Supporting Information

Solvent-controlled 4CzBnBN-catalyzed Intramolecular Photocyclization and Dehydrogenative Photocyclization of Indolecarboxamides for the switchable synthesis of indoloquinolones and dihydroindoloquinolones

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CONTENT

1. General information

All reactions were carried out under Argon atmosphere in Schlenk tubes. Anhydrous solvents (including DCM, MeCN, DMSO, MeOH, DMF, DCE, THF, 1,4-Dioxane, Water < 0.005%) were purchased from Energy and used as received. Solvent (including TFE, HFIP, Acetone and EtOH, reagent grade) and commercially available compounds were purchased from Adamas-beta®, Bide Pharmatech, Energy Chemical, Acmec Biochemical Technology, and Inno-Chem Science & Technology as reagent grade and used without further purification unless otherwise stated.

Photosensitizers Ir[dF(CF_3)ppy](dtbbpy)PF_6 (PC-I) and 2CzPN were purchased from Bide Pharmatech. 2CzPN, 4CzBnBN, 4CzBnBN and 4CzIPN were prepared according to literature.[1] 3CzClIPN[2] and 3CzEPAIPN[3] were prepared according to literature.

^{1}H NMR, ^{13}C NMR and ^{19}F NMR spectra were obtained with a Bruker AV II-400 spectrometer (^{1}H: 400 MHz, ^{13}C: 101 MHz, ^{19}F: 376 MHz). The chemical shifts (δ) were expressed in ppm and *J* values were given in Hz using tetramethylsilane as the internal reference. The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, dd = doublet of doublets, dt = doublet of triplets, td = triplet of doublets ddt = doublet of doublets of triplets and br = broad. TLC was performed using commercially prepared silica gel plates (GF_{254}), and visualized under UV light 254 nm. Flash column chromatography was performed on silica gel (100-200 mesh). All mixed solvent eluents are reported as v/v solutions. UV/Vis spectra were obtained using an Agilent Cary 60 spectrometer. Emission intensities were recorded using PerkinElmer LS55 Fluorescence Spectrometer. Cyclic voltammetry tests were carried out with a CHI700E electrochemical workstation. Mass analysis data were acquired on a SCIEX UPLC (EXion) – Q-TOF (X500R). Melting points were measured using a Hanon MP470 apparatus.

2. Involved substrates

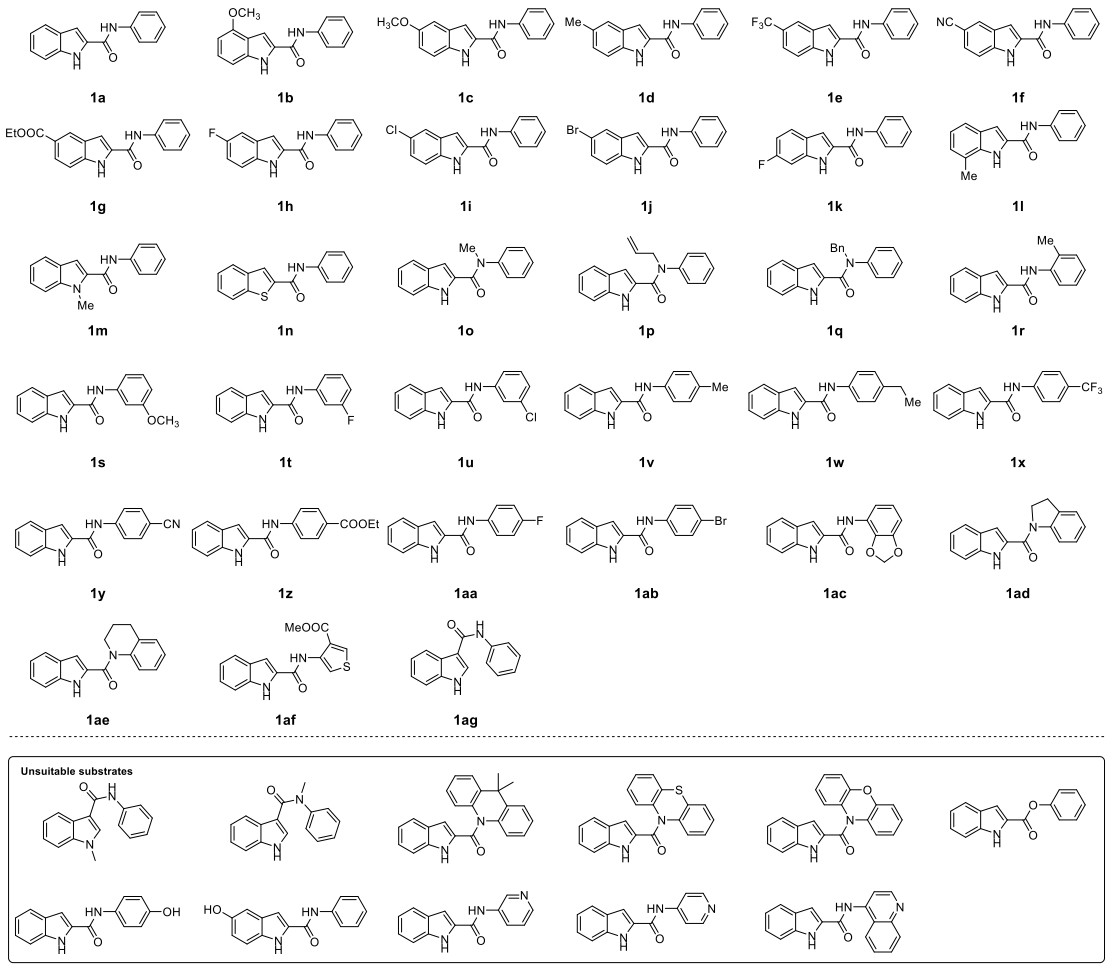
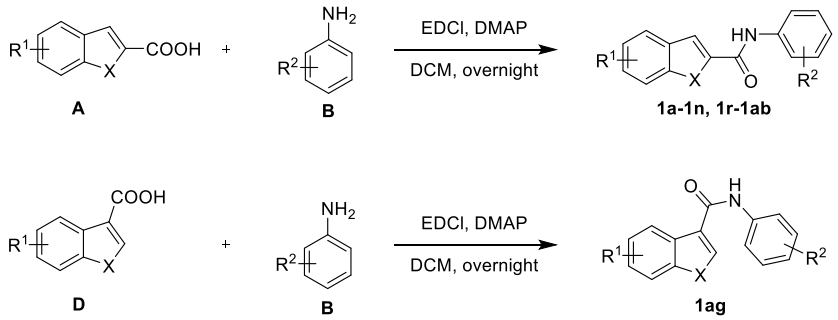


Figure S1. Substrates tested in the photocyclization and dehydrogenative photocyclization

3. The general synthetic route and characterization data of substrates



3.1 General Procedure A (synthetic route of substrates 1a-1n, 1r-1ab and 1ag)

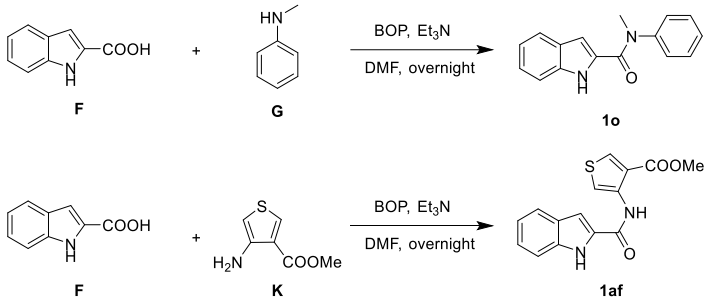
Substrates **1a-1l**, **1p-1x** and **1ab-1af** were synthesized according to the literature.[4]

In a typical procedure, a mixture of indolecarboxylic acids **A** or **D** (5 mmol), 4-

(dimethylamino)-pyridine (DMAP, 1.2equiv, 6mmol), 1-ethyl-(3-dimethylaminopropyl)carbodiimide hydrochloride (EDCI, 1.0 equiv., 5 mmol), and anilines **B** (1.0 equiv., 5 mmol) were dissolved in 25 mL of DCM; Then, the solution was stirred at room temperature overnight. After that, water was added to the solution and extracted with DCM (20 mL × 3). The combined organic phase was washed with 2 M HCl to remove the extra DMAP; then, the organic phase was dried with anhydrous Na_2SO_4, evaporated under reduced pressure, and finally recrystallized from ethyl acetate to obtain the target indole-3-carboxamides.

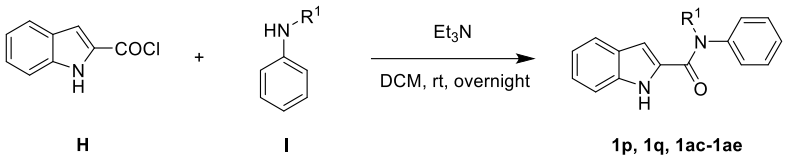
3.2 General Procedure B (Synthetic route of substrate 1o and 1af)

Substrate **1o** and **1af** was synthesized according to the literature.[5]



Under N_2 atmosphere, indole-2-carboxylic acid **F** (3.2 g, 20 mmol) and BOP reagent (8.8 g, 20 mmol) were added to a 100 mL Schlenk tube, then anhydrous DMF (20 mL), *N*-methyl aniline **G** (4.3 mL, 40 mmol) and triethylamine (8.3 mL, 60 mmol) were added in it. The reaction mixture was stirred at room temperature overnight, then diluted with water and extracted with ethyl acetate. The organic layer was washed with saturated brine and dried with anhydrous Na_2SO_4, and evaporated under vacuum. The product was obtained by column chromatography with petroleum ether/ethyl acetate = 3/1 as the eluent.

3.3 General Procedure C (synthetic route of substrate 1p, 1q, 1ac-1ae)

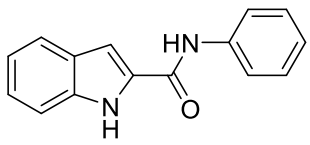


The substrates were synthesized according to the literature.[4]

The acyl chloride **H** (5.5 mmol, 1.1 equiv.) was dissolved in DCM (10 mL) at 0°C under Ar atmosphere. Aniline **I** (5.0 mmol, 1.0 equiv.) and triethylamine (1.05 mL, 7.5 mmol, 1.5 equiv.) were dissolved in DCM (10 mL) and were added slowly at 0°C and the reaction mixture was stirred at room temperature overnight. After the completion of the reaction, it was cooled in an ice bath and was slowly quenched with water (10-15 mL). The aqueous phase was extracted with diethyl ether (3 x 20 mL) and the combined organic phases were dried over Na_2SO_4 and volatiles were removed under reduced pressure. The obtained crude was subjected to column chromatography on silica for further purification**.**

3.4 Characterization data of the substrates

***N*-phenyl-1*H*-indole-2-carboxamide (1a)**



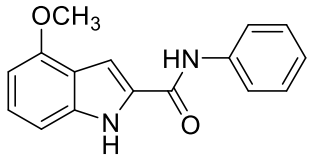
Physical state: White solid.

Yield： 40%.

^{1}H NMR (400 MHz, DMSO-*d6*) δ 11.80 (s, 1H), 10.26 (s, 1H), 7.85 (d, *J* = 7.9 Hz, 2H), 7.70 (d, *J* = 8.0 Hz, 1H), 7.48 (dd, *J* = 12.3, 4.8 Hz, 2H), 7.39 (t, *J* = 7.9 Hz, 2H), 7.24 (t, *J* = 7.5 Hz, 1H), 7.15 – 7.05 (m, 2H).

^{13}C NMR (101 MHz, DMSO-*d6*) δ 160.22, 139.44, 137.30, 131.97, 129.18, 127.51, 124.24, 124.00, 122.21, 120.62, 120.39, 112.87, 104.35. (The substrate is a known compound. The spectroscopic data is consistent with that previously reported[6].)

4-methoxy-*N*-phenyl-1*H*-indole-2-carboxamide (1b)



Physical state: White solid.

Yield： 79%.

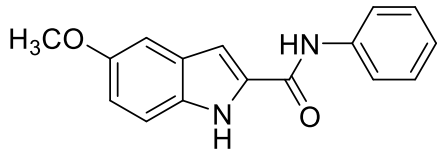
Melting Point: 192.4 °C-192.5 °C

^{1}H NMR (400 MHz, DMSO-*d6*) δ 11.77 (s, 1H), 10.15 (s, 1H), 7.84 (d, *J* = 7.8 Hz, 2H), 7.57 (d, *J* = 1.7 Hz, 1H), 7.37 (t, *J* = 7.9 Hz, 2H), 7.20 – 7.03 (m, 3H), 6.54 (d, *J* = 7.6 Hz, 1H), 3.91 (s, 3H).

^{13}C NMR (101 MHz, DMSO-*d6*) δ 160.10, 154.22, 139.56, 138.66, 130.54, 129.17, 125.35, 123.87, 120.41, 118.64, 105.95, 102.04, 99.78, 55.54.

HRMS (ESI)**:** calcd for $C_{16}H_{15}O_2N_2$ $[M+H]^+$ *m/z* 267.1128, found 267.1133.

5-methoxy-*N*-phenyl-1*H*-indole-2-carboxamide (1c)



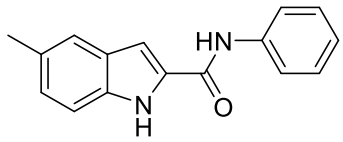
Physical state: Yellow solid.

Yield： 56%.

^{1}H NMR (400 MHz, DMSO-*d6*) δ 11.61 (s, 1H), 10.17 (s, 1H), 7.81 (d, *J* = 8.0 Hz, 2H), 7.41 – 7.32 (m, 4H), 7.14 (d, *J* = 2.0 Hz, 1H), 7.10 (t, *J* = 7.4 Hz, 1H), 6.88 (dd, *J* = 8.8, 2.3 Hz, 1H), 3.78 (s, 3H).

^{13}C NMR (101 MHz, DMSO-*d6*) δ 160.16, 154.33, 139.45, 132.61, 132.22, 129.16, 127.81, 123.96, 120.63, 115.52, 113.69, 104.03, 102.55, 55.76. (The substrate is a known compound. The spectroscopic data is consistent with that previously reported[6])

5-methyl-*N*-phenyl-1*H*-indole-2-carboxamide (1d)



Physical state: White solid.

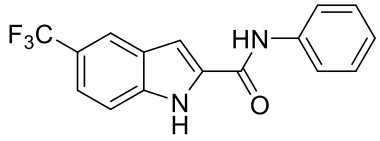
Yield： 58%.

Melting point: 226.2-226.5 °C.

^{1}H NMR (400 MHz, DMSO-*d6*) δ 11.64 (s, 1H), 10.17 (s, 1H), 7.81 (d, *J* = 7.9 Hz, 2H), 7.45 (s, 1H), 7.42 – 7.32 (m, 4H), 7.15 – 6.99 (m, 2H), 2.39 (s, 3H).

^{13}C NMR (101 MHz, DMSO-*d6*) δ 160.25, 139.48, 135.73, 131.91, 129.16, 128.97, 127.75, 126.14, 123.94, 121.41, 120.56, 112.59, 103.83, 21.63. (The substrate is a known compound. The spectroscopic data is consistent with that previously reported[7])

***N*-phenyl-5-(trifluoromethyl)-1*H*-indole-2-carboxamide (1e)**



Physical state: White solid.

Yield： 22%。

Melting point: 190.3-190.5 °C.

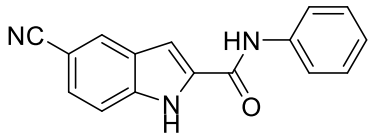
^{1}H NMR (400 MHz, DMSO-*d6*) δ 12.31 (s, 1H), 10.47 (s, 1H), 8.20 (s, 1H), 7.90 (d, *J* = 7.7 Hz, 2H), 7.71 (dd, *J* = 15.3, 5.0 Hz, 2H), 7.56 (dd, *J* = 8.7, 1.3 Hz, 1H), 7.43 (t, *J* = 7.9 Hz, 2H), 7.16 (t, *J* = 7.4 Hz, 1H).

^{19}F NMR (377 MHz, DMSO-*d6*) δ -58.83.

^{13}C NMR (101 MHz, DMSO-*d6*) δ 159.78, 139.24, 138.57, 134.13, 129.17, 126.83, 125.84 (q, *J* = 271.6 Hz), 124.22, 121.32 (q, *J* = 31.4 Hz), 120.34 (q, *J* = 3.2 Hz),120.22 (q, *J* = 4.5 Hz), 113.73, 105.20.

HRMS (ESI)**:** calcd for $C_{16}H_{12}OF_3N_2$ $[M+H]^+$ *m/z* 305.0896, found 305.0905.

5-cyano-*N*-phenyl-1*H*-indole-2-carboxamide (1f)



Physical state: White solid

Yield： 61%

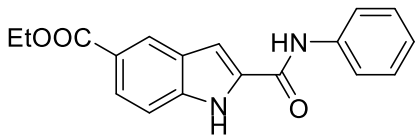
Melting point: >300 °C.

^{1}H NMR (400 MHz, DMSO-*d6*) δ 12.34 (s, 1H) , 10.40 (s, 1H), 8.34 (s, 1H), 7.82 (d, J = 9.9 Hz, 2H), 7.65 – 7.55 (m, 3H), 7.40 (t, J = 8.0 Hz, 2H), 7.14 (t, J = 7.3 Hz, 1H)

^{13}C NMR (101 MHz, DMSO-*d6*) δ 159.53, 139.14, 138.72, 134.40, 129.22, 128.49, 127.26, 126.44, 124.32, 120.75, 114.14, 104.97, 102.63.

HRMS (ESI)**:** calcd for $C_{16}H_{12}N_3O$ $[M+H]^+$ *m/z* 262.0974, found 262.0987.

ethyl 2-(phenylcarbamoyl)-1*H*-indole-5-carboxylate (1g)



Physical state: Yellow solid.

Yield： 66%.

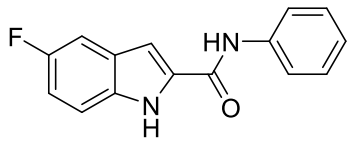
Melting point: 252.4-256.6 °C.

^{1}H NMR (400 MHz, DMSO-*d6*) δ 12.21 (s, 1H), 10.40 (s, 1H), 8.41 (s, 1H), 7.89 – 7.79 (m, 3H), 7.59 (s, 1H), 7.54 (d, J = 8.5 Hz, 2H), 7.39 (t, J = 8.2 Hz, 2H), 7.13 (t, J = 7.4 Hz, 1H), 4.33 (q, J = 7.1 Hz, 2H), 1.35 (t, J = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, DMSO-*d6*) δ 165.84, 160.50, 143.93, 137.51, 131.50, 130.64, 127.44, 124.87, 124.57, 122.37, 120.51, 119.78, 112.93, 105.08, 60.92, 14.70.

HRMS (ESI)**:** calcd for $C_{18}H_{17}N_2O_3$ $[M+H]^+$ *m/z* 309.1233, found 309.1245.

5-fluoro-*N*-phenyl-1*H*-indole-2-carboxamide (1h)



Physical state: White solid.

Yield： 60%.

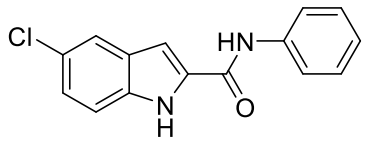
Melting point: 210.8-211.1 °C.

^{1}H NMR (400 MHz, DMSO-*d6*) δ 11.89 (s, 1H), 10.27 (s, 1H), 7.82 (d, *J* = 7.7 Hz, 2H), 7.52 – 7.42 (m, 3H), 7.38 (t, *J* = 7.9 Hz, 2H), 7.10 (ddd, *J* = 11.5, 8.4, 3.5 Hz, 2H).

^{19}F NMR (377 MHz, DMSO-*d6*) δ -123.68.

^{13}C NMR (101 MHz, DMSO-*d6*) δ 159.91, 157.69 (d, *J* = 233.0 Hz), 139.31, 134.02, 133.66, 129.19, 127.55 (d, *J* = 10.5 Hz), 124.13, 120.67, 114.12, 114.02, 113.00 (d, *J* = 26.7 Hz), 106.46, 106.23, 104.32 (d, *J* = 5.2 Hz). (The substrate is a known compound. The spectroscopic data is consistent with that previously reported[7])

5-chloro-*N*-phenyl-1*H*-indole-2-carboxamide (1i)



Physical state: White solid.

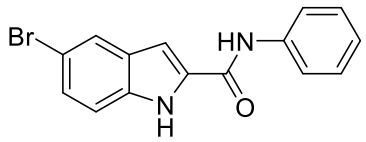
Yield： 45%.

Melting point: 260.6-260.9 °C.

^{1}H NMR (400 MHz, DMSO-*d6*) δ 11.99 (s, 1H), 10.31 (s, 1H), 7.86 – 7.76 (m, 3H), 7.49 (d, *J* = 8.7 Hz, 1H), 7.44 (d, *J* = 1.4 Hz, 1H), 7.38 (t, *J* = 7.8 Hz, 2H), 7.24 (d, *J* = 8.7 Hz, 1H), 7.12 (t, *J* = 7.3 Hz, 1H).

^{13}C NMR (101 MHz, DMSO-*d6*) δ 159.84, 139.28, 135.66, 133.46, 129.20, 128.53, 124.88, 124.35, 124.16, 121.28, 120.68, 114.46, 103.87. (The substrate is a known compound. The spectroscopic data is consistent with that previously reported[7])

5-bromo-*N*-phenyl-1*H*-indole-2-carboxamide (1j)



Physical state: Yellow solid.

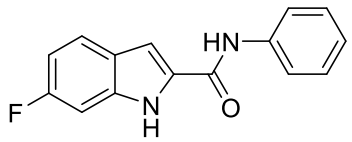
Yield： 28%.

Melting point: 275.6-275.9 °C.

^{1}H NMR (400 MHz, DMSO-*d6*) δ 12.01 (s, 1H), 10.33 (s, 1H), 7.94 (s, 1H), 7.83 (d, *J* = 7.9 Hz, 2H), 7.46 (d, *J* = 7.7 Hz, 2H), 7.38 (dd, *J* = 17.8, 8.7 Hz, 3H), 7.13 (t, *J* = 7.3 Hz, 1H).

^{13}C NMR (101 MHz, DMSO-*d6*) δ 159.82, 139.28, 135.87, 133.28, 129.29, 129.19, 126.82, 124.37, 124.16, 120.69, 114.88, 112.84, 103.75. (The substrate is a known compound. The spectroscopic data is consistent with that previously reported[7])

6-fluoro-*N*-phenyl-1*H*-indole-2-carboxamide (1k)



Physical state: White solid.

Yield： 63%.

Melting point: 240.0-240.3 °C.

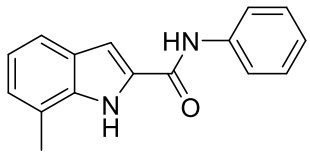
^{1}H NMR (400 MHz, DMSO-*d6*) δ 11.86 (s, 1H), 10.24 (s, 1H), 7.81 (d, *J* = 8.3 Hz, 2H), 7.72 (dd, *J* = 8.7, 5.5 Hz, 1H), 7.47 (s, 1H), 7.38 (t, *J* = 7.7 Hz, 2H), 7.20 (dd, *J* = 9.9, 1.8 Hz, 1H), 7.11 (t, *J* = 10.8, 3.9 Hz, 1H), 6.97 (td, *J* = 8.8, 4.7 Hz, 1H).

^{19}F NMR (377 MHz, DMSO-*d6*) δ -117.95.

^{13}C NMR (101 MHz, DMSO-*d6*) δ 160.62 (d, *J* = 237.7 Hz), 159.92, 139.36, 137.24 (d, *J* = 13.1 Hz), 132.78 (d, *J* = 3.6 Hz), 129.18, 124.38, 124.05, 123.83, 123.73, 120.63, 109.55 (d, *J* = 25.0 Hz), 104.55, 98.45, 98.20.

HRMS (ESI)**:** calcd for $C_{15}H_{12}OFN_2$ $[M+H]^+$ *m/z* 255.0928, found 255.0939.

7-methyl-*N*-phenyl-1*H*-indole-2-carboxamide (1l)



Physical state: White solid.

Yield： 22%.

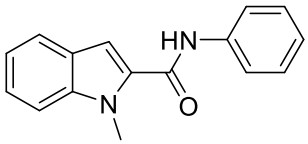
Melting point: 132.8-133.1 °C.

^{1}H NMR (400 MHz, DMSO-*d6*) δ 11.64 (s, 1H), 10.30 (s, 1H), 7.94 (d, *J* = 7.8 Hz, 2H), 7.62 – 7.49 (m, 2H), 7.41 (t, *J* = 7.5 Hz, 2H), 7.13 (t, *J* = 7.1 Hz, 1H), 7.06 – 6.99 (m, 2H), 2.61 (s, 3H).

^{13}C NMR (101 MHz, DMSO-*d6*) δ 160.34, 139.59, 137.14, 132.20, 129.22, 127.36, 124.85, 124.01, 122.44, 120.75, 120.64, 119.72, 105.63, 17.69. (The substrate is a known compound. The

spectroscopic data is consistent with that previously reported[8])

1-methyl-*N*-phenyl-1*H*-indole-2-carboxamide (1m)



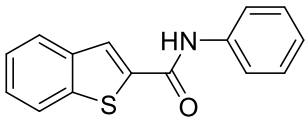
Physical state: White solid.

Yield： 40%.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (s, 1H), 7.62 (dd, *J* = 8.0, 3.0 Hz, 3H), 7.42 – 7.29 (m, 4H), 7.15 (q, *J* = 7.6 Hz, 2H), 6.94 (s, 1H), 4.02 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 160.69, 139.35, 137.78, 132.04, 129.17, 125.98, 124.57, 124.51, 121.99, 120.74, 120.12, 110.28, 104.41, 31.62. (The substrate is a known compound. The spectroscopic data is consistent with that previously reported[4])

***N*-phenylbenzo[*b*]thiophene-2-carboxamide (1n)**



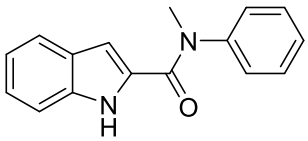
Physical state: White solid.

Yield： 47%.

^{1}H NMR (400 MHz, DMSO-*d6*) δ 10.55 (s, 1H), 8.39 (s, 1H), 8.05 (dd, *J* = 16.8, 7.0 Hz, 2H), 7.80 (d, *J* = 7.9 Hz, 2H), 7.55 – 7.45 (m, 2H), 7.40 (t, *J* = 7.8 Hz, 2H), 7.14 (t, *J* = 7.3 Hz, 1H).

^{13}C NMR (101 MHz, DMSO-*d6*) δ 160.79, 140.97, 140.55, 139.61, 139.10, 129.23, 126.97, 126.29, 125.88, 125.53, 124.44, 123.33, 120.80. (The substrate is a known compound. The spectroscopic data is consistent with that previously reported[9])

***N*-methyl-*N*-phenyl-1*H*-indole-2-carboxamide (1o)**



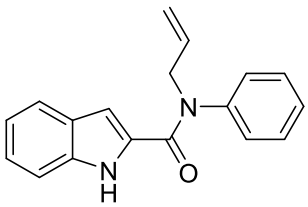
Physical state: White solid.

Yield： 38%.

^{1}H NMR (400 MHz, DMSO-*d6*) δ 11.63 (s, 1H), 7.53 – 7.34 (m, 6H), 7.29 (d, *J* = 8.0 Hz, 1H), 7.13 (t, *J* = 7.6 Hz, 1H), 6.91 (t, *J* = 7.4 Hz, 1H), 5.28 (s, 1H), 3.39 (s, 3H).

^{13}C NMR (101 MHz, DMSO-*d6*) δ 161.92, 144.76, 136.04, 130.55, 130.19, 128.45, 128.27, 127.19, 123.96, 121.91, 120.09, 112.61, 106.00, 38.93. (The substrate is a known compound. The spectroscopic data is consistent with that previously reported[10])

***N*-allyl-*N*-phenyl-1*H*-indole-2-carboxamide (1p)**



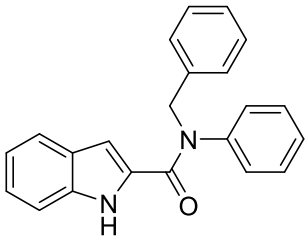
Physical state: Orange solid.

Yield： 40%.

^{1}H NMR (400 MHz, DMSO-*d6*) δ 11.64 (s, 1H), 7.52 – 7.43 (m, 3H), 7.41 (d, *J* = 8.3 Hz, 1H), 7.34 (dd, *J* = 7.8, 1.6 Hz, 2H), 7.29 (d, *J* = 8.0 Hz, 1H), 7.13 (t, *J* = 7.6 Hz, 1H), 6.91 (t, *J* = 7.5 Hz, 1H), 6.00 – 5.82 (m, 1H), 5.25 (s, 1H), 5.19 – 5.15 (m, 1H), 5.14 (s, 1H), 4.47 (d, *J* = 5.9 Hz, 2H).

^{13}C NMR (101 MHz, DMSO-*d6*) δ 161.63, 143.08, 136.10, 133.85, 130.45, 130.03, 129.09, 128.57, 127.17, 124.05, 121.95, 120.12, 118.20, 112.60, 106.08, 53.27. (The substrate is a known compound. The spectroscopic data is consistent with that previously reported[11])

***N*-benzyl-*N*-phenyl-1*H*-indole-2-carboxamide (1q)**



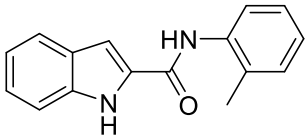
Physical state: Pink solid.

Yield： 39%.

^{1}H NMR (400 MHz, DMSO-*d6*) δ 11.74 (s, 1H), 7.47 – 7.36 (m, 4H), 7.33 – 7.19 (m, 8H), 7.14 (t, *J* = 7.5 Hz, 1H), 6.92 (t, *J* = 7.5 Hz, 1H), 5.27 (s, 1H), 5.10 (s, 2H).

^{13}C NMR (101 MHz, DMSO-*d6*) δ 162.13, 143.02, 137.81, 136.17, 130.39, 129.98, 128.95, 128.84, 128.57, 128.54, 127.69, 127.18, 124.12, 121.98, 120.17, 112.62, 106.26, 53.96. (The substrate is a known compound. The spectroscopic data is consistent with that previously reported[5])

***N*-(o-tolyl)-1*H*-indole-2-carboxamide (1r)**



Physical state: Yellow solid.

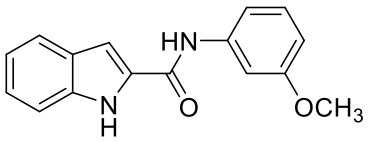
Yield： 31%.

Melting point: 185.3-185.6 °C.

^{1}H NMR (400 MHz, DMSO-*d6*) δ 11.75 (s, 1H), 9.90 (s, 1H), 7.67 (d, *J* = 8.0 Hz, 1H), 7.47 (d, *J* = 8.2 Hz, 1H), 7.39 (d, *J* = 8.3 Hz, 2H), 7.33 – 7.15 (m, 4H), 7.07 (t, *J* = 7.5 Hz, 1H), 2.28 (s, 3H).

^{13}C NMR (101 MHz, DMSO-*d6*) δ 160.29, 137.18, 136.41, 134.16, 131.88, 130.87, 127.56, 127.07, 126.56, 126.48, 124.08, 122.11, 120.35, 112.86, 103.99, 18.42. (The substrate is a known compound. The spectroscopic data is consistent with that previously reported[7])

***N*-(3-methoxyphenyl)-1*H*-indole-2-carboxamide (1s)**



Physical state: White solid.

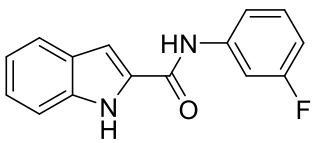
Yield： 69%.

Melting point: 168.4-168.7 °C.

^{1}H NMR (400 MHz, DMSO-*d6*) δ 11.78 (s, 1H), 10.20 (s, 1H), 7.69 (d, *J* = 8.0 Hz, 1H), 7.55 – 7.41 (m, 4H), 7.26 (dt, *J* = 17.7, 7.7 Hz, 2H), 7.08 (t, *J* = 7.5 Hz, 1H), 6.70 (dd, *J* = 8.1, 2.2 Hz, 1H), 3.78 (s, 3H).

^{13}C NMR (101 MHz, DMSO-*d6*) δ 160.24, 159.95, 140.63, 137.32, 131.94, 129.97, 127.50, 124.29, 122.24, 120.41, 112.87, 112.83, 109.38, 106.39, 104.36, 55.47. (The substrate is a known compound. The spectroscopic data is consistent with that previously reported[12])

***N*-(3-fluorophenyl)-1*H*-indole-2-carboxamide (1t)**



Physical state: Yellow solid.

Yield： 22%.

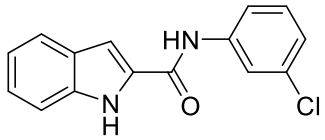
Melting point: 201.1-201.3 °C.

^{1}H NMR (400 MHz, DMSO-*d6*) δ 11.83 (s, 1H), 10.41 (s, 1H), 7.83 (d, *J* = 11.8 Hz, 1H), 7.71 (d, *J* = 8.0 Hz, 1H), 7.62 (d, *J* = 8.3 Hz, 1H), 7.49 (dd, *J* = 11.1, 4.9 Hz, 2H), 7.42 (dd, *J* = 15.3, 8.1 Hz, 1H), 7.25 (t, *J* = 7.6 Hz, 1H), 7.09 (t, *J* = 7.5 Hz, 1H), 6.95 (td, *J* = 8.5, 2.4 Hz, 1H).

^{13}C NMR (101 MHz, DMSO-*d6*) δ 162.59 (d, *J* = 241.0 Hz), 160.43, 141.25 (d, *J* = 11.1 Hz), 137.44, 131.57, 130.79 (d, *J* = 9.5 Hz), 127.44, 124.46, 122.31, 120.48, 116.20 (d, *J* = 2.5 Hz), 112.91, 110.40 (d, *J* = 21.1 Hz), 107.21 (d, *J* = 26.3 Hz), 104.74. (The substrate is a known

compound. The spectroscopic data is consistent with that previously reported[12])

***N*-(3-chlorophenyl)-1*H*-indole-2-carboxamide (1u)**



Physical state: White solid.

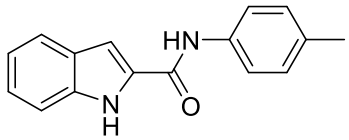
Yield： 29%.

Melting point: 170.1-170.4 °C.

^{1}H NMR (400 MHz, DMSO-*d6*) δ 11.81 (s, 1H), 10.38 (s, 1H), 8.03 (t, *J* = 1.9 Hz, 1H), 7.77 (d, *J* = 7.3 Hz, 1H), 7.71 (d, *J* = 8.0 Hz, 1H), 7.48 (dd, *J* = 13.3, 4.9 Hz, 2H), 7.41 (t, *J* = 8.1 Hz, 1H), 7.25 (t, *J* = 7.3 Hz, 1H), 7.17 (dd, *J* = 7.9, 1.3 Hz, 1H), 7.09 (t, *J* = 7.4 Hz, 1H).

^{13}C NMR (101 MHz, DMSO-*d6*) δ 160.41, 140.97, 137.44, 133.50, 131.52, 130.88, 127.44, 124.48, 123.64, 122.33, 120.49, 119.90, 118.84, 112.92, 104.79. (The substrate is a known compound. The spectroscopic data is consistent with that previously reported[7])

***N*-(*p*-tolyl)-1*H*-indole-2-carboxamide (1v)**



Physical state: White solid.

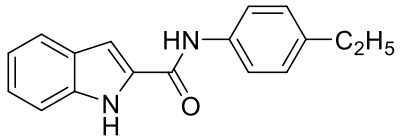
Yield： 65%.

Melting point: 241.1-241.4 °C

^{1}H NMR (400 MHz, DMSO-*d6*) δ 11.74 (s, 1H), 10.16 (s, 1H), 7.69 (t, *J* = 9.1 Hz, 3H), 7.48 (d, *J* = 8.2 Hz, 1H), 7.42 (d, *J* = 0.9 Hz, 1H), 7.27 – 7.15 (m, 3H), 7.07 (t, *J* = 7.4 Hz, 1H), 2.29 (s, 3H).

^{13}C NMR (101 MHz, DMSO-*d6*) δ 160.06, 137.25, 136.89, 132.97, 132.08, 129.57, 127.53, 124.16, 122.17, 120.65, 120.36, 112.85, 104.12, 20.98. (The substrate is a known compound. The spectroscopic data is consistent with that previously reported[13])

***N*-(4-ethylphenyl)-1*H*-indole-2-carboxamide (1w)**



Physical state: White solid.

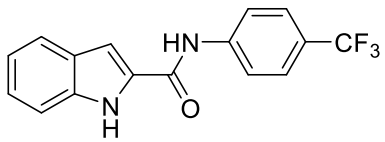
Yield： 59%.

Melting point: 214.1-214.4 °C

^{1}H NMR (400 MHz, DMSO-*d6*) δ 11.82 (s, 1H), 10.24 (s, 1H), 7.79 (d, *J* = 8.1 Hz, 2H), 7.71 (d, *J* = 7.9 Hz, 1H), 7.55 (d, *J* = 8.2 Hz, 1H), 7.50 (s, 1H), 7.29 – 7.17 (m, 3H), 7.10 (t, *J* = 7.4 Hz, 1H), 2.58 (q, *J* = 7.4 Hz, 2H), 1.18 (t, *J* = 7.5 Hz, 3H).

^{13}C NMR (101 MHz, DMSO-*d6*) δ 160.16, 139.51, 137.33, 137.13, 132.16, 128.38, 127.62, 124.18, 122.19, 120.81, 120.39, 112.90, 104.22, 28.19, 16.21. (The substrate is a known compound. The spectroscopic data is consistent with that previously reported[7])

***N*-(4-(trifluoromethyl)phenyl)-1*H*-indole-2-carboxamide (1x)**



Physical state: White solid.

Yield： 22%.

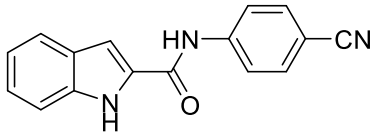
^{1}H NMR (400 MHz, DMSO-*d6*) δ 11.86 (s, 1H), 10.57 (s, 1H), 8.08 (d, *J* = 8.3 Hz, 2H), 7.72 (dd, *J* = 15.0, 8.3 Hz, 3H), 7.52 (d, *J* = 6.4 Hz, 2H), 7.25 (t, *J* = 7.5 Hz, 1H), 7.09 (t, *J* = 7.4 Hz, 1H).

^{19}F NMR (377 MHz, DMSO-*d6*) δ -60.37.

^{13}C NMR (101 MHz, DMSO-*d6*) δ 160.61, 143.13, 137.52, 131.44, 127.45, 126.43 (q, *J* = 3.7 Hz),

124.89 (q, *J* = 271.3 Hz), 124.57, 123.96 (q, *J* = 32.0 Hz), 122.36, 120.52, 120.34, 112.94, 105.10. (The substrate is a known compound. The spectroscopic data is consistent with that previously reported[13])

***N*-(4-cyanophenyl)-*1H*-indole-2-carboxamide (1y)**



Physical state: Yellow solid

Yield： 17%

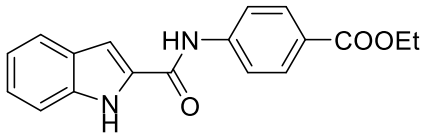
Melting point: 296.7-300 °C.

^{1}H NMR (400 MHz, DMSO-*d6*) δ 11.84 (s, 1H), 10.58 (s, 1H), 8.04 (d, J = 8.8 Hz, 2H), 7.84 (d, J = 8.8 Hz, 2H), 7.71 (d, J = 7.9 Hz, 1H), 7.48 (d, J = 8.3 Hz, 2H), 7.25 (t, J = 7.3 Hz, 1H), 7.09 (t, J = 7.3 Hz, 1H).

^{13}C NMR (101 MHz, DMSO-*d6*) δ 160.63, 143.83, 137.58, 133.69, 131.25, 127.36, 124.72, 122.43, 120.58, 120.39, 119.60, 112.95, 105.58, 105.36.

HRMS (ESI)**:** calcd for $C_{16}H_{12}N_3O$ $[M+H]^+$ *m/z* 262.0974, found 262.0968.

ethyl 4-(1*H*-indole-2-carboxamido)benzoate (1z)



Physical state: White solid.

Yield： 45%.

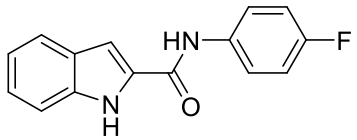
Melting point: 203.5-205.2 °C.

^{1}H NMR (400 MHz, DMSO-*d6*) δ 11.83 (s, 1H), 10.53 (s, 1H), 7.99 (s, 4H), 7.71 (d, J = 8.0 Hz, 1H), 7.49 (d, J = 11.5 Hz, 2H), 7.25 (t, J = 8.1 Hz, 1H), 7.09 (t, J = 7.5 Hz, 1H), 4.31 (q, J = 7.1 Hz, 2H), 1.33 (t, J = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, DMSO-*d6*) δ 165.84, 160.49, 143.93, 137.50, 131.49, 130.65, 127.43, 124.86, 124.58, 122.38, 120.52, 119.78, 112.93, 105.08, 60.93, 15.10.

HRMS (ESI)**:** calcd for $C_{18}H_{17}N_2O_3$ $[M+H]^+$ *m/z* 309.1233, found 309.1244.

***N*-(4-fluorophenyl)-1*H*-indole-2-carboxamide (1aa)**



Physical state: White solid.

Yield： 43%.

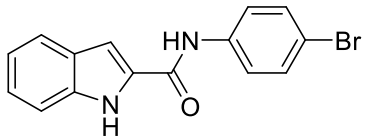
Melting point: 217.3-217.6 °C.

^{1}H NMR (400 MHz, DMSO-*d6*) δ 11.79 (s, 1H), 10.30 (s, 1H), 7.85 (dd, *J* = 8.8, 5.1 Hz, 2H), 7.69 (d, *J* = 8.0 Hz, 1H), 7.49 (d, *J* = 8.2 Hz, 1H), 7.43 (s, 1H), 7.23 (dd, *J* = 12.2, 5.4 Hz, 3H), 7.08 (t, *J* = 7.4 Hz, 1H).

^{19}F NMR (377 MHz, DMSO-*d6*) δ -119.00.

^{13}C NMR (101 MHz, DMSO-*d6*) δ 160.16, 158.70 (d, *J* = 240.1 Hz), 137.31, 135.79 (d, *J* = 2.5 Hz), 131.81, 127.49, 124.27, 122.40 (d, *J* = 7.8 Hz), 122.21, 120.41, 115.77 (d, *J* = 22.2 Hz), 112.88, 104.33. (The substrate is a known compound. The spectroscopic data is consistent with that previously reported[7])

***N*-(4-bromophenyl)-1*H*-indole-2-carboxamide (1ab)**



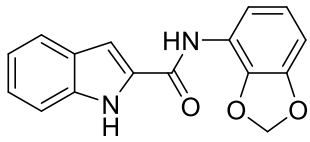
Physical state: White solid.

Yield： 25%.

^{1}H NMR (400 MHz, DMSO-*d6*) δ 11.80 (s, 1H), 10.35 (s, 1H), 7.82 (d, *J* = 8.9 Hz, 2H), 7.69 (d, *J* = 8.0 Hz, 1H), 7.57 (d, *J* =

8.8 Hz, 2H), 7.47 (dd, *J* = 14.1, 4.9 Hz, 2H), 7.23 (t, *J* = 11.3, 3.9 Hz, 1H), 7.08 (t, *J* = 7.5 Hz, 1H). **^{13}C NMR** (101 MHz, DMSO-*d6*) δ 160.28, 138.86, 137.38, 132.01, 131.66, 127.45, 124.40, 122.43, 122.28, 120.46, 115.65, 112.90, 104.62. (The substrate is a known compound. The spectroscopic data is consistent with that previously reported[13])

***N*-(benzo[*d*][1,3]dioxol-4-yl)-1*H*-indole-2-carboxamide (1ae)**



Physical state: Yellow solid.

Yield： 53%.

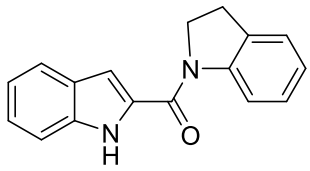
Melting point: 250.8-251.1 °C.

^{1}H NMR (400 MHz, DMSO-*d6*) δ 11.75 (s, 1H), 10.15 (s, 1H), 7.67 (d, *J* = 7.9 Hz, 1H), 7.54 – 7.44 (m, 2H), 7.39 (s, 1H), 7.22 (t, *J* = 7.5 Hz, 2H), 7.07 (t, *J* = 7.4 Hz, 1H), 6.93 (d, *J* = 8.4 Hz, 1H), 6.03 (s, 2H).

^{13}C NMR (101 MHz, DMSO-*d6*) δ 159.97, 147.50, 143.66, 137.24, 133.70, 131.97, 127.50, 124.16, 122.16, 120.36, 113.59, 112.84, 108.50, 104.07, 102.80, 101.50.

HRMS (ESI)**:** calcd for $C_{16}H_{13}O_3N_2$ $[M+H]^+$ *m/z* 281.0921, found 281.0926.

(1*H*-indol-2-yl)(indolin-1-yl)methanone (1ad)



Physical state: Red solid.

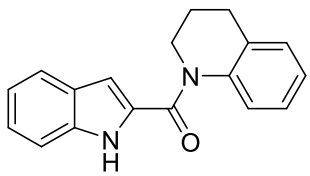
Yield： 33%.

Melting point: 210.7-211.0 °C.

^{1}H NMR (400 MHz, DMSO-*d6*) δ 11.76 (s, 1H), 8.20 (d, *J* = 7.9 Hz, 1H), 7.68 (d, *J* = 8.0 Hz, 1H), 7.51 (d, *J* = 8.2 Hz, 1H), 7.30 (d, *J* = 7.3 Hz, 1H), 7.24 (q, *J* = 15.2, 7.4 Hz, 2H), 7.14 (d, *J* = 0.8 Hz, 1H), 7.07 (q, *J* = 7.6 Hz, 2H), 4.51 (t, *J* = 8.3 Hz, 2H), 3.23 (t, *J* = 8.2 Hz, 2H).

^{13}C NMR (101 MHz, DMSO-*d6*) δ 160.71, 143.82, 136.63, 132.78, 131.23, 127.77, 127.42, 125.35, 124.44, 124.31, 122.36, 120.34, 117.45, 112.73, 106.00, 50.16, 28.67. (The substrate is a known compound. The spectroscopic data is consistent with that previously reported[14])

(3,4-dihydroquinolin-1(2*H*)-yl)(1*H*-indol-2-yl)methanone (1ae)



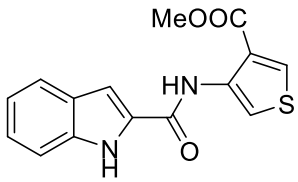
Physical state: Yellow solid.

Yield： 44%.

^{1}H NMR (400 MHz, DMSO-*d6*) δ 11.67 (s, 1H), 7.49 (d, *J* = 8.0 Hz, 1H), 7.43 (d, *J* = 8.2 Hz, 1H), 7.25 (d, *J* = 7.3 Hz, 1H), 7.17 (dd, *J* = 15.9, 7.8 Hz, 2H), 7.09 (t, *J* = 7.2 Hz, 1H), 7.01 (dd, *J* = 13.4, 6.7 Hz, 2H), 6.34 (s, 1H), 3.93 (t, *J* = 6.3 Hz, 2H), 2.81 (t, *J* = 6.5 Hz, 2H), 2.08 – 1.77 (m, 2H).

^{13}C NMR (101 MHz, DMSO-*d6*) δ 163.16, 139.46, 136.57, 134.07, 132.00, 131.33, 129.04, 127.07, 125.99, 125.24, 125.15, 123.97, 123.31, 121.97, 120.25, 113.96, 112.64, 109.62, 105.96, 45.36, 26.60, 24.23. (The substrate is a known compound. The spectroscopic data is consistent with that previously reported[5])

methyl 4-(1*H*-indole-2-carboxamido)thiophene-3-carboxylate (1af)



Physical state: White solid.

Yield： 25%.

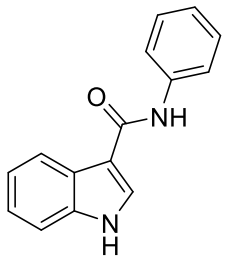
Melting point: 196.5-198.3 °C.

^{1}H NMR (400 MHz, DMSO-*d6*) δ 11.99 (s, 1H), 10.84 (s, 1H), 8.45 (d, J = 3.5 Hz, 1H), 8.07 (d, J = 3.5 Hz, 1H), 7.74 (d, J = 7.8 Hz, 1H), 7.50 (d, J = 9.4 Hz, 1H), 7.27 (t, J = 7.7 Hz, 1H), 7.15 – 7.07 (m, 2H), 3.93 (s, 3H).

^{13}C NMR (101 MHz, DMSO-*d6*) δ 164.64, 158.92, 137.69, 135.99, 134.67, 131.15, 127.51, 124.63, 122.40, 121.84, 120.71, 112.98, 111.29, 103.05, 52.80.

HRMS (ESI)**:** calcd for $C_{15}H_{13}N_2O_3S$ $[M+H]^+$ *m/z* 301.0641, found 301.0637.

***N*-phenyl-1*H*-indole-3-carboxamide (1ag)**



Physical state: White solid.

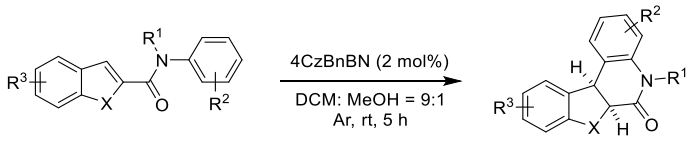
Yield： 57%.

^{1}H NMR (400 MHz, DMSO-*d6*) δ 11.84 (s, 1H), 10.31 (s, 1H), 7.86 (d, *J* = 8.2 Hz, 2H), 7.69 (d, *J* = 8.0 Hz, 1H), 7.49 (d, *J* = 9.0 Hz, 2H), 7.38 (t, *J* = 7.9 Hz, 2H), 7.24 (t, *J* = 7.5 Hz, 1H), 7.10 (dt, *J* = 12.2, 7.4 Hz, 2H).

^{13}C NMR (101 MHz, DMSO-*d6*) δ 164.96, 144.24, 142.05, 136.76, 133.91, 132.25, 129.00, 128.74, 126.97, 125.38, 125.14, 117.62, 109.27. (The substrate is a known compound. The spectroscopic data is consistent with that previously reported[15])

4. General procedures and characterization data of products

4.1 Photocyclization of indolecarboxamides

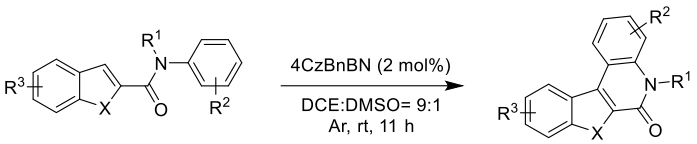


1a-1ag **2a-2ag**

Condition A:

An oven-dried Schlenk tube (10 mL) containing a stirring bar was charged with the substrate (0.2 mmol) and 4CzBnBN (3.3 mg, 2 mol%). The Schlenk tube was then connected to a vacuum line where it was evacuated and back-filled with argon for 3 times. Then Ultra-dry solvent (DCM: MeOH = 9:1, 2 mL) were added to the reaction in sequence under argon flow. Then, the reaction was degassed by three consecutive freeze-pump-thaw cycles. After backfilling with argon, the reaction mixture in sealed tube was placed at a distance of 2 ~ 3 cm from a 30 W blue LED and stirred at room temperature for 5 h. Then, the mixture was concentrated in vacuo. The resulting residue was purified by flash column chromatography on silica gel with DCM/MeOH as eluent to afford the desired product.

Condition B:



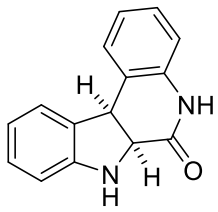
1a-1ag 3a-3ag

An oven-dried Schlenk tube (10 mL) containing a stirring bar was charged with the substrate (0.2 mmol) and 4CzBnBN (3.3 mg, 2 mol%). The Schlenk tube was then connected to a vacuum line where it was evacuated and back-filled with argon for 3 times. Then Ultra-dry solvent (DCE: DMSO = 9:1, 8 mL) were added to the reaction in sequence under argon flow. Then, the reaction was degassed by three consecutive freeze-pump-thaw cycles. After backfilling with argon, the reaction mixture in sealed tube was placed at a distance of 2 ~ 3 cm from a 30 W blue LED and stirred at room temperature for 11 h. Then, the reaction mixture was transferred to a separating funnel, diluted with water and extracted three times with EtOAc. The combined organic layers were washed with brine, dried over anhydrous sodium sulfate, filtered and concentrated to give the crude product which was purified by flash column chromatography on silica gel with DCM/MeOH as eluent to afford the desired product.

4.2 Characterization data for products

4.2.1 Characterization data for products of hydrogenative product

5,6a,7,11b-tetrahydro-6*H*-indolo[2,3-*c*]quinolin-6-one (2a)



Physical state: White solid.

Yield: 41.5 mg, 88%.

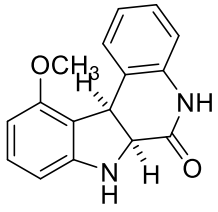
Melting point: 226.1-226.7 °C.

^{1}H NMR (400 MHz, DMSO-*d6*) δ 10.40 (s, 1H), 7.46 (d, *J* = 7.3 Hz, 1H), 7.27 – 7.17 (m, 1H), 7.07 (t, *J* = 7.3 Hz, 1H), 6.98 (t, *J* = 7.6 Hz, 1H), 6.89 (d, *J* = 7.7 Hz, 1H), 6.82 (d, *J* = 7.3 Hz, 1H), 6.72 (d, *J* = 7.7 Hz, 1H), 6.60 (t, *J* = 7.3 Hz, 1H), 6.15 (s, 1H), 4.57 (d, *J* = 9.4 Hz, 1H), 4.33 (d, *J* = 9.4 Hz, 1H).

^{13}C NMR (101 MHz, DMSO-*d6*) δ 170.46, 150.80, 136.86, 129.90, 129.58, 128.34, 128.28, 123.67, 122.92, 121.35, 118.74, 115.92, 110.25, 59.73, 43.95.

HRMS (ESI)**:** calcd for $C_{15}H_{13}ON_2$ $[M+H]^+$ *m/z* 237.1022, found 237.1033.

11-methoxy-5,6a,7,11b-tetrahydro-6*H*-indolo[2,3-*c*]quinolin-6-one (2b)



Physical state: White solid.

Yield: 27.0 mg, 54%.

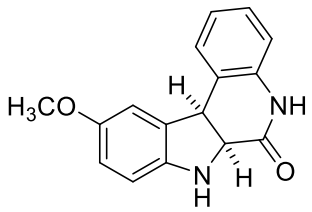
Melting point: 222.4-222.7 °C.

^{1}H NMR (400 MHz, DMSO-*d6*) δ 10.34 (s, 1H), 7.47 (d, *J* = 7.6 Hz, 1H), 7.13 (t, *J* = 7.6 Hz, 1H), 6.98 (t, *J* = 8.0 Hz, 1H), 6.92 (td, *J* = 7.6, 0.8 Hz, 1H), 6.87 (d, *J* = 7.9 Hz, 1H), 6.38 (d, *J* = 8.2 Hz, 1H), 6.31 (d, *J* = 7.7 Hz, 1H), 6.23 (s, 1H), 4.67 (d, *J* = 8.6 Hz, 1H), 4.18 (d, *J* = 8.6 Hz, 1H), 3.75 (s, 3H).

^{13}C NMR (101 MHz, DMSO-*d6*) δ 168.85, 156.95, 152.77, 136.98, 130.49, 129.72, 127.88, 122.63, 122.49, 116.82, 115.47, 104.04, 102.83, 61.45, 55.58, 41.79.

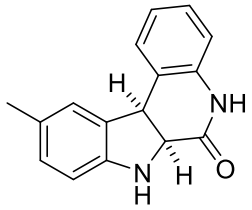
HRMS (ESI): calcd for $C_{16}H_{15}O_2N_2$ $[M+H]^+$ *m/z* 267.1128, found 267.1126.

10-methoxy-5,6a,7,11b-tetrahydro-6*H*-indolo[2,3-*c*]quinolin-6-one (2c)



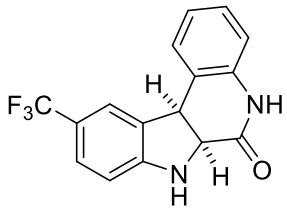
Physical state: White solid.
Yield: 17.0 mg, 32%.
Melting point: 188.7-189.0 °C.
^{1}H NMR (400 MHz, DMSO-*d6*) δ 10.41 (s, 1H), 7.47 (d, *J* = 7.3 Hz, 1H), 7.23 (t, *J* = 7.5 Hz, 1H), 7.08 (t, *J* = 7.3 Hz, 1H), 6.89 (d, *J* = 7.8 Hz, 1H), 6.67 (d, *J* = 8.3 Hz, 1H), 6.60 (d, *J* = 8.3 Hz, 1H), 6.42 (s, 1H), 5.76 (s, 1H), 4.55 (d, *J* = 9.2 Hz, 1H), 4.28 (d, *J* = 9.2 Hz, 1H), 3.58 (s, 3H).
^{13}C NMR (101 MHz, DMSO-*d6*) δ 170.70, 153.48, 144.52, 136.93, 130.99, 129.89, 128.44, 122.97, 121.20, 115.93, 113.33, 110.86, 110.48, 60.19, 55.97, 44.32.
HRMS (ESI): calcd for $C_{16}H_{15}O_2N_2$ $[M+H]^+$ *m/z* 267.1128, found 267.1125.

10-methyl-5,6a,7,11b-tetrahydro-6*H*-indolo[2,3-*c*]quinolin-6-one (2d)



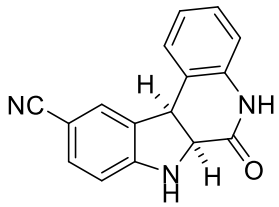
Physical state: White solid.
Yield: 48.5 mg, 97%.
Melting point: 257.1-257.4 °C.
^{1}H NMR (400 MHz, DMSO-*d6*) δ 10.40 (s, 1H), 7.46 (d, *J* = 7.4 Hz, 1H), 7.23 (t, *J* = 7.6 Hz, 1H), 7.08 (t, *J* = 7.4 Hz, 1H), 6.89 (d, *J* = 7.8 Hz, 1H), 6.80 (d, *J* = 7.8 Hz, 1H), 6.68 – 6.59 (m, 2H), 4.53 (d, *J* = 9.3 Hz, 1H), 4.29 (d, *J* = 9.3 Hz, 1H), 2.11 (s, 3H).
^{13}C NMR (101 MHz, DMSO-*d6*) δ 170.68, 148.43, 136.89, 129.95, 129.78, 128.61, 128.34, 127.58, 124.20, 122.92, 121.40, 115.92, 110.26, 59.91, 44.06, 20.89.
HRMS (ESI): calcd for $C_{16}H_{15}ON_2$ $[M+H]^+$ *m/z* 251.1179, found 251.1175.

10-(trifluoromethyl)-5,6a,7,11b-tetrahydro-6*H*-indolo[2,3-*c*]quinolin-6-one (2e)



Physical state: White solid.
Yield: 30.8 mg, 50%.
Melting point: 281.1-281.4 °C.
^{1}H NMR (400 MHz, DMSO-*d6*) δ 10.49 (s, 1H), 7.56 (d, *J* = 7.3 Hz, 1H), 7.35 (d, *J* = 8.1 Hz, 1H), 7.27 (dd, *J* = 10.9, 4.3 Hz, 1H), 7.11 (dd, *J* = 7.4, 6.8 Hz, 1H), 7.04 (d, *J* = 4.9 Hz, 2H), 6.92 (t, *J* = 7.7 Hz, 1H), 6.82 (d, *J* = 8.2 Hz, 1H), 4.70 (d, *J* = 9.9 Hz, 1H), 4.53 (d, *J* = 9.9 Hz, 1H).
^{19}F NMR (377 MHz, DMSO-*d6*) δ -58.93.
^{13}C NMR (101 MHz, DMSO-*d6*) δ 169.58, 154.30, 136.82, 130.46, 129.93, 128.68, 126.39 (q, *J* = 3.9 Hz), 125.54 (q, *J* = 270.6 Hz), 123.17, 120.32 (q, *J* = 3.4 Hz), 118.42 (q, *J* = 31.6 Hz), 116.09, 109.25, 59.79, 43.40.
HRMS (ESI): calcd for $C_{16}H_{12}OF_3N_2$ $[M+H]^+$ *m/z* 305.0896, found 305.0900.

(6aS,11bR)-6-oxo-6,6a,7,11b-tetrahydro-5*H*-indolo[2,3-*c*]quinoline-10-carbonitrile (2f)



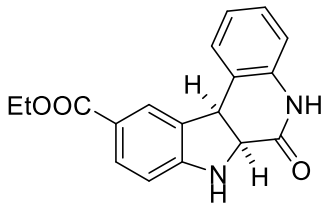
Physical State: White solid .
Yield: 16.2 mg, 62%.
Melting Point: 289.9-292.5 °C.
^{1}H NMR (400 MHz, DMSO-*d6*) δ 10.45 (s, 1H), 7.54 (d, J = 7.5 Hz, 1H), 7.42 (d, J = 8.2 Hz, 1H), 7.37 (s, 1H), 7.25 (t, J = 7.8 Hz, 1H), 7.16 (s, 1H), 7.09 (t, J = 7.5 Hz, 1H), 6.91 (d, J = 7.9 Hz, 1H), 6.74 (d, J = 8.1

Hz, 1H), 4.70 (d, J = 10.2 Hz, 1H), 4.56 (d, J = 8.1 Hz, 1H).

^{13}C NMR (101 MHz, DMSO-*d6*) δ 169.04, 154.84, 136.69, 134.02, 130.84, 129.97, 128.68, 127.24, 123.22, 120.66, 120.19, 116.05, 109.48, 98.79, 59.54, 43.12.

HRMS (ESI): calcd for $C_{16}H_{12}N_3O$ $[M+H]^+$ *m/z* 262.0975, found 262.0986.

ethyl (6aS,11bR)-6-oxo-6,6a,7,11b-tetrahydro-5*H*-indolo[2,3-*c*]quinoline-10-carboxylate (2g)



Physical State: White solid.

Yield: 37.6 mg, 61%.

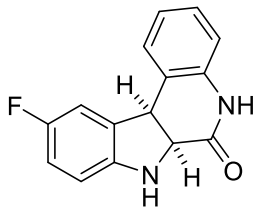
Melting Point: 268.6-275.3 °C.

^{1}H NMR (400 MHz, DMSO--*d6*) δ 10.47 (s, 1H), 7.67 (d, J = 10.0 Hz, 1H), 7.54 (d, J = 9.1 Hz, 1H), 7.36 (s, 1H), 7.26 (t, J = 7.7 Hz, 1H), 7.20 (s, 1H), 7.13 (t, J = 8.1 Hz, 1H), 6.91 (d, J = 9.2 Hz, 1H), 6.72 (d, J = 8.2 Hz, 1H), 4.66 (d, J = 9.8 Hz, 1H), 4.52 (d, J = 9.9 Hz, 1H), 4.222 – 4.142 (q, J = 6.9 Hz,2H), 1.22 (t, J = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, DMSO-*d6*) δ 169.66, 166.14, 155.38, 136.79, 131.32, 129.96, 129.82, 128.64, 124.70, 123.15, 120.69, 119.30, 116.05, 108.74, 60.29, 59.78, 55.41, 43.29, 14.80.

HRMS (ESI): calcd for $C_{18}H_{17}N_2O_3$ $[M+H]^+$ *m/z* 309.1234, found 309.1244.

10-fluoro-5,6a,7,11b-tetrahydro-6*H*-indolo[2,3-*c*]quinolin-6-one (2h)



Physical state: White solid.

Yield: 49.8 mg, 98%.

Melting point: 259.5-260.0 °C.

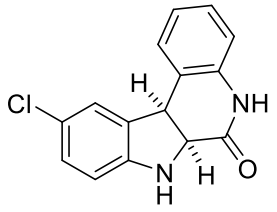
^{1}H NMR (400 MHz, DMSO-*d6*) δ 10.45 (s, 1H), 7.48 (d, *J* = 7.3 Hz, 1H), 7.24 (t, *J* = 7.2 Hz, 1H), 7.08 (t, *J* = 7.2 Hz, 1H), 6.91 (d, *J* = 7.8 Hz, 1H), 6.82 (td, *J* = 9.0, 2.2 Hz, 1H), 6.71 (dd, *J* = 8.5, 4.5 Hz, 1H), 6.67 – 6.61 (m, 1H), 6.10 (s, 1H), 4.58 (dd, *J* = 26.3, 9.5 Hz, 1H), 4.37 (d, *J* = 9.5 Hz, 1H).

^{19}F NMR (377 MHz, DMSO-*d6*) δ -126.41.

^{13}C NMR (101 MHz, DMSO-*d6*) δ 170.23, 156.64 (d, *J* = 233.3 Hz), 147.13, 136.91, 131.53 (d, *J* = 7.7 Hz), 129.85, 128.57, 123.06, 120.73, 115.99, 114.37 (d, *J* = 22.9 Hz), 111.15, 110.91, 110.64 (d, *J* = 8.1 Hz), 60.30, 44.08.

HRMS (ESI): calcd for $C_{15}H_{12}OFN_2$ $[M+H]^+$ *m/z* 255.0928, found 255.0940.

10-chloro-5,6a,7,11b-tetrahydro-6*H*-indolo[2,3-*c*]quinolin-6-one (2i)



Physical state: White solid.

Yield: 37.0 mg, 73%.

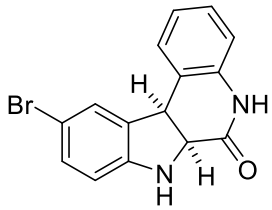
Melting point: 284.3-284.6 °C.

^{1}H NMR (400 MHz, DMSO-*d6*) δ 10.45 (s, 1H), 7.50 (d, *J* = 7.3 Hz, 1H), 7.25 (t, *J* = 7.3 Hz, 1H), 7.09 (t, *J* = 7.3 Hz, 1H), 7.02 (dd, *J* = 8.2, 1.5 Hz, 1H), 6.90 (d, *J* = 7.8 Hz, 1H), 6.77 (s, 1H), 6.72 (d, *J* = 8.3 Hz, 1H), 6.41 (s, 1H), 4.63 (d, *J* = 9.6 Hz, 1H), 4.40 (d, *J* = 9.6 Hz, 1H).

^{13}C NMR (101 MHz, DMSO-*d6*) δ 169.99, 149.86, 136.85, 132.03, 129.90, 128.61, 128.01, 123.59, 123.09, 121.99, 120.61, 116.01, 111.28, 60.01, 43.86.

HRMS (ESI): calcd for $C_{15}H_{12}OClN_2$ $[M+H]^+$ *m/z* 271.0633, found 271.0637.

10-bromo-5,6a,7,11b-tetrahydro-6*H*-indolo[2,3-*c*]quinolin-6-one (2j)



Physical state: White solid.

Yield: 47.0 mg, 74%.

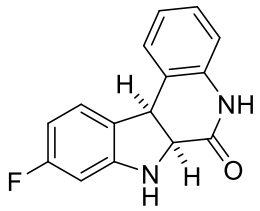
Melting point: 270.9-281.1 °C.

^{1}H NMR (400 MHz, DMSO-*d6*) δ 10.45 (s, 1H), 7.50 (d, *J* = 7.2 Hz, 1H), 7.25 (t, *J* = 7.4 Hz, 1H), 7.17 – 6.98 (m, 2H), 7.00 – 6.79 (m, 2H), 6.68 (d, *J* = 8.2 Hz, 1H), 6.44 (s, 1H), 4.63 (d, *J* = 9.5 Hz, 1H), 4.39 (d, *J* = 9.6 Hz, 1H).

^{13}C NMR (101 MHz, DMSO-*d6*) δ 169.98, 150.26, 136.84, 132.52, 130.84, 129.92, 128.63, 126.30, 126.21, 123.10, 120.60, 116.01, 111.90, 109.29, 59.92, 43.84.

HRMS (ESI): calcd for $C_{15}H_{12}OBrN_2$ $[M+H]^+$ *m/z* 315.0128, found 315.0134.

9-fluoro-5,6a,7,11b-tetrahydro-6*H*-indolo[2,3-*c*]quinolin-6-one (2k)



Physical state: White solid.

Yield: 49.5 mg, 97%.

Melting point: 241.9-242.1 °C.

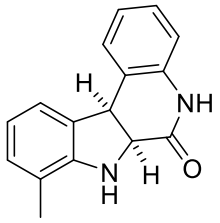
^{1}H NMR (400 MHz, DMSO-*d6*) δ 10.44 (s, 1H), 7.46 (d, *J* = 7.4 Hz, 1H), 7.23 (t, *J* = 7.6 Hz, 1H), 7.07 (t, *J* = 7.3 Hz, 1H), 6.90 (d, *J* = 7.8 Hz, 1H), 6.78 (t, 1H), 6.49 (dd, *J* = 10.2, 2.0 Hz, 1H), 6.43 – 6.29 (m, 1H), 4.56 (d, *J* = 9.5 Hz, 1H), 4.40 (d, *J* = 9.5 Hz, 1H).

^{19}F NMR (377 MHz, DMSO-*d6*) δ -115.25.

^{13}C NMR (101 MHz, DMSO-*d6*) δ 170.02, 163.28 (d, *J* = 239.4 Hz), 152.65 (d, *J* = 12.5 Hz), 136.76, 129.85, 128.44, 125.59, 124.48 (d, *J* = 10.7 Hz), 123.01, 121.06, 115.98, 104.42 (d, *J* = 22.9 Hz), 97.64, 97.37, 60.26, 43.18.

HRMS (ESI): calcd for $C_{15}H_{12}OFN_2$ $[M+H]^+$ *m/z* 255.0928, found 255.0930.

8-methyl-5,6a,7,11b-tetrahydro-6*H*-indolo[2,3-*c*]quinolin-6-one (2l)



Physical state: White solid.

Yield: 48.4 mg, 97%.

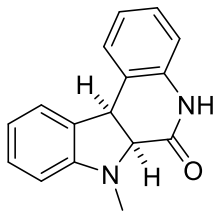
Melting point: 253.0-253.1 °C.

^{1}H NMR (400 MHz, DMSO-*d6*) δ 10.42 (s, 1H), 7.44 (d, *J* = 7.4 Hz, 1H), 7.22 (dd, *J* = 11.0, 4.3 Hz, 1H), 7.06 (t, *J* = 7.1 Hz, 1H), 6.90 (d, *J* = 7.8 Hz, 1H), 6.84 (d, *J* = 7.4 Hz, 1H), 6.72 (d, *J* = 7.3 Hz, 1H), 6.58 (t, *J* = 7.4 Hz, 1H), 4.58 (d, *J* = 9.3 Hz, 1H), 4.34 (d, *J* = 9.3 Hz, 1H), 2.13 (s, 3H).

^{13}C NMR (101 MHz, DMSO-*d6*) δ 170.42, 148.86, 136.87, 129.80, 129.35, 129.17, 128.31, 122.95, 121.48, 121.37, 119.45, 119.36, 115.93, 59.64, 44.12, 16.91.

HRMS (ESI): calcd for $C_{16}H_{15}ON_2$ $[M+H]^+$ *m/z* 251.1179, found 251.1173.

7-methyl-5,6a,7,11b-tetrahydro-6*H*-indolo[2,3-*c*]quinolin-6-one (2m)



Physical state: White solid.

Yield: 46 mg, 92%.

Melting point: 306.3-306.6 °C.

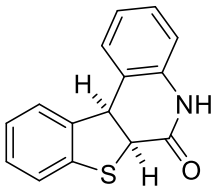
^{1}H NMR (400 MHz, DMSO-*d6*) δ 10.42 (s, 1H), 7.38 (d, *J* = 7.2 Hz, 1H), 7.32 (d, *J* = 7.6 Hz, 1H), 7.17 – 7.07 (m, 2H), 6.94 (t, *J* = 7.4 Hz, 1H), 6.87

(d, *J* = 7.9 Hz, 1H), 6.75 (t, *J* = 7.3 Hz, 1H), 6.57 (d, *J* = 7.8 Hz, 1H), 4.60 (d, *J* = 8.5 Hz, 1H), 3.85 (d, *J* = 8.6 Hz, 1H), 2.85 (s, 3H).

^{13}C NMR (101 MHz, DMSO-*d6*) δ 167.25, 152.12, 136.87, 131.27, 128.78, 128.58, 127.95, 125.19, 122.88, 121.77, 119.07, 115.62, 108.44, 67.86, 42.39, 35.52.

HRMS (ESI)**:** calcd for $C_{16}H_{15}ON_2$ $[M+H]^+$ *m/z* 251.1179, found 251.1168.

6a,11b-dihydrobenzo[4,5]thieno[2,3-*c*]quinolin-6(5*H*)-one (2n)



Physical State: White solid.

Yield: 27.8 mg, 55%.

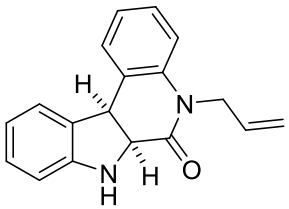
Melting Point: 245.2-245.5 °C.

^{1}H NMR (400 MHz, DMSO-*d6*) δ 10.55 (s, 1H), 7.33 (dd, *J* = 9.6, 8.2 Hz, 2H), 7.26 (dd, *J* = 11.0, 4.3 Hz, 1H), 7.20 (t, *J* = 7.4 Hz, 1H), 7.07 (q, *J* = 6.6 Hz, 2H), 7.00 (d, *J* = 7.5 Hz, 1H), 6.96 (d, *J* = 7.7 Hz, 1H), δ 4.82 (d, *J* = 8.1 Hz, 1H), 4.79 (d, *J* = 8.0 Hz, 1H)..

^{13}C NMR (101 MHz, DMSO-*d6*) δ 167.52, 140.55, 139.47, 137.30, 129.48, 128.69, 128.67, 125.33, 125.19, 122.92, 122.52, 120.88, 115.98, 52.17, 49.61.

HRMS (ESI)**:** calcd for $C_{15}H_{12}ONS$ $[M+H]^+$ *m/z* 254.0634, found 254.0637.

5-allyl-5,6a,7,11b-tetrahydro-6*H*-indolo[2,3-*c*]quinolin-6-one (2p)



Physical State: White solid.

Yield: 43.8 mg, 79%.

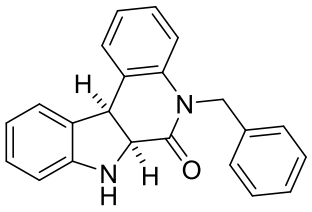
Melting Point: 148.5-148.8 °C.

^{1}H NMR (400 MHz, DMSO-*d6*) δ 7.50 (t, *J* = 9.9 Hz, 1H), 7.31 (dd, *J* = 11.4, 4.0 Hz, 1H), 7.16 (t, *J* = 7.4 Hz, 1H), 7.06 – 6.96 (m, 2H), 6.84 (d, *J* = 7.3 Hz, 1H), 6.75 (d, *J* = 7.7 Hz, 1H), 6.62 (t, *J* = 7.3 Hz, 1H), 5.85 – 5.70 (m, 1H), 5.07 – 4.98 (m, 1H), 4.93 – 4.83 (m, 1H), δ 4.69 – 4.61 (m, 1H), 4.58 (d, J = 9.2 Hz, 1H), 4.45 (d, J = 9.2 Hz, 1H), 4.39 – 4.30 (m, 1H).

^{13}C NMR (101 MHz, DMSO-*d6*) δ 169.90, 150.69, 137.64, 132.85, 130.38, 129.40, 128.48, 128.39, 123.54, 123.38, 122.68, 118.91, 116.07, 116.05, 110.41, 59.93, 44.35, 43.65.

HRMS (ESI)**:** calcd for $C_{18}H_{17}ON_2$ $[M+H]^+$ *m/z* 277.1335, found 277.1333.

5-benzyl-5,6a,7,11b-tetrahydro-6*H*-indolo[2,3-*c*]quinolin-6-one (2q)



Physical State: White solid.

Yield: 39.8 mg, 61%.

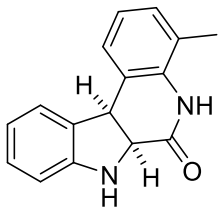
Melting Point: 198.0-198.7 °C.

^{1}H NMR (400 MHz, DMSO-*d6*) δ 7.53 (d, *J* = 7.3 Hz, 1H), 7.25 – 7.16 (m, 4H), 7.13 (t, *J* = 7.4 Hz, 1H), 7.04 (t, *J* = 7.8 Hz, 3H), 6.94 (d, *J* = 8.2 Hz, 1H), 6.85 (d, *J* = 7.3 Hz, 1H), 6.79 (d, *J* = 7.7 Hz, 1H), 6.66 (t, *J* = 7.4 Hz, 1H), 6.29 (s, 1H), 5.24 (d, *J* = 16.5 Hz, 1H), 5.06 (d, *J* = 16.5 Hz, 1H), 4.62 (d, *J* = 9.1 Hz, 1H), 4.57 (d, *J* = 9.1 Hz, 1H).

^{13}C NMR (101 MHz, DMSO-*d6*) δ 170.66, 150.77, 137.64, 137.03, 130.42, 129.50, 128.94, 128.43, 127.31, 126.56, 123.64, 123.50, 123.09, 118.96, 116.21, 110.49, 60.25, 45.28, 43.71.

HRMS (ESI)**:** calcd for $C_{22}H_{19}ON_2$ $[M+H]^+$ *m/z* 327.1492, found 327.1485.

4-methyl-5,6a,7,11b-tetrahydro-6*H*-indolo[2,3-*c*]quinolin-6-one (2r)



Physical State: White solid.

Yield: 46.0 mg, 92%.

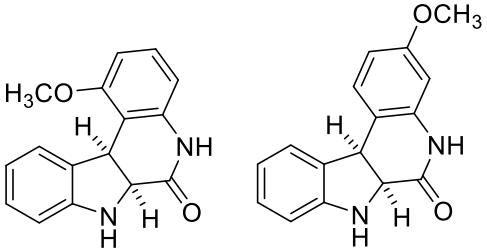
Melting Point: 244.8-245.1 °C.

^{1}H NMR (400 MHz, DMSO-*d6*) δ 9.60 (s, 1H), 7.30 (d, *J* = 6.9 Hz, 1H), 7.09 (d, *J* = 6.9 Hz, 1H), 6.99 (dd, *J* = 13.4, 6.7 Hz, 2H), 6.77 (dd, *J* = 18.7, 7.2 Hz, 2H), 6.60 (t, *J* = 7.0 Hz, 1H), 4.54 (d, *J* = 9.1 Hz, 1H), 4.31 (d, *J* = 9.2 Hz, 1H), 2.21 (s, 3H).

^{13}C NMR (101 MHz, DMSO-*d6*) δ 171.34, 150.85, 134.93, 130.07, 129.61, 128.29, 127.83, 124.19, 123.55, 122.78, 121.44, 118.80, 110.37, 59.66, 44.31, 17.81.

HRMS (ESI): calcd for $C_{16}H_{15}ON_2$ $[M+H]^+$ *m/z* 251.1179, found 251.1173.

1-methoxy-5,6a,7,11b-tetrahydro-6*H*-indolo[2,3-*c*]quinolin-6-one and 4-methoxy-5,6a,7,11b-tetrahydro-6*H*-indolo[2,3-*c*]quinolin-6-one (4:3) (2s+2s′)



Physical State: White solid.

Yield: 47.0 mg, 88%.

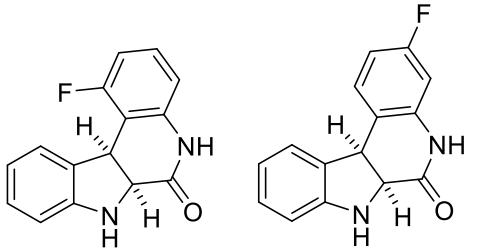
Melting Point: 195.0-195.3 °C.

^{1}H NMR (400 MHz, DMSO-*d6*) δ 10.39 (s, 0.76H), 10.34 (s, 1H), 7.38 (d, *J* = 8.4 Hz, 1H), 7.21 (t, *J* = 8.1 Hz, 0.85H), 6.97 (dd, *J* = 12.7, 7.4 Hz, 1.79H), 6.85 – 6.75 (m, 2.65H), 6.75 – 6.70 (m, 1.77H), 6.67 (dd, *J* = 8.3, 2.5 Hz, 1H), 6.63 – 6.55 (m, 2H), 6.53 (d, *J* = 7.9 Hz, 0.75H), 6.48 (d, *J* = 2.5 Hz, 1H), 6.12 (s, 1H), 6.08 (s, 0.78H), 4.73 (d, *J* = 9.7 Hz, 0.79H), 4.52 (s, 1H), 4.29 (d, *J* = 9.4 Hz, 1H), 4.25 (d, *J* = 9.7 Hz, 0.77H), 3.89 (s, 2.36H), 3.73 (s, 3H).

^{13}C NMR (101 MHz, DMSO-*d6*) δ 170.85, 170.70, 159.46, 158.04, 151.04, 150.75, 137.87, 137.77, 130.77, 130.00, 129.28, 129.06, 128.18, 128.13, 124.09, 123.63, 118.77, 118.73, 113.57, 110.22, 110.20, 109.76, 108.75, 108.22, 105.87, 101.80, 59.81, 59.20, 56.16, 55.57, 43.31, 39.07.

HRMS (ESI): calcd for $C_{16}H_{15}O_2N_2$ $[M+H]^+$ *m/z* 267.1128, found 267.1118.

3-fluoro-5,6a,7,11b-tetrahydro-6*H*-indolo[2,3-*c*]quinolin-6-one and 4-fluoro-5,6a,7,11b-tetrahydro-6*H*-indolo[2,3-*c*]quinolin-6-one (5:4) (2t+2t′)



Physical State: White solid.

Yield: 44.0 mg, 86%.

Melting Point: 253.8-254.1 °C.

^{1}H NMR (400 MHz, DMSO-*d6*) δ 10.64 (s, 1H), 10.52 (s, 0.80H), 7.56 – 7.47 (m, 1H), 7.29 (dd, *J* = 14.5, 8.0 Hz, 1H), 7.05 – 6.95 (m, 3H), 6.90 (td, *J* = 8.6, 2.5 Hz, 1H), 6.86 – 6.67 (m, 5.42H), 6.61 (t, *J* = 7.3 Hz, 1.64H), 4.78 (d, *J* = 9.7 Hz, 1H), 4.58 (d, *J* = 9.4 Hz, 1H), 4.35 (dd, *J* = 9.5, 7.2 Hz, 1.87H).

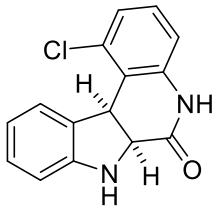
^{19}F NMR (377 MHz, DMSO-*d6*) δ -114.52, -119.14.

^{13}C NMR (101 MHz, DMSO-*d6*) δ 170.66, 170.61, 162.84 (d, *J* = 84.5 Hz), 160.43 (d, *J* = 85.2 Hz), 150.91, 150.70, 138.83 (d, *J* = 7.3 Hz), 138.50 (d, *J* = 11.1 Hz), 131.57 (d, *J* = 9.5 Hz), 130.03, 129.98 (d, *J* = 9.9 Hz), 129.41, 128.57, 128.37, 128.03, 123.64, 118.98, 118.81, 117.61, 117.58, 111.97, 111.94, 110.38, 110.26, 109.65 (d, *J* = 21.7 Hz), 109.27 (d, *J* = 21.4 Hz), 102.92, 102.66,

59.63, 58.96, 43.35, 38.55.

HRMS (ESI): calcd for $C_{15}H_{12}OFN_2$ $[M+H]^+$ *m/z* 255.0928, found 255.0921.

4-chloro-5,6a,7,11b-tetrahydro-6*H*-indolo[2,3-*c*]quinolin-6-one (2u)



Physical State: White solid.

Yield: 38.1 mg, 70%.

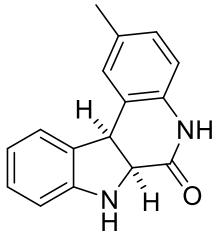
Melting Point: 253.8-254.1 °C.

^{1}H NMR (400 MHz, DMSO-*d6*) δ 10.54 (s, 1H), 7.50 (d, *J* = 8.1 Hz, 1H), 7.12 (dd, *J* = 8.1, 2.0 Hz, 1H), 6.99 (t, *J* = 7.5 Hz, 1H), 6.93 (d, *J* = 2.0 Hz, 1H), 6.83 (d, *J* = 7.3 Hz, 1H), 6.72 (d, *J* = 7.7 Hz, 1H), 6.61 (t, *J* = 7.3 Hz, 1H), 6.23 (s, 1H), 4.59 (d, *J* = 9.4 Hz, 1H), 4.34 (d, *J* = 9.4 Hz, 1H).

^{13}C NMR (101 MHz, DMSO-*d6*) δ 170.58, 150.73, 138.40, 132.48, 131.55, 129.12, 128.44, 123.65, 122.50, 120.45, 118.79, 115.36, 110.25, 59.59, 43.46.

HRMS (ESI): calcd for $C_{15}H_{12}OClN_2$ $[M+H]^+$ *m/z* 271.0633, found 271.0625.

2-methyl-5,6a,7,11b-tetrahydro-6*H*-indolo[2,3-*c*]quinolin-6-one (2v)



Physical State: White solid.

Yield: 46.0 mg, 90%.

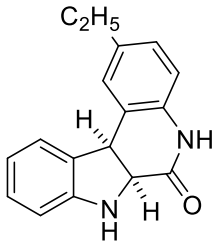
Melting Point: 205.9-206.1 °C.

^{1}H NMR (400 MHz, DMSO-*d6*) δ 10.32 (s, 1H), 7.27 (s, 1H), 7.06 – 6.95 (m, 2H), 6.85 (d, *J* = 7.3 Hz, 1H), 6.78 (d, *J* = 8.0 Hz, 1H), 6.73 (d, *J* = 7.7 Hz, 1H), 6.61 (t, *J* = 7.3 Hz, 1H), 4.52 (d, *J* = 9.4 Hz, 1H), 4.29 (d, *J* = 9.4 Hz, 1H), 2.31 (s, 3H).

^{13}C NMR (101 MHz, DMSO-*d6*) δ 170.20, 150.68, 134.40, 131.85, 130.31, 129.68, 128.76, 128.25, 123.72, 121.15, 118.83, 115.81, 110.32, 59.75, 43.95, 20.89.

HRMS (ESI): calcd for $C_{16}H_{15}ON_2$ $[M+H]^+$ *m/z* 251.1179, found 251.1173.

2-ethyl-5,6a,7,11b-tetrahydro-6*H*-indolo[2,3-*c*]quinolin-6-one (2w)



Physical State: White solid.

Yield: 50.5 mg, 91%.

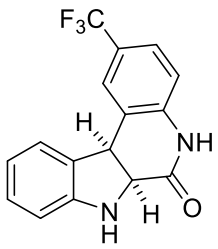
Melting Point: 234.6-234.9 °C.

^{1}H NMR (400 MHz, DMSO-*d6*) δ 10.34 (s, 1H), 7.36 (d, *J* = 7.7 Hz, 1H), 6.97 (t, *J* = 7.6 Hz, 1H), 6.92 (d, *J* = 7.6 Hz, 1H), 6.82 (d, *J* = 7.3 Hz, 1H), 6.72 (d, *J* = 7.6 Hz, 2H), 6.60 (t, *J* = 7.3 Hz, 1H), 6.13 (s, 1H), 4.53 (d, *J* = 9.4 Hz, 1H), 4.29 (d, *J* = 9.5 Hz, 1H), 2.55 (q, *J* = 7.6 Hz, 2H), 1.16 (t, *J* = 7.6 Hz, 3H).

^{13}C NMR (101 MHz, DMSO-*d6*) δ 170.58, 150.79, 144.02, 136.78, 129.82, 129.76, 128.22, 123.69, 122.43, 118.72, 118.70, 115.17, 110.23, 59.79, 43.65, 28.38, 15.97.

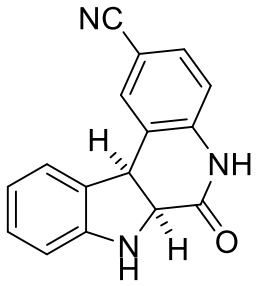
HRMS (ESI): calcd for $C_{17}H_{17}ON_2$ $[M+H]^+$ *m/z* 265.1335, found 265.1329.

2-(trifluoromethyl)-5,6a,7,11b-tetrahydro-6*H*-indolo[2,3-*c*]quinolin-6-one (2x)



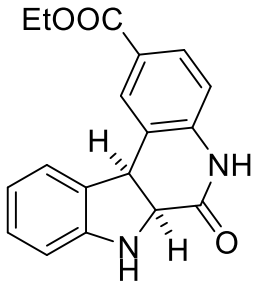
Physical State: White solid.
Yield: 49.4 mg, 82%.
Melting Point: 244.9-245.1 °C.
^{1}H NMR (400 MHz, DMSO-*d6*) δ 10.78 (s, 1H), 7.87 (s, 1H), 7.61 (d, *J* = 8.3 Hz, 1H), 7.07 (d, *J* = 8.3 Hz, 1H), 7.01 (t, *J* = 7.5 Hz, 1H), 6.81 (d, *J* = 7.3 Hz, 1H), 6.74 (d, *J* = 7.7 Hz, 1H), 6.63 (t, *J* = 7.3 Hz, 1H), 6.28 (s, 1H), 4.72 (d, *J* = 9.3 Hz, 1H), 4.39 (d, *J* = 9.4 Hz, 1H).
^{19}F NMR (377 MHz, DMSO-*d6*) δ -60.02.
^{13}C NMR (101 MHz, DMSO) δ 170.91, 150.74, 140.51, 128.87, 128.53, 126.84 (q, *J* = 3.9 Hz), 126.16 (q, *J* = 271.2 Hz), 125.66 (q, *J* = 3.3 Hz), 123.21 (q, *J* = 31.9 Hz), 122.30, 118.88, 116.29, 110.30, 59.57, 43.64.
HRMS (ESI): calcd for $C_{16}H_{12}OF_3N_2$ $[M+H]^+$ *m/z* 305.0896, found 305.0891.

(6aS,11bS)-6-oxo-6,6a,7,11b-tetrahydro-5H-indolo[2,3-c]quinoline-2-carbonitrile (2y)



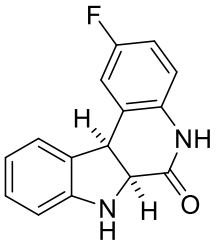
Physical State: White solid.
Yield: 5.0 mg, 10%.
Melting Point: 265.5-267.6 °C.
^{1}H NMR (400 MHz, DMSO-*d6*) δ 10.84 (s, 1H), 8.00 (s, 1H), 7.71 (dd, J = 8.3, 1.9 Hz, 1H), 7.00 (t, J = 7.7 Hz, 2H), 6.89 (d, J = 7.4 Hz, 1H), 6.72 (d, J = 7.7 Hz, 1H), 6.62 (t, J = 7.4 Hz, 1H), 6.30 (s, 1H), 4.65 (d, J = 9.4 Hz, 1H), 4.39 (d, J = 9.4 Hz, 1H).
^{13}C NMR (101 MHz, DMSO-*d6*) δ 170.96, 150.69, 141.22, 133.82, 132.85, 128.60, 123.85, 122.74, 119.61, 118.86, 116.61, 110.23, 104.79, 59.49, 43.45.
HRMS (ESI): calcd for $C_{16}H_{12}N_3O$ $[M+H]^+$ *m/z* 262.0975, found 262.0982.

ethyl (6aS,11bS)-6-oxo-6,6a,7,11b-tetrahydro-5*H*-indolo[2,3-*c*]quinoline-2-carboxylate (2z)



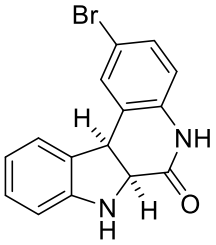
Physical State: White solid.
Yield: 44.3mg, 72%.
Melting Point: 273.8-276.5 °C.
^{1}H NMR (400 MHz, DMSO-*d6*) δ 10.81 (s, 1H), 8.07 (s, 1H), 7.85 (d, J = 10.3 Hz, 1H), 6.99 (t, J = 9.2 Hz, 2H), 6.79 (d, J = 7.3 Hz, 1H), 6.73 (d, J = 7.8 Hz, 1H), 6.62 (t, J = 7.4 Hz, 1H), 6.30 (s, 1H), 4.70 (d, J = 9.3 Hz, 1H), 4.38 (d, J = 9.4 Hz, 1H), 4.32 (m, 2H), 1.34 (t, J = 7.1 Hz, 3H).
^{13}C NMR (101 MHz, DMSO-*d6*) δ 171.08, 165.84, 150.78, 140.70, 130.99, 129.92, 129.10, 128.47, 124.20, 123.49, 121.56, 118.84, 115.92, 110.28, 61.02, 59.65, 43.62, 14.26.
HRMS (ESI): calcd for $C_{18}H_{17}N_2O_3$ $[M+H]^+$ *m/z* 309.1234, found 309.1244.

2-fluoro-5,6a,7,11b-tetrahydro-6*H*-indolo[2,3-*c*]quinolin-6-one (2aa)



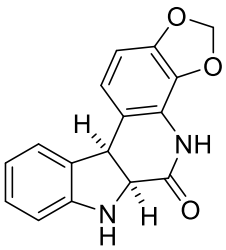
Physical State: White solid.
Yield: 43.9 mg, 86%.
Melting Point: 274.6-274.9 °C.
^{1}H NMR (400 MHz, DMSO-*d6*) δ 10.45 (s, 1H), 7.39 (dd, *J* = 9.1, 2.7 Hz, 1H), 7.09 (td, *J* = 8.6, 2.8 Hz, 1H), 7.00 (t, *J* = 7.5 Hz, 1H), 6.90 (dd, *J* = 8.5, 5.6 Hz, 2H), 6.73 (d, *J* = 7.7 Hz, 1H), 6.62 (t, *J* = 7.3 Hz, 1H), 6.19 (s, 1H), 4.59 (d, *J* = 9.4 Hz, 1H), 4.32 (d, *J* = 9.4 Hz, 1H).
^{19}F NMR (377 MHz, DMSO-*d6*) δ -119.90.
^{13}C NMR (101 MHz, DMSO-*d6*) δ 170.14, 158.11 (d, *J* = 238.4 Hz), 150.76, 133.41 (d, *J* = 2.1 Hz), 129.00, 128.43, 123.80, 123.39, 123.31, 118.80, 117.13 (d, *J* = 8.2 Hz), 116.49 (d, *J* = 23.1 Hz), 114.96 (d, *J* = 22.6 Hz), 110.26, 59.39 , 43.88.
HRMS (ESI): calcd for $C_{15}H_{12}OFN_2$ $[M+H]^+$ *m/z* 255.0928, found 255.0926.

2-bromo-5,6a,7,11b-tetrahydro-6*H*-indolo[2,3-*c*]quinolin-6-one (2ab)



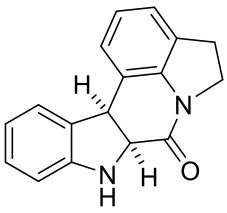
Physical State: Yellow solid.
Yield: 57.7 mg, 90%.
Melting Point: 252.6-252.9 °C.
^{1}H NMR (400 MHz, DMSO-*d6*) δ 10.52 (s, 1H), 7.69 (d, *J* = 2.0 Hz, 1H), 7.42 (dd, *J* = 8.5, 2.2 Hz, 1H), 7.00 (t, *J* = 7.6 Hz, 1H), 6.85 (t, *J* = 7.1 Hz, 2H), 6.72 (d, *J* = 7.7 Hz, 1H), 6.63 (t, *J* = 7.4 Hz, 1H), 6.21 (s, 1H), 4.60 (d, *J* = 9.3 Hz, 1H), 4.32 (d, *J* = 9.4 Hz, 1H).
^{13}C NMR (101 MHz, DMSO-*d6*) δ 170.35, 150.75, 136.38, 132.24, 131.10, 129.00, 128.46, 124.00, 123.74, 118.84, 117.87, 114.31, 110.26, 59.53, 43.59.
HRMS (ESI): calcd for $C_{15}H_{12}OBrN_2$ $[M+H]^+$ *m/z* 315.0128, found 315.0125

4,5a,6,10b-tetrahydro-5*H*-[1,3]dioxolo[4,5-*h*]indolo[2,3-*c*]quinolin-5-one (2ac)



Physical State: White solid.
Yield: 43.8 mg, 82%.
Melting Point: 272.6-272.9 °C.
^{1}H NMR (400 MHz, DMSO-*d6*) δ 10.21 (s, 1H), 7.09 (s, 1H), 6.98 (t, *J* = 7.6 Hz, 1H), 6.87 (d, *J* = 7.3 Hz, 1H), 6.72 (d, *J* = 7.7 Hz, 1H), 6.62 (t, *J* = 7.3 Hz, 1H), 6.50 (s, 1H), 6.00 (d, *J* = 7.3 Hz, 2H), 4.47 (d, *J* = 9.5 Hz, 1H), 4.25 (d, *J* = 9.5 Hz, 1H).
^{13}C NMR (101 MHz, DMSO-*d6*) δ 170.10, 150.68, 147.09, 143.07, 131.02, 129.78, 128.22, 123.74, 118.81, 113.51, 110.25, 109.77, 101.56, 97.72, 59.50, 43.86.
HRMS (ESI): calcd for $C_{16}H_{13}O_3N_2$ $[M+H]^+$ *m/z* 281.0921, found 281.0916.

4,5,8,12b-tetrahydroindolo[2,3-*c*]pyrrolo[3,2,1-*ij*]quinolin-7(7a*H*)-one (2ad)



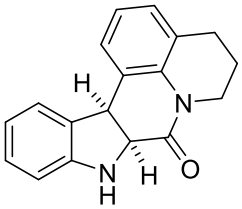
Physical State: White solid.
Yield: 52.9 mg, 87%.
Melting Point: 272.6-272.9 °C.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 (d, *J* = 7.3 Hz, 1H), 7.14 (d, *J* = 7.4 Hz, 1H), 7.07 (dd, *J* = 12.3, 7.4 Hz, 2H), 6.98 (d, *J* = 7.3 Hz, 1H), 6.83 – 6.69 (m, 2H), 5.15 (s, 1H), 4.71 (d, *J* = 9.4 Hz, 1H), 4.42 (d, *J* = 9.4 Hz, 1H), 4.14 –

4.03 (m, 1H), 4.01 – 3.90 (m, 1H), 3.30 – 3.17 (m, 1H), 3.11 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 167.06, 149.50, 139.46, 129.88, 128.67, 128.33, 126.38, 124.16, 124.07, 123.60, 119.73, 118.98, 110.71, 61.92, 45.40, 44.00, 27.57.

HRMS (ESI): calcd for $C_{17}H_{15}ON_2$ $[M+H]^+$ *m/z* 263.1179, found 263.1173.

5,6,9,13b-tetrahydro-4*H*-indolo[2,3-*c*]pyrido[3,2,1-*ij*]quinolin-8(8a*H*)-one (2ae)



Physical State: Yellow solid.

Yield: 46.0 mg, 83%.

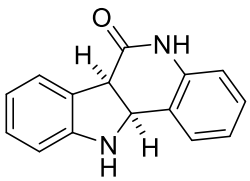
Melting Point: 250.5-250.9 °C.

^{1}H NMR (400 MHz, DMSO-*d6*) δ 7.32 (d, *J* = 7.1 Hz, 1H), 7.12 (d, *J* = 7.0 Hz, 1H), 7.06 (t, *J* = 7.4 Hz, 1H), 6.98 (t, *J* = 7.6 Hz, 1H), 6.80 (d, *J* = 7.3 Hz, 1H), 6.72 (d, *J* = 7.7 Hz, 1H), 6.60 (t, *J* = 7.3 Hz, 1H), 6.19 (s, 1H), 4.52 (d, *J* = 9.4 Hz, 1H), 4.34 (d, *J* = 9.4 Hz, 1H), 4.07 – 3.93 (m, 1H), 3.56 – 3.41 (m, 1H), 2.79 – 2.69 (m, 2H), 1.86 – 1.73 (m, 2H).

^{13}C NMR (101 MHz, DMSO-*d6*) δ 169.17, 150.76, 134.30, 129.55, 128.99, 128.34, 128.28, 125.62, 123.59, 122.92, 122.13, 118.79, 110.32, 59.68, 43.47, 41.60, 27.22, 20.83.

HRMS (ESI): calcd for $C_{18}H_{17}ON_2$ $[M+H]^+$ *m/z* 277.1335, found 277.1323.

5,6a,11,11a-tetrahydro-6*H*-indolo[3,2-*c*]quinolin-6-one (2ag)



Physical State: White solid.

Yield: 29.3 mg, 62%.

Melting Point: 265.3-265.6 °C.

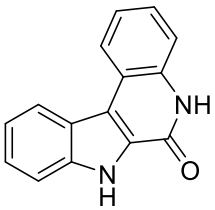
^{1}H NMR (400 MHz, DMSO-*d6*) δ 10.41 (s, 1H), 7.46 (d, *J* = 7.3 Hz, 1H), 7.22 (t, *J* = 7.3 Hz, 1H), 7.07 (t, *J* = 7.3 Hz, 1H), 6.98 (t, *J* = 7.5 Hz, 1H), 6.89 (d, *J* = 7.8 Hz, 1H), 6.82 (d, *J* = 7.3 Hz, 1H), 6.73 (d, *J* = 7.7 Hz, 1H), 6.60 (t, *J* = 7.3 Hz, 1H), 6.16 (s, 1H), 4.57 (d, *J* = 9.4 Hz, 1H), 4.33 (d, *J* = 9.4 Hz, 1H).

^{13}C NMR (101 MHz, DMSO-*d6*) δ 170.47, 150.80, 136.86, 129.90, 129.58, 128.34, 128.29, 123.67, 122.93, 121.35, 118.74, 115.92, 110.25, 59.73, 43.95.

HRMS (ESI): calcd for $C_{15}H_{13}N_2O$ $[M+H]^+$ *m/z* 237.1022, found 277.1032.

4.2.2 Characterization data for products of dehydrogenative products

5,7-dihydro-6*H*-indolo[2,3-*c*]quinolin-6-one (3a)



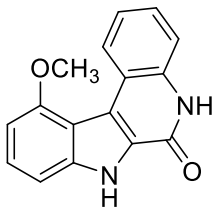
Physical State: White solid.

Yield: 40.6 mg, 87%.

^{1}H NMR (400 MHz, DMSO-*d6*) δ 12.37 (s, 1H), 11.89 (s, 1H), 8.51 – 8.42 (m, 2H), 7.67 (d, *J* = 8.3 Hz, 1H), 7.54 (d, *J* = 8.0 Hz, 1H), 7.48 (t, *J* = 7.6 Hz, 1H), 7.41 (dd, *J* = 11.2, 4.1 Hz, 1H), 7.33 (dd, *J* = 17.4, 7.6 Hz, 2H).

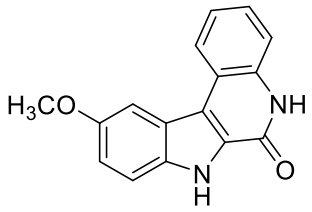
^{13}C NMR (101 MHz, DMSO-*d6*) δ 156.24, 139.35, 135.45, 128.11, 126.41, 126.15, 123.48, 122.83, 122.75, 121.17, 118.74, 118.55, 116.61, 113.56. (The substrate is a known compound. The spectroscopic data is consistent with that previously reported[16])

11-methoxy-5,7-dihydro-6*H*-indolo[2,3-*c*]quinolin-6-one (3b)



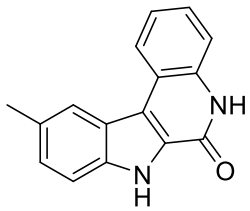
Physical State: White solid.
Yield: 17.2 mg, 33%.
Melting Point: 298.8-299.1 °C.
^{1}H NMR (400 MHz, DMSO-*d6*) δ 12.40 (s, 1H), 11.85 (s, 1H), 9.20 (d, *J* = 8.0 Hz, 1H), 7.48 (d, *J* = 8.0 Hz, 1H), 7.41 – 7.34 (m, 2H), 7.31 – 7.21 (m, 2H), 6.79 (d, *J* = 7.8 Hz, 1H), 4.08 (s, 3H).
^{13}C NMR (101 MHz, DMSO-*d6*) δ 155.88, 155.06, 141.26, 135.57, 127.57, 127.40, 127.19, 126.29, 122.30, 119.77, 118.31, 116.50, 113.61, 106.49, 101.41, 55.89.
HRMS (ESI): calcd for $C_{16}H_{13}O_2N_2$ $[M+H]^+$ *m/z* 265.0972, found 265.0969.

