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Supporting information

Selectivity-tunable oxidation of tetrahydro-β-carboline over OMS-2 composite catalyst: preparation and catalytic performance

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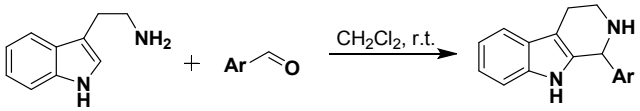
CONTENTS

1. General Information

All reagents were purchased from commercial suppliers and used without further purification. All experiments were carried out under air or using O_2 balloon. Flash chromatography was carried out with Merck silica gel 60 (200-300 mesh). Analytical TLC was performed with Merck silica gel 60 F254 plates, and the products were visualized by UV detection. ^1H NMR and ^{13}C NMR (400 and 100 MHz respectively) spectra were recorded in $CDCl_3$. Chemical shifts (δ) are reported in ppm using TMS as internal standard, and spin-spin coupling constants (J) are given in Hz.

2. Synthesis raw



Scheme 1. The procedure of synthesis of tetrahydro-β-carbolines derivatives 1a-1k.

To a solution of tryptamine (1.0 g, 6.3 mmol), aldehyde (7.5 mmol) in CH_2Cl_2 (10 mL) was added trifluoroacetic acid (0.7 mL). The reaction mixture was stirred at room temperature until the disappearance of the reactants (monitored by TLC). Then, the reaction mixture was adjusted to pH 11-12 with 1 M aqueous NaOH solution and extracted with CH_2Cl_2 (3 × 10 mL). The combined organic layer was dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel (eluent: petroleum ether/ethyl acetate) to afford 1a-1k.

3. catalyst characterization

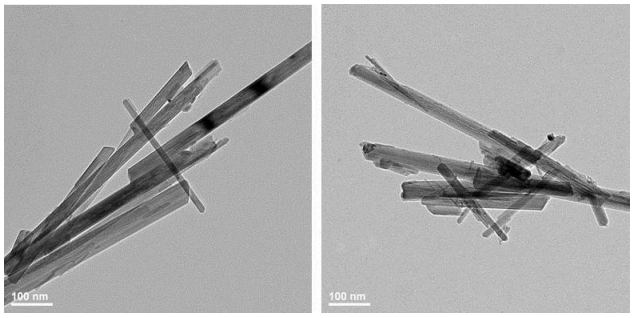


Fig. S1. TEM images of OMS-2.

As shown in the figure S1, the original OMS-2 has a typical and uniform nanorod morphology.

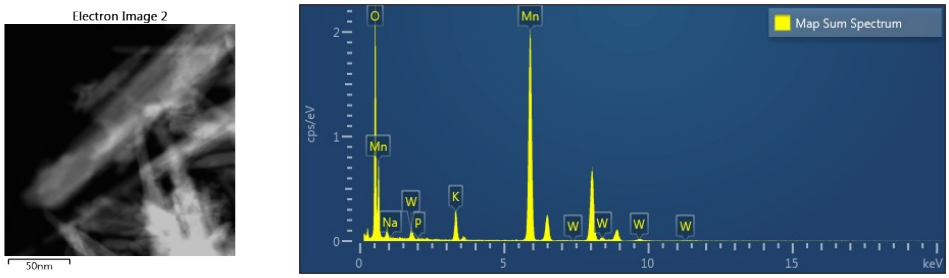


Fig. S2. TEM EDX analysis of [PW]-OMS-2.

Table S1. Element analysis of [PW]-OMS-2.

Element	Line Type	k factor	Absorption Correction	Wt%	Wt% Sigma
O	K series	1.86867	1.00	36.54	0.39
Na	K series	1.19124	1.00	0.00	0.00
P	K series	1.01332	1.00	0.10	0.06
K	K series	0.96973	1.00	4.96	0.13
Mn	K series	1.17370	1.00	53.82	0.39
W	L series	2.47844	1.00	4.58	0.30
Total:				100.00	

EDX results illustrated that the doped elements (P and W) were evenly distributed on the catalyst surface. However, there were no Na ions existed on the sample.

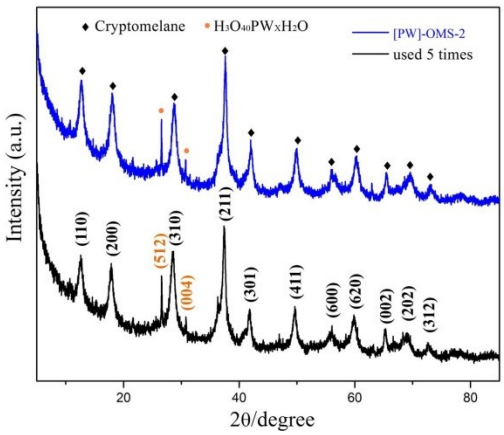


Fig. S3. The XRD patterns of fresh [PW]-OMS-2 and [PW]-OMS-2 reuse for 5 times.

The change of retrieved catalyst was measured by XRD, which confirms that the mixed crystal phase of cryptomelane/phosphotungstic acid were retained well after five recycles.

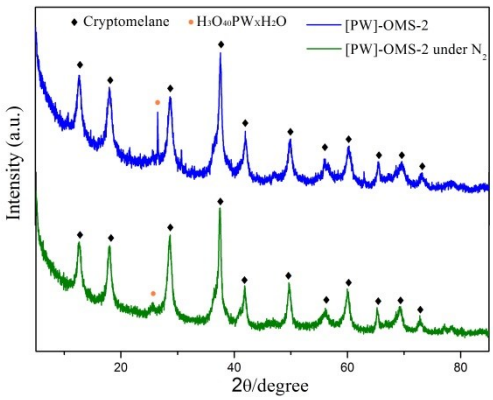


Fig. S4. The XRD patterns of fresh [PW]-OMS-2 and [PW]-OMS-2 that has reacted under N_2.

The XRD result showed that the diffraction peak of phosphotungstic acid of [PW]-OMS-2 became not obvious after 8 hours of reaction in nitrogen atmosphere, while the diffraction peak of cryptomelane has no obvious change.

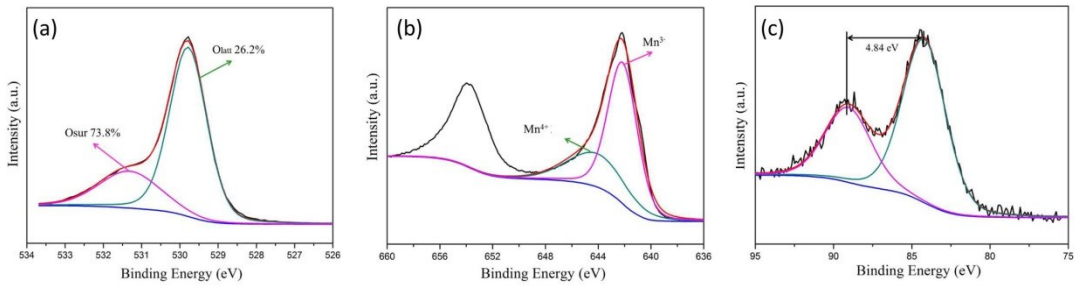


Fig. S5. The O1s (a), Mn2p (b) and Mn3s (c) XPS patterns of [PW]-OMS-2 that has reacted under N_2.

X-ray photoelectron spectroscopy was employed to analyze the surface elemental species of [PW]-OMS-2 used under N_2. The O 1s XPS spectra were fitted into two peaks including surface adsorbed unsaturated oxygen species at 531.32 eV and saturated lattice oxygen at 529.78 eV. Through analysis of the Mn 3s XPS spectra, the average oxidation state (AOS) of Mn was 3.50 (AOS calculated based on the following formula: AOS=8.956-1.126×ΔE, where ΔE is the binding energy difference between the doublet Mn 3s peaks).

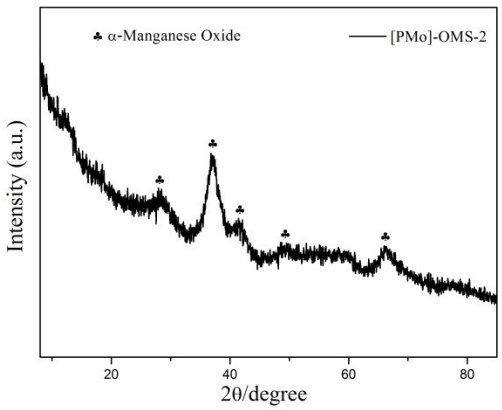
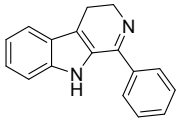


Fig. S6. The XRD patterns of [PMo]-OMS-2.

We prepared OMS-2-based nanocomposite doped by 2mol% phosphomolybdic acid hydrate and the catalyst was labeled as [PMo]-OMS-2. From the analysis of XRD spectra, [PMo]-OMS-2 were crystallized with alpha-Manganese Oxide (JCPDS file #53-633). Under the standard conditions of table 4 entry 12, the reaction catalyzed by [PMo]-OMS-2 obtained 83% conversion, 47% selectivity of 2a, and 53% selectivity of 3a. We speculate that this is caused by the crystal type of catalyst is not typical cryptomelane structure.

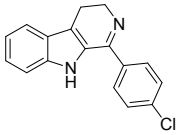
4. Spectrum data of the products

1-phenyl-dihydro-β-carboline (2a)



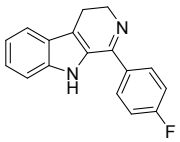
Yellow solid, isolated yield 94%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.48 (s, 1H), 7.75 – 7.70 (m, 2H), 7.66 (d, J = 8.0 Hz, 1H), 7.47 (d, J = 5.2 Hz, 3H), 7.33 (d, J = 8.2 Hz, 1H), 7.27 (d, J = 8.1 Hz, 1H), 7.18 (t, J = 7.4 Hz, 1H), 4.02 (t, J = 8.3 Hz, 2H), 2.97 (t, J = 8.3 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.41, 136.51, 135.55, 128.91, 127.75, 126.83, 124.50, 123.52, 119.33, 118.95, 116.82, 110.99, 47.72, 18.22.

1-(4-chlorophenyl)-dihydro-β-carboline (2b)



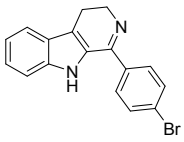
Yellow solid, isolated yield 81%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.34 (s, 1H), 7.57 (d, *J* = 8.4 Hz, 3H), 7.34 (d, *J* = 8.4 Hz, 2H), 7.28 – 7.19 (m, 2H), 7.11 (t, *J* = 7.4 Hz, 1H), 3.96 – 3.89 (m, 2H), 2.92 – 2.84 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.38, 135.66, 134.98, 128.18, 127.97, 126.46, 124.52, 123.77, 119.51, 119.04, 117.24, 111.01, 59.38, 47.79, 18.20.

1-(4-fluorophenyl)-dihydro-β-carboline (2c)



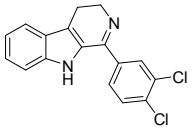
Yellow solid, isolated yield 96%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.35 (s, 1H), 7.67 – 7.59 (m, 2H), 7.56 (d, *J* = 8.1 Hz, 1H), 7.26 (dd, *J* = 7.4, 0.8 Hz, 1H), 7.22 – 7.17 (m, 1H), 7.11 – 7.02 (m, 3H), 3.95 – 3.86 (m, 2H), 2.89 – 2.84 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.06, 161.58, 157.39, 135.63, 132.65, 128.87, 126.57, 123.71, 119.02, 117.20, 114.86, 114.65, 111.00, 47.38, 18.20.

1-(4-bromophenyl)-dihydro-β-carboline (2d)



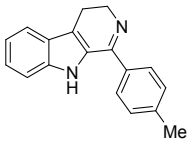
Yellow solid, isolated yield 86%. 1H NMR (400 MHz, DMSO) δ 11.15 (s, 1H), 7.77 – 7.69 (m, 4H), 7.63 (d, J = 8.0 Hz, 1H), 7.43 (d, J = 8.2 Hz, 1H), 7.24 – 7.20 (m, 1H), 7.11 – 7.07 (m, 1H), 3.93 – 3.85 (m, 2H), 2.90 – 2.85 (m, 2H). ^{13}C NMR (101 MHz, DMSO) δ 158.24, 137.46, 136.98, 131.91, 130.58, 127.66, 125.21, 124.35, 123.75, 120.10, 117.14, 113.19, 48.82, 19.30.

1-(3, 4-dichlorophenyl)-dihydro-β-carboline (2e)



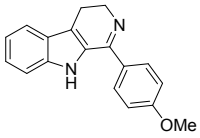
White crystalline, isolated yield 76%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.51 (s, 1H), 7.72 (d, *J* = 1.9 Hz, 1H), 7.59 (d, *J* = 8.0 Hz, 1H), 7.48 – 7.41 (m, 2H), 7.31 – 7.28 (m, 1H), 7.26 – 7.22 (m, 1H), 7.12 (ddd, *J* = 8.0, 6.9, 1.1 Hz, 1H), 3.99 – 3.90 (m, 2H), 2.93 – 2.86 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.43, 136.21, 135.82, 133.21, 132.06, 129.67, 128.78, 126.03, 124.44, 123.99, 119.63, 119.11, 117.66, 111.10, 47.78, 18.16.

1-(p-tolyl)-dihydro-β-carboline (2f)



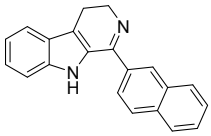
White crystalline, isolated yield 76%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.29 (s, 1H), 7.55 (t, *J* = 8.9 Hz, 3H), 7.25 – 7.16 (m, 4H), 7.08 (t, *J* = 7.4 Hz, 1H), 3.98 – 3.82 (m, 2H), 2.92 – 2.82 (m, 2H), 2.32 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.29, 139.04, 135.47, 133.69, 128.45, 126.82, 124.54, 123.46, 119.31, 118.94, 116.75, 110.96, 47.67, 20.37, 18.23.

1-(4-methoxyphenyl)-dihydro-β-carboline (2g)



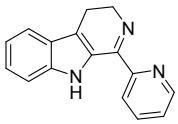
Pale yellow solid, isolated yield 99%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.52 (s, 1H), 7.62 – 7.51 (m, 3H), 7.24 (d, *J* = 8.2 Hz, 1H), 7.18 – 7.15 (m, 1H), 7.10 – 7.05 (m, 1H), 6.89 – 6.80 (m, 2H), 3.91 – 3.83 (m, 2H), 3.72 (s, 3H), 2.88 – 2.80 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.01, 157.83, 135.56, 129.03, 128.35, 126.95, 124.54, 123.41, 119.27, 118.90, 116.84, 113.07, 111.00, 54.33, 47.49, 18.25.

1-naphthyl-dihydro-β-carboline (2h)



Pale yellow solid, isolated yield 99%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.45 (s, 1H), 8.05 (s, 1H), 7.80 – 7.69 (m, 4H), 7.56 (d, *J* = 8.0 Hz, 1H), 7.45 – 7.38 (m, 2H), 7.25 (d, *J* = 8.2 Hz, 1H), 7.18 (ddd, *J* = 8.2, 7.0, 1.1 Hz, 1H), 7.11 – 7.07 (m, 1H), 3.97 – 3.90 (m, 2H), 2.89 – 2.83 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.47, 135.66, 133.62, 133.00, 131.94, 127.60, 126.77, 125.99, 125.52, 124.51, 124.10, 123.62, 119.39, 119.01, 117.06, 111.07, 47.71, 18.23.

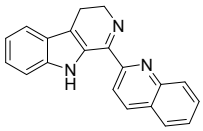
1-pyridyl-dihydro-β-carboline (2i)



Pale yellow solid, isolated yield 78%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.81 (s, 1H), 8.64 (ddd, *J* = 4.8, 1.6, 0.8 Hz, 1H), 8.26 (d, *J* = 8.1 Hz, 1H), 7.76 (td, *J* = 7.8, 1.8 Hz, 1H), 7.56 (dd, *J* = 8.0, 0.6 Hz, 1H), 7.42 (d, *J* = 8.3 Hz, 1H), 7.32 (ddd, *J* = 7.5, 4.9, 1.1 Hz, 1H), 7.22 (ddd, *J* = 13.8, 7.4, 3.9 Hz, 1H), 7.13 – 7.02 (m, 1H), 4.09 (dd, *J* = 9.3, 8.0 Hz, 2H), 2.93 (dd, *J* = 9.3, 8.0 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.40, 154.79, 146.94, 135.90, 135.42,

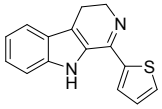
127.34, 123.91, 123.38, 120.30, 118.77, 116.20, 111.26, 48.11, 18.26.

1-quinolyl-dihydro-β-carboline (2j)



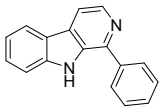
Pale yellow solid, isolated yield 85%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.04 (s, 1H), 8.36 (d, *J* = 8.7 Hz, 1H), 8.18 (dd, *J* = 8.4, 3.1 Hz, 2H), 7.79 (d, *J* = 8.0 Hz, 1H), 7.74 – 7.69 (m, 1H), 7.63 – 7.48 (m, 3H), 7.24 (dd, *J* = 11.1, 4.0 Hz, 1H), 7.12 – 7.05 (m, 1H), 4.15 (dd, *J* = 9.3, 8.0 Hz, 2H), 2.96 (dd, *J* = 9.3, 8.0 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.33, 154.98, 145.74, 137.27, 135.91, 128.76, 128.52, 127.42, 126.78, 126.42, 123.95, 123.40, 118.83, 117.80, 116.32, 111.30, 48.35, 18.28.

1- thienyl-dihydro-β-carboline (2k)



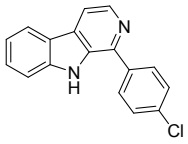
Light yellow oily liquid, isolated yield 72%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.69 (s, 1H), 7.57 (d, *J* = 8.0 Hz, 1H), 7.50 (dd, *J* = 3.6, 0.8 Hz, 1H), 7.37 – 7.30 (m, 2H), 7.25 – 7.19 (m, 1H), 7.13 – 7.08 (m, 1H), 7.02 (dd, *J* = 5.1, 3.7 Hz, 1H), 3.91 – 3.82 (m, 2H), 2.84 (dd, *J* = 9.0, 7.5 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 152.21, 141.07, 135.77, 127.49, 126.63, 126.29, 124.56, 123.72, 119.51, 118.98, 117.45, 111.16, 47.41, 18.20.

1-phenyl-β-carboline (3a)



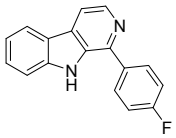
Yellow solid, isolated yield 99%. ^{1}H NMR (400 MHz, DMSO) δ 11.55 (s, 1H), 8.48 (d, *J* = 5.2 Hz, 1H), 8.26 (d, *J* = 7.9 Hz, 1H), 8.12 (d, *J* = 5.2 Hz, 1H), 8.08 – 8.03 (m, 2H), 7.70 – 7.51 (m, 5H), 7.30 – 7.24 (m, 1H). ^{13}C NMR (101 MHz, DMSO) δ 142.6, 141.59, 138.87, 133.49, 129.65, 129.20, 128.92, 128.63, 122.06, 121.31, 119.98, 114.35, 112.91.

