Supporting Information

Rearrangement of 2-(Benzofuran-2-yl)-3-Phenylpyridines *via* Photoinduced 6π-Electrocyclization

Jin Xi, Ding Wang, Jinxia Hu, Huan Shen,Tao Wang and Zunting Zhang*

Key Laboratory of the Ministry of Education for Medicinal Resources and Natural Pharmaceutical Chemistry, National Engineering Laboratory for Resource Development of Endangered Crude Drugs in Northwest of China, and School of Chemistry and Chemical Engineering, Shaanxi Normal University, Xi'an 710119, People's Republic of China.

Contents

1. General information

^{1}H NMR and ^{13}C NMR were recorded on a Bruker - 400 MHz, 600 MHz Spectrometer (^{1}H: 400 MHz, ^{13}C: 101 MHz), (^{1}H: 600 MHz, ^{13}C: 151 MHz), using $CDCl_3$ and DMSO-d_6 as the solvent at room temperature. The chemical shifts (δ) were expressed in ppm and the coupling constants (*J*) were expressed in Hz. High-resolution mass spectra (HRMS) were recorded on a Bruker MAXIS spectrometer. The irradiation experiments were performed in a photo-chemical reactor equipped with 64 W (8 x 8 w) of 313 nm UV light and 64 W of 254 nm UV light under an argon atmosphere in quartz tubes.

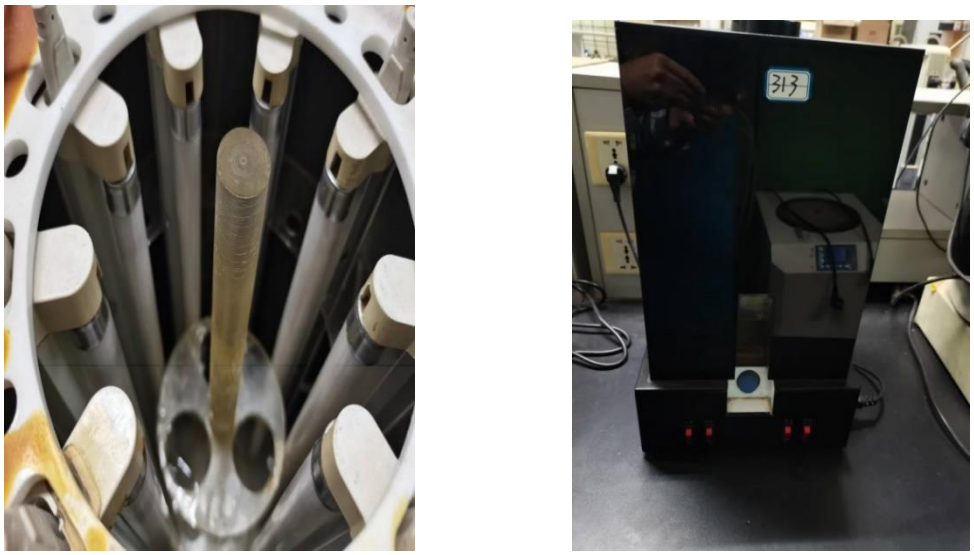


Figure S1. 313 nm ultraviolet lamp (64 W)

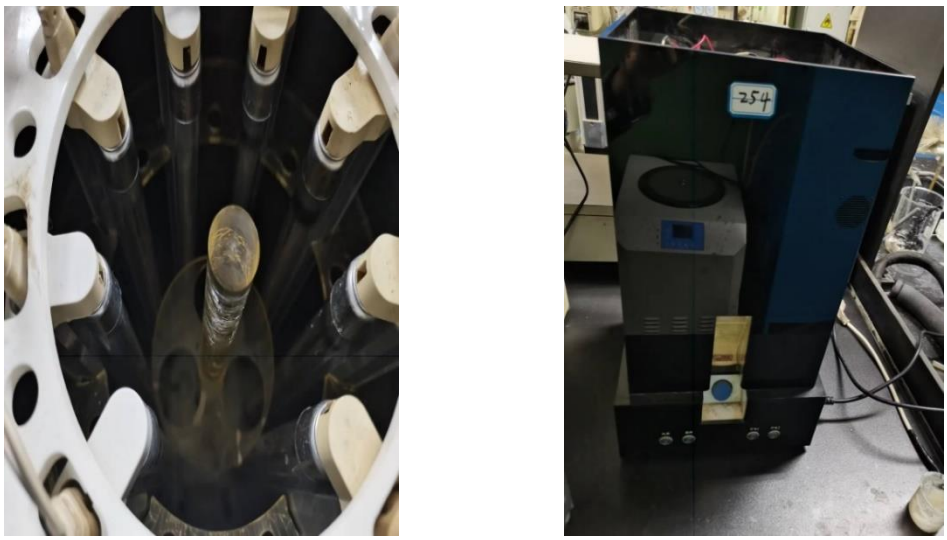
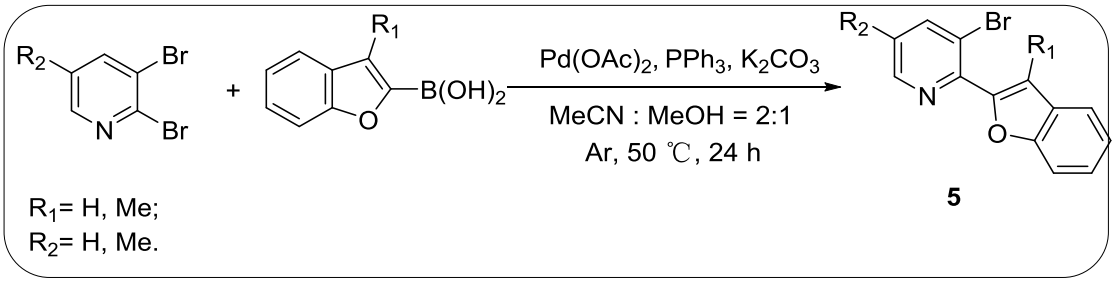


Figure S2. 254 nm ultraviolet lamp (64 W)

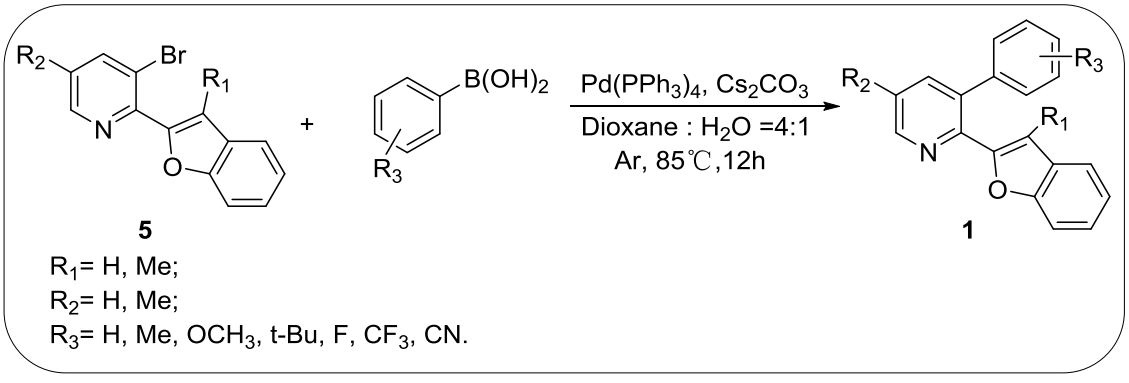
2. Synthetic schemes

Scheme S1. Synthesis of 2-(benzofuran-2-yl)-3-bromopyridines **(5a-5d)**.



A mixture of 2, 3-dibromopyridine (3 mmol, 708 mg), benzofuran-2-ylboronic acid (1.1 eq, 3.3 mmol) was dissolved in a mixed solvent of MeCN : MeOH = 2:1 (20 mL : 10 mL) followed with the addition of PPh_3 (20%, 0.6 mmol, 157 mg), $Pd(OAc)_2$ (10%, 0.3 mmol, 68 mg) and K_2CO_3 (2 eq, 6 mmol, 828 mg). The resulting mixture was flushed with argon, sealed, and stirred at 50 ℃ for 12-24 h in an oil bath. The volatiles was removed under reduced pressure after being cooled at room temperature. The residue was dissolved in CH_2Cl_2 (20 mL) and washed with water (40 mL × 3). The organic layer was dried (Na_2SO_4), concentrated and the residue was purified by column chromatography (EtOAc / Petroleum ether = 1/200 ~ 1/100) to give 2-(benzofuran-2-yl)-3-bromopyridine **5.**[1]

Scheme S2. Synthesis of 2-(benzofuran-2-yl)-3-phenylpyridines **(1a-1u)**.



The mixture of 2-(benzofuran-2-yl)-3-bromopyridine **5** (1 mmol), arylboronic acid (3 eq, 3 mmol) was dissolved in a mixed solvent of dioxane : H_2O = 4:1 (12 mL : 3mL) followed with the addition of $Pd(PPh_3)$ (5% mmol, 58 mg) and Cs_2CO_3 (5 eq, 5 mmol,

1.63 g). The resulting mixture was stirred at 85 ℃ for 12 h under an argon atmosphere. The volatiles was removed under reduced pressure after the reaction mixture was cooled at room temperature. The residue was dissolved in ethyl acetate (20 mL) and washed with water (30 mL × 3). The organic layer was dried (Na_2SO_4), concentrated and the residue was purified by column chromatography (EtOAc / Petroleum ether = 1/75~ 1/25) to give the desired product **1.** [2]

3. UV absorption spectra of 1a, 1l, 2l, 3l and 4a

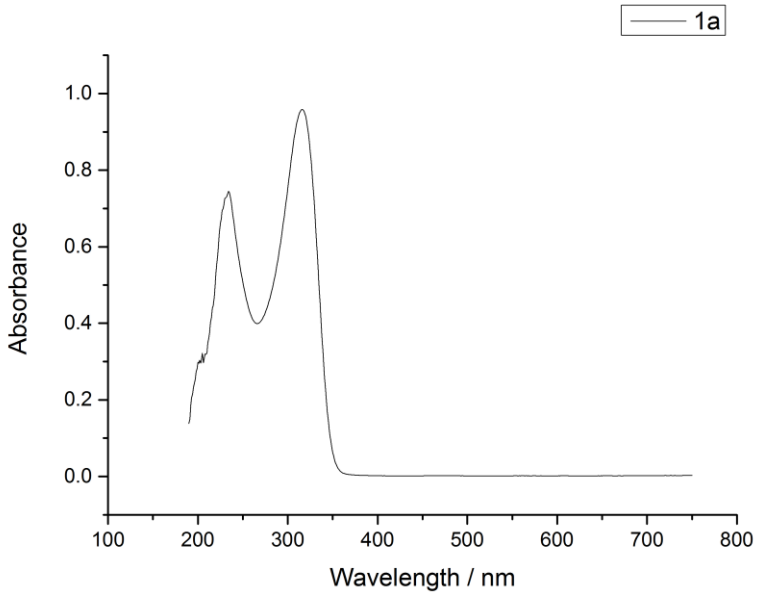


Figure S3. UV absorption spectra of **1a** in DCM (10^{-5} M).

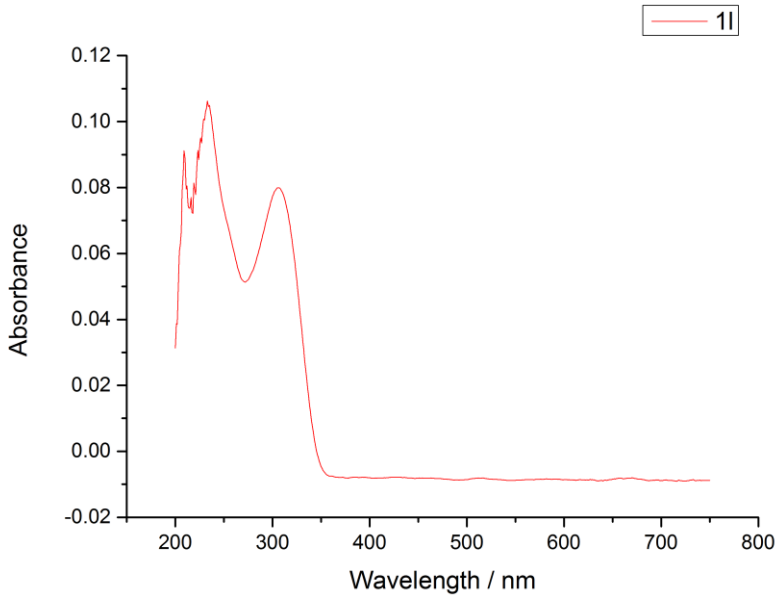


Figure S4. UV absorption spectra of **1l** in DCM (10^{-5} M).

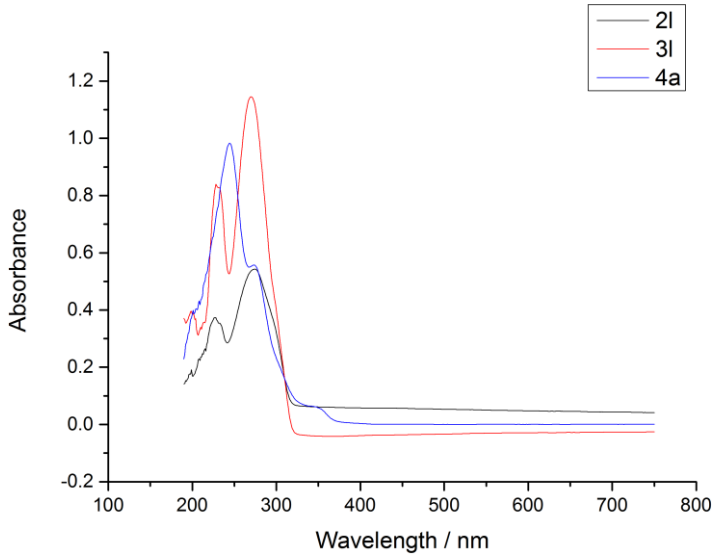
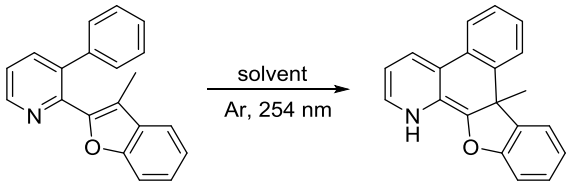


Figure S5. UV absorption spectra of **2l**, **3l** and **4a** in DCM (10^{-5} M).

4. Conditions optimization

The solution **1l** (0.2 mmol) in CH_2Cl_2 (40 mL, 5 mM) was irradiated by 254 nm UV light for 2 hours under an argon atmosphere at room temperature to give **4a** in 62% yield (Table 1, entry 1). Various solvents were explored, such as ethanol, acetonitrile, 1,2-dichloroethane, **4a** was obtained in 50%, 57% and 56% yield (entries 2-4). Extending the irradiation time to 3 hours led to the formation of **4a** in higher yield (65%, entry 5). Further increase of the exposure time to 9 h boosted the yield of **4a** to 79% (entry 6). However, either higher or lower substrate (**1l**) concentrations resulted in a lower yield of **4a** (entries 7-9). In consequence, irradiation of **1l-1u** (5 mM) in CH_2Cl_2 with a 254 nm UV lamp under an argon atmosphere at room temperature is the optimal condition for the synthesis of **4**.

Table 1 Optimization of reaction conditions for the synthesis of **4a**[a]



1l **4a**

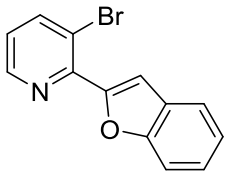
Entry	Solvent	*C* (mol/L)	Time (h)	Yield[b] (%)
1	CH_2Cl_2	0.005	2	62
2	EtOH	0.005	2	50
3	CH_3CN	0.005	2	57
4	DCE	0.005	2	56
5	CH_2Cl_2	0.005	3	65
6	CH_2Cl_2	0.005	9	79
7	CH_2CL_2	0.003	9	76
8	CH_2Cl_2	0.007	9	70
9	CH_2Cl_2	0.01	9	64

[a] Irradiation of **1l** (0.2 mmol) in various solvents (40 mL, 5 mM) with a 254 nm UV lamp (64 W) under an argon atmosphere at r.t. [b] Isolated yield.

5. Characterization data for products

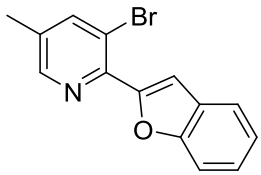
The data of 5a-5d

2-(Benzofuran-2-yl)-3-bromopyridine (5a)



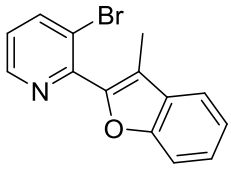
Yield: 74% (608 mg). Yellow solid. R_f = 0.39 (EtOAc / Petroleum ether = 1/10). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.71 (d, *J* = 16.5 Hz, 1H), 8.06 – 7.92 (m, 1H), 7.89 – 7.78 (m, 1H), 7.67 (s, 2H), 7.38 (d, *J* = 6.4 Hz, 1H), 7.29 (s, 1H), 7.16 – 7.02 (m, 1H).[3]

2-(Benzofuran-2-yl)-3-bromo-5-methylpyridine (5b)



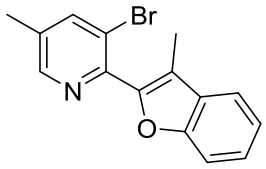
Yield: 67% (579 mg). White solid. m.p. 76.5-77.9 ℃. R_f = 0.40 (EtOAc / Petroleum ether = 1/10). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.55 (s, 1H), 7.87 – 7.75 (m, 2H), 7.66 (d, *J* = 7.2 Hz, 2H), 7.37 (t, *J* = 7.2 Hz, 1H), 7.28 (s, 1H), 2.37 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.8, 152.4, 148.8, 144.8, 142.5, 133.9, 128.4, 125.7, 123.2, 121.8, 117.9, 111.9, 109.4, 17.8. HRMS (ESI) m/z calcd for. $C_{14}H_{11}BrNO^+$ $[M+H]^+$ 288.0019, found 288.0018.

3-Bromo-2-(3-methylbenzofuran-2-yl)pyridine (5c)



Yield: 60% (519 mg). Colorless oil. R_f = 0.39 (EtOAc / Petroleum ether = 1/10). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.68 (dd, *J* = 4.6, 1.3 Hz, 1H), 8.00 (dd, *J* = 8.1, 1.2 Hz, 1H), 7.61 (s, 1H), 7.56 (d, *J* = 8.2 Hz, 1H), 7.39 – 7.34 (m, 1H), 7.33 – 7.28 (m, 1H), 7.17 (dd, *J* = 8.1, 4.6 Hz, 1H), 2.40 (s, 3H).[3]

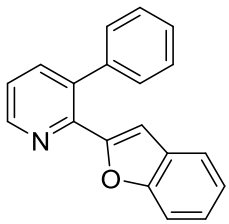
3-Bromo-5-methyl-2-(3-methylbenzofuran-2-yl)pyridine (5d)



Yield: 40% (363 mg). White solid. m.p. 81.2-82.7 ℃. R_f = 0.40 (EtOAc / Petroleum ether = 1/10). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.54 (d, *J* = 1.2 Hz, 1H), 7.88 (d, *J* = 1.0 Hz, 1H), 7.62 (d, *J* = 7.1 Hz, 1H), 7.55 (d, *J* = 8.1 Hz, 1H), 7.39 – 7.34 (m, 1H), 7.33 – 7.28 (m, 1H), 2.42 (s, 3H), 2.39 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.4, 148.9, 148.8, 147.0, 141.7, 134.8, 130.0, 125.1, 122.6, 120.8, 120.0, 115.9, 111.6, 18.0, 9.5. HRMS (APCI) m/z calcd for. $C_{15}H_{13}BrNO^+$ $[M+H]^+$ 302.0175, found 302.0171.

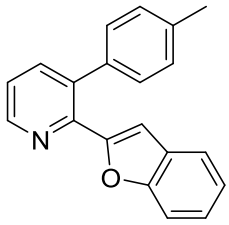
The data of 1a-1u

2-(Benzofuran-2-yl)-3-phenylpyridine (1a)



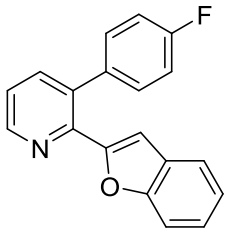
Yield: 90% (244 mg). Colorless oil. R_f = 0.47 (EtOAc / Petroleum ether = 1/10). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.79 – 8.75 (m, 1H), 7.64 – 7.58 (m, 1H), 7.52 (d, *J* = 8.3 Hz, 1H), 7.44 – 7.38 (m, 4H), 7.33 (dd, *J* = 3.6, 1.9 Hz, 2H), 7.26 (ddd, *J* = 7.5, 3.3, 2.0 Hz, 2H), 7.18 – 7.11 (m, 1H), 6.31 (s, 1H).[3]

2-(Benzofuran-2-yl)-3-(p-tolyl)pyridine (1b)



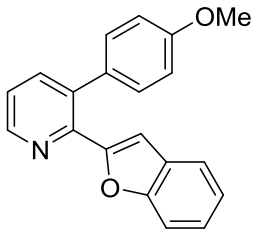
Yield: 93% (265 mg). White solid. m.p. 76.9-78.6 ℃. R_f = 0.47 (EtOAc / Petroleum ether = 1/10). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.76 (dd, *J* = 4.6, 1.4 Hz, 1H), 7.61 (d, *J* = 7.6 Hz, 1H), 7.54 (d, *J* = 8.2 Hz, 1H), 7.42 (d, *J* = 7.7 Hz, 1H), 7.31 – 7.22 (m, 6H), 7.16 (t, *J* = 7.5 Hz, 1H), 6.30 (s, 1H), 2.44 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.6, 153.8, 148.5, 146.8, 138.8, 137.9, 136.6, 136.4, 129.5, 128.8, 128.4, 125.1, 122.9, 122.4, 121.5, 111.7, 108.5, 21.3. HRMS (ESI) m/z calcd for. $C_{20}H_{16}NO^+$ $[M+H]^+$ 286.1226, found 286.1224.

2-(Benzofuran-2-yl)-3-(4-fluorophenyl)pyridine (1c)



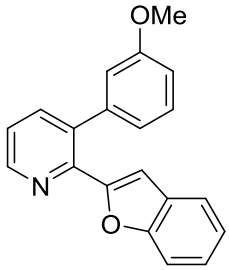
Yield: 97% (280 mg). Yellow oil. R_f = 0.47 (EtOAc / Petroleum ether = 1/10). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.75 (dd, *J* = 2.9, 1.8 Hz, 1H), 7.58 (d, *J* = 7.7 Hz, 1H), 7.46 (dd, *J* = 13.7, 8.0 Hz, 2H), 7.27 (dt, *J* = 7.3, 4.5 Hz, 4H), 7.18 – 7.08 (m, 3H), 6.39 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.6 (d, ^1J = 247.4 Hz), 154.6 (s), 153.7 (s), 148.8 (s), 146.8(s), 138.8 (s), 135.5 (d, ^4J = 3.5 Hz), 135.1, 130.6 (d, ^3J = 8.2 Hz), 128.2, 125.2, 123.0, 122.4, 121.5, 115.7 (d, ^2J = 21.5 Hz), 111.6, 108.4. HRMS (ESI) m/z calcd for. $C_{19}H_{13}FNO^+$ $[M+H]^+$ 290.0976, found 290.0972.

2-(Benzofuran-2-yl)-3-(4-methoxyphenyl)pyridine (1d)



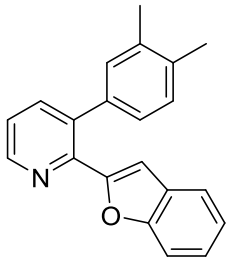
Yield: 92% (277 mg). White solid. m.p. 94.7-96.6 ℃. R_f = 0.46 (EtOAc / Petroleum ether = 1/10). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.76 (d, *J* = 3.7 Hz, 1H), 7.63 (d, *J* = 7.5 Hz, 1H), 7.55 (d, *J* = 8.2 Hz, 1H), 7.45 (d, *J* = 7.7 Hz, 1H), 7.29 (dd, *J* = 14.1, 6.5 Hz, 4H), 7.18 (t, *J* = 7.4 Hz, 1H), 6.98 (d, *J* = 8.5 Hz, 2H), 6.33 (s, 1H), 3.88 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.6, 154.6, 153.9, 148.5, 147.0, 139.0, 136.1, 131.9, 130.1, 128.5, 125.2, 122.9, 122.5, 121.5, 114.2, 111.7, 108.5, 55.4. HRMS (ESI) m/z calcd for. $C_{20}H_{16}NO_2^+$ $[M+H]^+$ 302.1176, found 302.1172.

2-(Benzofuran-2-yl)-3-(3-methoxyphenyl)pyridine (1e)



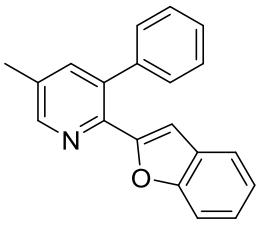
Yield: 90% (271 mg). Colorless oil. R_f = 0.46 (EtOAc / Petroleum ether = 1/10). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.65 (dd, *J* = 4.7, 0.8 Hz, 1H), 7.51 (d, *J* = 7.6 Hz, 1H), 7.40 (d, *J* = 8.3 Hz, 1H), 7.30 (d, *J* = 7.8 Hz, 1H), 7.22 (t, *J* = 7.9 Hz, 1H), 7.15 (dd, *J* = 14.4, 7.4 Hz, 2H), 7.03 (t, *J* = 7.5 Hz, 1H), 6.86 (dd, *J* = 8.3, 2.4 Hz, 1H), 6.78 (dd, *J* = 10.0, 4.7 Hz, 2H), 6.24 (s, 1H), 3.63 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.8, 154.6, 153.6, 148.7, 146.7, 140.9, 138.6, 136.1, 129.8, 128.4, 125.2, 122.9, 122.3, 121.5, 121.3, 114.3, 113.7, 111.7, 108.5, 55.3. HRMS (ESI) m/z calcd for. $C_{20}H_{16}NO_2^+$ $[M+H]^+$ 302.1176, found 302.1171.

2-(Benzofuran-2-yl)-3-(3,4-dimethylphenyl)pyridine (1f)



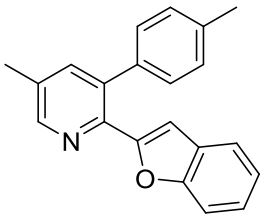
Yield: 93% (278 mg). White solid. m.p. 88-89.6 ℃. R_f = 0.46 (EtOAc / Petroleum ether = 1/10). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.69 (dd, *J* = 4.7, 1.6 Hz, 1H), 7.54 (dd, *J* = 7.7, 1.6 Hz, 1H), 7.48 (d, *J* = 8.2 Hz, 1H), 7.35 (d, *J* = 7.7 Hz, 1H), 7.22 – 7.17 (m, 2H), 7.14 – 7.04 (m, 3H), 6.99 (dd, *J* = 7.7, 1.4 Hz, 1H), 6.22 (d, *J* = 0.4 Hz, 1H), 2.28 (s, 3H), 2.22 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.6, 153.8, 148.5, 146.8, 138.9, 137.1, 137.1, 136.6, 130.0, 130.0, 128.5, 126.3, 125.1, 122.9, 122.4, 121.5, 111.8, 108.5, 19.9, 19.7. HRMS (ESI) m/z calcd for. $C_{21}H_{18}NO^+$ $[M+H]^+$ 300.1383, found 300.1377.

2-(Benzofuran-2-yl)-5-methyl-3-phenylpyridine (1g)



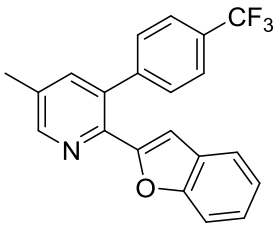
Yield: 90% (257 mg). White solid. m.p. 99.5-101.8 ℃. R_f = 0.46 (EtOAc / Petroleum ether = 1/10). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.63 (s, 1H), 7.53 (d, *J* = 8.2 Hz, 1H), 7.46 (dd, *J* = 7.6, 4.7 Hz, 4H), 7.41 (d, *J* = 7.7 Hz, 1H), 7.36 (dd, *J* = 6.3, 2.8 Hz, 2H), 7.27 (t, *J* = 7.1 Hz, 1H), 7.17 (t, *J* = 7.4 Hz, 1H), 6.23 (s, 1H), 2.44 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.6, 154.0, 149.3, 144.3, 139.8, 139.3, 136.0, 132.4, 129.0, 128.8, 128.6, 128.1, 125.0, 122.9, 121.4, 111.7, 107.8, 18.2. HRMS (ESI) m/z calcd for. $C_{20}H_{16}NO^+$ $[M+H]^+$ 286.1226, found 286.1222.

2-(Benzofuran-2-yl)-5-methyl-3-(p-tolyl)pyridine (1h)



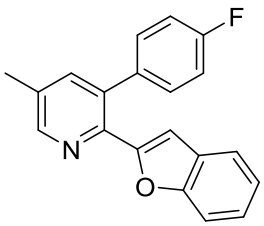
Yield: 98% (293 mg). White solid. m.p. 115.4-118.1 ℃. R_f = 0.46 (EtOAc / Petroleum ether = 1/10). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.62 (d, *J* = 1.7 Hz, 1H), 7.55 (d, *J* = 8.2 Hz, 1H), 7.44 (dd, *J* = 12.5, 4.6 Hz, 2H), 7.31 – 7.23 (m, 5H), 7.17 (t, *J* = 7.5 Hz, 1H), 6.25 (s, 1H), 2.46 (s, 3H), 2.43 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.6, 154.0, 149.1, 144.4, 139.4, 137.8, 136.8, 136.0, 132.3, 129.5, 128.8, 128.6, 124.9, 122.8, 121.4, 111.7, 107.8, 21.4, 18.2. HRMS (ESI) m/z calcd for. $C_{21}H_{18}NO^+$ $[M+H]^+$ 300.1383, found 300.1379.

2-(Benzofuran-2-yl)-5-methyl-3-(4-(trifluoromethyl)phenyl)pyridine (1i)



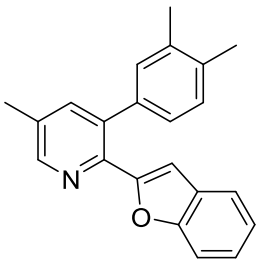
Yield: 95% (335 mg). White solid. m.p. 105.3-107.4 ℃. R_f = 0.47 (EtOAc / Petroleum ether = 1/10). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.65 (s, 1H), 7.72 (d, *J* = 8.0 Hz, 2H), 7.49 (d, *J* = 7.5 Hz, 4H), 7.43 (d, *J* = 8.2 Hz, 1H), 7.29 (d, *J* = 6.3 Hz, 1H), 7.20 (t, *J* = 7.4 Hz, 1H), 6.46 (s, 1H), 2.46 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ154.7, 153.9, 149.9, 144.2, 143.6, 139.2, 134.4, 132.7, 130.2 (q, ^2J = 32.8 Hz), 129.6, 128.4, 125.6 (q, ^3J = 3.7 Hz), 125.2, 123.1, 121.5, 111.7, 107.9, 18.3. HRMS (ESI) m/z calcd for. $C_{21}H_{15}F_3NO^+$ $[M+H]^+$ 354.1100, found 354.1097.

2-(Benzofuran-2-yl)-3-(4-fluorophenyl)-5-methylpyridine (1j)



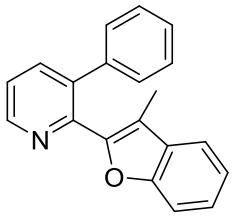
Yield: 90% (273 mg). White solid. m.p. 77.8-80.6 ℃. R_f = 0.47 (EtOAc / Petroleum ether = 1/10). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.62 (d, *J* = 1.5 Hz, 1H), 7.52 – 7.48 (m, 1H), 7.46 (dd, *J* = 3.9, 2.3 Hz, 2H), 7.34 – 7.27 (m, 3H), 7.20 – 7.11 (m, 3H), 6.33 (s, 1H), 2.43 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.7 (d, ^1J = 247.3 Hz), 154.6, 153.9, 149.4, 144.3, 139.4, 135.7 (d, ^4J = 3.5 Hz), 134.8, 132.4, 130.7 (d, ^3J = 8.1 Hz), 128.5, 125.0, 123.0, 121.4, 115.7 (d, ^2J = 21.5 Hz), 111.7, 107.7, 18.2. HRMS (ESI) m/z calcd for. $C_{20}H_{15}FNO^+$ $[M+H]^+$ 304.1132, found 304.1128.

2-(Benzofuran-2-yl)-3-(3,4-dimethylphenyl)-5-methylpyridine (1k)



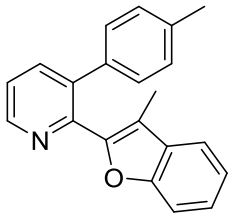
Yield: 91% (285 mg). White solid. m.p. 116.1-118.2 ℃. R_f = 0.47 (EtOAc / Petroleum ether = 1/10). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.58 (d, *J* = 1.7 Hz, 1H), 7.53 (dd, *J* = 8.3, 0.5 Hz, 1H), 7.42 (dt, *J* = 12.9, 5.5 Hz, 2H), 7.26 – 7.10 (m, 4H), 7.05 (dd, *J* = 7.6, 1.6 Hz, 1H), 6.21 (dd, *J* = 4.5, 0.7 Hz, 1H), 2.39 (s, 3H), 2.34 (s, 3H), 2.28 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ154.6, 154.1, 149.0, 144.3, 139.5, 137.3, 137.1, 136.5, 136.2, 132.2, 130.1, 130.0, 128.7, 126.4, 124.9, 122.8, 121.4, 111.8, 107.8, 19.9, 19.7, 18.2. HRMS (ESI) m/z calcd for. $C_{22}H_{20}NO^+$ $[M+H]^+$ 314.1539, found 314.1536.

2-(3-Methylbenzofuran-2-yl)-3-phenylpyridine (1l)



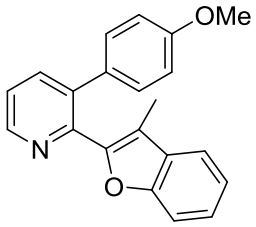
Yield: 91% (260 mg). Colorless oil. R_f = 0.46 (EtOAc / Petroleum ether = 1/10). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.75 (dd, *J* = 4.7, 1.4 Hz, 1H), 7.80 (dd, *J* = 7.8, 1.5 Hz, 1H), 7.43 (d, *J* = 7.6 Hz, 1H), 7.37 (dd, *J* = 8.5, 6.2 Hz, 2H), 7.28 – 7.23 (m, 6H), 7.20 (t, *J* = 7.3 Hz, 1H), 1.91 (s, 3H).[3]

2-(3-Methylbenzofuran-2-yl)-3-(p-tolyl)pyridine (1m)



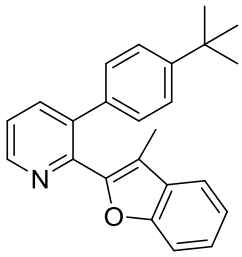
Yield: 83% (248 mg). White solid. m.p. 85.9-87.1 ℃. R_f = 0.46 (EtOAc / Petroleum ether = 1/10). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.75 (dd, *J* = 4.7, 1.7 Hz, 1H), 7.81 (dd, *J* = 7.9, 1.7 Hz, 1H), 7.46 – 7.37 (m, 3H), 7.30 – 7.26 (m, 1H), 7.23 (dd, *J* = 7.5, 1.0 Hz, 1H), 7.20 – 7.15 (m, 2H), 7.09 (d, *J* = 7.9 Hz, 2H), 2.33 (s, 3H), 1.86 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.5, 149.9, 148.3, 148.0, 138.5, 137.8, 137.3, 136.3, 130.2, 129.3, 128.6, 124.7, 123.3, 122.3, 119.8, 114.8, 111.5, 21.2, 8.5. HRMS (APCI) m/z calcd for. $C_{21}H_{18}NO^+$ $[M+H]^+$ 300.1383, found 300.1380.

3-(4-Methoxyphenyl)-2-(3-methylbenzofuran-2-yl)pyridine (1n)



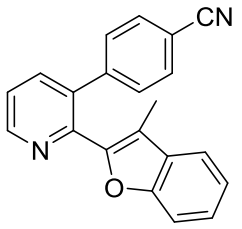
Yield: 70% (220 mg). Colorless oil. R_f = 0.46 (EtOAc / Petroleum ether = 1/10). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.75 (dd, *J* = 4.6, 1.3 Hz, 1H), 7.82 – 7.78 (m,1H), 7.47 (dd, *J* = 11.0, 8.0 Hz, 2H), 7.38 (dd, *J* = 7.8, 4.7 Hz, 1H), 7.30 (dd, *J* = 10.4, 4.5 Hz, 1H), 7.23 (d, *J* = 8.8 Hz, 3H), 6.84 (d, *J* = 8.7 Hz, 2H), 3.78 (s, 3H), 1.92 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.1, 154.4, 149.8, 148.0, 147.8, 138.2, 137.3, 131.5, 130.1, 129.8, 124.6, 123.2, 122.3, 119.7, 114.6, 113.9, 111.4, 55.2, 8.4. HRMS (APCI) m/z calcd for. $C_{21}H_{18}NO_2^+$ $[M+H]^+$ 316.1332, found 316.1330.

3-(4-(Tert-butyl)phenyl)-2-(3-methylbenzofuran-2-yl)pyridine (1o)



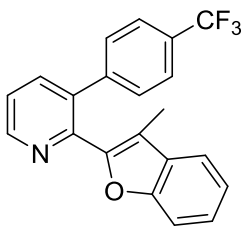
Yield: 85% (290 mg). Colorless oil. R_f = 0.45 (EtOAc / Petroleum ether = 1/10). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.78 (dd, *J* = 4.7, 1.6 Hz, 1H), 7.85 (dd, *J* = 7.8, 1.7 Hz, 1H), 7.48 (dd, *J* = 7.6, 0.6 Hz, 1H), 7.43 – 7.39 (m, 2H), 7.35 (dd, *J* = 9.2, 2.4 Hz, 2H), 7.32 – 7.28 (m, 1H), 7.26 (ddd, *J* = 4.5, 3.4, 1.5 Hz, 2H), 7.24 (d, *J* = 2.3 Hz, 1H), 1.88 (s, 3H), 1.34 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.5, 150.6, 149.9, 148.3, 148.1, 138.5, 137.6, 136.3, 130.2, 128.5, 125.4, 124.7, 123.2, 122.3, 119.8, 114.9, 111.5, 34.6, 31.4, 8.4. HRMS (APCI) m/z calcd for. $C_{24}H_{24}NO^+$ $[M+H]^+$ 342.1852, found 342.1853.

4-(2-(3-Methylbenzofuran-2-yl)pyridin-3-yl)benzonitrile (1p)



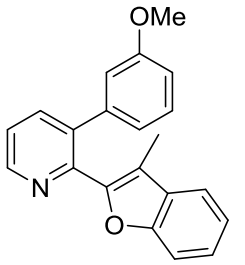
Yield: 90% (279 mg). White solid. m.p. 112.1-113.1 ℃. R_f = 0.46 (EtOAc / Petroleum ether = 1/10). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.82 (dd, *J* = 4.6, 1.4 Hz, 1H), 7.80 (dd, *J* = 7.8, 1.4 Hz, 1H), 7.61 (d, *J* = 8.2 Hz, 2H), 7.54 – 7.50 (m, 1H), 7.44 (dd, *J* = 7.8, 4.7 Hz, 1H), 7.39 (d, *J* = 8.2 Hz, 2H), 7.31 – 7.24 (m, 3H), 2.16 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ154.2, 149.4, 148.9, 148.1, 144.4, 138.3, 135.5, 132.2, 130.0, 129.5, 125.3, 123.1, 122.7, 120.0, 118.8, 116.2, 111.3, 111.3, 8.9. HRMS (APCI) m/z calcd for. $C_{21}H_{15}N_2O^+$ $[M+H]^+$ 311.1179, found 311.1179.

2-(3-Methylbenzofuran-2-yl)-3-(4-(trifluoromethyl)phenyl)pyridine (1q)



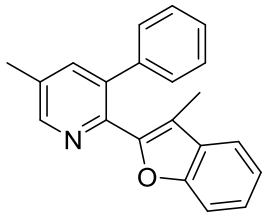
Yield: 92% (325 mg). Colorless oil. R_f = 0.47 (EtOAc / Petroleum ether = 1/10). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.83 (dd, *J* = 4.7, 1.6 Hz, 1H), 7.82 (dd, *J* = 7.8, 1.7 Hz, 1H), 7.59 (d, *J* = 8.2 Hz, 2H), 7.52 (d, *J* = 7.6 Hz, 1H), 7.46 – 7.39 (m, 3H), 7.32 – 7.23 (m, 3H), 2.10 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.3, 149.1, 148.2, 143.2, 138.4, 136.0, 130.0, 129.6 (q, ^2J = 32.5 Hz), 129.1, 125.4 (q, ^3J = 3.7 Hz), 125.1, 124.2 (q, ^1J = 272.1 Hz), 123.1, 122.6, 119.9, 115.8, 111.4, 8.8. HRMS (APCI) m/z calcd for. $C_{21}H_{15}F_3NO^+$ $[M+H]^+$ 354.1100, found 354.1093.

3-(3-Methoxyphenyl)-2-(3-methylbenzofuran-2-yl)pyridine (1r)



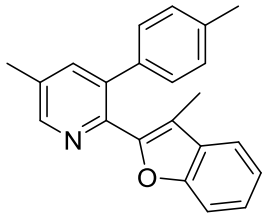
Yield: 90% (284 mg). Yellow oil. R_f = 0.47 (EtOAc / Petroleum ether = 1/10). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.78 (d, *J* = 4.7 Hz, 1H), 7.85 (d, *J* = 7.8 Hz, 1H), 7.48 (d, *J* = 7.6 Hz, 1H), 7.40 (dd, *J* = 11.4, 5.9 Hz, 2H), 7.29 (t, *J* = 7.7 Hz, 1H), 7.22 (dt, *J* = 12.0, 7.6 Hz, 2H), 6.89 (d, *J* = 7.7 Hz, 1H), 6.85 (d, *J* = 7.3 Hz, 2H), 3.61 (s, 3H), 1.97 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 159.5, 154.3, 149.5, 148.5, 148.0, 140.5, 138.4, 137.6, 130.0, 129.5, 124.7, 123.2, 122.3, 121.2, 119.7, 115.1, 114.0, 113.4. 111.3, 55.1, 8.4. HRMS (APCI) m/z calcd for. $C_{21}H_{18}NO_2^+$ $[M+H]^+$ 316.1332, found 316.1331.

5-Methyl-2-(3-methylbenzofuran-2-yl)-3-phenylpyridine (1s)



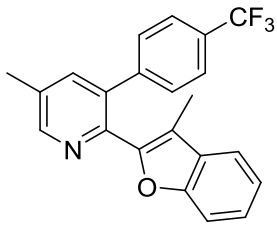
Yield: 91% (272 mg). Colorless oil. R_f = 0.47 (EtOAc / Petroleum ether = 1/10). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.64 – 8.61 (m, 1H), 7.65 (d, *J* = 1.4 Hz, 1H), 7.43 (dd, *J* = 14.8, 7.8 Hz, 2H), 7.31 – 7.27 (m, 6H), 7.22 (t, *J* = 7.3 Hz, 1H), 2.47 (s, 3H), 1.86 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.4, 149.8, 149.1, 145.3, 139.3, 138.9, 137.2, 133.1, 130.2, 128.8, 128.5, 127.4, 124.5, 122.3, 119.6, 114.5, 111.4, 18.4, 8.4. HRMS (APCI) m/z calcd for. $C_{21}H_{18}NO^+$ $[M+H]^+$ 300.1383, found 300.1380.

5-Methyl-2-(3-methylbenzofuran-2-yl)-3-(p-tolyl)pyridine (1t)



Yield: 96% (300 mg). White solid. m.p. 85.9-87.1 ℃. R_f = 0.47 (EtOAc / Petroleum ether = 1/10). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.61 (s, 1H), 7.64 (s, 1H), 7.45 (d, *J* = 7.8 Hz, 2H), 7.32 – 7.27 (m, 1H), 7.24 (d, *J* = 7.6 Hz, 1H), 7.18 (d, *J* = 8.1 Hz, 2H), 7.11 (d, *J* = 7.9 Hz, 2H), 2.47 (s, 3H), 2.35 (s, 3H), 1.83 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.5, 150.0, 148.9, 145.3, 138.9, 137.3, 137.2, 136.4, 133.1, 130.3, 129.1, 128.6, 124.5, 122.2, 119.6, 114.3, 114.5, 21.2, 18.4, 8.4. HRMS (APCI) m/z calcd for. $C_{22}H_{20}NO^+$ $[M+H]^+$ 314.1539, found 314.1536.

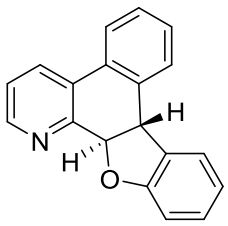
5-Methyl-2-(3-methylbenzofuran-2-yl)-3-(4-(trifluoromethyl)phenyl)pyridine (1u)



Yield: 92% (338 mg). Colorless oil. R_f = 0.47 (EtOAc / Petroleum ether = 1/10). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.67 (d, *J* = 1.1 Hz, 1H), 7.63 (d, *J* = 1.0 Hz, 1H), 7.58 (d, *J* = 8.1 Hz, 2H), 7.49 (d, *J* = 7.2 Hz, 1H), 7.41 (d, *J* = 8.1 Hz, 2H), 7.35 – 7.22 (m, 3H), 2.49 (s, 3H), 2.03 (s, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 154.3, 149.8, 149.3, 145.4, 143.3, 138.8, 135.6, 133.1, 130.1, 129.5 (q, ^2J = 32.5 Hz), 129.1, 125.3 (q, ^3J = 3.6 Hz), 124.9, 124.2 (q, ^1J = 272.0 Hz), 122.5, 119.8, 115.2, 111.3, 18.3, 8.7. HRMS (APCI) m/z calcd for. $C_{22}H_{17}F_3NO^+$ $[M+H]^+$ 368.1257, found 368.1257.

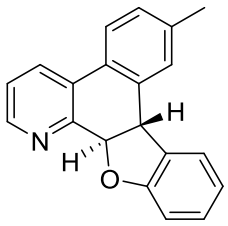
The data of 2a-2u

***trans*-8b,13a-Dihydrobenzo[*f*]benzofuro[3,2-*h*]quinoline (2a)**



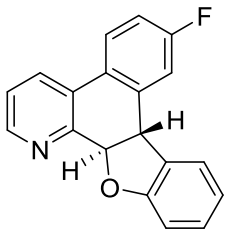
Yield: 85% (69 mg). White solid. R_f = 0.47 (EtOAc / Petroleum ether = 1/5). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.63 (s, 1H), 8.08 (d, *J* = 6.9 Hz, 1H), 7.92 (s, 1H), 7.82 – 7.69 (m, 2H), 7.43 (d, *J* = 23.4 Hz, 3H), 7.30 (d, *J* = 7.0 Hz, 1H), 7.20 – 7.06 (m, 2H), 5.31 (d, *J* = 16.1 Hz, 1H), 4.63 (d, *J* = 16.2 Hz, 1H). [3]

***trans*-7-Methyl-8b,13a-dihydrobenzo[*f*]benzofuro[3,2-*h*]quinoline (2b)**



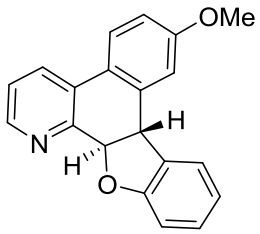
Yield: 90% (78 mg). White solid. m.p. 184.3-185.6 ℃. R_f = 0.47 (EtOAc / Petroleum ether = 1/5). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.54 (d, *J* = 4.5 Hz, 1H), 7.97 (d, *J* = 7.7 Hz, 1H), 7.71 – 7.59 (m, 3H), 7.32 (dd, *J* = 7.6, 5.0 Hz, 1H), 7.21 (dd, *J* = 12.6, 8.3 Hz, 2H), 7.10 (d, *J* = 8.0 Hz, 1H), 7.05 (t, *J* = 7.4 Hz, 1H), 5.21 (d, *J* = 16.3 Hz, 1H), 4.53 (d, *J* = 16.3 Hz, 1H), 2.43 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.5, 155.5, 148.1, 139.2, 135.5, 131.7, 130.3, 129.3, 128.7, 128.5, 127.7, 125.4, 125.0, 124.7, 123.3, 121.7, 111.6, 86.2, 48.3, 21.7. HRMS (ESI) m/z calcd for. $C_{20}H_{16}NO^+$ $[M+H]^+$ 286.1226, found 286.1223.

***trans*-7-Fluoro-8b,13a-dihydrobenzo[*f*]benzofuro[3,2-*h*]quinoline (2c)**



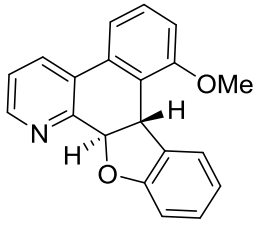
Yield: 74% (67 mg). White solid. m.p. 184.3-186.6 ℃. R_f = 0.47 (EtOAc / Petroleum ether = 1/5). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.60 (d, *J* = 4.4 Hz, 1H), 7.99 (d, *J* = 7.8 Hz, 1H), 7.74 (dd, *J* = 8.3, 5.5 Hz, 1H), 7.66 (d, *J* = 7.2 Hz, 1H), 7.59 (d, *J* = 8.3 Hz, 1H), 7.38 (dd, *J* = 7.4, 5.1 Hz, 1H), 7.29 (t, *J* = 7.7 Hz, 1H), 7.18 – 7.06 (m, 3H), 5.26 (d, *J* = 16.3 Hz, 1H), 4.57 (d, *J* = 16.3 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.9 (d, ^1J = 250.1 Hz), 161.4, 155.2, 148.4, 138.0 (d, ^3J = 8.1 Hz), 131.9, 129.3 (d, ^4J = 3.5 Hz), 129.0, 128.6, 127.3 (d, ^3J = 8.8 Hz), 126.9, 124.3, 123.4, 122.0, 114.8 (d, ^2J = 21.8 Hz), 112.2, 112.0, 85.7, 48.4. HRMS (ESI) m/z calcd for. $C_{19}H_{13}FNO^+$ $[M+H]^+$ 290.0976, found 290.0976.

***trans*-7-Methoxy-8b,13a-dihydrobenzo[*f*]benzofuro[3,2-*h*]quinoline (2d)**



Yield: 75% (67 mg). White solid. m.p. 156.5-157.6 ℃. R_f = 0.46 (EtOAc / Petroleum ether = 1/5). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.55 (dd, *J* = 4.8, 1.2 Hz, 1H), 7.95 (dd, *J* = 7.9, 1.2 Hz, 1H), 7.68 (dd, *J* = 7.9, 3.3 Hz, 2H), 7.42 (d, *J* = 1.3 Hz, 1H), 7.36 – 7.26 (m, 2H), 7.15 (d, *J* = 7.9 Hz, 1H), 7.08 (t, *J* = 7.4 Hz, 1H), 6.93 (dd, *J* = 8.5, 2.4 Hz, 1H), 5.24 (d, *J* = 16.3 Hz, 1H), 4.54 (d, *J* = 16.3 Hz, 1H), 3.90 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ161.4, 160.1, 154.8, 147.5, 137.2, 131.2, 129.2, 128.7, 127.5, 126.8, 125.6, 124.4, 123.2, 121.7, 112.3, 111.8, 110.9, 86.0, 55.5, 48.4. HRMS (ESI) m/z calcd for. $C_{20}H_{16}NO_2^+$ $[M+H]^+$ 302.1176, found 302.1173.

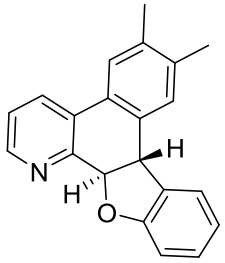
***trans*-8-Methoxy-8b,13a-dihydrobenzo[*f*]benzofuro[3,2-*h*]quinoline (2e)**



Yield: 76% (68 mg). White solid. m.p. 121.5-123 ℃. R_f = 0.47 (EtOAc / Petroleum ether = 1/5). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.53 (d, *J* = 4.3 Hz, 1H), 7.94 (d, *J* = 7.8 Hz, 1H), 7.71 (d, *J* = 8.3 Hz, 1H), 7.60 (d, *J* = 7.3 Hz, 1H), 7.30 (dd, *J* = 7.7, 5.0 Hz, 1H), 7.20 (dd, *J* = 14.8, 4.9 Hz, 2H), 7.06 (d, *J* = 7.9 Hz, 1H), 6.99 (t, *J* = 7.4 Hz, 1H), 6.88 (dd, *J* = 8.3, 2.1 Hz, 1H), 5.16 (d, *J* = 16.2 Hz, 1H), 4.44 (d, *J* = 16.2 Hz, 1H), 3.80 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.4, 159.3, 155.8, 148.5, 134.4, 132.1, 129.1, 128.6, 127.9, 127.8, 125.2, 124.5,

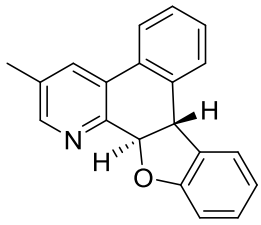
123.3, 121.7, 113.5, 111.9, 111.8, 86.3, 55.6, 47.7. HRMS (ESI) m/z calcd for. $C_{20}H_{16}NO_2^+$ $[M+H]^+$ 302.1176, found 302.1173.

***trans*-6,7-Dimethyl-8b,13a-dihydrobenzo[*f*]benzofuro[3,2-*h*]quinoline (2f)**



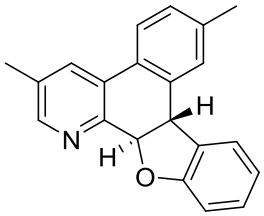
Yield: 75% (68 mg). White solid. m.p. 188.2-190.1 ℃. R_f = 0.47 (EtOAc / Petroleum ether = 1/5). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.57 (d, *J* = 4.7 Hz, 1H), 8.02 (d, *J* = 7.8 Hz, 1H), 7.73 (d, *J* = 7.3 Hz, 1H), 7.63 (s, 1H), 7.53 (s, 1H), 7.35 (dd, *J* = 7.7, 5.0 Hz, 1H), 7.27 (d, *J* = 6.5 Hz, 1H), 7.14 (d, *J* = 7.9 Hz, 1H), 7.08 (t, *J* = 7.4 Hz, 1H), 5.22 (d, *J* = 16.3 Hz, 1H), 4.53 (d, *J* = 16.3 Hz, 1H), 2.37 (s, 3H), 2.35 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.5, 155.6, 147.9, 137.8, 136.1, 133.0, 131.6, 130.6, 129.4, 128.6, 128.0, 126.7, 125.6, 124.6, 123.2, 121.7, 111.8, 86.4, 48.0, 20.0, 19.9. HRMS (ESI) m/z calcd for. $C_{21}H_{18}NO^+$ $[M+H]^+$ 300.1383, found 300.1381.

***trans*-3-Methyl-8b,13a-dihydrobenzo[*f*]benzofuro[3,2-*h*]quinoline (2g)**



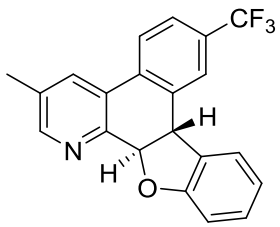
Yield: 73% (63 mg). Yellow solid. m.p. 105.7-108.2 ℃. R_f = 0.47 (EtOAc / Petroleum ether = 1/5). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.40 (s, 1H), 7.89 – 7.81 (m, 2H), 7.73 (dd, *J* = 5.4, 3.6 Hz, 1H), 7.68 (d, *J* = 7.4 Hz, 1H), 7.44 – 7.36 (m, 2H), 7.23 (d, *J* = 7.6 Hz, 1H), 7.11 (d, *J* = 7.9 Hz, 1H), 7.04 (t, *J* = 7.4 Hz, 1H), 5.22 (d, *J* = 16.3 Hz, 1H), 4.54 (d, *J* = 16.3 Hz, 1H), 2.41 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.5, 152.9, 148.6, 135.6, 133.2, 132.7, 128.8, 128.7, 128.6, 128.6, 127.8, 127.6, 125.3, 124.5, 124.2, 121.6, 111.8, 85.9, 48.5, 18.6. HRMS (ESI) m/z calcd for. $C_{20}H_{16}NO^+$ $[M+H]^+$ 286.1226, found 286.1223.

***trans*-3,7-Dimethyl-8b,13a-dihydrobenzo[*f*]benzofuro[3,2-*h*]quinoline (2h)**



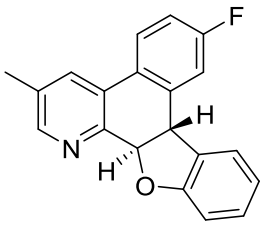
Yield: 83% (75 mg). White solid. m.p. 182.6-184.5 ℃. R_f = 0.48 (EtOAc / Petroleum ether = 1/5). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.42 (s, 1H), 7.84 (s, 1H), 7.74 (d, *J* = 7.3 Hz, 1H), 7.69 (s, 1H), 7.66 (d, *J* = 7.9 Hz, 1H), 7.29 (t, *J* = 7.7 Hz, 1H), 7.24 (d, *J* = 7.8 Hz, 1H), 7.16 (d, *J* = 7.9 Hz, 1H), 7.10 (t, *J* = 7.4 Hz, 1H), 5.22 (d, *J* = 16.3 Hz, 1H), 4.53 (d, *J* = 16.2 Hz, 1H), 2.47 (s, 3H), 2.44 (s, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 161.5, 152.7, 148.2, 138.9, 135.5, 132.6, 132.4, 130.4, 128.7, 128.6, 128.4, 127.8, 125.3, 125.0, 124.6, 121.6, 111.8, 86.1, 48.4, 21.7, 18.7. HRMS (ESI) m/z calcd for. $C_{21}H_{18}NO^+$ $[M+H]^+$ 300.1383, found 300.1386.

***trans*-3-Methyl-7-(trifluoromethyl)-8b,9,10,13a-tetrahydrobenzo[*f*]benzofuro[3,2-*h*]quinoline (2i)**



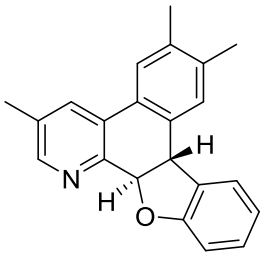
Yield: 70% (74 mg). White solid. m.p. 255.7-257.9 ℃. R_f = 0.48 (EtOAc / Petroleum ether = 1/5). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.50 (s, 1H), 8.11 (s, 1H), 7.93 – 7.85 (m, 2H), 7.71 (t, *J* = 7.8 Hz, 2H), 7.31 (t, *J* = 7.7 Hz, 1H), 7.14 (dd, *J* = 16.5, 7.9 Hz, 2H), 5.27 (d, *J* = 16.3 Hz, 1H), 4.61 (d, *J* = 16.3 Hz, 1H), 2.47 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.5, 153.3, 149.8, 136.9, 136.6, 133.3, 133.2, 130.6 (q, ^2J = 32.5 Hz), 129.1, 127.5, 126.8, 125.8, 125.0 (q, ^3J = 4.1 Hz), 124.5, 124.0 (q, ^1J = 271.8 Hz), 122.1, 121.3 (dd, *J* = 7.2, 3.5 Hz), 112.1, 85.5, 48.6, 18.7. HRMS (ESI) m/z calcd for. $C_{21}H_{15}F_3NO^+$ $[M+H]^+$ 354.1100, found 354.1100.

***trans*-7-Fluoro-3-methyl-8b,11,12,13a-tetrahydrobenzo[*f*]benzofuro[3,2-*h*]quinoline (2j)**



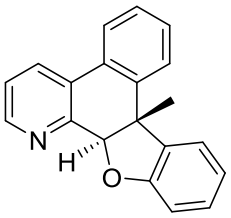
Yield: 80% (73 mg). White solid. m.p. 165.3-167.5 ℃. R_f = 0.47 (EtOAc / Petroleum ether = 1/5). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.44 (s, 1H), 7.82 (s, 1H), 7.74 (dd, *J* = 8.5, 5.4 Hz, 1H), 7.67 (d, *J* = 7.4 Hz, 1H), 7.62 – 7.56 (m, 1H), 7.29 (d, *J* = 7.4 Hz, 1H), 7.17 – 7.07 (m, 3H), 5.23 (d, *J* = 16.3 Hz, 1H), 4.54 (d, *J* = 16.3 Hz, 1H), 2.45 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.8 (d, ^1J = 249.8 Hz), 161.5, 152.4, 148.6, 138.1 (d, ^3J = 8.1 Hz), 132.9, 132.6, 129.4 (d, ^4J = 3.3 Hz), 128.9, 128.0, 127.2 (d, ^3J = 8.7 Hz), 127.0, 124.3, 121.9, 114.6 (d, ^2J = 21.6 Hz), 112.2, 112.0, 85.7, 48.6, 18.7. HRMS (ESI) m/z calcd for. $C_{20}H_{15}FNO^+$ $[M+H]^+$ 304.1132, found 304.1132.

***trans*-3,6,7-Trimethyl-8b,13a-dihydrobenzo[*f*]benzofuro[3,2-*h*]quinoline (2k)**



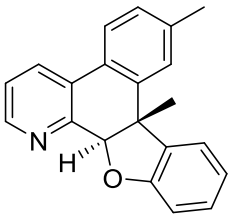
Yield: 58% (54.5 mg). White solid. m.p. 169-171 ℃. R_f = 0.48 (EtOAc / Petroleum ether = 1/5). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.33 (s, 1H), 7.77 (s, 1H), 7.66 (d, *J* = 7.3 Hz, 1H), 7.56 (s, 1H), 7.46 (s, 1H), 7.21 – 7.15 (m, 1H), 7.11 – 6.91 (m, 2H), 5.12 (d, *J* = 16.2 Hz, 1H), 4.43 (d, *J* = 16.2 Hz, 1H), 2.36 (s, 3H), 2.31 (s, 3H), 2.28 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.6, 152.9, 148.2, 137.6, 136.0, 133.1, 132.6, 132.4, 130.7, 128.8, 128.6, 128.1, 126.7, 125.6, 124.6, 121.6, 111.8, 86.4, 48.2, 20.0, 19.9, 18.7. HRMS (ESI) m/z calcd for. $C_{22}H_{20}NO^+$ $[M+H]^+$ 314.1539, found 314.1531.

***trans*-8b-Methyl-8b,13a-dihydrobenzo[*f*]benzofuro[3,2-*h*]quinoline (2l)**



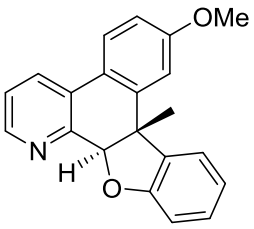
Yield: 93% (79 mg). White solid. m.p. 131.5-132.6 ℃. R_f = 0.47 (EtOAc / Petroleum ether = 1/5). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.62 (dd, *J* = 4.9, 1.3 Hz, 1H), 8.05 (dd, *J* = 7.9, 1.3 Hz, 1H), 7.91 (dd, *J* = 5.8, 3.1 Hz, 1H), 7.80 (dd, *J* = 6.0, 3.1 Hz, 1H), 7.75 (d, *J* = 7.5 Hz, 1H), 7.47 – 7.41 (m, 2H), 7.38 (ddd, *J* = 7.8, 5.0, 0.7 Hz, 1H), 7.30 – 7.26 (m, 1H), 7.16 (d, *J* = 7.9 Hz, 1H), 7.09 (td, *J* = 7.5, 0.9 Hz, 1H), 5.45 (s, 1H), 1.04 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.1, 153.5, 148.6, 142.3, 134.5, 132.0, 131.6, 129.5, 129.2, 128.6, 127.8, 126.1, 124.2, 123.9, 123.1, 122.1, 112.4, 87.9, 49.7, 24.5. HRMS (ESI) m/z calcd for. $C_{20}H_{16}NO^+$ $[M+H]^+$ 286.1226, found 286.1226.

***trans*-7,8b-Dimethyl-8b,13a-dihydrobenzo[*f*]benzofuro[3,2-*h*]quinoline (2m)**



Yield: 76% (68 mg). White solid. m.p. 119.3-121.3 ℃. R_f = 0.47 (EtOAc / Petroleum ether = 1/5). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.57 (d, *J* = 3.9 Hz, 1H), 7.98 (d, *J* = 7.6 Hz, 1H), 7.75 (d, *J* = 7.2 Hz, 1H), 7.71 – 7.62 (m, 2H), 7.37 – 7.31 (m, 1H), 7.23 (dd, *J* = 17.6, 7.2 Hz, 2H), 7.14 (d, *J* = 7.8 Hz, 1H), 7.08 (t, *J* = 7.3 Hz, 1H), 5.39 (s, 1H), 2.45 (s, 3H), 1.01 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.1, 153.3, 148.2, 142.2, 139.3, 134.6, 131.2, 129.6, 129.2, 128.5, 128.4, 126.0, 124.6, 124.2, 123.0, 122.0, 112.3, 88.0, 49.6, 24.5, 21.7. HRMS (ESI) m/z calcd for. $C_{21}H_{18}NO^+$ $[M+H]^+$ 300.1383, found 300.1383.

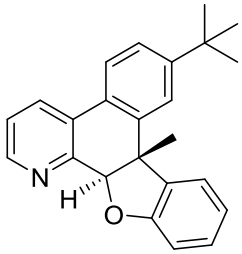
***trans*-7-Methoxy-8b-methyl-8b,13a-dihydrobenzo[*f*]benzofuro[3,2-*h*]quinoline (2n)**



Yield: 91% (86 mg). Colorless oil. R_f = 0.47 (EtOAc / Petroleum ether = 1/5). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.52 (d, *J* = 4.7 Hz, 1H), 7.92 (d, *J* = 7.8 Hz, 1H), 7.71 – 7.65 (m, 2H), 7.41 (d, *J* = 2.5 Hz, 1H), 7.31 (dd, *J* = 7.7, 5.0 Hz, 1H), 7.23 (d, *J* = 5.9 Hz, 1H), 7.12 (d, *J* = 7.9 Hz, 1H), 7.06 (d, *J* = 7.5 Hz, 1H), 6.89 (dd, *J* = 8.6, 2.4 Hz, 1H), 5.36 (s, 1H), 3.88 (s, 3H), 0.99 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.2, 160.1, 152.8, 147.7, 144.0, 134.4,

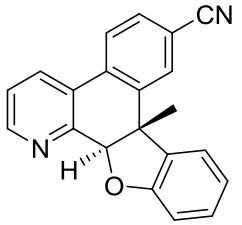
130.8, 129.5, 128.6, 127.4, 124.5, 124.0, 123.0, 122.1, 112.3, 112.1, 110.7, 88.0, 55.6, 49.8, 24.4. HRMS (ESI) m/z calcd for. $C_{21}H_{18}NO_2^+$ $[M+H]^+$ 316.1332, found 316.1332.

***trans*-7-(Tert-butyl)-8b-methyl-8b,13a-dihydrobenzo[*f*]benzofuro[3,2-*h*]quinoline (2o)**



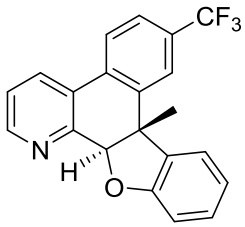
Yield: 87% (89 mg). White solid. m.p. 152-153.9 ℃. R_f = 0.47 (EtOAc / Petroleum ether = 1/5). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.61 (d, *J* = 4.9 Hz, 1H), 8.04 (d, *J* = 7.8 Hz, 1H), 7.96 (d, *J* = 1.8 Hz, 1H), 7.76 (dd, *J* = 14.1, 7.8 Hz, 2H), 7.47 (dd, *J* = 8.2, 1.9 Hz, 1H), 7.37 (dd, *J* = 7.8, 5.0 Hz, 1H), 7.30 (dd, *J* = 13.5, 5.7 Hz, 1H), 7.19 (d, *J* = 7.9 Hz, 1H), 7.14 (t, *J* = 7.4 Hz, 1H), 5.46 (s, 1H), 1.44 (s, 9H), 1.07 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.1, 153.4, 152.5, 148.2, 141.9, 134.8, 131.2, 129.5, 129.1, 128.5, 125.7, 124.7, 124.1, 123.0, 122.1, 120.7, 112.3, 88.1, 49.8, 35.1, 31.4, 24.6. HRMS (ESI) m/z calcd for. $C_{24}H_{24}NO^+$ $[M+H]^+$ 342.1852, found 342.1851.

***trans*-8b-Methyl-8b,13a-dihydrobenzo[*f*]benzofuro[3,2-*h*]quinoline-7-carbonitrile (2p)**



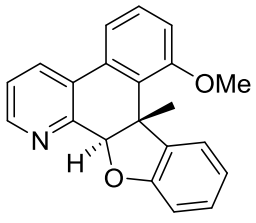
Yield: 84% (78 mg). White solid. m.p. 211.4.1-212.6 ℃. R_f = 0.47 (EtOAc / Petroleum ether = 1/5). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.68 (dd, *J* = 4.9, 1.1 Hz, 1H), 8.14 (d, *J* = 1.3 Hz, 1H), 8.07 (dd, *J* = 7.9, 1.2 Hz, 1H), 7.88 (d, *J* = 8.1 Hz, 1H), 7.73 – 7.68 (m, 2H), 7.43 (dd, *J* = 7.8, 5.0 Hz, 1H), 7.33 – 7.27 (m, 1H), 7.17 – 7.11 (m, 2H), 5.39 (s, 1H), 1.02 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.8, 153.7, 150.1, 143.3, 136.6, 133.0, 132.3, 131.6, 129.1, 127.8, 127.6, 126.6, 123.9, 123.4, 122.5, 118.6, 112.5, 112.4, 87.1, 49.6, 24.1. HRMS (ESI) m/z calcd for. $C_{21}H_{15}N_2O^+$ $[M+H]^+$ 311.1179, found 311.1182.

***trans*-8b-Methyl-7-(trifluoromethyl)-8b,13a-dihydrobenzo[*f*]benzofuro[3,2-*h*]quinoline (2q)**



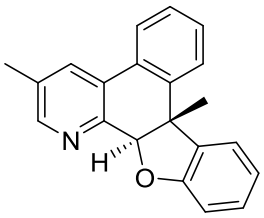
Yield: 90% (95.4 mg). White solid. m.p. 169.1-170 ℃. R_f = 0.47 (EtOAc / Petroleum ether = 1/5). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.67 (dd, *J* = 4.9, 1.1 Hz, 1H), 8.12 (s, 1H), 8.08 (dd, *J* = 7.9, 1.2 Hz, 1H), 7.89 (d, *J* = 8.1 Hz, 1H), 7.74 (d, *J* = 7.1 Hz, 1H), 7.68 (d, *J* = 8.1 Hz, 1H), 7.42 (dd, *J* = 7.6, 5.1 Hz, 1H), 7.30 (dd, *J* = 11.5, 4.1 Hz, 1H), 7.18 – 7.10 (m, 2H), 5.43 (s, 1H), 1.05 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.9, 153.7, 149.6, 143.0, 135.6, 133.5, 132.1, 130.9 (q, ^2J = 32.5 Hz), 128.9, 128.3, 126.4, 124.8 (dd, ^3J = 7.7, ^4J=3.8 Hz), 124.0, 124.0 (q, ^1J = 272.4 Hz), 123.3, 122.4, 120.9 (q, ^4J = 3.5 Hz), 112.5, 87.4, 49.7, 24.2. HRMS (ESI) m/z calcd for. $C_{21}H_{15}F_3NO^+$ $[M+H]^+$ 354.1100, found 354.1104.