10-methoxy-5,7-dihydro-6*H*-indolo[2,3-*c*]quinolin-6-one (3c)



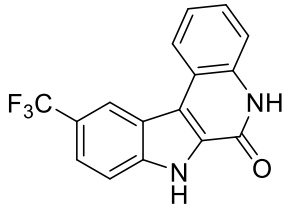
Physical State: White solid.
Yield: 14.9 mg, 28%.
Melting Point: 248.6-248.9 °C.
^{1}H NMR (400 MHz, DMSO-*d6*) δ 12.30 (s, 1H), 11.88 (s, 1H), 8.48 (d, *J* = 7.6 Hz, 1H), 7.87 (d, *J* = 1.9 Hz, 1H), 7.59 (d, *J* = 8.9 Hz, 1H), 7.54 (d, *J* = 7.6 Hz, 1H), 7.40 (dt, *J* = 14.7, 7.1 Hz, 2H), 7.17 (dd, *J* = 8.9, 2.2 Hz, 1H), 3.96 (s, 3H).
^{13}C NMR (101 MHz, DMSO-*d6*) δ 156.23, 154.85, 135.22, 134.45, 128.44, 126.15, 123.53, 122.88, 122.78, 118.67, 118.29, 117.03, 116.50, 114.39, 103.68, 56.16. (The substrate is a known compound. The spectroscopic data is consistent with that previously reported[16])

10-methyl-5,7-dihydro-6*H*-indolo[2,3-*c*]quinolin-6-one (3d)



Physical State: White solid.
Yield: 49.1 mg, 97%.
Melting Point: 306.8-307.1 °C.
^{1}H NMR (400 MHz, DMSO-*d6*) δ 12.26 (s, 1H), 11.87 (s, 1H), 8.45 (d, *J* = 7.6 Hz, 1H), 8.28 (s, 1H), 7.53 (t, *J* = 7.6 Hz, 2H), 7.40 (t, *J* = 7.4 Hz, 1H), 7.32 (dd, *J* = 20.0, 7.9 Hz, 2H), 3.43 (s, 3H).
^{13}C NMR (101 MHz, DMSO-*d6*) δ 156.24, 137.69, 135.36, 130.06, 128.11, 127.88, 126.23, 123.48, 122.94, 122.75, 122.18, 118.68, 118.25, 116.55, 113.21, 21.74. (The substrate is a known compound. The spectroscopic data is consistent with that previously reported[17])

10-(trifluoromethyl)-5,7-dihydro-6*H*-indolo[2,3-*c*]quinolin-6-one (3e)

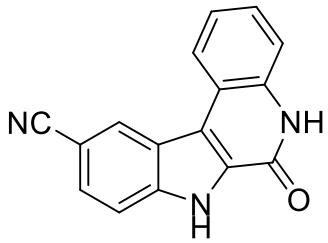


Physical State: White solid.
Yield: 53.6 mg, 88%.
Melting Point: 280.1-280.4 °C.
^{1}H NMR (400 MHz, DMSO-*d6*) δ 12.87 (s, 1H), 12.07 (s, 1H), 8.82 (s, 1H), 8.54 (d, *J* = 7.8 Hz, 1H), 7.87 (d, *J* = 8.7 Hz, 1H), 7.80 (d, *J* = 8.7 Hz, 1H), 7.57 (d, *J* = 8.0 Hz, 1H), 7.49 (t, *J* = 7.6 Hz, 1H), 7.41 (t, *J* = 7.5 Hz, 1H).
^{19}F NMR (377 MHz, DMSO-*d6*) δ -58.48.
^{13}C NMR (101 MHz, DMSO-*d6*) δ 155.97, 140.75, 135.58, 129.69, 127.05, 125.67 (q, *J* = 271.9 Hz), 123.78, 123.13, 122.44 (q, *J* = 3.1 Hz), 121.99, 121.89 (q, *J* = 31.4 Hz), 120.41 (q, *J* = 3.8 Hz),

119.26, 117.78, 116.71, 114.47.

HRMS (ESI): calcd for $C_{16}H_90F_3N_2$ $[M+H]^+$ *m/z* 303.0740, found 303.0749.

6-oxo-6,7-dihydro-5*H*-indolo[2,3-*c*]quinoline-10-carbonitrile (3f)



Physical State: Yellow solid.

Yield: 40.4 mg, 78%.

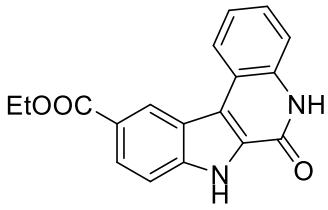
Melting Point: >300°C.

^{1}H NMR (400 MHz, DMSO-*d6*) δ 12.91 (s, 1H), 12.04 (s, 1H), 9.13 (s, 1H), 8.59 (d, J = 7.9 Hz, 1H), 7.84 – 7.75 (m, 2H), 7.54 (d, J = 9.0 Hz, 1H), 7.46 (t, J = 7.2 Hz, 1H), 7.36 (t, J = 7.5 Hz, 1H).

^{13}C NMR (101 MHz, DMSO-*d6*) δ 155.85, 140.83, 135.76, 129.75, 128.85, 128.53, 127.22, 124.07, 123.06, 122.49, 120.58, 119.23, 117.55, 116.67, 114.72, 103.37.

HRMS (ESI): calcd for $C_{16}H_{10}N_3O$ $[M+H]^+$ *m/z* 260.0818, found 260.0831.

ethyl 6-oxo-6,7-dihydro-5*H*-indolo[2,3-*c*]quinoline-10-carboxylate (3g)



Physical State: Yellow solid.

Yield: 46.6 mg, 90%.

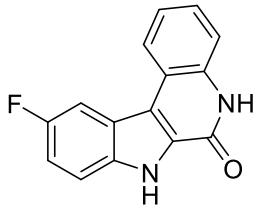
Melting Point: >300 °C.

^{1}H NMR (400 MHz, DMSO-*d6*) δ 12.83 (s, 1H), 12.05 (s, 1H), 9.02 (d, J = 1.6 Hz, 1H), 8.38 (d, J = 9.3 Hz, 1H), 8.08 (dd, J = 8.7, 1.5 Hz, 1H), 7.72 (d, J = 8.7 Hz, 1H), 7.56 (d, J = 6.6 Hz, 1H), 7.508 – 7.382 (m, 2H), 4.41 (q, J = 7.1 Hz, 2H), 1.41 (t, J = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, DMSO-*d6*) δ 166.71, 155.95, 141.71, 135.67, 129.50, 127.01, 126.65, 124.85, 123.26, 123.12, 122.80, 122.35, 119.48, 117.96, 116.79, 113.58, 60.55, 15.80.

HRMS (ESI): calcd for $C_{18}H_{15}N_2O_3$ $[M+H]^+$ *m/z* 307.1077, found 307.1089.

10-fluoro-5,7-dihydro-6*H*-indolo[2,3-*c*]quinolin-6-one (3h)



Physical State: White solid.

Yield: 44.0 mg, 87%.

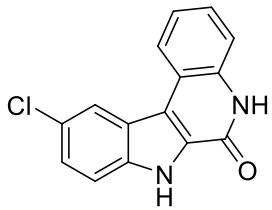
Melting Point: 332.0-332.3 °C.

^{1}H NMR (400 MHz, DMSO-*d6*) δ 12.48 (s, 1H), 11.91 (s, 1H), 8.44 (d, *J* = 7.8 Hz, 1H), 8.37 – 8.29 (m, 1H), 7.67 (dd, *J* = 8.9, 4.7 Hz, 1H), 7.53 (d, *J* = 8.0 Hz, 1H), 7.43 (t, *J* = 7.5 Hz, 1H), 7.37 (dt, *J* = 15.9, 4.7 Hz, 2H).

^{19}F NMR (377 MHz, DMSO-*d6*) δ -122.03.

^{13}C NMR (101 MHz, DMSO-*d6*) δ 157.98 (d, *J* = 234.3 Hz), 156.09, 135.99, 135.31, 129.51, 126.51, 123.52, 122.90, 122.56 (d, *J* = 10.3 Hz), 118.68 (d, *J* = 5.0 Hz), 118.18, 116.56, 114.85 (d, *J* = 15.6 Hz), 114.67, 107.62 (d, *J* = 24.0 Hz). (The substrate is a known compound. The spectroscopic data is consistent with that previously reported[17])

10-chloro-5,7-dihydro-6*H*-indolo[2,3-*c*]quinolin-6-one (3i)



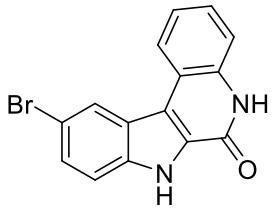
Physical State: White solid.

Yield: 39.5 mg, 73%.

^{1}H NMR (400 MHz, DMSO-*d6*) δ 12.57 (s, 1H), 11.94 (s, 1H), 8.55 (s, 1H), 8.47 (d, *J* = 7.8 Hz, 1H), 7.67 (d, *J* = 8.8 Hz, 1H), 7.56 – 7.47 (m, 2H), 7.44 (t, *J* = 7.5 Hz, 1H), 7.35 (t, *J* = 7.4 Hz, 1H).

^{13}C NMR (101 MHz, DMSO-*d6*) δ 156.03, 137.73, 135.44, 129.21, 126.69, 126.30, 125.70, 123.69, 123.58, 122.97, 121.93, 118.22, 118.02, 116.60, 115.08. (The substrate is a known compound. The spectroscopic data is consistent with that previously reported[18])

10-bromo-5,7-dihydro-6*H*-indolo[2,3-*c*]quinolin-6-one (3j)



Physical State: Yellow solid.

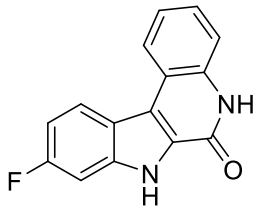
Yield: 52.1 mg, 83%.

Melting Point: 310.3-310.6 °C.

^{1}H NMR (400 MHz, DMSO-*d6*) δ 12.57 (s, 1H), 11.93 (s, 1H), 8.68 (s, 1H), 8.46 (d, *J* = 7.8 Hz, 1H), 7.61 (s, 2H), 7.52 (d, *J* = 8.0 Hz, 1H), 7.43 (t, *J* = 7.5 Hz, 1H), 7.35 (t, *J* = 7.5 Hz, 1H).

^{13}C NMR (101 MHz, DMSO-*d6*) δ 155.99, 137.96, 135.45, 129.02, 128.84, 126.72, 124.89, 124.28, 123.72, 122.99, 118.08, 118.00, 116.60, 115.50, 113.59. (The substrate is a known compound. The spectroscopic data is consistent with that previously reported[19])

9-fluoro-5,7-dihydro-6*H*-indolo[2,3-*c*]quinolin-6-one (3k)



Physical State: White solid.

Yield: 43.9 mg, 86%.

Melting Point: 292.9-293.1 °C.

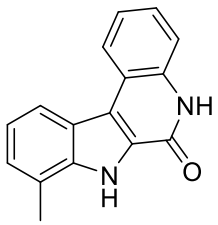
^{1}H NMR (400 MHz, DMSO-*d6*) δ 12.47 (s, 1H), 11.91 (s, 1H), 8.53 (dd, *J* = 8.9, 5.4 Hz, 1H), 8.44 (d, *J* = 7.7 Hz, 1H), 7.54 (d, *J* = 7.9 Hz, 1H), 7.44 (t, *J* = 7.3 Hz, 1H), 7.39 – 7.31 (m, 2H), 7.19 (td, *J* = 9.3, 2.3 Hz, 1H).

^{19}F NMR (377 MHz, DMSO-*d6*) δ -115.26.

^{13}C NMR (101 MHz, DMSO-*d6*) δ 161.43 (d, *J* = 240.6 Hz), 155.88, 139.80 (d, *J* = 12.9 Hz), 135.58, 128.80 (d, *J* = 2.7 Hz), 126.73, 124.55 (d, *J* = 10.5 Hz), 123.43, 122.86, 119.66, 118.93, 118.04, 116.64, 110.02 (d, *J* = 24.7 Hz), 99.14 (d, *J* = 25.5 Hz).

HRMS (ESI): calcd for $C_{15}H_{10}OFN_2$ $[M+H]^+$ *m/z* 253.0772, found 253.0779.

8-methyl-5,7-dihydro-6*H*-indolo[2,3-*c*]quinolin-6-one (3l)



Physical State: White solid.

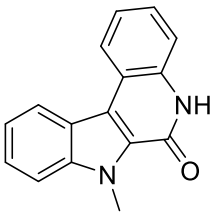
Yield: 35.8 mg, 72%.

Melting Point: 250.5-250.8 °C.

^{1}H NMR (400 MHz, DMSO-*d6*) δ 12.39 (s, 1H), 11.89 (s, 1H), 8.55 (d, *J* = 8.1 Hz, 1H), 8.27 (s, 1H), 7.68 (d, *J* = 8.2 Hz, 1H), 7.53 – 7.43 (m, 2H), 7.34 (t, *J* = 7.5 Hz, 1H), 7.25 (d, *J* = 8.2 Hz, 1H), 2.51 (s, 3H).

^{13}C NMR (101 MHz, DMSO-*d6*) δ 156.06, 139.30, 133.35, 131.86, 128.19, 127.51, 126.05, 123.20, 122.97, 122.76, 121.03, 118.57, 118.48, 116.52, 113.51, 21.26. (The substrate is a known compound. The spectroscopic data is consistent with that previously reported[17])

7-methyl-5,7-dihydro-6*H*-indolo[2,3-*c*]quinolin-6-one (3m)



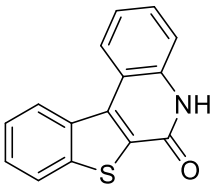
Physical State: White solid.

Yield: 34.7 mg, 69%.

^{1}H NMR (400 MHz, DMSO-*d6*) δ 11.91 (s, 1H), 8.54 (d, *J* = 8.1 Hz, 1H), 8.47 (d, *J* = 7.7 Hz, 1H), 7.77 (d, *J* = 8.4 Hz, 1H), 7.57 (t, *J* = 7.7 Hz, 1H), 7.51 (d, *J* = 8.0 Hz, 1H), 7.44 – 7.28 (m, 3H), 4.34 (s, 3H).

^{13}C NMR (101 MHz, DMSO-*d6*) δ 156.88, 140.58, 135.41, 126.57, 126.42, 123.43, 123.00, 122.86, 121.70, 121.56, 119.13, 118.30, 116.30, 111.60, 31.75. (The substrate is a a known compound. The spectroscopic data is consistent with that previously reported[20])

benzo[4,5]thieno[2,3-*c*]quinolin-6(5*H*)-one (3n)



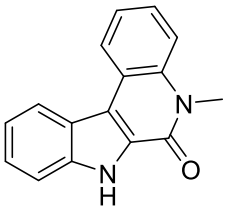
Physical State: Green solid.

Yield: 30.0 mg, 59%.

^{1}H NMR (400 MHz, DMSO-*d6*) δ 12.27 (s, 1H), 8.91 (dd, *J* = 6.1, 3.0 Hz, 1H), 8.76 (d, *J* = 8.2 Hz, 1H), 8.26 (dd, *J* = 5.8, 3.2 Hz, 1H), 7.68 (dd, *J* = 6.1, 3.1 Hz, 2H), 7.63 – 7.53 (m, 2H), 7.41 (t, *J* = 7.1 Hz, 1H).

^{13}C NMR (101 MHz, DMSO-*d6*) δ 158.37, 141.77, 138.08, 136.43, 135.95, 132.69, 129.35, 127.96, 126.41, 126.27, 124.63, 124.07, 123.23, 117.87, 117.20. (The substrate is a known compound. The spectroscopic data is consistent with that previously reported[21])

5-methyl-5,7-dihydro-6*H*-indolo[2,3-*c*]quinolin-6-one (3o)



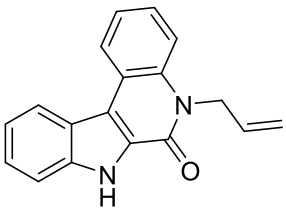
Physical State: White solid.

Yield: 43.5 mg, 87%.

^{1}H NMR (400 MHz, DMSO-*d6*) δ 12.39 (s, 1H), 8.53 (d, *J* = 7.5 Hz, 1H), 8.49 (d, *J* = 8.1 Hz, 1H), 7.66 (t, *J* = 9.1 Hz, 2H), 7.53 (t, *J* = 7.5 Hz, 1H), 7.50 – 7.40 (m, 2H), 7.32 (t, *J* = 7.5 Hz, 1H), 3.83 (s, 3H).

^{13}C NMR (101 MHz, DMSO-*d6*) δ 155.82, 139.45, 136.34, 127.50, 126.82, 126.23, 124.00, 123.13, 122.93, 122.54, 121.25, 119.40, 117.47, 116.17, 113.56, 29.75. (The substrate is a known compound. The spectroscopic data is consistent with that previously reported[22])

5-allyl-5,7-dihydro-6*H*-indolo[2,3-*c*]quinolin-6-one (3p)



Physical State: White solid.

Yield: 45.5 mg, 83%.

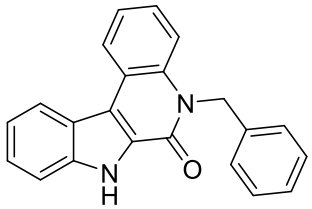
Melting Point: 233.5-233.7 °C.

^{1}H NMR (400 MHz, DMSO-*d6*) δ 12.44 (s, 1H), 8.54 (dd, *J* = 15.8, 7.8 Hz, 2H), 7.68 (d, *J* = 8.2 Hz, 1H), 7.59 (d, *J* = 8.4 Hz, 1H), 7.50 (t, *J* = 7.7 Hz, 2H), 7.43 (t, *J* = 7.4 Hz, 1H), 7.35 (t, *J* = 7.5 Hz, 1H), 6.05 (ddd, *J* = 15.0, 9.8, 4.5 Hz, 1H), 5.23 – 5.10 (m, 3H), 5.00 (d, *J* = 17.4 Hz, 1H).

^{13}C NMR (101 MHz, DMSO-*d6*) δ 155.60, 139.57, 135.41, 133.53, 127.26, 126.70, 126.32, 124.13, 123.10, 122.96, 122.52, 121.30, 119.58, 117.81, 116.67, 116.62, 113.59, 44.14.

HRMS (ESI): calcd for $C_{18}H_{14}0N_2$ $[M+H]^+$ *m/z* 275.1179, found 275.1181.

5-benzyl-5,7-dihydro-6*H*-indolo[2,3-*c*]quinolin-6-one (3q)



Physical State: Yellow solid.

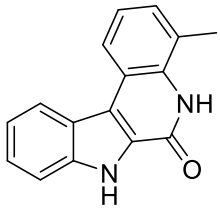
Yield: 38.9 mg, 60%.

Melting Point: 245.8-246.1 °C.

^{1}H NMR (400 MHz, DMSO-*d6*) δ 12.54 (s, 1H), 8.59 – 8.49 (m, 2H), 7.69 (d, *J* = 8.3 Hz, 1H), 7.51 (mi, 2H), 7.39 (dd, *J* = 6.1, 3.2 Hz, 2H), 7.34 (d, *J* = 8.0 Hz, 1H), 7.30 (d, *J* = 6.9 Hz, 2H), 7.24 (d, *J* = 7.2 Hz, 3H), 5.76 (s, 2H).

^{13}C NMR (101 MHz, DMSO-*d6*) δ 156.18, 139.66, 137.63, 135.41, 129.15, 127.48, 127.21, 126.87, 126.77, 126.46, 124.25, 123.25, 123.01, 122.51, 121.39, 119.75, 117.98, 116.72, 113.64, 45.17. (The substrate is a known compound. The spectroscopic data is consistent with that previously reported[22])

4-methyl-5,7-dihydro-6*H*-indolo[2,3-*c*]quinolin-6-one (3r)



Physical State: White solid.

Yield: 43.4 mg, 82%.

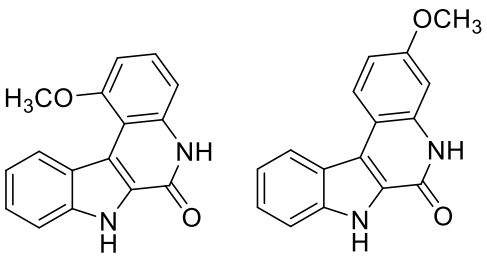
Melting Point:265.4-265.7 °C.

^{1}H NMR (400 MHz, DMSO-*d6*) δ 12.47 (s, 1H), 10.94 (s, 1H), 8.49 (d, *J* = 8.2 Hz, 1H), 8.35 (t, 1H), 7.69 (d, *J* = 8.2 Hz, 1H), 7.50 (t, *J* = 7.6 Hz, 1H), 7.33 (t, *J* = 7.5 Hz, 1H), 7.30 – 7.23 (m, 2H), 2.58 (s, 3H).

^{13}C NMR (101 MHz, DMSO-*d6*) δ 156.51, 139.51, 133.64, 128.08, 127.92, 126.19, 124.62, 122.93, 122.78, 122.66, 121.55, 121.14, 119.10, 118.61, 113.57, 18.67.

HRMS (ESI): calcd for $C_{16}H_{13}ON_2$ $[M+H]^+$ *m/z* 249.1022, found 249.1020.

3-methoxy-5,7-dihydro-6*H*-indolo[2,3-*c*]quinolin-6-one and 4-methoxy-5,7-dihydro-6*H*-indolo[2,3-*c*]quinolin-6-one (3:1) (3s+3s′)



Physical State: White solid.

Yield: 52.1 mg, 98%.

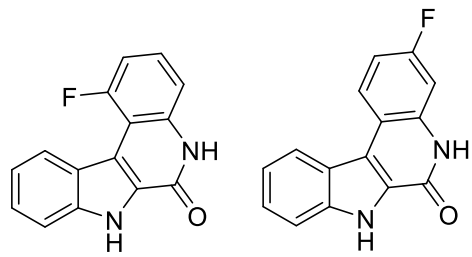
Melting Point: 269.1-269.4 °C.

^{1}H NMR (400 MHz, DMSO) δ 12.40 (s, 0.32H), 12.22 (s,1H), 11.93 (s, 0.34H), 11.76 (s, 1H), 8.69 (d, *J* = 8.5 Hz, 0.33H), 8.42 (d, *J* = 8.2 Hz, 1H), 8.34 (d, *J* = 8.8 Hz, 1H), 7.61 (t, *J* = 7.2 Hz, 1.3H), 7.45 (t, *J* = 7.6 Hz, 1H), 7.41 (t, *J* = 7.6 Hz, 0.4H), 7.34 (t, *J* = 8.1 Hz, 0.39H), 7.28 (t, *J* = 7.4 Hz, 1H), 7.22 (t, *J* = 7.3 Hz, 0.37H), 7.14 (d, *J* = 8.0 Hz, 0.34H), 7.07 (d, *J* = 2.4 Hz, 1H), 6.96 (dd, *J* = 8.7, 2.5 Hz, 1H), 6.92 (d, *J* = 7.9 Hz, 0.36H), 4.09 (s, 1H), 3.84 (s, 3H).

^{13}C NMR (101 MHz, DMSO-*d6*) δ 158.17, 156.43, 156.01, 155.58, 139.69, 139.37, 136.93, 136.85, 128.16, 127.02, 126.58, 126.14, 125.79, 124.62, 123.66, 122.74, 122.43, 120.87, 120.34, 120.20, 119.17, 118.97, 117.64, 113.44, 113.00, 112.29, 110.78, 109.83, 109.45, 104.42, 100.34, 55.68.

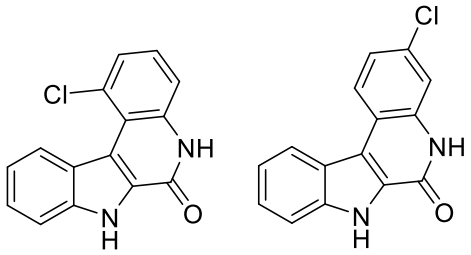
HRMS (ESI): calcd for $C_{16}H_{13}O_2N_2$ $[M+H]^+$ *m/z* 265.0972, found 265.0968.

3-fluoro-5,7-dihydro-6*H*-indolo[2,3-*c*]quinolin-6-one and 4-fluoro-5,7-dihydro-6*H*-indolo[2,3-*c*]quinolin-6-one (1:1) (3t+3t′)



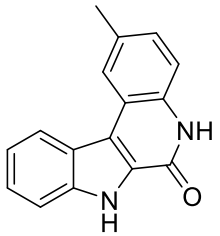
Physical State: White solid.
Yield: 42.4 mg, 83%.
Melting Point: 335.2-335.5 °C.
^{1}H NMR (400 MHz, DMSO-*d6*) δ 12.68 (s, 1H), 12.44 (s, 1H), 12.24 (s, 1H), 12.09 (s, 1H), 8.54 – 8.39 (m, 3H), 7.70 (dd, *J* = 8.2, 4.2 Hz, 2H), 7.50 (dd, *J* = 14.4, 7.0 Hz, 2H), 7.46 – 7.42 (m, 2H), 7.41 – 7.28 (m, 3H), 7.25 – 7.16 (m, 2H).
^{19}F NMR (377 MHz, DMSO-*d6*) δ -110.35, -115.04.
^{13}C NMR (101 MHz, DMSO-*d6*) δ 160.63 (d, *J* = 241.7 Hz), 157.94 (d, *J* = 244.2 Hz), 156.33, 155.94, 139.58, 139.34, 137.35 (d, *J* = 9.5 Hz), 136.79 (d, *J* = 11.4 Hz), 128.49, 127.35, 126.99 (d, *J* = 10.1 Hz), 126.31, 126.26, 125.30 (d, *J* = 9.7 Hz), 124.54, 124.27, 122.62, 122.42 (d, *J* = 4.0 Hz), 121.17 (d, *J* = 7.0 Hz), 118.41, 115.27 (d, *J* = 25.2 Hz), 113.59, 113.48, 113.07, 113.05, 110.36 (d, *J* = 22.5 Hz), 108.81 (d, *J* = 22.6 Hz), 107.55 (d, *J* = 22.3 Hz).
HRMS (ESI): calcd for $C_{15}H_{10}OFN_2$ $[M+H]^+$ *m/z* 253.0772, found 253.0774.

3-chloro-5,7-dihydro-6*H*-indolo[2,3-*c*]quinolin-6-one and 4-chloro-5,7-dihydro-6*H*-indolo[2,3-*c*]quinolin-6-one (1:1) (3u+3u′)



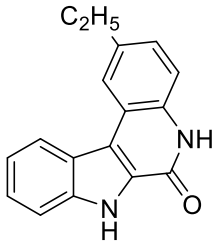
Physical State: White solid.
Yield: 29.4 mg, 54%.
Melting Point: 294.5-294.8 °C.
^{1}H NMR (400 MHz, DMSO-*d6*) δ 12.77 (s, 1H), 12.52 (s, 1H), 12.21 (s, 1H), 12.04 (s, 1H), 8.87 (d, *J* = 7.9 Hz, 1H), 8.46 (d, *J* = 7.6 Hz, 2H), 7.71 (s, 2H), 7.63 – 7.22 (m, 9H).
^{13}C NMR (101 MHz, DMSO-*d6*) δ 156.15, 155.68, 139.72, 139.35, 137.46, 136.46, 130.47, 130.11, 127.98, 127.19, 126.96, 126.38, 125.77, 125.06, 124.98, 122.67, 122.49, 121.35, 120.42, 118.13, 117.70, 117.36, 116.49, 116.12, 115.83, 113.64, 113.41.
HRMS (ESI): calcd for $C_{15}H_9OClN_2$ $[M+H]^+$ *m/z* 269.0476, found 269.0481.

2-methyl-5,7-dihydro-6*H*-indolo[2,3-*c*]quinolin-6-one (3v)



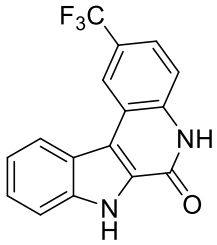
Physical State: White solid.
Yield: 40.4 mg, 81%.
^{1}H NMR (400 MHz, DMSO-*d6*) δ 12.34 (s, 1H), 11.81 (s, 1H), 8.53 (d, *J* = 8.1 Hz, 1H), 8.25 (s, 1H), 7.65 (d, *J* = 8.2 Hz, 1H), 7.47 (t, *J* = 7.6 Hz, 1H), 7.42 (d, *J* = 8.2 Hz, 1H), 7.32 (t, *J* = 7.5 Hz, 1H), 7.23 (d, *J* = 8.2 Hz, 1H), 2.50 (s, 3H).
^{13}C NMR (101 MHz, DMSO-*d6*) δ 156.07, 139.30, 133.33, 131.89, 128.18, 127.54, 126.08, 123.22, 122.98, 122.76, 121.05, 118.58, 118.47, 116.48, 113.49, 21.26. (The substrate is a known compound. The spectroscopic data is consistent with that previously reported[10])

2-ethyl-5,7-dihydro-6*H*-indolo[2,3-*c*]quinolin-6-one (3w)



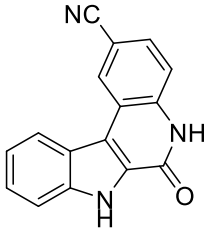
Physical State: White solid.
Yield: 43.1 mg, 82%.
Melting Point: 268.2-268.4 °C.
^{1}H NMR (400 MHz, DMSO-*d6*) δ 12.42 (s, 1H), 11.89 (s, 1H), 8.57 (d, *J* = 8.1 Hz, 1H), 8.28 (s, 1H), 7.70 (d, *J* = 8.2 Hz, 1H), 7.57 – 7.47 (m, 2H), 7.37 (t, *J* = 7.5 Hz, 1H), 7.30 (dd, *J* = 8.3, 1.4 Hz, 1H), 2.83 (q, *J* = 7.5 Hz, 2H), 1.32 (t, *J* = 7.6 Hz, 3H).
^{13}C NMR (101 MHz, DMSO-*d6*) δ 156.13, 139.32, 138.42, 133.54, 128.19, 126.37, 126.08, 123.00, 122.78, 122.07, 121.07, 118.69, 118.53, 116.63, 113.50, 28.42, 16.66.
HRMS (ESI): calcd for $C_{17}H_{15}ON_2$ $[M+H]^+$ *m/z* 263.1179, found 263.1177.

2-(trifluoromethyl)-5,7-dihydro-6*H*-indolo[2,3-*c*]quinolin-6-one (3x)



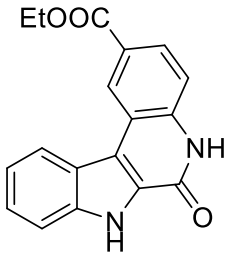
Physical State: Yellow solid.
Yield: 51.7 mg, 85%.
Melting Point: 287.8-290.0 °C.
^{1}H NMR (400 MHz, DMSO-*d6*) δ 12.63 (s, 1H), 12.30 (s, 1H), 8.61 (s, 1H), 8.46 (d, *J* = 8.1 Hz, 1H), 7.83 – 7.67 (m, 3H), 7.54 (t, *J* = 7.6 Hz, 1H), 7.40 (t, *J* = 7.5 Hz, 1H).
^{19}F NMR (377 MHz, DMSO-*d6*) δ -59.63.
^{13}C NMR (101 MHz, DMSO-*d6*) δ 156.26, 139.33, 137.96, 128.60, 126.51, 125.09 (q, *J* = 271.7 Hz), 123.18 (q, *J* = 32.0 Hz), 122.75 (q, *J* = 3.3 Hz), 122.54, 122.37, 121.68, 120.00 (q, *J* = 3.2 Hz), 118.38, 117.72, 117.39, 113.76.
HRMS (ESI): calcd for $C_{16}H_9OF_3N_2$ $[M+H]^+$ *m/z* 303.0740, found 303.0749.

6-oxo-6,7-dihydro-5*H*-indolo[2,3-*c*]quinoline-3-carbonitrile (3y)



Physical State: Red solid.
Yield: 44.5 mg, 86%.
Melting Point: 247.2-253.6 °C.
^{1}H NMR (400 MHz, DMSO-*d6*) δ 12.58 (s, 1H), 12.27 (s, 1H), 8.87 (d, J = 1.8 Hz, 1H), 8.65 (d, J = 8.2 Hz, 1H), 7.80 (dd, J = 8.5, 1.8 Hz, 1H), 7.65 (dd, J = 16.7, 8.4 Hz, 2H), 7.51 (t, J = 7.7 Hz, 1H), 7.35 (t, J = 7.0 Hz, 1H).
^{13}C NMR (101 MHz, DMSO-*d6*) δ 156.18, 139.33, 138.38, 129.50, 128.47, 127.84, 126.61, 123.11, 122.38, 121.61, 119.83, 118.75, 117.52, 117.48, 113.61.
HRMS (ESI): calcd for $C_{16}H_{10}N_3O$ $[M+H]^+$ *m/z* 260.0818, found 260.0822.

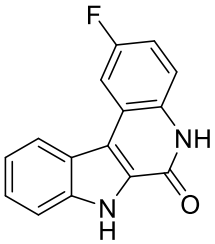
ethyl 6-oxo-6,7-dihydro-5*H*-indolo[2,3-*c*]quinoline-2-carboxylate (3z)



Physical State: Red solid.
Yield: 43.0 mg, 83%.
Melting Point: 204.2-208.5 °C.
^{1}H NMR (400 MHz, DMSO-*d6*) δ 12.58 (s, 1H), 12.26 (s, 1H), 8.90 (s, 1H), 8.31 (d, J = 8.1 Hz, 1H), 7.98 (s, 1H), 7.68 (d, J = 8.3 Hz, 1H), 7.58 (d, J = 8.6 Hz, 1H), 7.52 (t, J = 7.4 Hz, 1H), 7.40 (t, J = 7.5 Hz ,1H), 4.39 (q, J = 7.1 Hz, 2H), 1.39 (t, J = 7.1 Hz, 3H).
^{13}C NMR (101 MHz, DMSO-*d6*) δ 166.08, 156.32, 139.37, 138.39, 128.27, 126.96, 126.51, 124.46,

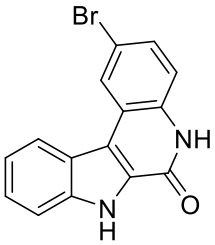
123.99, 122.43, 122.12, 121.70, 118.18, 118.04, 116.77, 113.87, 61.22, 14.40.
HRMS (ESI): calcd for $C_{18}H_{15}N_2O_3$ $[M+H]^+$ *m/z* 307.1077, found 307.1078.

2-fluoro-5,7-dihydro-6*H*-indolo[2,3-*c*]quinolin-6-one (3aa)



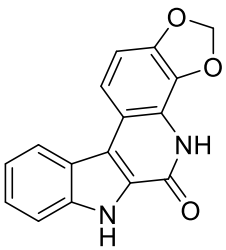
Physical State: Red solid.
Yield: 38.4 mg, 75%.
^{1}H NMR (400 MHz, DMSO-*d6*) δ 12.49 (s, 1H), 11.97 (s, 1H), 8.52 (d, *J* = 8.1 Hz, 1H), 8.20 (dd, *J* = 9.8, 2.2 Hz, 1H), 7.66 (d, *J* = 8.3 Hz, 1H), 7.58 – 7.47 (m, 2H), 7.37 – 7.25 (m, 2H).
^{19}F NMR (377 MHz, DMSO-*d6*) δ -119.97.
^{13}C NMR (101 MHz, DMSO-*d6*) δ 158.28 (d, *J* = 237.7 Hz), 155.85, 139.23, 132.02, 128.62, 126.29, 122.75, 122.56, 121.39, 119.29 (d, *J* = 9.4 Hz), 118.12 (d, *J* = 8.9 Hz), 117.98 (d, *J* = 3.0 Hz), 113.96 (d, *J* = 24.0 Hz), 113.55 (s), 108.83 (d, *J* = 23.8 Hz).
HRMS (ESI): calcd for $C_{15}H_{10}OFN_2$ $[M+H]^+$ *m/z* 253.0772, found 253.0771.

2-bromo-5,7-dihydro-6*H*-indolo[2,3-*c*]quinolin-6-one (3ab)



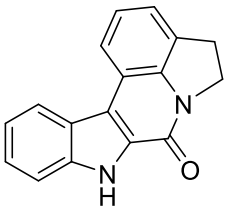
Physical State: Yellow solid.
Yield: 59.7 mg, 95%.
Melting Point: 298.1-298.4 °C.
^{1}H NMR (400 MHz, DMSO-*d6*) δ 12.56 (s, 1H), 12.10 (s, 1H), 8.49 (dd, *J* = 13.0, 5.0 Hz, 2H), 7.70 (d, *J* = 8.3 Hz, 1H), 7.59 (dd, *J* = 8.7, 1.9 Hz, 1H), 7.55 – 7.48 (m, 2H), 7.36 (t, *J* = 7.5 Hz, 1H).
^{13}C NMR (101 MHz, DMSO-*d6*) δ 155.96, 139.28, 134.50, 128.98, 128.55, 126.35, 125.14, 122.67, 122.43, 121.50, 120.34, 118.65, 117.35, 114.87, 113.65.
HRMS (ESI): calcd for $C_{15}H_{10}OBrN_2$ $[M+H]^+$ *m/z* 312.9971, found 312.9963.

4,6-dihydro-5*H*-[1,3]dioxolo[4,5-*h*]indolo[2,3-*c*]quinolin-5-one (3ac)



Physical State: Red solid.
Yield: 39.5 mg, 71%.
Melting Point: >300 °C.
^{1}H NMR (400 MHz, DMSO-*d6*) δ 12.23 (s, 1H), 11.81 (s, 1H), 8.48 (d, *J* = 8.1 Hz, 1H), 7.93 (s, 1H), 7.62 (d, *J* = 8.2 Hz, 1H), 7.46 (t, *J* = 7.5 Hz, 1H), 7.28 (t, *J* = 7.4 Hz, 1H), 7.09 (s, 1H), 6.13 (s, 2H).
^{13}C NMR (101 MHz, DMSO-*d6*) δ 155.70, 146.72, 144.14, 139.32, 130.96, 126.95, 126.13, 122.85, 122.42, 120.80, 119.41, 113.32, 112.15, 102.16, 101.83, 97.13.
HRMS (ESI): calcd for $C_{16}H_{11}O_3N_2$ $[M+H]^+$ *m/z* 279.0764, found 279.0768.

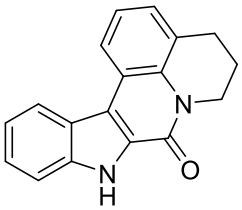
4,5-dihydroindolo[2,3-*c*]pyrrolo[3,2,1-*ij*]quinolin-7(8*H*)-one (3ad)



Physical State: White solid.
Yield: 14.9 mg, 28%.
^{1}H NMR (400 MHz, DMSO-*d6*) δ 12.40 (s, 1H), 8.42 (d, *J* = 8.0 Hz, 1H), 8.15 (dd, *J* = 7.9, 5.7 Hz, 1H), 7.64 (d, *J* = 8.3 Hz, 1H), 7.47 (t, *J* = 7.5 Hz, 1H), 7.37 – 7.27 (m, 3H), 4.47 (t, *J* = 8.1 Hz, 2H), 3.49 (t, *J* = 8.0 Hz, 2H).
^{13}C NMR (101 MHz, DMSO-*d6*) δ 154.33, 139.28, 138.74, 131.48, 129.47,

126.00, 123.93, 122.73, 122.58, 121.72, 121.10, 120.08, 118.07, 115.87, 113.51, 46.53, 28.04. (The substrate is a known compound. The spectroscopic data is consistent with that previously reported[10])

5,6-dihydro-4*H*-indolo[2,3-*c*]pyrido[3,2,1-*ij*]quinolin-8(9*H*)-one (3ae)



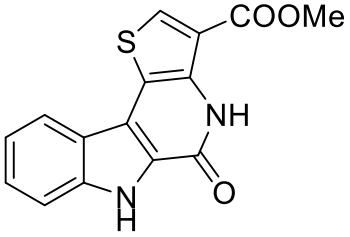
Physical State: White solid.

Yield: 43.3 mg, 78%.

^{1}H NMR (400 MHz, DMSO-*d6*) δ 12.36 (s, 1H), 8.47 (d, *J* = 8.1 Hz, 1H), 8.35 (d, *J* = 7.0 Hz, 1H), 7.65 (d, *J* = 8.2 Hz, 1H), 7.48 (t, *J* = 7.6 Hz, 1H), 7.36 – 7.22 (m, 3H), 4.30 (t, 2H), 3.03 (t, *J* = 5.9 Hz, 2H), 2.16 – 2.04 (m, 2H).

^{13}C NMR (101 MHz, DMSO-*d6*) δ 155.30, 139.46, 132.82, 127.39, 126.56, 126.25, 126.12, 122.95, 122.64, 121.95, 121.14, 119.29, 117.55, 113.51, 42.48, 28.24, 20.99. (The substrate is a known compound. The spectroscopic data is consistent with that previously reported[10])

methyl 5-oxo-5,6-dihydro-4*H*-thieno[2',3':5,6]pyrido[3,4-b]indole-3-carboxylate (3af)



Physical State: Yellow solid.

Yield: 17.9mg, 30%.

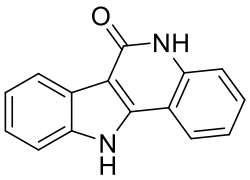
Melting Point: 181.2-187.5 °C

^{1}H NMR (400 MHz, DMSO-*d6*) δ 12.52 (s, 1H), 10.62 (s, 1H), 8.59 (s, 1H), 8.03 (d, J = 7.9 Hz, 1H), 7.63 (d, J = 8.3 Hz, 1H), 7.52 (t, J = 7.6 Hz, 1H), 7.35 (t, J = 7.5 Hz, 1H), 3.95 (s, 3H).

^{13}C NMR (101 MHz, DMSO-*d6*) δ 163.17, 154.89, 139.35, 133.69, 133.17, 127.30, 126.23, 121.57, 121.28, 120.72, 120.03, 118.31, 114.42, 113.67, 52.83.

HRMS (ESI): calcd for $C_{15}H_{11}N_2O_3S$ $[M+H]^+$ *m/z* 299.0485, found 299.0492.

5,11-dihydro-6*H*-indolo[3,2-*c*]quinolin-6-one (3ag)



Physical State: White solid.

Yield: 40.8 mg, 86%.

^{1}H NMR (400 MHz, DMSO-*d6*) δ 12.41 (s, 1H), 11.93 (s, 1H), 8.48 (dd, *J* = 11.8, 8.0 Hz, 2H), 7.68 (d, *J* = 8.2 Hz, 1H), 7.55 (d, *J* = 7.6 Hz, 1H), 7.50 (t, *J* = 7.5 Hz, 1H), 7.43 (t, *J* = 7.1 Hz, 1H), 7.35 (dd, *J* = 17.0, 8.1 Hz, 2H).

^{13}C NMR (101 MHz, DMSO-*d6*) δ 156.21, 139.33, 135.44, 128.10, 126.41, 126.15, 123.48, 122.83, 122.73, 121.17, 118.71, 118.53, 116.60, 113.55. (The substrate is a known compound. The spectroscopic data is consistent with that previously reported[23])

5. Preliminary mechanistic studies

5.1 UV-Vis spectroscopy of 4CzBnBN

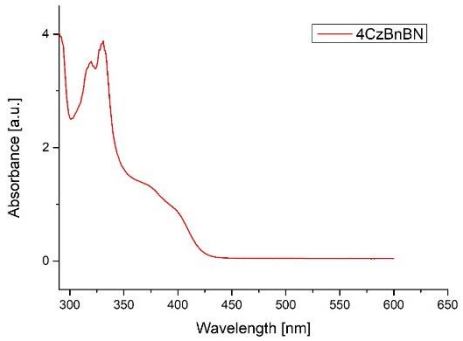


Figure S2. UV-Vis spectroscopy of 4CzBnBN in MeCN (0.02 mM)

UV-vis absorption spectra were recorded using a Shimadzu UV-3600 Plus atomic absorption spectrophotometer. Spectra were recorded at a concentration of 20 μM in MeCN.

5.2 Stern-Volmer quenching studies

Stern-Volmer experiments were conducted on a PerkinElmer LS55 Fluorescence Spectrophotometer. Before each set of experiments, each component was prepared in DCM: MeOH (9:1) and DCE: DMSO (9:1). The solutions were irradiated at 360 nm and the luminescence was measured at 370 nm. Linear regression of I_0/I against concentration was performed in Origin.

Species	Solvent	Concentration (mM)
4CzBnBN	DCM/MeOH	0.02
1a	DCM/MeOH	Varied

Substrate (mM)	0.000	0.005	0.0249	0.0498	0.099	0.196
I_0/I in Solvent (DCM/MeOH)	1.000	1.034	1.055	1.089	1.145	1.239

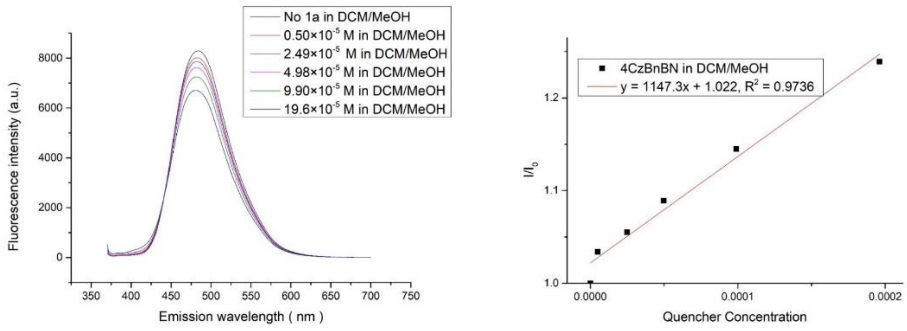


Figure S3. Stern-Volmer quenching experiments of **4CzBnBN** with **1a** in DCM /MeOH (0.02 mM, λ_{ex} = 360 nm, λ_{em} = 370 nm)

Species	Solvent	Concentration (mM)
4CzBnBN	DCE/DMSO	0.02

	2a		DCE/DMSO		Varied	
Substrate (mM)	0.000	0.0244	0.0476	0.0698	0.091	0.111
I_0/I in Solvent (**DCE/DMSO**)	1.000	1.108	1.207	1.300	1.384	1.461

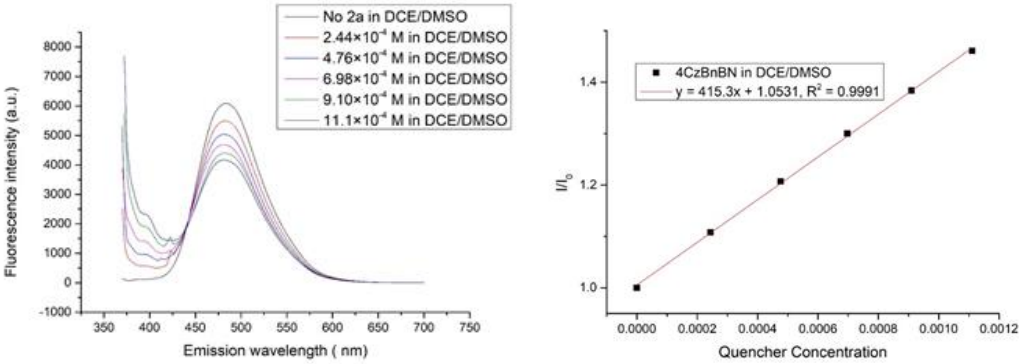


Figure S4. Stern-Volmer quenching experiments of **4CzBnBN** with **2a** in DCM /DMSO (0.02 mM, λ_{ex} = 360 nm, λ_{em} = 370 nm).

5.3 Cyclic voltammetry test

Cyclic voltammetry test was performed in a three-electrode cell under argon at room temperature. All cyclic voltammograms were measured using Ag/Ag^+ (0.01 M $AgNO_3$ in CH_3CN) reference electrode, a platinum (Pt) wire counter electrode and a glassy carbon working electrode. The conditions of the experiments were as follows: testing compounds are in solution of 0.1 M tetrabutylammonium tetrafluoroborate ($^nBu_4NBF_4$) in DCM/MeOH and DCE/DMSO at a scan rate of 50 mV/s; Prior to each measurement, solutions were purged with argon (Ar) for 10 minutes to ensure the oxygen-free conditions.

Measuring the Fc/Fc^+ redox couple afforded $E_{1/2}$ = +0.154 V vs Ag/Ag^+ (DCM/MeOH) and $E_{1/2}$ = +0.17 V vs Ag/Ag^+ (DCE/DMSO) under our experimental conditions. The obtained value was referenced to Ag/Ag^+ and converted to SCE by subtracting 0.266 V and 0.25 V, providing a value of +0.42 V for the Fc/Fc^+ couple.[21]

The oxidation half-peak potential of **1a** in DCM/MeOH was measured as +1.145 V (vs Ag/Ag^+), and calculated to +1.411 V (vs SCE); The oxidation half-peak potential of **1a** in DCE/DMSO was measured as +1.109 V (vs Ag/Ag^+), and calculated to +1.359 V (vs SCE); The oxidation half-peak potential of **2a** in DCE/DMSO was measured as +0.68 V, +1.014 V (vs Ag/Ag^+), and calculated to +0.93 V , +1.354 V (vs SCE).

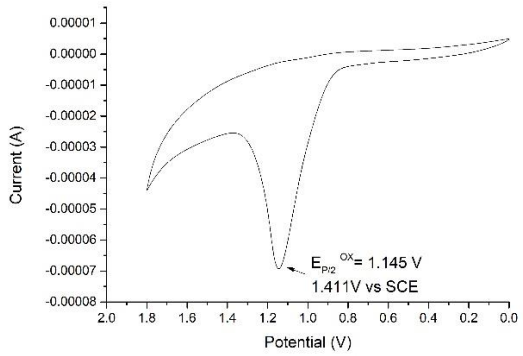


Figure S5. Cyclic voltammetry of **1a** (0.005 M) in DCM/MeOH (vs Ag/Ag^+) with $^nBu_4NPF_6$ (0.1 M) under argon at a glassy carbon electrode at a scan rate of 50 mV/s.

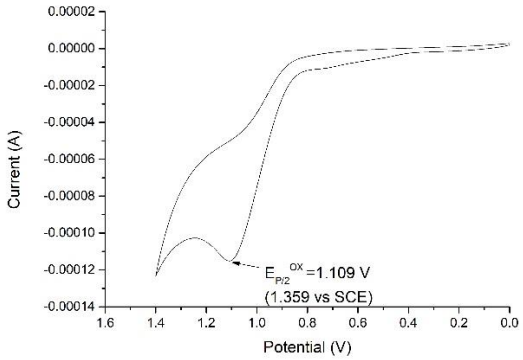


Figure S6. Cyclic voltammetry of **1a** (0.005 M) in DCE/DMSO (vs Ag/Ag^+) with $^nBu_4NPF_6$ (0.1 M) under argon at a glassy carbon electrode at a scan rate of 50 mV/s.

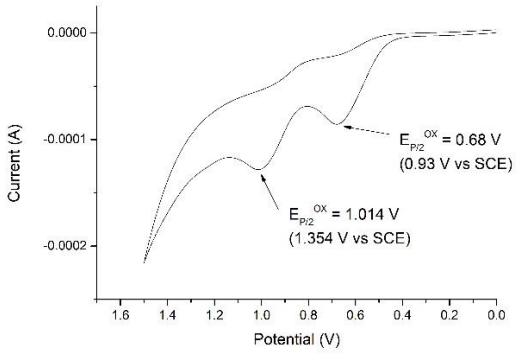
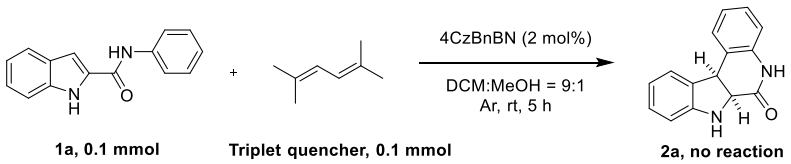


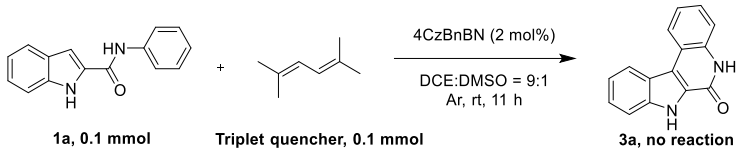
Figure S7. Cyclic voltammetry of **2a** (0.005 M) in DCE/DMSO (vs Ag/Ag^+) with $^nBu_4NPF_6$ (0.1 M) under argon at a glassy carbon electrode at a scan rate of 50 mV/s.

5.4 Control experiments with triplet quencher

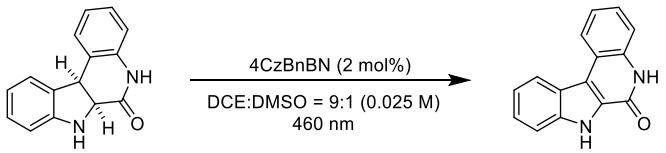


An oven-dried Schlenk tube (10 mL) containing a stirring bar was charged with the substrate

1a (19.9 mg, 0.1 mmol) and 4CzBnBN (1.6 mg, 2 mol%). The Schlenk tube was then connected to a vacuum line where it was evacuated and back-filled with argon for 3 times. Then, Ultra-dry solvent (DCM:MeOH) and 2,5-dimethylhexa-2,4-diene (known as a triplet quencher[21], 14.3 μL, 0.1 mmol) were added to the reaction in sequence under argon flow. Then, the reaction was degassed by three consecutive freeze-pump-thaw cycles. After backfilling with argon, the reaction mixture in sealed tube was placed at a distance of 2 ~ 3 cm from a 30 W blue LED and stirred at room temperature for 5 h. Then, the mixture was concentrated in vacuo. The yield of the product was determined by ^{1}H-NMR spectroscopy using dibromomethane (17.8 mg, 0.1 mmol) as internal standard. The reaction (condition A) was completely inhibited in the presence of 1.0 equivalent of 2,5-dimethylhexa-2,4-diene.



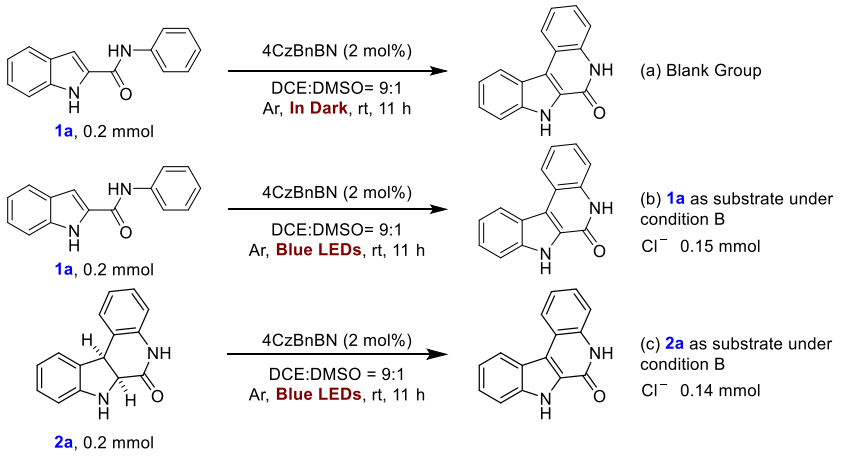
An oven-dried Schlenk tube (10 mL) containing a stirring bar was charged with the indole derivative **1a** (19.9 mg, 0.1 mmol) and 4CzBnBN (1.6 mg, 2 mol%). The Schlenk tube was then connected to a vacuum line where it was evacuated and back-filled with argon for 3 times. Then Ultra-dry solvent (DCE:DMSO) and 2,5-dimethylhexa-2,4-diene (known as a triplet quencher[21], 14.3 μL, 0.1 mmol), were added to the reaction in sequence under argon flow. Then, the reaction was degassed by three consecutive freeze-pump-thaw cycles. After backfilling with argon, the reaction mixture in sealed tube was placed at a distance of 2 ~ 3 cm from a 30 W blue LED and stirred at room temperature for 11 h. Then, the reaction mixture was transferred to a separating funnel, diluted with water and extracted three times with EtOAc. The combined organic layers were washed with brine, dried over anhydrous sodium sulfate, filtered and concentrated to give the crude product. Then, the yield of the product was determined by ^{1}H-NMR spectroscopy using dibromomethane (17.8 mg, 0.1 mmol) as internal standard. The reaction (condition B) was completely inhibited in the presence of 1.0 equivalent of 2,5-dimethylhexa-2,4-diene.



An oven-dried Schlenk tube (10 mL) containing a stirring bar was charged with the indole derivative **2a** (19.9 mg, 0.1 mmol) and 4CzBnBN (1.6 mg, 2 mol%). The Schlenk tube was then connected to a vacuum line where it was evacuated and back-filled with argon for 3 times. Then Ultra-dry solvent (DCE:DMSO) and 2,5-dimethylhexa-2,4-diene (known as a triplet quencher[21], 14.3 μL, 0.1 mmol), were added to the reaction in sequence under argon flow. Then, the reaction was degassed by three consecutive freeze-pump-thaw cycles. After backfilling with argon, the reaction mixture in sealed tube was placed at a distance of 2 ~ 3 cm from a 30 W blue LED and stirred at room temperature for 11 h. Then, the reaction mixture was transferred to a separating funnel, diluted with water and extracted three times with EtOAc. The combined organic layers were washed with brine, dried over anhydrous sodium sulfate, filtered and concentrated to give the crude

product. Then, the yield of the product was determined by ^{1}H-NMR spectroscopy using dibromomethane (17.8 mg, 0.1 mmol) as internal standard. The product **3a** was obtained in 63% yield. Notably, the product **3a** was obtained in 44% and 73%, respectively, after 5 and 11 hours in the absence of 1.0 equivalent of 2,5-dimethylhexa-2,4-diene.

5.5 Determination of chloride ion content



Transferring the blank control group (Reaction a), the solution after substrate **1a** dehydrogenative 6π cyclization reaction (Reaction b), and the solution after **2a** dehydrogenation (Reaction c) to a round bottom flask, and adding 100 μL of concentrated nitric acid to each to maintain a nitric acid concentration between 0.1-1 mol/L. Then, 10 mL of prepared 0.1 mmol/mL silver nitrate solution was added to the round bottom flask, shaking evenly under ultrasound to precipitate silver chloride. Following this, 200 μL of an 8% ferric ammonium sulfate indicator was added to the flask. A 0.1 mmol/mL ammonium thiocyanate solution was prepared using ultrapure water. Titrate the solution in the flask with the ammonium thiocyanate solution until the reaction solution changes from white to red and this red color persists even after shaking, indicating the end point. Under the principle of Volhard method, the blank control group consumed 10 mL of 0.1 mmol/mL ammonium thiocyanate solution, reaction b with substrate **1a** consumed 8.5 mL of 0.1 mmol/mL ammonium thiocyanate solution, and reaction c with substrate **2a** consumed 8.6 mL of 0.1 mmol/mL ammonium thiocyanate solution. The calculations show that reactions b and c produced 0.15 mmol and 0.14 mmol of chloride ions, respectively.

Principle of Volhard method:

Titration Reaction: $Ag^+ + X^- \rightarrow AgX\downarrow$ $Ag^+ + SCN^- \rightarrow AgSCN\downarrow$ （white）

Indicate endpoint response: $Fe^{3+} + SCN^- \rightarrow [Fe(SCN)]^{2+}$（red）

5.6 GC spectrum for the detection of Chloroethane

After the completion of dehydrogenative photocyclization substrate **1a** under condition B, the reaction solution was subjected to gas quality detection. Under the conditions of gas chromatography-mass spectrometry detector (Agilent 7890B-5977B), chromatographic column model DB-5ms, injection volume 1μL, injection port temperature 230 °C, chromatographic column flow rate 1 mL/min, and column temperature 26 °C, compared with the gas chromatography-mass spectrometry detection results of standard chloroethane (**Figure S8**), it was found that chloroethane was present in the reaction solution (**Figure S9**).

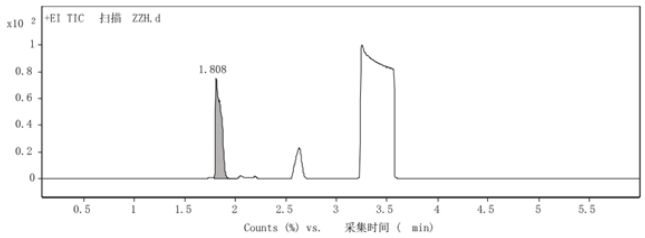


Figure S8. GC spectrum for standard chloroethane

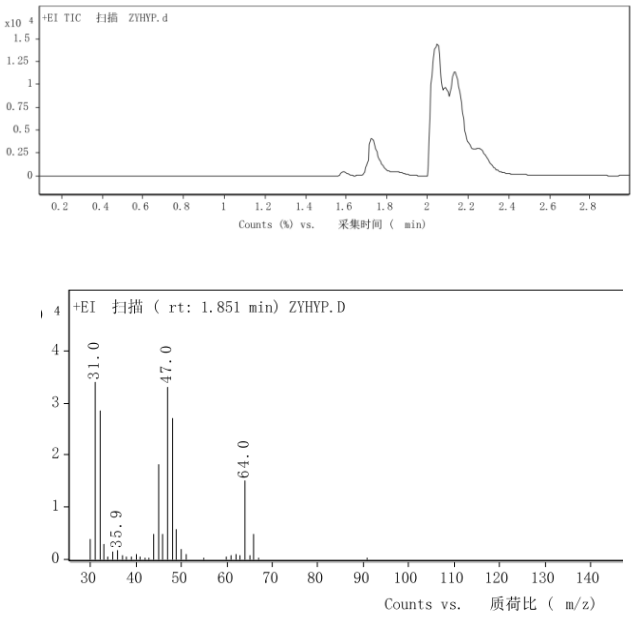


Figure S9. GC-MS analysis of the model reaction under dehydrogenative photocyclization conditions

5.7 Gas chromatography (GC) analysis

Gas chromatography (GC) analysis was performed on the reaction (Figure S10, a) reported in the literature (J. Org. Chem. 2024, 89, 14887), as well as the reactions (Figure S10, b) corresponding to Table 1, Entry 11, and Table 1, Entry 4 in our study. The results show that hydrogen gas was detected in the previously reported reaction, whereas no hydrogen gas was detected in the reactions performed in this work (Figure S11).

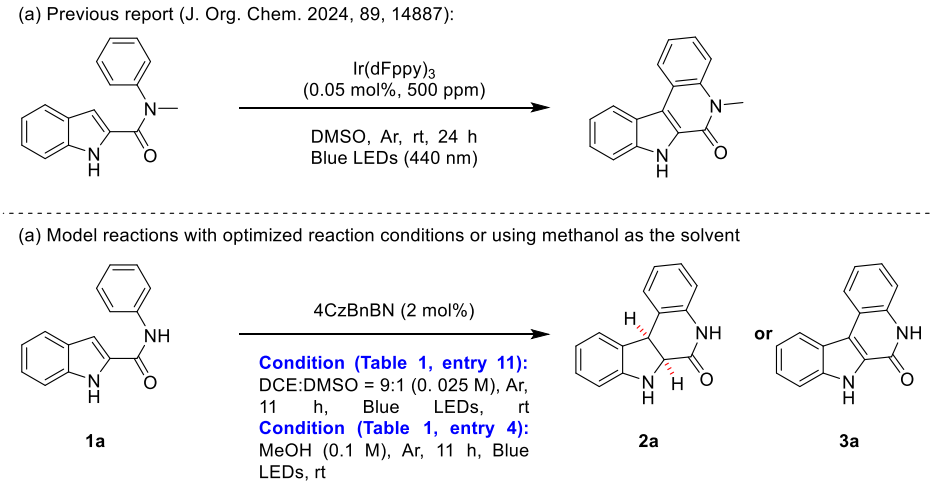


Figure S10. The reactions which was analyzed by gas chromatography (GC) analysis

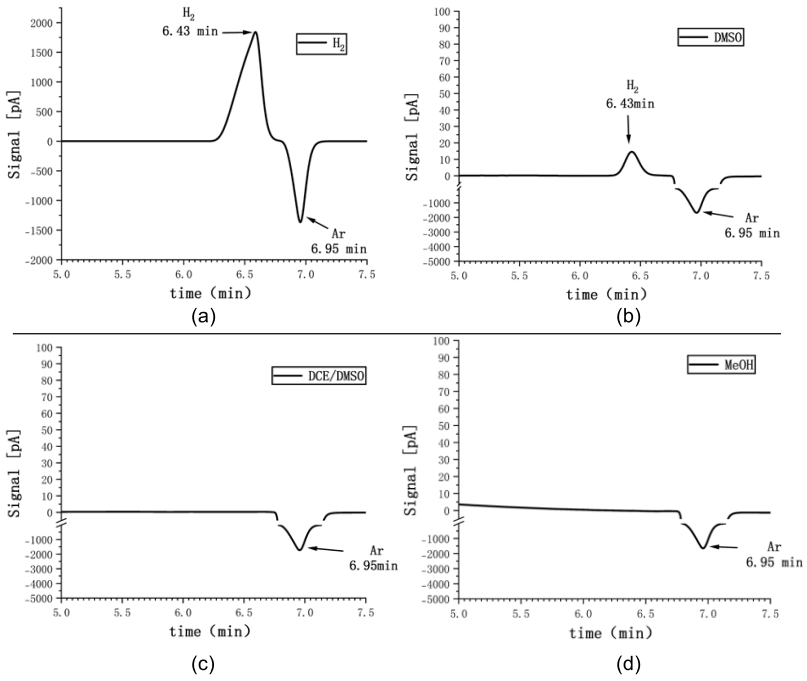
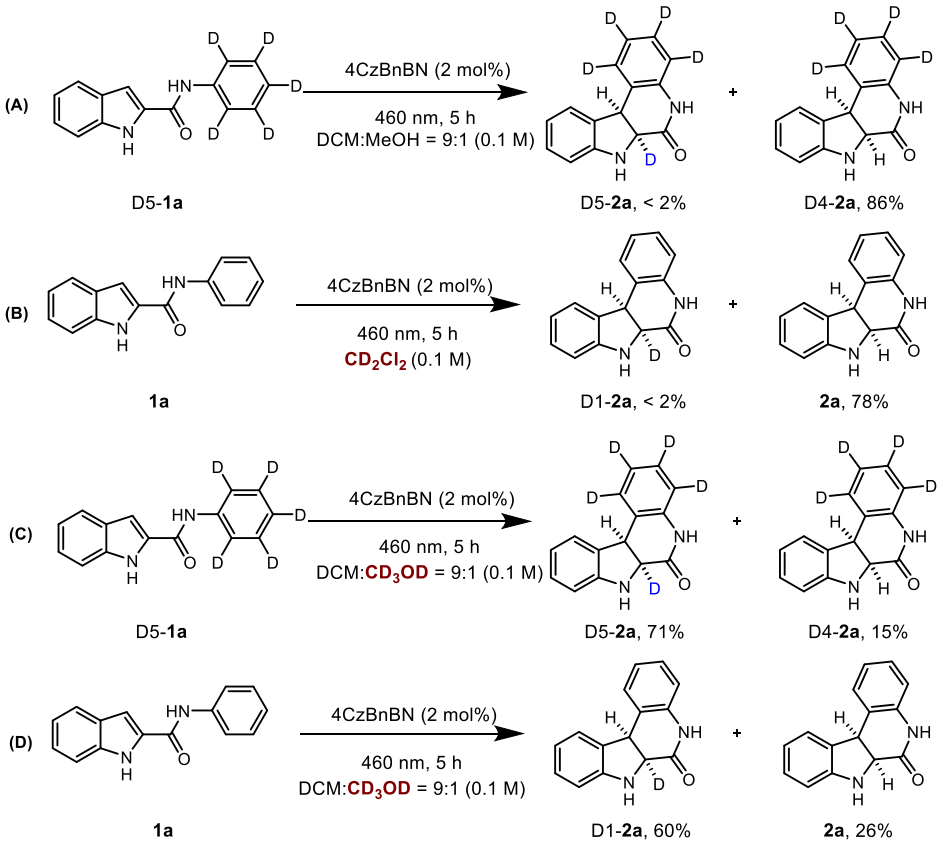


Figure S11. Gas Chromatography (GC) Analysis. (a) GC chromatogram of the standard hydrogen sample; (b) GC chromatogram of the reaction reported in the literature; (c) GC chromatogram of the optimized dehydrogenative photocyclization reaction (Table 1, Entry 11); (d) GC chromatogram of the reaction conducted in methanol as the solvent (Table 1, Entry 4).

5.8 Isotopic labeling Experiments



D5-**1a** is prepared according to the general procedure A using indole-2-carboxylate and phenyl-D5-amine. According to the general experimental procedure, the experiment is conducted using substrate D5-**1a** (reaction A) or using CD_2Cl_2 (reaction B) or CD_3OD (reactions C and D) as solvents, and the crude reaction mixture is analyzed by ^1H NMR to determine the extent of deuterium transfer from the para-position of the aniline to the α-carbonyl position and the source of hydrogen at the nitrogen α-position of the indole nucleus. The results show that the incorporation rate of deuterium at the C-6a position is related to the solvent.

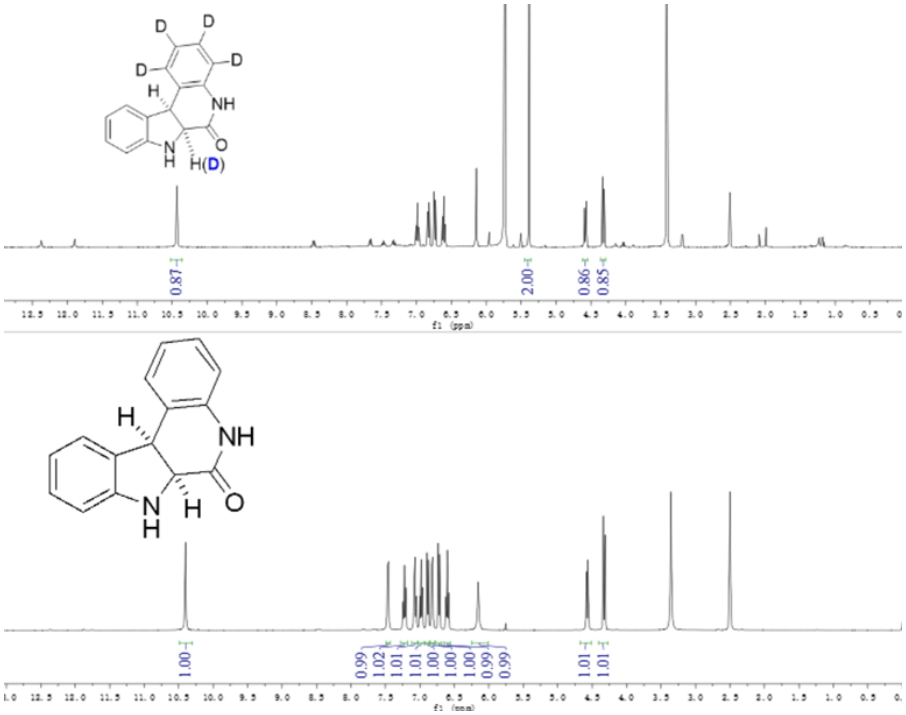


Figure S12. Top, Crude ^1H NMR spectrum of the product of the photocyclization using the corresponding D5-**1a** substrate. Bottom, purified ^1H NMR spectrum of product **2a** for comparison.

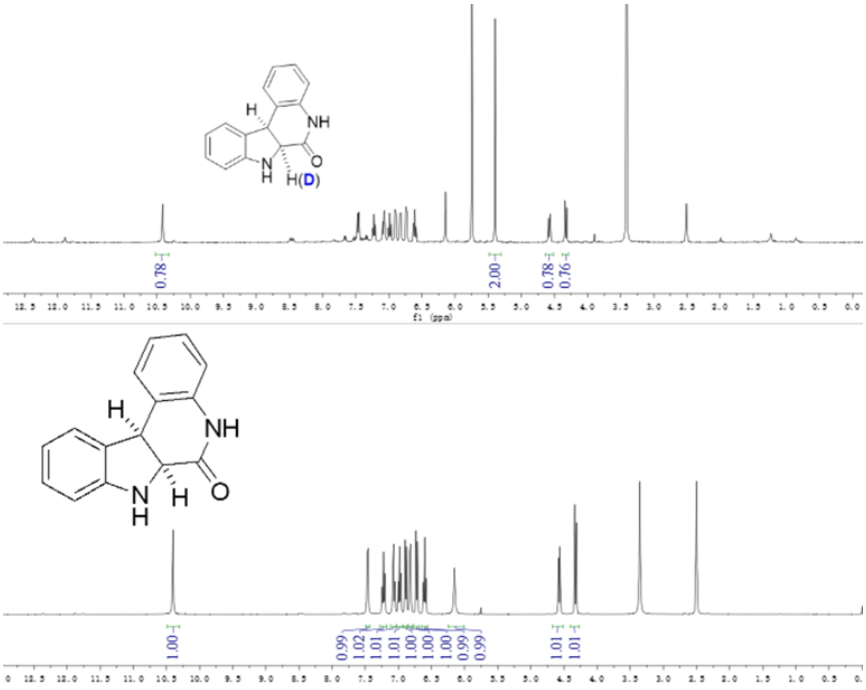


Figure S13. Top, Crude ^{1}H NMR spectrum of the product of the photocyclization using the CD_2Cl_2 as solvent. Bottom, purified ^{1}H NMR spectrum of product **2a** for comparison.

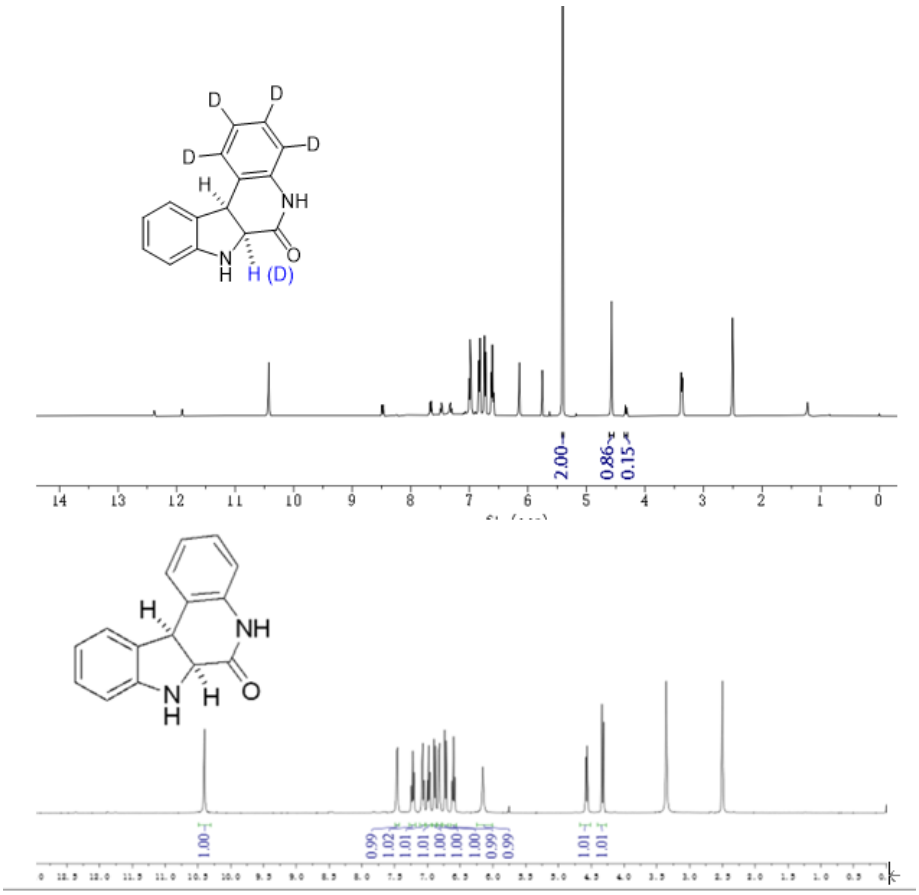


Figure S14. Top, Crude 1H NMR spectrum of the product of the photocyclization using the DCM:CD3OD=9:1(0.1M) as solvent and the corresponding D5-1a substrate. Bottom, purified 1H NMR spectrum of product 2a for comparison.

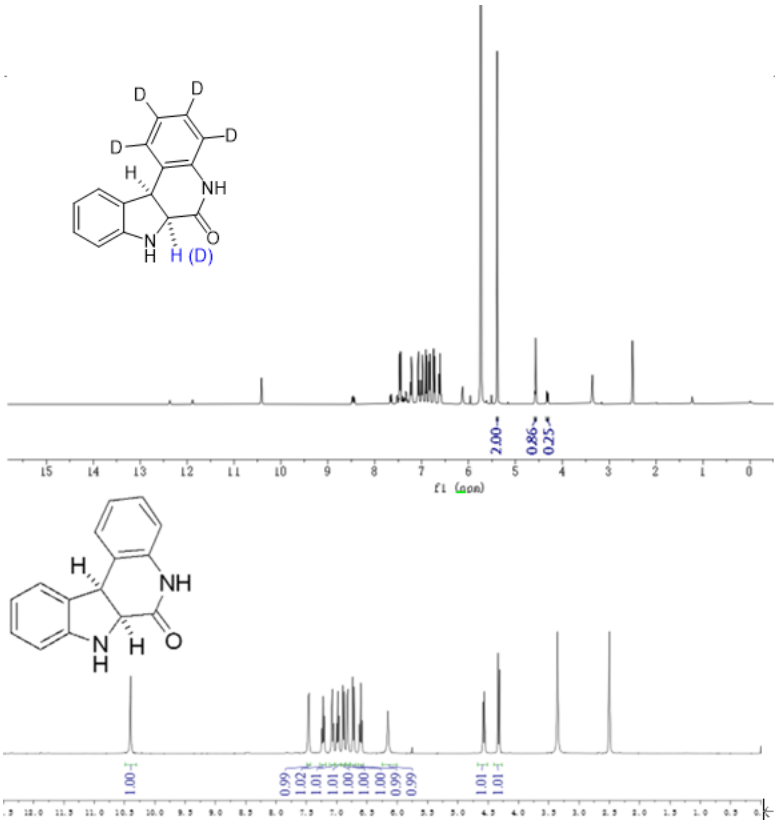
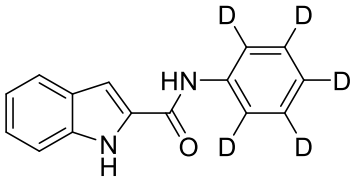


Figure S15. Top, Crude 1H NMR spectrum of the product of the photocyclization using the DCM:CD3OD=9:1(0.1M) as solvent. Bottom, purified 1H NMR spectrum of product 2a for comparison.

***N*-(phenyl-d5)-1*H*-indole-2-carboxamide (D5-1a)**



Physical State: white solid.

Yield： 77%.

^{1}H NMR (400 MHz, DMSO) δ 11.83 (s, 1H), 10.28 (s, 1H), 7.72 (d, J = 8.0 Hz, 1H), 7.54 – 7.47 (m, 2H), 7.26 (t, J = 7.6 Hz, 1H), 7.12 (d, J = 7.6 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 164.96, 144.04, 142.05, 136.72, 132.26, 129.00, 126.97, 125.15, 117.62, 109.08.

6. DFT Calculations

6.1 Reaction mechanism

DFT calculations were performed using the Gaussian 16 quantum chemistry software package. The calculation of photosensitizer is based on (U)ωB97X-D[24]/6-311+g(d, p)[25] SMD ($ClCH_2CH_2Cl$)[26]// (U)B3LYP[27]/6-31g(d) empiricaldispersion = gd3bj level using the Gaussian 16 program[28]. The rest of the calculations were performed at the (U)ωB97X-D/def2-TZPP[29], SMD (CH_2Cl_2 or $ClCH_2CH_2Cl$) //(U) ωB97XD/6-31+G(d,p) SMD (CH_2Cl_2 or $ClCH_2CH_2Cl$) level. A modified version of Harvey[30] code (sobMECP)[31] interfaced with Gaussian16 was used to search for the minimum energy crossing point (MECP). In addition, we also used Multiwfn to calculate relevant data.[32]

For the hydrogenation product **2a** (Figure S16): the substrate **1a** undergoes energy transfer with

the triplet state of the photocatalyst to form the triplet state **1a-T1** (59.12 kcal/mol). The triplet state **1a-T1** then passes through the transition state **TS1** (14.12 kcal/mol) to form the intermediate **INT1** (52.36 kcal/mol). The intermediate **INT1** undergoes intersystem crossing (**MECP**, ΔG = 6.69 kcal/mol) to form the intermediate **INT1-OSS**, which collapses to **INT1-CSS** (59.93 kcal/mol). Then, three possible reaction pathways (Path A, Path B, and Path C) were calculated. For the initially proposed Path A in the manuscript, we attempted multiple times to locate the transition states for stepwise or concerted proton transfer between **INT-CSS** and the substrate **1a**, but all attempts failed. For Path B, which involves a 1,5-hydrogen shift, we successfully calculated the corresponding transition state **TS2** with an energy barrier of 9.75 kcal/mol and the trans-hydrogenation product ***trans*-2a** (7.6 kcal/mol). The ***trans*-2a** undergoes keto-enol tautomerization to form ***cis*-2a** (1.23 kcal/mol). This pathway is commonly observed in 6π-photocyclization reactions. However, this pathway cannot explain why we failed to obtain the product with deuterium labeling at the C-6a position when using the indole amide substrate **D5-1a**, in which all aromatic hydrogens of aniline were deuterated (Scheme 2c, manuscript). We also hypothesized that the hydrogen at C-6a might readily exchange with H_2O, leading to the undetectable deuterium labeling at C-6a position. However, our NMR experiments using **2a** with deuterated water D_2O did not detect any deuterium incorporation at the C-6a position. For Path C, which involves intermolecular proton transfer, we calculated the transition state **TS3** with an energy barrier of 4.75 kcal/mol and the corresponding intermediates **INT2-1** and **INT2-2** (40.22 kcal/mol). Although this pathway appears feasible, we were unable to locate the subsequent transition state **TS4** for further proton transfer.

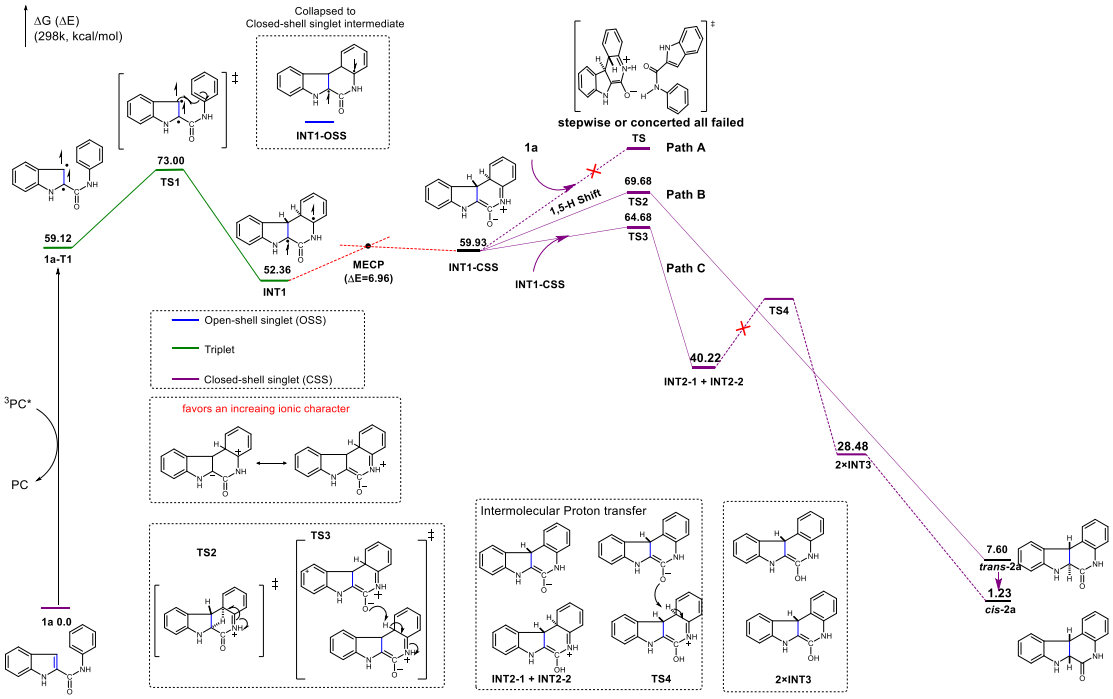


Figure S16. Computational analysis. Energy profile of the photocyclization of indolecarboxamide **1a** yielding *cis*-**2a**. Computational method: ωB97X-D/def2-TZVPP, SMD(CH_2Cl_2)// ωB97X-D/6-31+G(d,p), SMD(CH_2Cl_2).

	Zero-point Energy Correction [ωB97X-D/6-31+G (d, p),	**ΔG [ωB97X-D/6-31+G (d, p), SMD(CH_2Cl_2)]**	**E [ωB97X-D/6-31+G (d, p), SMD(CH_2Cl_2)]**	**E [ωB97X-D/def2-TZVPP, SMD(CH_2Cl_2)]**	**G_{HFIP} (ΔG+E)**

	SMD(CH_2Cl_2)]				
1a	0.240464	0.197281	-763.39836	-763.6320762	-763.3916122
1a-T1	0.234832	0.189922	-763.44152	-763.5305	-763.340578
TS1	0.236719	0.19581	-763.28325	-763.51427	-763.31846
INT1	0.238705	0.197916	-763.31889	-763.54928	-763.351364
MECP			-763.30779		
INT1-CSS	0.240166	0.200792	-763.30957	-763.54009	-763.339298
TS2	0.235903	0.197223	-763.29047	-763.52083	-763.323607
TS3	0.47798	0.419274	-1526.6325	-1527.0903	-1526.67102
INT2-1+INT2-2	0.482559	0.423807	-1526.67399	-1527.1338	-1526.70999
TS4	0.479996	0.422417	-1526.6786	-1527.1396	-1526.71718
INT3	0.241322	0.201995	-763.35922	-763.5914	-763.389405
cis-2a	0.243082	0.203869	-763.40662	-763.6367	-763.432831
trans-2a	0.242837	0.203886	-763.39616	-763.62658	-763.422694

The formation pathway of product **3a** (Figure S17): the mechanism for the formation of product **3a** from substrate **1a** is identical to that of product **2a** up to the intermediate **INT-CSS**. The difference lies in the subsequent steps for the formation of product **3a**. Specifically, the intermediate **INT-CSS** undergoes a single-electron transfer (SET) with the excited state photocatalyst to form intermediate **IND1** (20.72 kcal/mol), while the reduced state of the photocatalyst reduces 1,2-dichloroethane ($ClCH_2CH_2Cl$) to generate a chloroethyl radical and a chloride ion Cl^-. Subsequently, the intermediate **IND1** reacts with the chloride ion Cl^- through a barrierless transition state **TS5** (-0.8 kcal/mol) to form the intermediate **IND2** and a molecule of HCl (-5.04 kcal/mol). The intermediate **IND2** then undergoes a hydrogen atom transfer (HAT) reaction with the previously generated chloroethyl radical ($ClCH_2CH_2$•) *via* **TS6** (19.56 kcal/mol) to produce the final product **3a** (-81.98 kcal/mol) and a molecule of chloroethane.

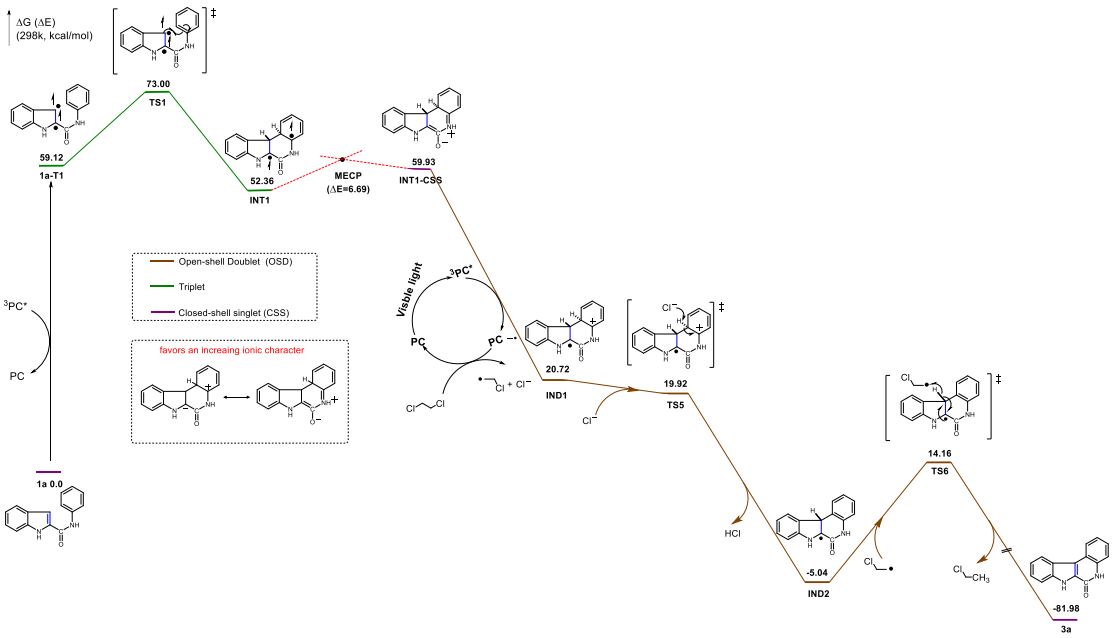
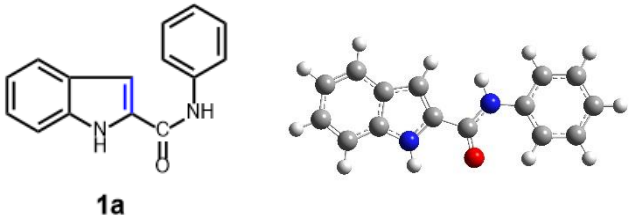


Figure S17. Computational analysis. Energy profile of the dehydrogenative photocyclization of indolecarboxamide **1a** yielding **3a**. Computational method: ωB97X-D/def2-TZVPP, SMD(CH_2Cl_2)//ωB97X-D/6-31+G(d,p), SMD(CH_2Cl_2).

	Zero-point Energy Correction [ωB97X-D/6-31+G (d, p), SMD(DCE)]	ΔG [ωB97X-D/6-31+G (d, p), SMD(DCE)]	E [ωB97X-D/6-31+G (d, p), SMD(DCE)]	E [ωB97X-D/def2-TZVPP, SMD(DCE)]	G_{HFIP} (ΔG+E)
DCE	**0.05472**	**0.022166**	**-998.97893**	**-999.06351**	**-999.041344**
HCl	**0.006691**	**-0.011199**	**-460.79029**	**-460.82317**	**-460.834369**
Cl^-	**0**	**-0.015023**	**-460.35118**	**-460.37044**	**-460.385463**
CH_3CH_2Cl	**0.063277**	**0.034354**	**-539.39769**	**-539.45177**	**-539.417416**
$ClCH_2CH_2$•	**0.048859**	**0.019025**	**-538.72213**	**-538.77592**	**-538.756895**
IND1	**0.242166**	**0.202579**	**-763.17166**	**-763.40341**	**-763.200831**
TS5	**0.237962**	**0.195313**	**-1223.5383**	**-1223.7958**	**-1223.600487**
IND2	**0.229548**	**0.189716**	**-762.76478**	**-762.99561**	**-762.805894**
TS6	**0.279348**	**0.229404**	**-1301.4792**	**-1301.7616**	**-1301.5321**
3a	**0.219774**	**0.181069**	**-762.216896**	**-762.44906**	**-762.267991**

	Zero-point Energy Correction [B3LYP/6-31G (d, p), empiricaldispersion=gd3bj, SMD(DCE)]	ΔG [B3LYP/6-31G (d, p), empiricaldispersion=gd3bj, SMD(DCE)]	E [B3LYP/6-31G (d, p), empiricaldispersion=gd3bj, SMD(DCE)]	E [B3LYP/6-311+G(d, p), SMD(DCE)]	G_{HFIP} (ΔG+E)
4CzBnBN	**0.837976**	**0.752517**	**-2660.313032**	**-2659.7399**	**-2658.98748**
^{3}4CzBnBN*	**0.834259**	**0.747386**	**-2660.289043**	**-2659.6323**	**-2658.8849**
4CzBnBN$^{\cdot-}$	**0.833924**	**0.747036**	**-2660.154950**	**-2659.8329**	**-2659.0858**

6.2 Cartesian coordinates and energies of all optimized structures



1a

SCF Done: E(RωB97XD) = -763.6320762a.u.

Zero-point correction = 0.240464(Hartree/Particle)

Sum of electronic and thermal Free Energies = -763.3916122a.u.

C, 0, 5.247656,1.084272, 0.031181

C, 0, 5.422569, -0.3183, -0.02965

C, 0, 4.341718, -1.181532, -0.059069

C, 0, 3.061768, -0.608952, -0.026002

C, 0, 2.86331, 0.793974, 0.034959

C, 0, 3.984523, 1.646228, 0.063774

N, 0, 1.82875, -1.200143, -0.042692

C, 0, 0.856946, -0.228531, 0.003688

C, 0, 1.449726, 1.012842, 0.053736

C, 0, -0.55549, -0.675186, -0.000729

N, 0, -1.479977, 0.322733, -0.023926

O, 0, -0.822346, -1.877202 ,0.013795

C, 0, -2.885415, 0.230534, -0.012971

C, 0, -3.597071, 1.437271, -0.074823

C,0, -4.986469,1.434825, -0.06274

C, 0, -5.689104, 0.231423, 0.010331

C, 0, -4.979643, -0.965035, 0.070829

C, 0, -3.584838, -0.979883, 0.059733

H, 0, 6.123691, 1.725471, 0.051834

H, 0, 6.429026, -0.725347, -0.053876

H, 0, 4.475488, -2.257714, -0.105632

H, 0, 3.855396, 2.723655, 0.110111

H, 0, 1.629966, -2.190189, -0.080742

H, 0, 0.950132, 1.970996, 0.107562

H, 0, -1.1183,1.266748, -0.057629

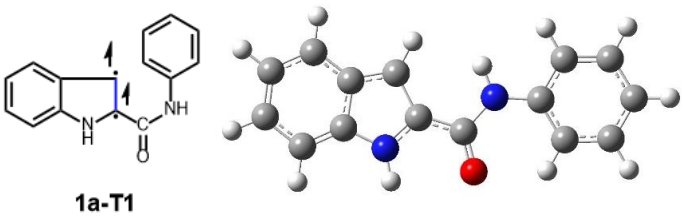
H, 0, -3.0571, 2.379182, -0.132476

H, 0, -5.520558, 2.378941, -0.111155

H, 0, -6.774506, 0.228826, 0.019693

H, 0, -5.512106, -1.909803, 0.128209

H, 0, -3.044879, -1.914968, 0.106583



1a-T1

SCF Done: E(UωB97XD) = -763.5305a.u.

Zero-point correction = 0.234832 (Hartree/Particle)

Sum of electronic and thermal Free Energies = -763.340578a.u.

C, 0, -5.260316, 1.09354, 0.000103

C, 0, -5.433139, -0.27757, 0.000454

C, 0, -4.313844, -1.169199, 0.000452

C, 0, -3.073379, -0.615396, 0.000112

C, 0, -2.857613,0.802983, -0.000252

C, 0, -3.975988, 1.659388, -0.000258

N, 0, -1.814136, -1.228259, -0.000028

C, 0, -0.81343, -0.306459, -0.000291

C, 0, -1.484868, 1.030048, -0.000555

C, 0, 0.546329, -0.723864, -0.000137

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C, 0, 2.87219, 0.233832, -0.000104

C, 0, 3.575993, 1.449138, 0.000395

C, 0, 4.961468, 1.463534, 0.000563

C, 0, 5.681253, 0.270451, 0.000259

C, 0, 4.986064, -0.933068, -0.00022

C, 0, 3.594905, -0.966368, -0.000415

H, 0, -6.128029, 1.743311, 0.000113

H, 0, -6.432689, -0.696697, 0.000732

H, 0, -4.460762, -2.242662, 0.000707

H, 0, -3.841448, 2.73482, -0.000514

H, 0, -1.64338, -2.224143, 0.000563

H, 0, -0.984177, 1.987665, -0.000965

H, 0, 1.10845, 1.243748, -0.00033

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H, 0, 6.765306, 0.281779, 0.000396

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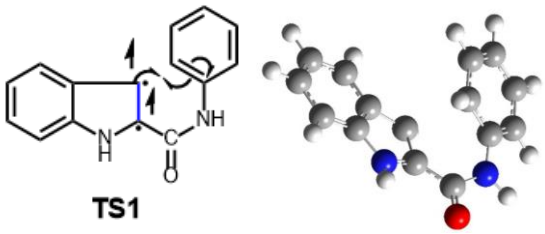
H, 0, 3.064443, -1.906663, -0.00079



TS1

SCF Done: E(UωB97XD) = -763.5142679a.u.

Zero-point correction = 0.236719 (Hartree/Particle)

Sum of electronic and thermal Free Energies = -763.31846a.u.

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C, 0, 3.654869, 0.457477, 0.361098
C, 0, 2.3161, 0.57496, 0.039276
C, 0, 1.548814, -0.518196, -0.426972
C, 0, 2.154138, -1.762844, -0.578681
N, 0, 1.496281, 1.710182, 0.067373
C, 0, 0.218632, 1.387311, -0.29096
C, 0, 0.201661, -0.041863, -0.68275
C, 0, -0.887733, 2.24504, -0.036497
N, 0, -2.139518, 1.625696, -0.102818
O, 0, -0.786528, 3.473027, 0.190363
C, 0, -2.365541, 0.275929, 0.104055
C, 0, -3.497121, -0.346834, -0.439024
C, 0, -3.664385, -1.718571, -0.31803
C, 0, -2.702749, -2.505482, 0.348633
C, 0, -1.599647, -1.902916, 0.915712
C, 0, -1.381464, -0.506948, 0.783267
H, 0, 3.991103, -2.866897, -0.351906
H, 0, 5.292156, -0.936086, 0.468206
H, 0, 4.232393, 1.31087, 0.70185
H, 0, 1.583173, -2.612079, -0.942173
H, 0, 1.746572, 2.593709, 0.490542
H, 0, -0.378115, -0.393012, -1.529345
H, 0, -2.927887, 2.225457, -0.313836
H, 0, -4.23033, 0.253683, -0.970423
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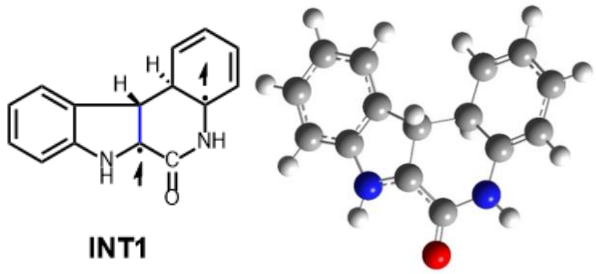
H, 0, -2.850109, -3.577113, 0.439807
H, 0, -0.874924, -2.489402, 1.472304
H, 0, -0.727835, -0.016406, 1.499078



INT1

SCF Done: E(URωB97XD) = -763.5492805a.u.

Zero-point correction = 0.238705 (Hartree/Particle)

Sum of electronic and thermal Free Energies = -763.351364a.u.

C, 0, 3.441987, -1.896223, 0.060038

C, 0, 4.215758, -0.763049, -0.202225

C, 0, 3.646374, 0.511355, -0.223223

C, 0, 2.278929, 0.604479, 0.00954

C, 0, 1.478892, -0.524262, 0.25504

C, 0, 2.067956, -1.779807, 0.300025

N, 0, 1.488835, 1.751308, 0.062663

C, 0, 0.184769, 1.41764, 0.293742

C, 0, 0.059514, -0.064361, 0.508961

C, 0, -0.917057, 2.28129, 0.024033

N, 0, -2.144318, 1.634006, -0.044548

O, 0, -0.830422, 3.511875, -0.137889

C, 0, -2.321701, 0.253619, -0.097198

C, 0, -3.552114, -0.314734, 0.118775

C, 0, -3.721359, -1.715345, 0.094915

C, 0, -2.599938, -2.557254, -0.128827

C, 0, -1.359171, -2.04084, -0.358953

C, 0, -1.093615, -0.566765, -0.420916

H, 0, 3.910204, -2.875206, 0.082171

H, 0, 5.280604, -0.870666, -0.385715

H, 0, 4.246016, 1.396007, -0.412251

H, 0, 1.477227, -2.66298, 0.521799

H, 0,1.790577,2.672665, -0.224371

H, 0, -0.234153, -0.296688, 1.542725

H, 0, -2.962898, 2.230148, -0.026656

H, 0, -4.402194, 0.329535, 0.330462

H, 0, -4.702132, -2.143631, 0.271031

H, 0, -2.737595, -3.635271, -0.121957

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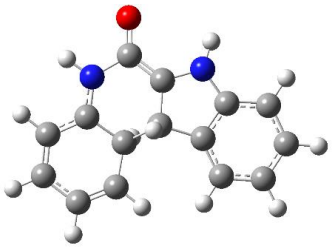
H, 0, -0.769521, -0.310704, -1.44562



MECP

SCF Done: E(RωB97XD) = -763.30779 a.u.

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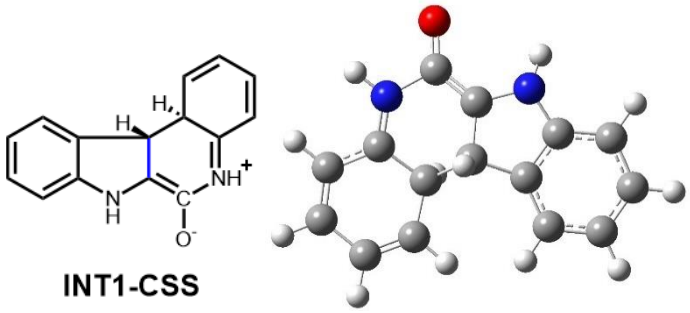
C 4.23616700 -0.78230100 -0.23178500
C 3.68069600 0.49782900 -0.17744700
C 2.31045500 0.60228600 0.04228100
C 1.49398000 -0.53448000 0.20609000
C 2.07008100 -1.79542800 0.18059000
N 1.54484200 1.75783500 0.15620700
C 0.20694800 1.41493000 0.21746900
C 0.08071900 -0.06173300 0.51163500
C -0.85871400 2.26792100 -0.00401500
N -2.10913000 1.59232600 0.04075500
O -0.84898500 3.51519800 -0.20460400
C -2.31219700 0.27425500 -0.05425000
C -3.61550800 -0.26652600 -0.03015000
C -3.79777100 -1.62596900 -0.04712400
C -2.67480400 -2.52762100 -0.04776500
C -1.41023000 -2.05979000 -0.11238600
C -1.10435100 -0.60247100 -0.28868800
H 3.89890300 -2.90408700 -0.08575400
H 5.30238800 -0.89071700 -0.41077500
H 4.29620300 1.38338900 -0.30136800
H 1.47442900 -2.68773500 0.34579600
H 1.84982100 2.66177200 -0.17734400
H -0.12191300 -0.22720200 1.58805000
H -2.91920400 2.20538600 0.07049900
H -4.46305500 0.41028600 0.03341800
H -4.80324100 -2.03255000 -0.02013000
H -2.86028500 -3.59513900 0.02125300
H -0.57343800 -2.74859800 -0.11728000
H -0.84837700 -0.44309400 -1.36222000



INT1-CSS

SCF Done: E(RωB97XD) = -763.5400937a.u.

Zero-point correction = 0.240166 (Hartree/Particle)

Sum of electronic and thermal Free Energies = -763.339298a.u.

