

Supporting Information for

**Lewis Acid-Catalyzed Regioselective C–H Carboxamidation of Indolizines with
Dioxazolones via Acyl Nitrene Type Rearrangement**

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1. General considerations

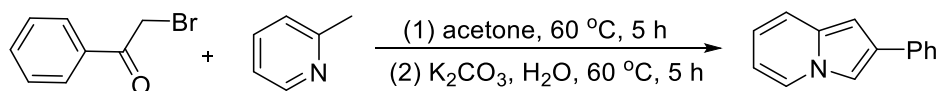
^1H and ^{13}C NMR spectra were recorded using a Bruker DRX-400 spectrometer using CDCl_3 as solvent. Chemical shifts were recorded in parts per million (ppm, δ) relative to tetramethylsilane (δ 0.00) or chloroform (δ = 7.26, singlet). The data of HRMS was carried out on a high-resolution mass spectrometer (LCMS-IT-TOF). IR spectra were obtained either as potassium bromide pellets or as liquid films between two potassium bromide pellets with a Bruker TENSOR 27 spectrometer. Melting points were determined with a Büchi Melting Point B-545 instrument. The instrument for electrolysis is dual display potentiostat (CHI 660E) (made in China). Unless otherwise noted, materials were obtained from commercial suppliers and used without further purification.

2. Experimental procedures and characterization data

2.1 Experimental procedures

Synthesis of substrate 1 according to the following procedure:

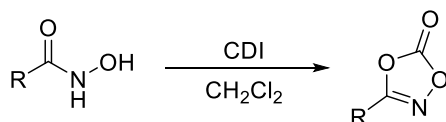
The substrates **1a-1ag** are known and were prepared according to the procedures in the literature.¹⁻³ As exemplified for **1a**:



A solution of 2-picoline (0.93 g, 10 mmol, 1.0 equiv.) and 2-bromoacetophenone (1.99 g, 10 mmol, 1.0 equiv.) in acetone (50 mL) were added to a 100 mL round bottom flask and heated with a heating mantle at 60 °C for 5 hours. The precipitate obtained by filtration separation was redissolved in 20 mL of hot water (60 °C). Then, K₂CO₃ (1.38 g, 10 mmol, 1.0 equiv.) was added and heated at 60 °C for 5 hours. After filtration and drying in vacuo, a white solid compound was obtained in 50% overall yield (0.965 g, 5 mmol) without further purification.

Synthesis of 3-substituted-1,4,2-dioxazol-5-ones according to the following procedure:

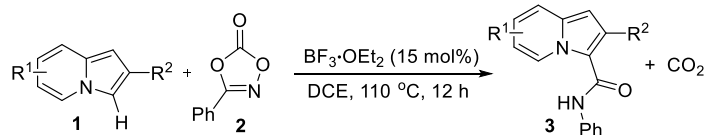
The substrates **2a-2m** are known and were prepared according to the procedures in the literature.⁴⁻⁶



To a stirred solution of hydroxamic acid (5.0 mmol) in dichloromethane (50 mL) was added 1,1'-carbonyldiimidazole (0.81 g, 5.0 mmol) in one portion at room temperature. After stirring for 30 min, the reaction mixture was quenched with 1 N HCl (30 mL), extracted with dichloromethane three times (50 mL x 3) and dried over sodium sulfate. The solvent was removed under reduced pressure to afford 3-substituted 1,4,2-dioxazol-5-ones. Product was recrystallized with acetone/hexane, if necessary.

Synthesis of product 3 according to the following procedure:

As exemplified for **3a**:



A pressure tube was charged with 2-phenylindazine **1a** (0.058 g, 0.3 mmol), dioxazolone **2a** (0.734 g, 0.45 mmol) and DCE (2 mL). $\text{BF}_3 \cdot \text{OEt}_2$ (0.006 g, 0.045 mmol) was added and the mixtures were heated with a heating mantle at 110 °C for 12 h. After cooling to room temperature, the solvent was volatilized and the crude product was purified by flash column chromatography on silica gel (eluent: PE/DCM = 1/1, v/v), and the target compound **3a** was obtained.

Scale-up experiment:

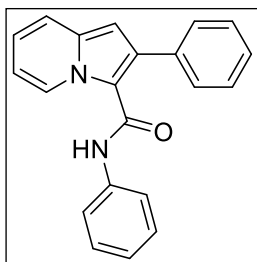
An oven-dried 50 mL Schlenk flask was charged with a stirring bar, 2-phenylindazine **1a** (1.158 g, 6.0 mmol), dioxazolone **2a** (1.467 g, 9.0 mmol) and DCE (15 mL). $\text{BF}_3 \cdot \text{OEt}_2$ (0.127 g, 0.9 mmol) was added and the mixture was heated with a heating mantle at 110 °C for 12 h. After cooling to room temperature, the solution was then diluted with EtOAc and water, extracted with EtOAc. The combined organic extracts were dried over anhydrous Na_2SO_4 , filtered, and concentrated. The crude product was purified by flash column chromatography on silica gel (eluent: PE/DCM = 1/1, v/v), and the target compound **3a** (1.634 g, 87% yield) was obtained.

Fluorescence experimental procedure:

Weigh compound **4k** of 0.05 g, add 1 mL DCM into EP tube to dissolve, then transfer to 100 mL volumetric bottle, continue to dilute with DCM to scale, shake well, and set aside. Take 1 mL of the above solution, transfer it to a 100 mL volumetric bottle and dilute it to the scale, then mix it into $10^{-6} \text{ mol} \cdot \text{L}^{-1}$ standard reserve solution for fluorescence test. Turn on the power, turn on the fluorophotometer and the computer, preheat the instrument, initialize the instrument, and measure the fluorescence intensity according to the excitation and emission fluorescence spectrometry. Determine the fluorescence intensity of compound **4k** in different solvents, replace DCM with other solvents and repeat the above experimental steps.

2.2 Characterization data

***N*,2-Diphenylindolizine-3-carboxamide (3a)**



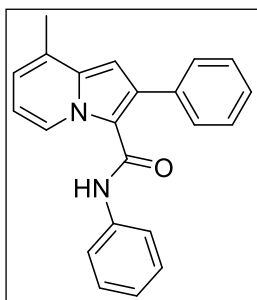
Flash column chromatography on silica gel (eluent: PE/DCM = 1/1, v/v) to afford **3a**.

Yellow liquid (81.7 mg, 87%). ¹H NMR (400 MHz, CDCl₃) δ 9.74 (m, *J* = 7.3, 1.2 Hz, 1H), 7.55 (m, *J* = 6.6, 2.3 Hz, 2H), 7.52 – 7.47 (m, 3H), 7.45 (dd, *J* = 8.8, 1.3 Hz, 1H), 7.21 (dd, *J* = 8.4, 7.0 Hz, 3H), 7.17 – 7.11 (m, 2H), 7.03 – 6.96 (m, 2H), 6.76 (td, *J* = 7.0, 1.4 Hz, 1H), 6.48 (s, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 160.1, 138.3,

136.1, 135.6, 133.5, 130.2, 129.1, 128.9, 128.6, 127.9, 123.5, 121.9, 119.2, 118.4, 113.8, 112.6, 102.9.

HRMS MALDI (*m/z*): calcd for C₂₁H₁₆N₂O [*M* + *H*]⁺: 313.1341, found: 313.1341.

8-Methyl-*N*,2-diphenylindolizine-3-carboxamide (3b)

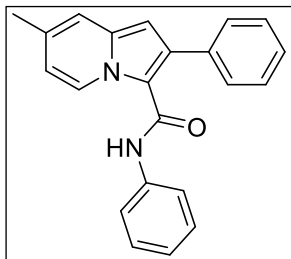


Flash column chromatography on silica gel (eluent: PE/DCM = 1/1, v/v) to afford

3b. Brown solid (83.4 mg, 85%), mp 148.3-149.2 °C. ¹H NMR (400 MHz, CDCl₃) δ 9.62 (d, *J* = 7.1 Hz, 1H), 7.59 – 7.54 (m, 2H), 7.54 – 7.47 (m, 3H), 7.21 (dd, *J* = 8.6, 7.1 Hz, 3H), 7.17 – 7.12 (m, 2H), 7.02 – 6.97 (m, 1H), 6.81 (dt, *J* = 6.8, 1.2 Hz, 1H), 6.71 (t, *J* = 7.0 Hz, 1H), 6.48 (s, 1H), 2.45 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 160.2, 138.4, 136.8, 135.8, 133.1, 130.3, 129.1, 128.9, 128.5, 127.4, 125.8, 123.5,

121.2, 119.2, 114.2, 112.8, 101.5, 18.2. HRMS MALDI (*m/z*): calcd for C₂₂H₁₈N₂O [*M* + *H*]⁺: 327.1497, found: 327.1500.

7-Methyl-*N*,2-diphenylindolizine-3-carboxamide (3c)



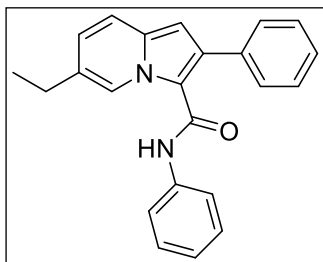
Flash column chromatography on silica gel (eluent: PE/DCM = 1/1, v/v) to afford

3c. Green solid (83.4 mg, 85%), mp 162.2-163.0 °C. ¹H NMR (400 MHz, CDCl₃) δ 9.67 (d, *J* = 7.3 Hz, 1H), 7.56 (m, *J* = 7.9, 2.4, 2.0 Hz, 2H), 7.52 (m, *J* = 7.1, 4.4, 1.4 Hz, 3H), 7.26 – 7.19 (m, 4H), 7.17 – 7.11 (m, 2H), 7.00 (td, *J* = 7.2, 1.3 Hz, 1H), 6.64 (dd, *J* = 7.4, 2.0 Hz, 1H), 6.37 (s, 1H), 2.37 (s, *J* = 1.0 Hz, 3H). ¹³C

NMR (100 MHz, CDCl₃) δ 160.2, 138.5, 136.7, 135.9, 133.8, 132.7, 130.3, 129.2,

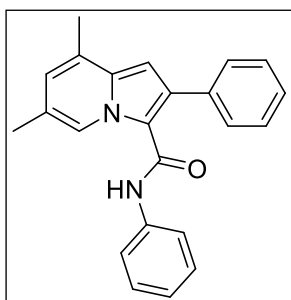
129.0, 128.6, 127.5, 123.4, 119.2, 116.8, 115.4, 113.1, 101.8, 21.2. HRMS MALDI (*m/z*): calcd for C₂₂H₁₈N₂O [*M* + *H*]⁺: 327.1497, found: 327.1492.

6-Ethyl-*N*,2-diphenylindolizine-3-carboxamide (**3d**)



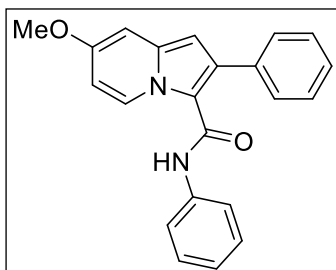
Flash column chromatography on silica gel (eluent: PE/DCM = 1/1, v/v) to afford **3d**. Brown solid (81.8 mg, 80%), mp 116.4-117.2 °C. ¹H NMR (400 MHz, CDCl₃) δ 9.61 (q, *J* = 1.1 Hz, 1H), 7.57 – 7.48 (m, 5H), 7.40 (dd, *J* = 9.0, 0.9 Hz, 1H), 7.26 – 7.17 (m, 3H), 7.17 – 7.13 (m, 2H), 7.00 (m, *J* = 8.6, 7.2, 1.3 Hz, 1H), 6.93 (dd, *J* = 9.0, 1.5 Hz, 1H), 6.44 (s, 1H), 2.66 (q, *J* = 7.5, 0.9 Hz, 2H), 1.29 (t, *J* = 7.6 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 160.2, 138.4, 135.9, 135.2, 133.3, 130.3, 129.1, 129.0, 128.7, 128.5, 125.1, 124.1, 123.5, 119.2, 118.0, 113.5, 102.6, 26.5, 15.5. HRMS MALDI (*m/z*): calcd for C₂₃H₂₀N₂O [*M* + *H*]⁺: 341.1654, found: 314.1657.

6,8-Dimethyl-*N*,2-diphenylindolizine-3-carboxamide (**3e**)



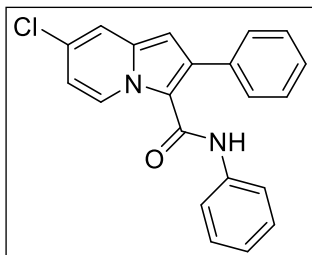
Flash column chromatography on silica gel (eluent: PE/DCM = 1/1, v/v) to afford **3e**. Brown solid (87.0 mg, 85%), mp 177.6-178.1 °C. ¹H NMR (400 MHz, CDCl₃) δ 9.45 (s, 1H), 7.59 – 7.54 (m, 2H), 7.54 – 7.44 (m, 3H), 7.25 – 7.18 (m, 3H), 7.18 – 7.12 (m, 2H), 6.99 (m, *J* = 7.1, 1.3 Hz, 1H), 6.70 (d, *J* = 1.4 Hz, 1H), 6.43 (s, 1H), 2.42 (s, 3H), 2.31 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 160.3, 138.5, 136.0, 135.7, 132.7, 130.3, 129.1, 128.9, 128.4, 126.7, 124.6, 123.6, 123.5, 122.3, 119.2, 113.9, 101.2, 18.8, 18.01. HRMS MALDI (*m/z*): calcd for C₂₃H₂₀N₂O [*M* + *H*]⁺: 341.1654, found: 341.1650.

7-Methoxy-*N*,2-diphenylindolizine-3-carboxamide (**3f**)



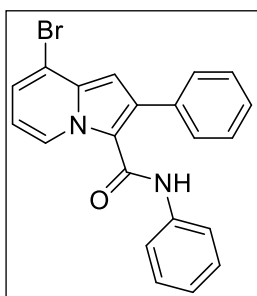
Flash column chromatography on silica gel (eluent: PE/DCM = 1/1, v/v) to afford **3f**. Purple solid (85.4 mg, 83%), mp 198.6-199.3 °C. ¹H NMR (400 MHz, CDCl₃) δ 9.67 (d, *J* = 7.8 Hz, 1H), 7.59 – 7.50 (m, 5H), 7.26 – 7.17 (m, 3H), 7.15 – 7.10 (m, 2H), 6.99 (t, *J* = 7.3 Hz, 1H), 6.73 (d, *J* = 2.7 Hz, 1H), 6.53 (m, *J* = 7.8, 2.7 Hz, 1H), 6.31 (s, 1H), 3.86 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 160.1, 155.5, 138.6, 137.7, 135.9, 134.5, 130.2, 129.5, 129.2, 129.0, 128.6, 123.4, 119.2, 112.5, 107.3, 101.3, 95.4, 55.4. HRMS MALDI (*m/z*): calcd for C₂₂H₁₈N₂O₂ [*M* + *H*]⁺: 343.1447, found: 343.1446.

2-(2-Fluorophenyl)-8-methyl-*N*-phenylindolizine-3-carboxamide (3g)



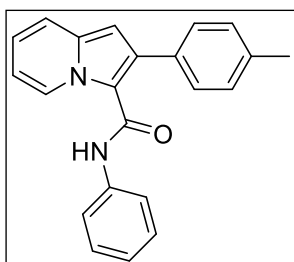
Flash column chromatography on silica gel (eluent: PE/DCM = 1/1, v/v) to afford **3g**. Brown solid (79.1 mg, 76%), mp 151.6-152.4 °C. ¹H NMR (400 MHz, CDCl₃) δ 9.72 (d, *J* = 7.6 Hz, 1H), 7.54 (m, *J* = 4.8, 4.2, 2.9 Hz, 5H), 7.46 (d, *J* = 2.3 Hz, 1H), 7.28 (s, 1H), 7.23 (dd, *J* = 8.5, 7.2 Hz, 2H), 7.17 – 7.11 (m, 2H), 7.02 (td, *J* = 7.3, 1.3 Hz, 1H), 6.76 (dd, *J* = 7.7, 2.3 Hz, 1H), 6.46 (s, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 159.8, 138.1, 136.0, 135.2, 134.3, 130.2, 129.3, 129.1, 128.9, 128.8, 128.3, 123.8, 119.3, 117.1, 114.1, 114.0, 102.8. HRMS MALDI (*m/z*): calcd for C₂₁H₁₅N₂OCl [*M* + *H*]⁺: 347.0951, found: 347.0955.

8-Bromo-*N*,2-diphenylindolizine-3-carboxamide (3h)



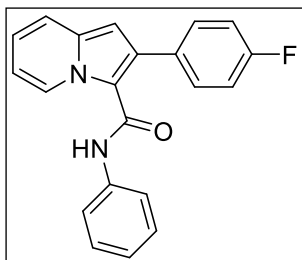
Flash column chromatography on silica gel (eluent: PE/DCM = 1/1, v/v) to afford **3h**. Brown solid (88.0 mg, 75%), mp 159.8-160.2 °C. ¹H NMR (400 MHz, CDCl₃) δ 9.74 (d, *J* = 7.2 Hz, 1H), 7.60 – 7.52 (m, 5H), 7.32 (s, 1H), 7.26 (s, 1H), 7.25 – 7.21 (m, 2H), 7.16 – 7.12 (m, 2H), 7.03 (td, *J* = 7.3, 1.2 Hz, 1H), 6.72 (s, 1H), 6.67 (t, *J* = 7.2 Hz, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 160.0, 138.1, 135.1, 135.0, 133.7, 130.3, 129.3, 129.1, 128.9, 127.1, 124.4, 123.9, 119.5, 119.4, 115.6, 112.5, 104.6. HRMS MALDI (*m/z*): calcd for C₂₁H₁₅N₂OBr [*M* + *H*]⁺: 391.0446, found: 391.0452.

6-Bromo-2-methyl-4-(phenylselanyl)isoquinolin-1(2*H*)-one (3i)



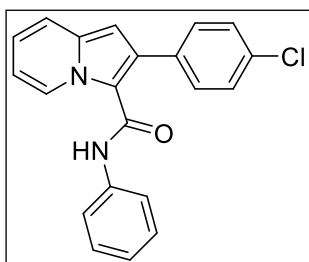
Flash column chromatography on silica gel (eluent: PE/DCM = 1/1, v/v) to afford **3i**. Green solid (73.6 mg, 75%), mp 110.2-110.8 °C. ¹H NMR (400 MHz, CDCl₃) δ 9.76 (dd, *J* = 7.3, 1.1 Hz, 1H), 7.46 (dd, *J* = 7.9, 1.8 Hz, 3H), 7.41 – 7.31 (m, 3H), 7.25 – 7.21 (m, 2H), 7.19 – 7.15 (m, 2H), 7.06 – 6.96 (m, 2H), 6.77 (td, *J* = 6.9, 1.4 Hz, 1H), 6.48 (s, 1H), 2.47 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 160.2, 138.5, 138.4, 136.2, 133.6, 132.6, 130.1, 129.9, 129.0, 128.1, 123.6, 121.9, 119.4, 118.4, 113.7, 112.6, 103.0, 21.5. HRMS MALDI (*m/z*): calcd for C₂₂H₁₈N₂O [*M* + *H*]⁺: 327.1497, found: 327.1496.

2-(4-Fluorophenyl)-*N*-phenylindolizine-3-carboxamide (**3j**)



Flash column chromatography on silica gel (eluent: PE/DCM = 1/1, v/v) to afford **3j**. Brown solid (75.5 mg, 76%), mp 129.4-130.3 °C. ¹H NMR (400 MHz, CDCl₃) δ 9.71 (dd, *J* = 7.2, 1.1 Hz, 1H), 7.58 – 7.53 (m, 2H), 7.48 (dt, *J* = 8.8, 1.2 Hz, 1H), 7.26 – 7.22 (m, 4H), 7.19 (dd, *J* = 8.8, 1.7 Hz, 3H), 7.04 (m, *J* = 7.8, 6.7, 3.8, 1.2 Hz, 2H), 6.80 (td, *J* = 7.0, 1.4 Hz, 1H), 6.49 (s, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 163.0 (d, *J* = 249.0 Hz), 160.0, 138.2, 136.2, 132.0 (d, *J* = 8.0 Hz), 132.0 (d, *J* = 67.0 Hz), 129.1, 128.0, 123.8, 122.1, 119.3, 118.5, 116.3 (d, *J* = 22.0 Hz), 112.8, 103.0. HRMS MALDI (*m/z*): calcd for C₂₁H₁₅N₂OF [M + H]⁺: 331.1247, found: 331.1250.

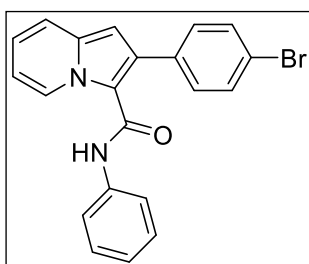
2-(4-Chlorophenyl)-*N*-phenylindolizine-3-carboxamide (**3k**)



Flash column chromatography on silica gel (eluent: PE/DCM = 1/1, v/v) to afford **3k**. Green solid (80.2 mg, 77%), mp 172.9-173.3 °C. ¹H NMR (400 MHz, CDCl₃) δ 9.66 (d, *J* = 7.3 Hz, 1H), 7.51 – 7.44 (m, 5H), 7.27 – 7.23 (m, 2H), 7.22 – 7.16 (m, 3H), 7.07 – 6.99 (m, 2H), 6.78 (td, *J* = 7.0, 1.3 Hz, 1H), 6.47 (s, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 160.0, 138.1, 136.2, 134.7, 134.6, 134.1, 132.0, 131.5, 129.4, 129.1, 127.9, 123.9, 122.1, 119.5, 118.5, 112.9, 102.9.

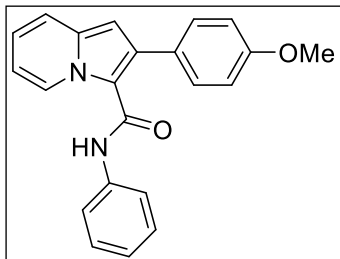
HRMS MALDI (*m/z*): calcd for C₂₁H₁₅N₂OCl [M + H]⁺: 347.0951, found: 347.0948.

2-(4-Bromophenyl)-*N*-phenylindolizine-3-carboxamide (**3l**)



Flash column chromatography on silica gel (eluent: PE/DCM = 1/1, v/v) to afford **3l**. Green solid (82.1 mg, 70%), mp 169.8-170.5 °C. ¹H NMR (400 MHz, CDCl₃) δ 9.67 (d, *J* = 7.2 Hz, 1H), 7.65 (dd, *J* = 8.5, 2.1 Hz, 2H), 7.50 – 7.44 (m, 3H), 7.30 – 7.26 (m, 2H), 7.23 – 7.19 (m, 2H), 7.17 (s, 1H), 7.04 (m, *J* = 15.3, 8.4, 4.0 Hz, 2H), 6.80 (t, *J* = 6.9 Hz, 1H), 6.49 (d, *J* = 1.9 Hz, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 160.0, 138.1, 136.2, 134.5, 132.4, 132.0, 131.8, 129.2, 127.9, 124.0, 122.9, 122.1, 119.5, 118.5, 113.7, 112.9, 102.8. HRMS MALDI (*m/z*): calcd for C₂₁H₁₅N₂OBr [M + H]⁺: 391.0446, found: 391.0447.

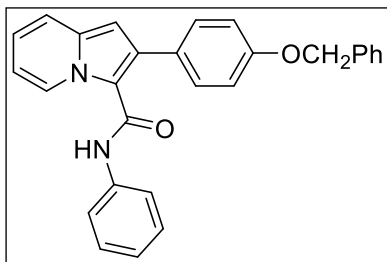
2-(4-Methoxyphenyl)-*N*-phenylindolizine-3-carboxamide (**3m**)



Flash column chromatography on silica gel (eluent: PE/DCM = 1/1, v/v) to afford **3m**. Green solid (78.2 mg, 76%), mp 158.2-160.0 °C. ¹H NMR (400 MHz, CDCl₃) δ 9.74 (dd, *J* = 7.2, 1.1 Hz, 1H), 7.50 – 7.40 (m, 4H), 7.24 – 7.19 (m, 4H), 7.08 – 6.94 (m, 4H), 6.75 (td, *J* = 6.9, 1.4 Hz, 1H), 6.44 (s, 1H), 3.87 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 160.2 159.9 138.4 136.1, 133.3, 131.4, 129.0, 128.0, 127.6, 123.5, 121.8, 119.3, 118.3, 114.6, 113.7, 112.5,

103.1, 55.5. HRMS MALDI (*m/z*): calcd for C₂₂H₁₈N₂O₂ [*M* + *H*]⁺: 343.1447, found: 343.1449.

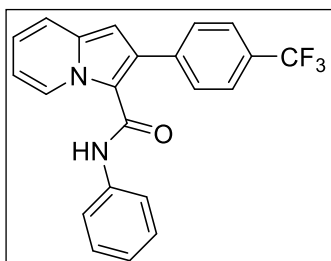
2-(4-(Benzyloxy)phenyl)-*N*-phenylindolizine-3-carboxamide (**3n**)



Flash column chromatography on silica gel (eluent: PE/DCM = 1/1, v/v) to afford **3n**. Green solid (95.5 mg, 76%), mp 148.2-149.0 °C. ¹H NMR (400 MHz, CDCl₃) δ 9.76 (d, *J* = 7.3 Hz, 1H), 7.52 – 7.45 (m, 4H), 7.42 (dd, *J* = 9.1, 7.2 Hz, 4H), 7.36 (t, *J* = 7.2 Hz, 1H), 7.26 – 7.15 (m, 4H), 7.15 – 7.11 (m, 2H), 7.07 – 6.97 (m, 2H), 6.78 (td, *J* = 7.0, 1.4 Hz, 1H), 6.47 (s, 1H), 5.17 (s, 2H). ¹³C NMR (100 MHz, CDCl₃) δ 160.2, 159.0,

138.4, 136.7, 136.2, 133.3, 131.5, 129.0, 128.8, 128.3, 128.1, 127.9, 127.6, 123.6, 121.9, 119.4, 118.4, 115.6, 113.7, 112.6, 103.1, 70.2. HRMS MALDI (*m/z*): calcd for C₂₈H₂₂N₂O₂ [*M* + *H*]⁺: 419.1760, found: 419.1760.

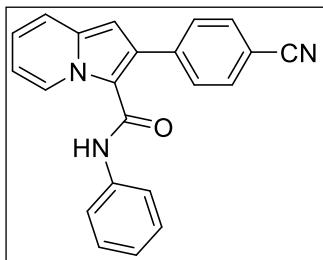
N-Phenyl-2-(4-(trifluoromethyl)phenyl)indolizine-3-carboxamide (**3o**)



Flash column chromatography on silica gel (eluent: PE/DCM = 1/1, v/v) to afford **3o**. Brown solid (91.4 mg, 80%), mp 177.2-178.1 °C. ¹H NMR (400 MHz, CDCl₃) δ 9.59 (d, *J* = 7.3 Hz, 1H), 7.75 (d, *J* = 8.1 Hz, 2H), 7.68 (d, *J* = 8.1 Hz, 2H), 7.47 (dd, *J* = 8.9, 1.2 Hz, 1H), 7.27 – 7.19 (m, 2H), 7.15 (d, *J* = 7.2 Hz, 2H), 7.08 – 6.98 (m, 3H), 6.83 – 6.74 (m, 1H), 6.51 (s, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 159.8, 139.4, 138.0, 136.2, 131.6, 130.6, 130.5 (q, *J* =

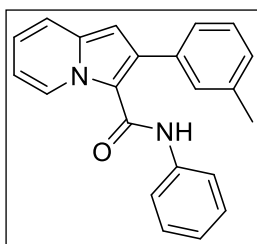
33.0 Hz), 129.1, 127.7, 126.0 (q, *J* = 4.0 Hz), 124.1 (q, *J* = 271.0 Hz), 124.1, 122.2, 119.4, 118.6, 114.0, 113.0, 102.7. HRMS MALDI (*m/z*): calcd for C₂₂H₁₅N₂OF₃ [*M* + *H*]⁺: 381.1215, found: 381.1218.

2-(4-Cyanophenyl)-*N*-phenylindolizine-3-carboxamide (3p)



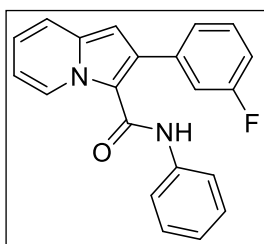
Flash column chromatography on silica gel (eluent: PE/DCM = 1/1, v/v) to afford **3p**. Green solid (71.0 mg, 70%), mp 209.8-210.3 °C. ¹H NMR (400 MHz, CDCl₃) δ 9.50 (d, *J* = 7.2 Hz, 1H), 7.76 (d, *J* = 7.9 Hz, 2H), 7.68 (d, *J* = 7.3 Hz, 2H), 7.48 (d, *J* = 9.0 Hz, 1H), 7.28 – 7.24 (m, 2H), 7.19 (d, *J* = 8.0 Hz, 2H), 7.10 – 6.98 (m, 3H), 6.79 (t, *J* = 7.1 Hz, 1H), 6.51 (s, 1H). ¹³C NMR (100 Hz, CDCl₃) δ 159.6, 140.4 137.8, 136.2, 132.7, 130.8, 129.2, 127.6 127.2, 124.3, 122.3, 119.4, 118.7, 118.6, 113.9, 113.2, 112.0, 102.5. HRMS MALDI (*m/z*): calcd for C₂₂H₁₅N₃O [*M* + *H*]⁺: 338.1293, found: 338.1293.

N-Phenyl-2-(*m*-tolyl)indolizine-3-carboxamide (3q)



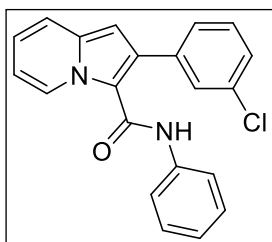
Flash column chromatography on silica gel (eluent: PE/DCM = 1/1, v/v) to afford **3q**. Brown solid (81.4 mg, 83%), mp 102.2-103.0 °C. ¹H NMR (400 MHz, CDCl₃) δ 9.76 (d, *J* = 7.2 Hz, 1H), 7.39 (m, *J* = 26.1, 9.1 Hz, 5H), 7.30 (d, *J* = 7.5 Hz, 1H), 7.21 (d, *J* = 7.5 Hz, 2H), 7.15 (d, *J* = 8.0 Hz, 2H), 7.04 – 6.94 (m, 2H), 6.76 (t, *J* = 7.0 Hz, 1H), 6.47 (s, 1H), 2.40 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 160.1, 139.0, 138.4, 136.1, 135.6, 133.7, 130.9, 129.3, 129.0, 128.9, 128.0, 127.3, 123.5, 121.8, 119.2, 118.4, 113.8, 112.5, 102.9, 21.5. HRMS MALDI (*m/z*): calcd for C₂₂H₁₈N₂O [*M* + *H*]⁺: 327.1497, found: 327.1496.

2-(3-Fluorophenyl)-*N*-phenylindolizine-3-carboxamide (3r)



Flash column chromatography on silica gel (eluent: PE/DCM = 1/1, v/v) to afford **3r**. Brown solid (73.5 mg, 74%), mp 127.7-128.2 °C. ¹H NMR (400 MHz, CDCl₃) δ 9.65 (d, *J* = 7.3 Hz, 1H), 7.75 (d, *J* = 1.7 Hz, 1H), 7.65 – 7.57 (m, 1H), 7.52 – 7.42 (m, 2H), 7.35 (t, *J* = 7.8 Hz, 1H), 7.26 – 7.19 (m, 5H), 7.08 – 6.96 (m, 2H), 6.81 – 6.74 (m, 1H), 6.48 (s, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 159.8, 137.9 (d, *J* = 30.0 Hz), 136.1, 133.0 (d, *J* = 2.0 Hz), 131.6 (d, *J* = 10.0 Hz), 130.5, 129.1, 128.9, 128.9, 127.9, 123.9 (d, *J* = 2.0 Hz), 123.2, 122.1, 122.1, 119.6, 118.6, 118.5, 113.8 (d, *J* = 7.0 Hz), 112.9, 102.8. HRMS MALDI (*m/z*): calcd for C₂₁H₁₅N₂OF [*M* + *H*]⁺: 331.1247, found: 331.1246.

2-(3-Chlorophenyl)-*N*-phenylindolizine-3-carboxamide (3s)

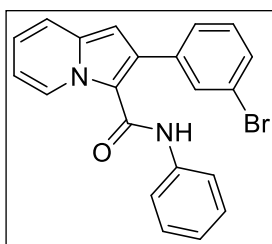


Flash column chromatography on silica gel (eluent: PE/DCM = 1/1, v/v) to afford

3s. Green solid (79.1 mg, 76%), mp 126.8-127.3 °C. ^1H NMR (400 MHz, CDCl_3) δ 9.68 (d, J = 7.2 Hz, 1H), 7.60 (d, J = 2.0 Hz, 1H), 7.50 – 7.45 (m, 3H), 7.27 – 7.24 (m, 3H), 7.24 – 7.17 (m, 3H), 7.10 – 6.99 (m, 2H), 6.81 (t, J = 6.3 Hz, 1H), 6.50 (s, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ 159.9, 138.1, 137.5, 136.2, 135.1, 131.8, 130.4,

130.2, 129.3, 129.1, 128.7, 128.5, 127.9, 124.0, 122.2, 119.6, 118.6, 113.0, 102.8. HRMS MALDI (m/z): calcd for $\text{C}_{21}\text{H}_{15}\text{N}_2\text{OCl}$ [$\text{M} + \text{H}$] $^+$: 347.0951, found: 347.0949.

2-(3-Bromophenyl)-N-phenylindolizine-3-carboxamide (3t)

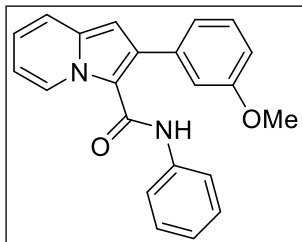


Flash column chromatography on silica gel (eluent: PE/DCM = 1/1, v/v) to afford

3t. Brown solid (82.1 mg, 70%), mp 103.3-103.9 °C. ^1H NMR (400 MHz, CDCl_3) δ 9.65 (d, J = 7.2 Hz, 1H), 7.74 (s, 1H), 7.61 (d, J = 8.0 Hz, 1H), 7.47 (dd, J = 11.6, 8.3 Hz, 2H), 7.35 (t, J = 8.0 Hz, 1H), 7.26 – 7.19 (m, 5H), 7.02 (dt, J = 15.5, 7.7 Hz, 2H), 6.77 (t, J = 7.1 Hz, 1H), 6.48 (s, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ

159.9, 138.2, 136.2, 130.7, 129.1, 127.9, 126.1, 123.9, 122.1, 119.5, 118.6, 117.4, 117.4, 117.4, 117.2, 115.6, 115.4, 112.9, 102.8. HRMS MALDI (m/z): calcd for $\text{C}_{21}\text{H}_{15}\text{N}_2\text{OBr}$ [$\text{M} + \text{H}$] $^+$: 391.0446, found: 391.0443.

2-(3-Methoxyphenyl)-N-phenylindolizine-3-carboxamide (3u)

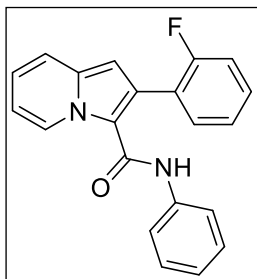


Flash column chromatography on silica gel (eluent: PE/DCM = 1/1, v/v) to

afford **3u.** Brown liquid (80.3 mg, 78%). ^1H NMR (400 MHz, CDCl_3) δ 9.73 (d, J = 7.3 Hz, 1H), 7.41 (t, J = 10.8 Hz, 3H), 7.22 – 7.16 (m, 4H), 7.12 (d, J = 7.6 Hz, 1H), 7.07 (s, 1H), 6.99 (dt, J = 16.0, 8.3 Hz, 3H), 6.75 (t, J = 7.0 Hz, 1H), 6.48 (s, 1H), 3.77 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 160.0, 160.0, 138.3,

136.9, 136.0, 133.3, 130.2, 128.9, 127.9, 123.5, 122.4, 121.9, 119.2, 118.4, 115.3, 114.5, 113.7, 112.6, 102.8, 55.4. HRMS MALDI (m/z): calcd for $\text{C}_{22}\text{H}_{18}\text{N}_2\text{O}_2$ [$\text{M} + \text{H}$] $^+$: 343.1447, found: 343.1444.

2-(2-Fluorophenyl)-N-phenylindolizine-3-carboxamide (3v)

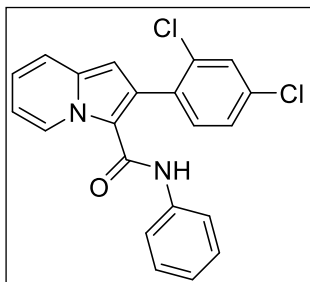


Flash column chromatography on silica gel (eluent: PE/DCM = 1/1, v/v) to afford **3v.**

Brown solid (71.5 mg, 72%), mp 109.7-110.6 °C. ^1H NMR (400 MHz, CDCl_3) δ 9.66 (d, J = 7.3 Hz, 1H), 7.56 – 7.43 (m, 3H), 7.30 (t, J = 7.5 Hz, 1H), 7.25 – 7.20 (m, 4H), 7.17 (d, J = 7.1 Hz, 2H), 7.01 (q, J = 8.8, 8.0 Hz, 2H), 6.77 (td, J = 7.0, 1.4 Hz, 1H), 6.53 (s, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ 160.0 (d, J = 248.0 Hz), 160.0,

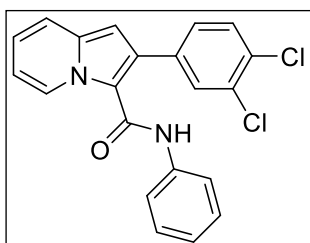
138.2, 136.2, 132.5, 130.8 (d, $J = 8.0$ Hz), 129.0, 127.8, 125.8, 124.8, 123.8, 123.2 (d, $J = 19.0$ Hz), 121.8 (d, $J = 2.0$ Hz), 119.5, 118.6, 116.6 (d, $J = 22.0$ Hz), 114.6, 112.7, 103.2. HRMS MALDI (m/z): calcd for $C_{21}H_{15}N_2OF$ $[M + H]^+$: 331.1247, found: 331.1247.

2-(2,4-Dichlorophenyl)-*N*-phenylindolizine-3-carboxamide (3w)



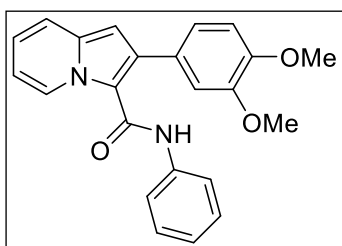
Flash column chromatography on silica gel (eluent: PE/DCM = 1/1, v/v) to afford **3w**. Green solid (77.7 mg, 68%), mp 67.0-68.3 °C. 1H NMR (400 MHz, $CDCl_3$) δ 9.68 (d, $J = 7.3$ Hz, 1H), 7.62 (d, $J = 2.0$ Hz, 1H), 7.51 – 7.39 (m, 3H), 7.26 (t, $J = 3.8$ Hz, 2H), 7.20 – 7.16 (m, 2H), 7.08 – 6.98 (m, 3H), 6.84 – 6.78 (m, 1H), 6.46 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.8, 138.1, 136.2, 135.5, 135.4, 133.3, 130.2, 129.1, 128.5, 127.9, 127.8, 124.0, 122.1, 119.7, 118.7, 114.5, 113.0, 103.1. HRMS MALDI (m/z): calcd for $C_{21}H_{14}N_2OCl_2$ $[M + H]^+$: 381.0561, found: 381.0560.

