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Supporting Information

Practical Synthesis of Polysubstituted Unsymmetric 1,10-Phenanthrolines by Palladium Catalyzed Intramolecular Oxidative Cross Coupling of C(sp^2)-H and C(sp^3)-H Bonds of Carboxamides

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Contents of Supporting Information

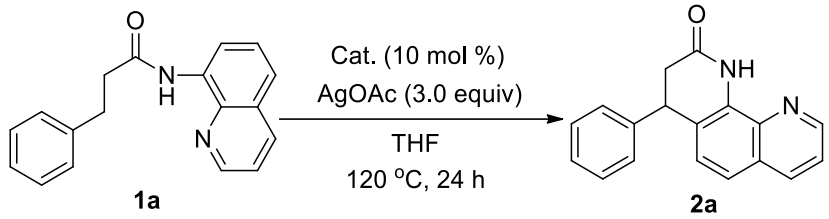
Experiment Section

General Methods. All Reactions were performed in sealed tube (capacity 25 mL) sealed with a cap. NMR spectra were recorded on Bruker DPX-400, DRX-500 instruments and calibrated using residual solvent peaks as internal reference, for example $CDCl_3$ solutions. High resolution mass spectra were performed on API STAR Pulsar. X-ray diffraction was obtained by APEX DUO. TLC analyses were performed on commercial glass plates bearing 0.25 mm layer of Merck Silica gel $60F_{254}$. Silica gel (Wakogel 300 - 400 mesh) was used for column chromatography. Visualization of the developed chromatogram was performed by fluorescence quenching or $KMnO_4$ staining.

Unless otherwise noted, materials obtained from commercial suppliers were used without further purification. $Pd(OAc)_2$, anhydrous AgOAc and DMAP were purchased from Alfar Aesar company and Shanghai Titan Polytron Technologies Inc. All aminoquinoline carboxamides were synthesized from the corresponding acids or acid chlorides with 8-aminoquinoline. All reactions were carried out under an air atmosphere.

Reaction Optimization

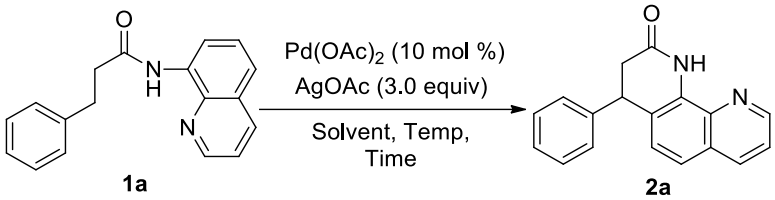
Table S1. Screening of catalyst.



1a **2a**

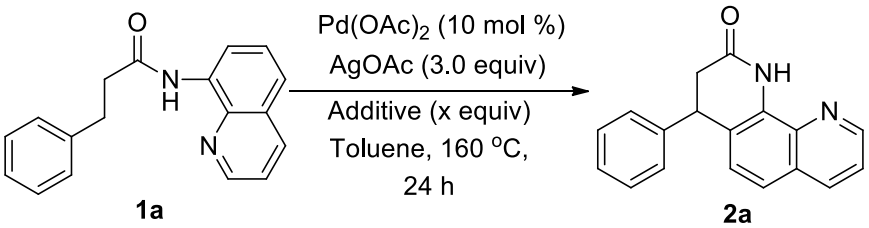
Entry	Solvent	Temp [°C]	Time [h]	Yield [%]
1	$Pd(OAc)_2$	120	24	14
2	$PdCl_2$	120	24	8
3	$PdCl_2(Ph_3P)_2$	120	24	18
4	$Pd(OAc)_2(Ph_3P)_2$	120	24	4
5	$Pd_2(dba)_3$	120	24	6
6	$PdCl_2(dppf)_2$	120	24	11
7	$PdCl_2(dippp)$	120	24	14
8	$PdCl_2(dppe)$	120	24	10
9	$PdCl_2(dppb)$	120	24	8
10	$PdCl_2(MeCN)_2$	120	24	9
11	$Pd(PhCN)_2Cl_2$	120	24	11
12	$PdCl_2[P(cy)_3]_2$	120	24	Trace
13	$RhCl(Ph_3P)_3$	120	24	0
14	$RuCl_2(Ph_3P)_2$	120	24	0

Table S2. Screening of temperature and solvent.



Entry	Solvent	Temp [°C]	Time [h]	Yield [%]
1	toluene	120	24	9
2	toluene	90	24	0
3	THF	120	24	14
4	EtOAc	120	24	17
5	CH_3CN	120	24	20
6	MeOH	120	24	15
7	EtOH	120	24	20
8	pyridine	120	34	10
9	toluene	160	24	29
10	n-BuOH	160	42	21
11	*t*-Amyl alcohol	160	24	27
12	1,4-dioxane	160	24	25
13	DMF	160	24	trace
14	DMA	160	15	trace
15	DMSO	160	24	trace
16	H_2O	160	34	8

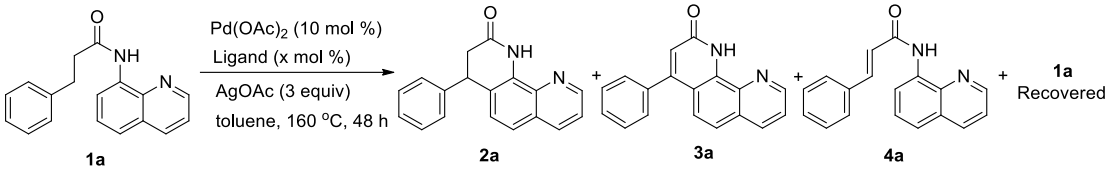
Table S3. Screening of the amount of additive.



Entry	Additive	Temp [°C]	Time [h]	Yield [%]
1	$Cu(OAc)_2$ (1 eq)	120	24	0
2	$SnCl_4$ (0.2 eq)	160	46	0
3	$Fe(NO_3)_3$ (1 eq)	160	24	0

4	$FeCl_3$ (0.2 eq)	160	24	17
5	$FeCl_3$ (1eq)	160	24	0
6	FeF_2 (0.2 eq)	160	24	31
7	FeF_2 (0.5 eq)	160	24	0
8	$FeBr_2$ (0.2 eq)	160	24	0
9	$FeBr_3$ (0.2 eq)	160	24	0

Table S4. Screening of the amount of ligand.



Entry	Ligand (x mol%)	**2a** [%]	**3a** [%]	**4a** [%]	Recovered **1a** [%]
1	**L1** (10)	37	0	16	38
2	**L2** (10)	52	0	15	24
3	**L3** (10)	53	0	13	20
4[a]	**L3** (15)	62	0	11	18
5[b]	**L3** (20)	69	0	11	16
6	**L4** (20)	7	0	5	76
7[a]	**L4** (15)	30	0	10	46
8	**L5** (10)	52	0	10	31
9[a]	**L5** (15)	58	0	17	16
10[a]	**L6** (15)	70	0	10	18
11[a]	**L7** (15)	71	0	7	19
12[a]	**L8** (15)	21	0	0	72
13	**L9** (20)	26	0	38	28
14[a]	**L9** (15)	55	0	18	12
15[a]	**L10** (15)	27	0	10	50
16[a]	**L11** (15)	23	0	4	61
17	**L12**(20)	12	6	0	68

18	**L13**(20)	58	6	0	18
19	**L14**(20)	42	0	0	40
20	**L14**(100)	26	0	0	50
21	**L15**(10)	20	0	16	53

[a] $Pd(OAc)_2$ (15 mol%) was used. [b] $Pd(OAc)_2$ (20 mol%) was used.

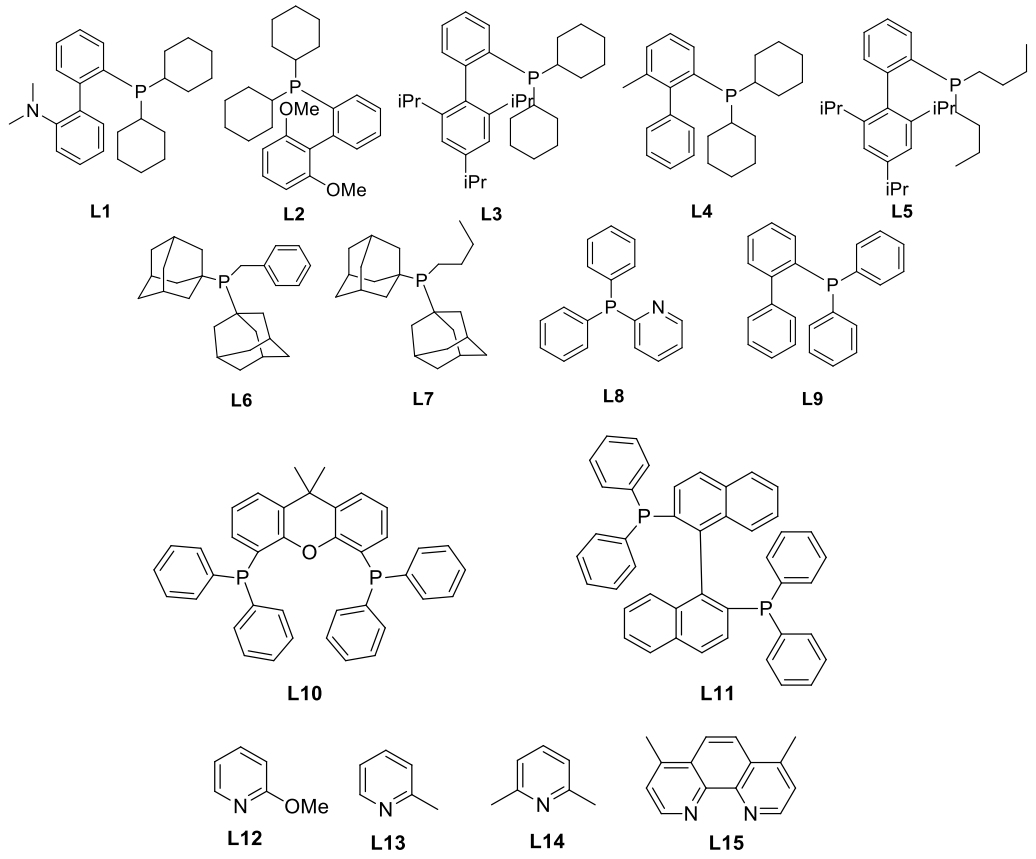
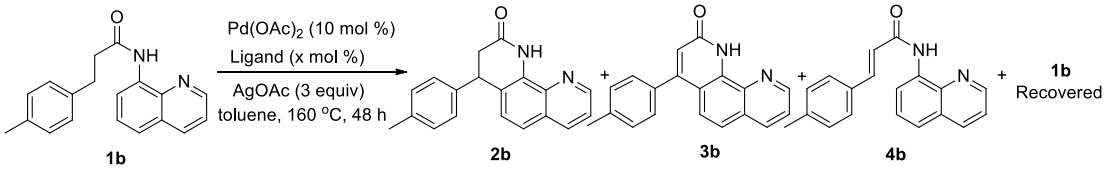


Table S5. Screening of the amount of ligand.



Entry	Ligand (x mol%)	**2b** [%]	**3b** [%]	**4b** [%]	Recovered **1b** [%]
1	**L16** (20)	48	7	0	28
2	**L17** (20)	26	7	0	41
3	**L18** (20)	48	1	7	39
4	**L19** (20)	27	0	15	45
5	**L20** (20)	36	0	15	34

6	**L21** (20)	37	0	0	54
7	**L22** (20)	41	0	7	32
8	**L23** (20)	25	0	15	51
9	DMAP (20)	48	13	0	10
10	DMAP (10)	50	15	0	20
11	DMAP (30)	50	26	0	12
12	DMAP (40)	72	13	0	6
13	DMAP (50)	45	12	0	30
14	DMAP (60)	42	11	0	31
15 [a]	DMAP (60)	65	0	0	21

[a] $Pd(OAc)_2$ (15 mol%), AgOAc (1.5 equiv), DMAP (15 mol%), toluene, 160 °C, 40h.

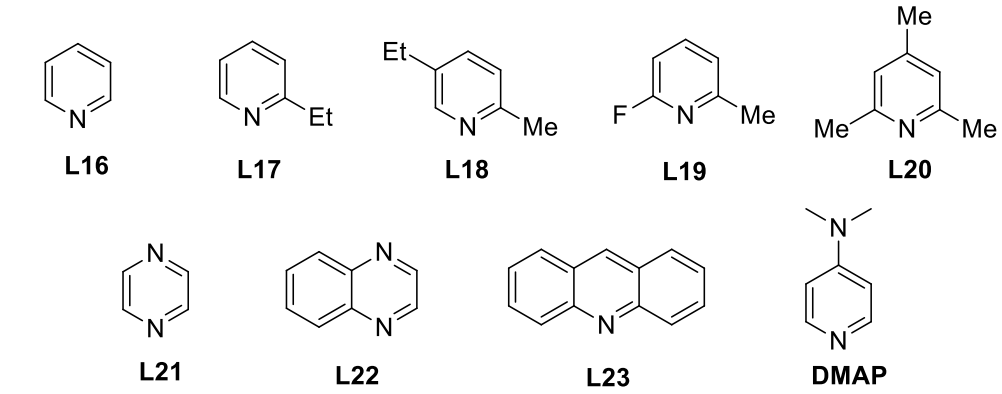
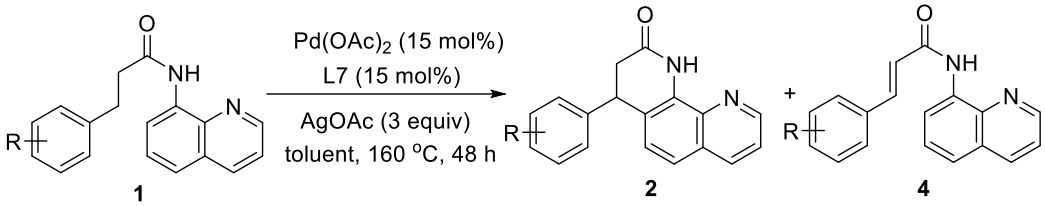


Table S6. Synthesis of δ-Lactams derivative by phosphine ligand.

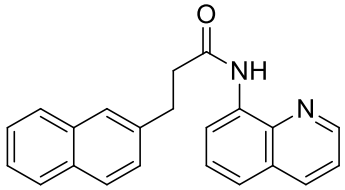


Entry	R	Yield[a] [%] of **2** / **4** / **1**	Entry	R	Yield[a] [%] of **2** / **4** / **1**
1	H	71 / 7 / 19	6	*m*-F	37 / 25 / 27
2	*p*-Me	41 / 25 / 25	7	*p*-F	41 / 20/ 27
3	*o*-OMe	22 / 55/ 10	8	*o*-Cl	33 / 2 / 52
4	*m*-OMe	63 / 12 / 10	9	*p*-Cl	55 / 17 / 15
5	*p*-OMe	42 / 41 / 7	10	*m*-NO_2	35 / 1 / 54

[a] Isolated yields.

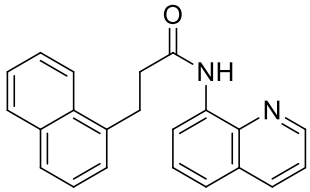
Preparation of aminoquinoline carboxamides subsrates

All carboxamides except **1w** were prepared according to literature procedure.[1] **1w** was prepared according to literature procedure.[2] Among them, substrates **1a**, **1b**, **1c**, **1d**, **1e**, **1f**, **1g**, **1h**, **1i**, **1j**, **1k, 1l**, **1m, 1n,** and **1o** were known[1].



3-(Naphthalen-2-yl)-*N*-(quinolin-8-yl)propanamide (1p):

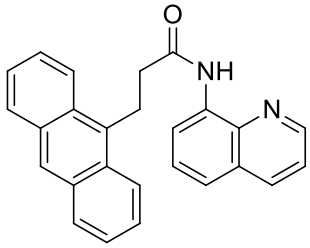
To a solution of 3-(2-naphthalenyl)propanoic acid (200.2 mg, 1.0 mmol), 8-aminoquinoline (173.0 mg, 1.2 mmol) in anhydrous DCM (2 mL) was added EDCI (287.6 mg, 1.5 mmol) and DMAP (12.2 mg, 0.1 mmol). The mixture was stirred at room temperature for 24 h. The reaction mixture was then diluted with DCM (30 mL), washed with aq. HCl (1 M, 2 x 30 mL) and brine, dried over anhydrous Na_2SO_4, and concentrated. Purification by flash chromatography (Silica gel, DCM as eluent) afforded the product **1p** as a white solid (212.3 mg, 65% yield). mp 131-132 ^oC. ^1H NMR (400 MHz, $CDCl_3$) δ 9.80 (bs, 1H), 8.80 (dd, J = 7.4 and 1.5 Hz, 1H), 8.68 (dd, J = 4.2 and 1.7 Hz, 1H), 8.13 (dd, J = 8.3 and 1.6 Hz, 1H), 7.83 – 7.20 (m, 4H), 7.63 – 7.32 (m, 6H), 3.32 (t, J = 7.8 Hz, 2H), 2.98 (t, J = 7.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.83, 148.18, 138.40, 138.38, 136.43, 134.54, 133.79, 132.31, 128.31, 128.02, 127.73, 127.65, 127.52, 127.22, 126.73, 126.10, 125.45, 121.68, 121.59, 116.62, 39.78, 31.79; HRMS(EI) Calcd for $C_{22}H_{18}N_2O$ [M^+]: 326.1419, Found 326.1405; IR (KBr) ν_{max} (cm^{-1}) : 3443, 1691, 1524, 1483, 1323, 698.



3-(Naphthalen-1-yl)-*N*-(quinolin-8-yl)propanamide (1q):

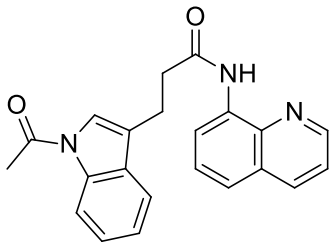
To a solution of 3-(1-naphthalenyl)propanoic acid (400.5 mg, 2.0 mmol), 8-aminoquinoline (288.2.0 mg, 1.0 mmol) in anhydrous DCM (2 mL) was added EDCI (575.1 mg, 3.0 mmol) and DMAP (24.4 mg, 0.2 mmol). The mixture was stirred at room temperature for 24 h. The reaction mixture was then diluted with DCM (30 mL), washed with aq. HCl (1 M, 2 x 30 mL) and brine, dried over anhydrous Na_2SO_4, and concentrated. Purification by flash chromatography (Silica gel, DCM as eluent) afforded the product **1q** as a white solid (455.7 mg, 70% yield). mp 131-132 ^oC. ^1H NMR (400 MHz, $CDCl_3$) δ 9.81 (bs, 1H), 8.87 (d, J = 7.3 Hz, 1H), 8.72 (dd, J = 4.2 and 1.7 Hz, 1H), 8.17 (d, J = 8.3 Hz, 1H), 8.09 (dd, J = 8.3 and 1.7 Hz, 1H), 7.88 (dd, J = 8.0 and 1.4 Hz, 1H), 7.74 (d, J = 7.9 Hz, 1H), 7.62 – 7.33 (m, 7H), 3.63 (t, J = 8.0 Hz, 2H), 3.02 (t, J = 8.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.86,

148.09, 138.25, 136.85, 136.31, 134.44, 133.96, 131.69, 128.91, 127.90, 127.40, 127.12, 126.13, 126.11, 125.66, 125.62, 123.57, 121.58, 121.52, 116.49, 38.87, 28.53; HRMS(EI) Calcd for $C_{22}H_{18}N_2O$ [M^+]: 326.1419, Found 326.1414; IR (KBr) ν_{max} (cm^{-1}) : 3442, 1697, 1523, 1325, 781, 660.



3-(Anthracen-9-yl)-*N*-(quinolin-8-yl)propanamide (1r):

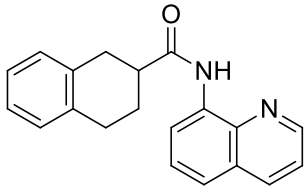
To a solution of 3-(9-anthracenyl)propanoic acid (100.1 mg, 0.4 mmol), 8-aminoquinoline (69.2 mg, 0.48 mmol) in anhydrous DCM (2 mL) was added EDCI (115.0 mg, 0.6 mmol) and DMAP (4.9 mg, 0.04 mmol). The mixture was stirred at room temperature for 24 h. The reaction mixture was then diluted with DCM (30 mL), washed with aq. HCl (1 M, 2 x 30 mL) and brine, dried over anhydrous Na_2SO_4, and concentrated. Purification by flash chromatography (Silica gel, DCM as eluent) afforded the product **1r** as a white solid (123.7 mg, 82% yield). mp 160-162 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.80 (bs, 1H), 8.88 (d, *J* = 7.5 Hz, 1H), 8.70 (dd, *J* = 4.2 and 1.7 Hz, 1H), 8.49 – 8.30 (m, 3H), 8.11 (dd, *J* = 8.3 and 1.7 Hz, 1H), 8.01 (d, *J* = 8.3 Hz, 2H), 7.66 – 7.34 (m, 7H), 4.17 (t, *J* = 8.4 Hz, 2H), 3.03 (t, *J* = 8.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.96, 148.16, 138.33, 136.37, 134.49, 132.95, 131.71, 129.64, 129.39, 127.96, 127.49, 126.37, 126.02, 125.01, 124.16, 121.65, 121.62, 116.57, 38.95, 23.57; HRMS(EI) Calcd for $C_{26}H_{20}N_2O$ [M^+]: 376.1576, Found 376.1577; IR (KBr) ν_{max} (cm^{-1}) : 3441, 1690, 1526, 1484, 1325, 1159.



3-(1-Acetyl-1H-indol-3-yl)-*N*-(quinolin-8-yl)propanamide (1s):

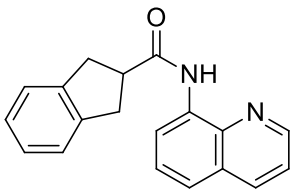
3-(3-Indolyl)-N-(8-quinolinyl)propanamide (157.7 mg, 0.5 mmol) and DMAP (12.2 mg, 0.1 mmol) were dissolved in DCE (2 mL). To this solution were added triethylamine (75.9 mg, 0.75 mmol) and acetic anhydride (204.2, 2.0 mmol). The reaction mixture was stirred at 60 °C for 24 h. After cooling down to room temperature, the reaction mixture was diluted with ethyl acetate (5 mL), quenched with a saturated solution of NH_4Cl (10 mL), and extracted with ethyl acetate (3 x 10 mL). The combined organic layers were dried over $MgSO_4$ and the volatiles were removed under reduced pressure. Purification by flash chromatography (Silica gel, DCM as eluent) afforded the product **1s** a yellow oil (124.9 mg, 70% yield). ^{1}H NMR

(400 MHz, $CDCl_3$) δ 9.76 (bs, 1H), 8.76 (d, *J* = 7.5 Hz, 1H), 8.70 – 8.60 (m, 1H), 8.40 (d, *J* = 8.2 Hz, 1H), 8.10 – 8.00 (m, 1H), 7.65 – 7.13 (m, 7H), 3.21 – 3.11 (m, 2H), 3.04 – 2.82 (m, 2H), 2.44 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.51, 168.33, 148.05, 138.11, 136.24, 135.88, 134.22, 130.22, 127.80, 127.23, 125.22, 123.42, 122.28, 121.55, 121.31, 118.70, 116.62, 116.40, 37.24, 23.84, 20.68; HRMS(EI) Calcd for $C_{22}H_{19}N_3O_2$ [M^+]: 357.1477, Found 357.1478; IR (KBr) ν_{max} (cm^{-1}) : 3377, 1688, 1510, 1451, 1383, 750.



***N*-(Quinolin-8-yl)-1,2,3,4-tetrahydronaphthalene-2-carboxamide (1t):**

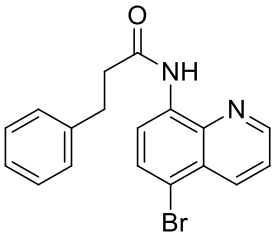
To a solution of 1,2,3,4-tetrahydronaphthalene-2-carboxylic acid (176.2 mg, 1.0 mmol) and 8-aminoquinoline (173.0 mg, 1.2 mmol) in anhydrous DCM (2 mL) was added EDCI (287.6 mg, 1.5 mmol) and DMAP (12.2 mg, 0.1 mmol). The mixture was stirred at room temperature for 24 h. The reaction mixture was then diluted with DCM (30 mL), washed with aq. HCl (1 M, 2 x 30 mL) and brine, dried over anhydrous Na_2SO_4, and concentrated. Purification by flash chromatography (Silica gel, DCM as eluent) afforded the product **1t** a white solid (276.1 mg, 91% yield). mp 189-191 ^oC. ^1H NMR (400 MHz, $CDCl_3$) δ 10.00 (bs, 1H), 8.83 (dd, *J* = 7.6 and 1.4 Hz, 1H), 8.76 (dd, *J* = 4.0 and 1.2 Hz, 1H), 8.09 (dd, *J* = 8.2 and 1.7 Hz, 1H), 7.57 – 7.26 (m, 3H), 7.17 – 7.00 (m, 4H), 3.29 – 3.05 (m, 2H), 3.00 – 2.79 (m, 3H), 2.40 – 2.25 (m, 1H), 2.20 – 1.92 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.96, 148.17, 138.43, 136.36, 135.69, 135.07, 134.51, 129.16, 128.88, 127.92, 127.41, 125.97, 125.86, 121.62, 121.50, 116.51, 43.39, 32.50, 28.73, 26.70; HRMS(EI) Calcd for $C_{20}H_{18}N_2O$ [M^+]: 302.1419, Found 302.1425; IR (KBr) ν_{max} (cm^{-1}) : 3335, 1680, 1523, 1324, 830, 757.



***N*-(Quinolin-8-yl)-2,3-dihydro-1H-indene-2-carboxamide (1u):**

To a solution of 2,3-dihydro-1H-indene-2-carboxylic acid (486.6 mg, 3.0 mmol) and 8-aminoquinoline (518.0 mg, 3.6 mmol) in anhydrous DCM (2 mL) was added EDCI (862.7 mg, 4.5 mmol) and DMAP (36.7 mg, 0.3 mmol). The mixture was stirred at room temperature for 24 h. The reaction mixture was then diluted with DCM (30 mL), washed with aq. HCl (1 M, 2 x 30 mL) and brine, dried over anhydrous Na_2SO_4, and concentrated. Purification by flash chromatography (Silica gel, DCM as eluent) afforded the product **1u** as a white solid (588.2 mg, 68% yield). mp 174-176 ^oC. ^1H NMR (400 MHz, $CDCl_3$) δ 9.98 (bs, 1H), 8.88 – 8.74 (m, 2H), 8.13 (dd, *J* = 8.3 and 1.7 Hz, 1H), 7.60 – 7.34 (m, 3H), 7.30 – 7.12 (m, 4H), 3.67 – 3.25 (m, 5H); ^{13}C NMR

(100 MHz, $CDCl_3$) δ 173.45, 148.24, 141.82, 138.46, 136.44, 134.60, 128.00, 127.49, 126.75, 124.49, 121.69, 121.56, 116.58, 47.33, 36.93; HRMS(EI) Calcd for $C_{19}H_{16}N_2O$ [M^+]: 288.1263, Found 288.1260; IR (KBr) ν_{max} (cm^{-1}) : 3327, 1681, 1524, 1425, 1160, 791.

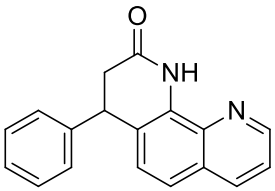


***N*-(5-Bromoquinolin-8-yl)-3-phenylpropanamide (1w):**

To a solution of **1a** (12.7107 g, 46 mmol) in DMF (50 mL) was added NBS (8.1871 g, 46 mmol). The reaction mixture was stirred at 80 °C for 24 h. After cooling down to room temperature, the reaction mixture was quenched with water, and extracted with ethyl acetate (3 x 100 mL). The organic layer was washed with brine, dried over anhydrous Na_2SO_4, and concentrated. Purification by flash chromatography (Silica gel, DCM as eluent) afforded the product **1w** as a white solid (12.50 g, 84% yield). mp 189-191 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 9.71 (bs, 1H), 8.73 (dd, J = 4.2 and 1.6 Hz, 1H), 8.64 (d, *J* = 8.4 Hz, 1H), 8.45 (dd, *J* = 8.5 and 1.7 Hz, 1H), 7.73 (d, *J* = 8.3 Hz, 1H), 7.49 (dd, *J* = 8.5 and 4.1 Hz, 1H), 7.31 – 7.13 (m, 5H), 3.11 (t, *J* = 7.8 Hz, 2H), 2.85 (t, *J* = 7.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.85, 148.65, 140.73, 139.02, 136.01, 134.41, 130.99, 128.68, 128.50, 127.20, 126.40, 122.73, 117.02, 114.22, 39.80, 31.48; HRMS(EI) Calcd for $C_{18}H_{15}N_2OBr$ [M+]: 354.0368, Found 354.0370; IR (KBr) ν_{max} (cm^{-1}) : 3442, 1687, 1523, 1477, 1364, 701.

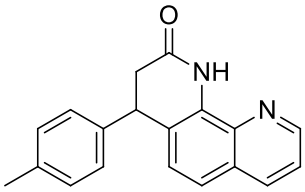
Typical procedure to make *δ*-Lactams via palladium catalyzed unactivated sp^3 C-H/sp^2C-H bonds activation and intramolecular cyclization of carboxamides:

General procedure: Carboxamide **1** (0.1 mmol), $Pd(OAc)_2$ (3.4 mg, 0.015 mmol), AgOAc (25 mg, 0.15 mmol), DMAP (7.3 mg, 0.06 mmol) and anhydrous toluene (2 mL) were added in turn into a 25 mL of glass sealed tube. The tube was tightly capped. The reaction mixture was stirred for 5 minutes at room temperature and then stirred at 160 °C in a pre-heated oil bath for 40 h. After cooling down to room temperature, the reaction mixture was concentrated under vacuum. Purification by preparative TLC plate (petroleum ether : ethyl acetate = 4 : 1 as eluent) afforded the product **2**.



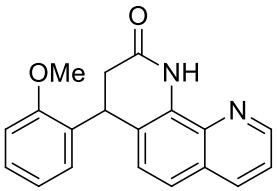
4-Phenyl-3,4-dihydro-1,10-phenanthrolin-2(1H)-one (2a):

1a (27.6 mg, 0.1 mmol), $Pd(OAc)_2$ (3.4 mg, 0.015 mmol), AgOAc (25.0 mg, 0.15 mmol), DMAP (7.3 mg, 0.06 mmol) and anhydrous toluene (2 mL) were added in turn into a 25 mL of glass sealed tube. The tube was tightly capped. The reaction mixture was stirred for 5 minutes at room temperature and then stirred at 160 °C in a pre-heated oil bath for 40 h. After cooling down to room temperature, the reaction mixture was concentrated under vacuum. Purification by preparative TLC plate (petroleum ether : ethyl acetate = 2 : 1 as eluent) afforded the product **2a** as a white solid (21.4 mg, 78% yield). mp 135-136 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.35 (bs, 1H), 8.83 (dd, *J* = 4.2 and 1.7 Hz, 1H), 8.11 (dd, *J* = 8.3 and 1.7 Hz, 1H), 7.45 – 7.37 (m, 2H), 7.36 – 7.28 (m, 2H), 7.29 – 7.20 (m, 3H), 7.15 (d, *J* = 8.4 Hz, 1H), 4.48 (t, *J* = 7.3 Hz, 1H), 3.10 (dd, *J* = 16.4 and 6.9 Hz, 1H), 3.00 (dd, *J* = 16.4 and 7.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.01, 149.35, 141.90, 136.72, 136.03, 133.19, 129.16, 127.84, 127.47, 126.89, 123.59, 121.88, 121.14, 42.70, 38.84; HRMS(EI) Calcd for $C_{18}H_{14}N_2O$ [M^+]: 274.1106, Found 274.1091; IR (KBr) ν_{max} (cm^{-1}) : 3432, 1682, 1510, 1472, 832, 671.



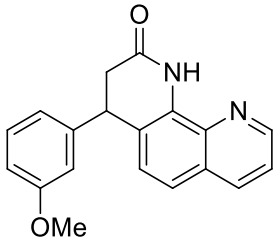
4-(*p*-Tolyl)-3,4-dihydro-1,10-phenanthrolin-2(1H)-one (2b):

1b (29.0 mg, 0.1 mmol), $Pd(OAc)_2$ (2.3 mg, 0.01 mmol), AgOAc (33.4 mg, 0.2 mmol), DMAP (4.9 mg, 0.04 mmol) and anhydrous toluene (2 mL) were added in turn into a 25 mL of glass sealed tube. The tube was tightly capped. The reaction mixture was stirred for 5 minutes at room temperature and then stirred at 160 °C in a pre-heated oil bath for 40 h. After cooling down to room temperature, the reaction mixture was concentrated under vacuum. Purification by preparative TLC plate (petroleum ether : ethyl acetate = 2 : 1 as eluent) afforded the product **2b** as a yellow solid (18.7 mg, 65% yield). mp 94-95 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.35 (bs, 1H), 8.83 (dd, *J* = 4.2 and 1.6 Hz, 1H), 8.11 (dd, *J* = 8.3 and 1.6 Hz, 1H), 7.49 – 7.35 (m, 2H), 7.20 – 7.06 (m, 5H), 4.46 (t, *J* = 7.4 Hz, 1H), 3.09 (dd, *J* = 16.4 and 6.9 Hz, 1H), 2.99 (dd, *J* = 16.4 and 7.9 Hz, 1H), 2.33 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.16, 149.34, 138.87, 137.14, 136.75, 136.03, 133.13, 129.83, 127.73, 127.46, 126.91, 123.92, 121.84, 121.11, 42.33, 38.91, 21.17; HRMS(EI) Calcd for $C_{19}H_{16}N_2O$ [M^+]: 288.1263, Found 288.1263; IR (KBr) ν_{max} (cm^{-1}) : 3433, 1688, 1510, 1472, 1380, 820.



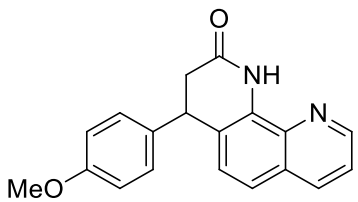
4-(2-Methoxyphenyl)-3,4-dihydro-1,10-phenanthrolin-2(1H)-one (2c):

1c (30.6 mg, 0.1 mmol), $Pd(OAc)_2$ (2.3 mg, 0.01 mmol), AgOAc (50.0 mg, 0.3 mmol), DMAP (4.9 mg, 0.04 mmol) and anhydrous toluene (2 mL) were added in turn into a 25 mL of glass sealed tube. The tube was tightly capped. The reaction mixture was stirred for 5 minutes at room temperature and then stirred at 160 °C in a pre-heated oil bath for 40 h. After cooling down to room temperature, the reaction mixture was concentrated under vacuum. Purification by preparative TLC plate (petroleum ether : ethyl acetate = 2 : 1 as eluent) afforded the product **2c** as a yellow solid (25.3 mg, 83% yield). mp 144-145 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.35 (bs, 1H), 8.86 (dd, *J* = 4.2 and 1.6 Hz, 1H), 8.14 (dd, *J* = 8.3 and 1.6 Hz, 1H), 7.50 – 7.38 (m, 2H), 7.28 – 7.17 (m, 2H), 6.97 – 6.82 (m, 3H), 4.92 (t, *J* = 6.9 Hz, 1H), 3.88 (s, 3H), 3.10 – 3.03 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.66, 156.99, 149.19, 136.74, 135.99, 133.53, 129.77, 128.61, 128.55, 127.42, 127.08, 123.38, 121.71, 121.01, 120.94, 110.89, 55.41, 37.09, 36.58; HRMS(EI) Calcd for $C_{19}H_{16}N_2O_2$ [M^+]: 304.1212, Found 304.1194; IR (KBr) ν_{max} (cm^{-1}) : 3440, 1680, 1510, 1488, 1244, 752.



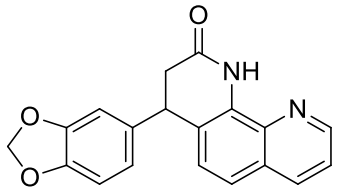
4-(3-Methoxyphenyl)-3,4-dihydro-1,10-phenanthrolin-2(1H)-one (2d):

1d (30.6 mg, 0.1 mmol), $Pd(OAc)_2$ (3.4 mg, 0.015 mmol), AgOAc (25.0 mg, 0.15 mmol), DMAP (7.3 mg, 0.06 mmol) and anhydrous toluene (2 mL) were added in turn into a 25 mL of glass sealed tube. The tube was tightly capped. The reaction mixture was stirred for 5 minutes at room temperature and then stirred at 160 °C in a pre-heated oil bath for 40 h. After cooling down to room temperature, the reaction mixture was concentrated under vacuum. Purification by preparative TLC plate (petroleum ether : ethyl acetate = 2 : 1 as eluent) afforded the product **2d** as a yellow solid (22.9 mg, 75% yield). mp 91-93 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.35 (bs, 1H), 8.83 (dd, *J* = 4.2 and 1.6 Hz, 1H), 8.11 (dd, *J* = 8.3 and 1.5 Hz, 1H), 7.47 – 7.37 (m, 2H), 7.30 – 7.13 (m, 2H), 6.88 – 6.71 (m, 3H), 4.46 (t, *J* = 7.4 Hz, 1H), 3.77 (s, 3H), 3.10 (dd, *J* = 16.4 and 6.9 Hz, 1H), 3.00 (dd, *J* = 16.4 and 7.9 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.98, 160.17, 149.35, 143.51, 136.73, 136.03, 133.20, 130.20, 127.51, 126.90, 123.45, 121.89, 121.15, 120.19, 114.02, 112.40, 55.34, 42.73, 38.80; HRMS(EI) Calcd for $C_{19}H_{16}N_2O_2$ [M^+]: 304.1212, Found 304.1219; IR (KBr) ν_{max} (cm^{-1}) : 3440, 1680, 1510, 1487, 1442, 1262.



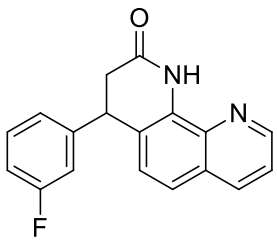
4-(4-Methoxyphenyl)-3,4-dihydro-1,10-phenanthrolin-2(1H)-one (2e):

1e (30.6 mg, 0.1 mmol), $Pd(OAc)_2$ (3.4 mg, 0.015 mmol), AgOAc (25.0 mg, 0.15 mmol), DMAP (7.3 mg, 0.06 mmol) and anhydrous toluene (2 mL) were added in turn into a 25 mL of glass sealed tube. The tube was tightly capped. The reaction mixture was stirred for 5 minutes at room temperature and then stirred at 160 ºC in a pre-heated oil bath for 40 h. After cooling down to room temperature, the reaction mixture was concentrated under vacuum. Purification by preparative TLC plate (petroleum ether : ethyl acetate = 2 : 1 as eluent) afforded the product **2e** as a yellow solid (21.3 mg, 70% yield). mp 95-97 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.34 (bs, 1H), 8.83 (dd, *J* = 4.2 and 1.6 Hz, 1H), 8.11 (dd, *J* = 8.3 and 1.6 Hz, 1H), 7.47 – 7.37 (m, 2H), 7.19 – 7.09 (m, 3H), 6.92 – 6.83 (m, 2H), 4.44 (t, *J* = 7.3 Hz, 1H), 3.79 (s, 3H), 3.08 (dd, *J* = 16.4 and 6.8 Hz, 1H), 2.97 (dd, *J* = 16.4 and 7.9 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.16, 158.92, 149.33, 136.74, 136.03, 133.89, 133.07, 128.86, 127.44, 126.87, 124.06, 121.83, 121.12, 114.52, 55.41, 41.91, 39.02; HRMS(EI) Calcd for $C_{19}H_{16}N_2O_2$ [M^+]: 304.1212, Found 304.1234; IR (KBr) ν_{max} (cm^{-1}) : 3439, 1683, 1510, 1471, 1247, 830.



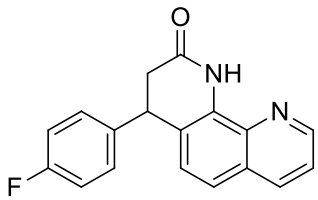
4-(Benzo[d][1,3]dioxol-5-yl)-3,4-dihydro-1,10-phenanthrolin-2(1H)-one (2f):

1f (32.0 mg, 0.1 mmol), $Pd(OAc)_2$ (3.4 mg, 0.015 mmol), AgOAc (25.0 mg, 0.15 mmol), DMAP (7.3 mg, 0.06 mmol) and anhydrous toluene (2 mL) were added in turn into a 25 mL of glass sealed tube. The tube was tightly capped. The reaction mixture was stirred for 5 minutes at room temperature and then stirred at 160 ºC in a pre-heated oil bath for 40 h. After cooling down to room temperature, the reaction mixture was concentrated under vacuum. Purification by preparative TLC plate (petroleum ether : ethyl acetate = 2 : 1 as eluent) afforded the product **2f** as a yellow solid (27.6 mg, 87% yield). mp 182-184 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.34 (bs, 1H), 8.86 – 8.78 (m, 1H), 8.11 (d, *J* = 8.3 Hz, 1H), 7.47 – 7.31 (m, 2H), 7.17 (d, *J* = 8.4 Hz, 1H), 6.79 – 6.65 (m, 3H), 5.93 (s, 2H), 4.40 (t, *J* = 7.1 Hz, 1H), 3.07 (dd, *J* = 16.4 and 6.8 Hz, 1H), 2.93 (dd, *J* = 16.3 and 7.7 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.95, 149.36, 148.28, 146.91, 136.71, 136.02, 135.72, 133.09, 127.49, 126.84, 123.65, 121.89, 121.19, 121.03, 108.70, 108.07, 101.24, 42.42, 39.09; HRMS(EI) Calcd for $C_{19}H_{14}N_2O_3$ [M^+]: 318.1004, Found 318.1006; IR (KBr) ν_{max} (cm^{-1}) : 3441, 1668, 1506, 1488, 1247,1037.



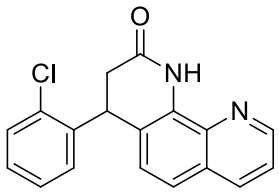
4-(3-Fluorophenyl)-3,4-dihydro-1,10-phenanthrolin-2(1H)-one (2g):

1g (29.4 mg, 0.1 mmol), $Pd(OAc)_2$ (3.4 mg, 0.015 mmol), AgOAc (25.0 mg, 0.15 mmol), DMAP (7.3 mg, 0.06 mmol) and anhydrous toluene (2 mL) were added in turn into a 25 mL of glass sealed tube. The tube was tightly capped. The reaction mixture was stirred for 5 minutes at room temperature and then stirred at 160 °C in a pre-heated oil bath for 40 h. After cooling down to room temperature, the reaction mixture was concentrated under vacuum. Purification by preparative TLC plate (petroleum ether : ethyl acetate = 2 : 1 as eluent) afforded the product **2g** as a yellow solid (19.6 mg, 67% yield). mp 118-120 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.28 (bs, 1H), 8.77 (d, *J* = 3.7 Hz, 1H), 8.06 (d, *J* = 8.3 Hz, 1H), 7.42 – 7.31 (m, 2H), 7.26 – 7.17 (m, 1H), 7.09 (d, *J* = 8.4 Hz, 1H), 6.97 – 6.78 (m, 3H), 4.42 (t, *J* = 7.0 Hz, 1H), 3.05 (dd, *J* = 16.4 and 6.9 Hz, 1H), 2.90 (dd, *J* = 16.4 and 7.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.59, 163.27 (d, $J_{c\text{-}f}$ = 245.2 Hz), 149.50, 144.48 (d, $J_{c\text{-}f}$ = 6.8 Hz, 1H), 136.75, 136.09, 133.31, 130.73 (d, $J_{c\text{-}f}$ = 8.3 Hz), 127.64, 126.75, 123.48 (d, $J_{c\text{-}f}$ = 2.8 Hz), 122.72, 122.07, 121.36, 114.84 (d, $J_{c\text{-}f}$ = 21.7 Hz), 114.47 (d, $J_{c\text{-}f}$ = 21.0 Hz), 42.44, 38.73; ^{19}F NMR (376 MHz, $CDCl_3$) δ -112.06; HRMS(EI) Calcd for $C_{18}H_{13}N_2OF$ [M^+]: 292.1012, Found 292.1025; IR (KBr) ν_{max} (cm^{-1}) : 3365, 1671, 1508, 1323, 791, 665.



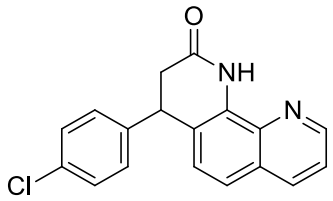
4-(4-Fluorophenyl)-3,4-dihydro-1,10-phenanthrolin-2(1H)-one (2h):

1h (29.4 mg, 0.1 mmol), $Pd(OAc)_2$ (3.4 mg, 0.015 mmol), AgOAc (25.0 mg, 0.15 mmol), DMAP (7.3 mg, 0.06 mmol) and anhydrous toluene (2 mL) were added in turn into a 25 mL of glass sealed tube. The tube was tightly capped. The reaction mixture was stirred for 5 minutes at room temperature and then stirred at 160 °C in a pre-heated oil bath for 40 h. After cooling down to room temperature, the reaction mixture was concentrated under vacuum. Purification by preparative TLC plate (petroleum ether : ethyl acetate = 2 : 1 as eluent) afforded the product **2h** as a yellow solid (18.1 mg, 62% yield). mp 118-120 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.35 (bs, 1H), 8.84 (dd, *J* = 4.2 and 1.6 Hz, 1H), 8.12 (dd, *J* = 8.3 and 1.6 Hz, 1H), 7.50 – 7.37 (m, 2H), 7.21 – 7.12 (m, 3H), 7.05 – 6.95 (m, 2H), 4.48 (t, *J* = 7.1 Hz, 1H), 3.10 (dd, *J* = 16.4 and 6.9 Hz, 1H), 2.96 (dd, *J* = 16.4 and 7.5 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.77, 162.11 (d, $J_{c\text{-}f}$ = 244.5 Hz), 149.46, 137.65 (d, $J_{c\text{-}f}$ = 3.2 Hz), 136.74, 136.07, 133.20, 129.37 (d, $J_{c\text{-}f}$ = 8.0 Hz), 127.56, 126.73, 123.32, 122.00, 121.29, 116.03 (d, $J_{c\text{-}f}$ = 21.3 Hz), 41.99, 38.99; ^{19}F NMR (376 MHz, $CDCl_3$) δ -115.16; HRMS(EI) Calcd for $C_{18}H_{13}N_2OF$ [M^+]: 292.1012, Found 292.1023; IR (KBr) ν_{max} (cm^{-1}) : 3441, 1686, 1509, 1471, 1222, 832.



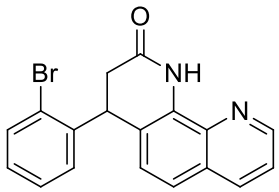
4-(2-Chlorophenyl)-3,4-dihydro-1,10-phenanthrolin-2(1H)-one (2i):

1i (31.1 mg, 0.1 mmol), $Pd(OAc)_2$ (3.4 mg, 0.015 mmol), AgOAc (25.0 mg, 0.15 mmol), DMAP (7.3 mg, 0.06 mmol) and anhydrous toluene (2 mL) were added in turn into a 25 mL of glass sealed tube. The tube was tightly capped. The reaction mixture was stirred for 5 minutes at room temperature and then stirred at 160 ^oC in a pre-heated oil bath for 40 h. After cooling down to room temperature, the reaction mixture was concentrated under vacuum. Purification by preparative TLC plate (petroleum ether : ethyl acetate = 2 : 1 as eluent) afforded the product **2i** as a yellow solid (23.1 mg, 75% yield). mp 120-121 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 9.37 (bs, 1H), 8.86 (dd, *J* = 4.2 and 1.6 Hz, 1H), 8.14 (dd, *J* = 8.3 and 1.6 Hz, 1H), 7.52 – 7.38 (m, 3H), 7.24 – 7.10 (m, 3H), 6.95 (dd, *J* = 7.7 and 1.6 Hz, 1H), 5.05 (t, *J* = 6.9 Hz, 1H), 3.12 (dd, *J* = 16.5 and 7.3 Hz, 1H), 3.02 (dd, *J* = 16.5 and 6.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.65, 149.45, 139.05, 136.75, 136.09, 133.83, 133.73, 130.27, 129.18, 128.75, 127.68, 127.62, 126.87, 122.27, 122.05, 121.42, 39.14, 37.28; HRMS(EI) Calcd for $C_{18}H_{13}N_2OCl$ [M^+]: 308.0716, Found 308.0719; IR (KBr) ν_{max} (cm^{-1}) : 3440, 1684, 1510, 1471, 738, 646.



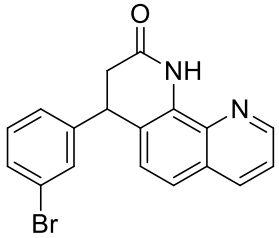
4-(4-Chlorophenyl)-3,4-dihydro-1,10-phenanthrolin-2(1H)-one (2j):

1j (31.1 mg, 0.1 mmol), $Pd(OAc)_2$ (3.4 mg, 0.015 mmol), AgOAc (25.0 mg, 0.15 mmol), DMAP (7.3 mg, 0.06 mmol) and anhydrous toluene (2 mL) were added in turn into a 25 mL of glass sealed tube. The tube was tightly capped. The reaction mixture was stirred for 5 minutes at room temperature and then stirred at 160 ^oC in a pre-heated oil bath for 40 h. After cooling down to room temperature, the reaction mixture was concentrated under vacuum. Purification by preparative TLC plate (petroleum ether : ethyl acetate = 2 : 1 as eluent) afforded the product **2j** as a yellow solid (20.5 mg, 66% yield). mp 94-96 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 9.35 (bs, 1H), 8.84 (dd, *J* = 4.2 and 1.6 Hz, 1H), 8.13 (dd, *J* = 8.3 and 1.5 Hz, 1H), 7.49 – 7.38 (m, 2H), 7.33 – 7.23 (m, 2H), 7.19 – 7.10 (m, 3H), 4.47 (t, *J* = 7.1 Hz, 1H), 3.10 (dd, *J* = 16.4 and 6.9 Hz, 1H), 2.95 (dd, *J* = 16.4 and 7.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.64, 149.49, 140.42, 136.73, 136.08, 133.32, 133.26, 129.33, 129.19, 127.59, 126.68, 122.95, 122.05, 121.34, 42.13, 38.79; HRMS(EI) Calcd for $C_{18}H_{13}N_2OCl$ [M^+]: 308.0716, Found 308.0717; IR (KBr) ν_{max} (cm^{-1}) : 3433, 1682, 1510, 1490, 1380, 830.



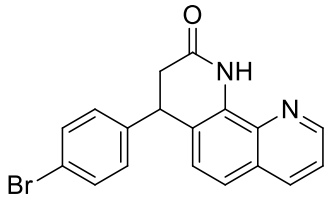
4-(2-Bromophenyl)-3,4-dihydro-1,10-phenanthrolin-2(1H)-one (2k):

1k (35.6 mg, 0.1 mmol), $Pd(OAc)_2$ (2.3 mg, 0.015 mmol), AgOAc (50.0 mg, 0.3 mmol), DMAP (4.9 mg, 0.04 mmol) and anhydrous toluene (2 mL) were added in turn into a 25 mL of glass sealed tube. The tube was tightly capped. The reaction mixture was stirred for 5 minutes at room temperature and then stirred at 160 °C in a pre-heated oil bath for 40 h. After cooling down to room temperature, the reaction mixture was concentrated under vacuum. Purification by preparative TLC plate (petroleum ether : ethyl acetate = 2 : 1 as eluent) afforded the product **2k** as a yellow solid (23.1 mg, 65% yield). mp 144-146 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.37 (bs, 1H), 8.86 (dd, *J* = 4.2 and 1.6 Hz, 1H), 8.14 (dd, *J* = 8.3 and 1.6 Hz, 1H), 7.64 (dd, *J* = 7.8 and 1.4 Hz, 1H), 7.53 – 7.35 (m, 2H), 7.27 – 7.06 (m, 3H), 6.95 (dd, *J* = 7.6 and 1.7 Hz, 1H), 5.04 (t, *J* = 7.0 Hz, 1H), 3.12 (dd, *J* = 16.5 and 7.4 Hz, 1H), 3.01 (dd, *J* = 16.5 and 6.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.54, 149.45, 140.74, 136.75, 136.09, 133.80, 133.59, 129.28, 129.04, 128.27, 127.68, 126.89, 124.41, 122.34, 122.06, 121.42, 41.70, 37.46; HRMS(EI) Calcd for $C_{18}H_{13}N_2OBr$ [M^+]: 352.0211, Found 352.0215; IR (KBr) ν_{max} (cm^{-1}) : 3442, 1678, 1510, 1472, 767, 662.



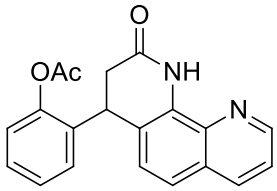
4-(3-Bromophenyl)-3,4-dihydro-1,10-phenanthrolin-2(1H)-one (2l):

1l (35.5 mg, 0.1 mmol), $Pd(OAc)_2$ (3.4 mg, 0.015 mmol), AgOAc (25.0 mg, 0.15 mmol), DMAP (7.3 mg, 0.06 mmol) and anhydrous toluene (2 mL) were added in turn into a 25 mL of glass sealed tube. The tube was tightly capped. The reaction mixture was stirred for 5 minutes at room temperature and then stirred at 160 °C in a pre-heated oil bath for 40 h. After cooling down to room temperature, the reaction mixture was concentrated under vacuum. Purification by preparative TLC plate (petroleum ether : ethyl acetate = 2 : 1 as eluent) afforded the product **2l** as a yellow solid (25.2 mg, 71% yield). mp 114-116 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.36 (bs, 1H), 8.85 (dd, *J* = 4.2 and 1.4 Hz, 1H), 8.13 (dd, *J* = 8.3 and 1.4 Hz, 1H), 7.50 – 7.34 (m, 4H), 7.24 – 7.10 (m, 3H), 4.46 (t, *J* = 7.1 Hz, 1H), 3.11 (dd, *J* = 16.4 and 7.0 Hz, 1H), 2.97 (dd, *J* = 16.4 and 7.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.50, 149.51, 144.32, 136.75, 136.10, 133.33, 130.96, 130.78, 130.71, 127.65, 126.71, 126.47, 123.21, 122.57, 122.10, 121.41, 42.43, 38.74; HRMS(EI) Calcd for $C_{18}H_{13}N_2OBr$ [M^+]: 352.0211, Found 352.0209; IR (KBr) ν_{max} (cm^{-1}) : 3443, 1675, 1511, 1473, 1385, 685.



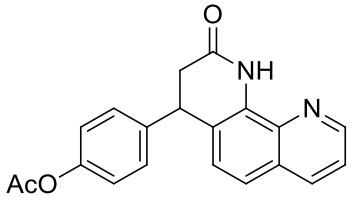
4-(4-Bromophenyl)-3,4-dihydro-1,10-phenanthrolin-2(1H)-one (2m):

1m (35.5 mg, 0.1 mmol), $Pd(OAc)_2$ (3.4 mg, 0.015 mmol), AgOAc (25.0 mg, 0.15 mmol), DMAP (7.3 mg, 0.06 mmol) and anhydrous toluene (2 mL) were added in turn into a 25 mL of glass sealed tube. The tube was tightly capped. The reaction mixture was stirred for 5 minutes at room temperature and then stirred at 160 ºC in a pre-heated oil bath for 40 h. After cooling down to room temperature, the reaction mixture was concentrated under vacuum. Purification by preparative TLC plate (petroleum ether : ethyl acetate = 2 : 1 as eluent) afforded the product **2m** as a yellow solid (26.1 mg, 74% yield). mp 145-146 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.36 (bs, 1H), 8.88 – 8.81 (m, 1H), 8.13 (d, *J* = 8.3 Hz, 1H), 7.55 – 7.35 (m, 4H), 7.17 – 7.06 (m, 3H), 4.46 (t, *J* = 6.9 Hz, 1H), 3.18 – 3.04 (m, 1H), 3.01 – 2.88 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.61, 149.49, 140.95, 136.72, 136.08, 133.26, 132.28, 129.56, 127.59, 126.66, 122.84, 122.05, 121.38, 121.35, 42.20, 38.71; HRMS(EI) Calcd for $C_{18}H_{13}N_2OBr$ [M^+]: 352.0211, Found 352.0213; IR (KBr) ν_{max} (cm^{-1}) : 3450, 1677, 1510, 1383, 825, 646.



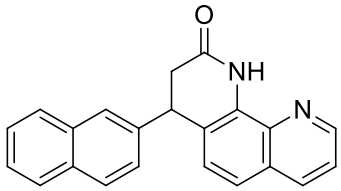
2-(2-oxo-1,2,3,4-Tetrahydro-1,10-phenanthrolin-4-yl)phenyl acetate (2n):

1n (33.4 mg, 0.1 mmol), $Pd(OAc)_2$ (3.4 mg, 0.015 mmol), AgOAc (50.0 mg, 0.3 mmol), DMAP (7.3 mg, 0.06 mmol) and anhydrous toluene (2 mL) were added in turn into a 25 mL of glass sealed tube. The tube was tightly capped. The reaction mixture was stirred for 5 minutes at room temperature and then stirred at 160 ºC in a pre-heated oil bath for 40 h. After cooling down to room temperature, the reaction mixture was concentrated under vacuum. Purification by preparative TLC plate (petroleum ether : ethyl acetate = 2 : 1 as eluent) afforded the product **2n** as a yellow solid (17.3 mg, 52% yield). mp 151-152 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.39 (bs, 1H), 8.83 (dd, *J* = 4.2 and 1.5 Hz, 1H), 8.10 (dd, *J* = 8.3 and 1.5 Hz, 1H), 7.46 – 7.27 (m, 3H), 7.21 – 7.04 (m, 4H), 4.65 (t, *J* = 8.0 Hz, 1H), 3.15 – 2.90 (m, 2H), 2.21 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.33, 168.76, 149.35, 148.68, 136.56, 136.05, 133.59, 133.29, 129.20, 128.58, 127.47, 126.81, 126.63, 123.22, 122.53, 121.92, 121.25, 37.66, 36.88, 21.03; HRMS(EI) Calcd for $C_{20}H_{16}N_2O_3$ [M^+]: 332.1161, Found 332.1153; IR (KBr) ν_{max} (cm^{-1}) : 3345, 1753, 1678, 1510, 1472, 1210.



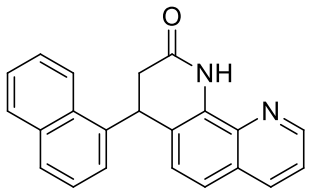
4-(2-oxo-1,2,3,4-Tetrahydro-1,10-phenanthrolin-4-yl)phenyl acetate (2o):

1o (33.4 mg, 0.1 mmol), $Pd(OAc)_2$ (3.4 mg, 0.015 mmol), AgOAc (25.0 mg, 0.15 mmol), DMAP (7.3 mg, 0.06 mmol) and anhydrous toluene (2 mL) were added in turn into a 25 mL of glass sealed tube. The tube was tightly capped. The reaction mixture was stirred for 5 minutes at room temperature and then stirred at 160 ºC in a pre-heated oil bath for 40 h. After cooling down to room temperature, the reaction mixture was concentrated under vacuum. Purification by preparative TLC plate (petroleum ether : ethyl acetate = 2 : 1 as eluent) afforded the product **2o** as a yellow solid (18.3 mg, 55% yield). mp 87-88 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.38 (bs, 1H), 8.91 – 8.77 (m, 1H), 8.14 (d, *J* = 8.3 Hz, 1H), 7.49 – 7.39 (m, 2H), 7.31 – 7.15 (m, 3H), 7.12 – 7.00 (m, 2H), 4.51 (t, *J* = 7.1 Hz, 1H), 3.13 (dd, *J* = 16.4 and 6.9 Hz, 1H), 3.00 (dd, *J* = 16.3 and 7.5 Hz, 1H), 2.31 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.55, 168.84, 149.90, 149.40, 139.38, 136.70, 136.05, 133.13, 128.84, 127.52, 126.84, 123.24, 122.22, 121.95, 121.25, 42.11, 38.81, 21.23; HRMS(EI) Calcd for $C_{20}H_{16}N_2O_3$ [M^+]: 332.1161, Found 332.1169; IR (KBr) ν_{max} (cm^{-1}) : 3440, 1758, 1682, 1509, 1198, 833.



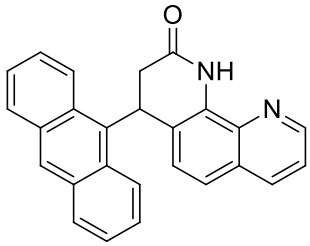
4-(Naphthalen-2-yl)-3,4-dihydro-1,10-phenanthrolin-2(1H)-one (2p):

1p (32.6 mg, 0.1 mmol), $Pd(OAc)_2$ (3.4 mg, 0.015 mmol), AgOAc (25.0 mg, 0.15 mmol), DMAP (7.3 mg, 0.06 mmol) and anhydrous toluene (2 mL) were added in turn into a 25 mL of glass sealed tube. The tube was tightly capped. The reaction mixture was stirred for 5 minutes at room temperature and then stirred at 160 ºC in a pre-heated oil bath for 40 h. After cooling down to room temperature, the reaction mixture was concentrated under vacuum. Purification by preparative TLC plate (petroleum ether : ethyl acetate = 2 : 1 as eluent) afforded the product **2P** as a yellow solid (23.8 mg, 73% yield). mp 173-174 °C. ^{1}H NMR (400 MHz, $CDCl_3$) 9.42 (bs, 1H), 8.86 (d, *J* = 4.0 Hz, 1H), 8.12 (d, *J* = 8.3 Hz, 1H), 7.87 – 7.61 (m, 4H), 7.53 – 7.33 (m, 5H), 7.16 (d, *J* = 8.4 Hz, 1H), 4.66 (t, *J* = 7.5 Hz, 1H), 3.24 – 3.05 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.99, 149.39, 139.18, 136.74, 136.05, 133.65, 133.25, 132.77, 129.10, 127.91, 127.78, 127.52, 126.92, 126.71, 126.49, 126.14, 125.80, 123.47, 121.92, 121.18, 42.88, 38.77; HRMS(EI) Calcd for $C_{22}H_{16}N_2O$ [M^+]: 324.1263, Found 324.1264; IR (KBr) ν_{max} (cm^{-1}) : 3442, 1675, 1509, 1380, 757, 646.



4-(Naphthalen-1-yl)-3,4-dihydro-1,10-phenanthrolin-2(1H)-one (2q):

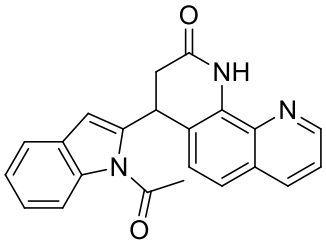
1q (32.6 mg, 0.1 mmol), $Pd(OAc)_2$ (3.4 mg, 0.015 mmol), AgOAc (25.0 mg, 0.15 mmol), DMAP (7.3 mg, 0.06 mmol) and anhydrous toluene (2 mL) were added in turn into a 25 mL of glass sealed tube. The tube was tightly capped. The reaction mixture was stirred for 5 minutes at room temperature and then stirred at 160 ^oC in a pre-heated oil bath for 40 h. After cooling down to room temperature, the reaction mixture was concentrated under vacuum. Purification by preparative TLC plate (petroleum ether : ethyl acetate = 2 : 1 as eluent) afforded the product **2q** as a yellow solid (19.9 mg, 61% yield). mp 160-161 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 9.43 (bs, 1H), 8.88 (dd, *J* = 4.2 and 1.7 Hz, 1H), 8.13 (dd, *J* = 8.2 and 1.1 Hz, 1H), 8.11 – 8.03 (m, 1H), 7.98 – 7.89 (m, 1H), 7.79 (d, *J* = 8.2 Hz, 1H), 7.60 – 7.31 (m, 5H), 7.13 – 7.06 (m, 2H), 5.33 (t, *J* = 7.4 Hz, 1H), 3.22 (d, *J* = 7.5 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.00, 149.40, 136.89, 136.78, 136.06, 134.49, 133.73, 131.12, 129.48, 128.27, 127.57, 127.10, 126.56, 125.89, 125.83, 125.75, 123.38, 123.29, 121.94, 121.30, 38.79, 38.13; HRMS(EI) Calcd for $C_{22}H_{16}N_2O$ [M^+]: 324.1263, Found 324.1268; IR (KBr) ν_{max} (cm^{-1}) : 3432, 1683, 1510, 1471, 1318, 777.



4-(Anthracen-9-yl)-3,4-dihydro-1,10-phenanthrolin-2(1H)-one (2r):

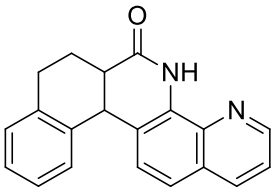
1r (37.6 mg, 0.1 mmol), $Pd(OAc)_2$ (3.4 mg, 0.015 mmol), AgOAc (33.4 mg, 0.20 mmol), DMAP (7.3 mg, 0.06 mmol) and anhydrous toluene (2 mL) were added in turn into a 25 mL of glass sealed tube. The tube was tightly capped. The reaction mixture was stirred for 5 minutes at room temperature and then stirred at 160 ^oC in a pre-heated oil bath for 40 h. After cooling down to room temperature, the reaction mixture was concentrated under vacuum. Purification by preparative TLC plate (petroleum ether : ethyl acetate = 2 : 1 as eluent) afforded the product **2r** as a colorless solid (3.3 mg, 9% yield) and recovered **1r** (20.6 mg, 69%). mp 120-121 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 9.65 (s, 1H), 8.89 (d, *J* = 3.3 Hz, 1H), 8.54 (s, 1H), 8.38 (d, *J* = 8.7 Hz, 1H), 8.18 – 8.02 (m, 3H), 7.87 (d, *J* = 9.0 Hz, 1H), 7.65 – 7.50 (m, 2H), 7.45 (dd, *J* = 8.2 and 4.3 Hz, 1H), 7.40 (t, *J* = 7.5 Hz, 1H), 7.18 (d, *J* = 8.4 Hz, 2H), 6.73 (d, *J* = 8.5 Hz, 1H), 6.24 (dd, *J* = 14.8 and 7.2 Hz, 1H), 3.71 (dd, *J* = 17.2 and 15.0 Hz, 1H), 3.05 (dd, *J* = 17.4 and 7.2 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.31, 149.39, 136.83, 136.11, 132.52, 132.11, 131.83, 131.66, 131.20, 130.16, 129.90, 128.92, 128.54, 127.29, 127.04, 126.77, 126.33, 125.34, 125.27, 124.85, 124.45,

122.86, 121.78, 121.17, 37.16, 36.50.; HRMS(EI) Calcd for $C_{26}H_{18}N_2O$ [M^+]: 374.1416, Found 374.1419; IR (KBr) ν_{max} (cm^{-1}) : 3440, 1676, 1510, 1473, 1284, 1050.



4-(1-Acetyl-1H-indol-3-yl)-3,4-dihydro-1,10-phenanthrolin-2(1H)-one (2s):

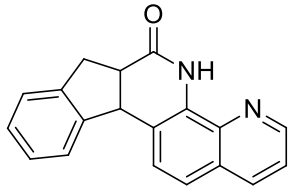
1s (35.7 mg, 0.1 mmol), $Pd(OAc)_2$ (3.4 mg, 0.015 mmol), AgOAc (25.0 mg, 0.15 mmol), DMAP (7.3 mg, 0.06 mmol) and anhydrous toluene (2 mL) were added in turn into a 25 mL of glass sealed tube. The tube was tightly capped. The reaction mixture was stirred for 5 minutes at room temperature and then stirred at 160 °C in a pre-heated oil bath for 40 h. After cooling down to room temperature, the reaction mixture was concentrated under vacuum. Purification by preparative TLC plate (petroleum ether : ethyl acetate = 2 : 1 as eluent) afforded the product **2s** as a yellow solid (12.6 mg, 34% yield) and recovered **1s** (17.1 mg, 46%). mp 79-80 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.55 (bs, 1H), 9.02 (dd, *J* = 4.2 and 1.7 Hz, 1H), 8.61 (d, *J* = 8.3 Hz, 1H), 8.29 (dd, *J* = 8.3 and 1.7 Hz, 1H), 7.67 – 7.51 (m, 4H), 7.46 – 7.40 (m, 3H), 4.92 (t, *J* = 7.2 Hz, 1H), 3.35 (dd, *J* = 16.3 and 7.8 Hz, 1H), 3.27 (dd, *J* = 16.3 and 6.8 Hz, 1H), 2.69 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 169.00, 168.52, 149.49, 136.76, 136.55, 136.12, 133.15, 128.88, 127.67, 126.52, 125.79, 123.80, 123.04, 122.43, 122.16, 122.06, 121.39, 119.40, 117.17, 37.22, 34.16, 24.17; HRMS(EI) Calcd for $C_{22}H_{17}N_3O_2$ [M^+]: 355.1321, Found 355.1319; IR (KBr) ν_{max} (cm^{-1}) : 3436, 1687, 1450, 1327, 1215, 1019.



6,7,8,12-Tetrahydronaphtho[2,1][1,10]phenanthrolin-6(5H)-one (2t):

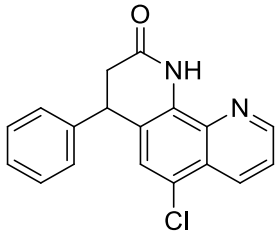
1t (32.8 mg, 0.1 mmol), $Pd(OAc)_2$ (3.4 mg, 0.015 mmol), AgOAc (25.0 mg, 0.15 mmol), DMAP (7.3 mg, 0.06 mmol) and anhydrous toluene (2 mL) were added in turn into a 25 mL of glass sealed tube. The tube was tightly capped. The reaction mixture was stirred for 5 minutes at room temperature and then stirred at 160 °C in a pre-heated oil bath for 40 h. After cooling down to room temperature, the reaction mixture was concentrated under vacuum. Purification by preparative TLC plate (petroleum ether : ethyl acetate = 2 : 1 as eluent) afforded the product **2t** as a colorless solid (8.6 mg, 26% yield) and recovered **1t** (21.6 mg, 66%). mp 203-204 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.27 (bs, 1H), 8.81 (dd, *J* = 4.2 and 1.7 Hz, 1H), 8.13 (dd, *J* = 8.3 and 1.7 Hz, 1H), 7.55 – 7.02 (m, 7H), 4.47 (d, *J* = 5.7 Hz, 1H), 3.20 – 2.85 (m,

3H), 2.38 – 2.18 (m, 1H), 2.18 – 2.00 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.03, 149.31, 136.80, 136.70, 136.01, 134.05, 132.25, 129.72, 129.70, 127.49, 127.37, 127.25, 125.81, 123.56, 121.76, 120.76, 40.72, 40.49, 26.98, 21.47; HRMS(EI) Calcd for $C_{20}H_{16}N_2O$ [M^+]: 300.1263, Found 300.1265; IR (KBr) ν_{max} (cm^{-1}) : 3340, 1673, 1511, 1474, 1383, 658.



6,7-Dihydro-5H-indeno[2,1][1,10]phenanthrolin-6(11H)-one (2u):

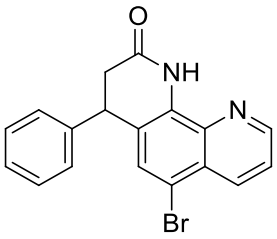
1u (28.8 mg, 0.1 mmol), $Pd(OAc)_2$ (3.4 mg, 0.015 mmol), AgOAc (25.0 mg, 0.15 mmol), DMAP (7.3 mg, 0.06 mmol) and anhydrous toluene (2 mL) were added in turn into a 25 mL of glass sealed tube. The tube was tightly capped. The reaction mixture was stirred for 5 minutes at room temperature and then stirred at 160 °C in a pre-heated oil bath for 40 h. After cooling down to room temperature, the reaction mixture was concentrated under vacuum. Purification by preparative TLC plate (petroleum ether : ethyl acetate = 2 : 1 as eluent) afforded the product **2u** as a colorless solid (5.6 mg, 20% yield) and recovered **1u** (15.7 mg, 55%). mp 228-230 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.34 (bs, 1H), 8.79 (dd, *J* = 4.2 and 1.7 Hz, 1H), 8.16 (dd, *J* = 8.3 and 1.7 Hz, 1H), 7.63 (d, *J* = 8.3 Hz, 1H), 7.56 (d, *J* = 8.3 Hz, 1H), 7.43 (dd, *J* = 8.4 and 4.2 Hz, 1H), 7.36 – 7.26 (m, 1H), 7.25 – 7.05 (m, 3H), 4.72 (d, *J* = 8.0 Hz, 1H), 3.77 (dd, *J* = 15.8 and 2.6 Hz, 1H), 3.57 (td, *J* = 7.8 and 2.6 Hz, 1H), 3.38 (dd, *J* = 15.8 and 7.6 Hz, 1H), ^{13}C NMR (150 MHz, $CDCl_3$) δ 170.81, 149.23, 143.08, 141.66, 136.73, 136.03, 132.10, 127.61, 127.55, 127.52, 126.90, 124.94, 123.84, 121.82, 120.99, 120.06, 47.27, 45.03, 35.67. HRMS(EI) Calcd for $C_{19}H_{14}N_2O$ [M^+]: 286.1106, Found 286.1105; IR (KBr) ν_{max} (cm^{-1}) : 3364, 1667, 1511, 1477, 1290, 690.



6-Chloro-4-phenyl-3,4-dihydro-1,10-phenanthrolin-2(1H)-one (2v):

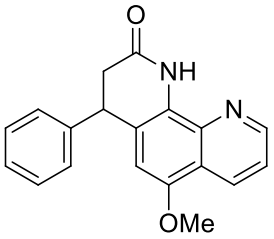
1v (31.1 mg, 0.1 mmol), $Pd(OAc)_2$ (2.3 mg, 0.01 mmol), AgOAc (33.0 mg, 0.2 mmol), DMAP (4.9 mg, 0.04 mmol) and anhydrous toluene (2 mL) were added in turn into a 25 mL of glass sealed tube. The tube was tightly capped. The reaction mixture was stirred for 5 minutes at room temperature and then stirred at 160 °C in a pre-heated oil bath for 40 h. After cooling down to room temperature, the reaction mixture was concentrated under vacuum. Purification by preparative TLC plate (petroleum ether : ethyl acetate = 2 : 1 as eluent) afforded the product **2v** as a yellow solid (24.8 mg, 80%

yield). mp 138-140 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.24 (bs, 1H), 8.82 – 8.75 (m, 1H), 8.41 (d, *J* = 8.5 Hz, 1H), 7.51 – 7.42 (m, 1H), 7.34 – 7.10 (m, 6H), 4.37 (t, *J* = 7.4 Hz, 1H), 3.08 – 2.86 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.66, 149.85, 141.20, 137.17, 133.16, 132.52, 129.34, 127.80, 127.77, 126.65, 125.46, 124.18, 123.88, 122.61, 42.62, 38.75; HRMS(EI) Calcd for $C_{18}H_{13}N_2OCl$ [M^+]: 308.0716, Found 308.0713; IR (KBr) ν_{max} (cm^{-1}) : 3441, 1701, 1505, 1466, 1365, 703.



6-Bromo-4-phenyl-3,4-dihydro-1,10-phenanthrolin-2(1H)-one (2w):

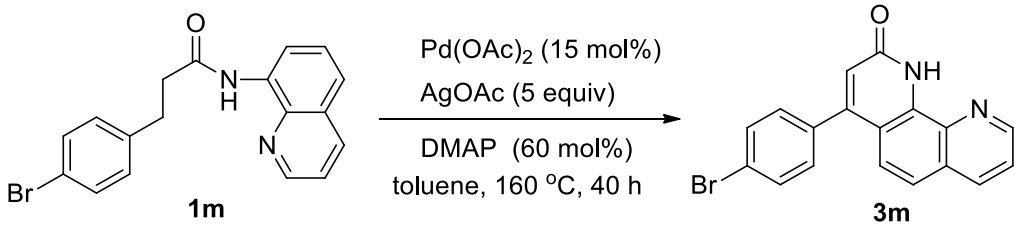
1w (35.5 mg, 0.1 mmol), $Pd(OAc)_2$ (3.4 mg, 0.015 mmol), AgOAc (33.0 mg, 0.2 mmol), DMAP (7.3 mg, 0.06 mmol) and anhydrous toluene (2 mL) were added in turn into a 25 mL of glass sealed tube. The tube was tightly capped. The reaction mixture was stirred for 5 minutes at room temperature and then stirred at 160 °C in a pre-heated oil bath for 40 h. After cooling down to room temperature, the reaction mixture was concentrated under vacuum. Purification by preparative TLC plate (petroleum ether : ethyl acetate = 2 : 1 as eluent) afforded the product **2w** as a yellow solid (30.1 mg, 85% yield). mp 144-146 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.34 (bs, 1H), 8.85 (dd, *J* = 4.2 and 1.5 Hz, 1H), 8.46 (dd, *J* = 8.5 and 1.6 Hz, 1H), 7.54 (dd, *J* = 8.5 and 4.2 Hz, 1H), 7.45 – 7.18 (m, 6H), 4.46 (t, *J* = 7.4 Hz, 1H), 3.10 (dd, *J* = 16.5 and 6.9 Hz, 1H), 3.00 (dd, *J* = 16.5 and 7.9 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.64, 149.86, 141.22, 137.30, 135.71, 133.23, 130.22, 129.36, 127.79, 126.75, 124.43, 122.96, 113.99, 42.56, 38.80; HRMS(EI) Calcd for $C_{18}H_{13}N_2OBr$ [M^+]: 352.0211, Found 352.0223; IR (KBr) ν_{max} (cm^{-1}) : 3440, 1698, 1502, 1464, 927, 703.



6-Methoxy-4-phenyl-3,4-dihydro-1,10-phenanthrolin-2(1H)-one (2x):

1x (30.6 mg, 0.1 mmol), $Pd(OAc)_2$ (3.4 mg, 0.015 mmol), AgOAc (25.0 mg, 0.15 mmol), DMAP (7.3 mg, 0.06 mmol) and anhydrous toluene (2 mL) were added in turn into a 25 mL of glass sealed tube. The tube was tightly capped. The reaction mixture was stirred for 5 minutes at room temperature and then stirred at 160 °C in a pre-heated oil bath for 40 h. After cooling down to room temperature, the reaction mixture was concentrated under vacuum. Purification by preparative TLC plate (petroleum ether : ethyl acetate = 2 : 1 as eluent) afforded the product **2x** as a yellow solid (19.8 mg, 65% yield). mp 66-68 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.16 (bs, 1H),

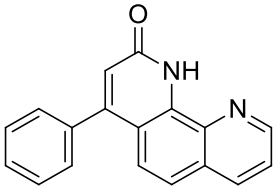
8.83 (dd, *J* = 4.2 and 1.5 Hz, 1H), 8.50 (dd, *J* = 8.4 and 1.5 Hz, 1H), 7.41 (dd, *J* = 8.4 and 4.2 Hz, 1H), 7.36 – 7.16 (m, 5H), 6.48 (s, 1H), 4.43 (t, *J* = 6.9 Hz, 1H), 3.83 (s, 3H), 3.11 (dd, *J* = 16.3 and 7.0 Hz, 1H), 2.96 (dd, *J* = 16.3 and 6.9 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.58, 150.37, 149.78, 141.94, 137.41, 131.10, 129.09, 127.76, 127.42, 126.50, 123.31, 120.93, 119.96, 104.70, 55.84, 43.23, 39.15; HRMS(EI) Calcd for $C_{19}H_{16}N_2O_2$ [M^+]: 304.1212, Found 304.1220; IR (KBr) ν_{max} (cm^{-1}) : 3382, 1680, 1478, 1130, 1096, 702.



4-(4-Bromophenyl)-1,10-phenanthrolin-2(1H)-one(3m):

1m (35.5 mg, 0.1 mmol), $Pd(OAc)_2$ (3.4 mg, 0.015 mmol), AgOAc (83.5 mg, 0.5 mmol), DMAP (7.3 mg, 0.06 mmol) and anhydrous toluene (2 mL) were added in turn into a 25 mL of glass sealed tube. The tube was tightly capped. The reaction mixture was stirred for 5 minutes at room temperature and then stirred at 160 °C in a pre-heated oil bath for 40 h. After cooling down to room temperature, the reaction mixture was concentrated under vacuum. Purification by preparative TLC plate (petroleum ether : ethyl acetate = 1 : 2 as eluent) afforded the product **3m** as a yellow solid (29.1 mg, 83% yield). mp 214-216 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.85 (bs, 1H), 8.93 (dd, *J* = 4.1 and 1.3 Hz, 1H), 8.20 (dd, *J* = 8.2 and 1.3 Hz, 1H), 7.68 (d, *J* = 8.3 Hz, 2H), 7.58 (dd, *J* = 8.2 and 4.2 Hz, 1H), 7.54 (d, *J* = 8.9 Hz, 1H), 7.47 (d, *J* = 8.9 Hz, 1H), 7.37 (d, *J* = 8.3 Hz, 2H), 6.76 (s, 1H); 13C NMR (100 MHz, CDCl3) δ 161.40, 151.81, 149.60, 136.92, 136.10, 136.02, 135.94, 132.16, 130.58, 128.32, 123.83, 123.62, 123.49, 123.15, 120.80, 116.66; HRMS(EI) Calcd for $C_{18}H_{11}N_2OBr$ [M^+]: 350.0055, Found 350.0060; IR (KBr) ν_{max} (cm^{-1}) : 3440, 1681, 1664, 1461, 1009, 743.

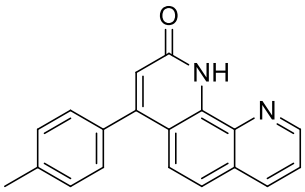
Typical procedure for preparing the compound 3



4-Phenyl-1,10-phenanthrolin-2(1H)-one (3a):

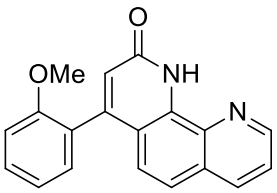
A mixture of the **2a** (109.0 mg, 0.4 mmol) and DDQ (272.4 mg, 1.2 mmol) in toluene (2 mL) was stirred under refluxing condition for 12 h. After cooling down to room temperature, aqueous NaOH solution (2 M) was added slowly to the reaction mixture. The reaction mixture was extracted with CH_2Cl_2 (3 x 30 mL), dried over anhydrous Na_2SO_4, and concentrated. The residue was purified by flash chromatography (Silica gel, eluent: $CHCl_3$/MeOH = 40/1) to get the product **3a** as a yellow solid (81.2 mg,

76% yield). mp 83-85 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.86 (bs, 1H), 8.92 (dd, *J* = 4.2 and 1.5 Hz, 1H), 8.19 (dd, *J* = 8.2 and 1.5 Hz, 1H), 7.65 – 7.40 (m, 8H), 6.80 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.67, 153.10, 149.48, 137.06, 136.97, 136.06, 135.89, 129.07, 128.97, 128.88, 128.26, 124.25, 123.49, 123.03, 120.62, 117.10; HRMS(EI) Calcd for $C_{18}H_{12}N_2O$ [M^+]: 272.0950, Found 272.0945; IR (KBr) ν_{max} (cm^{-1}) : 3441, 1657, 1464, 1380, 772, 704.



4-(*p*-Tolyl)-1,10-phenanthrolin-2(1H)-one (3b):

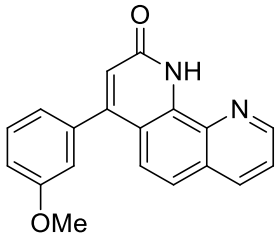
A mixture of the **2b** (103.0 mg, 0.36 mmol) and DDQ (245.0 mg, 1.2 mmol) in toluene (2 mL) was stirred under refluxing condition for 12 h. After cooling down to room temperature, aqueous NaOH solution (2 M) was added slowly to the reaction mixture. The reaction mixture was extracted with CH_2Cl_2 (3 x 30 mL), dried over anhydrous Na_2SO_4, and concentrated. The residue was purified by flash chromatography (Silica gel, eluent: $CHCl_3$/MeOH = 40/1) to get the product **3b** as a yellow solid (93.1 mg, 90% yield). mp 167-169 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.80 (bs, 1H), 8.90 (dd, *J* = 4.3 and 1.6 Hz, 1H), 8.17 (dd, *J* = 8.2 and 1.6 Hz, 1H), 7.62 (d, *J* = 8.9 Hz, 1H), 7.55 (dd, *J* = 8.2 and 4.3 Hz, 1H), 7.44 (d, *J* = 8.9 Hz, 1H), 7.40 – 7.31 (m, 4H), 6.77 (s, 1H), 2.46 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.66, 153.07, 149.38, 139.05, 136.92, 136.00, 135.82, 134.12, 129.53, 128.87, 128.18, 124.30, 123.39, 122.83, 120.47, 117.14, 21.43; HRMS(EI) Calcd for $C_{19}H_{14}N_2O$ [M^+]: 286.1106, Found 286.1102; IR (KBr) ν_{max} (cm^{-1}) : 3441, 1660, 1374, 819, 744, 646.



4-(2-Methoxyphenyl)-1,10-phenanthrolin-2(1H)-one (3c):

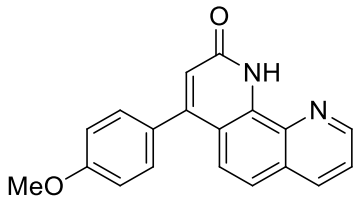
A mixture of the **2c** (97.4 mg, 0.32 mmol) and DDQ (217.9 mg, 0.96 mmol) in toluene (2 mL) was stirred under refluxing condition for 12 h. After cooling down to room temperature, aqueous NaOH solution (2 M) was added slowly to the reaction mixture. The reaction mixture was extracted with CH_2Cl_2 (3 x 30 mL), dried over anhydrous Na_2SO_4, and concentrated. The residue was purified by flash chromatography (Silica gel, eluent: $CHCl_3$/MeOH = 40/1) to get the product **3c** as a yellow solid (76.1 mg, 79% yield). mp 179-180 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.81 (bs, 1H), 8.88 (d, *J* = 3.1 Hz, 1H), 8.15 (dd, *J* = 8.2 and 1.2 Hz, 1H), 7.58 – 7.44 (m, 2H), 7.40 (d, *J* = 8.8 Hz, 1H), 7.33 – 7.26 (m, 2H), 7.15 – 7.03 (m, 2H), 6.77 (s, 1H), 3.73 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.94, 156.59, 150.78, 149.19, 136.99, 135.92, 135.14, 130.61, 128.18, 126.02, 124.77, 123.75, 123.19, 121.10,

120.29, 117.80, 111.22, 55.61; HRMS(EI) Calcd for $C_{19}H_{14}N_2O_2$ [M^+]: 302.1055, Found 302.1050; IR (KBr) ν_{max} (cm^{-1}) : 3441, 1653, 1462, 1377, 1257, 832.