C, 0, 3.436684, -1.921517, -0.076334

C, 0, 4.227575, -0.785898, -0.253842

C, 0, 3.677544, 0.495222, -0.177131

C, 0, 2.31015, 0.60838, 0.06096

C, 0, 1.491484, -0.528834, 0.212672

C, 0, 2.063834, -1.791887, 0.171468

N, 0, 1.566547, 1.772992, 0.221835

C, 0, 0.2055, 1.423545, 0.225061

C, 0, 0.079335, -0.055961, 0.531743

C, 0, -0.838972, 2.265858, -0.015189

N, 0, -2.109069, 1.57107, 0.037218

O, 0, -0.878608, 3.514948, -0.246713

C, 0, -2.306145, 0.277488, -0.058195

C, 0, -3.625874, -0.272284, -0.041819

C, 0, -3.788753, -1.619972, -0.040596

C, 0, -2.661989, -2.529465, -0.044942

C, 0, -1.403416, -2.060614, -0.11105

C, 0, -1.100231, -0.603379, -0.267026

H, 0, 3.884808, -2.909022, -0.123537

H, 0, 5.291124, -0.895383, -0.445944

H, 0, 4.296315, 1.379658, -0.294956

H, 0, 1.46851, -2.684119, 0.336257

H, 0, 1.855801, 2.632952, -0.224629

H, 0, -0.118338, -0.225931, 1.608728

H, 0, -2.917237, 2.188519, 0.076214

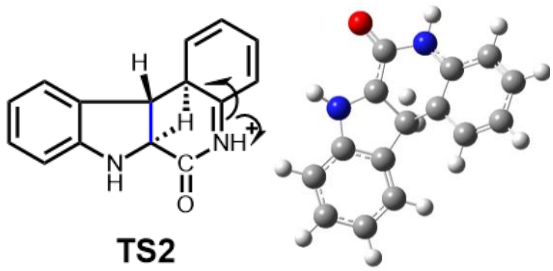
H, 0, -4.474812, 0.403057, 0.005498

H, 0, -4.791944, -2.034, -0.013269

H, 0, -2.852974, -3.59583, 0.01361

H, 0, -0.565228, -2.747188, -0.129771

H, 0, -0.849843, -0.444806, -1.342552



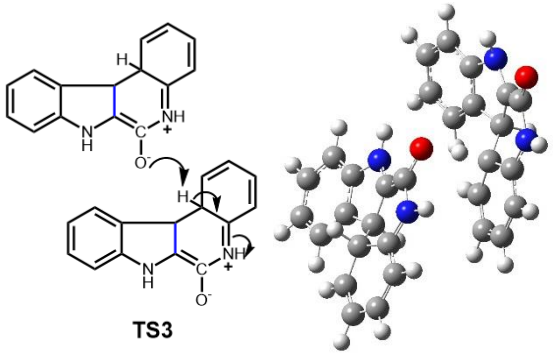
TS2

SCF Done: E(RωB97XD) = -763.52083a.u.

Zero-point correction = 0.235903 (Hartree/Particle)

Sum of electronic and thermal Free Energies = -763.323607a.u.

C, 3.50338200, -1.78995700, 0.21527000
C, 4.20446000, -0.69390800, -0.28741000
C, 3.58494200, 0.54795100, -0.45828800
C, 2.23984700, 0.65160800, -0.12599600
C, 1.51314100, -0.45069000, 0.36211500
C, 2.14921100, -1.66635500, 0.55398500
N, 1.42235900, 1.78653800, -0.17415900
C, 0.11005900, 1.36779300, 0.00896800
C, 0.11136000, 0.01747000, 0.70486300
C, -1.02259100, 2.21540700, 0.04663400
N, -2.19817600, 1.50351600, 0.32330300
O, -1.06272700, 3.44523200, -0.17492100
C, -2.31116000, 0.15701100, 0.18814500
C, -3.56624500, -0.46897000, 0.05365000
C, -3.62821300, -1.80366200, -0.27052000
C, -2.44466200, -2.56973200, -0.45600200
C, -1.21514600, -2.00076400, -0.28455200
C, -1.07533100, -0.58304900, -0.02309900
H, 4.00853900, -2.74121800, 0.34928800
H, 5.25394500, -0.80052300, -0.54586500
H, 4.13684700, 1.40385700, -0.83405400
H, 1.60932000, -2.51543900, 0.96339500
H, 1.64027200, 2.57154000, -0.77250900
H, -0.02507900, 0.06673400, 1.79883500
H, -3.04633700, 2.06131900, 0.32845000
H, -4.47024400, 0.11812300, 0.18772400
H, -4.59624200, -2.27971600, -0.39028700
H, -2.52735900, -3.62378500, -0.70183800
H, -0.31369600, -2.59576500, -0.38255500
H, -0.65576400, 0.16173400, -1.01180600



SCF Done: E(RωB97XD) = -1527.0903134a.u.

Zero-point correction = 0.47798 (Hartree/Particle)

Sum of electronic and thermal Free Energies = -1526.671026a.u.

C, 0, 4.440405, 3.610489, 0.419568

C, 0, 3.344263, 4.408398, 0.092587

C, 0, 2.10978, 3.842076, -0.234137

C, 0, 2.01412, 2.454768, -0.238479

C, 0, 3.1143, 1.631417, 0.074597

C, 0, 4.322586, 2.213879, 0.423881

N, 0, 0.897113, 1.676211, -0.512233

C, 0, 1.267542, 0.347533, -0.574315

C, 0, 2.626197, 0.189725, 0.073322

C, 0, 0.561755, -0.680006, -1.112362

N, 0, 1.240033, -1.933098, -1.053051

O, 0, -0.655649, -0.692663, -1.554916

C, 0, 2.516697, -2.12149, -0.814433

C, 0, 3.068558, -3.438761, -0.772489

C, 0, 4.364039, -3.607156, -0.404341

C, 0, 5.211514, -2.488947, -0.044109

C, 0, 4.75548, -1.227298, -0.128488

C, 0, 3.394953, -0.903664, -0.663291

H, 0, 5.38866, 4.070703, 0.678264

H, 0, 3.446593, 5.489604, 0.094532

H, 0, 1.252339, 4.460333, -0.480555

H, 0, 5.178036, 1.609256, 0.706627

H, 0, 0.057505, 2.030878, -0.947694

H, 0, 2.48624, -0.134113, 1.123618

H, 0, 0.651989, -2.741351, -1.246101

H, 0, 2.425259, -4.284162, -0.997725

H, 0, 4.776056, -4.610125, -0.353387

H, 0, 6.22032, -2.689881, 0.30032

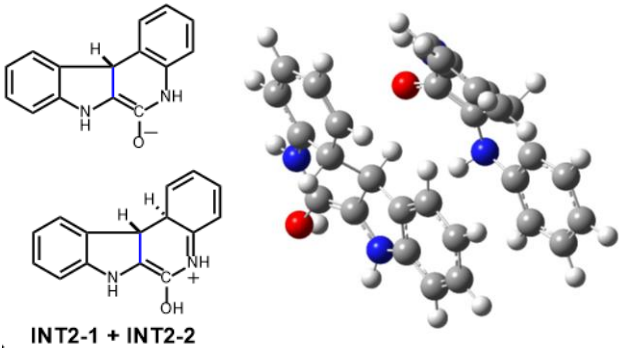
H, 0, 5.398984, -0.393354, 0.126234

H, 0, 3.539839, -0.550645, -1.709755

C, 0, -1.884468, 3.657833, 0.747127

C, 0, -2.801584, 4.068401, -0.220954

C, 0, -3.741074, 3.17835, -0.746298
C, 0, -3.727417, 1.859569, -0.294122
C, 0, -2.776074, 1.418372, 0.64802
C, 0, -1.879634, 2.327865, 1.189375
N, 0, -4.612376, 0.839377, -0.626964
C, 0, -4.067089, -0.375176, -0.118862
C, 0, -3.045071, -0.050376, 0.954096
C, 0, -4.331292, -1.615397, -0.602851
N, 0, -3.510821, -2.647414, 0.007481
O, 0, -5.14855, -2.009443, -1.499248
C, 0, -2.3609, -2.438449, 0.637352
C, 0, -1.533077, -3.528344, 1.028988
C, 0, -0.38241, -3.292869, 1.73181
C, 0, 0.024223, -1.973812, 2.094287
C, 0, -0.723436, -0.910149, 1.691749
C, 0, -1.89853, -1.056749, 0.830838
H, 0, -1.174454, 4.366816, 1.161961
H, 0, -2.797058, 5.099102, -0.564899
H, 0, -4.469871, 3.504723, -1.48244
H, 0, -1.165832, 2.027818, 1.949837
H, 0, -4.992021, 0.817137, -1.5653
H, 0, -3.470692, -0.122671, 1.973769
H, 0, -3.764892, -3.594617, -0.252157
H, 0, -1.852283, -4.540566, 0.79841
H, 0, 0.228964, -4.136727, 2.03961
H, 0, 0.919613, -1.832314, 2.69027
H, 0, -0.424104, 0.093587, 1.970928
H, 0, -1.429365, -0.868297, -0.296081



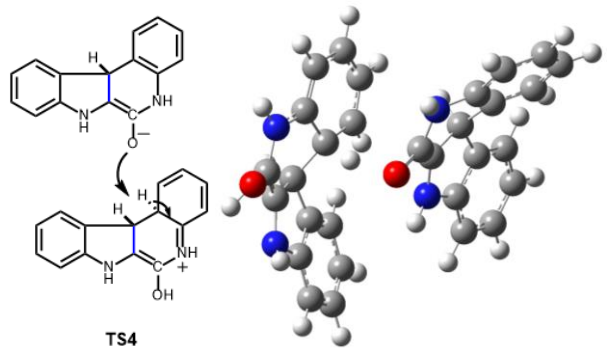
INT2-1 + INT2-2

SCF Done: E(RωB97XD) = -1527.1338a.u.
Zero-point correction = 0.482559 (Hartree/Particle)
Sum of electronic and thermal Free Energies = -1526.709993a.u.

C 1.79365600 -1.20336900 2.29445200
C 1.81482000 -2.59599500 2.30641400
C 0.79496700 -3.33845900 1.70323900
C -0.24739900 -2.63661300 1.11731600

C -0.30505200 -1.23504600 1.12659900
C 0.73562800 -0.51432700 1.68940100
N -1.34306400 -3.15782700 0.40987100
C -2.20438300 -2.13813300 0.09225900
C -1.51790100 -0.80498700 0.32881000
C -3.47322800 -2.19049300 -0.33944300
N -4.15652300 -0.96643000 -0.49691500
O -4.22585300 -3.30033200 -0.57729700
C -3.77066800 0.16992900 0.04036100
C -4.51576500 1.36706800 -0.16407400
C -4.03598300 2.53704700 0.33115200
C -2.78483600 2.61963000 1.05147800
C -2.06536600 1.51219300 1.29871800
C -2.55361300 0.14952900 0.92788500
H 2.61201000 -0.64460800 2.73686800
H 2.64719400 -3.11757300 2.76901000
H 0.82528000 -4.42323100 1.67952300
H 0.75586400 0.56893900 1.64442800
H -1.64247200 -4.11895600 0.49827000
H -1.20854500 -0.38336000 -0.64122000
H -5.00778000 -0.98507700 -1.05388000
H -5.43179300 1.32709600 -0.74428000
H -4.59736300 3.45066300 0.16126400
H -2.43022500 3.59227700 1.37325800
H -1.12958200 1.57199200 1.84263500
H -2.92253800 -0.30450000 1.87495000
C 4.78787000 -1.58506200 -0.20846000
C 4.03185500 -2.69363500 -0.59289400
C 2.79317300 -2.53813400 -1.21625900
C 2.31402800 -1.24560700 -1.42918600
C 3.04478400 -0.11809400 -1.00414300
C 4.29420300 -0.29177000 -0.42612500
N 1.15097500 -0.87479900 -2.09406100
C 0.97513600 0.53478000 -1.88139500
C 2.27394700 1.13653200 -1.38900300
C -0.18089700 1.23234600 -2.01239900
N -0.08222900 2.60980700 -1.58734700
O -1.33661000 0.82998300 -2.41171200
C 0.77347900 2.93658300 -0.53623400
C 0.46395400 3.99074800 0.33578800
C 1.29384000 4.28657000 1.41200200
C 2.44534800 3.53102200 1.63532700
C 2.76553300 2.49777600 0.75365700
C 1.95777600 2.19168900 -0.34021100

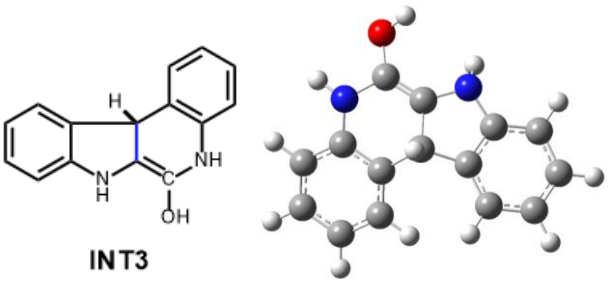
H 5.76039600 -1.72279800 0.25458700
H 4.41415800 -3.69501100 -0.41353100
H 2.21335500 -3.40188800 -1.52967000
H 4.89951900 0.56446600 -0.14252800
H 0.33755100 -1.46604000 -1.97156000
H 2.82726900 1.64776000 -2.20227000
H -1.00288600 3.02775100 -1.52436500
H -0.44339000 4.56559900 0.16831500
H 1.03466500 5.10296100 2.08052800
H 3.09464700 3.74946500 2.47777600
H 3.66672300 1.91963300 0.92757200
H -3.94990500 -3.72031600 -1.40465000



SCF Done: E(RωB97XD) = -1527.1396a.u.
Zero-point correction = 0.479996 (Hartree/Particle)
Sum of electronic and thermal Free Energies = -1526.717183a.u.

C -2.02946000 3.72666800 0.28702200
C -2.86855700 3.94837500 -0.80498800
C -3.70542300 2.93829100 -1.28657200
C -3.65492800 1.69741200 -0.66192200
C -2.77793200 1.44243800 0.40388700
C -1.98902900 2.46966100 0.90150500
N -4.46229400 0.58126300 -0.93361900
C -3.96754400 -0.48891900 -0.16285200
C -2.96632600 0.01052100 0.86541100
C -4.17714600 -1.79663100 -0.31989700
N -3.41227700 -2.70475400 0.42254900
O -5.00226700 -2.40870500 -1.21731300
C -2.22371300 -2.36948300 0.98814700
C -1.44286800 -3.30107300 1.65078800
C -0.26621300 -2.88619600 2.29124100
C 0.15340400 -1.55865800 2.29157700
C -0.53934800 -0.61070600 1.54548300
C -1.76824300 -0.96461300 0.81027700
H -1.40392700 4.52970300 0.66378600
H -2.88825600 4.92495700 -1.28000400

H -4.38260600 3.11861600 -2.11588800
H -1.33969700 2.31303800 1.75637700
H -4.70638600 0.40114800 -1.90059400
H -3.39069800 -0.00309000 1.88015800
H -1.76479300 -4.33662400 1.70643900
H 0.31033600 -3.62484800 2.84136600
H 1.02145300 -1.26996200 2.87409500
H -0.30691600 0.43947000 1.66157100
H -3.73929200 -3.66093400 0.47965200
H -5.83533000 -1.92248100 -1.27863800
H -1.44135100 -0.96294900 -0.31496400
C 4.07391000 3.59619800 0.85659300
C 3.03962400 4.32162200 0.26350500
C 1.90047300 3.68366600 -0.23262700
C 1.83507100 2.29506700 -0.13505700
C 2.88943500 1.54431700 0.42060600
C 3.99371000 2.19946300 0.94382100
N 0.78966600 1.46324700 -0.49491000
C 1.16304900 0.13133200 -0.30693100
C 2.49420300 0.07622200 0.41059300
C 0.62470500 -0.94649900 -0.97525800
N 1.35561000 -2.14690500 -0.85802900
O -0.48609700 -0.93920300 -1.60782600
C 2.75342100 -2.09127600 -0.81015000
C 3.52141000 -3.14173600 -1.32634700
C 4.91027200 -3.06954900 -1.30883000
C 5.54665800 -1.94179400 -0.79160600
C 4.77931700 -0.90026600 -0.27035100
C 3.38728400 -0.96169200 -0.25335500
H 4.94230100 4.11286100 1.25318600
H 3.11288500 5.40329900 0.19370400
H 1.08738800 4.24882800 -0.67784000
H 4.79382900 1.64464200 1.42476900
H 0.07400000 1.72612400 -1.15661800
H 2.34828100 -0.25600800 1.45290700
H 3.02012800 -4.00648100 -1.75372400
H 5.49396700 -3.89082000 -1.71436500
H 6.63002200 -1.87350200 -0.78656000
H 5.27960100 -0.02858400 0.13763000
H 0.96174500 -2.90605700 -1.39953700



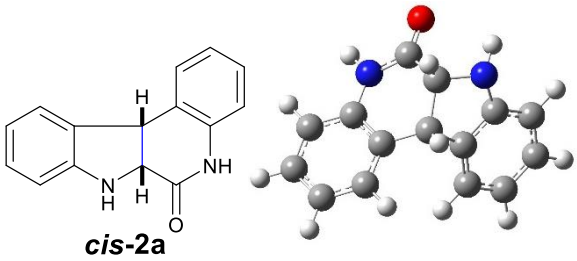
INT3

SCF Done: E(RωB97XD) = -763.5914a.u.

Zero-point correction = 0.241322 (Hartree/Particle)

Sum of electronic and thermal Free Energies = -763.389405a.u.

C 3.49021700 -1.77612300 0.14406400
C 4.15217100 -0.69823400 -0.44601100
C 3.52293300 0.53961200 -0.59393700
C 2.20726900 0.66182700 -0.15693900
C 1.51342500 -0.42562800 0.39698300
C 2.16654600 -1.63750500 0.57714400
N 1.42570900 1.82791800 -0.14915900
C 0.11782400 1.44215300 0.23727600
C 0.12140500 0.03054100 0.79058600
C -1.03066200 2.11121500 0.13160100
N -2.23133900 1.44562100 0.41655100
O -1.21699500 3.38699200 -0.31411700
C -2.28826100 0.06976700 0.15529800
C -3.49331400 -0.53845200 -0.21107600
C -3.52667300 -1.89928300 -0.49591000
C -2.35756900 -2.65784500 -0.43465800
C -1.16020500 -2.04942100 -0.06020000
C -1.10822400 -0.69379200 0.26032800
H 4.00317500 -2.72429800 0.27140400
H 5.17771300 -0.81580400 -0.78404500
H 4.04614400 1.38533700 -1.03006600
H 1.66425400 -2.47428600 1.05320600
H 1.51628000 2.44019300 -0.95199400
H 0.04559800 0.05047800 1.89112800
H -3.06444700 1.97612300 0.19625100
H -4.39510400 0.06365700 -0.28559200
H -4.46604400 -2.36320600 -0.78184100
H -2.37710800 -3.71765400 -0.66859100
H -0.25659100 -2.64702100 -0.00753200
H -0.47978900 3.94278500 -0.02842300



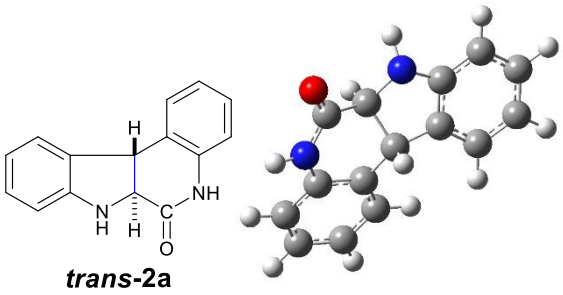
***cis*-2a**

SCF Done: E(RωB97XD) = -763.6367046a.u.

Zero-point correction = 0.243082 (Hartree/Particle)

Sum of electronic and thermal Free Energies = -763.432831a.u.

C, 0, 2.520328, -2.313875, -0.844179
C, 0, 3.586549, -1.413513, -0.820819
C, 0, 3.463683, -0.156537, -0.219811
C, 0, 2.241325, 0.173998, 0.356525
C, 0, 1.168693, -0.725923, 0.339364
C, 0, 1.296443, -1.968764, -0.256385
N, 0, 1.887862, 1.353378, 1.032467
C, 0, 0.423655, 1.399314, 1.043078
C, 0, 0.012365, -0.087082, 1.091886
C, 0, -0.092776, 2.134158, -0.200433
N, 0, -1.237914, 1.672986, -0.761501
O, 0, 0.493471, 3.121124, -0.636393
C, 0, -1.939327, 0.519056, -0.368756
C, 0, -3.198642, 0.262405, -0.912423
C, 0, -3.892926, -0.883047, -0.534738
C, 0, -3.340016, -1.764807, 0.393149
C, 0, -2.08443, -1.494169, 0.933748
C, 0, -1.365586, -0.360692, 0.555307
H, 0, 2.637762, -3.280887, -1.323268
H, 0, 4.529857, -1.687278, -1.284776
H, 0, 4.293564, 0.54383, -0.212831
H, 0, 0.458463, -2.660663, -0.276292
H, 0, 2.315121, 2.202909, 0.677548
H, 0, 0.057229, -0.419201, 2.136636
H, 0, -3.627456, 0.959884, -1.626731
H, 0, -4.871138, -1.08009, -0.962256
H, 0, -3.882824, -2.654465, 0.696028
H, 0, -1.647024, -2.173236, 1.661051
H, 0, 0.052572, 1.956248, 1.90901
H, 0, -1.609562, 2.216283, -1.532814



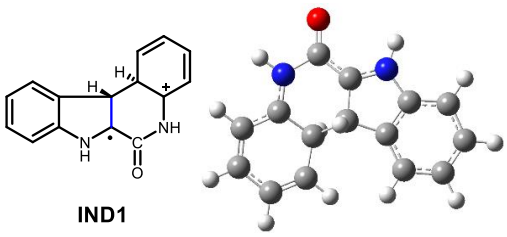
***trans*-2a**

SCF Done: E(RωB97XD) = -763.62658a.u.

Zero-point correction = 0.242822 (Hartree/Particle)

Sum of electronic and thermal Free Energies = -763.422694a.u.

C, 0, -3.451003, -1.904225, -0.199067
C, 0, -4.226378, -0.811775, 0.188405
C, 0, -3.658228, 0.454726, 0.35554
C, 0, -2.291528, 0.593325, 0.139668
C, 0, -1.493712, -0.507442, -0.228348
C, 0, -2.076344, -1.750701, -0.422502
N, 0, -1.529885, 1.774653, 0.197844
C, 0, -0.158662, 1.325316, 0.35771
C, 0, -0.102695, 0.03236, -0.470597
C, 0, 0.94873, 2.255286, -0.071387
N, 0, 2.127983, 1.58571, -0.259513
O, 0, 0.847936, 3.468251, -0.201149
C, 0, 2.308539, 0.194778, -0.08695
C, 0, 3.58646, -0.314661, 0.134228
C, 0, 3.761497, -1.687069, 0.299751
C, 0, 2.664483, -2.544002, 0.257125
C, 0, 1.387491, -2.028387, 0.027899
C, 0, 1.193745, -0.663429, -0.156764
H, 0, -3.912629, -2.877697, -0.33196
H, 0, -5.290809, -0.94204, 0.36141
H, 0, -4.265517, 1.30679, 0.646311
H, 0, -1.48614, -2.601031, -0.748512
H, 0, -1.842645, 2.465785, 0.869333
H, 0, 0.051147, 1.063545, 1.411239
H, 0, -0.056803, 0.329046, -1.533756
H, 0, 2.949381, 2.155381, -0.426632
H, 0, 4.435359, 0.361745, 0.181799
H, 0, 4.758076, -2.081634, 0.471996
H, 0, 2.797925, -3.611708, 0.399326
H, 0, 0.538094, -2.701322, -0.007952



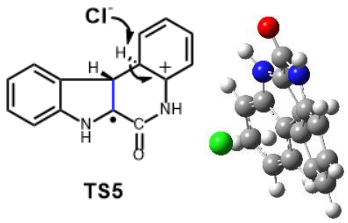
IND1

SCF Done: E(RωB97XD) = -763.40341a.u.

Zero-point correction = 0.242166 (Hartree/Particle)

Sum of electronic and thermal Free Energies = -763.200831a.u.

C 3.47482500 -1.87251900 0.07498900
C 4.24254600 -0.73766500 -0.19480100
C 3.66228900 0.53040400 -0.24102300
C 2.29343100 0.60604100 -0.02922800
C 1.49834700 -0.52215500 0.22173200
C 2.09807500 -1.77075100 0.29985200
N 1.48825800 1.75269600 -0.01339900
C 0.20176700 1.42170800 0.19621700
C 0.08473500 -0.05092000 0.49186400
C -0.90716100 2.27348500 0.04234900
N -2.15426400 1.56611200 0.10997900
O -0.91488200 3.49565500 -0.13879300
C -2.31445000 0.26126400 -0.04674300
C -3.60666500 -0.31807900 0.01679300
C -3.73019000 -1.67586400 -0.01618900
C -2.59938400 -2.56211500 -0.12813200
C -1.35768100 -2.05759800 -0.24255400
C -1.10538900 -0.59005700 -0.32312500
H 3.95244000 -2.84572100 0.11937200
H 5.31004000 -0.83894100 -0.36241600
H 4.25298100 1.42001100 -0.43208300
H 1.52243100 -2.65853000 0.53897400
H 1.80641100 2.68548600 -0.24858400
H -0.14466100 -0.19517600 1.55988400
H -2.98002200 2.15308700 0.21030600
H -4.47131800 0.32582300 0.13836700
H -4.72219700 -2.11049600 0.05969900
H -2.76899700 -3.63253700 -0.12252400
H -0.50083000 -2.71034900 -0.36364400
H -0.88575900 -0.40063400 -1.39507200



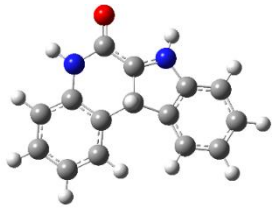
TS5

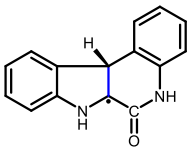
SCF Done: E(RωB97XD) = -1223.7958a.u.

Zero-point correction = 0.237962 (Hartree/Particle)

Sum of electronic and thermal Free Energies = -1223.600487a.u.

C -3.53048600 -1.86199500 -0.33476200
C -4.27490600 -0.75513100 0.07759800
C -3.70077700 0.51514500 0.14329600
C -2.36036000 0.62493600 -0.19949000
C -1.58814700 -0.47697100 -0.59848600
C -2.18358000 -1.72638300 -0.68813200
N -1.57214700 1.77972700 -0.22396200
C -0.29741900 1.46799300 -0.55613000
C -0.20642400 0.02480900 -0.97045800
C 0.81910800 2.31194200 -0.38705400
N 2.05929700 1.63098400 -0.50308200
O 0.80690400 3.52358800 -0.13374600
C 2.22296700 0.29312200 -0.44044000
C 3.51934300 -0.25732100 -0.36661900
C 3.67510700 -1.62137000 -0.33549000
C 2.56895800 -2.51301400 -0.39125400
C 1.30796500 -2.00603700 -0.45416400
C 1.05826500 -0.57800600 -0.34828600
H -4.00106400 -2.83850600 -0.38583900
H -5.31909600 -0.87996200 0.34683100
H -4.27499100 1.38250400 0.45177600
H -1.62505700 -2.59307300 -1.02560400
H -1.84500300 2.66557300 0.18260400
H -0.09602200 -0.03653600 -2.06581700
H 2.88102400 2.22109400 -0.41844100
H 4.37915200 0.40474400 -0.35450600
H 4.67904900 -2.03096300 -0.27875900
H 2.73972200 -3.58328400 -0.39244200
H 0.45059600 -2.66853200 -0.48689600
H 0.88230400 -0.49301600 0.87870100
Cl 0.53567200 -0.25082600 2.63570000





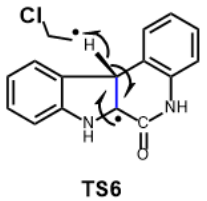
IND2

SCF Done: E(RωB97XD) = -762.99561a.u.

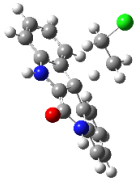
Zero-point correction = 0.229548 (Hartree/Particle)

Sum of electronic and thermal Free Energies = -762.805894a.u.

C 3.48461600 -1.79158500 0.11992900
C 4.16626700 -0.69989600 -0.42183200
C 3.54265100 0.54070600 -0.56477600
C 2.21524000 0.63884600 -0.16557000
C 1.50253600 -0.45395900 0.35638500
C 2.14989700 -1.66958800 0.52358100
N 1.39336800 1.76587900 -0.18276500
C 0.14222600 1.44008800 0.24355300
C 0.11628700 0.02437800 0.74574200
C -1.01764300 2.24504600 0.10109200
N -2.19980400 1.53645100 0.30991700
O -1.02710600 3.45583800 -0.18492500
C -2.28813600 0.14796000 0.10708100
C -3.51399600 -0.42481600 -0.24268300
C -3.60405400 -1.79437100 -0.46980100
C -2.47110200 -2.59897100 -0.36188900
C -1.25162800 -2.02607800 -0.00321200
C -1.14440400 -0.66025500 0.24674000
H 3.99496300 -2.74241600 0.23570200
H 5.20171000 -0.81133600 -0.72891100
H 4.07249400 1.39749000 -0.96839300
H 1.64024200 -2.51832000 0.96842600
H 1.62256000 2.63693800 -0.64210600
H 0.05675200 0.03627100 1.84959900
H -3.04086600 2.07495100 0.14071700
H -4.38969400 0.21019500 -0.34589700
H -4.56075800 -2.22898700 -0.74313300
H -2.53384600 -3.66594300 -0.55038600
H -0.37418900 -2.65688500 0.08767900

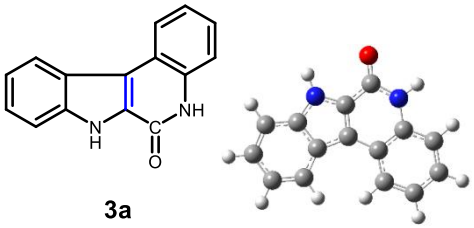


TS6



SCF Done: E(RωB97XD) = -1301.7616a.u.
Zero-point correction = 0.279348 (Hartree/Particle)
Sum of electronic and thermal Free Energies = -1301.532196a.u.

C 2.14250500 3.16327400 -0.86237800
C 2.82226200 3.15868600 0.35309700
C 2.46080000 2.27697700 1.37966400
C 1.39744000 1.42317700 1.14095900
C 0.67839600 1.42766900 -0.07119600
C 1.06942900 2.28794700 -1.08655200
N 0.87685400 0.43694300 1.98879200
C -0.17040100 -0.19147800 1.39686600
C -0.32847000 0.32687600 -0.00528300
C -1.04420300 -1.13637100 1.97952900
N -2.14222100 -1.43712700 1.16454300
O -0.89912400 -1.67474600 3.09400600
C -2.61417900 -0.57081200 0.16519100
C -3.94595600 -0.65035100 -0.24666100
C -4.42436100 0.19988400 -1.24016600
C -3.58272900 1.14731800 -1.82127100
C -2.25334700 1.22749100 -1.41368800
C -1.74693200 0.37463600 -0.42970000
H 2.44788100 3.84598700 -1.64881900
H 3.65071200 3.84252700 0.50970900
H 2.99468300 2.26033200 2.32421400
H 0.56626300 2.28543100 -2.04757300
H 1.14464800 0.30908900 2.95582800
H 0.21011400 -0.62852000 -0.68965700
H -2.82475800 -2.04750200 1.59683300
H -4.60498700 -1.37819200 0.21863500
H -5.46167400 0.12515900 -1.55179800
H -3.95625200 1.81830000 -2.58801800
H -1.60008500 1.96466700 -1.86746100
C 2.24654300 -1.67728300 -0.71162200
H 2.27094900 -1.82167500 0.36823000
H 2.77186400 -0.76112000 -0.98050100
C 0.87097500 -1.73292700 -1.26538100
H 0.76628000 -1.48364100 -2.32172500
H 0.25235500 -2.56794700 -0.93720800
Cl 3.29152500 -3.04070100 -1.39614900



3a

SCF Done: E(RωB97XD) = -762.44906a.u.

Zero-point correction = 0.219774 (Hartree/Particle)

Sum of electronic and thermal Free Energies = -762.267991a.u.

C -3.42666500 -1.94492400 0.01030800
C -4.25478900 -0.80235800 0.00171400
C -3.71786500 0.47247900 -0.00489800
C -2.32156900 0.58466300 -0.00454000
C -1.46547700 -0.54856100 0.00026900
C -2.04714600 -1.83070900 0.01015200
N -1.54817700 1.71751200 -0.00723800
C -0.23360000 1.34372600 -0.00418800
C -0.11476800 -0.03500500 -0.00186800
C 0.88136800 2.26670400 0.00049800
N 2.09355700 1.62989300 0.00773100
O 0.77699200 3.49809900 -0.00021500
C 2.30449300 0.25350600 0.00506200
C 3.61786600 -0.23548700 0.00835400
C 3.84582600 -1.60111800 0.00184100
C 2.76684700 -2.49466800 -0.01003200
C 1.46797200 -2.01360200 -0.01247200
C 1.20388300 -0.63250500 -0.00233100
H -3.88171200 -2.93046500 0.01792000
H -5.33337200 -0.92714500 0.00148600
H -4.34803000 1.35621400 -0.00964500
H -1.43582600 -2.72573400 0.02043200
H -1.88067600 2.67116700 -0.00853700
H 2.90731500 2.23485300 0.01287500
H 4.44730200 0.46621400 0.01529900
H 4.86477900 -1.97506500 0.00450800
H 2.94616400 -3.56499000 -0.01793100
H 0.64220000 -2.71451400 -0.02534900

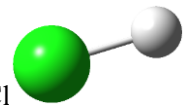
Cl^-

SCF Done: E(RωB97XD) = -460.37044a.u.

Zero-point correction = 0(Hartree/Particle)

Sum of electronic and thermal Free Energies = -460.385463a.u.

Cl 0.00000000 0.00000000 0.00000000

HCl 

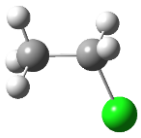
SCF Done: E(RωB97XD) = -460.82317a.u.

Zero-point correction = 0.006691 (Hartree/Particle)

Sum of electronic and thermal Free Energies = -460.834369a.u.

Cl 0.00000000 0.00000000 0.07155600

H 0.00000000 0.00000000 -1.21645000

CH_3CH_2Cl 

SCF Done: E(RωB97XD) = -539.45177a.u.

Zero-point correction = 0.063277 (Hartree/Particle)

Sum of electronic and thermal Free Energies = -539.417416a.u.

C 0 -1.50878800 0.63477900 0.00000000

H 0 -1.85356800 0.09905500 0.88922700

H 0 -1.85356800 0.09905500 -0.88922700

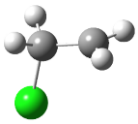
C -1 0.00000000 0.78797800 0.00000000

H 0 0.33944600 1.32877700 -0.88502200

H 0 0.33944600 1.32877700 0.88502200

Cl -1 0.82620700 -0.76604400 0.00000000

H 0 -1.96454800 1.63054700 0.00000000

$ClCH_2CH_2$ • 

SCF Done: E(RωB97XD) = -538.77592a.u.

Zero-point correction = 0.048859 (Hartree/Particle)

Sum of electronic and thermal Free Energies = -538.756895a.u.

C 0 1.47628600 0.76072400 0.00000000

H 0 2.01641900 0.65280900 -0.93525400

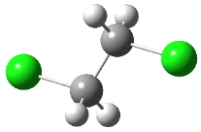
H 0 2.01641900 0.65280900 0.93525400

C -1 0.00000000 0.81864700 0.00000000

H 0 -0.38116600 1.32640500 0.88771400

H 0 -0.38116600 1.32640500 -0.88771400

Cl -1 -0.71342500 -0.79027400 0.00000000

$ClCH_2CH_2Cl$ 

SCF Done: E(RωB97XD) = -999.06351a.u.

Zero-point correction = 0.05472 (Hartree/Particle)

Sum of electronic and thermal Free Energies = -999.041344a.u.

C 0 -0.48293200 -0.58183000 -0.00018500

H 0 -0.38145800 -1.19753600 0.89337000

H 0 -0.38165900 -1.19739900 -0.89383700

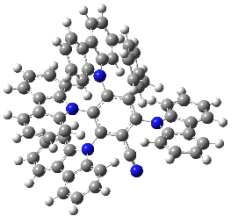
C -1 0.49716700 0.57519700 -0.00018300

H 0 0.38674900 1.19203800 -0.89228700

H 0 0.38658300 1.19208700 0.89186600

Cl -1 2.16204400 -0.06966500 0.00009100

Cl 0 -2.16766900 0.07264200 0.00009100



4CzBnBN

At (U) ωb97xd/6-311+g(d, p) scrf = (smd, solvent=dichloroethane)//(U)B3LYP/6-31g(d) empiricaldispersion = gd3bj level.

SCF Done: E(RωB97XD) = -2659.74a.u.

Zero-point correction = 0.837976 (Hartree/Particle)

Sum of electronic and thermal Free Energies = -2658.987483a.u.

C 1.21414400 -1.66787300 -0.71469200

C -0.17357100 -1.47623800 -0.58590200

C -0.66318000 -0.17153100 -0.35163000

C 0.24555300 0.90281800 -0.24016700

C 1.64098400 0.69996000 -0.27542900

C 2.10843900 -0.59431300 -0.53045700

N 3.49297300 -0.86579200 -0.56541000

C 2.59491100 1.81567400 0.10988800

N -0.25140800 2.20294800 -0.01957800

N -2.04379000 0.05549800 -0.20647000

N -1.03570500 -2.58135600 -0.69534700

C 1.72855200 -2.94954200 -1.08404900

N 2.15469300 -3.98535000 -1.39419900

C -2.19183800 -2.63729700 -1.49573200

C -2.99613800 -3.71647600 -1.06250400

C -2.30050100 -4.34952200 0.04172600

C -1.09483000 -3.63575100 0.24143900

C -2.86595700 -0.55021500 0.75819500

C -4.20427400 -0.15238000 0.52743000

C -4.19176200 0.73598500 -0.61840100

C -2.84695500 0.84346600 -1.04779800

C -0.09509600 3.28030100 -0.89899100
C -0.78526300 4.40071700 -0.37164100
C -1.36952900 3.98296200 0.88851100
C -1.01871900 2.62519500 1.07799500
C 4.39226500 -0.42265900 -1.54019600
C 5.69690200 -0.84249900 -1.17691300
C 5.57481600 -1.56476300 0.07606900
C 4.20111300 -1.55778800 0.42403100
C 2.29091300 2.35128500 1.49808600
C 1.98617500 3.69918100 1.69904900
C 1.64695900 4.16859100 2.96785700
C 1.62093200 3.29479000 4.05365000
C 1.94842200 1.95058900 3.86580200
C 2.28030200 1.48252700 2.59600100
C -5.19212700 1.41347900 -1.32007500
C -4.84249800 2.17521900 -2.43237900
C -3.50588500 2.25216800 -2.85445000
C -2.49196100 1.58123900 -2.17340300
C -2.51509100 -1.36935100 1.82745400
C -3.53997300 -1.83875000 2.64635700
C -4.87722500 -1.47863900 2.41762200
C -5.21441700 -0.62766500 1.36772900
C -2.61373400 -5.41831500 0.88466700
C -1.73249300 -5.75365800 1.90964300
C -0.54377000 -5.03122500 2.09454200
C -0.20771700 -3.96253900 1.26411400
C -2.54782400 -1.83877600 -2.57770200
C -3.76825000 -2.09826200 -3.19706200
C -4.59485300 -3.14758900 -2.76498500
C -4.20976300 -3.96838100 -1.70787100
C 0.57095300 3.33343900 -2.12289100
C 0.55273100 4.54254600 -2.81844200
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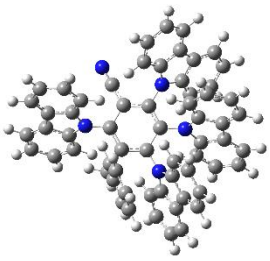

^{3}4CzBnBN*

At (U)wb97xd/6-311+g(d, p) scrf = (smd, solvent=dichloroethane)//(U)B3LYP/6-31g(d) empiricaldispersion = gd3bj level.

SCF Done: E(RωB97XD) = -2659.6323a.u.

Zero-point correction = 0.834259 (Hartree/Particle)

Sum of electronic and thermal Free Energies = -2658.884914a.u.

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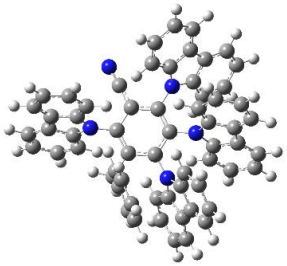

4CzBnBN$^{\bullet-}$

At (U) ωb97xd/6-311+g(d, p) scrf = (smd, solvent=dichloroethane)//(U)B3LYP/6-31g(d) empiricaldispersion=gd3bj level.

SCF Done: E(RωB97XD) = -2659.8329a.u.

Zero-point correction = 0.833924 (Hartree/Particle)

Sum of electronic and thermal Free Energies = -2659.085864a.u.

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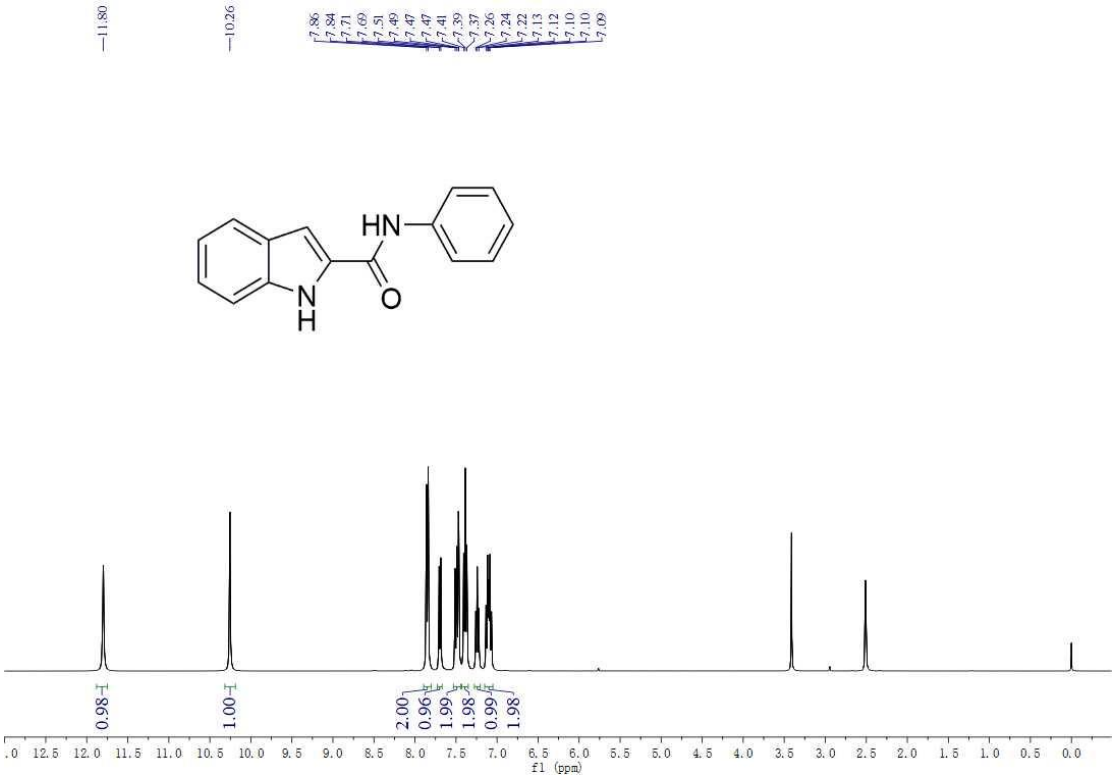
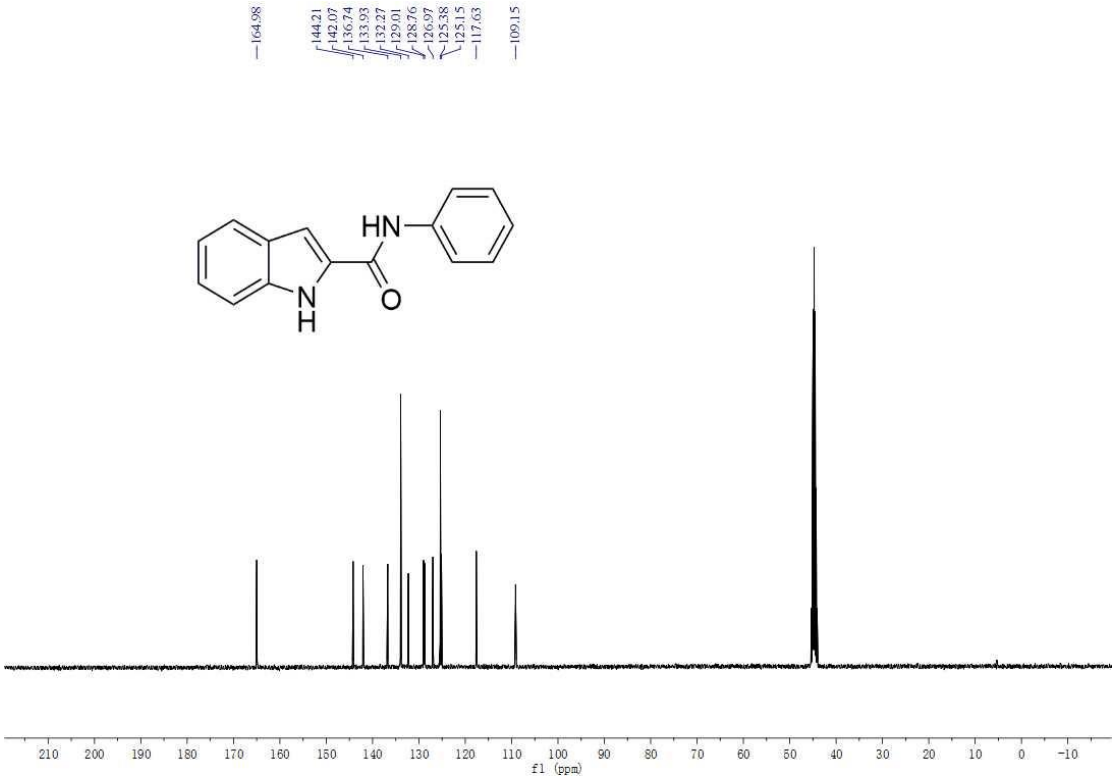
8. Copies of NMR spectra for substrates

^{1}H NMR spectrum of **1a**



^{13}C NMR spectrum of **1a**



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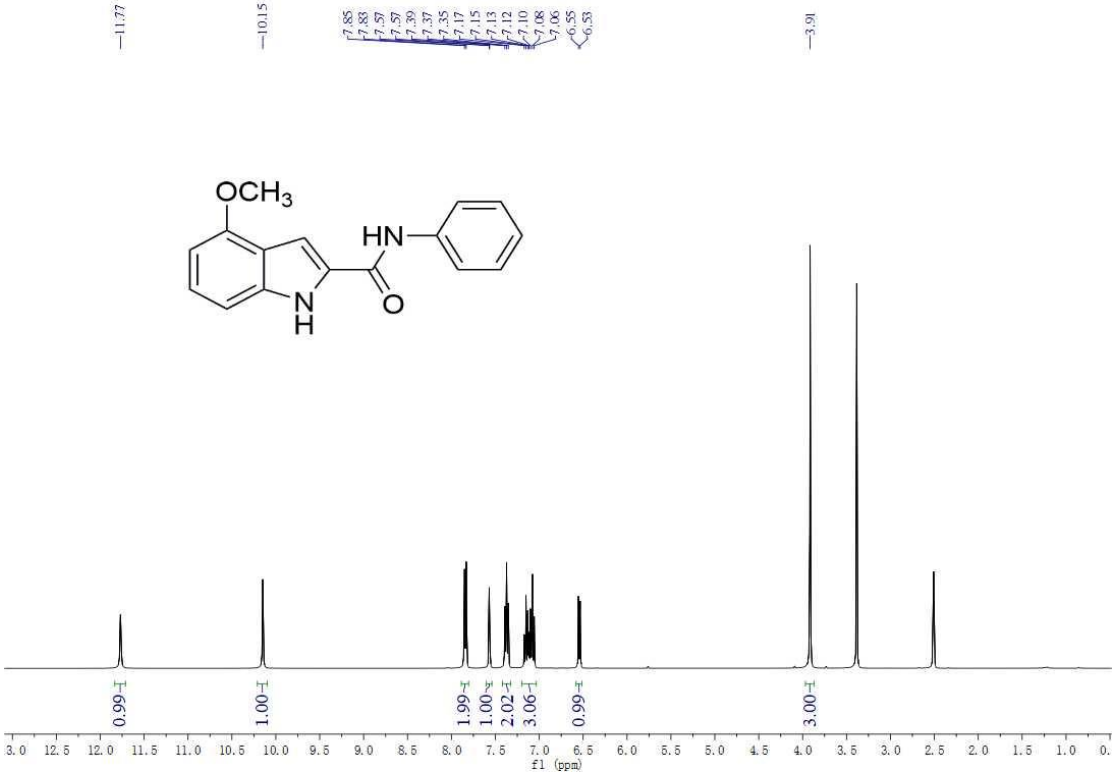

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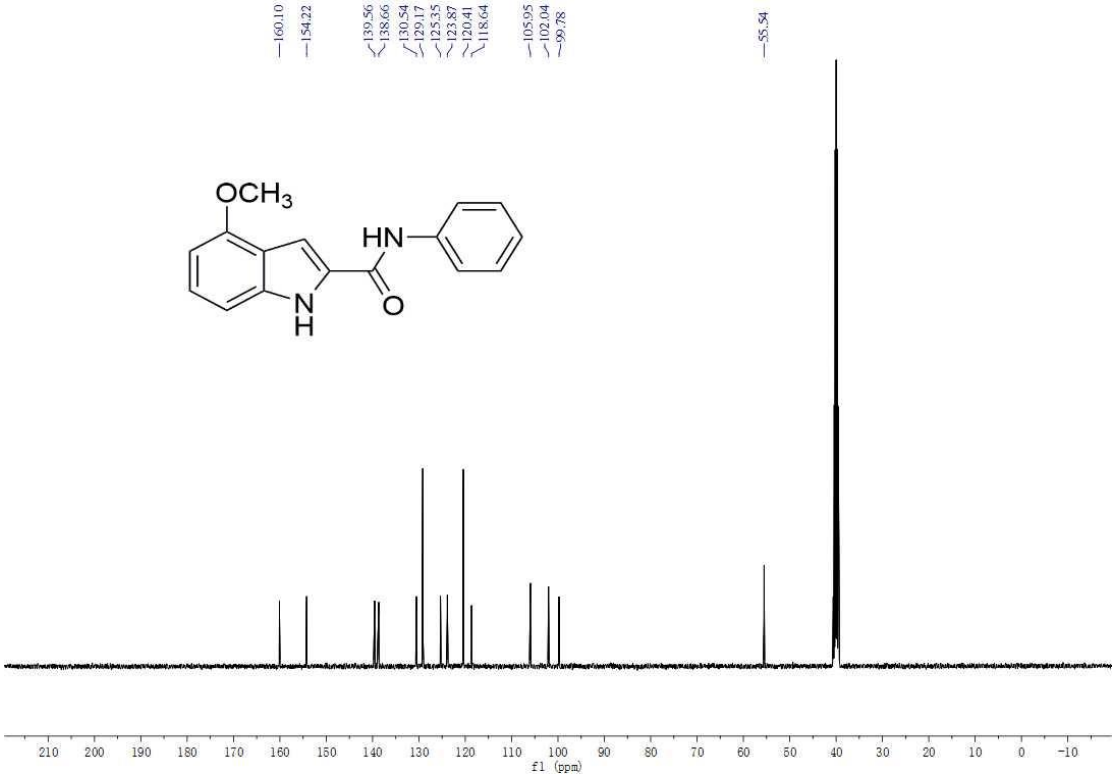

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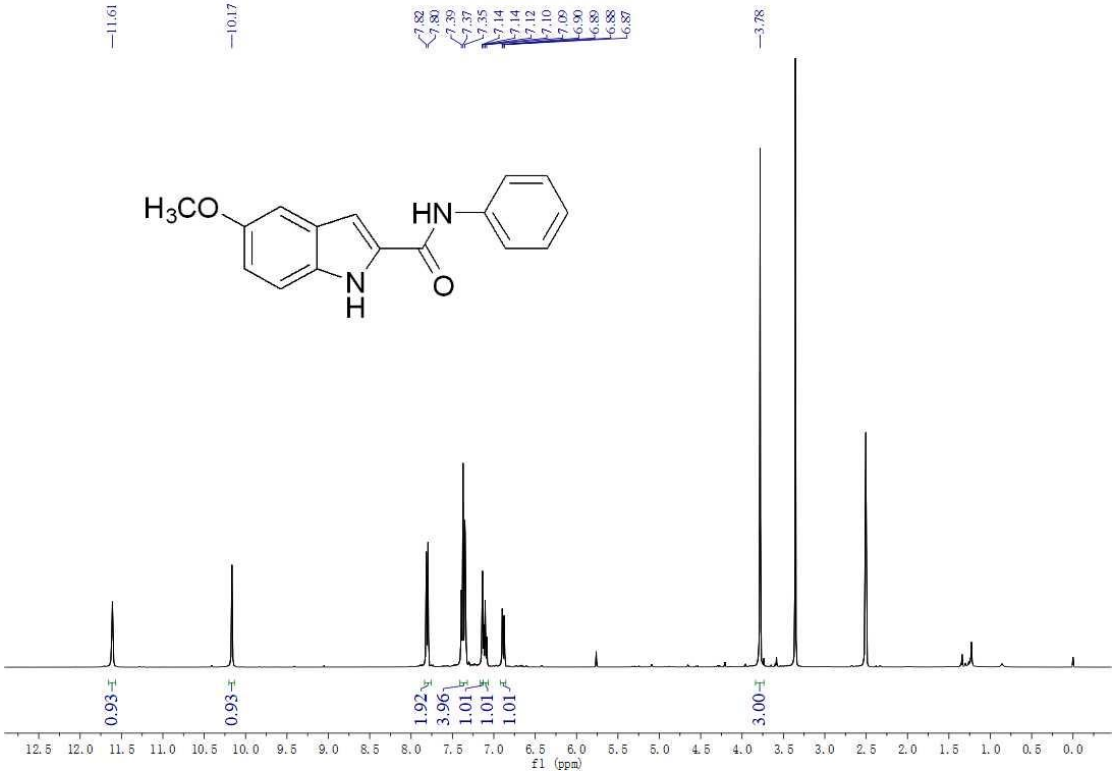

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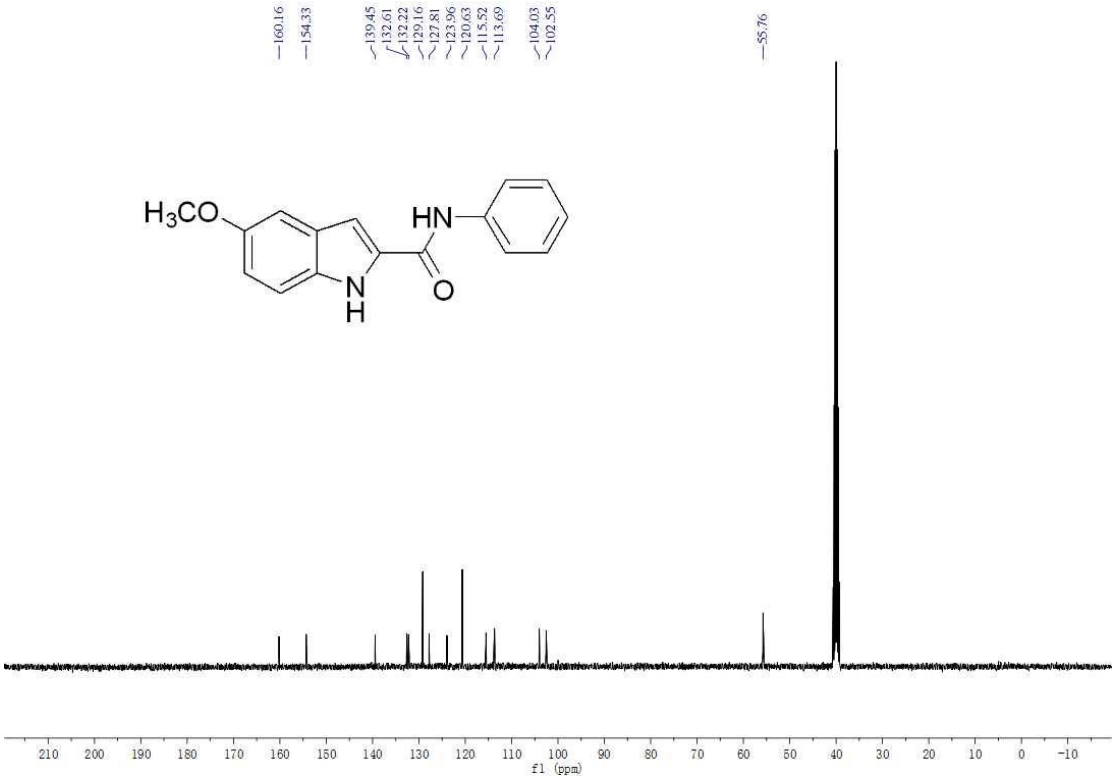

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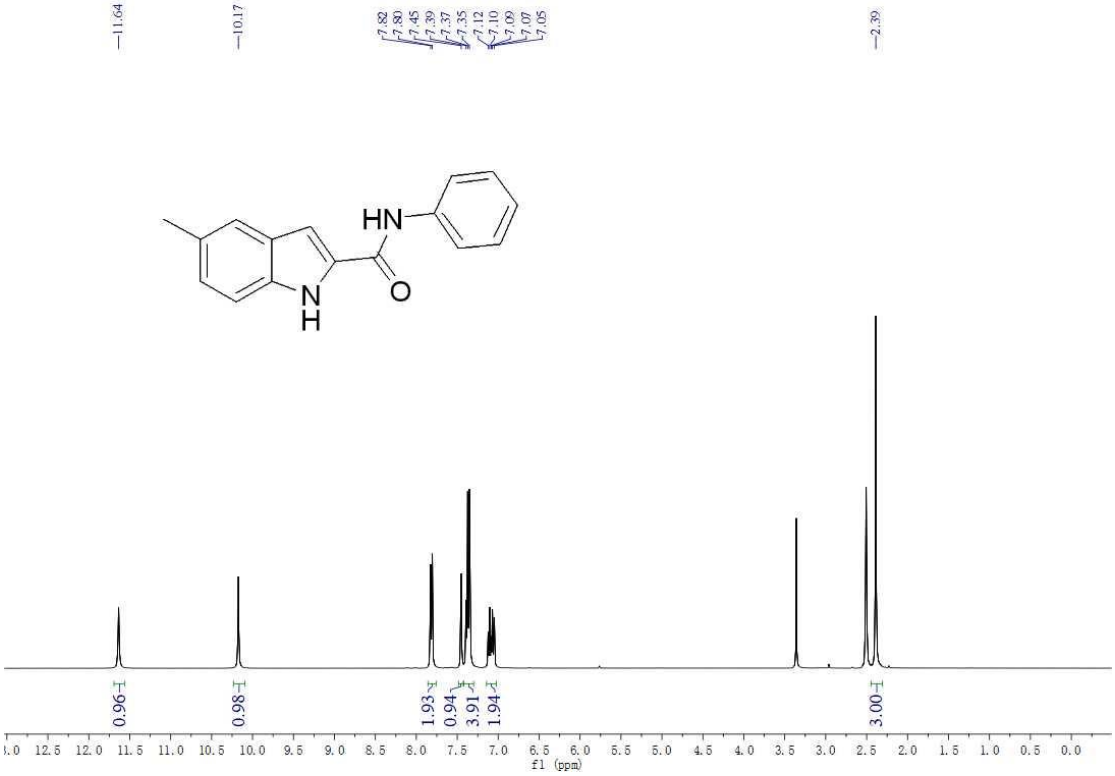

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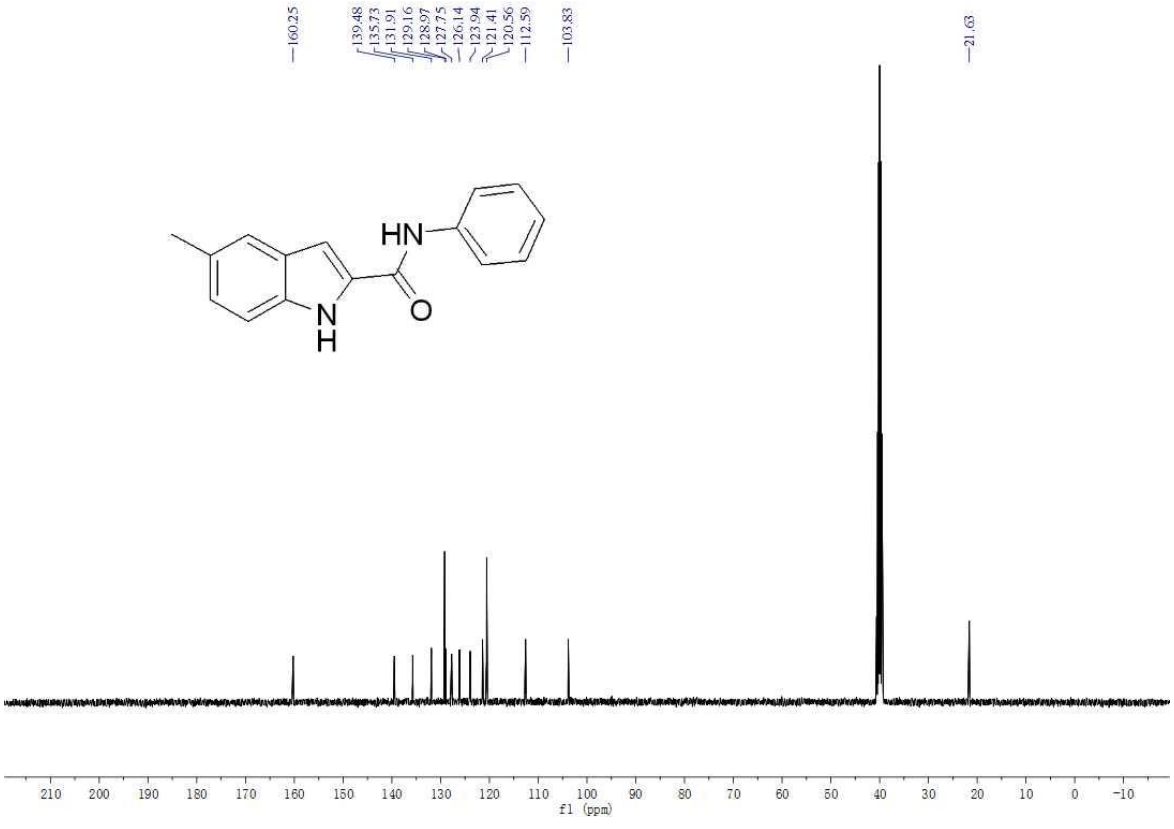

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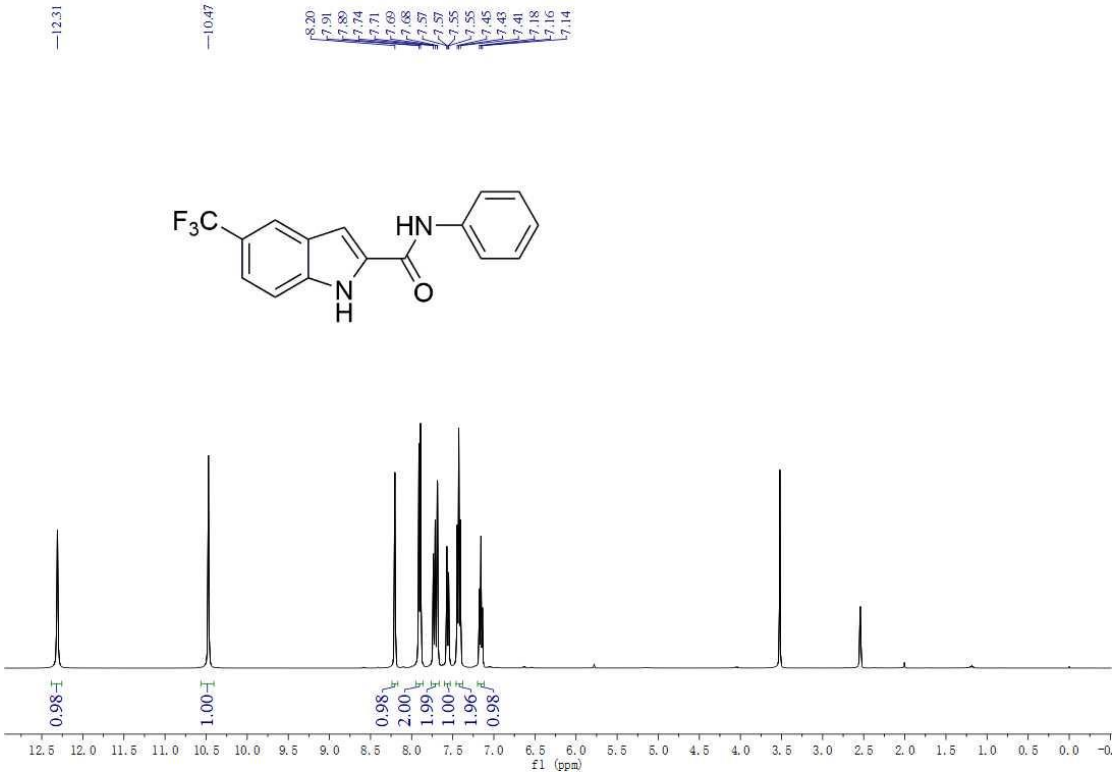

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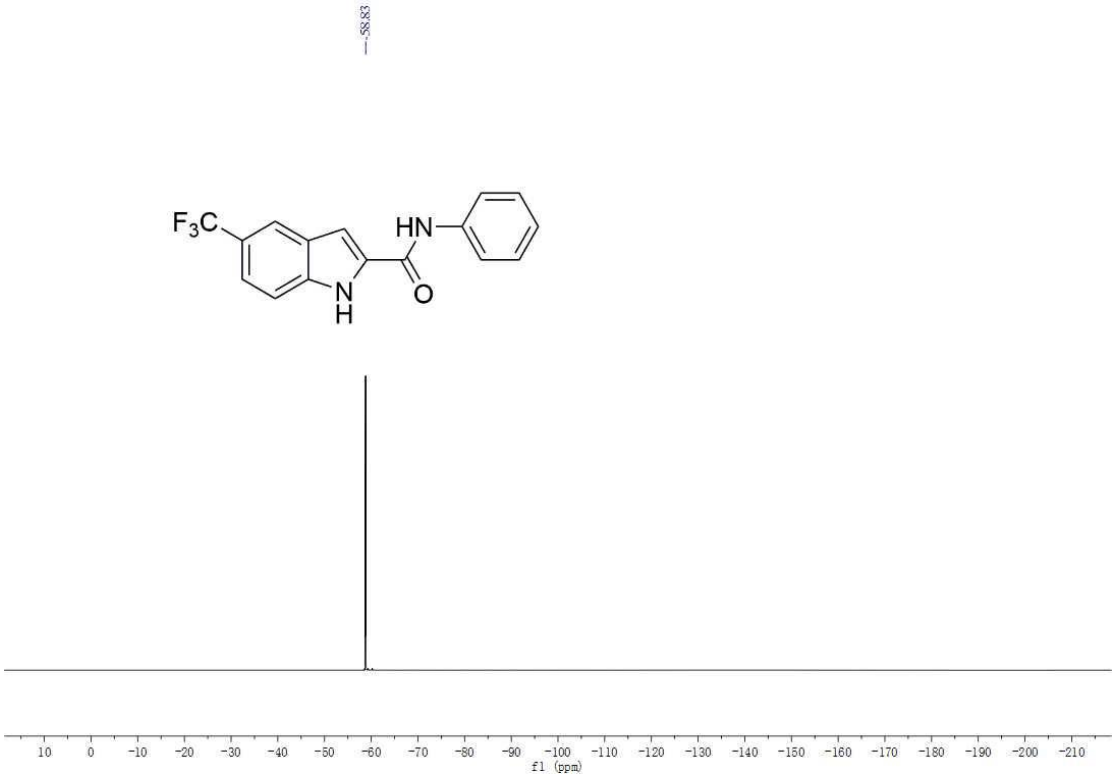

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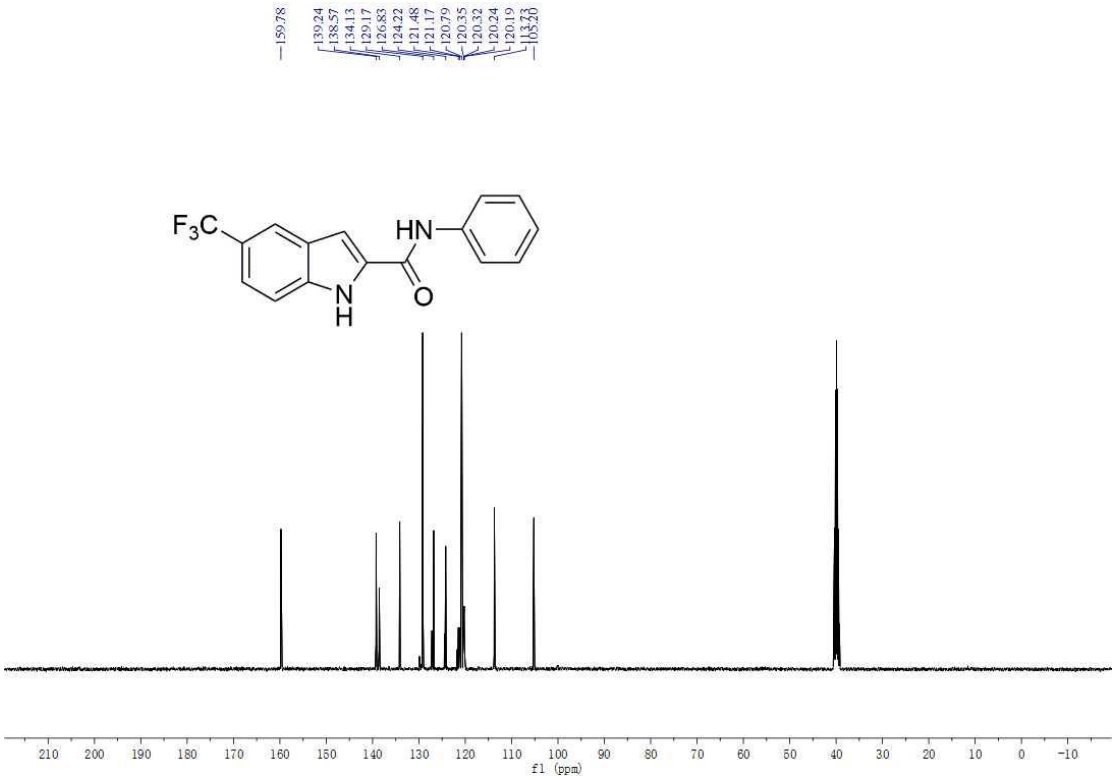

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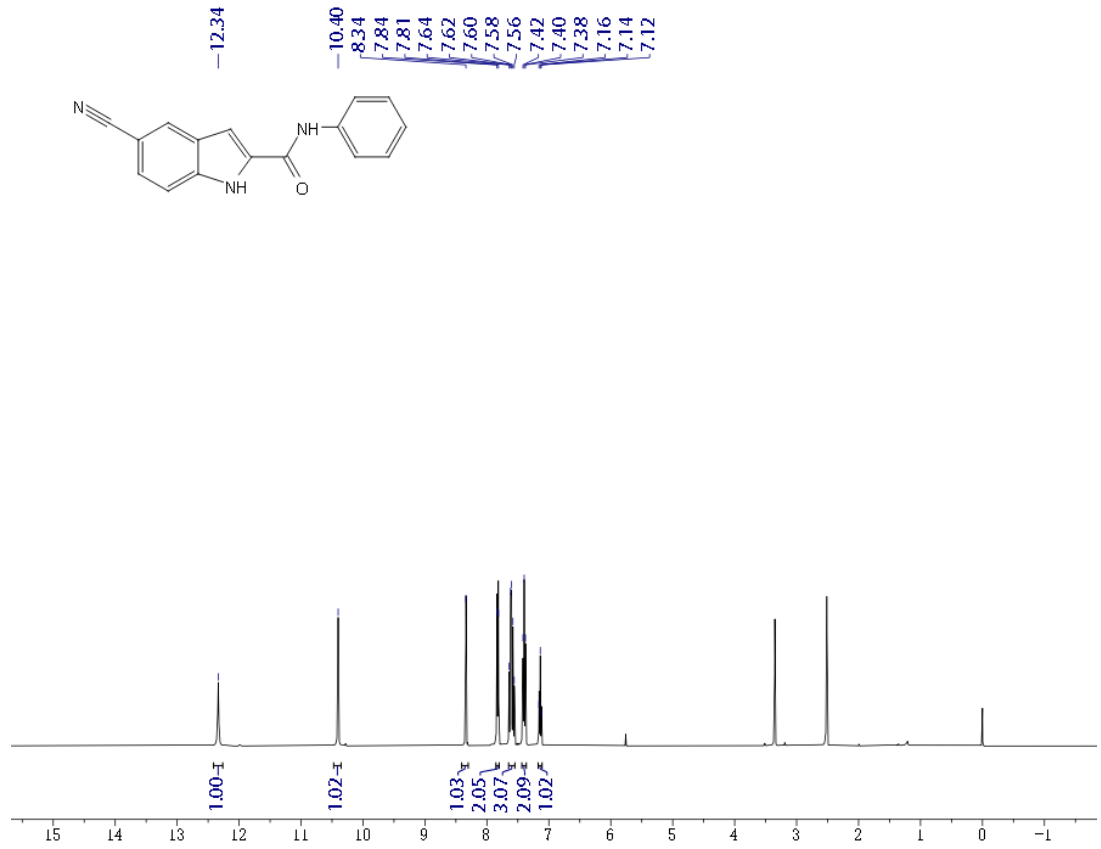

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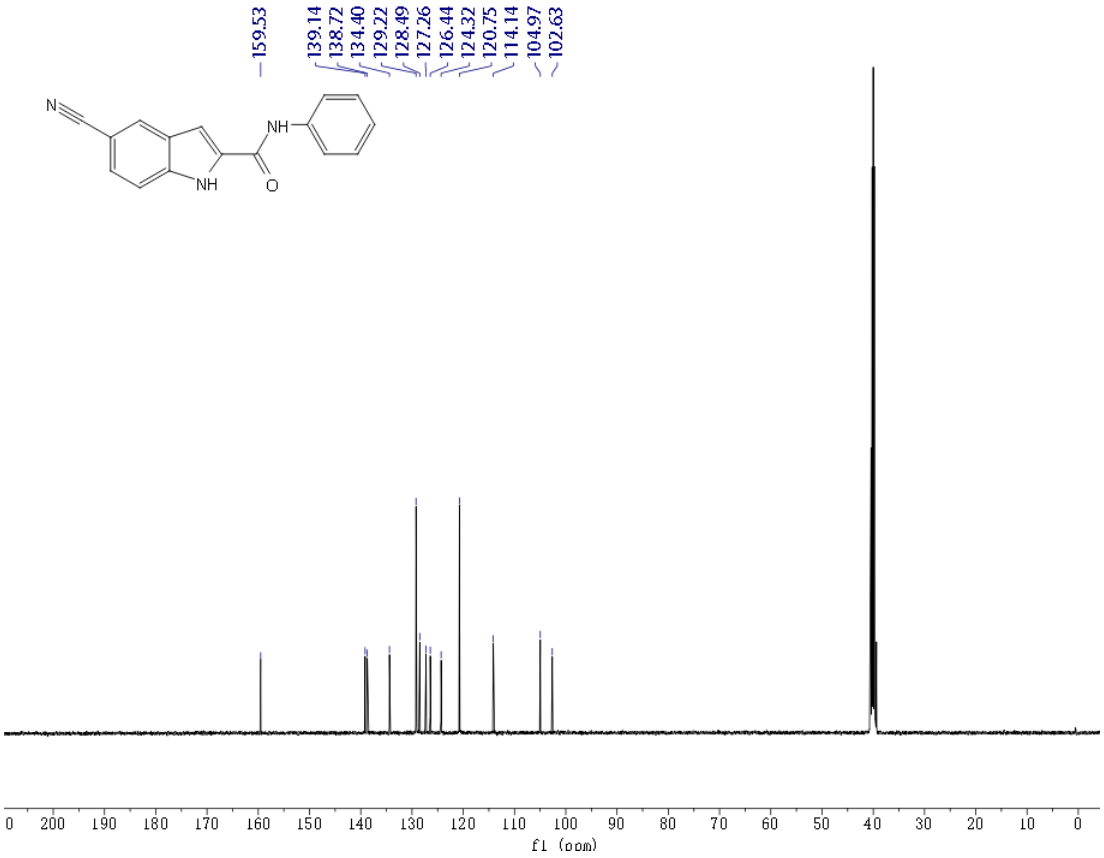

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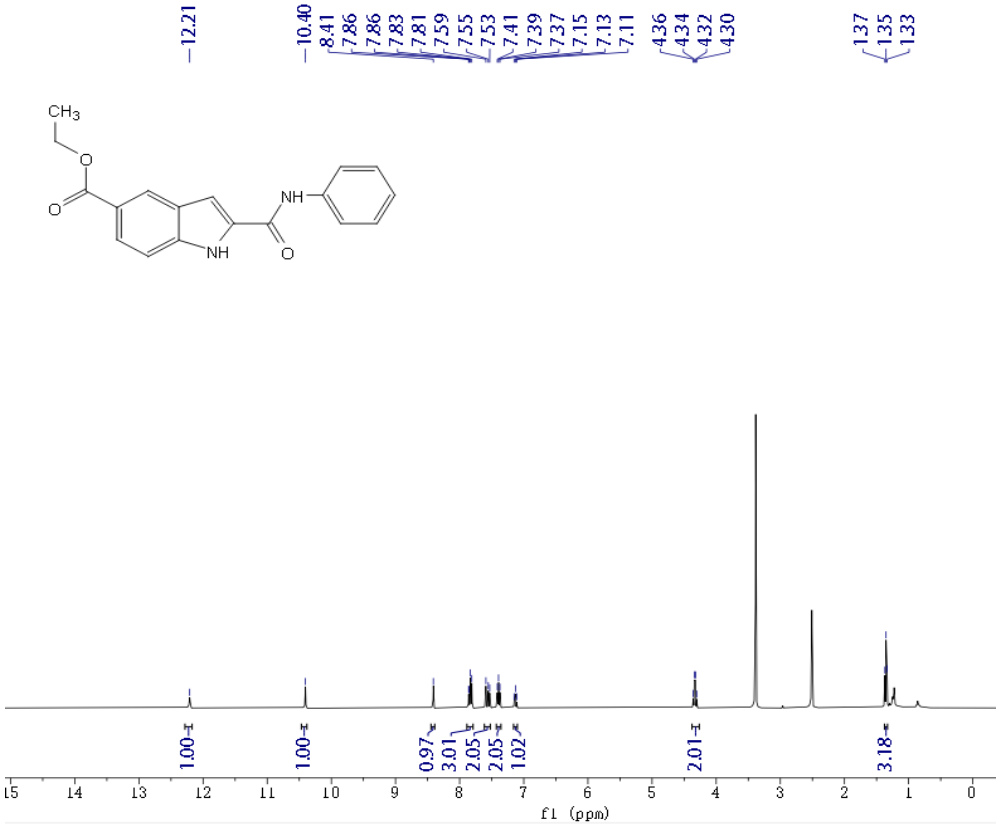

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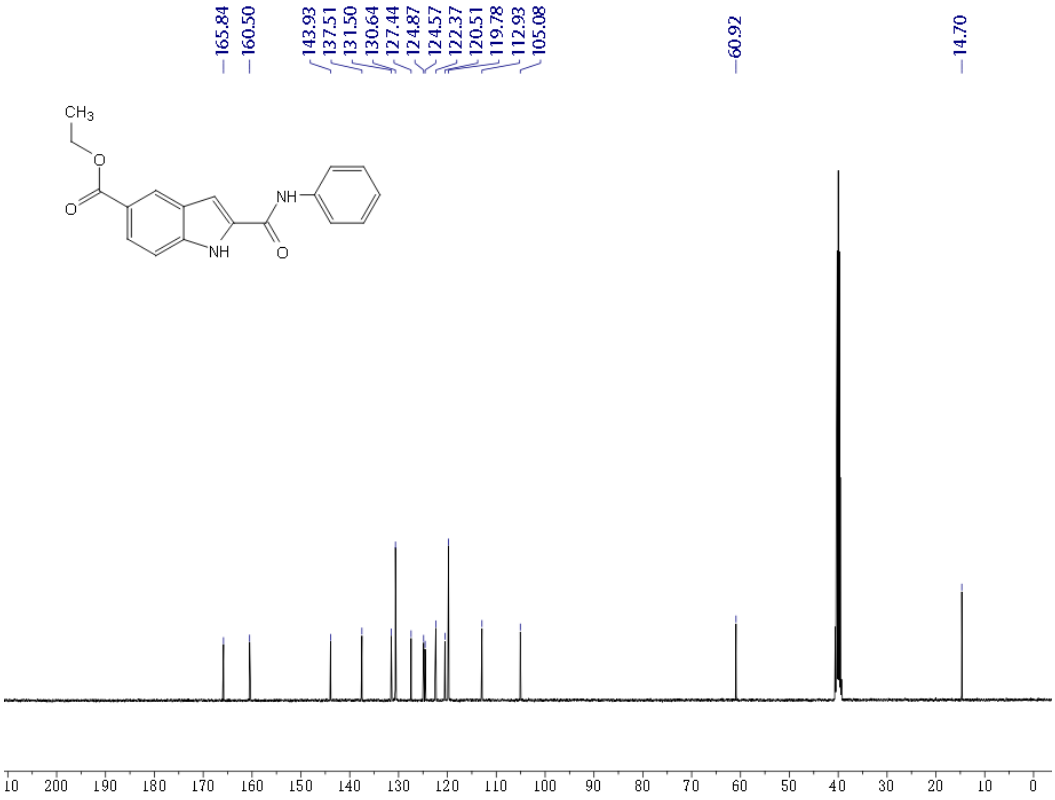
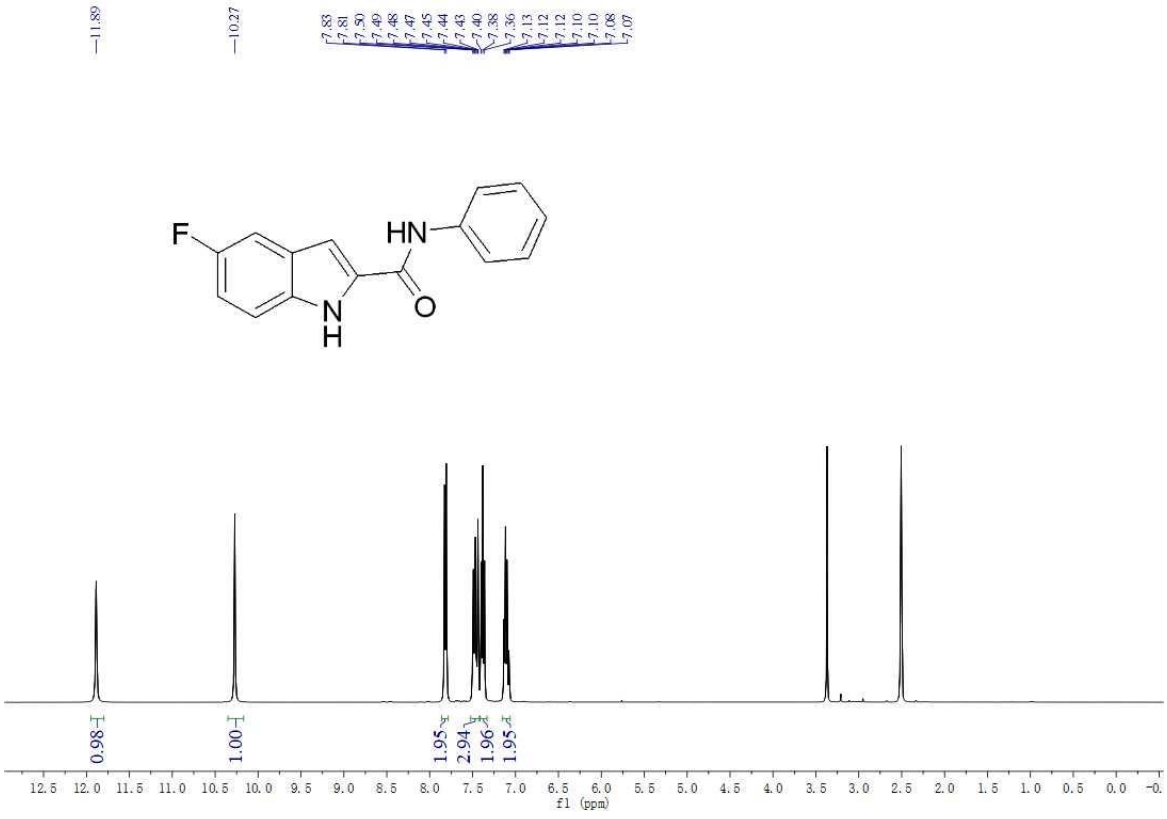


^{1}H NMR spectrum of **1h**



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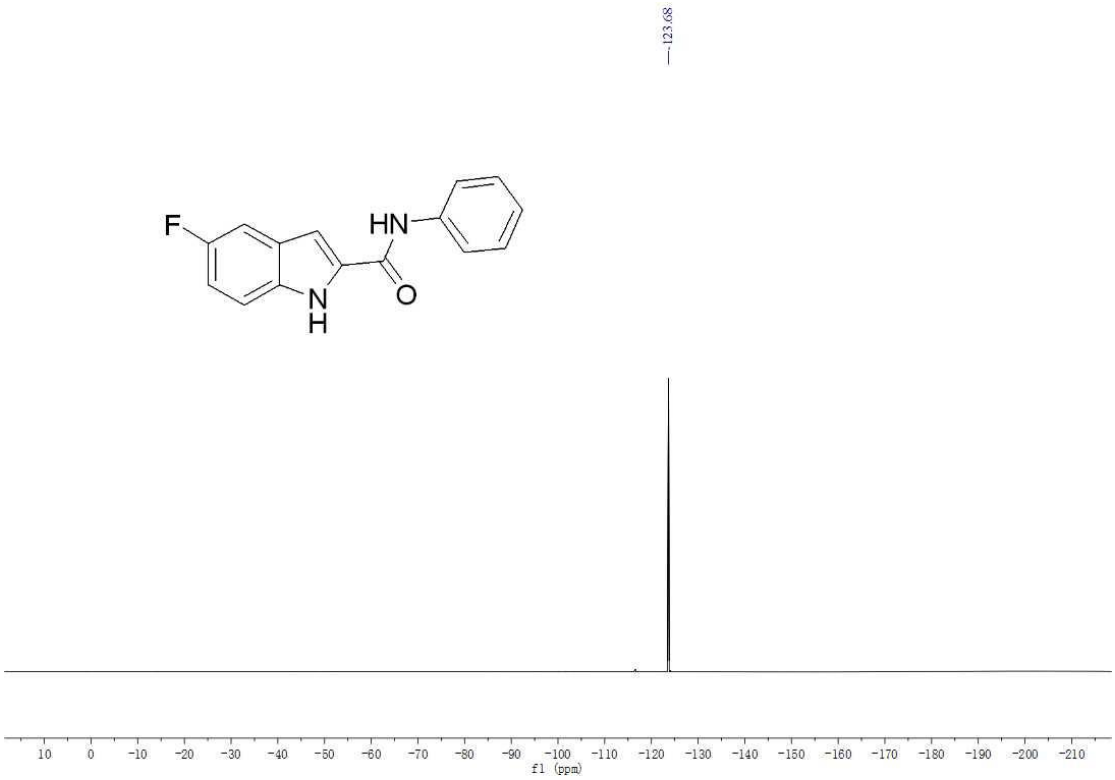

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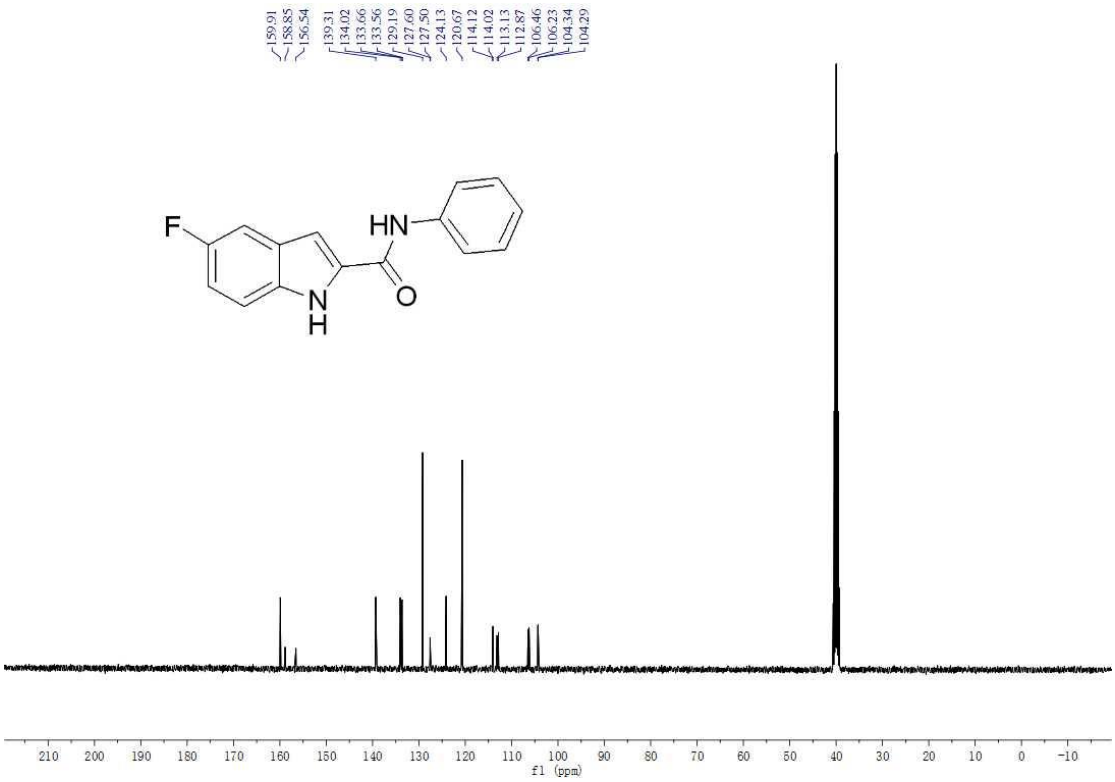

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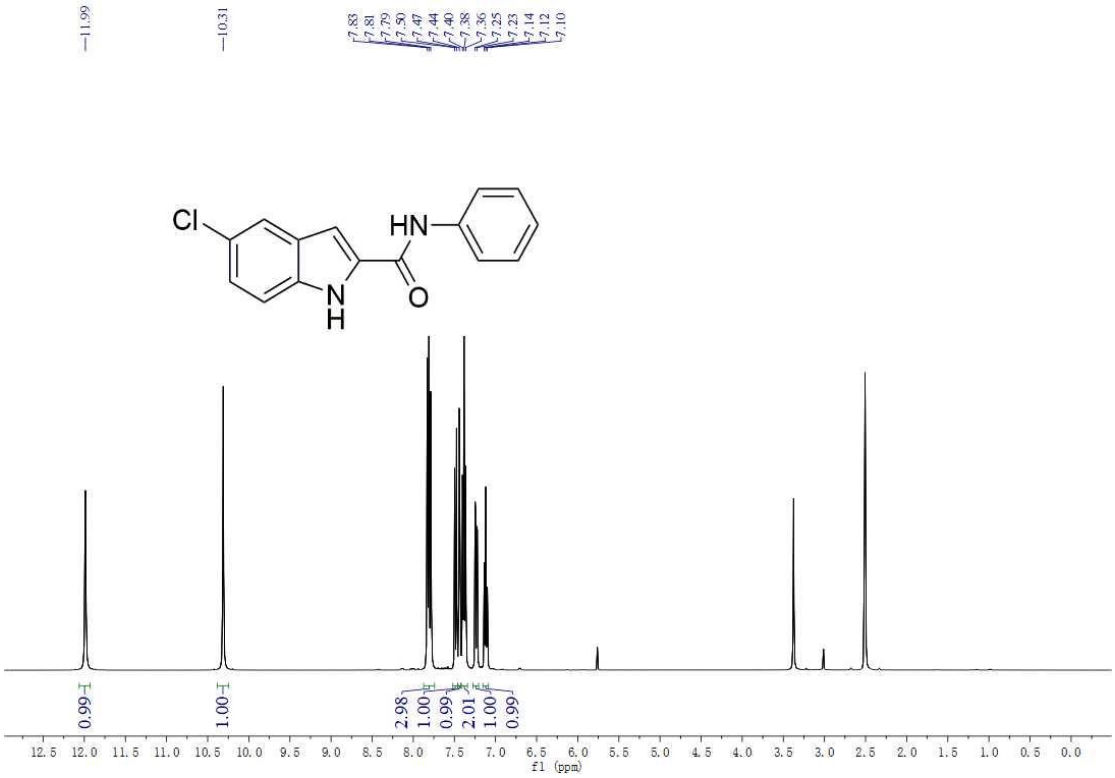

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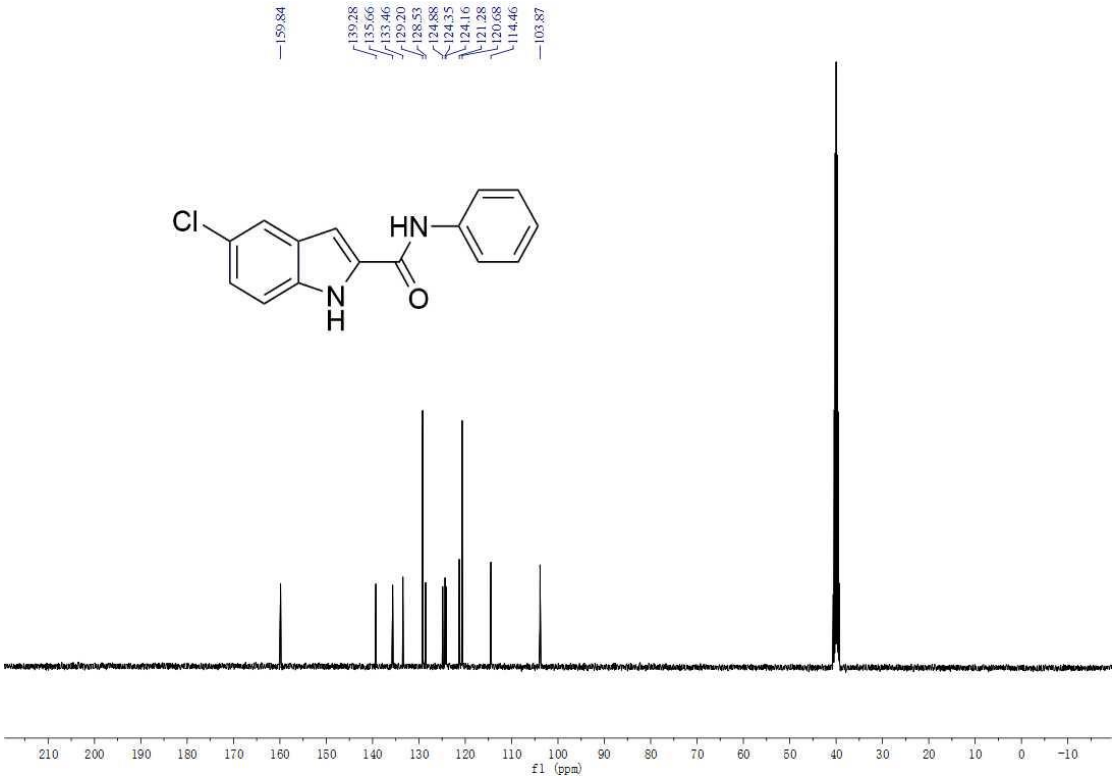

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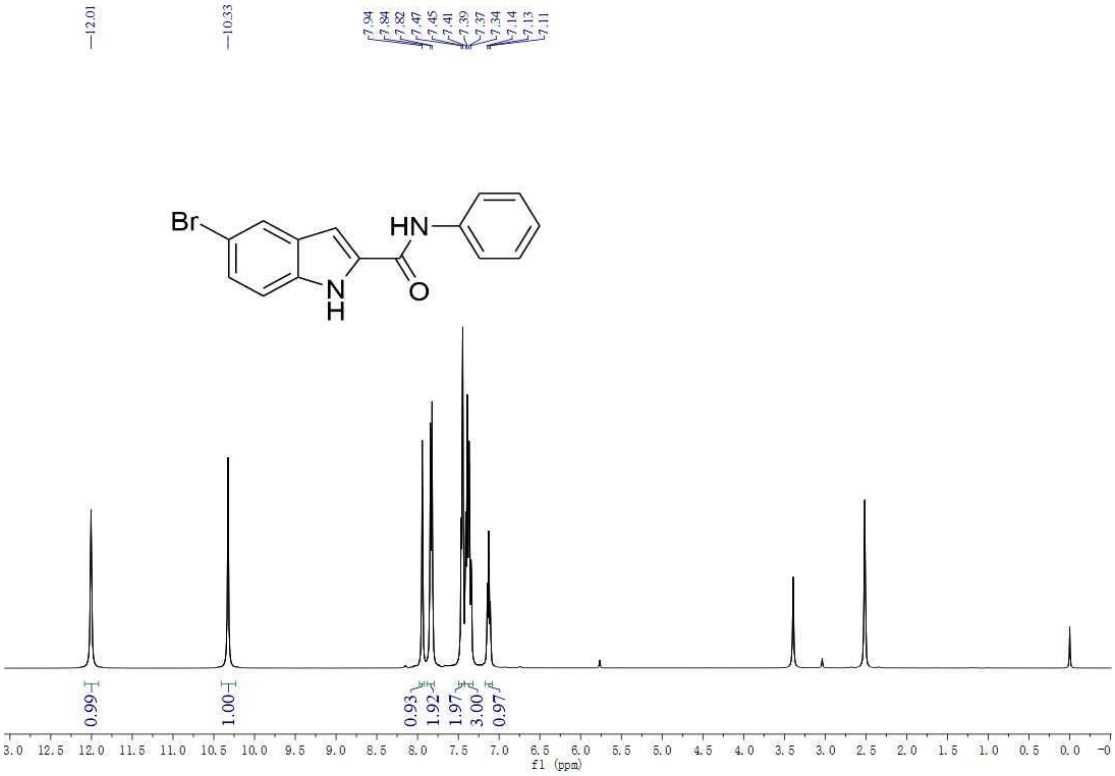

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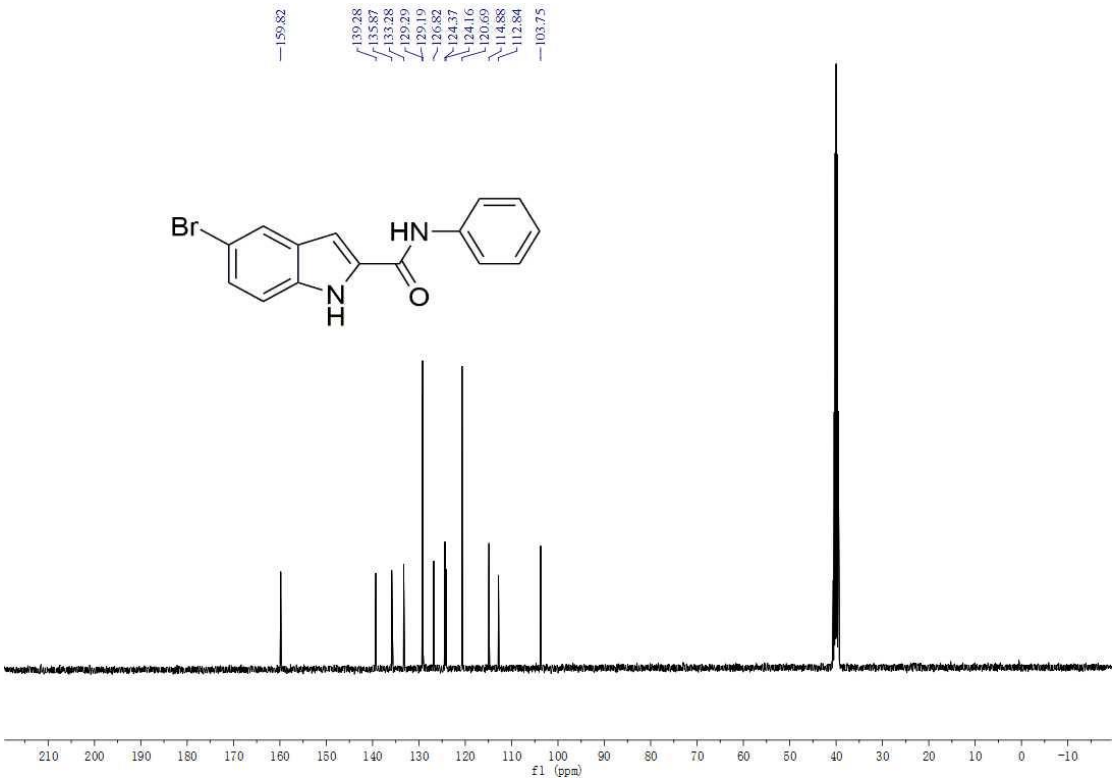

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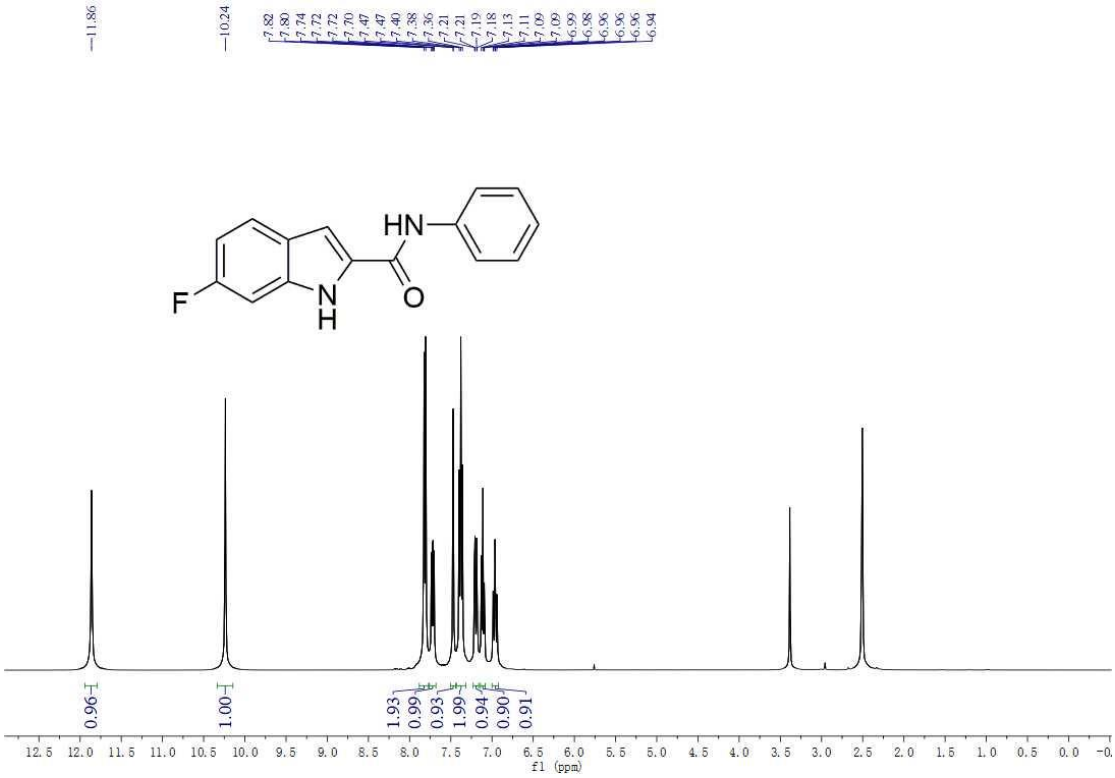

