Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information

Pd/Cu Catalyzed Carbonylation of *α*-Aminoaryl-Tethered Alkylidenecyclopropanes: Synthesis of Furoquinoline Derivatives

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Table of Contents

1. General Information

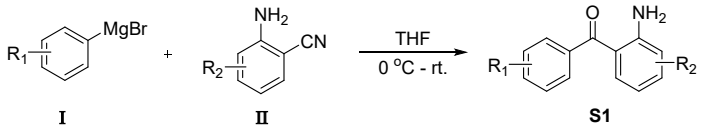
Reagents, solvents and analytical methods:

Unless otherwise noted, all reactions were carried out under the nitrogen and oxygen atmosphere. All reagents were from commercial sources and used as received without further purification. All solvents were dried by standard techniques and distilled prior to use. Column chromatography was performed on silica gel (200-300 meshes) using petroleum ether (bp. 60~90 °C) and ethyl acetate as eluent. ^{1}NMR spectra were recorded on a Bruker Avance operating at for ^{1}H NMR at 500 MHz, ^{13}C NMR at 126 MHz and ^{19}F NMR at 471 MHz and spectral data were reported in ppm relative to tetramethylsilane (TMS) as internal standard and $CDCl_3$ (^{1}H NMR δ 7.26, ^{13}C NMR δ 77.2) as solvent. High-resolution mass spectra (HRMS) is produced by Thermo Fisher Scientific. Its main body is composed of two parts: Thermo Scientific's UltiMate 3000 Series liquid system and Thermo Scientific Q-Exactive combined quadrupole Orbitrap mass spectrometer. All coupling constants (*J*) are reported in Hz. The following abbreviations were used to describe peak splitting patterns when appropriate: s = singlet, d = doublet, dd = double doublet, ddd = double doublet of doublets, t = triplet, dt = double triplet, q = quatriplet, m = multiplet, br = broad. Compounds **1a-1v** were prepared according to the previous literature.[S1, S2]

2 Preparation of the Compounds 1a-1t

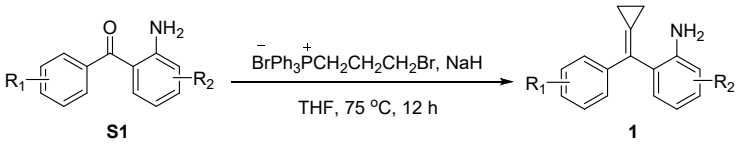
2.1 Preparation of the Compounds 1a-1r

Compounds **1a-1r** were prepared according to the previous literature.[S1, S2]



I **II** **S1**

A round-bottom flask was charged with compound **I** (30.0 mL, 1.0 M solution in THF, 30 mmol, 3.0 equiv) and THF (20 mL). The mixture was stirred at room temperature for 5 minutes under N_2 atmosphere. To a mixture of compound **II** (10 mmol, 1.0 equiv) in THF (10 mL) was added dropwise at 0 °C. Then the reaction mixture was stirred at room temperature for 12 hours. After completion, the reaction mixture was cooled down to 0 °C, HCl solution (20 mL, 3 M) was added dropwise and the mixture was stirred at room temperature for 30 minutes. Then reaction mixture was extracted with EA. The combined organic layer was washed with brine solution, dried over Na_2SO_4, and the solvent was evaporated under reduced pressure to afford a crude residue. The residue was purified by a flash column chromatograph on silica gel using petroleum ether / ethyl acetate as the eluent to yield the products **S1**.

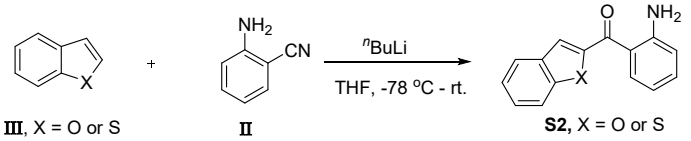


S1 **1**

A solution of (4-Bromobutyl)triphenylphosphonium bromide (4.64 g, 10 mmol, 2 equiv) and NaH (0.80 g, 20 mmol, 4 equiv) in 20 mL THF was stirred at 75 °C under N_2 atmosphere for 12 h. Afterwards, compound **S1** (5 mmol, 1.0 equiv) in 5 mL THF was added and the reaction solution was stirred at 75 °C. After completion, the reaction mixture was cooled to room temperature, and the mixture was filtered through a celite. The filtrate was concentrated under reduced pressure and the residue was purified by a flash column chromatography to afford the product **1**.

2.2 Preparation of the Compounds 1s-1t.

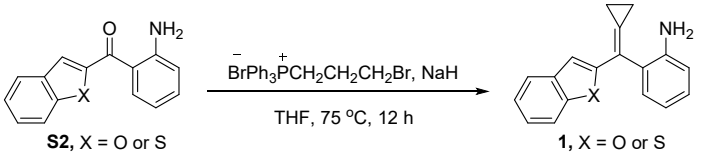
Compounds **1s-1t** were prepared according to the previous literature.[S2]



III, X = O or S **II** **S2**, X = O or S

A round-bottom flask was charged with compound **I** (30.0 mmol, 3.0 equiv) and THF (20 mL). The mixture was stirred at room temperature for 5 minutes under N_2 atmosphere. ^{n}BuLi (12.0 mL, 2.5 M solution in THF, 30.0 mmol, 3.0 equiv) was added dropwise at -78 °C. Then the reaction mixture was stirred at rt for 2 hours. To a mixture of compound **II** (1.18 g, 10 mmol, 1.0 equiv) in THF (10 mL) was added dropwise at 0 °C. The reaction mixture was stirred at room temperature for 12 hours. After completion, the reaction mixture was cooled down to 0 °C, HCl solution (20 mL, 3 M) was added dropwise and the mixture was stirred at room temperature for 30 minutes. Then reaction mixture was extracted with EA. The combined organic layer was washed with brine solution, dried over Na_2SO_4, and the solvent was evaporated under reduced pressure to afford a

crude residue. The residue was purified by a flash column chromatograph on silica gel using petroleum ether / ethyl acetate as the eluent to yield the products **S1**.



S2, X = O or S **1,** X = O or S

A solution of (4-Bromobutyl)triphenylphosphonium bromide (4.64 g, 10 mmol, 2 equiv) and NaH (0.80 g, 20 mmol, 4 equiv) in 20 mL THF was stirred at 75 °C under N_2 atmosphere for 12 h. Afterwards, compound **S2** (5 mmol, 1.0 equiv) in 5 mL THF was added and the reaction solution was stirred at 75 °C. After completion, the reaction mixture was cooled to room temperature, and the mixture was filtered through a celite. The filtrate was concentrated under reduced pressure and the residue was purified by a flash column chromatography to afford the product **1**.

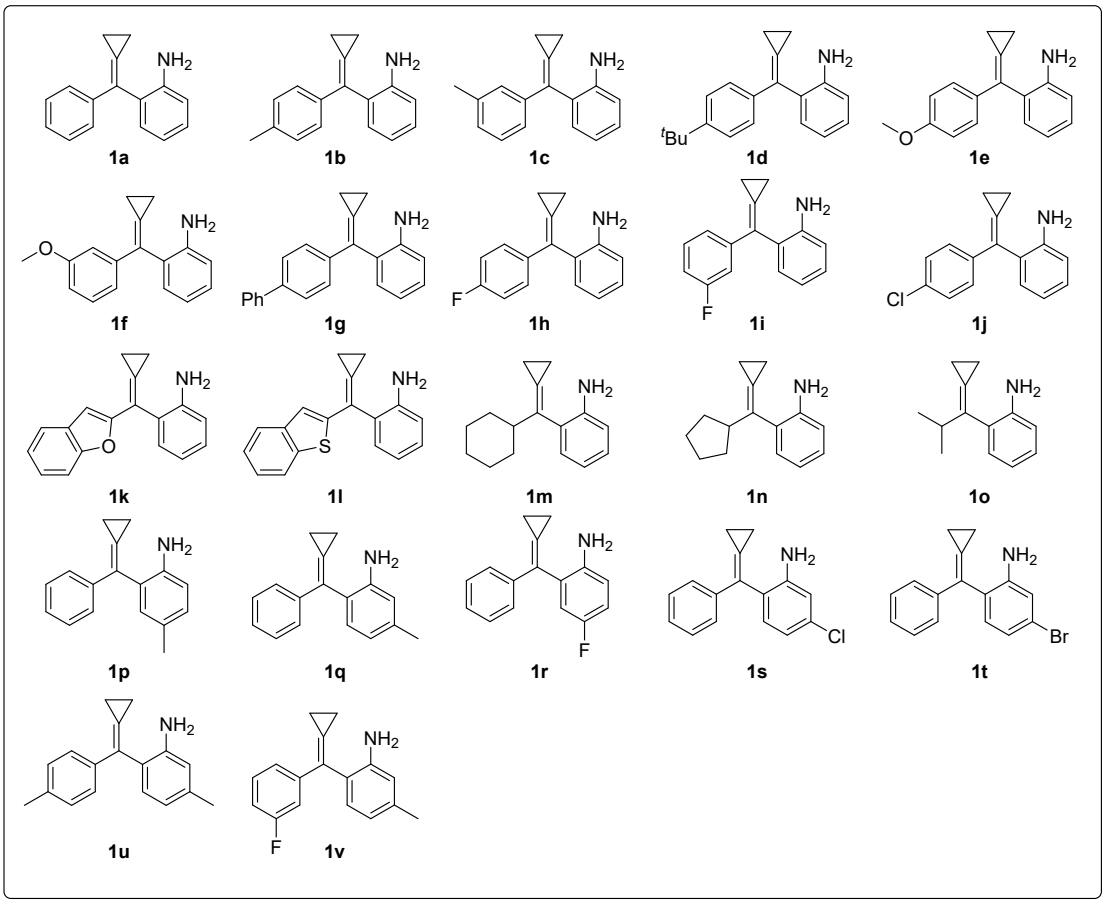
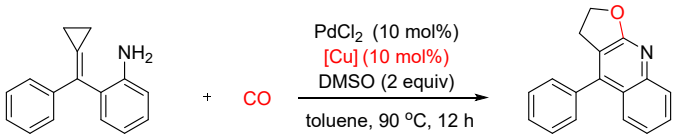


Figure S1 Substrates of 2-(cyclopropylidene(phenyl)methyl)aniline derivatives

3 Optimization of Reaction Conditions

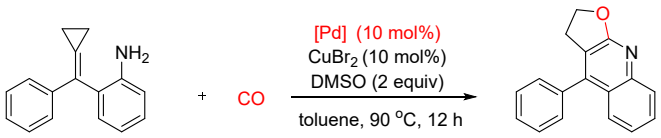
Table S1. Optimization of the Copper Catalyst.[a]



Entry	[Cu]	Yield (%)[b]
1[c]	-	trace
2	CuO	83
3	$CuBr_2$	99
4	$CuCl_2$	90
5	$Cu(OAc)_2$	76
10	$Cu(OTF)_2$	75

[a] Reaction conditions: **1a** (0.2 mmol), $PdCl_2$ (10 mol%), [Cu] (10 mol%), DMSO (2.0 equiv.), toluene (2 mL), O_2 atmosphere, [CO] (HCO_2H + Ac_2O, 2 mmol), 90 °C for 12 h. [b] Isolated yield. [c] N_2 atmosphere.

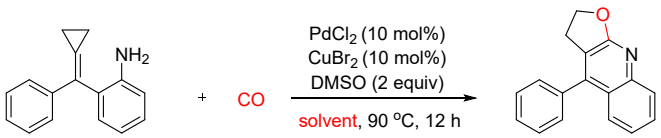
Table S2. Optimization of the Palladium Catalyst.[a]



Entry	[Pd]	Yield (%)[b]
1	$PdCl_2$	99
2	$Pd(OAc)_2$	97
3	$Pd(acac)_2$	92
4	$Pd(TFA)_2$	88
5	$Pd(PPh_3)_4$	95

[a] Reaction conditions: **1a** (0.2 mmol), [Pd] (10 mol%), $CuBr_2$ (10 mol%), DMSO (2.0 equiv.), toluene (2 mL), O_2 atmosphere, [CO] (HCO_2H + Ac_2O, 2 mmol), 90 °C for 12 h. [b] Isolated yield.

Table S3. Optimization of Solvent.[a]

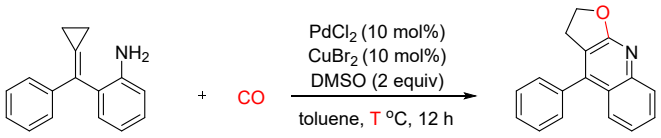


Entry	Solvent	Yield (%)[b]
1	toluene	99
2	THF	96
3	Dioxane	52
4	DCM	85
5	MeCN	77
6	DMSO	81

7	DMF	15

[a] Reaction conditions: **1a** (0.2 mmol), $PdCl_2$ (10 mol%), $CuBr_2$ (10 mol%), DMSO (2.0 equiv.), solvent (2 mL), O_2 atmosphere, [CO] (HCO_2H + Ac_2O, 2 mmol), 90 °C for 12 h. [b] Isolated yield.

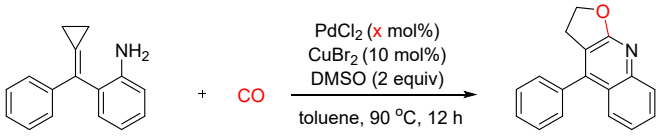
Table S4. Optimization of Temperature.[a]



Entry	Temp.	Yield (%)[b]
1	60	45
2	80	95
3	90	99
4	100	93
5	120	57

[a] Reaction conditions: **1a** (0.2 mmol), $PdCl_2$ (10 mol%), $CuBr_2$ (10 mol%), DMSO (2.0 equiv.), toluene (2 mL), O_2 atmosphere, [CO] (HCO_2H + Ac_2O, 2 mmol), T °C for 12 h. [b] Isolated yield.

Table S5. Optimization of the equivalent of Palladium Catalyst.[a]

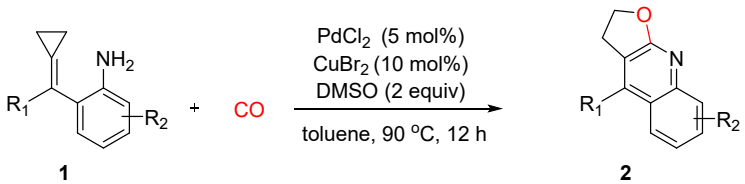


Entry	$PdCl_2$ (x mol%)	Yield (%)[b]
1	5	99
2	10	99

[a] Reaction conditions: **1a** (0.2 mmol), $PdCl_2$ (x mol%), $CuBr_2$ (10 mol%), DMSO (2.0 equiv.), toluene (2 mL), O_2 atmosphere, [CO] (HCO_2H + Ac_2O, 2 mmol), 90 °C for 12 h. [b] Isolated yield.

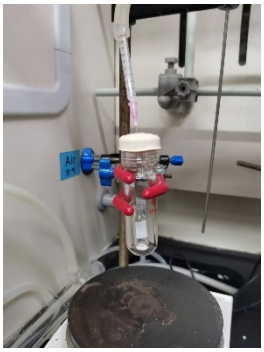
4 General Procedure

4.1. General Procedure

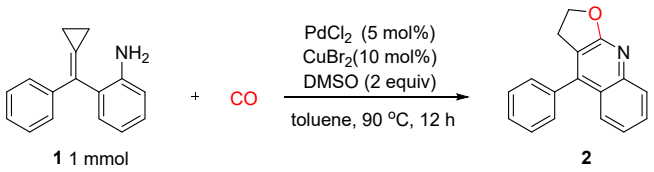


1 **2**

1 (44.3 mg, 0.2 mmol, 1 equiv), $PdCl_2$ (1.7 mg, 5 mol%), and $CuBr_2$ (4.5 mg, 10 mol%) were transferred into a 15 mL tube. A 2.0 mL vial was placed in the tube and the tube was sealed with a septum. The tube was evacuated and backfilled with O_2 (x3). Then, a solution of DMSO (29 μL, 0.4 mmol, 2.0 equiv) in toluene (2 mL) was added to the reaction tube. To the inner vial was added Et_3N (276 μL, 2 mmol) and HCO_2H/Ac_2O (75 μL/187 μL, 2 mmol). Then the reaction tube was sealed with a screw-top septum cap quickly and placed in a heating block that was preheated to 90 °C. After a time period of 12 h, the reaction tube was allowed cooled to room temperature. The mixture was concentrated under reduced pressure and the residue was purified by flash chromatography on silica gel eluting with petroleum ether / EtOAc (v/v = 8:1 to 4:1) to afford the products **2**.