2-(3,4-Dichlorophenyl)-*N*-phenylindolizine-3-carboxamide (3x)



Flash column chromatography on silica gel (eluent: PE/DCM = 1/1, v/v) to afford **3x**. Brown solid (84.6 mg, 74%), mp 167.4-168.3 °C. 1H NMR (400 MHz, $CDCl_3$) δ 9.55 (d, $J = 7.2$ Hz, 1H), 7.68 (d, $J = 2.0$ Hz, 1H), 7.54 (d, $J = 8.2$ Hz, 1H), 7.45 (d, $J = 8.9$ Hz, 1H), 7.38 (dd, $J = 8.3, 2.0$ Hz, 1H), 7.28 – 7.21 (m, 4H), 7.15 (s, 1H), 7.09 – 6.98 (m, 2H), 6.77 (td, $J = 7.0, 1.3$ Hz, 1H), 6.46 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.8, 137.8, 136.1, 135.5, 133.3, 132.7, 131.8, 130.9, 130.5, 129.4, 129.1, 127.7, 124.2, 122.2, 119.7, 118.6, 113.7, 113.0, 102.7. HRMS MALDI (m/z): calcd for $C_{21}H_{14}N_2OCl_2$ $[M + H]^+$: 381.0561, found: 381.0559.

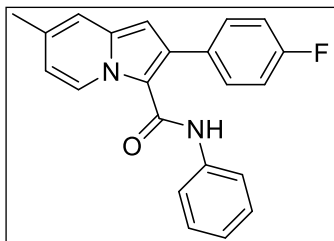
2-(3,4-Dimethoxyphenyl)-*N*-phenylindolizine-3-carboxamide (3y)



Flash column chromatography on silica gel (eluent: PE/DCM = 1/1, v/v) to afford **3y**. Green solid (77.2 mg, 69%), mp 49.6-50.2 °C. 1H NMR (400 MHz, $CDCl_3$) δ 9.79 – 9.73 (m, 1H), 7.53 – 7.42 (m, 2H), 7.26 – 7.22 (m, 4H), 7.14 (dd, $J = 8.1, 2.0$ Hz, 1H), 7.06 (d, $J = 2.0$ Hz, 1H), 7.07 – 6.97 (m, 3H), 6.78 (td, $J = 7.0, 1.4$ Hz, 1H), 6.49 (s, 1H), 3.97 (s, 3H), 3.82 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.2, 149.3, 138.4, 136.1, 133.4, 129.1, 128.0, 127.9, 123.6, 122.5, 122.0, 120.3,

119.3, 118.4, 113.7, 113.1, 112.6, 111.6, 103.0, 56.2, 56.1. HRMS MALDI (m/z): calcd for C₂₃H₂₀N₂O₃ [M + H]⁺: 373.1552, found: 373.1550.

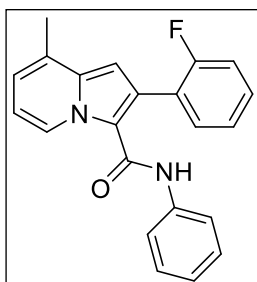
2-(4-Fluorophenyl)-7-methyl-N-phenylindolizine-3-carboxamide (3z)



Flash column chromatography on silica gel (eluent: PE/DCM = 1/1, v/v) to afford **3z**. Green solid (69.3 mg, 67%), mp 128.4-129.3 °C. ¹H NMR (400 MHz, CDCl₃) δ 9.61 (d, *J* = 7.3 Hz, 1H), 7.53 (dd, *J* = 8.5, 5.5 Hz, 2H), 7.26 – 7.17 (m, 8H), 7.04 – 7.00 (m, 1H), 6.63 (m, *J* = 7.4, 1.8 Hz, 1H), 6.33 (s, 1H), 2.36 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 162.9 (d, *J* = 249.0 Hz),

160.0, 138.3, 136.7, 132.8, 132.6, 132.0 (d, *J* = 8.0 Hz), 131.8 (d, *J* = 3.0 Hz), 129.1, 127.4, 123.7, 119.2, 116.8, 116.2 (d, *J* = 21.0 Hz), 115.5, 113.1, 101.8, 21.2. HRMS MALDI (m/z): calcd for C₂₂H₁₇N₂OF [M + H]⁺: 345.1403, found: 345.1405.

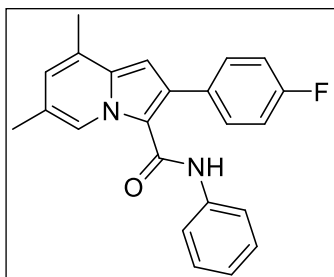
2-(2-Fluorophenyl)-8-methyl-N-phenylindolizine-3-carboxamide (3aa)



Flash column chromatography on silica gel (eluent: PE/DCM = 1/1, v/v) to afford **3aa**. Black solid (71.4 mg, 69%), mp 148.4-149.3 °C. ¹H NMR (400 MHz, CDCl₃) δ 9.54 (d, *J* = 7.2 Hz, 1H), 7.52 (td, *J* = 7.5, 1.8 Hz, 1H), 7.46 (m, *J* = 7.3, 5.2, 1.9 Hz, 1H), 7.29 (td, *J* = 7.6, 1.0 Hz, 1H), 7.22 (t, *J* = 7.8 Hz, 4H), 7.21 – 7.14 (m, 2H), 7.01 (t, *J* = 7.1 Hz, 1H), 6.80 (d, *J* = 6.7 Hz, 1H), 6.70 (t, *J* = 7.0 Hz, 1H), 6.52 (s, 1H), 2.44 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 160.1, 160.0 (d, *J* = 247.0 Hz),

138.3, 136.9, 132.5 (d, *J* = 2.0 Hz), 130.7 (d, *J* = 8.0 Hz), 129.0, 127.6, 125.6, 125.4, 124.8 (d, *J* = 4.0 Hz), 123.7, 123.4 (d, *J* = 16.0 Hz), 121.1, 119.4, 116.6 (d, *J* = 22.0 Hz), 115.0, 112.9, 101.7, 18.2. HRMS MALDI (m/z): calcd for C₂₂H₁₇N₂OF [M + H]⁺: 345.1403, found: 345.1403.

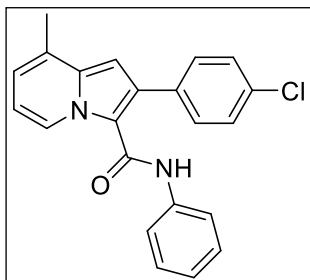
2-(4-Fluorophenyl)-6,8-dimethyl-N-phenylindolizine-3-carboxamide (3ab)



Flash column chromatography on silica gel (eluent: PE/DCM = 1/1, v/v) to afford **3ab**. Purple solid (70.0 mg, 65%), mp 144.8-145.0 °C. ¹H NMR (400 MHz, CDCl₃) δ 9.39 (s, 1H), 7.56 – 7.52 (m, 2H), 7.27 – 7.15 (m, 7H), 7.07 – 6.98 (m, 1H), 6.71 (s, 1H), 6.40 (s, 1H), 2.42 (s, 3H), 2.31 (s, 3H). ¹³C NMR

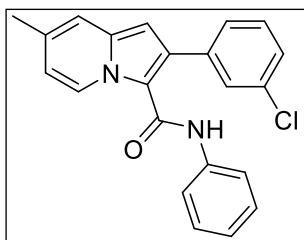
(100 MHz, CDCl₃) δ 162.8 (d, J = 249.0 Hz), 160.2, 149.3, 138.3, 135.8, 132.0 (d, J = 8.0 Hz), 131.9, 131.5, 129.1, 126.7, 124.7, 123.6 (d, J = 20.0 Hz), 122.5, 119.3, 116.1 (d, J = 21.0 Hz), 113.9, 101.3, 18.8, 18.1. HRMS MALDI (m/z): calcd for C₂₃H₁₉N₂OF [M + H]⁺: 359.1560, found: 359.1559.

2-(4-Chlorophenyl)-8-methyl-*N*-phenylindolizine-3-carboxamide (3ac)



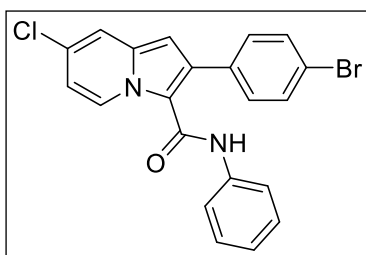
Flash column chromatography on silica gel (eluent: PE/DCM = 1/1, v/v) to afford **3ac**. Purple solid (84.5 mg, 78%), mp 123.9-124.8 °C. ¹H NMR (400 MHz, CDCl₃) δ 9.51 (d, J = 7.2 Hz, 1H), 7.53 – 7.45 (m, 4H), 7.27 – 7.20 (m, 2H), 7.23 – 7.16 (m, 3H), 7.03 (t, J = 7.1 Hz, 1H), 6.81 (d, J = 6.6 Hz, 1H), 6.70 (t, J = 7.0 Hz, 1H), 6.45 (s, 1H), 2.44 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 160.0, 138.2, 136.9, 134.6, 134.2, 131.5, 131.5, 129.3, 129.1, 127.5, 125.7, 123.8, 121.3, 119.4, 114.2, 112.9, 101.3, 18.2. HRMS MALDI (m/z): calcd for C₂₂H₁₇N₂OCl [M + H]⁺: 361.1108, found: 361.1107.

2-(3-Chlorophenyl)-7-methyl-*N*-phenylindolizine-3-carboxamide (3ad)



Flash column chromatography on silica gel (eluent: PE/DCM = 1/1, v/v) to afford **3ad**. Green solid (73.6 mg, 68%), mp 126.8-127.7 °C. ¹H NMR (400 MHz, CDCl₃) δ 9.58 (d, J = 7.3 Hz, 1H), 7.57 (d, J = 1.9 Hz, 1H), 7.50 – 7.39 (m, 3H), 7.27 – 7.14 (m, 6H), 7.03 (t, J = 7.1 Hz, 1H), 6.63 (dd, J = 7.4, 1.8 Hz, 1H), 6.34 (s, 1H), 2.35 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 159.9, 138.2, 137.7, 136.7, 135.0, 132.8, 132.0, 130.3, 130.2, 129.0, 128.5, 128.4, 127.4, 123.7, 119.4, 116.9, 115.6, 113.1, 101.6, 21.2. HRMS MALDI (m/z): calcd for C₂₂H₁₇N₂OCl [M + H]⁺: 361.1108, found: 361.1108.

2-(4-Bromophenyl)-7-chloro-*N*-phenylindolizine-3-carboxamide (3ae)

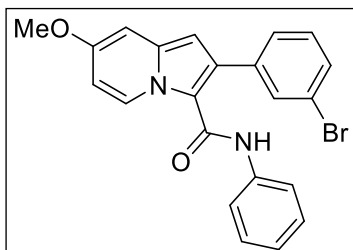


Flash column chromatography on silica gel (eluent: PE/DCM = 1/1, v/v) to afford **3ae**. Green liquid (89.2 mg, 70%). ¹H NMR (400 MHz, CDCl₃) δ 9.76 (d, J = 7.3 Hz, 1H), 7.60 – 7.47 (m, 4H), 7.47 (d, J = 8.8 Hz, 1H), 7.26 – 7.20 (m, 2H), 7.15 (d, J = 7.1 Hz, 2H), 7.06 – 6.96 (m, 2H), 6.79 (t, J = 7.0 Hz, 1H), 6.51 (s, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 160.1, 138.4,

136.2, 135.7, 133.5, 130.3, 129.2, 129.0, 128.6, 128.1, 123.6, 122.0, 119.3, 118.5, 113.8, 112.7, 103.0.

HRMS MALDI (m/z): calcd for $C_{21}H_{14}N_2OBrCl$ $[M + H]^+$: 425.0056, found: 425.0061.

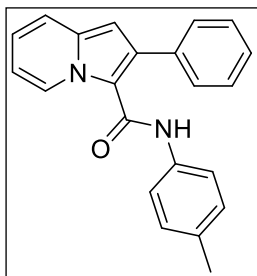
2-(3-Bromophenyl)-7-methoxy-*N*-phenylindolizine-3-carboxamide (3af)



Flash column chromatography on silica gel (eluent: PE/DCM = 1/1, v/v) to afford **3af**. Purple solid (91.0 mg, 72%), mp 179.4-180.1 °C. 1H NMR (400 MHz, $CDCl_3$) δ 9.59 (d, J = 7.8 Hz, 1H), 7.74 (t, J = 1.9 Hz, 1H), 7.64 – 7.60 (m, 1H), 7.49 (dt, J = 7.7, 1.3 Hz, 1H), 7.37 (t, J = 7.8 Hz, 1H), 7.26 – 7.22 (m, 2H), 7.22 – 7.17 (m, 2H), 7.13 (s, 1H), 7.07 – 6.98 (m, 1H), 6.71

(d, J = 2.7 Hz, 1H), 6.52 (dd, J = 7.9, 2.7 Hz, 1H), 6.28 (s, 1H), 3.85 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.8, 155.5, 138.3, 138.0, 137.7, 133.0, 132.5, 131.5, 130.5, 129.3, 129.1, 128.9, 123.7, 123.1, 119.4, 112.4, 107.6, 101.1, 95.4, 55.4. HRMS MALDI (m/z): calcd for $C_{22}H_{17}N_2O_2Br$ $[M + H]^+$: 421.0552, found: 421.0555.

2-Phenyl-*N*-(p-tolyl)indolizine-3-carboxamide (4a)

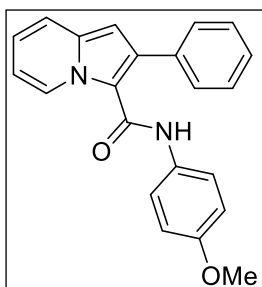


Flash column chromatography on silica gel (eluent: PE/DCM = 1/1, v/v) to afford **4a**.

Green solid (65.7 mg, 67%), mp 114.3-115.0 °C. 1H NMR (400 MHz, $CDCl_3$) δ 9.74 (d, J = 7.3 Hz, 1H), 7.58 – 7.50 (m, 5H), 7.48 (dd, J = 9.8, 2.2 Hz, 1H), 7.22 (s, 1H), 7.03 (d, J = 9.6 Hz, 5H), 6.78 (td, J = 7.0, 1.3 Hz, 1H), 6.50 (s, 1H), 2.27 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.1, 136.1, 135.8, 135.7, 133.4, 133.2, 130.3, 129.5, 129.2, 128.6, 128.0, 121.8, 119.3, 118.5, 113.9, 112.6, 102.8, 21.0. HRMS MALDI

(m/z): calcd for $C_{22}H_{18}N_2O$ $[M + H]^+$: 327.1497, found: 327.1498.

N-(4-Methoxyphenyl)-2-phenylindolizine-3-carboxamide (4b)

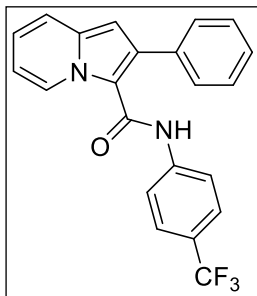


Flash column chromatography on silica gel (eluent: PE/DCM = 1/1, v/v) to afford

4b. Green solid (66.9 mg, 65%), mp 132.7-133.5 °C. 1H NMR (400 MHz, $CDCl_3$) δ 9.71 (dd, J = 7.3, 1.2 Hz, 1H), 7.56 (m, J = 7.8, 1.9 Hz, 2H), 7.53 – 7.47 (m, 3H), 7.49 – 7.41 (m, 1H), 7.17 (s, 1H), 7.11 – 7.06 (m, 2H), 7.03 – 6.94 (m, 1H), 6.82 – 6.71 (m, 3H), 6.49 (s, 1H), 3.74 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.0,

156.0, 136.0, 135.8, 133.2, 131.5, 130.3, 129.1, 128.5, 127.9, 121.7, 121.0, 118.4, 114.2, 113.9, 112.5, 102.8, 55.6. HRMS MALDI (m/z): calcd for C₂₂H₁₈N₂O₂ [M + H]⁺: 343.1447, found: 343.1445.

2-Phenyl-N-(4-(trifluoromethyl)phenyl)indolizine-3-carboxamide (4c)

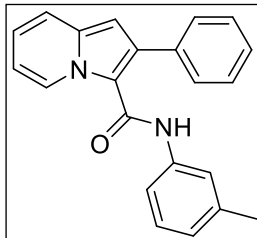


Flash column chromatography on silica gel (eluent: PE/DCM = 1/1, v/v) to afford **4c**.

Green solid (68.6 mg, 60%), mp 149.9-150.9 °C. ¹H NMR (400 MHz, CDCl₃) δ 9.75 (d, *J* = 7.2 Hz, 1H), 7.54 (d, *J* = 1.4 Hz, 5H), 7.52 – 7.38 (m, 4H), 7.21 (d, *J* = 8.4 Hz, 2H), 7.05 (m, *J* = 8.7, 6.8, 1.1 Hz, 1H), 6.81 (td, *J* = 7.0, 1.4 Hz, 1H), 6.51 (s, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 160.0, 141.5, 136.6, 135.6, 134.1, 130.3, 129.3, 128.9, 128.1, 126.2 (q, *J* = 4.0 Hz), 125.2, 124.9, 124.3 (q, *J* = 270.0 Hz), 122.5,

118.6, 118.5, 113.4, 113.0, 103.3. HRMS MALDI (m/z): calcd for C₂₂H₁₅N₂OF₃ [M + H]⁺: 381.1215, found: 381.1218.

2-Phenyl-N-(m-tolyl)indolizine-3-carboxamide (4d)

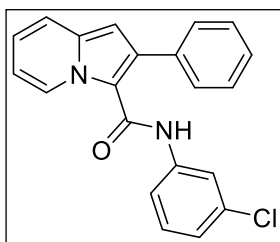


Flash column chromatography on silica gel (eluent: PE/DCM = 1/1, v/v) to afford

4d. Green solid (67.7 mg, 69%), mp 145.0-145.6 °C. ¹H NMR (400 MHz, CDCl₃) δ 9.75 (d, *J* = 7.3 Hz, 1H), 7.61 – 7.49 (m, 5H), 7.48 (d, *J* = 8.8 Hz, 1H), 7.19 – 7.07 (m, 3H), 7.02 (dd, *J* = 8.8, 6.7 Hz, 1H), 6.84 (d, *J* = 7.6 Hz, 1H), 6.79 (t, *J* = 6.8 Hz, 2H), 6.51 (s, 1H), 2.29 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 160.2, 139.0, 138.2,

136.2, 135.7, 133.5, 130.3, 129.2, 128.8, 128.6, 128.0, 124.8, 124.5, 122.0, 120.0, 118.5, 116.4, 112.7, 102.9, 21.7. HRMS MALDI (m/z): calcd for C₂₂H₁₈N₂O [M + H]⁺: 327.1497, found: 327.1501.

N-(3-Chlorophenyl)-2-phenylindolizine-3-carboxamide (4e)

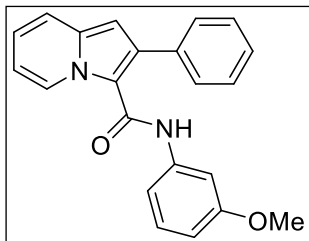


Flash column chromatography on silica gel (eluent: PE/DCM = 1/1, v/v) to afford

4e. Green solid (61.4 mg, 59%), mp 103.5-104.3 °C. ¹H NMR (400 MHz, CDCl₃) δ 9.76 (d, *J* = 7.3 Hz, 1H), 7.57 – 7.53 (m, 6H), 7.49 (d, *J* = 8.9 Hz, 1H), 7.42 (d, *J* = 2.1 Hz, 1H), 7.26 (s, 1H), 7.13 – 7.03 (m, 2H), 6.97 (d, *J* = 7.7 Hz, 1H), 6.81 (q, *J* = 7.4 Hz, 2H), 6.51 (s, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 160.0, 139.5, 136.4,

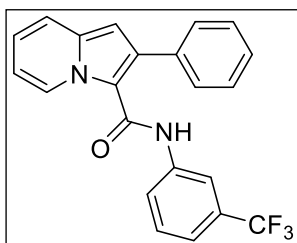
135.6, 134.7, 133.9, 130.3, 129.9, 129.3, 128.8, 128.1, 123.5, 122.3, 119.3, 118.5, 117.1, 113.5, 112.9, 103.2. HRMS MALDI (m/z): calcd for C₂₁H₁₅N₂OCl [M + H]⁺: 347.0951, found: 347.0950.

N-(3-Methoxyphenyl)-2-phenylindolizine-3-carboxamide (4f)



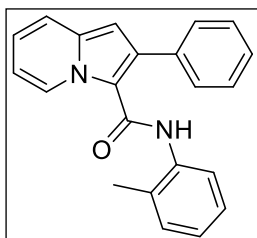
Flash column chromatography on silica gel (eluent: PE/DCM = 1/1, v/v) to afford **4f**. Green liquid (45.7 mg, 60%). ^1H NMR (400 MHz, CDCl_3) δ 9.76 (d, $J = 7.2$ Hz, 1H), 7.61 – 7.44 (m, 7H), 7.09 (t, $J = 8.1$ Hz, 1H), 7.07 – 6.98 (m, 1H), 6.97 (t, $J = 2.3$ Hz, 1H), 6.80 (td, $J = 7.0, 1.4$ Hz, 1H), 6.59 – 6.49 (m, 3H), 3.77 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 160.2, 160.1, 139.6, 136.2, 135.8, 133.6, 130.4, 129.7, 129.2, 128.6, 128.1, 122.0, 118.5, 113.9, 112.7, 111.5, 109.6, 104.8, 103.0, 55.4. HRMS MALDI (m/z): calcd for $\text{C}_{22}\text{H}_{18}\text{N}_2\text{O}_2$ [$\text{M} + \text{H}$] $^+$: 343.1447, found: 343.1443.

2-Phenyl-N-(3-(trifluoromethyl)phenyl)indolizine-3-carboxamide (4g)



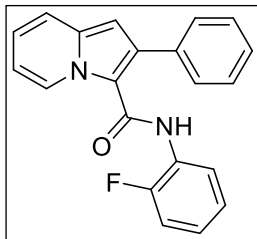
Flash column chromatography on silica gel (eluent: PE/DCM = 1/1, v/v) to afford **4g**. Green solid (70.9 mg, 62%), mp 143.2-144.0 °C. ^1H NMR (400 MHz, CDCl_3) δ 9.76 (d, $J = 7.2$ Hz, 1H), 7.55 (d, $J = 1.6$ Hz, 6H), 7.49 (d, $J = 9.0$ Hz, 1H), 7.36 (s, 1H), 7.30 (t, $J = 7.9$ Hz, 1H), 7.25 (s, 1H), 7.15 (dd, $J = 7.9, 1.9$ Hz, 1H), 7.06 (dd, $J = 8.8, 6.6$ Hz, 1H), 6.82 (td, $J = 7.0, 1.4$ Hz, 1H), 6.52 (s, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ 160.1, 139.0, 136.5, 135.6, 134.0, 131.37 (q, $J = 32.0$ Hz), 130.3, 129.4, 129.3, 128.8, 128.1, 124.01 (q, $J = 270.0$ Hz), 122.4, 122.01, 120.0 (q, $J = 4.0$ Hz), 118.5, 115.9 (q, $J = 4.0$ Hz), 113.5, 113.0, 103.2. HRMS MALDI (m/z): calcd for $\text{C}_{22}\text{H}_{15}\text{N}_2\text{OF}_3$ [$\text{M} + \text{H}$] $^+$: 381.1215, found: 381.1218.

2-Phenyl-N-(o-tolyl)indolizine-3-carboxamide (4h)



Flash column chromatography on silica gel (eluent: PE/DCM = 1/1, v/v) to afford **4h**. Brown liquid (62.8 mg, 64%). ^1H NMR (400 MHz, CDCl_3) δ 9.76 (d, $J = 7.2$ Hz, 1H), 8.15 (d, $J = 8.1$ Hz, 1H), 7.61 – 7.53 (m, 2H), 7.52 – 7.40 (m, 4H), 7.22 – 7.17 (m, 2H), 7.07 – 6.98 (m, 2H), 6.96 (td, $J = 7.4, 1.2$ Hz, 1H), 6.79 (td, $J = 7.0, 1.4$ Hz, 1H), 6.49 (s, 1H), 1.50 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 160.3, 136.5, 136.1, 135.9, 133.5, 130.4, 130.3, 129.3, 128.6, 128.1, 127.5, 126.7, 124.0, 121.9, 121.4, 118.4, 114.0, 112.7, 103.3, 16.7. HRMS MALDI (m/z): calcd for $\text{C}_{22}\text{H}_{18}\text{N}_2\text{O}$ [$\text{M} + \text{H}$] $^+$: 327.1497, found: 327.1496.

***N*-(2-Fluorophenyl)-2-phenylindolizine-3-carboxamide (4i)**

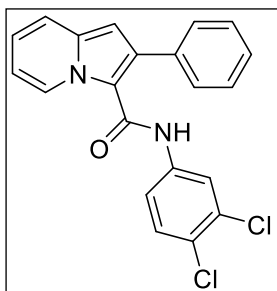


Flash column chromatography on silica gel (eluent: PE/DCM = 1/1, v/v) to afford **4i**.

Green solid (59.6 mg, 60%), mp 87.6-88.3 °C. ¹H NMR (400 MHz, CDCl₃) δ 9.78 (d, *J* = 7.3 Hz, 1H), 8.43 (td, *J* = 8.1, 1.5 Hz, 1H), 7.60 – 7.46 (m, 7H), 7.13 – 7.00 (m, 2H), 6.99 – 6.85 (m, 2H), 6.81 (td, *J* = 6.9, 1.3 Hz, 1H), 6.50 (s, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 160.1, 152.2 (d, *J* = 244.0 Hz), 135.3 (d, *J* = 214.0 Hz), 135.2,

130.0, 129.3, 128.6, 128.1, 127.0 (d, *J* = 10.0 Hz), 124.4 (d, *J* = 4.0 Hz), 123.4 (d, *J* = 7.0 Hz), 122.2, 121.3, 118.5, 114.7 (d, *J* = 19.0 Hz), 113.6, 112.8, 103.5. HRMS MALDI (*m/z*): calcd for C₂₁H₁₅N₂OF [M + H]⁺: 331.1247, found: 331.1248.

***N*-(3,4-Dichlorophenyl)-2-phenylindolizine-3-carboxamide (4j)**

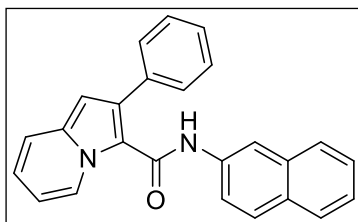


Flash column chromatography on silica gel (eluent: PE/DCM = 1/1, v/v) to afford

4j. Green solid (67.4 mg, 59%), mp 164.6-165.2 °C. ¹H NMR (400 MHz, CDCl₃) δ 9.71 (d, *J* = 7.2 Hz, 1H), 7.54 (s, 5H), 7.52 (d, *J* = 2.5 Hz, 1H), 7.50 – 7.46 (m, 1H), 7.25 – 7.19 (m, 2H), 7.05 (dd, *J* = 8.8, 6.6 Hz, 1H), 6.81 (td, *J* = 7.0, 1.4 Hz, 1H), 6.74 (dd, *J* = 8.7, 2.5 Hz, 1H), 6.51 (s, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 159.9, 137.9, 136.6, 135.6, 134.0, 132.7, 130.4, 130.3, 129.3, 128.9, 128.0, 126.4,

122.5, 120.7, 118.6, 118.3, 113.4, 113.0, 103.3. HRMS MALDI (*m/z*): calcd for C₂₁H₁₄N₂OCl₂ [M + H]⁺: 381.0561, found: 381.0560.

***N*-(Naphthalen-2-yl)-2-phenylindolizine-3-carboxamide (4k)**



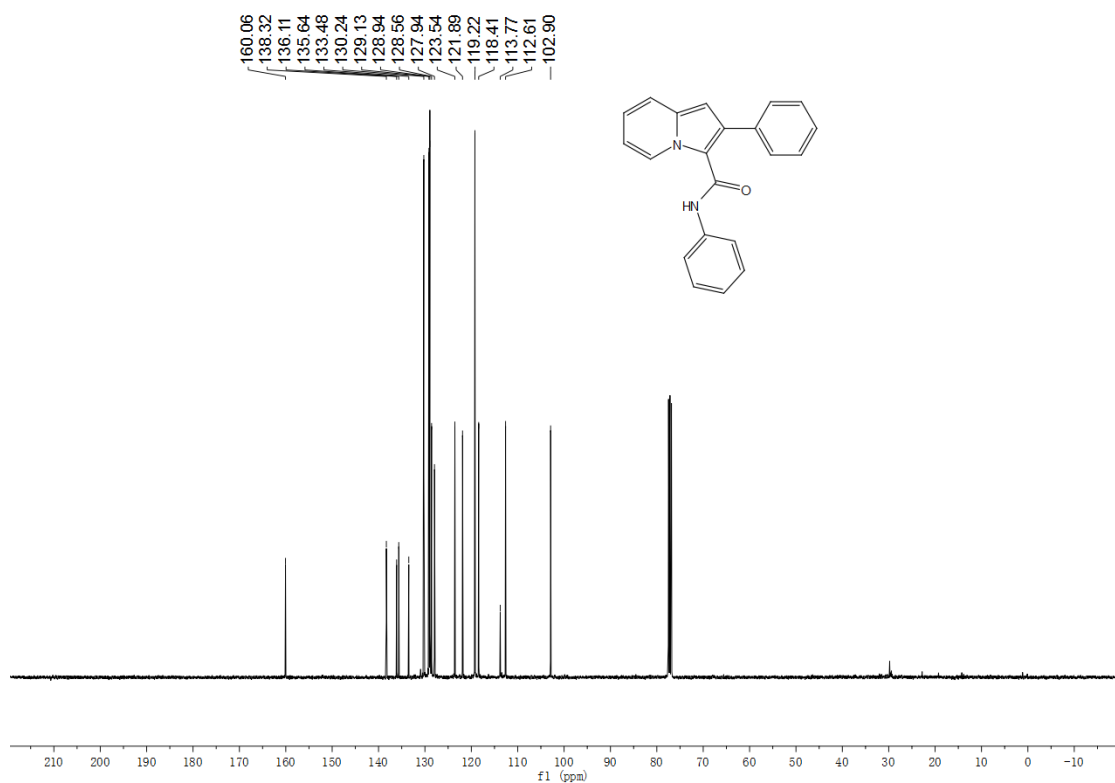
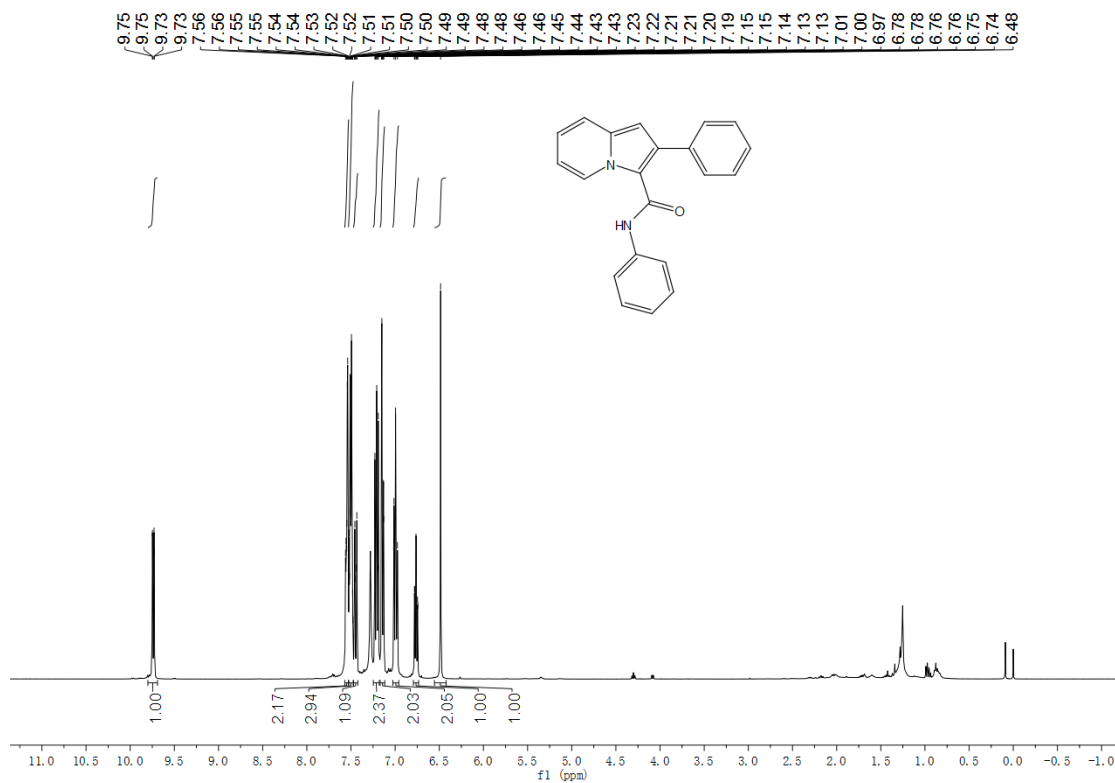
Flash column chromatography on silica gel (eluent: PE/DCM = 1/1, v/v) to

afford **4k**. Green solid (76.23 mg, 70%), mp 129.6-130.1 °C. ¹H NMR (400 MHz, CDCl₃) δ 9.79 (d, *J* = 7.2 Hz, 1H), 8.10 (d, *J* = 2.1 Hz, 1H), 7.71 (dd, *J* = 16.9, 8.1 Hz, 2H), 7.62 (d, *J* = 8.8 Hz, 1H), 7.57 (dd, *J* = 6.7, 3.1 Hz, 2H), 7.52 (q, *J* = 3.2, 2.5 Hz, 3H), 7.49 – 7.36 (m, 3H), 7.37 – 7.28 (m, 1H),

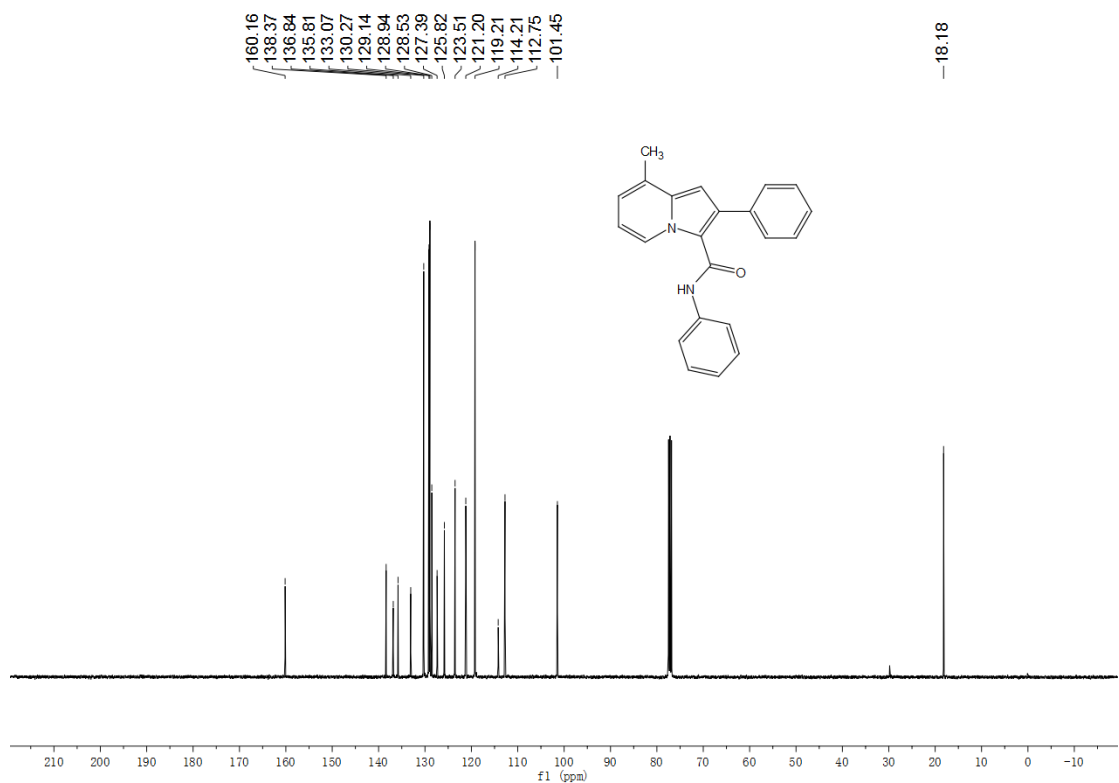
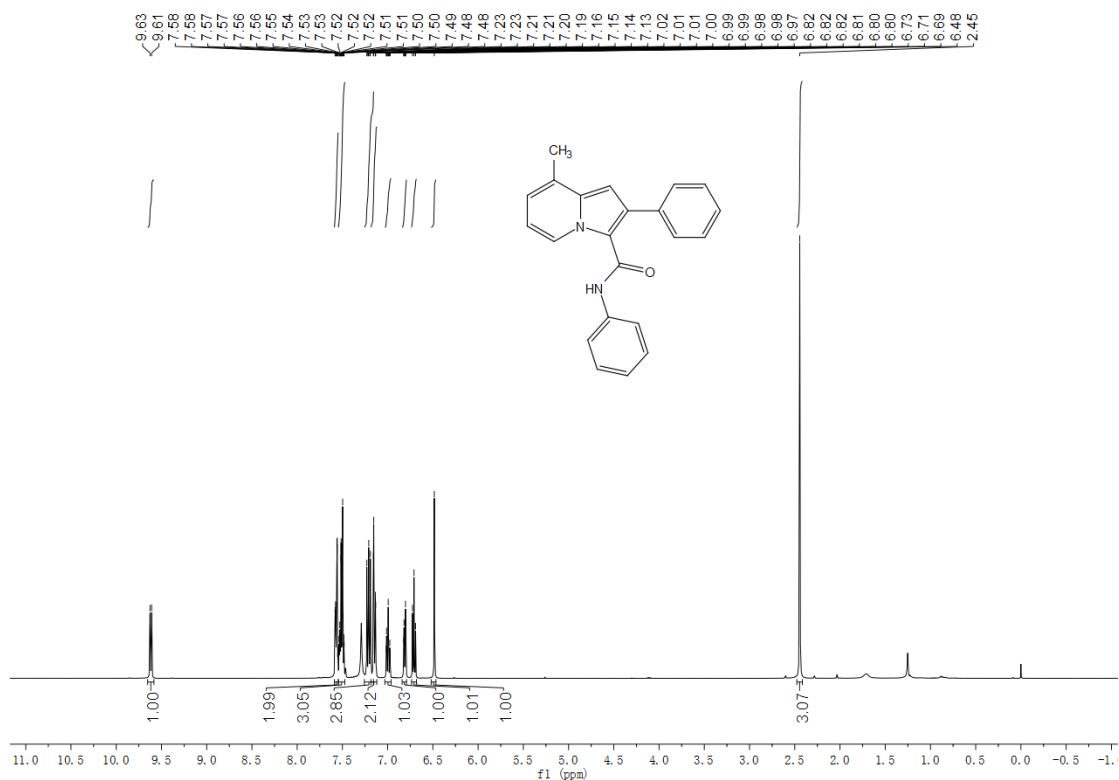
7.04 – 6.95 (m, 1H), 6.82 – 6.73 (m, 2H), 6.50 (s, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 160.2, 136.2, 135.8, 135.7, 134.1, 133.6, 130.3, 129.2, 128.6, 128.6, 128.0, 127.7, 127.6, 126.5, 124.7, 122.0, 119.6, 118.5, 115.5, 113.9, 112.7, 103.0. HRMS MALDI (*m/z*): calcd for C₂₅H₁₈N₂O [M + H]⁺: 363.1497, found: 363.1492.