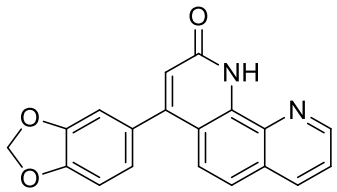
4-(3-Methoxyphenyl)-1,10-phenanthrolin-2(1H)-one (3d):

A mixture of the **2d** (91.3 mg, 0.3 mmol) and DDQ (204.3 mg, 0.96 mmol) in toluene (2 mL) was stirred under refluxing condition for 12 h. After cooling down to room temperature, aqueous NaOH solution (2 M) was added slowly to the reaction mixture. The reaction mixture was extracted with CH_2Cl_2 (3 x 30 mL), dried over anhydrous Na_2SO_4, and concentrated. The residue was purified by flash chromatography (Silica gel, eluent: $CHCl_3$/MeOH = 40/1) to get the product **3d** as a yellow solid (83.6 mg, 92% yield). mp 157-158 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.82 (bs, 1H), 8.87 (dd, *J* = 4.2 and 1.4 Hz, 1H), 8.15 (dd, *J* = 8.2 and 1.5 Hz, 1H), 7.59 (d, *J* = 8.9 Hz, 1H), 7.53 (dd, *J* = 8.2 and 4.3 Hz, 1H),7.46 – 7.39 (m, 2H), 7.07– 6.95 (m, 3H), 6.77 (s, 1H), 3.85 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.58, 159.81, 152.86, 149.37, 138.25, 136.80, 135.99, 135.71, 129.89, 128.17, 124.14, 123.41, 122.78, 121.24, 120.58, 116.93, 114.58, 114.43, 55.46; HRMS(EI) Calcd for $C_{19}H_{14}N_2O_2$ [M^+]: 302.1055, Found 302.1056; IR (KBr) ν_{max} (cm^{-1}) : 3437, 1663, 1465, 1269, 1026, 716.



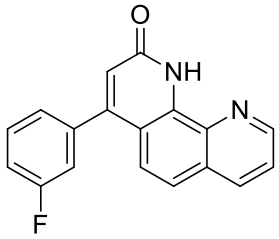
4-(4-Methoxyphenyl)-1,10-phenanthrolin-2(1H)-one (3e):

A mixture of the **2e** (122.0 mg, 0.4 mmol) and DDQ (272.4 mg, 1.2 mmol) in toluene (2 mL) was stirred under refluxing condition for 12 h. After cooling down to room temperature, aqueous NaOH solution (2 M) was added slowly to the reaction mixture. The reaction mixture was extracted with CH_2Cl_2 (3 x 30 mL), dried over anhydrous Na_2SO_4, and concentrated. The residue was purified by flash chromatography (Silica gel, eluent: $CHCl_3$/MeOH = 40/1) to get the product **3e** as a yellow solid (76.1 mg, 84% yield). mp 220-222 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.79 (bs, 1H), 8.89 (dd, *J* = 4.2 and 1.5 Hz, 1H), 8.17 (dd, *J* = 8.2 and 1.5 Hz, 1H), 7.64 (d, *J* = 8.9 Hz, 1H), 7.55 (dd, *J* = 8.2 and 4.3 Hz, 1H), 7.48– 7.38 (m, 3H), 7.08– 7.12 (m, 2H), 6.76 (s, 1H), 3.89 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.69, 160.33, 152.73, 149.39, 136.95, 136.01, 135.87, 130.32, 129.31, 128.18, 124.30, 123.40, 122.72, 120.47, 117.21, 114.31, 55.54; HRMS(EI) Calcd for $C_{19}H_{14}N_2O_2$ [M^+]: 302.1055, Found 302.1052; IR (KBr) ν_{max} (cm^{-1}) : 3448, 1653, 1515, 1465, 1253, 831.



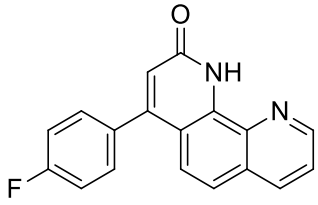
4-(Benzo[d][1,3]dioxol-5-yl)-1,10-phenanthrolin-2(1H)-one (3f):

A mixture of the **2f** (31.8 mg, 0.1 mmol) and DDQ (68.1 mg, 0.3 mmol) in toluene (2 mL) was stirred under refluxing condition for 12 h. After cooling down to room temperature, aqueous NaOH solution (2 M) was added slowly to the reaction mixture. The reaction mixture was extracted with CH_2Cl_2 (3 x 30 mL), dried over anhydrous Na_2SO_4, and concentrated. The residue was purified by flash chromatography (Silica gel, eluent: $CHCl_3$/MeOH = 40/1) to get the product **3f** as a yellow solid (16.2 mg, 51% yield). mp 202-204 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.84 (bs, 1H), 8.90 (d, *J* = 3.3 Hz, 1H), 8.23 – 8.14 (m, 1H), 7.66 (d, *J* = 8.9 Hz, 1H), 7.56 (dd, *J* = 8.2 and 4.2 Hz, 1H), 7.46 (d, *J* = 8.9 Hz, 1H), 6.96 (s, 3H), 6.76 (s, 1H), 6.07 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.67, 149.46, 148.42, 148.08, 136.96, 136.04, 135.88, 130.76, 128.23, 124.20, 123.48, 122.88, 120.60, 117.15, 109.48, 108.81, 101.65; HRMS(EI) Calcd for $C_{19}H_{12}N_2O_3$ [M^+]: 316.0848, Found 316.0848; IR (KBr) ν_{max} (cm^{-1}) : 3440, 1658, 1506, 1489, 1250, 1034.



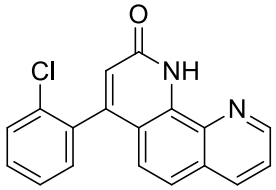
4-(3-Fluorophenyl)-1,10-phenanthrolin-2(1H)-one (3g):

A mixture of the **2g** (87.7 mg, 0.3 mmol) and DDQ (204.3 mg, 0.9 mmol) in toluene (2 mL) was stirred under refluxing condition for 12 h. After cooling down to room temperature, aqueous NaOH solution (2 M) was added slowly to the reaction mixture. The reaction mixture was extracted with CH_2Cl_2 (3 x 30 mL), dried over anhydrous Na_2SO_4, and concentrated. The residue was purified by flash chromatography (Silica gel, eluent: $CHCl_3$/MeOH = 40/1) to get the product **3g** as a yellow solid (68.8 mg, 79% yield). mp 188-190 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.82 (bs, 1H), 8.88 (d, *J* = 3.7 Hz, 1H), 8.17 (dd, *J* = 8.2 and 1.0 Hz, 1H), 7.61 – 7.39 (m, 4H), 7.29 – 7.11 (m, 3H), 6.75 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ162.78 (d, $J_{c\text{-}f}$ = 246.4 Hz), 161.32, 151.56 (d, $J_{c\text{-}f}$ = 1.9 Hz), 149.50, 139.01 (d, $J_{c\text{-}f}$ = 7.7 Hz), 136.78, 136.04, 135.86, 130.59 (d, $J_{c\text{-}f}$ = 8.3 Hz), 128.23, 124.69 (d, $J_{c\text{-}f}$ = 3.1 Hz), 123.73, 123.55, 123.13, 120.78, 116.53, 116.13 (d, $J_{c\text{-}f}$ = 4.0 Hz), 115.92 (d, $J_{c\text{-}f}$ = 2.5 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ -111.86; HRMS(EI) Calcd for $C_{18}H_{11}N_2OF$ [M^+]: 290.0855, Found 290.0854; IR (KBr) ν_{max} (cm^{-1}) : 3441, 1664, 1264, 826, 735, 718.



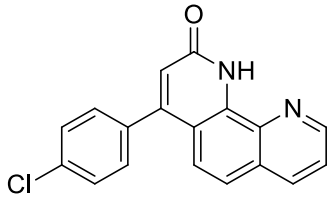
4-(4-Fluorophenyl)-1,10-phenanthrolin-2(1H)-one (3h):

A mixture of the **2h** (117.0 mg, 0.4 mmol) and DDQ (272.4 mg, 1.2 mmol) in toluene (2 mL) was stirred under refluxing condition for 12 h. After cooling down to room temperature, aqueous NaOH solution (2 M) was added slowly to the reaction mixture. The reaction mixture was extracted with CH_2Cl_2 (3 x 30 mL), dried over anhydrous Na_2SO_4, and concentrated. The residue was purified by flash chromatography (Silica gel, eluent: $CHCl_3$/MeOH = 40/1) to get the product **3h** as a yellow solid (82.8 mg, 71% yield). mp 166-168 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.82 (bs, 1H), 8.90 (dd, *J* = 4.2 and 1.5 Hz, 1H), 8.18 (dd, *J* = 8.3 and 1.5 Hz, 1H), 7.64 – 7.39 (m, 5H), 7.26 – 7.18 (m, 2H), 6.75 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.24 (d, $J_{c\text{-}f}$ = 247.4 Hz), 161.44, 151.94, 149.53, 136.88, 136.06, 135.91, 133.00 (d, $J_{c\text{-}f}$ = 3.5 Hz), 130.77 (d, $J_{c\text{-}f}$ = 8.2 Hz), 128.25, 123.90, 123.54, 123.19, 120.71, 116.89, 116.00 (d, $J_{c\text{-}f}$ = 21.6 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ -112.24; HRMS(EI) Calcd for $C_{18}H_{11}N_2OF$ [M^+]: 290.0855, Found 290.0861; IR (KBr) ν_{max} (cm^{-1}) : 3440, 1686, 1663, 1513, 1225, 842.



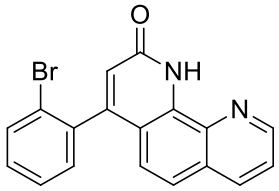
4-(2-Chlorophenyl)-1,10-phenanthrolin-2(1H)-one (3i):

A mixture of the **2i** (77.2 mg, 0.25 mmol) and DDQ (170.3 mg, 0.75 mmol) in toluene (2 mL) was stirred under refluxing condition for 12 h. After cooling down to room temperature, aqueous NaOH solution (2 M) was added slowly to the reaction mixture. The reaction mixture was extracted with CH_2Cl_2 (3 x 30 mL), dried over anhydrous Na_2SO_4, and concentrated. The residue was purified by flash chromatography (Silica gel, eluent: $CHCl_3$/MeOH = 40/1) to get the product **3i** as a yellow solid (67.5 mg, 87% yield). mp 200-202 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.86 (bs, 1H), 8.90 (dd, *J* = 4.2 and 1.4 Hz, 1H), 8.17 (dd, *J* = 8.2 and 1.4 Hz, 1H), 7.62 – 7.31 (m, 6H), 7.19 (d, *J* = 8.8 Hz, 1H), 6.76 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.59, 150.59, 149.45, 136.89, 136.06, 135.84, 135.46, 132.98, 130.76, 130.38, 130.04, 128.36, 127.31, 124.04, 123.87, 123.46, 120.81, 117.07; HRMS(EI) Calcd for $C_{18}H_{11}N_2OCl$ [M^+]: 306.0560, Found 306.0572; IR (KBr) ν_{max} (cm^{-1}) : 3443, 1654, 1622, 1463, 832, 764.



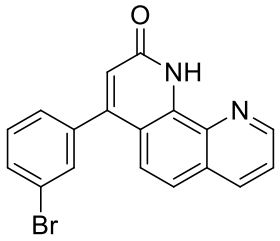
4-(4-Chlorophenyl)-1,10-phenanthrolin-2(1H)-one (3j):

A mixture of the **2j** (93.8 mg, 0.3 mmol) and DDQ (204.3 mg, 0.9 mmol) in toluene (2 mL) was stirred under refluxing condition for 12 h. After cooling down to room temperature, aqueous NaOH solution (2 M) was added slowly to the reaction mixture. The reaction mixture was extracted with CH_2Cl_2 (3 x 30 mL), dried over anhydrous Na_2SO_4, and concentrated. The residue was purified by flash chromatography (Silica gel, eluent: $CHCl_3$/MeOH = 40/1) to get the product **3j** as a yellow solid (86.2 mg, 94% yield). mp 210-211 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.84 (bs, 1H), 8.92 (dd, *J* = 4.2 and 1.4 Hz, 1H), 8.19 (dd, *J* = 8.3 and 1.5 Hz, 1H), 7.62 – 7.38 (m, 7H), 6.76 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.41, 151.79, 149.58, 136.91, 136.09, 135.99, 135.45, 135.31, 130.31, 129.20, 128.30, 123.83, 123.60, 123.19, 120.78, 116.73; HRMS(EI) Calcd for $C_{18}H_{11}N_2OCl$ [M^+]: 306.0560, Found 306.0572; IR (KBr) ν_{max} (cm^{-1}) : 3441, 1685, 1664, 1460, 1093, 825. HRMS(EI) Calcd for $C_{14}H_{17}N_3O_4$ [M^+]: 291.1235, Found 291.1235; IR (KBr) ν_{max} (cm^{-1}) : 3441, 1685, 1664, 1460, 1093, 825.



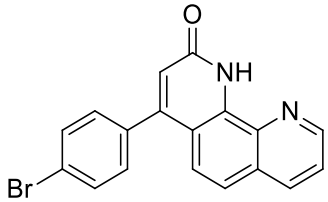
4-(2-Bromophenyl)-1,10-phenanthrolin-2(1H)-one (3k):

A mixture of the **2k** (106.0 mg, 0.3 mmol) and DDQ (204.3 mg, 0.9 mmol) in toluene (2 mL) was stirred under refluxing condition for 12 h. After cooling down to room temperature, aqueous NaOH solution (2 M) was added slowly to the reaction mixture. The reaction mixture was extracted with CH_2Cl_2 (3 x 30 mL), dried over anhydrous Na_2SO_4, and concentrated. The residue was purified by flash chromatography (Silica gel, eluent: $CHCl_3$/MeOH = 40/1) to get the product **3k** as a yellow solid (86.5 mg, 82% yield). mp 155-156 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.85 (bs, 1H), 8.92 (dd, *J* = 4.3 and 1.5 Hz, 1H), 8.19 (dd, *J* = 8.2 and 1.6 Hz, 1H), 7.69 – 7.36 (m, 7H), 6.76 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.33, 151.36, 149.59, 139.01, 136.85, 136.10, 135.95, 132.15, 131.81, 130.48, 128.31, 127.61, 123.76, 123.62, 123.30, 122.93, 120.88, 116.60; HRMS(EI) Calcd for $C_{18}H_{11}N_2OBr$ [M^+]: 350.0055, Found 350.0060; IR (KBr) ν_{max} (cm^{-1}) : 3441, 1657, 1623, 1465, 839, 715.



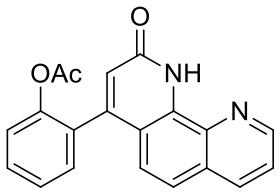
4-(3-Bromophenyl)-1,10-phenanthrolin-2(1H)-one (3l):

A mixture of the **2l** (115.0 mg, 0.33 mmol) and DDQ (227.0 mg, 0.99 mmol) in toluene (2 mL) was stirred under refluxing condition for 12 h. After cooling down to room temperature, aqueous NaOH solution (2 M) was added slowly to the reaction mixture. The reaction mixture was extracted with CH_2Cl_2 (3 x 30 mL), dried over anhydrous Na_2SO_4, and concentrated. The residue was purified by flash chromatography (Silica gel, eluent: $CHCl_3$/MeOH = 40/1) to get the product **3l** as a yellow solid (93.0 mg, 82% yield). mp 185-187 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.87 (bs, 1H), 8.94 (dd, *J* = 4.2 and 1.4 Hz, 1H), 8.20 (dd, *J* = 8.2 and 1.4 Hz, 1H), 7.70 – 7.38 (m, 7H), 6.77 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.37, 151.40, 149.63, 139.06, 136.91, 136.12, 136.00, 132.17, 131.85, 130.50, 128.35, 127.63, 123.80, 123.65, 123.35, 122.96, 120.89, 116.65; HRMS(EI) Calcd for $C_{18}H_{11}N_2OBr$ [M^+]: 350.00555, Found 350.0051; IR (KBr) ν_{max} (cm^{-1}) : 3441, 1656, 1623, 1466, 840, 716.



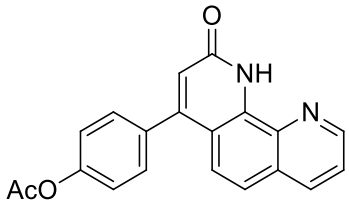
4-(4-Bromophenyl)-1,10-phenanthrolin-2(1H)-one(3m):

A mixture of the **2m** (40.0 mg, 0.11 mmol) and DDQ (77.0 mg, 0.33 mmol) in toluene (2 mL) was stirred refluxing condition for 12 h. After cooling down to room temperature, aqueous NaOH solution (2 M) was added slowly to the reaction mixture. The reaction mixture was extracted with CH_2Cl_2 (3 x 30 mL), dried over anhydrous Na_2SO_4, and concentrated. The residue was purified by flash chromatography (Silica gel, eluent: CHCl3/MeOH = 40/1) to get the product **3m** as a yellow solid (29.1 mg, 75% yield). mp 214-216 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.85 (bs, 1H), 8.93 (dd, *J* = 4.1 and 1.3 Hz, 1H), 8.20 (dd, *J* = 8.2 and 1.3 Hz, 1H), 7.68 (d, *J* = 8.3 Hz, 2H), 7.58 (dd, *J* = 8.2 and 4.2 Hz, 1H), 7.54 (d, *J* = 8.9 Hz, 1H), 7.47 (d, *J* = 8.9 Hz, 1H), 7.37 (d, *J* = 8.3 Hz, 2H), 6.76 (s, 1H); 13C NMR (100 MHz, CDCl3) δ 161.40, 151.81, 149.60, 136.92, 136.10, 136.02, 135.94, 132.16, 130.58, 128.32, 123.83, 123.62, 123.49, 123.15, 120.80, 116.66; HRMS(EI) Calcd for $C_{18}H_{11}N_2OBr$ [M^+]: 350.0055, Found 350.0060; IR (KBr) ν_{max} (cm^{-1}) : 3440, 1681, 1664, 1461, 1009, 743.



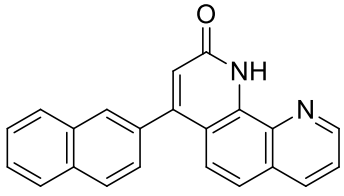
2-(2-oxo-1,2-Dihydro-1,10-phenanthrolin-4-yl)phenyl acetate (3n):

A mixture of the **2n** (30.0 mg, 0.09 mmol) and DDQ (61.5 mg, 0.27 mmol) in toluene (2 mL) was stirred under refluxing condition for 12 h. After cooling down to room temperature, aqueous NaOH solution (2 M) was added slowly to the reaction mixture. The reaction mixture was extracted with CH_2Cl_2 (3 x 30 mL), dried over anhydrous Na_2SO_4, and concentrated. The residue was purified by flash chromatography (Silica gel, eluent: $CHCl_3$/MeOH = 40/1) to get the product **3n** as a yellow solid (18.9 mg, 64% yield). mp 100-102 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.87 (bs, 1H), 8.92 (d, *J* = 3.0 Hz, 1H), 8.18 (dd, *J* = 8.2 and 1.4 Hz, 1H), 7.62 – 7.49 (m, 2H), 7.47 – 7.22 (m, 5H), 6.77 (s, 1H), 1.90 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.05, 161.49, 149.48, 148.99, 147.98, 136.83, 136.12, 135.45, 130.68, 130.36, 129.83, 128.36, 126.42, 124.20, 123.83, 123.51, 123.30, 120.75, 117.16, 20.80; HRMS(EI) Calcd for $C_{20}H_{14}N_2O_3$ [M^+]: 330.1004, Found 330.1008; IR (KBr) ν_{max} (cm^{-1}) : 3440, 1768, 1664, 1463, 1370, 1188.



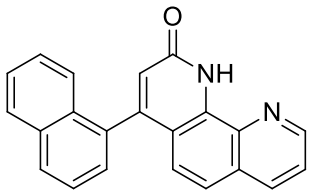
4-(2-oxo-1,2-Dihydro-1,10-phenanthrolin-4-yl)phenyl acetate (3o):

A mixture of the **2o** (66.5 mg, 0.2 mmol) and DDQ (136.2 mg, 0.6 mmol) in toluene (2 mL) was stirred under refluxing condition for 12 h. After cooling down to room temperature, aqueous NaOH solution (2 M) was added slowly to the reaction mixture. The reaction mixture was extracted with CH_2Cl_2 (3 x 30 mL), dried over anhydrous Na_2SO_4, and concentrated. The residue was purified by flash chromatography (Silica gel, eluent: $CHCl_3$/MeOH = 40/1) to get the product **3o** as a yellow solid (40.2 mg, 62% yield). mp 104-106 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.86 (bs, 1H), 8.89 (s, 1H), 8.18 (d, *J* = 8.0 Hz, 1H), 7.69 – 7.37 (m, 5H), 7.27 (d, *J* = 8.2 Hz, 2H), 6.78 (s, 1H), 2.37 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.44, 161.49, 152.09, 151.28, 149.45, 136.85, 136.03, 135.85, 134.51, 130.10, 128.23, 124.03, 123.50, 123.09, 122.13, 120.68, 116.86, 21.28; HRMS(EI) Calcd for $C_{20}H_{14}N_2O_3$ [M^+]: 330.1004, Found 330.0999; IR (KBr) ν_{max} (cm^{-1}) : 3448, 1751, 1664, 1375, 1200, 837.



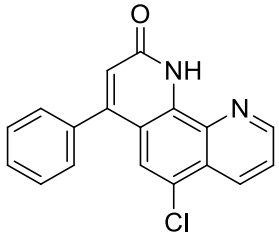
4-(Naphthalen-2-yl)-1,10-phenanthrolin-2(1H)-one (3p):

A mixture of the **2p** (64.9 mg, 0.2 mmol) and DDQ (136.2 mg, 0.6 mmol) in toluene (2 mL) was stirred refluxing condition for 12 h. After cooling down to room temperature, aqueous NaOH solution (2 M) was added slowly to the reaction mixture. The reaction mixture was extracted with CH_2Cl_2 (3 x 30 mL), dried over anhydrous Na_2SO_4, and concentrated. The residue was purified by flash chromatography (Silica gel, eluent: $CHCl_3$/MeOH = 40/1) to get the product **3p** as a yellow solid (54.6 mg, 85% yield). mp 189-190 °C . ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.88 (bs, 1H), 8.98 – 8.86 (m, 1H), 8.17 (d, *J* = 8.1 Hz, 1H), 8.05 – 7.85 (m, 4H), 7.69 – 7.39 (m, 6H), 6.88 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.58, 153.01, 149.44, 136.92, 136.01, 135.88, 134.47, 133.34, 133.26, 128.50, 128.37, 128.29, 128.23, 127.93, 127.04, 126.94, 126.48, 124.24, 123.45, 123.26, 120.63, 117.14; HRMS(EI) Calcd for $C_{22}H_{14}N_2O$ [M^+]: 322.1106, Found 322.1102; IR (KBr) ν_{max} (cm^{-1}) : 3350, 1663, 1464, 1030, 828, 749.



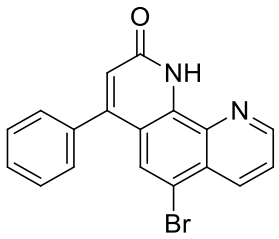
4-(Naphthalen-1-yl)-1,10-phenanthrolin-2(1H)-one (3q):

A mixture of the **2q** (64.9 mg, 0.2 mmol) and DDQ (136.2 mg, 0.6 mmol) in toluene (2 mL) was stirred refluxing condition for 12 h. After cooling down to room temperature, aqueous NaOH solution (2 M) was added slowly to the reaction mixture. The reaction mixture was extracted with CH_2Cl_2 (3 x 30 mL), dried over anhydrous Na_2SO_4, and concentrated. The residue was purified by flash chromatography (Silica gel, eluent: $CHCl_3$/MeOH = 40/1) to get the product **3q** as a yellow solid (46.9 mg, 73% yield). mp 206-207 °C . ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.95 (bs, 1H), 8.95 (d, *J* = 4.3 Hz, 1H), 8.15 (dd, *J* = 8.2 and 1.6 Hz, 1H), 7.99 (dd, *J* = 16.2 and 8.2 Hz, 2H), 7.69 – 7.45 (m, 5H), 7.38 (t, J = 7.5 Hz, 1H), 7.31 (d, J = 8.9 Hz, 1H), 7.08 (d, *J* = 8.8 Hz, 1H), 6.91 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.75, 152.09, 149.50, 137.00, 136.09, 135.50, 134.65, 133.63, 131.47, 129.37, 128.59, 128.40, 126.92, 126.83, 126.50, 125.83, 125.56, 124.66, 124.42, 123.47, 120.69, 118.26; HRMS(EI) Calcd for $C_{22}H_{14}N_2O$ [M^+]: 322.1106, Found 322.1098; IR (KBr) ν_{max} (cm^{-1}) : 3443, 1656, 1464, 1372, 781, 653.



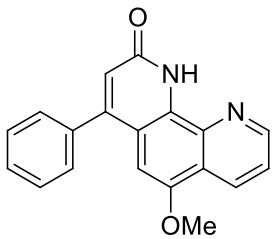
6-Chloro-4-phenyl-1,10-phenanthrolin-2(1H)-one (3v):

A mixture of the **2v** (92.6 mg, 0.3 mmol) and DDQ (204.3 mg, 0.9 mmol) in toluene (2 mL) was stirred under refluxing condition for 12 h. After cooling down to room temperature, aqueous NaOH solution (2 M) was added slowly to the reaction mixture. The reaction mixture was extracted with CH_2Cl_2 (3 x 30 mL), dried over anhydrous Na_2SO_4, and concentrated. The residue was purified by flash chromatography (Silica gel, eluent: $CHCl_3$/MeOH = 40/1) to get the product **3v** as a yellow solid (68.5 mg, 74% yield). mp 130-132 °C . ^{1}H NMR (600 MHz, $CDCl_3$) δ 10.83 (bs, 1H), 8.99 (d, *J* = 3.4 Hz, 1H), 8.60 (dd, *J* = 8.4 and 1.5 Hz, 1H), 7.73 – 7.67 (m, 2H), 7.61 – 7.44 (m, 5H), 6.81 (s, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 161.36, 152.25, 150.03, 137.44, 136.42, 135.03, 133.47, 129.37, 129.12, 128.88, 126.43, 124.35, 124.15, 123.85, 123.71, 117.07; HRMS(EI) Calcd for $C_{18}H_{11}N_2OCl$ [M^+]: 306.0560, Found 306.0575; IR (KBr) ν_{max} (cm^{-1}) : 3441, 1670, 1461, 1386, 748, 698.



6-Bromo-4-phenyl-1,10-phenanthrolin-2(1H)-one (3w):

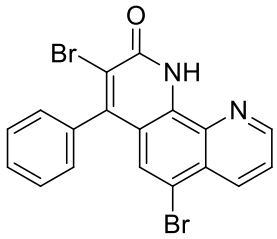
A mixture of the **2w** (92.6 mg, 0.3 mmol) and DDQ (204.3 mg, 0.9 mmol) in toluene (2 mL) was stirred under refluxing condition for 12 h. After cooling down to room temperature, aqueous NaOH solution (2 M) was added slowly to the reaction mixture. The reaction mixture was extracted with CH_2Cl_2 (3 x 30 mL), dried over anhydrous Na_2SO_4, and concentrated. The residue was purified by flash chromatography (Silica gel, eluent: $CHCl_3$/MeOH = 40/1) to get the product **3w** as a yellow solid (68.5 mg, 74% yield). mp 180-182 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.82 (bs, 1H), 8.94 (d, *J* = 4.2 Hz, 1H), 8.55 (dd, *J* = 8.5 and 1.5 Hz, 1H), 7.87 (s, 1H), 7.73 – 7.42 (m, 6H), 6.80 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.29, 152.08, 149.98, 137.43, 136.40, 135.98, 135.60, 129.36, 129.12, 128.88, 127.54, 127.36, 124.39, 123.86, 117.69, 114.09; HRMS(EI) Calcd for $C_{18}H_{11}N_2OBr$ [M^+]: 350.0055, Found 350.0050; IR (KBr) ν_{max} (cm^{-1}) : 3450, 1676, 1659, 1385, 748, 698.



6-Methoxy-4-phenyl-1,10-phenanthrolin-2(1H)-one (3x):

A mixture of the **2x** (30.4 mg, 0.1 mmol) and DDQ (68.1 mg, 0.3 mmol) in toluene (2 mL) was stirred under refluxing condition for 12 h. After cooling down to room temperature, aqueous NaOH solution (2 M) was added slowly to the reaction mixture. The reaction mixture was extracted with CH_2Cl_2 (3 x 30 mL), dried over anhydrous

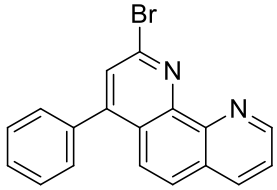
Na_2SO_4, and concentrated. The residue was purified by flash chromatography (Silica gel, eluent: $CHCl_3$/MeOH = 40/1) to get the product **3x** as a yellow solid (21.0 mg, 70% yield). mp 150-151 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.70 (bs, 1H), 8.91 (d, *J* = 4.3 Hz, 1H), 8.56 (d, *J* = 8.2 Hz, 1H), 7.64 – 7.40 (m, 6H), 6.80 (d, *J* = 18.6 Hz, 2H), 3.83 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.25, 152.59, 149.86, 149.70, 137.53, 137.33, 131.29, 130.67, 129.03, 128.91, 128.80, 123.45, 122.82, 122.02, 116.80, 100.29, 55.79; HRMS(EI) Calcd for $C_{19}H_{14}N_2O_2$ [M^+]: 302.1055, Found 302.1059; IR (KBr) ν_{max} (cm^{-1}) : 3440, 1656, 1606, 1124, 1102, 613.



3,6-Dibromo-4-phenyl-1,10-phenanthrolin-2(1H)-one (9):

A solution of Bromine (119.0 mg, 0.296 mmol) in bromobenzene (1 mL) was added dropwise to a solution of **2a** (204.0 mg, 0.74 mmol) in bromobenzene (3 mL) at room temperature. The reaction mixture was stirred at 160 °C for 12 h. After cooling down to room temperature, the reaction mixture was concentrated under vacuum, diluted with DCM (50 mL), washed with aq. NH_4OH (30 mL) and brine, dried over anhydrous Na_2SO4, and concentrated. Purification by flash chromatography (Silica gel, DCM as eluent) afforded the product **9** as a yellow solid (276.7 mg, 87% yield). mp 225-226 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.96 (bs, 1H), 8.93 (d, *J* = 3.5 Hz, 1H), 8.50 (d, *J* = 7.7 Hz, 1H), 7.68 (dd, *J* = 8.5 and 4.2 Hz, 1H), 7.64 – 7.50 (m, 3H), 7.42 (s, 1H), 7.32 (d, *J* = 6.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.58, 151.20, 150.24, 137.00, 136.44, 136.02, 133.78, 129.28, 129.17, 128.53, 127.58, 127.42, 124.56, 121.94, 118.51, 114.64; HRMS(EI) Calcd for $C_{18}H_{10}N_2OBr_2$ [M^+]: 427.9160, Found 427.9147; IR (KBr) ν_{max} (cm^{-1}) : 3443, 1664, 1540, 1444, 1388, 929.

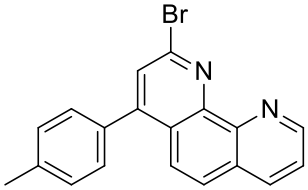
General procedure for preparing unsymmetric polysubstituted 1,10-phenanthrolines:



2-Bromo-4-phenyl-1,10-phenanthroline (5a):

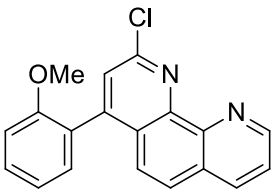
3a (81.7 mg, 0.3 mmol) was suspended in dry toluene (2 mL). $POBr_3$ (430.0 mg, 1.5 mmol) was added. The reaction mixture was vigorously stirred at 100 °C for 12 h under nitrogen atmosphere. Then the reaction mixture was neutralized by addition of aqueous saturated sodium bicarbonate and extracted with CH_2Cl_2. The combined extracts were dried over Na_2SO_4 and concentrated. Purification by flash chromatography (Silica gel, eluent: petroleum ether : ethyl acetate = 1 : 1) afforded

the product **5a** as a yellow solid (79.9 mg, 80% yield). mp 173-175 °C . ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.20 (dd, *J* = 4.2 and 1.5 Hz, 1H), 8.18 (dd, *J* = 8.0 and 1.4 Hz, 1H), 7.83 – 7.65 (m, 3H), 7.60 (dd, *J* = 8.0 and 4.4 Hz, 1H), 7.55 – 7.42 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.08, 150.93, 147.15, 145.24, 142.21, 136.60, 135.93, 129.56, 129.05, 128.85, 128.73, 127.86, 126.79, 125.96, 123.92, 123.58; HRMS(EI) Calcd for $C_{18}H_{11}N_2Br$ [M^+]: 334.0106, Found 334.0094; IR (KBr) ν_{max} (cm^{-1}) : 3440, 1539, 1486, 1130, 869, 700.



2-Bromo-4-(p-tolyl)-1,10-phenanthroline (5b):

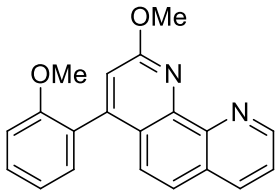
3b (80.0 mg, 0.28 mmol) was suspended in dry toluene (2 mL). $POBr_3$(400.0 mg, 1.4 mmol) was added. The reaction mixture was vigorously stirred at 100 °C for 12 h under nitrogen atmosphere. Then the reaction mixture was neutralized by addition of aqueous saturated sodium bicarbonate and extracted with CH_2Cl_2. The combined extracts were dried over Na_2SO_4 and concentrated. Purification by flash chromatography (Silica gel, eluent: petroleum ether : ethyl acetate = 1 : 1) afforded the product **5b** as a yellow solid (64.3 mg, 67% yield). mp 171-173 °C . ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.22 (dd, *J* = 4.3 and 1.7 Hz, 1H), 8.21 (dd, *J* = 8.1 and 1.6 Hz, 1H), 7.86 (d, *J* = 9.1 Hz, 1H), 7.72 (d, *J* = 9.1 Hz, 1H), 7.69 (s, 1H), 7.63 (dd, *J* = 8.1 and 4.3 Hz, 1H), 7.41 – 7.32 (m, 4H), 2.46 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.27, 150.96, 147.23, 145.35, 142.32, 139.16, 135.96, 133.77, 129.60, 129.56, 128.78, 127.90, 126.69, 126.14, 124.13, 123.60, 21.43; HRMS(EI) Calcd for $C_{19}H_{13}N_2Br$ [M^+]: 348.0262, Found 348.0264; IR (KBr) ν_{max} (cm^{-1}) : 3429, 1727, 1538, 1491, 1131, 868, 733.



2-Chloro-4-(2-methoxyphenyl)-1,10-phenanthroline (5c):

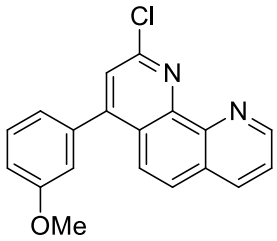
3c (30.2 mg, 0.1 mmol), PCl_5(41.6 mg, 0.2 mmol) and anhydrous DCM (2 mL) were added in turn into a 25 mL of glass sealed tube. The tube was then tightly capped. The reaction mixture was stirred at 80 ^{o}C for 12 h. After cooling down to room temperature, the reaction mixture was neutralized by addition of aqueous saturated sodium bicarbonate and extracted with CH_2Cl_2. The combined extracts were dried over Na_2SO_4 and concentrated. Purification by flash chromatography (Silica gel, eluent: petroleum ether : ethyl acetate = 1 : 1) afforded the product **5c** as a yellow solid (26.0 mg, 81% yield). mp 111-113 °C . ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.23 (dd, *J* = 4.2 and 1.4 Hz, 1H), 8.22 (dd, *J* = 8.0 and 1.3 Hz, 1H), 7.69 (d, *J* = 9.0 Hz, 1H),

7.64 (dd, *J* = 8.0 and 4.3 Hz, 1H), 7.56 (t, *J* = 4.5 Hz, 2H), 7.54 – 7.48 (m, 1H), 7.30 (dd, *J* = 7.3 and 1.5 Hz, 1H), 7.13 (t, *J* = 7.4 Hz, 1H), 7.09 (d, *J* = 8.4 Hz, 1H), 3.72 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.74, 151.16, 150.77, 149.18, 146.32, 145.55, 135.93, 131.24, 130.80, 128.93, 126.79, 126.24, 125.79, 125.26, 124.66, 123.47, 121.03, 111.33, 55.65; HRMS(EI) Calcd for $C_{19}H_{13}N_2OCl$ [M^+]: 320.0716, Found 320.0724; IR (KBr) ν_{max} (cm^{-1}) : 3441, 1546, 1489, 1131, 840, 736.



2-Methoxy-4-(2-methoxyphenyl)-1,10-phenanthroline (14):

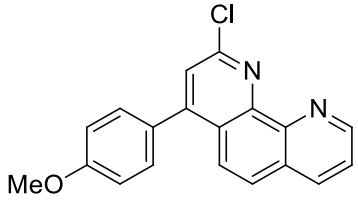
Into a 25mL of round-bottomed flask was charged with **3c** (60.4 mg, 0.2 mmol) and $NaHCO_3$ (75.6 mg, 0.9 mmol). Then 5 mL of CH_2Cl_2 was added to the flask, followed by addition of BF_4OMe_3 (88.8 mg, 0.6 mmol). Then the reaction mixture was stirred at refluxing condition under N_2 atmosphere for 48 h. The reaction mixture was neutralized by addition of aqueous saturated sodium bicarbonate and extracted with CH_2Cl_2. The combined extracts were dried over Na_2SO_4 and concentrated. Purification by preparative TLC plate ($CHCl_3$: MeOH = 30 : 1 as eluent) afforded the product **14** as a yellow solid (17.8 mg, 28% yield). mp 120-121 °C . ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.18 (dd, *J* = 4.2 and 1.5 Hz, 1H), 8.18 (dd, *J* = 8.0 and 1.5 Hz, 1H), 7.70 – 7.41 (m, 4H), 7.29 (dd, *J* = 7.4 and 1.5 Hz, 1H), 7.16 – 6.98 (m, 3H), 4.35 (s, 3H), 3.70 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.95, 156.83, 149.96, 149.01, 145.67, 144.60, 136.03, 131.24, 130.21, 128.98, 127.01, 125.02, 124.38, 123.04, 122.42, 120.89, 114.66, 111.24, 55.64, 53.98; HRMS(ESI) Calcd for $C_{20}H_{16}N_2O_2$ [M+H]$^+$: 317.1290, Found 317.1290; IR (KBr) ν_{max} (cm^{-1}) : 3441, 1591, 1561, 1365, 1210, 1020.



2-Chloro-4-(3-methoxyphenyl)-1,10-phenanthroline (5d):

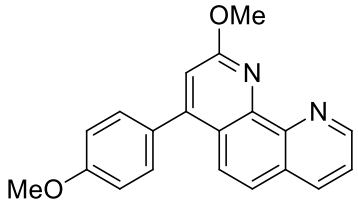
3d (30.2 mg, 0.1 mmol), PCl_5(41.6 mg, 0.2 mmol) and anhydrous DCM (2 mL) were added in turn into a 25 mL of glass sealed tube. The tube was then tightly capped. The reaction mixture was stirred at 80 ^{o}C for 12 h. After cooling down to room temperature, the reaction mixture was neutralized by addition of aqueous saturated sodium bicarbonate and extracted with CH_2Cl_2. The combined extracts were dried over Na_2SO_4 and concentrated. Purification by flash chromatography (Silica gel, eluent: petroleum ether : ethyl acetate = 1 : 1) afforded the product **5d** as a yellow solid (27.3 mg, 85% yield). mp 140-142 °C . ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.23 (d, *J*

= 3.0 Hz, 1H), 8.23 (d, *J* = 8.0 Hz, 1H), 7.87 (d, *J* = 9.1 Hz, 1H), 7.73 (d, *J* = 9.1 Hz, 1H), 7.65 (dd, *J* = 8.0 and 4.3 Hz, 1H), 7.58 (s, 1H), 7.46 (t, *J* = 7.8 Hz, 1H), 7.15 – 6.95 (m, 3H), 3.87 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.92, 151.62, 151.17, 150.92, 146.68, 145.33, 138.20, 136.07, 130.02, 128.90, 126.70, 125.85, 124.32, 123.99, 123.68, 122.01, 115.28, 114.58, 55.58; HRMS(EI) Calcd for $C_{19}H_{13}N_2OCl$ [M^+]: 320.0716, Found 320.0718; IR (KBr) ν_{max} (cm^{-1}) : 3441, 1547, 1488, 1230, 1132, 836.



2-Chloro-4-(4-methoxyphenyl)-1,10-phenanthroline (5e):

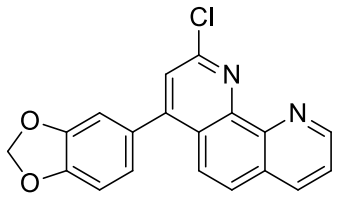
3e (30.2 mg, 0.1 mmol), PCl_5(41.6 mg, 0.2 mmol) and anhydrous DCM (2 ml) were added in turn into a 25 mL of glass sealed tube. The tube was then tightly capped. The reaction mixture was stirred at 80 ^oC for 12 h. After cooling down to room temperature, the reaction mixture was neutralized by addition of aqueous saturated sodium bicarbonate and extracted with CH_2Cl_2. The combined extracts were dried over Na_2SO_4 and concentrated. Purification by flash chromatography (Silica gel, eluent: petroleum ether : ethyl acetate = 1 : 1) afforded the product **5e** as a yellow solid (25.3 mg, 79% yield). mp 114-115 °C . ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.21 (d, *J* = 2.9 Hz, 1H), 8.20 (d, *J* = 7.1 Hz, 1H), 7.88 (d, *J* = 9.1 Hz, 1H), 7.70 (d, *J* = 9.1 Hz, 1H), 7.61 (dd, *J* = 8.0 and 4.3 Hz, 1H), 7.53 (s, 1H), 7.43 (d, *J* = 8.5 Hz, 2H), 7.06 (d, *J* = 8.5 Hz, 2H), 3.89 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.37, 151.47, 151.16, 150.86, 146.77, 145.41, 135.91, 130.97, 129.08, 128.80, 126.48, 125.93, 124.27, 123.97, 123.55, 114.39, 55.54; HRMS(ESI) Calcd for $C_{19}H_{13}N_2OCl$ [M^+]: 321.0795, Found 321.0793; IR (KBr) ν_{max} (cm^{-1}) : 3442, 1608, 1543, 1494, 1248, 838.



2-Methoxy-4-(4-methoxyphenyl)-1,10-phenanthroline (15):

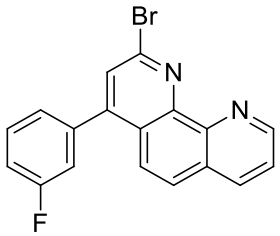
Into a 25mL of round-bottomed flask was charged with **3e** (30.2 mg, 0.1 mmol). Then 1 mL of CH_2Cl_2 was added to the flask, followed by addition of BF_4OMe_3 (74.0 mg, 0.5 mmol). Then the reaction mixture was stirred at refluxing condition under N_2 atmosphere for 48 h. The reaction mixture was neutralized by addition of aqueous saturated sodium bicarbonate and extracted with CH_2Cl_2. The combined extracts were dried over Na_2SO_4 and concentrated. Purification by preparative TLC plate ($CHCl_3$: MeOH = 30 : 1 as eluent) afforded the product **15** as a yellow solid (8.6 mg, 27% yield). mp 116-118 °C . ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.18 (dd, *J* = 4.3 and 1.6 Hz, 1H), 8.22 (dd, *J* = 8.1 and 1.6 Hz, 1H), 7.86 (d, *J* = 9.0 Hz, 1H), 7.65 – 7.54 (m, 2H),

7.48 – 7.42 (m, 2H), 7.10 – 7.04 (m, 3H), 4.35 (s, 3H), 3.91 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.96, 160.01, 151.49, 150.13, 145.62, 145.21, 136.16, 130.91, 130.44, 128.98, 124.55, 123.80, 123.29, 122.65, 114.21, 113.83, 55.56, 54.04; HRMS(EI) Calcd for $C_{20}H_{16}N_2O_2$ [M^+]: 316.1212, Found 316.1212; IR (KBr) ν_{max} (cm^{-1}) : 3441, 1614, 1591, 1364, 1213, 835.



4-(Benzo[d][1,3]dioxol-5-yl)-2-chloro-1,10-phenanthroline (5f):

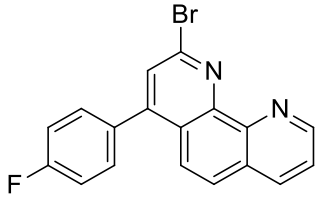
3f (31.6 mg, 0.1 mmol), PCl_5(41.6 mg, 0.2 mmol) and anhydrous DCM (2 ml) were added in turn into a 25 mL of glass sealed tube. The tube was then tightly capped. The reaction mixture was stirred at 80 ^oC for 12 h. After cooling down to room temperature, the reaction mixture was neutralized by addition of aqueous saturated sodium bicarbonate and extracted with CH_2Cl_2. The combined extracts were dried over Na_2SO_4 and concentrated. Purification by flash chromatography (Silica gel, eluent: petroleum ether : ethyl acetate = 1 : 1) afforded the product **5f** as a yellow solid (25.9 mg, 77% yield). mp 192-194 °C . ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.27 (dd, *J* = 4.3 and 1.6 Hz, 1H), 8.28 (dd, *J* = 8.0 and 1.6 Hz, 1H), 7.95 (d, *J* = 9.1 Hz, 1H), 7.78 (d, *J* = 9.1 Hz, 1H), 7.69 (dd, *J* = 8.0 and 4.4 Hz, 1H), 7.58 (s, 1H), 7.01 (s, 3H), 6.11 (s, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 151.38, 151.27, 150.88, 148.54, 148.23, 146.65, 145.21, 136.26, 130.54, 128.90, 126.64, 125.98, 124.47, 124.03, 123.74, 123.71, 110.11, 108.90, 101.76; HRMS(ESI) Calcd for $C_{19}H_{12}N_2O_2Cl$ [M+H]$^+$: 335.0587, Found 335.0587; IR (KBr) ν_{max} (cm^{-1}) : 3441, 1630, 1488, 1251, 1230, 1036.



2-Bromo-4-(3-fluorophenyl)-1,10-phenanthroline (5g):

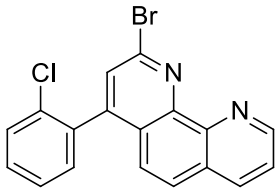
3g (61.3 mg, 0.21 mmol) was suspended in dry toluene (2 mL). $POBr_3$ (303.0 mg, 1.01 mmol) was added. The reaction mixture was vigorously stirred at 100 °C for 12 h under nitrogen atmosphere. Then the reaction mixture was neutralized by addition of aqueous saturated sodium bicarbonate and extracted with CH_2Cl_2. The combined extracts were dried over Na_2SO_4 and concentrated. Purification by flash chromatography (Silica gel, eluent: petroleum ether : ethyl acetate = 1 : 1) afforded the product **5g** as a yellow solid (73.7 mg, 99% yield). mp 203-205 °C . ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.25 (dd, *J* = 4.3 and 1.7 Hz, 1H), 8.24 (dd, *J* = 8.1 and 1.7 Hz, 1H), 7.78 (dd, *J* = 14.3 and 9.12 Hz, 2H), 7.71 (s, 1H), 7.66 (dd, *J* = 8.1 and 4.3 Hz, 1H),

7.59 – 7.49 (m, 1H), 7.33 – 7.18 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ162.80 (d, $J_{c\text{-}f}$ = 246.8 Hz), 151.12, δ149.59 (d, $J_{c\text{-}f}$ = 1.9 Hz), 147.22, 145.21, 142.18, δ138.67 (d, $J_{c\text{-}f}$ = 7.8 Hz), 136.02, δ130.64 (d, $J_{c\text{-}f}$ = 8.3 Hz), 128.81, 127.79, 127.19, 125.70, δ125.42 (d, $J_{c\text{-}f}$ = 3.1 Hz), 123.76, 123.53, δ116.73 (d, $J_{c\text{-}f}$ = 22.3 Hz), δ116.11 (d, $J_{c\text{-}f}$ = 20.9 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ -111.74; HRMS(EI) Calcd for $C_{18}H_{10}N_2FBr$ [M^+]: 352.0011, Found 352.0008; IR (KBr) ν_{max} (cm^{-1}) : 3433, 1728, 1545, 1480, 1126, 796.



2-Bromo-4-(4-fluorophenyl)-1,10-phenanthroline (5h):

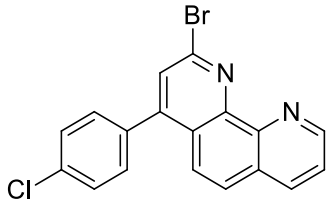
3h (67.0 mg, 0.23 mmol) was suspended in dry toluene (2 mL). $POBr_3$ (330.8 mg, 1.15 mmol) was added. The reaction mixture was vigorously stirred at 100 °C for 12 h under nitrogen atmosphere. Then the reaction mixture was neutralized by addition of aqueous saturated sodium bicarbonate and extracted with CH_2Cl_2. The combined extracts were dried over Na_2SO_4 and concentrated. Purification by flash chromatography (Silica gel, eluent: petroleum ether : ethyl acetate = 1 : 1) afforded the product **5h** as a yellow solid (60.9 mg, 75% yield). mp 197-199 °C . ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.23 (dd, *J* = 4.3 and 1.7 Hz, 1H), 8.22 (dd, *J* = 8.1 and 1.7 Hz, 1H), 7.76 (dd, *J* = 14.8 and 9.1 Hz, 2H), 7.68 (s, 1H), 7.64 (dd, *J* = 8.1 and 4.4 Hz, 1H), 7.53 – 7.43 (m, 2H), 7.30 – 7.20 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.30 (d, $J_{c\text{-}f}$ = 248.0 Hz), 151.12, 150.03, 147.25, 145.28, 142.27, 136.02, 132.66 (d, $J_{c\text{-}f}$ = 3.5 Hz), 131.46 (d, $J_{c\text{-}f}$ = 8.2 Hz), 128.81, 127.97, 127.06, 126.00, 123.74, 123.67, 116.09 (d, $J_{c\text{-}f}$ = 21.6 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ -112.02; HRMS(EI) Calcd for $C_{18}H_{10}N_2FBr$ [M^+]: 352.0011, Found 352.0013; IR (KBr) ν_{max} (cm^{-1}) : 3441, 1602, 1541, 1492, 1225, 1131, 837.



2-Bromo-4-(2-chlorophenyl)-1,10-phenanthroline (5i):

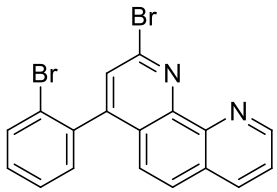
3i (15.3 mg, 0.05 mmol) was suspended in dry toluene (2 mL). $POBr_3$ (71.7 mg, 0.25 mmol) was added. The reaction mixture was vigorously stirred at 100 °C for 12 h under nitrogen atmosphere. Then the reaction mixture was neutralized by addition of aqueous saturated sodium bicarbonate and extracted with CH_2Cl_2. The combined extracts were dried over Na_2SO_4 and concentrated. Purification by flash chromatography (Silica gel, eluent: petroleum ether : ethyl acetate = 1 : 1) afforded the product **5i** as a yellow solid (14.2 mg, 78% yield). mp 192-193 °C . ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.28 (d, *J* = 4.3 Hz, 1H), 8.28 (d, *J* = 8.0 Hz, 1H), 7.82 – 7.64 (m, 3H),

7.62 – 7.32 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.80, 148.50, 146.63, 144.91, 142.14, 136.59, 135.40, 133.31, 131.29, 130.63, 130.14, 129.06, 128.47, 127.25, 127.14, 126.43, 124.13, 123.85; HRMS(EI) Calcd for $C_{18}H_{10}N_2ClBr$ [M^+]: 367.9716, Found 367.9709; IR (KBr) ν_{max} (cm^{-1}) : 3441, 1619, 1543, 1468, 1126, 836.



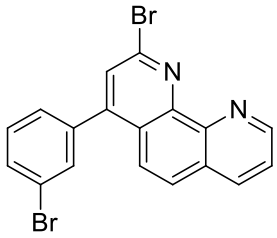
2-Bromo-4-(4-chlorophenyl)-1,10-phenanthroline (5j):

3j (61.0 mg, 0.20 mmol) was suspended in dry toluene (2 mL). $POBr_3$ (286.7 mg, 1.00 mmol) was added. The reaction mixture was vigorously stirred at 100 °C for 12 h under nitrogen atmosphere. Then the reaction mixture was neutralized by addition of aqueous saturated sodium bicarbonate and extracted with CH_2Cl_2. The combined extracts were dried over Na_2SO_4 and concentrated. Purification by flash chromatography (Silica gel, eluent: petroleum ether : ethyl acetate = 1 : 1) afforded the product **5j** as a yellow solid (50.0 mg, 67% yield). mp 219-220 °C . ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.23 (dd, *J* = 4.3 and 1.7 Hz, 1H), 8.22 (dd, *J* = 8.1 and 1.7 Hz, 1H), 7.80 – 7.72 (m, 2H), 7.70 – 7.61 (m, 2H), 7.56 – 7.50 (m, 2H), 7.47 – 7.40 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.14, 149.82, 147.25, 145.25, 142.25, 136.05, 135.48, 135.07, 130.95, 129.23, 128.83, 127.82, 127.15, 125.82, 123.79, 123.57; HRMS(EI) Calcd for $C_{18}H_{10}N_2ClBr$ [M^+]: 367.9716, Found 367.9697; IR (KBr) ν_{max} (cm^{-1}) : 3441, 1630, 1539, 1486, 1133, 1059, 836.



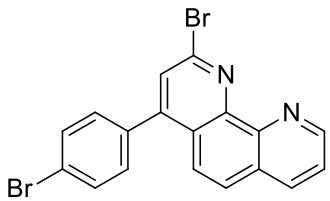
2-Bromo-4-(2-bromophenyl)-1,10-phenanthroline (5k):

3k (35.1 mg, 0.10 mmol) was suspended in dry toluene (2 mL). $POBr_3$ (143.0 mg, 0.50 mmol) was added. The reaction mixture was vigorously stirred at 100 °C for 12 h under nitrogen atmosphere. Then the reaction mixture was neutralized by addition of aqueous saturated sodium bicarbonate and extracted with CH_2Cl_2. The combined extracts were dried over Na_2SO_4 and concentrated. Purification by flash chromatography (Silica gel, eluent: petroleum ether : ethyl acetate = 1 : 1) afforded the product**5k** as a yellow solid (38.0 mg, 92% yield). mp 190-191 °C . ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.28 – 9.18 (m, 1H), 8.29 – 8.14 (m, 1H), 7.84 – 7.58 (m, 6H), 7.46 – 7.36 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.16, 149.33, 147.22, 145.21, 142.19, 138.63, 136.05, 132.41, 132.19, 130.45, 128.83, 128.28, 127.83, 127.28, 125.70, 123.79, 123.48, 123.01; HRMS(EI) Calcd for $C_{18}H_{10}N_2Br_2$ [M^+]: 411.9211, Found 411.9214; IR (KBr) ν_{max} (cm^{-1}) : 3440, 1620, 1542, 1129, 1059, 870, 833.



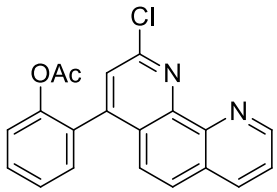
2-Bromo-4-(3-bromophenyl)-1,10-phenanthroline (5l):

3l (70.4 mg, 0.20 mmol) was suspended in dry toluene (2 mL). $POBr_3$ (286.7 mg, 1.00 mmol) was added. The reaction mixture was vigorously stirred at 100 °C for 12 h under nitrogen atmosphere. Then the reaction mixture was neutralized by addition of aqueous saturated sodium bicarbonate and extracted with CH_2Cl_2. The combined extracts were dried over Na_2SO_4 and concentrated. Purification by flash chromatography (Silica gel, eluent: petroleum ether : ethyl acetate = 1 : 1) afforded the product **5l** as a yellow solid (53.2 mg, 64% yield). mp 233-235 °C . ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.22 (d, *J* = 3.3 Hz, 1H), 8.23 (d, *J* = 7.6 Hz, 1H), 7.84 – 7.57 (m, 6H), 7.40 (d, *J* = 4.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.96, 149.30, 147.00, 144.94, 142.10, 138.52, 136.23, 132.34, 132.16, 130.42, 128.81, 128.24, 127.79, 127.22, 125.67, 123.81, 123.48, 122.96; HRMS(EI) Calcd for $C_{18}H_{10}N_2Br_2$ [M^+]: 411.9211, Found 411.9216; IR (KBr) ν_{max} (cm^{-1}) : 3442, 1631, 1543, 1473, 1129, 1060.



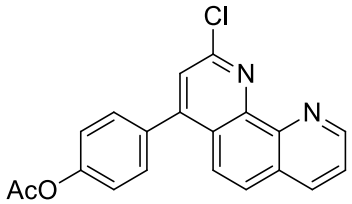
2-Bromo-4-(4-bromophenyl)-1,10-phenanthroline (5m):

3m (7.1 mg, 0.02 mmol) was suspended in dry toluene (1 mL). $POBr_3$ (28.6 mg, 0.10 mmol) was added. The reaction mixture was vigorously stirred at 100 °C for 12 h under nitrogen atmosphere. Then the reaction mixture was neutralized by addition of aqueous saturated sodium bicarbonate and extracted with CH_2Cl_2. The combined extracts were dried over Na_2SO_4 and concentrated. Purification by flash chromatography (Silica gel, eluent: petroleum ether : ethyl acetate = 1 : 1) afforded the product **5m** as a yellow solid (5.2 mg, 63% yield). mp 222-224 °C . ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.30 – 9.20 (m, 1H), 8.27 – 8.21 (m, 1H), 7.73 – 7.56 (m, 6H), 7.42 – 7.34 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.11, 149.84, 147.21, 145.18, 142.26, 136.15, 135.55, 132.21, 131.22, 128.87, 127.78, 127.18, 125.77, 123.83, 123.69, 123.60; HRMS(EI) Calcd for $C_{18}H_{10}N_2Br_2$ [M^+]: 411.9211, Found 411.9221; IR (KBr) ν_{max} (cm^{-1}) : 3441, 1622, 1538, 1486, 1133, 834.



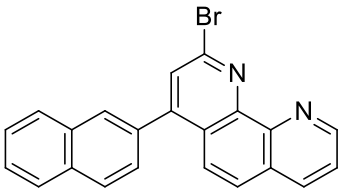
2-(2-Chloro-1,10-phenanthrolin-4-yl)phenyl acetate (5n):

3n (16.5 mg, 0.05 mmol), PCl_5 (31.2 mg, 0.15 mmol) and anhydrous DCM (2 mL) were added in turn into a 25 mL of glass sealed tube. The tube was then tightly capped. The reaction mixture was stirred at 80 ^oC for 12 h. After cooling down to room temperature, the reaction mixture was neutralized by addition of aqueous saturated sodium bicarbonate and extracted with CH_2Cl_2. The combined extracts were dried over Na_2SO_4 and concentrated. Purification by flash chromatography (Silica gel, eluent: petroleum ether : ethyl acetate = 1 : 1) afforded the product **5n** as a yellow solid (12.4 mg, 71% yield). mp 93-95 °C . ^1H NMR (400 MHz, $CDCl_3$) δ 9.23 (dd, *J* = 4.3 and 1.5 Hz, 1H), 8.24 (dd, *J* = 8.1 and 1.4 Hz, 1H), 7.73 (d, *J* = 9.1 Hz, 1H), 7.66 (dd, *J* = 8.1 and 4.3 Hz, 1H), 7.63 – 7.52 (m, 3H), 7.47 – 7.39 (m, 2H), 7.30 (d, *J* = 8.2 Hz, 1H), 1.78 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.97, 151.08, 151.00, 148.19, 147.47, 146.43, 145.30, 136.14, 131.18, 130.64, 129.89, 129.01, 126.88, 126.54, 126.16, 124.93, 123.98, 123.75, 123.33, 20.61; HRMS(EI) Calcd for $C_{20}H_{13}N_2O_2Cl$ [M^+]: 348.0666, Found 348.0671; IR (KBr) ν_{max} (cm^{-1}) : 3441, 1766, 1547, 1489, 1188, 838.



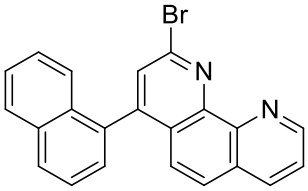
4-(2-Chloro-1,10-phenanthrolin-4-yl)phenyl acetate (5o):

3o (33.0 mg, 0.1 mmol), PCl_5(41.6 mg, 0.2 mmol) and anhydrous DCM (2 ml) were added in turn into a 25 mL of glass sealed tube. The tube was then tightly capped. The reaction mixture was stirred at 80 ^oC for 12 h. After cooling down to room temperature, the reaction mixture was neutralized by addition of aqueous saturated sodium bicarbonate and extracted with CH_2Cl_2. The combined extracts were dried over Na_2SO_4 and concentrated. Purification by flash chromatography (Silica gel, eluent: petroleum ether : ethyl acetate = 1 : 1) afforded the product **5o** as a yellow solid (21.6 mg, 62% yield). mp 153-155 °C . ^1H NMR (600 MHz, $CDCl_3$) δ 9.26 (dd, *J* = 4.3, 1.7 Hz, 1H), 8.27 (dd, *J* = 8.0 and 1.6 Hz, 1H), 7.89 (d, *J* = 9.1 Hz, 1H), 7.78 (d, *J* = 9.1 Hz, 1H), 7.69 (dd, *J* = 8.0 and 4.3 Hz, 1H), 7.60 (s, 1H), 7.56 (d, *J* = 8.5 Hz, 2H), 7.32 (d, *J* = 8.5 Hz, 2H), 2.39 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 169.55, 151.39, 151.23, 151.07, 150.79, 146.77, 145.35, 136.11, 134.46, 130.85, 128.93, 126.91, 125.79, 124.50, 123.80, 122.30, 21.37; HRMS(EI) Calcd for $C_{20}H_{13}N_2O_2Cl$ [M^+]: 348.0666, Found 348.0670; IR (KBr) ν_{max} (cm^{-1}) : 3440, 1752, 1546, 1493, 1201, 839.



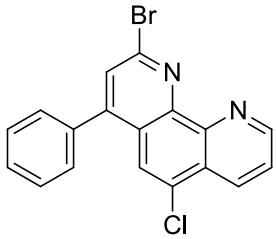
2-Bromo-4-(naphthalen-2-yl)-1,10-phenanthroline (5p):

3p (96.7 mg, 0.3 mmol) was suspended in dry toluene (3 mL). $POBr_3$ (430.0 mg, 1.5 mmol) was added. The reaction mixture was vigorously stirred at 100 °C for 12 h under nitrogen atmosphere. Then the reaction mixture was neutralized by addition of aqueous saturated sodium bicarbonate and extracted with CH_2Cl_2. The combined extracts were dried over Na_2SO_4 and concentrated. Purification by flash chromatography (Silica gel, eluent: petroleum ether : ethyl acetate = 1 : 1) afforded the product **5p** as a yellow solid (86.1 mg, 74% yield). mp 78-80 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.24 – 9.14 (m, 1H), 8.15 (d, *J* = 7.9 Hz, 1H), 7.99 – 7.81 (m, 4H), 7.81 – 7.43 (m, 7H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.97, 150.86, 147.07, 145.13, 142.15, 135.89, 133.90, 133.10, 133.05, 128.97, 128.66, 128.47, 128.24, 127.97, 127.82, 127.09, 126.96, 126.87, 126.81, 126.00, 123.88, 123.55. HRMS(EI) Calcd for $C_{22}H_{13}N_2Br$ [M^+]: 384.0262, Found 384.0259; IR (KBr) ν_{max} (cm^{-1}) : 3441, 1620, 1564, 1541, 1489, 1125, 863.



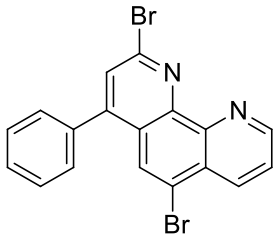
2-Bromo-4-(naphthalen-1-yl)-1,10-phenanthroline (5q):

3q (96.7 mg, 0.3 mmol) was suspended in dry toluene (3 mL). $POBr_3$ (430.0 mg, 1.5 mmol) was added. The reaction mixture was vigorously stirred at 100 °C for 12 h under nitrogen atmosphere. Then the reaction mixture was neutralized by addition of aqueous saturated sodium bicarbonate and extracted with CH_2Cl_2. The combined extracts were dried over Na_2SO_4 and concentrated. Purification by flash chromatography (Silica gel, eluent: petroleum ether : ethyl acetate = 1 : 1) afforded the product **5q** as a yellow solid (95.5 mg, 83% yield). mp 93-95 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.25 (dd, *J* = 4.3 and 1.8 Hz, 1H), 8.15 (dd, *J* = 8.1 and 1.8 Hz, 1H), 8.01 (d, *J* = 8.3 Hz, 1H), 7.96 (d, *J* = 8.2 Hz, 1H) 7.78 (s, 1H), 7.70 – 7.39 (m, 5H), 7.39 – 7.20 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.82, 149.86, 146.69, 145.07, 142.15, 135.88, 133.91, 133.34, 131.42, 129.35, 128.79, 128.75, 128.42, 127.47, 127.16, 126.82, 126.78, 126.34, 125.39, 125.22, 124.21, 123.51; HRMS(EI) Calcd for $C_{22}H_{13}N_2Br$ [M^+]: 384.0262, Found 384.0270; IR (KBr) ν_{max} (cm^{-1}) : 3427, 1563, 1540, 1489, 1127, 778.



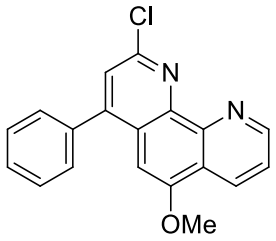
2-Bromo-6-chloro-4-phenyl-1,10-phenanthroline (5v):

3v (30.7 mg, 0.1 mmol) was suspended in dry toluene (1 mL). $POBr_3$ (143.4 mg, 0.5 mmol) was added. The reaction mixture was vigorously stirred at 100 °C for 12 h under nitrogen atmosphere. Then the reaction mixture was neutralized by addition of aqueous saturated sodium bicarbonate and extracted with CH_2Cl_2. The combined extracts were dried over Na_2SO_4 and concentrated. Purification by flash chromatography (Silica gel, eluent: petroleum ether : ethyl acetate = 1 : 1) afforded the product **5v** as a yellow solid (31.4 mg, 85% yield). mp 205-207 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.26 (dd, *J* = 4.4 and 1.7 Hz, 1H), 8.63 (dd, *J* = 8.3 and 1.7 Hz, 1H), 7.90 (s, 1H), 7.78 – 7.67 (m, 2H), 7.62 – 7.43 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.53, 150.39, 146.17, 145.68, 142.49, 136.05, 133.27, 130.69, 129.52, 129.37, 129.11, 128.51, 127.04, 125.75, 124.14, 123.35; HRMS(EI) Calcd for $C_{18}H_{10}N_2ClBr$ [M^+]: 367.9716, Found 367.9710; IR (KBr) ν_{max} (cm^{-1}) : 3441, 1631, 1601, 1540, 1488, 1388, 1131, 879.



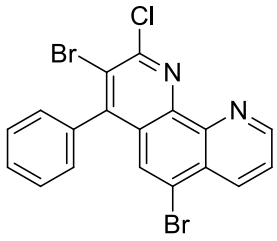
2,6-Dibromo-4-phenyl-1,10-phenanthroline (5w):

In a 25 mL round-bottomed flask was placed substrate **3w** (25.0 mg, 0.07 mmol) and $POBr_3$ (500 mg). Then the reaction mixture was stirred at 80 ºC for 24 h. The reaction mixture was neutralized by addition of aqueous saturated sodium bicarbonate and extracted with CH_2Cl_2. The combined extracts were dried over Na_2SO_4 and concentrated. Purification by flash chromatography (Silica gel, eluent: petroleum ether : ethyl acetate = 4 : 1) afforded the product **5w** as a yellow solid (24.0 mg, 83% yield). mp 278-280 °C.^{1}H NMR (400 MHz, $CDCl_3$) δ 9.27 (dd, *J* = 4.3 and 1.6 Hz, 1H), 8.65 (dd, *J* = 8.3 and 1.6 Hz, 1H), 8.16 (s, 1H), 7.80 – 7.71 (m, 2H), 7.63 – 7.47 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.65, 150.37, 146.65, 145.74, 142.71, 136.09, 136.06, 129.60, 129.45, 129.19, 128.64, 128.22, 127.32, 126.36, 124.50, 121.59; HRMS(ESI) Calcd for $C_{18}H_{11}N_2Br_2$ [M+H]$^+$: 412.9289, Found 412.9282; IR (KBr) ν_{max} (cm^{-1}) : 3440, 1631, 1597, 1538, 1487, 1129, 878, 701.



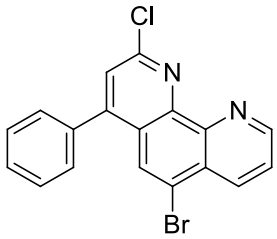
2-Chloro-6-methoxy-4-phenyl-1,10-phenanthroline (5x):

3x (15.1 mg, 0.05 mmol), PCl_5 (20.8 mg, 0.1 mmol) and anhydrous DCM (2 ml) were added in turn into a 25 mL of glass sealed tube. The tube was then tightly capped. The reaction mixture was stirred at 80 ^oC for 12 h. After cooling down to room temperature, the reaction mixture was neutralized by addition of aqueous saturated sodium bicarbonate and extracted with CH_2Cl_2. The combined extracts were dried over Na_2SO_4 and concentrated. Purification by flash chromatography (Silica gel, eluent: petroleum ether : ethyl acetate = 1 : 1) afforded the product **5x** as a yellow solid (12.3 mg, 83% yield). mp 185-187 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 9.23 (dd, *J* = 4.2 and 1.5 Hz, 1H), 8.66 – 8.62 (m, 1H), 7.75 – 7.45 (m, 7H), 7.02 (s, 1H), 3.90 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.17, 151.17, 150.12, 148.50, 145.73, 143.02, 137.28, 130.85, 129.25, 128.89, 126.30, 124.41, 123.52, 123.11, 98.47, 55.68; HRMS(EI) Calcd for $C_{19}H_{13}N_2OCl$ $[M^+]$: 320.0716, Found 320.0706; IR (KBr) ν_{max} (cm^{-1}) : 3443, 1619, 1547, 1397, 1259, 1114.



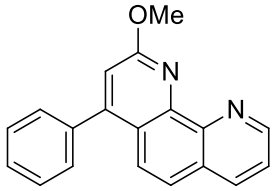
3,6-Dibromo-2-chloro-4-phenyl-1,10-phenanthroline (10):

In a 25 mL of round-bottomed flask was placed substrate **9** (27.2 mg, 0.063 mmol) and $POCl_3$(1 mL). Then the reaction mixture was refluxed for 8 h. The reaction mixture was neutralized by addition of aqueous saturated sodium bicarbonate and extracted with CH_2Cl_2. The combined extracts were dried over Na_2SO_4 and concentrated. Purification by flash chromatography (Silica gel, eluent: petroleum ether : ethyl acetate = 4 : 1) afforded the product **10** as a yellow solid (25.7 mg, 91% yield). mp 273-275 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 9.25 (dd, *J* = 4.3 and 1.4 Hz, 1H), 8.60 (dd, *J* = 8.3 and 1.3 Hz, 1H), 7.75 (dd, *J* = 8.3 and 4.3 Hz, 1H), 7.70 – 7.53 (m, 4H), 7.37 – 7.28 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.83, 151.46, 151.15, 145.30, 143.76, 137.01, 136.11, 129.40, 129.13, 129.06, 128.15, 127.88, 127.60, 124.62, 122.37, 122.22; HRMS(ESI) Calcd for $C_{18}H_{10}N_2ClBr_2$ $[M+H]^+$: 446.8899, Found 446.8892; IR (KBr) ν_{max} (cm^{-1}) : 3451, 1635, 1482, 1381, 1172, 912.



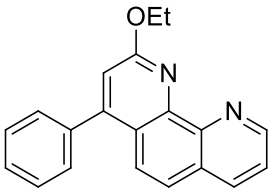
6-Bromo-2-chloro-4-phenyl-1,10-phenanthroline (11):

In a 25 mL of round-bottomed flask was placed substrate **3w** (25.0 mg, 0.07 mmol) and $POCl_3$(1 mL). Then the reaction mixture was stirred at 80 ºC for 8 h. The reaction mixture was neutralized by addition of aqueous saturated sodium bicarbonate and extracted with CH_2Cl_2. The combined extracts were dried over Na_2SO_4 and concentrated. Purification by flash chromatography (Silica gel, eluent: petroleum ether : ethyl acetate = 2 : 1) afforded the product **11** as a yellow solid (21.9 mg, 85% yield). mp 185-187 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.26 (dd, *J* = 4.3 and 1.5 Hz, 1H), 8.64 (dd, *J* = 8.3 and 1.5 Hz, 1H), 8.16 (s, 1H), 7.76 (dd, *J* = 8.3 and 4.3 Hz, 1H), 7.67 – 7.41 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.61, 151.57, 150.97, 146.21, 145.80, 136.27, 136.02, 129.57, 129.45, 129.18, 128.26, 127.19, 126.14, 125.07, 124.46, 121.44; HRMS(ESI) Calcd for $C_{18}H_{11}N_2ClBr$ $[M+H]^+$: 368.9794, Found 368.9789; IR (KBr) ν_{max} (cm^{-1}) : 3441, 1631, 1600, 1543, 1489, 1134, 885.



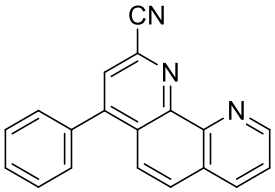
2-Methoxy-4-phenyl-1,10-phenanthroline (6):

5a (33.5 mg, 0.1 mmol), $PdCl_2$ (0.9 mg, 0.005 mmol), K_2CO_3 (41.5 mg, 0.3 mmol) and MeOH (2 mL) were added in turn into a 25 mL of glass sealed tube. The tube was then tightly capped. The reaction mixture was stirred for 5 minutes at room temperature and then stirred at 80 ºC in a pre-heated oil bath for 24 h. After cooling down to room temperature, the reaction mixture was concentrated under vacuum. Purification by preparative TLC plate (petroleum ether : ethyl acetate = 2 : 1 as eluent) afforded the product **6** as a yellow solid (24.3 mg, 85% yield). mp 143-145 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.19 (dd, *J* = 4.4 and 1.8 Hz, 1H), 8.19 (dd, *J* = 8.1 and 1.8 Hz, 1H), 7.79 (d, *J* = 9.0 Hz, 1H), 7.66 – 7.41 (m, 7H), 7.07 (s, 1H), 4.35 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.84, 151.68, 150.12, 145.54, 145.13, 138.08, 136.10, 129.57, 128.93, 128.67, 128.54, 124.38, 123.53, 123.37, 122.63, 113.89, 54.01; HRMS(EI) Calcd for $C_{19}H_{14}N_2O$ $[M^+]$: 286.1106, Found 286.1092; IR (KBr) ν_{max} (cm^{-1}) : 3441, 1619, 1590, 1557, 1460, 1367, 1217.



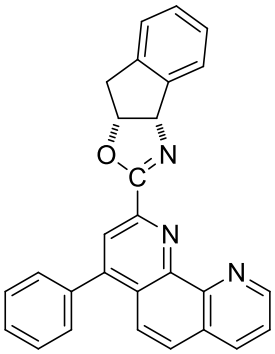
2-Ethoxy-4-phenyl-1,10-phenanthroline (7):

5a (16.8 mg, 0.05 mmol), $PdCl_2$ (0.4 mg, 0.0025 mmol), K_2CO_3 (20.7 mg, 0.15 mmol) and EtOH (2 mL) were added in turn into a 25 mL of glass sealed tube. The tube was then tightly capped. The reaction mixture was stirred for 5 minutes at room temperature and then stirred at 80 ^oC in a pre-heated oil bath for 24 h. After cooling down to room temperature, the reaction mixture was concentrated under vacuum. Purification by preparative TLC plate (petroleum ether : ethyl acetate = 2 : 1 as eluent) afforded the product the product **7** as a yellow solid (12.8 mg, 85% yield). mp 87-89 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 9.18 (dd, *J* = 4.4 and 1.8 Hz, 1H), 8.20 (dd, *J* = 8.1 and 1.8 Hz, 1H), 7.80 (d, *J* = 9.0 Hz, 1H), 7.64 – 7.44 (m, 7H), 7.07 (s, 1H), 4.85 (q, *J* = 7.1 Hz, 2H), 1.52 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.68, 151.62, 150.11, 145.60, 145.22, 138.18, 136.11, 129.60, 128.96, 128.68, 128.53, 124.42, 123.46, 123.26, 122.61, 114.04, 62.35, 14.76, HRMS(EI) Calcd for $C_{20}H_{16}N_2O$ [M^+]: 300.1263, Found 300.1257; IR (KBr) ν_{max} (cm^{-1}) : 3440, 1619, 1589, 1556, 1376, 1210, 706.

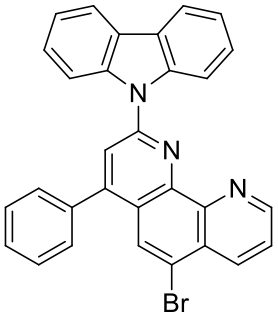


4-Phenyl-1,10-phenanthroline-2-carbonitrile (8):

In a 10 mL of glass tube was placed substrate **5a** (106.0 mg, 0.32 mmol), CuCN (28.3 mg, 0.32 mmol) and DMF (1 mL). After the reaction mixture was mixed well with stirring at room temperature for about 5 min, the glass tube was placed into the CEM microwave reactor and sealed with a pressure lock. The reaction mixture was stirred at 160 ^oC for 0.5 h. After cooling down to room temperature, the reaction mixture was concentrated under vacuum. The residue was dissolved with DCM (30 mL), washed with aq. NH_4OH (3 x 30 mL) and brine, dried over anhydrous Na_2SO_4, and concentrated. Purification by flash chromatography (Silica gel, $CHCl_3$: MeOH= 50 : 1) afforded the product **8** as a yellow solid (82.6 mg, 92% yield). mp 208-210 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 9.29 – 9.20 (m, 1H), 8.26 (dd, *J* = 8.0 and 3.2 Hz, 1H), 7.96 – 7.79 (m, 3H), 7.74 – 7.64 (m, 1H), 7.63 – 7.42 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.30, 150.35, 147.29, 145.53, 136.22, 136.17, 132.98, 129.59, 129.52, 129.46, 129.08, 128.89, 128.20, 126.64, 124.25, 123.70, 117.59; HRMS(EI) Calcd for $C_{19}H_{11}N_3$ [M^+]: 281.0953, Found 281.0954; IR (KBr) ν_{max} (cm^{-1}) : 3441, 1615, 1486, 1374, 843, 705.

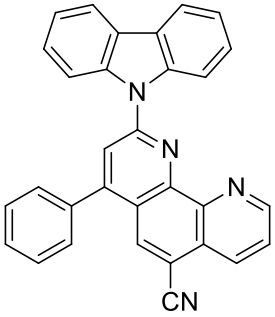


(3a*S*,8a*R*)-2-(4-Phenyl-1,10-phenanthrolin-2-yl)-8,8a-dihydro-3aH-indeno[1,2-d] oxazole (16): In a 25mL of sealed tube was placed substrate **8** (28.1 mg, 0.10 mmol) and amino (22.4 mg, 0.15 mmol). Then 2 mL of anhydrous toluene was added to the tube, followed by addition of $ZnCl_2$ (1.4 mg, 0.01 mmol). The tube was tightly capped. The reaction mixture was stirred at 140 ^oC in a pre-heated oil bath for 48 h. After cooling down to room temperature, the reaction mixture was concentrated under vacuum. Purification by preparative TLC plate ($CHCl_3$: MeOH = 4 : 1 as eluent) afforded the product **16** as a yellow solid (31.8 mg, 77% yield). mp 258-260 °C. $[\alpha]^{25}_D$ +196.8 (*c* 1.20, $CHCl_3$).^{1}H NMR (400 MHz, $CDCl_3$) δ 9.37 (dd, *J* = 4.7 and 1.5 Hz, 1H), 8.45 (dd, *J* = 8.2 and 1.5 Hz, 1H), 8.25 – 8.12 (m, 2H), 8.07 – 7.88 (m, 3H), 7.71 – 7.48 (m, 5H), 7.42 – 7.23 (m, 3H), 6.12 (d, *J* = 7.8 Hz, 1H), 6.01 – 5.92 (m, 1H), 3.77 – 3.44 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.48, 154.54, 150.69, 141.79, 140.87, 140.54, 139.24, 138.69, 137.73, 135.64, 130.29, 129.58, 129.45, 129.38, 128.89, 128.68, 128.24, 128.20, 128.15, 126.66, 124.88, 123.93, 122.11, 90.20, 74.27, 39.16; HRMS(EI) Calcd for $C_{28}H_{19}N_3O$ [M^+]: 413.1528, Found 413.1522; IR (KBr) ν_{max} (cm^{-1}) : 3454, 1642, 1615, 1461, 1386, 1165, 999.



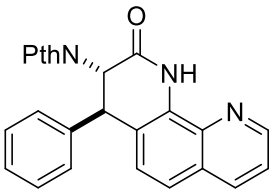
6-Bromo-2-(9H-carbazol-9-yl)-4-phenyl-1,10-phenanthroline (12):
NaH (60% dispersion in mineral oil, 4.4 mg, 0.11 mmol) was added in portions at 0 °C to a stirred solution of carbazole (16.7 mg, 0.1 mmol) in DMF (2 mL). After the reaction was stirred at 0 °C for 30 min, **5w** (37.0 g, 0.1 mmol) was added to the reaction mixture. The reaction mixture was stirred at 130 °C for 24 h. Then, the reaction mixture was cooled down to ambient temperature, poured into H_2O (3 mL) and extracted with EtOAc (3 x 10 mL). The combined organic phase was dried over Na_2SO_4 and concentrated under vacuum. Purification by flash chromatography (Silica gel, $CHCl_3$: MeOH= 50 : 1) afforded the product **12** as a yellow solid (37.1 mg, 74% yield). mp 125-127 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.26 (dd, *J* = 4.3 and 1.7 Hz,

1H), 8.67 (dd, *J* = 8.3 and 1.7 Hz, 1H), 8.27 (d, *J* = 9.2 Hz, 3H), 8.13 (d, *J* = 7.7 Hz, 2H), 7.98 (s, 1H), 7.76 (dd, *J* = 8.3 and 4.3 Hz, 1H), 7.65 – 7.53 (m, 5H), 7.50 (t, *J* = 7.7 Hz, 2H), 7.36 (t, *J* = 7.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.24, 151.08, 150.74, 146.53, 146.20, 139.70, 137.18, 135.81, 129.63, 129.53, 129.21, 129.16, 128.28, 127.30, 126.68, 125.22, 124.91, 124.15, 121.56, 120.34, 120.28, 119.37, 111.91; HRMS(EI) Calcd for $C_{30}H_{18}N_3Br$ [M^+]: 499.0684, Found 499.0699; IR (KBr) ν_{max} (cm^{-1}) : 3440, 1630, 1602, 1490, 1449, 1391, 1172, 752.



9-(9H-Carbazol-9-yl)-7-phenyl-1,10-phenanthroline-5-carbonitrile (13):

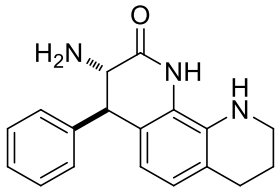
In a 10 mL of glass tube was placed substrate **12** (25.0 mg, 0.05 mmol), CuCN (4.5 mg, 0.05 mmol) and DMF (1 mL). After the reaction mixture was mixed well with stirring at room temperature for about 5 min, the glass tube was placed into the CEM microwave reactor and sealed with a pressure lock. The reaction mixture was stirred at 160 °C for 0.5 h. After cooling down to room temperature, the reaction mixture was concentrated under vacuum. The residue was dissolved with DCM (10 mL), washed with aq. NH_4OH (3 x 10mL) and brine, dried over anhydrous Na_2SO_4, and concentrated. Purification by flash chromatography (Silica gel, $CHCl_3$: MeOH= 50 : 1) afforded the product **13** as a yellow solid (12.5 mg, 56% yield). mp 223-225 °C . ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.35 (dd, *J* = 4.2 and 1.6 Hz, 1H), 8.65 (dd, *J* = 8.3 and 1.7 Hz, 1H), 8.43 (s, 1H), 8.35 (d, *J* = 8.3 Hz, 2H), 8.22 – 8.03 (m, 3H), 7.84 (dd, *J* = 8.2 and 4.3 Hz, 1H), 7.74 – 7.58 (m, 5H), 7.51 (t, *J* = 7.7 Hz, 2H), 7.38 (t, *J* = 7.5 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.27, 152.47, 152.08, 148.38, 145.64, 139.49, 136.56, 133.67, 132.66, 129.72, 129.66, 129.42, 126.96, 125.36, 124.61, 123.30, 122.22, 120.41, 119.22, 117.03, 112.30, 108.02, HRMS(EI) Calcd for $C_{31}H_{18}N_4$ [M^+]: 446.1531, Found 446.1539; IR (KBr) ν_{max} (cm^{-1}) : 3441, 1584, 1549, 2220, 1491, 1449, 1382, 751.



2-((3S,4R)-2-oxo-4-phenyl-1,2,3,4-tetrahydro-1,10-phenanthrolin-3-yl)isoindoline -1,3-dione

1y (42.1 mg, 0.1 mmol), $Pd(OAc)_2$ (3.4 mg, 0.015 mmol), AgOAc (25 mg, 0.15 mmol), NaOAc (8.2 mg, 0.1 mmol), DMAP (7.3 mg, 0.06 mmol) and anhydrous

toluene (10 ml) were added in turn into a 25 ml glass sealed tube, the reaction mixture was then tightly capped and stirred for 5 minutes at room temperature for proper mixing of the reactants, then submerged into an oil bath pre-heated to 160 °C for 48 hours. After cooling to room temperature, the reaction mixture was concentrated under vacuum, use preparative TLC plate (petroleum ether : ethyl acetate = 4 : 1 as eluent) to get the product **2y** (26.5 mg, 63% yield). $[\alpha]^{25}_D$ -32.6 (*c* 1.35, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ 9.56 (s, 1H), 8.86 (dd, *J* = 4.2, 1.6 Hz, 1H), 8.13 (dd, *J* = 8.3, 1.6 Hz, 1H), 7.81 – 7.62 (m, 4H), 7.46 (dd, *J* = 8.3, 4.2 Hz, 1H), 7.41 – 7.24 (m, 6H), 6.83 (d, *J* = 8.5 Hz, 1H), 5.52 (d, *J* = 14.4, 1H), 5.46 (d, *J* = 14.4, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.72, 164.99, 149.63, 137.71, 136.43, 136.08, 134.40, 134.15, 132.31, 131.81, 129.36, 129.25, 128.19, 127.52, 126.30, 123.69, 123.63, 123.46, 122.13, 121.46, 54.92, 45.78; HRMS(EI) Calcd for $C_{26}H_{17}N_3O_2$ [M^+]: 419.1270, Found 419.1278; IR (KBr) V(cm^{-1}) : 1717, 1632, 1471, 1390, 1115.