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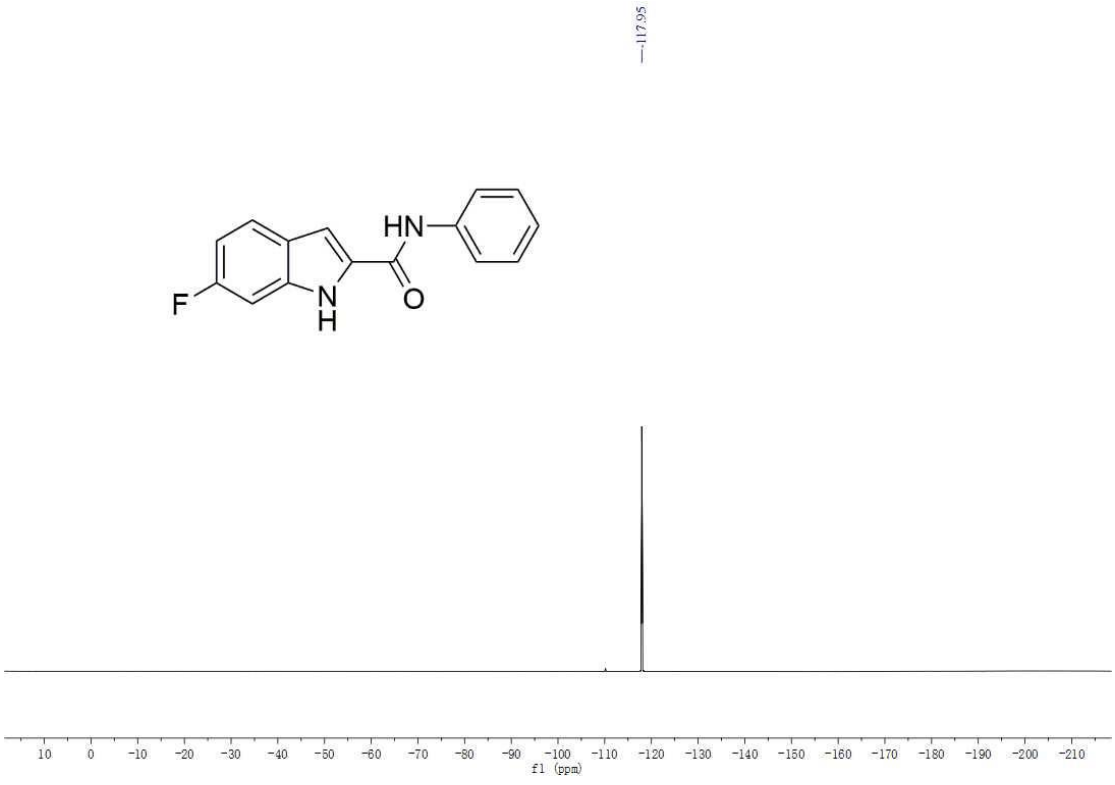

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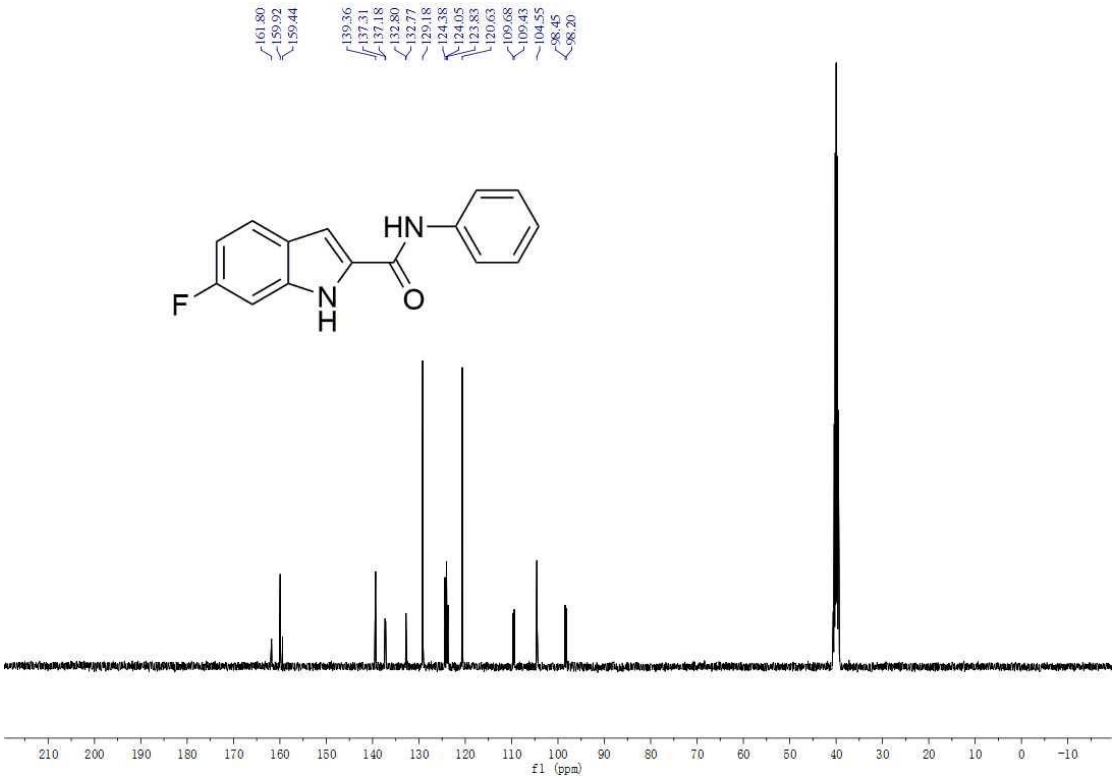

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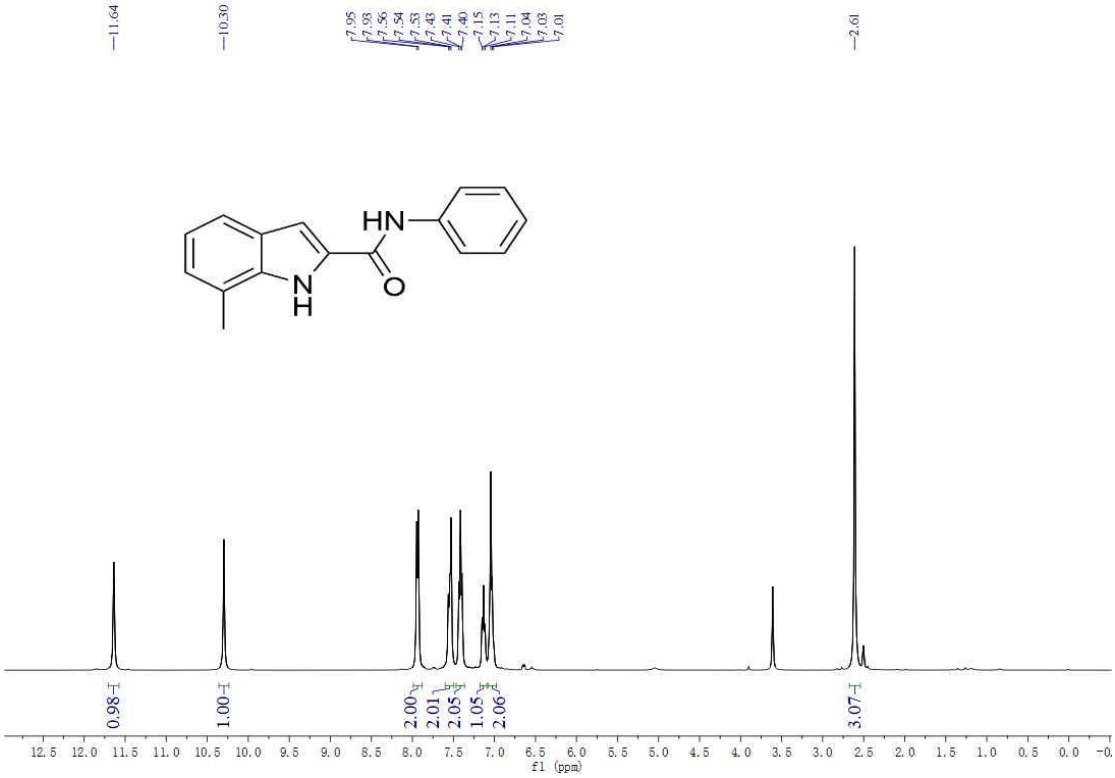

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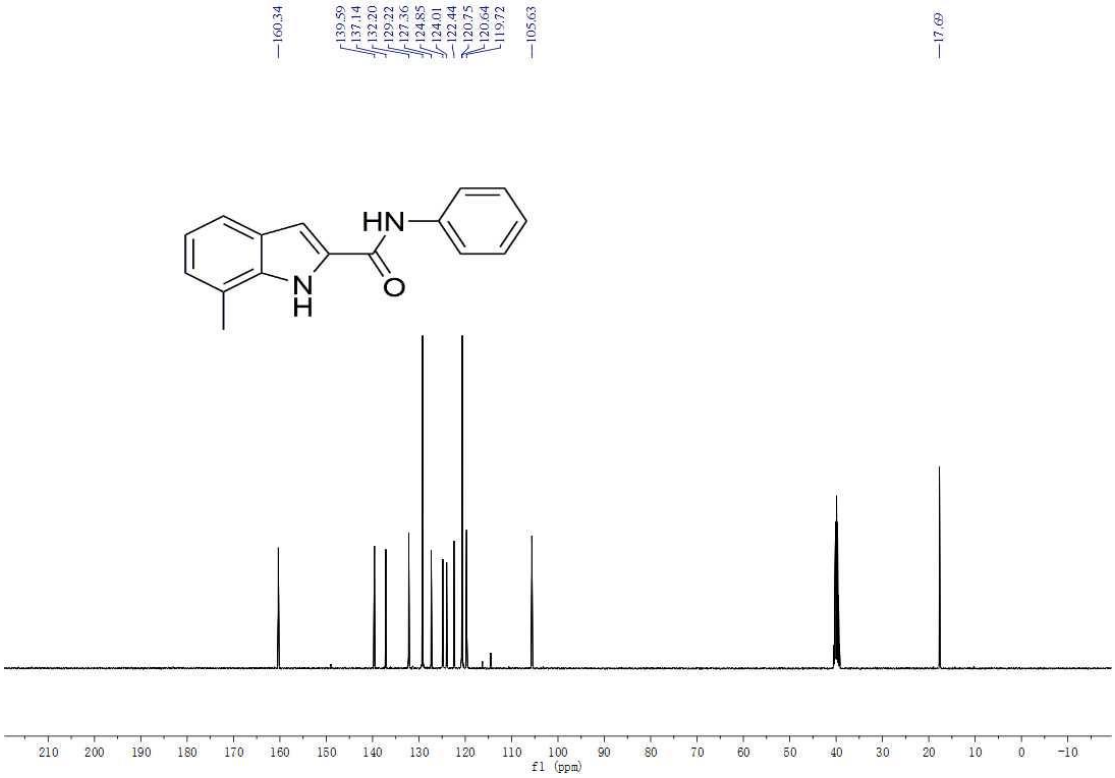

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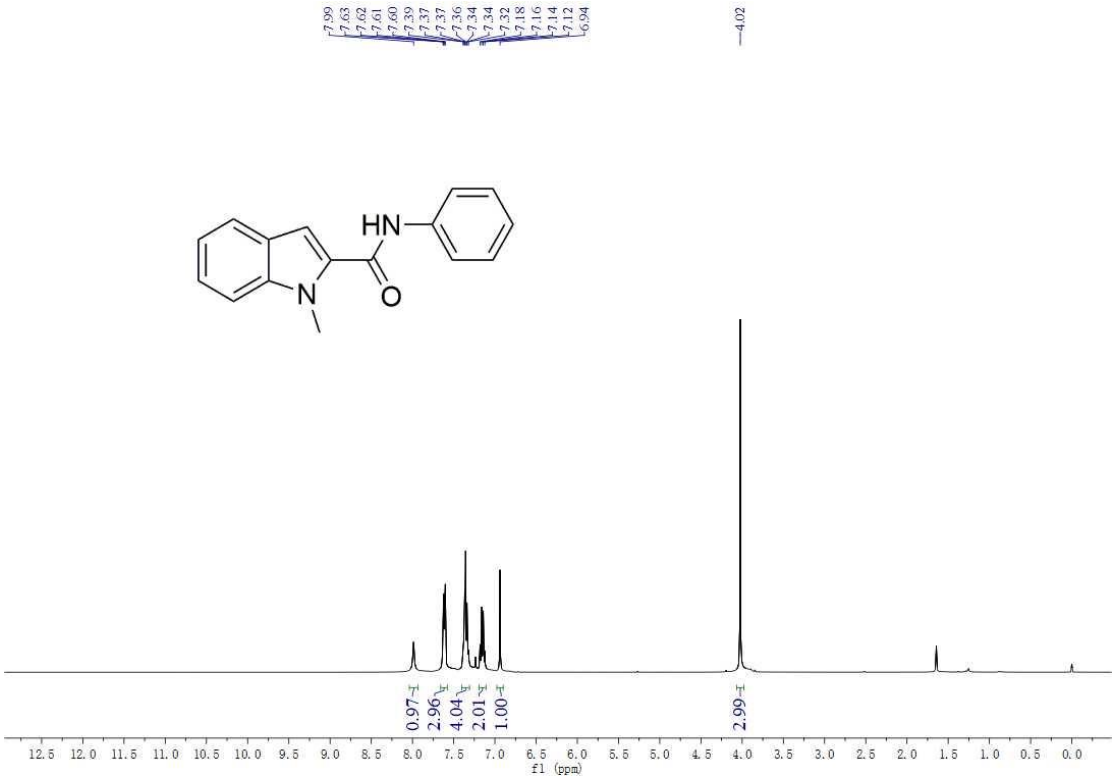

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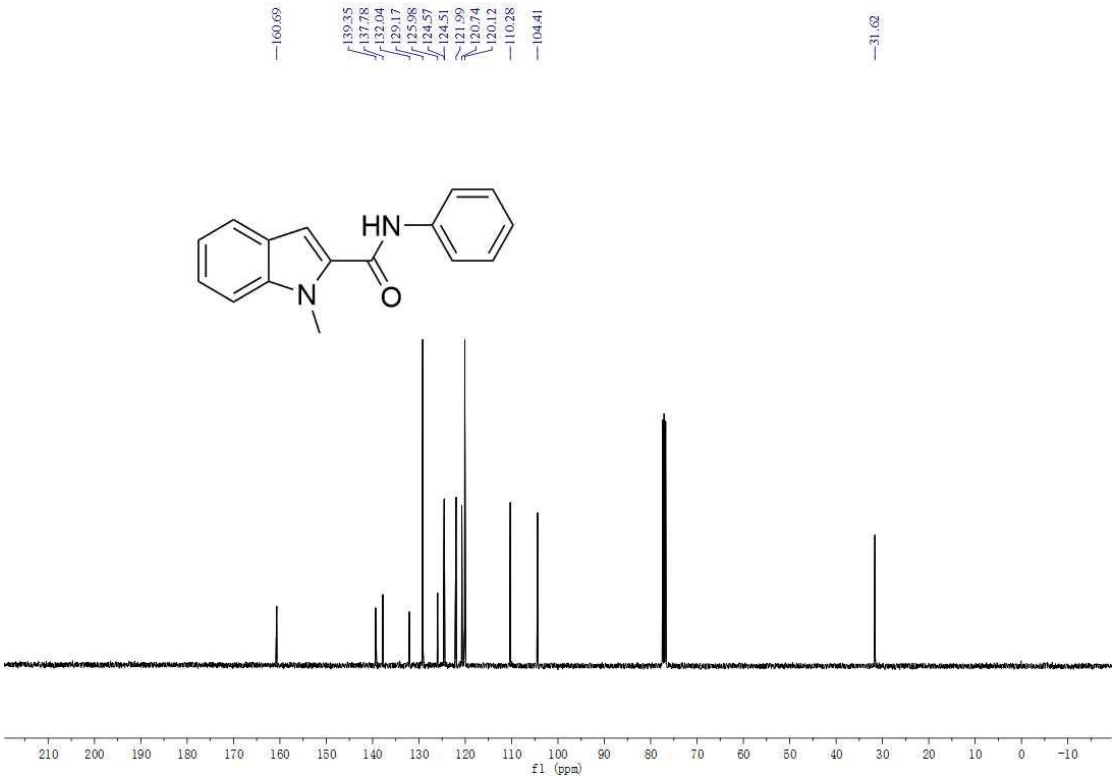

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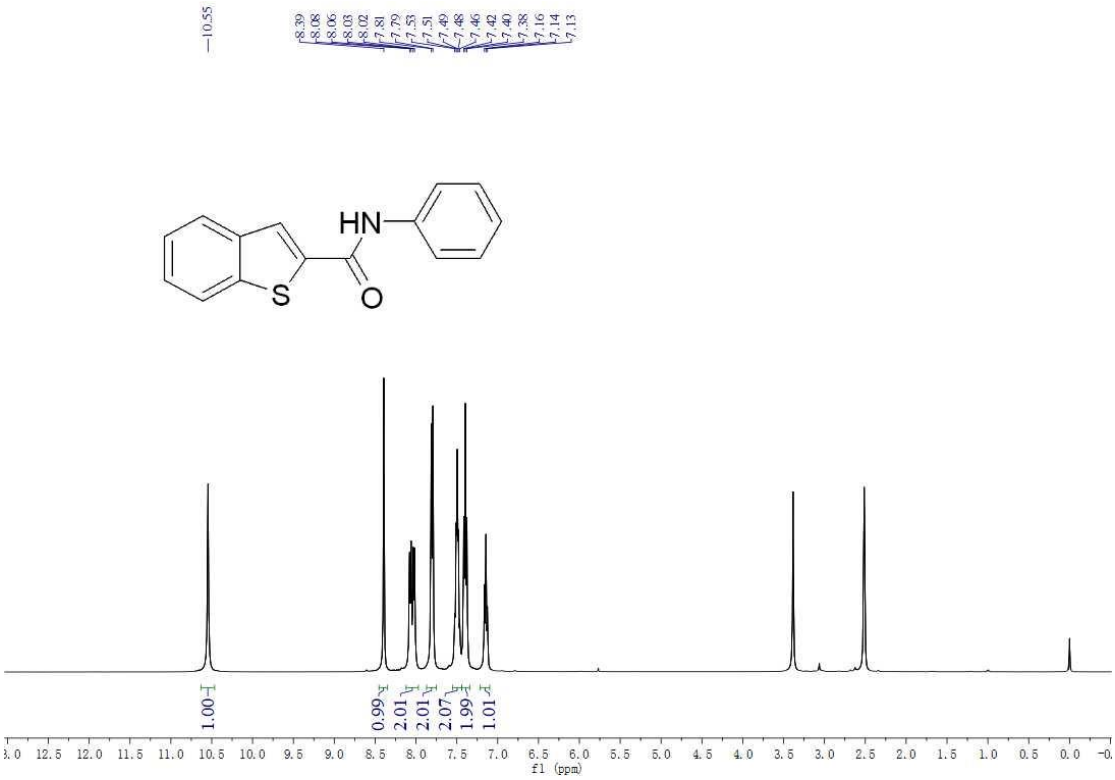

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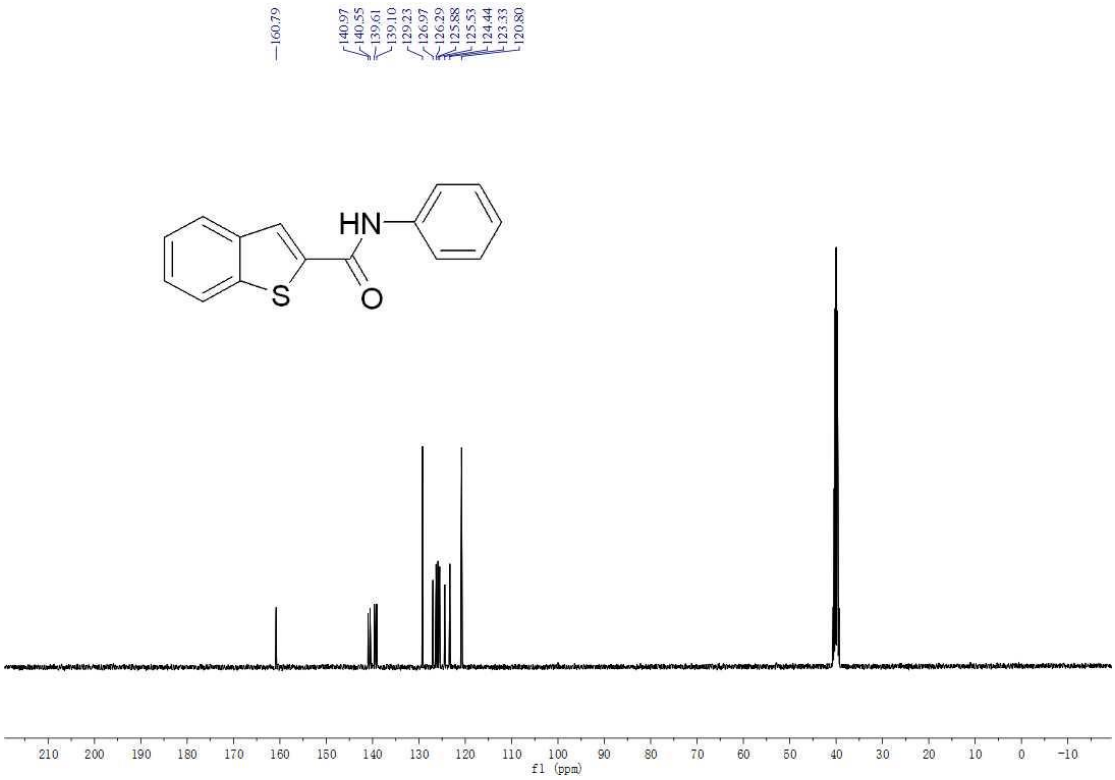

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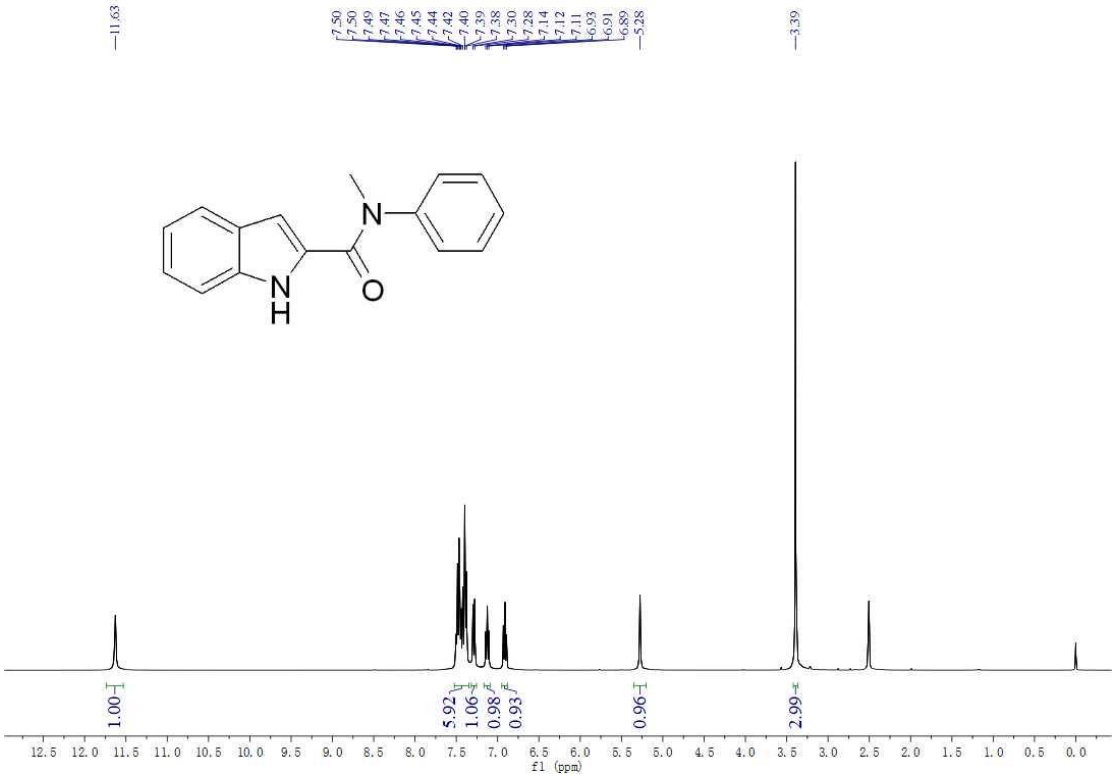

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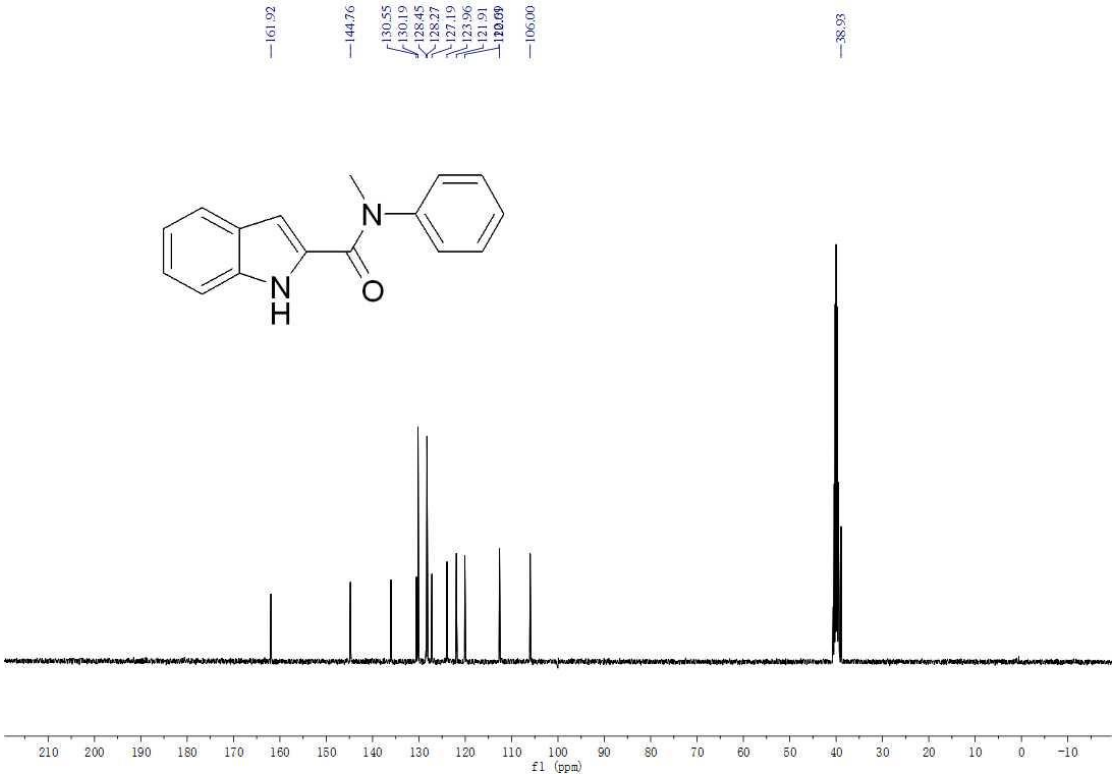

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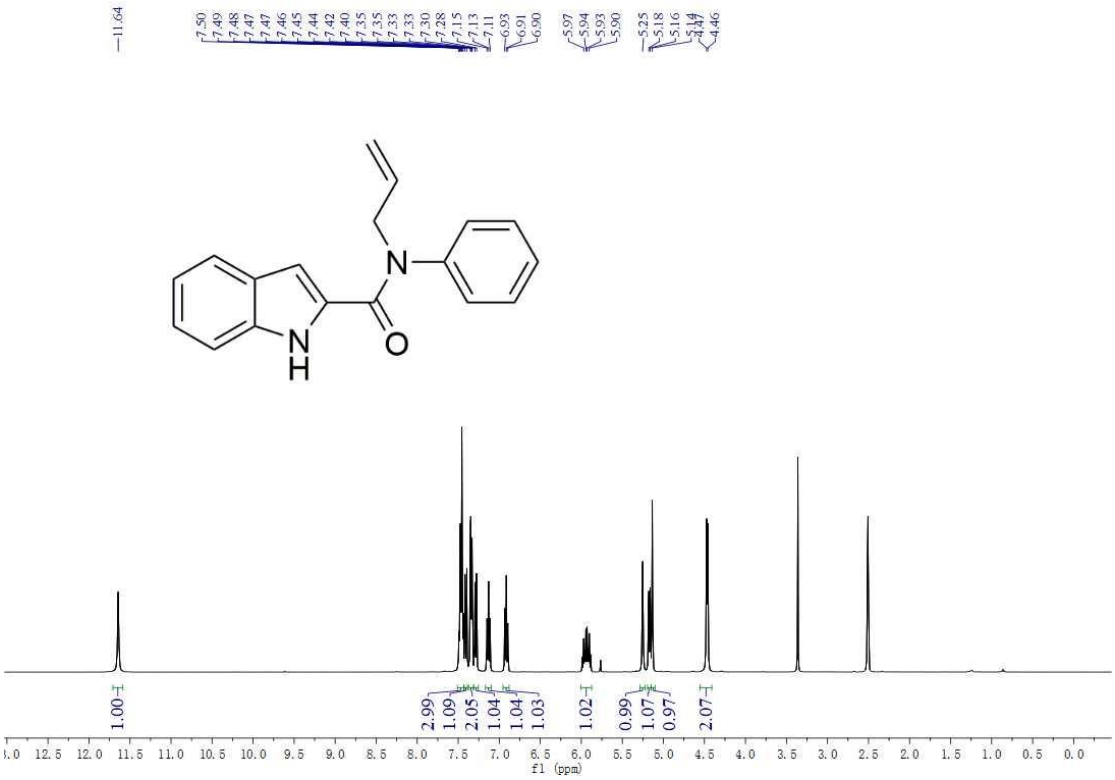

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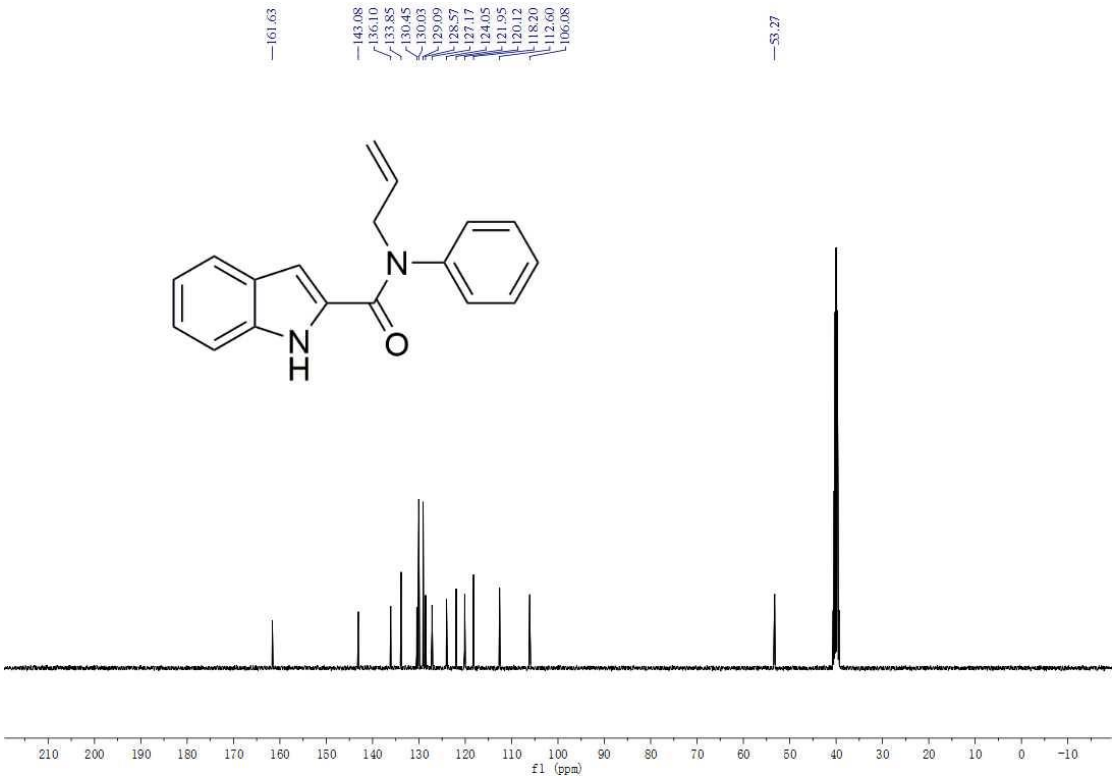

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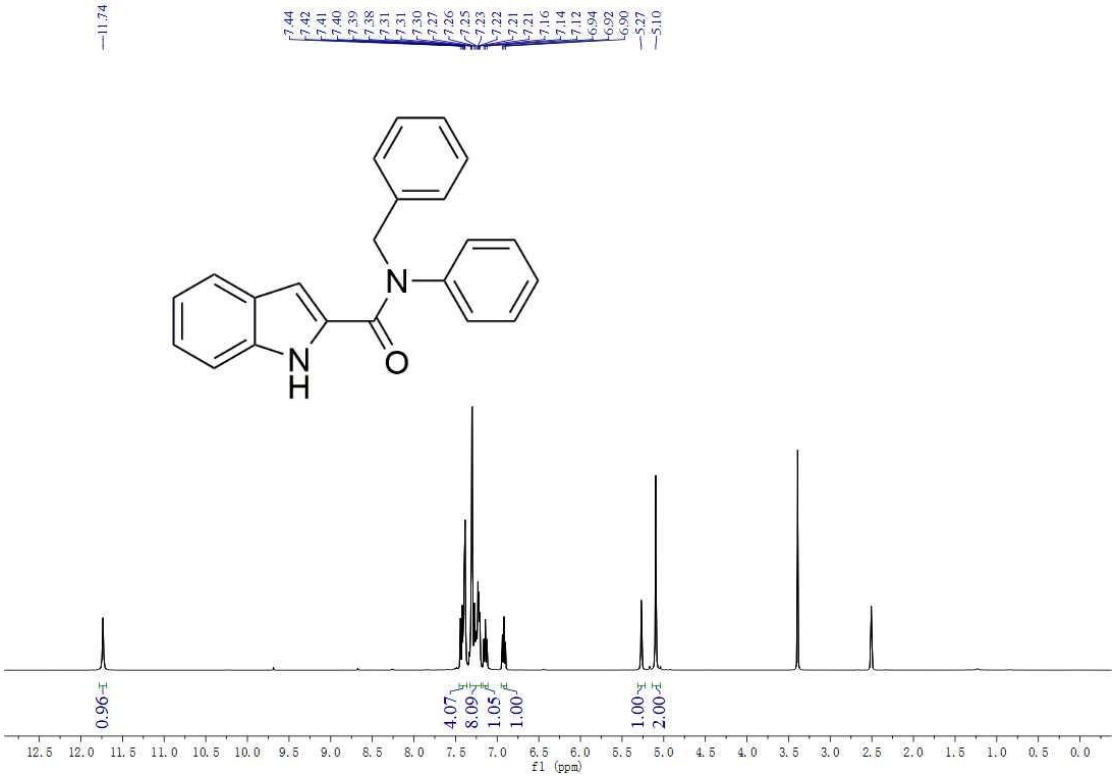

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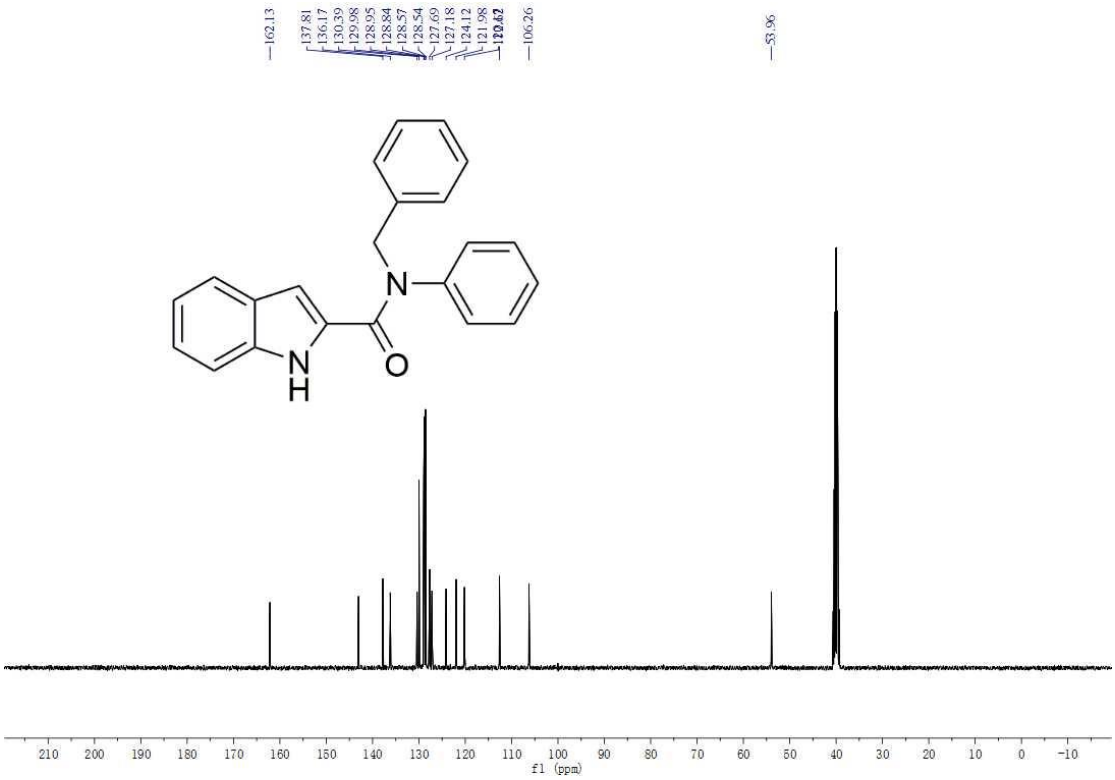

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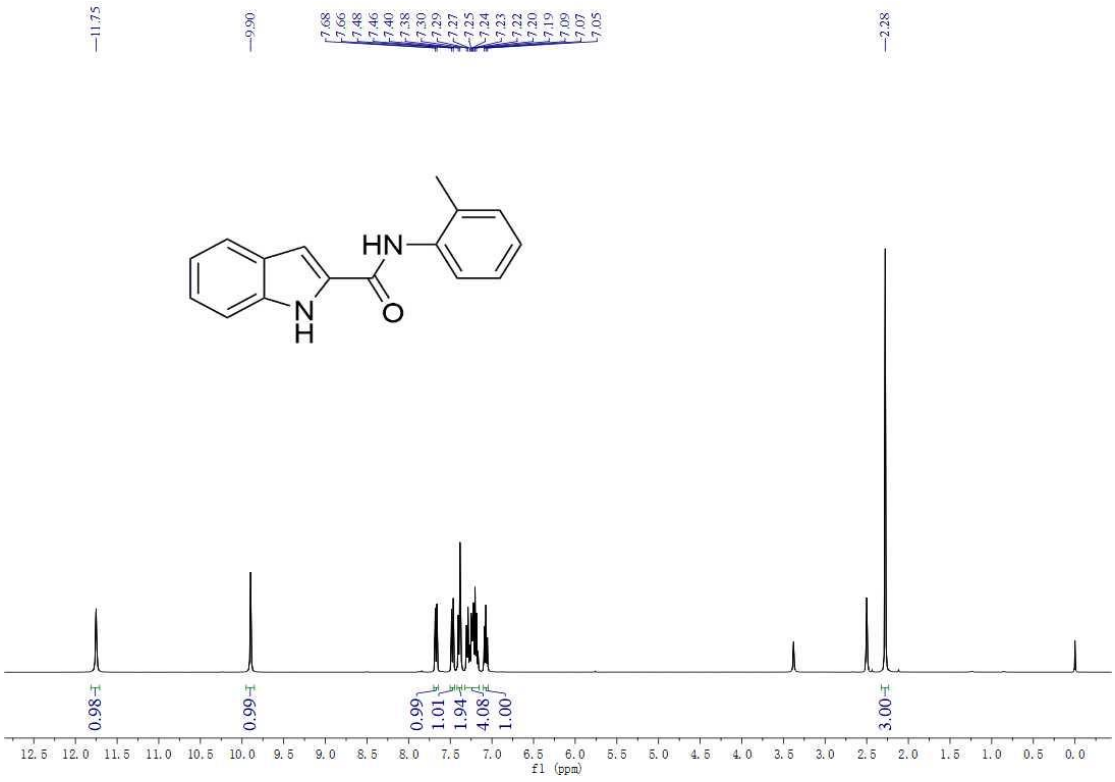

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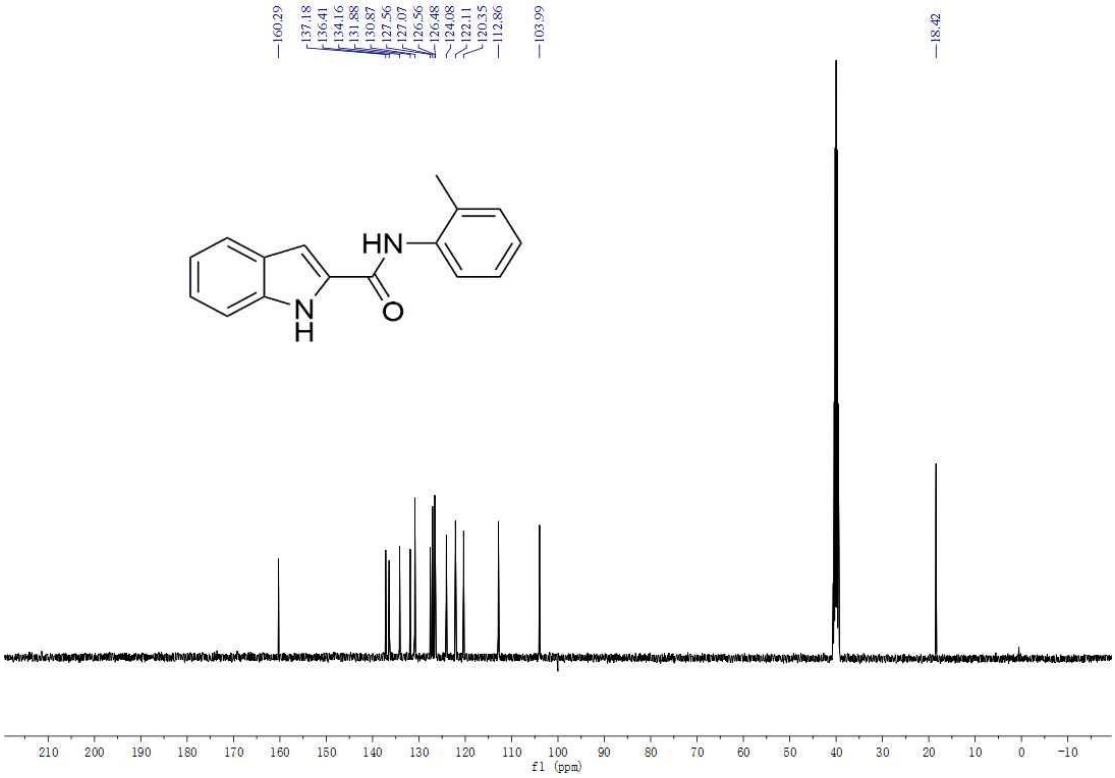

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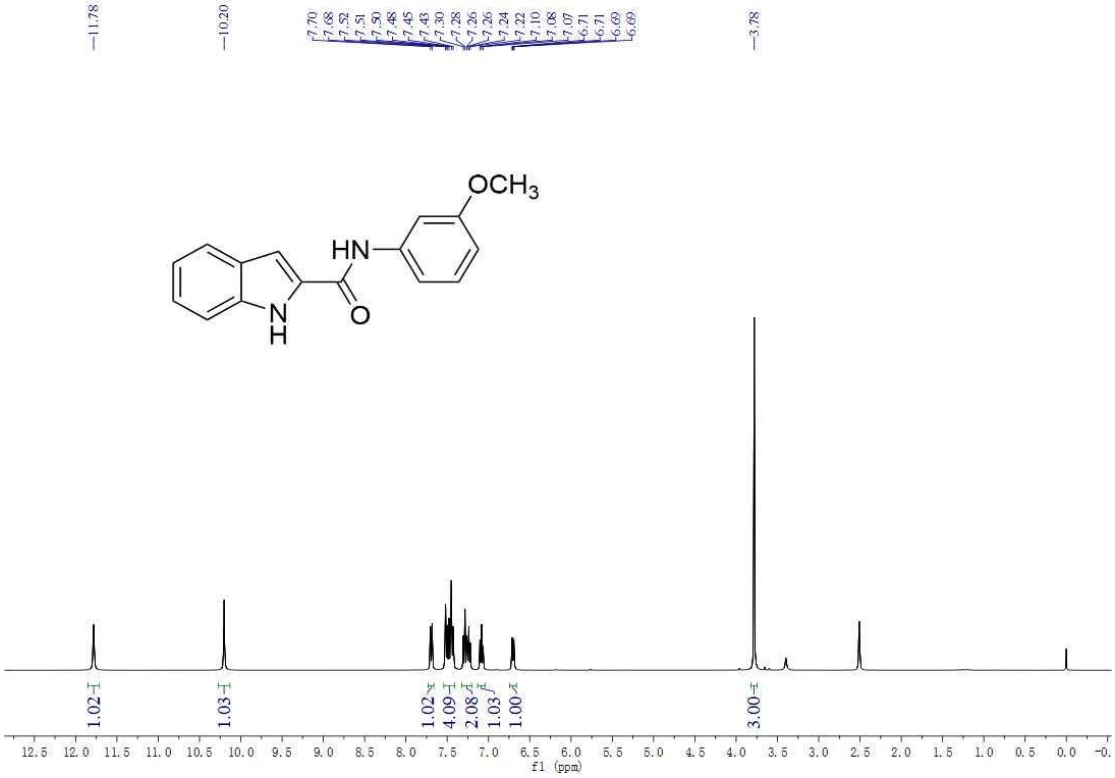

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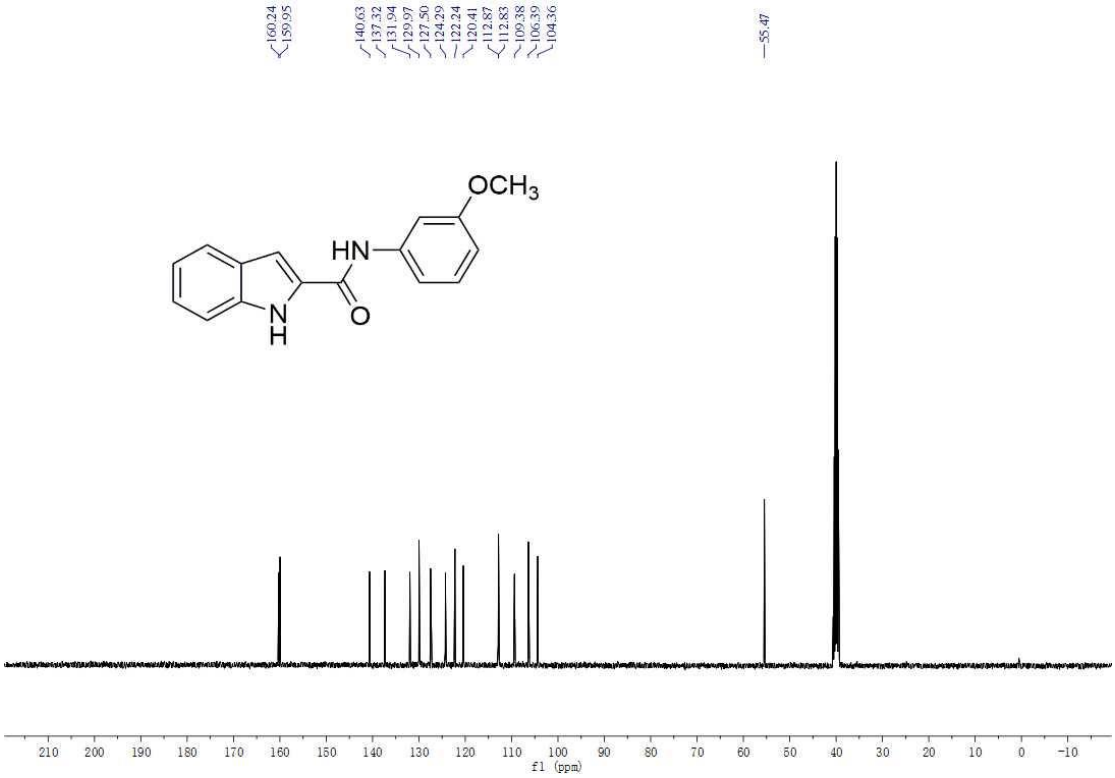

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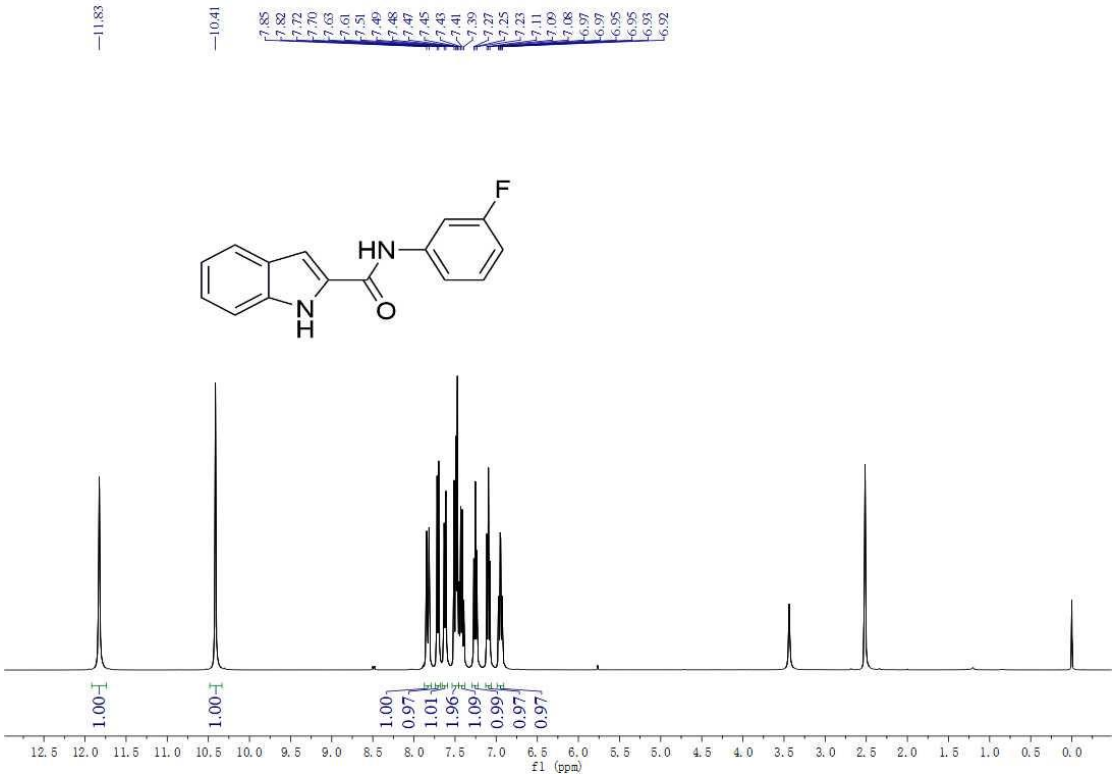

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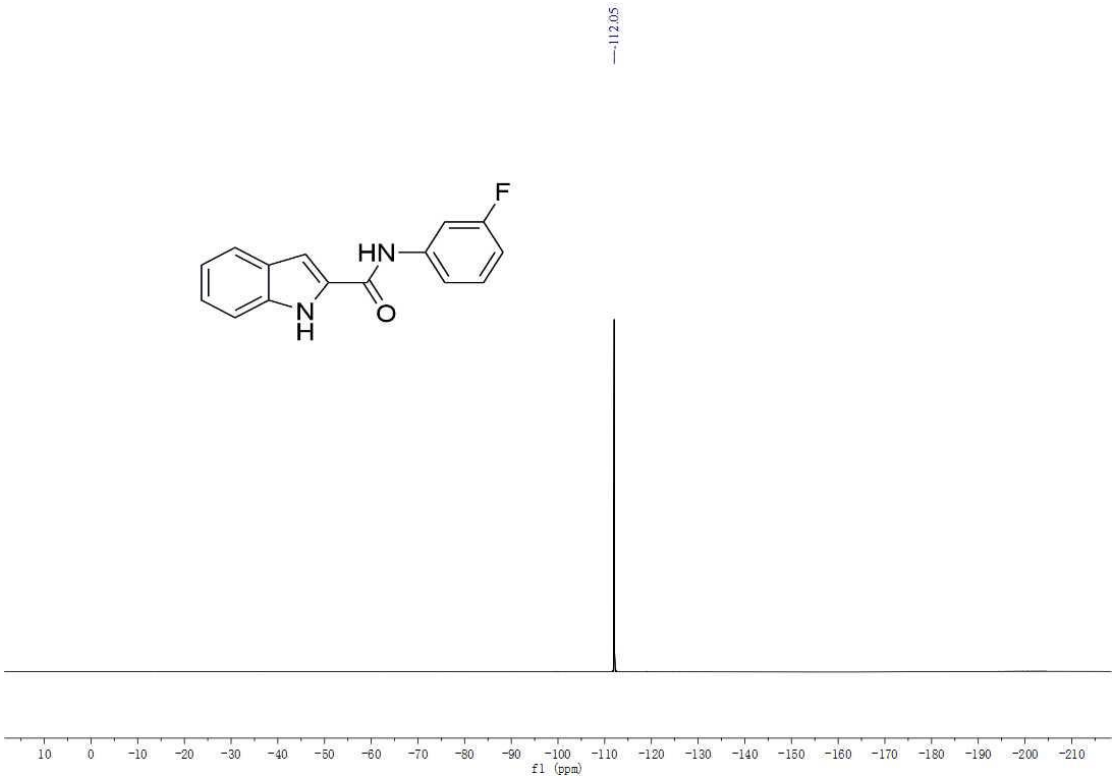

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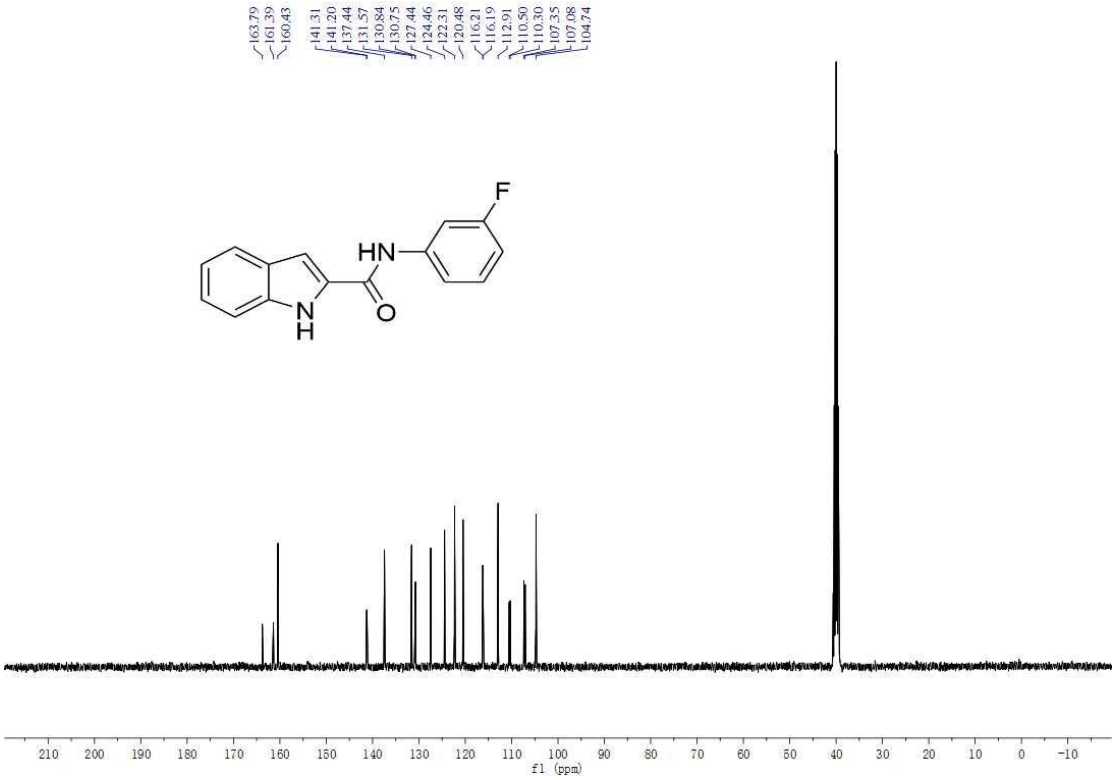

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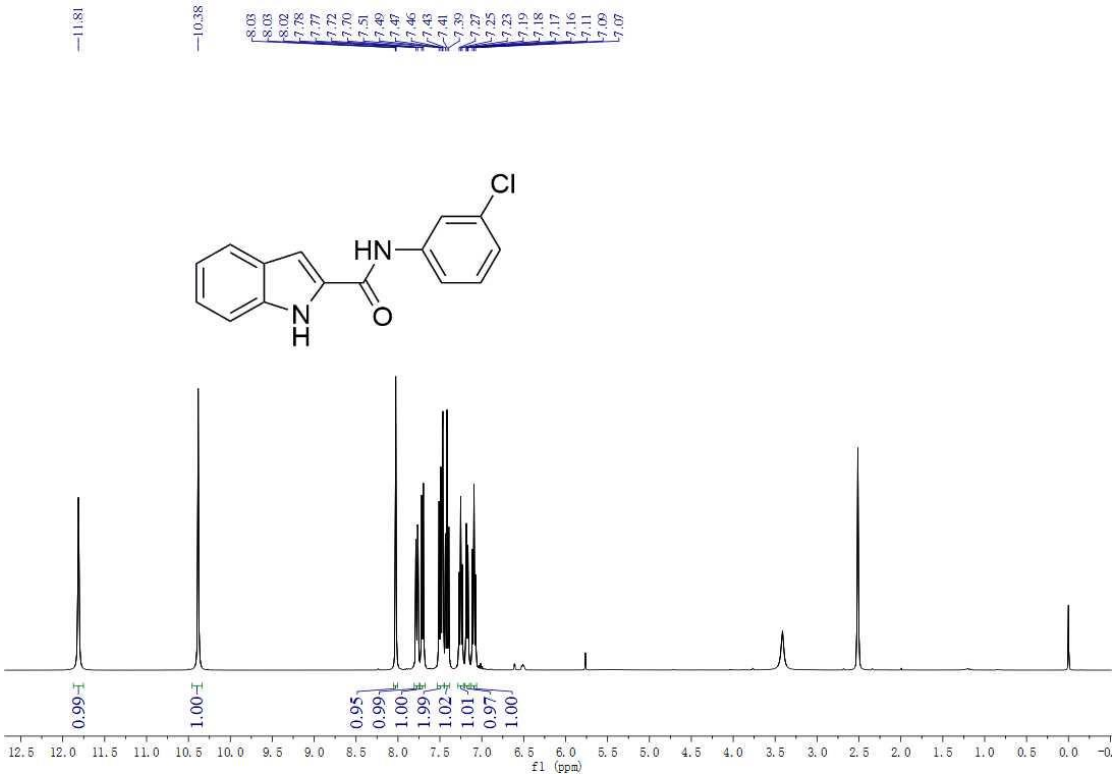

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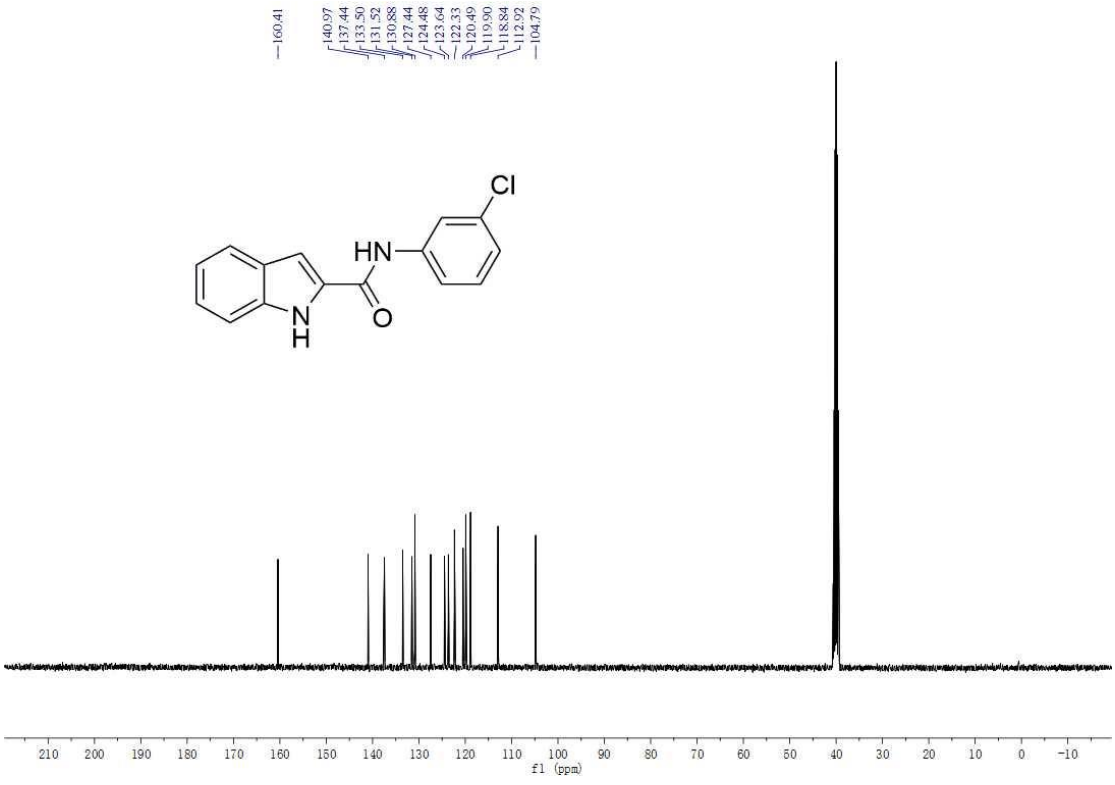

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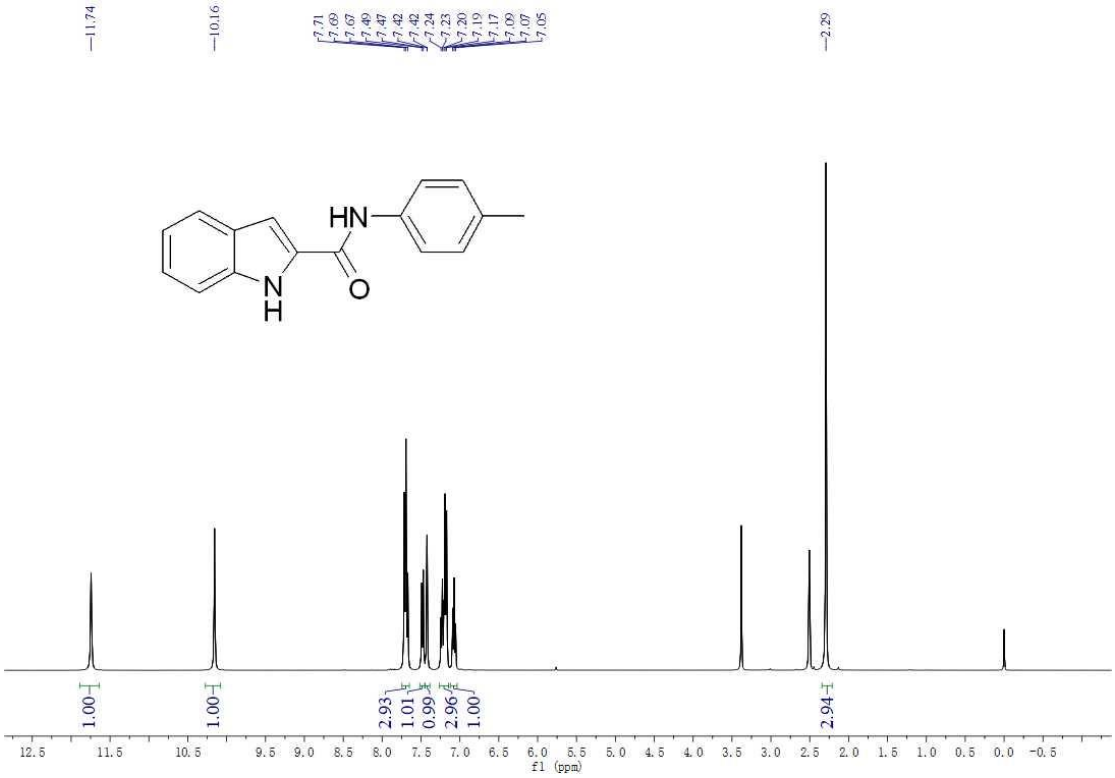

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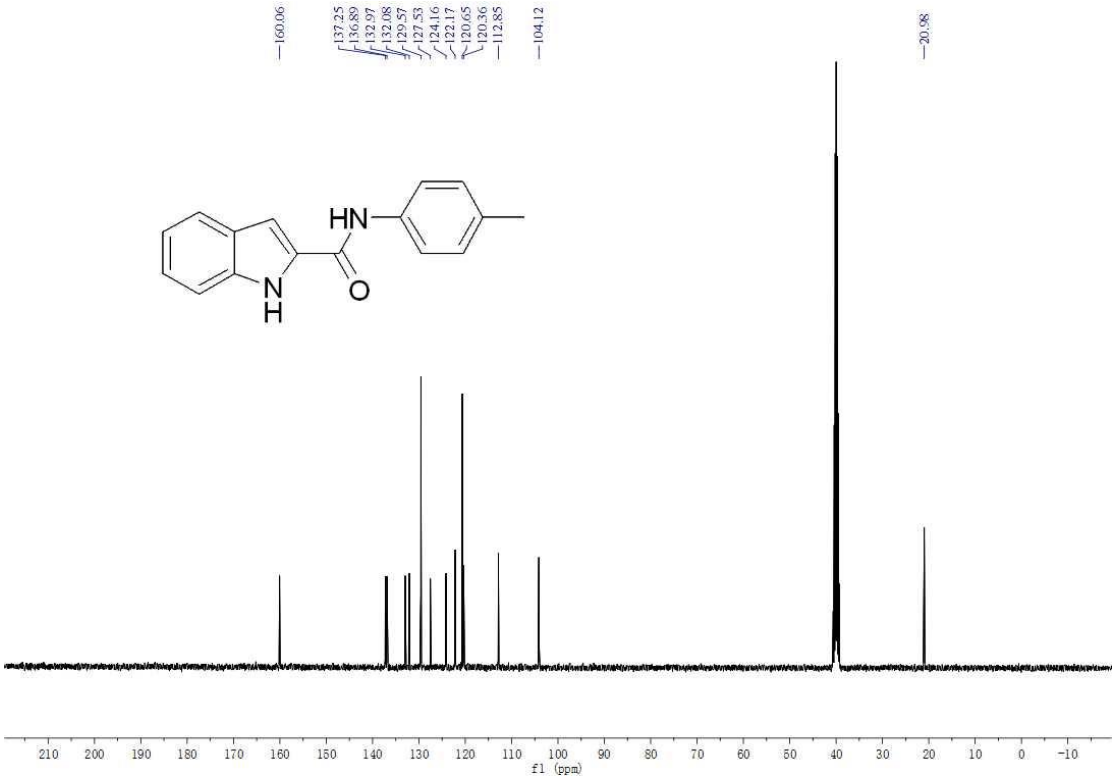

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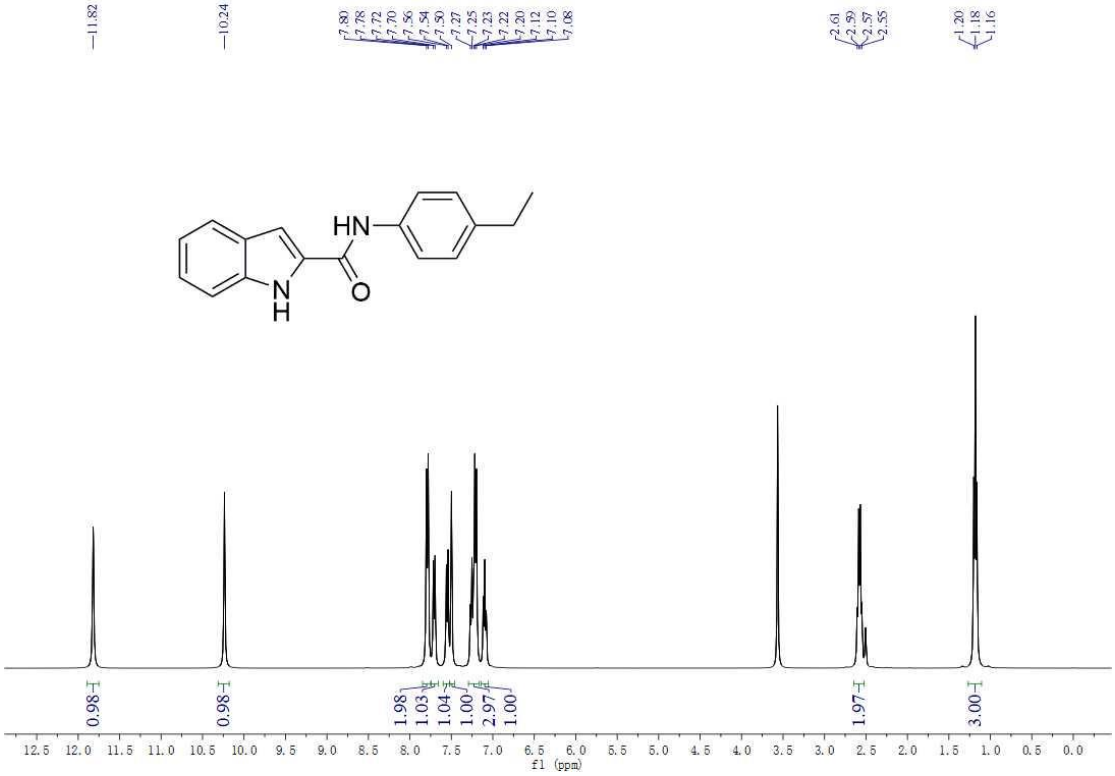
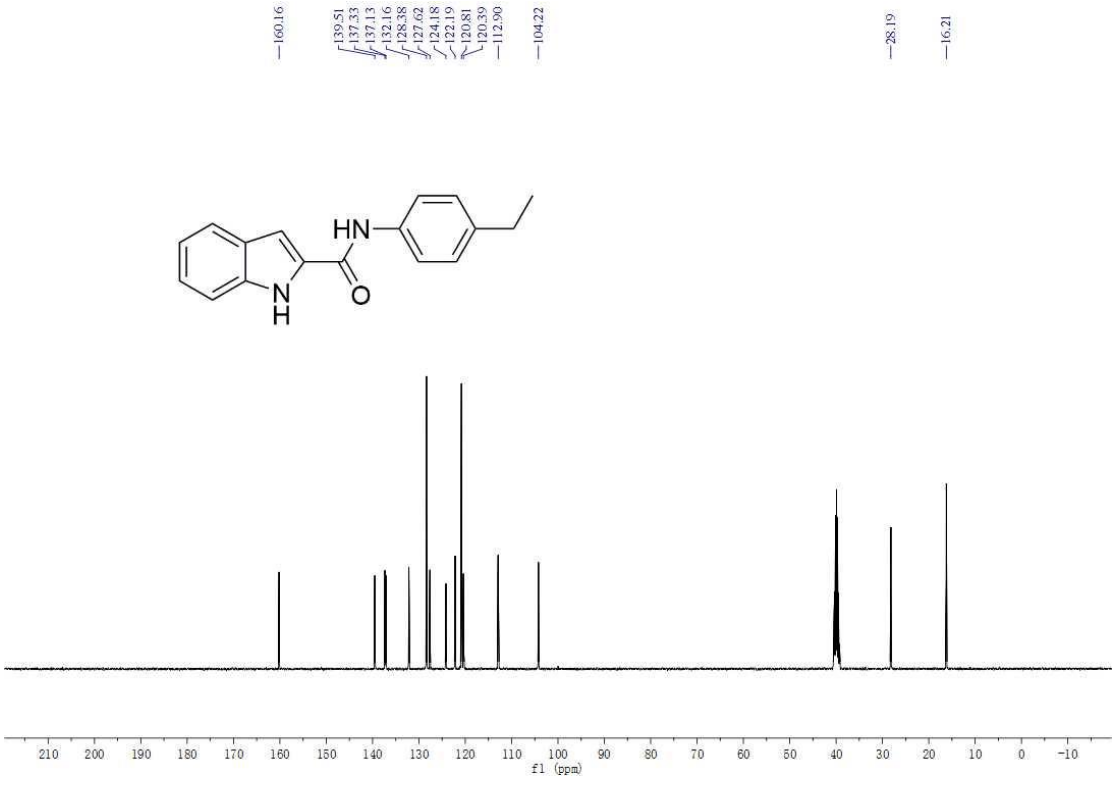
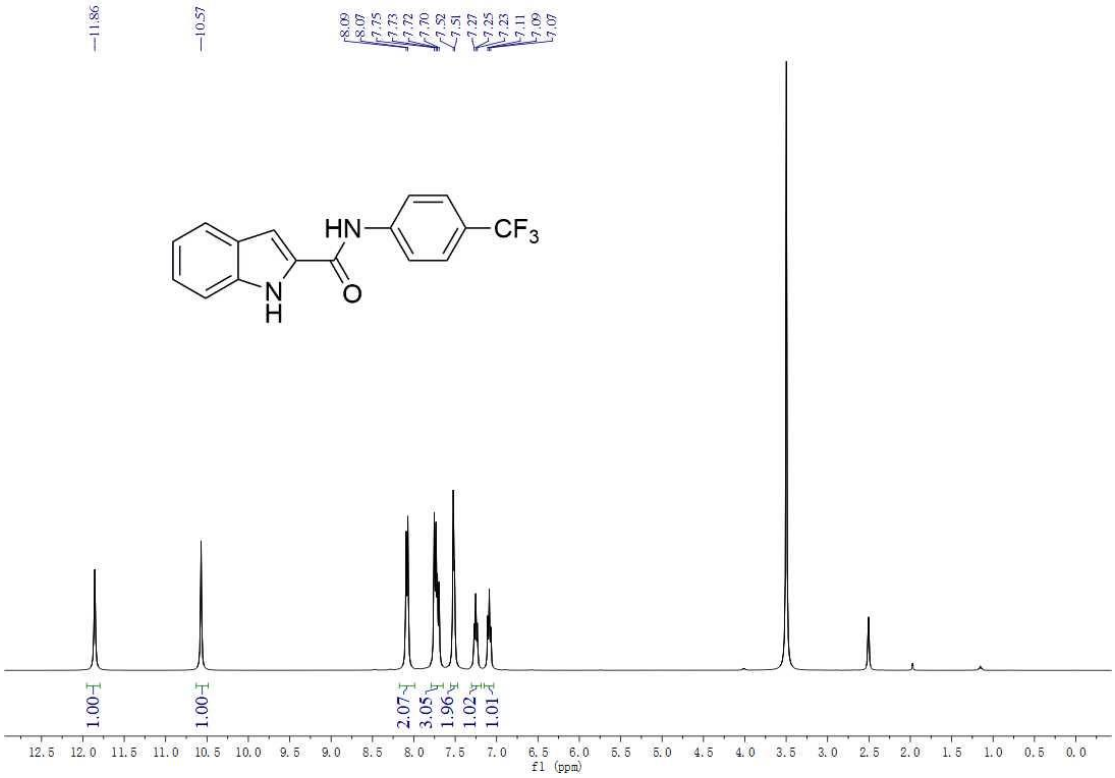