***trans*-8-Methoxy-8b-methyl-8b,13a-dihydrobenzo[*f*]benzofuro[3,2-*h*]quinoline (2r)**



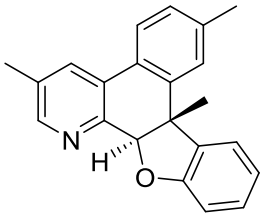
Yield: 52% (49 mg). Yellow solid. m.p. 59.6-62.8 ℃. R_f = 0.48 (EtOAc / Petroleum ether = 1/5). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.66 – 8.62 (m, 1H), 8.06 – 8.01 (m, 1H), 7.84 (d, *J* = 8.4 Hz, 1H), 7.73 (d, *J* = 7.1 Hz, 1H), 7.40 (dd, *J* = 7.6, 5.1 Hz, 1H), 7.35 (d, *J* = 2.5 Hz, 1H), 7.30 (dd, *J* = 9.5, 1.9 Hz, 1H), 7.18 (d, *J* = 7.9 Hz, 1H), 7.11 (t, *J* = 7.4 Hz, 1H), 6.97 (dd, *J* = 8.4, 2.5 Hz, 1H), 5.43 (s, 1H), 3.91 (s, 3H), 1.02 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 160.1, 159.1, 153.7, 148.7, 134.8, 134.7, 133.3, 131.6, 129.4, 128.5, 124.9, 124.0, 123.0 122.0, 113.7, 112.4, 112.3, 88.3, 55.6, 49.1, 24.7. HRMS (ESI) m/z calcd for. $C_{21}H_{18}NO_2^+$ $[M+H]^+$ 316.1332, found 316.1335.

***trans*-3,8b-Dimethyl-8b,13a-dihydrobenzo[*f*]benzofuro[3,2-*h*]quinoline (2s)**



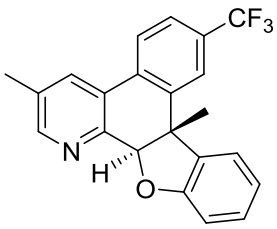
Yield: 90% (81 mg). White solid. m.p. 147.3-148.4 ℃. R_f = 0.48 (EtOAc / Petroleum ether = 1/5). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.35 (s, 1H), 7.81 (d, *J* = 3.1 Hz, 1H), 7.76 (s, 1H), 7.69 (d, *J* = 4.1 Hz, 1H), 7.65 (d, *J* = 7.3 Hz, 1H), 7.32 (d, *J* = 3.2 Hz, 2H), 7.18 (t, *J* = 7.6 Hz, 1H), 7.06 (d, *J* = 7.9 Hz, 1H), 6.99 (t, *J* = 7.3 Hz, 1H), 5.30 (s, 1H), 2.35 (s, 3H), 0.93 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.1, 150.7, 148.7, 142.3, 134.6, 132.5, 132.3, 132.1, 129.0, 128.4, 127.7, 125.9, 124.1, 123.9, 122.0, 112.3, 87.9, 49.7, 24.5, 18.7. HRMS (ESI) m/z calcd for. $C_{21}H_{18}NO^+$ $[M+H]^+$ 300.1383, found 300.1386.

***trans*-3,7,8b-Trimethyl-8b,13a-dihydrobenzo[*f*]benzofuro[3,2-*h*]quinoline (2t)**



Yield: 73% (69 mg). White solid. m.p. 230.8-232.5 ℃. R_f = 0.48 (EtOAc / Petroleum ether = 1/5). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.44 (s, 1H), 7.83 (s, 1H), 7.78 (d, *J* = 7.3 Hz, 1H), 7.73 – 7.66 (m, 2H), 7.28 (d, *J* = 7.1 Hz, 1H), 7.23 (d, *J* = 7.7 Hz, 1H), 7.17 (d, *J* = 7.9 Hz, 1H), 7.12 (d, *J* = 7.4 Hz, 1H), 5.38 (s, 1H), 2.48 (s, 3H), 2.45 (s, 3H), 1.03 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.1, 150.5, 148.3, 142.3, 139.1, 134.6, 132.4, 131.9, 129.2, 129.0, 128.4, 128.3, 125.9, 124.6, 124.2, 121.9, 112.2, 88.0, 49.6, 24.5, 21.7, 18.7. HRMS (ESI) m/z calcd for. $C_{22}H_{20}NO^+$ $[M+H]^+$ 314.1539, found 314.1543.

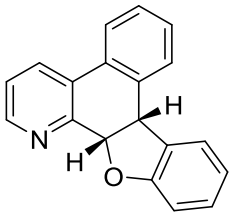
***trans*-3,8b-Dimethyl-7-(trifluoromethyl)-8b,13a-dihydrobenzo[*f*]benzofuro[3,2-*h*]quinoline (2u)**



Yield: 89% (98 mg). White solid. m.p. 208.9-210.3 ℃. R_f = 0.48 (EtOAc / Petroleum ether = 1/5). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.51 (s, 1H), 8.11 (s, 1H), 7.89 (d, *J* = 6.4 Hz, 2H), 7.74 (d, *J* = 7.0 Hz, 1H), 7.68 (d, *J* = 8.0 Hz, 1H), 7.32 – 7.27 (m, 1H), 7.18 – 7.10 (m, 2H), 5.40 (s, 1H), 2.47 (s, 3H), 1.04 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.0, 150.9, 149.9, 143.1, 135.8, 133.7, 132.9, 130.7 (q, ^2J = 34.5 Hz), 128.9, 127.8, 126.3, 124.7 (q, ^3J = 3.7 Hz), 124.0 (q, ^1J = 272.4 Hz), 124.0, 122.4, 120.9 (q, ^3J = 3.5 Hz), 112.5, 87.4, 49.8, 24.3, 18.7. HRMS (ESI) m/z calcd for. $C_{22}H_{17}F_3NO^+$ $[M+H]^+$ 368.1257, found 368.1263.

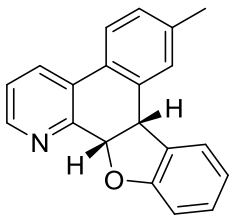
The data of 3a-3u

***cis*-8b,13a-Dihydrobenzo[*f*]benzofuro[3,2-*h*]quinoline (3a)**



Yield: 64% (17 mg). White solid. R_f = 0.46 (Acetone / Petroleum ether = 1/5). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.66 (s, 1H), 8.15 (d, *J* = 7.4 Hz, 1H), 7.83 (d, *J* = 6.3 Hz, 1H), 7.55 (d, *J* = 5.9 Hz, 1H), 7.35 (d, *J* = 20.3 Hz, 4H), 7.13 (t, *J* = 7.0 Hz, 1H), 6.91 (d, *J* = 7.5 Hz, 2H), 6.02 (d, *J* = 8.8 Hz, 1H), 4.91 (d, *J* = 8.8 Hz, 1H).[3]

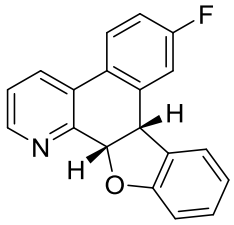
***cis*-7-Methyl-8b,13a-dihydrobenzo[*f*]benzofuro[3,2-*h*]quinoline (3b)**



Yield: 50% (15 mg). White solid. m.p. 184.5-185.3 ℃. R_f = 0.46 (Acetone / Petroleum ether = 1/5). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.62 (d, *J* = 3.1 Hz, 1H), 8.11 (d, *J* = 7.8 Hz, 1H), 7.71 (d, *J* = 7.9 Hz, 1H), 7.33 (d, *J* = 8.2 Hz, 3H), 7.15 (dd, *J* = 15.9, 7.8 Hz, 2H), 6.91 (d, *J* = 5.7 Hz, 2H), 6.00 (d, *J* = 9.0 Hz, 1H), 4.86 (d, *J* = 8.9 Hz, 1H), 2.41 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$)

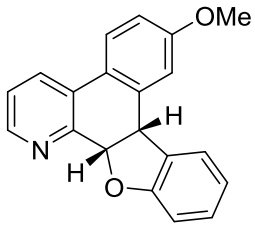
δ 158.8, 150.4, 149.2, 139.3, 132.7, 130.3, 130.2, 130.2, 128.9, 128.8, 128.7, 126.9, 125.0, 124.3, 123.7, 121.1, 110.4, 82.5, 44.8, 21.5. HRMS (ESI) m/z calcd for. $C_{20}H_{16}NO^+$ $[M+H]^+$ 286.1226, found 286.1222.

***cis*-7-Fluoro-8b,13a-dihydrobenzo[*f*]benzofuro[3,2-*h*]quinoline (3c)**



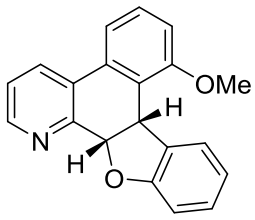
Yield: 57% (16.5 mg). White solid. m.p. 182.3-183.5 ℃. R_f = 0.45 (Acetone / Petroleum ether = 1/5). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.68 (d, *J* = 3.3 Hz, 1H), 8.12 (d, *J* = 7.8 Hz, 1H), 7.88 – 7.79 (m, 1H), 7.39 (d, *J* = 7.0 Hz, 2H), 7.28 (s, 1H), 7.19 (t, *J* = 7.4 Hz, 1H), 7.08 (t, *J* = 7.2 Hz, 1H), 6.95 (dd, *J* = 16.0, 7.7 Hz, 2H), 6.00 (d, *J* = 8.7 Hz, 1H), 4.87 (d, *J* = 8.6 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.2 (d, ^1J = 249.8 Hz), 158.9, 150.0, 149.5, 135.6 (d, ^3J = 7.3 Hz), 130.5, 129.5, 129.1, 128.0, 125.9 (d, ^4J = 3.2 Hz), 125.7 (d, ^3J = 8.6 Hz), 125.0, 124.5, 121.4, 116.3 (d, ^2J = 22.2 Hz), 115.2 (d, ^2J = 21.7 Hz), 110.5, 82.4, 44.7. HRMS (ESI) m/z calcd for. $C_{19}H_{13}FNO^+$ $[M+H]^+$ 290.0976, found 290.0972.

***cis*-7-Methoxy-8b,13a-dihydrobenzo[*f*]benzofuro[3,2-*h*]quinoline (3d)**



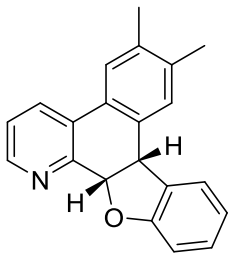
Yield: 45% (13.5 mg). Yellow solid. m.p. 151.5-153.2 ℃. R_f = 0.45 (Acetone / Petroleum ether = 1/5). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.51 (d, *J* = 4.2 Hz, 1H), 7.97 (d, *J* = 7.9 Hz, 1H), 7.67 (d, *J* = 8.7 Hz, 1H), 7.28 (d, *J* = 7.5 Hz, 1H), 7.24 – 7.19 (m, 1H), 7.07 (t, *J* = 7.6 Hz, 1H), 6.98 (d, *J* = 2.3 Hz, 1H), 6.87 – 6.77 (m, 3H), 5.91 (d, *J* = 9.0 Hz, 1H), 4.77 (d, *J* = 9.0 Hz, 1H), 3.79 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.4, 158.8, 149.7, 148.6, 134.6, 130.0, 129.9, 128.9, 128.6, 125.2, 124.9 124.3, 122.4, 121.2, 114.9, 113.4, 110.4, 82.6, 55.5, 45.0. HRMS (ESI) m/z calcd for. $C_{20}H_{16}NO_2^+$ $[M+H]^+$ 302.1176, found 302.1171.

***cis*-8-Methoxy-8b,13a-dihydrobenzo[*f*]benzofuro[3,2-*h*]quinoline (3e)**



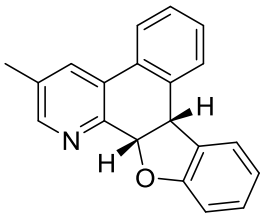
Yield: 54% (16.2 mg). Yellow solid. m.p. 151.6-153.6 ℃. R_f = 0.45 (Acetone / Petroleum ether = 1/5). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.66 (d, *J* = 3.9 Hz, 1H), 8.11 (d, *J* = 7.9 Hz, 1H), 7.46 (d, *J* = 8.4 Hz, 1H), 7.33 (dd, *J* = 18.8, 7.5 Hz, 3H), 7.13 (t, *J* = 7.5 Hz, 1H), 6.92 (dd, *J* = 20.2, 6.7 Hz, 3H), 5.99 (d, *J* = 9.0 Hz, 1H), 4.86 (d, *J* = 8.8 Hz, 1H), 3.87 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.5, 158.8, 151.0, 149.7, 130.8, 130.7, 130.7, 130.5, 128.7, 128.5, 125.1, 124.9, 124.3, 121.2, 114.7, 110.4, 109.4, 82.5, 55.6, 44.2. HRMS (ESI) m/z calcd for. $C_{20}H_{16}NO_2^+$ $[M+H]^+$ 302.1176, found 302.1174.

***cis*-6,7-Dimethyl-8b,13a-dihydrobenzo[*f*]benzofuro[3,2-*h*]quinoline (3f)**



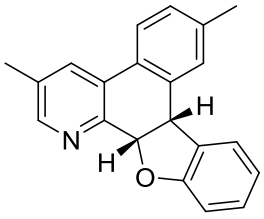
Yield: 43% (13 mg). White solid. m.p. 176.3-177.2 ℃. R_f = 0.44 (Acetone / Petroleum ether = 1/5). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.61 (dd, *J* = 4.6, 1.4 Hz, 1H), 8.12 (d, *J* = 7.6 Hz, 1H), 7.58 (s, 1H), 7.35 – 7.28 (m, 3H), 7.13 (t, *J* = 7.7 Hz, 1H), 6.90 (dd, *J* = 7.4, 5.6 Hz, 2H), 5.98 (d, *J* = 9.0 Hz, 1H), 4.83 (d, *J* = 9.0 Hz, 1H), 2.32 (s, 3H), 2.31 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.9, 150.5, 149.0, 138.1, 136.3, 130.7, 130.5, 130.3, 130.2, 128.8, 128.7, 127.1, 125.0, 124.8, 124.2, 121.1, 110.3, 82.7, 44.4, 19.9, 19.8. HRMS (ESI) m/z calcd for. $C_{21}H_{18}NO^+$ $[M+H]^+$ 300.1383, found 300.1382.

***cis*-3-Methyl-8b,13a-dihydrobenzo[*f*]benzofuro[3,2-*h*]quinoline (3g)**



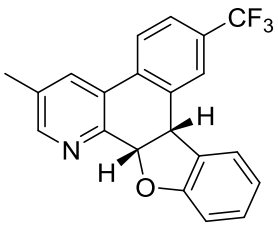
Yield: 40% (12 mg). White solid. m.p. 172.3-172.7 ℃. R_f = 0.44 (Acetone / Petroleum ether = 1/5). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.48 (s, 1H), 7.94 (s, 1H), 7.85 – 7.79 (m, 1H), 7.55 – 7.50 (m, 1H), 7.39 – 7.33 (m, 2H), 7.30 (d, *J* = 7.6 Hz, 1H), 7.12 (t, *J* = 7.6 Hz, 1H), 6.88 (t, *J* = 7.5 Hz, 2H), 6.00 (d, *J* = 9.0 Hz, 1H), 4.88 (d, *J* = 9.0 Hz, 1H), 2.39 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.8, 150.2, 147.9, 133.9, 133.0, 131.0, 130.2, 129.7, 129.6, 129.1, 128.8, 127.9, 127.9, 124.9, 123.6, 121.1, 110.4, 82.3, 44.9, 18.6. HRMS (ESI) m/z calcd for. $C_{20}H_{16}NO^+$ $[M+H]^+$ 286.1226, found 286.1225.

***cis*-3,7-Dimethyl-8b,13a-dihydrobenzo[*f*]benzofuro[3,2-*h*]quinoline (3h)**



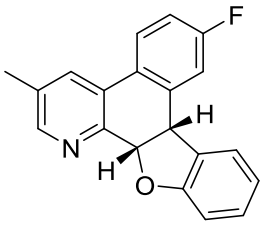
Yield: 43% (13 mg). White solid. m.p. 189.8-190.8 ℃. R_f = 0.45 (Acetone / Petroleum ether = 1/5). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.45 (s, 1H), 7.91 (s, 1H), 7.72 (d, *J* = 8.1 Hz, 1H), 7.32 (d, *J* = 8.7 Hz, 2H), 7.14 (dd, *J* = 16.9, 8.4 Hz, 2H), 6.96 – 6.83 (m, 2H), 5.98 (d, *J* = 9.0 Hz, 1H), 4.83 (d, *J* = 9.0 Hz, 1H), 2.41 (s, 3H), 2.39 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.9, 149.8, 147.6, 139.1, 133.9, 132.7, 130.7, 130.3, 130.1, 128.8, 128.7, 128.1, 127.0, 125.0, 123.6, 121.0, 110.4, 82.5, 44.9, 21.5, 18.6. HRMS (ESI) m/z calcd for. $C_{21}H_{18}NO^+$ $[M+H]^+$ 300.1383, found 300.1382.

***cis*-3-Methyl-7-(trifluoromethyl)-8b,13a-dihydrobenzo[*f*]benzofuro[3,2-*h*]quinoline (3i)**



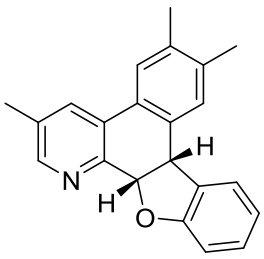
Yield: 40% (14 mg). White solid. m.p. 229.1-230.1 ℃. R_f = 0.45 (Acetone / Petroleum ether = 1/5). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.55 (s, 1H), 7.98 – 7.91 (m, 2H), 7.78 (s, 1H), 7.60 (d, *J* = 8.3 Hz, 1H), 7.31 (d, *J* = 7.4 Hz, 1H), 7.16 (t, *J* = 7.7 Hz, 1H), 6.95 – 6.89 (m, 2H), 6.02 (d, *J* = 9.0 Hz, 1H), 4.92 (d, *J* = 9.0 Hz, 1H), 2.42 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.8, 151.4, 148.3, 134.3, 133.9, 133.4, 131.5, 130.9 (q, ^2J = 32.9 Hz), 129.3, 129.19 (s), 126.69 (s), 126.43 (q, ^3J = 3.7 Hz), 124.8, 124.8 (q, ^3J = 3.6 Hz), 124.1, 124.0 (q, ^1J = 272.5 Hz), 121.5, 110.6, 82.0, 44.8, 18.6. HRMS (ESI) m/z calcd for. $C_{21}H_{15}F_3NO^+$ $[M+H]^+$ 354.1100, found 354.1097.

***cis*-7-Fluoro-3-methyl-8b,13a-dihydrobenzo[*f*]benzofuro[3,2-*h*]quinoline (3j)**



Yield: 40% (12 mg). White solid. m.p. 190.3-191.3 ℃. R_f = 0.45 (Acetone / Petroleum ether = 1/5). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.52 (s, 1H), 7.93 (s, 1H), 7.85 (dd, *J* = 8.5, 5.6 Hz, 1H), 7.40 (d, *J* = 7.2 Hz, 1H), 7.29 (d, *J* = 4.0 Hz, 1H), 7.19 (t, *J* = 7.6 Hz, 1H), 7.08 (t, *J* = 7.2 Hz, 1H), 6.95 (dd, *J* = 16.7, 7.8 Hz, 2H), 5.99 (d, *J* = 8.8 Hz, 1H), 4.86 (d, *J* = 8.6 Hz, 1H), 2.44 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.2 (d, ^1J = 248.6 Hz), 159.0, 150.1, 147.2, 135.7 (d, ^3J = 7.4 Hz), 134.2, 130.9, 129.7, 129.1, 127.4, 126.1 (d, ^4J = 3.0 Hz), 125.6 (d, ^3J = 8.6 Hz), 125.0, 121.3, 116.2 (d, ^2J = 22.1 Hz), 115.1 (d, ^2J = 21.9 Hz), 110.5, 82.3, 44.8, 18.7. HRMS (ESI) m/z calcd for. $C_{20}H_{15}FNO^+$ $[M+H]^+$ 304.1132, found 304.1129.

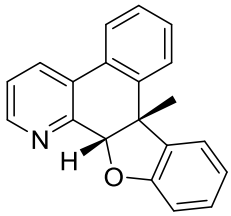
***cis*-3,6,7-Trimethyl-8b,13a-dihydrobenzo[*f*]benzofuro[3,2-*h*]quinoline (3k)**



Yield: 53% (17 mg). Yellow solid. m.p. 188.4-189.3 ℃. R_f = 0.45 (Acetone / Petroleum ether = 1/5). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.37 (s, 1H), 7.86 (s, 1H), 7.51 (s, 1H), 7.26 (d, *J* = 7.6 Hz, 1H), 7.20 (d, *J* = 7.4 Hz, 1H), 7.04 (t, *J* = 7.6 Hz, 1H), 6.81 (t, *J* = 7.1 Hz, 2H), 5.89 (d, *J* = 9.0 Hz, 1H), 4.73 (d, *J* = 8.9 Hz, 1H), 2.32 (s, 3H), 2.25 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.9, 149.7, 147.7, 137.9, 136.2, 133.8, 130.7, 130.6, 130.4, 128.6, 128.2,

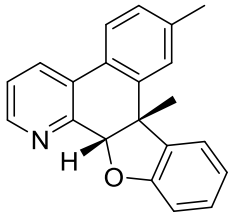
127.2, 125.0, 124.7, 121.0, 110.3, 82.6, 44.5, 19.9, 19.8, 18.6. HRMS (ESI) m/z calcd for. $C_{22}H_{20}NO^+$ $[M+H]^+$ 314.1539, found 314.1537.

***cis*-8b-Methyl-8b,13a-dihydrobenzo[*f*]benzofuro[3,2-*h*]quinoline (3l)**



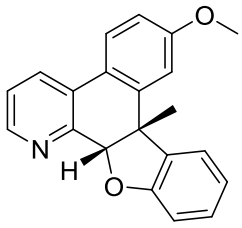
Yield: 92% (26 mg). White solid. m.p. 112.1-113.1 ℃. R_f = 0.49 (Acetone / Petroleum ether = 1/5). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.69 (dd, *J* = 4.6, 1.1 Hz, 1H), 8.26 (d, *J* = 7.9 Hz, 1H), 7.84 (dd, *J* = 6.3, 2.8 Hz, 1H), 7.62 (d, *J* = 7.2 Hz, 1H), 7.52 (dd, *J* = 6.3, 2.7 Hz, 1H), 7.47 (dd, *J* = 8.0, 4.7 Hz, 1H), 7.34 – 7.27 (m, 2H), 7.18 (dd, *J* = 11.1, 4.3 Hz, 1H), 7.04 (t, *J* = 7.3 Hz, 1H), 6.85 (d, *J* = 7.9 Hz, 1H), 5.41 (s, 1H), 1.67 (s, 3H).[3]

***cis*-7,8b-Dimethyl-8b,13a-dihydrobenzo[*f*]benzofuro[3,2-*h*]quinoline (3m)**



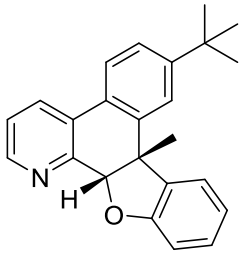
Yield: 80% (24 mg). White solid. m.p. 163.5-164.9 ℃. R_f = 0.49 (Acetone / Petroleum ether = 1/5). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.65 (d, *J* = 4.0 Hz, 1H), 8.21 (d, *J* = 7.9 Hz, 1H), 7.73 (d, *J* = 8.0 Hz, 1H), 7.63 (d, *J* = 7.2 Hz, 1H), 7.43 (dd, *J* = 7.9, 4.7 Hz, 1H), 7.29 (s, 1H), 7.18 (t, *J* = 7.5 Hz, 1H), 7.12 – 7.01 (m, 2H), 6.86 (d, *J* = 7.8 Hz, 1H), 5.39 (s, 1H), 2.32 (s, 3H), 1.65 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.6, 149.1, 148.5, 139.6, 138.7, 135.0, 130.7, 129.4, 128.9, 128.5, 128.4, 126.0, 125.1, 124.4, 123.6, 121.4, 110.4, 90.2, 48.1, 25.9, 21.6. HRMS (ESI) m/z calcd for. $C_{21}H_{18}NO^+$ $[M+H]^+$ 300.1383, found 300.1388.

***cis*-7-Methoxy-8b-methyl-8b,13a-dihydrobenzo[*f*]benzofuro[3,2-*h*]quinoline (3n)**



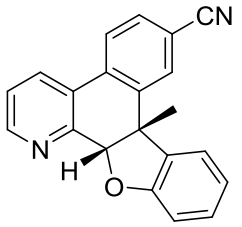
Yield: 90% (28 mg). White solid. m.p. 138.8-140.5 ℃. R_f = 0.49 (Acetone / Petroleum ether = 1/5). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.64 – 8.60 (m, 1H), 8.15 (dd, *J* = 8.1, 1.1 Hz, 1H), 7.76 (d, *J* = 8.7 Hz, 1H), 7.60 (s, 1H), 7.42 (dd, *J* = 8.1, 4.7 Hz, 1H), 7.18 (s, 1H), 7.06 – 7.00 (m, 2H), 6.88 – 6.80 (m, 2H), 5.38 (s, 1H), 3.79 (s, 3H), 1.65 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.6, 159.5, 148.6, 148.0, 140.7, 134.8, 130.4, 129.3, 128.5, 125.1, 124.2, 121.7, 121.4, 114.2, 112.8, 110.4, 90.2, 55.4, 48.4, 25.7. HRMS (ESI) m/z calcd for. $C_{21}H_{18}NO_2^+$ $[M+H]^+$ 316.1332, found 316.1341.

***cis*-7-(Tert-butyl)-8b-methyl-8b,13a-dihydrobenzo[*f*]benzofuro[3,2-*h*]quinoline (3o)**



Yield: 81% (27.6 mg). White solid. m.p. 113.5-114.7 ℃. R_f = 0.50 (Acetone / Petroleum ether = 1/5). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.66 (dd, *J* = 4.7, 1.3 Hz, 1H), 8.22 (d, *J* = 8.0 Hz, 1H), 7.77 (d, *J* = 8.3 Hz, 1H), 7.63 (d, *J* = 7.3 Hz, 1H), 7.57 (d, *J* = 1.8 Hz, 1H), 7.43 (dd, *J* = 8.0, 4.7 Hz, 1H), 7.32 (dd, *J* = 8.3, 2.0 Hz, 1H), 7.17 (td, *J* = 7.8, 1.1 Hz, 1H), 7.05 (t, *J* = 7.2 Hz, 1H), 6.86 (d, *J* = 7.9 Hz, 1H), 5.41 (s, 1H), 1.68 (s, 3H), 1.29 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.5, 152.6, 149.1, 148.7, 138.3, 135.1, 130.8, 129.3, 128.3, 126.0, 125.2, 125.1, 124.7, 124.2, 123.2, 121.3, 110.4, 90.2, 48.3, 34.9, 31.3, 26.2. HRMS (ESI) m/z calcd for. $C_{24}H_{24}NO^+$ $[M+H]^+$ 342.1852, found 342.1861.

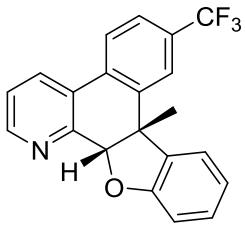
***cis*-8b-Methyl-8b,13a-dihydrobenzo[*f*]benzofuro[3,2-*h*]quinoline-7-carbonitrile (3p)**



Yield: 76% (24 mg). White solid. m.p. 197.7-199 ℃. R_f = 0.50 (Acetone / Petroleum ether = 1/5). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.78 (s, 1H), 8.26 (d, *J* = 7.4 Hz, 1H), 7.92 (d, *J* = 7.8 Hz, 1H), 7.78 (s, 1H), 7.62 (d, *J* = 6.8 Hz, 1H), 7.55 (dd, *J* = 14.4, 6.3 Hz, 2H), 7.22 (t, *J* = 7.2 Hz, 1H), 7.11 (d, *J* = 6.8 Hz, 1H), 6.87 (d, *J* = 7.5 Hz, 1H), 5.41 (s, 1H), 1.67 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.6, 151.0, 149.4, 140.2, 133.4, 133.2, 132.7, 131.8, 130.9, 129.0,

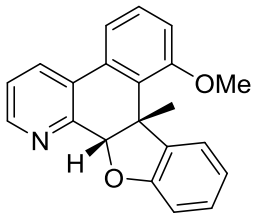
127.5, 125.4, 124.4, 124.3, 122.1, 118.6, 113.0, 110.6, 89.4, 48.0, 25.3. HRMS (ESI) m/z calcd for. $C_{21}H_{15}N_2O^+$ $[M+H]^+$ 311.1179, found 311.1175.

***cis*-8b-Methyl-7-(trifluoromethyl)-8b,13a-dihydrobenzo[*f*]benzofuro[3,2-*h*]quinoline (3q)**



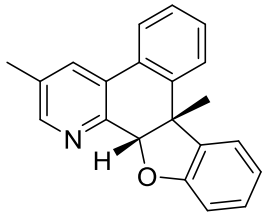
Yield: 90% (32 mg). White solid. m.p. 159.6-161.1 ℃. R_f = 0.49 (Acetone / Petroleum ether = 1/5). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.75 (dd, *J* = 4.6, 1.0 Hz, 1H), 8.27 (d, *J* = 7.9 Hz, 1H), 7.94 (d, *J* = 8.3 Hz, 1H), 7.75 (s, 1H), 7.64 (d, *J* = 7.3 Hz, 1H), 7.54 – 7.48 (m, 2H), 7.20 (t, *J* = 7.4 Hz, 1H), 7.08 (t, *J* = 7.4 Hz, 1H), 6.87 (d, *J* = 7.9 Hz, 1H), 5.43 (s, 1H), 1.69 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.6, 150.6, 149.3, 139.7, 133.9, 132.2, 131.6, 131.4 (q, ^2J = 32.7 Hz), 128.8, 127.9, 125.5 (q, ^4J = 3.7 Hz), 125.3, 124.4 (dd, ^3J = 7.2, ^4J=3.5 Hz), 124.3, 124.1, 123.9 (q, ^1J = 272.6 Hz), 121.9, 110.6, 89.6, 48.2, 25.6. HRMS (ESI) m/z calcd for. $C_{21}H_{15}F_3NO^+$ $[M+H]^+$ 354.1100, found 354.1096.

***cis*-8-Methoxy-8b-methyl-8b,13a-dihydrobenzo[*f*]benzofuro[3,2-*h*]quinoline (3r)**



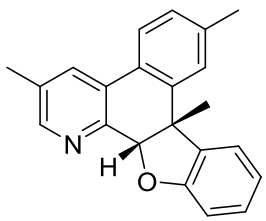
Yield: 75% (24 mg). White solid. m.p. 189.6-190.3 ℃. R_f = 0.48 (Acetone / Petroleum ether = 1/5). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.68 (s, 1H), 8.21 (d, *J* = 7.8 Hz, 1H), 7.59 (d, *J* = 7.0 Hz, 1H), 7.48 – 7.40 (m, 2H), 7.33 (s, 1H), 7.16 (t, *J* = 7.4 Hz, 1H), 7.03 (t, *J* = 7.0 Hz, 1H), 6.86 (dd, *J* = 13.8, 8.4 Hz, 2H), 5.38 (s, 1H), 3.83 (s, 3H), 1.64 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.6, 158.9, 150.2, 149.6, 149.3, 135.1, 131.1, 129.9, 129.7, 129.2, 128.3, 125.1, 124.2, 121.3, 115.3, 110.4, 108.9, 90.2, 55.5, 47.7, 25.8. HRMS (ESI) m/z calcd for. $C_{21}H_{18}NO_2^+$ $[M+H]^+$ 316.1332, found 316.1329.

***cis*-3,8b-Dimethyl-8b,13a-dihydrobenzo[*f*]benzofuro[3,2-*h*]quinoline (3s)**



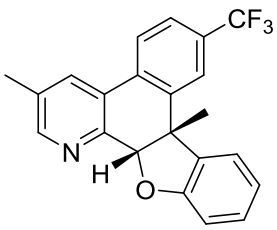
Yield: 85% (25 mg). White solid. m.p. 175.3-177 ℃. R_f = 0.50 (Acetone / Petroleum ether = 1/5). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.52 (s, 1H), 8.05 (s, 1H), 7.84 (d, *J* = 6.2 Hz, 1H), 7.62 (d, *J* = 7.2 Hz, 1H), 7.54 – 7.49 (m, 1H), 7.32 – 7.26 (m, 2H), 7.17 (t, *J* = 7.5 Hz, 1H), 7.04 (t, *J* = 7.3 Hz, 1H), 6.84 (d, *J* = 7.8 Hz, 1H), 5.39 (s, 1H), 2.46 (s, 3H), 1.65 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.7, 150.1, 146.1, 138.9, 134.9, 134.9, 131.4, 129.4, 128.8, 128.6, 128.4, 128.4, 127.4, 124.4, 123.5, 121.3, 110.4, 90.0, 48.1, 25.7, 18.8. HRMS (ESI) m/z calcd for. $C_{21}H_{18}NO^+$ $[M+H]^+$ 300.1383, found 300.1378.

***cis*-3,7,8b-Trimethyl-8b,13a-dihydrobenzo[*f*]benzofuro[3,2-*h*]quinoline (3t)**



Yield: 74% (23 mg). White solid. m.p. 170.6-172 ℃. R_f = 0.50 (Acetone / Petroleum ether = 1/5). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.49 (s, 1H), 8.01 (s, 1H), 7.73 (d, *J* = 7.9 Hz, 1H), 7.63 (d, *J* = 7.2 Hz, 1H), 7.29 (s, 1H), 7.17 (t, *J* = 7.4 Hz, 1H), 7.06 (dd, *J* = 19.7, 7.7 Hz, 2H), 6.85 (d, *J* = 7.8 Hz, 1H), 5.37 (s, 1H), 2.45 (s, 3H), 2.32 (s, 3H), 1.64 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.6, 149.7, 145.8, 139.4, 138.8, 135.1, 134.8, 131.1, 128.9, 128.7, 128.4, 128.3, 126.1, 124.4, 123.5, 121.2, 110.4, 90.1, 48.1, 25.9, 21.6, 18.8. HRMS (ESI) m/z calcd for. $C_{22}H_{20}NO^+$ $[M+H]^+$ 314.1539, found 314.1536.

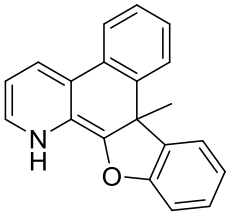
***cis*-3,8b-Dimethyl-7-(trifluoromethyl)-8b,13a-dihydrobenzo[*f*]benzofuro[3,2-*h*]quinoline (3u)**



Yield: 80% (29 mg). White solid. m.p. 249.1-251 ℃. R_f = 0.50 (Acetone / Petroleum ether = 1/5). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.57 (s, 1H), 8.04 (s, 1H), 7.92 (d, *J* = 8.2 Hz, 1H), 7.74 (s, 1H), 7.63 (d, *J* = 7.4 Hz, 1H), 7.51 (d, *J* = 8.1 Hz, 1H), 7.20 (t, *J* = 7.7 Hz, 1H), 7.08 (t, *J* = 7.5 Hz, 1H), 6.87 (d, *J* = 7.9 Hz, 1H), 5.41 (s, 1H), 2.45 (s, 3H), 1.66 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 159.7, 151.2, 146.5, 139.8, 135.2, 134.0, 132.3, 131.9, 131.1 (q, ^2J = 33.0 Hz), 128.8, 127.3, 125.4 (dd, ^3J = 7.3, ^4J= 3.6 Hz), 124.3, 124.3, 124.0, 124.0 (q, ^1J = 272.1 Hz), 121.8, 110.5, 89.6, 48.2, 25.6, 18.7. HRMS (ESI) m/z calcd for. $C_{22}H_{17}F_3NO^+$ $[M+H]^+$ 368.1257, found 368.1253.

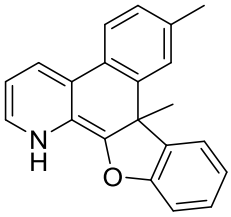
The data of 4a-4j, 6a-6b

8b-Methyl-1,8b-dihydrobenzo[*f*]benzofuro[3,2-*h*]quinoline (4a)



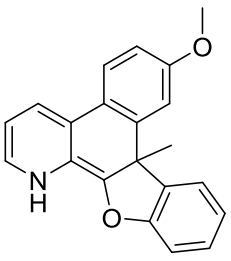
Yield: 79% (45 mg). White solid. m.p. 212.9-213.5 ℃. R_f = 0.45 (EtOAc / CH_2Cl_2 = 1/15). ^{1}H NMR (400 MHz, DMSO) δ 9.23 (d, *J* = 8.1 Hz, 1H), 8.99 (s, 1H), 8.92 (d, *J* = 4.9 Hz, 1H), 8.77 (d, *J* = 2.6 Hz, 1H), 8.21 (d, *J* = 3.2 Hz, 1H), 7.77 (s, 2H), 7.59 (dd, *J* = 7.9, 4.0 Hz, 1H), 7.23 (t, *J* = 7.5 Hz, 1H), 7.03 (d, *J* = 7.1 Hz, 1H), 6.97 – 6.86 (m, 2H), 2.46 (s, 3H).[3]

7,8b-Dimethyl-1,8b-dihydrobenzo[*f*]benzofuro[3,2-*h*]quinoline (4b)



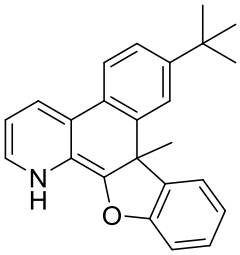
Yield: 56% (34 mg). White solid. m.p. 203.6-205 ℃. R_f = 0.45 (EtOAc / CH_2Cl_2 = 1/15). ^{1}H NMR (400 MHz, DMSO) δ 9.16 (d, *J* = 8.2 Hz, 1H), 8.96 (s, 1H), 8.84 – 8.76 (m, 1H), 8.73 (d, *J* = 3.0 Hz, 1H), 8.00 (s, 1H), 7.60 (d, *J* = 8.2 Hz, 1H), 7.56 (dd, *J* = 8.1, 4.1 Hz, 1H), 7.23 (t, *J* = 7.5 Hz, 1H), 7.02 (d, *J* = 7.1 Hz, 1H), 6.95 (d, *J* = 7.6 Hz, 1H), 6.89 (t, *J* = 7.2 Hz, 1H), 2.59 (s, 3H), 2.44 (s, 3H). ^{13}C NMR (101 MHz, DMSO) δ 154.9, 148.6, 146.9, 137.0, 135.3, 134.2, 131.7, 131.3, 130.5, 128.4, 127.9, 127.0, 126.8, 124.7, 123.9, 123.3, 120.7, 118.5, 115.3, 21.5, 17.1. HRMS (ESI) m/z calcd for. $C_{21}H_{18}NO^+$ $[M+H]^+$ 300.1383, found 300.1385.

7-Methoxy-8b-methyl-1,8b-dihydrobenzo[*f*]benzofuro[3,2-*h*]quinoline (4c)



Yield: 55% (35 mg). White solid. m.p. 206.3-207.2 ℃. R_f = 0.45 (EtOAc / CH_2Cl_2 = 1/15). ^{1}H NMR (400 MHz, DMSO) δ 9.12 (d, *J* = 8.2 Hz, 1H), 8.97 (s, 1H), 8.83 (d, *J* = 9.1 Hz, 1H), 8.69 (d, *J* = 4.0 Hz, 1H), 7.55 (dd, *J* = 6.5, 3.1 Hz, 2H), 7.40 (dd, *J* = 9.0, 2.3 Hz, 1H), 7.22 (t, *J* = 7.6 Hz, 1H), 7.02 (d, *J* = 7.1 Hz, 1H), 6.94 (d, *J* = 8.1 Hz, 1H), 6.89 (t, *J* = 7.4 Hz, 1H), 3.97 (s, 3H), 2.43 (s, 3H). ^{13}C NMR (101 MHz, DMSO) δ 158.7, 154.9, 148.1, 148.0, 134.0 (d, *J* = 1.7 Hz), 132.8，131.6, 127.9, 126.9, 125.1, 124.0, 123.7, 123.0, 120.8, 118.5, 116.6, 115.3, 106.2, 55.4, 17.2. HRMS (ESI) m/z calcd for. $C_{21}H_{17}NO_2$ $[M+H]^+$ 316.1332, found 316.1334. HRMS (ESI) m/z calcd for. $C_{21}H_{18}NO_2^+$ $[M+H]^+$ 316.1332, found 316.1334.

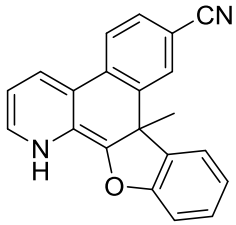
7-(Tert-butyl)-8b-methyl-1,8b-dihydrobenzo[*f*]benzofuro[3,2-*h*]quinoline (4d)



Yield: 49% (33 mg). Yellow solid. m.p. 78-80.2 ℃. R_f = 0.44 (EtOAc / CH_2Cl_2 = 1/15). ^{1}H NMR (400 MHz, DMSO) δ 9.18 (d, *J* = 8.1 Hz, 1H), 8.94 (s, 1H), 8.84 (d, *J* = 8.8 Hz, 1H), 8.74 (d, *J* = 3.2 Hz, 1H), 8.11 (d, *J* = 1.4 Hz, 1H), 7.86 (dd, *J* = 8.7, 1.5 Hz, 1H), 7.57 (dd, *J* = 8.3, 4.3 Hz, 1H), 7.22 (t, *J* = 7.7 Hz, 1H), 7.02 (d, *J* = 6.4 Hz, 1H), 6.95 (d, *J* = 8.1 Hz, 1H), 6.90 (t, *J* = 7.3 Hz,

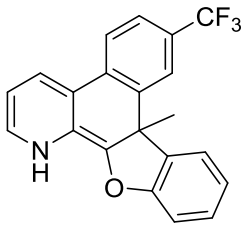
1H), 2.47 (s, 3H), 1.45 (s, 9H). ^{13}C NMR (101 MHz, DMSO) δ 154.9, 149.9, 148.7, 135.3, 134.6, 131.7, 130.9, 130.6, 127.9, 127.0, 126.8, 124.9, 123.7, 123.2, 120.7, 120.5, 118.5, 115.3, 34.9, 31.2, 17.1. HRMS (ESI) m/z calcd for. $C_{24}H_{24}NO^+$ $[M+H]^+$ 342.1852, found 342.1854.

8b-Methyl-1,8b-dihydrobenzo[*f*]benzofuro[3,2-*h*]quinoline-7-carbonitrile (4e)



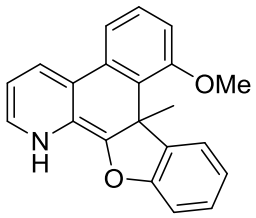
Yield: 50% (31 mg). White solid. m.p. 305.2-306.7 ℃. R_f = 0.45 (EtOAc / CH_2Cl_2 = 1/15). ^{1}H NMR (400 MHz, DMSO) δ 9.30 (d, *J* = 8.0 Hz, 1H), 9.09 (d, *J* = 8.8 Hz, 2H), 8.87 (d, *J* = 3.9 Hz, 1H), 8.72 (s, 1H), 8.10 (d, *J* = 8.5 Hz, 1H), 7.66 (dd, *J* = 8.2, 4.2 Hz, 1H), 7.25 (dd, *J* = 11.2, 4.1 Hz, 1H), 7.04 (d, *J* = 6.8 Hz, 1H), 6.97 (d, *J* = 8.1 Hz, 1H), 6.92 (t, *J* = 7.3 Hz, 1H), 2.50 (s, 3H). ^{13}C NMR (101 MHz, DMSO) δ 154.9, 150.7, 148.0, 137.3, 134.4, 131.9, 131.8, 131.5, 130.9, 130.7, 128.3, 128.2, 126.1, 124.8, 123.2, 121.4, 119.2, 118.6, 115.4, 110.0, 17.0. HRMS (ESI) m/z calcd for. $C_{21}H_{15}N_2O^+$ $[M+H]^+$ 311.1179, found 311.1180.

8b-Methyl-7-(trifluoromethyl)-1,8b-dihydrobenzo[*f*]benzofuro[3,2-*h*]quinoline (4f)



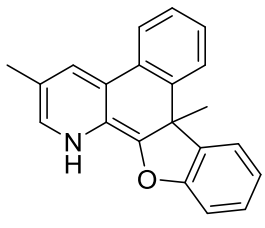
Yield: 46% (33 mg). White solid. m.p. 175.3-176.9 ℃. R_f = 0.46 (EtOAc / CH_2Cl_2 = 1/15). ^{1}H NMR (400 MHz, DMSO) δ 9.31 (d, *J* = 8.2 Hz, 1H), 9.15 (d, *J* = 8.5 Hz, 1H), 9.02 (s, 1H), 8.86 (d, *J* = 3.5 Hz, 1H), 8.50 (s, 1H), 8.05 (d, *J* = 8.5 Hz, 1H), 7.67 (dd, *J* = 7.6, 4.0 Hz, 1H), 7.25 (t, *J* = 7.6 Hz, 1H), 7.04 (d, *J* = 7.2 Hz, 1H), 6.96 (d, *J* = 8.1 Hz, 1H), 6.91 (t, *J* = 7.2 Hz, 1H), 2.52 (s, 3H). ^{13}C NMR (101 MHz, DMSO) δ 154.8, 150.3, 147.8, 137.09 (s), 134.6, 131.6, 131.5, 131.4, 130.7, 128.2, 126.3, 125.0, 123.2, 123.0 (d, *J* = 29.8 Hz), 122.2 (dd, *J* = 5.9, 2.5 Hz), 121.3, 121.2 (q, *J* = 250.1 Hz), 118.5, 115.3, 17.0. HRMS (ESI) m/z calcd for. $C_{21}H_{15}F_3NO^+$ $[M+H]^+$ 354.1100, found 354.1102.

8-Methoxy-8b-methyl-1,8b-dihydrobenzo[*f*]benzofuro[3,2-*h*]quinoline (4g)



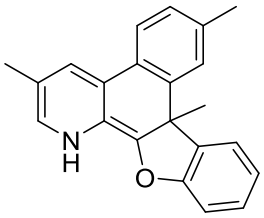
Yield: 35% (22 mg). White solid. m.p. 112.1-113.1 ℃. R_f = 0.46 (EtOAc / CH_2Cl_2 = 1/15). ^{1}H NMR (400 MHz, DMSO) δ 9.25 (d, *J* = 8.2 Hz, 1H), 8.93 (d, *J* = 3.0 Hz, 1H), 8.75 (d, *J* = 3.5 Hz, 1H), 8.31 (d, *J* = 1.9 Hz, 1H), 8.13 (d, *J* = 9.0 Hz, 1H), 7.55 (dd, *J* = 8.2, 4.2 Hz, 1H), 7.39 (d, *J* = 9.0 Hz, 1H), 7.21 (t, *J* = 7.5 Hz, 1H), 7.01 (d, *J* = 7.3 Hz, 1H), 6.94 (d, *J* = 7.8 Hz, 1H), 6.88 (t, *J* = 7.2 Hz, 1H), 4.03 (s, 3H), 2.42 (s, 3H). ^{13}C NMR (101 MHz, DMSO) δ 158.3, 155.1, 149.1, 147.6, 134.4, 132.9, 131.9, 131.2, 130.7, 127.9, 127.0, 126.8, 125.7, 123.5, 120.3, 118.5, 117.3, 115.3, 104.8, 55.6, 17.1. HRMS (ESI) m/z calcd for. $C_{21}H_{18}NO_2^+$ $[M+H]^+$ 316.1332, found 316.1335.

3,8b-Dimethyl-1,8b-dihydrobenzo[*f*]benzofuro[3,2-*h*]quinoline (4h)



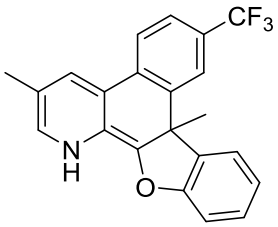
Yield: 61% (37 mg). White solid. m.p. 193.6-194.1 ℃. R_f = 0.47 (EtOAc / CH_2Cl_2 = 1/15). ^{1}H NMR (400 MHz, DMSO) δ 9.05 – 8.85 (m, 3H), 8.62 (s, 1H), 8.18 (s, 1H), 7.75 (s, 2H), 7.22 (s, 1H), 7.03 – 6.84 (m, 3H), 2.54 (s, 3H), 2.43 (s, 3H). ^{13}C NMR (101 MHz, DMSO) δ 155.0, 150.3, 145.2, 135.3, 133.2, 131.7, 131.4, 130.1, 130.0, 128.8, 127.0, 127.4, 127.0, 126.6, 125.1, 123.6, 123.3, 118.5, 115.3, 18.2, 17.0. HRMS (ESI) m/z calcd for. $C_{21}H_{18}NO^+$ $[M+H]^+$ 300.1383, found 300.1385.

3,7,8b-Trimethyl-1,8b-dihydrobenzo[*f*]benzofuro[3,2-*h*]quinoline (4i)



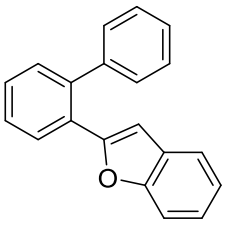
Yield: 35% (22 mg). Yellow solid. m.p. 230.4-231.3 ℃. R_f = 0.47 (EtOAc / CH_2Cl_2 = 1/15). ^{1}H NMR (400 MHz, DMSO) δ 8.97 (s, 1H), 8.93 (s, 1H), 8.78 (d, *J* = 8.4 Hz, 1H), 8.58 (s, 1H), 7.97 (s, 1H), 7.58 (d, *J* = 8.1 Hz, 1H), 7.21 (t, *J* = 7.2 Hz, 1H), 7.00 (d, *J* = 7.0 Hz, 1H), 6.93 (d, *J* = 8.0 Hz, 1H), 6.88 (t, *J* = 7.2 Hz, 1H), 2.58 (s, 3H), 2.52 (s, 3H), 2.41 (s, 3H). ^{13}C NMR (101 MHz, DMSO) δ 154.9, 149.9, 144.9, 136.8, 135.2, 132.9, 131.7, 131.5, 129.8, 129.8, 128.1, 127.9, 127.0, 126.6, 124.7, 123.6, 123.3, 118.5, 115.3, 21.5, 18.2, 17.0. HRMS (ESI) m/z calcd for. $C_{22}H_{20}NO^+$ $[M+H]^+$ 314.1539, found 314.1543.

3,8b-Dimethyl-7-(trifluoromethyl)-1,8b-dihydrobenzo[*f*]benzofuro[3,2-*h*]quinoline (4j)



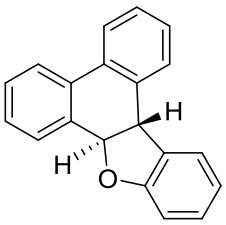
Yield: 76% (56 mg). Yellow solid. m.p. 237.9-239 ℃. R_f = 0.47 (EtOAc / CH_2Cl_2 = 1/15). ^{1}H NMR (400 MHz, DMSO) δ 9.07 – 8.99 (m, 3H), 8.66 (s, 1H), 8.40 (s, 1H), 7.95 (d, *J* = 7.7 Hz, 1H), 7.21 (t, *J* = 7.6 Hz, 1H), 6.98 (d, *J* = 7.2 Hz, 1H), 6.93 (d, *J* = 8.0 Hz, 1H), 6.86 (t, *J* = 7.3 Hz, 1H), 2.50 (s, 3H), 2.45 (s, 3H). ^{13}C NMR (101 MHz, DMSO) δ 155.9, 151.6, 145.8, 137.0, 133.3, 131.5, 131.4, 130.8, 130.7, 130.7, 128.2, 127.4 (q, ^2J = 31.3 Hz), 126.4, 124.9, 124.6 (q, ^1J = 272.3 Hz), 123.2, 122.1 (dd, *J* = 21.2, 1.9 Hz), 118.5, 115.3, 18.2, 16.9. HRMS (ESI) m/z calcd for. $C_{22}H_{17}F_3NO^+$ $[M+H]^+$ 368.1257, found 368.1257.

2-([1,1'-biphenyl]-2-yl)benzofuran (6a)



Yield: 40% (108 mg) Colorless oil. R_f = 0.49 (EtOAc / Petroleum ether = 1/10). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 – 7.99 (m, 1H), 7.50 – 7.38 (m, 7H), 7.37 – 7.34 (m, 3H), 7.26 – 7.21 (m, 1H), 7.15 (ddd, *J* = 8.6, 2.2, 1.1 Hz, 1H), 5.97 (d, *J* = 0.8 Hz, 1H).[4]

***trans*-8b,13b-dihydrophenanthro[9,10-*b*]benzofuran (6b)**



Yield: 62.5% (51 mg) White solid. m.p. 106.5-108.3 ℃. R_f = 0.48 (EtOAc / Petroleum ether = 1/5). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (d, J = 7.1 Hz, 1H), 7.85 – 7.79 (m, 2H), 7.76 – 7.69 (m, 2H), 7.48 – 7.39 (m, 4H), 7.30 (t, *J* = 7.8 Hz, 1H), 7.12 – 7.06 (m, 2H), 5.21 (d, *J* = 16.0 Hz, 1H), 4.42 (d, *J* = 16.0 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.6, 137.2, 135.7, 135.0, 133.4, 128.5, 128.4, 128.2, 128.1, 128.0, 127.8, 125.4, 125.0, 124.9, 124.1, 122.0, 121.7, 111.3, 86.7, 48.7. HRMS (APCI) m/z calcd for. $C_{20}H_{15}O^+$ $[M+H]^+$ 271.1117, found 271.1117.

6. References

[1] N. Shestakov, A. S. Pankova and M. A. Kuznetsov, *Chem. Heterocycl. Comp.*, **2017**, *53*, 1103-1113.

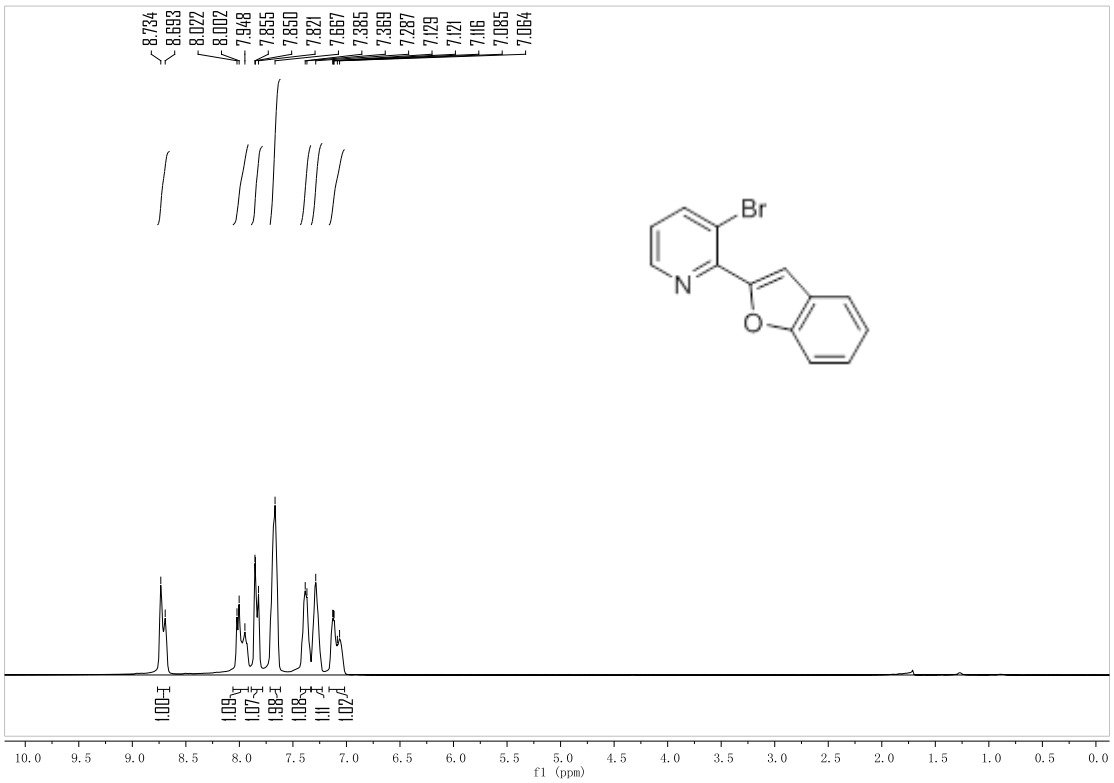
[2] F. Alonso, I. P. Beletskaya and M. Yus, *Tetrahedron.*, **2008**, *64*, 3047-3101.

[3] J. M. Fan, W. Zhang, W. X. Gao, T. Wang, W. L. Duan, Y. Liang, and Z. T. Zhang, *Org. Lett.*, **2019**, *21*, 9183-9187.

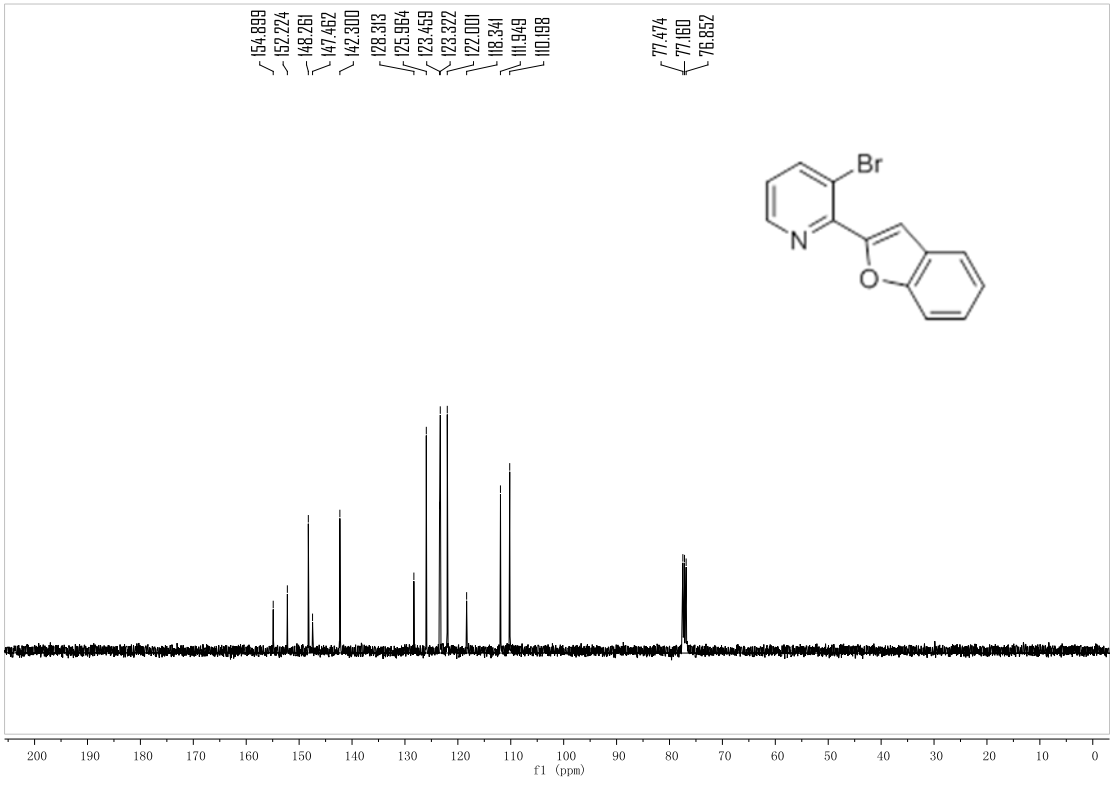
[4] J. Gicquiaud, A. Hacıhasanoğlu, P. Hermange, J. M. Sotiropoulos, and P. Y. Toullec, *Adv. Synth. Catal.*, **2019**, *361*, 2025-2030.

7. ^{1}H NMR and ^{13}C NMR Spectra

5a

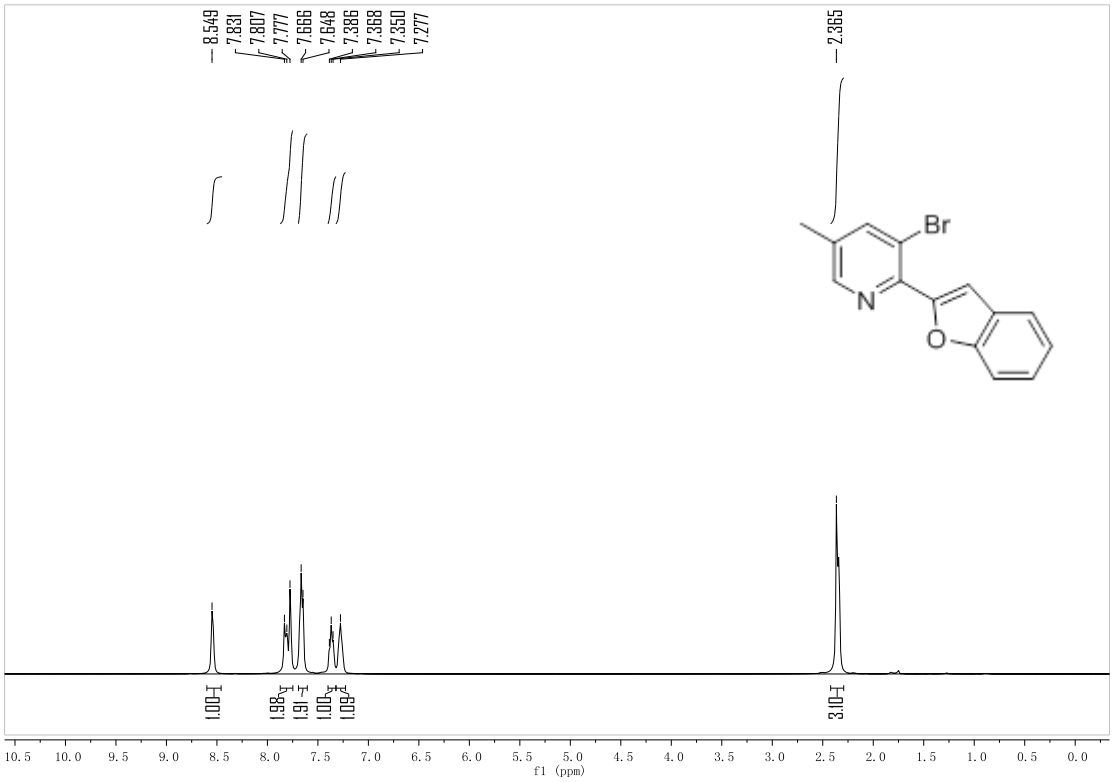


^{1}H NMR spectrum of **5a** ($CDCl_3$, 400 MHz)

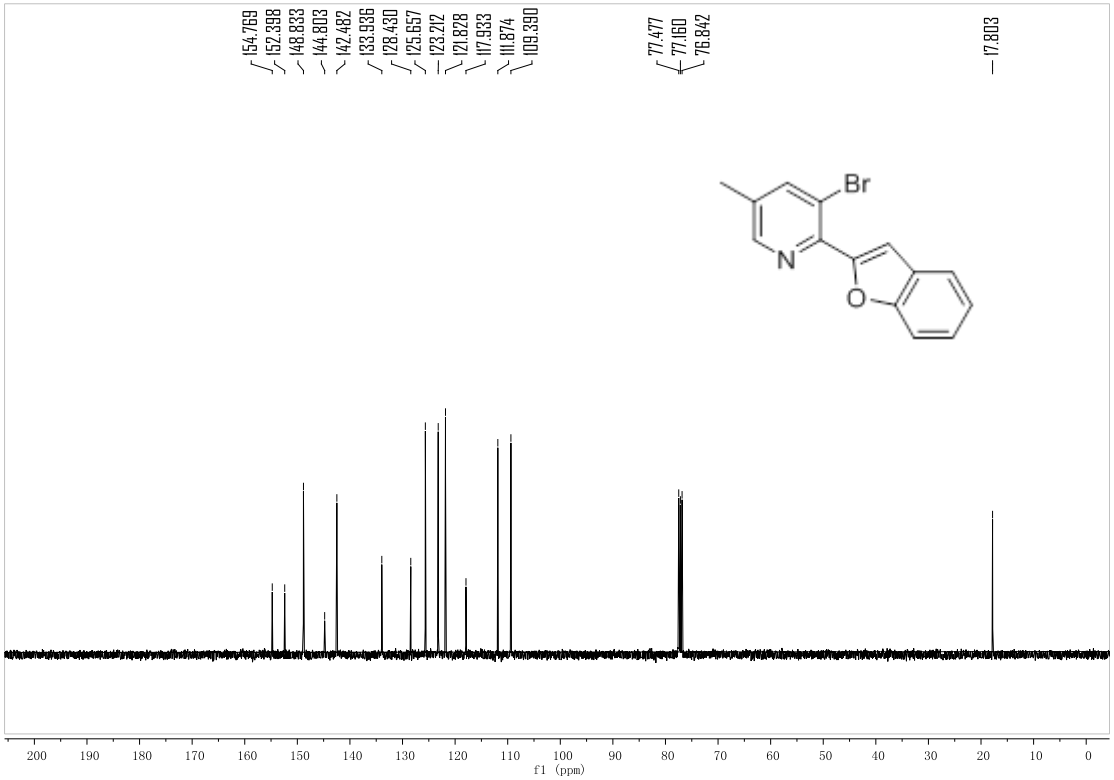


^{13}C NMR spectrum of **5a** ($CDCl_3$, 400 MHz)

5b

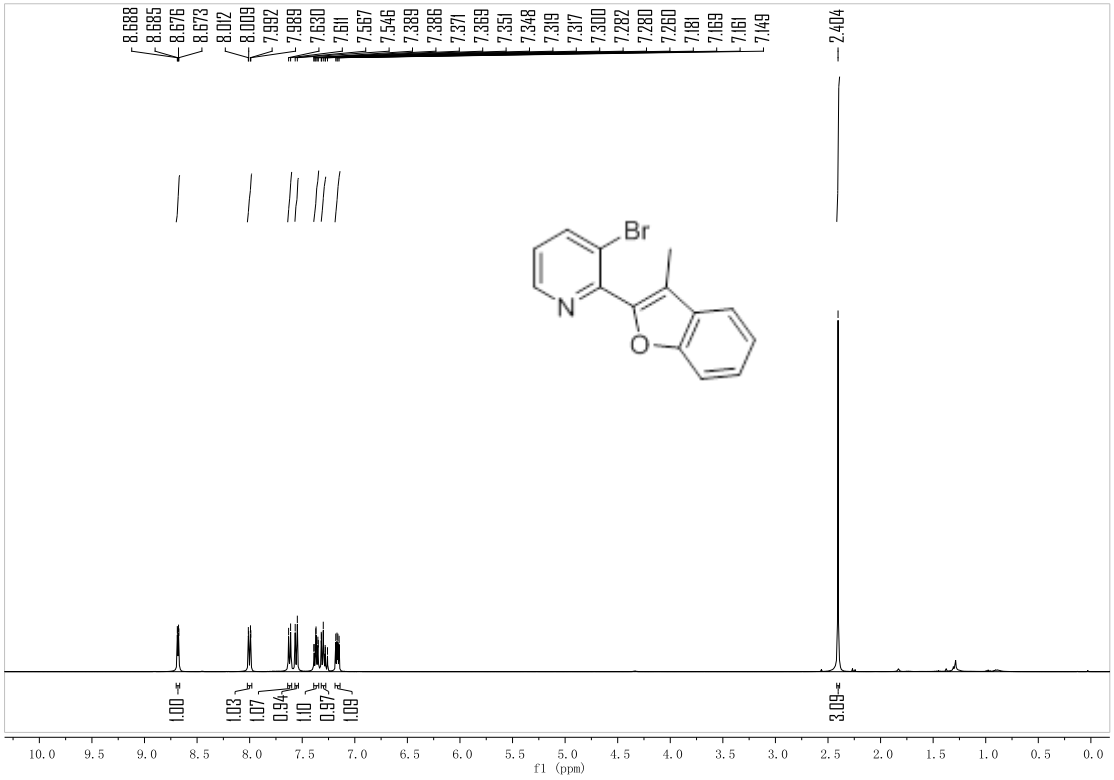


^{1}H NMR spectrum of **5b** ($CDCl_3$, 400 MHz)



^{13}C NMR spectrum of **5b** ($CDCl_3$, 400 MHz)