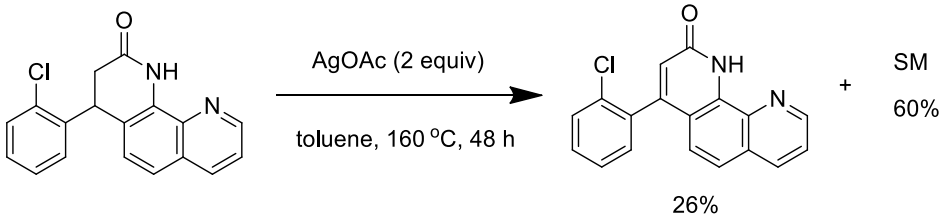


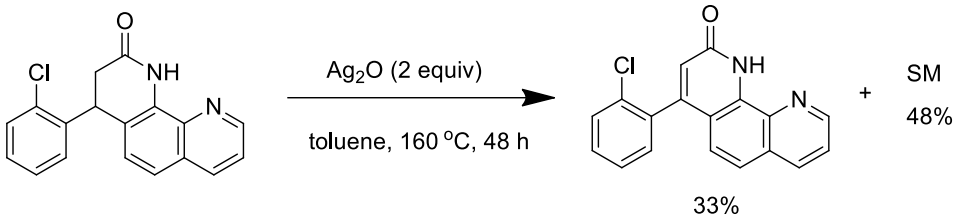
(3S,4R)-3-amino-4-phenyl-3,4,7,8,9,10-hexahydro-1,10-phenanthrolin-2(1H)-one

2y (78 mg, 0.19 mmol) was dissolved in MeOH (3 mL) and (5%) Pd/C (19.8 mg) was added. The reaction mixture was stirred at 40 °C for 24 hours under H_2 (balloon). The reaction mixture was filtered through celite, and washed with MeOH. The MeOH solution was concentrated in vacuum and used in the next step without further purification.

In a 10 mL of glass tube was placed substrate **2a**, $N_2H_4{\cdot}H_2O$ (95 mg, 1.9 mmol) and n-BuOH (5ml). Then the mixture was stirred at 90 °C for 1 h. The mixture was cooled to room temperature and concentrated under vacuum. Purification by flash chromatography (Silica gel, eluent: $CHCl_3$: MeOH = 4 : 1) to get the product **2y'** as a yellow solid (38.3 mg, 70% yield over two steps). $[\alpha]^{25}_D$ -49.4 (*c* 0.75, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ 9.52 (s, 1H), 7.49 – 7.12 (m, 5H), 6.58 (d, *J* = 7.8 Hz, 1H), 5.91 (d, *J* = 7.7 Hz, 1H), 4.02 (d, *J* = 12.4, 1H), 3.94 (d, *J* = 12.4, 1H), 3.40 – 3.31 (m, 2H), 2.73 (t, *J* = 5.9 Hz, 2H), 2.00 – 1.75 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.07, 139.67, 132.41, 129.39, 129.04, 127.54, 125.17, 125.14, 124.39, 122.79, 122.45, 116.80, 55.27, 50.95, 42.32, 27.26, 21.87; HRMS(EI) Calcd for $C_{18}H_{19}N_3O$ [M^+]: 293.1528, Found 293.1529; IR (KBr) V(cm^{-1}) : 1681, 1582, 1285, 750, 701.

Control experiment

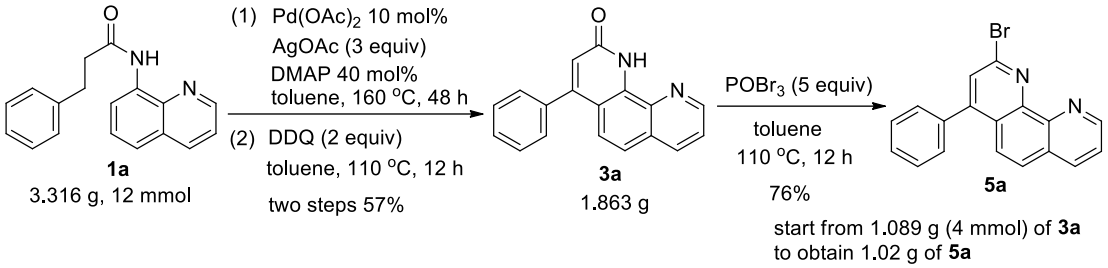




2i (5.2 mg, 0.017 mmol) and AgOAc (5.6 mg, 0.034 mmol) were added in turn into a 25 mL of glass sealed tube. The tube was then tightly capped. The reaction mixture was stirred for 5 minutes at room temperature. Then the reaction mixture was stirred at 160 °C in a pre-heated oil bath for 48 h. After cooling down to room temperature, the reaction mixture was concentrated under vacuum. Purification by preparative TLC plate (petroleum ether : ethyl acetate = 1 : 1 as eluent) afforded the product **3i** as a yellow solid (1.3 mg, 26% yield) with recovered starting material **2i** (3.1 mg, 60%).

2i (5.6 mg, 0.018 mmol) and Ag_2O (8.4 mg, 0.036 mmol) were added in turn into a 25 mL of glass sealed tube. The tube was then tightly capped. The reaction mixture was stirred for 5 minutes at room temperature. Then the reaction mixture was stirred at 160 °C in a pre-heated oil bath for 48 h. After cooling down to room temperature, the reaction mixture was concentrated under vacuum. Purification by preparative TLC plate (petroleum ether : ethyl acetate = 1 : 1 as eluent) afforded the product **3i** as a yellow solid (1.8 mg, 33% yield) with recovered starting material **2i**(2.7 mg, 48%).

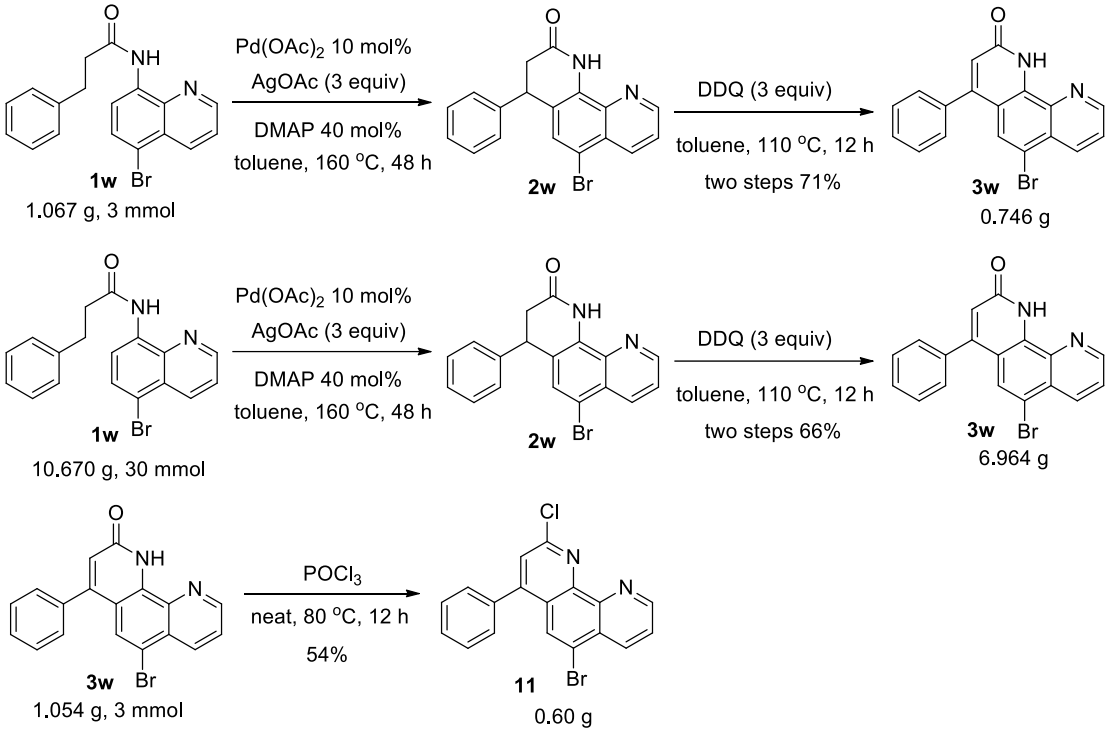
Large scale reaction:



1a (3.3158 g, 12 mmol), $Pd(OAc)_2$ (269.4 mg, 1.2 mmol), AgOAc (6.0091 g, 36 mmol), DMAP (586.4 mg, 4.8 mmol) and anhydrous toluene (60 mL) were added in turn into a 150 mL of glass sealed tube. The tube was tightly capped. The reaction mixture was stirred for 5 minutes at room temperature and then stirred at 160 °C in a pre-heated oil bath for 48 hours. After cooling down to room temperature, DDQ (5.448 g, 24 mmol) was added into the reaction mixture. The reaction mixture was stirred under refluxing condition for 12 h. After cooling down to room temperature, aqueous NaOH solution (2 M) was added slowly to the reaction mixture. The reaction mixture was extracted with CH_2Cl_2 (3 x 100 mL), dried over anhydrous Na_2SO_4, and concentrated. The residue was purified by flash chromatography (Silica gel, eluent: $CHCl_3$/MeOH = 40/1) to get the product **3a** as a yellow solid (1.863 g, 57% yield).

3a (1.0892 g, 4 mmol) was suspended in dry toluene (30 mL). $POBr_3$ (5.7336 g, 20 mmol) was added. The reaction mixture was vigorously stirred at 110 °C for 12 h

under nitrogen atmosphere. Then the reaction mixture was neutralized by addition of aqueous saturated sodium bicarbonate and extracted with CH_2Cl_2. The combined extracts were dried over Na_2SO_4 and concentrated. Purification by flash chromatography (Silica gel, eluent: petroleum ether : ethyl acetate = 1 : 1) afforded the product **5a** as a yellow solid (1.02 g, 76% yield).



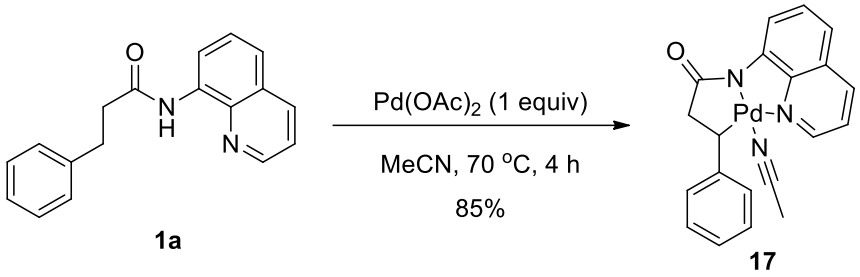
1w (1.067 g, 3 mmol), $Pd(OAc)_2$ (67.4 mg, 0.3 mmol), AgOAc (1.502 g, 9 mmol), DMAP (146.6 mg, 1.2 mmol) and anhydrous toluene (25 mL) were added in turn into a 50 mL of glass sealed tube. The tube was tightly capped. The reaction mixture was stirred for 5 minutes at room temperature and then stirred at 160 °C in a pre-heated oil bath for 48 hours. After cooling down to room temperature, DDQ (2.043 g, 9mmol) was added into the reaction mixture. The reaction mixture was stirred under refluxing condition for 12 h. After cooling down to room temperature, aqueous NaOH solution (2 M) was added slowly to the reaction mixture. The reaction mixture was extracted with CH_2Cl_2 (3 x 100 mL), dried over anhydrous Na_2SO_4, and concentrated. The residue was purified by flash chromatography (Silica gel, eluent: $CHCl_3$/MeOH = 40/1) to get the product **3w** as a yellow solid (746 mg, 71% yield).

1w (10.67 g, 30 mmol), $Pd(OAc)_2$ (0.674 g, 3 mmol), AgOAc (15.02 g, 90 mmol), DMAP (1.466 g, 1.2 mmol) and anhydrous toluene (150 mL) were added in turn into a 250 mL of glass sealed tube. The tube was tightly capped. The reaction mixture was stirred for 5 minutes at room temperature and then stirred at 160 °C in a pre-heated oil bath for 48 hours. After cooling down to room temperature, DDQ (20.43 g, 90 mmol) was added into the reaction mixture. The reaction mixture was stirred under refluxing condition for 12 h. After cooling down to room temperature, aqueous NaOH solution (2 M) was added slowly to the reaction mixture. The reaction mixture was extracted with CH_2Cl_2 (3 x 250 mL), dried over anhydrous Na_2SO_4, and concentrated. The

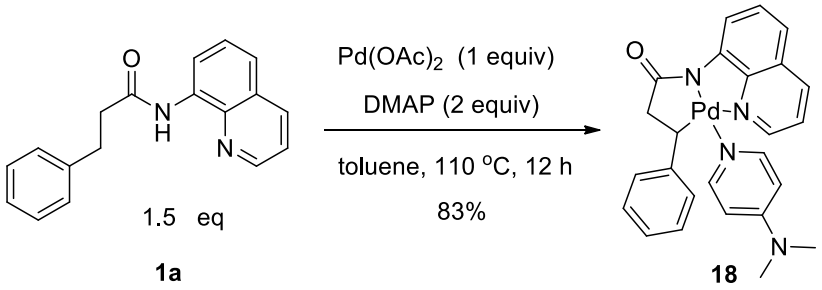
residue was purified by flash chromatography (Silica gel, eluent: $CHCl_3$/MeOH = 40/1) to get the product **3w** as a yellow solid (6.9638 g, 66% yield).

In a 25 mL of round-bottomed flask was placed substrate **3w** (1.054 g, 3 mmol) and $POCl_3$ (10 mL). Then the reaction mixture was stirred at 80 °C for 12 h. The reaction mixture was neutralized by addition of aqueous saturated sodium bicarbonate and extracted with CH_2Cl_2. The combined extracts were dried over Na_2SO_4 and concentrated. Purification by flash chromatography (Silica gel, eluent: petroleum ether : ethyl acetate = 2 : 1) afforded the product **11** as a yellow solid (0.6 g, 54% yield).

Mechanism Studies

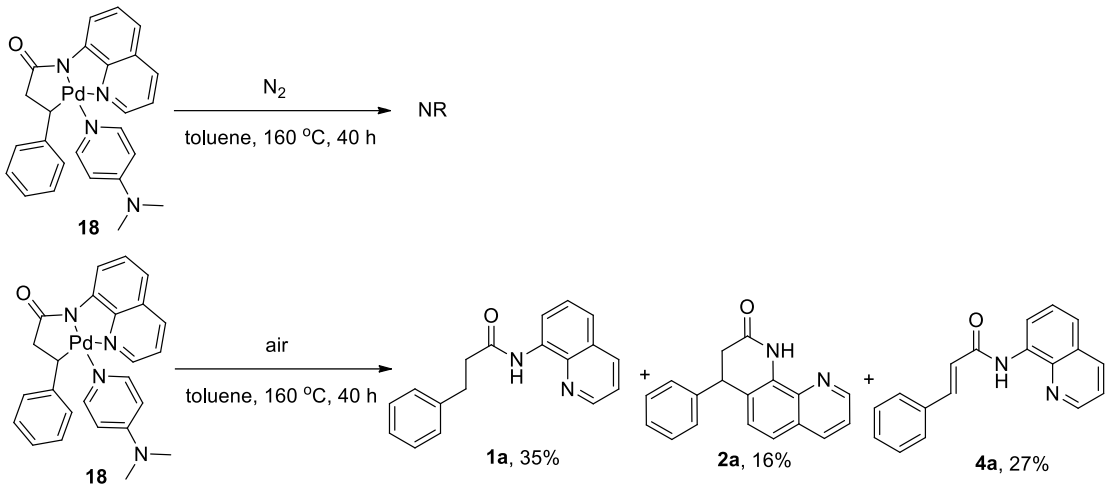


$Pd(OAc)_2$ (112.3 mg, 0.5 mmol) was added to a solution of **1a** (138.2 mg, 0.5 mmol) in CH_3CN (4 mL). The reaction mixture was stirred at 70 °C for 4 h, and then the solvent was removed under vacuum. Purification by preparative TLC plate (petroleum ether : ethyl acetate = 1 : 2 as eluent) afforded the product **17** (179.1 mg, 85% yield) as a green powder. ^{1}H NMR (400 MHz, DMSO) δ 9.04 (d, *J* = 4.1 Hz, 1H), 8.96 (d, *J* = 7.6 Hz, 1H), 8.53 (d, *J* = 8.1 Hz, 1H), 7.75 – 7.35 (m, 5H), 7.28 – 7.02 (m, 3H), 3.46 (dd, *J* = 17.0 and 8.3 Hz, 2H), 3.15 (d, *J* = 7.6 Hz, 1H), 2.36 (d, *J* = 16.9 Hz, 1H), 2.08 (s, 2H); ^{13}C NMR (100MHz, DMSO) δ 184.60, 151.49, 151.03, 146.22, 145.43, 139.99, 130.56, 129.54, 129.44, 128.35, 125.57, 122.63, 119.97, 119.94, 119.02, 51.53, 30.68, 2.10; HRMS(EI) Calcd for $C_{20}H_{17}NOPd$ [M^+]: 421.0406, Found 421.0408; IR (KBr) ν_{max} (cm^{-1}) : 3441, 2918, 1602, 1499, 1462, 1389, 825.



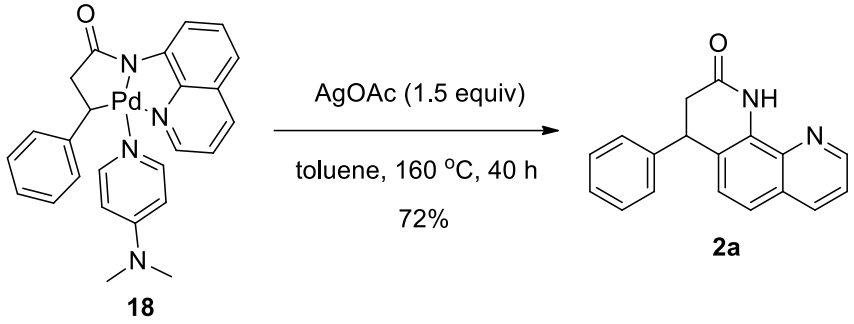
1a (82.9 mg, 0.3 mmol), $Pd(OAc)_2$ (45.0 mg, 0.2 mmol), DMAP (48.9 mg, 0.4 mmol) and anhydrous toluene (5 mL) were added in turn into a 100 mL of round-bottomed flask. The reaction mixture was stirred at 110 °C for 24 h, and then the solvent was removed under vacuum. Purification by preparative TLC plate (dichloromethane :

ethyl acetate = 6 : 1 as eluent) afforded the product **18** (83.1 mg, 83% yield) as a orange powder. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.11 (dd, *J* = 7.9 and 1.2 Hz, 1H), 8.10 (dd, *J* = 8.3 and 1.6 Hz, 1H), 7.97 (d, *J* = 7.0 Hz, 2H), 7.63 (dd, *J* = 4.6 and 1.6 Hz, 1H), 7.51 (t, *J* = 8.0 Hz, 1H), 7.22 (d, *J* = 8.1, 1H), 7.15 (dd, *J* = 8.3 and 4.6 Hz, 1H), 7.04 – 6.86 (m, 5H), 6.42 (d, *J* = 6.8 Hz, 2H), 3.50 – 3.31 (m, 2H), 3.12 – 3.00 (m, 7H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 186.49, 154.09, 152.42, 150.96, 146.66, 145.55, 137.80, 129.90, 129.36, 128.22, 126.33, 122.11, 120.63, 120.51, 118.20, 107.48, , 49.71, 39.36, 26.32; HRMS(ESI) Calcd for $C_{25}H_{25}N_4OPd$ [M^+]: 503.1063, Found 503.1053; IR (KBr) ν_{max} (cm^{-1}) : 3354, 2913, 1686, 1612, 1530, 1459, 1386, 1342, 1226, 825.

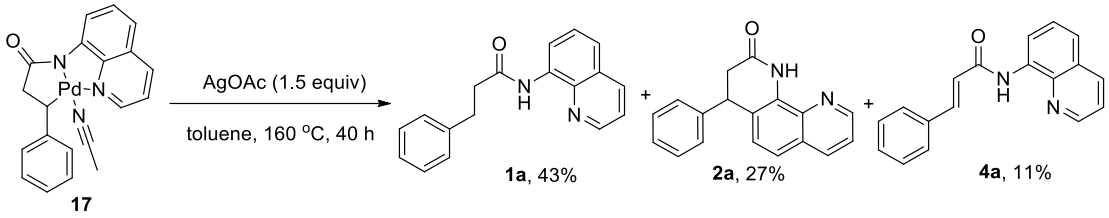


18 (50.3 mg, 0.1 mmol) and anhydrous toluene (2 mL) were added into a 10 mL of glass sealed tube under N_2. The tube was then tightly capped. The reaction mixture was stirred for 5 minutes at room temperature, and then stirred at 160 °C in a pre-heated oil bath for 40 h. After cooling down to room temperature, the reaction mixture was concentrated under vacuum and monitored by TLC and crude ^{1}H NMR. It indicated that there was no reaction occurred.

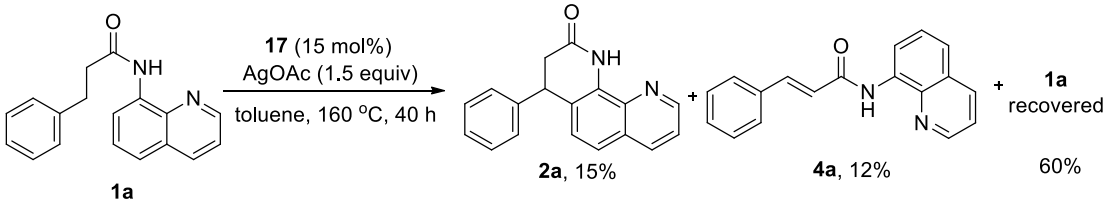
18 (10.1 mg, 0.02 mmol) and anhydrous toluene (2 mL) were added into a 10 mL of glass sealed tube in air. The tube was then tightly capped. The reaction mixture was stirred for 5 minutes at room temperature, and then stirred at 160 °C in a pre-heated oil bath for 40 h. After cooling down to room temperature, the reaction mixture was concentrated under vacuum. Purification by preparative TLC plate (petroleum ether : ethyl acetate = 4 : 1 as eluent) afforded the product **1a** (1.9 mg, 35% yield)，**2a** (0.9 mg, 16% yield)，**4a** (1.5 mg, 27% yield).



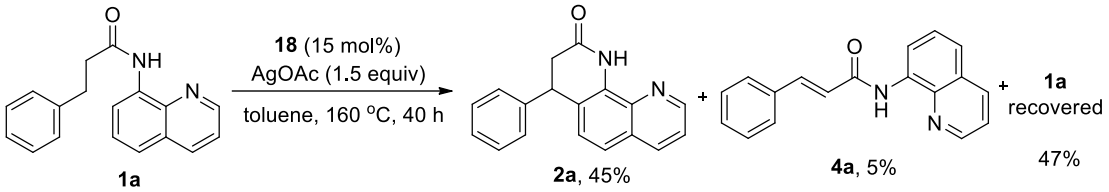
18 (25.1 mg, 0.05 mmol), AgOAc (12.5 mg, 0.075 mmol) and anhydrous toluene (5 mL) were added in turn into a 25 mL of glass sealed tube. The tube was then tightly capped. The reaction mixture was stirred for 5 minutes at room temperature, and then stirred at 160 °C in a pre-heated oil bath for 40 h. After cooling down to room temperature, the reaction mixture was concentrated under vacuum. Purification by preparative TLC plate (petroleum ether : ethyl acetate = 4 : 1 as eluent) afforded the product **1a** (9.9 mg, 72% yield).



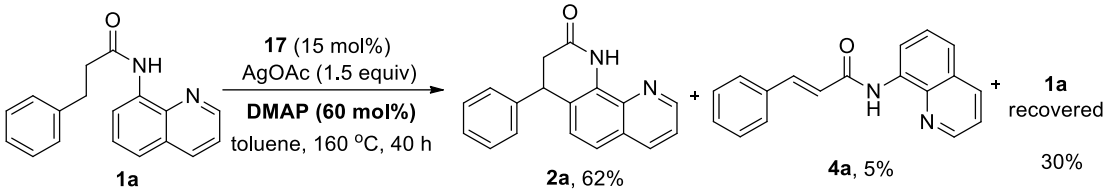
17 (42.2 mg, 0.1 mmol), AgOAc (25 mg, 0.15 mmol) and anhydrous toluene (2 mL) were added in turn into a 25 mL of glass sealed tube. The tube was then tightly capped. The reaction mixture was stirred for 5 minutes at room temperature, and then stirred at 160 °C in a pre-heated oil bath for 40 h. After cooling down to room temperature, the reaction mixture was concentrated under vacuum. Purification by preparative TLC plate (petroleum ether : ethyl acetate = 4 : 1 as eluent) afforded the product **2a** (7.5 mg, 27% yield)，**4a** (,3.0mg, 11% yield) and **1a** (11.8 mg, 43%).



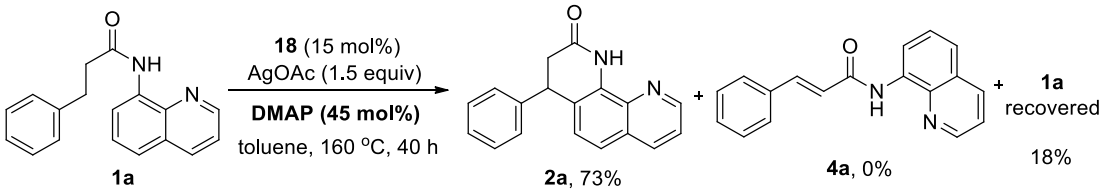
1a (27.6 mg, 0.1 mmol), 17 (6.3 mg, 0.015 mmol), AgOAc (25 mg, 0.15 mmol), and anhydrous toluene (2 mL) were added in turn into a 25 mL of glass sealed tube. The tube was tightly capped. The reaction mixture was stirred for 5 minutes at room temperature and then stirred at 160 °C in a pre-heated oil bath for 40 hours. After cooling down to room temperature, the reaction mixture was concentrated under vacuum. Purification by preparative TLC plate (petroleum ether : ethyl acetate = 2 : 1 as eluent) afforded the product the product **2a** (4.7 mg, 15% yield based on **1a** and **17**), **4a** (3.8 mg, 12% yield) and recovered starting material (18.9 mg, 60%).



1a (27.6 mg, 0.1 mmol), **18** (7.5 mg, 0.015 mmol), AgOAc (25 mg, 0.15 mmol), and anhydrous toluene (4 mL) were added in turn into a 25 mL of glass sealed tube. The tube was tightly capped. The reaction mixture was stirred for 5 minutes at room temperature and then stirred at 160 °C in a pre-heated oil bath for 40 hours. After cooling down to room temperature, the reaction mixture was concentrated under vacuum. Purification by preparative TLC plate (petroleum ether : ethyl acetate = 2 : 1 as eluent) afforded the product **2a** (14.2 mg, 45% yield based on **1a** and **18**) and recovered starting material (14.9 mg, 47%).



1a (27.6 mg, 0.1 mmol), **17** (6.3 mg, 0.015 mmol), AgOAc (25 mg, 0.15 mmol), DMAP (7.3 mg, 0.06 mmol) and anhydrous toluene (2 mL) were added in turn into a 25 mL of glass sealed tube. The tube was tightly capped. The reaction mixture was stirred for 5 minutes at room temperature and then stirred at 160 °C in a pre-heated oil bath for 40 hours. After cooling down to room temperature, the reaction mixture was concentrated under vacuum. Purification by preparative TLC plate (petroleum ether : ethyl acetate = 2 : 1 as eluent) afforded the product the product **2a** (19.5 mg, 62% yield based on **1a** and **17**), **4a** (1.6 mg, 5% yield) and recovered starting material (9.5 mg, 30%).



1a (27.6 mg, 0.1 mmol), **18** (7.5 mg, 0.015 mmol), AgOAc (25 mg, 0.15 mmol), DMAP (5.5 mg, 0.045 mmol) and anhydrous toluene (4 mL) were added in turn into a 25 mL of glass sealed tube. The tube was tightly capped. The reaction mixture was stirred for 5 minutes at room temperature and then stirred at 160 °C in a pre-heated oil bath for 40 hours. After cooling down to room temperature, the reaction mixture was concentrated under vacuum. Purification by preparative TLC plate (petroleum ether : ethyl acetate = 2 : 1 as eluent) afforded the product **2a** (23.0 mg, 73% yield based on **1a** and **18**) and recovered starting material (5.0 mg, 18%).

X-ray single-crystal analysis data of compound 18 and 5a.

X-ray single-crystal analysis data of compound **18** (Summary of Data CCDC 1472966).

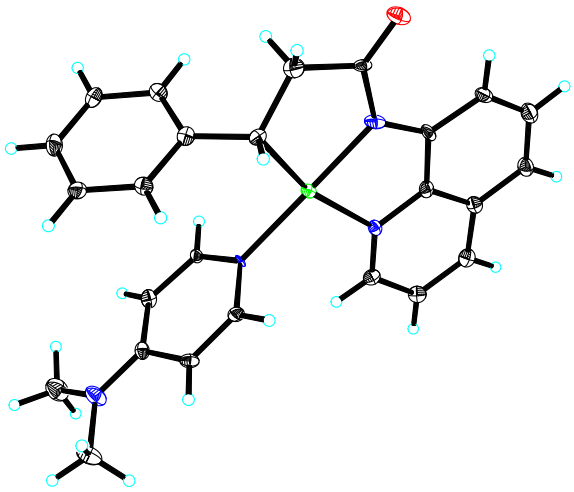


Figure 4. ORTEP view of compound 18.

Displacement ellipsoids are drawn at the 30% probability level.

Table 5. Crystal data and structure refinement for compound 18.

Empirical formula	C51 H56 Cl2 N8 O5 Pd2
Formula weight	1144.74
Temperature	100(2) K
Wavelength	0.71073 Å
Crystal system, space group	Orthorhombic, P n a 21
Unit cell dimensions	a = 25.795(4) Å alpha = 90°.
	b = 9.1440(15) Å beta = 90°.
	c = 21.256(4) Å gamma = 90°.
Volume	5013.7(15) $Å^3$
Z, Calculated density	4, 1.517 Mg/m^3
Absorption coefficient	0.879 mm^{-1}
F(000)	2336
Crystal size	1.46 x 0.18 x 0.10 mm
Theta range for data collection	1.85 to 30.55°.
Limiting indices	-35<=h<=35, -12<=k<=12, -29<=l<=26

Reflections collected / unique	49980 / 13756 [R(int) = 0.0498]
Completeness to theta = 30.55	95.0 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9172 and 0.3602
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	13756 / 409 / 617
Goodness-of-fit on F^2	1.088
Final R indices [I>2sigma(I)]	R1 = 0.0720, wR2 = 0.2088
R indices (all data)	R1 = 0.0827, wR2 = 0.2181
Absolute structure parameter	0.00
Largest diff. peak and hole	4.795 and -2.050 e. $Å^{-3}$

X-ray single-crystal analysis data of compound **5a** (Summary of Data CCDC 1472967).

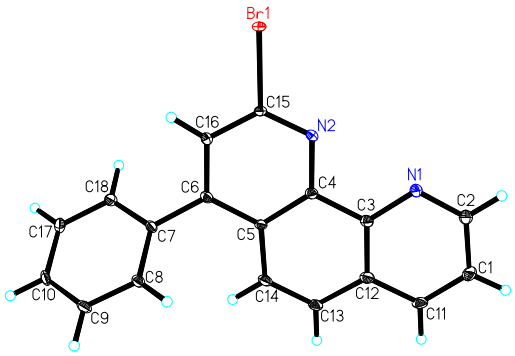


Figure 4. ORTEP view of compound 5a.

Displacement ellipsoids are drawn at the 30% probability level.

Table 5. Crystal data and structure refinement for compound 5a.

Empirical formula	C18 H11 Br N2
Formula weight	335.20
Temperature	100(2) K
Wavelength	0.71073 Å
Crystal system, space group	Monoclinic, C 2/c

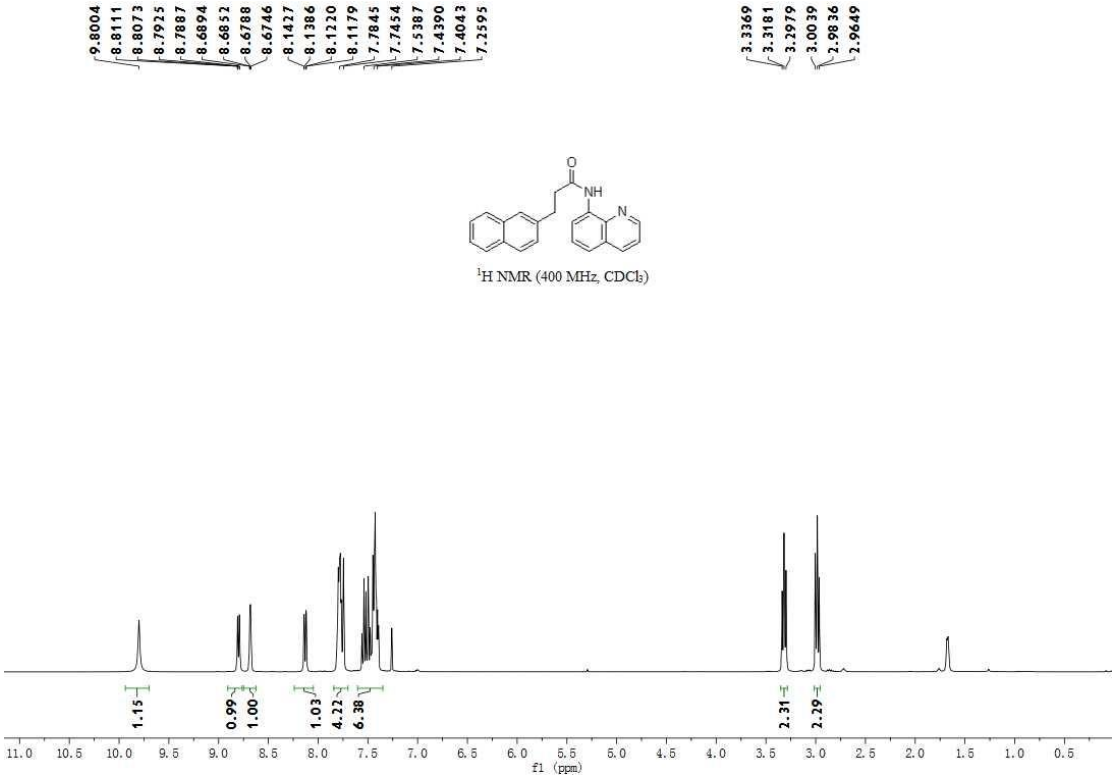
Unit cell dimensions	a = 26.203(4) Å alpha = 90°. b = 10.6440(15) Å beta = 106.633(2)°. c = 30.852(4) Å gamma = 90°.
Volume	8245(2) $Å^3$
Z, Calculated density	24, 1.620 Mg/m^3
Absorption coefficient	2.985 mm^{-1}
F(000)	4032
Crystal size	0.65 x 0.60 x 0.60 mm
Theta range for data collection	1.62 to 30.16°.
Limiting indices	-36<=h<=36, -14<=k<=14, -42<=l<=42
Reflections collected / unique	42824 / 11605 [R(int) = 0.0620]
Completeness to theta = 30.16	95.4 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.2675 and 0.2472
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	11605 / 0 / 568
Goodness-of-fit on F^2	1.022
Final R indices [I>2sigma(I)]	R1 = 0.0469, wR2 = 0.0980
R indices (all data)	R1 = 0.0794, wR2 = 0.1102
Largest diff. peak and hole	1.334 and -1.210 e. $Å^{-3}$

References

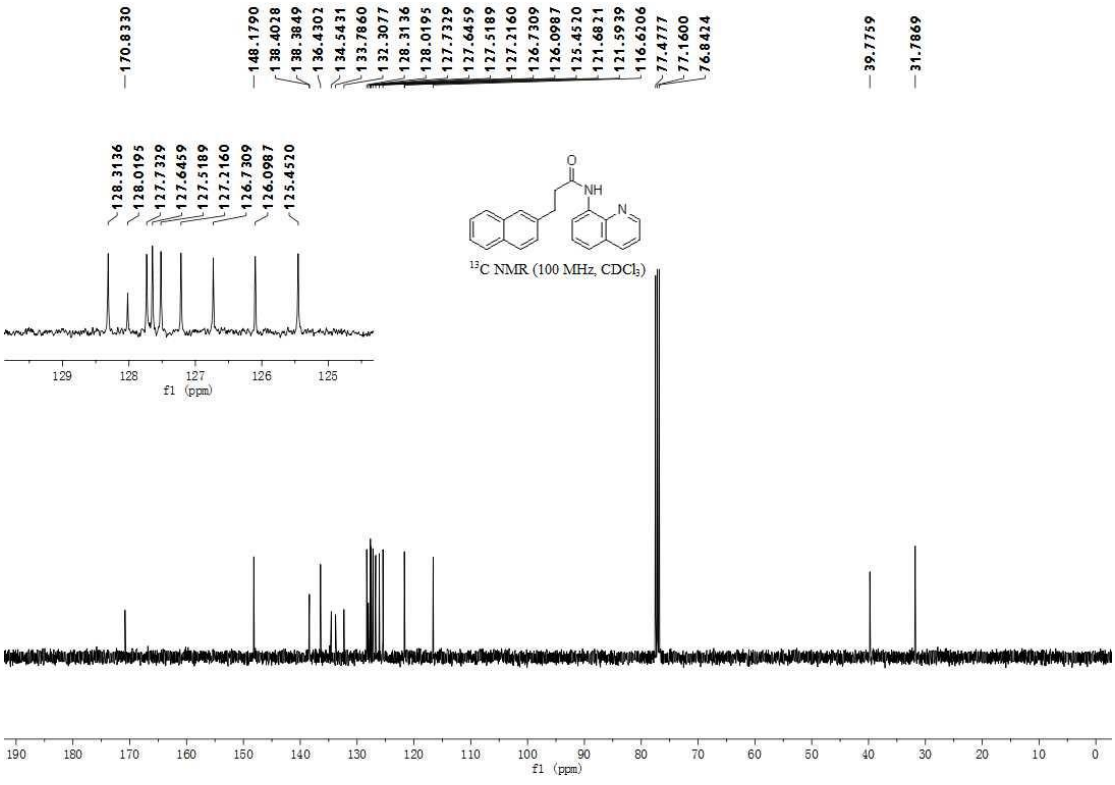
1. Sun, W.-W.; Cao, P.; Mei, R.-Q.; Li, Y.; Ma, Y.-L.; Wu, B. *Org. Lett.* 2014, *16*, 480-483.
2. Piscitelli, F.; Regina, G. L.; Silvestri, R. *Org. Prep. Proced. Int.* 2008, *40*, 204-208.

^{1}H NMR, ^{13}C NMR and ^{19}F NMR spectra of compounds

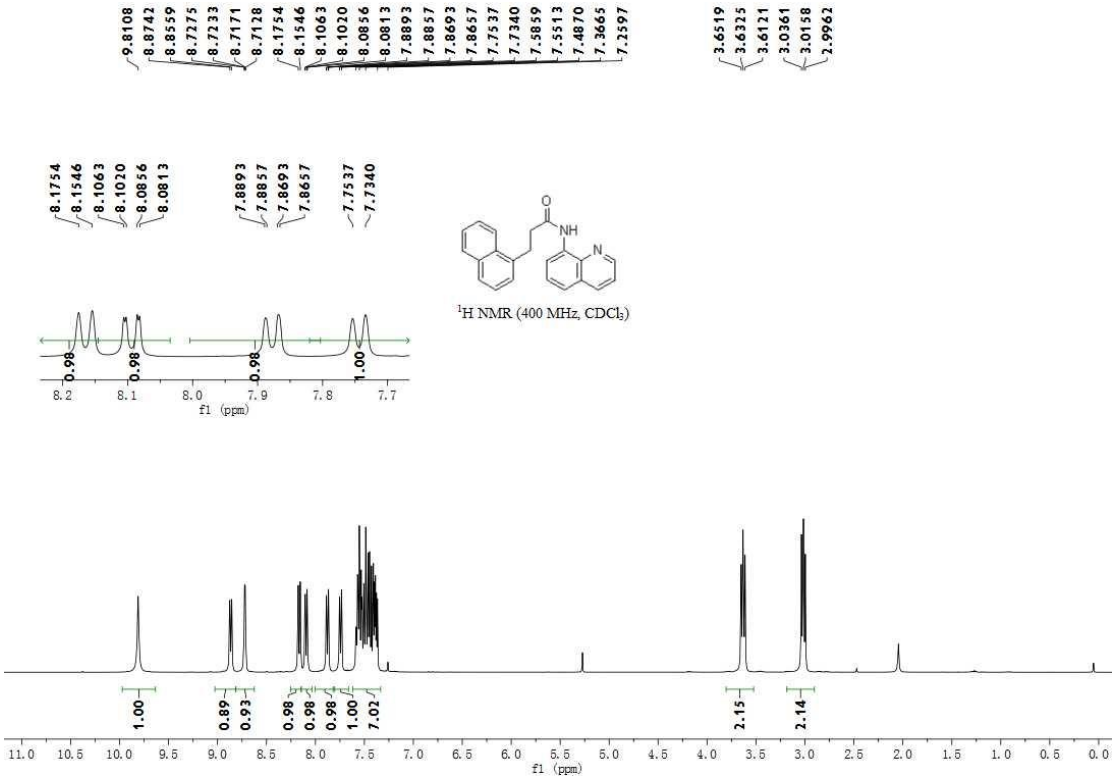
^{1}H NMR spectrum (400 MHz) of compound **1p** in $CDCl_3$



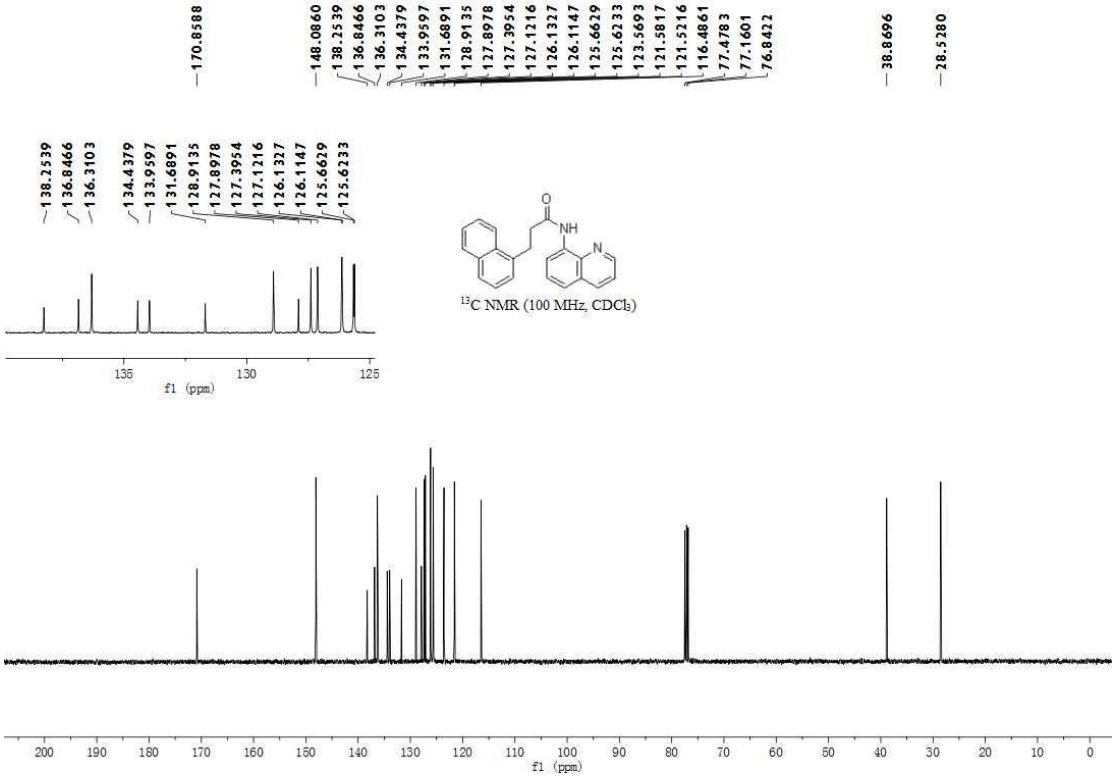
^{13}C NMR spectrum (100 MHz) of compound **1p** in $CDCl_3$



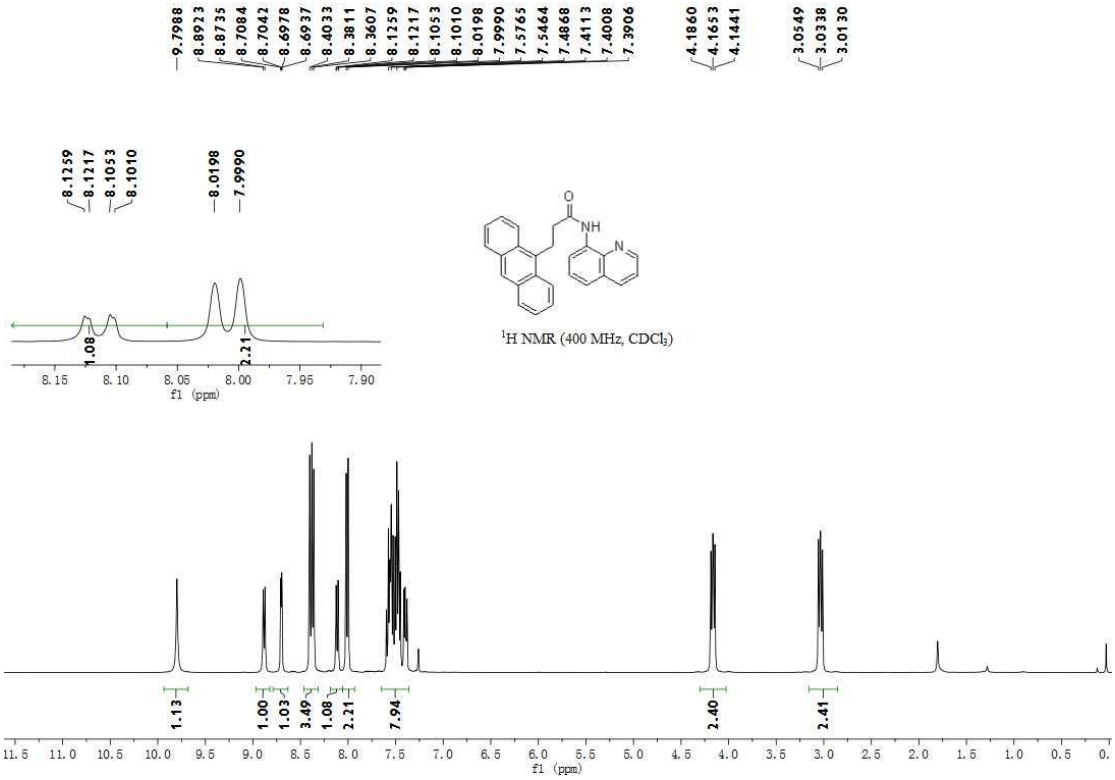
^{1}H NMR spectrum (400 MHz) of compound **1q** in $CDCl_3$



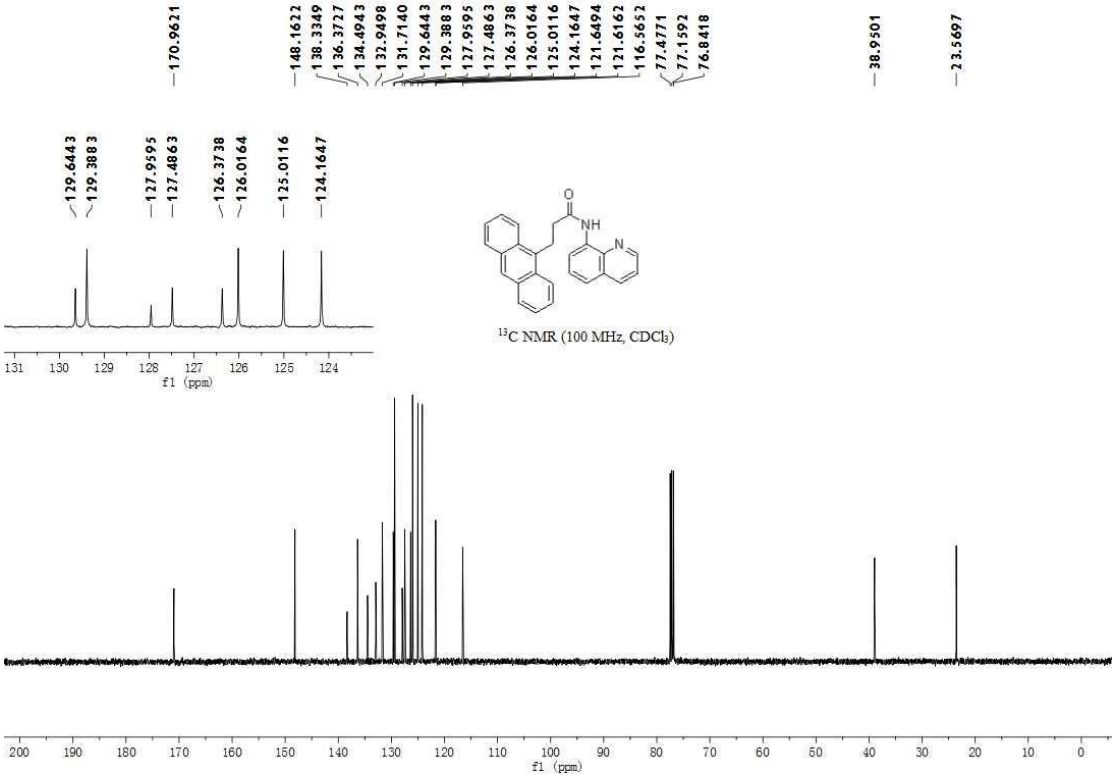
^{13}C NMR spectrum (100 MHz) of compound **1q** in $CDCl_3$



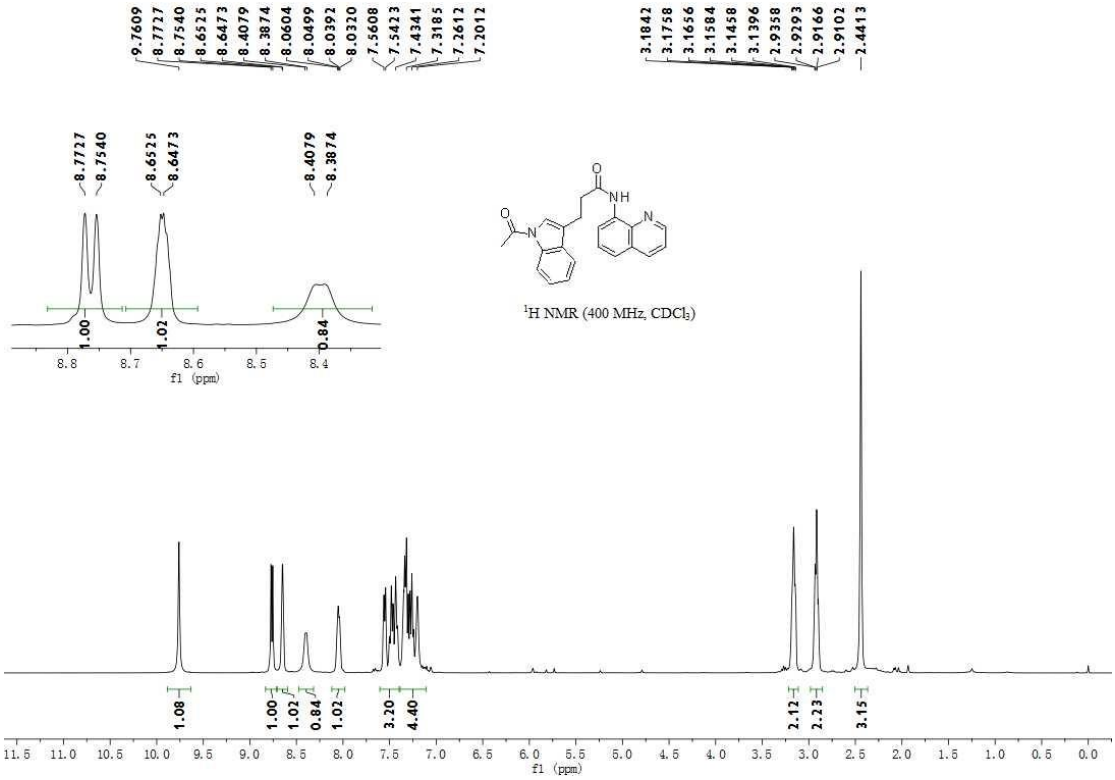
^{1}H NMR spectrum (400 MHz) of compound **1r** in $CDCl_3$



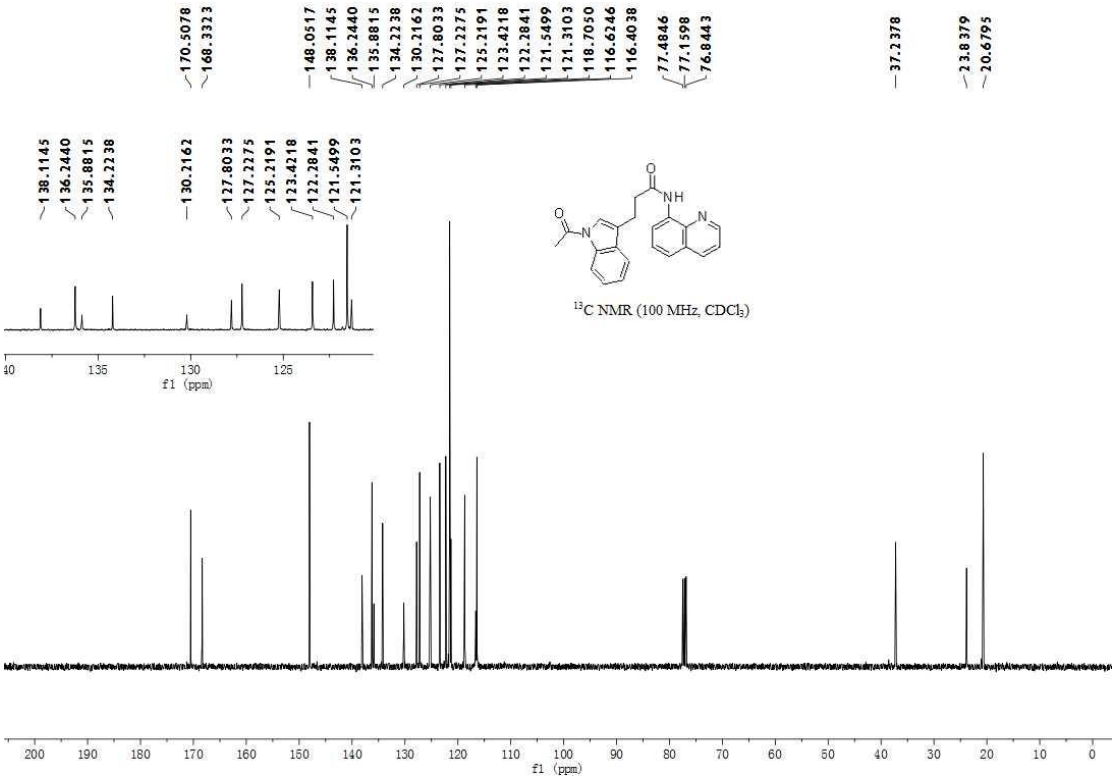
^{13}C NMR spectrum (100 MHz) of compound **1r** in $CDCl_3$



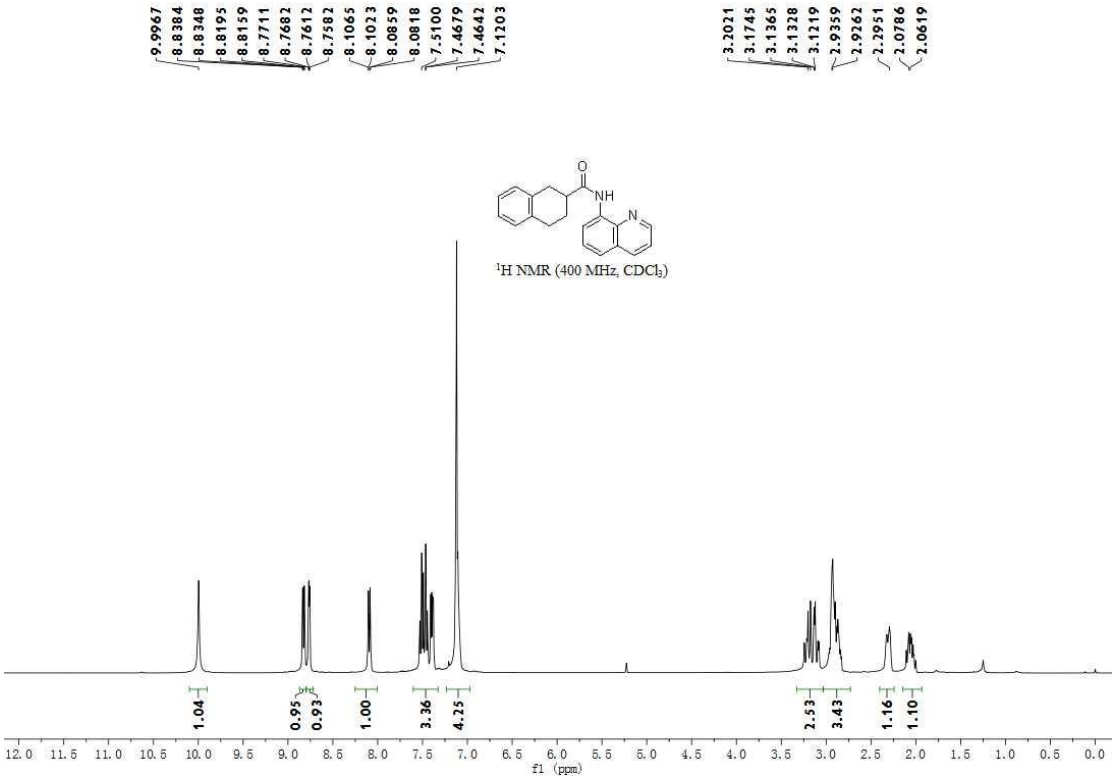
^{1}H NMR spectrum (400 MHz) of compound **1s** in $CDCl_3$



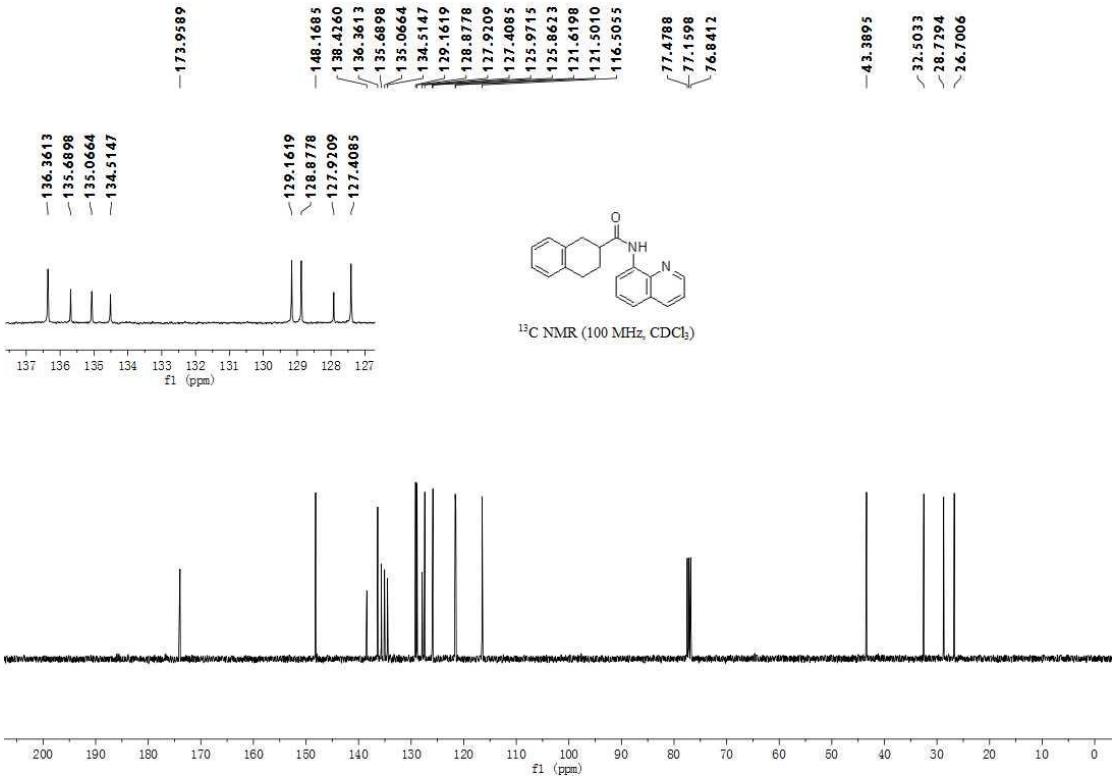
^{13}C NMR spectrum (100 MHz) of compound **1s** in $CDCl_3$



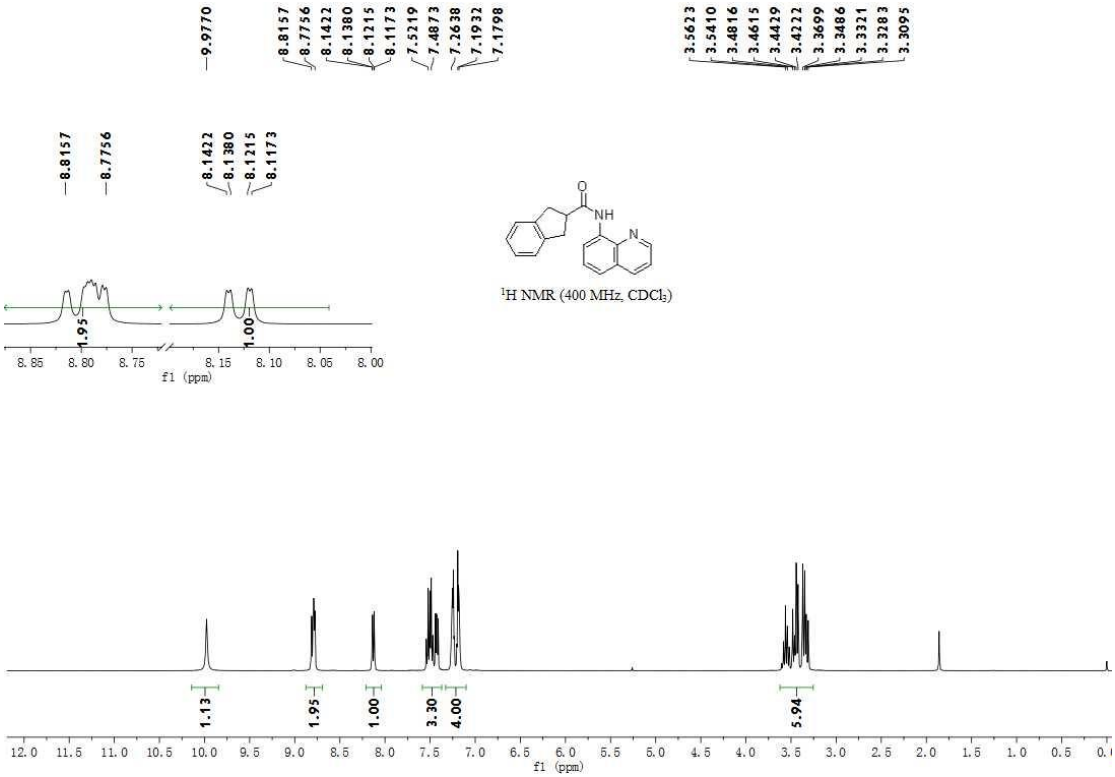
^{1}H NMR spectrum (400 MHz) of compound **1t** in $CDCl_3$



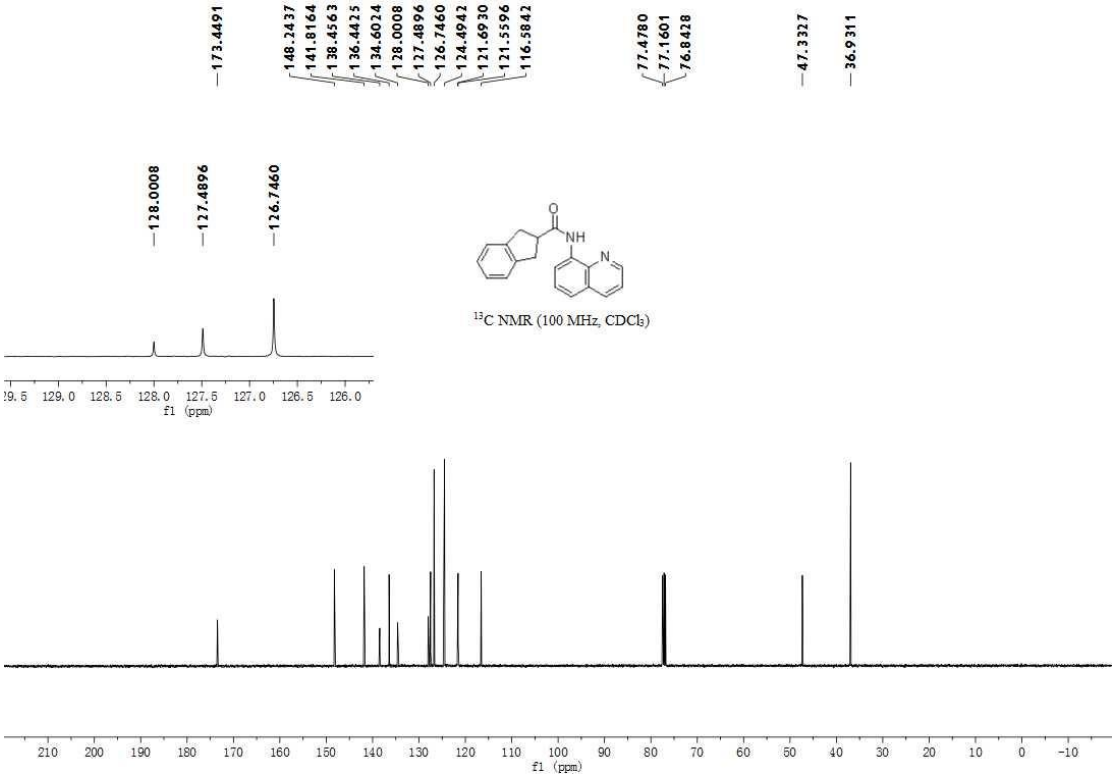
^{13}C NMR spectrum (100 MHz) of compound **1t** in $CDCl_3$



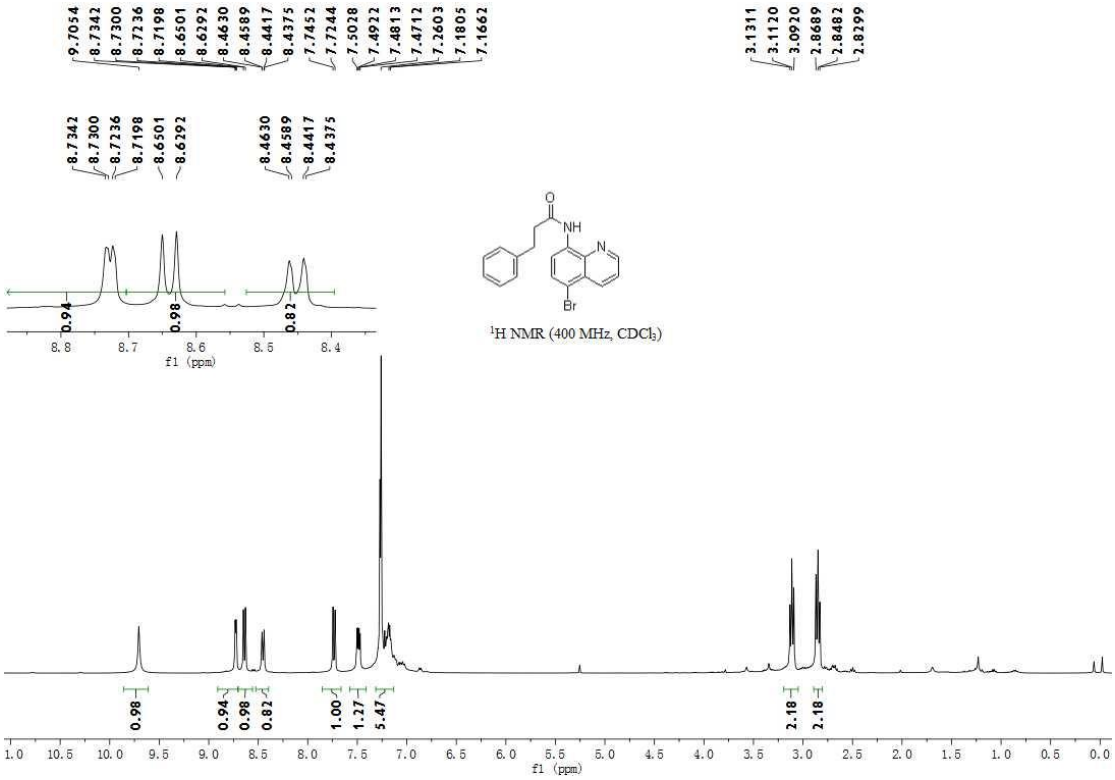
^{1}H NMR spectrum (400 MHz) of compound **1u** in $CDCl_3$



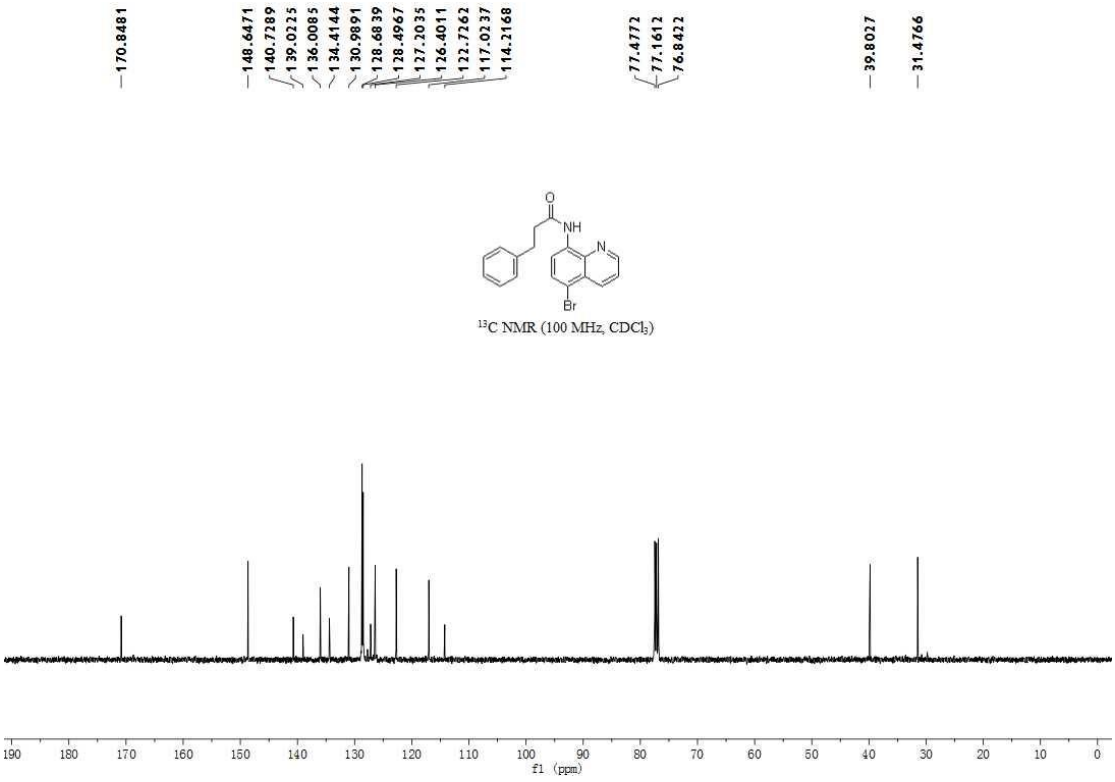
^{13}C NMR spectrum (100 MHz) of compound **1u** in $CDCl_3$



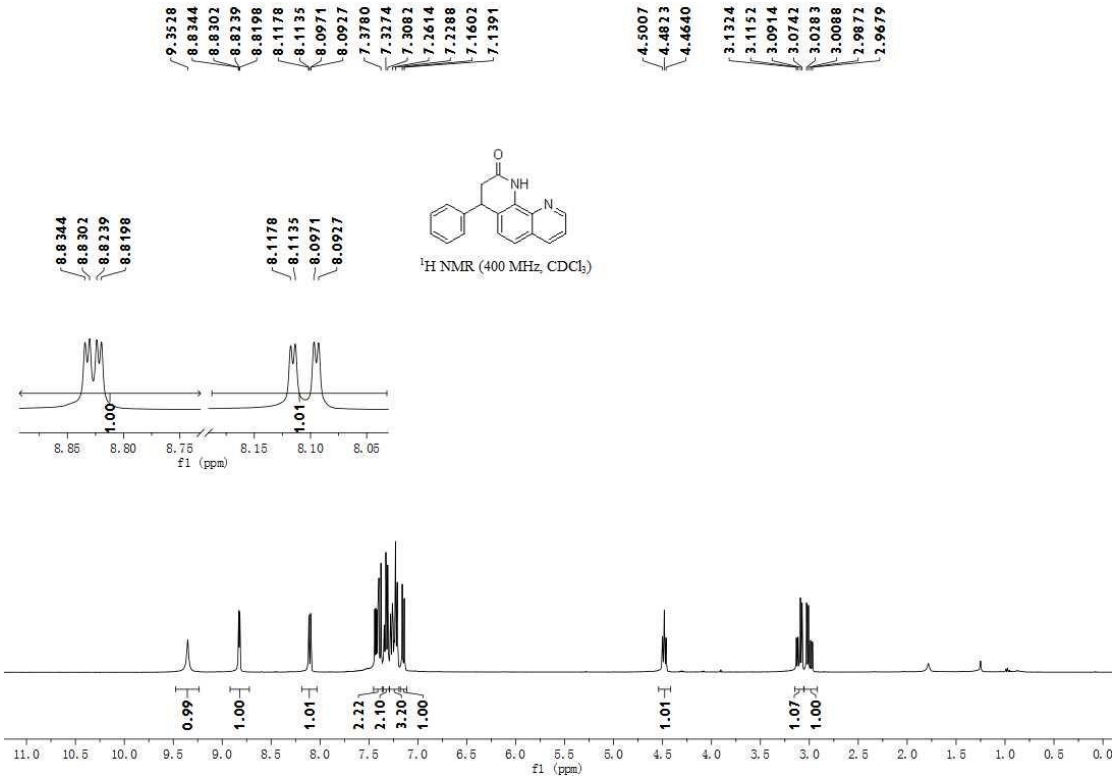
^{1}H NMR spectrum (400 MHz) of compound **1w** in $CDCl_3$



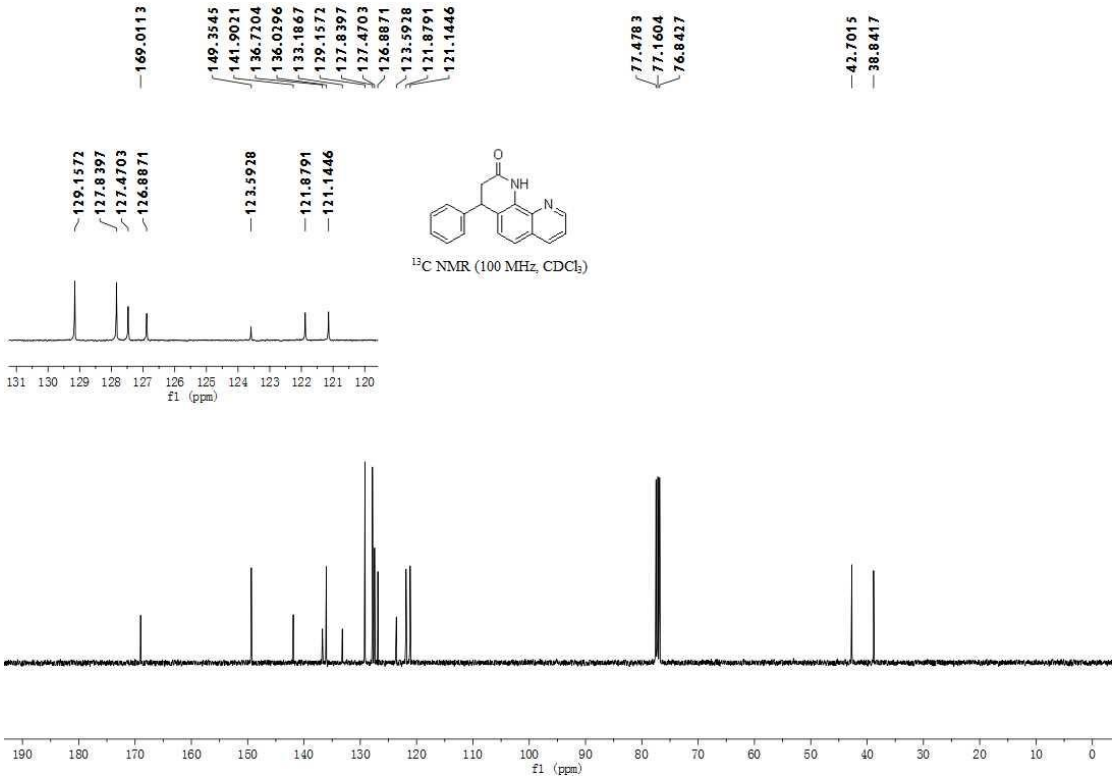
^{13}C NMR spectrum (100 MHz) of compound **1w** in $CDCl_3$



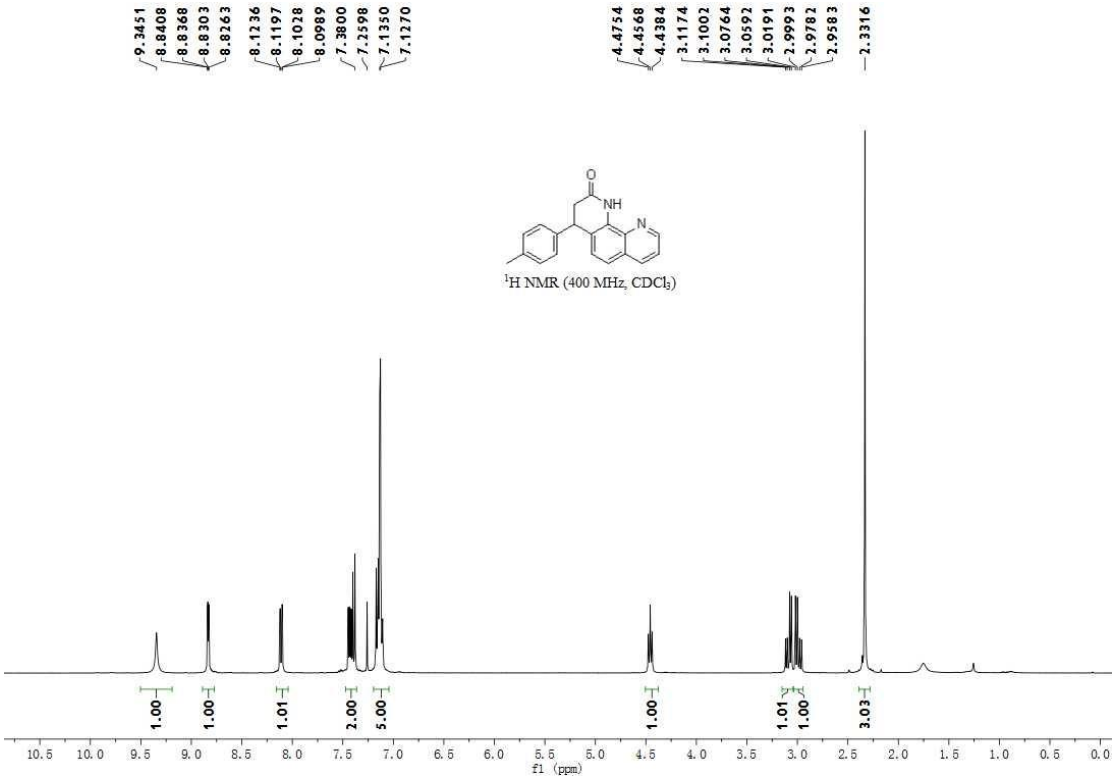
^{1}H NMR spectrum (400 MHz) of compound **2a** in $CDCl_3$



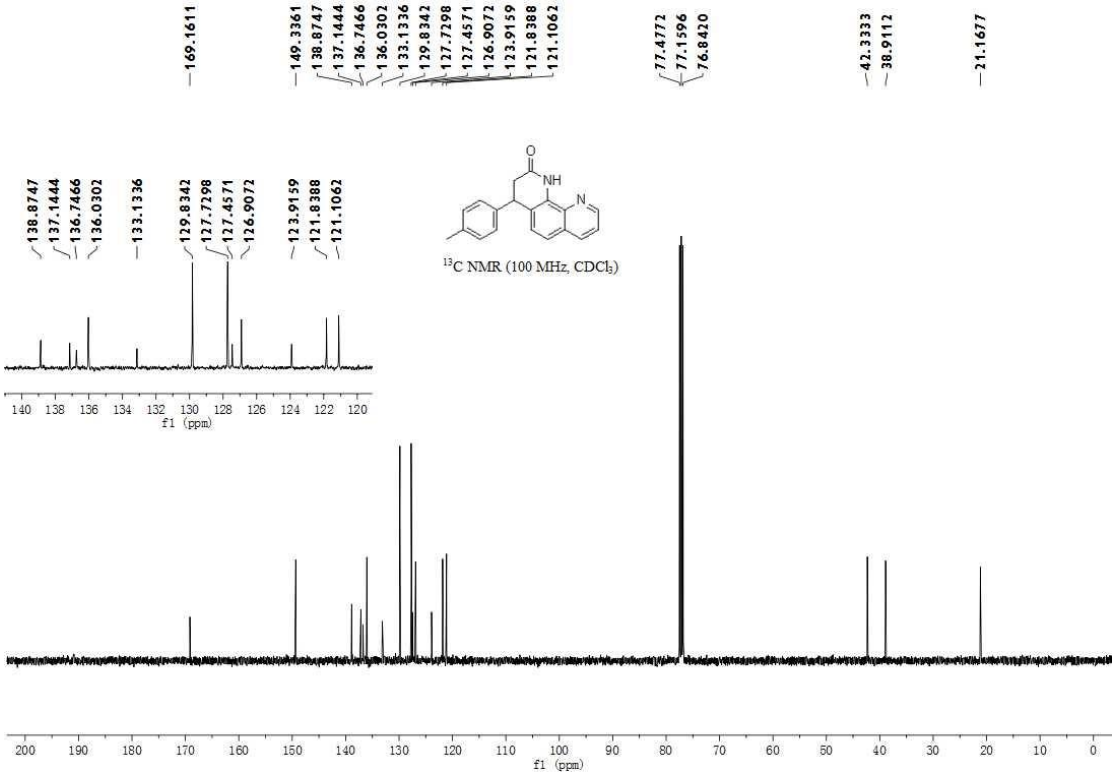
^{13}C NMR spectrum (100 MHz) of compound **2a** in $CDCl_3$



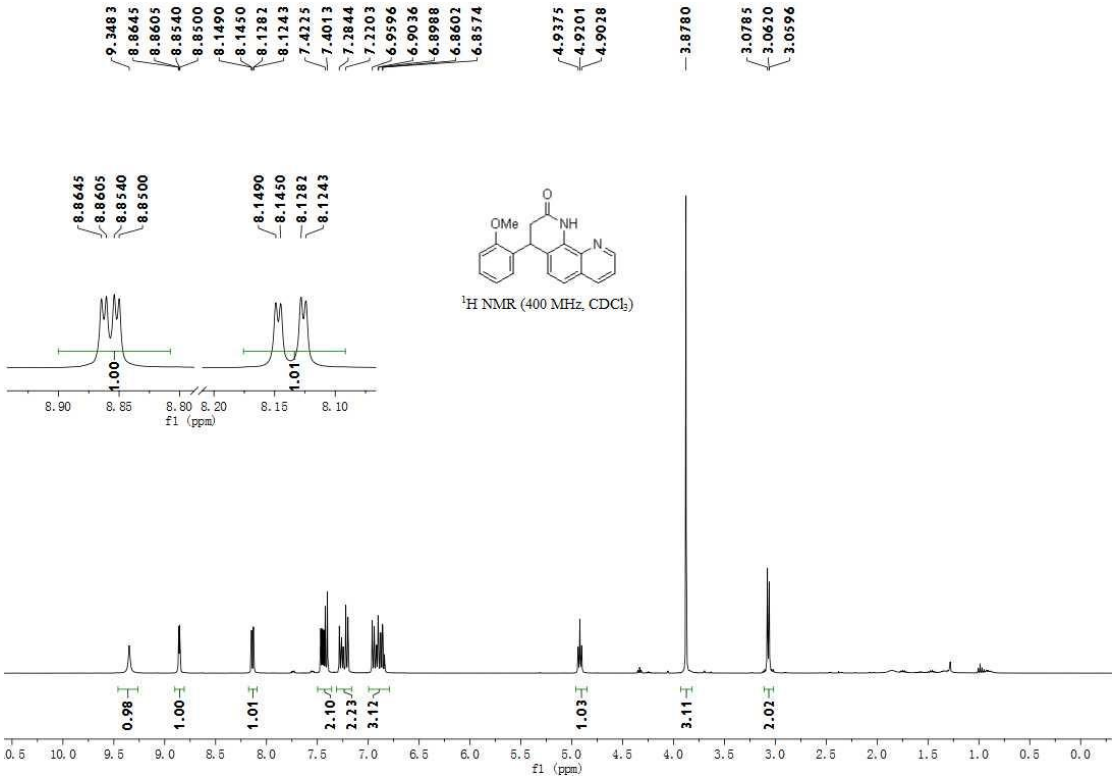
^{1}H NMR spectrum (400 MHz) of compound **2b** in $CDCl_3$