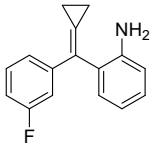

4.2. 1 mmol Scale Synthesis



1 1 mmol **2**

1 (221.3 mg, 1 mmol, 1 equiv), $PdCl_2$ (8.9 mg, 5 mol%), and $CuBr_2$ (22.3 mg, 10 mol%) were transferred into a 30 mL tube. A 5.0 mL vial was placed in the tube and the tube was sealed with a septum. The tube was evacuated and backfilled with O_2 (x3). Then, a solution of DMSO (142 μL, 2 mmol, 2.0 equiv) in toluene (10 mL) was added to the reaction tube. To the inner vial was added Et_3N (828 μL, 6 mmol) and HCO_2H/Ac_2O (225 μL/561 μL, 6 mmol). Then the reaction tube was sealed with a screw-top septum cap quickly and placed in a heating block that was preheated to 90 °C. After a time period of 12 h, the reaction tube was allowed cooled to room temperature. The mixture was concentrated under reduced pressure and the residue was purified by flash chromatography on silica gel eluting with petroleum ether / EtOAc (v/v = 8:1 to 4:1) to afford the products **2** (222.6 mg, 90%).

5 Experimental Characterization Data for the Starting Materials



2-(Cyclopropylidene(3-fluorophenyl)methyl)aniline (1i)

The compound was prepared according to the procedure to give a colorless liquid (0.63 g, 53% yield).

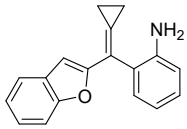
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.27 – 7.21 (m, 3H), 7.17 (m, 1H), 7.08 (dd, *J* = 7.5, 1.3 Hz, 1H), 6.93 (m, 1H), 6.81 (t, *J* = 7.4 Hz, 1H), 6.75 (d, *J* = 8.0 Hz, 1H), 3.52 (s, 2H), 1.62 (dd, *J* = 9.0, 6.8 Hz, 2H), 1.21 (dd, *J* = 9.0, 6.8 Hz, 2H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 163.3 (d, $J_{(C-F)}$ = 245.7 Hz), 144.3, 141.8 (d, $J_{(C-F)}$ = 7.6 Hz), 131.0, 129.9 (d, $J_{(C-F)}$ = 8.8 Hz), 128.7, 127.4, 126.4 (d, $J_{(C-F)}$ = 2.6 Hz), 126.1, 122.4 (d, $J_{(C-F)}$ = 2.5 Hz), 118.6, 115.8, 114.0 (d, $J_{(C-F)}$ = 20.2 Hz), 113.4 (d, $J_{(C-F)}$ = 22.7 Hz), 5.7, 1.9.

^{19}F NMR (471 MHz, CDCl3) δ -111.11 – -116.29 (m).

IR 3470, 3382, 2962, 2925, 1611, 1580, 1488, 1452, 1297, 1151, 785, 750 cm^{-1}.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{16}H_{15}FN^+$ 240.1183; Found 240.1187.



2-(Benzofuran-2-yl(cyclopropylidene)methyl)aniline (1k)

The compound was prepared according to the general procedure to give a white solid (0.91 g, 70% yield).

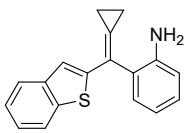
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.46 (m, 2H), 7.26 – 7.22 (m, 1H), 7.21 – 7.14 (m, 3H), 6.86 – 6.75 (m, 2H), 6.44 (s, 1H), 3.63 (dd, *J* = 23.5, 16.7 Hz, 2H), 1.71 (dd, *J* = 9.0, 6.9 Hz, 2H), 1.27 (dd, *J* = 8.9, 6.8 Hz, 2H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 156.3, 155.2, 144.6, 130.9, 129.1, 129.0, 128.9, 124.2, 123.9, 122.8, 121.0, 119.0, 118.4, 115.8, 111.2, 104.1, 5.7, 2.7.

IR 3463, 3381, 2971, 1613, 1494, 1451, 1301, 1257, 954, 747 cm^{-1}.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{18}H_{16}NO^+$ 262.1226; Found 262.1237.

Melting Point: 148.0 - 148.2 °C.



2-(Benzo[*b*]thiophen-2-yl(cyclopropylidene)methyl)aniline (1l)

The compound was prepared according to the general procedure to give a white solid (1.04 g, 75% yield).

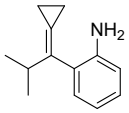
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.81 – 7.71 (m, 1H), 7.62 – 7.55 (m, 1H), 7.31 – 7.14 (m, 4H), 6.92 (s, 1H), 6.83 (m, 1H), 6.79 (d, *J* = 8.0 Hz, 1H), 3.46 (s, 2H), 1.63 (dd, *J* = 9.0, 6.6 Hz, 2H), 1.33 (dd, *J* = 9.0, 6.6 Hz, 2H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 145.1, 144.4, 140.1, 139.9, 130.7, 128.9, 128.0 125.2, 124.4, 124.4, 123.6, 123.4, 122.1, 121.4, 118.4, 115.8, 6.3, 3.7.

IR 3468, 3378, 2971, 1612, 1492, 1453, 1250, 1157, 1070, 1016, 829, 748 cm^{-1}.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{18}H_{16}NS^+$ 278.0998; Found 278.1007.

Melting Point: 161.1 - 161.6 °C.



2-(1-Cyclopropylidene-2-methylpropyl)aniline (1o)

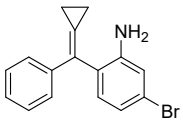
The compound was prepared according to the general procedure to give a colorless liquid (0.54 g, 58% yield).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.10 (m, 1H), 7.04 (dd, *J* = 7.5, 1.5 Hz, 1H), 6.77 (ddd, *J* = 15.0, 7.6, 1.0 Hz, 2H), 3.58 (s, 2H), 2.90 – 2.75 (m, 1H), 1.38 (ddd, *J* = 7.5, 5.6, 1.2 Hz, 2H), 1.21 (d, *J* = 6.9 Hz, 6H), 0.93 (ddd, *J* = 8.5, 5.6, 1.1 Hz, 2H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 143.9, 132.7, 129.0, 128.9, 127.5, 119.2, 117.9 115.3, 35.2, 21.9, 4.1, 0.7.

IR 3472, 3379, 2965, 1611, 1493, 1452, 1295, 1055, 952, 748, 645 cm^{-1}.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{13}H_{18}N^+$ 188.1434; Found 188.1430.



5-Bromo-2-(cyclopropylidene(phenyl)methyl)aniline (1t)

The compound was prepared according to the general procedure to give a white solid (0.71 g, 47% yield).

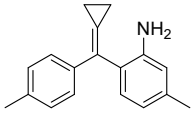
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.54 (d, *J* = 7.5 Hz, 2H), 7.36 (t, *J* = 7.6 Hz, 2H), 7.29 (t, *J* = 7.3 Hz, 1H), 6.99 (d, *J* = 8.0 Hz, 1H), 6.95 (dd, *J* = 8.0, 1.9 Hz, 1H), 6.90 (d, *J* = 1.9 Hz, 1H), 3.55 (s, 2H), 1.64 (dd, *J* = 8.9, 6.7 Hz, 2H), 1.22 (dd, *J* = 8.9, 6.7 Hz, 2H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 145.8, 138.8, 132.3, 128.6, 127.4, 126.6, 126.4, 126.3, 125.4, 121.8, 121.2, 118.0, 5.7, 1.8.

IR 3475, 3383, 2971, 1612, 1488, 1411, 1252, 1061, 908, 795, 765, 695 cm^{-1}.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{16}H_{15}BrN^+$ 300.0382; Found 300.0392.

Melting Point: 124.0 - 124.9 °C.

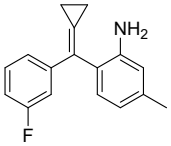


2-(cyclopropylidene(p-tolyl)methyl)-5-methylaniline (1u)

The compound was prepared according to the general procedure to give a yellow liquid (0.81 g, 65% yield).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.44 (d, *J* = 8.1 Hz, 2H), 7.15 (d, *J* = 8.0 Hz, 2H), 7.03 (d, *J* = 7.6 Hz, 1H), 6.66 (d, *J* = 7.6 Hz, 1H), 6.60 (s, 1H), 3.55 (d, *J* = 52.5 Hz, 2H), 2.37 (s, 3H), 2.35 (s, 3H), 1.65 – 1.55 (m, 2H), 1.26 – 1.17 (m, 2H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 144.2, 138.1, 136.9, 136.8, 130.9, 129.2, 126.9, 126.7, 124.5, 124.1, 119.3, 116.3, 21.4, 21.3, 5.5, 1.8.



2-(cyclopropylidene(3-fluorophenyl)methyl)-5-methylaniline (1v)

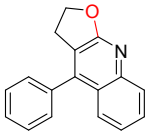
The compound was prepared according to the general procedure to give a yellow liquid (0.76 g, 60% yield).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.27 – 7.21 (m, 3H), 6.96 (t, J = 5.9 Hz, 1H), 6.94 – 6.89 (m, 1H), 6.63 (d, J = 7.6 Hz, 1H), 6.58 (s, 1H), 3.47 (s, 2H), 2.31 (s, 3H), 1.60 (dd, J = 8.9, 6.7 Hz, 2H), 1.23 – 1.17 (m, 2H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 163.24 (d, $J_{(C-F)}$ = 245.7 Hz), 144.2, 142.0 (d, $J_{(C-F)}$ = 7.6 Hz), 138.5, 130.8, 129.9 (d, $J_{(C-F)}$ = 7.6 Hz), 127.1, 126.3 (d, $J_{(C-F)}$ = 1.3 Hz), 123.3, 122.5 (d, $J_{(C-F)}$ = 2.5 Hz), 119.5, 116.5, 114.0 (d, $J_{(C-F)}$ = 21.4 Hz), 113.5 (d, $J_{(C-F)}$ = 22.7 Hz), 21.5, 5.7, 1.9.

^{19}F NMR (471 MHz, $CDCl_3$) δ -109.05 – -118.00 (m).

6 Experimental Characterization Data for the Products

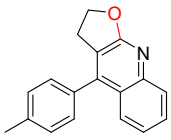


1-4-Phenyl-2,3-dihydrofuro[2,3-*b*]quinoline (2a)

From 2-(cyclopropylidene(phenyl)methyl)aniline (44.3 mg, 0.2 mmol), following the general procedure, the title compound (49.0 mg, 99%) was obtained as a white solid. $\mathbf{R}_f$ = 0.2 (petroleum ether / ethyl acetate = 8:1).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.91 (d, J = 8.3 Hz, 1H), 7.60 – 7.51 (m, 4H), 7.49 (t, J = 7.3 Hz, 1H), 7.42 – 7.36 (m, 2H), 7.31 – 7.25 (m, 1H), 4.69 (t, J = 8.1 Hz, 2H), 3.23 (t, J = 8.1 Hz, 2H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 167.2, 147.5, 145.5, 136.1, 129.2, 129.0, 128.9, 128.5, 127.8, 125.7, 124.7, 124.1, 119.9, 69.3, 27.8.

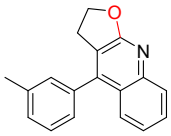


4-(*p*-Tolyl)-2,3-dihydrofuro[2,3-*b*]quinoline (2b)

From 2-(cyclopropylidene(*p*-tolyl)methyl)aniline (47.1 mg, 0.2 mmol), following the general procedure, the title compound (50.2 mg, 96%) was obtained as a white solid. $\mathbf{R}_f$ = 0.4 (petroleum ether / ethyl acetate = 4:1).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.91 (s, 1H), 7.57 (t, J = 8.6 Hz, 2H), 7.34 (d, J = 7.9 Hz, 2H), 7.27 (dd, J = 9.0, 6.7 Hz, 3H), 4.67 (t, J = 8.2 Hz, 2H), 3.22 (t, J = 8.2 Hz, 2H), 2.46 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 167.2, 147.4, 145.7, 138.4, 133.1, 129.5, 129.2, 128.9, 127.7, 125.7, 124.8, 124.0, 119.8, 69.3, 27.8, 21.5.

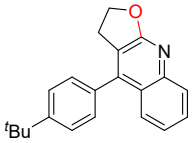


4-(*m*-Tolyl)-2,3-dihydrofuro[2,3-*b*]quinoline (2c)

From 2-(cyclopropylidene(*m*-tolyl)methyl)aniline (42.3 mg, 0.2 mmol), following the general procedure, the title compound (50.2 mg, 81%) was obtained as a white solid. $\mathbf{R}_f$ = 0.5 (petroleum ether / ethyl acetate = 4:1).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.92 – 7.85 (m, 1H), 7.56 (t, *J* = 7.6 Hz, 2H), 7.41 (t, *J* = 7.6 Hz, 1H), 7.31 – 7.24 (m, 2H), 7.21 – 7.15 (m, 2H), 4.68 (t, *J* = 8.2 Hz, 2H), 3.22 (t, *J* = 8.2 Hz, 2H), 2.44 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 167.2, 147.5, 145.7, 138.5, 136.1, 129.6, 129.2, 129.1, 128.7, 127.7, 126.1, 125.7, 124.8, 124.0, 119.8, 69.3, 27.8, 21.6.

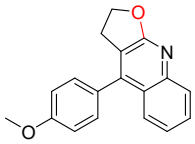


4-(4-(*tert*-Butyl)phenyl)-2,3-dihydrofuro[2,3-*b*]quinoline (2d)

From 2-((4-(*tert*-butyl)phenyl)(cyclopropylidene)methyl)aniline (55.5 mg, 0.2 mmol), following the general procedure, the title compound (49.2 mg, 81%) was obtained as a white solid. $\mathbf{R}_f$ = 0.8 (petroleum ether / ethyl acetate = 2:1).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.89 (d, *J* = 8.3 Hz, 1H), 7.62 (d, *J* = 8.2 Hz, 1H), 7.59 – 7.51 (m, 3H), 7.32 (d, *J* = 8.3 Hz, 2H), 7.30 – 7.25 (m, 1H), 4.67 (t, *J* = 8.2 Hz, 2H), 3.24 (t, *J* = 8.2 Hz, 2H), 1.41 (s, 9H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 167.2, 151.5, 147.6, 145.5, 133.0, 129.1, 128.8, 127.8, 125.8, 125.7, 124.8, 123.9, 119.8, 69.3, 34.9, 31.5, 27.9.

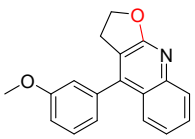


4-(4-Methoxyphenyl)-2,3-dihydrofuro[2,3-*b*]quinoline (2e)

From 2-(cyclopropylidene(4-methoxyphenyl)methyl)aniline (50.3 mg, 0.2 mmol), following the general procedure, the title compound (50.2 mg, 95%) was obtained as a white solid. $\mathbf{R}_f$ = 0.6 (petroleum ether / ethyl acetate = 2:1).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.88 (d, *J* = 8.3 Hz, 1H), 7.67 – 7.51 (m, 2H), 7.31 (t, *J* = 5.6 Hz, 2H), 7.27 (dd, *J* = 8.8, 6.4 Hz, 1H), 7.06 (d, *J* = 8.6 Hz, 2H), 4.67 (t, *J* = 8.2 Hz, 2H), 3.90 (s, 3H), 3.22 (t, *J* = 8.2 Hz, 2H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 167.2, 159.7, 147.5, 145.3, 130.4, 129.1, 128.2, 127.8, 125.7, 124.9, 124.0, 119.8, 114.3, 69.2, 55.5, 27.8.



4-(3-Methoxyphenyl)-2,3-dihydrofuro[2,3-*b*]quinoline (2f)

From 2-(cyclopropylidene(3-methoxyphenyl)methyl)aniline (50.3 mg, 0.2 mmol), following the general procedure, the title compound (49.9 mg, 90%) was obtained as a white solid. $\mathbf{R}_f$ = 0.6 (petroleum ether / ethyl acetate = 2:1).