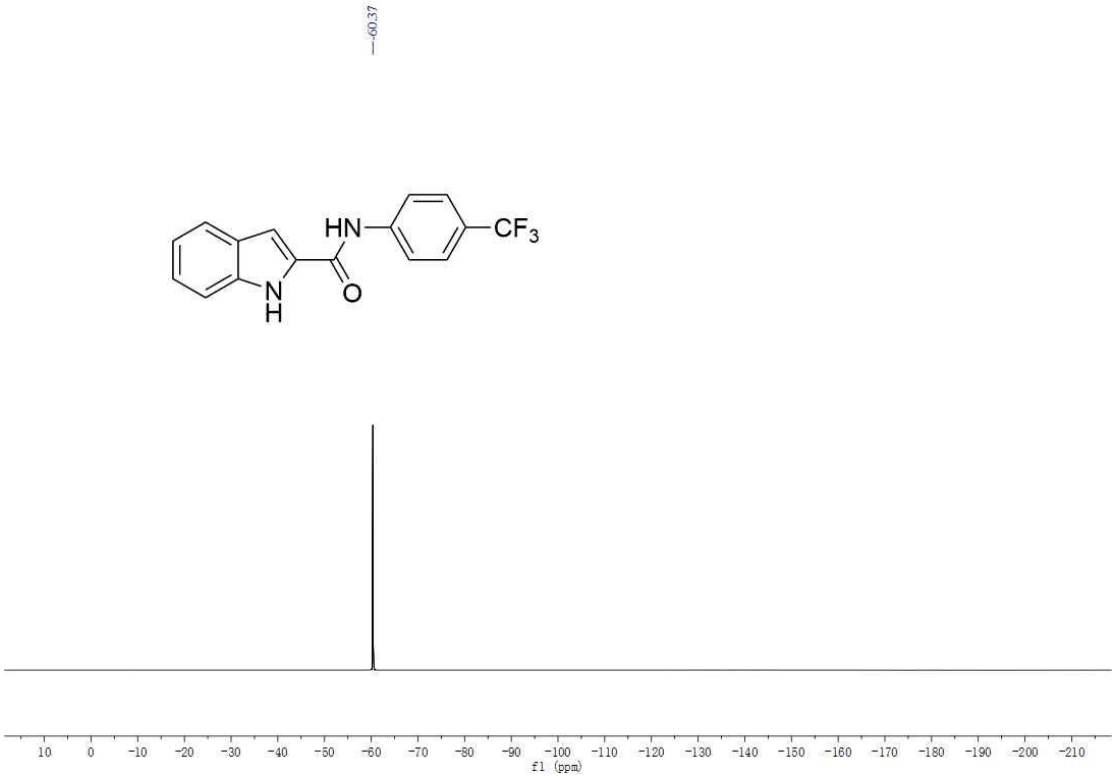
^{13}C NMR spectrum of **1w**



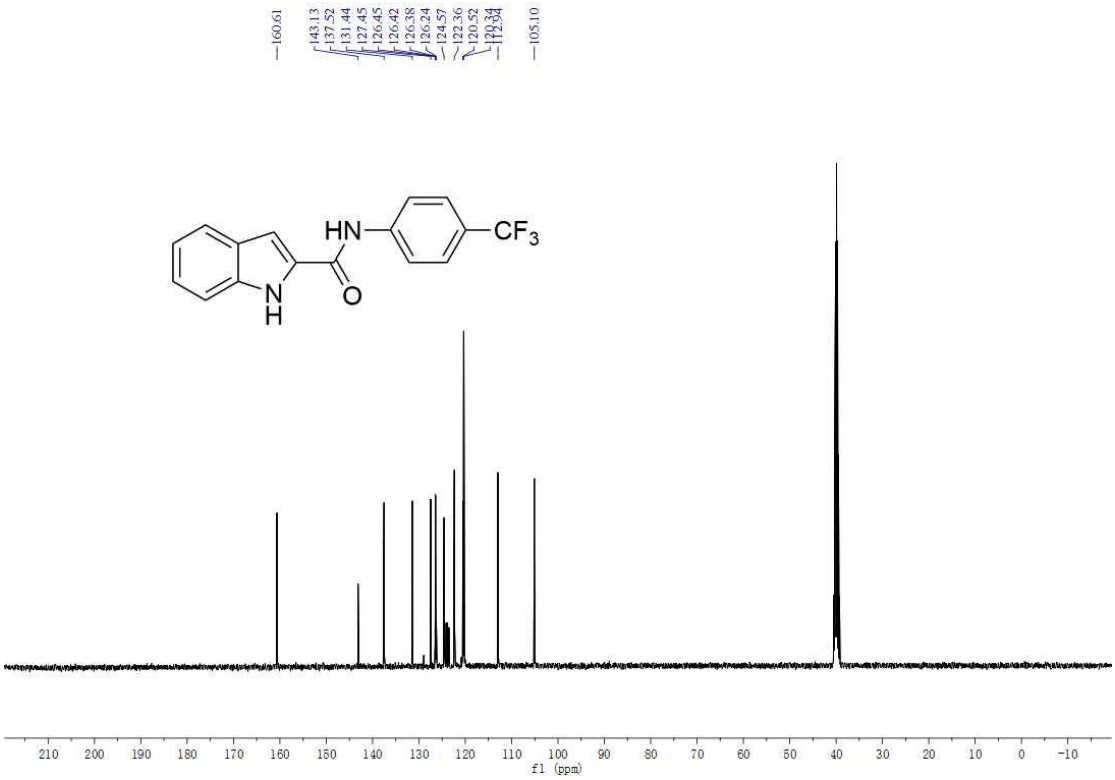
^{1}H NMR spectrum of **1x**



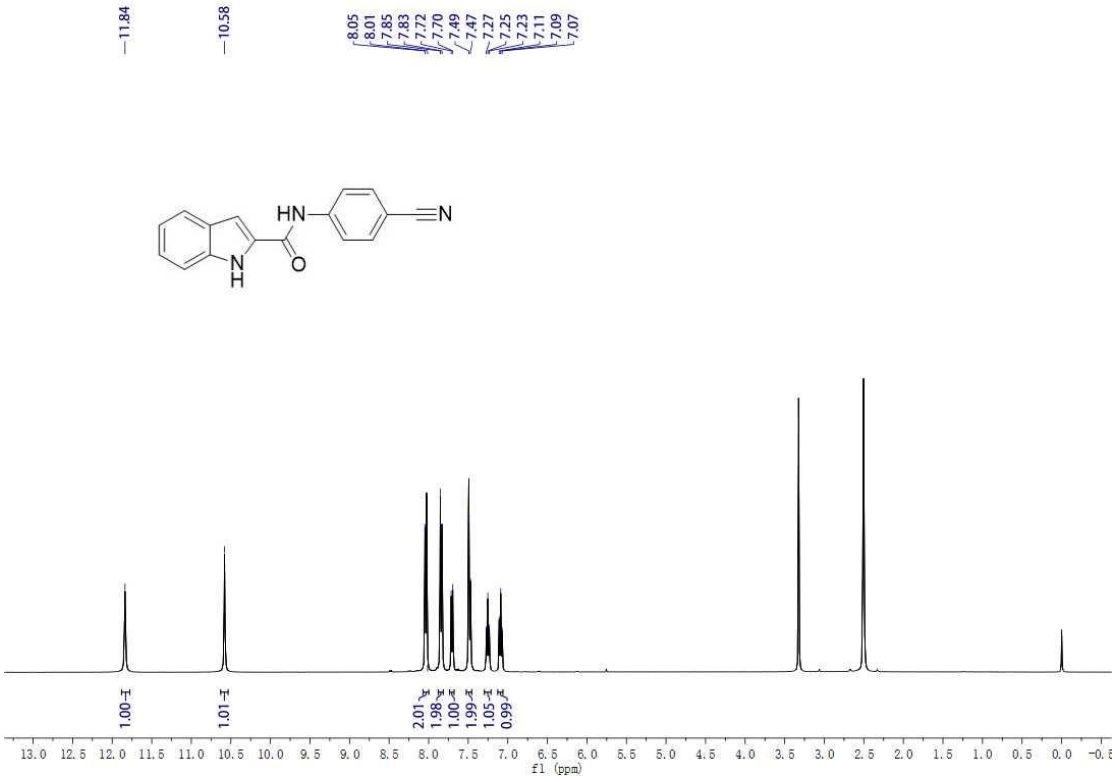
^{19}F NMR spectrum of **1x**



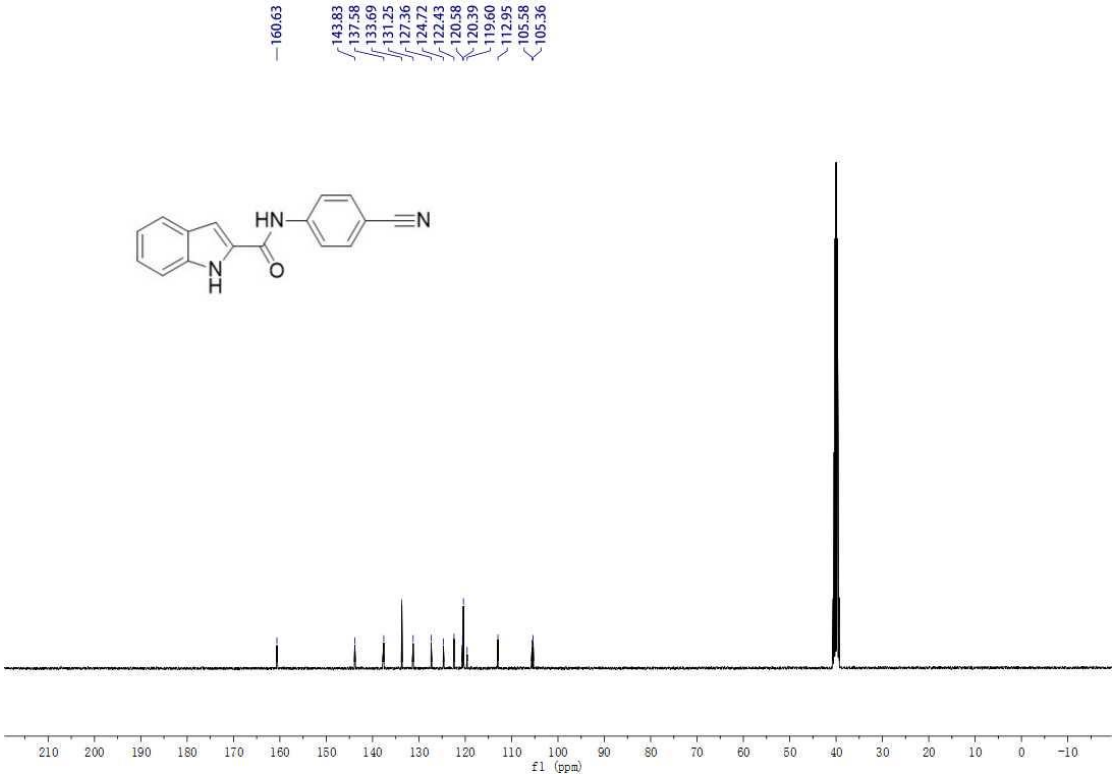
^{13}C NMR spectrum of **1x**



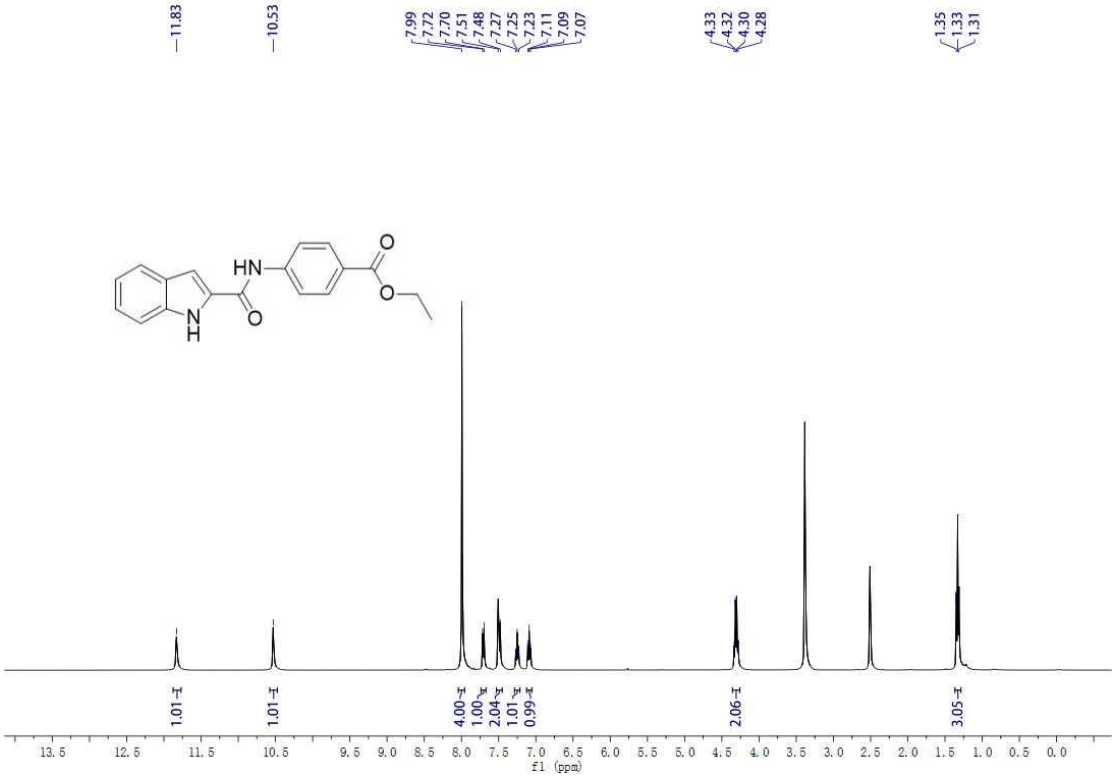
^{1}H NMR spectrum of **1y**



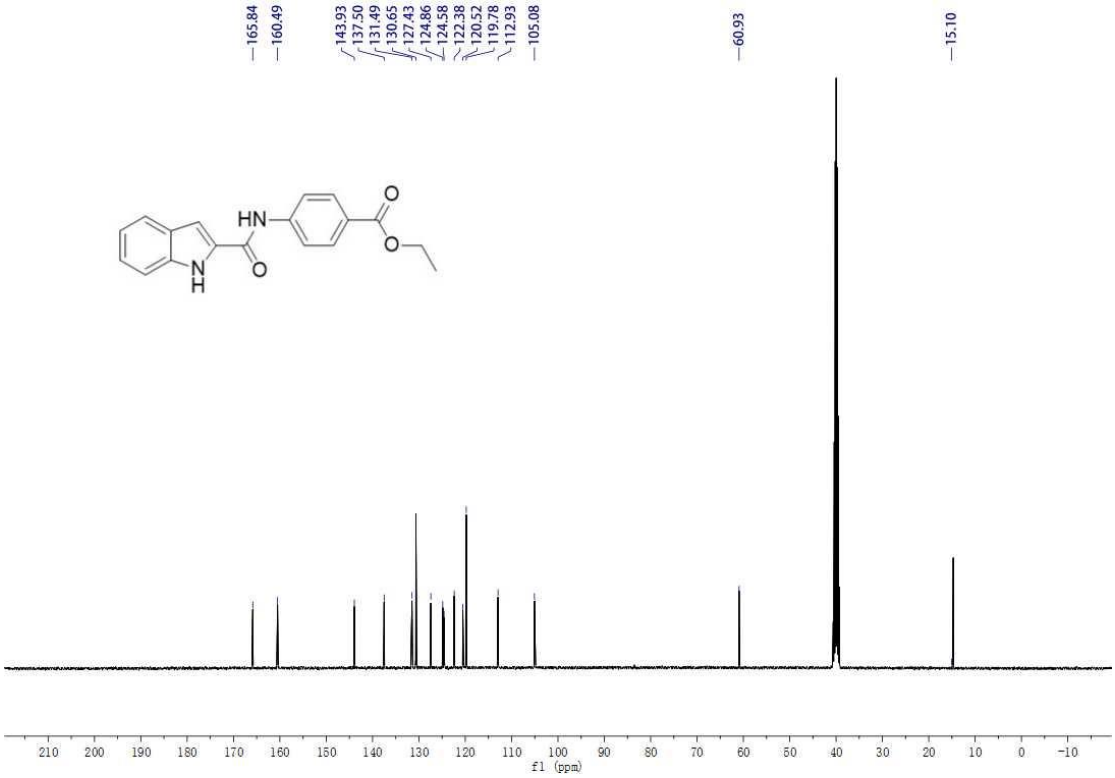
^{13}C NMR spectrum of **1y**



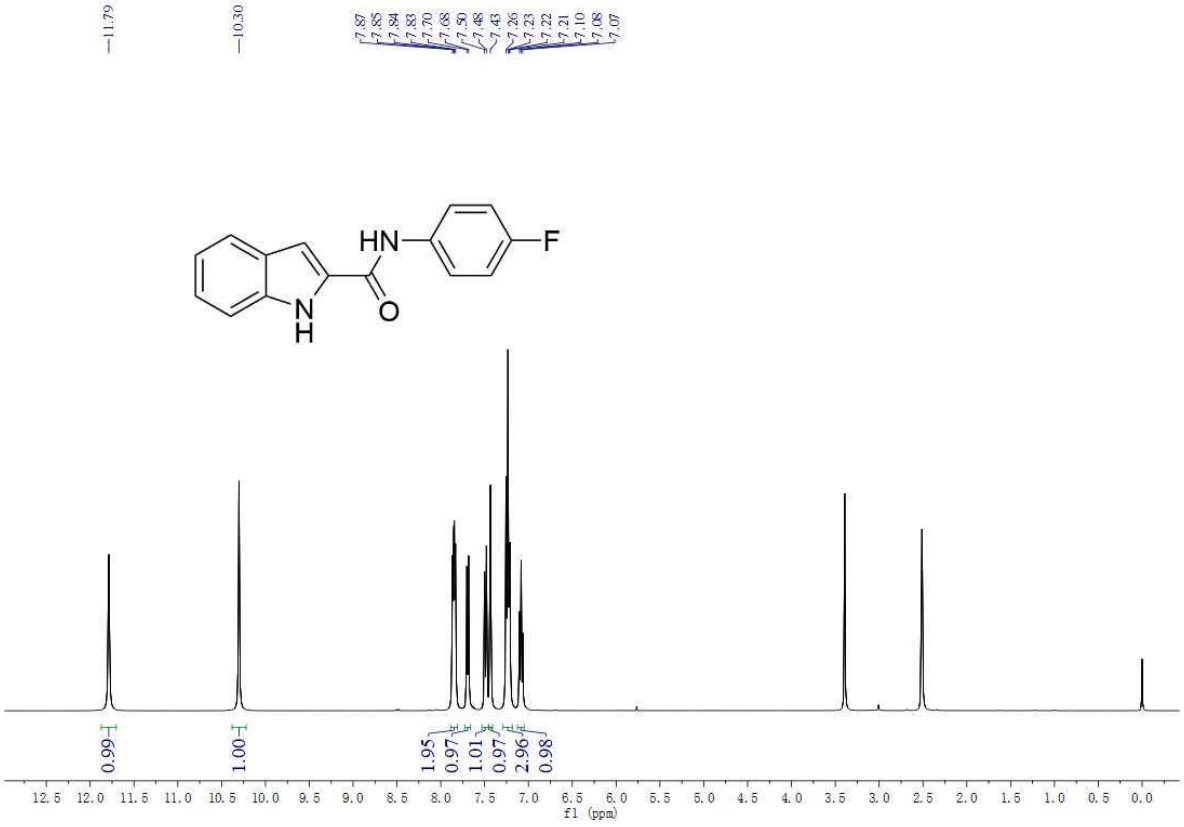
^{1}H NMR spectrum of **1z**



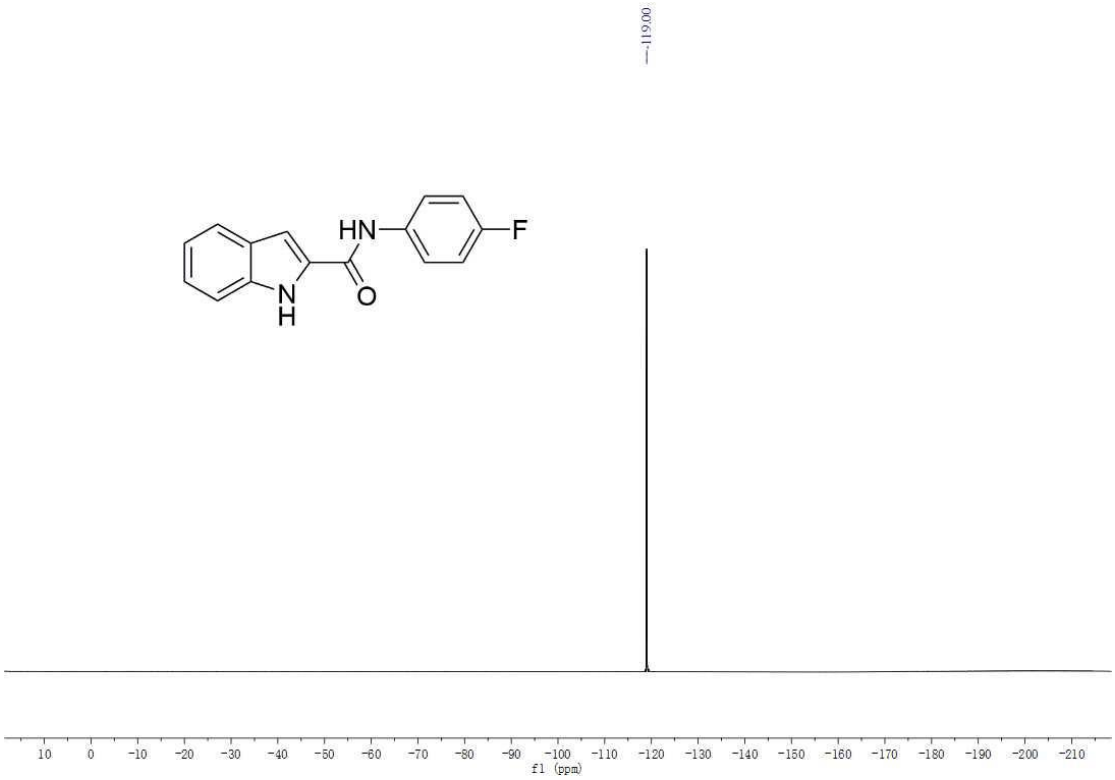
^{13}C NMR spectrum of **1z**



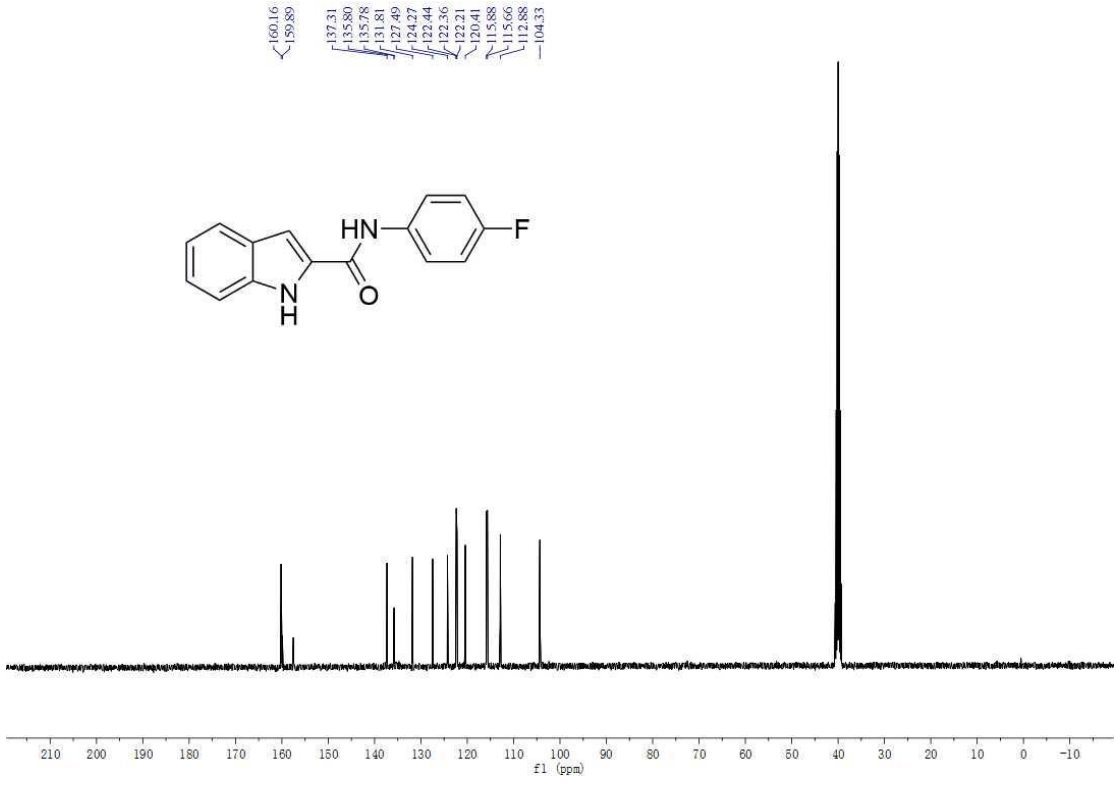
^{1}H NMR spectrum of **1aa**



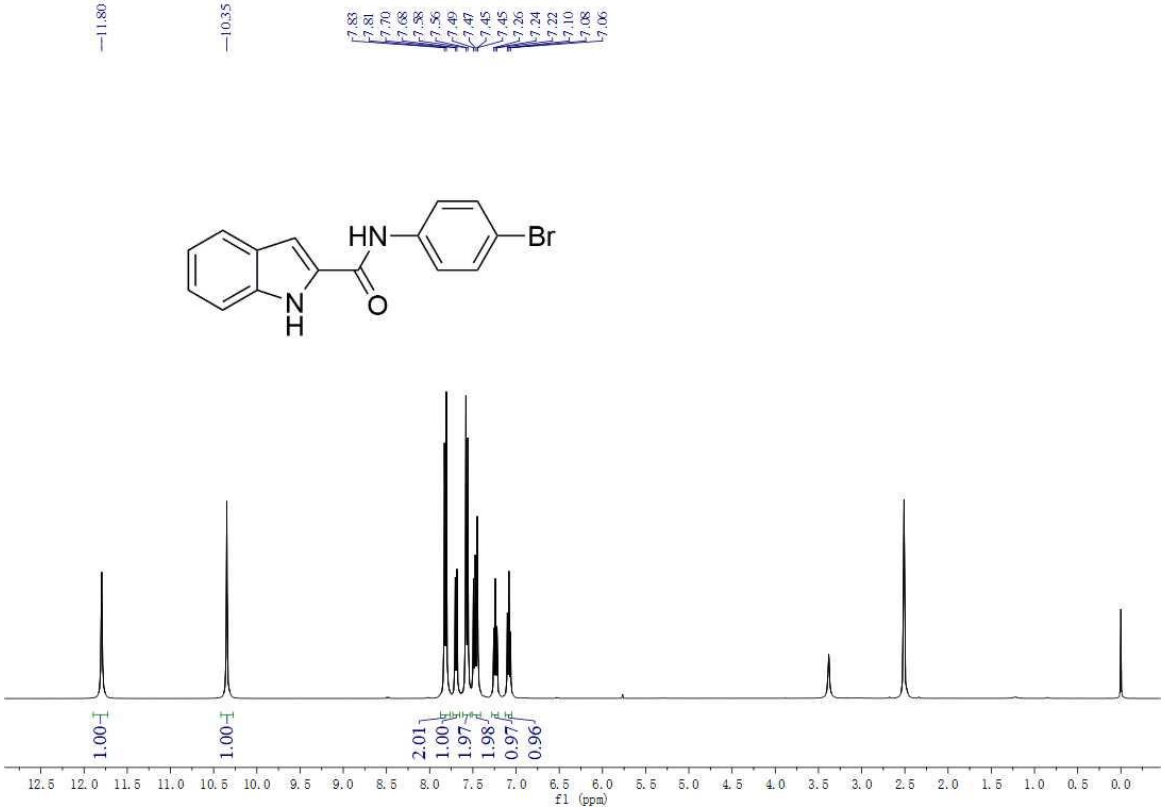
^{19}F NMR spectrum of **1aa**



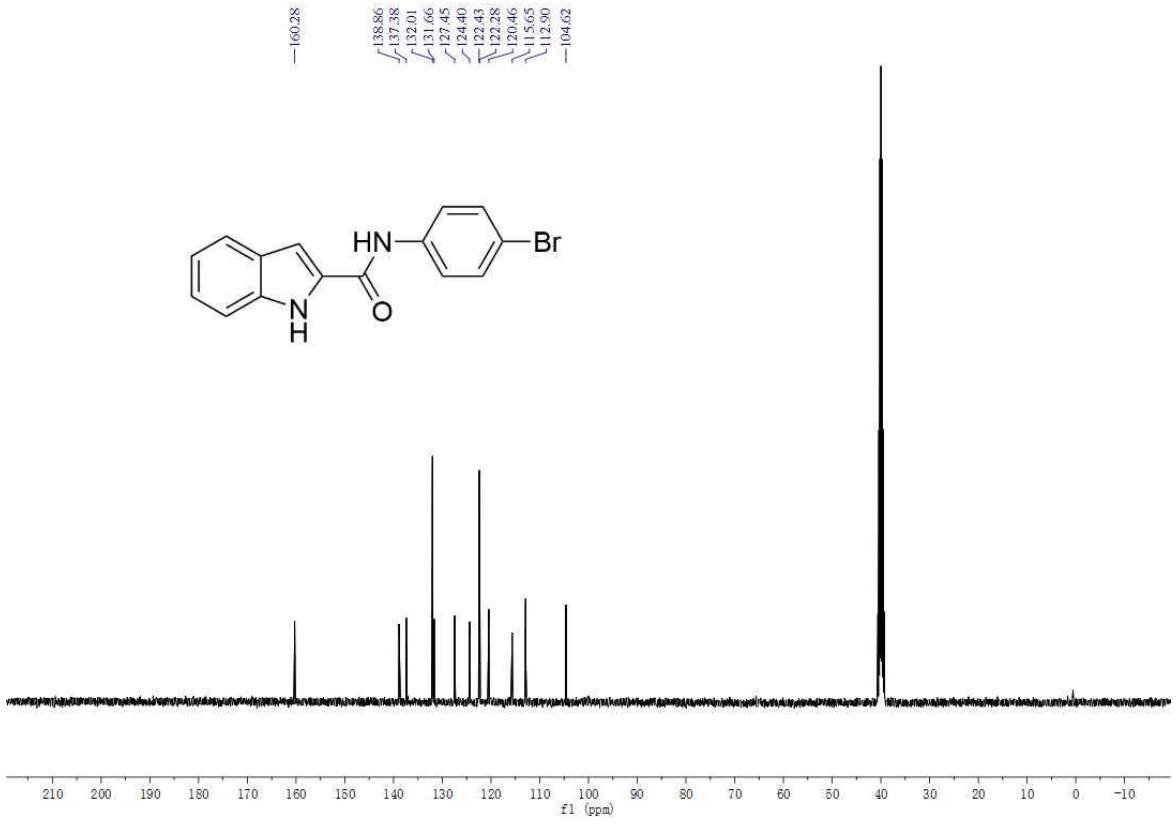
^{13}C NMR spectrum of **1aa**



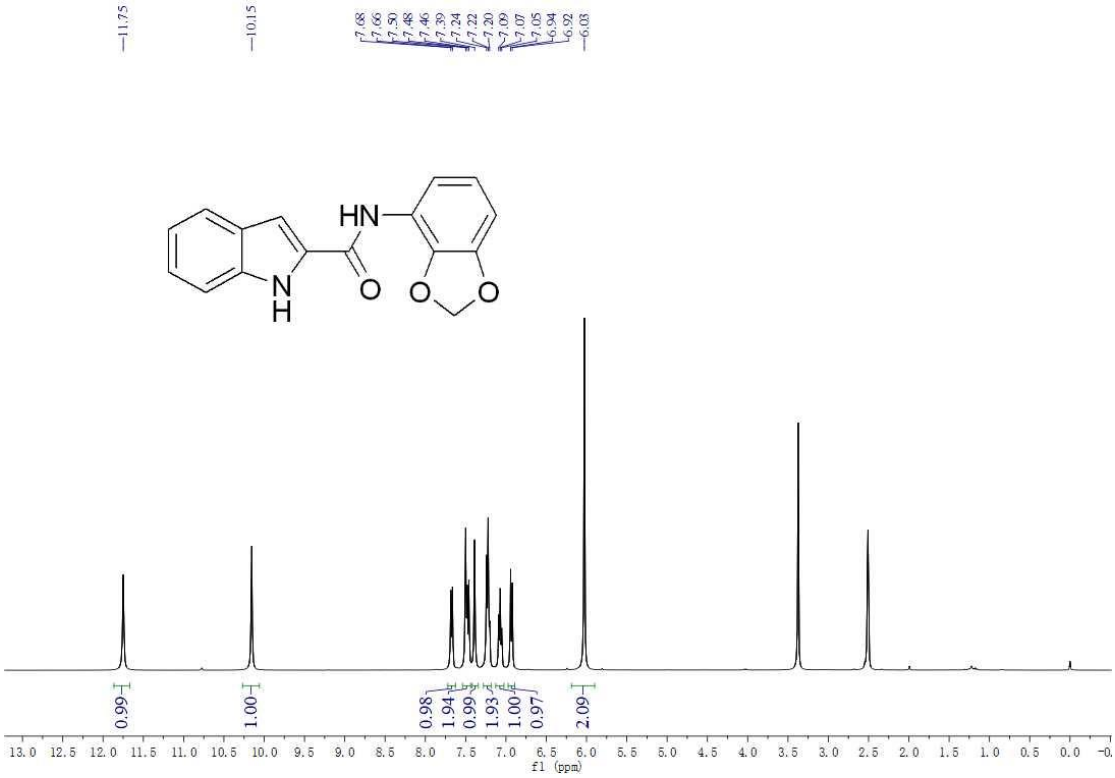
^{1}H NMR spectrum of **1ab**



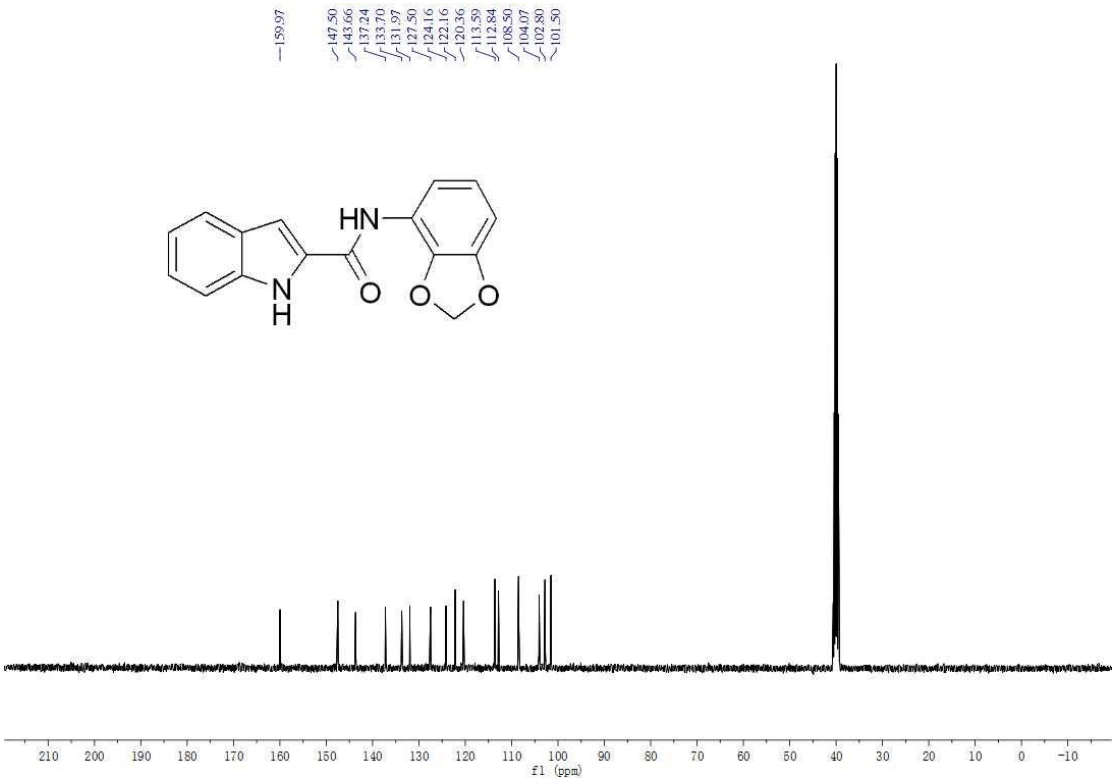
^{13}C NMR spectrum of **1ab**



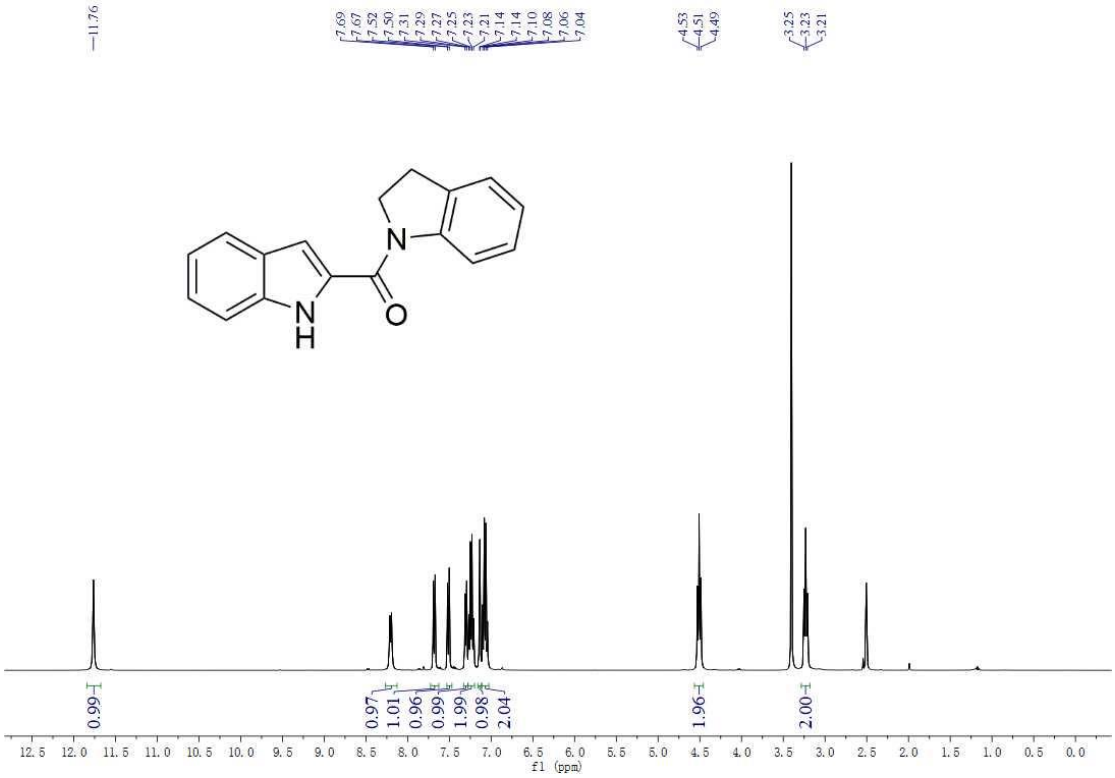
^{1}H NMR spectrum of **1ac**



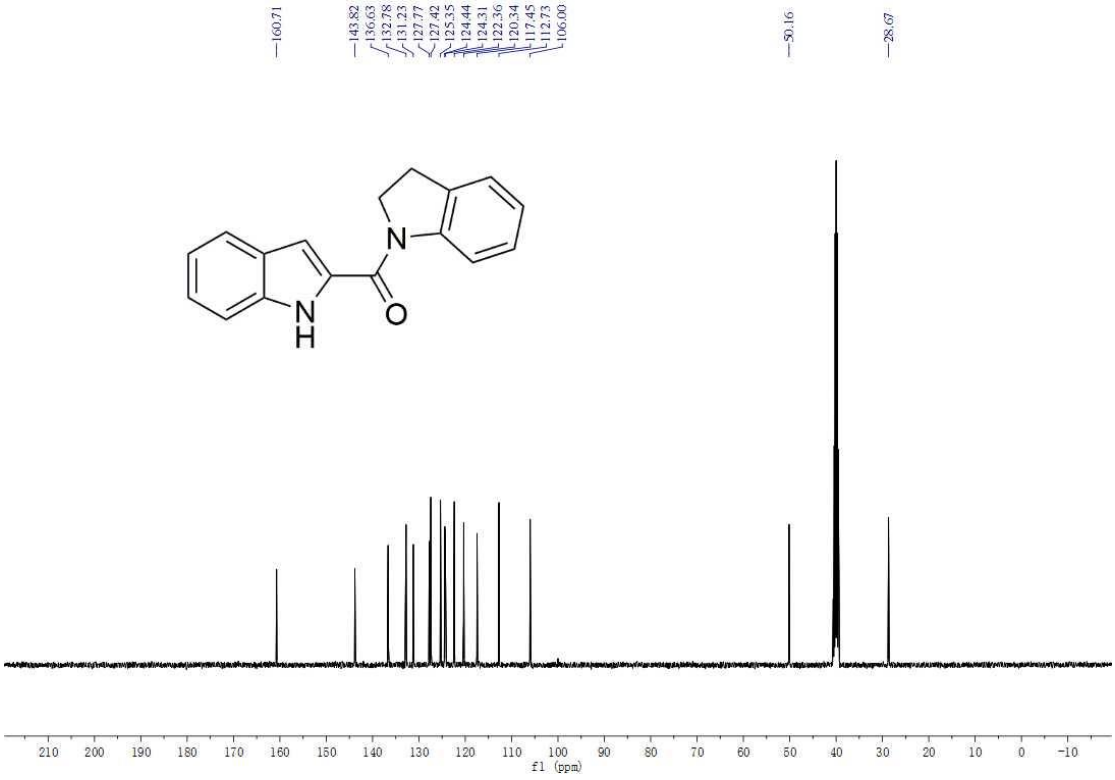
^{13}C NMR spectrum of **1ac**



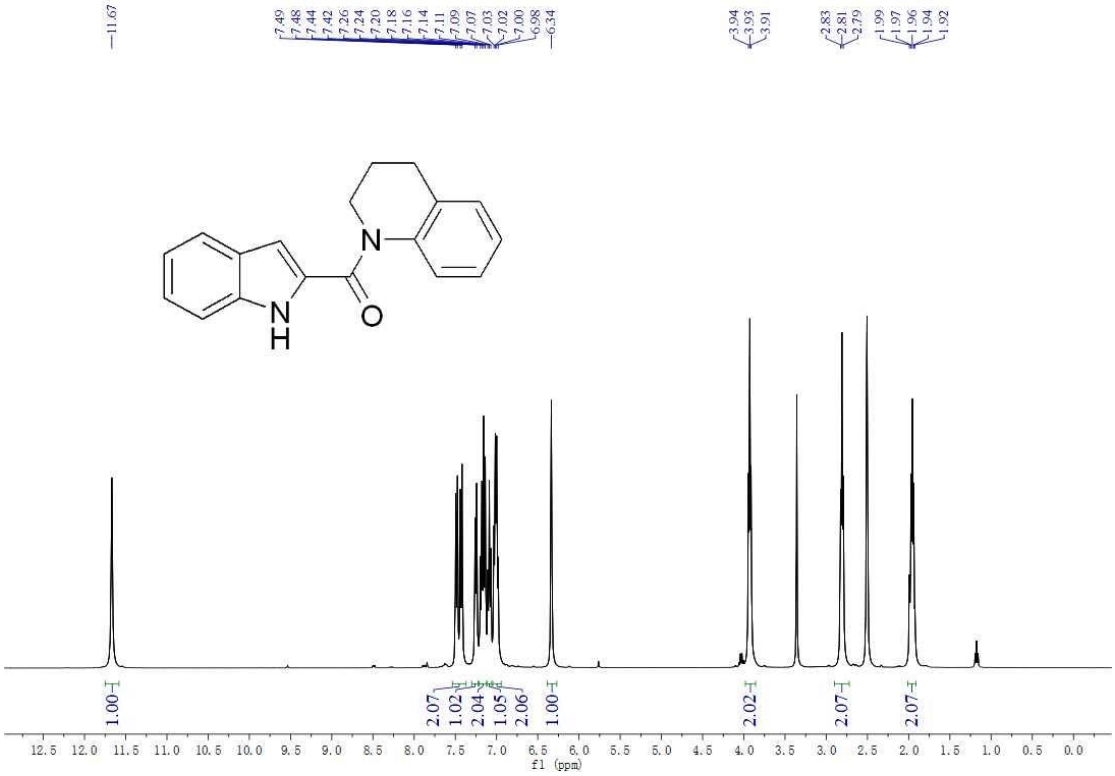
^{1}H NMR spectrum of **1ad**



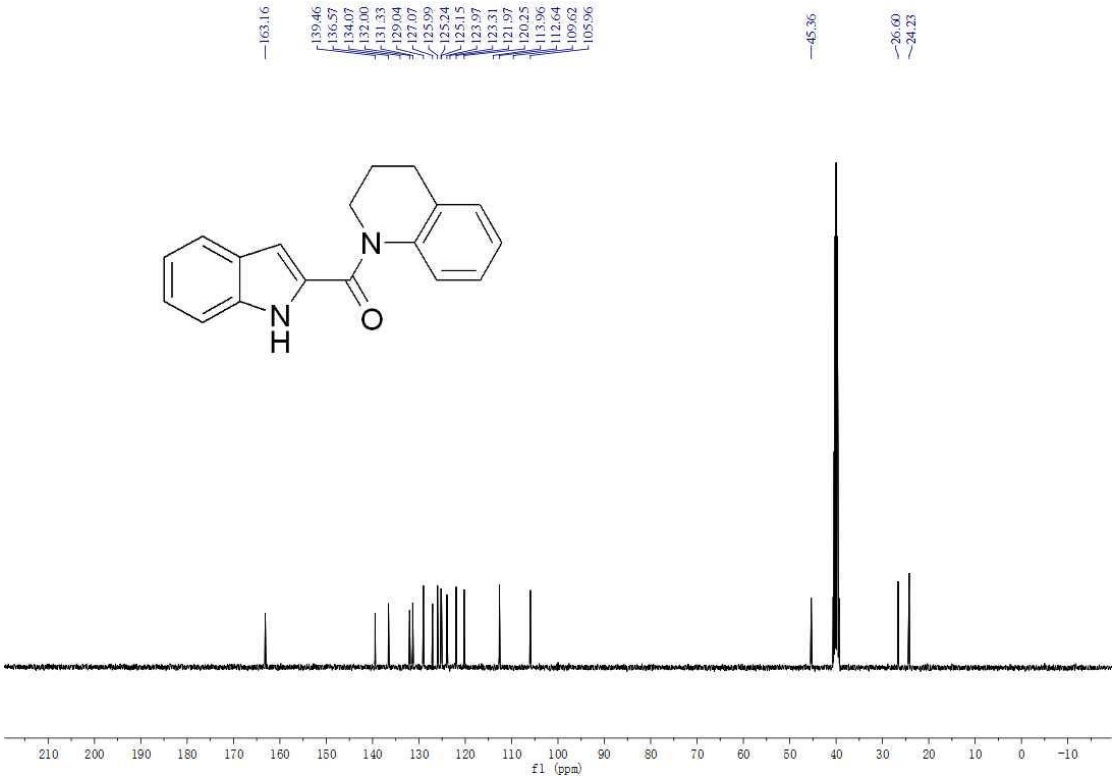
^{13}C NMR spectrum of **1ad**



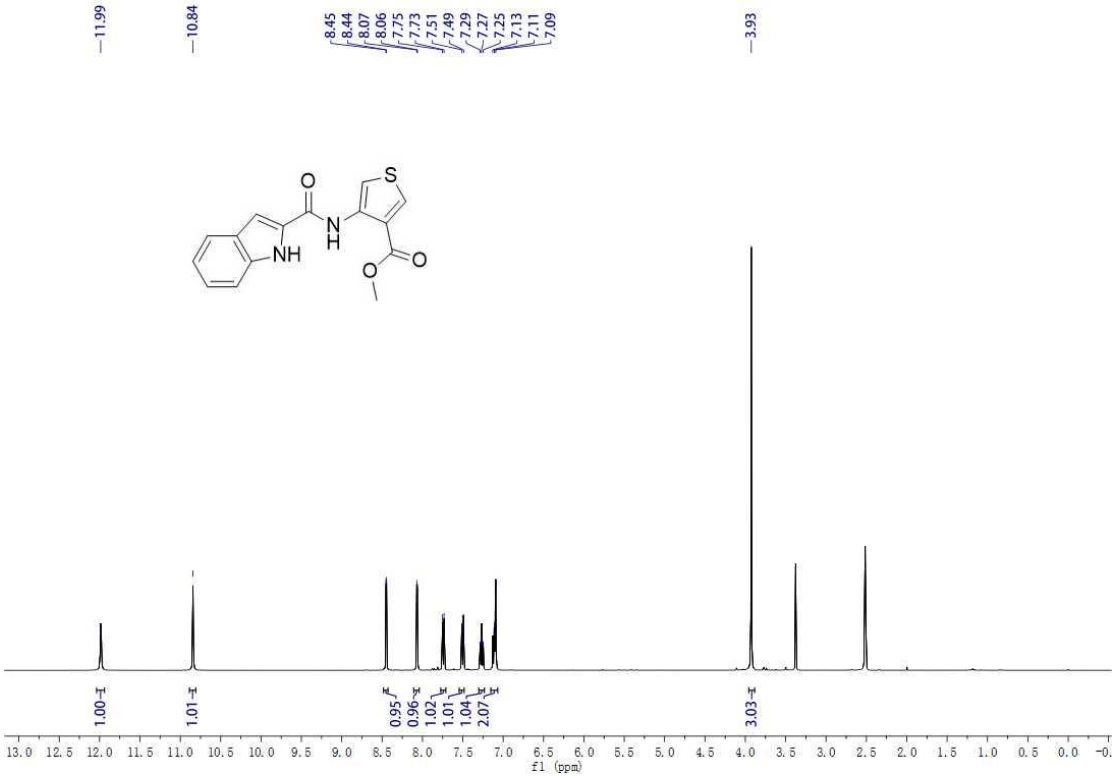
^{1}H NMR spectrum of **1ae**



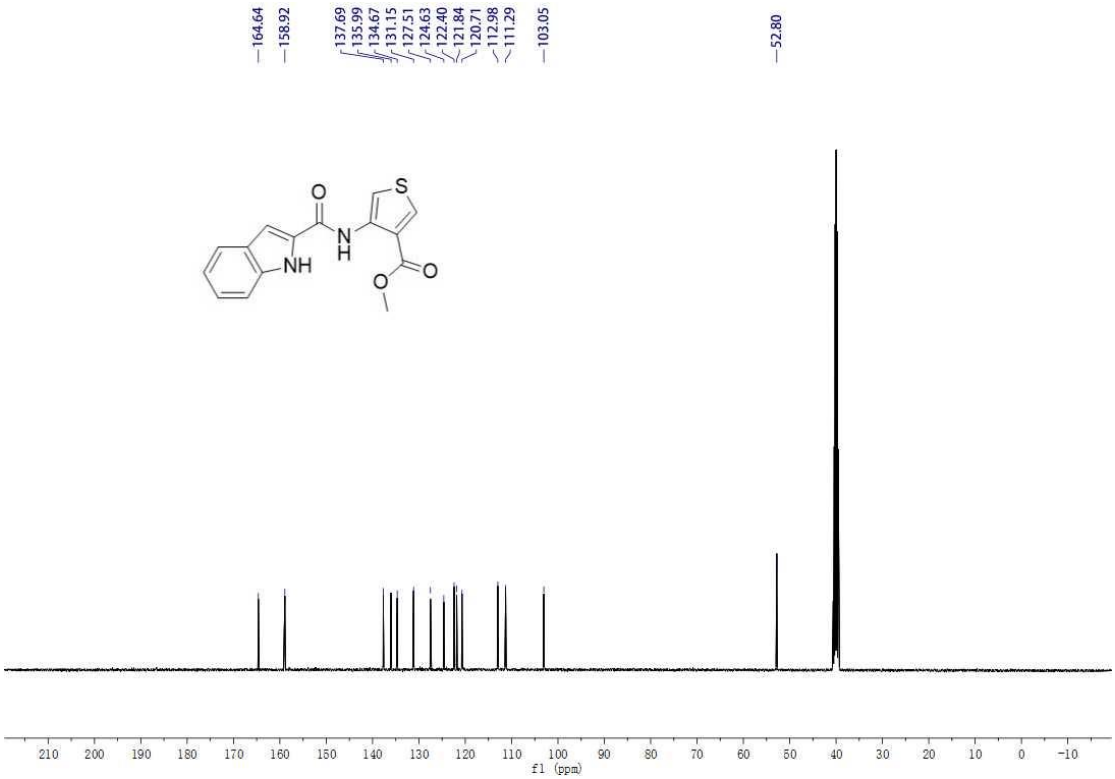
^{13}C NMR spectrum of **1ae**



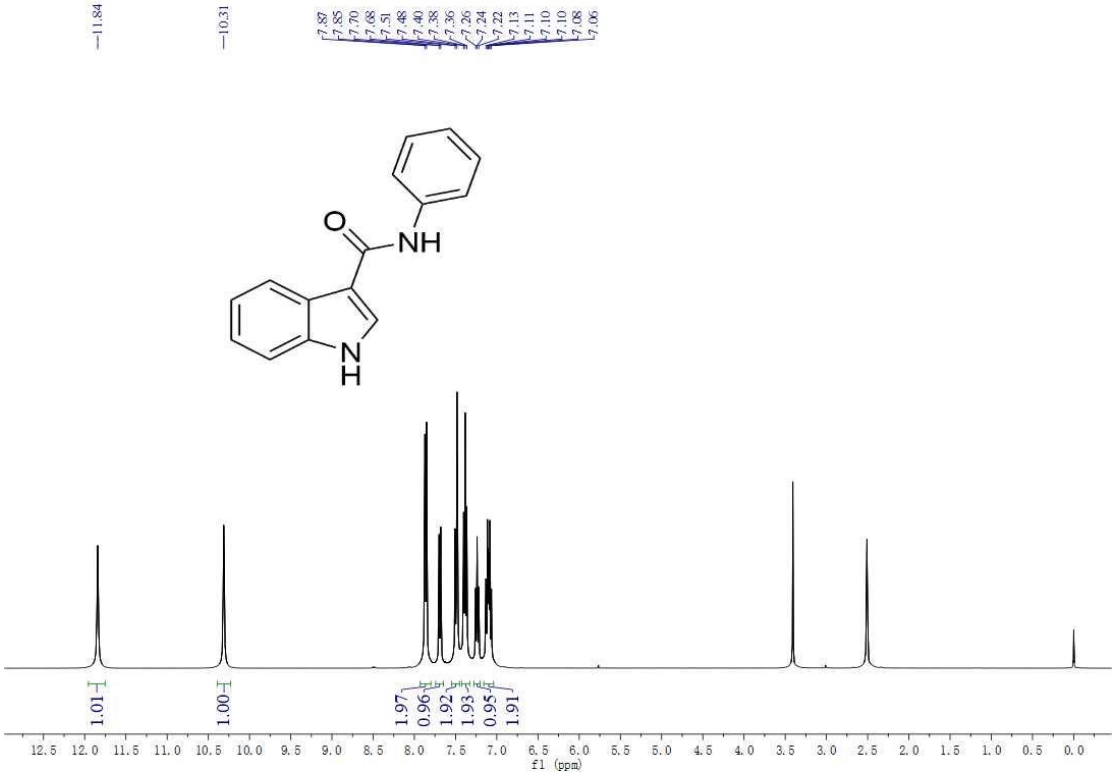
^{1}H NMR spectrum of **1af**



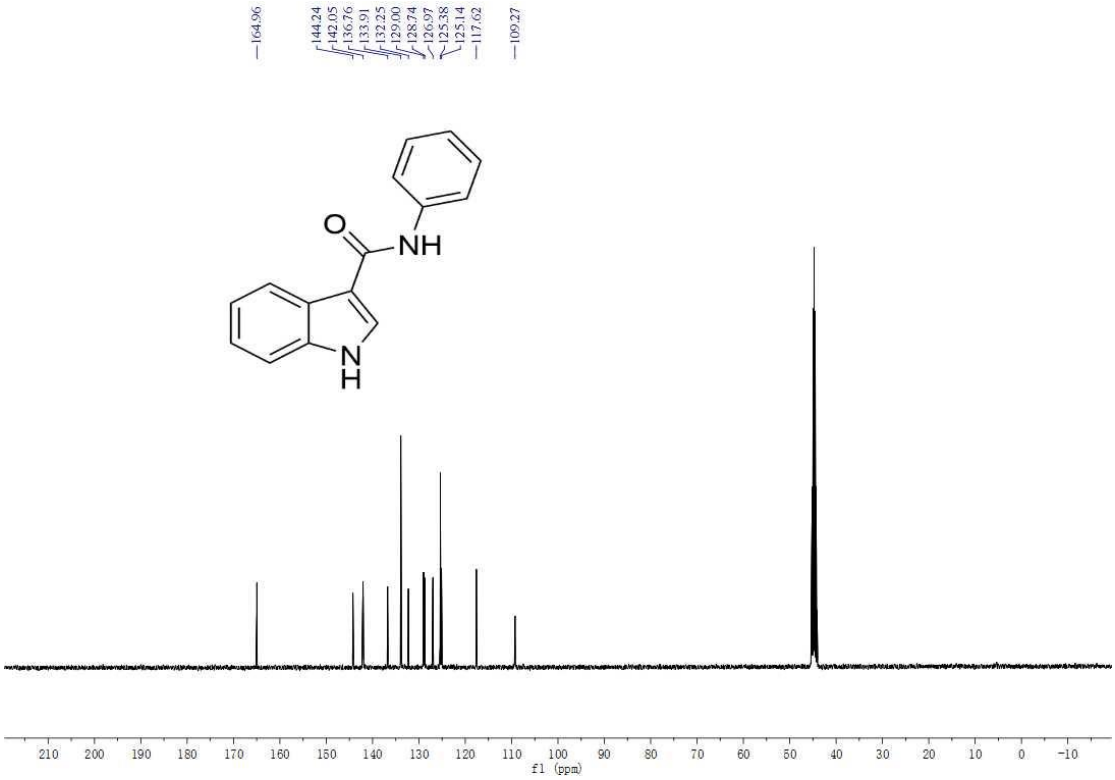
^{13}C NMR spectrum of **1af**



^{1}H NMR spectrum of **1ag**

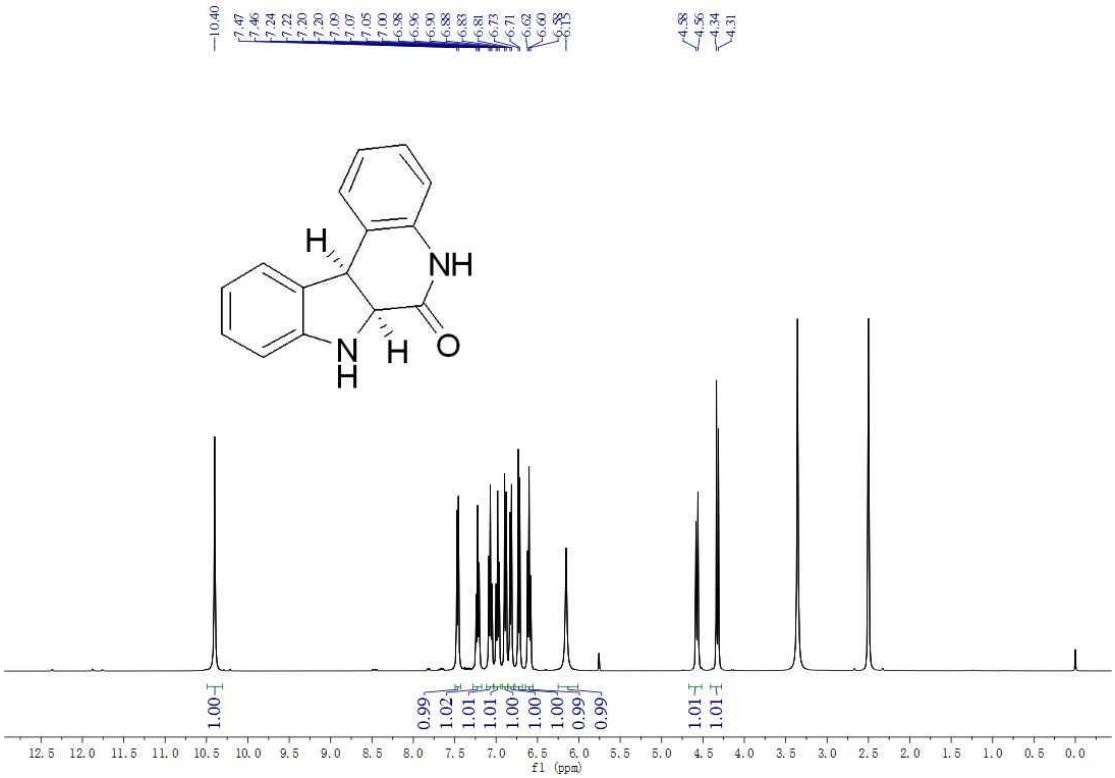


^{13}C NMR spectrum of **1ag**

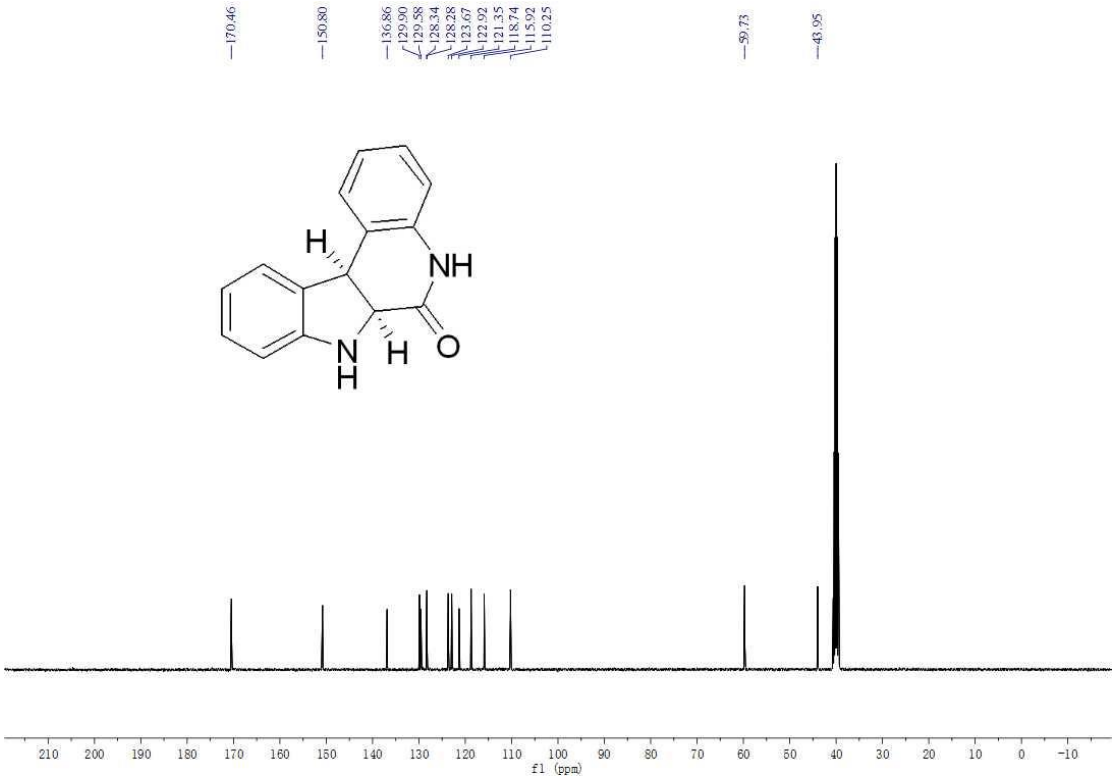


8. Copies of NMR spectra for the products

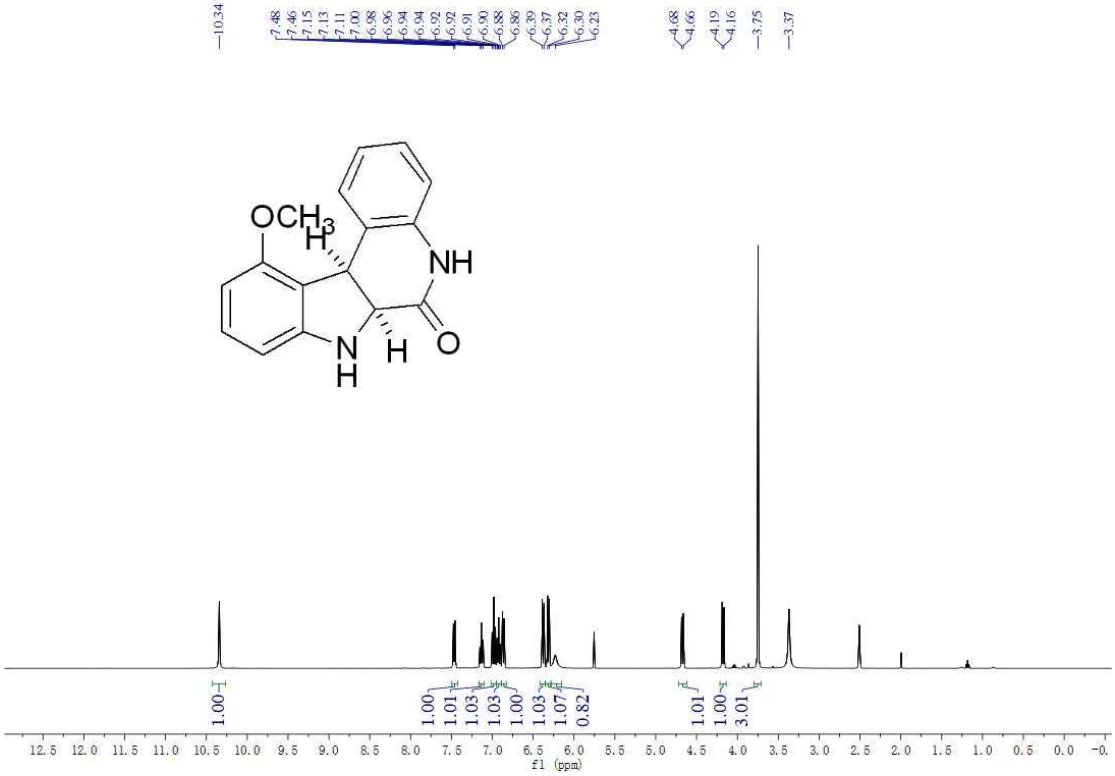
^{1}H NMR spectrum of **2a**



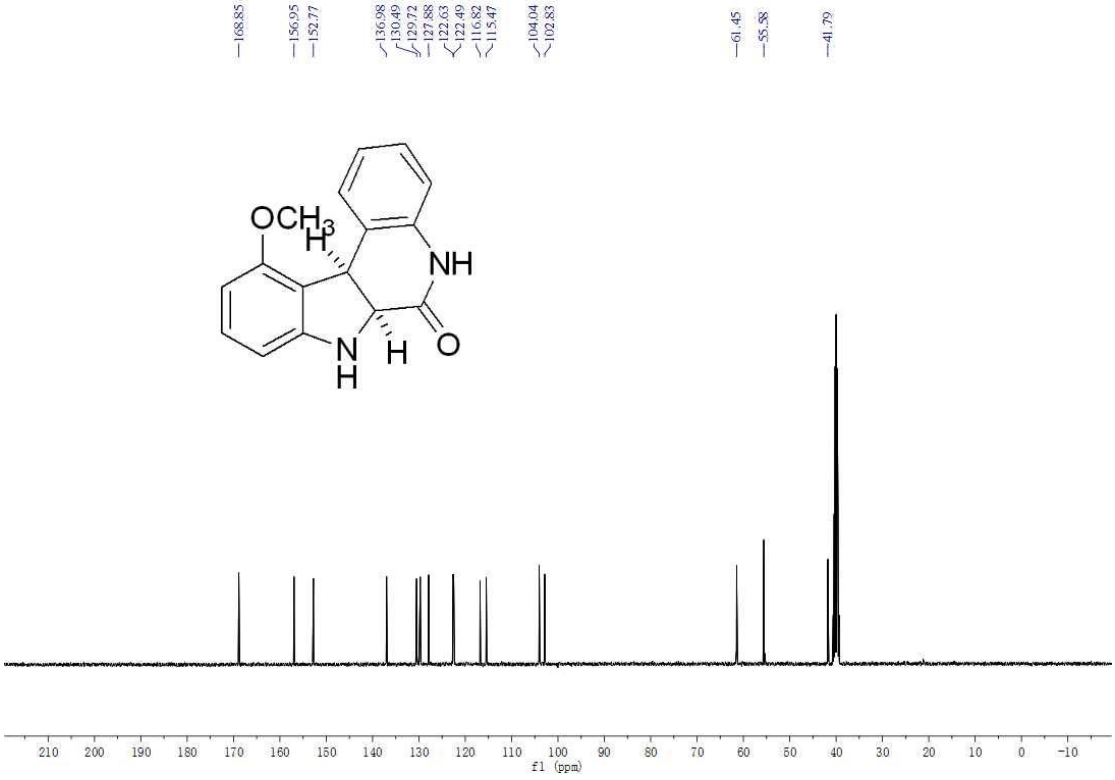
^{13}C NMR spectrum of **2a**



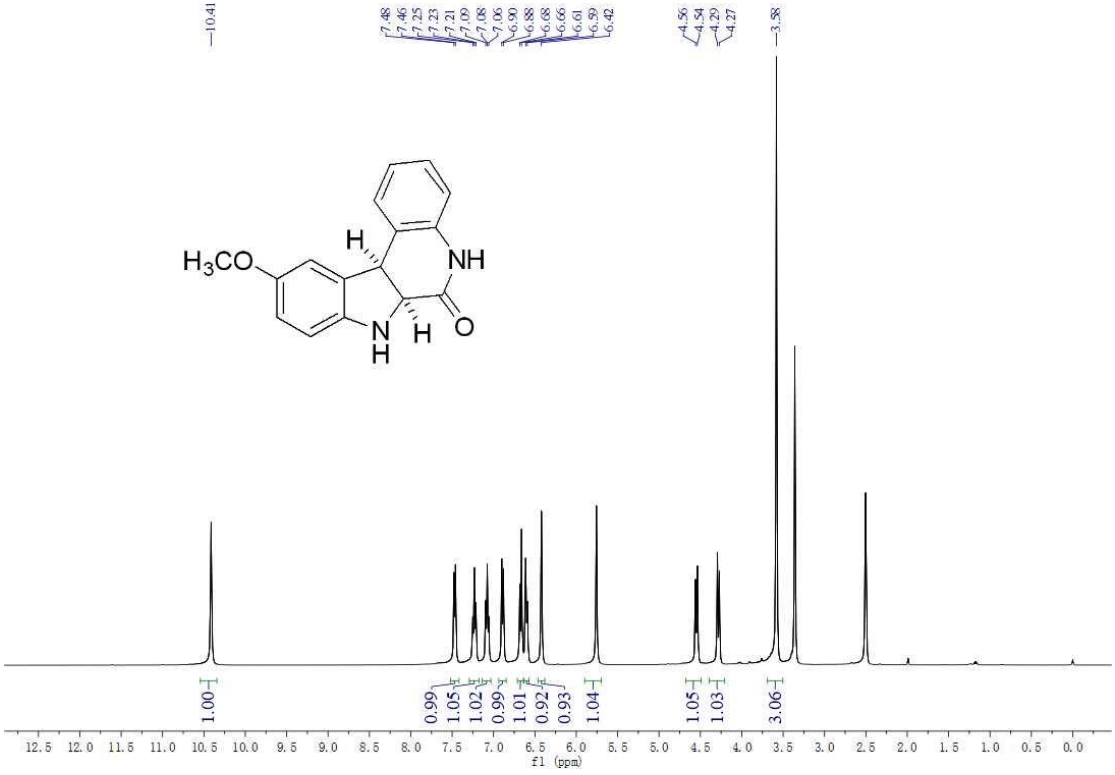
^{1}H NMR spectrum of **2b**



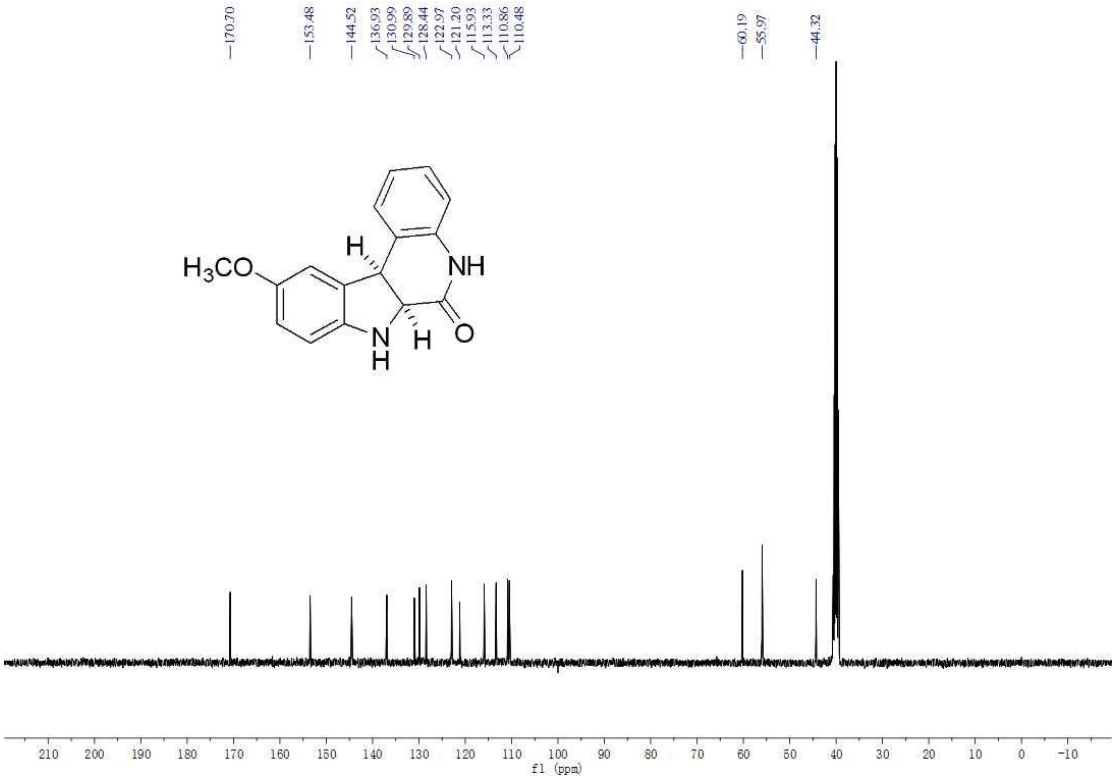
^{13}C NMR spectrum of **2b**



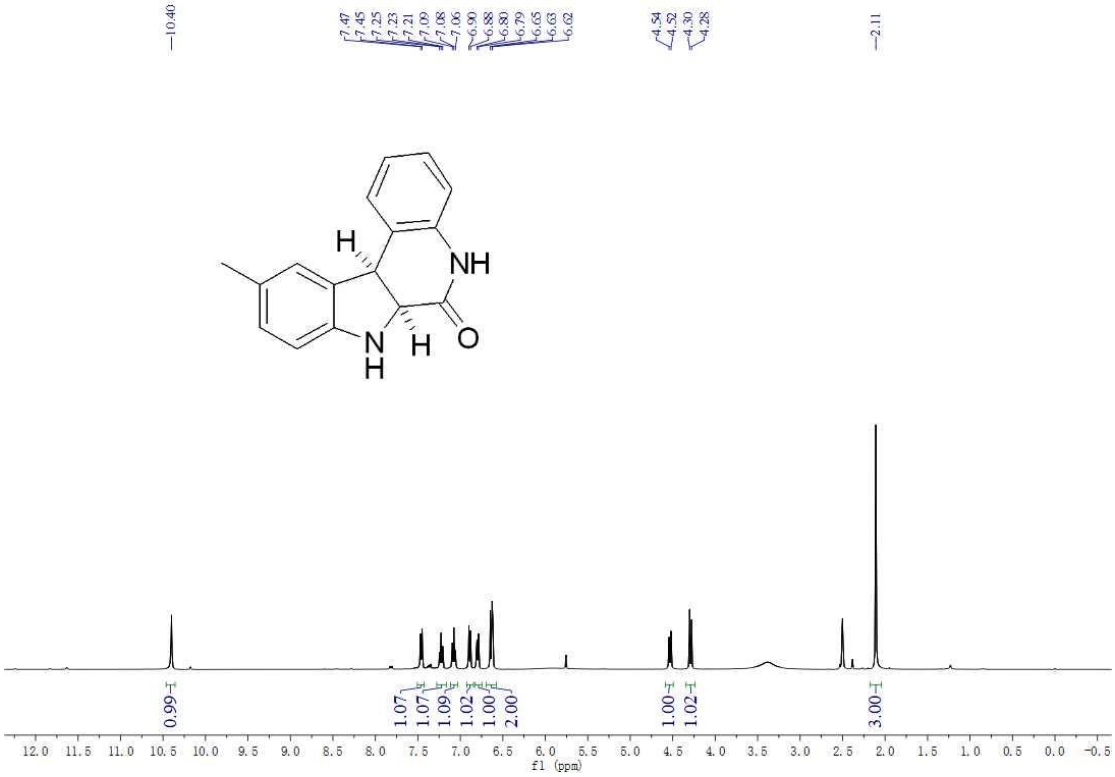
^{1}H NMR spectrum of **2c**



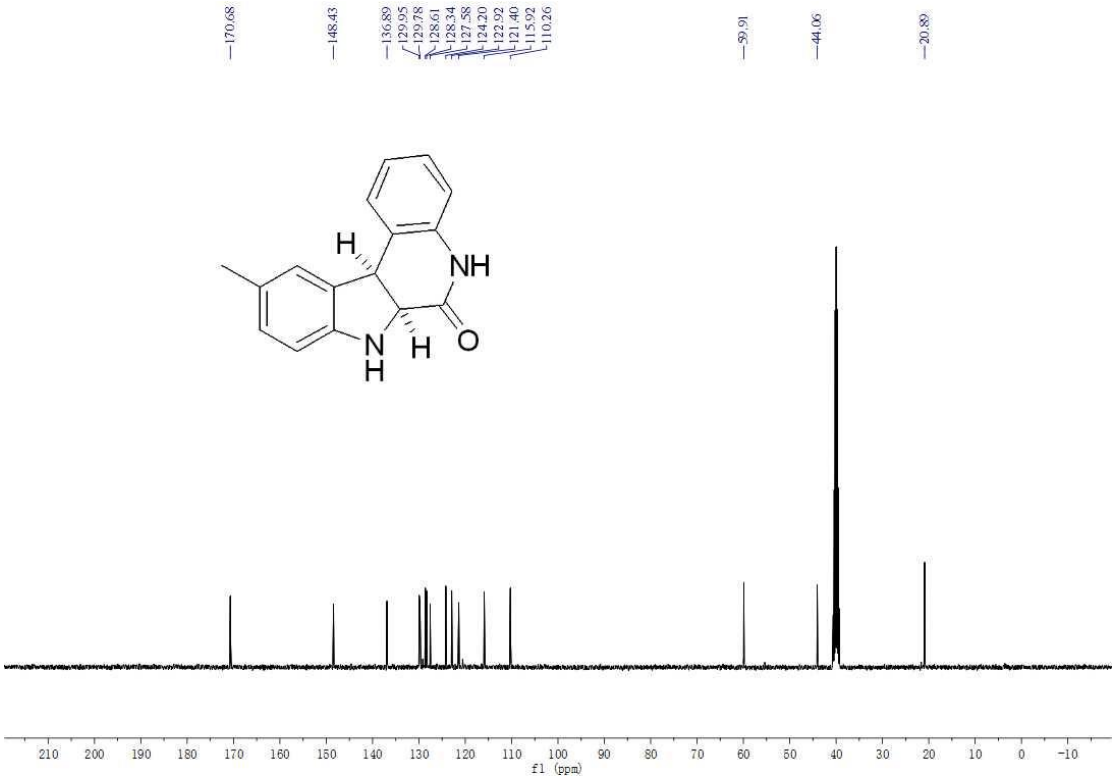
^{13}C NMR spectrum of **2c**



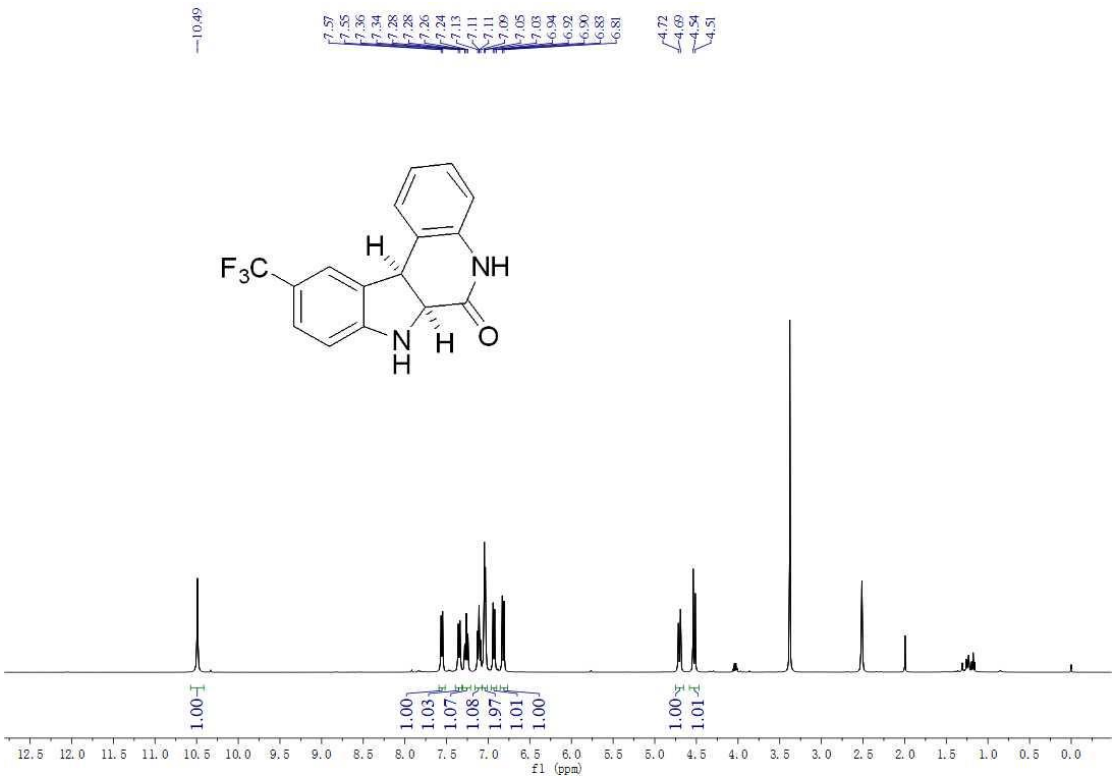
^{1}H NMR spectrum of **2d**



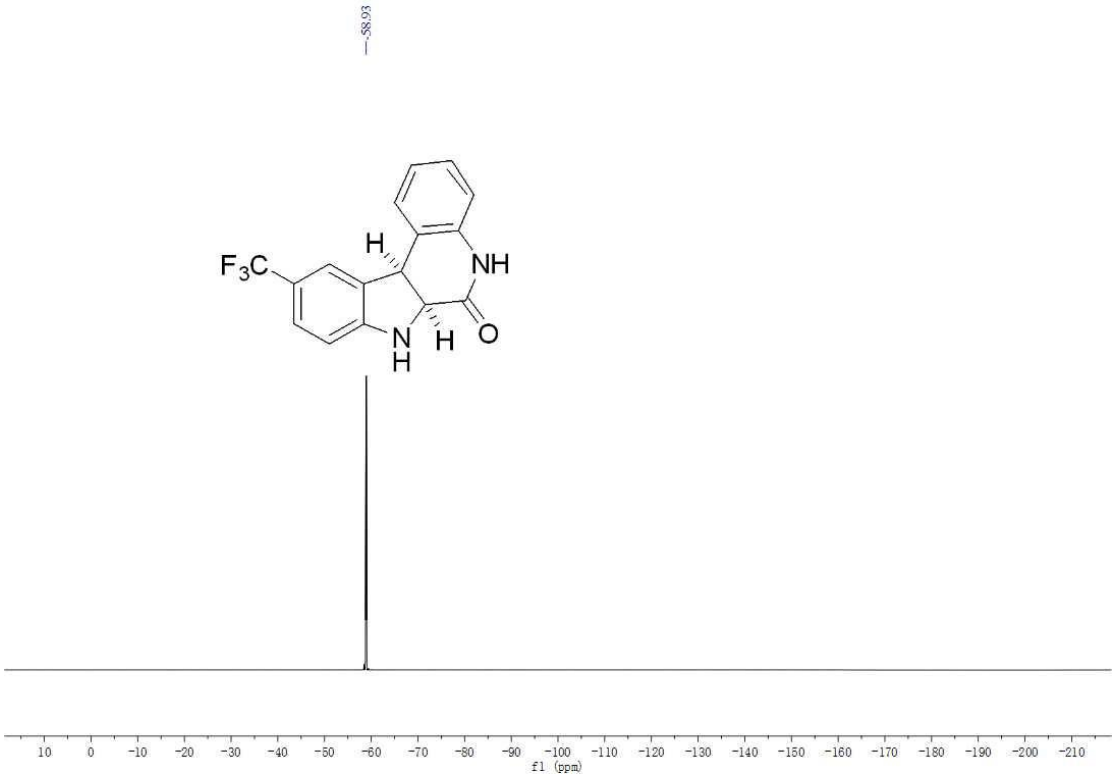
^{13}C NMR spectrum of **2d**



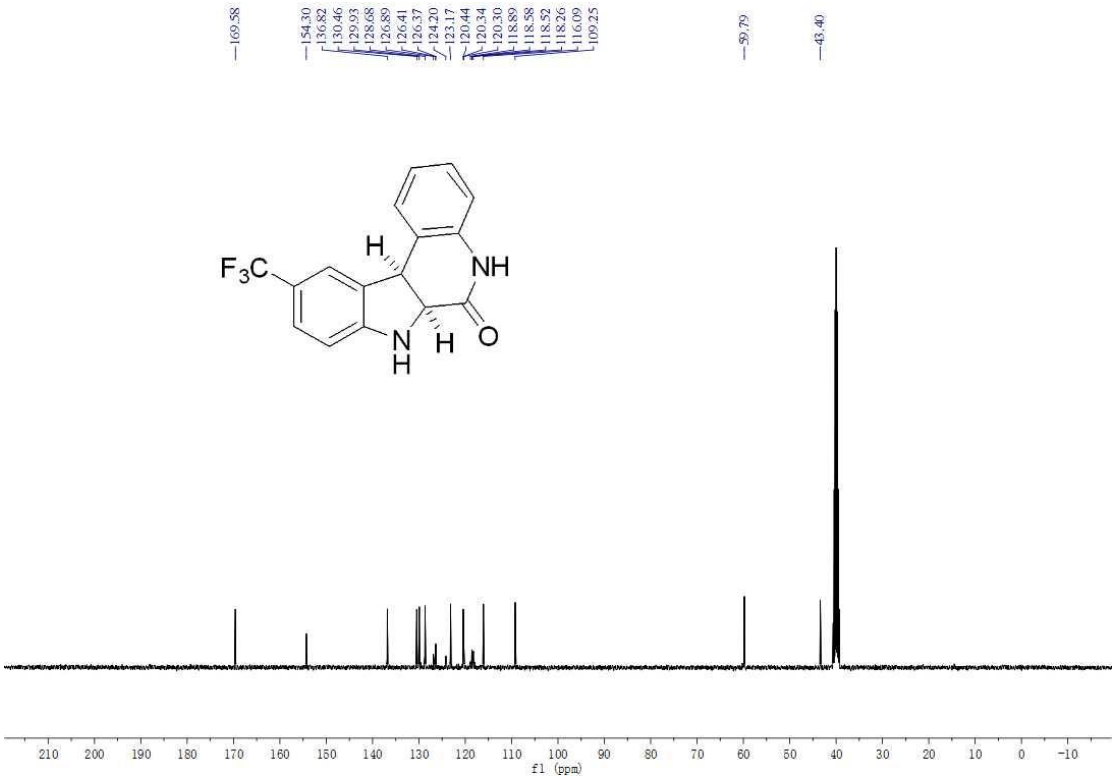
^{1}H NMR spectrum of **2e**



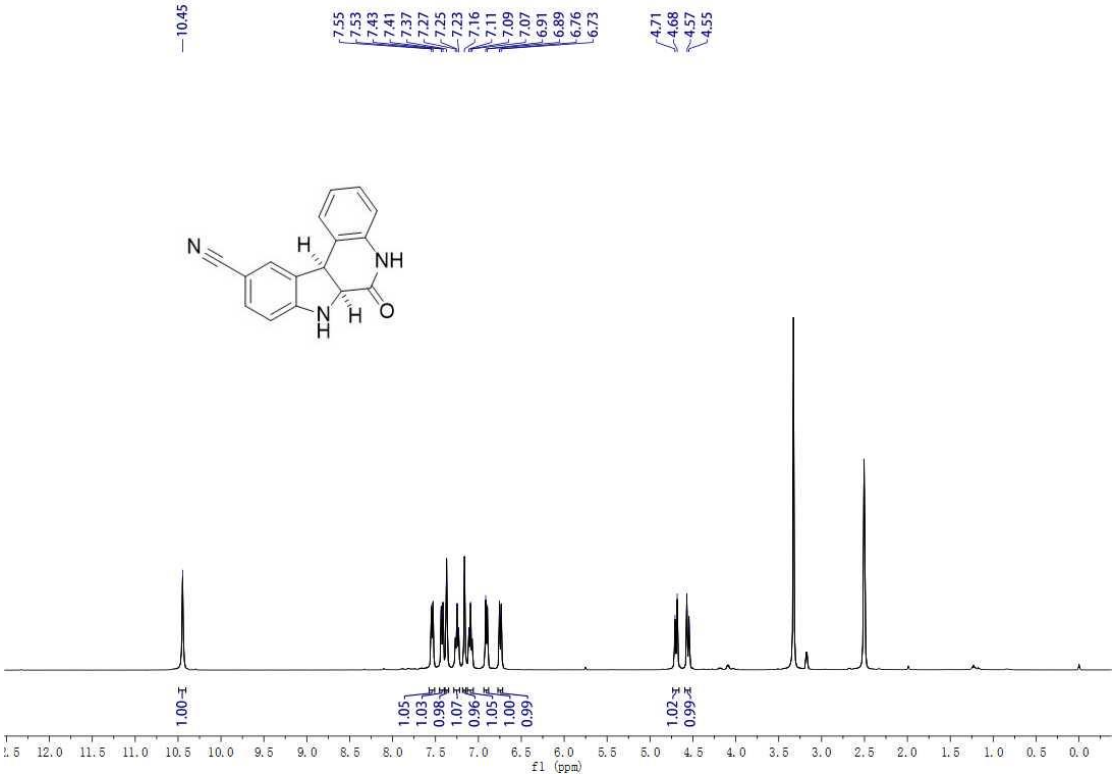
^{19}F NMR spectrum of **2e**



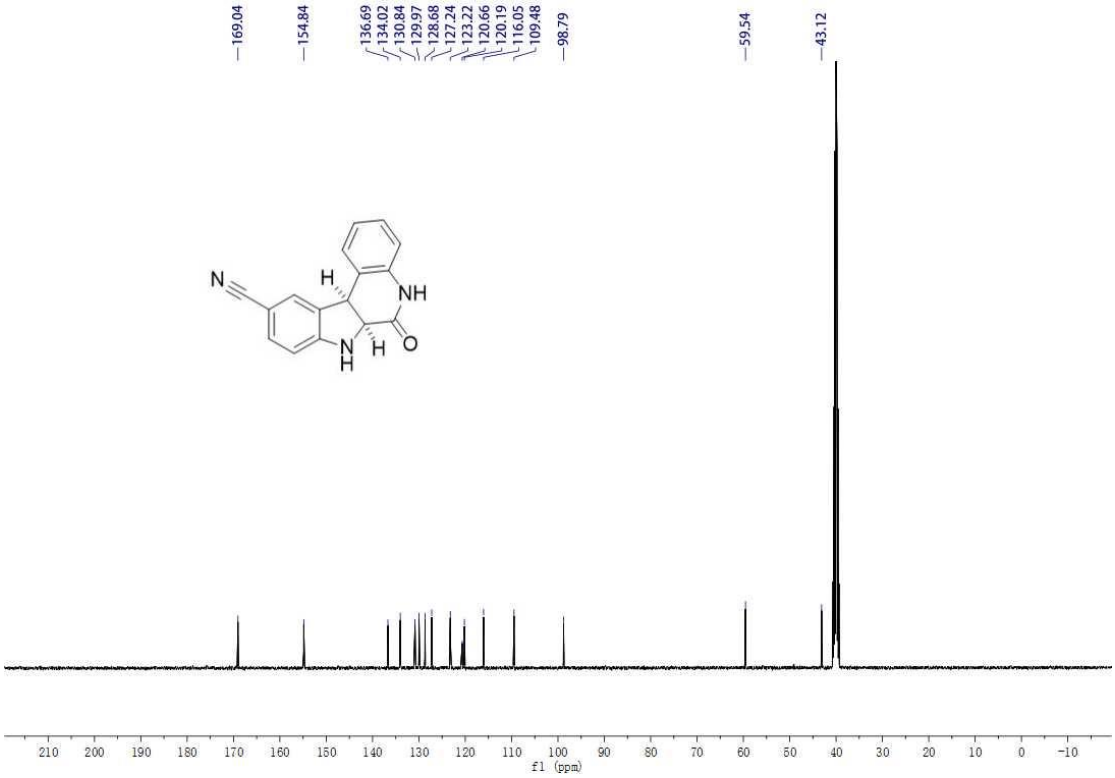
^{13}C NMR spectrum of **2e**



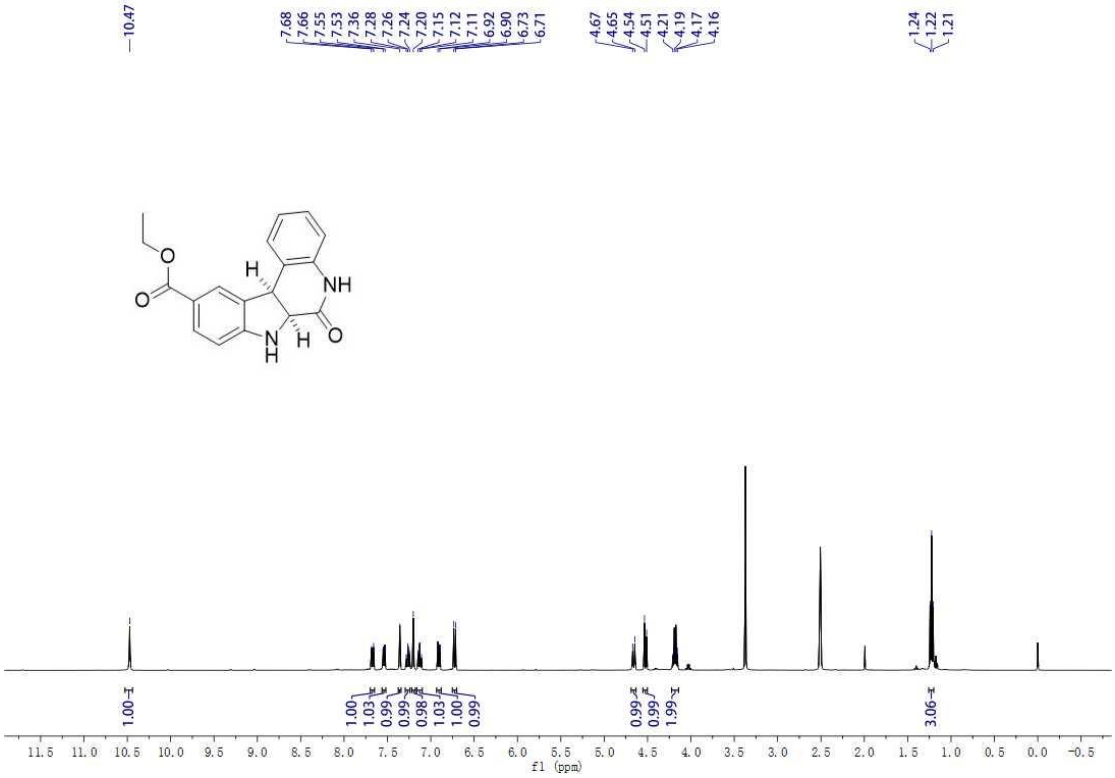
^{1}H NMR spectrum of **2f**



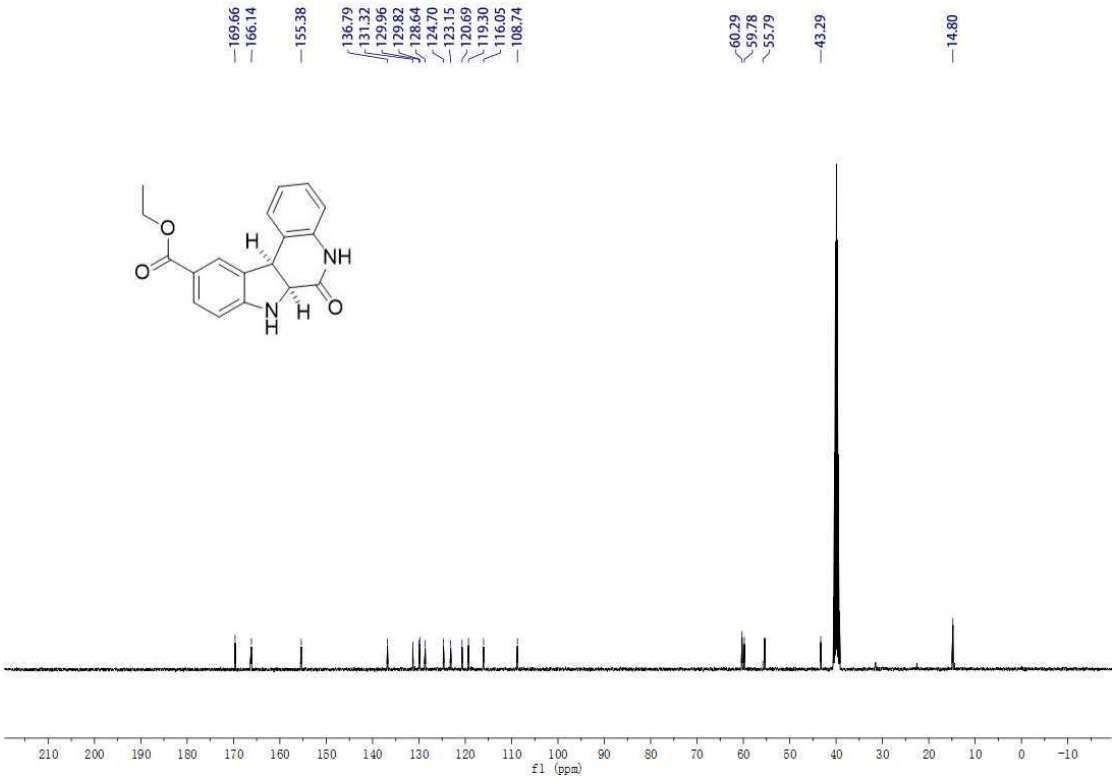
^{13}C NMR spectrum of **2f**



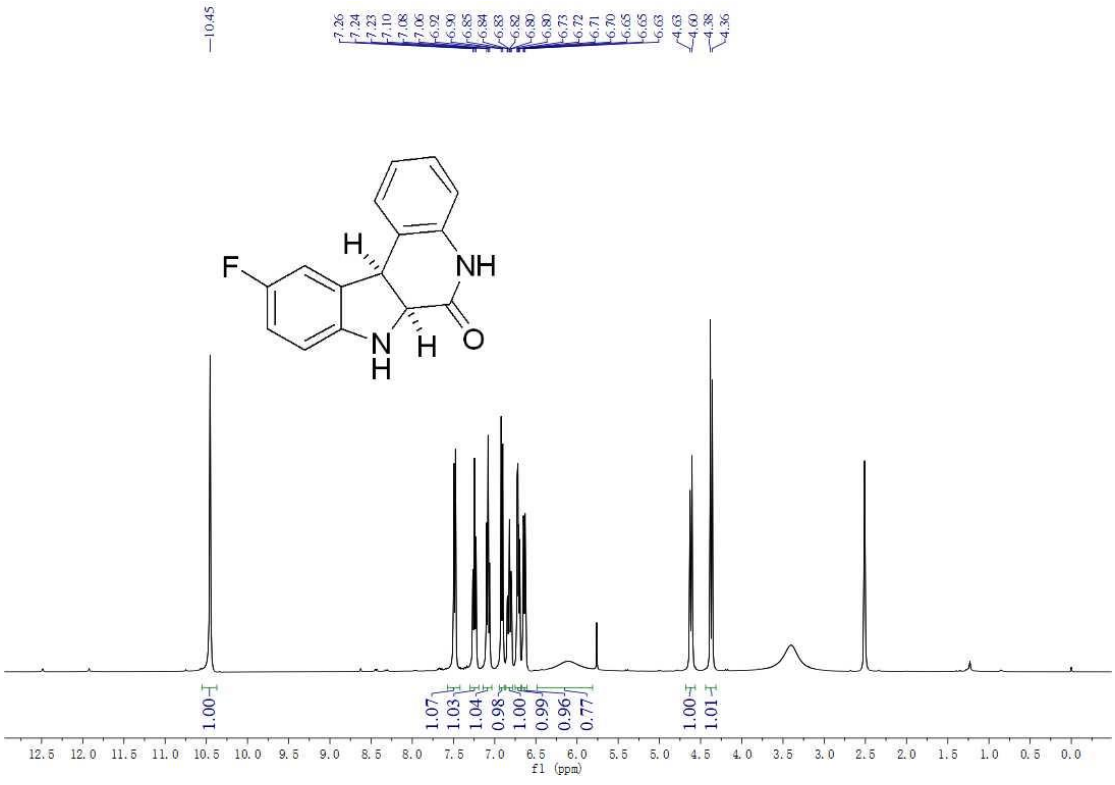
^{1}H NMR spectrum of **2g**



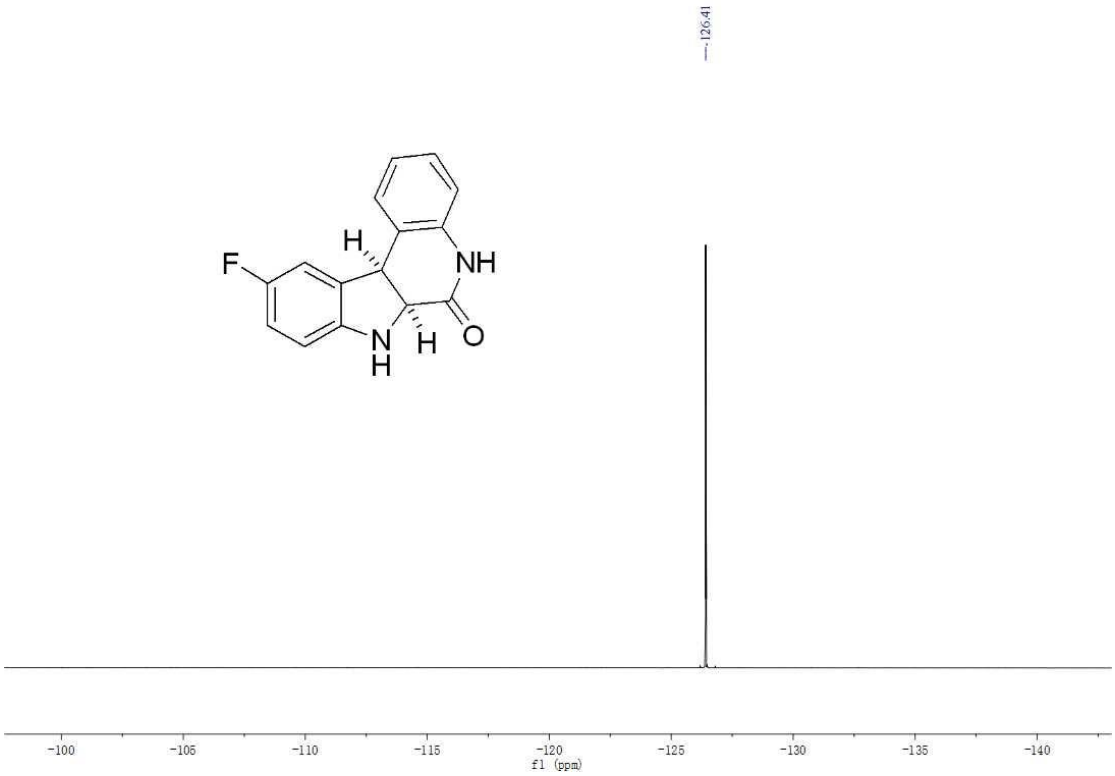
^{13}C NMR spectrum of **2g**



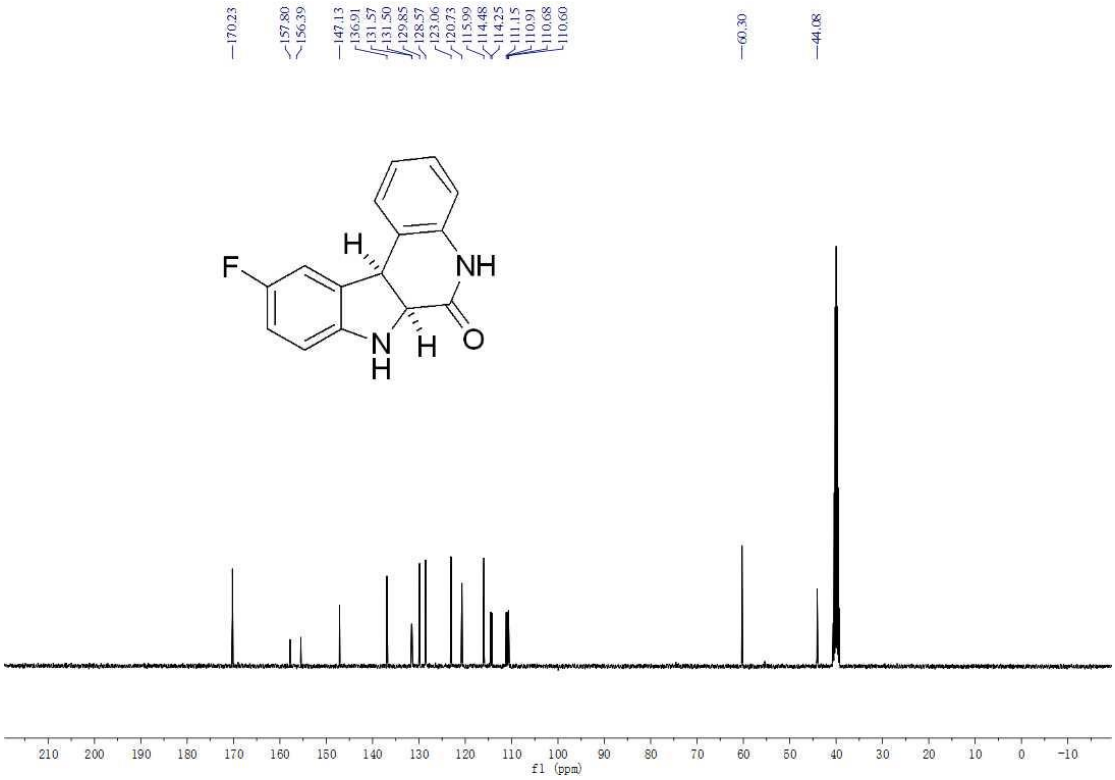
^{1}H NMR spectrum of **2h**



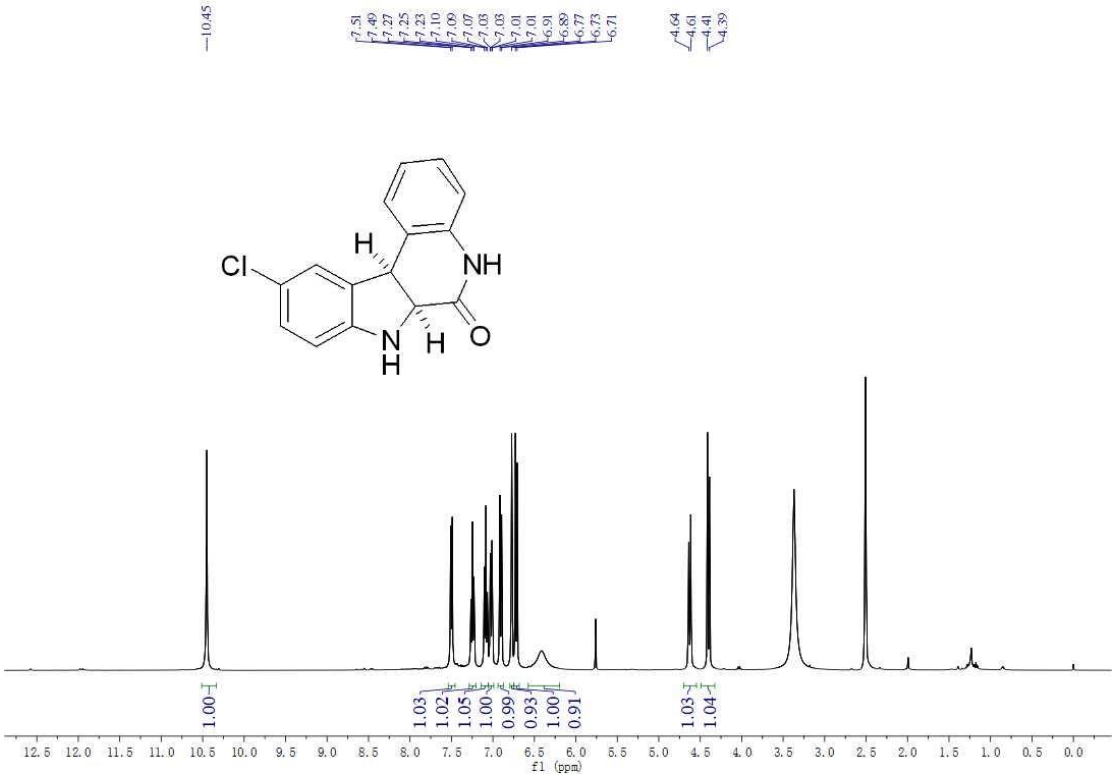
^{19}F NMR spectrum of **2h**



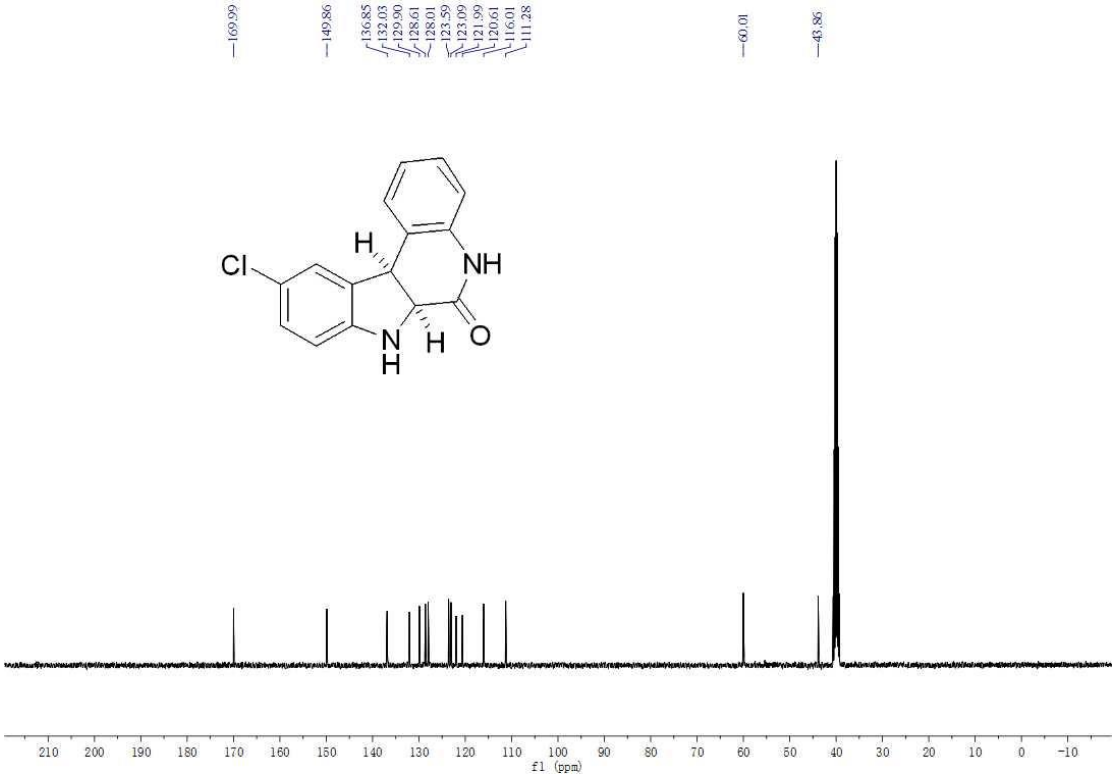