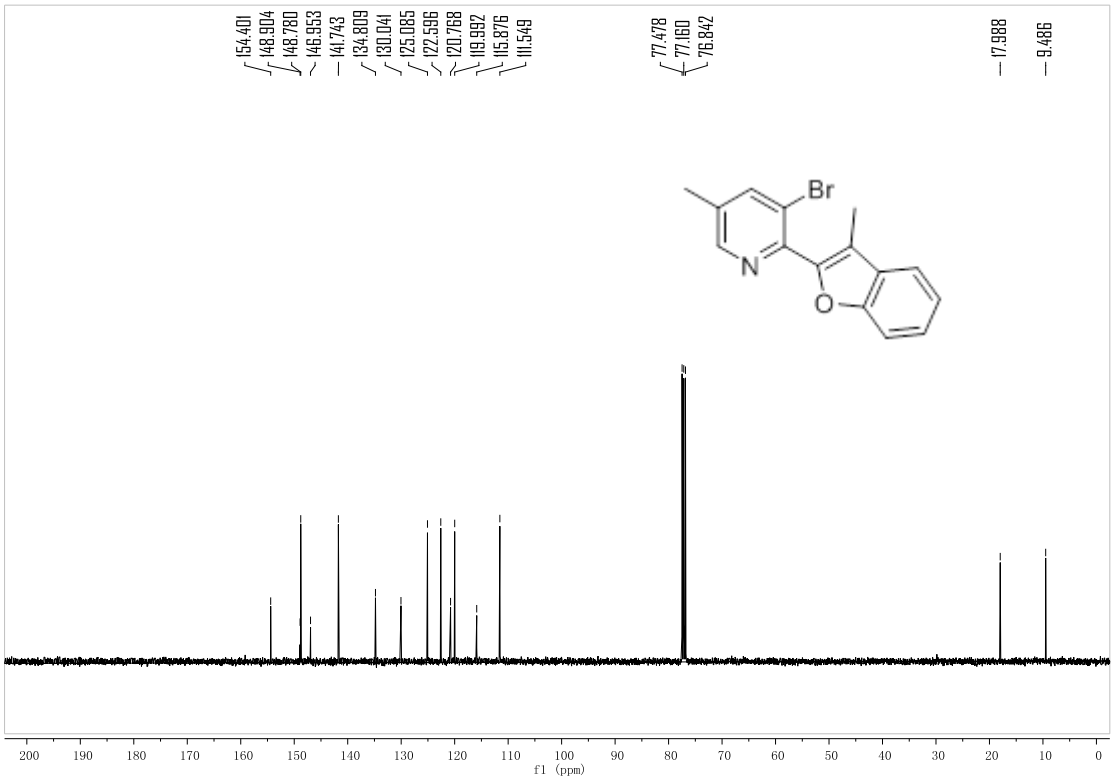
5c



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

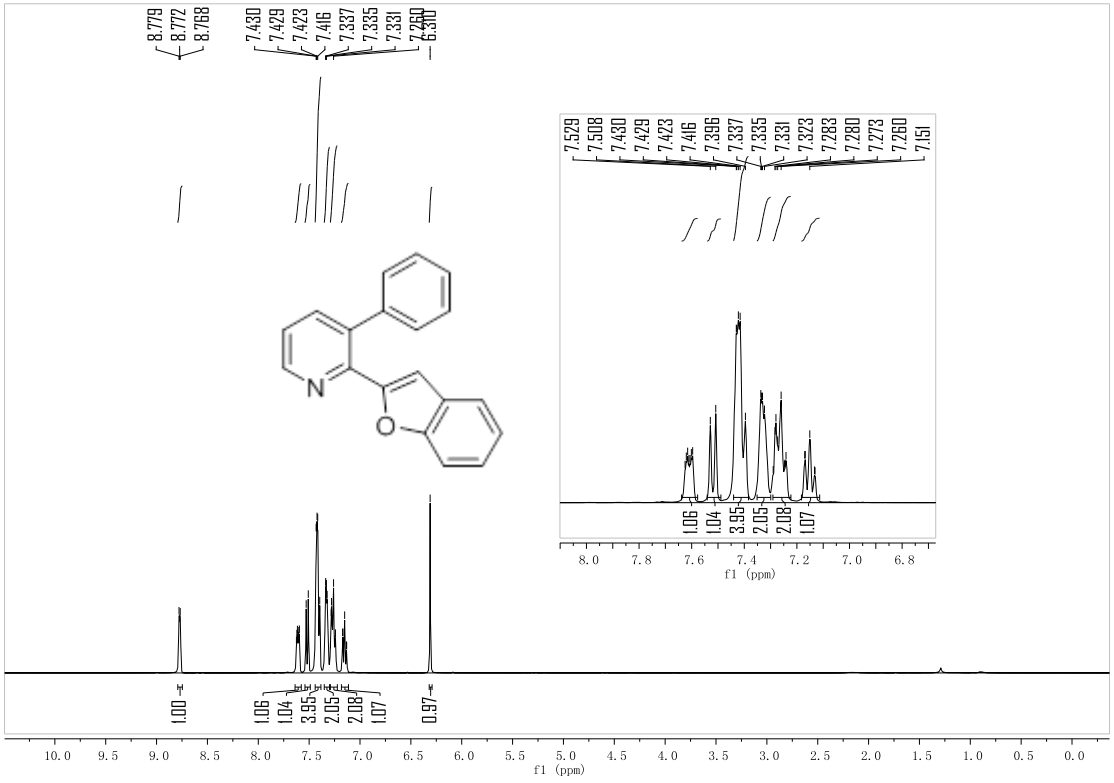
5d

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

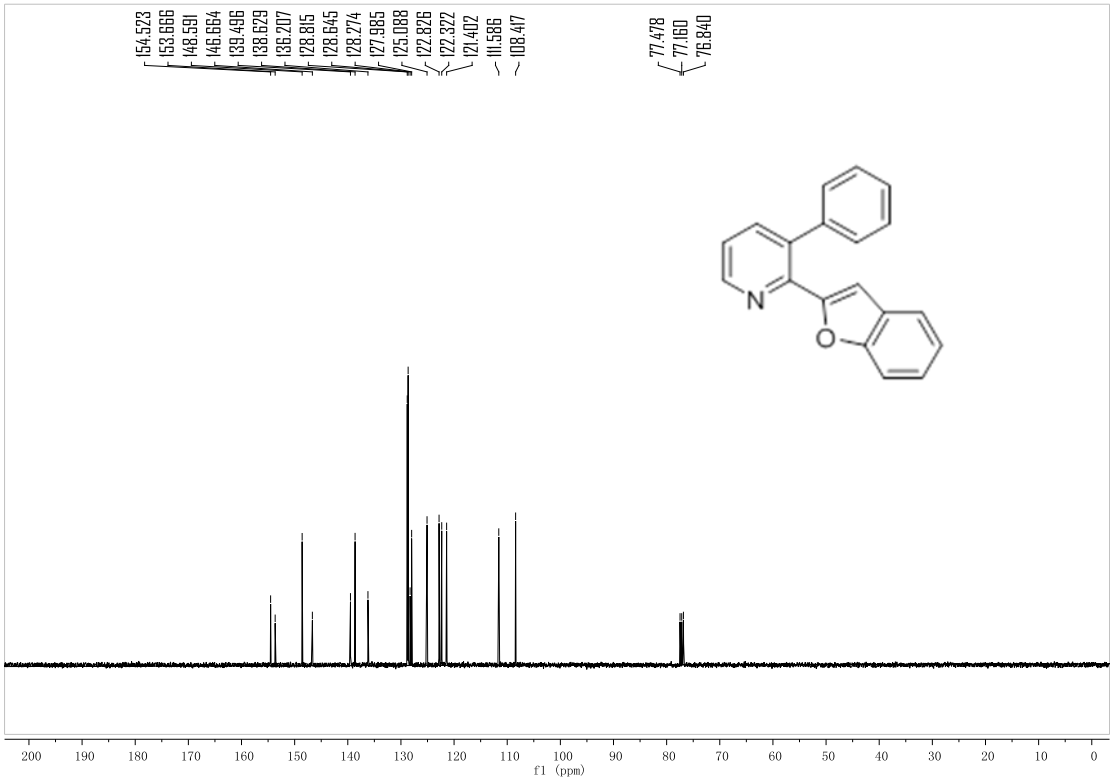


^{13}C NMR spectrum of **5d** ($CDCl_3$, 400 MHz)

1a

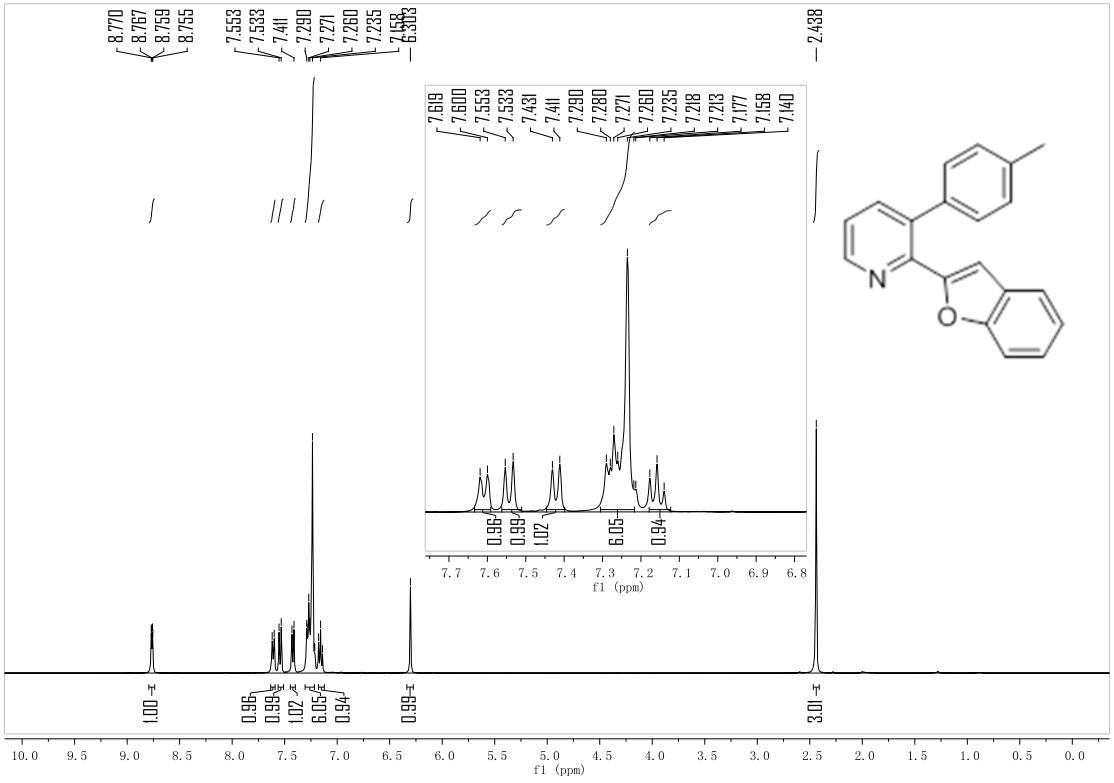


^{1}H NMR spectrum of **1a** ($CDCl_3$, 400 MHz)

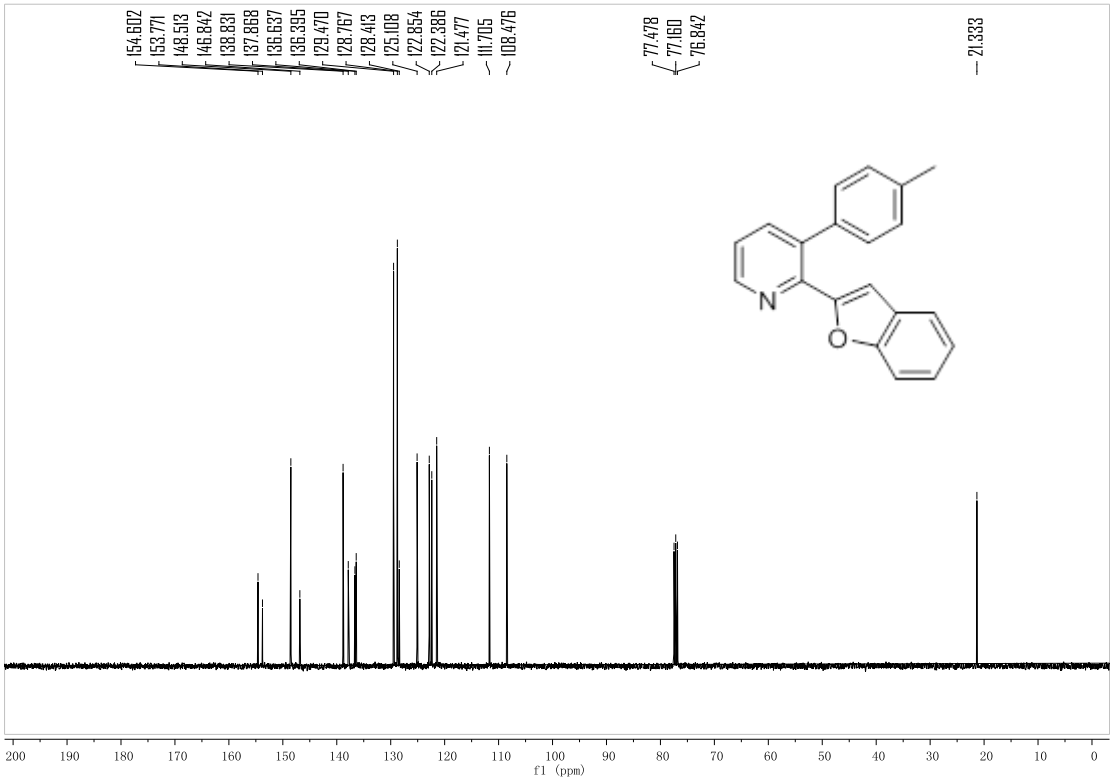


^{13}C NMR spectrum of **1a** ($CDCl_3$, 400 MHz)

1b

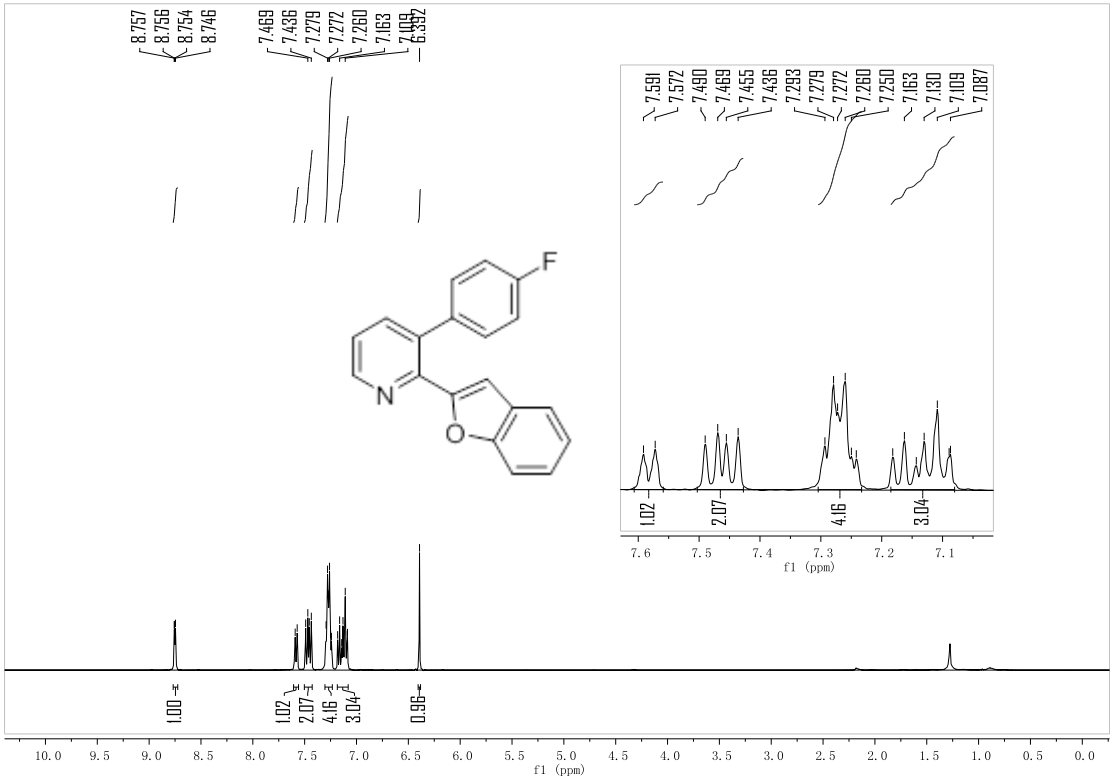


^{1}H NMR spectrum of **1b** ($CDCl_3$, 400 MHz)

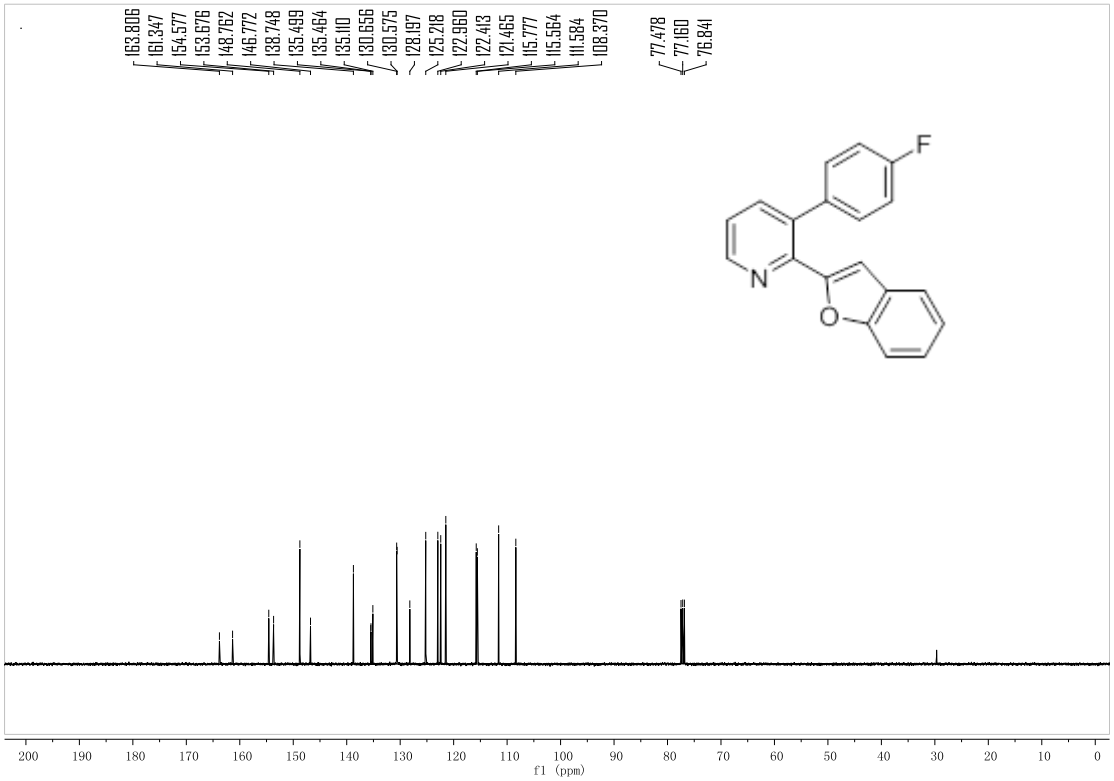


^{13}C NMR spectrum of **1b** ($CDCl_3$, 400 MHz)

1c

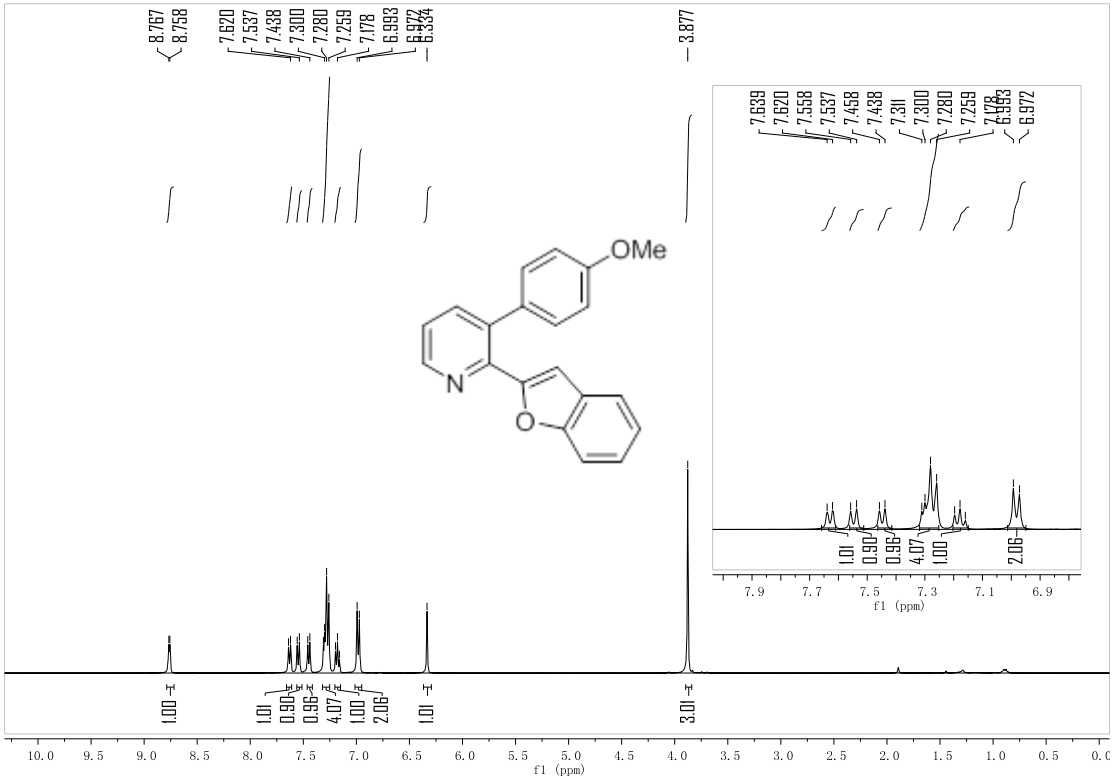


^{1}H NMR spectrum of **1c** ($CDCl_3$, 400 MHz)

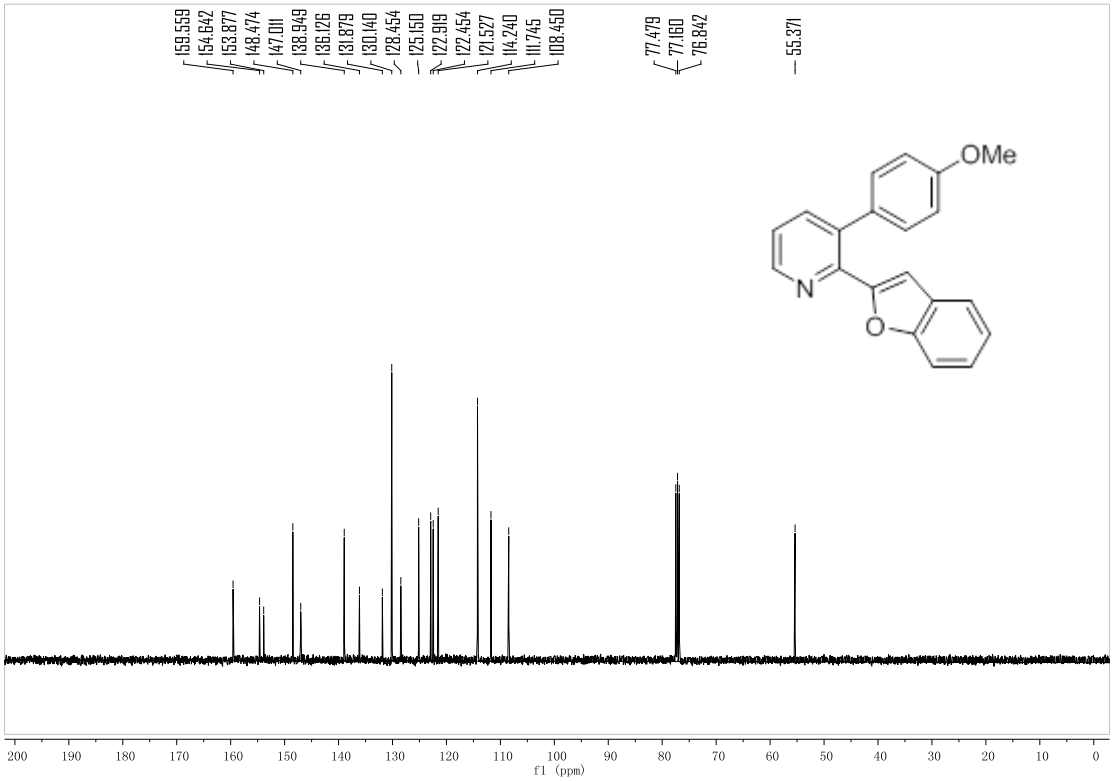


^{13}C NMR spectrum of **1c** ($CDCl_3$, 400 MHz)

1d

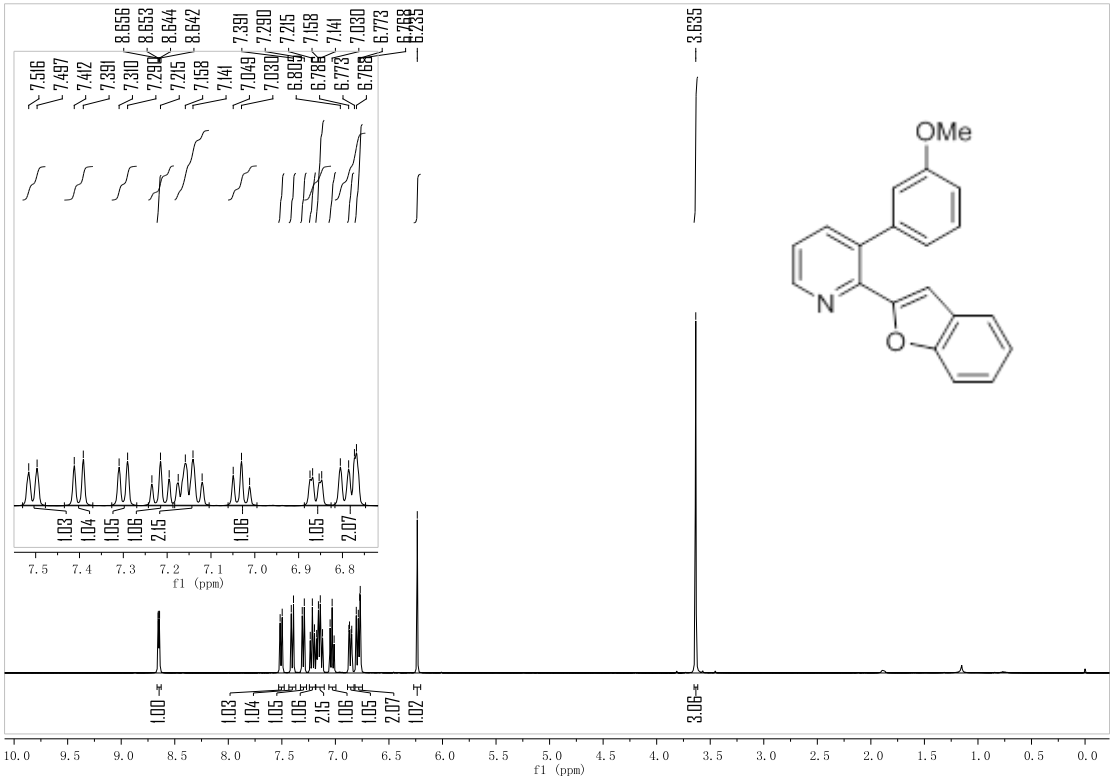


^{1}H NMR spectrum of **1d** ($CDCl_3$, 400 MHz)

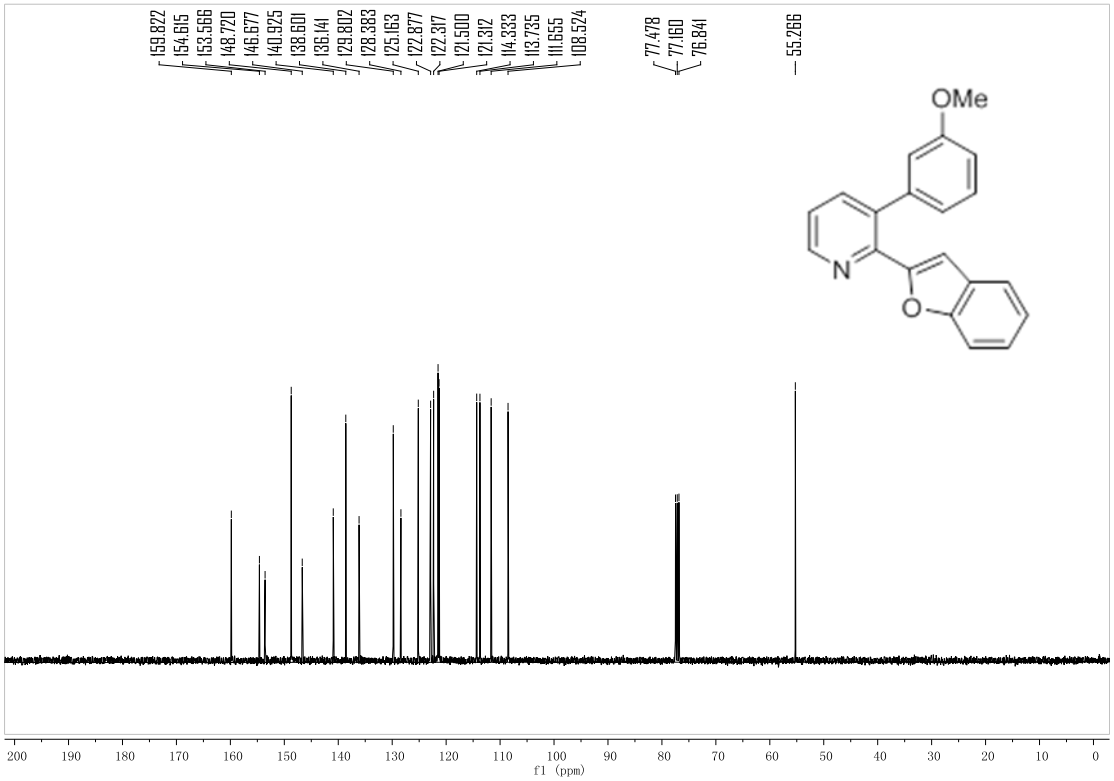


^{13}C NMR spectrum of **1d** ($CDCl_3$, 400 MHz)

1e

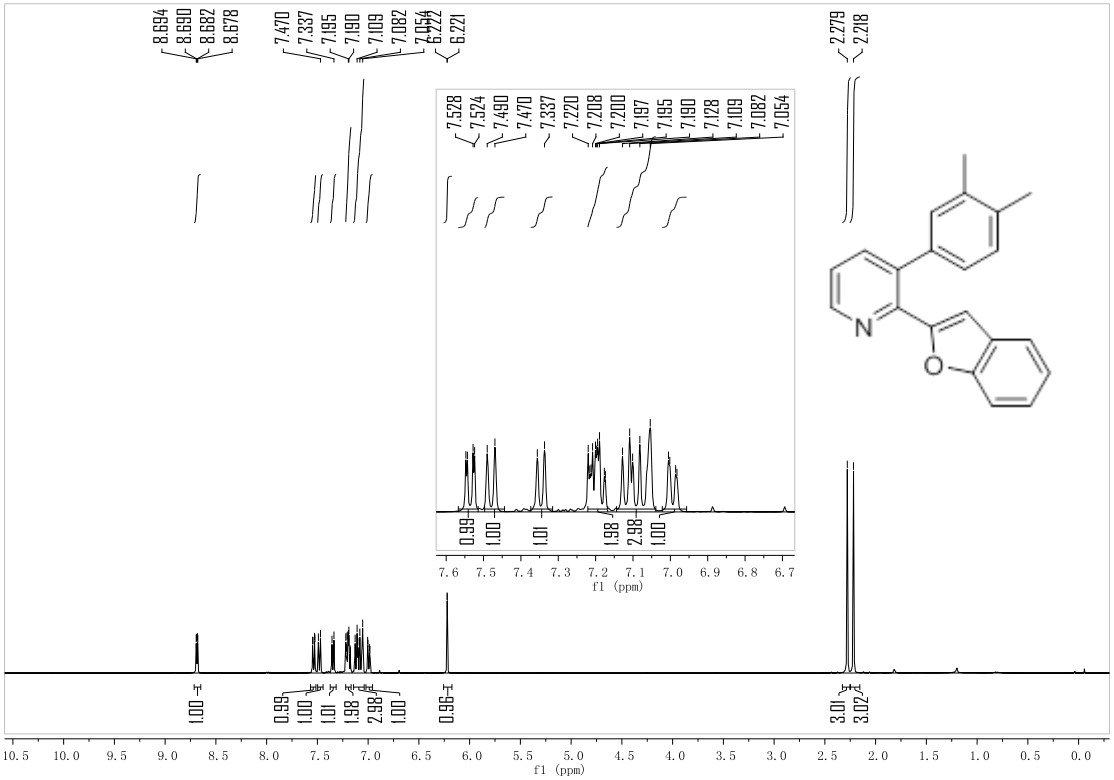


^{1}H NMR spectrum of **1e** ($CDCl_3$, 400 MHz)

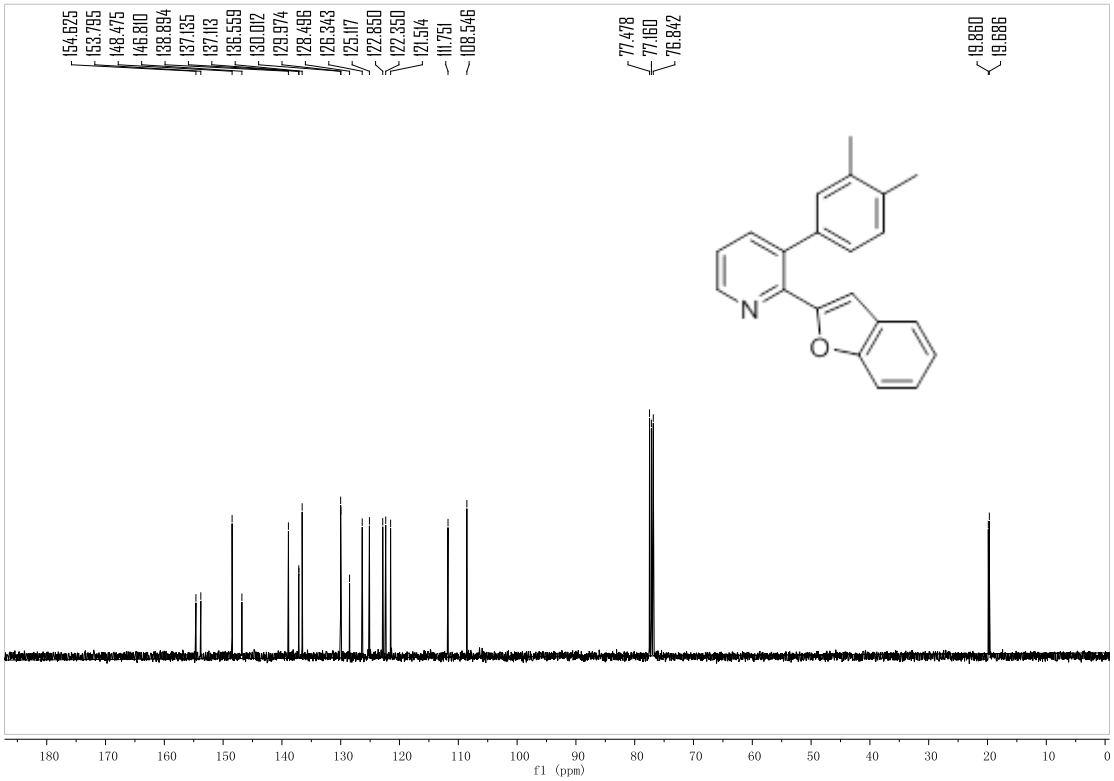


^{13}C NMR spectrum of **1e** ($CDCl_3$, 400 MHz)

1f

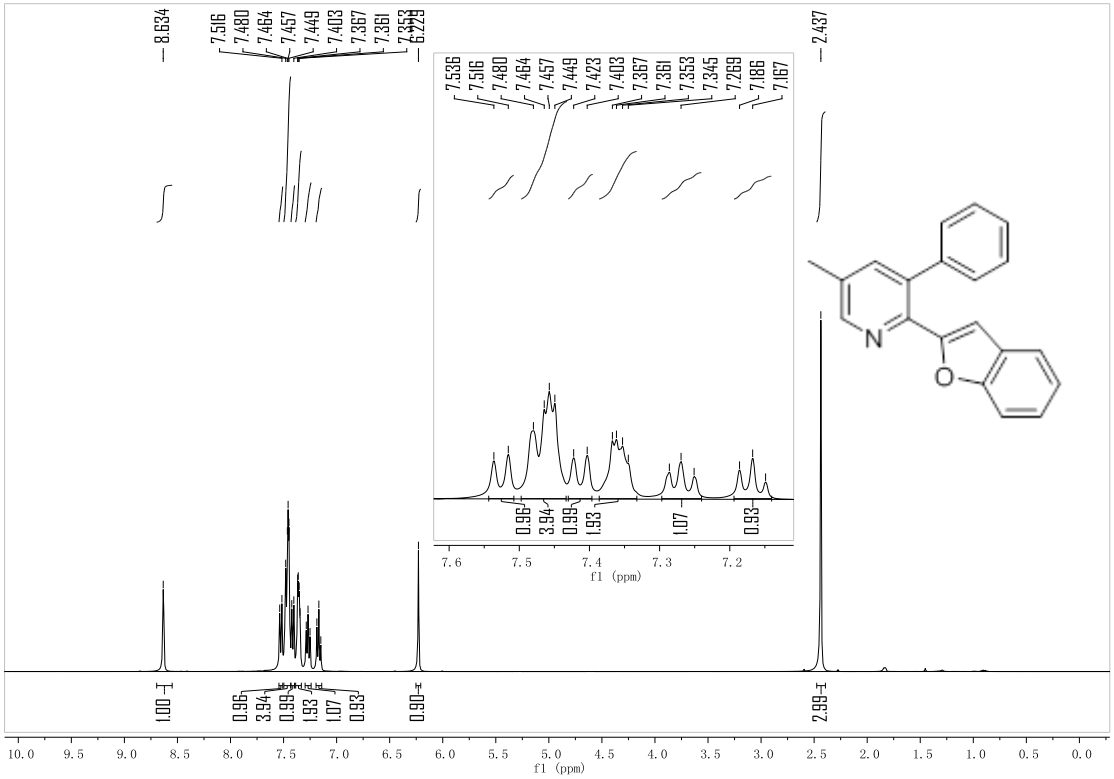


^{1}H NMR spectrum of **1f** ($CDCl_3$, 400 MHz)

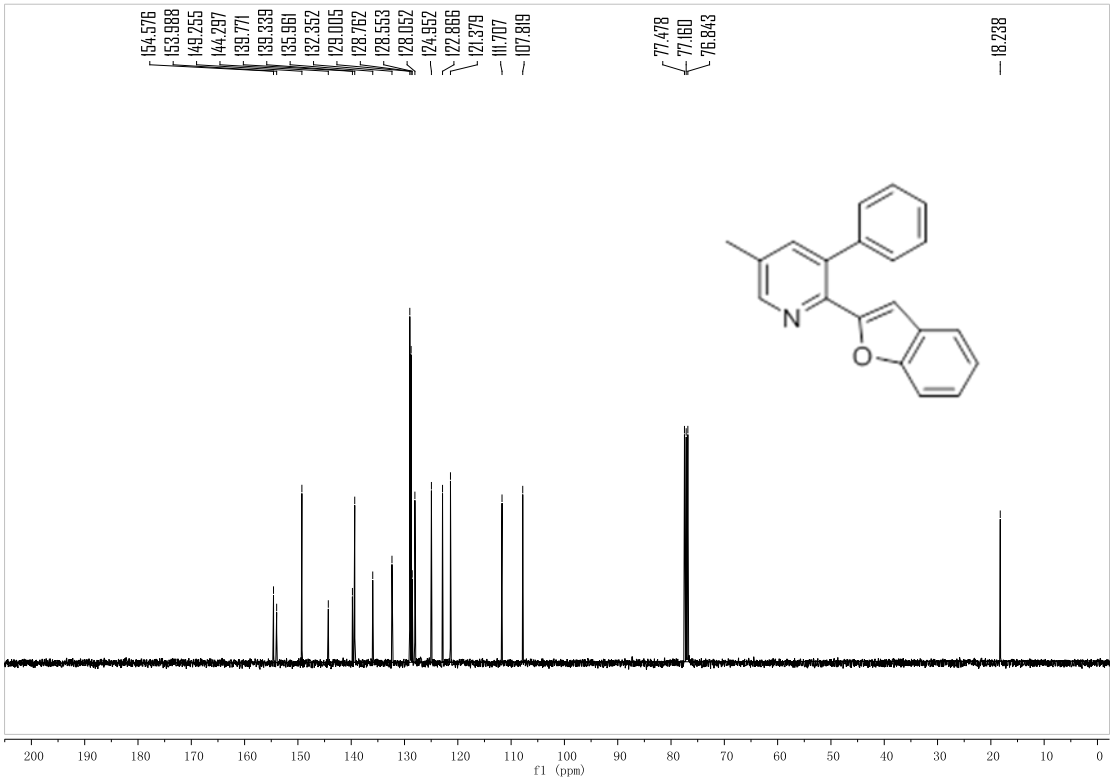


^{13}C NMR spectrum of **1f** ($CDCl_3$, 400 MHz)

1g

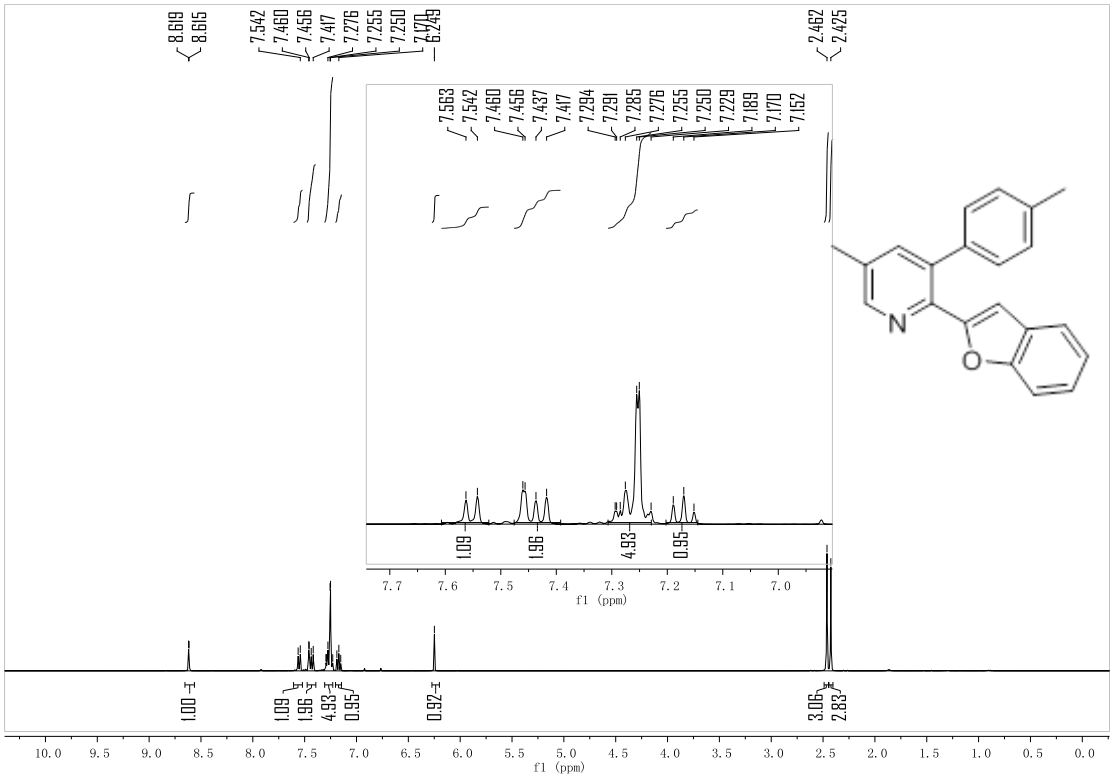


^{1}H NMR spectrum of **1g** ($CDCl_3$, 400 MHz)

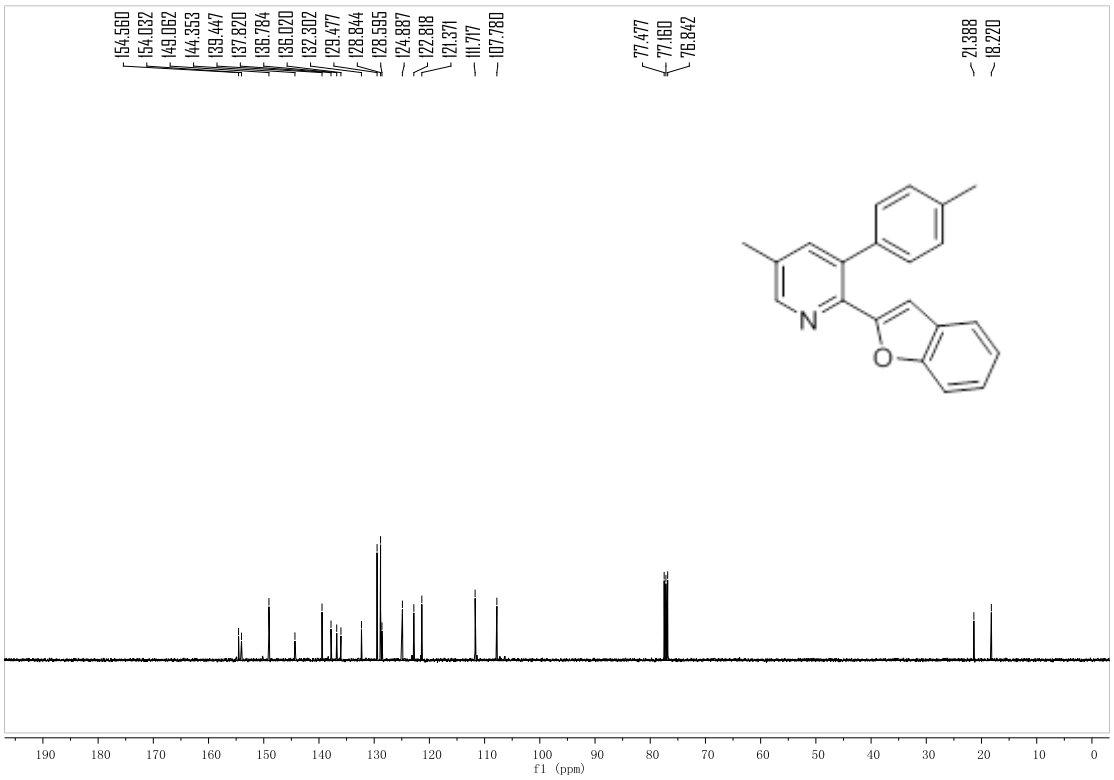


^{13}C NMR spectrum of **1g** ($CDCl_3$, 400 MHz)

1h

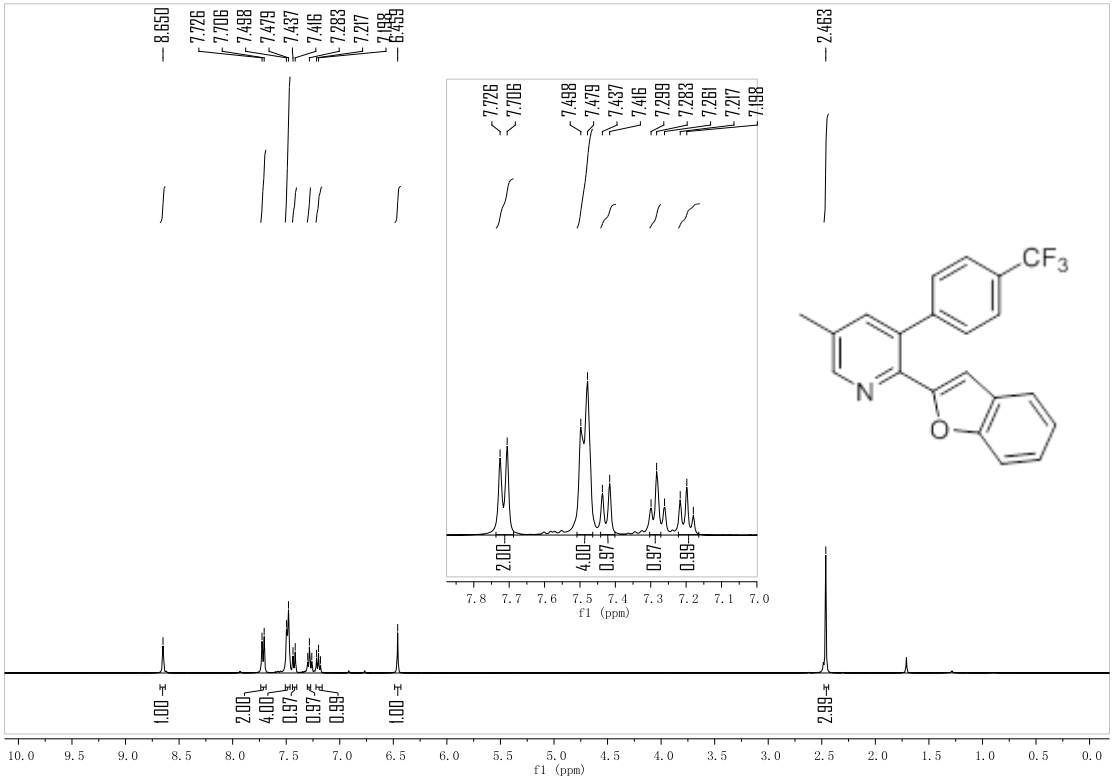


^{1}H NMR spectrum of **1h** ($CDCl_3$, 400 MHz)

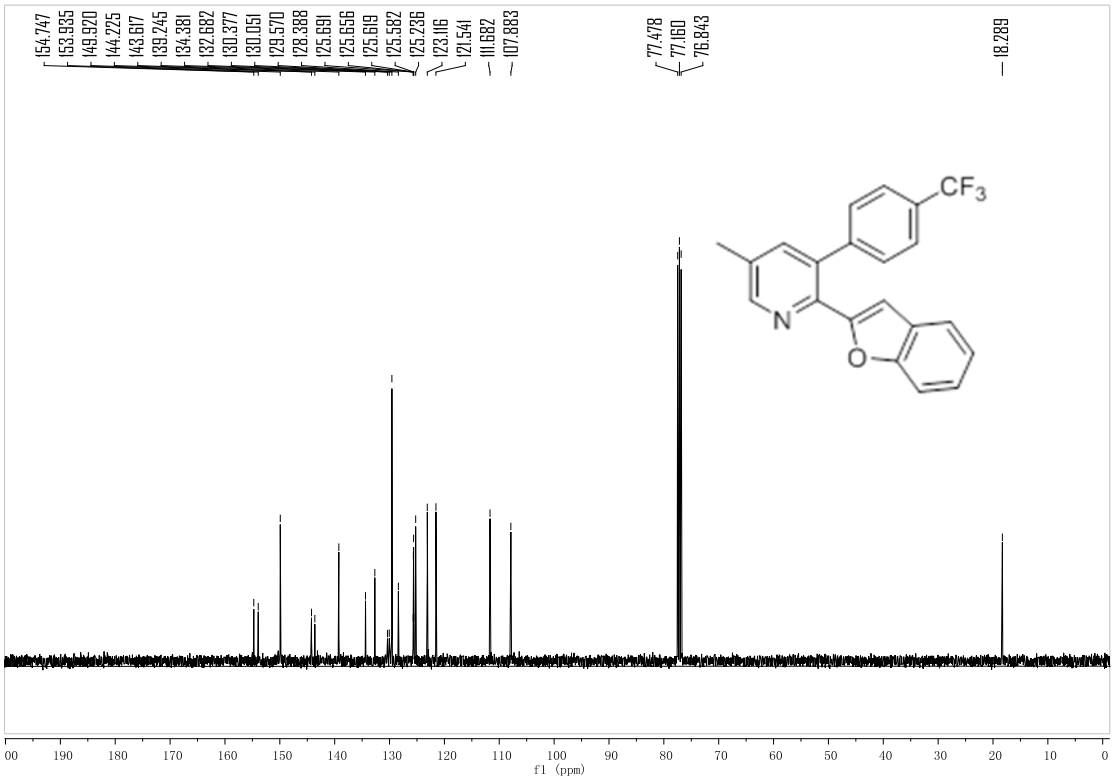


^{13}C NMR spectrum of **1h** ($CDCl_3$, 400 MHz)

1i

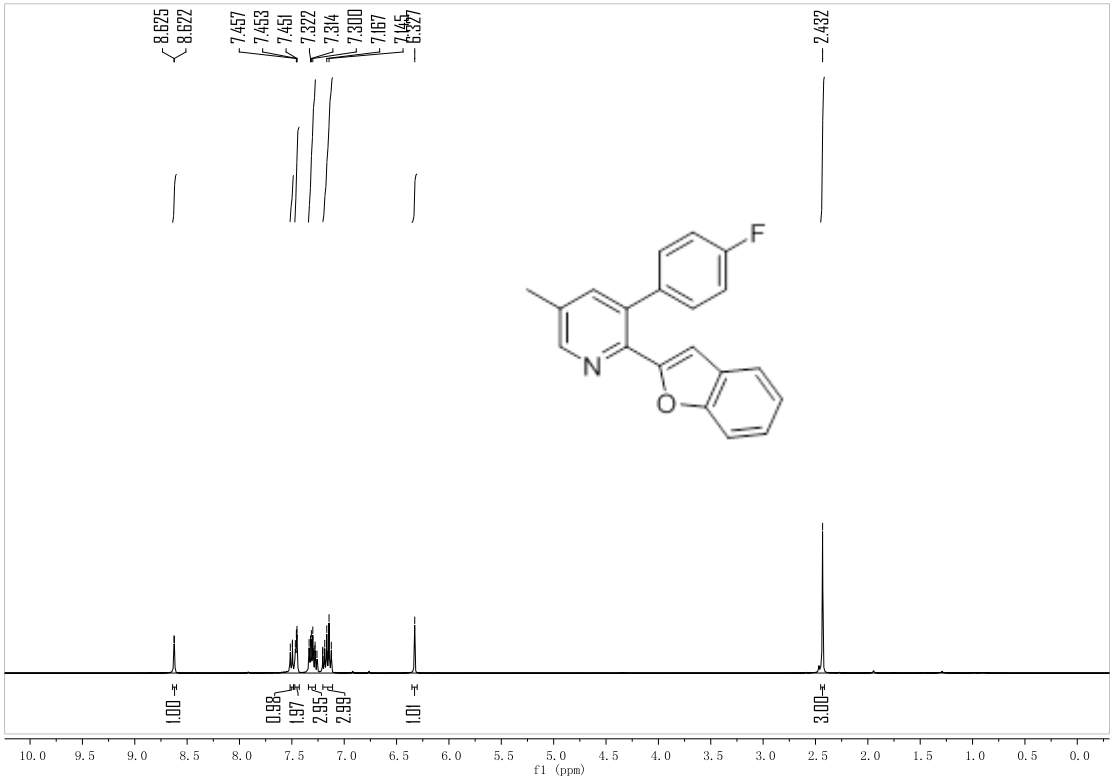


^{1}H NMR spectrum of **1i** ($CDCl_3$, 400 MHz)

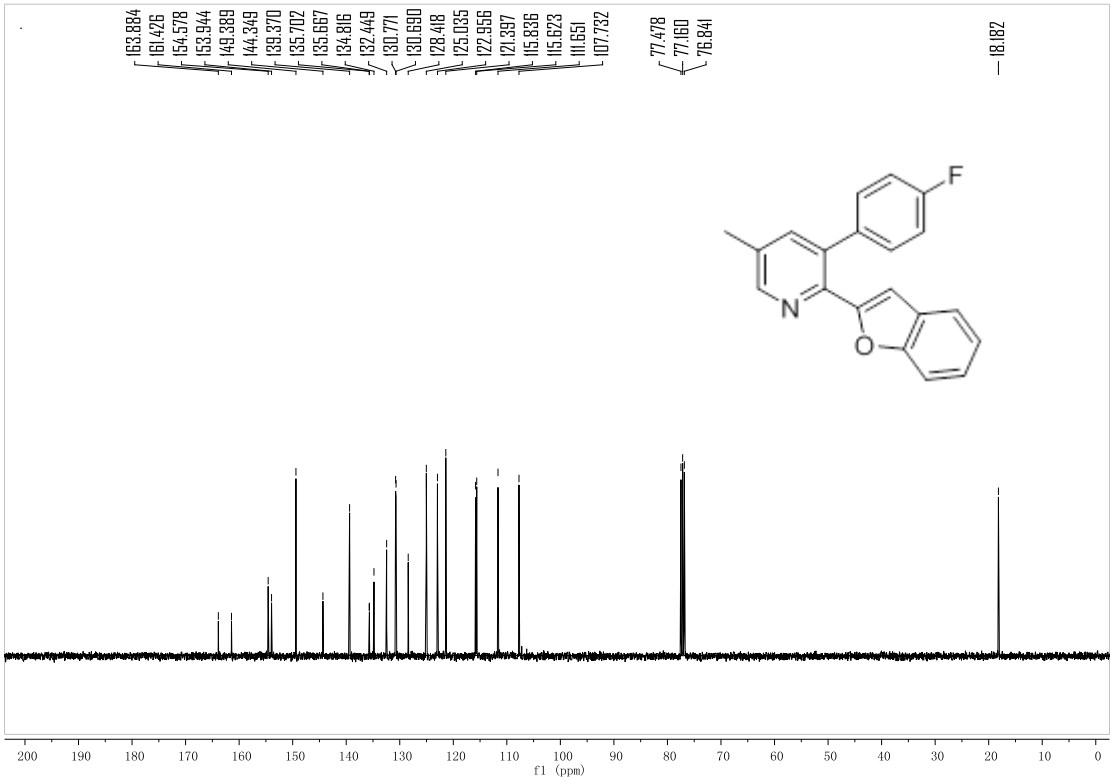


^{13}C NMR spectrum of **1i** ($CDCl_3$, 400 MHz)

1j

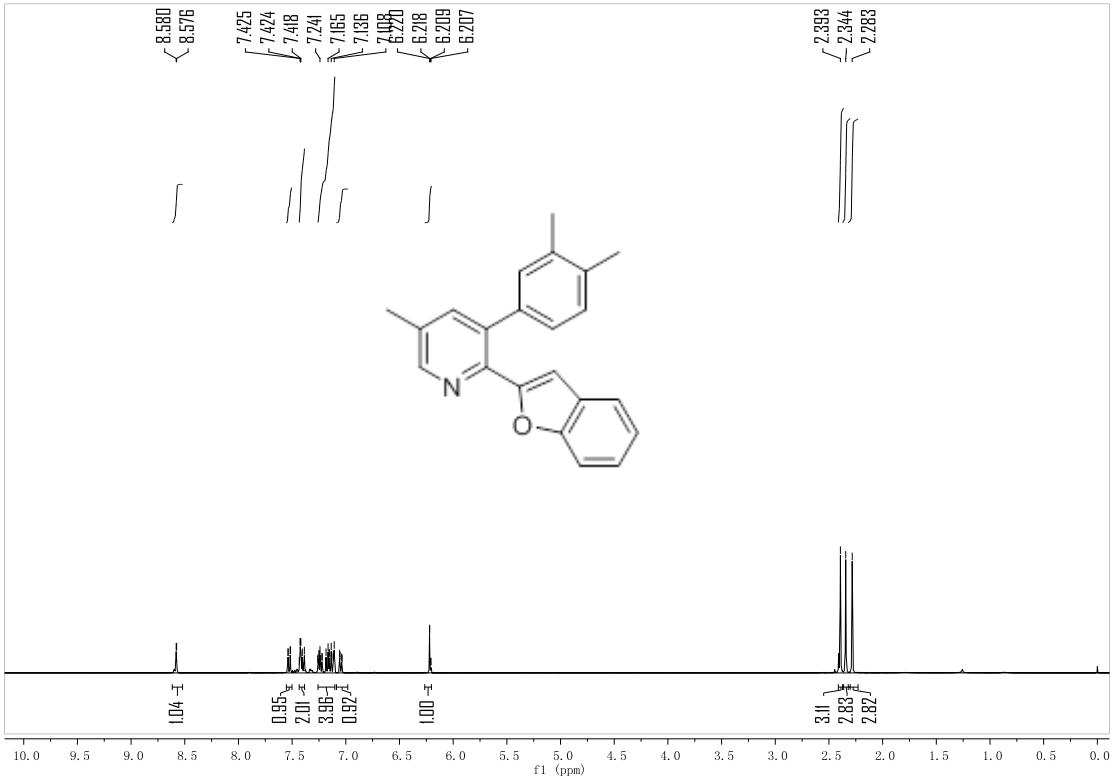


^{1}H NMR spectrum of **1j** ($CDCl_3$, 400 MHz)

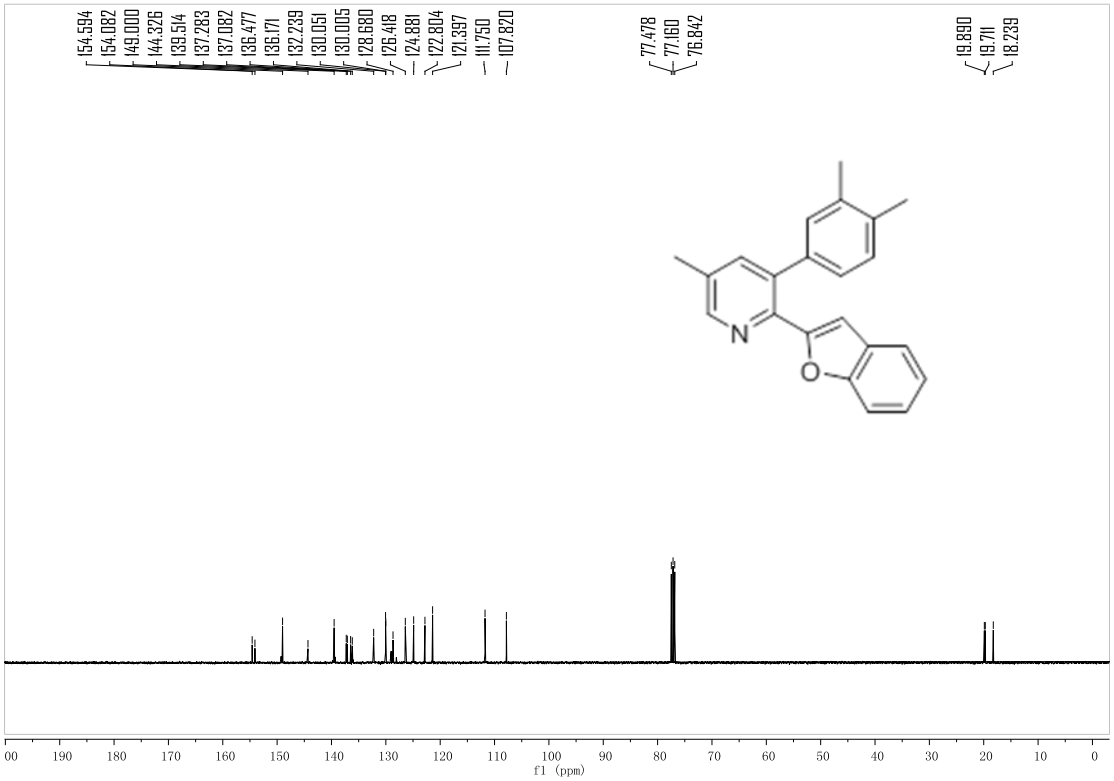


^{13}C NMR spectrum of **1j** ($CDCl_3$, 400 MHz)

1k

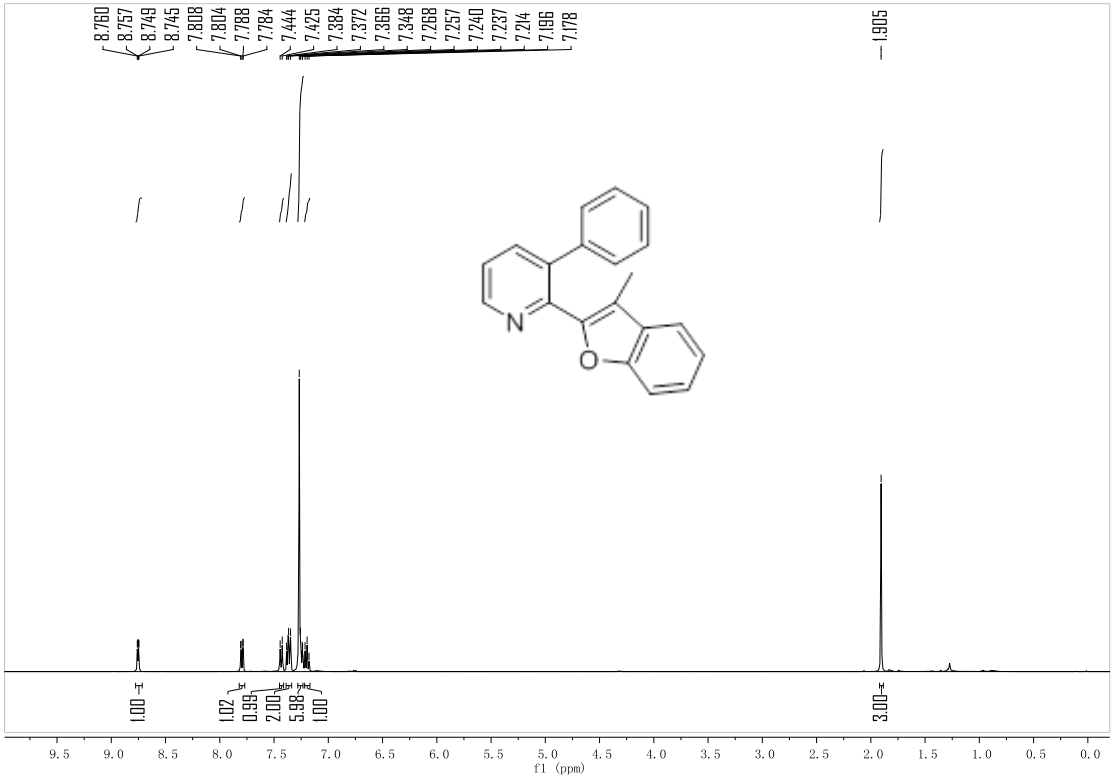


^{1}H NMR spectrum of **1k** ($CDCl_3$, 400 MHz)



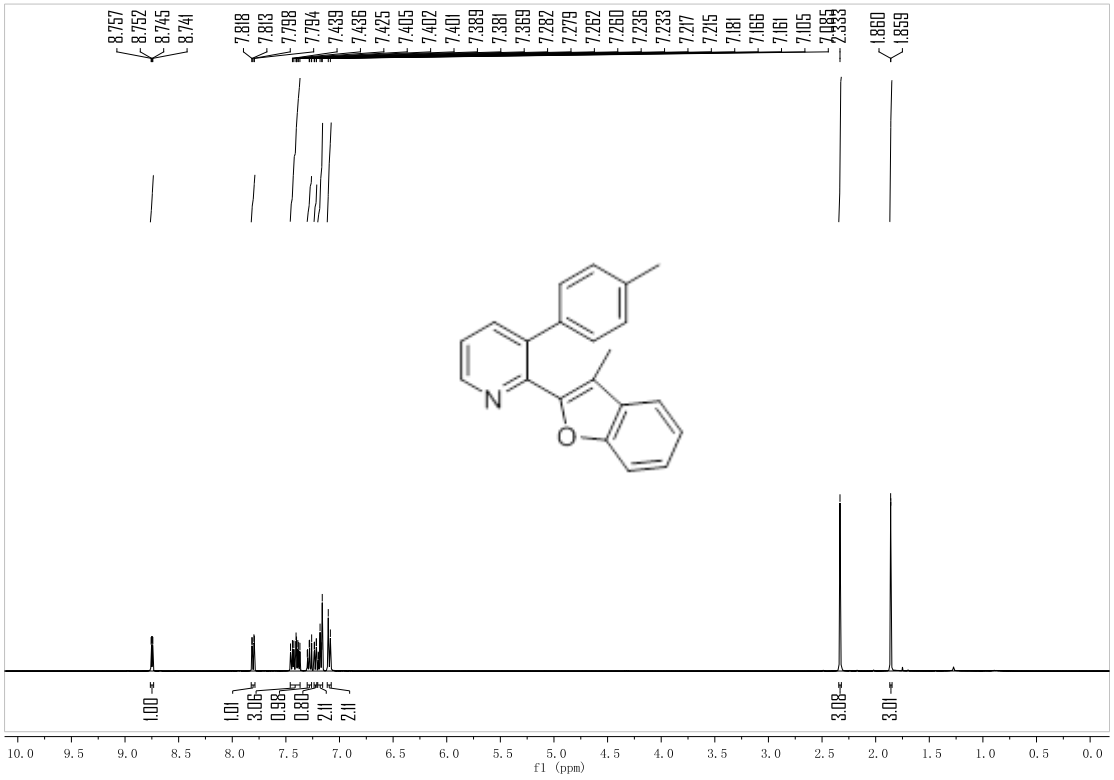
^{13}C NMR spectrum of **1k** ($CDCl_3$, 400 MHz)

1l

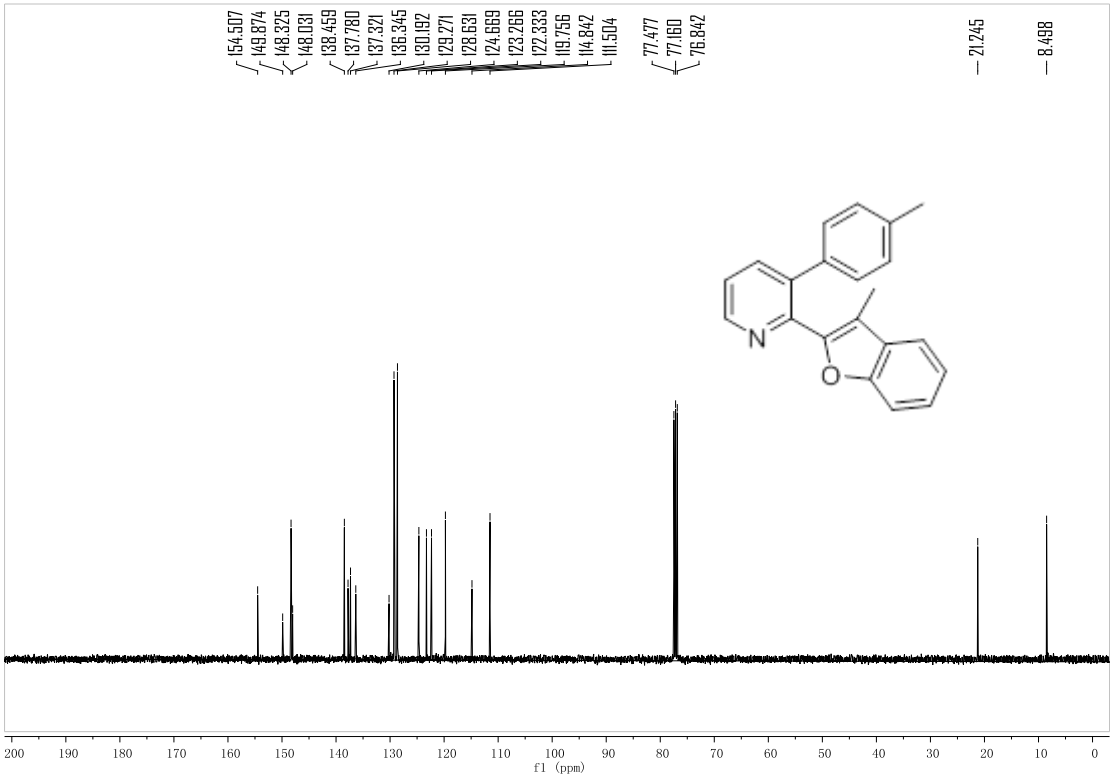


^{1}H NMR spectrum of **1l** ($CDCl_3$, 400 MHz)