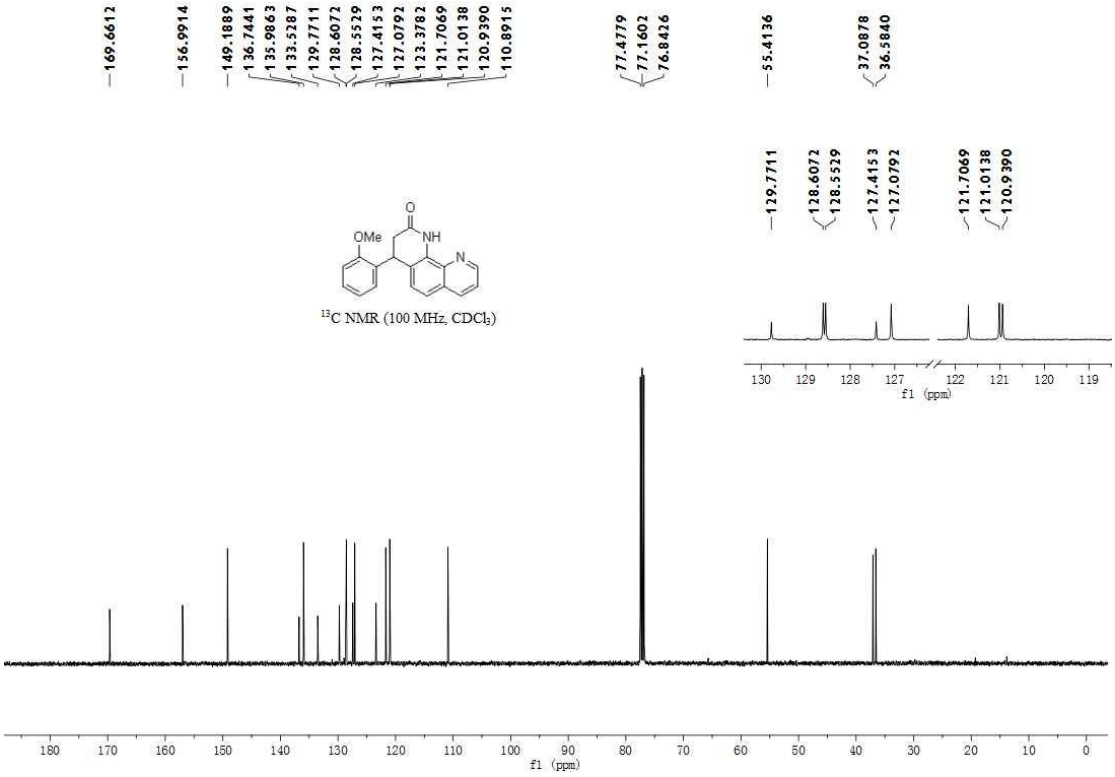
^{13}C NMR spectrum (100 MHz) of compound **2b** in $CDCl_3$



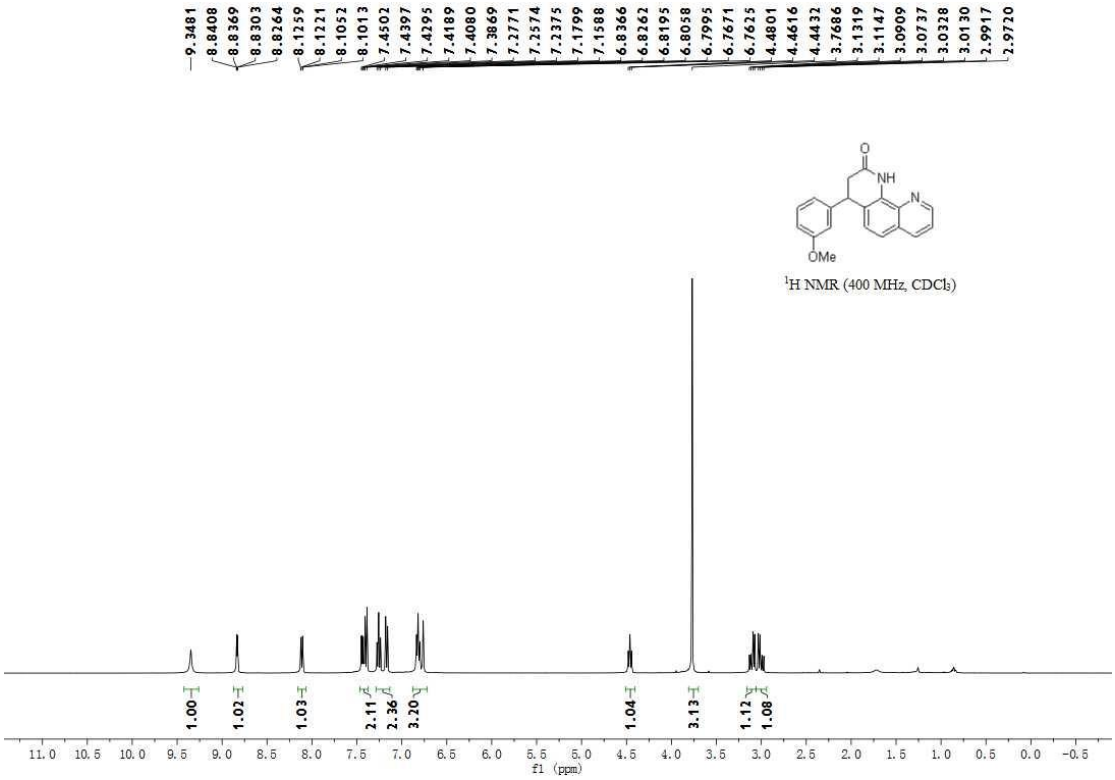
^{1}H NMR spectrum (400 MHz) of compound **2c** in $CDCl_3$



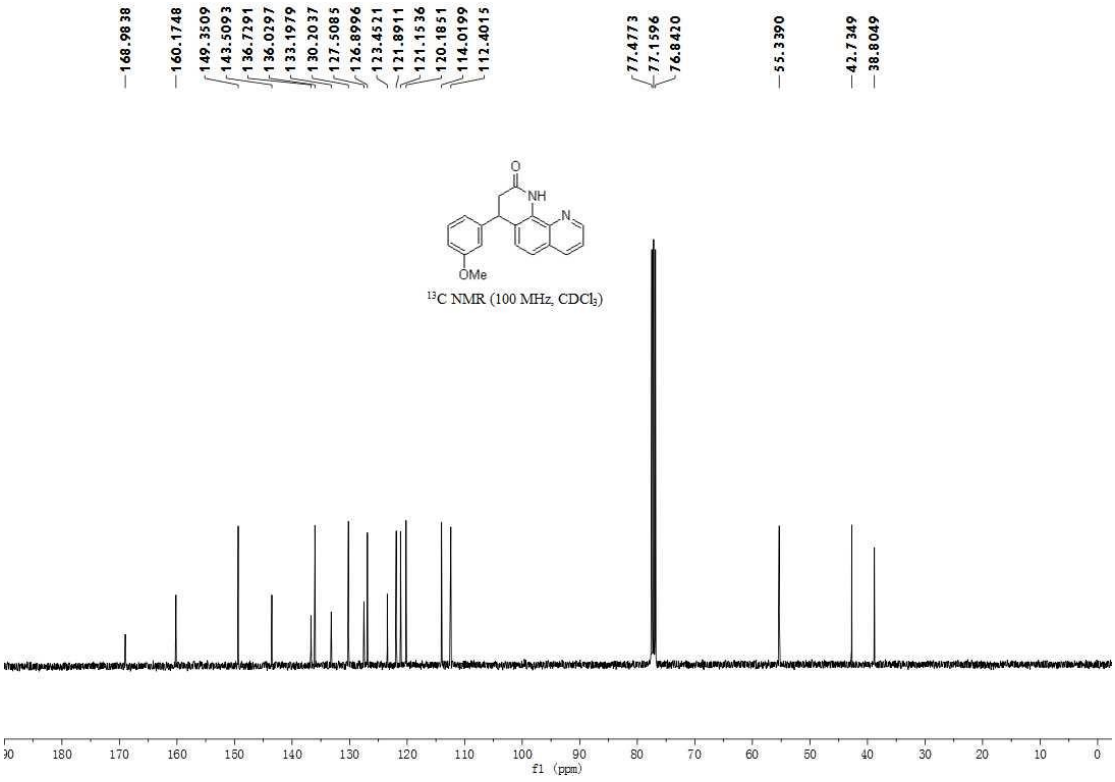
^{13}C NMR spectrum (100 MHz) of compound **2c** in $CDCl_3$



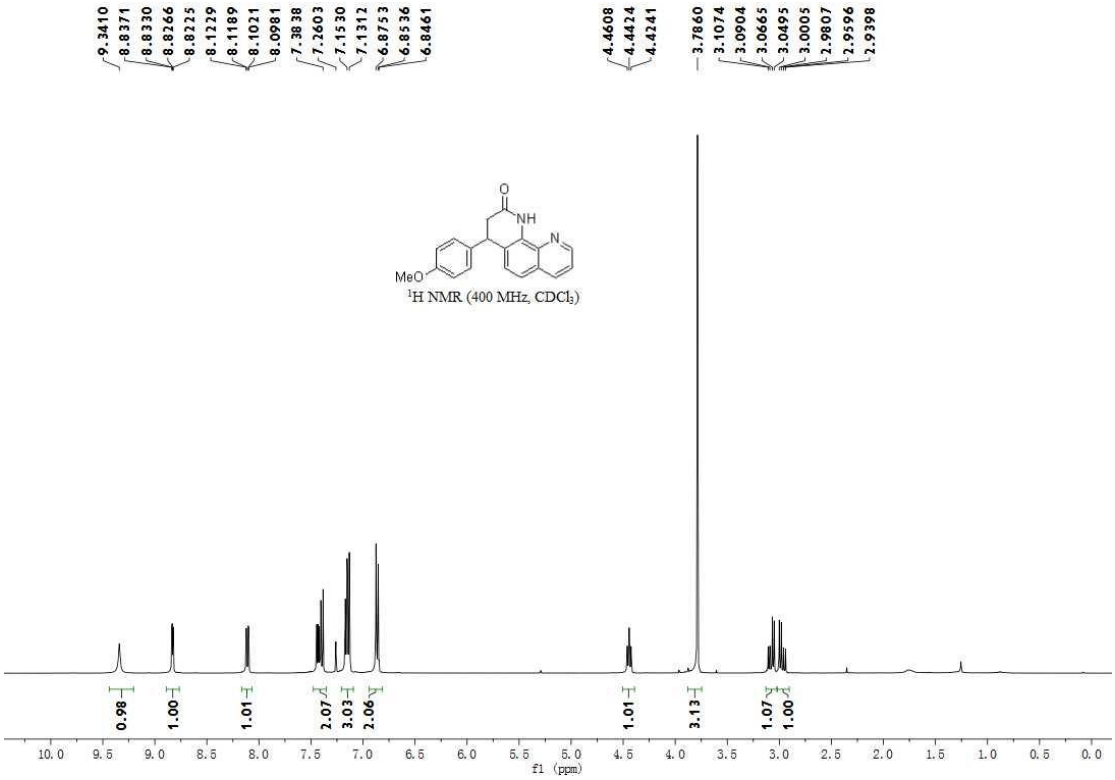
^{1}H NMR spectrum (400 MHz) of compound **2d** in $CDCl_3$



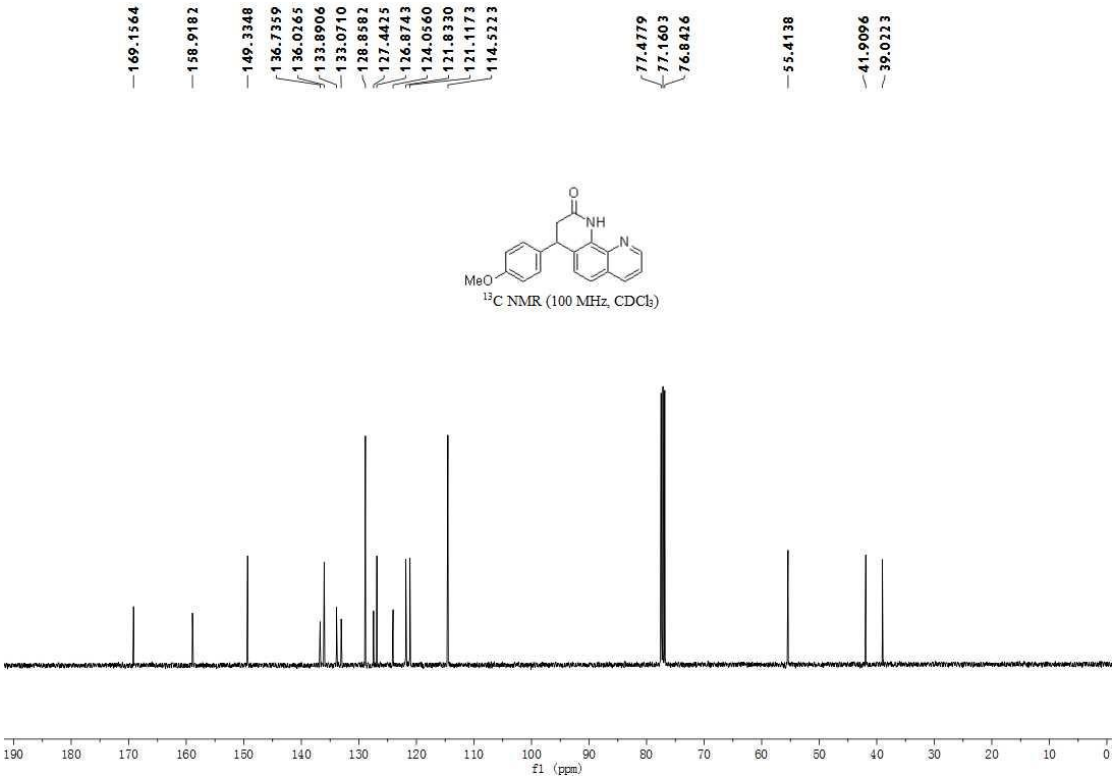
^{13}C NMR spectrum (100 MHz) of compound **2d** in $CDCl_3$



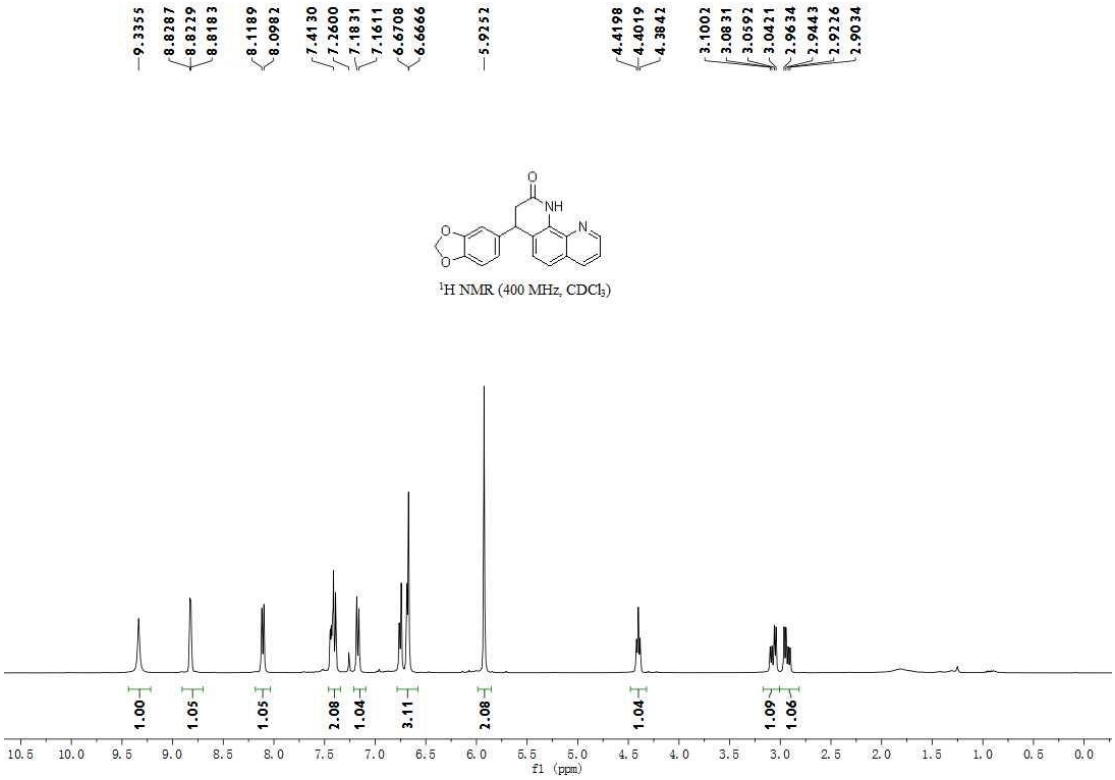
^{1}H NMR spectrum (400 MHz) of compound **2e** in $CDCl_3$



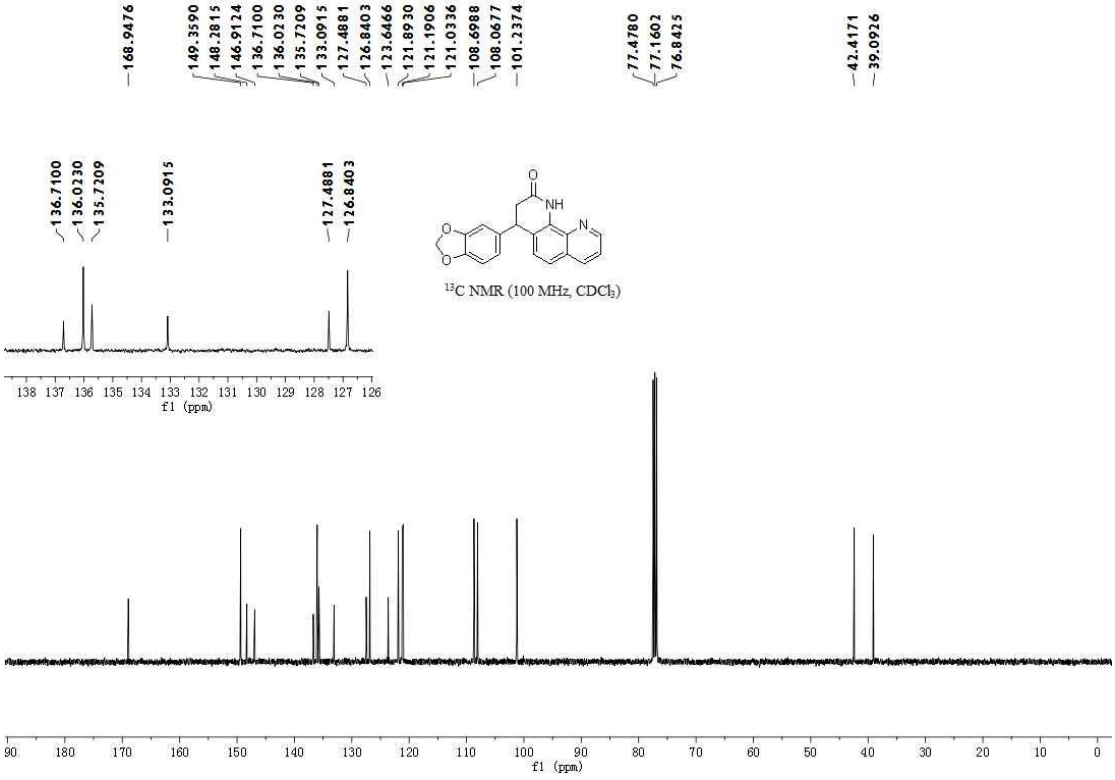
^{13}C NMR spectrum (100 MHz) of compound **2e** in $CDCl_3$



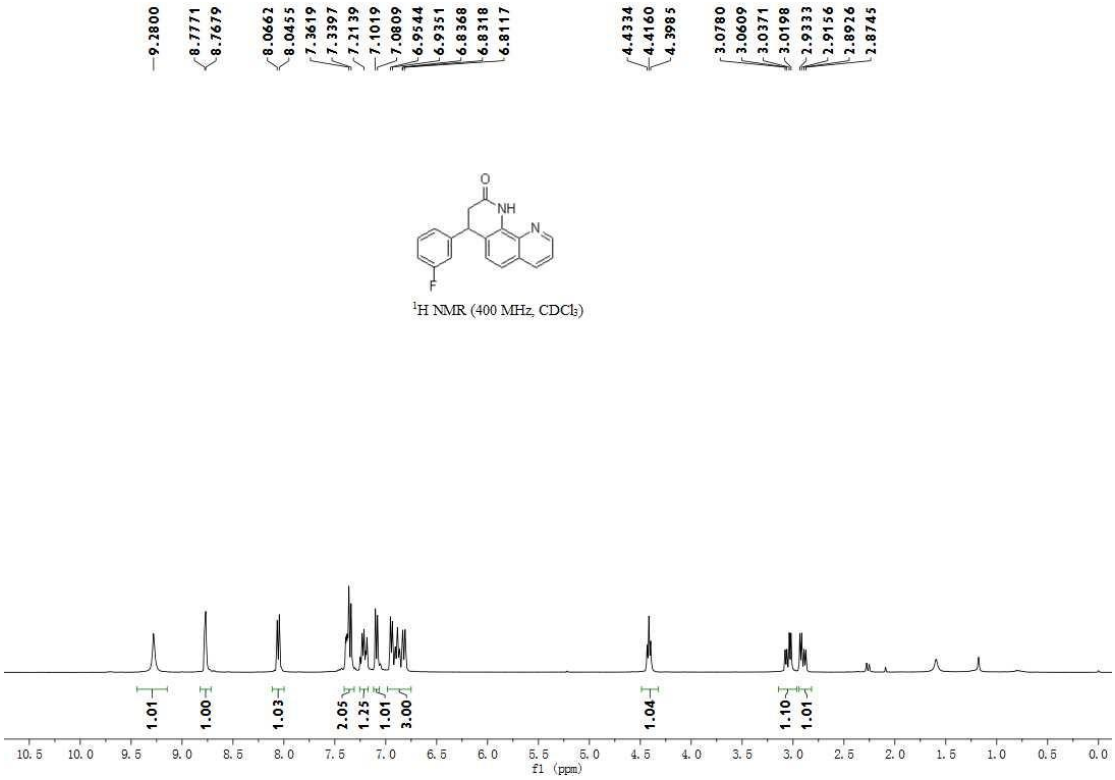
^{1}H NMR spectrum (400 MHz) of compound **2f** in $CDCl_3$



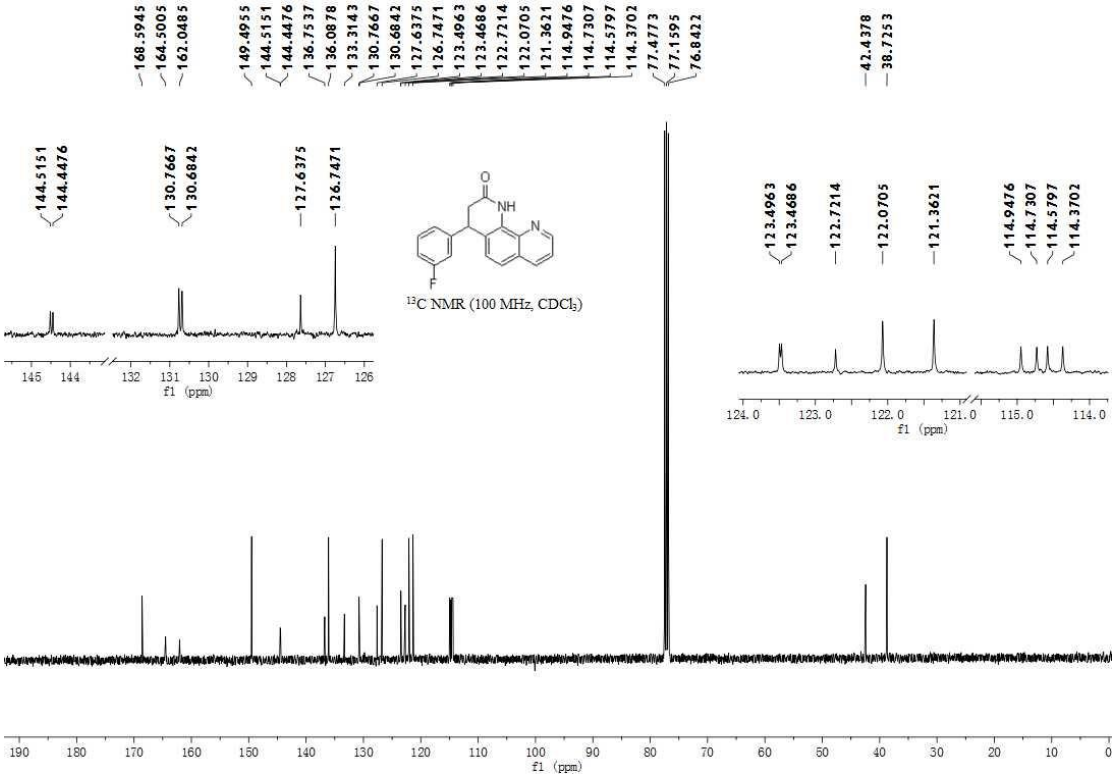
^{13}C NMR spectrum (100 MHz) of compound **2f** in $CDCl_3$



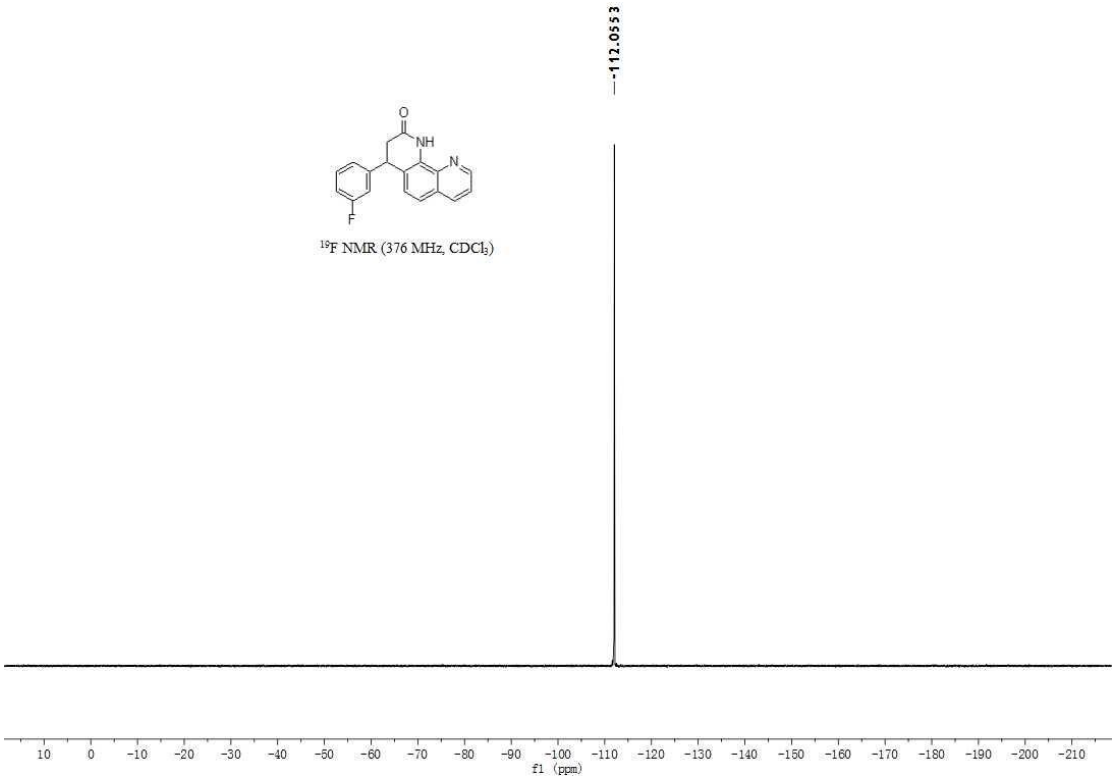
^{1}H NMR spectrum (400 MHz) of compound **2g** in $CDCl_3$



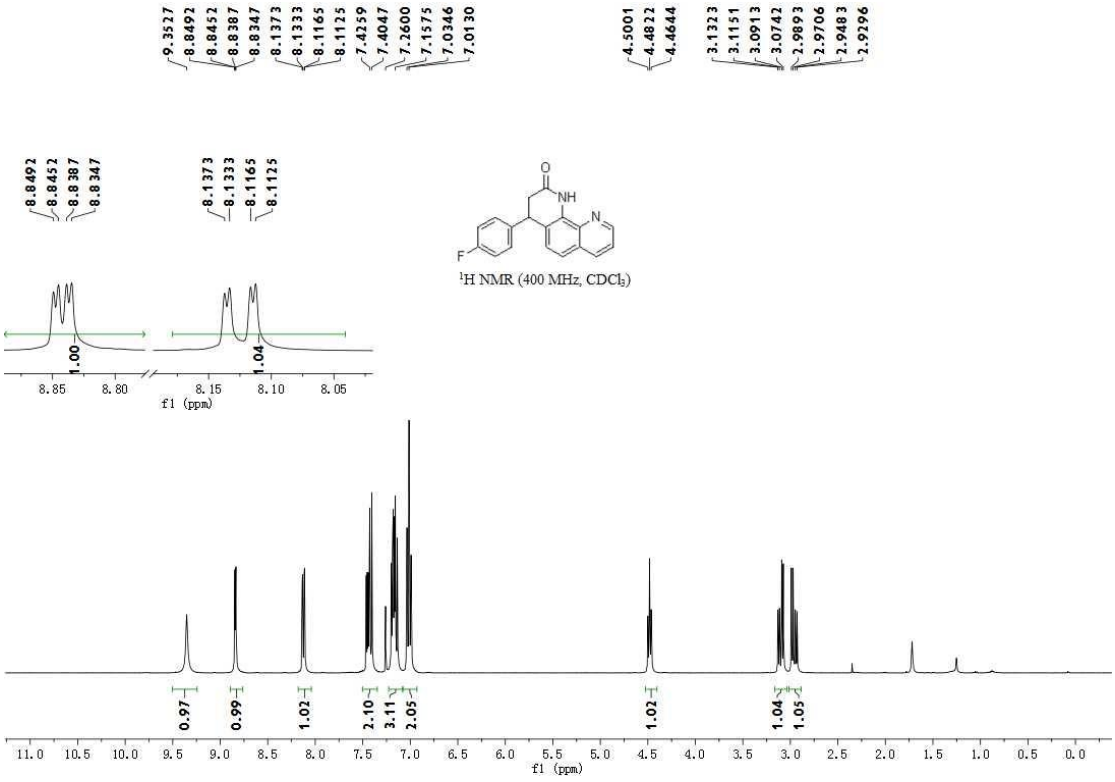
^{13}C NMR spectrum (100 MHz) of compound **2g** in $CDCl_3$



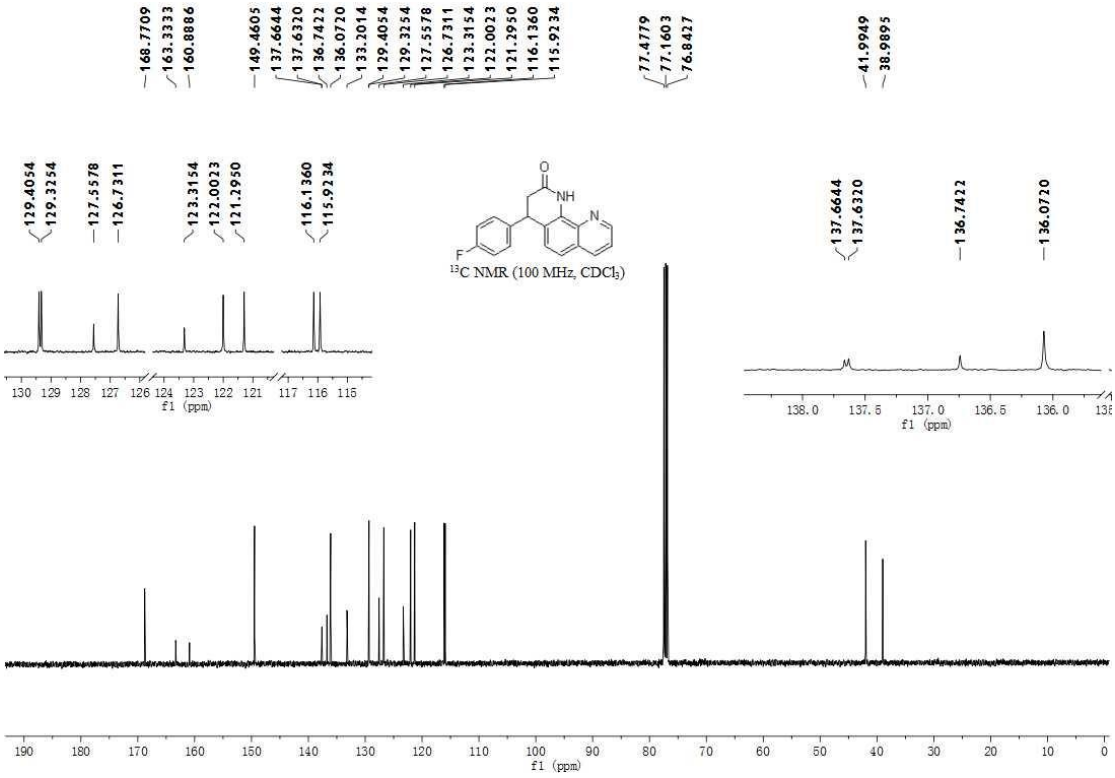
^{19}F NMR spectrum (376 MHz) of compound **2g** in $CDCl_3$



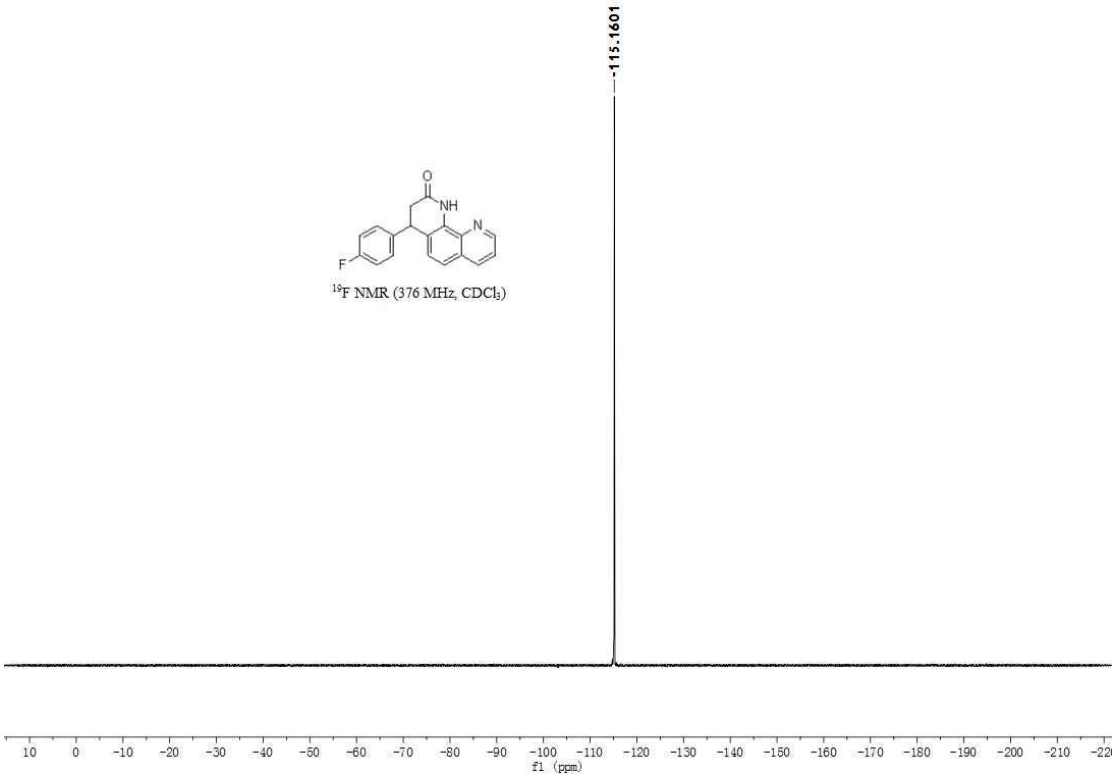
^{1}H NMR spectrum (400 MHz) of compound **2h** in $CDCl_3$



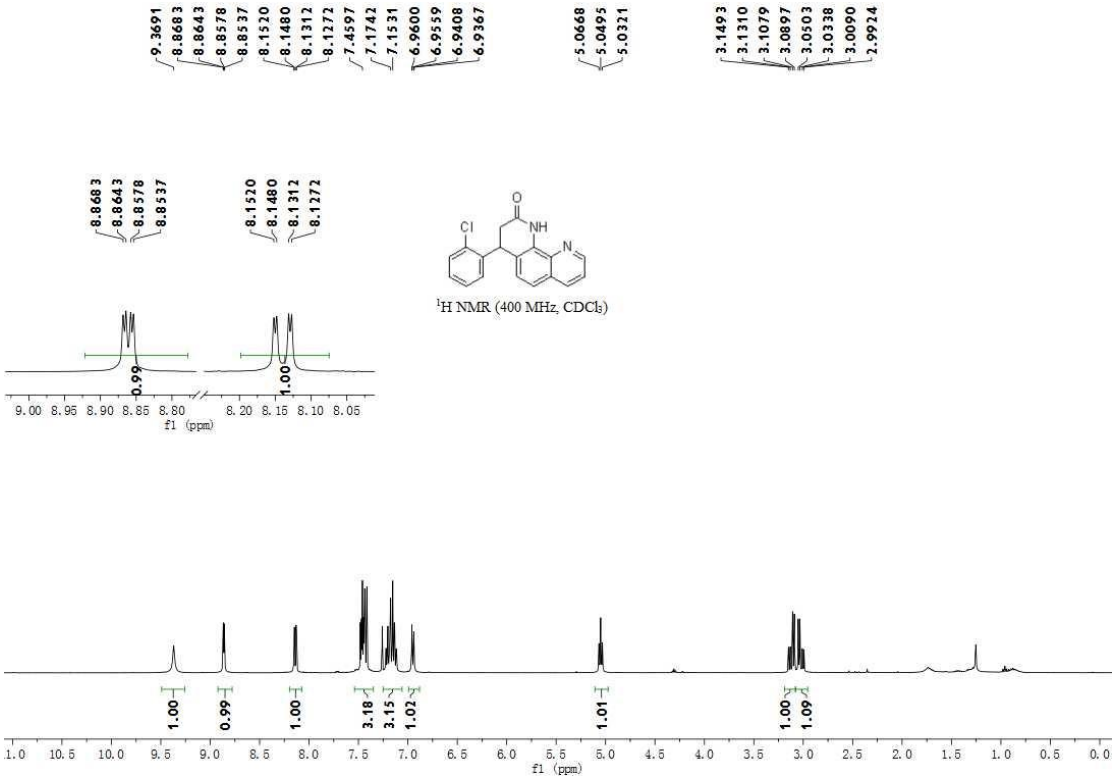
^{13}C NMR spectrum (100 MHz) of compound **2h** in $CDCl_3$



^{19}F NMR spectrum (376 MHz) of compound **2h** in $CDCl_3$

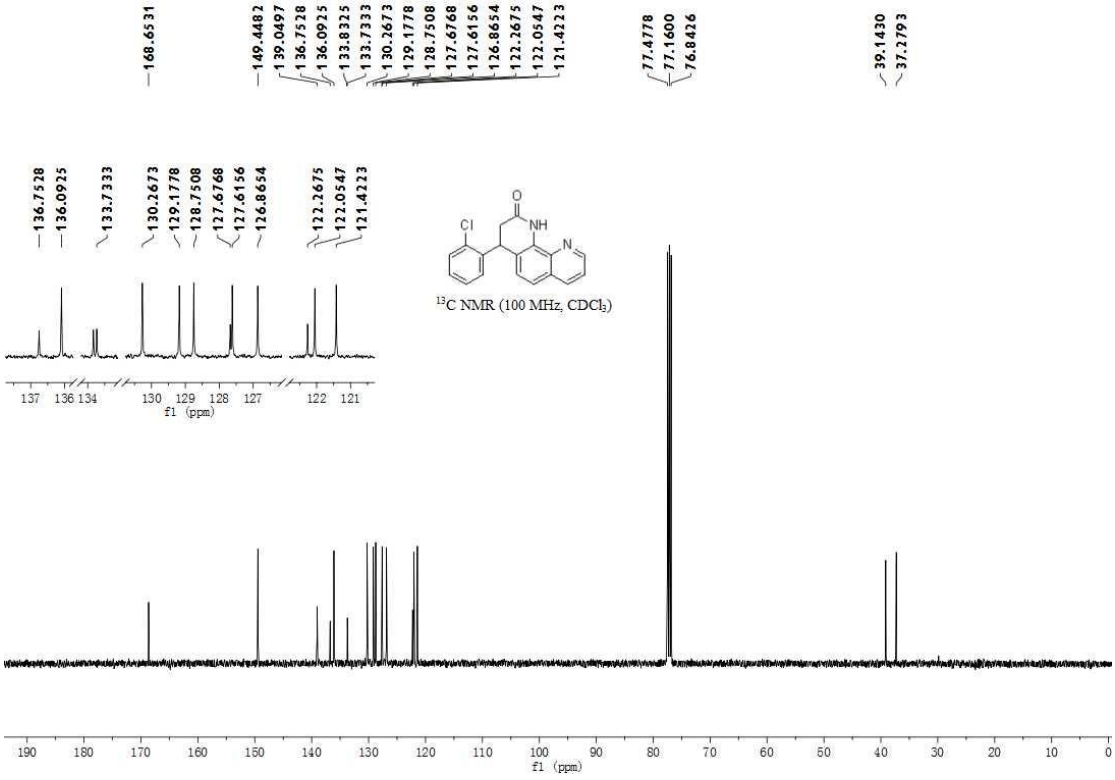


^{1}H NMR spectrum (400 MHz) of compound **2i** in $CDCl_3$



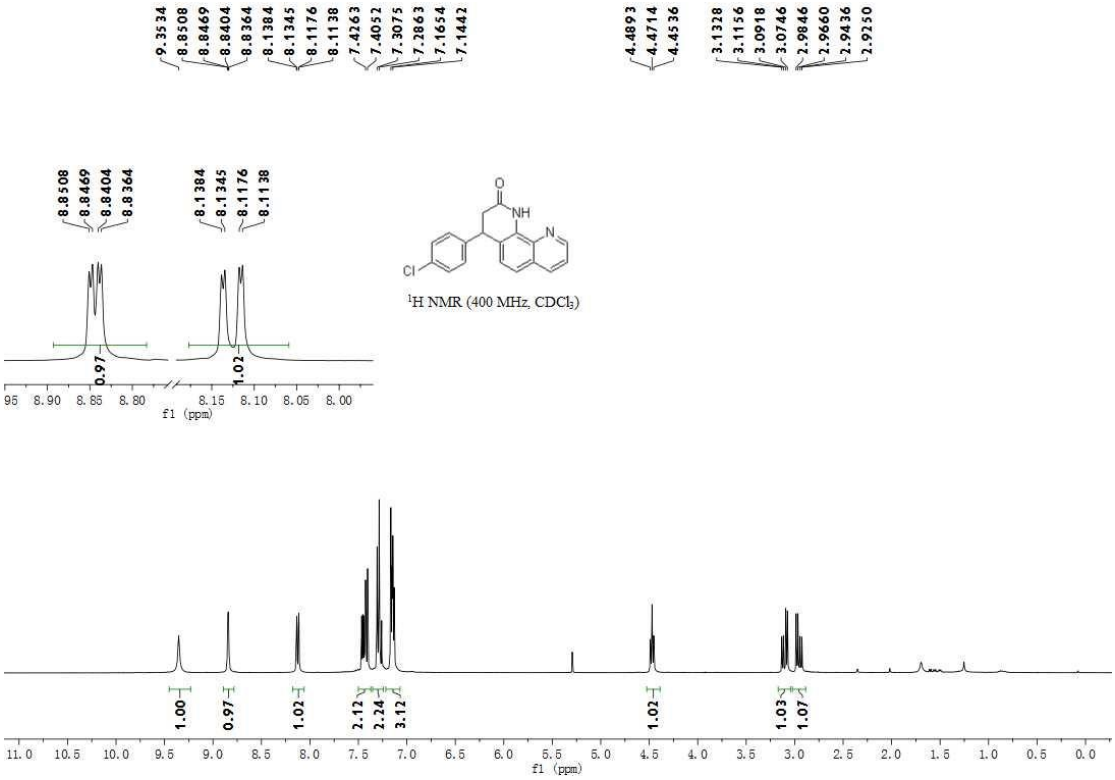
^{1}H NMR (400 MHz, $CDCl_3$)

^{13}C NMR spectrum (100 MHz) of compound **2i** in $CDCl_3$

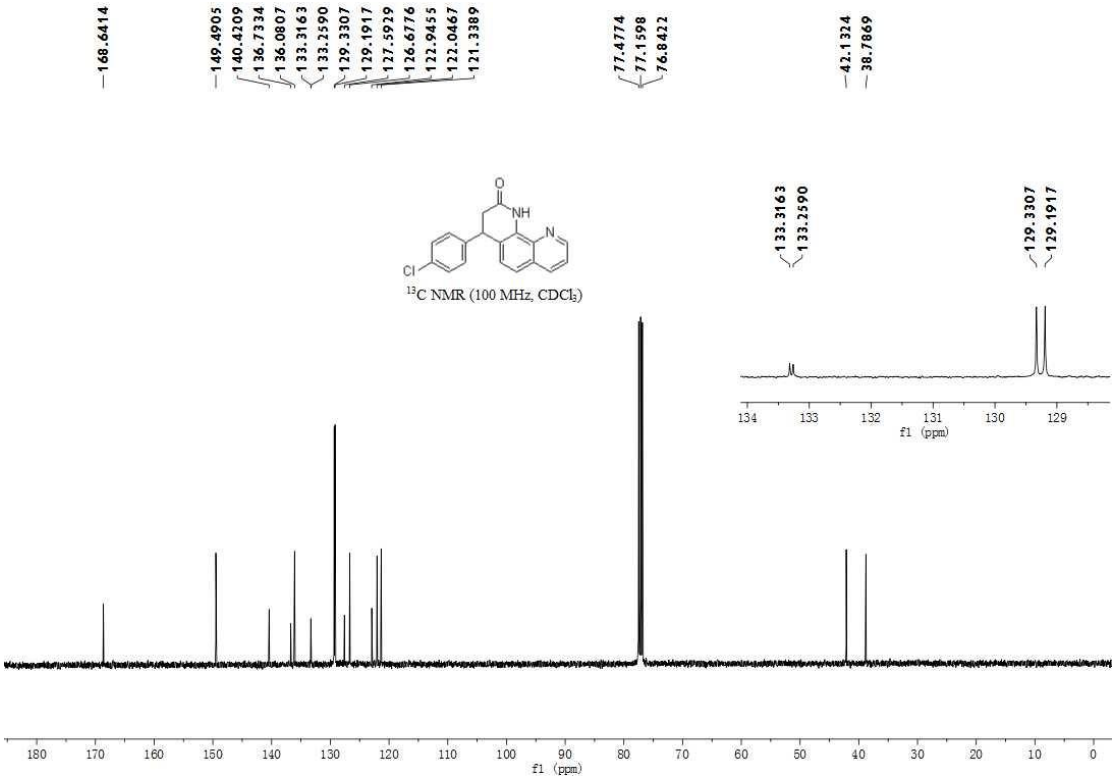


^{13}C NMR (100 MHz, $CDCl_3$)

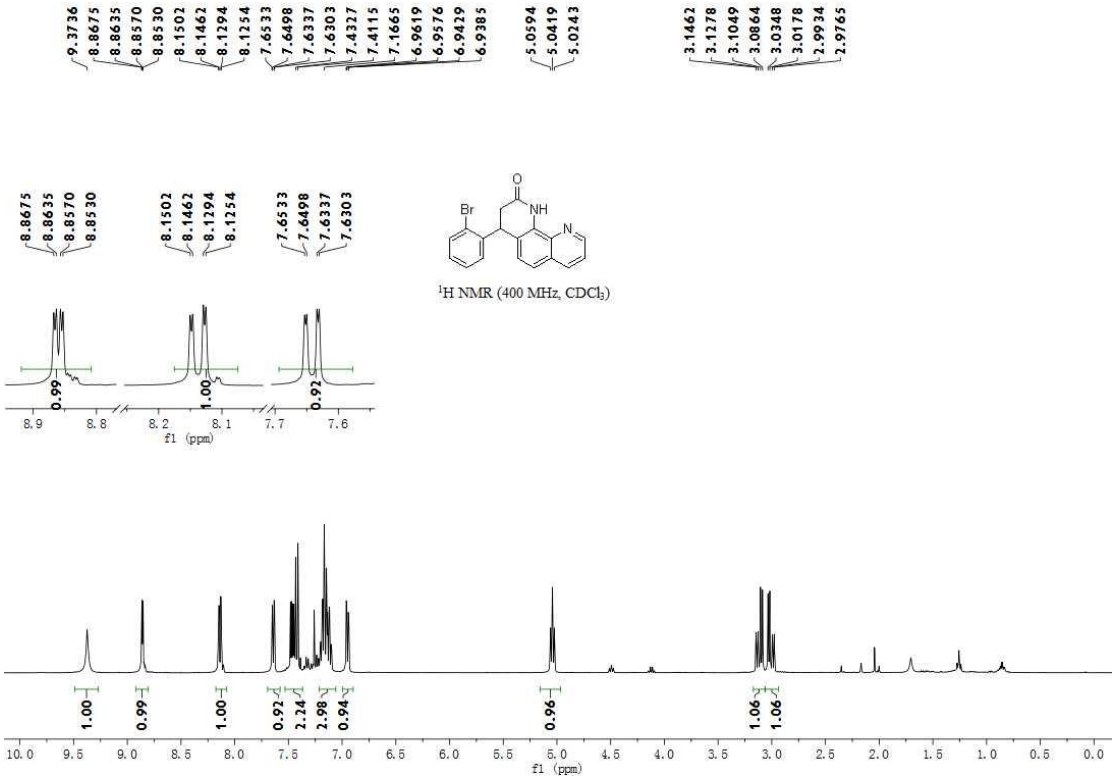
^{1}H NMR spectrum (400 MHz) of compound **2j** in $CDCl_3$



^{13}C NMR spectrum (100 MHz) of compound **2j** in $CDCl_3$

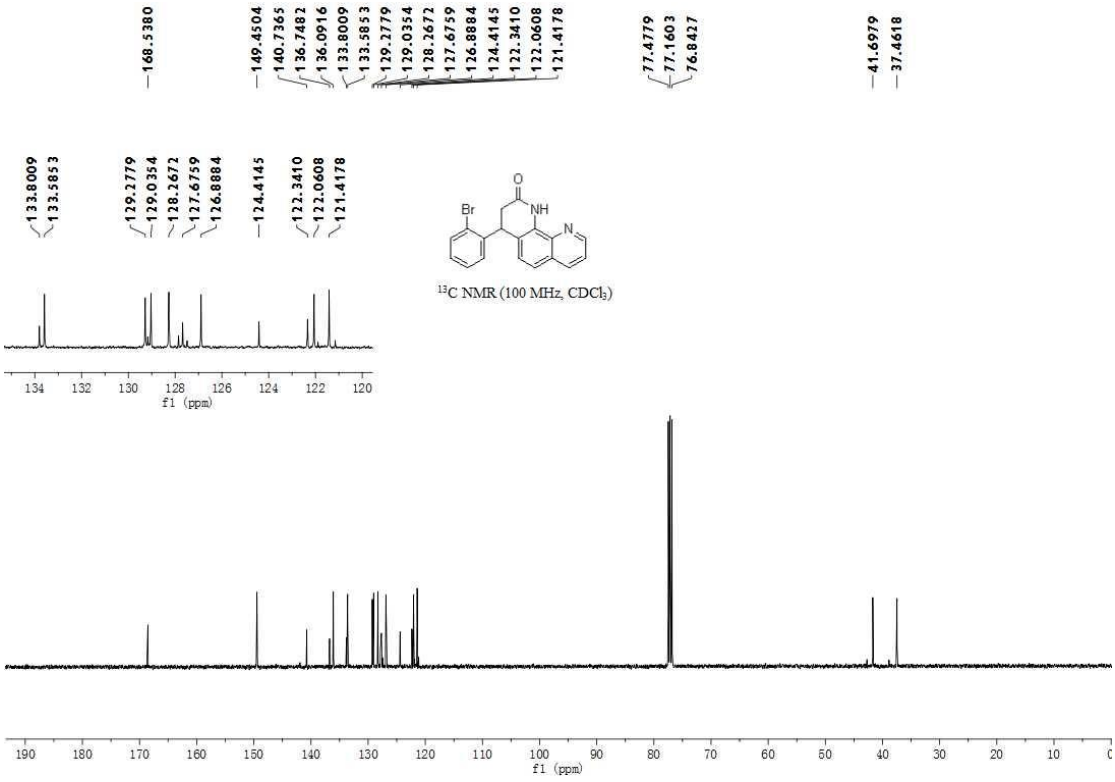


^{1}H NMR spectrum (400 MHz) of compound **2k** in $CDCl_3$



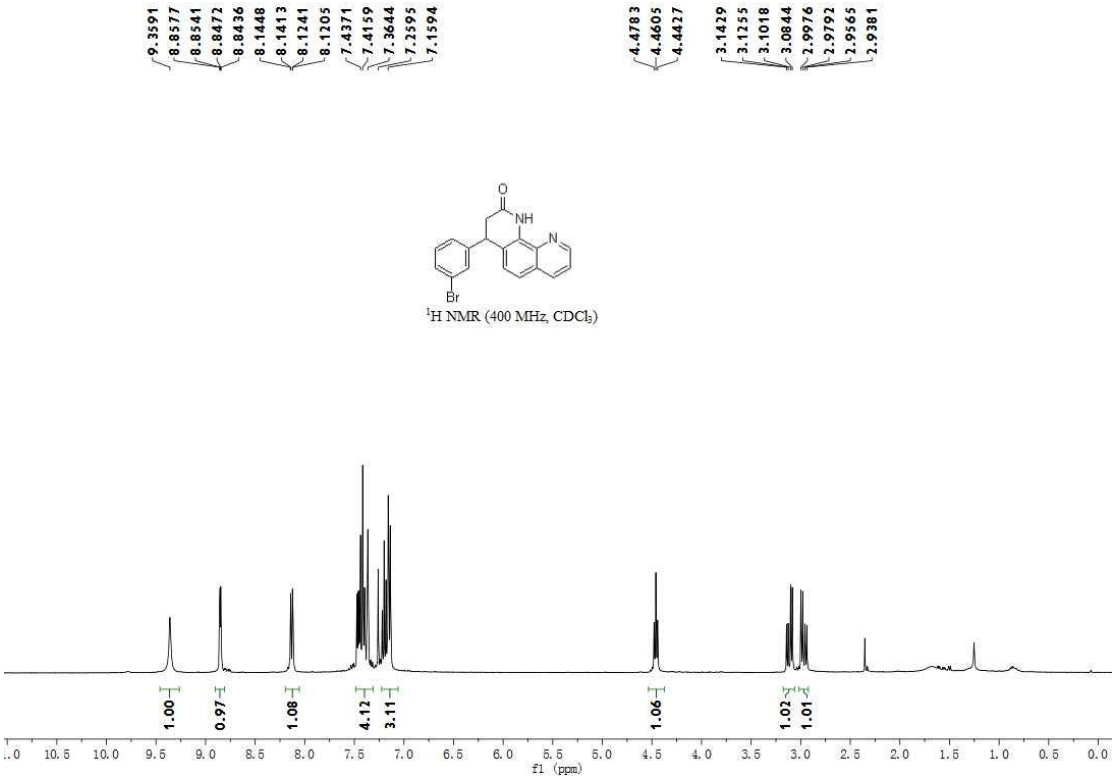
^{1}H NMR (400 MHz, $CDCl_3$)

^{13}C NMR spectrum (100 MHz) of compound **2k** in $CDCl_3$

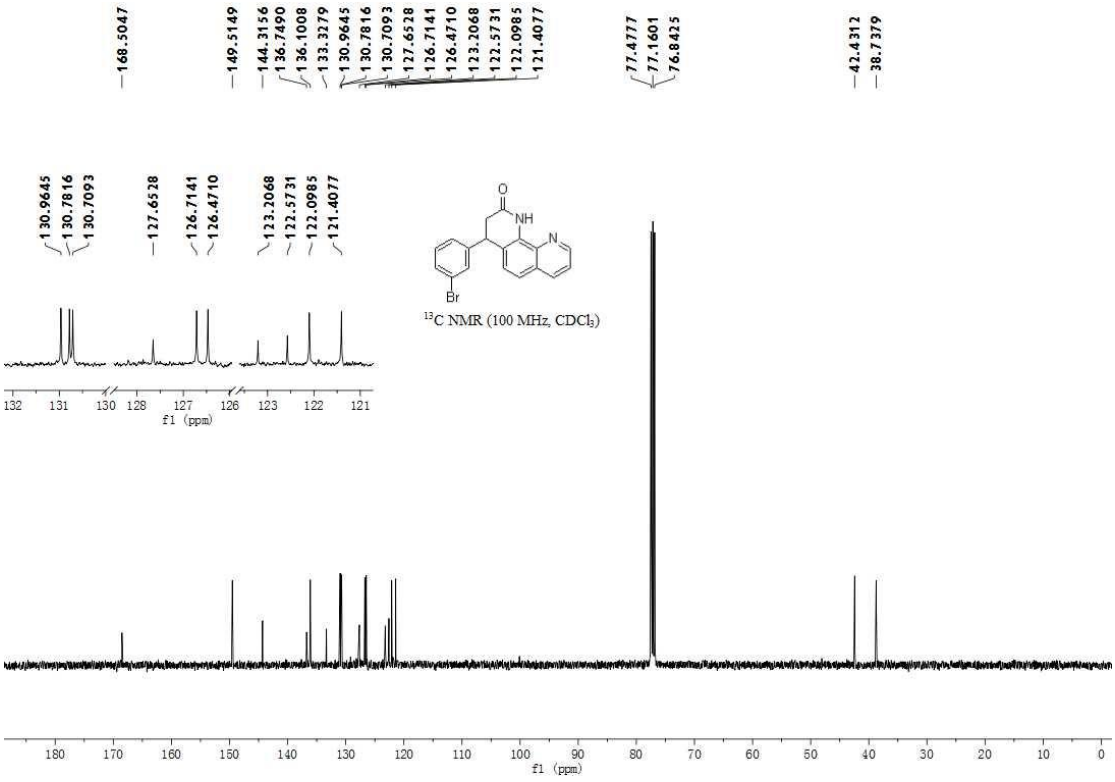


^{13}C NMR (100 MHz, $CDCl_3$)

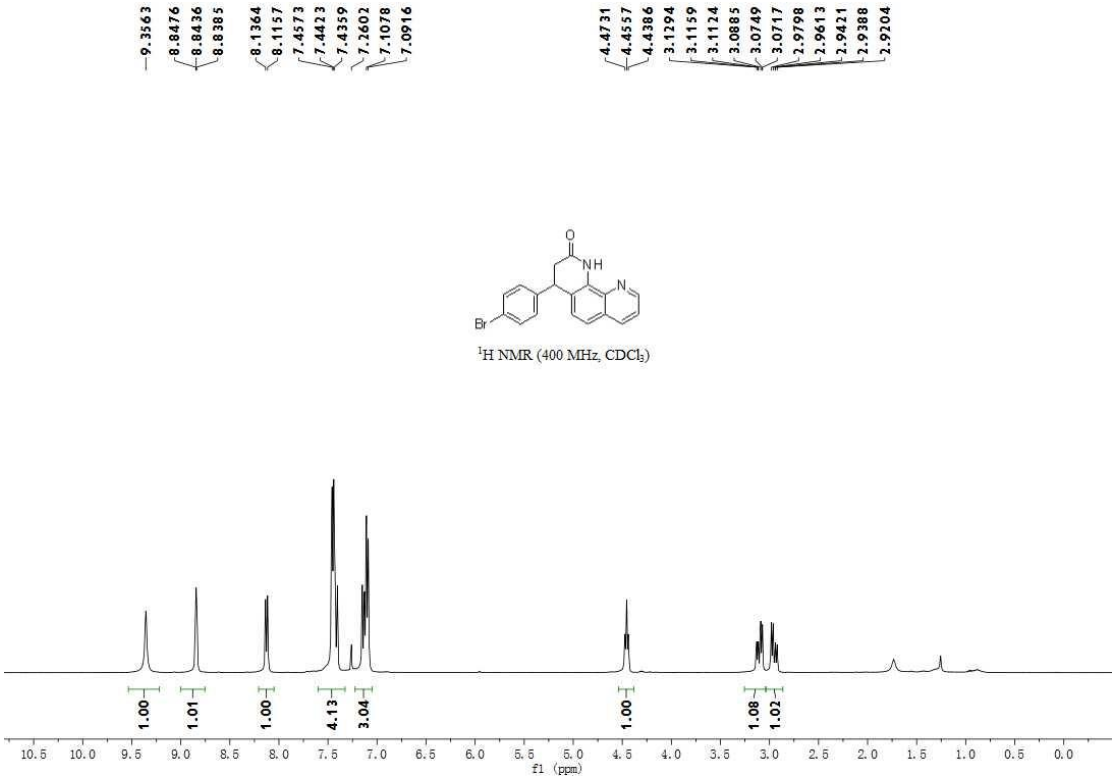
^{1}H NMR spectrum (400 MHz) of compound **2l** in $CDCl_3$



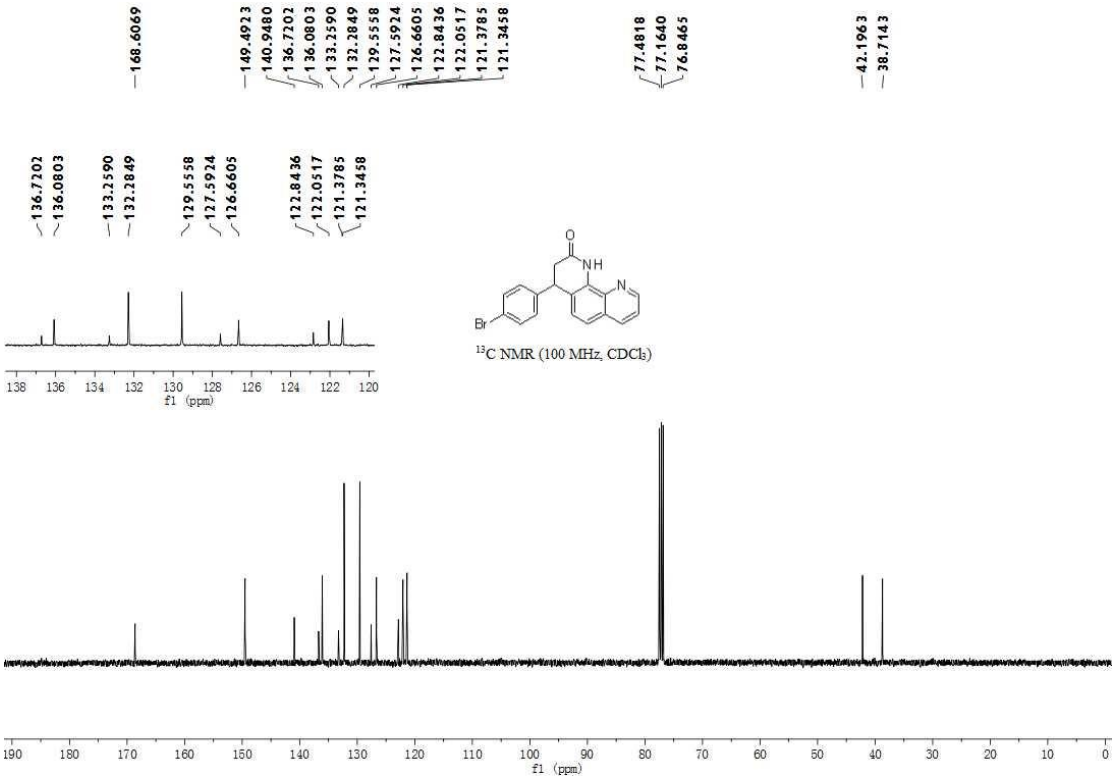
^{13}C NMR spectrum (100 MHz) of compound **2l** in $CDCl_3$



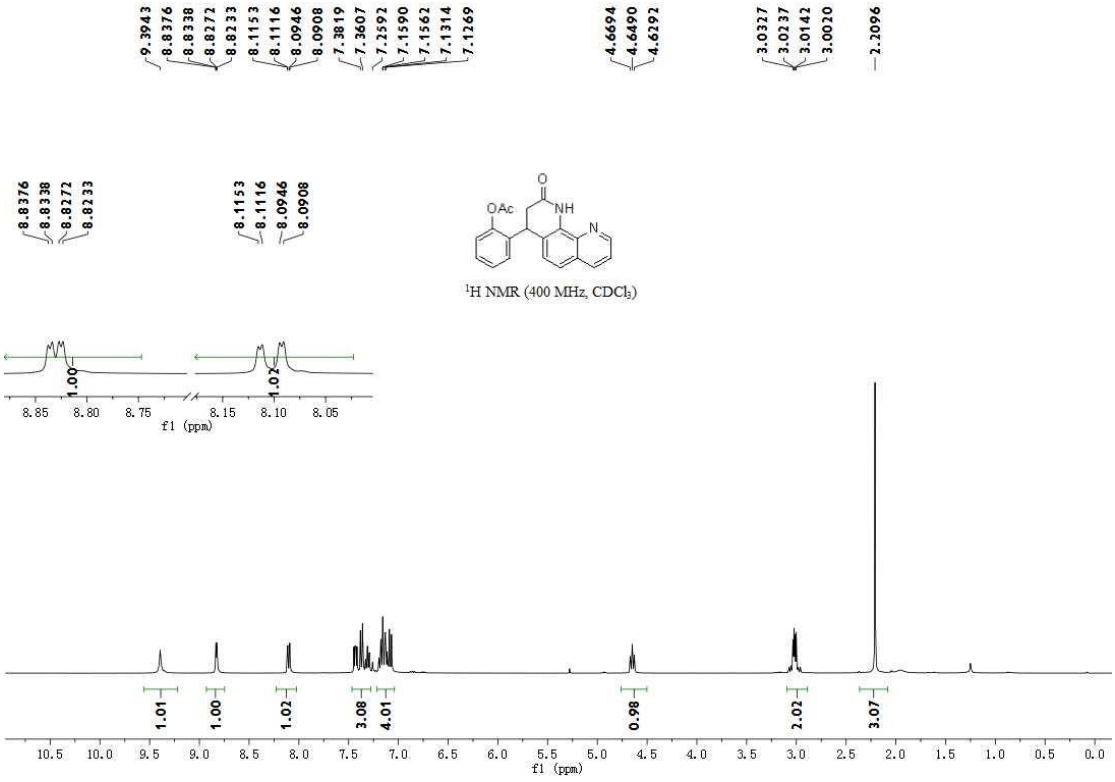
^{1}H NMR spectrum (400 MHz) of compound **2m** in $CDCl_3$



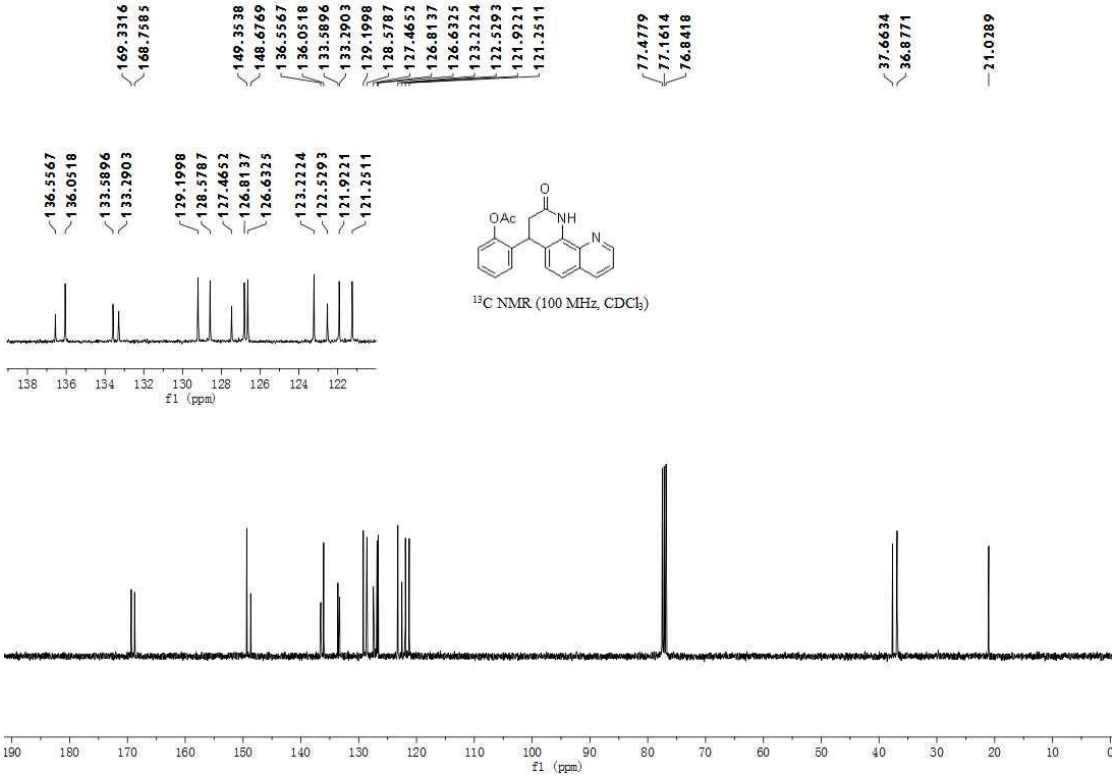
^{13}C NMR spectrum (100 MHz) of compound **2m** in $CDCl_3$



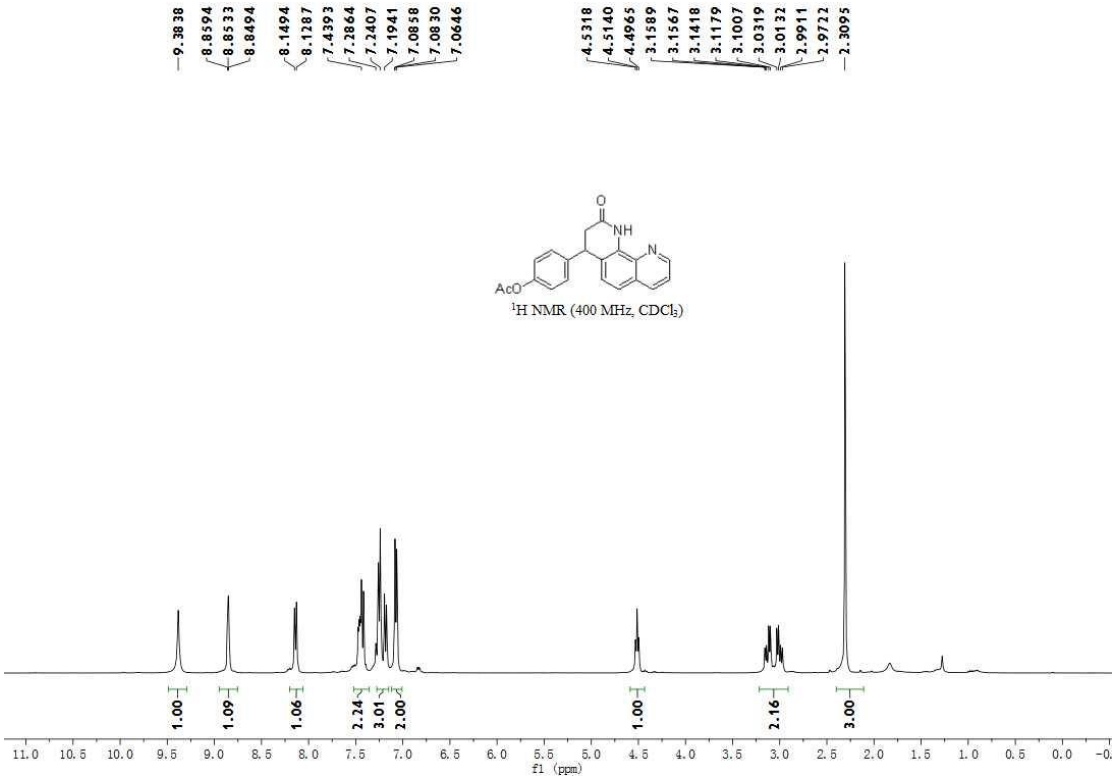
^{1}H NMR spectrum (400 MHz) of compound **2n** in $CDCl_3$



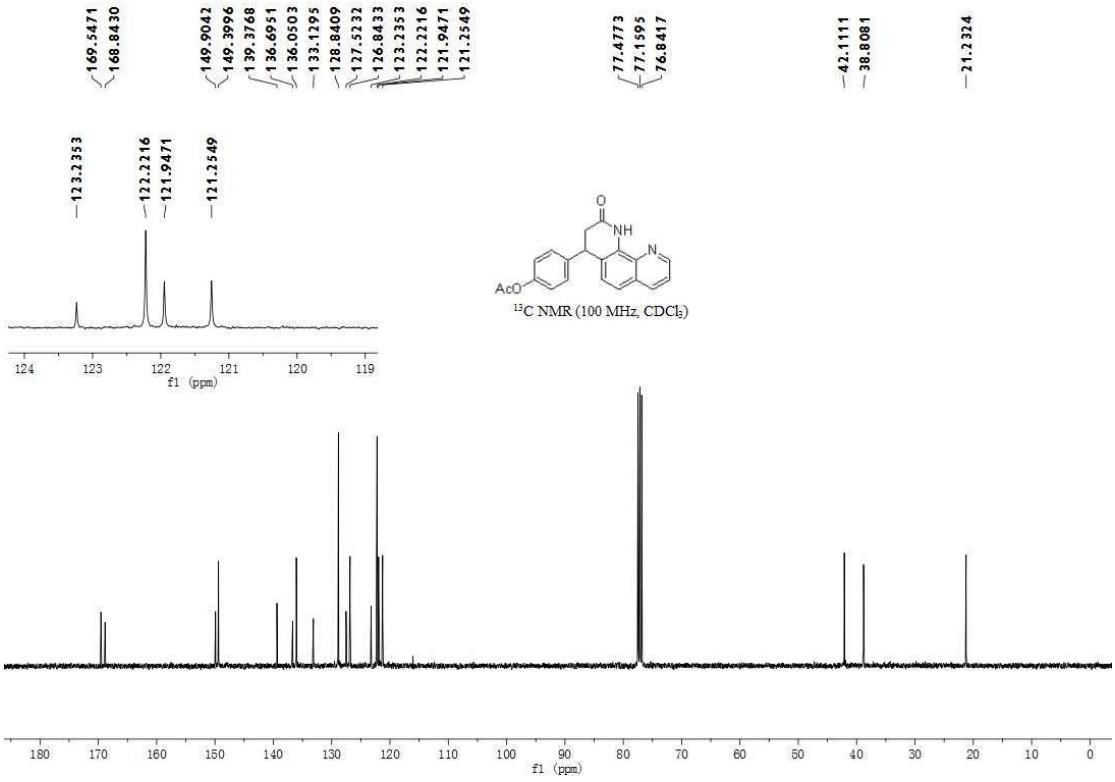
^{13}C NMR spectrum (100 MHz) of compound **2n** in $CDCl_3$



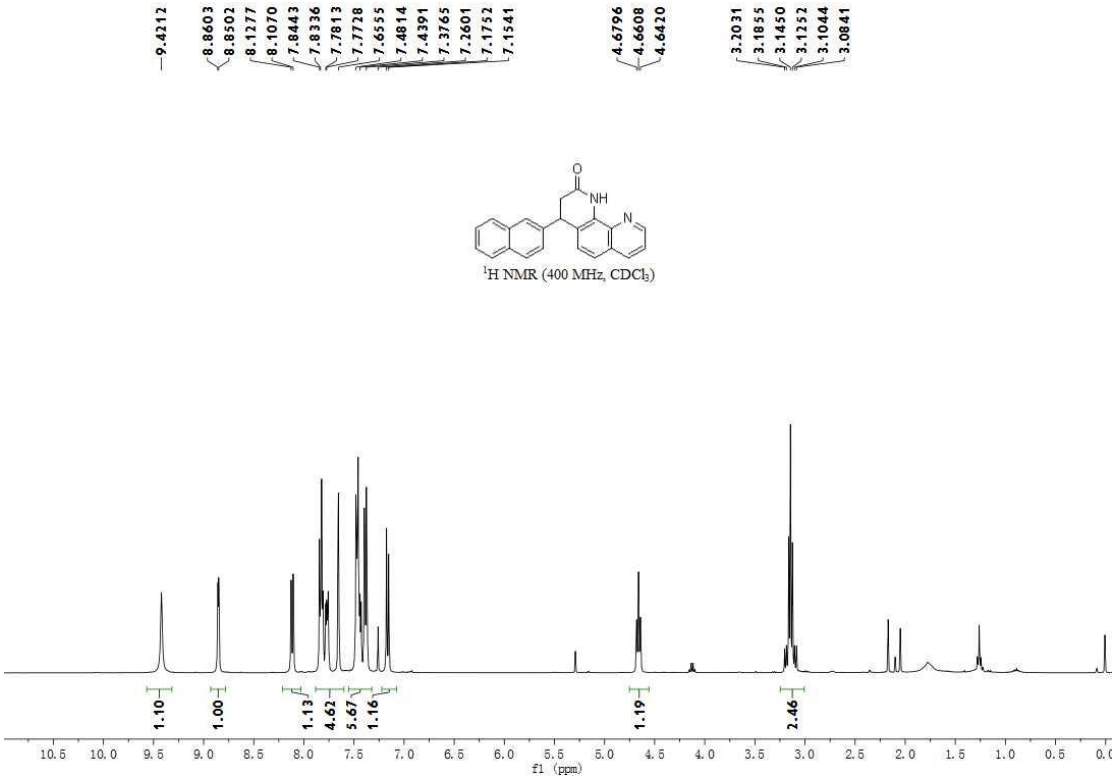
^{1}H NMR spectrum (400 MHz) of compound **2o** in $CDCl_3$



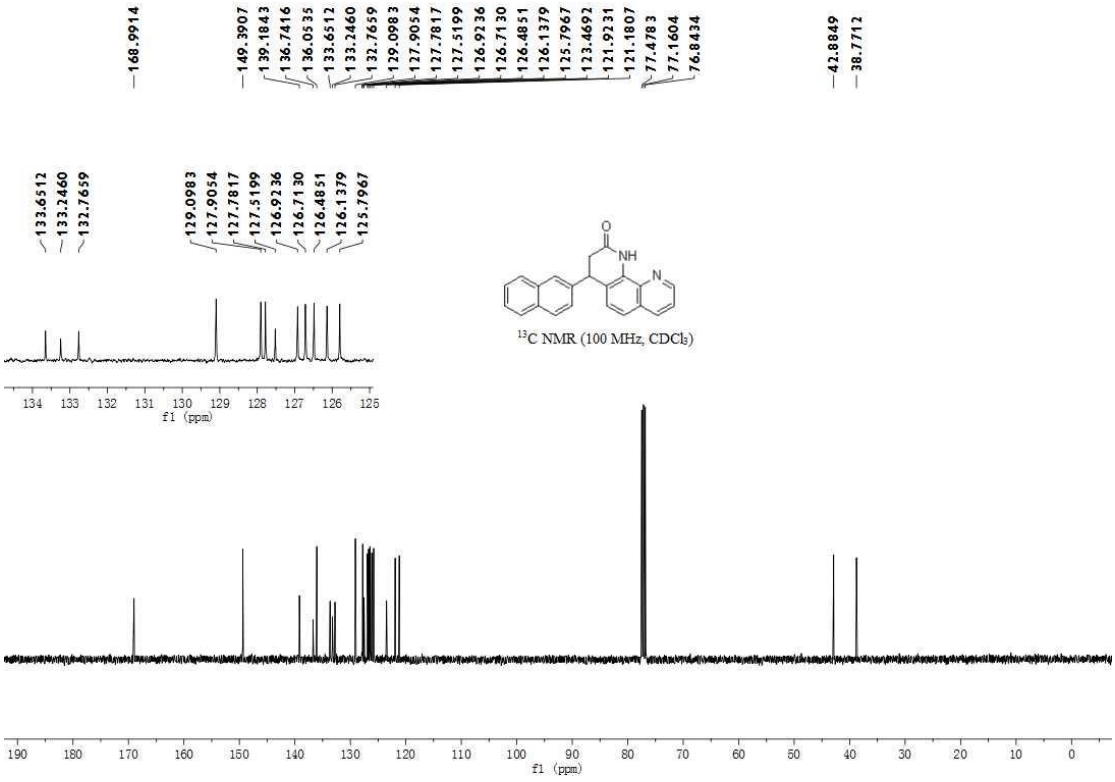
^{13}C NMR spectrum (100 MHz) of compound **2o** in $CDCl_3$



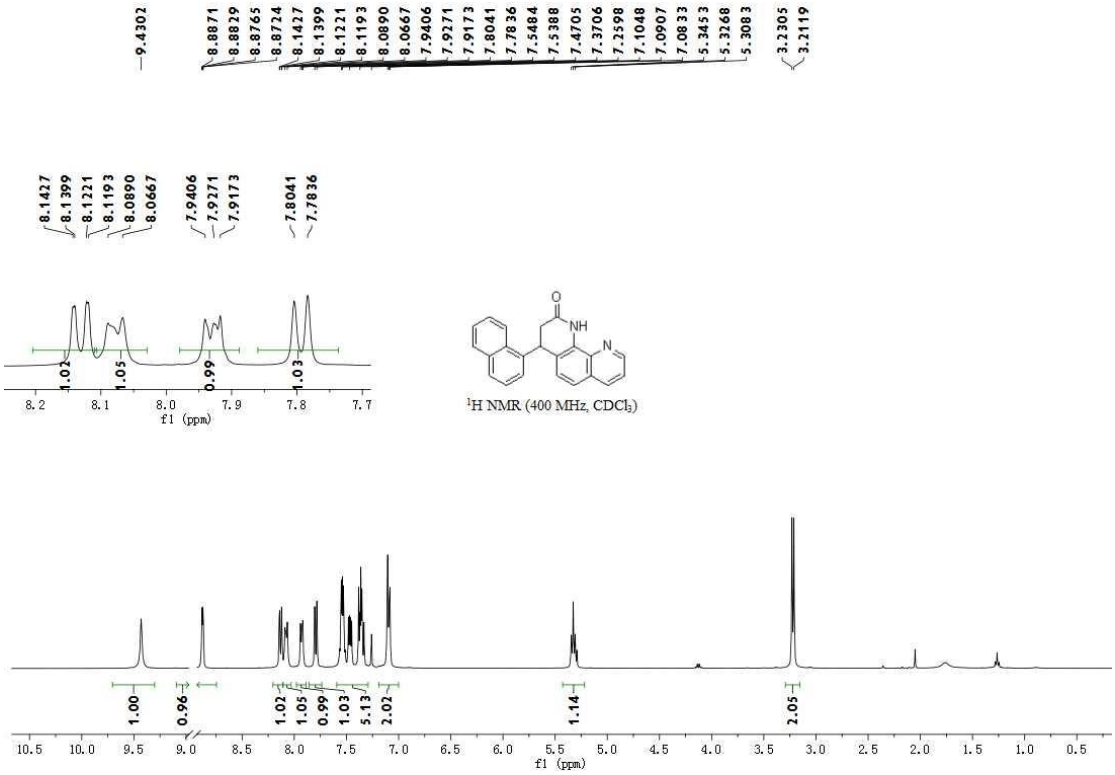
^{1}H NMR spectrum (400 MHz) of compound **2p** in $CDCl_3$



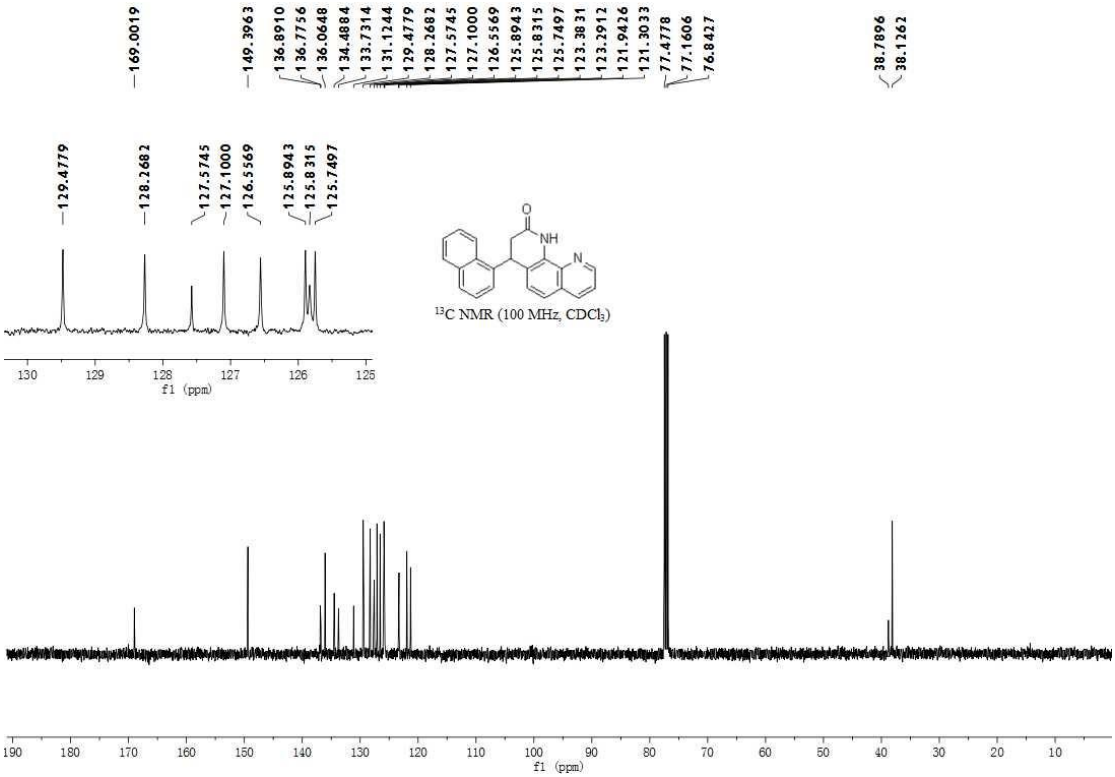
^{13}C NMR spectrum (100 MHz) of compound **2p** in $CDCl_3$



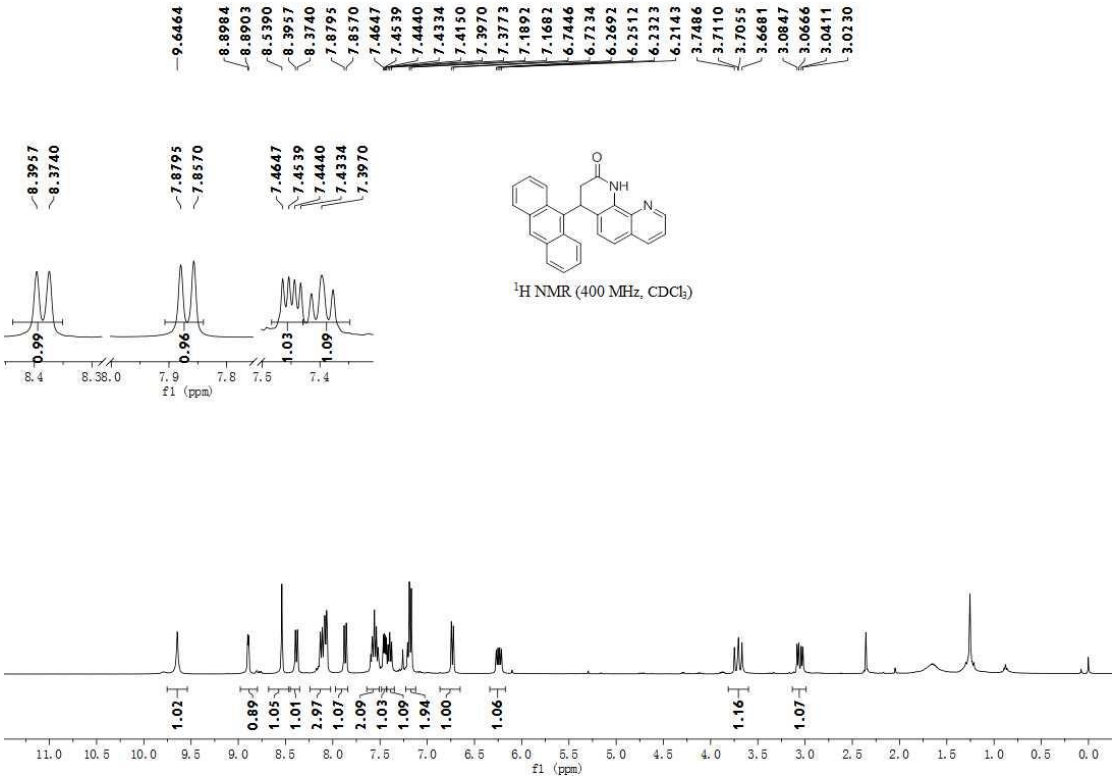
^{1}H NMR spectrum (400 MHz) of compound **2q** in $CDCl_3$