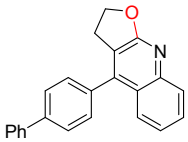
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.91 – 7.86 (m, 1H), 7.57 (dd, *J* = 12.3, 4.4 Hz, 2H), 7.47 – 7.41 (m, 1H), 7.30 – 7.25 (m, 1H), 7.02 (m, 1H), 6.96 (dd, *J* = 7.5, 0.9 Hz, 1H), 6.92 (dd, *J* = 2.3, 1.6 Hz, 1H), 4.68 (t, *J* = 8.2 Hz, 2H), 3.85 (s, 3H), 3.23 (t, *J* = 8.2 Hz, 2H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 167.2, 159.9, 147.5, 145.3, 137.5, 130.0, 129.2, 127.8, 125.7, 124.6, 124.1, 121.3, 119.8, 114.7, 113.9, 69.3, 55.5, 27.7.

IR 2918, 1623, 1583, 1459, 1416, 1315, 1248, 1141, 1035, 765, 700 cm^{-1}.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{18}H_{16}NO_2^+$ 278.1176; Found 278.1182.

Melting Point: 202.9 - 203.5 °C.



4-([1,1'-Biphenyl]-4-yl)-2,3-dihydrofuro[2,3-*b*]quinoline (2g)

From 2-([1,1'-biphenyl]-4-yl(cyclopropylidene)methyl)aniline (59.5 mg, 0.2 mmol), following the general procedure, the title compound (45.3 mg, 70%) was obtained as a white solid. $\mathbf{R}_f$ = 0.3 (petroleum ether / ethyl acetate = 4:1).

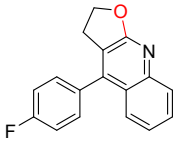
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.91 (d, *J* = 8.0 Hz, 1H), 7.78 – 7.73 (m, 2H), 7.71 – 7.66 (m, 2H), 7.64 (dd, *J* = 8.3, 1.0 Hz, 1H), 7.61 – 7.56 (m, 1H), 7.52 – 7.44 (m, 4H), 7.43 – 7.38 (m, 1H), 7.29 (m, 1H), 4.69 (t, *J* = 8.2 Hz, 2H), 3.26 (t, *J* = 8.2 Hz, 2H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 167.2, 147.6, 145.1, 141.4, 140.5, 135.0, 129.6, 129.2, 129.1, 127.8, 127.5, 127.2, 125.7, 124.7, 124.1, 119.9, 69.3, 27.8.

IR 2960, 2923, 1734, 1622, 1591, 1484, 1413, 1394, 1317, 1224, 1007, 766, 738, 699 cm^{-1}.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{23}H_{18}NO^+$ 324.1383; Found 324.1374.

Melting Point: 167.0 - 167.9 °C.



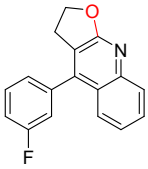
4-(4-Fluorophenyl)-2,3-dihydrofuro[2,3-*b*]quinoline (2h)

From 2-(cyclopropylidene(4-fluorophenyl)methyl)aniline (47.9 mg, 0.2 mmol), following the general procedure, the title compound (39.8 mg, 75%) was obtained as a white solid. $\mathbf{R}_f$ = 0.4 (petroleum ether / ethyl acetate = 4:1).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.88 (t, *J* = 5.6 Hz, 1H), 7.60 – 7.54 (m, 1H), 7.51 (dd, *J* = 8.3, 0.9 Hz, 1H), 7.45 – 7.33 (m, 2H), 7.31 – 7.20 (m, 3H), 4.68 (m, 2H), 3.21 (m, 2H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 167.2, 146.4 (d, $J_{(C-F)}$ = 307.4 Hz), 140.9 (d, $J_{(C-F)}$ = 113.4 Hz), 135.0, 129.6, 129.2, 129.01, 127.8, 127.5, 127.2, 124.9 (d, $J_{(C-F)}$ = 197.8 Hz), 124.7, 119.9, 69.3, 27.8.

^{19}F NMR (471 MHz, $CDCl_3$) δ -110.04 – -116.65 (m).



4-(3-Fluorophenyl)-2,3-dihydrofuro[2,3-*b*]quinoline (2i)

From 2-(cyclopropylidene(3-fluorophenyl)methyl)aniline (47.9 mg, 0.2 mmol), following the general procedure, the title compound (45.1 mg, 85%) was obtained as a white solid. $\mathbf{R}_f$ = 0.7 (petroleum ether / ethyl acetate = 2:1).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.94 – 7.84 (m, 1H), 7.62 – 7.54 (m, 1H), 7.51 (m, 2H), 7.29 (m, 1H), 7.22 – 7.15 (m, 2H), 7.13 – 7.08 (m, 1H), 4.69 (t, *J* = 8.2 Hz, 2H), 3.22 (dd, *J* = 8.6, 7.7 Hz, 2H).

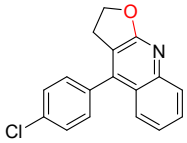
^{13}C NMR (126 MHz, $CDCl_3$) δ 167.1, 163.9, 162.0, 147.5, 144.0, 138.2 (d, $J_{(C-F)}$ = 7.6 Hz), 130.6 (d, $J_{(C-F)}$ = 8.8 Hz), 129.4, 127.9, 125.3, 124.8 (d, $J_{(C-F)}$ = 2.5 Hz), 124.3, 120.0, 116.2 (d, $J_{(C-F)}$ = 22.7 Hz), 115.6 (d, $J_{(C-F)}$ = 20.2 Hz), 69.2, 27.6.

^{19}F NMR (471 MHz, $CDCl_3$) δ -228.36 – -237.38 (m).

IR 3053, 2922, 1623, 1574, 1475, 1412, 1315, 1216, 1171, 1002, 763, 699 cm^{-1}.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{17}H_{13}FNO^+$ 266.0976; Found 266.0980.

Melting Point: 157.5 - 157.9 °C.

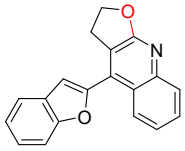


4-(4-Chlorophenyl)-2,3-dihydrofuro[2,3-*b*]quinoline (2g)

From 2-((4-chlorophenyl)(cyclopropylidene)methyl)aniline (51.1 mg, 0.2 mmol), following the general procedure, the title compound (45.6 mg, 81%) was obtained as a white solid. $\mathbf{R}_f$ = 0.3 (petroleum ether / ethyl acetate = 4:1).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.89 (d, *J* = 8.3 Hz, 1H), 7.58 (dd, *J* = 8.3, 7.0 Hz, 1H), 7.54 – 7.47 (m, 3H), 7.33 (dd, *J* = 8.5, 2.4 Hz, 2H), 7.31 – 7.25 (m, 1H), 4.68 (m, 2H), 3.20 (m, 2H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 167.1, 147.5, 144.2, 134.6, 134.5, 130.4, 129.3, 129.2, 127.9, 125.3, 124.4, 124.2, 120.0, 69.2, 27.7.



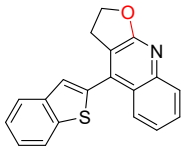
4-(Benzofuran-2-yl)-2,3-dihydrofuro[2,3-*b*]quinoline (2k)

From 2-(benzofuran-2-yl(cyclopropylidene)methyl)aniline (32.3 mg, 0.2 mmol), following the general procedure, the title compound (55.2 mg, 96%) was obtained as a white solid. $\mathbf{R}_f$ = 0.7 (petroleum ether / ethyl acetate = 2:1).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.24 (d, *J* = 8.4 Hz, 1H), 7.90 (d, *J* = 8.3 Hz, 1H), 7.70 (d, *J* = 7.7 Hz, 1H), 7.63 – 7.55 (m, 2H), 7.43 – 7.35 (m, 2H), 7.32 (dd, *J* = 11.0, 4.0 Hz, 1H), 7.14 (s, 1H), 4.71 (t, *J* = 8.2 Hz, 2H), 3.56 (t, *J* = 8.2 Hz, 2H).

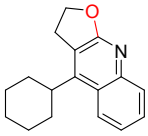
^{13}C NMR (126 MHz, $CDCl_3$) δ 167.4, 154.9, 151.1, 147.7, 133.2, 129.4, 128.2, 128.1, 125.6, 125.2, 124.6, 123.5, 122.6, 121.6, 120.7, 111.5, 109.6, 69.2, 29.2.

IR 3063, 2921, 1591, 1479, 1452, 1407, 1319, 1260, 1011, 964, 841, 756, 702 cm^{-1}.
HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{19}H_{14}NO_2^+$ 288.1019; Found 288.1028.
Melting Point: 119.1 - 120.1 °C.



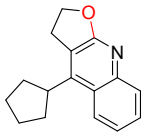
4-(Benzo[*b*]thiophen-2-yl)-2,3-dihydrofuro[2,3-*b*]quinoline (2l)

From 2-(benzo[*b*]thiophen-2-yl(cyclopropylidene)methyl)aniline (55.5 mg, 0.2 mmol), following the general procedure, the title compound (56.4 mg, 93%) was obtained as a white solid. $\mathbf{R}_f$ = 0.8 (petroleum ether / ethyl acetate = 2:1).
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.94 – 7.85 (m, 4H), 7.59 (t, *J* = 7.7 Hz, 1H), 7.47 – 7.39 (m, 3H), 7.32 (t, *J* = 7.6 Hz, 1H), 4.69 (t, *J* = 8.2 Hz, 2H), 3.37 (t, *J* = 8.2 Hz, 2H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 167.0, 147.4, 140.6, 139.7, 138.3, 136.4, 129.5, 127.9, 125.5, 125.4, 125.1, 124.9, 124.6, 124.5, 124.1, 122.3, 121.6, 69.3, 28.4.
IR 2919, 1621, 1589, 1439, 1409, 1314, 1225, 1090, 1006, 961, 758 cm^{-1}.
HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{19}H_{14}NOS^+$ 304.0791; Found 304.0794.
Melting Point: 180.4 - 181.4 °C.



4-Cyclohexyl-2,3-dihydrofuro[2,3-*b*]quinoline (2m)

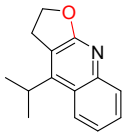
From 2-(cyclohexyl(cyclopropylidene)methyl)aniline (45.5 mg, 0.2 mmol), following the general procedure, the title compound (32.9 mg, 65%) was obtained as a white solid. $\mathbf{R}_f$ = 0.6 (petroleum ether / ethyl acetate = 2:1).
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.04 (s, 1H), 7.94 (d, *J* = 8.3 Hz, 1H), 7.58 (t, *J* = 7.6 Hz, 1H), 7.39 (t, *J* = 7.6 Hz, 1H), 4.70 (t, *J* = 8.1 Hz, 2H), 3.52 (s, 2H), 3.42 (s, 1H), 2.06 – 1.82 (m, 6H), 1.77 (s, 1H), 1.51 (dd, *J* = 25.4, 12.6 Hz, 2H), 1.43 – 1.29 (m, 1H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 167.1, 150.6, 145.8, 129.2, 127.4, 124.2, 124.1, 124.0, 123.1, 69.4, 31.1, 28.8, 28.7, 26.9, 26.2.
IR 2926, 2853, 1616, 1588, 1446, 1412, 1312, 1260, 1218, 1018, 757, 707 cm^{-1}.
HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{17}H_{20}NO^+$ 254.1539; Found 254.1533.
Melting Point: 102.4 - 103.1 °C.



4-Cyclopentyl-2,3-dihydrofuro[2,3-*b*]quinoline (2n)

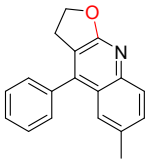
From 2-(cyclopentyl(cyclopropylidene)methyl)aniline (42.7 mg, 0.2 mmol), following the general procedure, the title compound (24.4 mg, 51%) was obtained as a white solid. $\mathbf{R}_f$ = 0.7 (petroleum ether / ethyl acetate = 2:1).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.99 (d, *J* = 8.4 Hz, 1H), 7.85 (d, *J* = 8.3 Hz, 1H), 7.55 (t, *J* = 7.6 Hz, 1H), 7.37 – 7.31 (m, 1H), 4.66 (t, *J* = 8.2 Hz, 2H), 3.79 – 3.59 (m, 1H), 3.43 (t, *J* = 8.2 Hz, 2H), 2.15 – 2.07 (m, 2H), 2.02 – 1.92 (m, 4H), 1.83 (t, *J* = 6.8 Hz, 2H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 167.5, 148.8, 147.4, 128.8, 128.4, 124.6, 123.8, 123.6, 118.5, 68.8, 41.2, 32.0, 28.3, 26.7.
IR 2956, 2869, 1660, 1616, 1588, 1410, 1315, 1224, 1016, 759, 708 cm^{-1}.
HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{16}H_{18}NO^+$ 240.1383; Found 240.1377.
Melting Point: 109.8 - 110.9 °C.



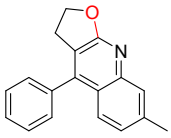
4-Isopropyl-2,3-dihydrofuro[2,3-*b*]quinoline (2o)

From 2-(1-cyclopropylidene-2-methylpropyl)aniline (37.5 mg, 0.2 mmol), following the general procedure, the title compound (32.0 mg, 75%) was obtained as a white solid. $\mathbf{R}_f$ = 0.5 (petroleum ether / ethyl acetate = 2:1).
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.01 (d, *J* = 8.4 Hz, 1H), 7.84 (d, *J* = 8.3 Hz, 1H), 7.55 (t, *J* = 7.6 Hz, 1H), 7.39 – 7.32 (m, 1H), 4.65 (t, *J* = 8.2 Hz, 2H), 3.83 – 3.69 (m, 1H), 3.46 (t, *J* = 8.2 Hz, 2H), 1.44 (d, *J* = 7.1 Hz, 6H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 167.7, 150.5, 147.6, 128.8, 128.5, 124.1, 123.7, 123.4, 117.8, 68.7, 29.2, 28.4, 21.3.
IR 2251, 2125, 1657, 1415, 1316, 1224, 1056, 824, 762 cm^{-1}.
HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{14}H_{16}NO^+$ 214.1226; Found 214.1233.
Melting Point: 87.9 - 88.7 °C.



6-Methyl-4-phenyl-2,3-dihydrofuro[2,3-*b*]quinoline (2p)

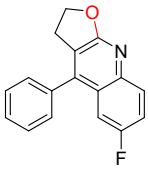
From 2-(cyclopropylidene(phenyl)methyl)-4-methylaniline (47.1 mg, 0.2 mmol), following the general procedure, the title compound (48.1 mg, 92%) was obtained as a colorless liquid. $\mathbf{R}_f$ = 0.6 (petroleum ether / ethyl acetate = 2:1).
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.78 (d, *J* = 8.5 Hz, 1H), 7.54 (m, 2H), 7.51 – 7.46 (m, 1H), 7.42 – 7.35 (m, 3H), 7.30 (s, 1H), 4.65 (t, *J* = 8.2 Hz, 2H), 3.18 (t, *J* = 8.2 Hz, 2H), 2.36 (s, 3H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 166.7, 145.8, 144.9, 136.3, 133.6, 131.1, 129.0, 128.8, 128.4, 127.5, 124.9, 124.5, 119.8, 69.1, 27.8, 21.5.



7-Methyl-4-phenyl-2,3-dihydrofuro[2,3-*b*]quinoline (2q)

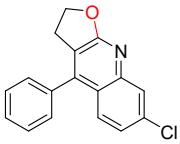
From 2-(cyclopropylidene(phenyl)methyl)-5-methylaniline (47.1 mg, 0.2 mmol), following the general procedure, the title compound (48.1 mg, 92%) was obtained as a white solid. $\mathbf{R}_f$ = 0.4 (petroleum ether / ethyl acetate = 4:1).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.69 (s, 1H), 7.46 (m, 4H), 7.36 (d, *J* = 6.9 Hz, 2H), 7.09 (d, *J* = 8.0 Hz, 1H), 4.65 (t, *J* = 8.0 Hz, 2H), 3.18 (t, *J* = 8.0 Hz, 2H), 2.48 (s, 3H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 167.3, 147.6, 145.3, 139.4, 136.2, 129.0, 128.8, 128.4, 127.2, 126.0, 125.3, 122.5, 118.8, 69.2, 27.6, 21.7.
IR 2919, 1619, 1591, 1488, 1440, 1402, 1317, 1221, 1169, 1001, 763, 712 cm^{-1}.
HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{18}H_{16}NO^+$ 262.1226; Found 262.1228.
Melting Point: 125.8 - 126.7 °C.