1m

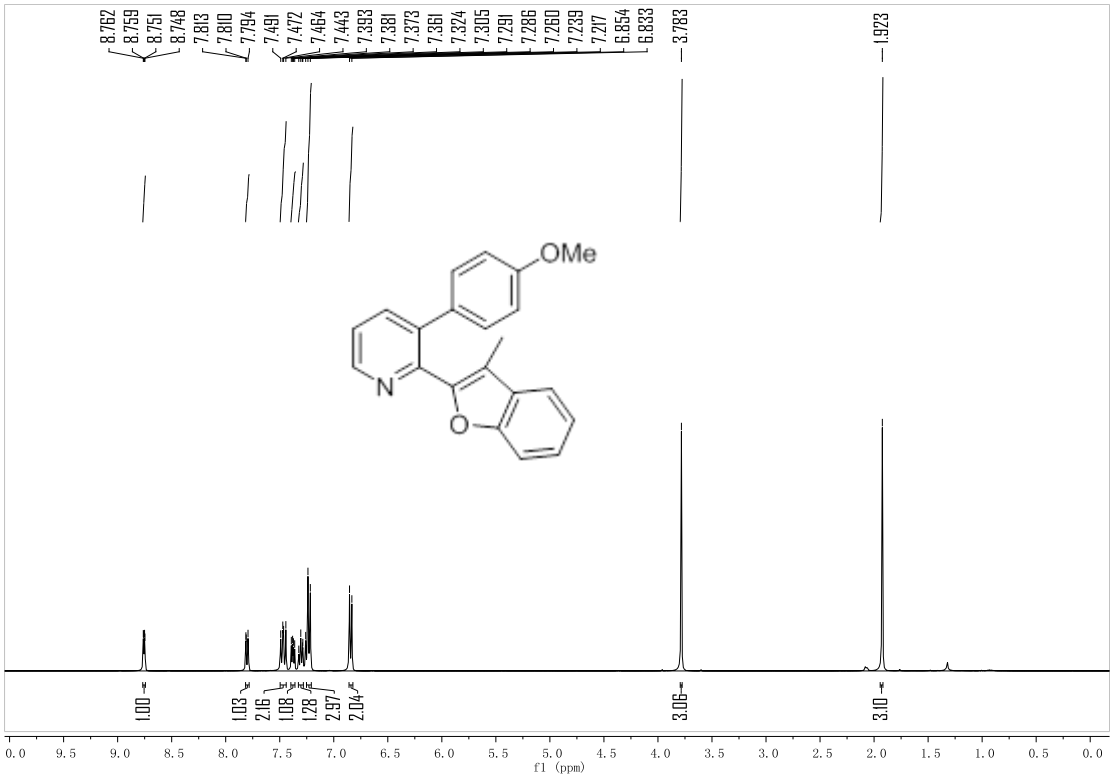


^{1}H NMR spectrum of **1m** ($CDCl_3$, 400 MHz)

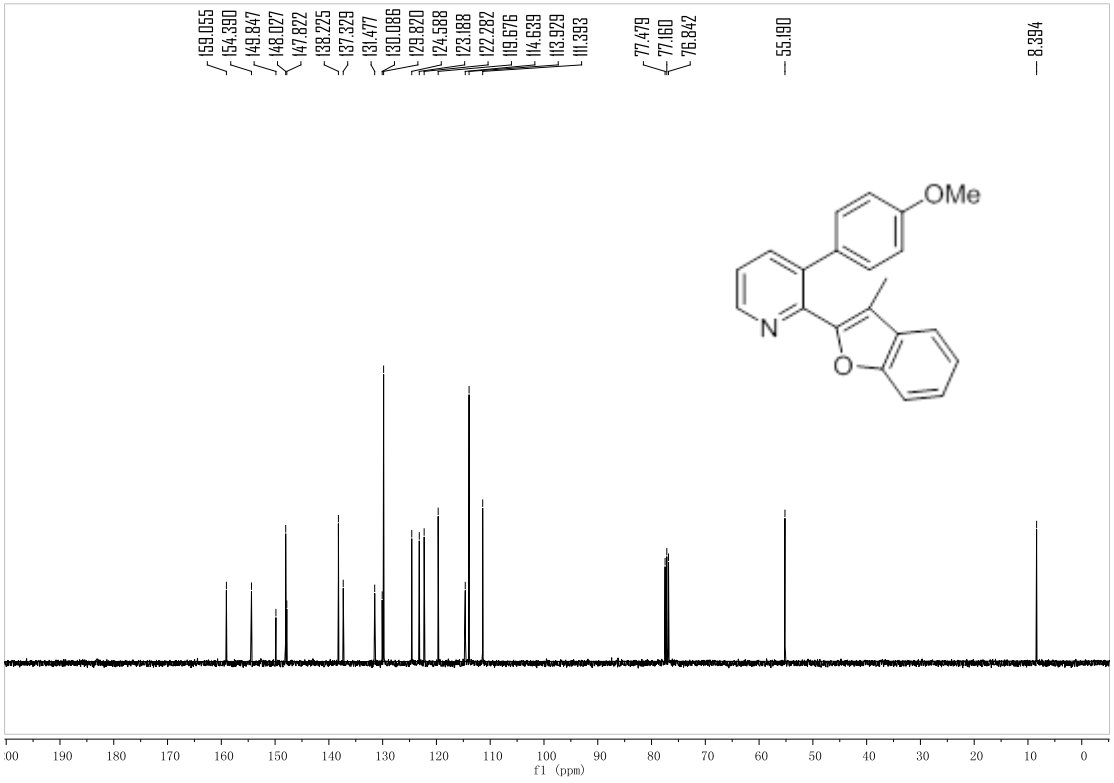


^{13}C NMR spectrum of **1m** ($CDCl_3$, 400 MHz)

1n

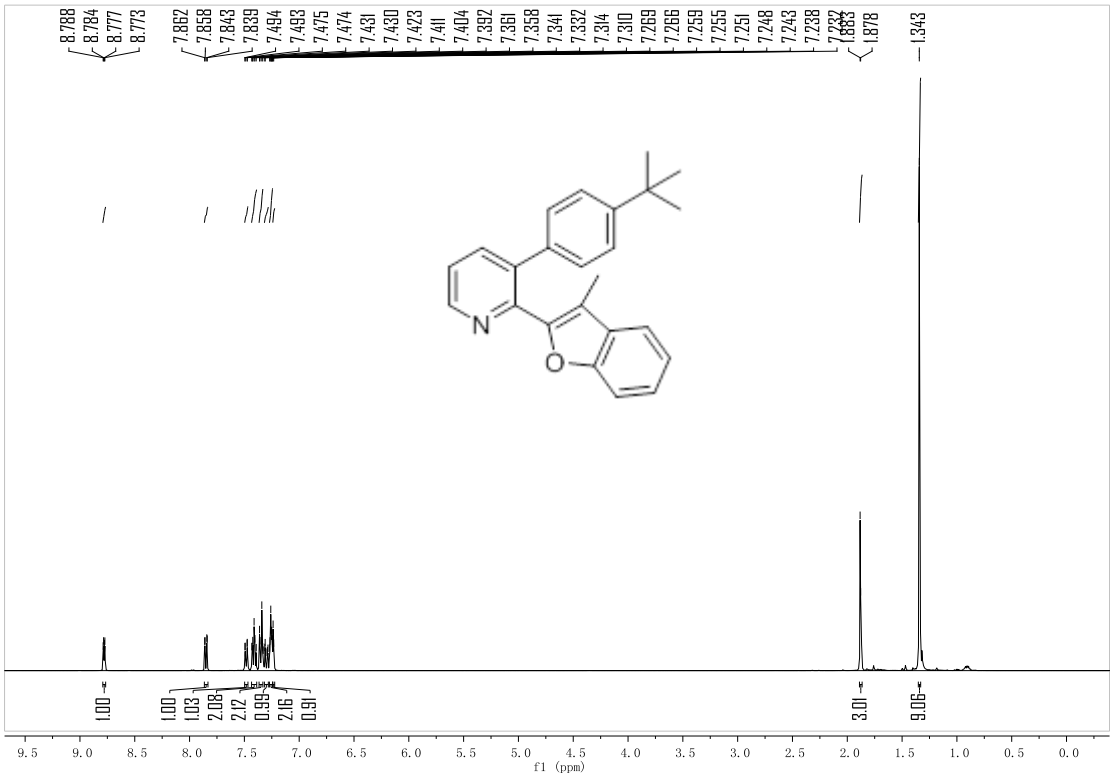


^{1}H NMR spectrum of **1n** ($CDCl_3$, 400 MHz)

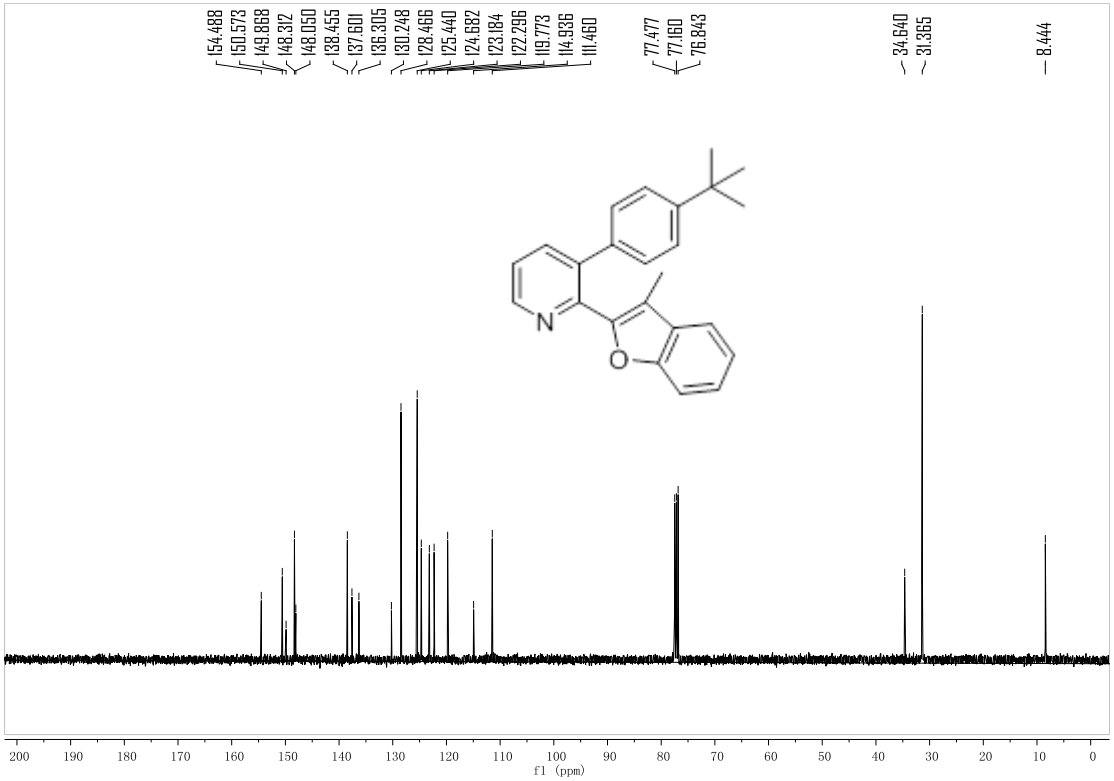


^{13}C NMR spectrum of **1n** ($CDCl_3$, 400 MHz)

1o

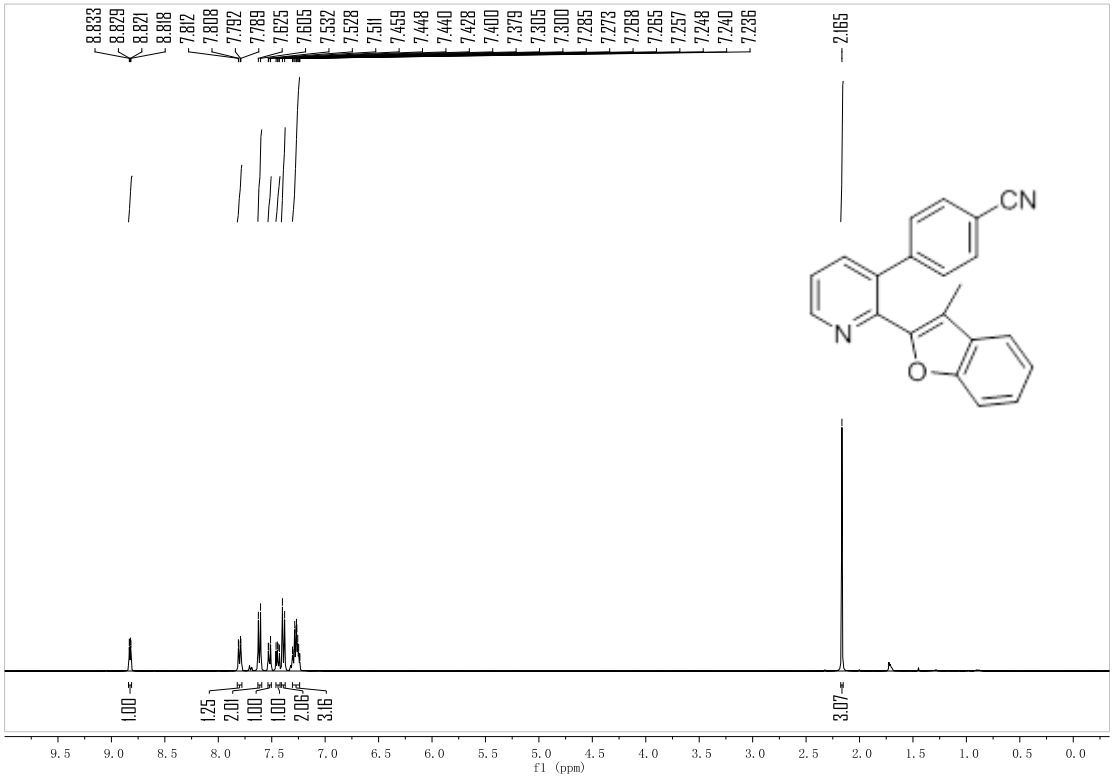


^{1}H NMR spectrum of **1o** ($CDCl_3$, 400 MHz)

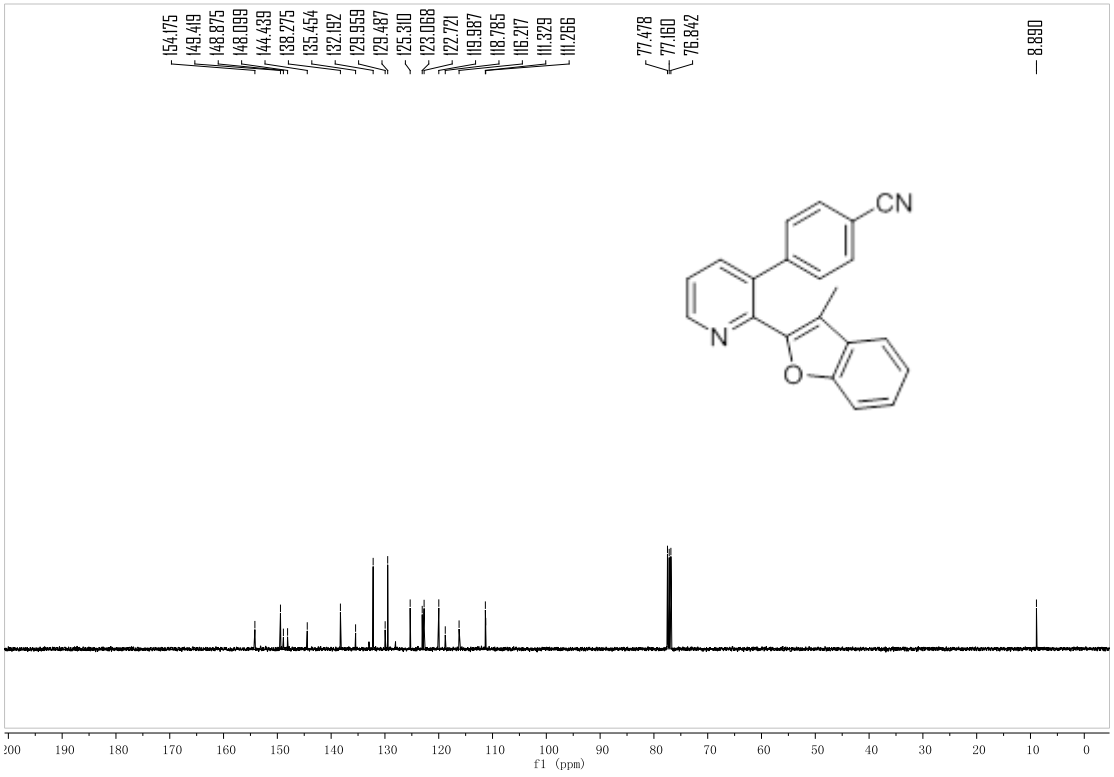


^{13}C NMR spectrum of **1o** ($CDCl_3$, 400 MHz)

1p

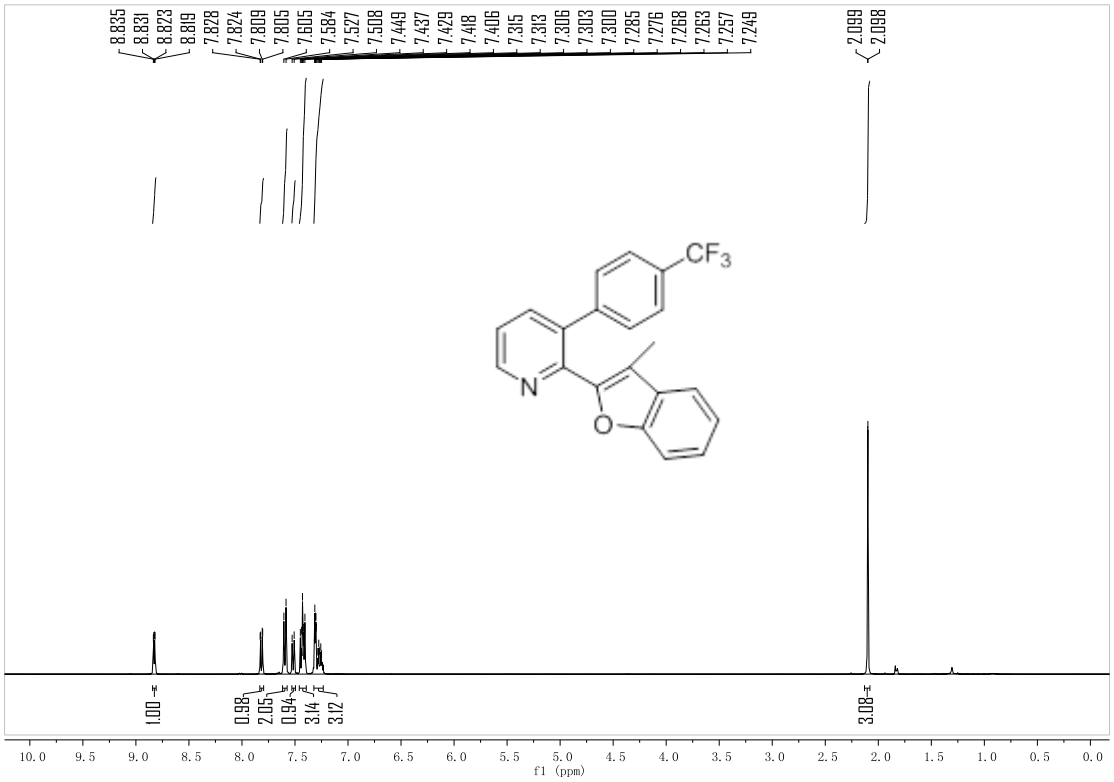


^{1}H NMR spectrum of **1p** ($CDCl_3$, 400 MHz)

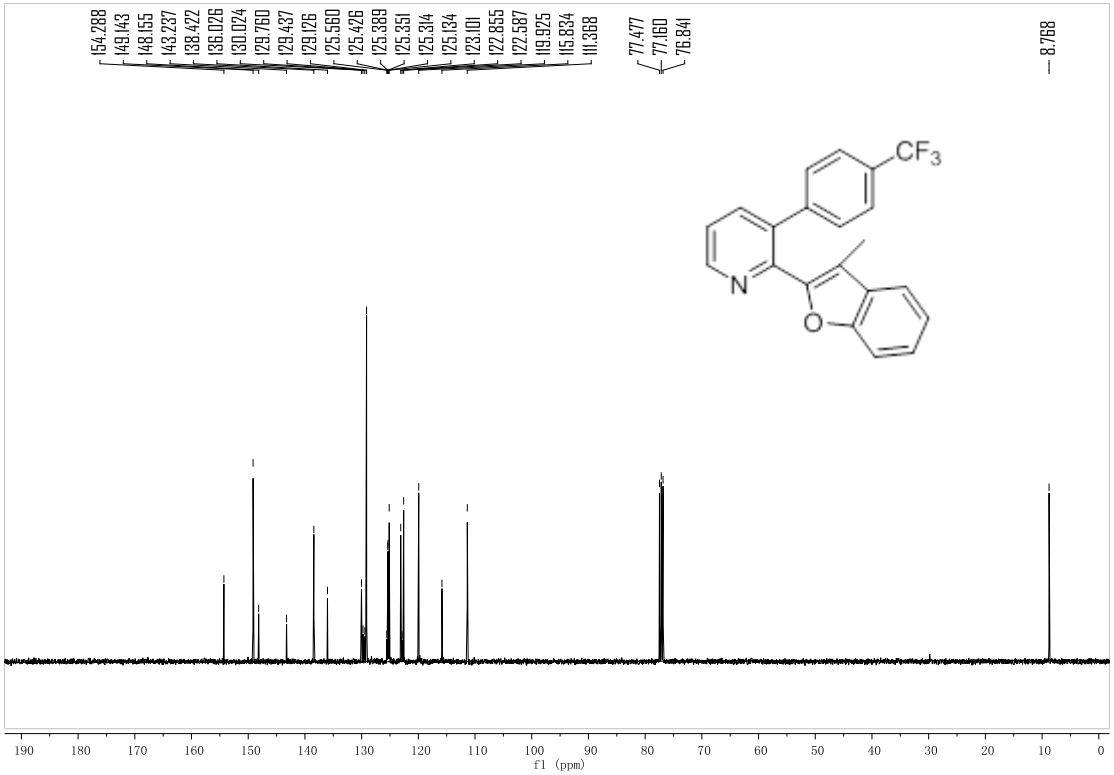


^{13}C NMR spectrum of **1p** ($CDCl_3$, 400 MHz)

1q

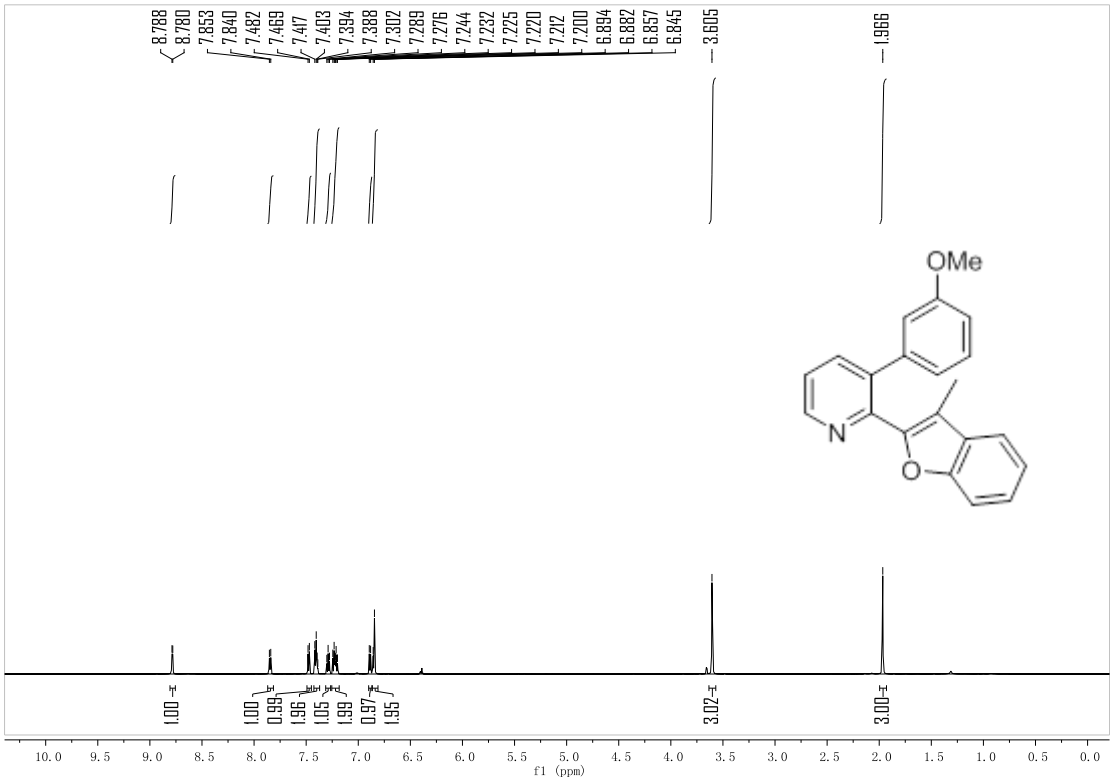


^{1}H NMR spectrum of **1q** ($CDCl_3$, 400 MHz)

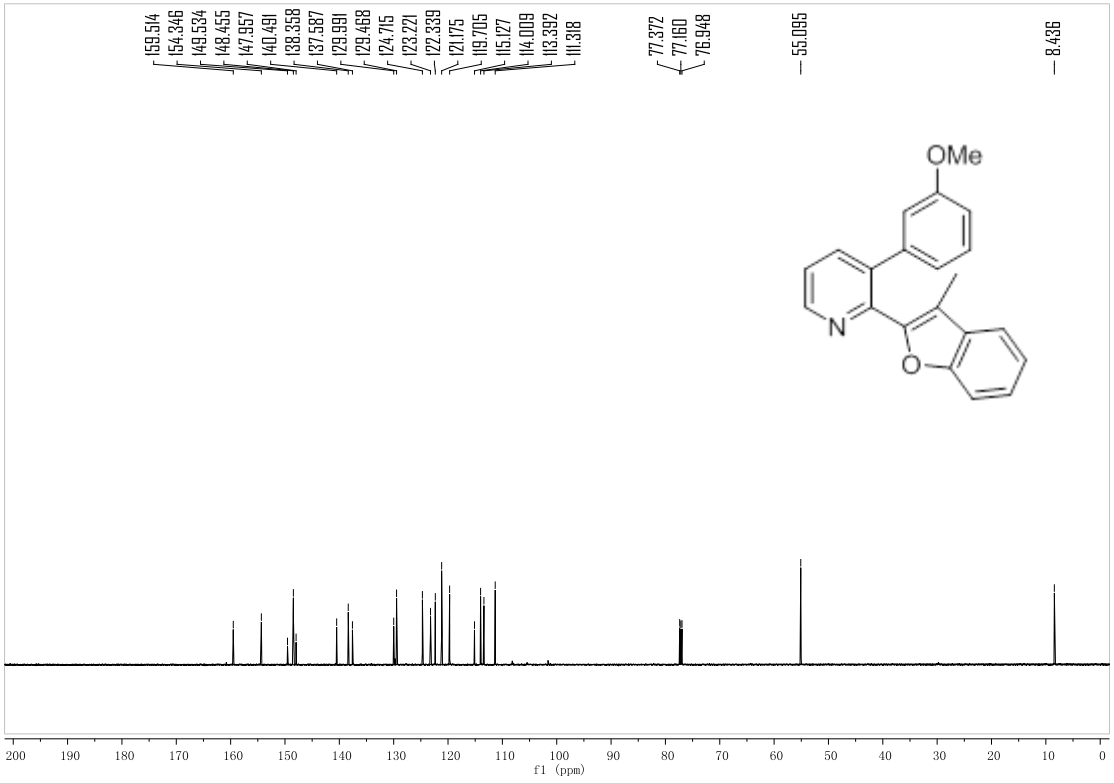


^{13}C NMR spectrum of **1q** ($CDCl_3$, 400 MHz)

1r

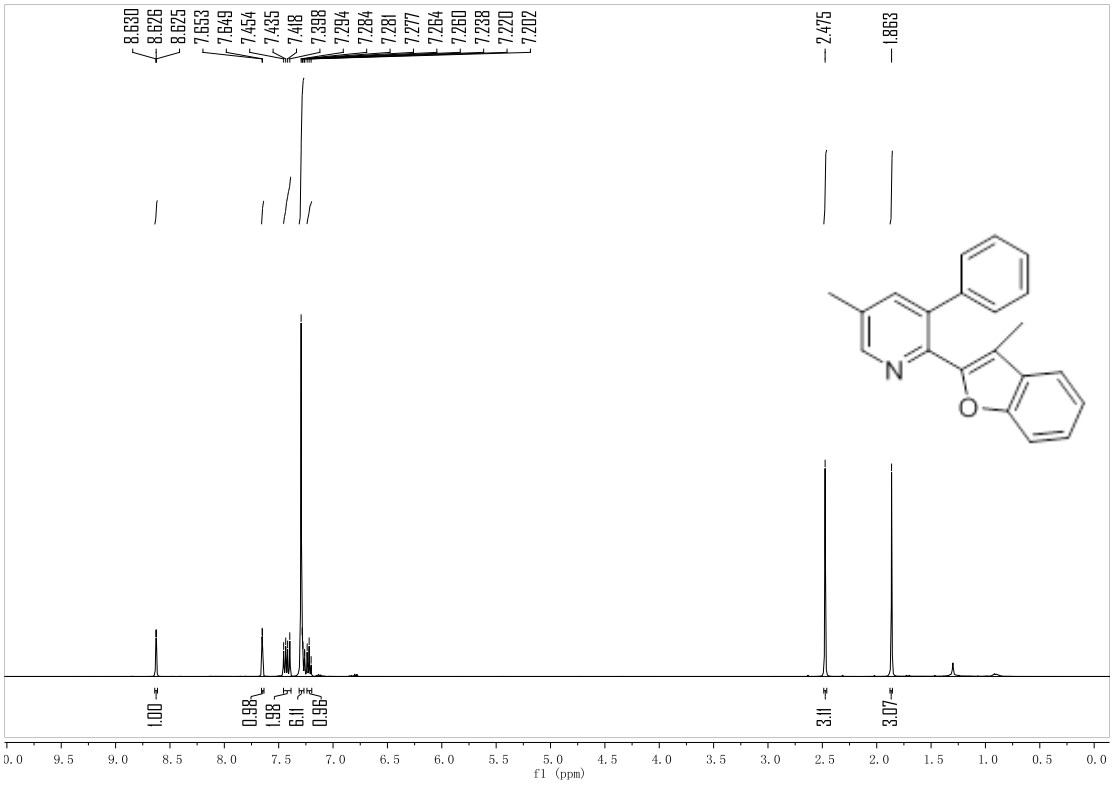


^{1}H NMR spectrum of **1r** ($CDCl_3$, 600 MHz)

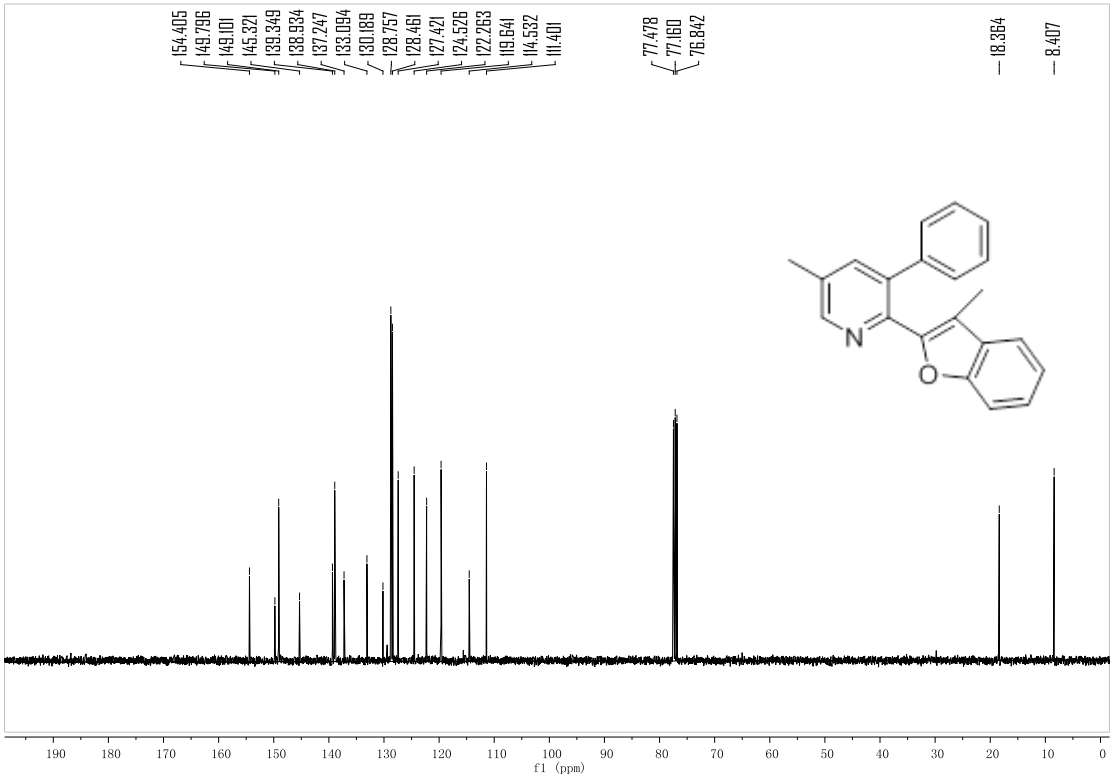


^{13}C NMR spectrum of **1r** ($CDCl_3$, 600 MHz)

1s



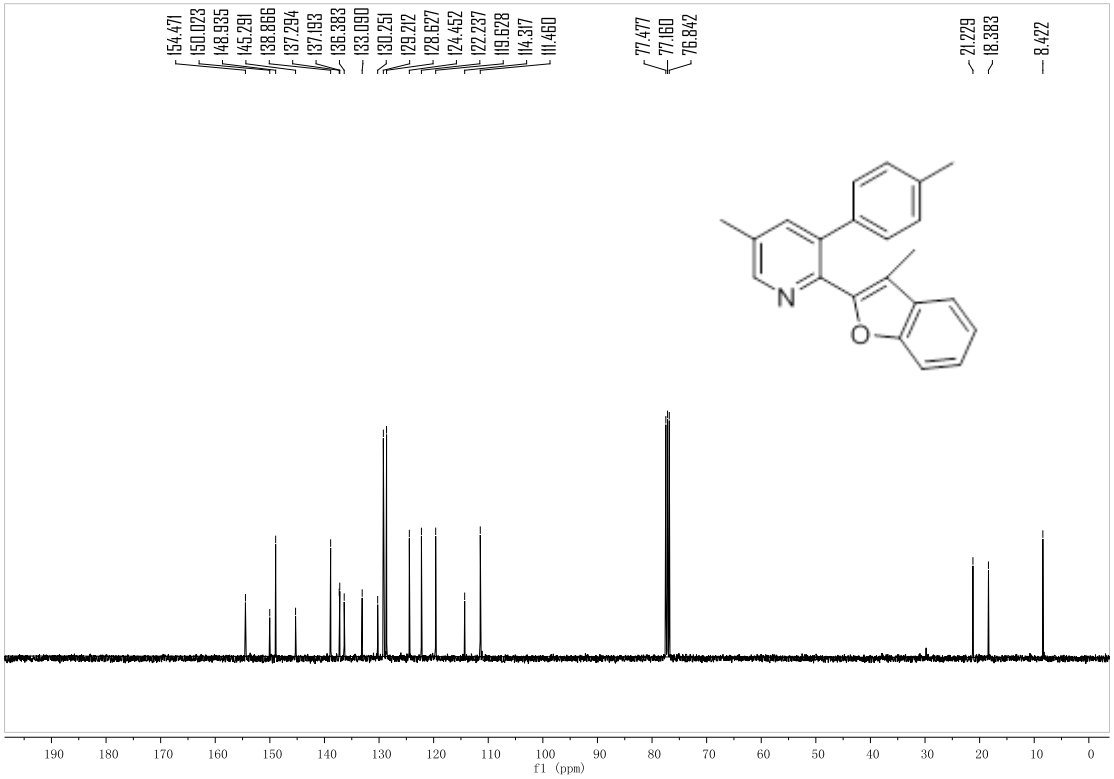
^{1}H NMR spectrum of **1s** ($CDCl_3$, 400 MHz)



^{13}C NMR spectrum of **1s** ($CDCl_3$, 400 MHz)

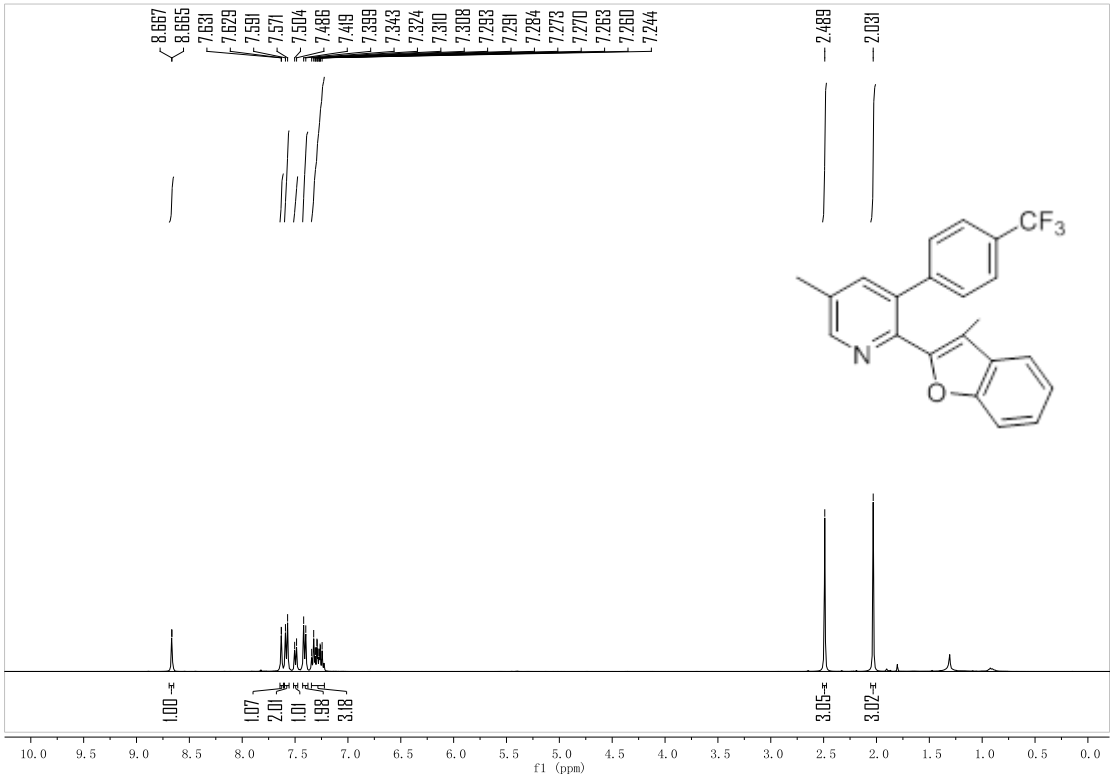
1t

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

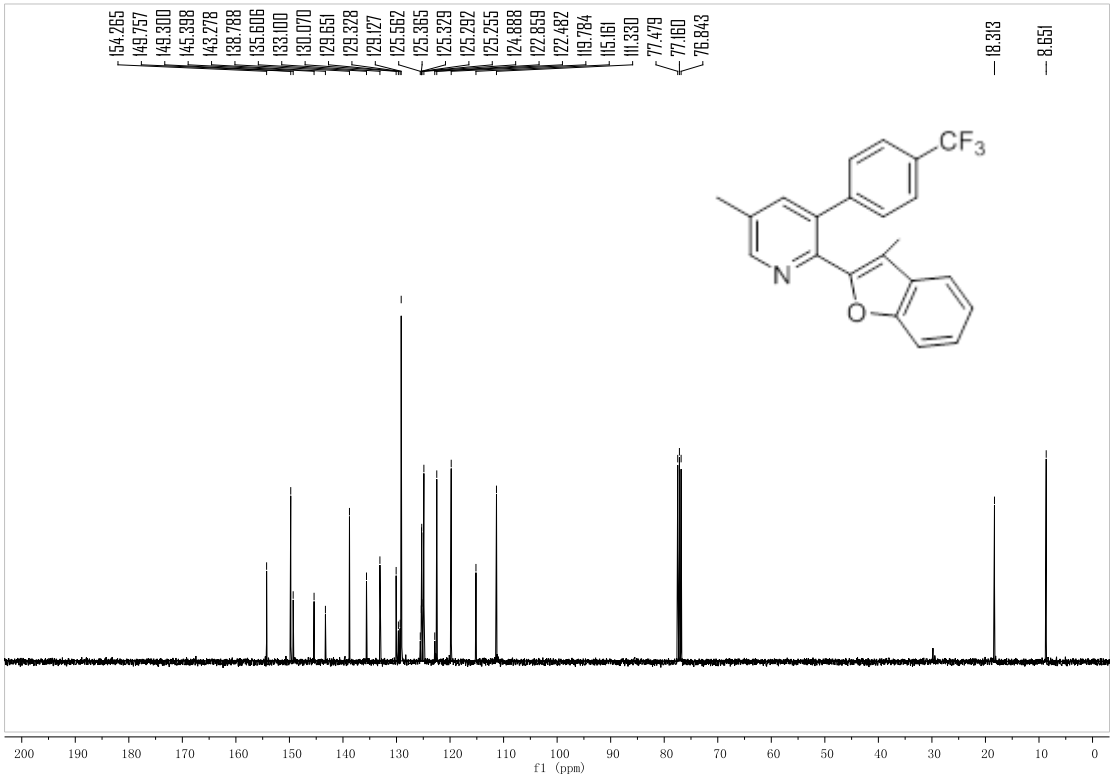


^{13}C NMR spectrum of **1t** ($CDCl_3$, 400 MHz)

1u

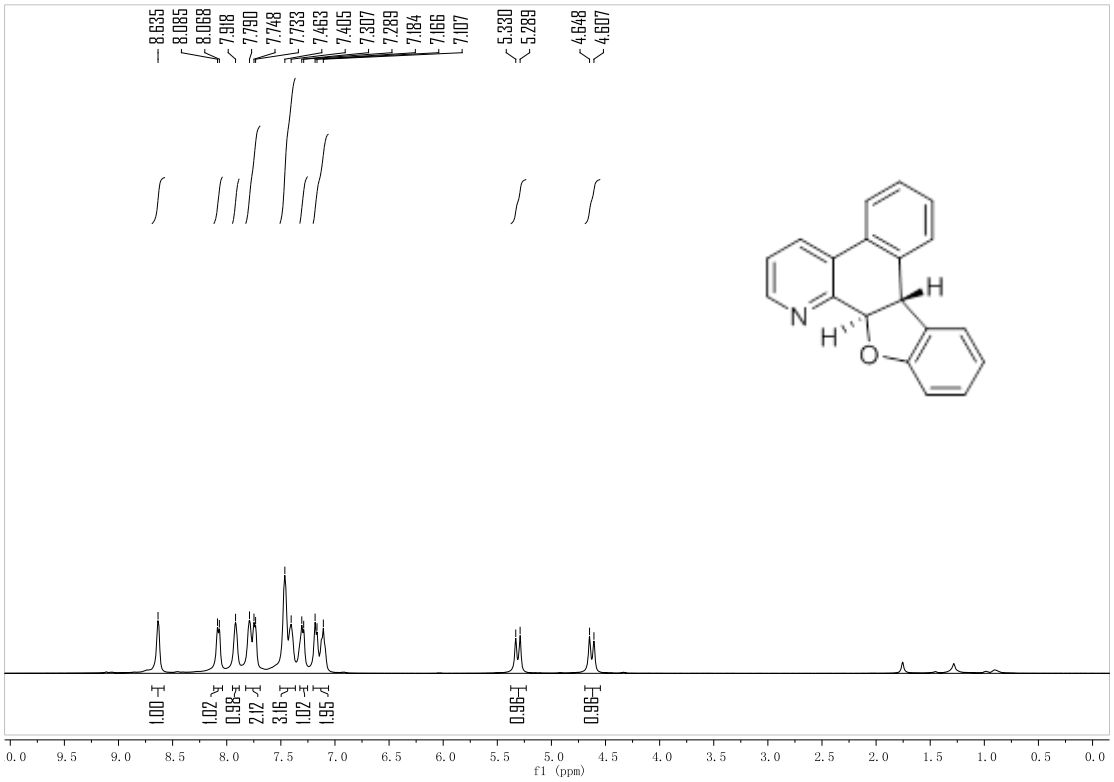


^{1}H NMR spectrum of **1u** ($CDCl_3$, 400 MHz)

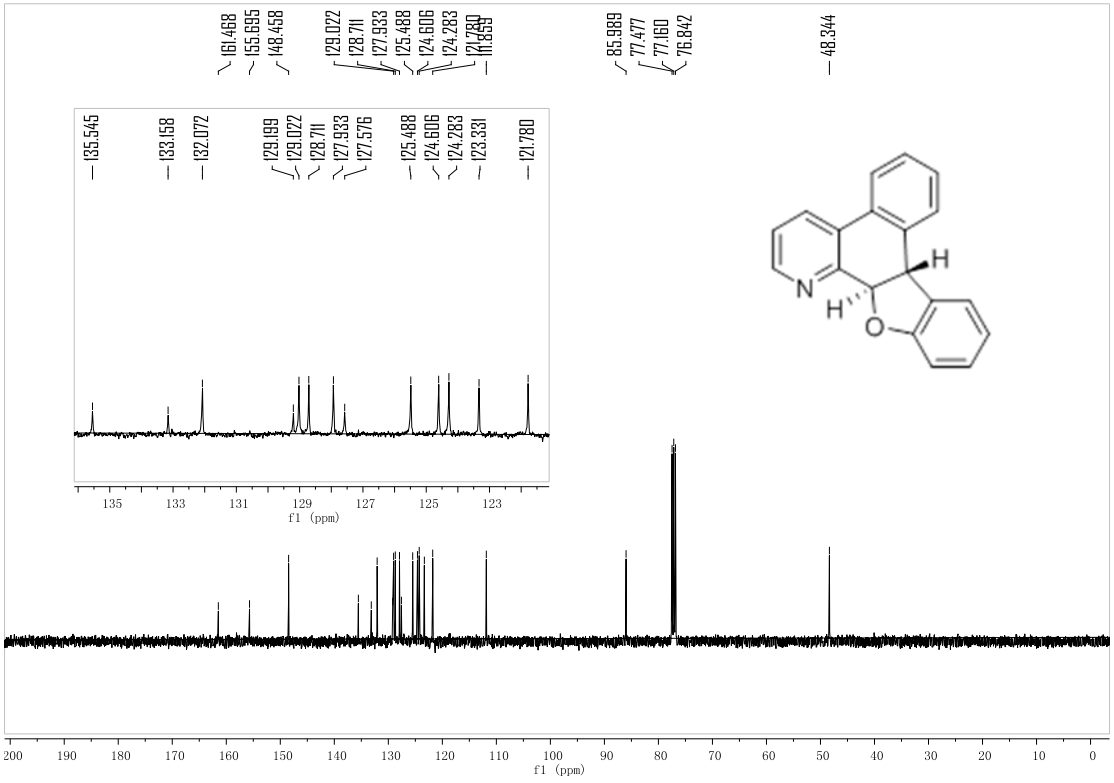


^{13}C NMR spectrum of **1u** ($CDCl_3$, 400 MHz)

2a

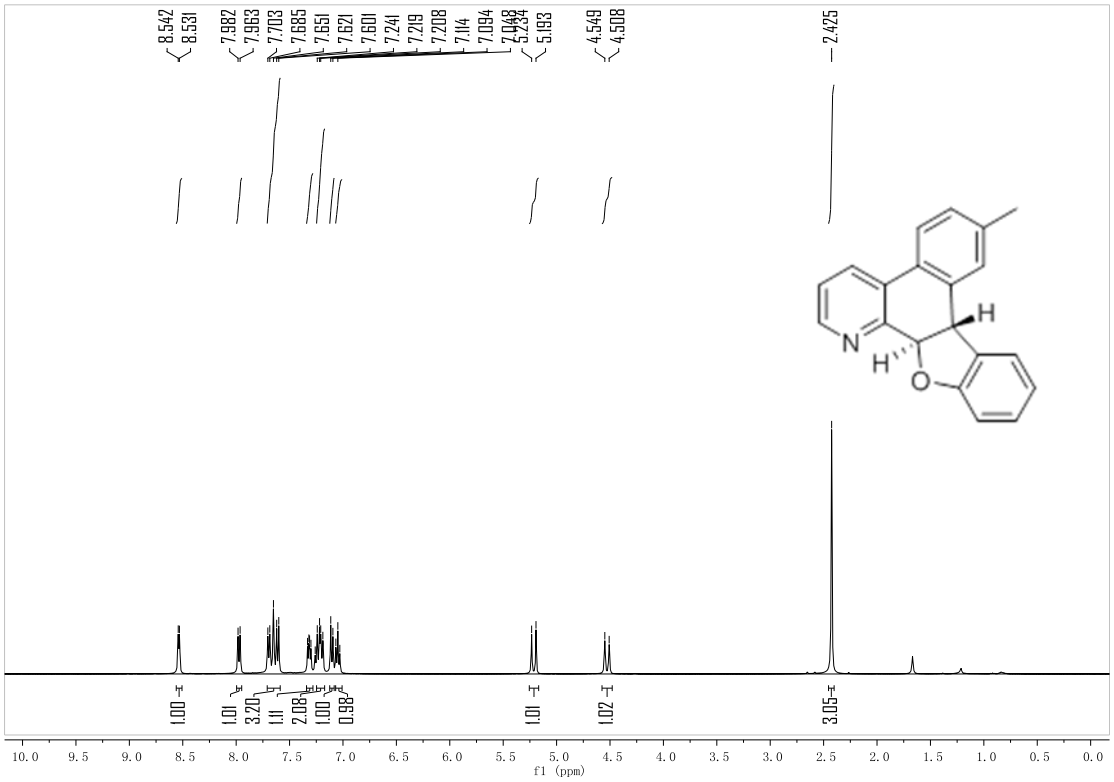


^{1}H NMR spectrum of **2a** ($CDCl_3$, 400 MHz)

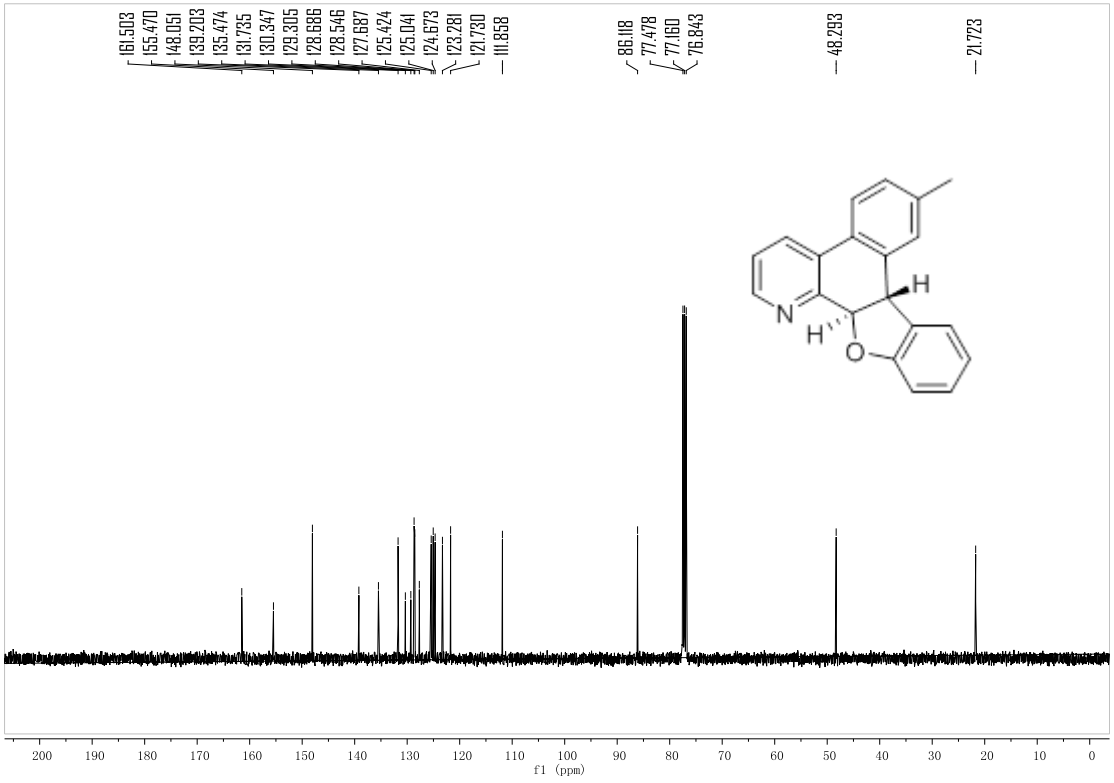


^{13}C NMR spectrum of **2a** ($CDCl_3$, 400 MHz)

2b

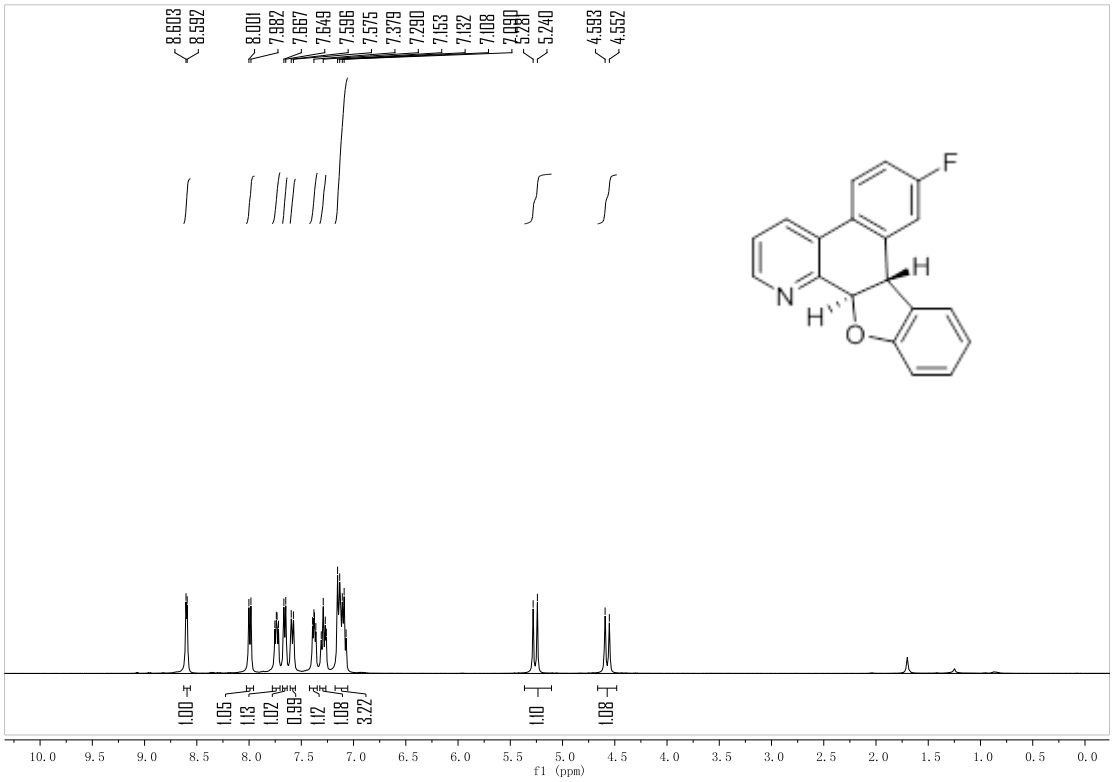


^{1}H NMR spectrum of **2b** ($CDCl_3$, 400 MHz)

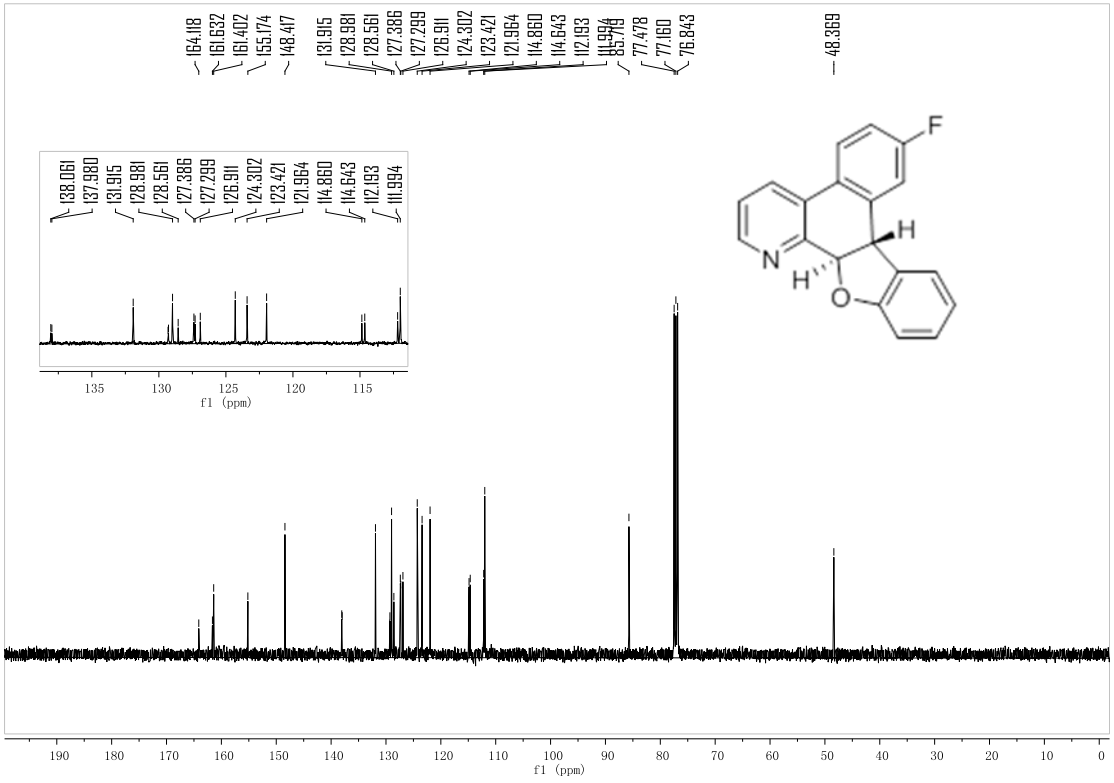


^{13}C NMR spectrum of **2b** ($CDCl_3$, 400 MHz)

2c

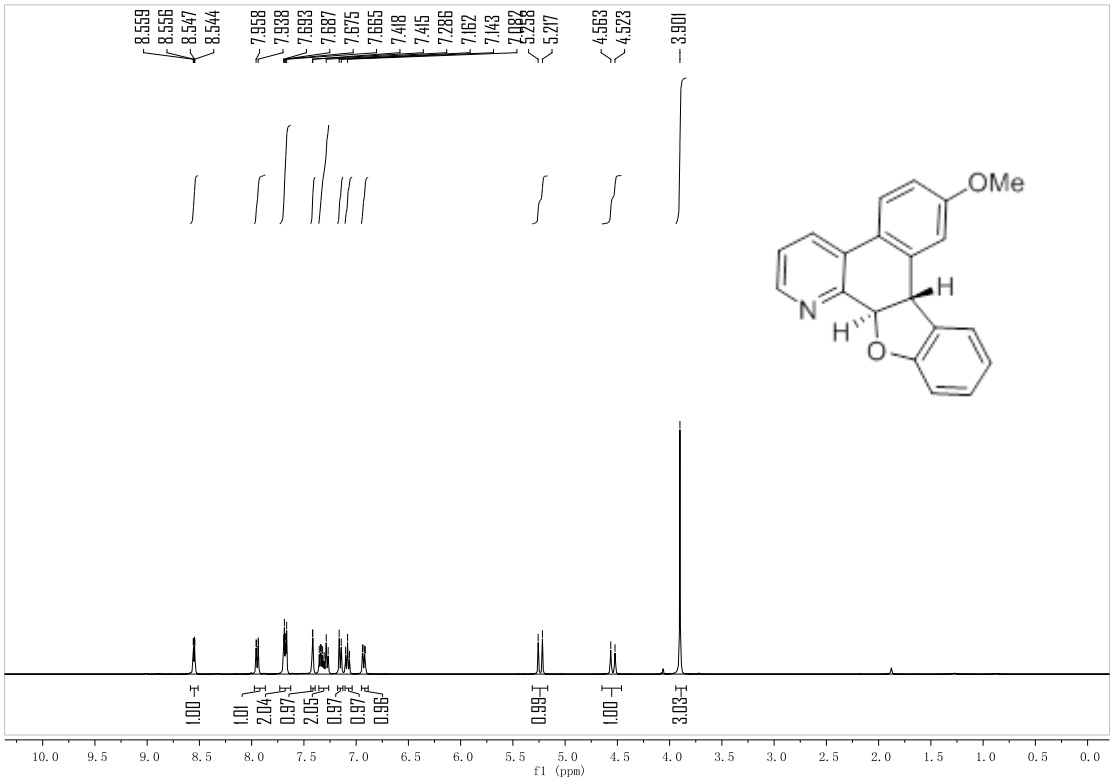


^{1}H NMR spectrum of **2c** ($CDCl_3$, 400 MHz)

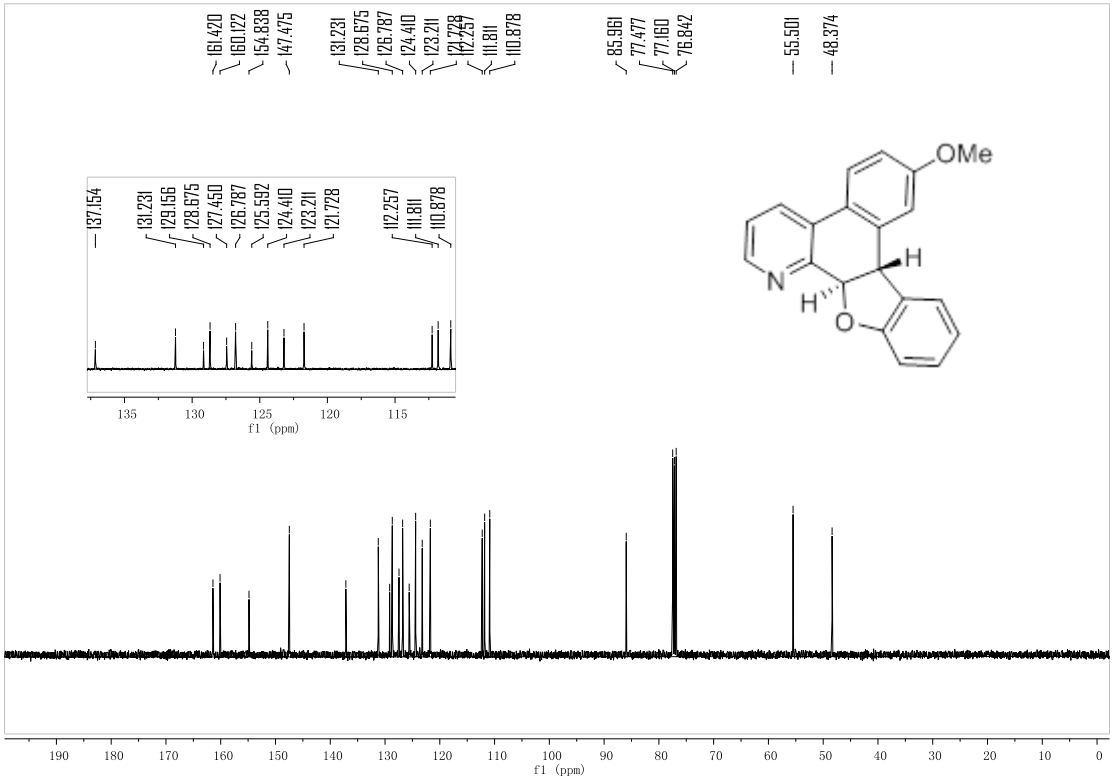


^{13}C NMR spectrum of **2c** ($CDCl_3$, 400 MHz)

2d

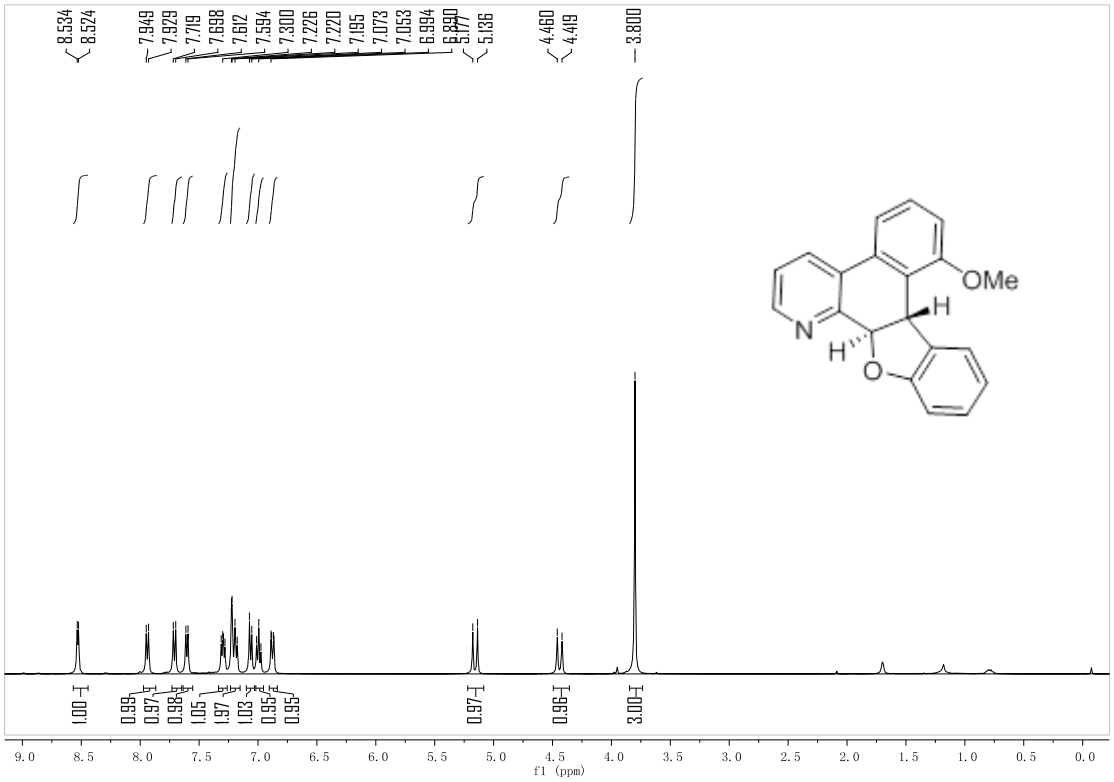


^{1}H NMR spectrum of **2d** ($CDCl_3$, 400 MHz)

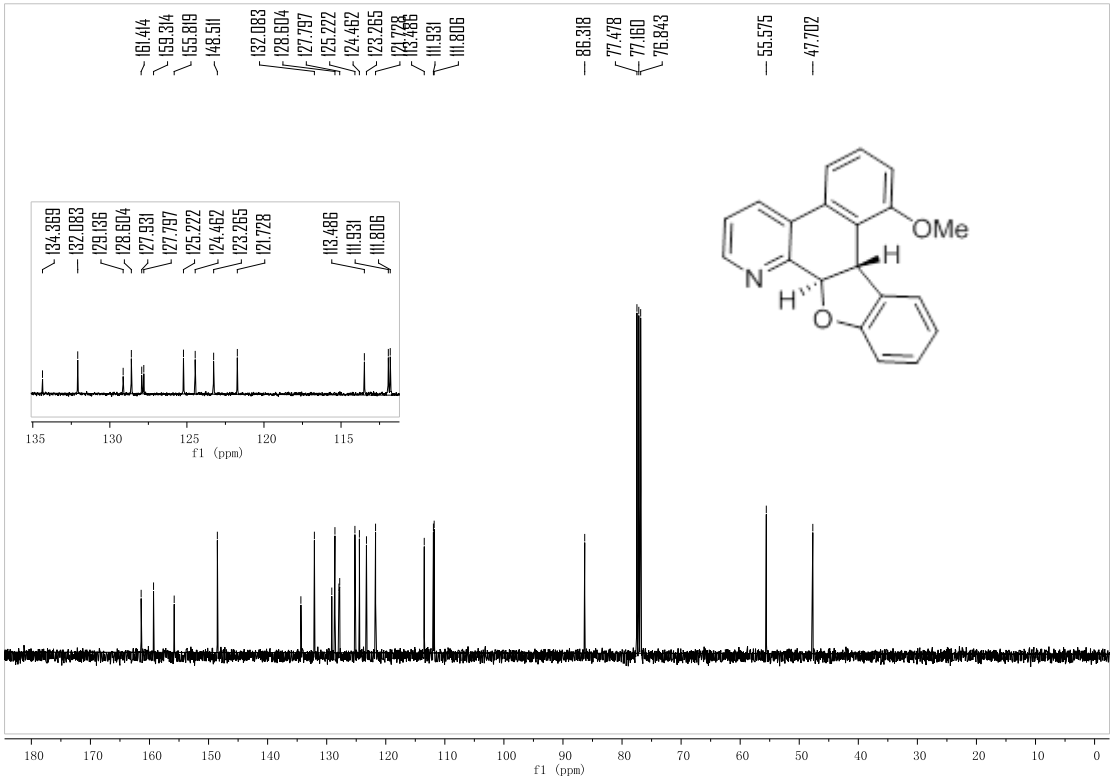


^{13}C NMR spectrum of **2d** ($CDCl_3$, 400 MHz)

2e

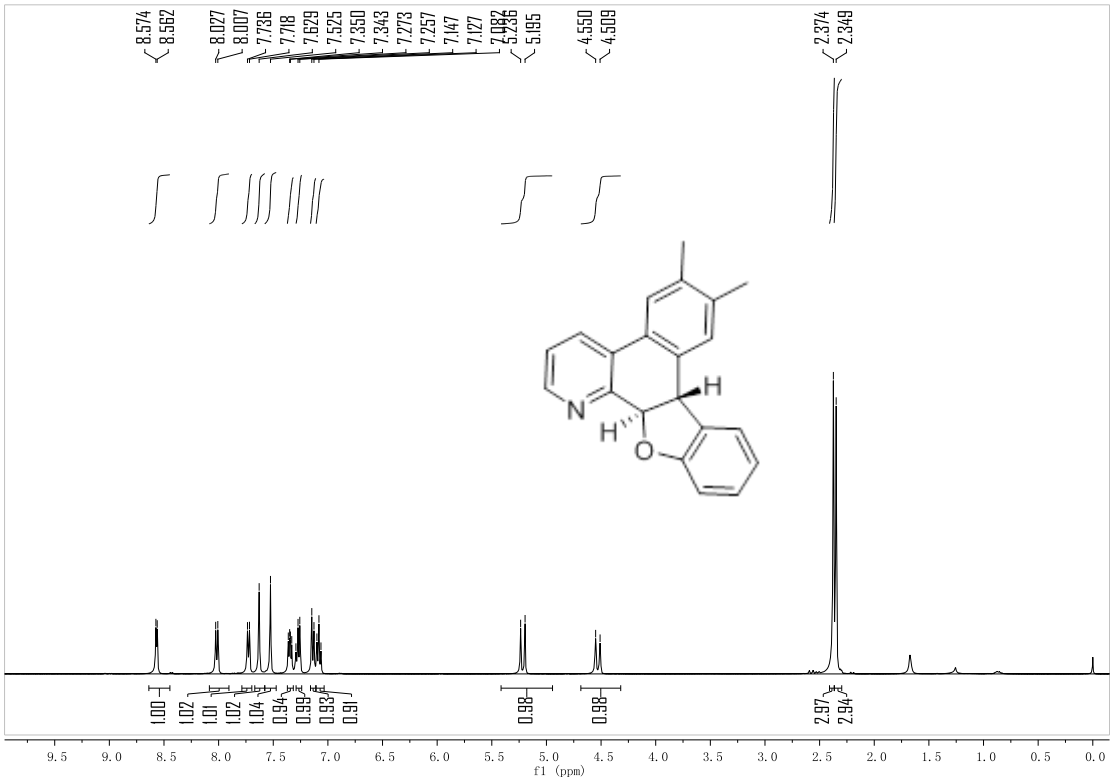


^{1}H NMR spectrum of **2e** ($CDCl_3$, 400 MHz)