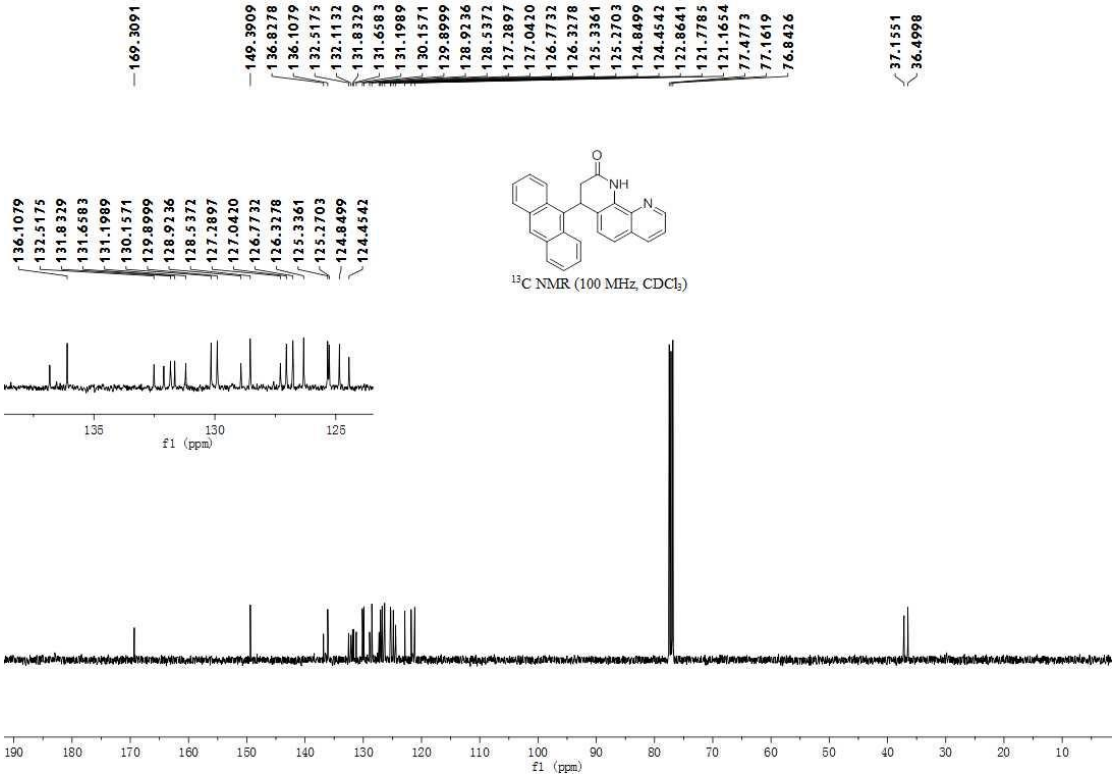
^{13}C NMR spectrum (100 MHz) of compound **2q** in $CDCl_3$



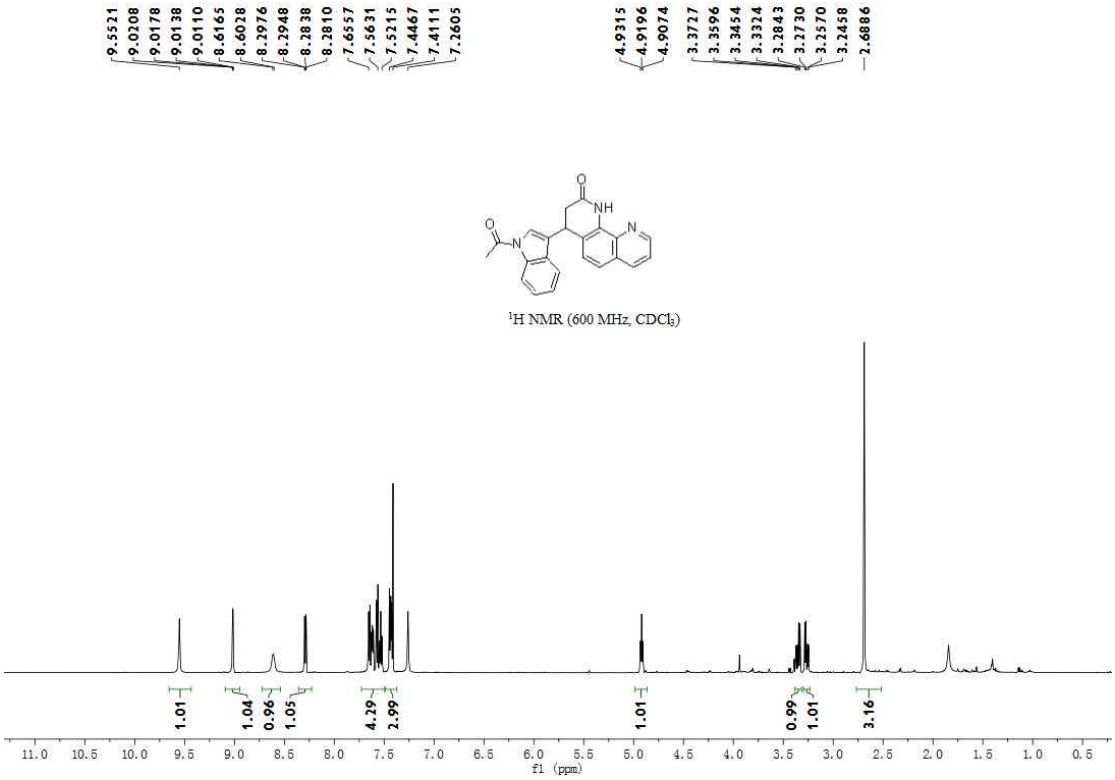
^{1}H NMR spectrum (400 MHz) of compound **2r** in $CDCl_3$



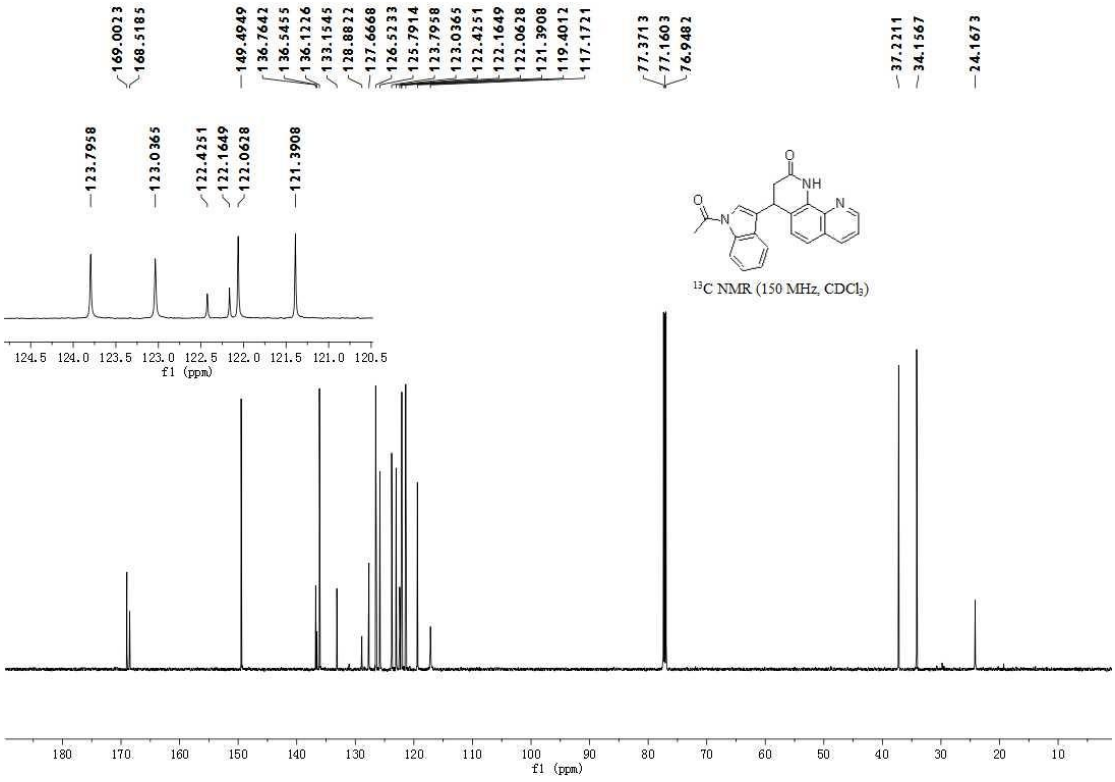
^{13}C NMR spectrum (100 MHz) of compound **2r** in $CDCl_3$



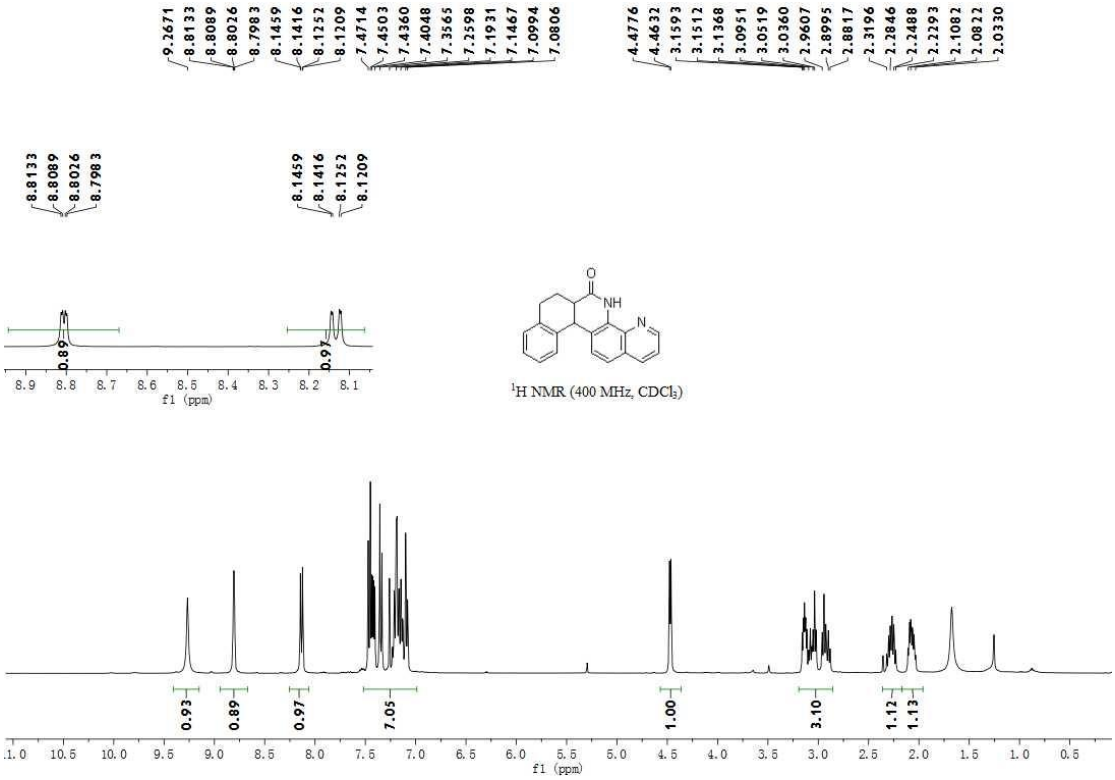
^{1}H NMR spectrum (400 MHz) of compound **2s** in $CDCl_3$



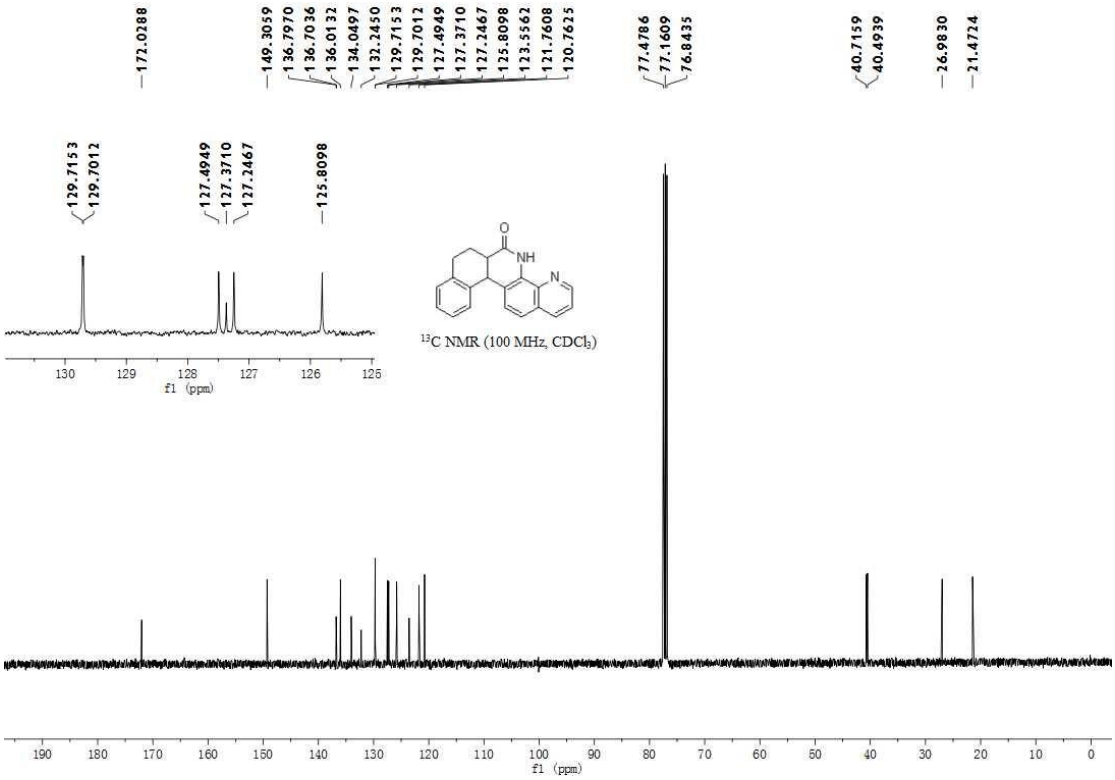
^{13}C NMR spectrum (100 MHz) of compound **2s** in $CDCl_3$



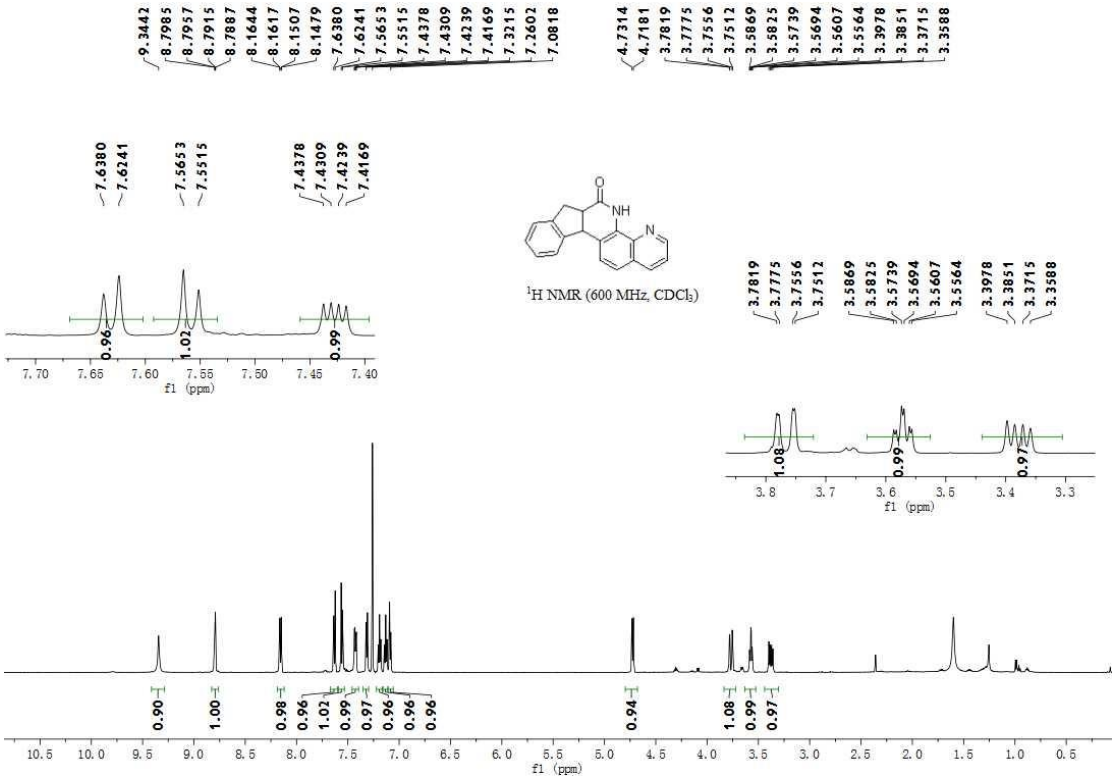
^{1}H NMR spectrum (400 MHz) of compound **2t** in $CDCl_3$



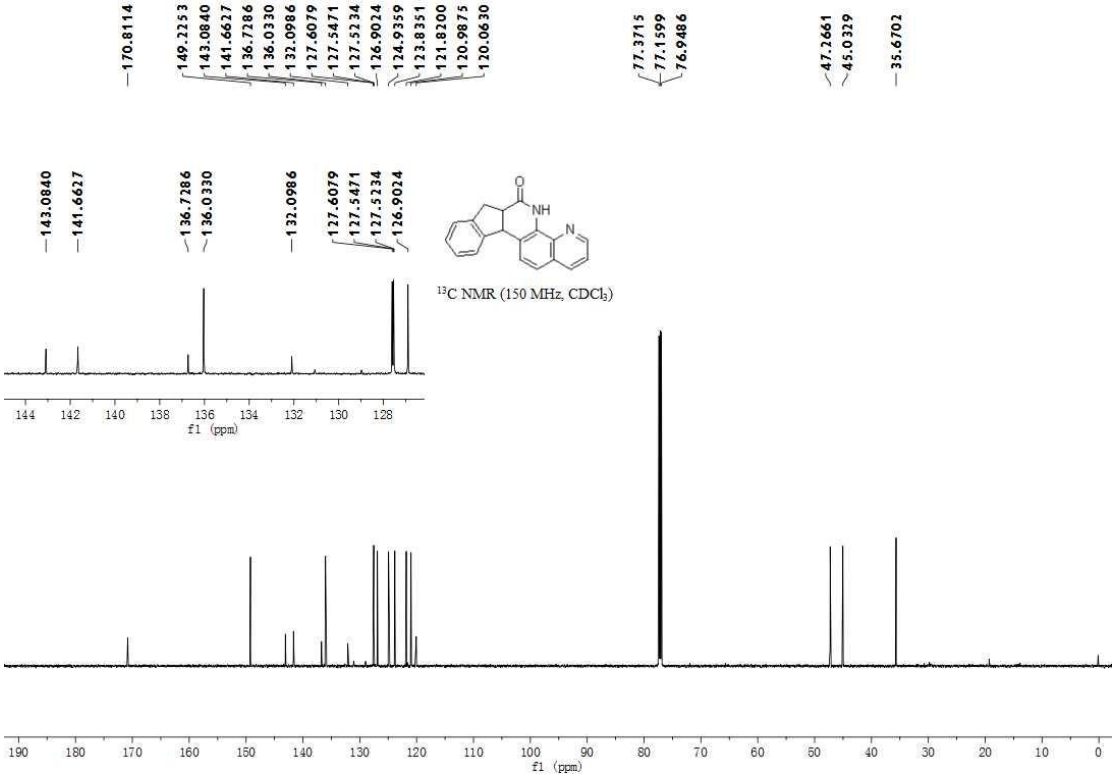
^{13}C NMR spectrum (100 MHz) of compound **2t** in $CDCl_3$



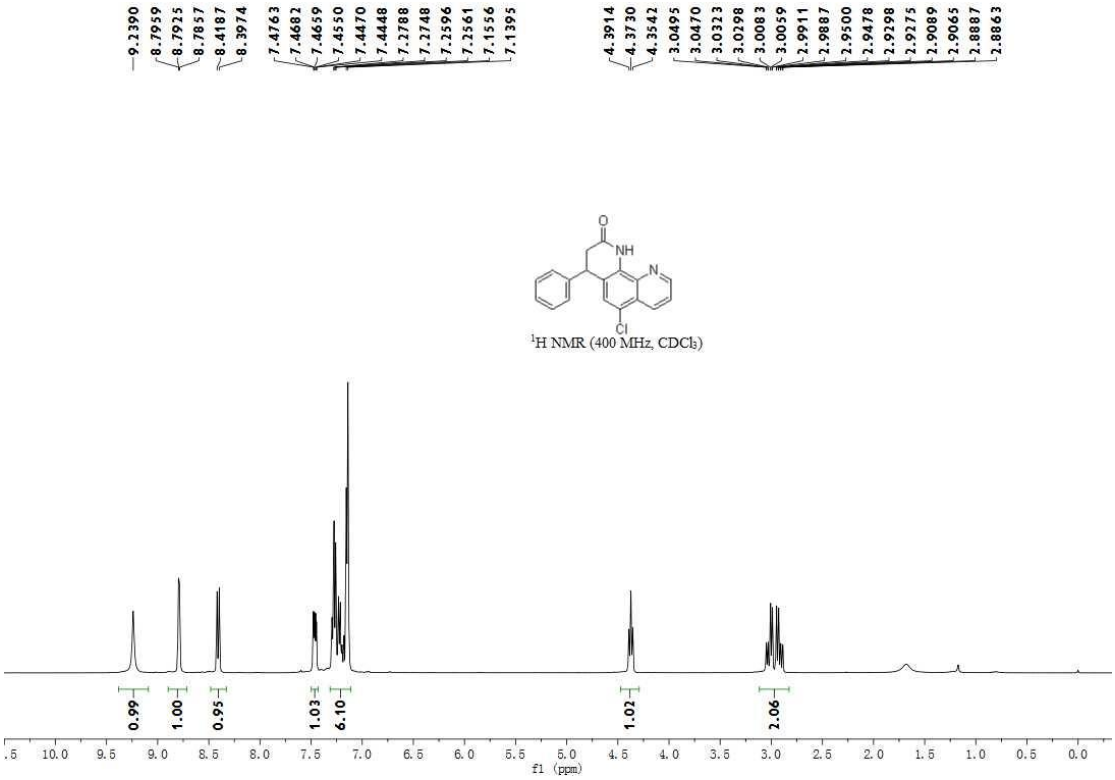
^{1}H NMR spectrum (400 MHz) of compound **2u** in $CDCl_3$



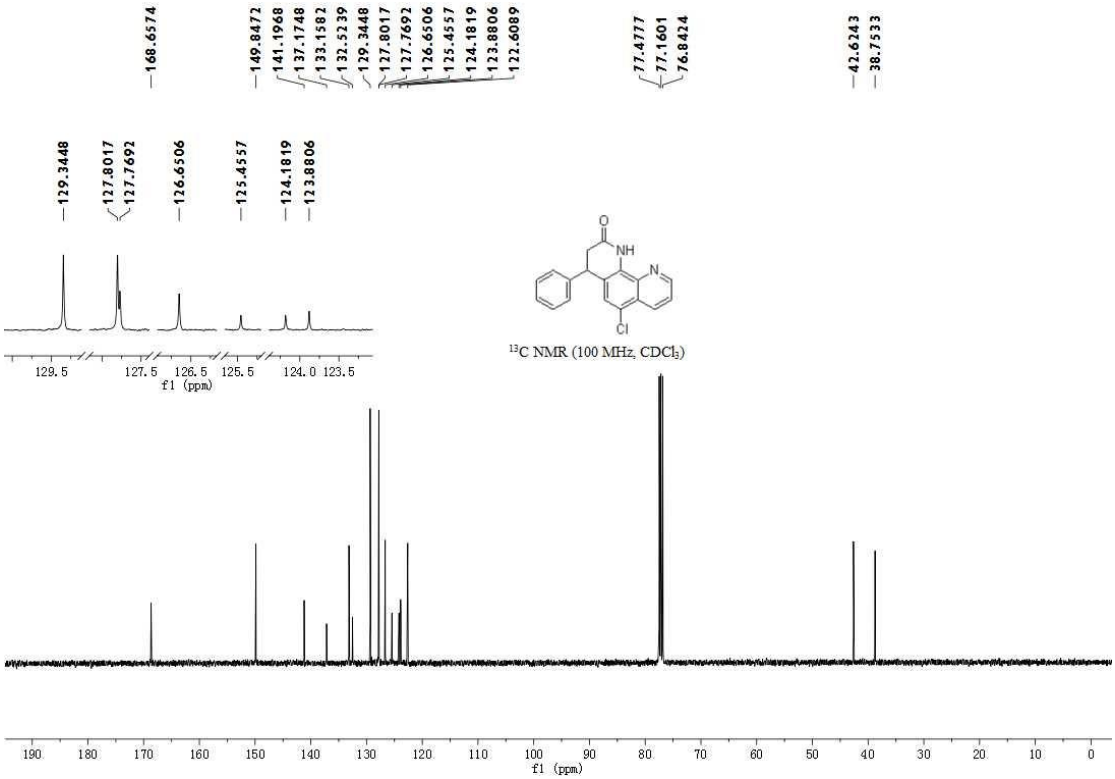
^{13}C NMR spectrum (100 MHz) of compound **2u** in $CDCl_3$



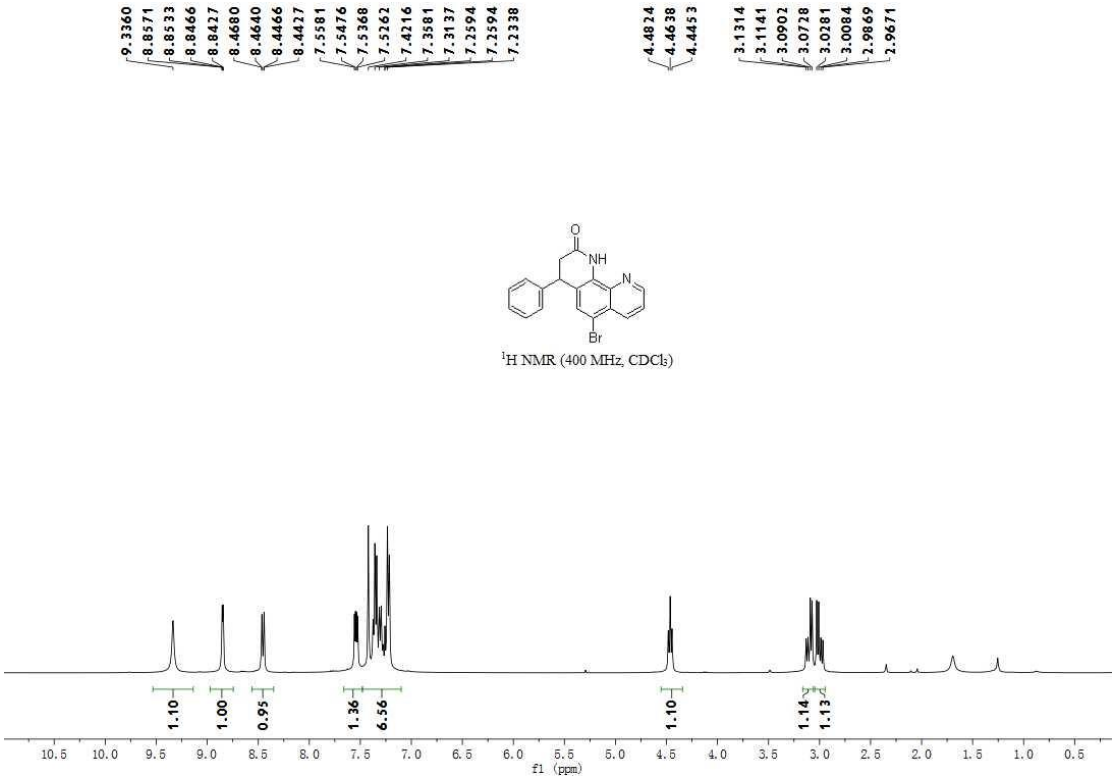
^{1}H NMR spectrum (400 MHz) of compound **2v** in $CDCl_3$



^{13}C NMR spectrum (100 MHz) of compound **2v** in $CDCl_3$

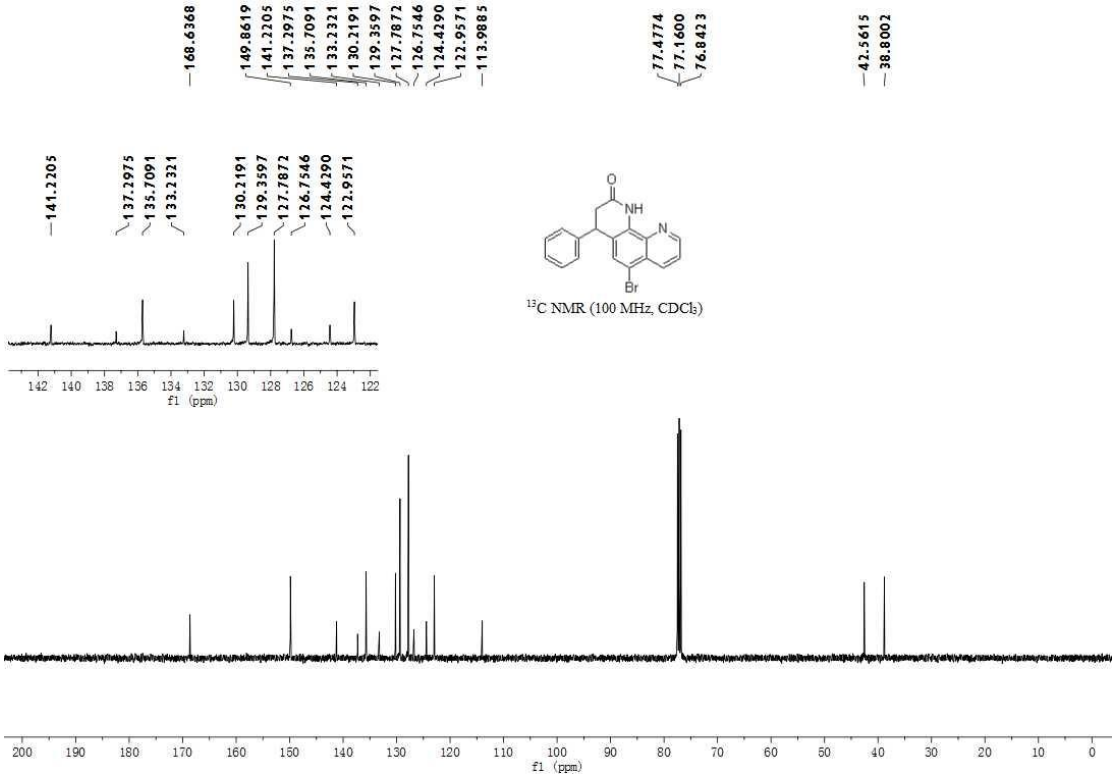


^{1}H NMR spectrum (400 MHz) of compound **2w** in $CDCl_3$



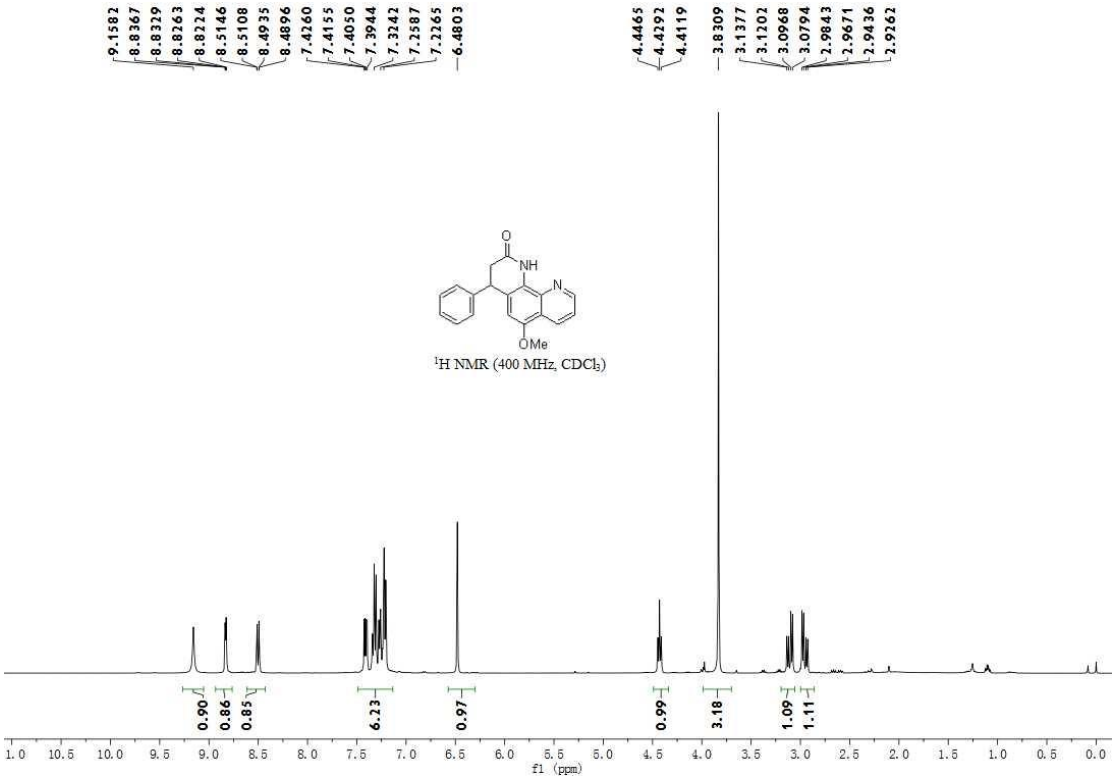
^{1}H NMR (400 MHz, $CDCl_3$)

^{13}C NMR spectrum (100 MHz) of compound **2w** in $CDCl_3$

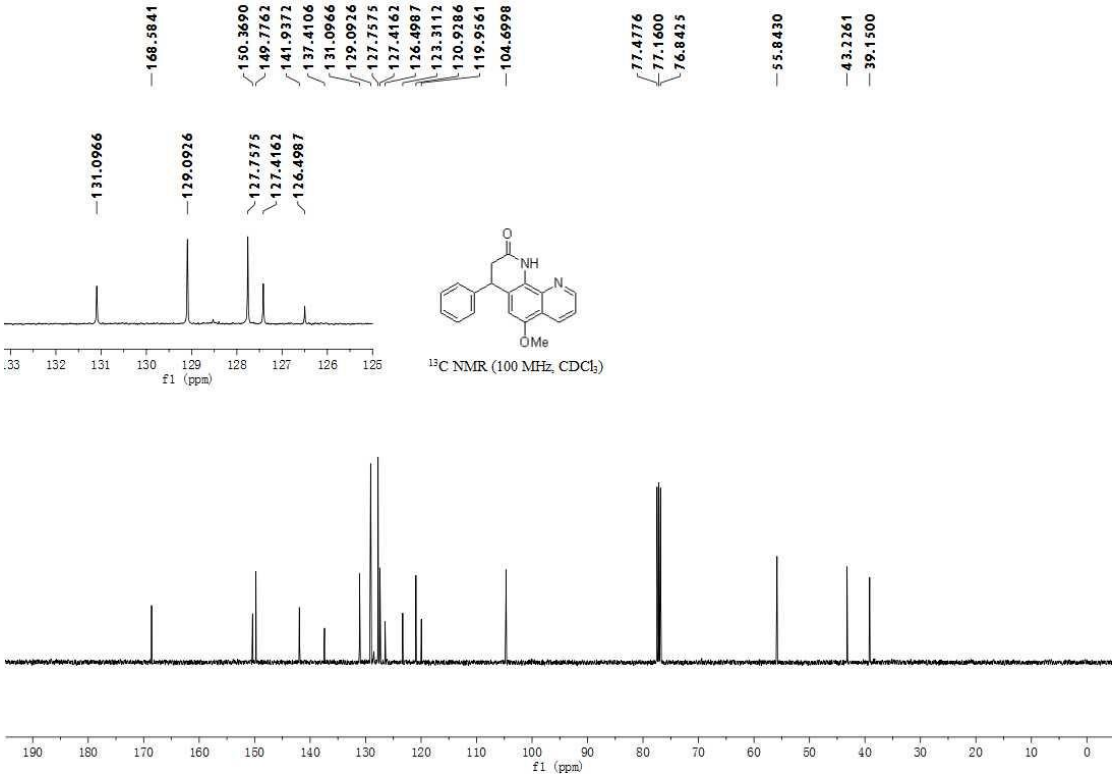


^{13}C NMR (100 MHz, $CDCl_3$)

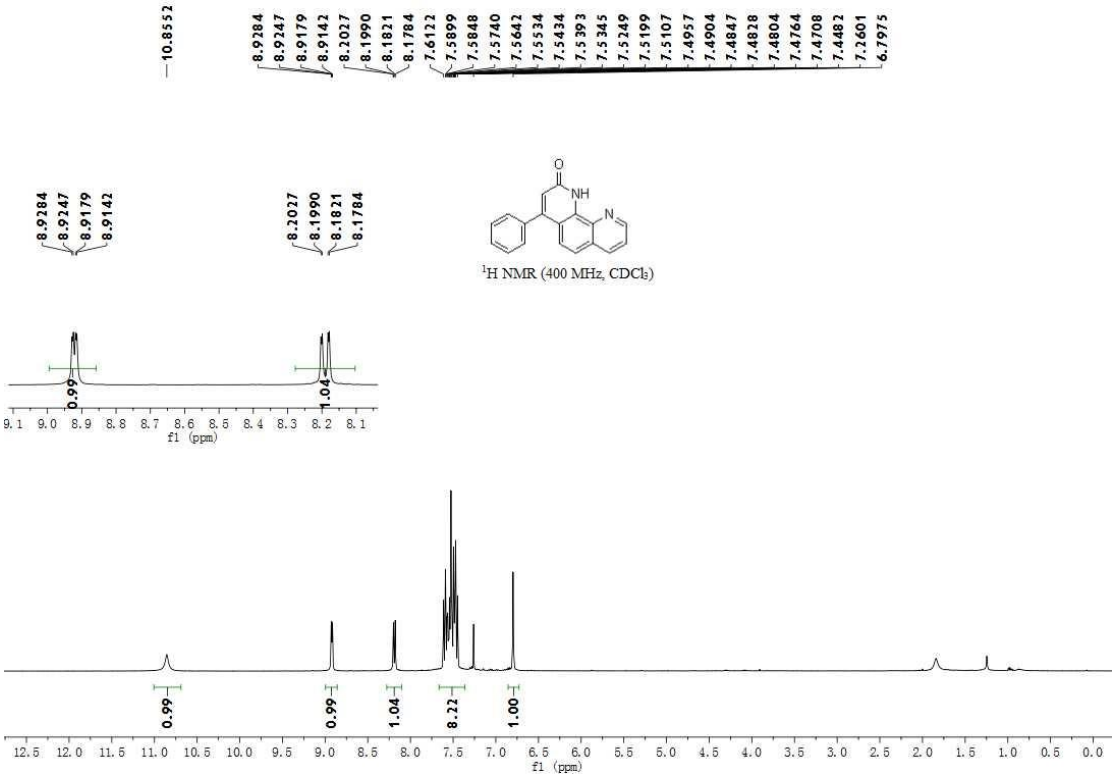
^{1}H NMR spectrum (400 MHz) of compound **2x** in $CDCl_3$



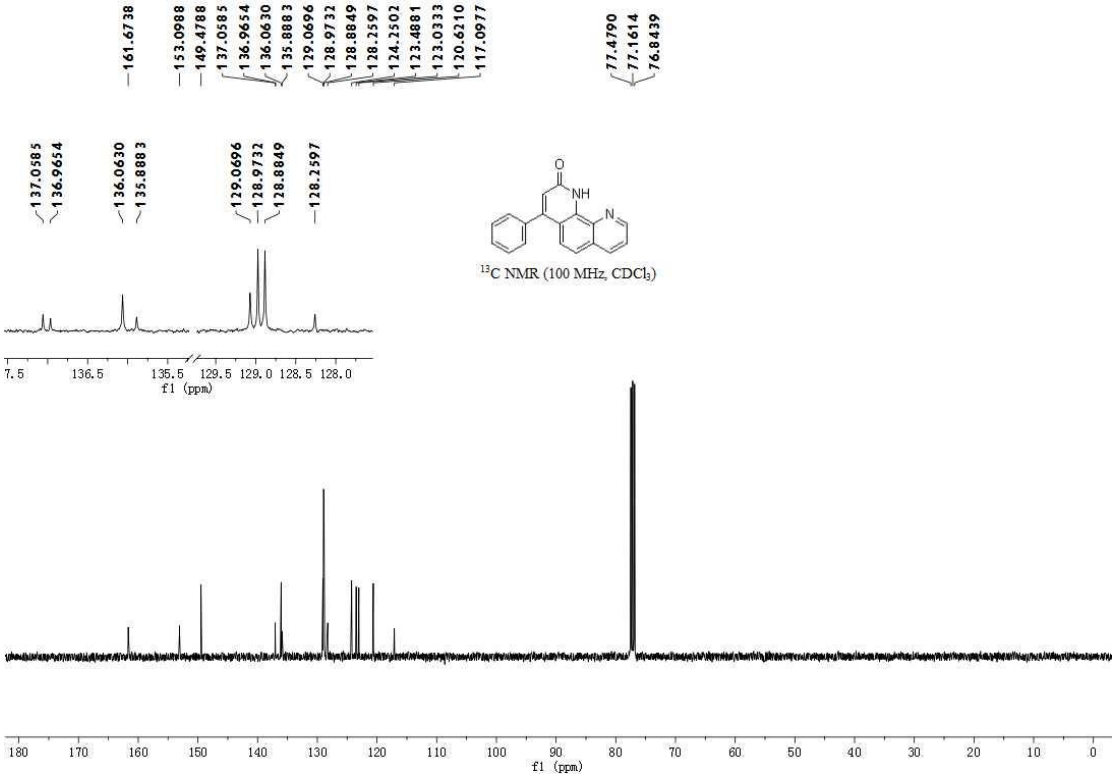
^{13}C NMR spectrum (100 MHz) of compound **2x** in $CDCl_3$



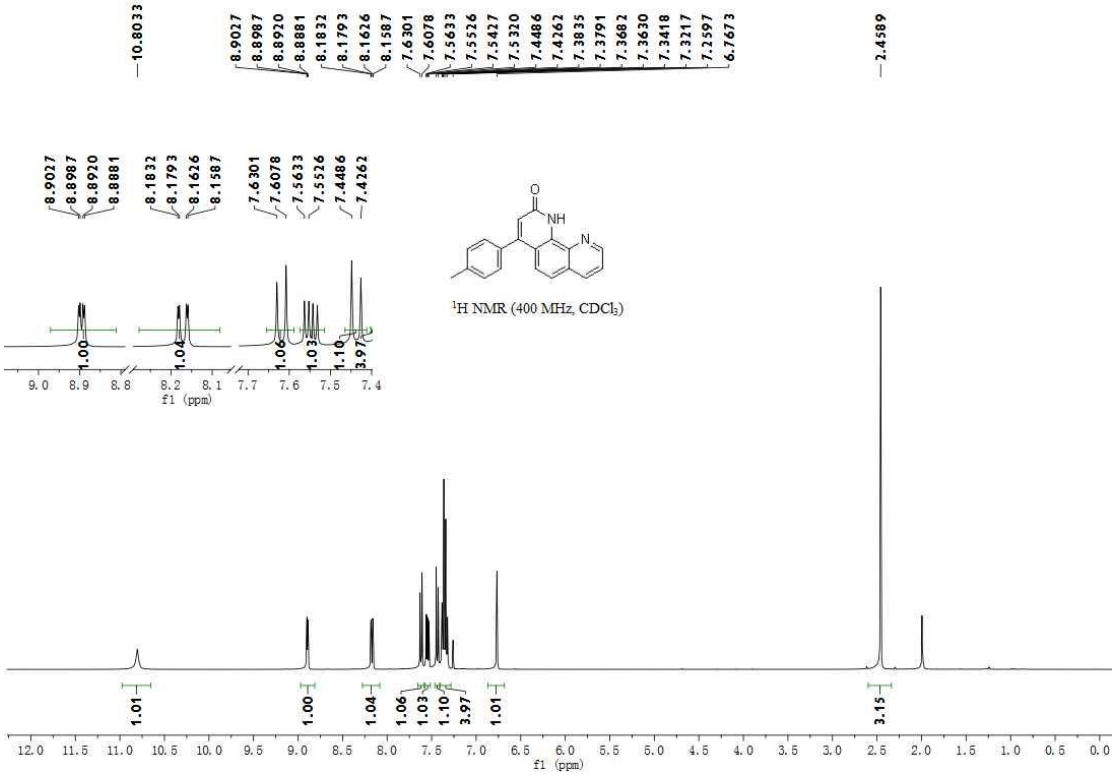
^{1}H NMR spectrum (400 MHz) of compound **3a** in $CDCl_3$



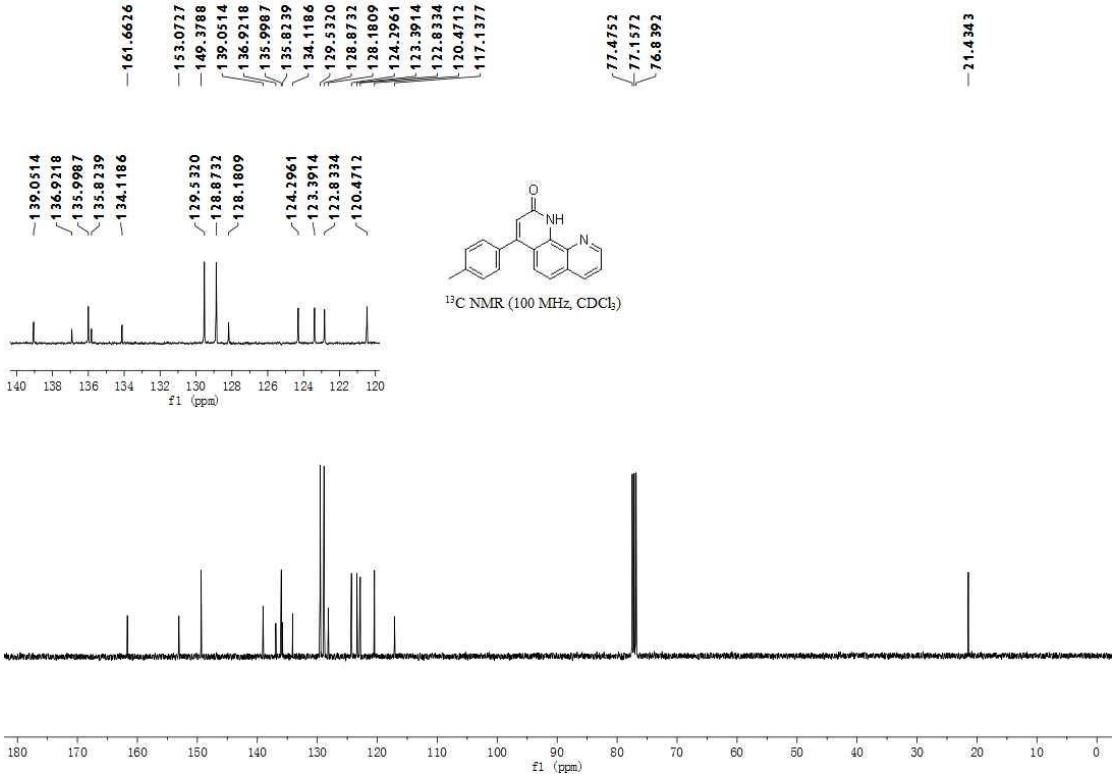
^{13}C NMR spectrum (100 MHz) of compound **3a** in $CDCl_3$



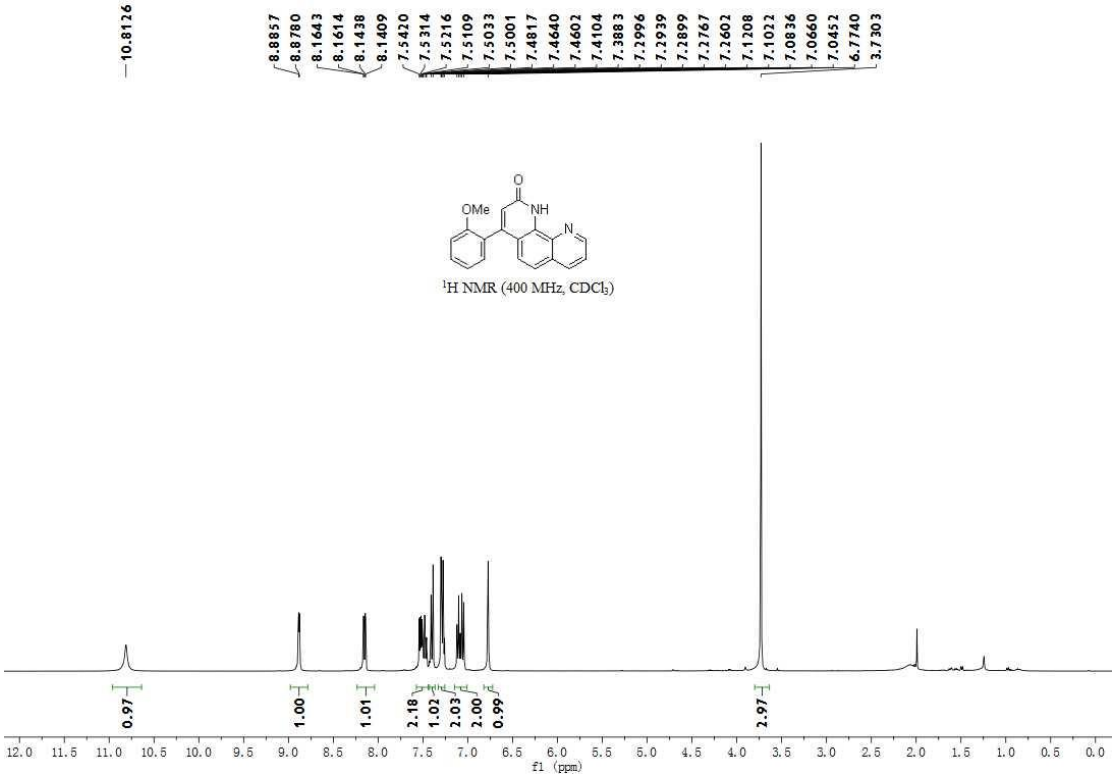
^{1}H NMR spectrum (400 MHz) of compound **3b** in $CDCl_3$



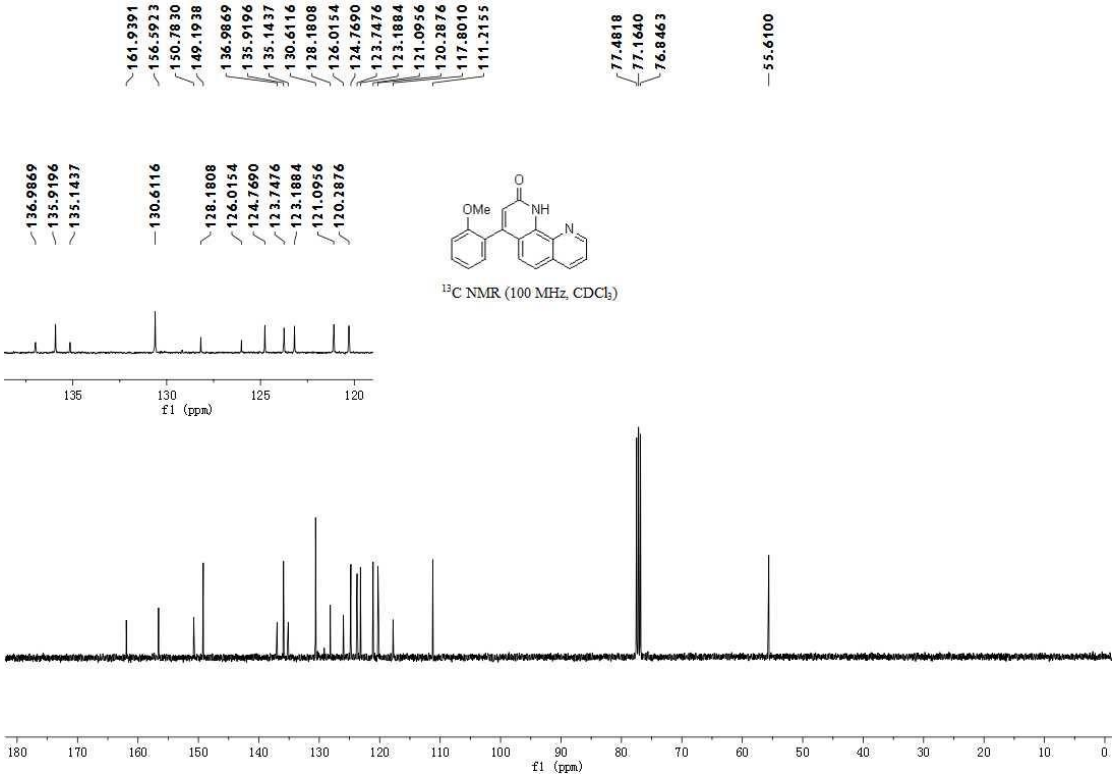
^{13}C NMR spectrum (100 MHz) of compound **3b** in $CDCl_3$



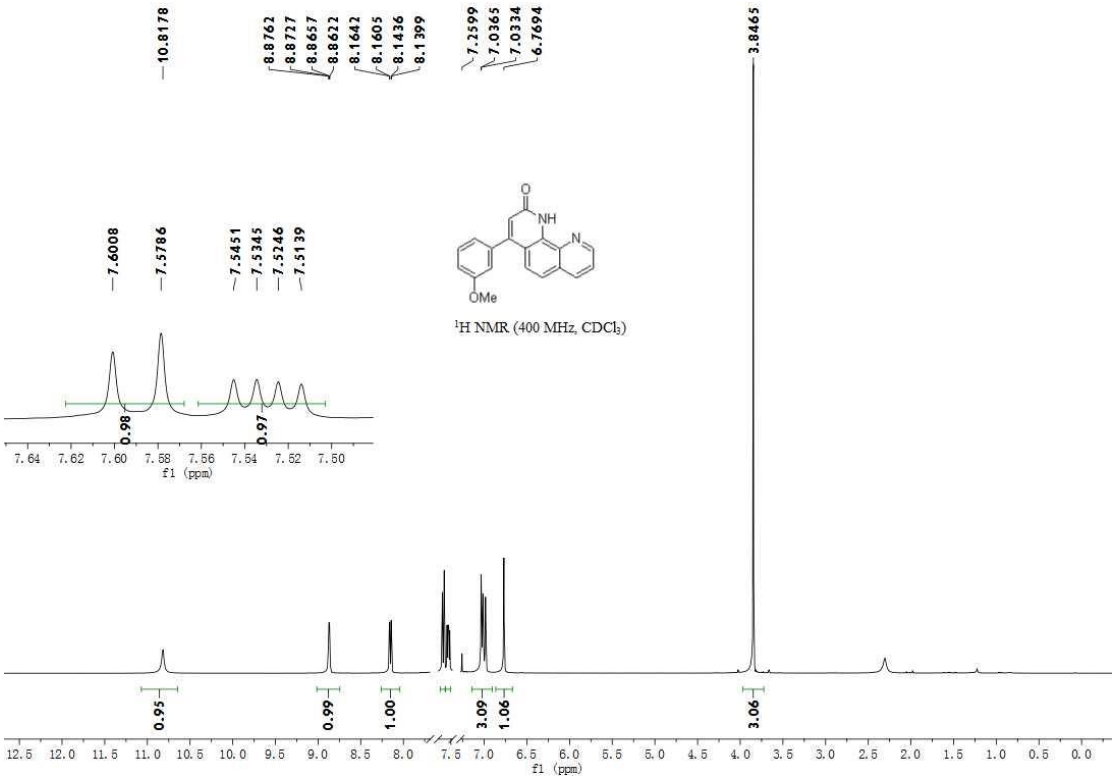
^{1}H NMR spectrum (400 MHz) of compound **3c** in $CDCl_3$



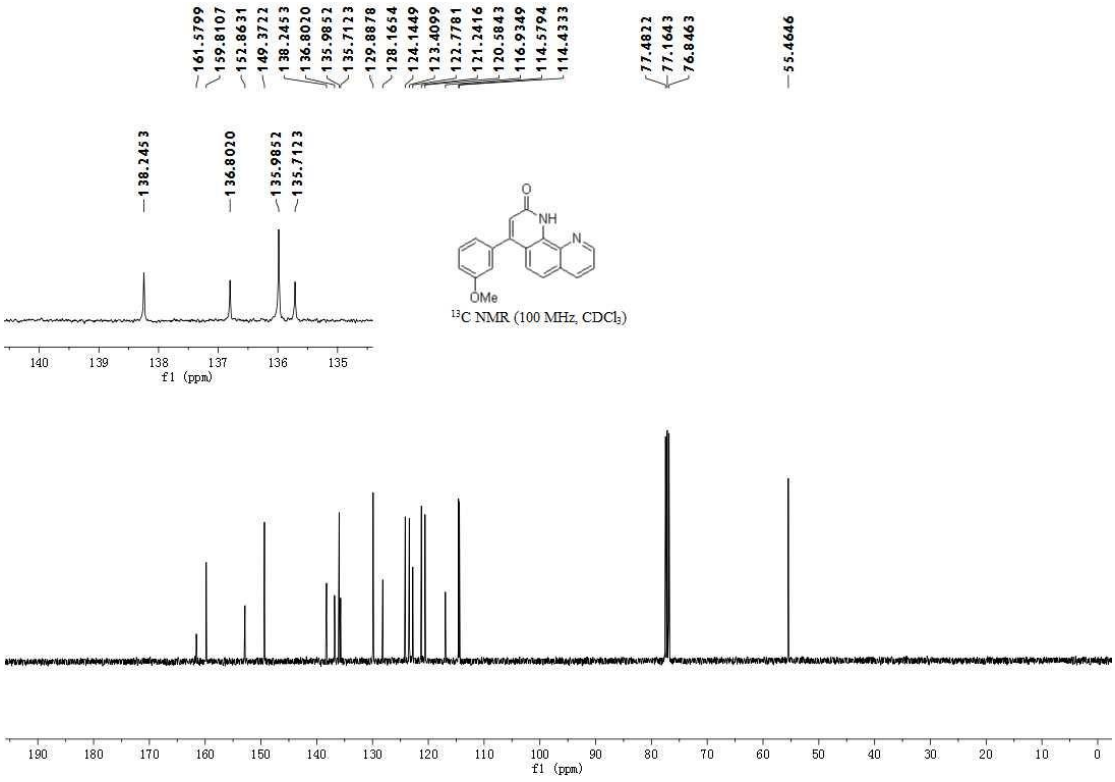
^{13}C NMR spectrum (100 MHz) of compound **3c** in $CDCl_3$



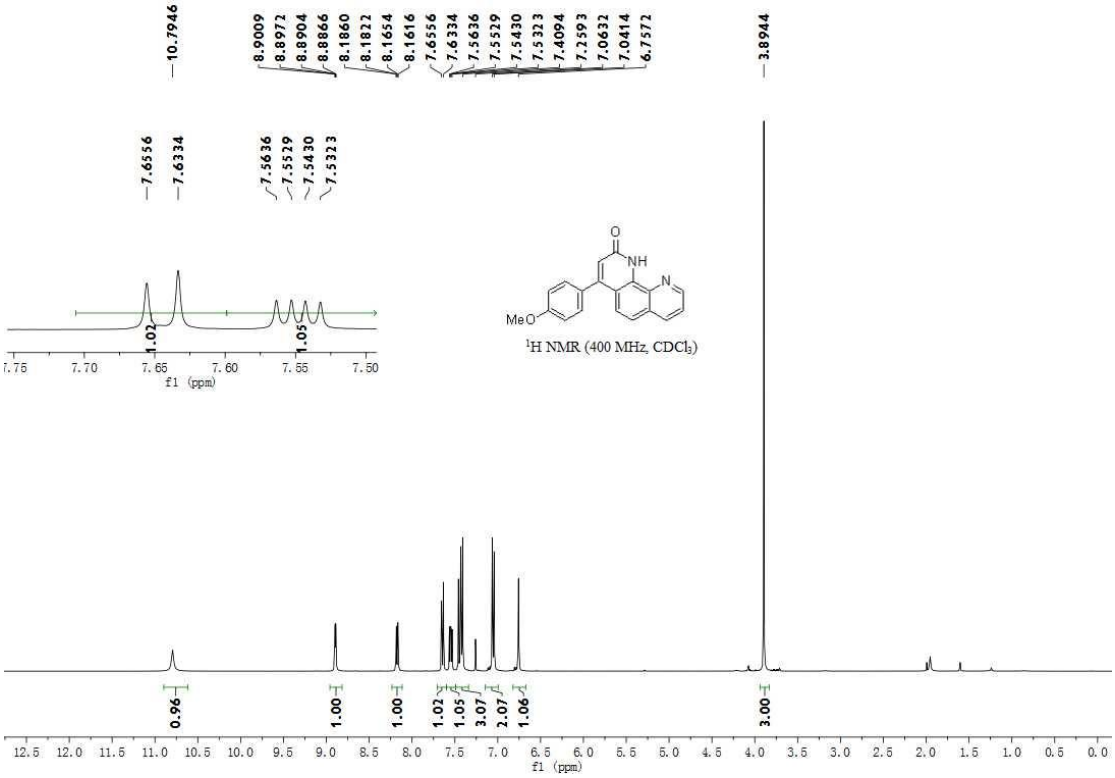
^{1}H NMR spectrum (400 MHz) of compound **3d** in $CDCl_3$



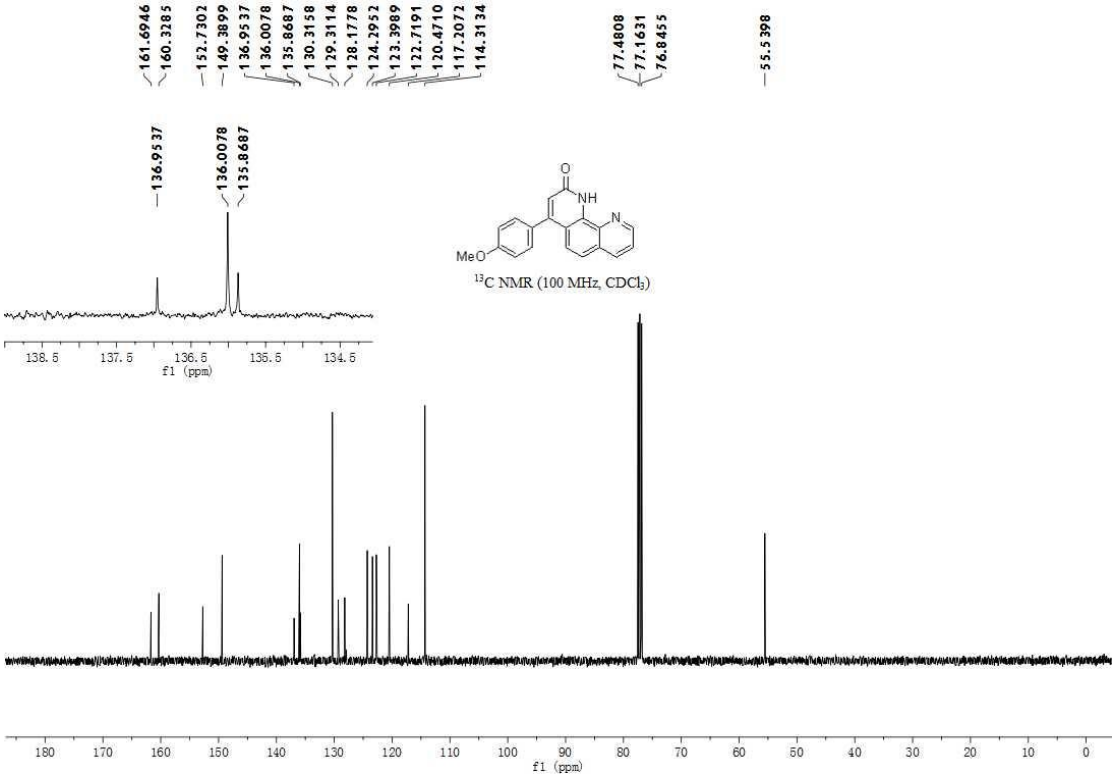
^{13}C NMR spectrum (100 MHz) of compound **3d** in $CDCl_3$



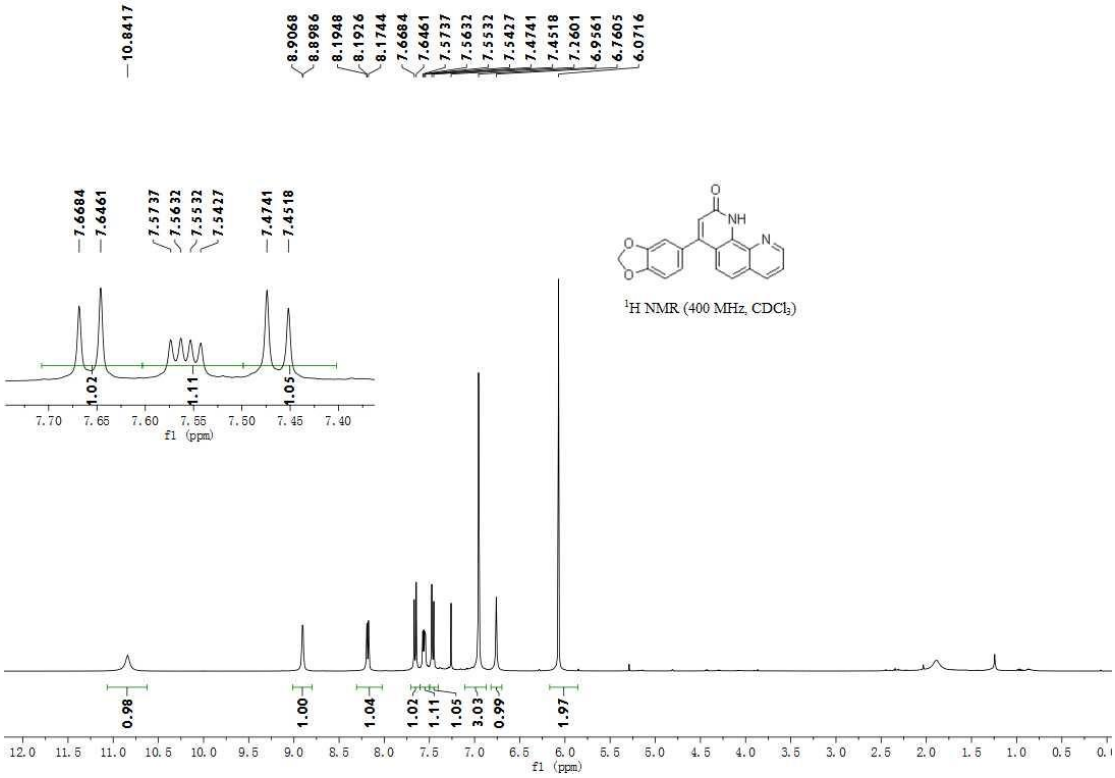
^{1}H NMR spectrum (400 MHz) of compound **3e** in $CDCl_3$



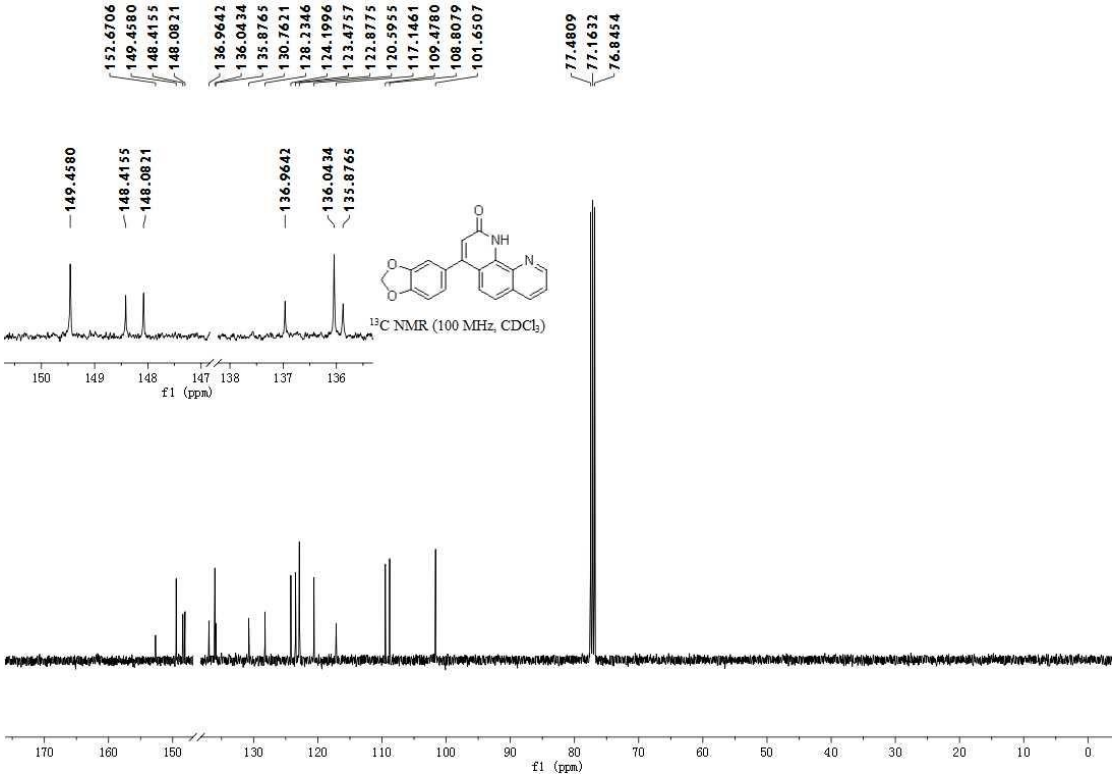
^{13}C NMR spectrum (100 MHz) of compound **3e** in $CDCl_3$



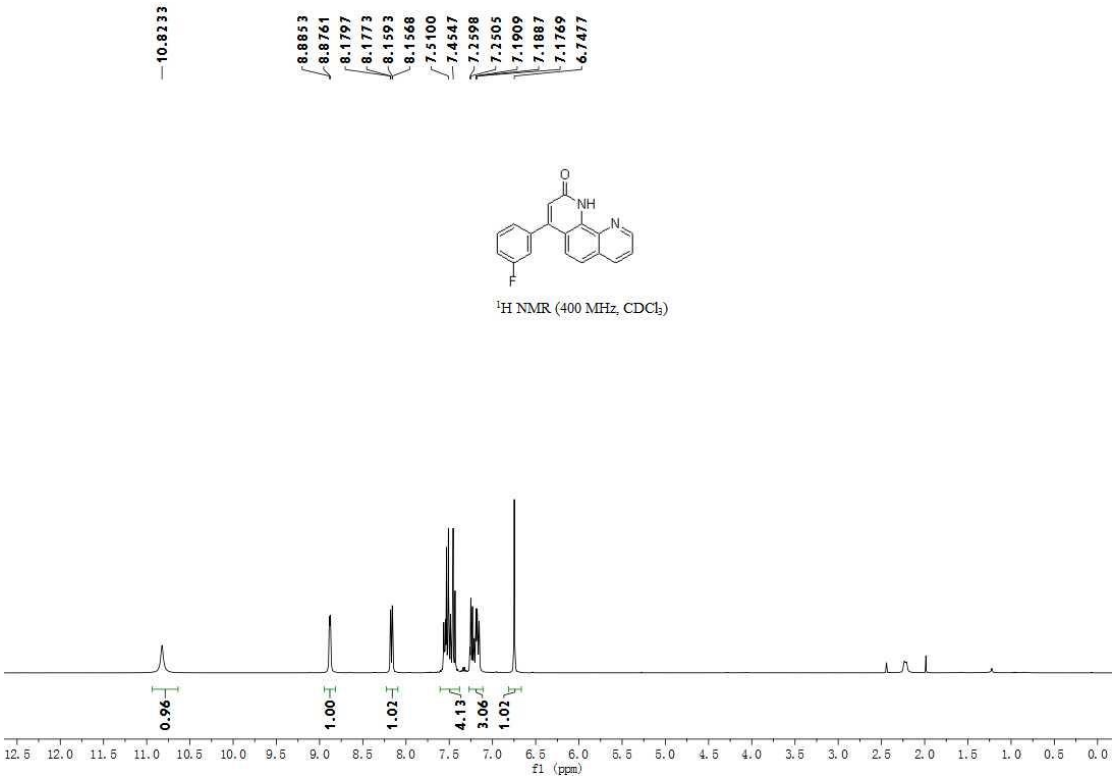
^{1}H NMR spectrum (400 MHz) of compound **3f** in $CDCl_3$



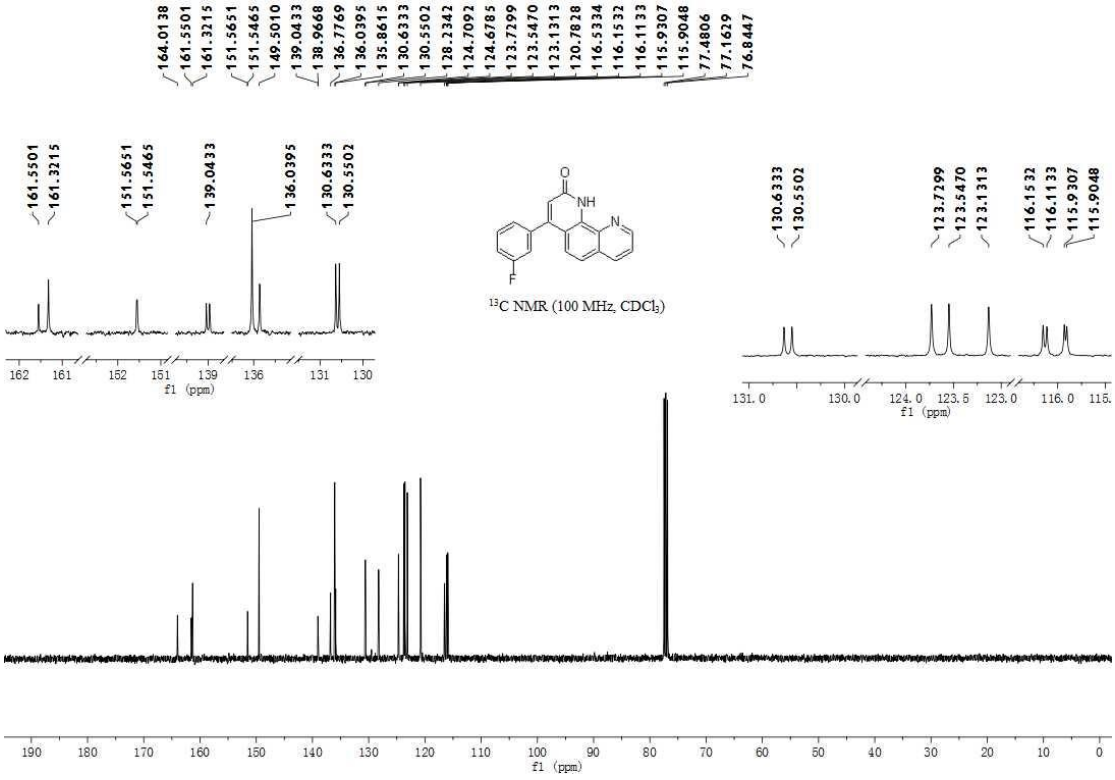
^{13}C NMR spectrum (100 MHz) of compound **3f** in $CDCl_3$



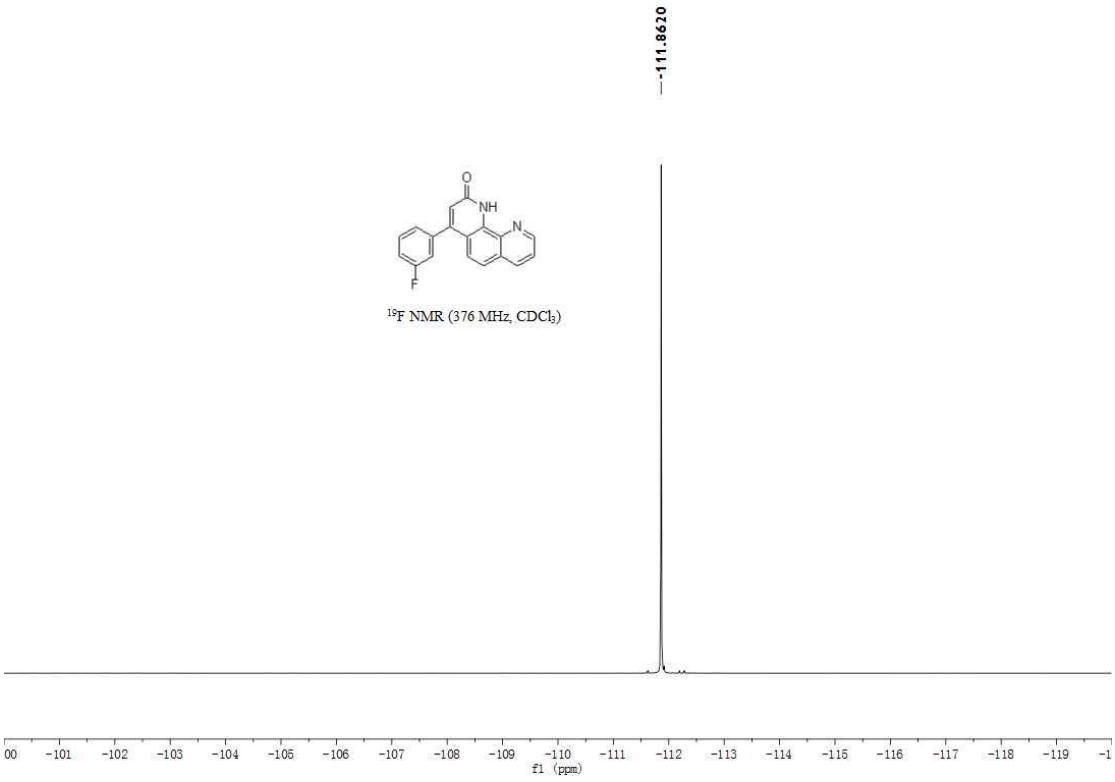
^{1}H NMR spectrum (400 MHz) of compound **3g** in $CDCl_3$



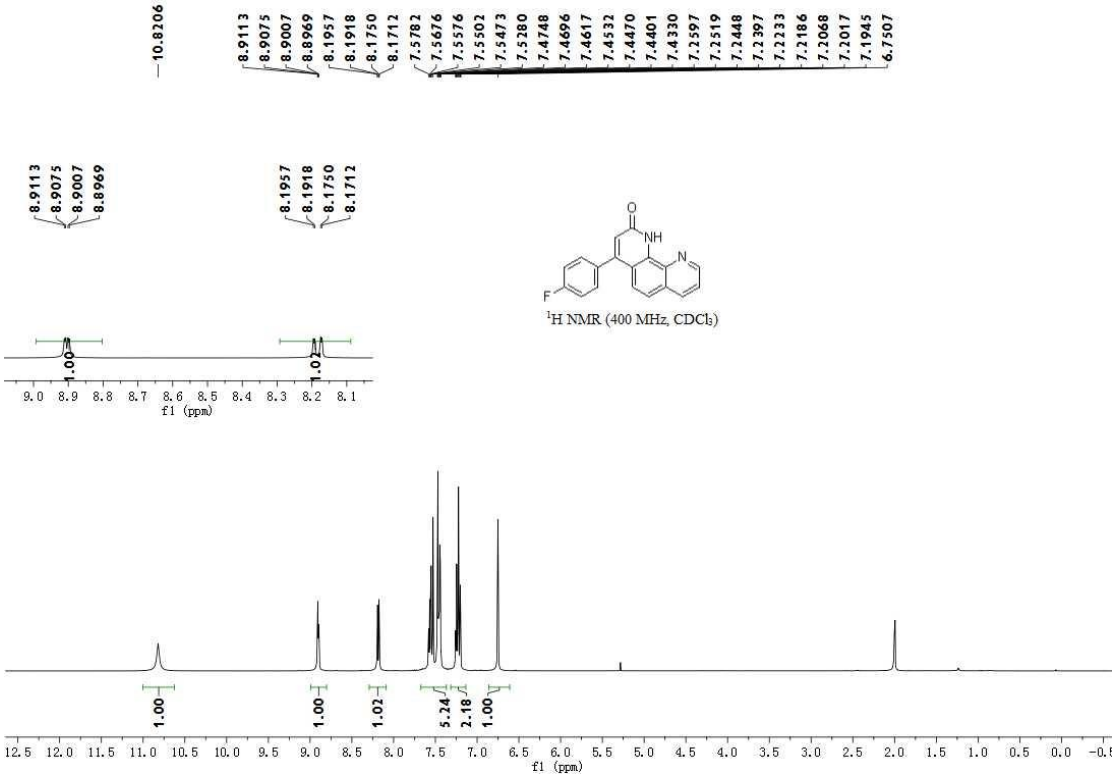
^{13}C NMR spectrum (100 MHz) of compound **3g** in $CDCl_3$



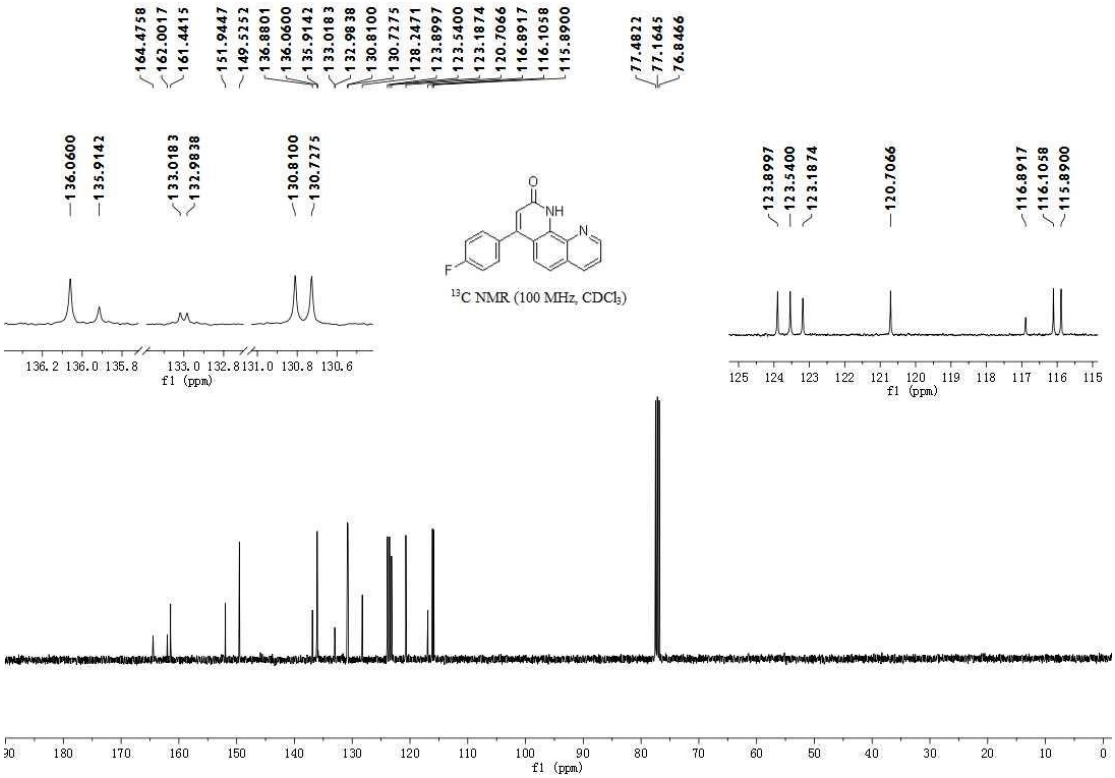
^{19}F NMR spectrum (376 MHz) of compound **3g** in $CDCl_3$



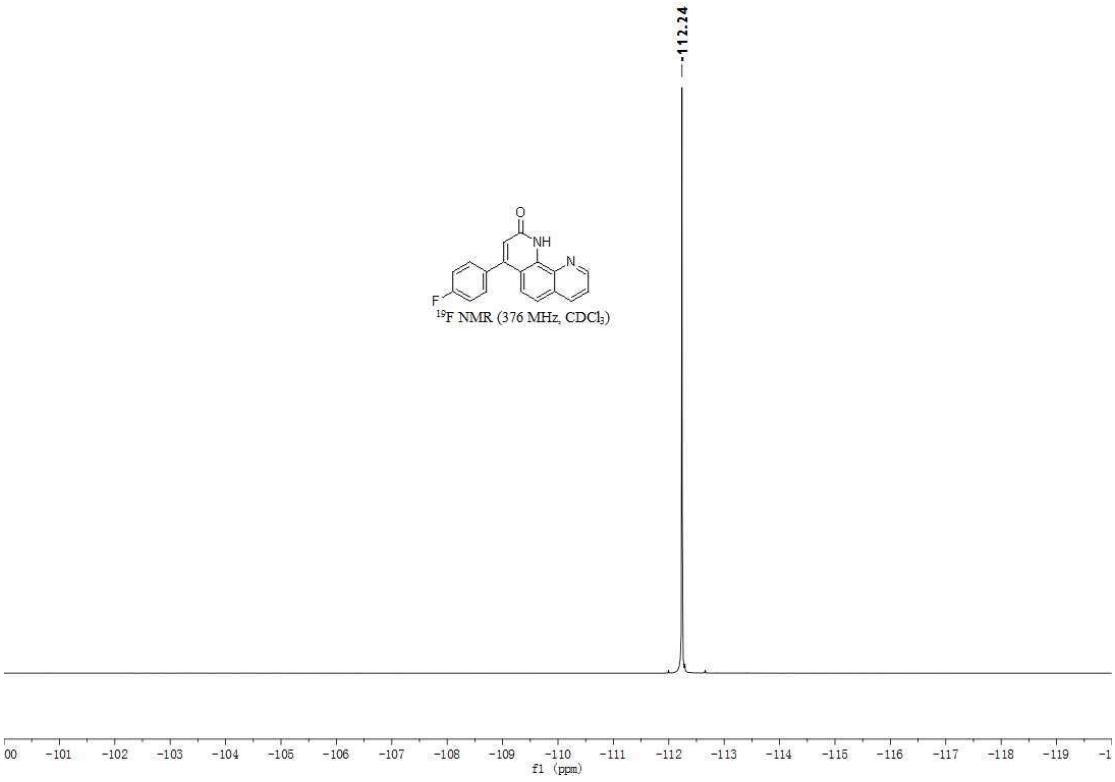
^{1}H NMR spectrum (400 MHz) of compound **3h** in $CDCl_3$