1-(4-chlorophenyl)-β-carboline (3b)



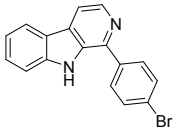
Yellow solid, isolated yield 96%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.67 (s, 1H), 8.49 (d, *J* = 5.2 Hz, 1H), 8.10 (d, *J* = 7.9 Hz, 1H), 7.88 (d, *J* = 5.2 Hz, 1H), 7.81 (d, *J* = 8.4 Hz, 2H), 7.50 (dd, *J* = 11.2, 3.9 Hz, 1H), 7.43 (dd, *J* = 8.3, 3.3 Hz, 3H), 7.26 (t, *J* = 7.4 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 140.70, 139.45, 138.54, 135.95, 133.78, 132.44, 129.13, 128.34, 127.65, 120.83, 119.41, 113.06, 110.59.

1-(4-fluorophenyl)-β-carboline (3c)



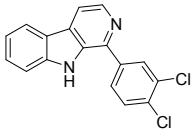
Yellow oily liquid, isolated yield 97%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.61 (s, 1H), 8.55 (d, *J* = 5.2 Hz, 1H), 8.16 (d, *J* = 8.0 Hz, 1H), 7.95 – 7.93 (m, 2H), 7.56 (ddd, *J* = 8.2, 7.0, 1.2 Hz, 1H), 7.50 (dt, *J* = 8.2, 0.8 Hz, 1H), 7.32 (ddd, *J* = 8.0, 7.0, 1.1 Hz, 1H), 7.27 – 7.23 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.30, 160.83, 140.99, 139.38, 138.54, 133.66, 132.39, 128.86, 127.59, 120.82, 119.38, 115.25, 112.84, 110.55.

1-(4-bromophenyl)-β-carboline (3d)



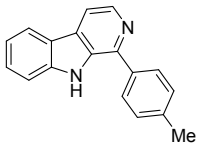
Yellow oily liquid, isolated yield 99%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.84 (s, 1H), 8.45 (d, *J* = 5.2 Hz, 1H), 8.06 (d, *J* = 7.9 Hz, 1H), 7.85 (d, *J* = 5.2 Hz, 1H), 7.68 (d, *J* = 8.4 Hz, 2H), 7.51 – 7.43 (m, 3H), 7.39 (d, *J* = 8.2 Hz, 1H), 7.25 – 7.20 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 140.69, 139.49, 138.44, 136.30, 132.41, 131.17, 129.14, 128.63, 127.64, 121.96, 120.79, 119.37, 113.10, 110.60.

1-(3, 4-dichlorophenyl)-β-carboline (3e)



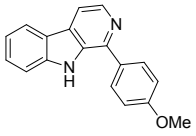
White crystalline, isolated yield 84%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.84 (s, 1H), 8.90 (s, 1H), 8.47 (d, *J* = 5.2 Hz, 1H), 8.07 (d, *J* = 7.9 Hz, 1H), 7.89 (dd, *J* = 11.8, 3.6 Hz, 2H), 7.64 (dd, *J* = 8.3, 2.0 Hz, 1H), 7.42 (dd, *J* = 8.2, 3.0 Hz, 2H), 7.24 (t, *J* = 7.4 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 139.57, 139.22, 138.47, 137.36, 132.33, 131.80, 130.23, 129.90, 129.47, 128.88, 127.81, 127.33, 126.67, 126.20, 120.77, 119.53, 113.49, 110.69.

1-(p-tolyl)-β-carboline (3f)



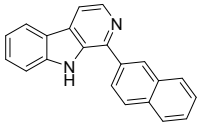
White crystalline, isolated yield 63%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.78 (s, 1H), 8.43 (d, *J* = 5.3 Hz, 1H), 8.04 (d, *J* = 7.9 Hz, 1H), 7.80 (d, *J* = 5.3 Hz, 1H), 7.74 – 7.71 (m, 2H), 7.42 (ddd, *J* = 8.2, 7.1, 1.1 Hz, 1H), 7.35 (d, *J* = 8.2 Hz, 1H), 7.23 – 7.18 (m, 3H), 2.30 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 142.15, 139.37, 138.32, 137.64 (s), 134.62, 132.48, 128.73, 127.31, 126.95, 120.77, 119.07, 112.48, 110.52, 20.29.

1-(4-methoxyphenyl)-β-carboline (3g)



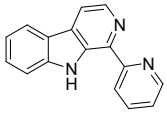
Yellow solid, isolated yield 93%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.52 (s, 1H), 8.46 (d, *J* = 5.3 Hz, 1H), 8.08 (d, *J* = 7.9 Hz, 1H), 7.85 – 7.81 (m, 3H), 7.49 – 7.41 (m, 2H), 7.23 (ddd, *J* = 8.0, 6.9, 1.2 Hz, 1H), 7.02 (d, *J* = 8.8 Hz, 2H), 3.81 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.12, 141.91, 139.31, 138.44, 132.36, 130.98, 130.06, 128.69, 128.36, 127.38, 120.77, 119.20, 113.60, 113.31, 112.31, 110.52, 54.41.

1-naphthyl-β-carboline (3h)



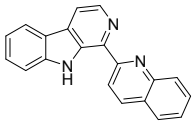
Pale yellow solid, isolated yield 99%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.08 (s, 1H), 8.46 (d, *J* = 5.2 Hz, 1H), 8.07 (s, 1H), 8.03 (d, *J* = 7.9 Hz, 1H), 7.81 (dd, *J* = 10.6, 3.6 Hz, 2H), 7.71 (d, *J* = 8.5 Hz, 1H), 7.67 (d, *J* = 8.1 Hz, 1H), 7.60 (d, *J* = 8.0 Hz, 1H), 7.34 (tddd, *J* = 16.2, 8.1, 6.9, 1.2 Hz, 4H), 7.18 (ddd, *J* = 8.0, 7.0, 1.1 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.92, 139.55, 138.28, 134.69, 132.79, 132.25, 128.86, 127.77, 127.40, 127.20, 126.68, 126.10, 125.35, 124.77, 120.76, 119.11, 112.75, 110.61.

1-pyridyl-β-carboline (3i)



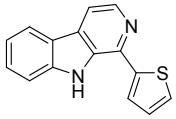
Yellow oily liquid, isolated yield 77%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.21 (s, 1H), 8.64 (dd, *J* = 10.5, 4.7 Hz, 2H), 8.43 (d, *J* = 5.1 Hz, 1H), 8.04 (d, *J* = 7.9 Hz, 1H), 7.88 (d, *J* = 5.1 Hz, 1H), 7.76 (td, *J* = 7.8, 1.8 Hz, 1H), 7.47 (ddd, *J* = 10.8, 9.2, 4.5 Hz, 2H), 7.18 (ddd, *J* = 12.3, 5.8, 2.7 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.96, 147.19, 139.56, 137.07, 135.77, 133.71, 129.41, 127.35, 121.83, 120.61, 120.16, 118.72, 114.38, 110.80.

1-quinolyl-β-carboline (3j)



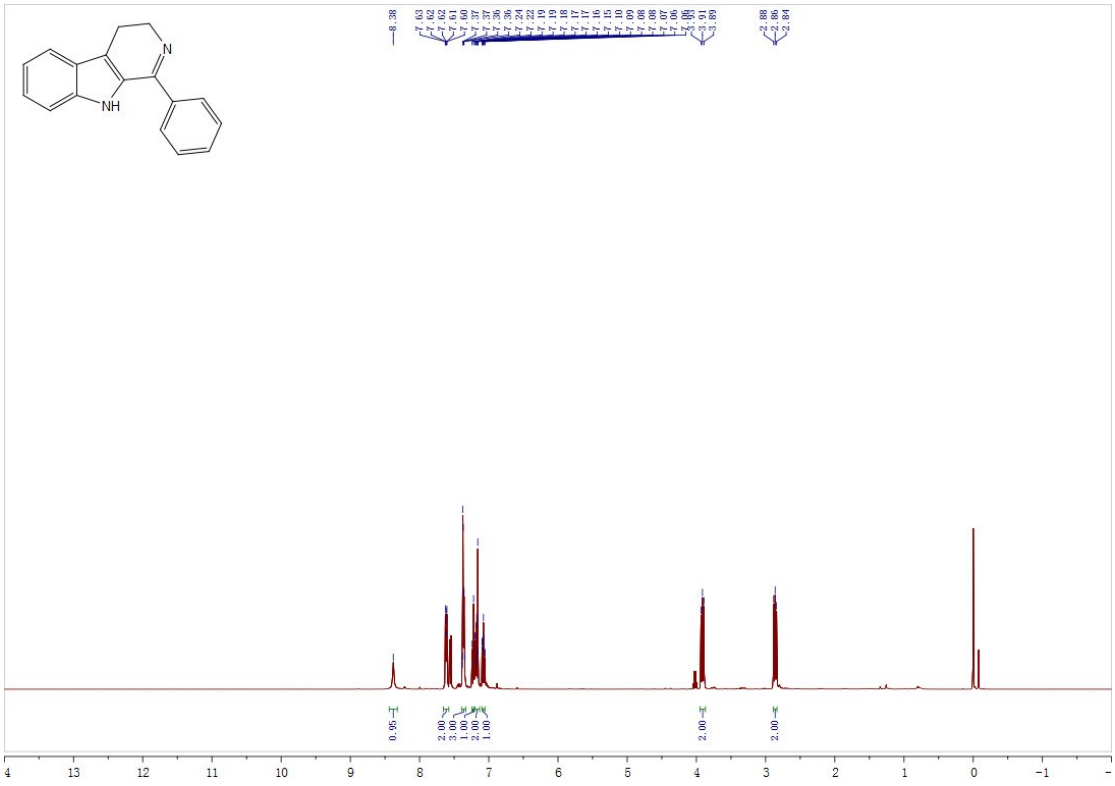
Light yellow solid, isolated yield 93%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.36 (s, 1H), 8.65 (d, *J* = 8.7 Hz, 1H), 8.39 (d, *J* = 5.0 Hz, 1H), 8.04 (d, *J* = 8.7 Hz, 1H), 8.00 (d, *J* = 8.4 Hz, 1H), 7.95 (d, *J* = 7.9 Hz, 1H), 7.78 (d, *J* = 5.0 Hz, 1H), 7.62 (d, *J* = 8.1 Hz, 1H), 7.56 (ddd, *J* = 8.3, 6.9, 1.4 Hz, 1H), 7.43 (tt, *J* = 8.2, 4.2 Hz, 2H), 7.38 – 7.32 (m, 1H), 7.13 (ddd, *J* = 7.7, 4.7, 1.5 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.96, 146.11, 139.48, 137.05, 136.72, 135.31, 134.11, 129.30, 128.40, 127.99, 127.31, 126.64, 125.48, 120.57, 120.08, 118.78, 118.03, 114.65, 110.83.

1-thienyl-β-carboline (3k)

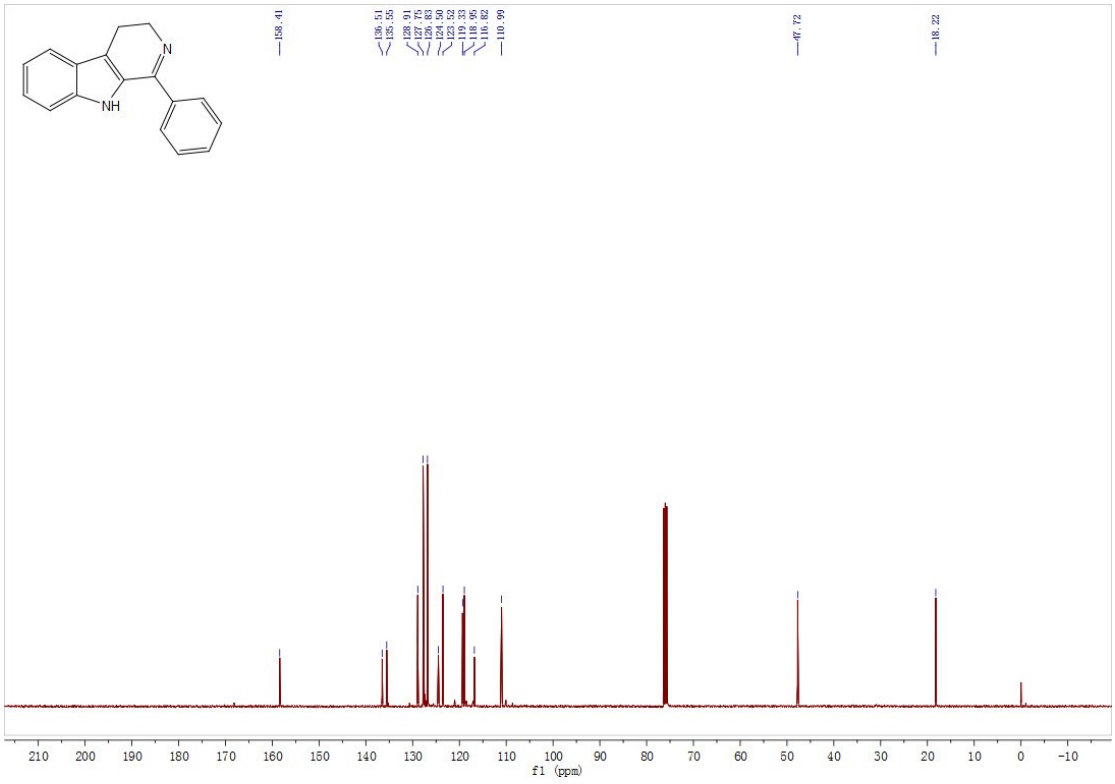


Light yellow oily liquid, isolated yield 79%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.65 (s, 1H), 8.42 (d, *J* = 5.2 Hz, 1H), 8.07 (d, *J* = 7.8 Hz, 1H), 7.82 (d, *J* = 5.2 Hz, 1H), 7.68 (dd, *J* = 3.6, 1.0 Hz, 1H), 7.52 – 7.47 (m, 2H), 7.43 (dd, *J* = 5.1, 1.0 Hz, 1H), 7.25 (ddd, *J* = 8.0, 6.0, 2.1 Hz, 1H), 7.17 (dd, *J* = 5.1, 3.7 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.89, 139.47, 138.37, 136.06, 131.22, 129.37, 127.65, 127.00, 126.17, 124.00, 120.82, 119.56, 112.75, 110.72.