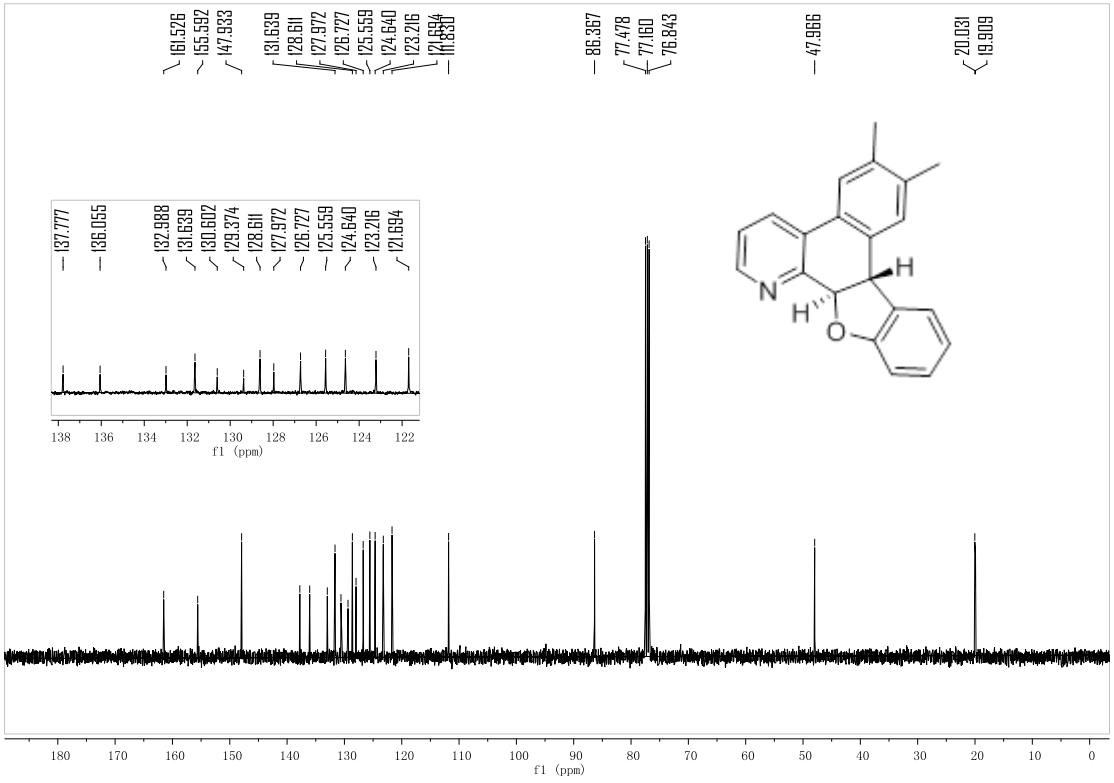


^{13}C NMR spectrum of **2e** ($CDCl_3$, 400 MHz)

2f

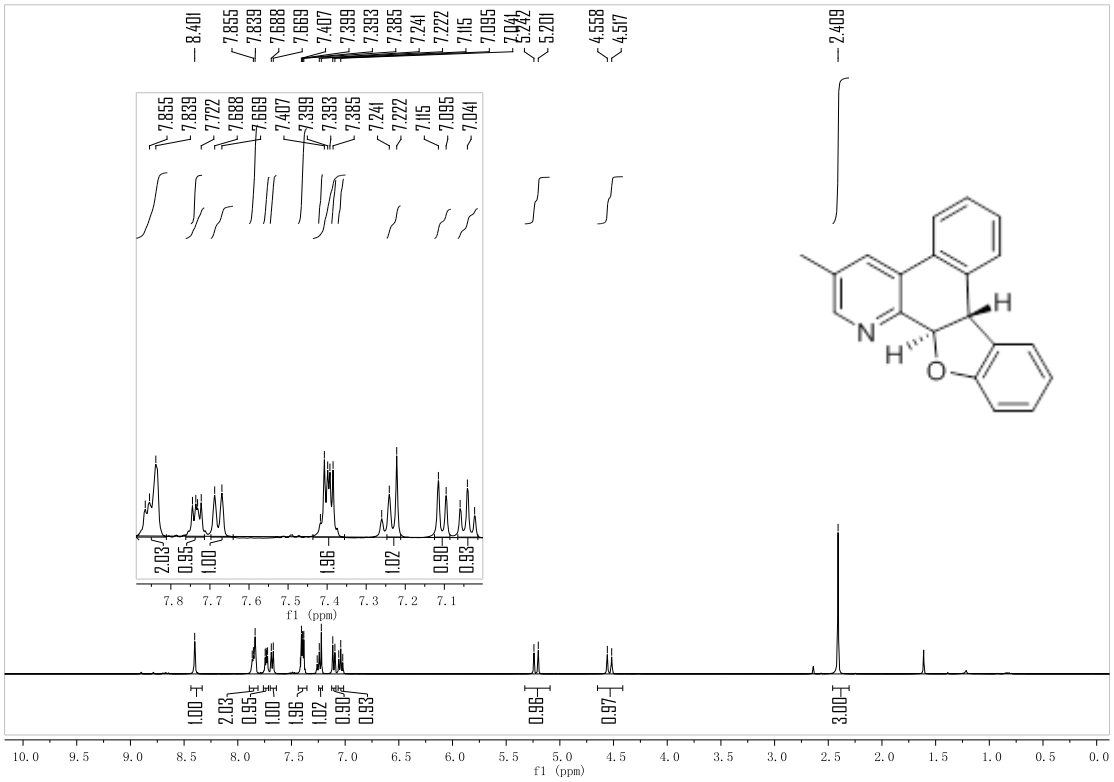


^{1}H NMR spectrum of **2f** ($CDCl_3$, 400 MHz)

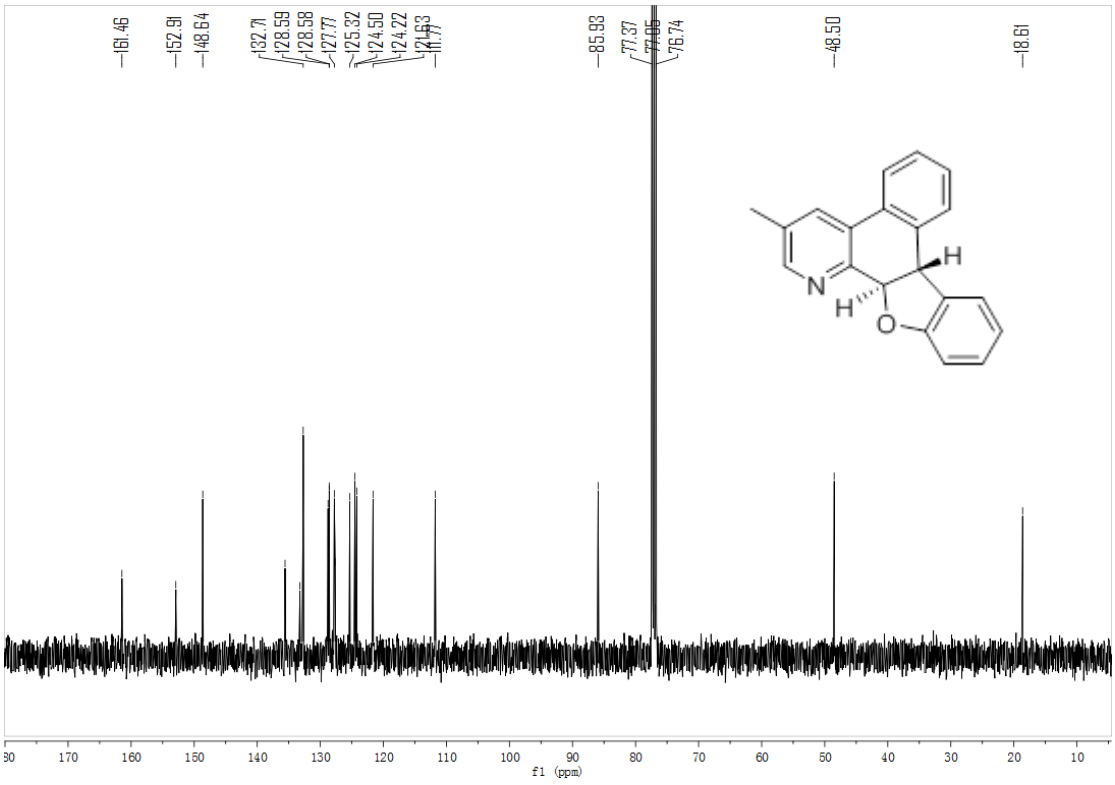


^{13}C NMR spectrum of **2f** ($CDCl_3$, 400 MHz)

2g

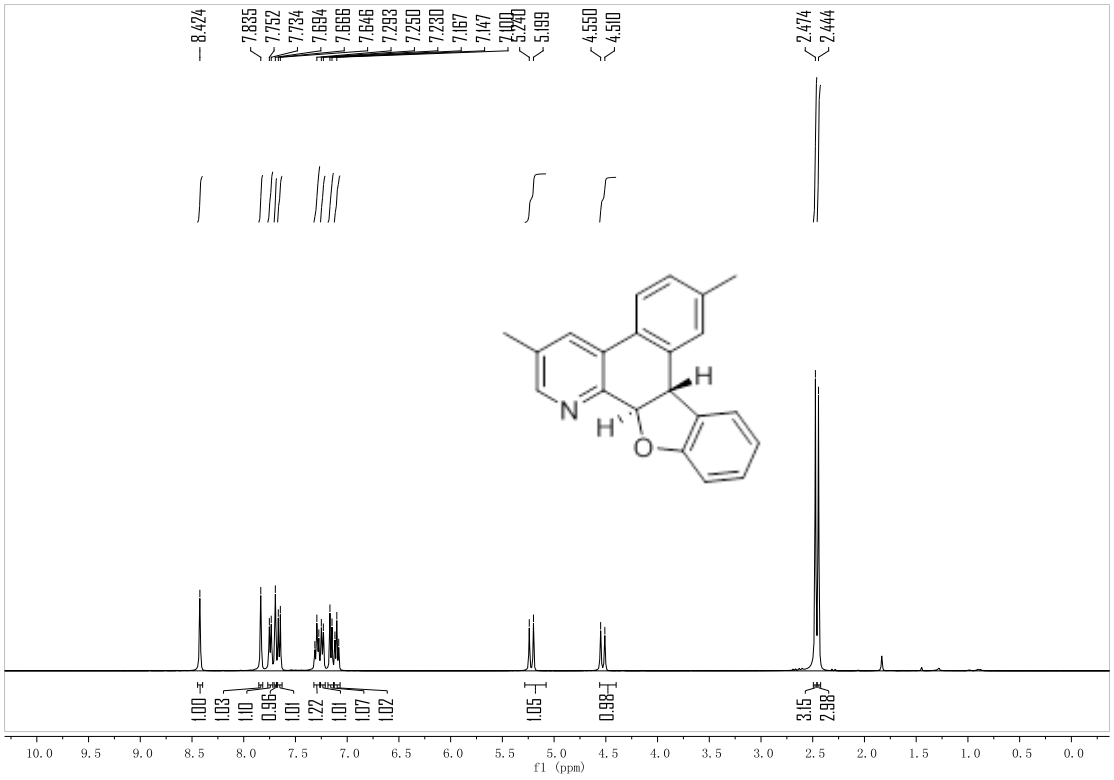


^{1}H NMR spectrum of **2g** ($CDCl_3$, 400 MHz)

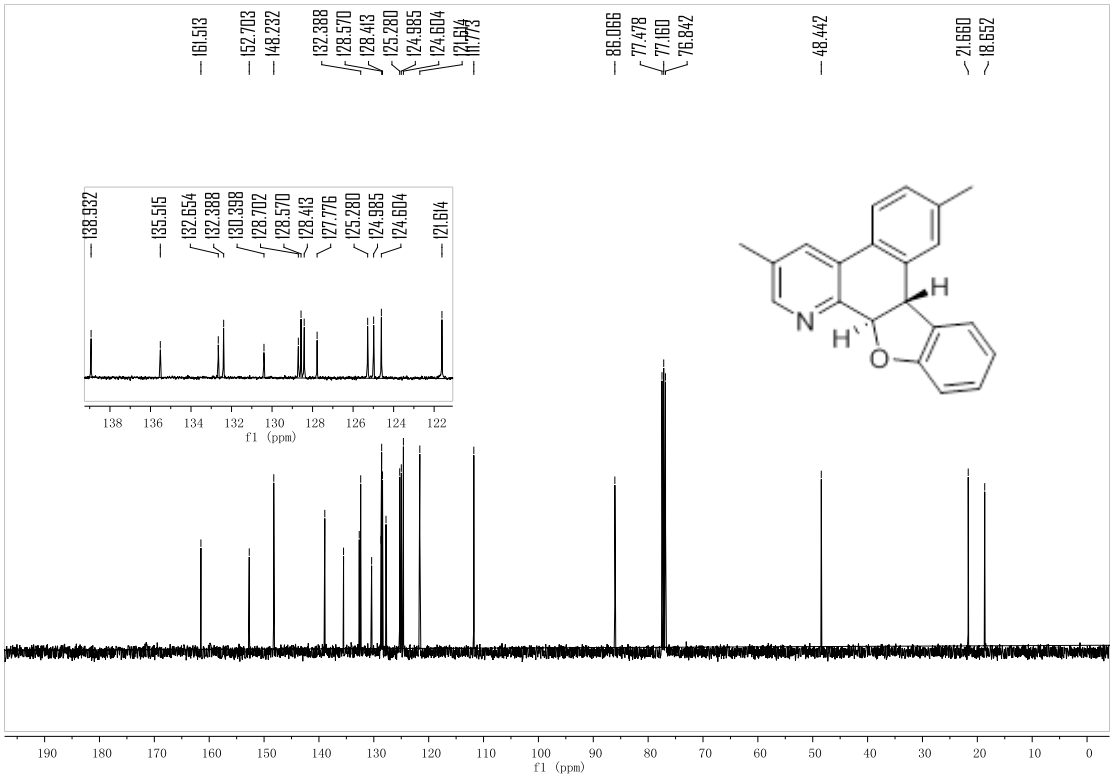


^{13}C NMR spectrum of **2g** ($CDCl_3$, 400 MHz)

2h

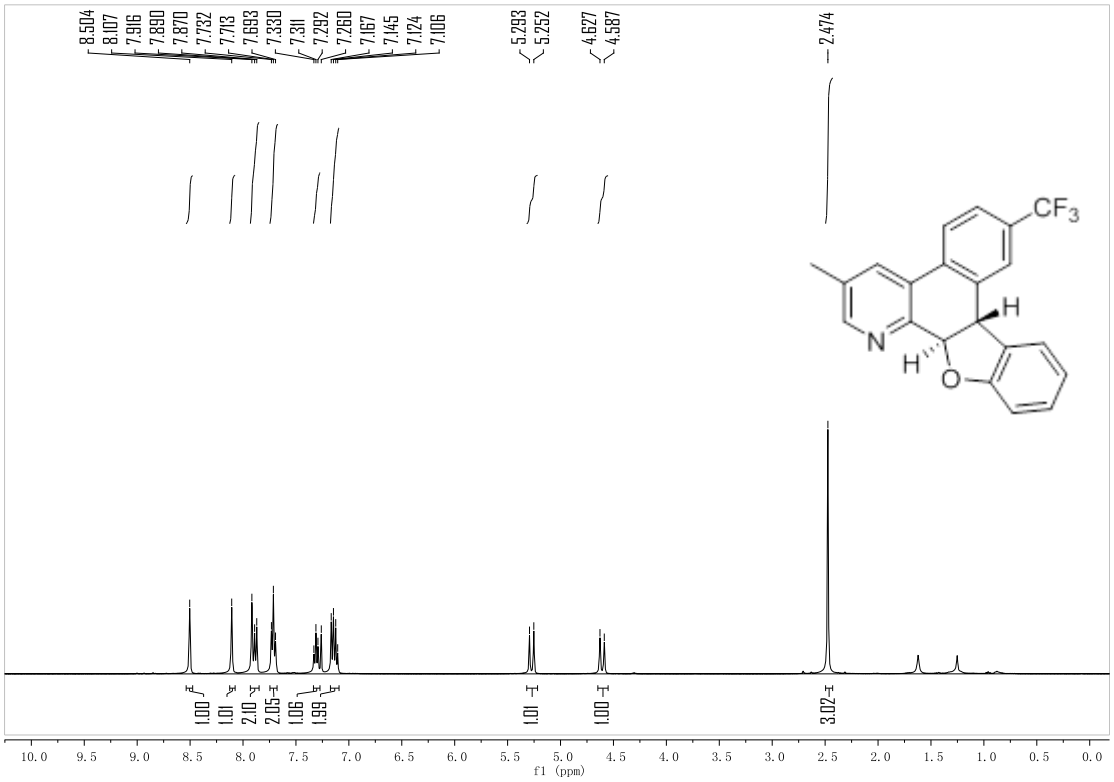


^{1}H NMR spectrum of **2h** ($CDCl_3$, 400 MHz)

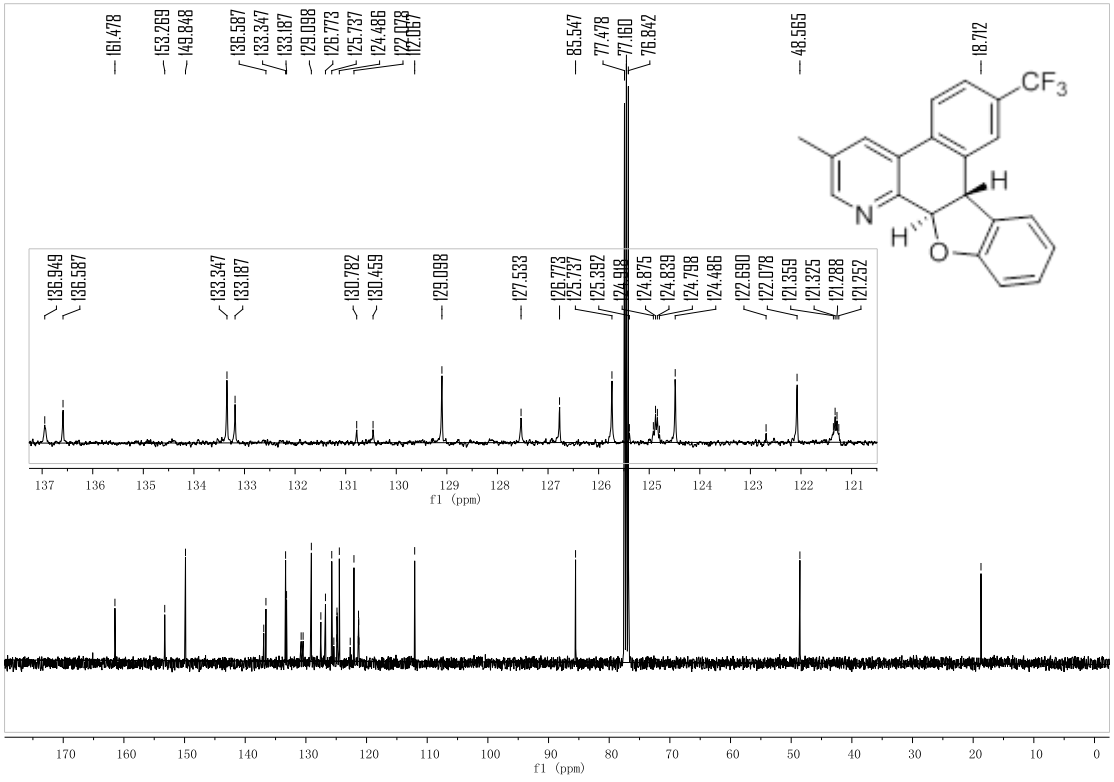


^{13}C NMR spectrum of **2h** ($CDCl_3$, 400 MHz)

2i

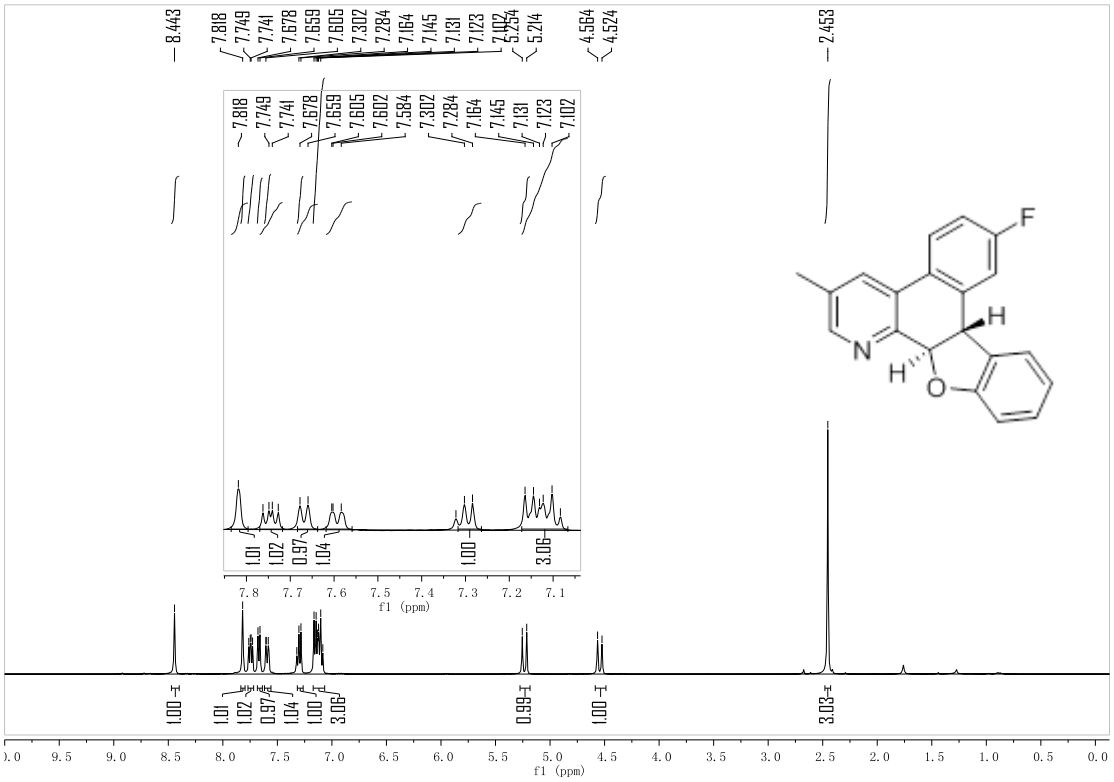


^{1}H NMR spectrum of **2i** ($CDCl_3$, 400 MHz)

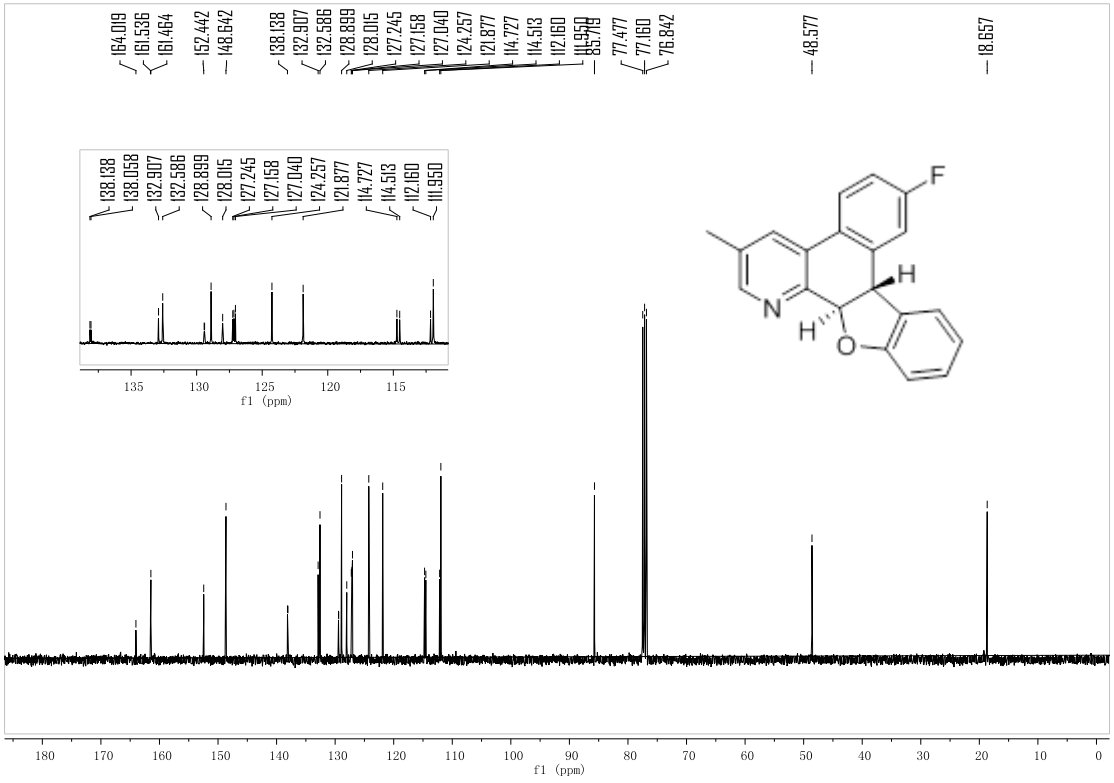


^{13}C NMR spectrum of **2i** ($CDCl_3$, 400 MHz)

2j

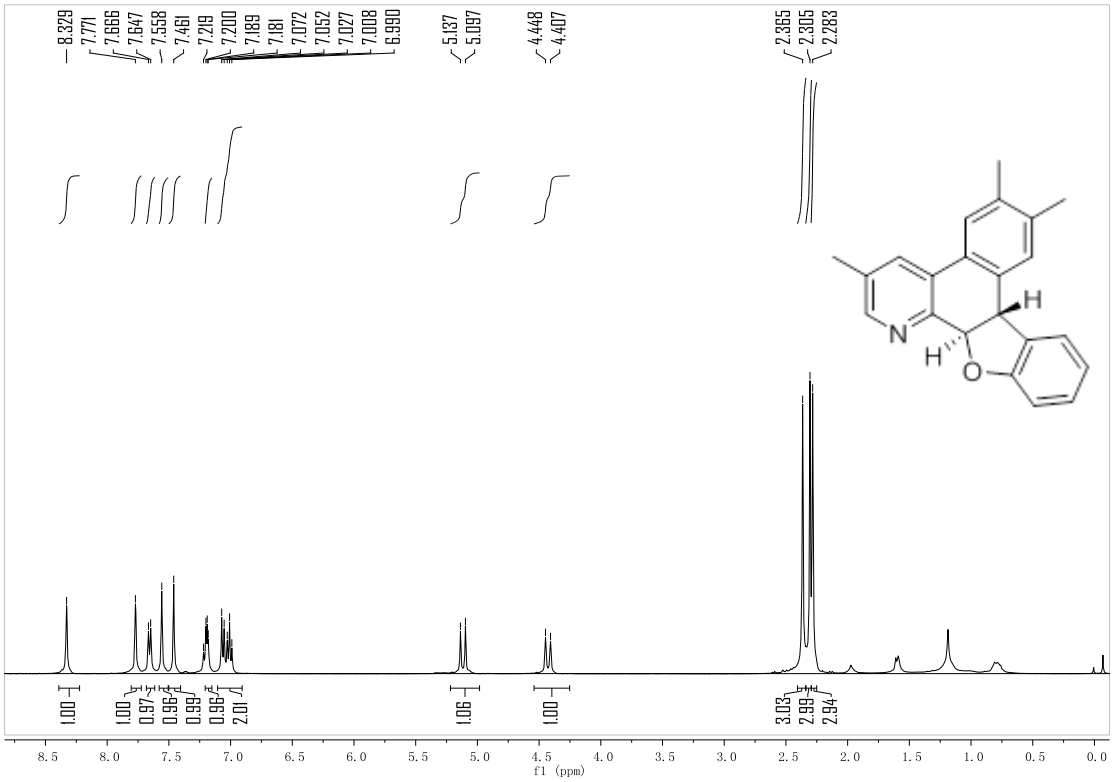


^{1}H NMR spectrum of **2j** ($CDCl_3$, 400 MHz)

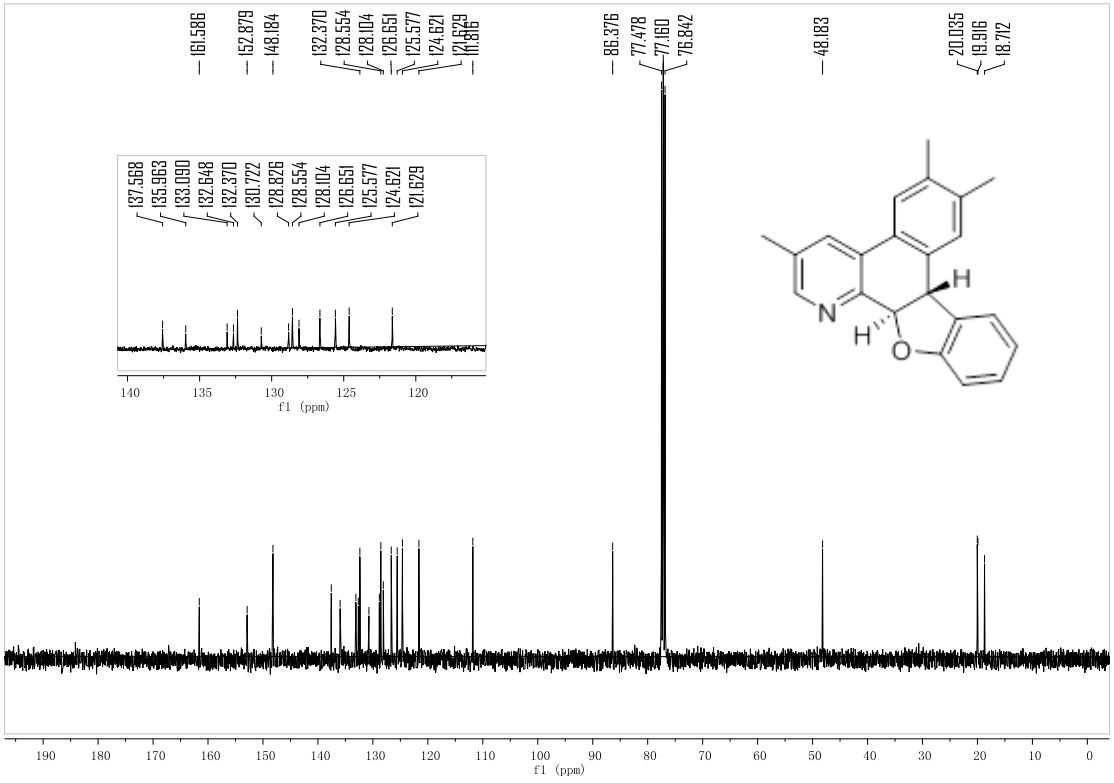


^{13}C NMR spectrum of **2j** ($CDCl_3$, 400 MHz)

2k

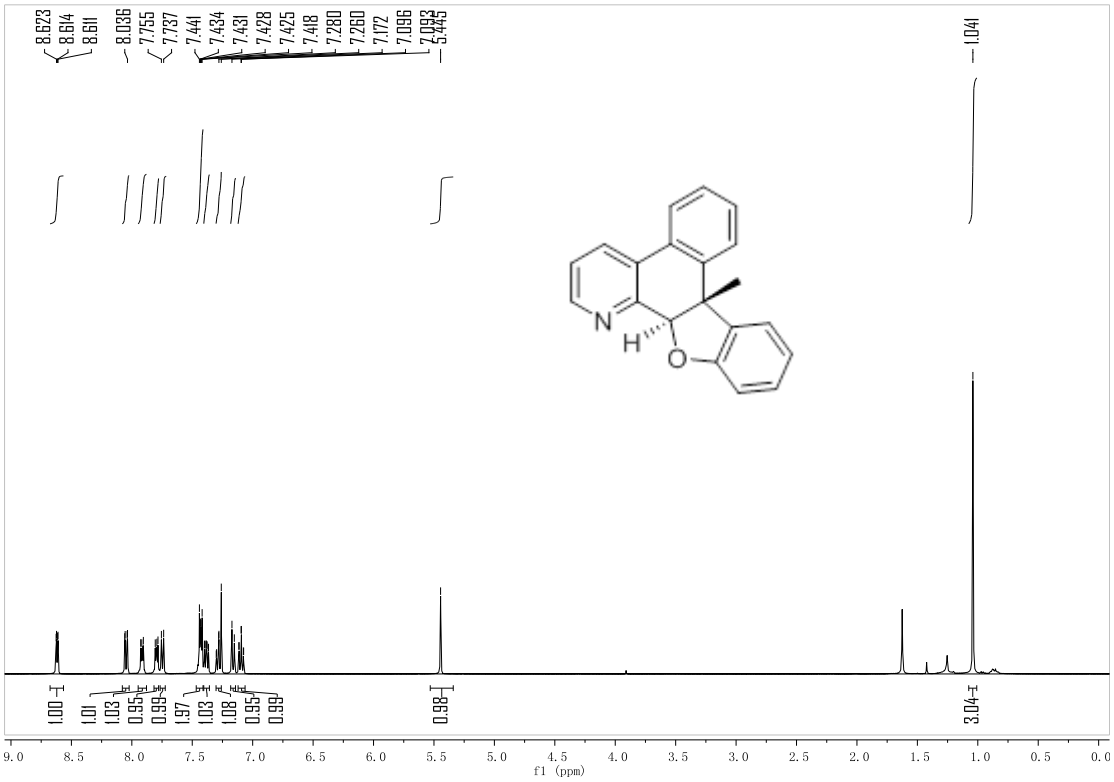


^{1}H NMR spectrum of **2k** ($CDCl_3$, 400 MHz)

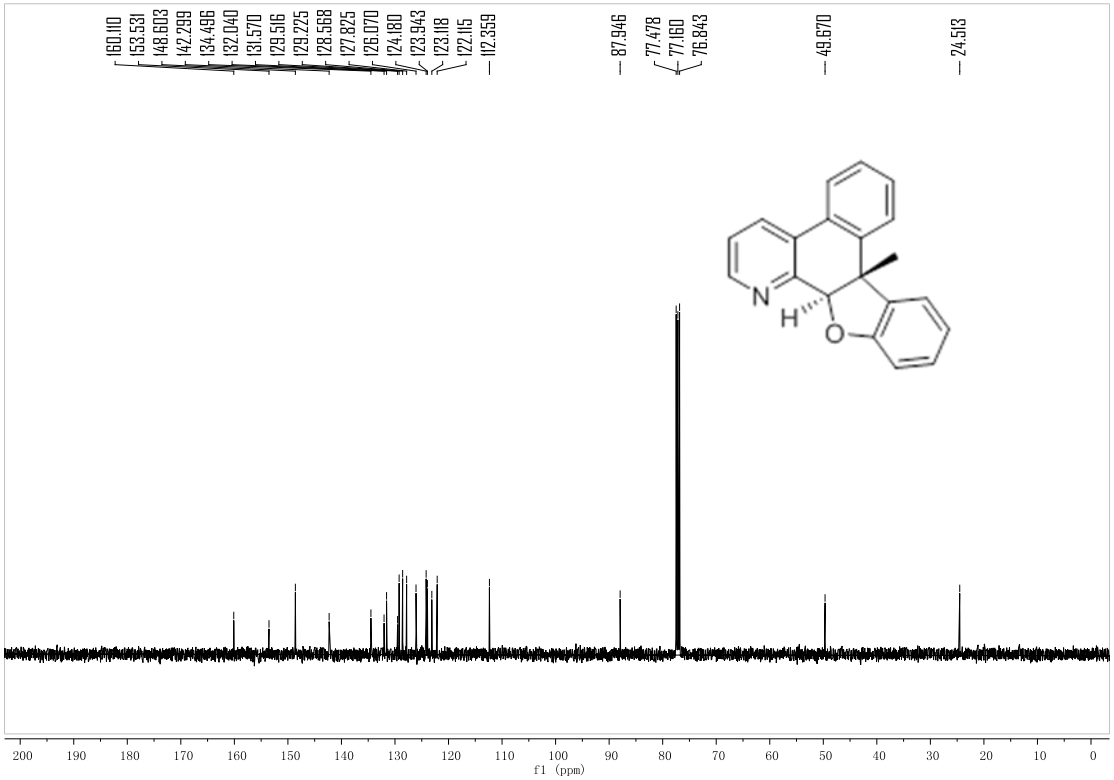


^{13}C NMR spectrum of **2k** ($CDCl_3$, 400 MHz)

2l

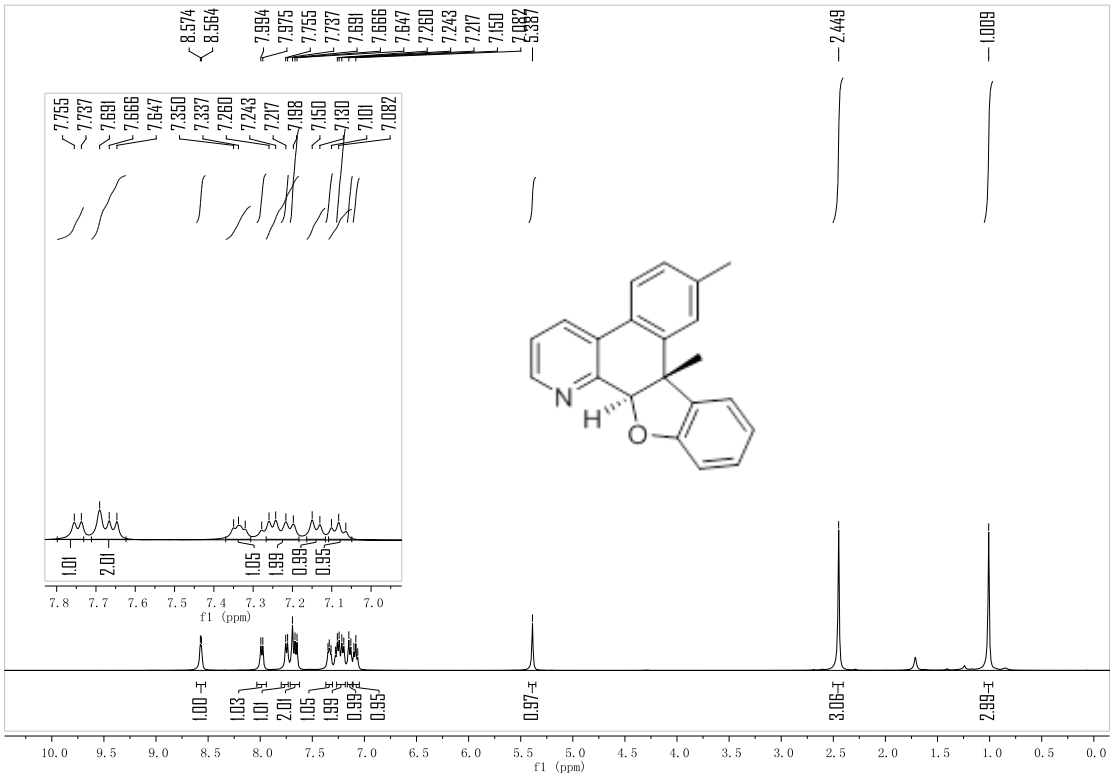


^{1}H NMR spectrum of **2l** ($CDCl_3$, 400 MHz)

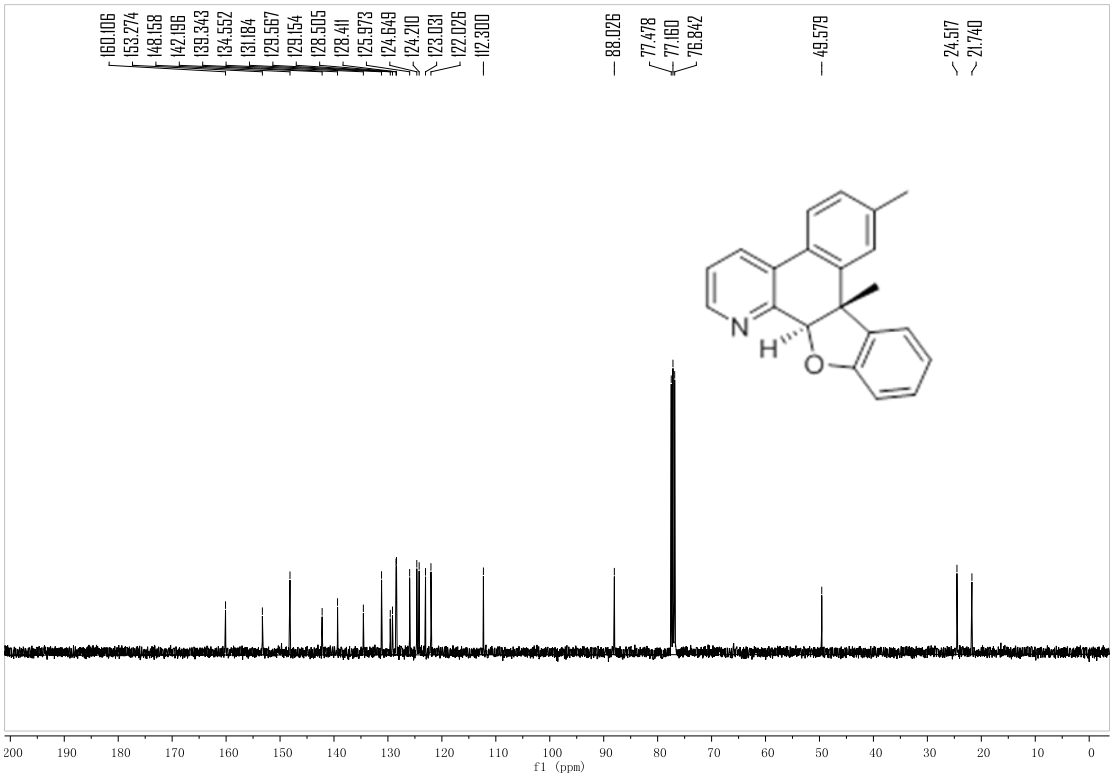


^{13}C NMR spectrum of **2l** ($CDCl_3$, 400 MHz)

2m

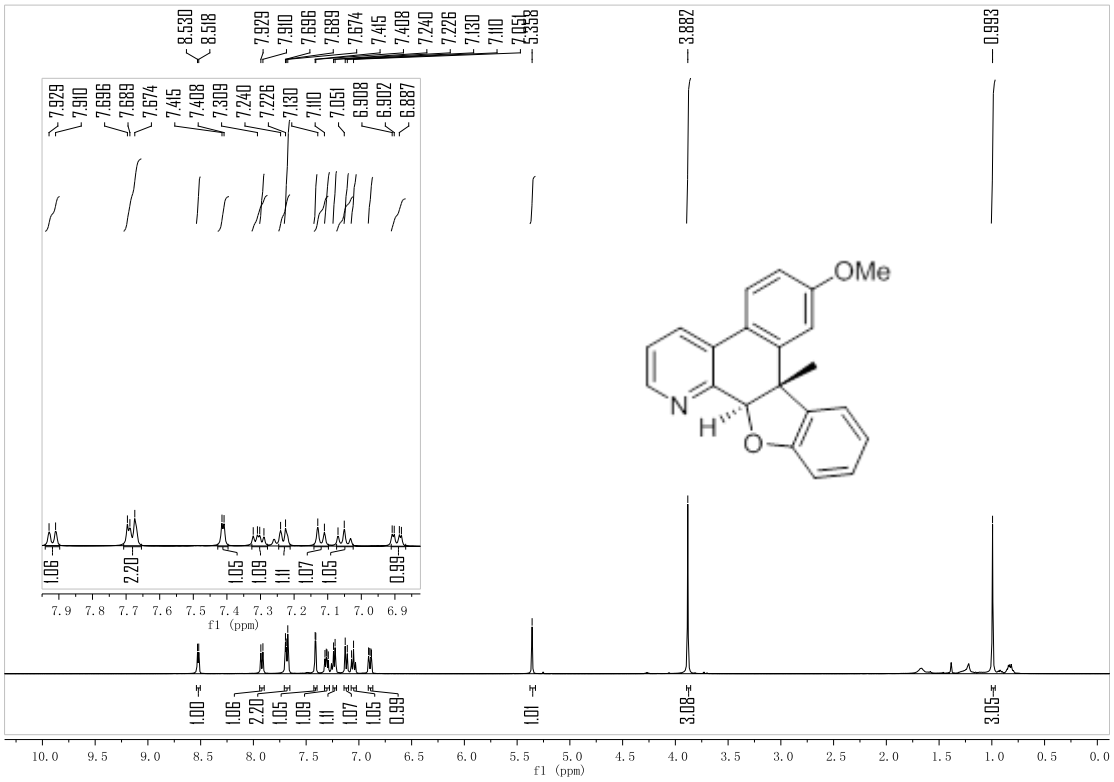


^{1}H NMR spectrum of **2m** ($CDCl_3$, 400 MHz)

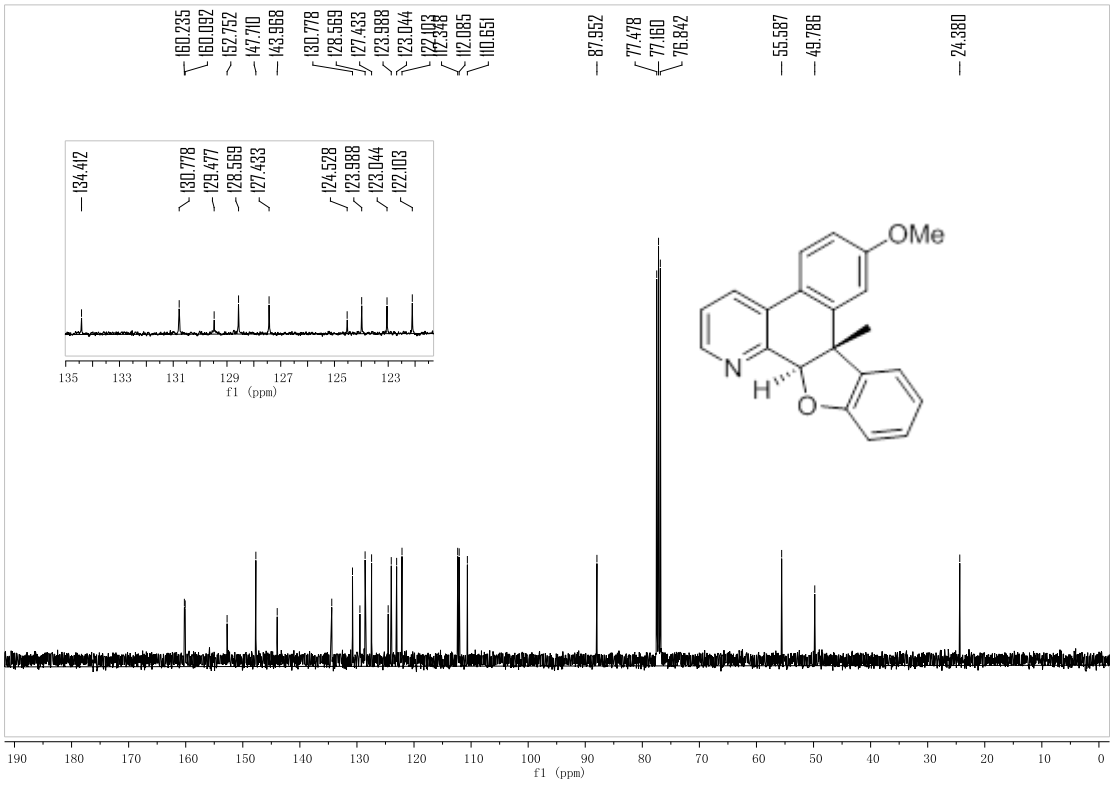


^{13}C NMR spectrum of **2m** ($CDCl_3$, 400 MHz)

2n



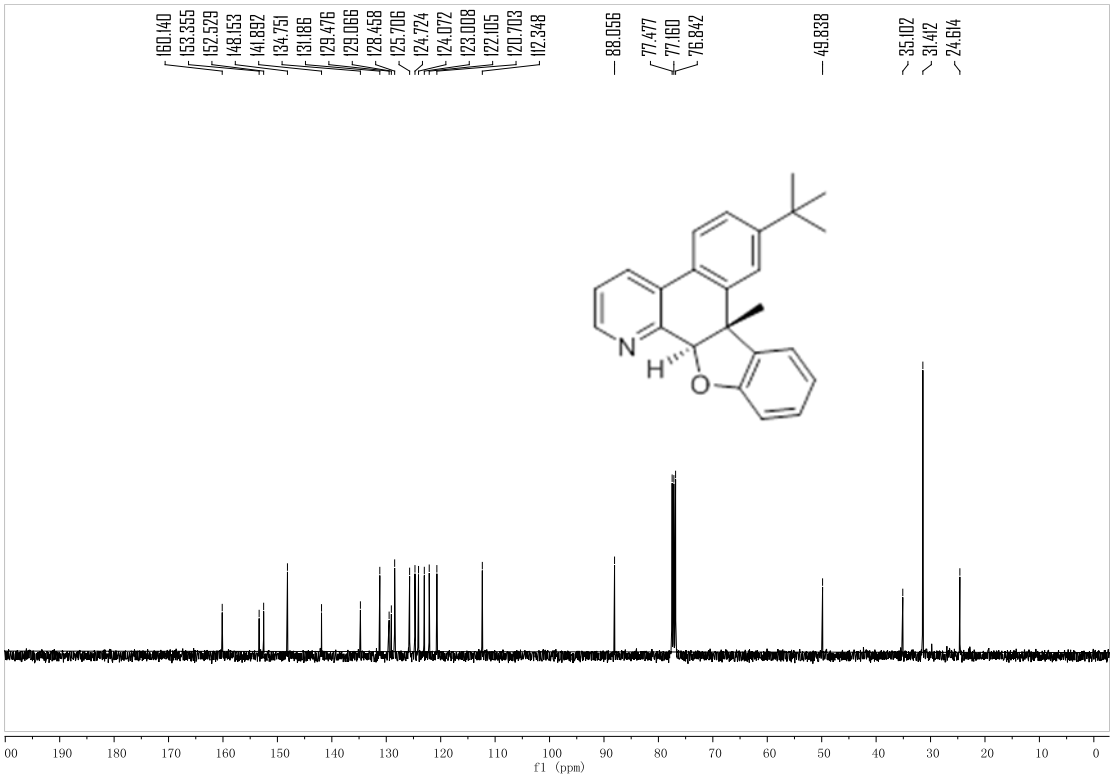
^{1}H NMR spectrum of **2n** ($CDCl_3$, 400 MHz)



^{13}C NMR spectrum of **2n** ($CDCl_3$, 400 MHz)

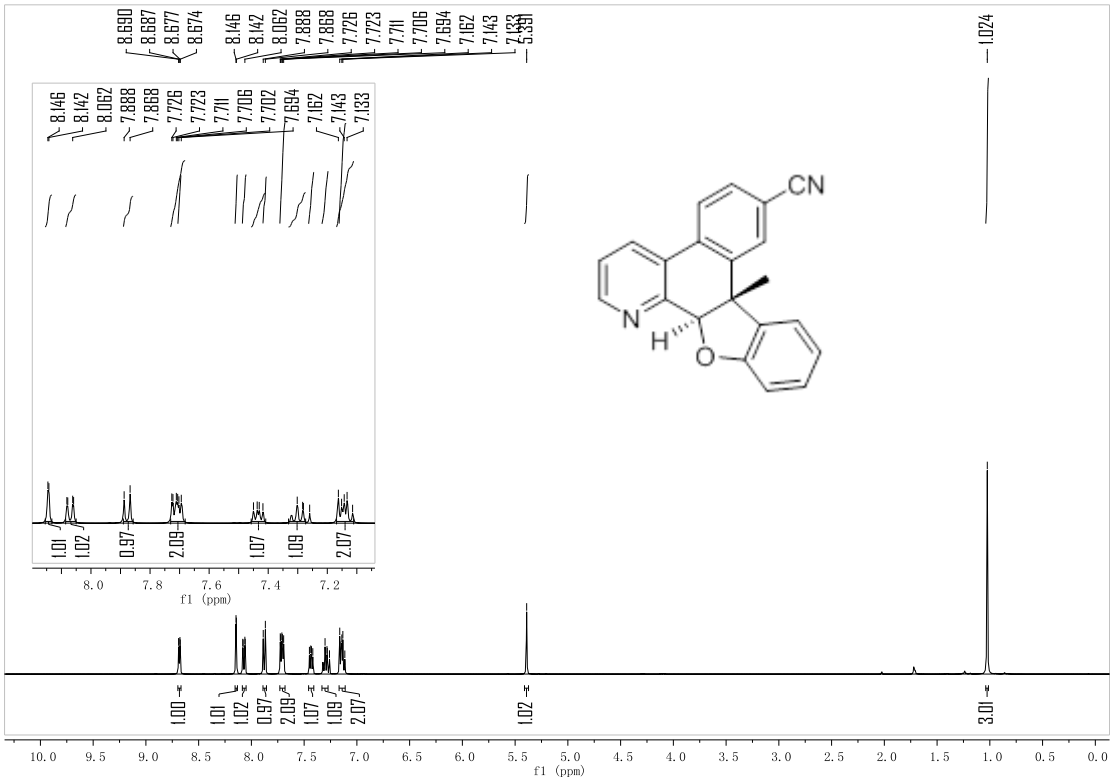
2o

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

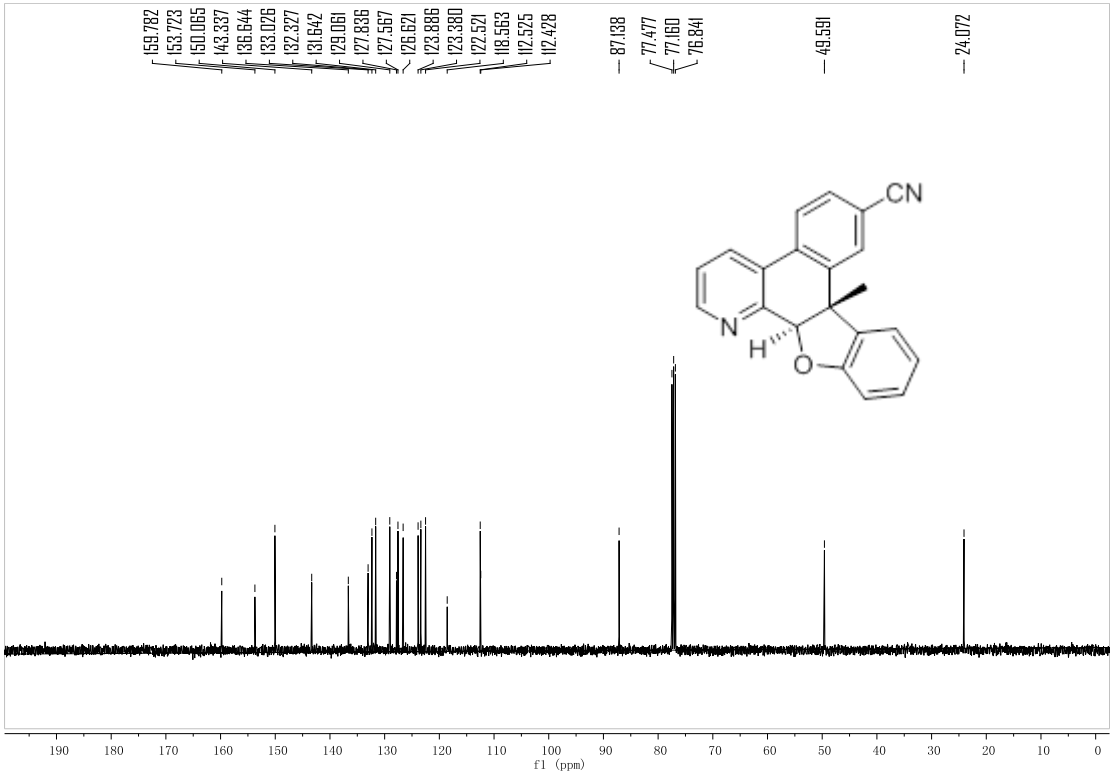


^{13}C NMR spectrum of **2o** ($CDCl_3$, 400 MHz)

2p

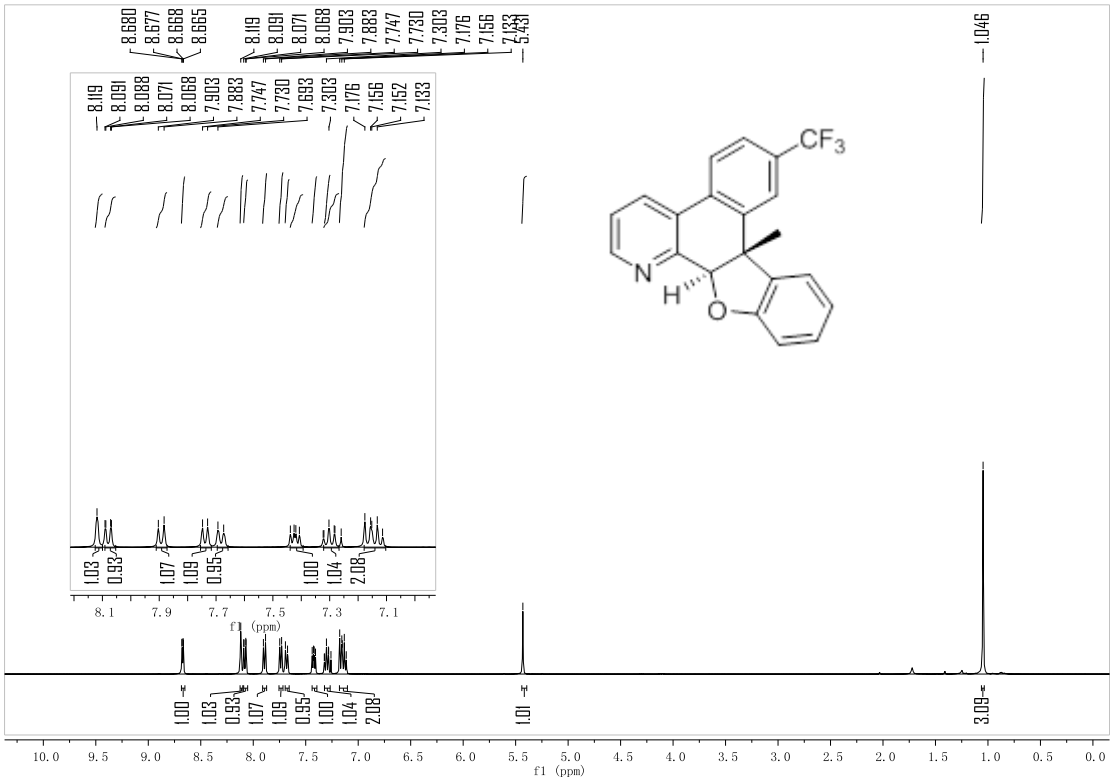


^{1}H NMR spectrum of **2p** ($CDCl_3$, 400 MHz)

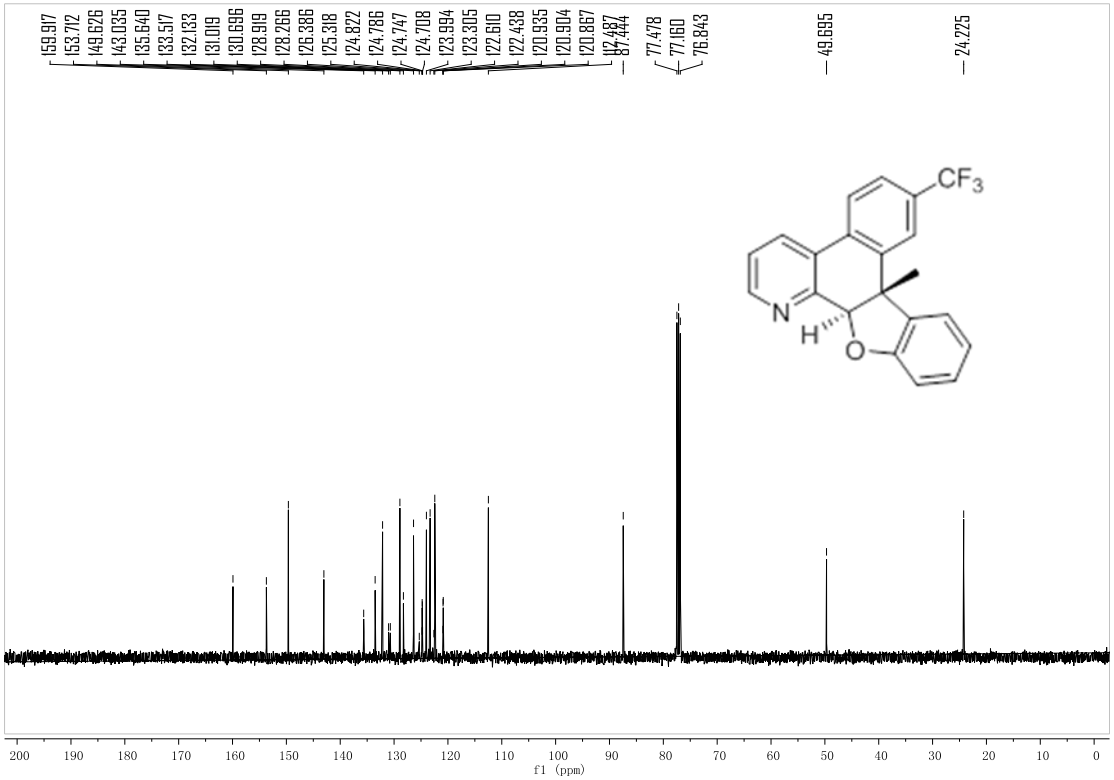


^{13}C NMR spectrum of **2p** ($CDCl_3$, 400 MHz)

2q

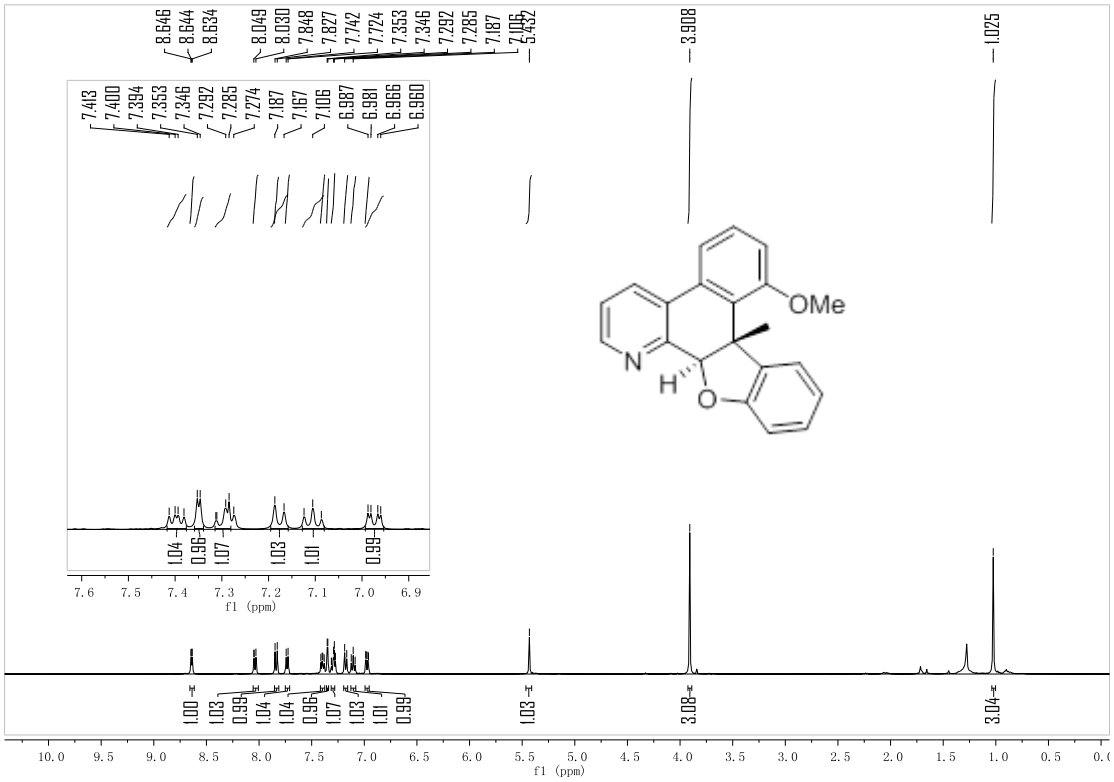


^{1}H NMR spectrum of **2q** ($CDCl_3$, 400 MHz)

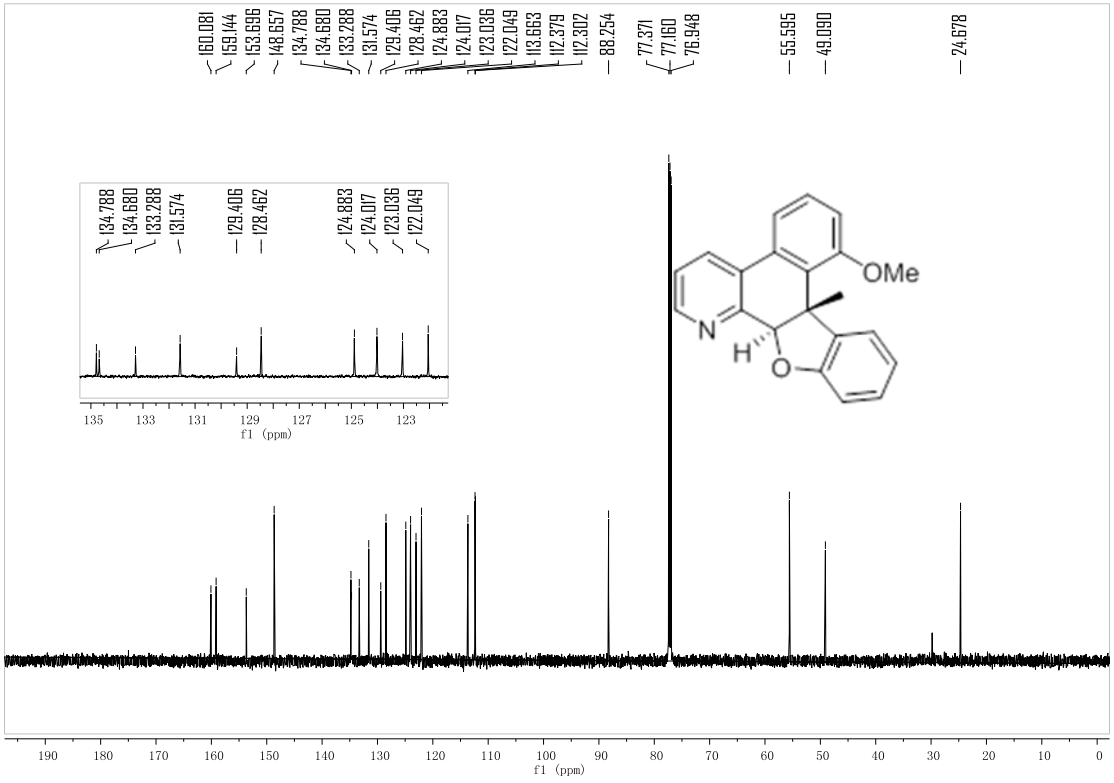


^{13}C NMR spectrum of **2q** ($CDCl_3$, 400 MHz)

2r

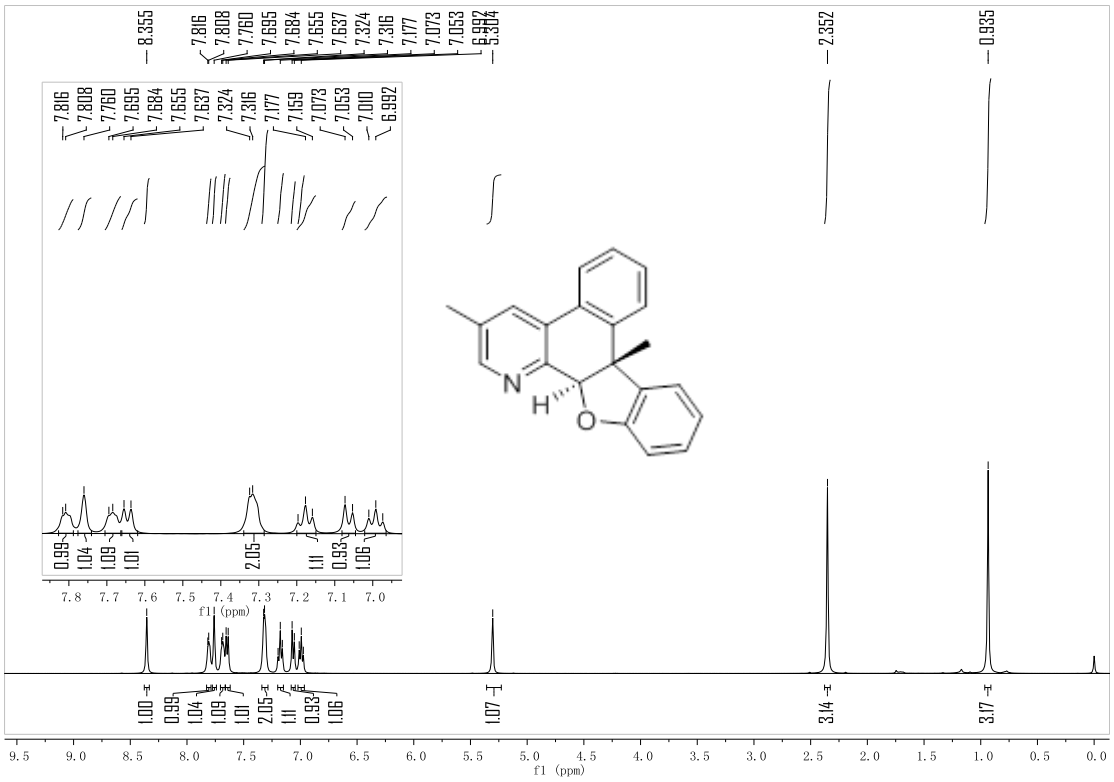


^{1}H NMR spectrum of **2r** ($CDCl_3$, 400 MHz)