3. NMR spectra for new compounds

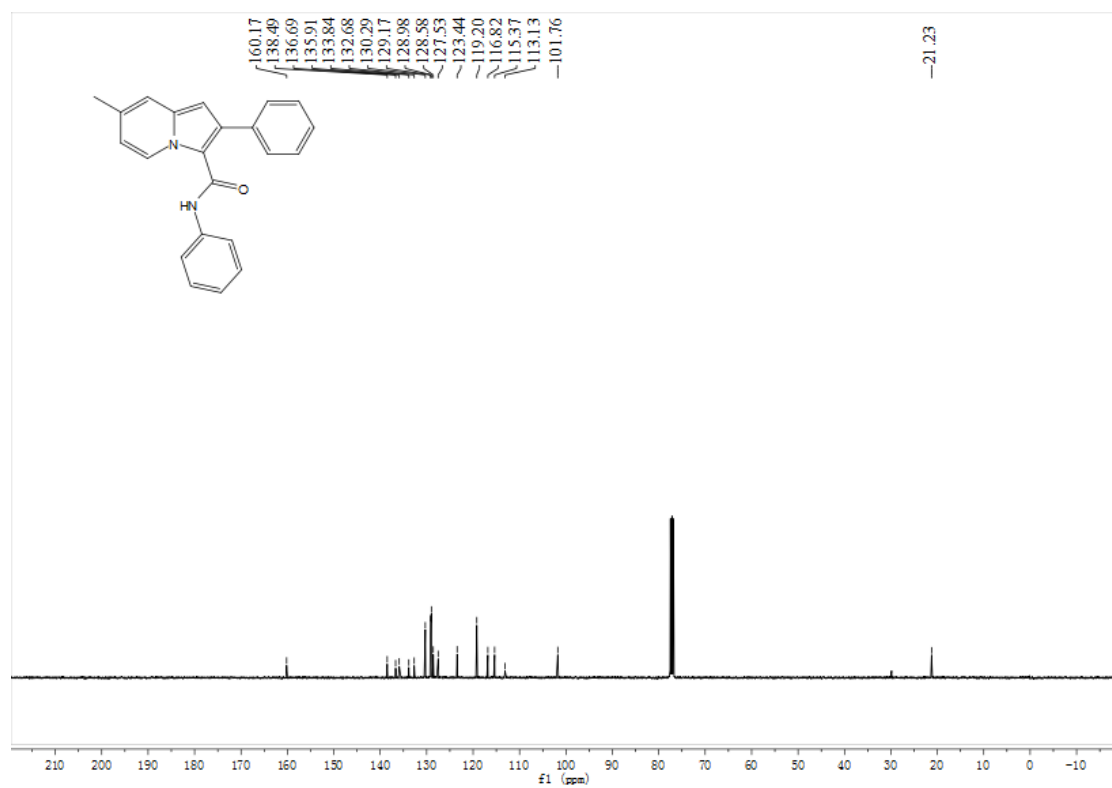
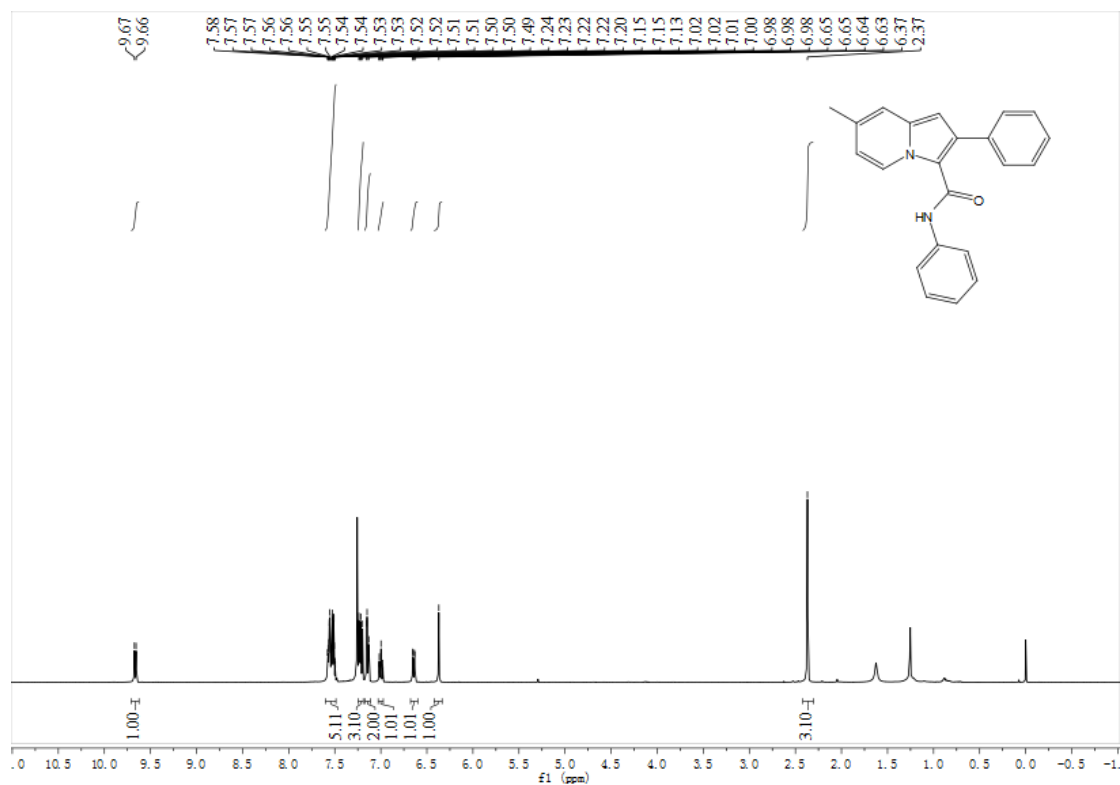
^1H NMR and ^{13}C NMR spectrum of compound **3a**



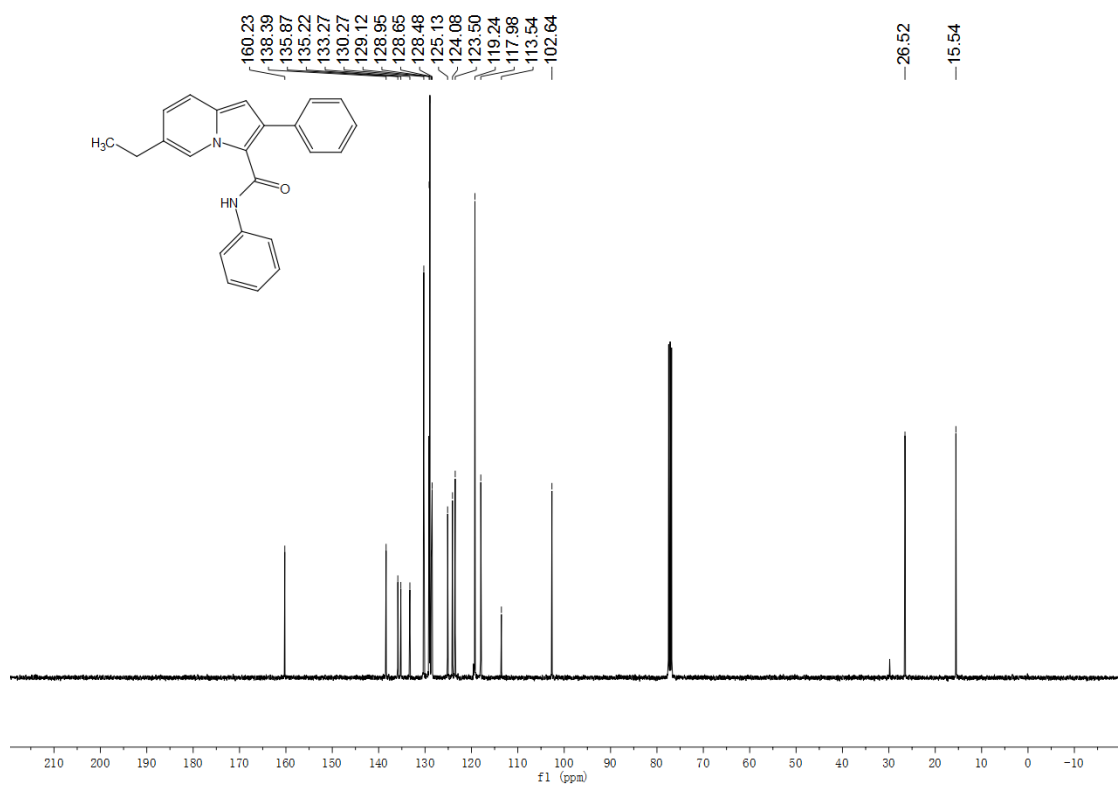
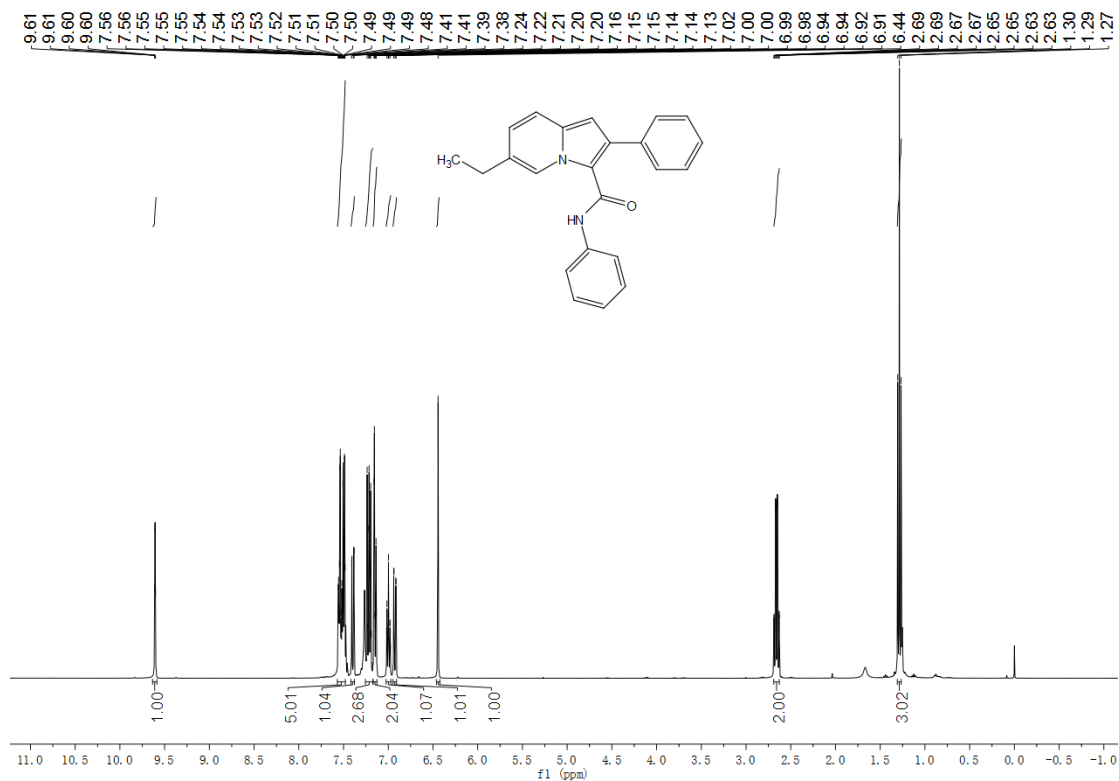
^1H NMR and ^{13}C NMR spectrum of compound **3b**



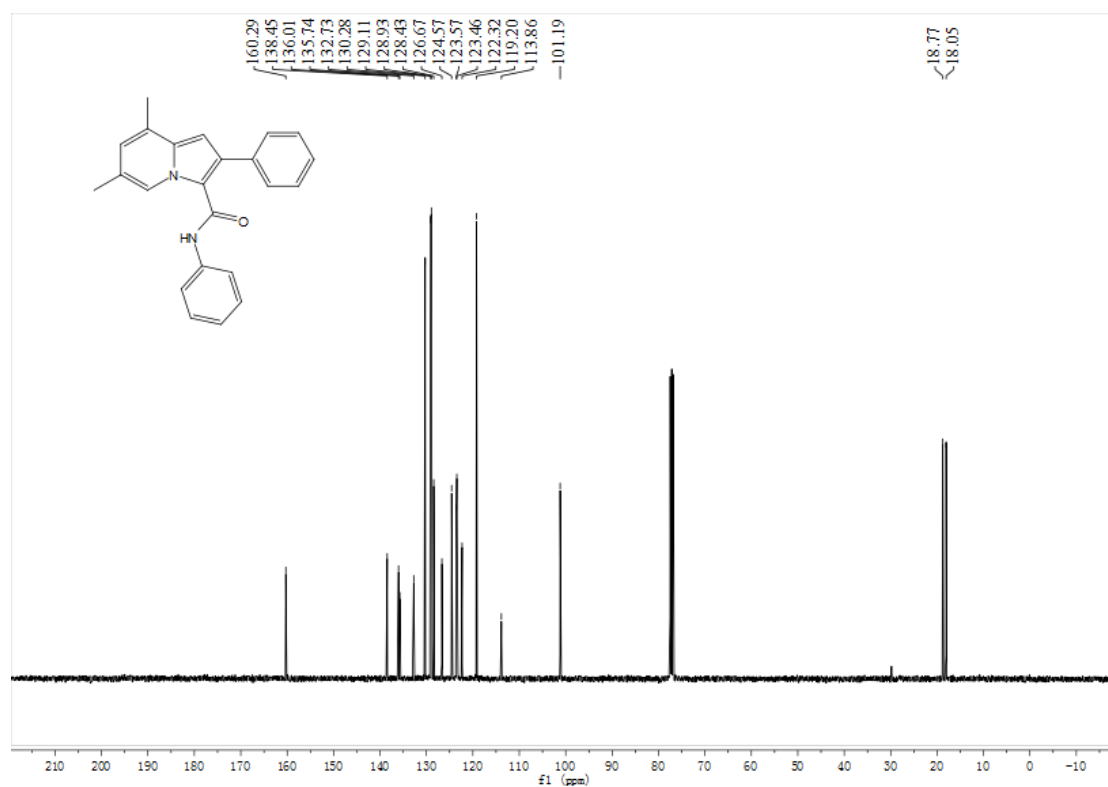
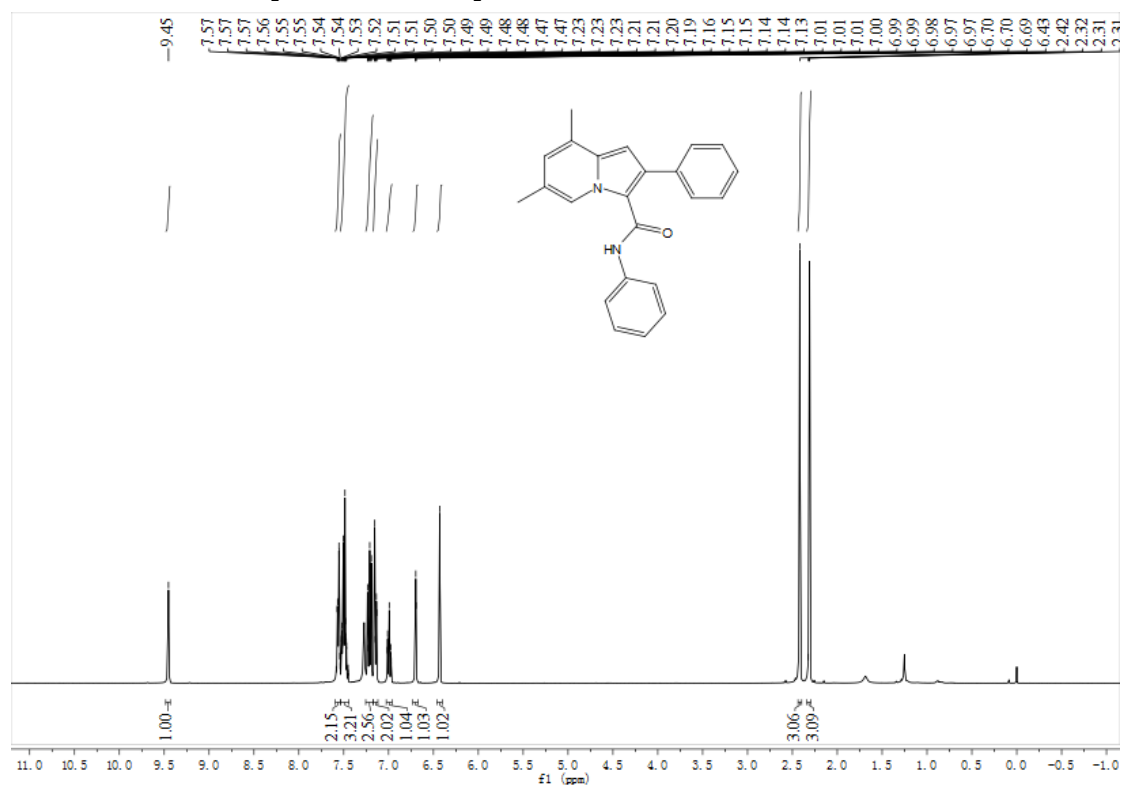
^1H NMR and ^{13}C NMR spectrum of compound **3c**



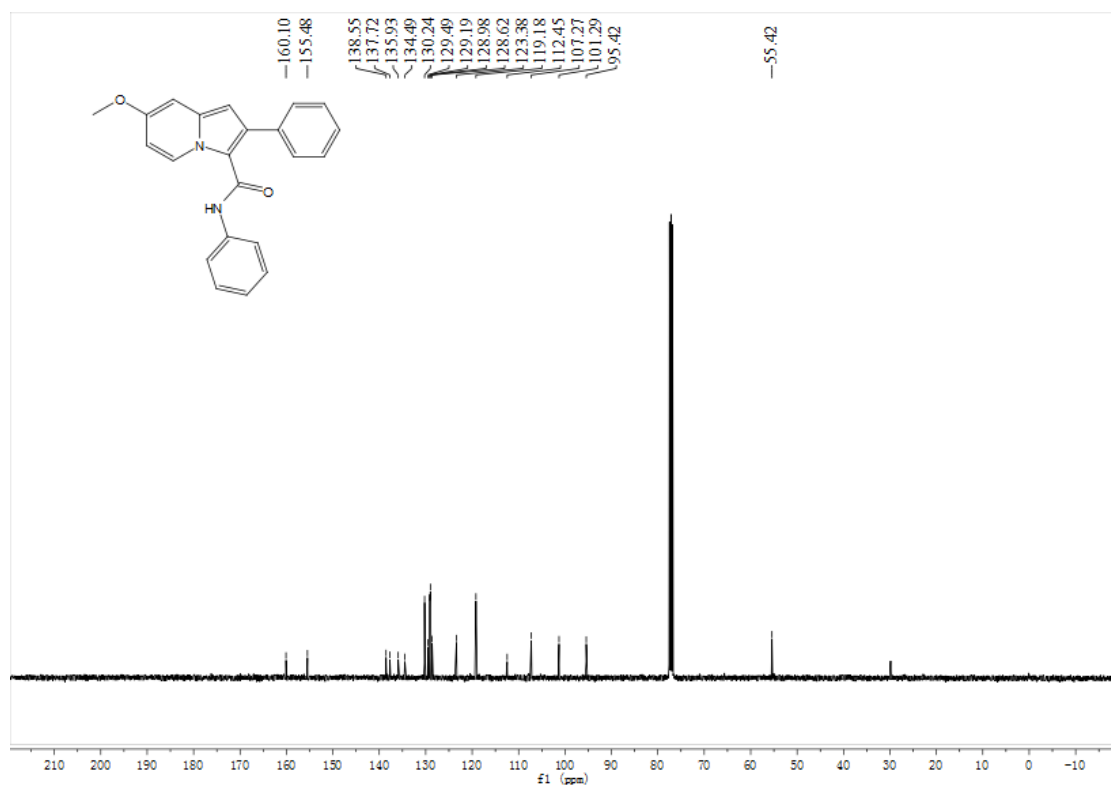
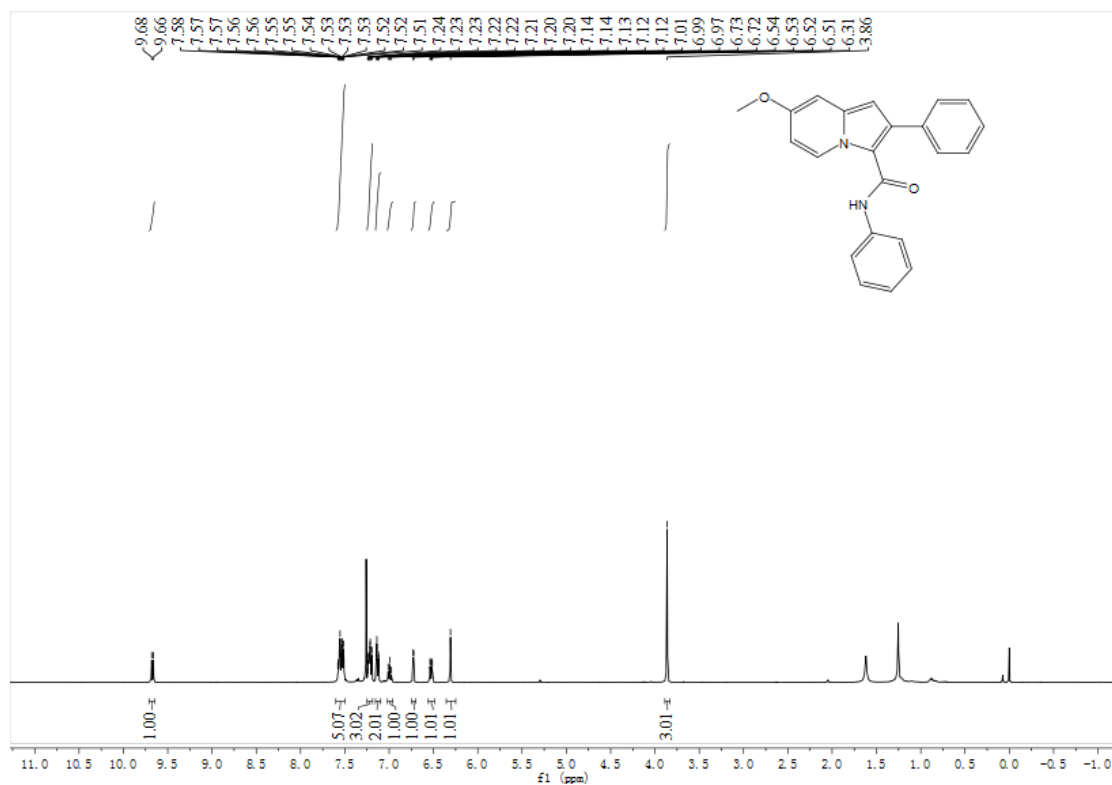
^1H NMR and ^{13}C NMR spectrum of compound **3d**



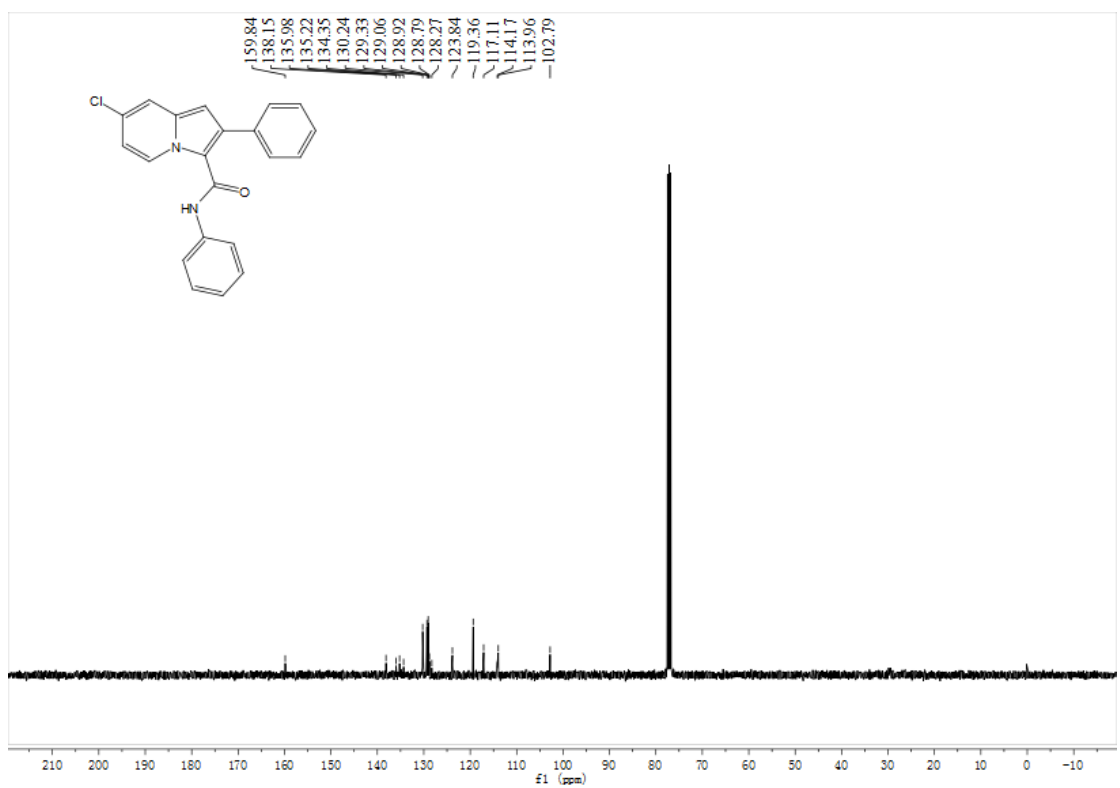
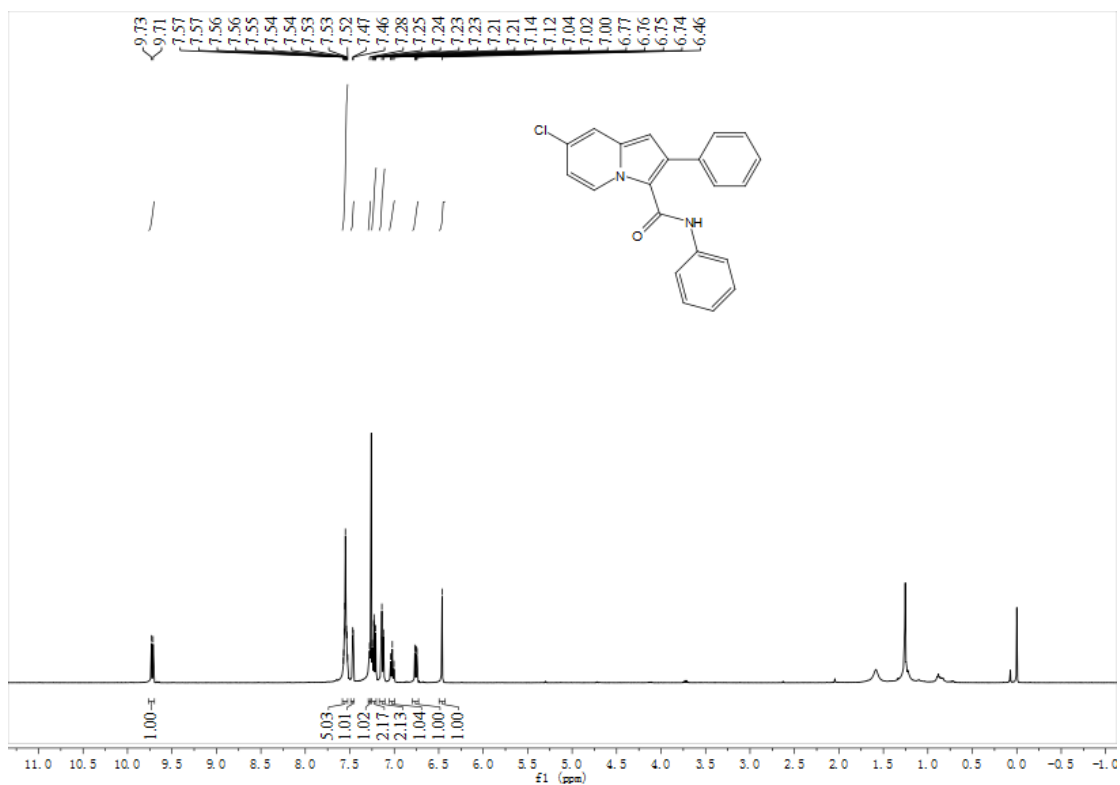
^1H NMR and ^{13}C NMR spectrum of compound **3e**



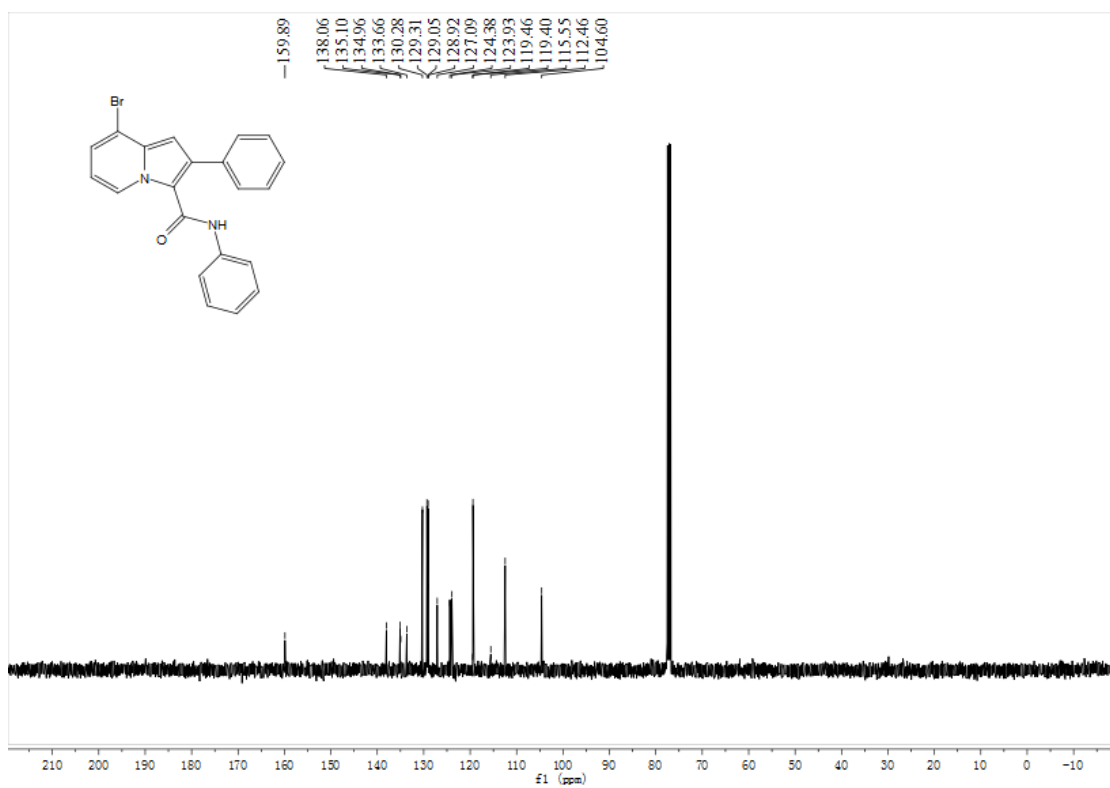
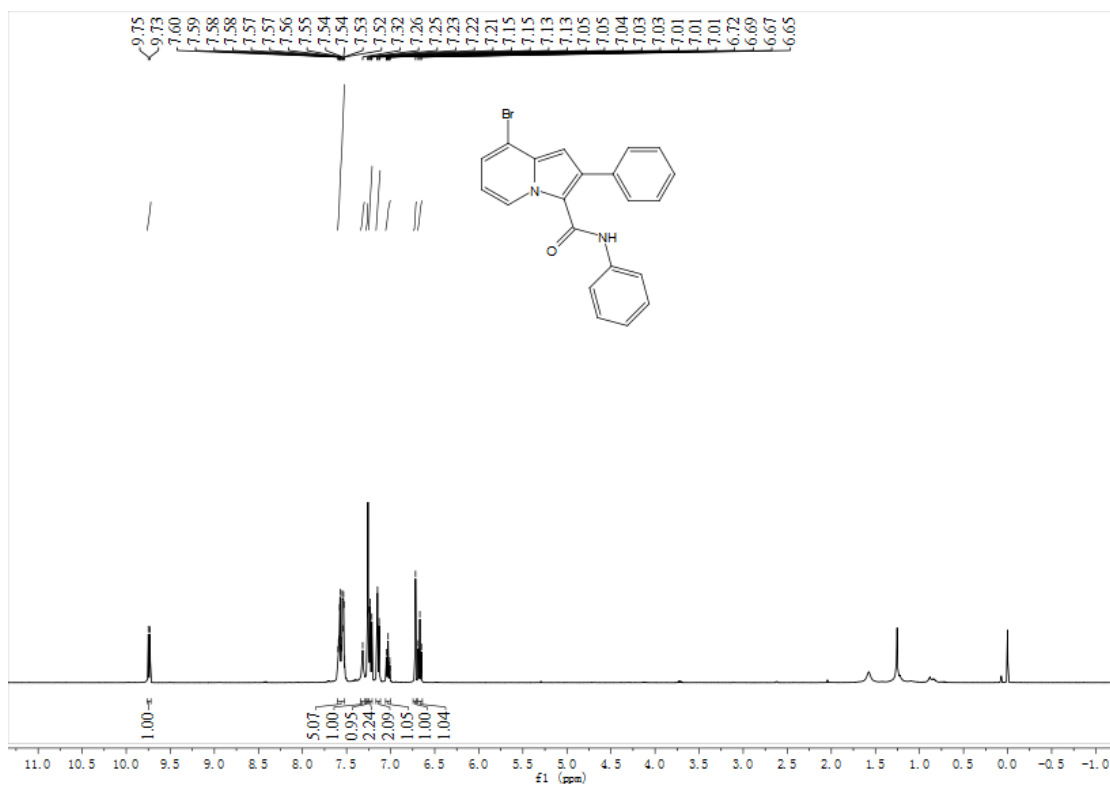
^1H NMR and ^{13}C NMR spectrum of compound **3f**



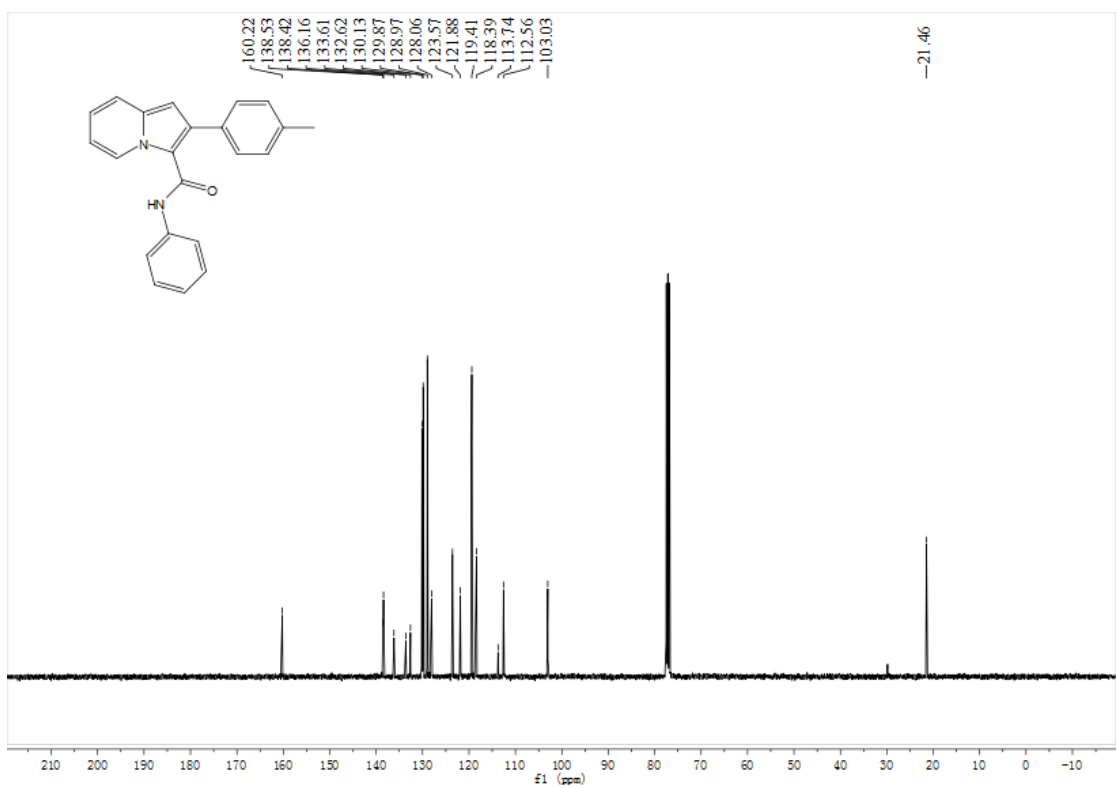
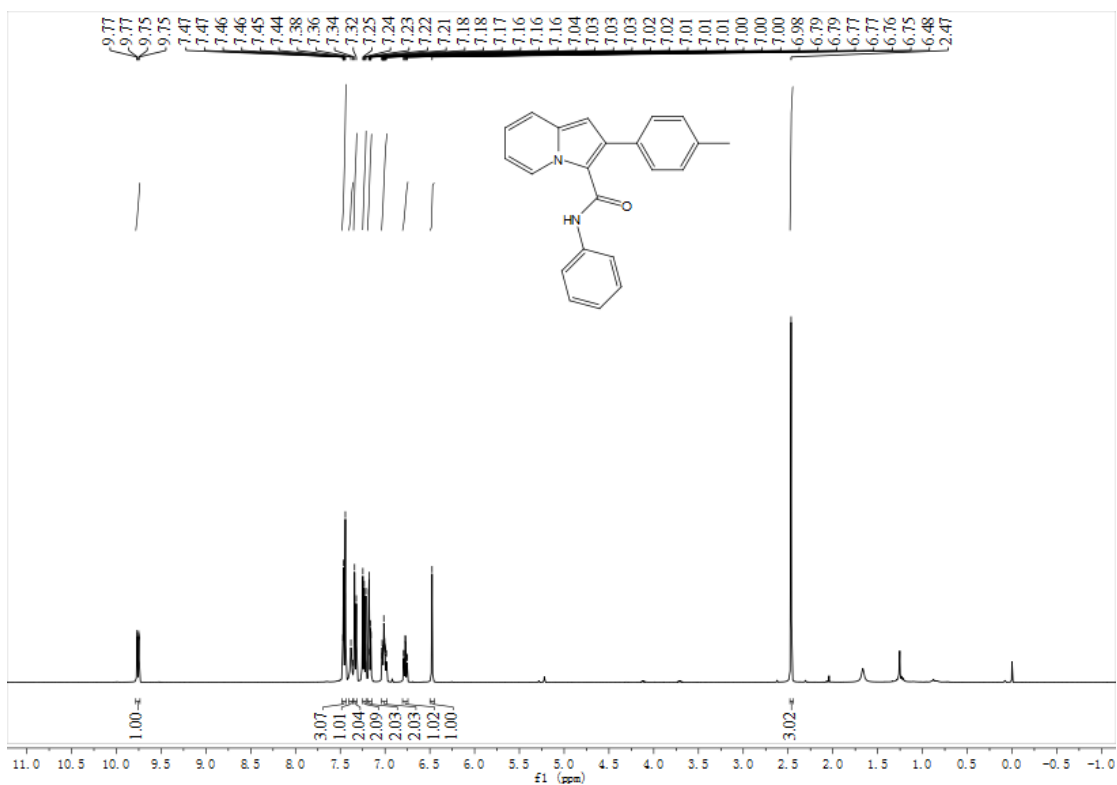
^1H NMR and ^{13}C NMR spectrum of compound **3g**



