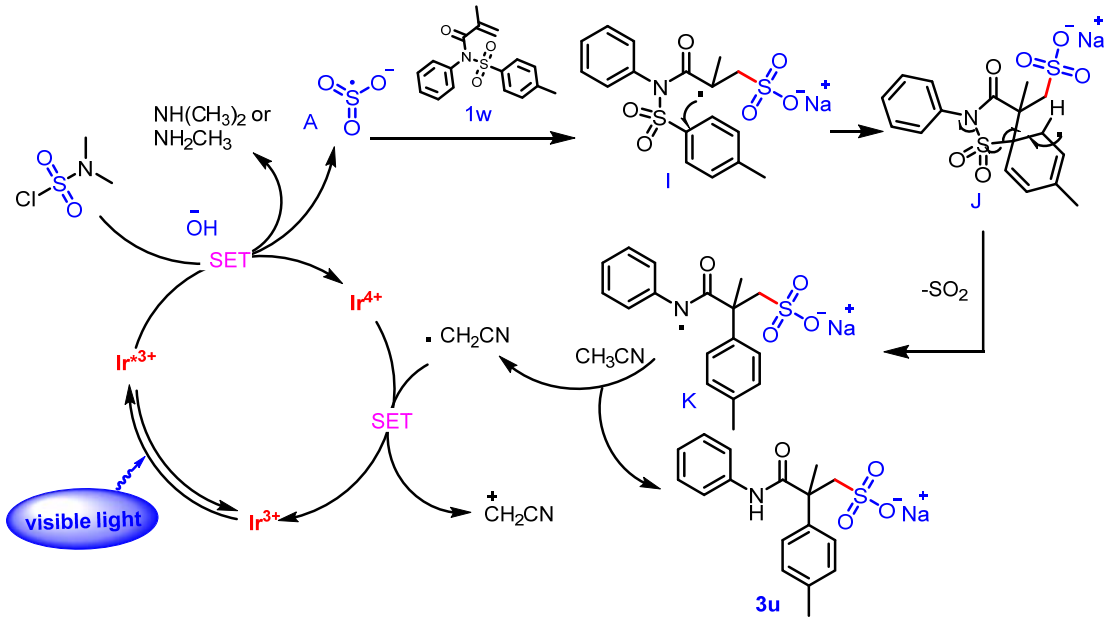
4.8 General Procedure 17 for Mechanistic Study (h)



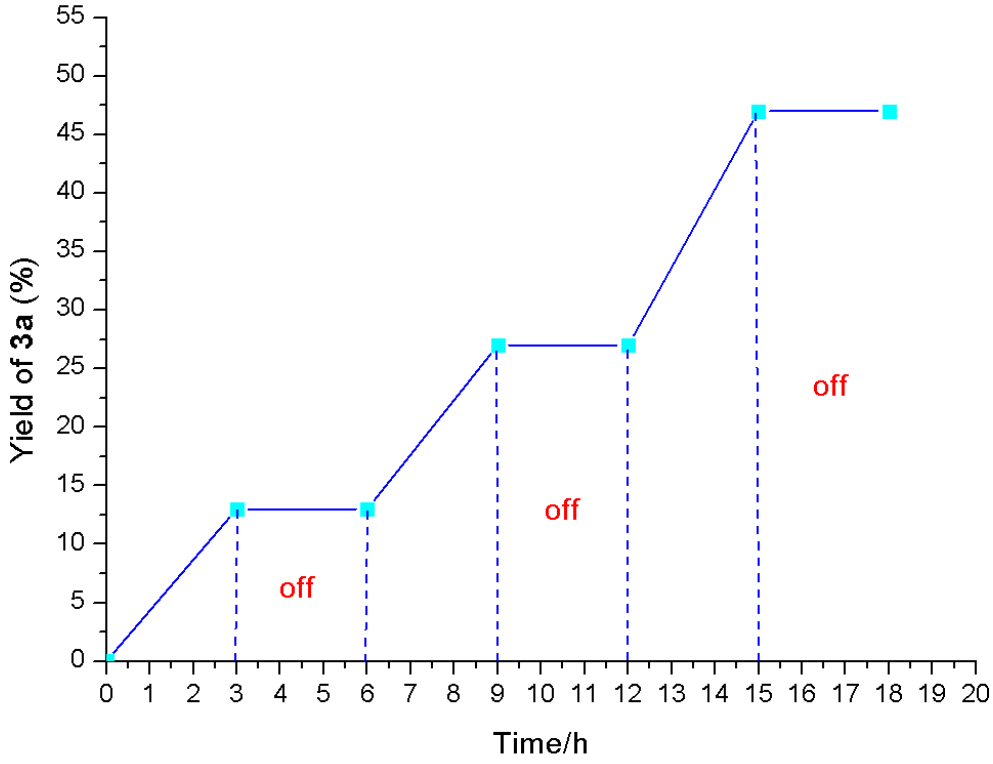
Under argon atmosphere, to a 10 mL Schlenk tube was added dimethylsulfamoyl chloride (0.75 mmol, 2.5 equiv), NaOAc (61.5 mg, 0.75 mmol, 2.5 equiv) and 2 mL MeCN. The reaction mixtue was stirred at room temperature for 24 hours. **1a** (52.6 mg, 0.3 mmol, 1.0 equiv) and $Ir(btp)_2Ala$ (4.5 mg, 0.06mmol, 2.0 mol%) were added

to the reaction mixture. The reaction mixture was stirred at room temperature under 25 W blue LED irradiation for 24 hours.

4.9 Scheme S1: Proposed Mechanism of **3t**



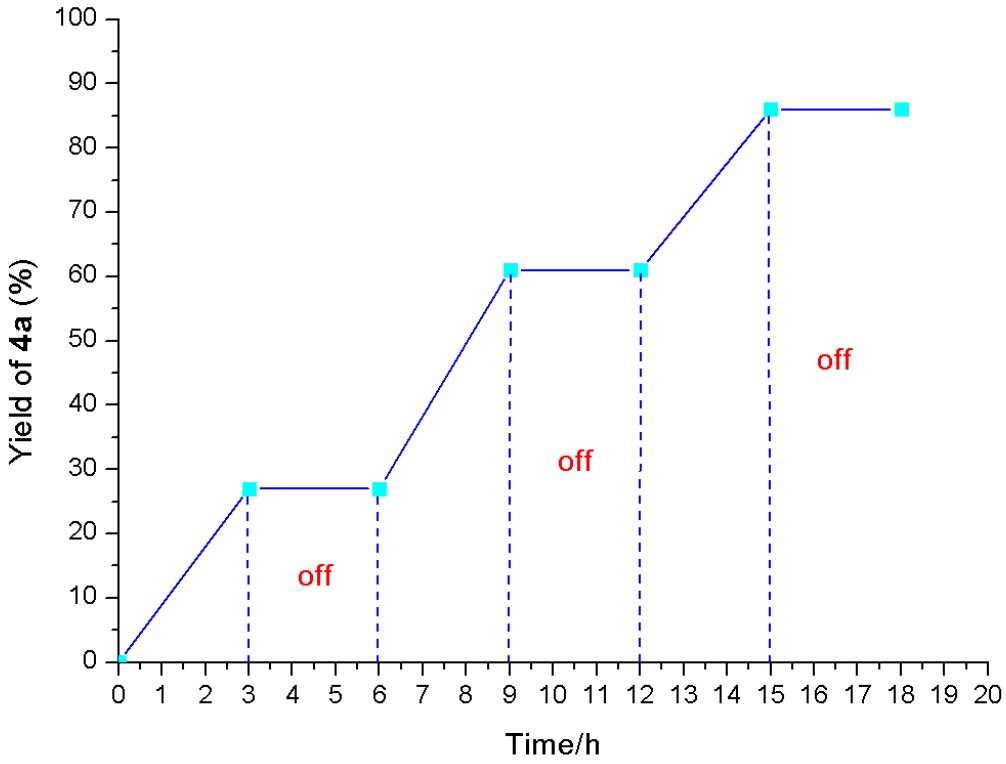
4.10 Light on/off experiment (3a)



Under argon atmosphere, Six standard reaction mixtures in 10 mL Schlenk tubes were charged with **1a** (52.5mg, 0.3 mmol, 1.0 equiv), dimethylsulfamoyl chloride (129.2 mg, 0.9 mmol, 3.0 equiv), Na_2CO_3 (95.4 mg, 0.9 mmol, 3.0 equiv),

$Ir\{dF(CF_3)ppy\}_2(dtbbpy)PF_6$ (6.7 mg, 0.06mmol, 2.0 mol%) and 2 mL MeCN. The mixtures were then stirred rapidly and irradiated with a 25 W Blue LED (approximately 2 cm away from the light source) at room temperature. After 3 h, the Blue LED was turned off, and one tube was removed from the irradiation setup for analysis. The remaining five tubes were stirred in the absence of light for an additional 3 h. Then, one tube was removed for analysis, and the Blue LED was turned back on to irradiate the remaining four reaction mixtures. After an additional 3 h of irradiation, the Blue LED was turned off, and one tube was removed for analysis. The remaining three tubes were stirred in the absence of light for an additional 3 h. Then, a tube was removed for analysis, and the Blue LED was turned back on to irradiate the remaining two reaction mixtures. After 3 h, the Blue LED was turned off, and one tube was removed for analysis. The last tube was stirred in the absence of light for an additional 3 h, and then it was analyzed. The yield was determined by flash chromatography on a silica gel using DCM and methanol (10:1, v/v).

4.11 Light on/off experiment (4a)

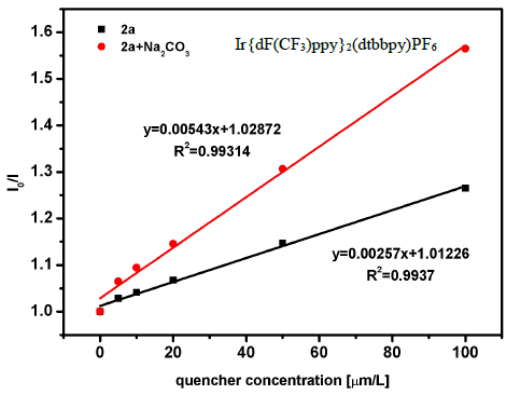


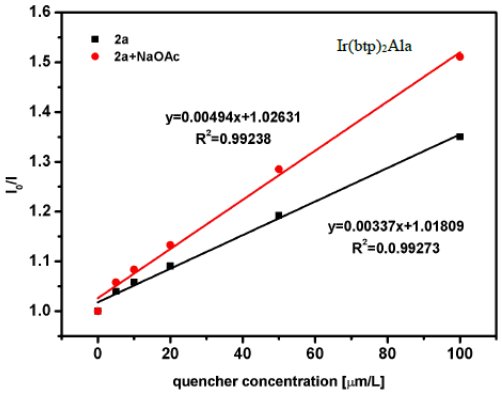
Under argon atmosphere, Six standard reaction mixtures in 10 mL Schlenk tubes were charged with **1a** (52.5mg, 0.3 mmol, 1.0 equiv), dimethylsulfamoyl chloride

(107.7 mg, 0.75 mmol, 2.5 equiv), NaOAc (61.5 mg, 0.75 mmol, 2.5 equiv), $Ir(btp)_2Ala$ (4.5 mg, 0.06mmol, 2.0 mol%) and 2 mL MeCN. The mixtures were then stirred rapidly and irradiated with a 25 W Blue LED (approximately 2 cm away from the light source) at room temperature. After 3 h, the Blue LED was turned off, and one tube was removed from the irradiation setup for analysis. The remaining five tubes were stirred in the absence of light for an additional 3 h. Then, one tube was removed for analysis, and the Blue LED was turned back on to irradiate the remaining four reaction mixtures. After an additional 3 h of irradiation, the Blue LED was turned off, and one tube was removed for analysis. The remaining three tubes were stirred in the absence of light for an additional 3 h. Then, a tube was removed for analysis, and the Blue LED was turned back on to irradiate the remaining two reaction mixtures. After 3 h, the Blue LED was turned off, and one tube was removed for analysis. The last tube was stirred in the absence of light for an additional 3 h, and then it was analyzed. The yield was determined by ^1H NMR with mesitylene as an internal standard.

4.12 Stern-Volmer measurements

Emission intensities were recorded using a F27000 (Hitachi Limited) luminescence spectrophotometer. All $Ir\{dF(CF_3)ppy\}_2(dtbbpy)PF_6$ and $Ir(btp)_2Ala$ solutions were excited at 350 nm and the emission intensity was collected at 475 nm. In a typical experiment, to a 1×10^{-5} mol/L solution of $Ir\{dF(CF_3)ppy\}_2(dtbbpy)PF_6$ or $Ir(btp)_2Ala$ in acetonitrile was added the appropriate amount of a quencher in a screw-top quartz cuvette. After degassing the sample with a stream of argon for 10 minutes, the emission of the sample was collected.



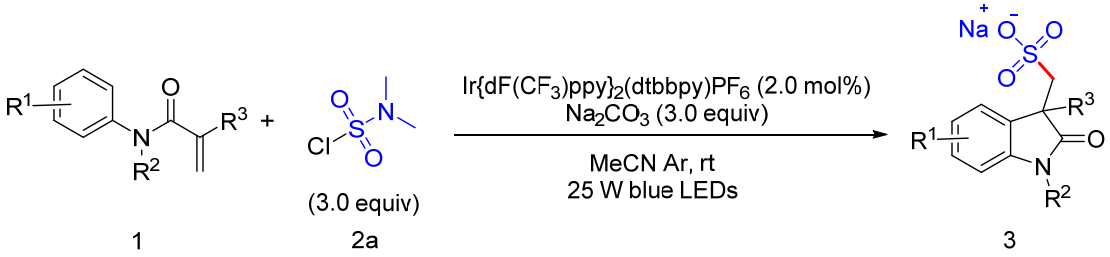


$Ir\{dF(CF_3)ppy\}_2(dtbbpy)PF_6$ emission quenching with **2a** or **2a** + Na_2CO_3

$Ir(btp)_2Ala$ emission quenching with **2a** or **2a** + NaOAc

5. Experimental Procedures and Product Characterization.

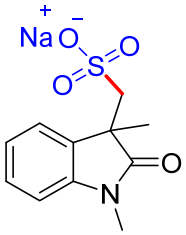
5.1 General Procedure 18 for Sulfonation of Substrates **1**.



1 2a 3

Under argon atmosphere, to a 10 mL Schlenk tube was added **1** (0.3 mmol, 1.0 equiv), dimethylsulfamoyl chloride (129.2 mg, 0.9 mmol, 3.0 equiv), Na_2CO_3 (95.4 mg, 0.9 mmol, 3.0 equiv), $Ir\{dF(CF_3)ppy\}_2(dtbbpy)PF_6$ (6.7 mg, 0.06mmol, 2.0 mol%) and 2 mL MeCN, The reaction mixture was stirred at room temperature under 25 W blue LED irradiation for 36 hours, and concentrated. The residue was purified by flash chromatography on a silica gel using DCM and methanol (10:1, v/v) as the eluent to give **3**.

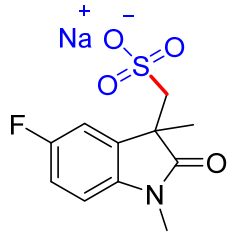
Sodium (1,3-dimethyl-2-oxoindolin-3-yl)methanesulfonate (3a)



General procedure 18 was followed to obtain **3a** (76.6 mg, 0.28 mmol, 92 %) as a colorless oil.

^{1}H NMR (400 MHz, DMSO-*d6*) δ 7.55 (d, J = 7.3 Hz, 1H, Ar-H), 7.22 – 7.18 (m, 1H, Ar-H), 6.97 – 6.91 (m, 2H, Ar-H), 3.08 (s, 3H, N-CH_3), 3.04 (d, J = 13.9 Hz, 1H, CH_2), 2.85 (d, J = 13.9 Hz, 1H, CH_2), 1.28 (s, 3H, CH_3). **^{13}C NMR** (100 MHz, DMSO-*d6*) δ 179.7, 143.3, 133.7, 127.5, 125.6, 121.8, 108.2, 57.3, 46.5, 26.5, 24.4. **HRMS** (ESI) calcd for $C_{11}H_{12}NO_4S$ $[M\text{-}Na]^-$ 254.0493, found 254.0497.

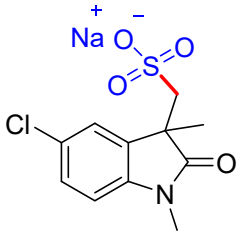
Sodium (5-fluoro-1,3-dimethyl-2-oxoindolin-3-yl)methanesulfonate (3b)



General procedure 18 was followed to obtain **3b** (79.7 mg, 0.27 mmol, 90 %) as a colorless oil.

^{1}H NMR (400 MHz, DMSO-*d6*) δ 7.44 (d, J = 7.7 Hz, 1H, Ar-H), 7.03 (d, J = 8.0 Hz, 1H, Ar-H), 6.91 (dd, J = 7.7, 4.1 Hz, 1H, Ar-H), 3.08 (s, 3H, N-CH_3), 3.08 (d, J = 13.8 Hz, 1H, CH_2), 2.88 (d, J = 13.8 Hz, 1H, CH_2), 1.29 (s, 3H, CH_3). **^{13}C NMR** (100 MHz, DMSO-*d6*) δ 179.0, 159.2, 156.9, 139.2, 135.0 (d, J = 8.0 Hz, 1C), 113.29 (d, J = 4.0 Hz, 1C), 108.2 (d, J = 8.0 Hz, 1C), 56.5, 46.4, 26.2, 23.7. **HRMS** (ESI) calcd for $C_{11}H_{11}FNO_4S$ $[M\text{-}Na]^-$ 272.0398, found 272.0391.

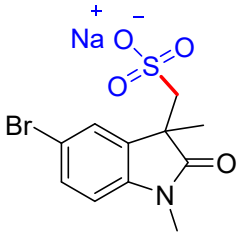
Sodium (5-chloro-1,3-dimethyl-2-oxoindolin-3-yl)methanesulfonate (3c)



General procedure 18 was followed to obtain **3c** (82.3 mg, 0.26 mmol, 88 %) as a white solid. **Mp** 248–249 °C.

^{1}H NMR (400 MHz, DMSO-*d6*) δ 7.60 (d, J = 2.0 Hz, 1H, Ar-H), 7.25 (dd, J = 8.3, 2.1 Hz, 1H, Ar-H), 6.94 (d, J = 8.3 Hz, 1H, Ar-H), 3.09 (d, J = 13.9 Hz, 1H, CH_2), 3.07 (s, 3H, N-CH_3), 2.87 (d, J = 13.9 Hz, 1H, CH_2), 1.27 (s, 3H, CH_3). **^{13}C NMR** (100 MHz, DMSO-*d6*) δ 178.9, 141.9, 135.2, 126.8, 125.4, 109.0, 56.6, 46.2, 26.1, 23.8. **HRMS** (ESI) calcd for $C_{11}H_{11}ClNO_4S$ $[M\text{-}Na]^-$ 288.0103, found 288.0109.

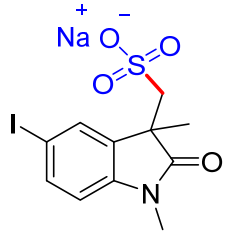
Sodium (5-bromo-1,3-dimethyl-2-oxoindolin-3-yl)methanesulfonate (3d)



General procedure 18 was followed to obtain **3d** (95.1 mg, 0.27 mmol, 89 %) as a white solid. **Mp** 285–287 °C.

^{1}H NMR (400 MHz, DMSO-*d6*) δ 7.72 (d, J = 1.8 Hz, 1H, Ar-H), 7.37 (dd, J = 8.3, 1.8 Hz, 1H, Ar-H), 6.89 (d, J = 8.3 Hz, 1H, Ar-H), 3.06 (s, 3H, N-CH_3), 3.05 (d, J = 13.8 Hz, 1H, CH_2), 2.85 (d, J = 13.8 Hz, 1H, CH_2), 1.27 (s, 3H, CH_3). **^{13}C NMR** (100 MHz, DMSO-*d6*) δ 178.7, 142.4, 135.6, 129.7, 128.0, 113.3, 109.6, 56.7, 46.2, 26.1, 23.8. **HRMS** (ESI) calcd for $C_{11}H_{11}BrNO_4S$ $[M\text{-}Na]^-$ 331.9598, found 331.9595.

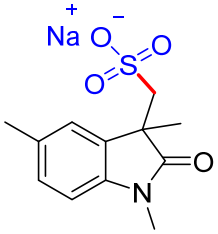
Sodium (5-iodo-1,3-dimethyl-2-oxoindolin-3-yl)methanesulfonate (3e)



General procedure 18 was followed to obtain **3e** (101.6 mg, 0.25 mmol, 84 %) as a white solid. **Mp** 191–193 °C.

^{1}H NMR (400 MHz, DMSO-*d6*) δ 7.85 (d, J = 1.7 Hz, 1H, Ar-H), 7.54 (dd, J = 8.1, 1.7 Hz, 1H, Ar-H), 6.79 (d, J = 8.2 Hz, 1H, Ar-H), 3.18 (d, J = 13.9 Hz, 1H, CH_2), 3.06 (s, 3H, N-CH_3), 2.88 (d, J = 13.9 Hz, 1H, CH_2), 1.26 (s, 3H, CH_3). **^{13}C NMR** (100 MHz, DMSO-*d6*) δ 178.6, 142.9, 135.9, 135.6, 133.4, 110.2, 84.5, 56.7, 46.1, 26.0, 23.9. **HRMS** (ESI) calcd for $C_{11}H_{11}INO_4S$ $[M\text{-}Na]^-$ 379.9459, found 379.9464.

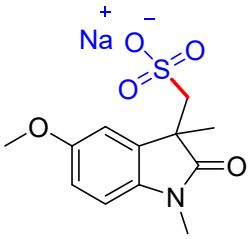
Sodium (1,3,5-trimethyl-2-oxoindolin-3-yl)methanesulfonate (3f)



General procedure 18 was followed to obtain **3f** (78.7 mg, 0.27 mmol, 90 %) as a colorless oil.

^{1}H NMR (400 MHz, DMSO-*d6*) δ 7.40 (s, 1H, Ar-H), 7.00 (d, J = 7.7 Hz, 1H, Ar-H), 6.80 (d, J = 7.9 Hz, 1H, Ar-H), 3.06 (s, 3H, N-CH_3), 3.04 (d, J = 13.8 Hz, 1H, CH_2), 2.82 (d, J = 13.8 Hz, 1H, CH_2), 2.26 (s, 3H, Ar-CH_3), 1.27 (s, 3H, CH_3). **^{13}C NMR** (100 MHz, DMSO-*d6*) δ 179.7, 141.0, 133.8, 130.3, 127.7, 126.4, 107.9, 57.3, 46.5, 26.5, 24.4, 21.4. **HRMS** (ESI) calcd for $C_{12}H_{14}NO_4S$ $[M\text{-}Na]^-$ 268.0649, found 268.0641.

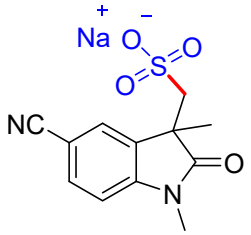
Sodium (5-methoxy-1,3-dimethyl-2-oxoindolin-3-yl)methanesulfonate (3g)



General procedure 18 was followed to obtain **3g** (84.8 mg, 0.28 mmol, 92 %) as a colorless oil.

^{1}H NMR (400 MHz, DMSO-*d6*) δ 7.30 (d, J = 2.5 Hz, 1H, Ar-H), 6.82 (d, J = 8.4 Hz, 1H, Ar-H), 6.76 (dd, J = 8.4, 2.6 Hz, 1H, Ar-H), 3.70 (s, 3H, O-CH_3), 3.05 (s, 3H, N-CH_3), 3.03 (d, J = 13.9 Hz, 1H, CH_2), 2.78 (d, J = 13.9 Hz, 1H, CH_2), 1.28 (s, 3H, CH_3). **^{13}C NMR** (100 MHz, DMSO-*d6*) δ 179.4, 155.3, 136.8, 135.1, 113.5, 111.8, 108.3, 57.1, 55.8, 46.9, 26.6, 24.2. **HRMS** (ESI) calcd for $C_{12}H_{14}NO_5S$ $[M\text{-}Na]^-$ 284.0598, found 284.0596.

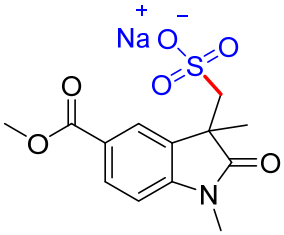
Sodium (5-cyano-1,3-dimethyl-2-oxoindolin-3-yl)methanesulfonate (3h)



General procedure 18 was followed to obtain **3h** (44.4 mg, 0.15 mmol, 49 %) as a white solid. **Mp** 217–219 °C.

^{1}H NMR (400 MHz, DMSO-*d6*) δ 7.86 (s, 1H), 7.69 (d, J = 7.9 Hz, 1H, Ar-H), 7.11 (d, J = 8.1 Hz, 1H, Ar-H), 3.17 (s, 1H, Ar-H), 3.15 (d, J = 13.8 Hz, 1H, CH_2), 3.12 (s, 3H, N-CH_3), 2.98 (d, J = 13.8 Hz, 1H, CH_2), 1.26 (s, 3H, CH_3). **^{13}C NMR** (100 MHz, DMSO-*d6*) δ 179.3, 147.4, 133.9, 132.5, 128.4, 120.0, 108.6, 102.9, 56.8, 45.7, 26.3, 24.0. **HRMS** (ESI) calcd for $C_{12}H_{11}N_2O_4S$ $[M\text{-}Na]^-$ 279.0445, found 279.0441.

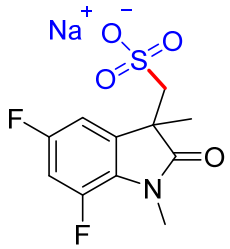
Sodium (5-(methoxycarbonyl)-1,3-dimethyl-2-oxoindolin-3-yl)methanesulfonate (3i)



General procedure 18 was followed to obtain **3i** (67.4 mg, 0.20 mmol, 67 %) as a white solid. **Mp** > 300 °C.

^{1}H NMR (400 MHz, DMSO-*d6*) δ 8.05 (d, J = 1.6 Hz, 1H, Ar-H), 7.87 (dd, J = 8.2, 1.8 Hz, 1H, Ar-H), 7.03 (d, J = 8.2 Hz, 1H, Ar-H), 3.82 (s, 3H, O-CH_3), 3.15 (d, J = 13.8 Hz, 1H, CH_2), 3.11 (s, 3H, N-CH_3), 2.95 (d, J = 13.8 Hz, 1H, CH_2), 1.26 (s, 3H, CH_3). **^{13}C NMR** (100 MHz, DMSO-*d6*) δ 180.1, 167.1, 148.1, 133.6, 130.1, 126.3, 122.9, 108.1, 57.5, 52.2, 46.3, 26.7, 25.5, 24.7. **HRMS** (ESI) calcd for $C_{13}H_{14}NO_6S$ $[M\text{-}Na]^-$ 312.0547, found 312.0556.

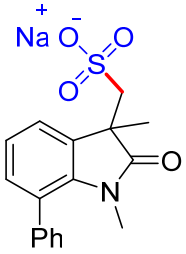
Sodium (5,7-difluoro-1,3-dimethyl-2-oxoindolin-3-yl)methanesulfonate (3j)



General procedure 18 was followed to obtain **3j** (33.8 mg, 0.11 mmol, 36 %) as a white solid. **Mp** 163–164 °C.

^{1}H NMR (400 MHz, DMSO-*d6*) δ 6.77 (dd, J = 9.3, 2.0 Hz, 1H, Ar-H), 6.63 (td, J = 10.4, 2.1 Hz, 1H, Ar-H), 3.06 (d, J = 4.9 Hz, 2H, CH_2), 3.04 (s, 3H, N-CH_3), 1.20 (s, 3H, CH_3). **^{13}C NMR** (100 MHz, DMSO-*d6*) δ 179.2, 104.2, 97.0, 96.7, 96.4, 93.8 (d, J = 3.3 Hz, 1C), 93.6 (d, J = 2.3 Hz, 1C), 57.4, 45.5, 27.1, 24.1. **HRMS** (ESI) calcd for $C_{11}H_{10}F_2NO_4S$ $[M\text{-}Na]^-$ 290.0304, found 290.0307.

Sodium (1,3-dimethyl-2-oxo-7-phenylindolin-3-yl)methanesulfonate (3k)

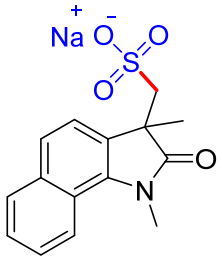


General procedure 18 was followed to obtain **3k** (94.3 mg, 0.27 mmol, 89 %) as a white solid. **Mp** 172–174 °C.

^{1}H NMR (400 MHz, DMSO-*d6*) δ 7.58 – 7.56 (m, 1H, Ar-H), 7.44 – 7.41 (m, 2H, Ar-H), 7.39 – 7.37 (m, 3H, Ar-H), 6.99 (d, J = 4.4 Hz, 2H, Ar-H), 3.10 (d, J = 13.8 Hz, 1H, CH_2), 2.95 (d, J = 13.8 Hz, 1H, CH_2), 2.58 (s, 3H, N-CH_3), 1.33 (s, 3H, CH_3). **^{13}C NMR** (100 MHz, DMSO-*d6*) δ 181.0, 140.3, 139.6, 134.7, 131.4, 130.3, 130.2, 128.2, 127.8, 124.8, 124.4, 121.3, 118.0, 57.6, 45.8, 30.6, 24.8. **HRMS** (ESI) calcd for $C_{17}H_{16}NO_4S$ $[M\text{-}Na]^-$ 330.0806, found 330.0809.

Sodium

(1,3-dimethyl-2-oxo-2,3-dihydro-1H-benzo[*g*]indol-3-yl)methanesulfonate (3l)

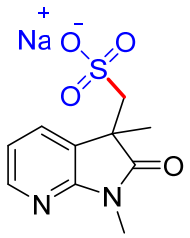


General procedure 18 was followed to obtain **3l** (70.7 mg, 0.22 mmol, 72 %) as a white solid. **Mp** > 300 °C.

^{1}H NMR (400 MHz, DMSO-*d6*) δ 7.68 (d, J = 7.8 Hz, 1H, Ar-H), 7.54 (d, J = 7.1 Hz, 1H, Ar-H), 7.51 – 7.45 (m, 2H, Ar-H), 7.40 (d, J = 7.9 Hz, 1H, Ar-H), 6.95 (d, J = 7.5 Hz, 1H, Ar-H), 3.69 (d, J = 13.6 Hz, 1H, CH_2), 3.37 (s, 3H, N-CH_3), 3.31 (d, J = 13.6 Hz, 1H, CH_2), 1.46 (s, 3H, CH_3). **^{13}C NMR** (100 MHz, DMSO-*d6*) δ 172.5, 137.5, 137.4, 133.2, 126.9, 126.4, 125.4, 124.8, 121.9, 119.6, 108.1, 62.3, 45.9, 33.6, 29.8. **HRMS** (ESI) calcd for $C_{15}H_{14}NO_4S$ $[M\text{-}Na]^-$ 304.0649, found 304.0657.

Sodium

(1,3-Dimethyl-2-oxo-2,3-dihydro-1*H*-pyrrolo[2,3-b]pyridin-3-yl)methanesulfonate (3m)

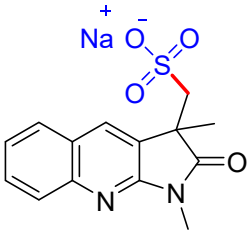


General procedure 18 was followed to obtain **3m** (44.2 mg, 0.16 mmol, 53 %) as a white solid. **Mp** 163–164 °C.

^{1}H NMR (400 MHz, DMSO-*d6*) δ 8.07 (dd, J = 5.2, 1.6 Hz, 1H, Ar-H), 7.77 (dd, J = 7.2, 1.5 Hz, 1H, Ar-H), 6.96 – 6.93 (m, 1H, Ar-H), 3.10 (s, 3H, N-CH_3), 3.06 (d, J = 13.8 Hz, 1H, CH_2), 2.95 (d, J = 13.8 Hz, 1H, CH_2), 1.28 (s, 3H, CH_3). **^{13}C NMR** (100 MHz, DMSO-*d6*) δ 179.6, 156.6, 146.0, 133.1, 127.9, 117.9, 56.9, 46.1, 25.5, 24.0. **HRMS** (ESI) calcd for $C_{10}H_{11}N_2O_4S$ $[M\text{-}Na]^-$ 255.0445, found 255.0441.

Sodium

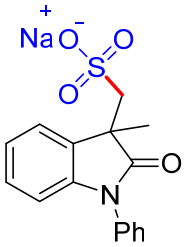
(1,3-dimethyl-2-oxo-2,3-dihydro-1*H*-pyrrolo[2,3-b]quinolin-3-yl)methanesulfonate (3n)



General procedure 18 was followed to obtain **3n** (56.1 mg, 0.17 mmol, 57 %) as a **Mp** 133–134 °C.

^{1}H NMR (400 MHz, DMSO-*d6*) δ 8.16 (s, 1H, Ar-H), 7.82 (d, J = 8.4 Hz, 2H, Ar-H), 7.63 – 7.60 (m, 1H, Ar-H), 7.42 – 7.38 (m, 1H, Ar-H), 3.20 (s, 3H, N-CH_3), 3.17 (d, J = 13.8 Hz, 1H, CH_2), 3.11 (d, J = 13.8 Hz, 1H, CH_2), 1.35 (s, 3H, CH_3). **^{13}C NMR** (100 MHz, DMSO-*d6*) δ 179.6, 156.9, 146.6, 131.7, 129.2, 128.9, 128.7, 127.3, 126.5, 124.2, 57.5, 45.6, 25.9, 24.7. **HRMS** (ESI) calcd for $C_{14}H_{13}N_2O_4S$ $[M\text{-}Na]^-$ 305.0602, found 305.0609.

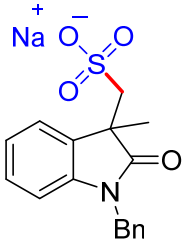
Sodium (3-methyl-2-oxo-1-phenylindolin-3-yl)methanesulfonate (3o)



General procedure 18 was followed to obtain **3o** (88.6 mg, 0.26 mmol, 87 %) as a white solid. **Mp** 232–234 °C.

^{1}H NMR (400 MHz, DMSO-*d6*) δ 7.56 – 7.50 (m, 3H, Ar-H), 7.45 – 7.40 (m, 3H, Ar-H), 7.14 – 7.10 (m, 1H, Ar-H), 7.00 – 6.97 (m, 1H, Ar-H), 6.62 (d, J = 7.8 Hz, 1H, Ar-H), 3.18 (d, J = 13.8 Hz, 1H, CH_2), 3.10 (d, J = 13.8 Hz, 1H, CH_2), 1.35 (s, 3H, CH_3). **^{13}C NMR** (100 MHz, DMSO-*d6*) δ 179.4, 143.4, 135.7, 133.2, 129.7, 128.1, 127.5, 127.4, 125.8, 122.1, 108.5, 58.0, 46.5, 25.4. **HRMS** (ESI) calcd for $C_{16}H_{14}NO_4S$ $[M\text{-}Na]^-$ 316.0649, found 316.0641.

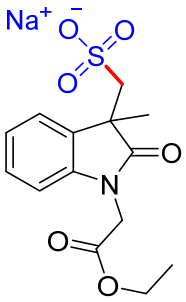
Sodium (1-benzyl-3-methyl-2-oxoindolin-3-yl)methanesulfonate (3p)



General procedure 18 was followed to obtain **3p** (85.9 mg, 0.24 mmol, 81 %) as a white solid. **Mp** 253–255 °C.

^{1}H NMR (400 MHz, DMSO-*d6*) δ 7.57 (d, J = 7.3 Hz, 1H, Ar-H), 7.41 – 7.28 (m, 4H, Ar-H), 7.26 – 7.22 (m, 1H, Ar-H), 7.10 – 7.07 (m, 1H, Ar-H), 6.95 – 6.91 (m, 1H, Ar-H), 6.72 (d, J = 7.7 Hz, 1H, Ar-H), 4.87 (q, J = 8.7 Hz, 2H, N-CH_2), 3.17 (d, J = 13.9 Hz, 1H, CH_2), 2.98 (d, J = 13.9 Hz, 1H, CH_2), 1.35 (s, 3H, CH_3). **^{13}C NMR** (100 MHz, DMSO-*d6*) δ 179.9, 142.2, 137.2, 133.6, 129.0, 127.6, 127.4, 125.8, 121.9, 108.9, 57.2, 46.6, 43.1, 25.0. **HRMS** (ESI) calcd for $C_{17}H_{16}NO_4S$ $[M\text{-}Na]^-$ 330.0806, found 330.0809.

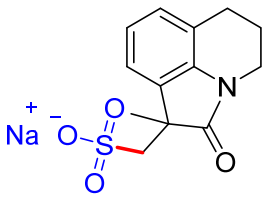
Sodium (1-(2-ethoxy-2-oxoethyl)-3-methyl-2-oxoindolin-3-yl)methanesulfonate (3q)



General procedure 18 was followed to obtain **3q** (91.2 mg, 0.26 mmol, 87 %) as a white solid. **Mp** 248–250 °C.

^{1}H NMR (400 MHz, DMSO-*d6*) δ 7.65 (d, J = 7.3 Hz, 1H), 7.19 – 7.15 (m, 1H), 6.98 – 6.95 (m, 1H), 6.92 (d, J = 7.8 Hz, 1H), 4.50 (q, J = 17.7 Hz, 2H), 4.13 (q, J = 7.1 Hz, 2H), 3.05 (d, J = 13.9 Hz, 1H), 2.80 (d, J = 13.9 Hz, 1H), 1.35 (s, 3H), 1.19 (t, J = 7.1 Hz, 3H). **^{13}C NMR** (100 MHz, DMSO-*d6*) δ 180.0, 168.5, 142.1, 133.5, 127.5, 126.1, 122.0, 108.4, 61.5, 56.9, 46.5, 41.5, 24.0, 14.5. **HRMS** (ESI) calcd for $C_{14}H_{16}NO_6S$ $[M\text{-}Na]^-$ 326.0704, found 326.0709.

Sodium (1-methyl-2-oxo-1,2,5,6-tetrahydro-4H-pyrrolo[3,2,1-ij]quinolin-1-yl)methanesulfonate (3r)

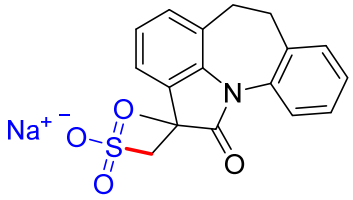


General procedure 18 was followed to obtain **3r** (76.4 mg, 0.25 mmol, 84 %) as a white solid. **Mp** 120–121 °C.

^{1}H NMR (400 MHz, DMSO-*d6*) δ 7.41 (d, J = 7.4 Hz, 1H, Ar-H), 6.95 (d, J = 7.6 Hz, 1H, Ar-H), 6.83 – 6.80 (m, 1H, Ar-H), 3.60 – 3.52 (m, 2H, N-CH_2), 2.99 (d, J = 13.8

Hz, 1H, CH_2), 2.77 (d, *J* = 13.8 Hz, 1H, CH_2), 2.71 (t, *J* = 6.0 Hz, 2H, Ar-H), 1.93 – 1.84 (m, 2H, NCH_2-CH_2), 1.30 (s, 3H, CH_3). **^{13}C NMR** (100 MHz, DMSO-*d6*) *δ* 178.5, 139.0, 132.4, 126.3, 123.9, 121.1, 119.5, 57.1, 47.7, 38.8, 24.6, 23.7, 21.2. **HRMS** (ESI) calcd for $C_{13}H_{14}NO_4S$ [M-Na]$^-$ 280.0649, found 280.0646.

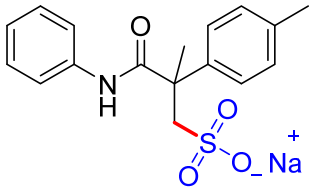
Sodium (7-methyl-6-oxo-6,7,11,12-tetrahydrobenzo[6,7]azepino[3,2,1-hi]indol-7-yl)methanesulfonate (3s)



General procedure 18 was followed to obtain **3s** (87.7 mg, 0.24 mmol, 80 %) as a white solid. **Mp** 216–217 °C.

^{1}H NMR (400 MHz, DMSO-*d6*) *δ* 7.83 (d, *J* = 7.7 Hz, 1H, Ar-H), 7.27 – 7.23 (m, 2H, Ar-H), 7.23 – 7.12 (m, 2H, Ar-H), 6.97 (d, *J* = 7.5 Hz, 1H, Ar-H),6.92 – 6.88 (m, 1H, Ar-H), 3.21 (d, *J* = 5.8 Hz, 2H, Ar-CH_2), 3.06 – 2.93 (m, 3H, Ar-CH_2, CH_2), 2.89 –2.82 (m, 1H, CH_2), 1.28 (s, 3H, CH_3). **^{13}C NMR** (100 MHz, DMSO-*d6*) *δ* 180.1, 140.2, 137.0, 133.7, 129.3, 129.2, 126.2, 124.9, 122.9, 121.7, 58.5, 46.1, 33.8, 33.4, 26.7. **HRMS** (ESI) calcd for $C_{18}H_{16}NO_4S$ [M-Na]$^-$ 342.0806, found 342.0801.

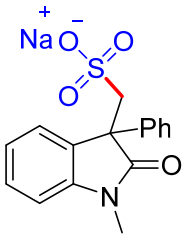
Sodium 2-methyl-3-oxo-3-(phenylamino)-2-(*p*-tolyl)propane-1-sulfonate (3t)



General procedure 18 was followed to obtain **3t** (46.9 mg, 0.13 mmol, 44 %) as a white solid. **Mp** > 300 °C.

^{1}H NMR (400 MHz, DMSO-*d6*) δ 9.88 (s, 1H, NH), 7.56 (d, *J* = 8.0 Hz, 2H, Ar-H), 7.29 – 7.19 (m, 4H, Ar-H), 7.09 (d, *J* = 8.2 Hz, 2H, Ar-H), 7.02 – 6.98 (m, 1H, Ar-H), 3.69 (d, *J* = 14.4 Hz, 1H, CH_2), 2.96 (d, *J* = 14.4 Hz, 1H, CH_2), 2.25 (s, 3H, Ar-CH_3), 1.72 (s, 3H, CH_3). **^{13}C NMR** (100 MHz, DMSO-*d6*) *δ* 174.0, 143.5, 140.1, 135.5, 129.1, 128.7, 126.3, 123.4, 120.5, 59.7, 50.2, 24.1, 21.0. **HRMS** (ESI) calcd for $C_{17}H_{18}NO_4S$ [M-Na]$^-$ 332.0962, found 332.0968.

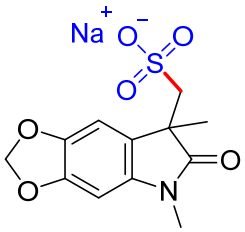
Sodium (1-methyl-2-oxo-3-phenylindolin-3-yl)methanesulfonate (3u)



General procedure 18 was followed to obtain **3u** (84.5 mg, 0.25 mmol, 83 %) as a white solid. **Mp** 214–216 °C.

^{1}H NMR (400 MHz, DMSO-*d6*) δ 7.31 (d, J = 7.2 Hz, 1H, Ar-H), 7.25 – 7.19 (m, 6H, Ar-H), 6.99 – 6.94 (m, 2H, Ar-H), 3.59 (d, J = 13.7 Hz, 1H, CH_2), 3.51 (d, J = 13.7 Hz, 1H, CH_2), 3.08 (s, 3H, CH_3). **^{13}C NMR** (100 MHz, DMSO-*d6*) δ 177.3, 141.2, 130.8, 128.2, 127.4, 126.8, 126.4, 126.4, 121.1, 107.9, 57.2, 54.0, 26.3. **HRMS** (ESI) calcd for $C_{16}H_{14}NO_4S$ $[M\text{-}Na]^-$ 316.0649, found 316.0653.

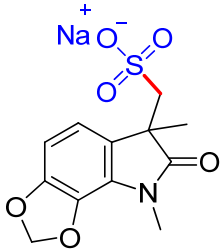
Sodium (5,7-dimethyl-6-oxo-6,7-dihydro-5H-[1,3]dioxolo[4,5-f]indol-7-yl)methanesulfonate (3v)



General procedure 18 was followed to obtain **3v** (66.5 mg, 0.21 mmol, 69 %) as a white solid. **Mp** 210–211 °C.

^{1}H NMR (400 MHz, DMSO-*d6*) δ 7.22 (s, 1H, Ar-H), 6.72 (s, 1H, Ar-H), 5.93 (d, J = 13.9 Hz, 2H, O-CH_2), 3.04 (s, 3H, N-CH_3), 3.00 (d, J = 13.8 Hz, 1H, CH_2), 2.79 (d, J = 13.8 Hz, 1H, CH_2), 1.26 (s, 3H, CH_3). **^{13}C NMR** (100 MHz, DMSO-*d6*) δ 180.0, 146.6, 142.1, 137.7, 125.7, 107.7, 100.9, 92.3, 57.4, 46.7, 26.8, 24.3. **HRMS** (ESI) calcd for $C_{12}H_{12}NO_6S$ $[M\text{-}Na]^-$ 298.0391, found 298.0396.

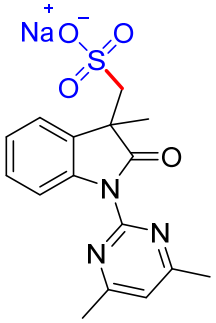
Sodium (6,8-dimethyl-7-oxo-7,8-dihydro-6H-[1,3]dioxolo[4,5-g]indol-6-yl)methanesulfonate (3v')



General procedure 18 was followed to obtain **3v'** (26.0 mg, 0.08 mmol, 27 %) as a white solid. **Mp** 210–211 °C.

^{1}H NMR (400 MHz, DMSO-*d6*) δ 6.70 (d, J = 8.0 Hz, 1H, Ar-H), 6.29 (d, J = 8.0 Hz, 1H, Ar-H), 5.96 (s, 1H, O-CH_2), 5.86 (s, 1H, O-CH_2), 3.10 (d, J = 13.8 Hz, 1H, CH_2), 3.01 (s, 3H, N-CH_3), 2.73 (d, J = 13.8 Hz, 1H), 1.19 (s, 3H, CH_3). **^{13}C NMR** (100 MHz, DMSO-*d6*) δ 178.3, 143.8, 143.6, 139.2, 114.2, 106.1, 101.4, 99.6, 57.2, 45.2, 26.9, 24.3. **HRMS** (ESI) calcd for $C_{12}H_{12}NO_6S$ $[M\text{-}Na]^-$ 298.0391, found 298.0396.

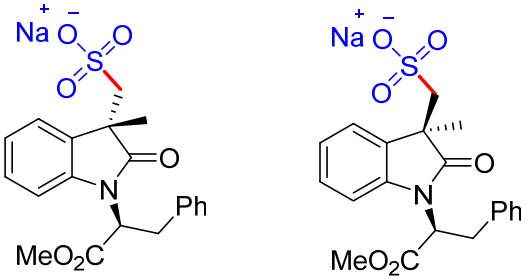
Sodium (1-(4,6-dimethylpyrimidin-2-yl)-3-methyl-2-oxoindolin-3-yl)methanesulfonate (3w)



General procedure 18 was followed to obtain **3w** (52.0 mg, 0.14 mmol, 47 %) as a colorless oil.

^{1}H NMR (400 MHz, DMSO-*d6*) δ 7.64 (dd, J = 7.5, 0.9 Hz, 1H, Ar-H), 7.33 (d, J = 7.7 Hz, 1H, Ar-H), 7.29 (s, 1H, Ar-H), 7.21 – 7.16 (m, 1H, Ar-H), 7.07 – 7.04 (m, 1H, Ar-H), 3.20 (d, J = 13.9 Hz, 1H, CH_2), 3.03 (d, J = 13.9 Hz, 1H, CH_2), 2.50 (s, 6H, Ar-CH_3), 1.41 (s, 3H, CH_3). **^{13}C NMR** (100 MHz, DMSO-*d6*) δ 178.3, 168.6, 154.7, 140.2, 132.6, 126.9, 125.3, 122.5, 118.3, 118.3, 111.2, 56.9, 46.5, 24.9, 23.4, 23.3. **HRMS** (ESI) calcd for $C_{16}H_{16}N_3O_4S$ $[M\text{-}Na]^-$ 346.0867, found 346.0864.

Sodium ((*R*/*S*)-1-((*S*)-1-methoxy-1-oxo-3-phenylpropan-2-yl)-3-methyl-2-oxoindolin-3-yl) methanesulfonate (3x)

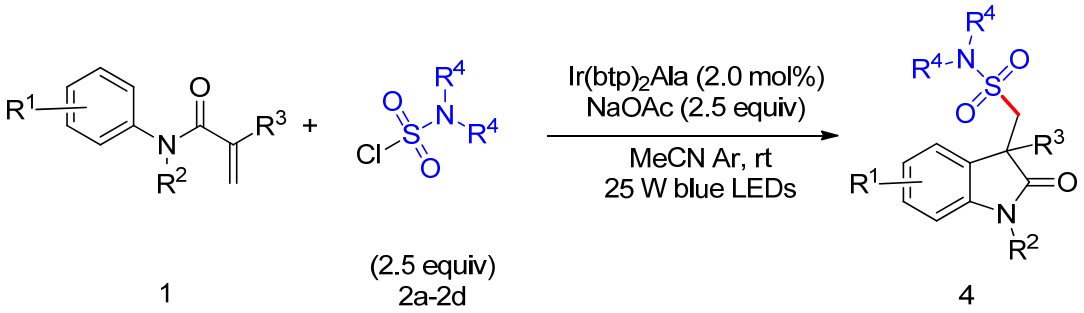


General procedure 18 was followed to obtain **3x** (106.2 mg, 0.25 mmol, 88 %) as a

colorless oil.

^{1}H NMR (400 MHz, DMSO-*d6*) δ 7.75 (dd, J = 7.5, 0.9 Hz, 1H, Ar-H), 7.17 – 7.07 (m, 6H, Ar-H), 6.92 – 6.88 (m, 1H, Ar-H), 6.82 (d, J = 3.2 Hz, 1H, Ar-H), 5.31 (t, J = 11.2 Hz, 1H, N-CH), 3.65 (s, 3H, O-CH_3), 3.35 – 3.31 (m, 2H), 2.84 (d, J = 14.0 Hz, 1H), 2.37 (d, J = 14.0 Hz, 1H), 1.32 (s, 3H). **^{1}H NMR** (400 MHz, DMSO-*d6*) δ 7.72 (dd, J = 7.4, 0.8 Hz, 1H, Ar-H), 7.17 – 7.07 (m, 6H, Ar-H), 6.92 – 6.88 (m, 1H, Ar-H), 6.84 (d, J = 3.2 Hz, 1H, Ar-H), 5.31 (t, J = 11.2 Hz, 1H, N-CH), 3.66 (s, 3H, O-CH_3), 3.46 – 3.42 (m, 2H), 2.96 (d, J = 14.0 Hz, 1H), 2.49 (d, J = 14.0 Hz, 1H), 1.14 (s, 3H). **^{13}C NMR** (100 MHz, DMSO-*d6*) δ 179.8, 170.2, 141.5, 137.4, 133.4, 129.5, 129.5, 128.5, 127.5, 126.9, 126.7, 121.9, 108.8, 56.5, 54.6, 52.9, 46.2, 33.8, 22.5. **HRMS** (ESI) calcd for $C_{20}H_{20}NO_6S$ $[M-Na]^-$ 402.1017, found 402.1019.

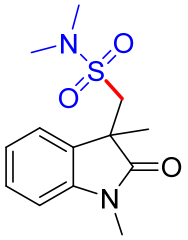
5.2 General Procedure 19 for Sulfonamidation of Substrates 1



1 (2.5 equiv) 2a-2d 4

Under argon atmosphere, to a 10 mL Schlenk tube was added **1** (0.3 mmol, 1.0 equiv), aliphatic sulfamoyl chloride (0.75 mmol, 2.5 equiv), NaOAc (61.5 mg, 0.75 mmol, 2.5 equiv), $Ir(btp)_2Ala$ (4.5 mg, 0.06mmol, 2.0 mol%) and 2 mL MeCN. The reaction mixtue was stirred at room temperature under 25 W blue LED irradiation for 24 hours, followed by the addition of H_2O (20 mL), and extracted with DCM (10 mL × 3). The combined organic layer was washed with brine (10 mL × 3), dried over Na_2SO_4, and concentrated. The residue was purified by flash chromatography on a silica gel using petroleum ether and ethyl acetate (4:1~2:1, v/v) as the eluent to give **4**.

1-(1,3-Dimethyl-2-oxoindolin-3-yl)-*N*,*N*-dimethylmethanesulfonamide (4a)

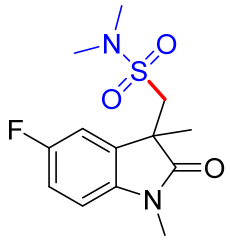


General procedure 19 was followed to obtain **4a** (79.7 mg, 0.28 mmol, 94 %) as a

white solid. **Mp** 104–106 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 – 7.24 (m, 2H, Ar-H), 7.08 – 7.04 (m, 1H, Ar-H), 6.85 (d, J = 7.7 Hz, 1H, Ar-H), 3.23 (s, 3H, CON-CH_3), 2.92 (d, J = 13.3 Hz, 1H, CH_2), 2.73 (d, J = 13.3 Hz, 1H, CH_2), 2.04 (s, 6H, N-CH_3), 1.28 (s, 3H, CH_3). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 178.3, 143.1, 130.6, 128.7, 124.1, 122.6, 108.5, 54.0, 45.6, 37.0, 26.6, 25.0. **HRMS** (ESI) calcd for $C_{13}H_{19}N_2O_3S$ $[M+H]^+$ 283.1111, found 283.1116.

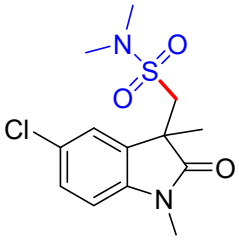
1-(5-Fluoro-1,3-dimethyl-2-oxoindolin-3-yl)-*N*,*N*-dimethylmethanesulfonamide (4b)



General procedure 19 was followed to obtain **4b** (76,7 mg, 0.26 mmol, 85%) as a white solid. **Mp** 124–125 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.18 (dd, J = 8.0, 2.6 Hz, 1H, Ar-H), 7.06 – 6.99 (m, 1H, Ar-H), 6.80 (dd, J = 8.5, 4.1 Hz, 1H, Ar-H), 3.53 (d, J = 14.1 Hz, 1H, CH_2), 3.38 (d, J = 14.1 Hz, 1H, CH_2), 3.24 (s, 3H, CON-CH_3), 2.71 (s, 6H, N-CH_3), 1.45 (s, 3H, CH_3). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 177.9, 159.2 (d, J = 240.7 Hz, 1C), 139.0, 132.2 (d, J = 7.3 Hz, 1C), 116.0 (d, J = 24.1 Hz, 1C), 112.5 (d, J = 15.4 Hz, 1C), 108.91 (d, J = 9.3 Hz, 1C), 53.5, 46.0, 37.1, 26.7, 24.8. **HRMS** (ESI) calcd for $C_{13}H_{18}FN_2O_3S$ $[M+H]^+$ 301.1017, found 301.1011.

1-(5-Chloro-1,3-dimethyl-2-oxoindolin-3-yl)-*N*,*N*-dimethylmethanesulfonamide (4c)

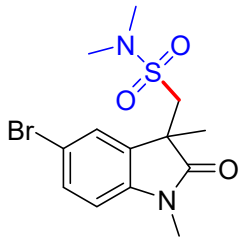


General procedure 19 was followed to obtain **4c** (84.6 mg, 0.27 mmol, 89 %) as a white solid. **Mp** 183–184 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 (d, J = 2.1 Hz, 1H, Ar-H), 7.29 (dd, J = 8.3, 2.1 Hz, 1H, Ar-H), 6.81 (d, J = 8.3 Hz, 1H, Ar-H), 3.54 (d, J = 14.2 Hz, 1H, CH_2), 3.39 (d, J = 14.2 Hz, 1H, CH_2), 3.24 (s, 3H, CON-CH_3), 2.70 (s, 6H, N-CH_3), 1.44 (s, 3H,

CH_3). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 177.6, 141.6, 132.0, 128.4, 127.8, 124.5, 109.2, 53.6, 45.6, 36.8, 26.5, 24.7. **HRMS** (ESI) calcd for $C_{13}H_{18}ClN_2O_3S$ $[M+H]^+$ 317.0721, found 317.0727.

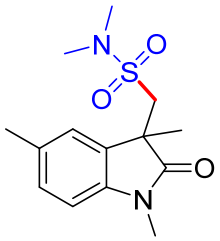
1-(5-Bromo-1,3-dimethyl-2-oxoindolin-3-yl)-*N*,*N*-dimethylmethanesulfonamide (4d)



General procedure 19 was followed to obtain **4d** (94.4 mg, 0.26 mmol, 87 %) as a white solid. **Mp** 207–210 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 (d, J = 1.9 Hz, 1H, Ar-H), 7.44 (dd, J = 8.3, 2.0 Hz, 1H, Ar-H), 6.76 (d, J = 8.3 Hz, 1H, Ar-H), 3.54 (d, J = 14.2 Hz, 1H, CH_2), 3.38 (d, J = 14.2 Hz, 1H, CH_2), 3.23 (s, 3H, CON-CH_3), 2.69 (s, 6H, N-CH_3), 1.43 (s, 3H, CH_3). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 177.7, 142.3, 132.6, 131.5, 127.4, 115.3, 109.9, 53.8, 45.7, 37.0, 26.7, 24.9. **HRMS** (ESI) calcd for $C_{13}H_{18}BrN_2O_3S$ $[M+H]^+$ 361.0216, found 361.0219.

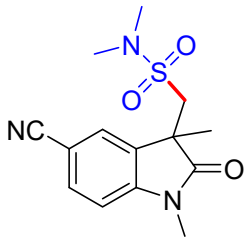
***N*,*N*-Dimethyl-1-(1,3,5-trimethyl-2-oxoindolin-3-yl)methanesulfonamide (4e)**



General procedure 19 was followed to obtain **4e** (79.2 mg, 0.27 mmol, 89 %) as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.21 (s, 1H, Ar-H), 7.11 (d, J = 7.9 Hz, 1H, Ar-H), 6.77 (d, J = 7.9 Hz, 1H, Ar-H), 3.54 (d, J = 14.2 Hz, 1H, CH_2), 3.40 (d, J = 14.2 Hz, 1H, CH_2), 3.23 (s, 3H, CON-CH_3), 2.66 (s, 6H, N-CH_3), 2.37 (s, 3H, CH_3), 1.43 (s, 3H, Ar-CH_3). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 178.2, 140.7, 132.1, 130.6, 129.0, 124.9, 108.2, 54.0, 45.6, 37.0, 26.6, 25.0, 21.2. **HRMS** (ESI) calcd for $C_{14}H_{21}N_2O_3S$ $[M+H]^+$ 297.1267, found 297.1262.

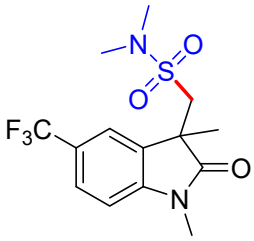
1-(5-Cyano-1,3-dimethyl-2-oxoindolin-3-yl)-*N*,*N*-dimethylmethanesulfonamide (4f)



General procedure 19 was followed to obtain **4f** (79.4 mg, 0.26 mmol, 86 %) as a white solid. **Mp** 224–226 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 (d, J = 1.4 Hz, 1H, Ar-H), 7.64 (s, 1H, Ar-H), 6.95 (d, J = 8.0 Hz, 1H, Ar-H), 3.56 (d, J = 14.1 Hz, 1H, CH_2), 3.40 (d, J = 14.1 Hz, 1H, CH_2), 3.28 (s, 3H, CON-CH_3), 2.74 (s, 6H, N-CH_3), 1.45 (s, 3H, CH_3). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 178.1, 147.1, 134.0, 131.6, 127.7, 119.1, 108.9, 105.9, 53.5, 45.3, 37.1, 26.8, 24.7. **HRMS** (ESI) calcd for $C_{14}H_{18}N_3O_3S$ $[M+H]^+$ 308.1063, found 308.1068.

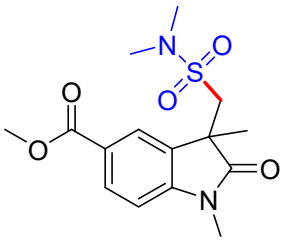
1-(1,3-Dimethyl-2-oxo-5-(trifluoromethyl)indolin-3-yl)-*N*,*N*-dimethylmethanesulfonamide (4g)



General procedure 19 was followed to obtain **4g** (96.8 mg, 0.28 mmol, 92 %) as a white solid. **Mp** 197–198 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (d, J = 8.0 Hz, 1H, Ar-H), 7.60 (s, 1H, Ar-H), 6.96 (d, J = 8.6 Hz, 1H, Ar-H), 3.59 (d, J = 14.2 Hz, 1H, CH_2), 3.44 (d, J = 14.2 Hz, 1H, CH_2), 3.29 (s, 3H, CON-CH_3), 2.67 (s, 6H, N-CH_3), 1.46 (s, 3H, CH_3). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 178.3, 146.3, 131.1, 130.9, 128.9, 126.4, 121.3, 108.3, 53.8, 45.5, 36.9, 26.8, 24.9. **HRMS** (ESI) calcd for $C_{14}H_{18}F_3N_2O_3S$ $[M+H]^+$ 351.0985, found 351.0987.

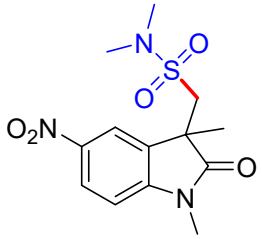
Methyl 3-((*N*,*N*-dimethylsulfamoyl)methyl)-1,3-dimethyl-2-oxoindoline-5-carboxylate (4h)



General procedure 19 was followed to obtain **4h** (90.0 mg, 0.26 mmol, 88 %) as a white solid. **Mp** 205–207 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (dd, J = 8.2, 1.5 Hz, 1H, Ar-H), 8.02 (d, J = 1.4 Hz, 1H, Ar-H), 6.93 (d, J = 8.2 Hz, 1H, Ar-H), 3.91 (s, 3H, -OCH_3), 3.61 (d, J = 14.1 Hz, 1H, CH_2), 3.45 (d, J = 14.2 Hz, 1H, CH_2), 3.29 (s, 3H, CON-CH_3), 2.66 (s, 6H, N-CH_3), 1.45 (s, 3H, CH_3). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 178.55, 166.76, 147.38, 131.41, 130.50, 125.23, 124.54, 108.10, 53.96, 52.08, 45.34, 36.95, 26.80, 25.02. **HRMS** (ESI) calcd for $C_{15}H_{21}N_2O_5S$ $[M+H]^+$ 341.1166, found 341.1163.

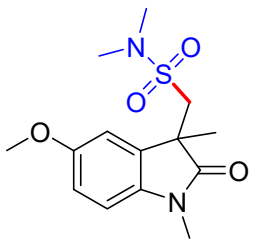
1-(1,3-Dimethyl-5-nitro-2-oxoindolin-3-yl)-*N,N*-dimethylmethanesulfonamid (4i)



General procedure 19 was followed to obtain **4i** (77.6 mg, 0.24 mmol, 79 %) as a white solid. **Mp** 209–210 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.31 (dd, J = 8.6, 2.2 Hz, 1H, Ar-H), 8.26 (d, J = 2.2 Hz, 1H, Ar-H), 6.97 (d, J = 8.6 Hz, 1H, Ar-H), 3.62 (d, J = 14.1 Hz, 1H, CH_2), 3.46 (d, J = 14.1 Hz, 1H, CH_2), 3.32 (s, 3H, CON-CH_3), 2.73 (s, 6H, N-CH_3), 1.48 (s, 3H, CH_3). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 178.5, 148.9, 131.4, 125.9, 124.7, 120.1, 108.1, 53.6, 45.5, 37.1, 27.0, 24.8. **HRMS** (ESI) calcd for $C_{13}H_{18}N_3O_5S$ $[M+H]^+$ 328.0962, found 328.0969.

1-(5-Methoxy-1,3-dimethyl-2-oxoindolin-3-yl)-N,N-dimethylmethanesulfonamide (4j)

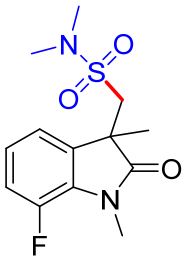


General procedure 19 was followed to obtain **4j** (49.7 mg, 0.16 mmol, 53 %) as a

white solid. **Mp** 126–127 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.05 (d, J = 2.4 Hz, 1H, Ar-H), 6.84 (dd, J = 8.5, 2.4 Hz, 1H, Ar-H), 6.78 (d, J = 8.5 Hz, 1H, Ar-H), 3.81 (s, 3H, -OCH_3), 3.52 (d, J = 14.1 Hz, 1H, CH_2), 3.40 (d, J = 14.2 Hz, 1H, CH_2), 3.23 (s, 3H, CON-CH_3), 2.69 (s, 6H, N-CH_3), 1.44 (s, 3H, CH_3). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 177.9, 156.0, 136.6, 132.0, 113.0, 111.8, 108.7, 55.9, 53.9, 46.0, 37.0, 26.6, 24.9. **HRMS** (ESI) calcd for $C_{14}H_{21}N_2O_4S$ $[M+H]^+$ 313.1217, found 313.1224.

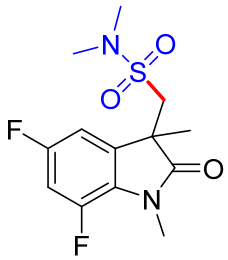
1-(7-Fluoro-1,3-dimethyl-2-oxoindolin-3-yl)-*N*,*N*-dimethylmethanesulfonamide (4k)



General procedure 19 was followed to obtain **4k** (36.9 mg, 0.12 mmol, 41 %) as a white solid. **Mp** 92–94 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.18 – 7.16 (m, 1H, Ar-H), 7.09 – 6.99 (m, 2H, Ar-H), 3.57 (d, J = 14.1 Hz, 1H, 3.46 (d, J = 2.7 Hz, 3H, CON-CH_3), CH_2), 3.39 (d, J = 14.1 Hz, 1H, CH_2), 2.71 (s, 6H, N-CH_3), 1.44 (s, 3H, CH_3). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 176.9, 146.9 (d, J = 242.1 Hz, 1C), 132.3 (d, J = 4.1 Hz, 1C), 128.8 (d, J = 4.2 Hz, 1C), 122.1 (d, J = 7.7 Hz, 1C), 118.9 (d, J = 3.5 Hz, 1C), 115.7, 115.5, 76.3, 76.0, 75.7, 52.9, 44.8, 36.0, 28.1, 24.2. **HRMS** (ESI) calcd for $C_{13}H_{18}FN_2O_3S$ $[M+H]^+$ 301.1017, found 301.1015.

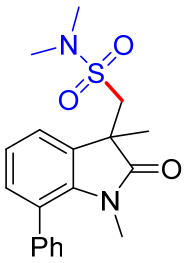
1-(5,7-Difluoro-1,3-dimethyl-2-oxoindolin-3-yl)-*N*,*N*-dimethylmethanesulfonamide (4l)



General procedure 19 was followed to obtain **4l** (45.9 mg, 0.14 mmol, 48 %) as a white solid. **Mp** 173–174 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.53 (dd, J = 9.6, 4.8 Hz, 1H, Ar-H), 6.47 (dd, J = 8.4 Hz 4.4 Hz, 1H, Ar-H), 3.58 (q, J = 14.0 Hz, 2H, CH_2), 3.23 (s, 3H, CON-CH_3), 2.70 (s, 6H, N-CH_3), 1.47 (s, 3H, CH_3). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 177.8, 145.88 – 145.75 (m, 1C), 111.5, 111.3 (d, J = 20.4 Hz, 1C), 97.6, 97.6 (d, J = 30.4 Hz, 1C), 93.7 (d, J = 26.6 Hz, 1C), 52.9, 44.3, 36.8, 26.9, 23.4. **HRMS** (ESI) calcd for $C_{13}H_{17}F_2N_2O_3S$ $[M+H]^+$ 319.0922, found 319.0927.

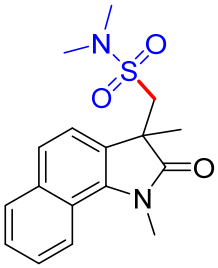
1-(1,3-Dimethyl-2-oxo-7-phenylindolin-3-yl)-*N*,*N*-dimethylmethanesulfonamide (4m)



General procedure 19 was followed to obtain **4m** (58.1 mg, 0.16 mmol, 54 %) as a white solid. **Mp** 140–141 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 – 7.35 (m, 6H, Ar-H), 7.15 – 7.12 (m, 2H, Ar-H), 3.53 (q, J = 14.1 Hz, 2H, CH_2), 2.77 (s, 3H, CON-CH_3), 2.69 (s, 6H, N-CH_3), 1.48 (s, 3H, CH_3). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 179.3, 140.2, 138.9, 131.7, 131.5, 127.8, 127.9, 125.9, 123.1, 121.9, 54.4, 45.0, 37.0, 30.6, 25.4. **HRMS** (ESI) calcd for $C_{19}H_{23}N_2O_3S$ $[M+H]^+$ 359.1424, found 359.1429.

1-(1,3-Dimethyl-2-oxo-2,3-dihydro-1H-benzo[g]indol-3-yl)-*N*,*N*-dimethylmethane sulfonamide (4n)

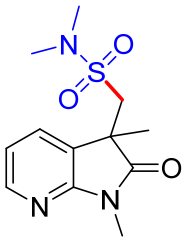


General procedure 19 was followed to obtain **4n** (60.9 mg, 0.18 mmol, 51 %) as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (d, J = 8.1 Hz, 1H, Ar-H), 7.58 – 7.54 (m, 1H, Ar-H), 7.52 (d, J = 8.2 Hz, 1H, Ar-H), 7.48 (d, J = 7.3 Hz, 1H, Ar-H), 7.45 – 7.41 (m, 1H, Ar-H), 6.98 (d, J = 7.6 Hz, 1H, Ar-H), 4.35 (d, J = 14.1 Hz, 1H, CH_2), 3.64 (d, J = 14.1 Hz, 1H, CH_2), 3.57 (s, 3H, CON-CH_3), 2.57 (s, 6H, N-CH_3), 1.67 (s, 3H, CH_3).

^{13}C NMR (100 MHz, $CDCl_3$) δ 171.3, 136.4, 134.5, 133.5, 126.9, 126.6, 126.5, 123.5, 122.8, 119.2, 108.9, 58.1, 45.6, 36.9, 33.6, 30.0. **HRMS** (ESI) calcd for $C_{17}H_{21}N_2O_3S$ $[M+H]^+$ 333.1267, found 333.1265.

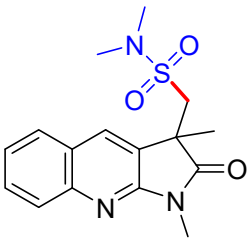
1-(1,3-Dimethyl-2-oxo-2,3-dihydro-1*H*-pyrrolo[2,3-*b*]pyridin-3-yl)-*N*,*N*-dimethyl methanesulfonamide (4o)



General procedure 19 was followed to obtain **4o** (52.7 mg, 0.19 mmol, 62 %) as a white solid. **Mp** 134–135 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.23 (d, J = 4.4 Hz, 1H, Ar-H), 7.70 (d, J = 6.4 Hz, 1H, Ar-H), 7.03 – 7.00 (m, 1H, Ar-H), 3.50 (d, J = 14.1 Hz, 1H, CH_2), 3.41 (d, J = 14.0 Hz, 1H, CH_2), 3.34 (s, 3H, CON-CH_3), 2.73 (s, 6H, N-CH_3), 1.49 (s, 3H, CH_3). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 177.8, 156.1, 147.3, 132.1, 124.9, 118.1, 52.9, 45.1, 36.9, 25.5, 23.9. **HRMS** (ESI) calcd for $C_{12}H_{18}N_3O_3S$ $[M+H]^+$ 284.1063, found 284.1068.

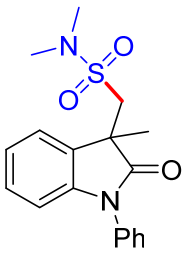
1-(1,3-Dimethyl-2-oxo-2,3-dihydro-1*H*-pyrrolo[2,3-*b*]quinolin-3-yl)-*N*,*N*-dimethyl methanesulfonamide (4p)



General procedure 19 was followed to obtain **4p** (67.1 mg, 0.20 mmol, 67 %) as a white solid. **Mp** 120–121 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (s, 1H, Ar-H), 7.95 (d, J = 8.4 Hz, 1H, Ar-H), 7.79 (d, J = 7.9 Hz, 1H, Ar-H), 7.69 – 7.62 (m, 1H, Ar-H), 7.45– 7.41 (m, 1H, Ar-H), 3.53 (q, J = 14.2 Hz, 2H, CH_2), 3.45 (s, 3H, CON-CH_3), 2.73 (s, 6H, N-CH_3), 1.57 (s, 3H, CH_3). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 178.2, 155.7, 147.1, 132.0, 129.9, 128.4, 127.7, 126.1, 125.6, 124.8, 53.2, 44.8, 37.2, 26.0, 24.6. **HRMS** (ESI) calcd for $C_{16}H_{20}N_3O_3S$ $[M+H]^+$ 334.1220, found 334.1223.

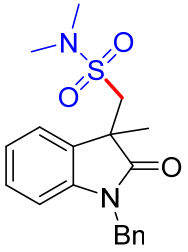
***N*,*N*-Dimethyl-1-(3-methyl-2-oxo-1-phenylindolin-3-yl)methanesulfonamide (4q)**



General procedure 19 was followed to obtain **4q** (81.6 mg, 0.24 mmol, 79 %) as a white solid. **Mp** 151–153 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 – 7.46 (m, 4H, Ar-H), 7.42 (d, J = 7.2 Hz, 2H, Ar-H), 7.23 (d, J = 7.7, 1H, Ar-H), 7.16– 7.12 (m, 1H, Ar-H), 6.83 (d, J = 7.8 Hz, 1H, Ar-H), 3.69 (d, J = 14.1 Hz, 1H, CH_2), 3.50 (d, J = 14.1 Hz, 1H, CH_2), 2.69 (s, 6H, N-CH_3), 1.55 (s, 3H, CH_3). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 177.8, 143.5, 134.6, 130.2, 129.6, 128.6, 128.2, 126.8, 124.1, 122.9, 109.9, 54.3, 45.7, 37.0, 25.5. **HRMS** (ESI) calcd for $C_{18}H_{21}N_2O_3S$ $[M+H]^+$ 345.1267, found 345.1271.

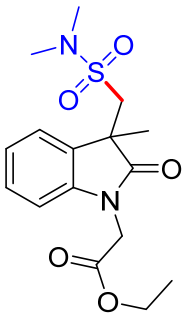
1-(1-Benzyl-3-methyl-2-oxoindolin-3-yl)-*N*,*N*-dimethylmethanesulfonamide (4r)



General procedure 19 was followed to obtain **4r** (80.7 mg, 0.23 mmol, 75 %) as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 (d, J = 7.1 Hz, 1H, Ar-H), 7.36 – 7.29 (m, 4H, Ar-H), 7.29 – 7.25 (m, 1H, Ar-H), 7.18 – 7.16(m, 1H, Ar-H), 7.09 – 7.05 (m, 1H, Ar-H), 6.74 (d, J = 7.8 Hz, 1H, Ar-H), 5.04 (d, J = 15.7 Hz, 1H, N-CH_2), 4.87 (d, J = 15.7 Hz, 1H, N-CH), 3.61 (d, J = 14.2 Hz, 1H, CH_2), 3.47 (d, J = 14.2 Hz, 1H, CH_2), 2.66 (s, 6H, N-CH_3), 1.50 (s, 3H, CH_3). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 178.4, 142.3, 135.8, 130.6, 128.8, 128.6, 127.6, 127.4, 124.1, 122.6, 109.7, 53.7, 45.7, 44.2, 37.0, 25.6. **HRMS** (ESI) calcd for $C_{19}H_{23}N_2O_3S$ $[M+H]^+$ 359.1424, found 359.1429.

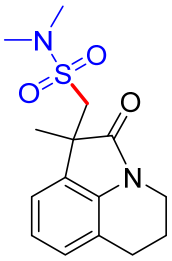
Ethyl 3-((*N*,*N*-dimethylsulfamoyl)methyl)-3-methyl-2-oxoindoline-1-carboxylate (4s)



General procedure 19 was followed to obtain **4s** (84.0 mg, 0.24 mmol, 79 %) as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 (d, J = 7.0 Hz, 1H, Ar-H), 7.31 – 7.29 (m, 1H, Ar-H), 7.15 – 7.11 (m, 1H, Ar-H), 6.77 (d, J = 7.8 Hz, 1H, Ar-H), 4.68 (d, J = 17.6 Hz, 1H, SO_2-CH_2), 4.30 (d, J = 17.6 Hz, 1H, SO_2-CH_2), 4.22 (q, J = 7.1 Hz, 2H, O-CH_2), 3.50 (dd, J = 36.8, 14.2 Hz, 2H, N-CH_2), 2.67 (s, 6H, N-CH_3), 1.50 (s, 3H, CH_3), 1.26 (d, J = 7.1 Hz, 3H, OCH_2-CH_3). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 178.3, 167.6, 141.8, 130.4, 128.7, 124.5, 123.0, 108.5, 61.8, 53.7, 45.7, 41.6, 37.0, 25.1, 14.1. **HRMS** (ESI) calcd for $C_{16}H_{23}N_2O_5S$ $[M+H]^+$ 355.1322, found 355.1328.

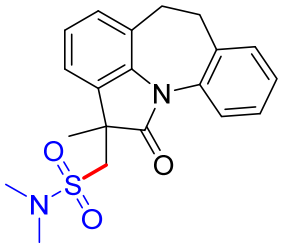
***N,N*-Dimethyl-1-(1-methyl-2-oxo-1,2,5,6-tetrahydro-4H-pyrrolo[3,2,1-ij]quinolin-1-yl)methanesulfonamide (4t)**



General procedure 19 was followed to obtain **4t** (84.2 mg, 0.27 mmol, 91 %) as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27 – 7.23 (d, J = 7.4 Hz, 1H, Ar-H), 7.06 (d, J = 7.4 Hz, 1H, Ar-H), 7.02 – 6.98 (m, 1H, Ar-H), 3.75 (t, J = 5.2 Hz, 2H, N-CH_2), 3.50 (d, J = 14.1 Hz, 1H, SO_2-CH_2), 3.40 (d, J = 14.1 Hz, 1H, SO_2-CH_2), 2.80 (t, J = 5.2 Hz, 2H, Ar-CH_2), 2.69 (s, 6H, N-CH_3), 2.06 – 1.99 (m, 2H, ArCH_2-CH_2), 1.46 (s, 3H, CH_3). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 177.1, 138.9, 129.2, 127.5, 122.09, 122.06, 120.5, 53.7, 46.7, 39.2, 37.0, 24.6, 24.5, 21.1. **HRMS** (ESI) calcd for $C_{15}H_{21}N_2O_3S$ $[M+H]^+$ 309.1267, found 309.1265.

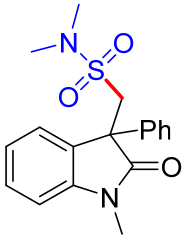
***N,N*-Dimethyl-1-(7-methyl-6-oxo-6,7,11,12-tetrahydrobenzo[6,7]azepino[3,2,1-hi] indol-7-yl)methanesulfonamide (4u)**



General procedure 19 was followed to obtain **4u** (97.8 mg, 0.26 mmol, 88 %) as a white solid. **Mp** 166–167 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (br, 1H, Ar-H), 7.32 – 7.27 (m, 1H, Ar-H), 7.24 – 7.15 (m, 3H, Ar-H), 7.10 – 7.02 (m, 2H, Ar-H), 3.74 (d, J = 14.1 Hz, 1H, SO_2-CH_2), 3.50 (d, J = 14.1 Hz, 1H, SO_2-CH_2), 3.07 – 3.03 (m, 4H, Ar-CH_2), 2.68 (s, 6H, N-CH_3), 1.51 (s, 3H, CH_3). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 178.5, 140.4, 130.6, 129.3, 126.6, 126.55, 125.3, 122.3, 121.5, 54.7, 45.4, 36.9, 33.8, 33.8, 26.3. **HRMS** (ESI) calcd for $C_{20}H_{23}N_2O_3S$ $[M+H]^+$ 371.1424, found 371.1427.

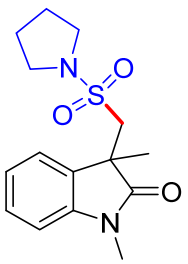
***N,N*-Dimethyl-1-(1-methyl-2-oxo-3-phenylindolin-3-yl)methanesulfonamide (4v)**



General procedure 19 was followed to obtain **4v** (33.0 mg, 0.1 mmol, 32 %) as a white solid. **Mp** 151–152 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 (d, J = 7.8 Hz, 1H, Ar-H), 7.42 – 7.36 (m, 3H, Ar-H), 7.33 – 7.28 (m, 3H, Ar-H), 7.21– 7.17 (m, 1H, Ar-H), 6.94 (d, J = 7.8 Hz, 1H, Ar-H), 4.14 (d, J = 14.1 Hz, 1H, CH_2), 3.77 (d, J = 14.1 Hz, 1H, CH_2), 3.25 (s, 3H, N-CH_3), 2.70 (s, 6H, N-CH_3). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 176.5, 144.2, 138.3, 129.2, 128.9, 128.1, 128.0, 126.6, 126.5, 122.4, 108.8, 54.8, 52.8, 37.1, 26.9. **HRMS** (ESI) calcd for $C_{18}H_{21}N_2O_3S$ $[M+H]^+$ 345.1267, found 345.1273.

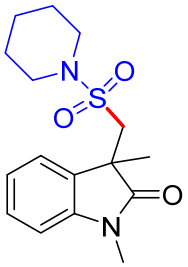
1,3-Dimethyl-3-((pyrrolidin-1-ylsulfonyl)methyl)indolin-2-one (4w)



General procedure 19 was followed to obtain **4w** (73.1 mg, 0.24 mmol, 79 %) as colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (d, J = 7.4 Hz, 1H, Ar-H), 7.33 – 7.31 (m, 1H, Ar-H), 7.12 – 7.09 (m, 1H, Ar-H), 6.89 (d, J = 7.8 Hz, 1H, Ar-H), 3.60 (d, J = 14.3 Hz, 1H, CH_2), 3.50 (d, J = 14.3 Hz, 1H, CH_2), 3.25 (s, 3H, N-CH_3), 3.16 – 3.10 (m, 2H, N-CH_2), 3.09 – 3.01 (m, 2H, N-CH_2), 1.83 – 1.77 (m, 4H, NCH_2-CH_2), 1.43 (s, 3H, CH_3). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 178.1, 143.0, 130.4, 128.4, 123.9, 122.3, 108.3, 55.0, 47.1, 45.5, 26.4, 25.6, 24.9. **HRMS** (ESI) calcd for $C_{15}H_{21}N_2O_3S$ $[M+H]^+$ 309.1267, found 309.1265.

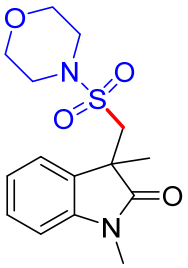
1,3-Dimethyl-3-((piperidin-1-ylsulfonyl)methyl)indolin-2-one (4x)



General procedure 19 was followed to obtain **4x** (80.3 mg, 0.25 mmol, 83 %) as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 (d, J = 7.4 Hz, 1H, Ar-H), 7.33– 7.29 (m, 1H, Ar-H), 7.13– 7.09 (m, 1H, Ar-H), 6.88 (d, J = 7.8 Hz, 1H, Ar-H), 3.51 (d, J = 14.1 Hz, 1H, CH_2), 3.38 (d, J = 14.1 Hz, 1H, CH_2), 3.25 (s, 3H, N-CH_3), 3.08 – 2.98 (m, 4H, N-CH_2), 1.54 (dd, J = 10.3, 5.5 Hz, 6H, NCH_2-CH_2CH_3), 1.44 (s, 3H, CH_3). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 178.3, 143.1, 130.6, 128.6, 124.3, 122.6, 108.4, 54.9, 46.3, 45.7, 26.6, 25.5, 24.9, 23.7. **HRMS** (ESI) calcd for $C_{16}H_{23}N_2O_3S$ $[M+H]^+$ 323.1424, found 323.1429.