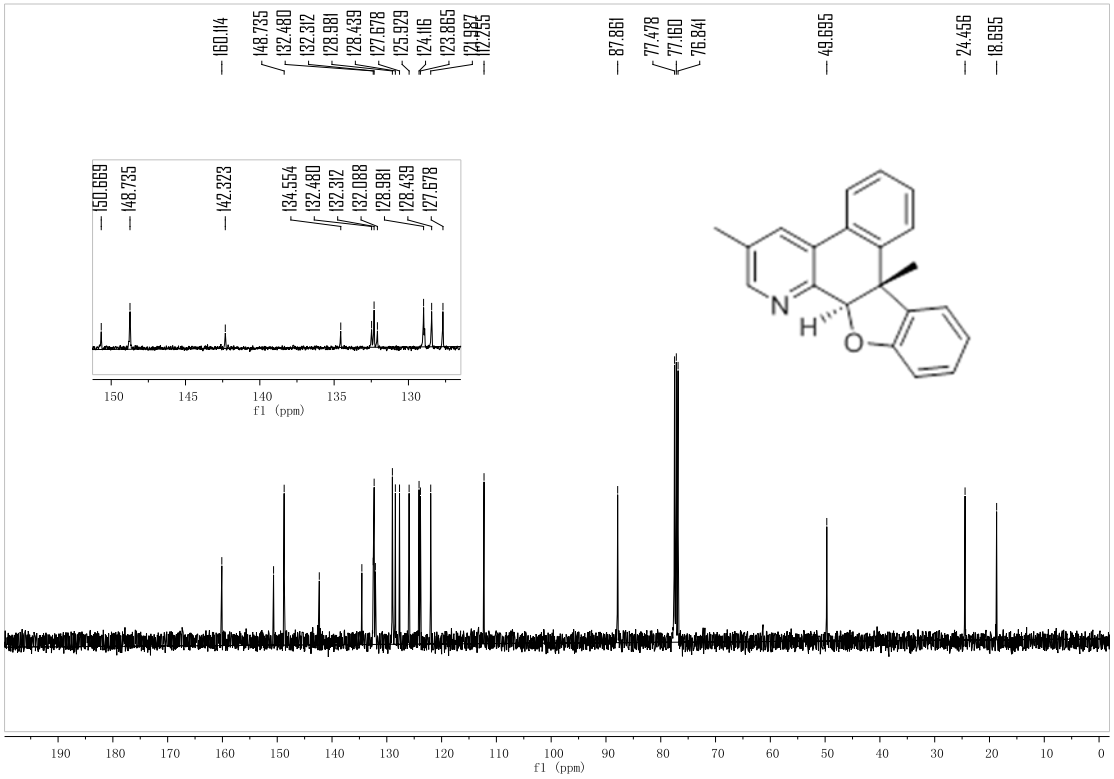


^{13}C NMR spectrum of **2r** ($CDCl_3$, 600 MHz)

2s

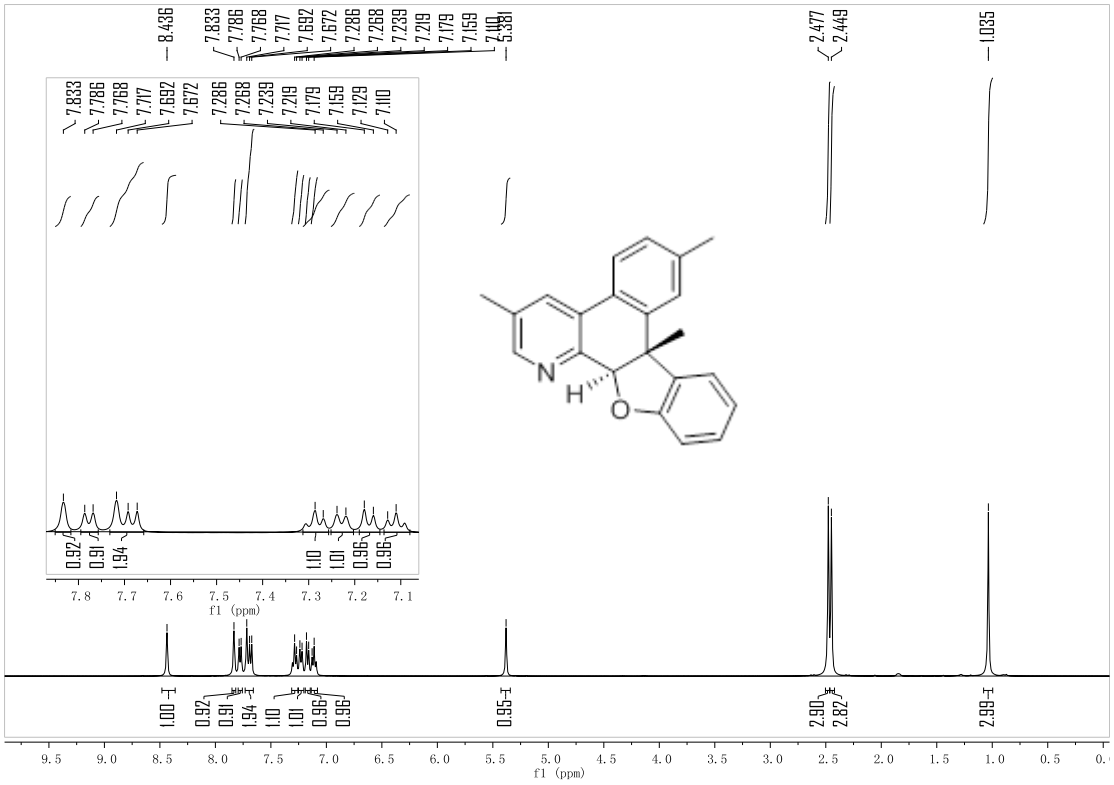


^{1}H NMR spectrum of **2s** ($CDCl_3$, 400 MHz)

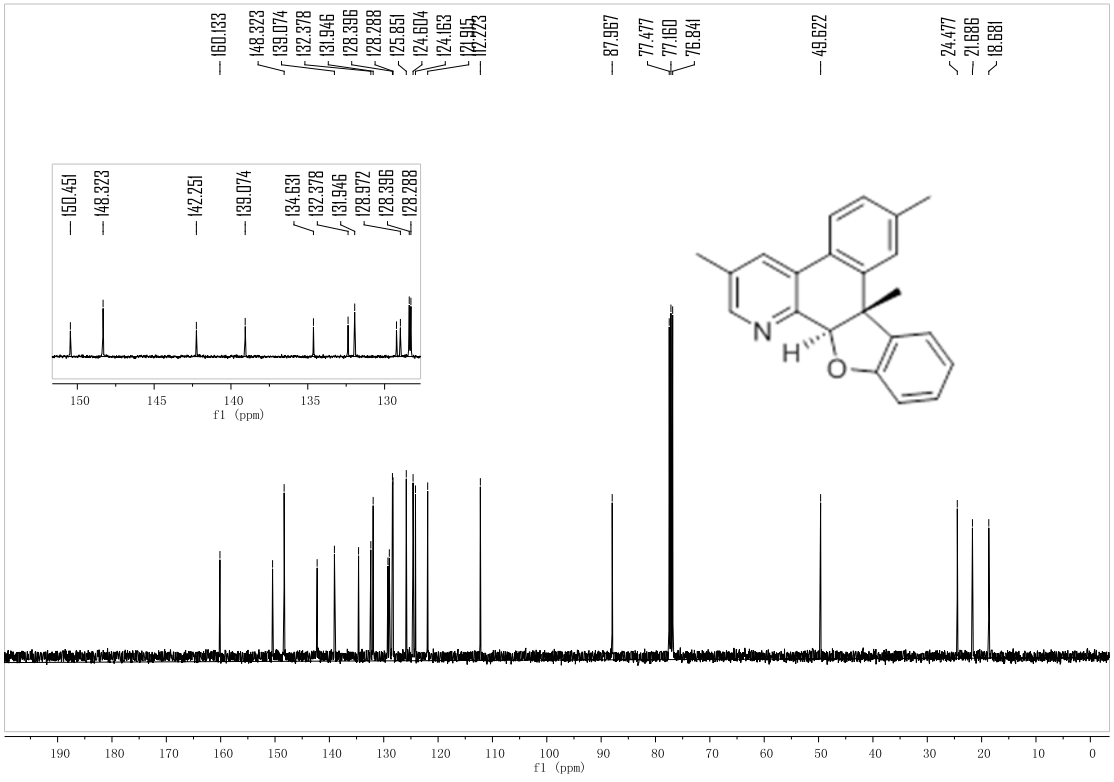


^{13}C NMR spectrum of **2s** ($CDCl_3$, 400 MHz)

2t

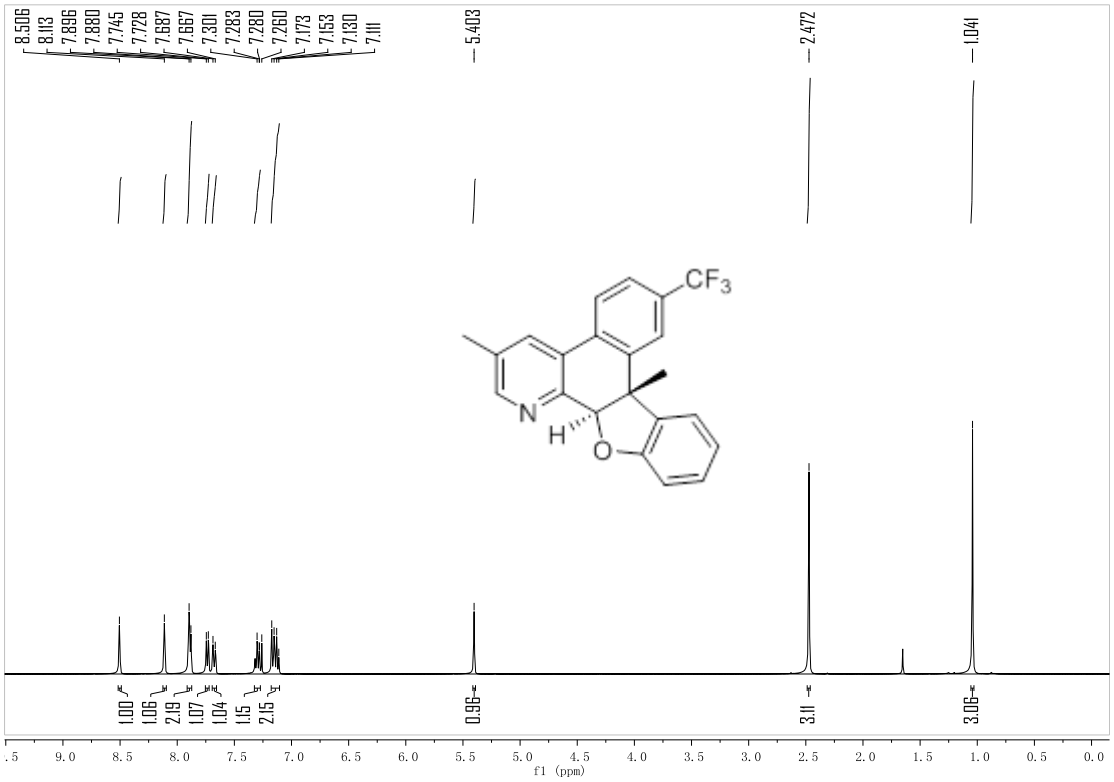


^{1}H NMR spectrum of **2t** ($CDCl_3$, 400 MHz)

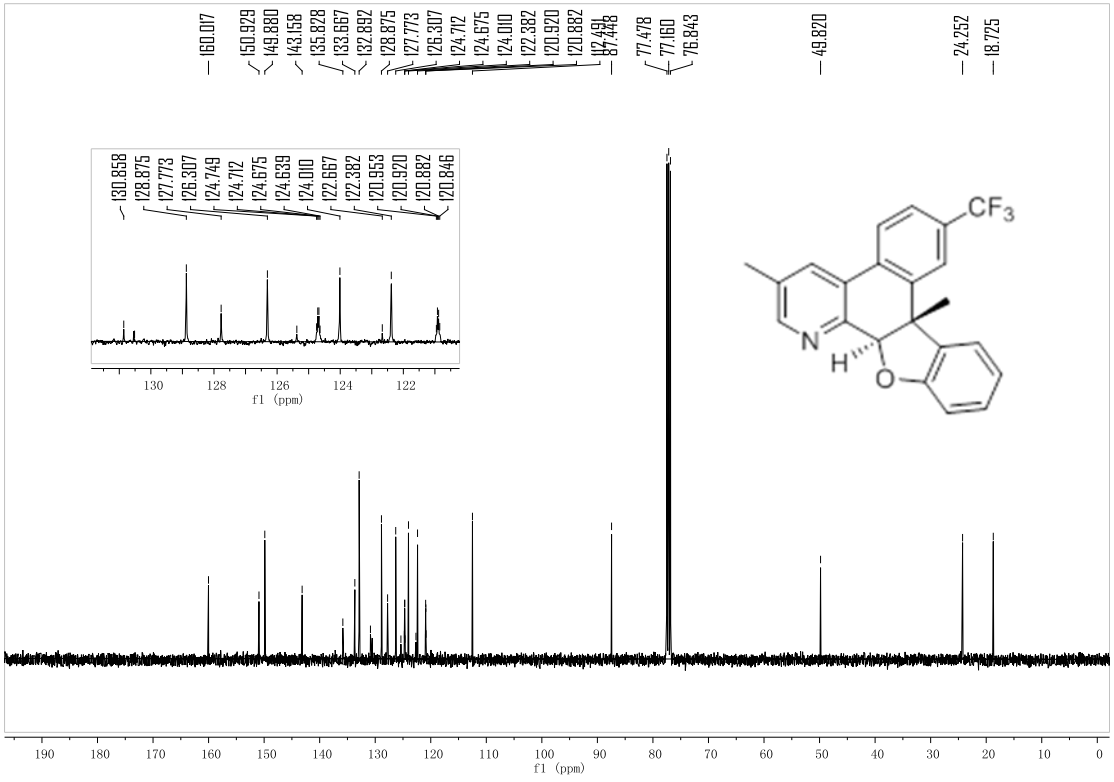


^{13}C NMR spectrum of **2t** ($CDCl_3$, 400 MHz)

2u

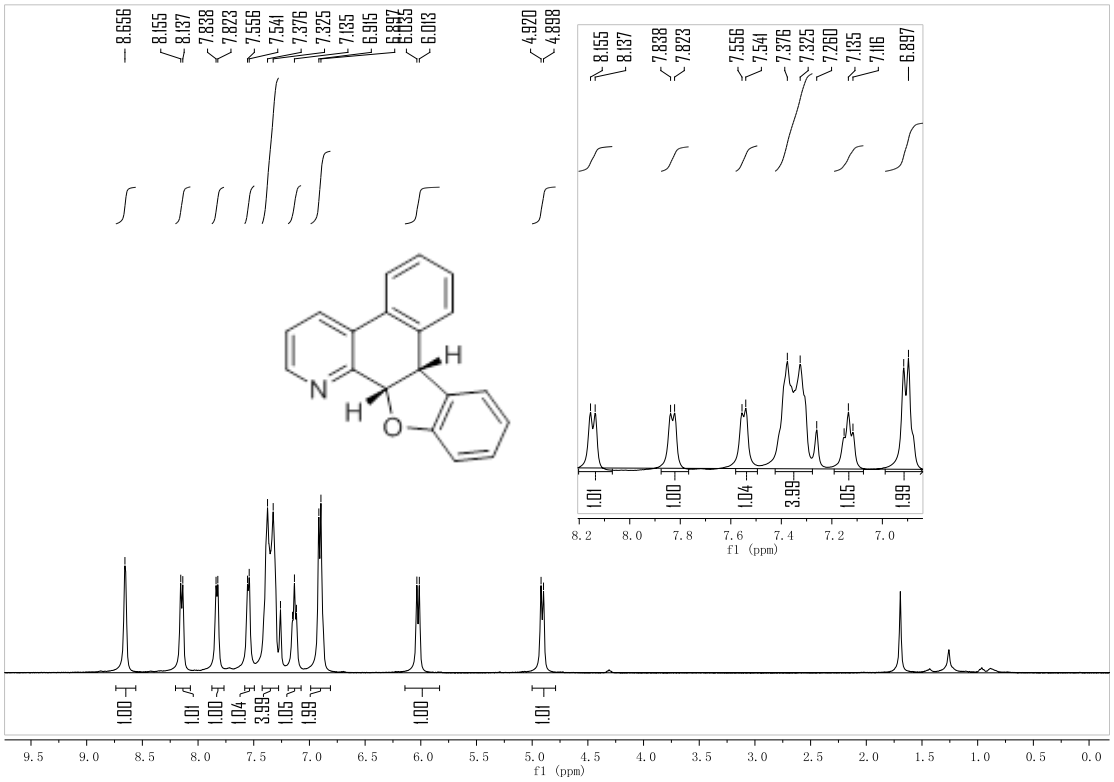


^{1}H NMR spectrum of **2u** ($CDCl_3$, 400 MHz)



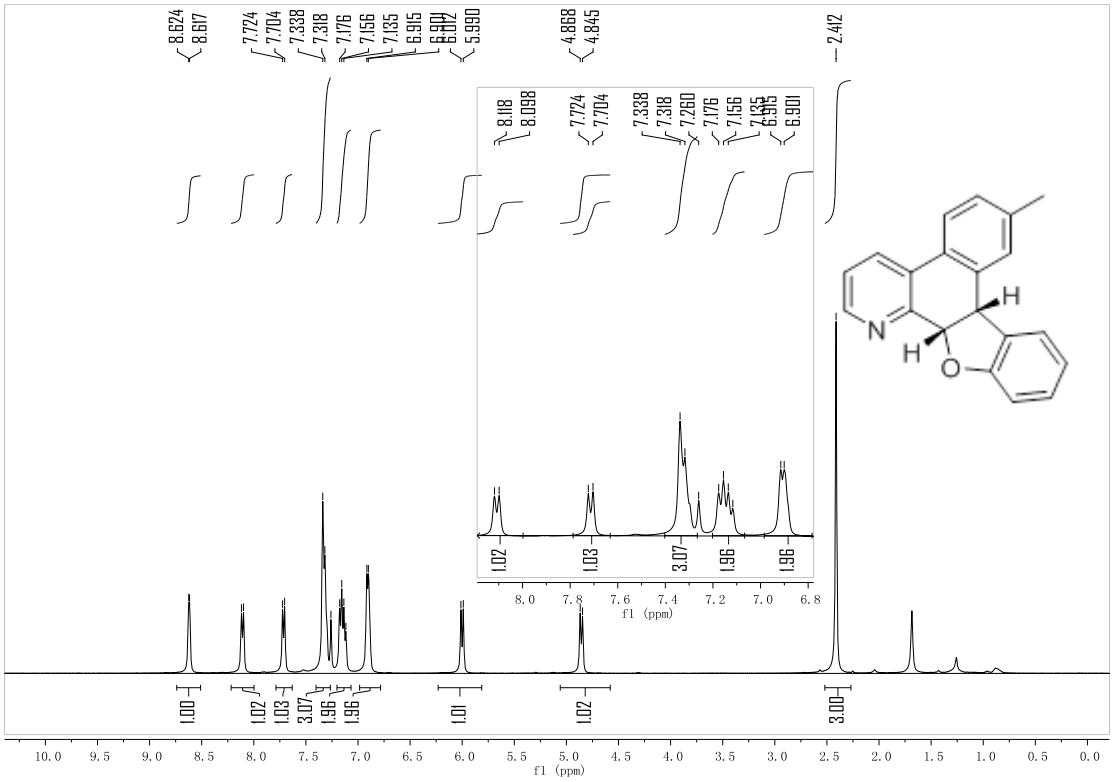
^{13}C NMR spectrum of **2u** ($CDCl_3$, 400 MHz)

3a

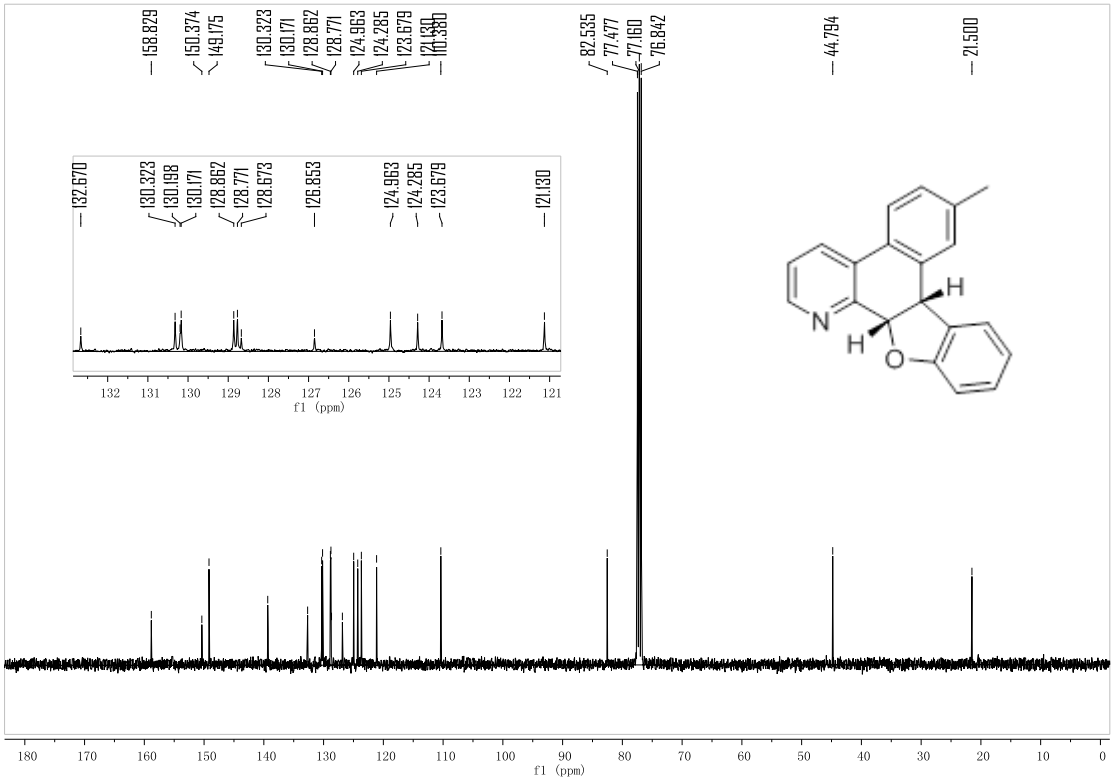


^{1}H NMR spectrum of **3a** ($CDCl_3$, 400 MHz)

3b

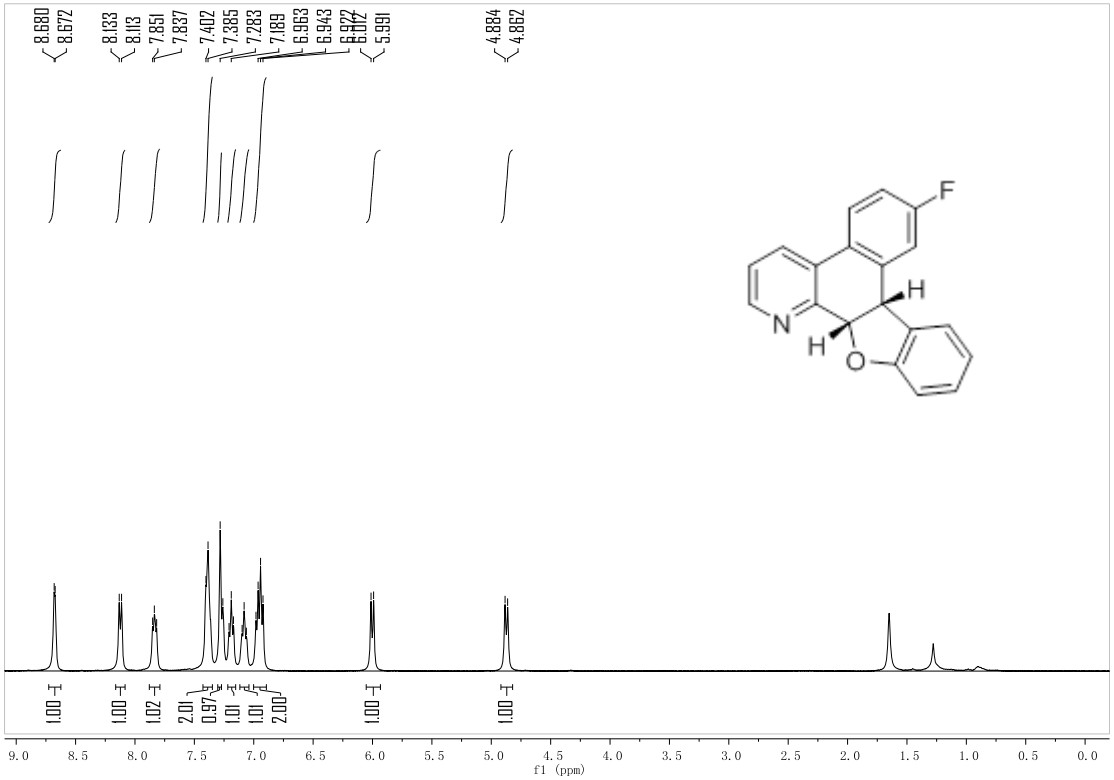


^{1}H NMR spectrum of **3b** ($CDCl_3$, 400 MHz)

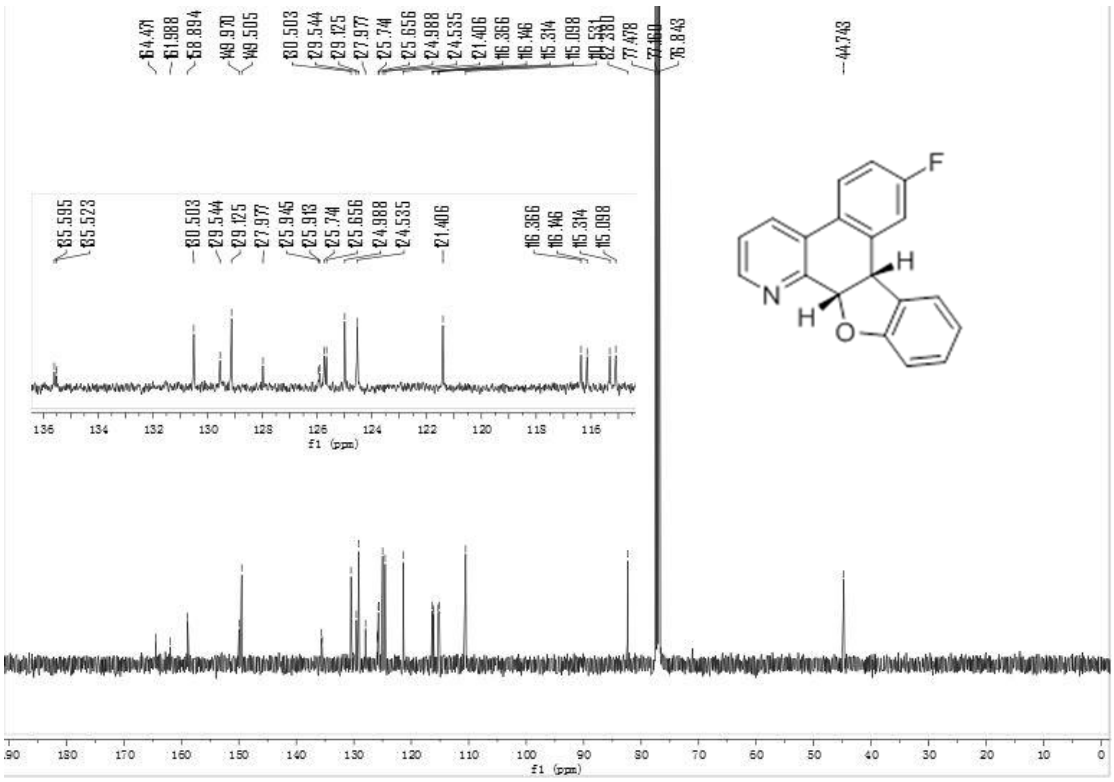


^{13}C NMR spectrum of **3b** ($CDCl_3$, 400 MHz)

3c

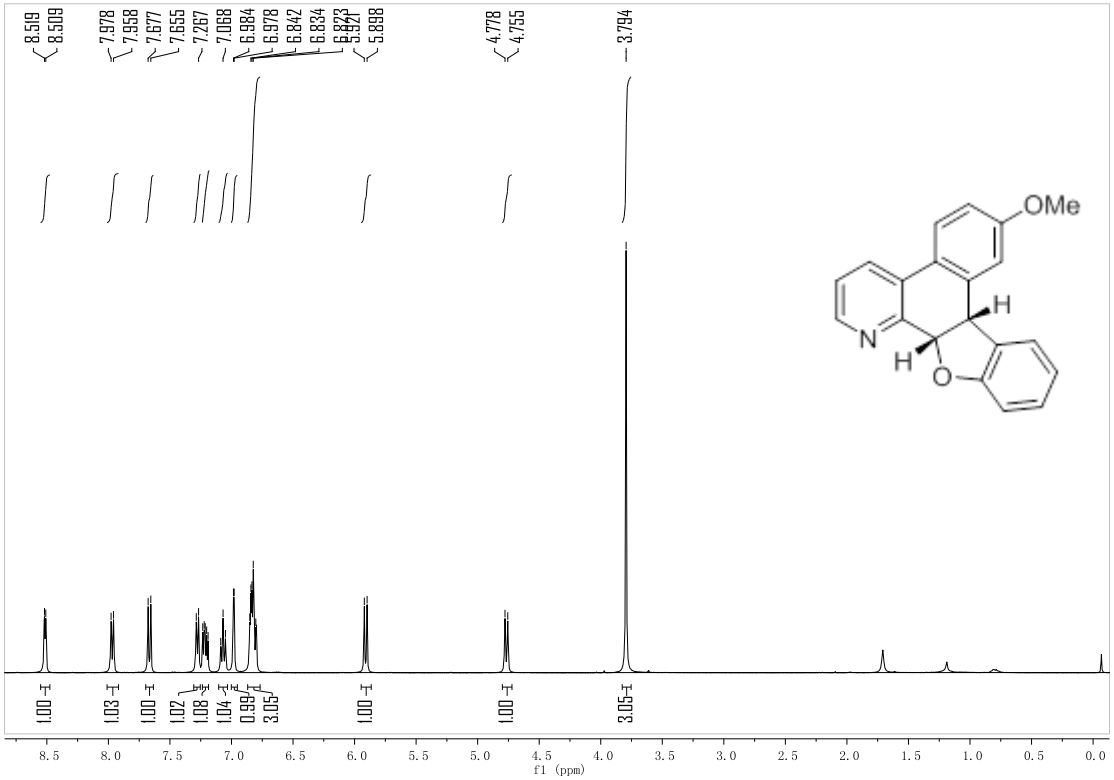


^{1}H NMR spectrum of **3c** ($CDCl_3$, 400 MHz)

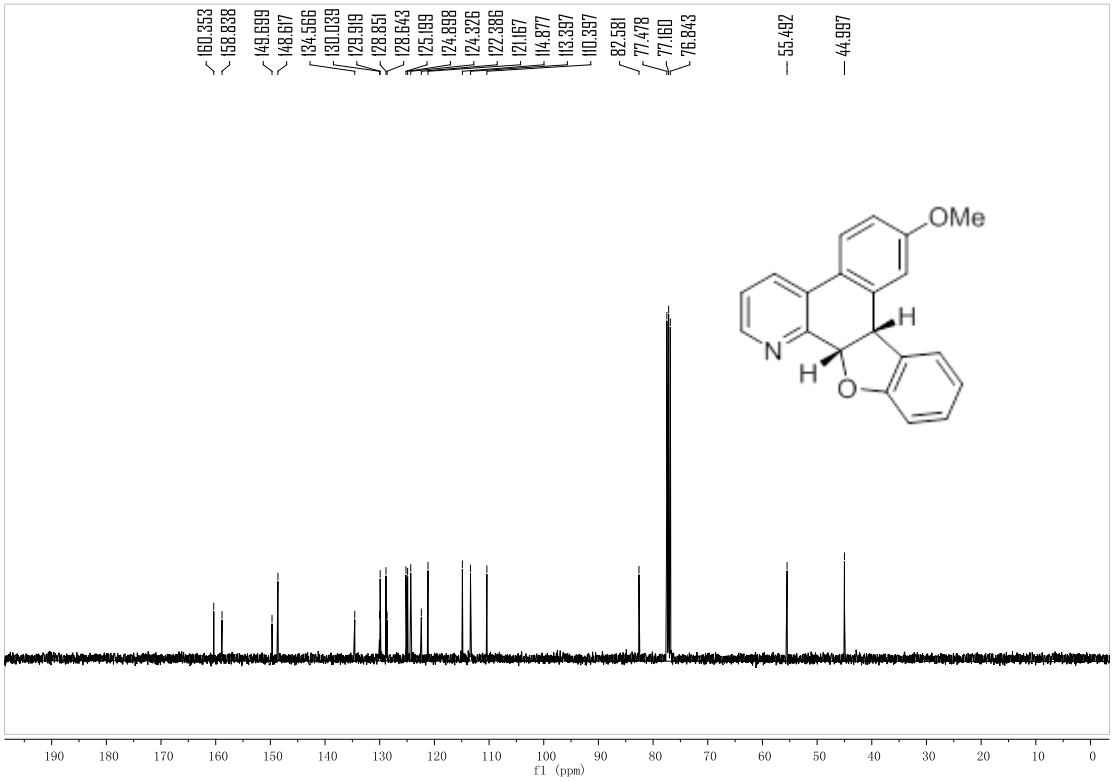


^{13}C NMR spectrum of **3c** ($CDCl_3$, 400 MHz)

3d

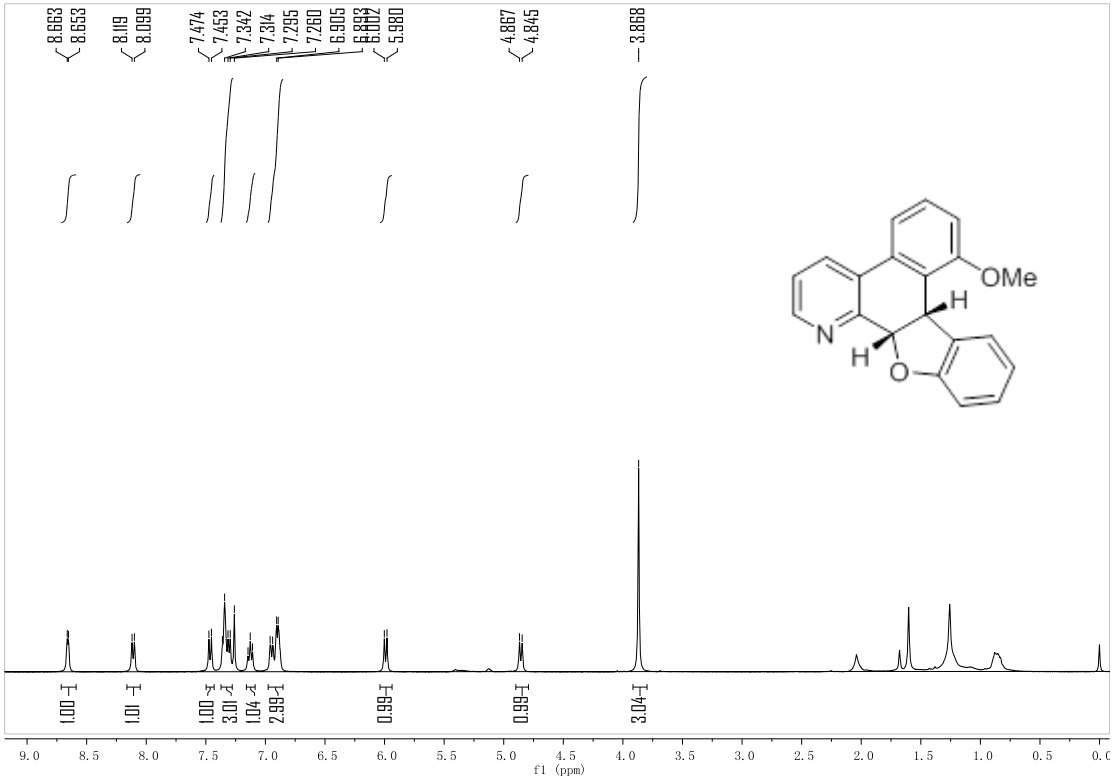


^{1}H NMR spectrum of **3d** ($CDCl_3$, 400 MHz)

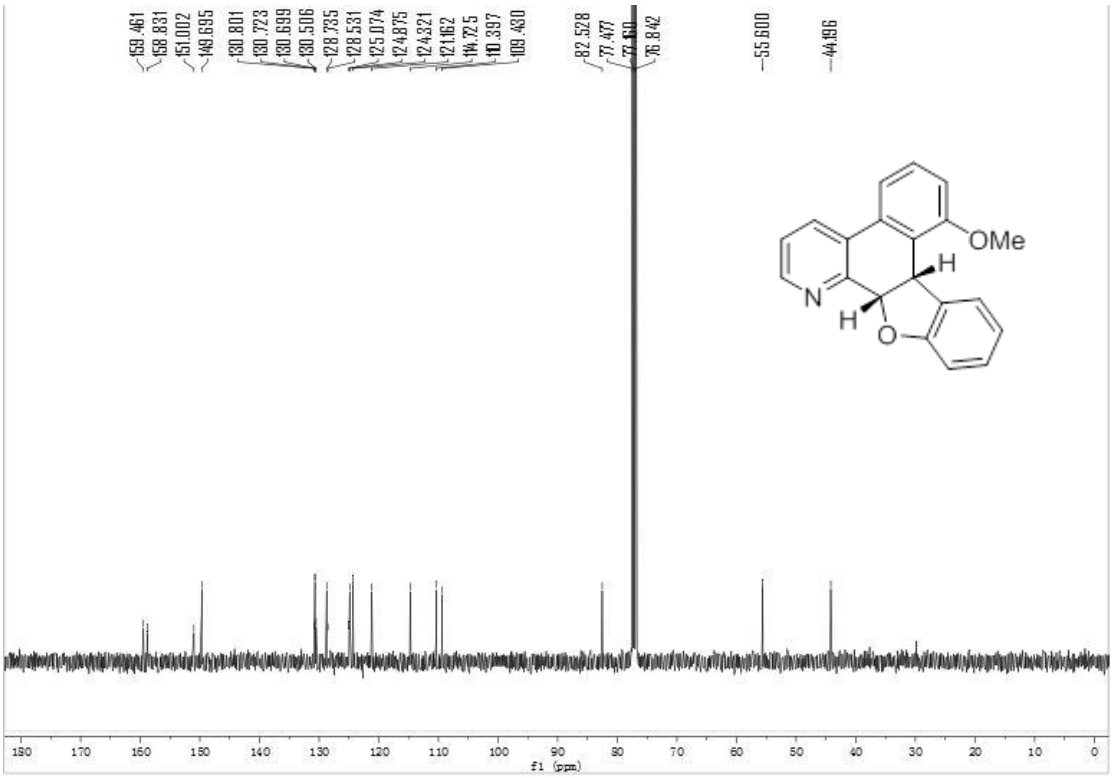


^{13}C NMR spectrum of **3d** ($CDCl_3$, 400 MHz)

3e

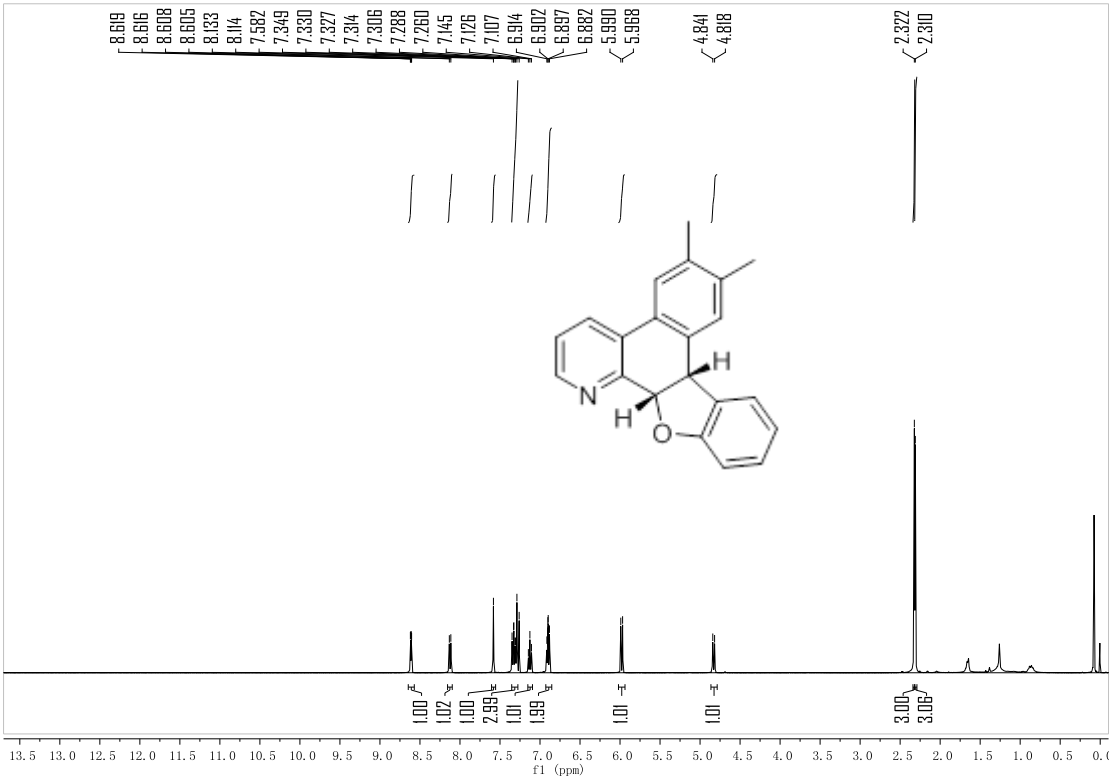


^{1}H NMR spectrum of **3e** ($CDCl_3$, 400 MHz)

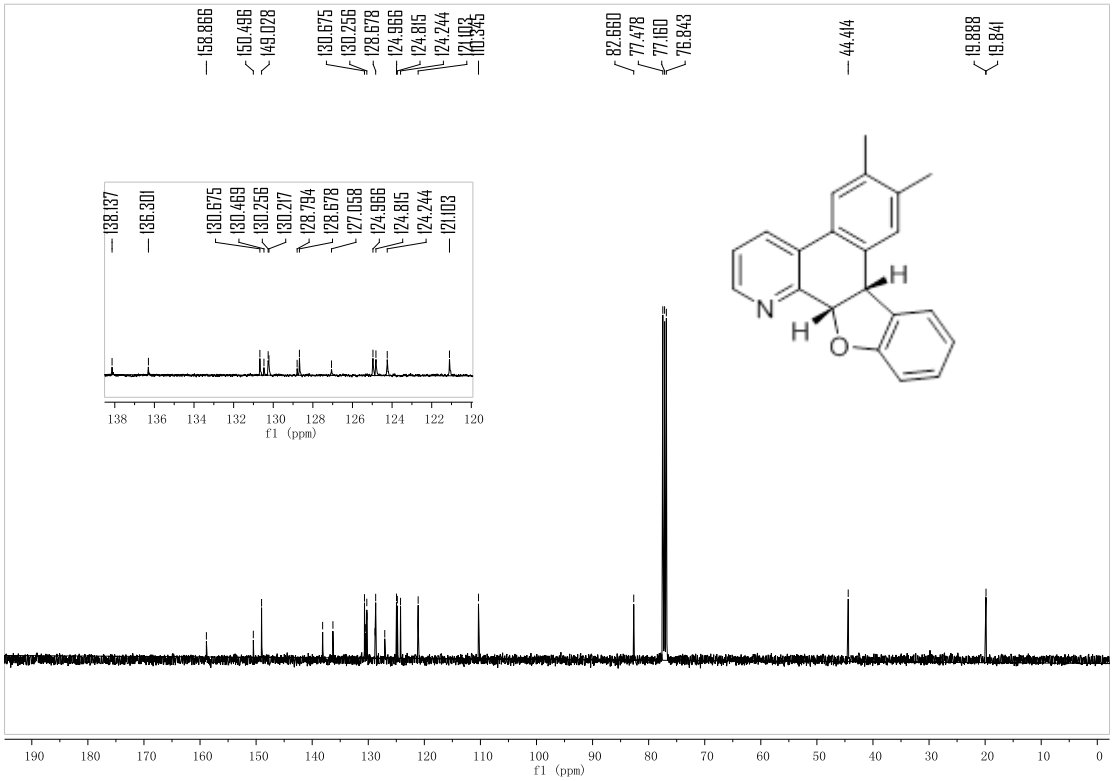


^{13}C NMR spectrum of **3e** ($CDCl_3$, 400 MHz)

3f

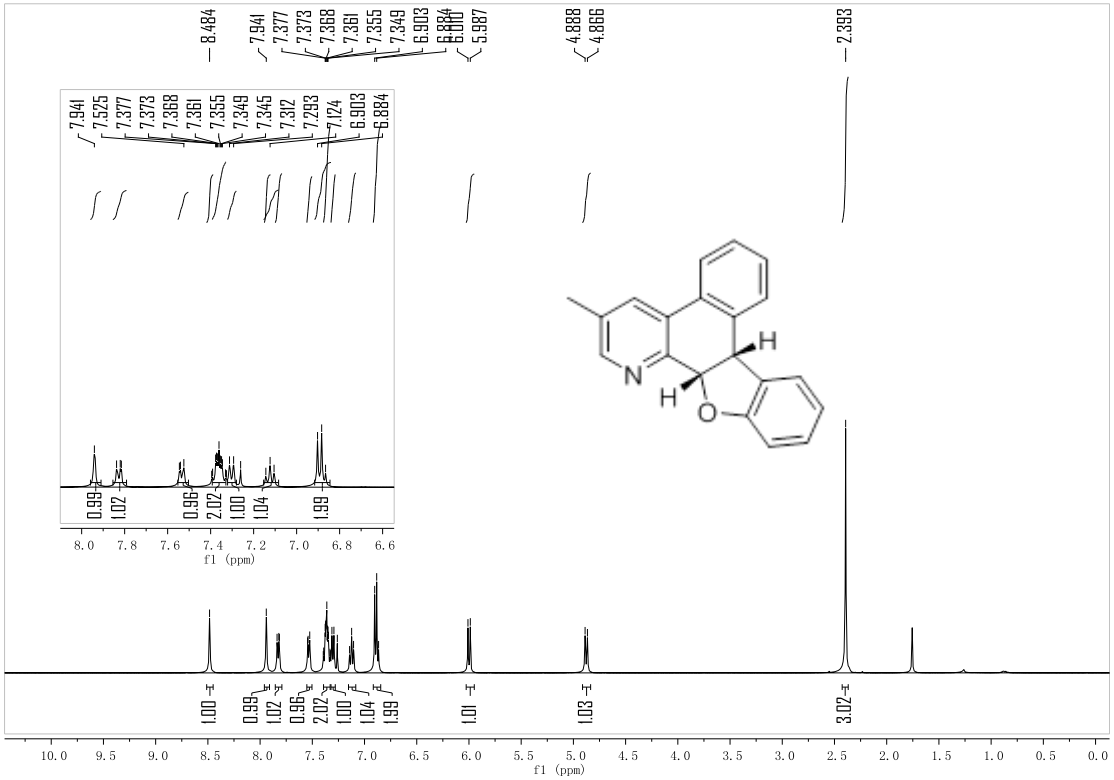


^{1}H NMR spectrum of **3f** ($CDCl_3$, 400 MHz)

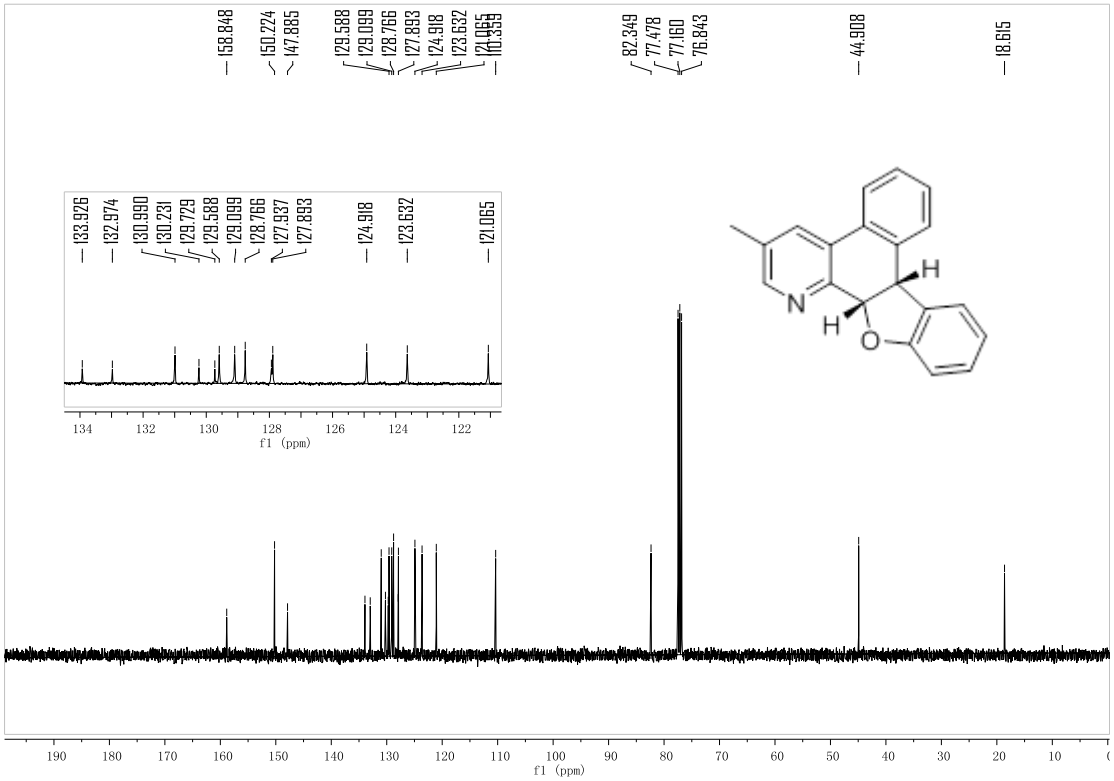


^{13}C NMR spectrum of **3f** ($CDCl_3$, 400 MHz)

3g

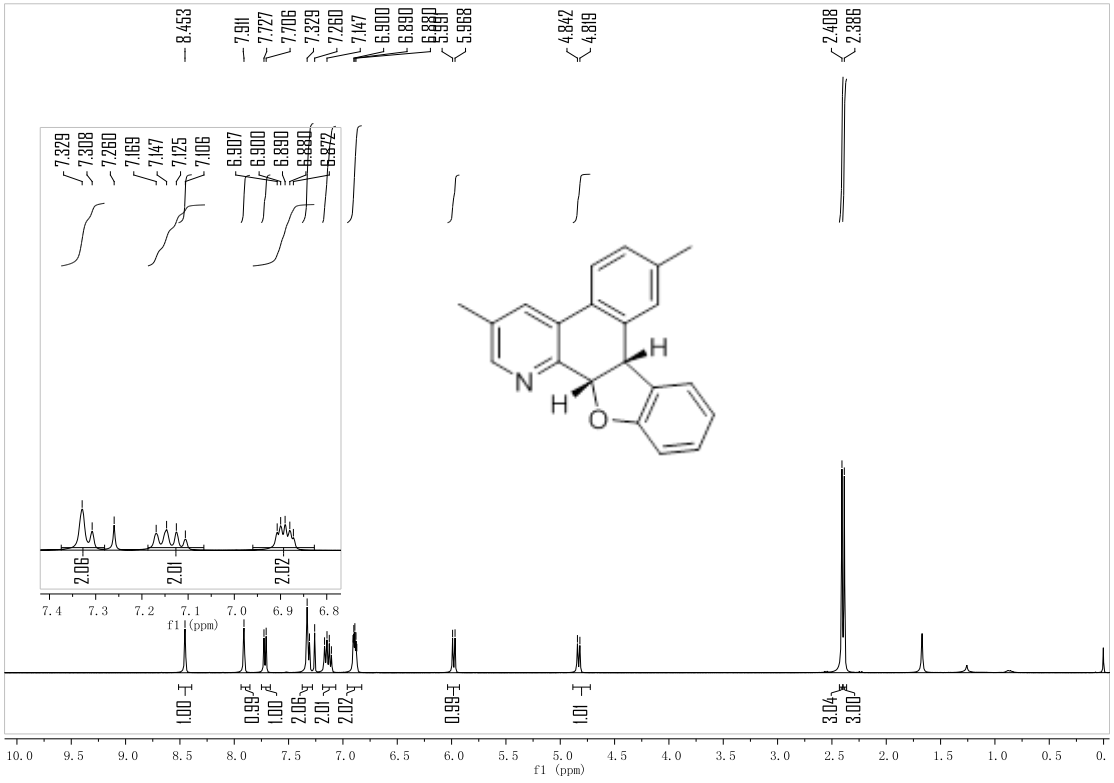


^{1}H NMR spectrum of **3g** ($CDCl_3$, 400 MHz)

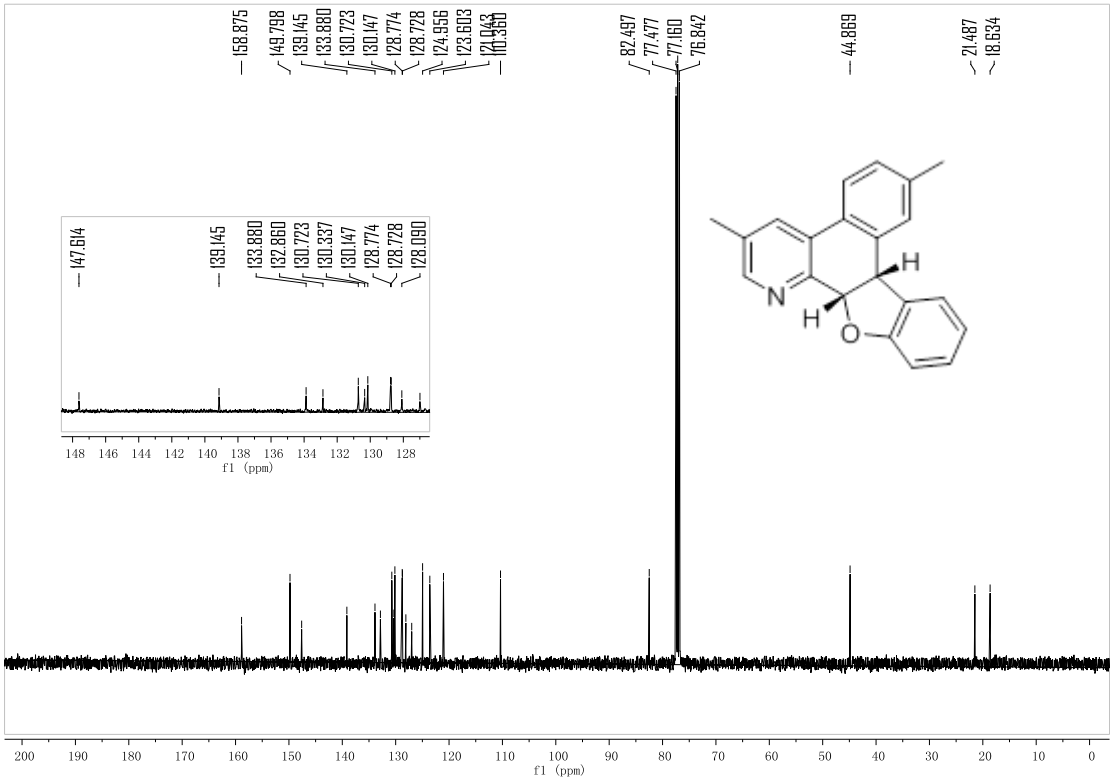


^{13}C NMR spectrum of **3g** ($CDCl_3$, 400 MHz)

3h

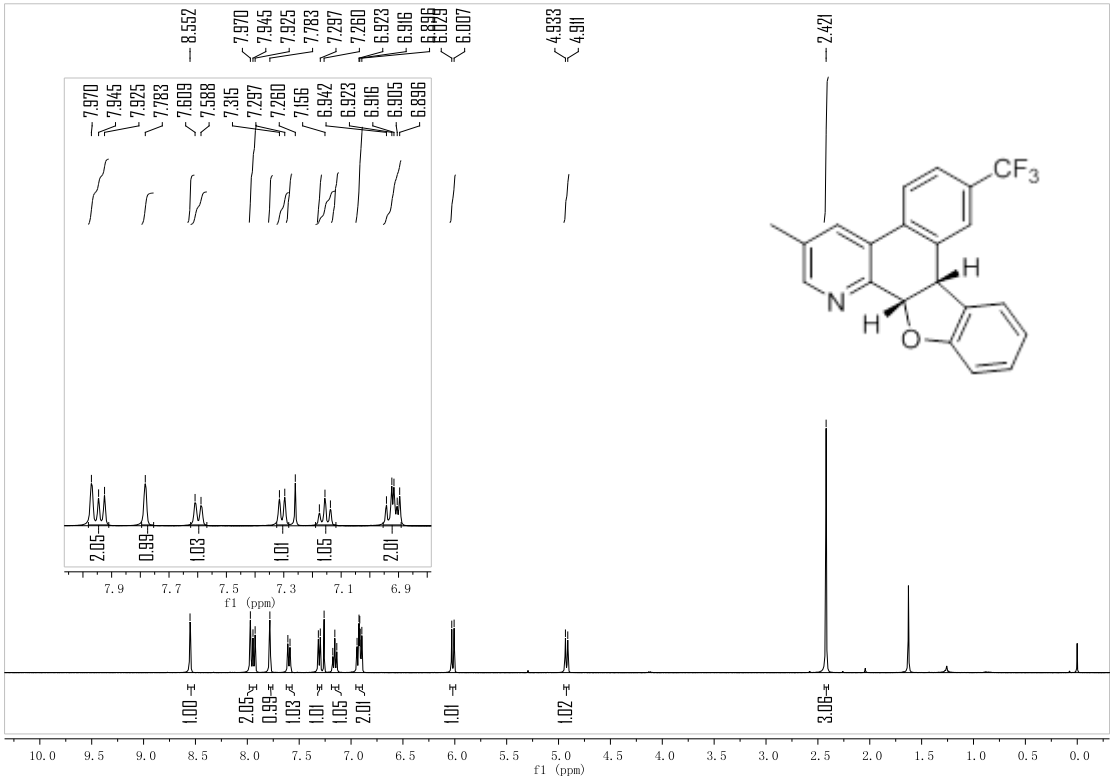


^{1}H NMR spectrum of **3h** ($CDCl_3$, 400 MHz)

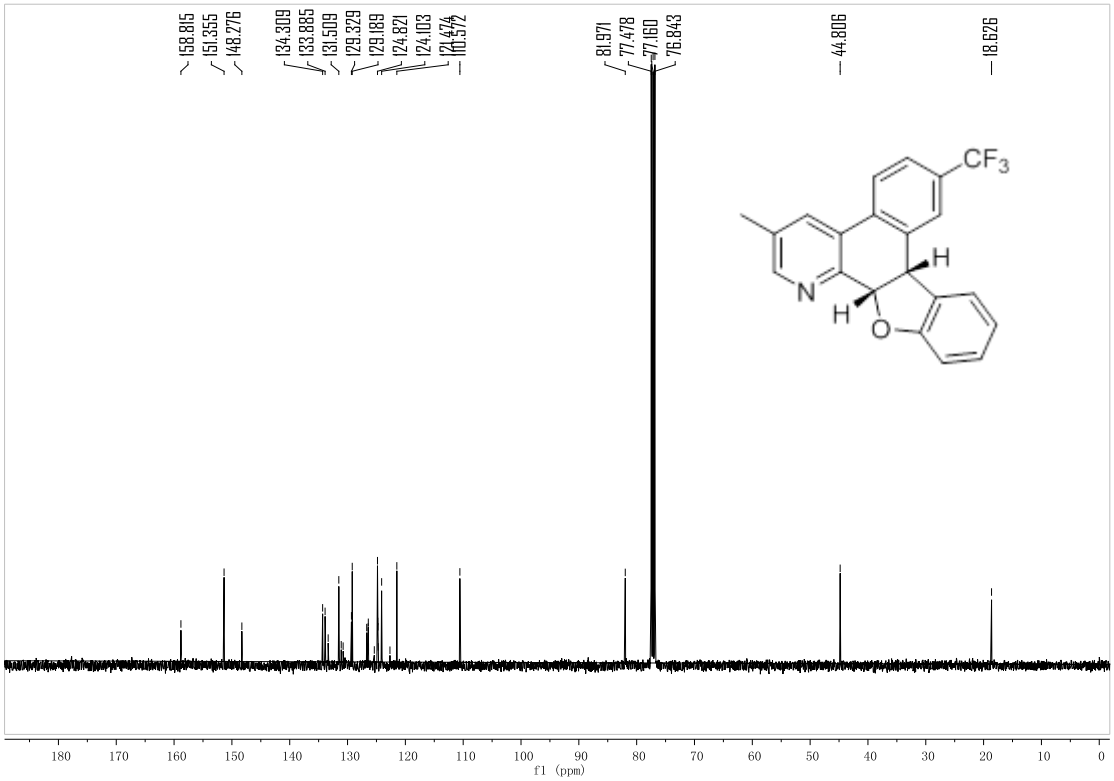


^{13}C NMR spectrum of **3h** ($CDCl_3$, 400 MHz)

3i

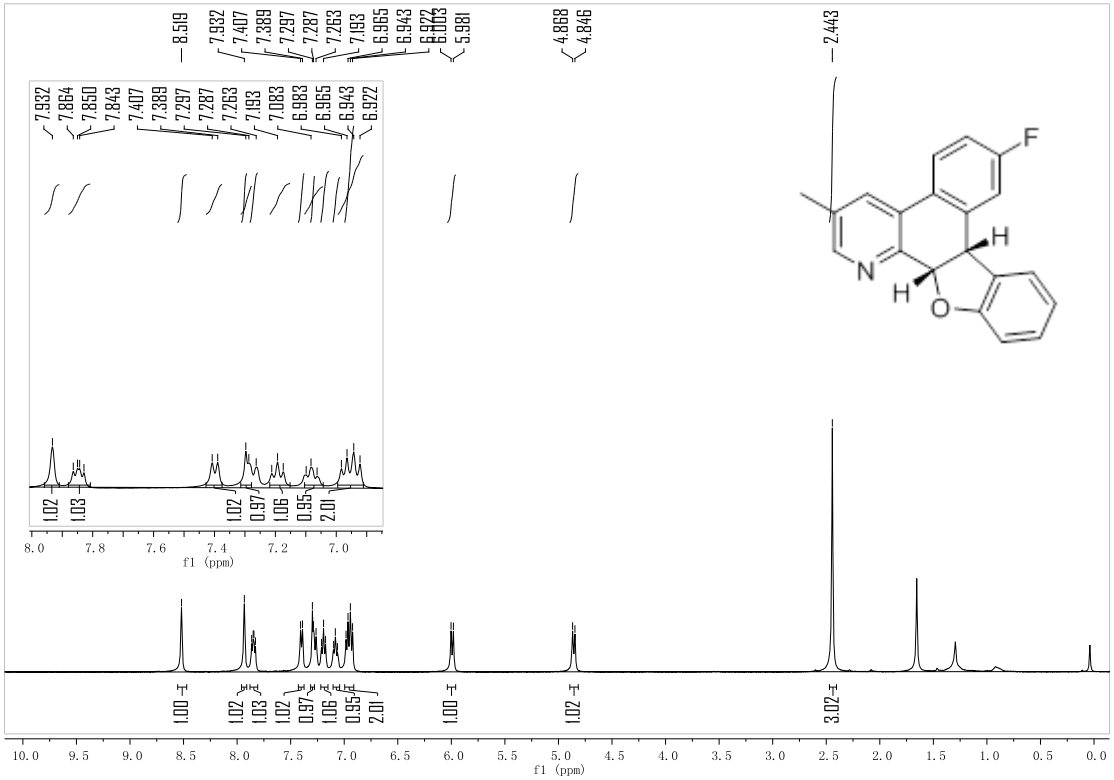


^{1}H NMR spectrum of **3i** ($CDCl_3$, 400 MHz)

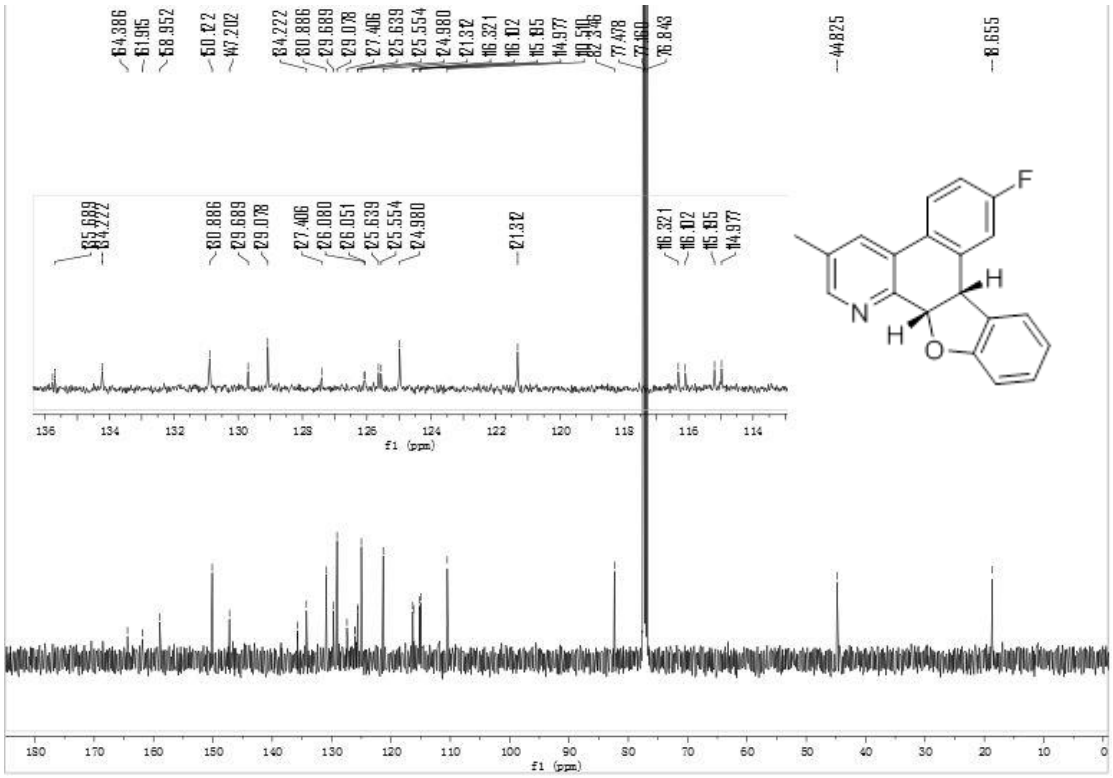


^{13}C NMR spectrum of **3i** ($CDCl_3$, 400 MHz)

3j



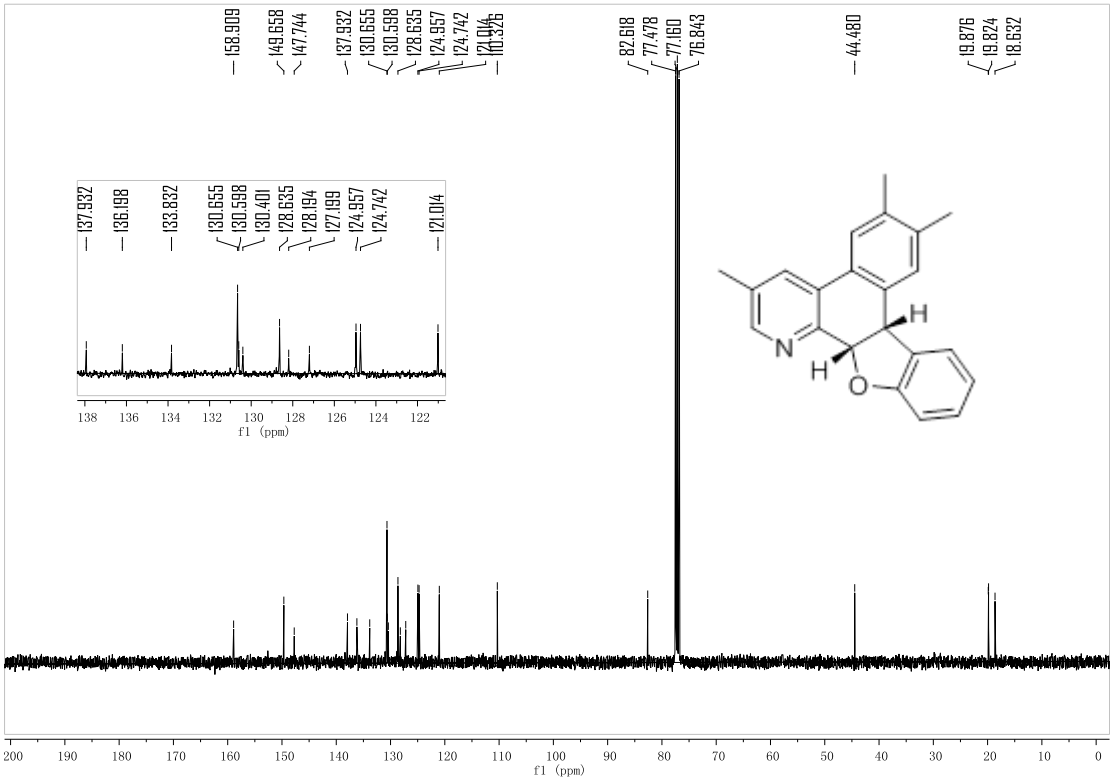
^{1}H NMR spectrum of **3j** ($CDCl_3$, 400 MHz)



^{13}C NMR spectrum of **3j** ($CDCl_3$, 400 MHz)