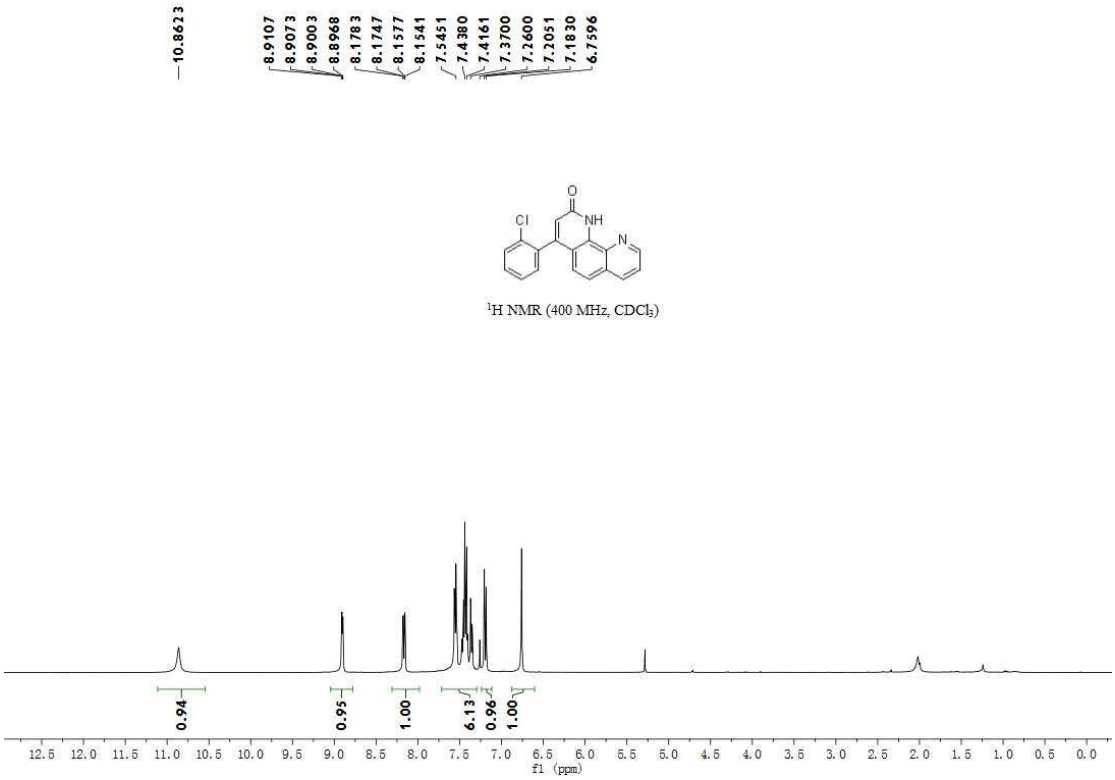
^{13}C NMR spectrum (100 MHz) of compound **3h** in $CDCl_3$



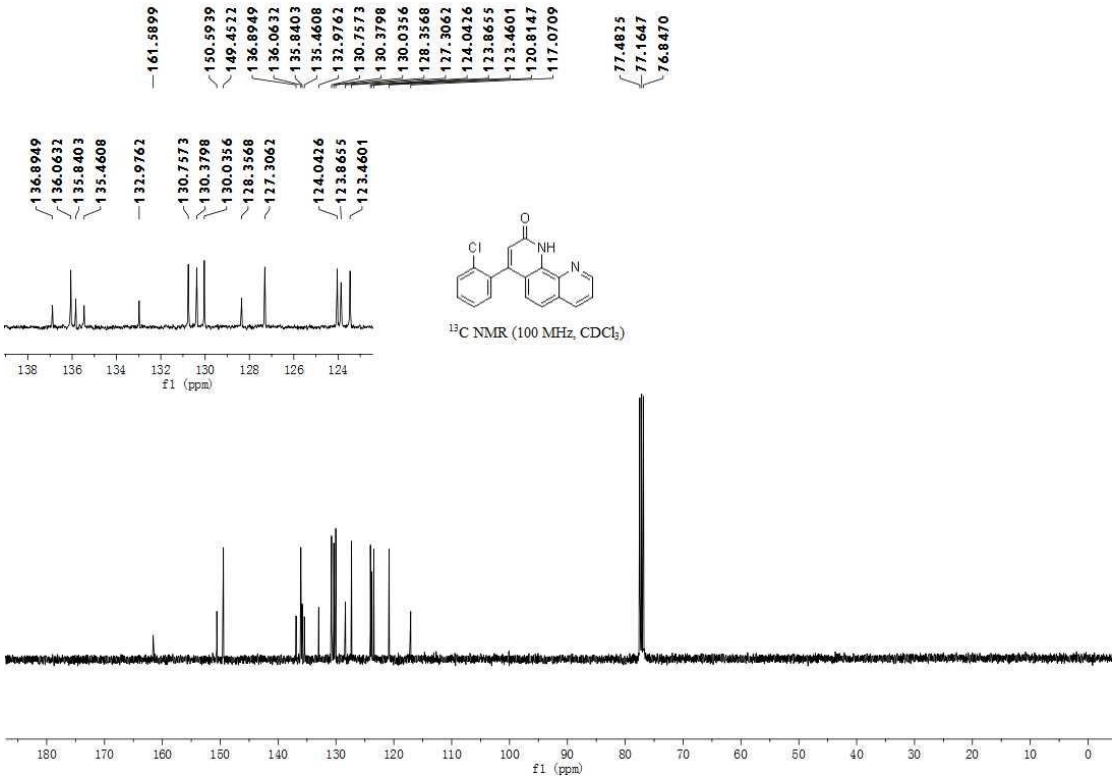
^{19}F NMR spectrum (376 MHz) of compound **3h** in $CDCl_3$



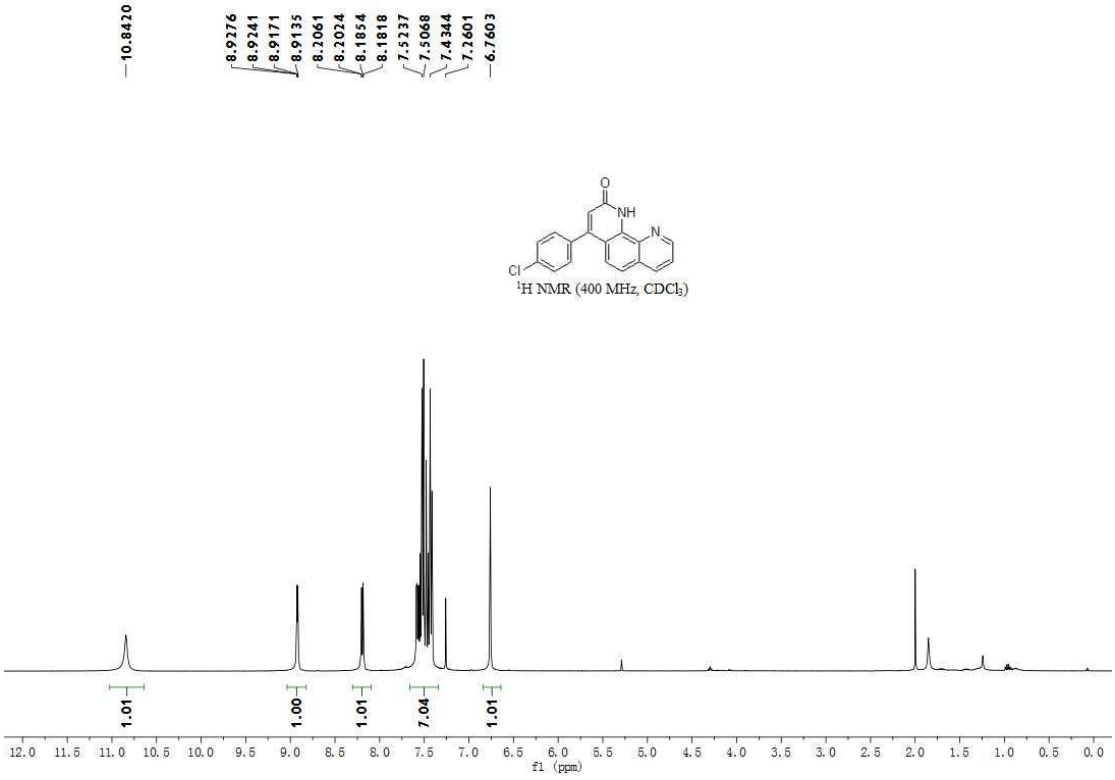
^{1}H NMR spectrum (400 MHz) of compound **3i** in $CDCl_3$



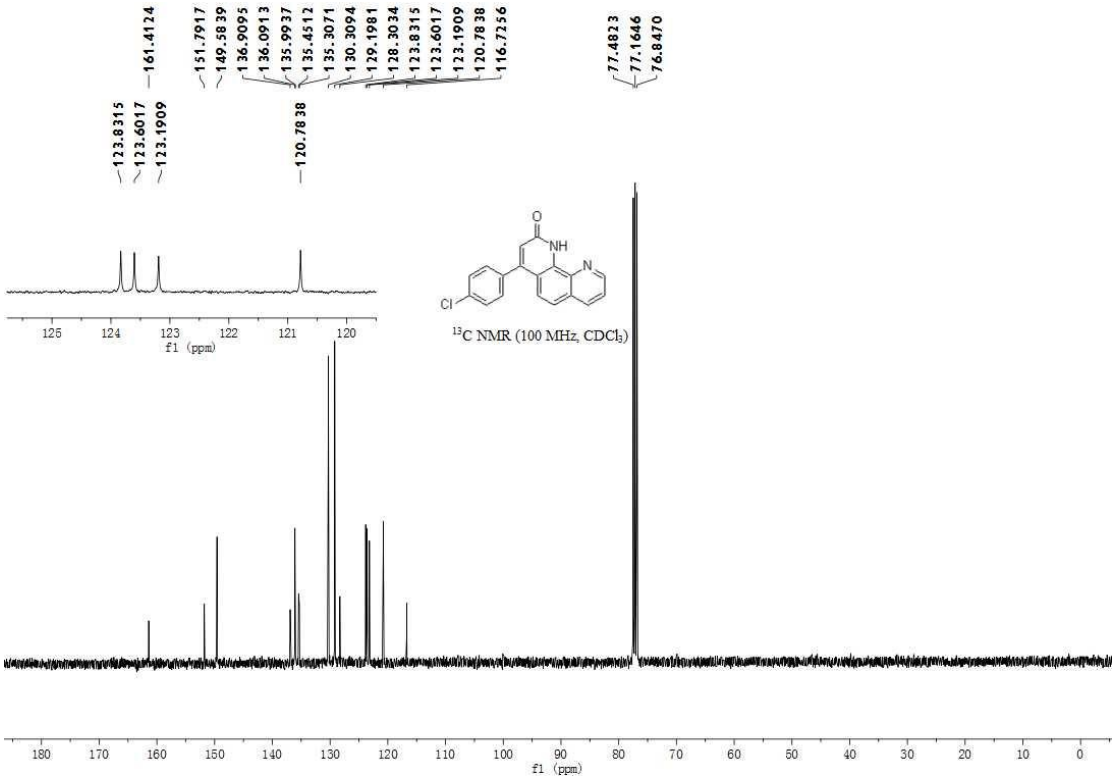
^{13}C NMR spectrum (100 MHz) of compound **3i** in $CDCl_3$



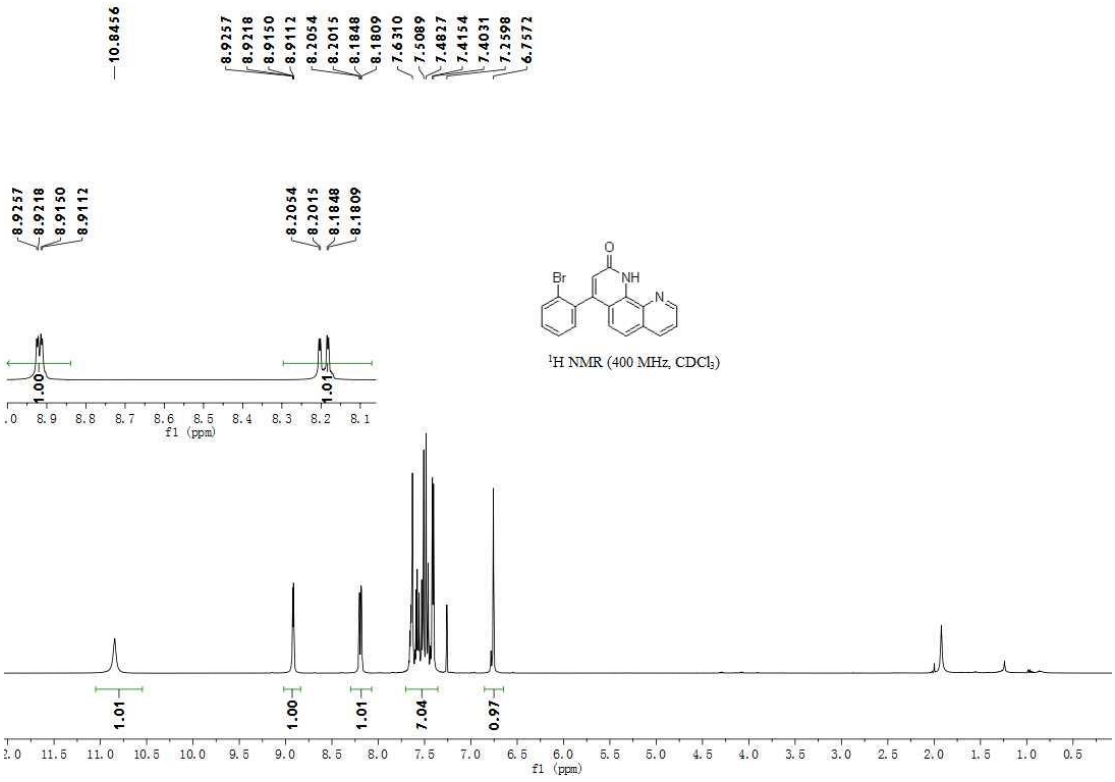
^{1}H NMR spectrum (400 MHz) of compound **3j** in $CDCl_3$



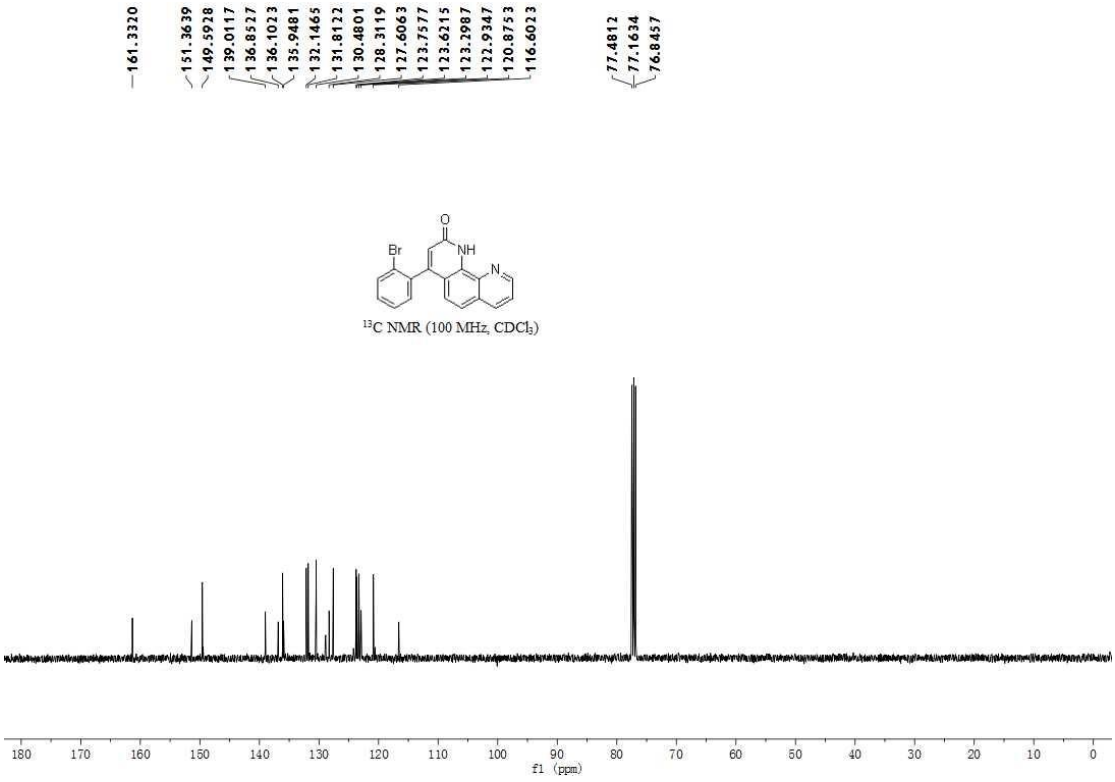
^{13}C NMR spectrum (100 MHz) of compound **3j** in $CDCl_3$



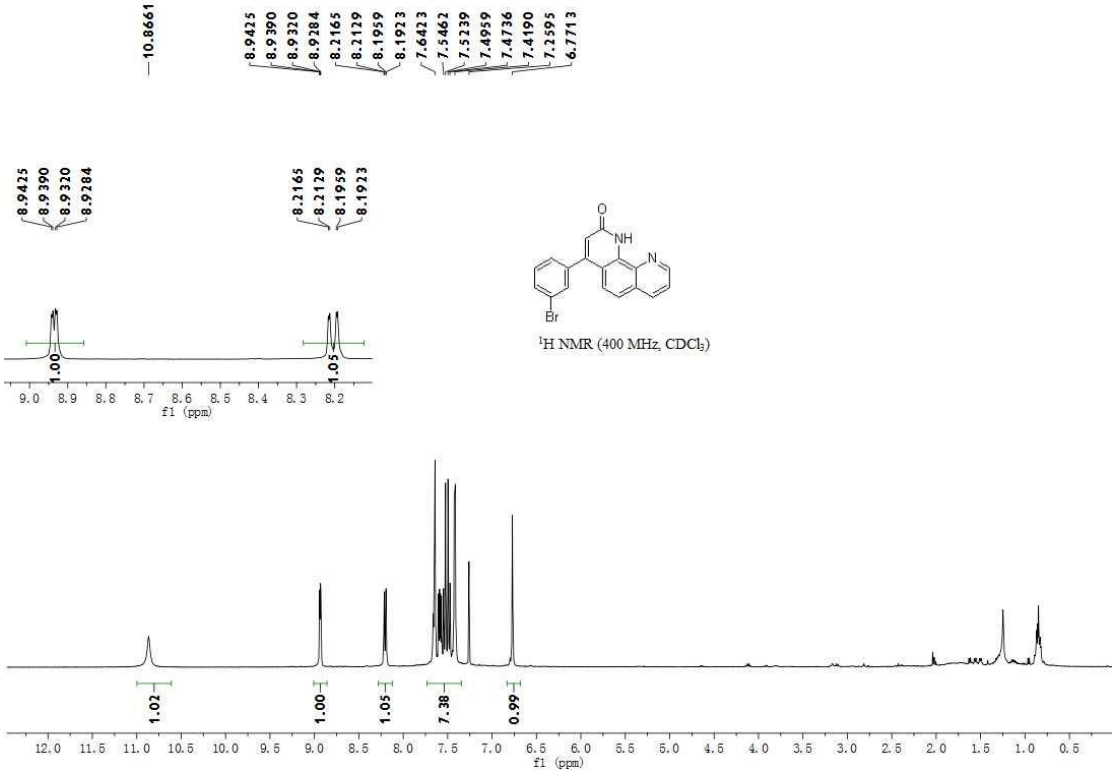
^{1}H NMR spectrum (400 MHz) of compound **3k** in $CDCl_3$



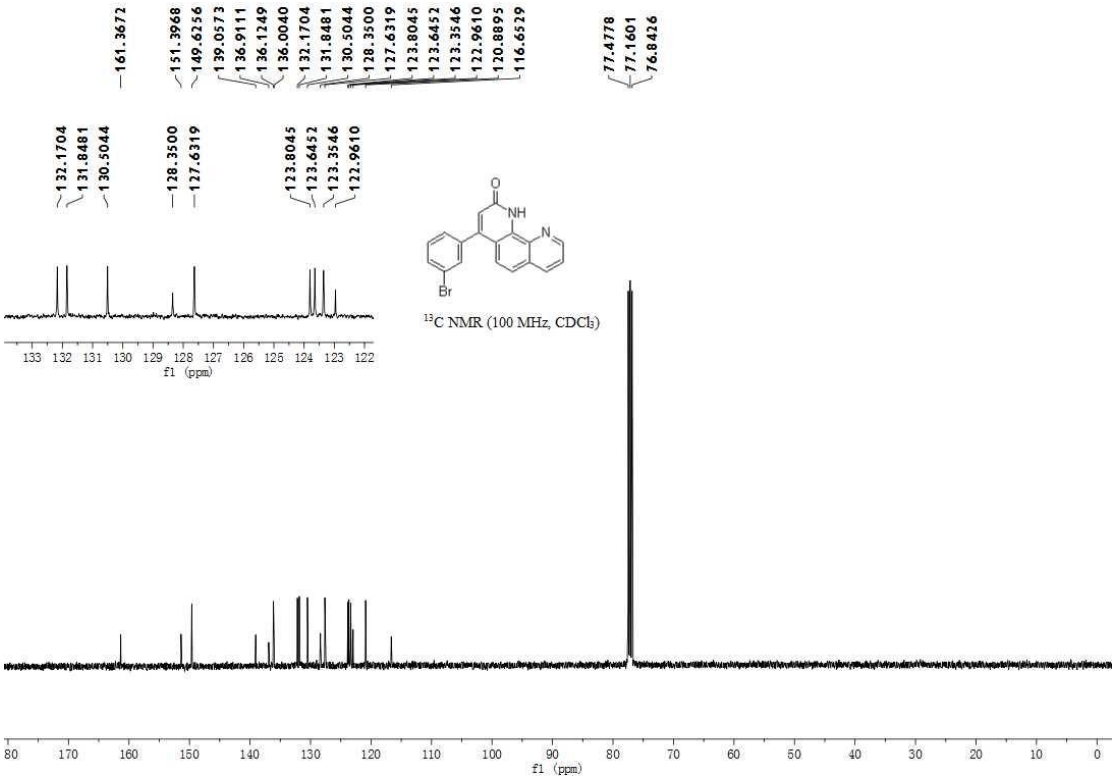
^{13}C NMR spectrum (100 MHz) of compound **3k** in $CDCl_3$



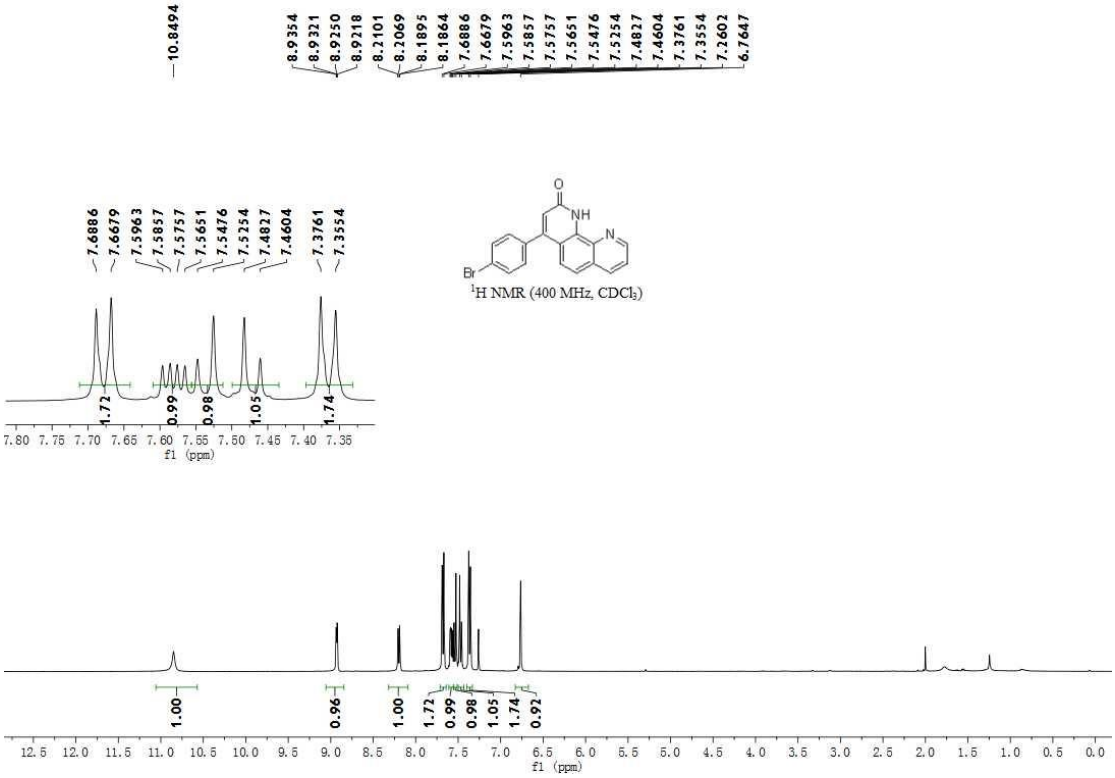
^{1}H NMR spectrum (400 MHz) of compound **3l** in $CDCl_3$



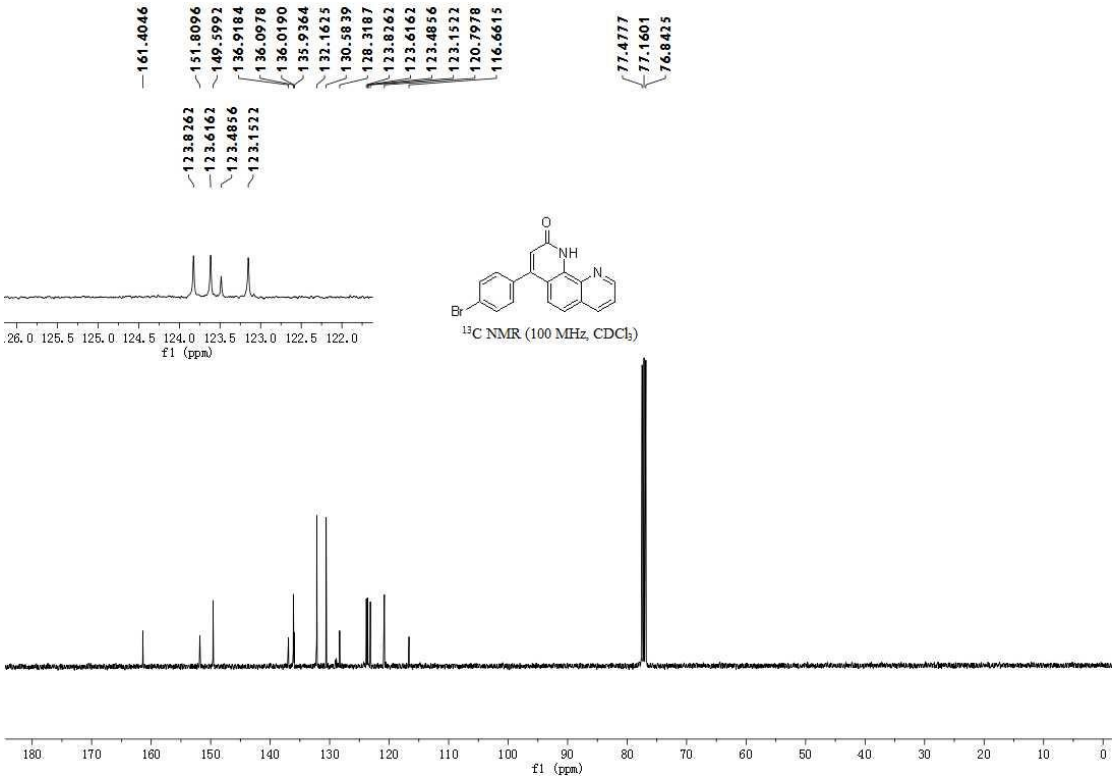
^{13}C NMR spectrum (100 MHz) of compound **3l** in $CDCl_3$



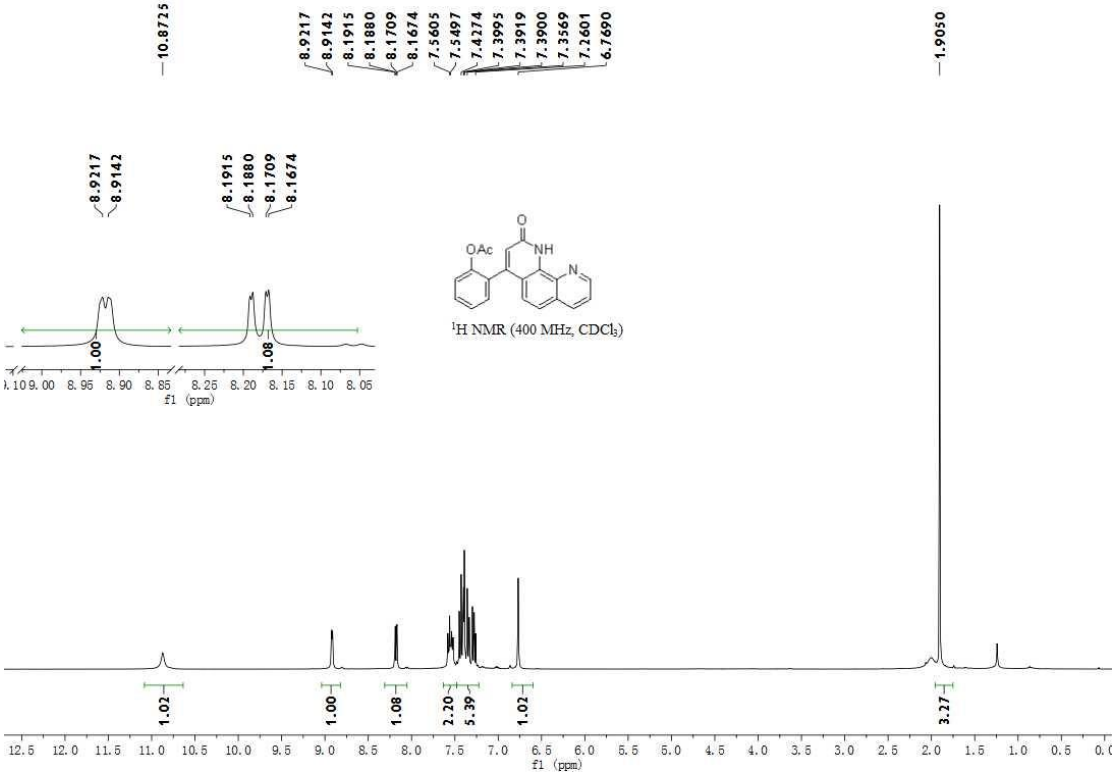
^{1}H NMR spectrum (400 MHz) of compound **3m** in $CDCl_3$



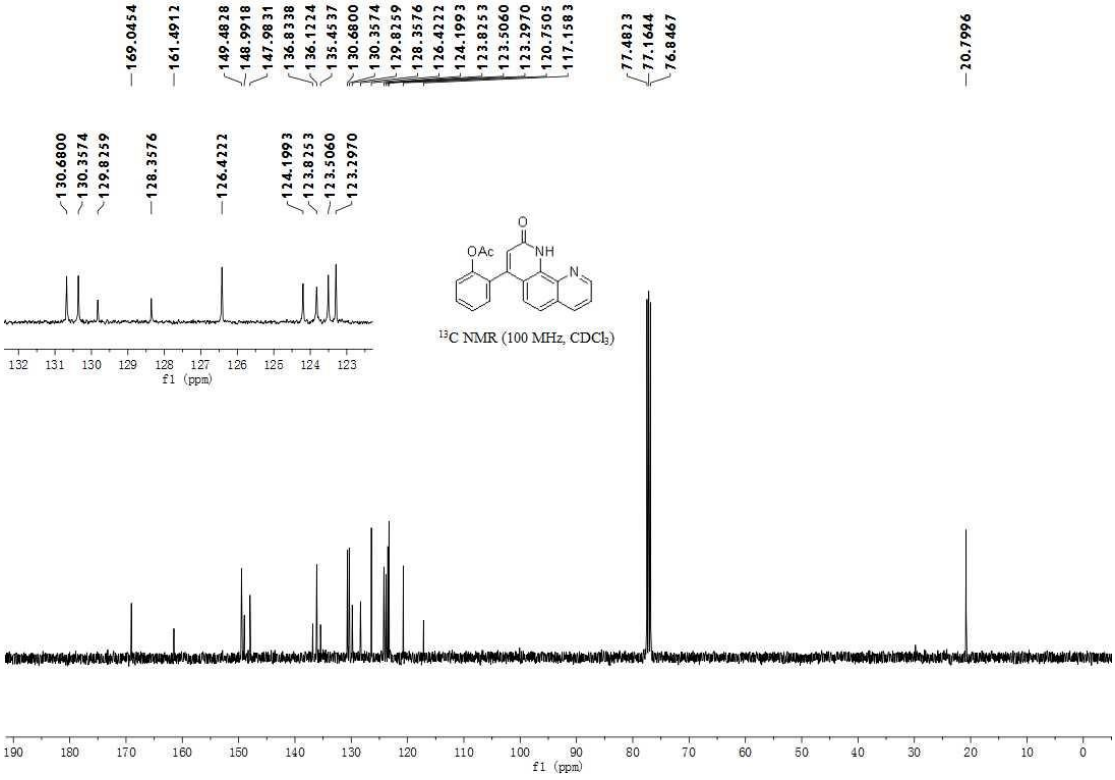
^{13}C NMR spectrum (100 MHz) of compound **3m** in $CDCl_3$



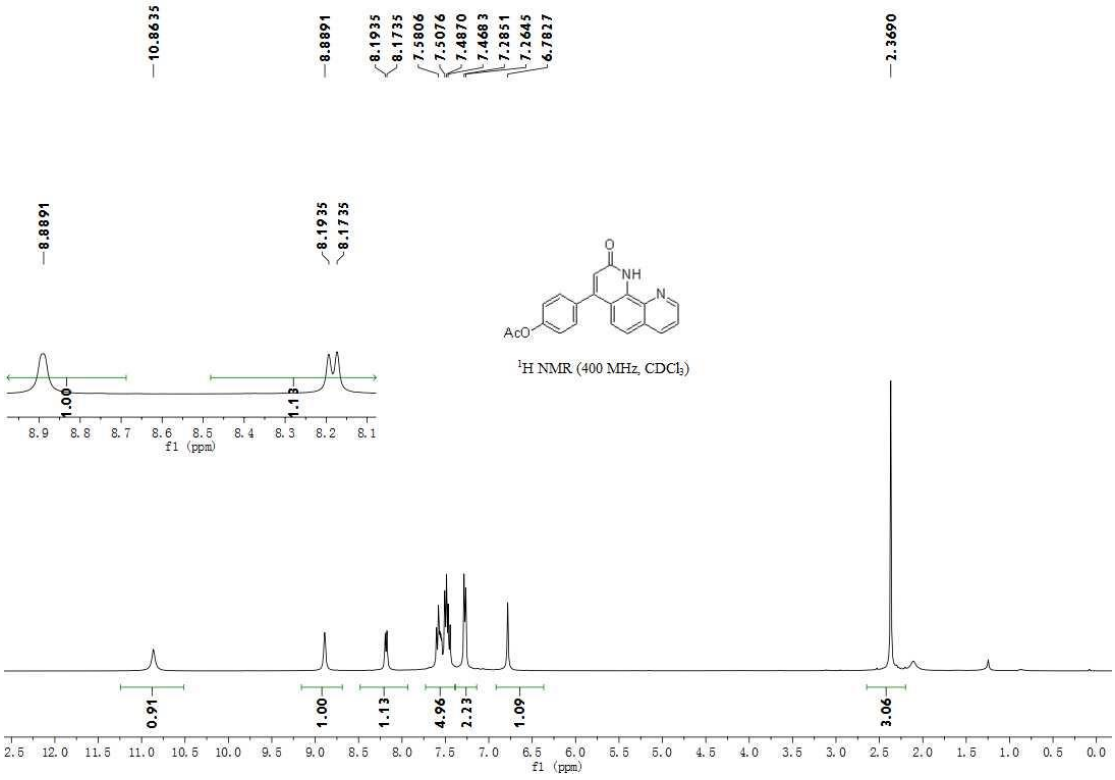
^{1}H NMR spectrum (400 MHz) of compound **3n** in $CDCl_3$



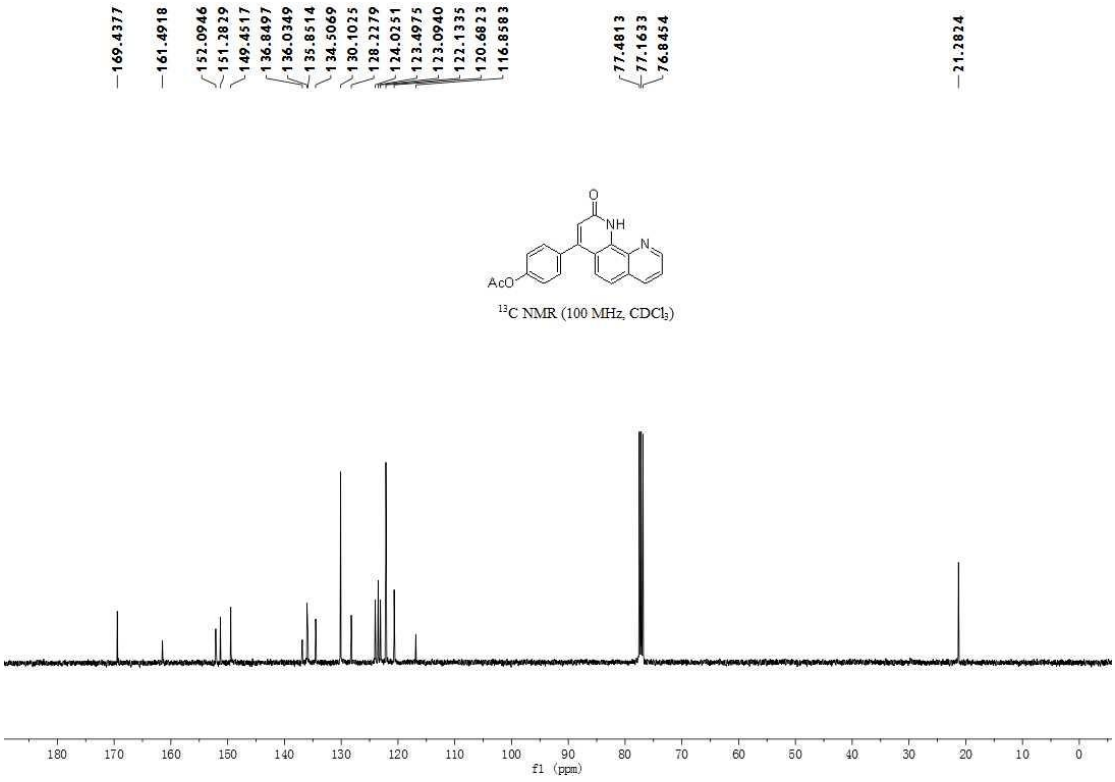
^{13}C NMR spectrum (100 MHz) of compound **3n** in $CDCl_3$



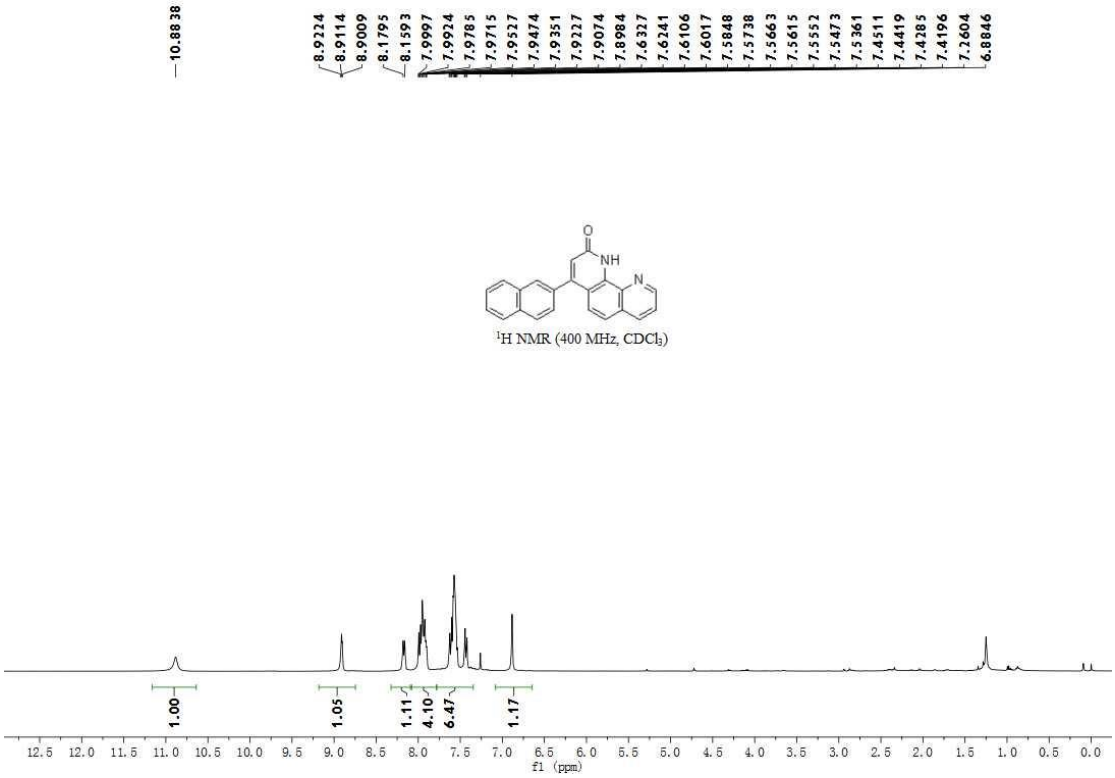
^{1}H NMR spectrum (400 MHz) of compound **3o** in $CDCl_3$



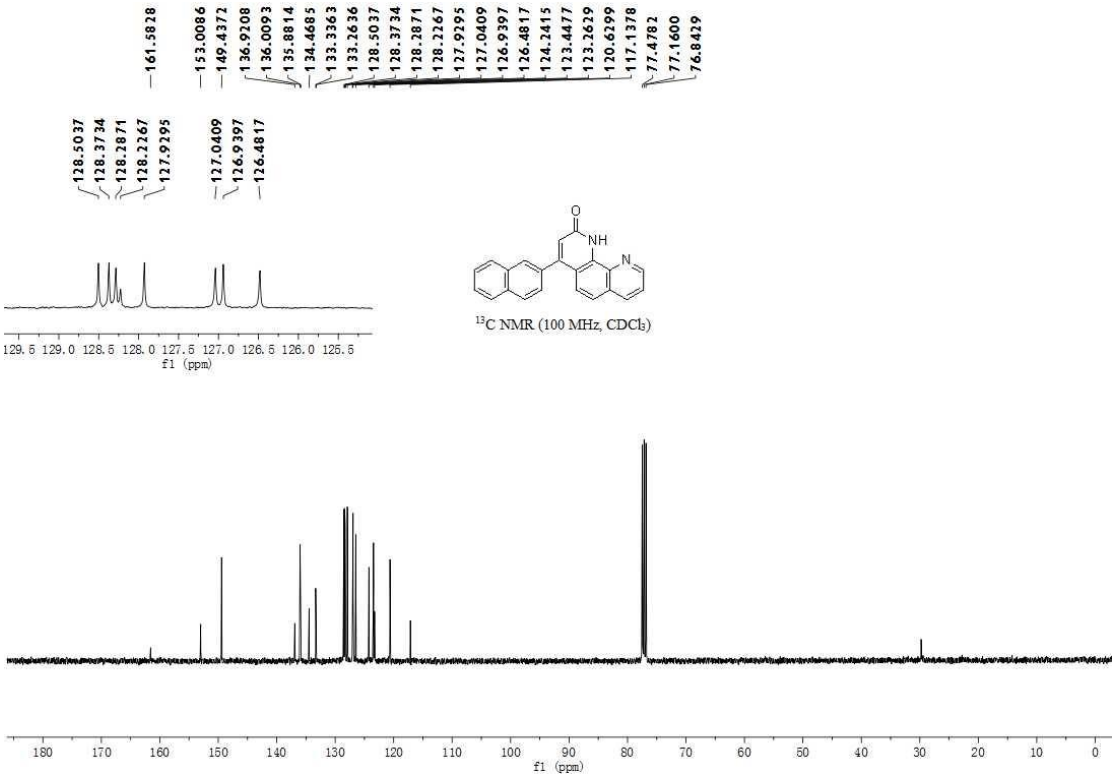
^{13}C NMR spectrum (100 MHz) of compound **3o** in $CDCl_3$



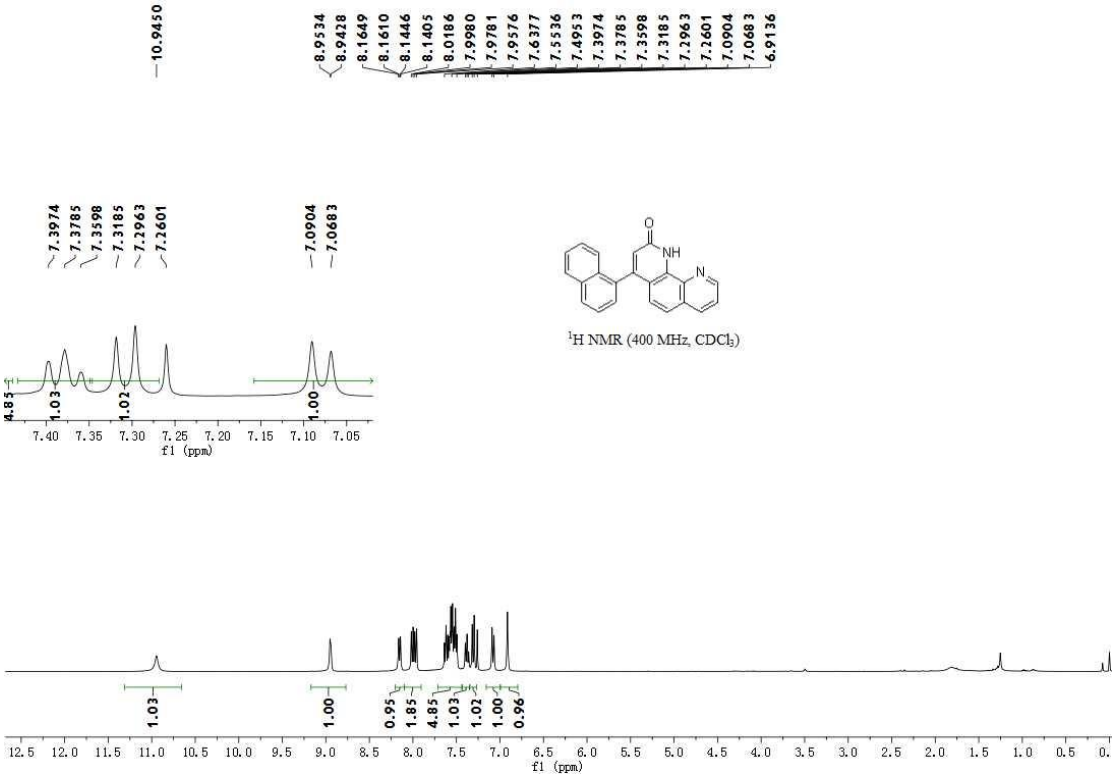
^{1}H NMR spectrum (400 MHz) of compound **3p** in $CDCl_3$



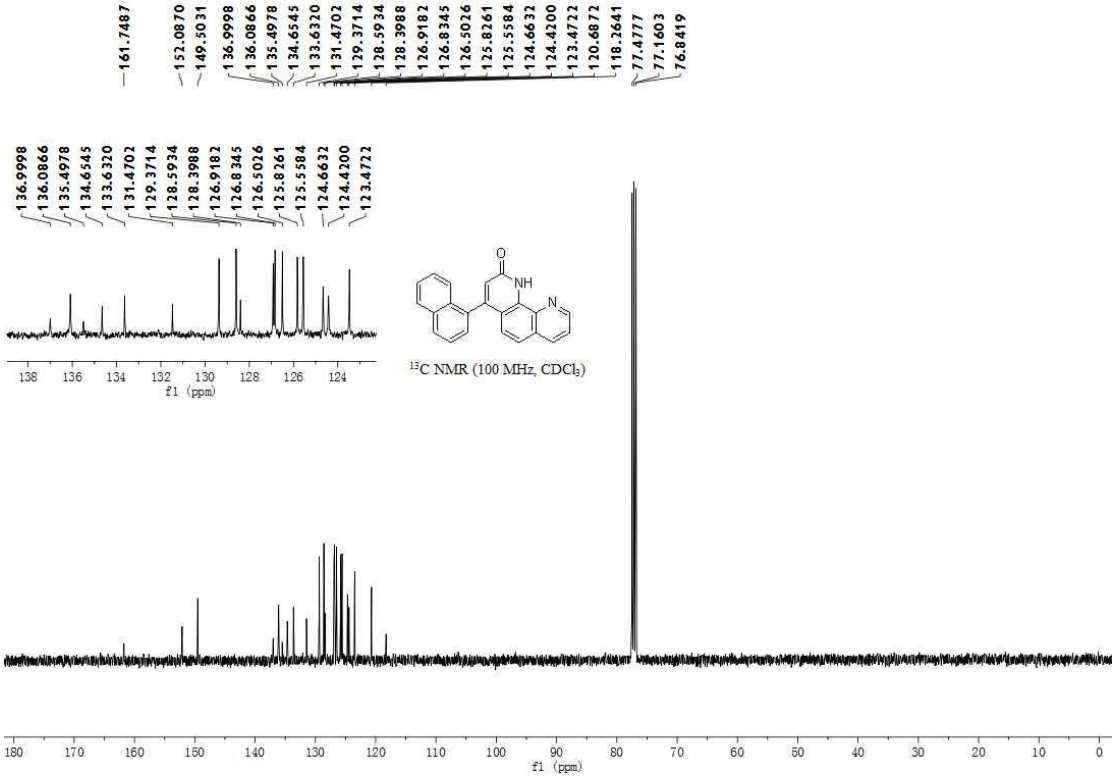
^{13}C NMR spectrum (100 MHz) of compound **3p** in $CDCl_3$



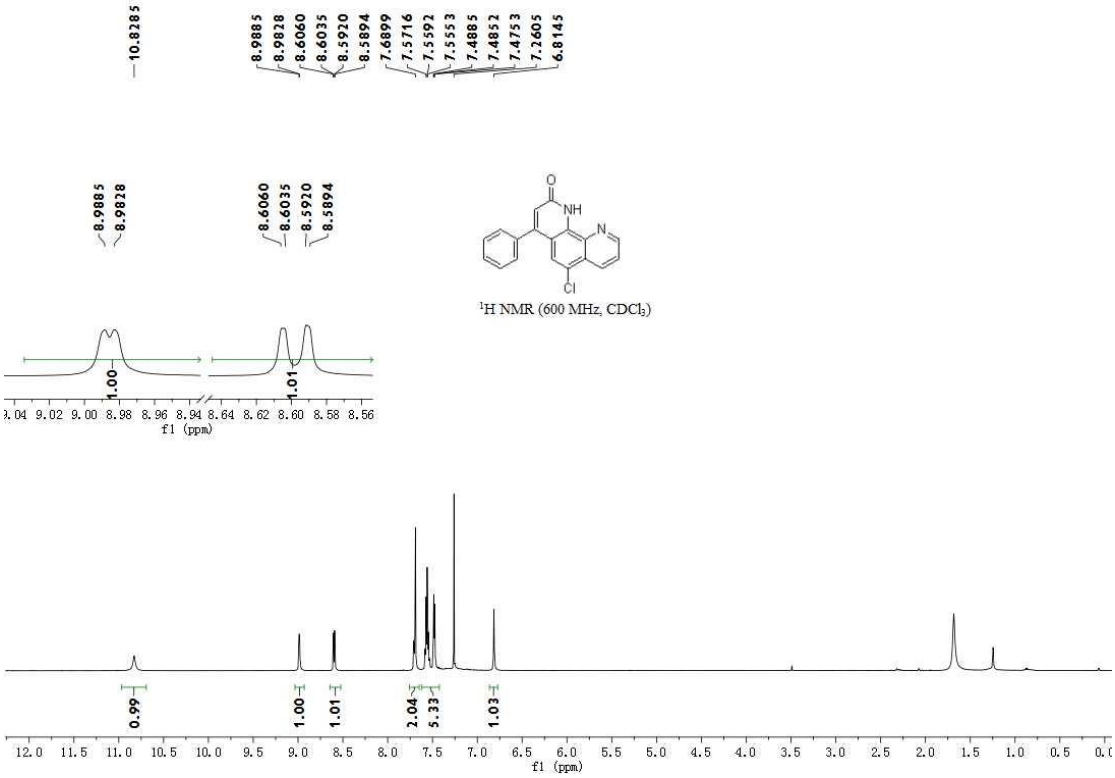
^{1}H NMR spectrum (400 MHz) of compound **3q** in $CDCl_3$



^{13}C NMR spectrum (100 MHz) of compound **3q** in $CDCl_3$

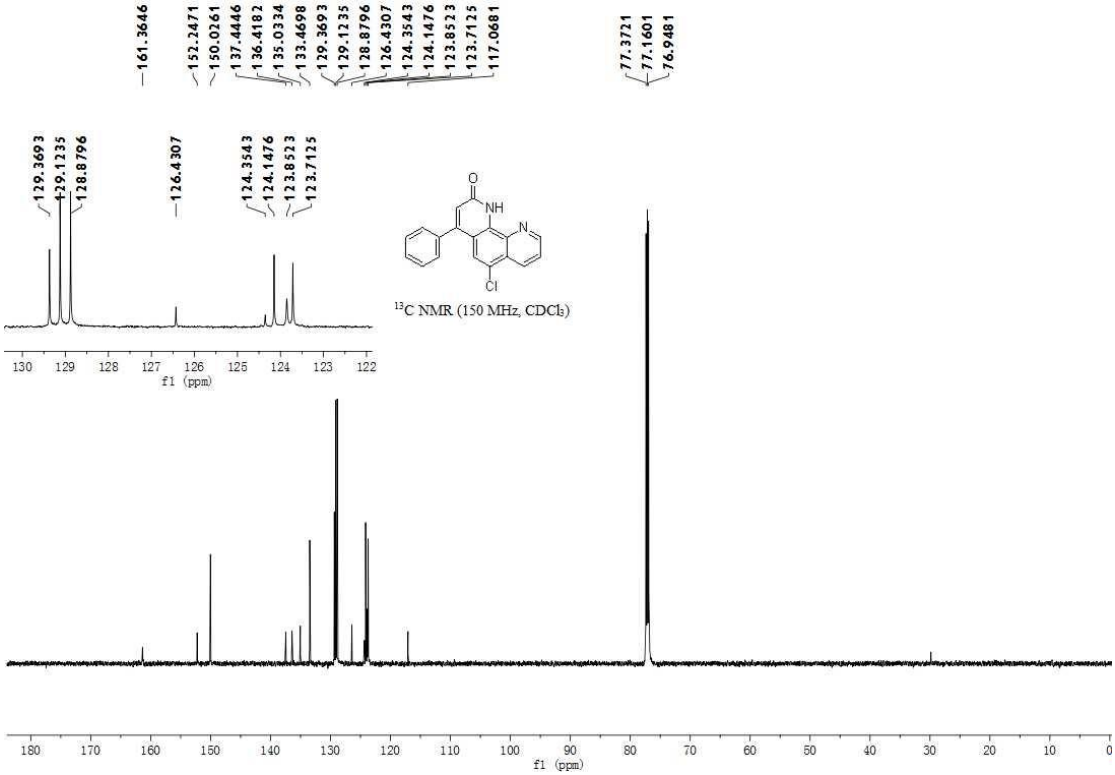


^{1}H NMR spectrum (400 MHz) of compound **3v** in $CDCl_3$



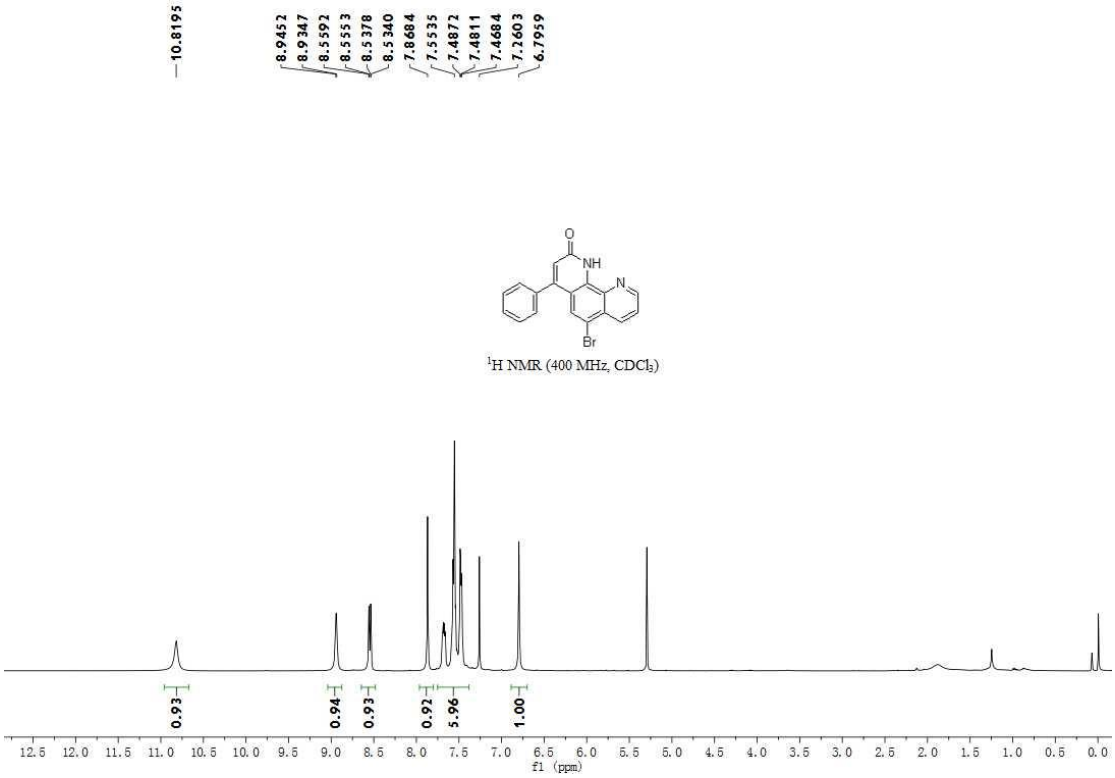
^{1}H NMR (600 MHz, $CDCl_3$)

^{13}C NMR spectrum (100 MHz) of compound **3v** in $CDCl_3$

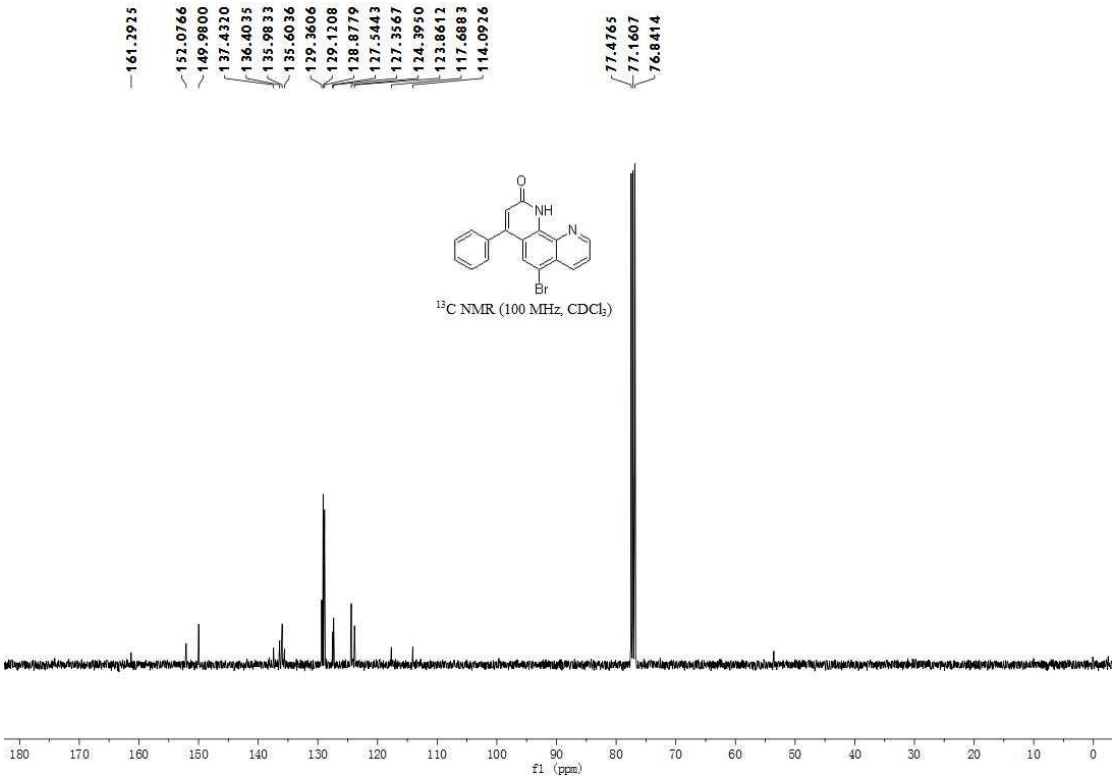


^{13}C NMR (150 MHz, $CDCl_3$)

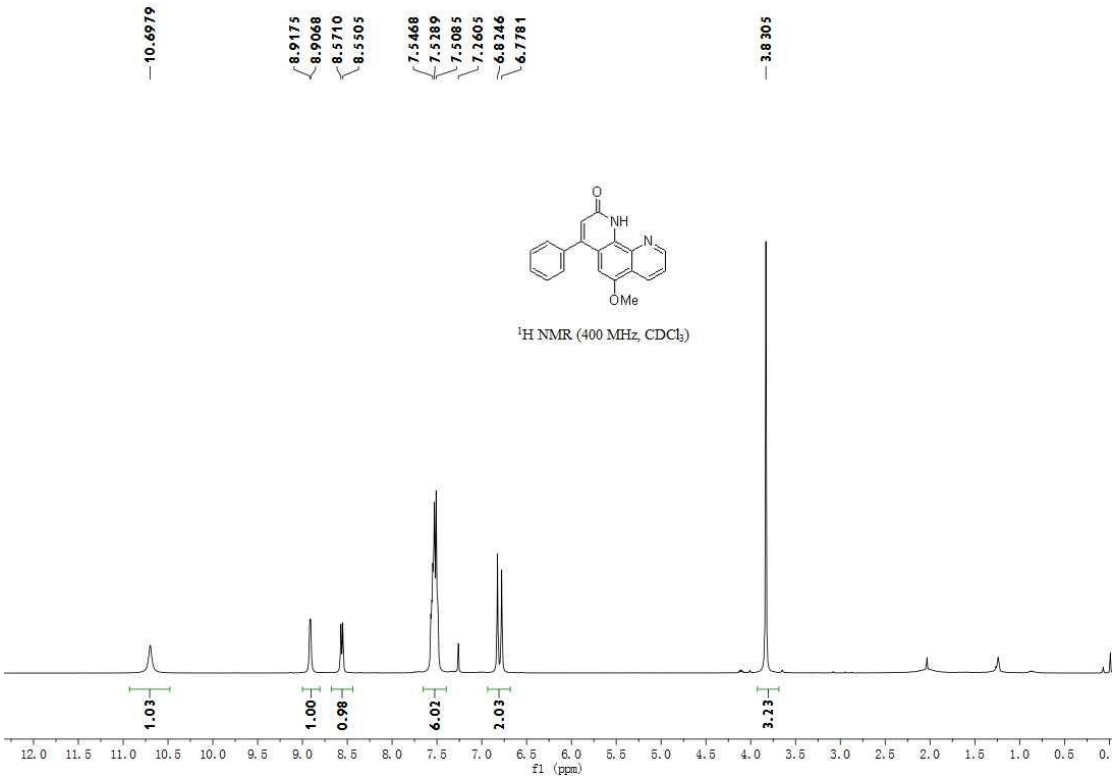
^{1}H NMR spectrum (400 MHz) of compound **3w** in $CDCl_3$



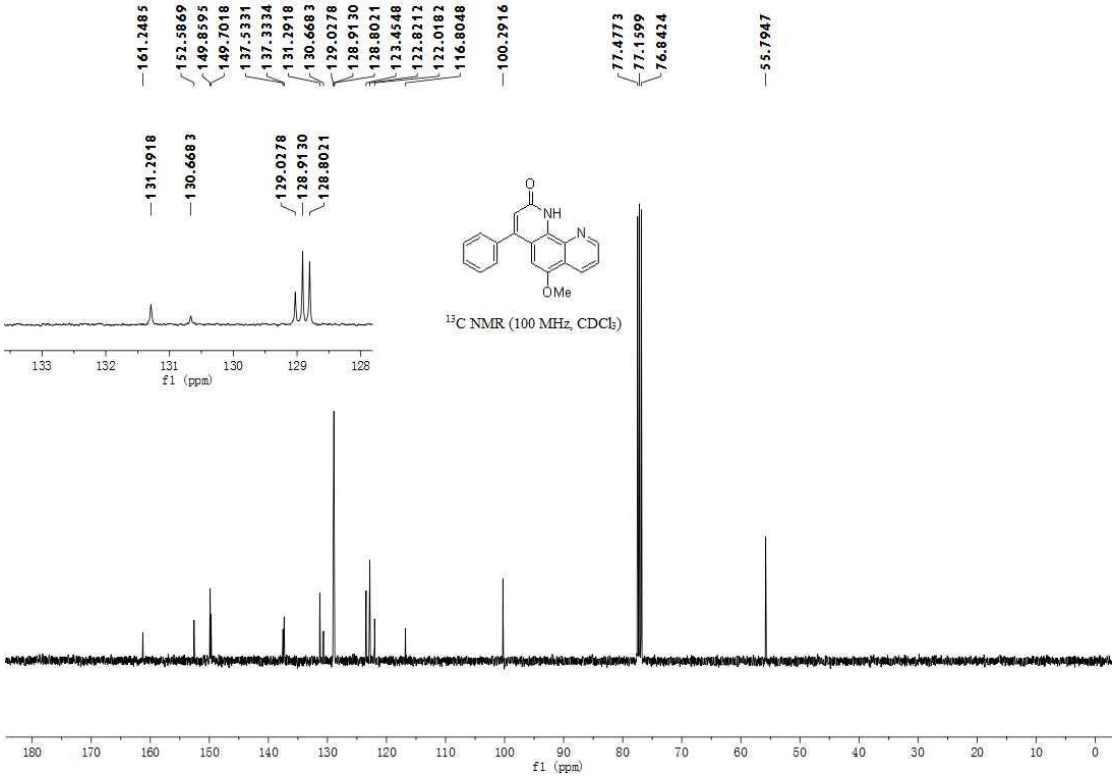
^{13}C NMR spectrum (100 MHz) of compound **3w** in $CDCl_3$



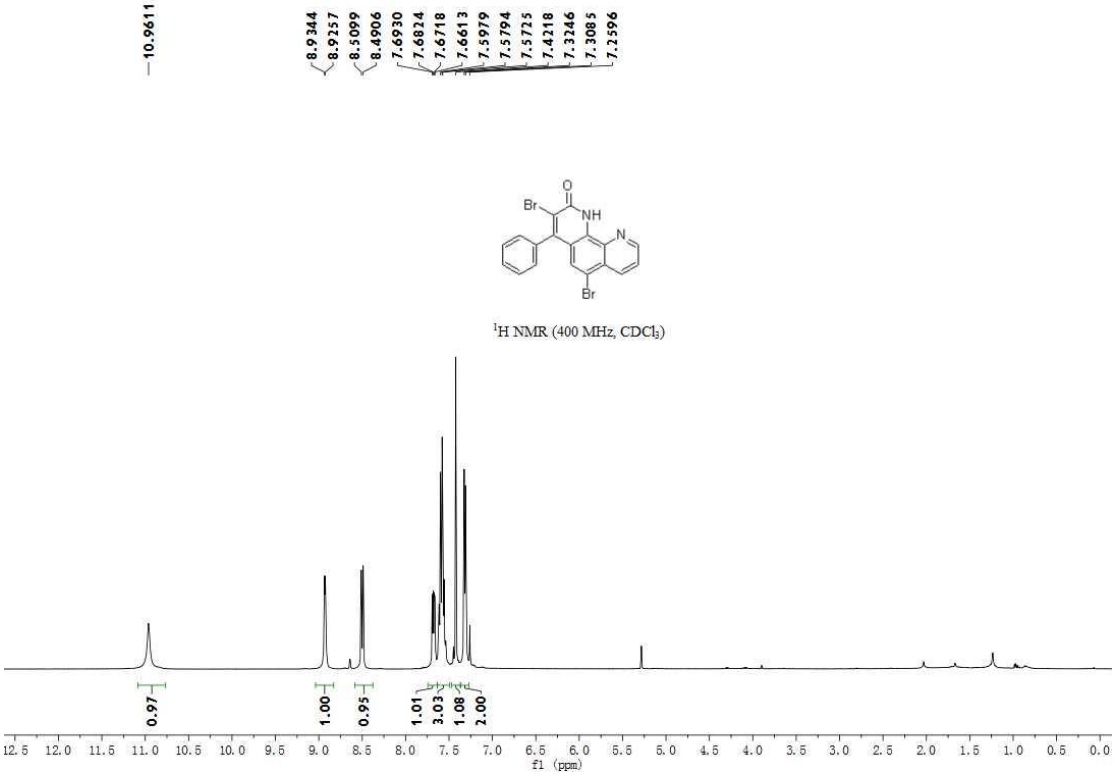
^{1}H NMR spectrum (400 MHz) of compound **3x** in $CDCl_3$



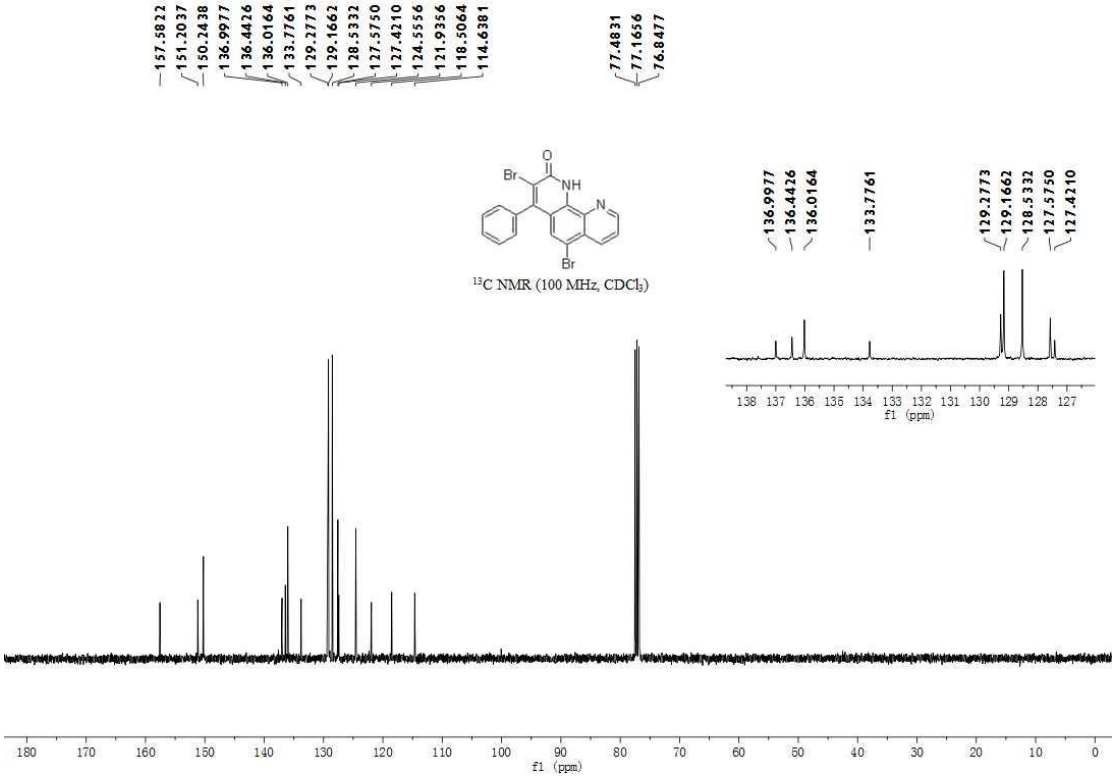
^{13}C NMR spectrum (100 MHz) of compound **3x** in $CDCl_3$



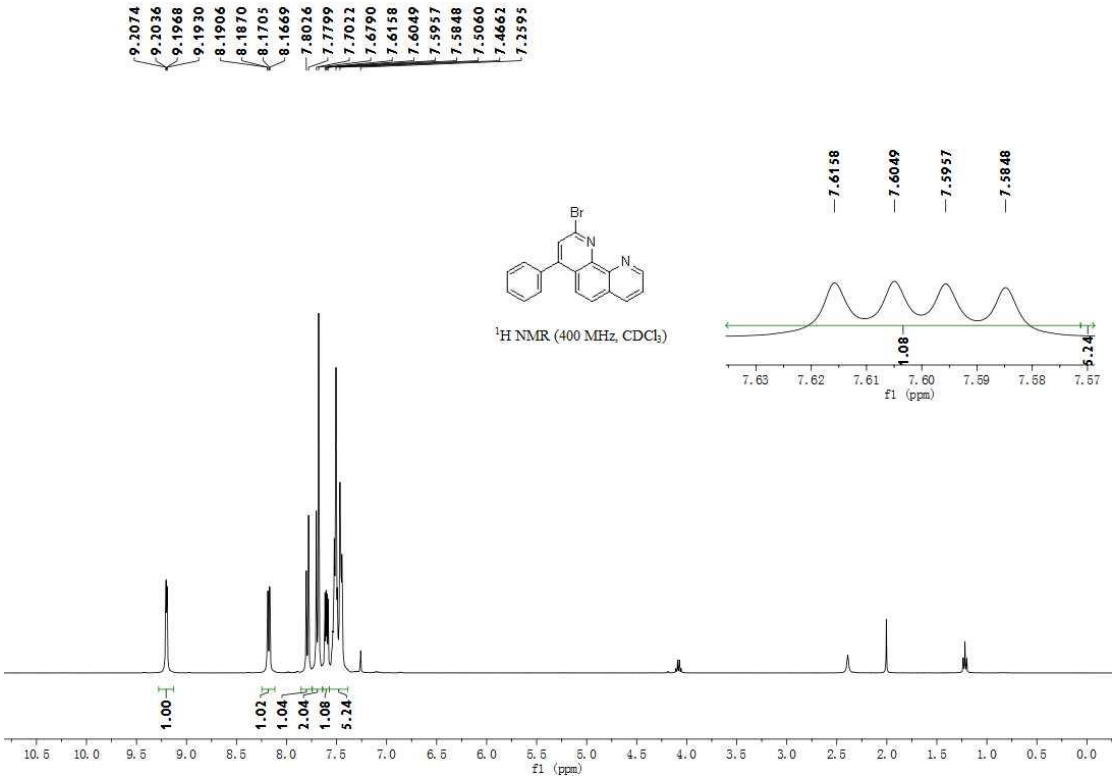
^{1}H NMR spectrum (400 MHz) of compound **9** in $CDCl_3$



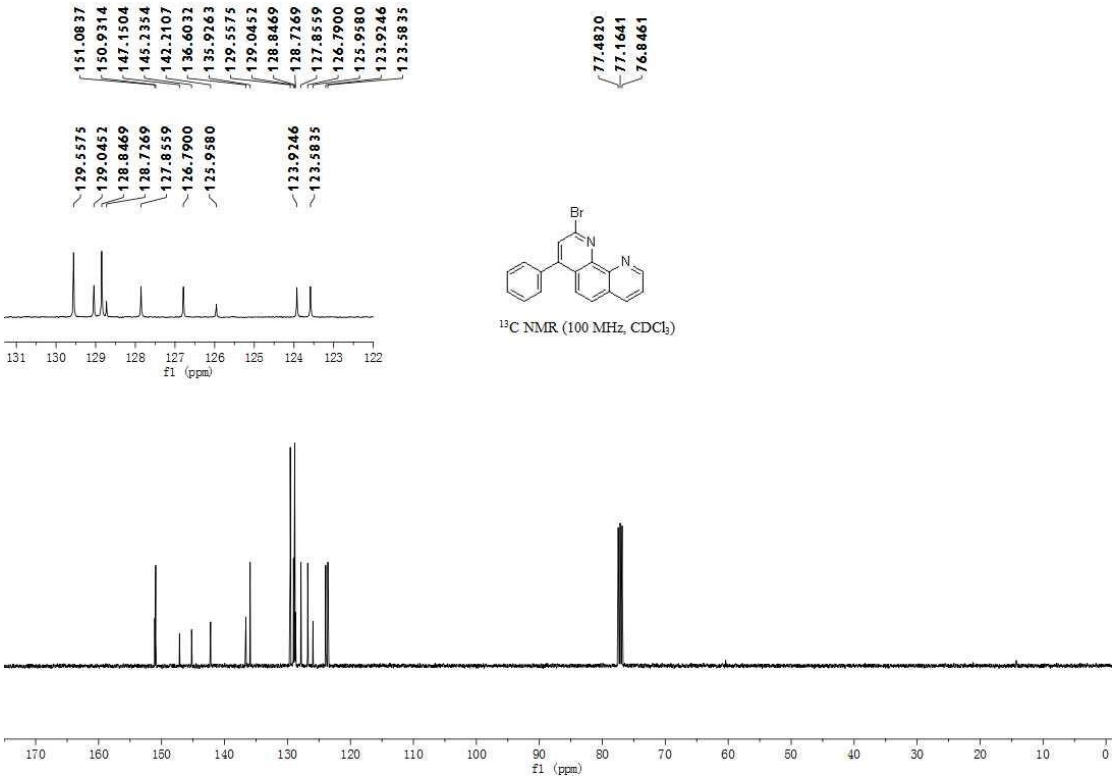
^{13}C NMR spectrum (100 MHz) of compound **9** in $CDCl_3$



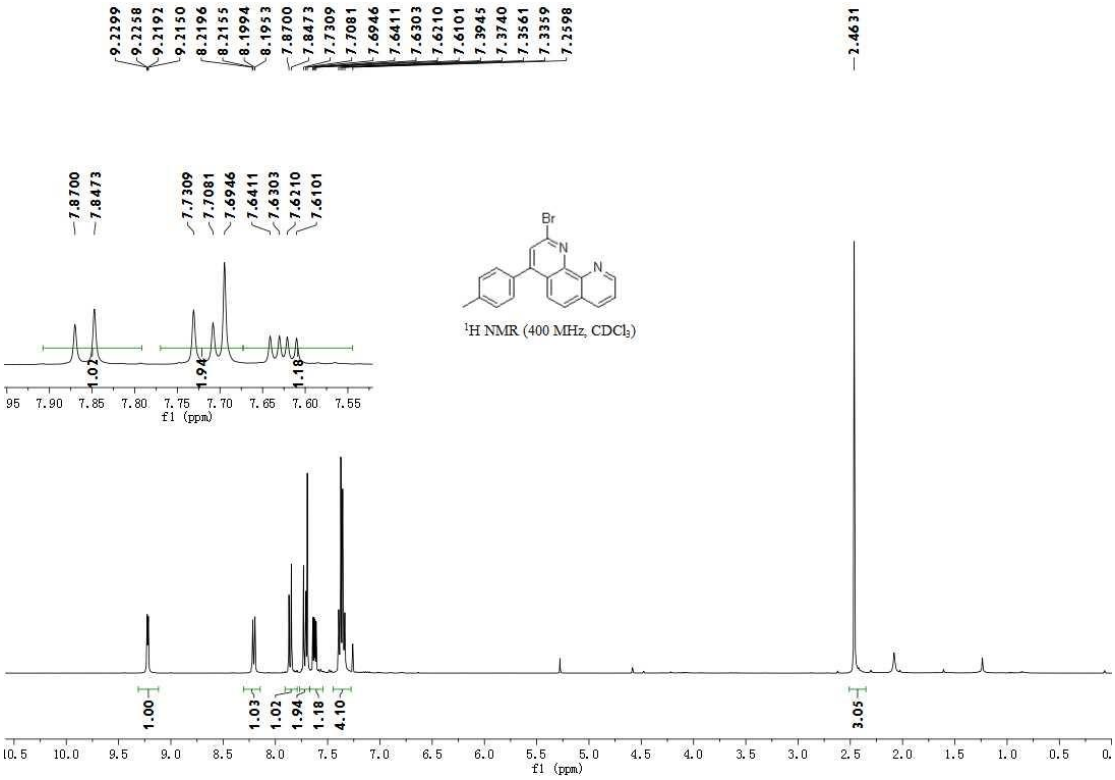
^{1}H NMR spectrum (400 MHz) of compound **5a** in $CDCl_3$



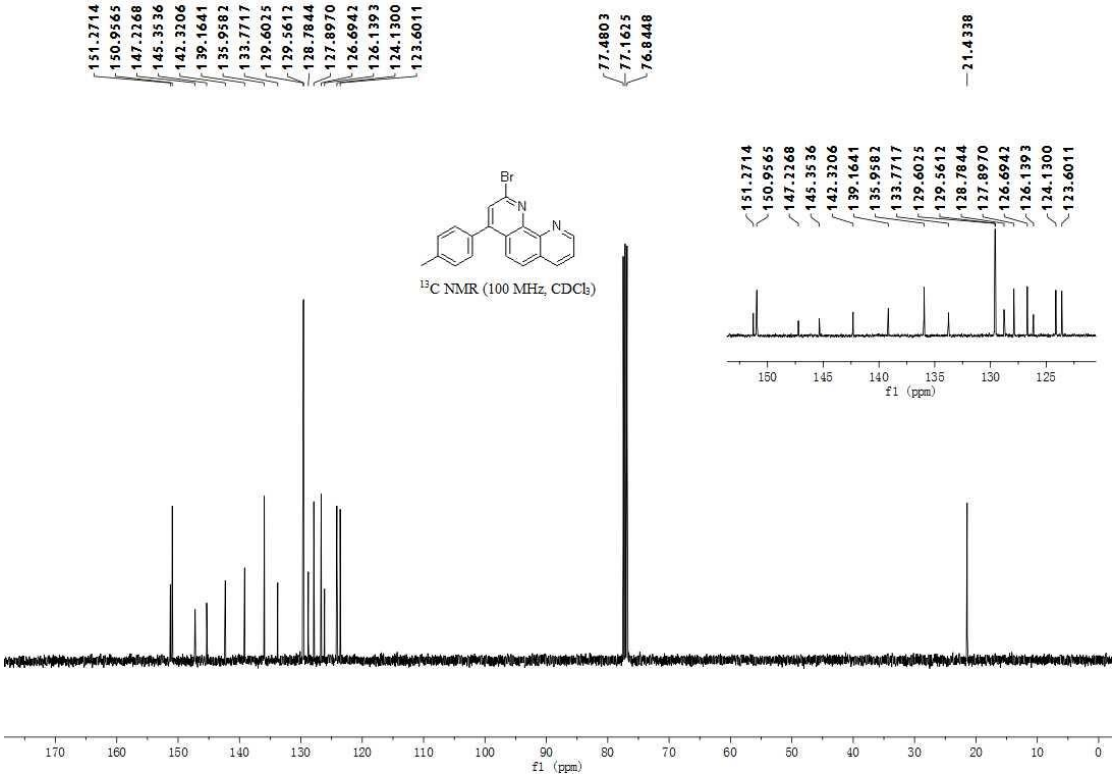
^{13}C NMR spectrum (100 MHz) of compound **5a** in $CDCl_3$



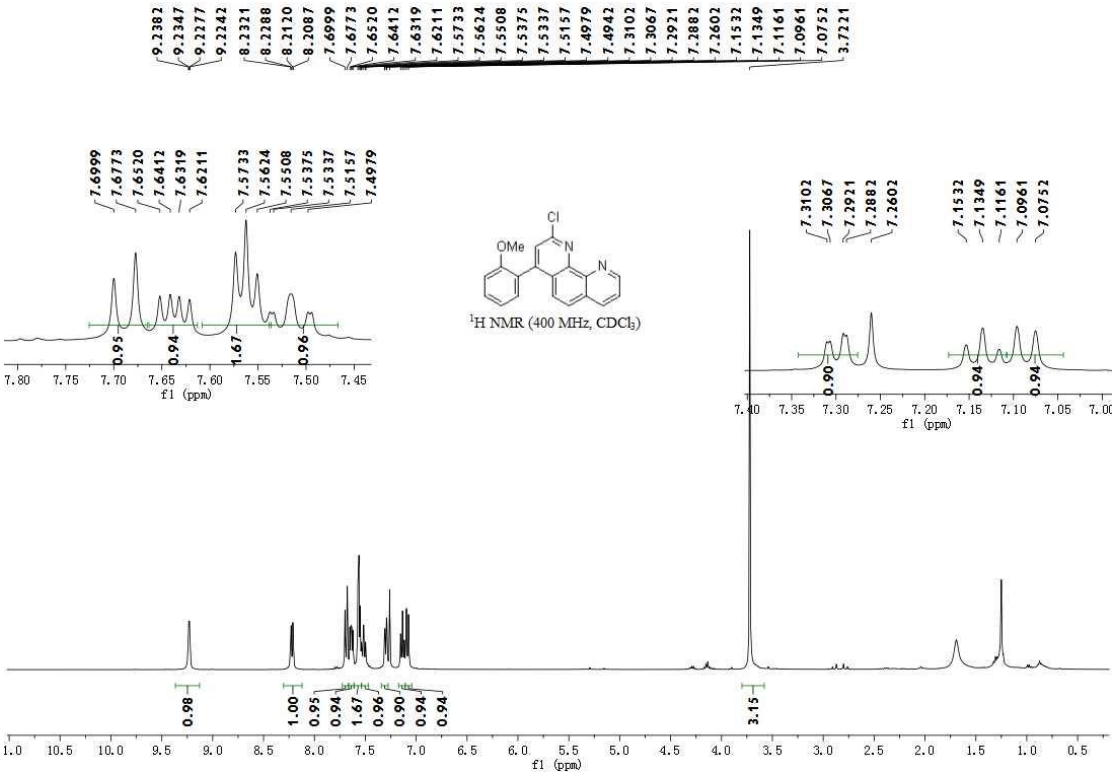
^{1}H NMR spectrum (400 MHz) of compound **5b** in $CDCl_3$