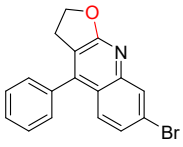
6-Fluoro-4-phenyl-2,3-dihydrofuro[2,3-*b*]quinoline (2r)

From 2-(cyclopropylidene(phenyl)methyl)-4-fluoroaniline (47.9 mg, 0.2 mmol), following the general procedure, the title compound (48.3 mg, 91%) was obtained as a white solid. $\mathbf{R_f}$ = 0.6 (petroleum ether / ethyl acetate = 2:1).
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.86 (dd, *J* = 9.1, 5.4 Hz, 1H), 7.57 – 7.52 (m, 2H), 7.52 – 7.47 (m, 1H), 7.37 (dd, *J* = 5.2, 3.2 Hz, 2H), 7.35 – 7.30 (m, 1H), 7.18 (dd, *J* = 10.2, 2.9 Hz, 1H), 4.69 (t, *J* = 8.2 Hz, 2H), 3.23 (t, *J* = 8.2 Hz, 2H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 166.9, 159.4 (d, $J_{(C-F)}$ = 244.4 Hz), 144.8 (d, $J_{(C-F)}$ = 3.8 Hz), 144.3, 135.6, 129.6 (d, $J_{(C-F)}$ = 8.8 Hz), 129.0, 128.9, 128.8, 125.3 (d, $J_{(C-F)}$ = 10.1 Hz), 120.9, 118.4(d, $J_{(C-F)}$ = 25.2 Hz), 109.7 (d, $J_{(C-F)}$ = 23.9 Hz), 69.3, 27.8.
^{19}F NMR (471 MHz, $CDCl_3$) δ -117.31 (dd, *J* = 14.6, 9.3 Hz).
IR 3050, 2922, 1627, 1595, 1525, 1422, 1397, 1323, 1227, 1099, 1007, 731, 702 cm^{-1}.
HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{17}H_{13}FNO^+$ 266.0976; Found 266.0980.
Melting Point: 154.0 - 154.5 °C.



7-Chloro-4-phenyl-2,3-dihydrofuro[2,3-*b*]quinoline (2s)

From 5-chloro-2-(cyclopropylidene(phenyl)methyl)aniline (51.1 mg, 0.2 mmol), following the general procedure, the title compound (50.1 mg, 89%) was obtained as a white solid. $\mathbf{R_f}$ = 0.7 (petroleum ether / ethyl acetate = 2:1).
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.85 (d, *J* = 2.0 Hz, 1H), 7.59 – 7.43 (m, 4H), 7.40 – 7.32 (m, 2H), 7.20 (dd, *J* = 8.8, 2.1 Hz, 1H), 4.69 (t, *J* = 8.2 Hz, 2H), 3.21 (t, *J* = 8.2 Hz, 2H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 167.9, 148.3, 145.3, 135.6, 135.0, 129.0, 128.9, 128.8, 126.9, 126.8, 124.7, 123.2, 120.2, 69.5, 27.6.



7-Bromo-4-phenyl-2,3-dihydrofuro[2,3-*b*]quinoline (2t)

From 5-bromo-2-(cyclopropylidene(phenyl)methyl)aniline (60.0 mg, 0.2 mmol), following the

general procedure, the title compound (48.3 mg, 74%) was obtained as a white solid. $\mathbf{R}_f$ = 0.7 (petroleum ether / ethyl acetate = 2:1).

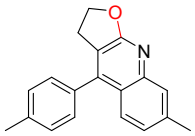
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.04 (s, 1H), 7.57 – 7.45 (m, 3H), 7.40 (d, *J* = 8.8 Hz, 1H), 7.34 (dd, *J* = 10.4, 3.7 Hz, 3H), 4.70 (t, *J* = 8.2 Hz, 2H), 3.20 (t, *J* = 8.2 Hz, 2H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 167.8, 148.5, 145.4, 135.6, 130.1, 129.0, 128.9, 128.8, 127.4, 127.0, 123.5, 123.3, 120.4, 69.5, 27.7.

IR 3055, 2923, 1624, 1589, 1438, 1400, 1315, 1206, 1139, 922, 867, 762, 730 cm^{-1}.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{17}H_{13}BrNO^+$ 326.0175; Found 326.0186.

Melting Point: 135.3 - 135.7 ºC.

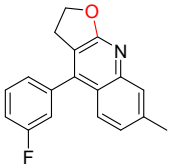


7-methyl-4-(p-tolyl)-2,3-dihydrofuro[2,3-b]quinoline (2u)

From 2-(cyclopropylidene(p-tolyl)methyl)-5-methylaniline (49.8 mg, 0.2 mmol), following the general procedure, the title compound (52.3 mg, 95%) was obtained as a yellow solid. $\mathbf{R}_f$ = 0.4 (petroleum ether / ethyl acetate = 4:1).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.67 (s, 1H), 7.46 (d, *J* = 8.4 Hz, 1H), 7.32 (d, *J* = 7.9 Hz, 2H), 7.28 – 7.24 (m, 2H), 7.09 (dd, *J* = 8.4, 1.3 Hz, 1H), 4.65 (t, *J* = 8.2 Hz, 2H), 3.20 (t, *J* = 8.2 Hz, 2H), 2.48 (s, 3H), 2.46 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 167.3, 147.7, 145.4, 139.3, 138.3, 133.3, 129.5, 129.0, 127.2, 125.9, 125.4, 122.7, 118.7, 69.2, 27.7, 21.7, 21.5.



4-(3-fluorophenyl)-7-methyl-2,3-dihydrofuro[2,3-b]quinoline (2v)

From 2-(cyclopropylidene(4-fluorophenyl)methyl)-5-methylaniline (50.6 mg, 0.2 mmol), following the general procedure, the title compound (50.2 mg, 90%) was obtained as a yellow solid. $\mathbf{R}_f$ = 0.3 (petroleum ether / ethyl acetate = 4:1).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.68 (s, 1H), 7.49 (m, *J* = 11.0, 5.5 Hz, 1H), 7.40 (d, *J* = 8.4 Hz, 1H), 7.20 – 7.13 (m, 2H), 7.13 – 7.06 (m, 2H), 4.68 (t, *J* = 8.2 Hz, 2H), 3.20 (t, *J* = 8.1 Hz, 2H), 2.49 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 167.2, 162.9 (d, $J_{(C-F)}$ = 248.2 Hz), 147.7, 143.9, 139.7, 138.4 (d, $J_{(C-F)}$ = 8.8 Hz), 130.6 (d, $J_{(C-F)}$ = 7.6 Hz), 127.3, 126.3, 125.0, 124.9 (d, $J_{(C-F)}$ = 2.5 Hz), 122.2, 118.9, 116.2 (d, $J_{(C-F)}$ = 22.7 Hz), 115.5 (d, $J_{(C-F)}$ = 21.4 Hz), 69.3, 27.6, 21.7.

^{19}F NMR (471 MHz, $CDCl_3$) δ -109.05 – -115.58 (m).

7 References

S1. J. H. Chen, Z. C. Chen, H. Zhao, T. Zhang, W. J. Wang, Y. Zou, X. J. Zhang and M. Yan, *Org. Biomol. Chem*., 2016, **14**, 4071.

S2. L. Z. Yu, X. B. Hu, Q. Xu and M. Shi, *Chem. Commun.*, 2016, **52**, 2701.

