Supporting information

Transition metal- and oxidant-free [3 + 2] cycloaddition of *N*-amino(iso)quinolinium salts utilizing vinyl acetate as acetylene surrogate

Hui Wu, Wenfeng Zhao, Nan Jiang, Mao Liu, Qingmei Ge,* and Hang Cong

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1. General information

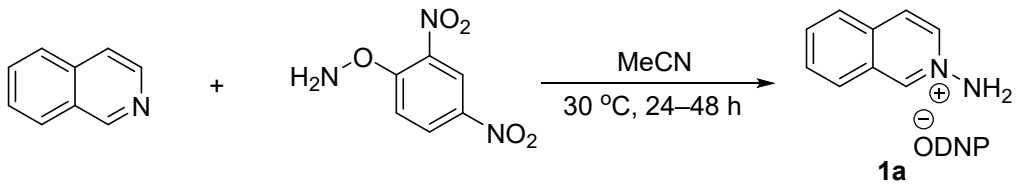
Unless otherwise noted, commercially available solvents and others reagents were used without further purification. Thin layer chromatography (TLC) was conducted on pre-coated, glass-backed silica gel plates. Visualization of the developed chromatogram was performed by UV absorbance (254 nm and 365 nm). For column chromatography, silica gel with a particle size of 200 – 300 mesh was used. Nuclear magnetic resonance (NMR) spectra were recorded on a JEOL JNM-ECZ400S spectrometer operating at 400 MHz for proton (^{1}H) and 101 MHz for carbon (^{13}C), using $CDCl_3$, DMSO-d_6, as solvents. Chemical shifts (δ) for all ^{1}H a nd ^{13}C NMR spectra were reported in parts per million (ppm). The residual solvent signals were used as references and the chemical shifts converted to the tetramethylsilane (TMS) scale ($CDCl_3$: 7.26 ppm for ^{1}H NMR, 77.2 ppm for ^{13}C NMR. DMSO-d_6: 2.50 ppm for ^{1}H NMR, 39.5 ppm for ^{13}C NMR.). All coupling constants (J) were reported in Hertz (Hz) and signal multiplicities were reported as singlet (s), doub let (d), triplet (t), quartet (q), double doublet (dd) and multiplet (m). "f1" in the NMR spectra represents the chemical shift "δ".

2. Experimental Procedures

2.1 General procedure for the preparation of N-amino(iso)quinolinium salts 1.

The substrates **1** were prepared according to the procedures in the literature.[1]

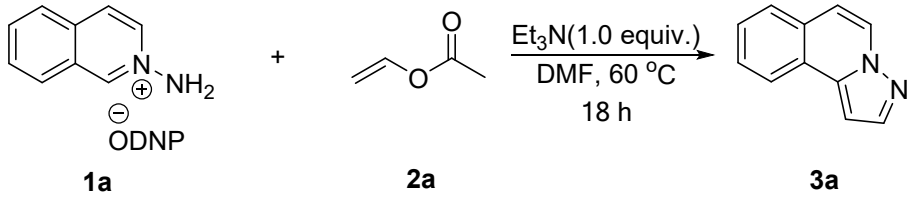
As exemplified for **1a**：



To a solution of isoquinoline (0.77 g, 6.0 mmol) in acetonitrile (25 mL) was added *O*-(2,4-dinitrophenyl)hydroxylamine (1.3 g, 6.6 mmol). The reaction flask was sealed with rubber plug, and the reaction mixture was stirred at 30 ℃ for 24 – 48 h, then upon filtering off the solvent, the solid was washed with diethyl ether, and dried in a vacuum oven. The orange solid **1a** was obtained.

2.2 General procedure for the synthesis of products 3.

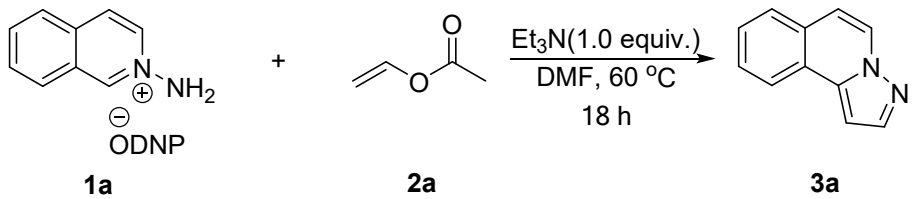
As exemplified for **3a**:



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

A 25 mL sealed tube with 3 mL DMF was charged with a stirring bar, **1a** (98.5 mg, 0.3 mmol), **2a** (38.7 mg, 1.5 equiv.) and Et_3N (30.7 mg, 1.0 equiv.) were added, and the mixture was stirred at 60 °C in an oil bath for 18 h. After cooling to room temperature, the reaction was diluted with sodium chloride aqueous solution (30 mL) and extracted with ethyl acetate (3×15 mL). Then, dried over anhydrous Na_2SO_4, and concentrated to dryness. The residue was purified through silica gel chromatography using *n*-hexane and ethyl acetate (*n*-hexane/EA = 10/1, v/v) as eluent, and the target compound **3a** was obtained.

2.3 Procedure for the scale-up synthesis of product 3a.

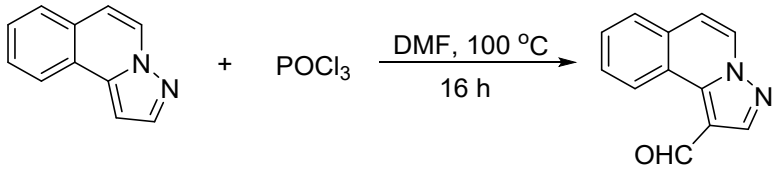


1a **2a** **3a**

A 100 mL sealed tube with 10 mL DMF was charged with a stirring bar, **1a** (328.3 mg, 1 mmol), **2a** (129.3 mg, 1.5 equiv.) and Et_3N (101.5 mg, 1.0 equiv.) were added, and

the mixture was stirred at 60 °C in an oil bath for 18 h. After cooling to room temperature, the reaction was diluted with sodium chloride aqueous solution (50 mL) and extracted with ethyl acetate (3×20 mL). Then, dried over anhydrous Na_2SO_4, and concentrated to dryness. The residue was purified through silica gel chromatography using *n*-hexane and ethyl acetate (*n*-hexane/EA = 10/1, v/v) as eluent, and the target compound **3a** (67.5 mg, 40%) was obtained.

2.4 Procedure for the synthesis of compound 4.[1a]

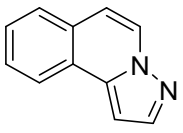


3a **4**

A 25 mL sealed tube with 2 mL DMF was charged with a stirring bar, pyrazolo[5,1-*a*]isoquinoline **3a** (50.6 mg, 0.3 mmol), $POCl_3$ (69.1 mg, 0.45 mmol) were added. The reaction was heated with a heating mantle at 100 °C for 16 h. The phases were separated and the aqueous phase was extracted with DCM (3×15 mL) and the combined organic layer was dried over anhydrous Na_2SO_4, filtered, and concentrated in vacuo. Finally, the crude product was purified by flash column chromatography on silica gel (*n*-hexane/EA = 15/1 – 5/1, v/v), affording the corresponding product **4**.

3. Characterization data

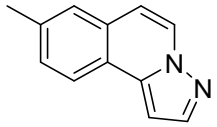
Pyrazolo[5,1-*a*]isoquinoline (3a)[1a]



3a was purified by silica gel chromatography (*n*-hexane/EA = 10/1, v/v). Yellow solid (30.5 mg, 60%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.26 (d, *J* = 7.4 Hz, 1H), 8.10 (d, *J* =

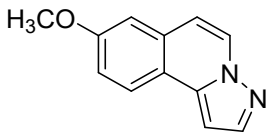
7.2 Hz, 1H), 7.98 (d, *J* = 2.2 Hz, 1H), 7.72 (dd, *J* = 1.9, 7.1 Hz, 1H), 7.56 (pd, *J* = 1.5, 7.1 Hz, 2H), 7.01 – 6.98 (m, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 141.3, 138.5, 128.8, 128.0, 127.7, 127.3, 126.5, 124.7, 123.8, 112.1, 97.6.

8-Methylpyrazolo[5,1-*a*]isoquinoline (3b)[1a]



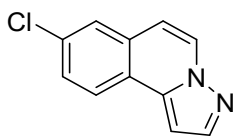
3b was purified by silica gel chromatography (*n*-hexane/EA = 10/1, v/v). Yellow solid (27.7 mg, 51%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.22 (d, *J* = 7.4 Hz, 1H), 7.99 – 7.94 (m, 2H), 7.49 (s, 1H), 7.38 (d, *J* = 8.1 Hz, 1H), 6.92 (d, *J* = 11.0 Hz, 2H), 2.50 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 141.2, 138.6, 138.0, 129.3, 129.0, 127.0, 126.5, 123.7, 122.4, 112.0, 97.1, 21.7.

8-Methoxypyrazolo[5,1-*a*]isoquinoline (3c)[2]



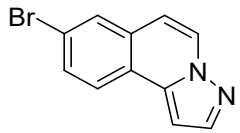
3c was purified by silica gel chromatography (*n*-hexane/EA = 10/1, v/v). Yellow solid (27.3 mg, 46%).**^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.22 (d, *J* = 7.4 Hz, 1H), 7.97 (d, *J* = 8.8 Hz, 1H), 7.93 (d, *J* = 2.2 Hz, 1H), 7.16 (dd, *J* = 2.6, 8.8 Hz, 1H), 7.08 (d, *J* = 2.6 Hz, 1H), 6.89 (d, *J* = 7.5 Hz, 1H), 6.85 (d, *J* = 2.1 Hz, 1H), 3.91 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 159.4, 141.4, 138.6, 130.5, 126.9, 125.4, 118.8, 117.4, 111.8, 108.3, 96.4, 55.5.

8-Chloropyrazolo[5,1-*a*]isoquinoline (3d)[1a]



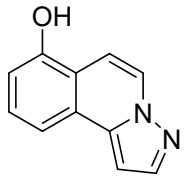
3d was purified by silica gel chromatography (*n*-hexane/EA = 10/1, v/v). Yellow solid (15.9 mg, 26%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.25 (d, *J* = 7.4 Hz, 1H), 8.00 – 7.95 (m, 2H), 7.66 (s, 1H), 7.49 (d, *J* = 8.3 Hz, 1H), 6.94 (d, *J* = 2.2 Hz, 1H), 6.87 (d, *J* = 7.3 Hz, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 141.6, 137.9, 133.8, 130.0, 128.1, 127.5, 126.5, 125.2, 123.0, 111.1, 97.9.

8-Bromopyrazolo[5,1-*a*]isoquinoline (3e)[1a]



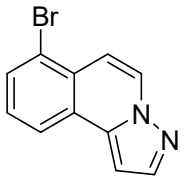
3e was purified by silica gel chromatography (*n*-hexane/EA = 10/1, v/v). Yellow solid (19.5 mg, 26%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.26 (d, *J* = 7.3 Hz, 1H), 7.98 (d, *J* = 2.1 Hz, 1H), 7.93 (d, *J* = 8.6 Hz, 1H), 7.85 (d, *J* = 2.1 Hz, 1H), 7.64 (dd, *J* = 2.0, 8.7 Hz, 1H), 6.96 (s, 1H), 6.88 (d, *J* = 7.4 Hz, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 141.6, 137.9, 130.9, 130.3, 129.6, 127.5, 125.3, 123.3, 121.9, 111.0, 97.9.

Pyrazolo[5,1-*a*]isoquinolin-7-ol (3f)[1a]



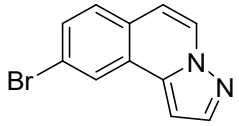
3f was purified by silica gel chromatography (*n*-hexane/EA = 3/1, v/v). Yellow solid (27.6 mg, 50%). **^{1}H NMR** (400 MHz, DMSO-d_6) δ 10.39 (s, 1H), 8.37 (d, *J* = 7.5 Hz, 1H), 7.99 (d, *J* = 2.0 Hz, 1H), 7.68 (d, *J* = 7.9 Hz, 1H), 7.43 (t, *J* = 7.9 Hz, 1H), 7.35 (d, *J* = 7.6 Hz, 1H), 7.17 (d, *J* = 2.2 Hz, 1H), 7.02 (d, *J* = 7.8 Hz, 1H). **^{13}C NMR** (101 MHz, DMSO-d_6) δ 153.9, 141.5, 138.1, 129.3, 125.8, 125.7, 118.4, 114.8, 112.7, 106.9, 98.5.

7-Bromopyrazolo[5,1-*a*]isoquinoline (3g)[1a]



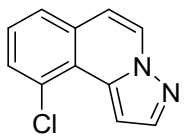
3g was purified by silica gel chromatography (*n*-hexane/EA = 20/1 – 10/1, v/v). Yellow solid (30.6 mg, 41%).**^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.33 (d, *J* = 7.5 Hz, 1H), 8.07 – 8.00 (m, 2H), 7.79 (d, *J* = 7.9 Hz, 1H), 7.41 (t, *J* = 7.8 Hz, 2H), 7.01 (s, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 141.9, 137.8, 131.9, 128.4, 128.2, 127.7, 126.1, 123.3, 122.3, 110.9, 98.3.

9-Bromopyrazolo[5,1-*a*]isoquinoline (3h)[1a]



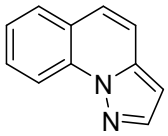
3h was purified by silica gel chromatography (*n*-hexane/EA = 10/1, v/v). Yellow solid (18.6 mg, 25%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.26 (d, *J* = 7.3 Hz, 1H), 8.21 (s, 1H), 7.98 (d, *J* = 2.1 Hz, 1H), 7.62 (d, *J* = 8.6 Hz, 1H), 7.56 (d, *J* = 8.6 Hz, 1H), 6.96 (d, *J* = 2.1 Hz, 1H), 6.93 (d, *J* = 7.5 Hz, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 141.5, 137.2, 131.1, 128.8, 127.4, 126.9, 126.4, 126.1, 121.5, 111.5, 98.1.

10-Chloropyrazolo[5,1-*a*]isoquinoline (3i)[1a]



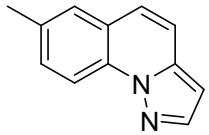
3i was purified by silica gel chromatography (*n*-hexane/EA = 10/1, v/v). White solid (19.8 mg, 33%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.28 (d, *J* = 7.3 Hz, 1H), 8.02 (s, 1H), 7.67 (s, 1H), 7.60 (t, *J* = 7.4 Hz, 2H), 7.41 (t, *J* = 8.0 Hz, 1H), 6.94 (d, *J* = 7.3 Hz, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 141.2, 135.8, 131.4, 130.8, 129.5, 127.9, 127.5, 126.1, 123.1, 112.0, 103.6.