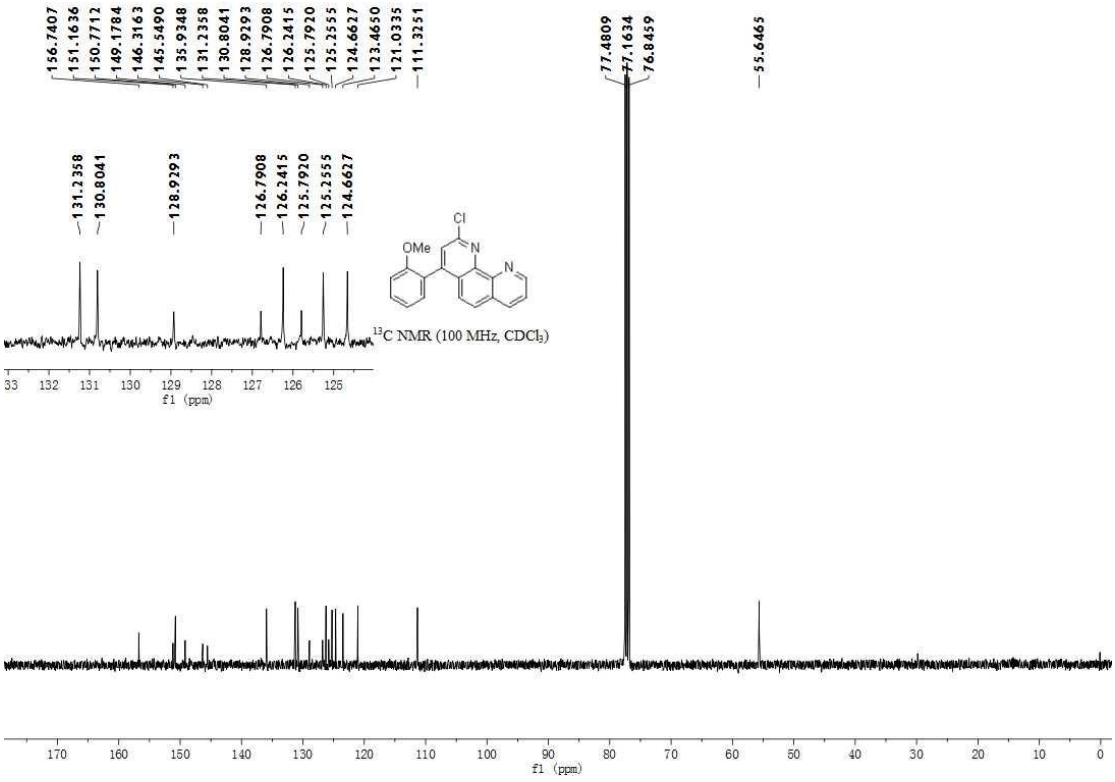
^{13}C NMR spectrum (100 MHz) of compound **5b** in $CDCl_3$



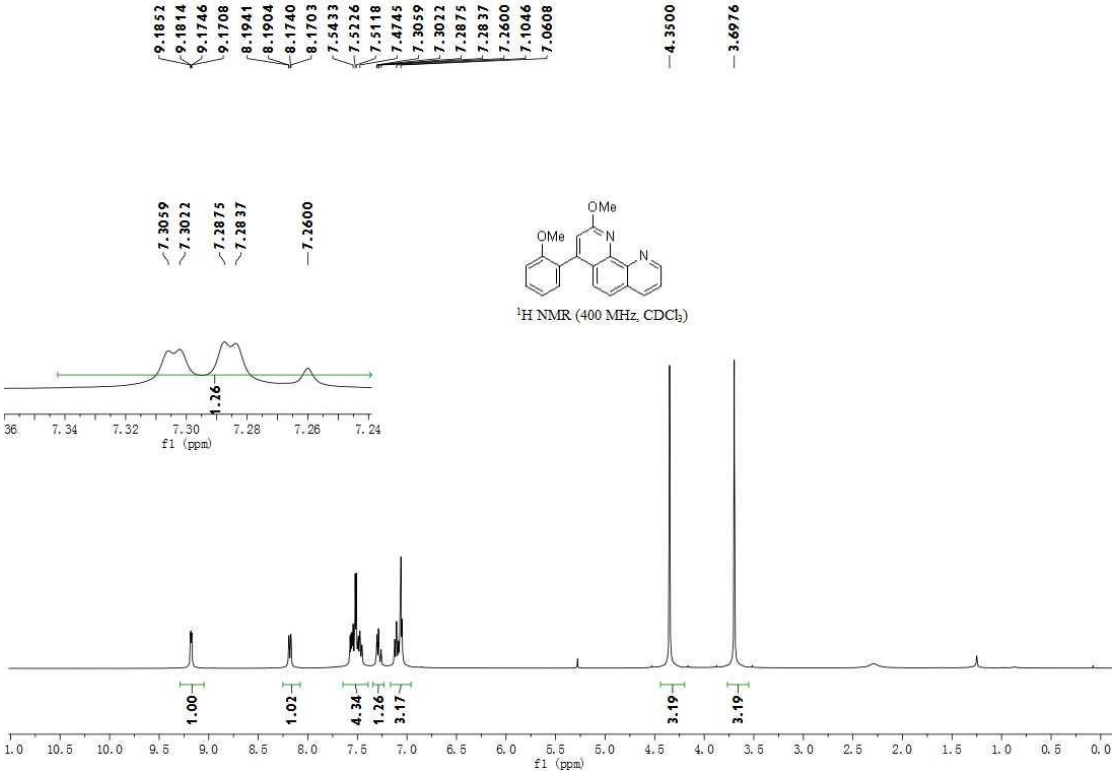
^{1}H NMR spectrum (400 MHz) of compound **5c** in $CDCl_3$



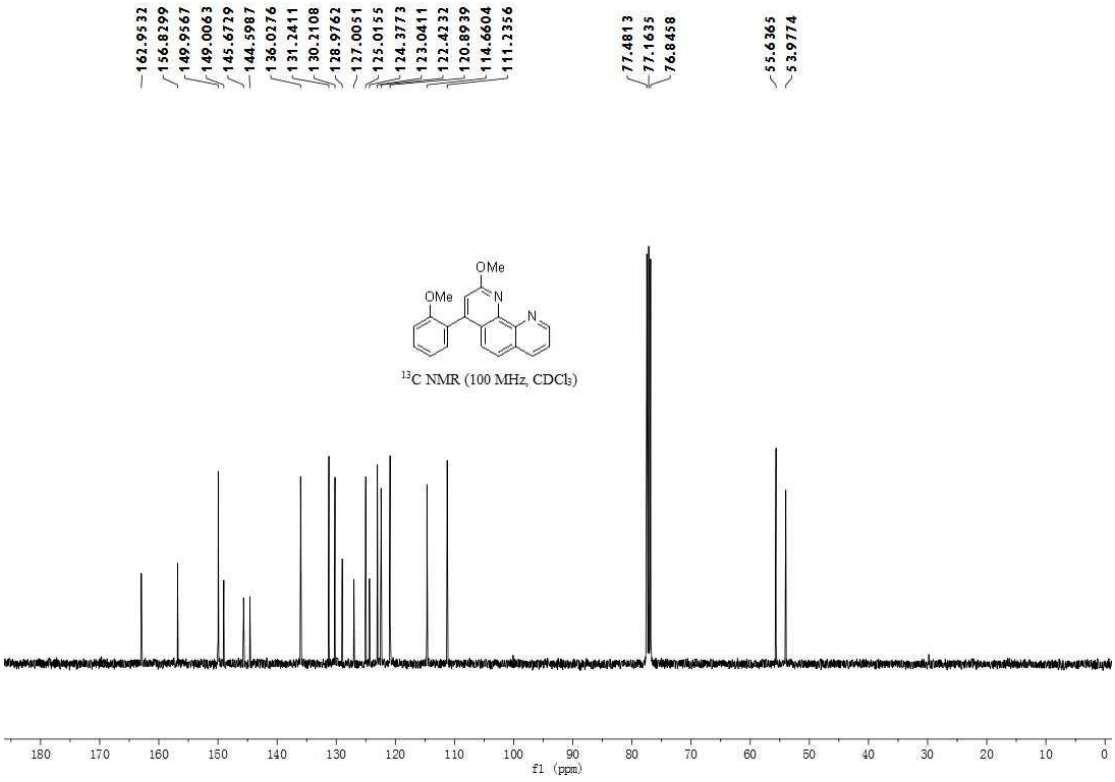
^{13}C NMR spectrum (100 MHz) of compound **5c** in $CDCl_3$



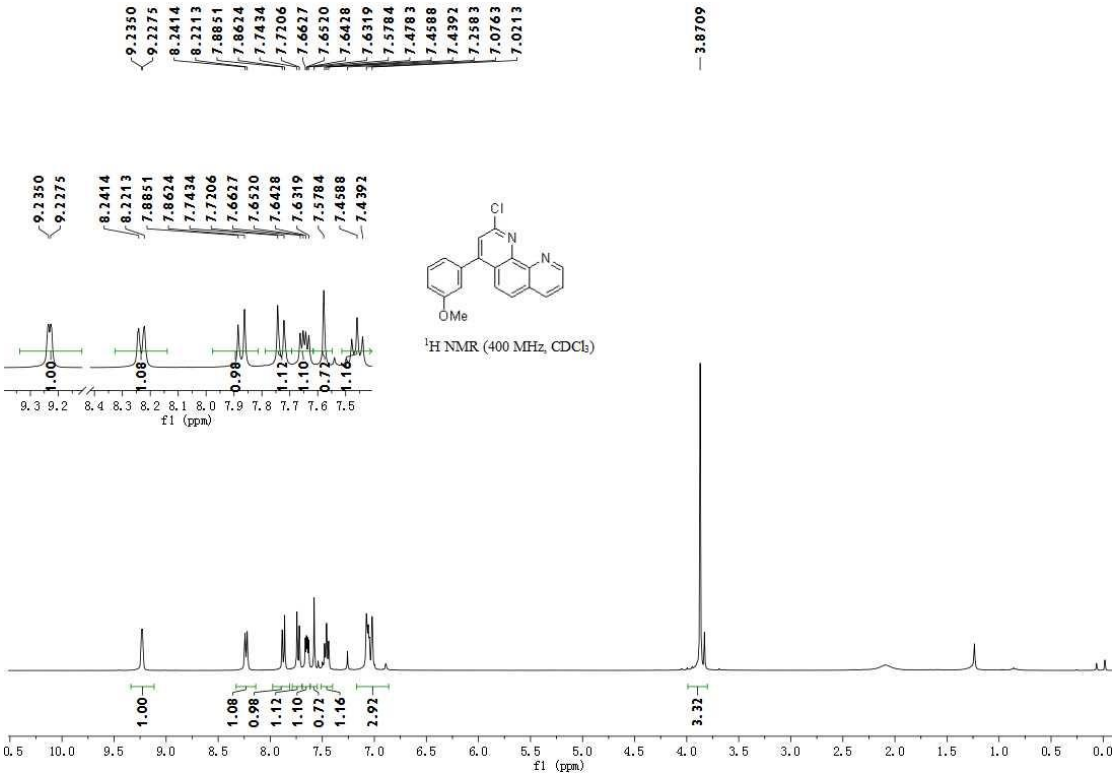
^{1}H NMR spectrum (400 MHz) of compound **14** in $CDCl_3$



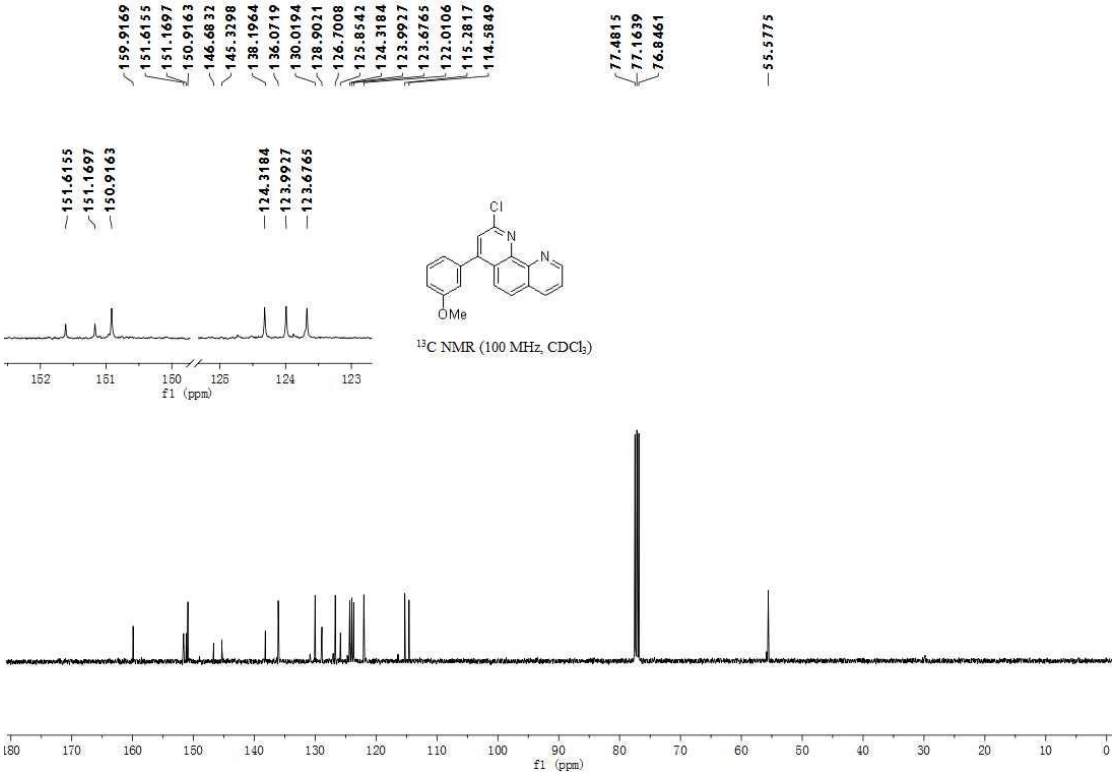
^{13}C NMR spectrum (100 MHz) of compound **14** in $CDCl_3$



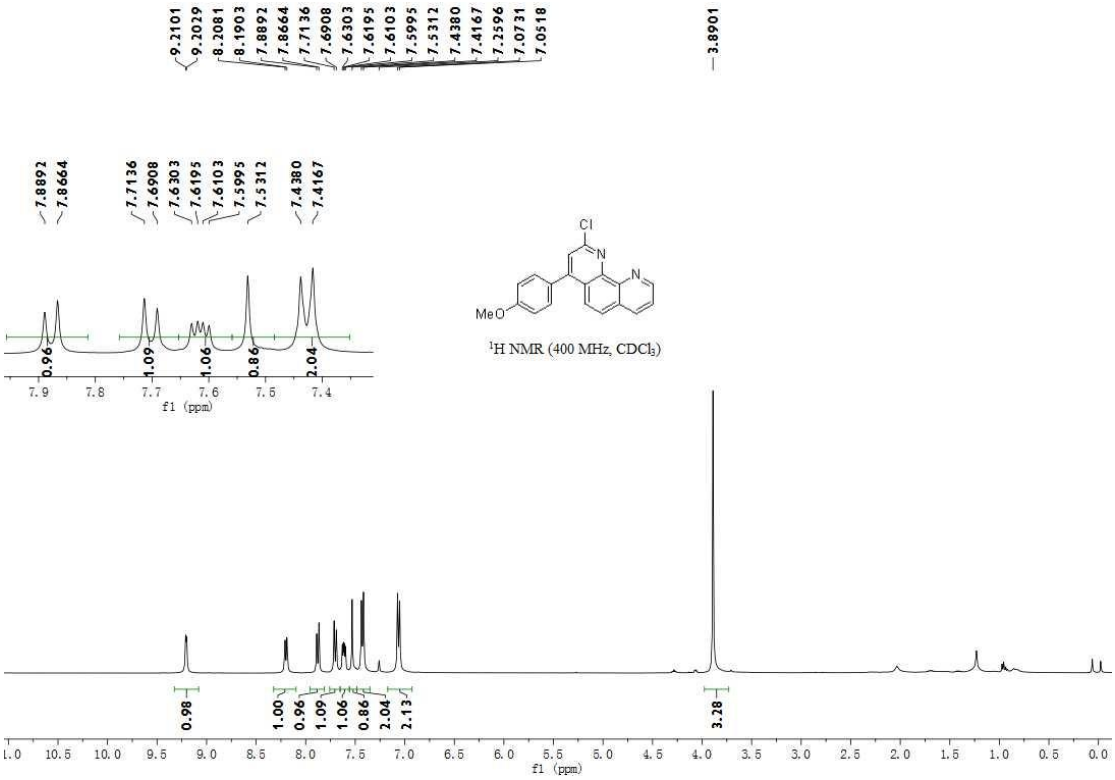
^{1}H NMR spectrum (400 MHz) of compound **5d** in $CDCl_3$



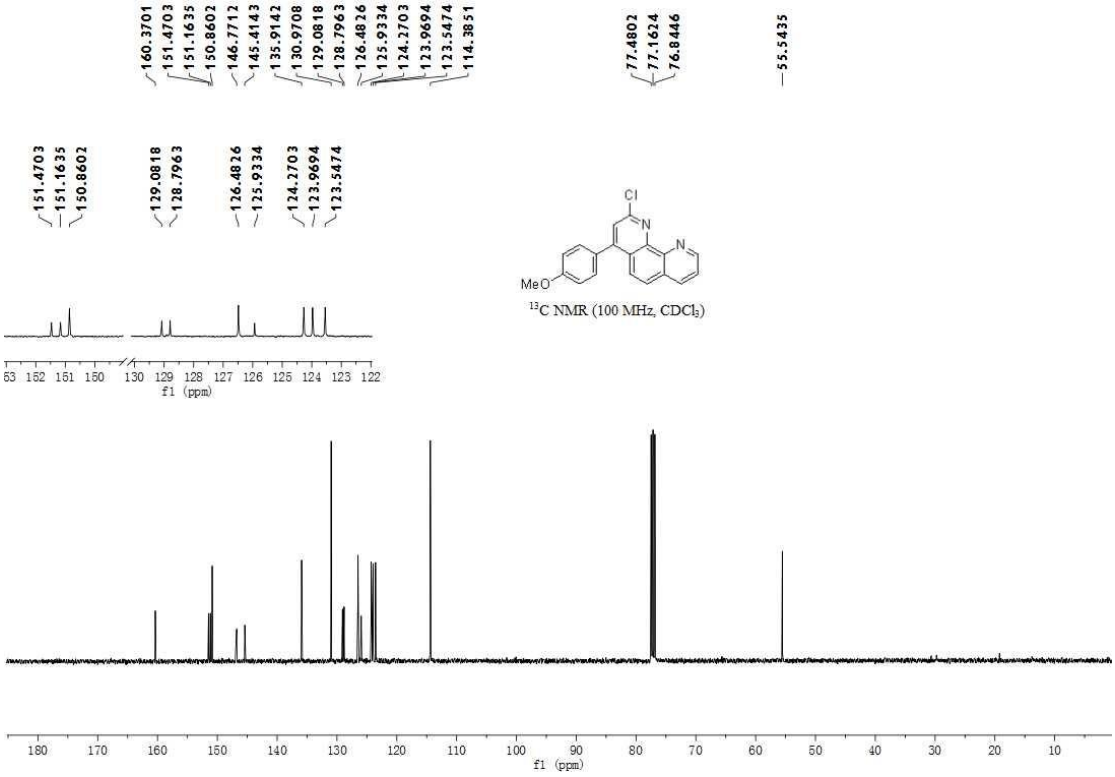
^{13}C NMR spectrum (100 MHz) of compound **5d** in $CDCl_3$



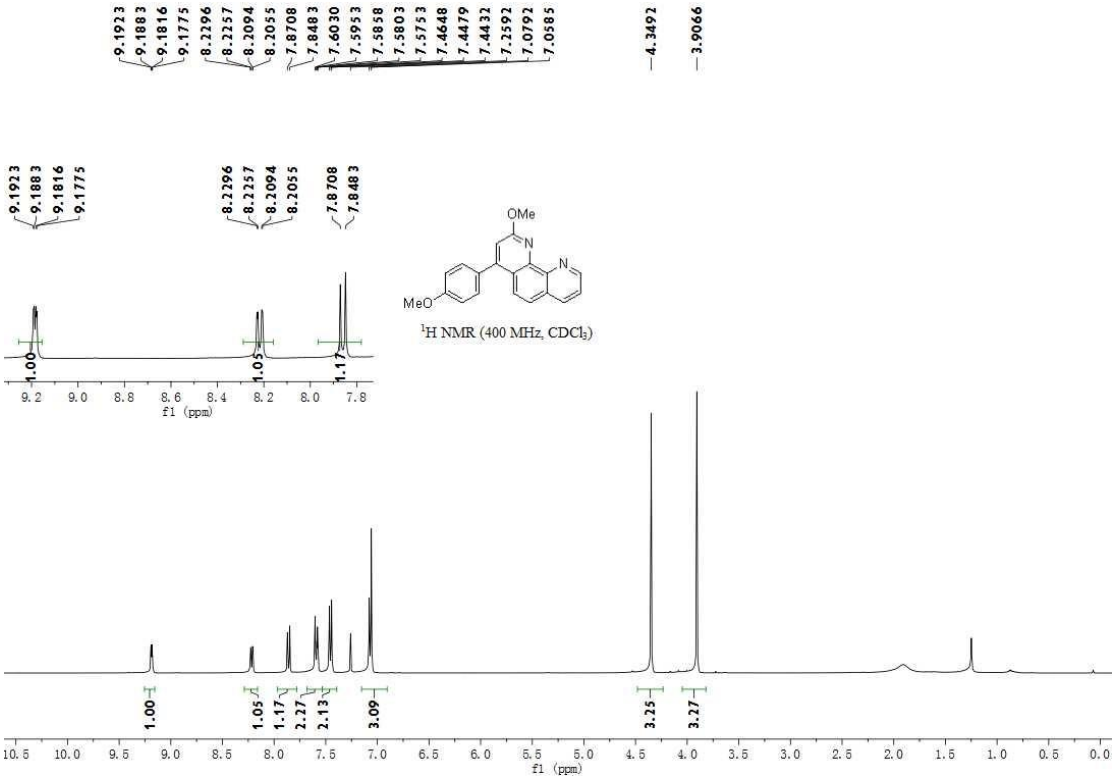
^{1}H NMR spectrum (400 MHz) of compound **5e** in $CDCl_3$



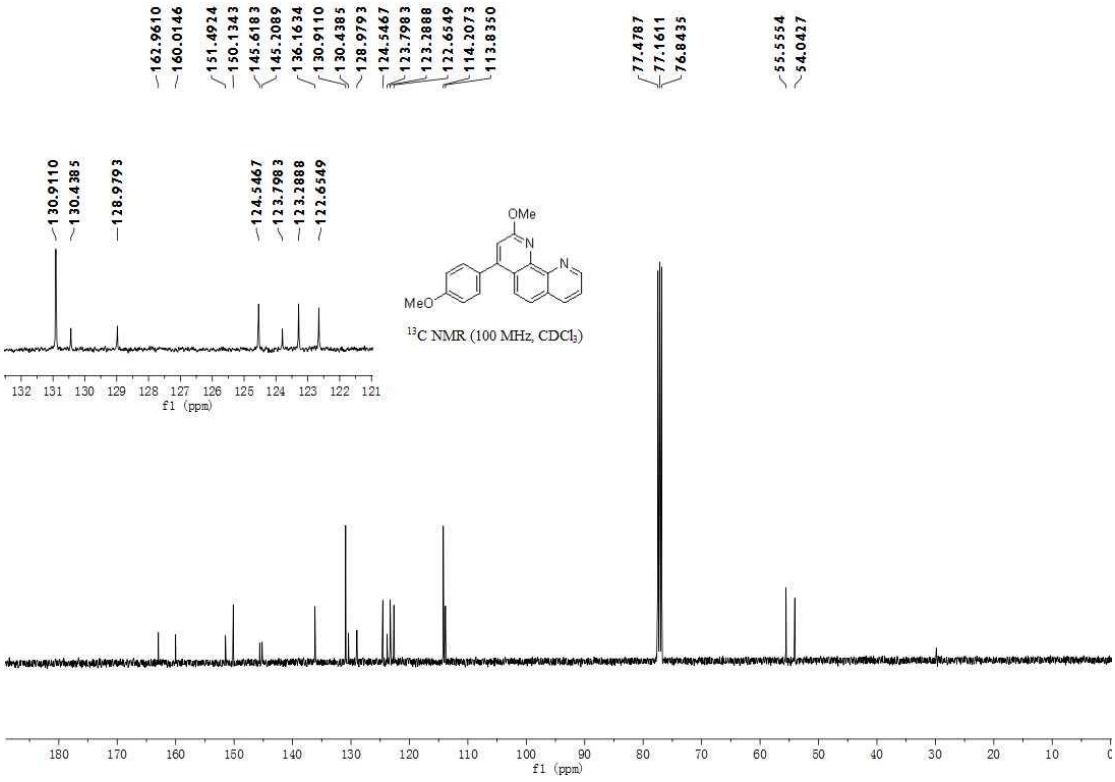
^{13}C NMR spectrum (100 MHz) of compound **5e** in $CDCl_3$



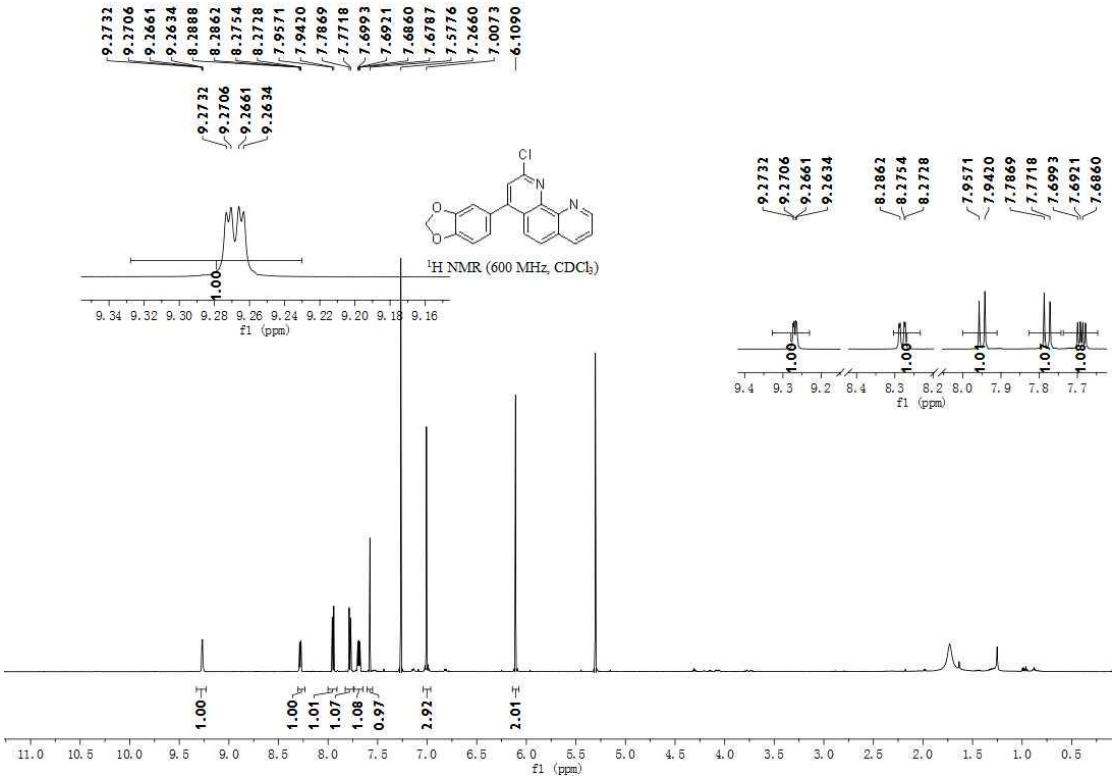
^{1}H NMR spectrum (400 MHz) of compound **15** in $CDCl_3$



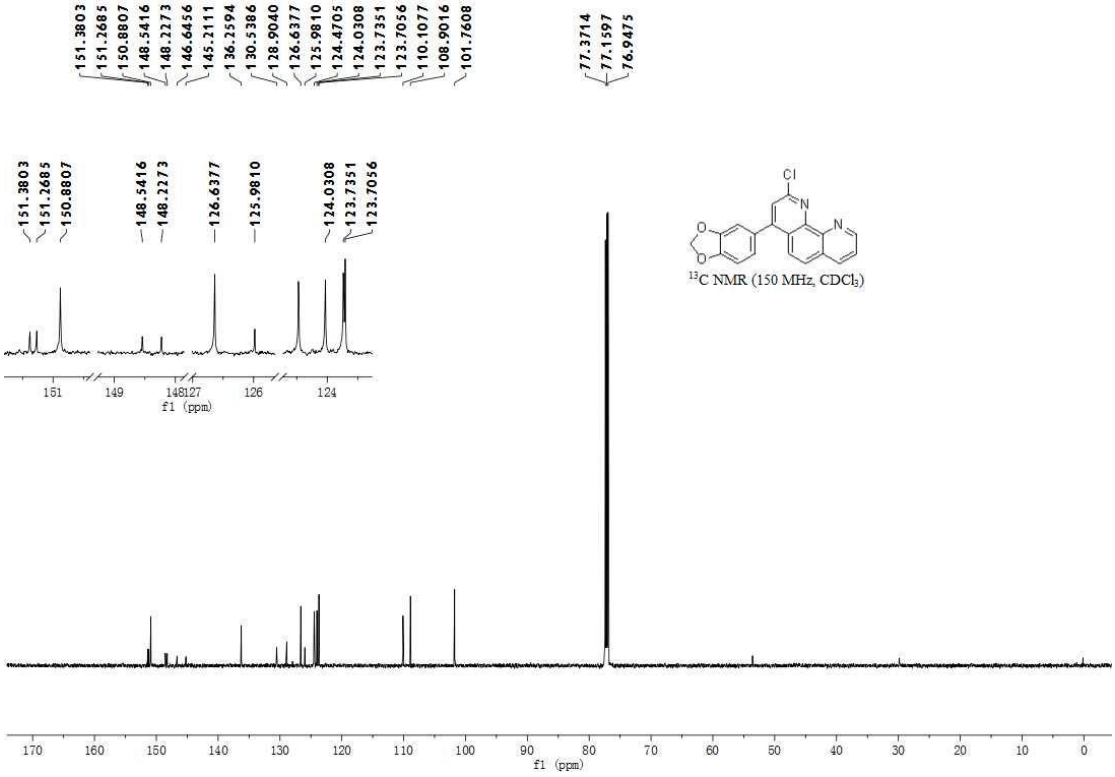
^{13}C NMR spectrum (100 MHz) of compound **15** in $CDCl_3$



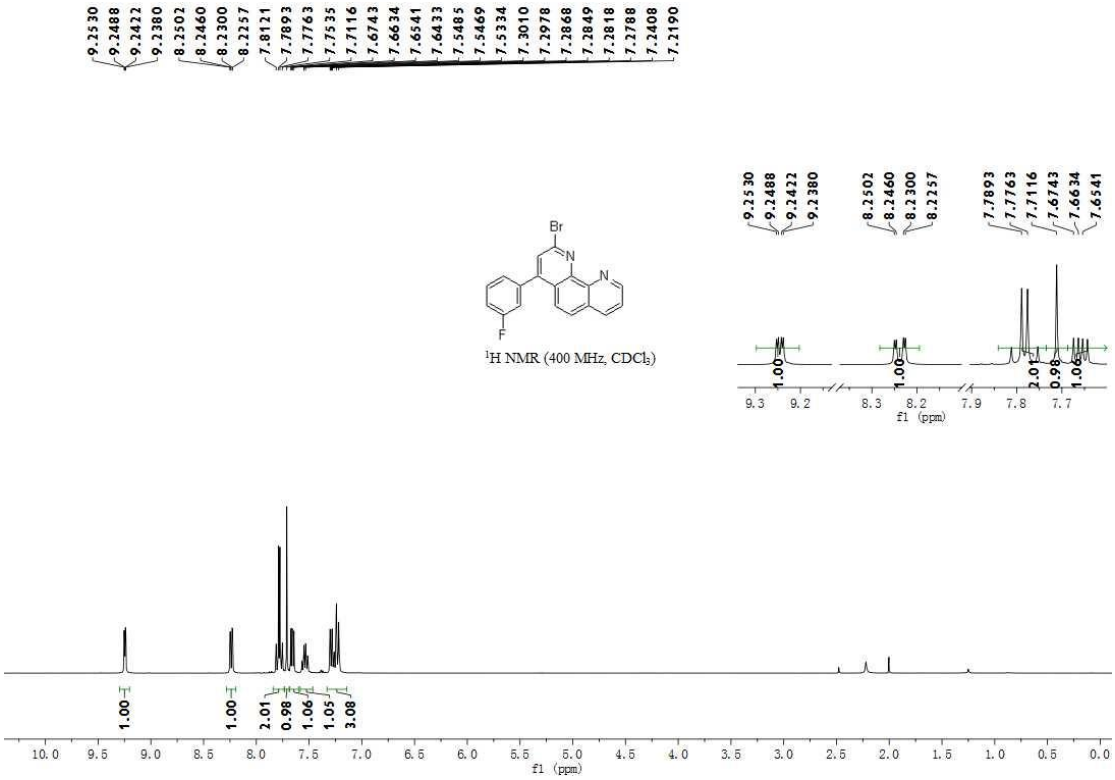
^{1}H NMR spectrum (400 MHz) of compound **5f** in $CDCl_3$



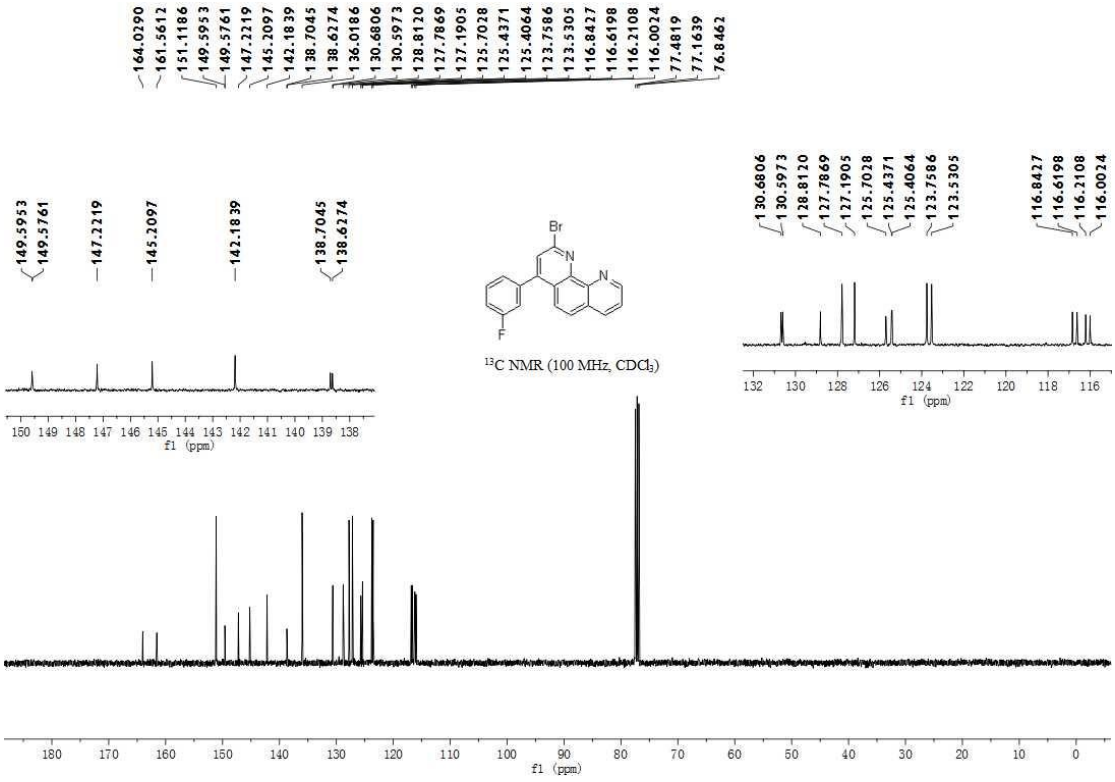
^{13}C NMR spectrum (100 MHz) of compound **5f** in $CDCl_3$



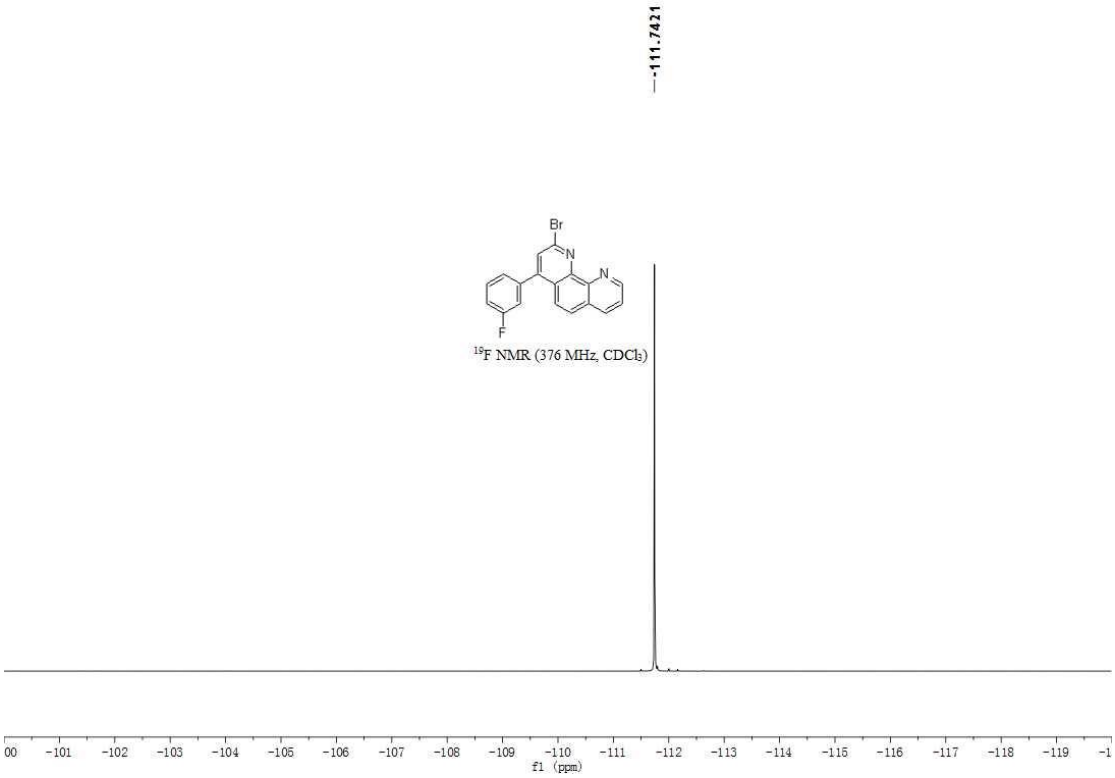
^{1}H NMR spectrum (400 MHz) of compound **5g** in $CDCl_3$



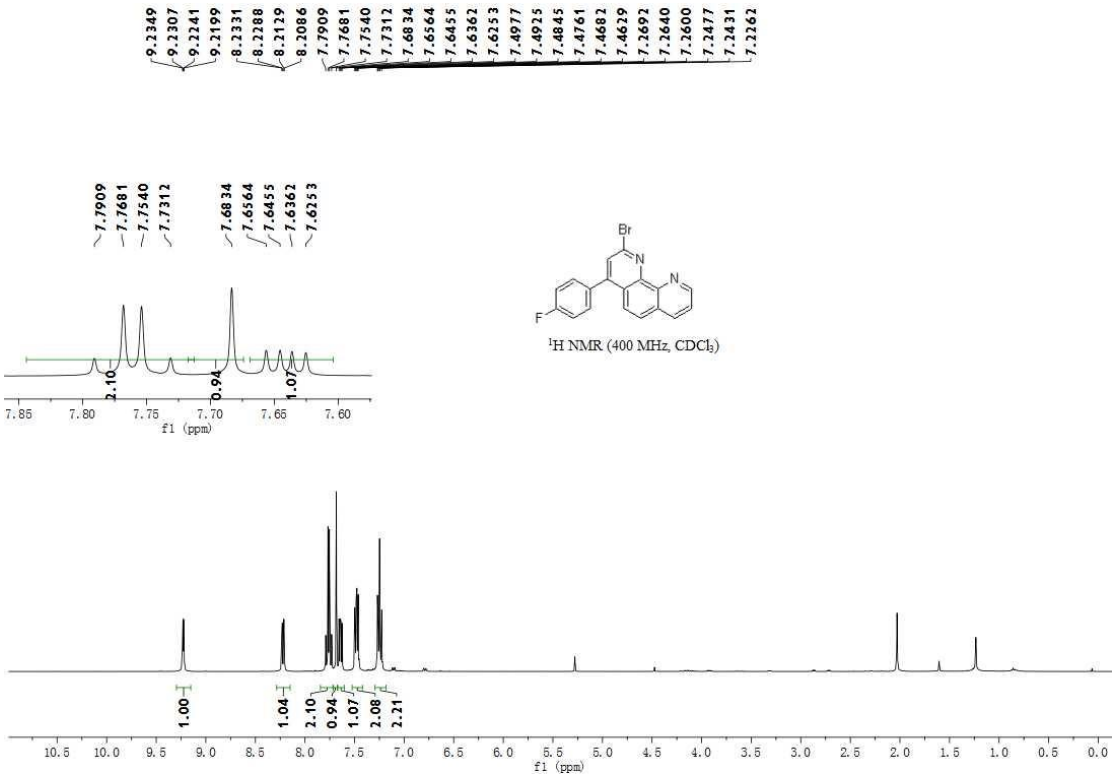
^{13}C NMR spectrum (100 MHz) of compound **5g** in $CDCl_3$



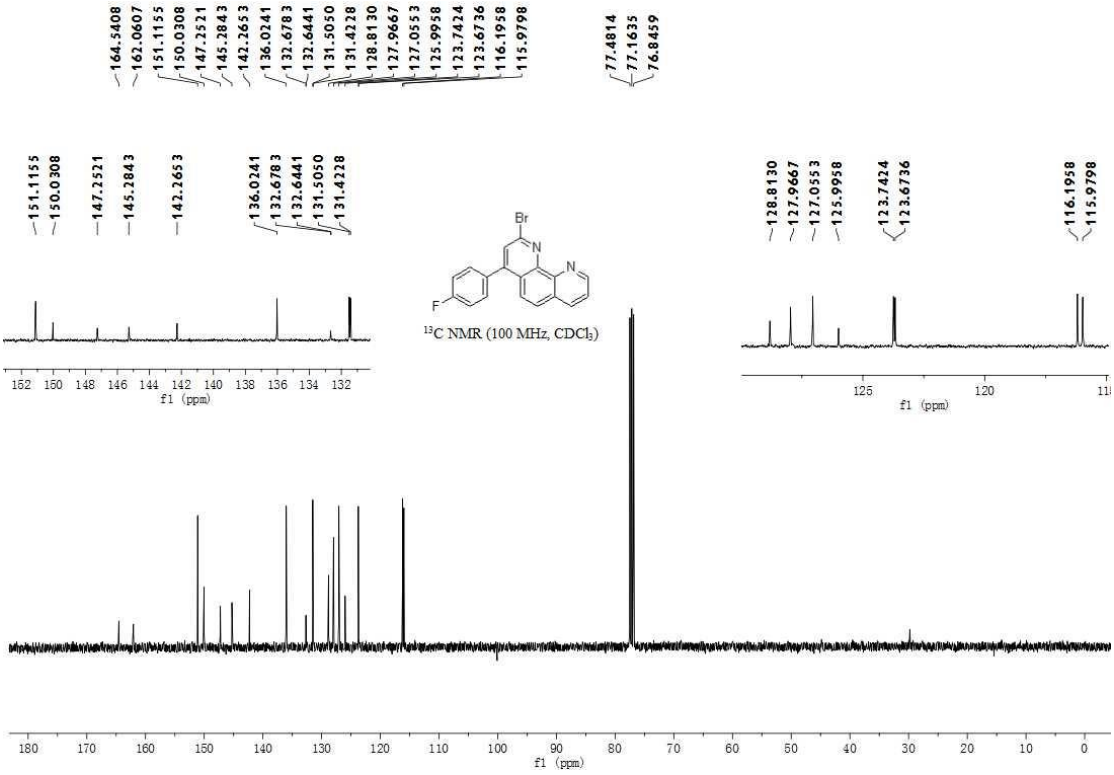
^{19}F NMR spectrum (376 MHz) of compound **5g** in $CDCl_3$



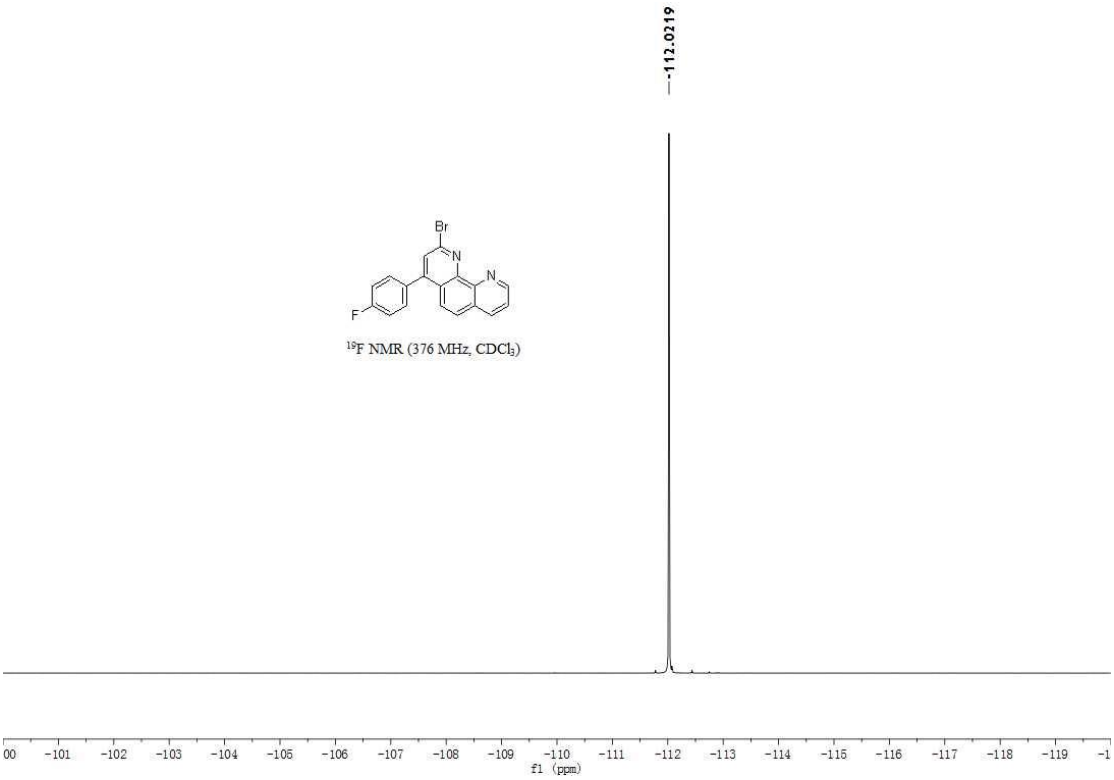
^{1}H NMR spectrum (400 MHz) of compound **5h** in $CDCl_3$



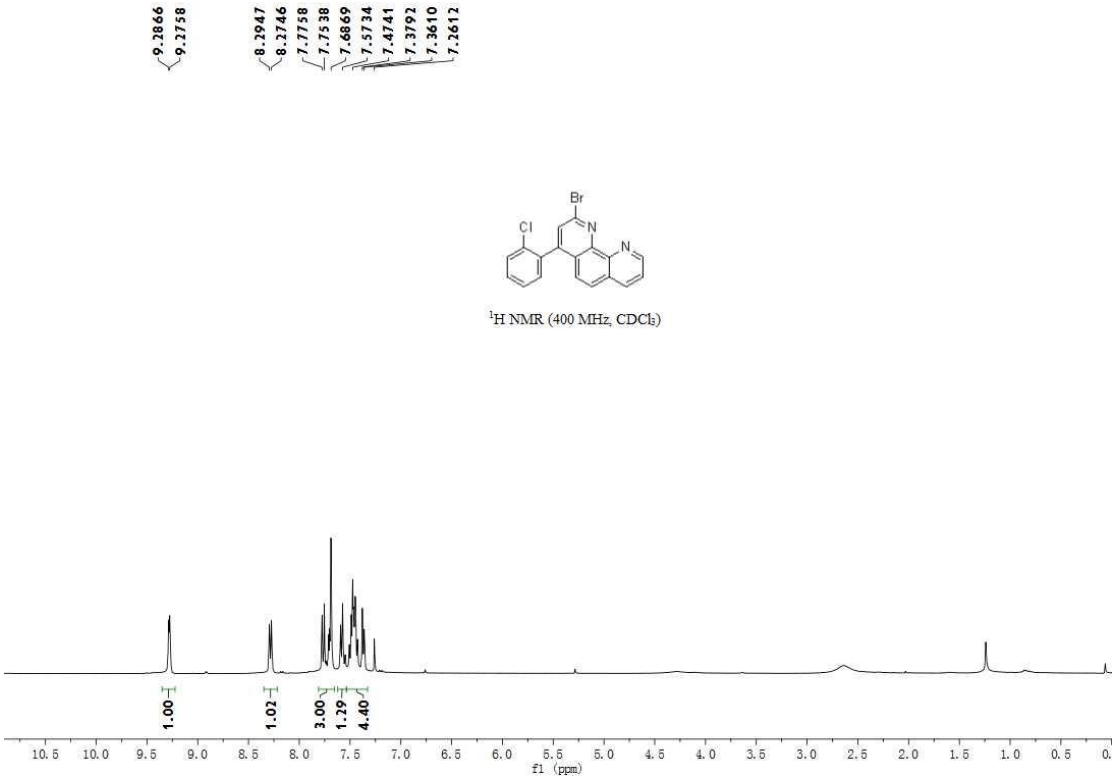
^{13}C NMR spectrum (100 MHz) of compound **5h** in $CDCl_3$



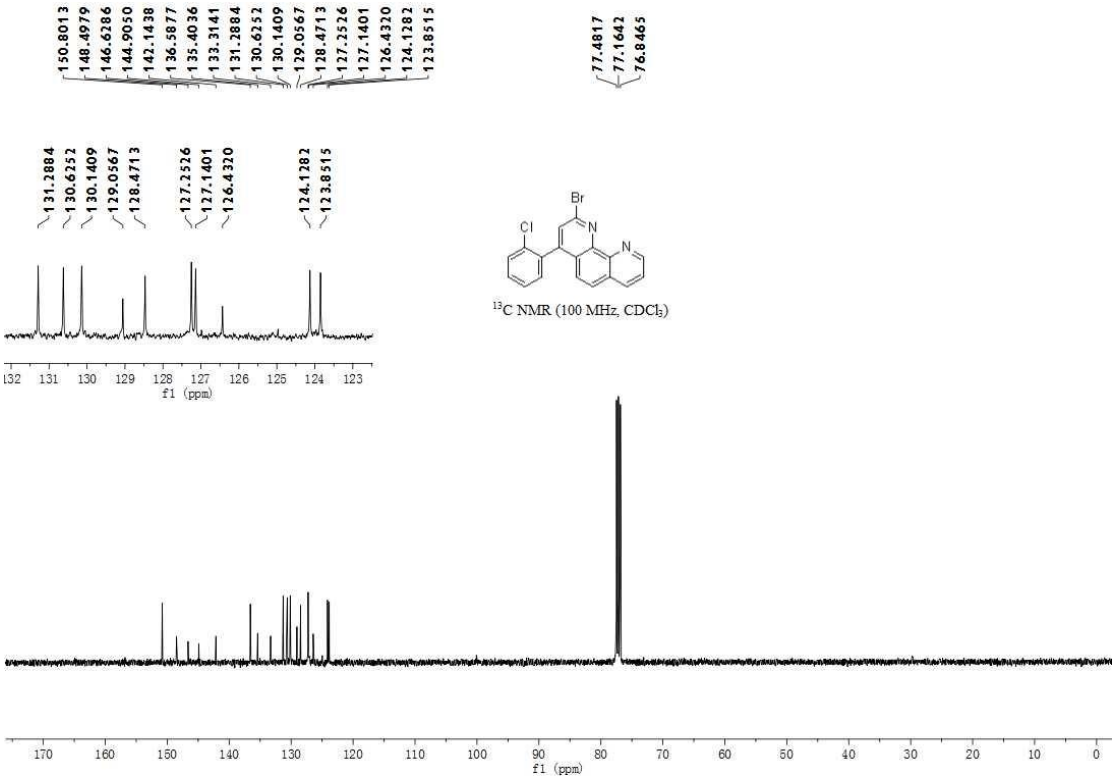
^{19}F NMR spectrum (376 MHz) of compound **5h** in $CDCl_3$



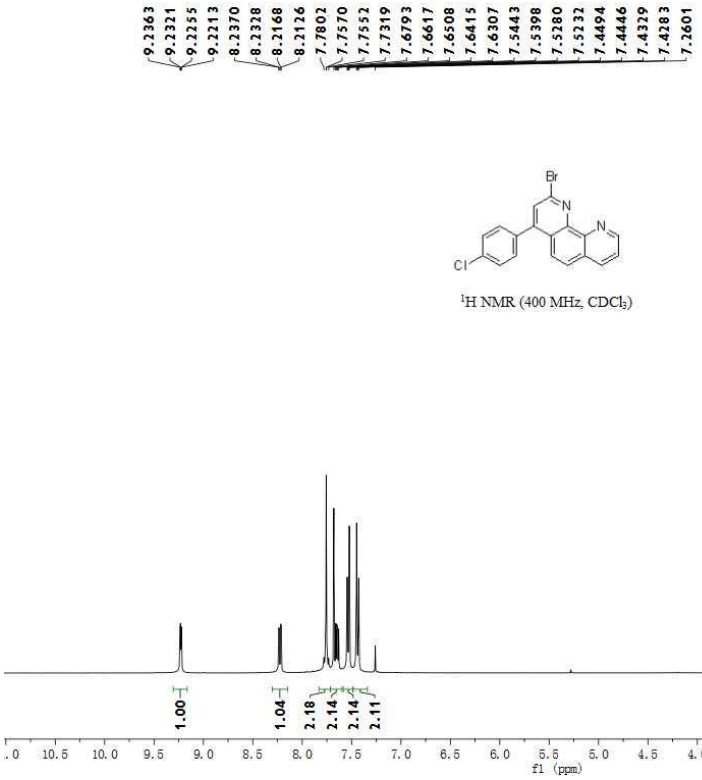
^{1}H NMR spectrum (400 MHz) of compound **5i** in $CDCl_3$



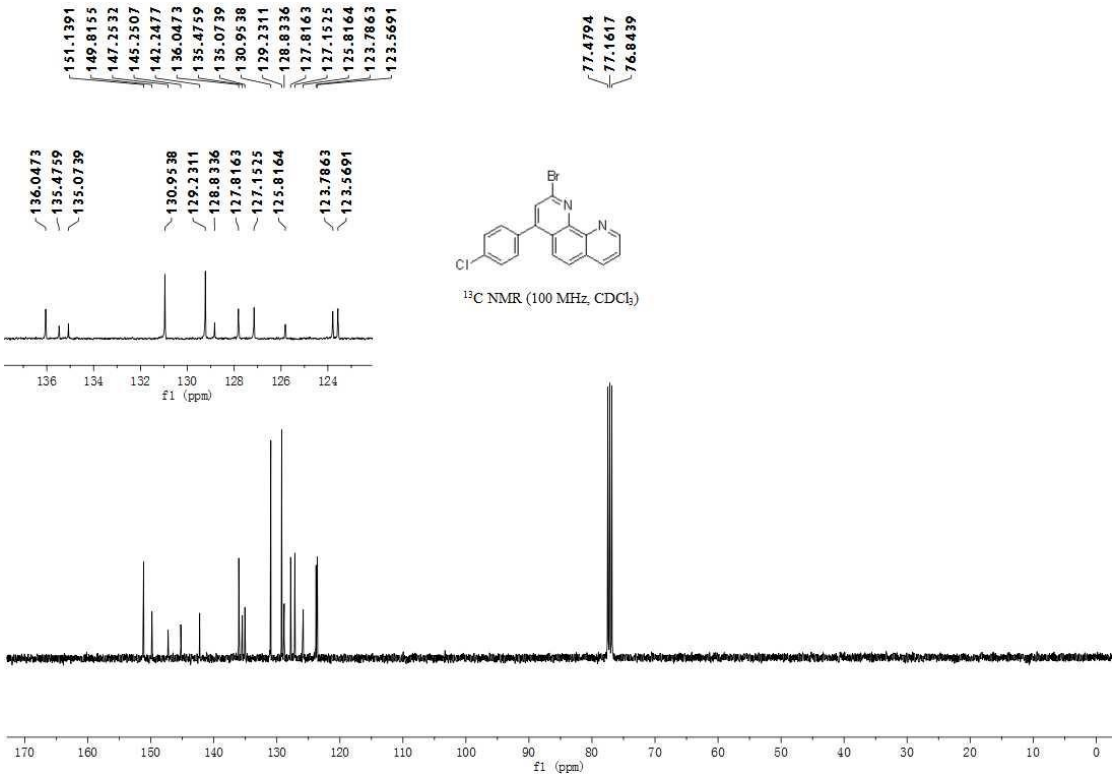
^{13}C NMR spectrum (100 MHz) of compound **5i** in $CDCl_3$



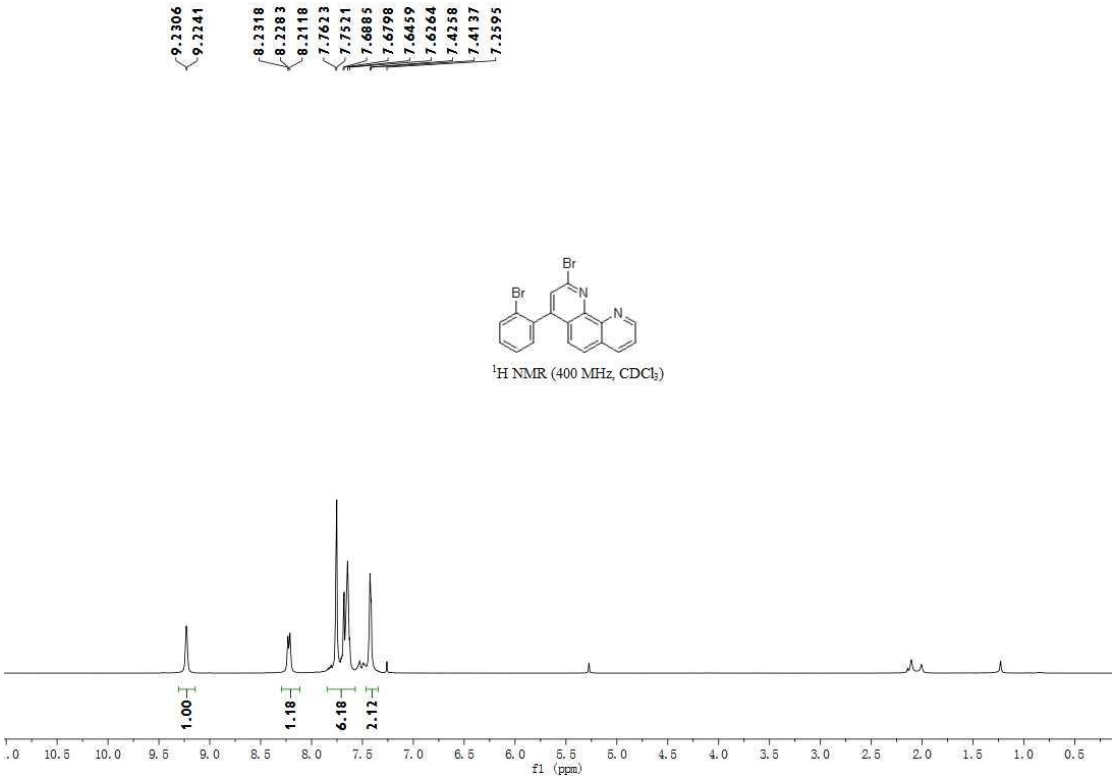
^{1}H NMR spectrum (400 MHz) of compound **5j** in $CDCl_3$



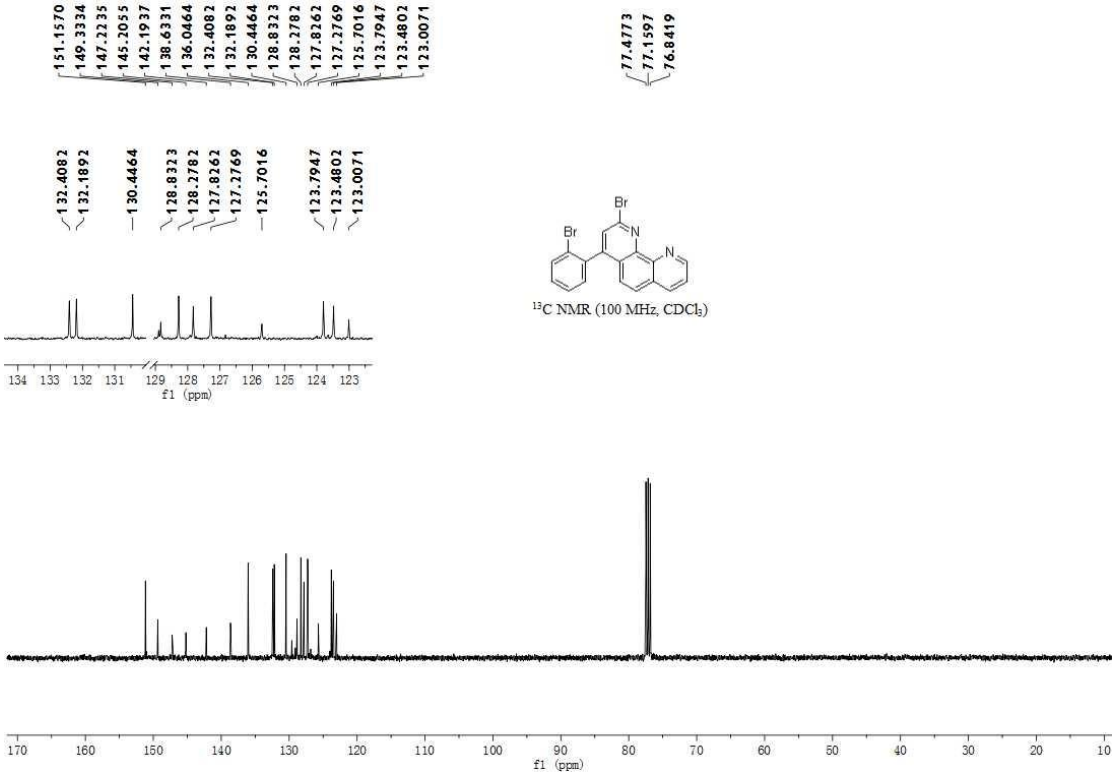
^{13}C NMR spectrum (100 MHz) of compound **5j** in $CDCl_3$



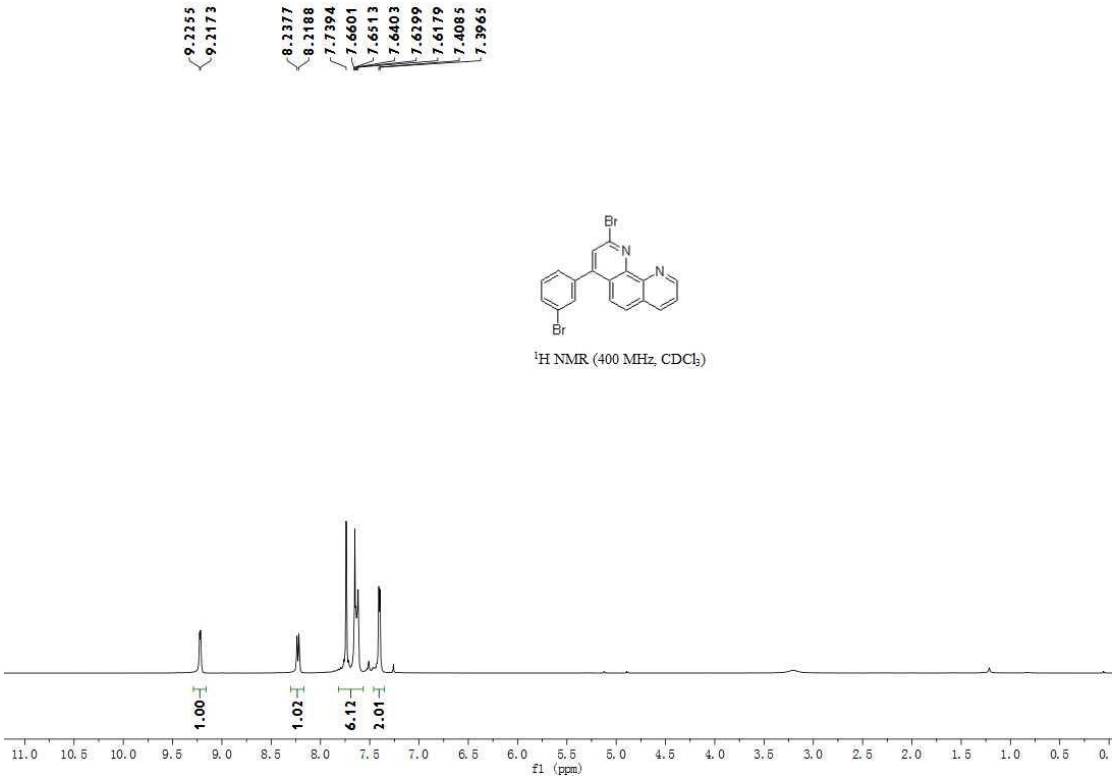
^{1}H NMR spectrum (400 MHz) of compound **5k** in $CDCl_3$



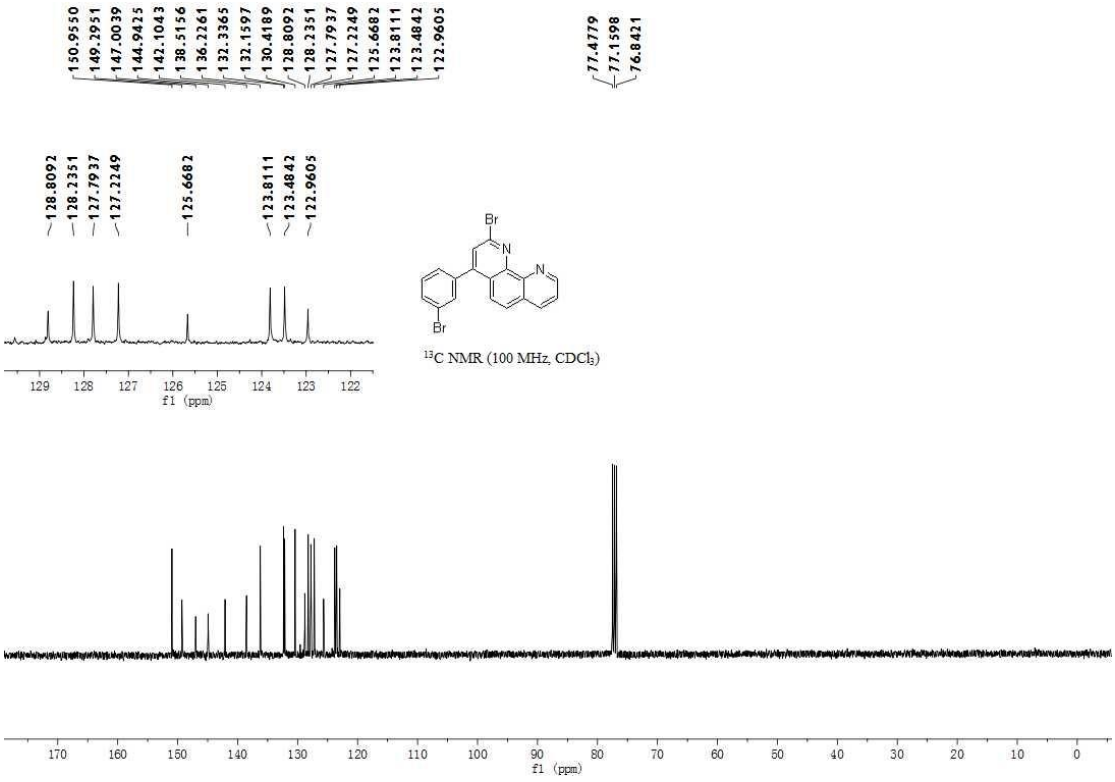
^{13}C NMR spectrum (100 MHz) of compound **5k** in $CDCl_3$



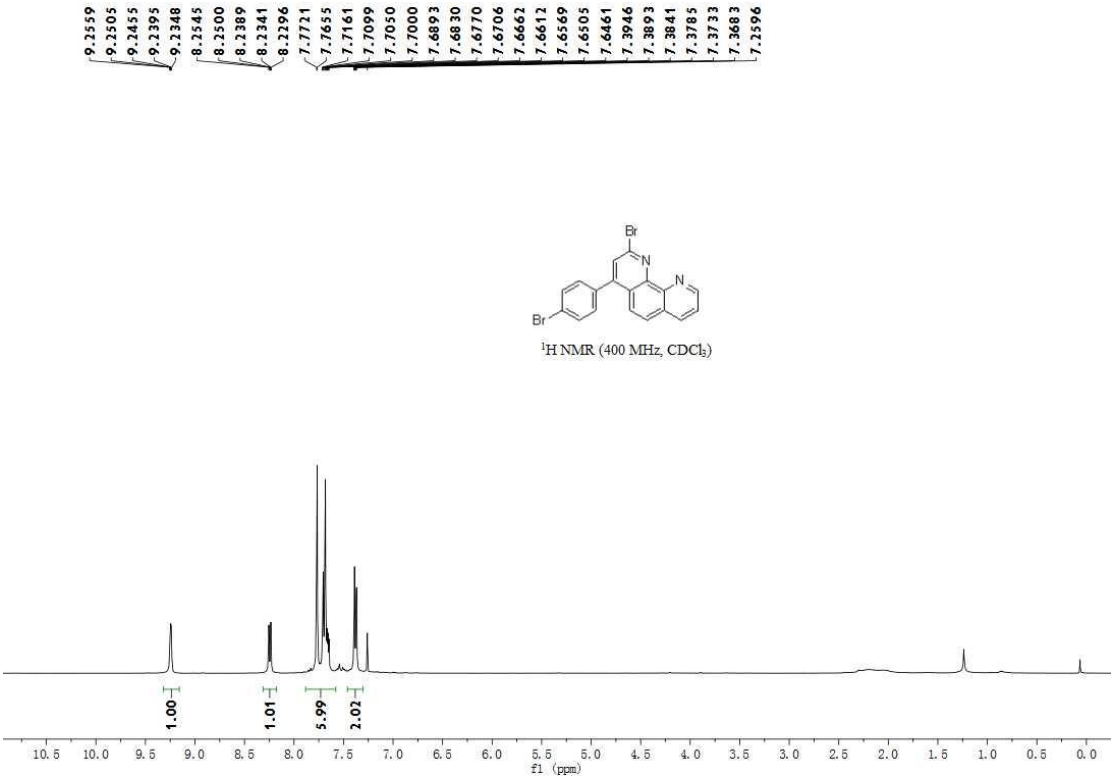
^{1}H NMR spectrum (400 MHz) of compound **5l** in $CDCl_3$



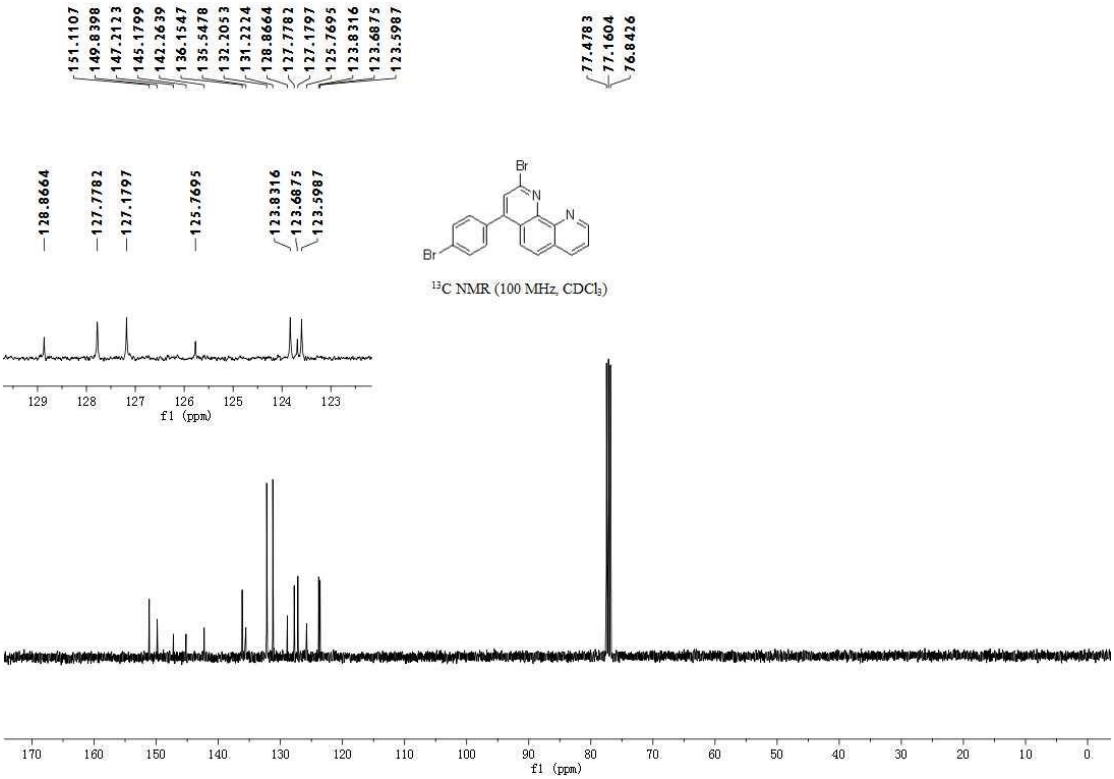
^{13}C NMR spectrum (100 MHz) of compound **5l** in $CDCl_3$



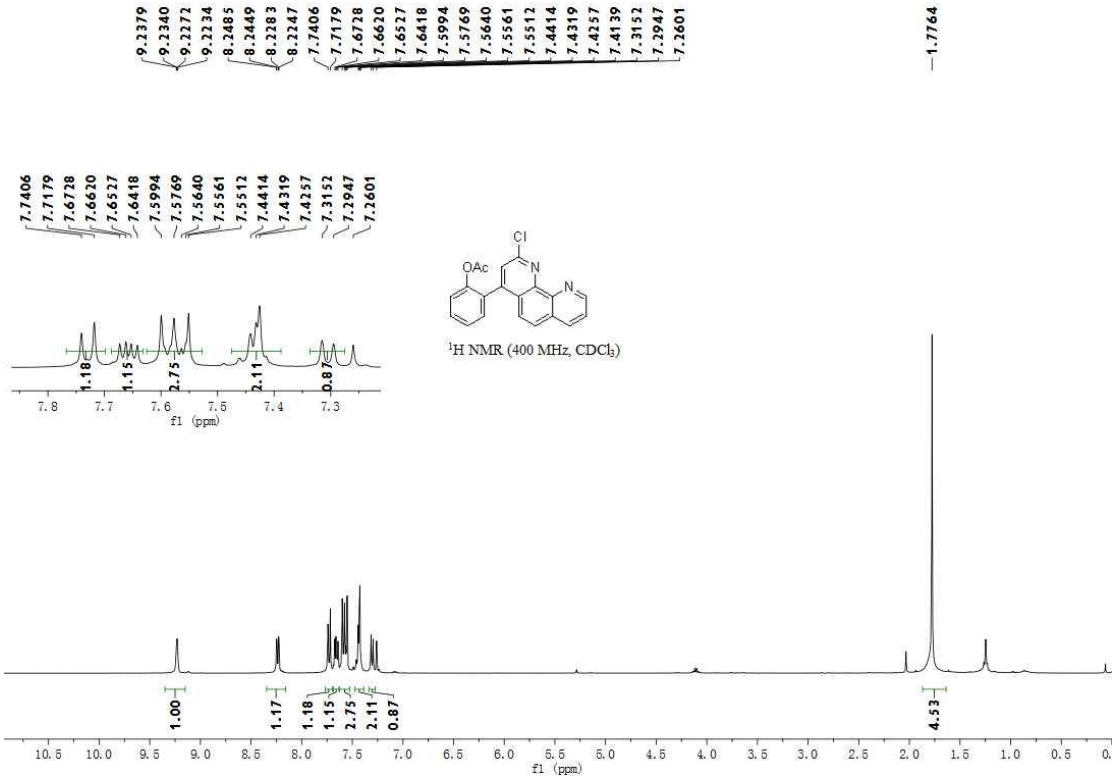
^{1}H NMR spectrum (400 MHz) of compound **5m** in $CDCl_3$



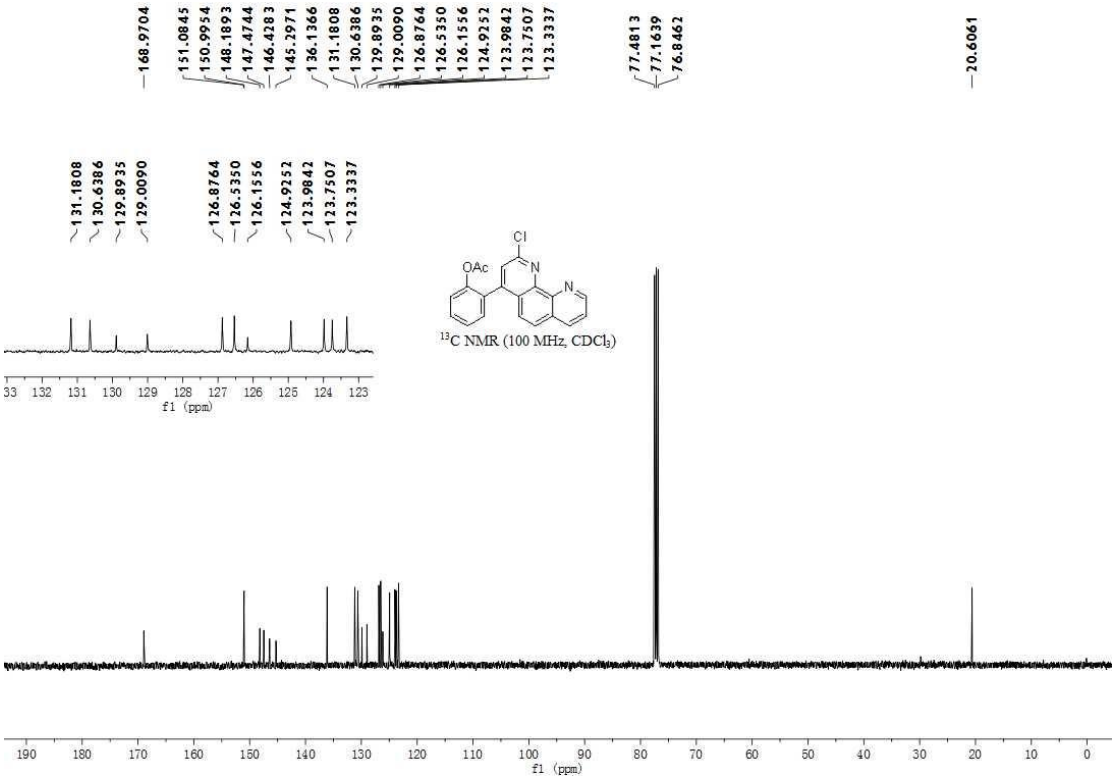
^{13}C NMR spectrum (100 MHz) of compound **5m** in $CDCl_3$



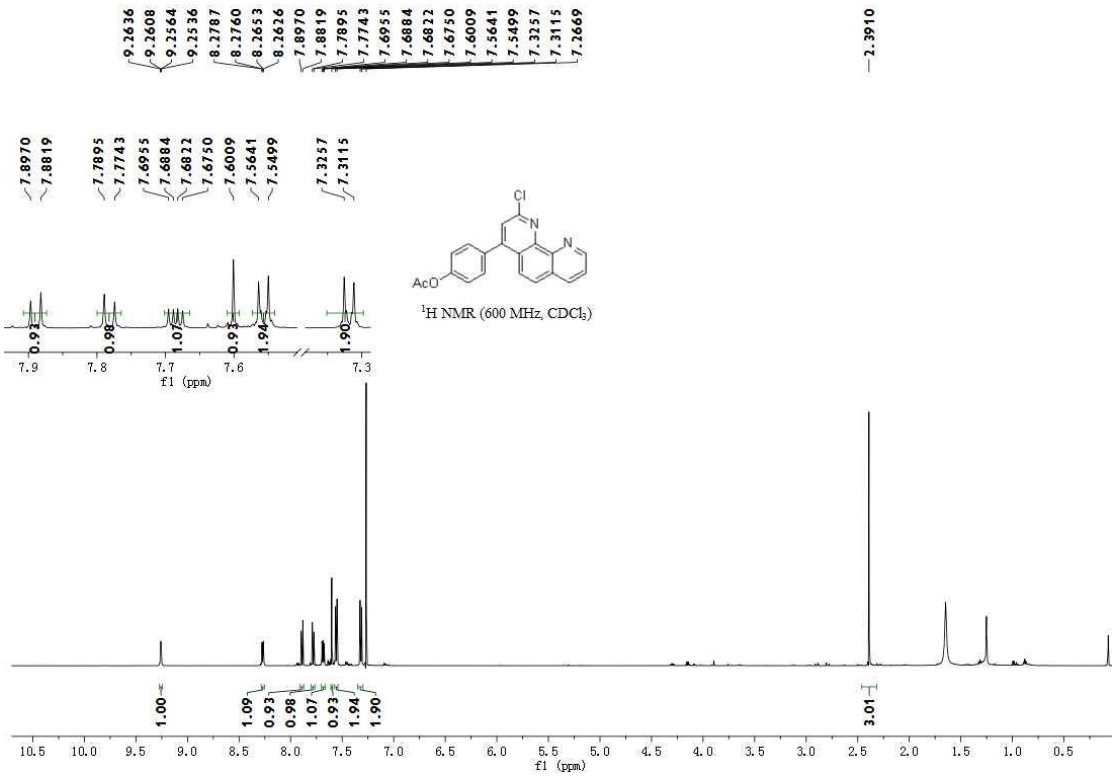
^{1}H NMR spectrum (400 MHz) of compound **5n** in $CDCl_3$



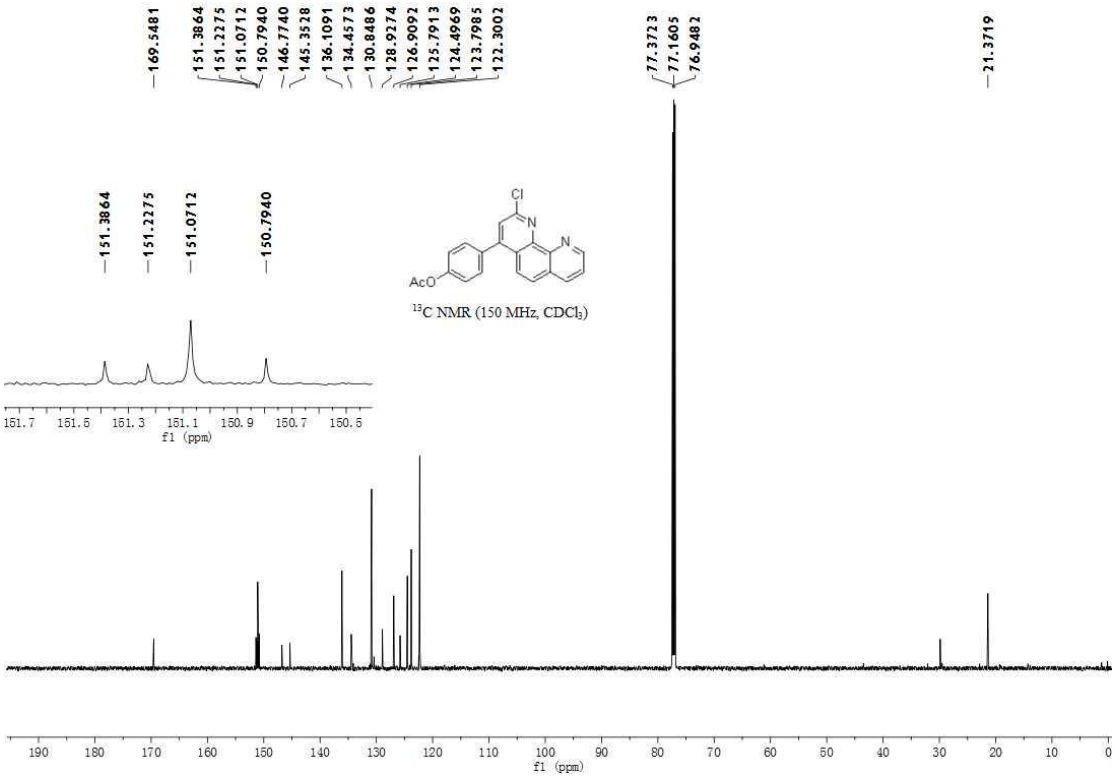
^{13}C NMR spectrum (100 MHz) of compound **5n** in $CDCl_3$



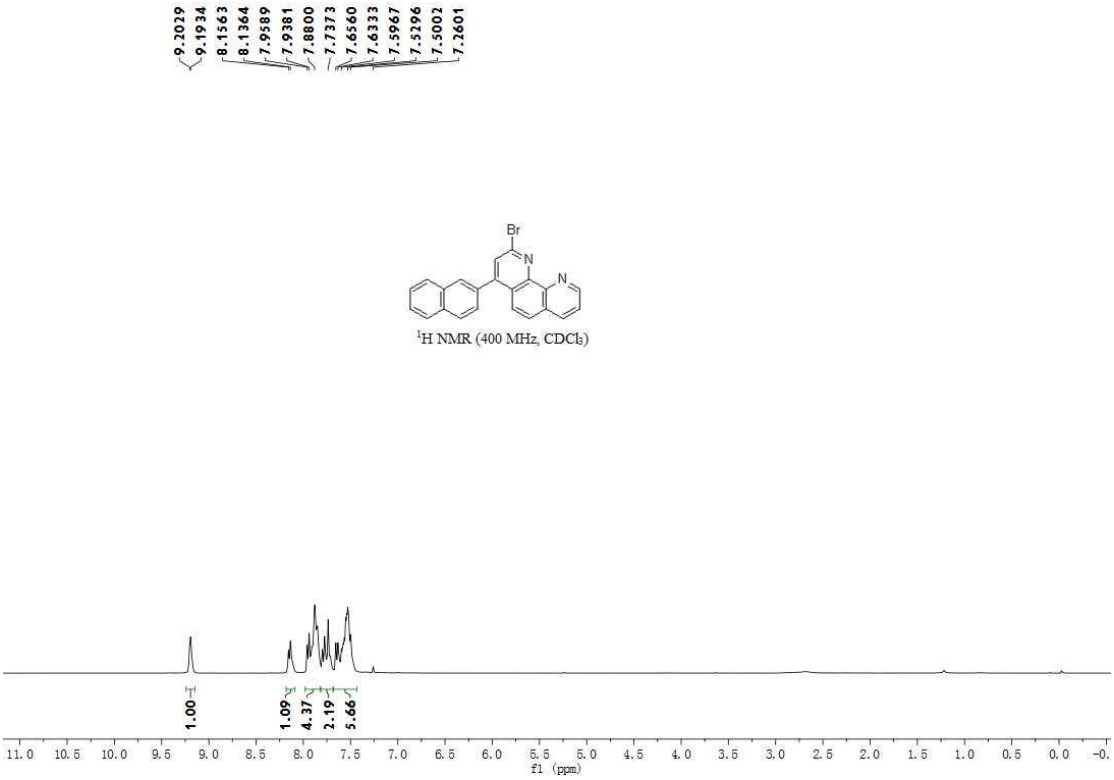
^{1}H NMR spectrum (400 MHz) of compound **5o** in $CDCl_3$