8 Copies of NMR Spectra for Compounds

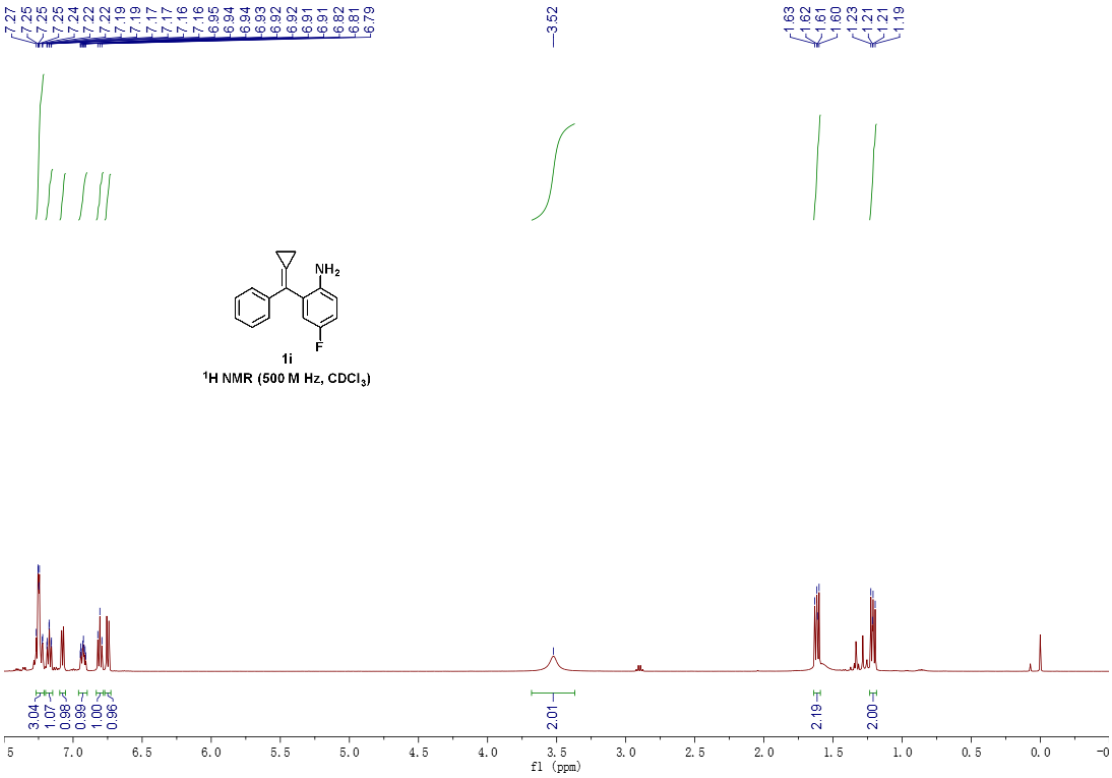


Figure S2. ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of 1i

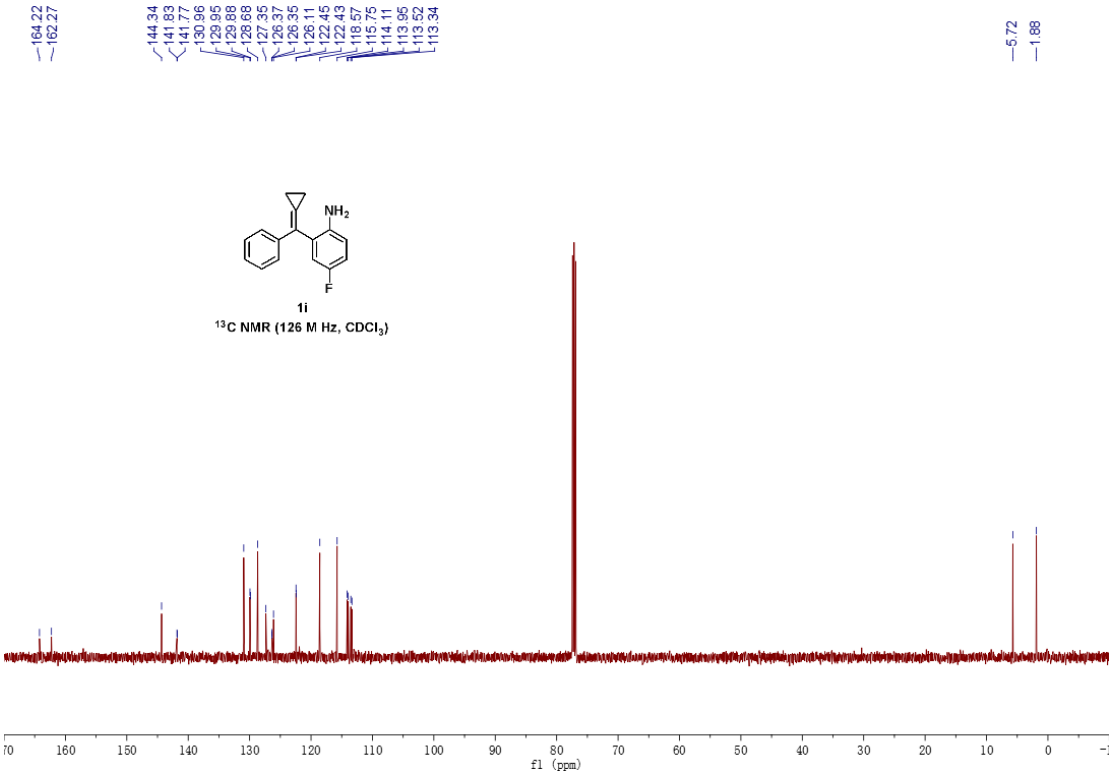


Figure S3. ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of 1i

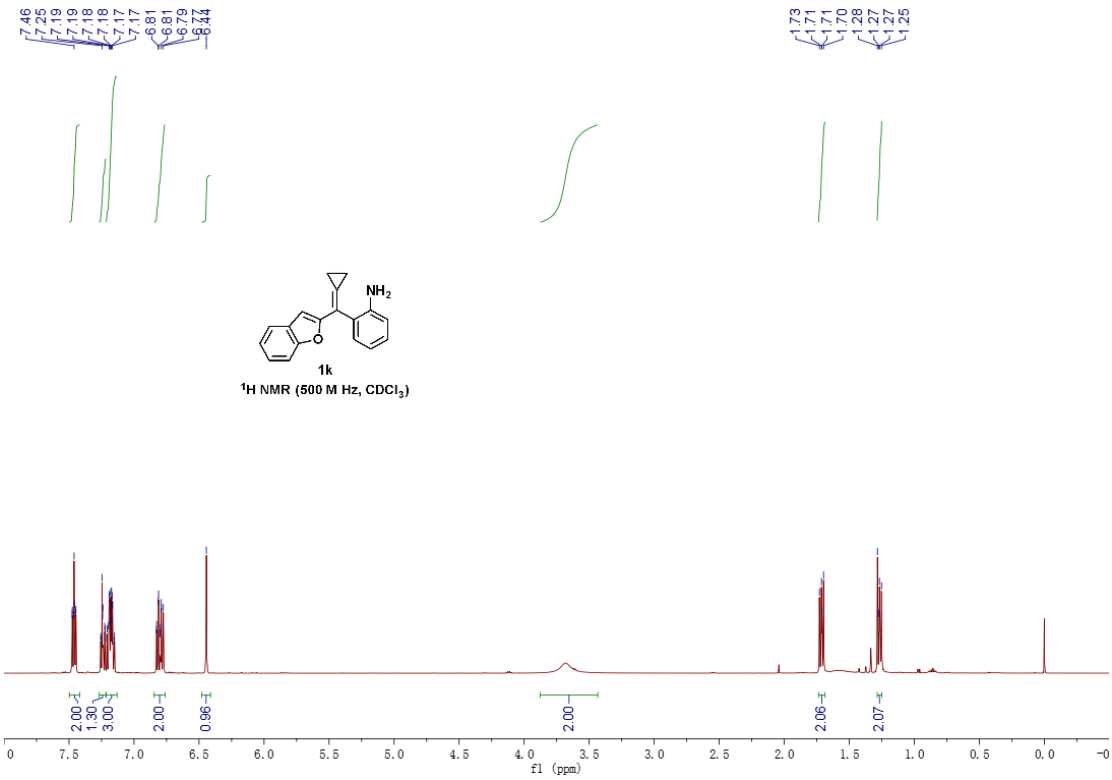


Figure S4. ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of 1k

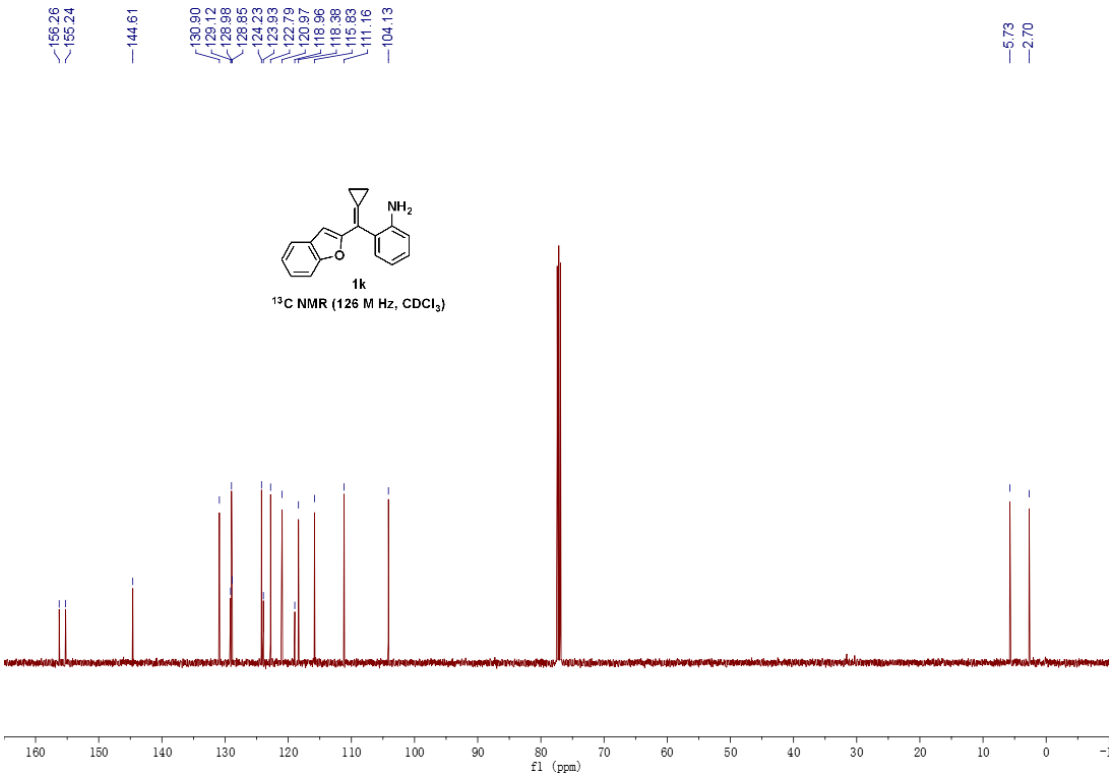


Figure S5. ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of 1k

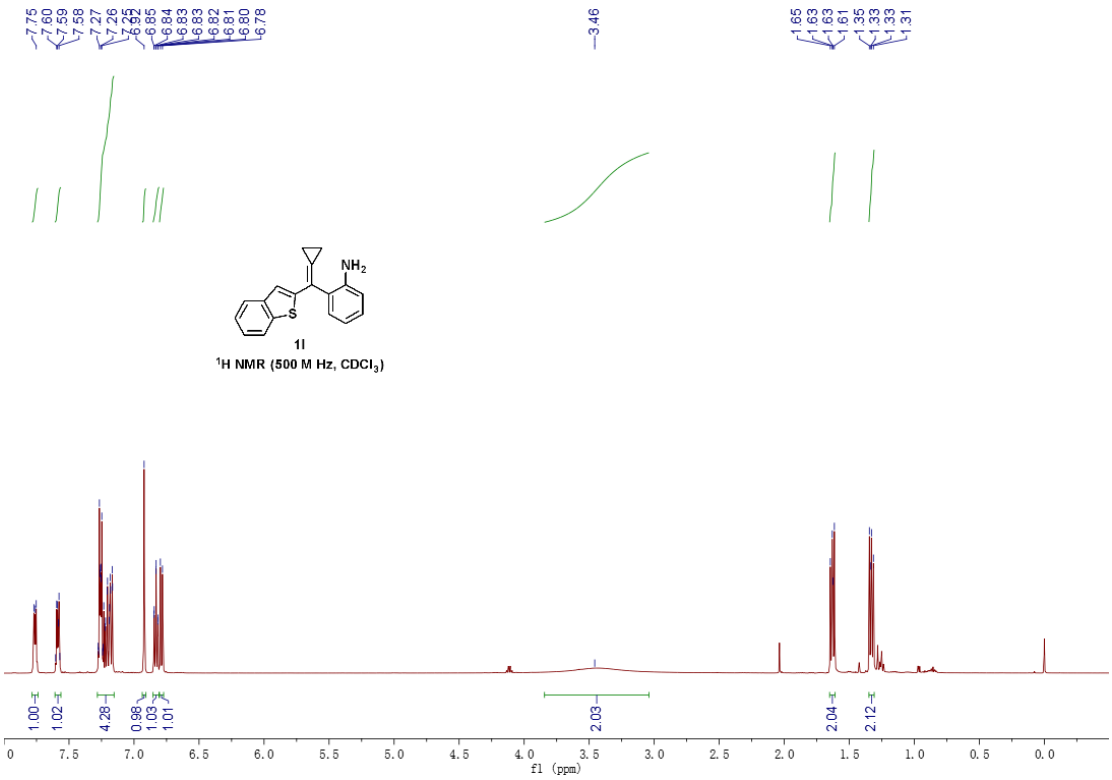


Figure S6. ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of 1l

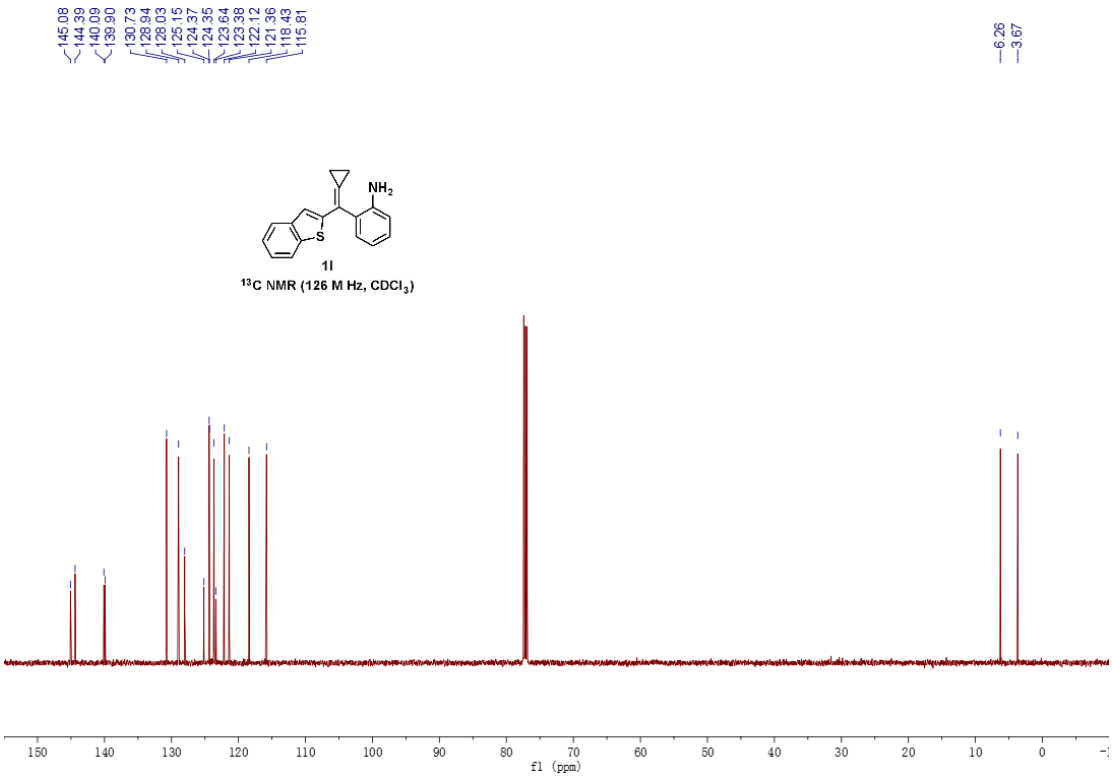


Figure S7. ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of 1l

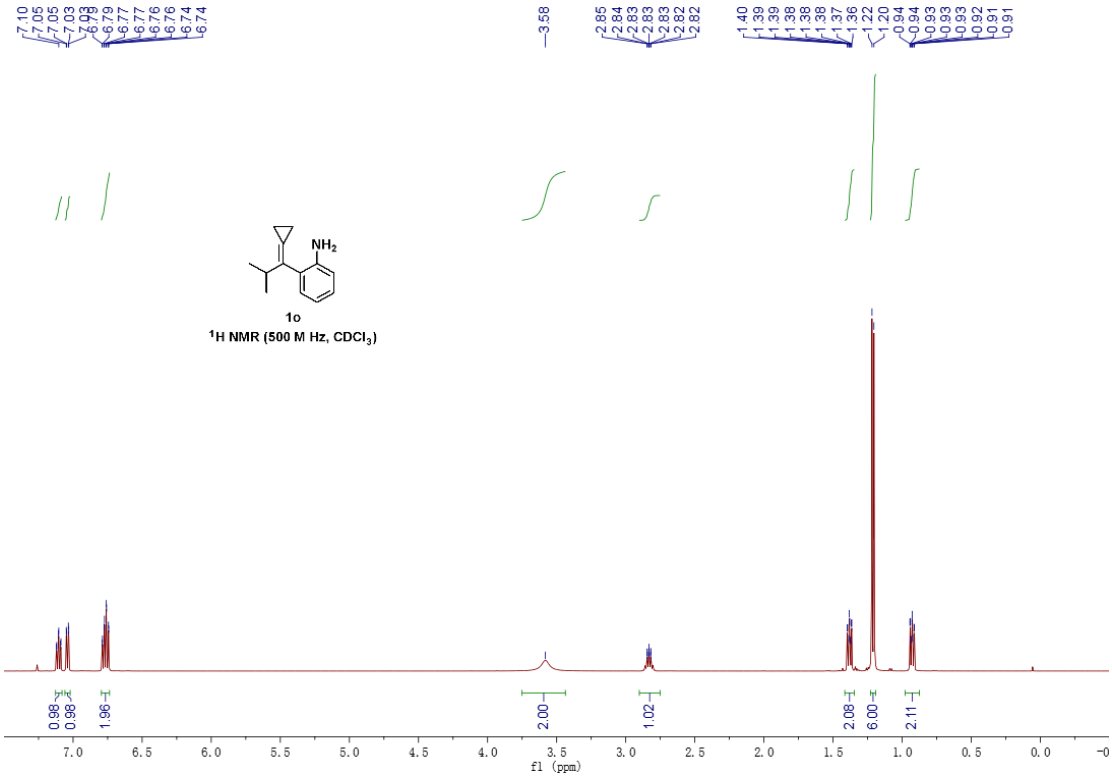