1,3-Dimethyl-3-((morpholinosulfonyl)methyl)indolin-2-one (4y)

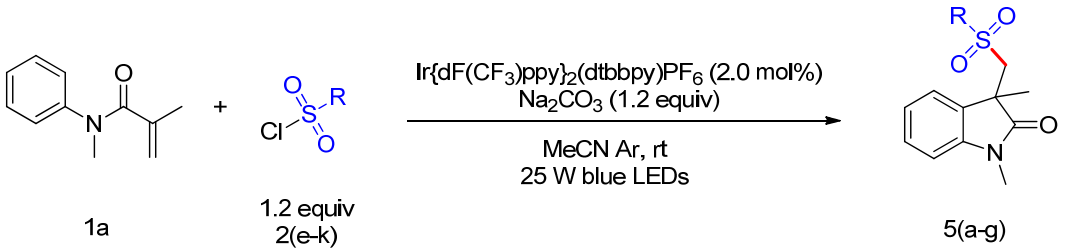


General procedure 19 was followed to obtain **4y** (86.6 mg, 0.27 mmol, 89 %) as a white solid. **Mp** 145–136 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 (d, J = 7.4 Hz, 1H, Ar-H), 7.37 – 7.29 (m, 1H, Ar-H), 7.14 – 7.11 (m, 1H, Ar-H), 6.89 (d, J = 7.8 Hz, 1H, Ar-H), 3.64 (t, J = 4.7 Hz, 4H, O-CH_2), 3.58 (d, J = 14.1 Hz, 1H, CH_2), 3.42 (d, J = 14.1 Hz, 1H, CH_2), 3.13 –

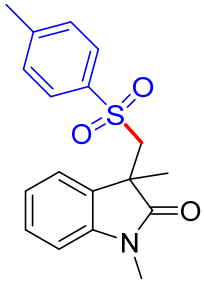
3.00 (m, 4H, N-CH_2), 1.44 (s, 3H, CH_3). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 178.0, 142.9, 130.1, 128.5, 124.0, 122.4, 108.3, 66.2, 54.5, 46.4, 45.2, 26.4, 24.8. **HRMS** (ESI) calcd for $C_{15}H_{21}N_2O_4S$ $[M+H]^+$ 325.1217, found 325.1213.

5.3 General Procedure 20 for Sulfonylation of Substrates **5a**–**5g**



Under argon atmosphere, to a 10 mL Schlenk tube was added **1** (0.3 mmol, 1.0 equiv), sulfonyl chloride (0.36 mmol, 1.2 equiv), Na_2CO_3 (38.2 mg, 0.36 mmol, 1.2 equiv), Ir{dF(CF_3)ppy}$_2$(dtbbpy)PF_6 (6.7 mg, 0.06 mmol, 2.0 mol%) and 2 mL MeCN, The reaction mixtue was stirred at room temperature under 25 W blue LED irradiation for 36 hours, followed by the addition of H_2O (20 mL), and extracted with DCM (10 mL × 3). The combined organic layer was washed with brine (10 mL × 3), dried over Na_2SO_4, and concentrated. The residue was purified by flash chromatography on a silica gel using petroleum ether and ethyl acetate (8:1~4:1, v/v) as the eluent to give **5**.

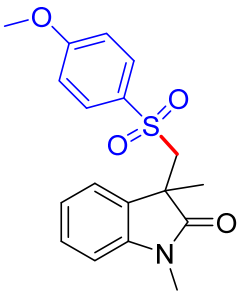
1,3-Dimethyl-3-(tosylmethyl)indolin-2-one (5a)



General procedure 20 was followed to obtain **5a** (89.9 mg, 0.27 mmol, 91 %) as a white solid. **Mp** 112–113 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (d, J = 8.3 Hz, 2H, Ar-H), 7.31 – 7.27 (m, 1H, Ar-H), 7.17 (d, J = 8.1 Hz, 2H, Ar-H), 7.09 (d, J = 7.1 Hz, 1H, Ar-H), 6.94 – 6.90 (m, J = 7.5 Hz, 1H, Ar-H), 6.84 (d, J = 7.8 Hz, 1H, Ar-H), 3.85 (d, J = 14.5 Hz, 1H, CH_2), 3.66 (d, J = 14.5 Hz, 1H, CH_2), 3.16 (s, 3H, N-CH_3), 2.39 (s, 3H, Ar-CH_3), 1.39 (s, 3H, CH_3). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 177.7, 144.4, 143.3, 137.0, 129.6, 129.5, 128.6, 127.8, 124.1, 122.5, 108.4, 61.9, 45.7, 26.6, 25.5, 21.6. **HRMS** (ESI) calcd for $C_{18}H_{20}NO_3S$ $[M+H]^+$ 330.1158, found 330.1163.

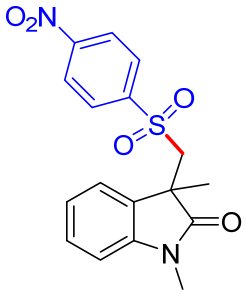
3-(((4-Methoxyphenyl)sulfonyl)methyl)-1,3-dimethylindolin-2-one (5b)



General procedure 20 was followed to obtain **5b** (90.2 mg, 0.26 mmol, 87 %) as a white solid. **Mp** 103–104 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 (d, J = 8.8 Hz, 2H, Ar-H), 7.31 – 7.27 (m, 1H, Ar-H), 7.10 (d, J = 7.4 Hz, 1H, Ar-H), 6.97 – 6.93 (m, 1H, Ar-H), 6.85 – 6.82 (m, 1H, Ar-H), 6.84 – 6.81 (d, J = 8.5 Hz, 2H, Ar-H), 3.86 (d, J = 14.5 Hz, 1H, CH_2), 3.84 (s, 3H, OCH_3), 3.65 (d, J = 14.5 Hz, 1H, CH_2), 3.15 (s, 3H, N-CH_3), 1.38 (s, 3H, CH_3). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 163.5, 143.3, 131.6, 130.1, 129.7, 128.6, 124.2, 122.5, 114.1, 108.4, 62.1, 55.7, 45.7, 26.5, 25.6. **HRMS** (ESI) calcd for $C_{18}H_{20}NO_4S$ $[M+H]^+$ 346.1108, found 346.1106.

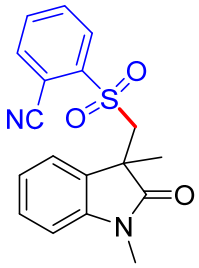
1,3-Dimethyl-3-(((4-nitrophenyl)sulfonyl)methyl)indolin-2-one (5c)



General procedure 20 was followed to obtain **5c** (76.8 mg, 0.21 mmol, 71 %) as a white solid. **Mp** 221–224 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19 (d, J = 8.8 Hz, 2H, Ar-H), 7.64 (d, J = 8.8 Hz, 2H, Ar-H), 7.33 – 7.29 (m, 1H, Ar-H), 6.90 – 6.88 (m, 2H, Ar-H), 6.83 – 6.80 (m, 1H, Ar-H), 3.97 (d, J = 14.8 Hz, 1H, CH_2), 3.76 (d, J = 14.8 Hz, 1H, CH_2), 3.22 (s, 3H, N-CH_3), 1.40 (s, 3H, CH_3). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 177.3, 150.5, 145.5, 143.5, 129.2, 129.0, 124.0, 123.7, 122.5, 108.7, 62.1, 45.5, 26.6, 25.4. **HRMS** (ESI) calcd for $C_{17}H_{17}N_2O_5S$ $[M+H]^+$ 361.0853, found 361.0857.

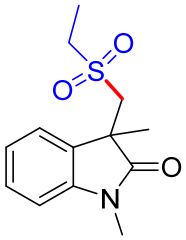
2-(((1,3-Dimethyl-2-oxoindolin-3-yl)methyl)sulfonyl)benzonitrile (5d)



General procedure 20 was followed to obtain **5d** (94.0 mg, 0.28 mmol, 92 %) as a white solid. **Mp** 240–242 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (d, J = 7.6 Hz, 1H, Ar-H), 7.63 – 7.59 (m, 1H, Ar-H), 7.48 – 7.44 (m, J = 7.7 Hz, 1H, Ar-H), 7.34 (d, J = 7.9 Hz, 1H, Ar-H), 7.21 – 7.19 (m, 1H, Ar-H), 6.83 (d, J = 7.9 Hz, 1H, Ar-H), 6.81 (d, J = 7.5 Hz, 1H, Ar-H), 6.68 – 6.64 (m, 1H, Ar-H), 4.09 (q, J = 15.1 Hz, 2H, CH_2), 3.23 (s, 3H, N-CH_3), 1.42 (s, 3H, CH_3). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 177.2, 143.4, 142.2, 134.9, 133.1, 132.9, 129.7, 129.0, 128.8, 123.2, 122.4, 115.7, 110.8, 108.6, 60.6, 45.4, 26.7, 25.2. **HRMS** (ESI) calcd for $C_{18}H_{17}N_2O_3S$ $[M+H]^+$ 341.0954, found 341.0959.

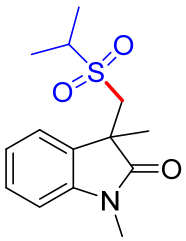
3-((Ethylsulfonyl)methyl)-1,3-dimethylindolin-2-one (5e)



General procedure 20 was followed to obtain **5e** (72.2 mg, 0.27 mmol, 90 %) as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.28 (m, 2H, Ar-H), 7.15 – 7.08 (m, 1H, Ar-H), 6.91 (d, J = 7.8 Hz, 1H, Ar-H), 3.59 (q, J = 14.5 Hz, 2H, CH_2), 3.26 (s, 3H, N-CH_3), 2.74 – 2.68 (m, 2H, CH_3-CH_2), 1.46 (s, 3H, CH_3), 1.27 (t, J = 7.4 Hz, 3H, SO_2CH_2-CH_3). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 178.0, 143.4, 130.4, 129.0, 123.5, 122.6, 108.8, 57.8, 49.5, 45.5, 26.6, 25.1, 6.4. **HRMS** (ESI) calcd for $C_{13}H_{18}NO_3S$ $[M+H]^+$ 268.1002, found 268.1008.

3-((Isopropylsulfonyl)methyl)-1,3-dimethylindolin-2-one (5f)

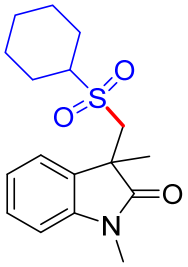


General procedure 20 was followed to obtain **5f** (58.2 mg, 0.21 mmol, 69 %) as a

colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 (d, J = 7.4 Hz, 1H, Ar-H), 7.35 – 7.30 (m, 1H, Ar-H), 7.13 – 7.09 (m, 1H, Ar-H), 6.90 (d, J = 7.8 Hz, 1H, Ar-H), 3.56 (q, J = 14.0 Hz, 2H, CH_2), 3.26 (s, 3H, N-CH_3), 2.91 – 2.84 (m, 1H, CH), 1.46 (s, 3H, CH_3), 1.31 (d, J = 3.8 Hz, 3H, CH-CH_3), 1.29 (d, J = 3.8 Hz, 3H, CH-CH_3). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 178.2, 143.3, 130.4, 128.9, 123.9, 122.6, 108.6, 77.4, 77.1, 76.7, 55.0, 45.3, 26.6, 25.2, 15.2, 15.0. **HRMS** (ESI) calcd for $C_{14}H_{20}NO_3S$ $[M+H]^+$ 282.1158, found 282.1164.

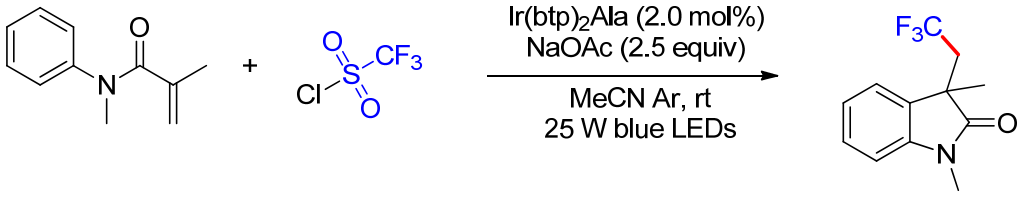
3-((Cyclohexylsulfonyl)methyl)-1,3-dimethylindolin-2-one (5g)



General procedure 20 was followed to obtain **5g** (55.9 mg, 0.17 mmol, 58 %) as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 (d, J = 7.8 Hz, 1H, Ar-H), 7.35 – 7.31 (m, 1H, Ar-H), 7.12 – 7.09 (m, 1H, Ar-H), 6.90 (d, J = 7.8 Hz, 1H, Ar-H), 3.61 (d, J = 14.0 Hz, 1H, CH_2), 3.48 (d, J = 14.0 Hz, 1H, CH_2), 3.26 (s, 3H, N-CH_3), 2.57 – 2.49 (m, J = 8.7, 4.4 Hz, 1H, CH), 2.09 – 2.04 (m, 2H, CH-CH_2), 1.89 – 1.85 (m, 2H, CH-CH_2), 1.71 – 1.63 (m, 2H, $CHCH_2$-CH_2), 1.46 (s, 3H, CH_3), 1.44 – 1.39 (m, 2H, $CHCH_2$-CH_2), 1.20 – 1.17 (m, 2H, $CHCH_2CH_2$-CH_2). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 178.3, 143.3, 130.4, 128.9, 123.8, 122.5, 108.7, 62.9, 55.2, 45.2, 26.6, 25.2, 25.01, 25.00, 24.9, 24.8, 24.76. **HRMS** (ESI) calcd for $C_{17}H_{24}NO_3S$ $[M+H]^+$ 322.1471, found 322.1477.

5.4 General Procedure 21 for Sulfonylation of Substrates **5k**

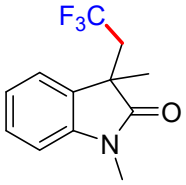


1a 2l 5h

Under argon atmosphere, to a 10 mL Schlenk tube was added **1a** (0.3 mmol, 1.0 equiv), trifluoromethanesulfonyl chloride (125.9 mg, 0.75 mmol, 2.5 equiv), NaOAc

(61.5 mg, 0.75 mmol, 2.5 equiv), $Ir(btp)_2Ala$ (4.5 mg, 0.06mmol, 2.0 mol%) and 2 mL MeCN. The reaction mixtue was stirred at room temperature under 25 W blue LED irradiation for 24 hours, followed by the addition of H_2O (20 mL), and extracted with DCM (10 mL). The combined organic layer was washed with brine (10 mL × 3), dried over Na_2SO_4, and concentrated. The residue was purified by flash chromatography on a silica gel using petroleum ether and ethyl acetate (5:1, v/v) as the eluent to give **5h**.

1,3-Dimethyl-3-(((trifluoromethyl)sulfonyl)methyl)indolin-2-one (5h)



General procedure 21 was followed to obtain **5h** (70.1 mg, 0.23 mmol, 76 %) as a yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 – 7.30 (m, 1H, Ar-H), 7.26 (d, J = 3.0 Hz, 1H, Ar-H), 7.11 – 7.07 (m, 1H, Ar-H), 6.88 (d, J = 7.8 Hz, 1H, Ar-H), 3.24 (s, 3H, N-CH_3), 2.86 – 2.76 (m, 1H, CH_2), 2.70 – 2.60 (m, 1H, CH_2), 1.41 (s, 3H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$) δ 178.5, 142.8, 131.0, 129.93 – 129.23 (m, 1C), 128.5, 123.6, 122.7, 108.5, 44.4, 40.6 (q, J = 24.1 Hz, 1C), 26.4, 25.0. **HRMS** (ESI) calcd for $C_{12}H_{13}FNO$ $[M+H]^+$ 244.0944, found 244.0947.

Reference:

1. (a) Connelly, N. G.; Geiger, W. E. Chemical redox agents for organometallic chemistry. *Chem. Rev.* **1996**, *96*, 877–910. (b) Choi, G. J.; Zhu, Q. L.; Miller, D. C.; Gu, C. J.; Knowles, R. R. Catalytic alkylation of remote C-H bonds enabled by proton-coupled electron transfer. *Nature* **2016**, *539*, 268–271.

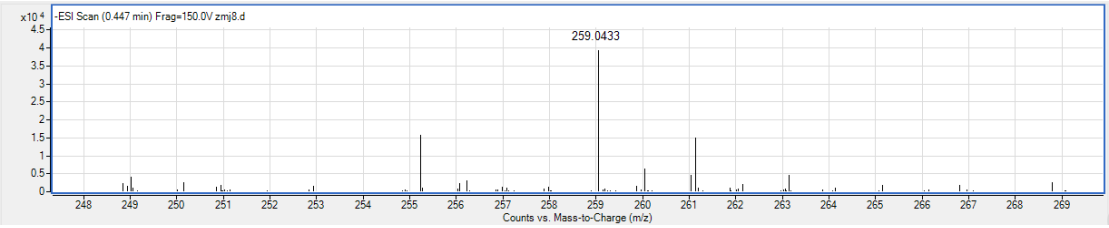
2. Brennan, J. L.; Keyes, T. E.; Forster, R. J. Photonic and electrochemical properties of adsorbed $[Ru(dpp)_2(Qbpy)]^{2+}$ luminophores. *Langmuir* **2006**, *22*, 10754–10761.

3. (a) Døssing, A.; Ryu, C. K.; Kudo, S.; Ford, P. C. Competitive bimolecular electron- and energy-transfer quenching of the excited state(s) of the tetranuclear copper(I) cluster $Cu_4I_4py_4$. Evidence for large reorganization energies in an excited-state electron transfer. *J. Am. Chem. Soc.* **1993**, *115*, 5132–5137. (b) Bruner, B.; Walker, M. B.; Ghimire, M. M.; Zhang, D.; Selke, M.; Klausmeyer, K. K.; Omary,

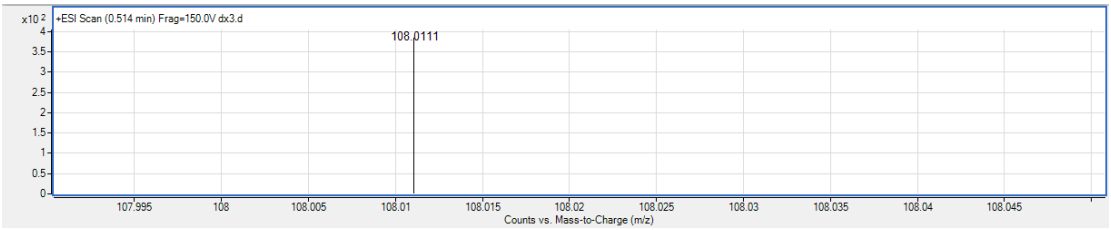
M. A.; Farmer, P. J. Ligand-based photooxidations of dithiomaltolato complexes of Ru(ii) and Zn(ii): photolytic CH activation and evidence of singlet oxygen generation and quenching. *Dalton Trans.* **2014**, *43*, 11548–11556. (c) Le, C.; Chen, T. Q.; Liang, T.; Zhang, P.; MacMillan, D. W. C. A radical approach to the copper oxidative addition problem: Trifluoromethylation of bromoarenes. Science **2018**, *360*, 1010–1014.

6. MS (ESI) spectrum

MS (ESI) spectrum of Intermediation 5

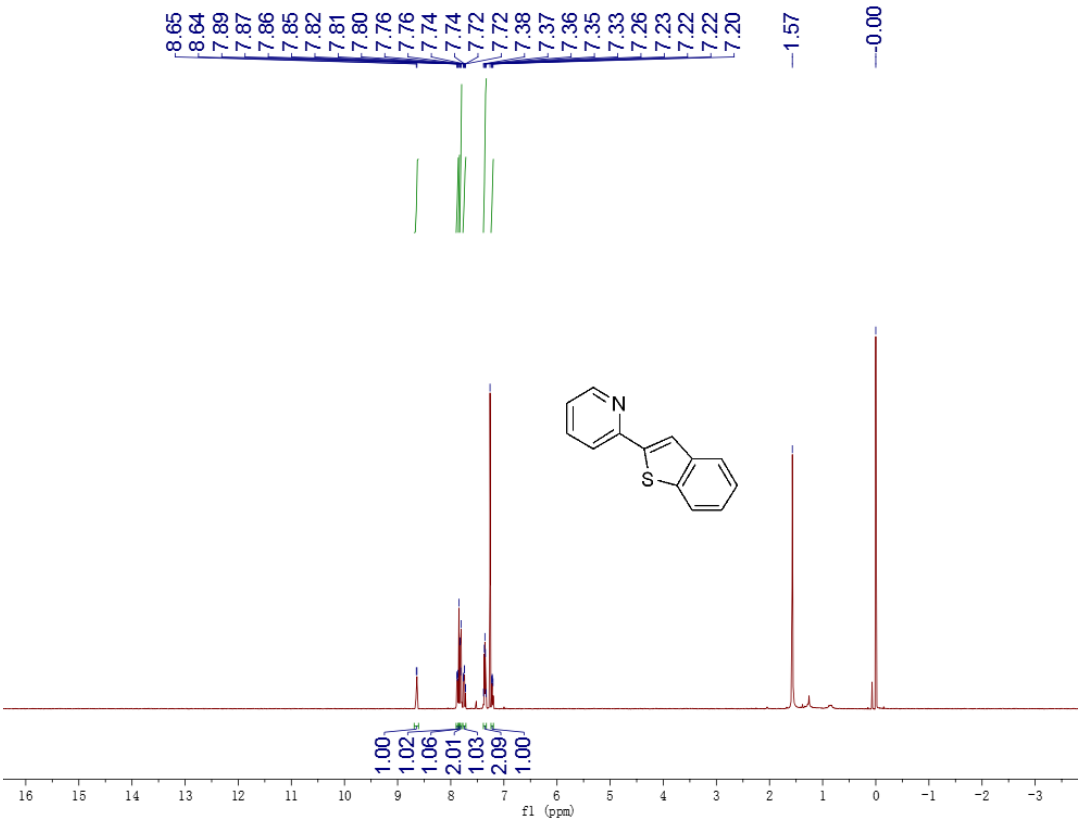


MS (ESI) spectrum of Intermediation A^1 and A^2

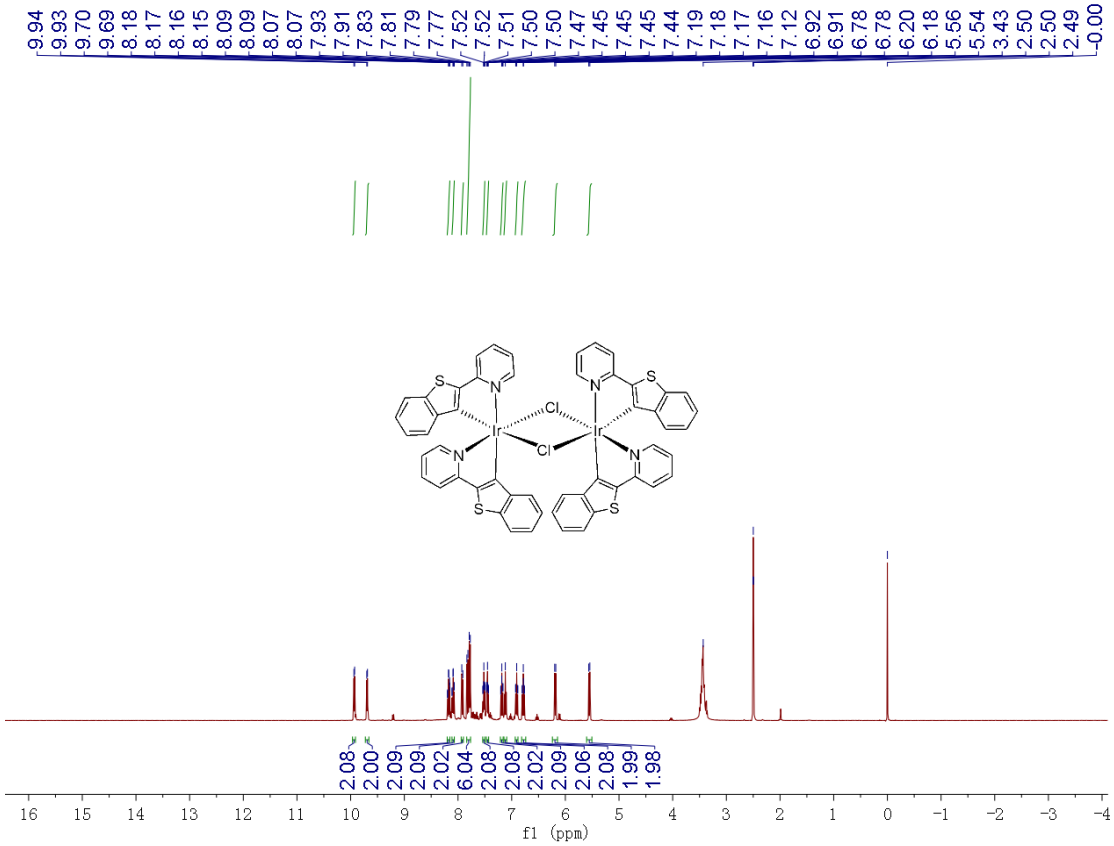


7. **^{1}H NMR and ^{13}C NMR spectrum of Photocatalysts**

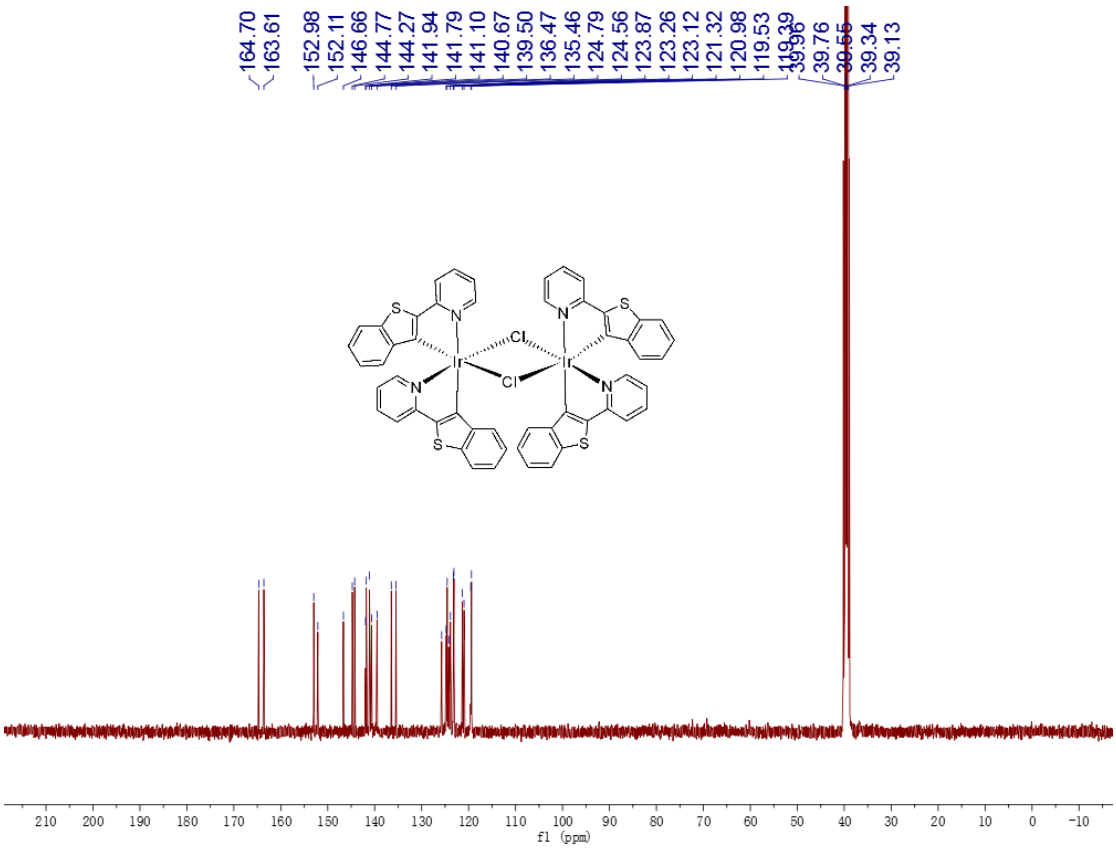
^{1}H NMR spectrum of compound L1



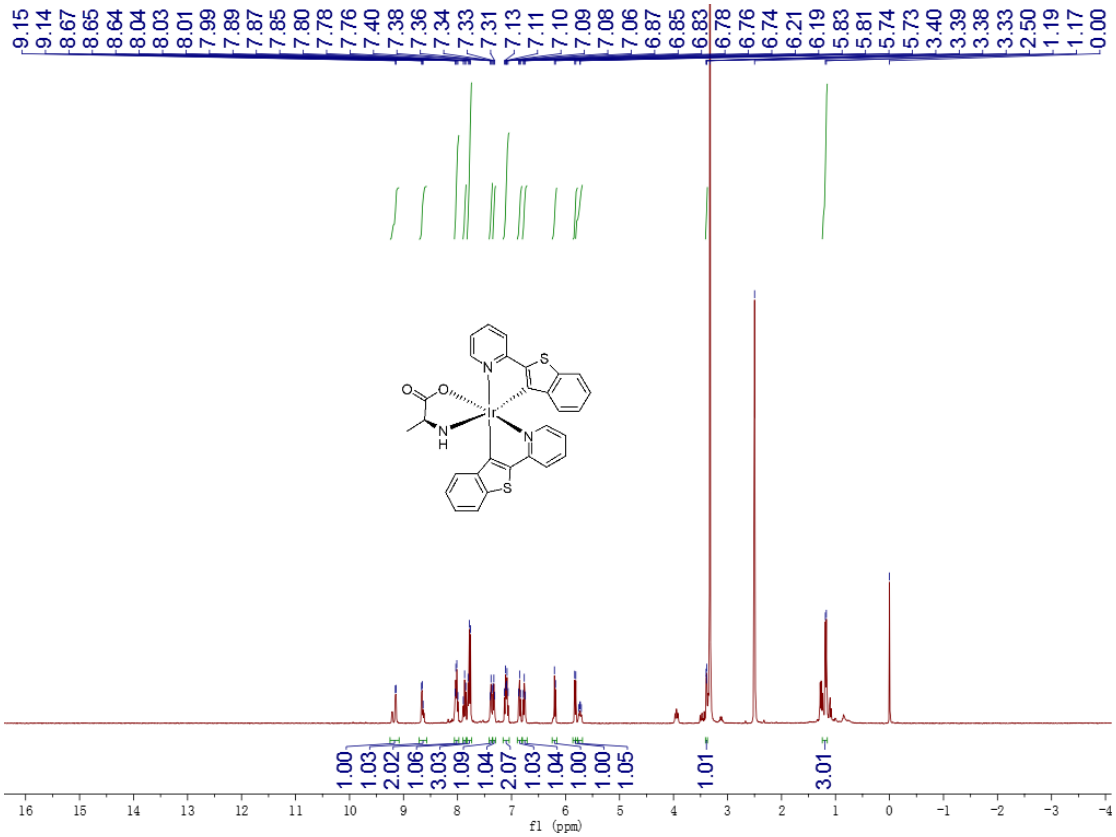
^{1}H NMR spectrum of photocatalyst Ir(btp)$_2$Cl



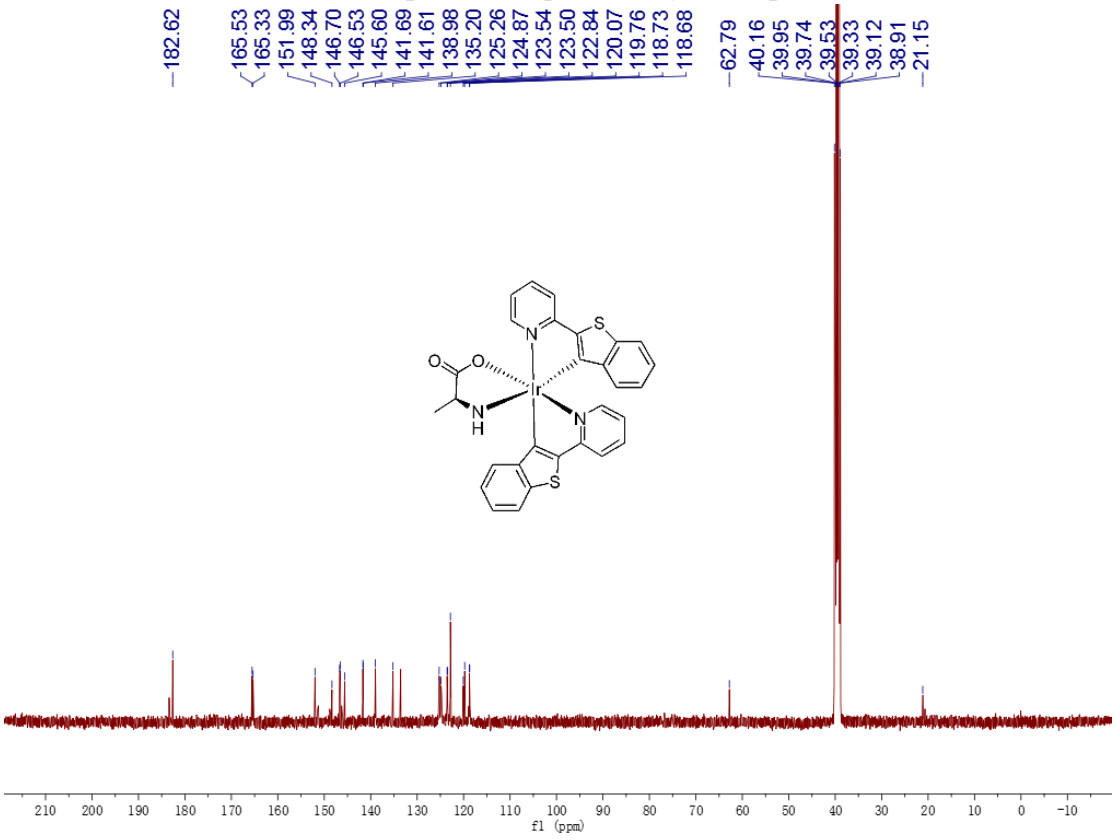
^{13}C NMR spectrum of photocatalyst Ir(btp)$_2$Cl



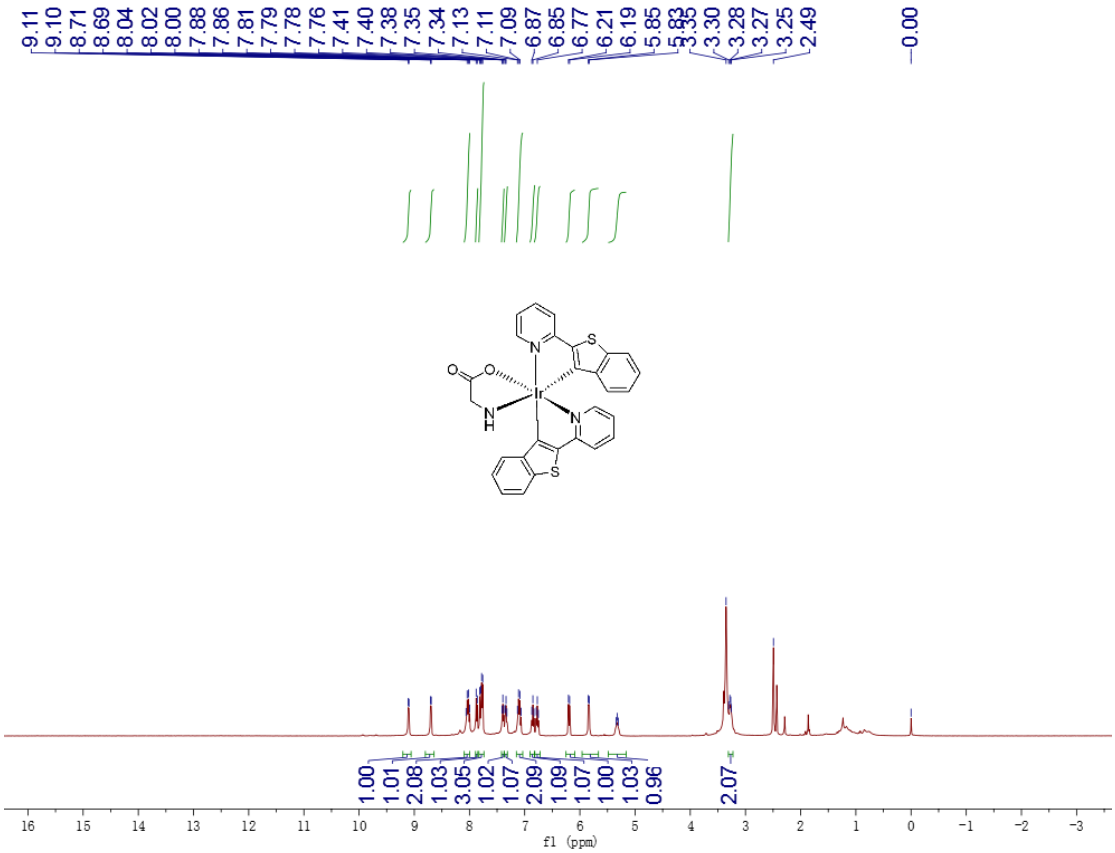
^{1}H NMR spectrum of photocatalyst Ir(btp)$_2$Ala



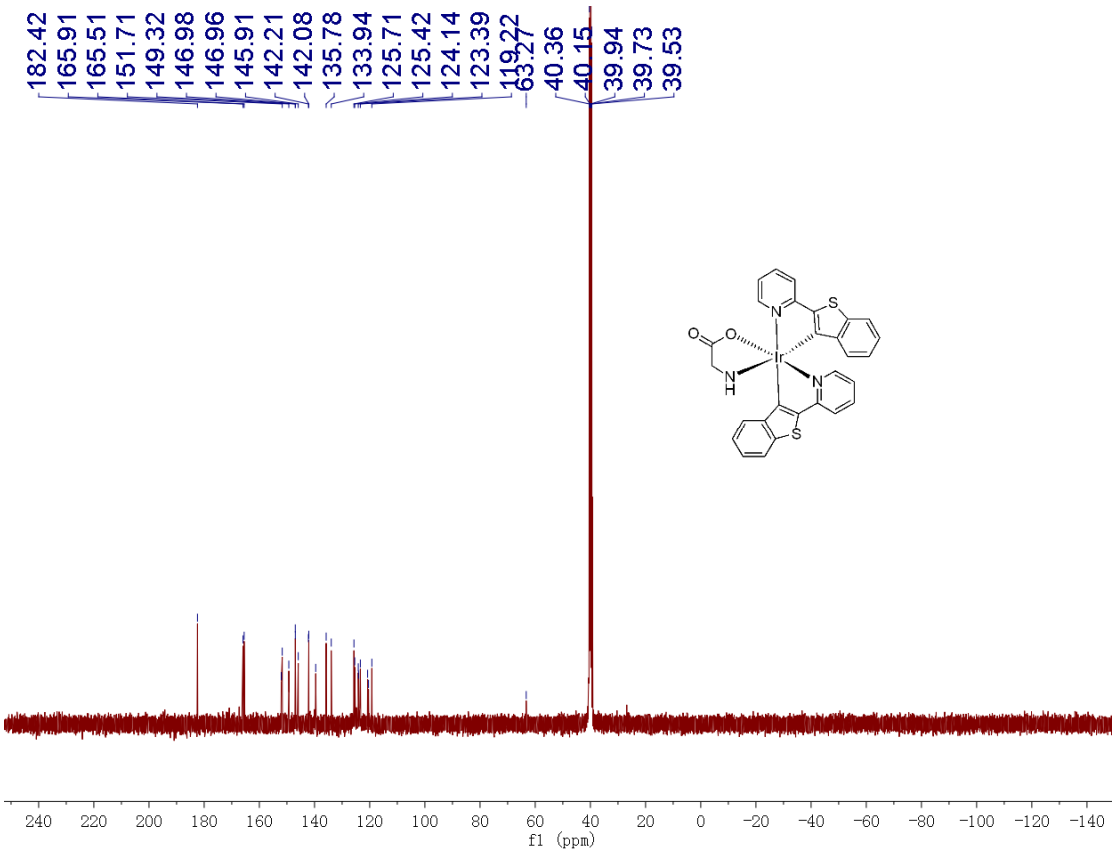
^{13}C NMR spectrum of photocatalyst Ir(btp)$_2$Ala



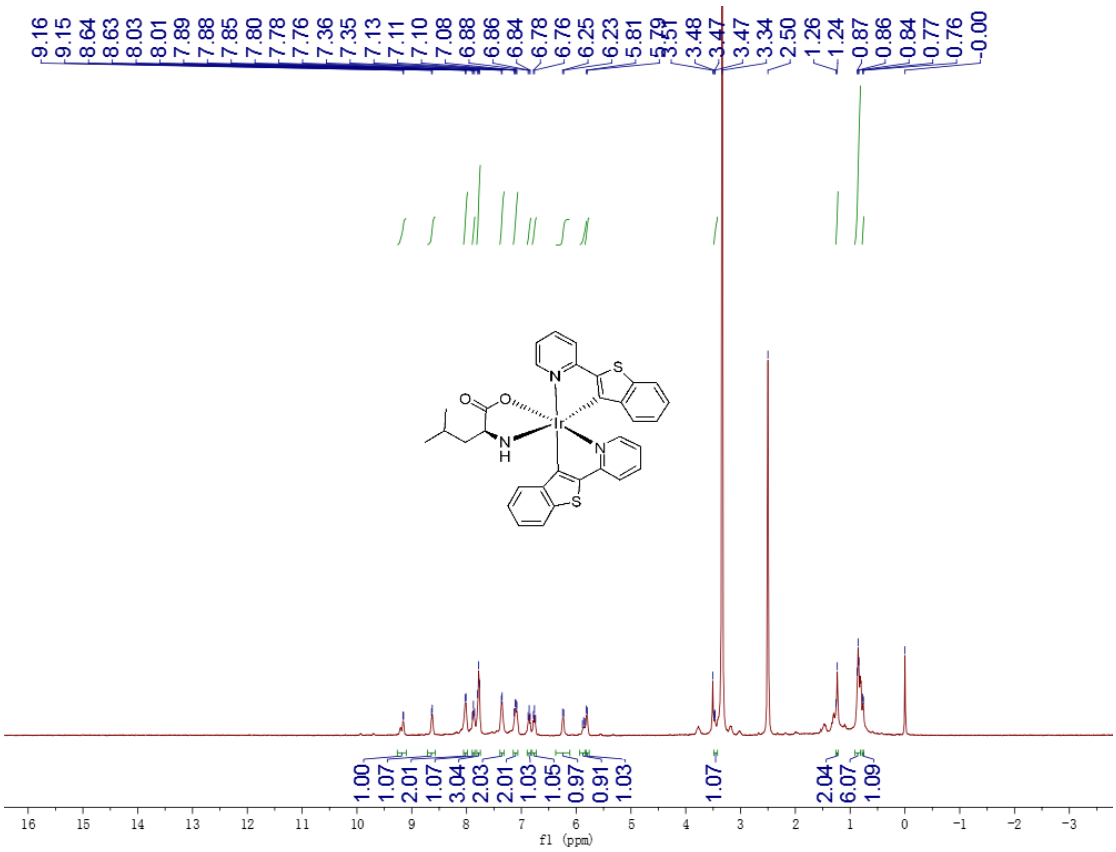
^{1}H NMR spectrum of photocatalyst Ir(btp)$_2$Gly



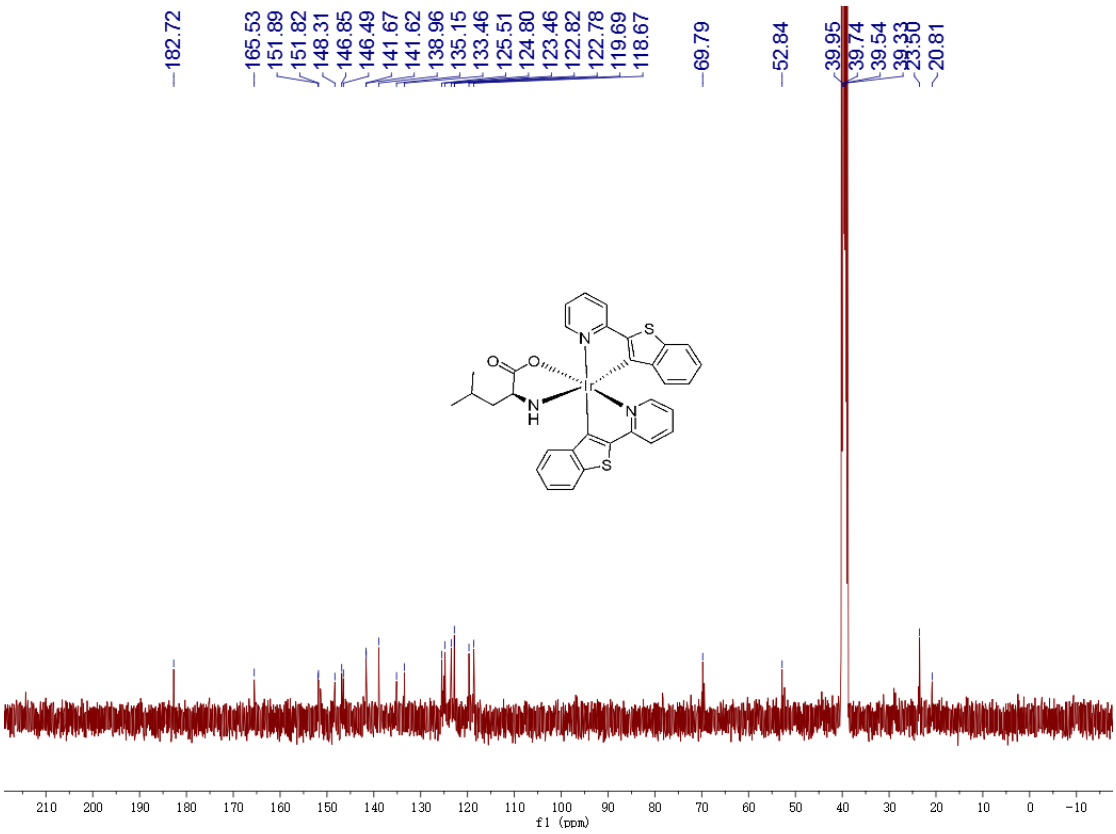
^{13}C NMR spectrum of photocatalyst Ir(btp)$_2$Gly



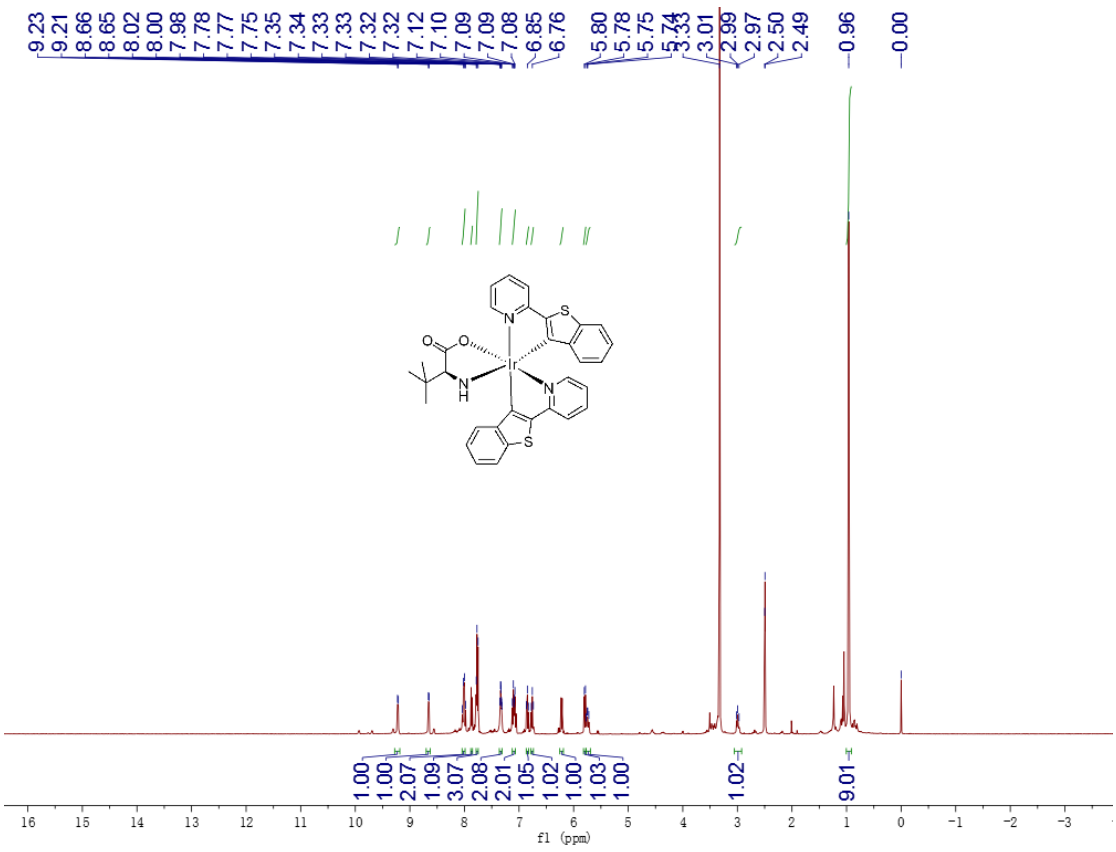
^{1}H NMR spectrum of photocatalyst Ir(btp)$_2$Leu



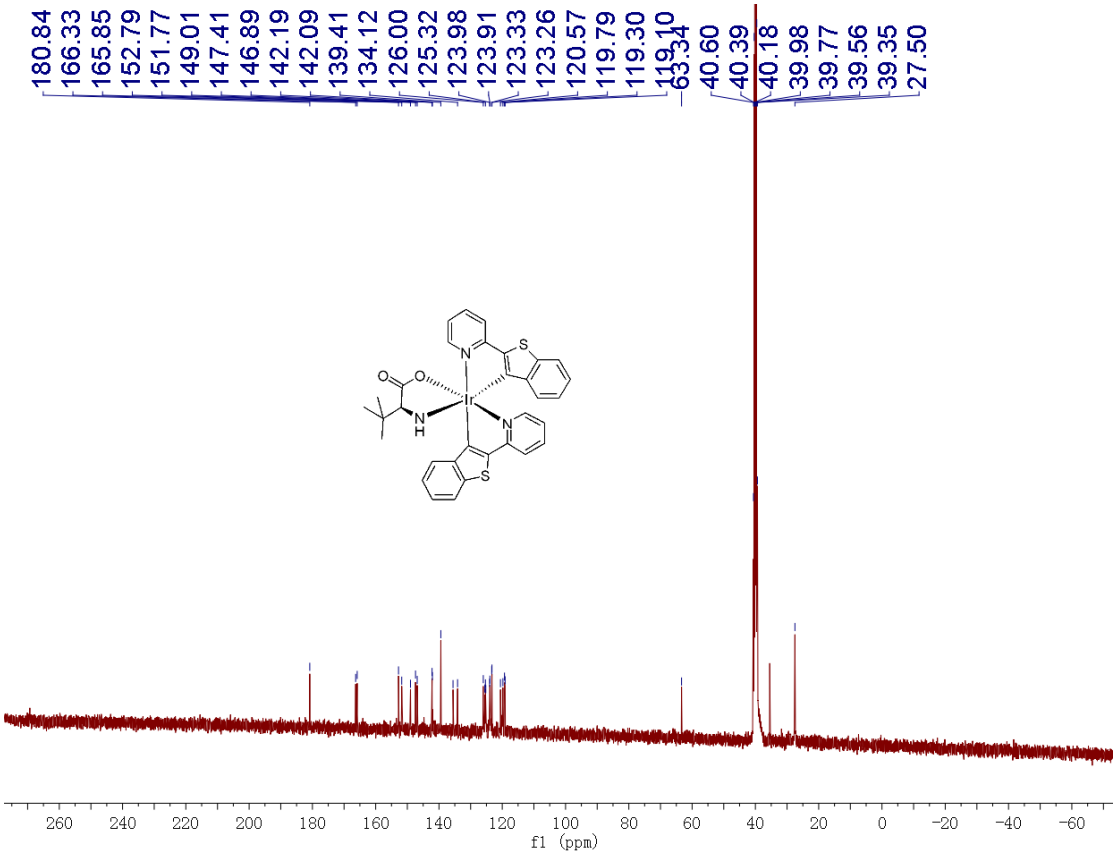
^{13}C NMR spectrum of photocatalyst Ir(btp)$_2$Leu



^{1}H NMR spectrum of compound Ir(btp)$_2$(t-Leu)

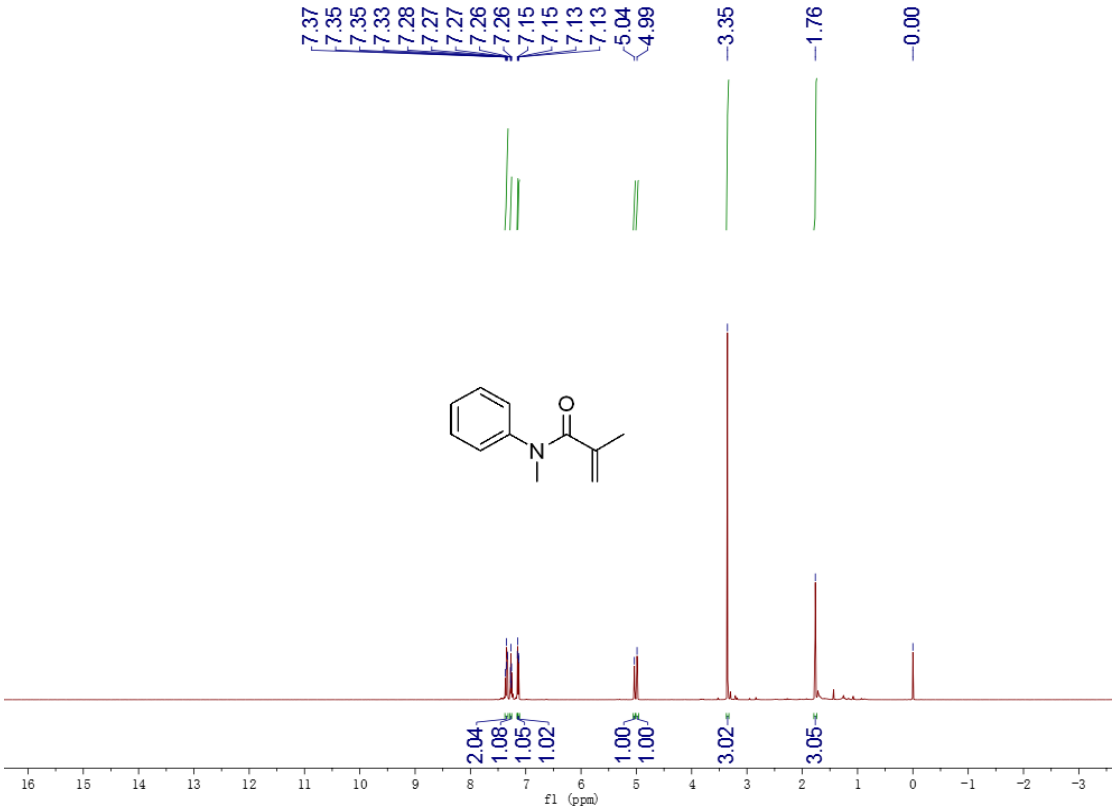


^{13}C NMR spectrum of photocatalyst Ir(btp)$_2$(t-Leu)