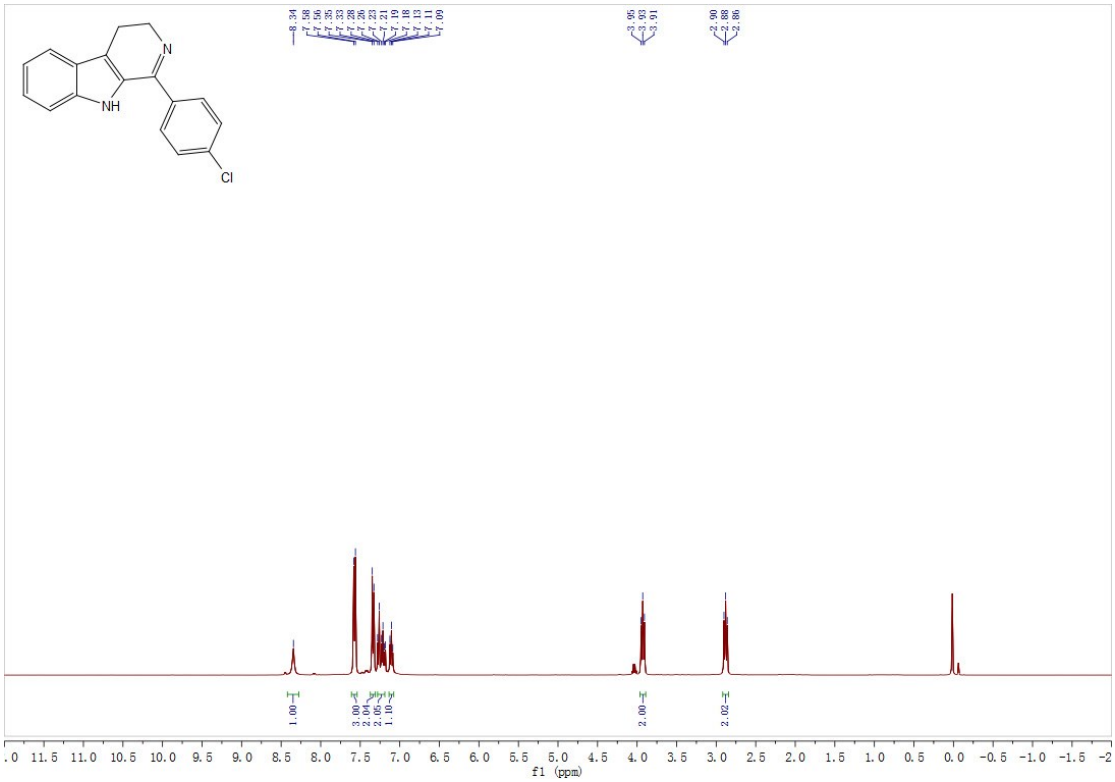
5. Copies of ^{1}H and ^{13}C Spectra



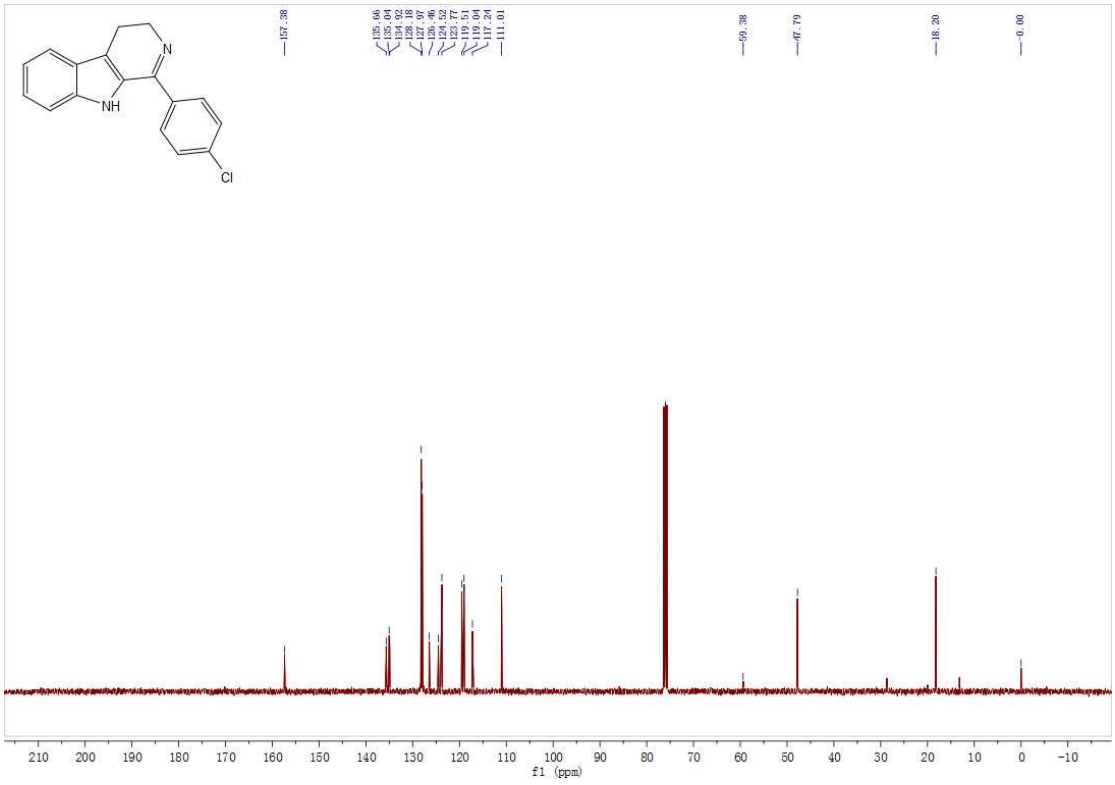
^{1}H NMR of **2a**



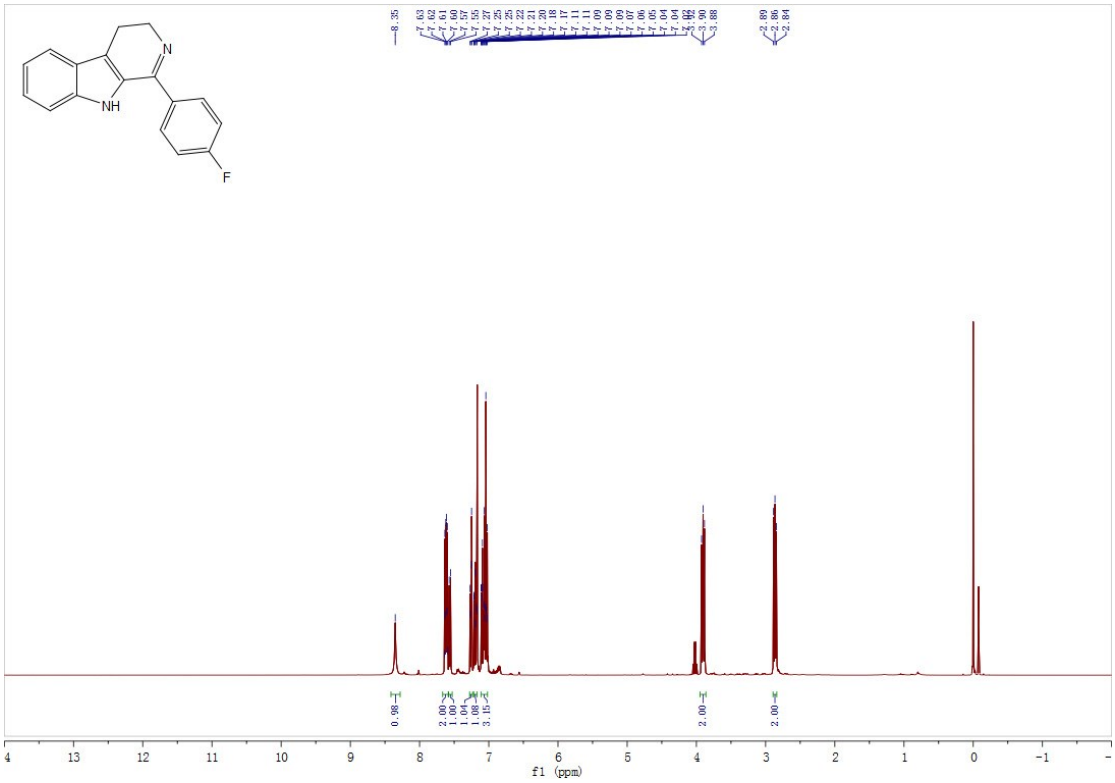
^{13}C NMR of **2a**



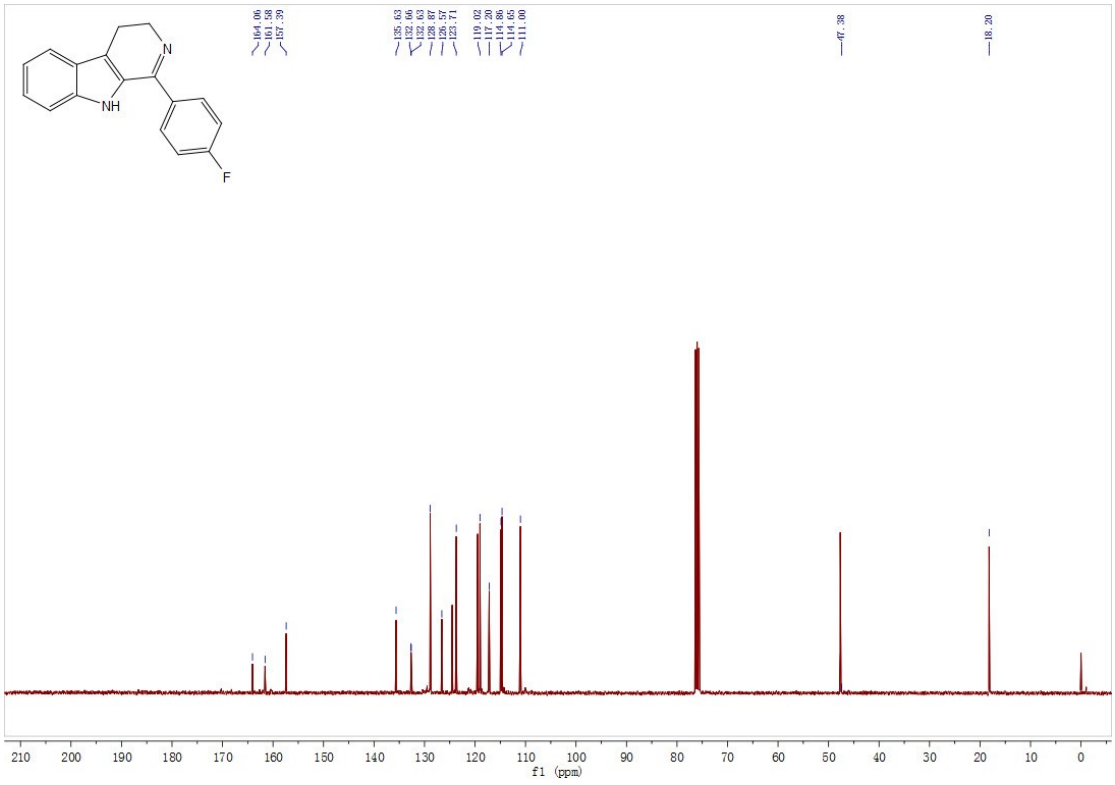
^{1}H NMR of **2b**



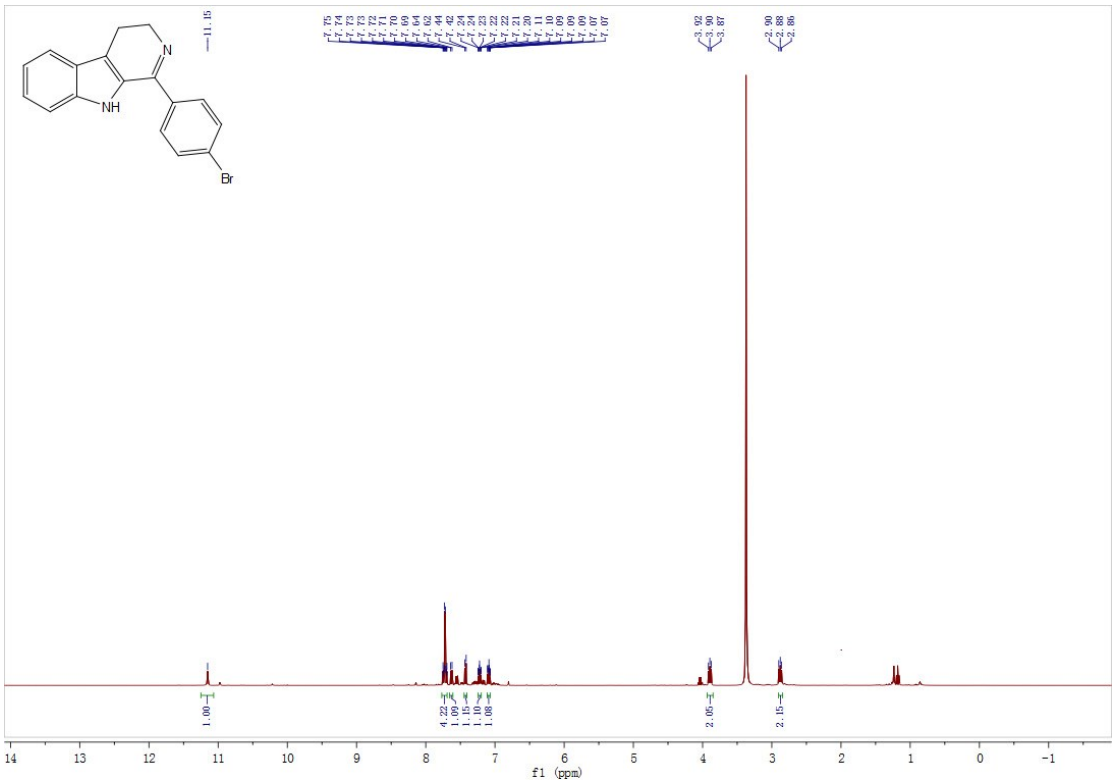
^{13}C NMR of **2b**



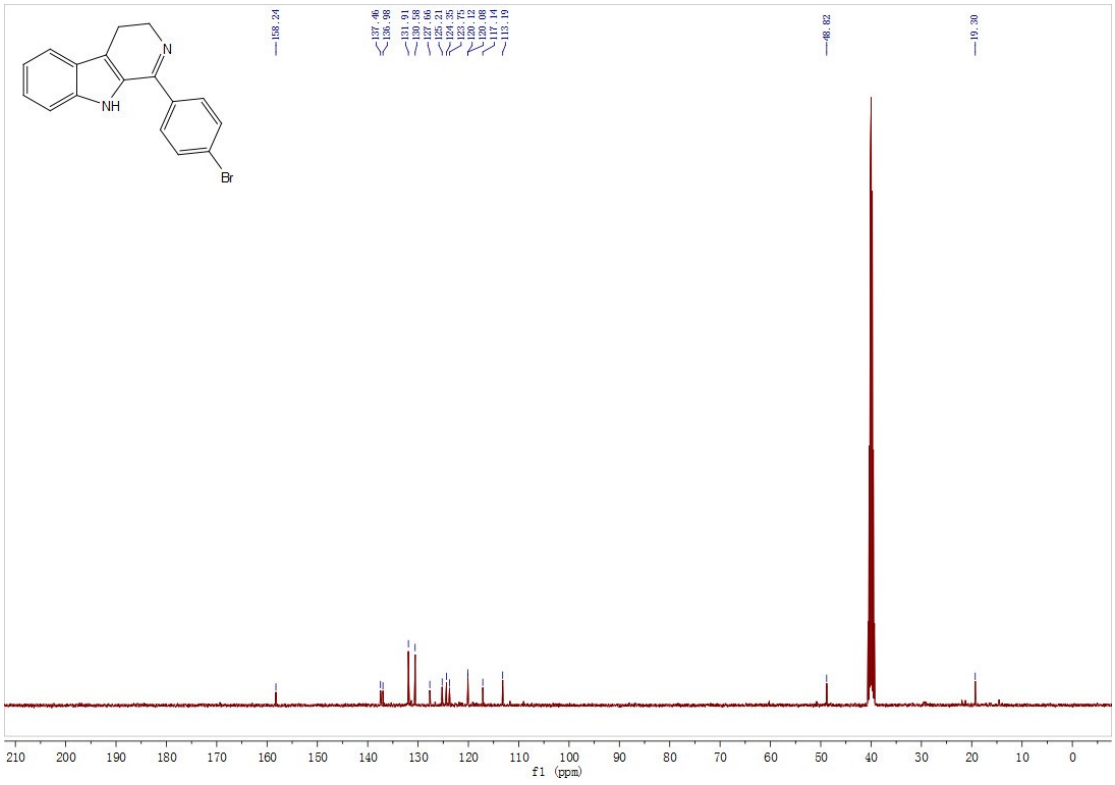
^{1}H NMR of **2c**



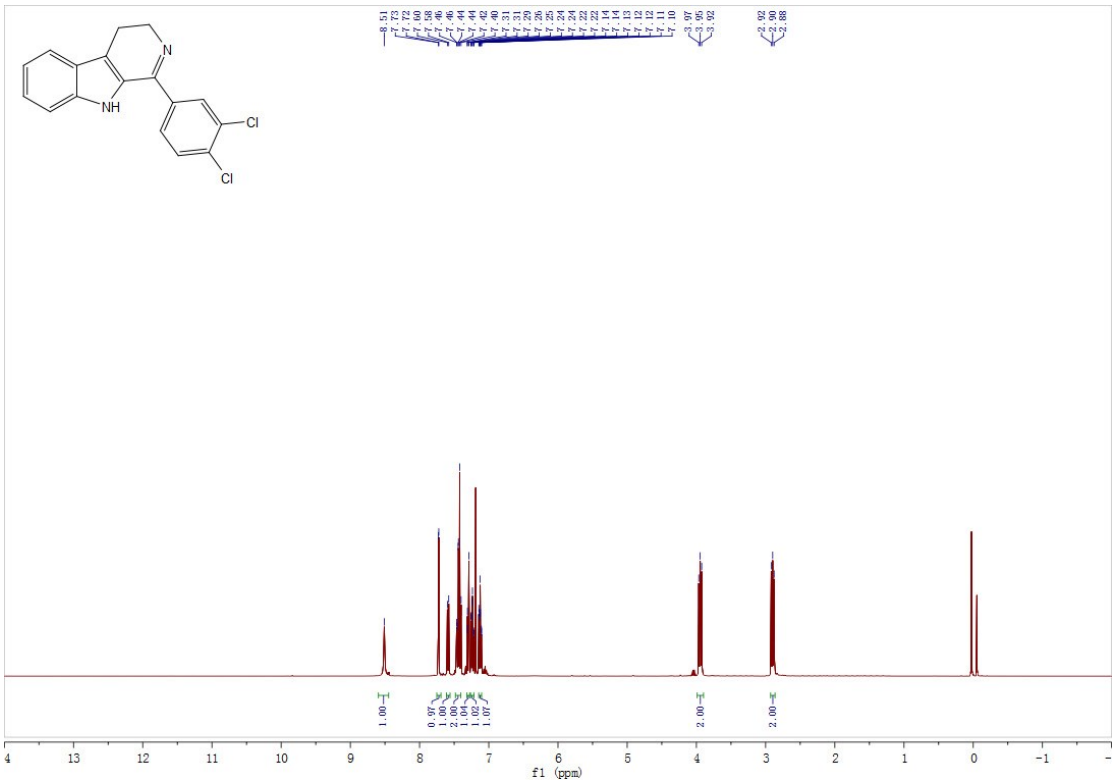
^{13}C NMR of **2c**