Pyrazolo[1,5-*a*]quinoline (3j)[1a]



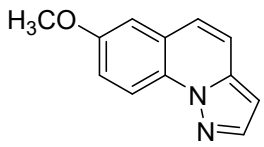
3j was purified by silica gel chromatography (*n*-hexane/EA = 80/1 – 40/1, v/v). Yellow liquid (23 mg, 46%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.58 (d, *J* = 8.3 Hz, 1H), 8.02 (d, *J* = 1.9 Hz, 1H), 7.72 (d, *J* = 7.9 Hz, 1H), 7.68 – 7.63 (m, 1H), 7.44 – 7.35 (m, 3H), 6.60 (d, *J* = 1.8 Hz, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 141.2, 138.1, 135.0, 129.4, 128.4, 124.7, 124.6, 123.3, 116.8, 115.5, 99.8.

7-Methylpyrazolo[1,5-*a*]quinoline (3k)[1a]



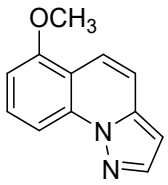
3k was purified by silica gel chromatography (*n*-hexane/EA = 80/1 – 40/1, v/v). Red liquid (26 mg, 48%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.46 (d, *J* = 8.4 Hz, 1H), 7.99 (d, *J* = 2.2 Hz, 1H), 7.50 (s, 1H), 7.47 (d, *J* = 8.7 Hz, 1H), 7.40 (d, *J* = 9.3 Hz, 1H), 7.31 (d, *J* = 9.2 Hz, 1H), 6.58 (d, *J* = 2.1 Hz, 1H), 2.48 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 140.9, 137.8, 134.3, 133.1, 130.8, 128.0, 124.4, 123.3, 116.7, 115.3, 99.6, 21.2.

7-Methoxypyrazolo[1,5-*a*]quinoline (3l)[3]



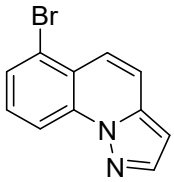
3l was purified by silica gel chromatography (*n*-hexane/EA = 35/1 – 25/1, v/v). White solid (27.2 mg, 46%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.49 (d, *J* = 8.6 Hz, 1H), 7.97 (s, 1H), 7.40 (d, *J* = 9.1 Hz, 1H), 7.31 – 7.25 (m, 2H), 7.11 (d, *J* = 1.9 Hz, 1H), 6.57 (d, *J* = 2.0 Hz, 1H), 3.89 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 156.7, 140.6, 137.3, 129.9, 124.3, 124.2, 118.5, 117.3, 116.9, 109.5, 99.5, 55.7.

6-Methoxypyrazolo[1,5-*a*]quinoline (3m)[1a]



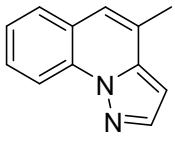
3m was purified by silica gel chromatography (*n*-hexane/EA = 35/1 – 25/1, v/v). White solid (22.8 mg, 38%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.17 (d, *J* = 8.4 Hz, 1H), 8.01 (d, *J* = 2.0 Hz, 1H), 7.82 (d, *J* = 8.9 Hz, 1H), 7.57 (t, *J* = 8.2 Hz, 1H), 7.40 (d, *J* = 9.5 Hz, 1H), 6.84 (d, *J* = 8.0 Hz, 1H), 6.59 (d, *J* = 2.0 Hz, 1H), 3.98 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 156.2, 141.3, 138.3, 135.8, 129.8, 118.9, 115.4, 114.3, 108.0, 104.7, 99.4, 55.9.

6-Bromopyrazolo[1,5-*a*]quinoline (3n)[1a]



3n was purified by silica gel chromatography (*n*-hexane/EA = 50/1 – 40/1, v/v). Yellow solid (20.8 mg, 28%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.57 (d, *J* = 8.3 Hz, 1H), 8.03 (d, *J* = 1.9 Hz, 1H), 7.78 (d, *J* = 9.6 Hz, 1H), 7.67 (d, *J* = 1.5 Hz, 1H), 7.53 – 7.45 (m, 2H), 6.63 (d, *J* = 2.1 Hz, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 141.9, 137.8, 135.9, 129.8, 128.8, 123.4, 123.0, 122.6, 118.0, 115.3, 100.2.

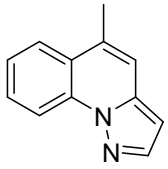
4-Methylpyrazolo[1,5-*a*]quinoline (3o)[1a]



3o was purified by silica gel chromatography (*n*-hexane/EA = 80/1 – 40/1, v/v). Yellow liquid (35.1 mg, 64%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.54 (d, *J* = 8.3 Hz, 1H), 8.02 (d, *J* = 2.0 Hz, 1H), 7.68 (d, *J* = 7.9 Hz, 1H), 7.61 (t, *J* = 7.7 Hz, 1H), 7.41 (t, *J* = 7.5

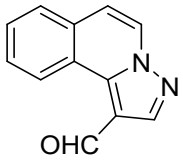
Hz, 1H), 7.17 (s, 1H), 6.60 (d, *J* = 2.0 Hz, 1H), 2.50 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 141.1, 139.8, 133.8, 128.4, 127.7, 126.2, 124.7, 123.8, 122.7, 115.4, 98.5, 18.5.

5-Methylpyrazolo[1,5-*a*]quinoline (3p)[1a]



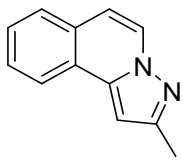
3p was purified by silica gel chromatography (*n*-hexane/EA = 80/1 – 40/1, v/v). White solid (22.3 mg, 41%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.59 (d, *J* = 8.2 Hz, 1H), 7.96 (s, 1H), 7.83 (d, *J* = 8.1 Hz, 1H), 7.65 (t, *J* = 7.6 Hz, 1H), 7.45 (t, *J* = 7.1 Hz, 1H), 7.25 (s, 1H), 6.48 (s, 1H), 2.56 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 141.2, 137.9, 134.7, 131.4, 129.2, 125.2, 124.6, 123.7, 116.0, 115.8, 98.7, 19.2.

Pyrazolo[5,1-*a*]isoquinoline-1-carbaldehyde (4)[1a]



4 was purified by silica gel chromatography (*n*-hexane/EA = 15/1 – 5/1, v/v). White solid (44.2 mg, 75%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 10.13 (s, 1H), 9.67 – 9.63 (m, 1H), 8.44 (s, 1H), 8.31 (d, *J* = 7.3 Hz, 1H), 7.81 – 7.77 (m, 1H), 7.73 – 7.69 (m, 2H), 7.27 (d, *J* = 7.3 Hz, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 183.2, 148.6, 138.0, 130.9, 130.4, 128.5, 128.0, 127.1, 126.2, 124.4, 117.5, 115.9.

2-Methylpyrazolo[5,1-*a*]isoquinoline (6)[4]



6 was purified by silica gel chromatography (*n*-hexane/EA = 10/1, v/v). Yellow solid (13.2 mg, 24%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.14 (d, *J* = 7.3 Hz, 1H), 8.01 (d, *J* = 6.8 Hz, 1H), 7.67 (d, *J* = 8.6 Hz, 1H), 7.55 – 7.48 (m, 2H), 6.89 (d, *J* = 7.3 Hz, 1H), 6.75 (s, 1H), 2.53 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 151.1, 139.3, 128.9, 127.8, 127.5, 127.2, 126.1, 124.3, 123.7, 111.1, 97.3, 14.1.

4. References

1 (a) W. Li, M. Zhang, J. Yan, L. Ni, H. Cao and X. Liu, *Org. Chem. Front.*, 2022, **9**, 2529-2533; (b) X. Shi, Y. Lin, J. Wei, L. Zhao, P. Guo, H. Cao and X. Liu, *Org. Chem. Front.*, 2023, **10**, 2892-2897.

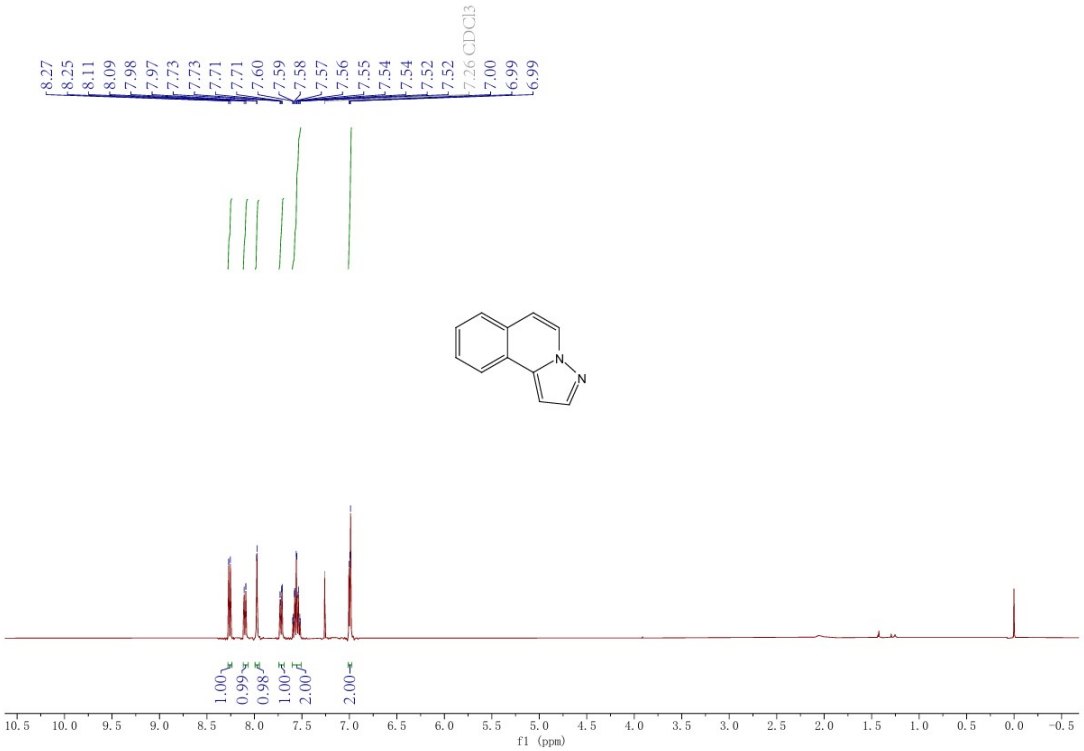
2 M. Kobayashi, K. Kondo and T. Aoyama, *Tetrahedron Lett.*, 2007, **48**, 7019-7021.

3 X. Liu, S. Ma, S. Yan, X. Shi, S. Li, Y. Ma and H. Cao, *Chin. J. Chem* . 2024, **42**, 3355-3361.

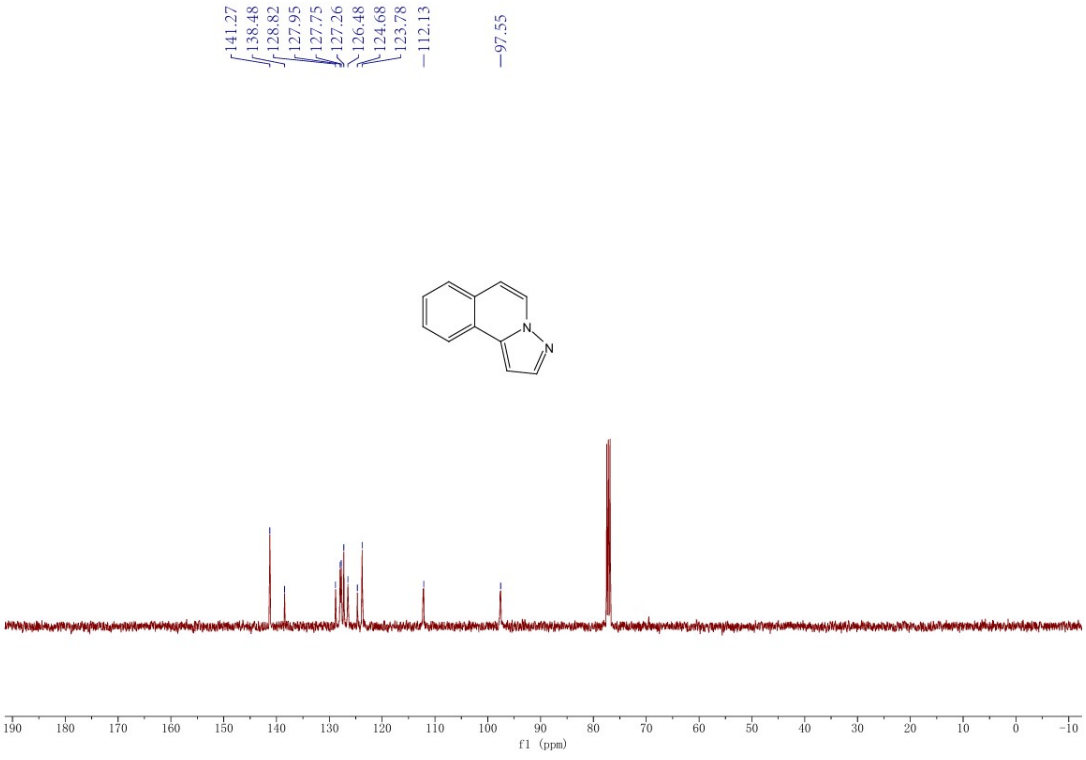
4 H. Gnichtel and B. Möller, *Liebigs Ann. Chem.*, 2006, **1981**, 1751-1759.