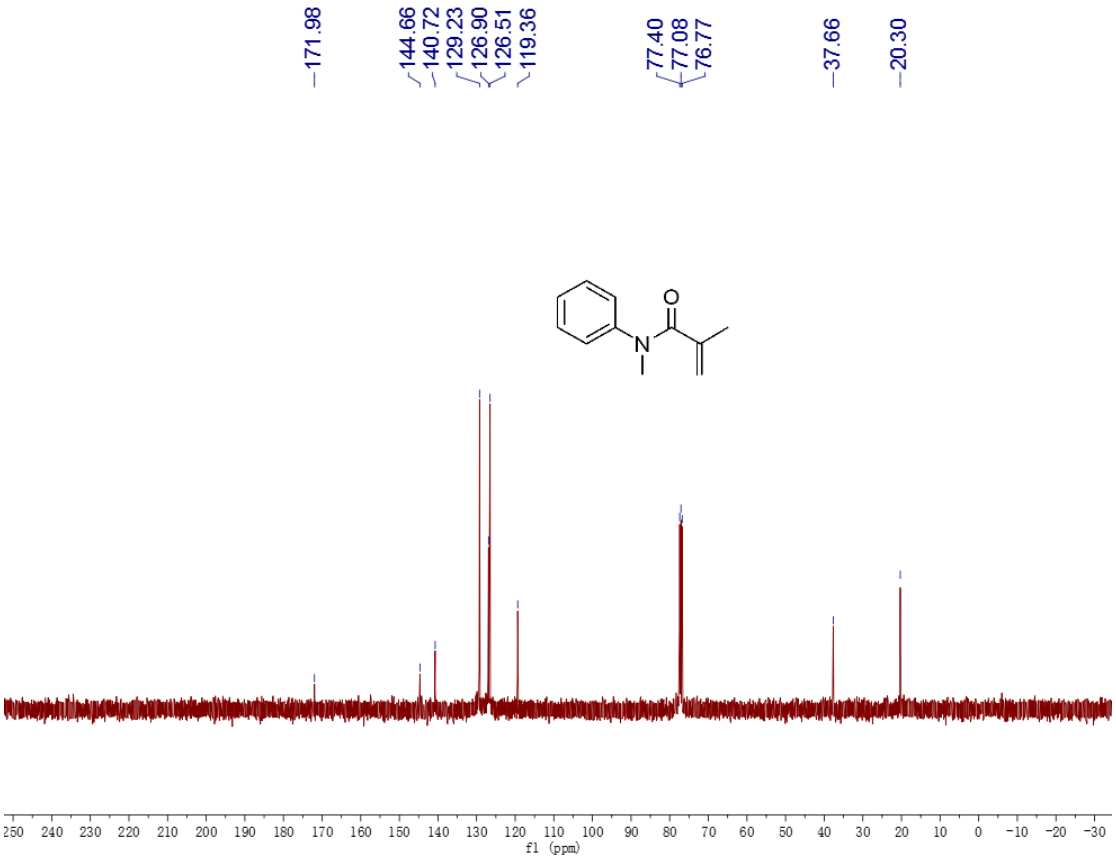


8. ^{1}H NMR and ^{13}C NMR spectrum of Substrates

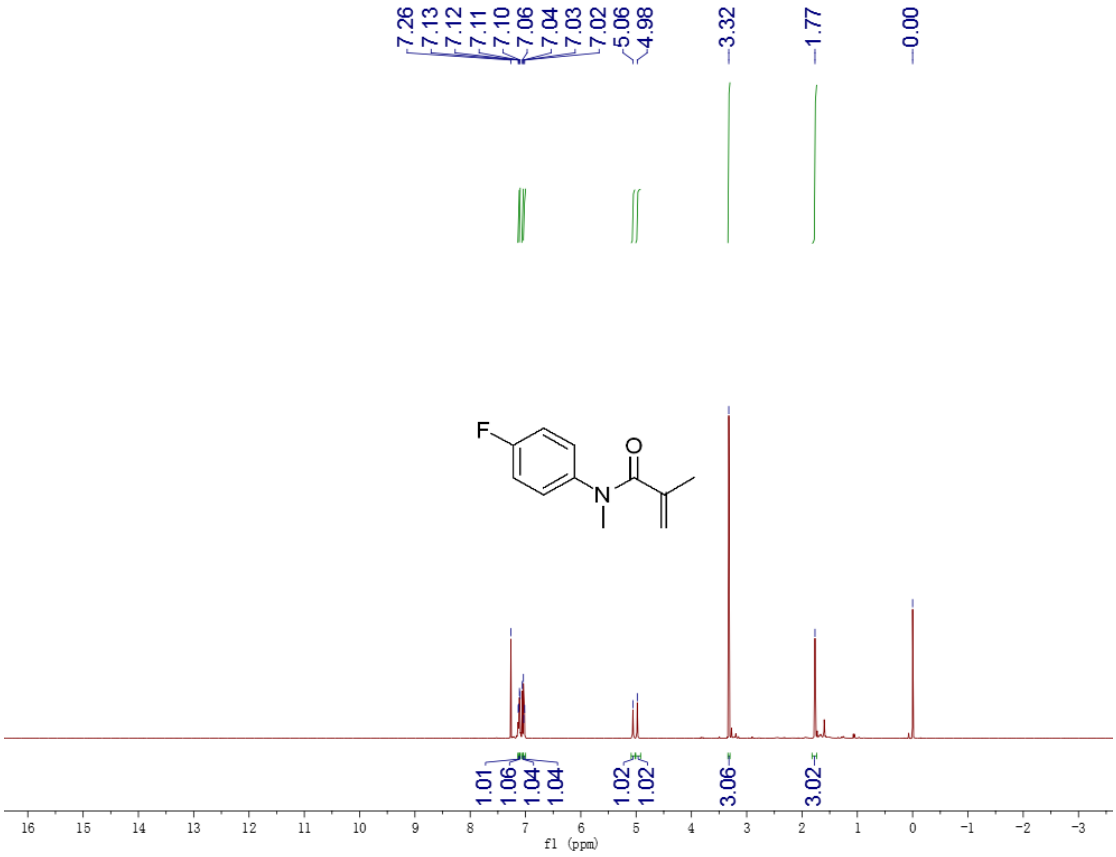
^{1}H NMR spectrum of compound 1a



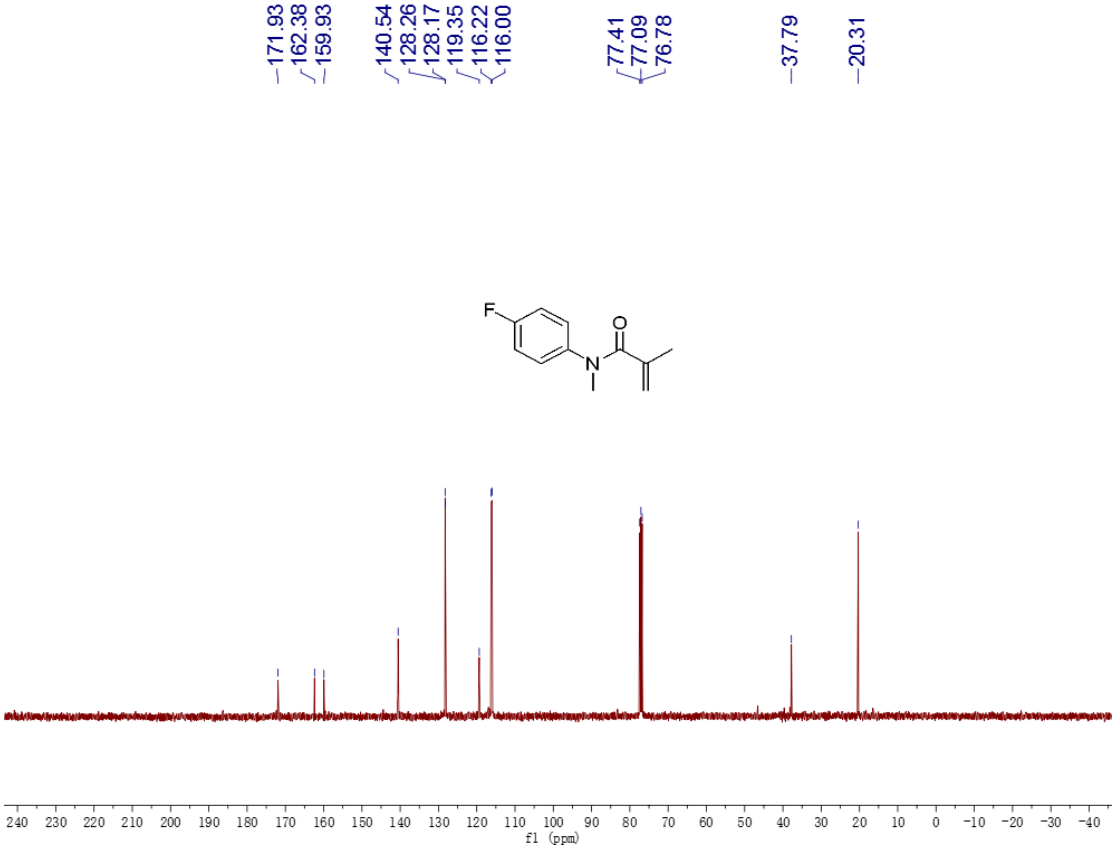
^{13}C NMR spectrum of compound 1a



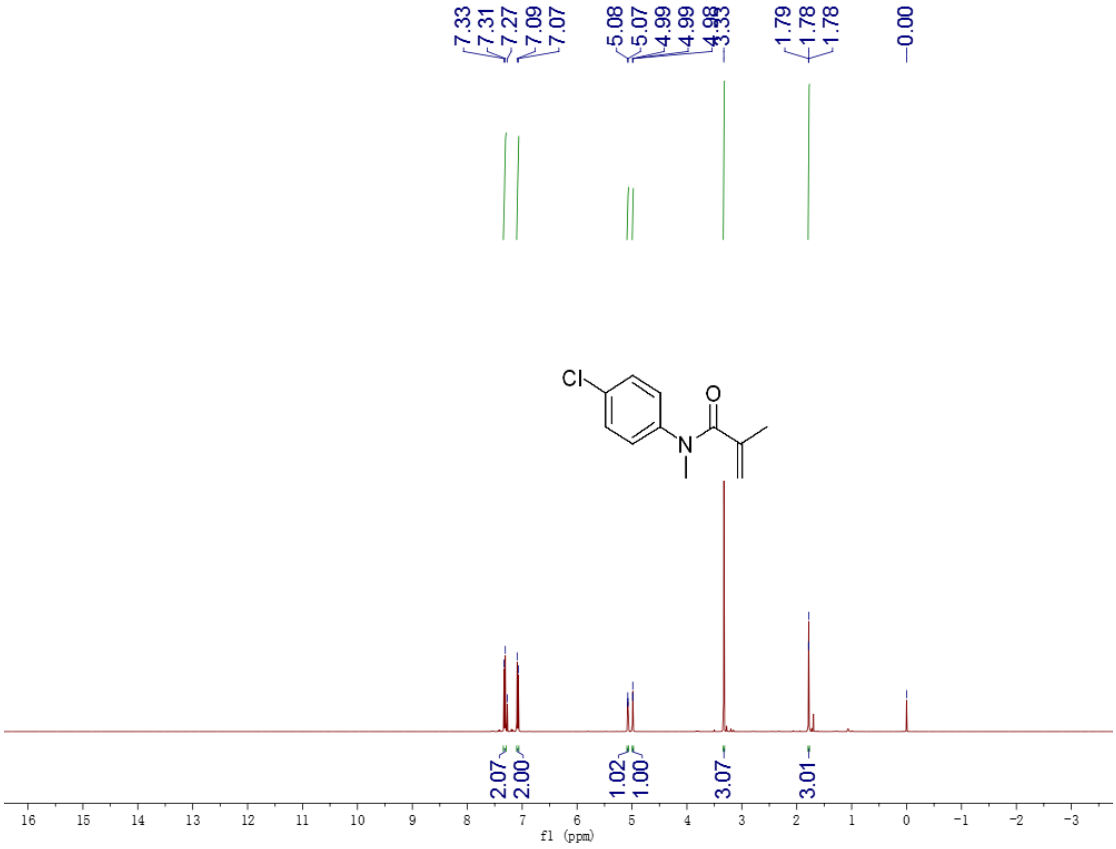
^{1}H NMR spectrum of compound 1b



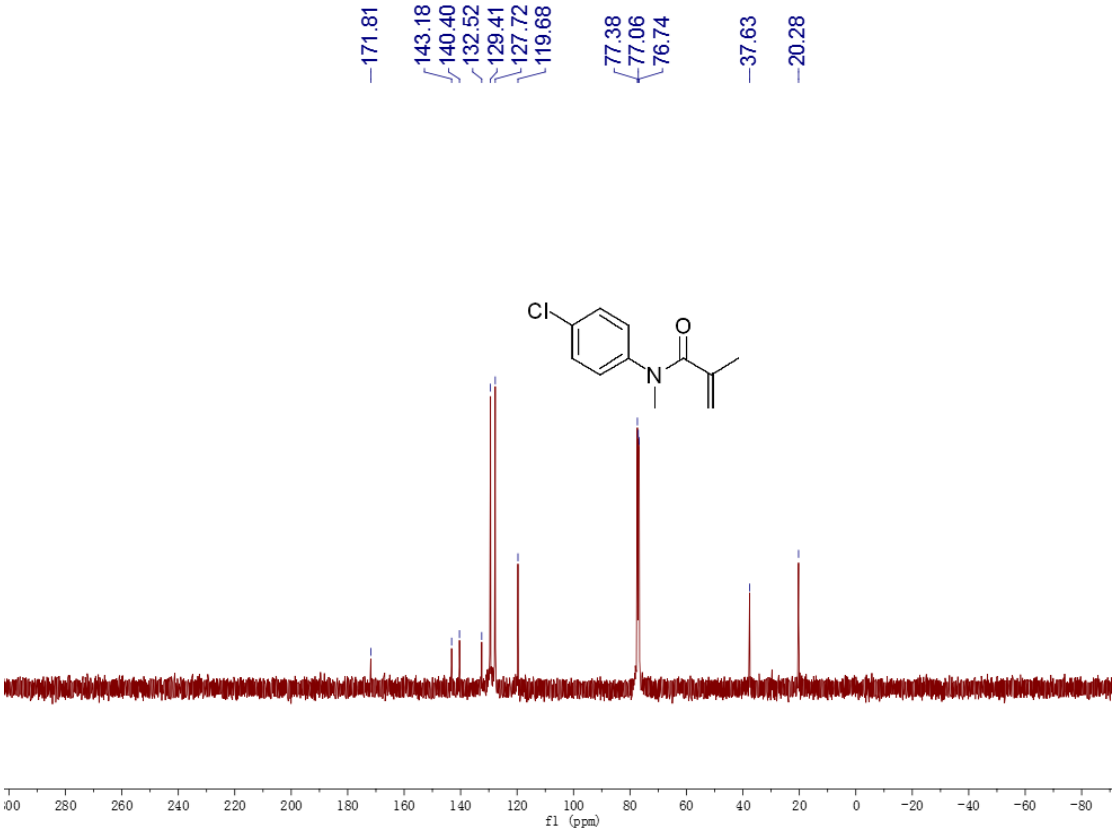
^{13}C NMR spectrum of compound 1b



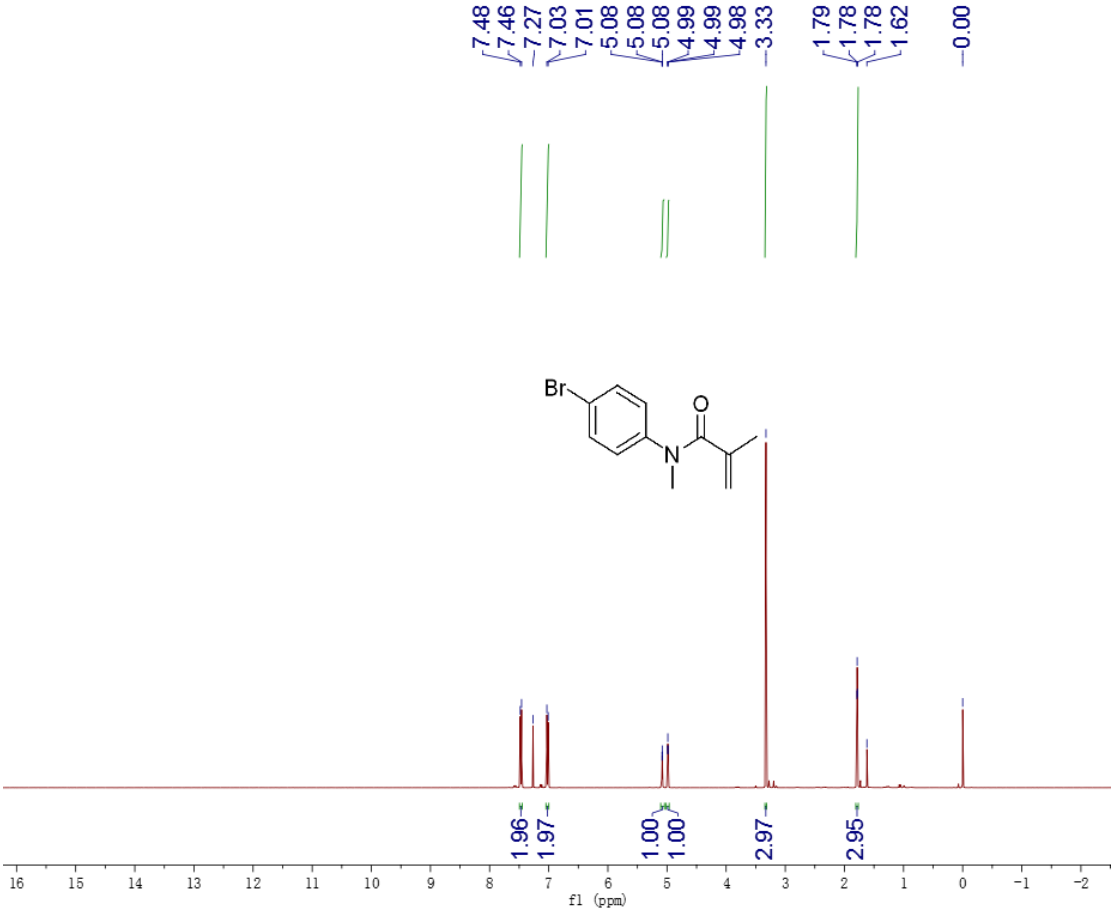
^{1}H NMR spectrum of compound 1c



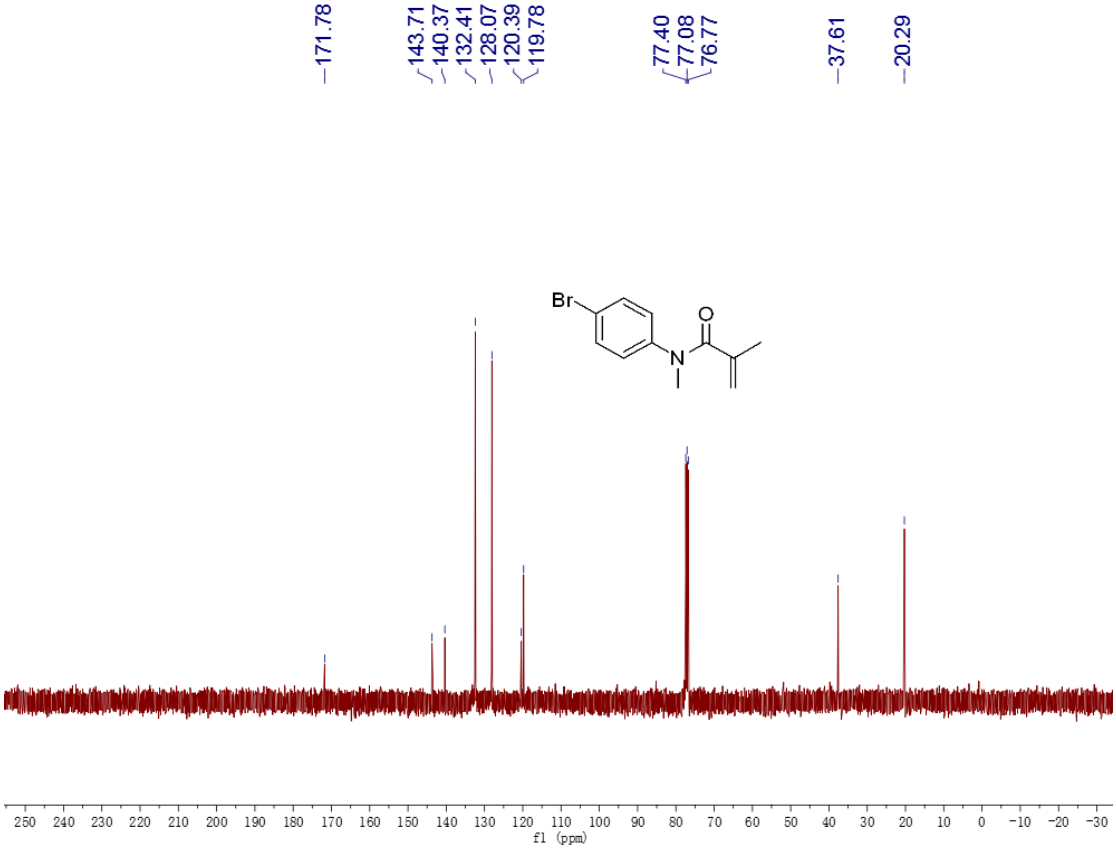
^{13}C NMR spectrum of compound 1c



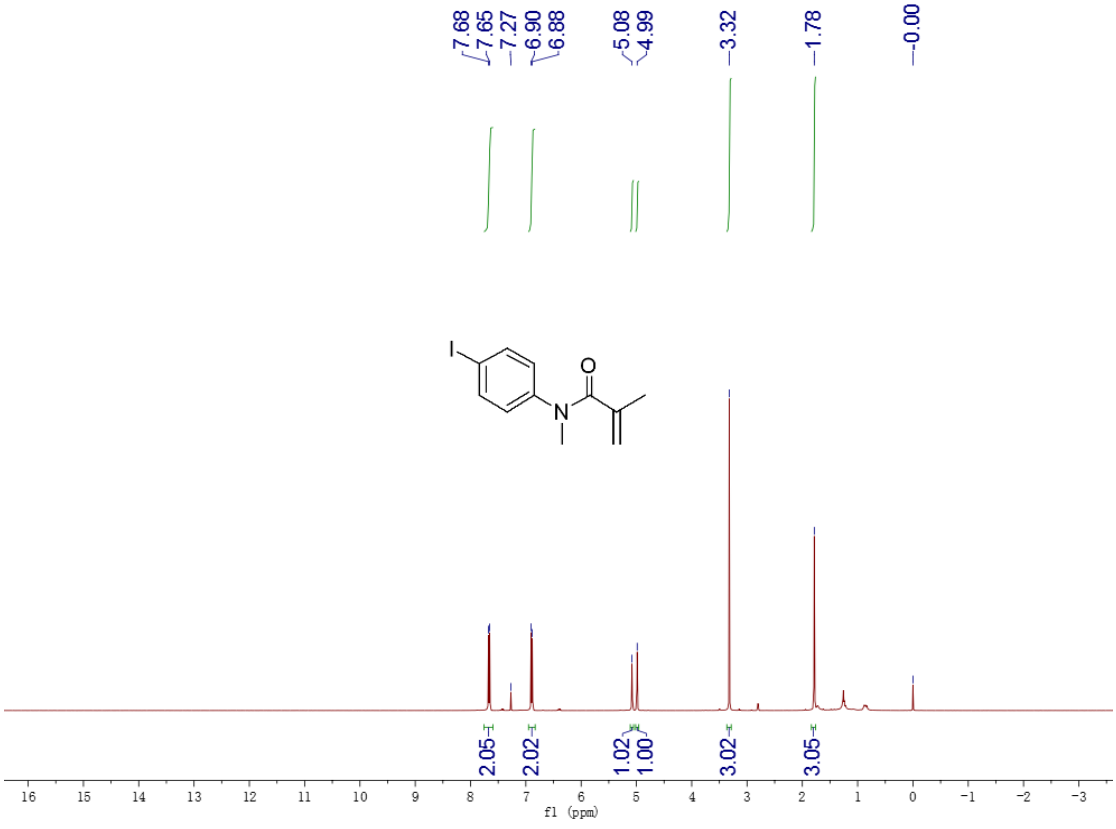
^{1}H NMR spectrum of compound 1d



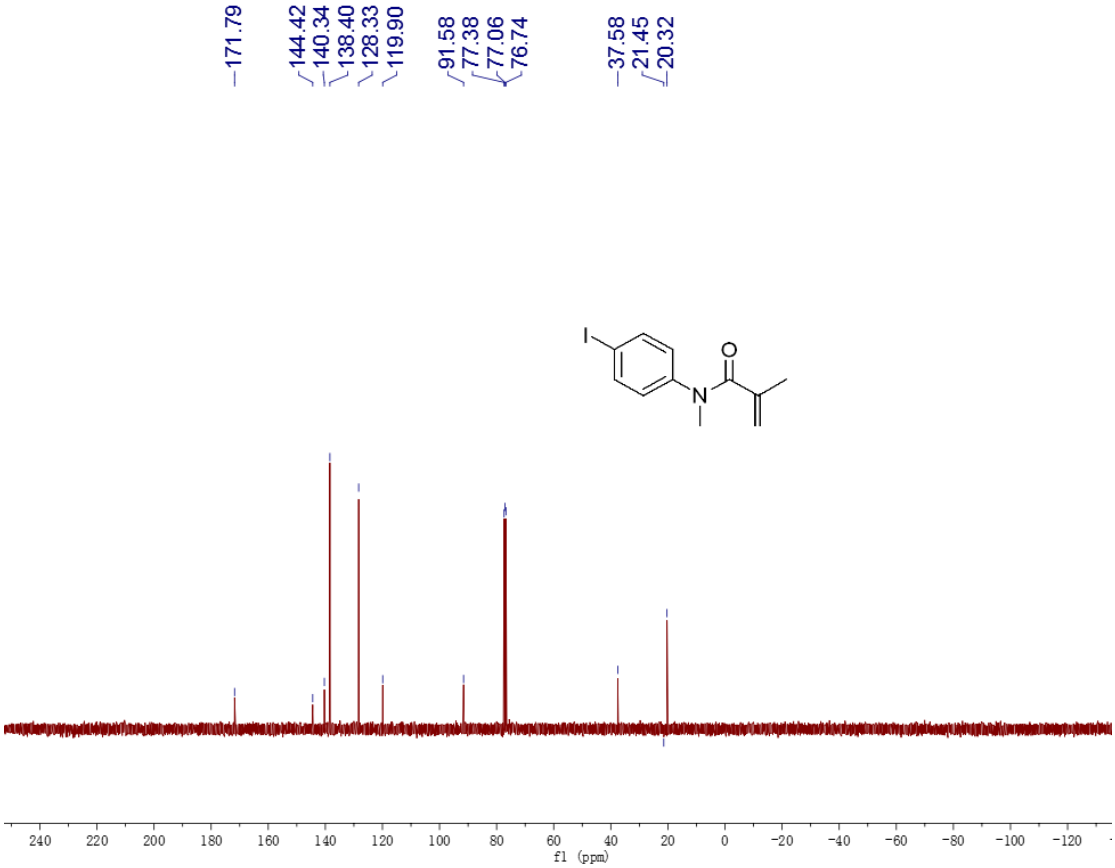
^{13}C NMR spectrum of compound 1d



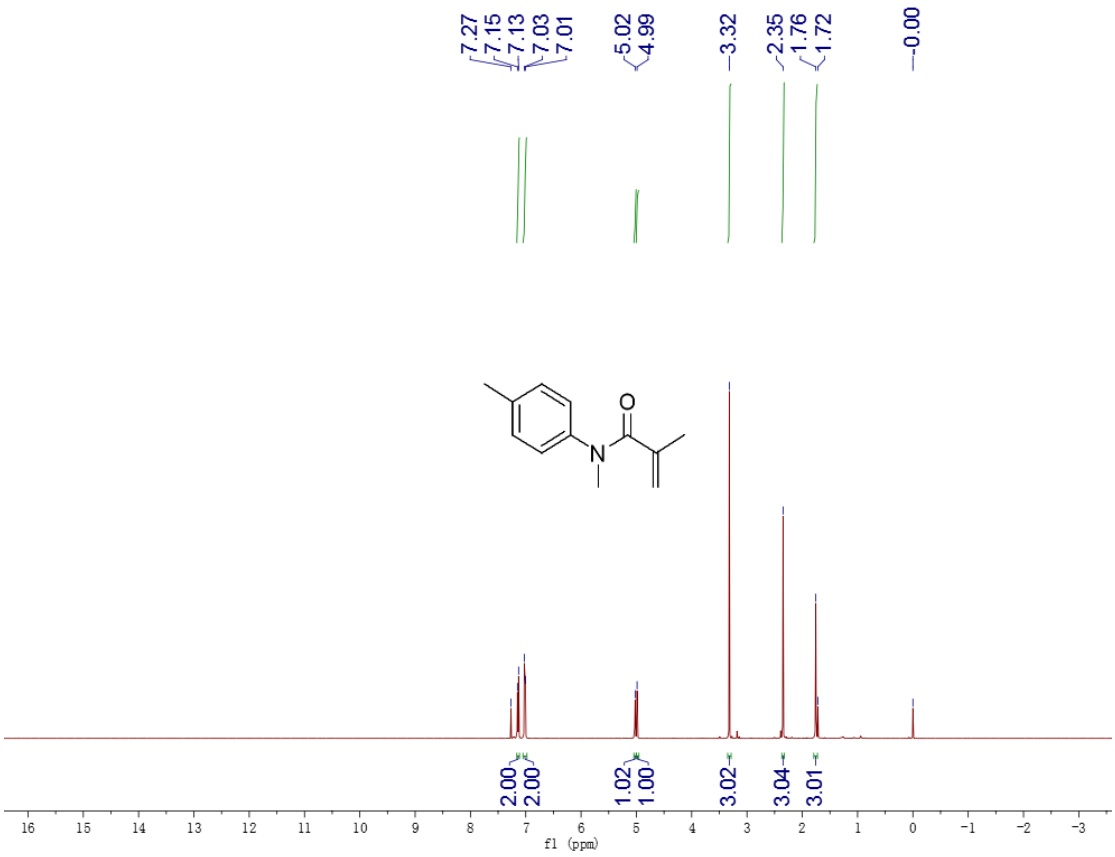
^{1}H NMR spectrum of compound 1e



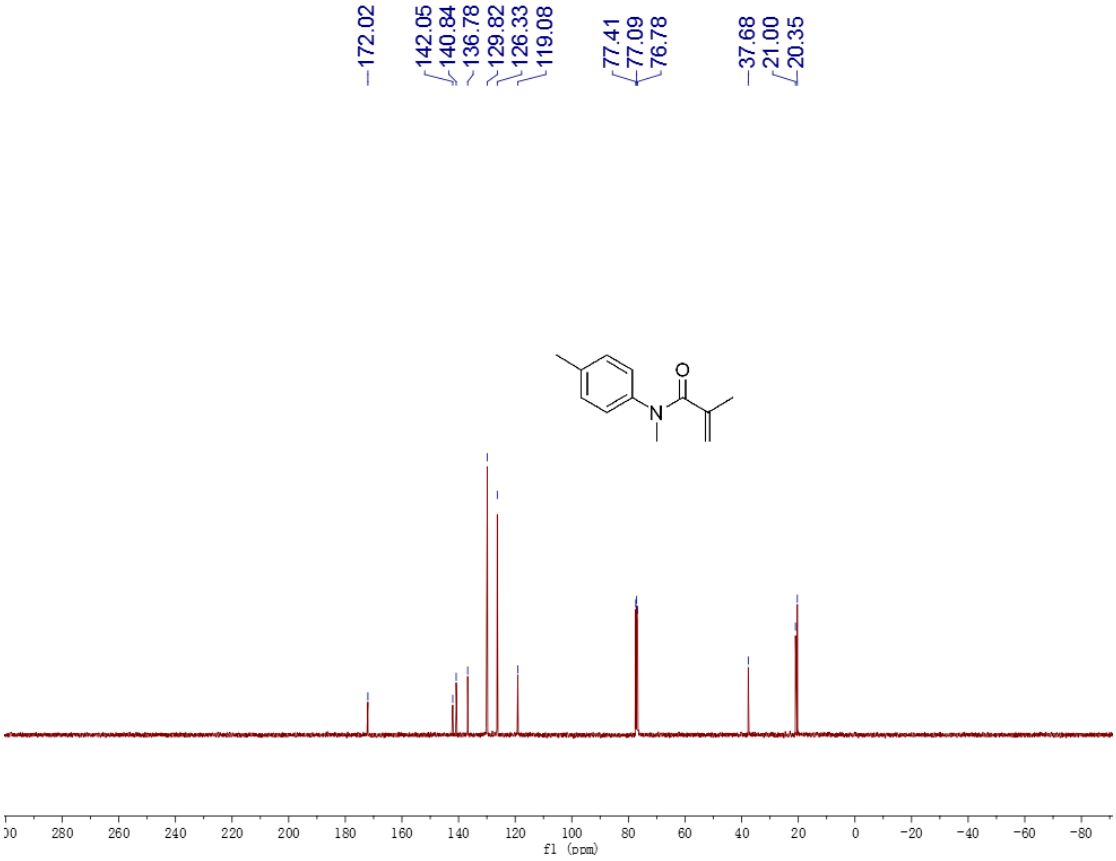
^{13}C NMR spectrum of compound 1e



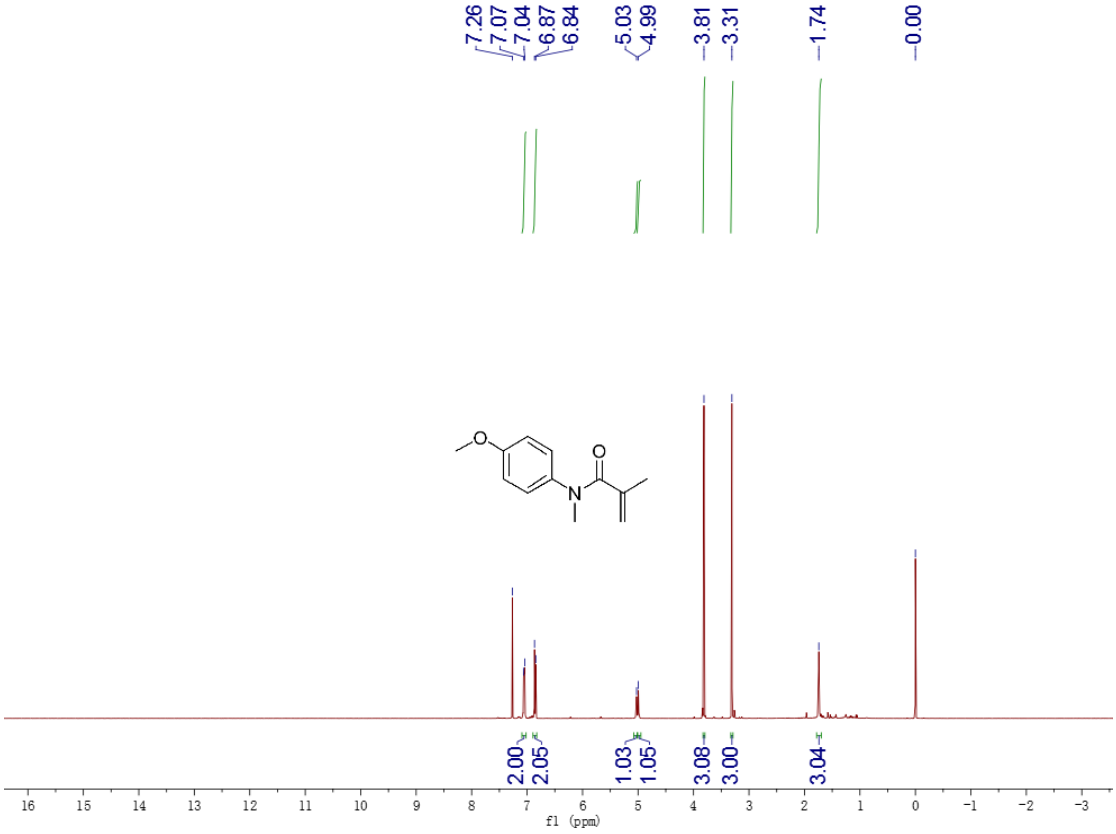
^{1}H NMR spectrum of compound 1f



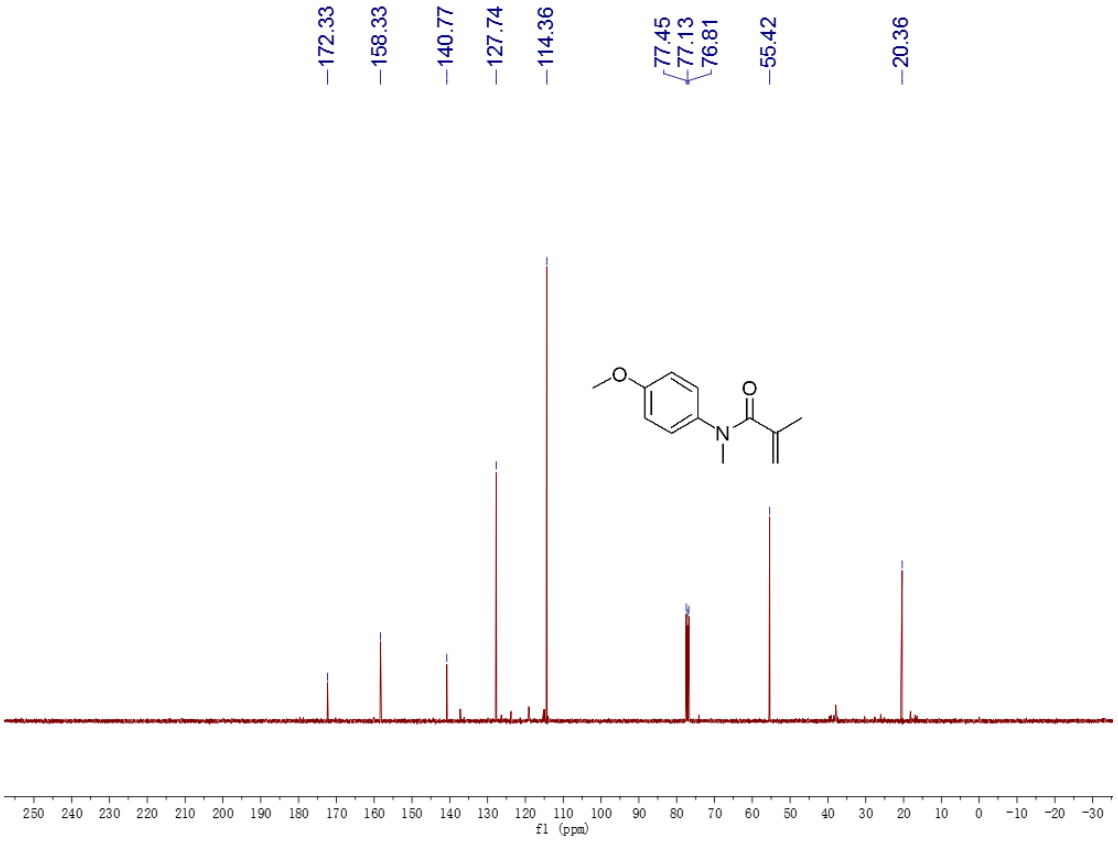
^{13}C NMR spectrum of compound 1f



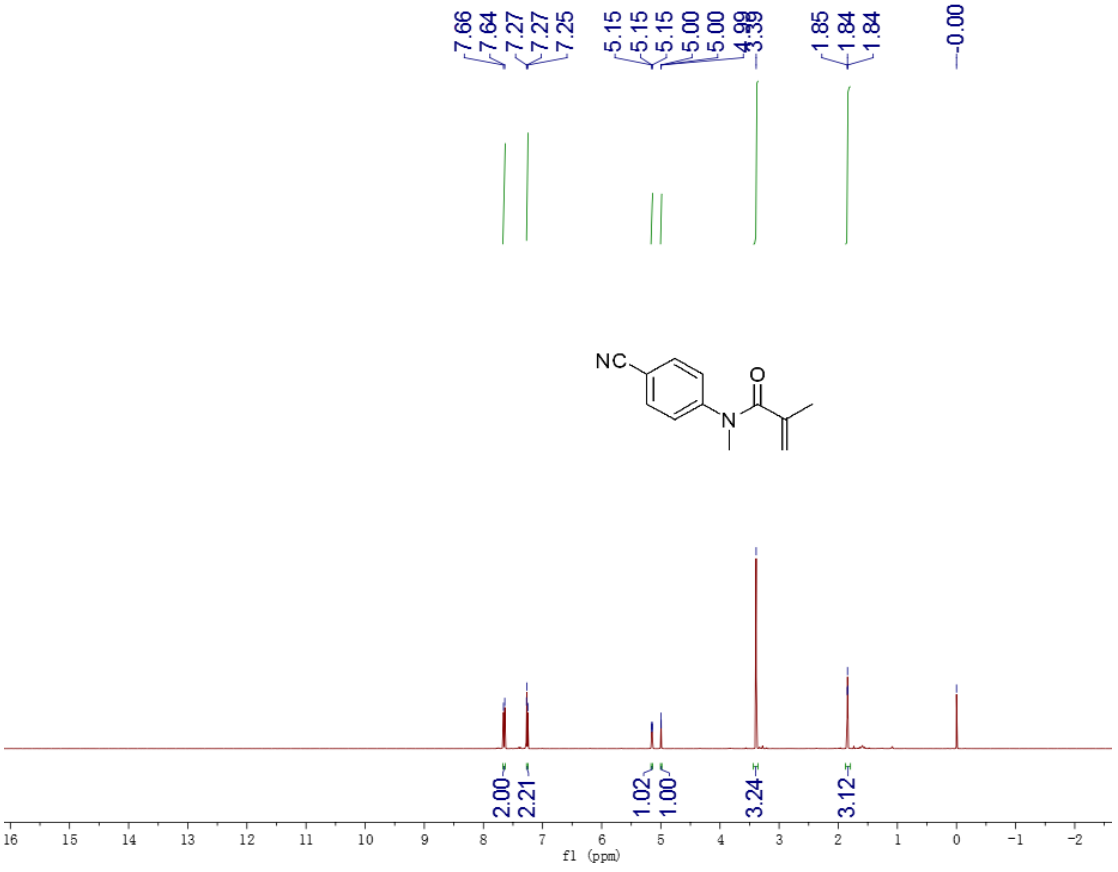
^{1}H NMR spectrum of compound 1g



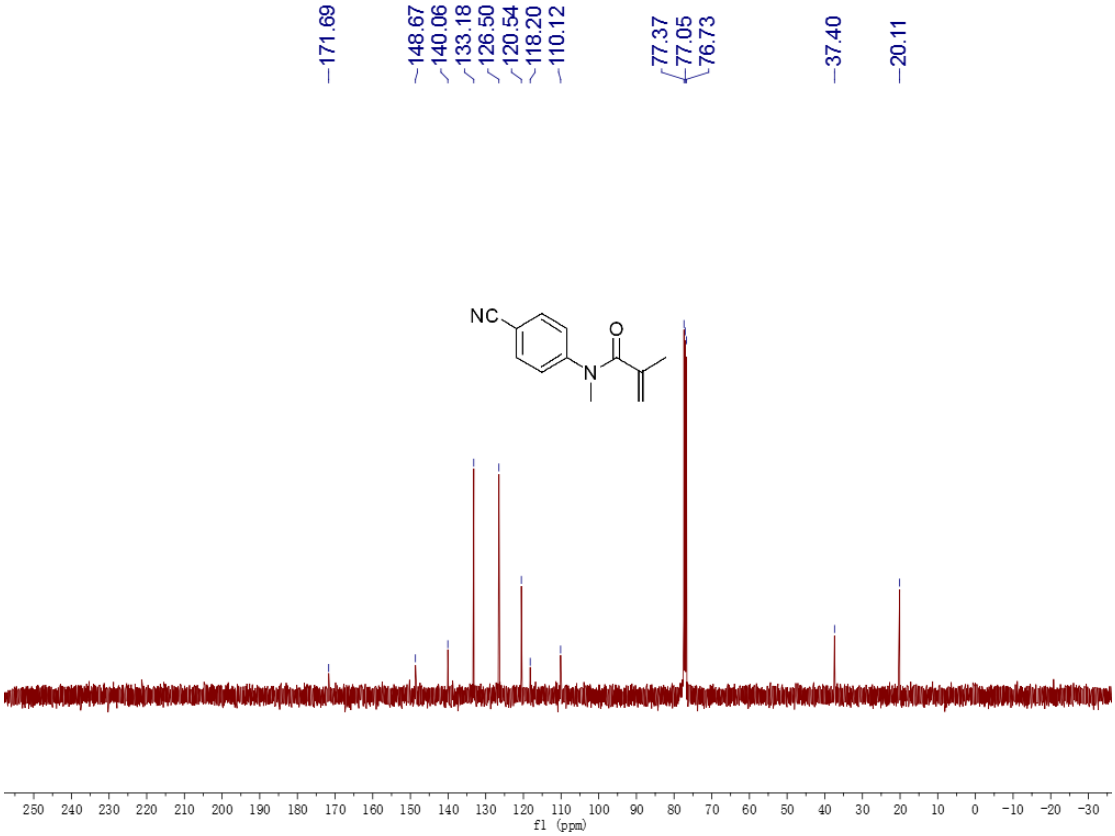
^{13}C NMR spectrum of compound 1g



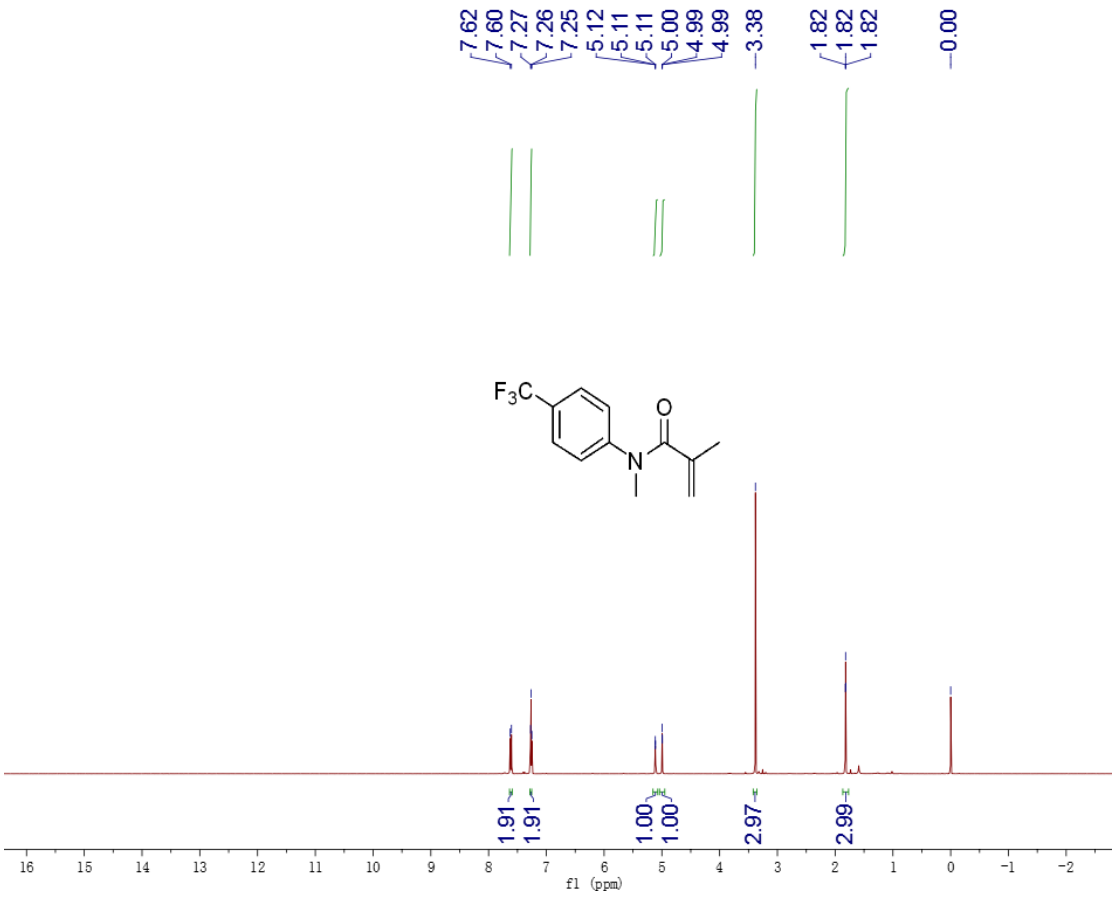
^{1}H NMR spectrum of compound 1h



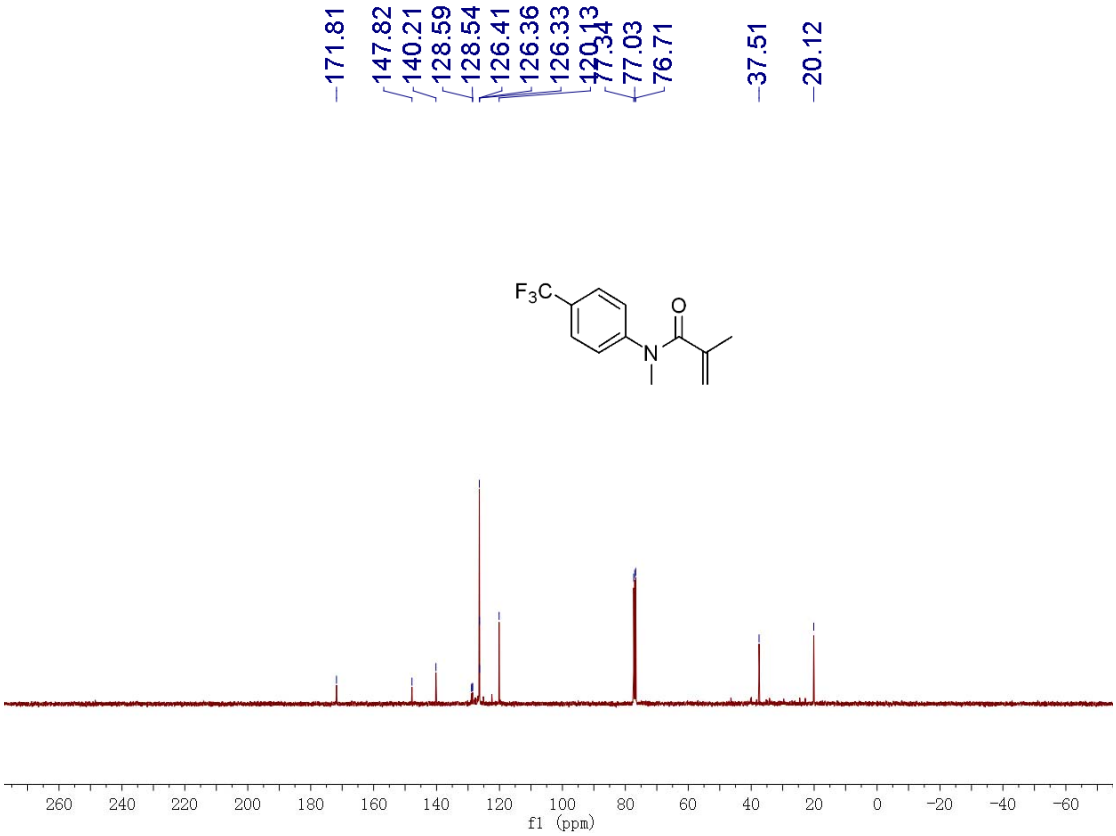
^{13}C NMR spectrum of compound 1h



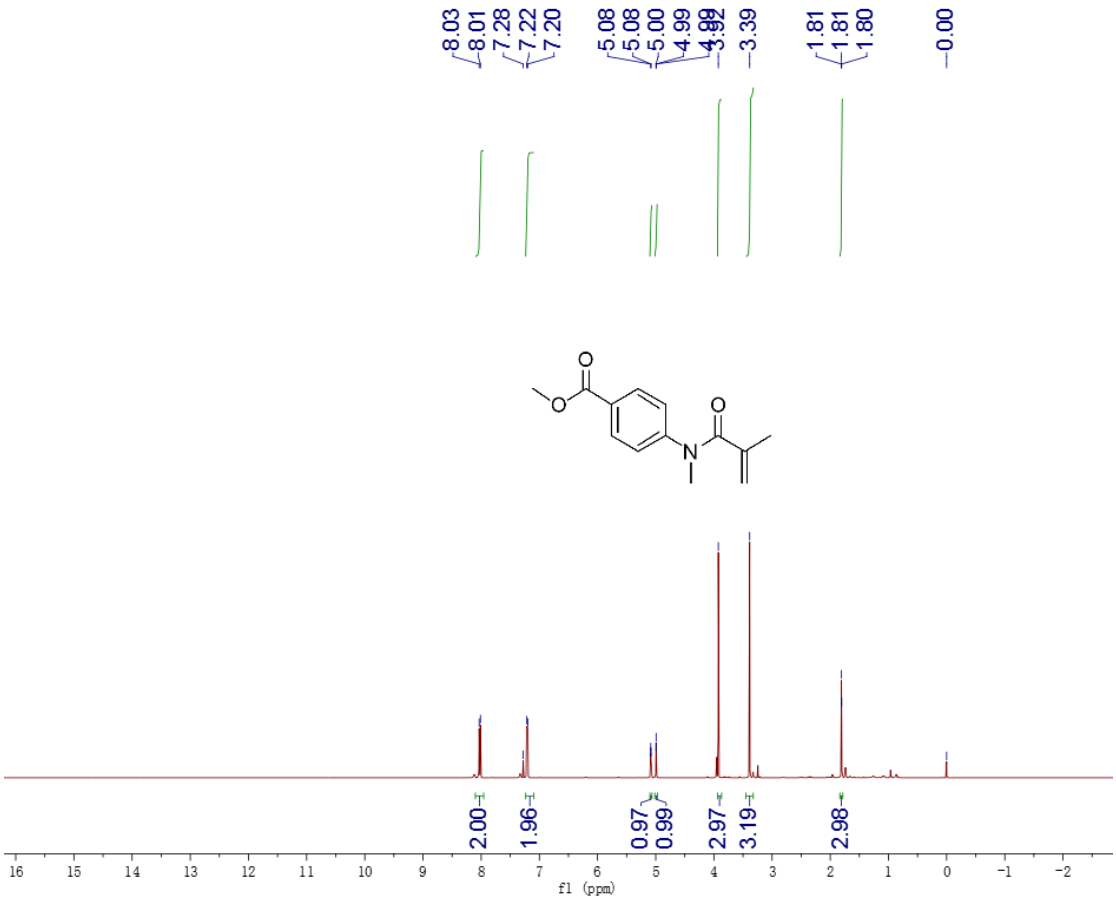
^{1}H NMR spectrum of compound 1i



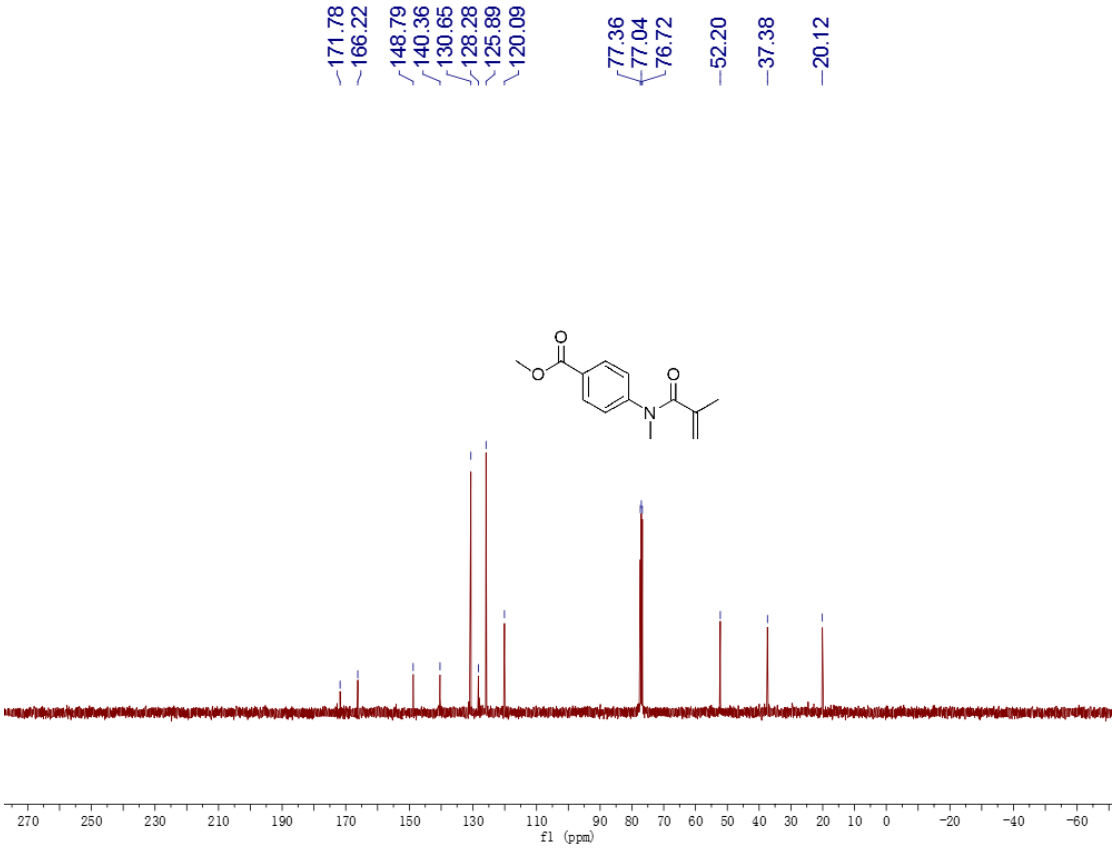
^{13}C NMR spectrum of compound 1i



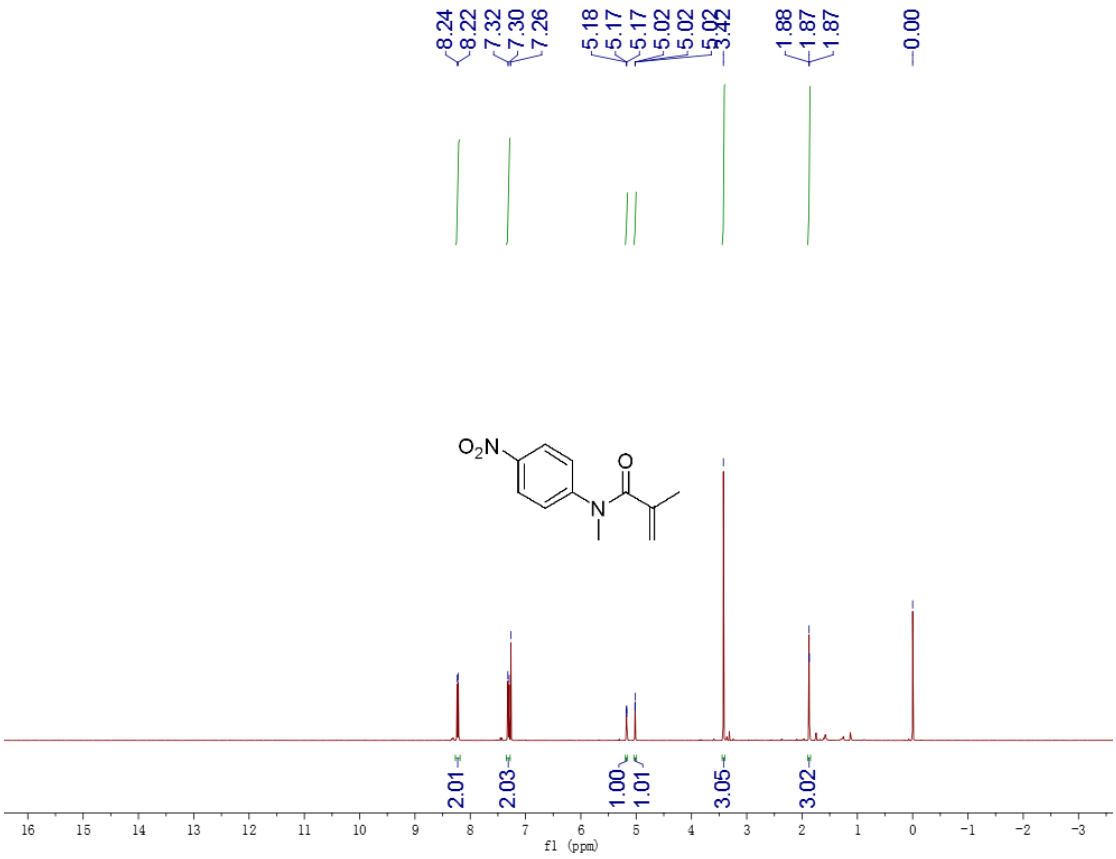
^{1}H NMR spectrum of compound 1j



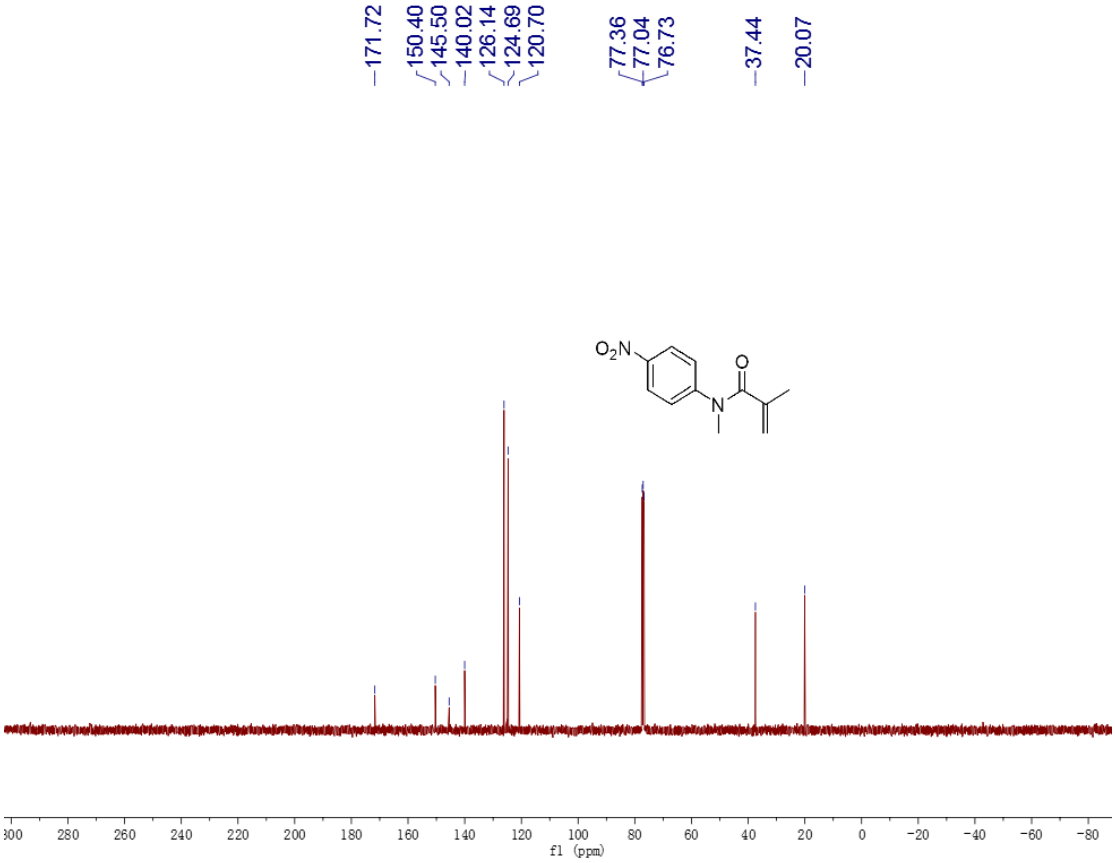
^{13}C NMR spectrum of compound 1j



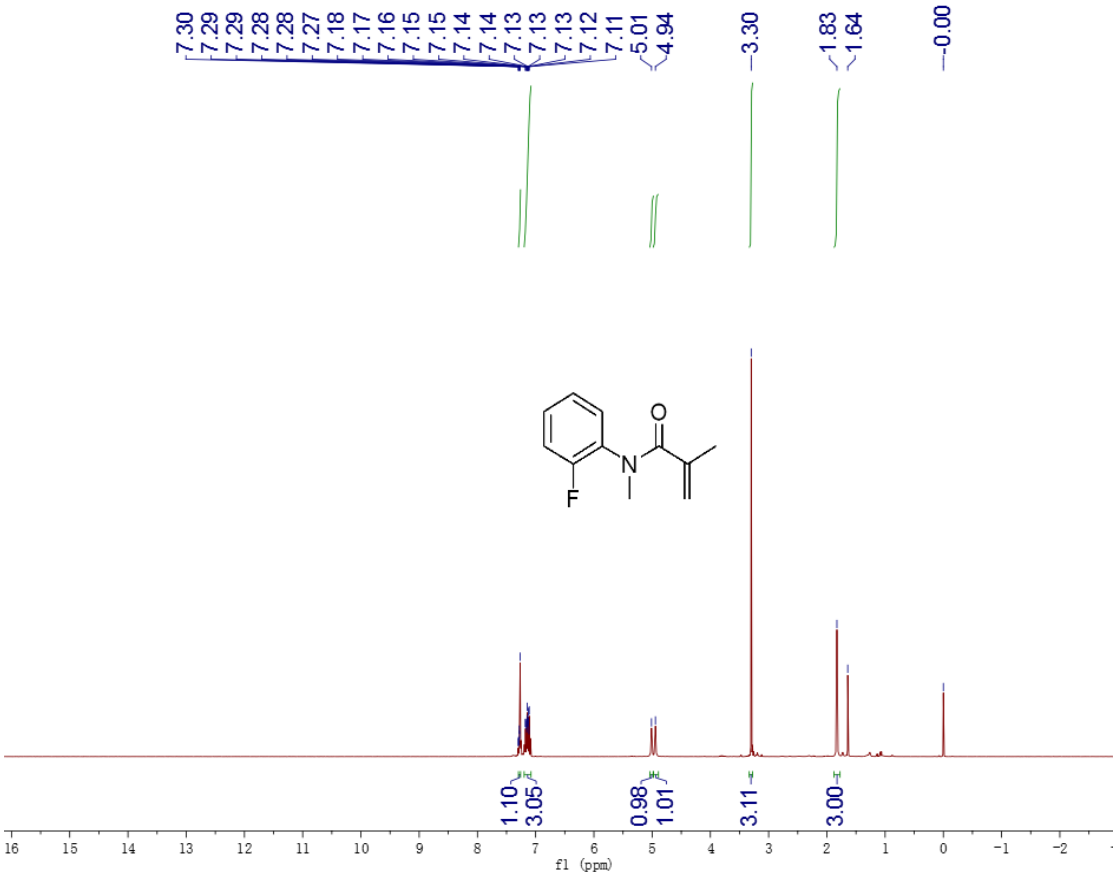
^{1}H NMR spectrum of compound 1k



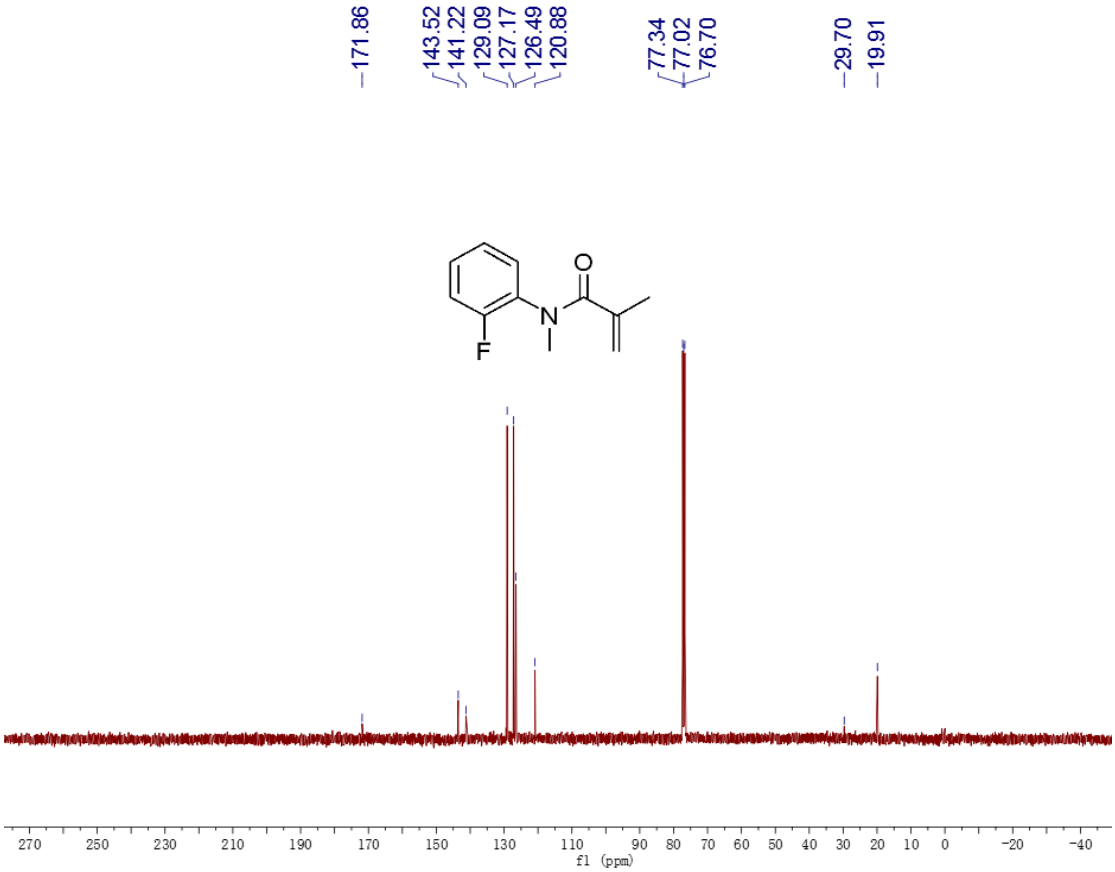
^{13}C NMR spectrum of compound 1k



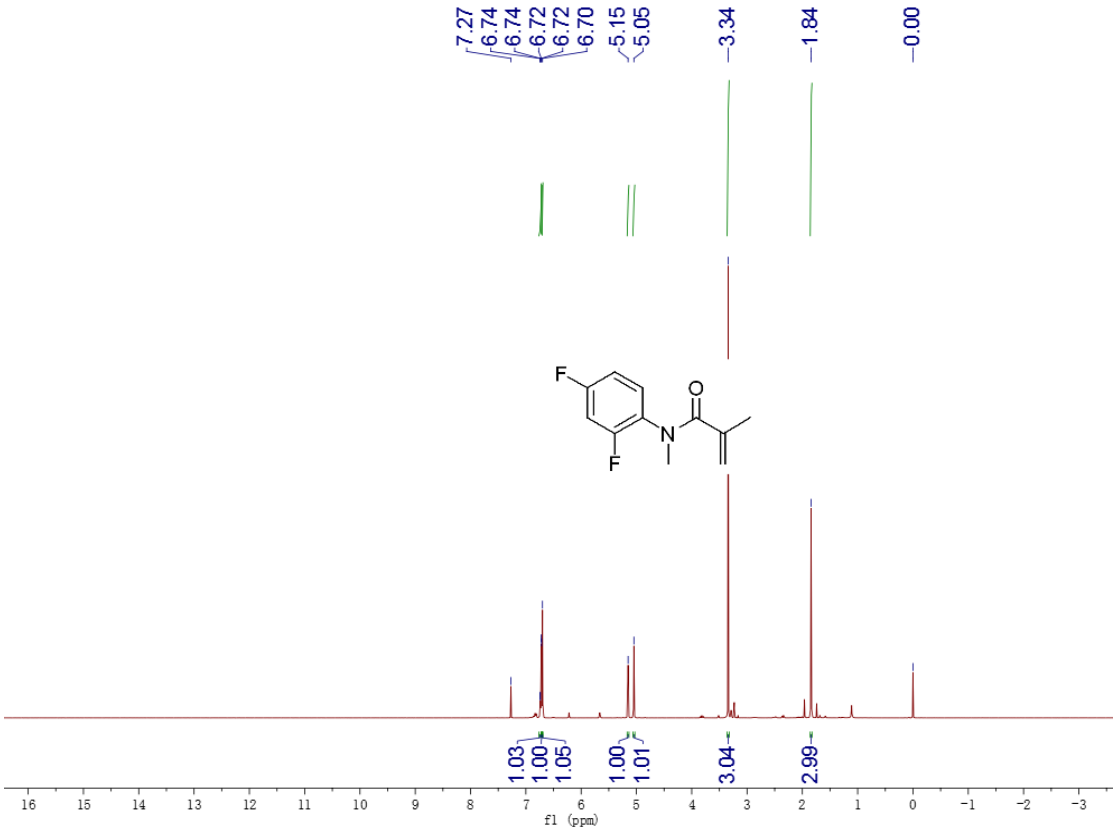
^{1}H NMR spectrum of compound 1l



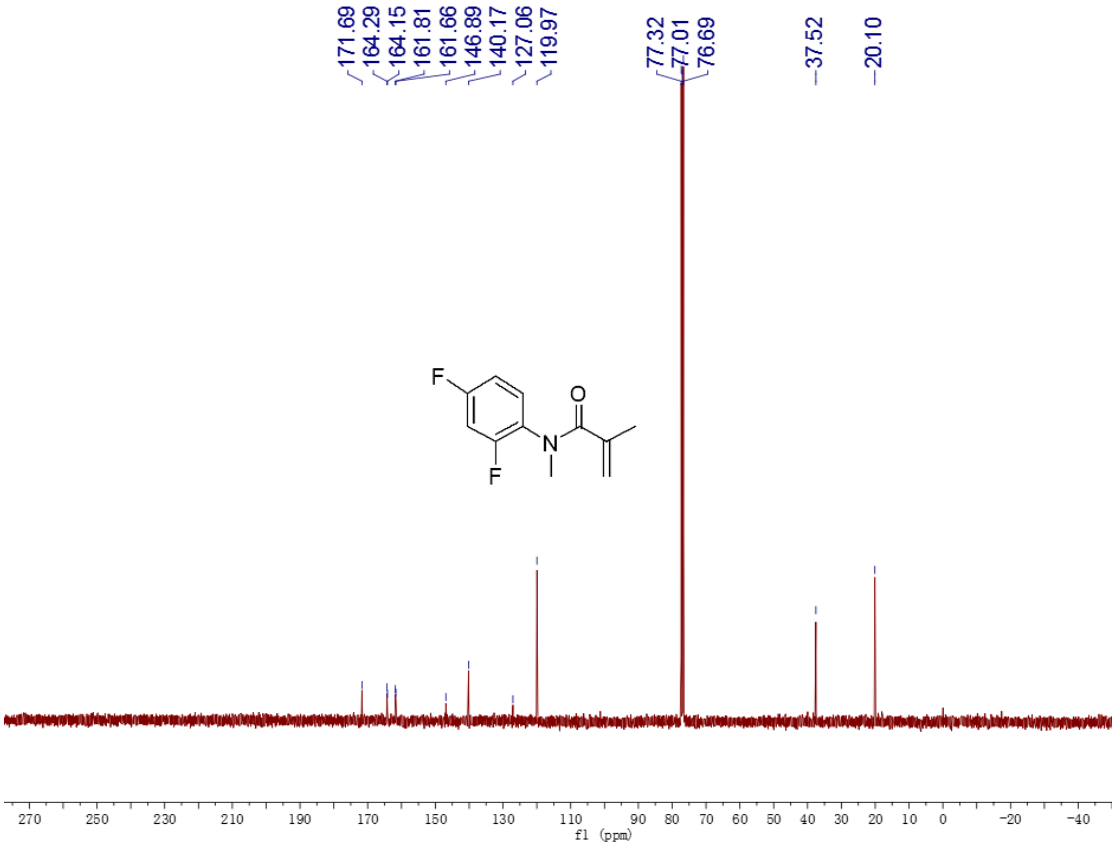
^{13}C NMR spectrum of compound 1l



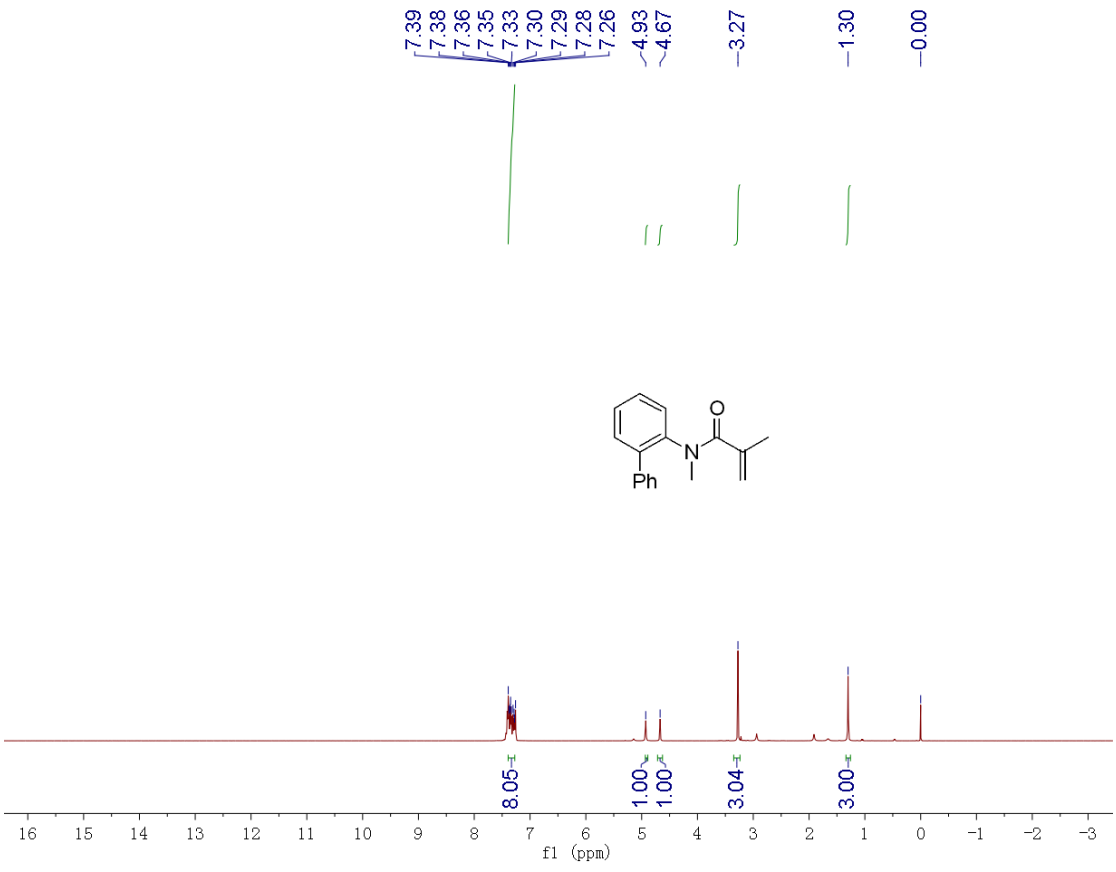
^{1}H NMR spectrum of compound 1m



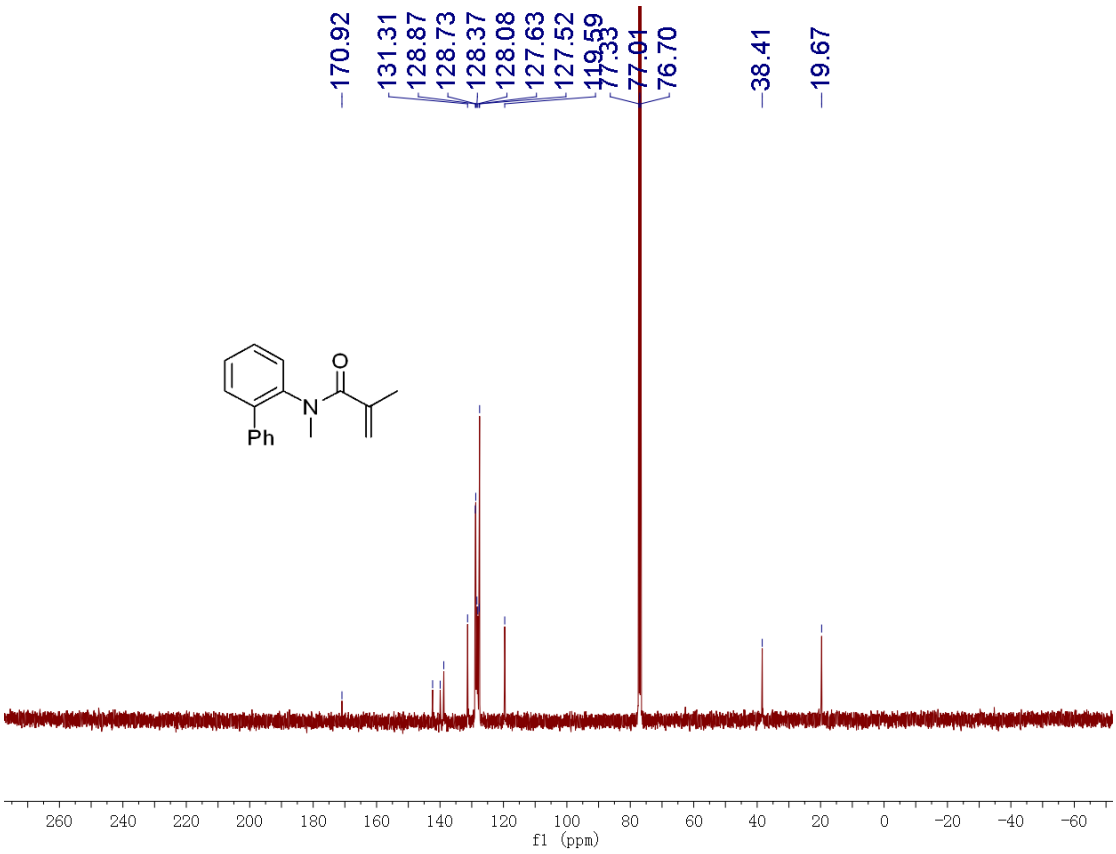
^{13}C NMR spectrum of compound 1m



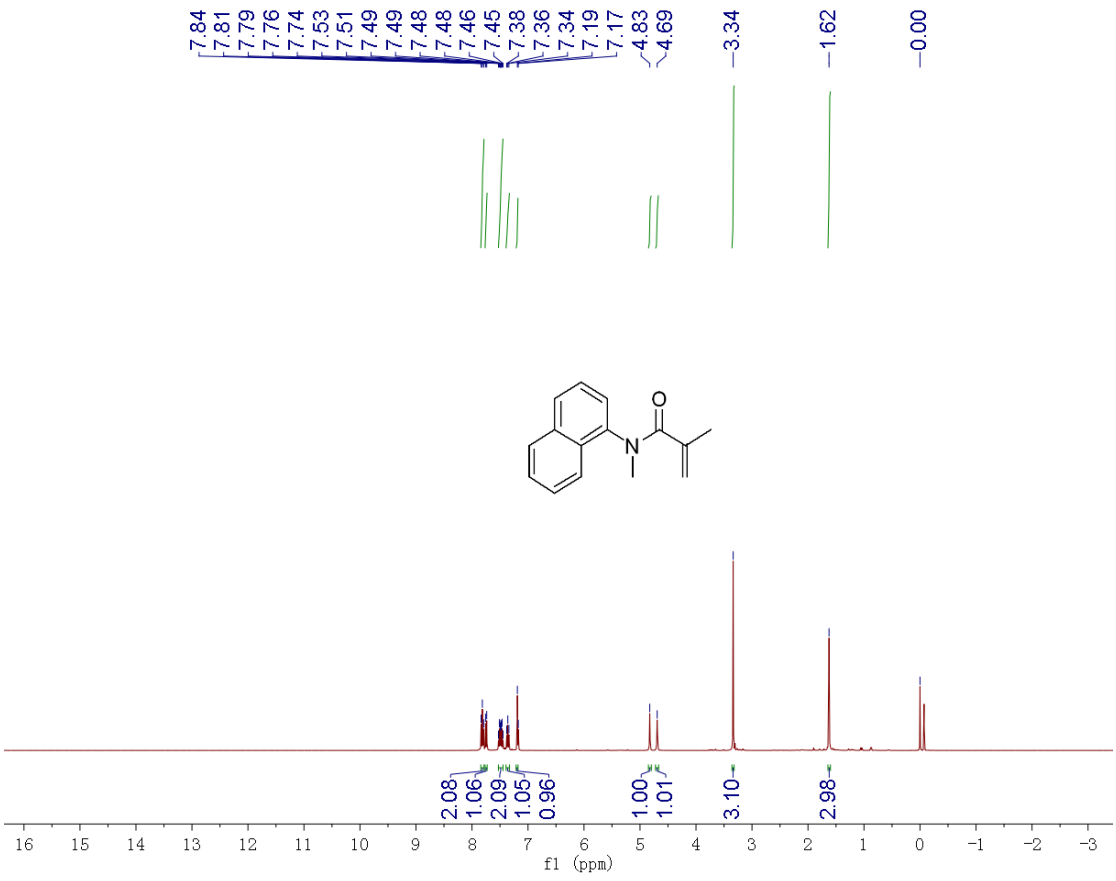
^{1}H NMR spectrum of compound 1n