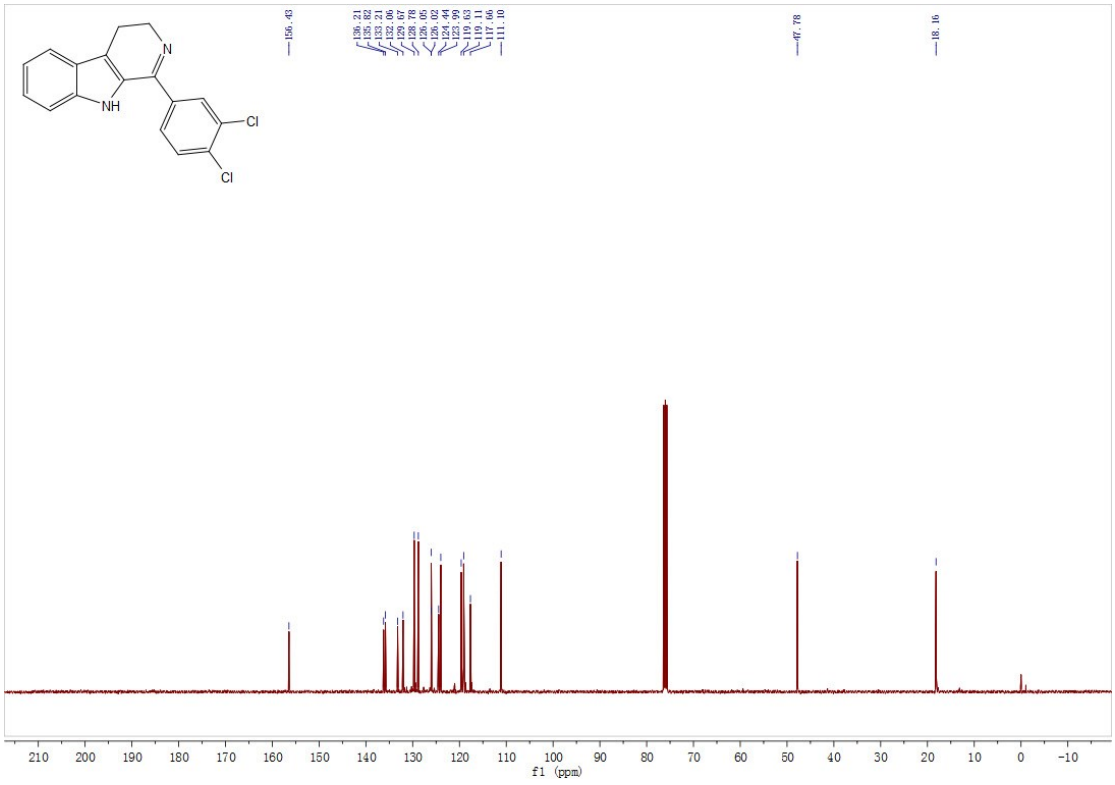
^{1}H NMR of **2d**



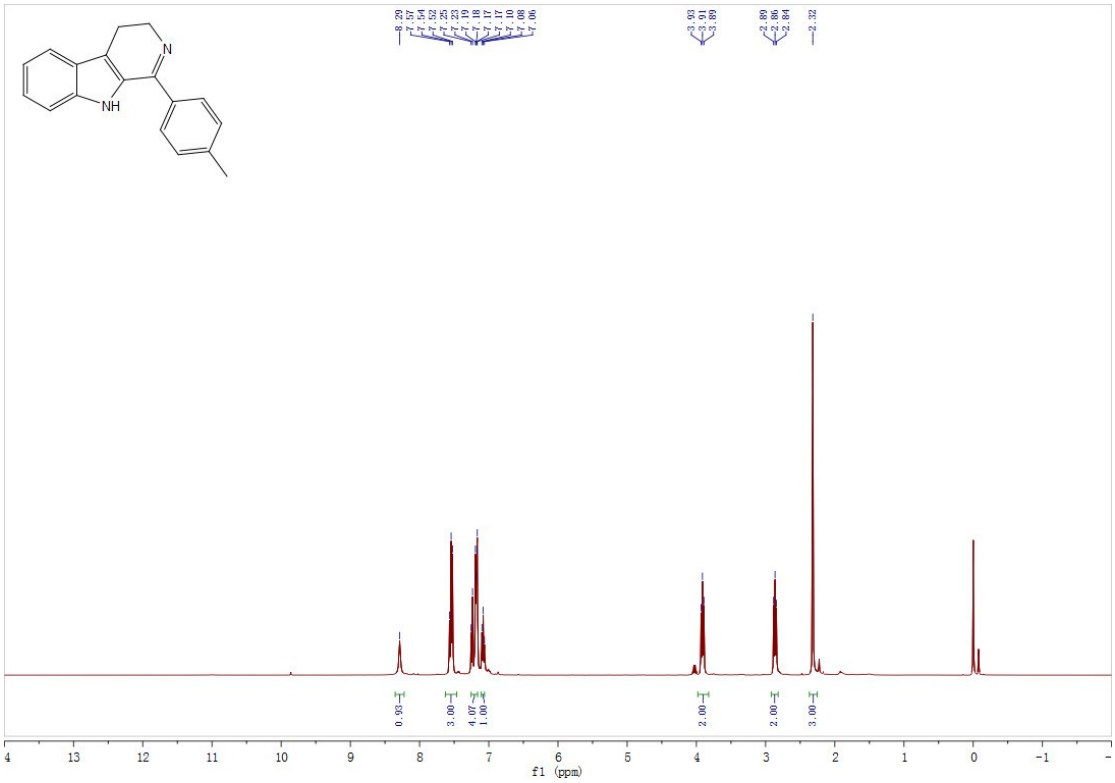
^{13}C NMR of **2d**



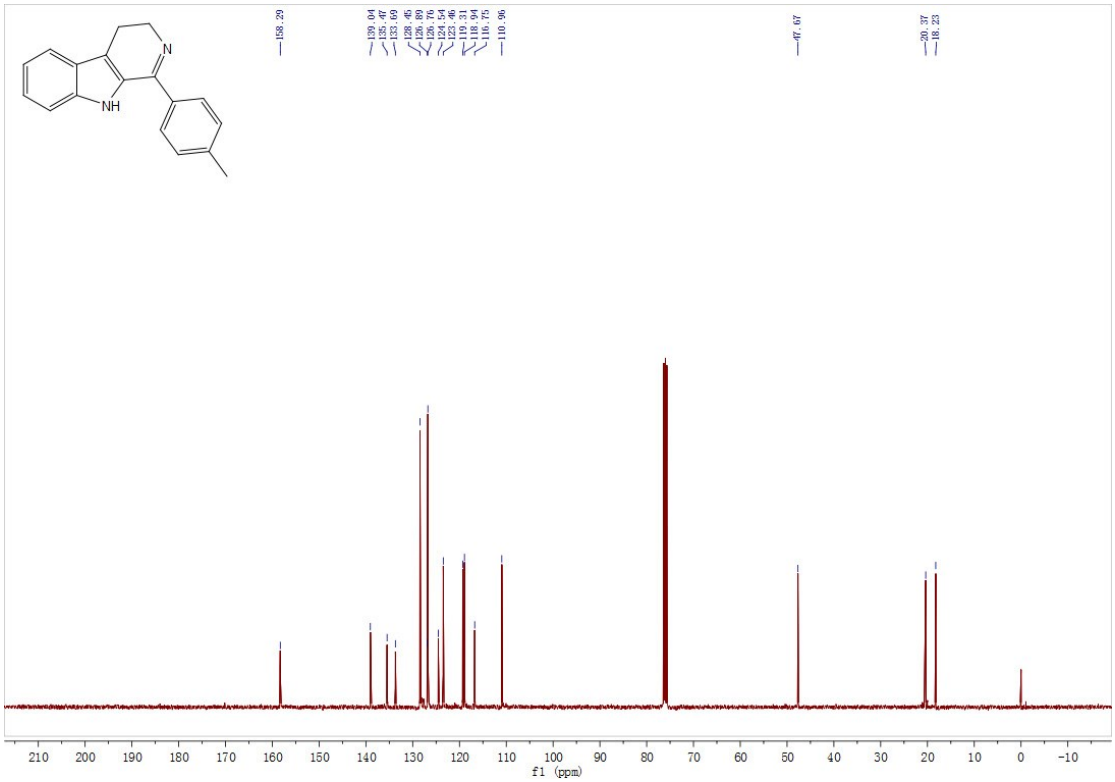
^{1}H NMR of **2e**



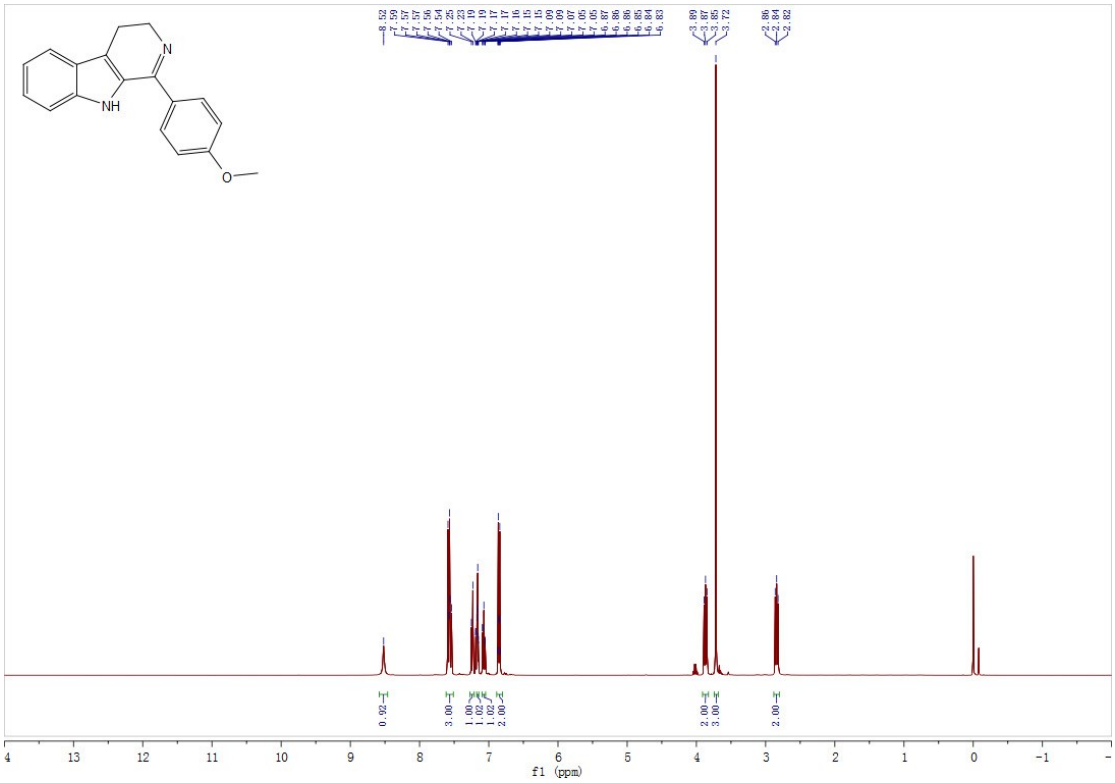
^{13}C NMR of **2e**



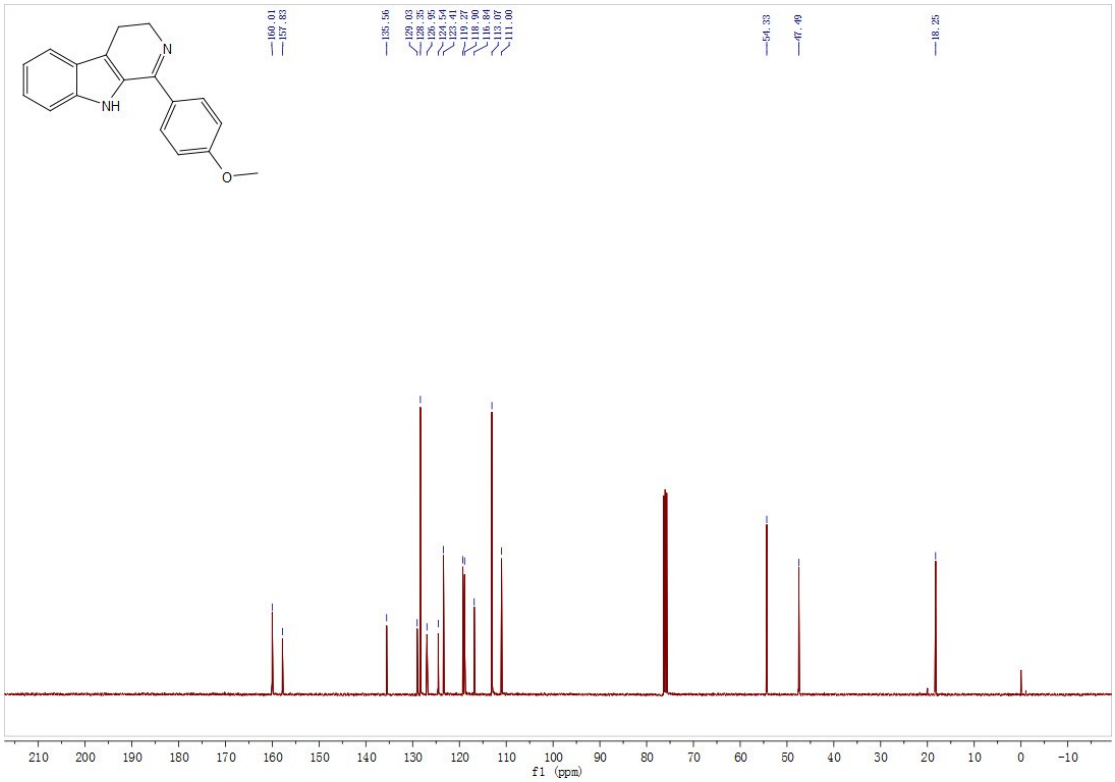
^{1}H NMR of **2f**



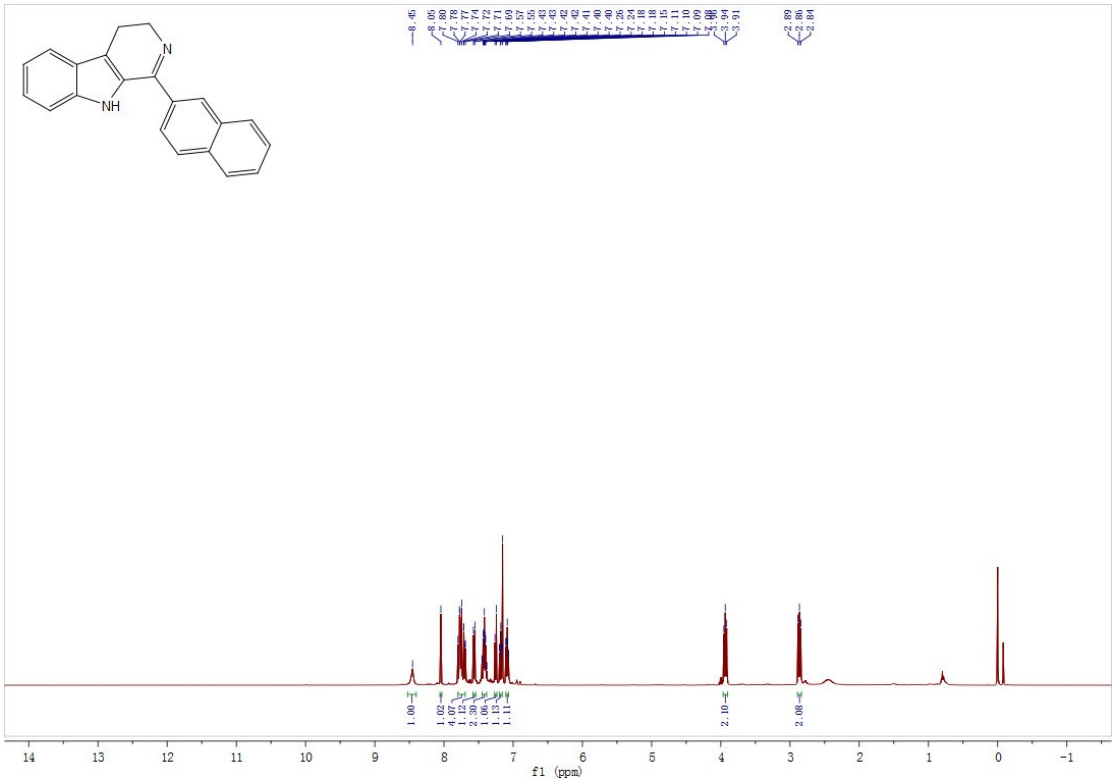
^{13}C NMR of **2f**



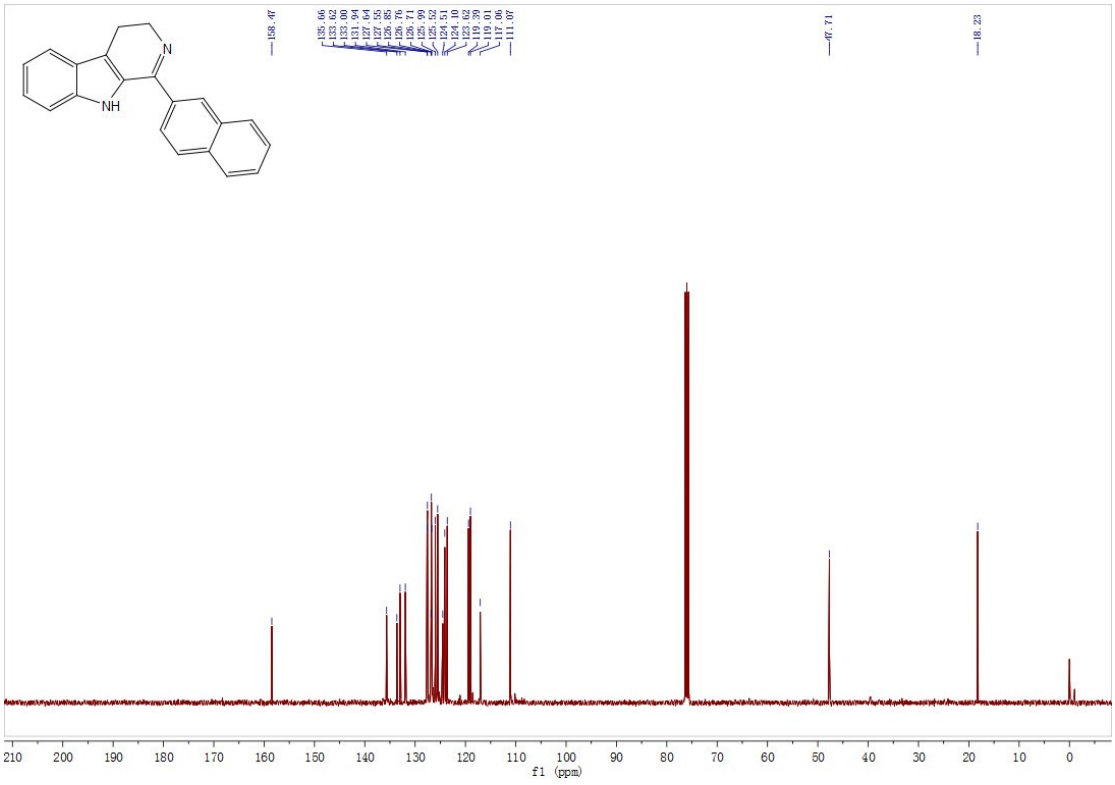
^{1}H NMR of **2g**



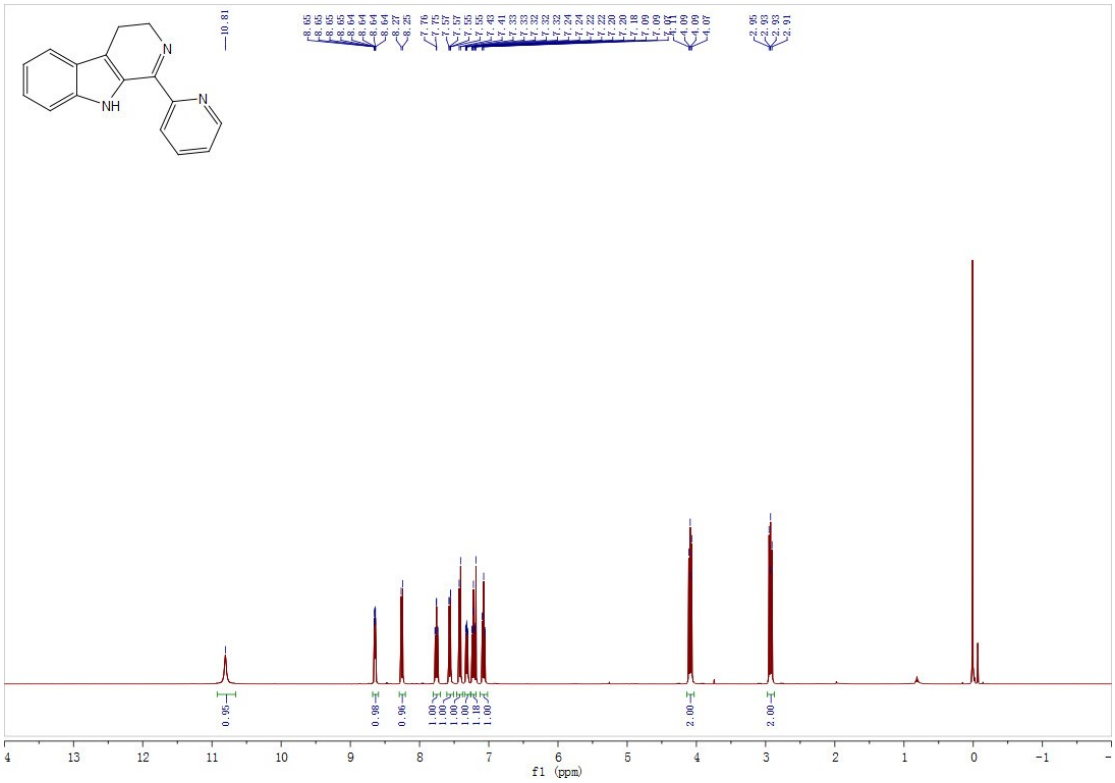