Figure S8. ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of 1o

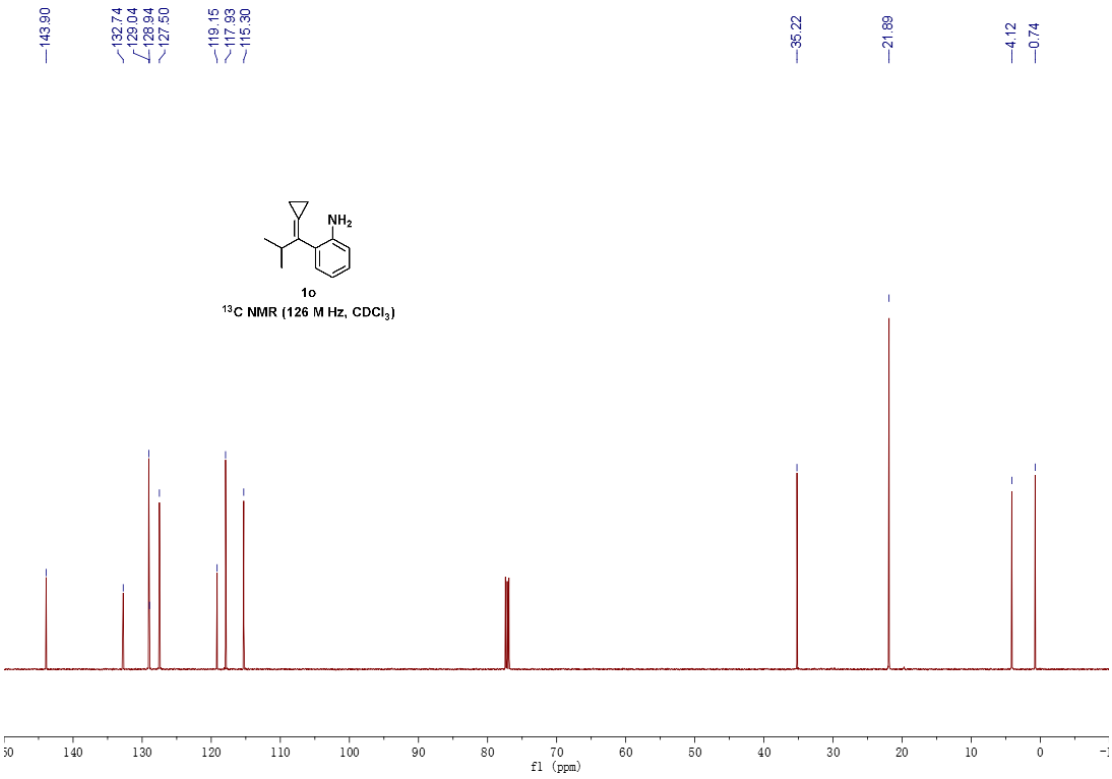


Figure S9. ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of 1o

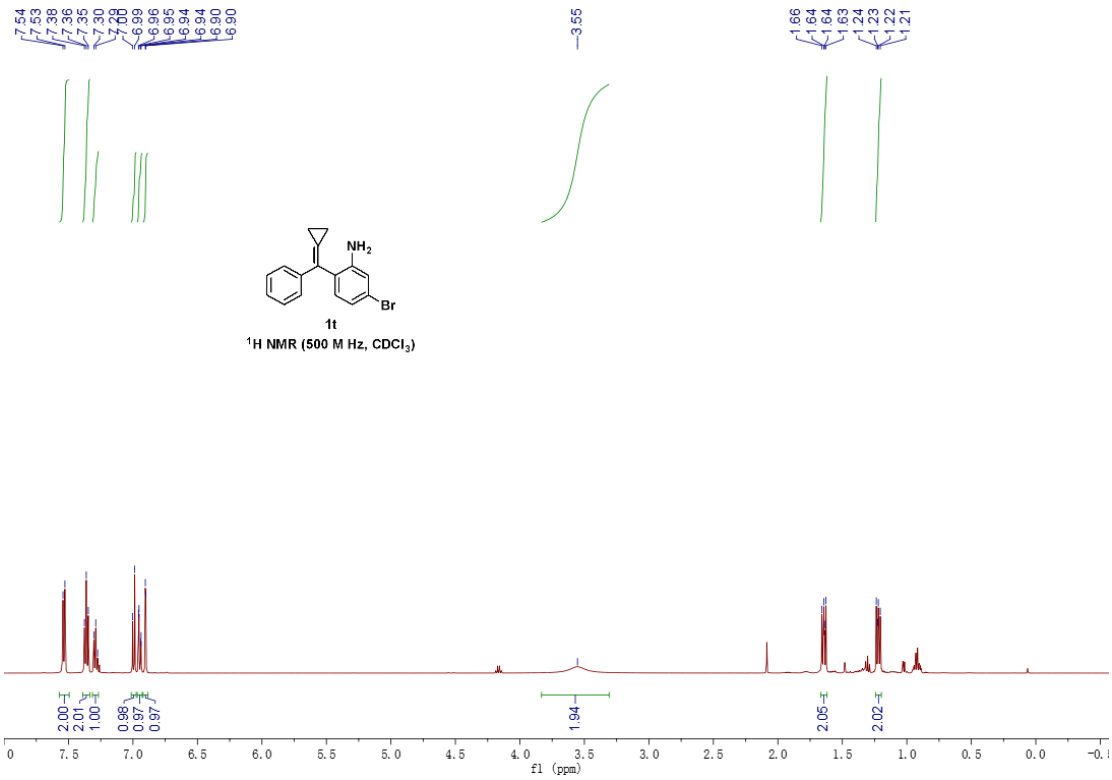


Figure S10. ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of 1t

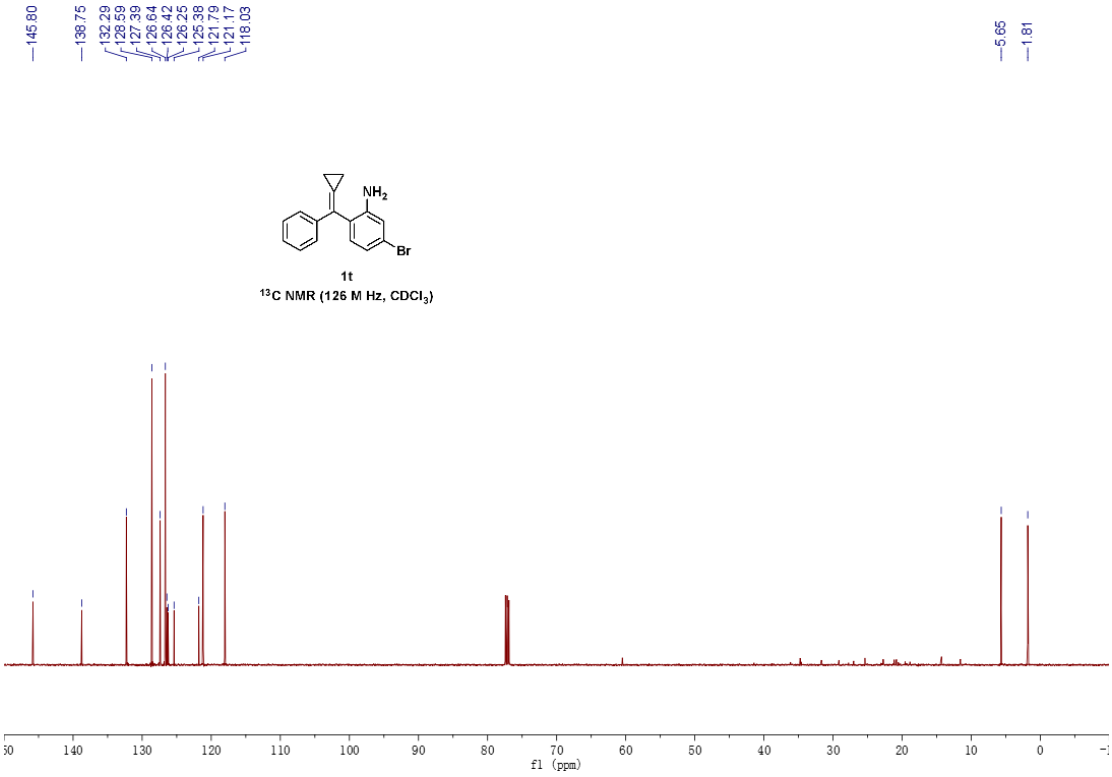


Figure S11. ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of 1t

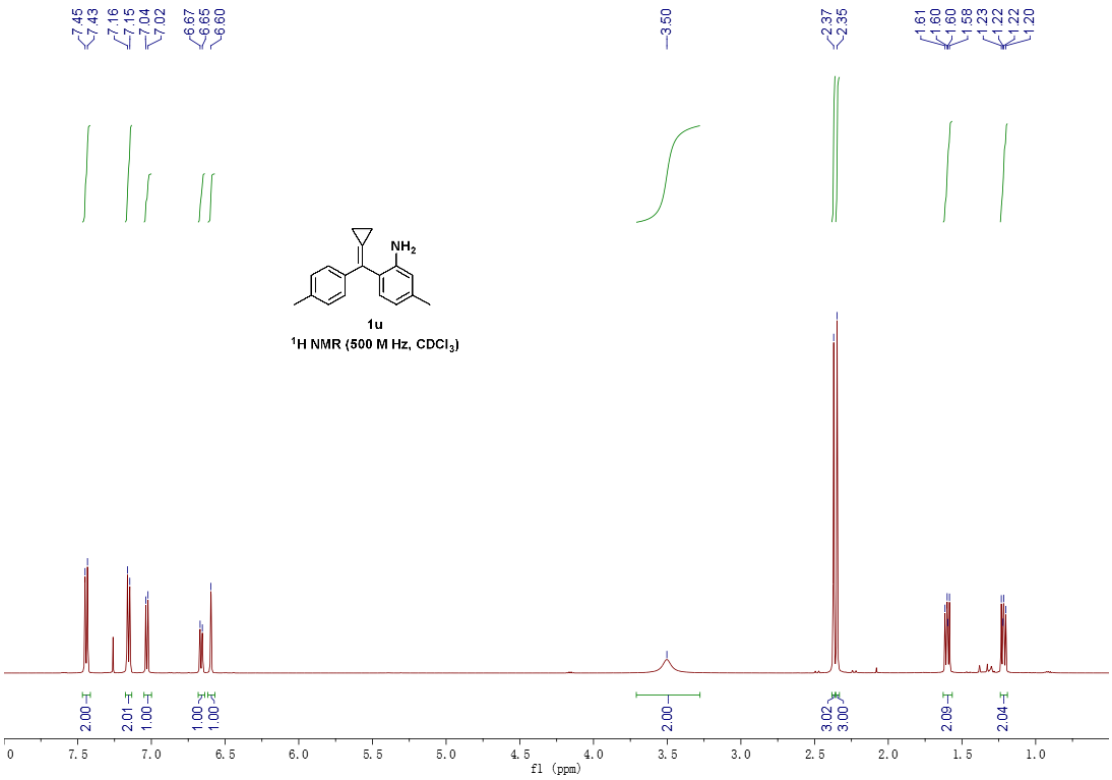


Figure S12. ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of 1u

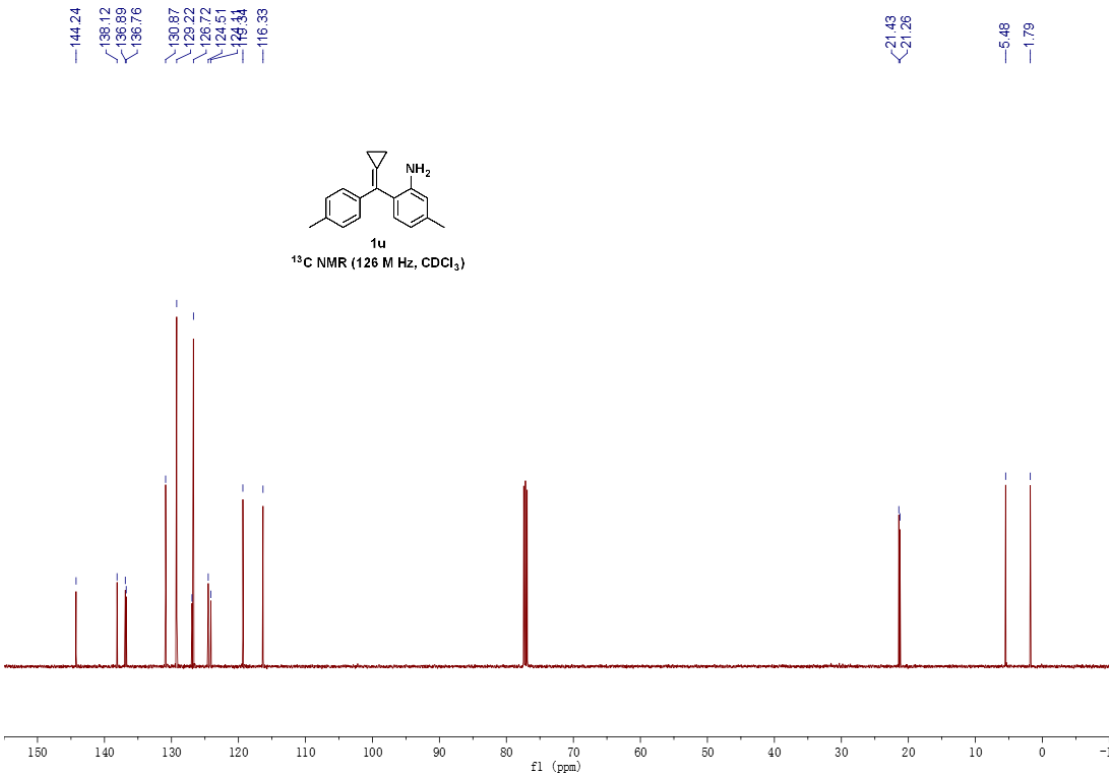


Figure S13. ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of 1u

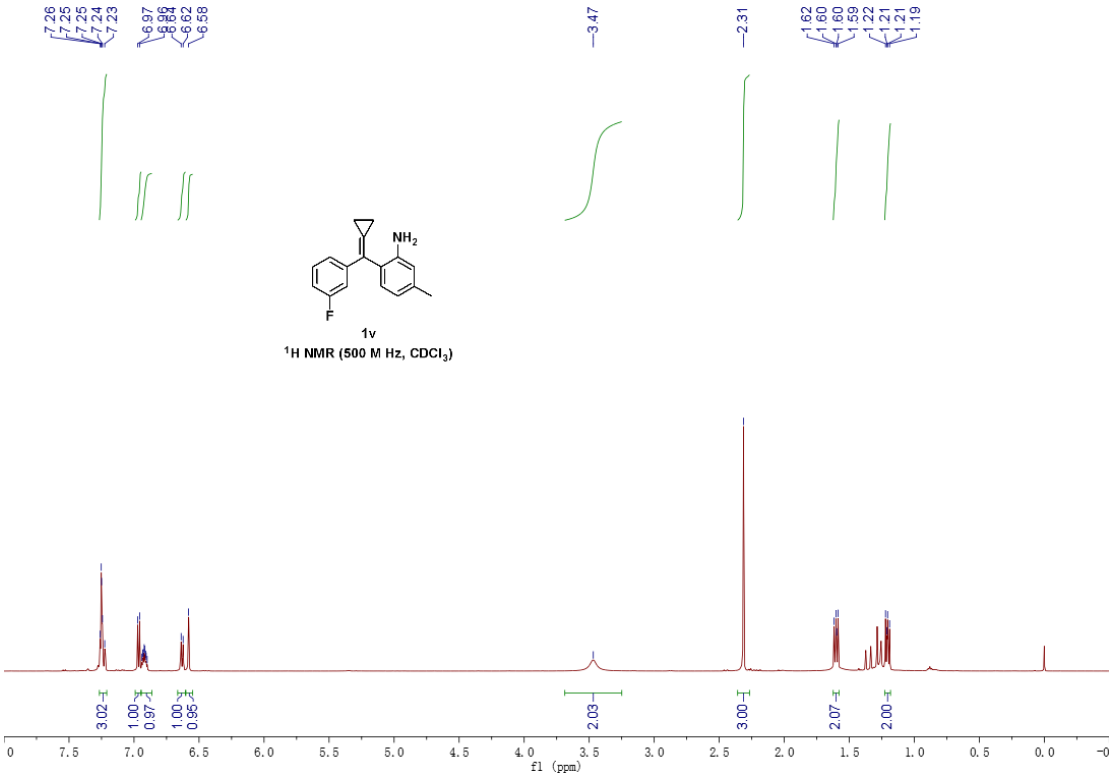


Figure S14. ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of 1v

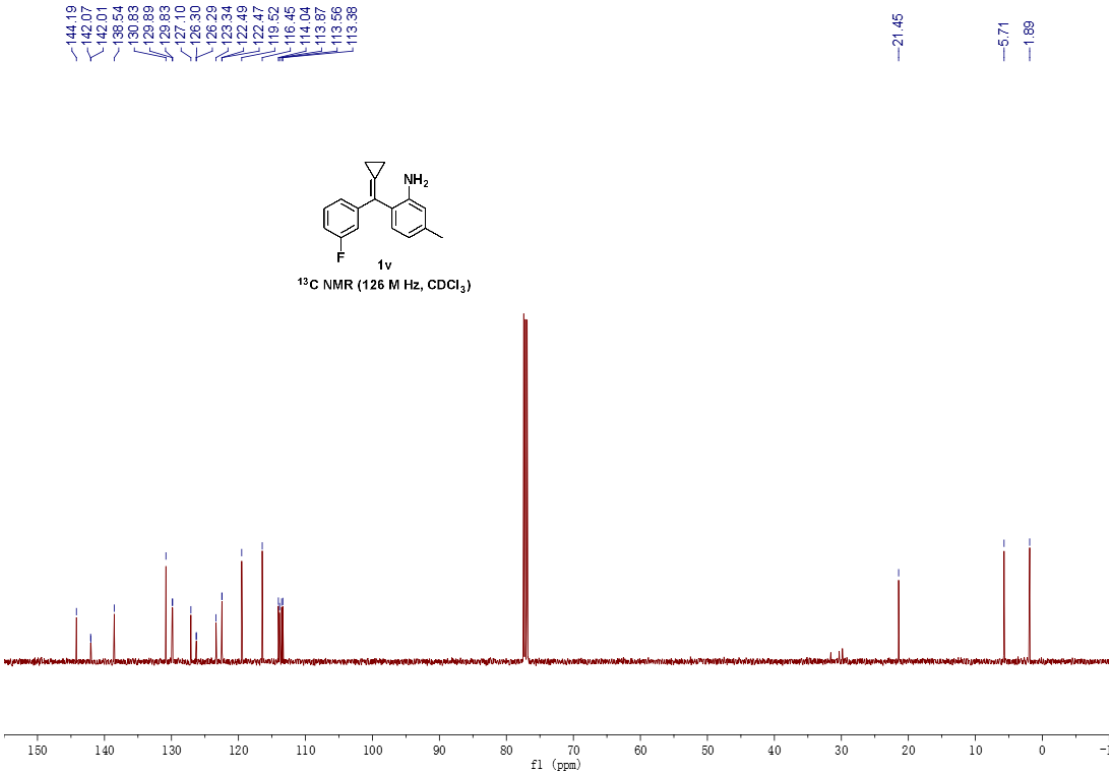