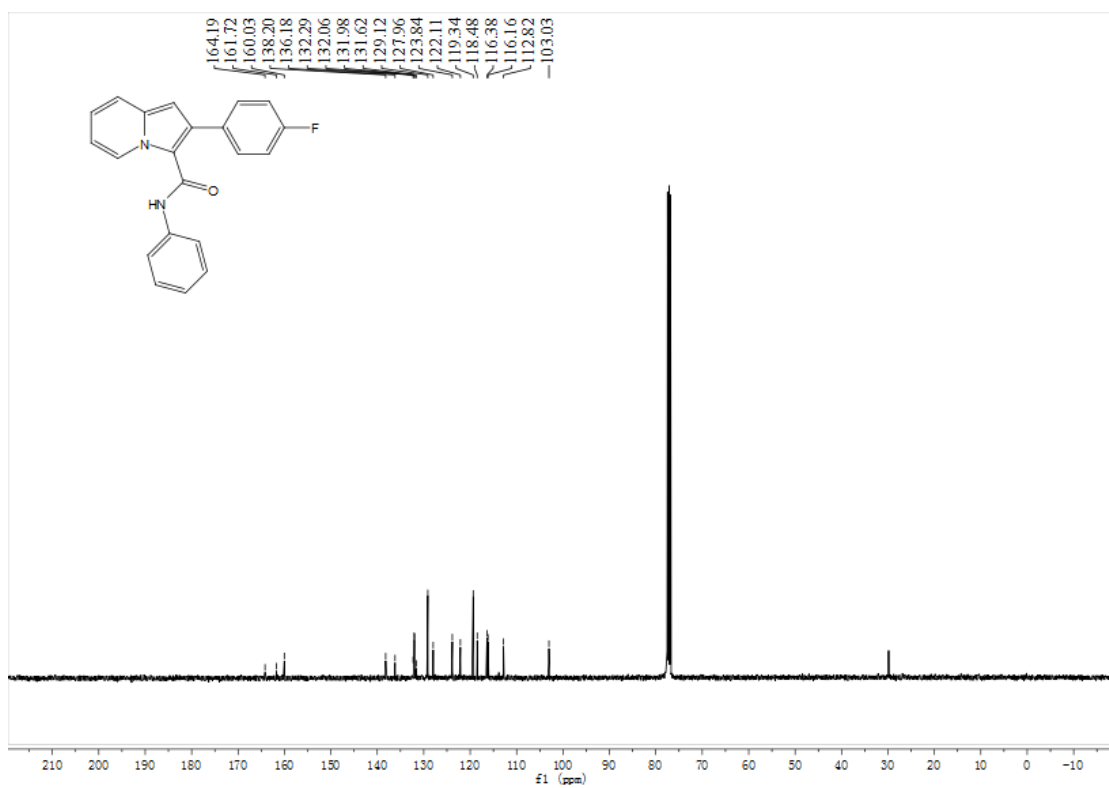
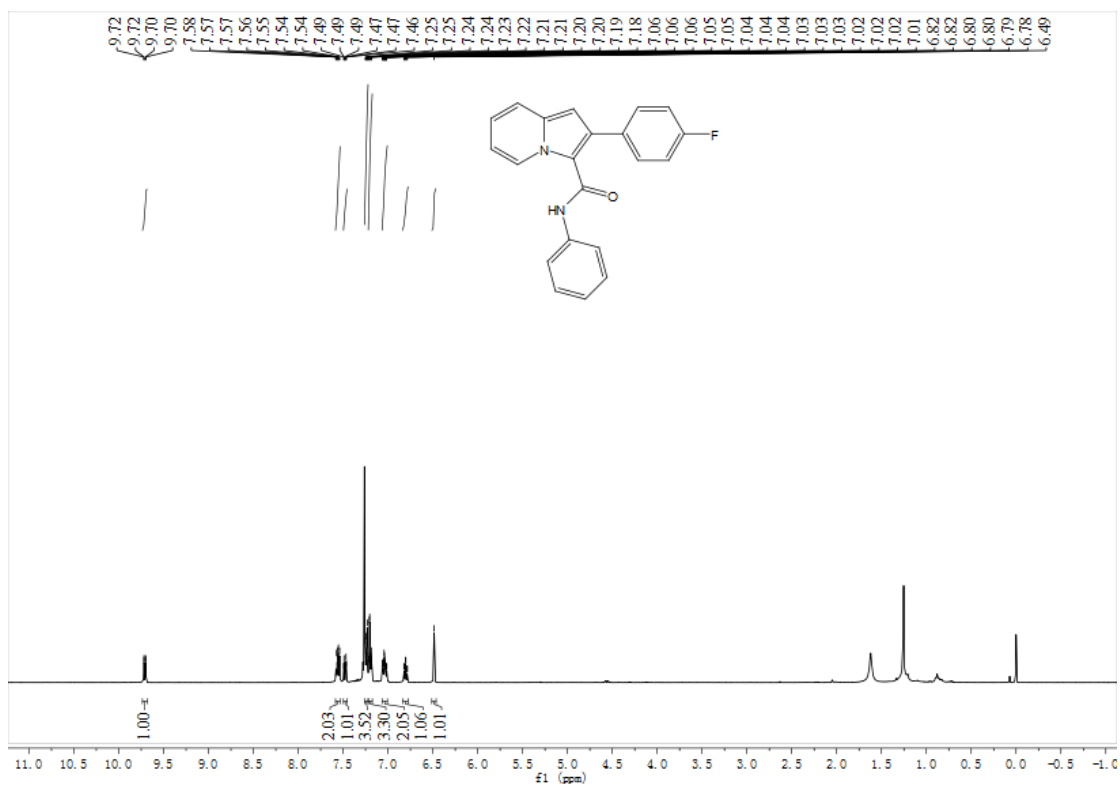
^1H NMR and ^{13}C NMR spectrum of compound **3h**



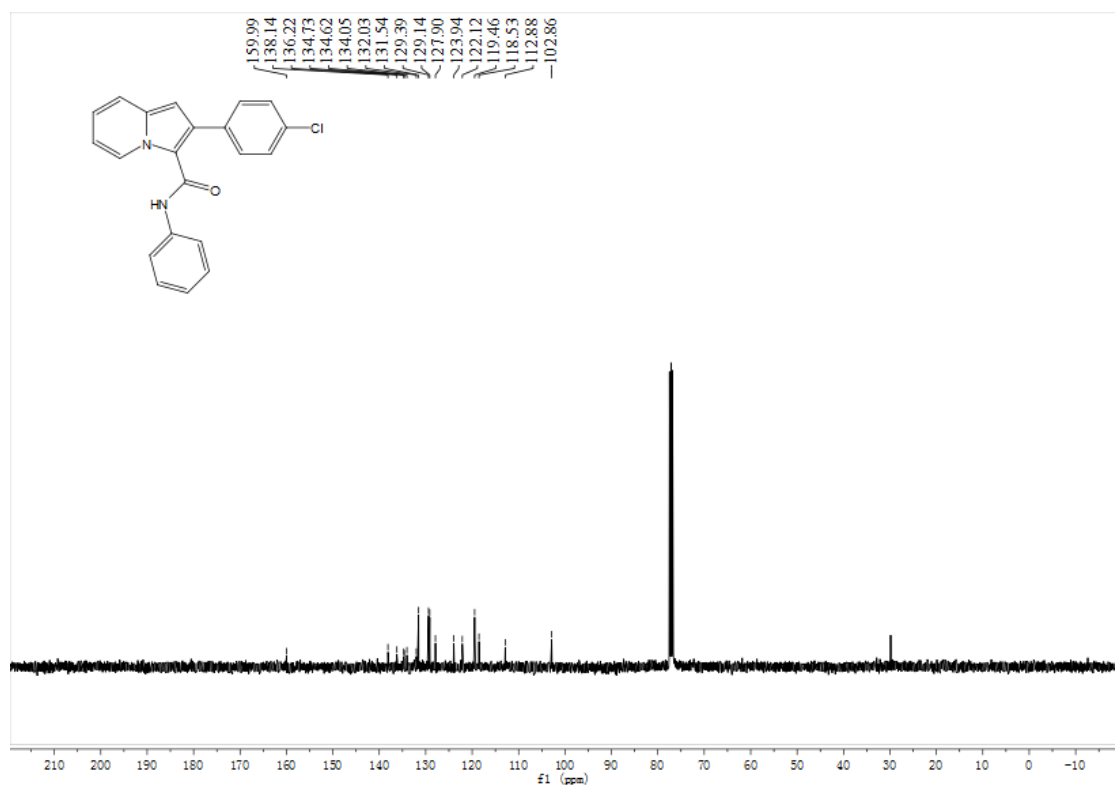
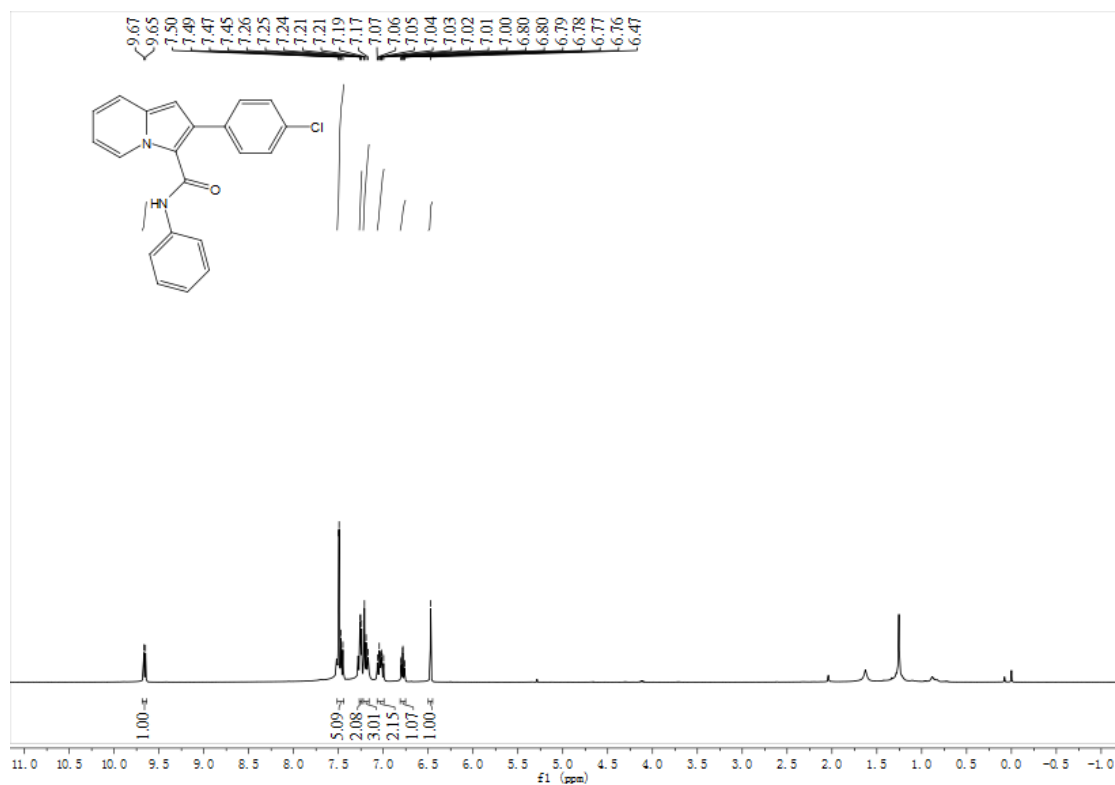
^1H NMR and ^{13}C NMR spectrum of compound **3i**



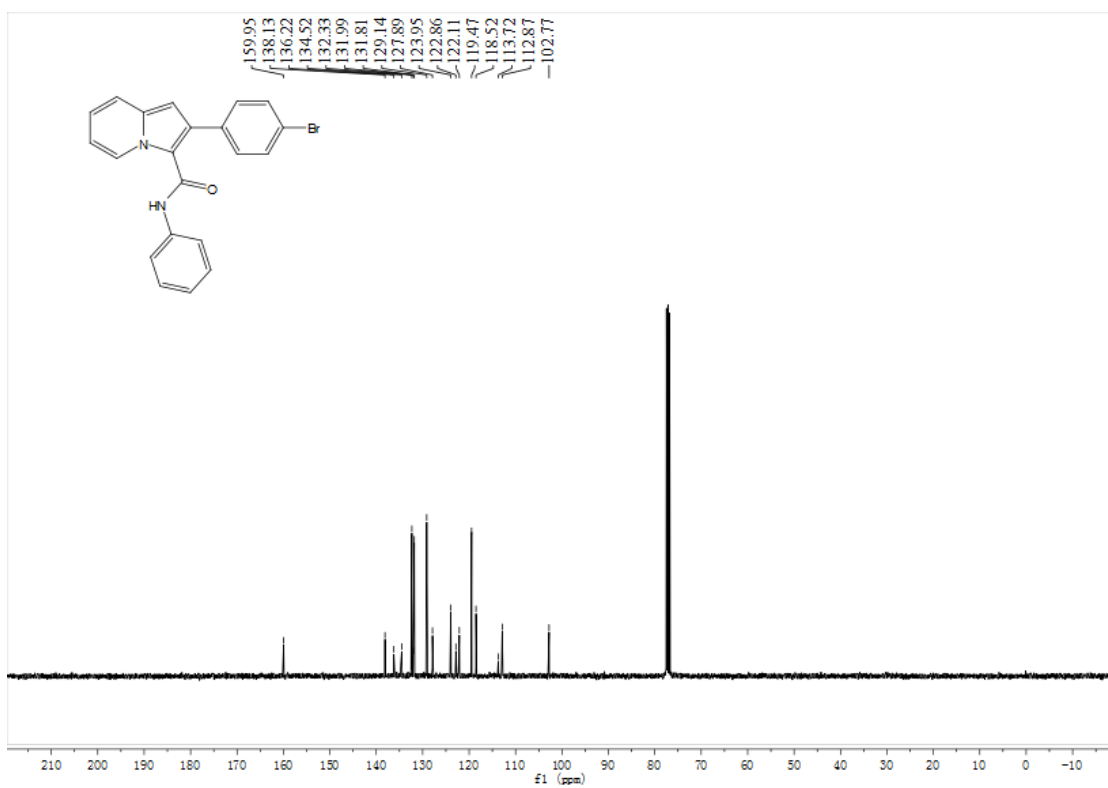
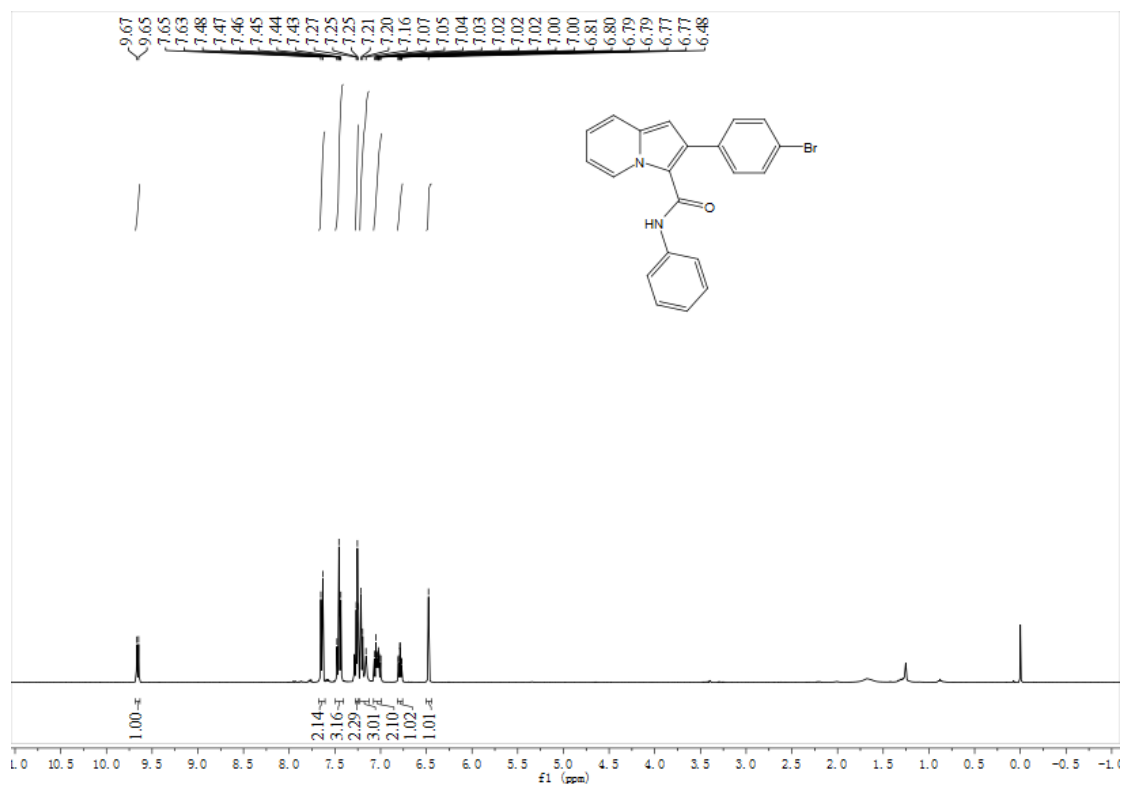
^1H NMR and ^{13}C NMR spectrum of compound **3j**



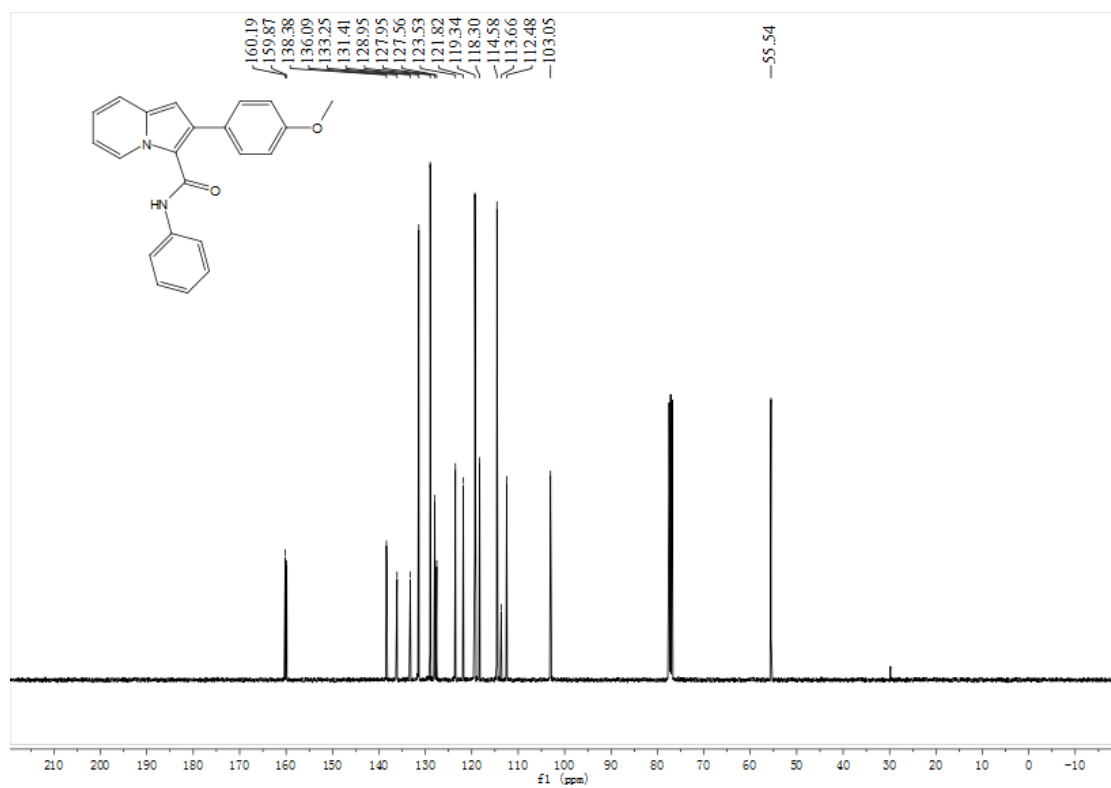
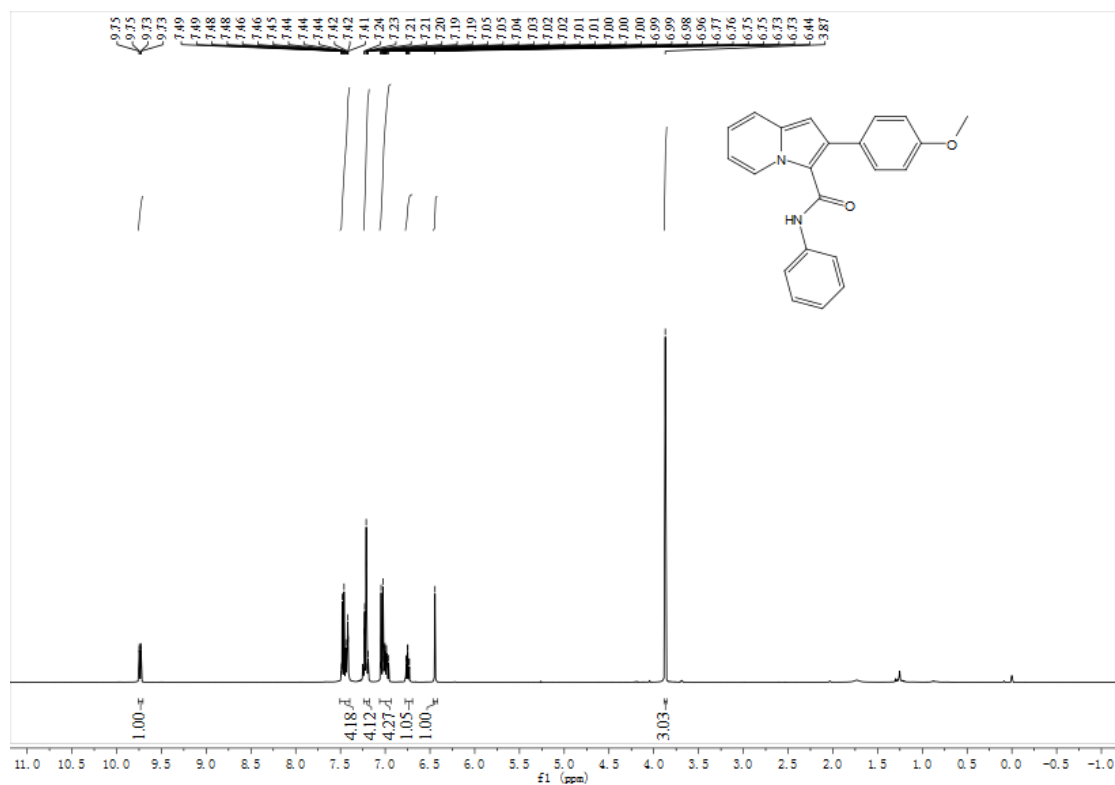
^1H NMR and ^{13}C NMR spectrum of compound **3k**



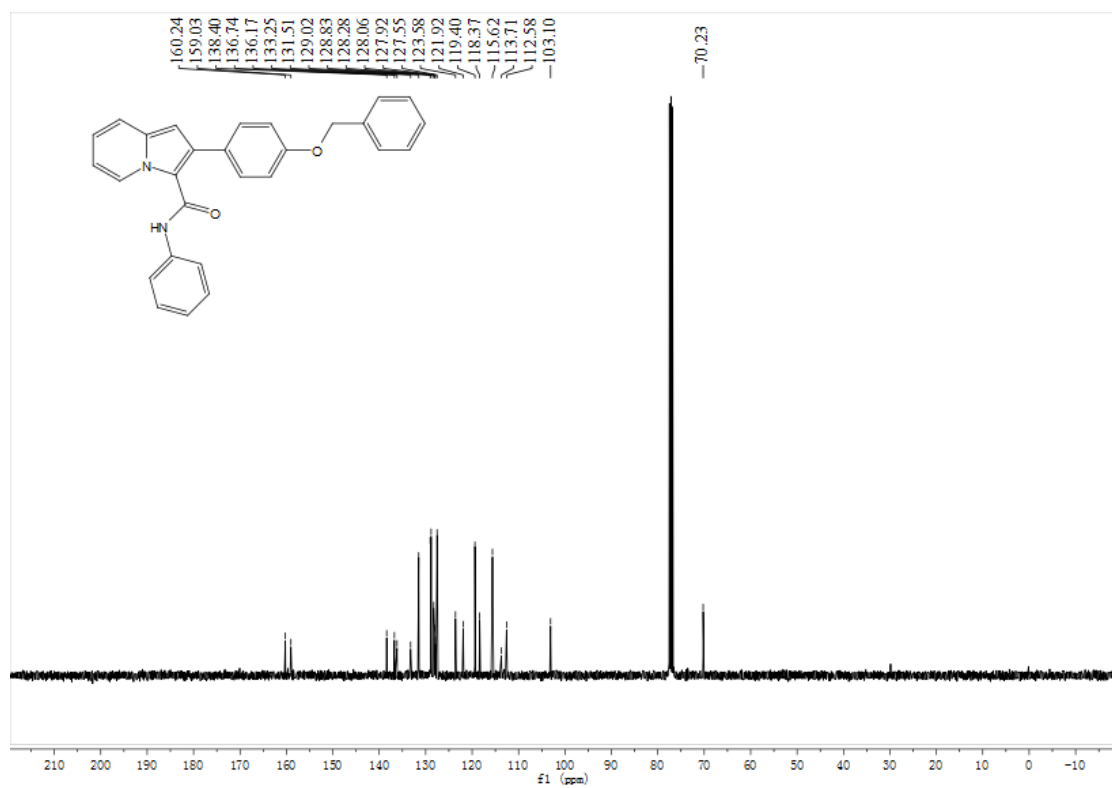
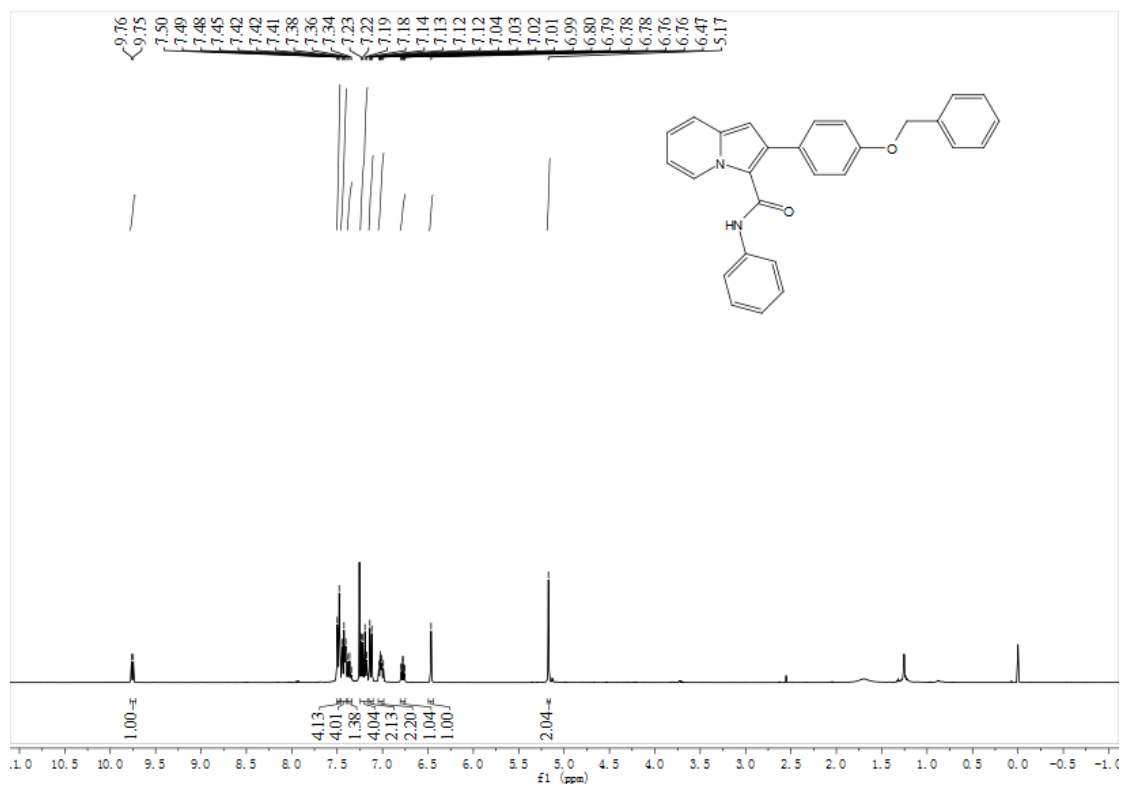
^1H NMR and ^{13}C NMR spectrum of compound **3l**



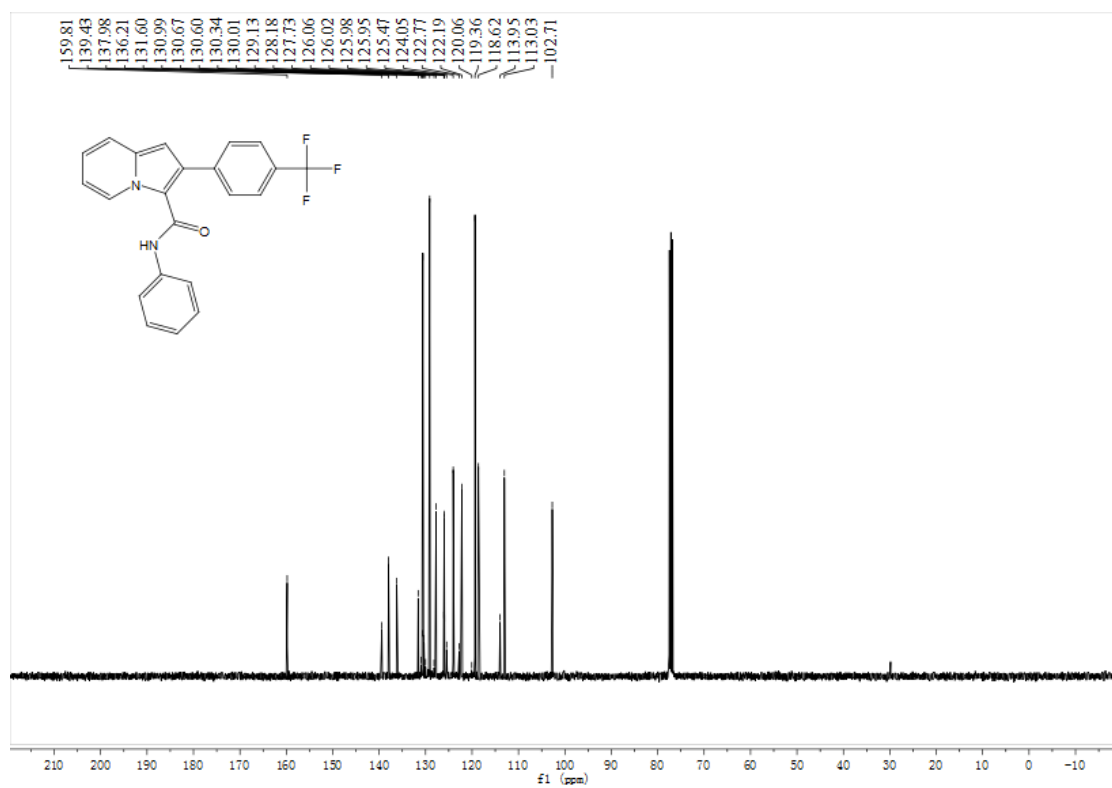
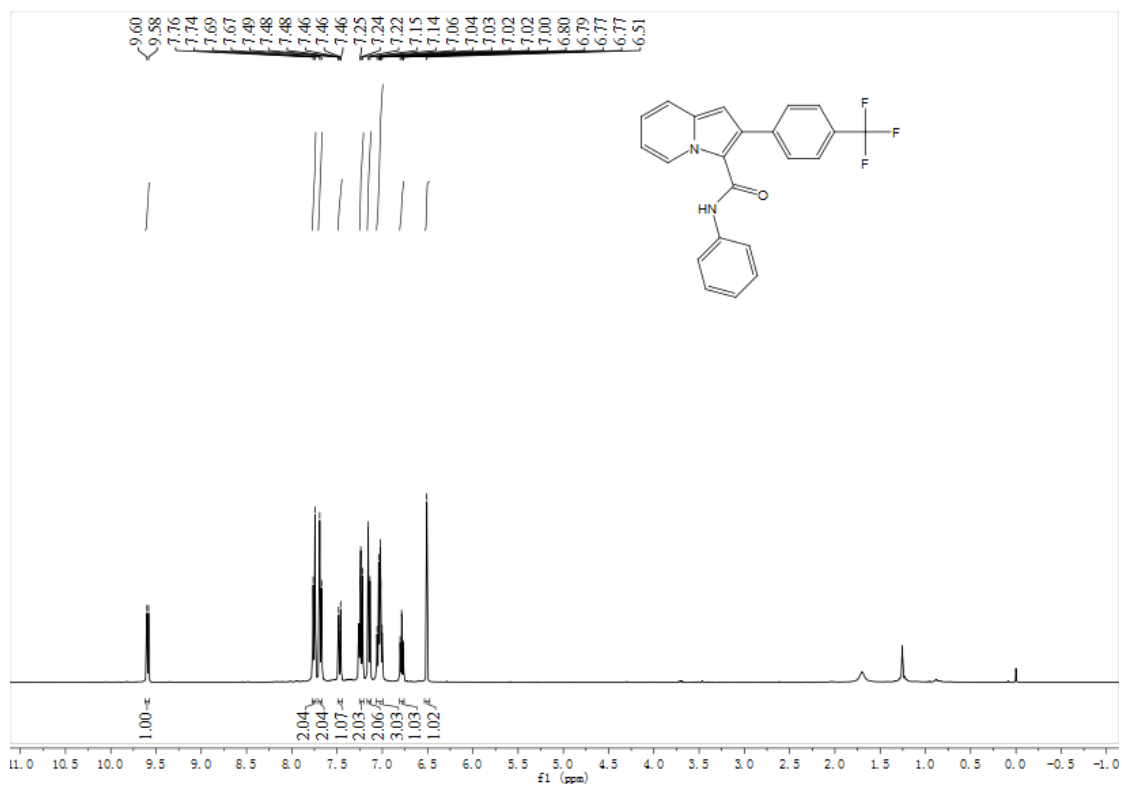
^1H NMR and ^{13}C NMR spectrum of compound **3m**



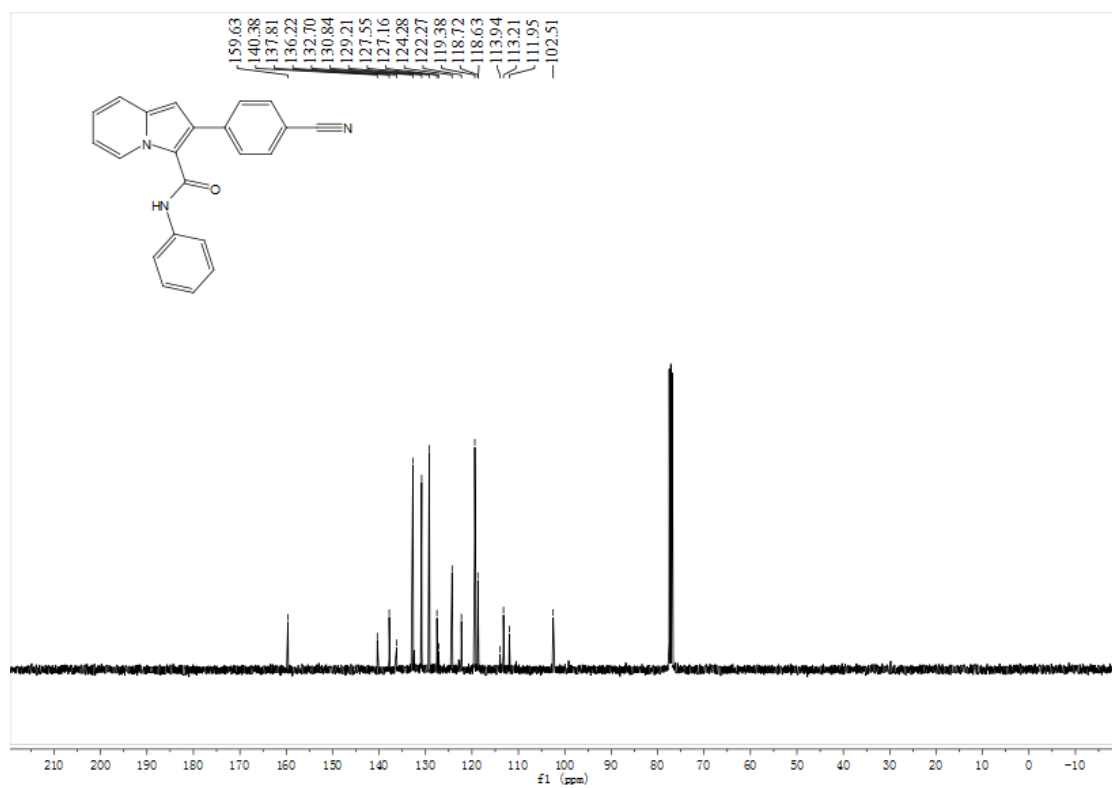
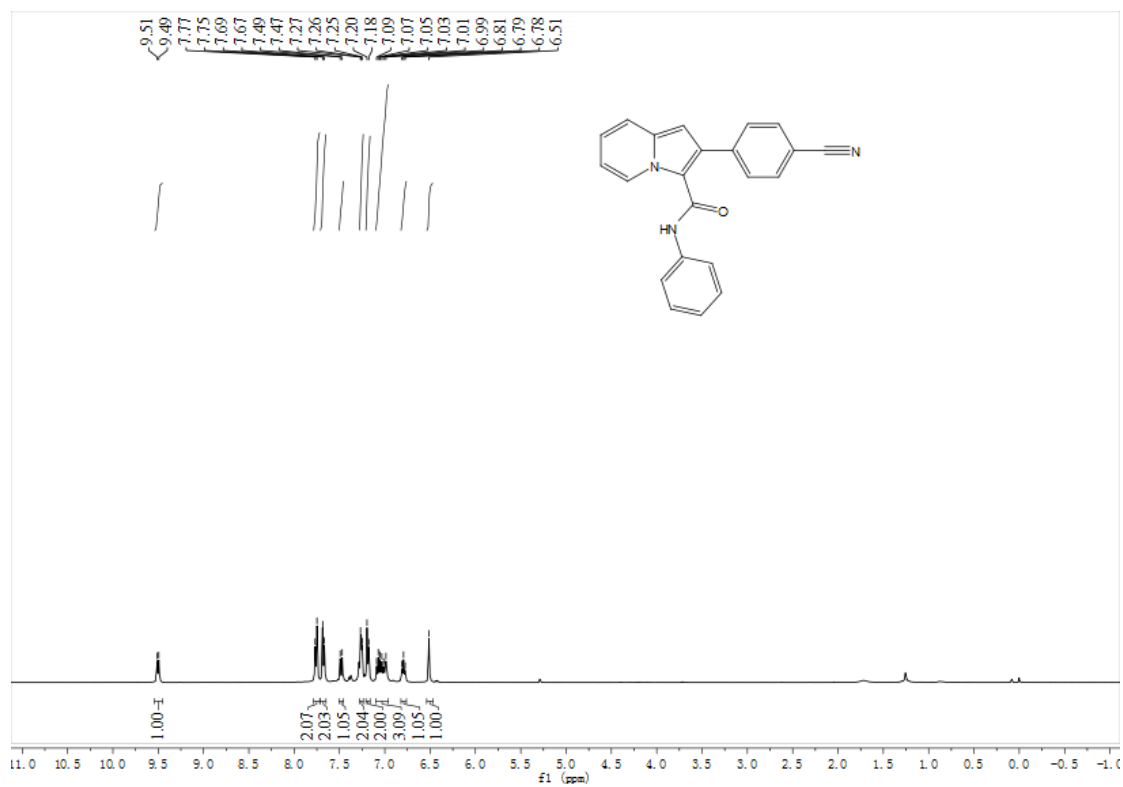
^1H NMR and ^{13}C NMR spectrum of compound **3n**