^{13}C NMR spectrum of **2h**



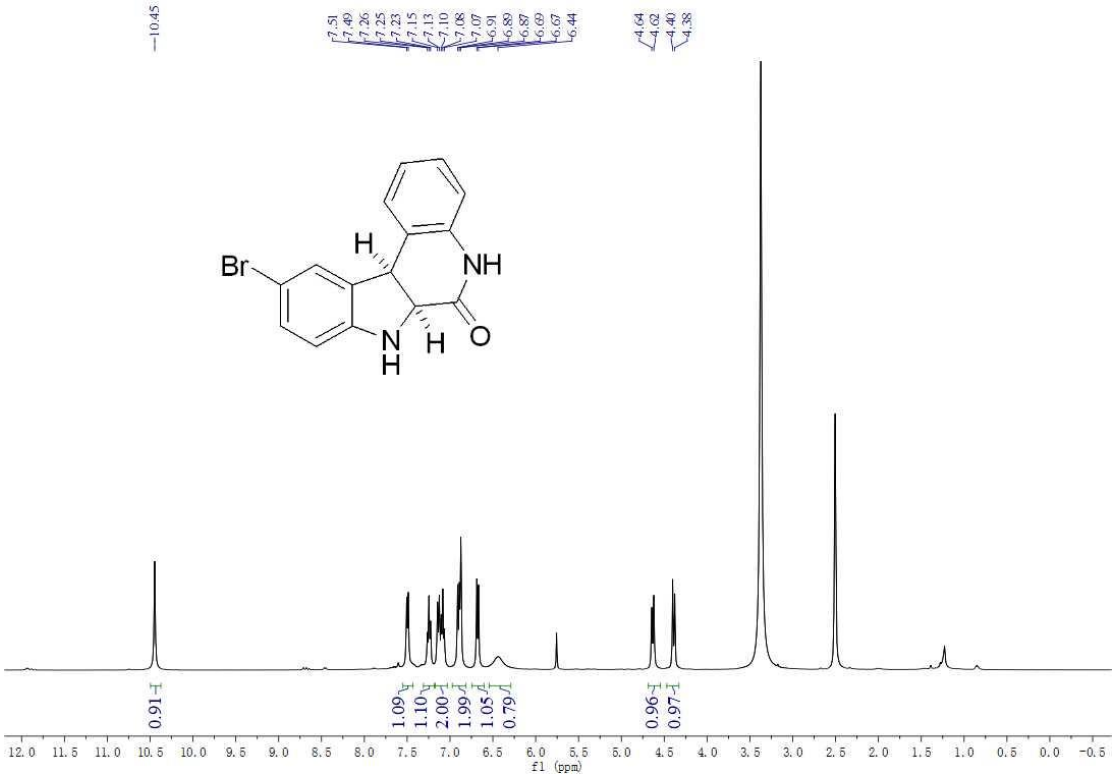
^{1}H NMR spectrum of **2i**



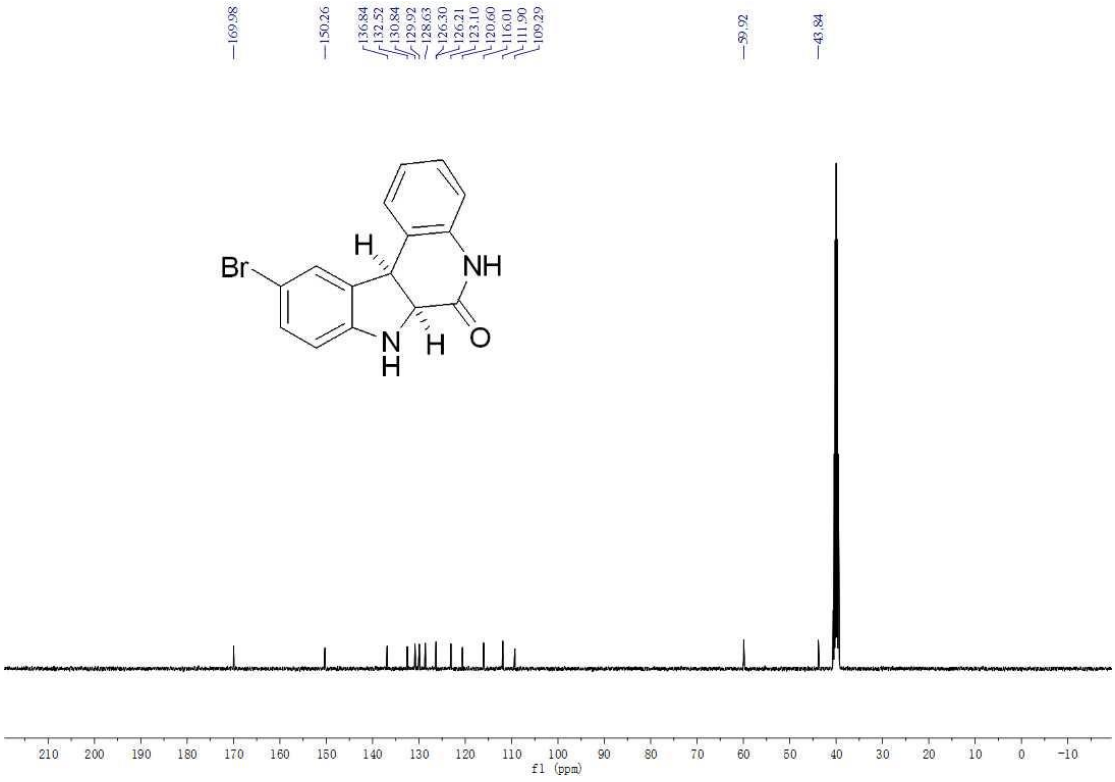
^{13}C NMR spectrum of **2i**



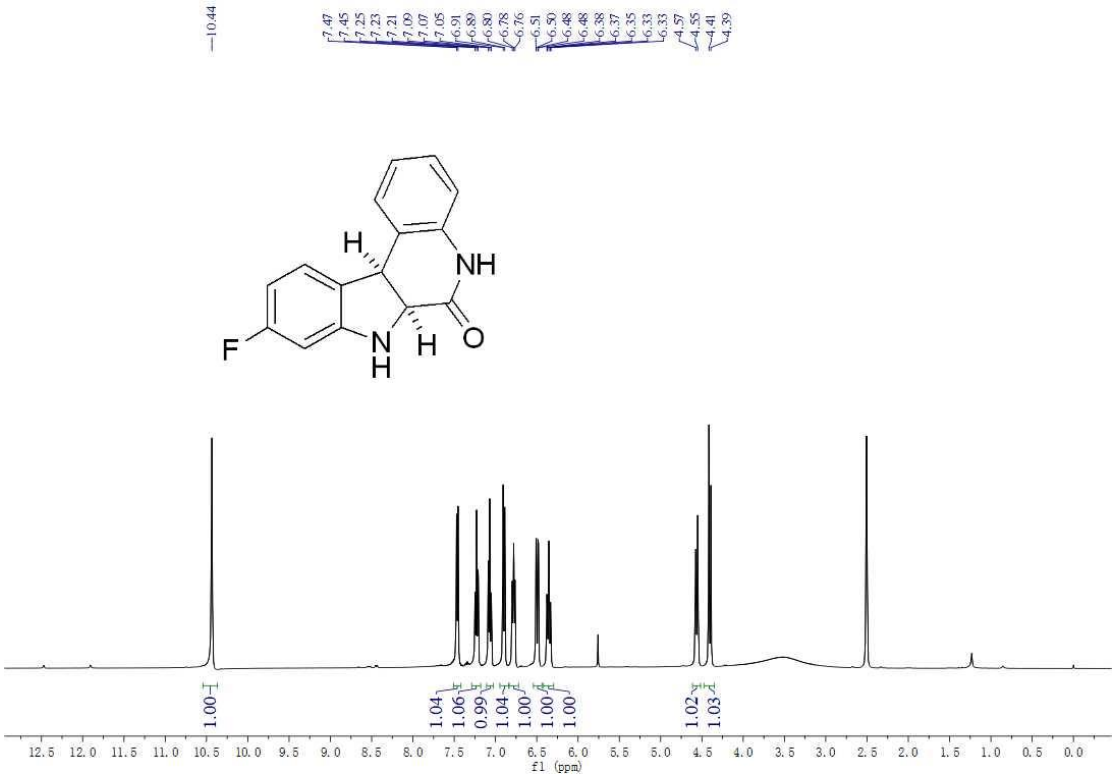
^{1}H NMR spectrum of **2j**



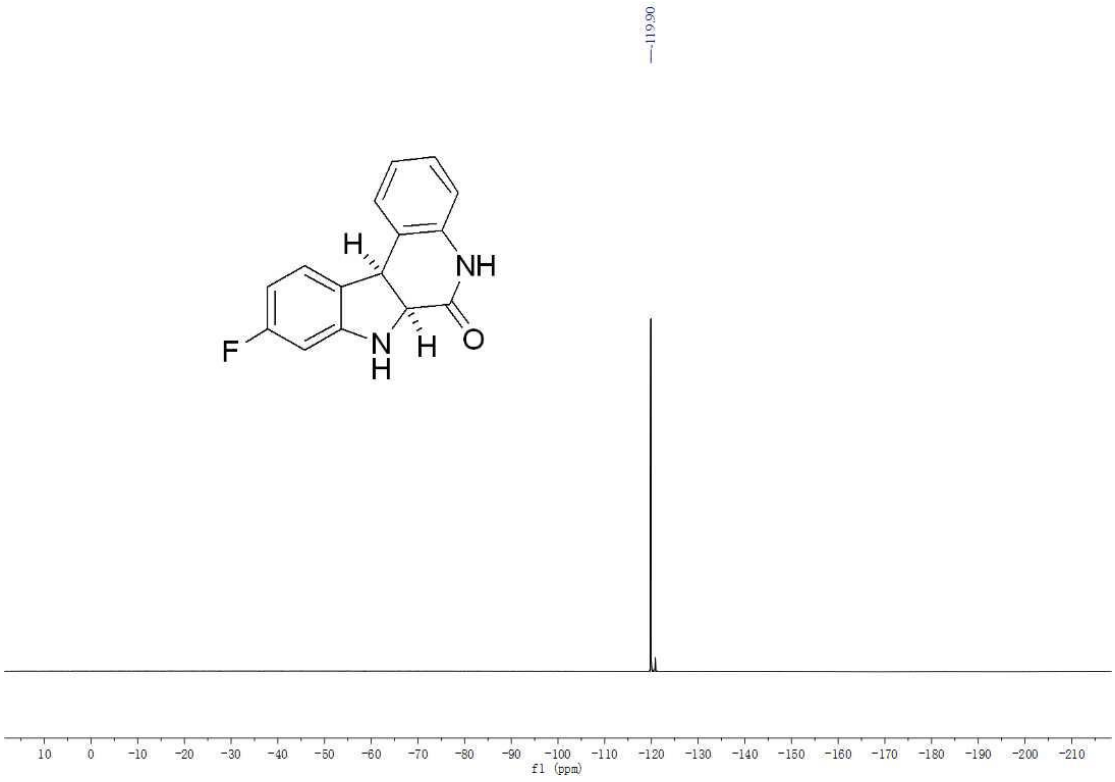
^{13}C NMR spectrum of **2j**



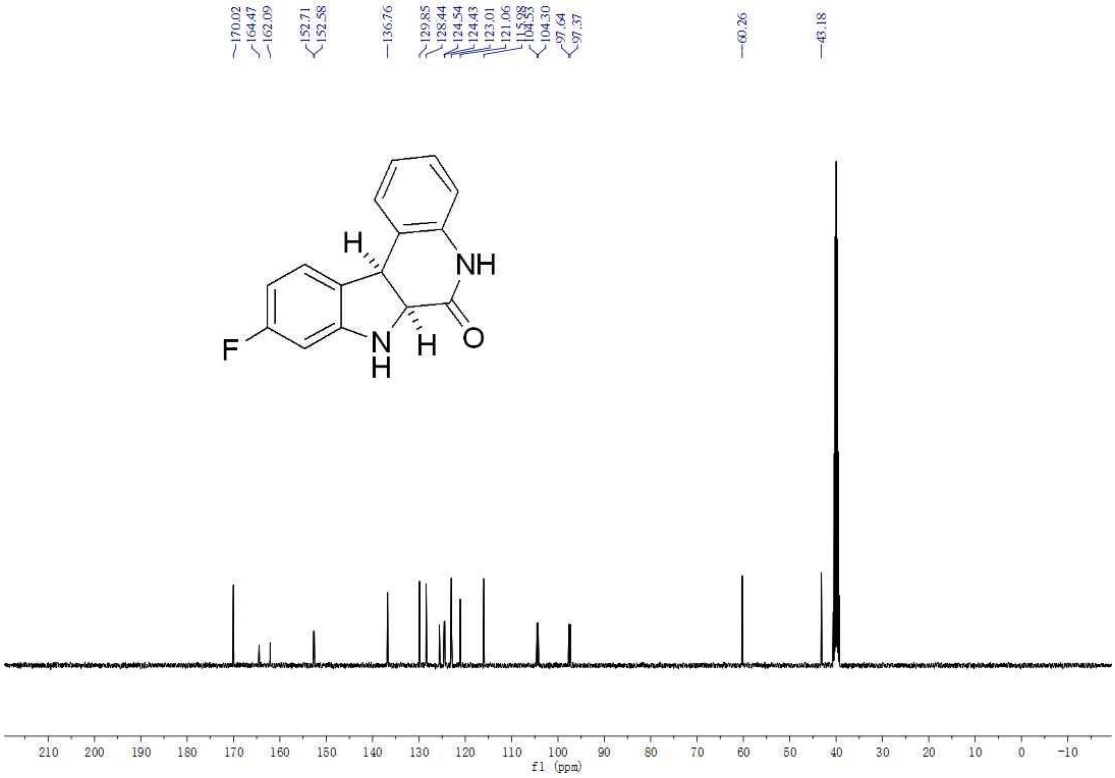
^{1}H NMR spectrum of **2k**



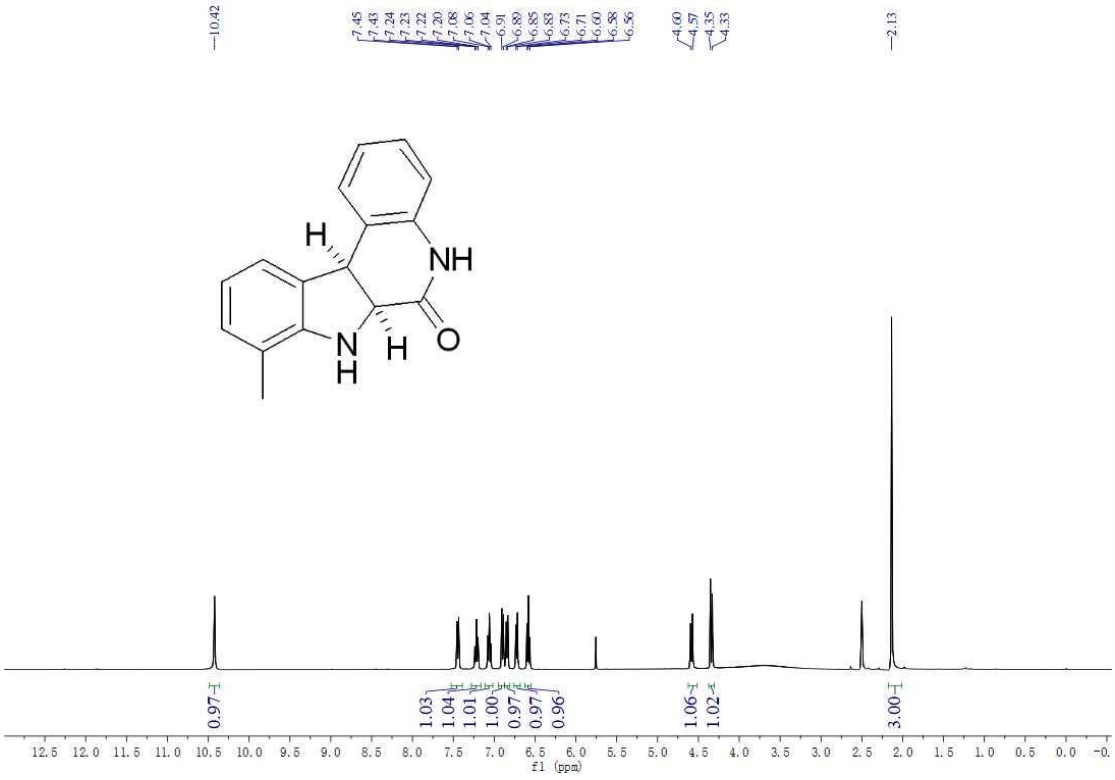
^{19}F NMR spectrum of **2k**



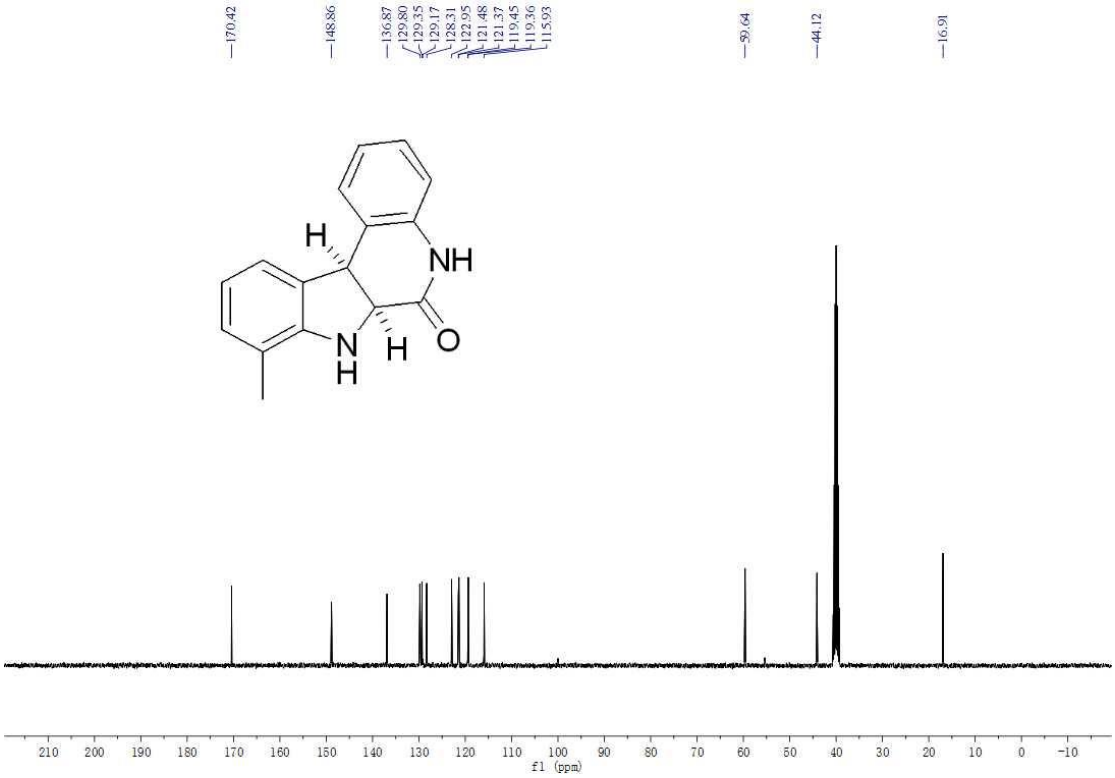
^{13}C NMR spectrum of **2k**



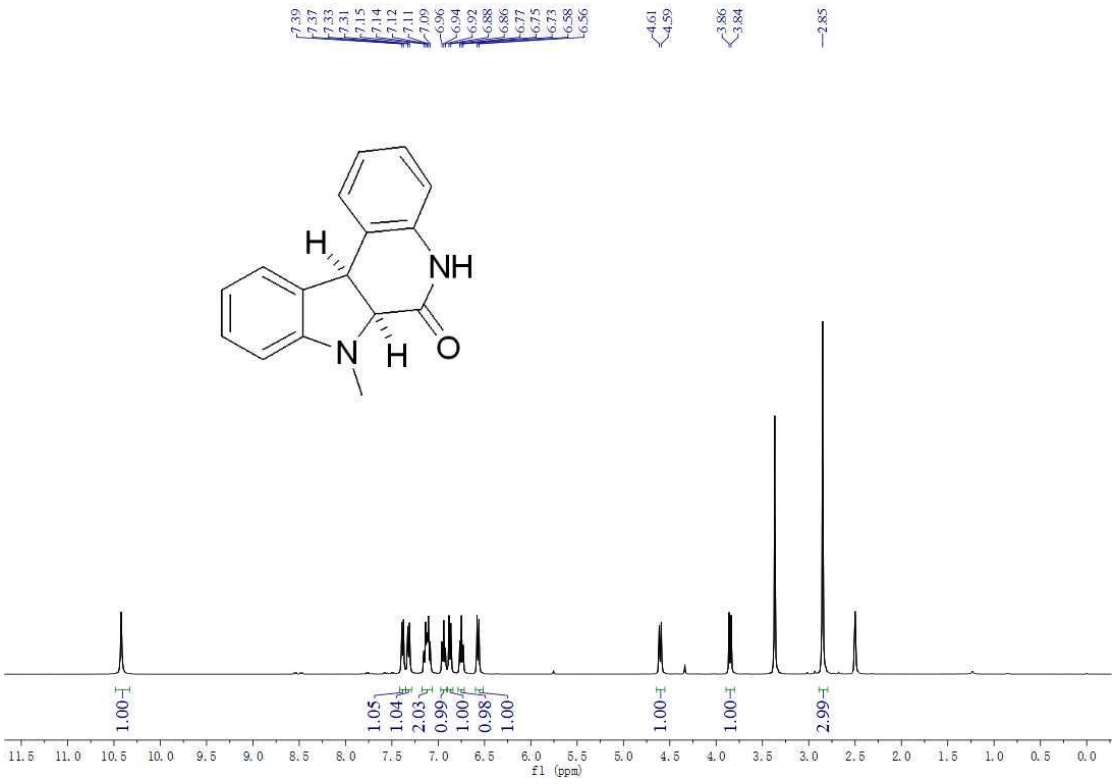
^{1}H NMR spectrum of **2l**



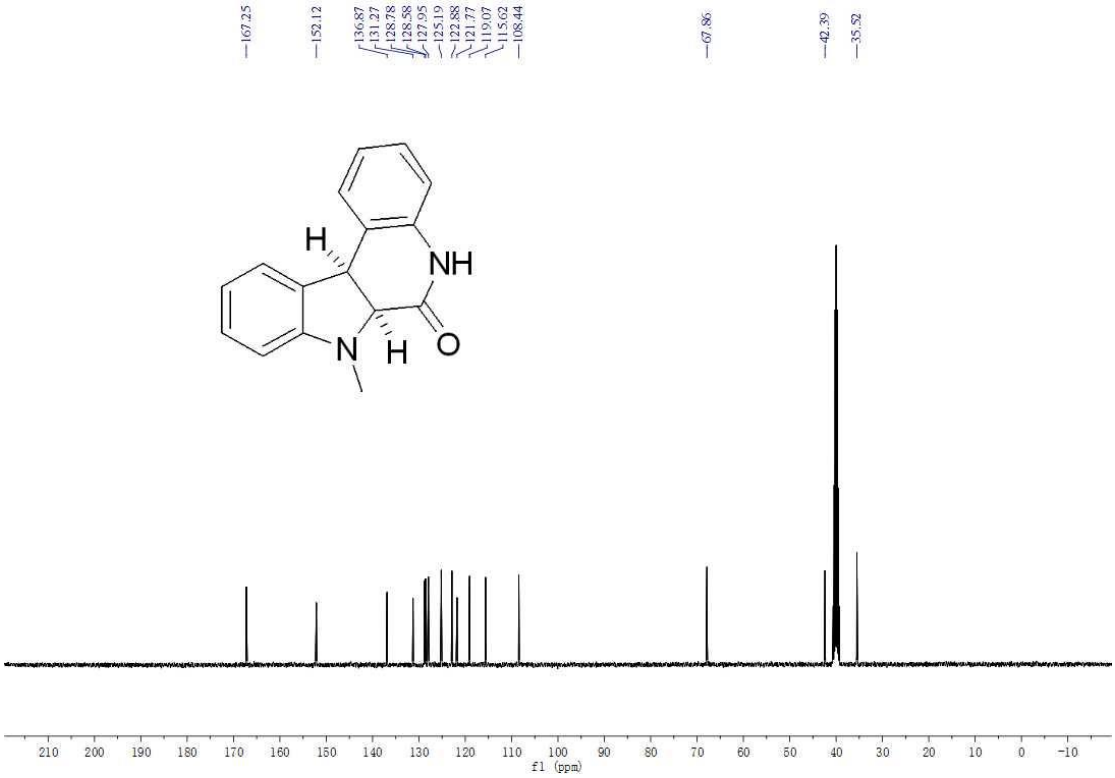
^{13}C NMR spectrum of **2l**



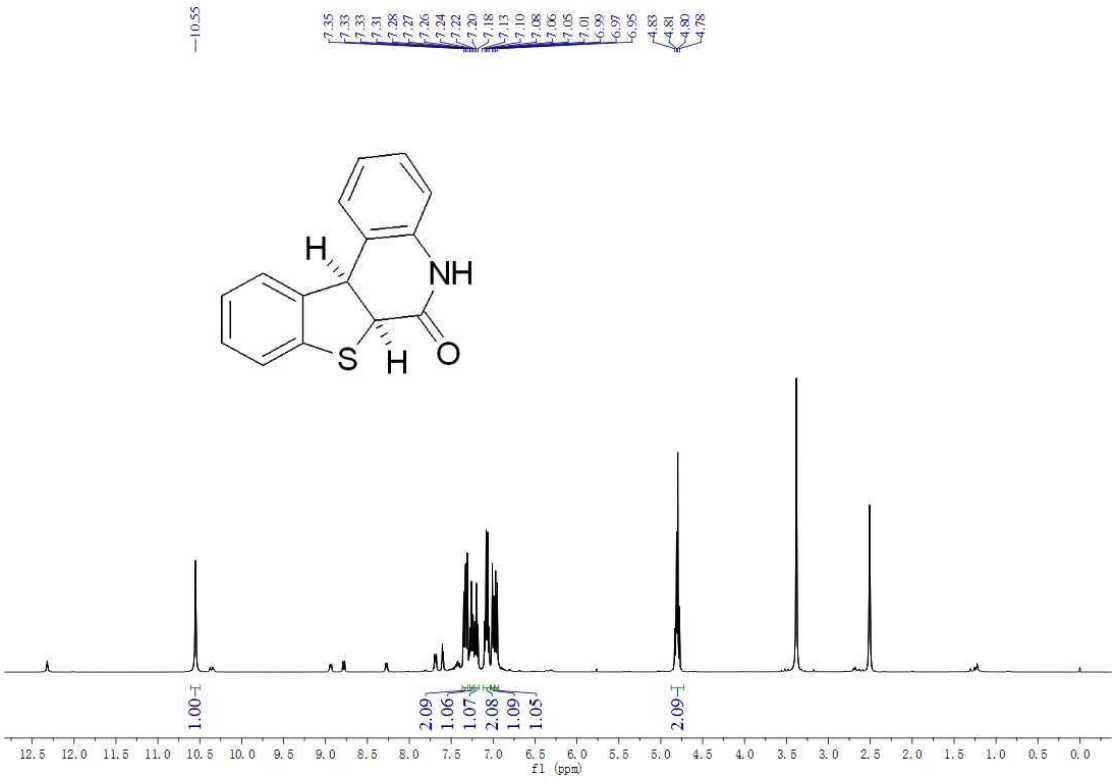
^{1}H NMR spectrum of **2m**



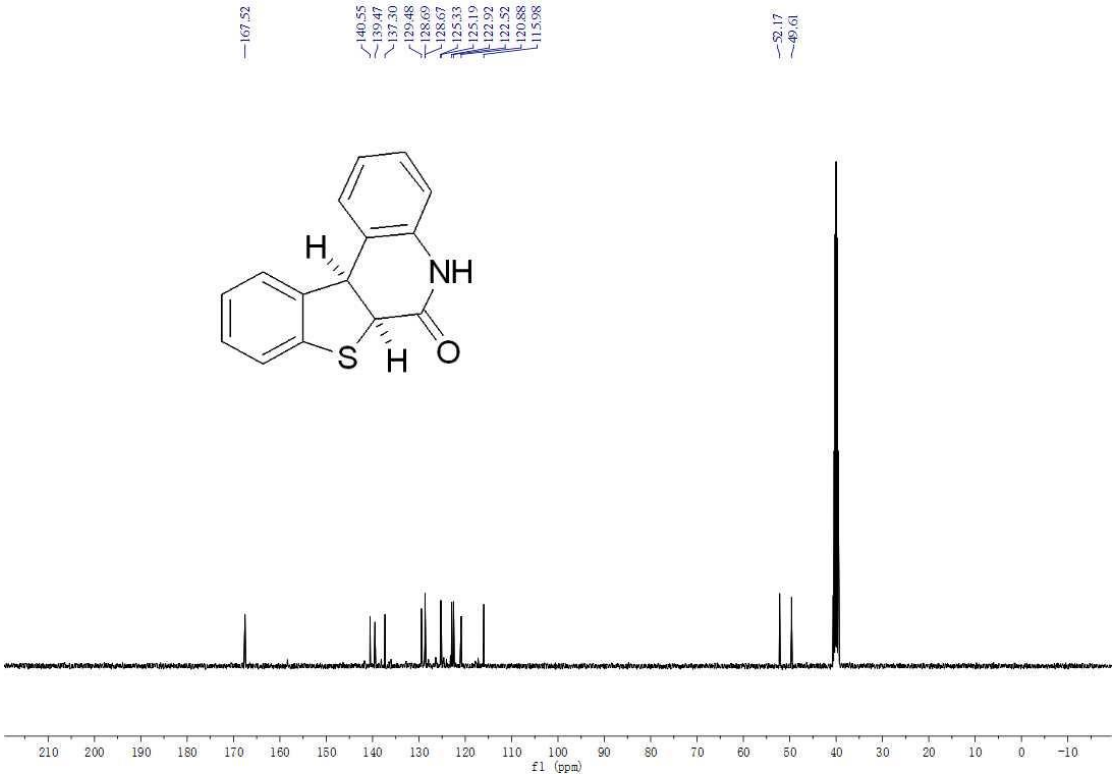
^{13}C NMR spectrum of **2m**



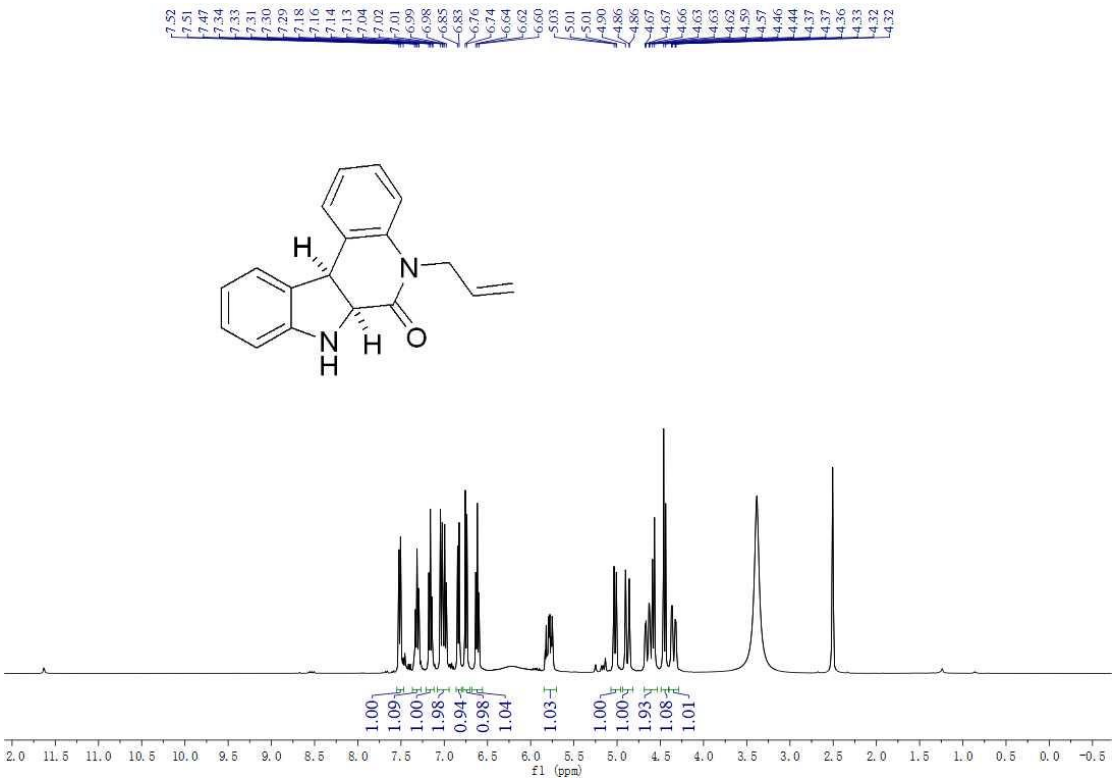
^{1}HNMR spectrum of **2n**



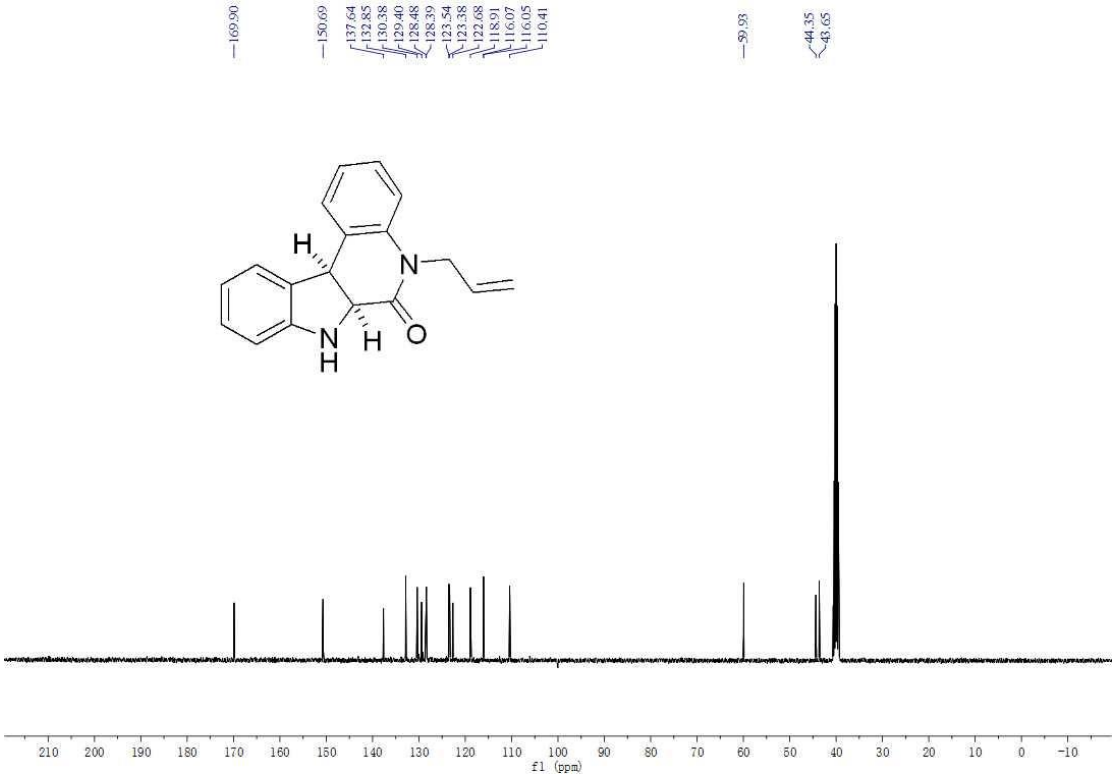
^{13}C NMR spectrum of **2n**



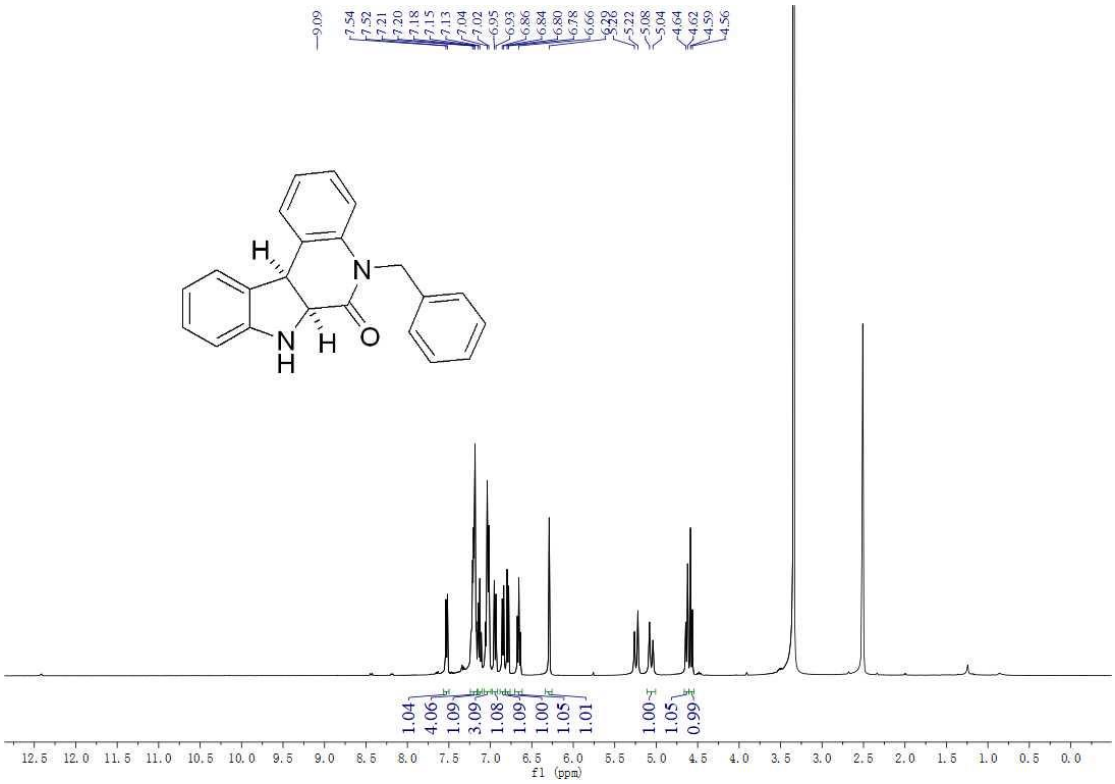
^{1}H NMR spectrum of **2p**



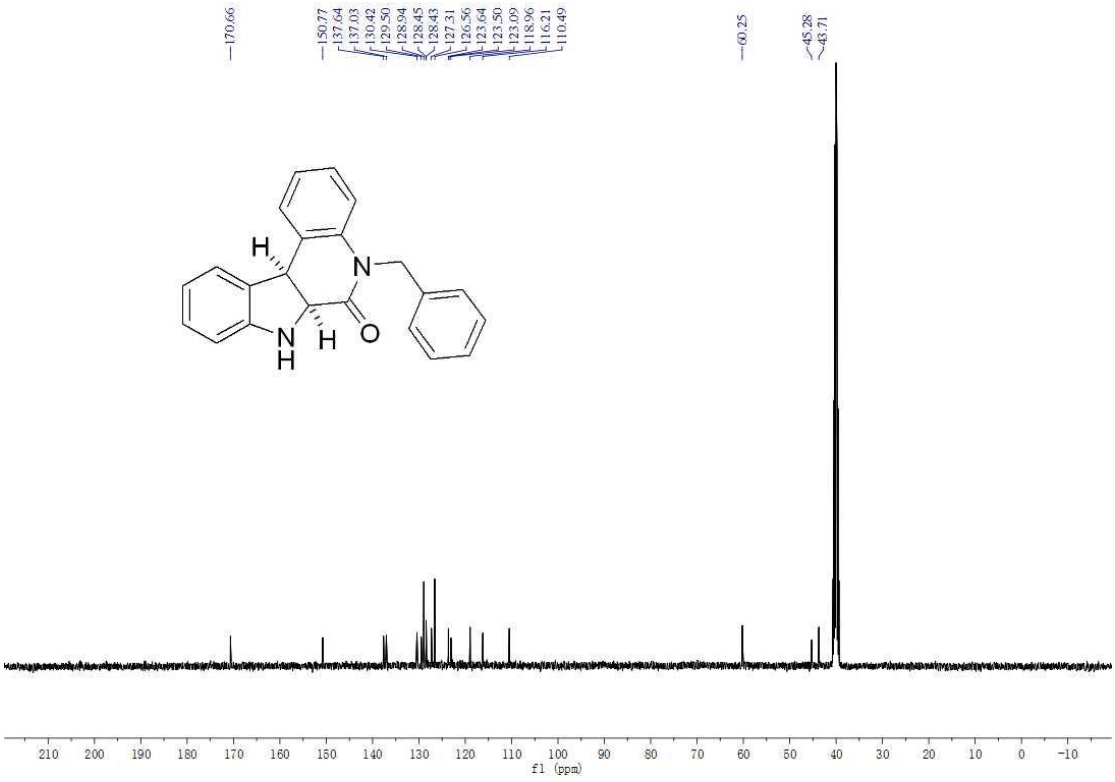
^{13}C NMR spectrum of **2p**



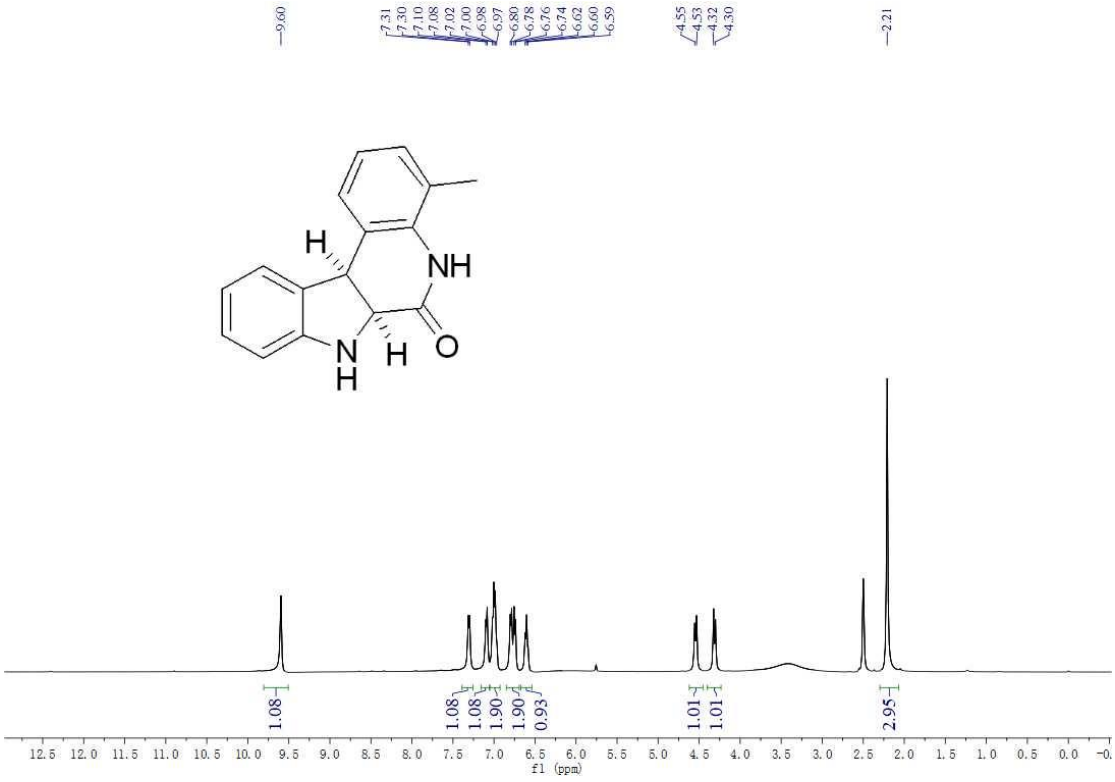
^{1}H NMR spectrum of **2q**



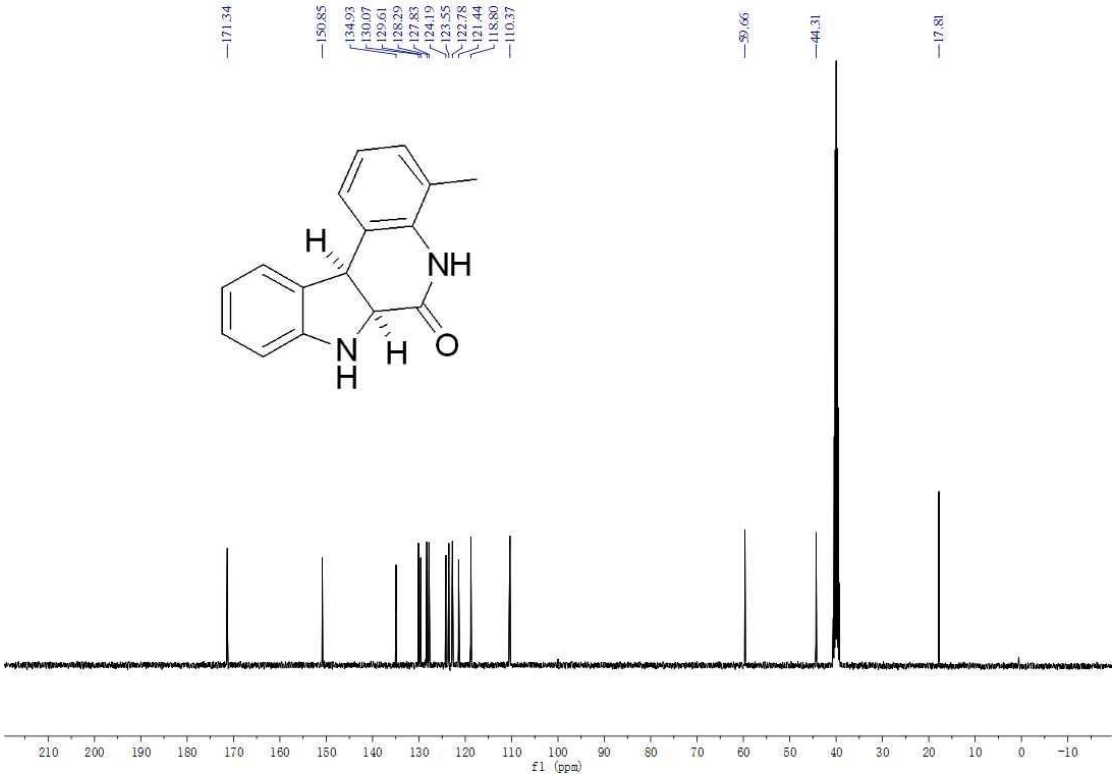
^{13}C NMR spectrum of **2q**



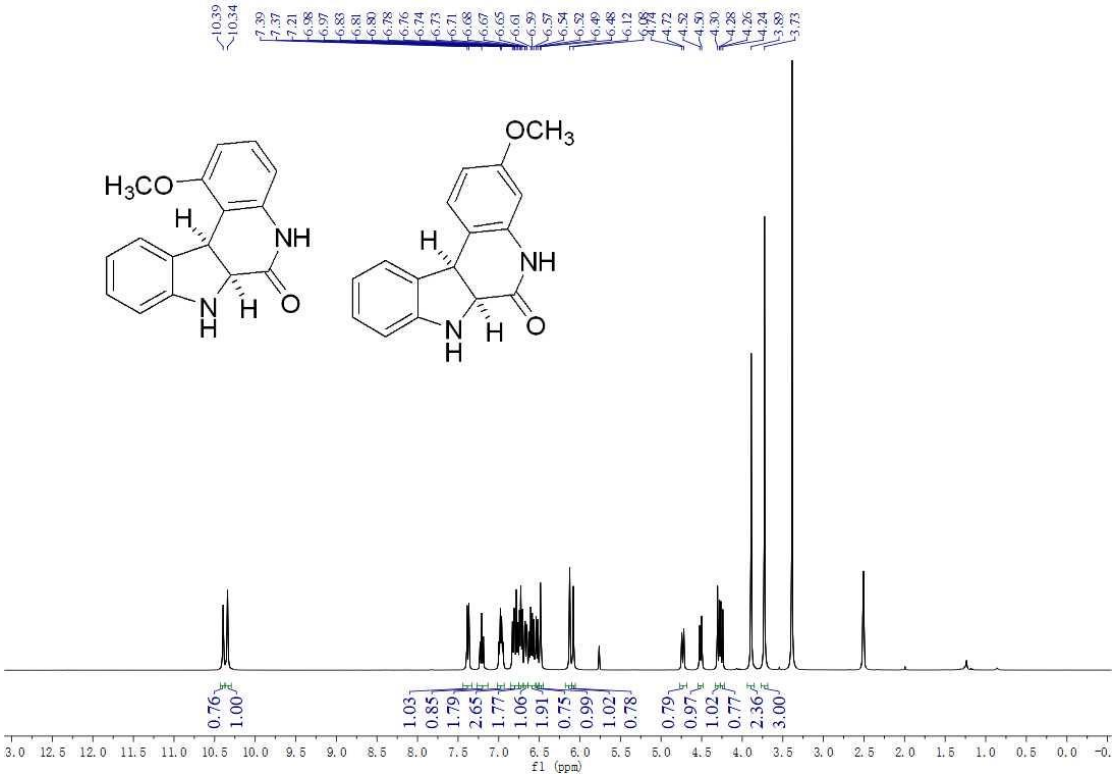
^{1}H NMR spectrum of **2r**



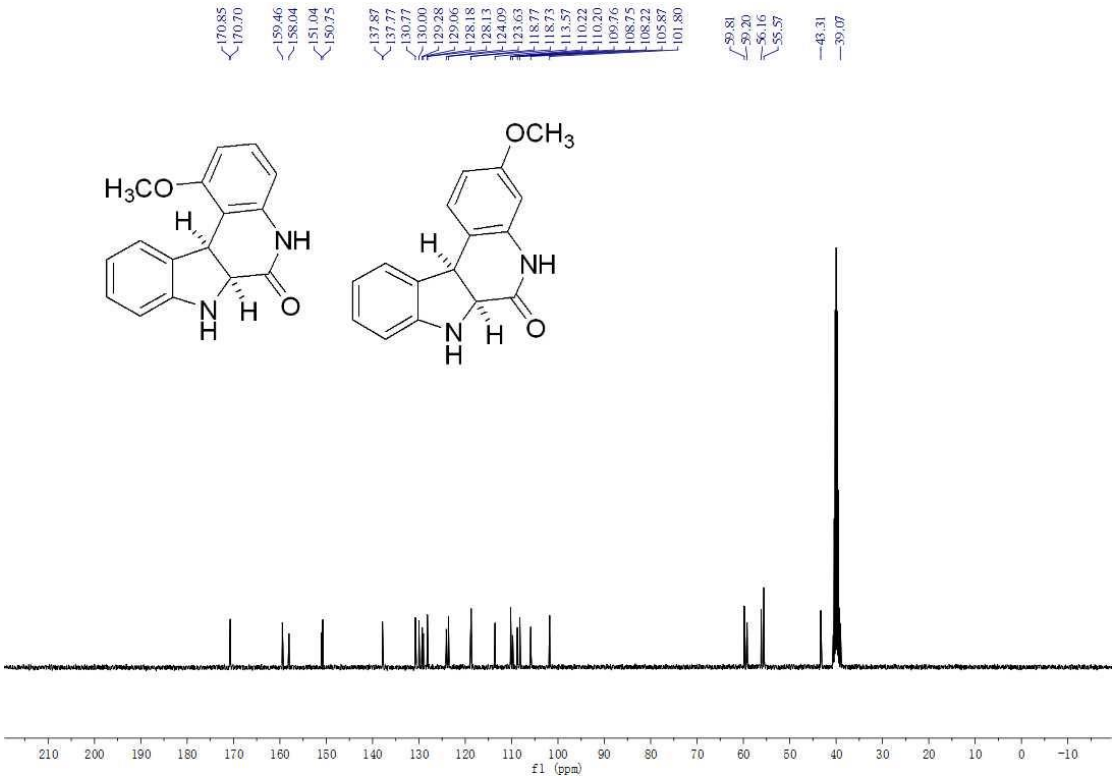
^{13}C NMR spectrum of **2r**



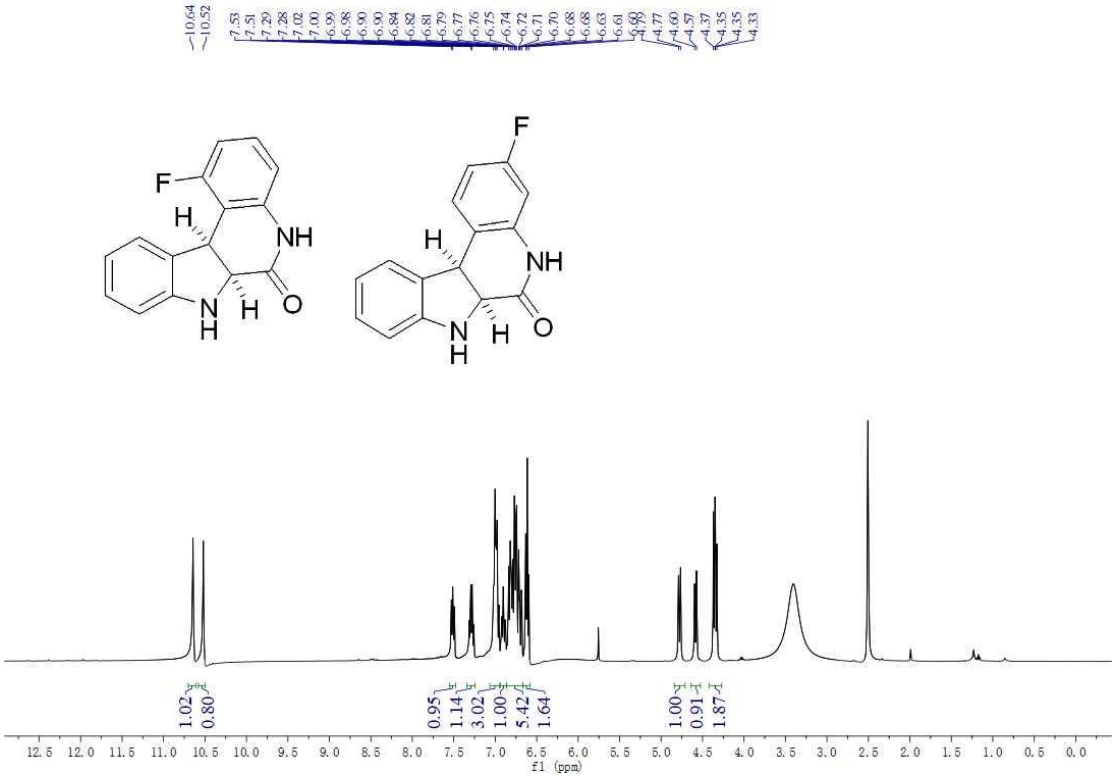
^{1}H NMR spectrum of **2s+2s′**



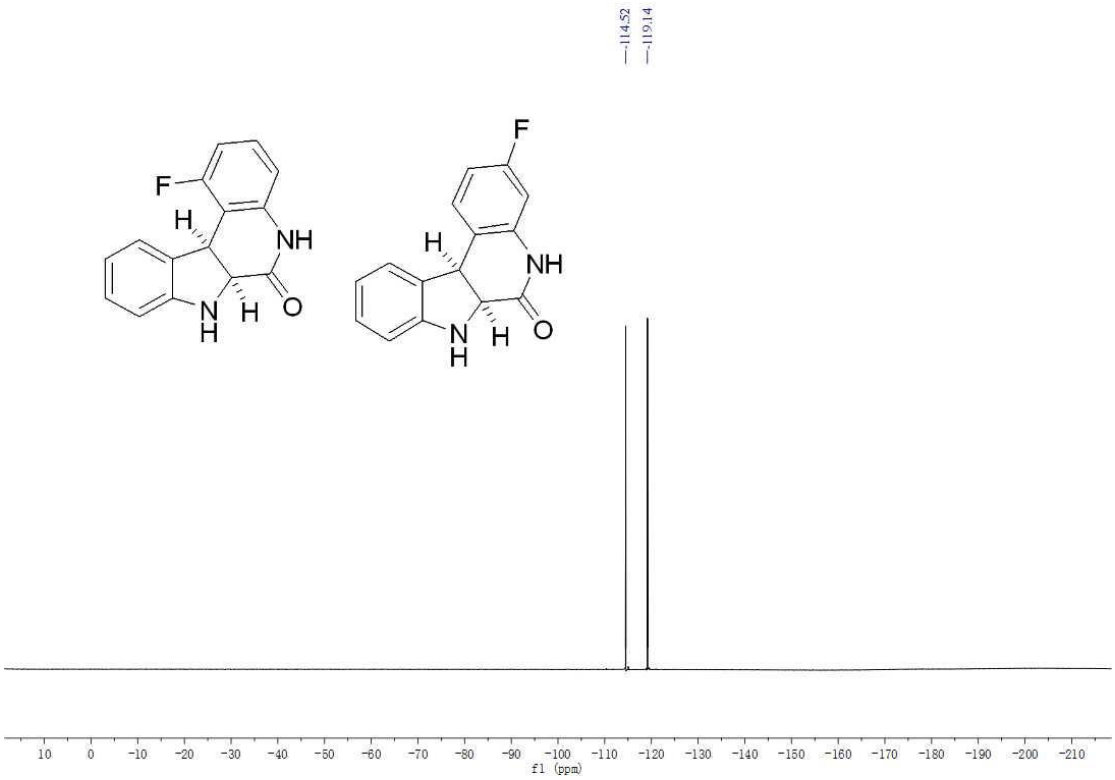
^{13}C NMR spectrum of **2s+2s′**



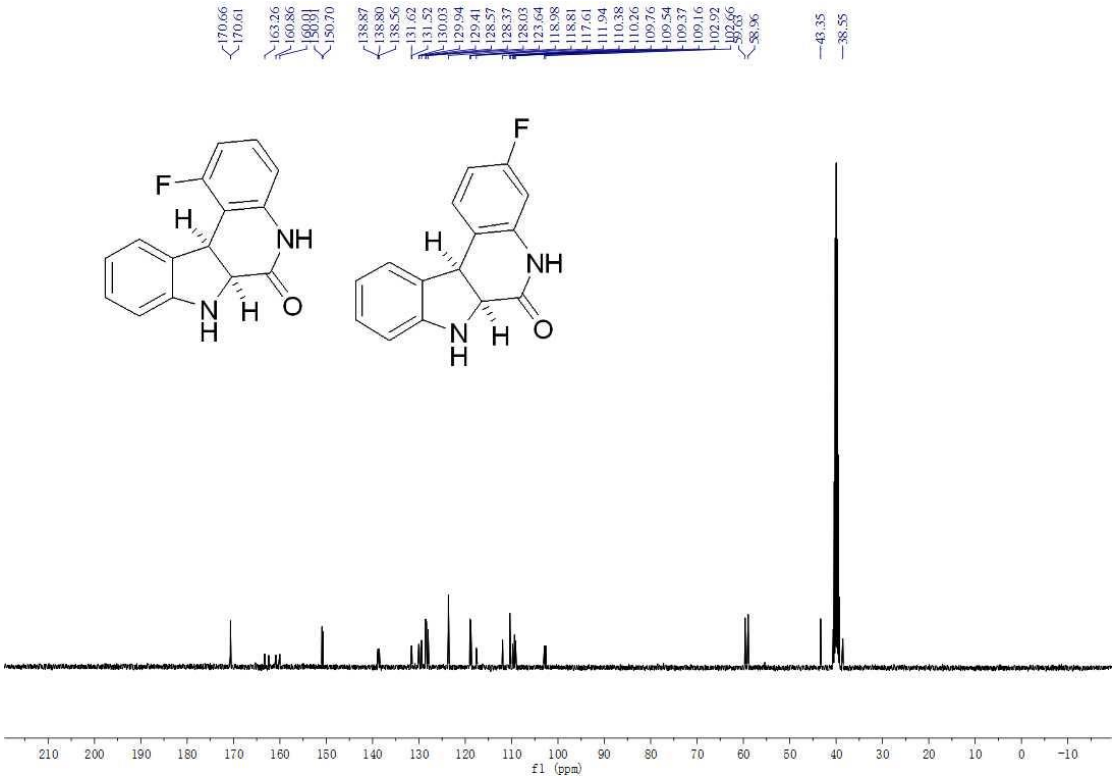
^{1}H NMR spectrum of **2t+2t′**



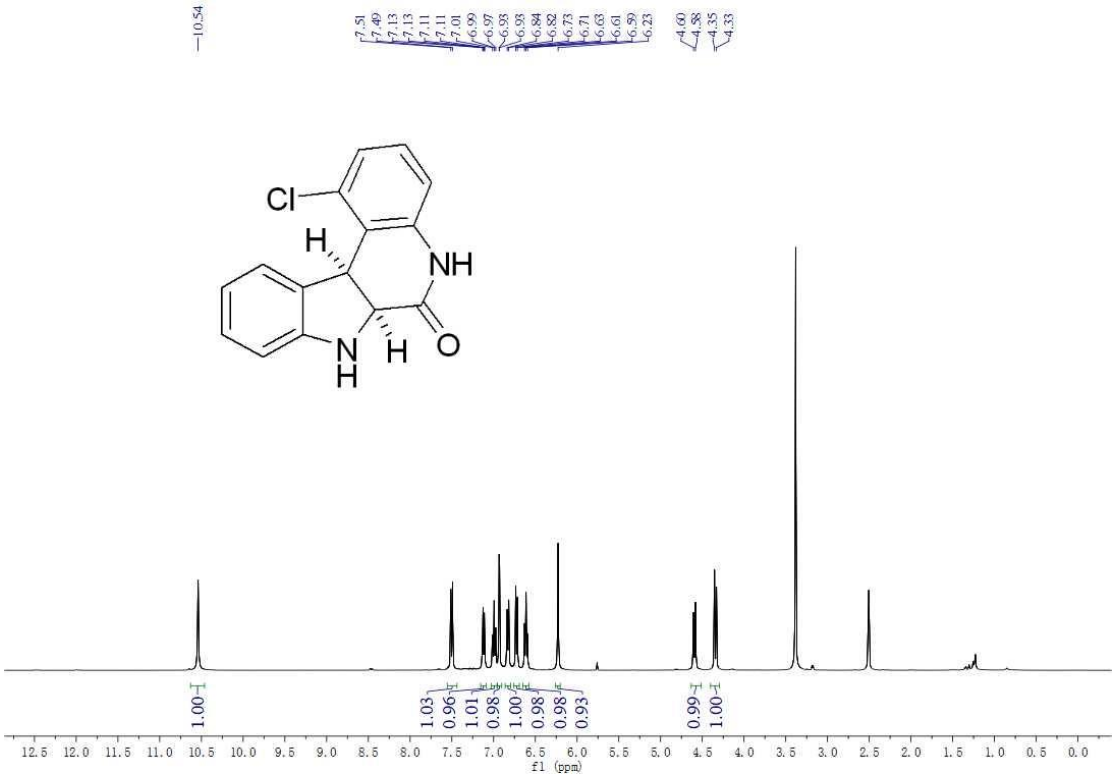
^{19}F NMR spectrum of **2t**+**2t′**



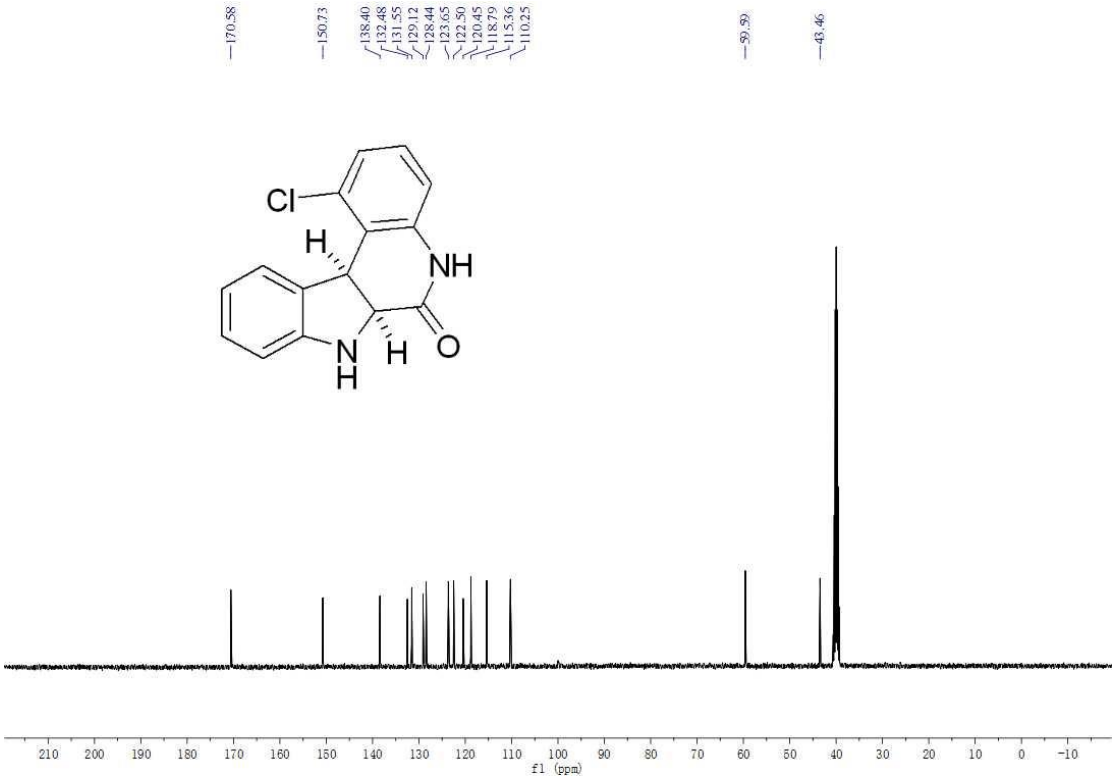
^{13}C NMR spectrum of **2t**+**2t′**



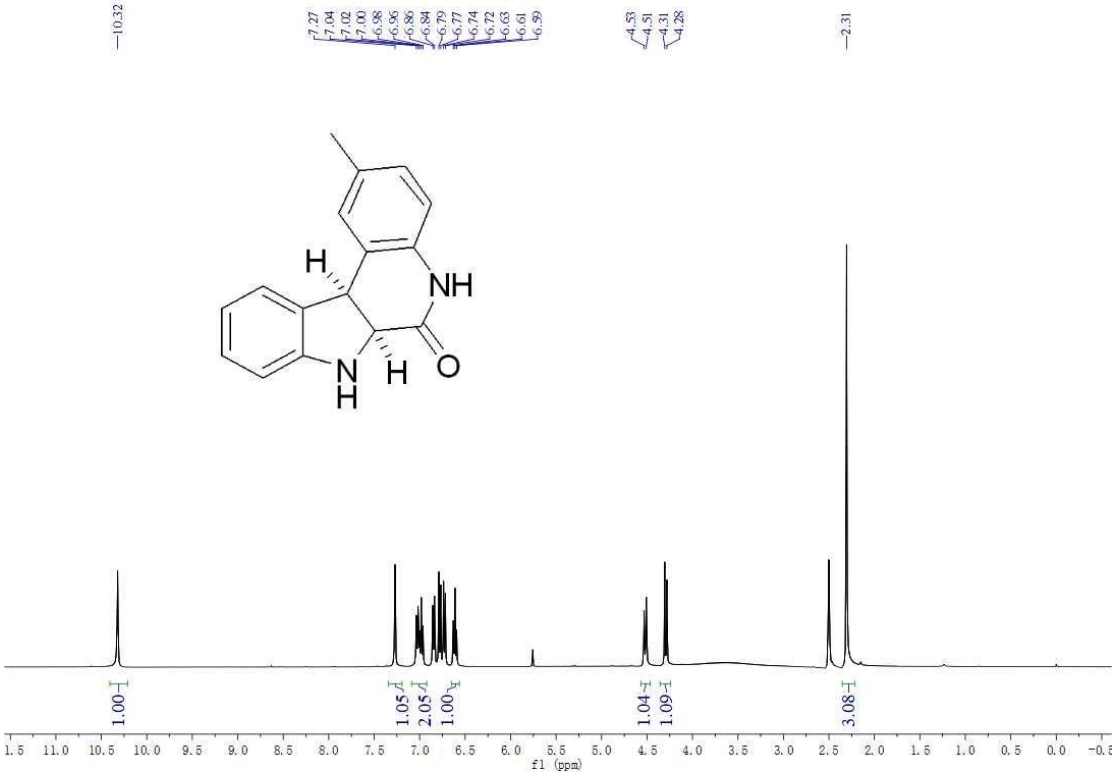
^{1}H NMR spectrum of **2u**



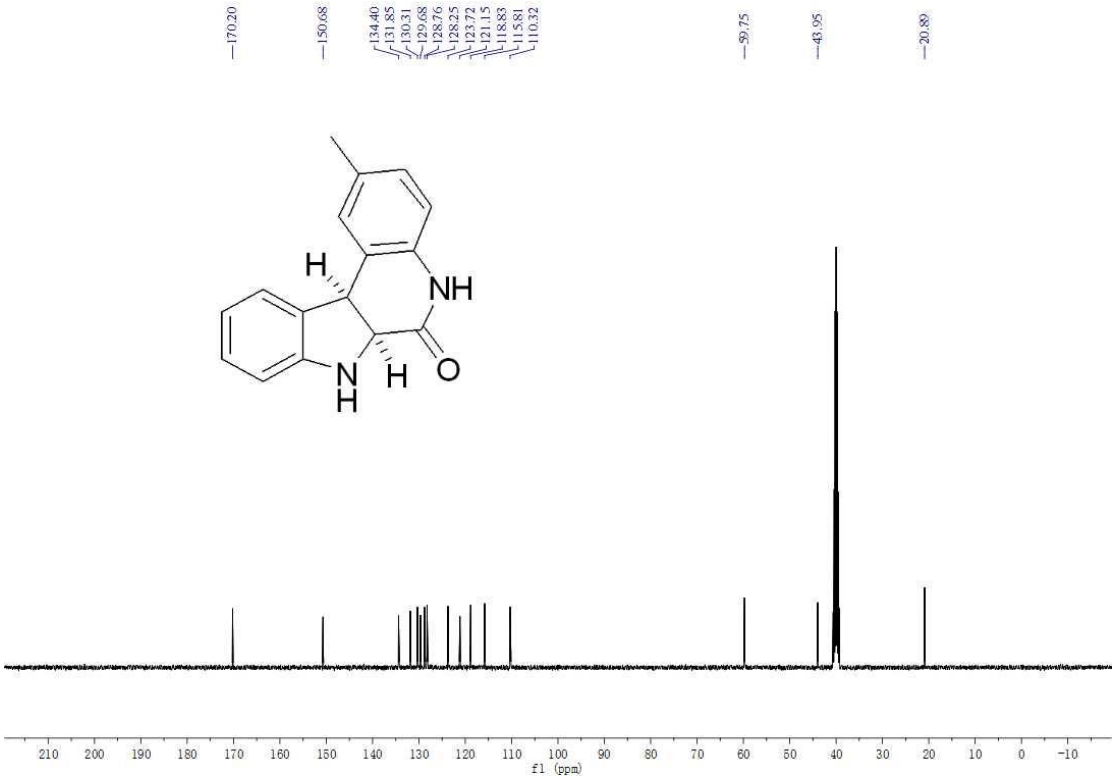
^{13}C NMR spectrum of **2u**



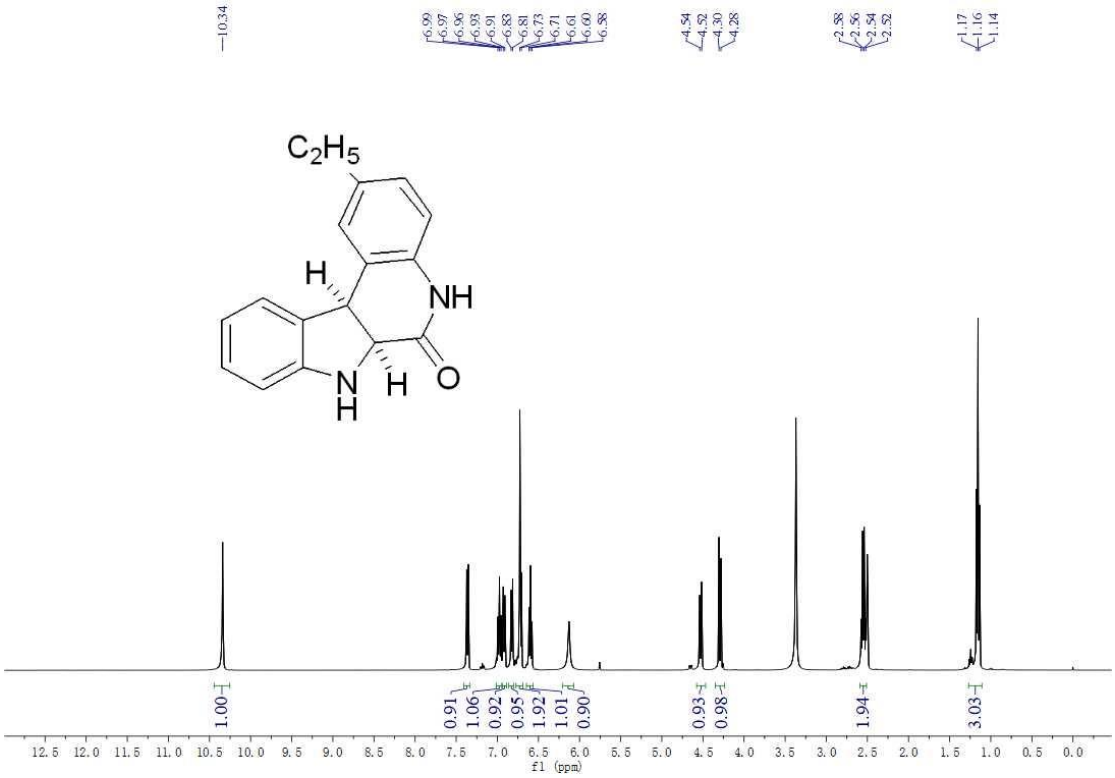
^{1}H NMR spectrum of **2v**



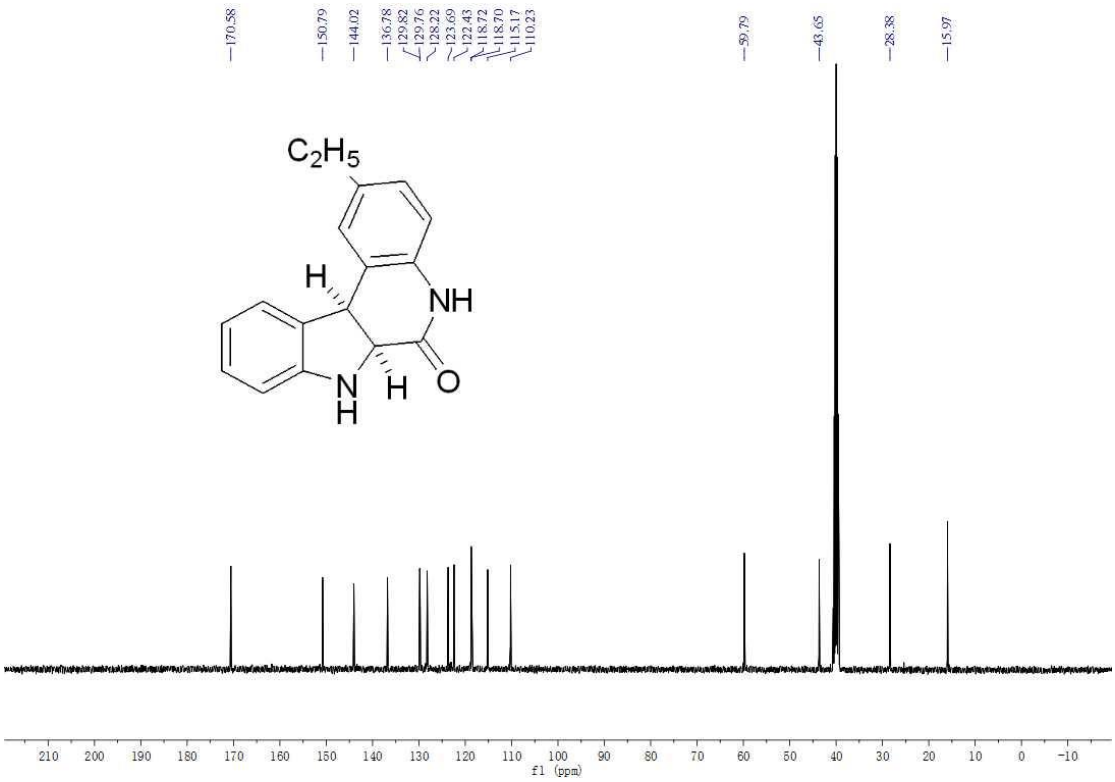
^{13}C NMR spectrum of **2v**



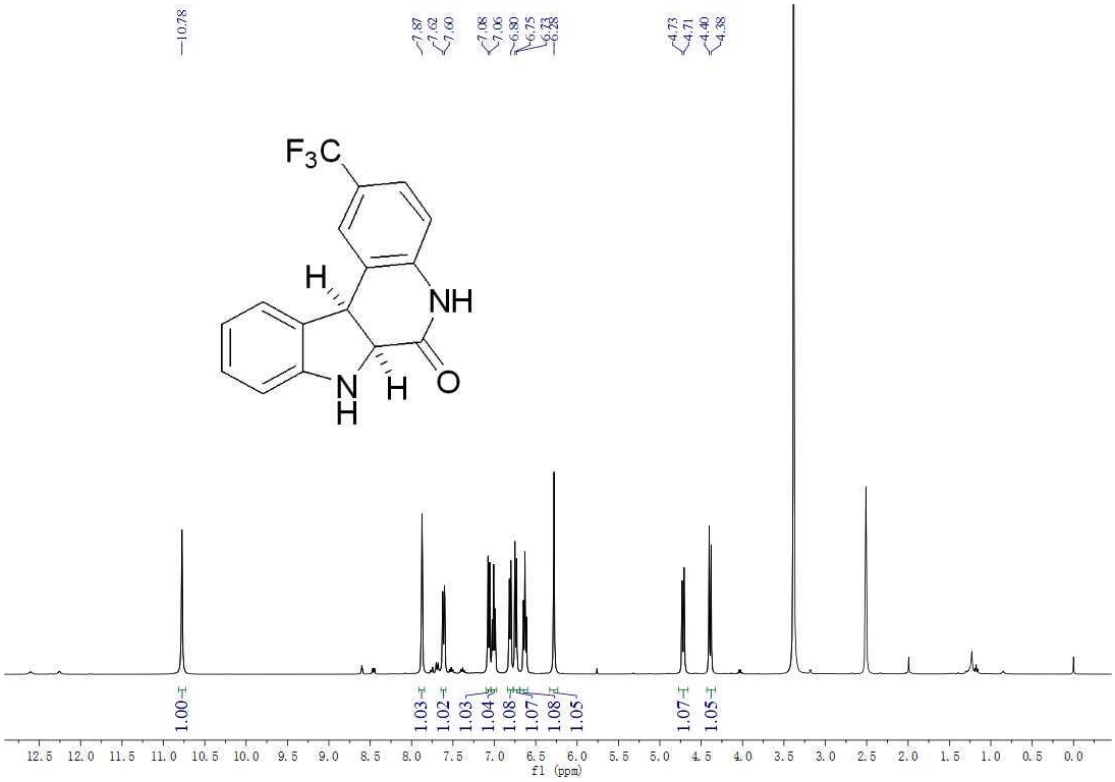
^{1}H NMR spectrum of **2w**



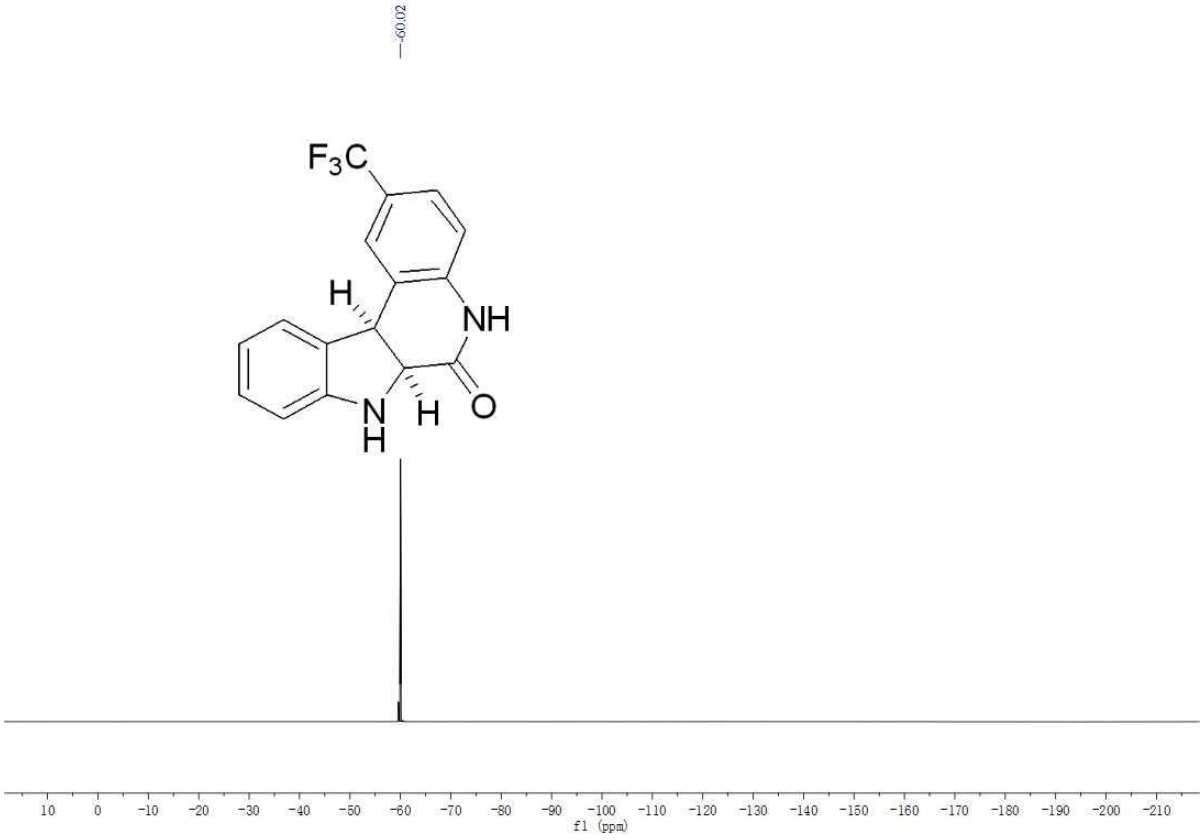
^{13}C NMR spectrum of **2w**



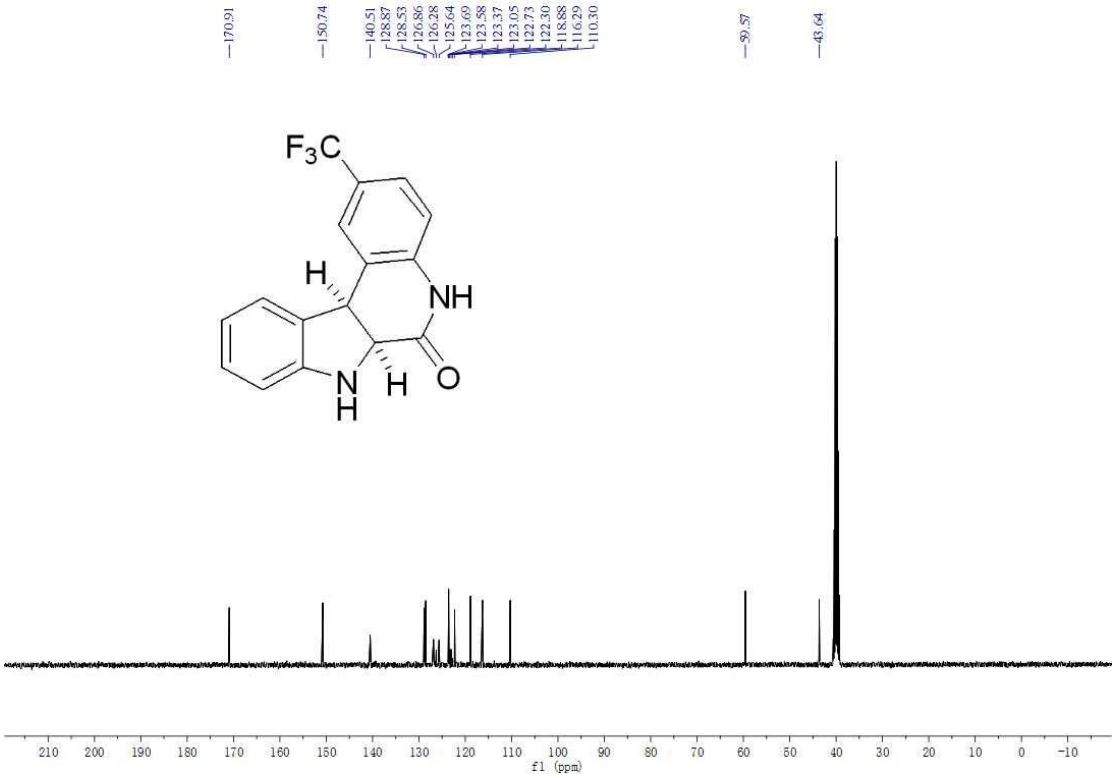
^{1}H NMR spectrum of **2x**



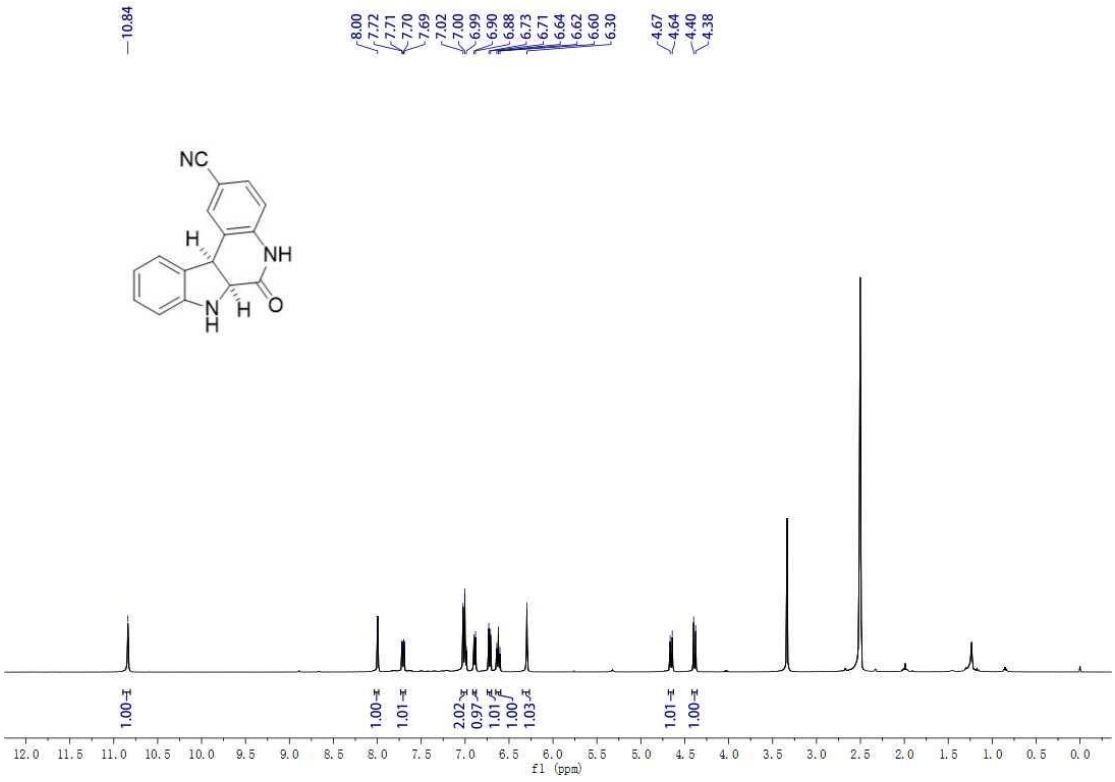
^{19}F NMR spectrum of **2x**



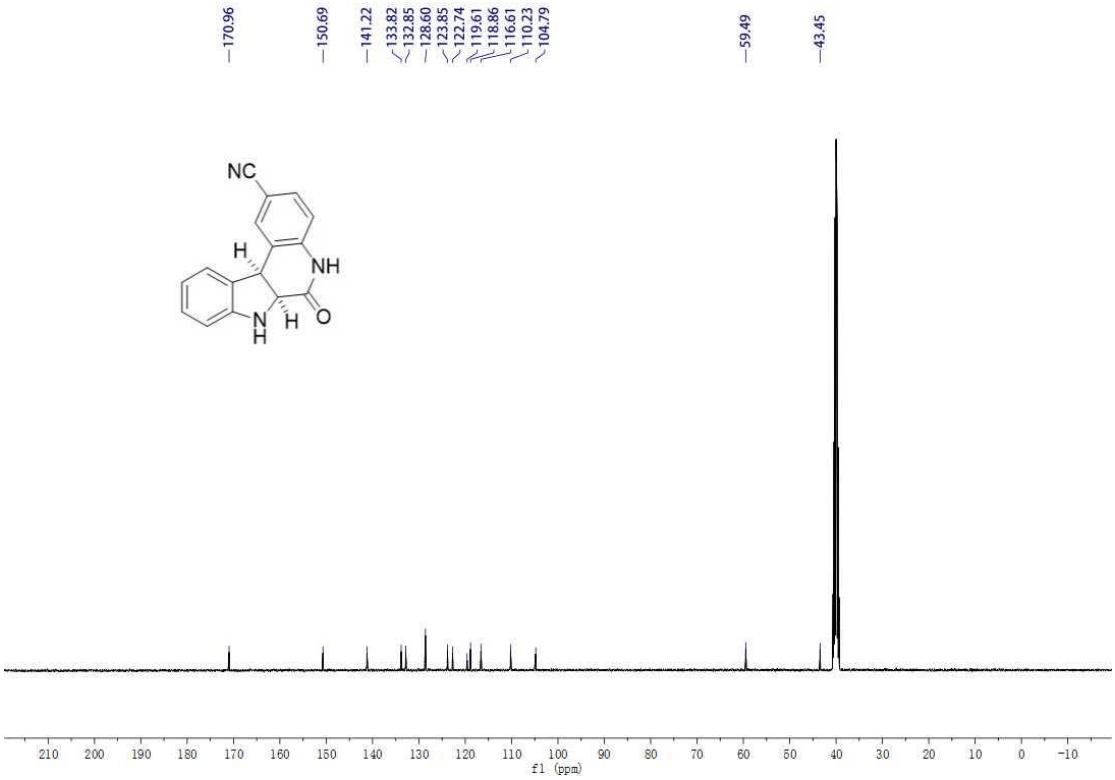
^{13}C NMR spectrum of **2x**



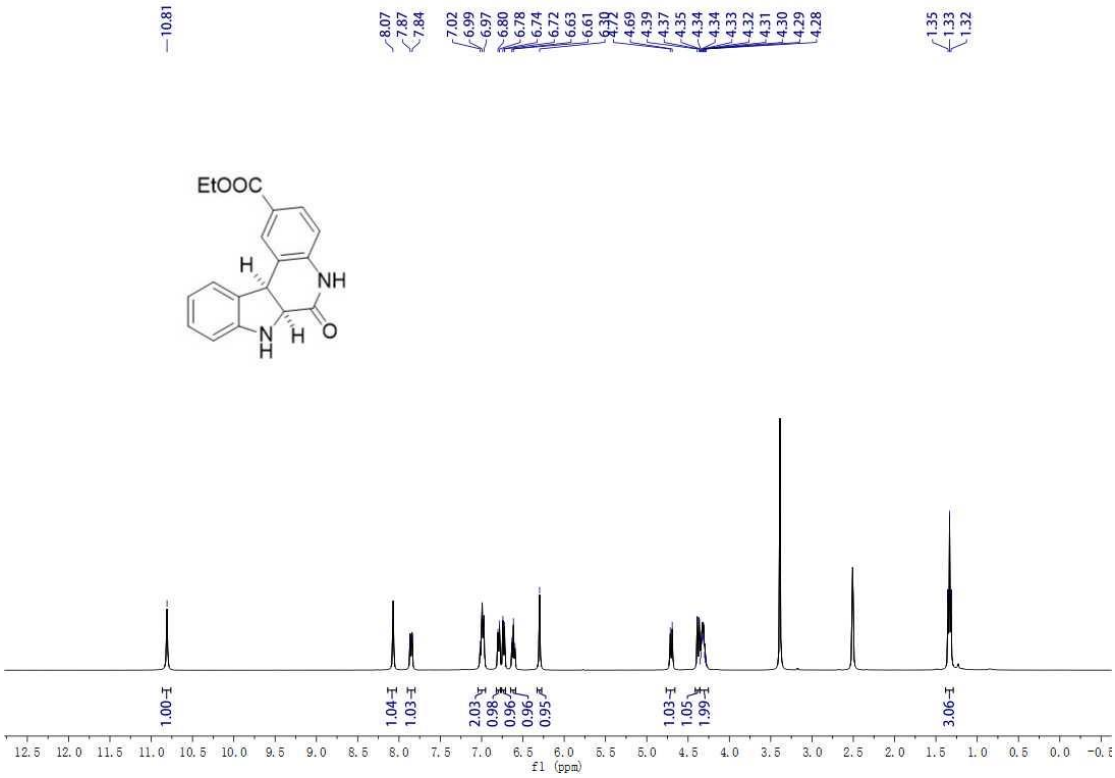
^{1}H NMR spectrum of **2y**



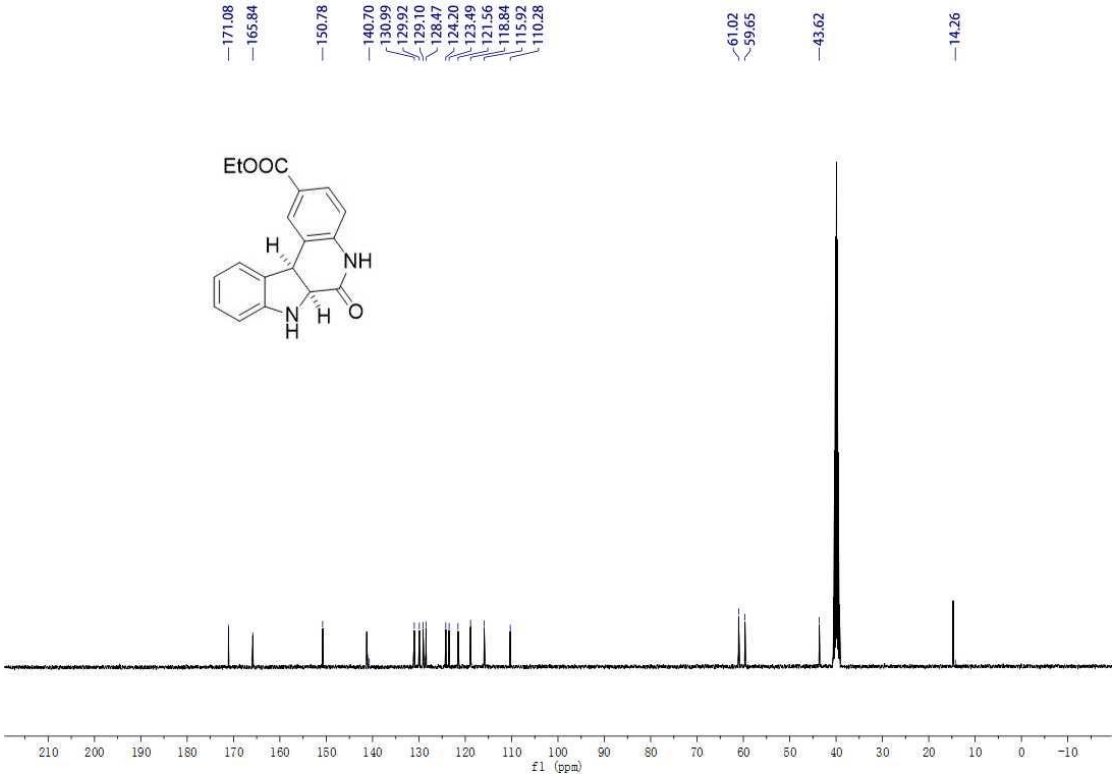
^{13}C NMR spectrum of **2y**



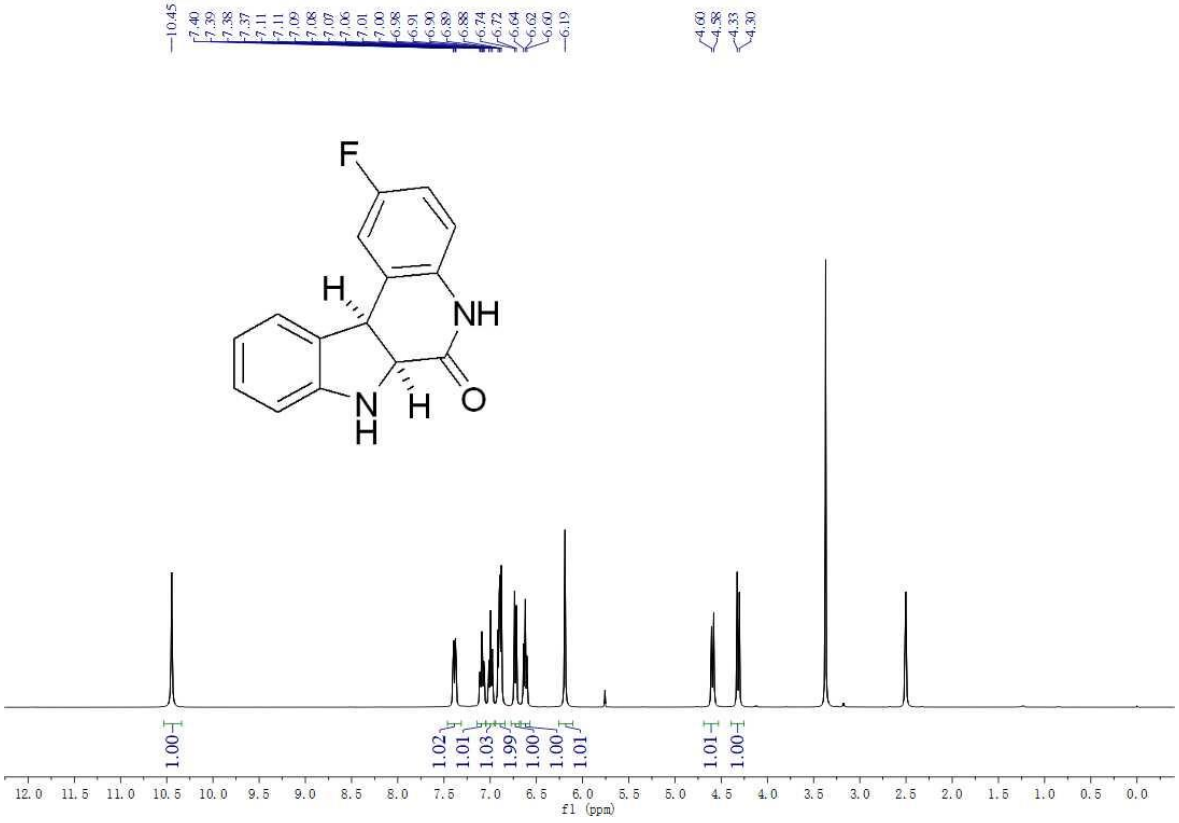
^{1}H NMR spectrum of **2z**



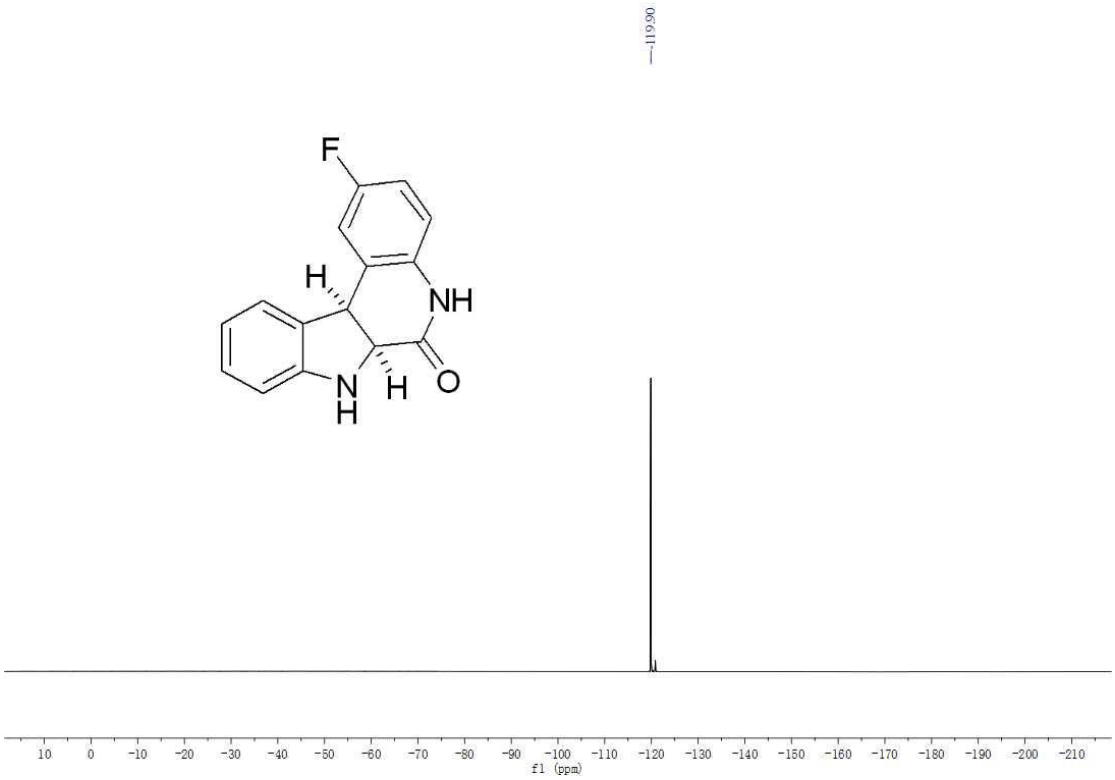
^{13}C NMR spectrum of **2z**



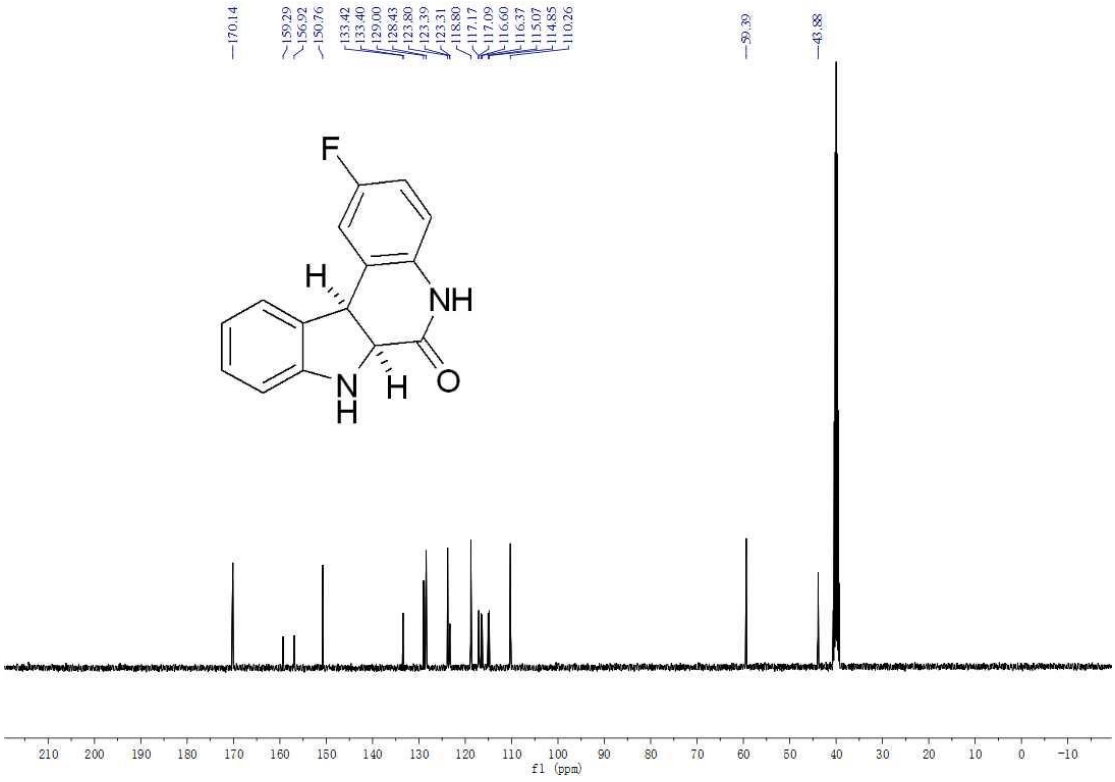
^{1}H NMR spectrum of **2aa**



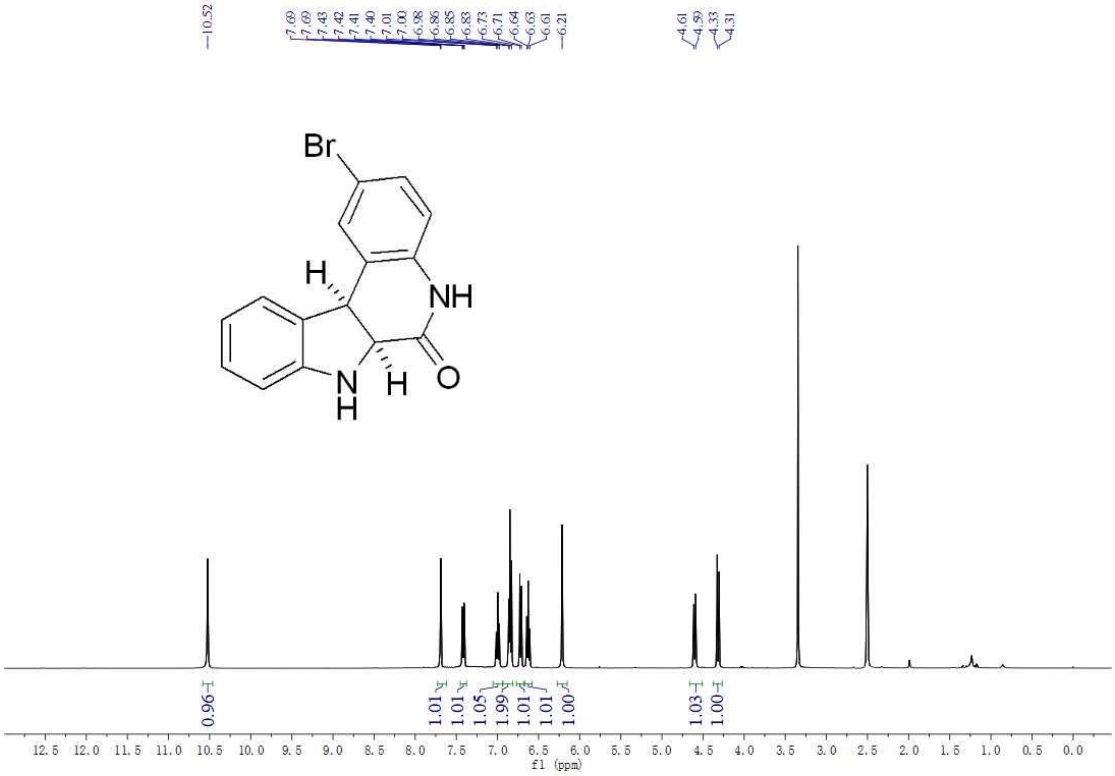
^{19}F NMR spectrum of **2aa**



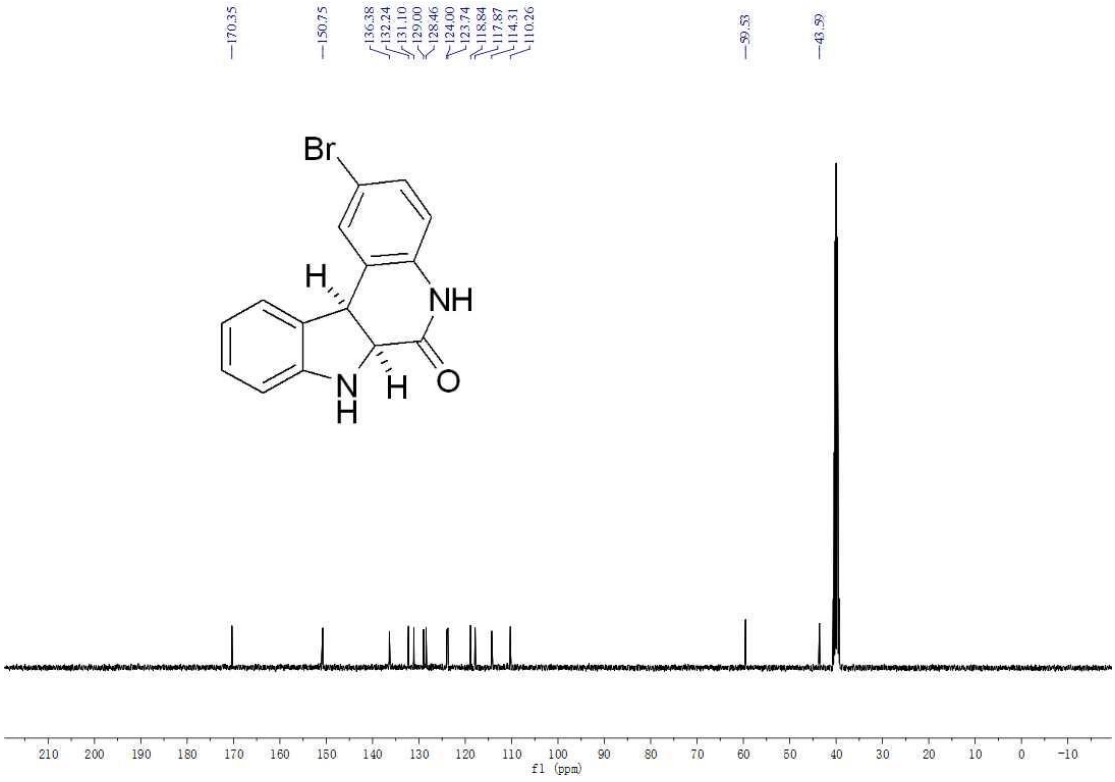
^{13}C NMR spectrum of **2aa**



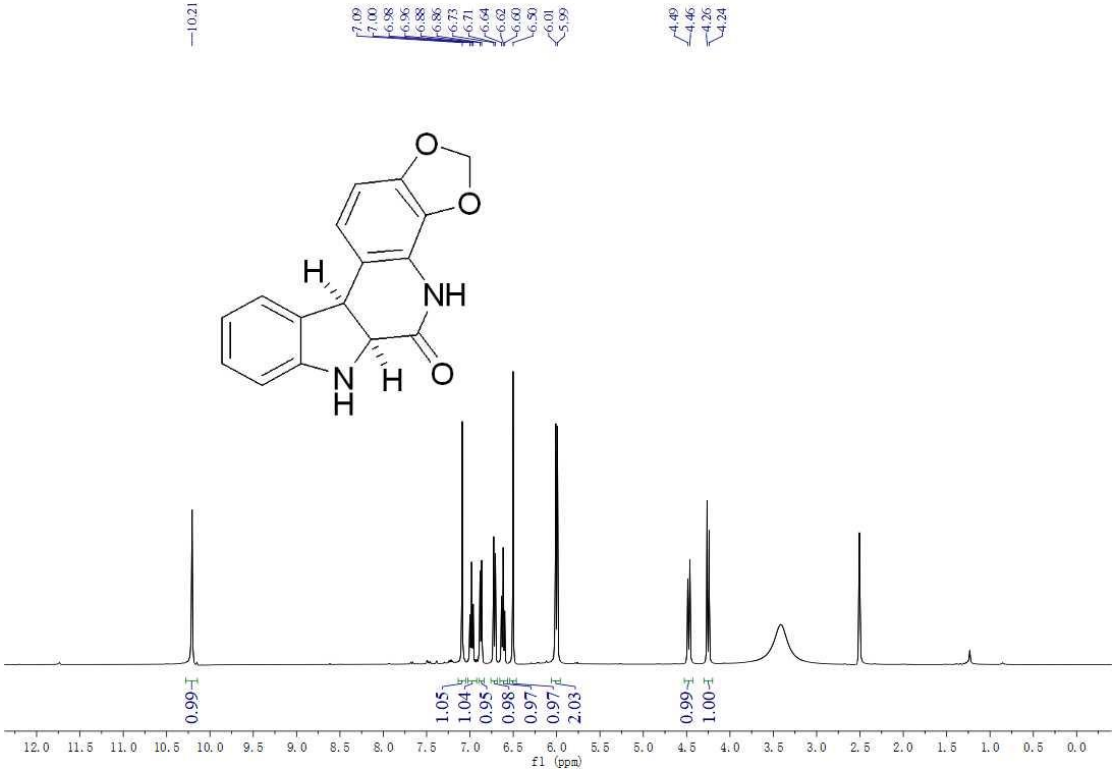