Figure S15. ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of 1v

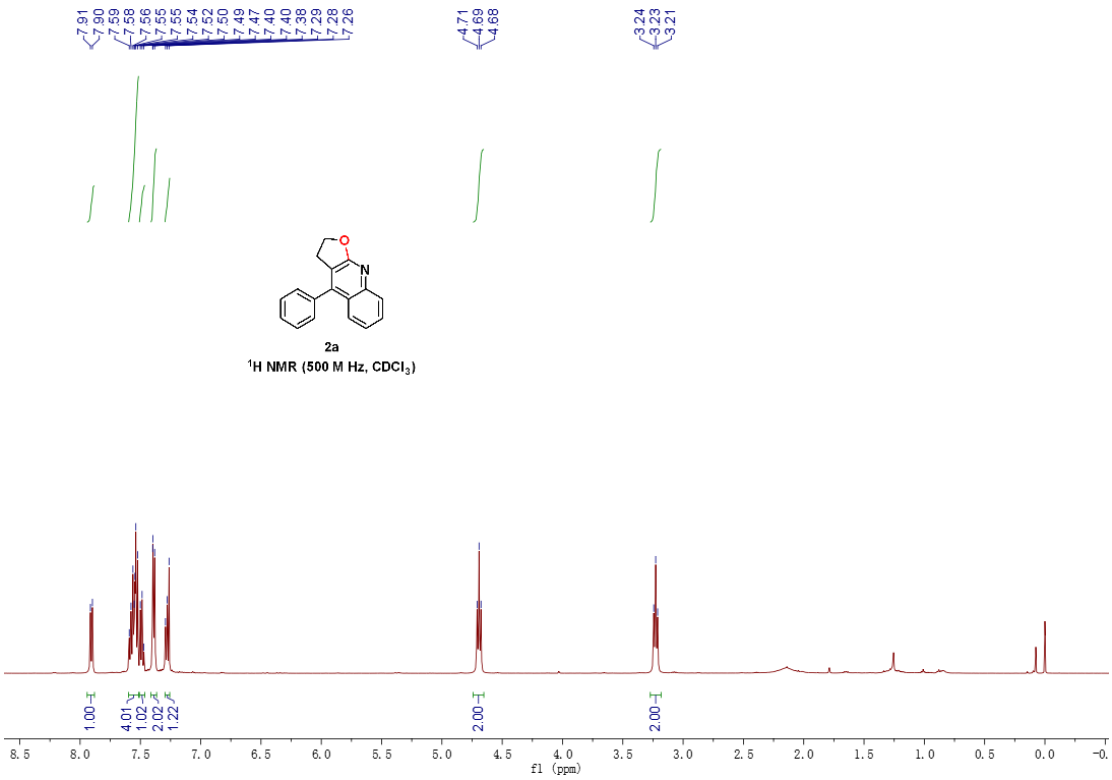


Figure S16. ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of 2a

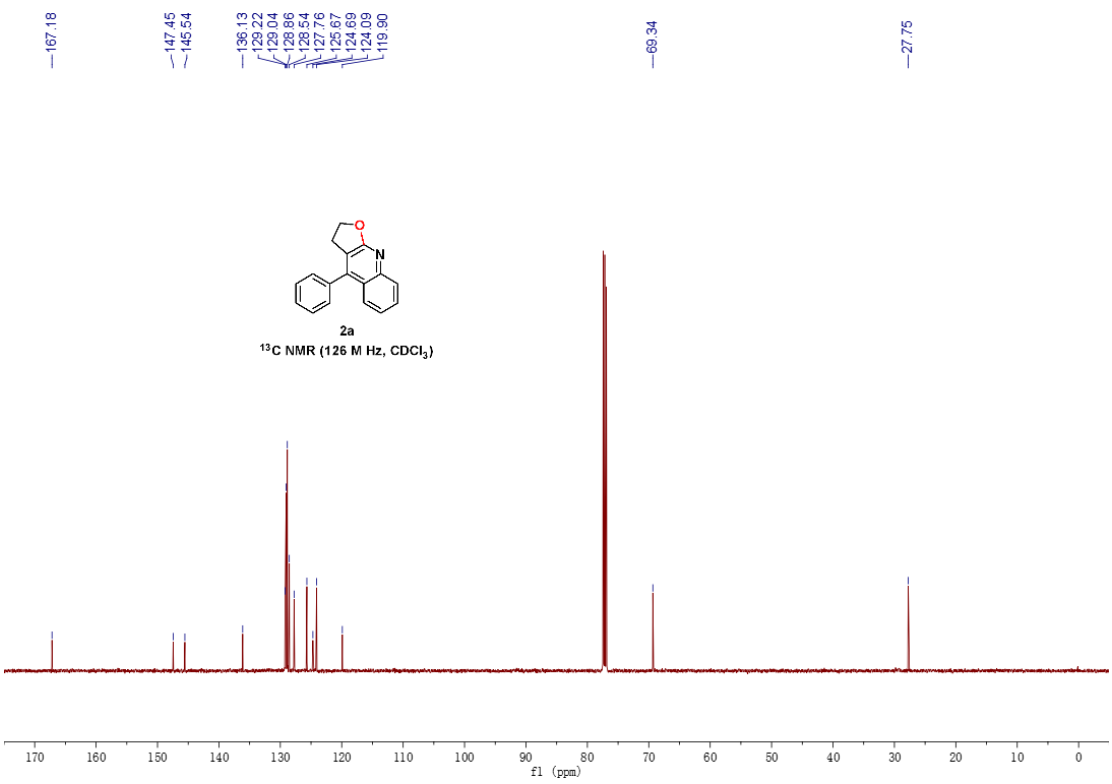


Figure S17. ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of 2a

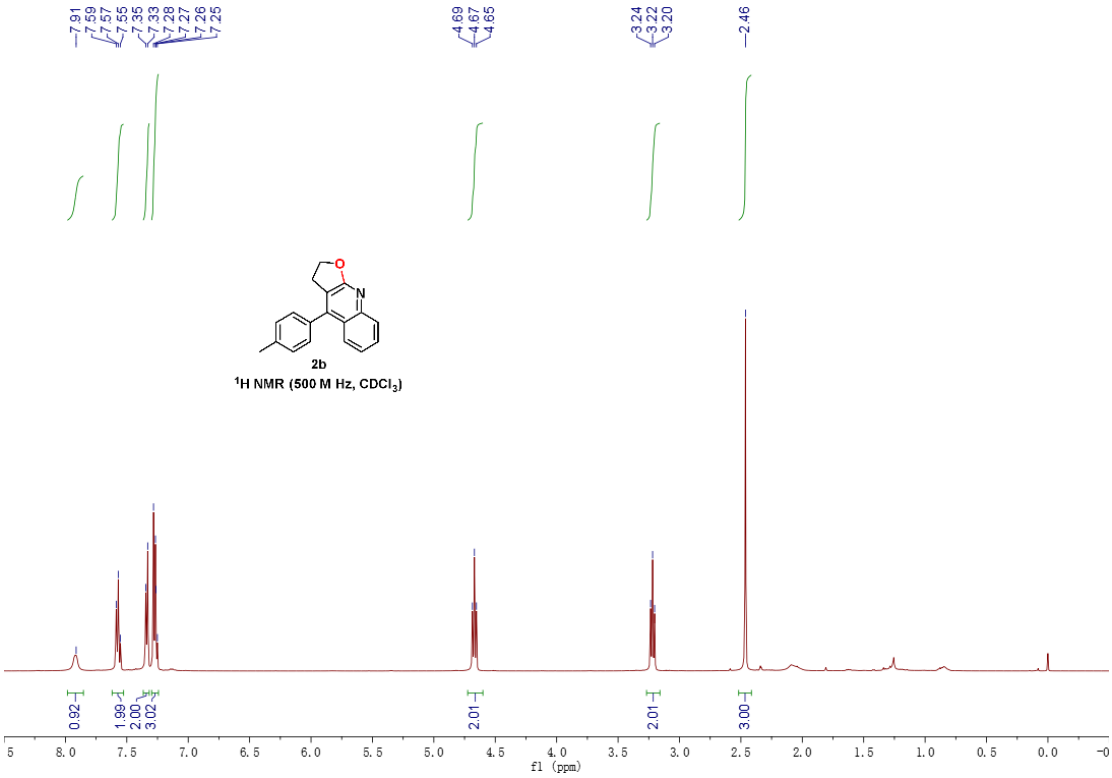


Figure S18. ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of 2b

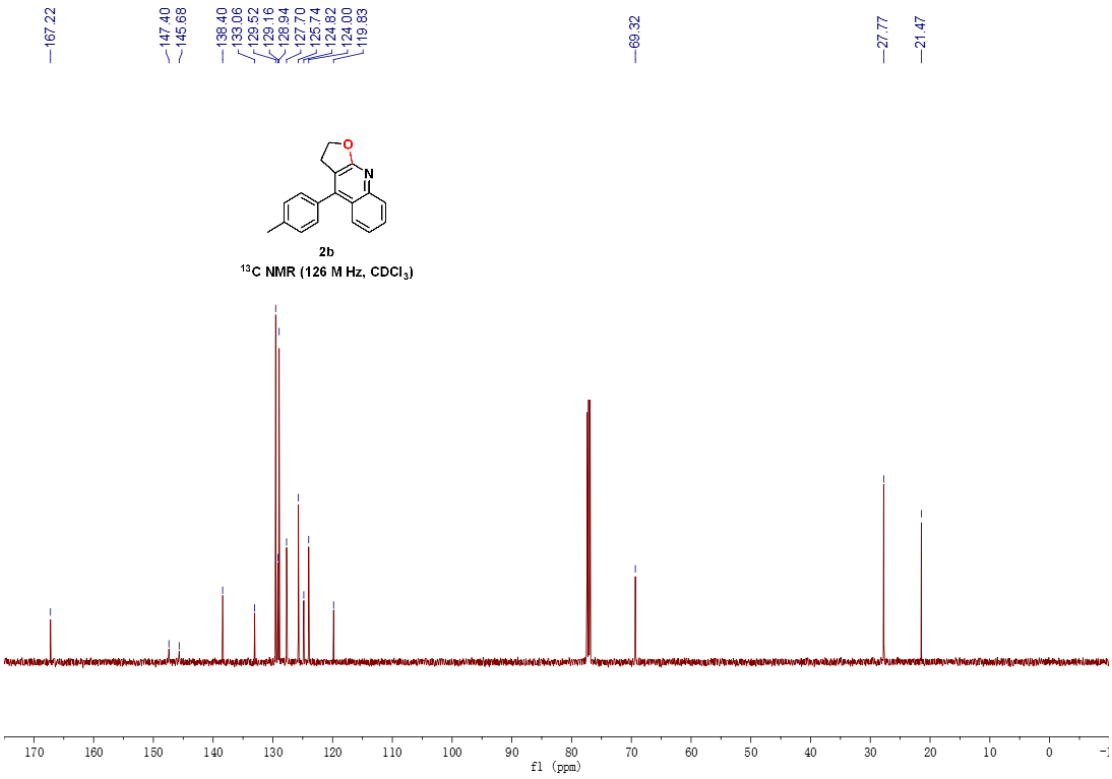


Figure S19. ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of 2b

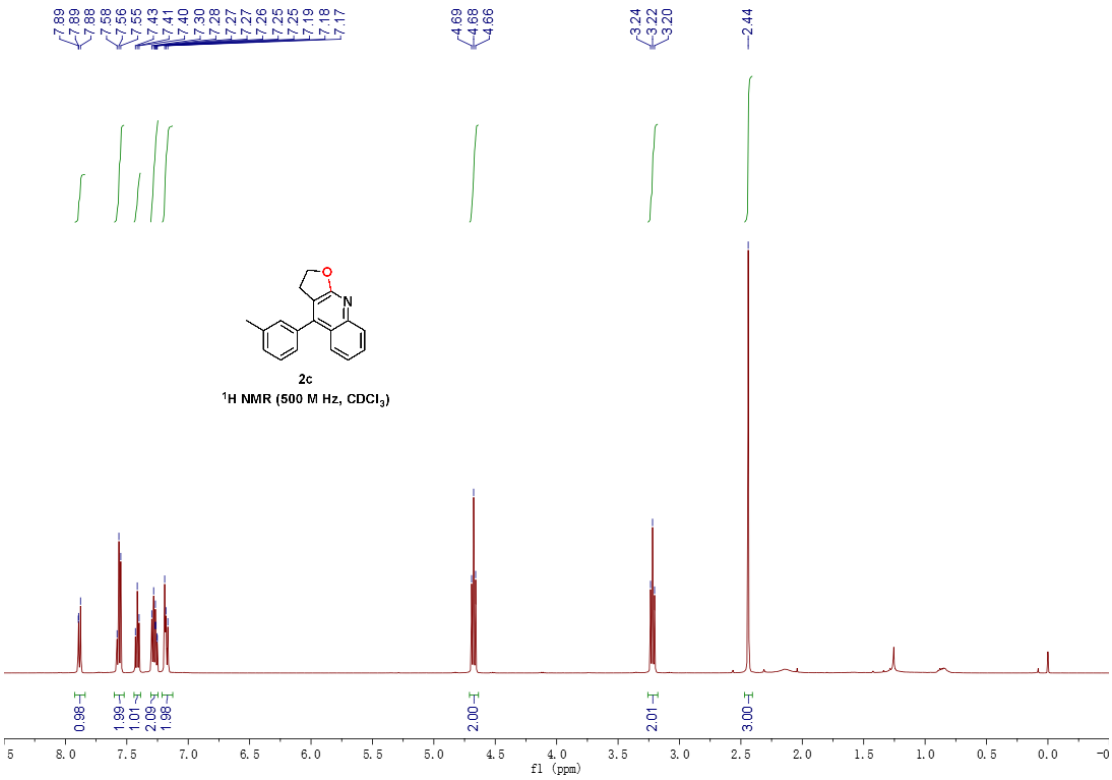


Figure S20. ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of 2c

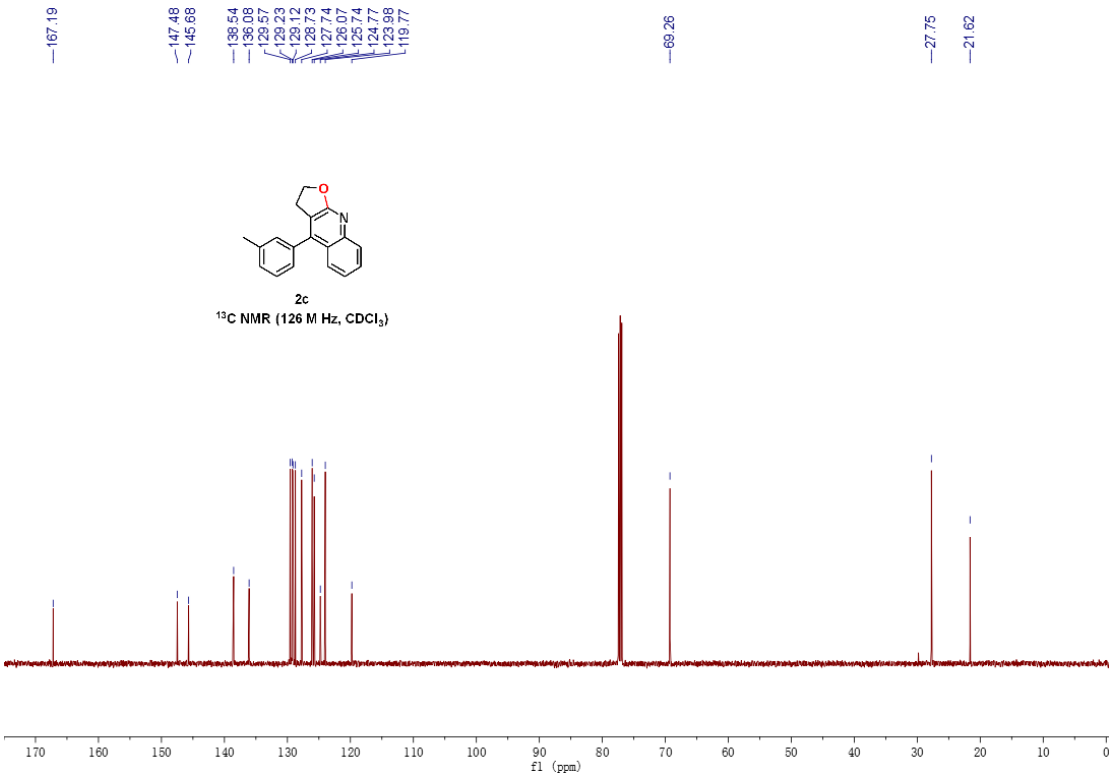


Figure S21. ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of 2c