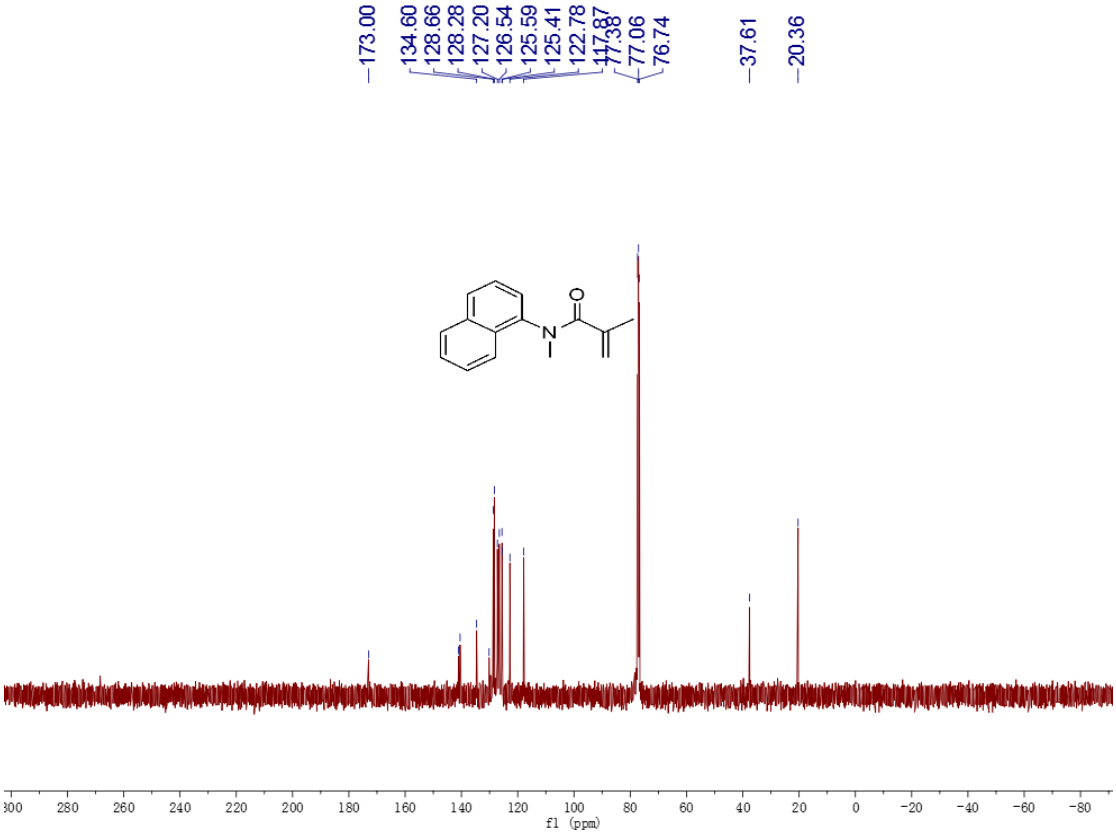
^{13}C NMR spectrum of compound 1n



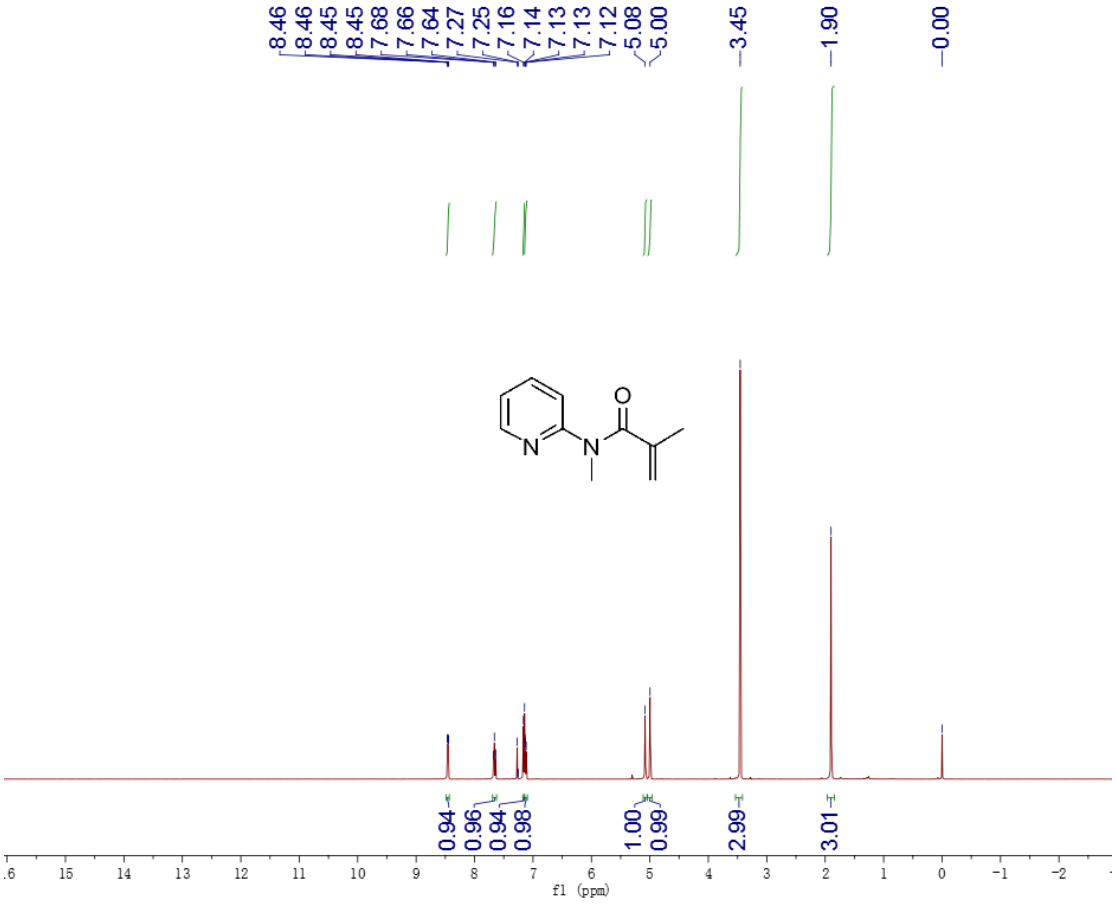
^{1}H NMR spectrum of compound 1o



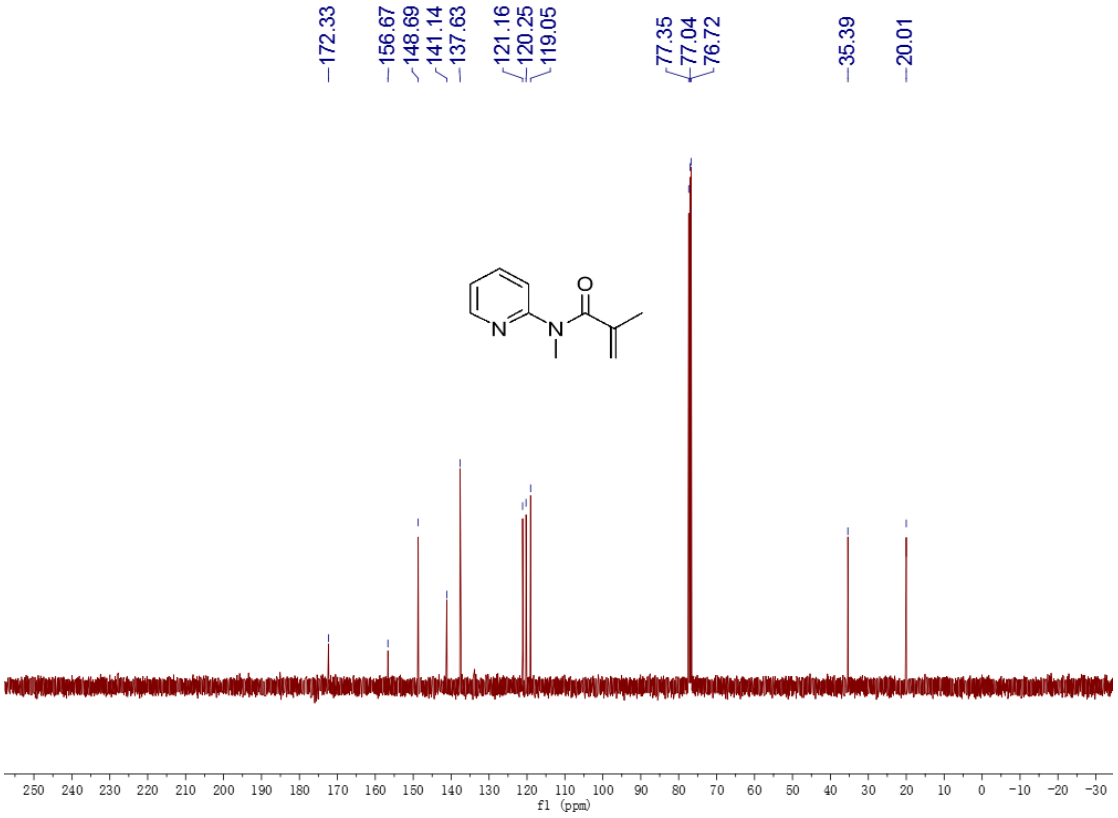
^{13}C NMR spectrum of compound 1o



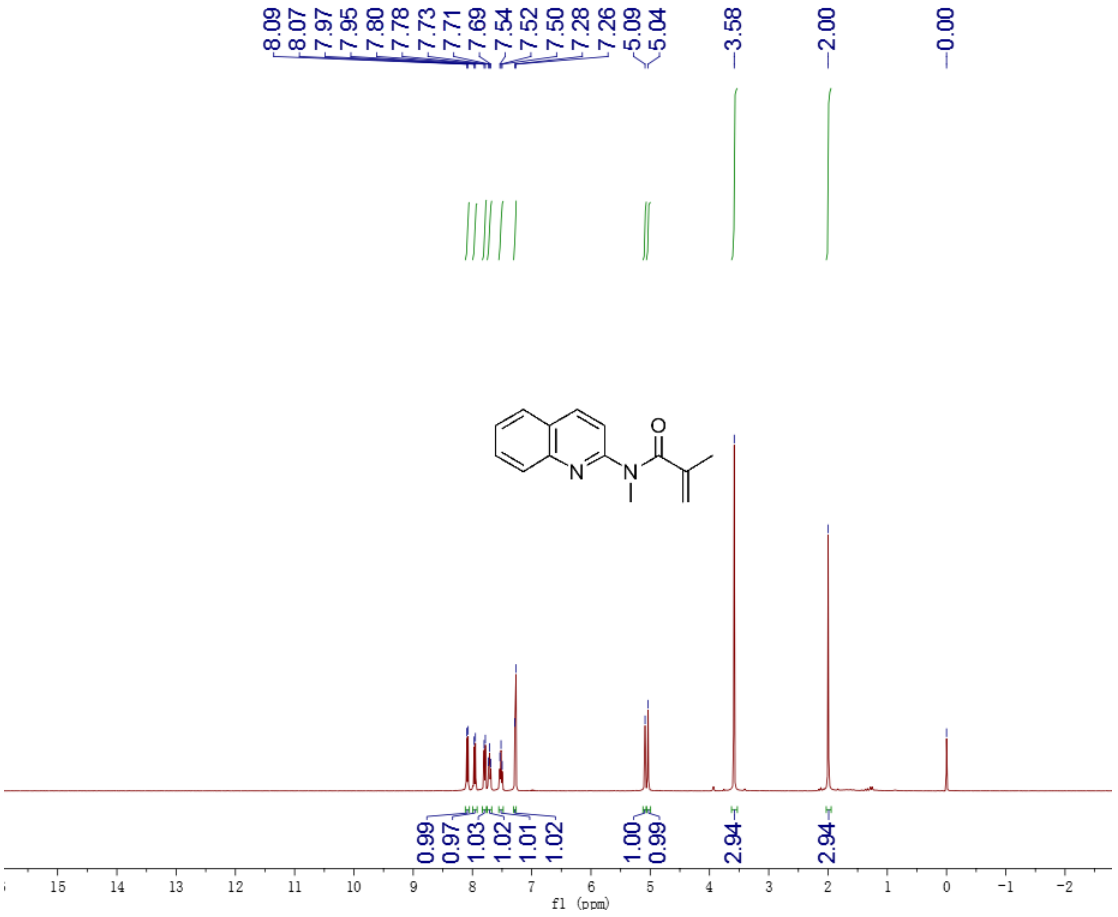
^{1}H NMR spectrum of compound 1p



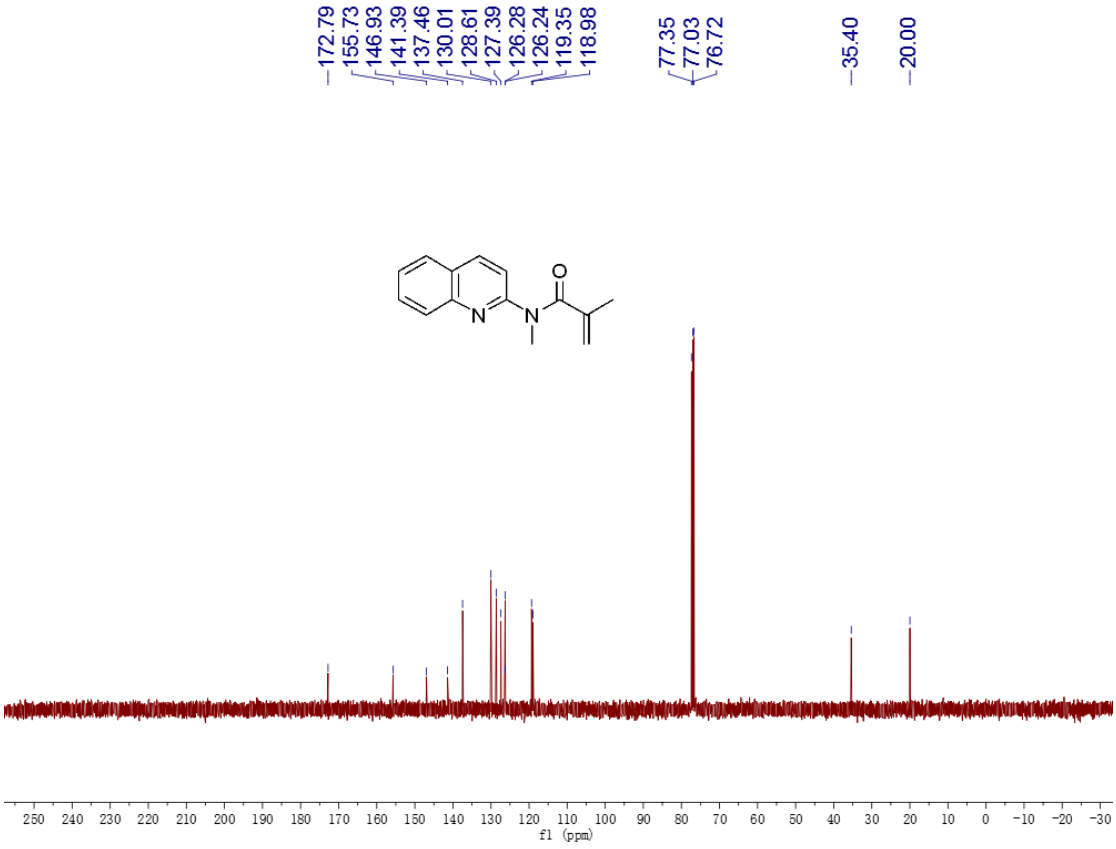
^{13}C NMR spectrum of compound 1p



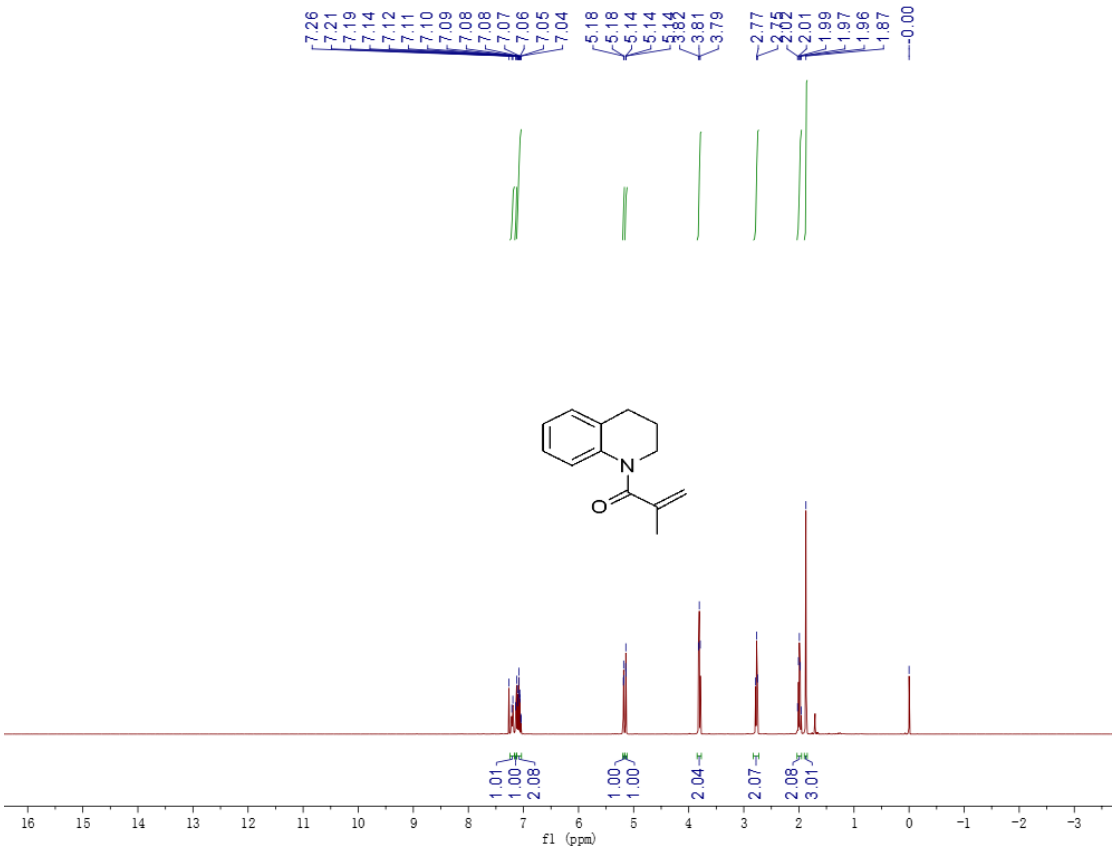
^{1}H NMR spectrum of compound 1q



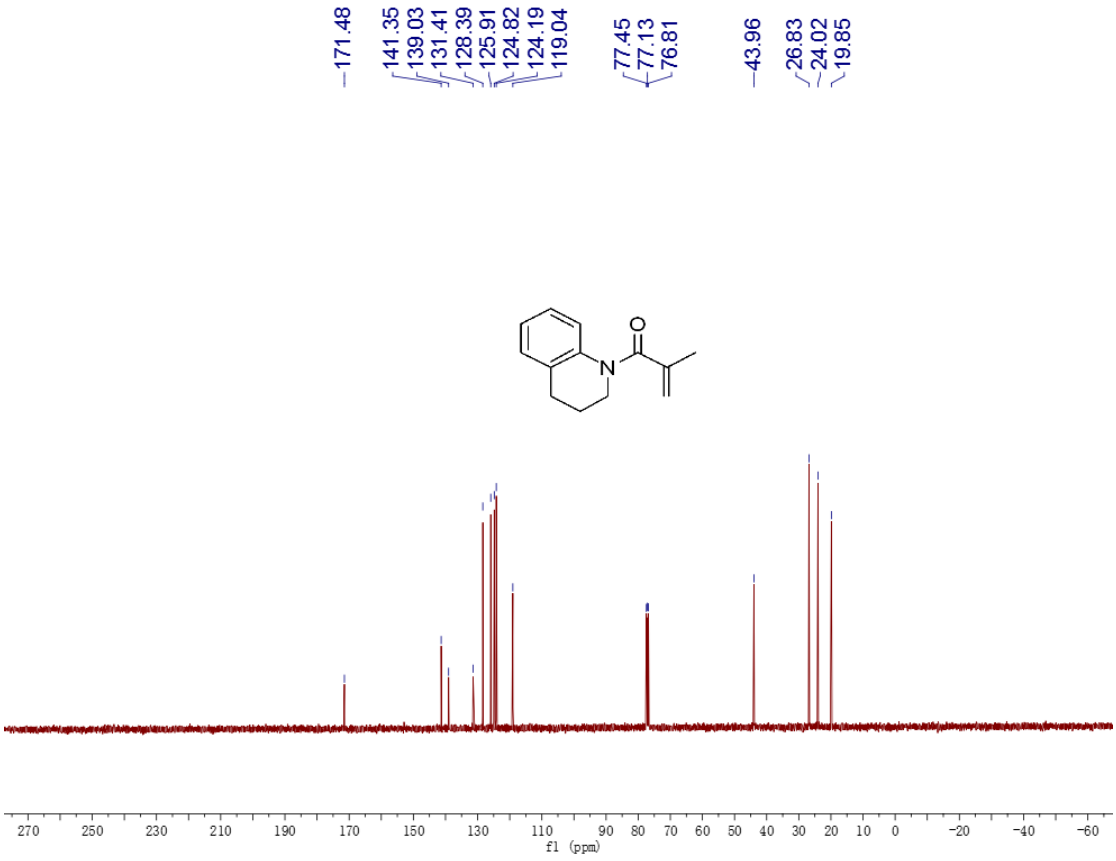
^{13}C NMR spectrum of compound 1q



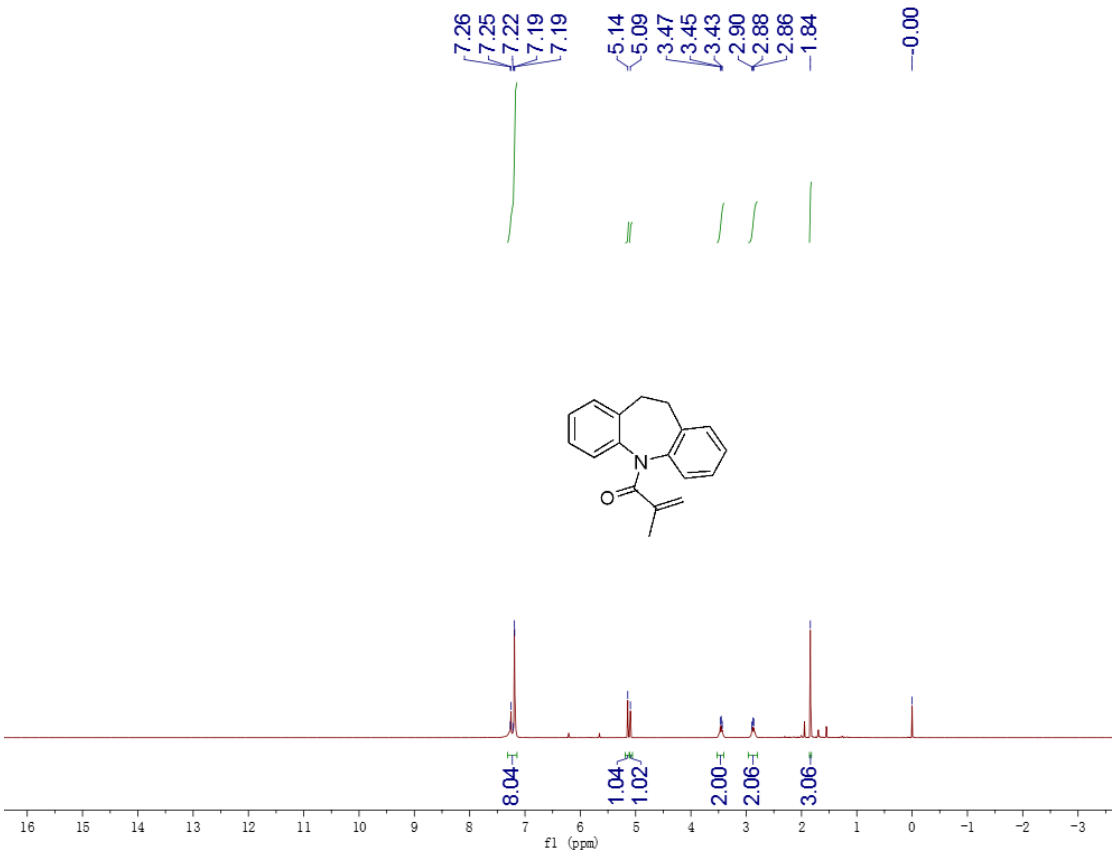
^{1}H NMR spectrum of compound 1r



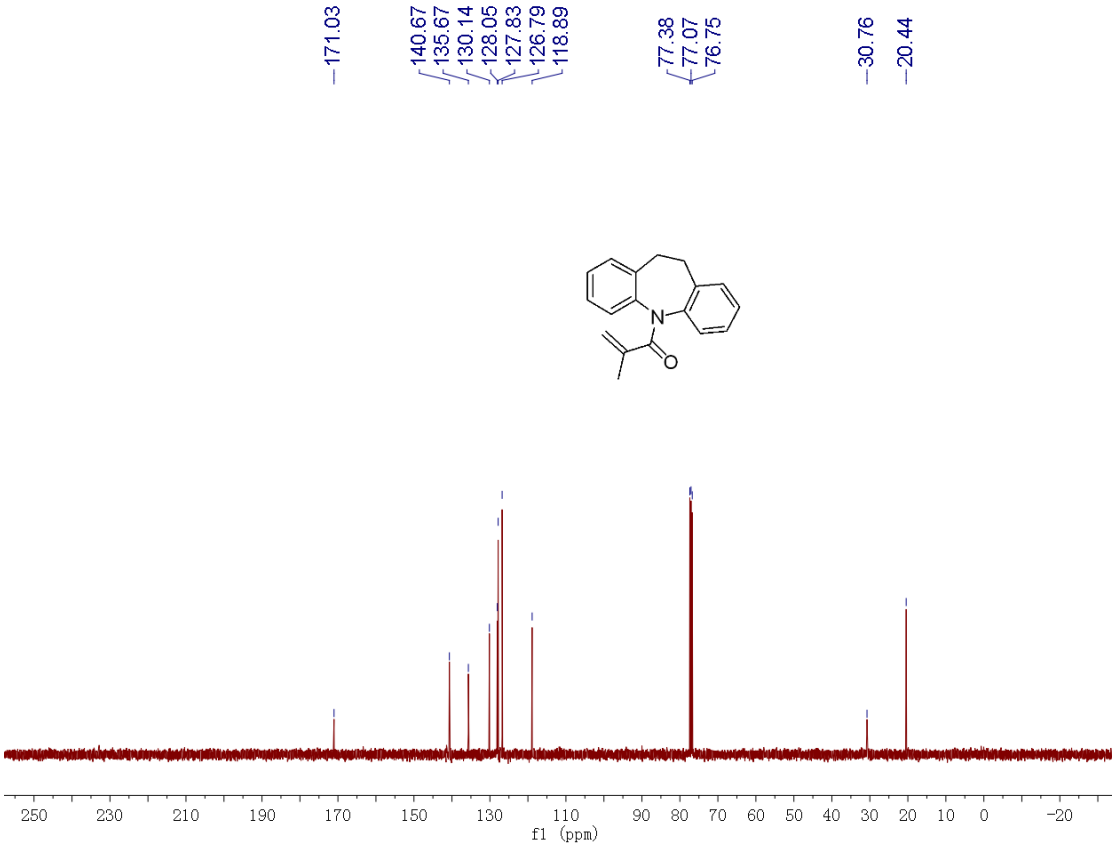
^{13}C NMR spectrum of compound 1r



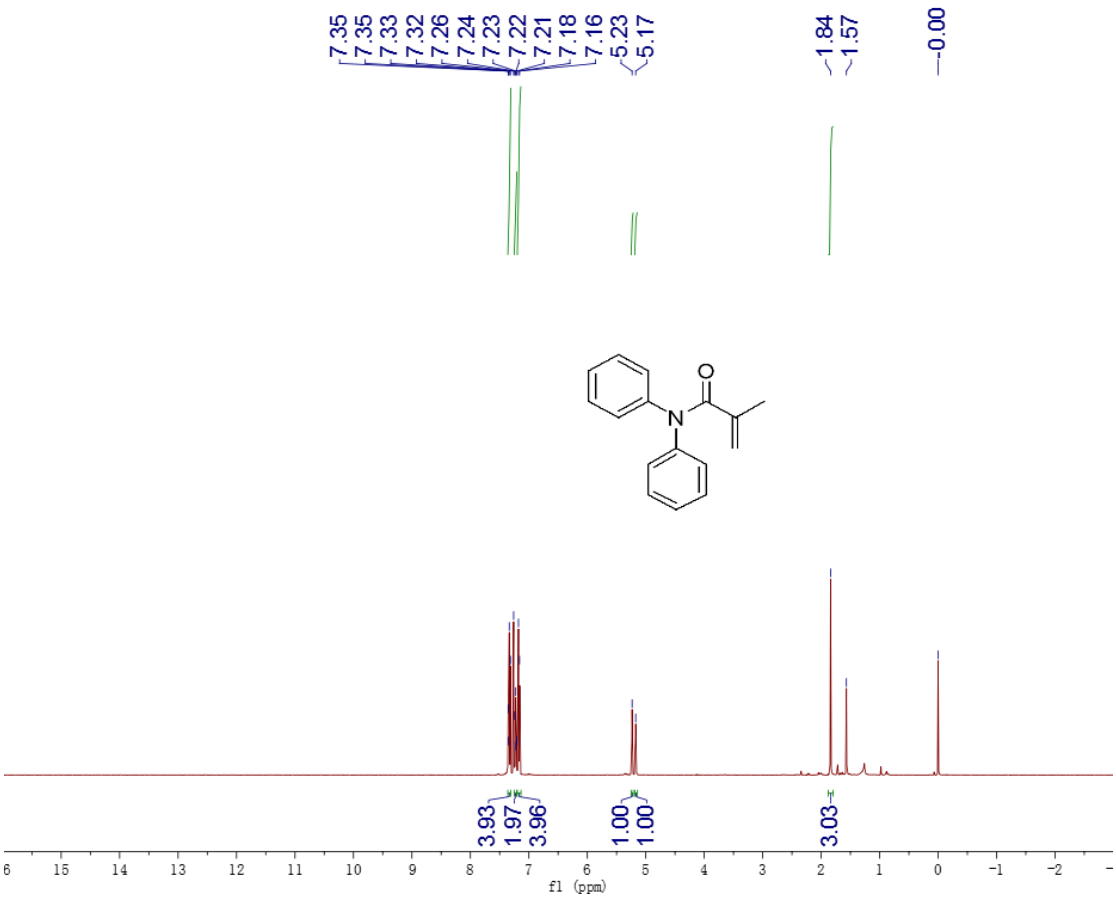
^{1}H NMR spectrum of compound 1s



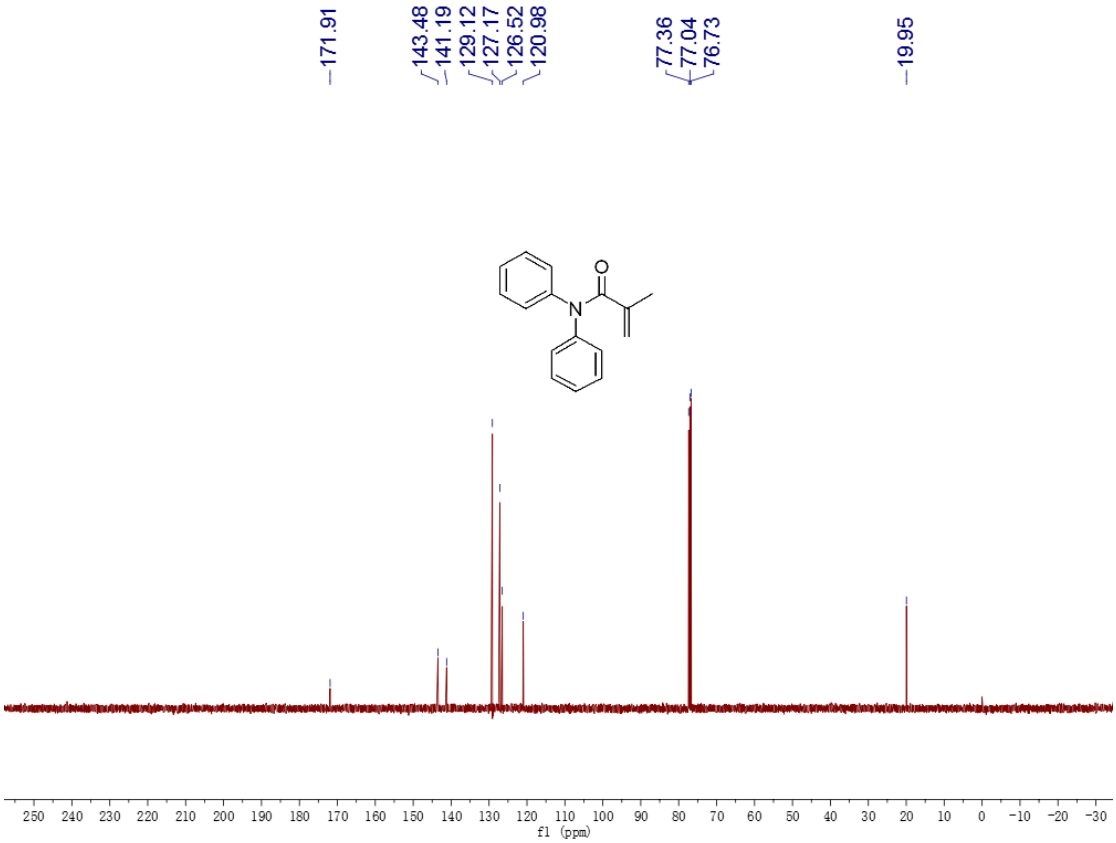
^{13}C NMR spectrum of compound 1s



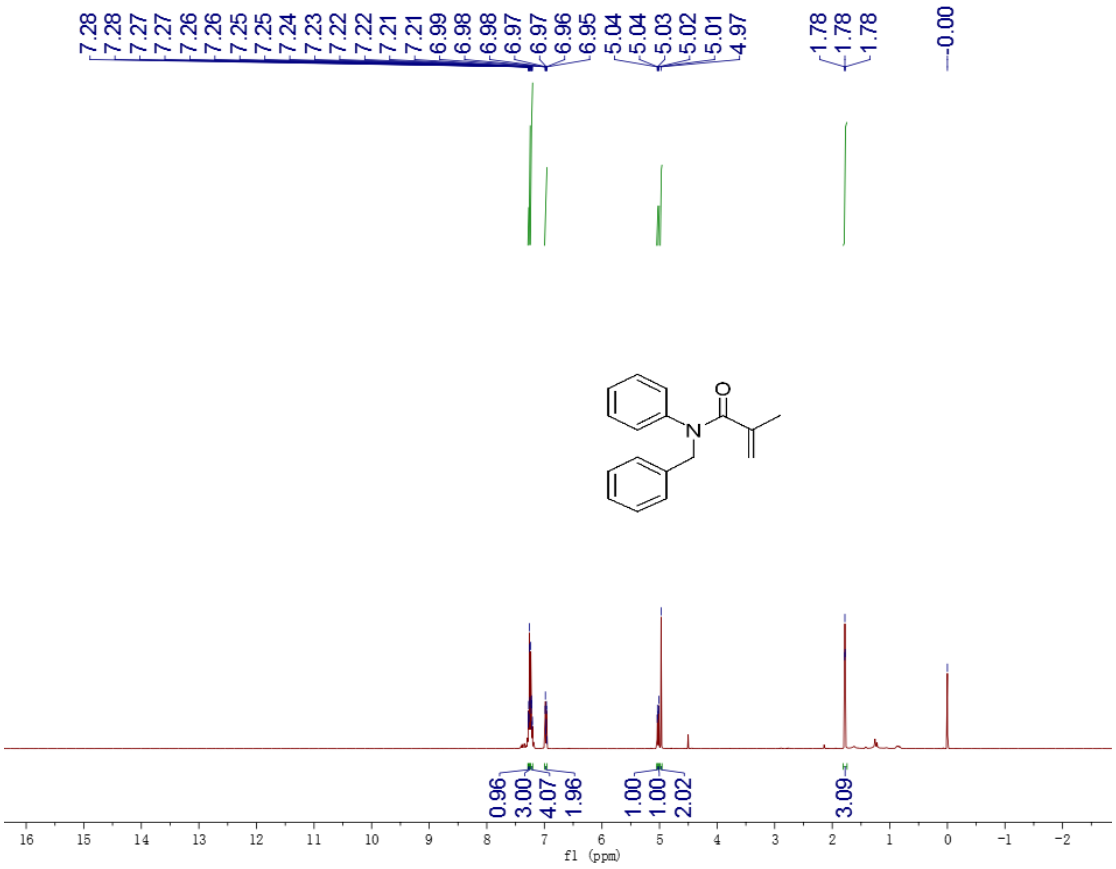
^{1}H NMR spectrum of compound 1t



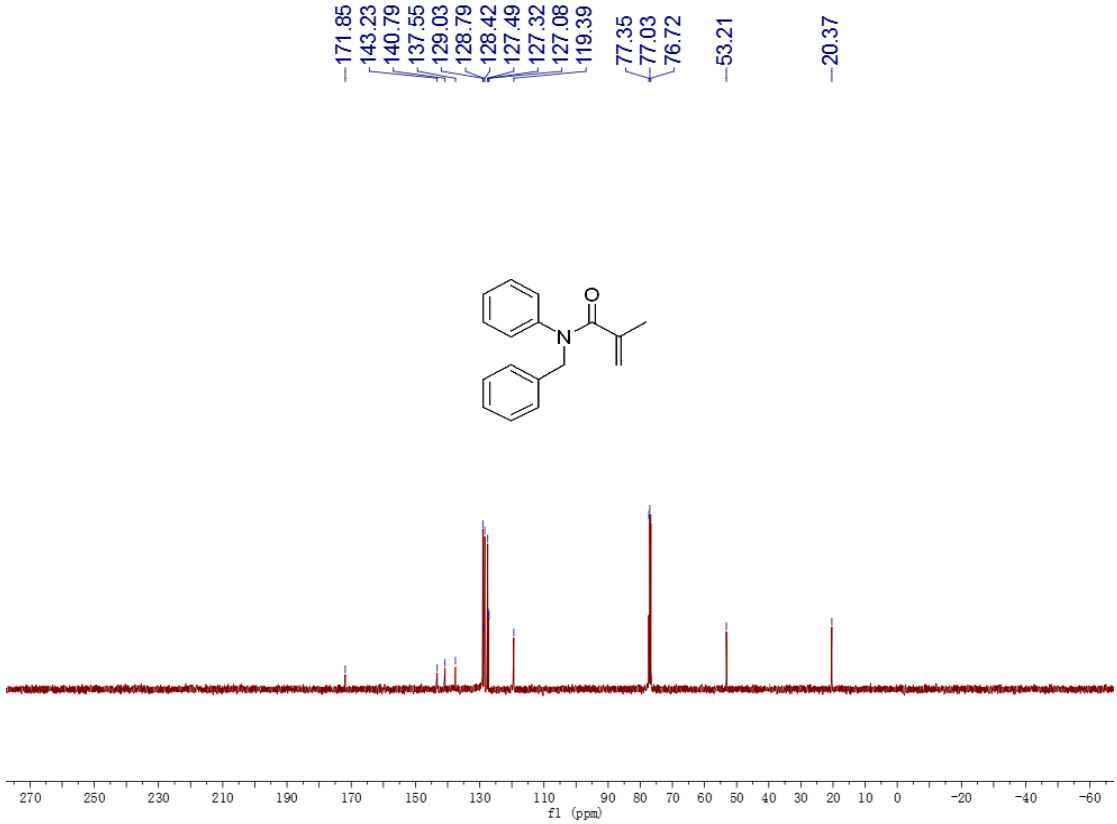
^{13}C NMR spectrum of compound 1t



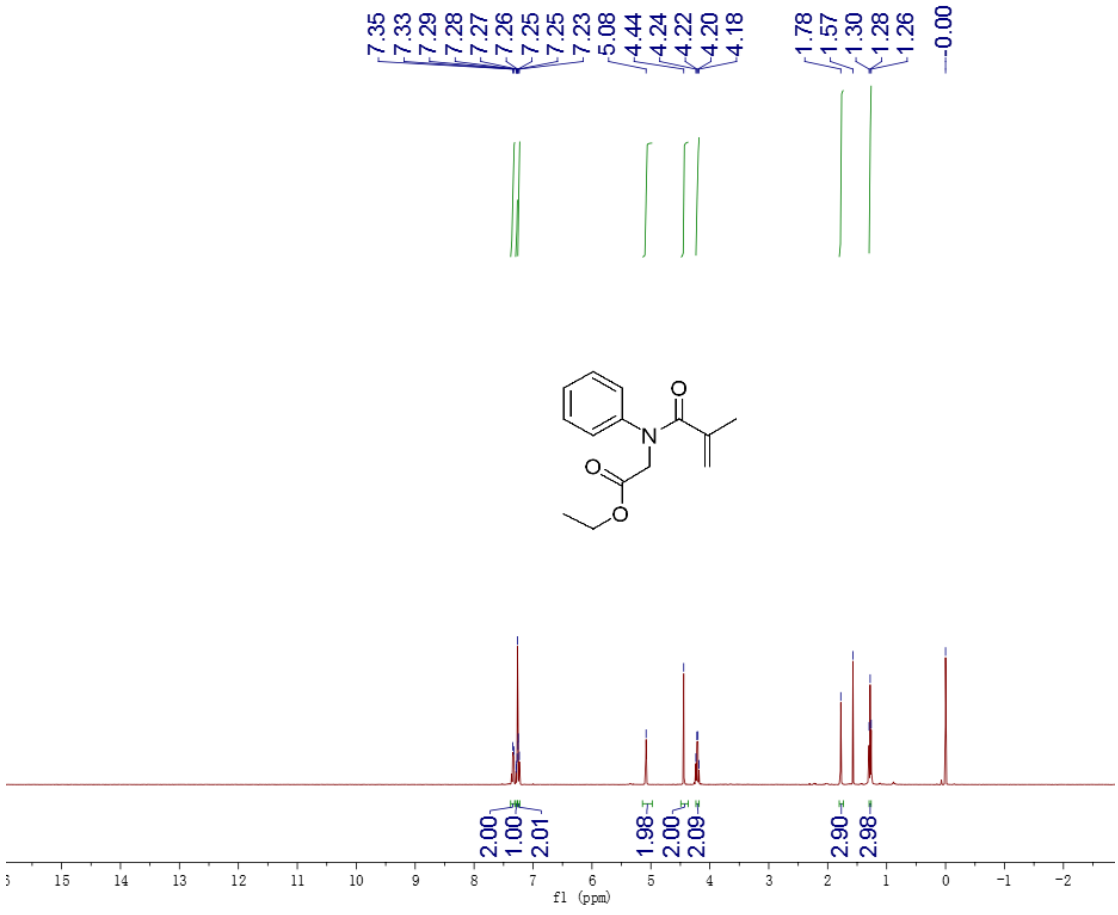
^{1}H NMR spectrum of compound 1u



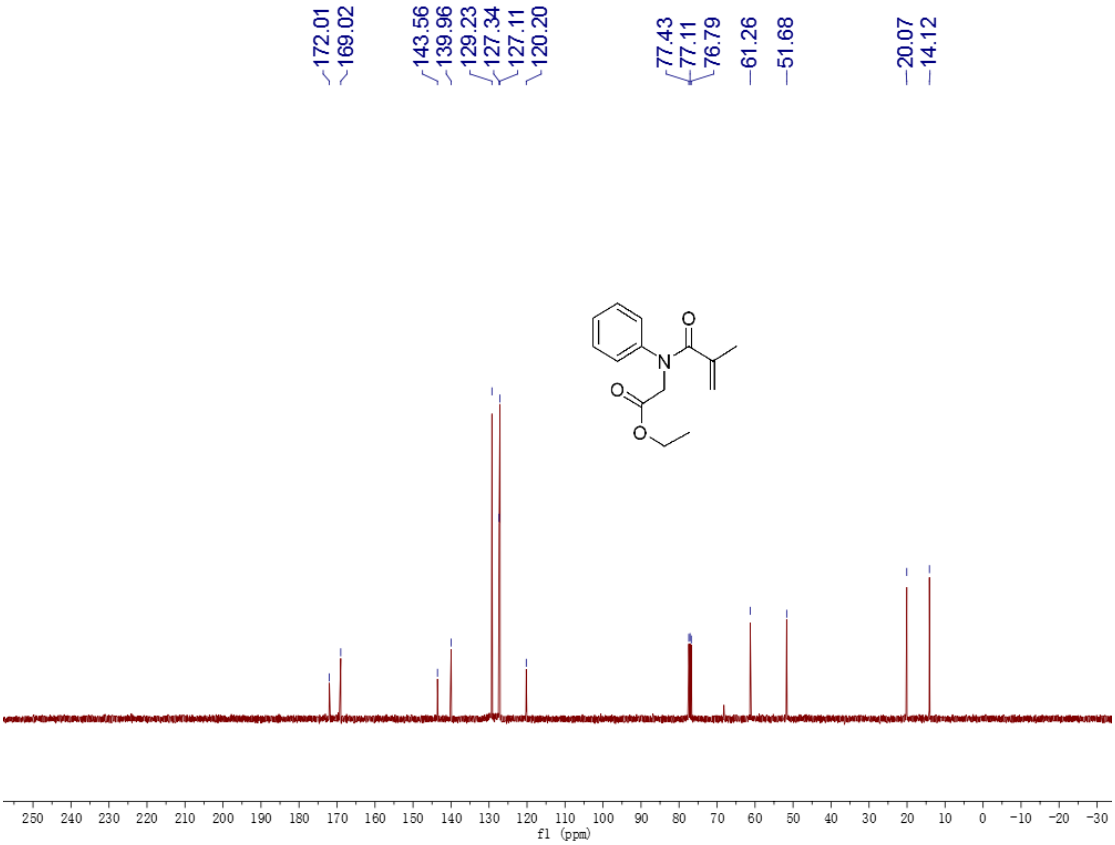
^{13}C NMR spectrum of compound 1u



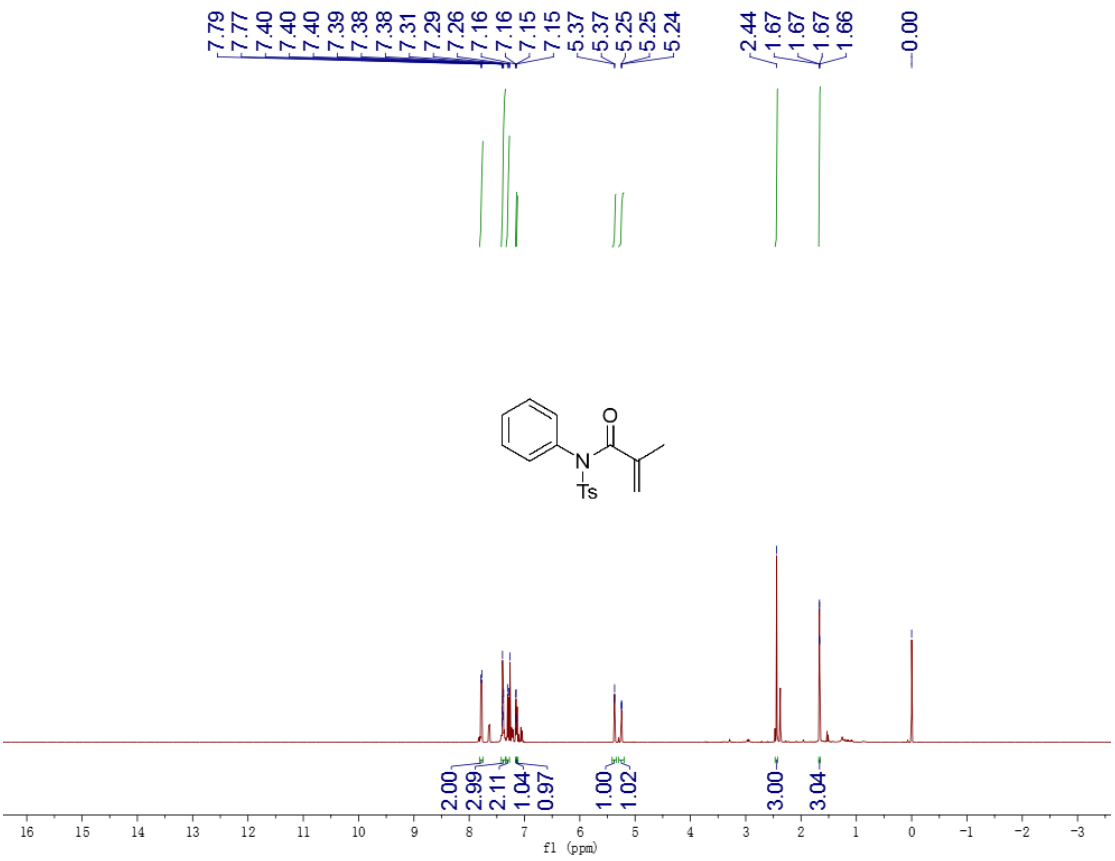
^{1}H NMR spectrum of compound 1v



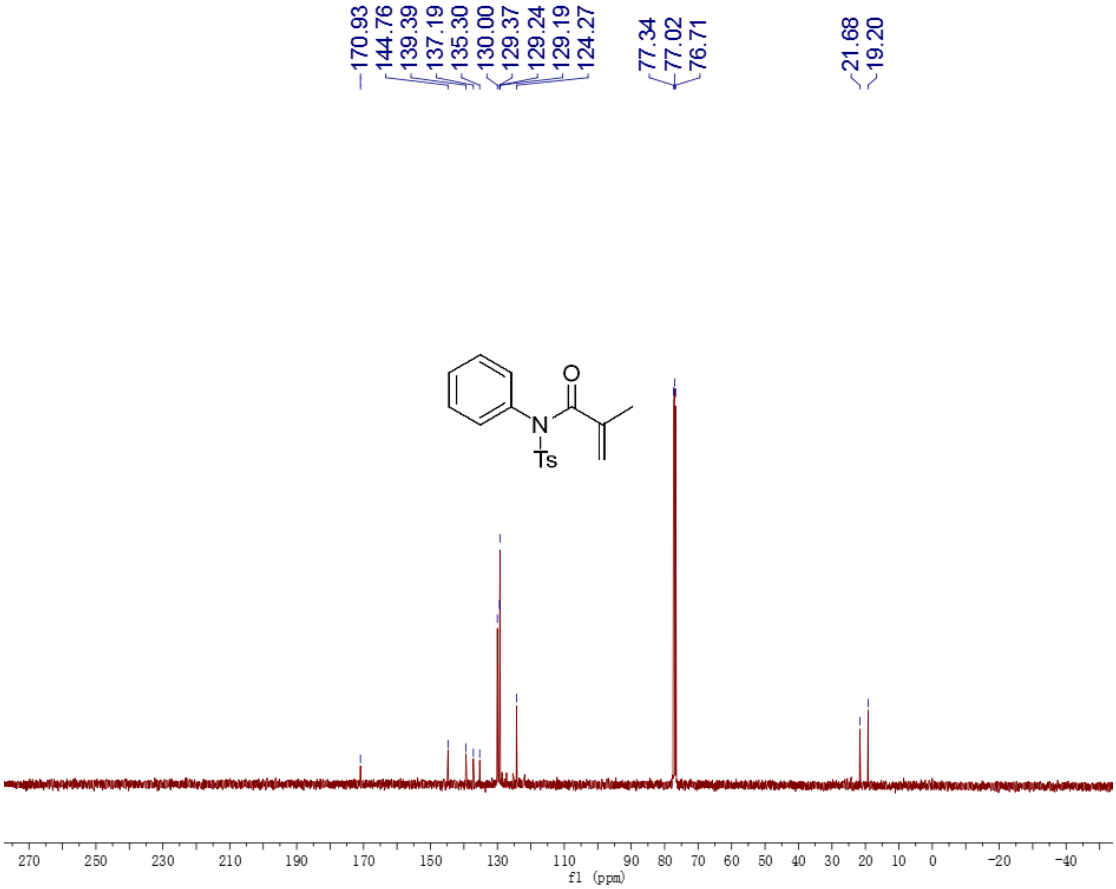
^{13}C NMR spectrum of compound 1v



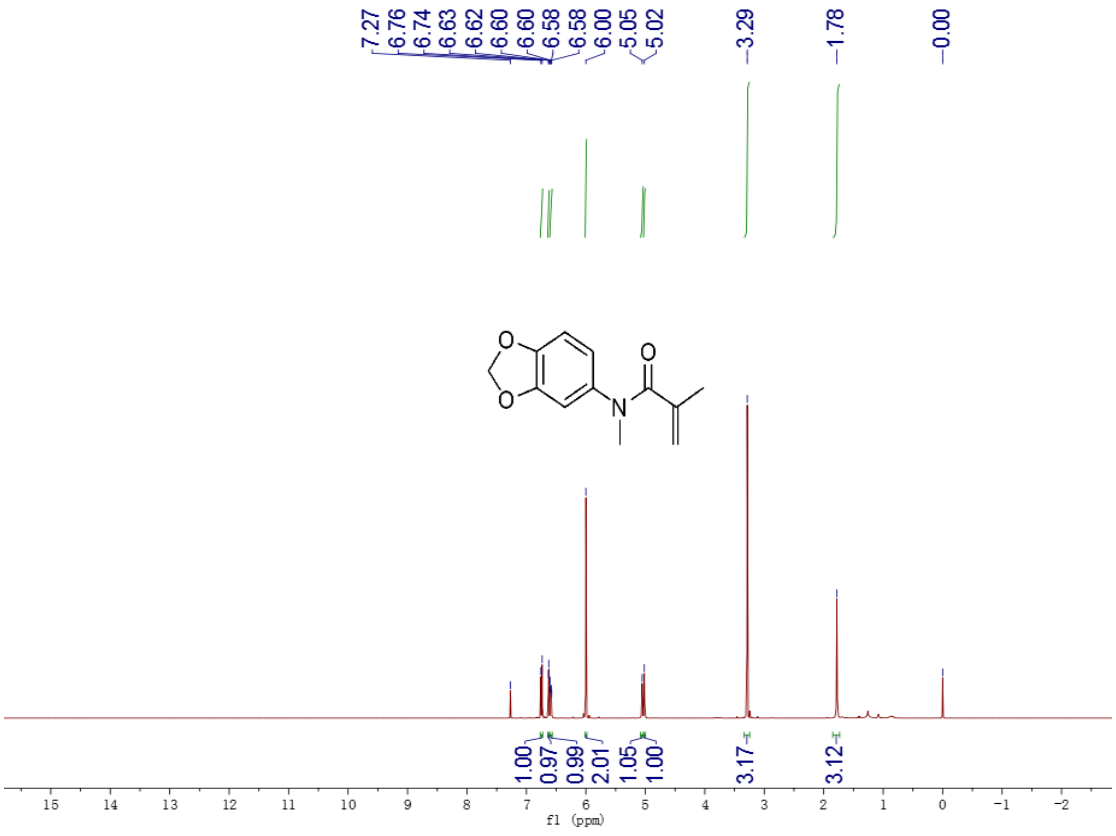
^{1}H NMR spectrum of compound 1w



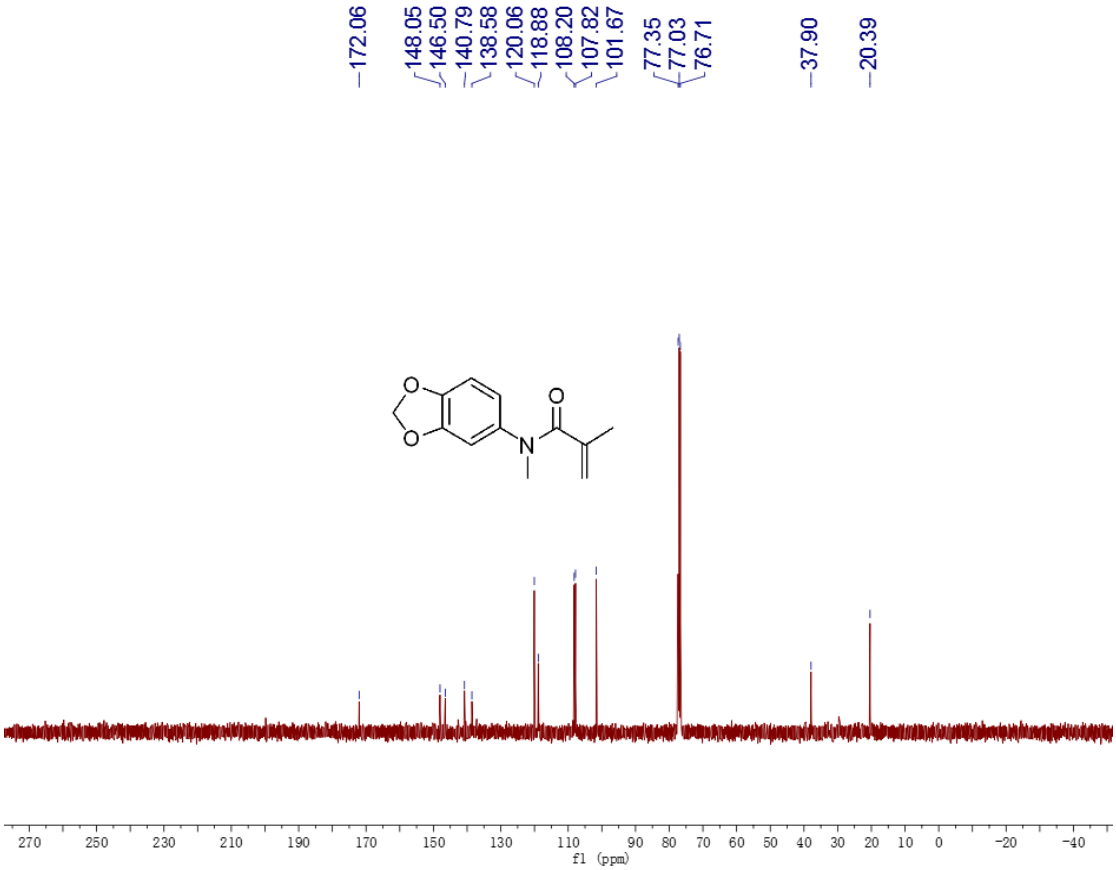
^{13}C NMR spectrum of compound 1w



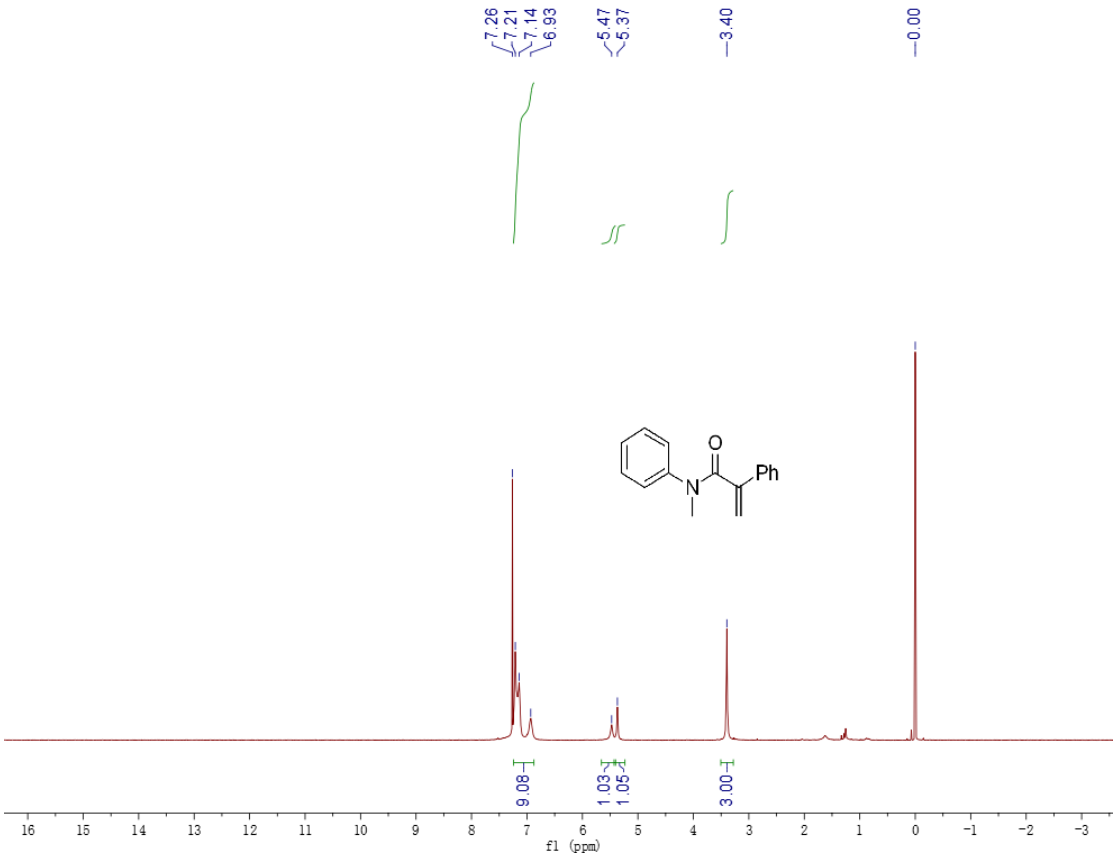
^{1}H NMR spectrum of compound 1x



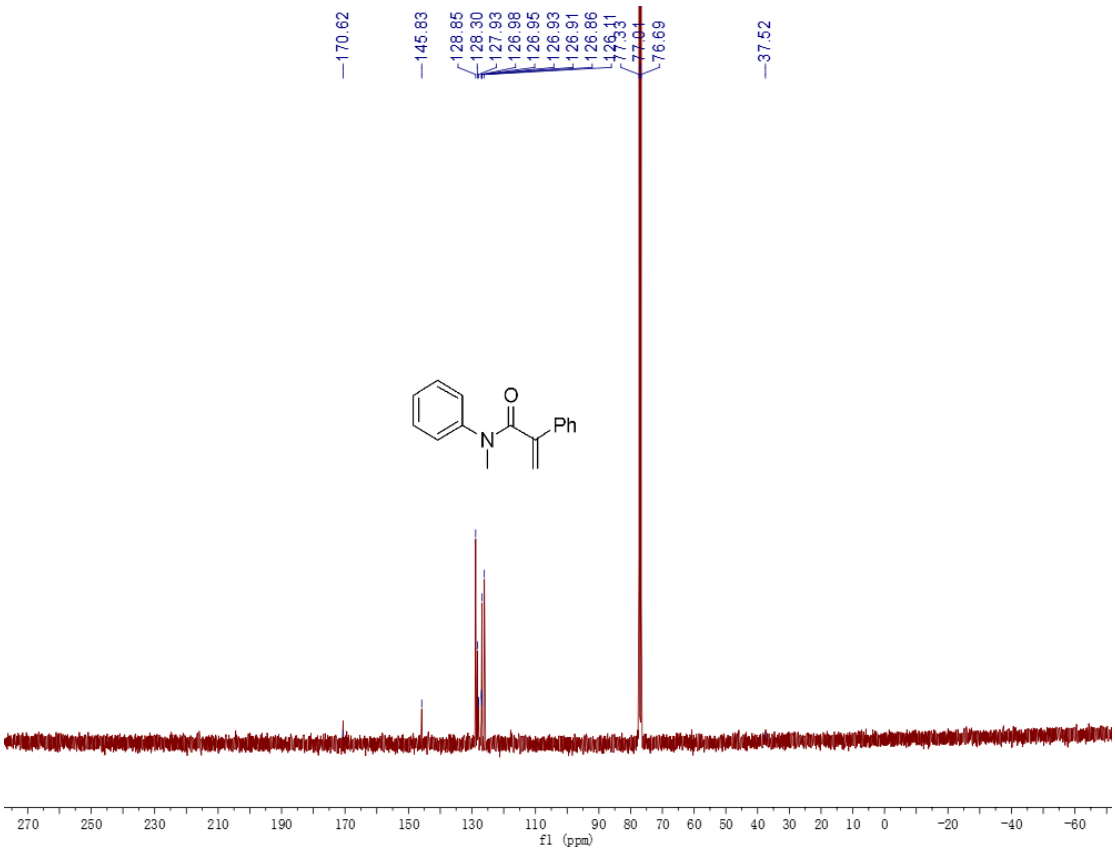
^{13}C NMR spectrum of compound 1x



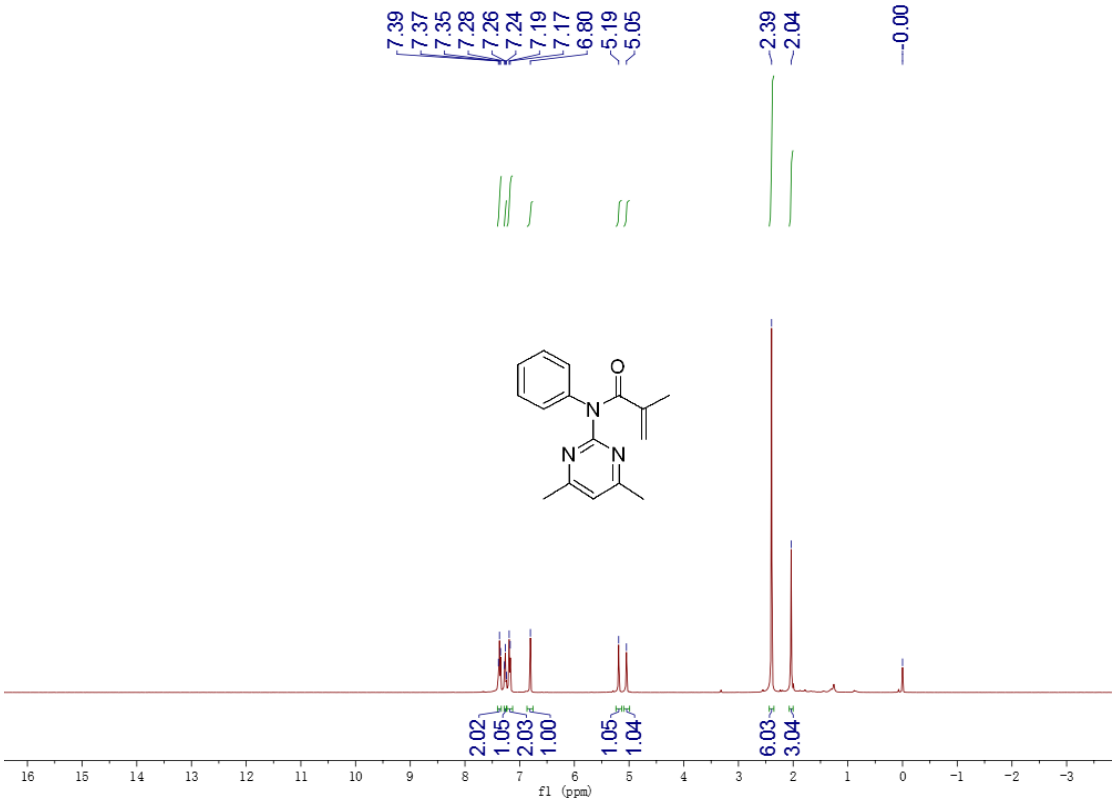
^{1}H NMR spectrum of compound 1y



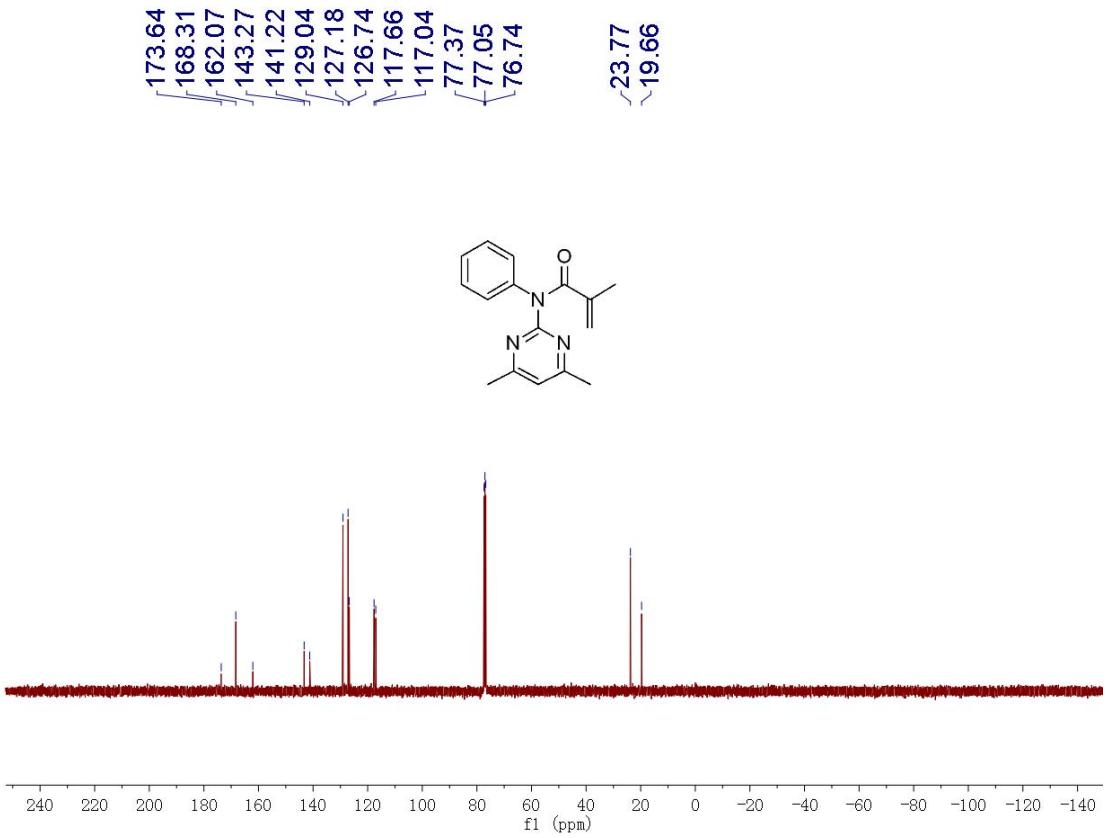
^{13}C NMR spectrum of compound 1y



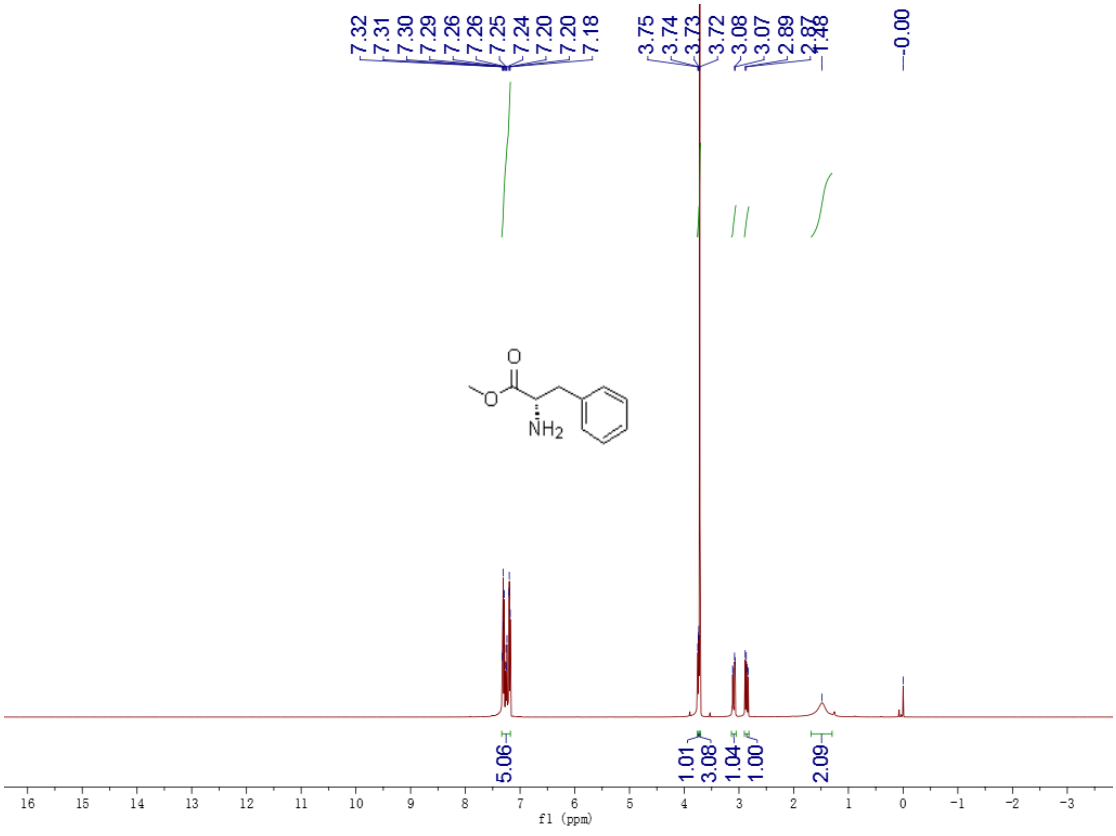
^{1}H NMR spectrum of compound 1z



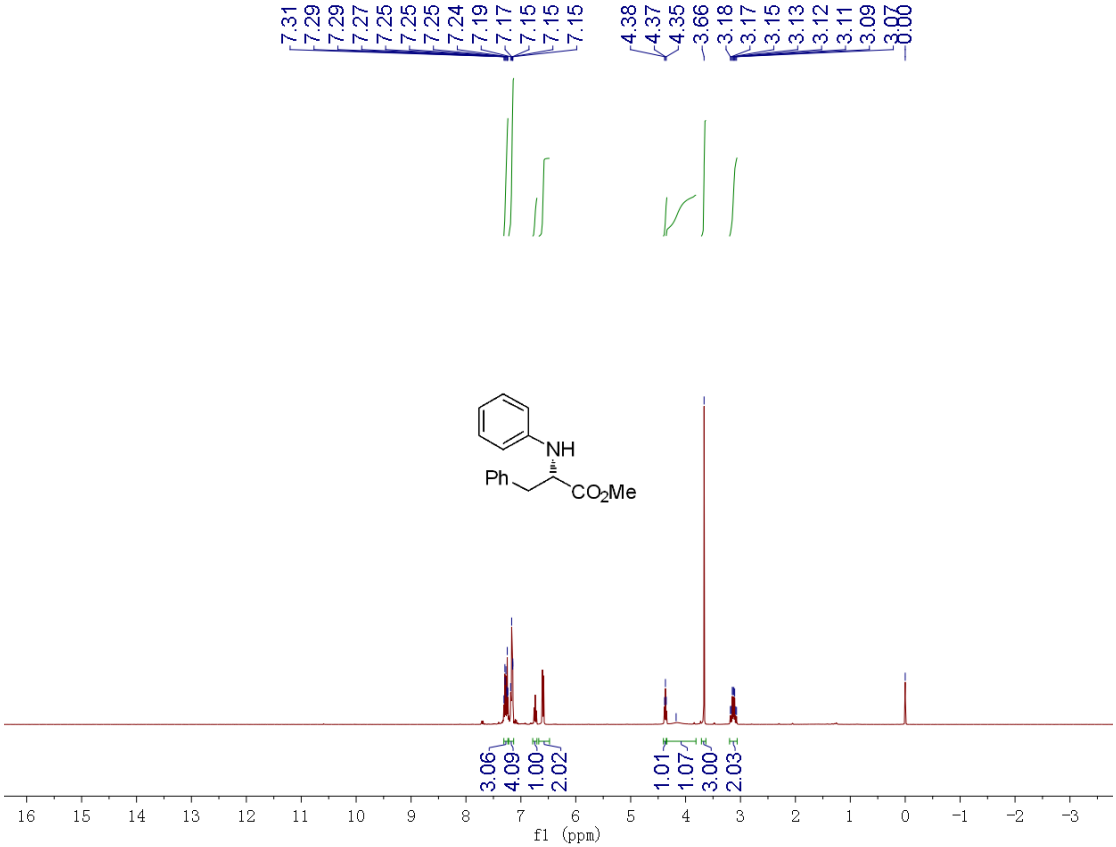
^{13}C NMR spectrum of compound 1z



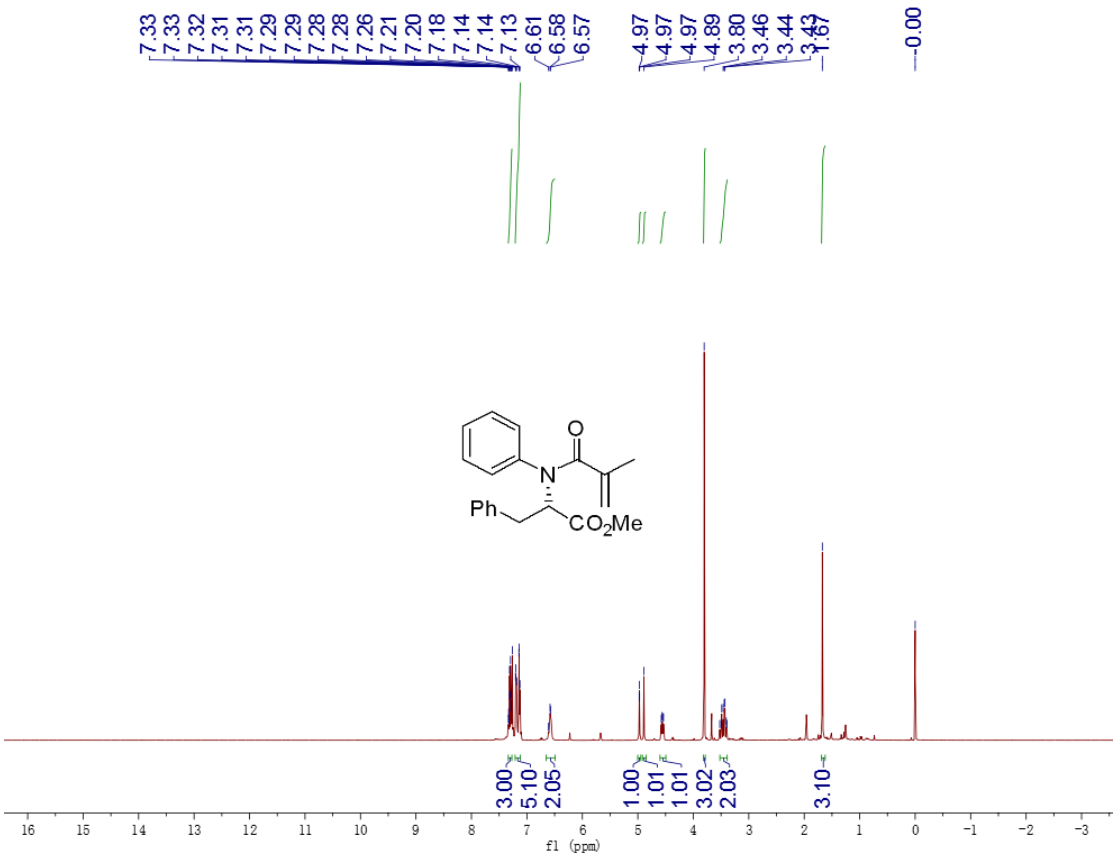
^{1}H NMR spectrum of compound 1aa



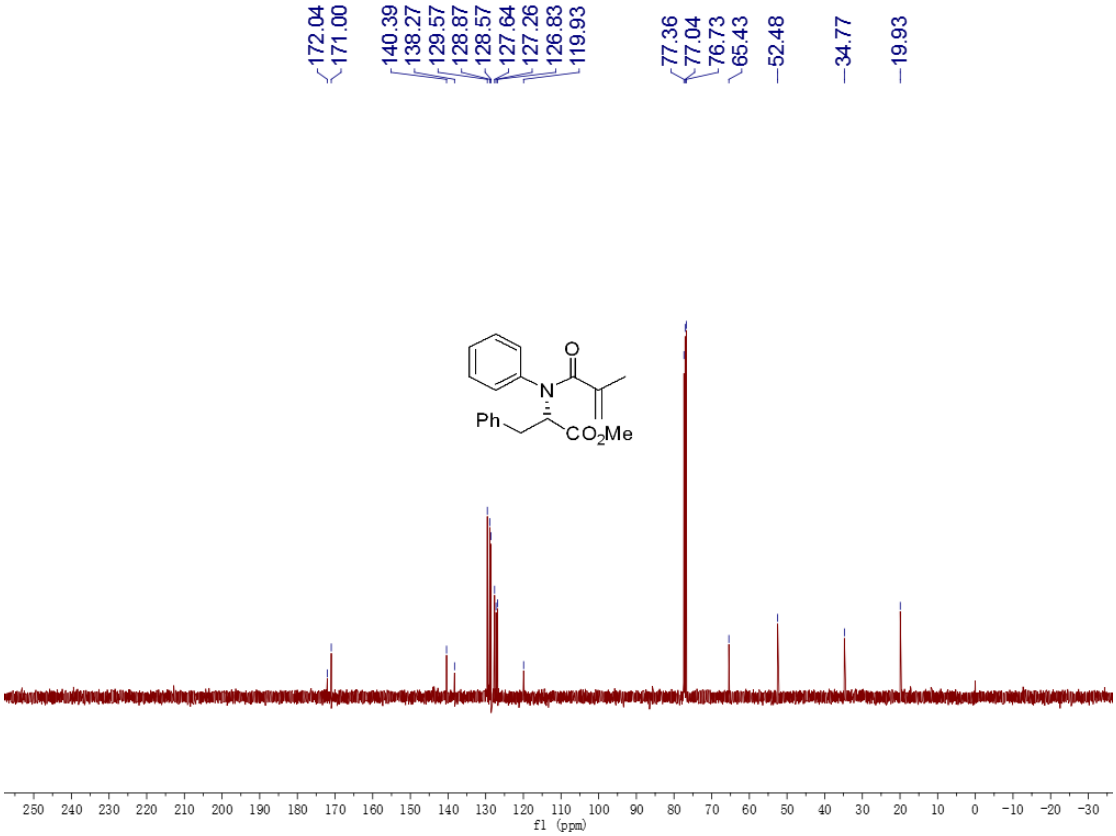
^{1}H NMR spectrum of compound 1bb



^{1}H NMR spectrum of compound 1cc

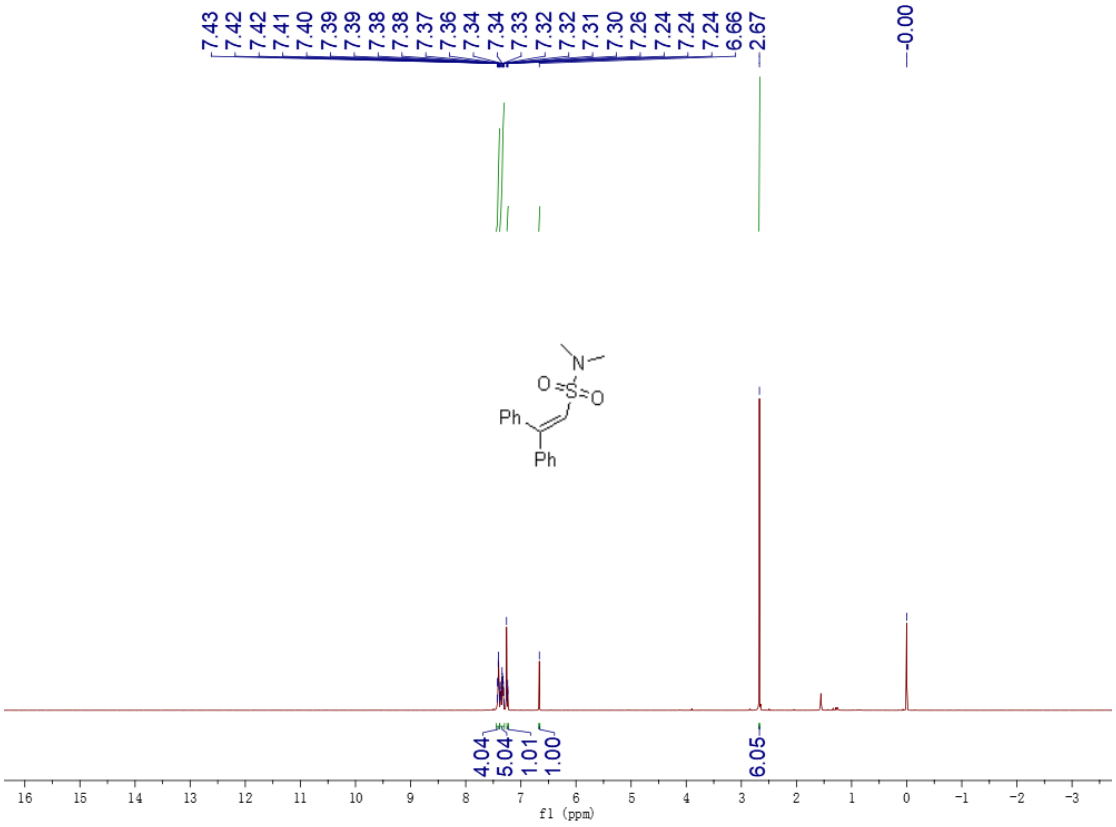