5. NMR spectra of compounds

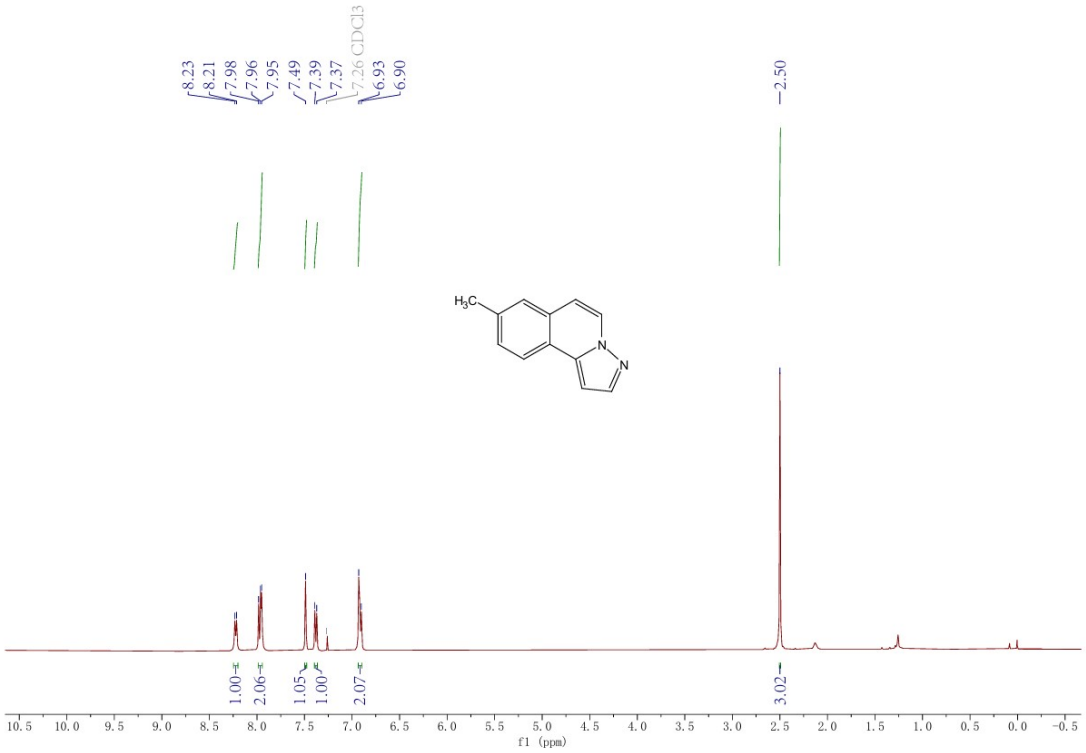
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **3a**



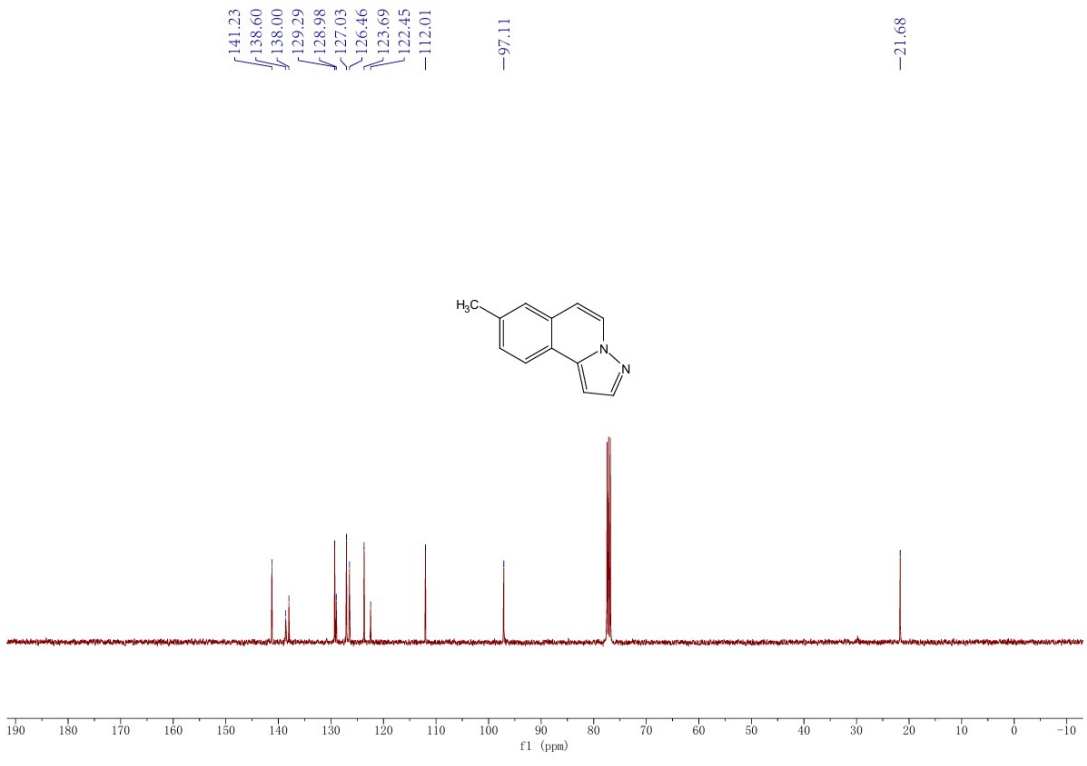
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of compound **3a**



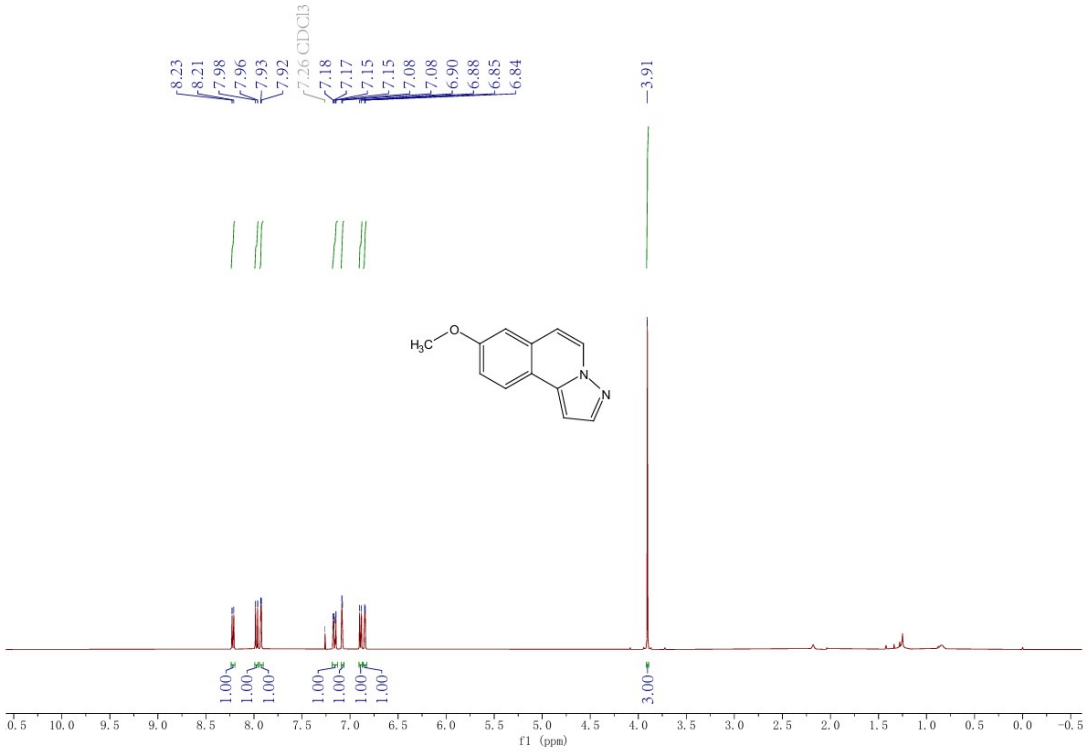
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **3b**



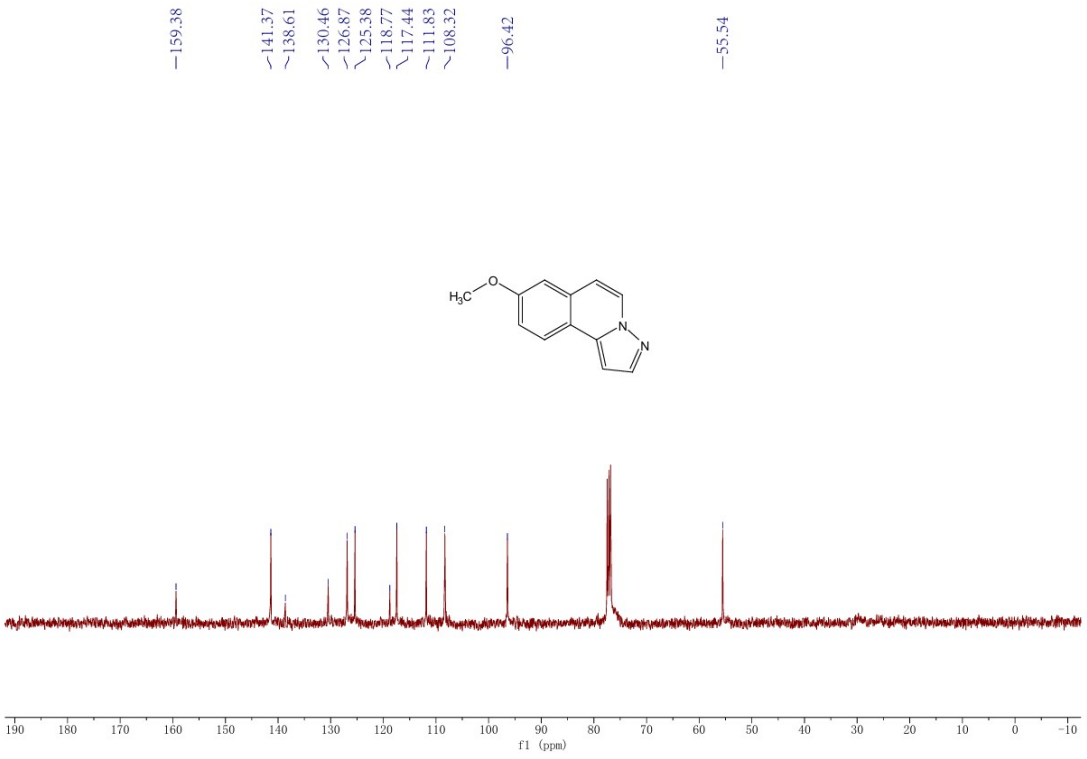
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of compound **3b**



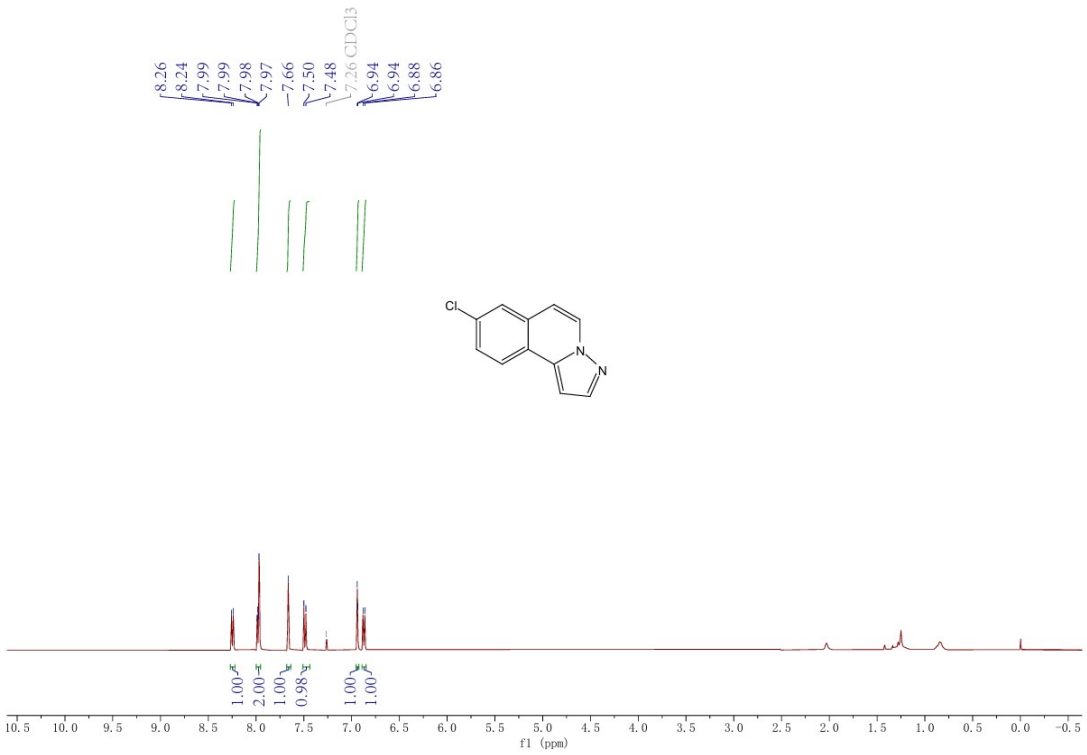
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **3c**



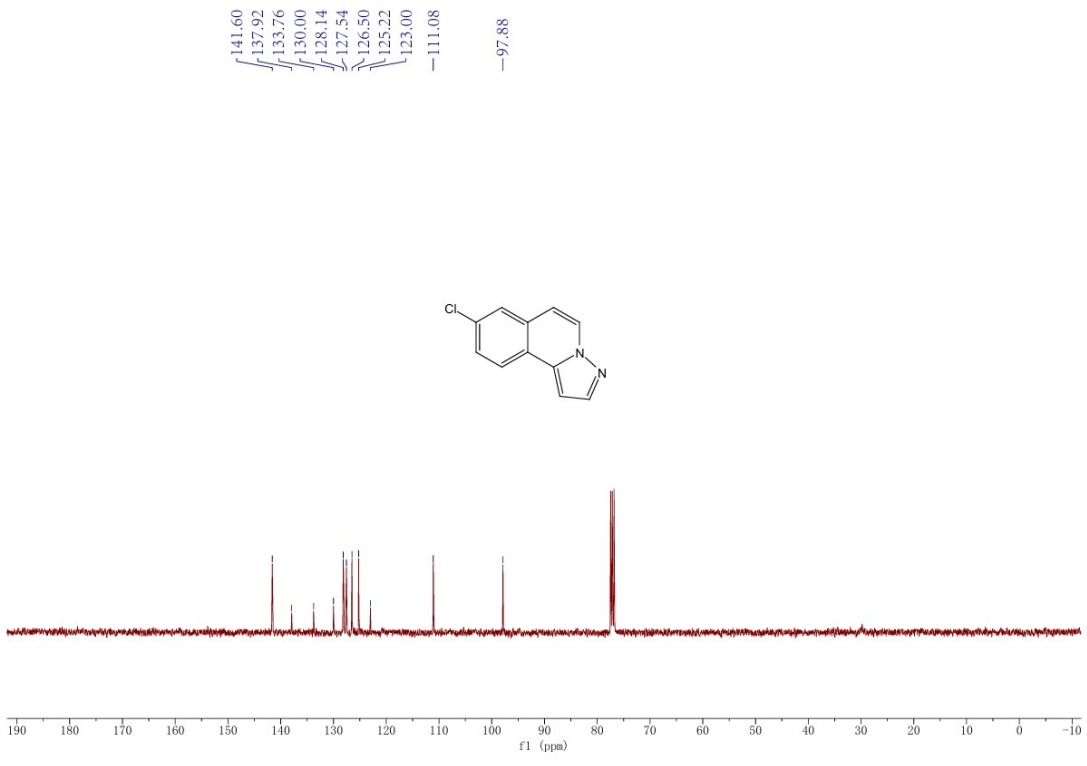
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of compound **3c**