^{1}H NMR spectrum of **2ab**



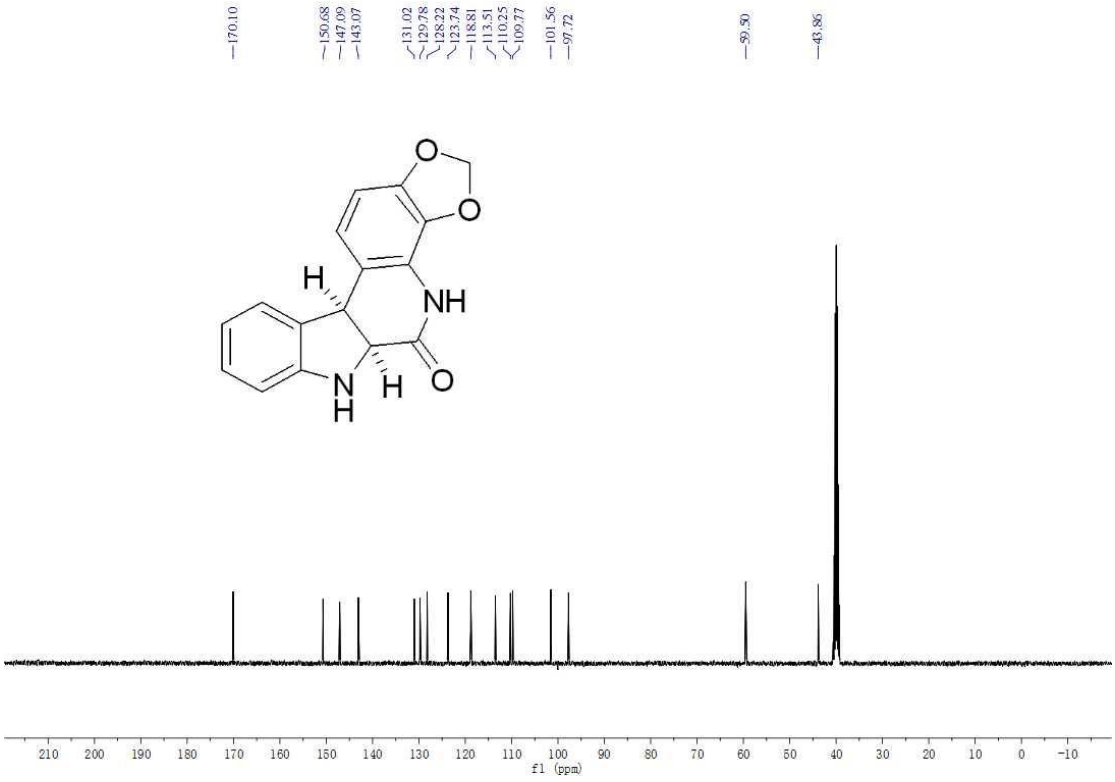
^{13}C NMR spectrum of **2ab**



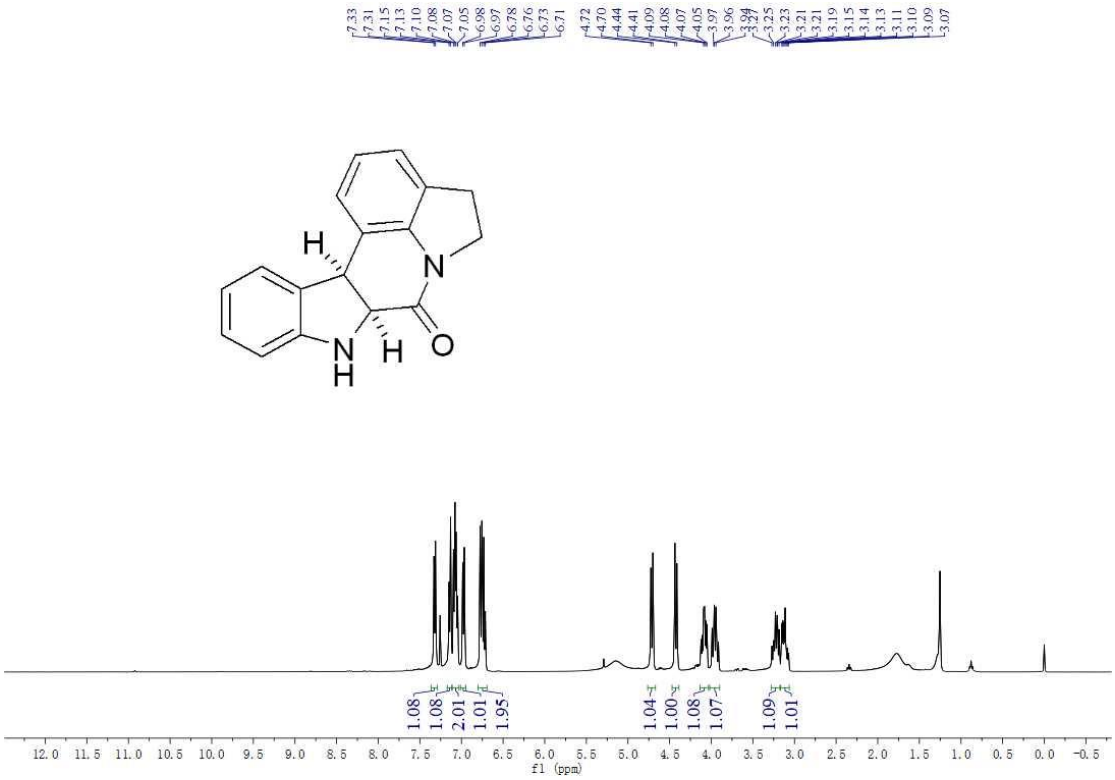
^{1}H NMR spectrum of **2ac**



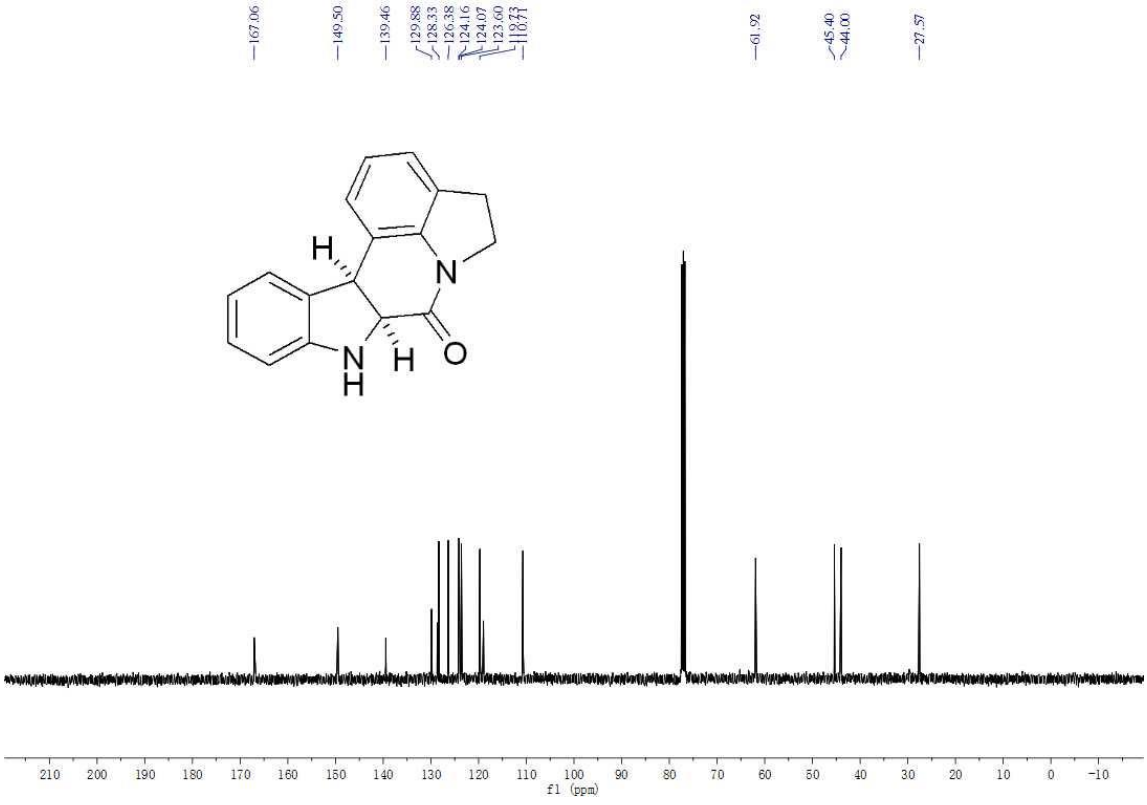
^{13}C NMR spectrum of **2ac**



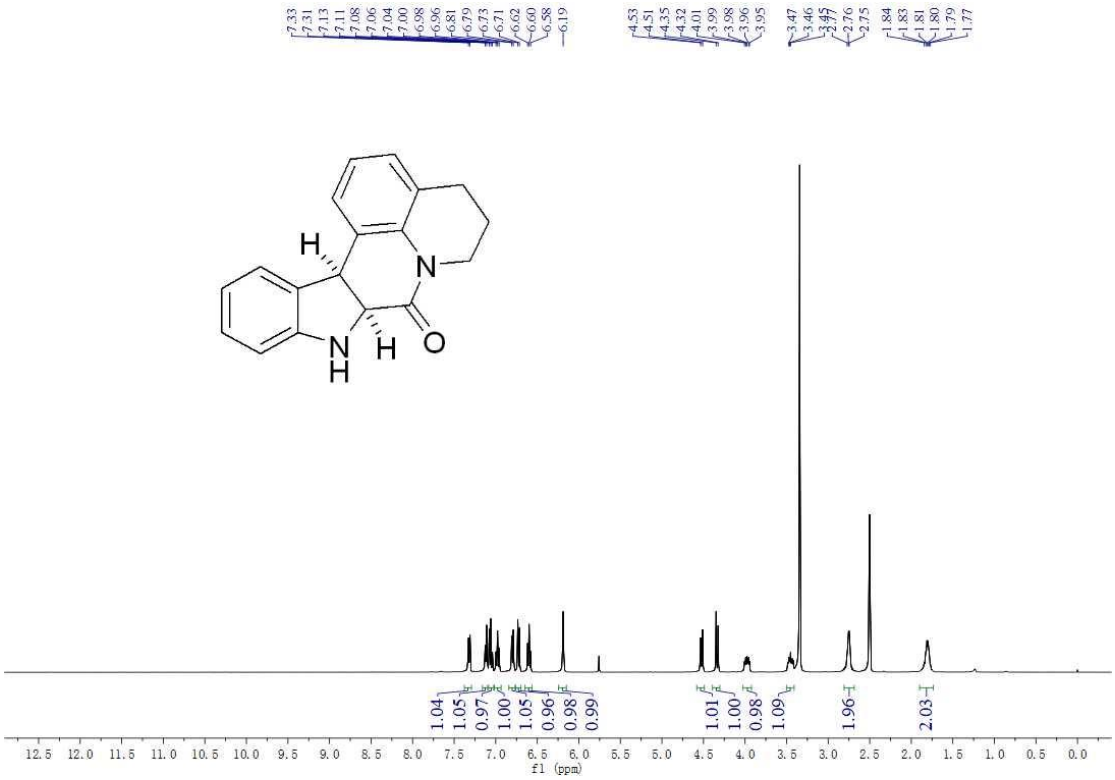
^{1}H NMR spectrum of **2ad**



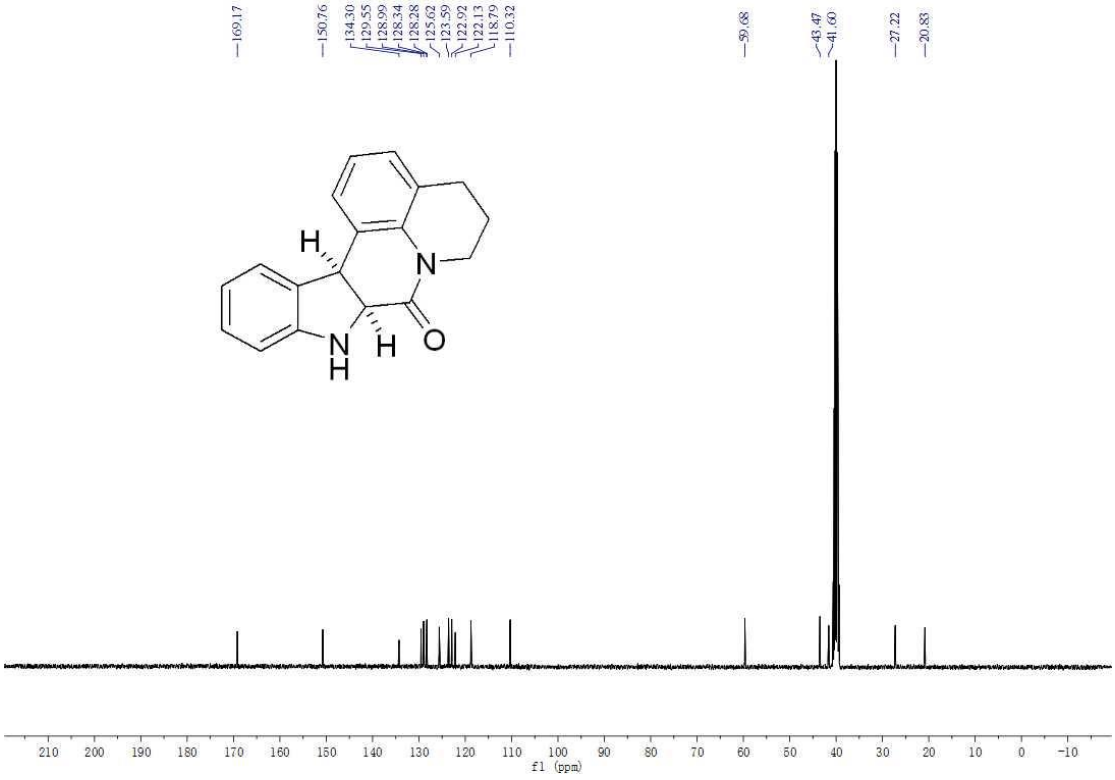
^{13}C NMR spectrum of **2ad**



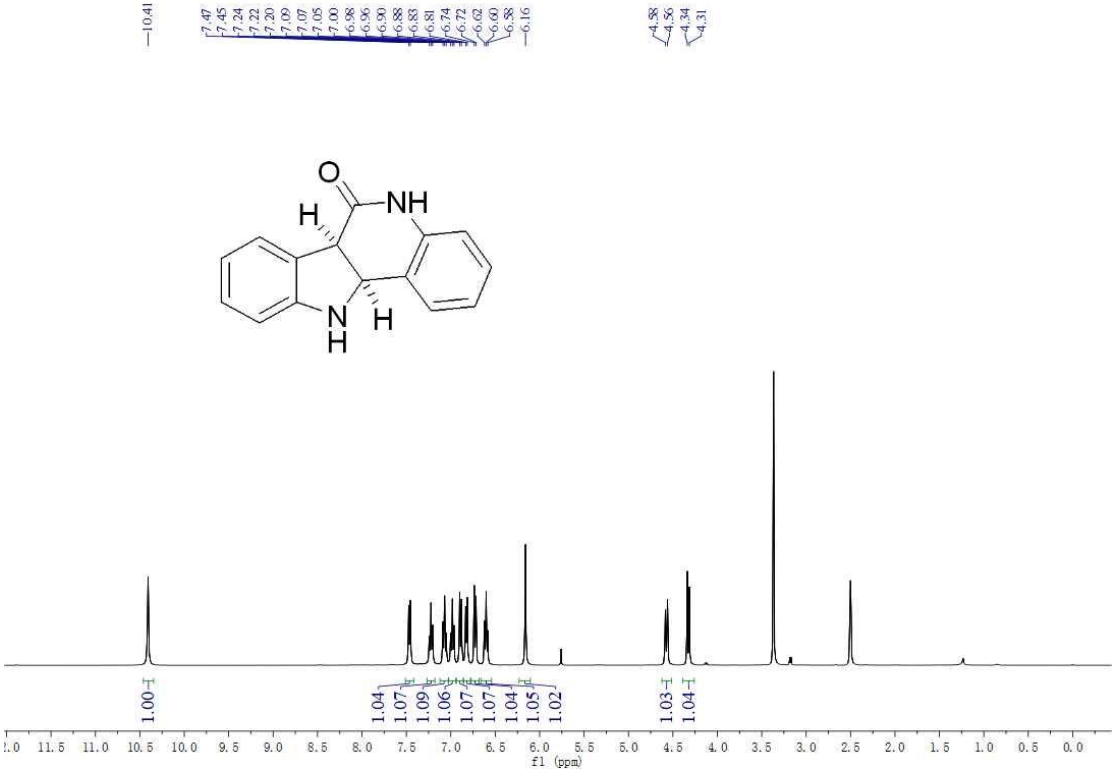
^{1}H NMR spectrum of **2ae**



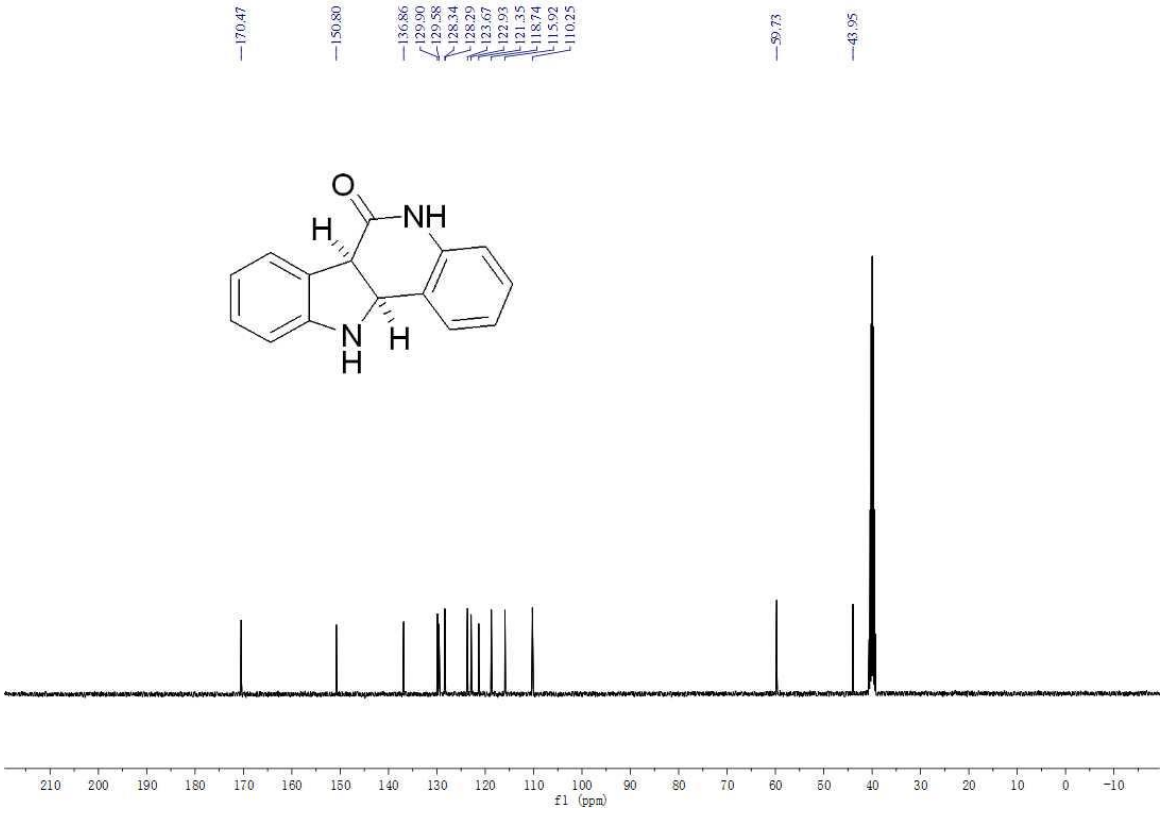
^{13}C NMR spectrum of **2ae**



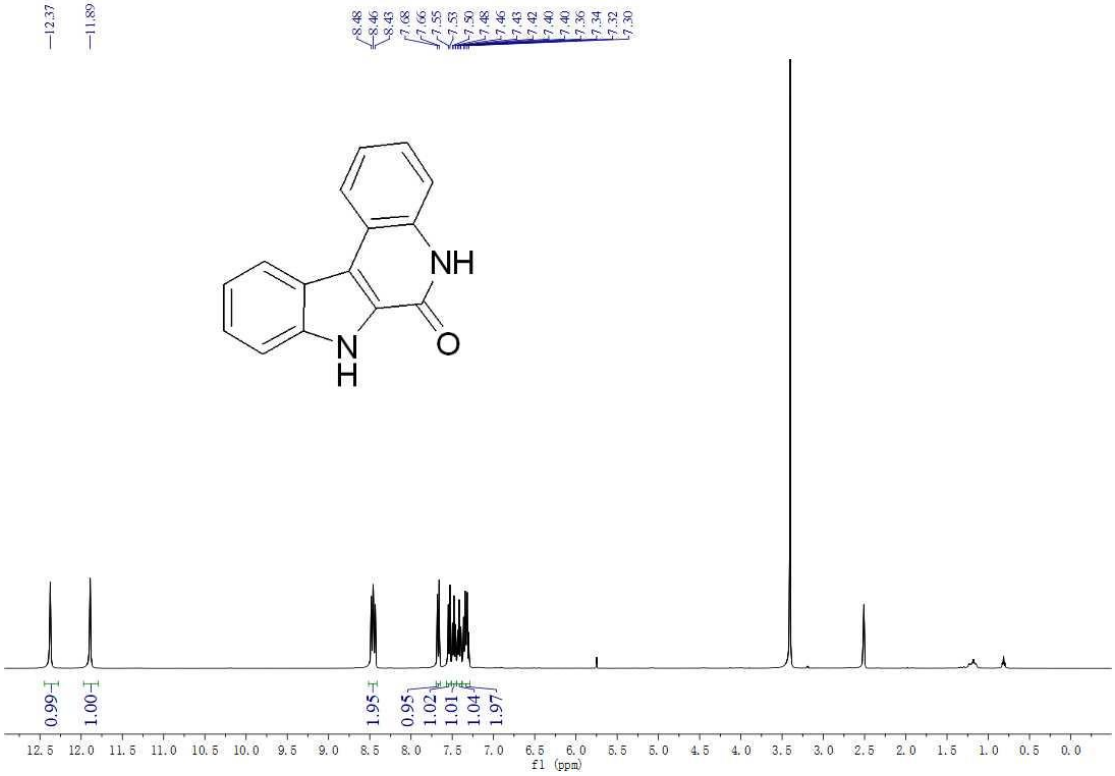
^{1}H NMR spectrum of **2ag**



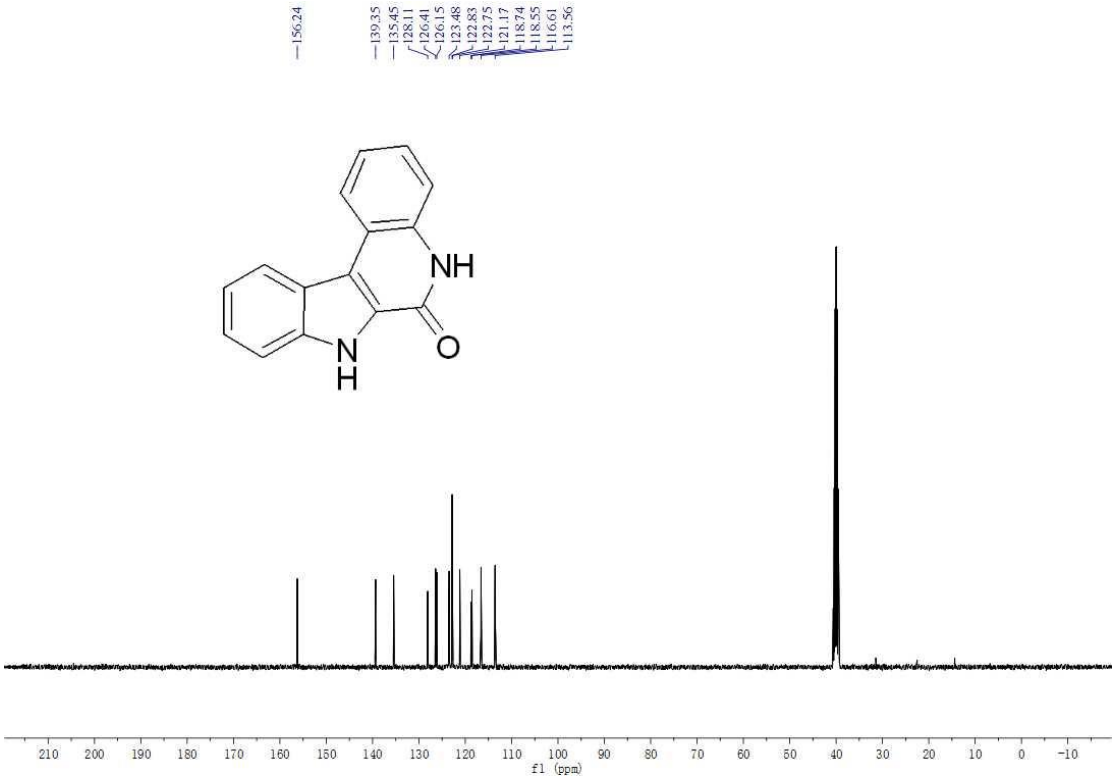
^{13}C NMR spectrum of **2ag**



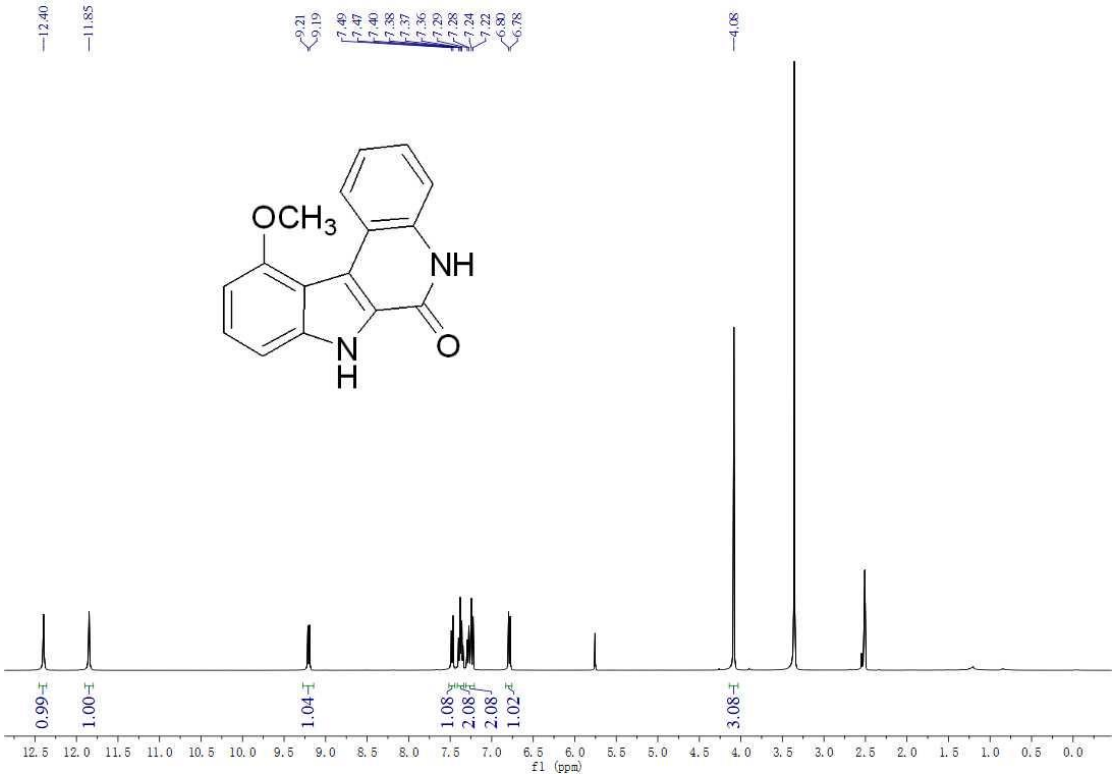
^{1}H NMR spectrum of **3a**



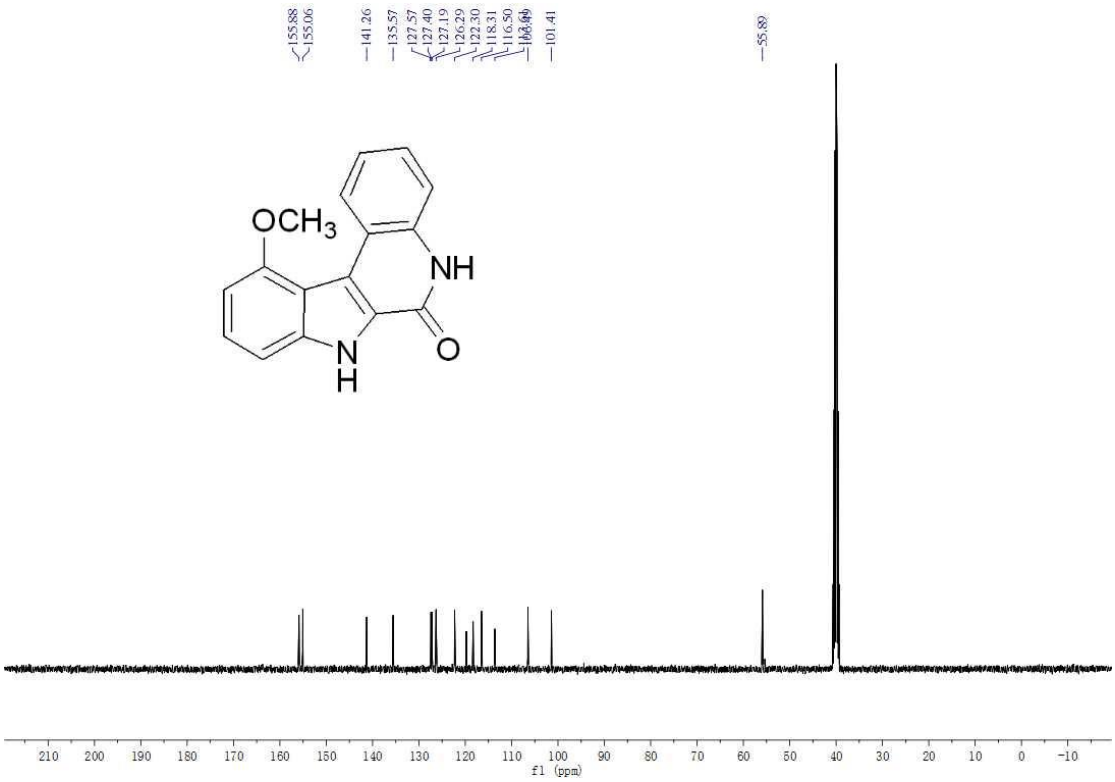
^{13}C NMR spectrum of **3a**



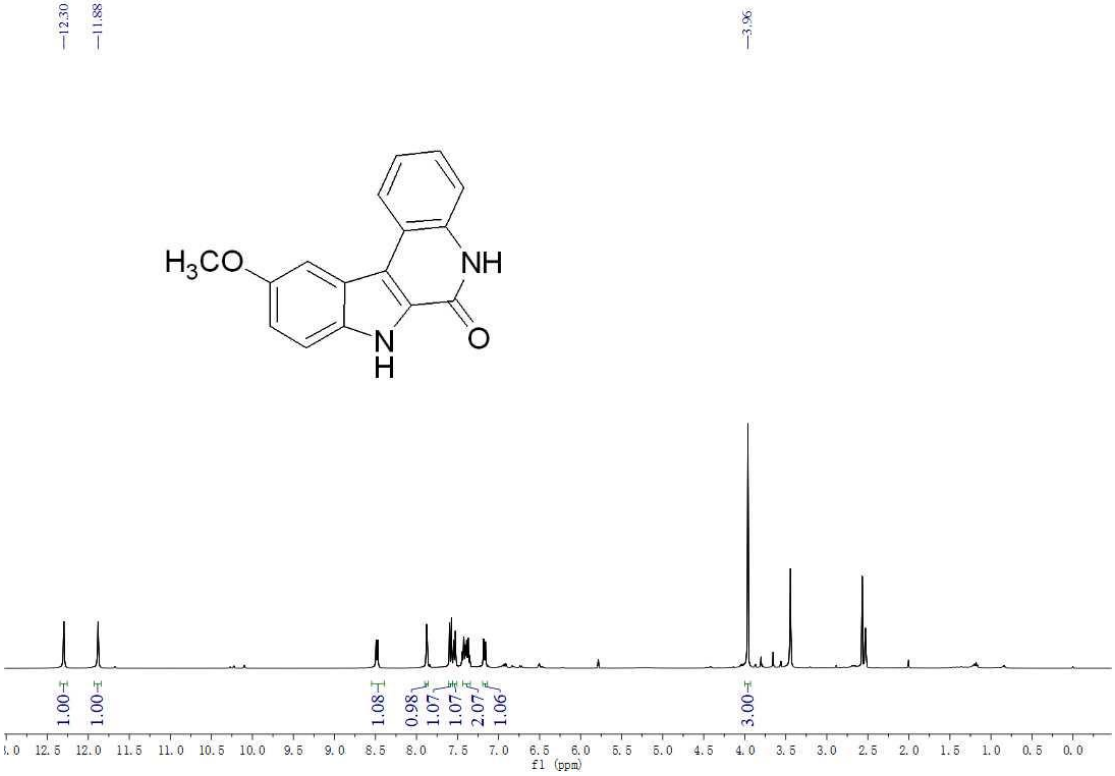
^{1}H NMR spectrum of **3b**



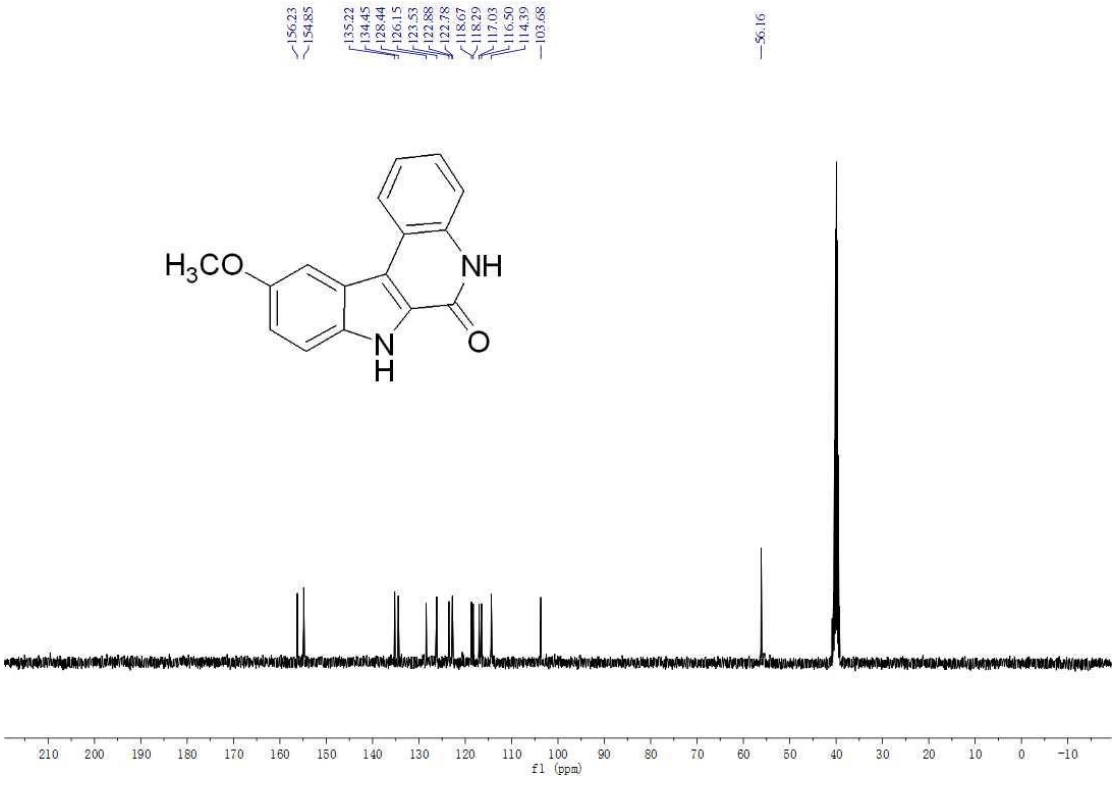
^{13}C NMR spectrum of **3b**



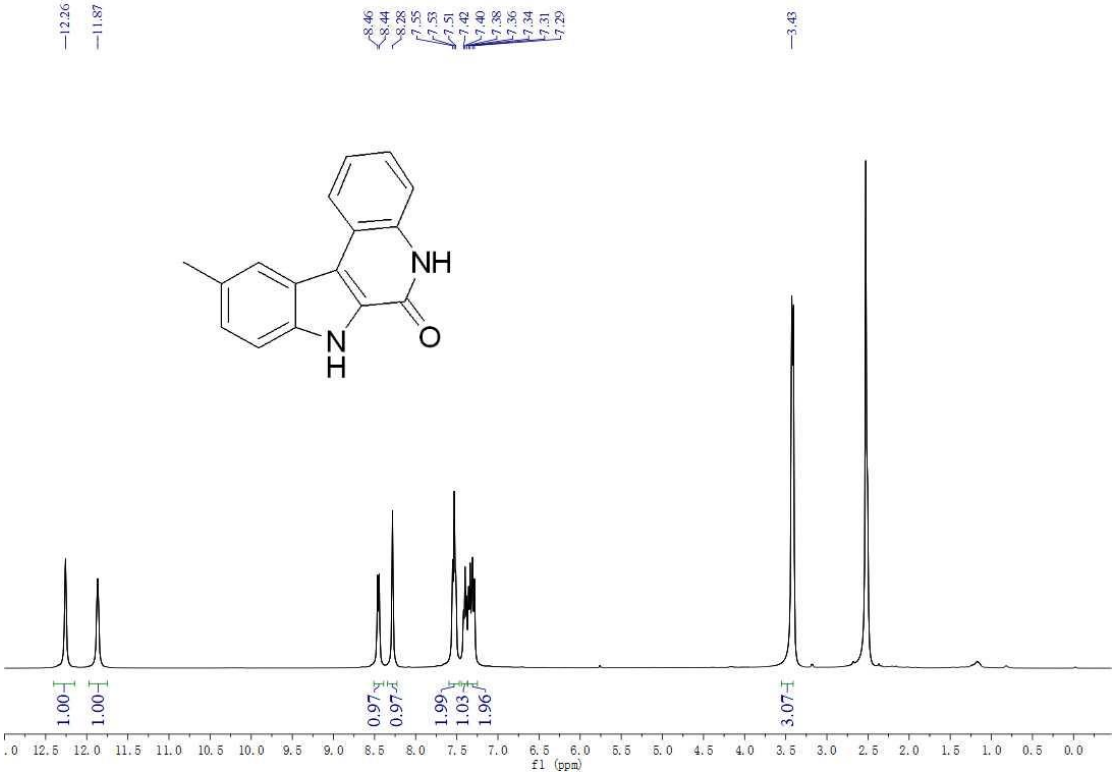
^{1}H NMR spectrum of **3c**



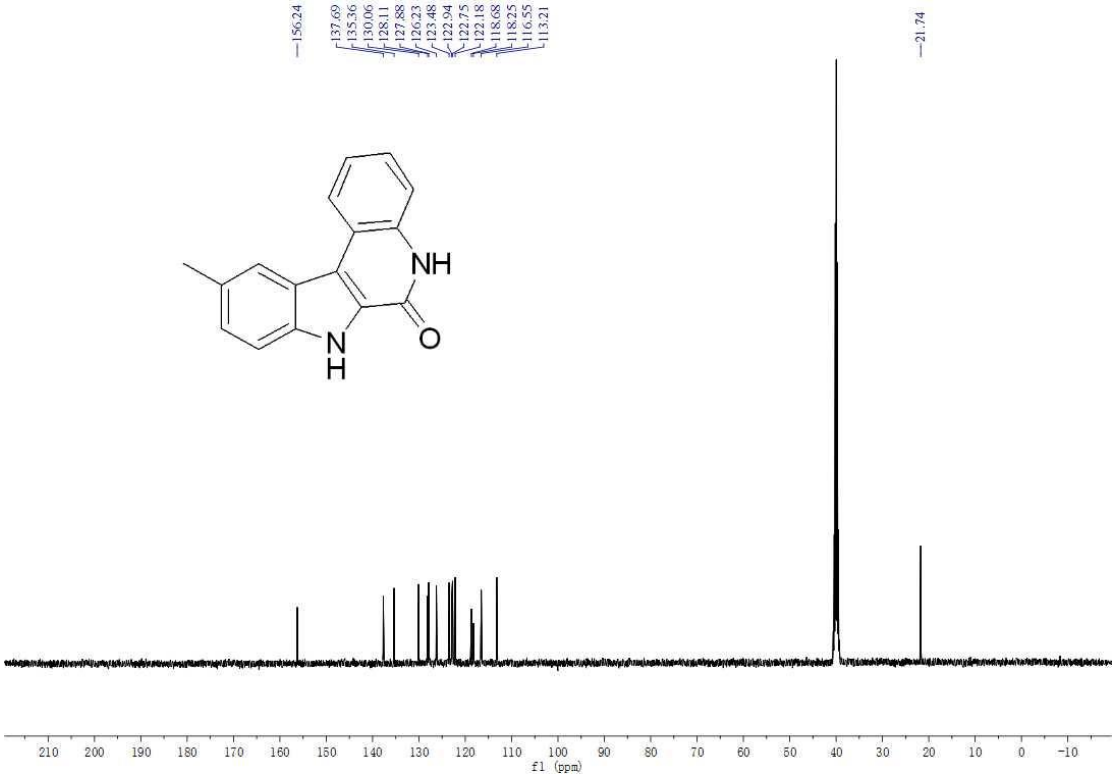
^{13}C NMR spectrum of **3c**



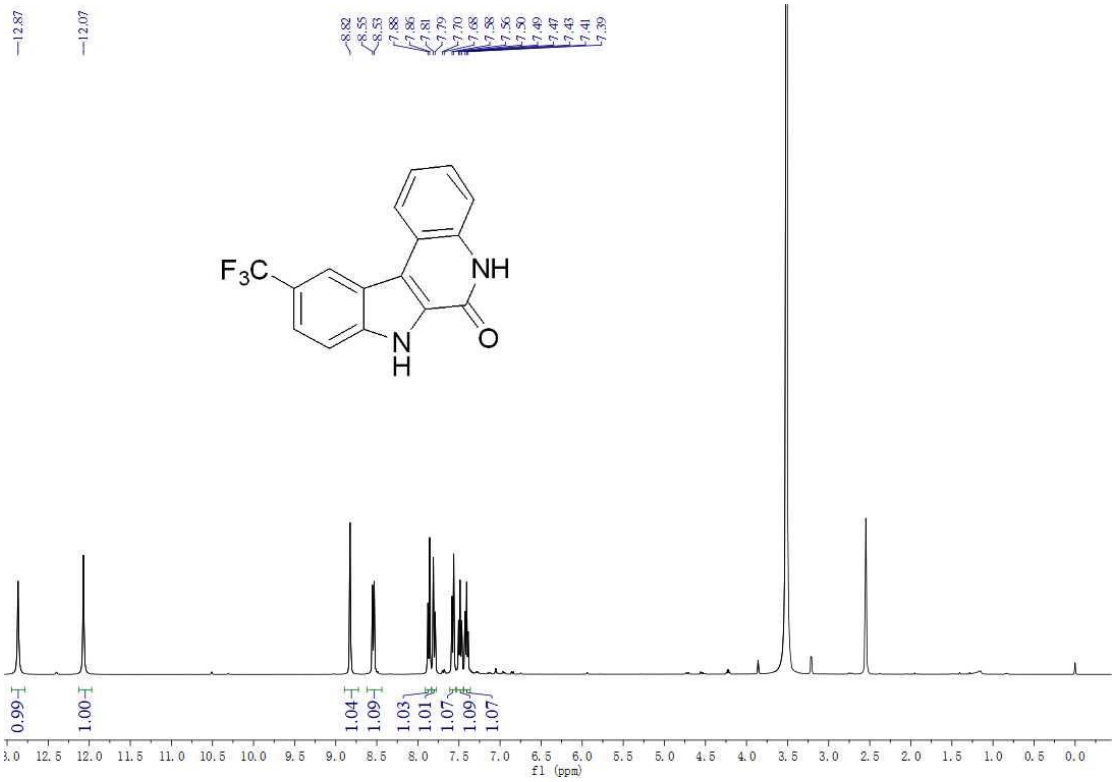
^{1}H NMR spectrum of **3d**



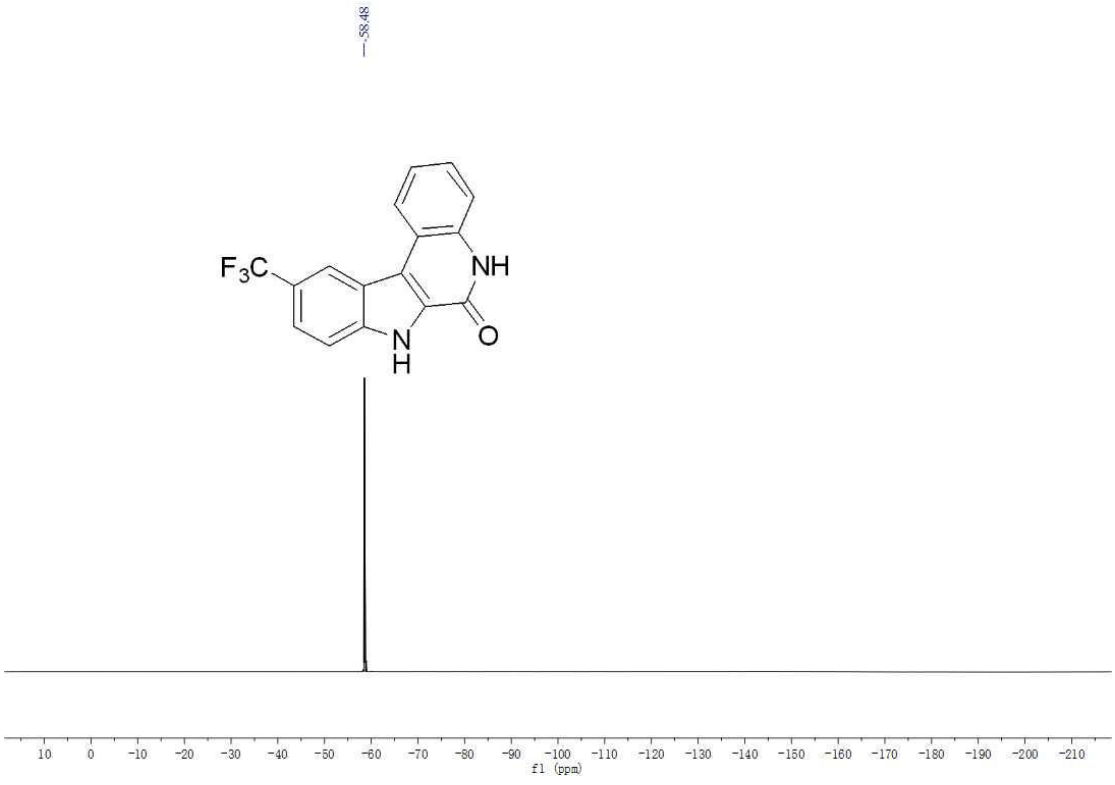
^{13}C NMR spectrum of **3d**



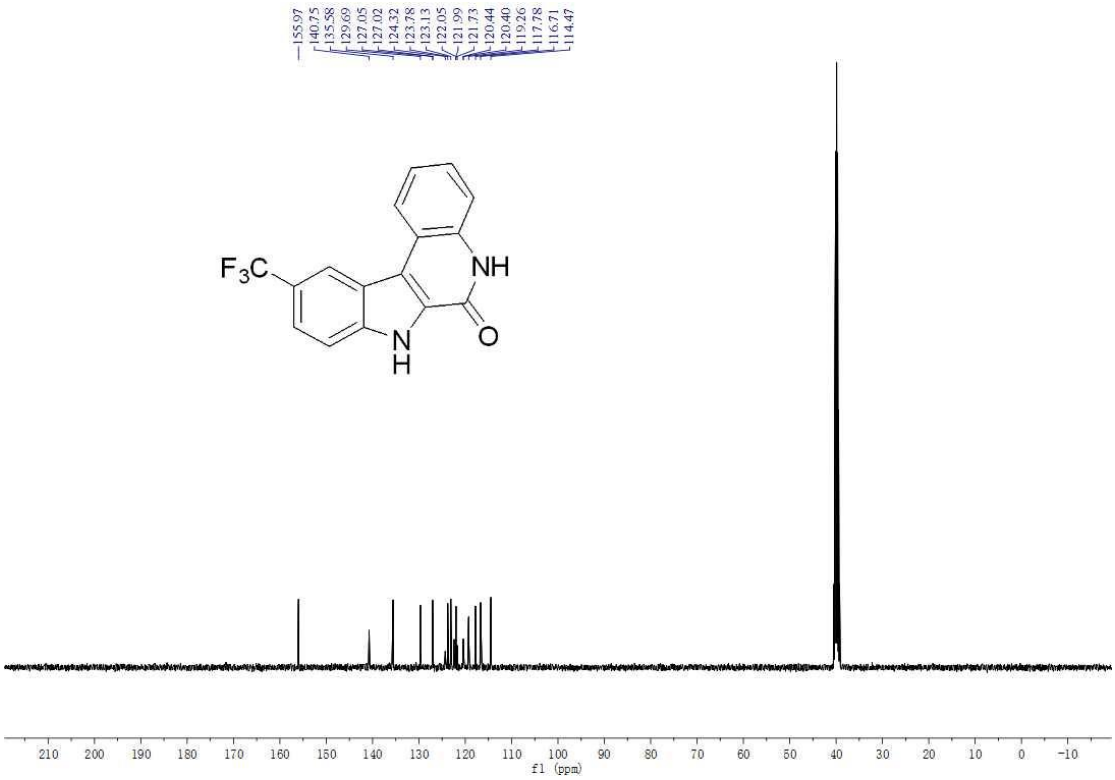
^{1}H NMR spectrum of **3e**



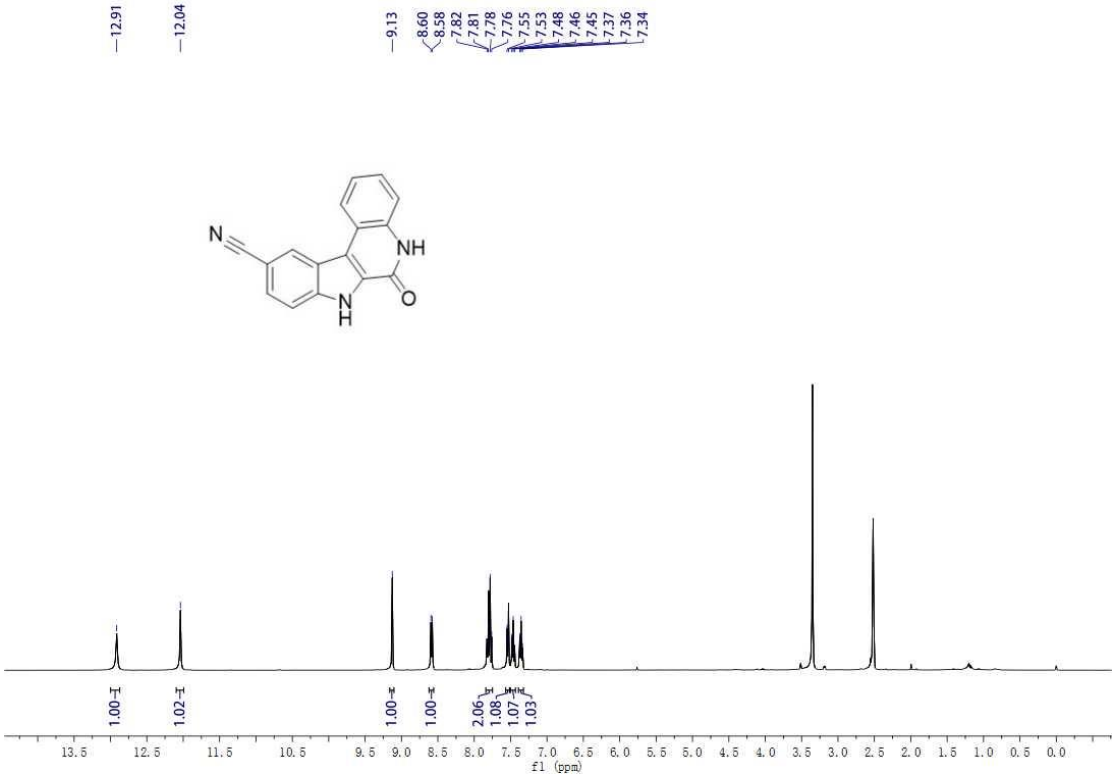
^{19}F NMR spectrum of **3e**



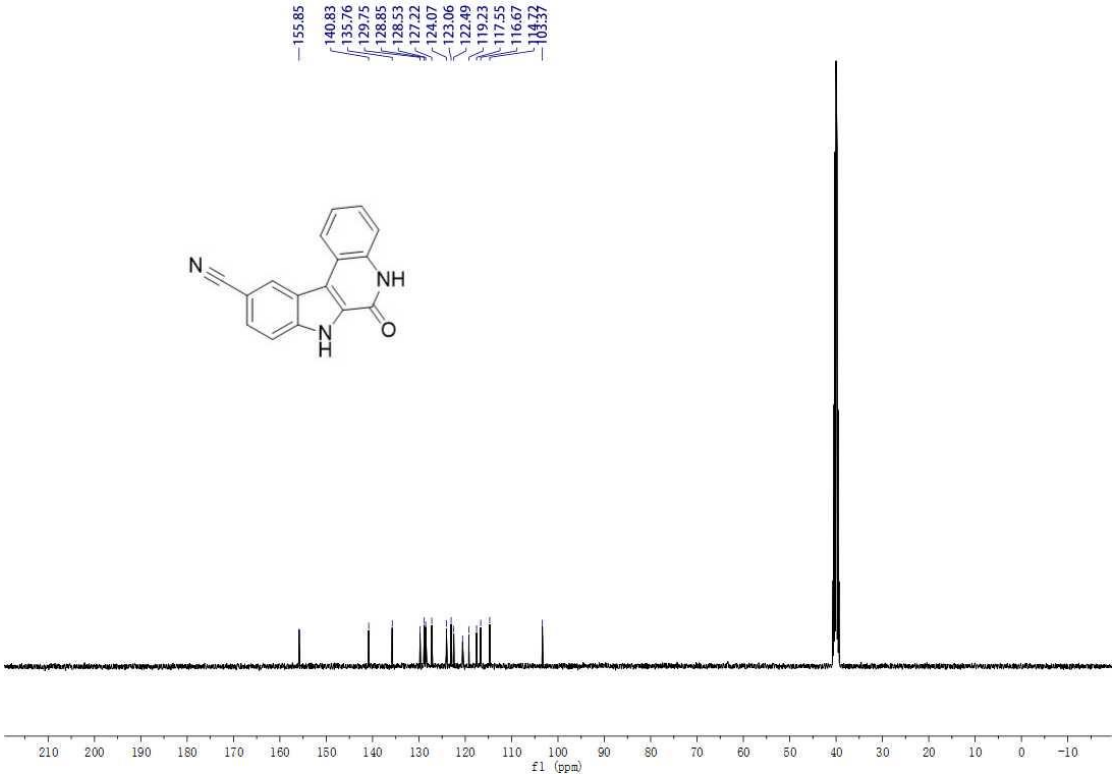
^{13}C NMR spectrum of **3e**



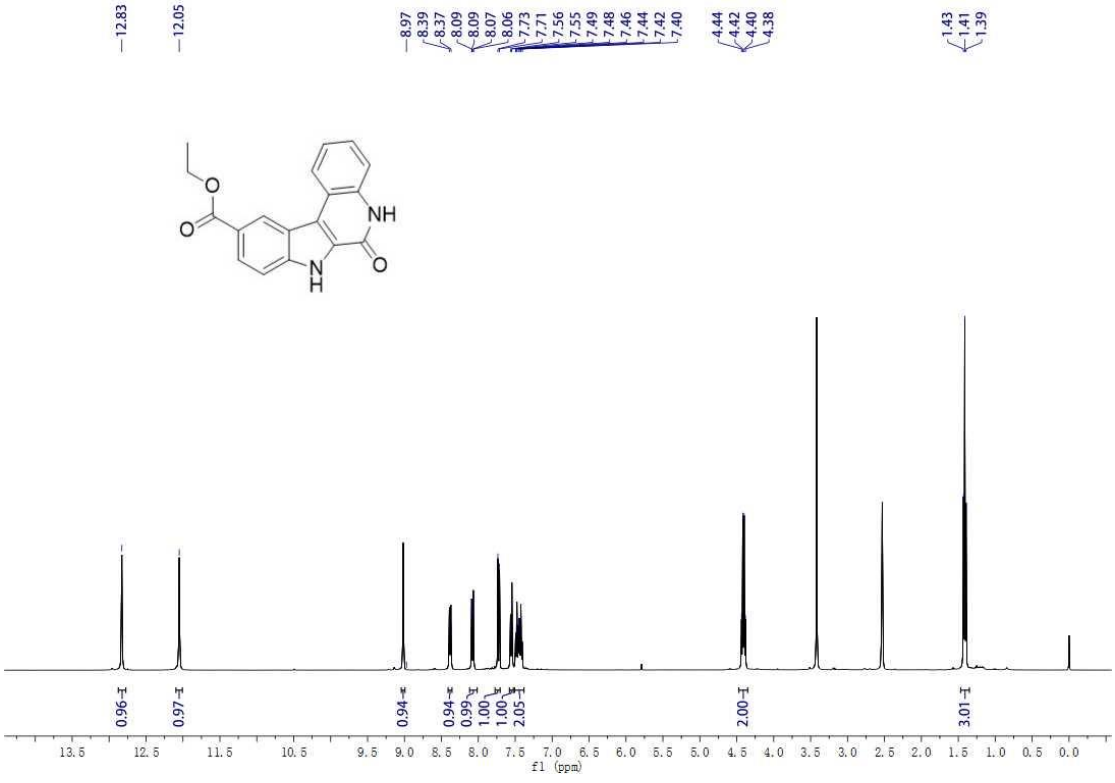
^{1}H NMR spectrum of **3f**



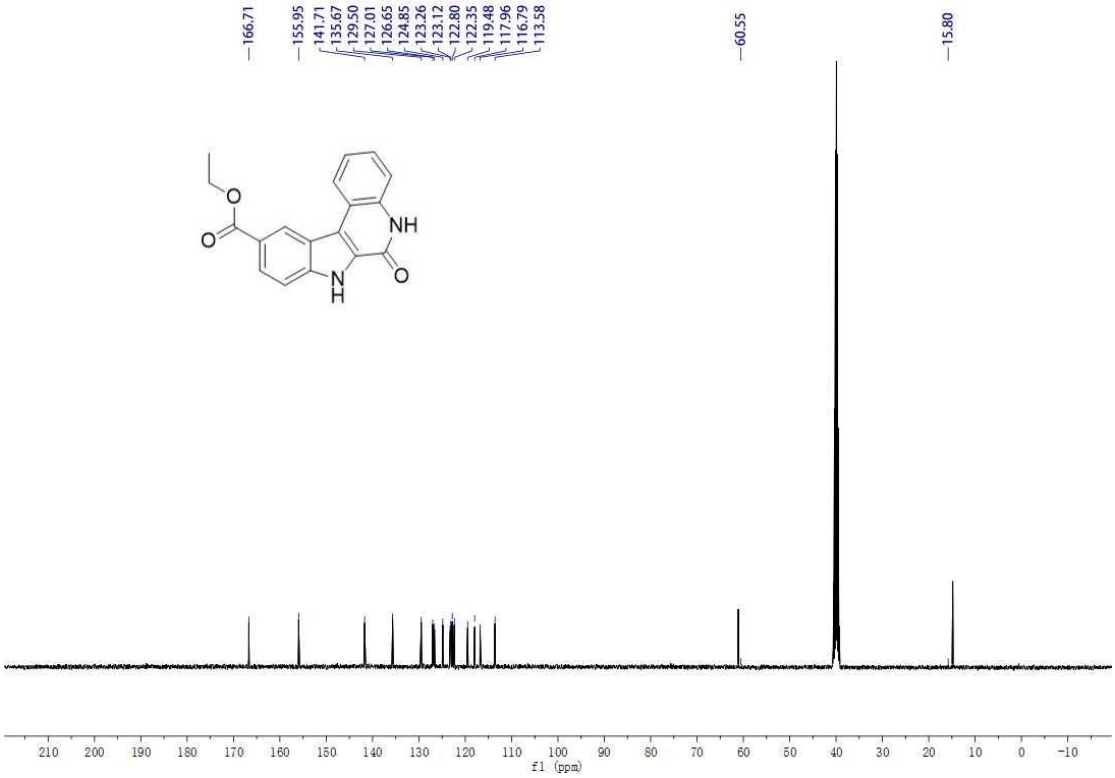
^{13}C NMR spectrum of **3f**



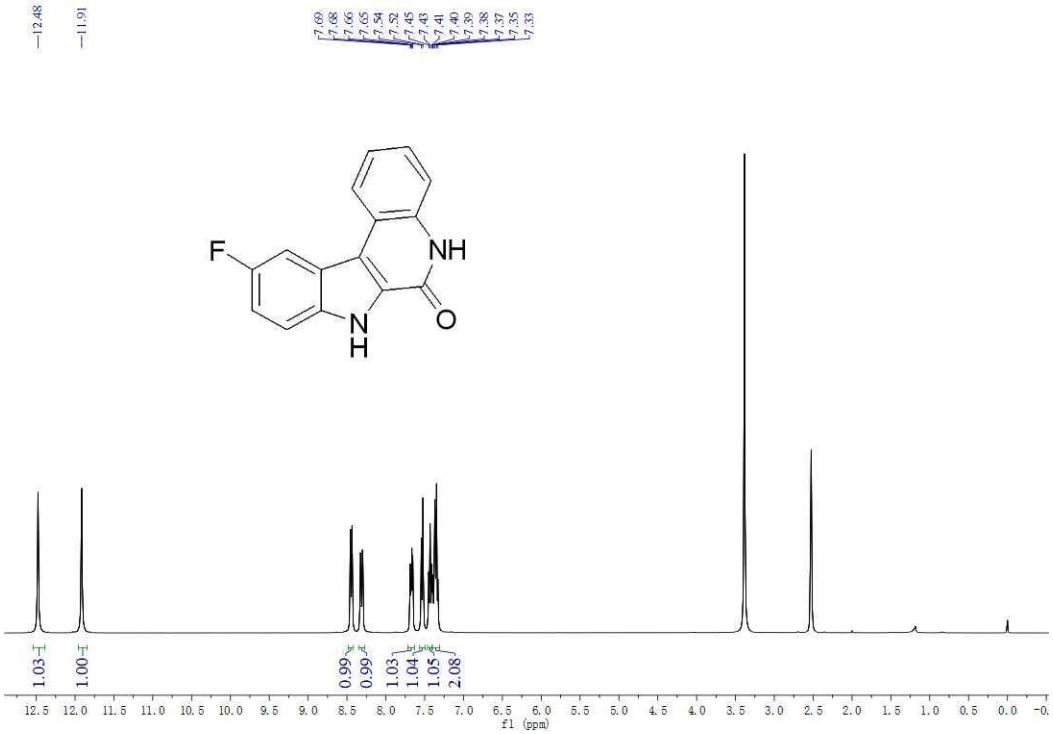
^{1}H NMR spectrum of **3g**



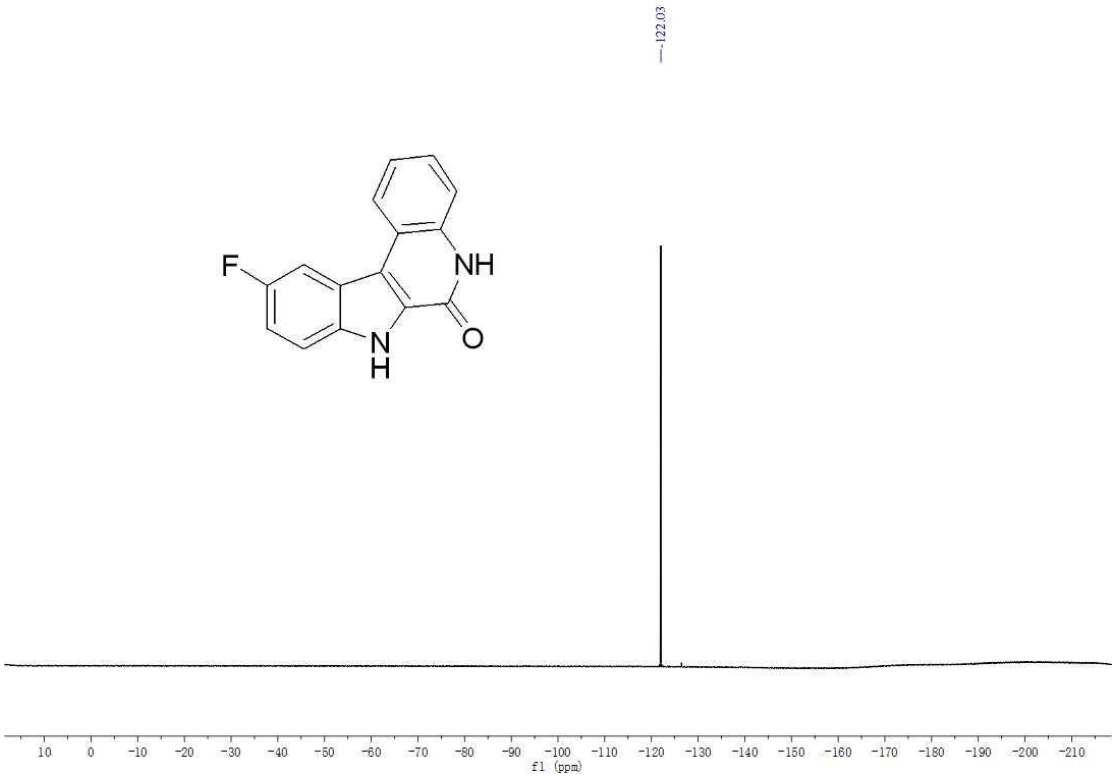
^{13}C NMR spectrum of **3g**



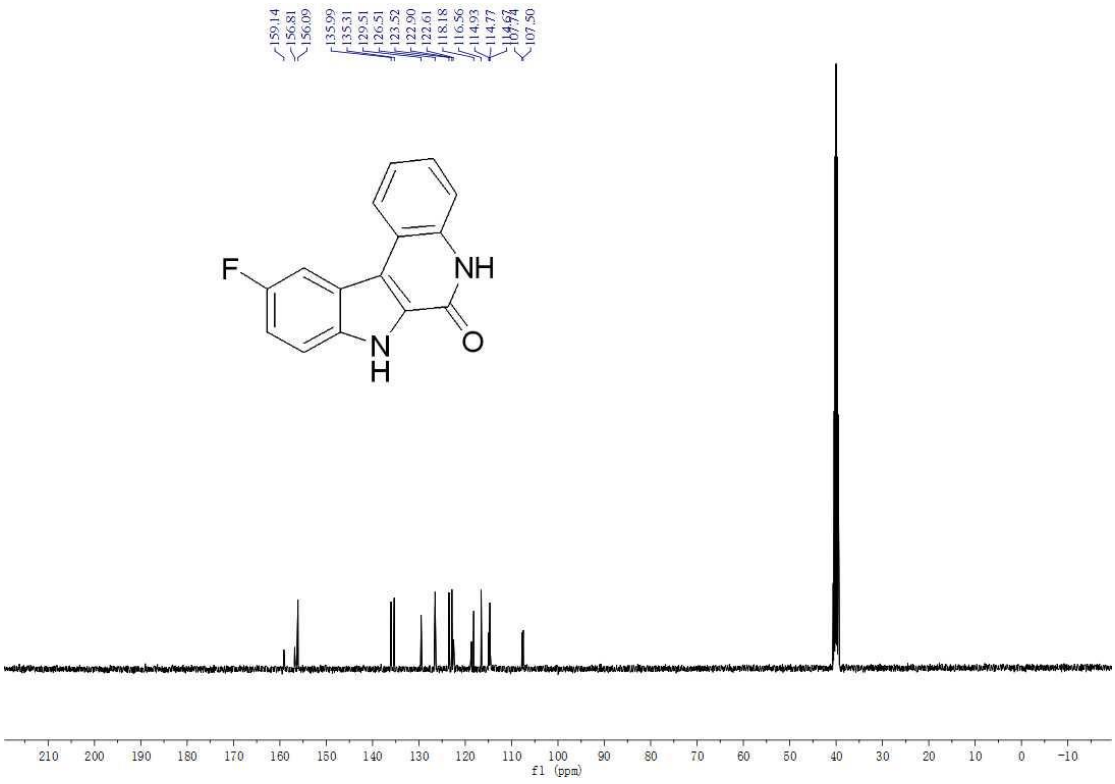
^{1}H NMR spectrum of **3h**



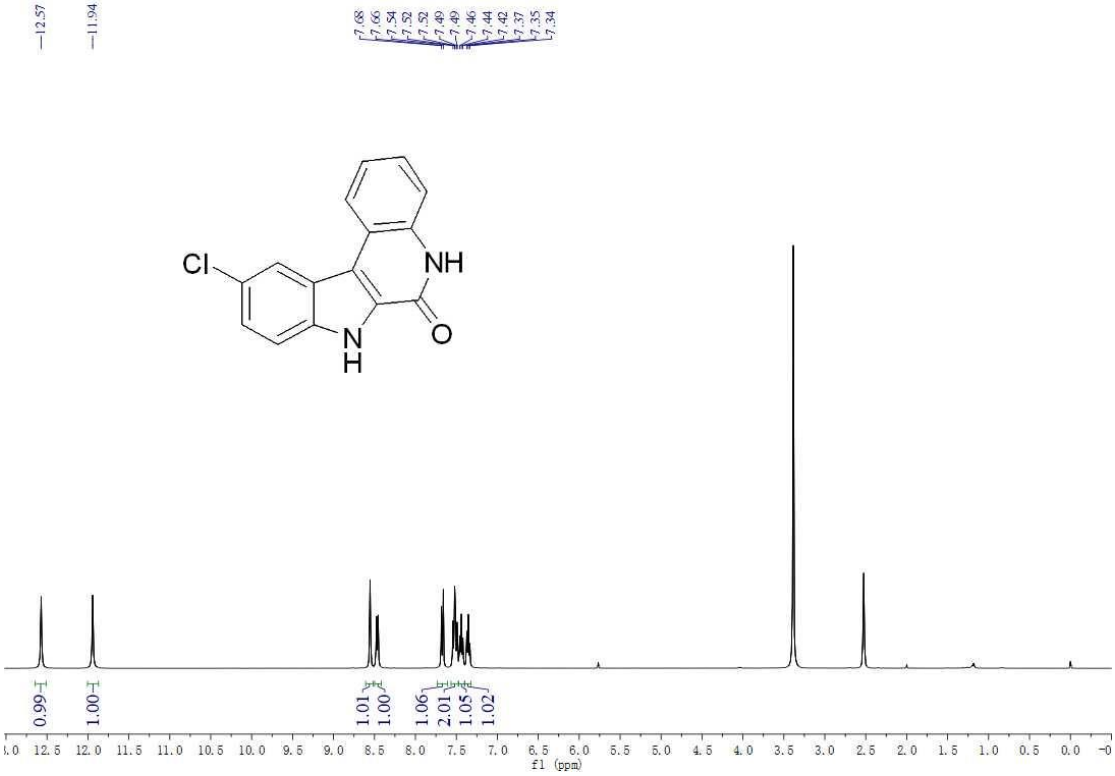
^{19}F NMR spectrum of **3h**



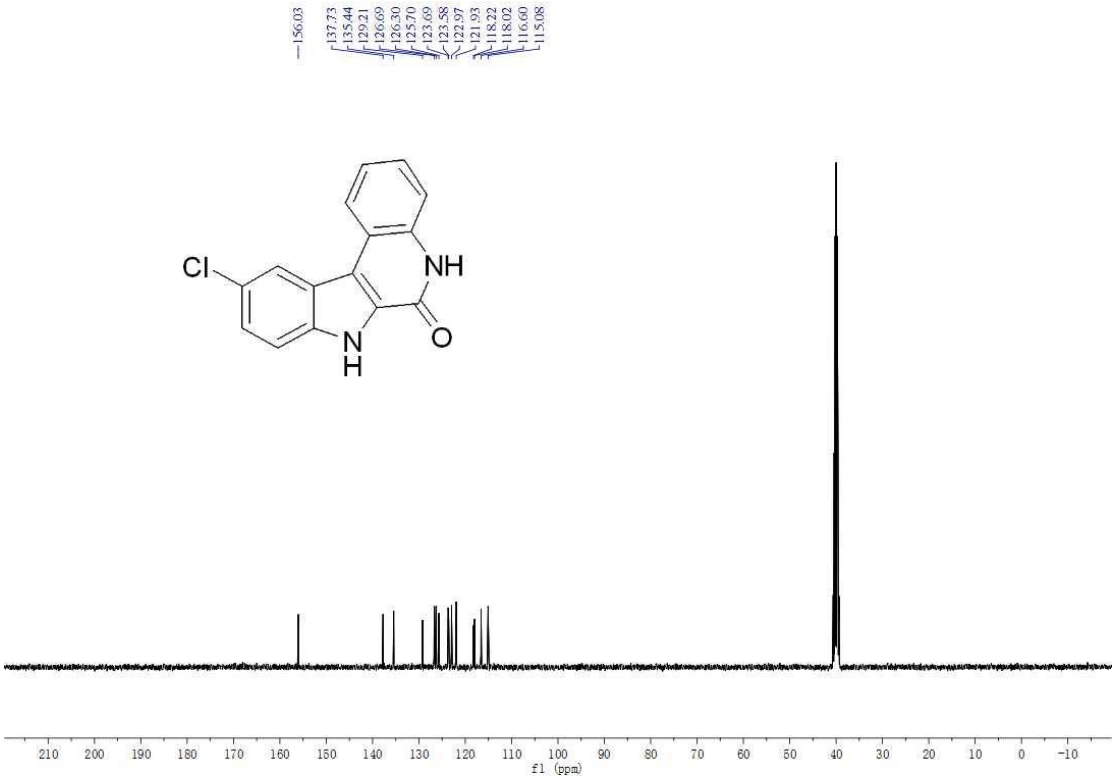
^{13}C NMR spectrum of **3h**



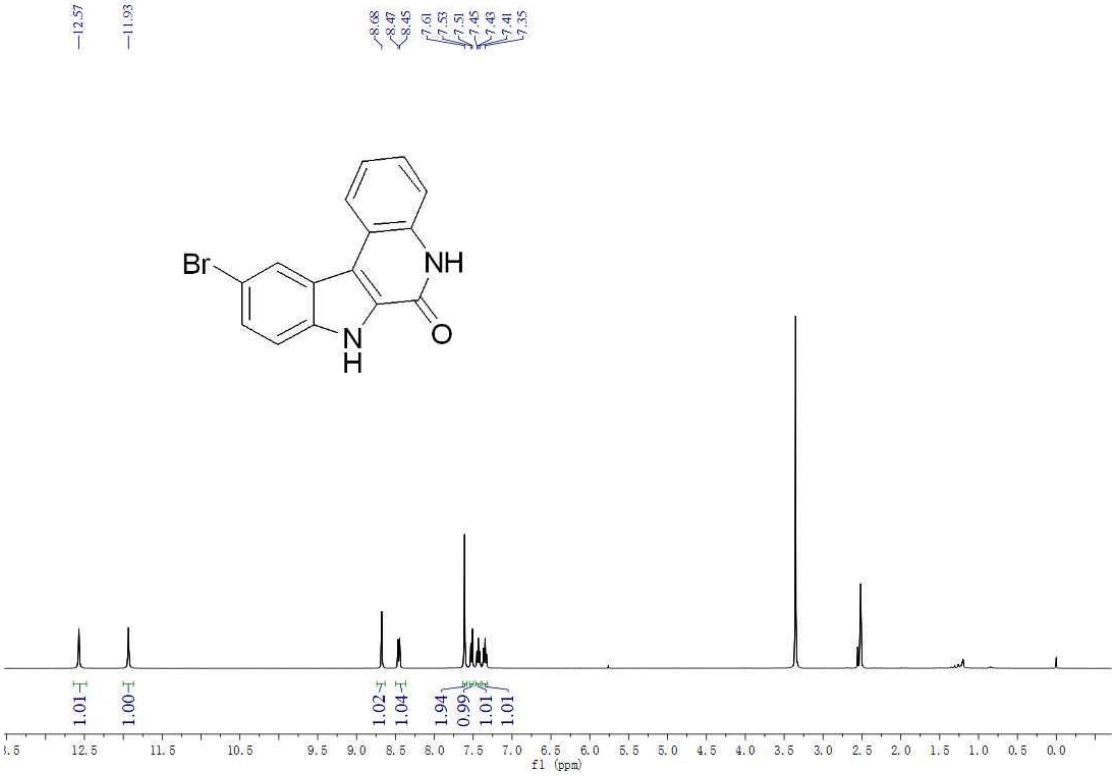
^{1}H NMR spectrum of **3i**



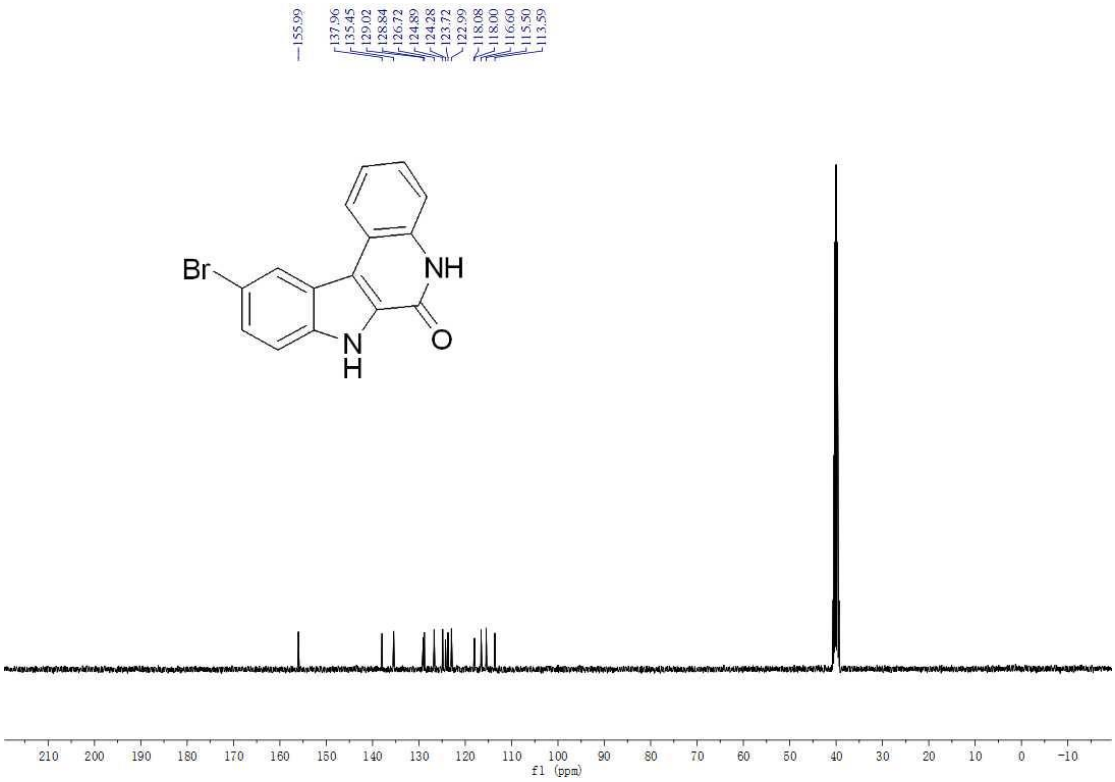
^{13}C NMR spectrum of **3i**



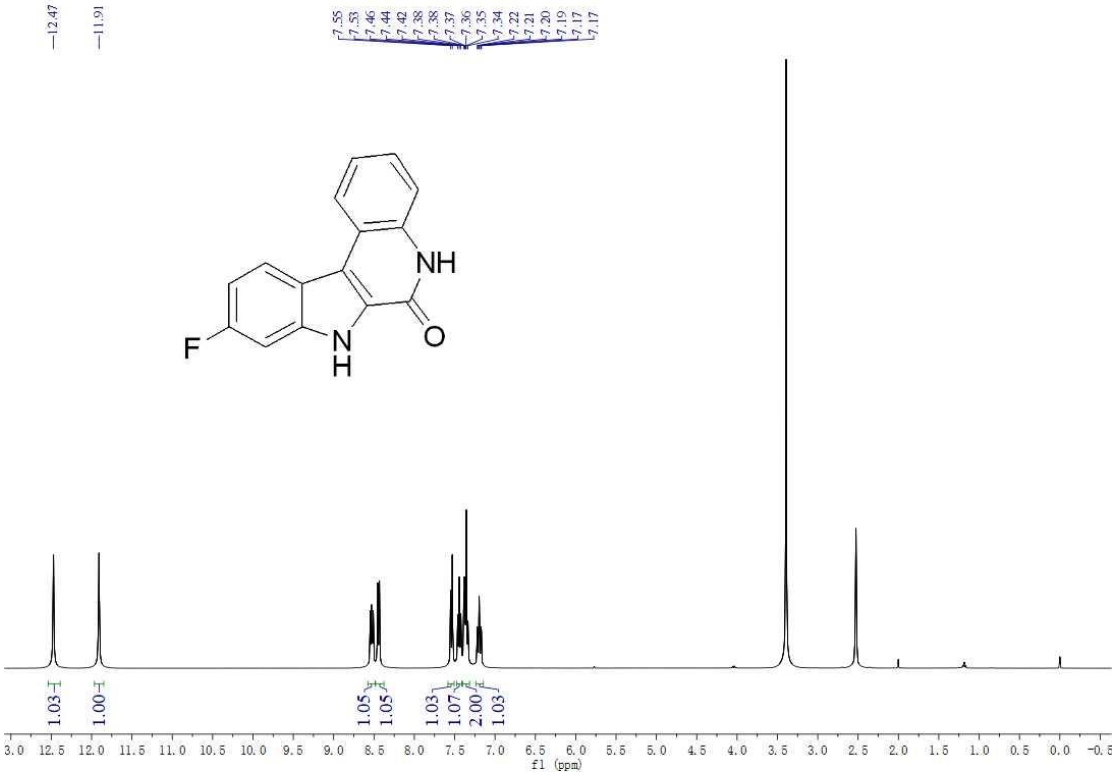
^{1}H NMR spectrum of **3j**



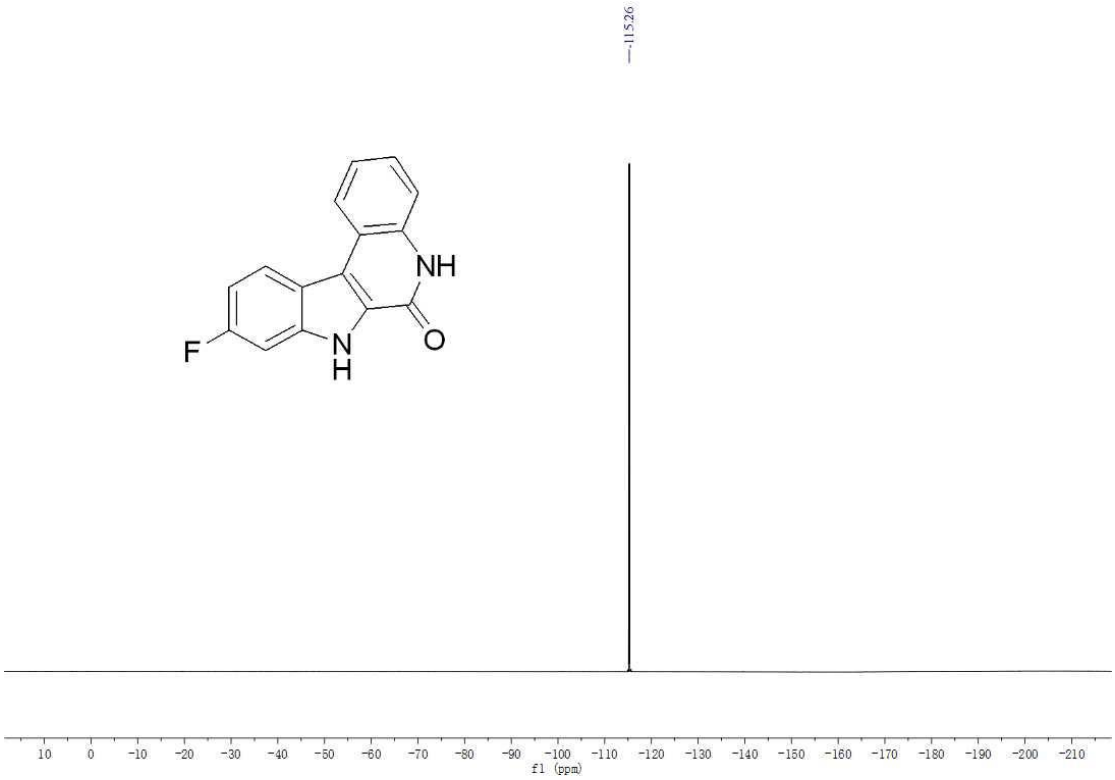
^{13}C NMR spectrum of **3j**



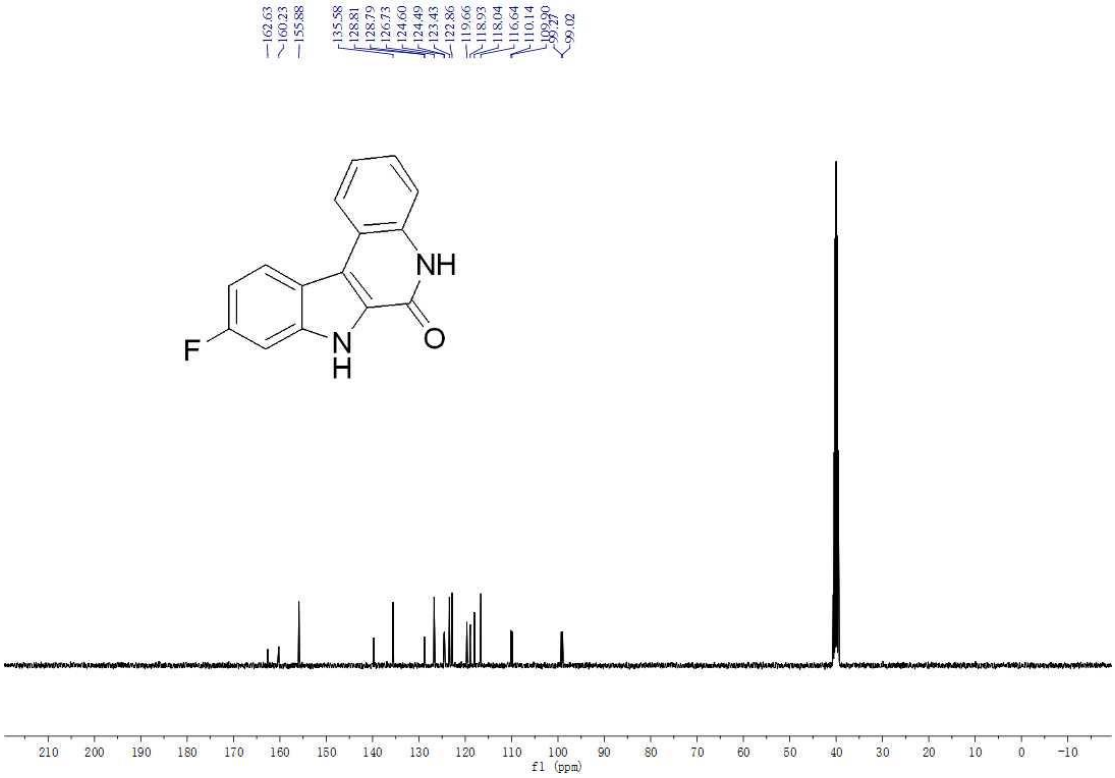
^{1}H NMR spectrum of **3k**



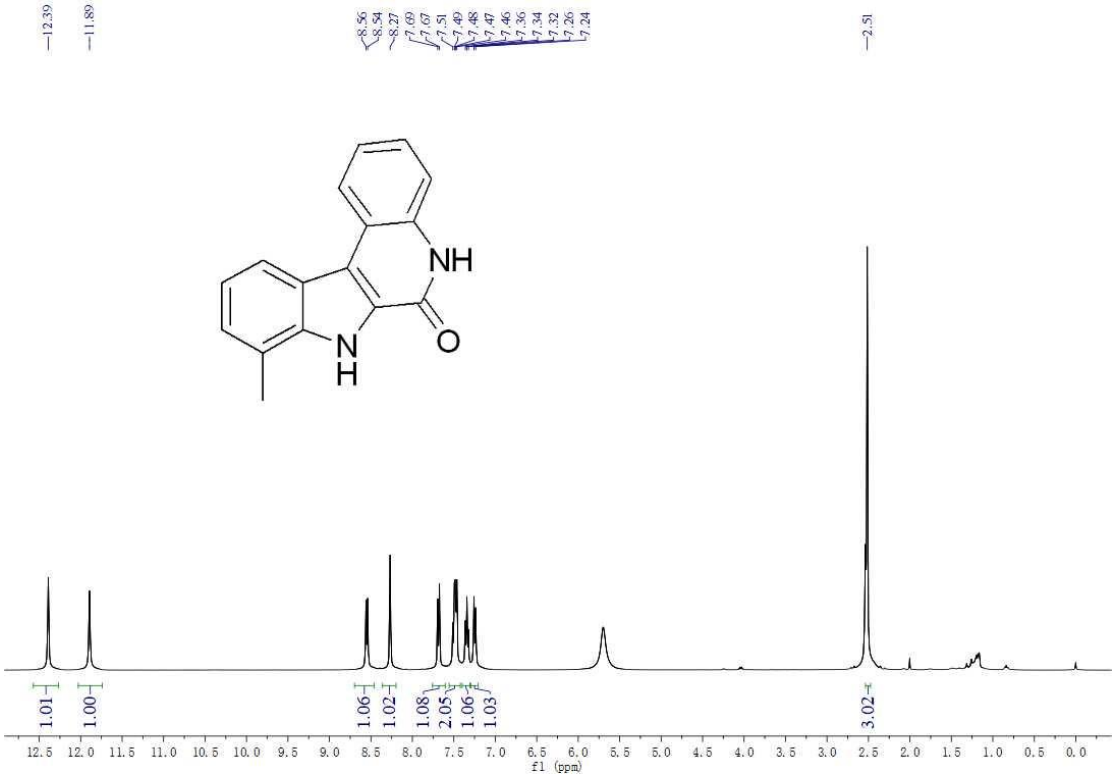
^{19}F NMR spectrum of **3k**



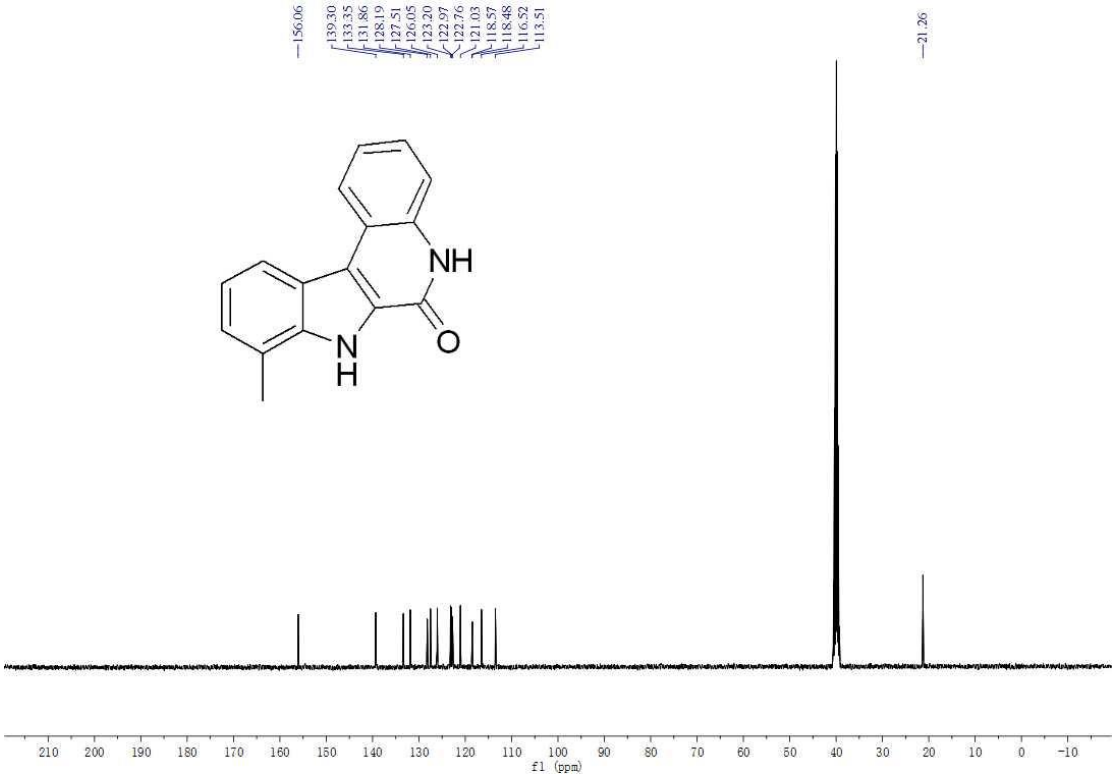
^{13}C NMR spectrum of **3k**



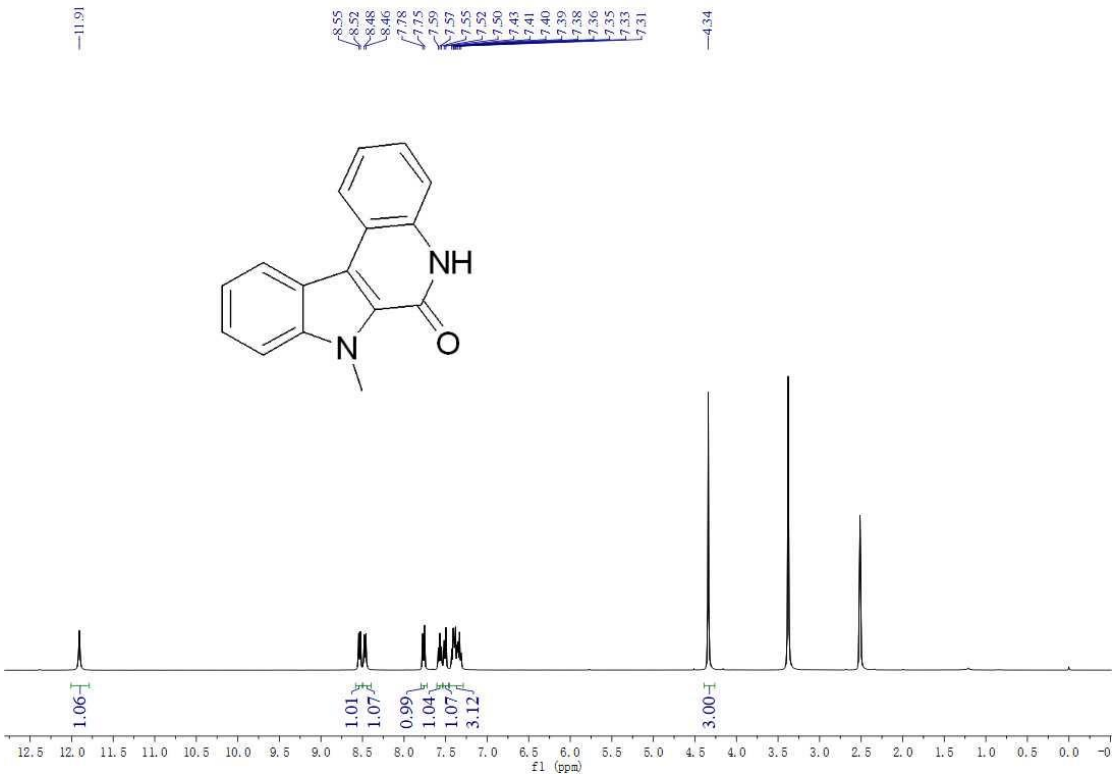
^{1}H NMR spectrum of **3l**



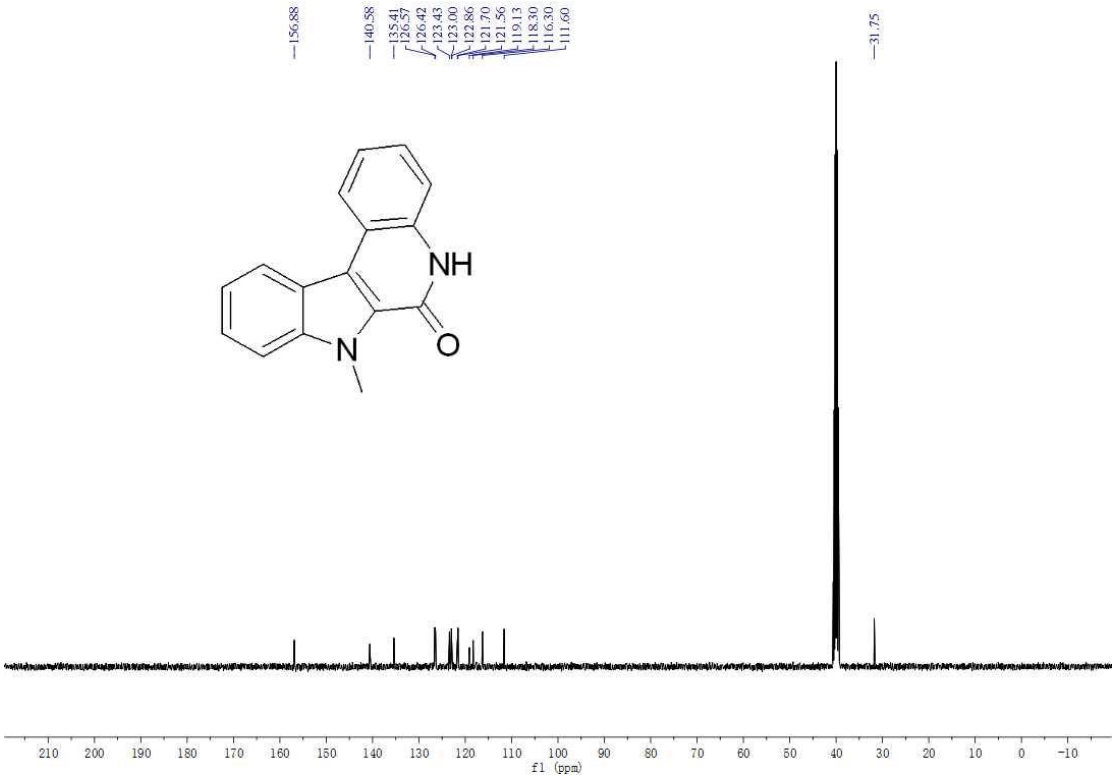
^{13}C NMR spectrum of **3l**



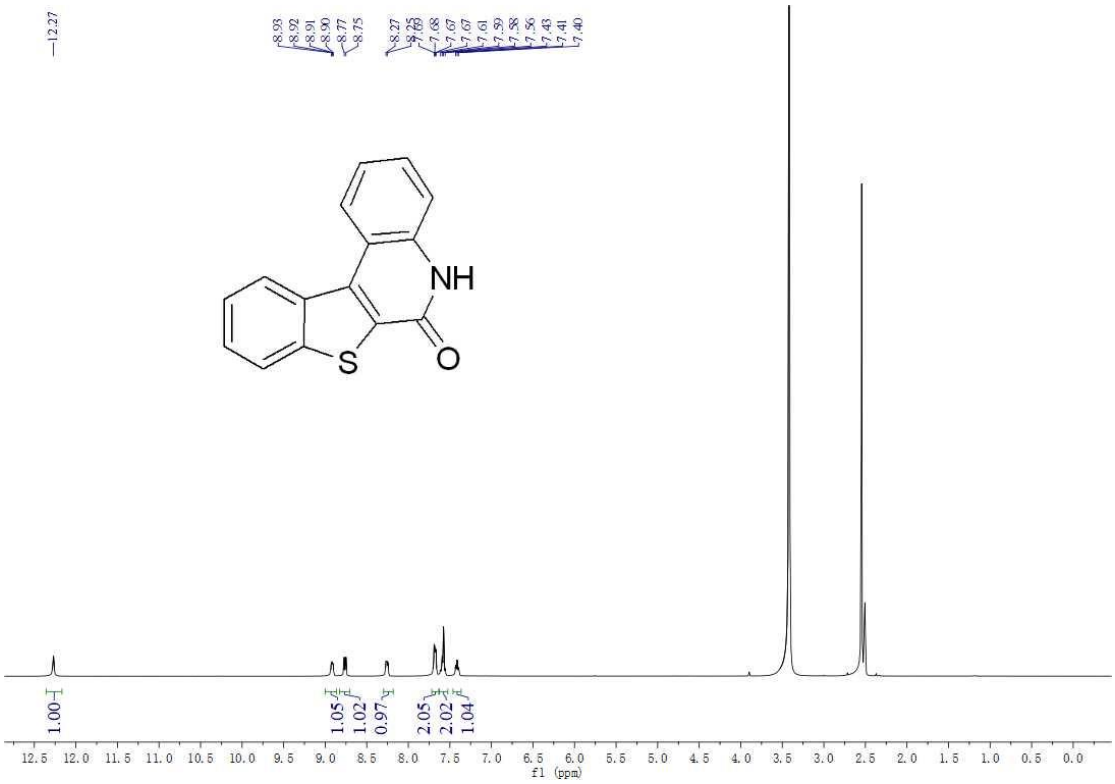
^{1}H NMR spectrum of **3m**



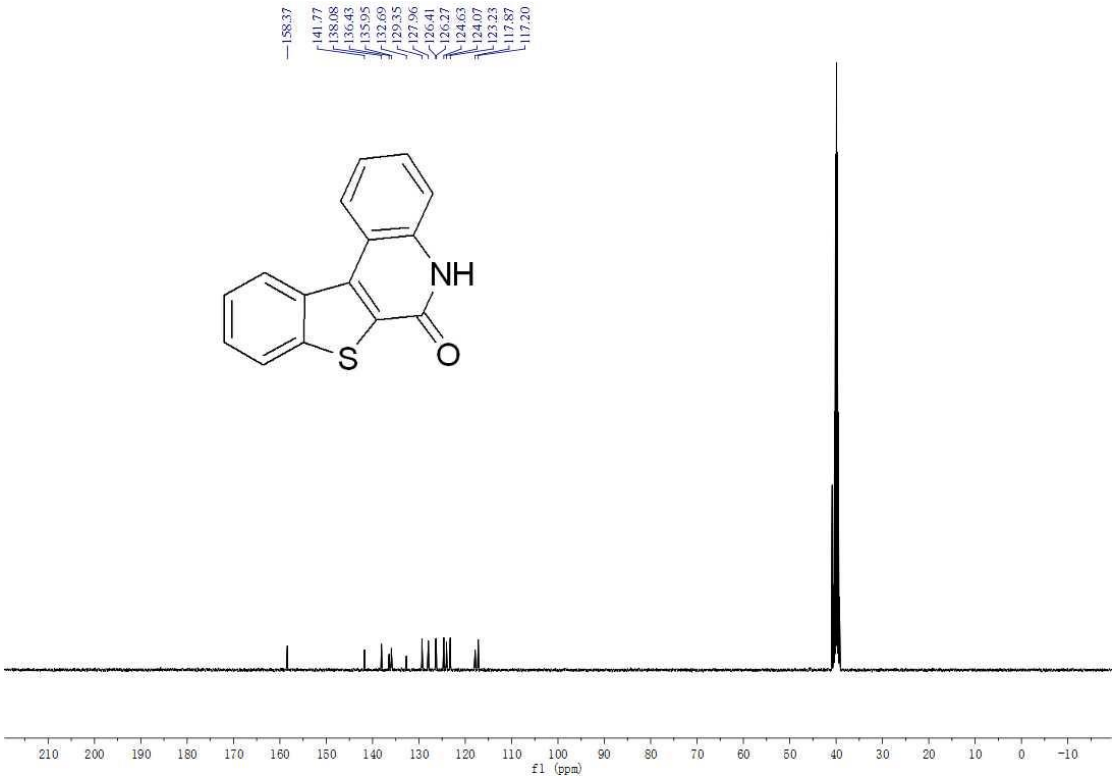
^{13}C NMR spectrum of **3m**



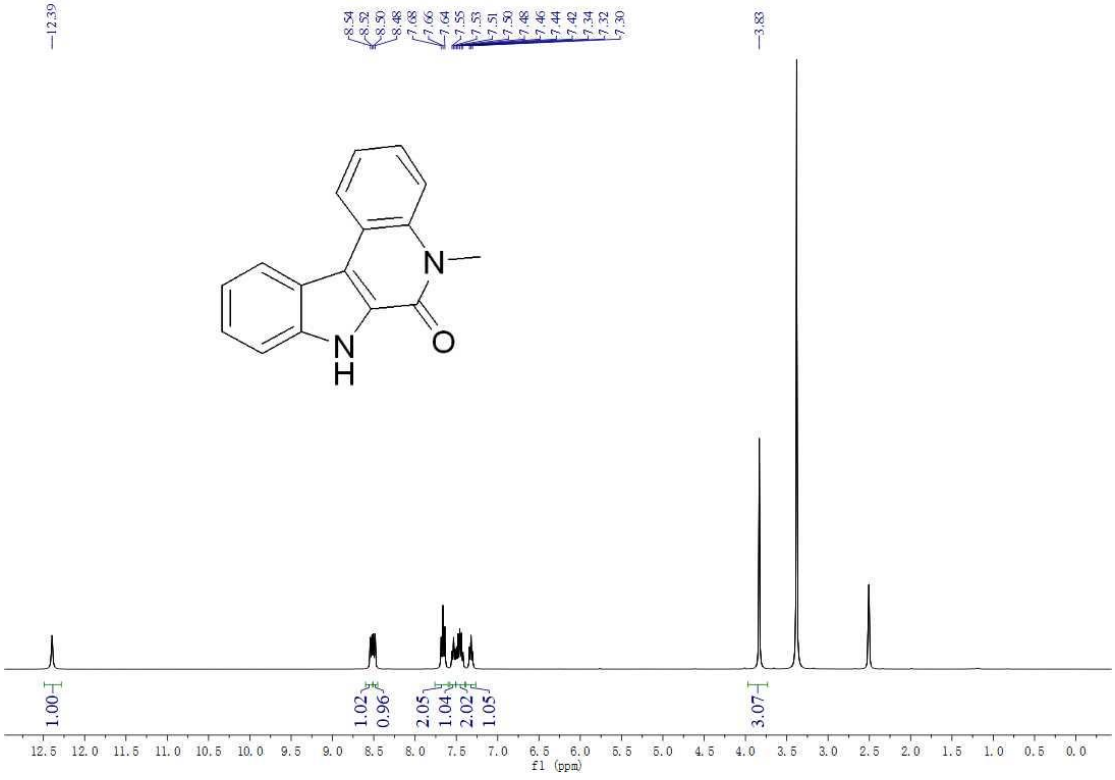
^{1}H NMR spectrum of **3n**



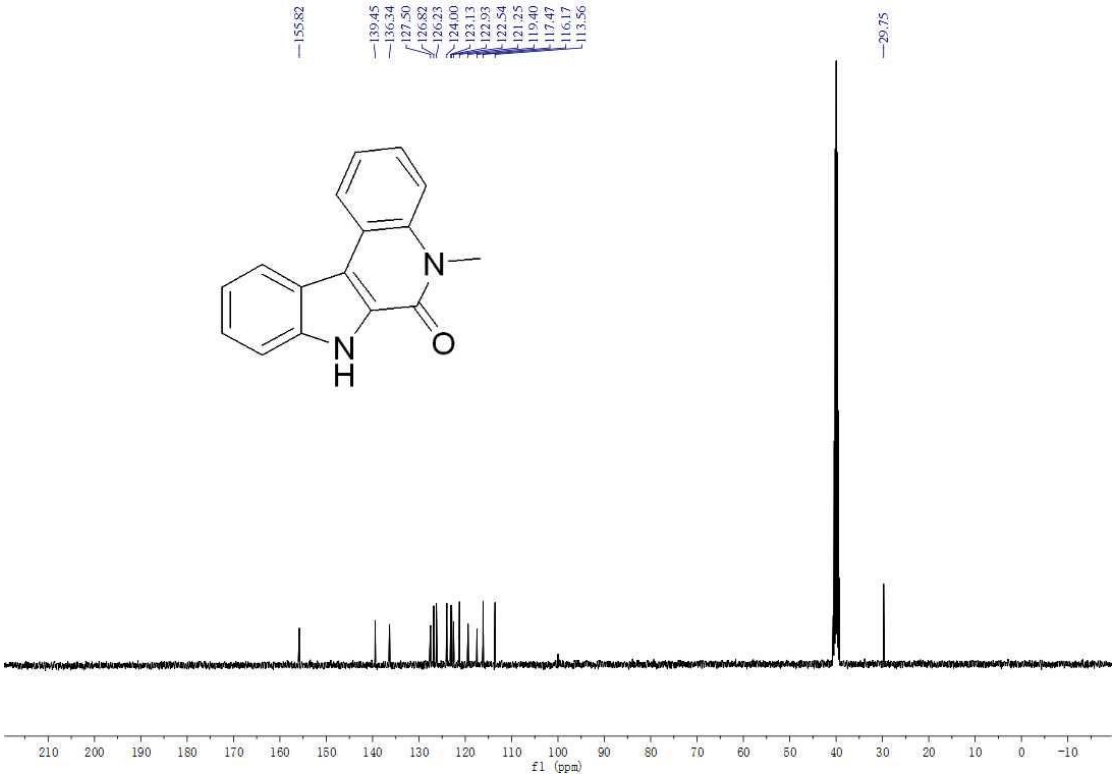
^{13}C NMR spectrum of **3n**



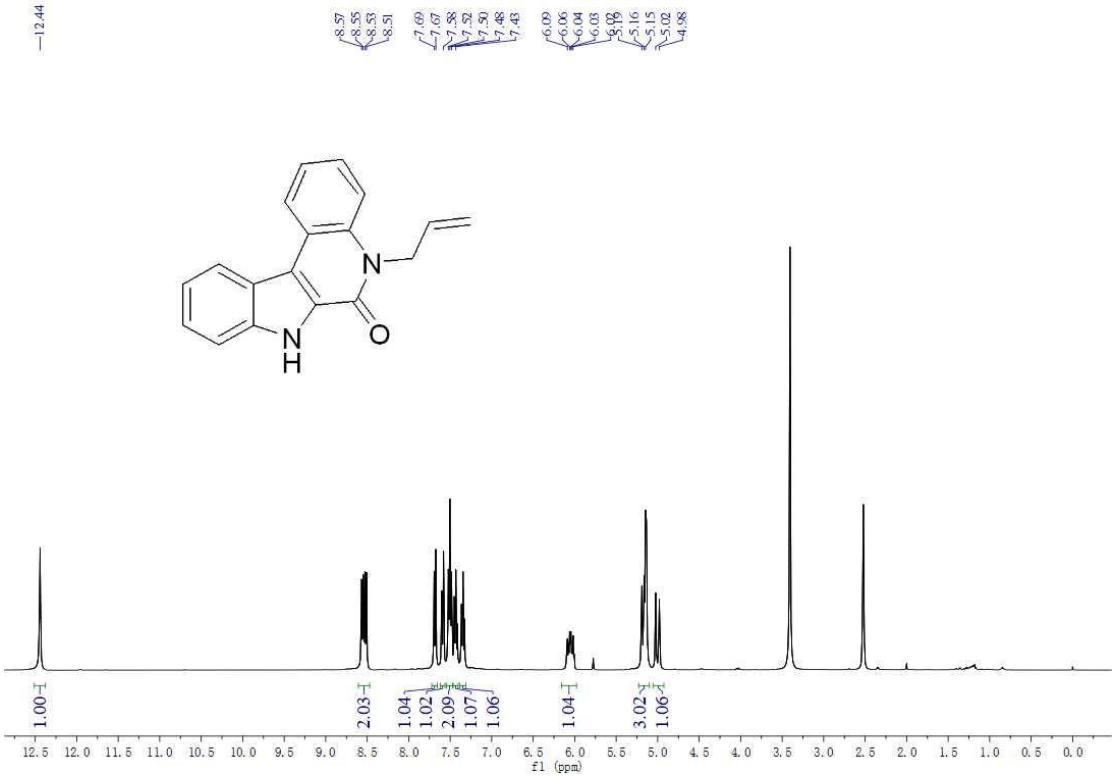