^{13}C NMR spectrum of compound 1cc

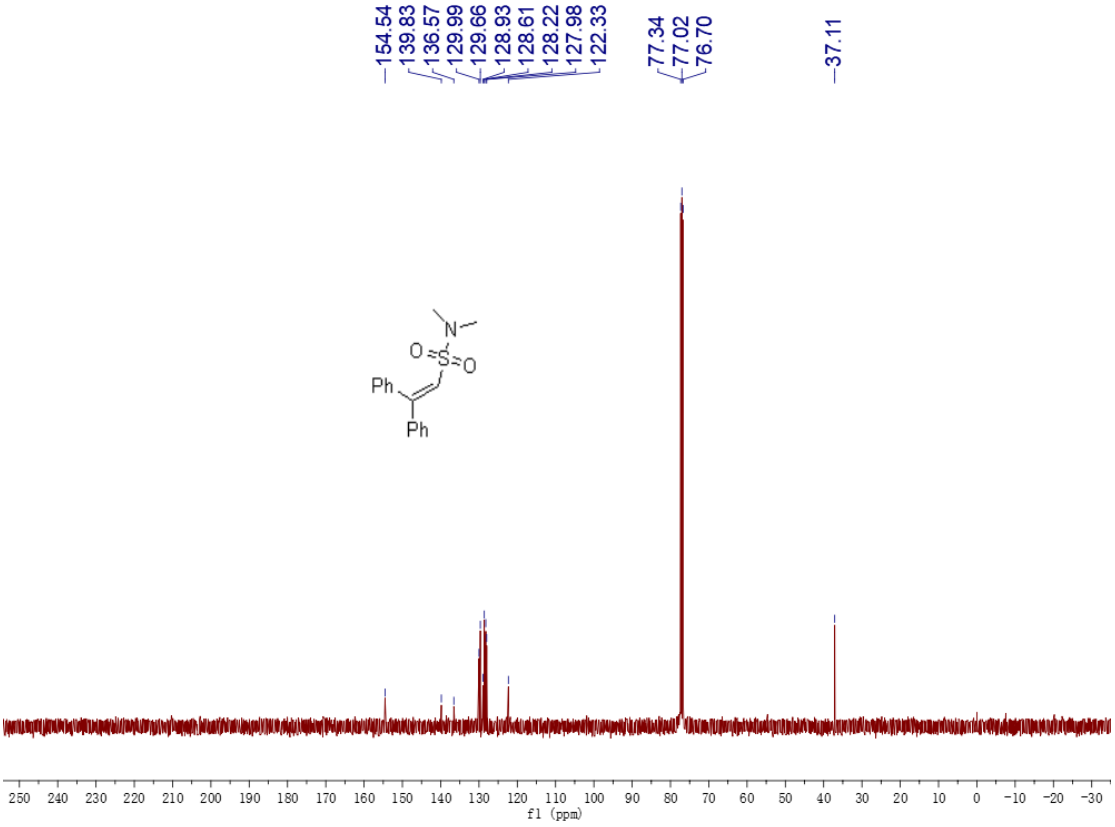


9. ^{1}H NMR and ^{13}C NMR spectrum of Mechanistic Study

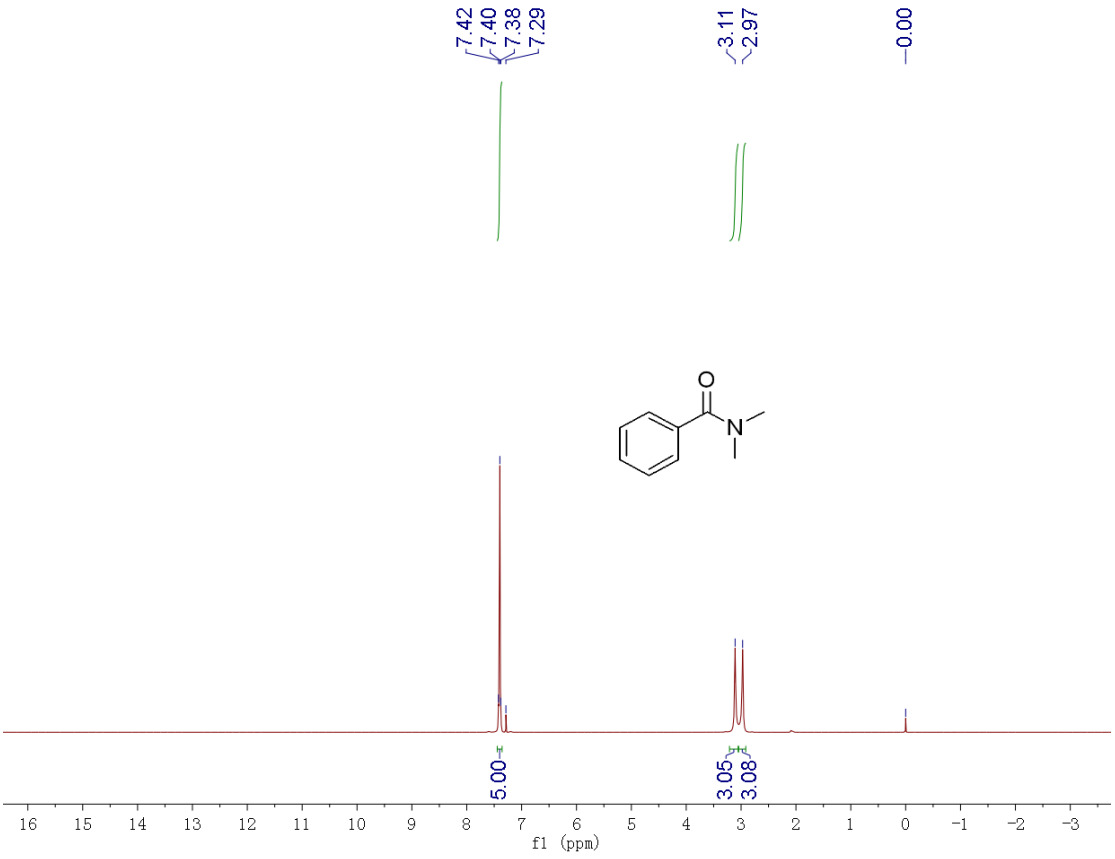
^{1}H NMR spectrum of compound 7



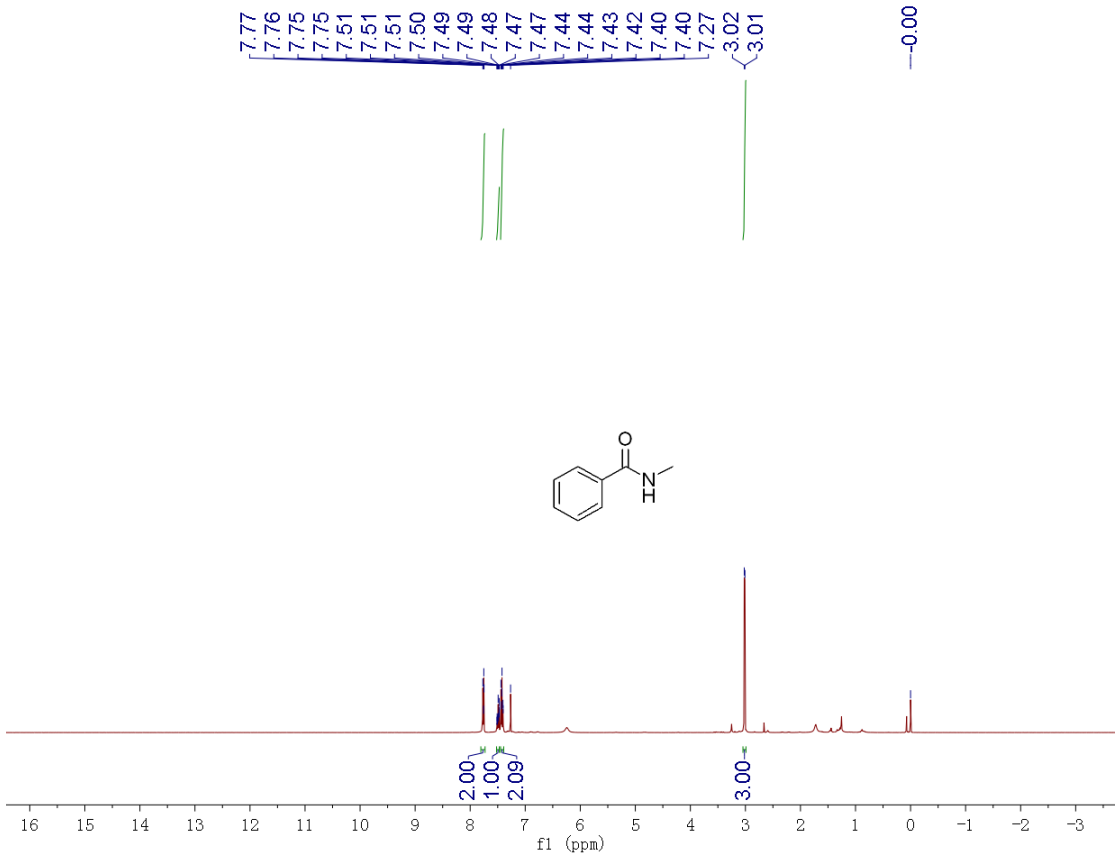
^{13}C NMR spectrum of compound 7



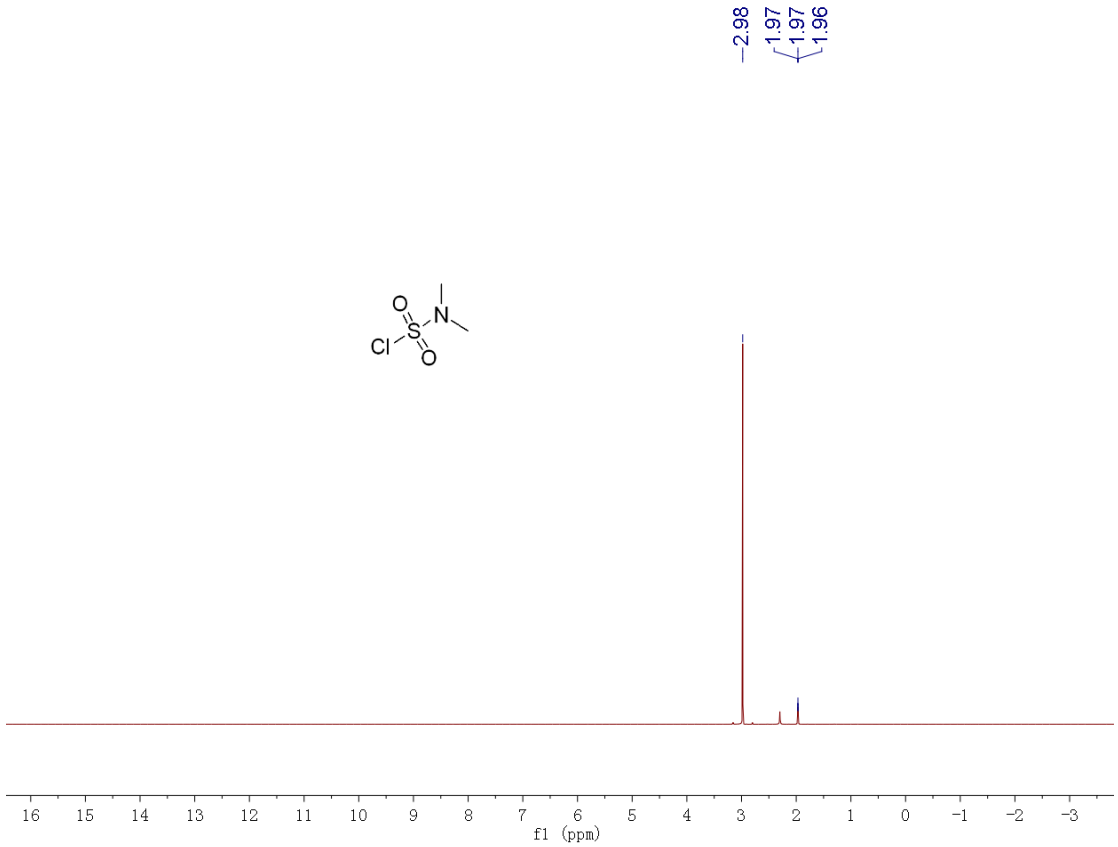
^{1}H NMR spectrum of compound 8



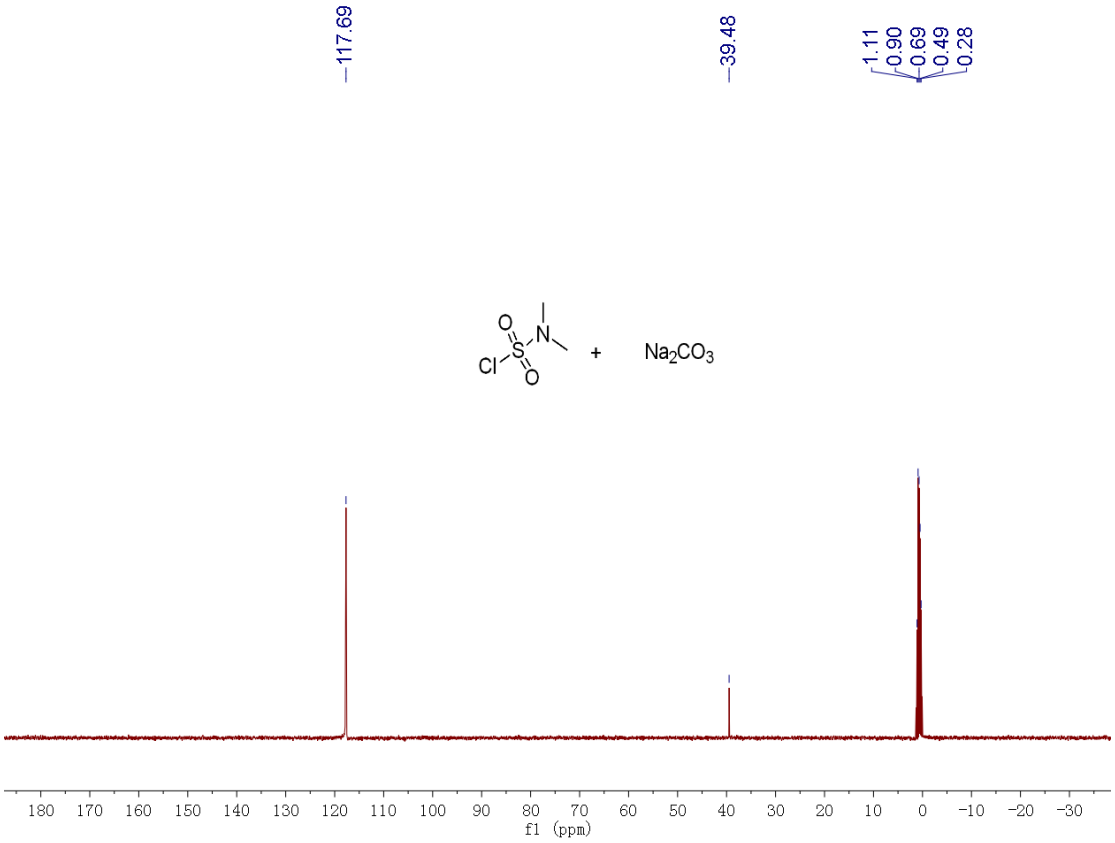
^{1}H NMR spectrum of compound 9



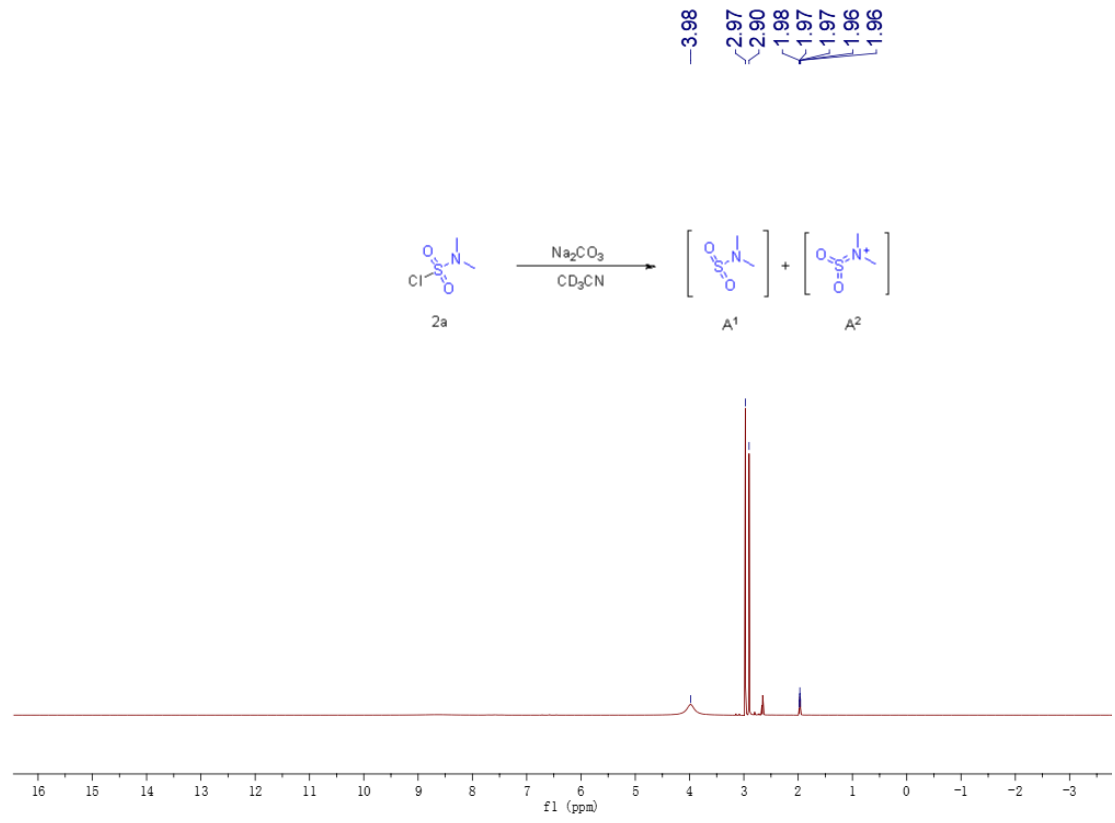
^{1}H NMR spectrum of compound 2a



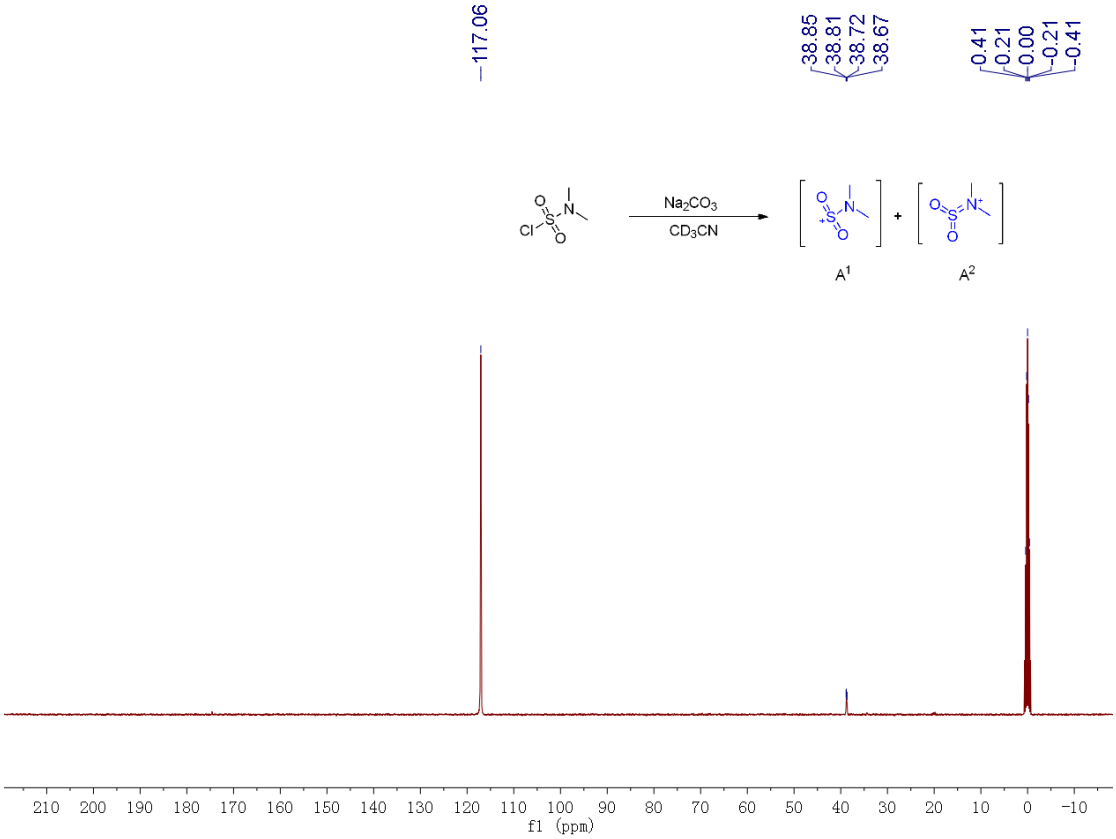
^{13}C NMR spectrum of compound 2a



^{1}H NMR spectrum of compound 2a, A^{1} and A^{2}

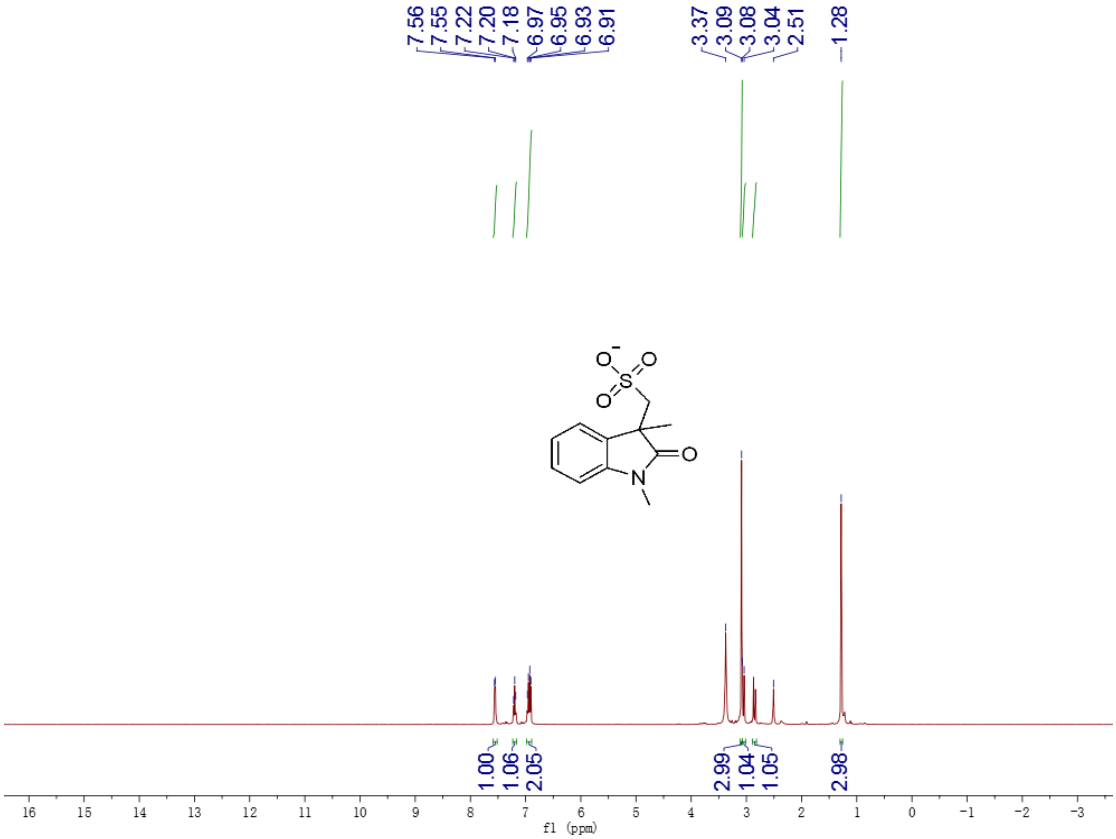


^{13}C NMR spectrum of compound 2a, A^1 and A^2

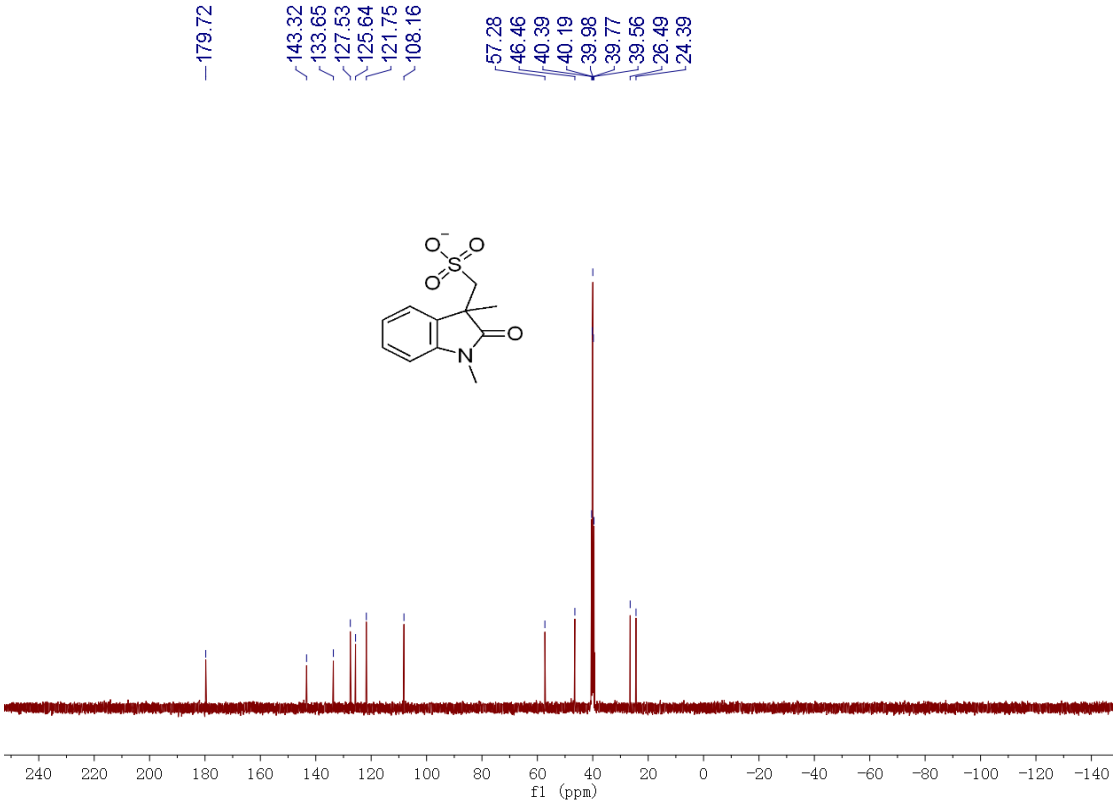


10. ^{1}H NMR and ^{13}C NMR spectrum of Sulfonate Products

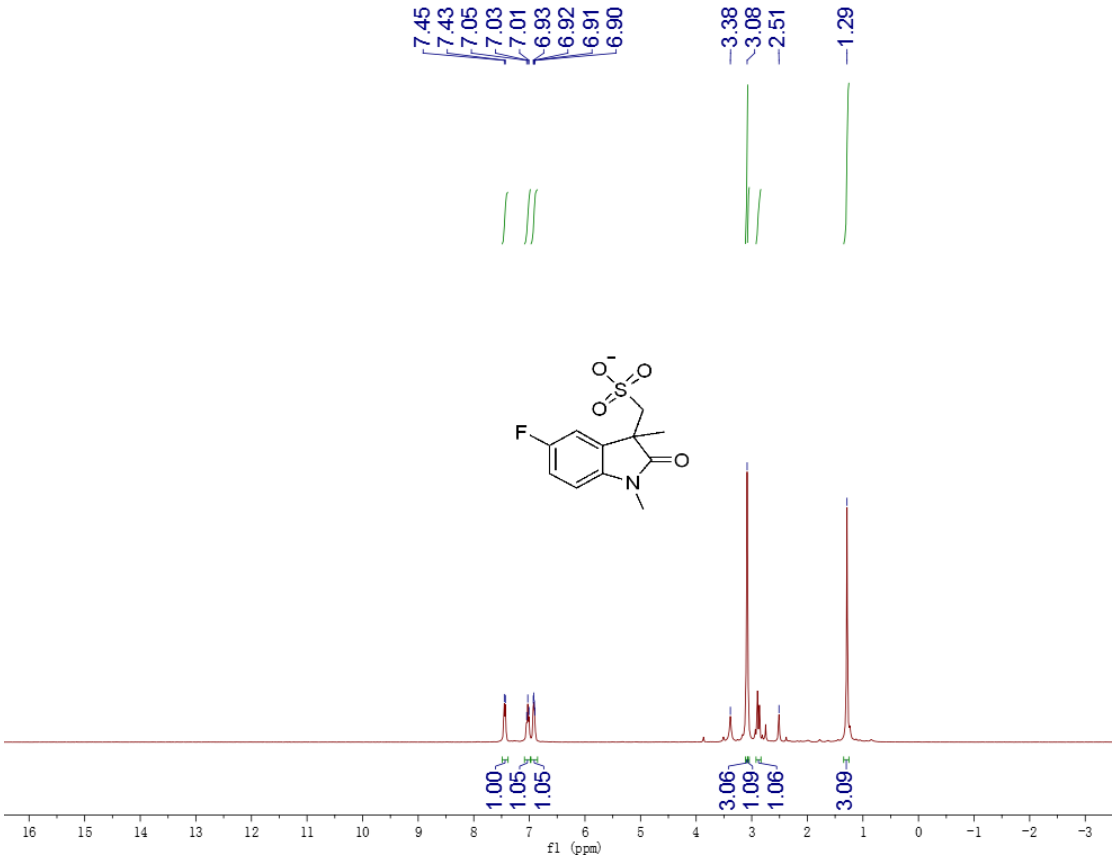
^{1}H NMR spectrum of compound 3a



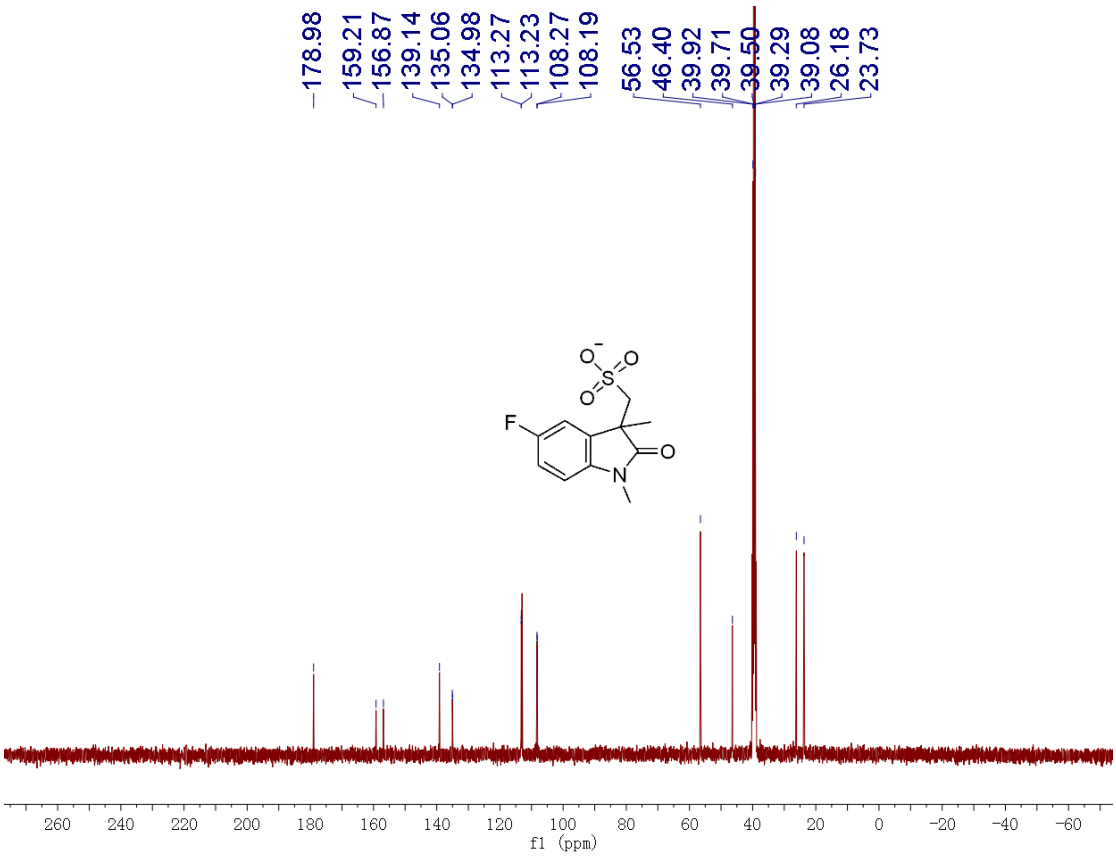
^{13}C NMR spectrum of compound 3a



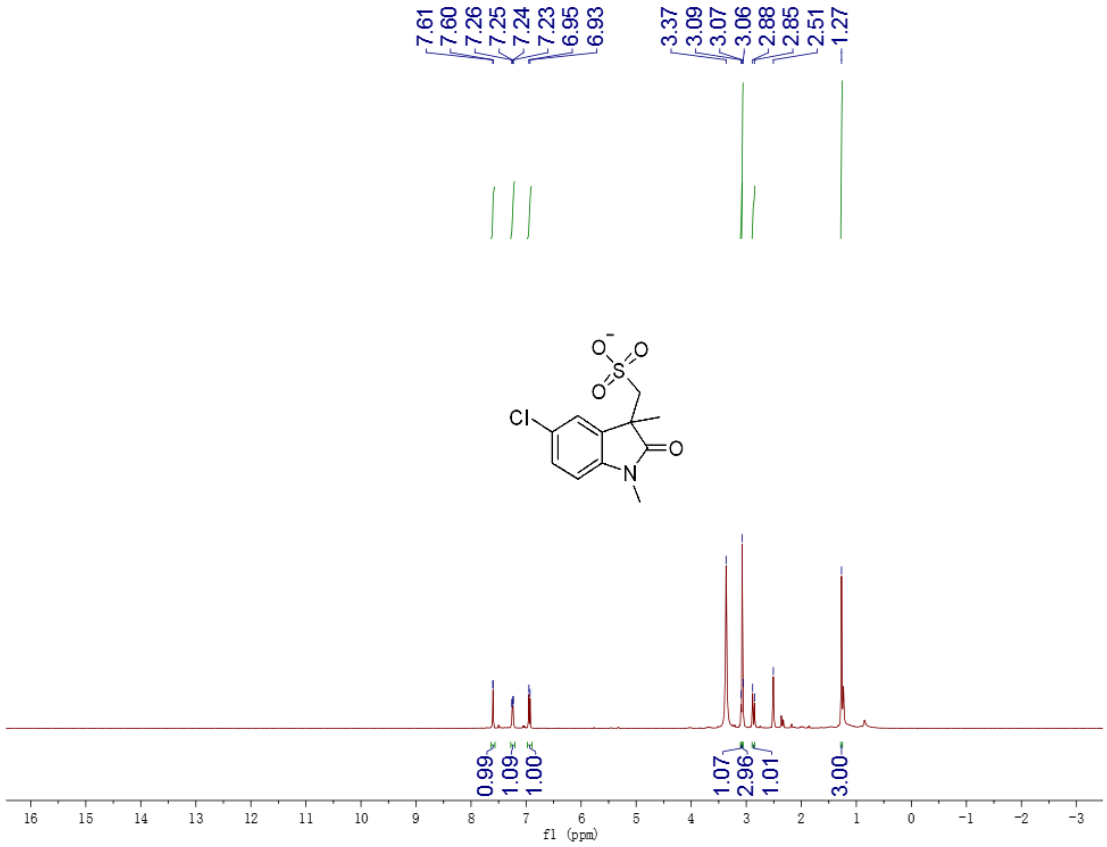
^{1}H NMR spectrum of compound 3b



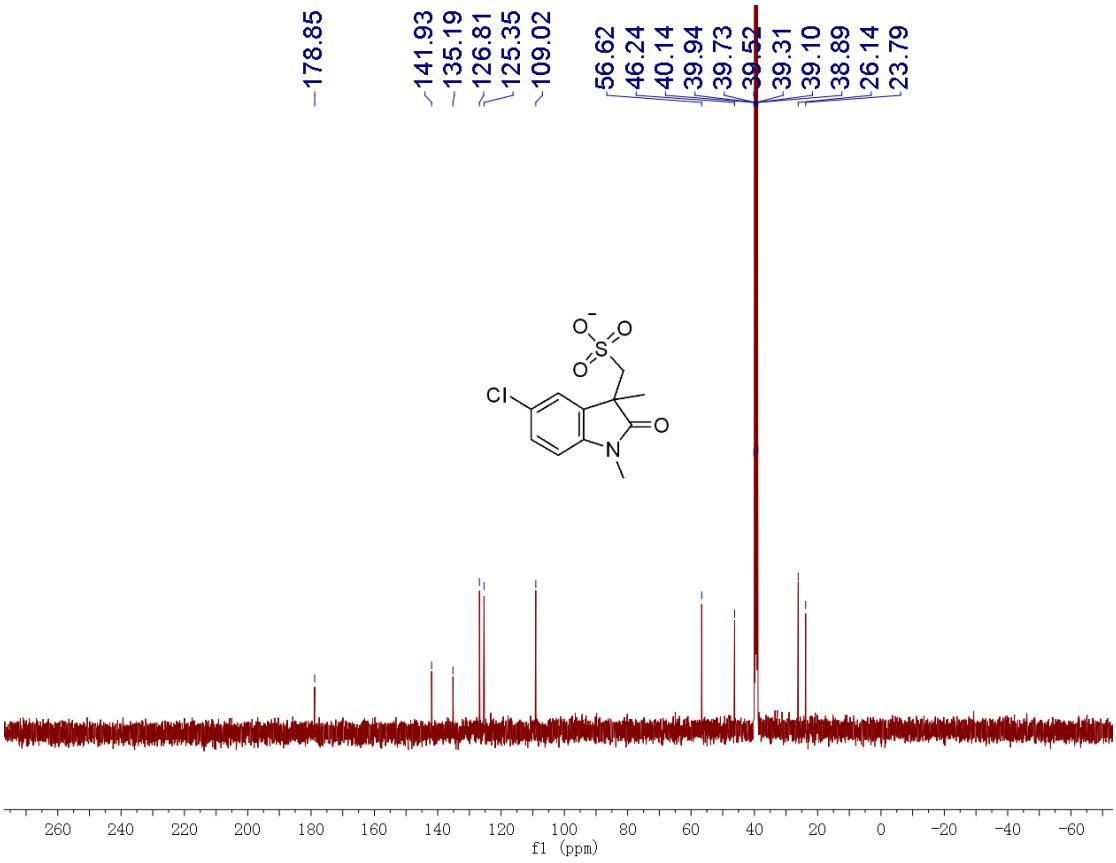
^{13}C NMR spectrum of compound 3b



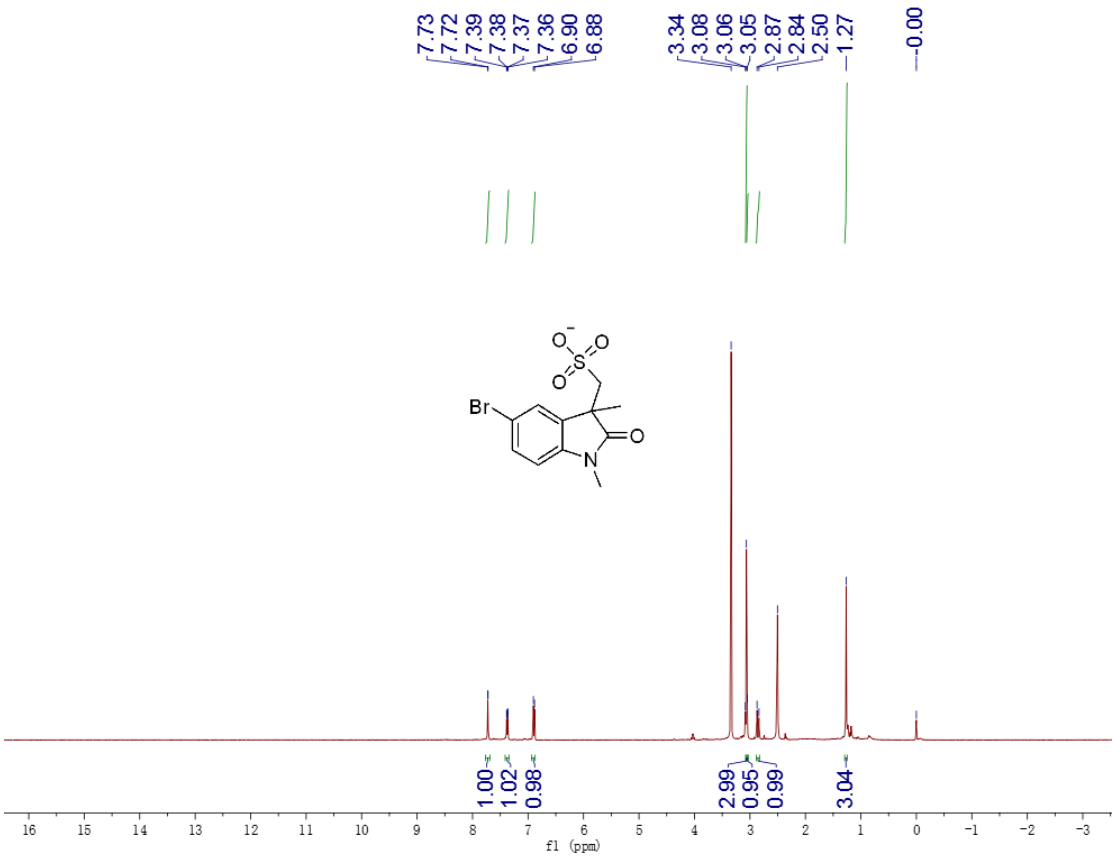
^{1}H NMR spectrum of compound 3c



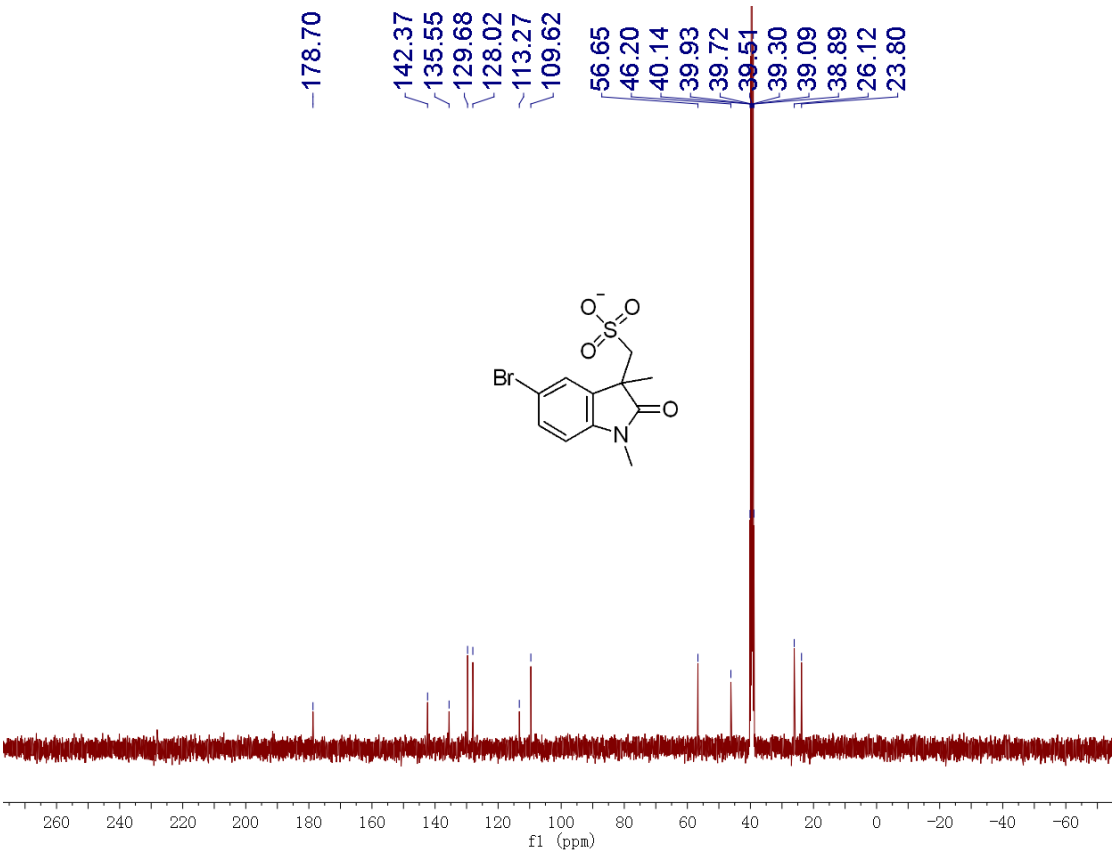
^{13}C NMR spectrum of compound 3c



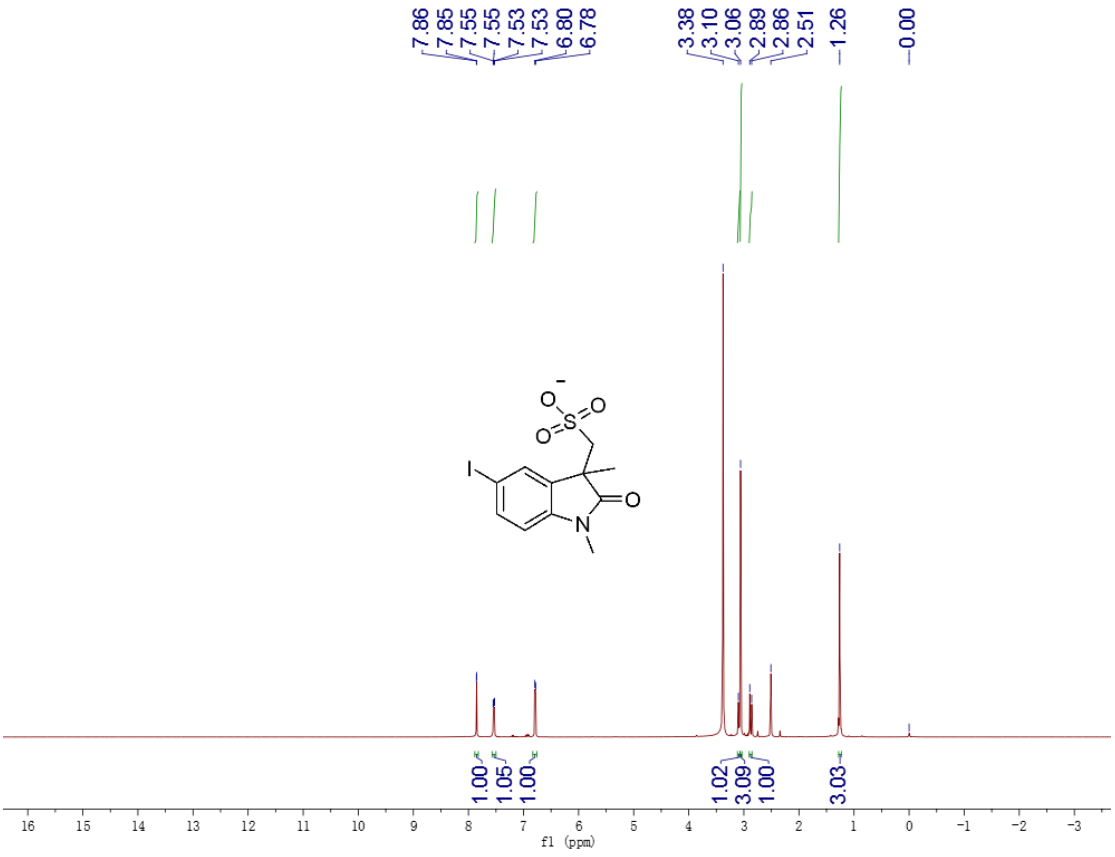
^{1}H NMR spectrum of compound 3d



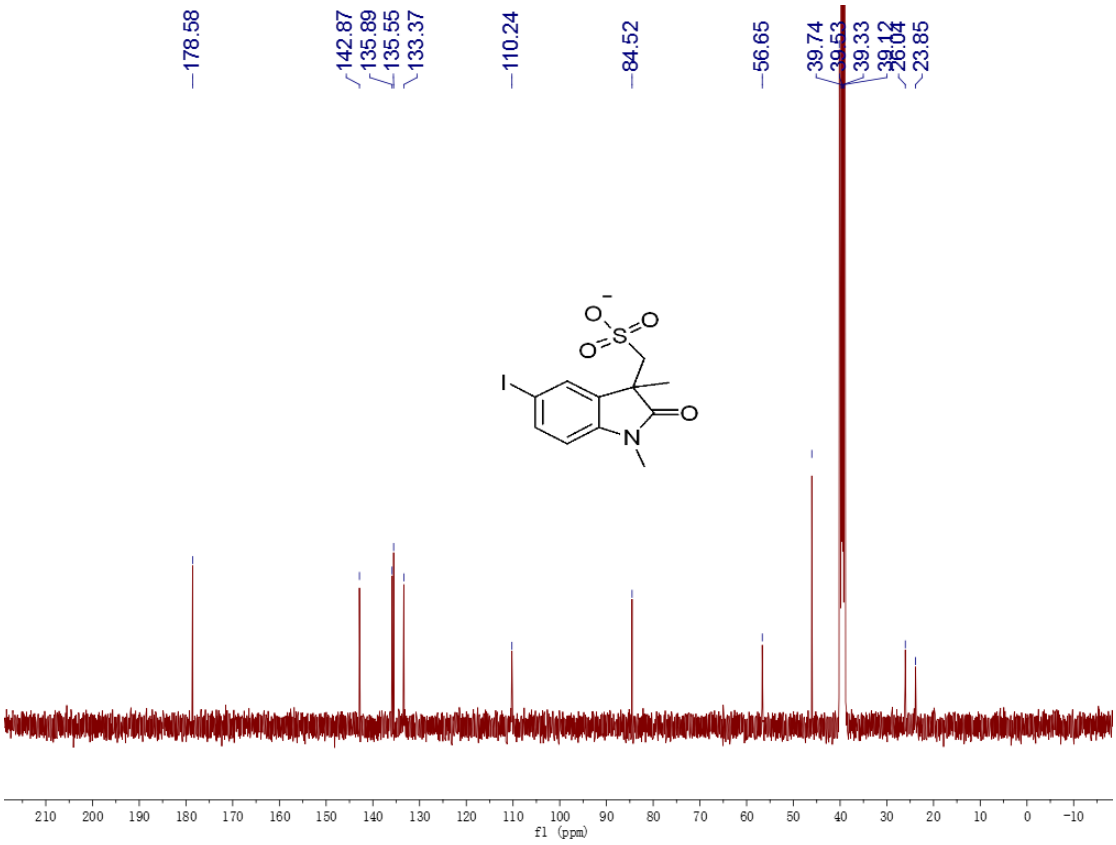
^{13}C NMR spectrum of compound 3d



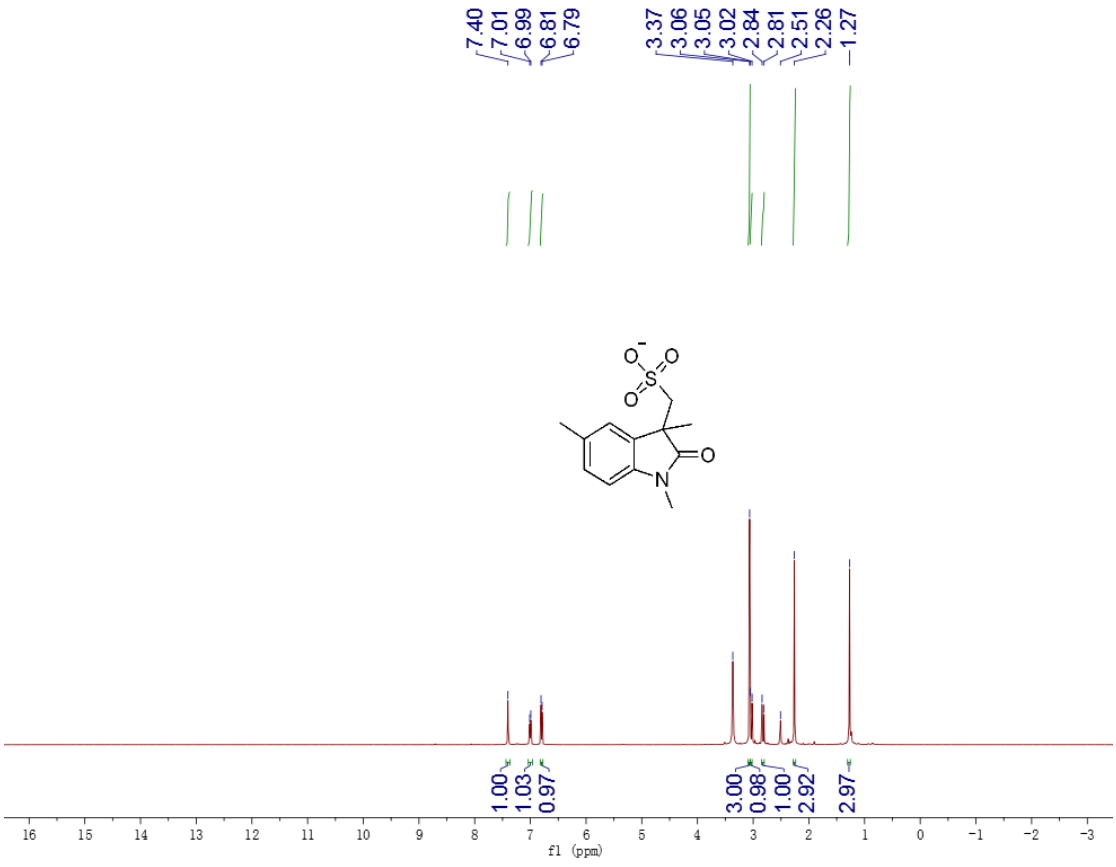
^{1}H NMR spectrum of compound 3e



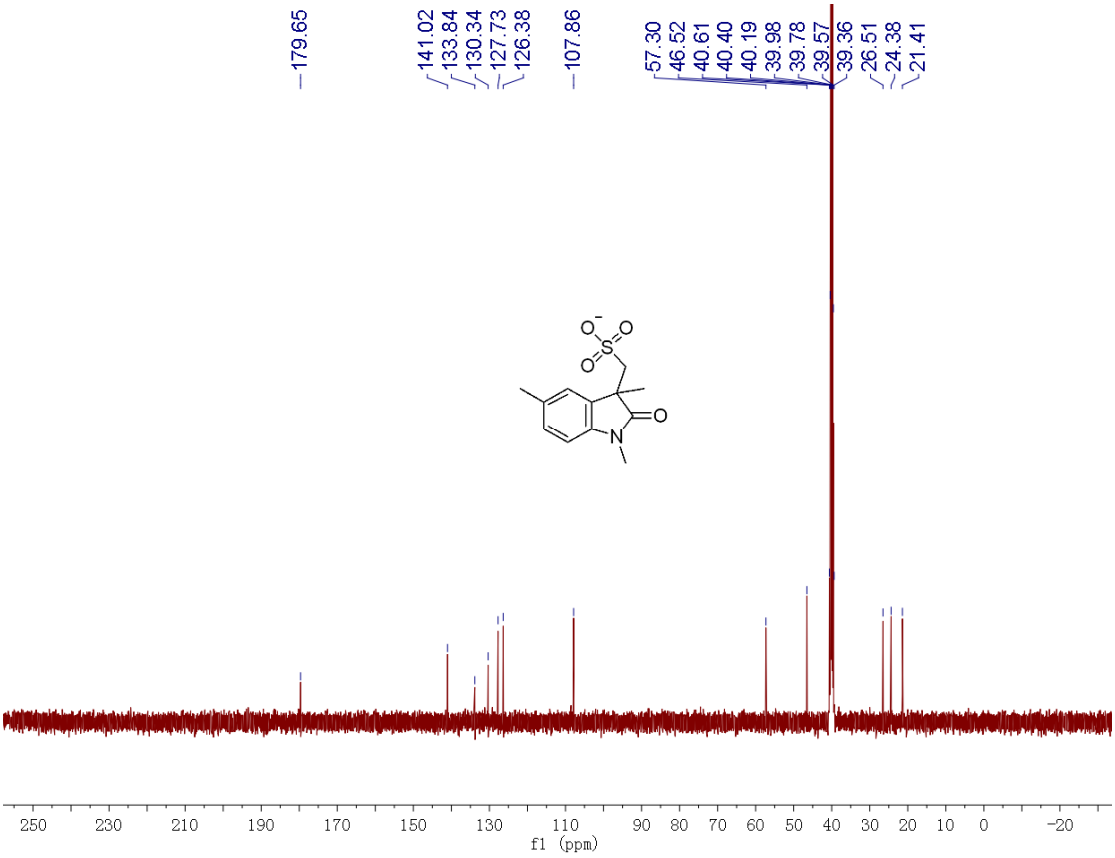
^{13}C NMR spectrum of compound 3e



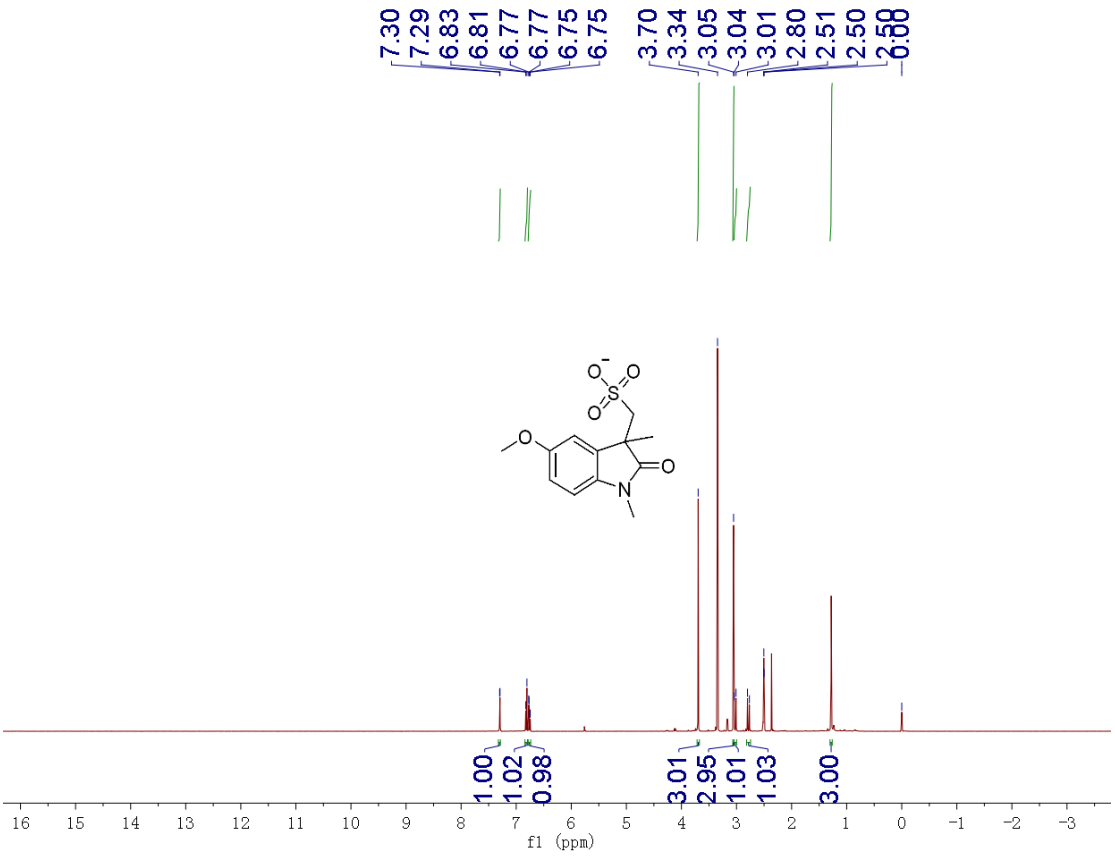
^{1}H NMR spectrum of compound 3f



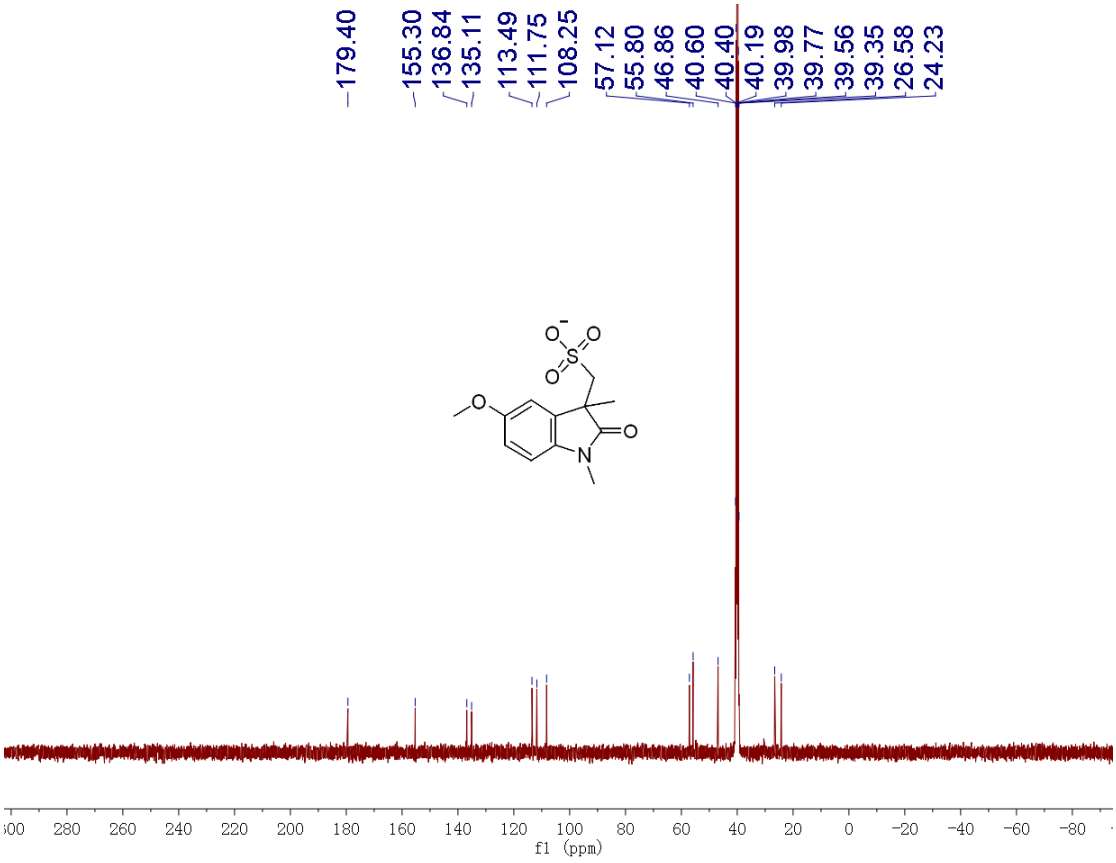
^{13}C NMR spectrum of compound 3f



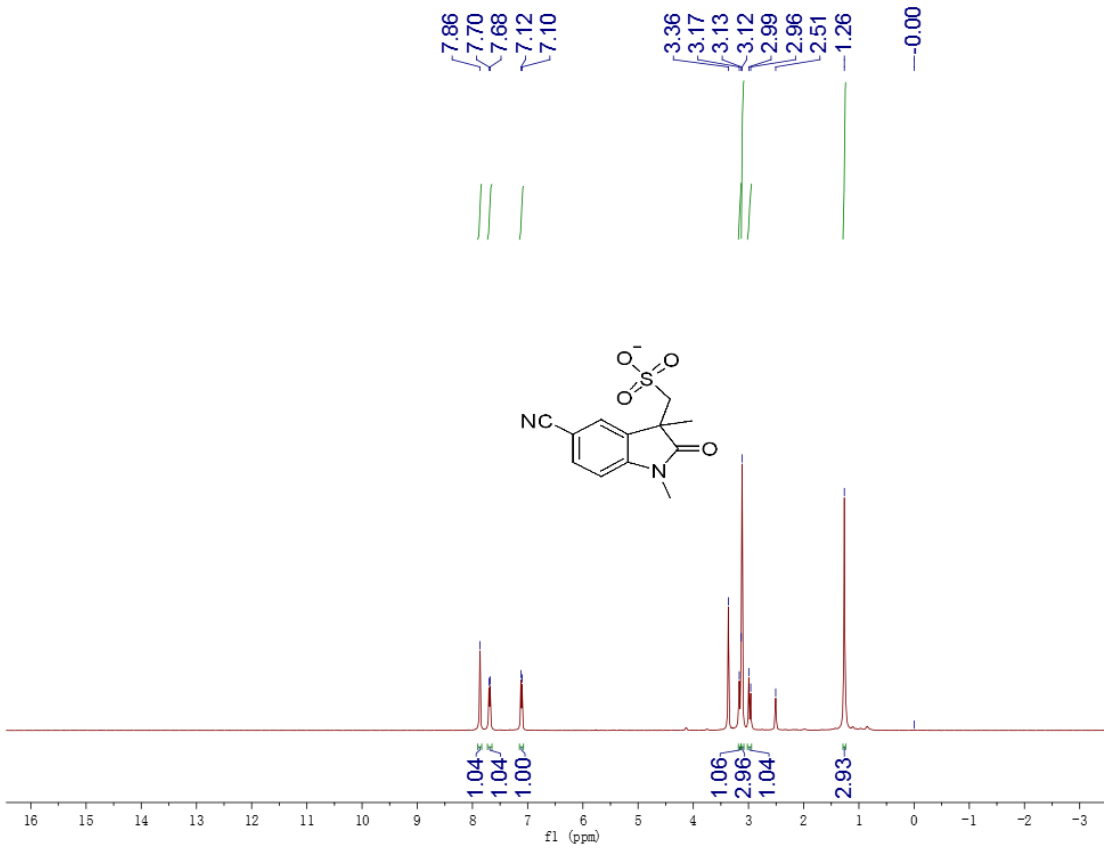
^{1}H NMR spectrum of compound 3g



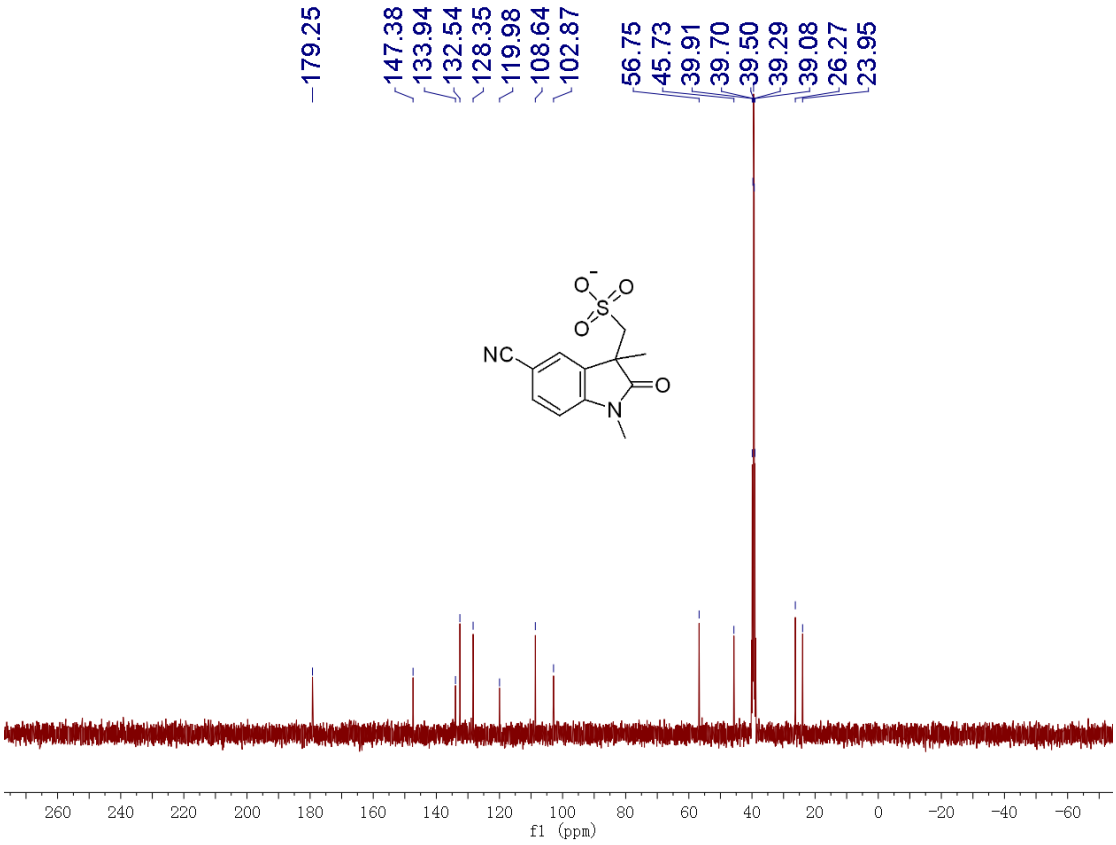
^{13}C NMR spectrum of compound 3g



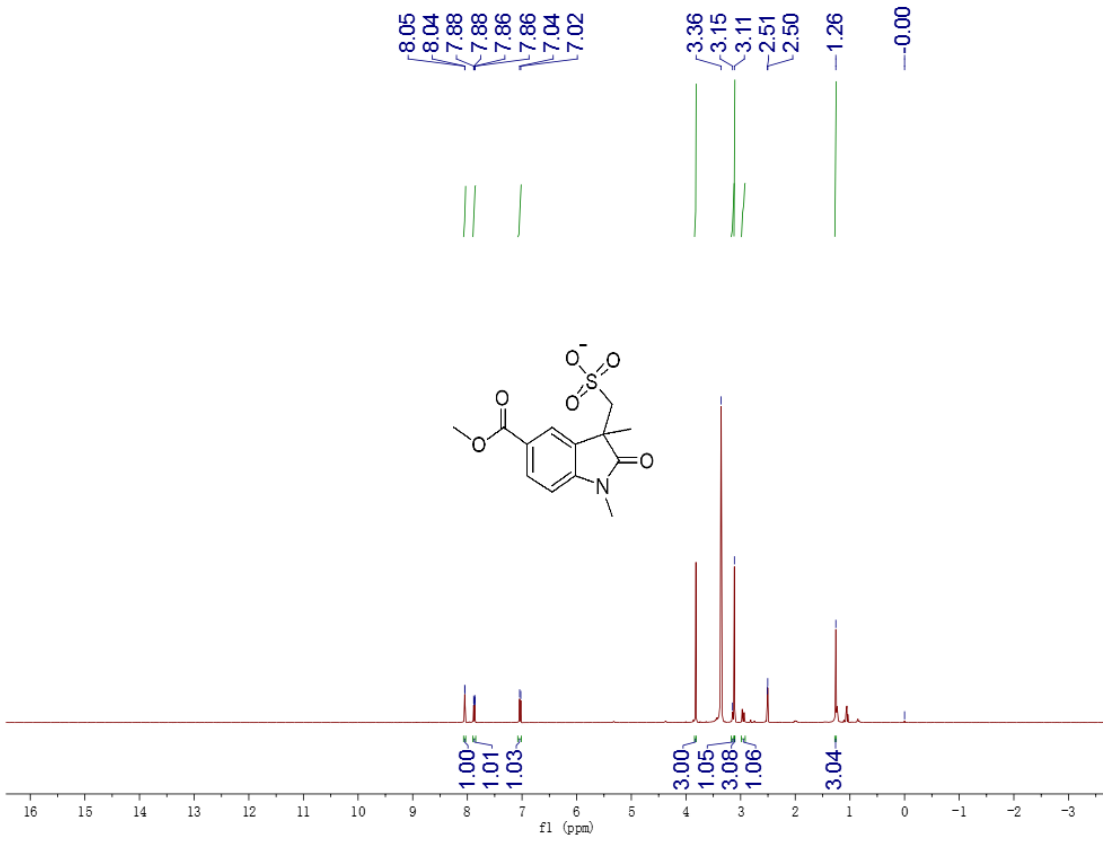
^{1}H NMR spectrum of compound 3h



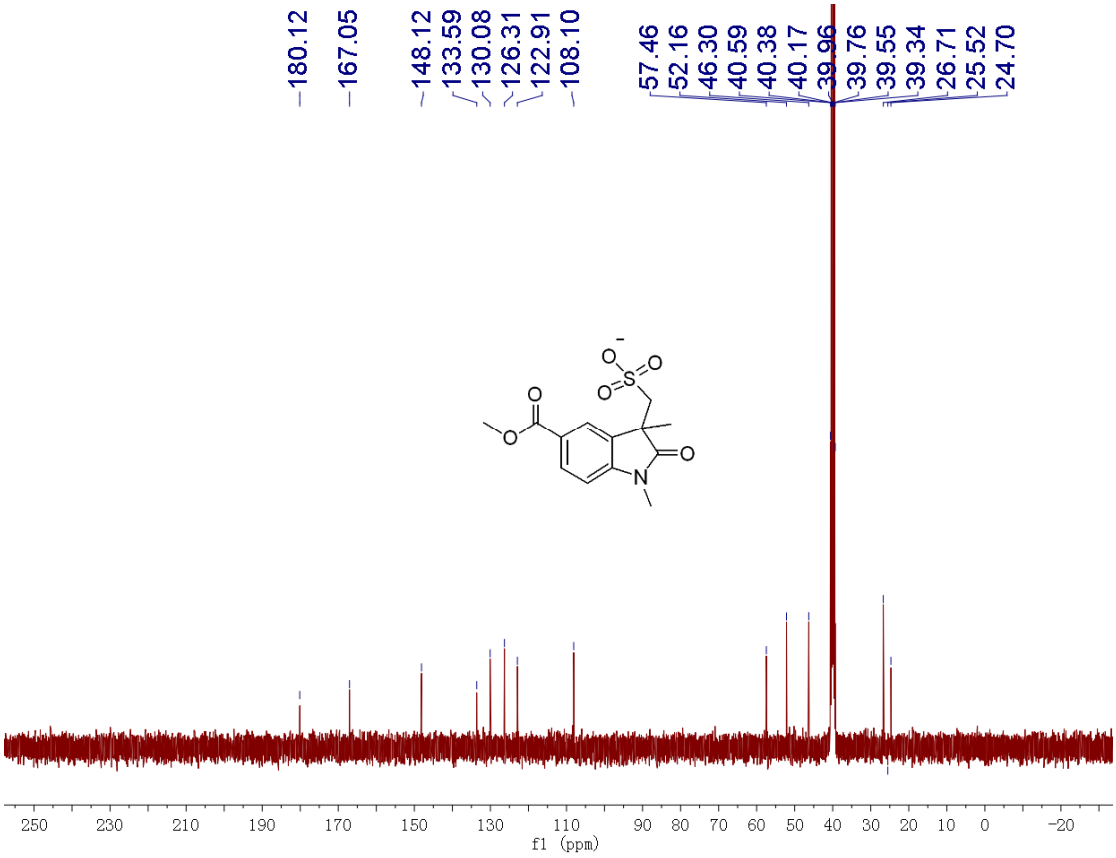
^{13}C NMR spectrum of compound 3h



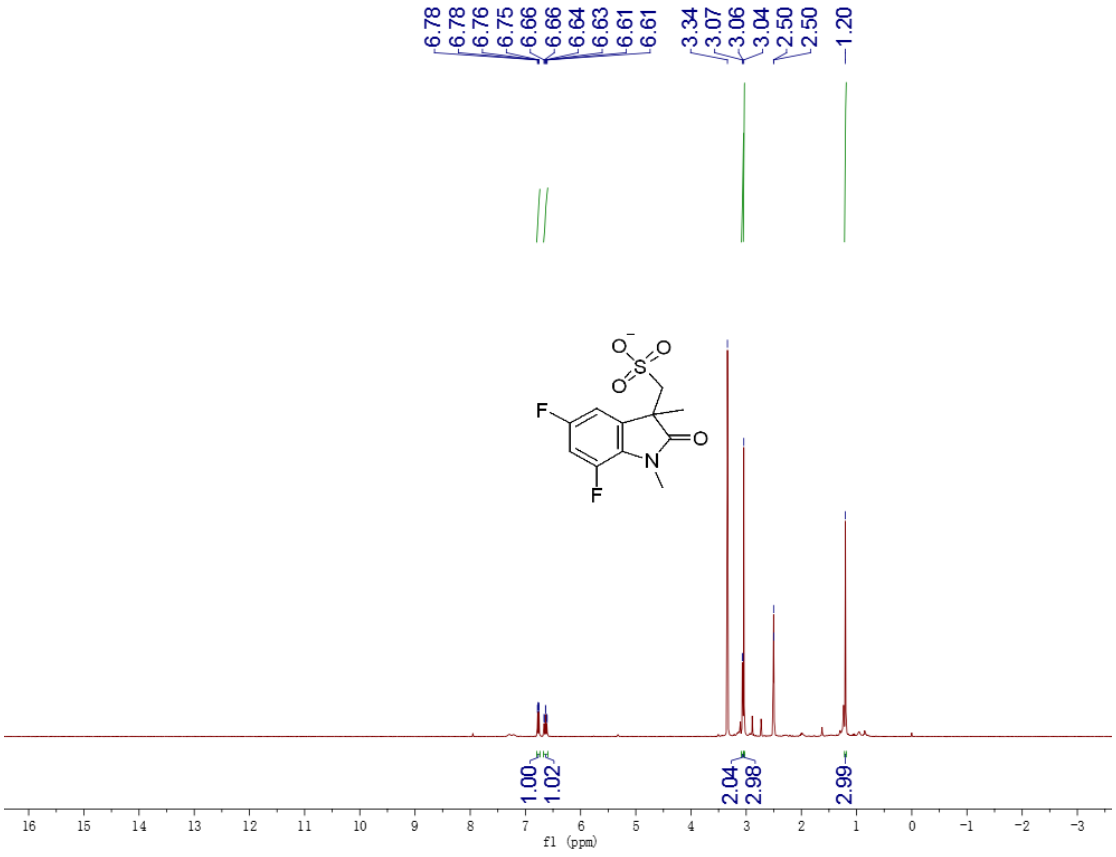
^{1}H NMR spectrum of compound 3i