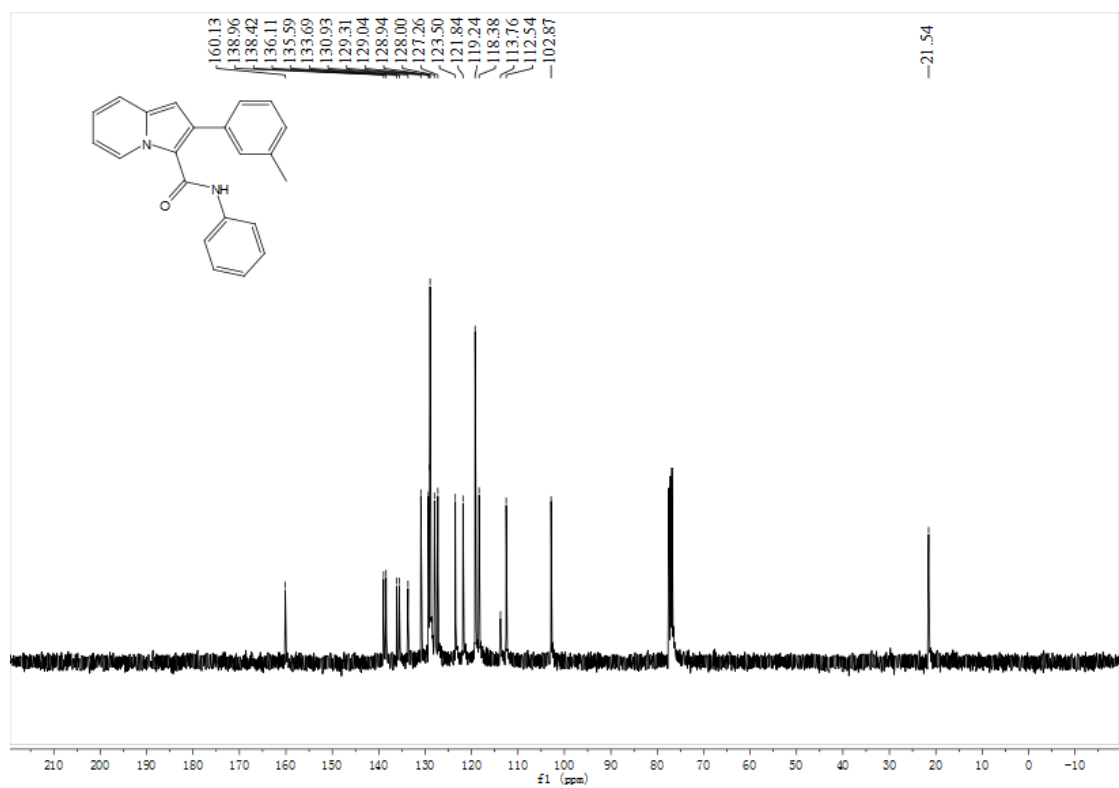
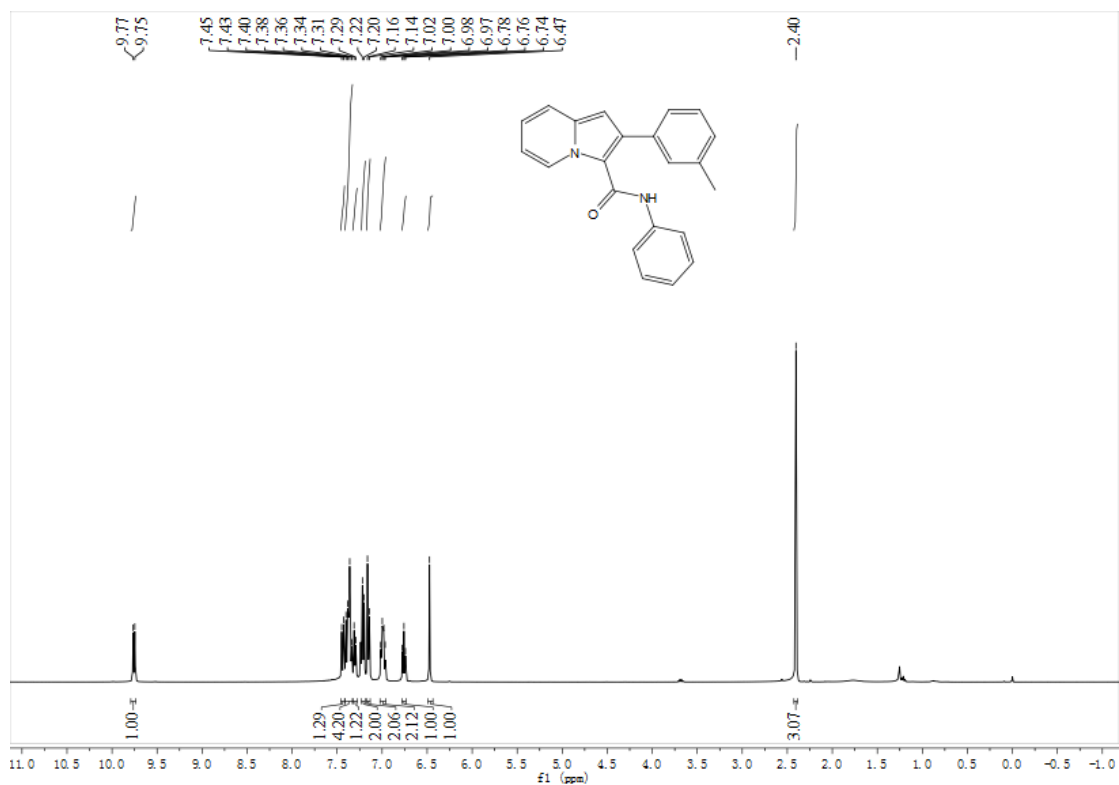
^1H NMR and ^{13}C NMR spectrum of compound **3o**



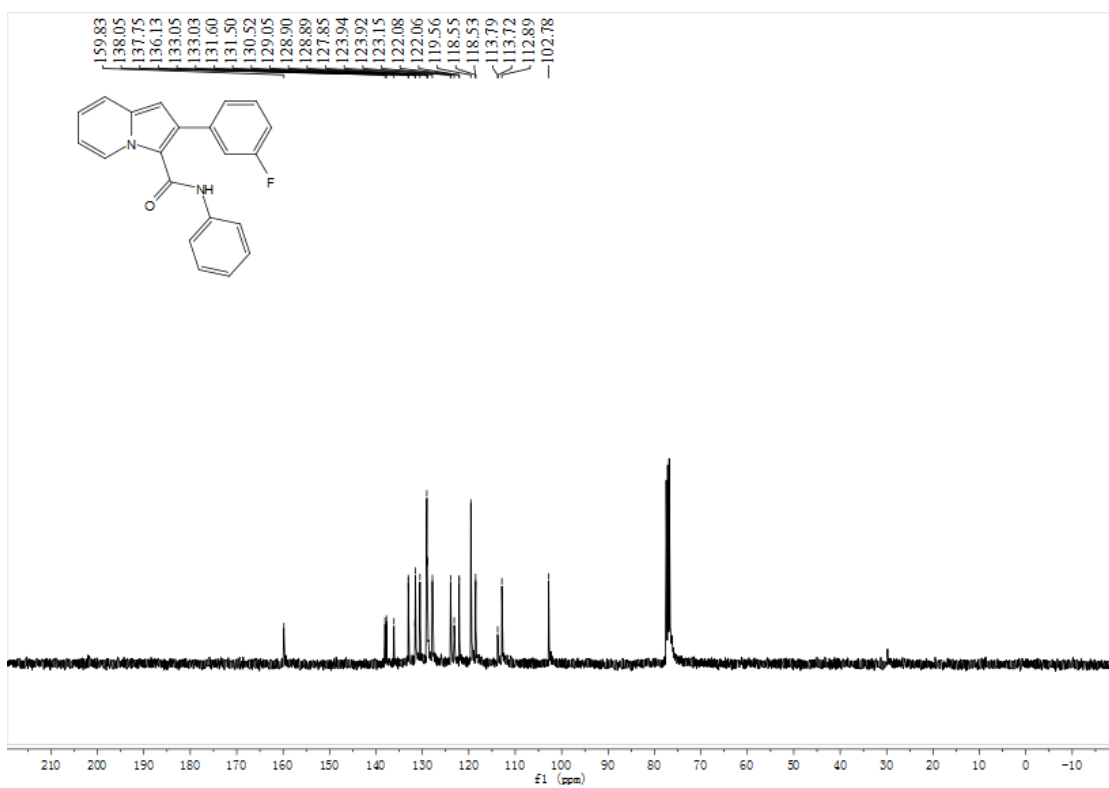
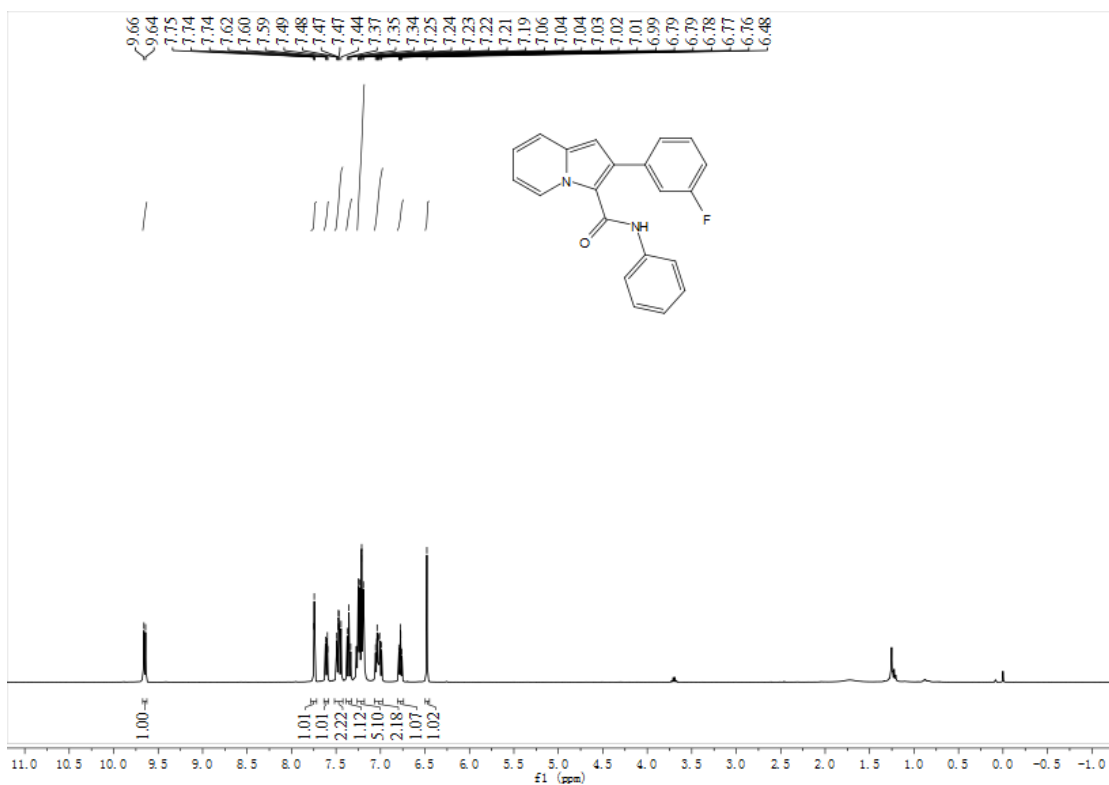
^1H NMR and ^{13}C NMR spectrum of compound **3p**



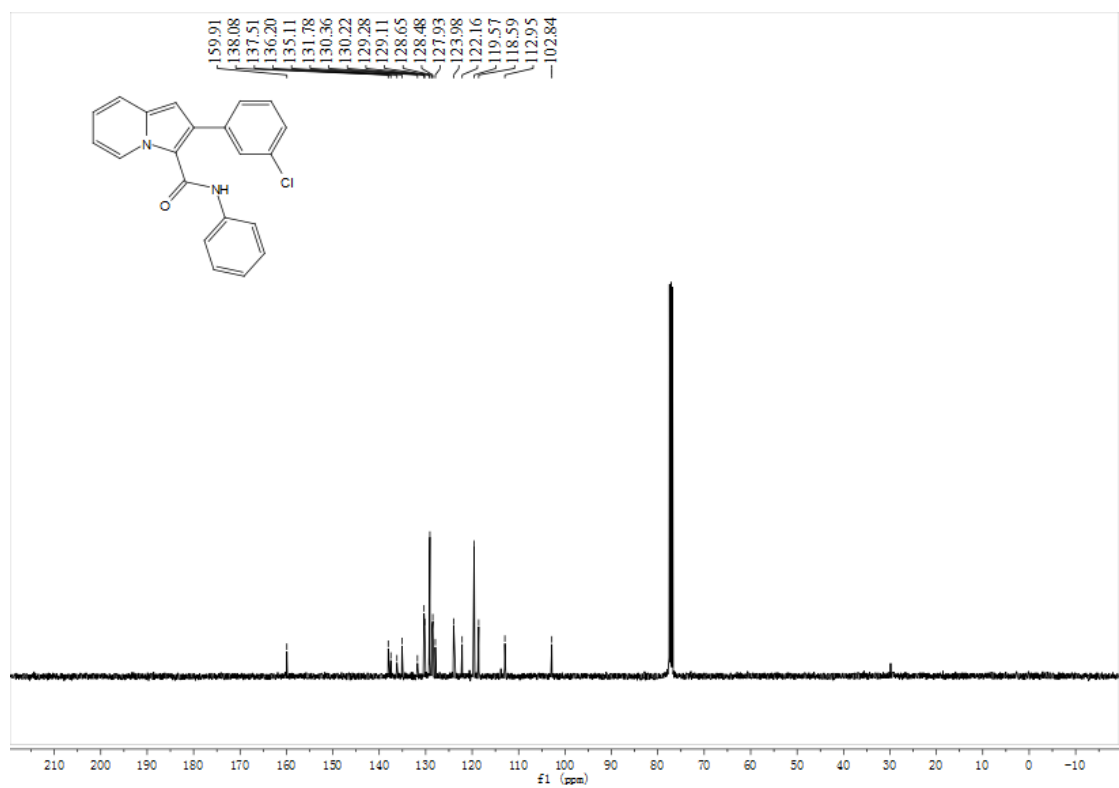
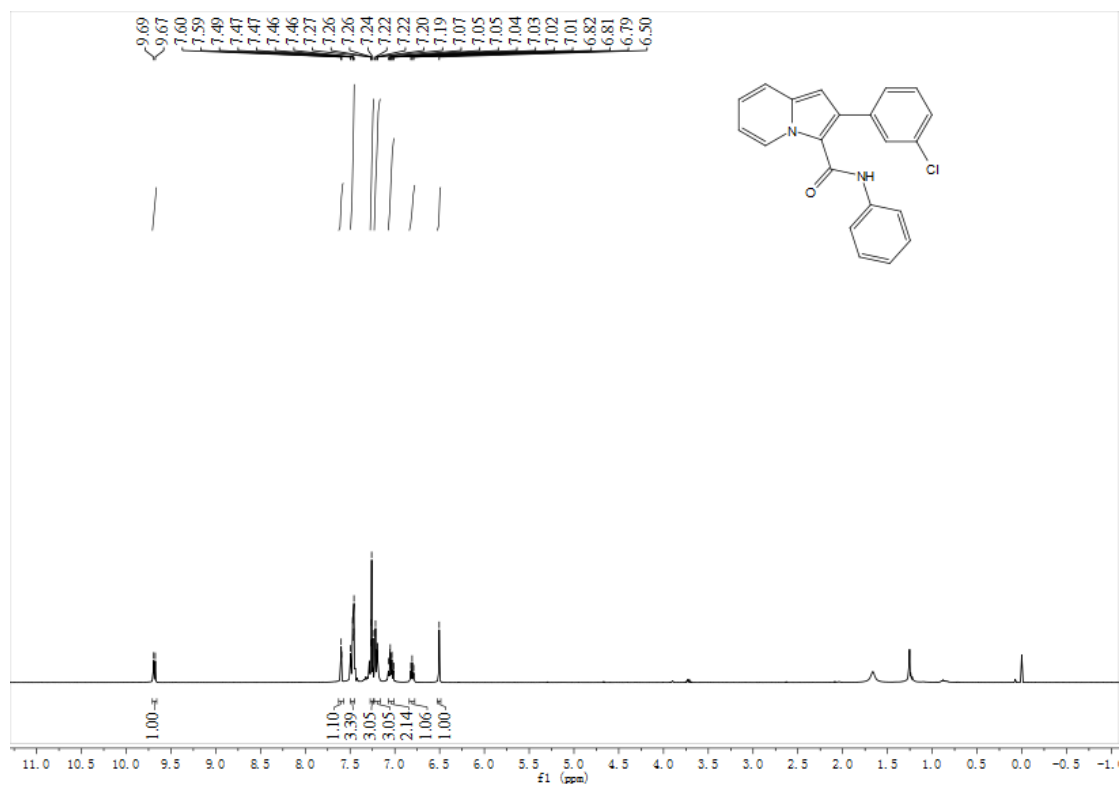
^1H NMR and ^{13}C NMR spectrum of compound **3q**



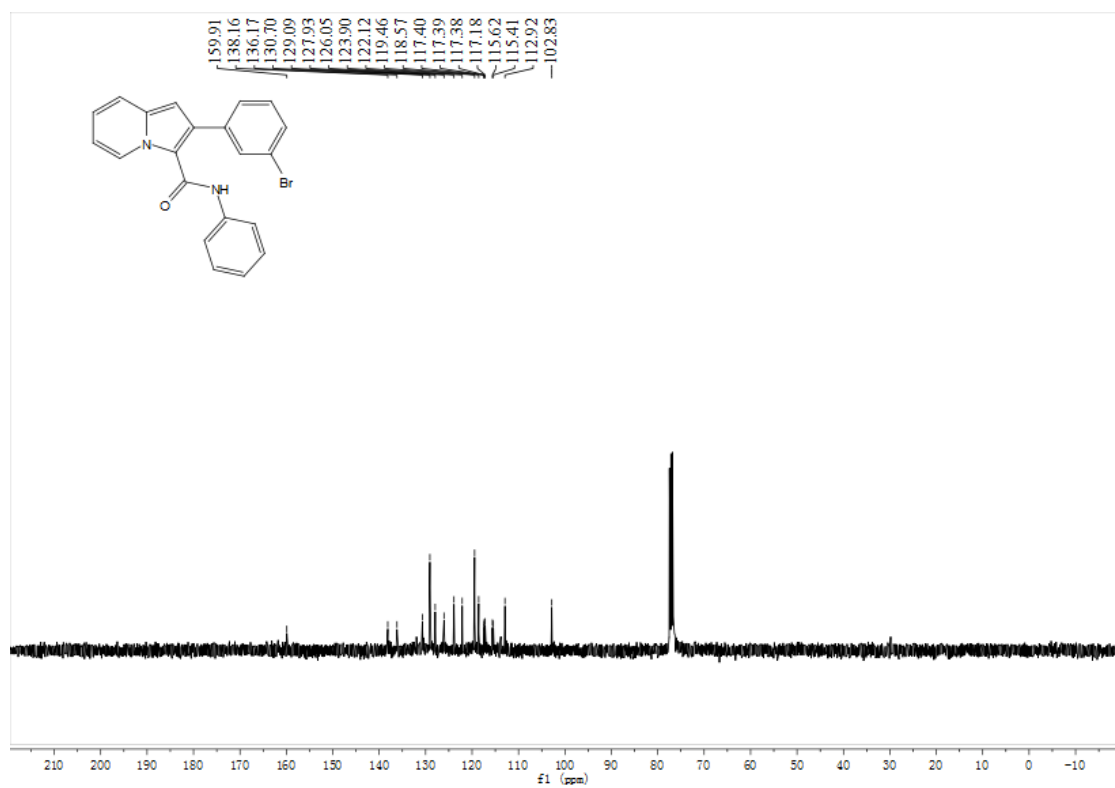
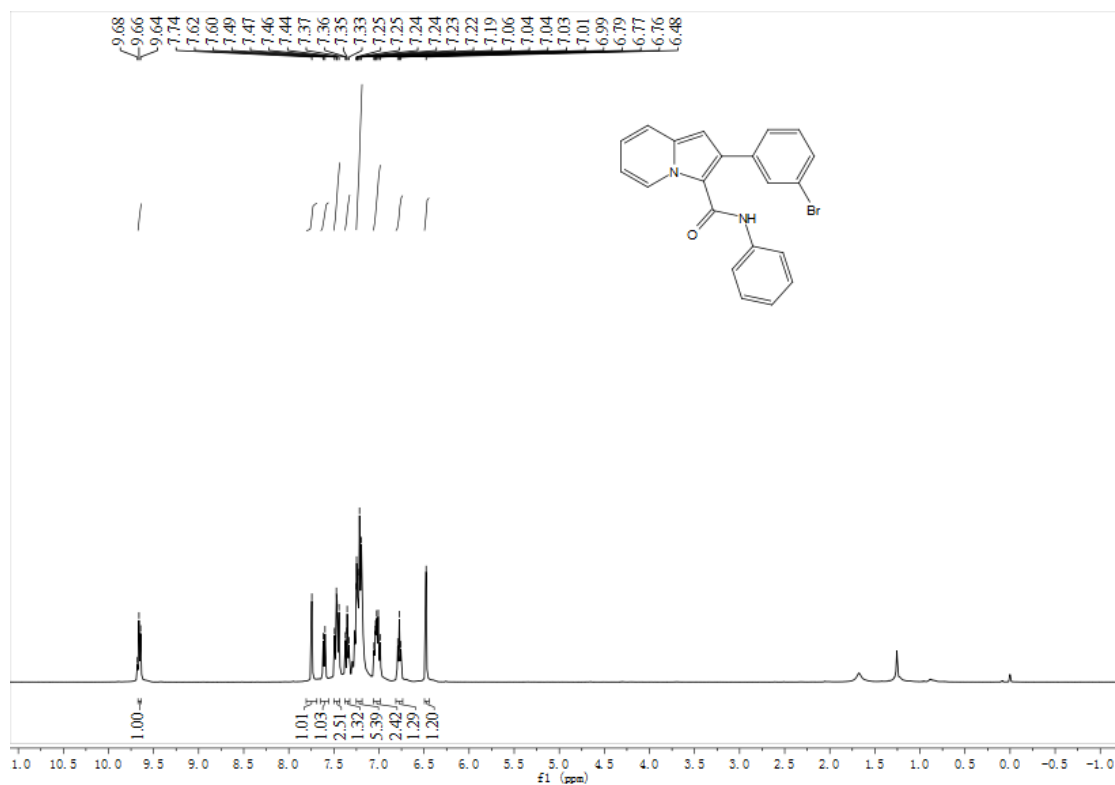
^1H NMR and ^{13}C NMR spectrum of compound **3r**



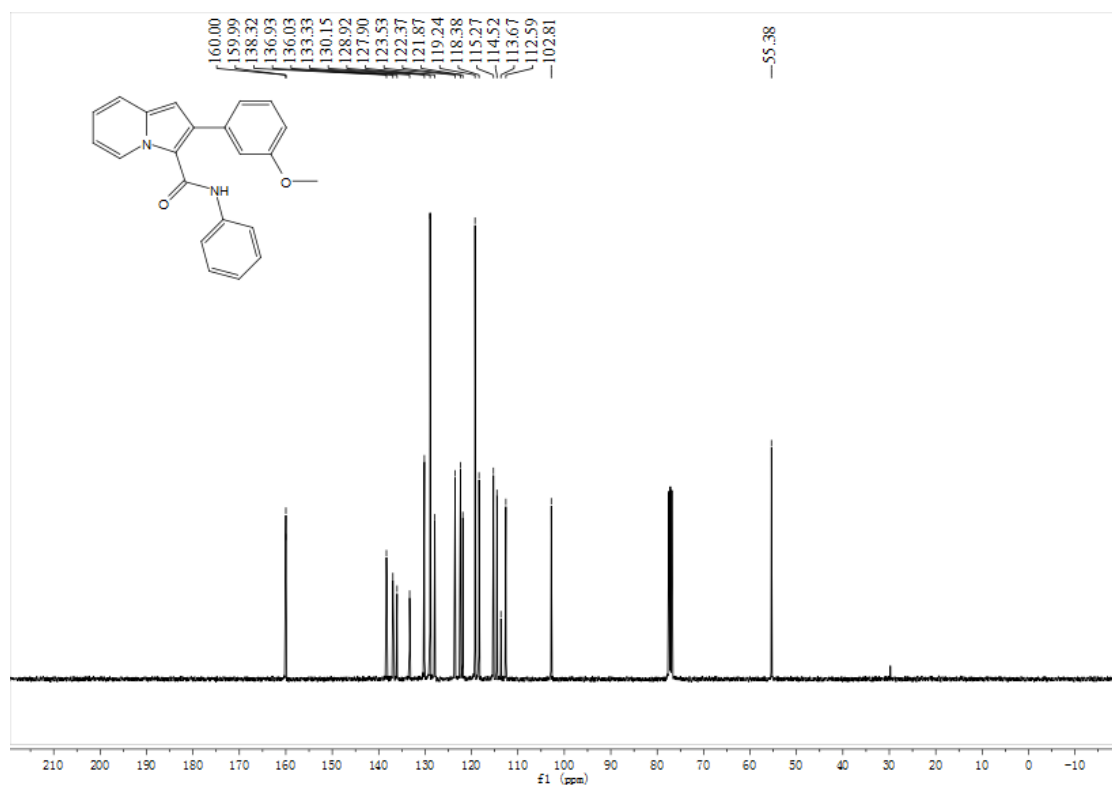
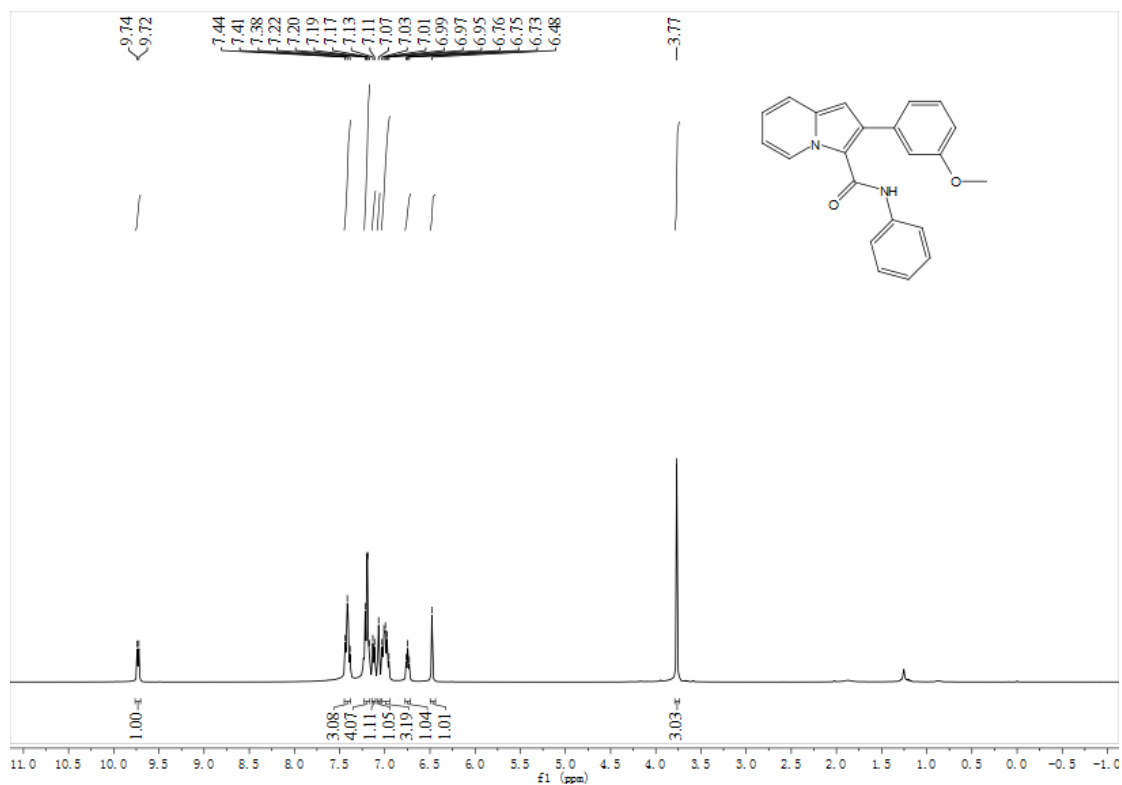
^1H NMR and ^{13}C NMR spectrum of compound **3s**



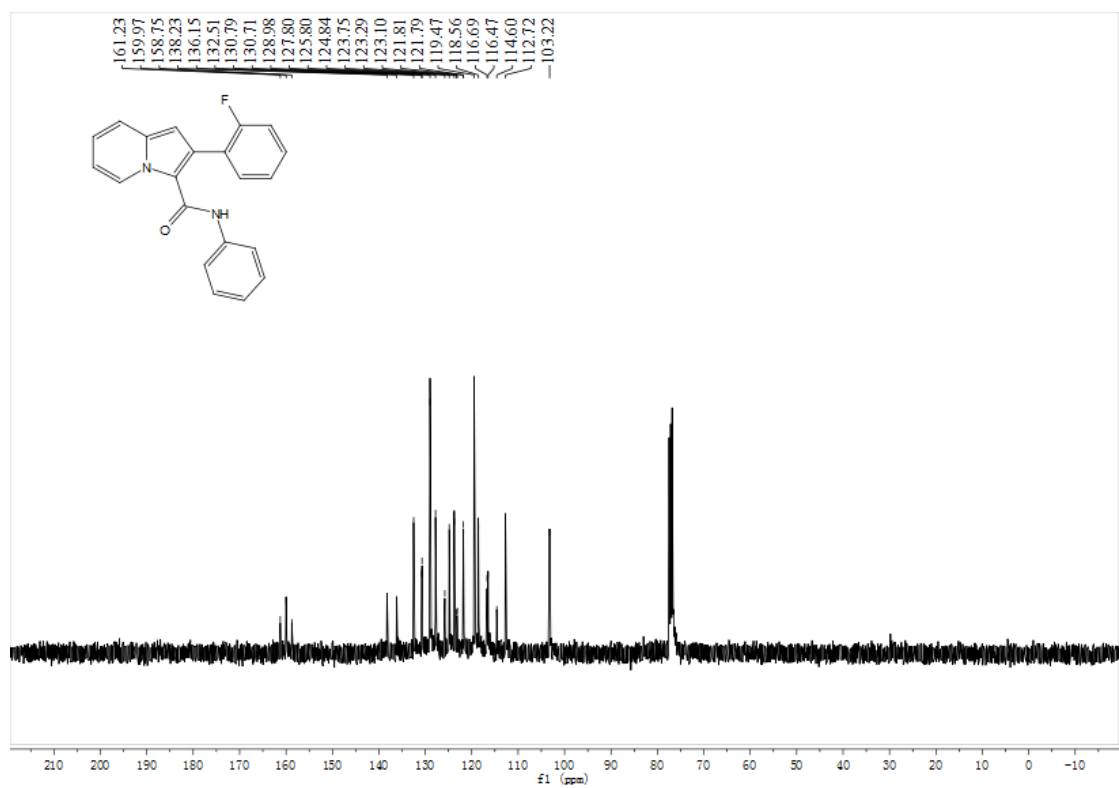
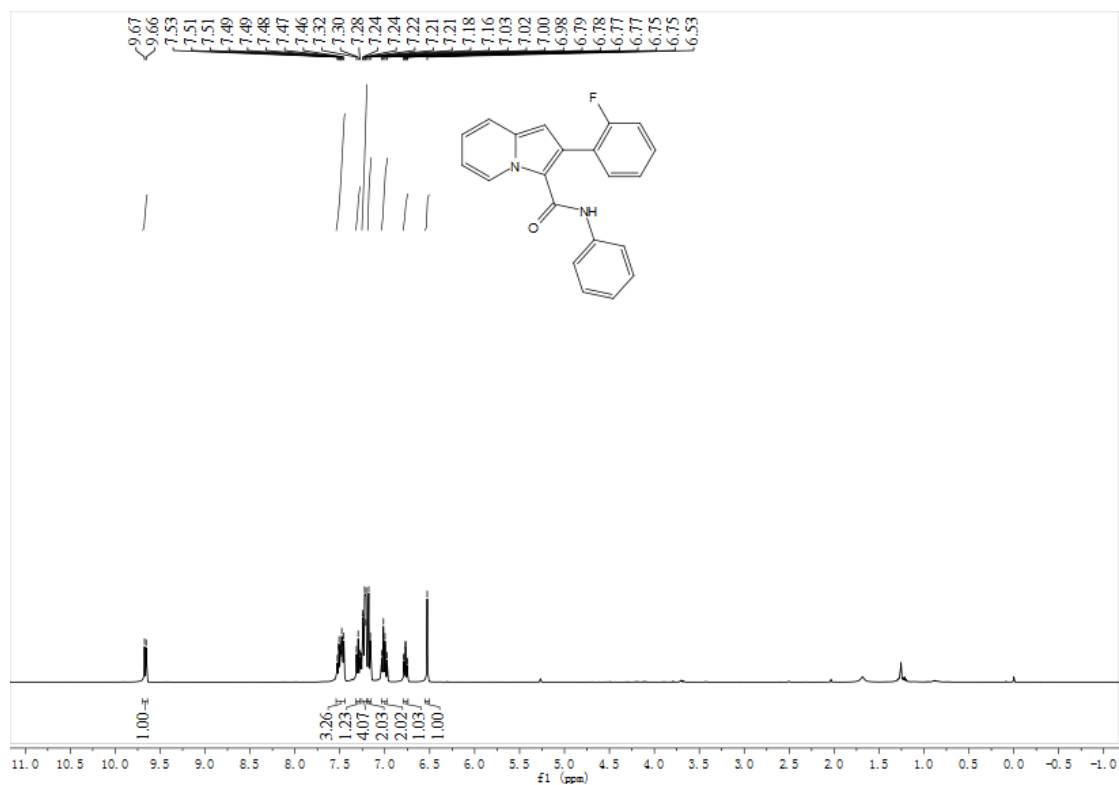
^1H NMR and ^{13}C NMR spectrum of compound **3t**



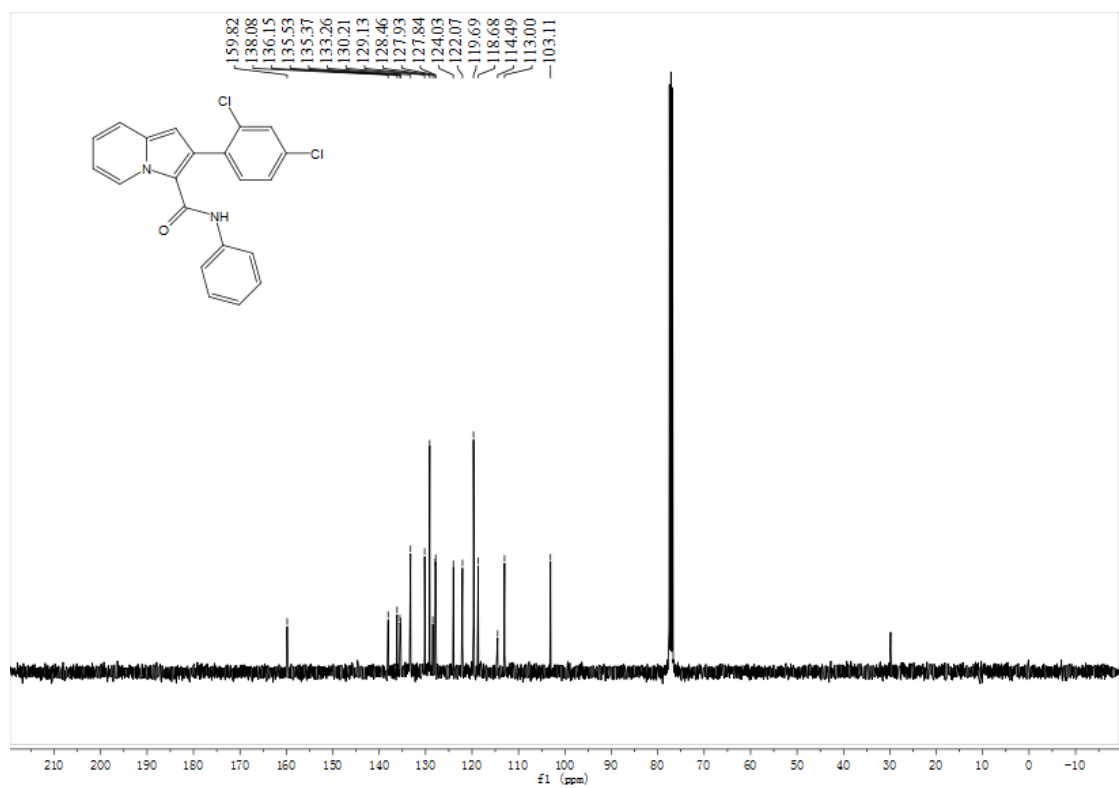
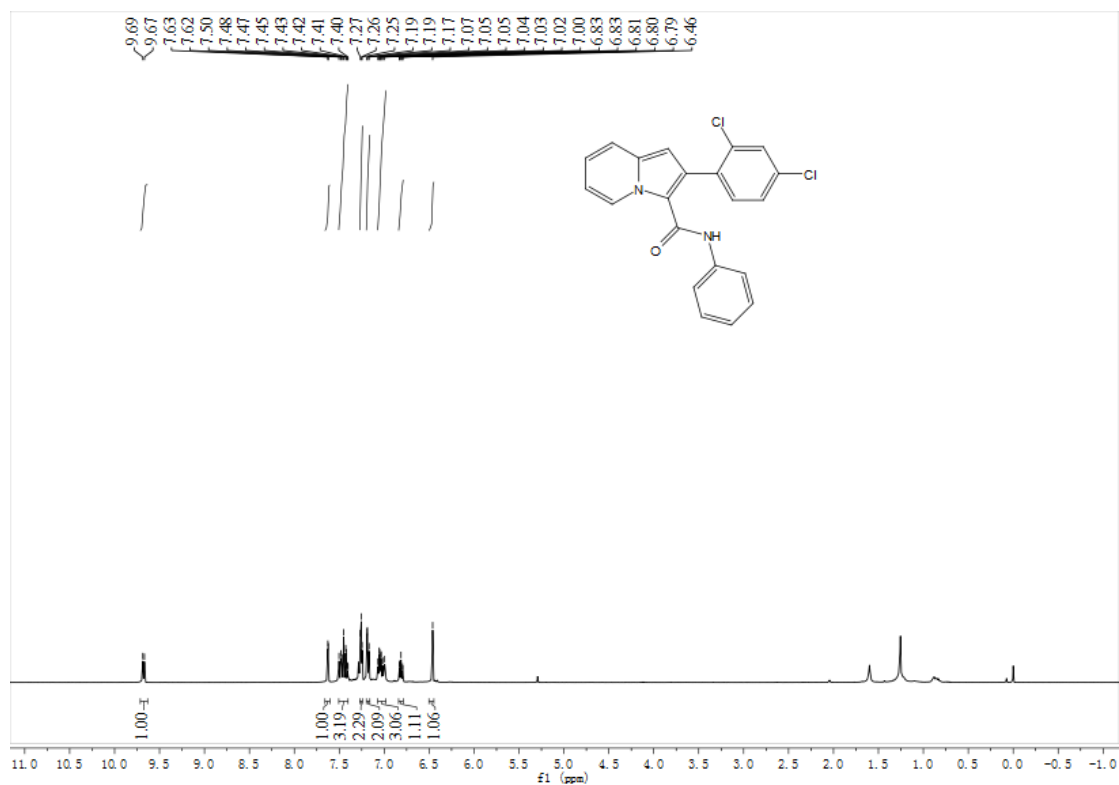
^1H NMR and ^{13}C NMR spectrum of compound **3u**