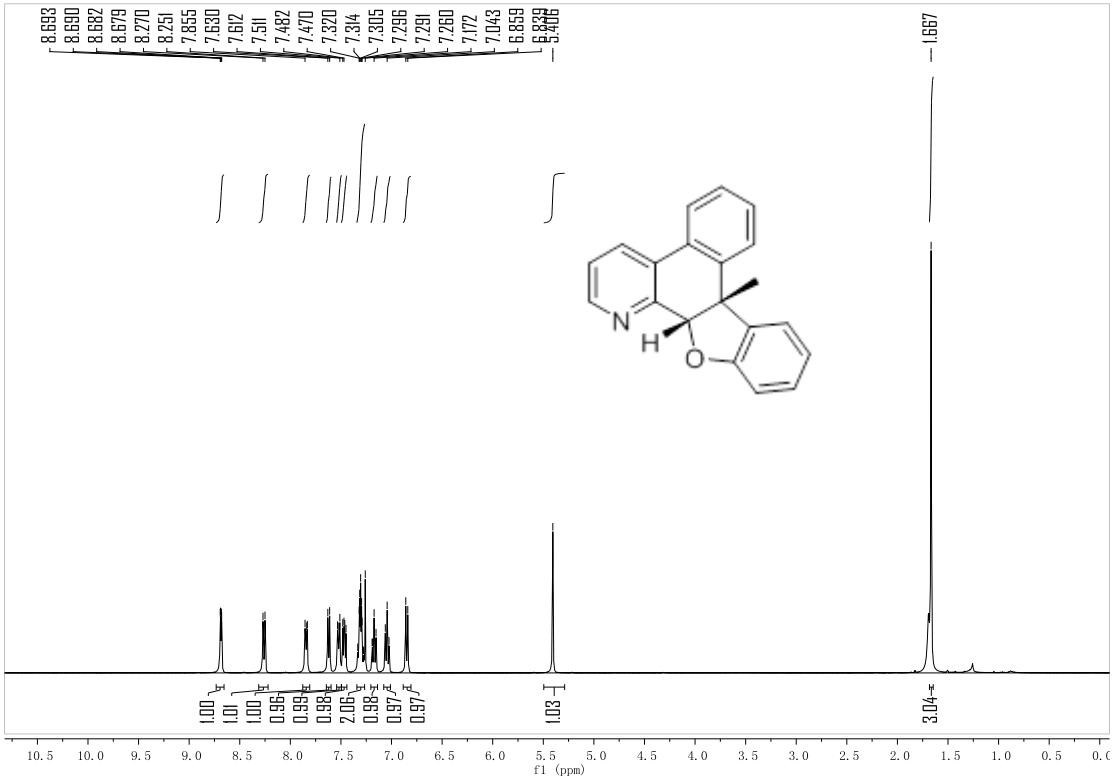
3k

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



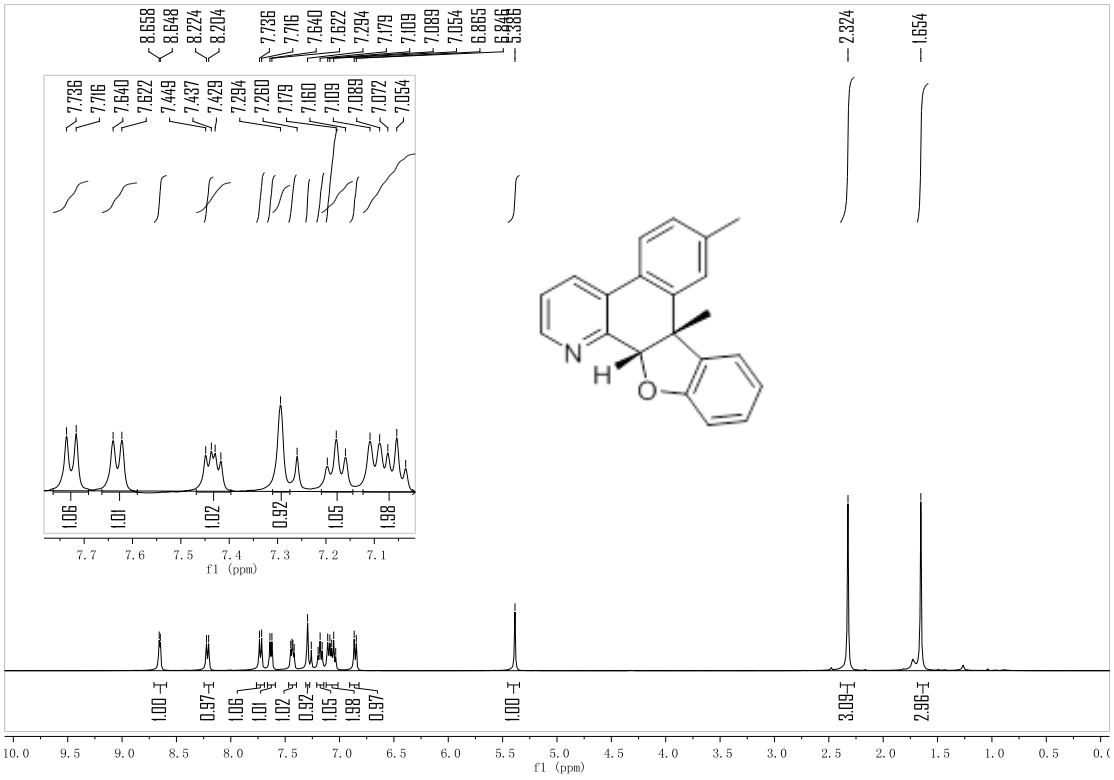
^{13}C NMR spectrum of **3k** ($CDCl_3$, 400 MHz)

3l

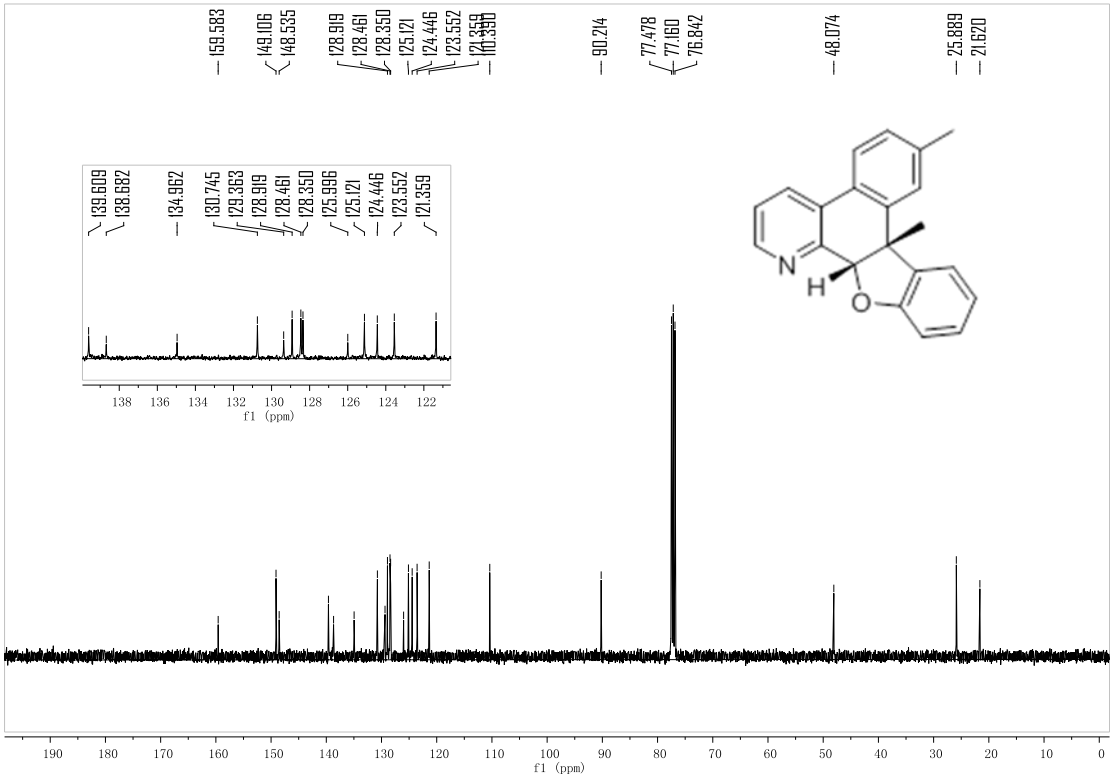


^{1}H NMR spectrum of **3l** ($CDCl_3$, 400 MHz)

3m

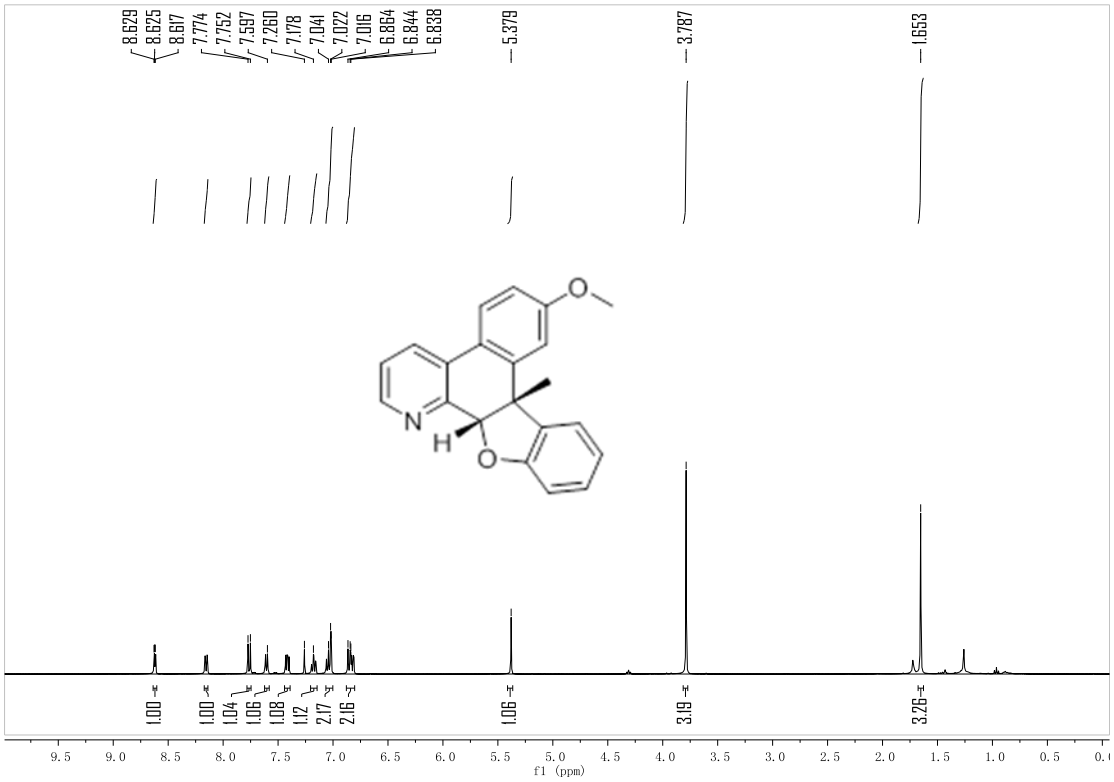


^{1}H NMR spectrum of **3m** ($CDCl_3$, 400 MHz)

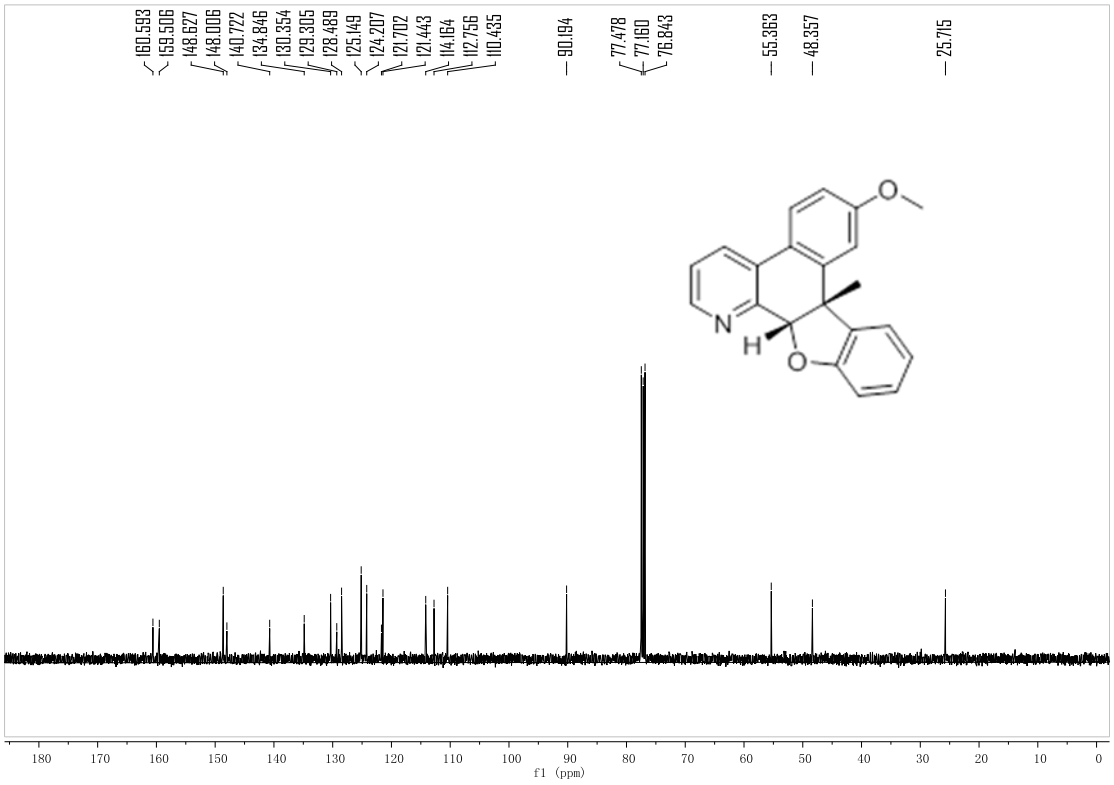


^{13}C NMR spectrum of **3m** ($CDCl_3$, 400 MHz)

3n

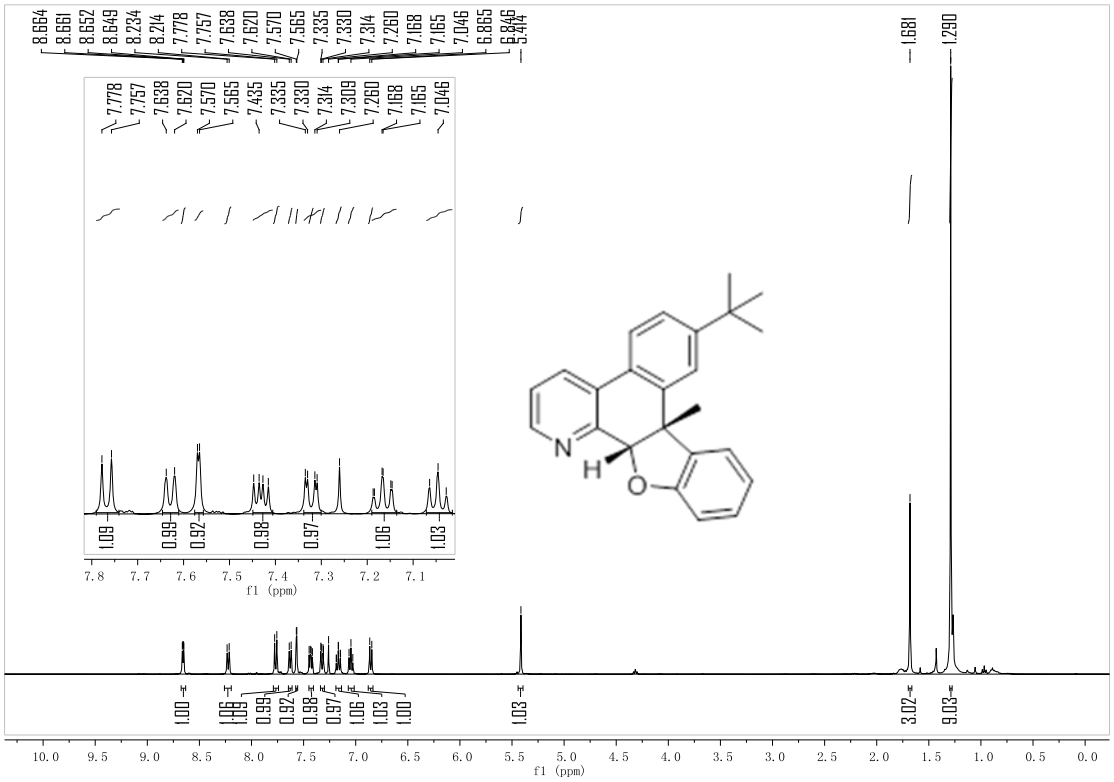


^{1}H NMR spectrum of **3n** ($CDCl_3$, 400 MHz)

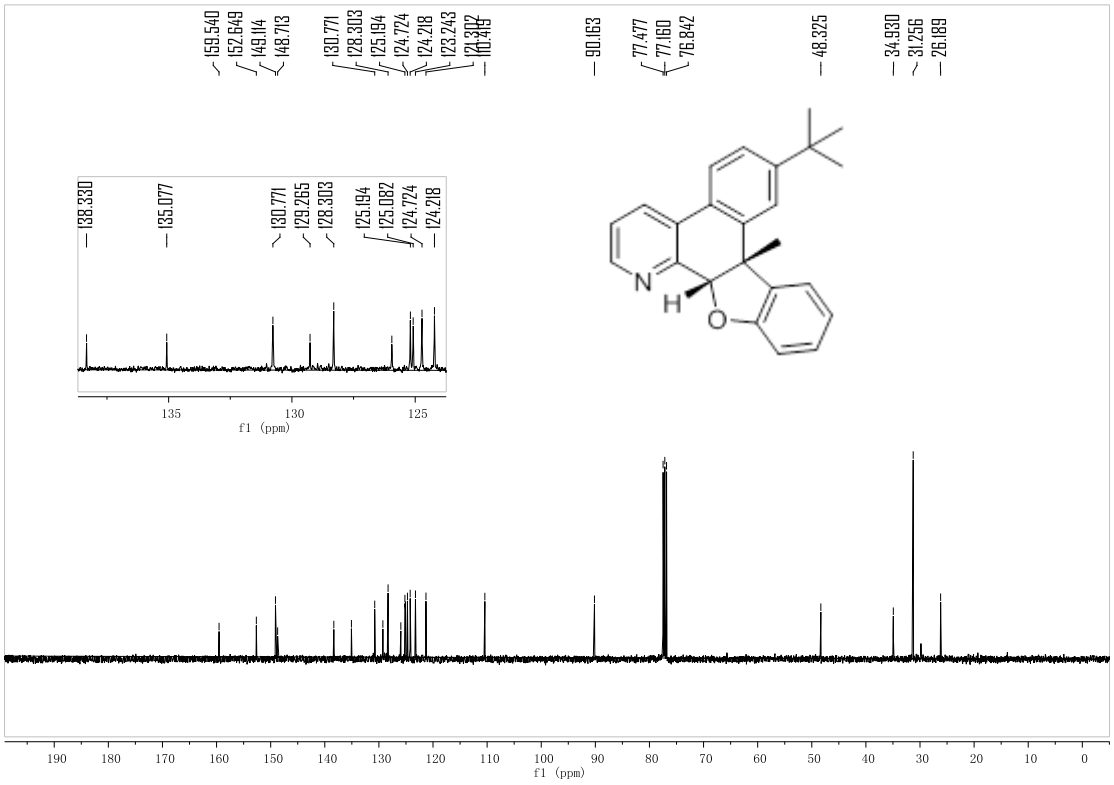


^{13}C NMR spectrum of **3n** ($CDCl_3$, 400 MHz)

3o



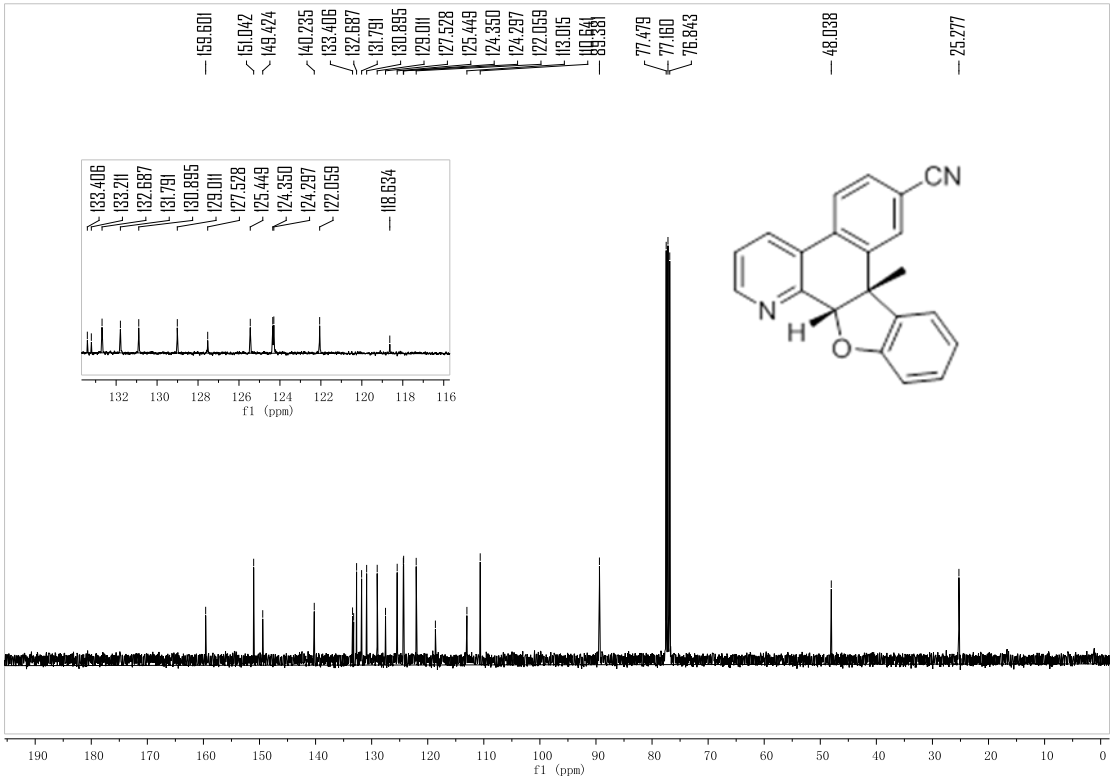
^{1}H NMR spectrum of **3o** ($CDCl_3$, 400 MHz)



^{13}C NMR spectrum of **3o** ($CDCl_3$, 400 MHz)

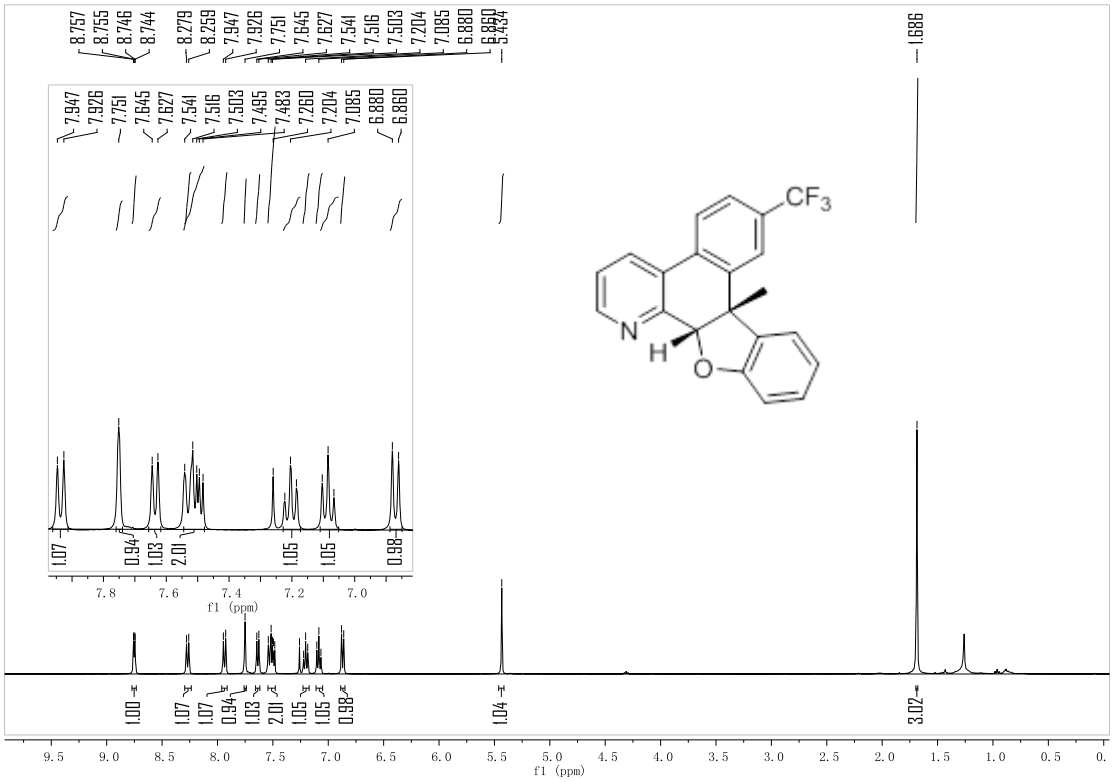
3p

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

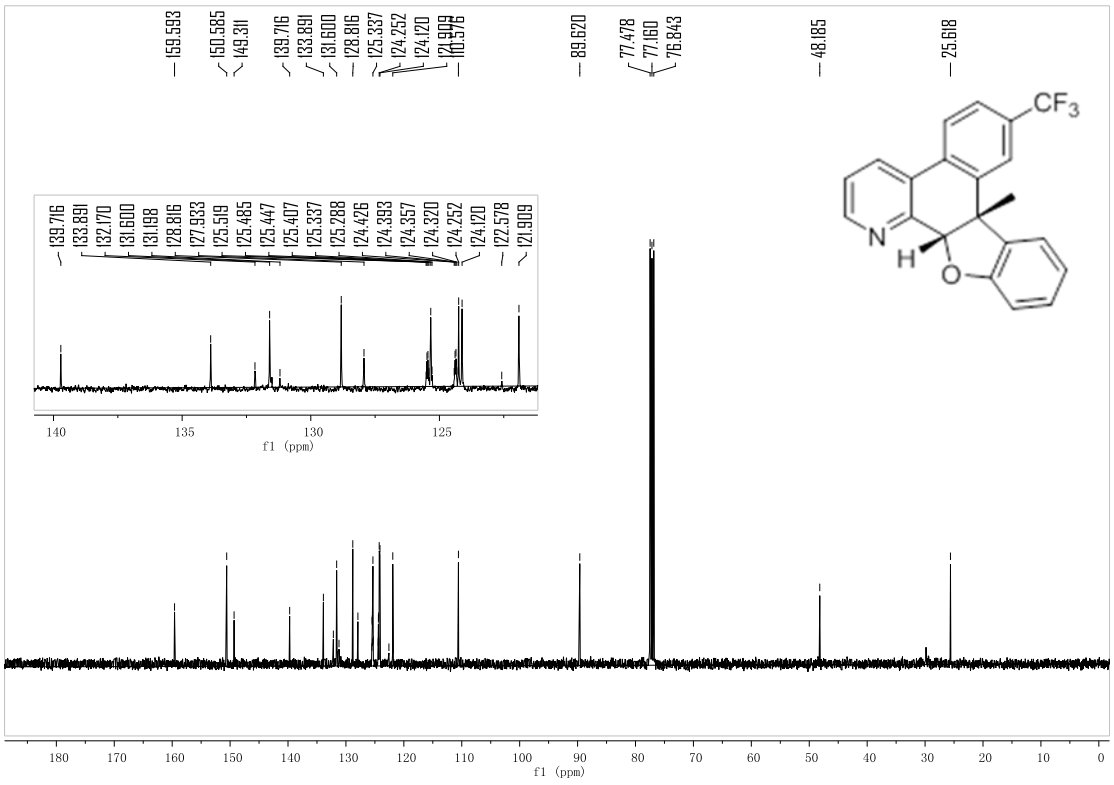


^{13}C NMR spectrum of **3p** ($CDCl_3$, 400 MHz)

3q

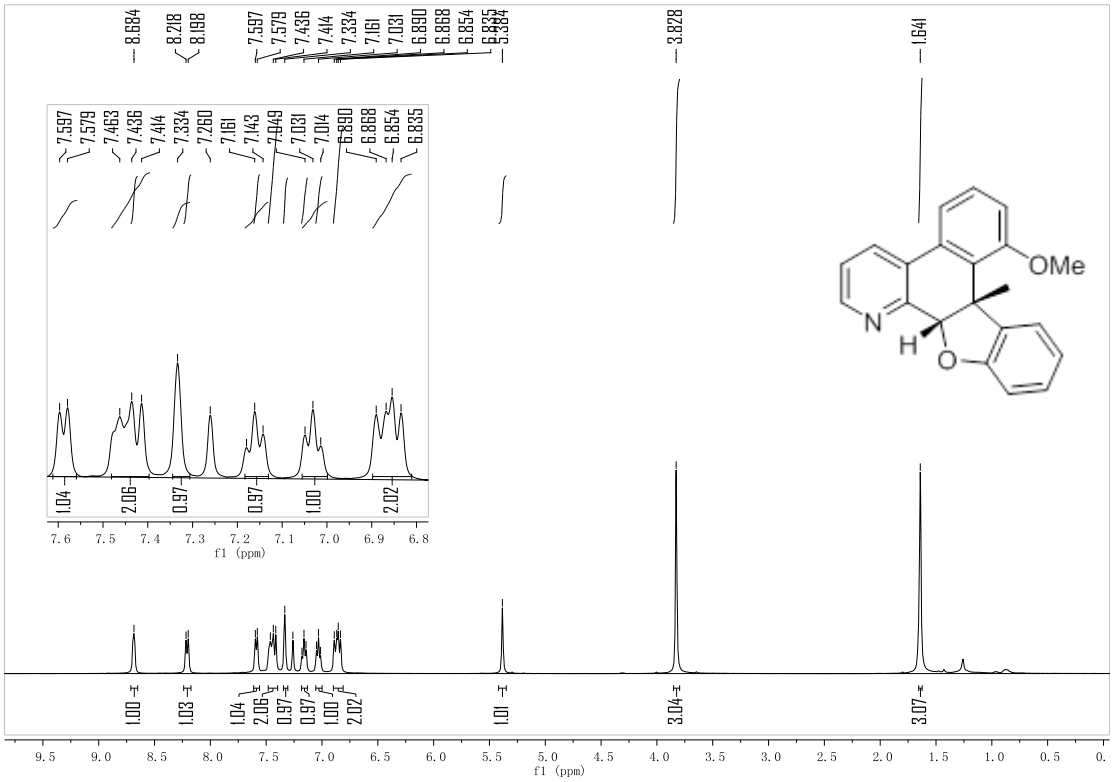


^{1}H NMR spectrum of **3q** ($CDCl_3$, 400 MHz)

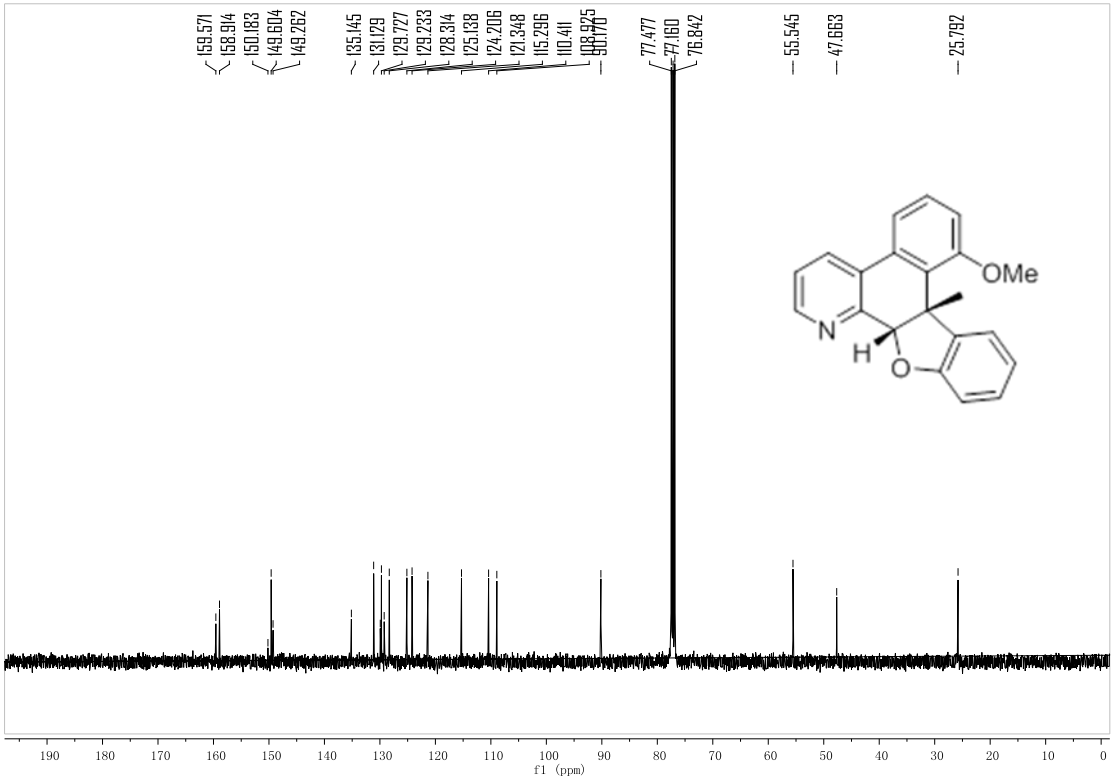


^{13}C NMR spectrum of **3q** ($CDCl_3$, 400 MHz)

3r

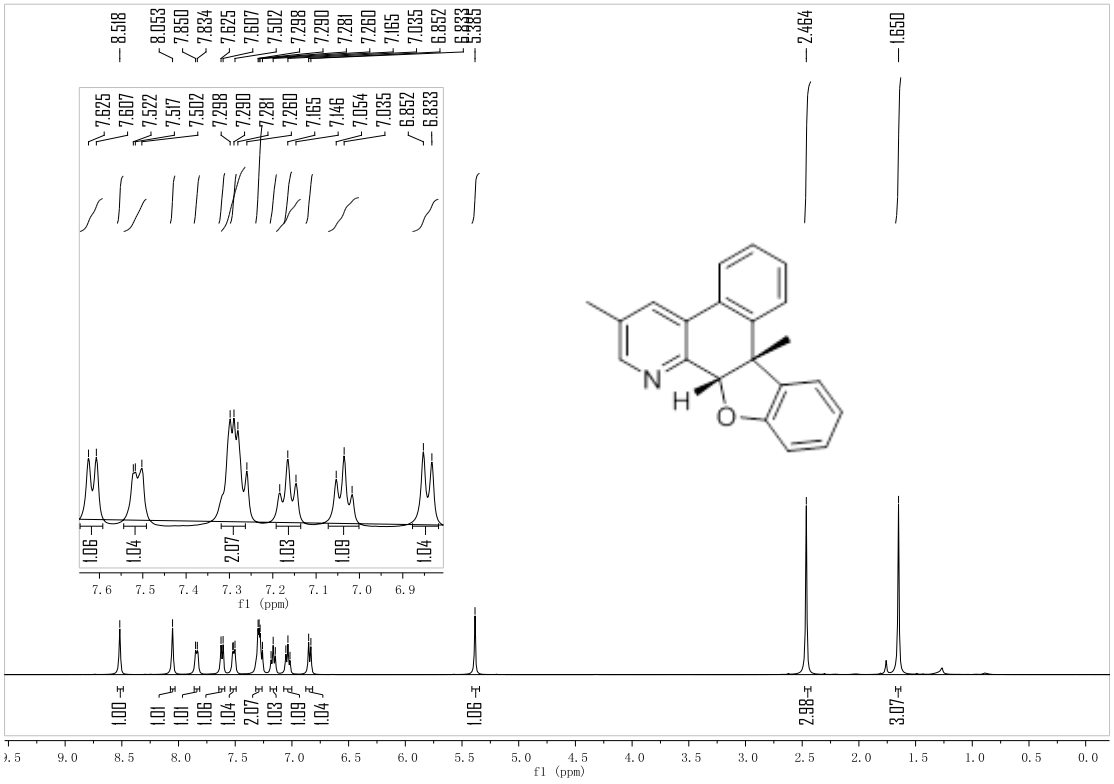


^{1}H NMR spectrum of **3r** ($CDCl_3$, 400 MHz)

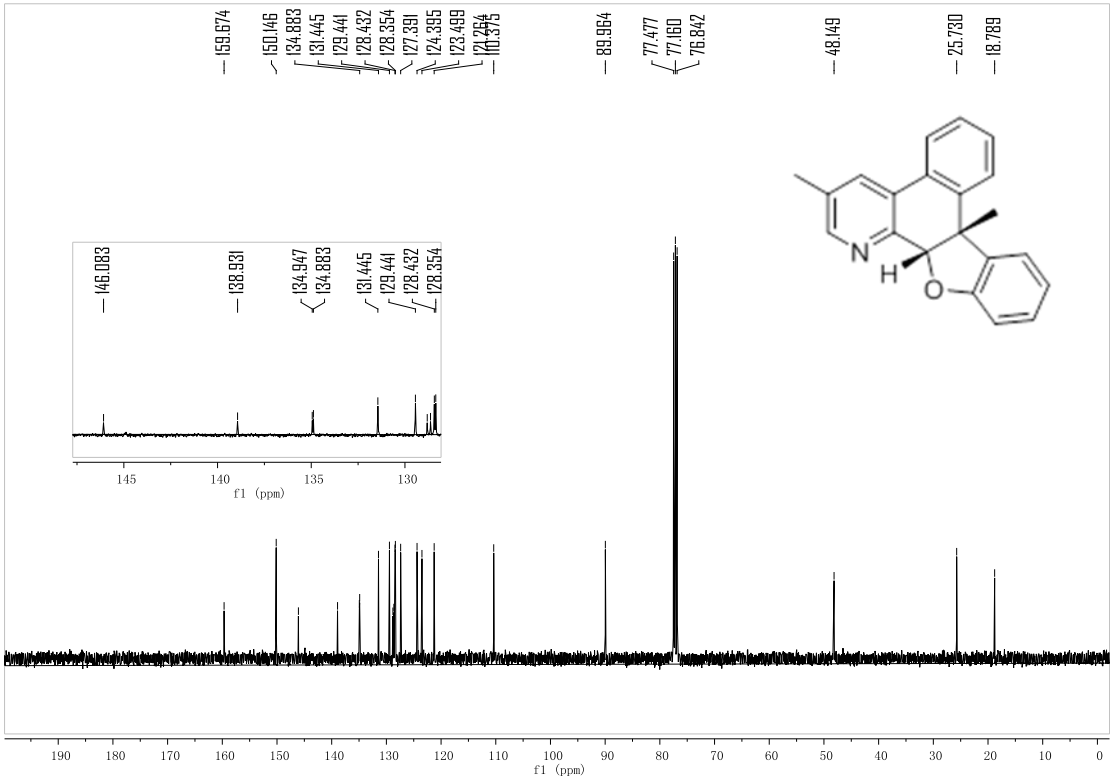


^{13}C NMR spectrum of **3r** ($CDCl_3$, 400 MHz)

3s

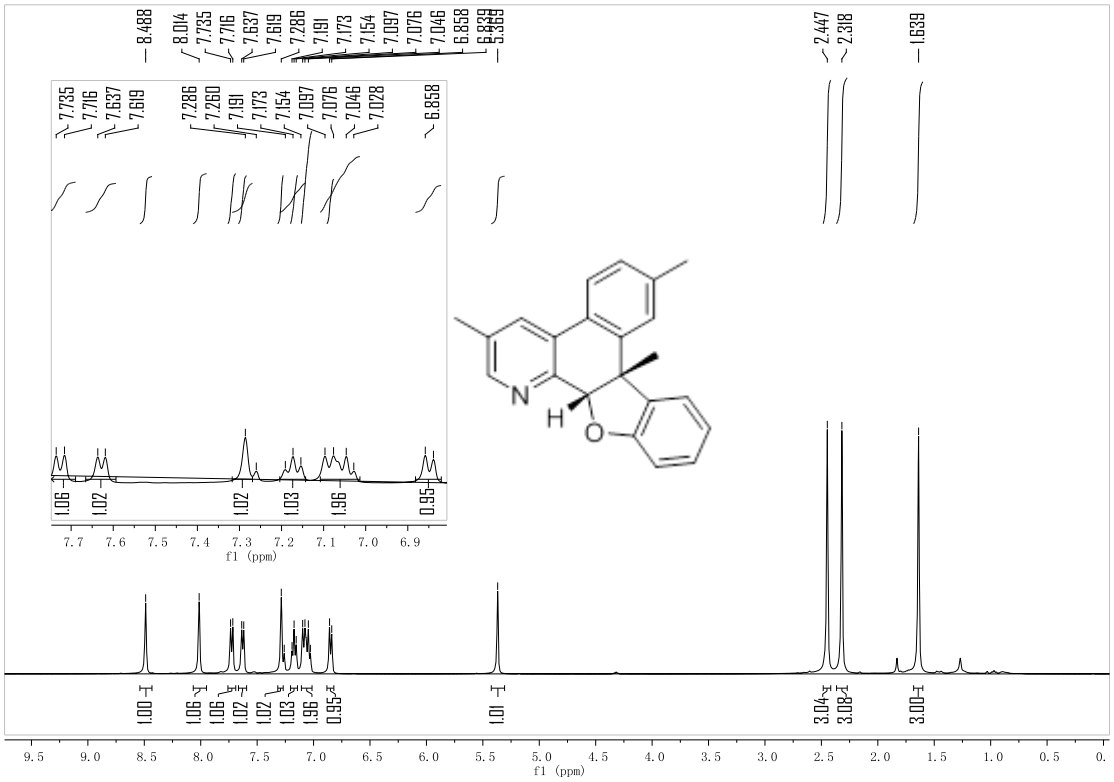


^{1}H NMR spectrum of **3s** ($CDCl_3$, 400 MHz)

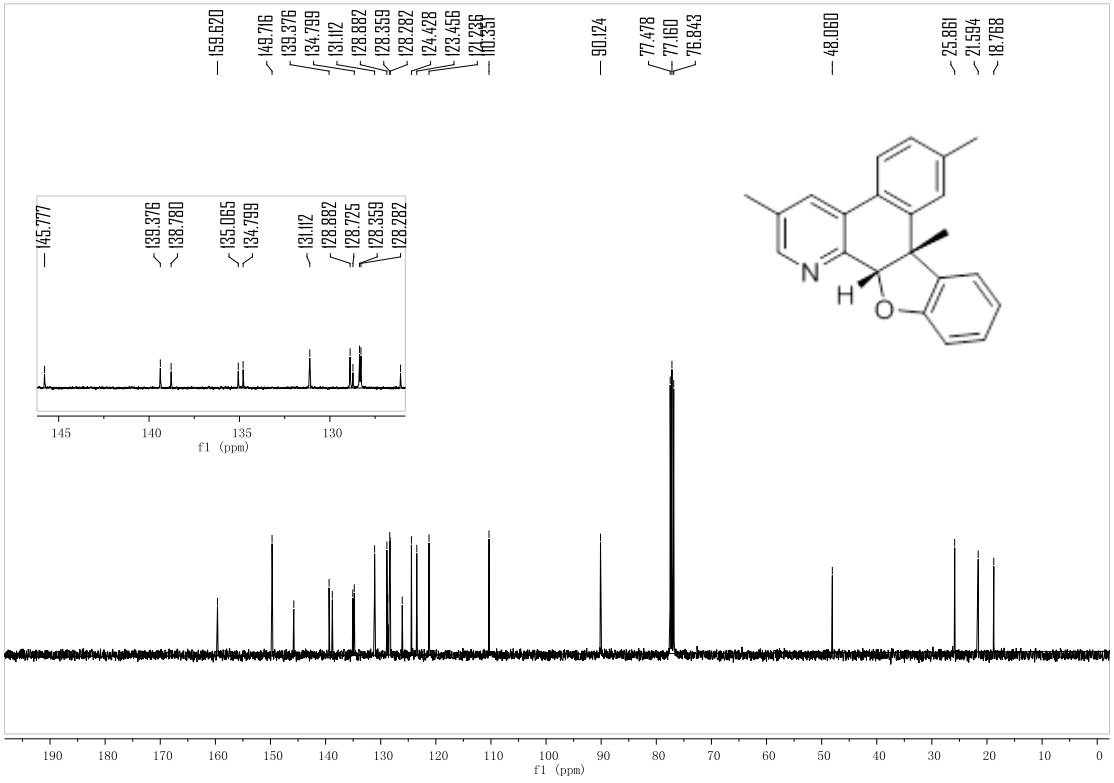


^{13}C NMR spectrum of **3s** ($CDCl_3$, 400 MHz)

3t

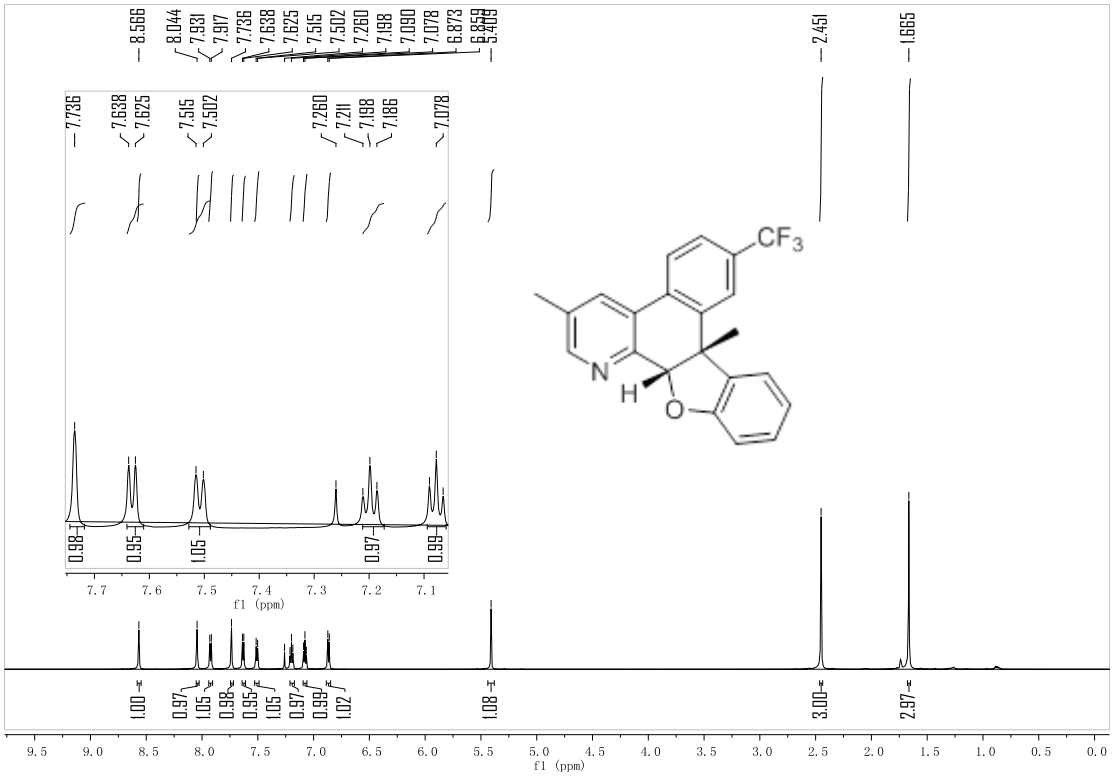


^{1}H NMR spectrum of **3t** ($CDCl_3$, 400 MHz)

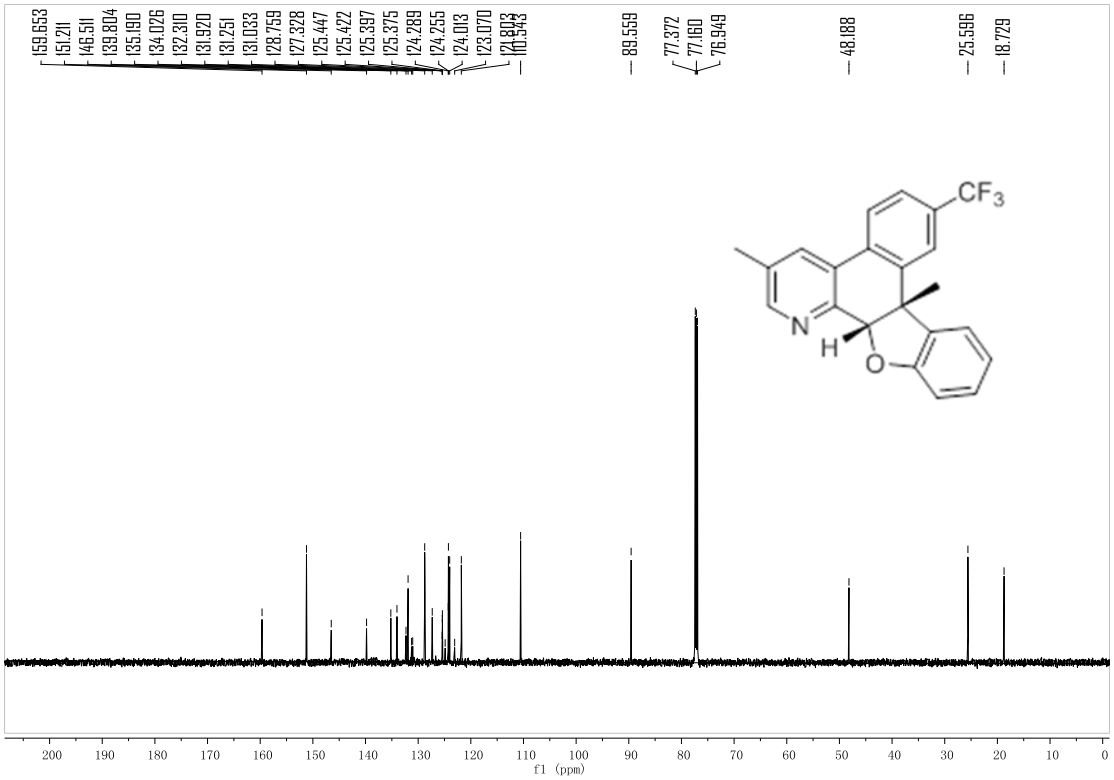


^{13}C NMR spectrum of **3t** ($CDCl_3$, 400 MHz)

3u

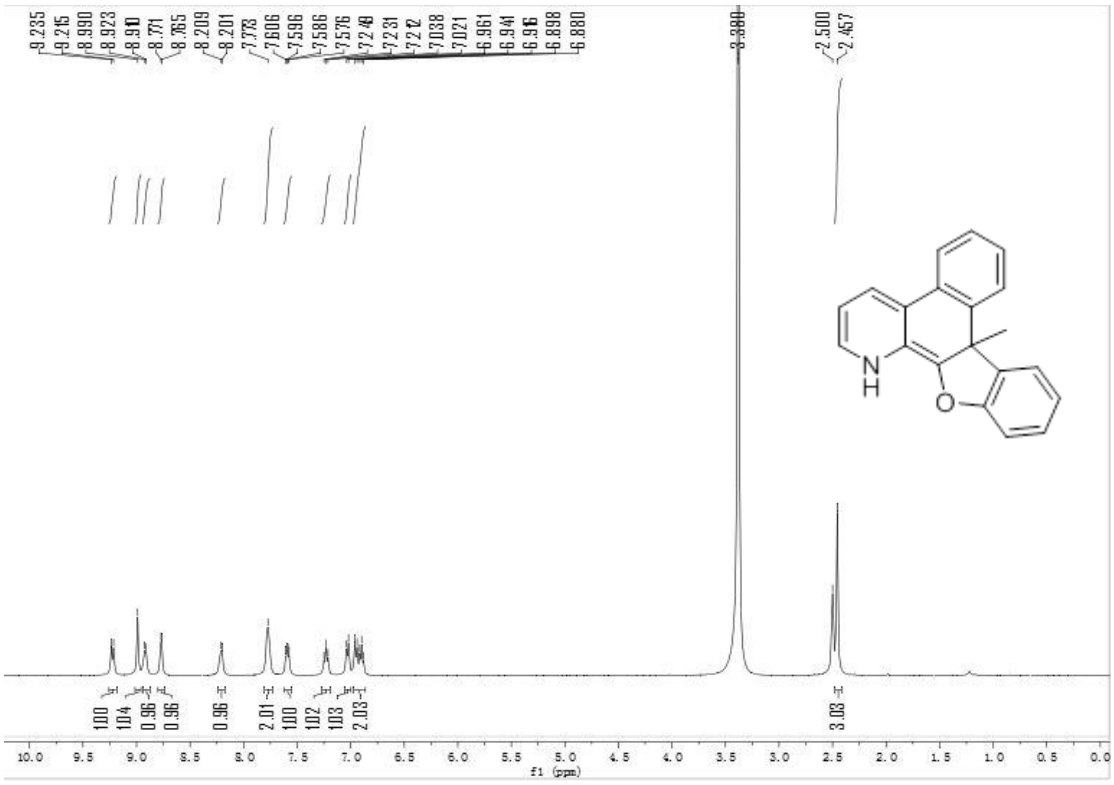


^{1}H NMR spectrum of **3u** ($CDCl_3$, 600 MHz)



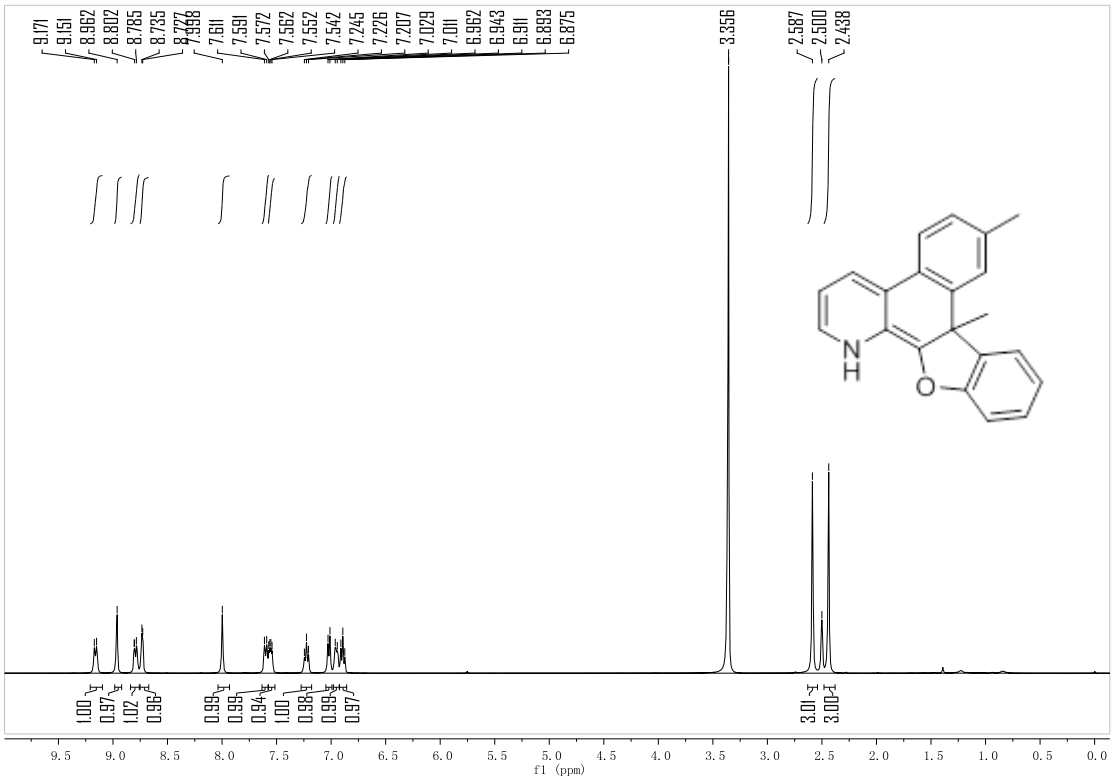
^{13}C NMR spectrum of **3u** ($CDCl_3$, 600 MHz)

4a

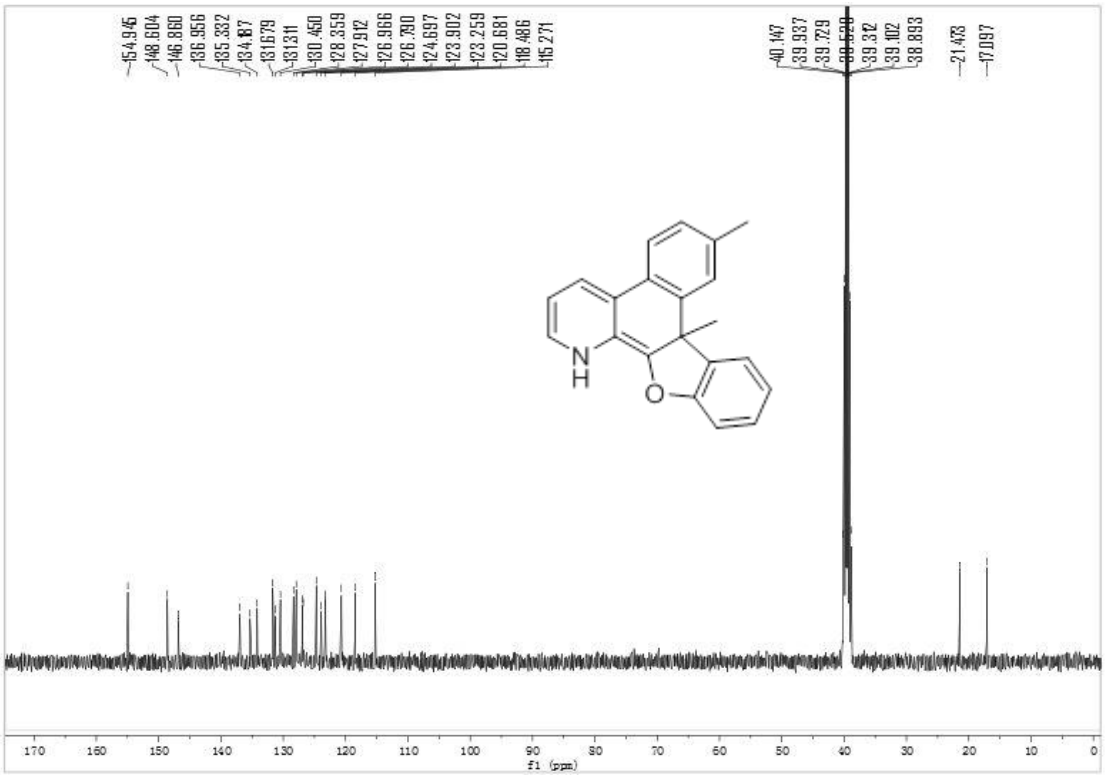


^{1}H NMR spectrum of **4a** (DMSO-d_6, 400 MHz)

4b

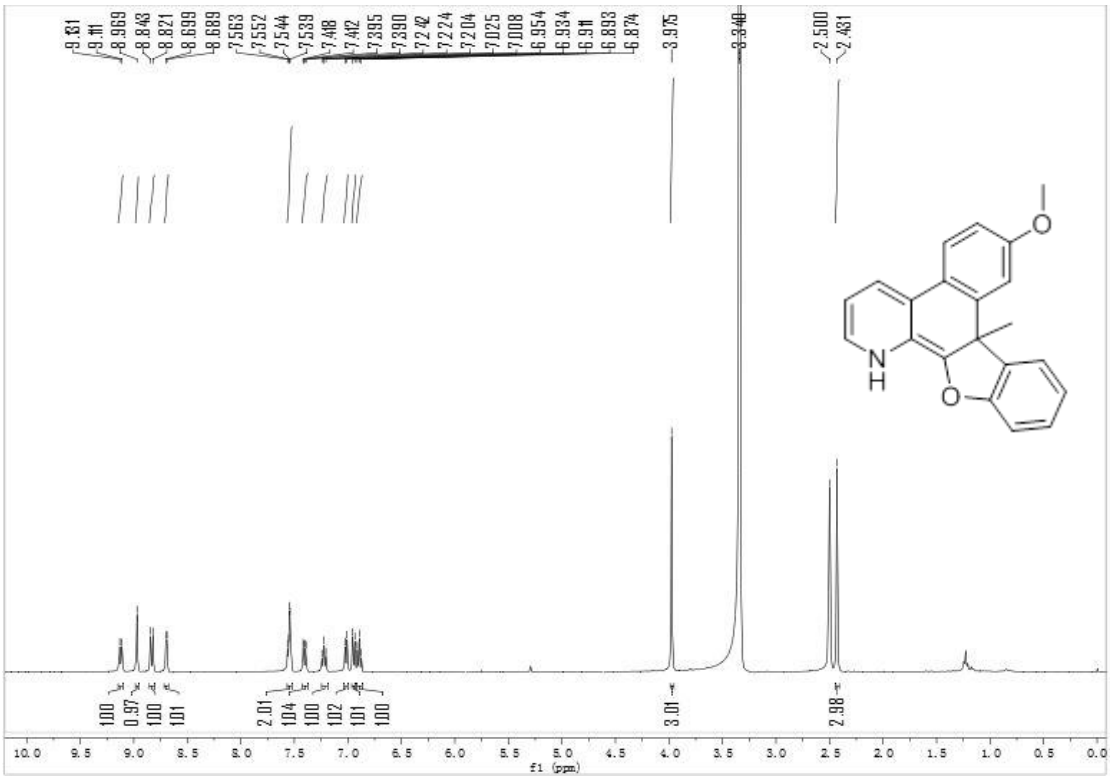


^{1}H NMR spectrum of **4b** (DMSO-d_6, 400 MHz)

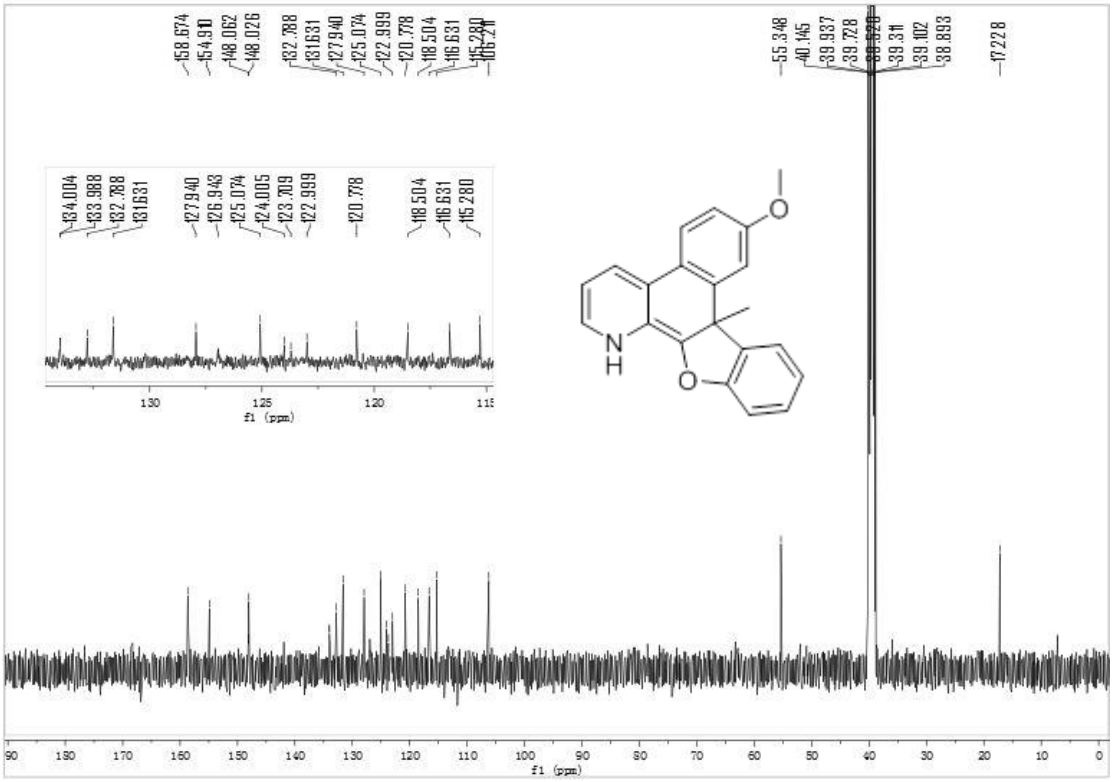


^{13}C NMR spectrum of **4b** (DMSO-d_6, 400 MHz)

4c

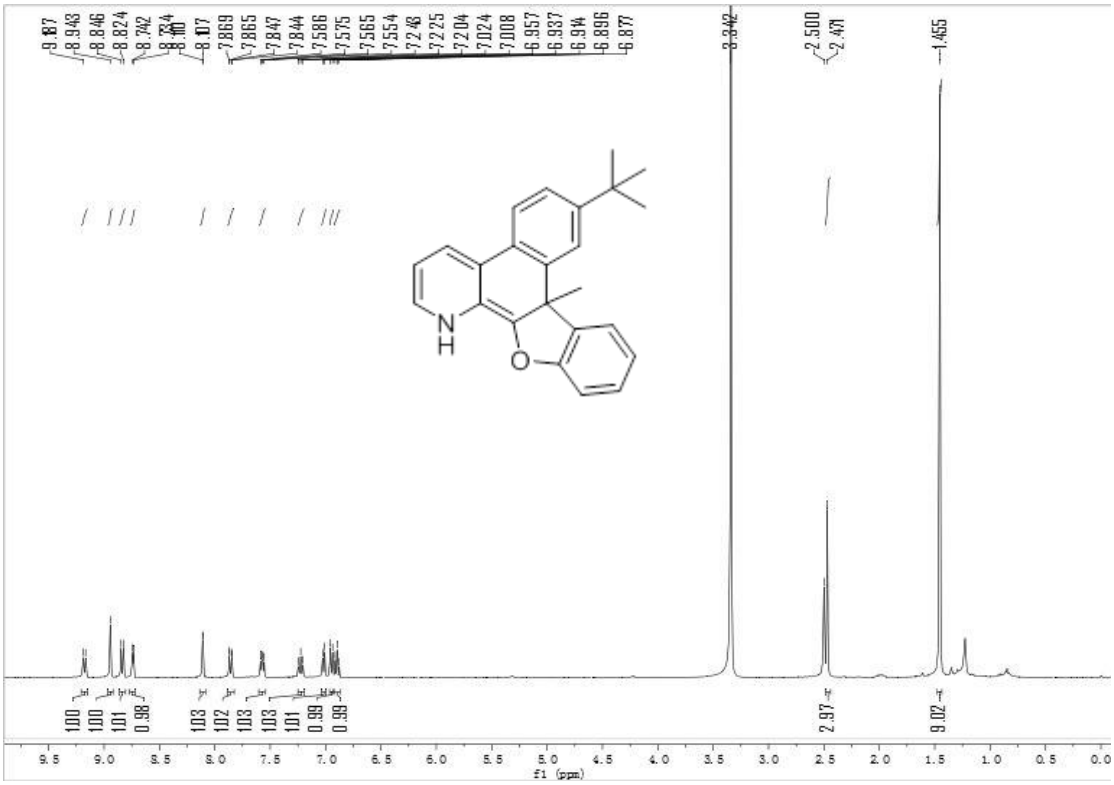


^{1}H NMR spectrum of **4c** (DMSO-d_6, 400 MHz)

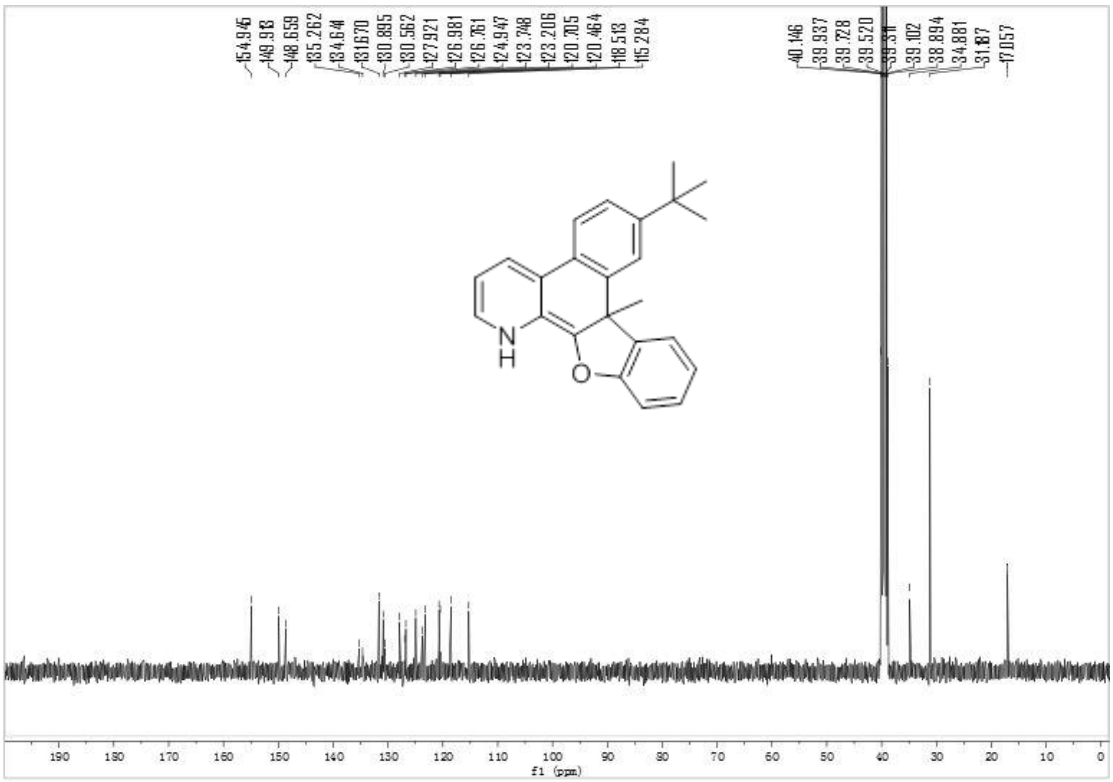


^{13}C NMR spectrum of **4c** (DMSO-d_6, 400 MHz)

4d

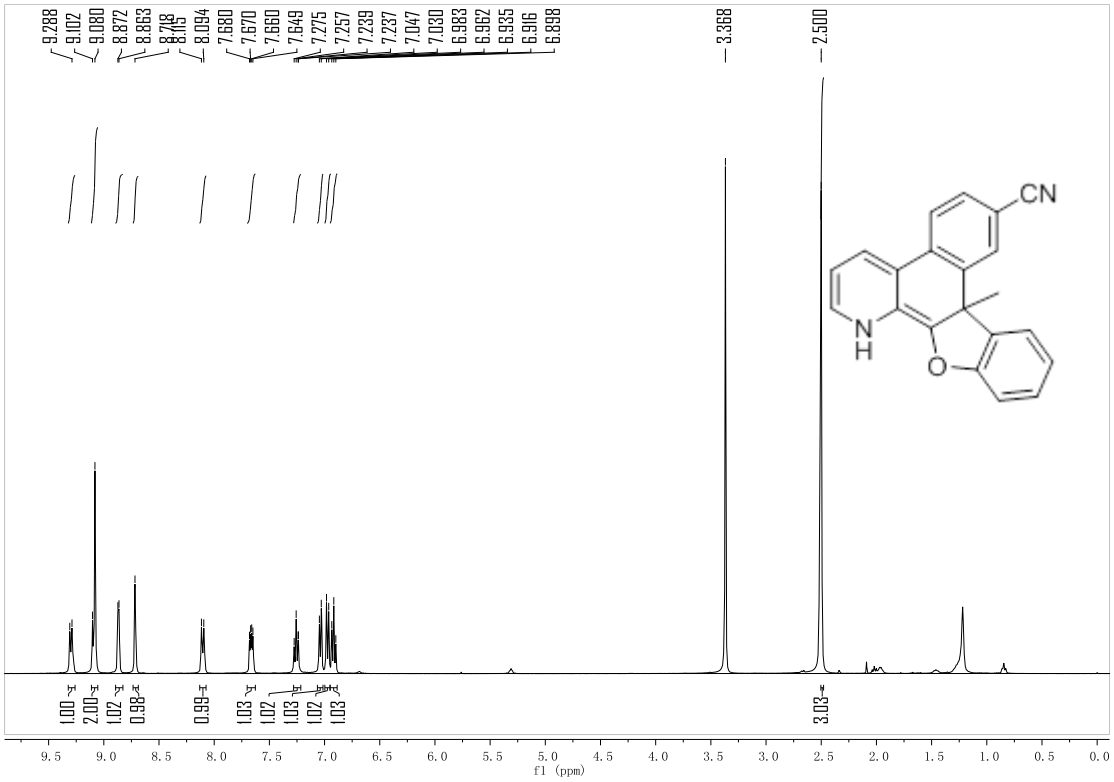


^{1}H NMR spectrum of **4d** (DMSO-d_6, 400 MHz)