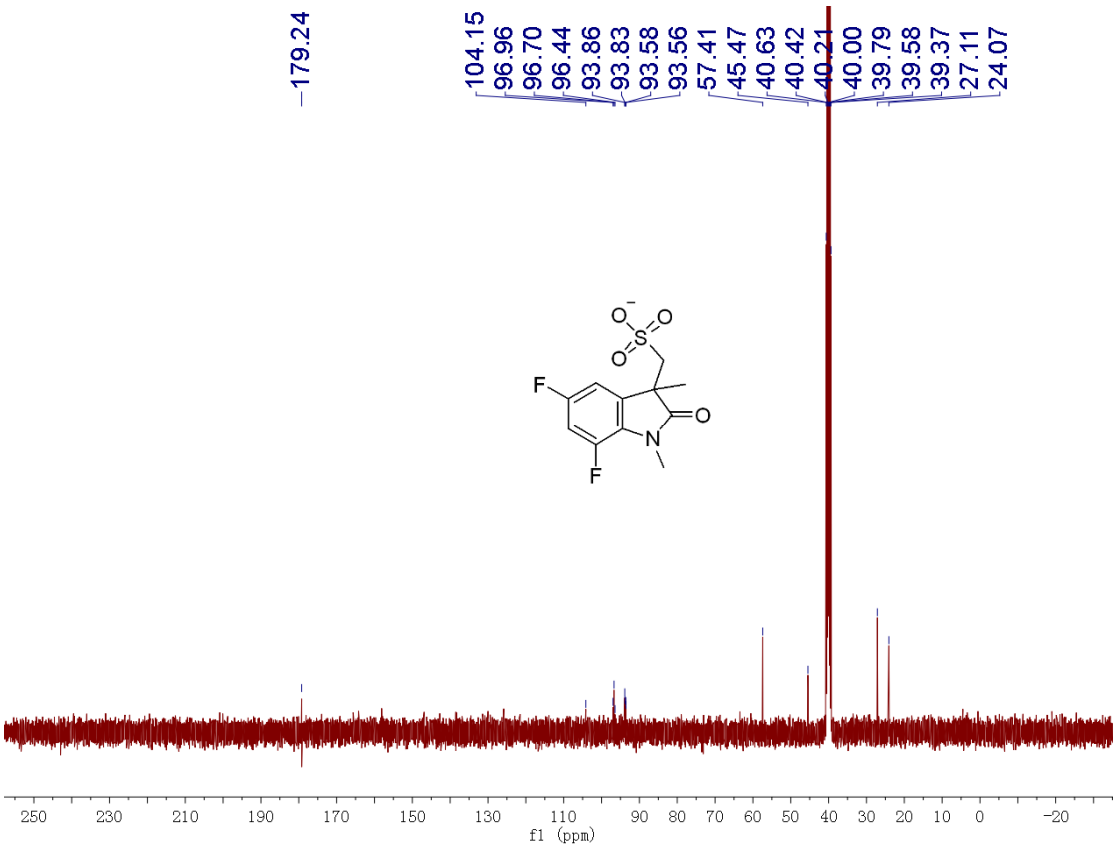
^{13}C NMR spectrum of compound 3i



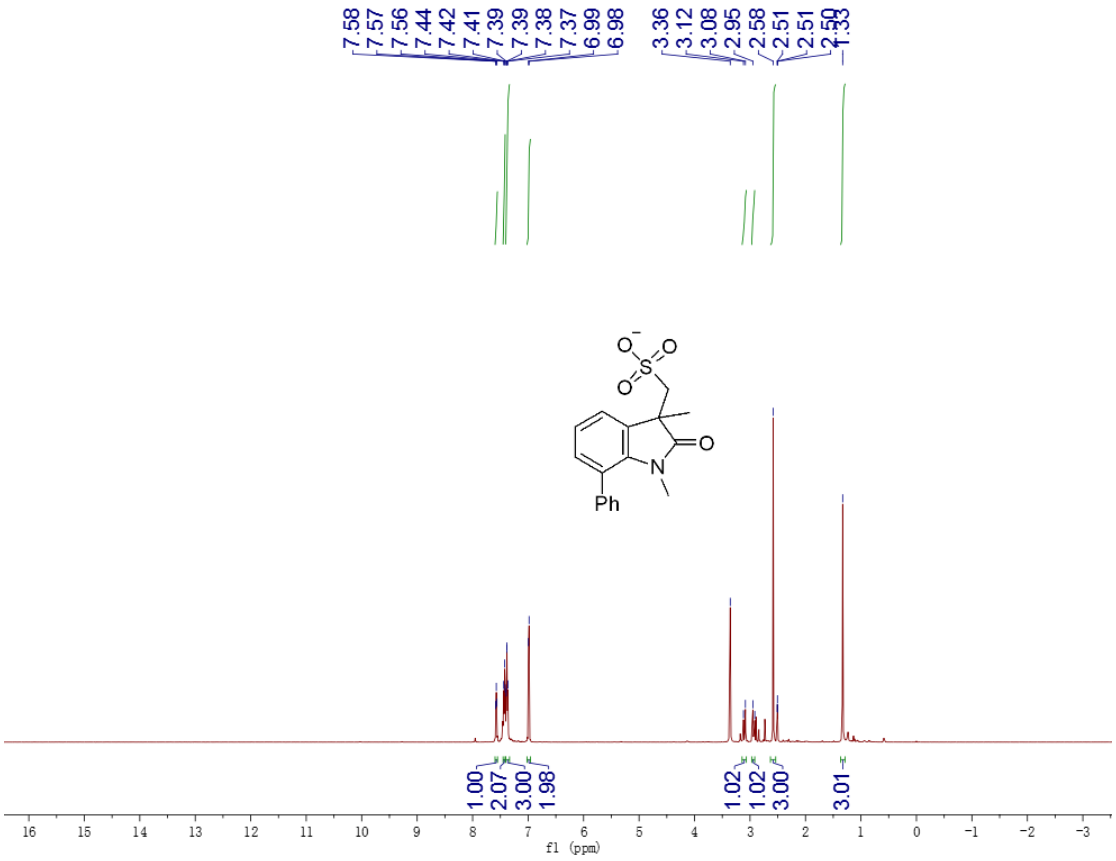
^{1}H NMR spectrum of compound 3j



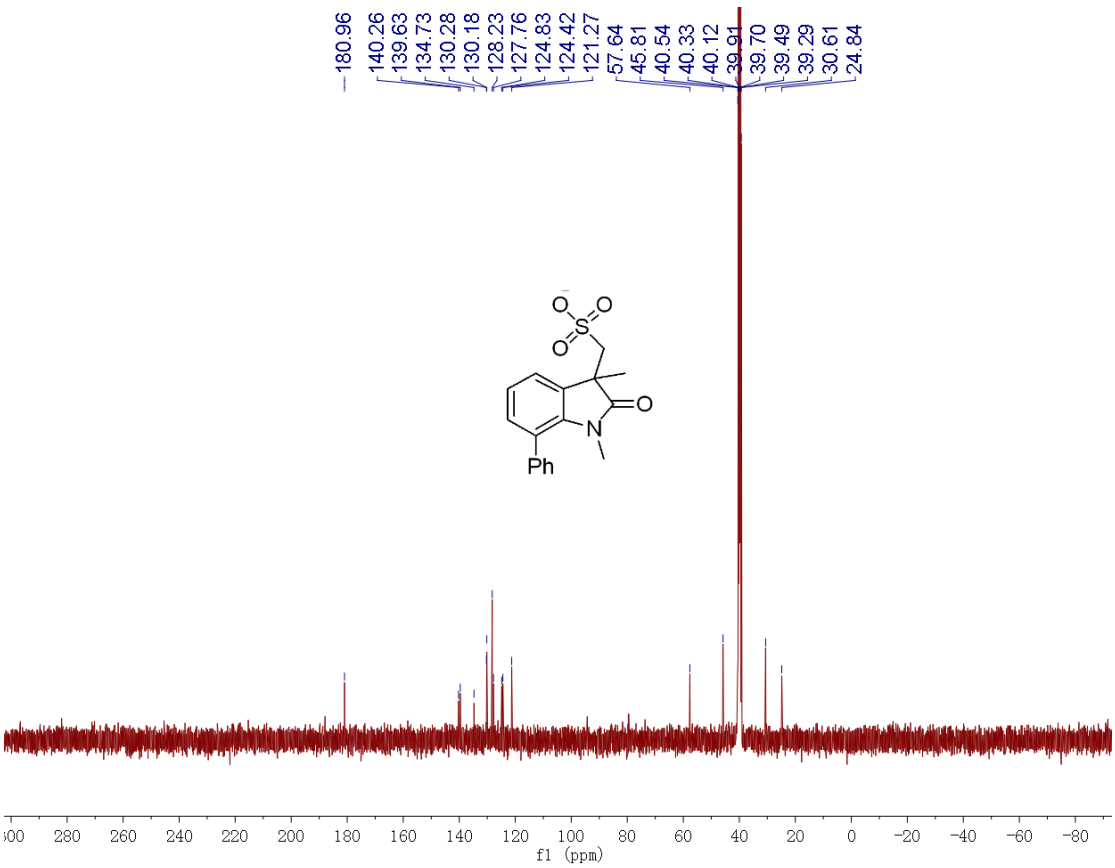
^{13}C NMR spectrum of compound 3j



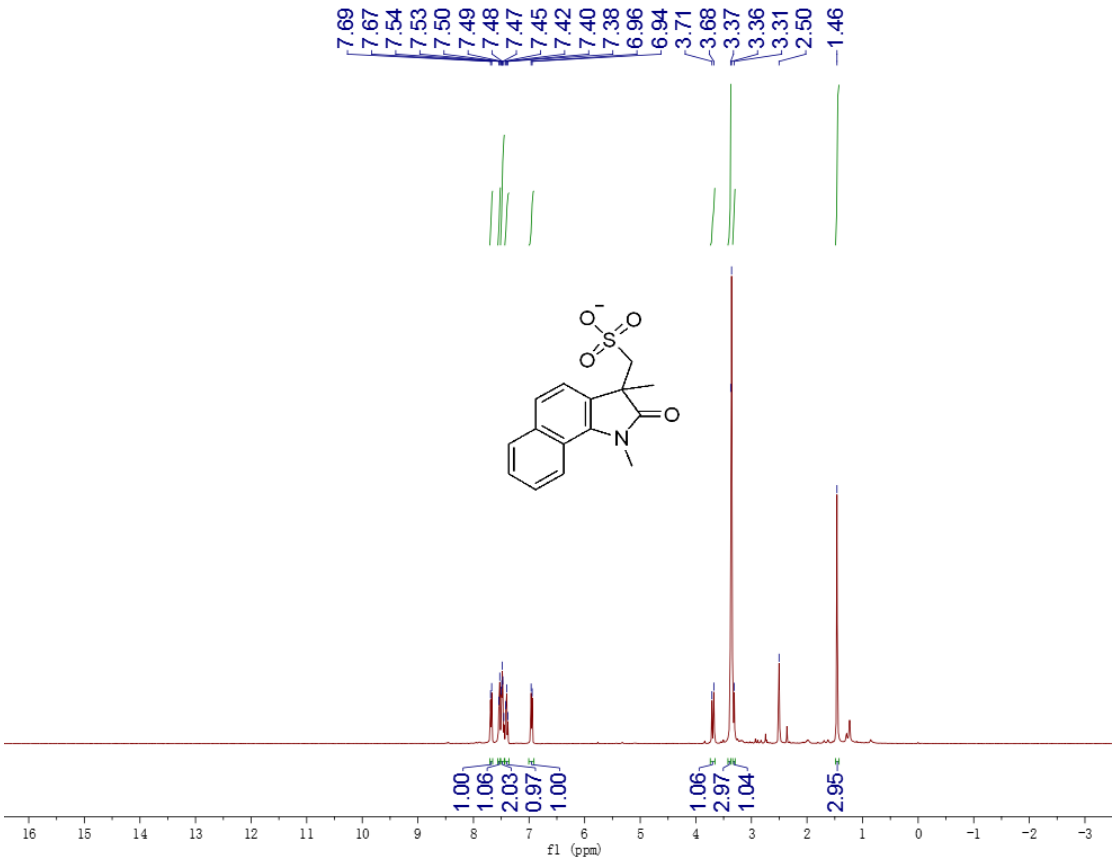
^{1}H NMR spectrum of compound 3k



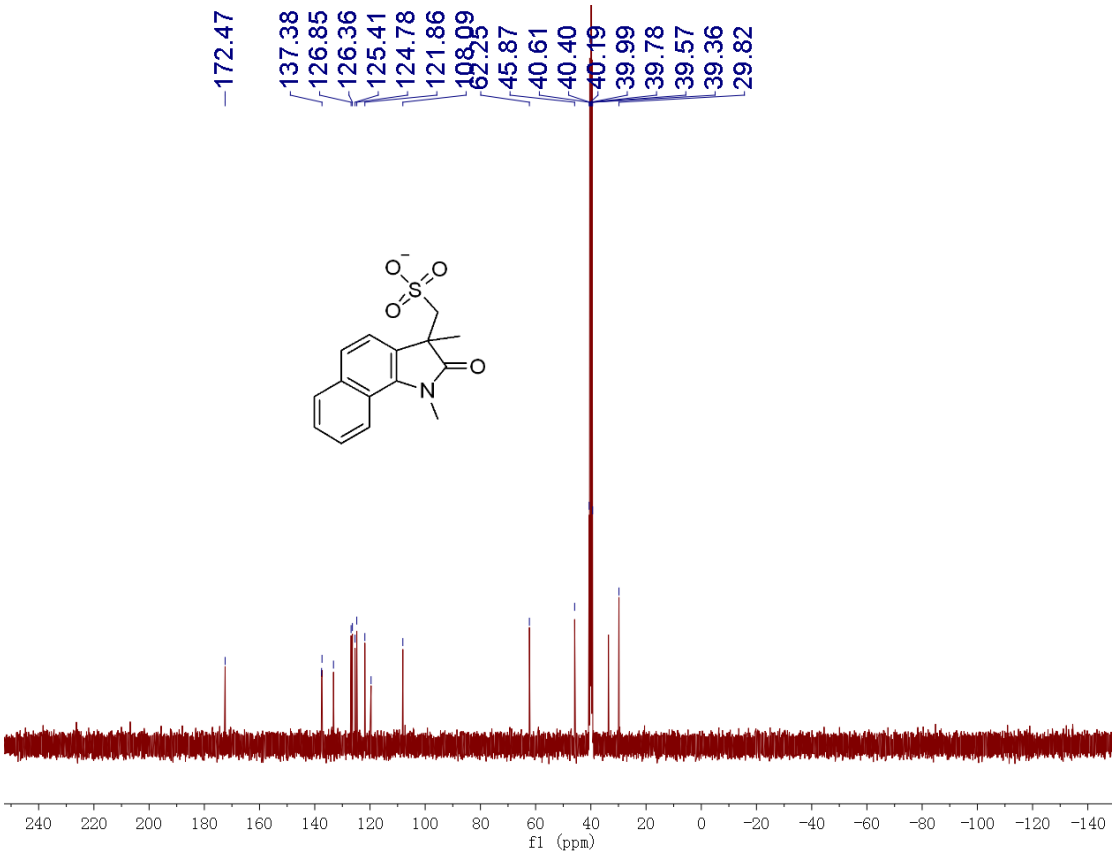
^{13}C NMR spectrum of compound 3k



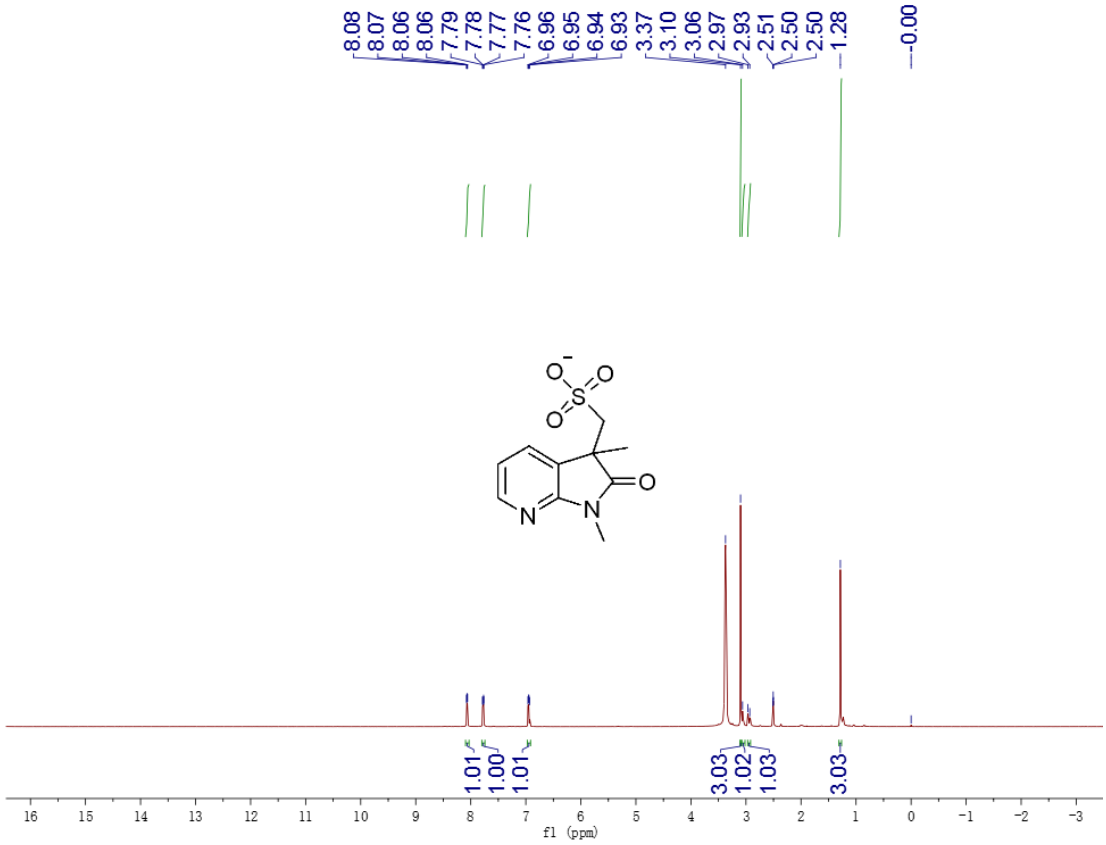
^{1}H NMR spectrum of compound 3l



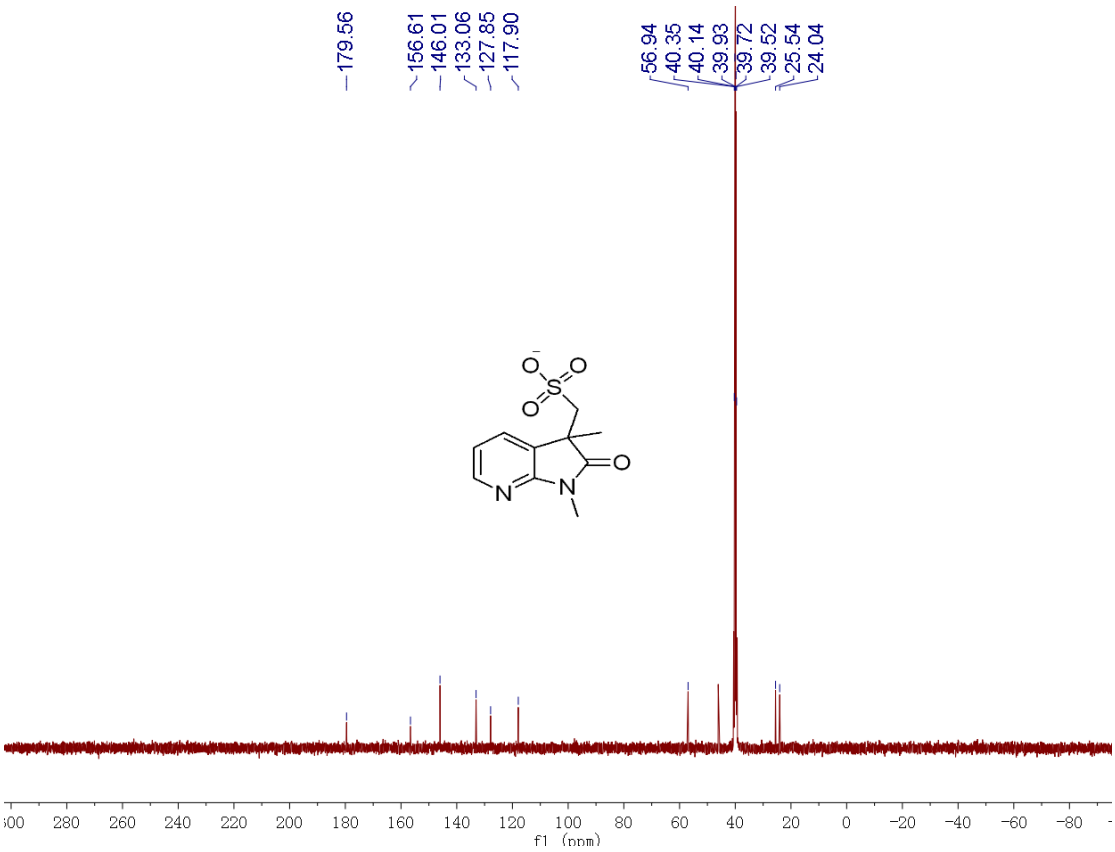
^{13}C NMR spectrum of compound 3l



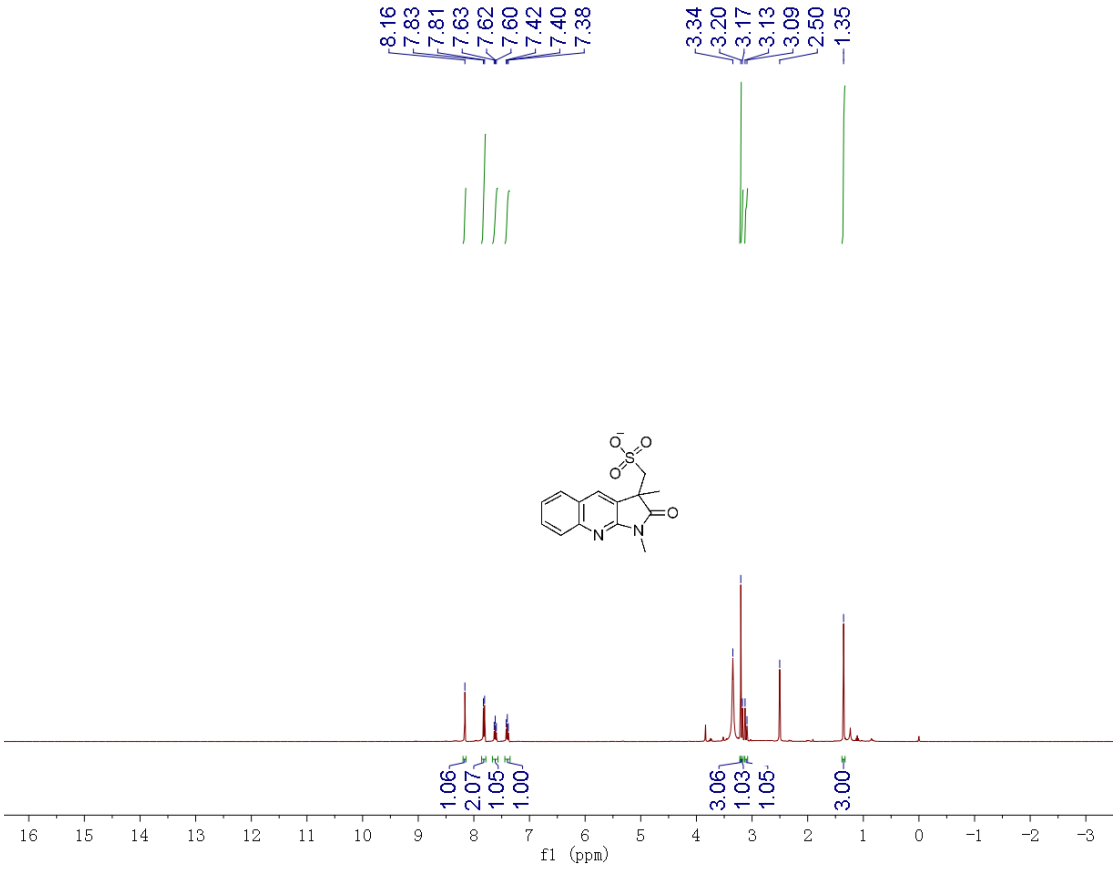
^{1}H NMR spectrum of compound 3m



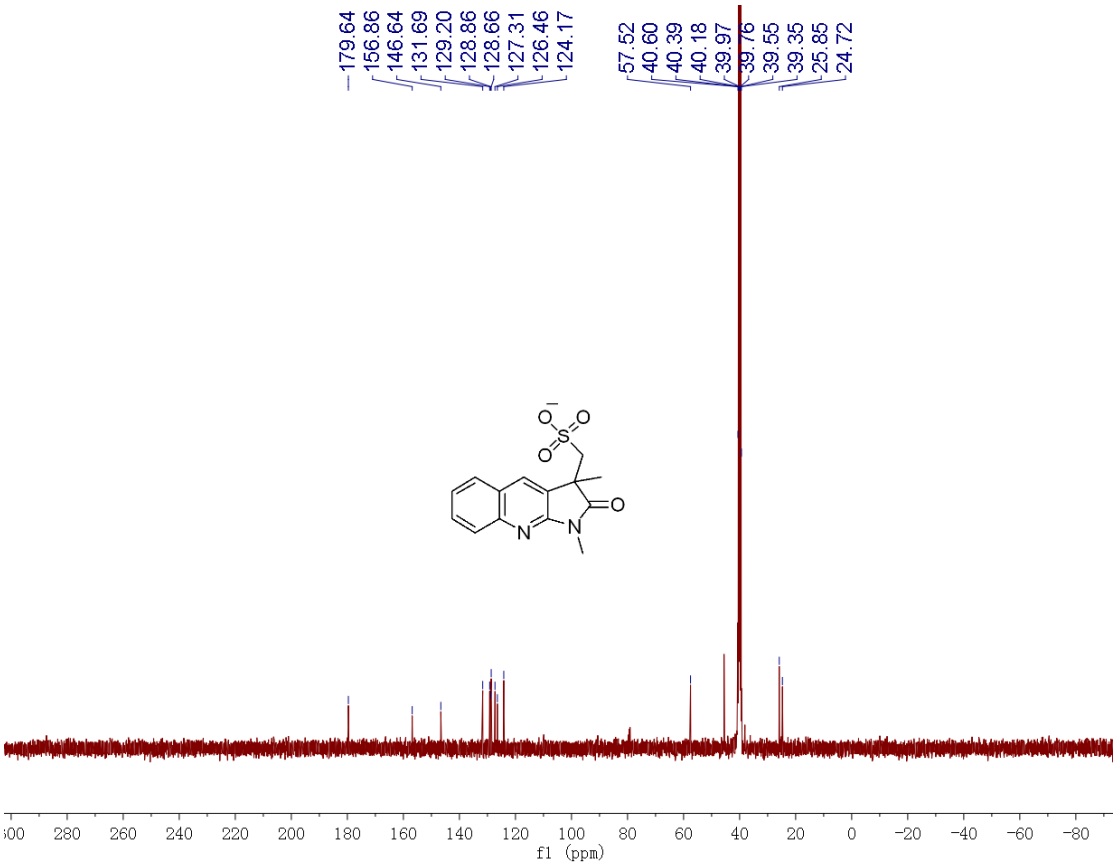
^{13}C NMR spectrum of compound 3m



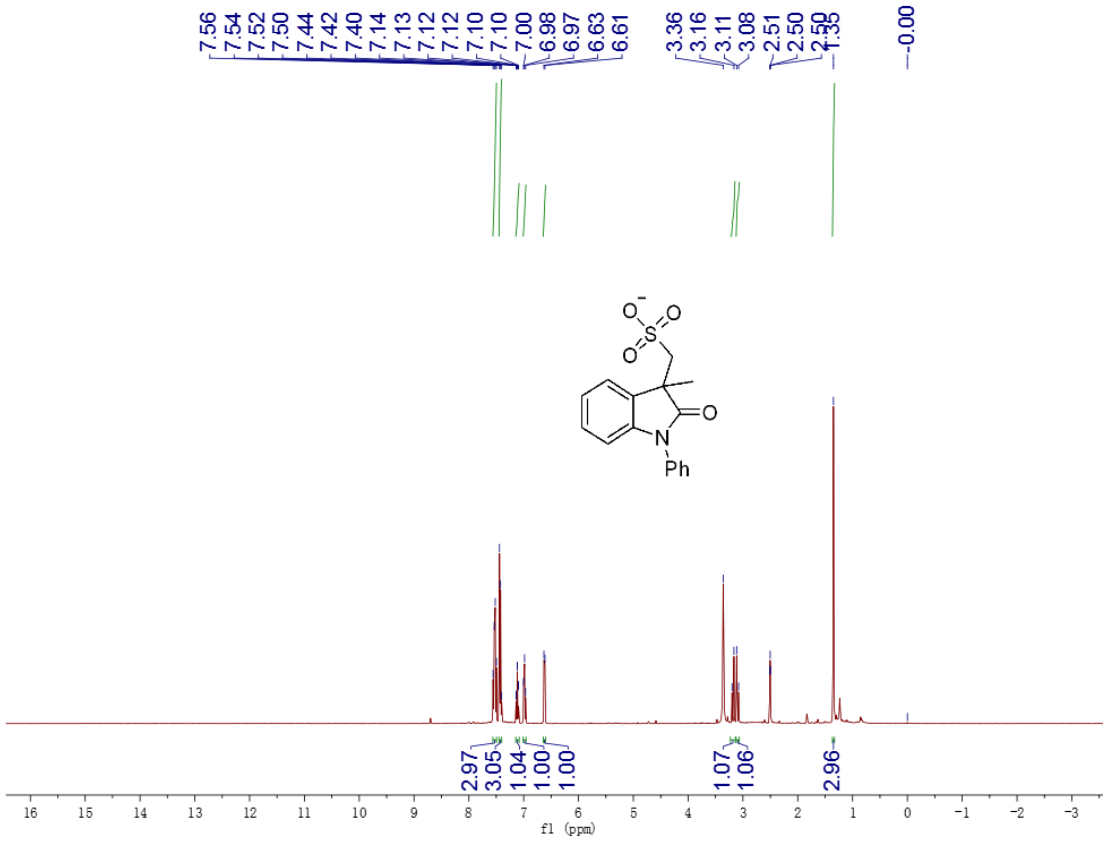
^{1}H NMR spectrum of compound 3n



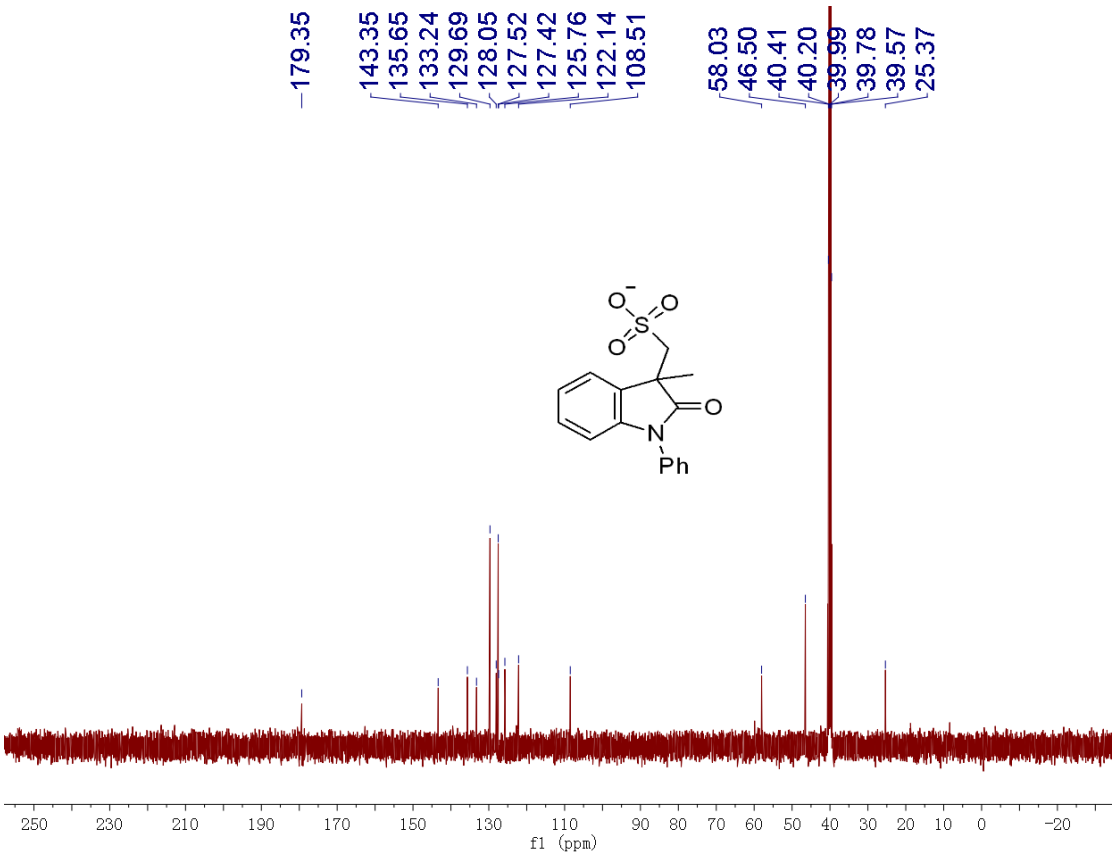
^{13}C NMR spectrum of compound 3n



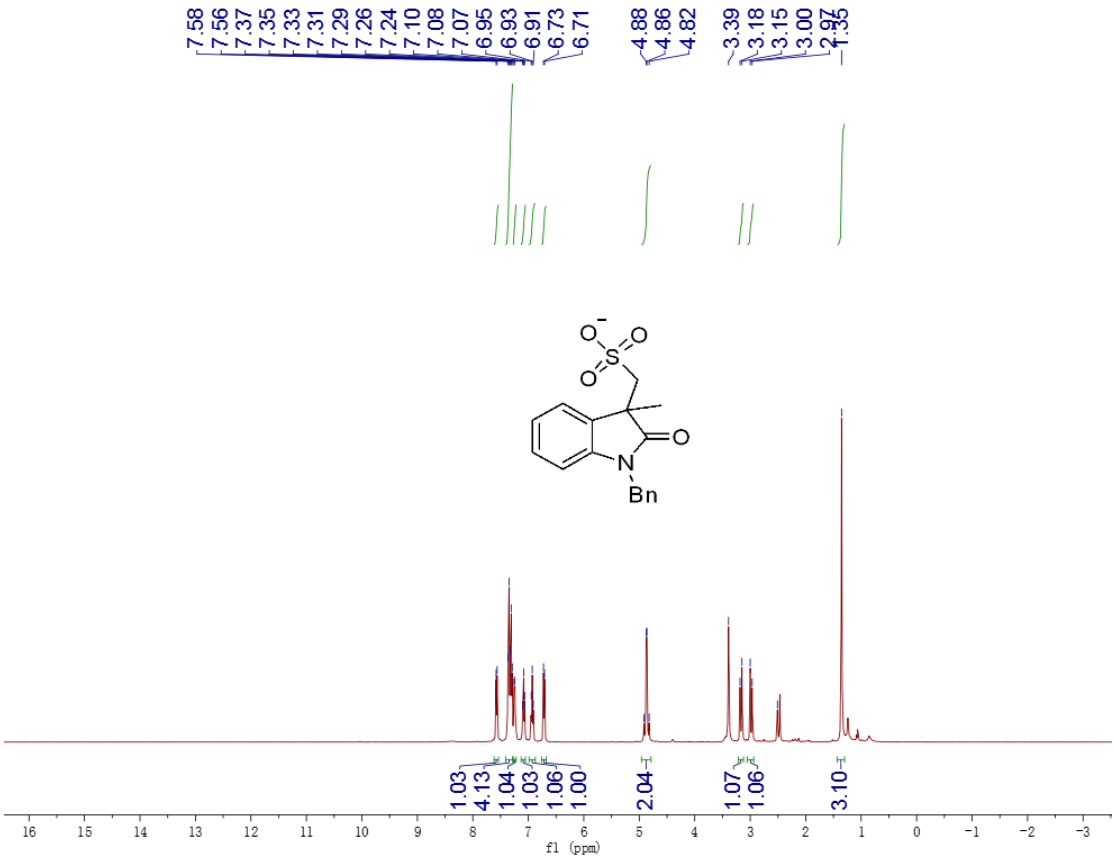
^{1}H NMR spectrum of compound 3o



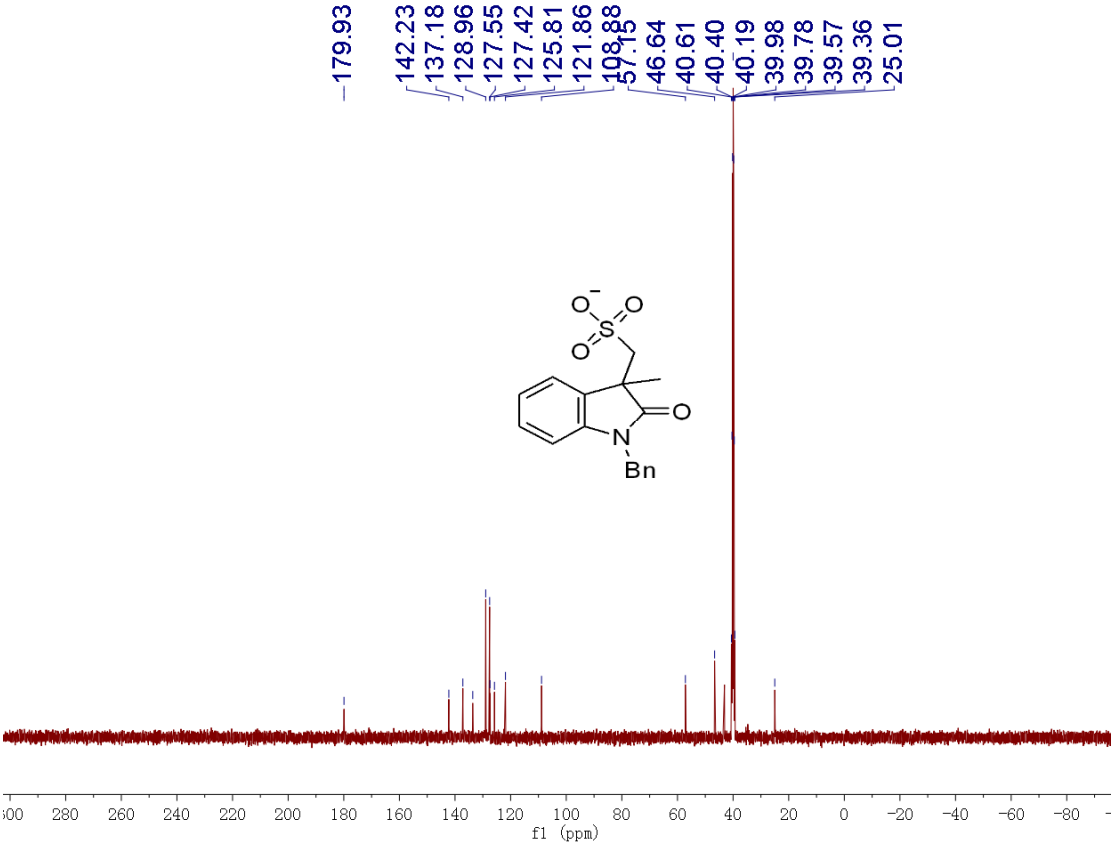
^{13}C NMR spectrum of compound 3o



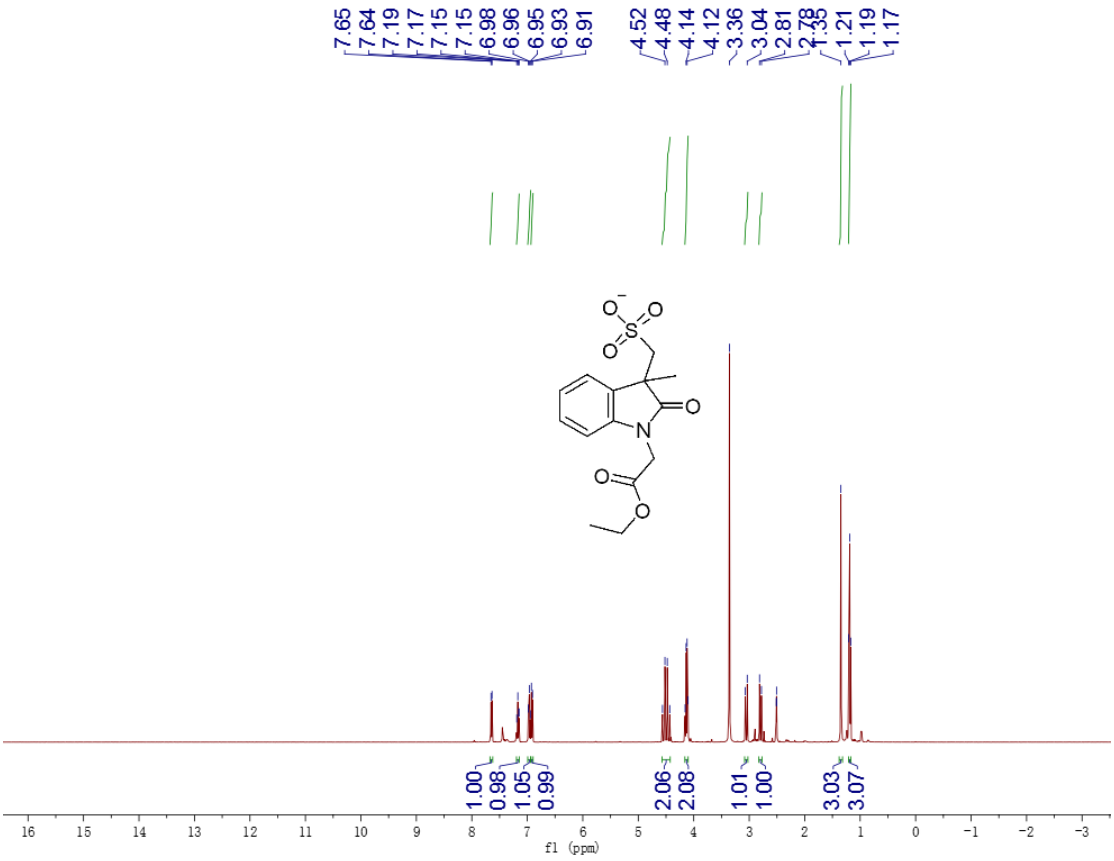
^{1}H NMR spectrum of compound 3p



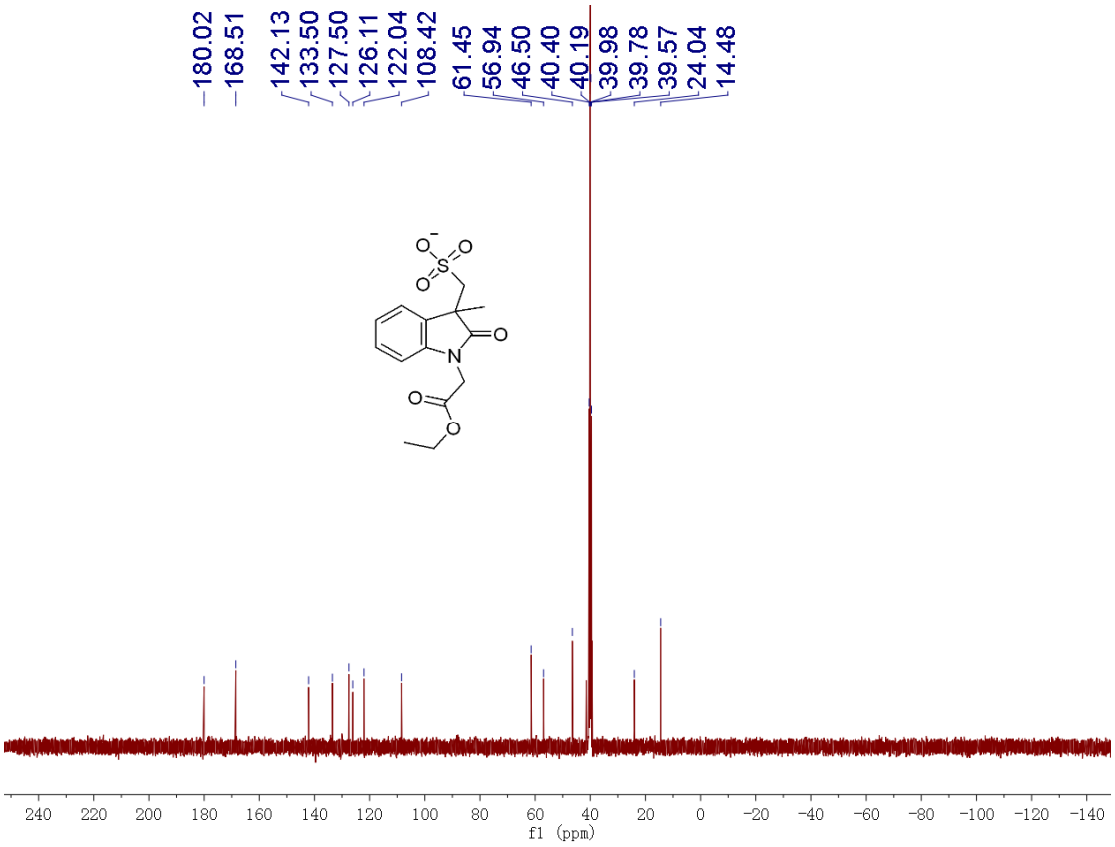
^{13}C NMR spectrum of compound 3p



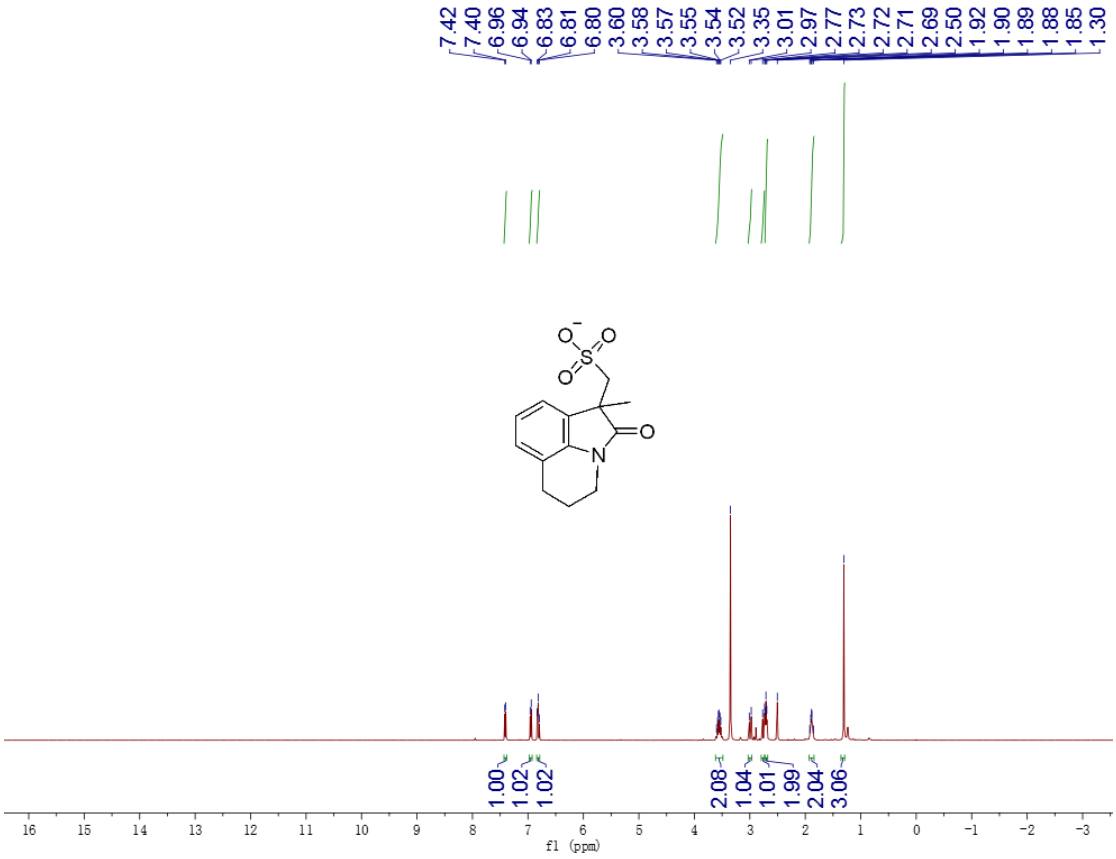
^{1}H NMR spectrum of compound 3q



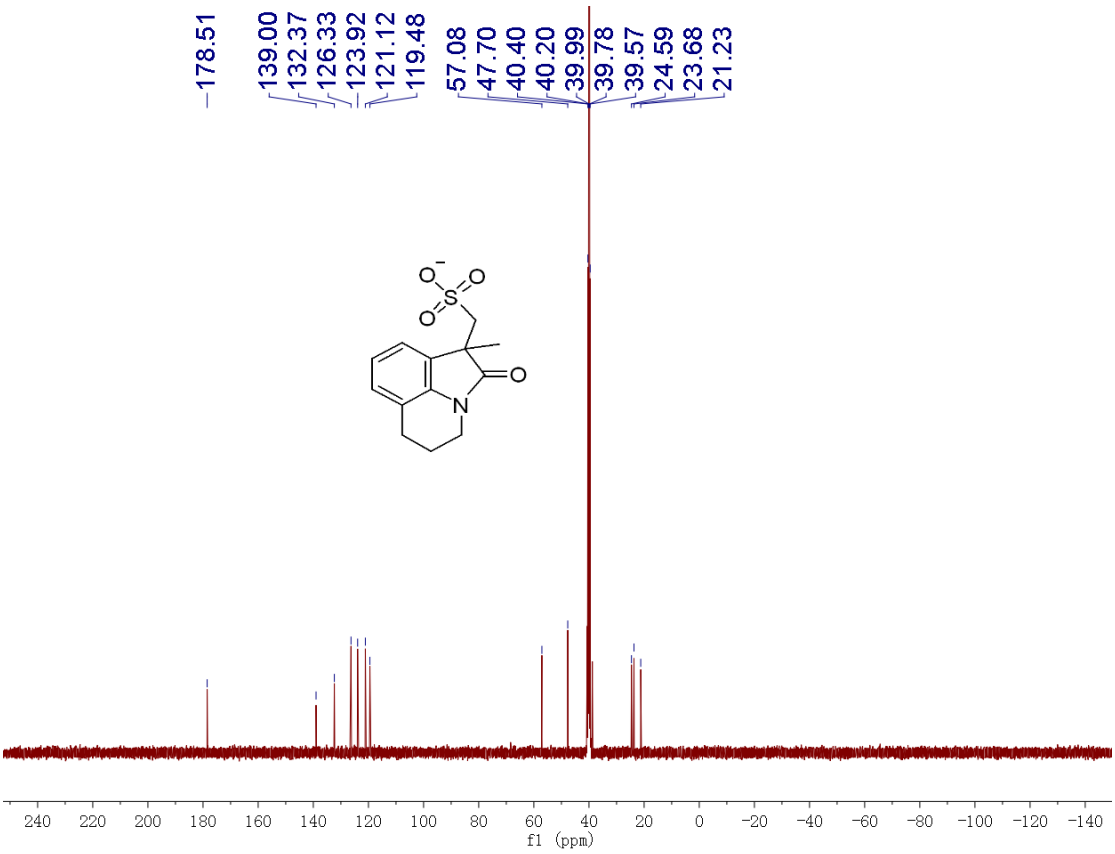
^{13}C NMR spectrum of compound 3q



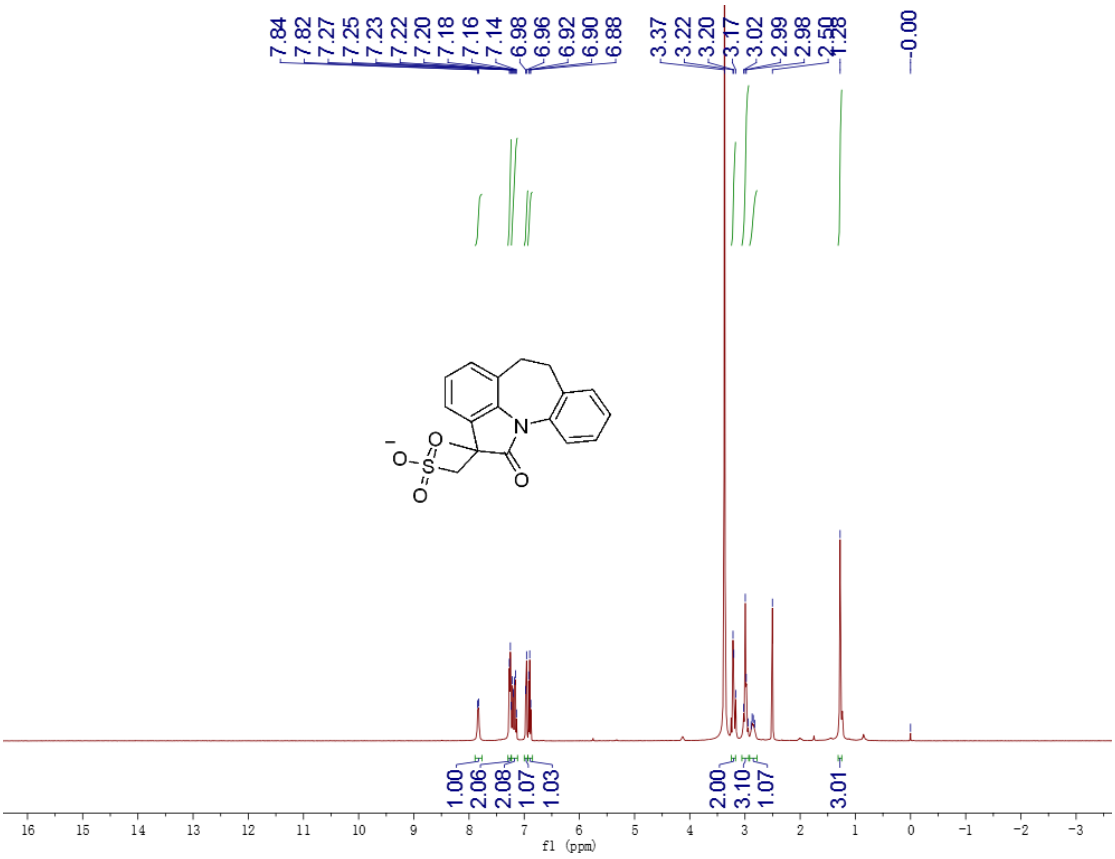
^{1}H NMR spectrum of compound 3r



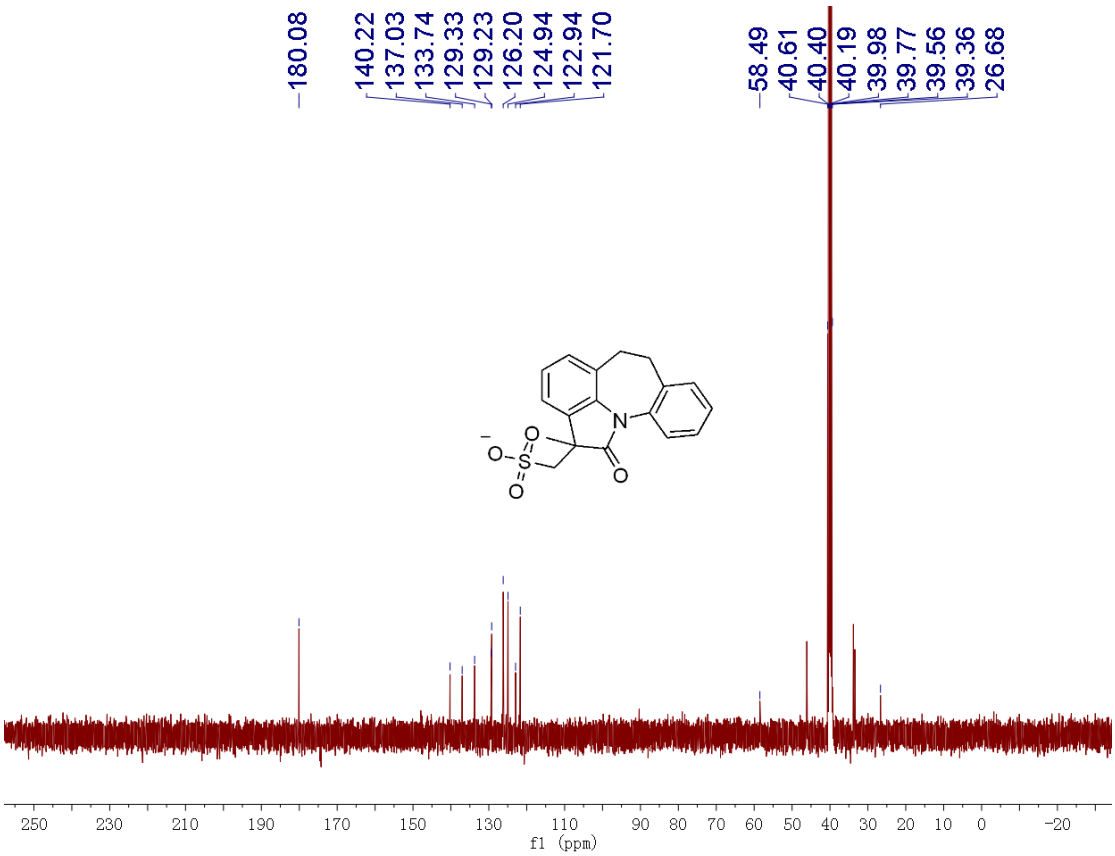
^{13}C NMR spectrum of compound 3r



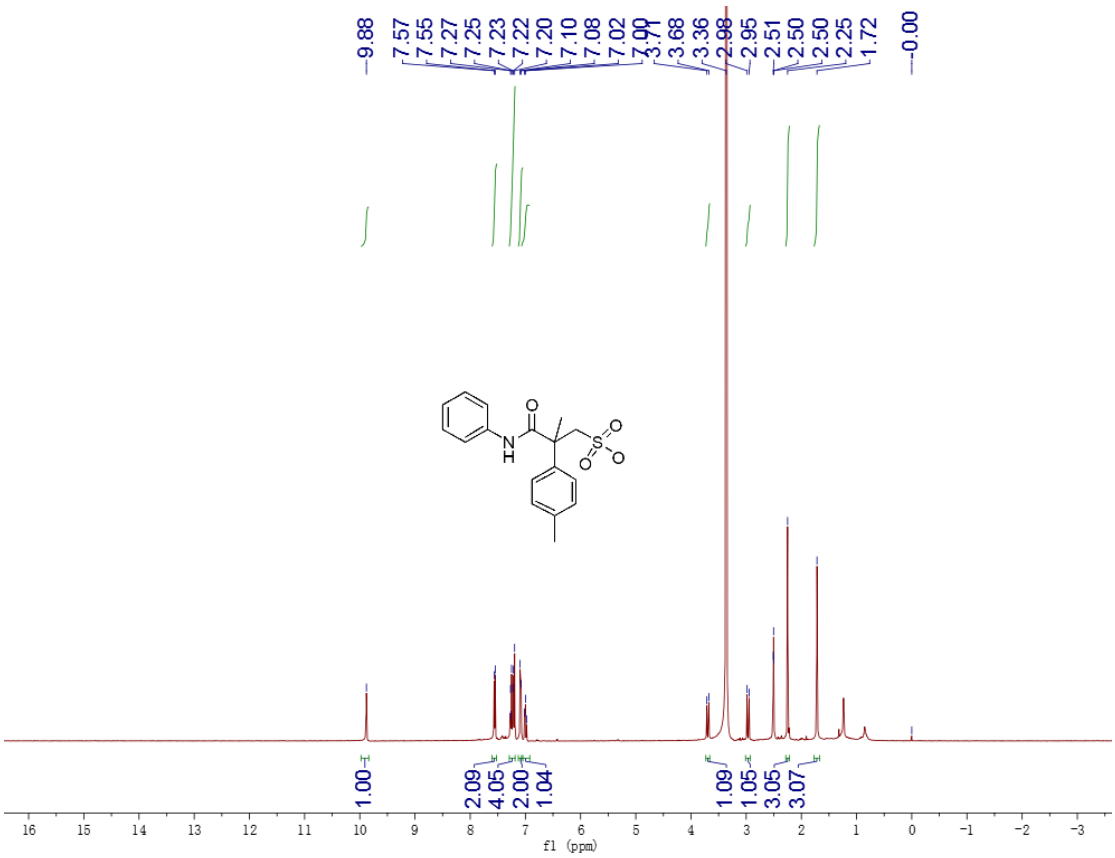
^{1}H NMR spectrum of compound 3s



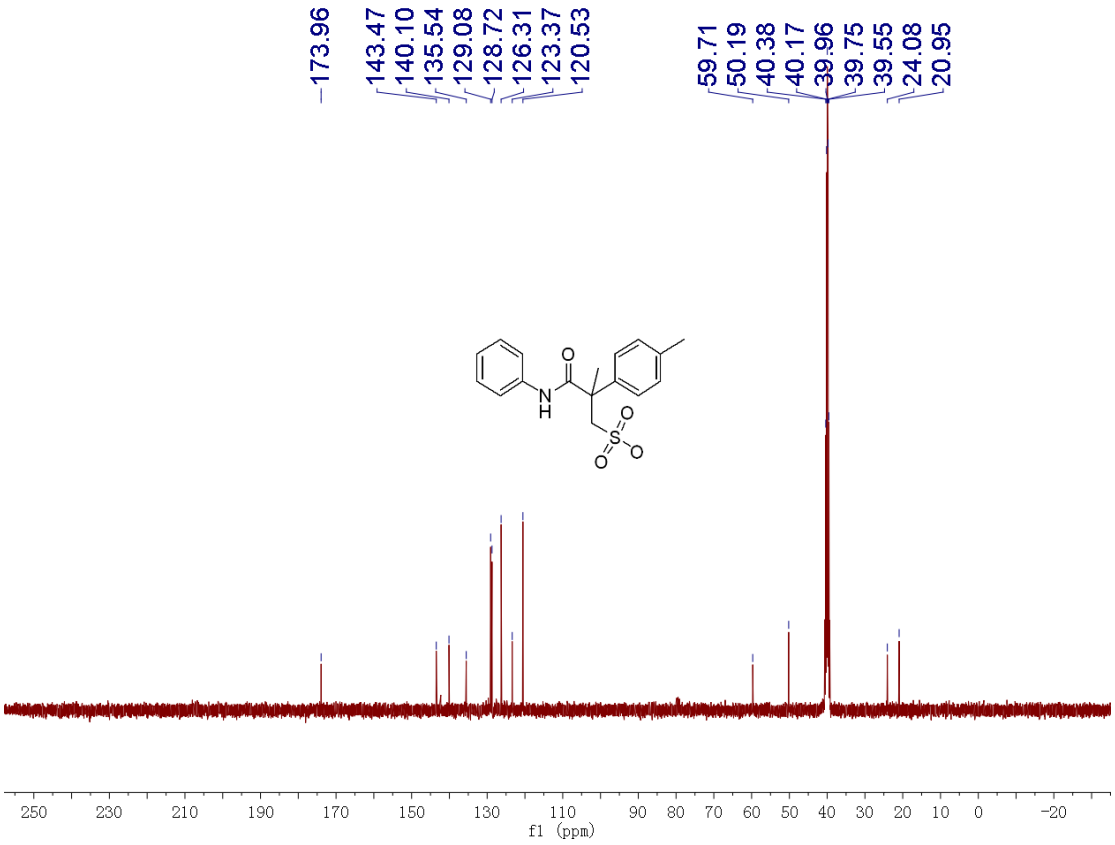
^{13}C NMR spectrum of compound 3s



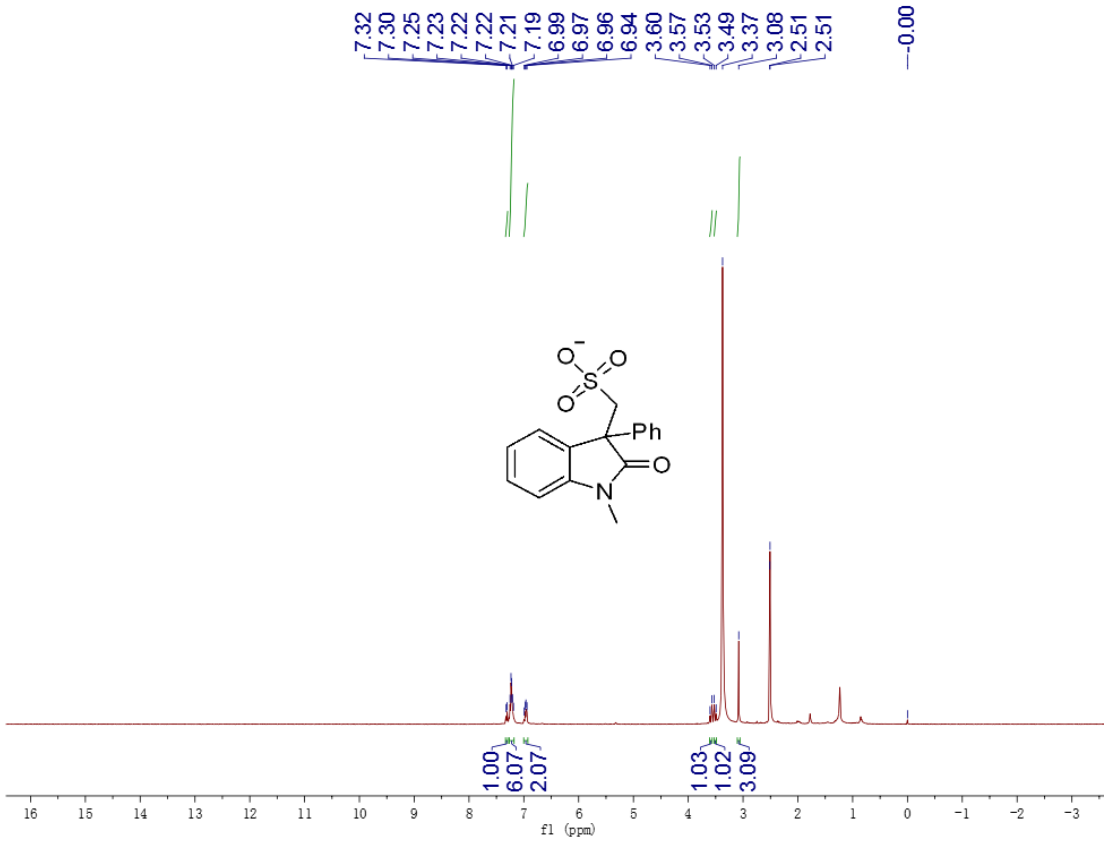
^{1}H NMR spectrum of compound 3t



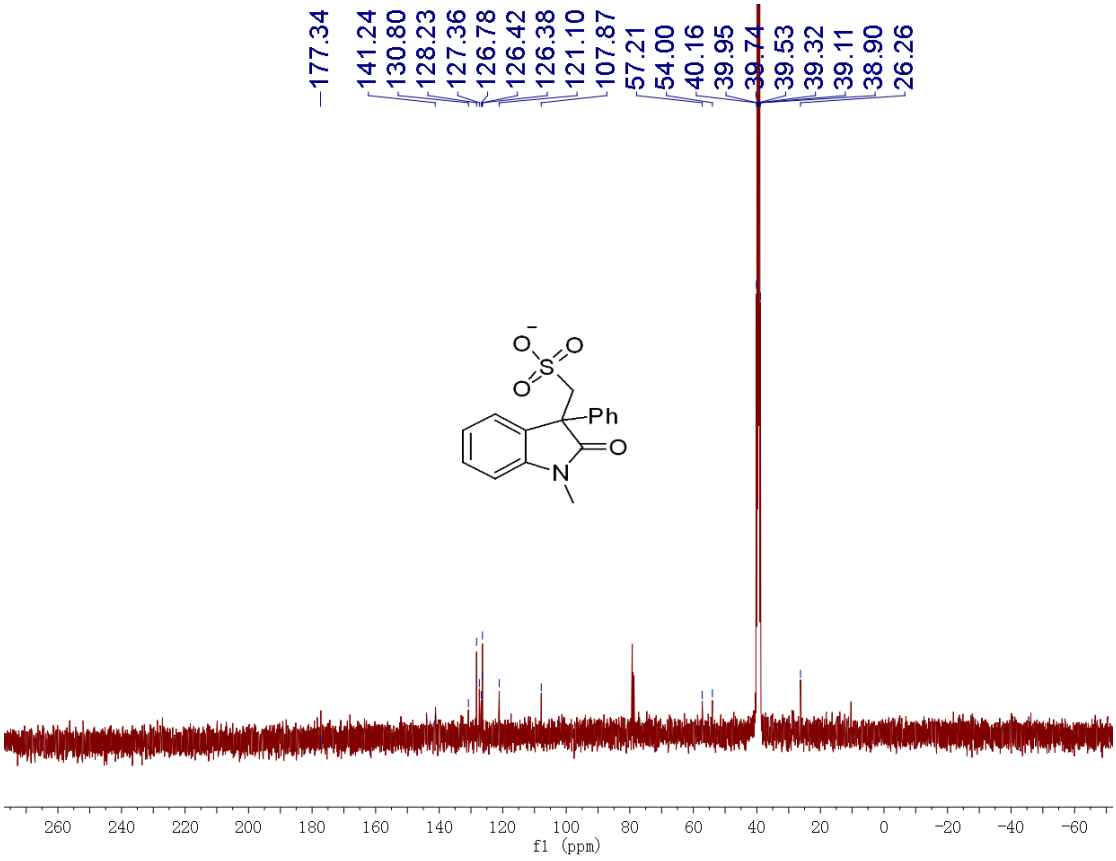
^{13}C NMR spectrum of compound 3t



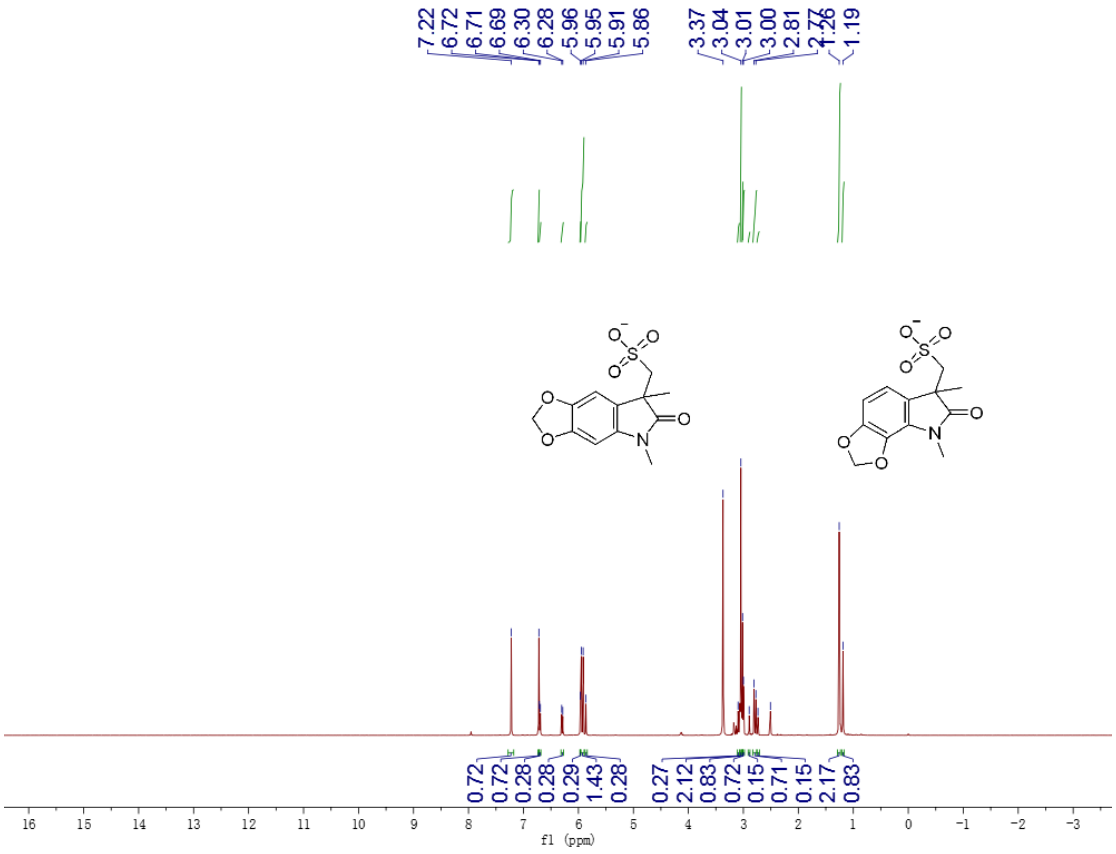
^{1}H NMR spectrum of compound 3u



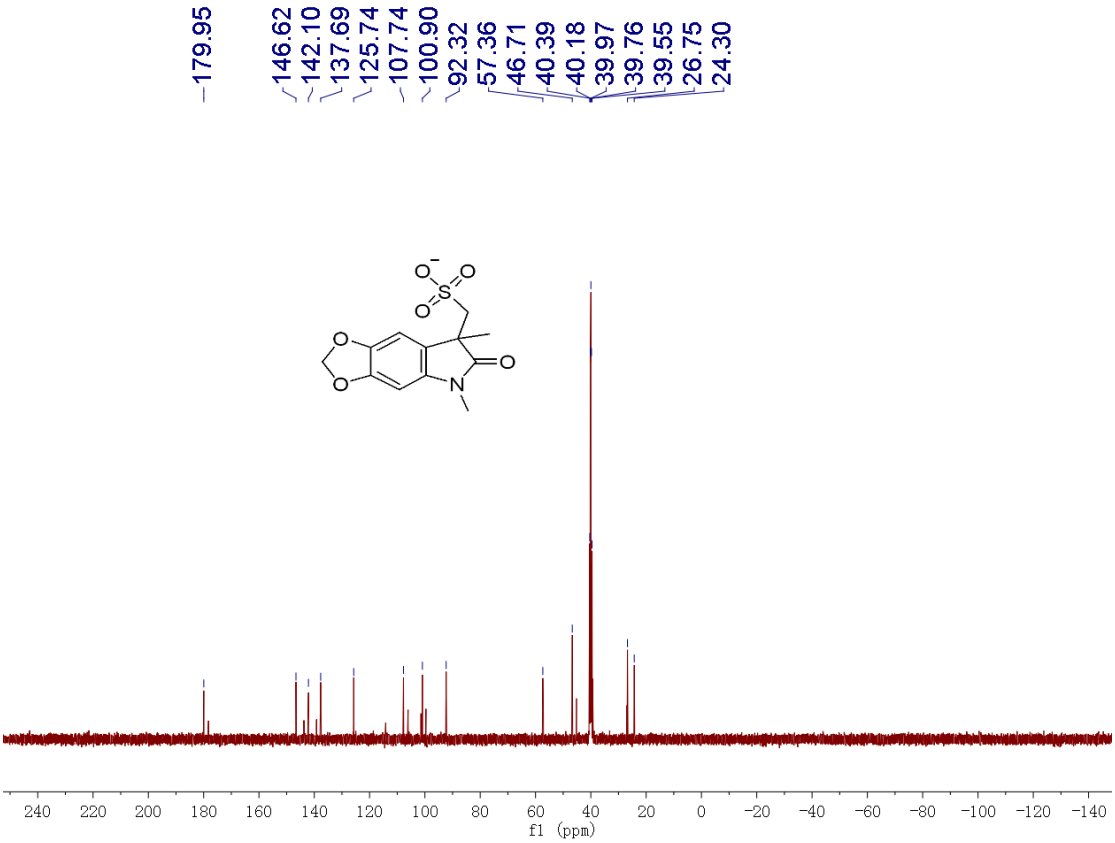
^{13}C NMR spectrum of compound 3u



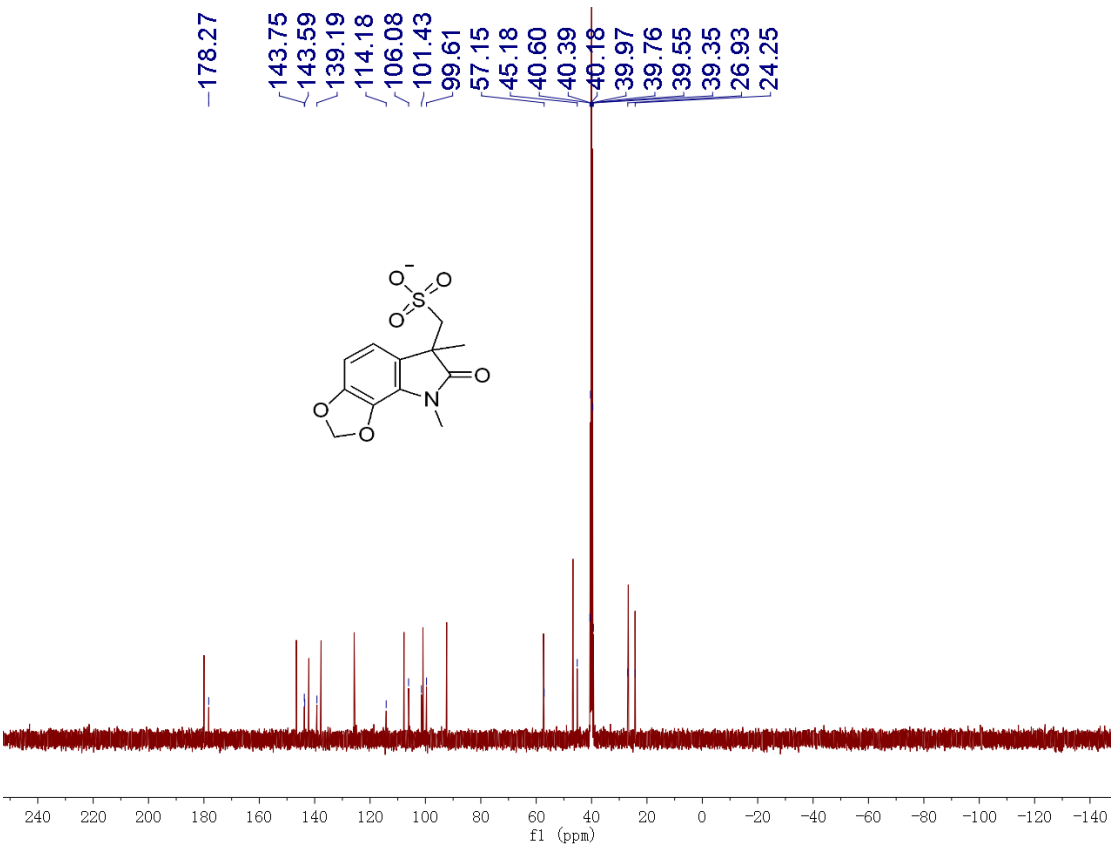
^{1}H NMR spectrum of compound 3v and 3v'



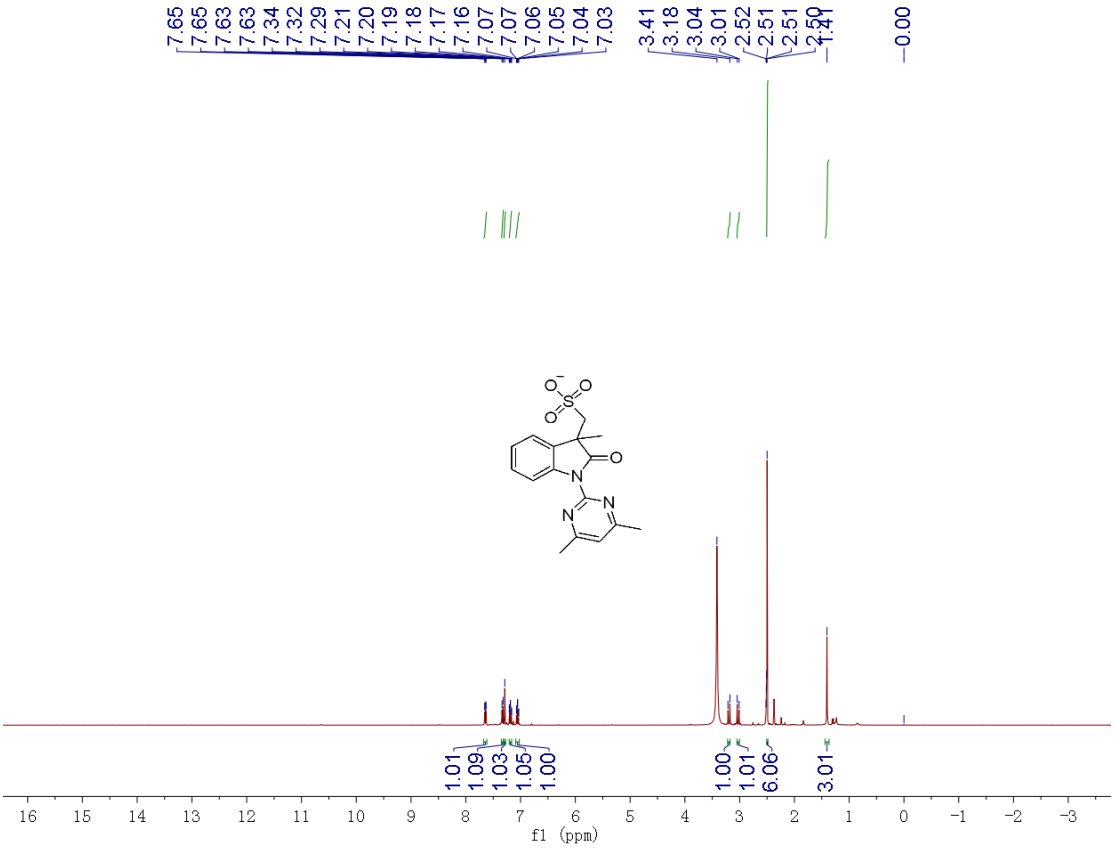
^{13}C NMR spectrum of compound 3v



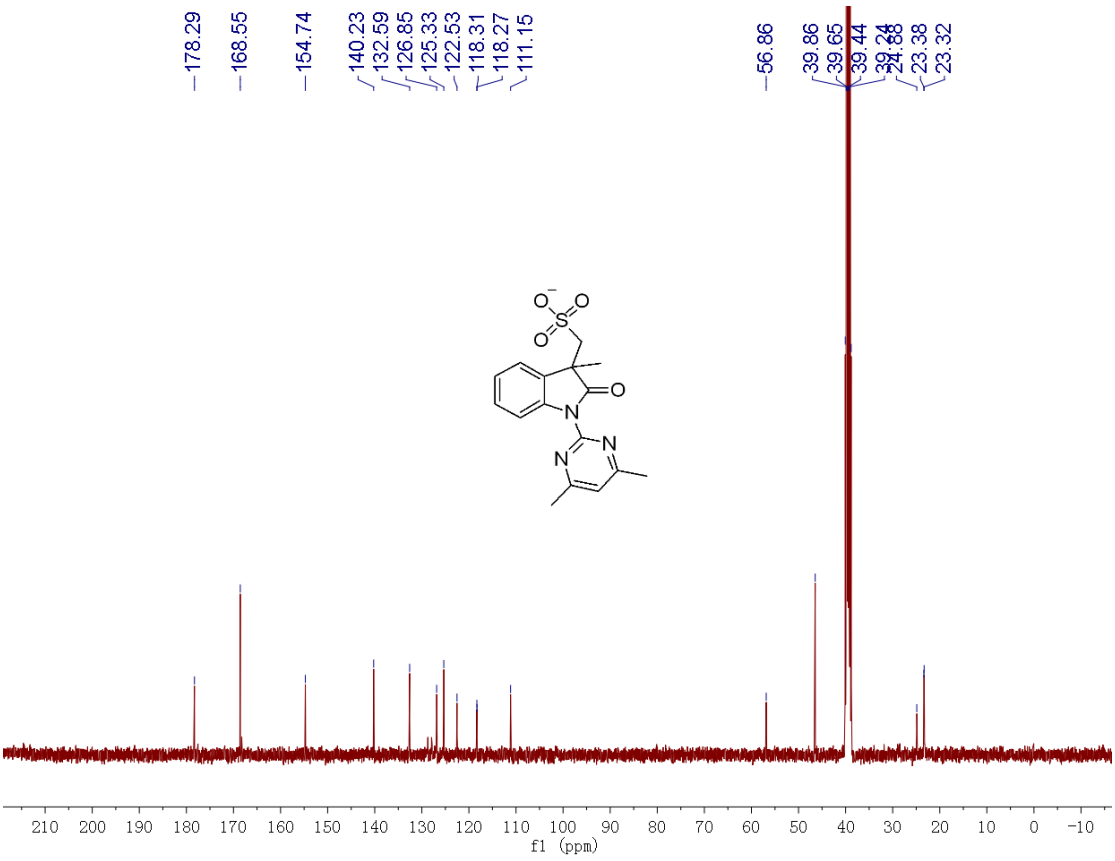
^{13}C NMR spectrum of compound 3v'