^{13}C NMR of **2g**



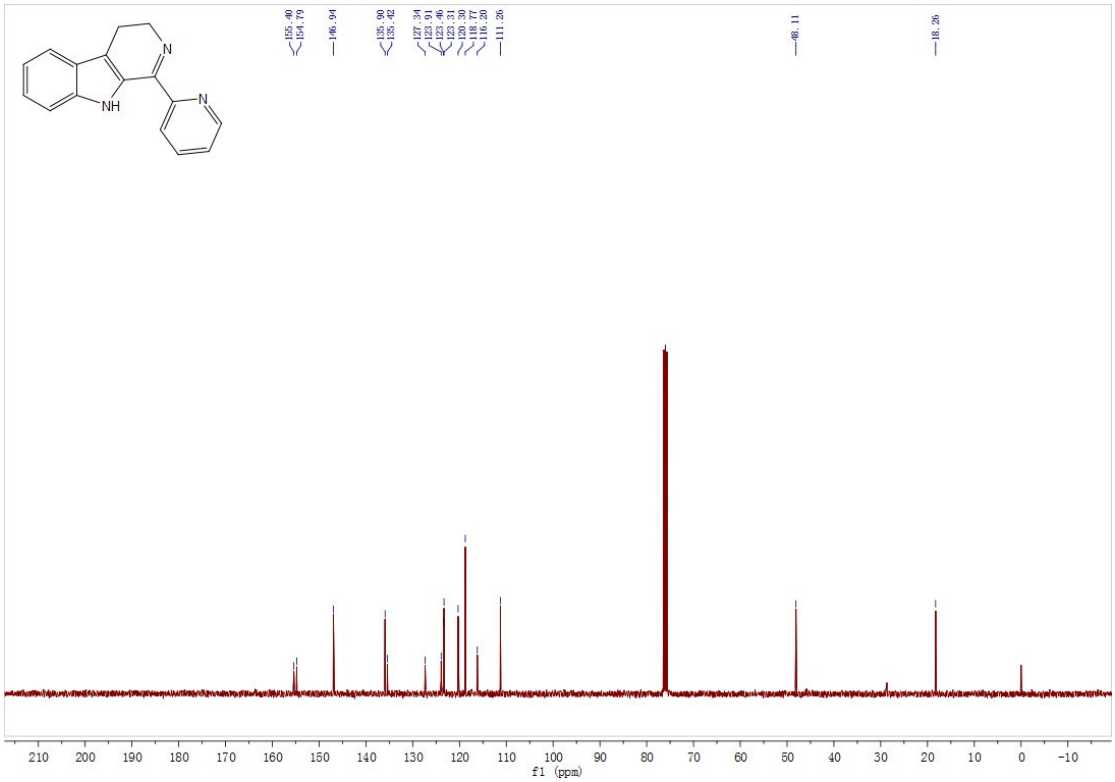
^{1}H NMR of **2h**



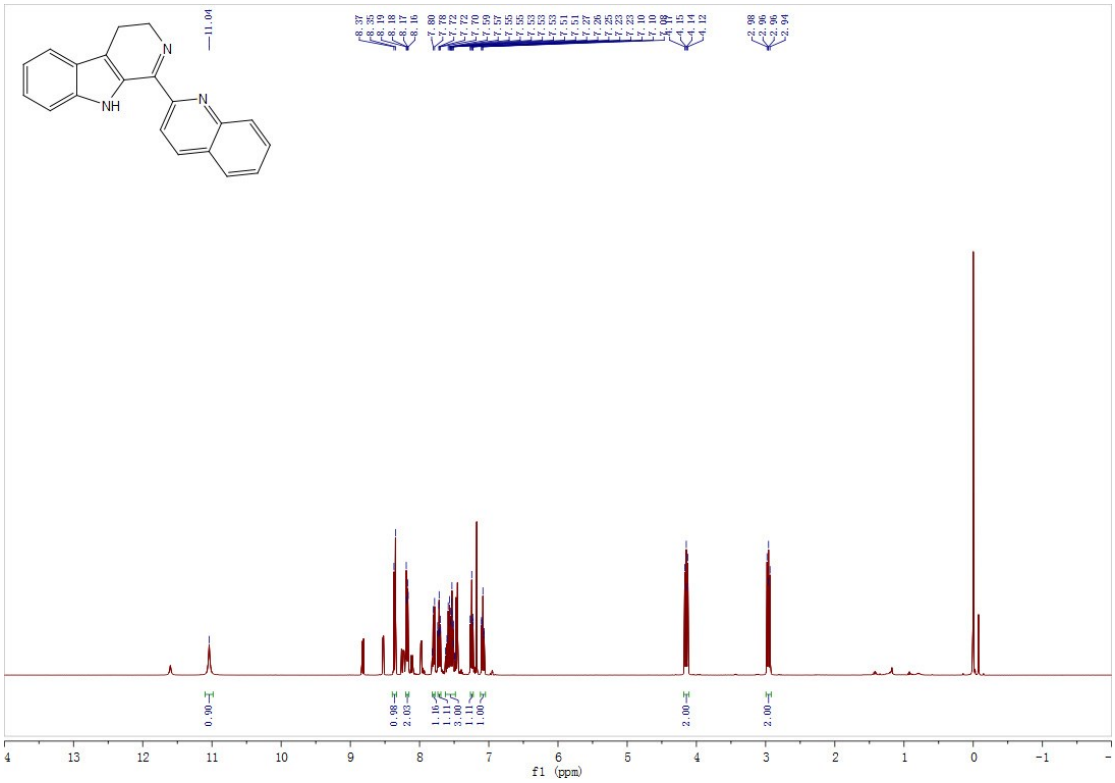
^{13}C NMR of **2h**



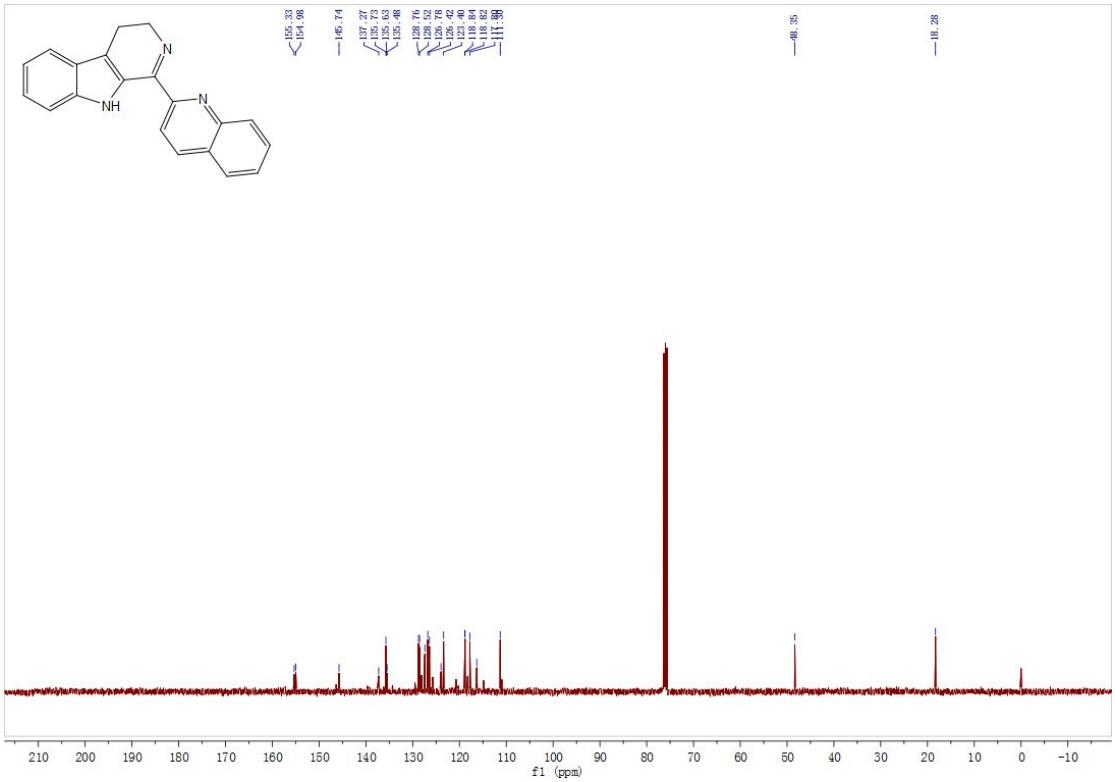
^{1}H NMR of **2i**



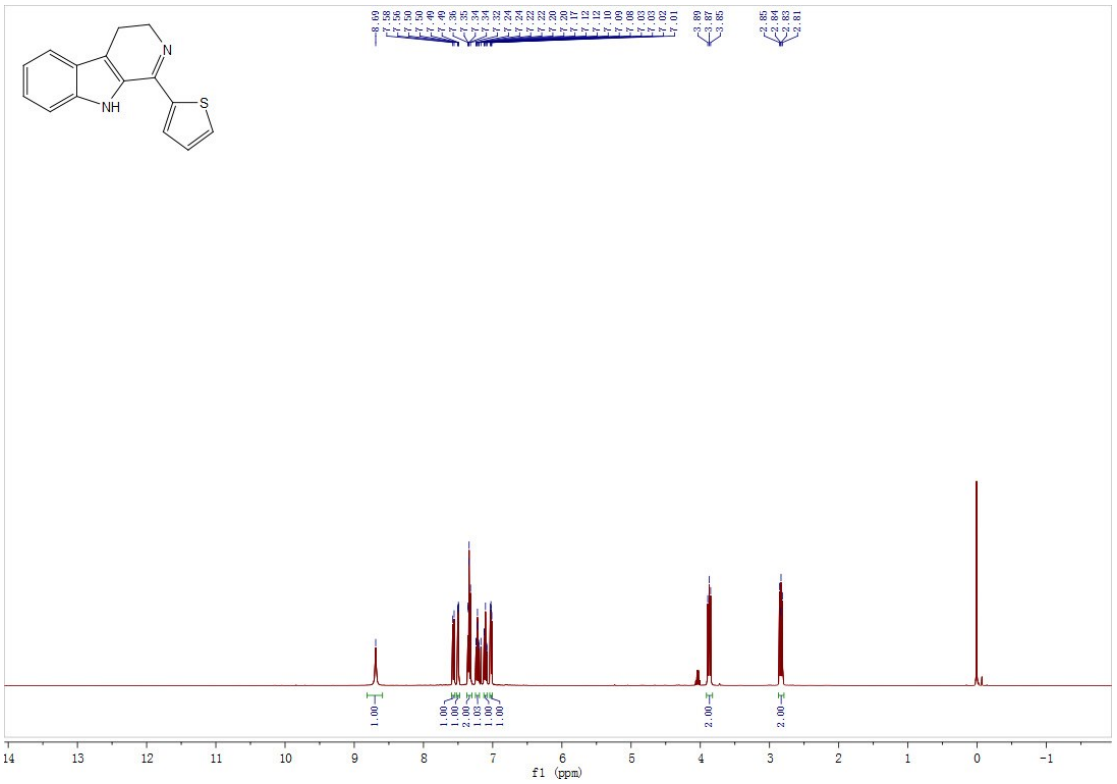
^{13}C NMR of **2i**



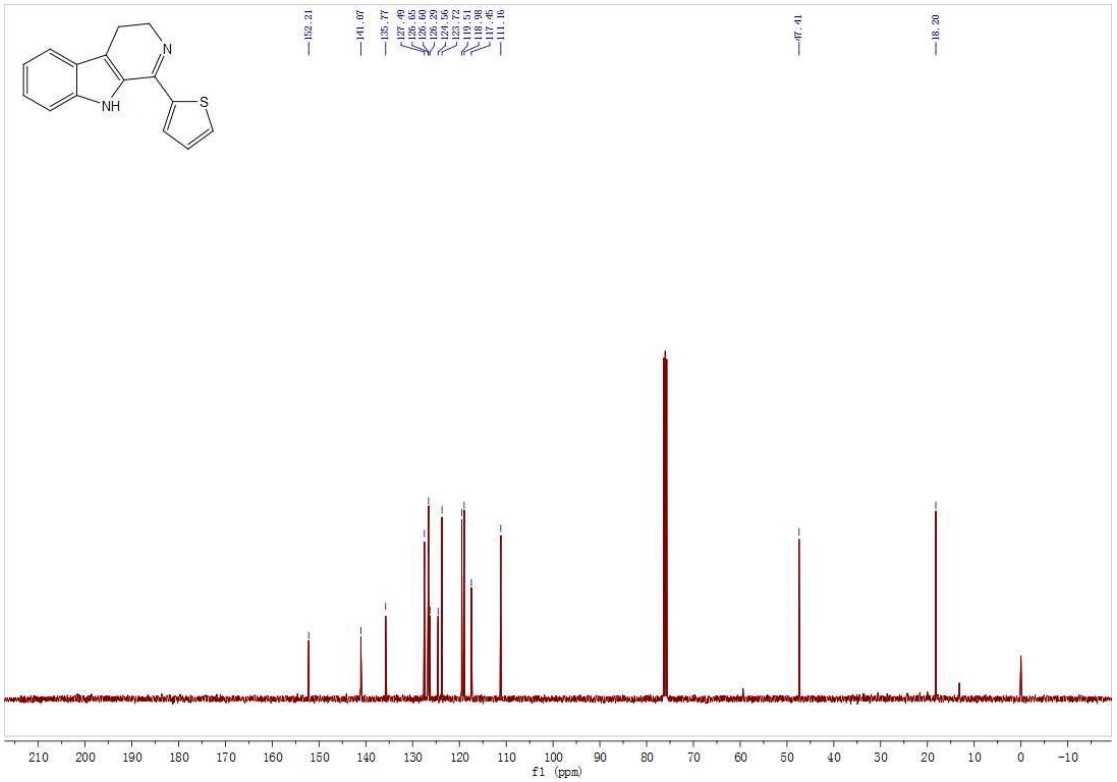
^{1}H NMR of **2j**



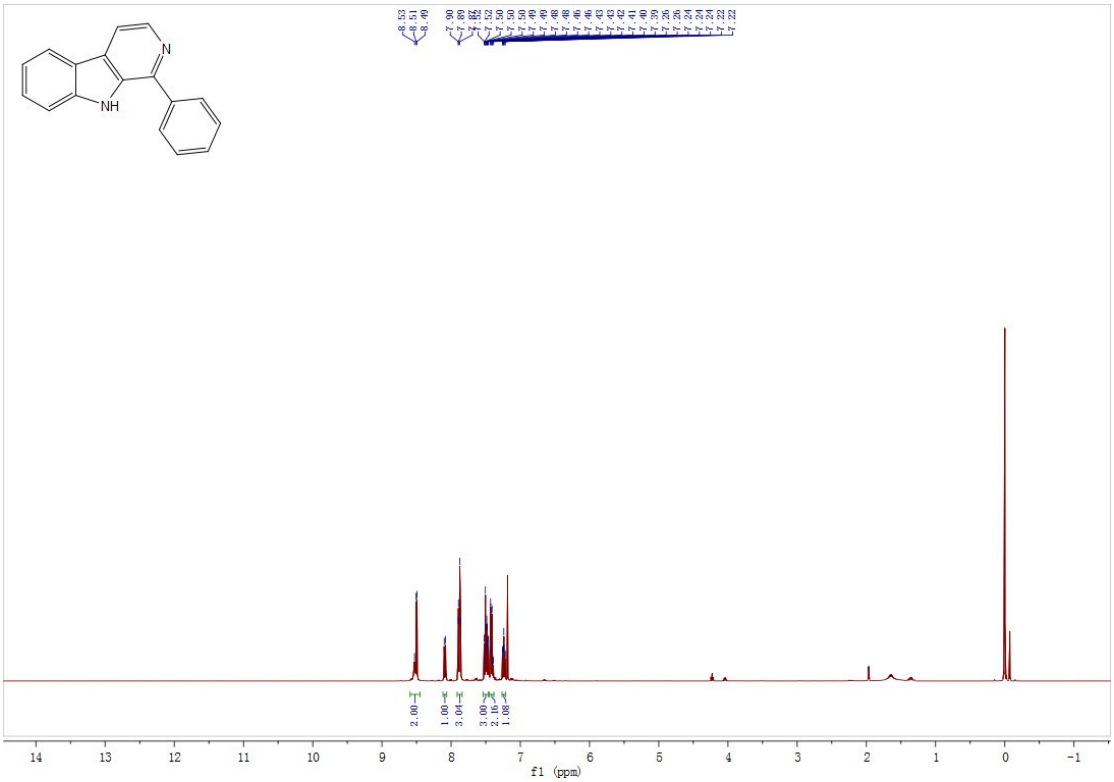
^{13}C NMR of **2j**



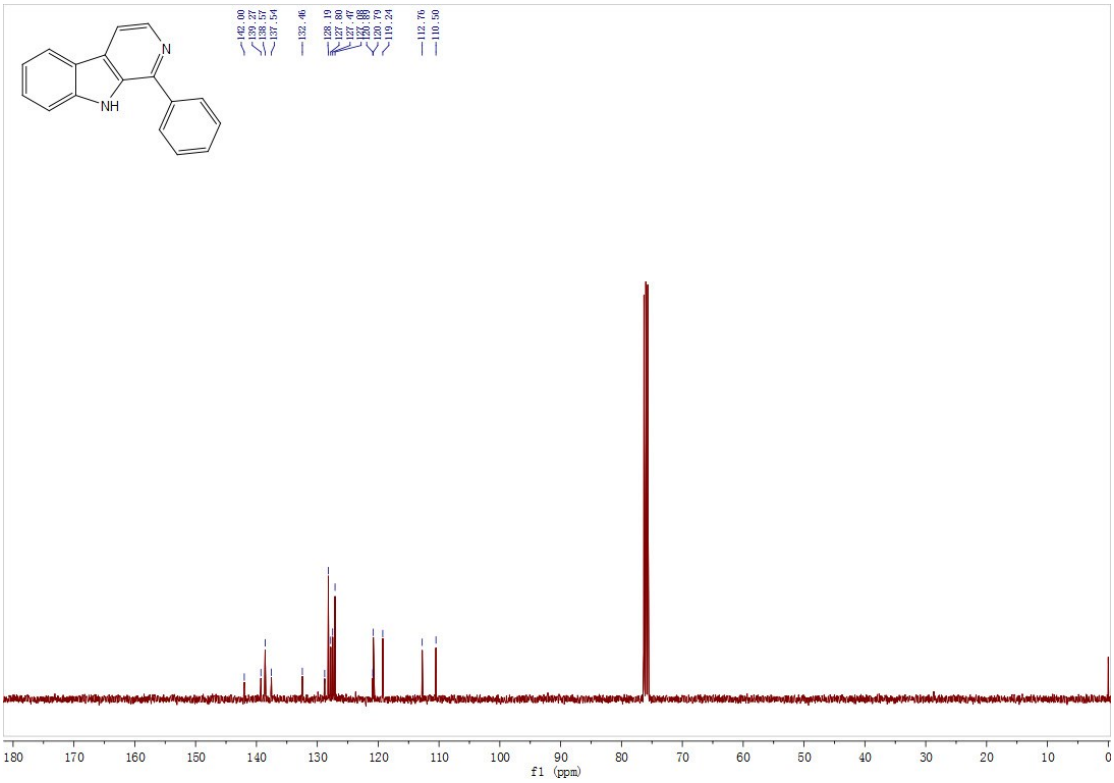
^{1}H NMR of **2k**