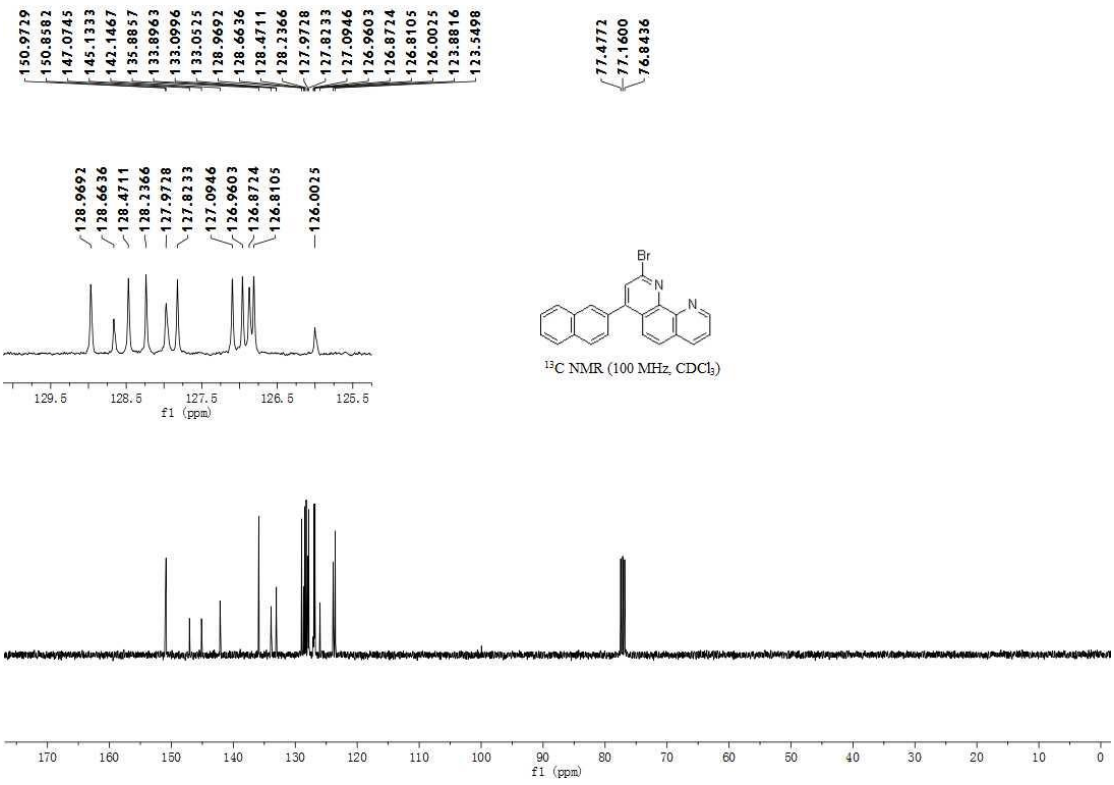
^{13}C NMR spectrum (100 MHz) of compound **5o** in $CDCl_3$



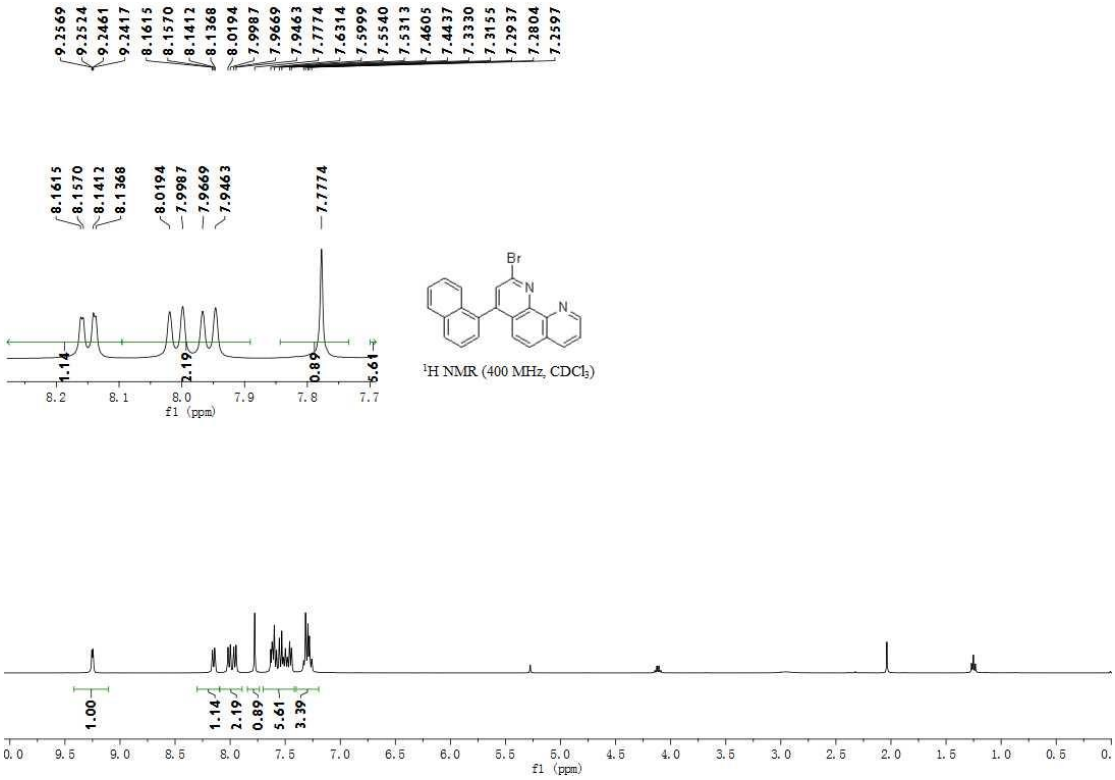
^{1}H NMR spectrum (400 MHz) of compound **5p** in $CDCl_3$



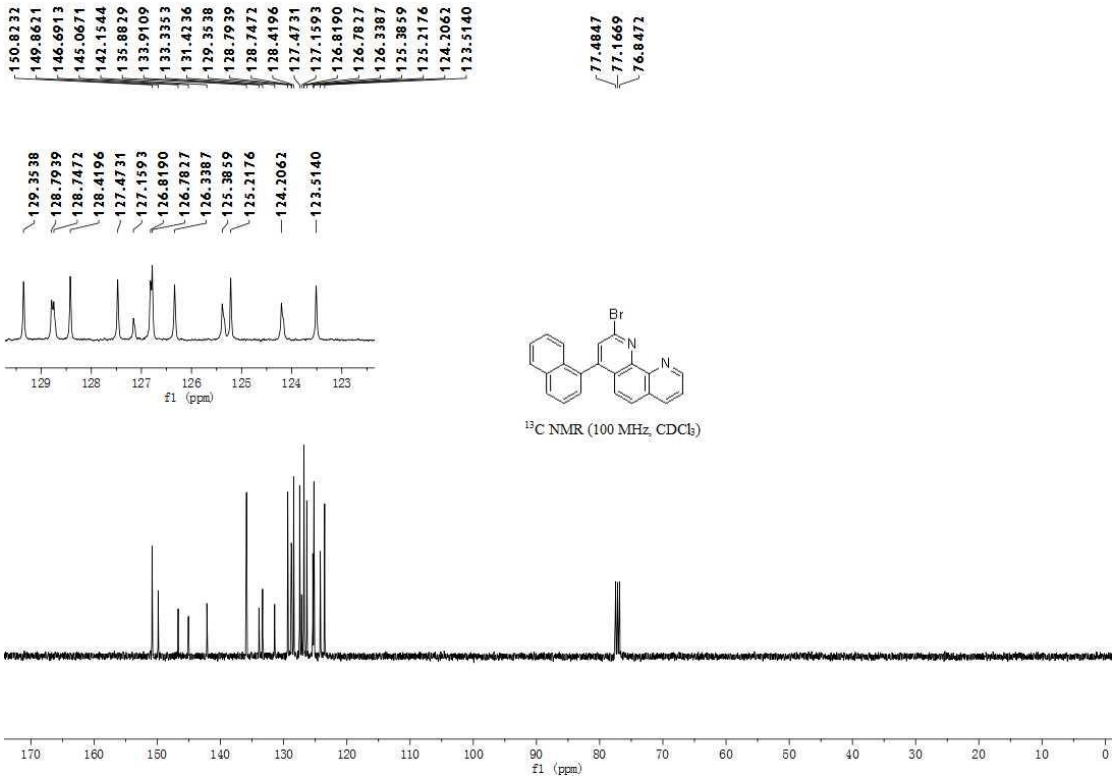
^{13}C NMR spectrum (100 MHz) of compound **5p** in $CDCl_3$



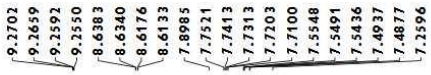
^{1}H NMR spectrum (400 MHz) of compound **5q** in $CDCl_3$

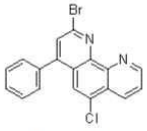


^{13}C NMR spectrum (100 MHz) of compound **5q** in $CDCl_3$

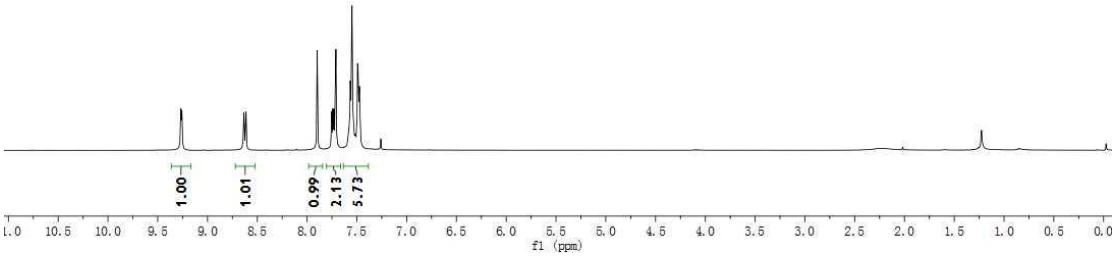


^{1}H NMR spectrum (400 MHz) of compound **5v** in $CDCl_3$

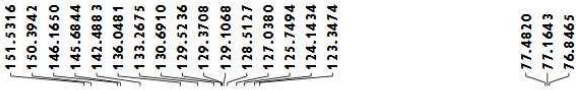


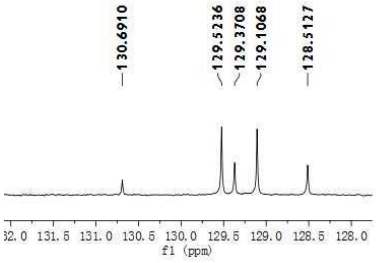


^{1}H NMR (400 MHz, $CDCl_3$)

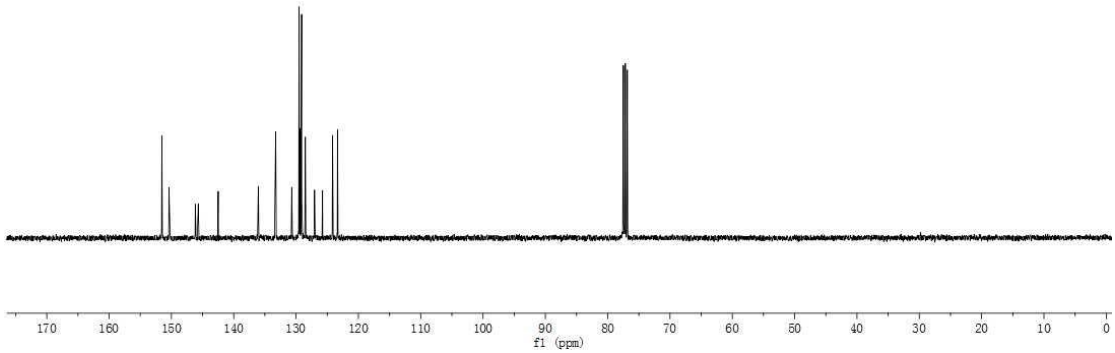


^{13}C NMR spectrum (100 MHz) of compound **5v** in $CDCl_3$

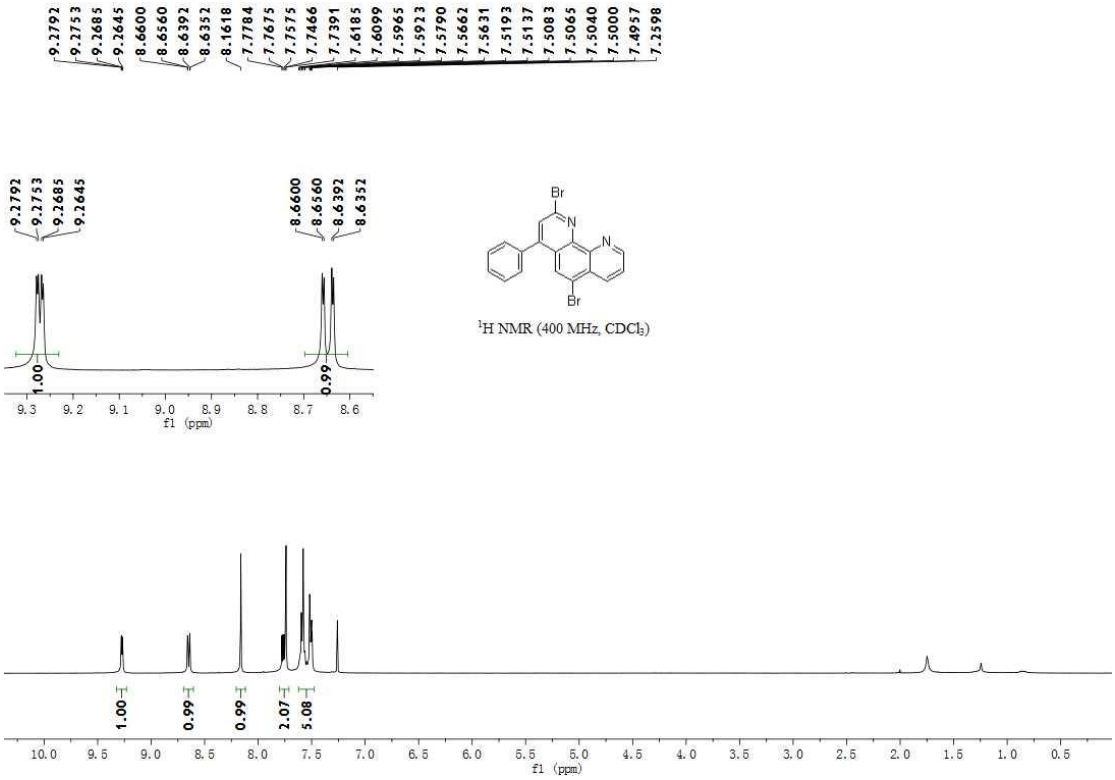




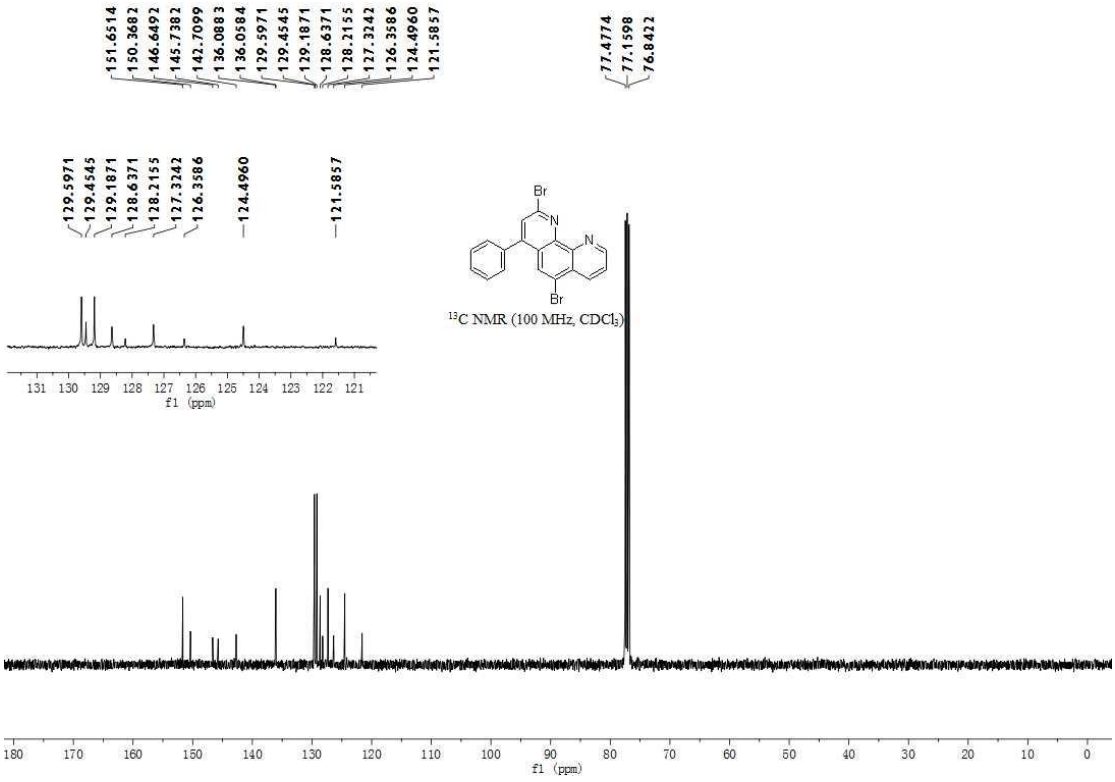
^{13}C NMR (100 MHz, $CDCl_3$)



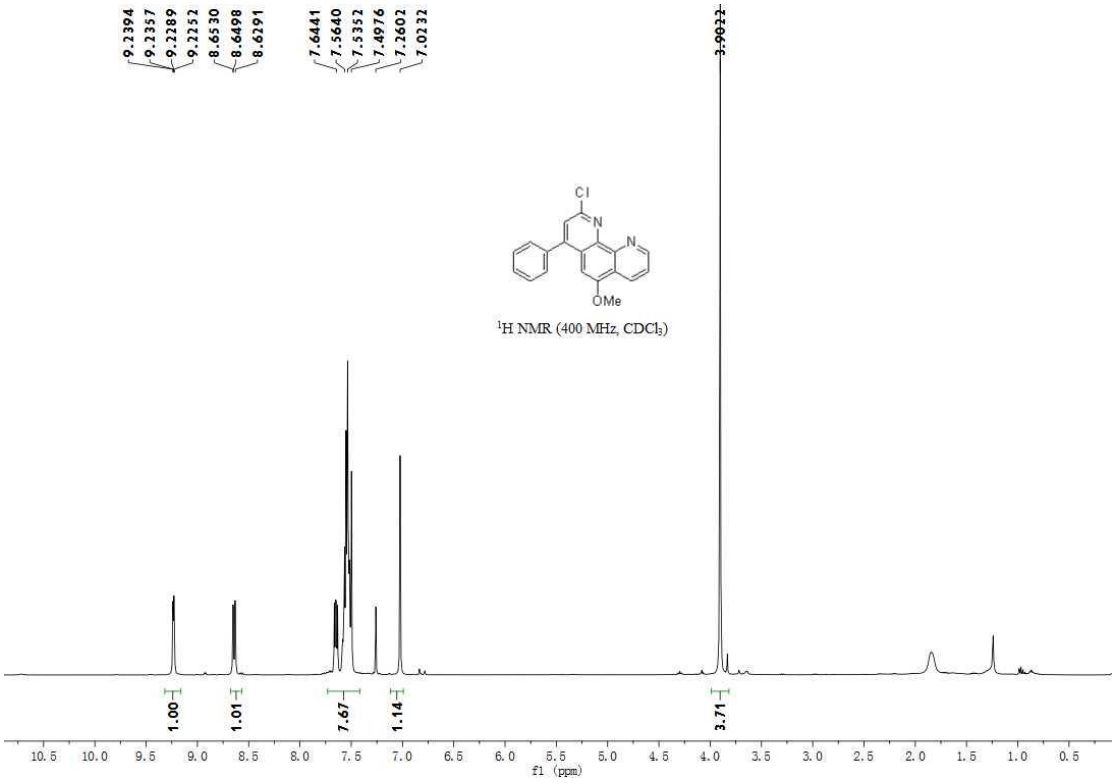
^{1}H NMR spectrum (400 MHz) of compound **5w** in $CDCl_3$



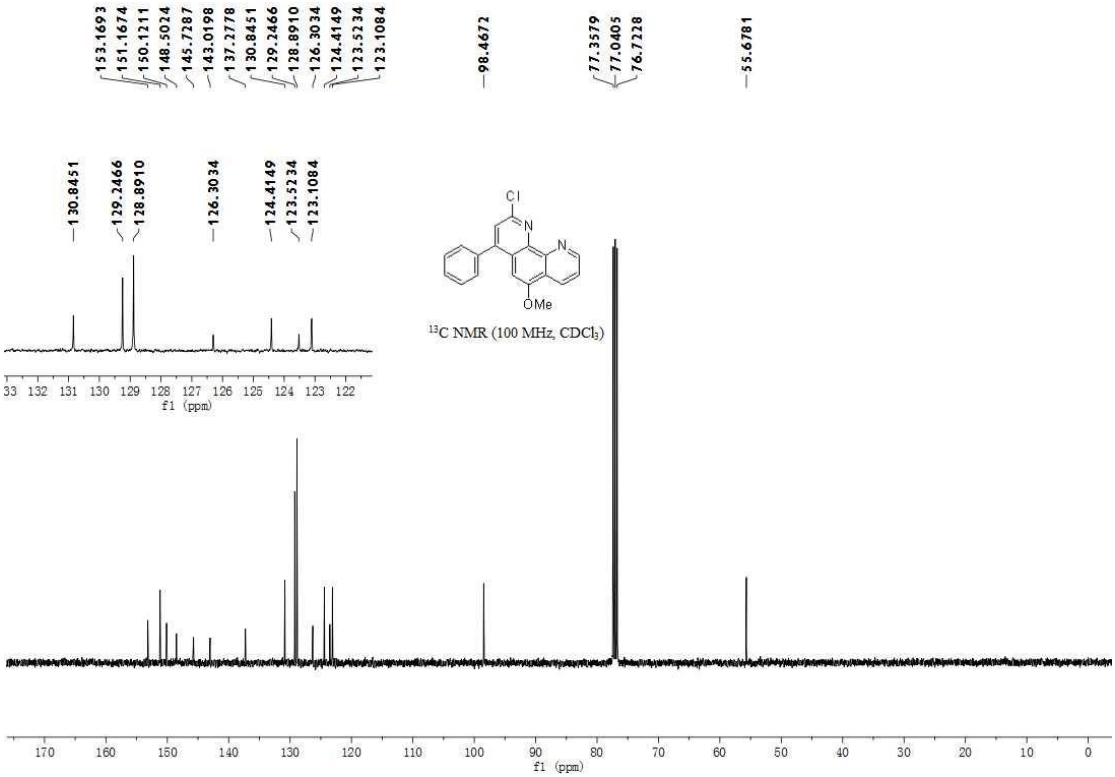
^{13}C NMR spectrum (100 MHz) of compound **5w** in $CDCl_3$



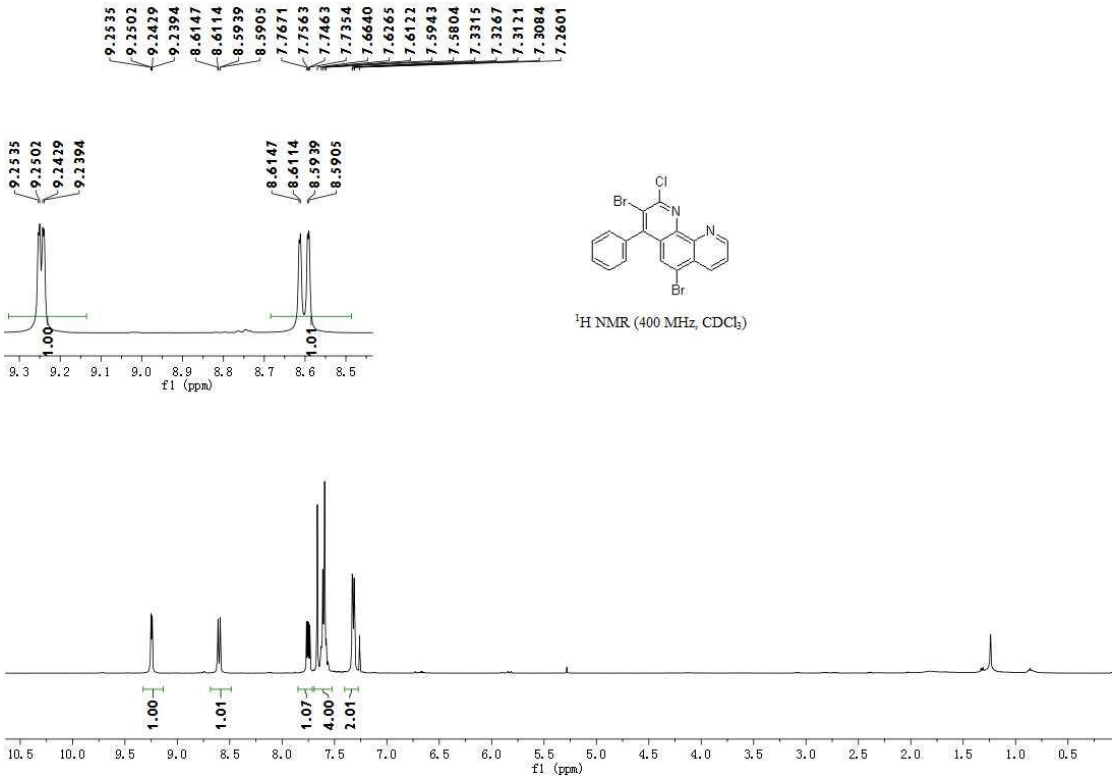
^{1}H NMR spectrum (400 MHz) of compound **5x** in $CDCl_3$



^{13}C NMR spectrum (100 MHz) of compound **5x** in $CDCl_3$

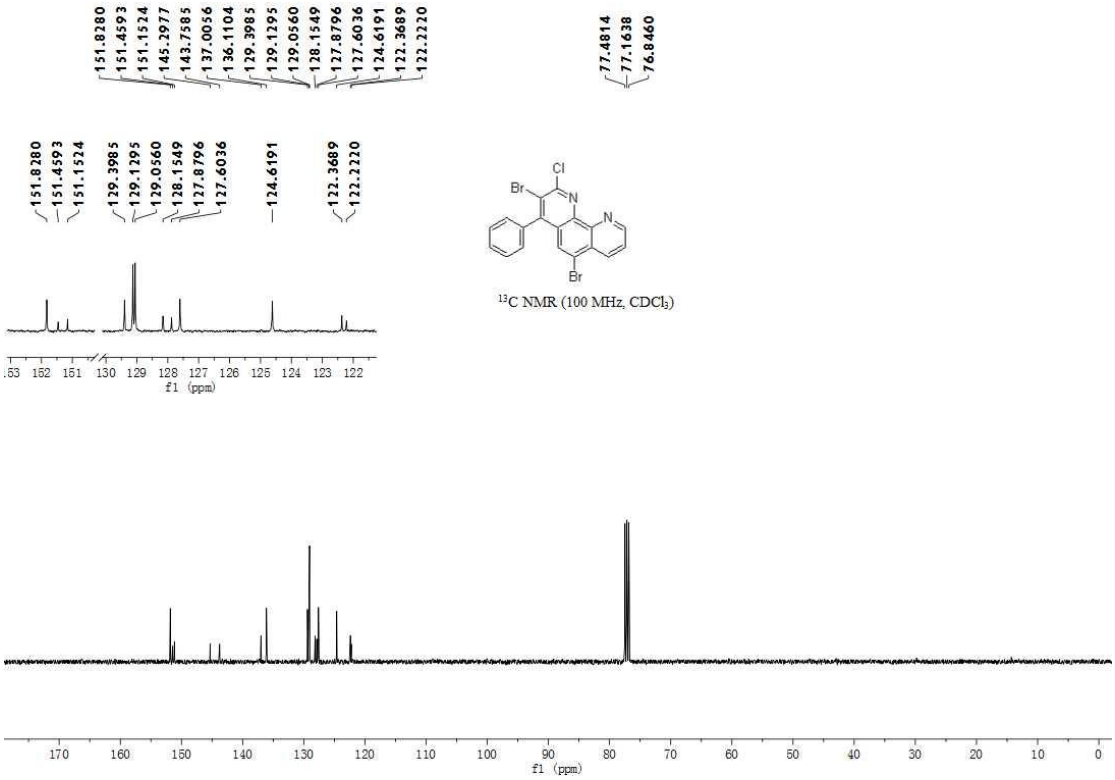


^{1}H NMR spectrum (400 MHz) of compound **10** in $CDCl_3$



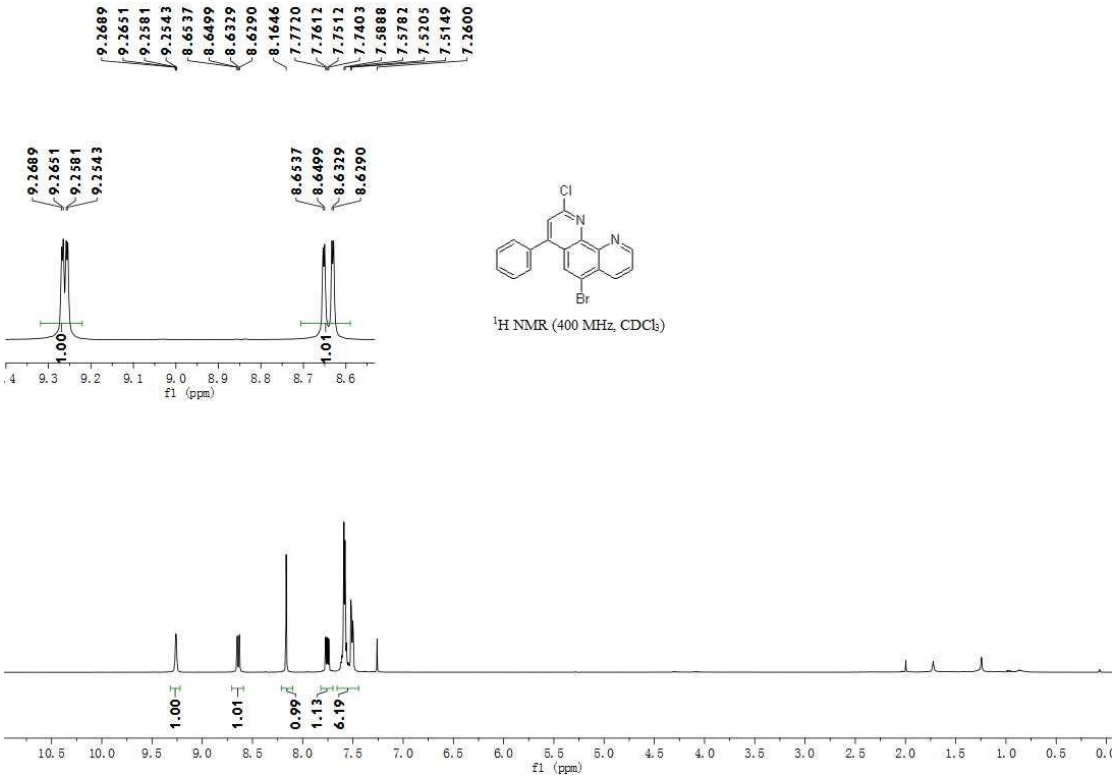
^{1}H NMR (400 MHz, $CDCl_3$)

^{13}C NMR spectrum (100 MHz) of compound **10** in $CDCl_3$

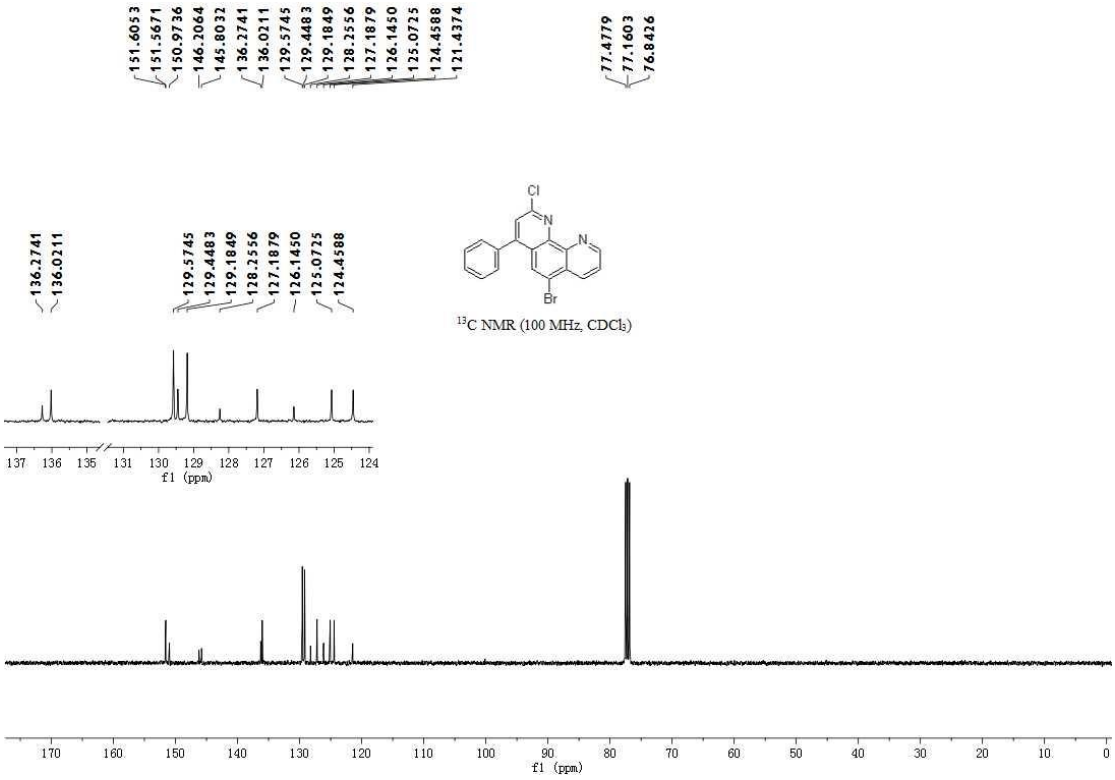


^{13}C NMR (100 MHz, $CDCl_3$)

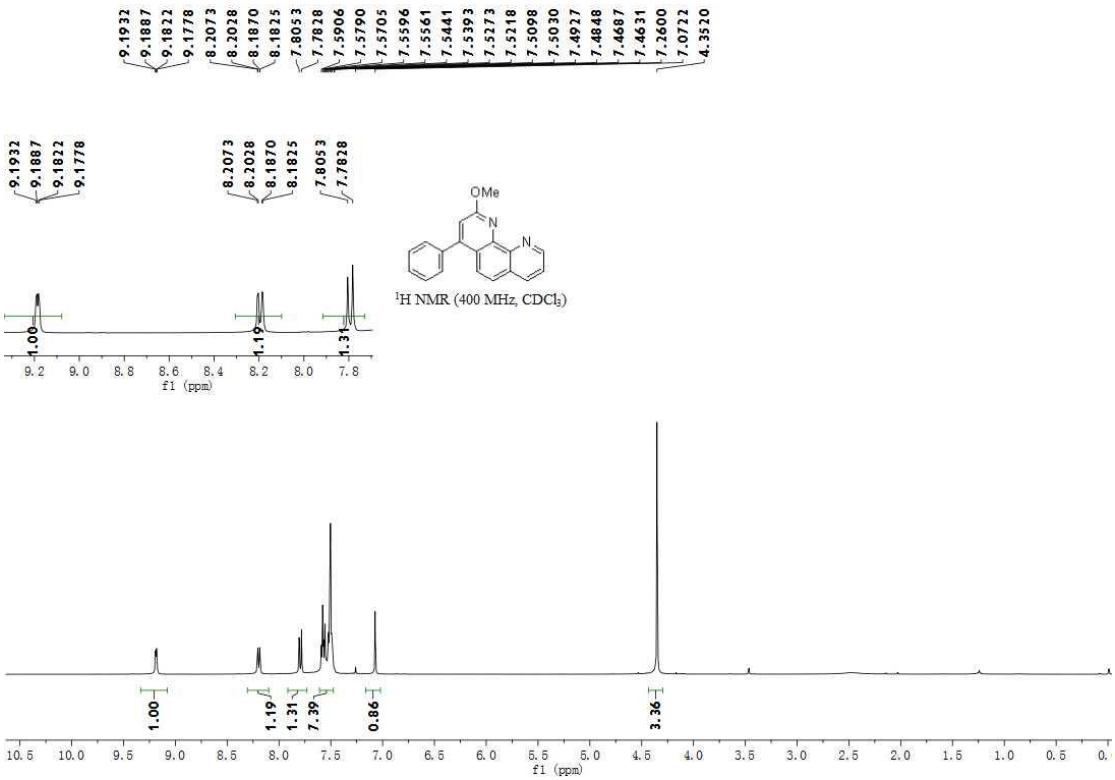
^{1}H NMR spectrum (400 MHz) of compound **11** in $CDCl_3$



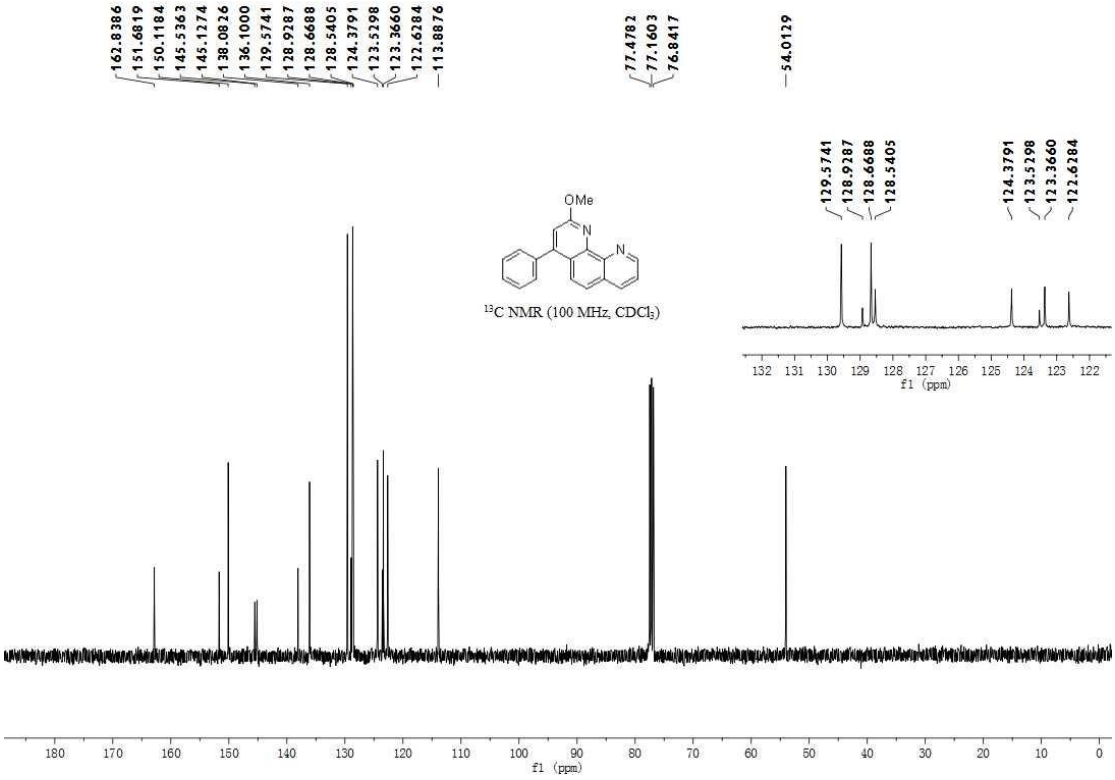
^{13}C NMR spectrum (100 MHz) of compound **11** in $CDCl_3$



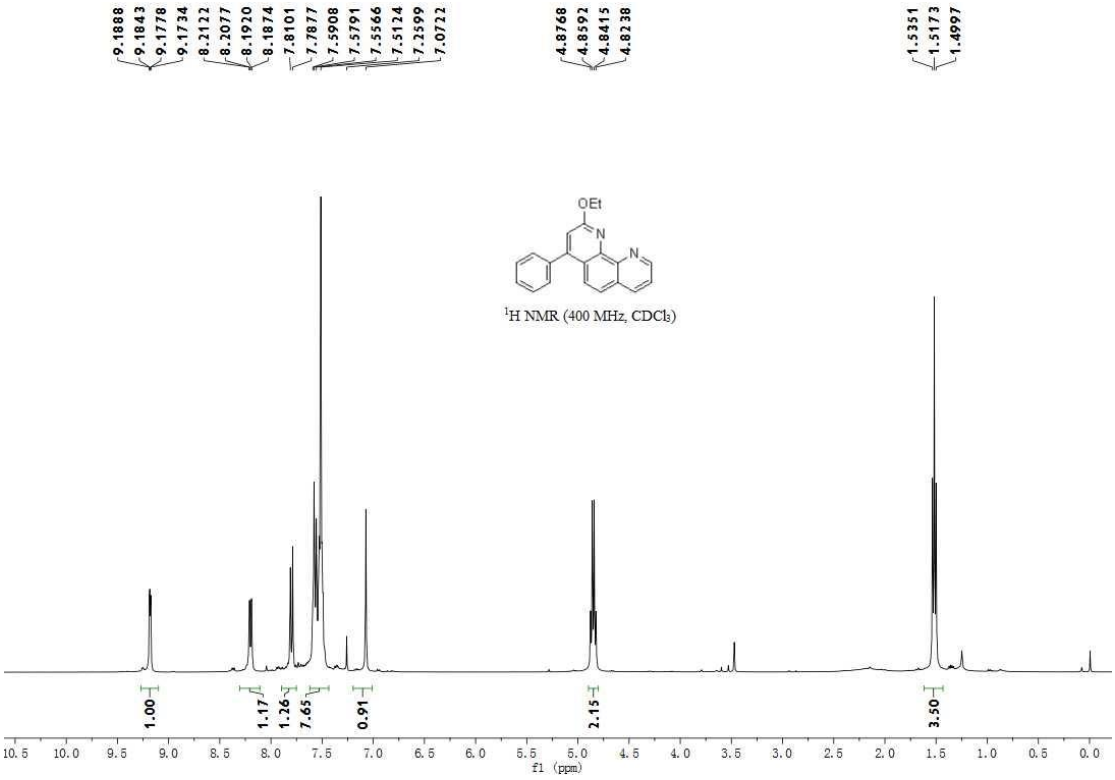
^{1}H NMR spectrum (400 MHz) of compound **6** in $CDCl_3$



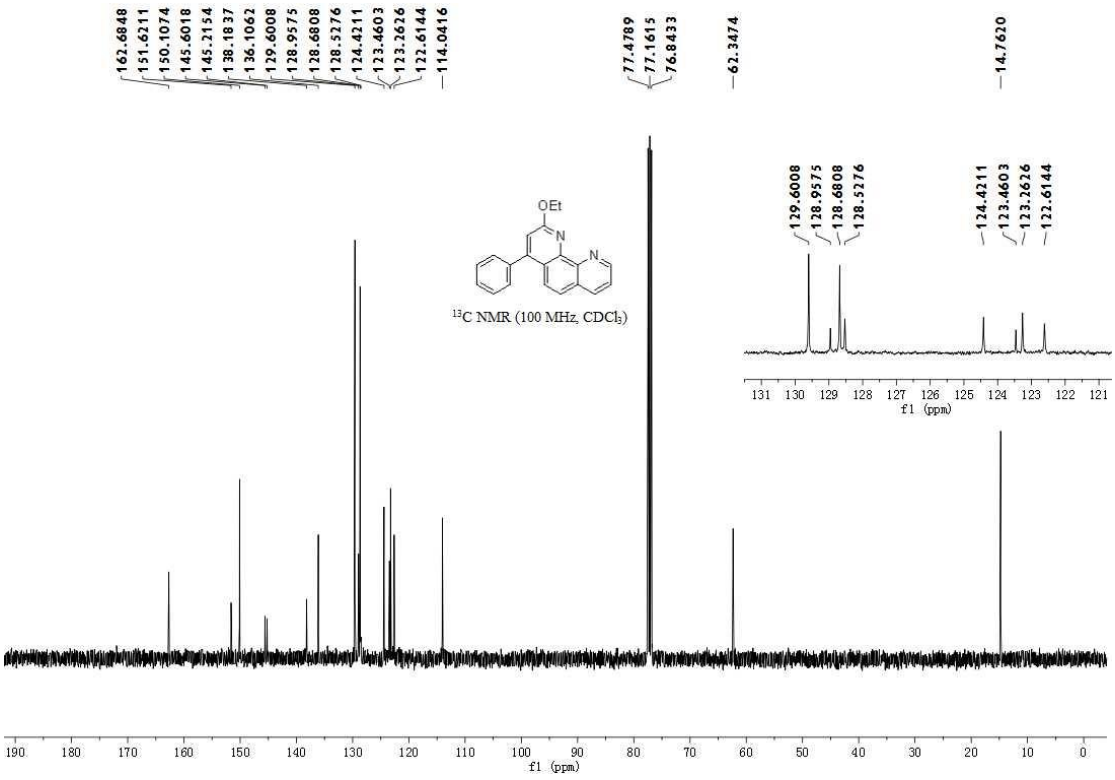
^{13}C NMR spectrum (100 MHz) of compound **6** in $CDCl_3$



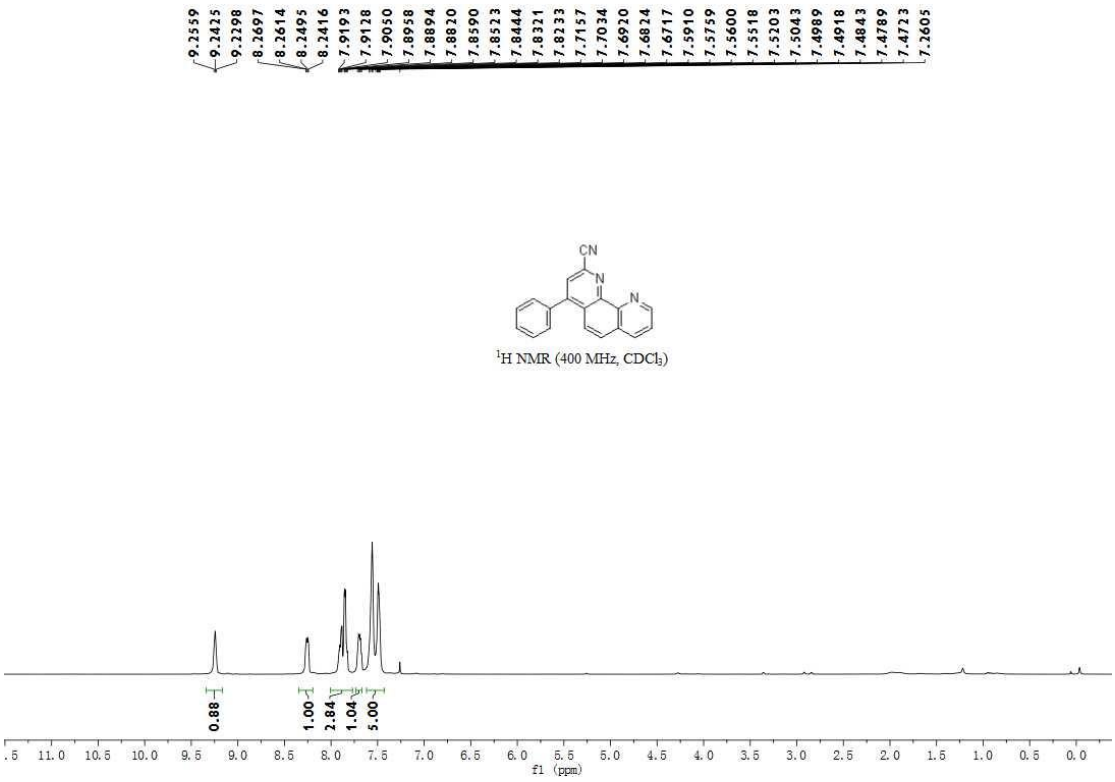
^{1}H NMR spectrum (400 MHz) of compound **7** in $CDCl_3$



^{13}C NMR spectrum (100 MHz) of compound **7** in $CDCl_3$

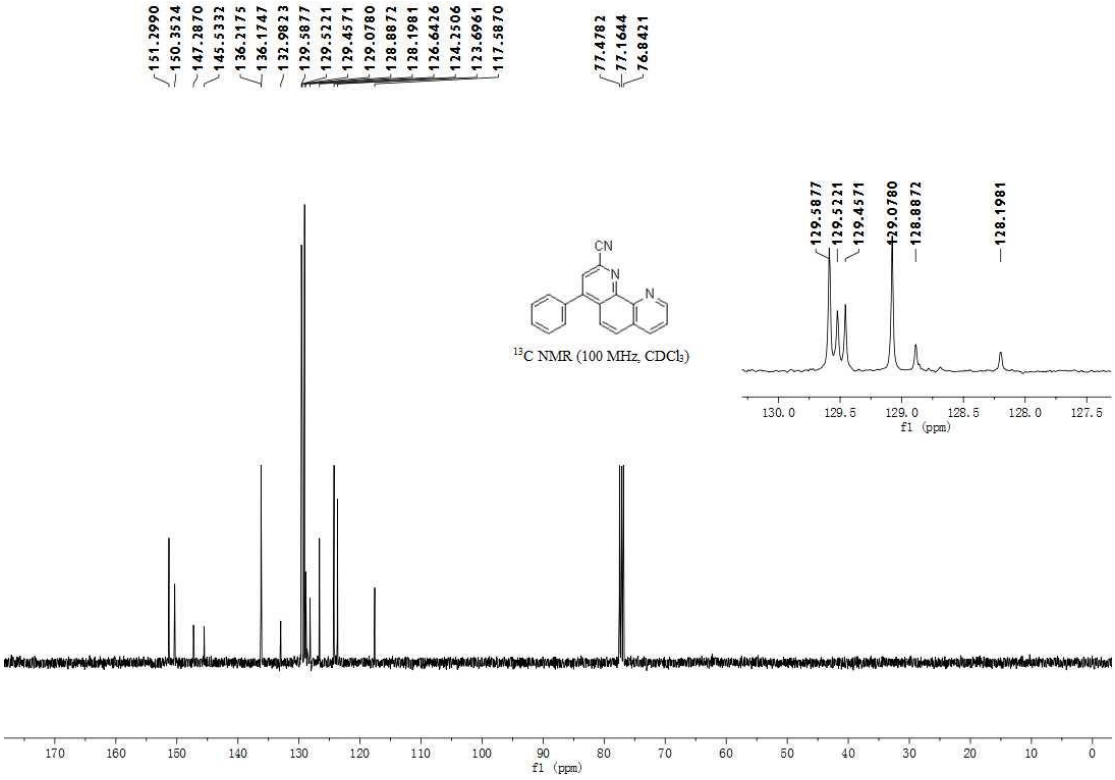


^{1}H NMR spectrum (400 MHz) of compound **8** in $CDCl_3$



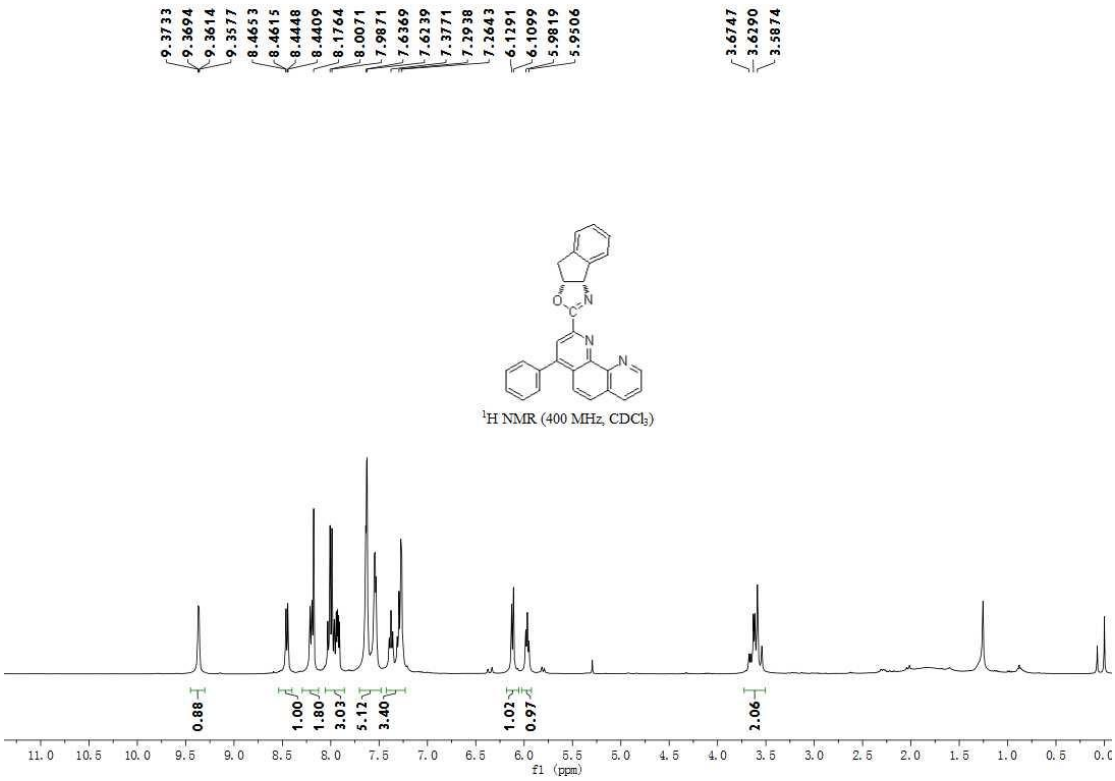
^{1}H NMR (400 MHz, $CDCl_3$)

^{13}C NMR spectrum (100 MHz) of compound **8** in $CDCl_3$



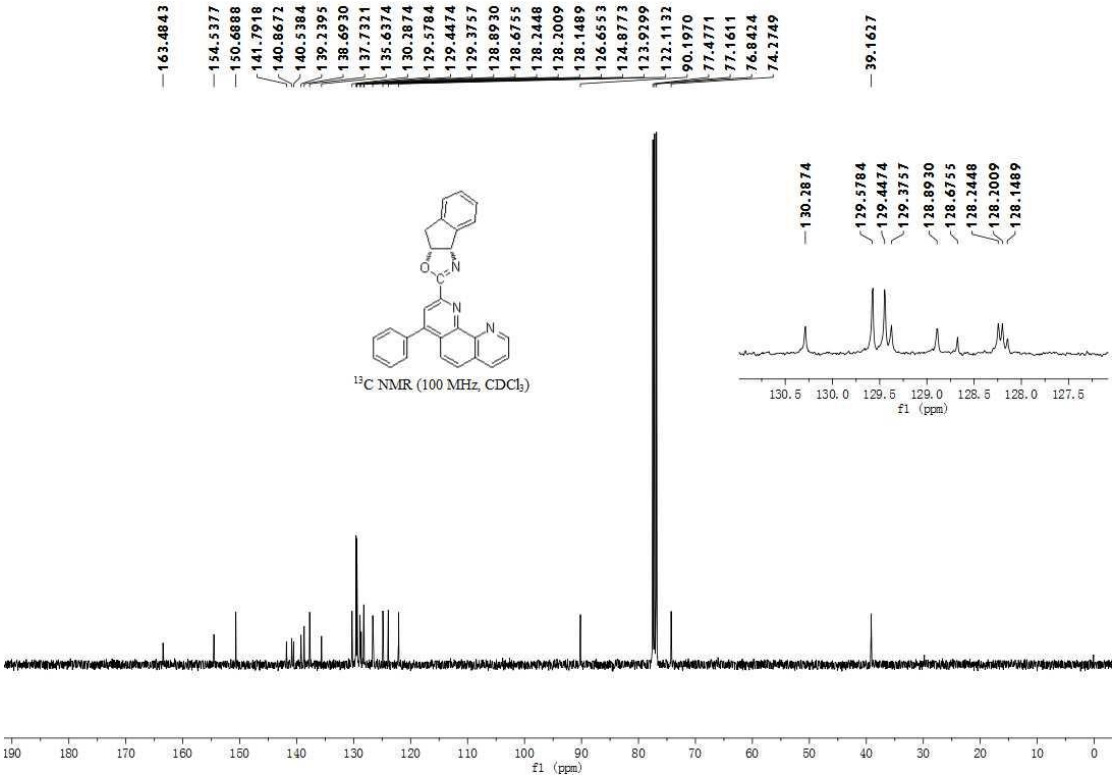
^{13}C NMR (100 MHz, $CDCl_3$)

^{1}H NMR spectrum (400 MHz) of compound **16** in $CDCl_3$



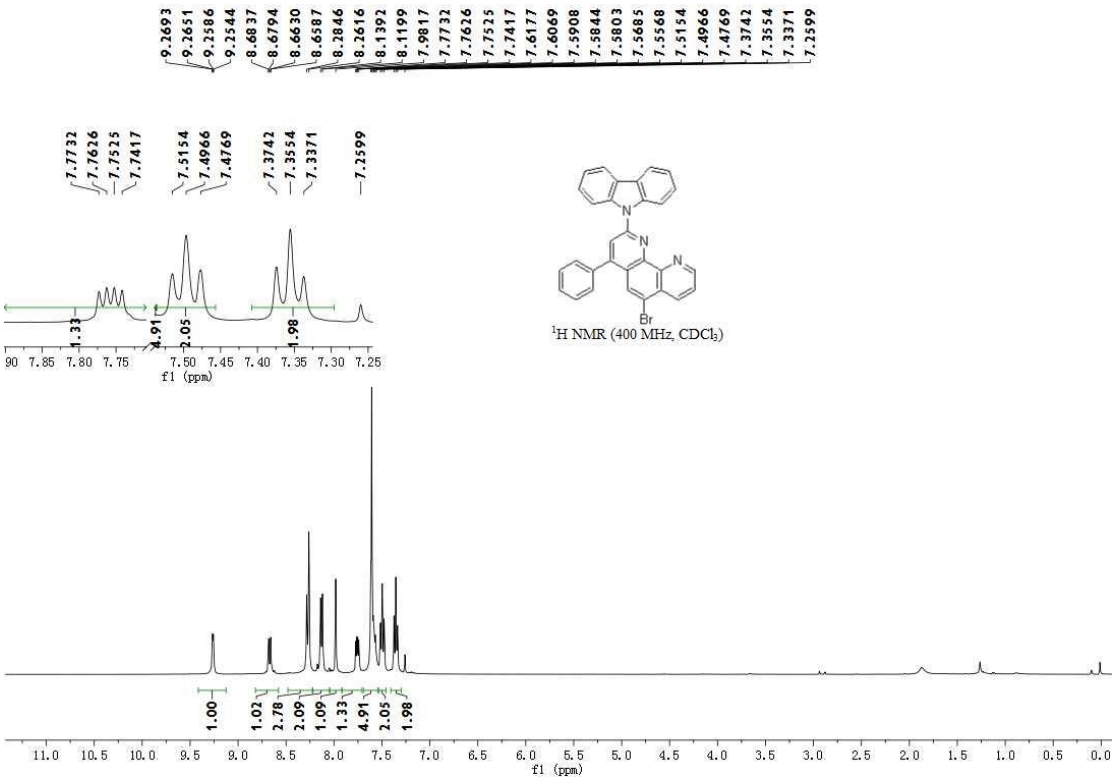
^{1}H NMR (400 MHz, $CDCl_3$)

^{13}C NMR spectrum (100 MHz) of compound **16** in $CDCl_3$

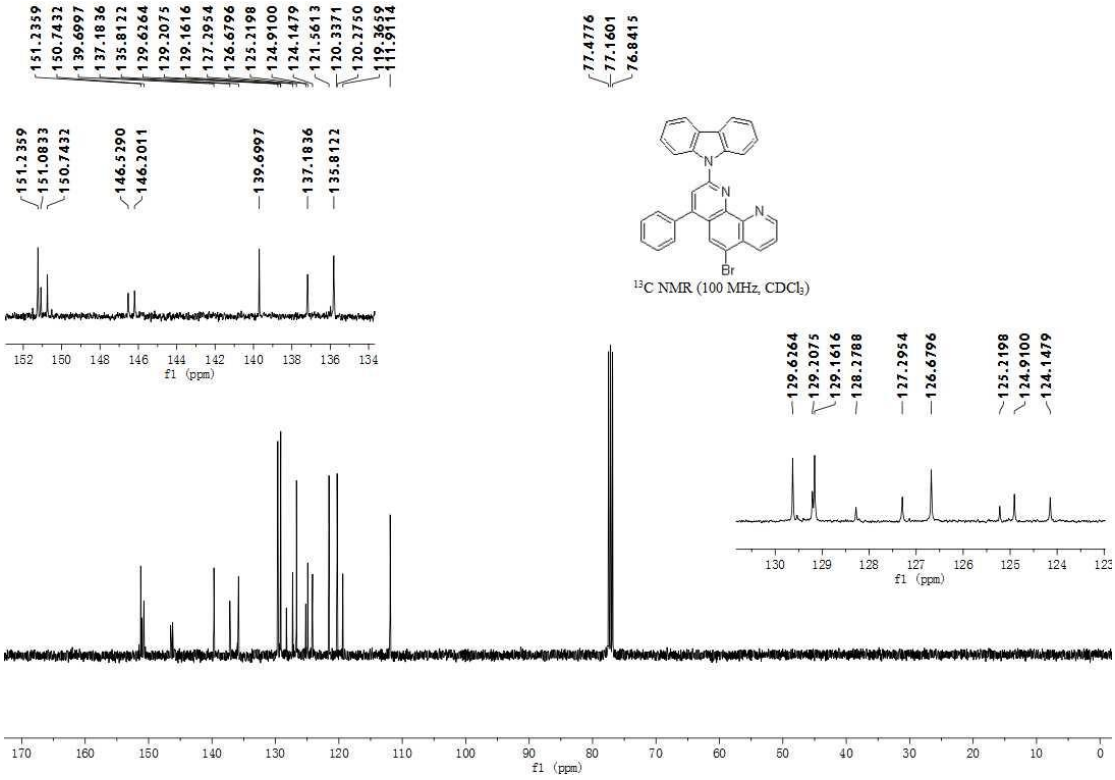


^{13}C NMR (100 MHz, $CDCl_3$)

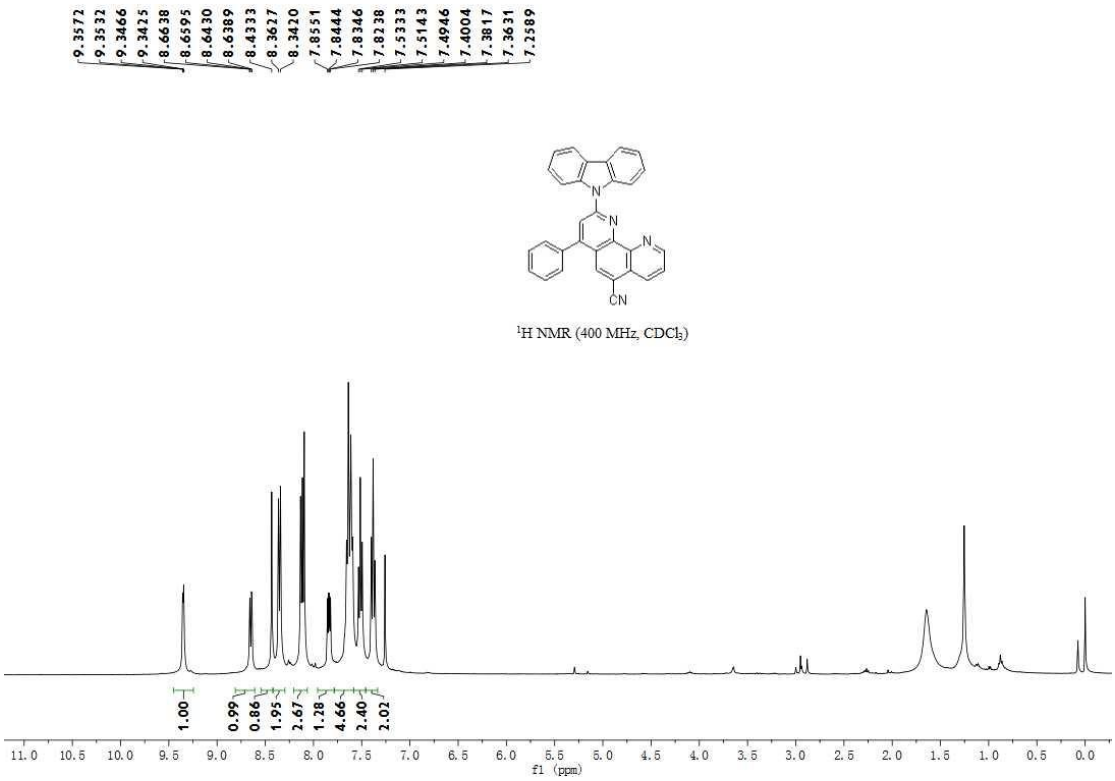
^{1}H NMR spectrum (400 MHz) of compound **12** in $CDCl_3$



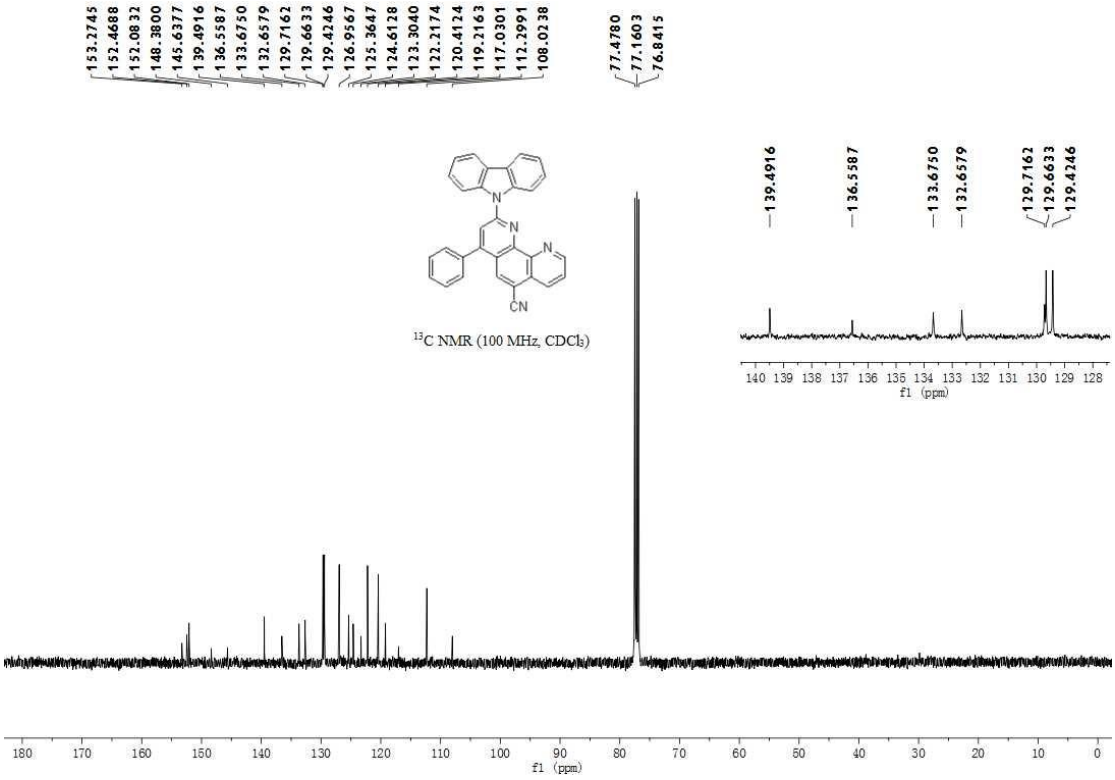
^{13}C NMR spectrum (100 MHz) of compound **12** in $CDCl_3$



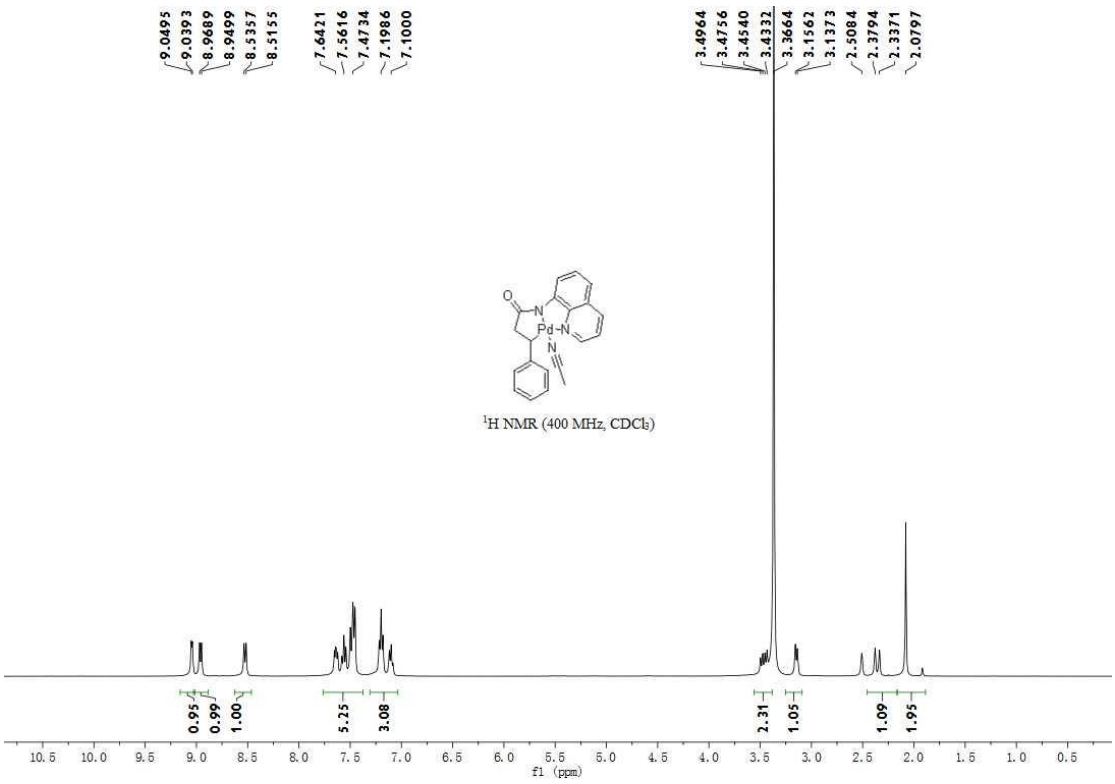
^{1}H NMR spectrum (400 MHz) of compound **13** in $CDCl_3$



^{13}C NMR spectrum (100 MHz) of compound **13** in $CDCl_3$

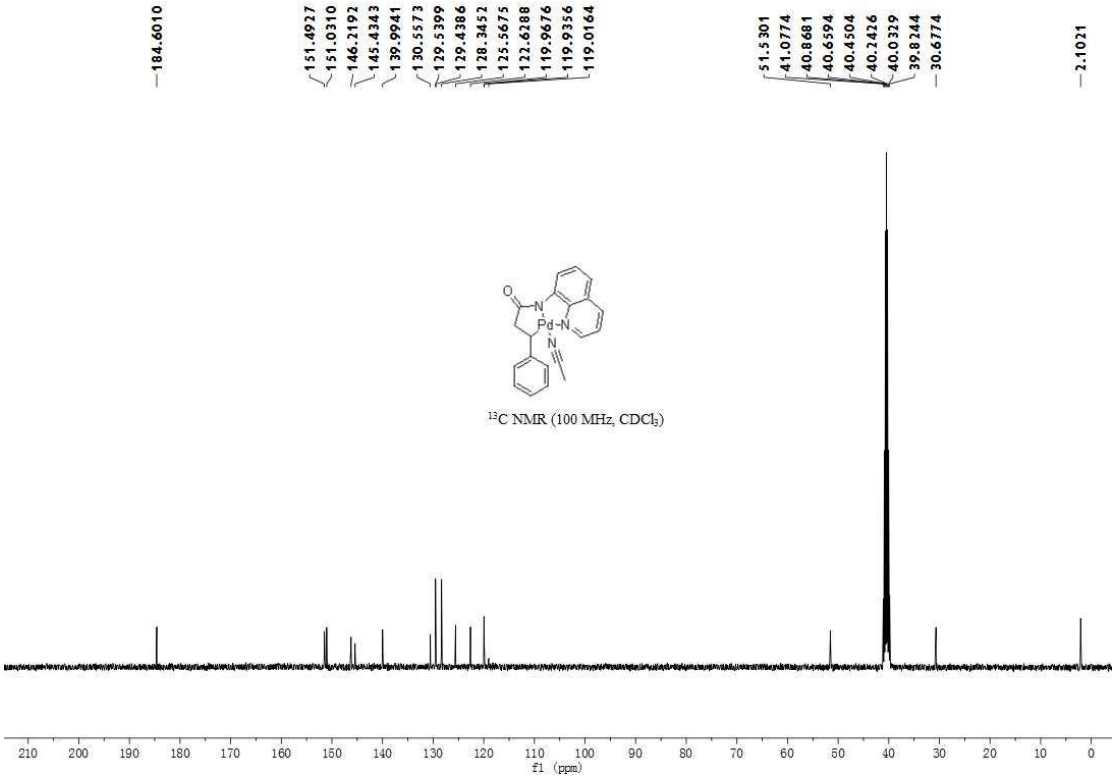


^{1}H NMR spectrum (400 MHz) of compound **17** in $CDCl_3$



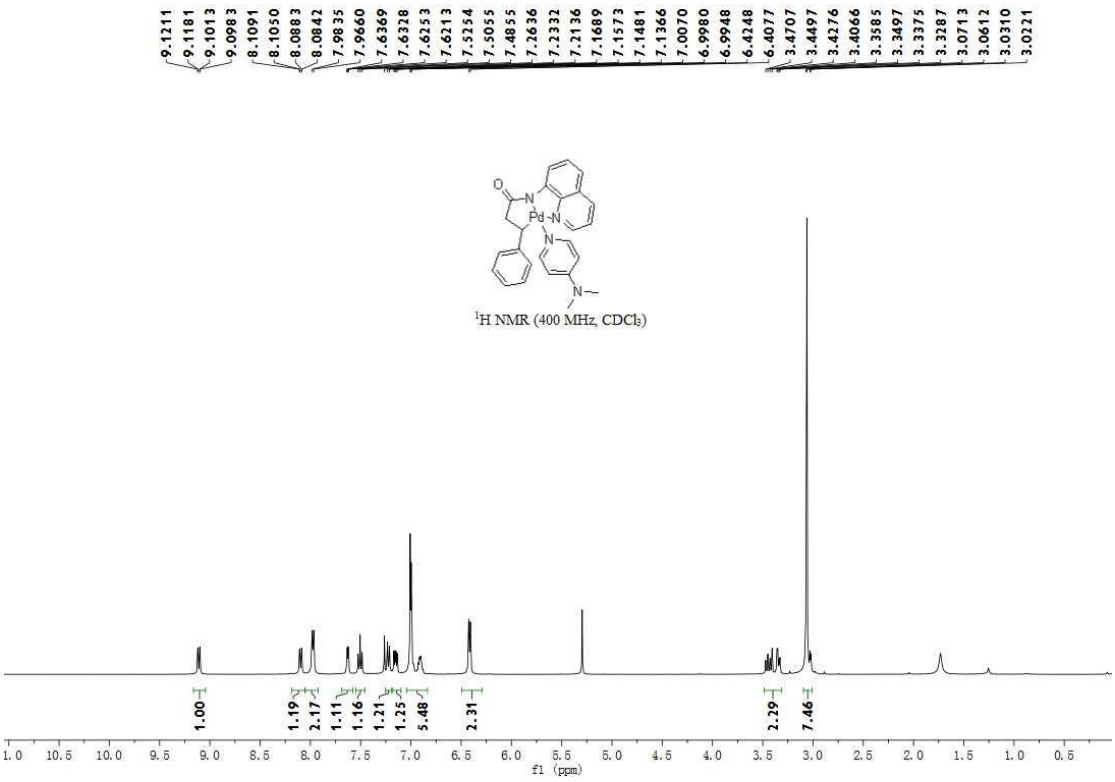
^{1}H NMR (400 MHz, $CDCl_3$)

^{13}C NMR spectrum (100 MHz) of compound **17** in $CDCl_3$

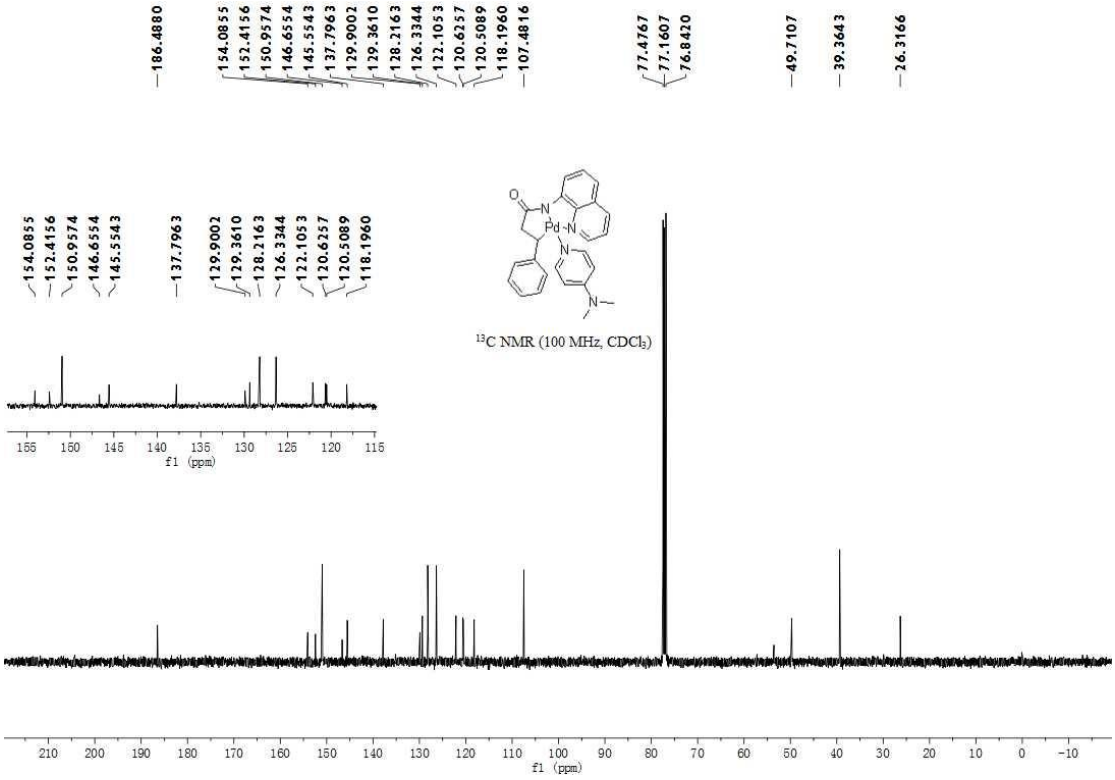


^{13}C NMR (100 MHz, $CDCl_3$)

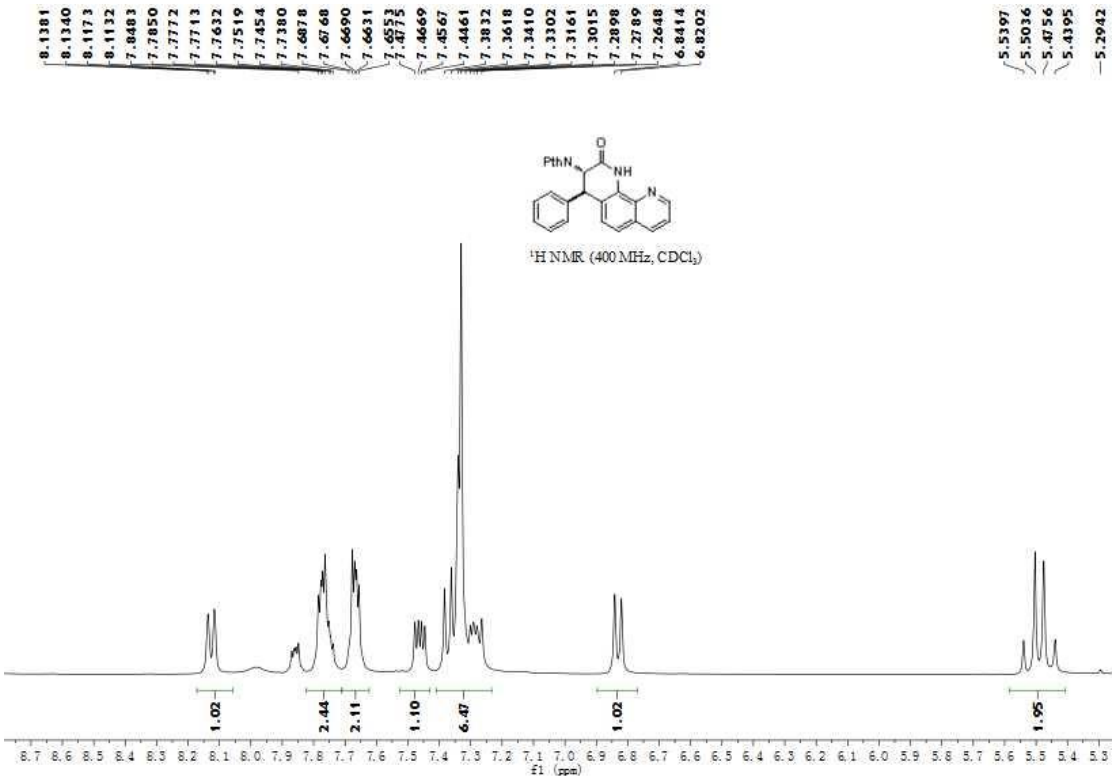
^{1}H NMR spectrum (400 MHz) of compound **18** in $CDCl_3$



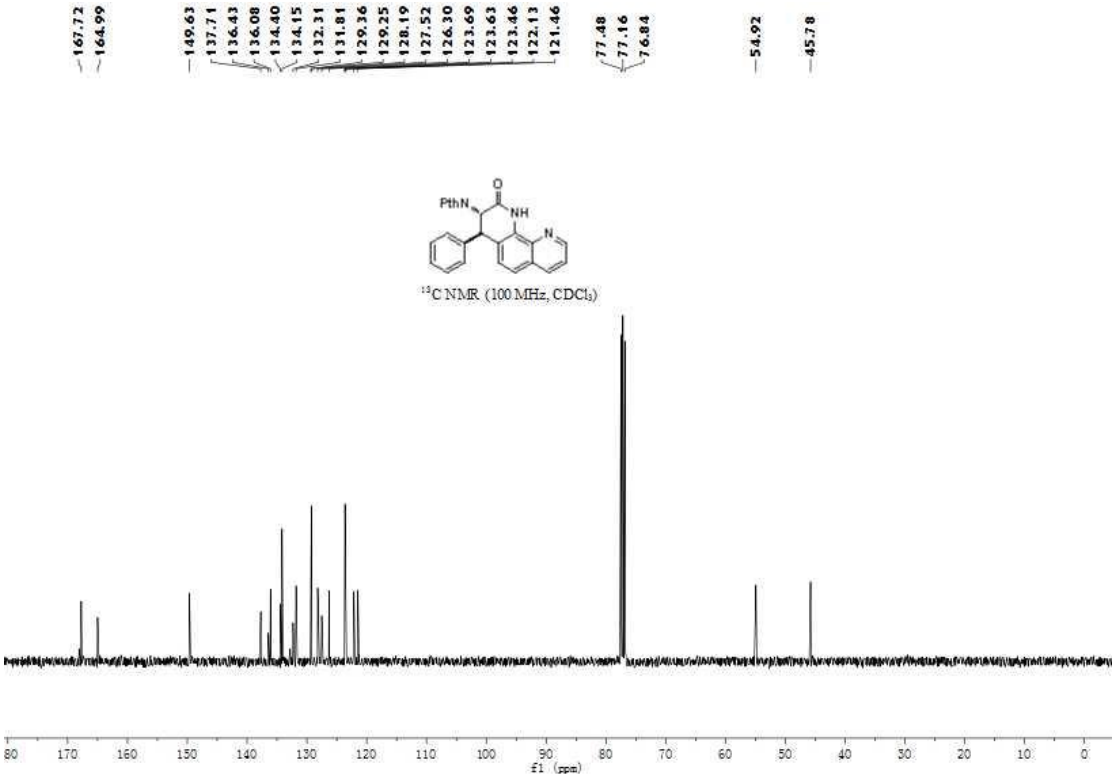
^{13}C NMR spectrum (100 MHz) of compound **18** in $CDCl_3$



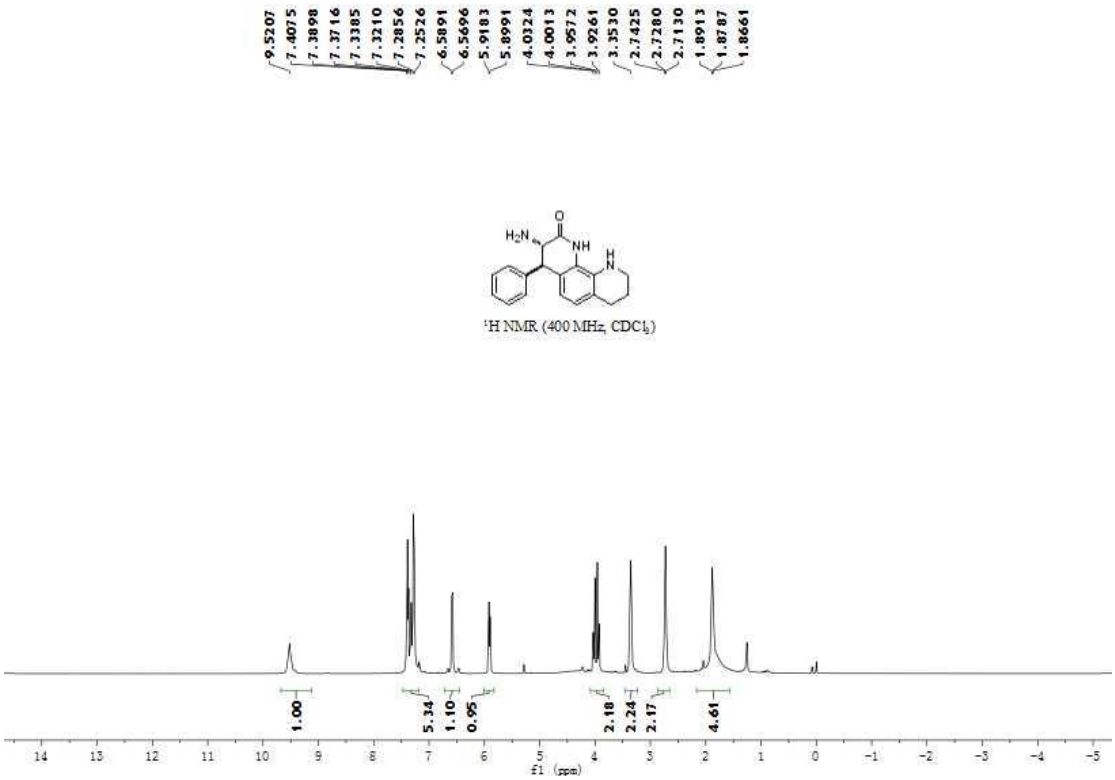
^{1}H NMR spectrum (400 MHz) of compound **2y** in $CDCl_3$



^{13}C NMR spectrum (100 MHz) of compound **2y** in $CDCl_3$



^{1}H NMR spectrum (400 MHz) of compound **2y'** in $CDCl_3$



^{13}C NMR spectrum (100 MHz) of compound **2y'** in $CDCl_3$