^{1}H NMR spectrum of **3e**



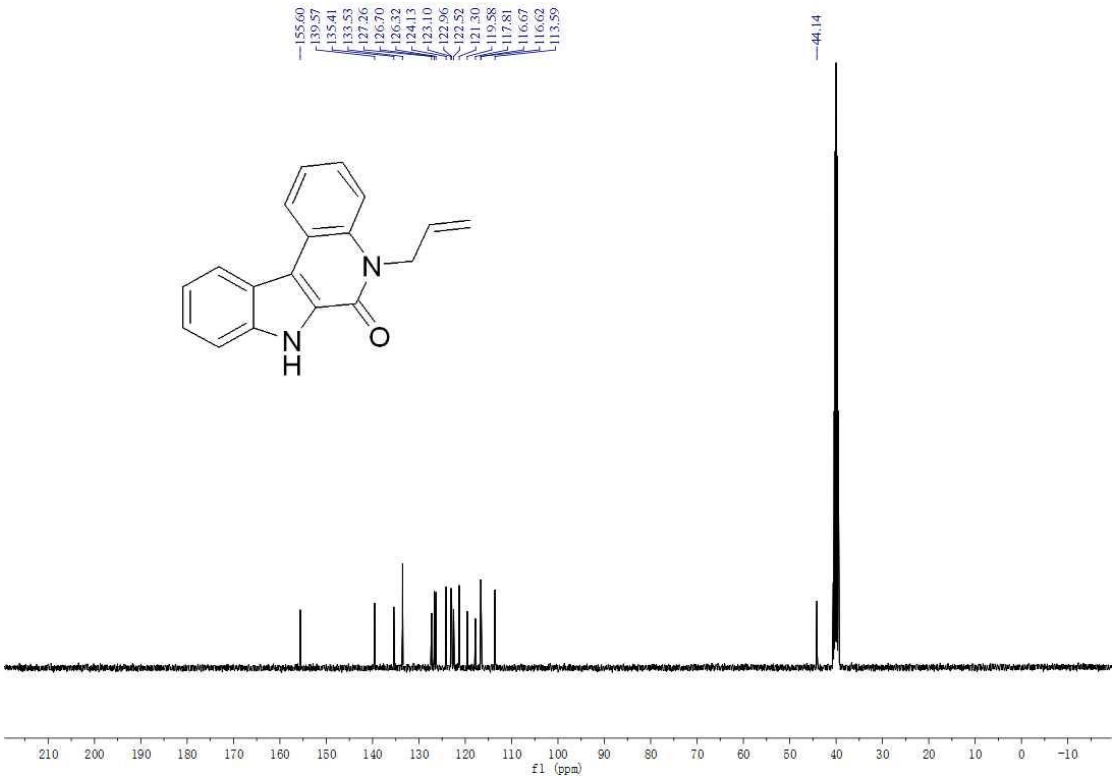
^{13}C NMR spectrum of **3e**



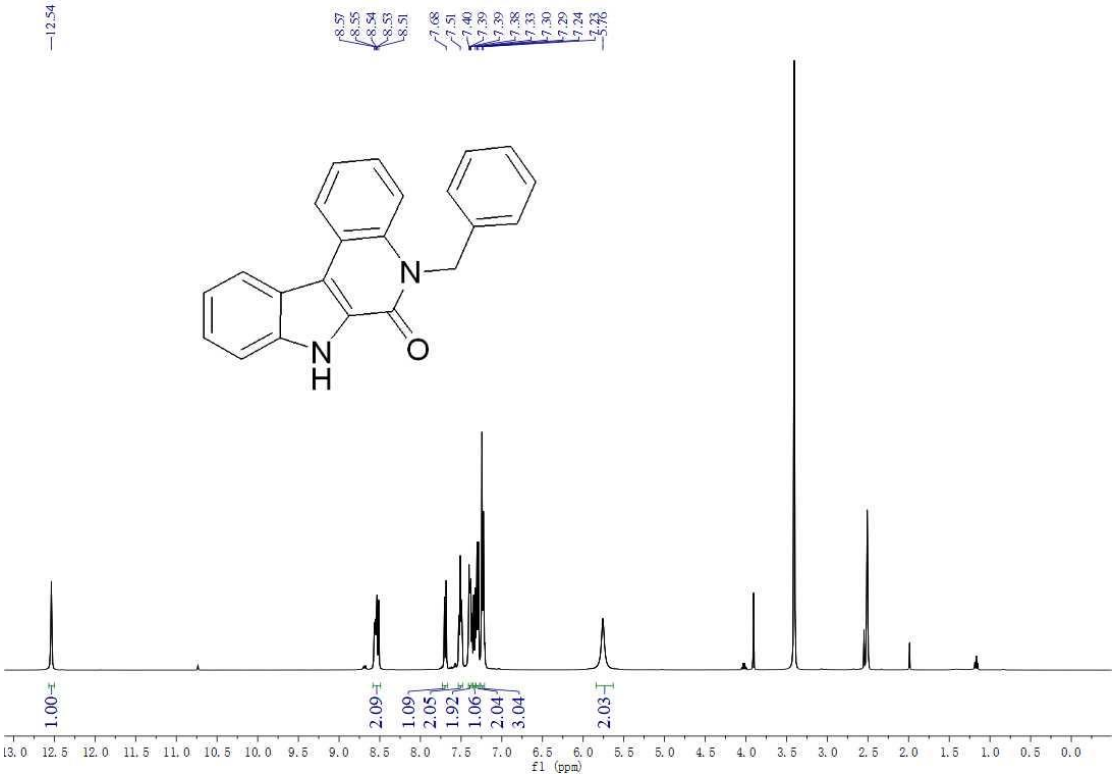
^{1}H NMR spectrum of **3p**



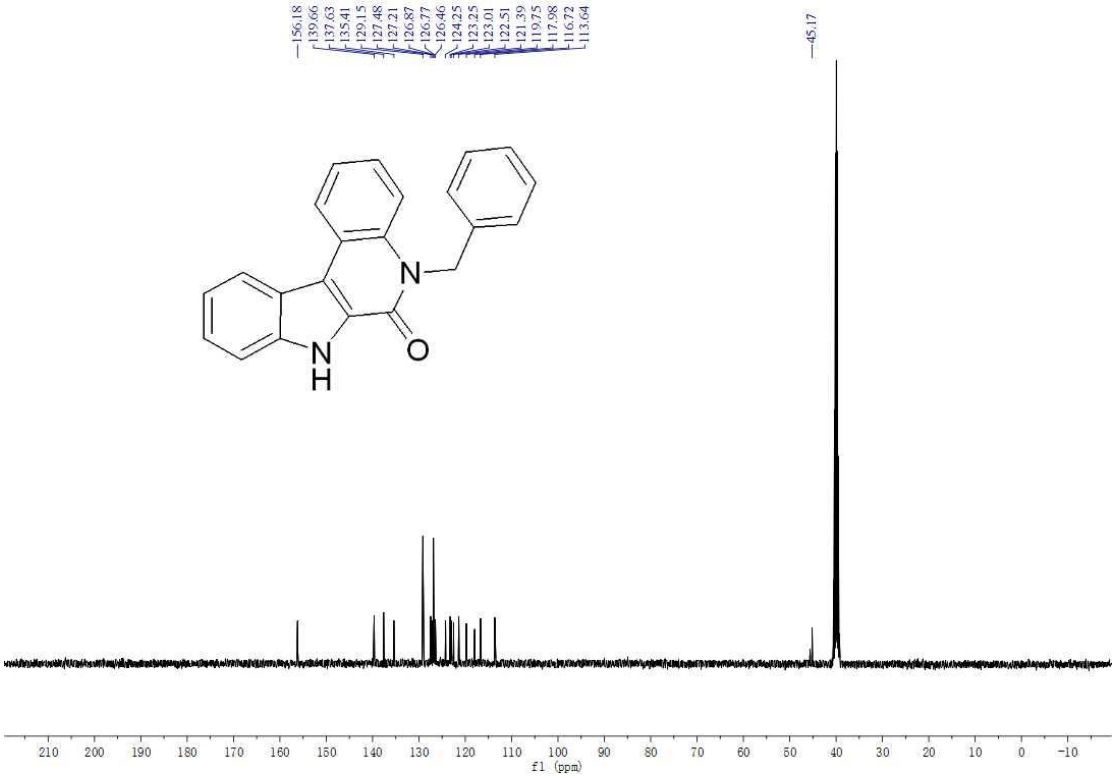
^{13}C NMR spectrum of **3p**



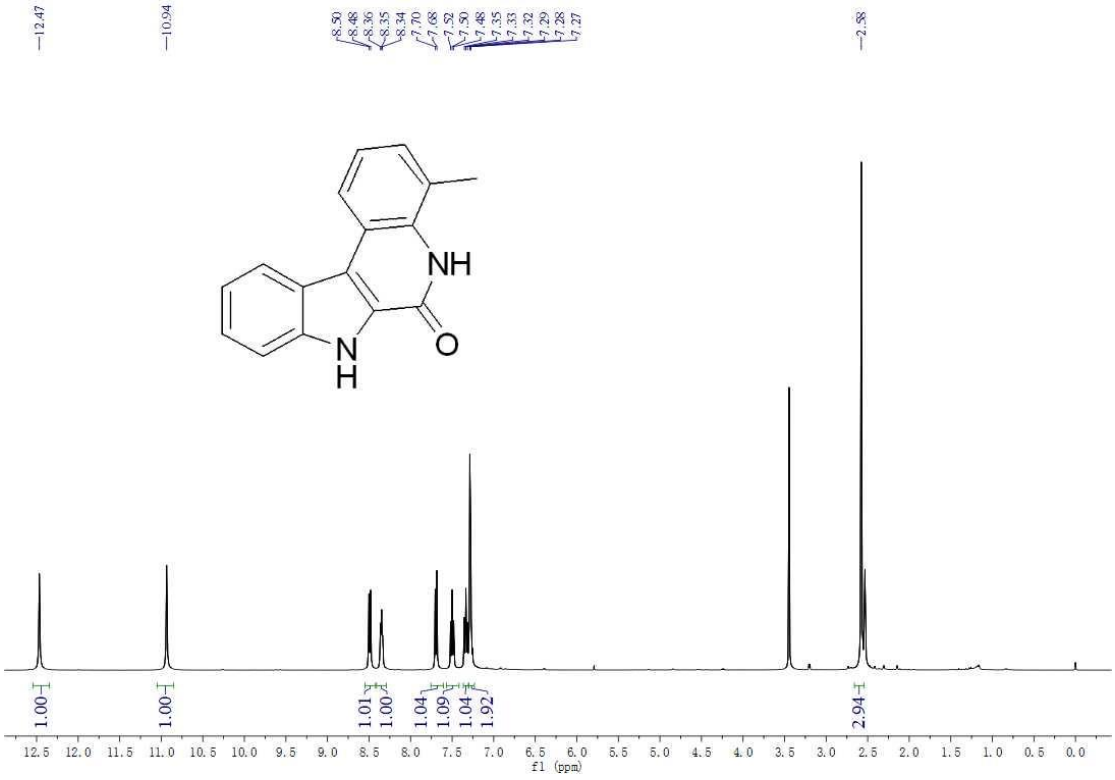
^{1}H NMR spectrum of **3q**



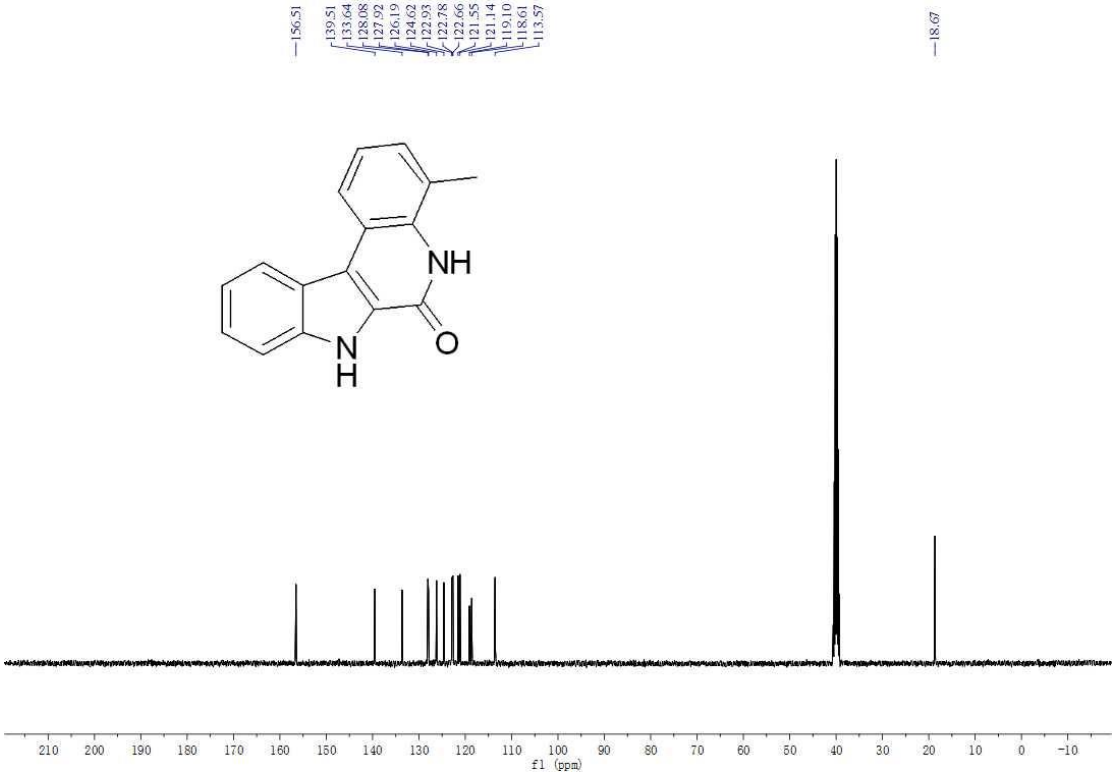
^{13}C NMR spectrum of **3q**



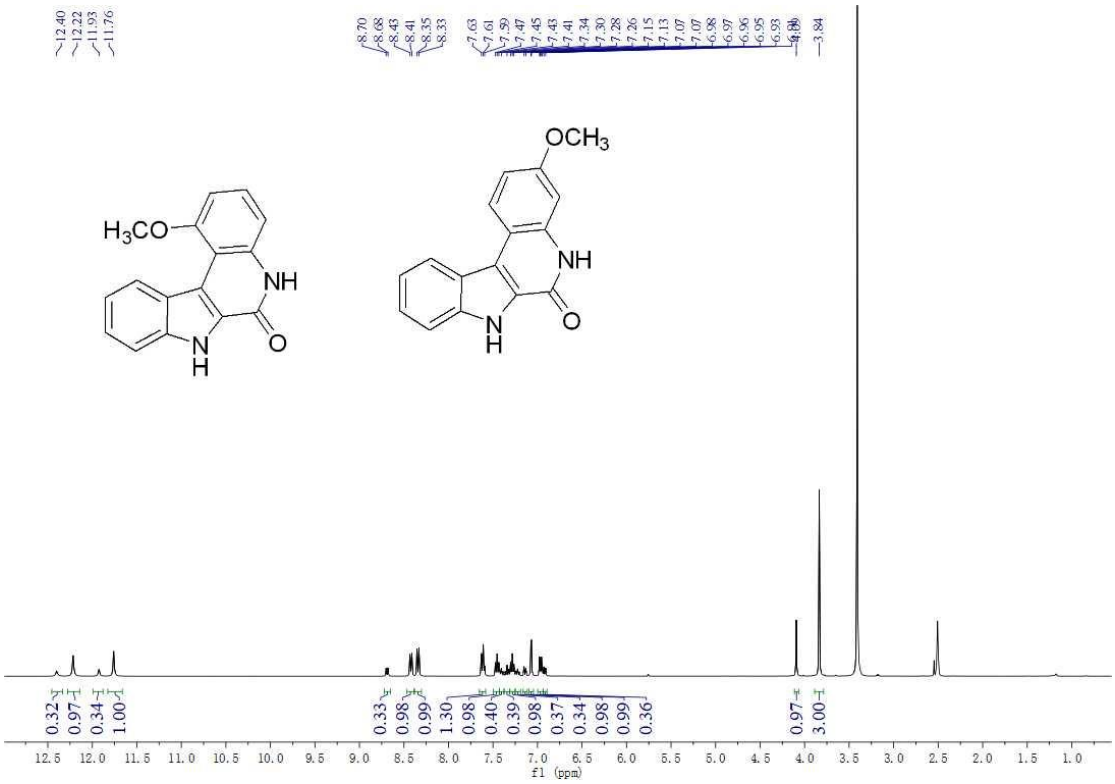
^{1}H NMR spectrum of **3r**



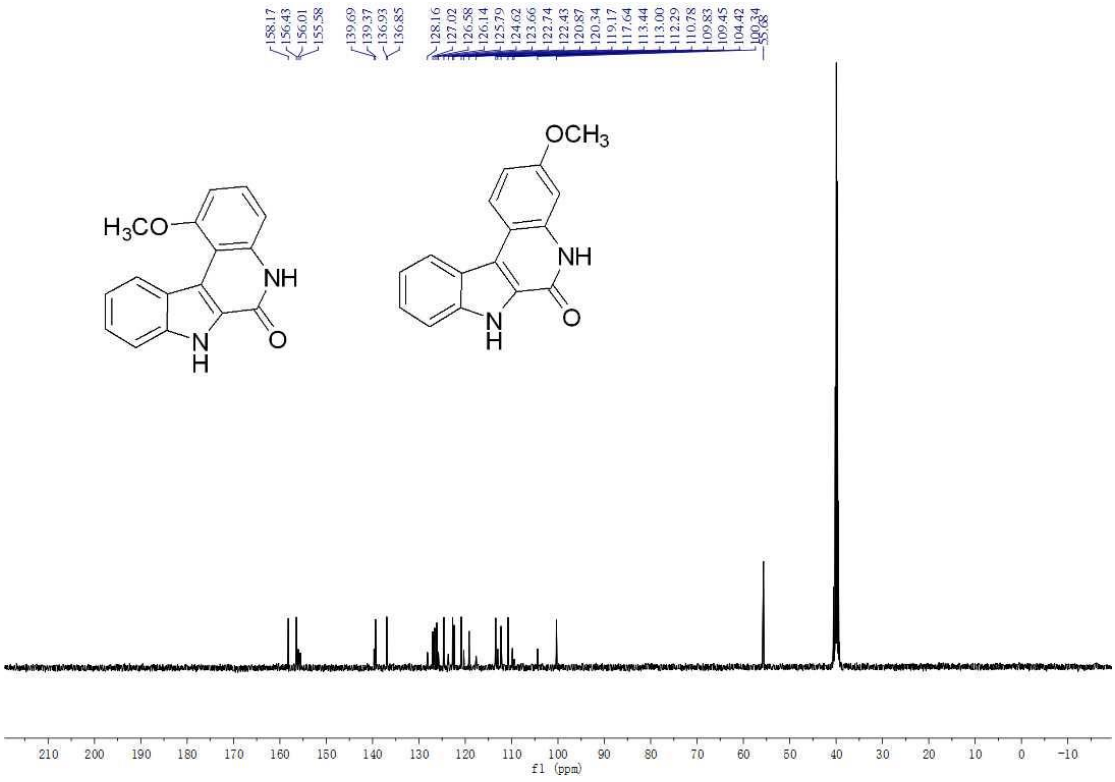
^{13}C NMR spectrum of **3r**



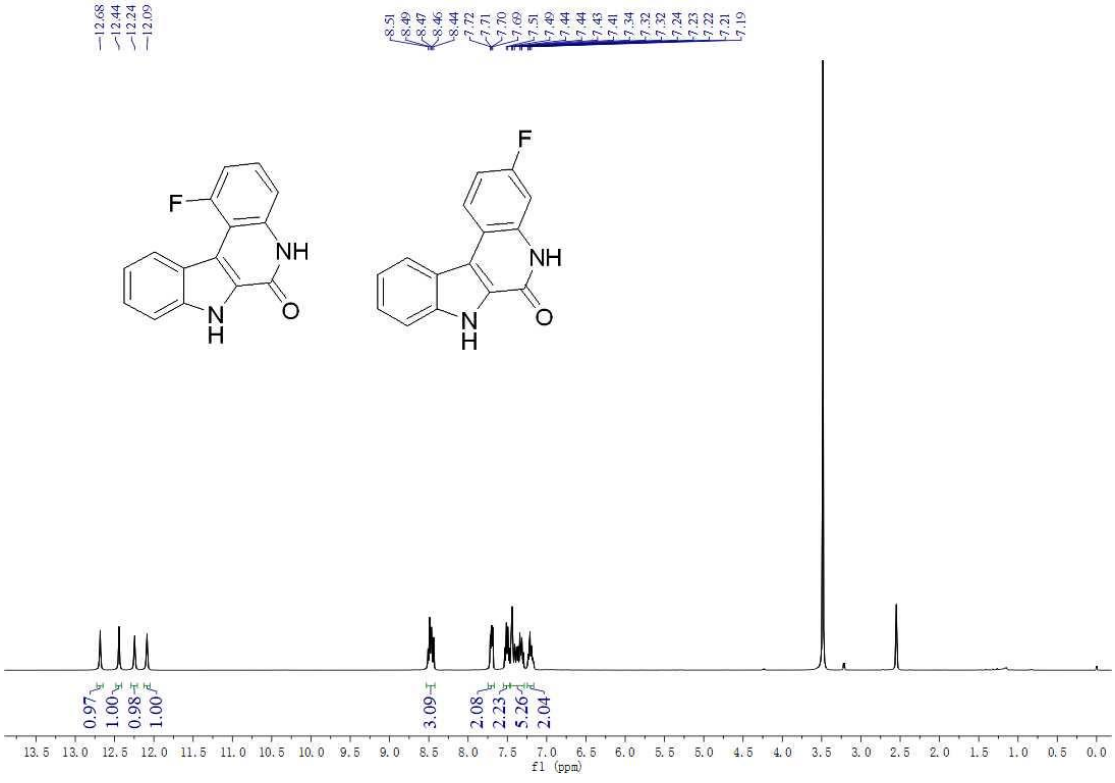
^{1}H NMR spectrum of **3s+3s′**



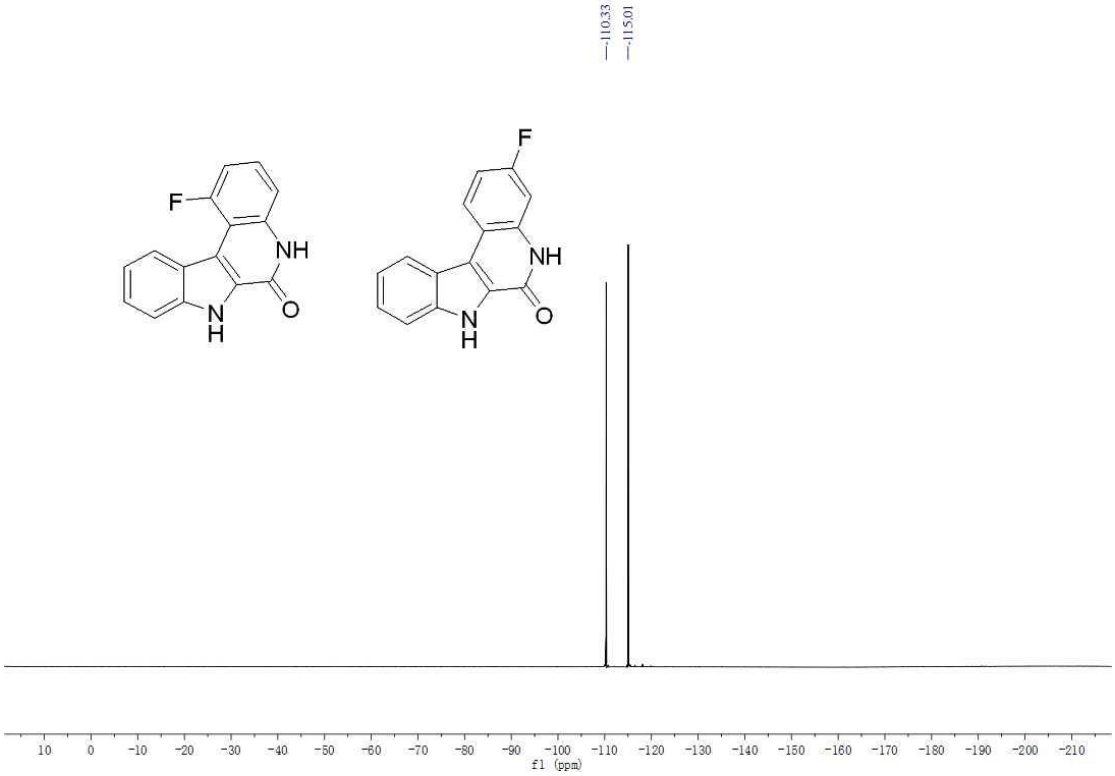
^{13}C NMR spectrum of **3s+3s′**



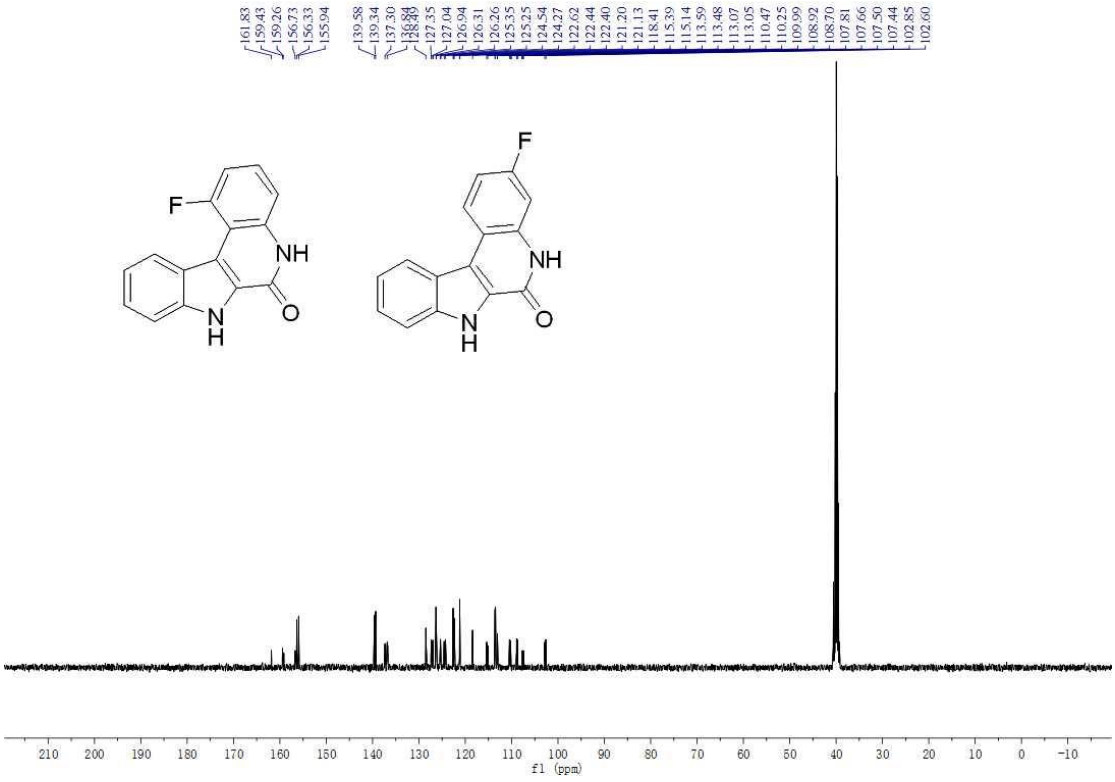
^{1}H NMR spectrum of **3t+3t′**



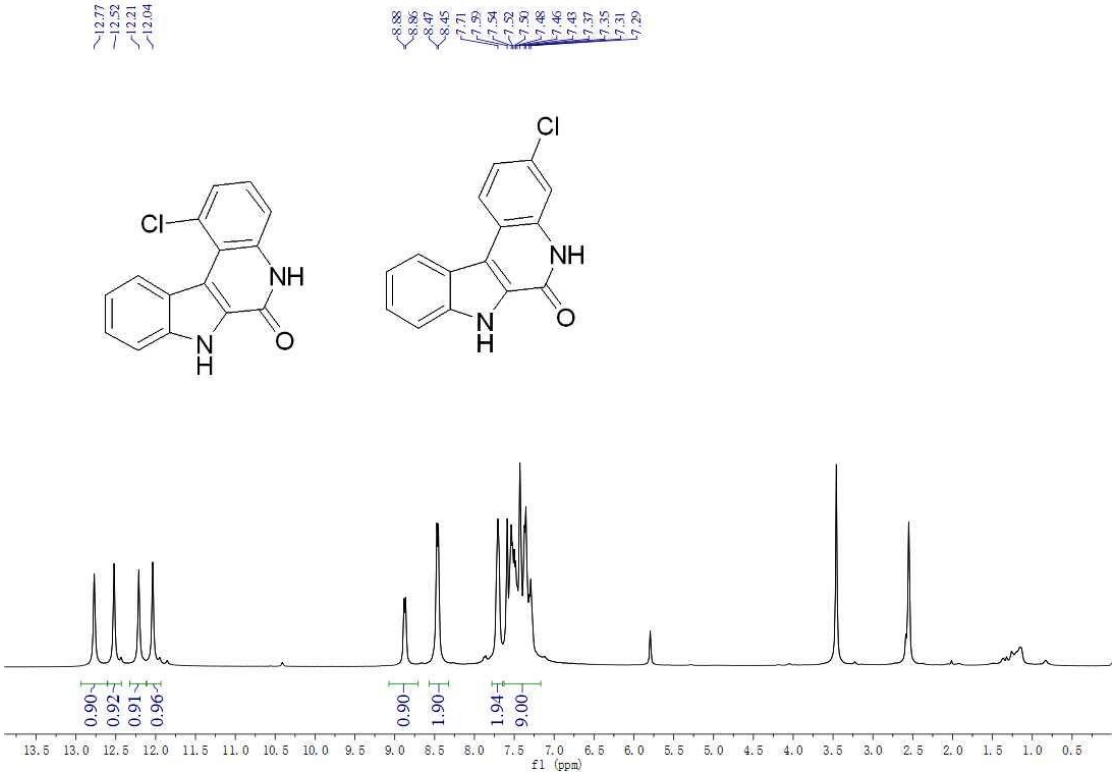
^{19}F NMR spectrum of **3t+3t′**



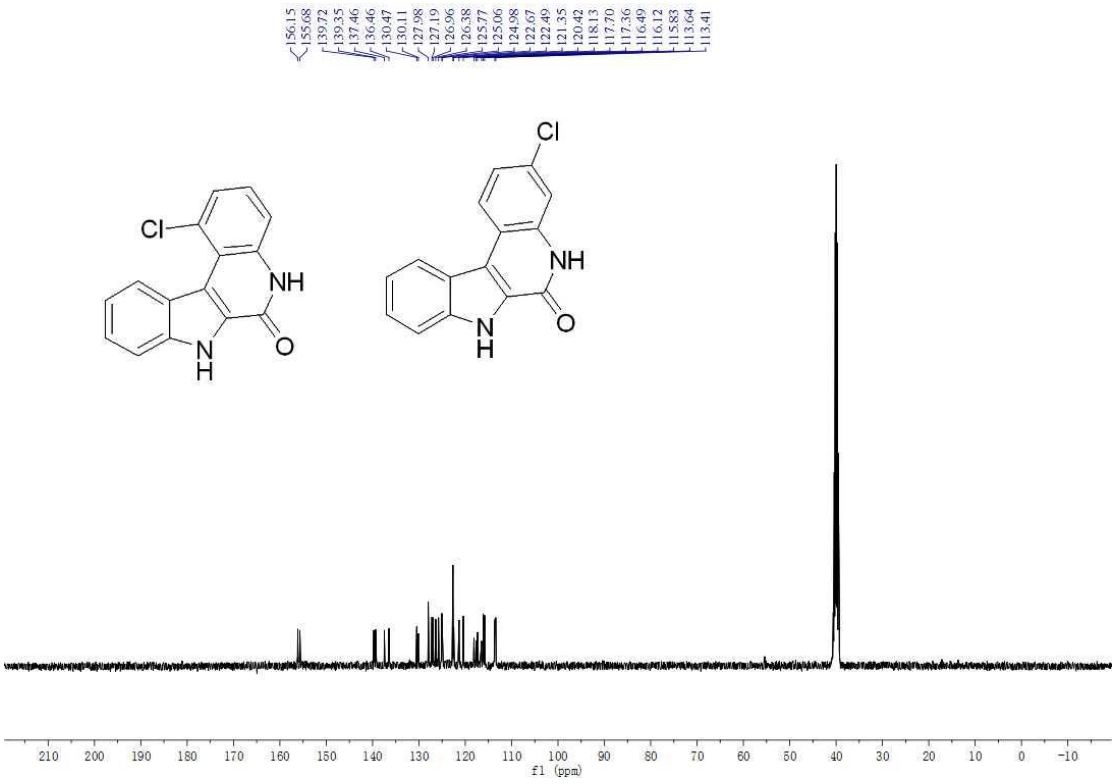
^{13}C NMR spectrum of **3t+3t′**



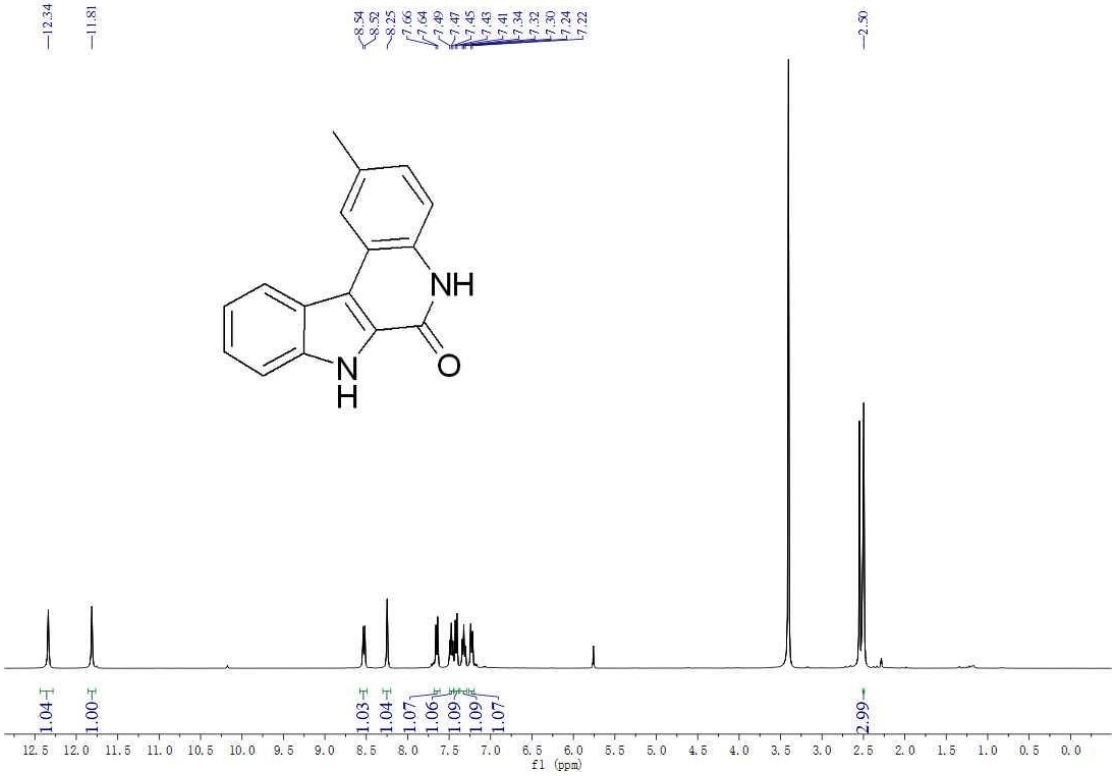
^{1}H NMR spectrum of **3u**+**3u′**



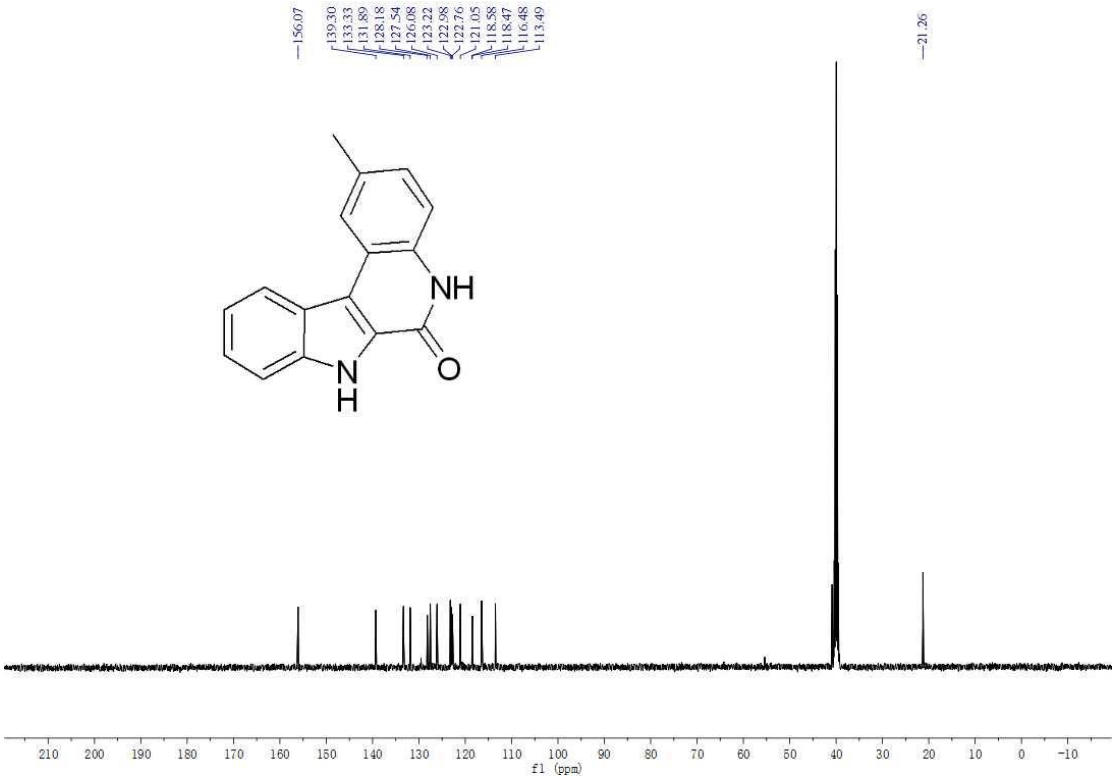
^{13}C NMR spectrum of **3u**+**3u′**



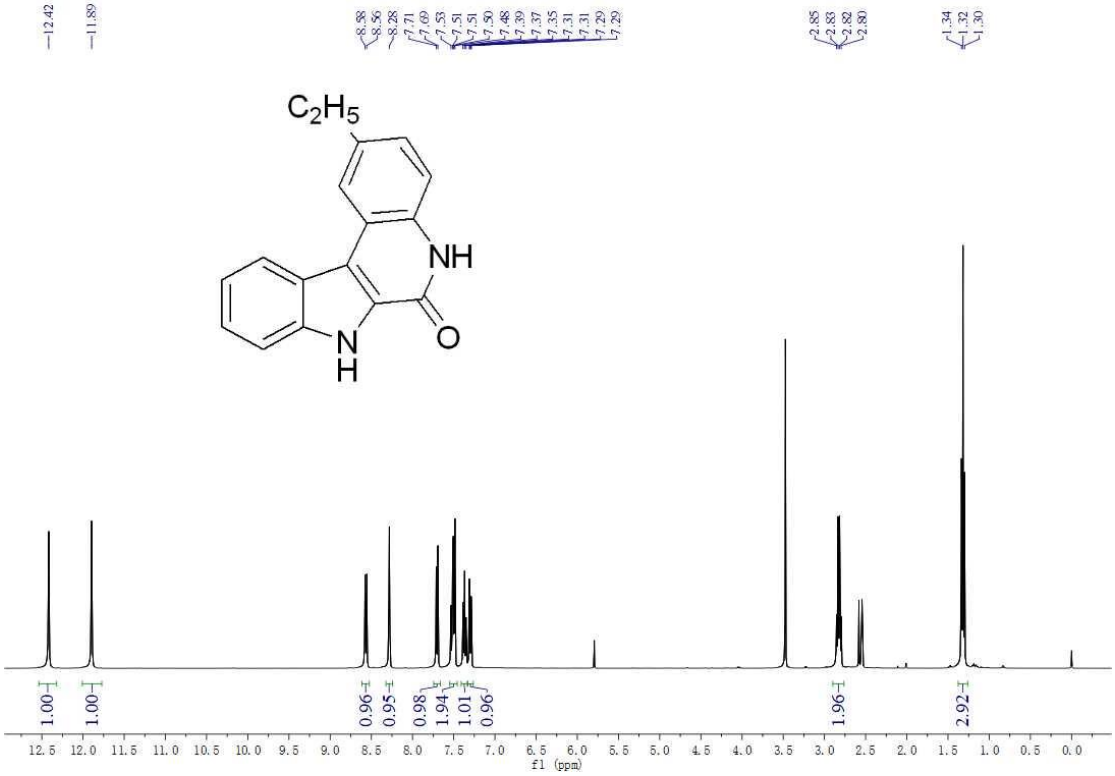
^{1}H NMR spectrum of **3v**



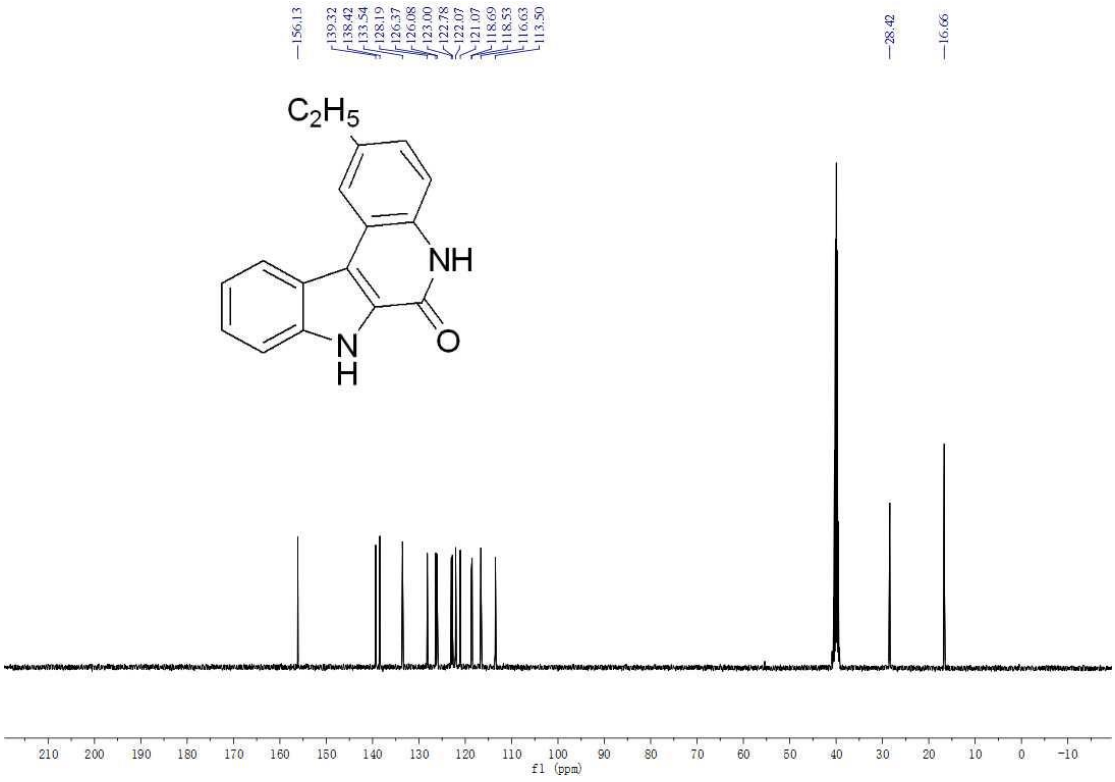
^{13}C NMR spectrum of **3v**



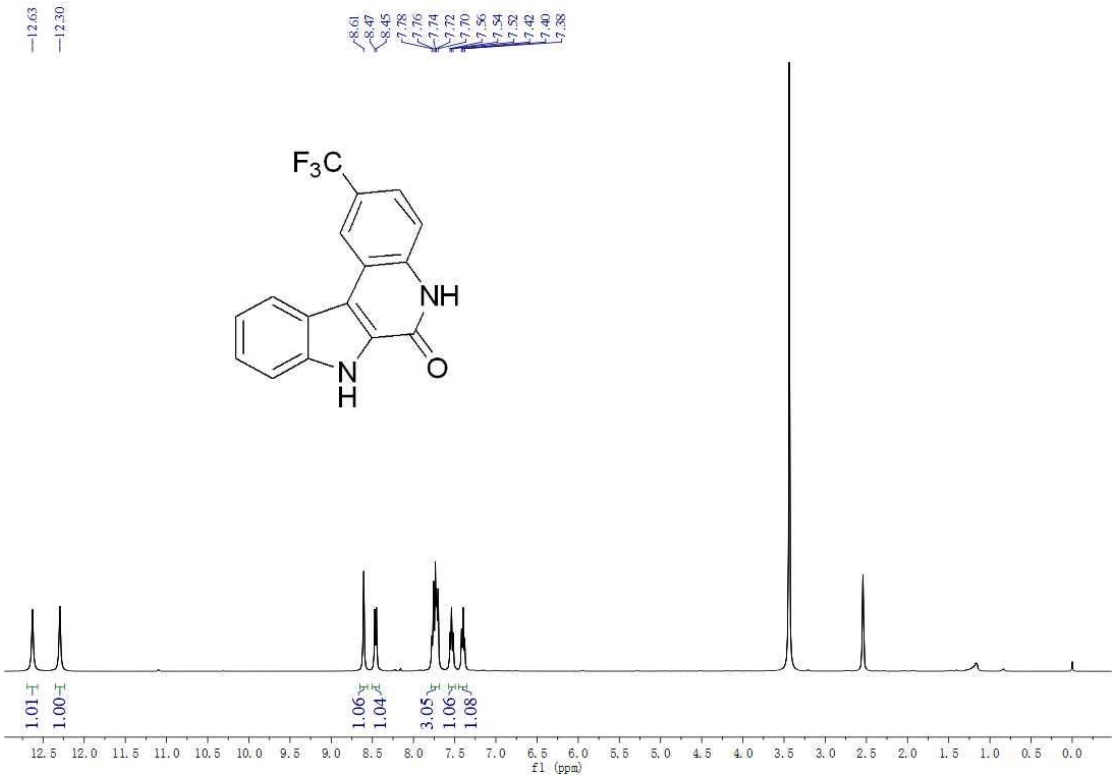
^{1}H NMR spectrum of **3w**



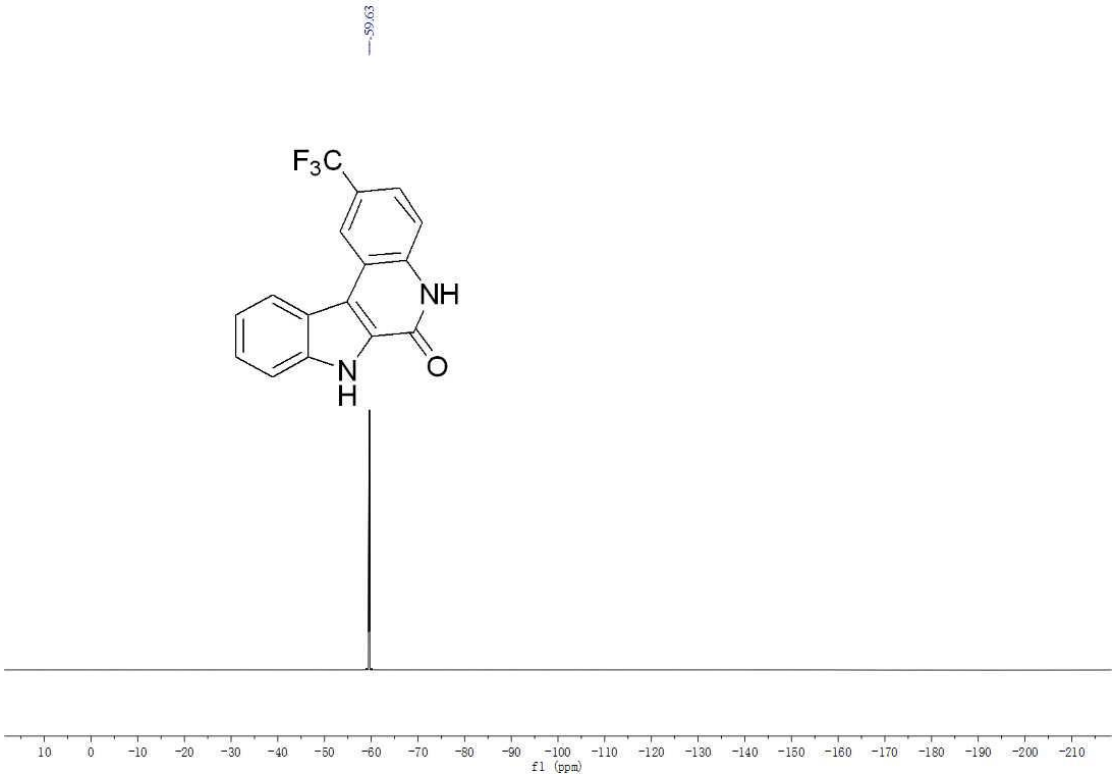
^{13}C NMR spectrum of **3w**



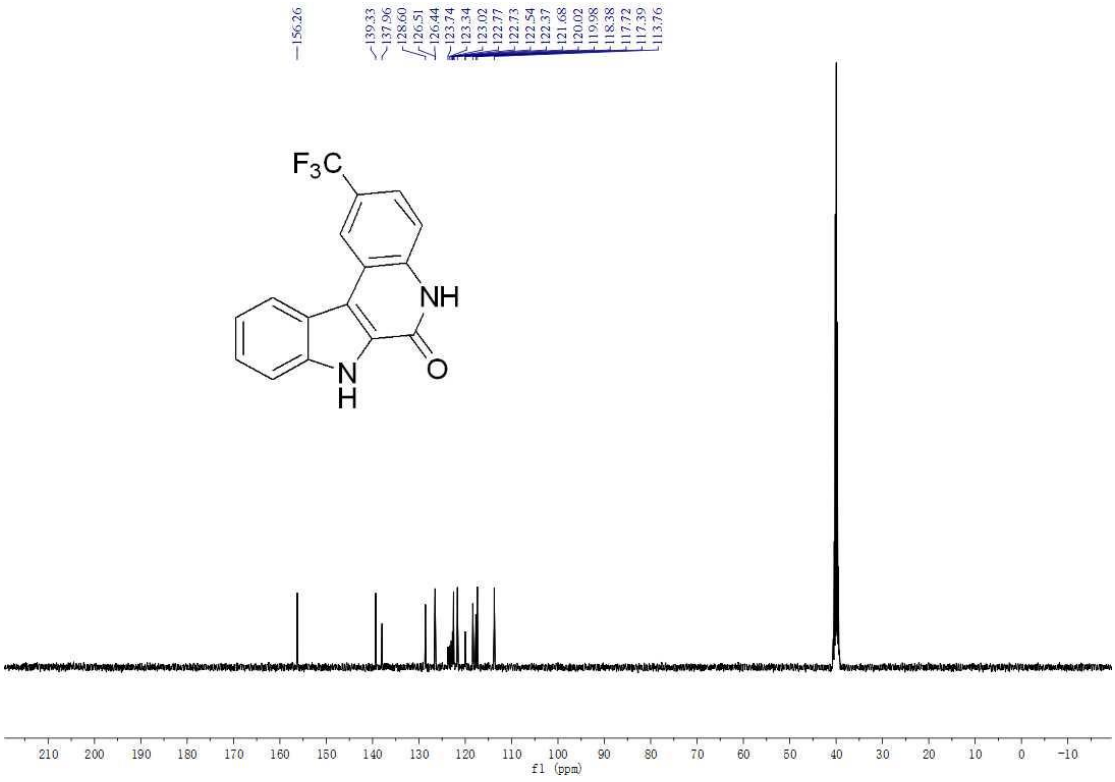
^{1}H NMR spectrum of **3x**



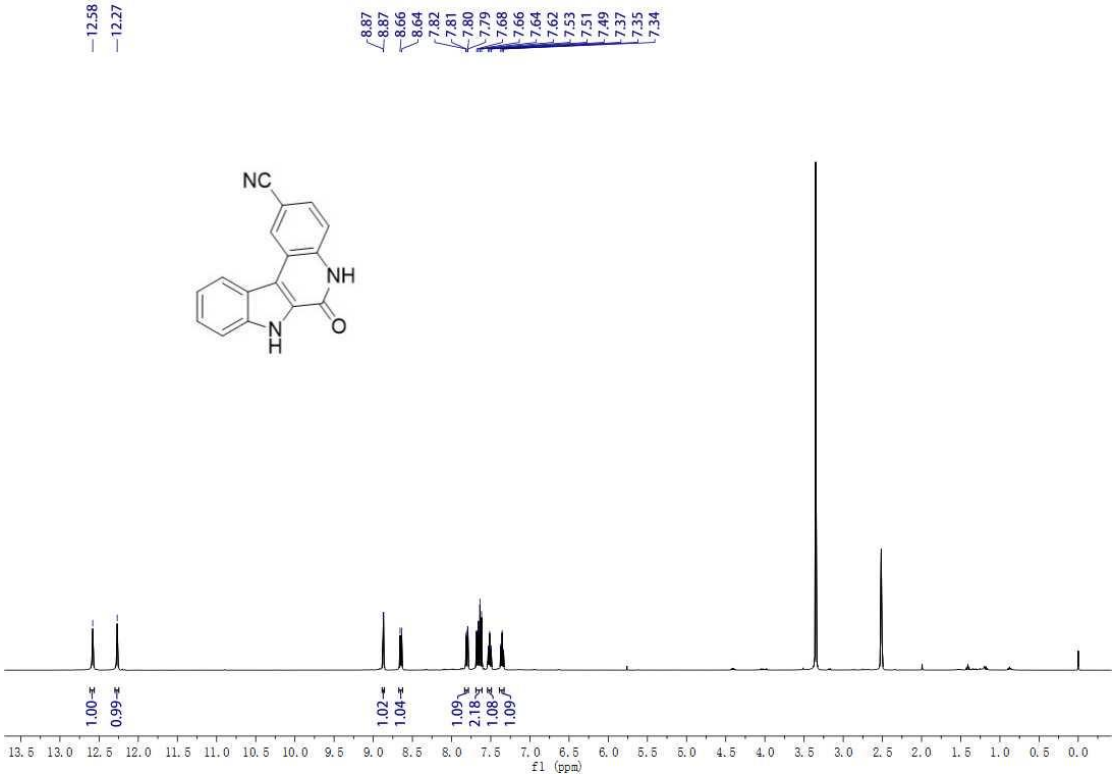
^{19}F NMR spectrum of **3x**



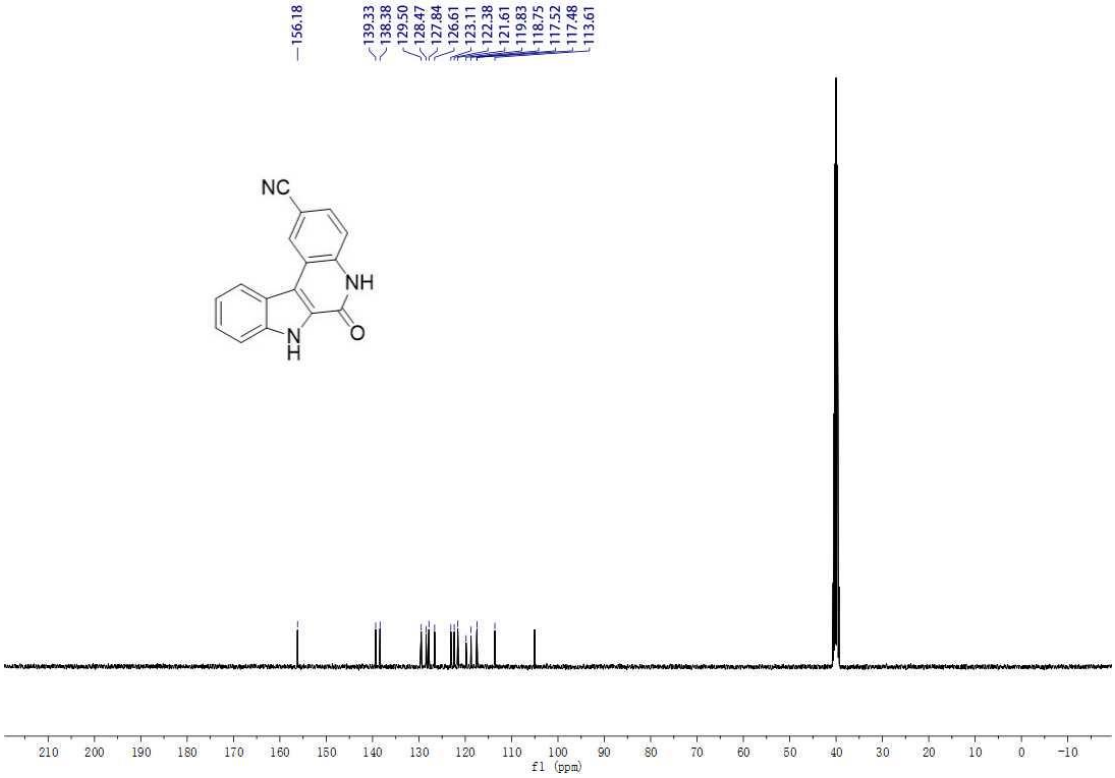
^{13}C NMR spectrum of **3x**



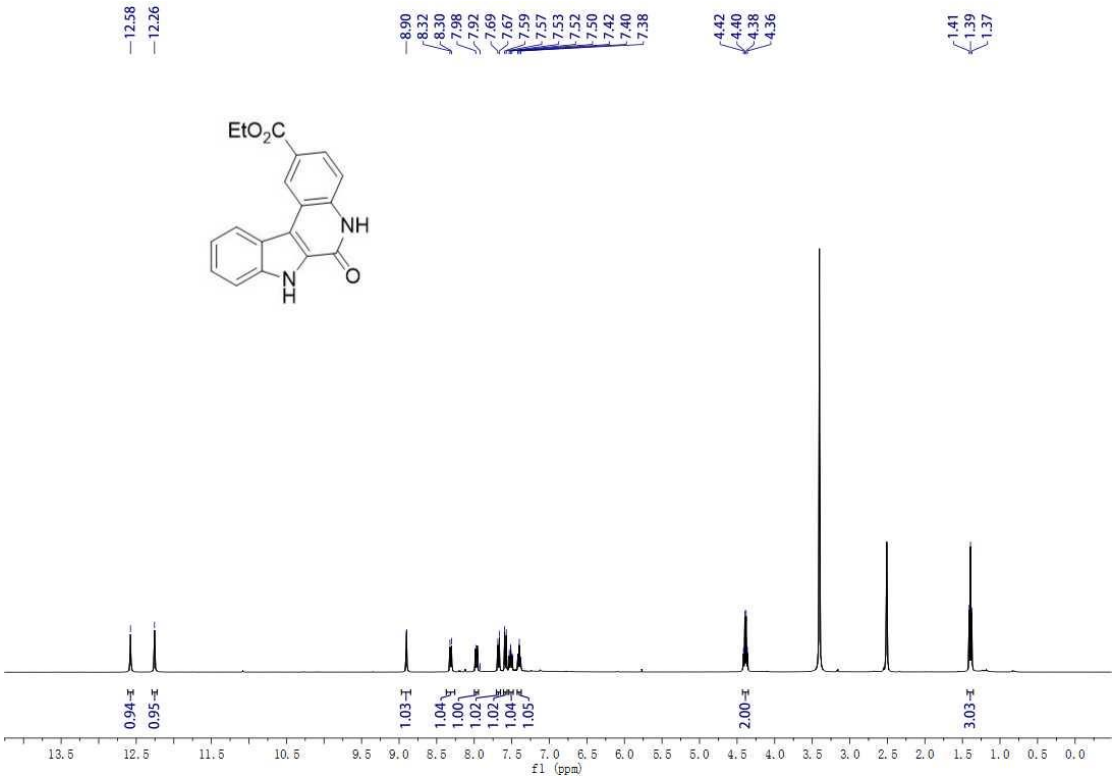
^{1}H NMR spectrum of **3y**



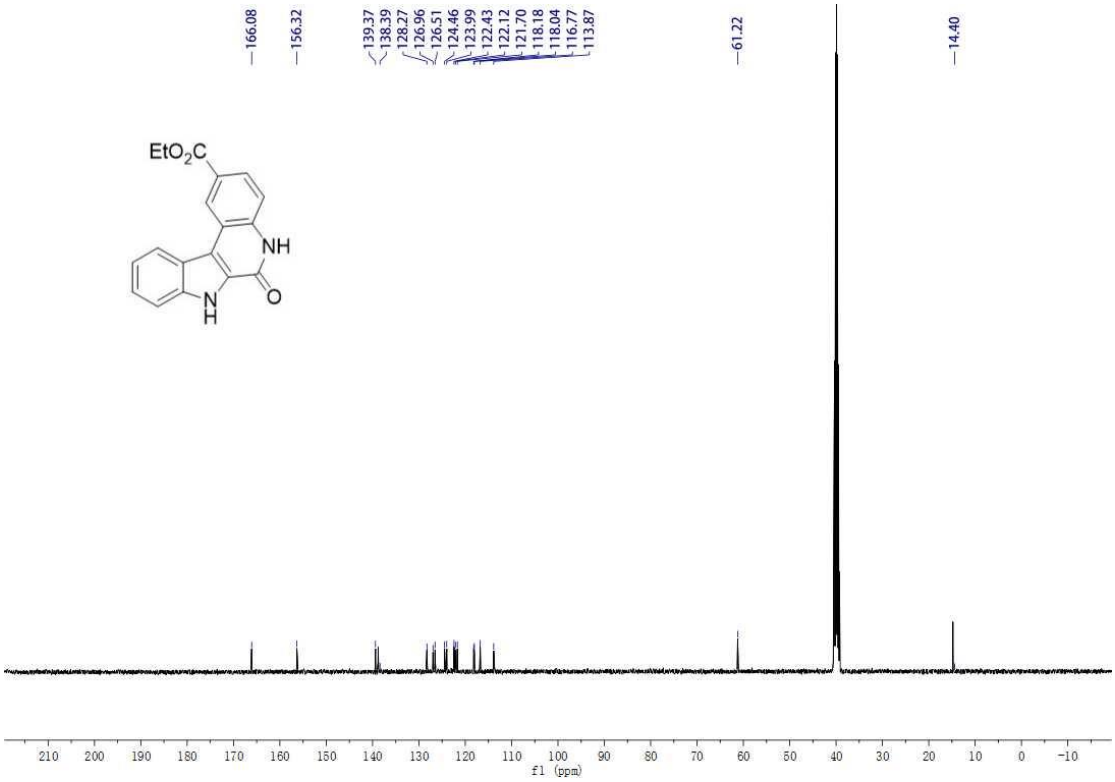
^{13}C NMR spectrum of **3y**



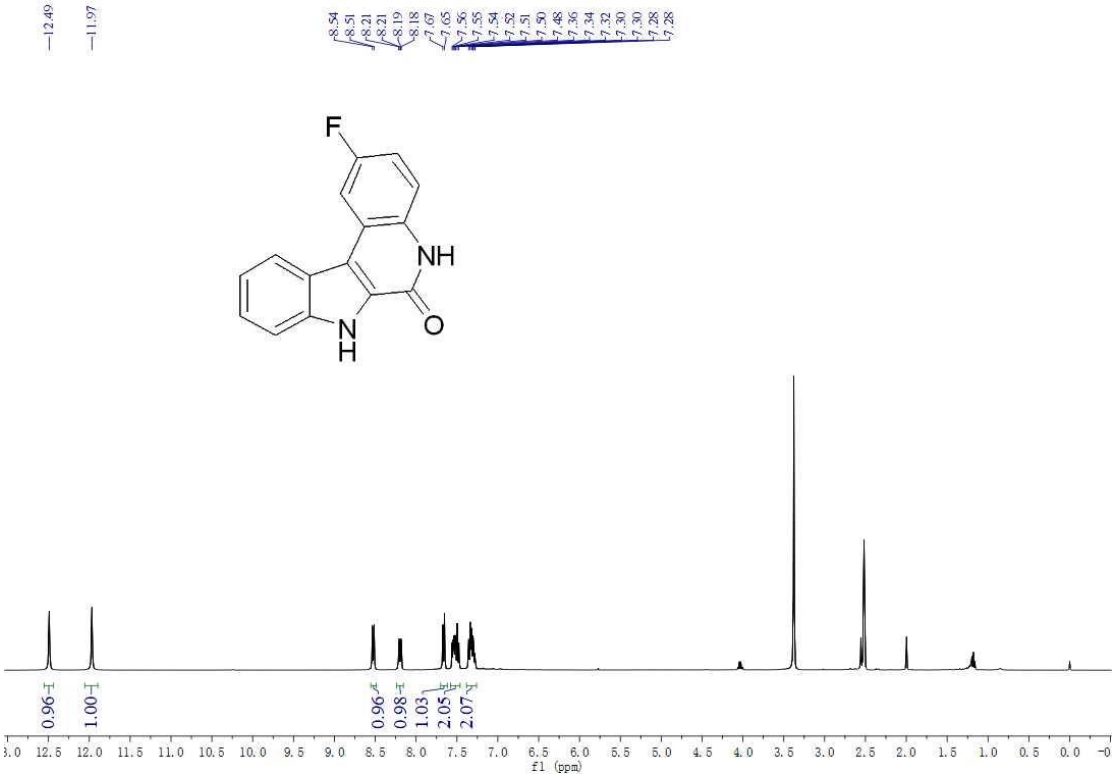
^{1}H NMR spectrum of **3z**



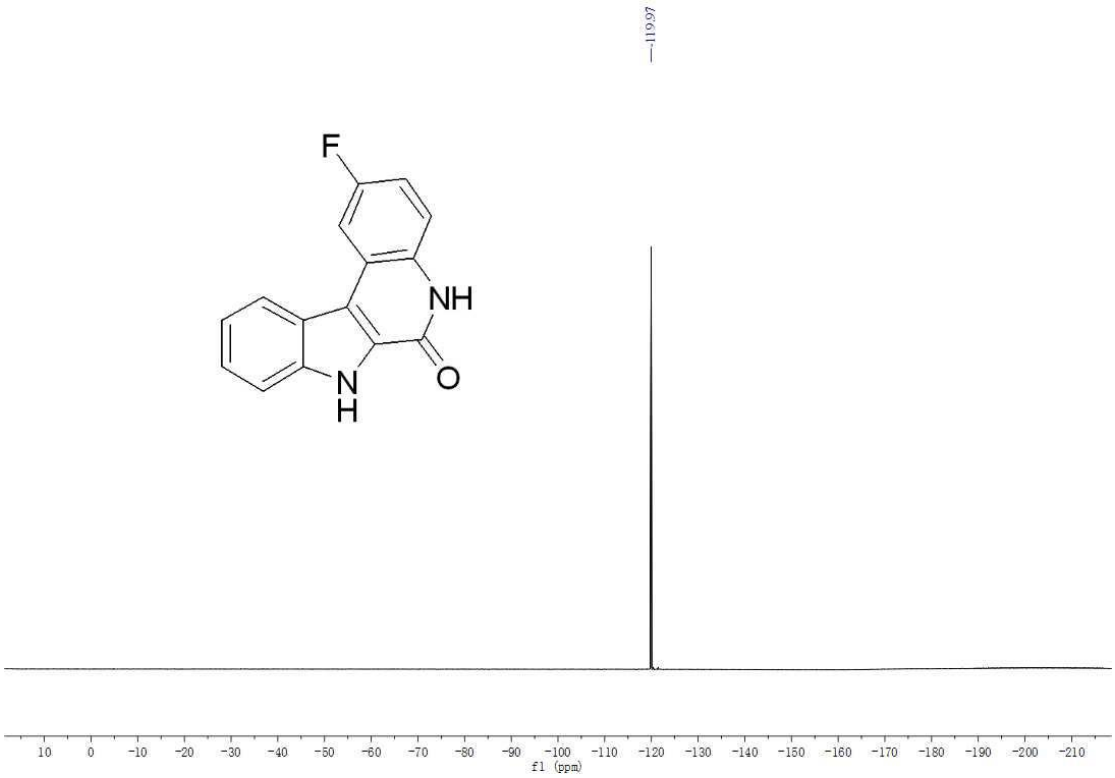
^{13}C NMR spectrum of **3z**



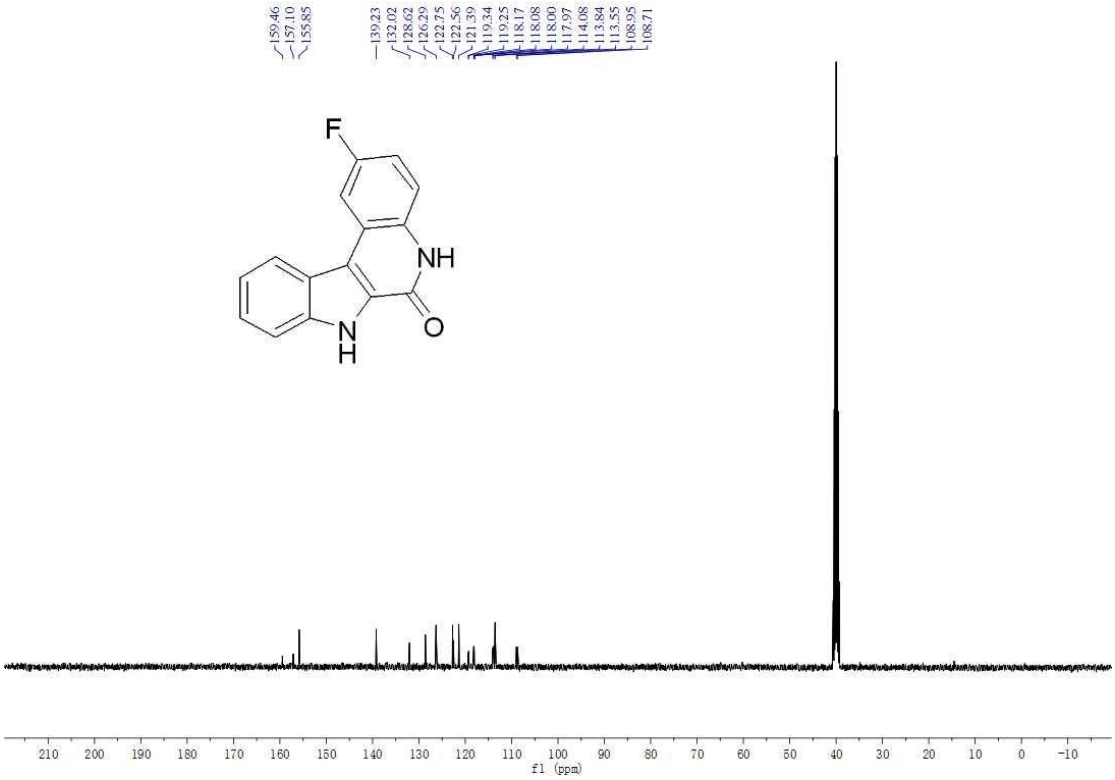
^{1}H NMR spectrum of **3aa**



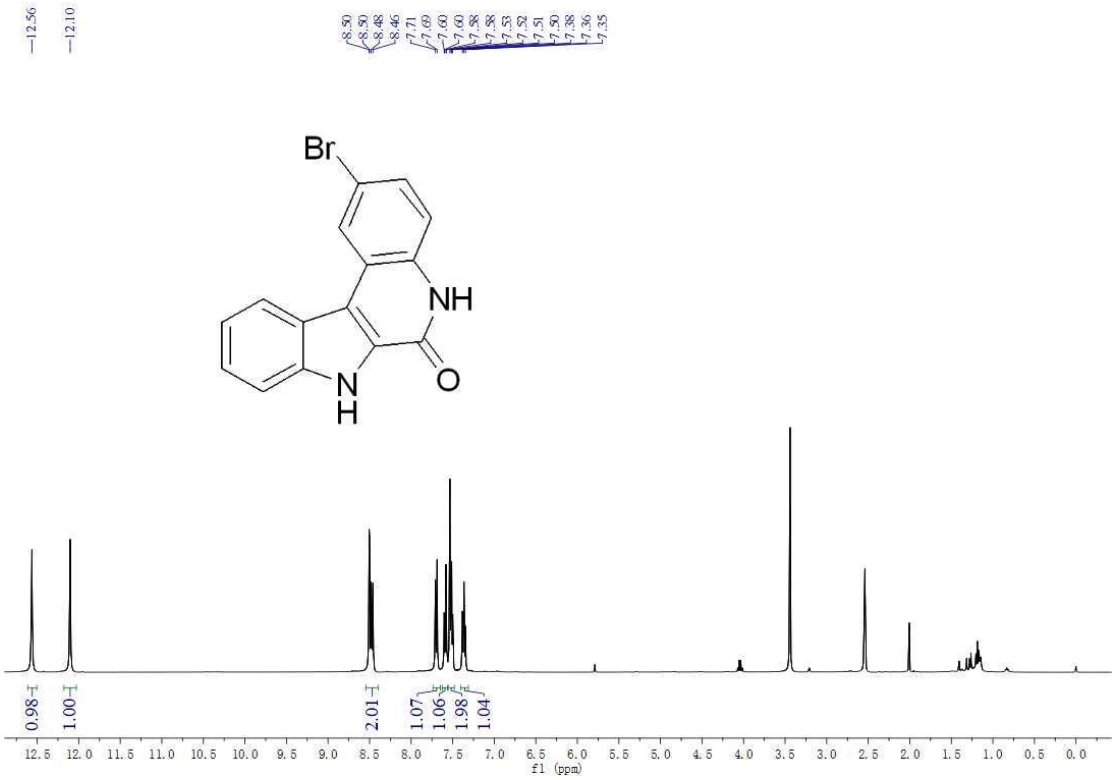
^{19}F NMR spectrum of **3aa**



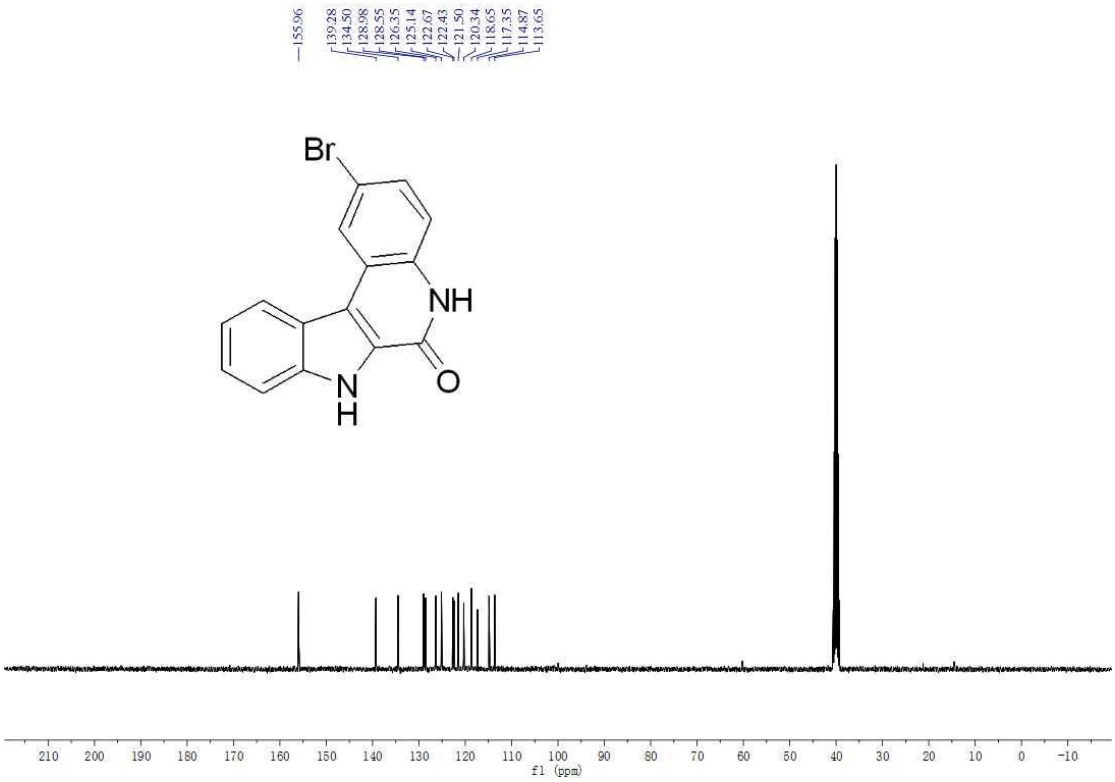
^{13}C NMR spectrum of **3aa**



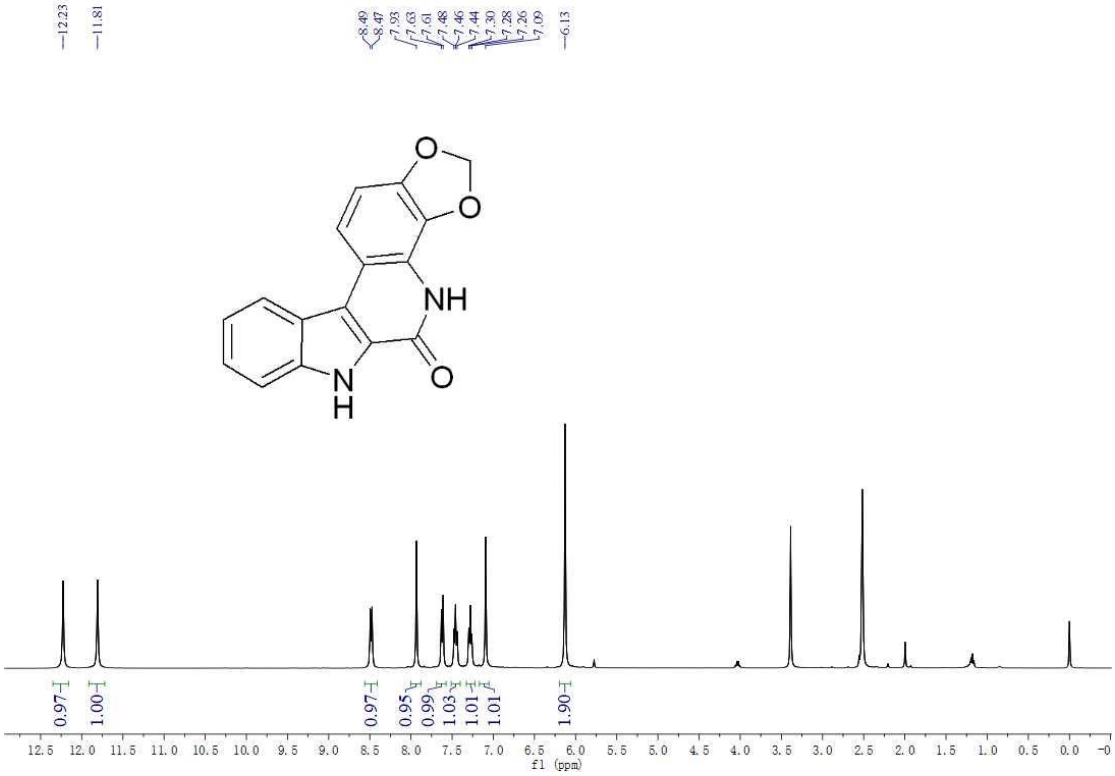
^{1}H NMR spectrum of **3ab**



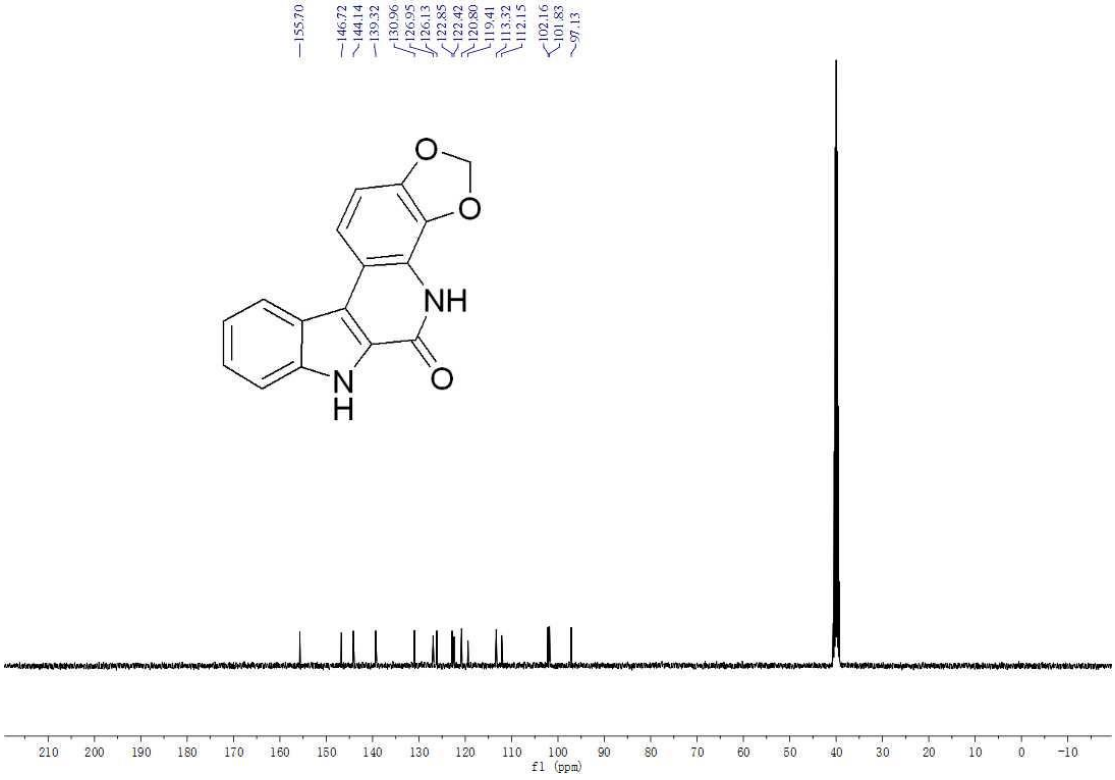
^{13}C NMR spectrum of **3ab**



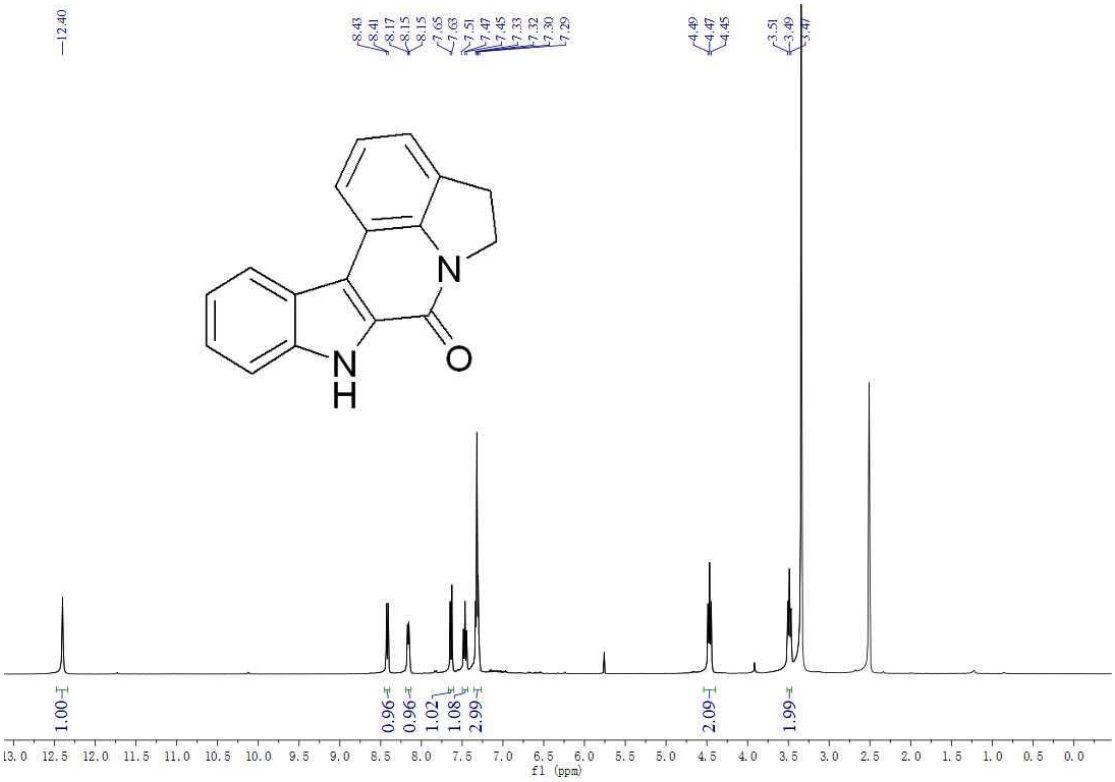
^{1}H NMR spectrum of **3ac**



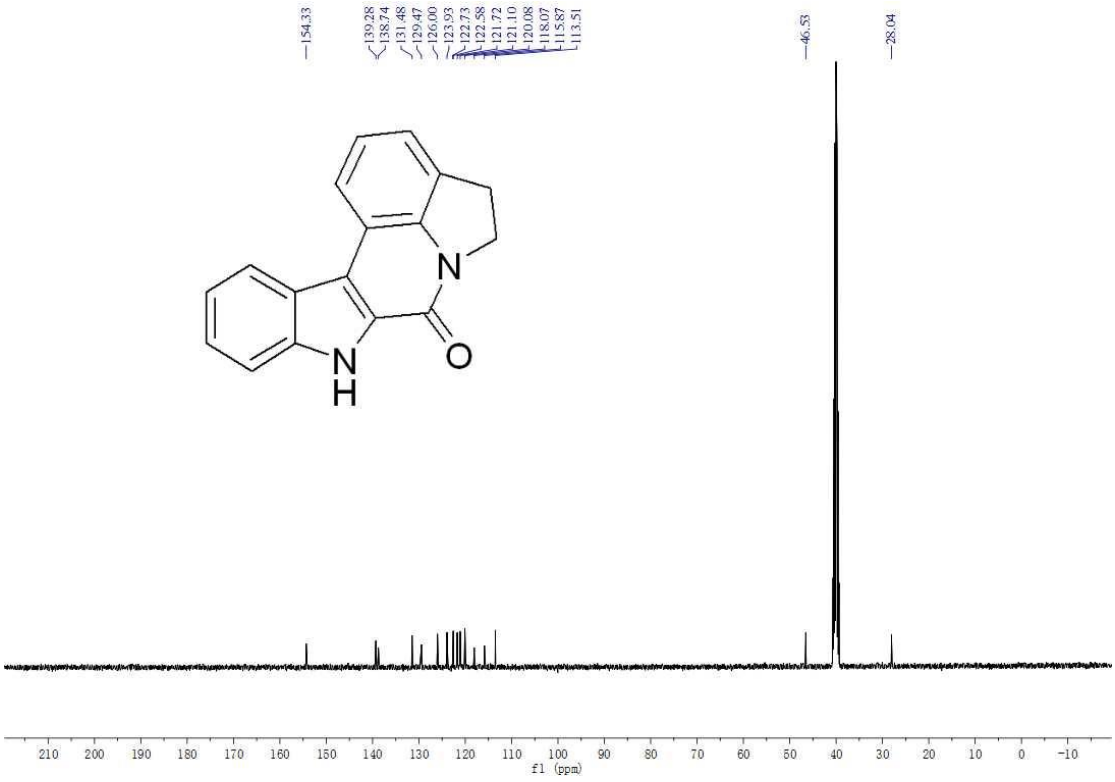
^{13}C NMR spectrum of **3ac**



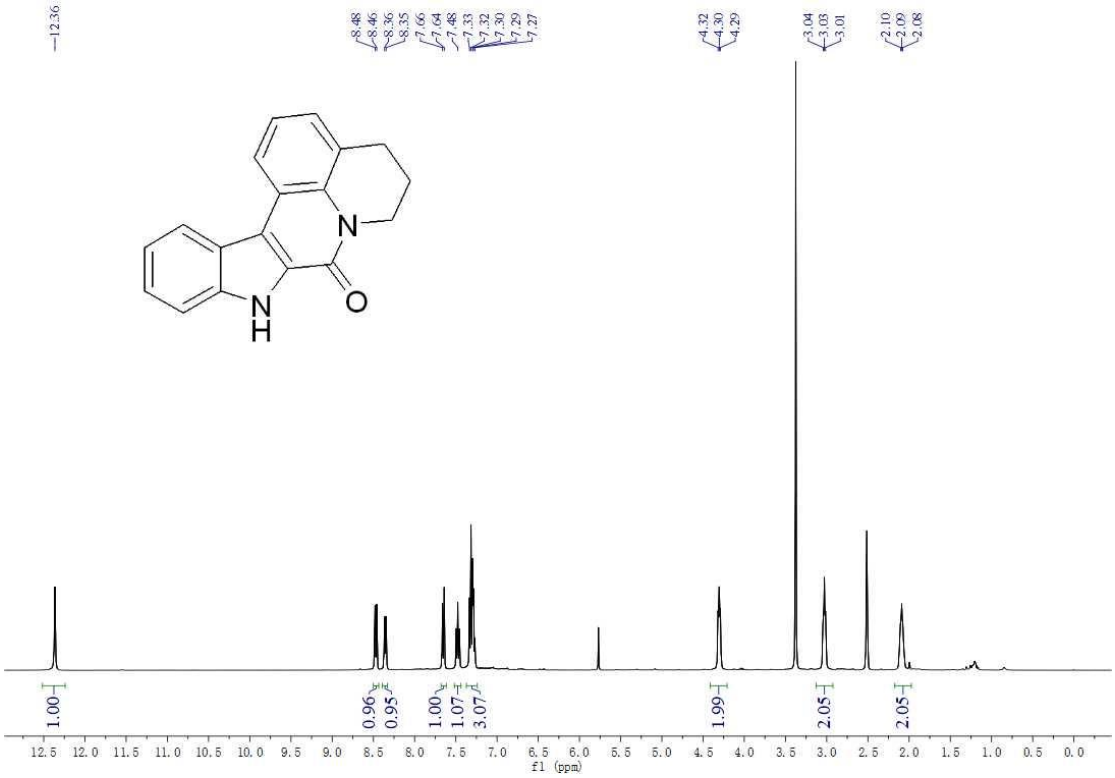
^{1}H NMR spectrum of **3ad**



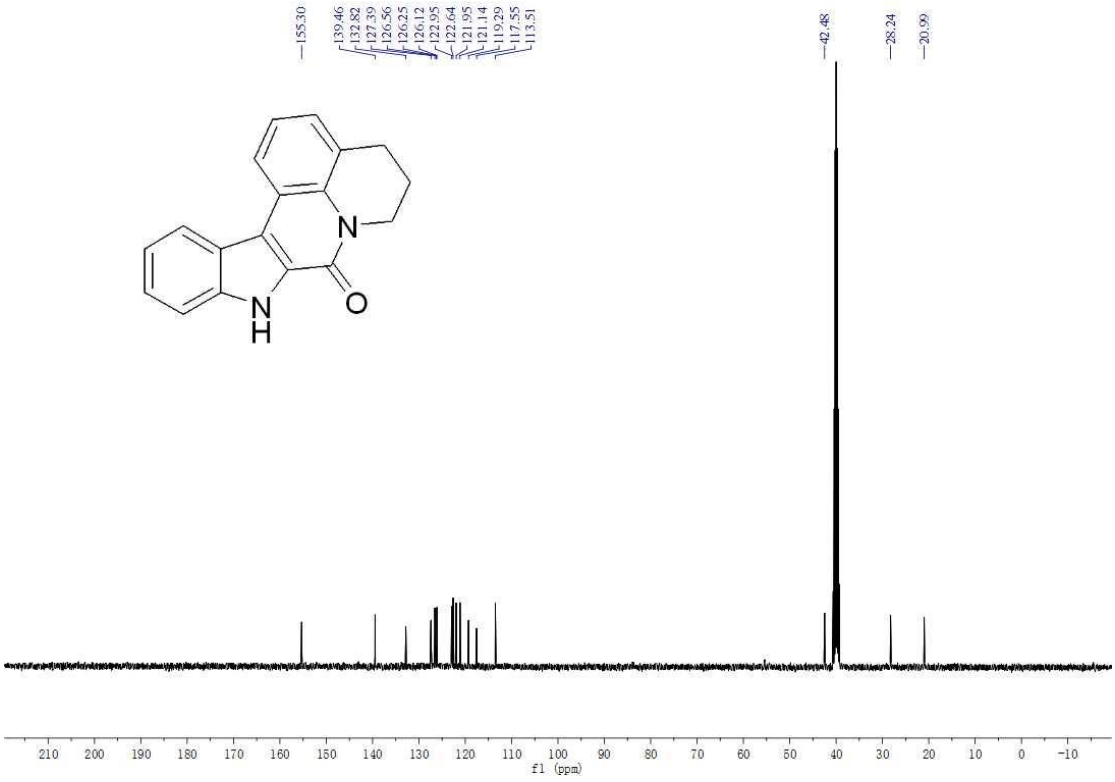
^{13}C NMR spectrum of **3ad**



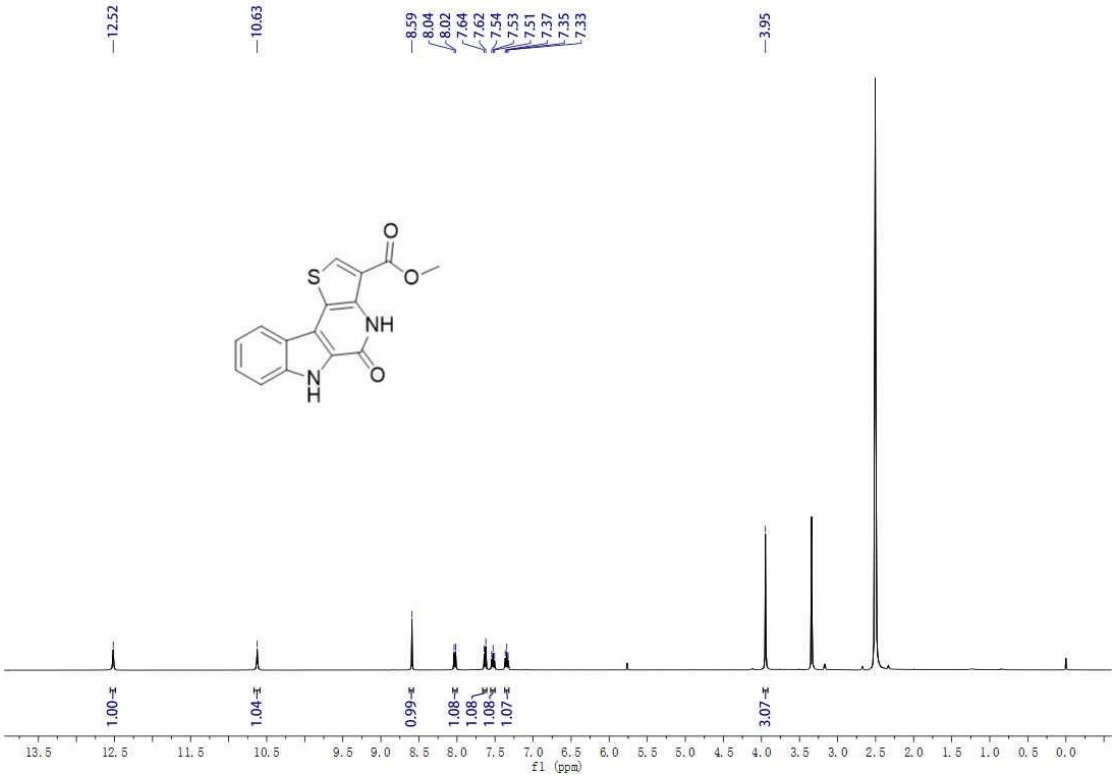
^{1}H NMR spectrum of **3ae**



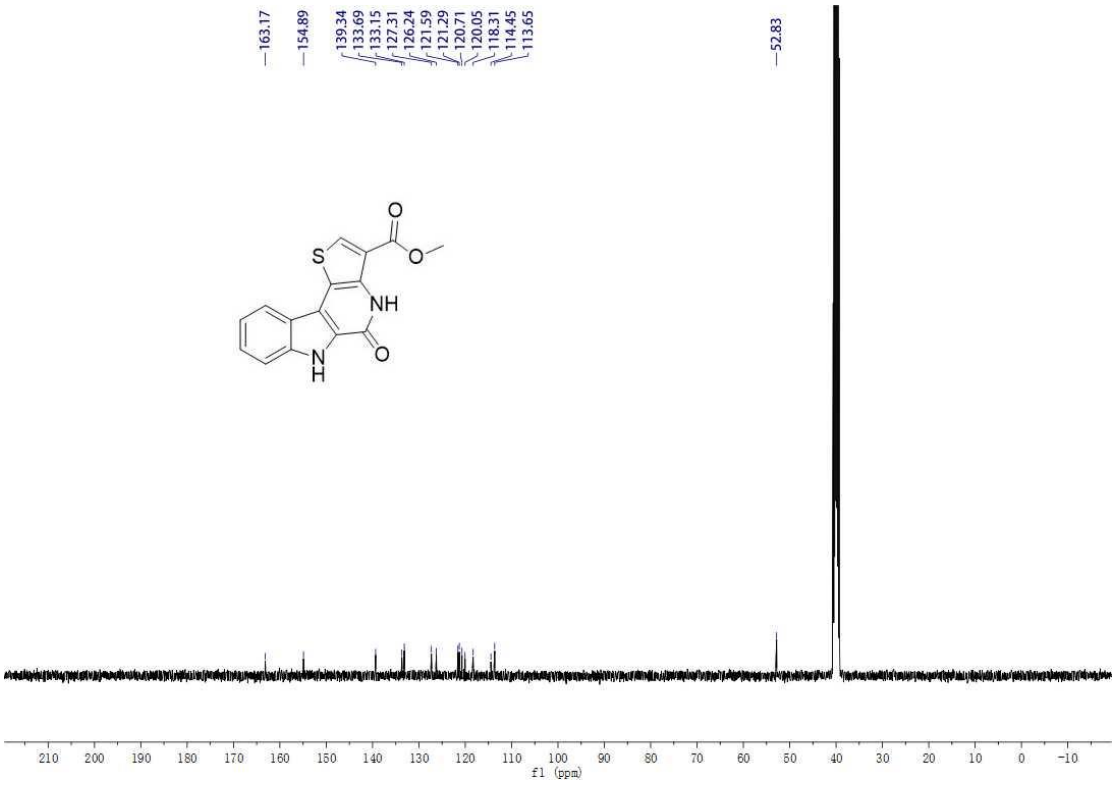
^{13}C NMR spectrum of **3ae**



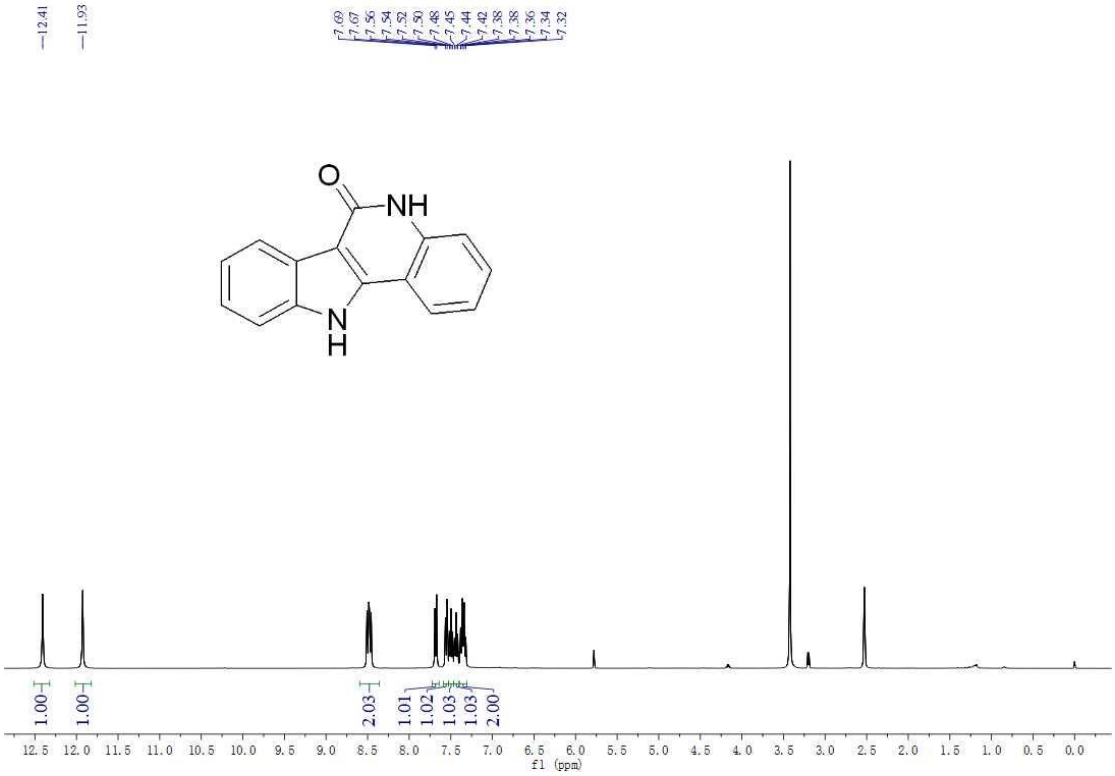
^{1}H NMR spectrum of **3af**



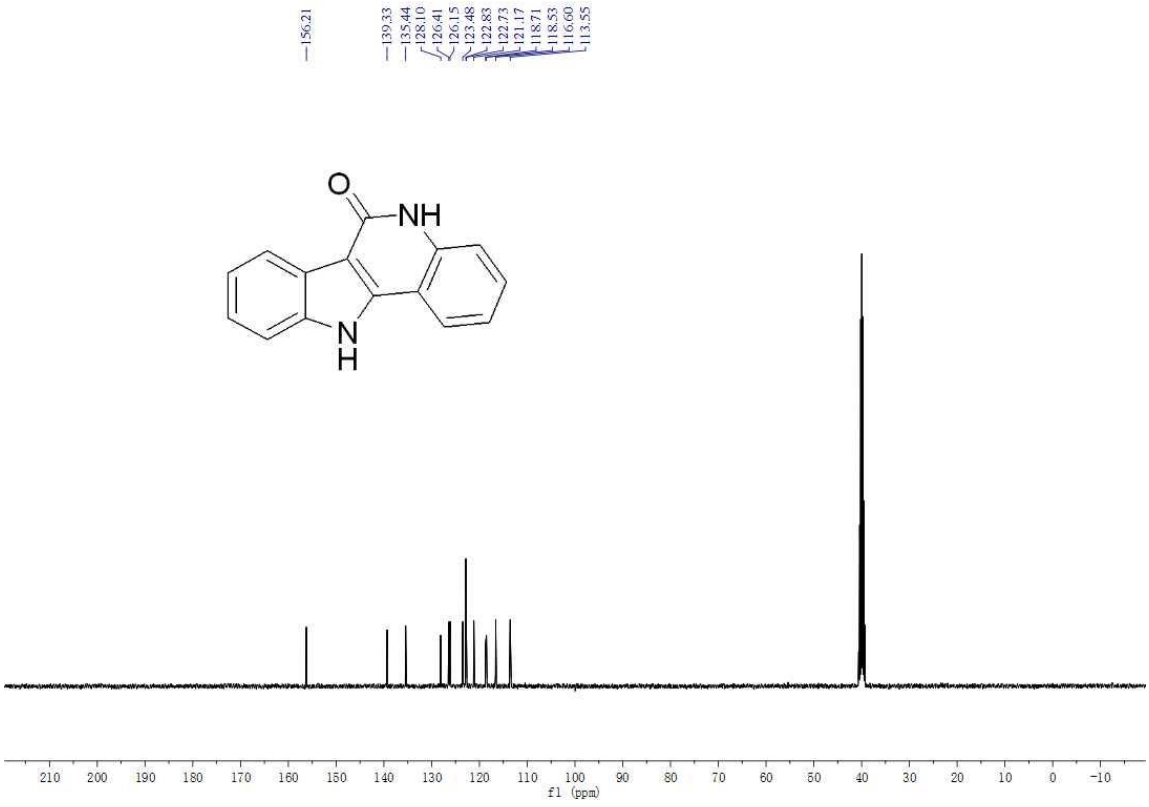
^{13}C NMR spectrum of **3af**



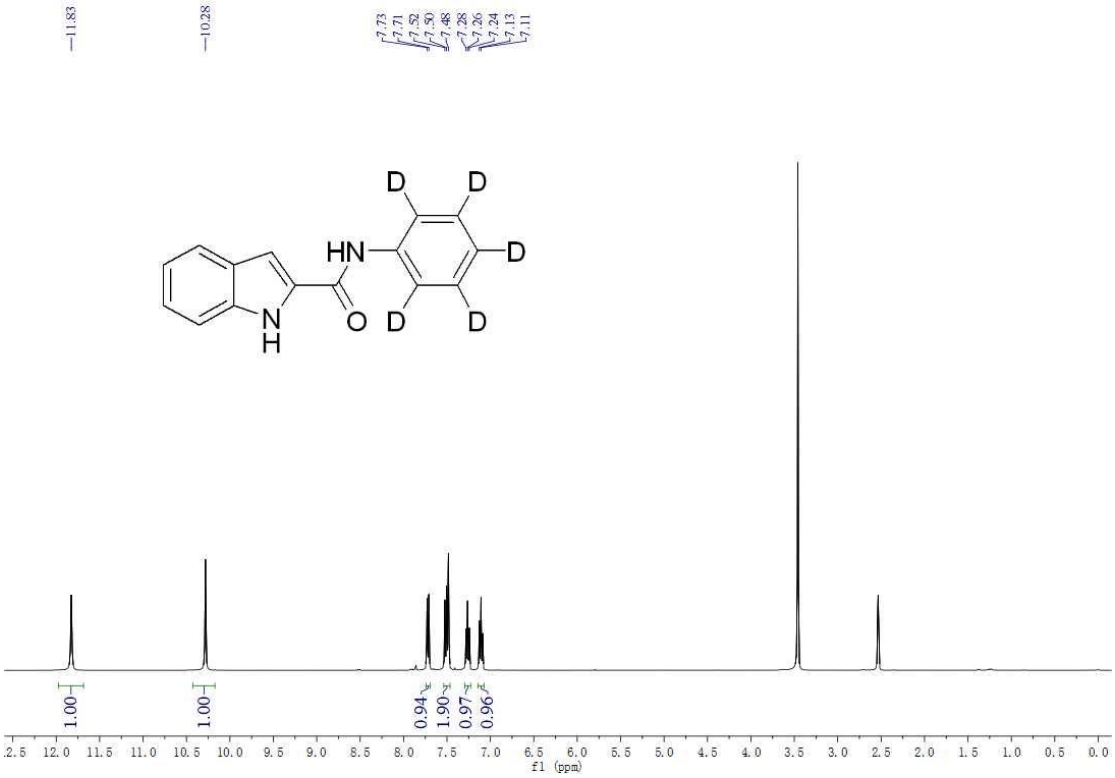
^{1}H NMR spectrum of **3ag**



^{13}C NMR spectrum of **3ag**



^{1}H NMR spectrum of D5-**1a**



^{13}C NMR spectrum of D5-**1a**