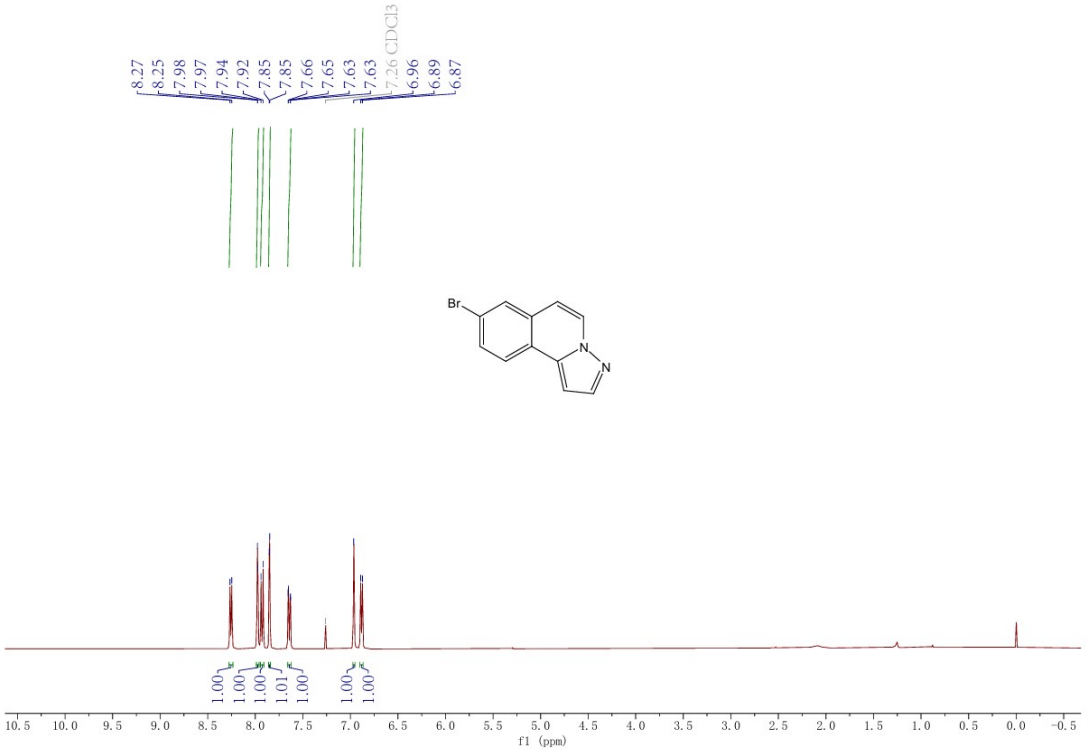
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **3d**



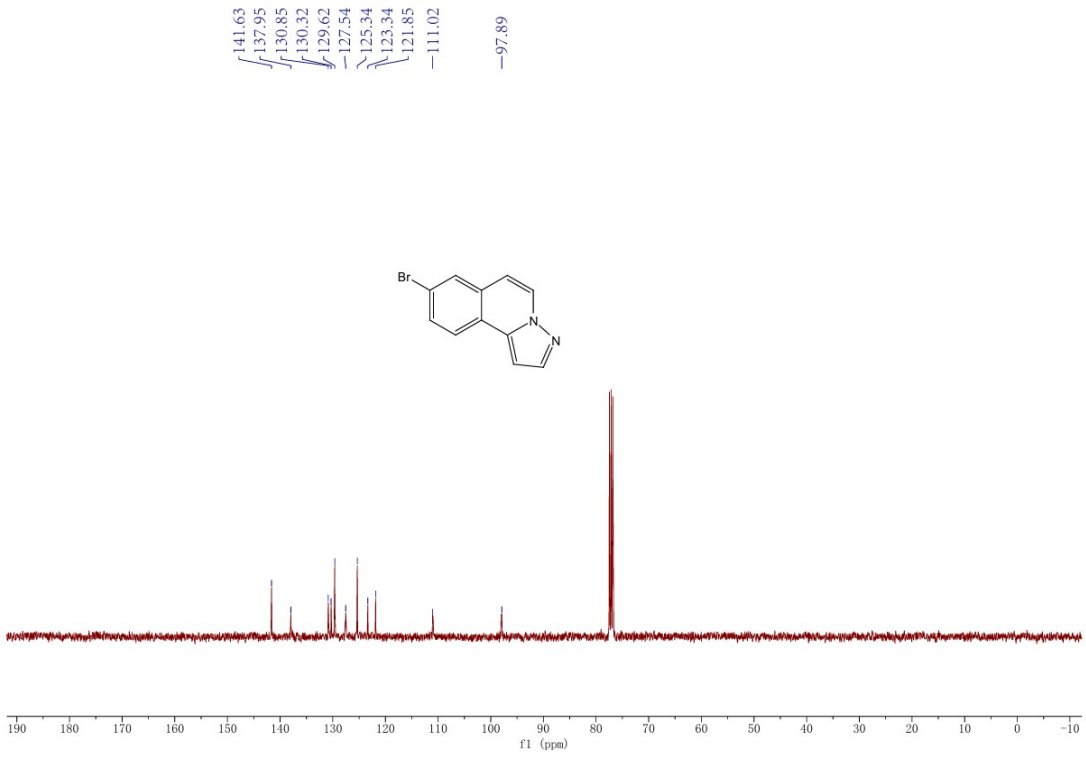
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of compound **3d**



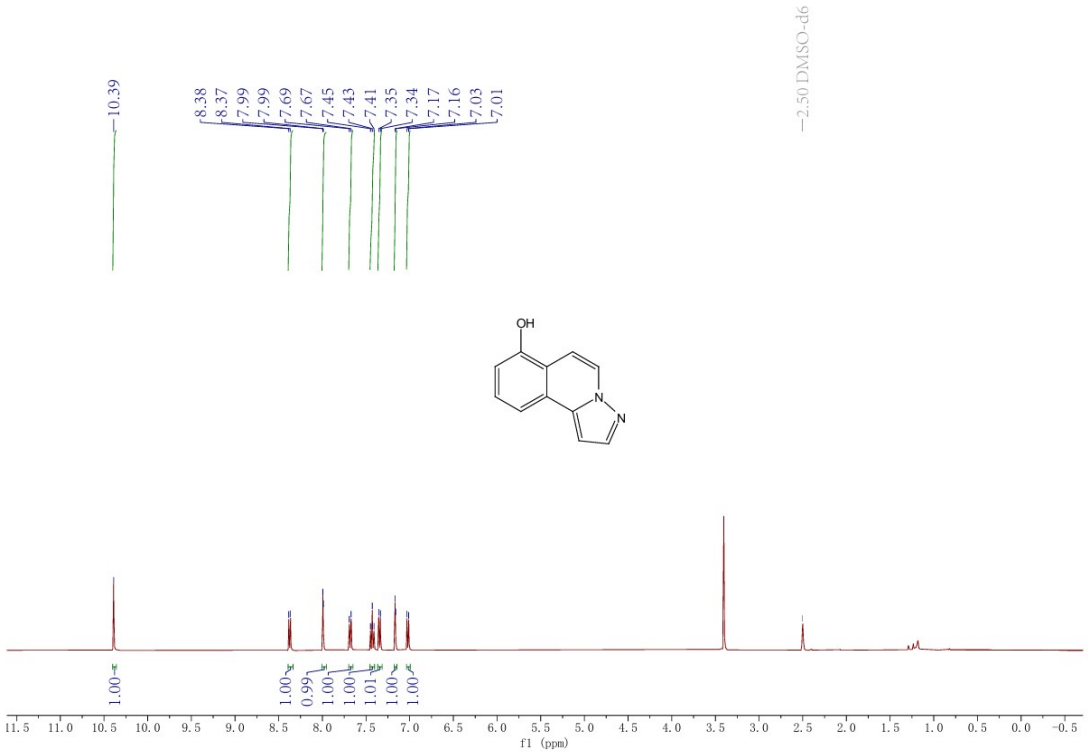
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **3e**



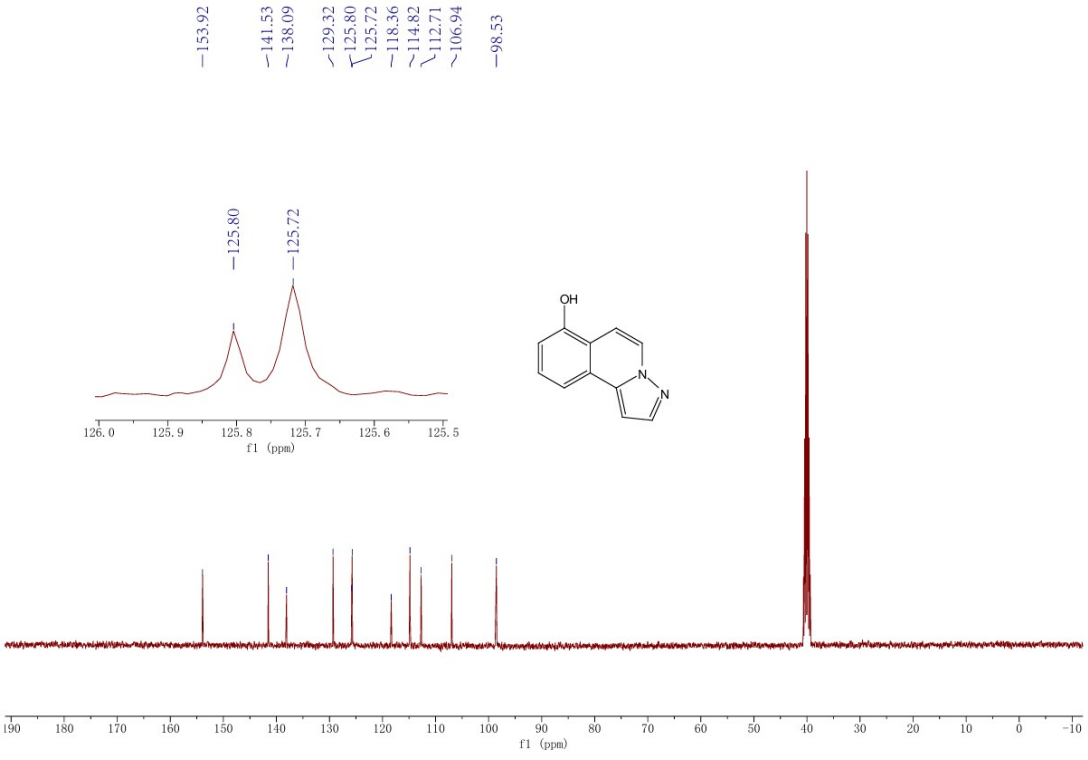
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of compound **3e**



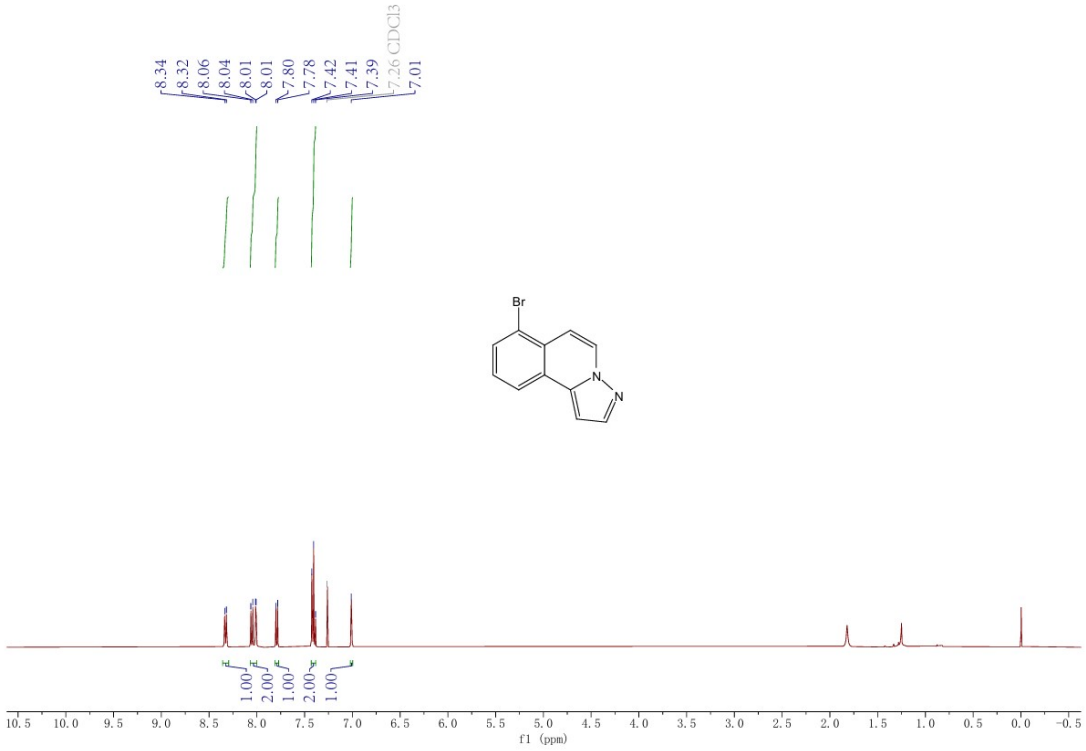
^{1}H NMR (400 MHz, DMSO-d_6) spectrum of compound **3f**