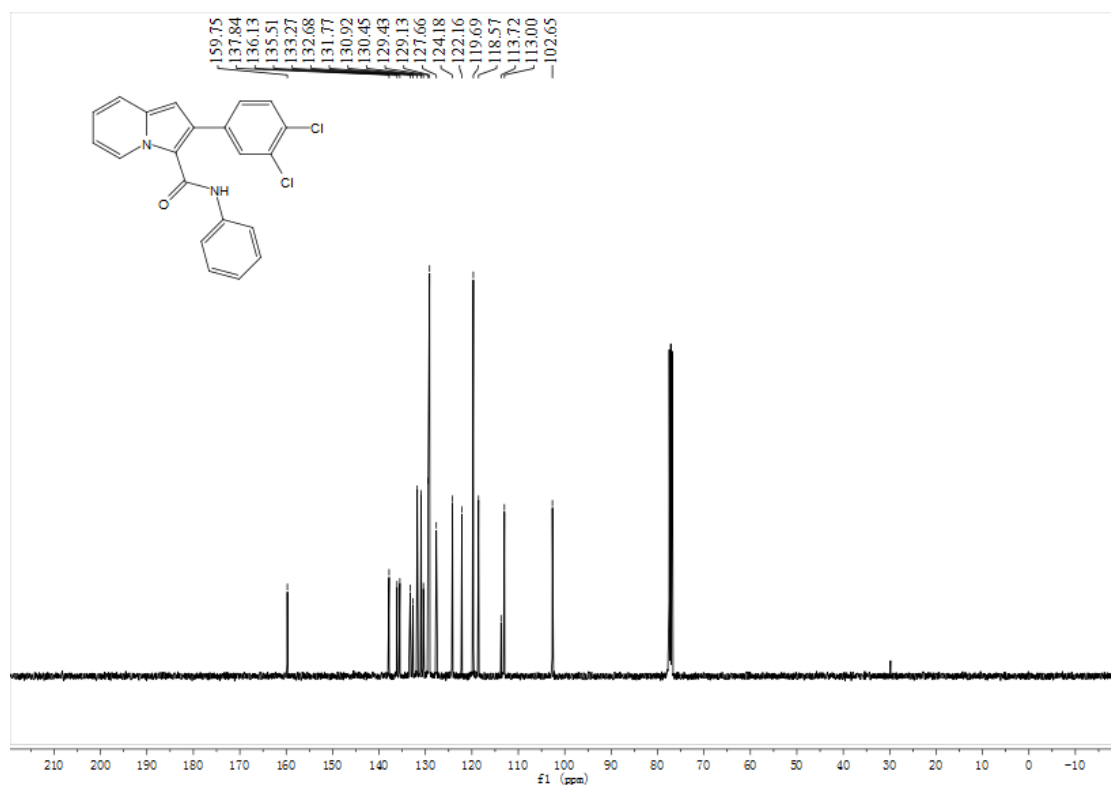
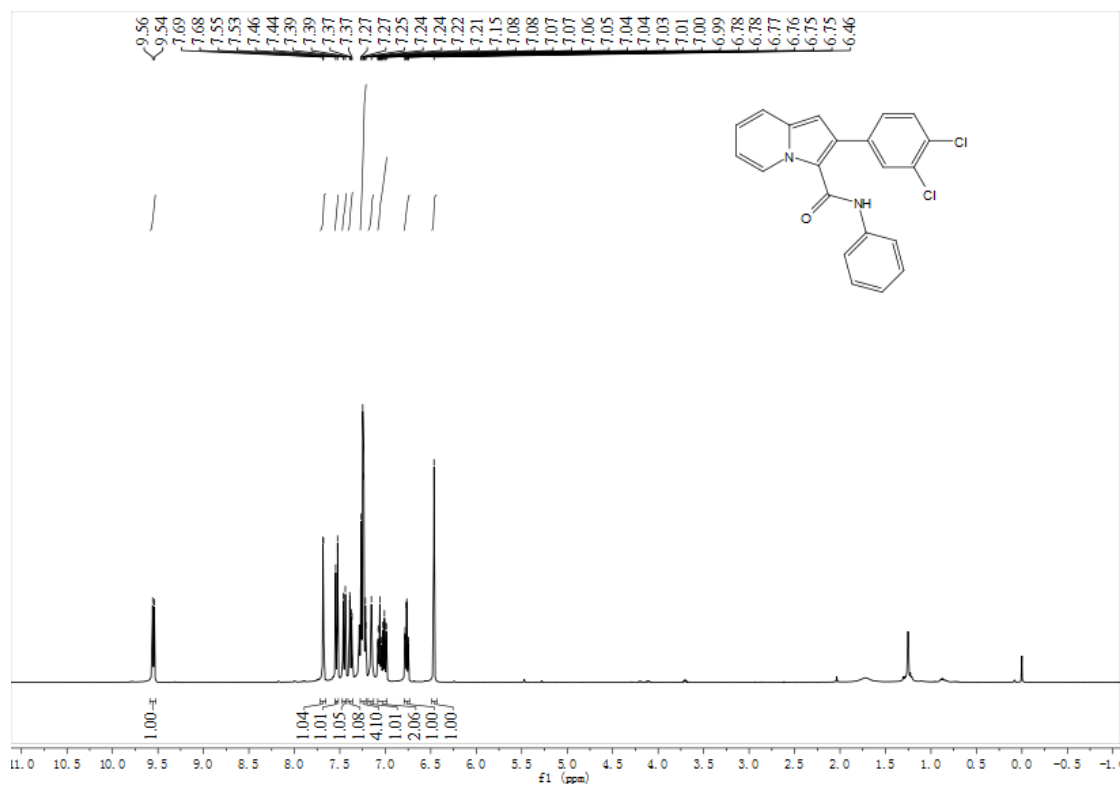
^1H NMR and ^{13}C NMR spectrum of compound **3v**



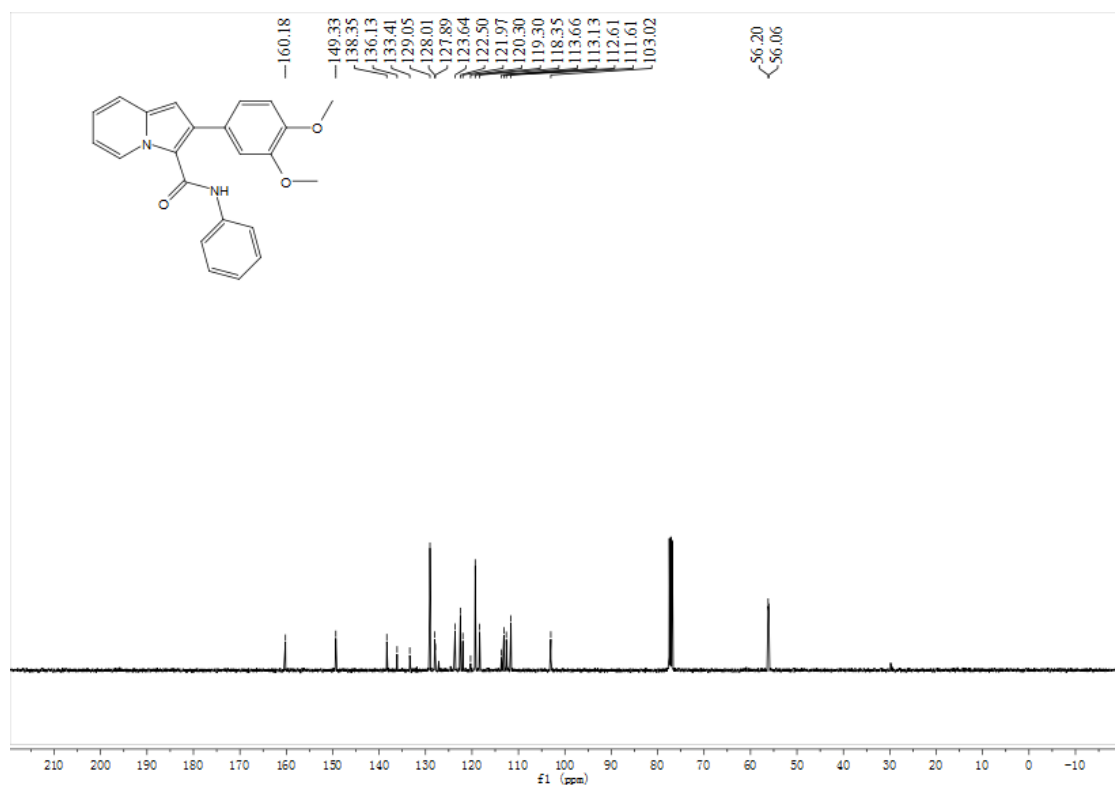
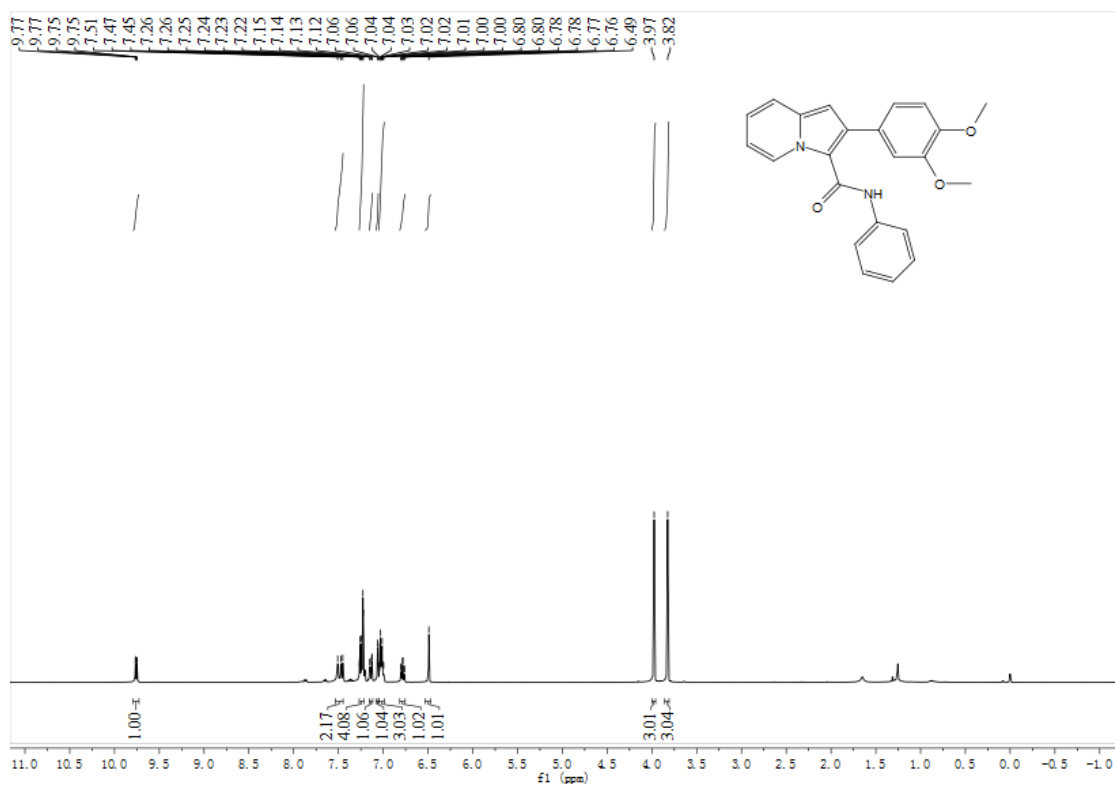
^1H NMR and ^{13}C NMR spectrum of compound **3w**



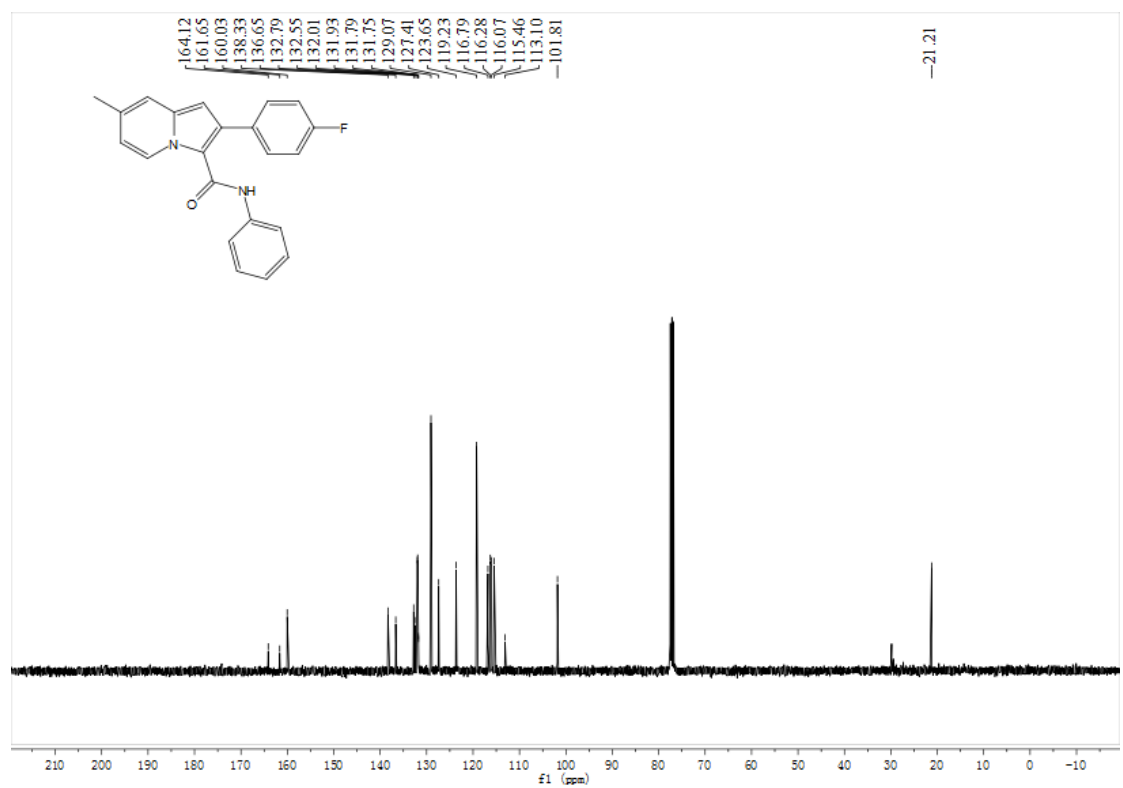
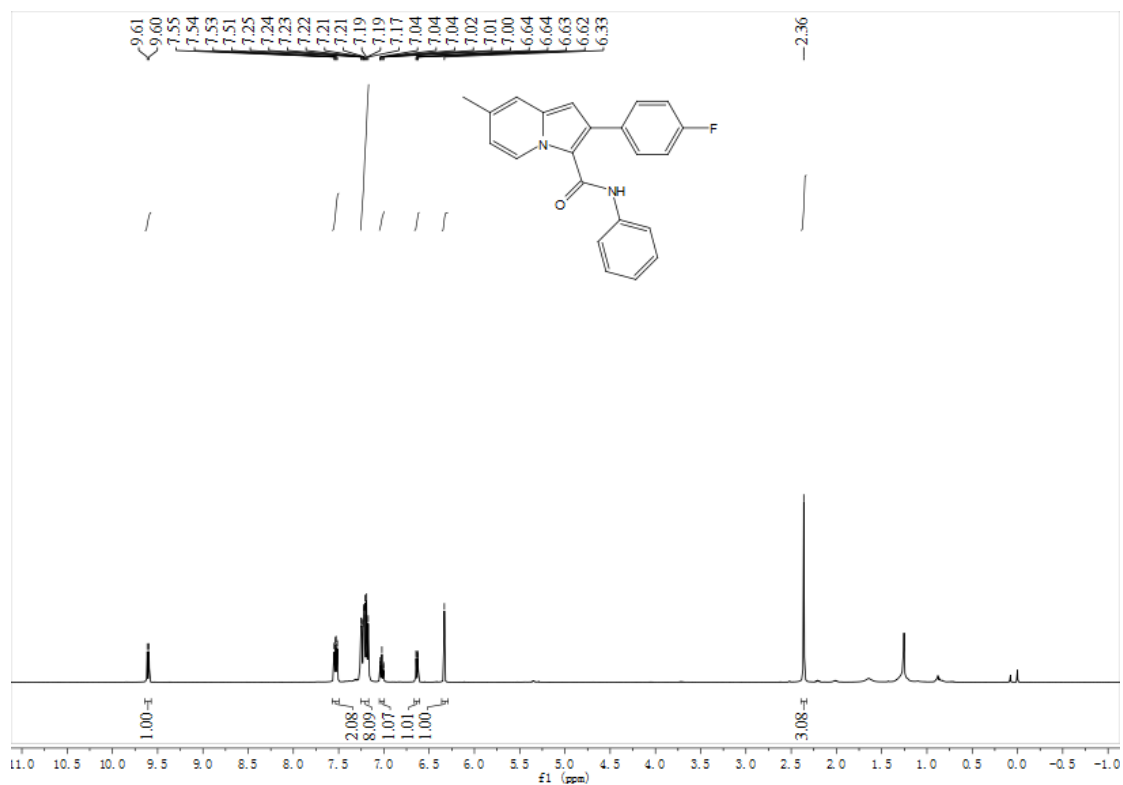
^1H NMR and ^{13}C NMR spectrum of compound **3x**



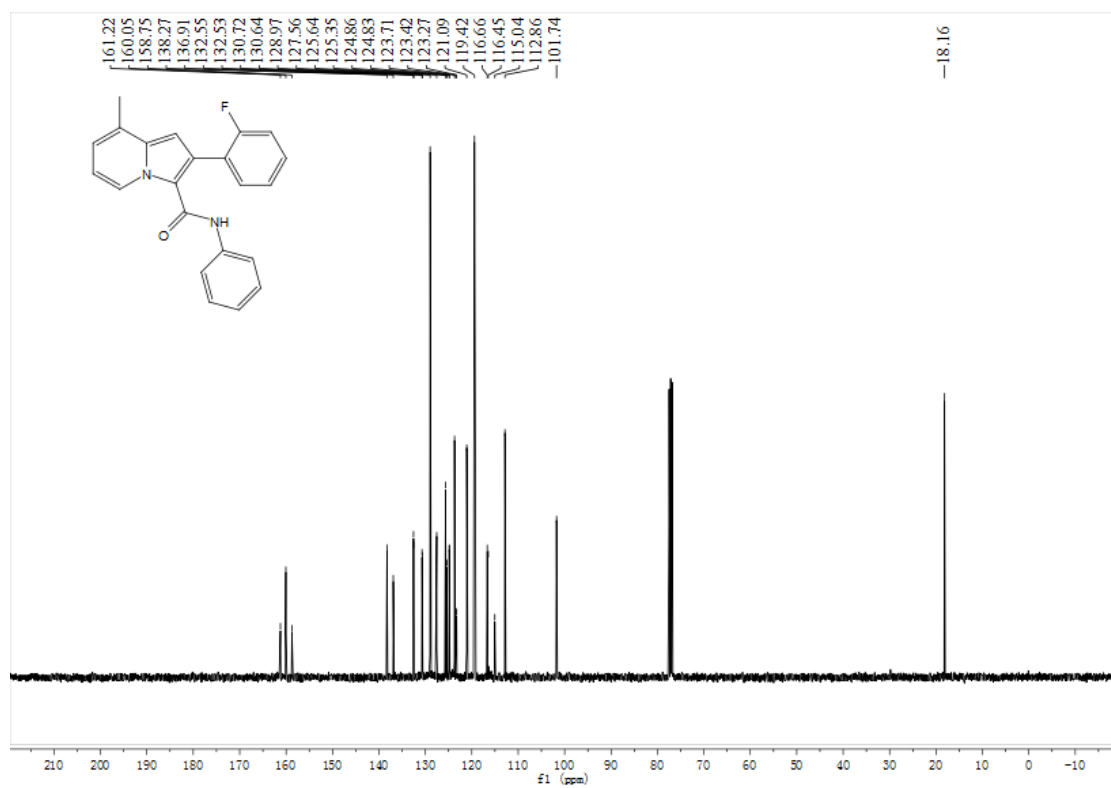
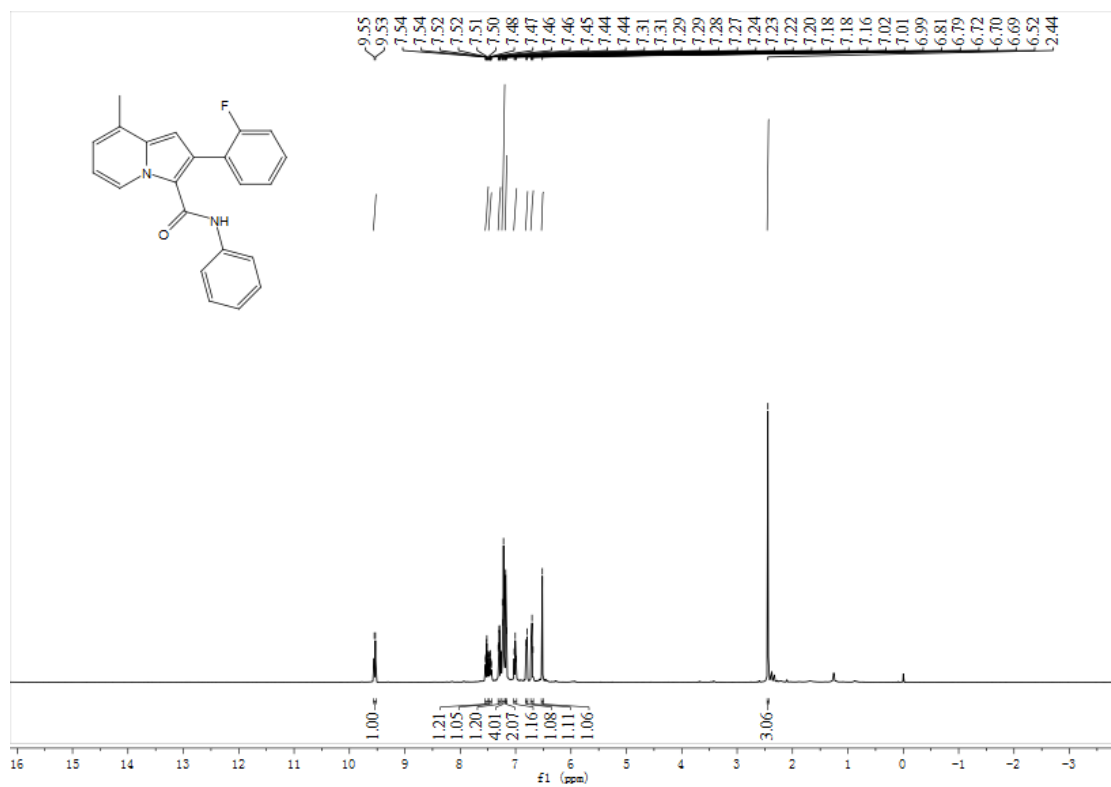
^1H NMR and ^{13}C NMR spectrum of compound **3y**



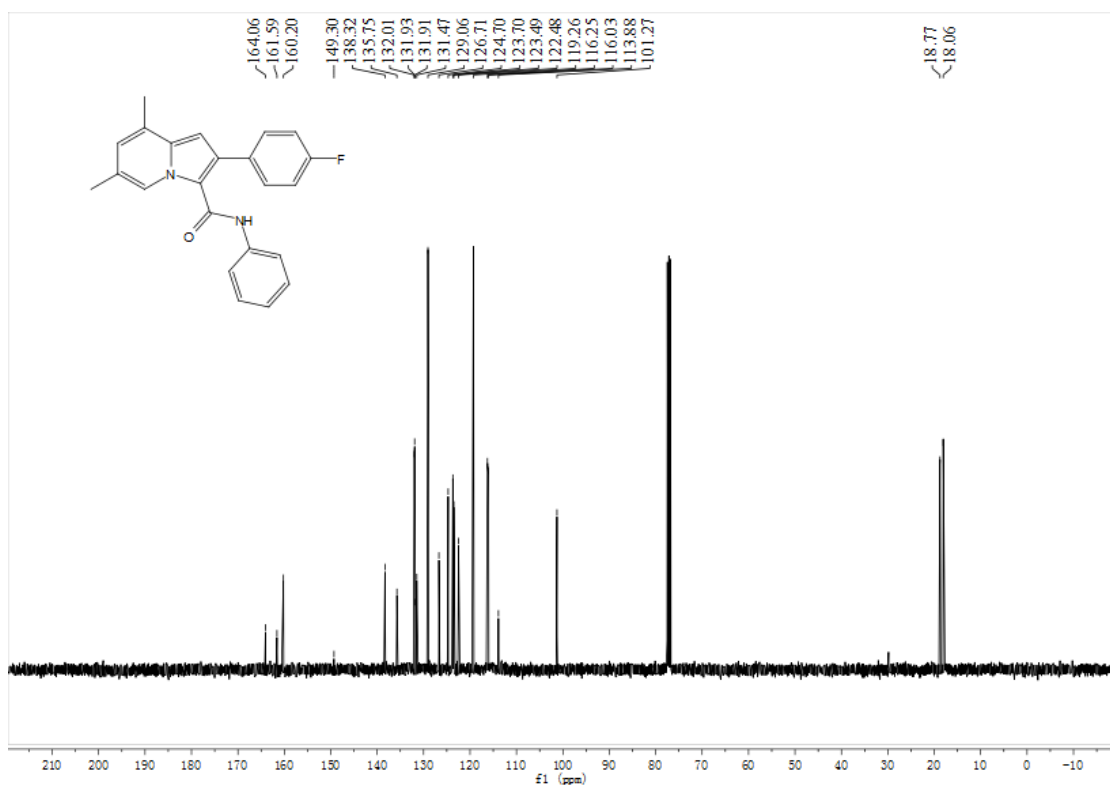
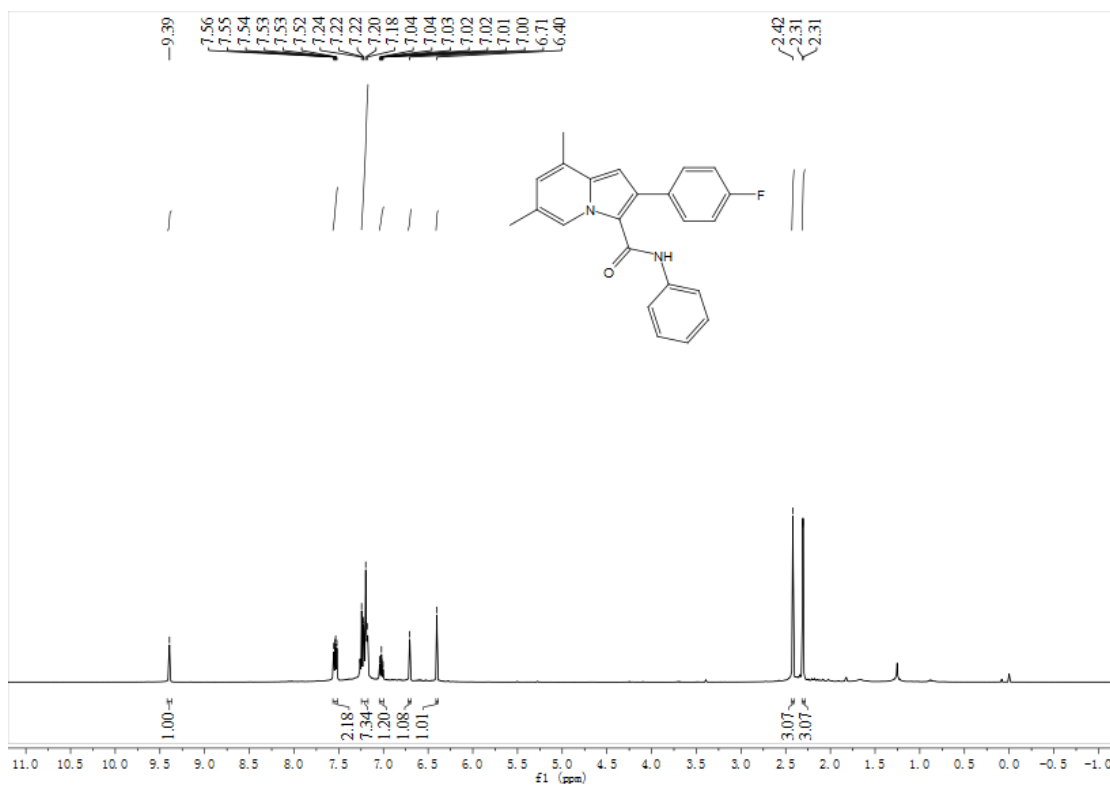
^1H NMR and ^{13}C NMR spectrum of compound **3z**



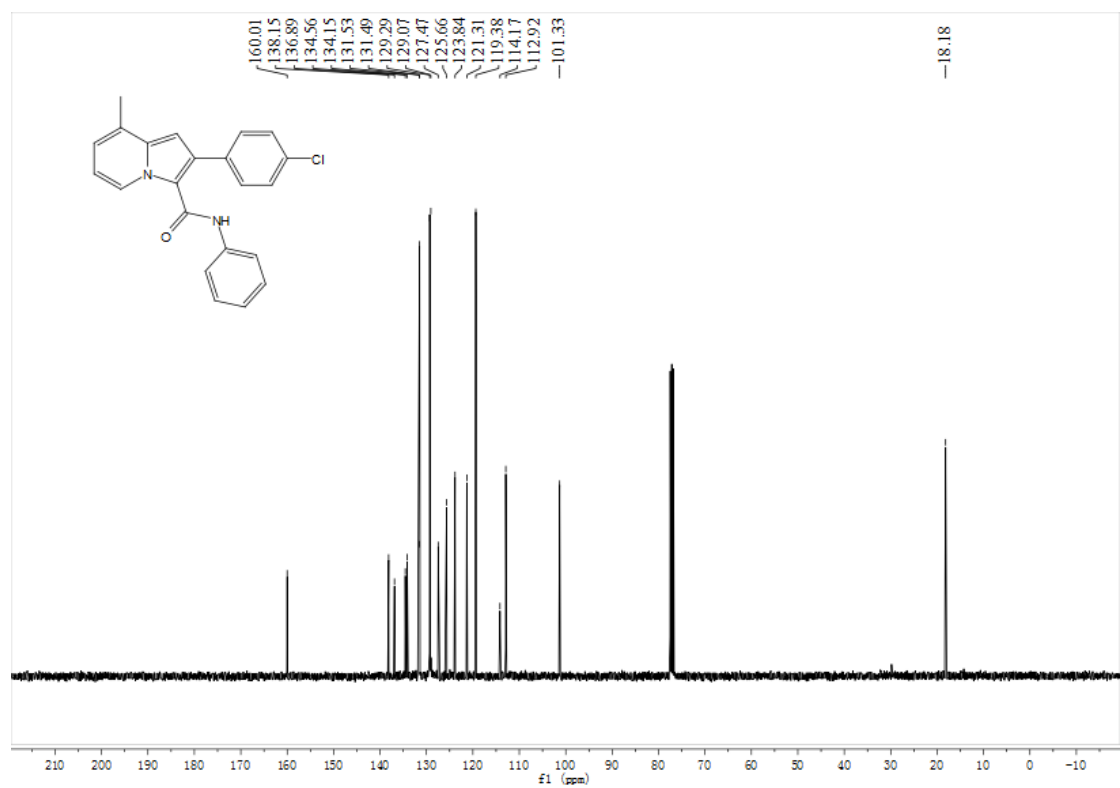
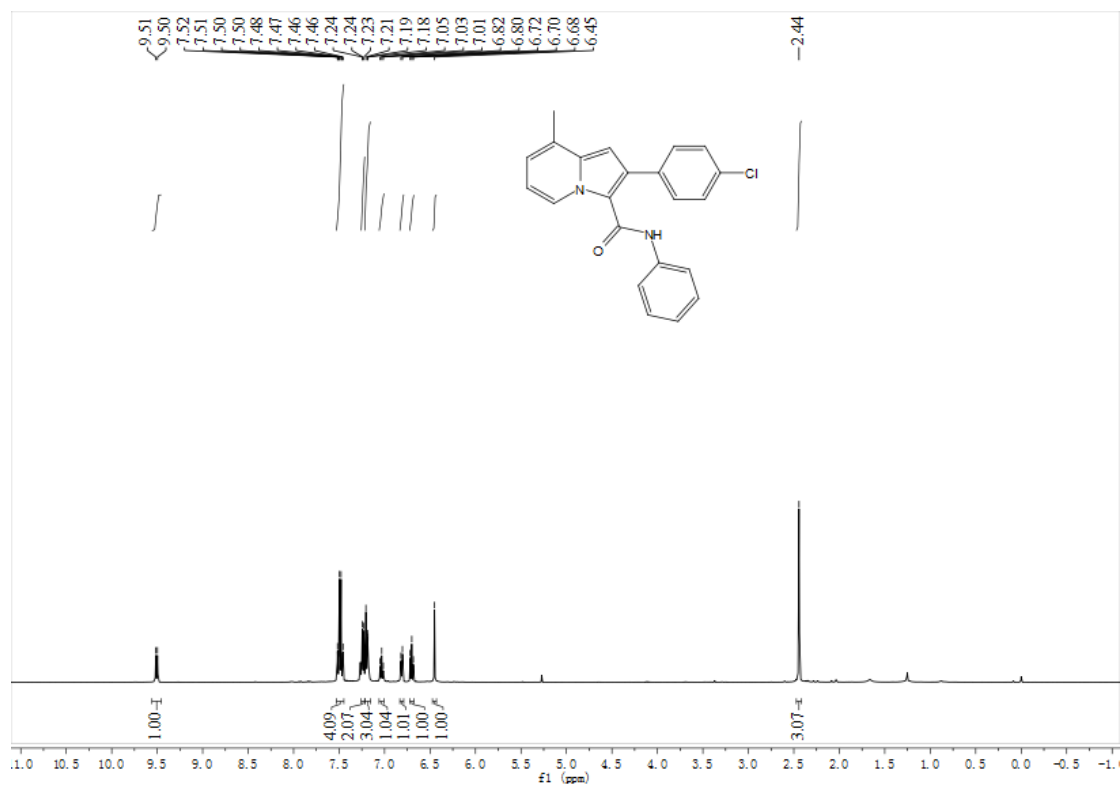
^1H NMR and ^{13}C NMR spectrum of compound **3aa**



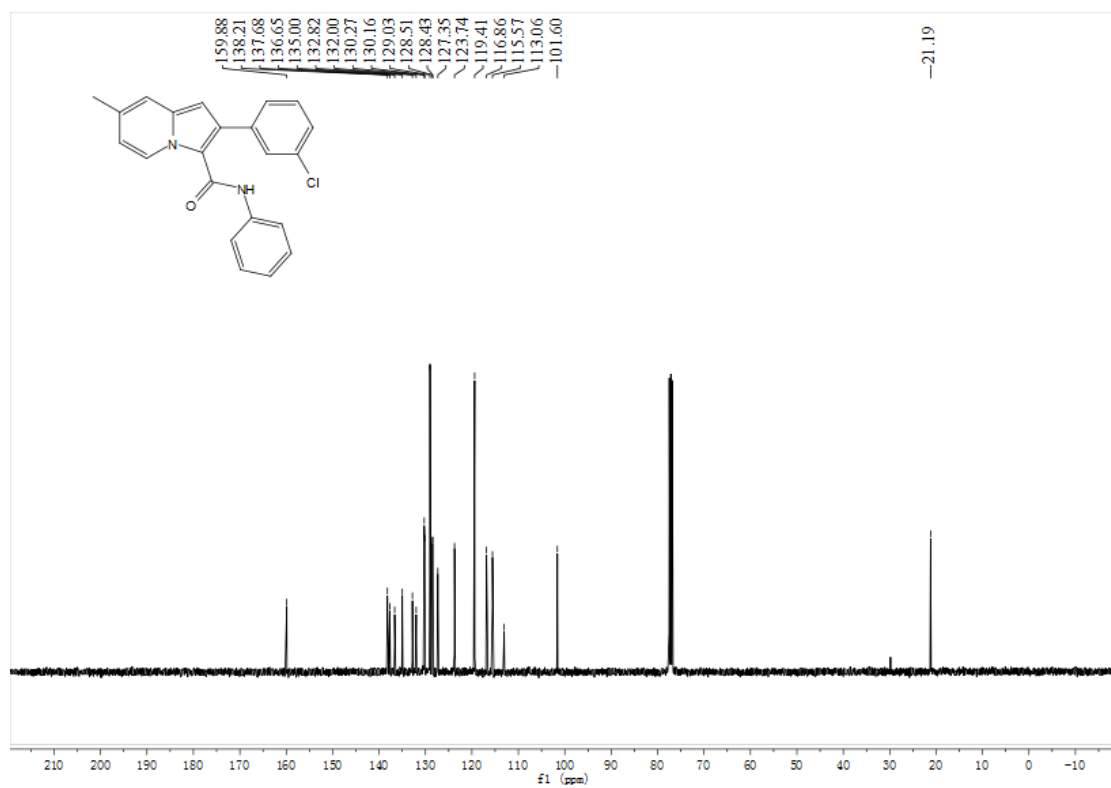
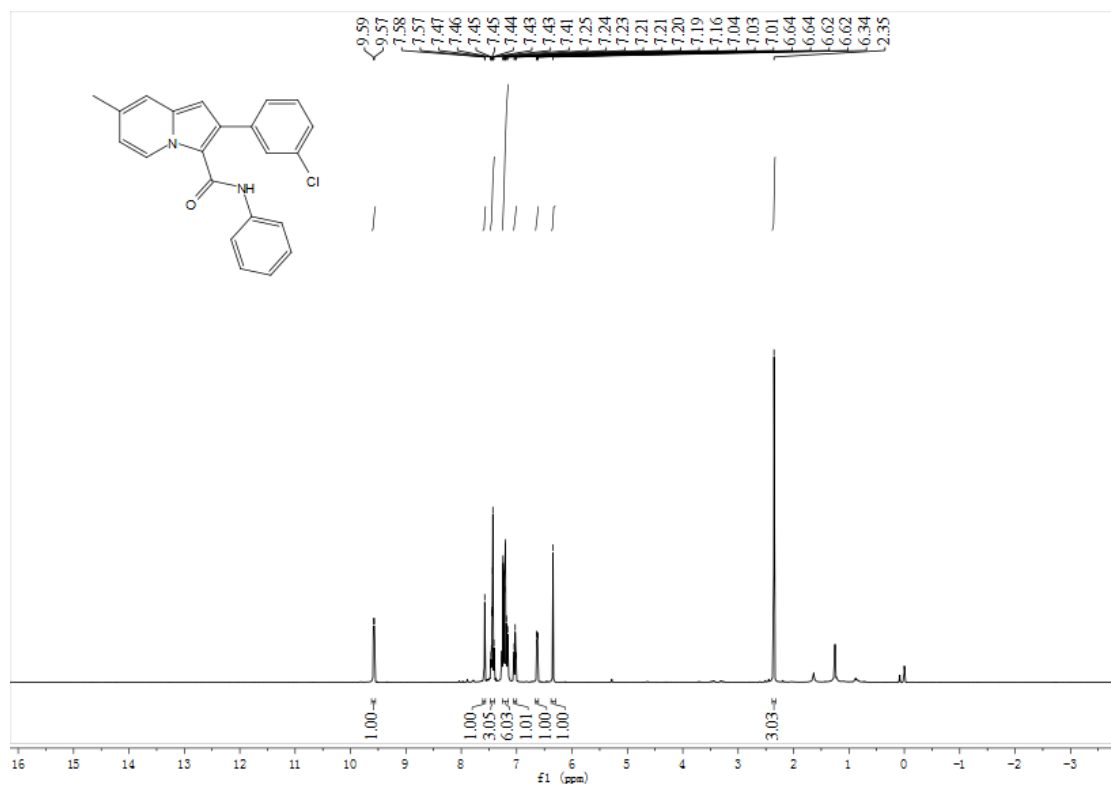
^1H NMR and ^{13}C NMR spectrum of compound **3ab**