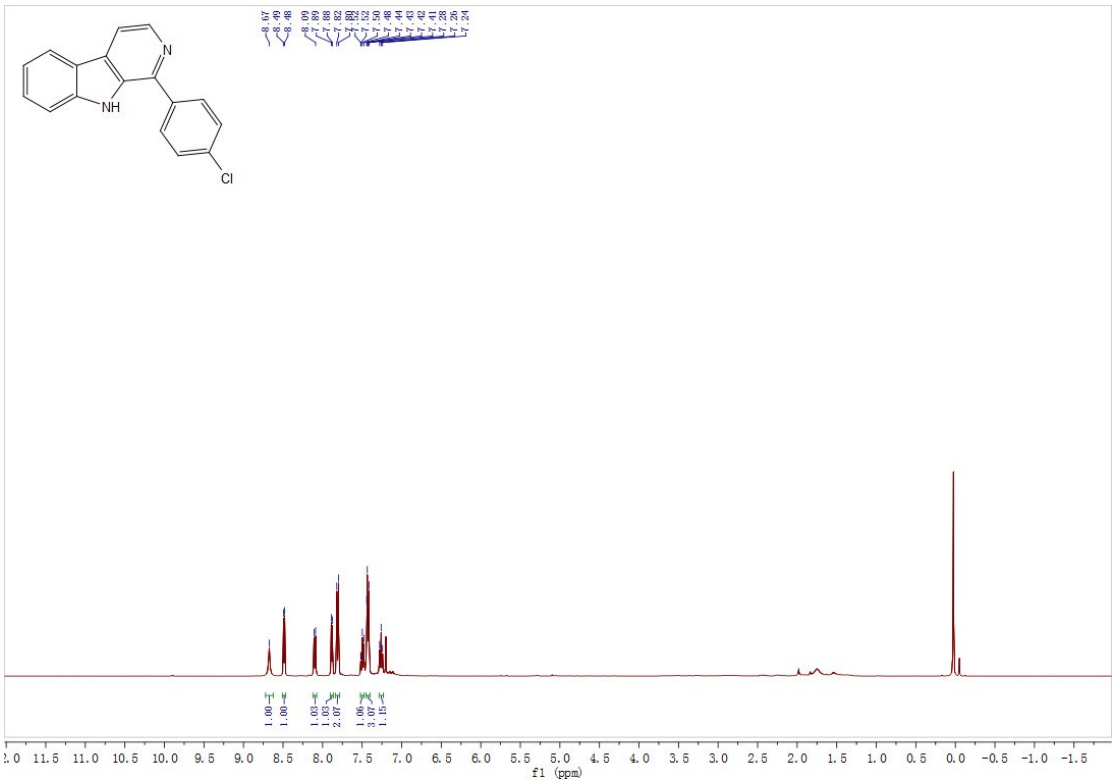
^{13}C NMR of **2k**



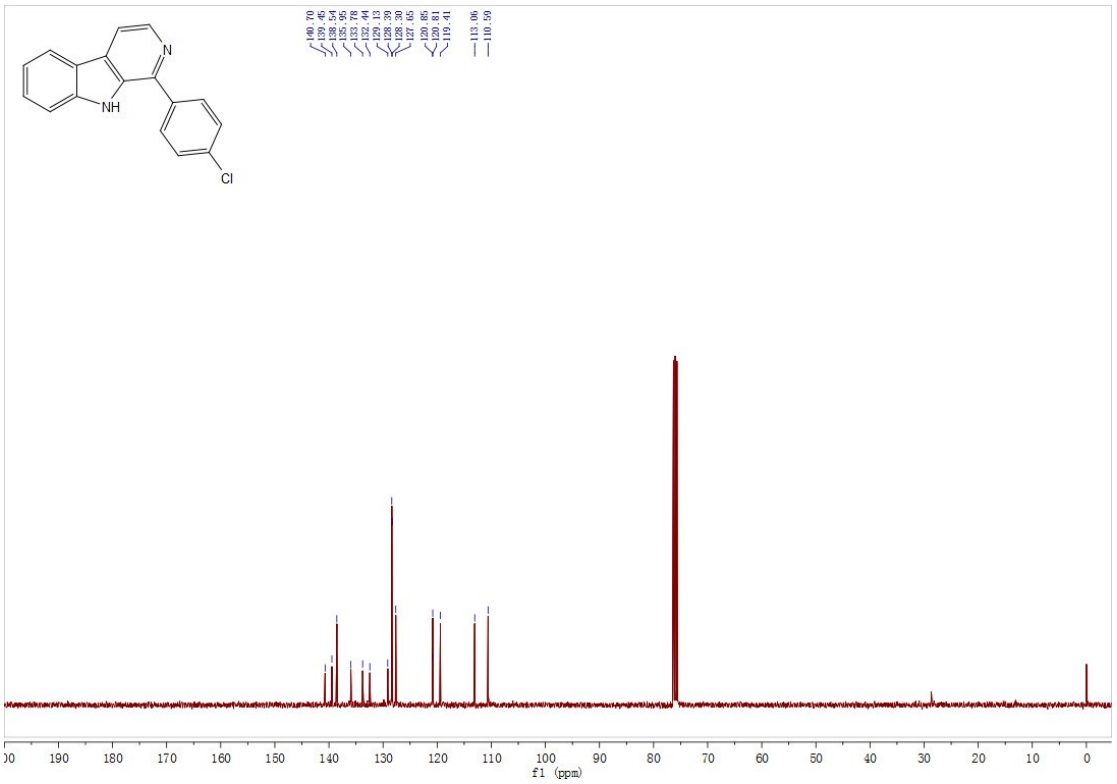
^{1}H NMR of **3a**



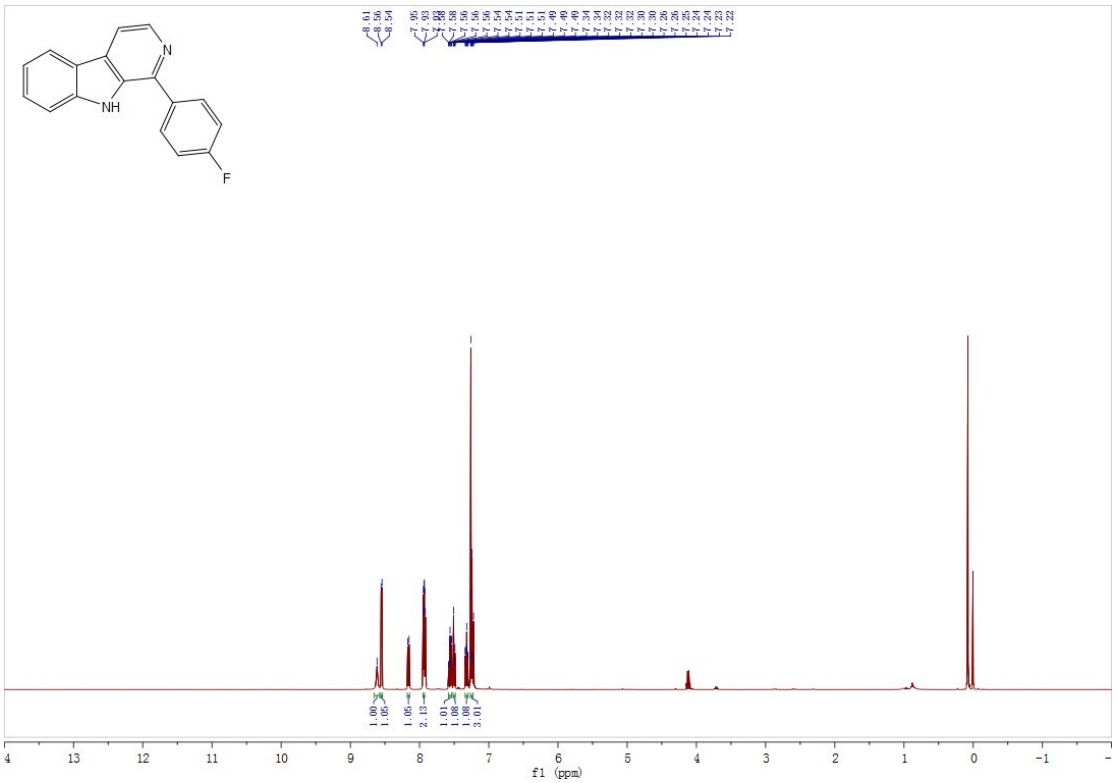
^{13}C NMR of **3a**



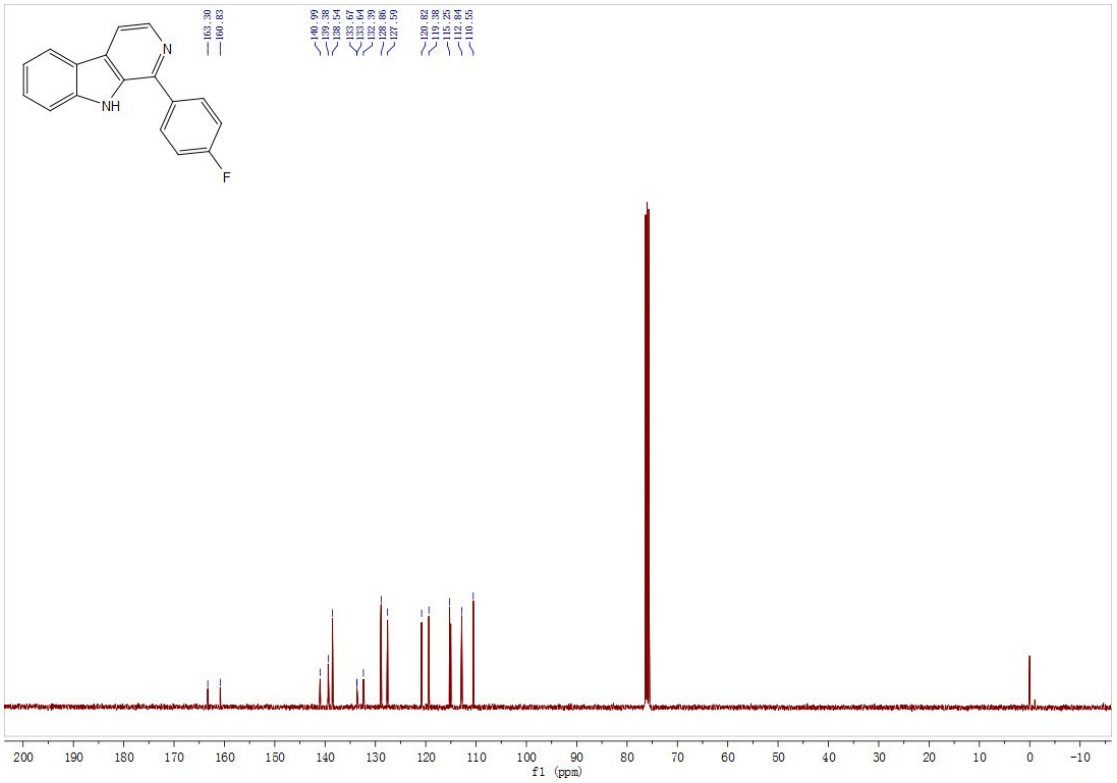
^{1}H NMR of **3b**



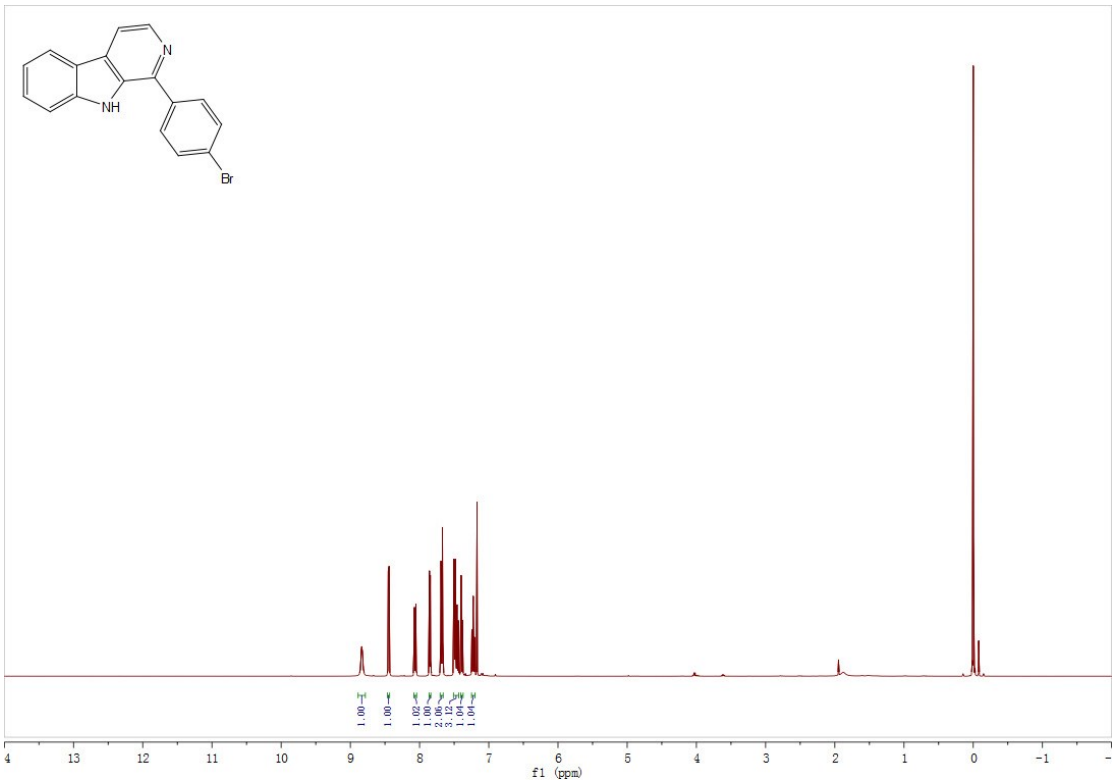
^{13}C NMR of **3b**



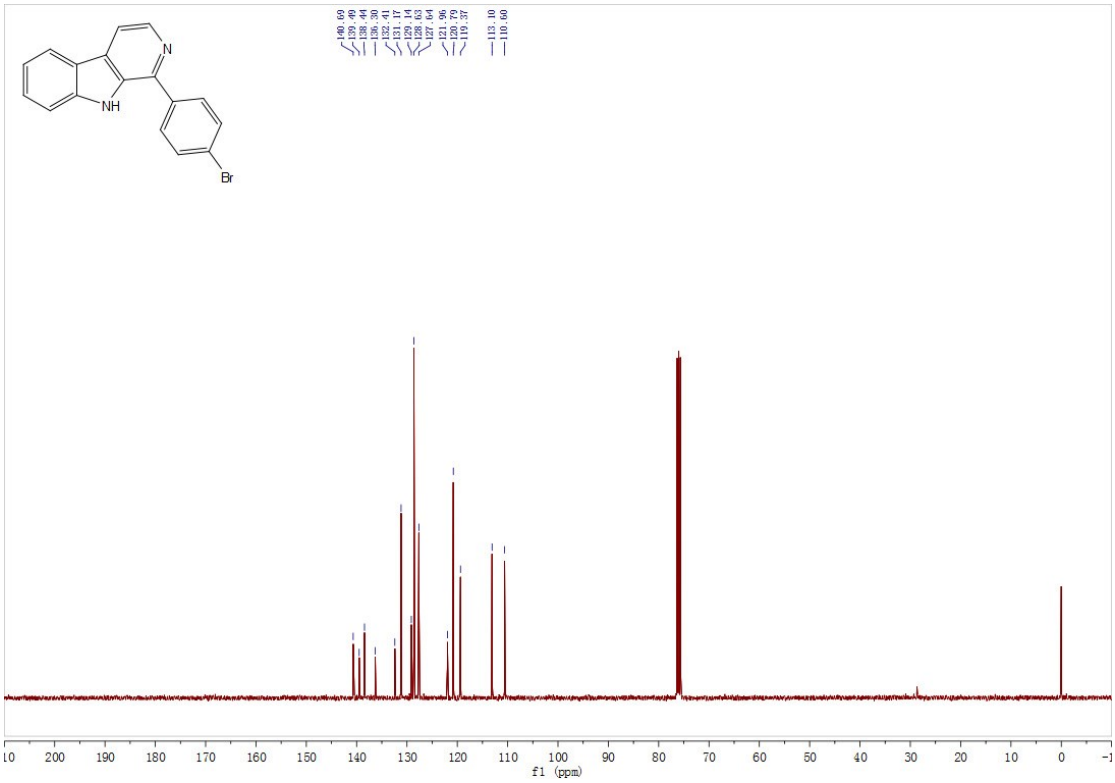
^{1}H NMR of **3c**



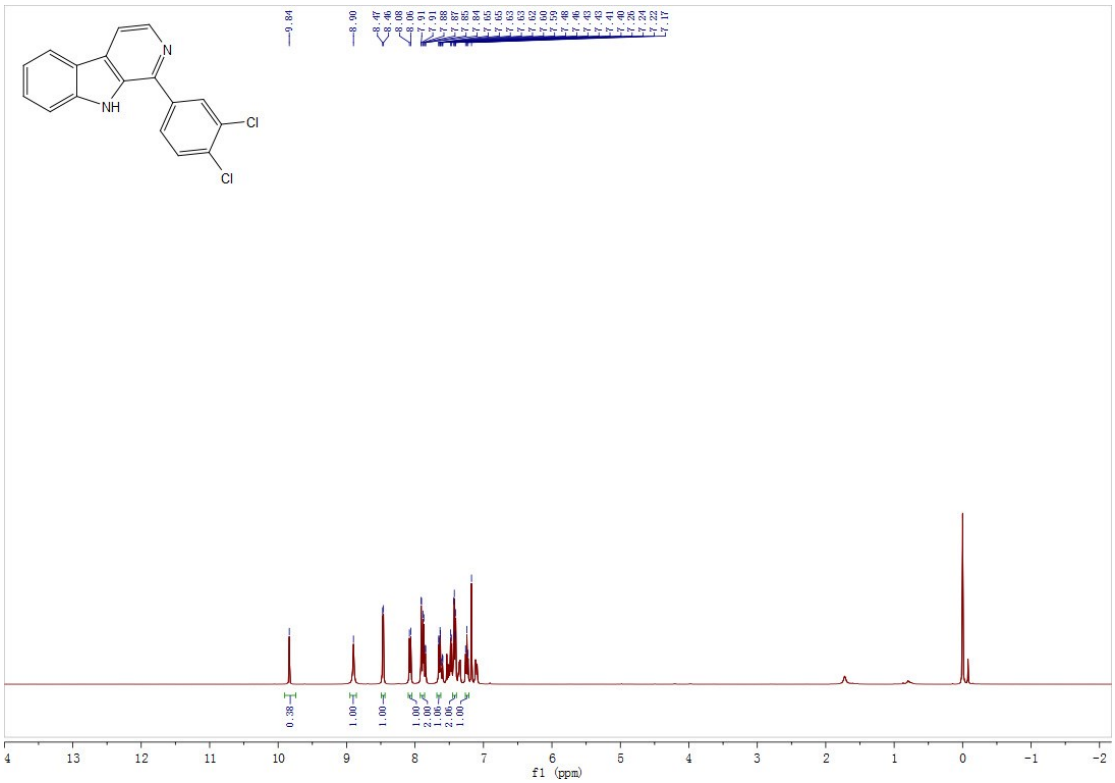
^{13}C NMR of **3c**



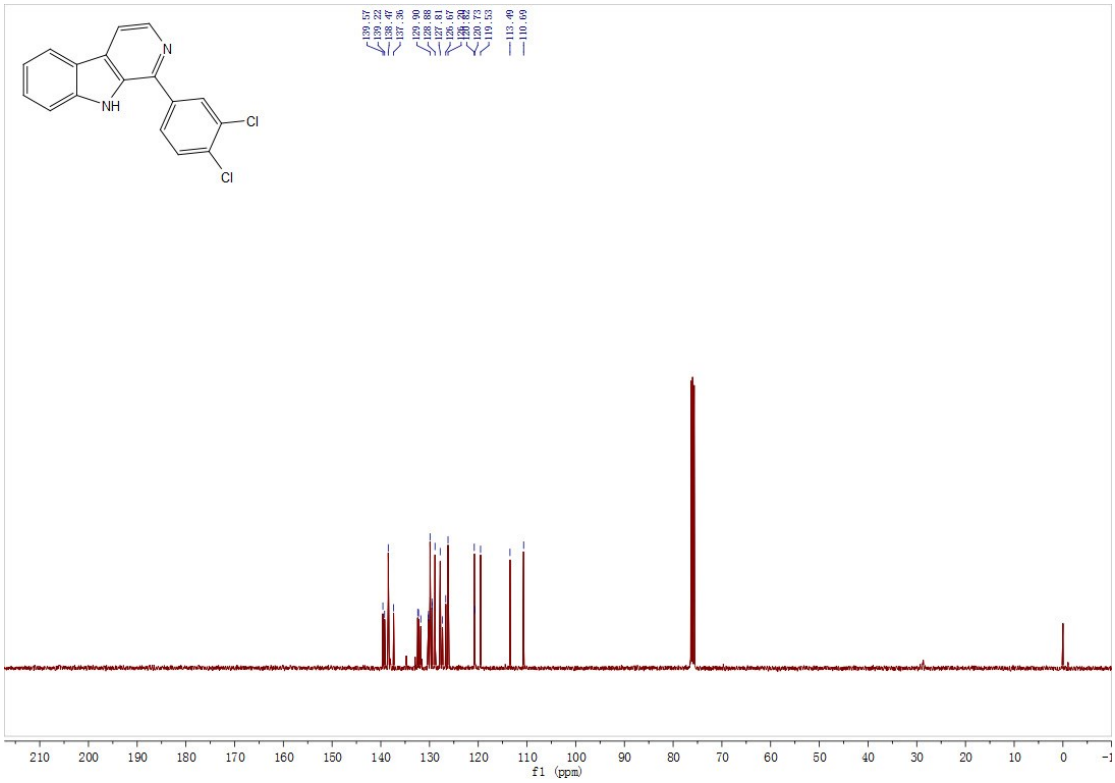