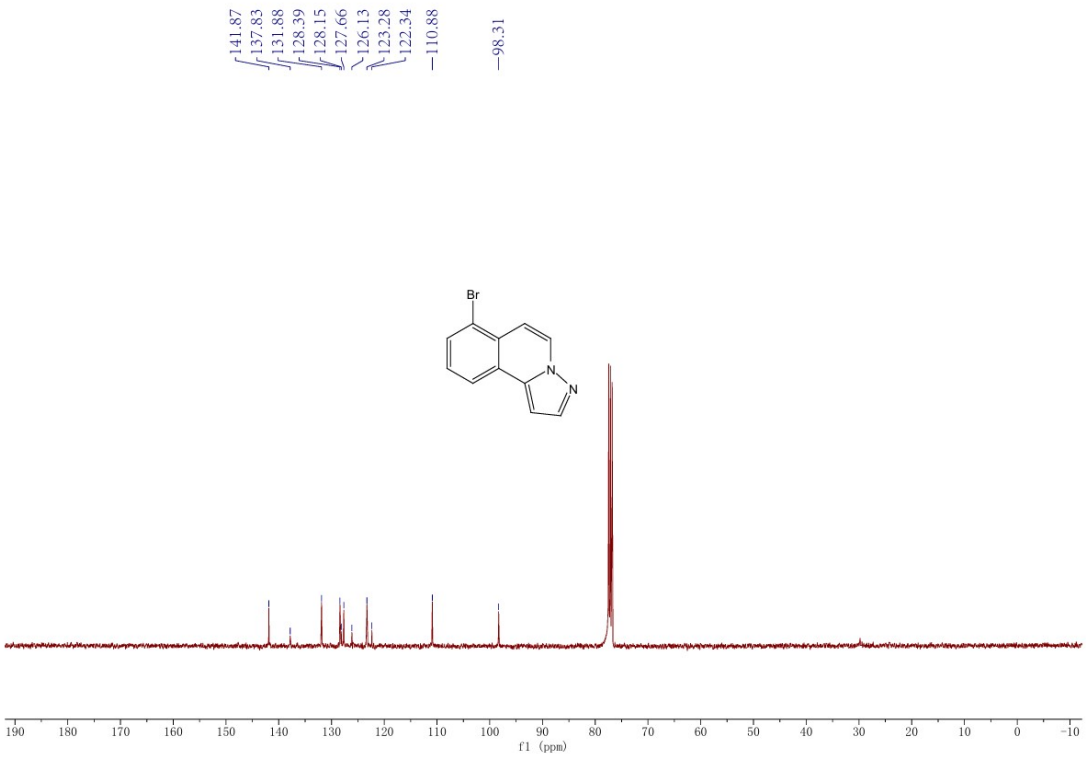
^{13}C NMR (101 MHz, DMSO-d_6) spectrum of compound **3f**



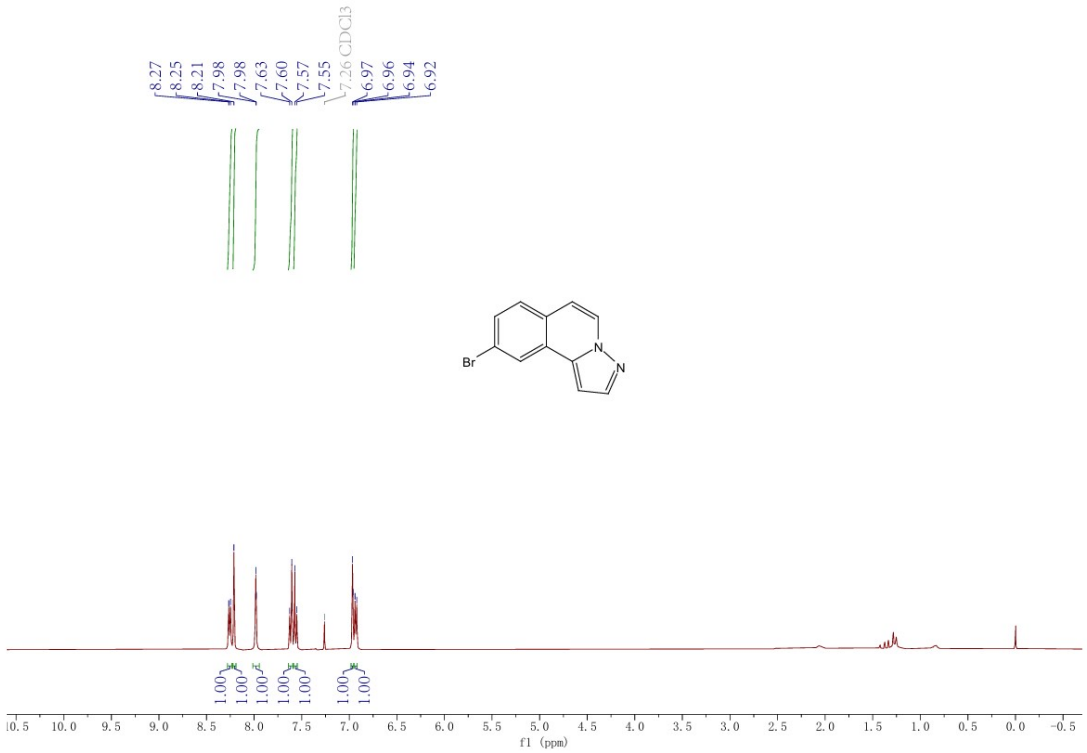
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **3g**



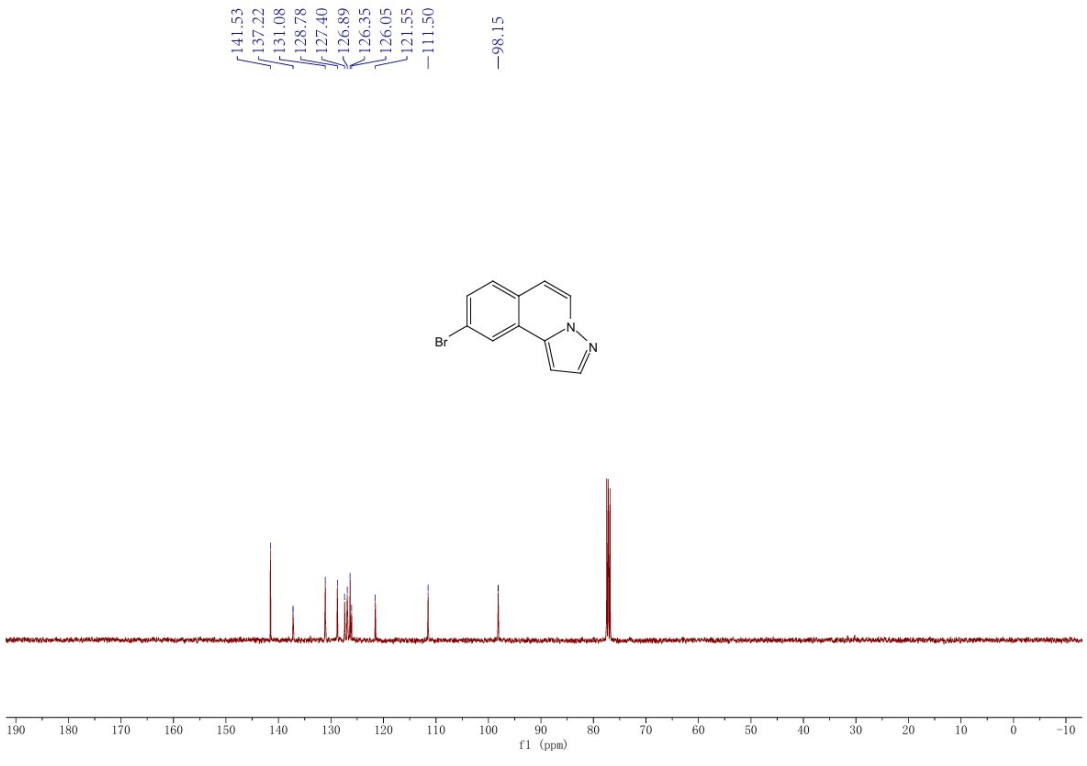
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of compound **3g**



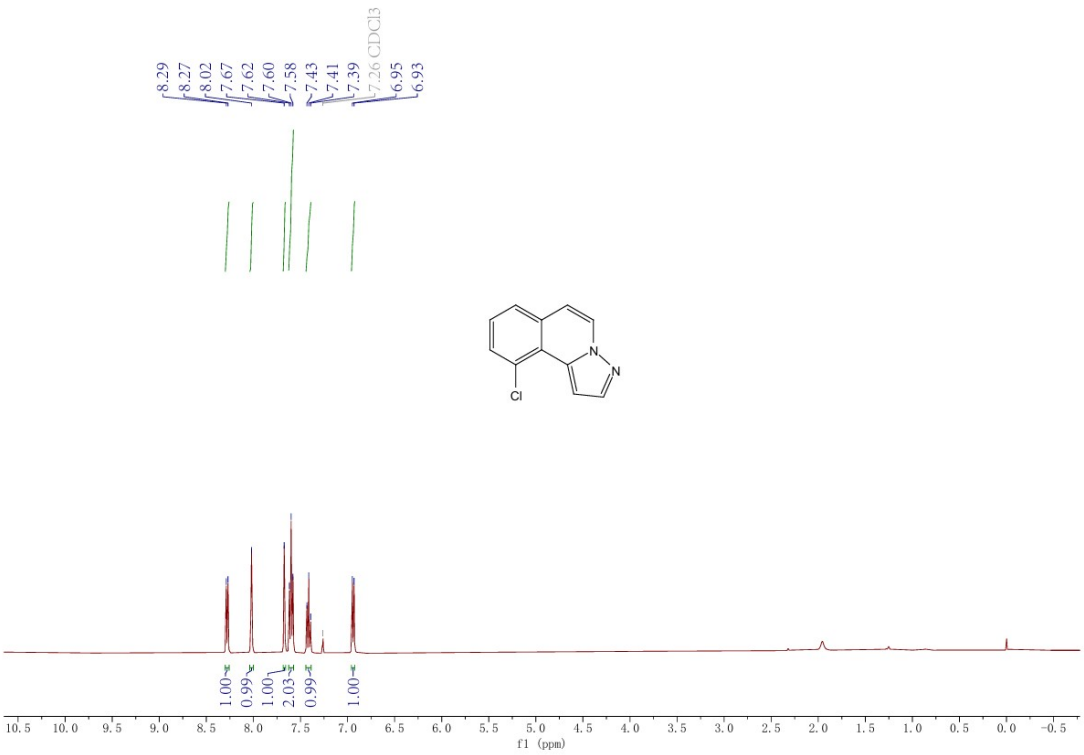
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **3h**



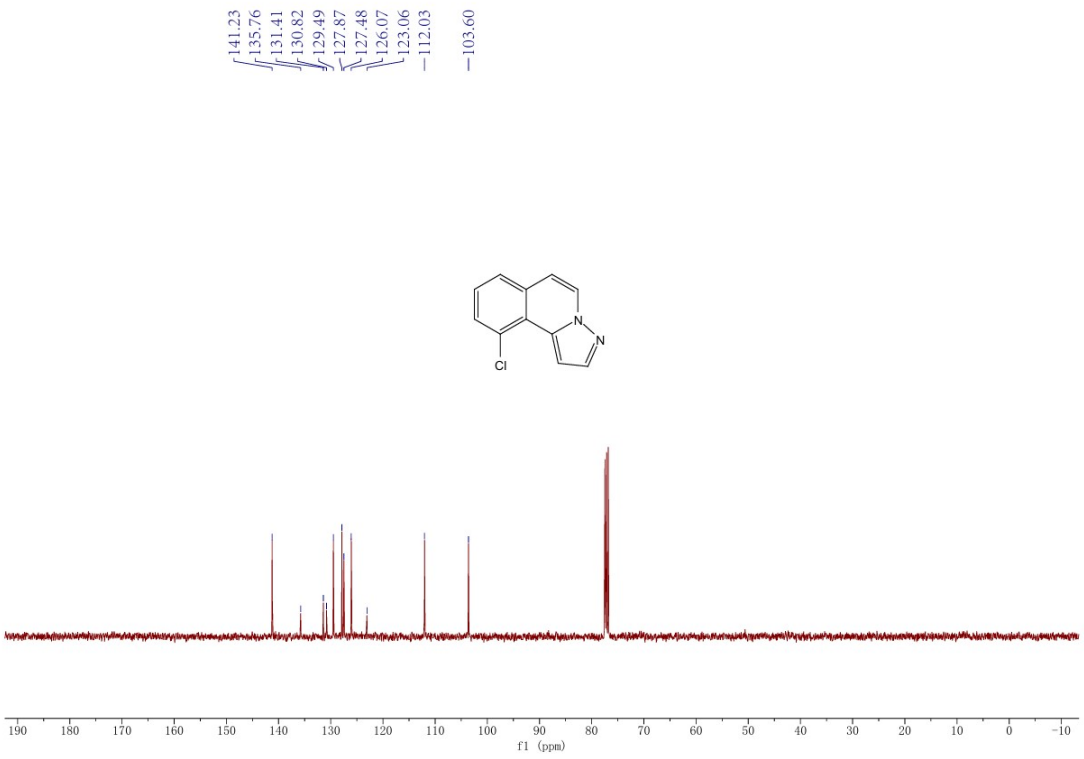
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of compound **3h**



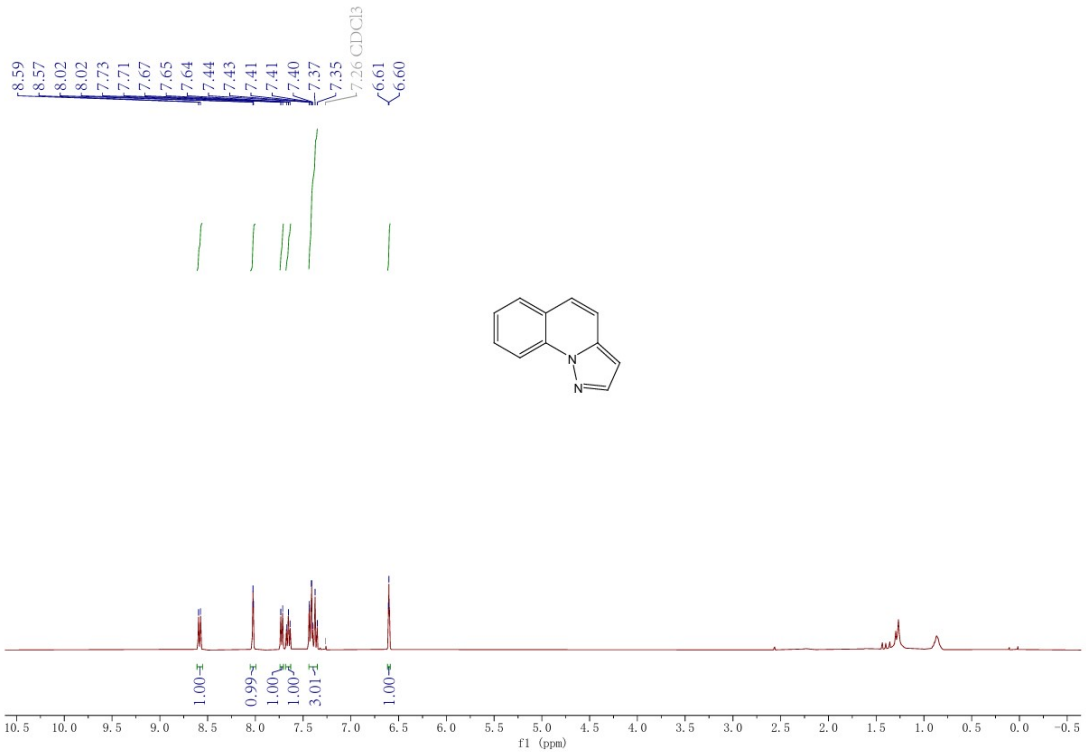
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **3i**