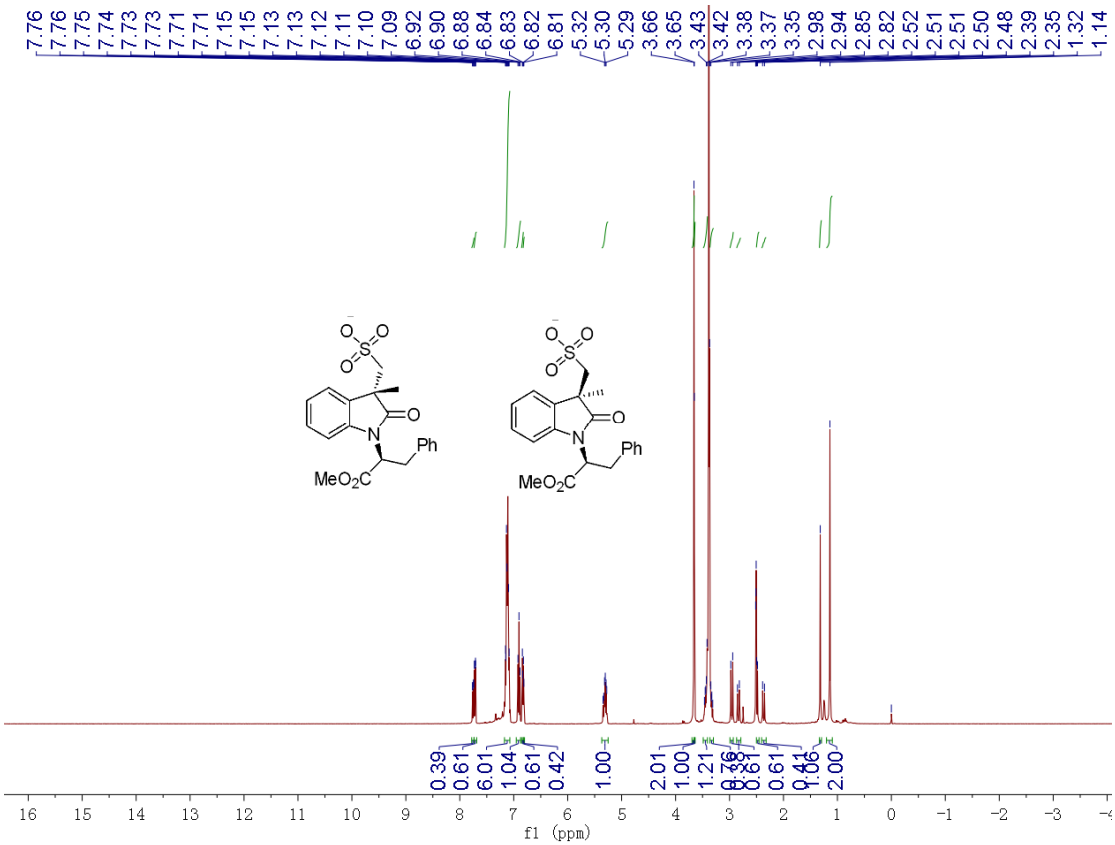
^{1}H NMR spectrum of compound 3w



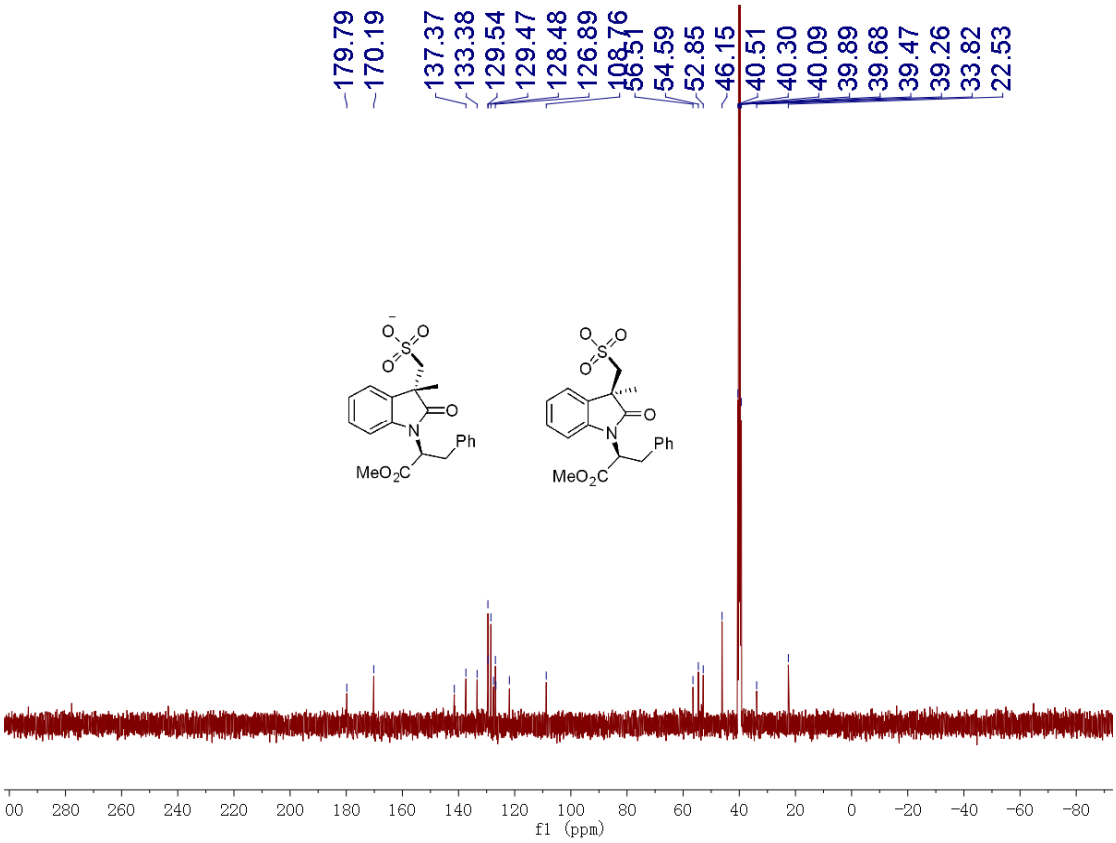
^{13}C NMR spectrum of compound 3w



^{1}H NMR spectrum of compound 3x

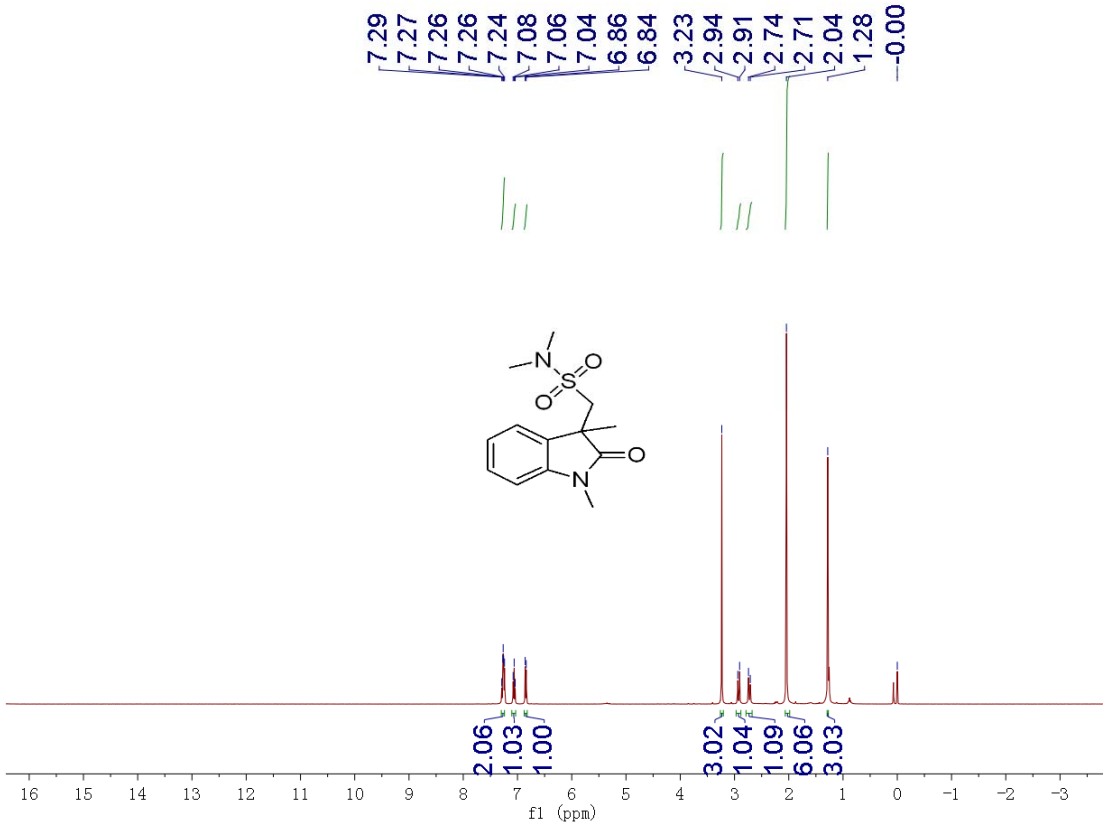


^{13}C NMR spectrum of compound 3x

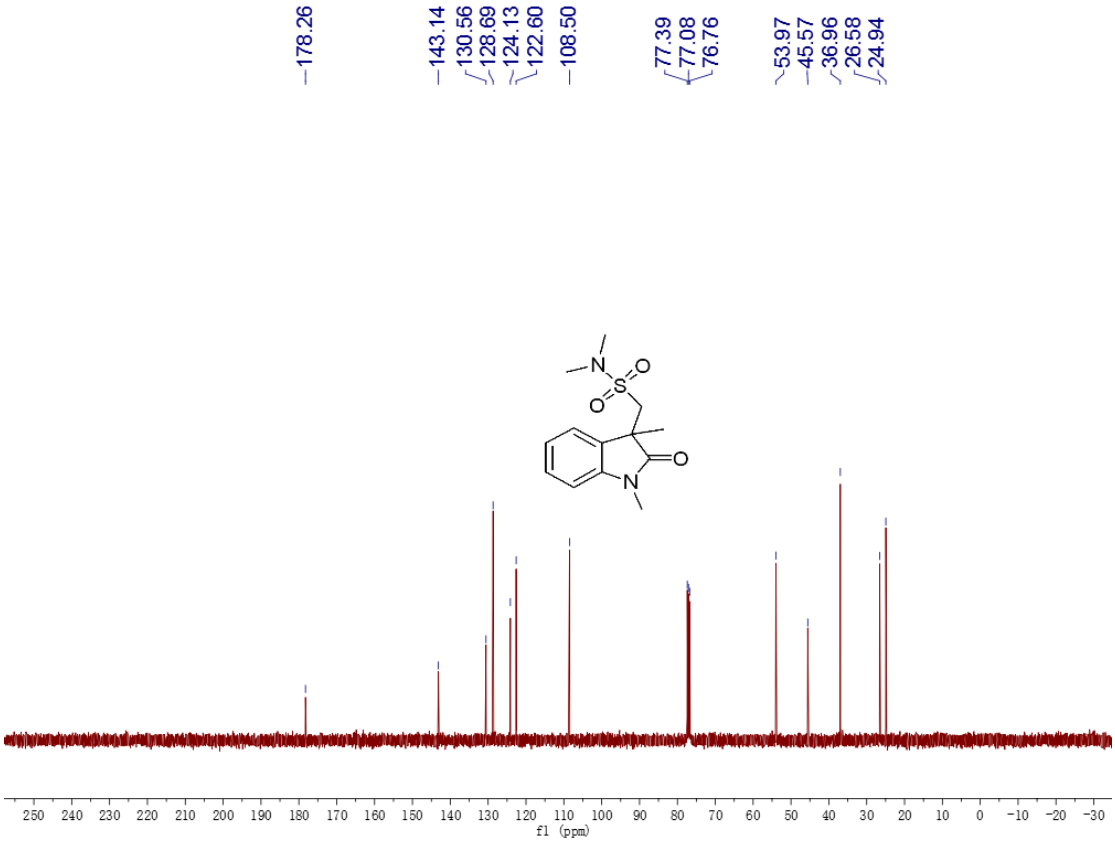


11. ^{1}H NMR and ^{13}C NMR spectrum of Alkylsulfonamide Products

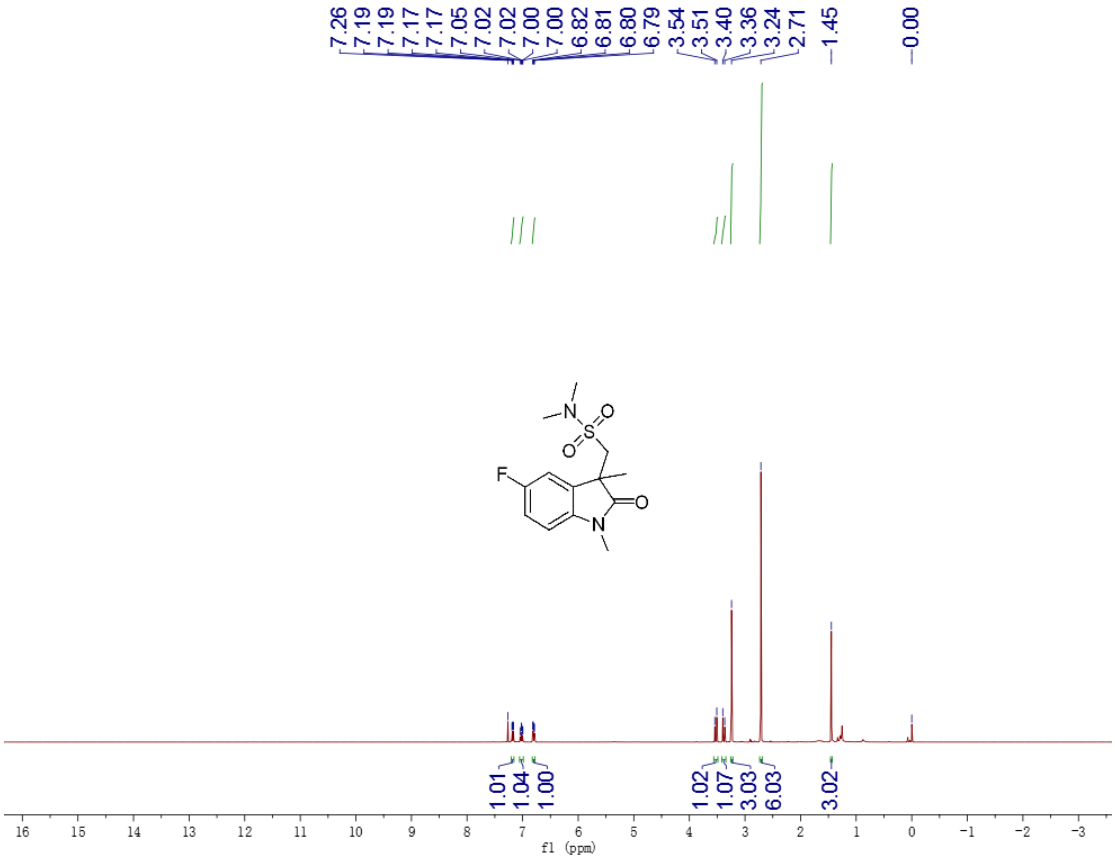
^{1}H NMR spectrum of compound 4a



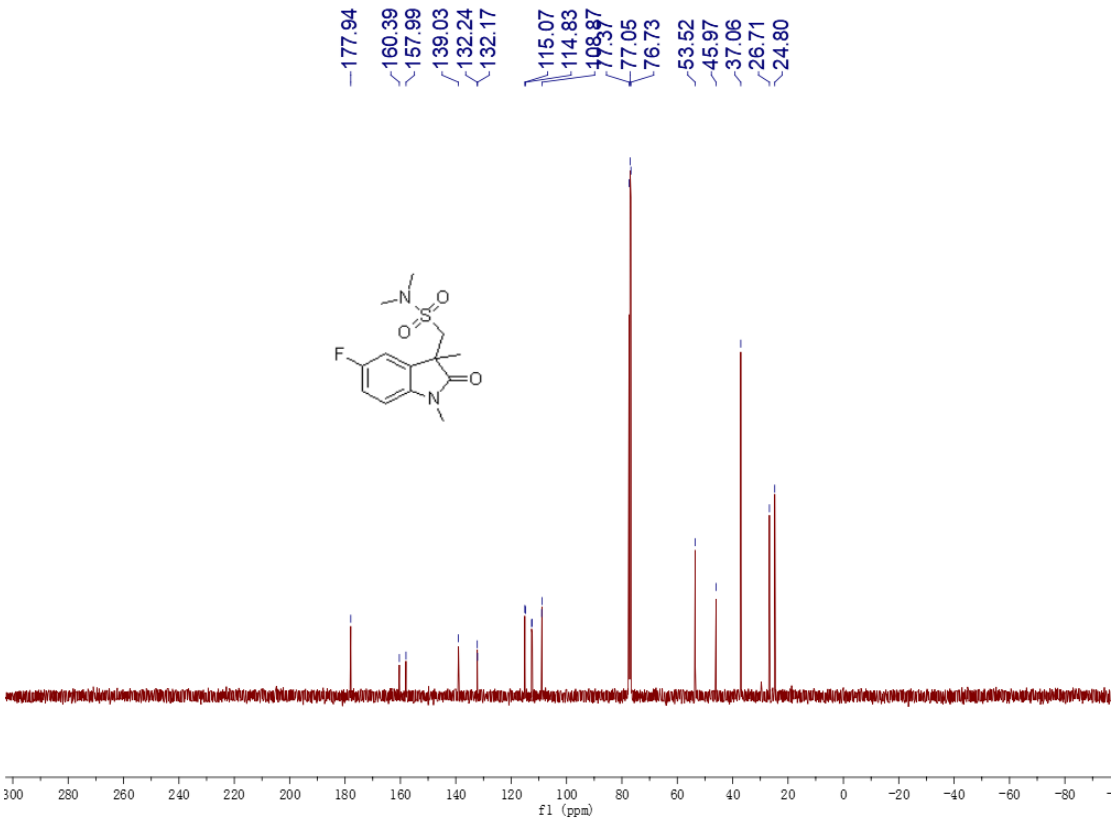
^{13}C NMR spectrum of compound 4a



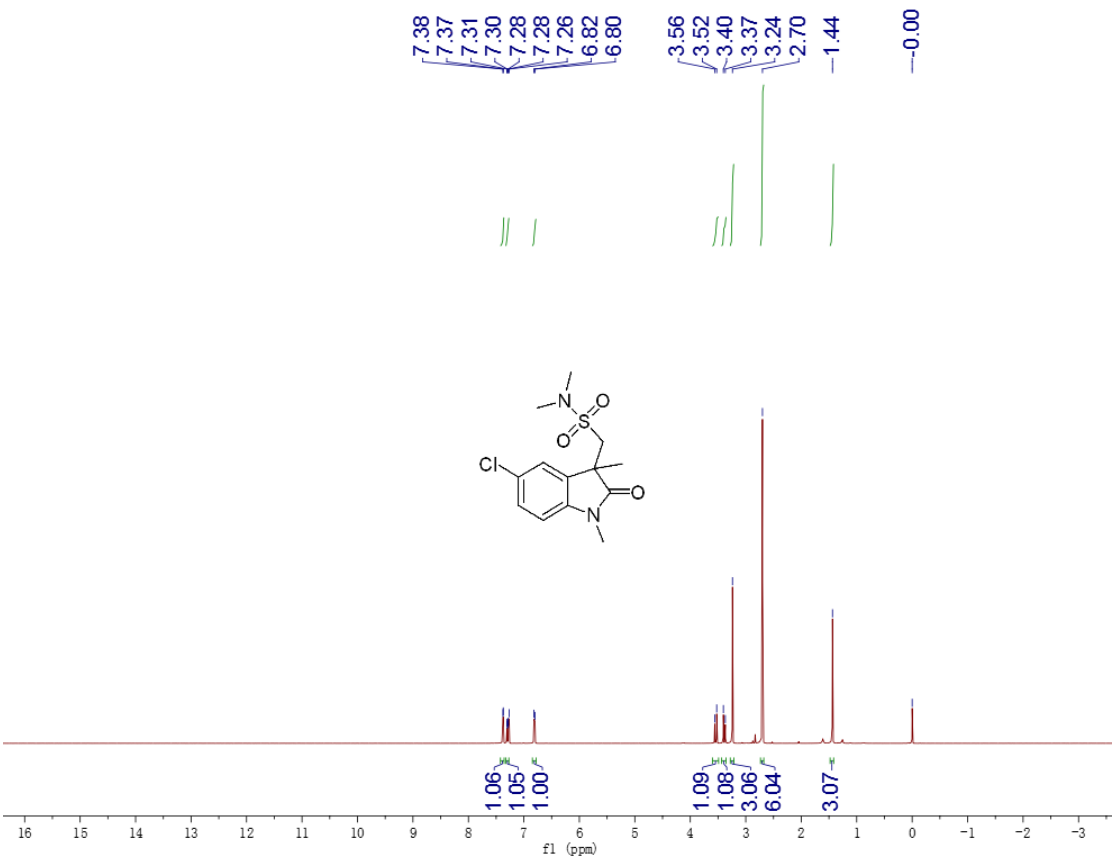
^{1}H NMR spectrum of compound 4b



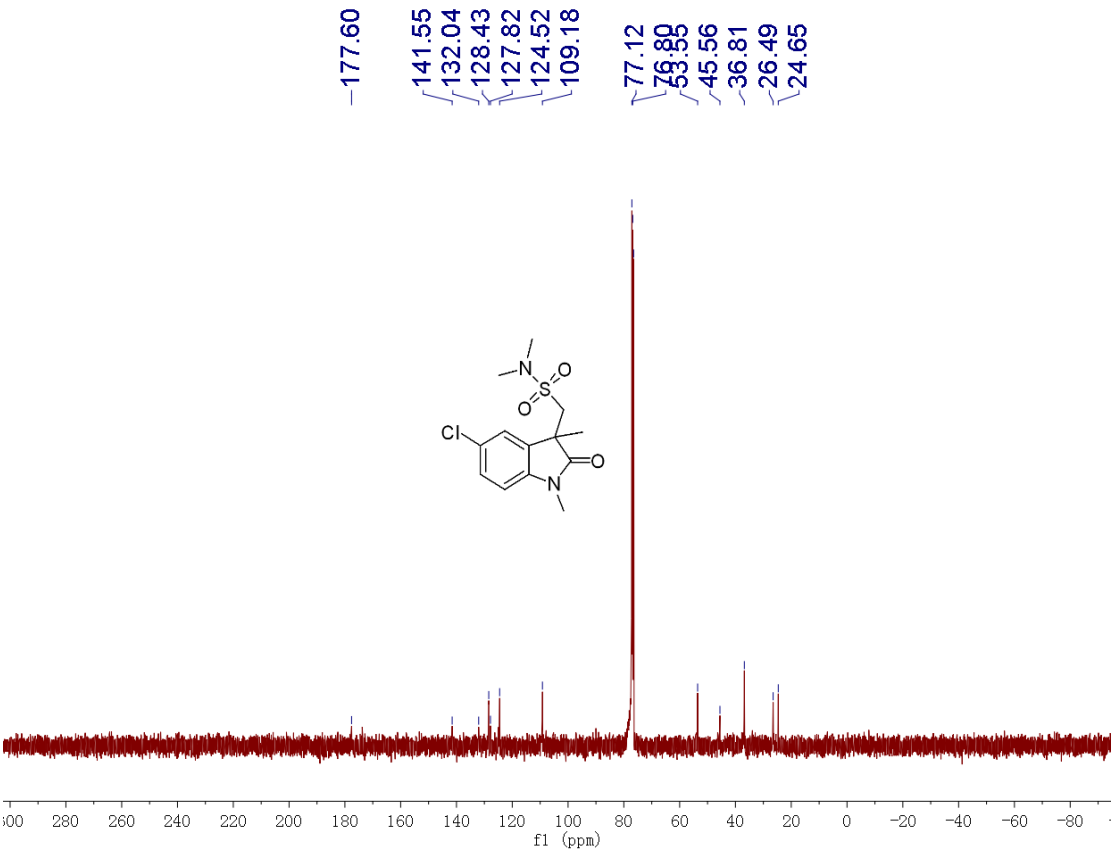
^{13}C NMR spectrum of compound 4b



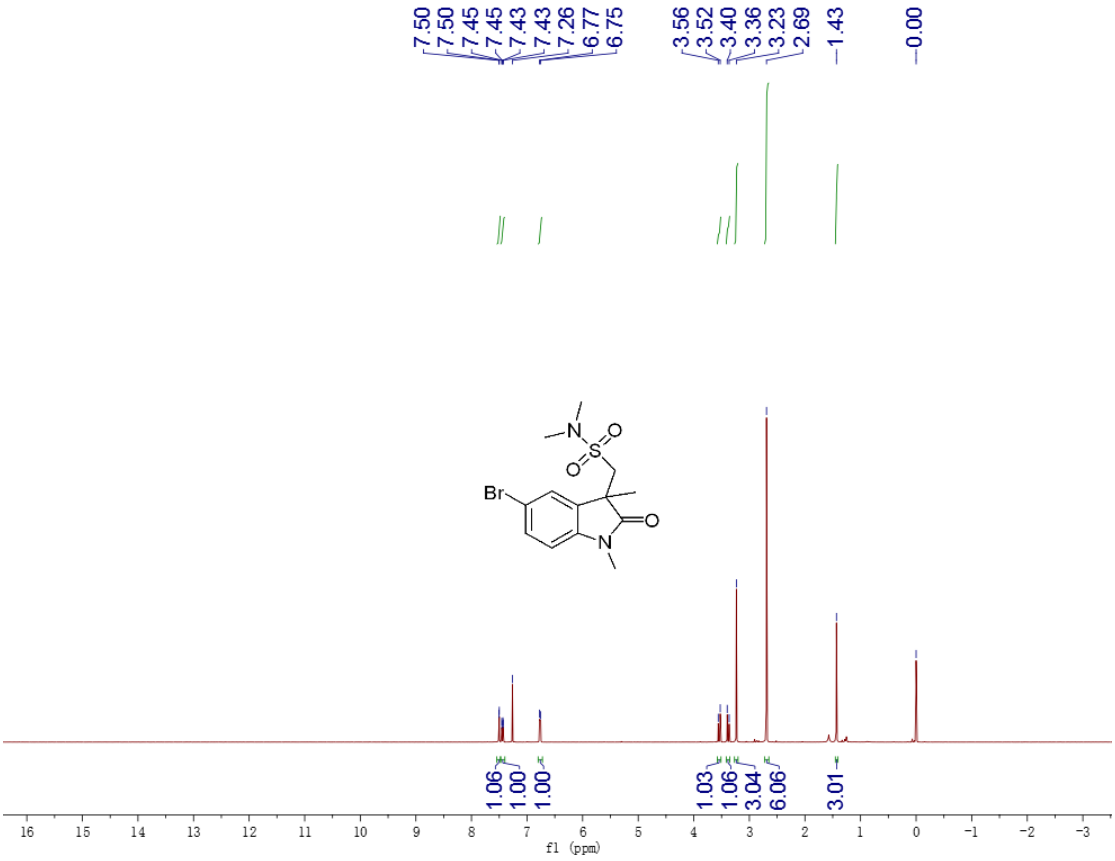
^{1}H NMR spectrum of compound 4c



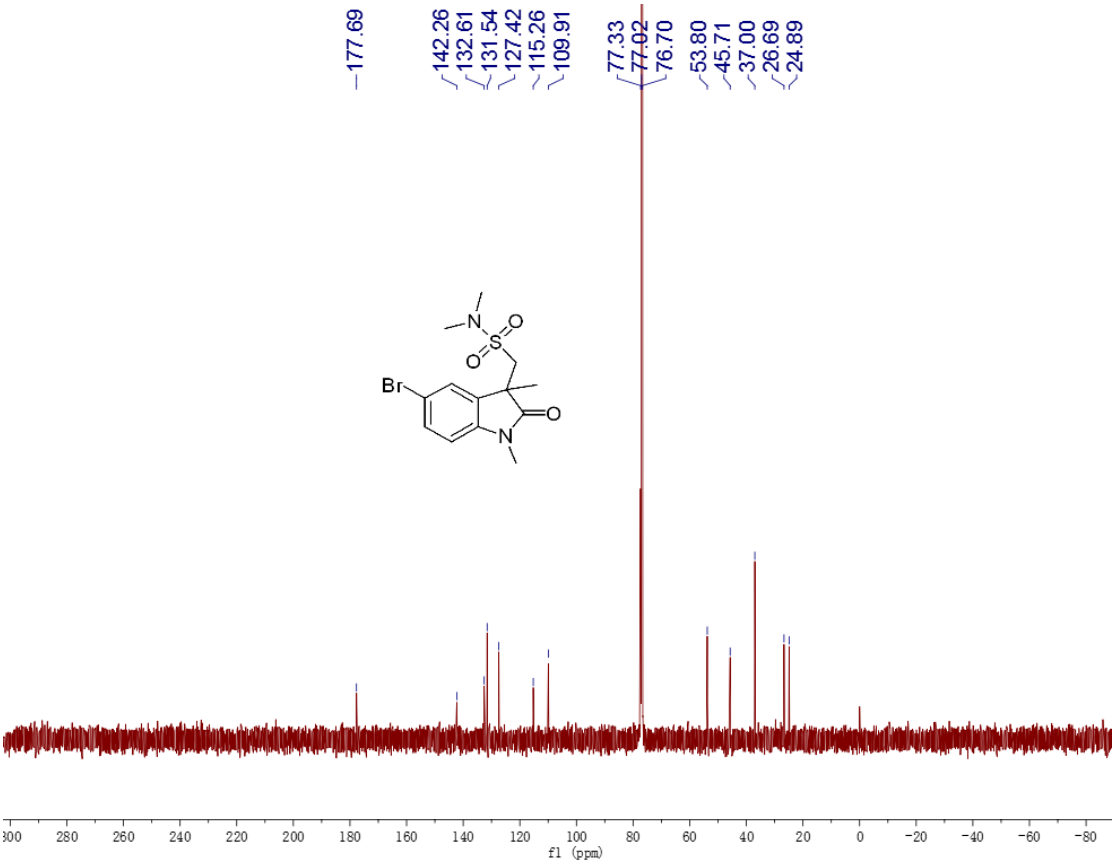
^{13}C NMR spectrum of compound 4c



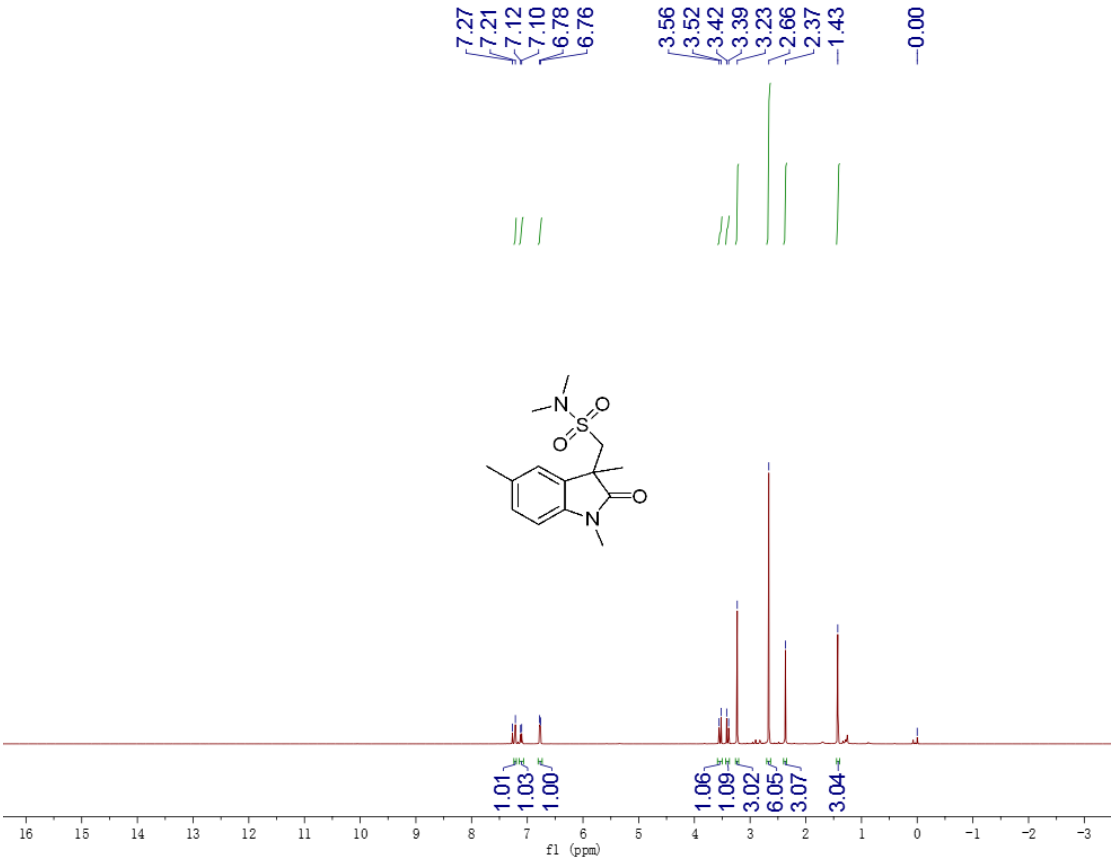
^{1}H NMR spectrum of compound 4d



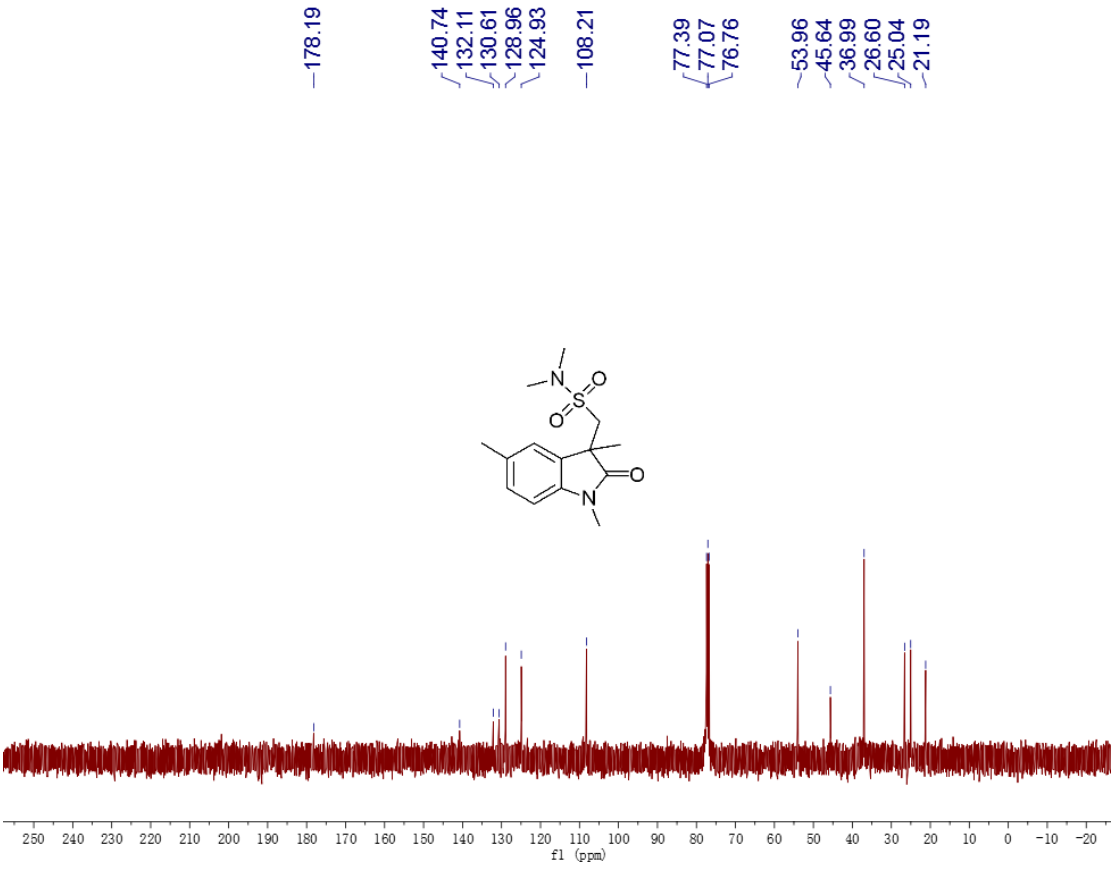
^{13}C NMR spectrum of compound 4d



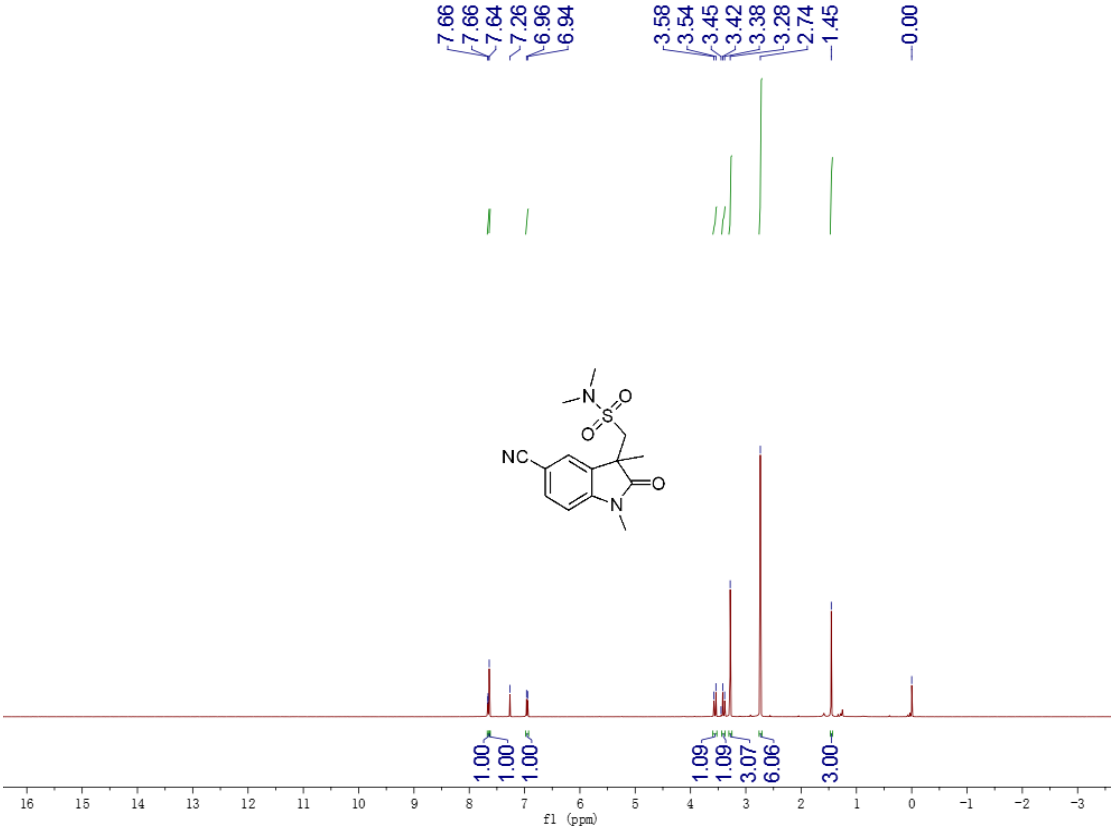
^{1}H NMR spectrum of compound 4e



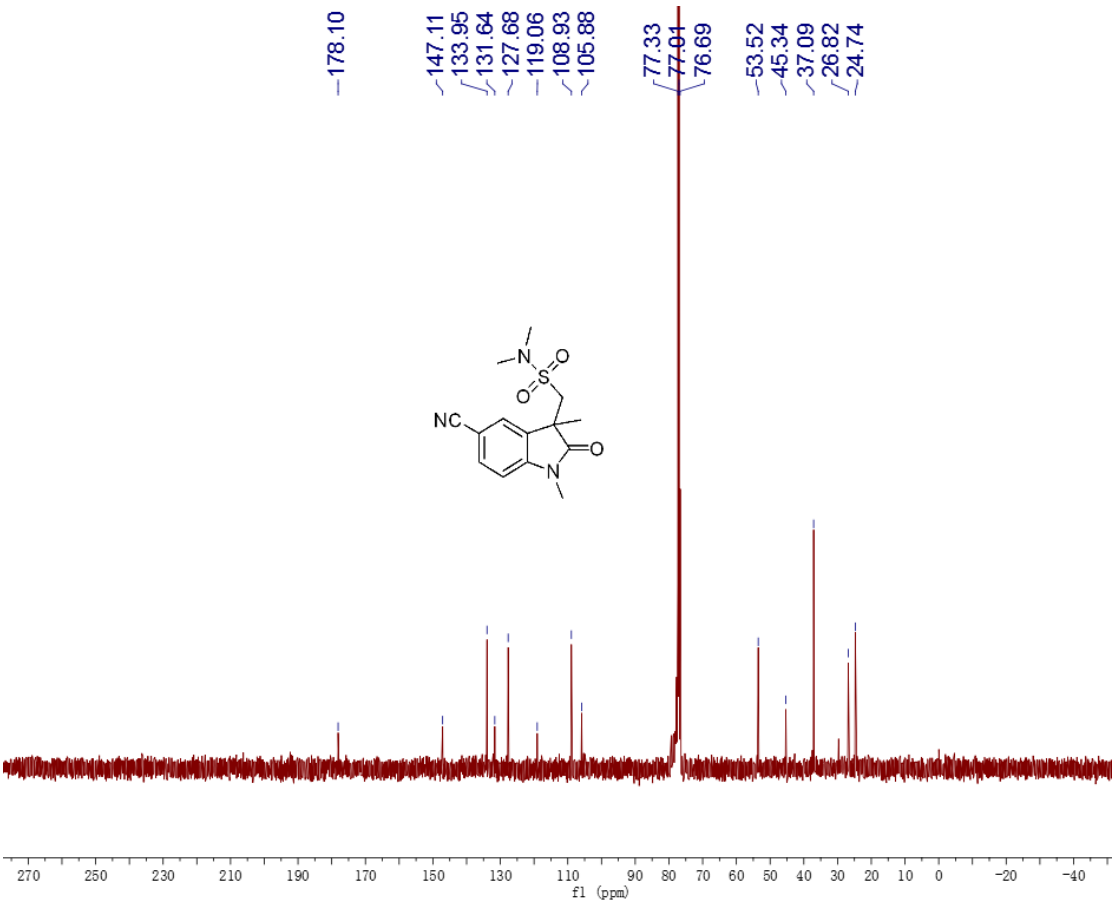
^{13}C NMR spectrum of compound 4e



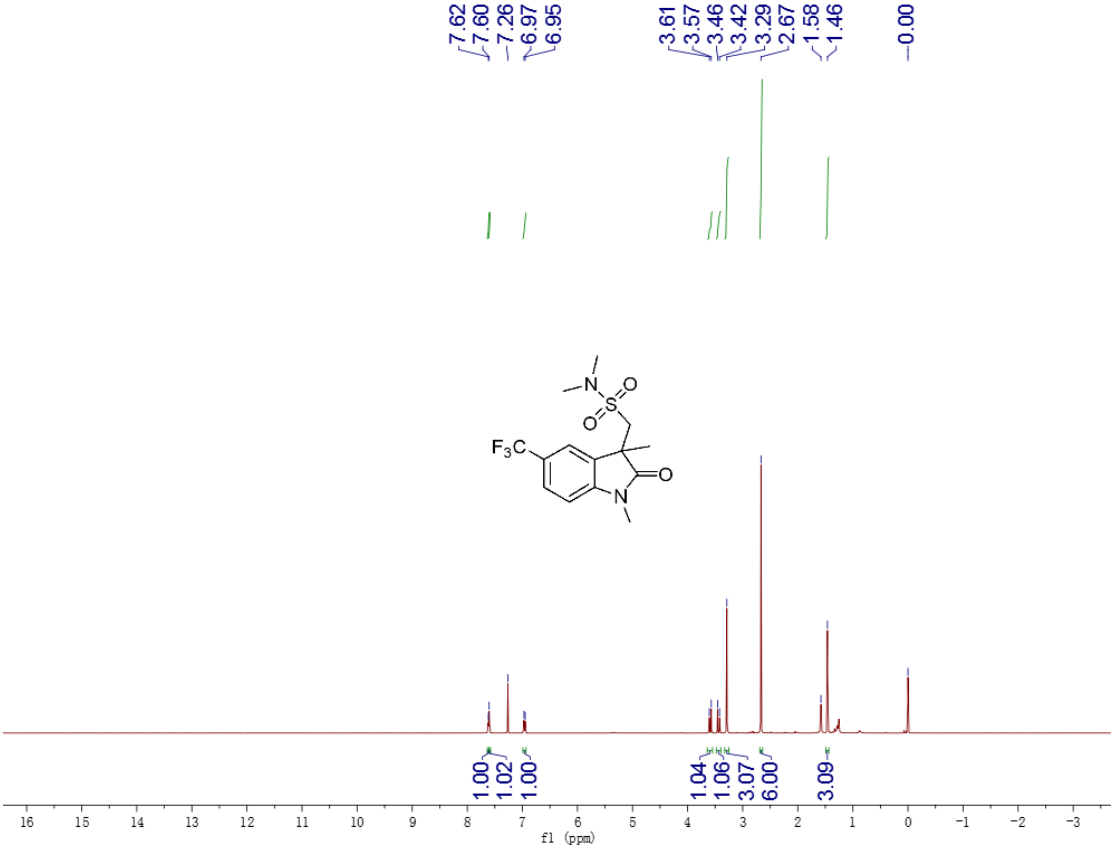
^{1}H NMR spectrum of compound 4f



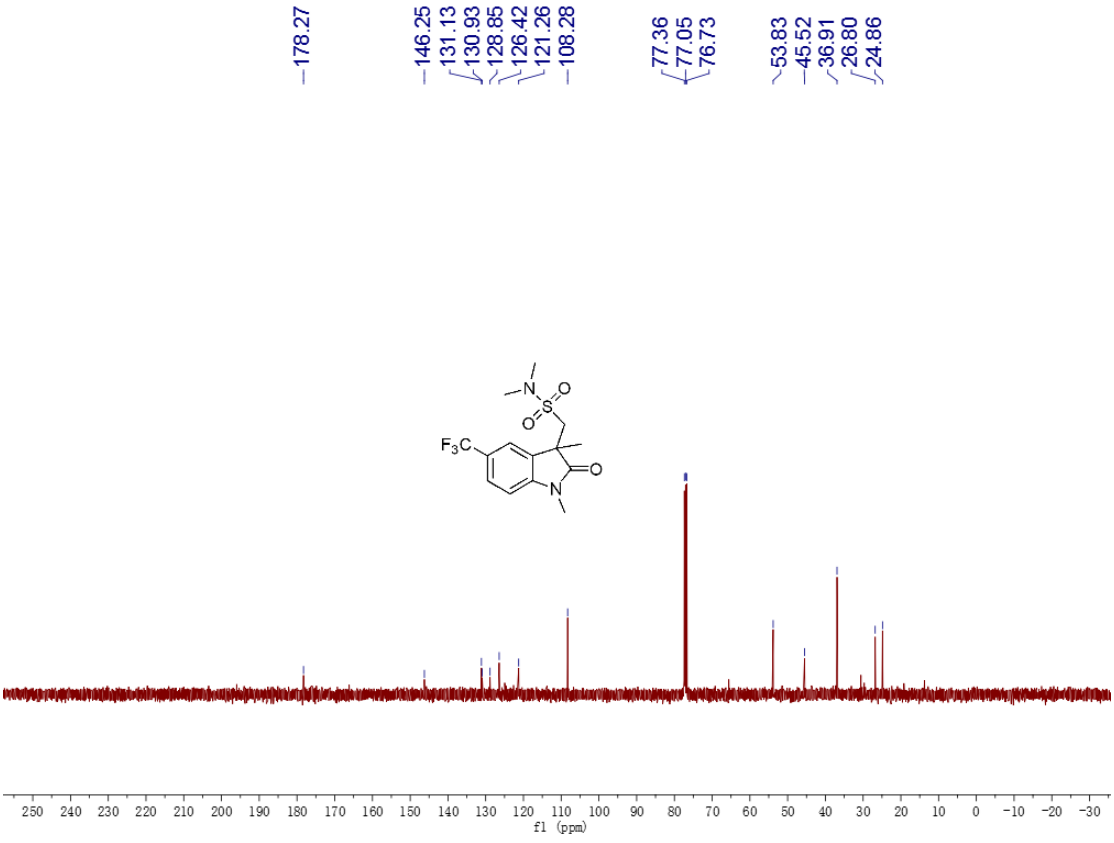
^{13}C NMR spectrum of compound 4f



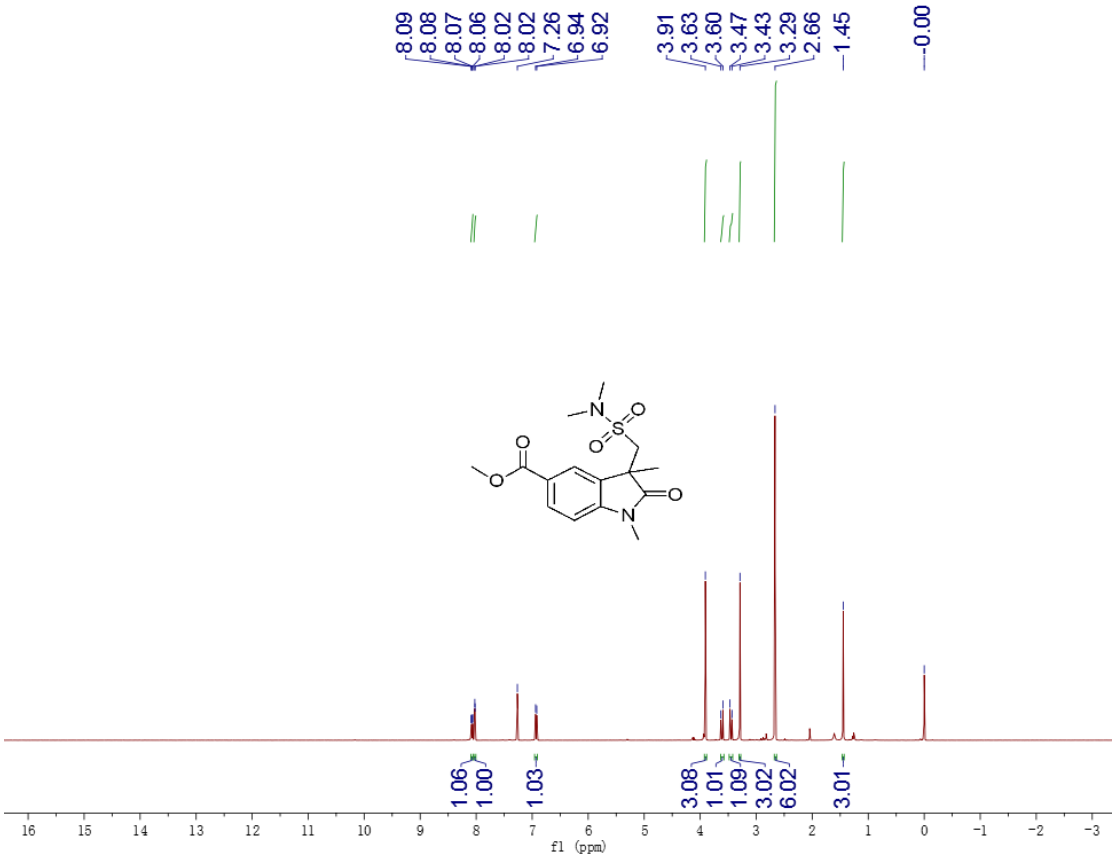
^{1}H NMR spectrum of compound 4g



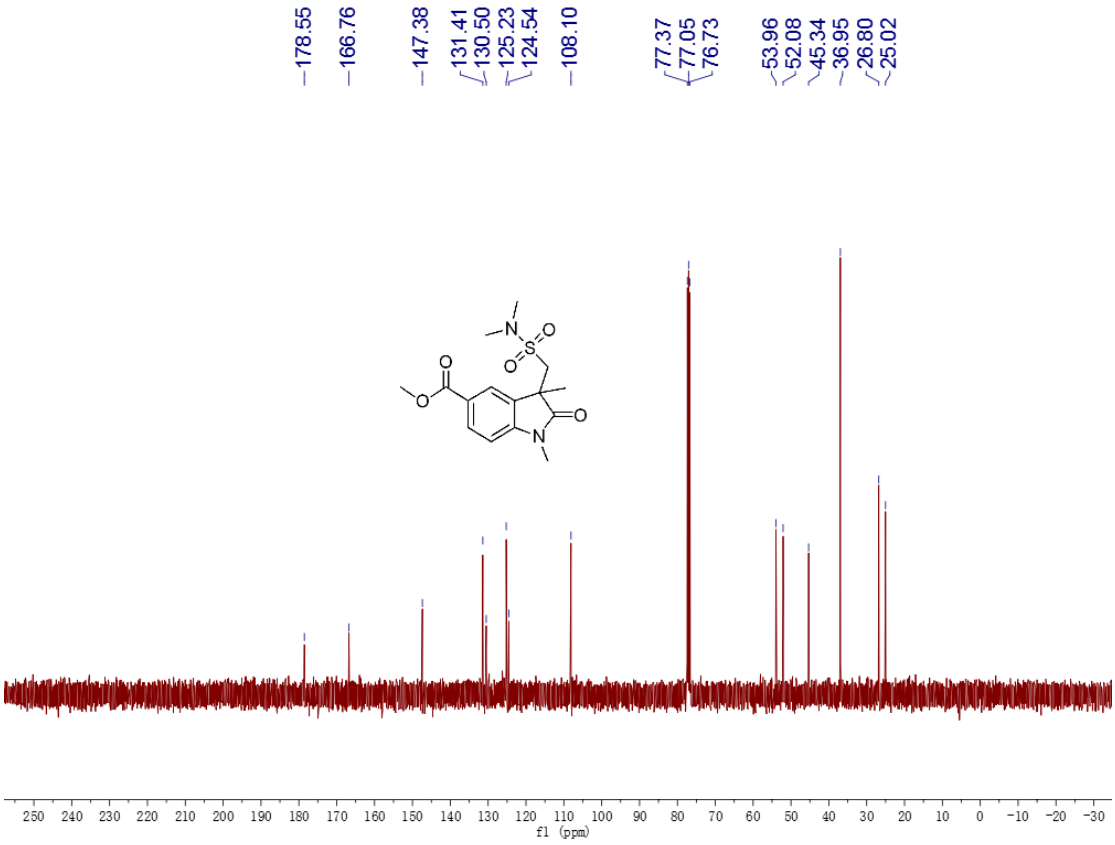
^{13}C NMR spectrum of compound 4g



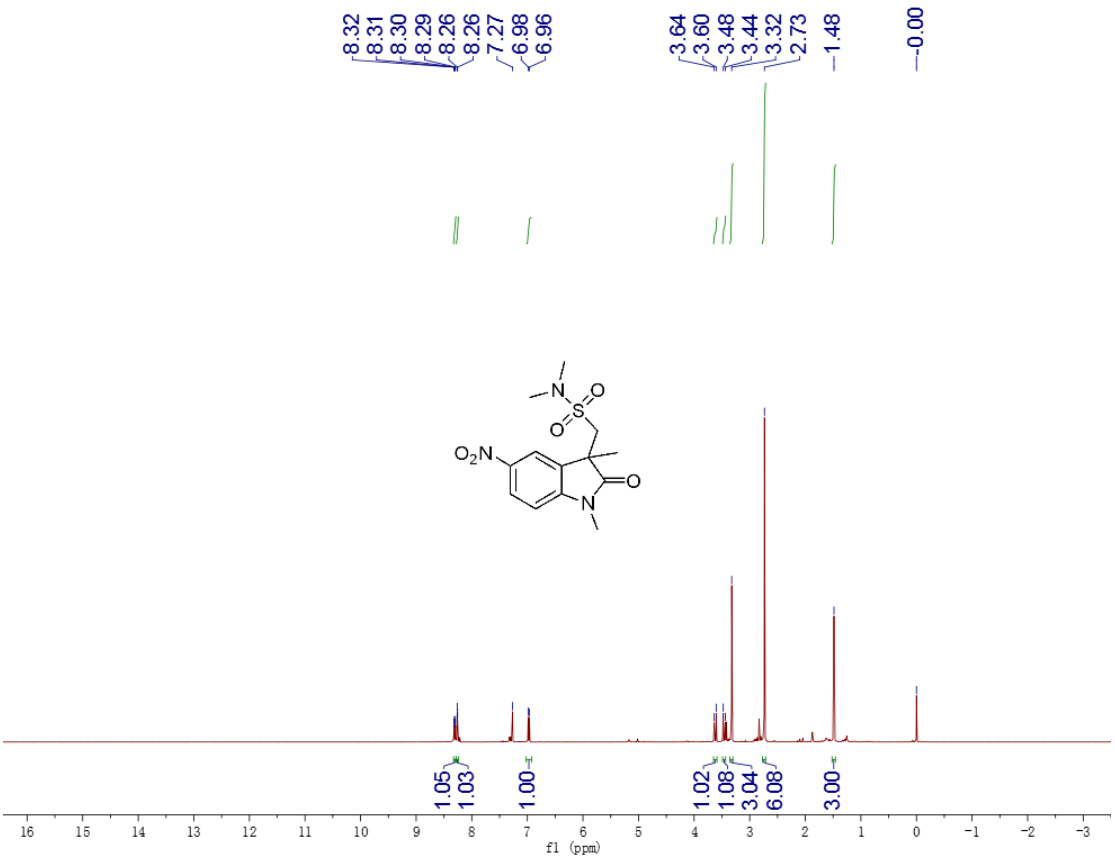
^{1}H NMR spectrum of compound 4h



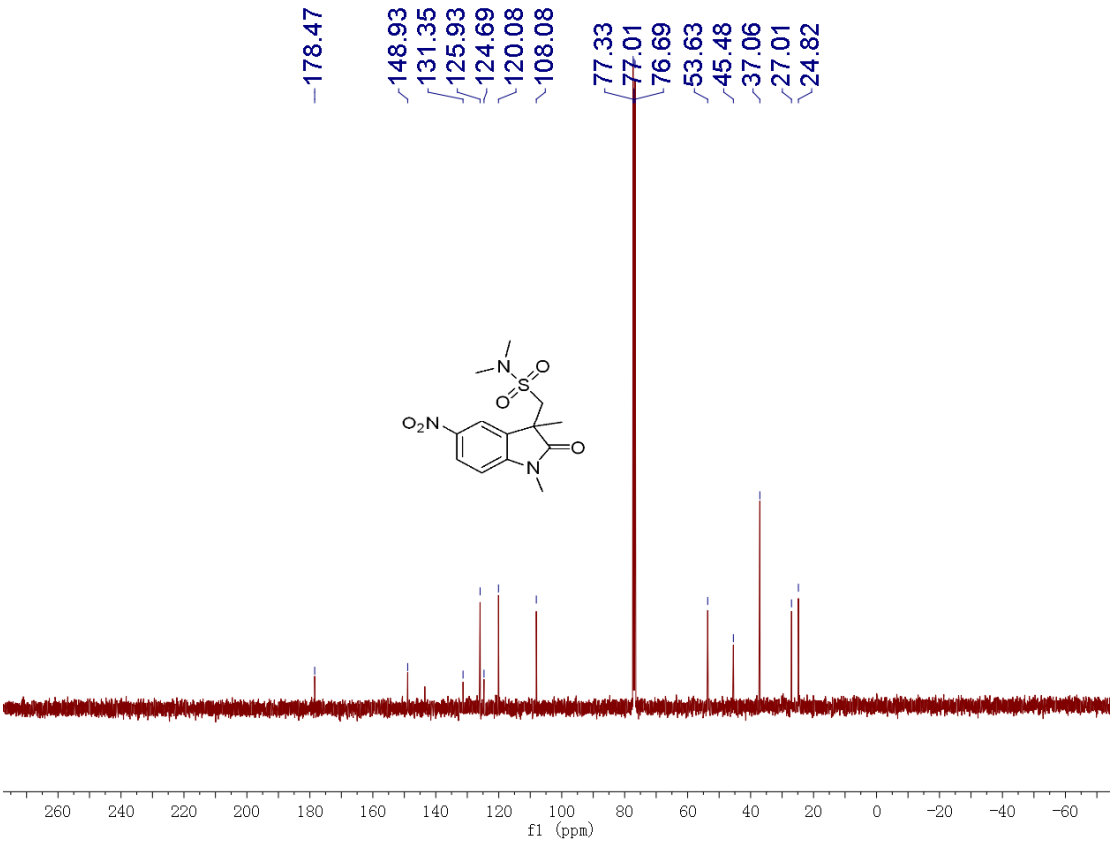
^{13}C NMR spectrum of compound 4h



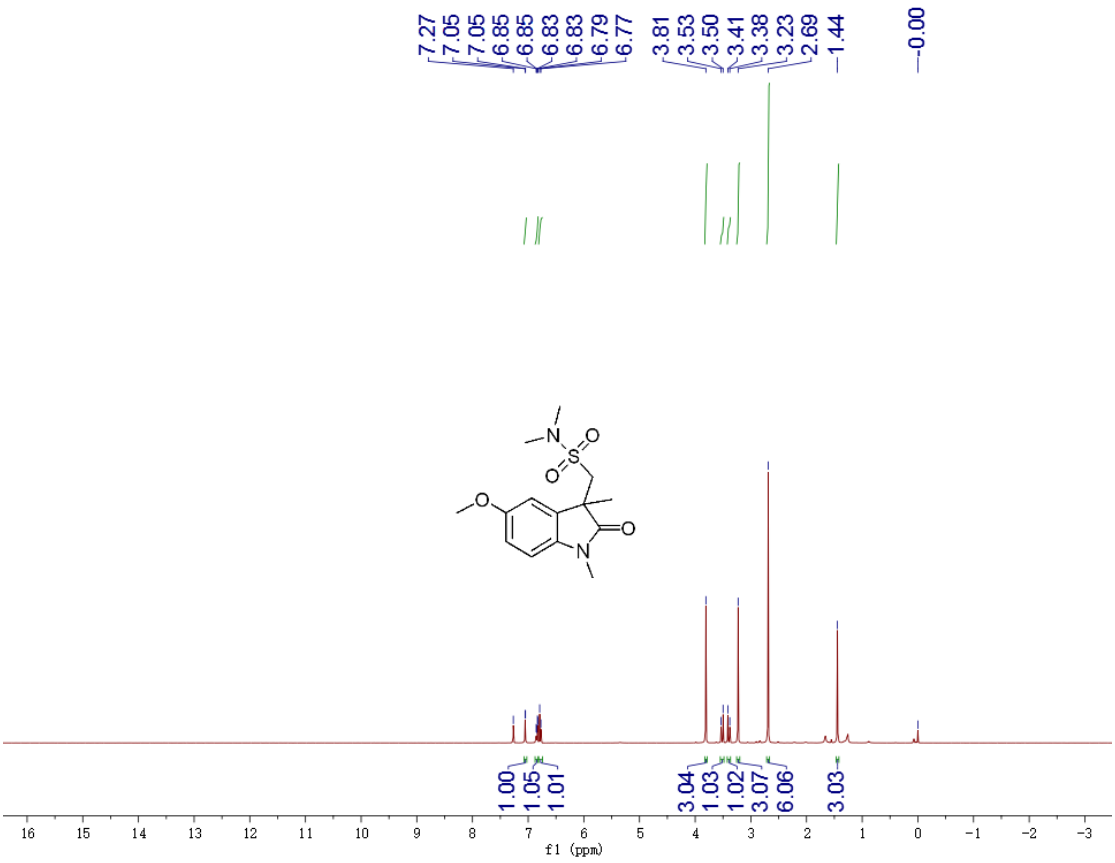
^{1}H NMR spectrum of compound 4i



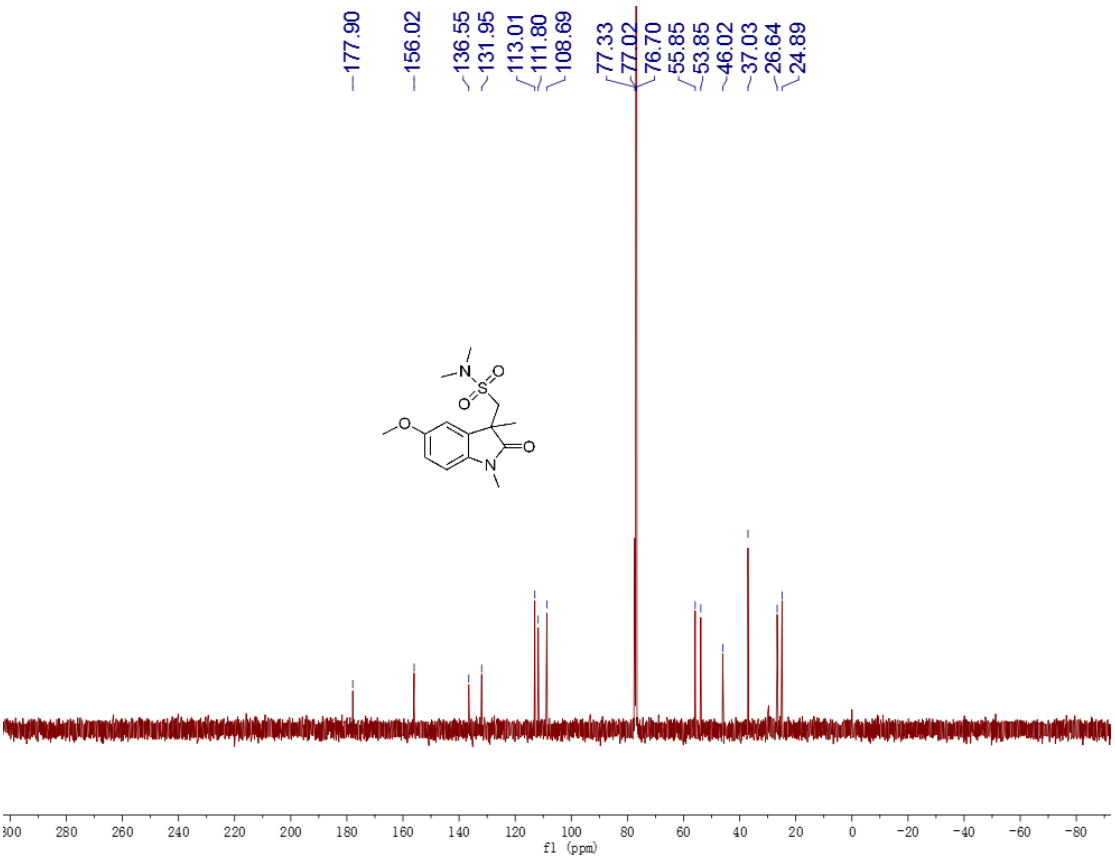
^{13}C NMR spectrum of compound 4i



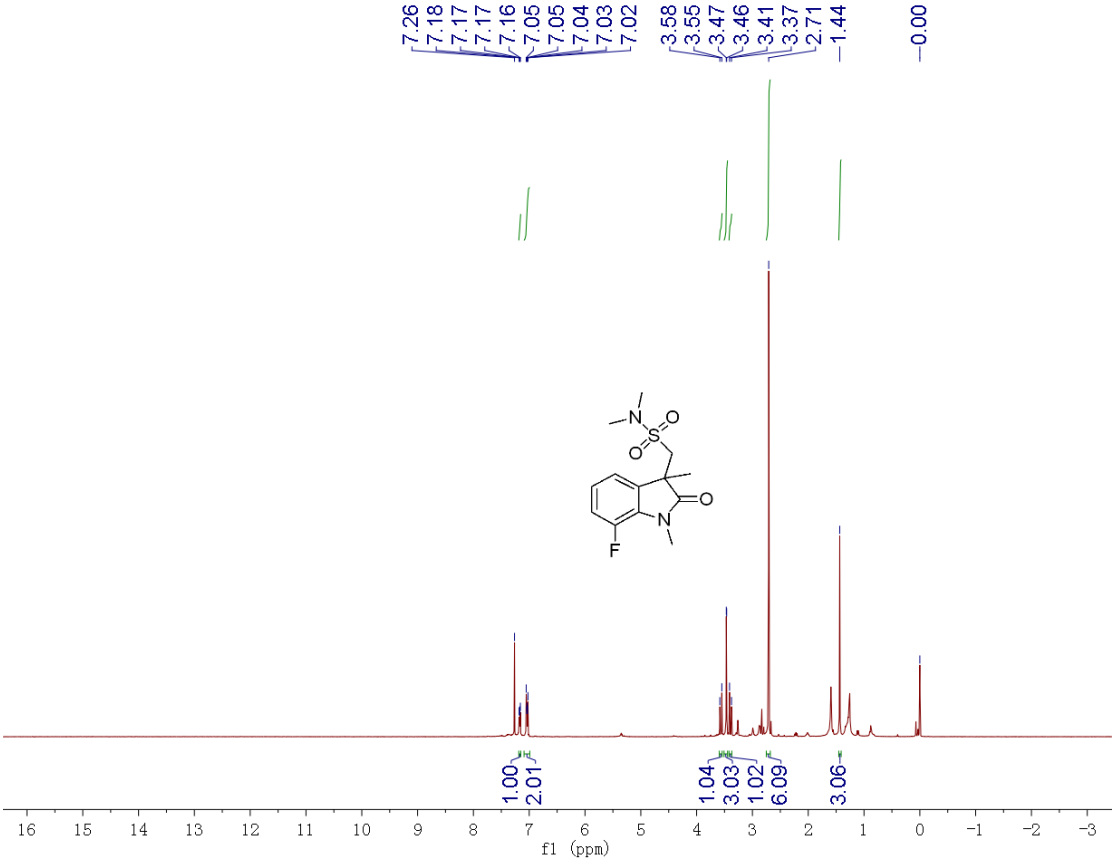
^{1}H NMR spectrum of compound 4j



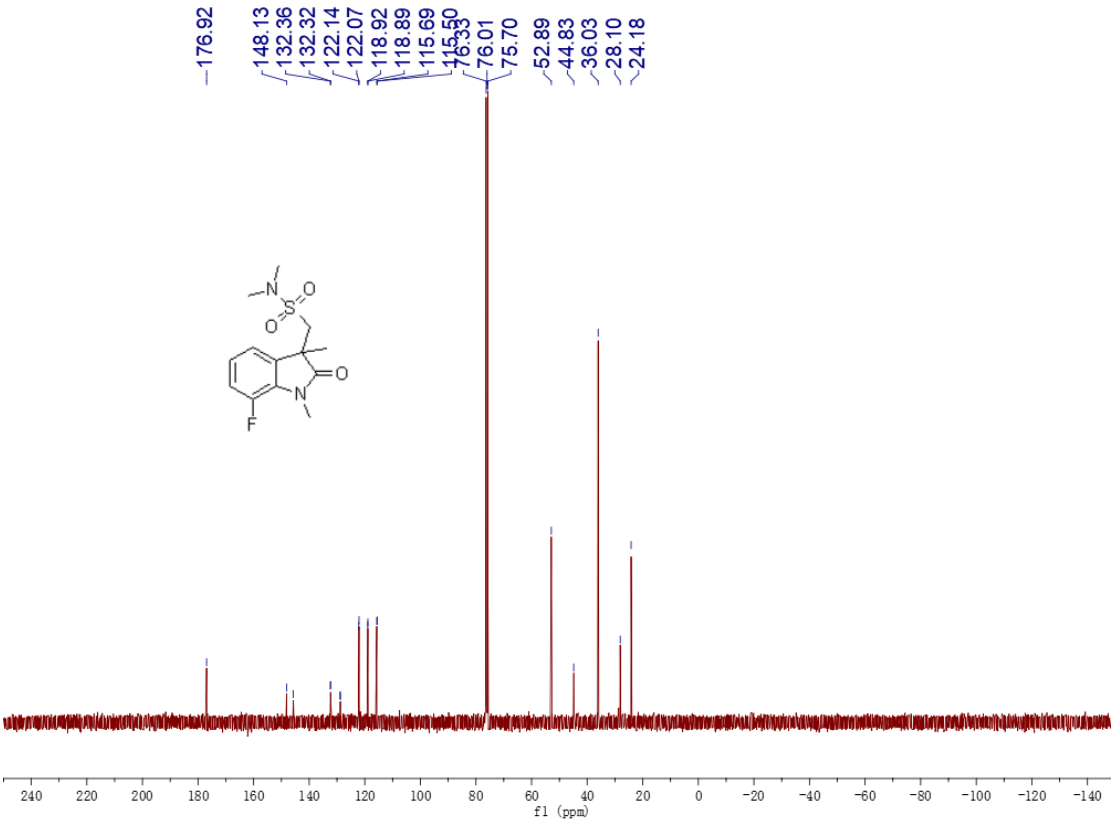
^{13}C NMR spectrum of compound 4j



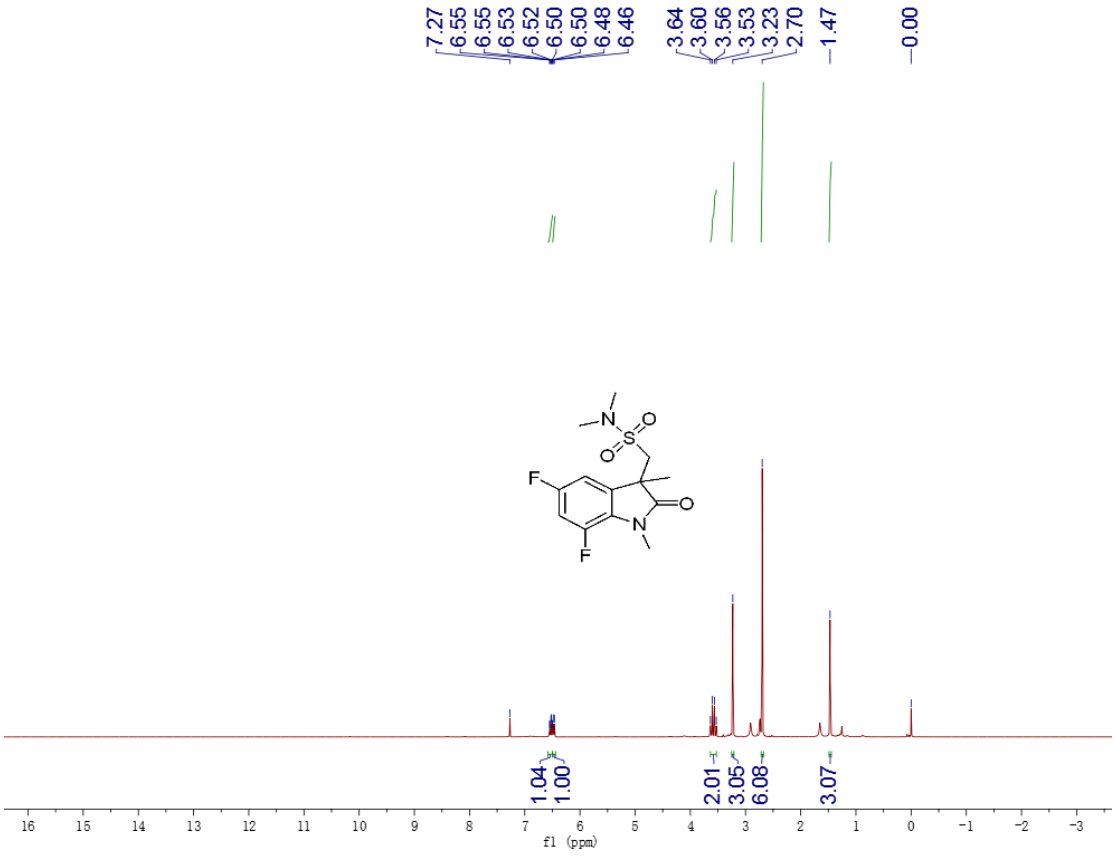
^{1}H NMR spectrum of compound 4k



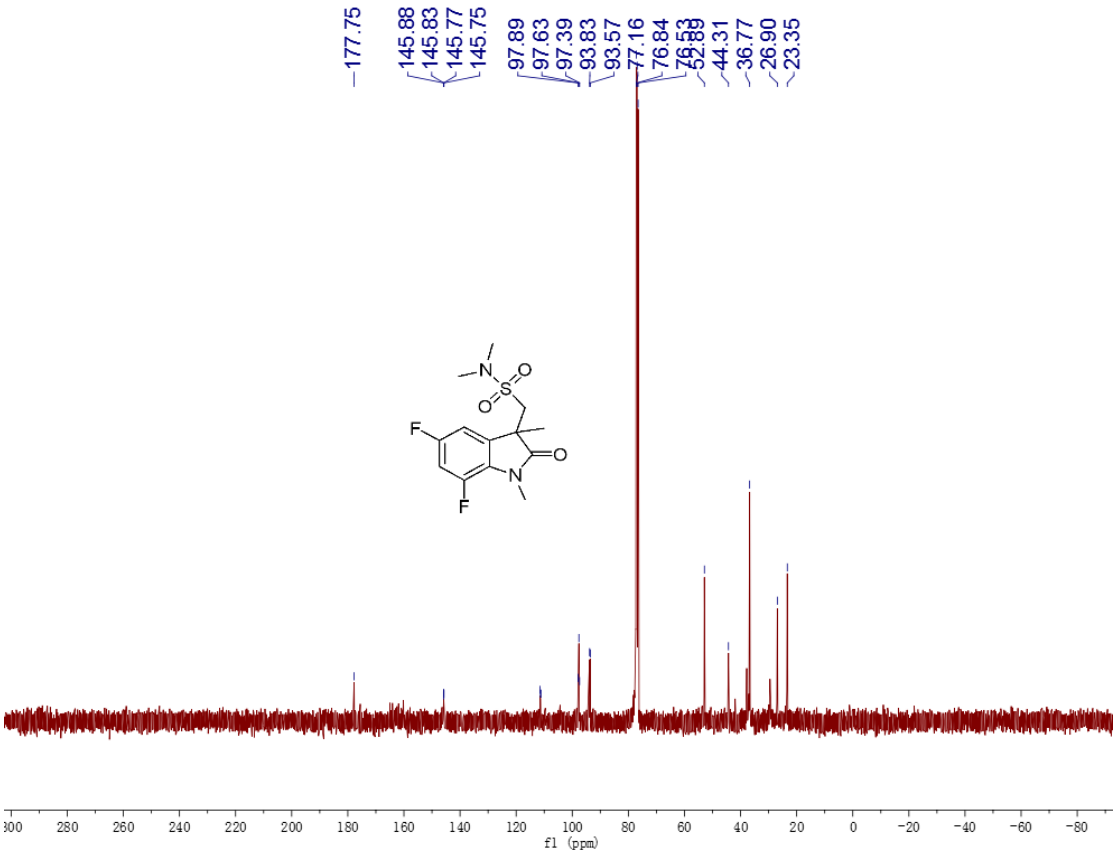
^{13}C NMR spectrum of compound 4k



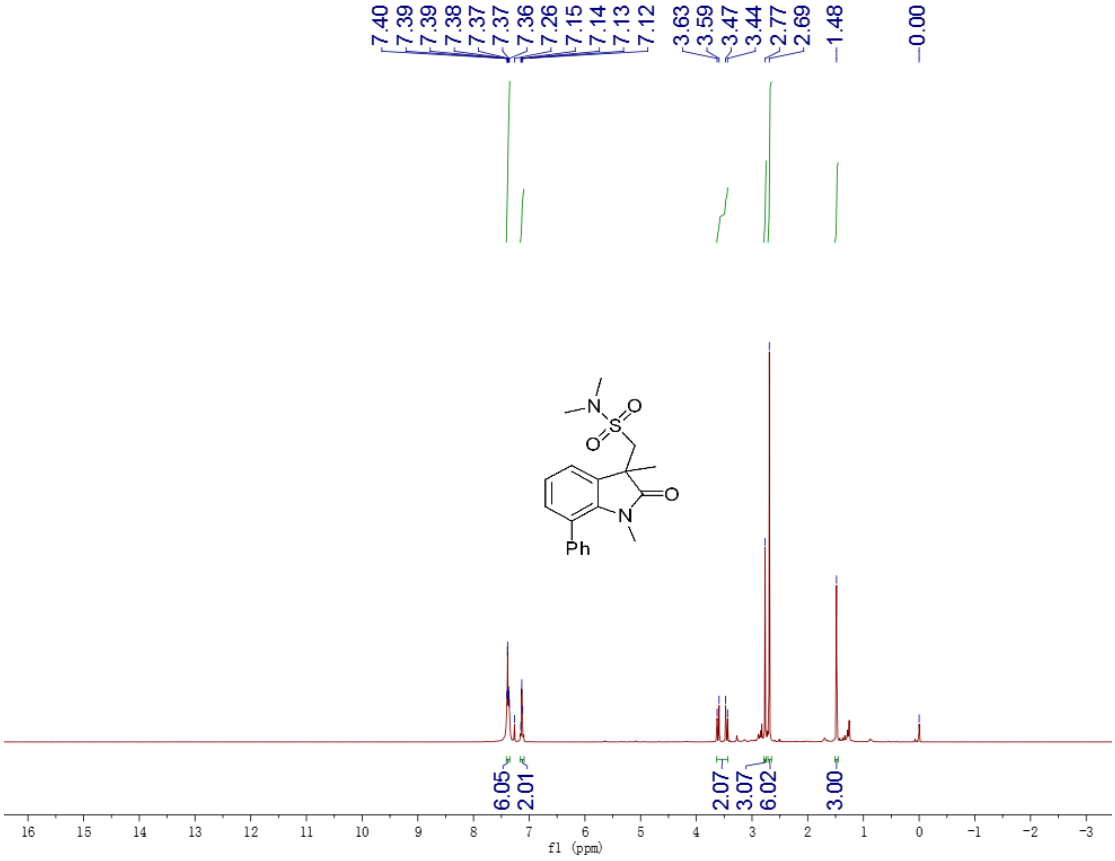
^{1}H NMR spectrum of compound 4l



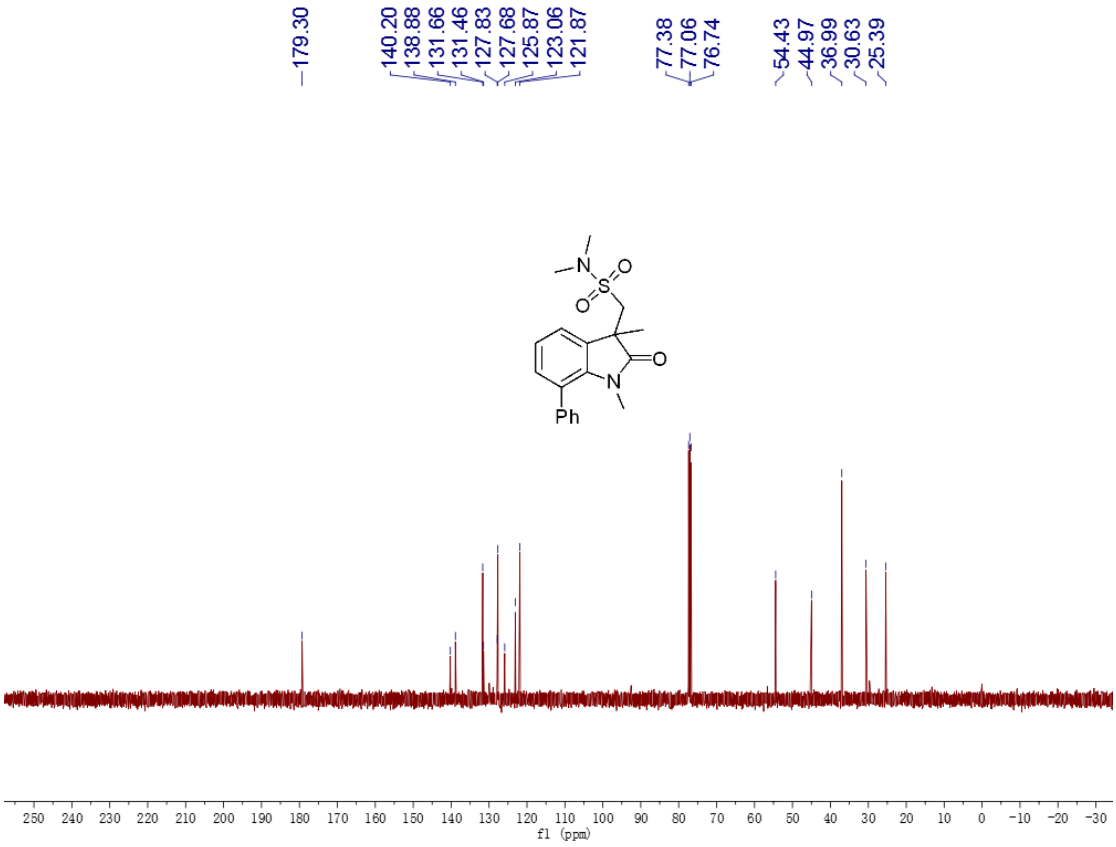
^{13}C NMR spectrum of compound 4l



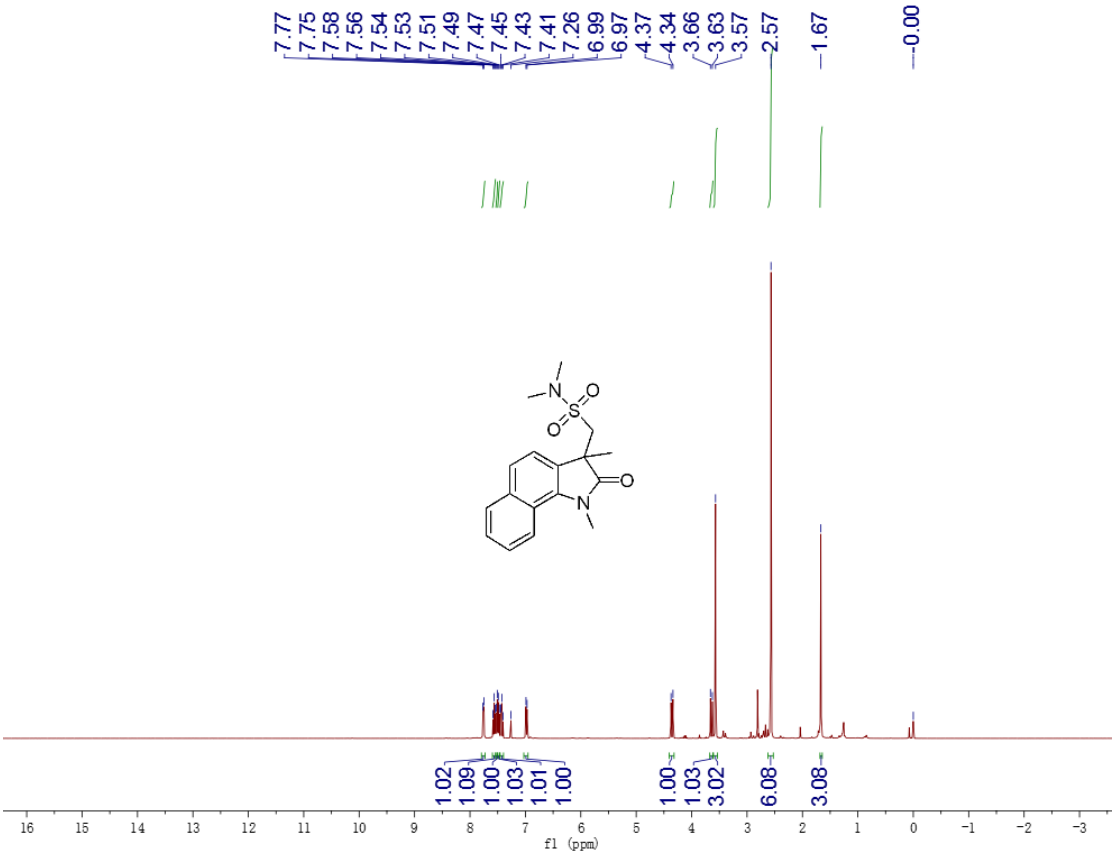
^{1}H NMR spectrum of compound 4m



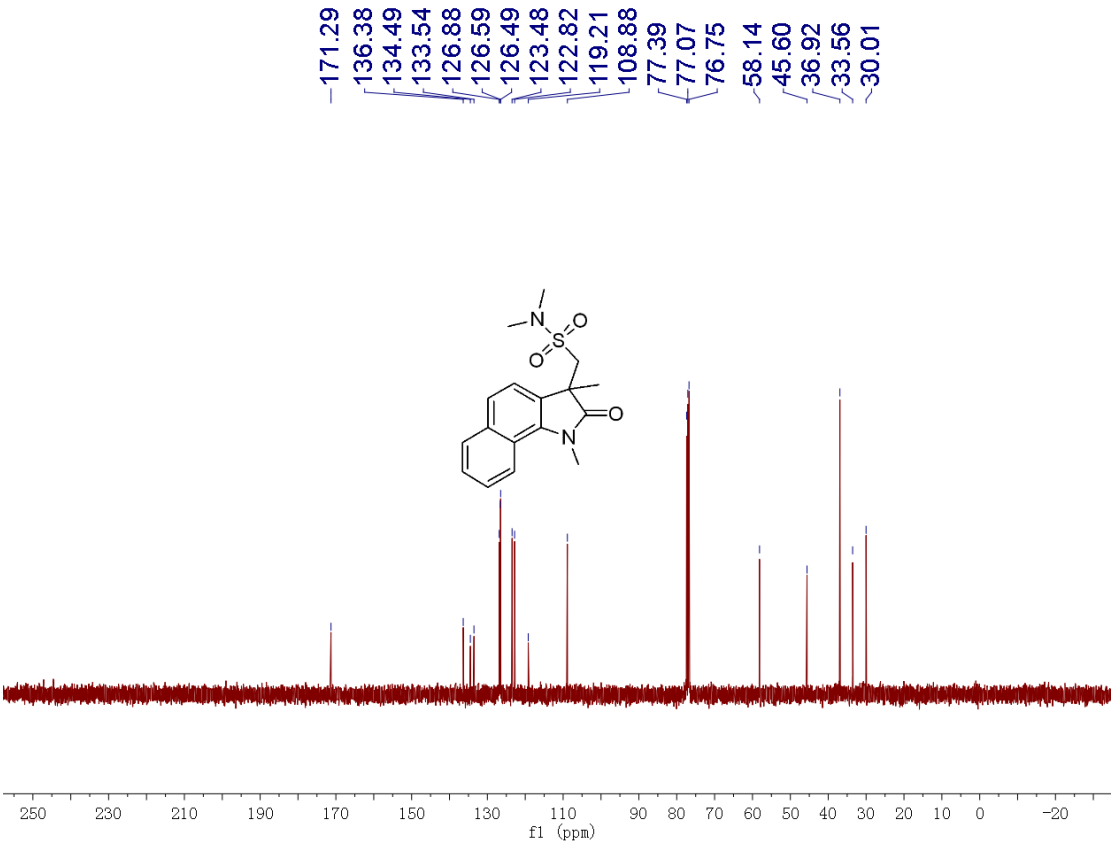
^{13}C NMR spectrum of compound 4m



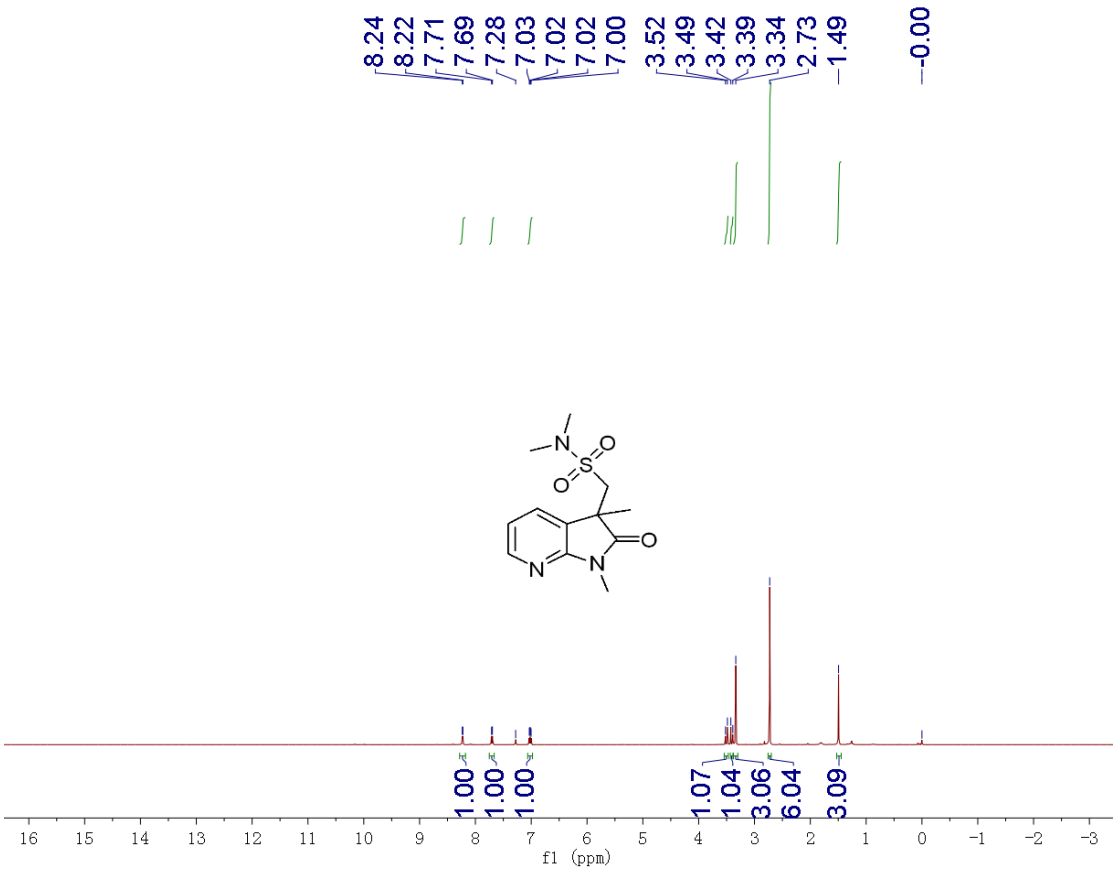
^{1}H NMR spectrum of compound 4n



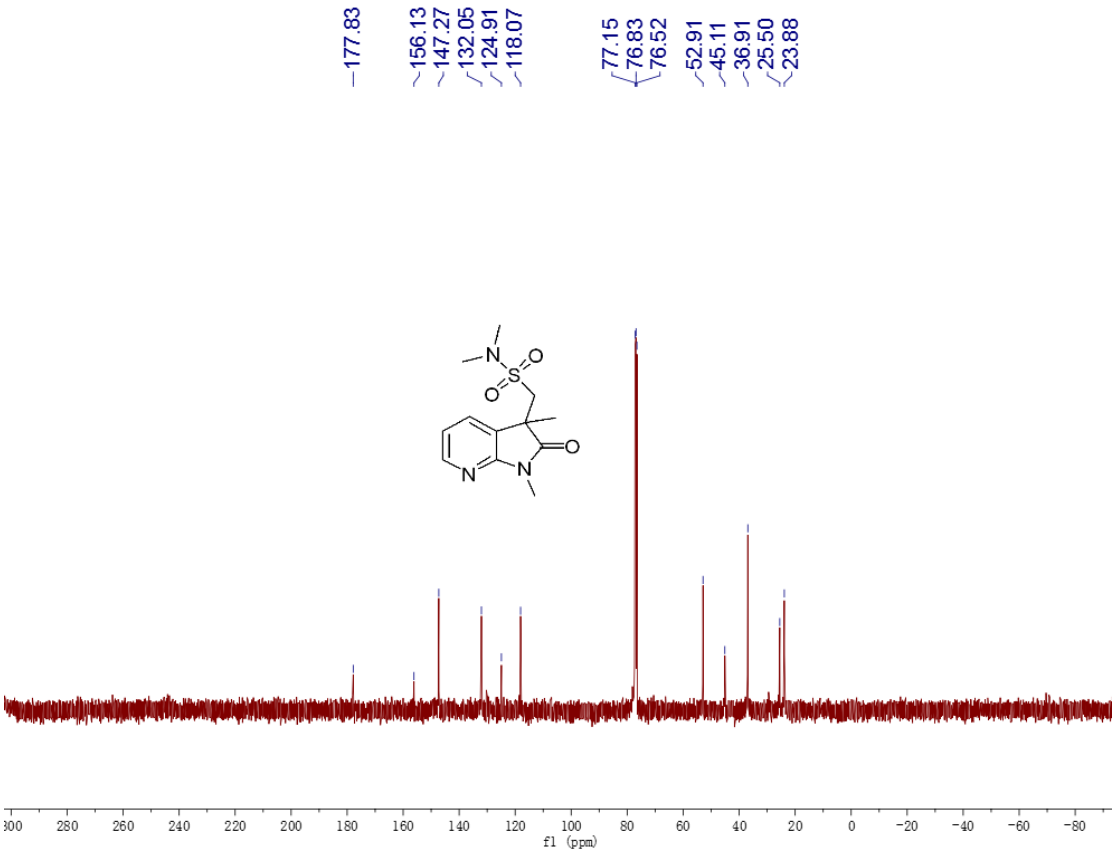
^{13}C NMR spectrum of compound 4n



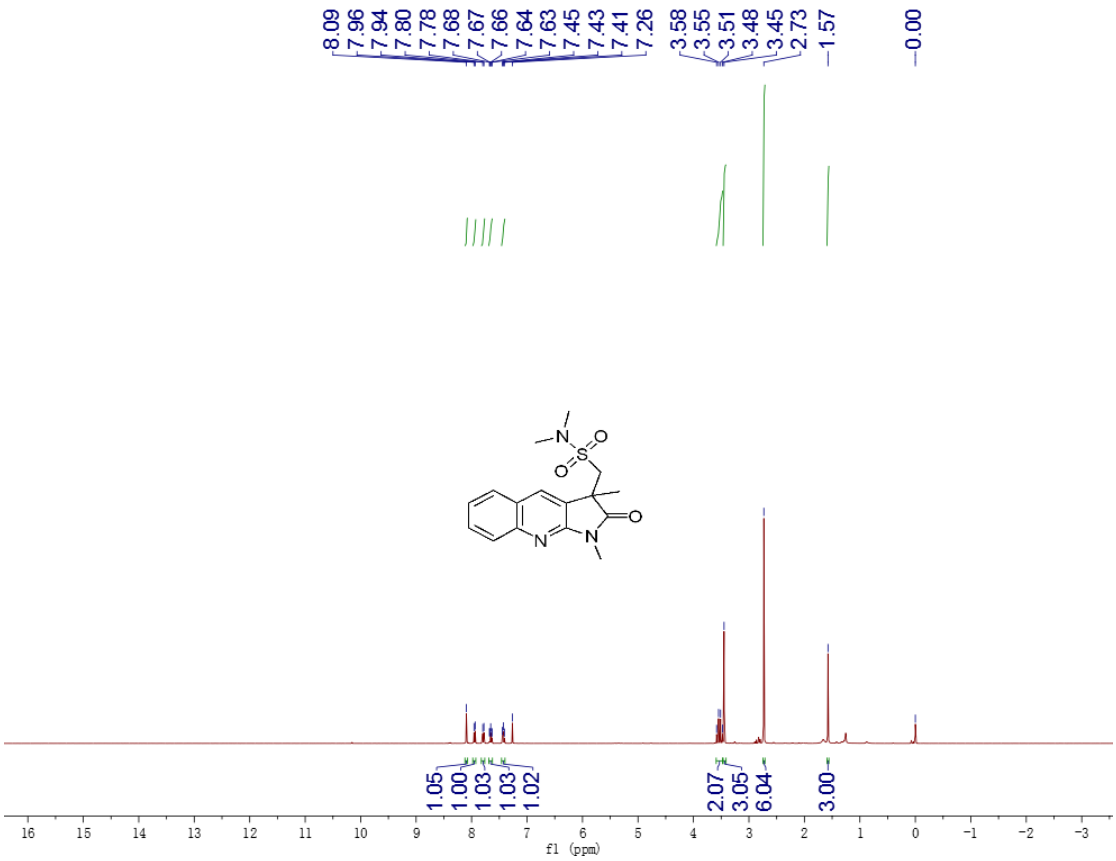
^{1}H NMR spectrum of compound 4o



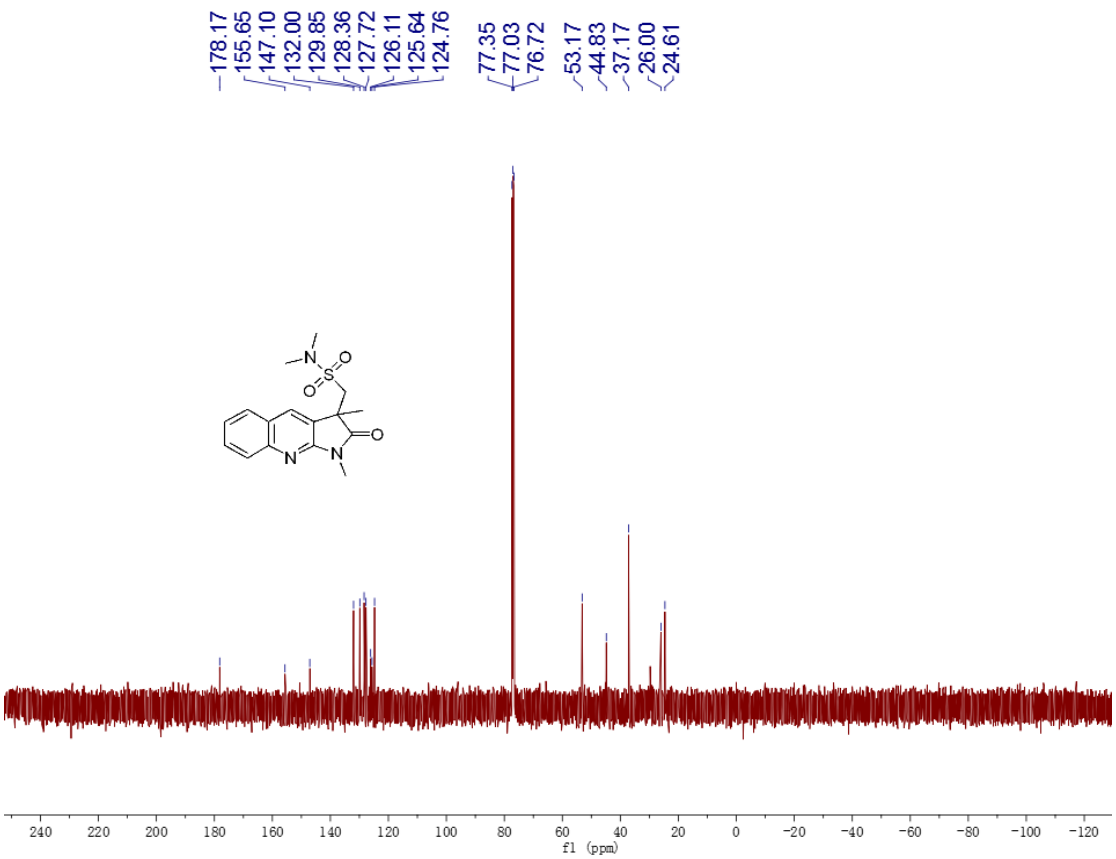
^{13}C NMR spectrum of compound 4o