^{1}H NMR of **3d**



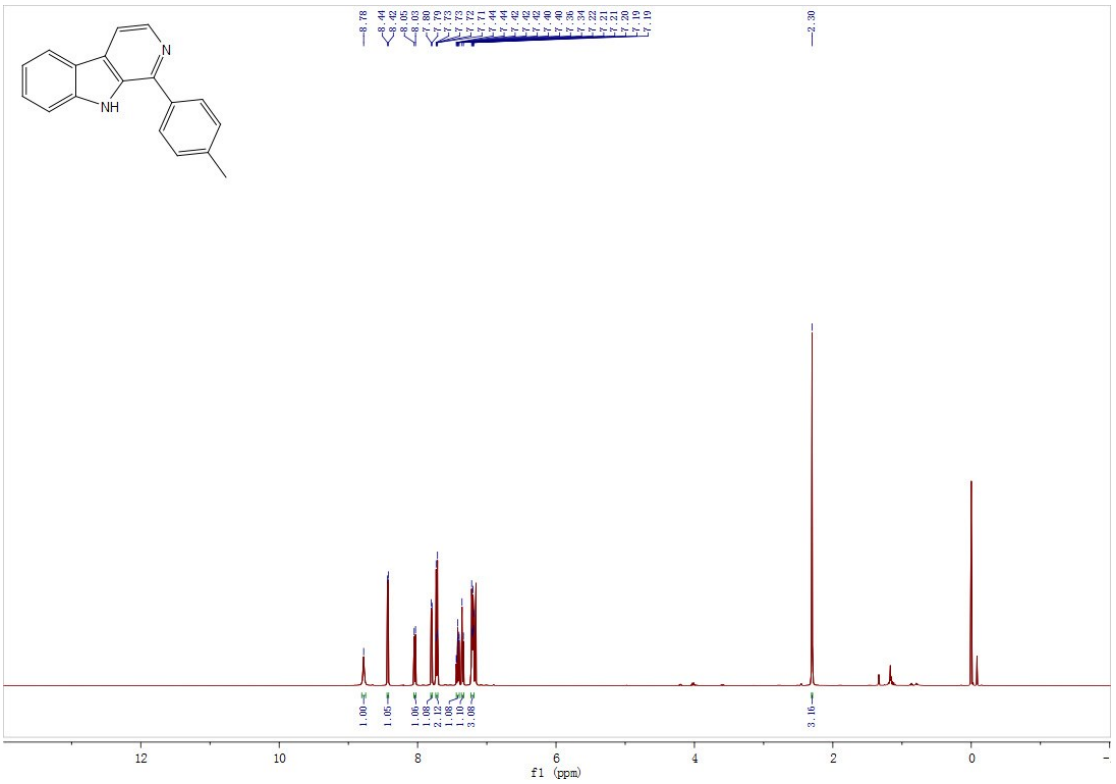
^{13}C NMR of **3d**



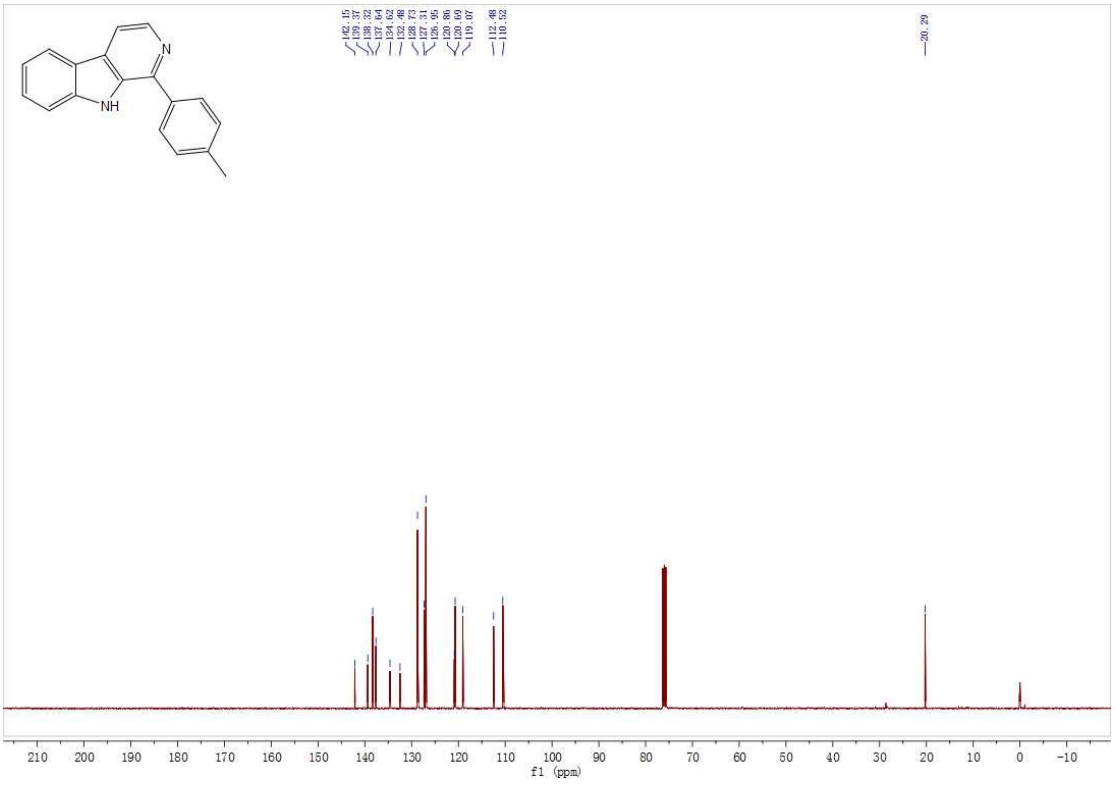
^{1}H NMR of **3e**



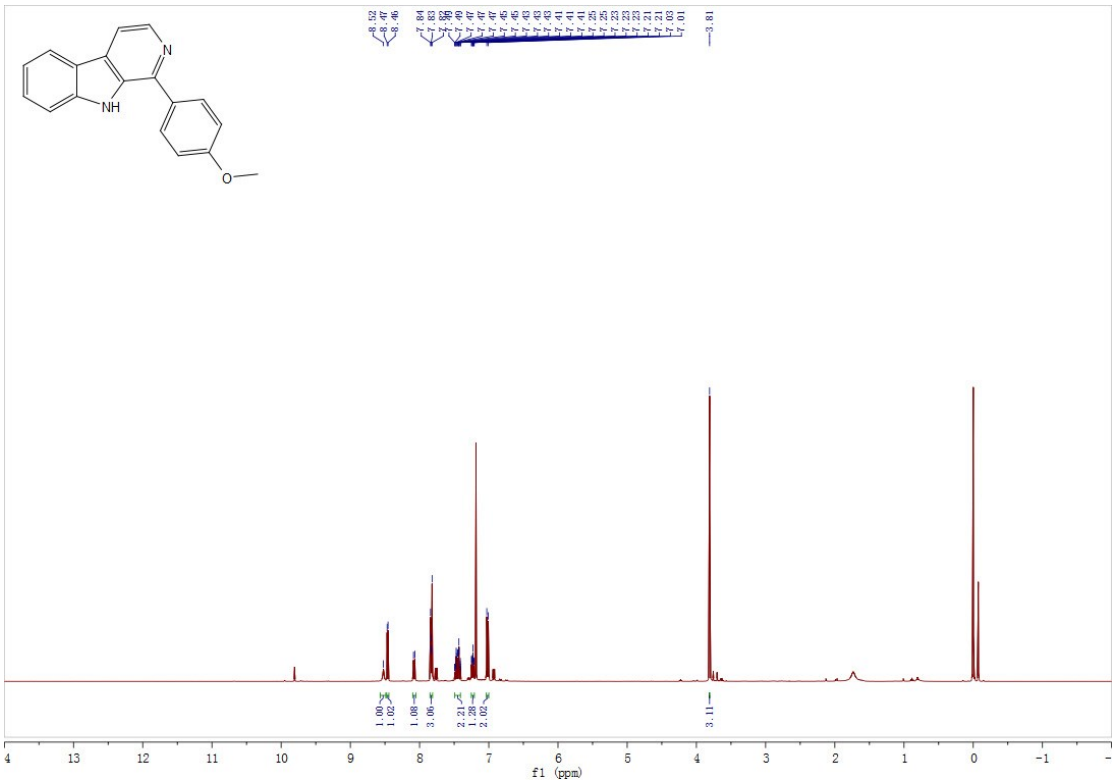
^{13}C NMR of **3e**



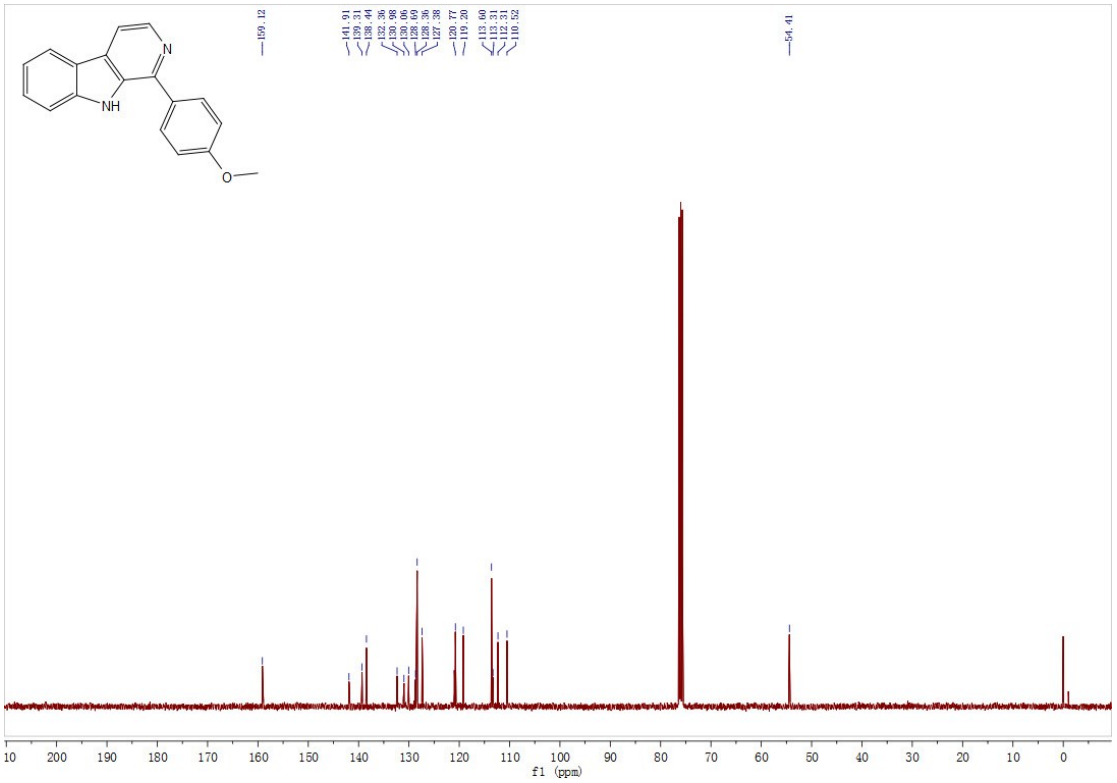
^{1}H NMR of **3f**



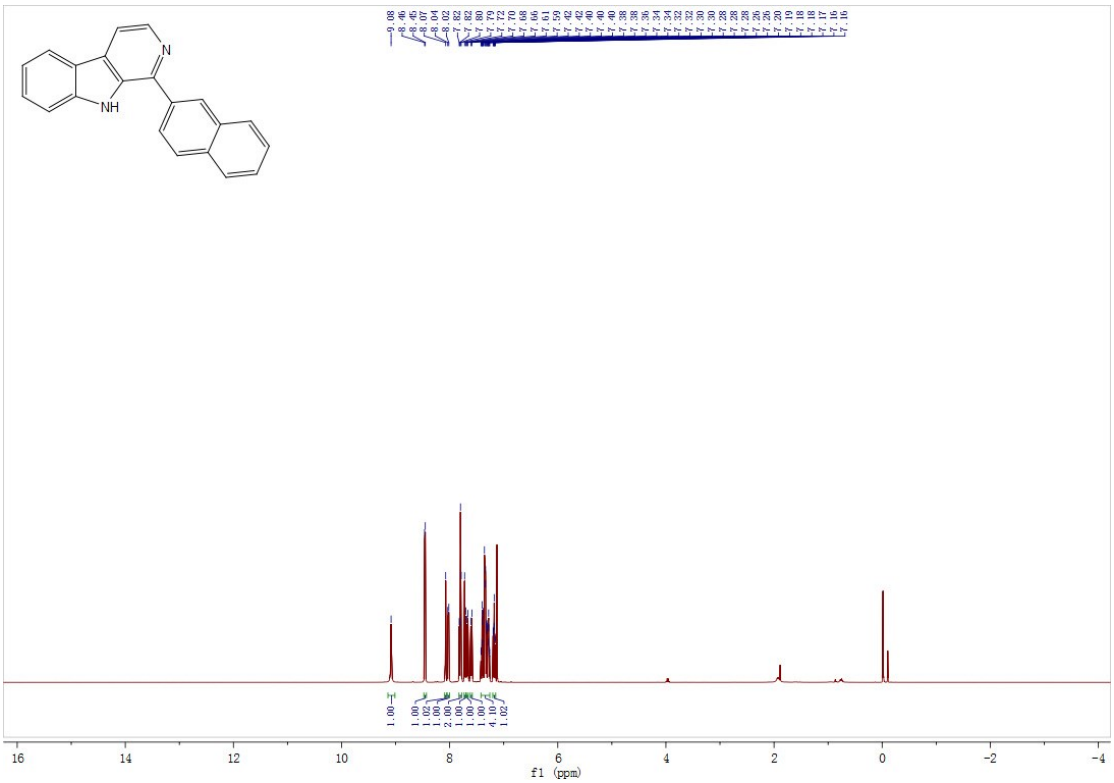
^{13}C NMR of **3f**



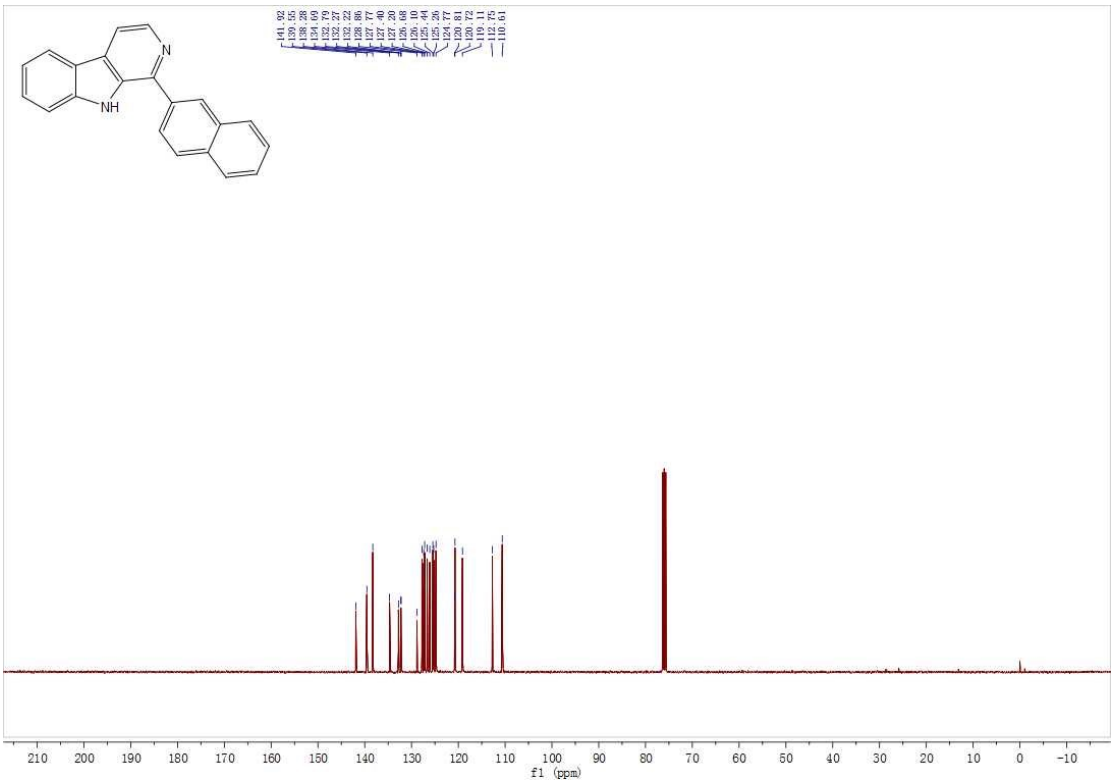
^{1}H NMR of **3g**



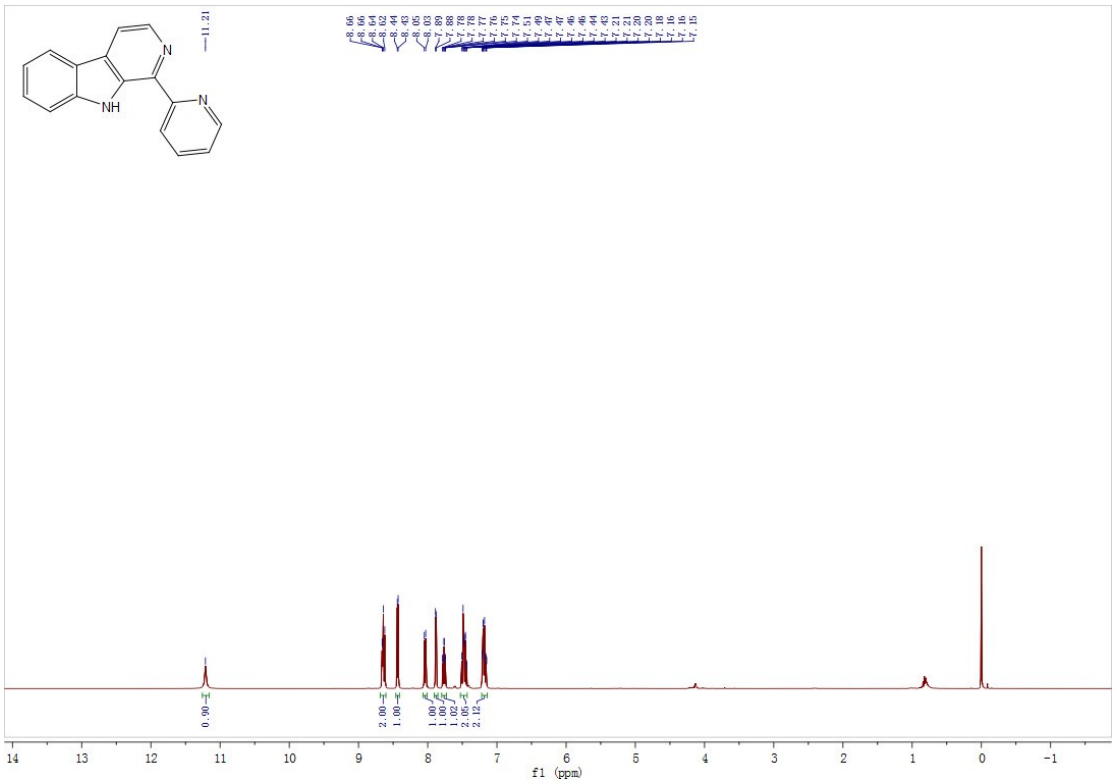
^{13}C NMR of **3g**