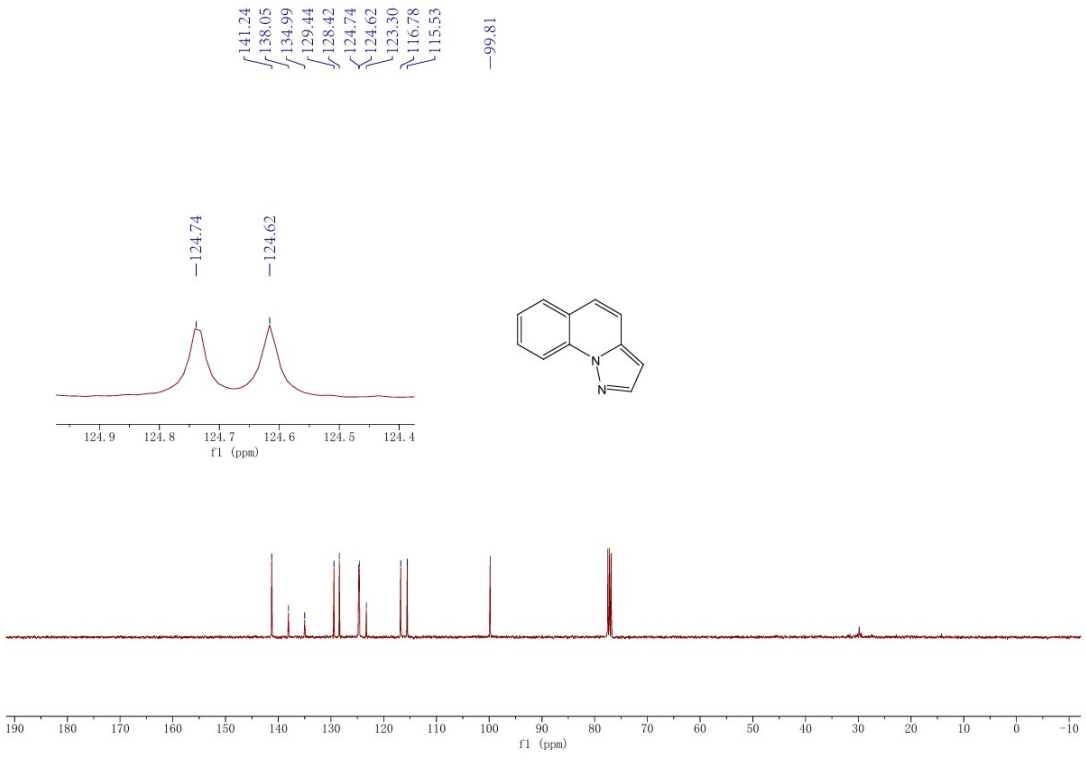
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of compound **3i**



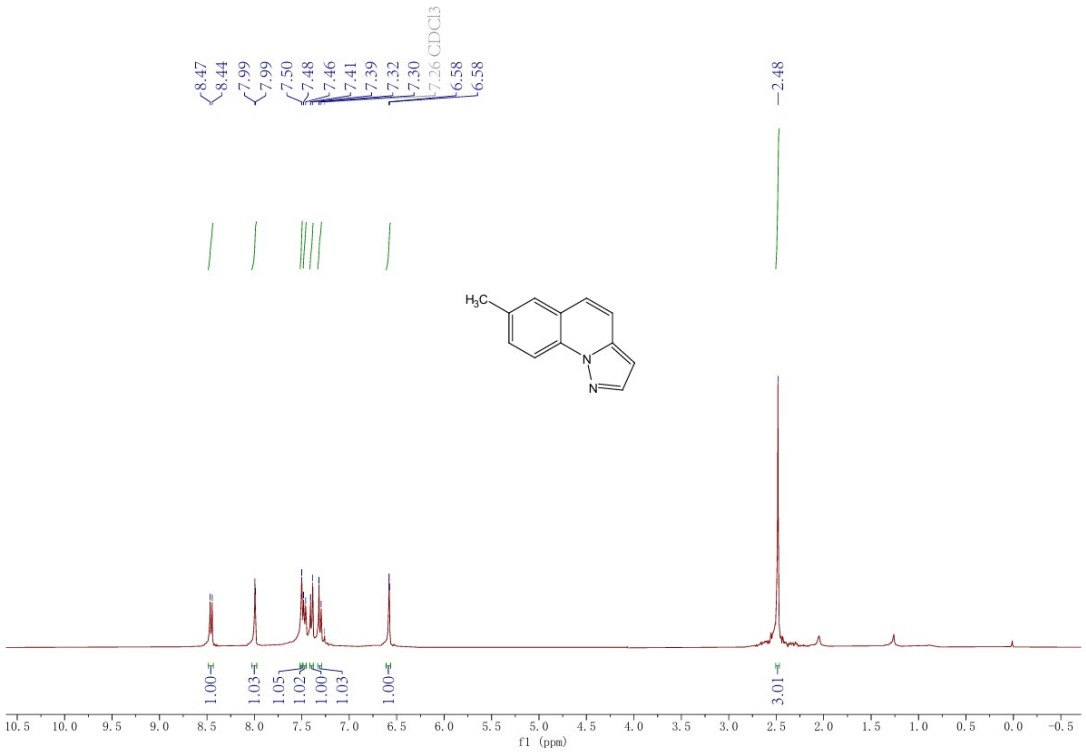
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **3j**



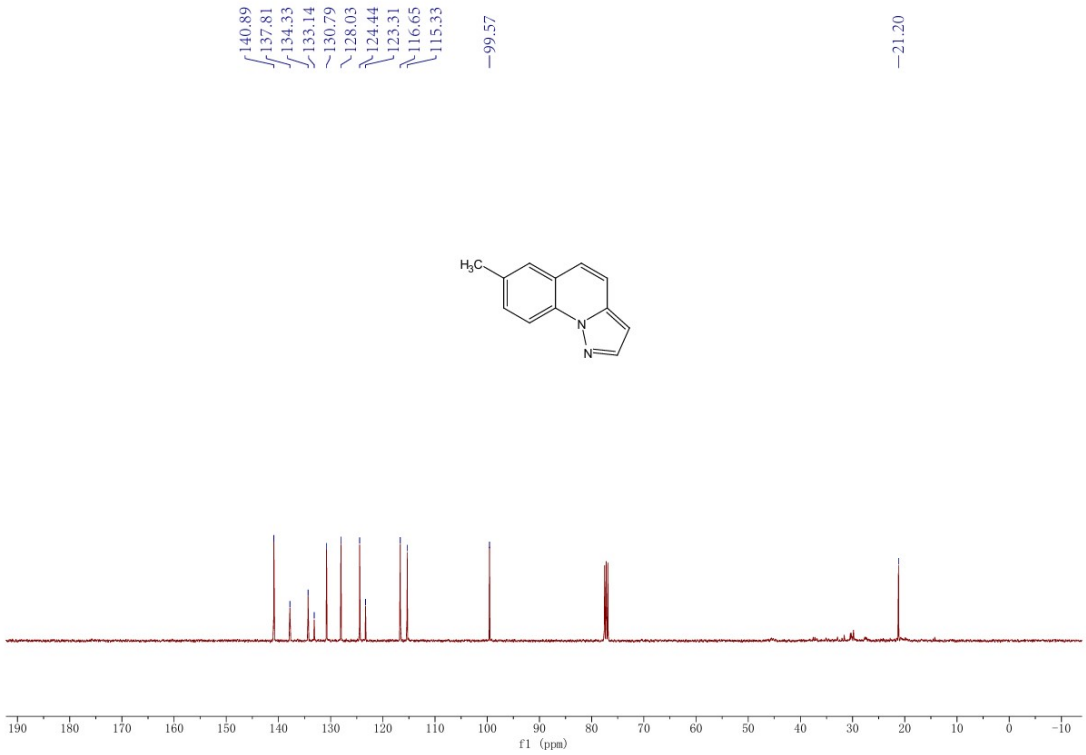
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of compound **3j**



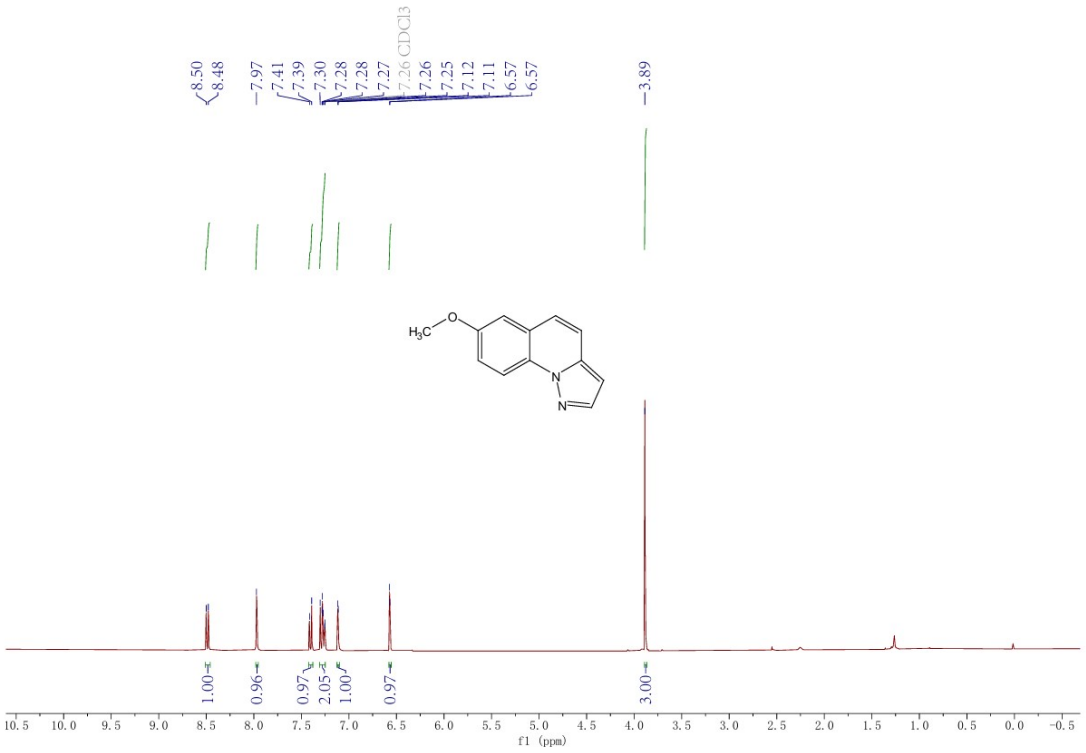
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **3k**



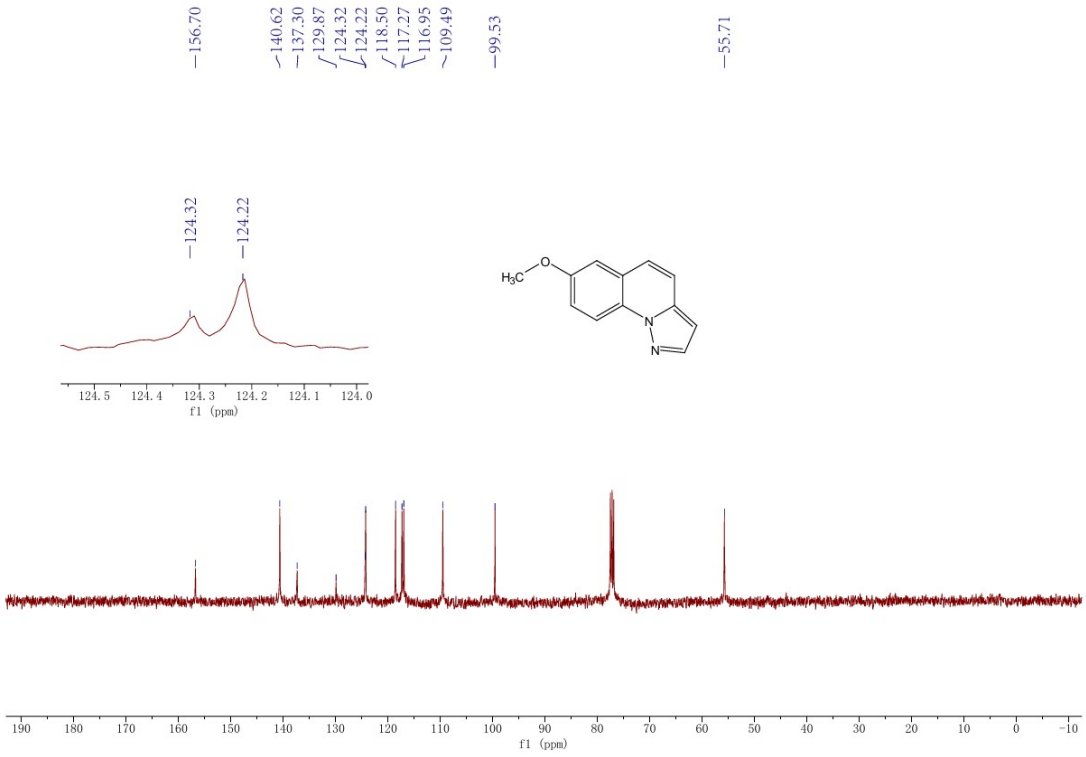
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of compound **3k**