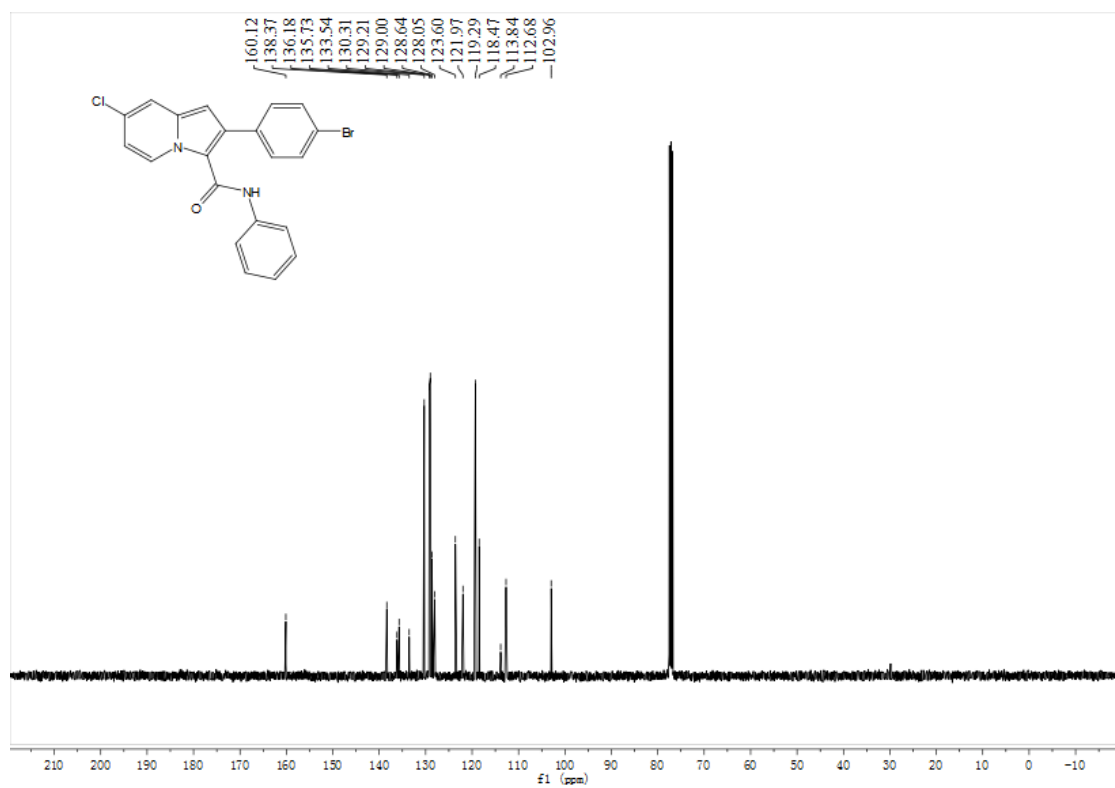
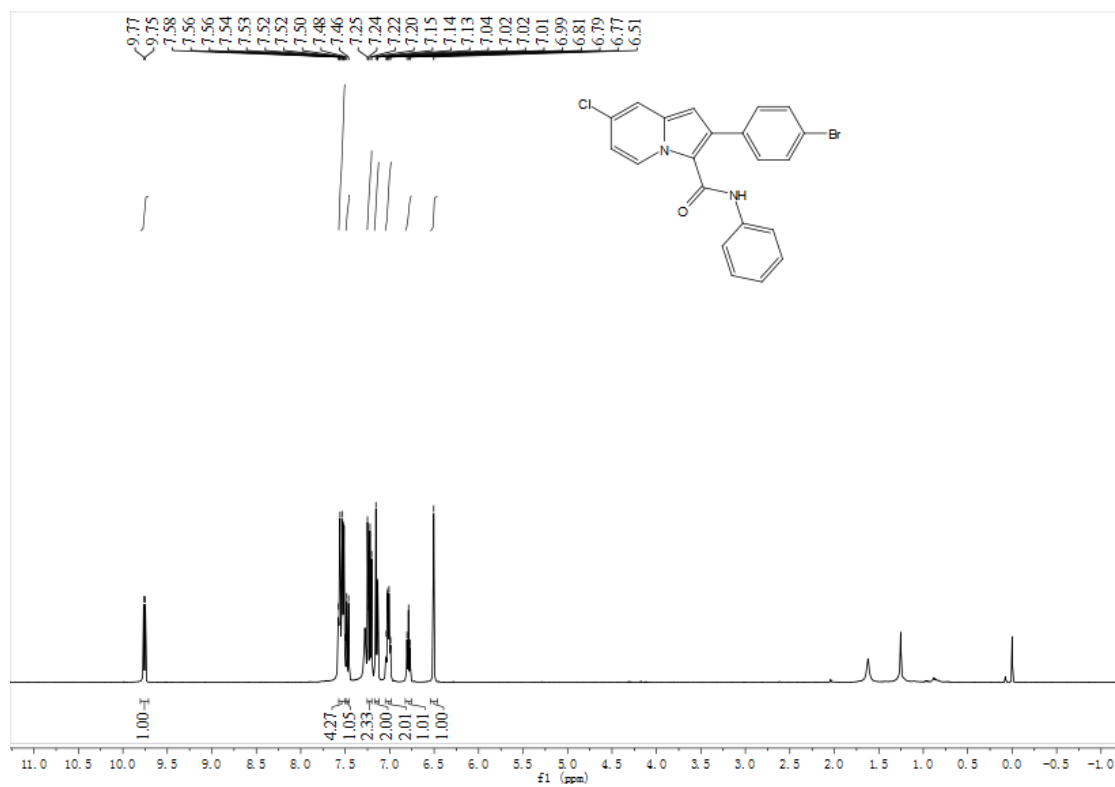
^1H NMR and ^{13}C NMR spectrum of compound **3ac**



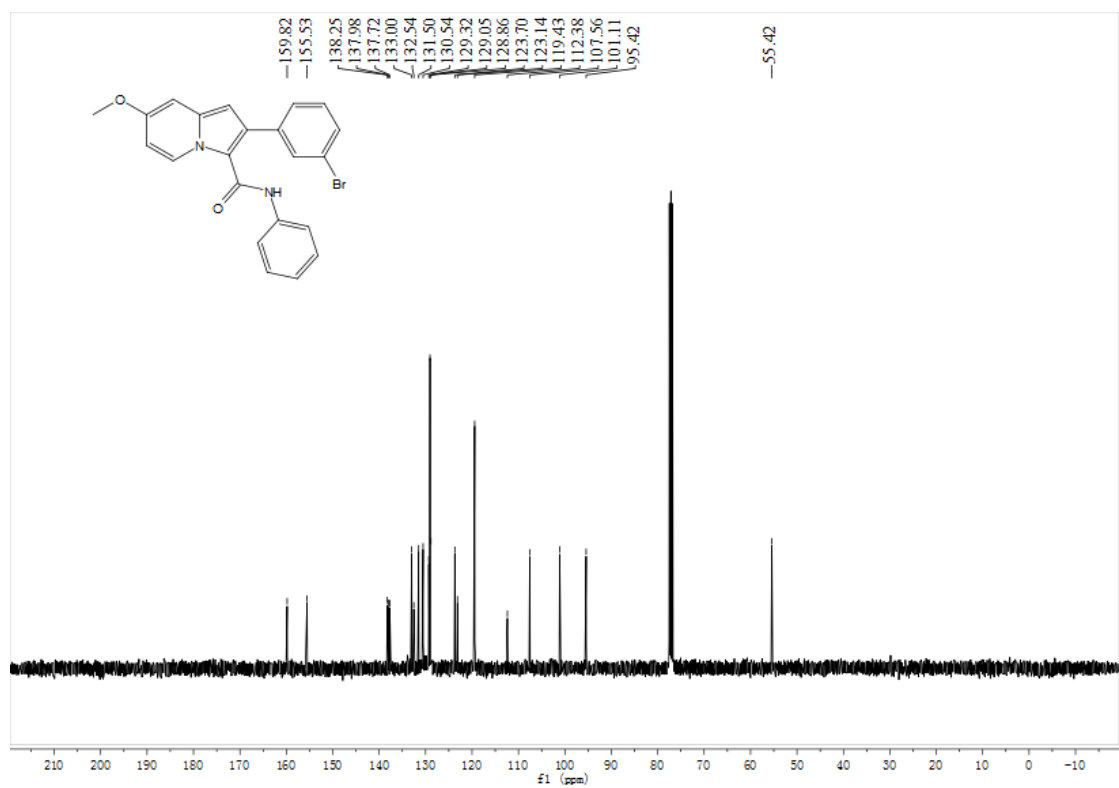
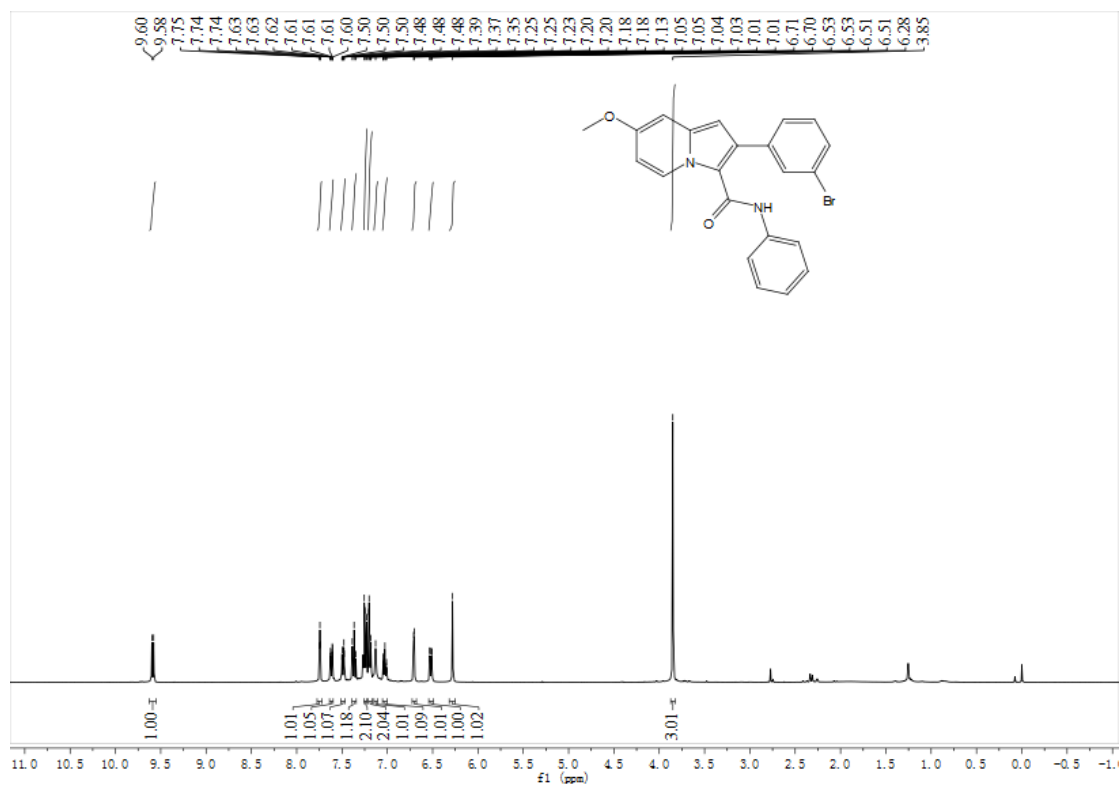
^1H NMR and ^{13}C NMR spectrum of compound **3ad**



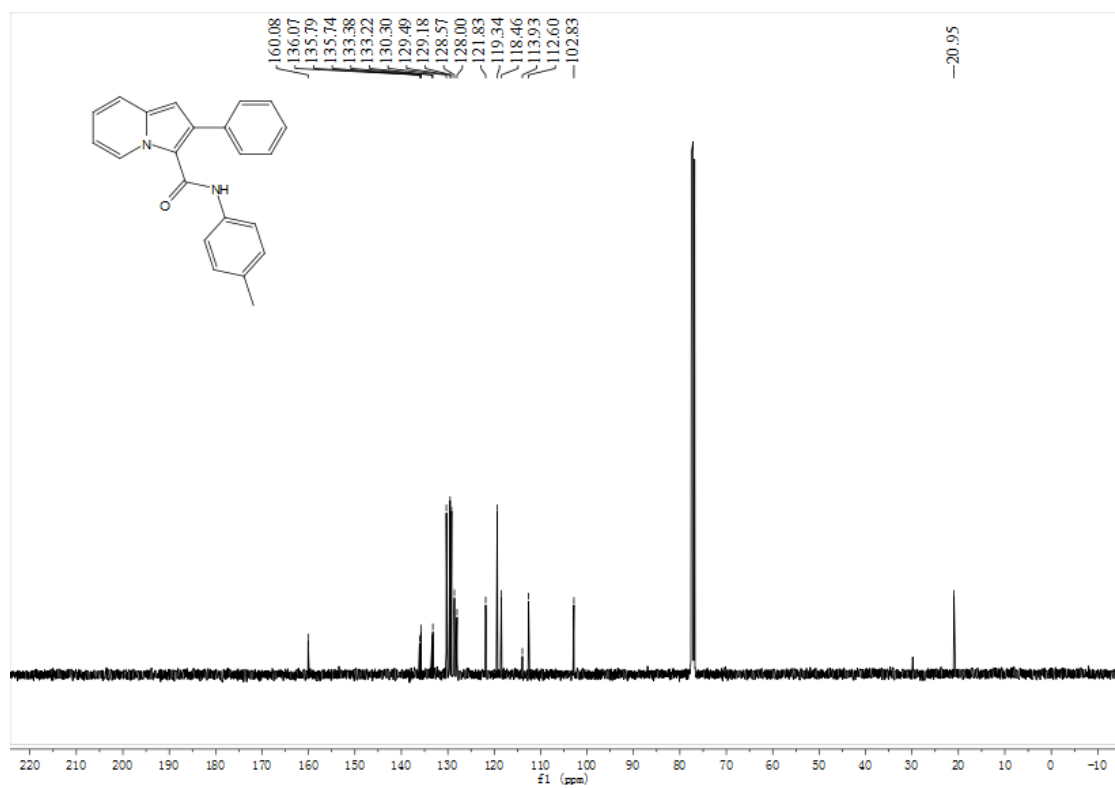
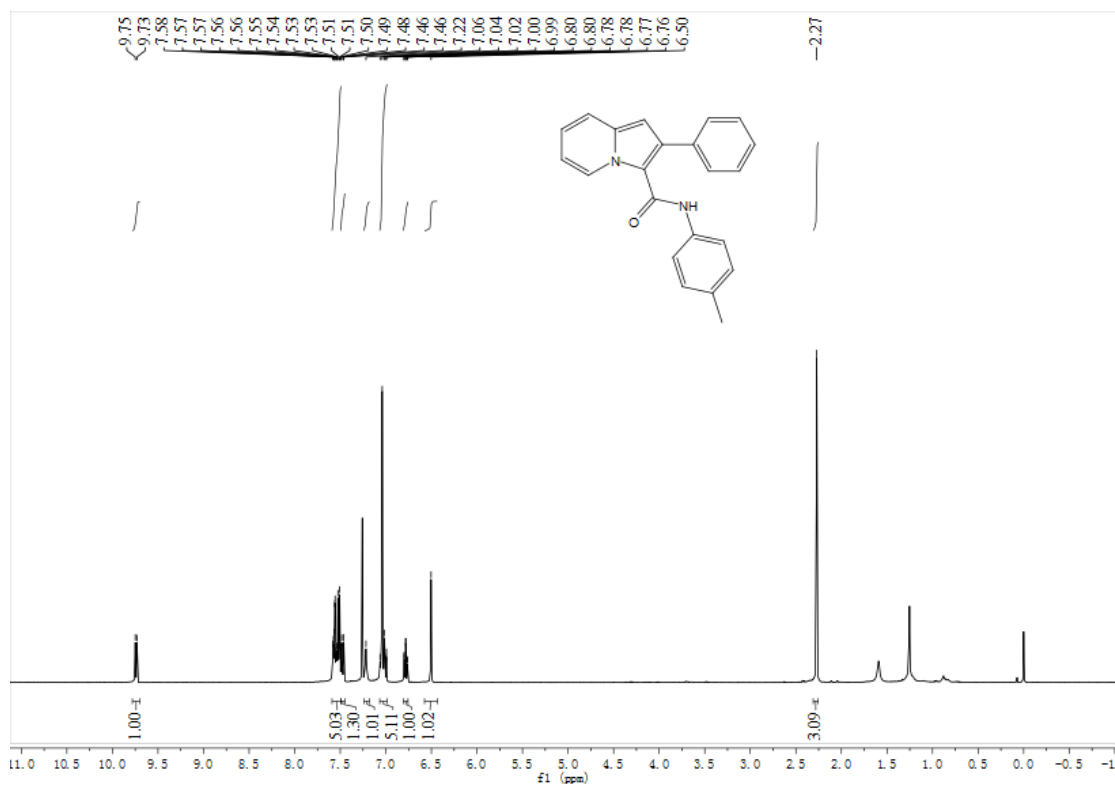
^1H NMR and ^{13}C NMR spectrum of compound **3ae**



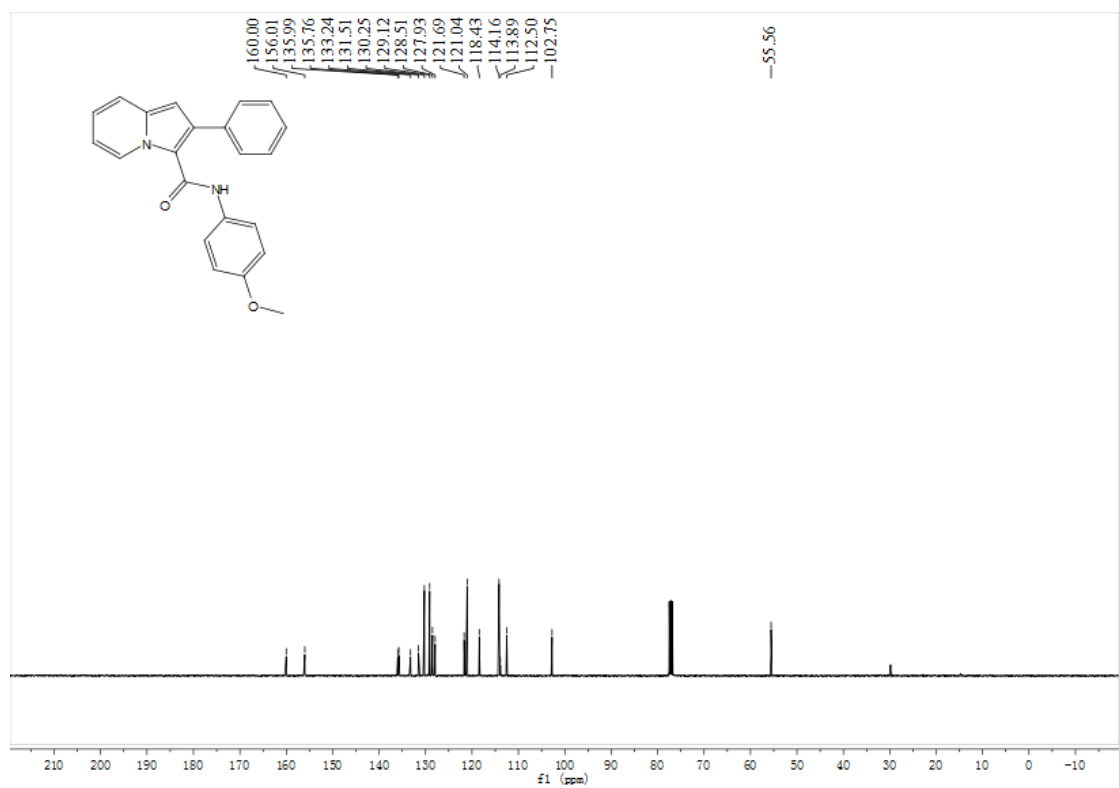
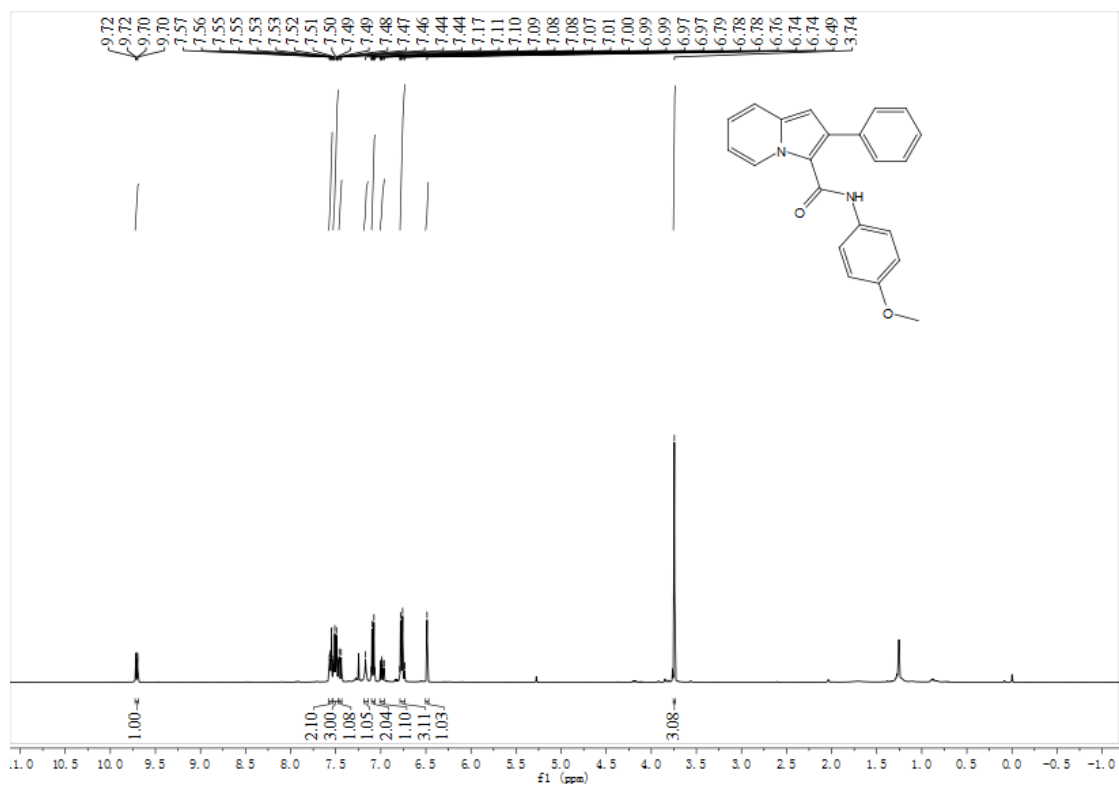
^1H NMR and ^{13}C NMR spectrum of compound **3af**



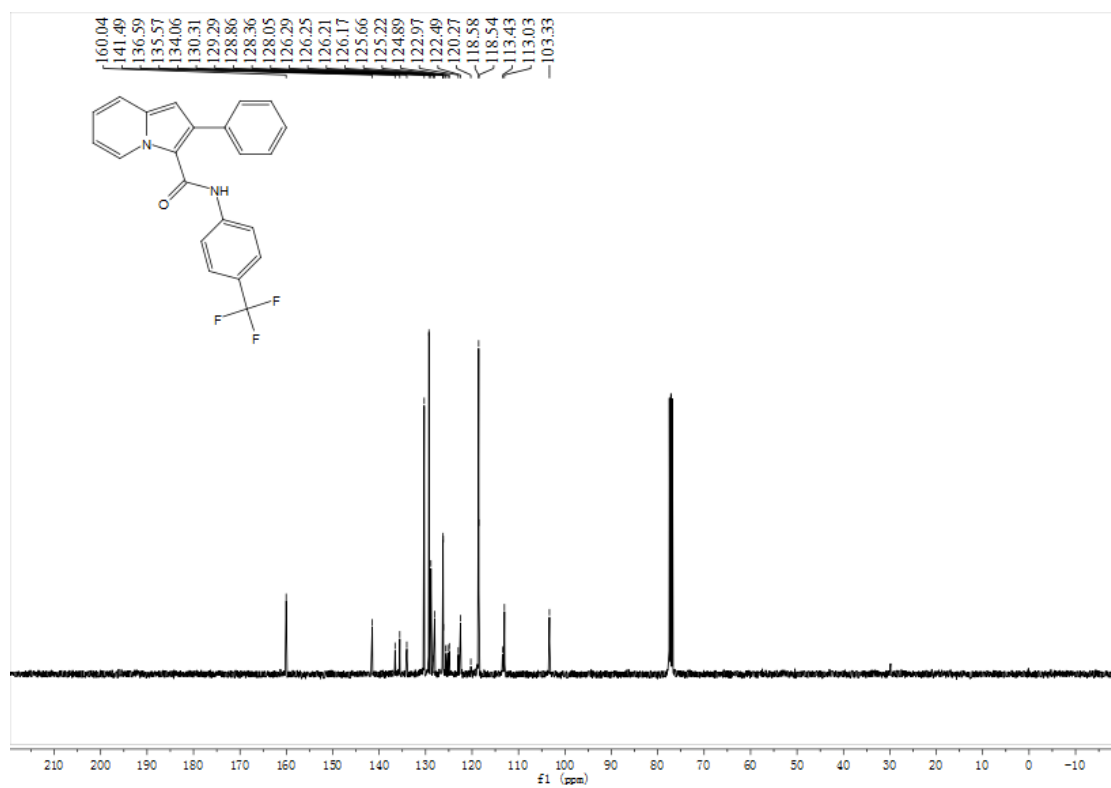
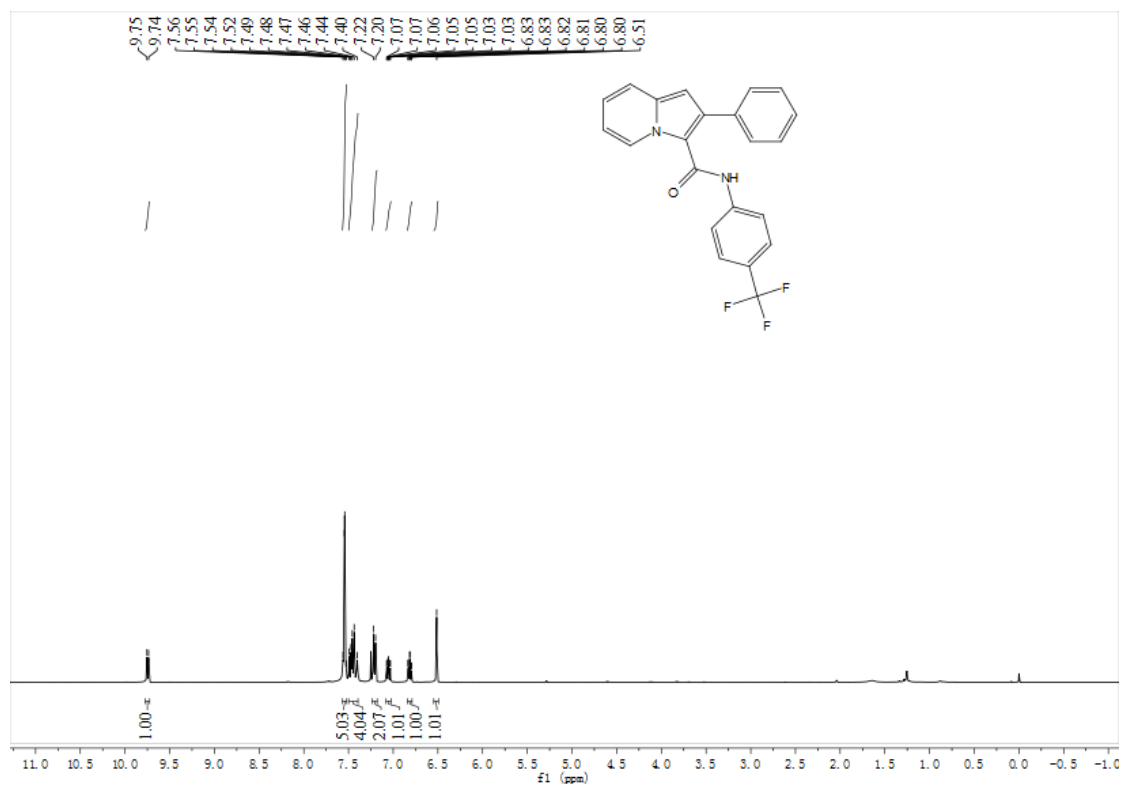
^1H NMR and ^{13}C NMR spectrum of compound **4a**



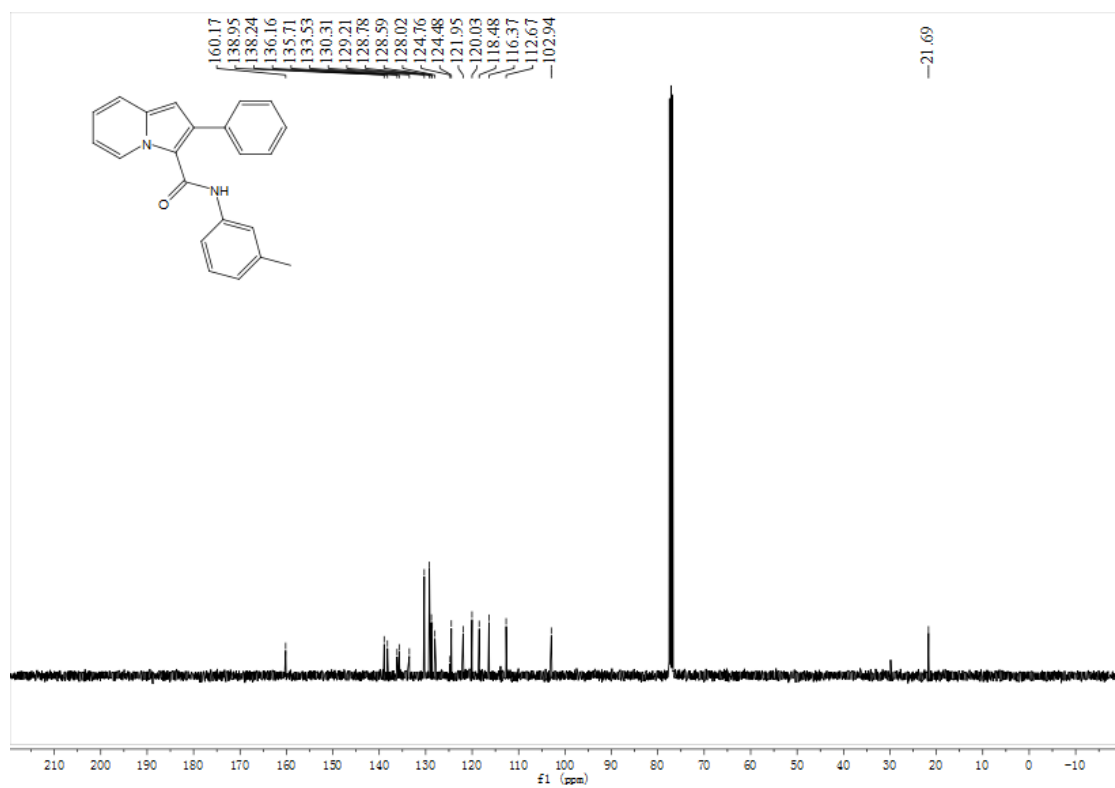
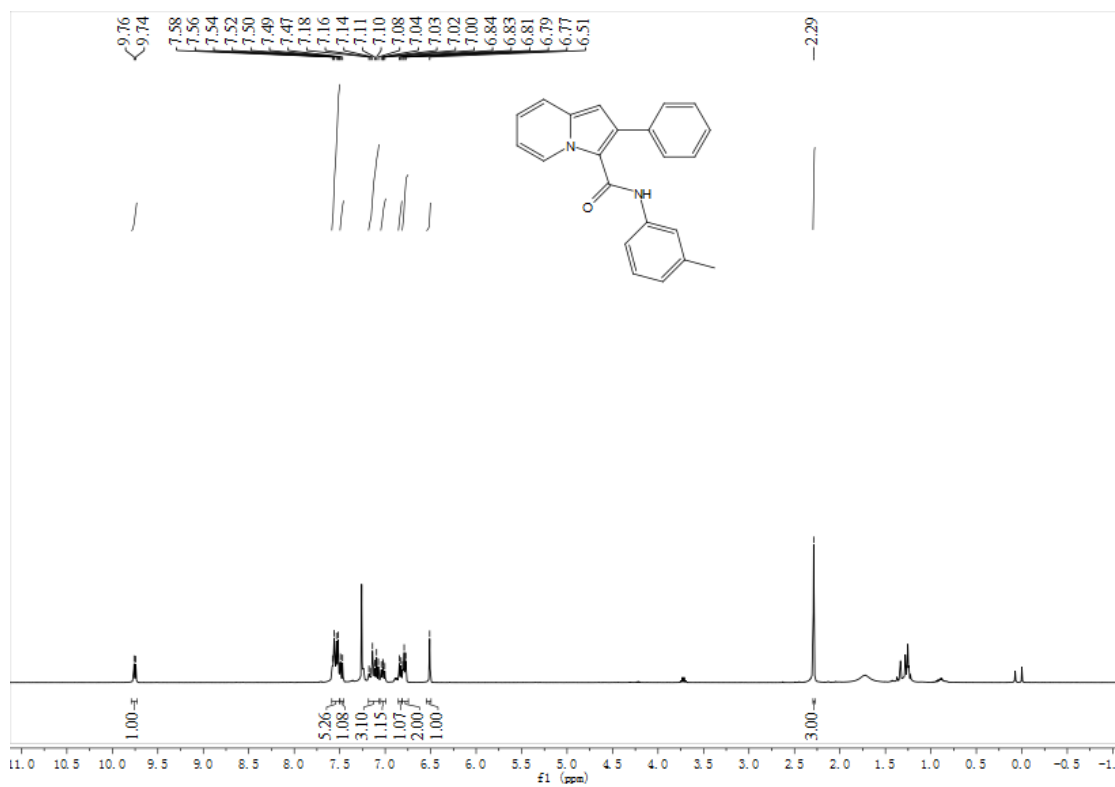
^1H NMR and ^{13}C NMR spectrum of compound **4b**



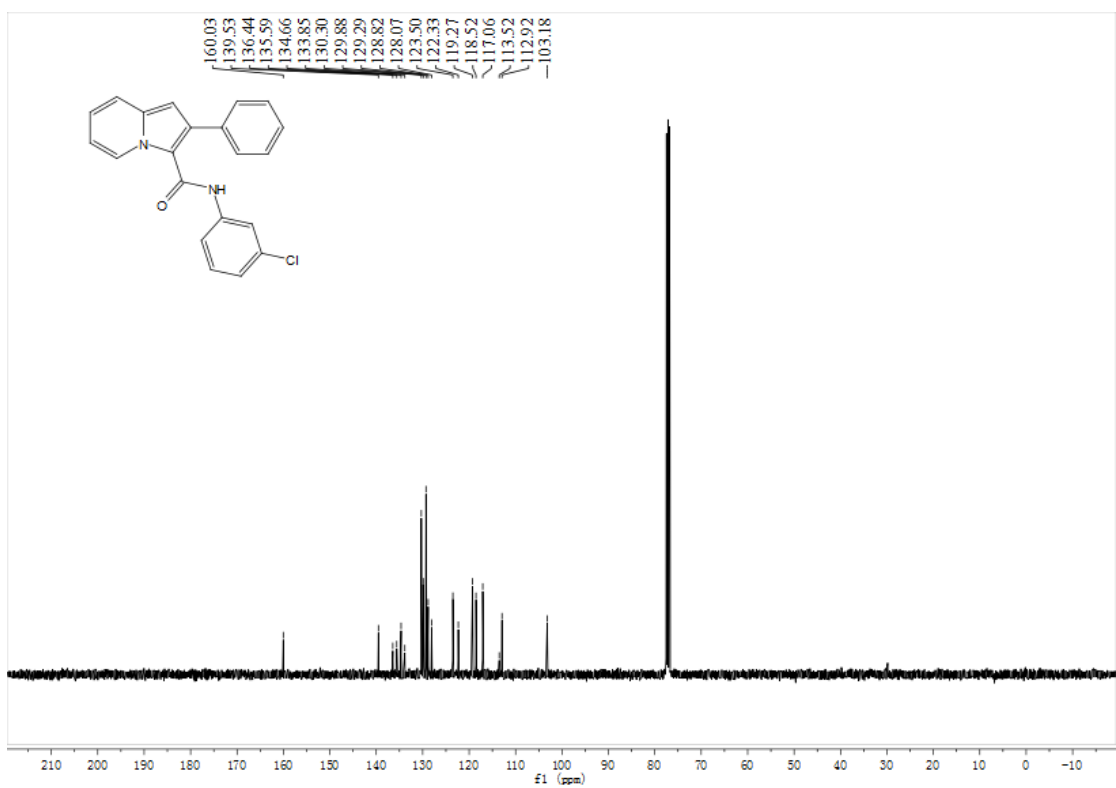
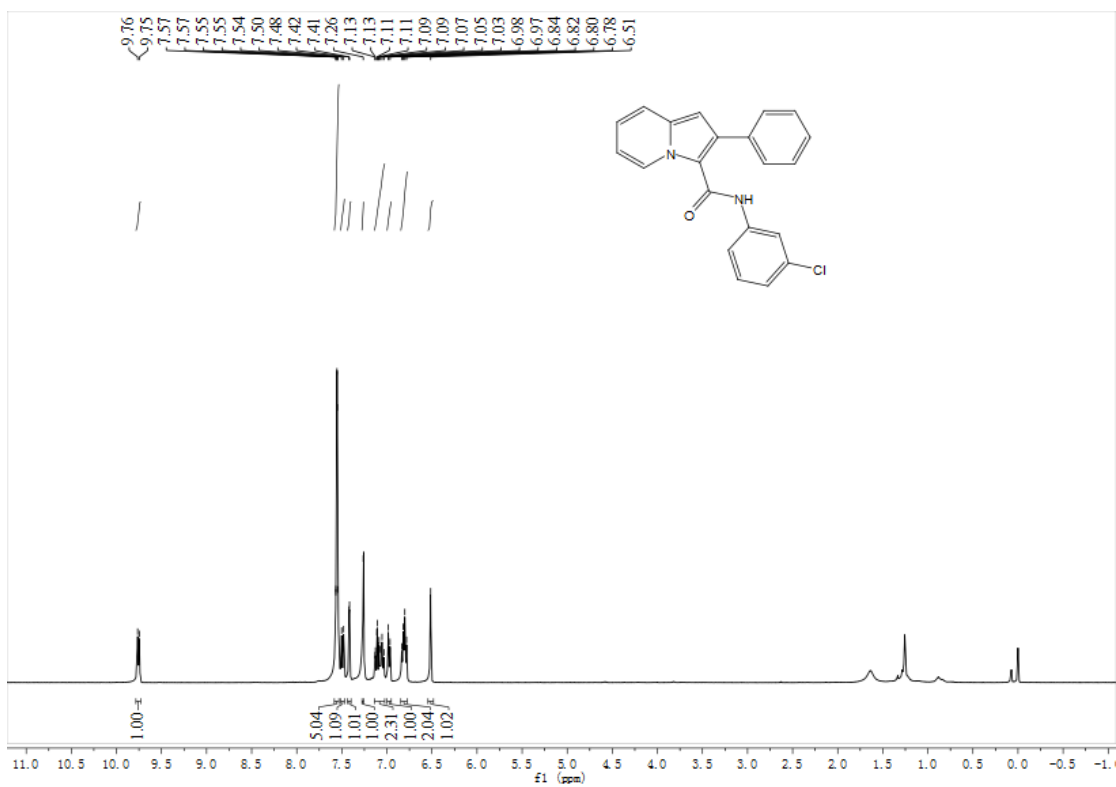
^1H NMR and ^{13}C NMR spectrum of compound **4c**