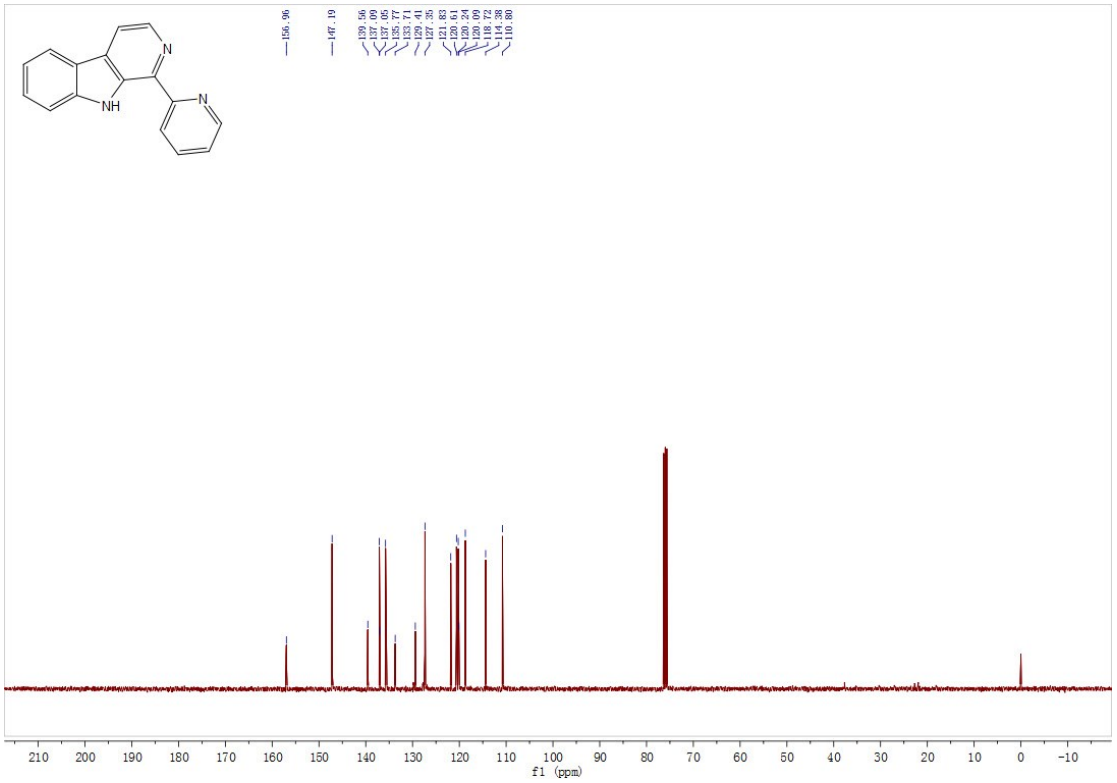
^{1}H NMR of **3h**



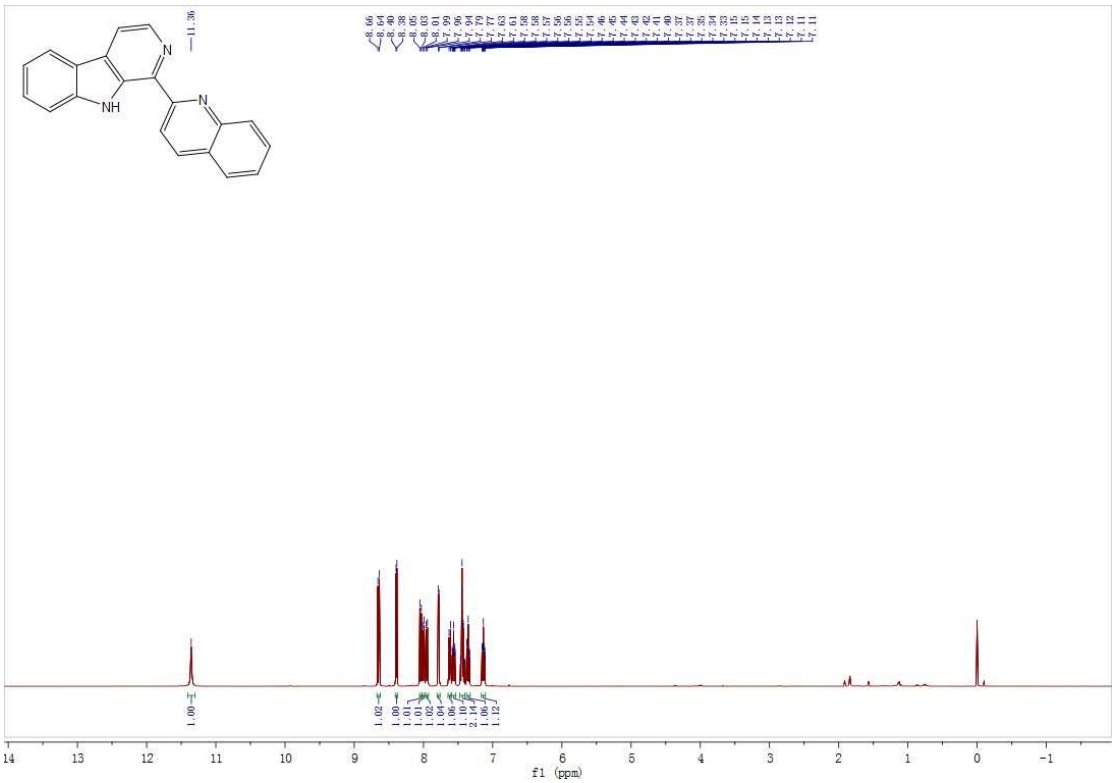
^{13}C NMR of **3h**



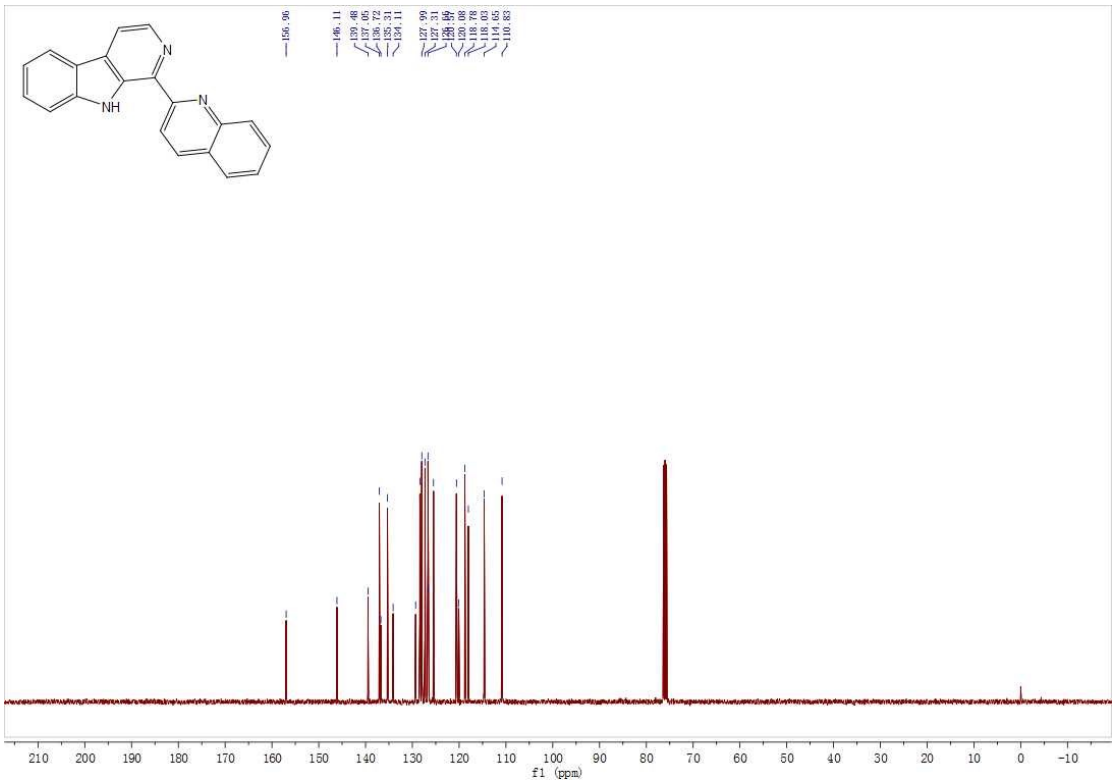
^{1}H NMR of **3i**



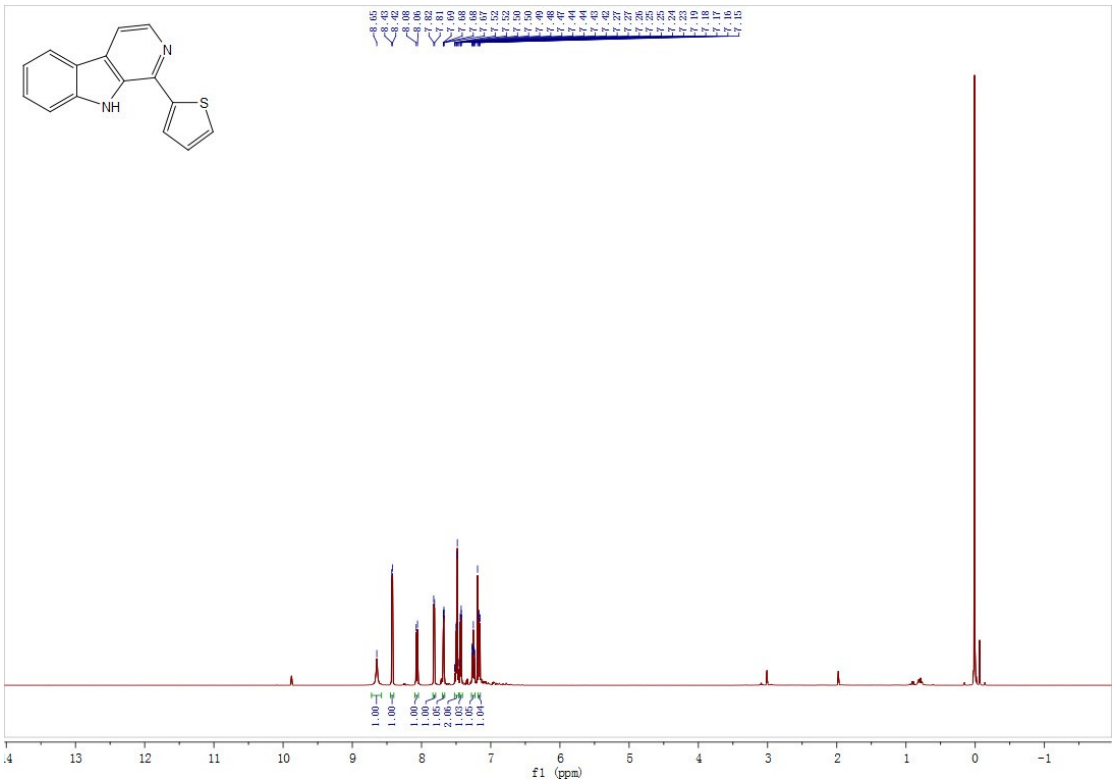
^{13}C NMR of **3i**



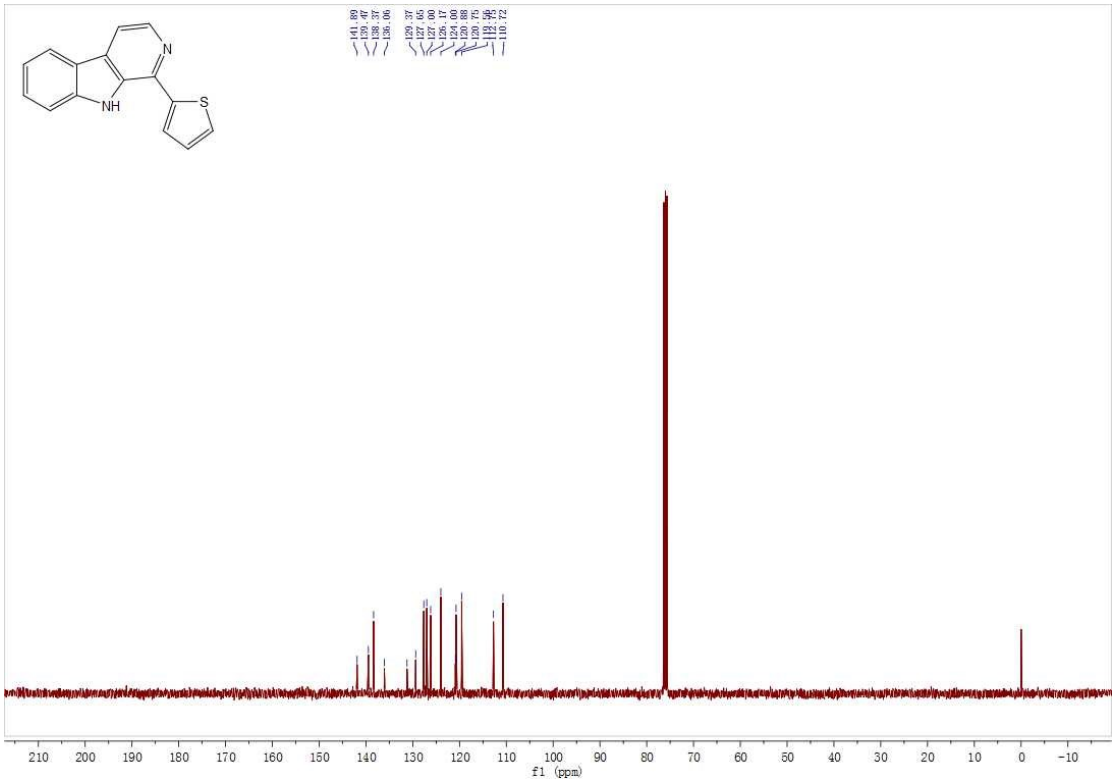
^{1}H NMR of **3j**



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



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



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