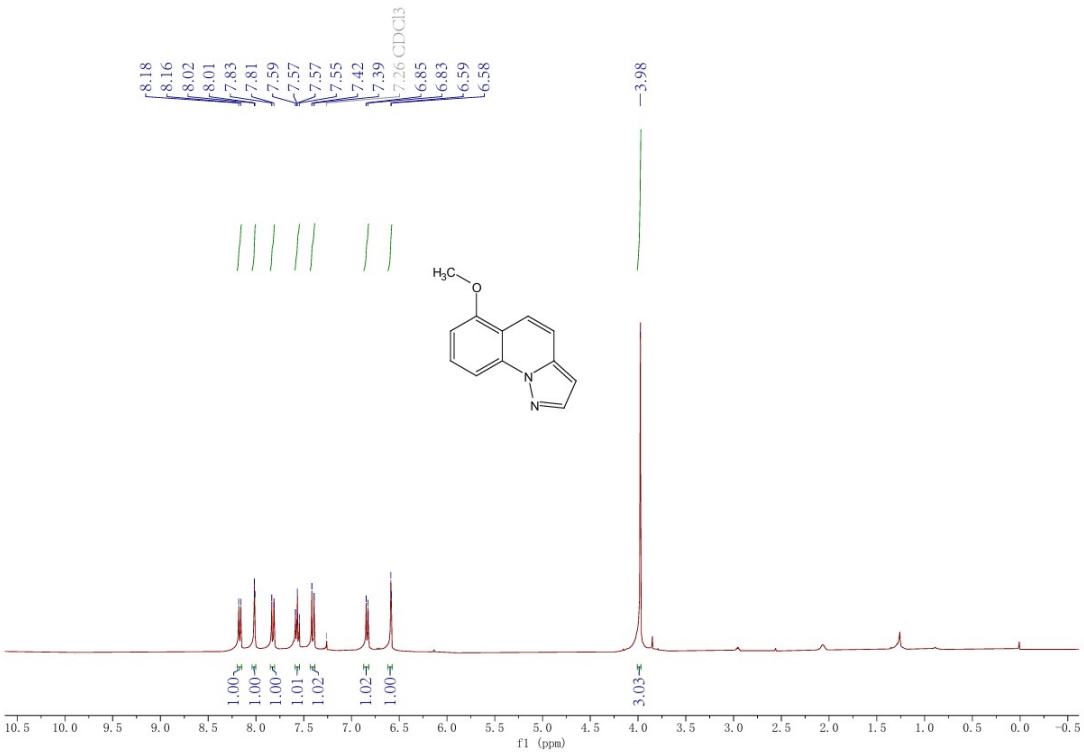
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **3l**



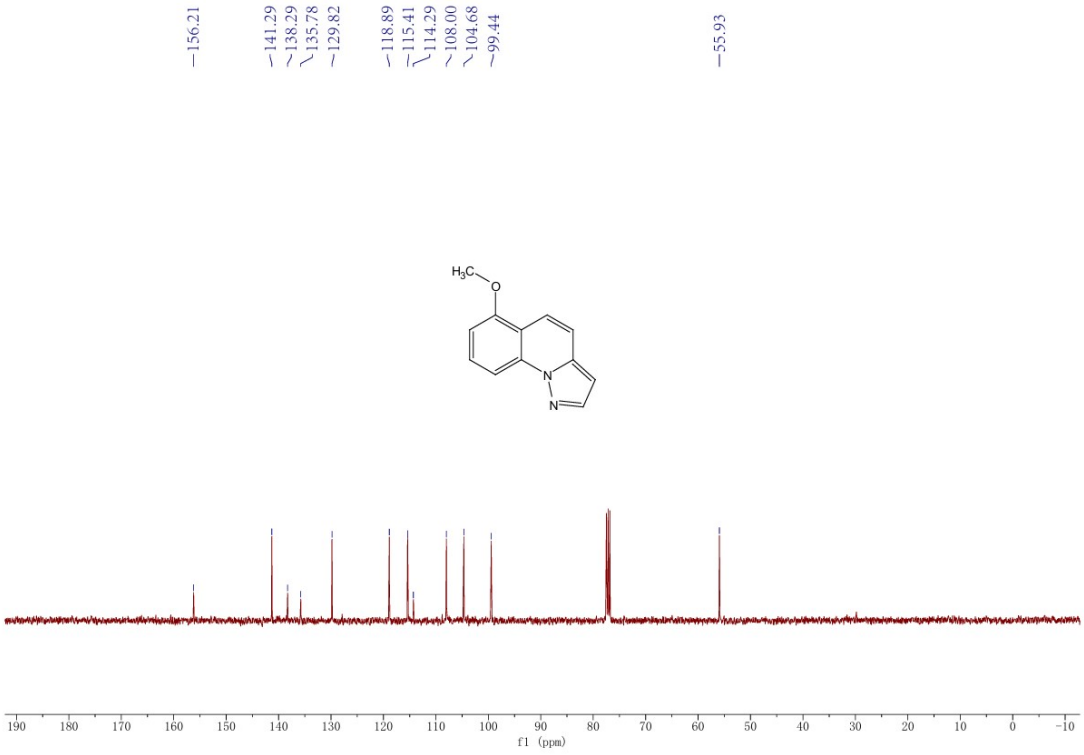
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of compound **3l**



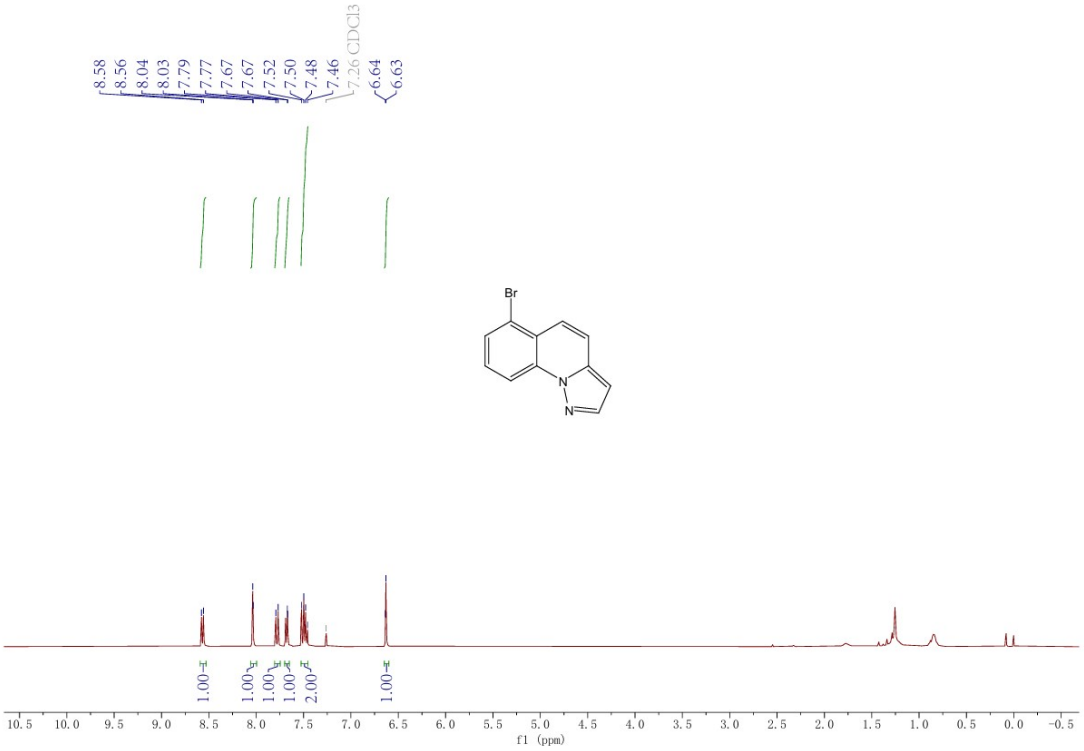
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **3m**



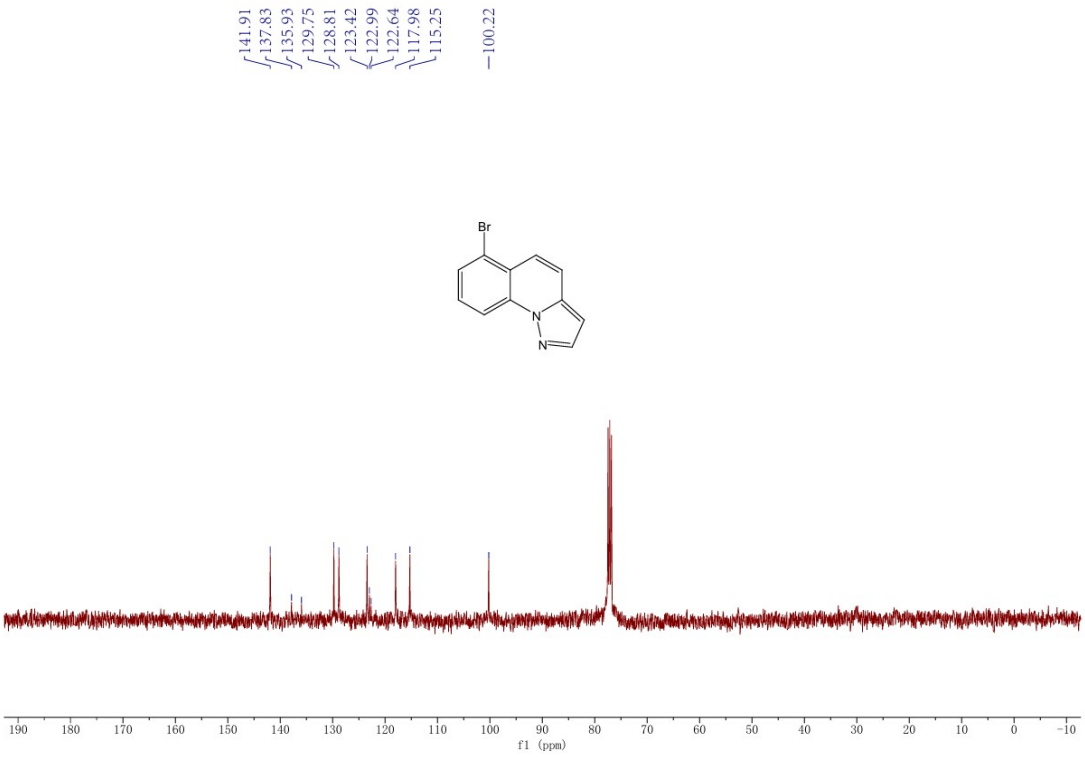
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of compound **3m**



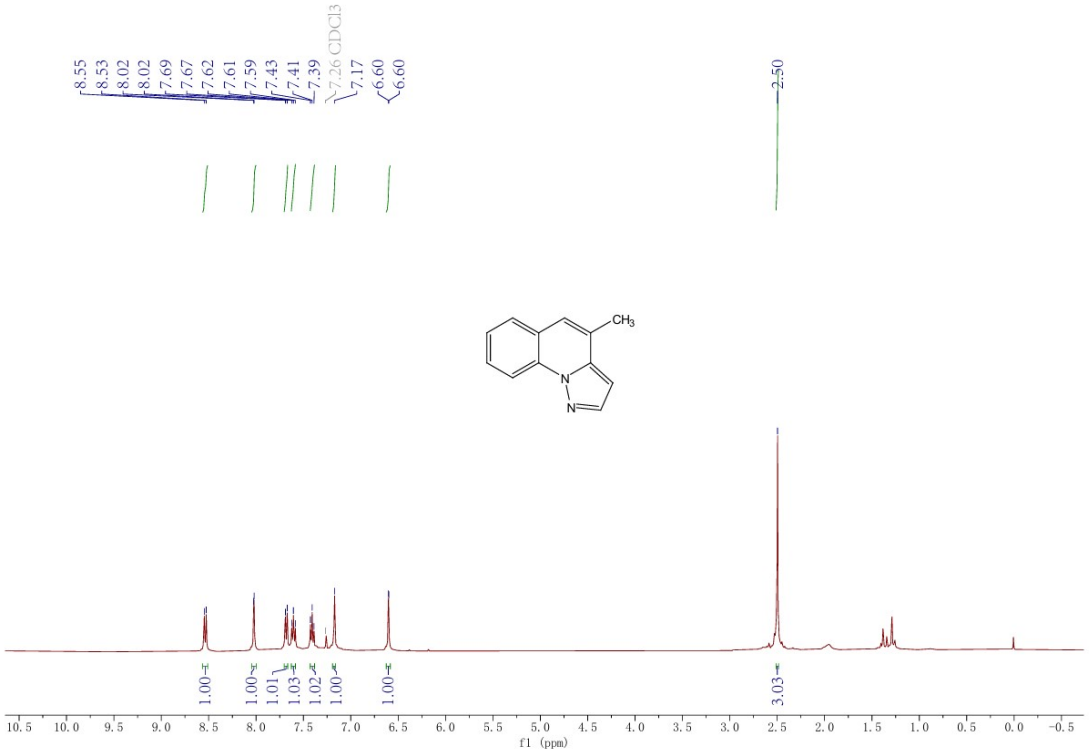
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **3n**



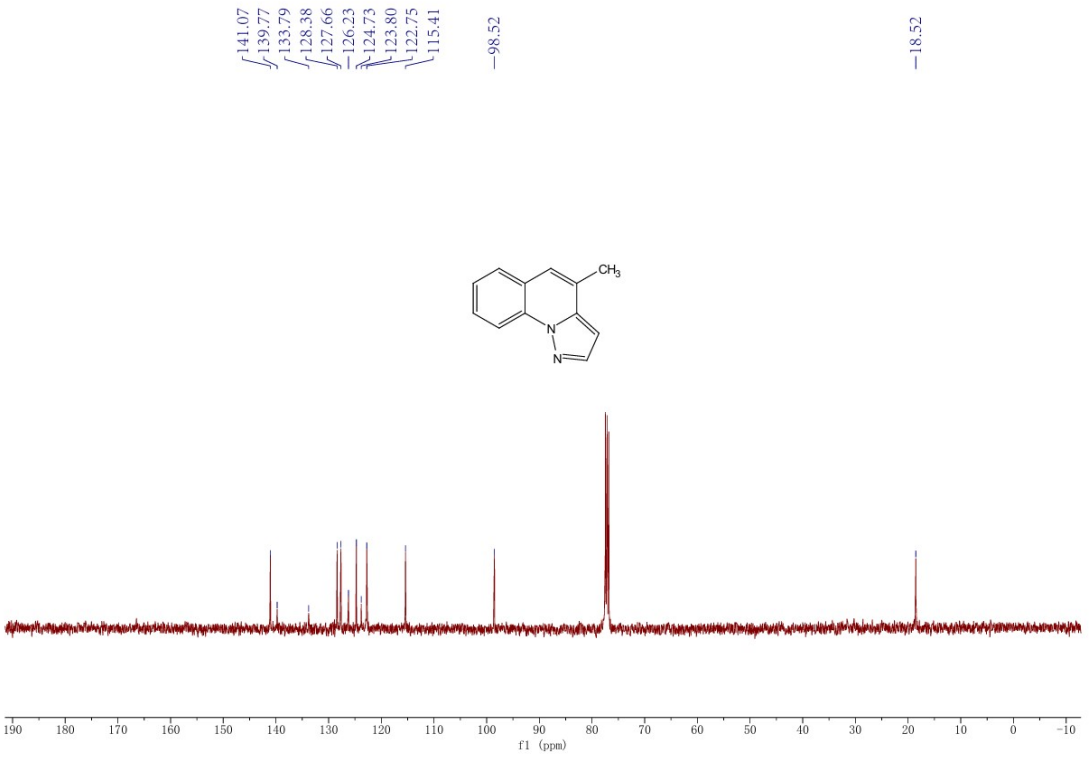
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of compound **3n**