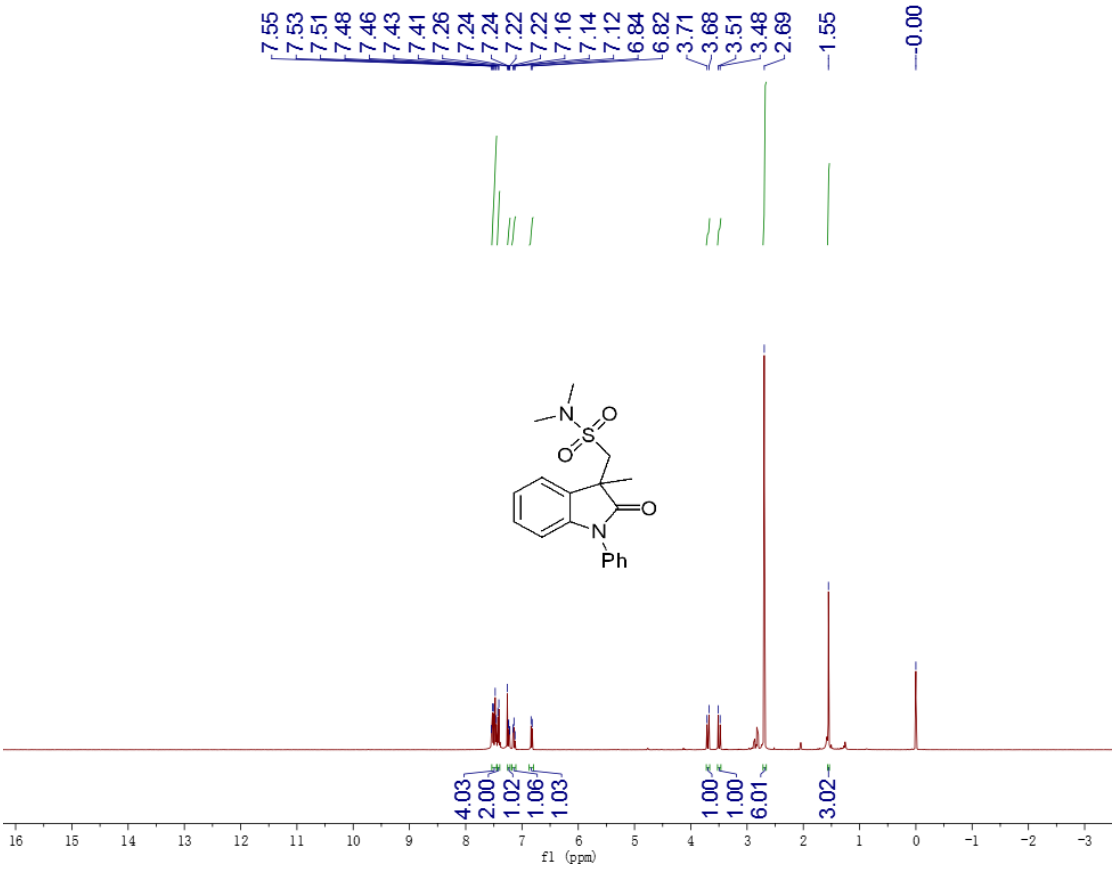
^{1}H NMR spectrum of compound 4p



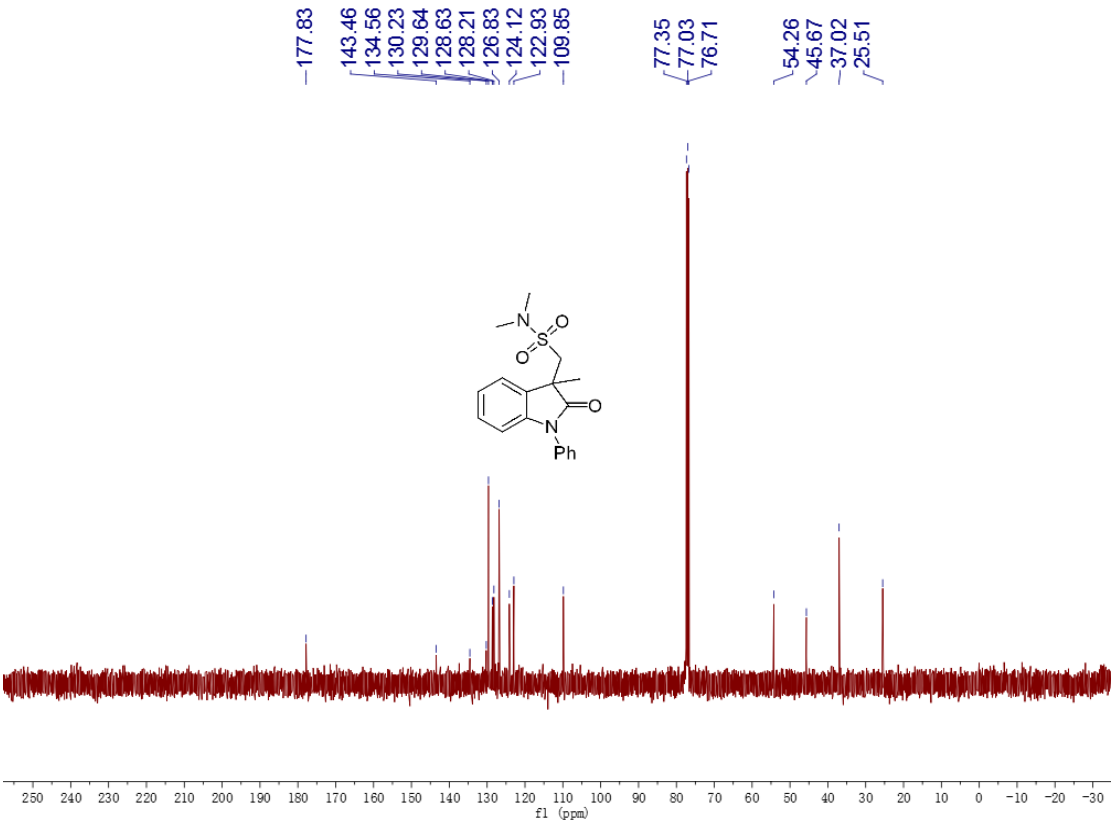
^{13}C NMR spectrum of compound 4p



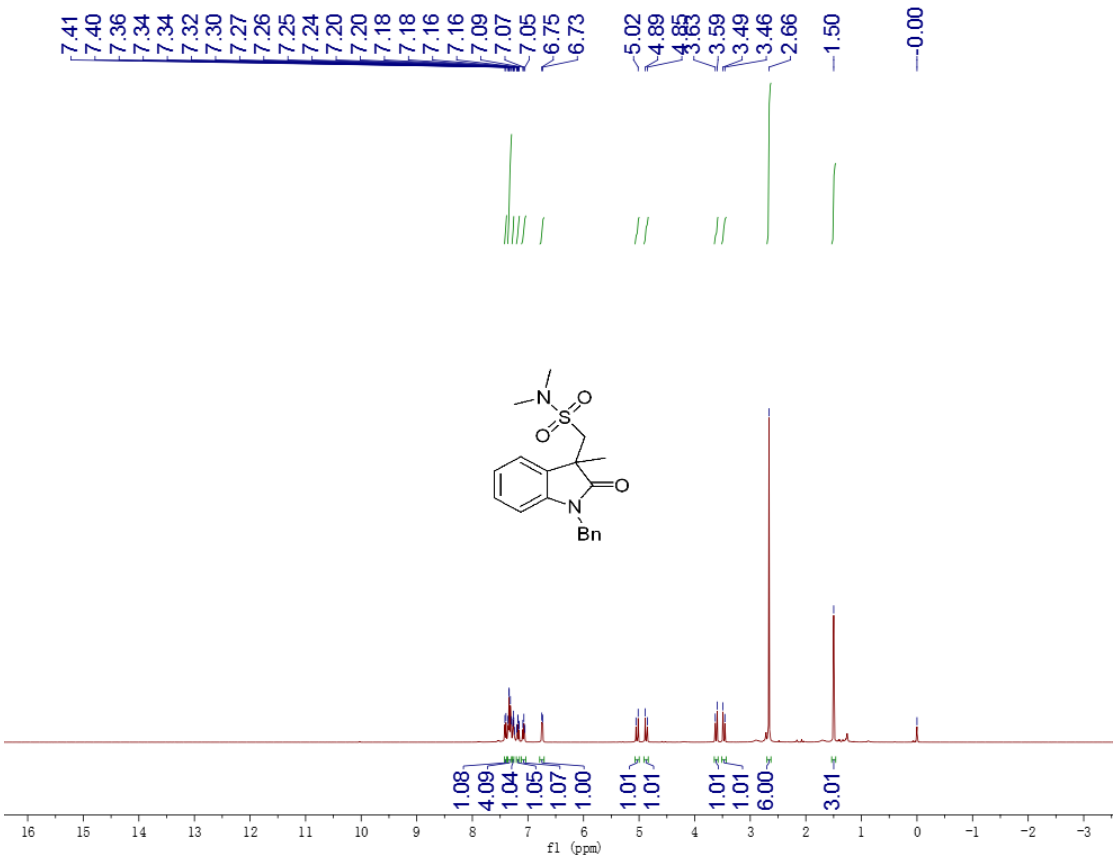
^{1}H NMR spectrum of compound 4q



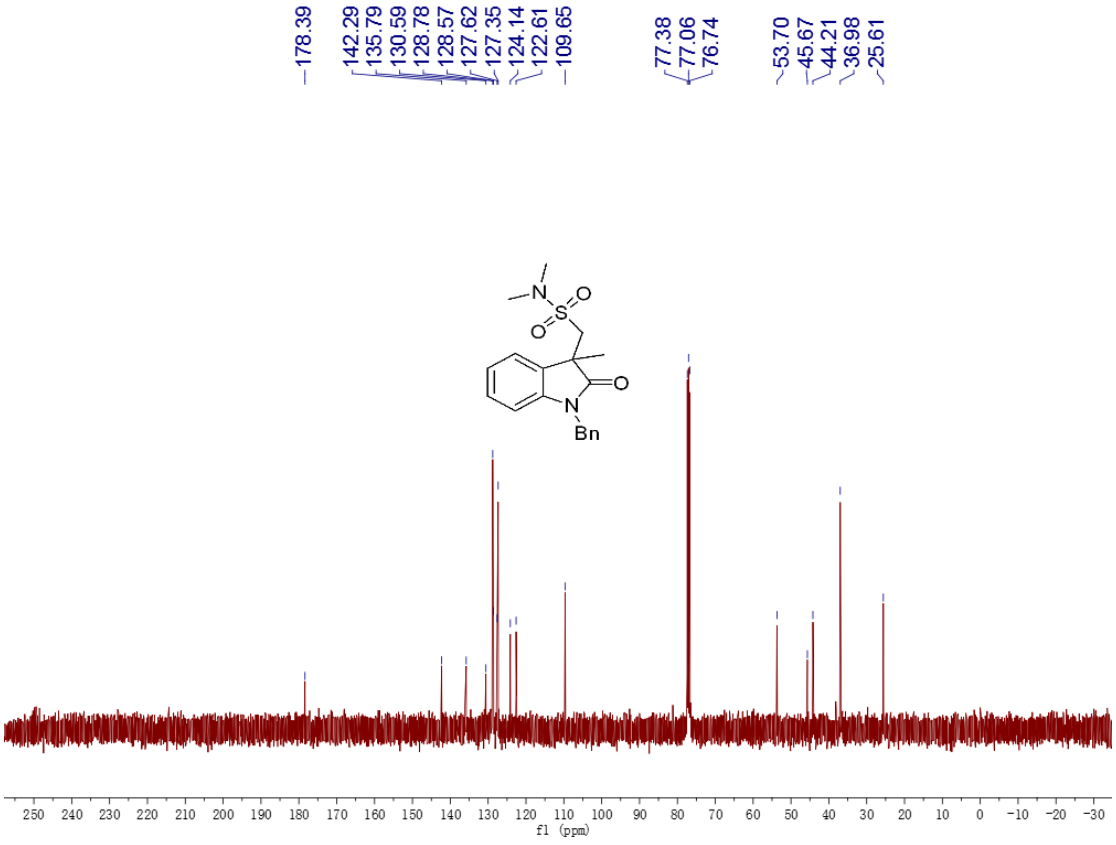
^{13}C NMR spectrum of compound 4q



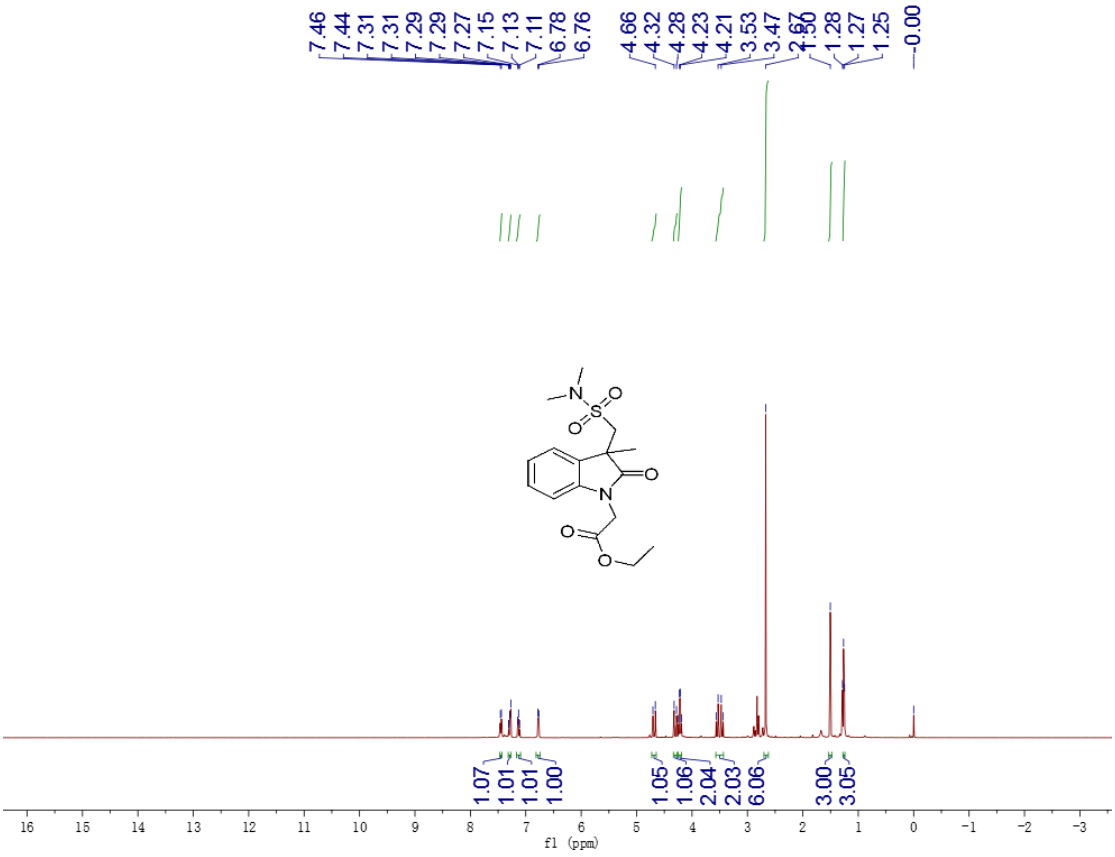
^{1}H NMR spectrum of compound 4r



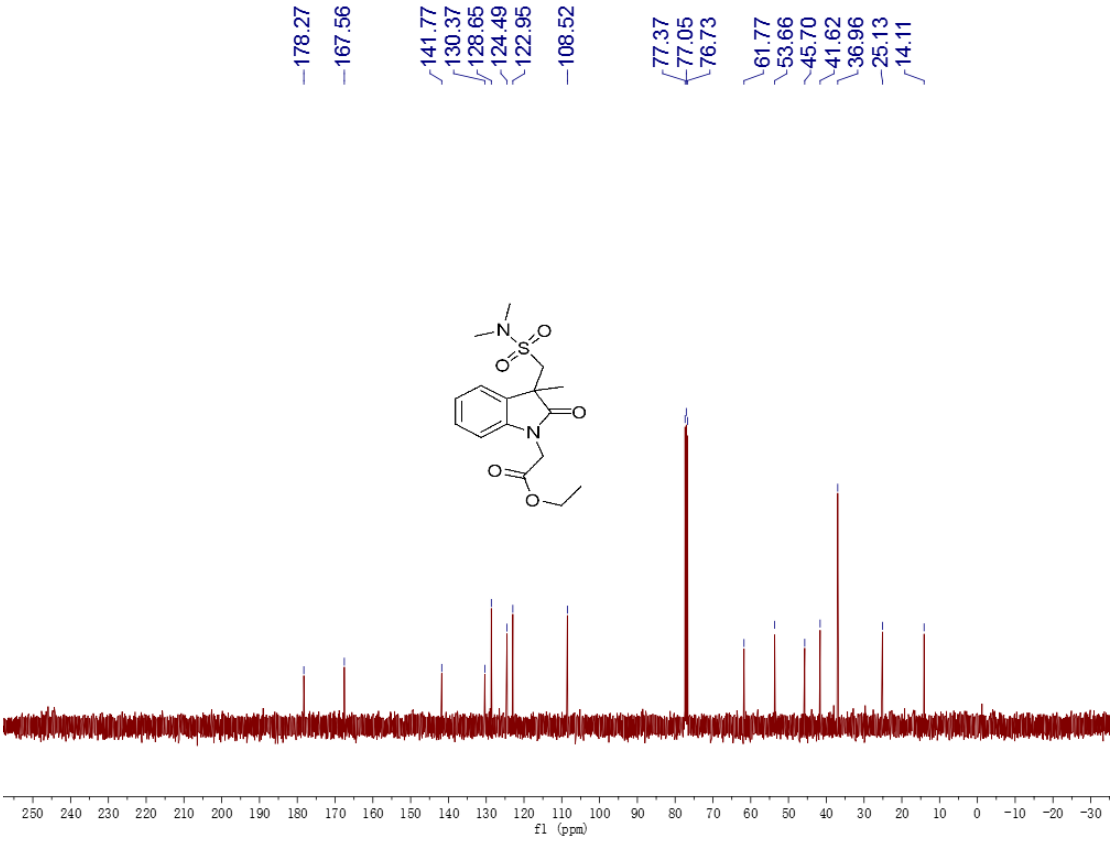
^{13}C NMR spectrum of compound 4r



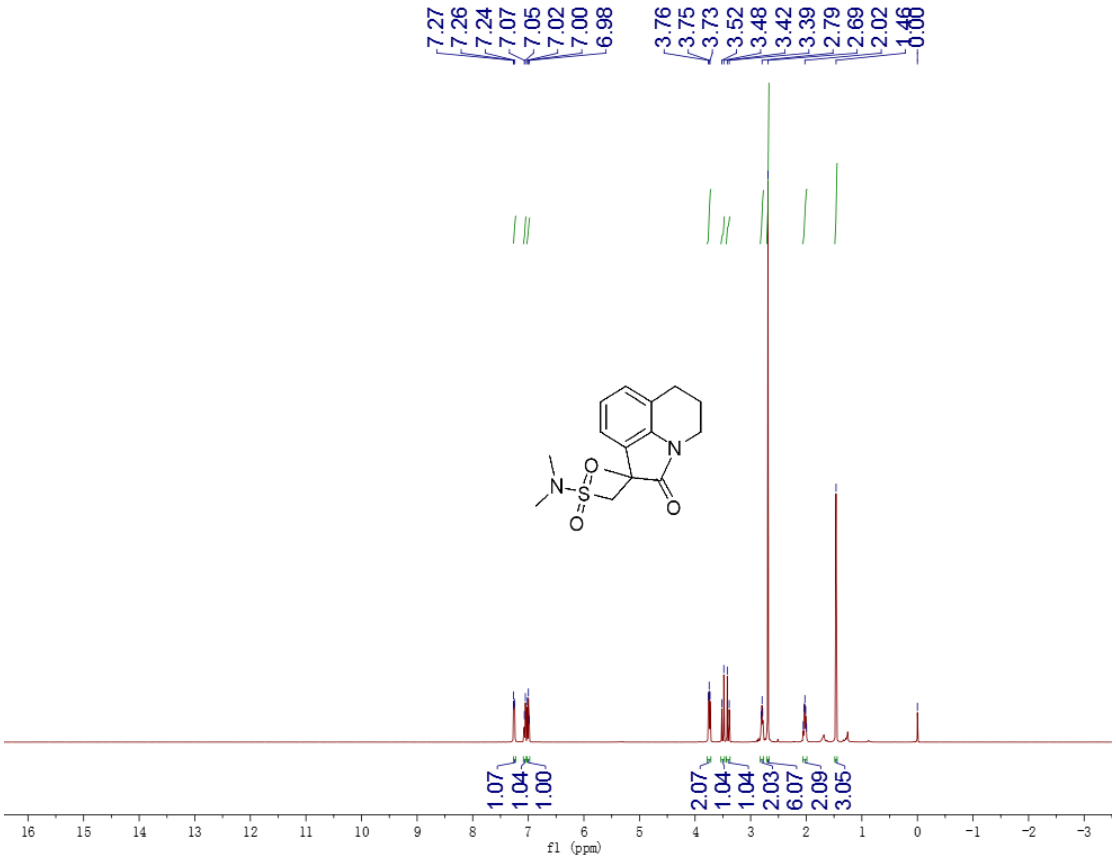
^{1}H NMR spectrum of compound 4s



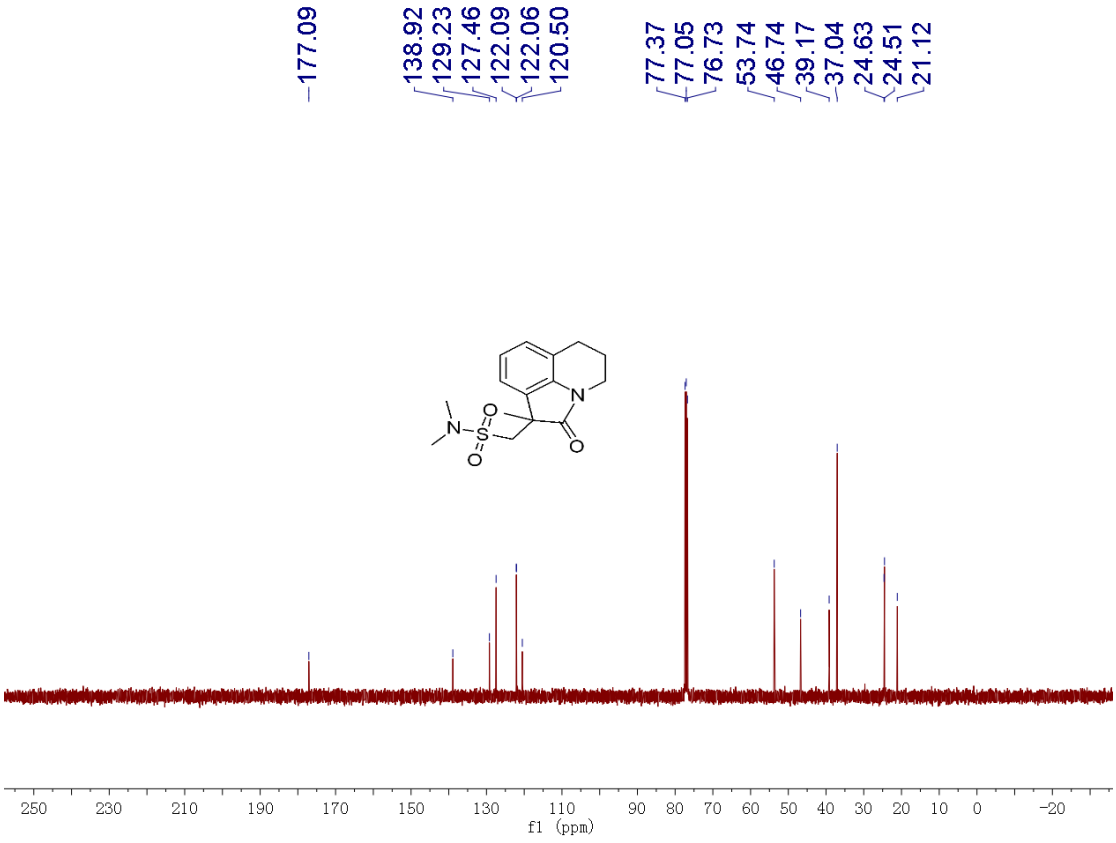
^{13}C NMR spectrum of compound 4s



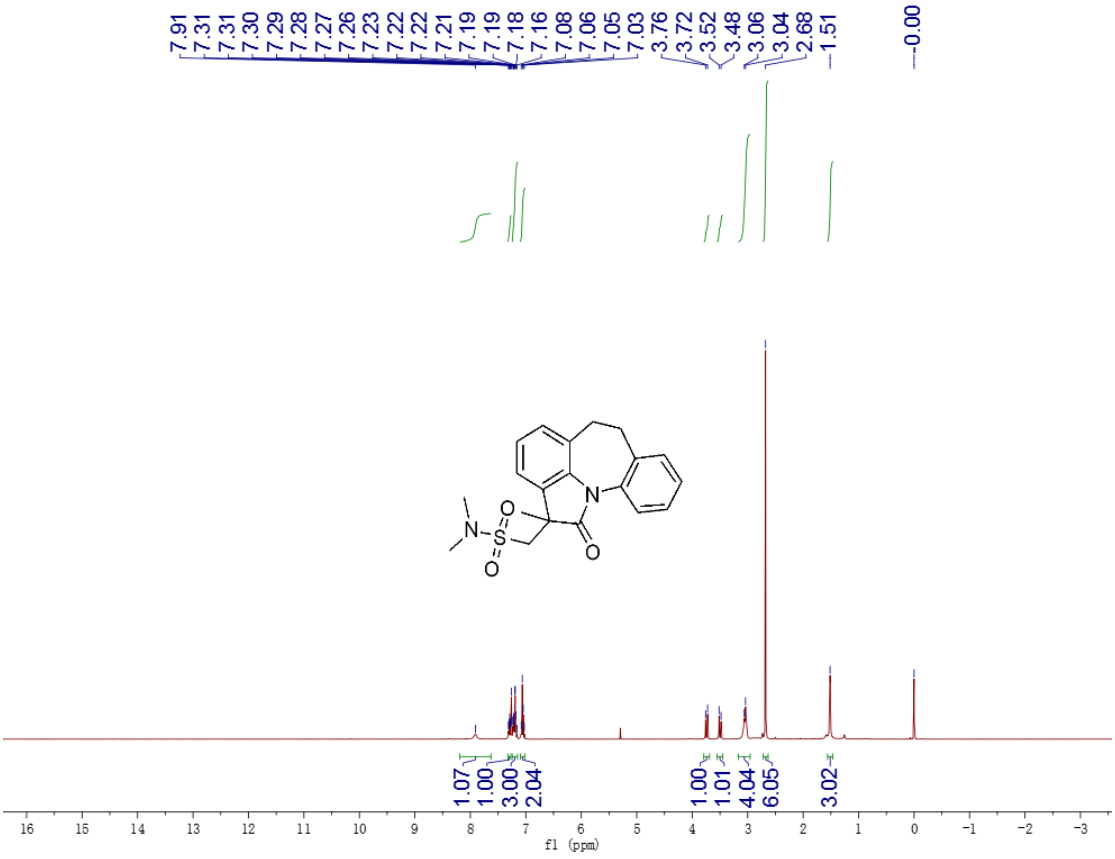
^{1}H NMR spectrum of compound 4t



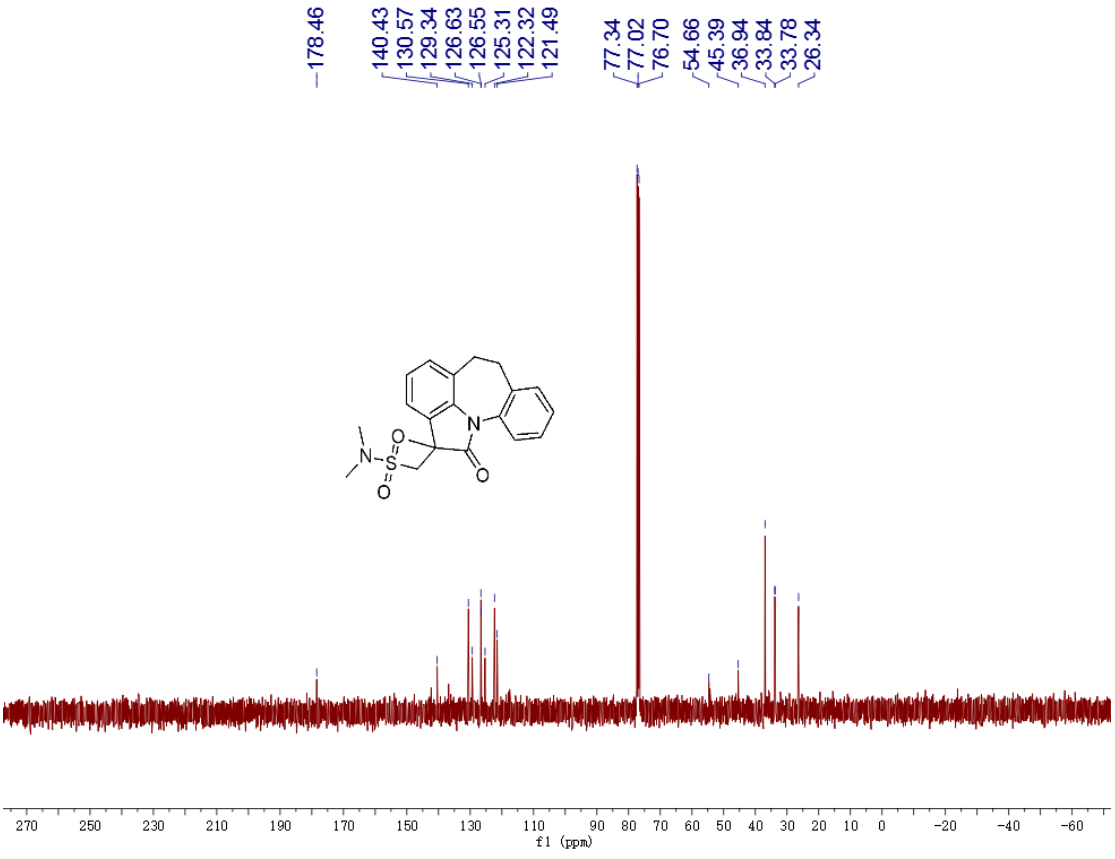
^{13}C NMR spectrum of compound 4t



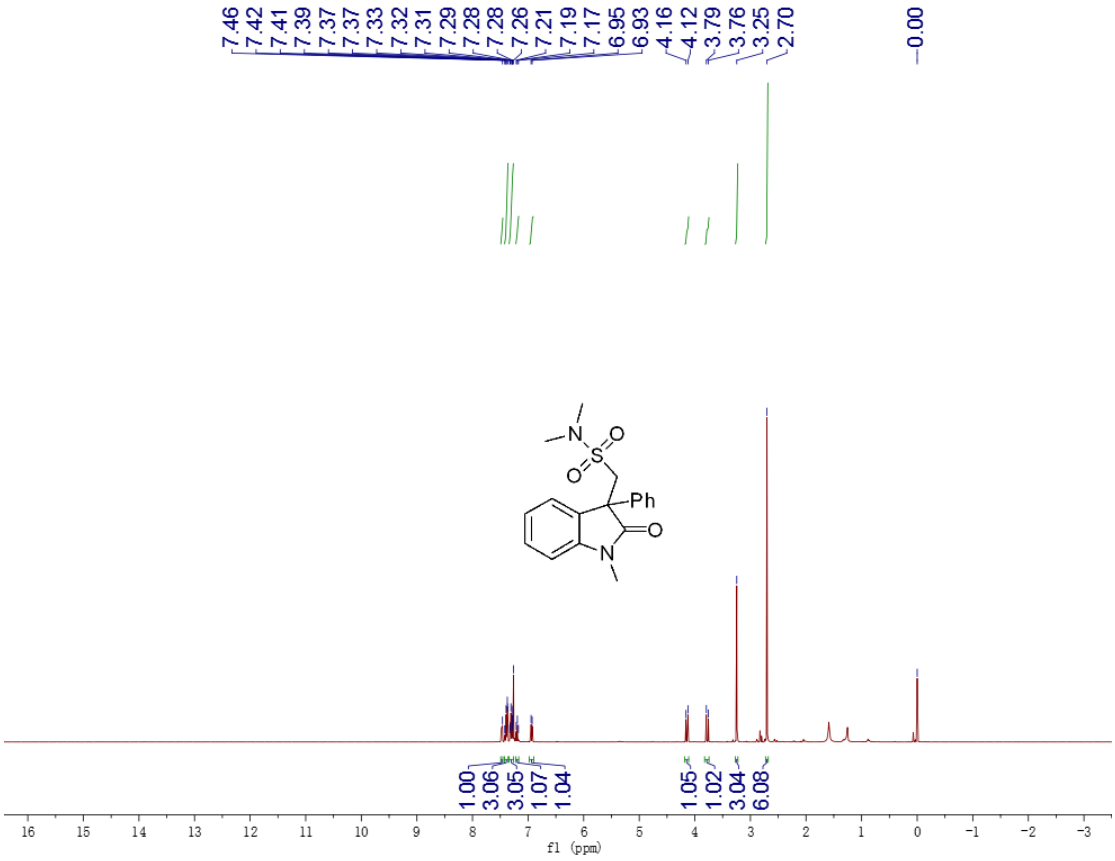
^{1}H NMR spectrum of compound 4u



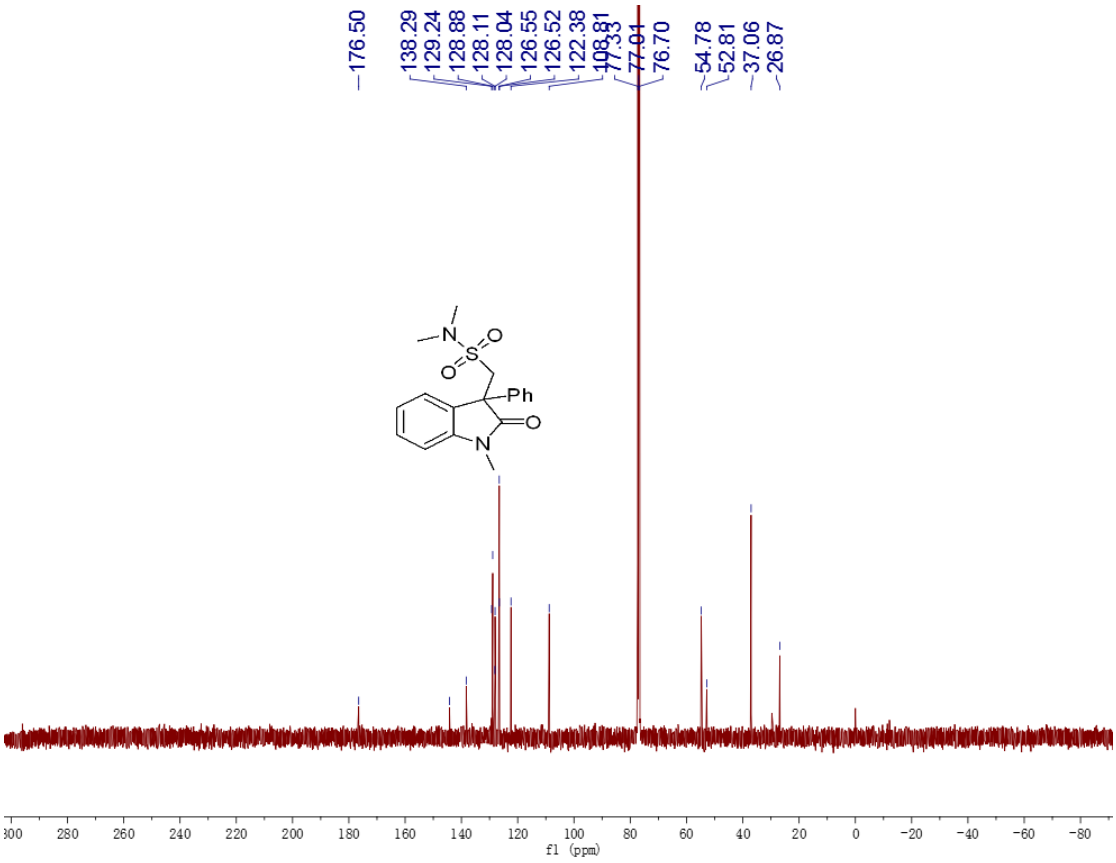
^{13}C NMR spectrum of compound 4u



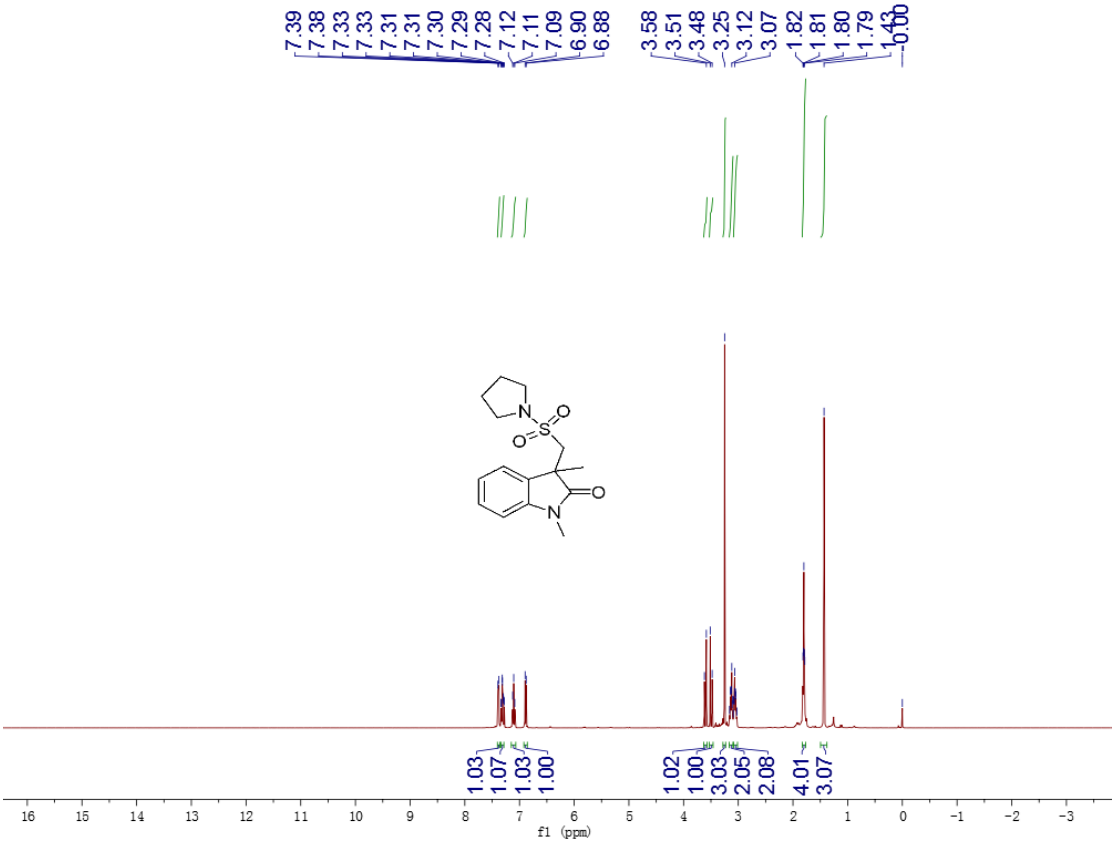
^{1}H NMR spectrum of compound 4v



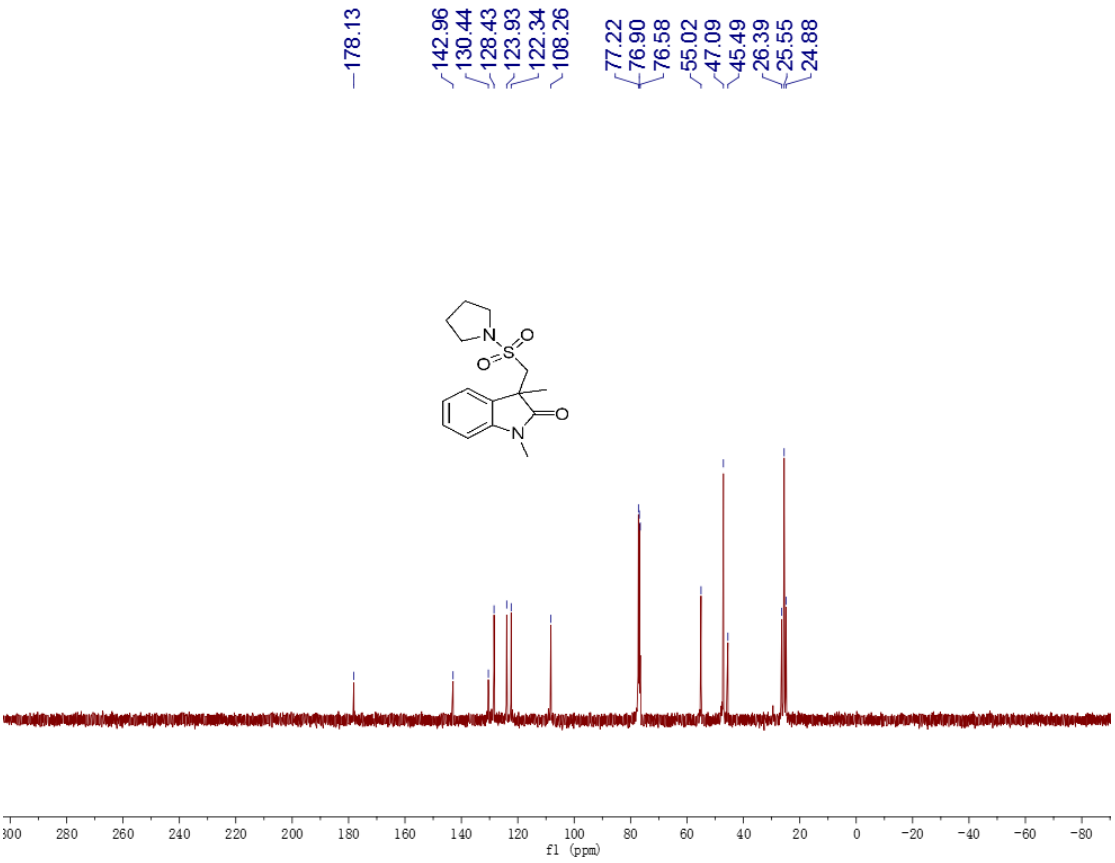
^{13}C NMR spectrum of compound 4v



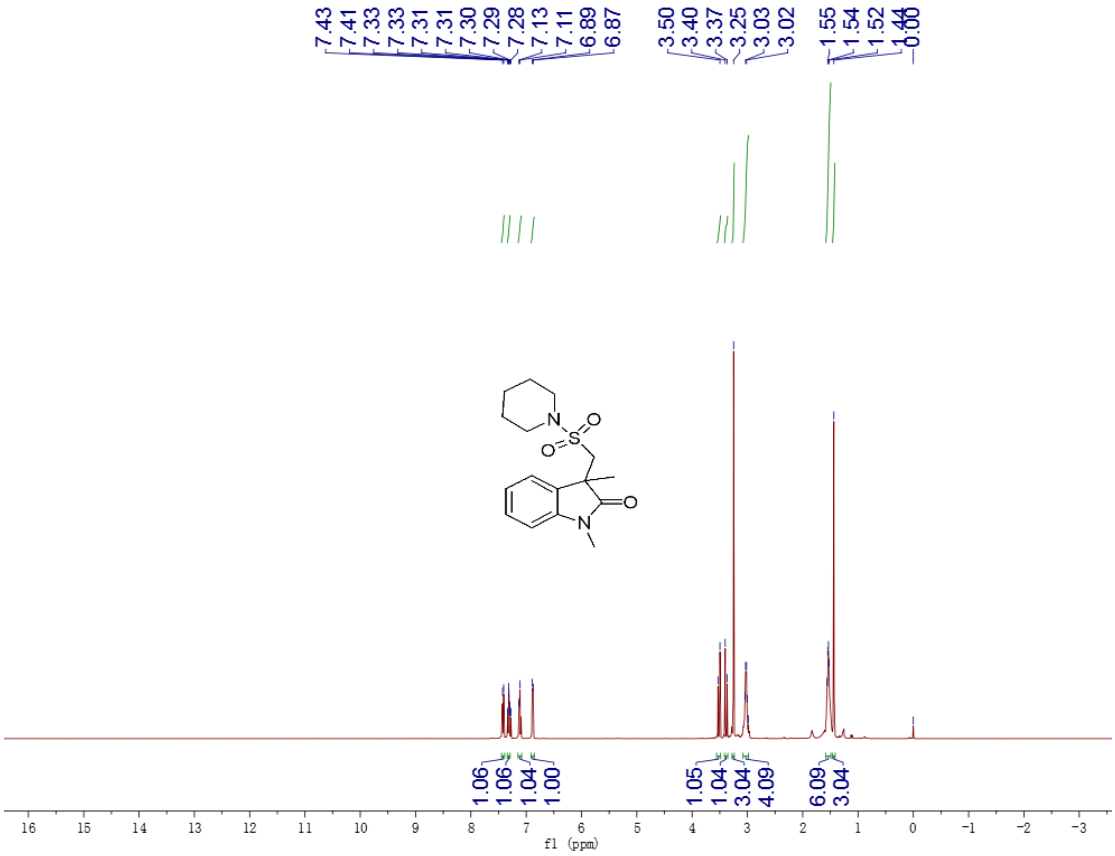
^{1}H NMR spectrum of compound 4w



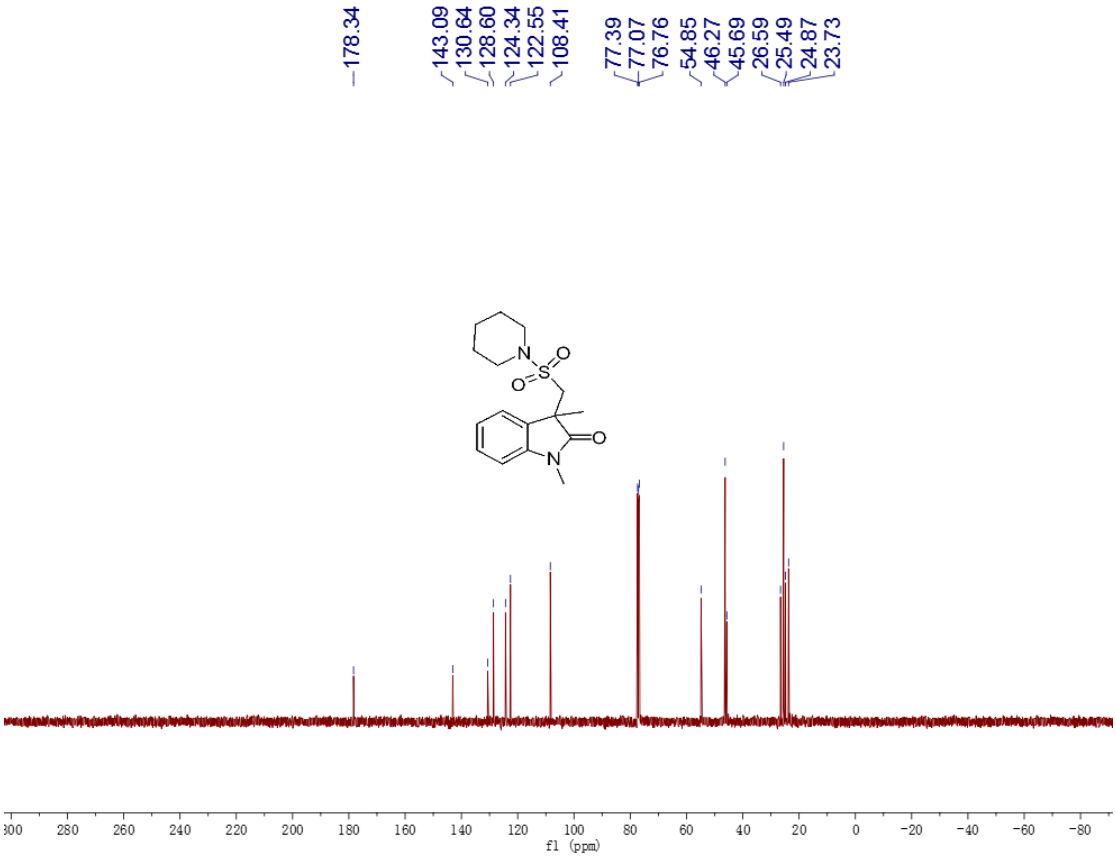
^{13}C NMR spectrum of compound 4w



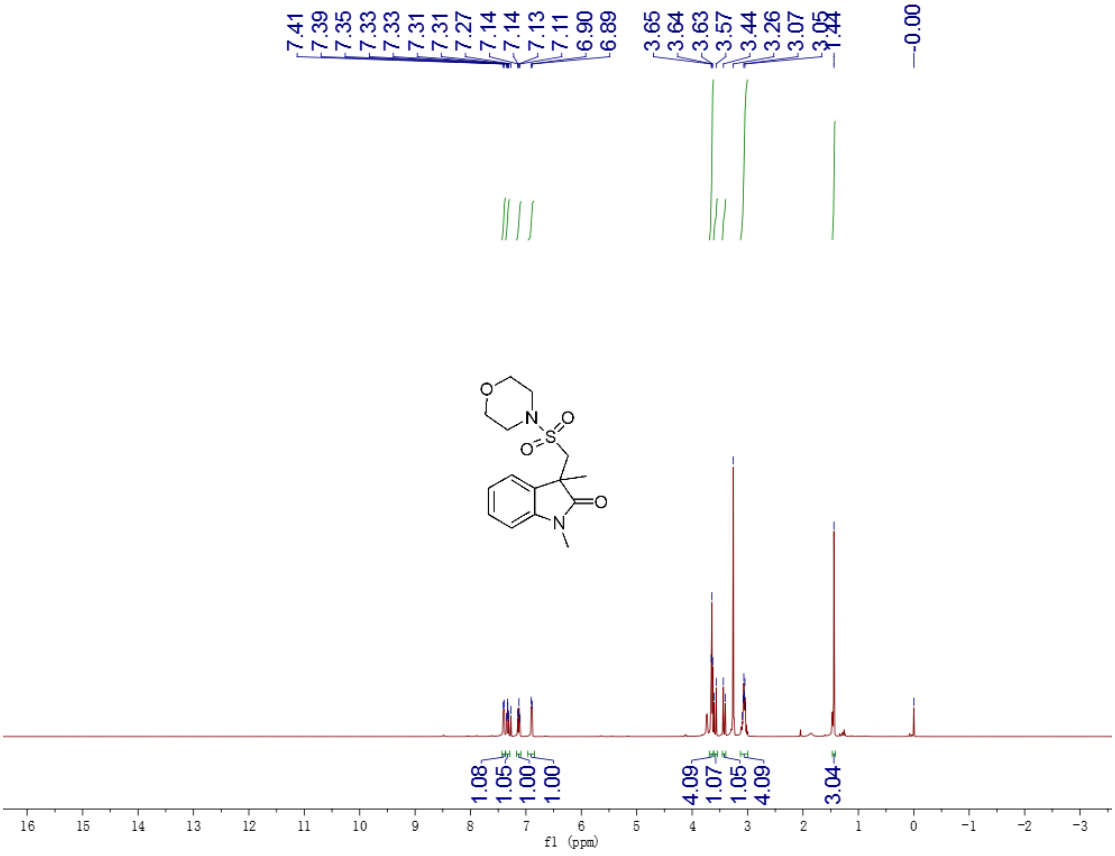
^{1}H NMR spectrum of compound 4x



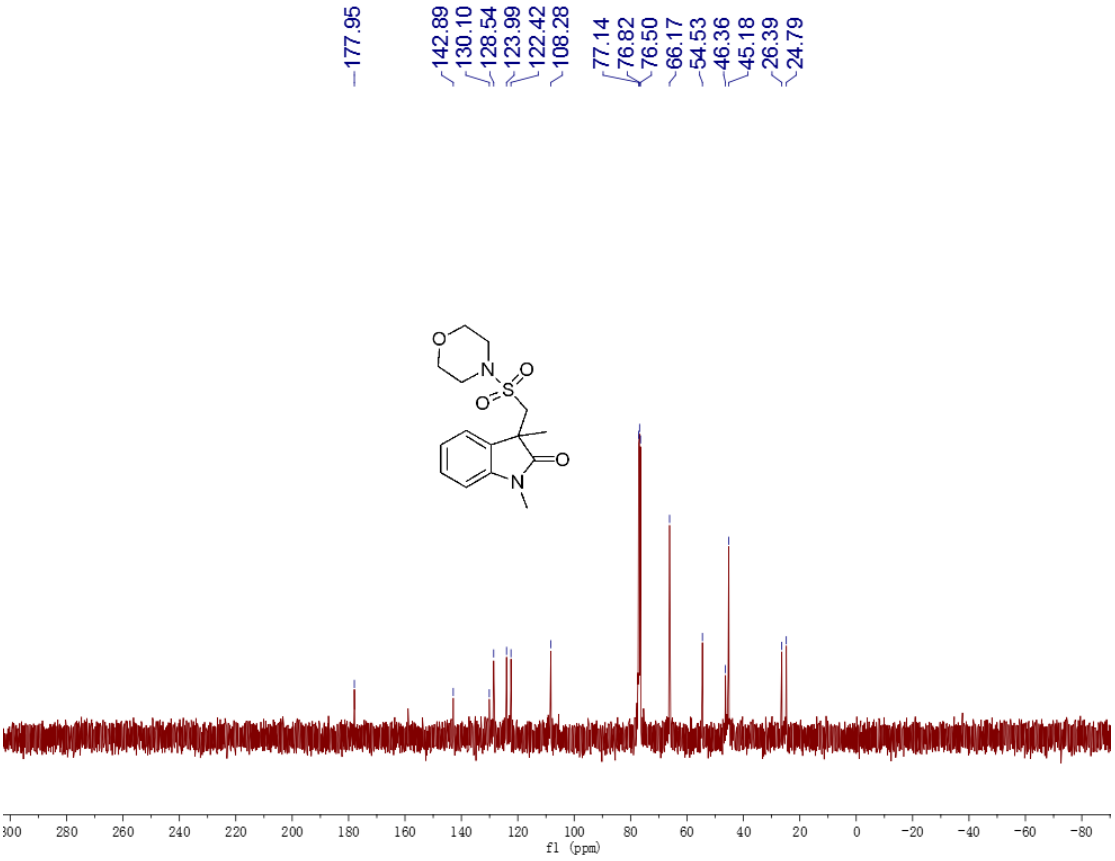
^{13}C NMR spectrum of compound 4x



^{1}H NMR spectrum of compound 4y

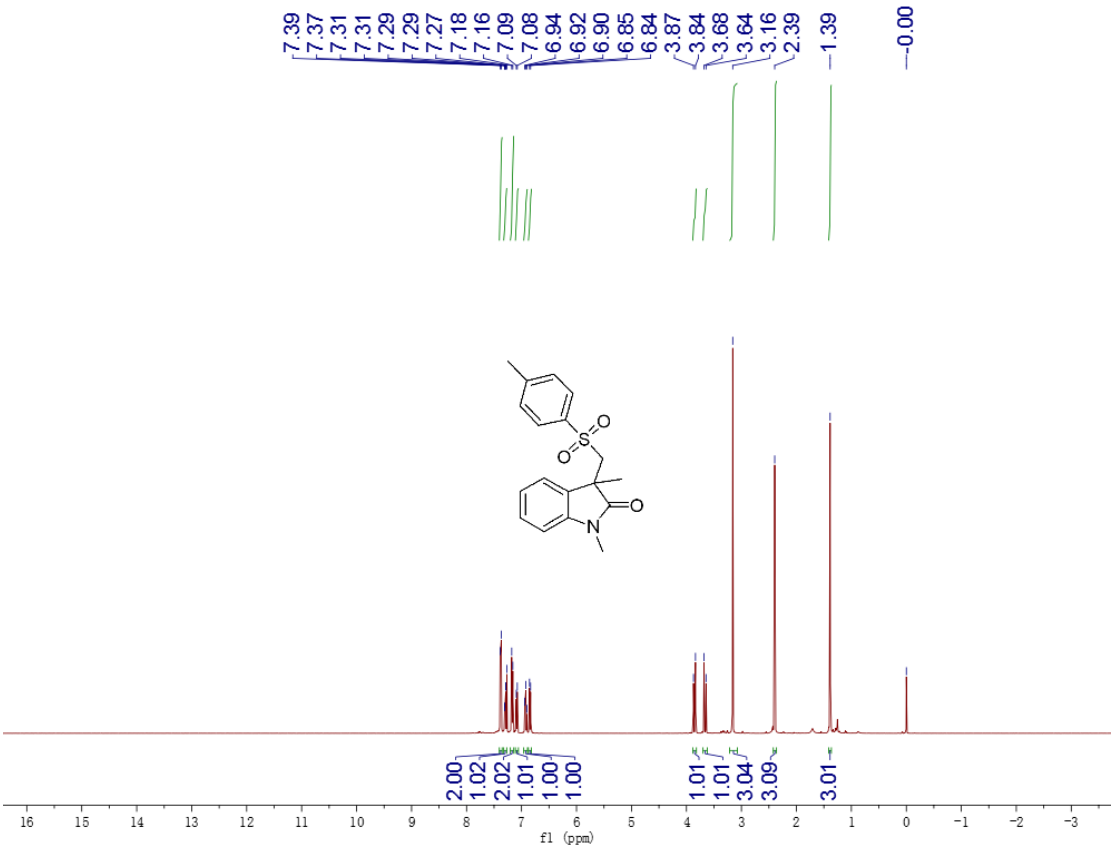


^{13}C NMR spectrum of compound 4y

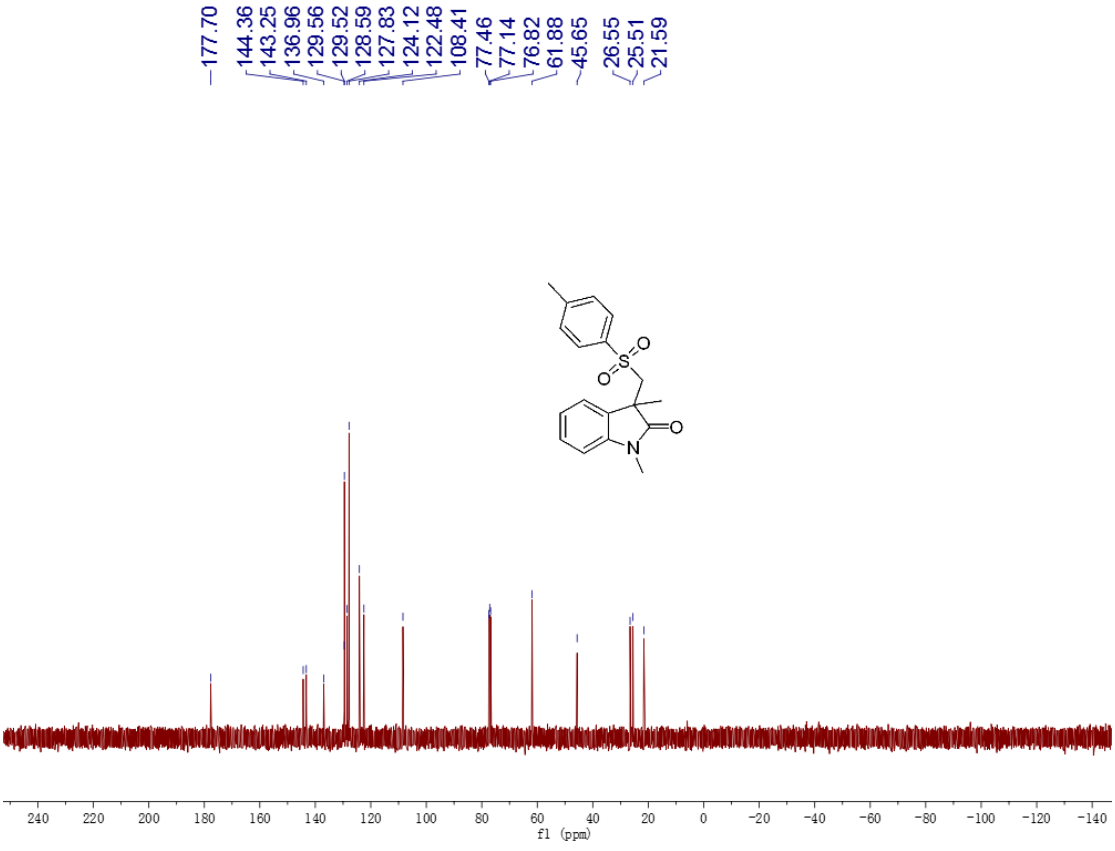


12. ^{1}H NMR and ^{13}C NMR spectrum of Sulfonyl Products

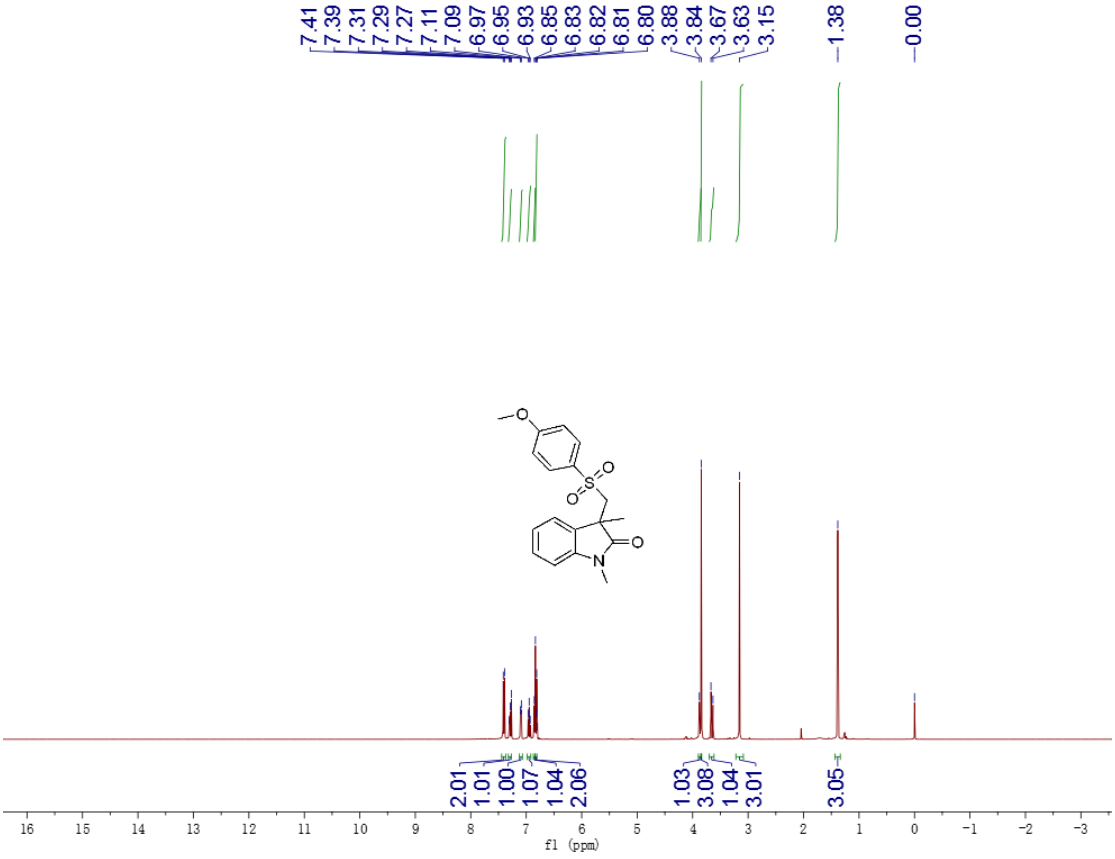
^{1}H NMR spectrum of compound 5a



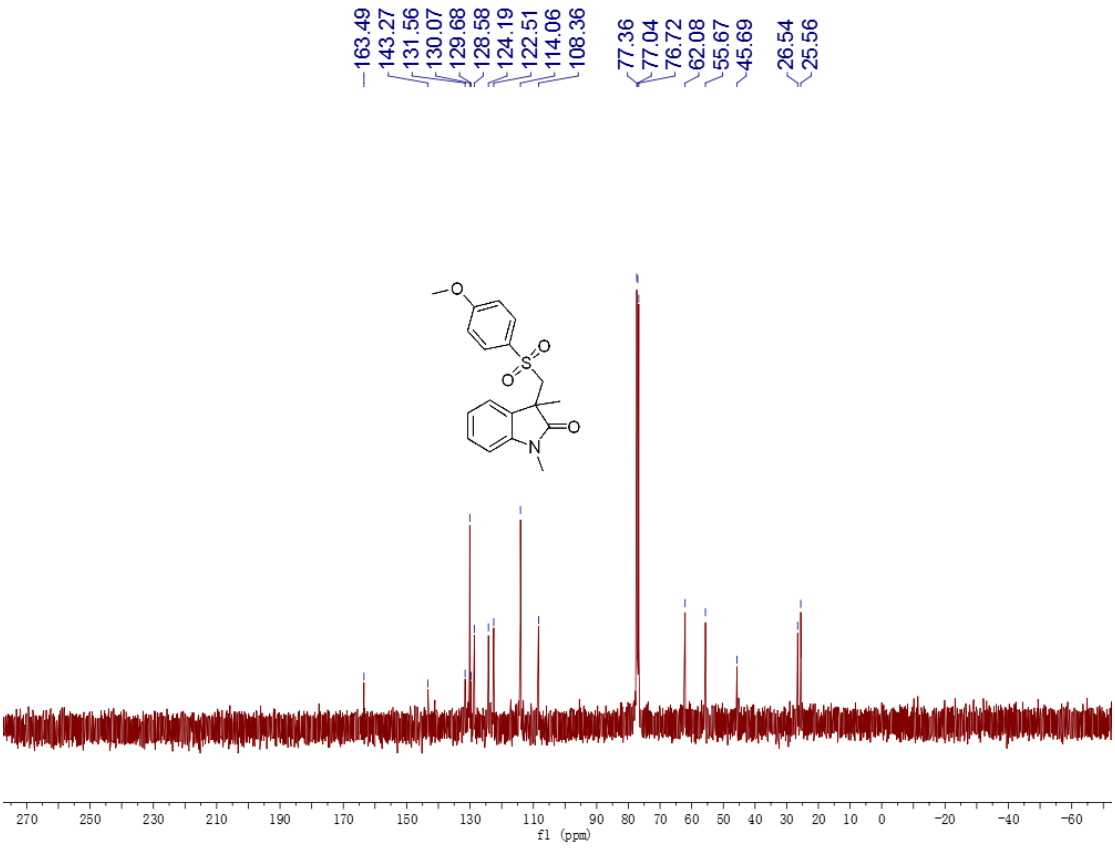
^{13}C NMR spectrum of compound 5a



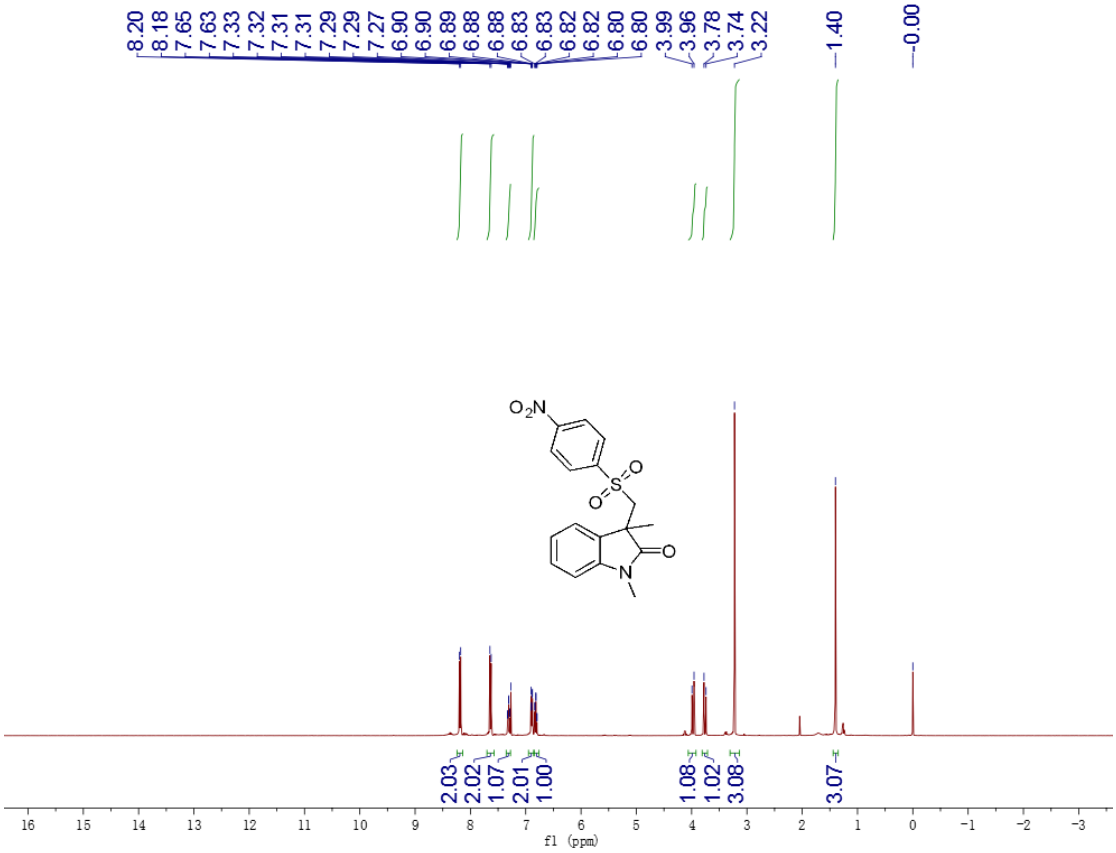
^{1}H NMR spectrum of compound 5b



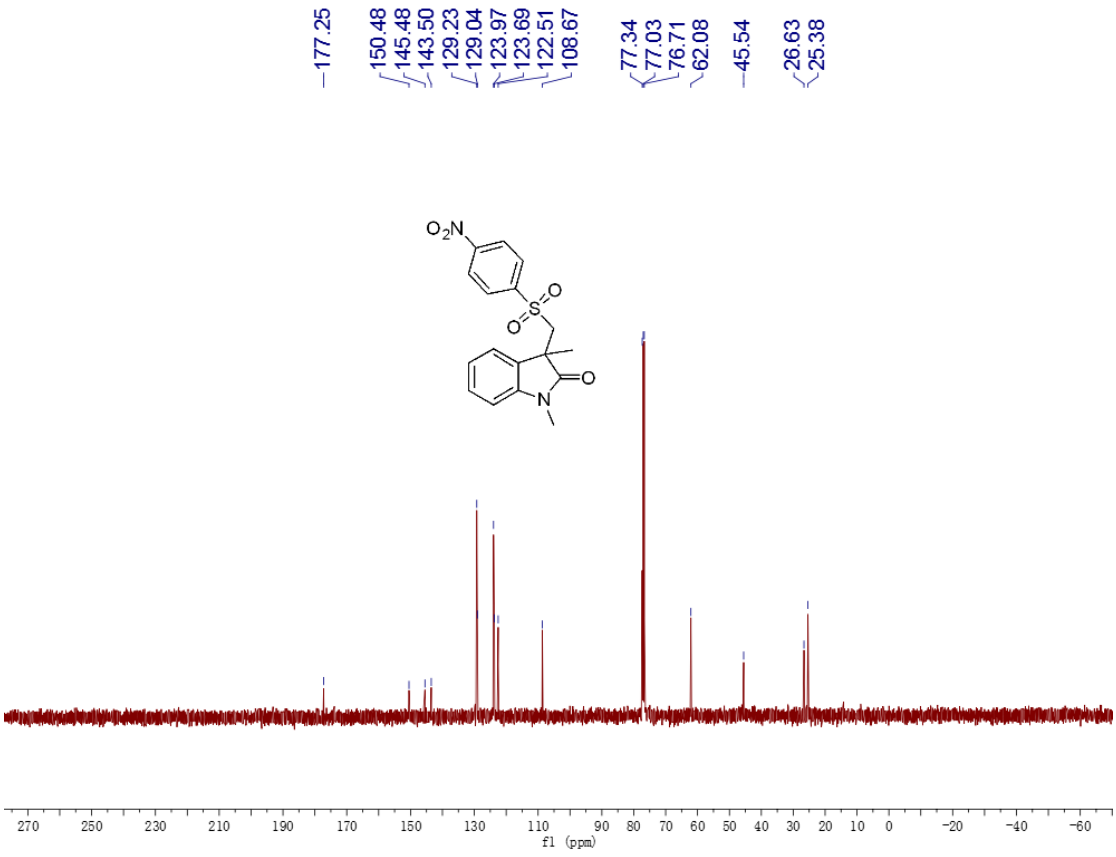
^{13}C NMR spectrum of compound 5b



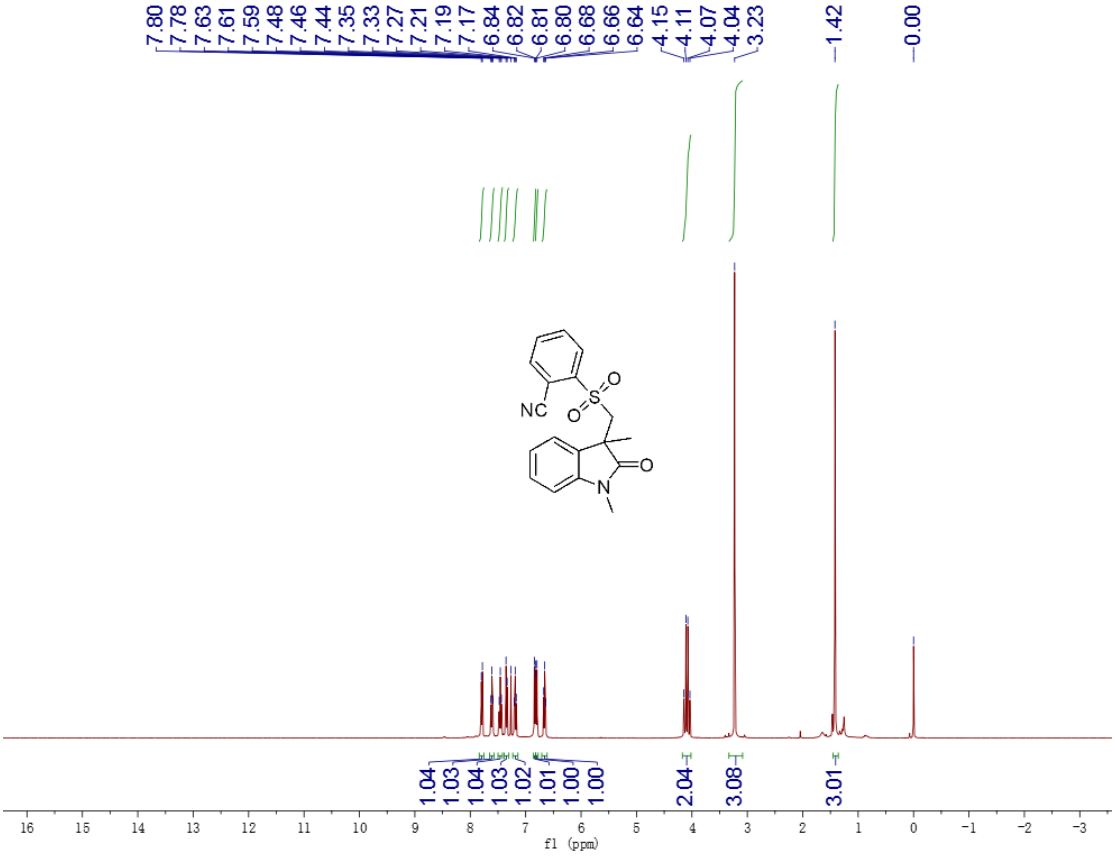
^{1}H NMR spectrum of compound 5c



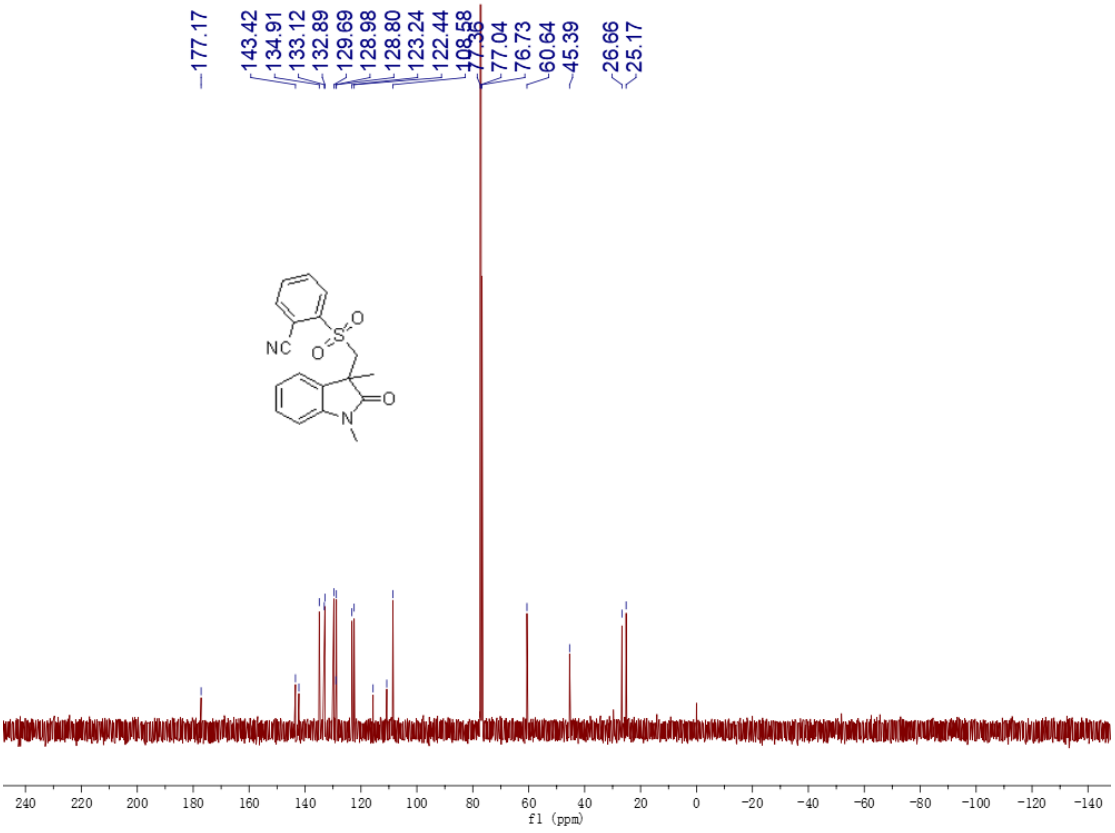
^{13}C NMR spectrum of compound 5c



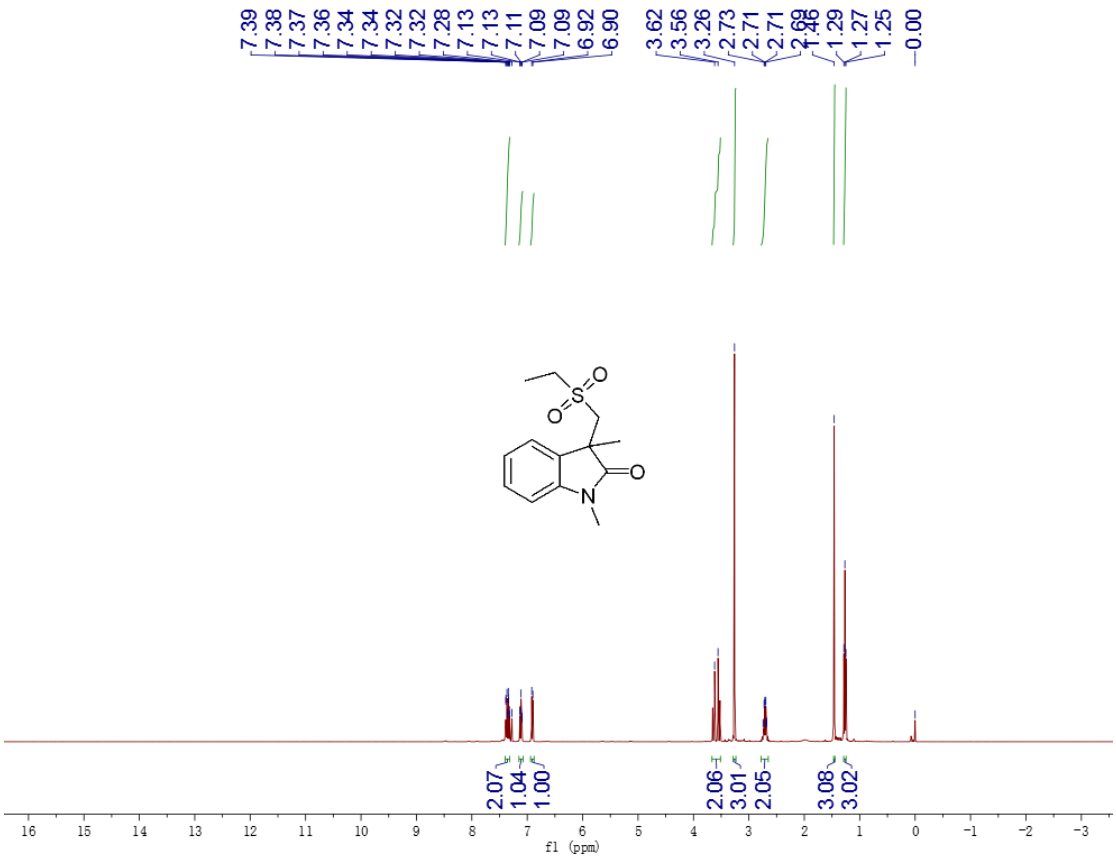
^{1}H NMR spectrum of compound 5d



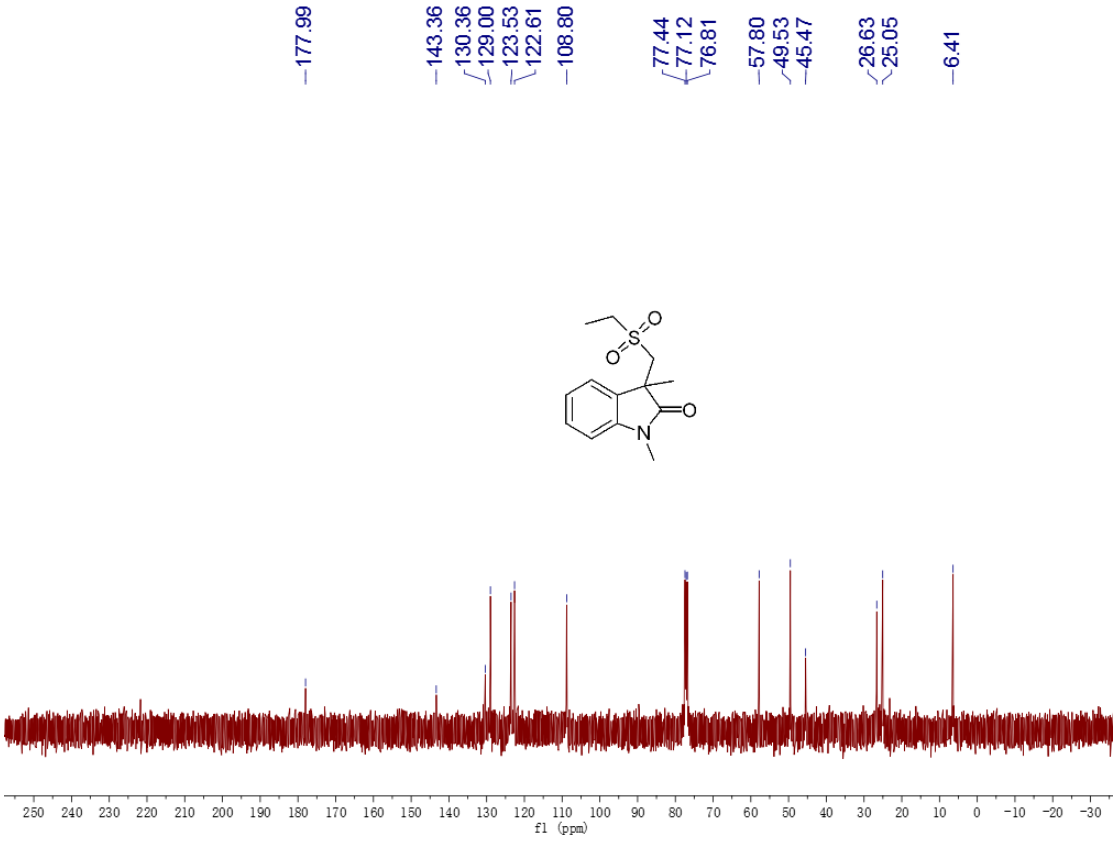
^{13}C NMR spectrum of compound 5d



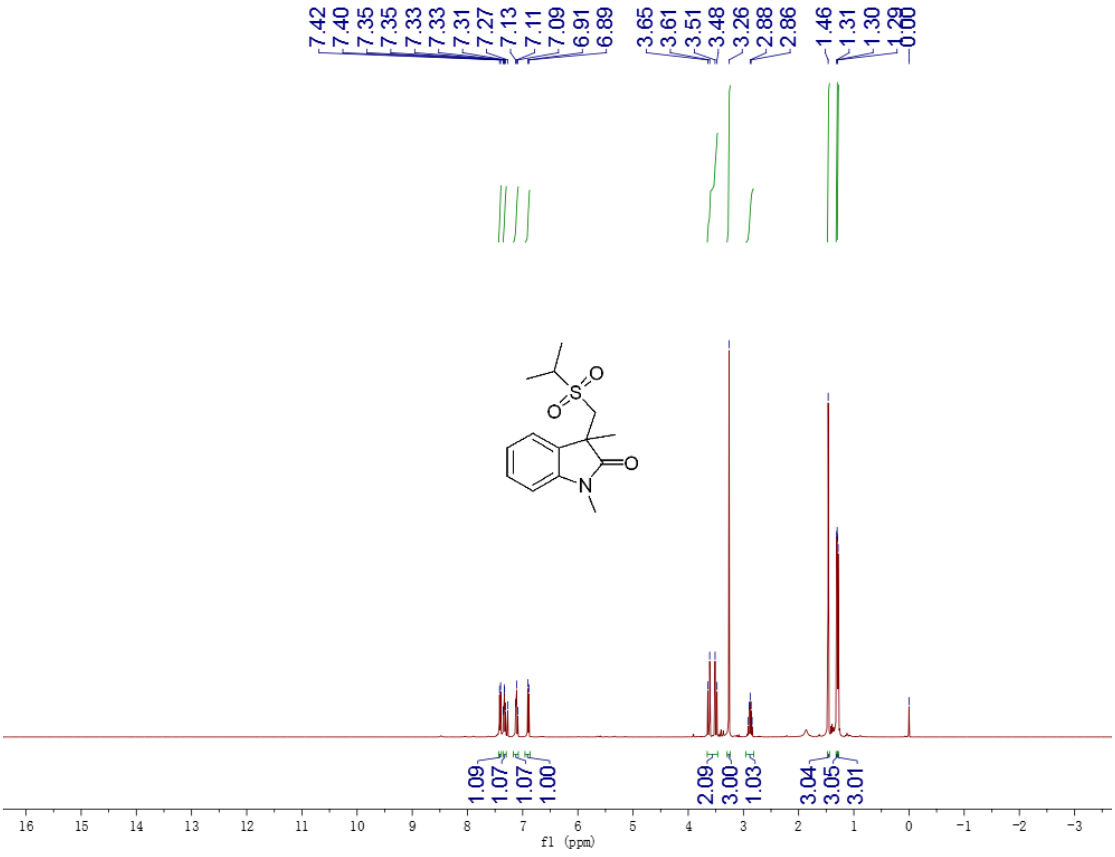
^{1}H NMR spectrum of compound 5e



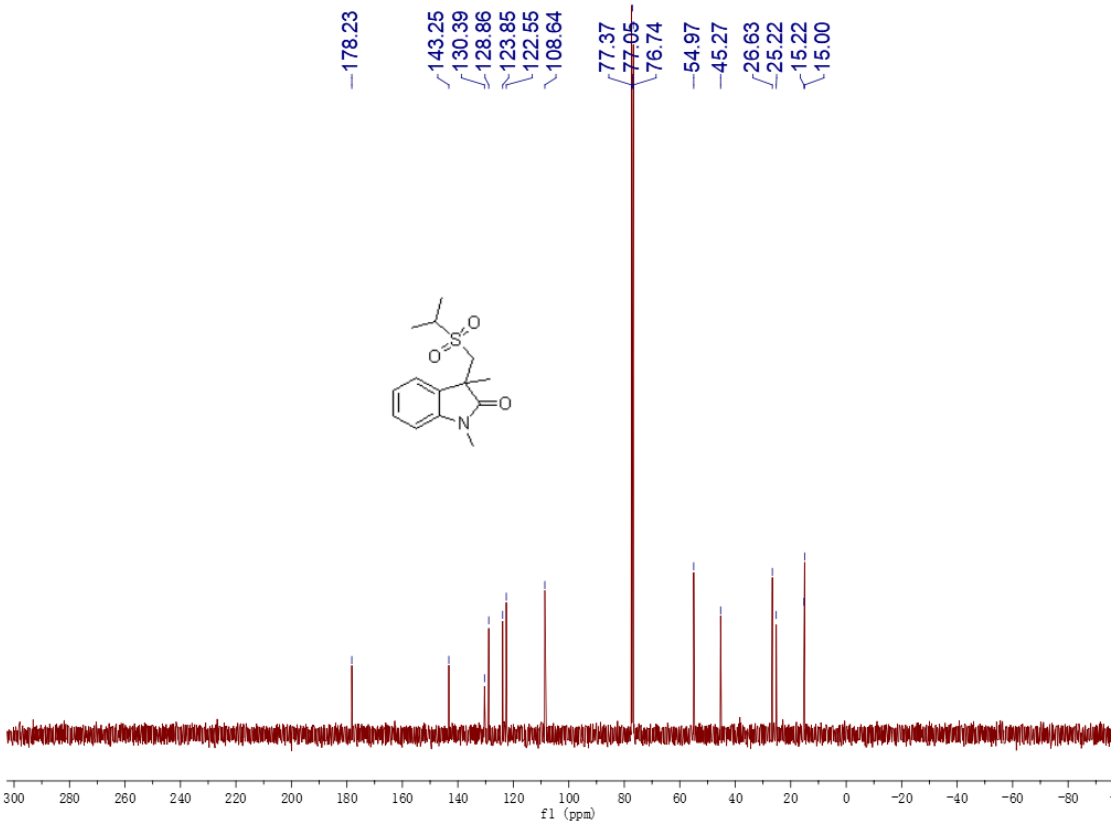
^{13}C NMR spectrum of compound 5e



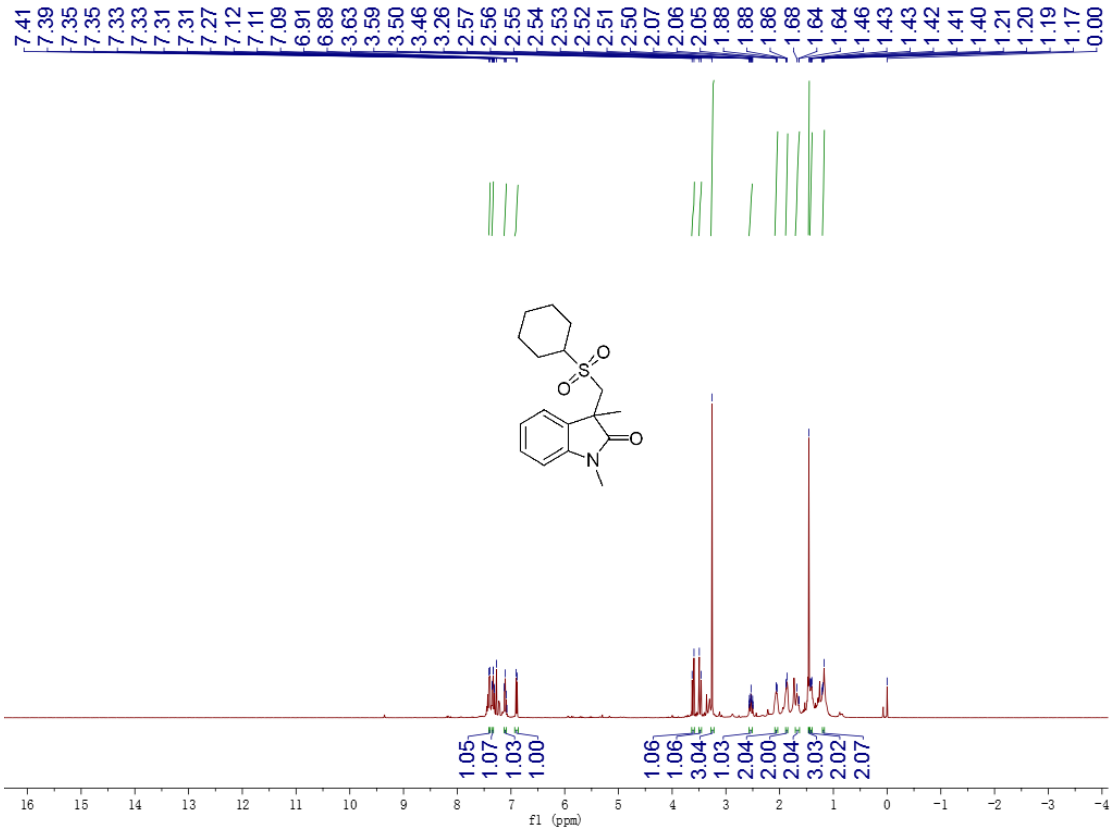
^{1}H NMR spectrum of compound 5f



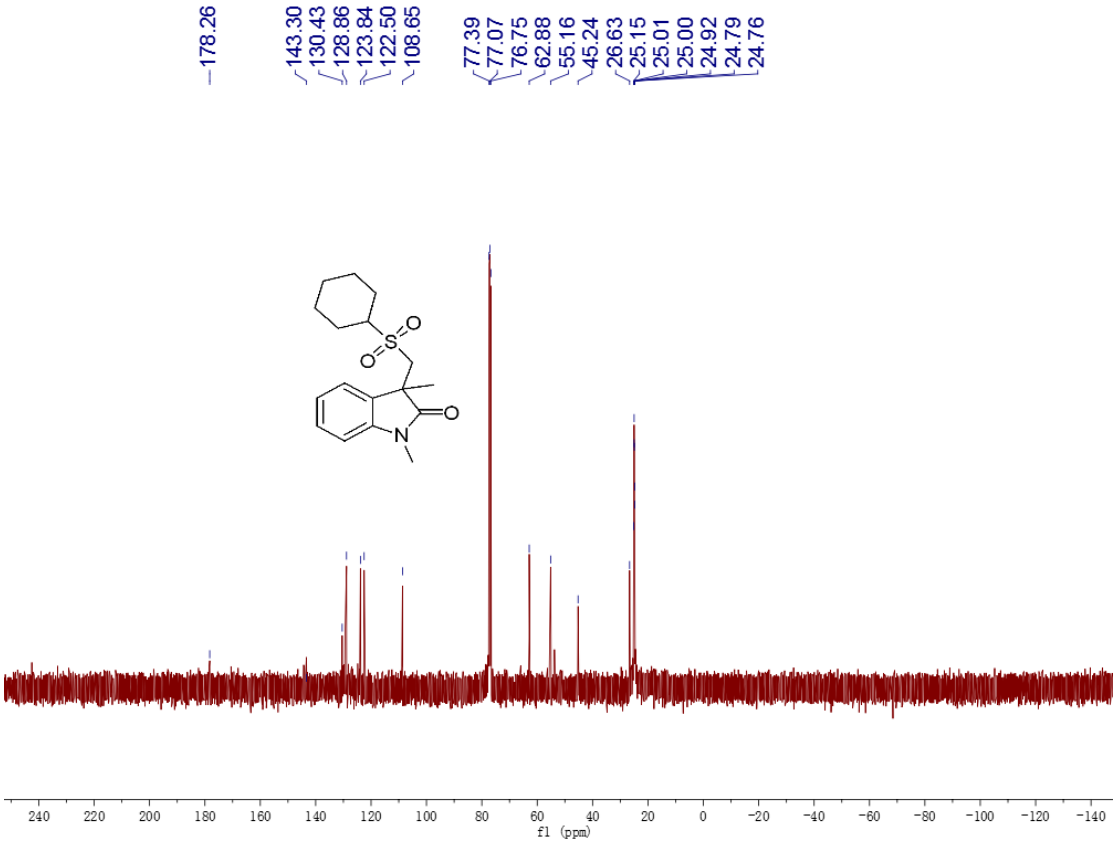
^{13}C NMR spectrum of compound 5f



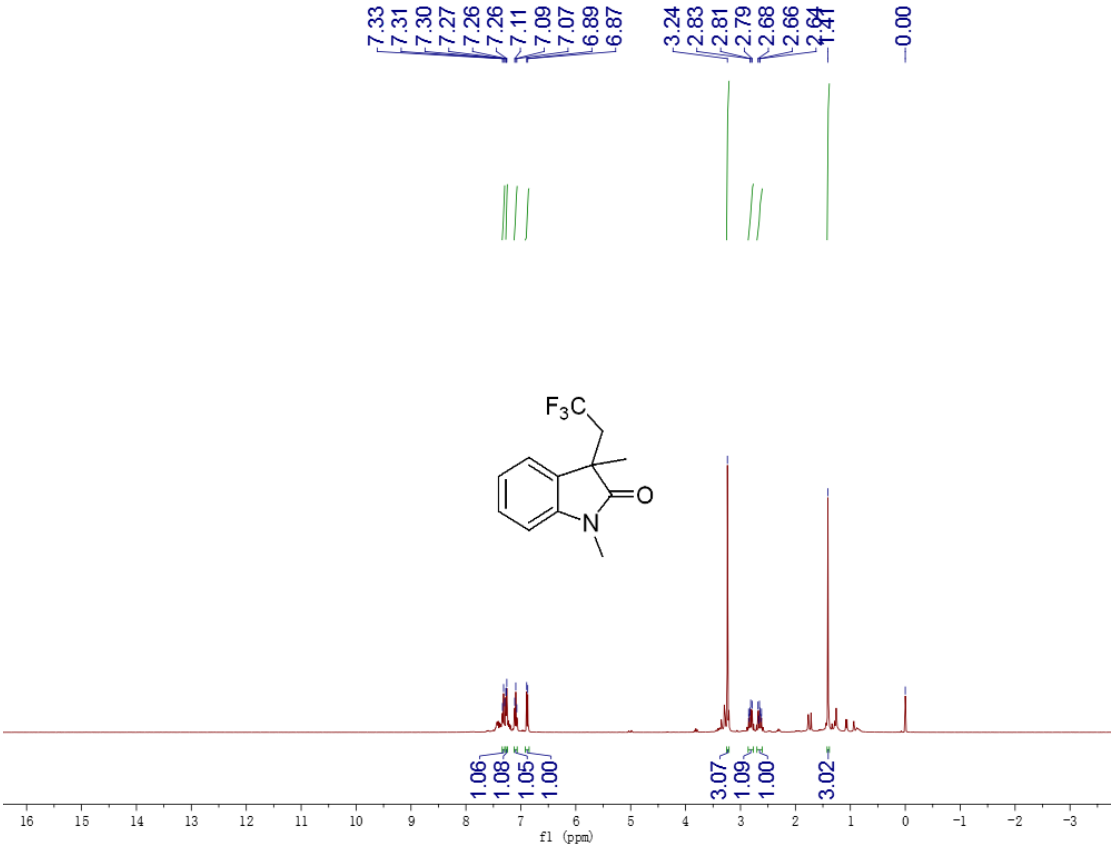
^{1}H NMR spectrum of compound 5g



^{13}C NMR spectrum of compound 5g



^{1}H NMR spectrum of compound 5h



^{13}C NMR spectrum of compound 5h