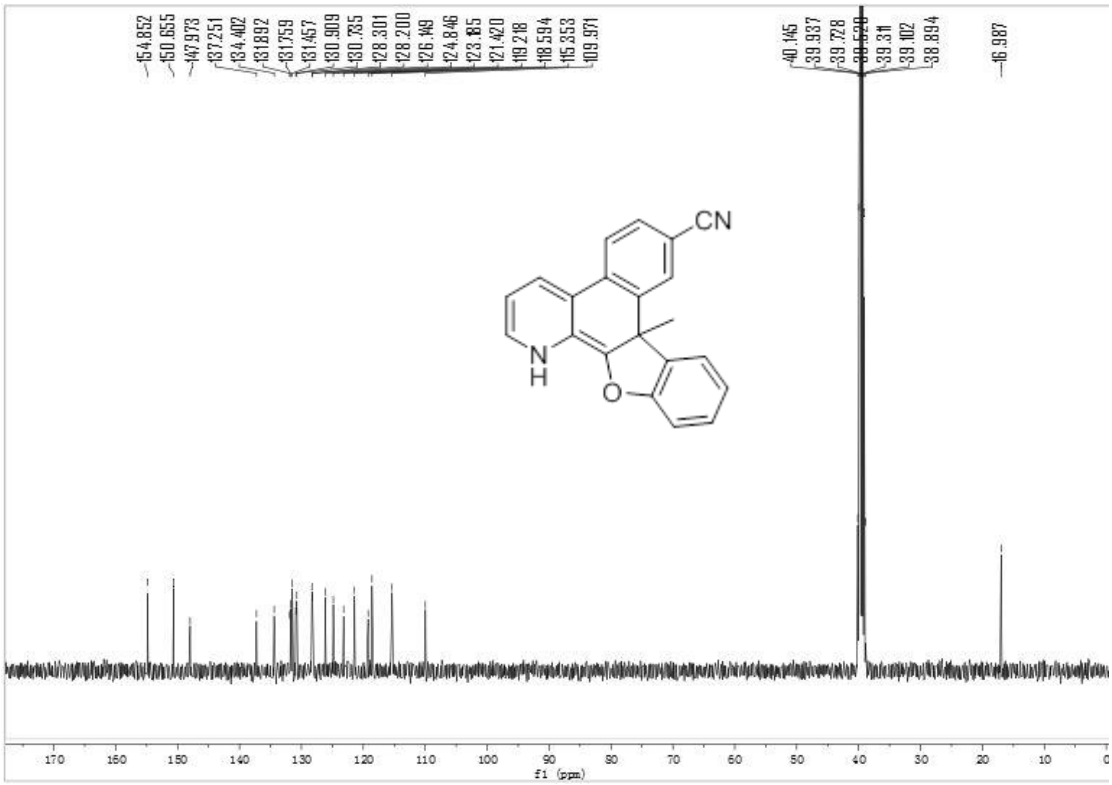


^{13}C NMR spectrum of **4d** (DMSO-d_6, 400 MHz)

4e

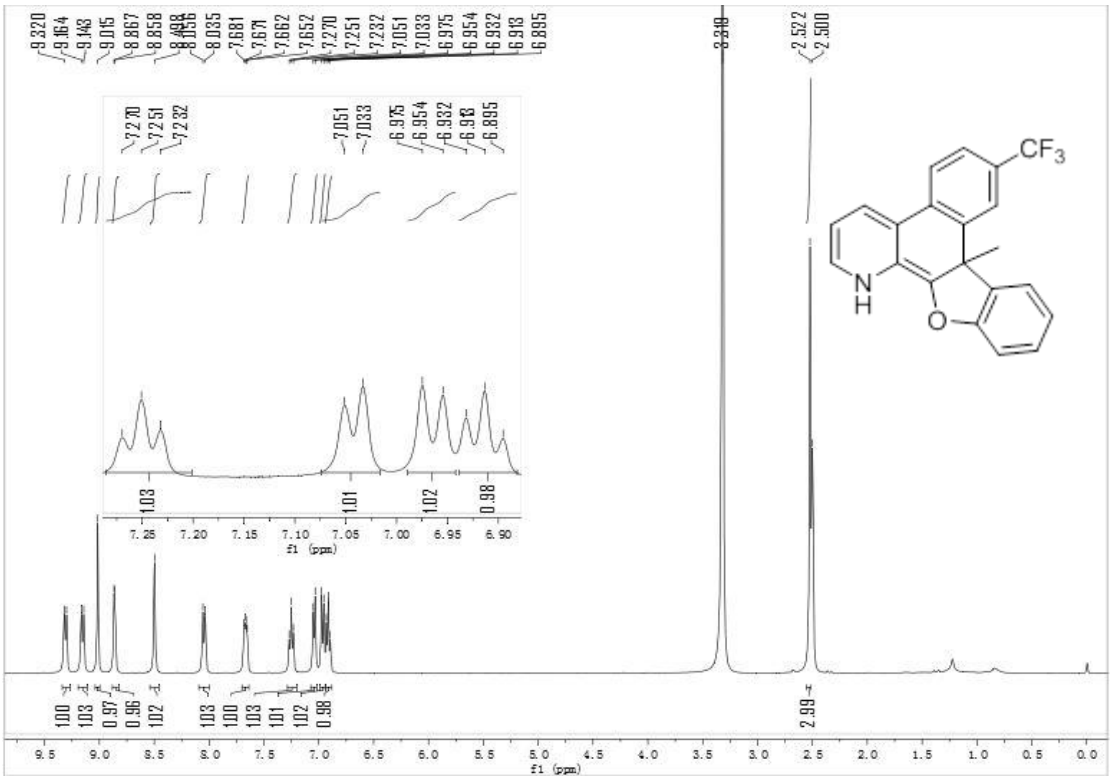


^{1}H NMR spectrum of **4e** (DMSO-d_6, 400 MHz)

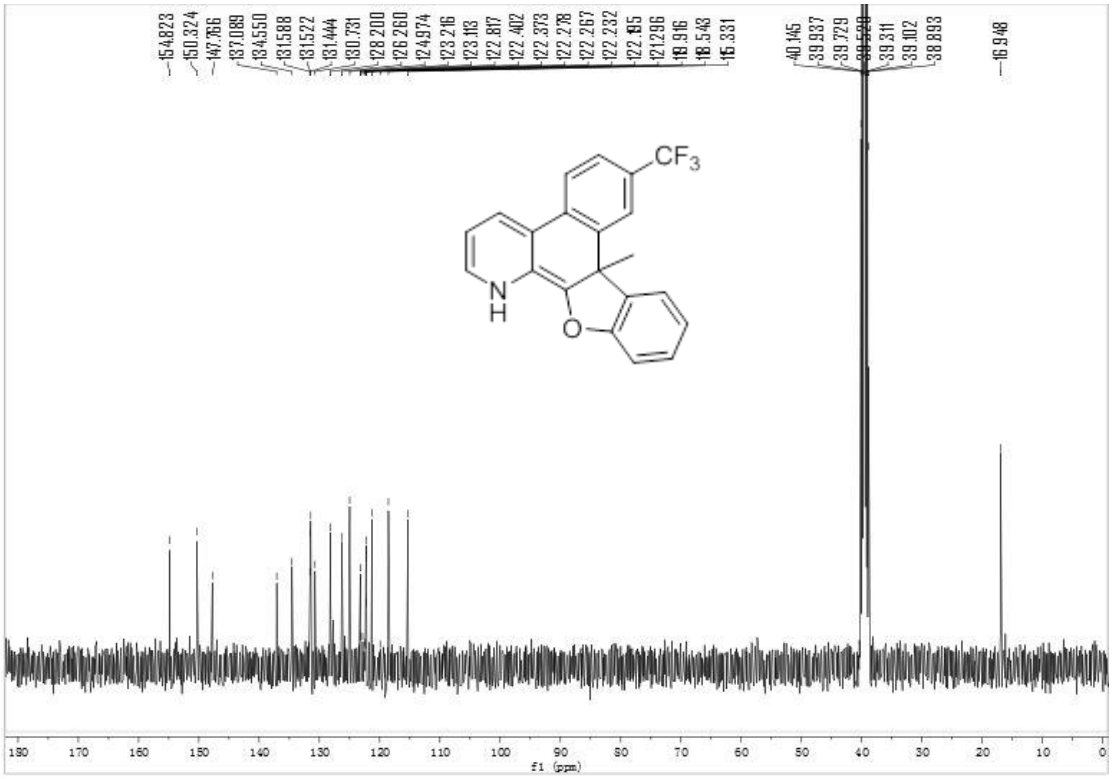


^{13}C NMR spectrum of **4e** (DMSO-d_6, 400 MHz)

4f

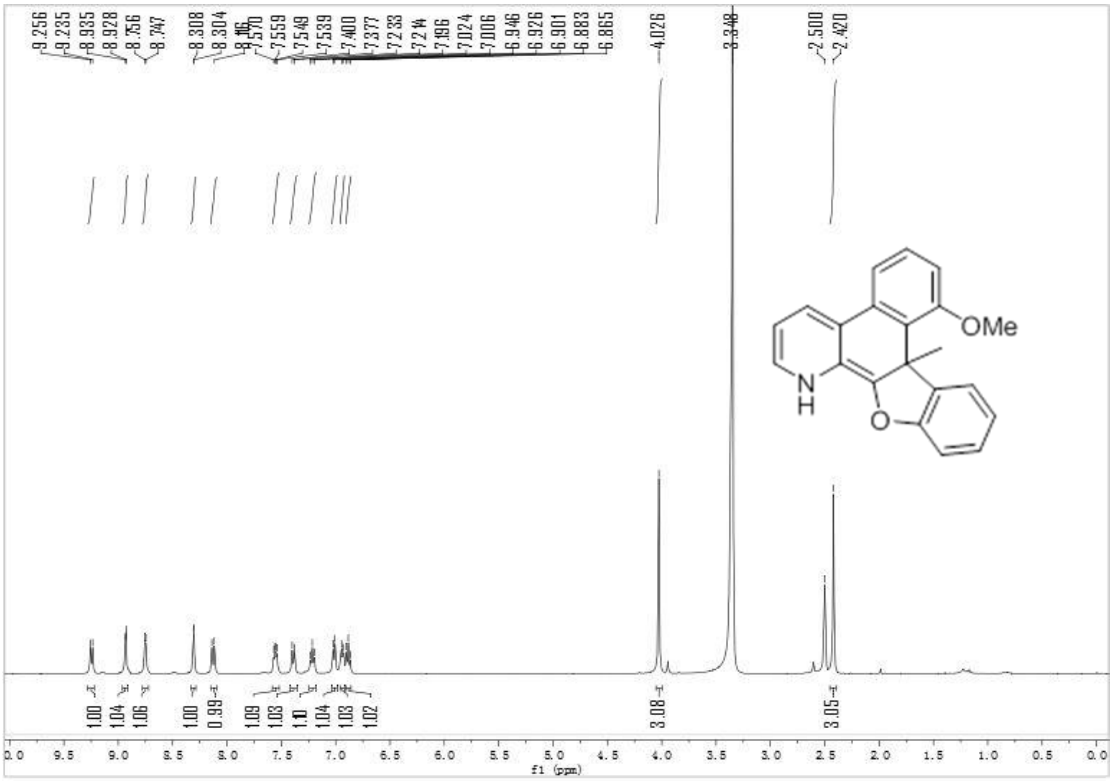


^{1}H NMR spectrum of **4f** (DMSO-d_6, 400 MHz)

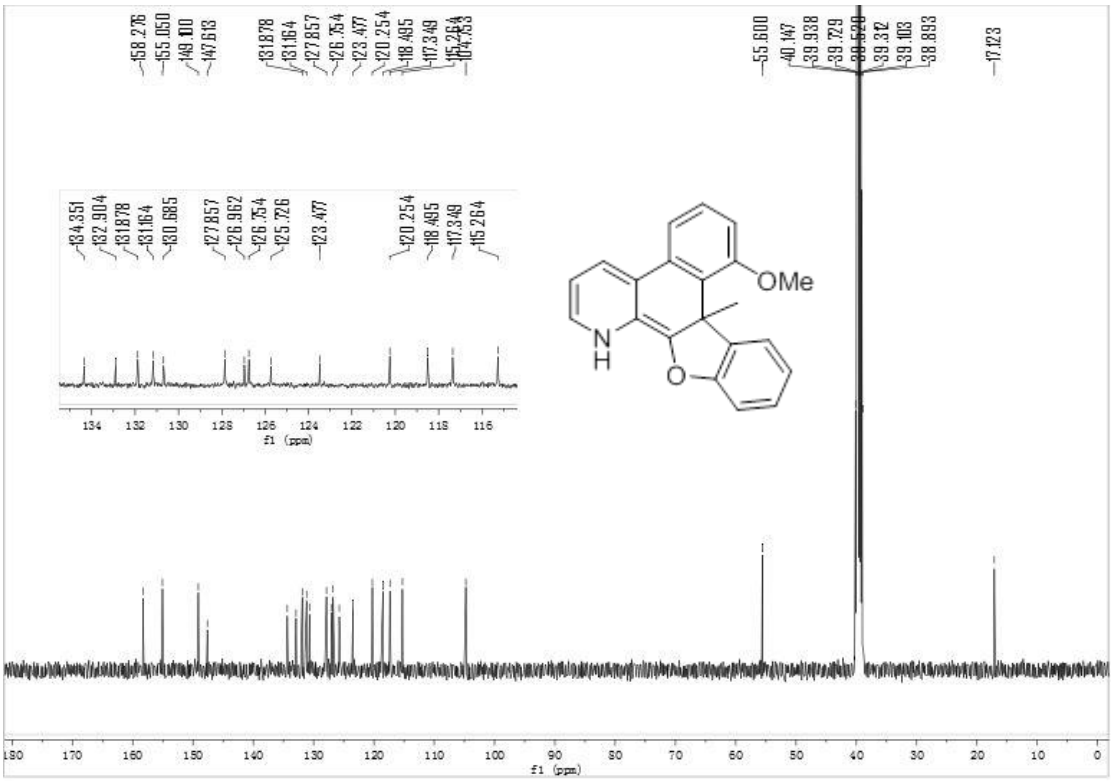


^{13}C NMR spectrum of **4f** (DMSO-d_6, 400 MHz)

4g

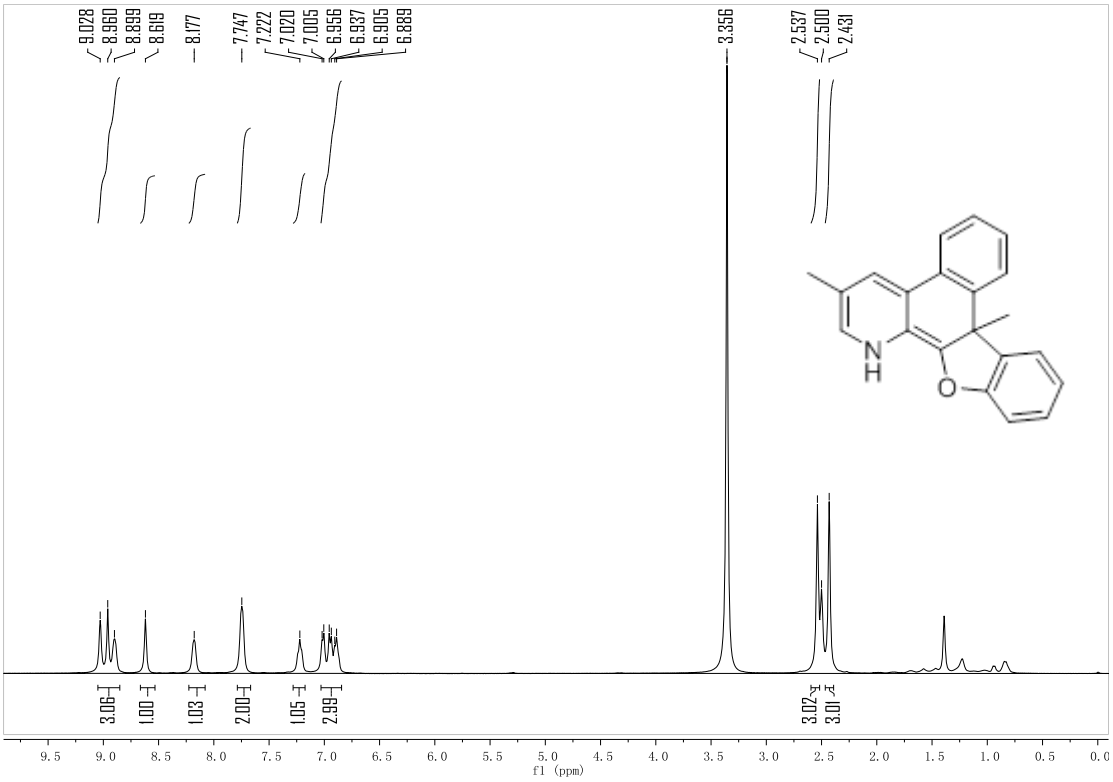


^{1}H NMR spectrum of **4g** (DMSO-d_6, 400 MHz)

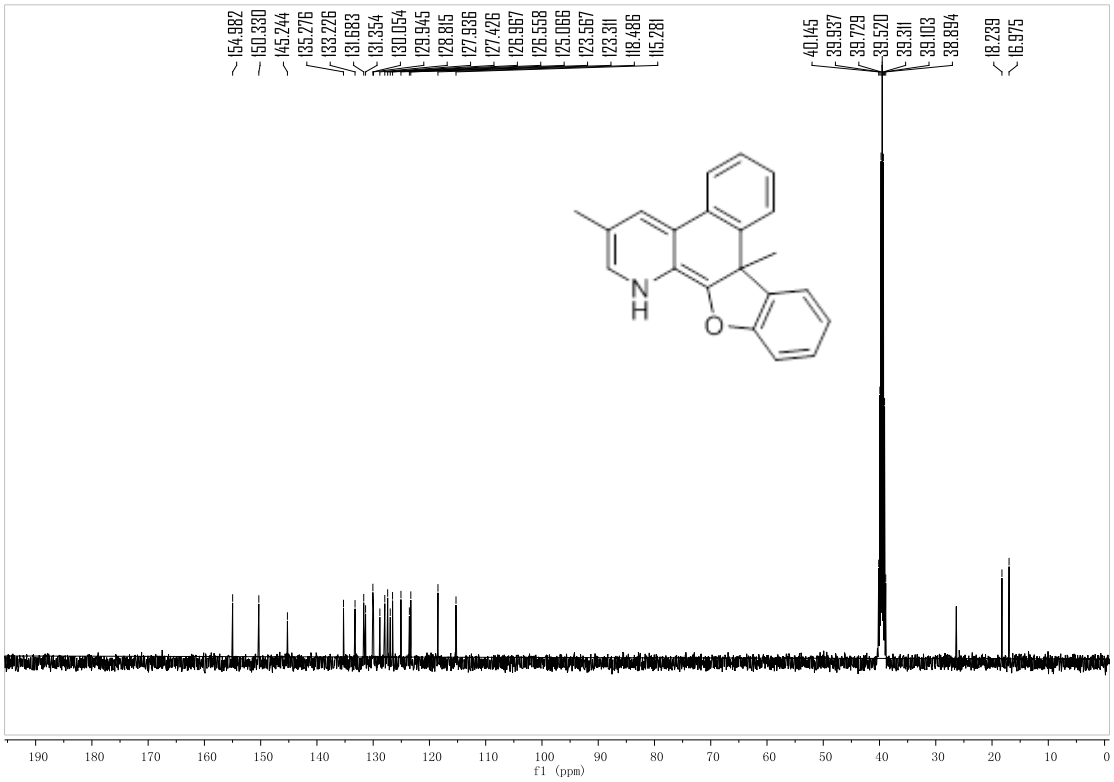


^{13}C NMR spectrum of **4g** (DMSO-d_6, 400 MHz)

4h

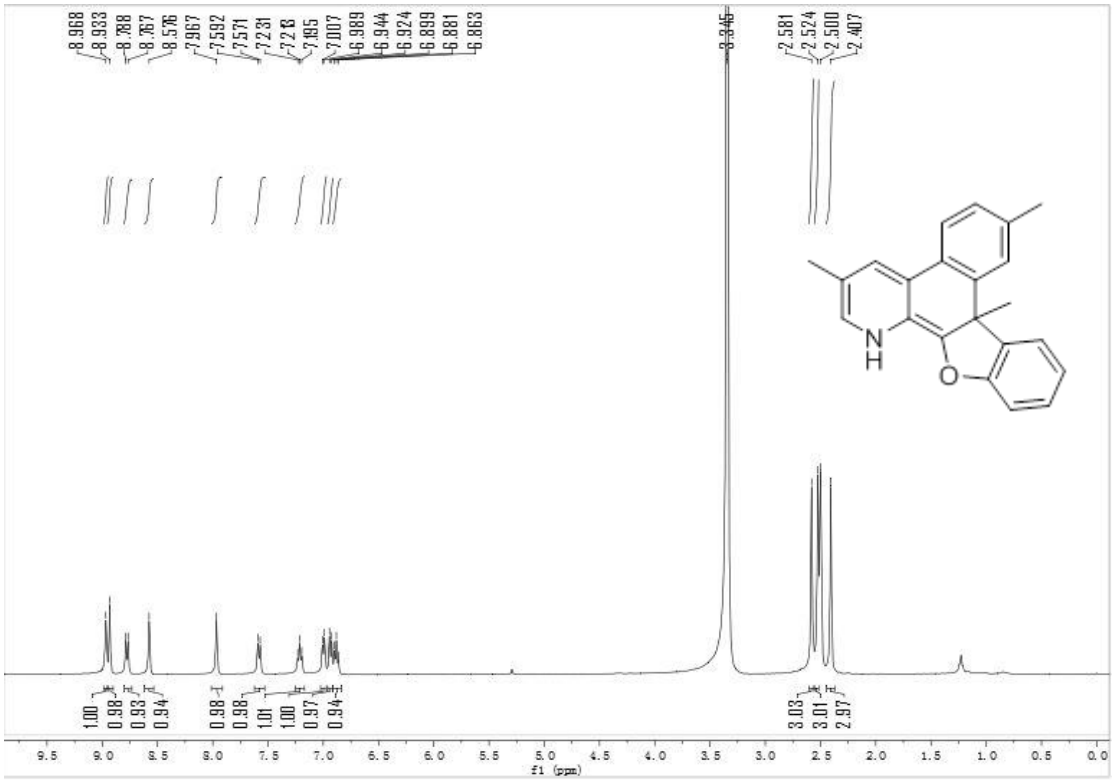


^{1}H NMR spectrum of **4h** (DMSO-d_6, 400 MHz)

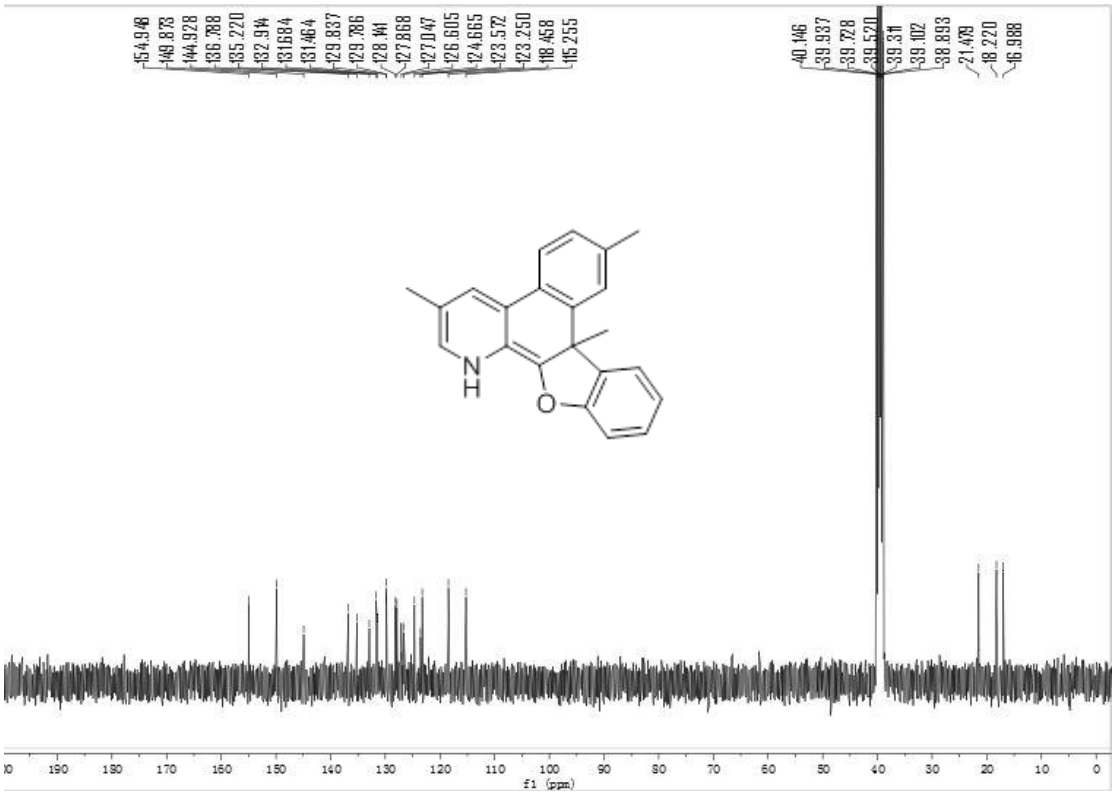


^{13}C NMR spectrum of **4h** (DMSO-d_6, 400 MHz)

4i

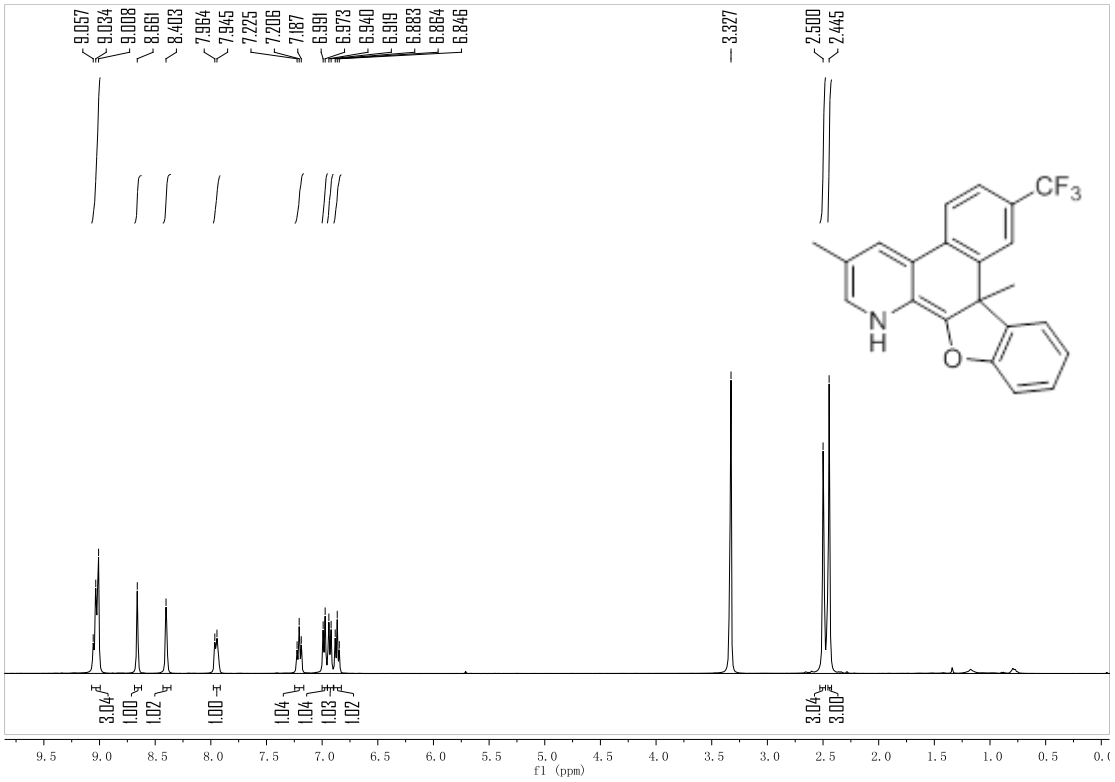


^{1}H NMR spectrum of **4i** (DMSO-d_6, 400 MHz)

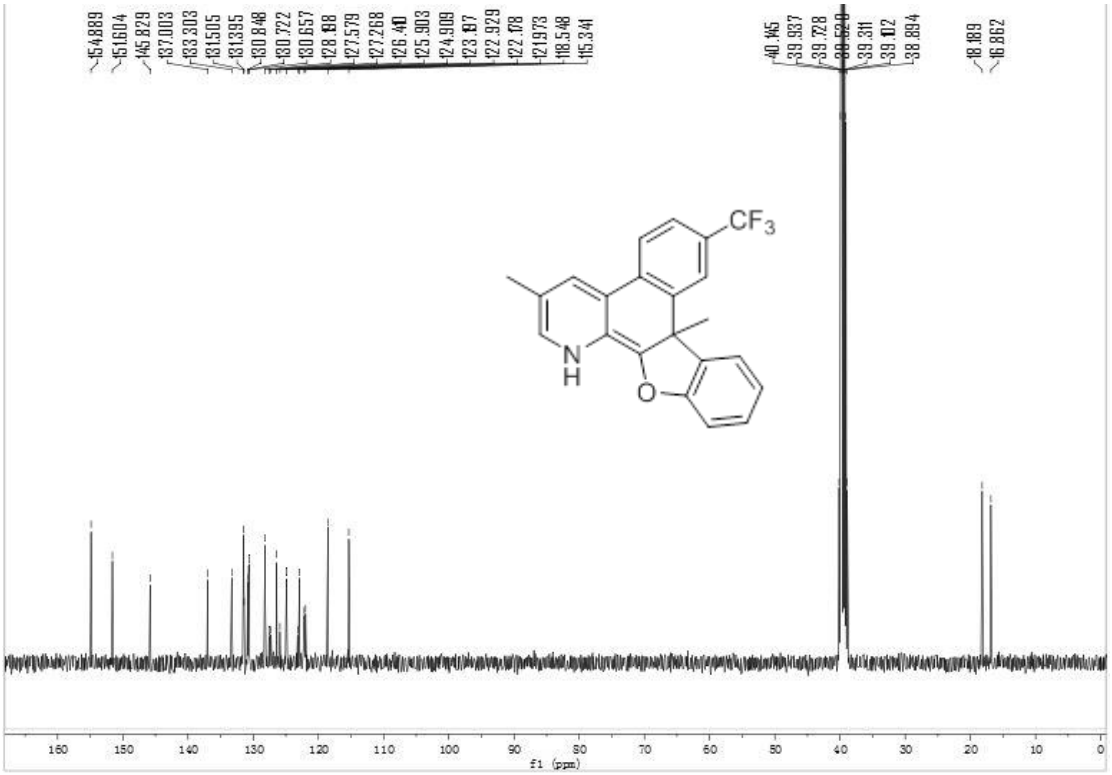


^{13}C NMR spectrum of **4i** (DMSO-d_6, 400 MHz)

4j

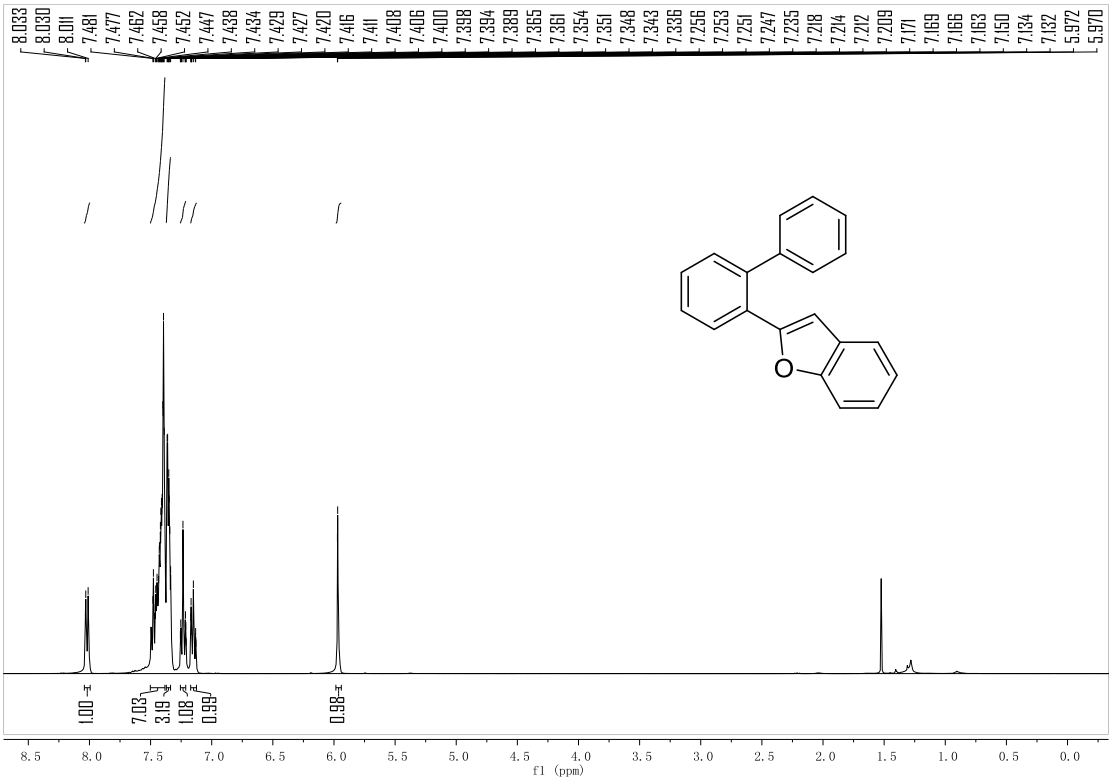


^{1}H NMR spectrum of **4j** (DMSO-d_6, 400 MHz)

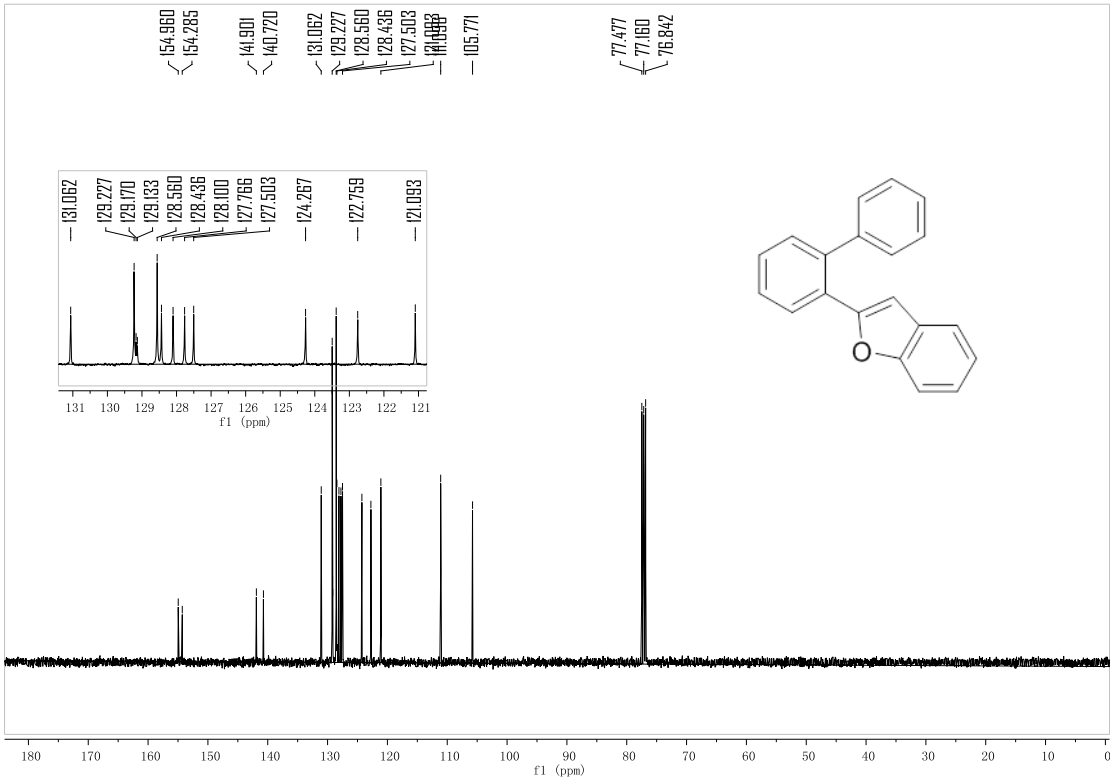


^{13}C NMR spectrum of **4j** (DMSO-d_6, 400 MHz)

6a

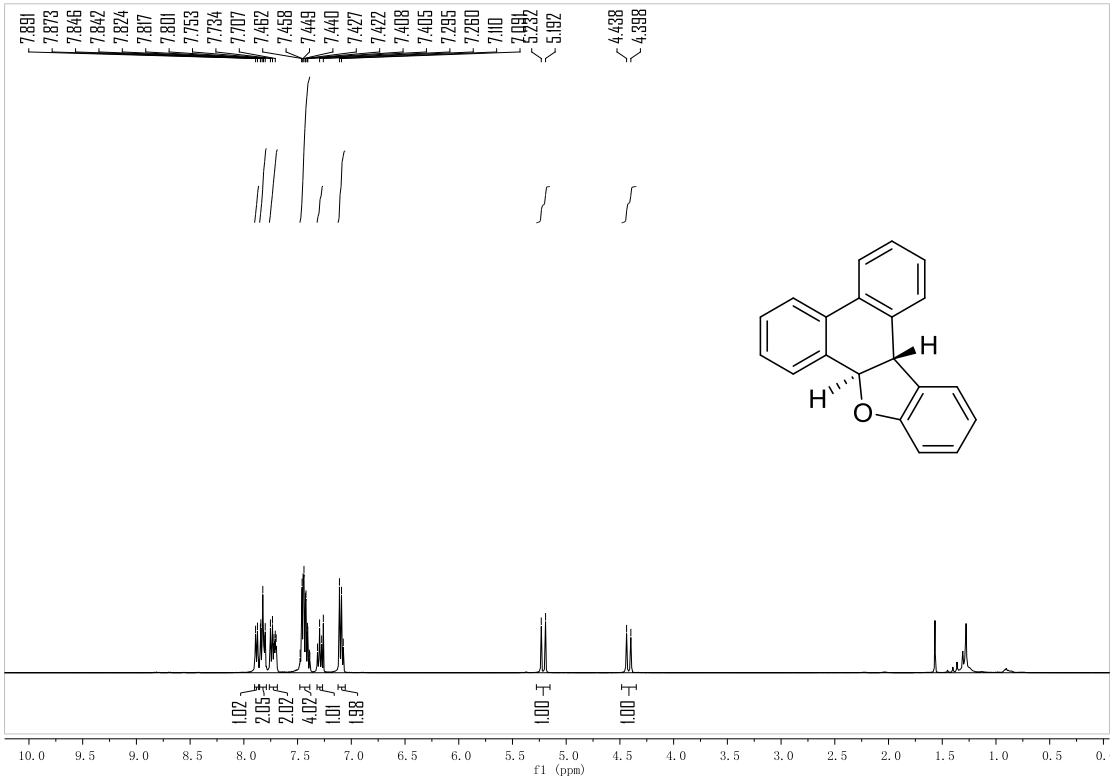


^{1}H NMR spectrum of **6a** ($CDCl_3$, 400 MHz)

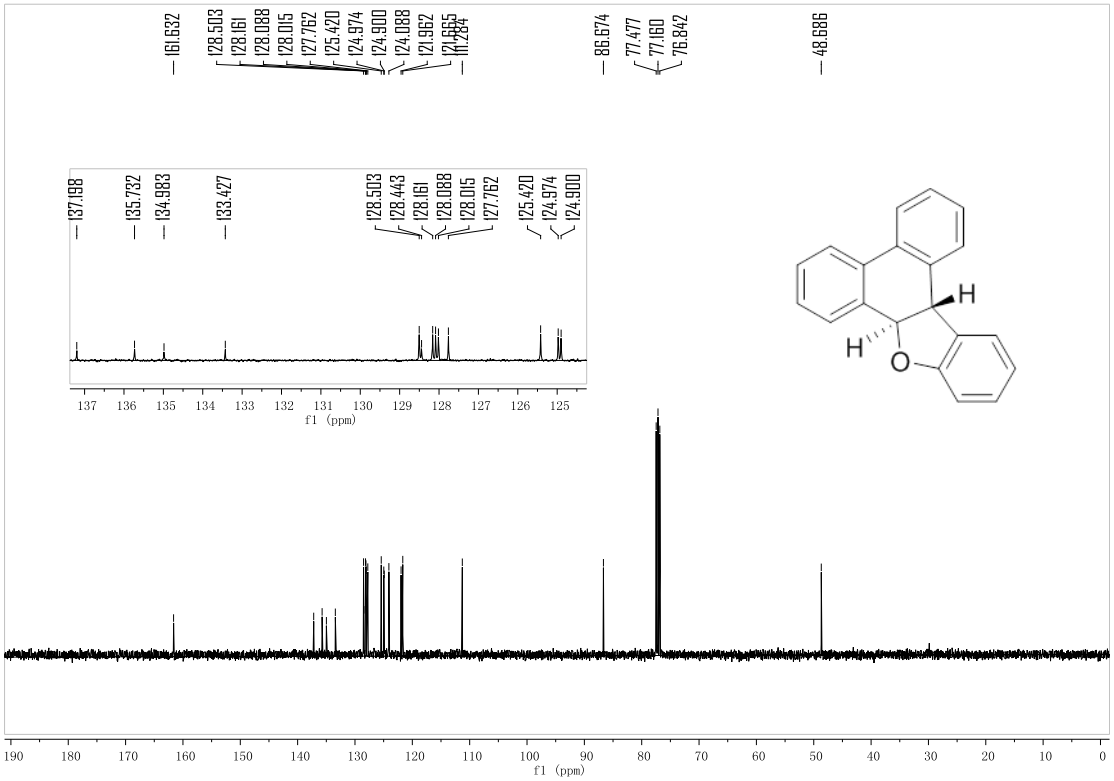


^{13}C NMR spectrum of **6a** ($CDCl_3$, 400 MHz)

6b



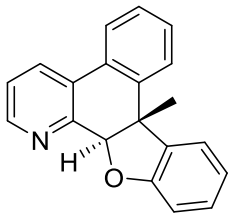
^{1}H NMR spectrum of **6b** ($CDCl_3$, 400 MHz)



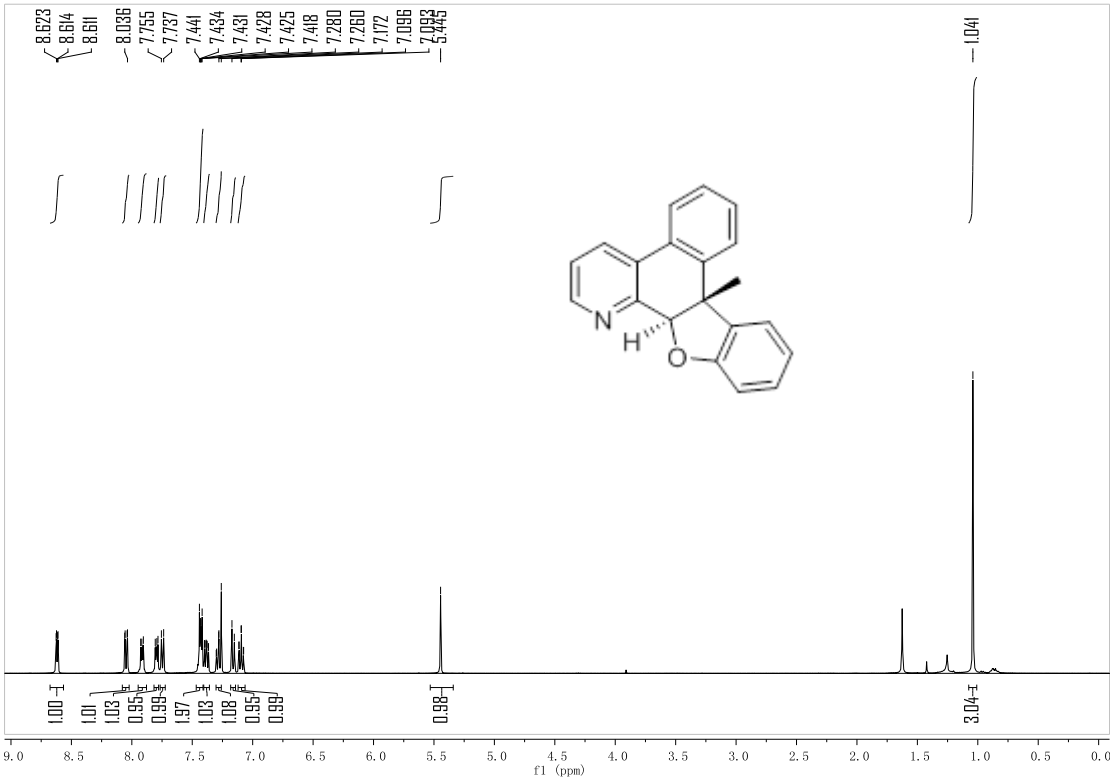
^{13}C NMR spectrum of **6b** ($CDCl_3$, 400 MHz)

8. Two-dimensional NMR of 2l

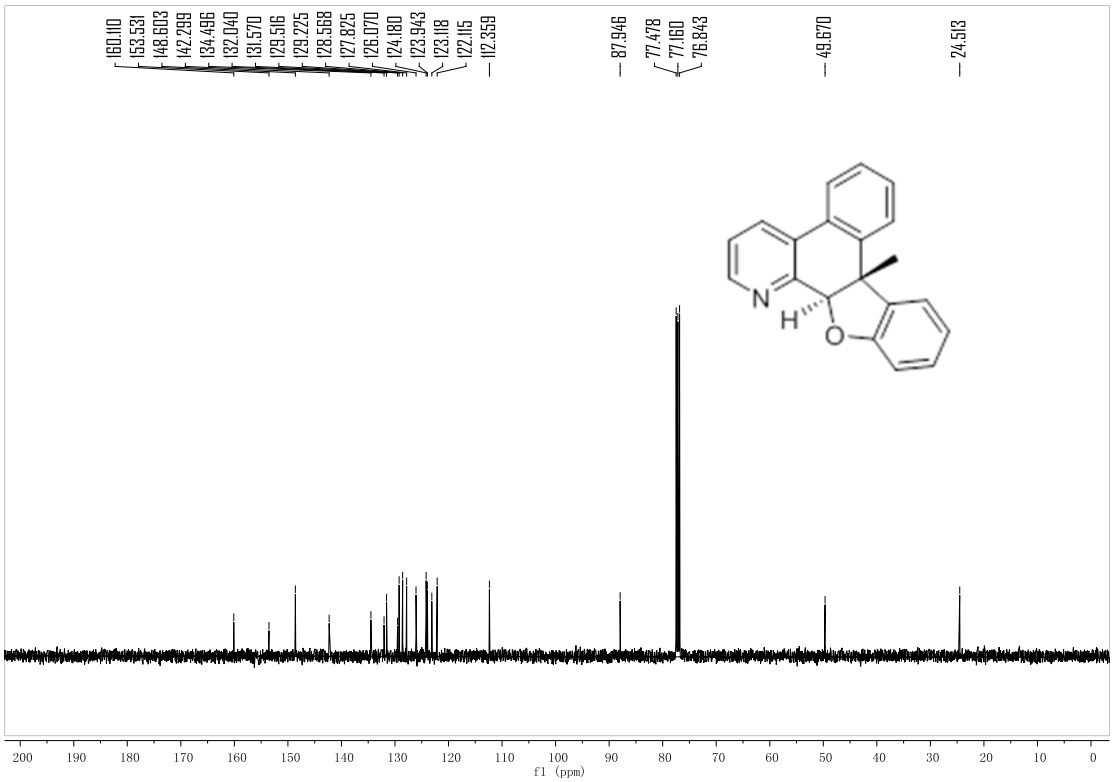
***trans*-8b-Methyl-8b,13a-dihydrobenzo[*f*]benzofuro[3,2-*h*]quinoline (2l)**



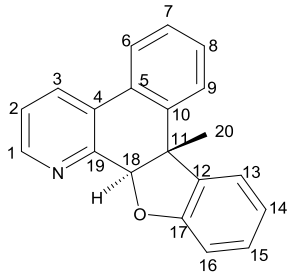
Yield: 93% (79 mg).White solid. m.p. 131.5-132.6 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.62 (dd, *J* = 4.9, 1.3 Hz, 1H), 8.05 (dd, *J* = 7.9, 1.3 Hz, 1H), 7.91 (dd, *J* = 5.8, 3.1 Hz, 1H), 7.80 (dd, *J* = 6.0, 3.1 Hz, 1H), 7.75 (d, *J* = 7.5 Hz, 1H), 7.47 – 7.41 (m, 2H), 7.38 (ddd, *J* = 7.8, 5.0, 0.7 Hz, 1H), 7.30 – 7.26 (m, 1H), 7.16 (d, *J* = 7.9 Hz, 1H), 7.09 (td, *J* = 7.5, 0.9 Hz, 1H), 5.45 (s, 1H), 1.04 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.1, 153.5, 148.6, 142.3, 134.5, 132.0, 131.6, 129.5, 129.2, 128.6, 127.8, 126.1, 124.2, 123.9, 123.1, 122.1, 112.4, 87.9, 49.7, 24.5.



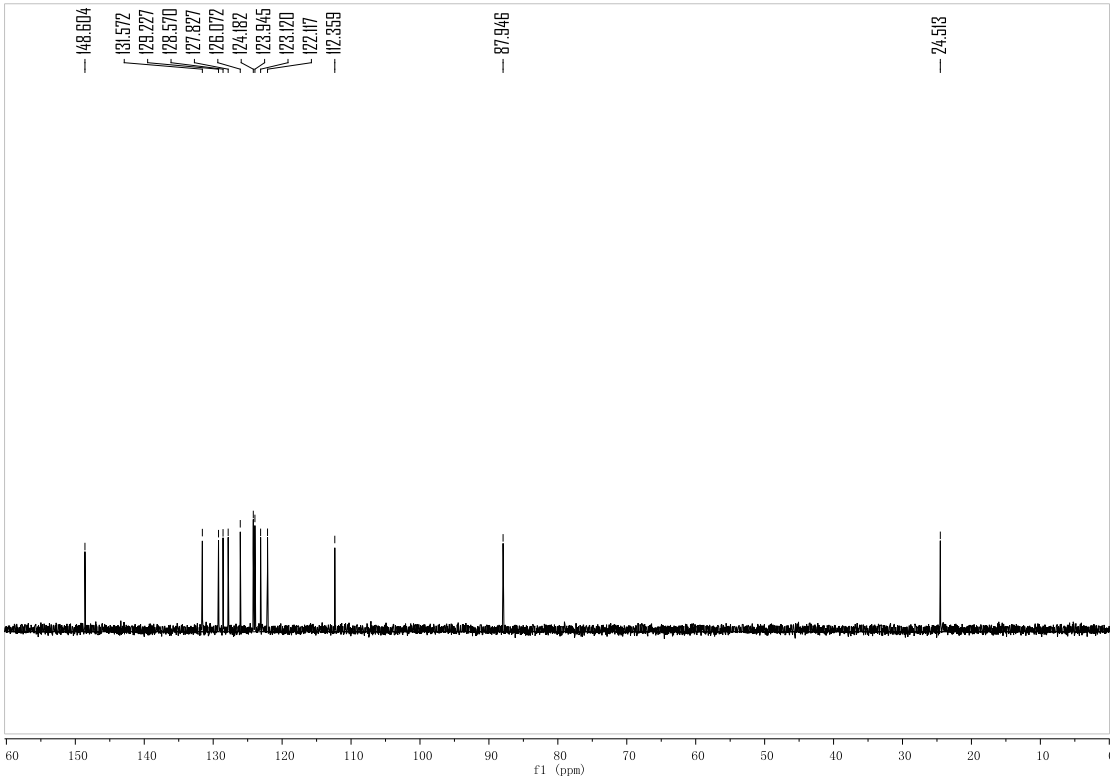
^{1}H NMR spectrum of **2l** ($CDCl_3$, 400 MHz)



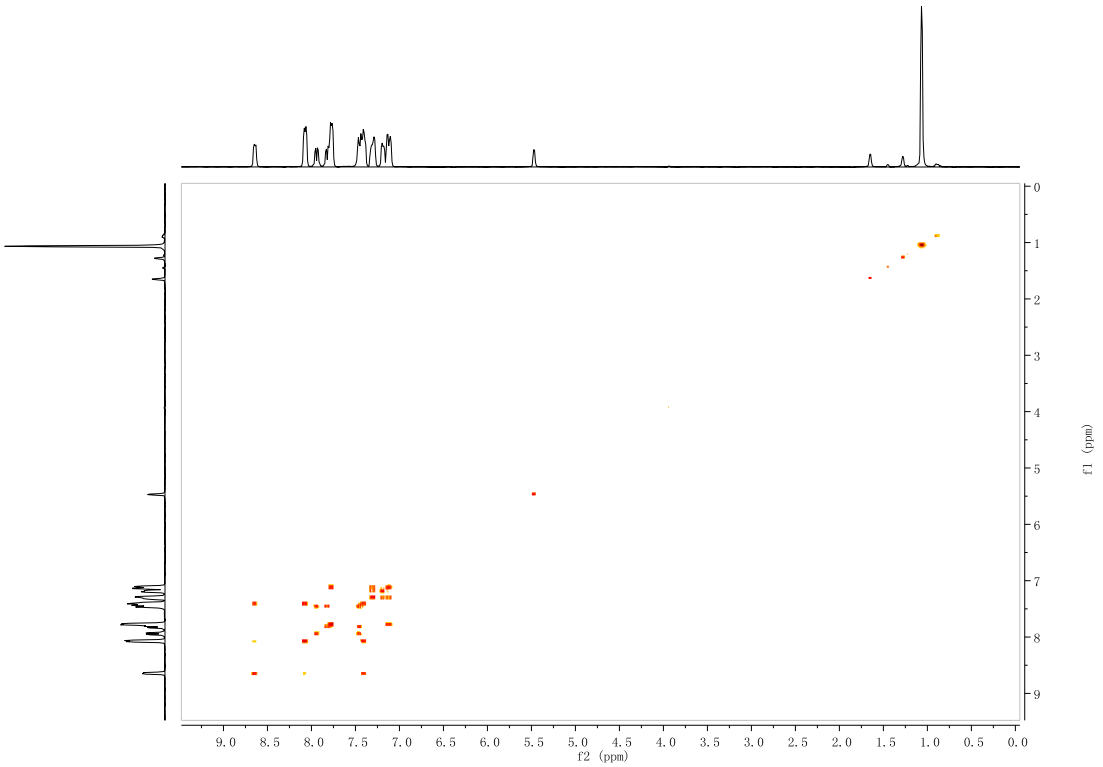
^{13}C NMR spectrum of **2l** ($CDCl_3$, 400 MHz)



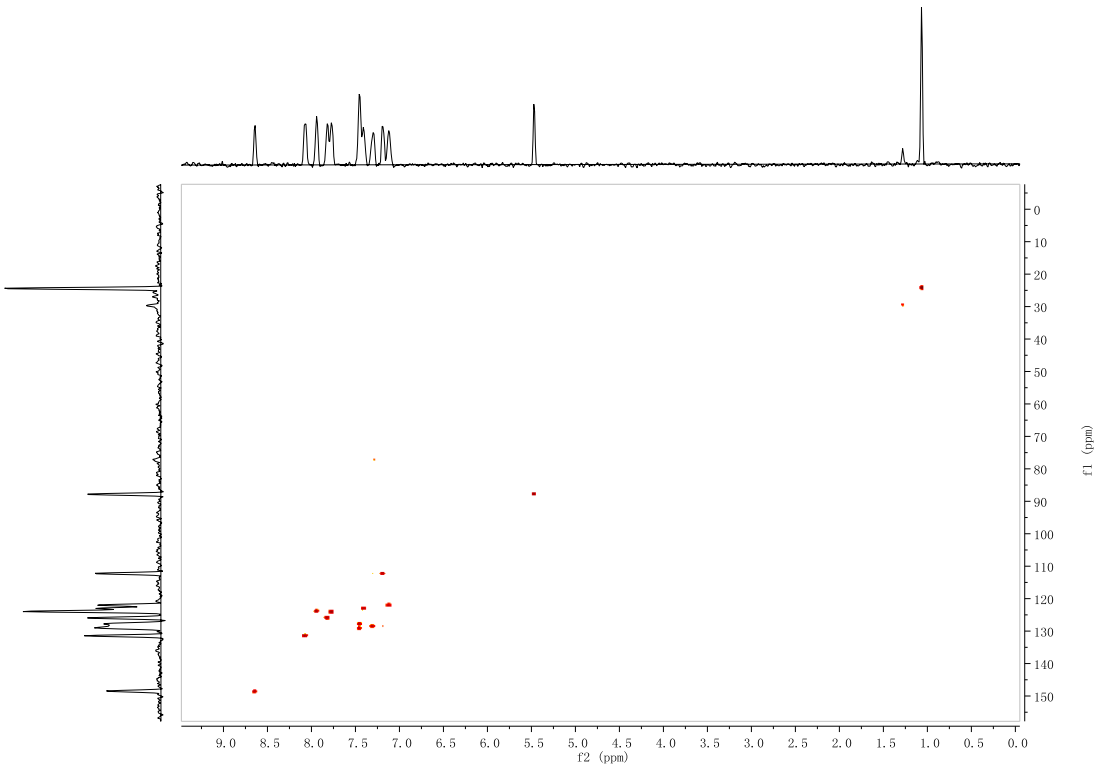
2l



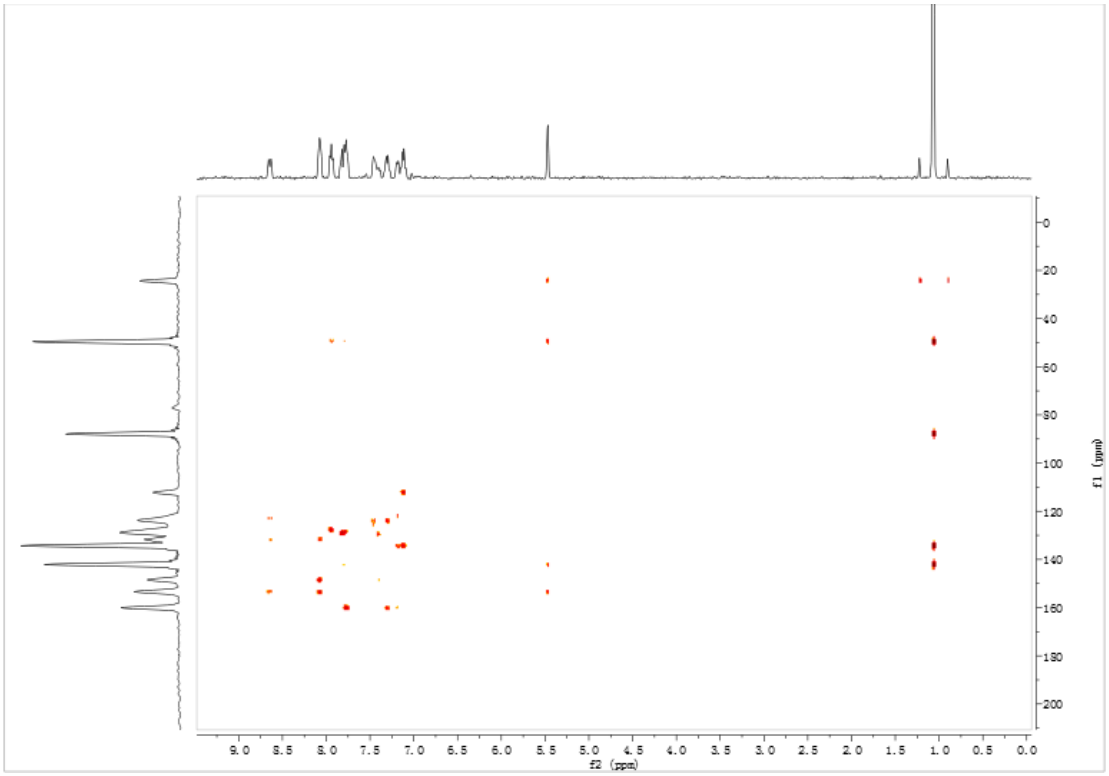
DEPT (135 ℃) spectrum of **2l** ($CDCl_3$, 400 MHz)



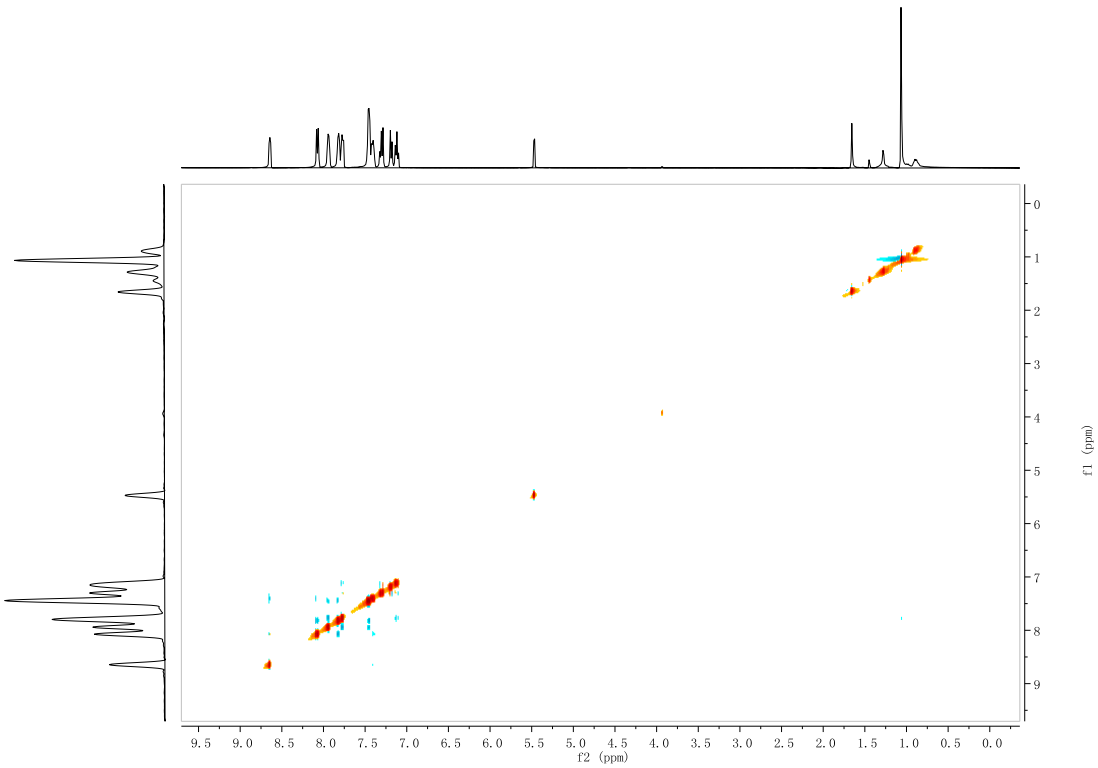
H,H-COSY spectrum of **2l** ($CDCl_3$, 400 MHz)



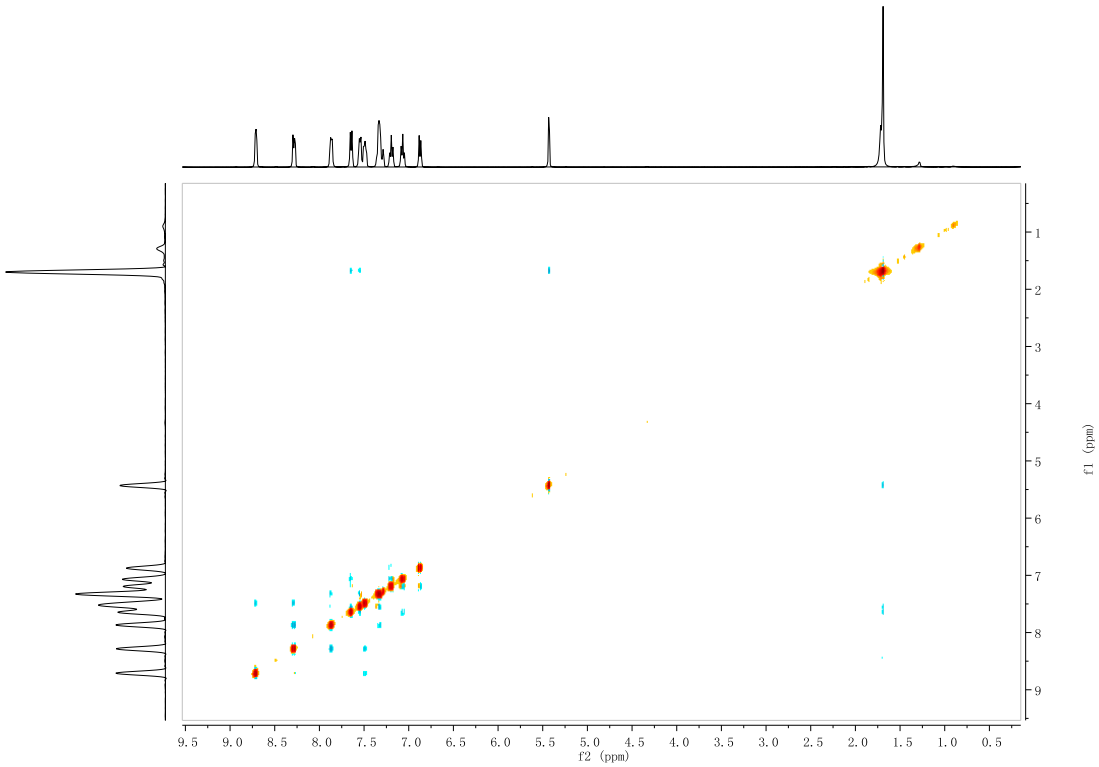
HSQC spectrum of **2l** ($CDCl_3$, 400 MHz)



HMBC spectrum of **2l** ($CDCl_3$, 400 MHz)



H,H-NOESY spectrum of **2l** ($CDCl_3$, 400 MHz)



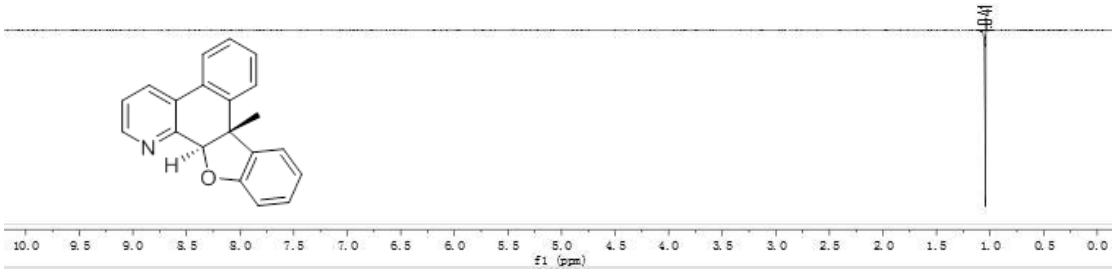
H,H-NOESY spectrum of **3l** ($CDCl_3$, 400 MHz)

Data analysis of DEPT (135 °), H,H-COSY, HSQC and HMBC of **2l** are shown in the table.

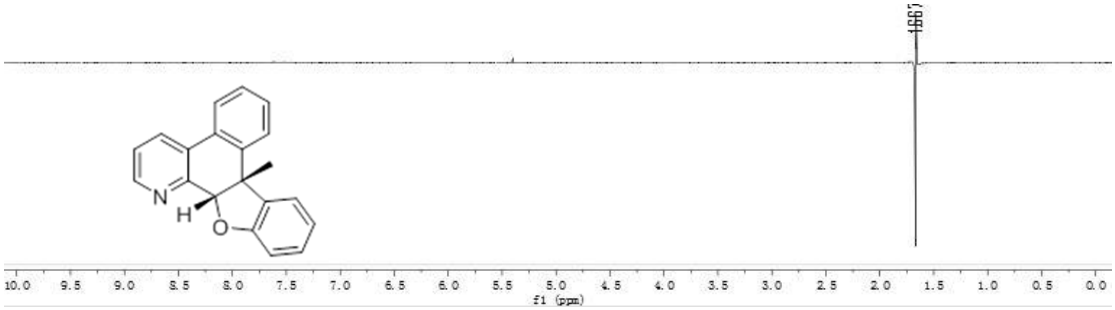
Position	δ_{Hppm}	δ_{Cppm}	DEPT (135 °) δ_{Cppm}	H,H-COSY cross-signal with δ_{Hppm}	HSQC cross-signal with $\delta_H(\delta_C)_{ppm}$	HMBC cross-signal with $\delta_H(\delta_C)_{ppm}$
1	8.62	148.6	148.6	7.38	8.62 (148.6)	8.62 (123.1) J^2, (131.6) J^3, (153.5) J^3
2	7.38	123.1	123.1		7.38 (123.1)	7.38 (148.6)J^2, (131.6) J^2
3	8.05	131.6	131.6	7.38	8.05 (131.6)	8.05 (132.0) J^2, (148.6) J^3, (153.5) J^3
4		132.0				
5		129.5				
6	7.80	126.1	126.1	7.42	7.80 (126.1)	7.80 (129.2) J^2, (129.5) J^2, (132.0) J^3, (142.3) J^3
7	7.42	129.2	129.2		7.42 (129.2)	7.42 (126.1)J^2, (123.9)J^3
8	7.45	127.8	127.8		7.45 (127.8)	7.45 (123.9) J^2, (142.3) J^3
9	7.91	123.9	123.9	7.45	7.91 (123.9)	7.91 (49.7) J^3, (127.8) J^2, (142.3) J^2
10		142.3				
11		49.7				
12		134.5				
13	7.75	124.2	124.2	7.09	7.75 (124.2)	7.75 (49.7) J^3, (128.6) J^3, (160.1) J^3
14	7.09	122.1	122.1		7.09 (122.1)	7.09 (112.4) J^3, (134.5) J^3
15	7.30	128.6	128.6	7.09 ; 7.16	7.30 (128.6)	7.30 (124.2) J^3, (160.1) J^3
16	7.16	112.4	112.4		7.16 (112.4)	7.16 (122.1) J^3, (134.5) J^3, (160.1) J^2
17		160.2				
18	5.45	87.9	87.9		5.45 (87.9)	5.45 (24.5) J^3, (49.7) J^2, (134.5) J^3, (142.3) J^3, (153.5) J^2
19		153.5				
20	1.04	24.5	24.5		1.04 (24.5)	1.04 (49.7) J^2, (87.9) J^3, (134.5) J^3, (142.3) J^3

9. 1D-NOE of 2l and 3l

Nuclear Overhauser Effect



Nuclear Overhauser Effect of **2l** ($CDCl_3$, 400 MHz)



Nuclear Overhauser Effect of **3l** ($CDCl_3$, 400 MHz)