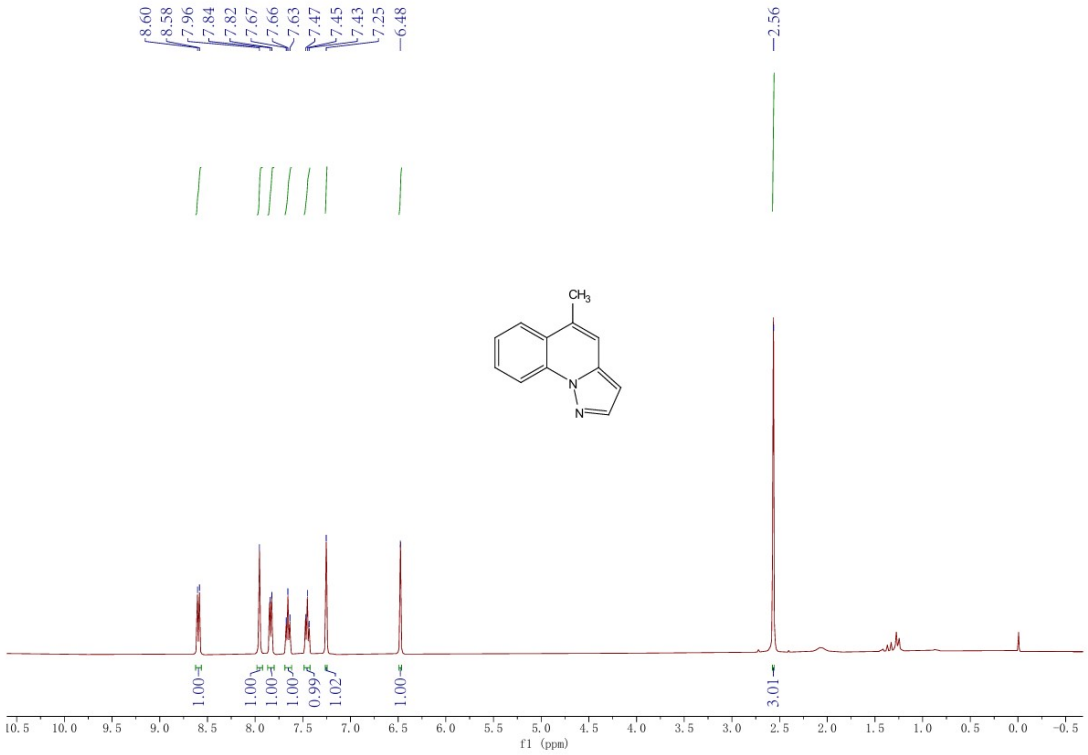
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **3o**



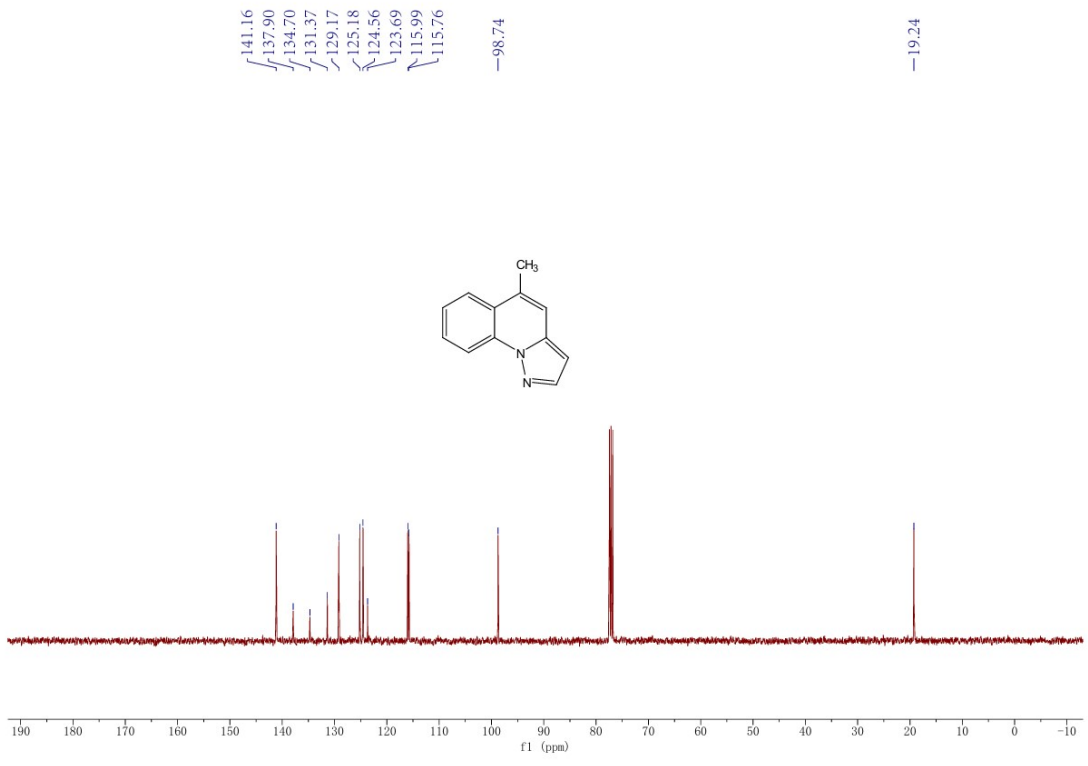
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of compound **3o**



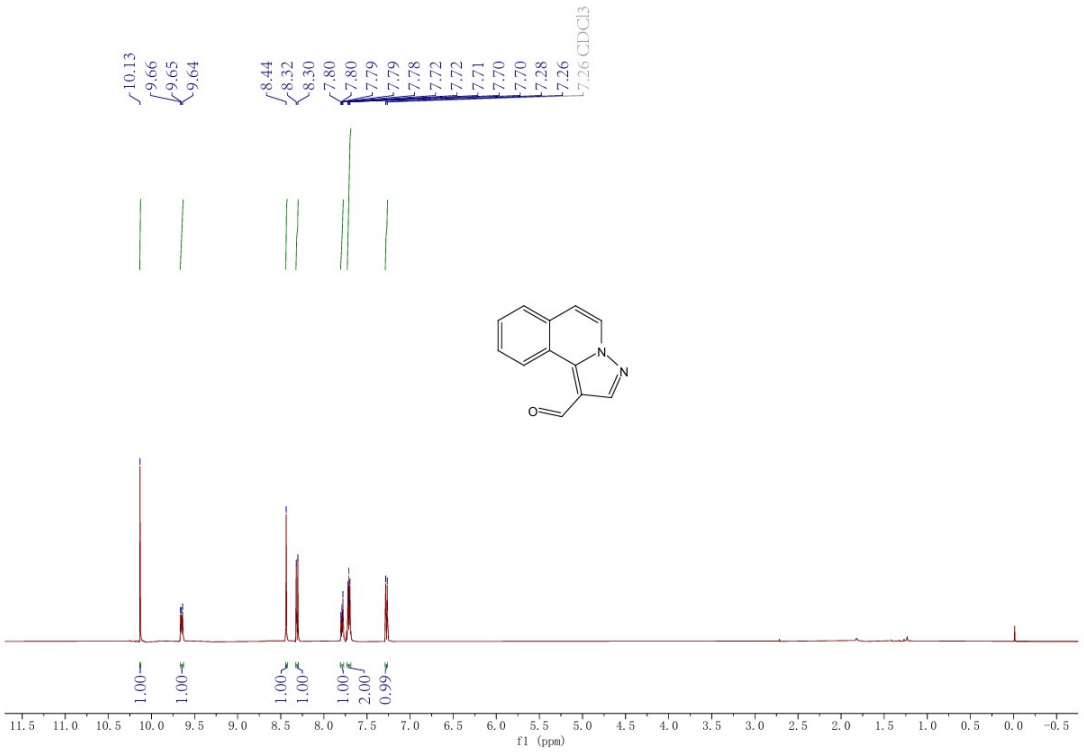
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **3p**



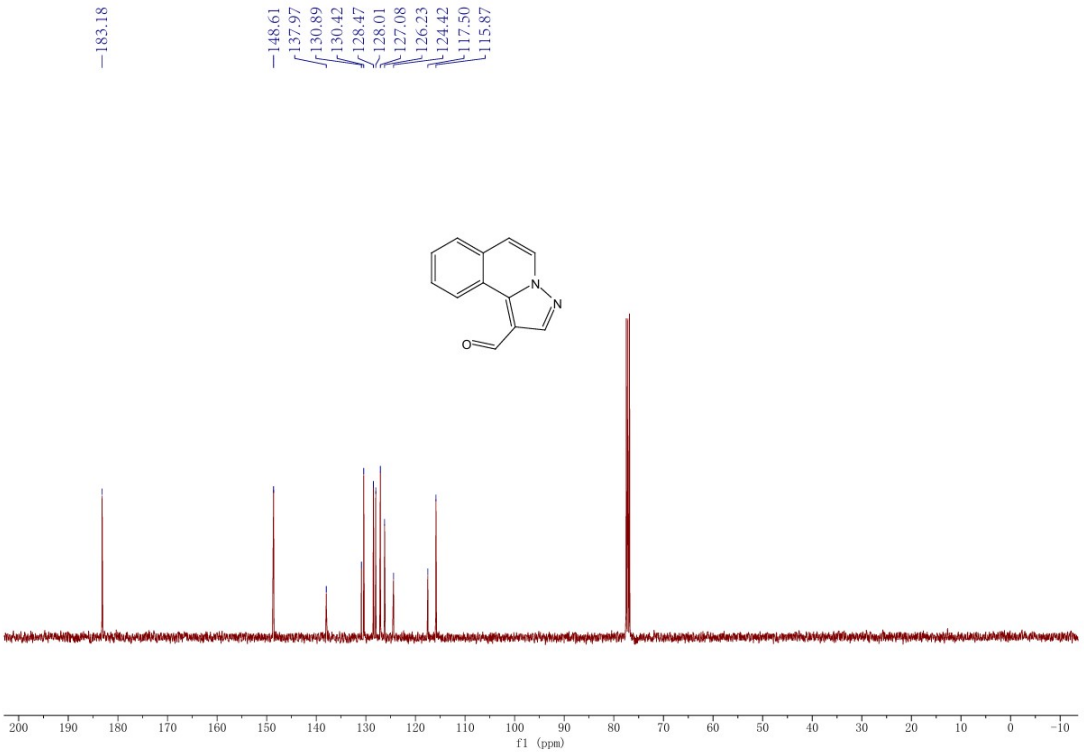
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of compound **3p**



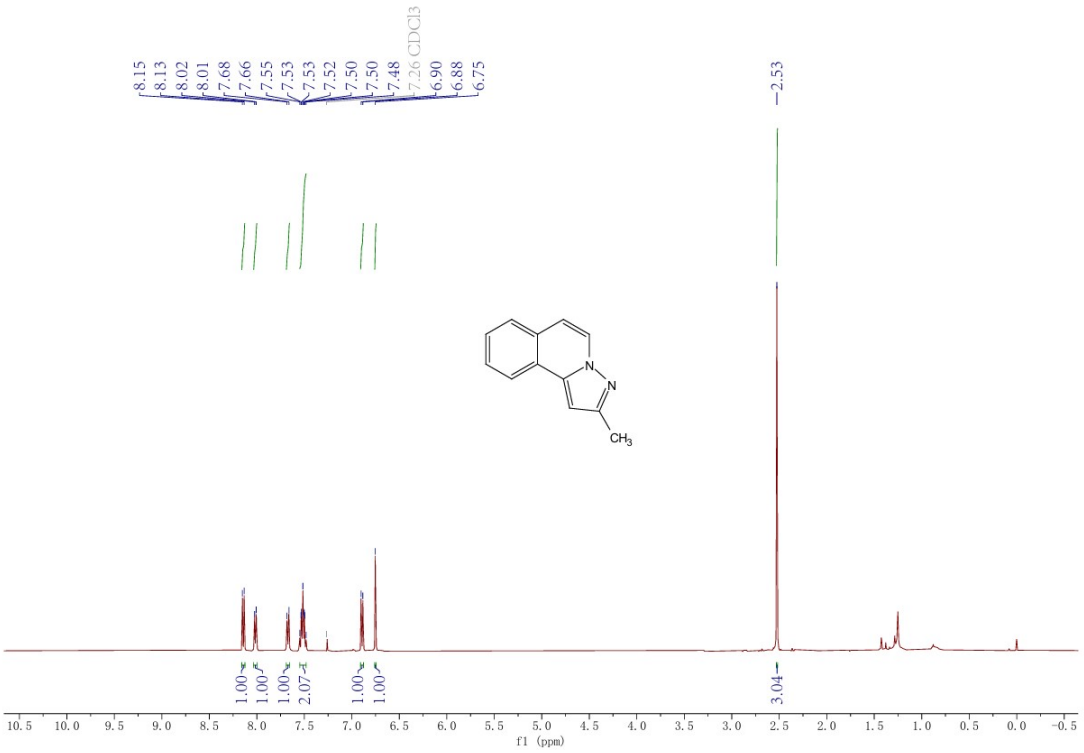
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **4**



^{13}C NMR (101 MHz, $CDCl_3$) spectrum of compound **4**



^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **6**



^{13}C NMR (101 MHz, $CDCl_3$) spectrum of compound **6**