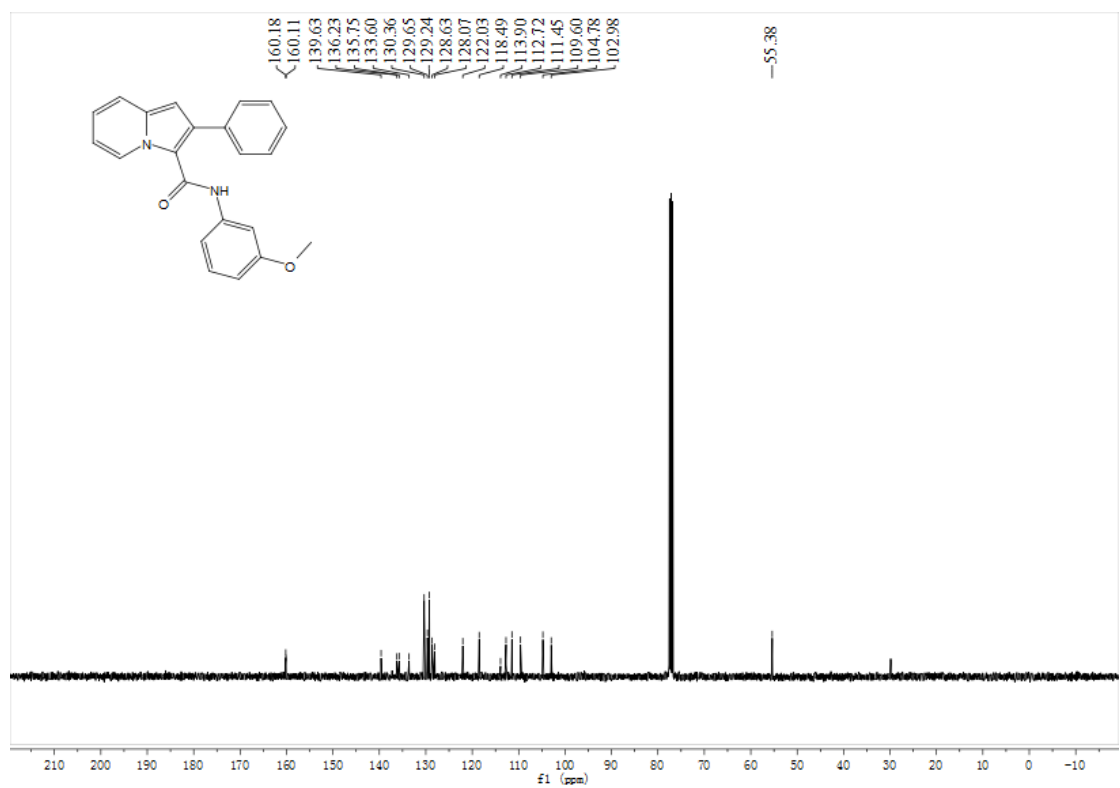
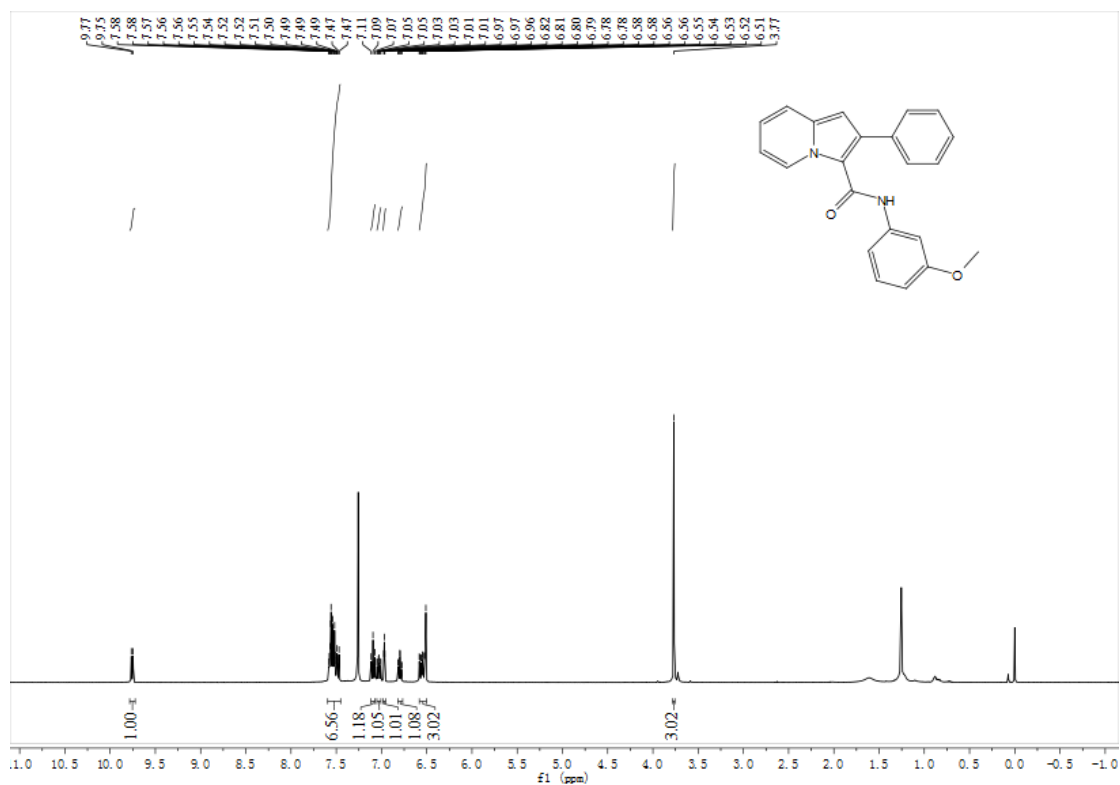
^1H NMR and ^{13}C NMR spectrum of compound **4d**



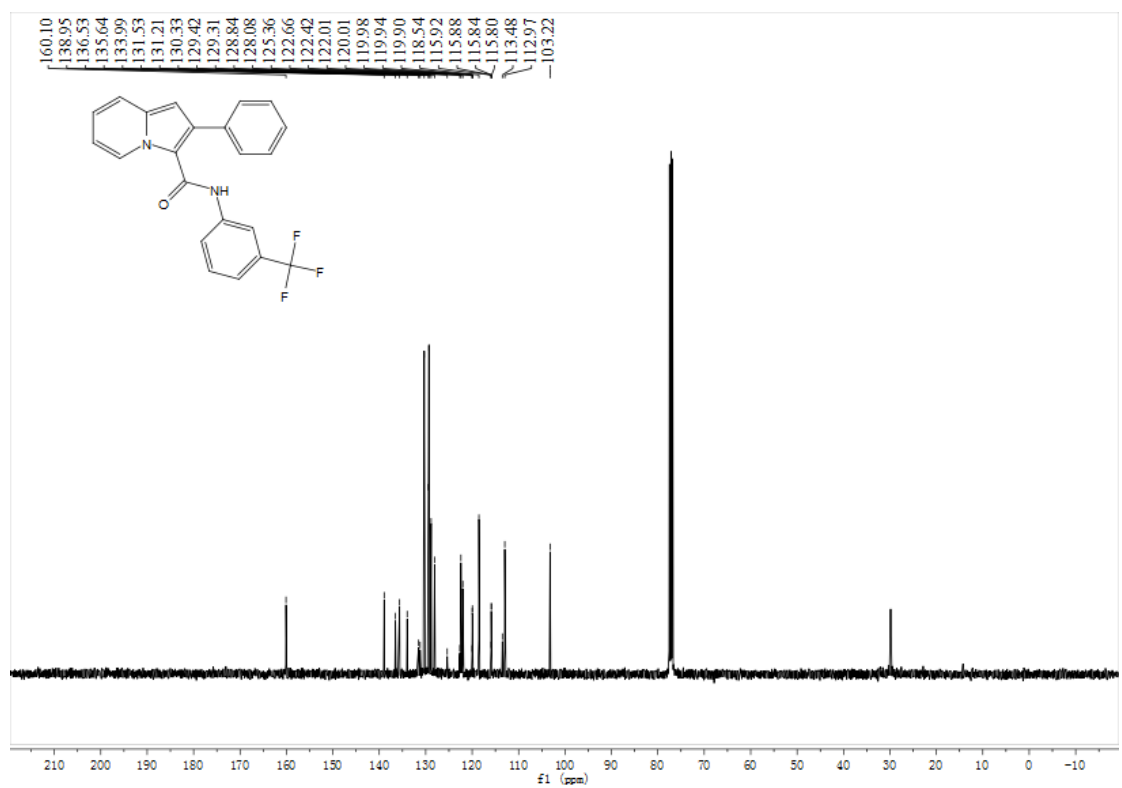
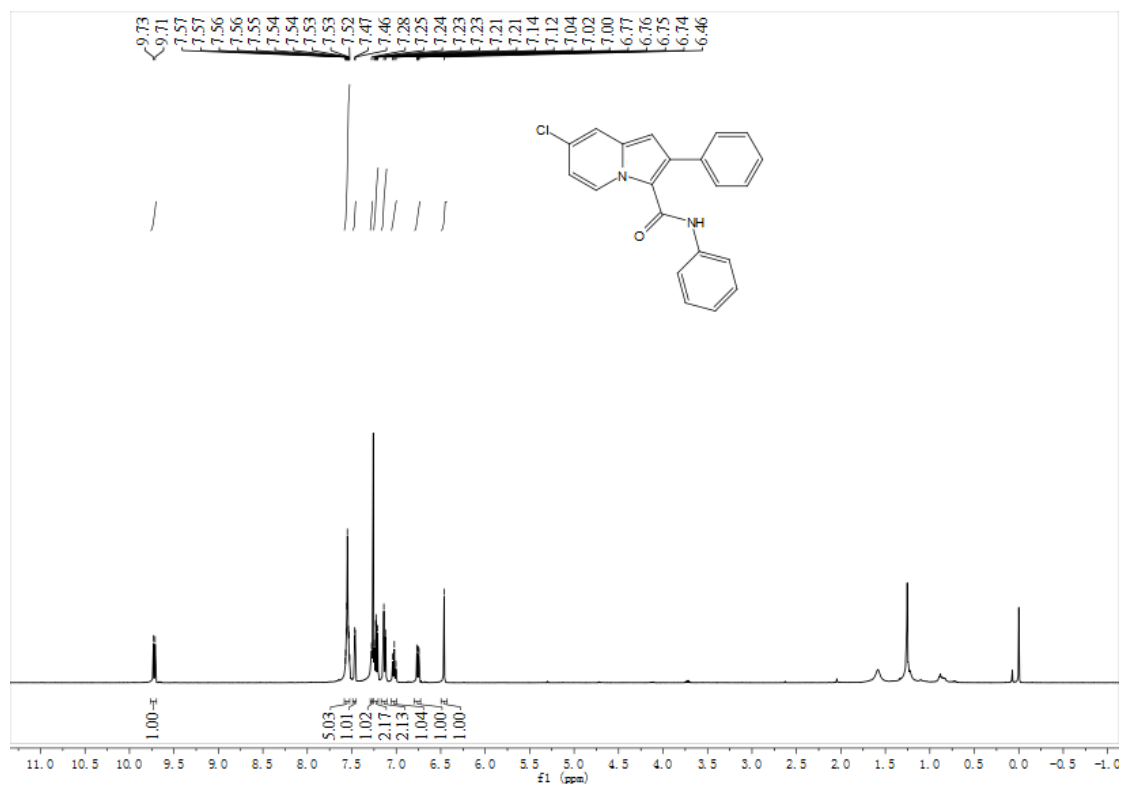
^1H NMR and ^{13}C NMR spectrum of compound **4e**



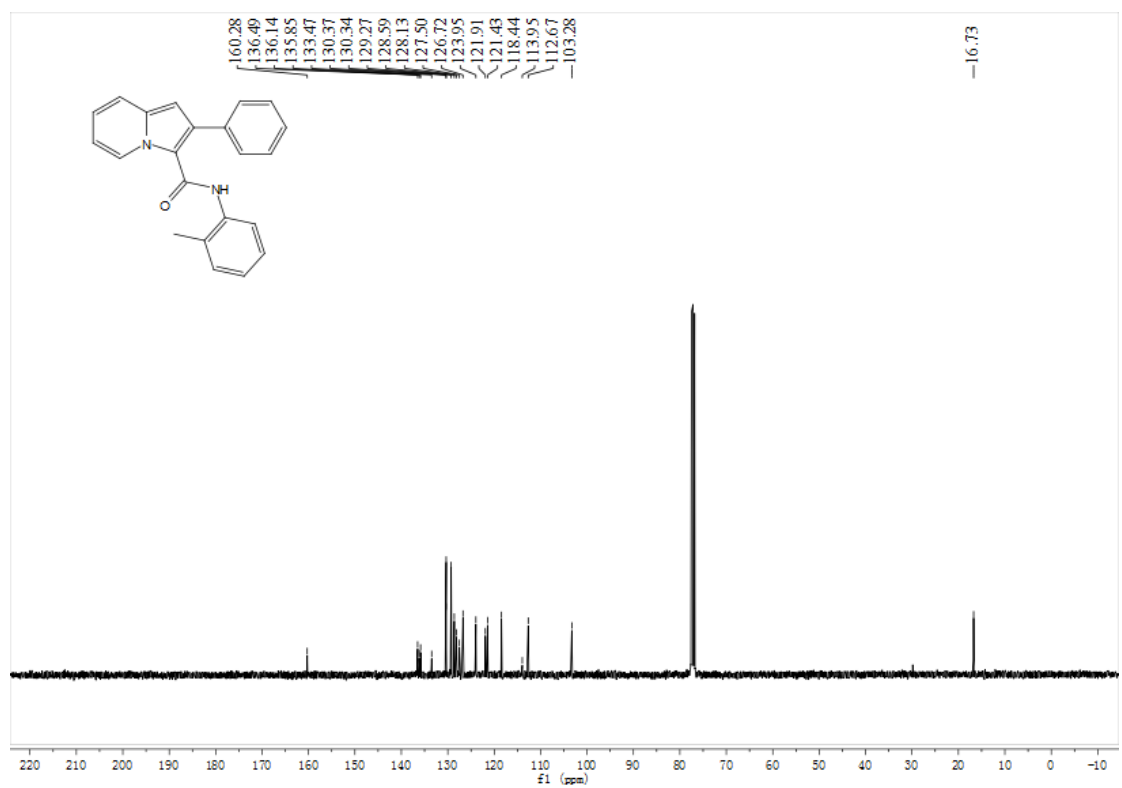
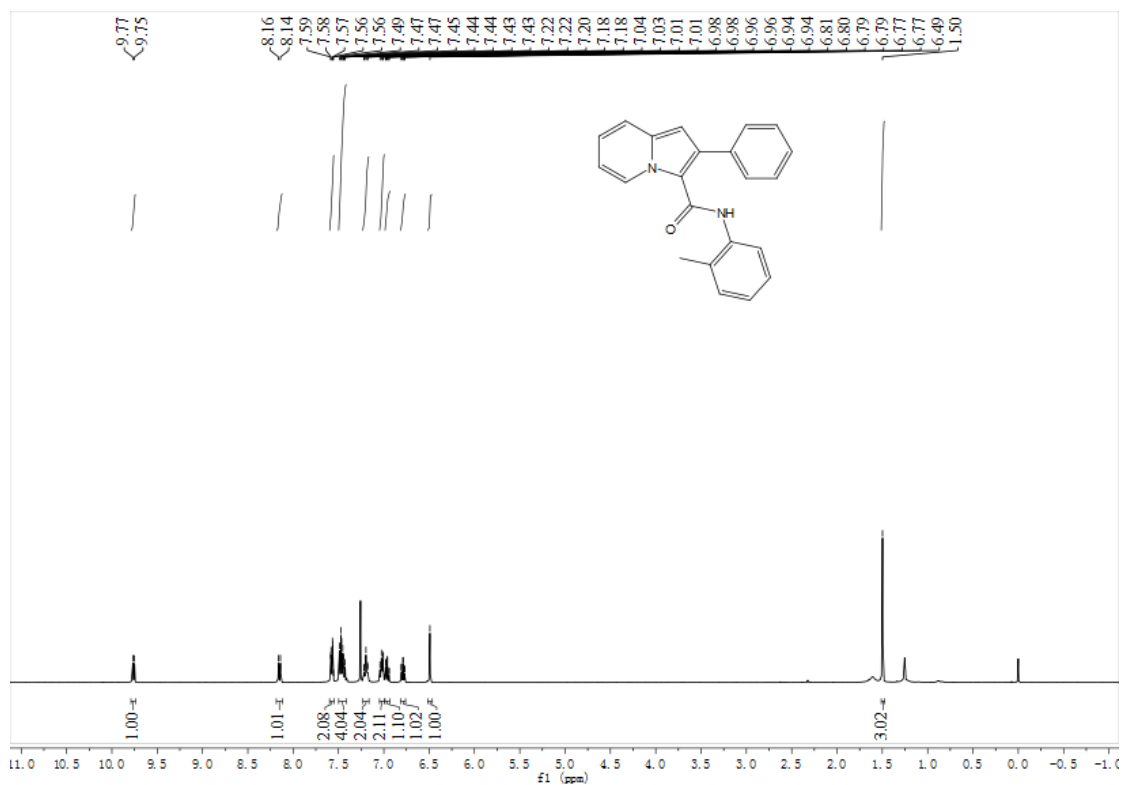
^1H NMR and ^{13}C NMR spectrum of compound **4f**



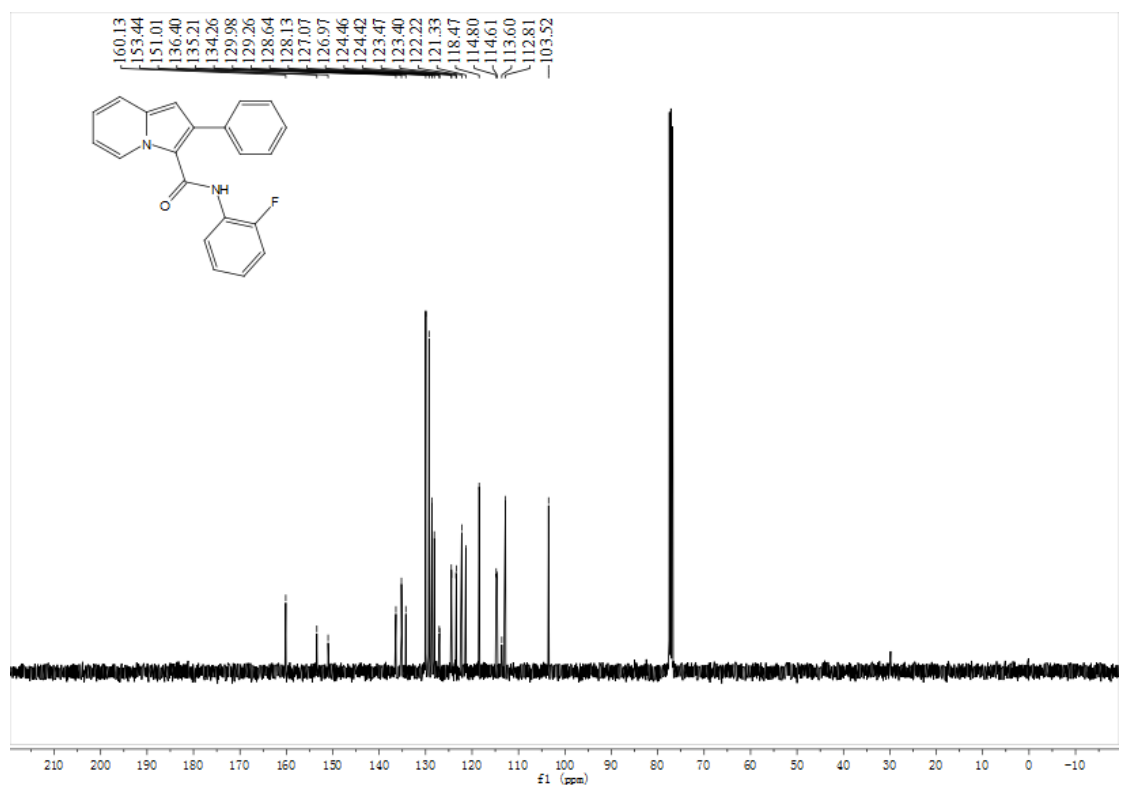
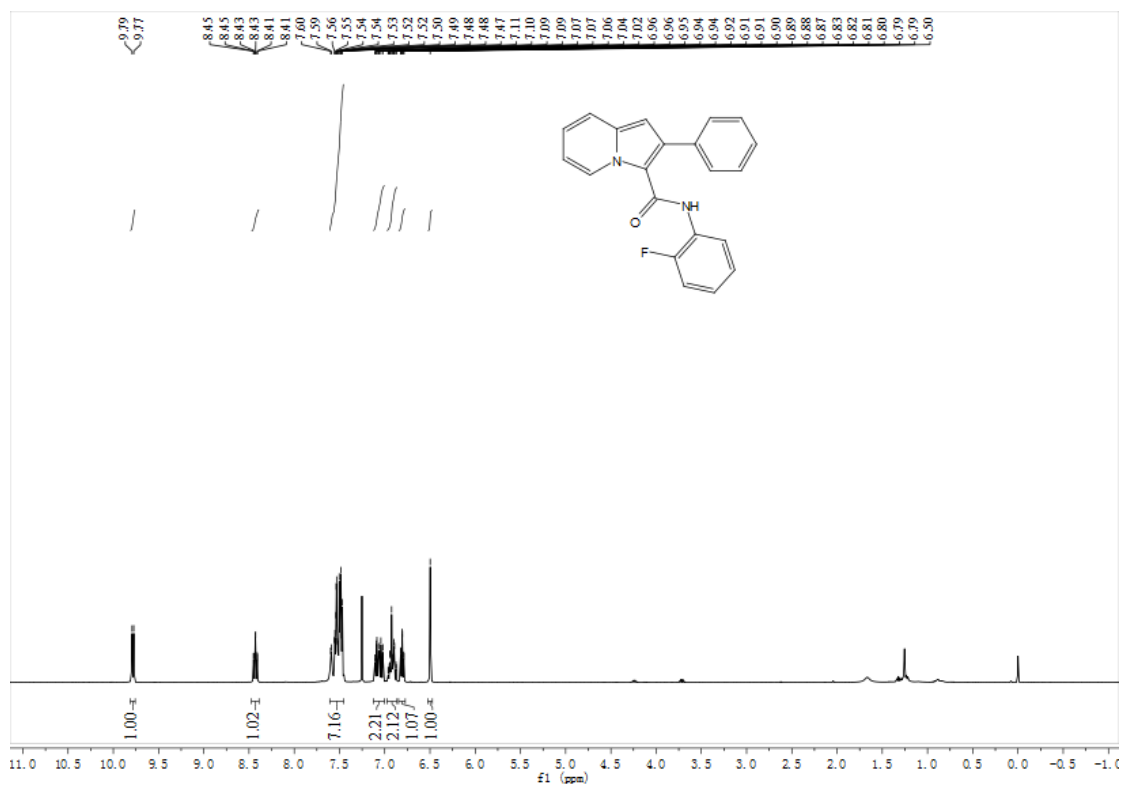
^1H NMR and ^{13}C NMR spectrum of compound **4g**



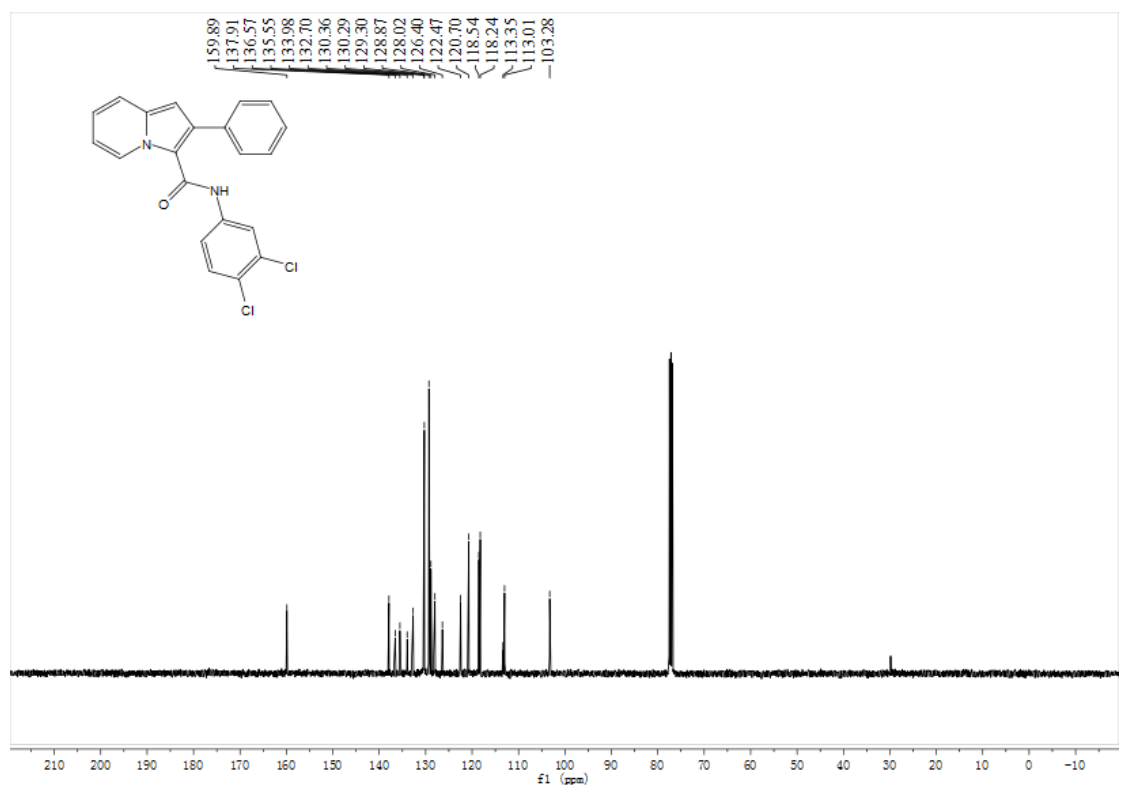
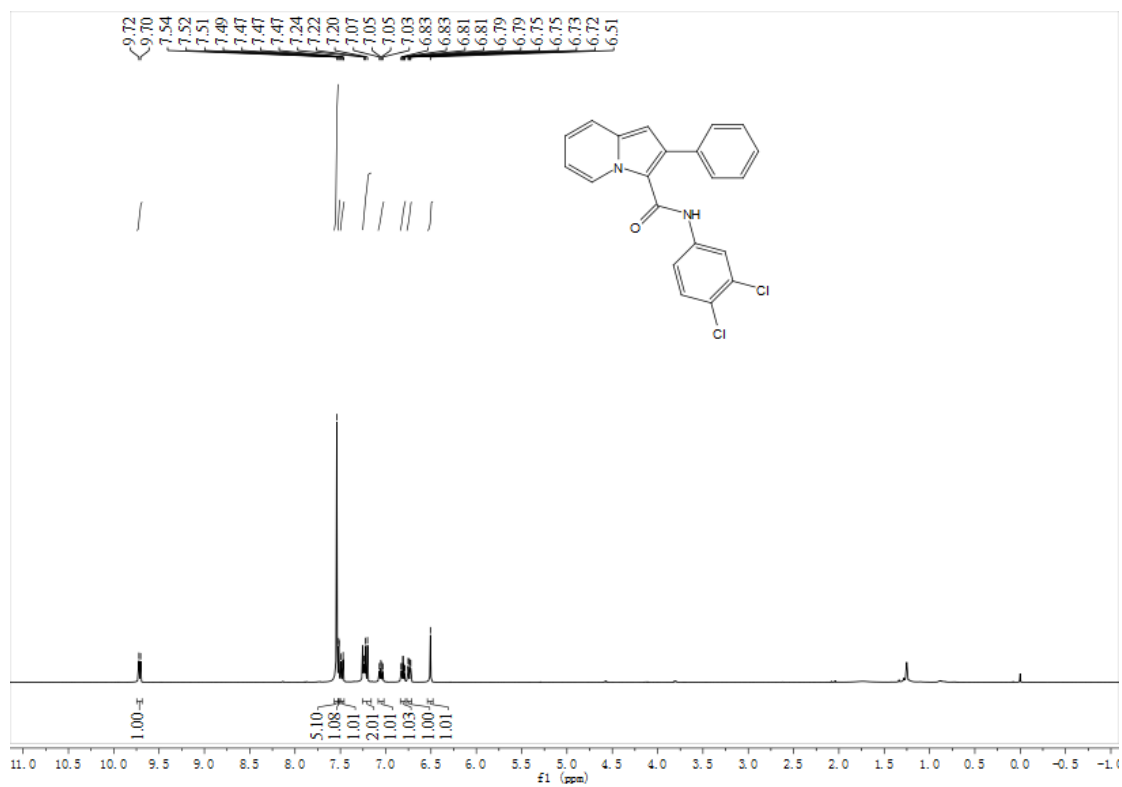
^1H NMR and ^{13}C NMR spectrum of compound **4h**



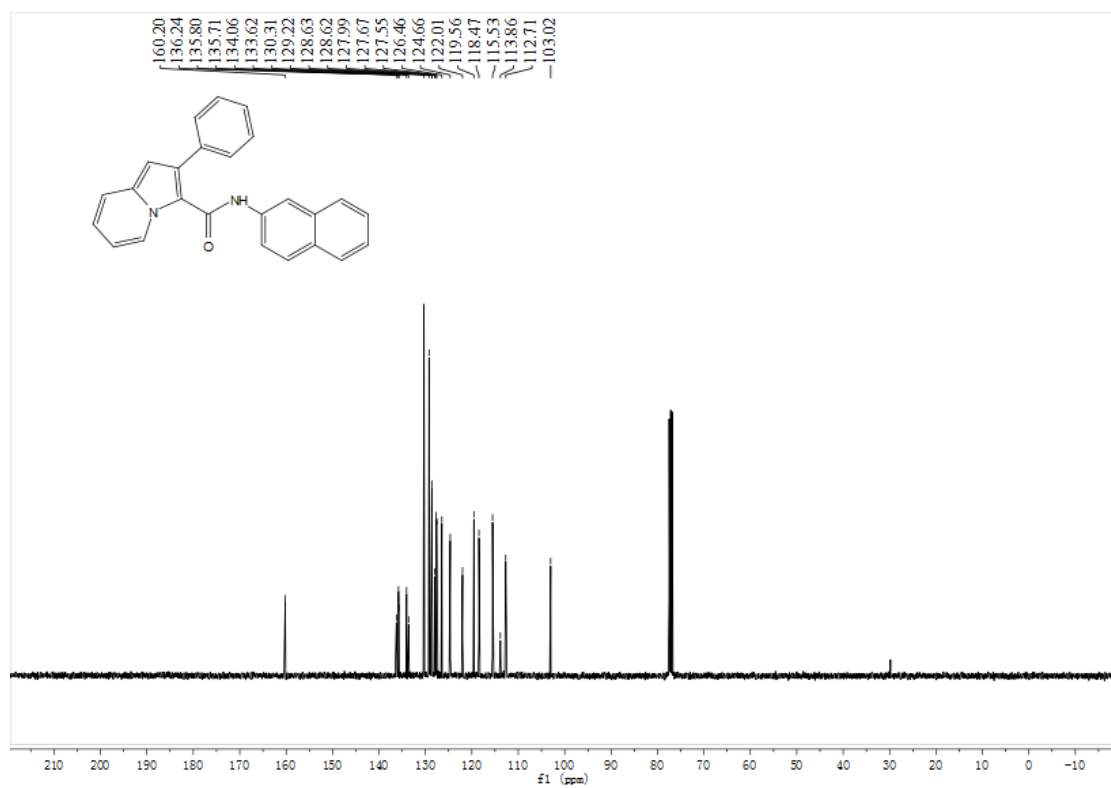
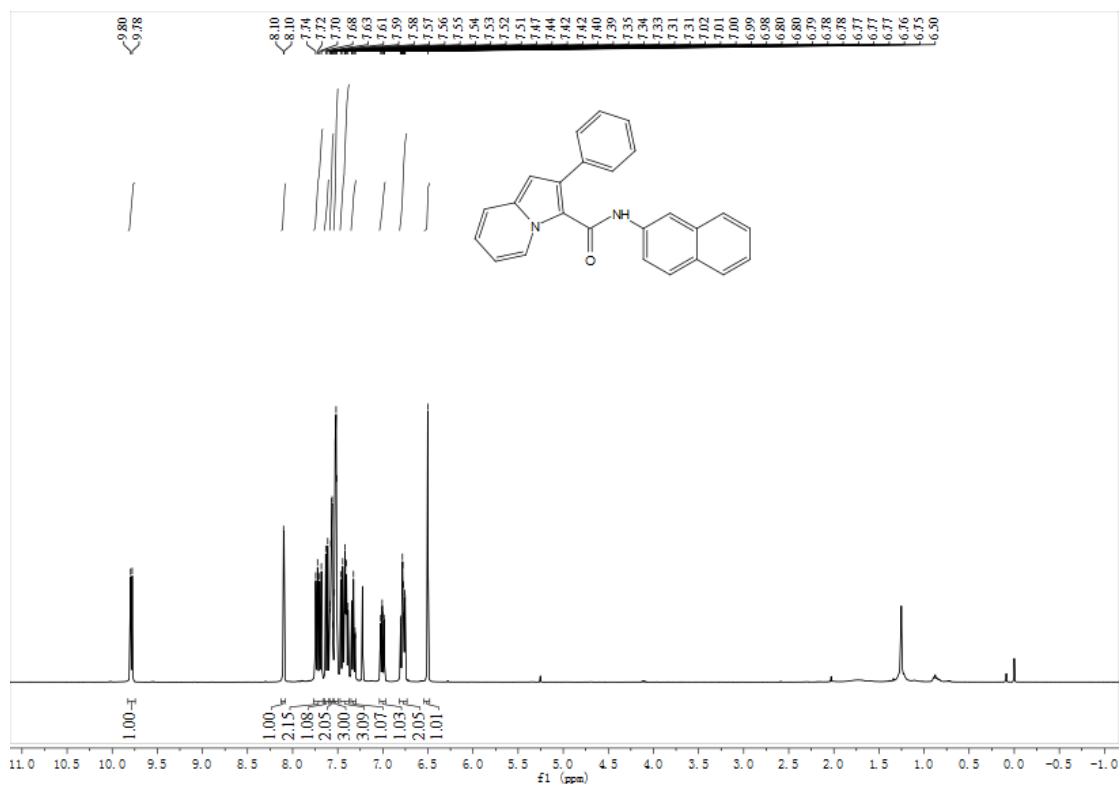
^1H NMR and ^{13}C NMR spectrum of compound **4i**



^1H NMR and ^{13}C NMR spectrum of compound **4j**

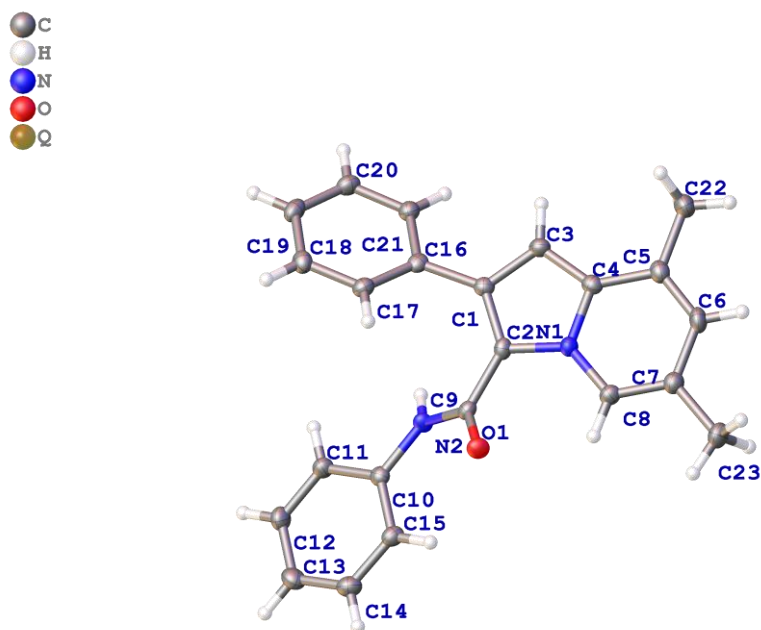


^1H NMR and ^{13}C NMR spectrum of compound **4k**



4. X-ray crystallographic data

Figure 1 X-ray single crystal structure of **3e**



Single crystals of **3e** were grown by slow evaporation of its DCM/PE solution. Single-crystal X-ray diffraction data were collected with a 'multiwire proportional' diffractometer. The crystal was kept at 100 K during data collection. Using Olex2, the structure was solved with the olex2.solve structure solution program using Charge Flipping and refined with the olex2.refine refinement package using Least Squares minimization. Supplementary crystallographic data have been deposited at the Cambridge Crystallographic Data Center (CCDC 2046530).

Table 1 Crystal data and structure refinement for **3e**

Identification code	148
Empirical formula	C ₂₃ H ₂₀ N ₂ O
Formula weight	340.41
Temperature/K	100.01(11)
Crystal system	monoclinic
Space group	P2 ₁ /c
a/Å	7.6733(7)
b/Å	23.983(2)
c/Å	9.7058(7)
α/°	90
β/°	100.517(7)
γ/°	90
Volume/Å ³	1756.1(3)
Z	4
ρ _{calc} /g/cm ³	1.288
μ/mm ⁻¹	0.079

F(000)	720.0
Crystal size/mm ³	0.14 × 0.12 × 0.11
Radiation	Mo K α (λ = 0.71073)
2 Θ range for data collection/°	4.594 to 49.992
Index ranges	-7 ≤ h ≤ 9, -27 ≤ k ≤ 28, -11 ≤ l ≤ 11
Reflections collected	7750
Independent reflections	3089 [R _{int} = 0.0351, R _{sigma} = 0.0513]
Data/restraints/parameters	3089/0/237
Goodness-of-fit on F ²	1.013
Final R indexes [I ≥ 2 σ (I)]	R ₁ = 0.0462, wR ₂ = 0.1074
Final R indexes [all data]	R ₁ = 0.0600, wR ₂ = 0.1177

Table 2 Bond Lengths for **3e**

Atom	Atom	Length/Å	Atom	Atom	Length/Å
O1	C9	1.2409(19)	C7	C8	1.350(3)
N1	C2	1.389(2)	C7	C23	1.506(2)
N1	C4	1.396(2)	C10	C11	1.395(2)
N1	C8	1.384(2)	C10	C15	1.391(2)
N2	C9	1.352(2)	C11	C12	1.375(3)
N2	C10	1.417(2)	C12	C13	1.384(3)
C1	C2	1.402(2)	C13	C14	1.381(3)
C1	C3	1.403(3)	C14	C15	1.384(3)
C1	C16	1.479(2)	C16	C17	1.395(3)
C2	C9	1.470(3)	C16	C21	1.402(2)
C3	C4	1.384(2)	C17	C18	1.385(3)
C4	C5	1.426(3)	C18	C19	1.387(3)
C5	C6	1.357(3)	C19	C20	1.380(3)
C5	C22	1.503(3)	C20	C21	1.381(2)
C6	C7	1.421(3)			

Table 3 Bond Angles for **3e**

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C2	N1	C4	108.92(14)	C7	C8	N1	120.29(17)
C8	N1	C2	129.72(16)	O1	C9	N2	122.55(17)
C8	N1	C4	121.34(15)	O1	C9	C2	122.03(16)
C9	N2	C10	127.50(14)	N2	C9	C2	115.41(14)
C2	C1	C3	107.45(15)	C11	C10	N2	117.28(15)
C2	C1	C16	128.06(17)	C11	C10	C15	119.43(18)
C3	C1	C16	124.29(16)	C15	C10	N2	123.25(16)
N1	C2	C1	107.50(16)	C12	C11	C10	120.39(17)
N1	C2	C9	120.05(15)	C11	C12	C13	120.44(18)
C1	C2	C9	132.42(16)	C14	C13	C12	119.1(2)
C4	C3	C1	108.66(16)	C13	C14	C15	121.32(18)
N1	C4	C5	118.71(16)	C14	C15	C10	119.26(17)
C3	C4	N1	107.41(16)	C17	C16	C1	122.53(15)
C3	C4	C5	133.88(18)	C17	C16	C21	117.93(16)
C4	C5	C22	118.28(16)	C21	C16	C1	119.44(17)
C6	C5	C4	118.28(18)	C18	C17	C16	120.88(16)
C6	C5	C22	123.42(17)	C17	C18	C19	120.34(18)
C5	C6	C7	122.22(18)	C20	C19	C18	119.39(17)
C6	C7	C23	120.75(17)	C21	C20	C19	120.57(17)
C8	C7	C6	119.15(17)	C20	C21	C16	120.87(18)
C8	C7	C23	120.10(18)				

5. References

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5. Liu, D.; Ding, Q.; Fu, Y.; Song, Z.; Peng, Y. *Org. Lett.* **2019**, *21*, 2523-2527.
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