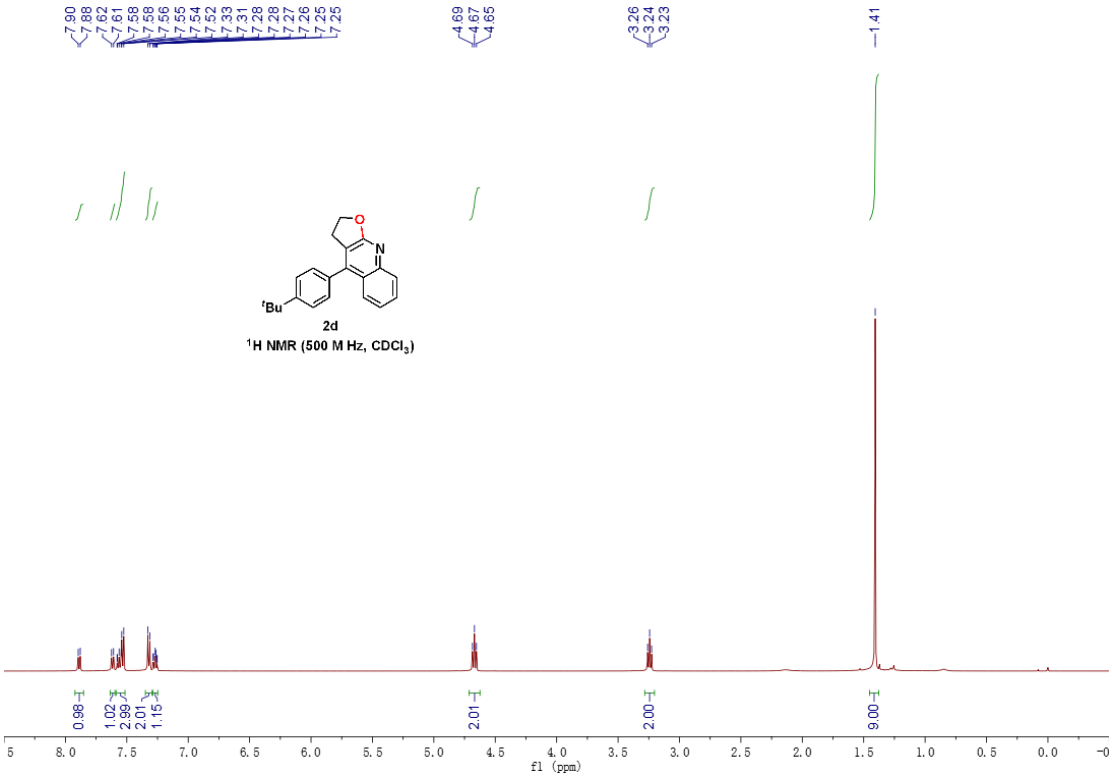


Figure S22. ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of 2d

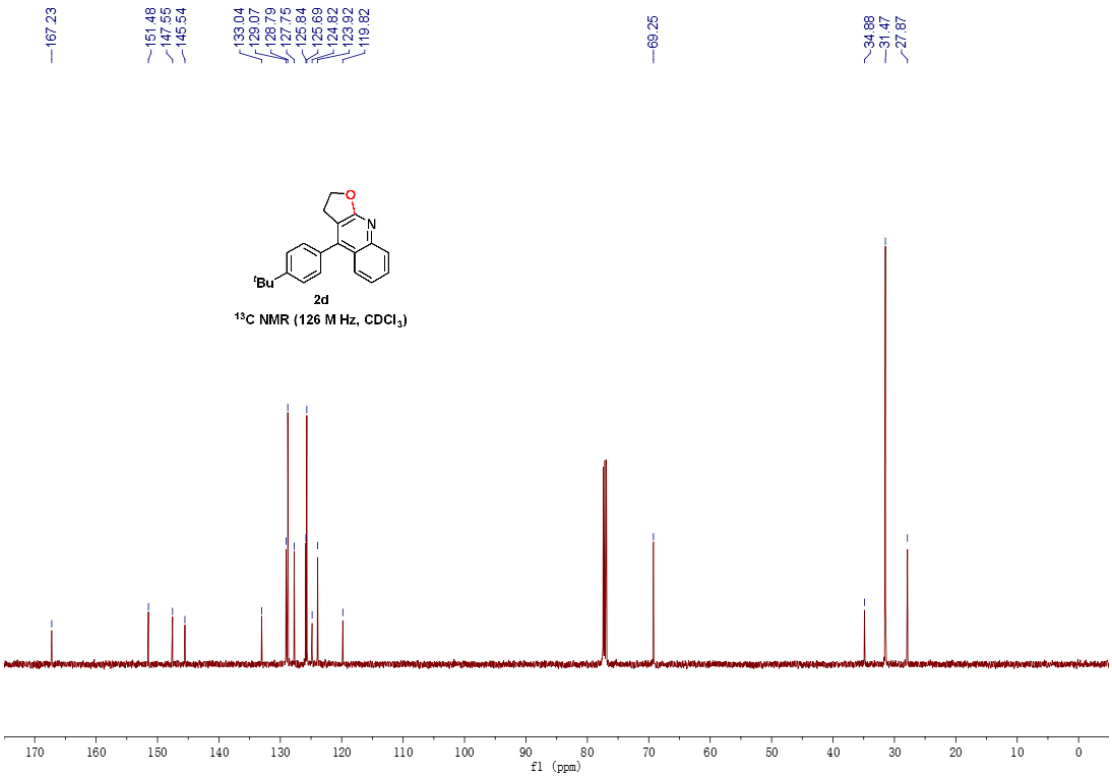


Figure S23. ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of 2d

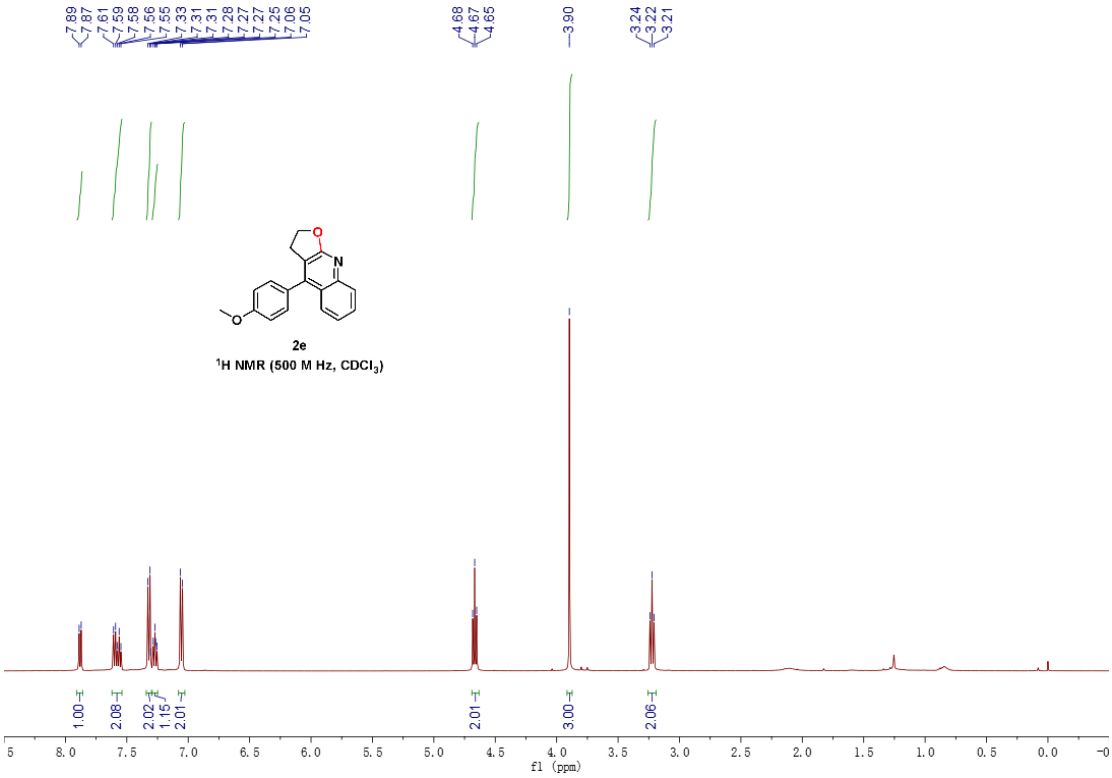


Figure S24. ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of 2e

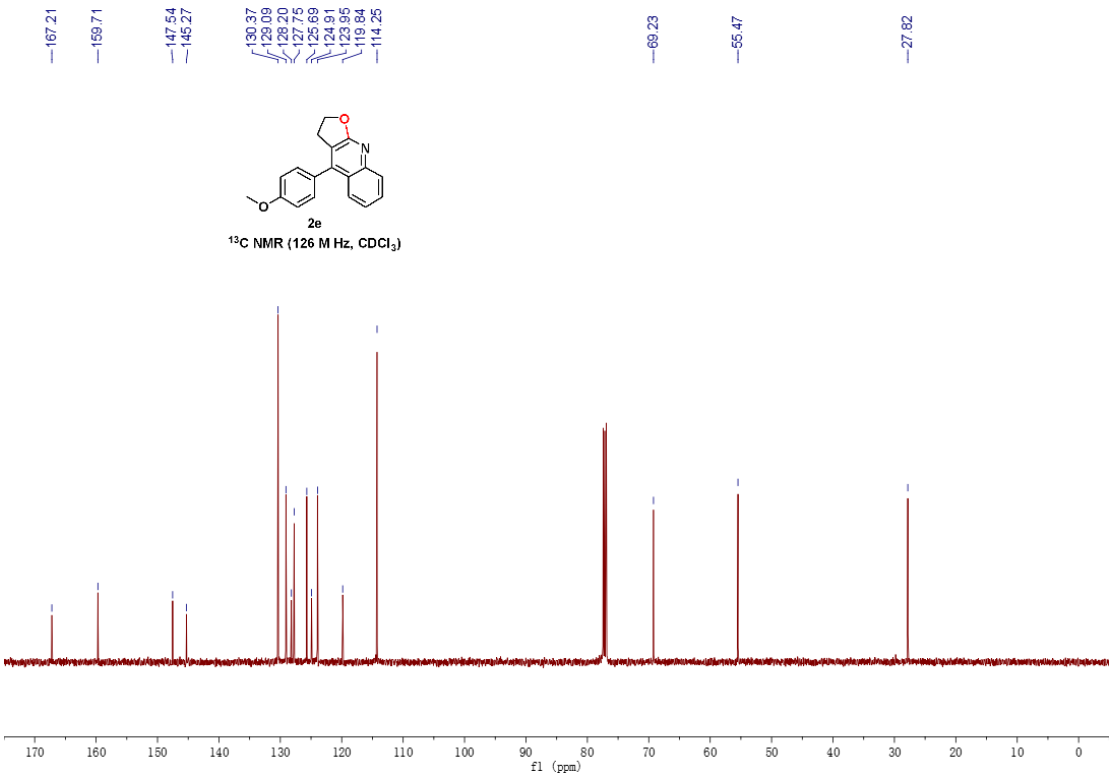


Figure S25. ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of 2e

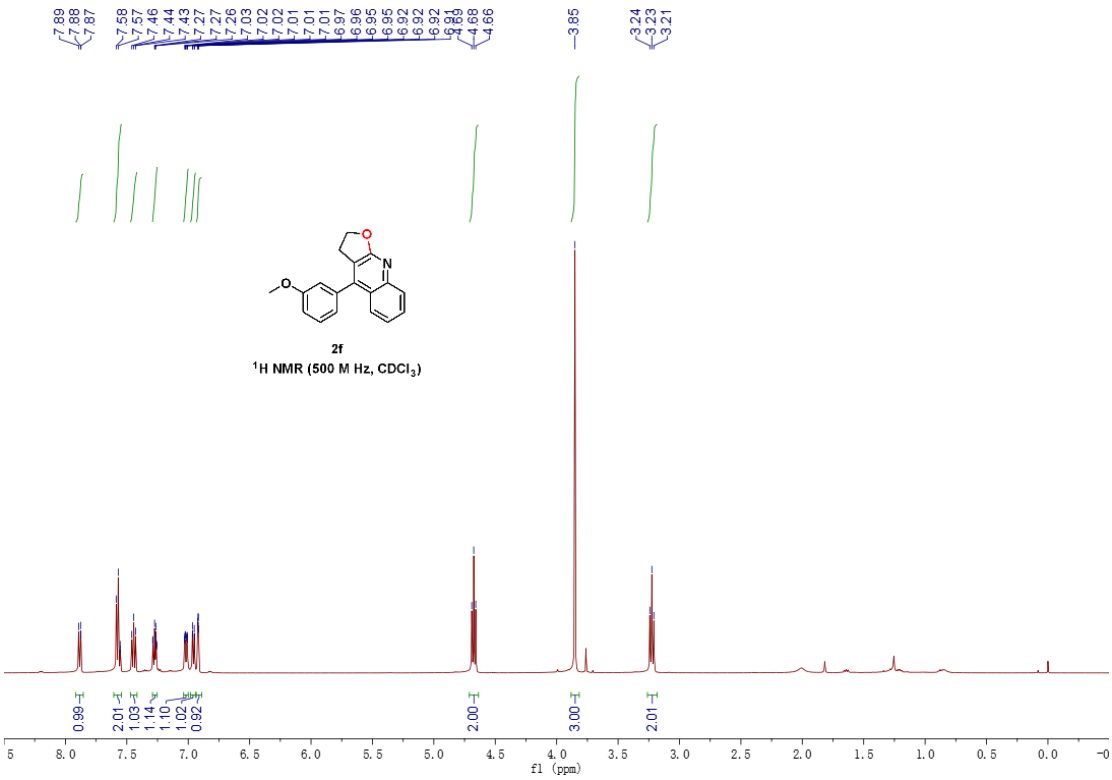


Figure S26. ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of 2f

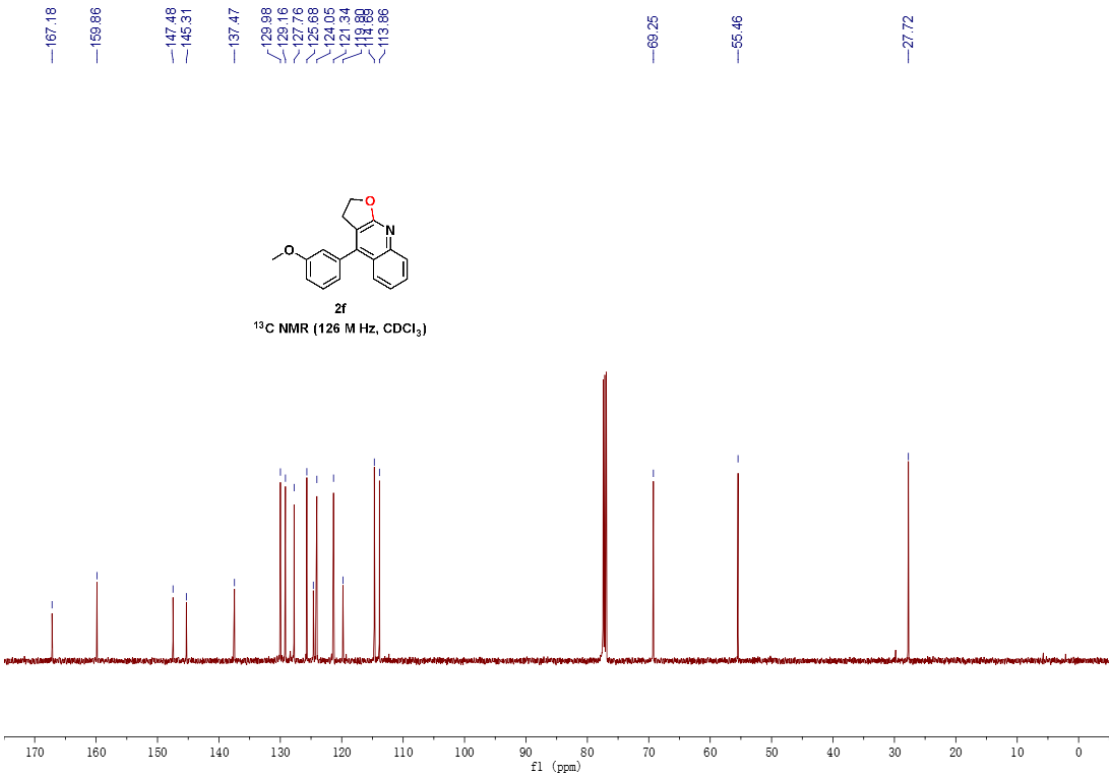


Figure S27. ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of 2f

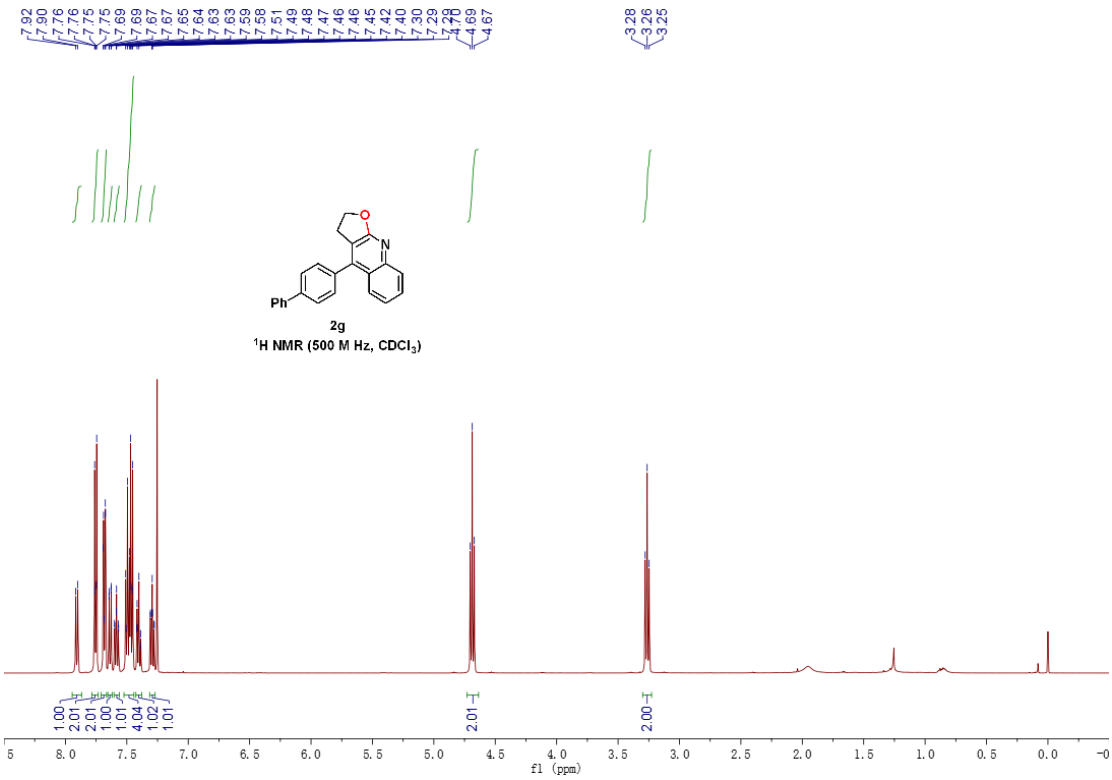


Figure S28. ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of 2g

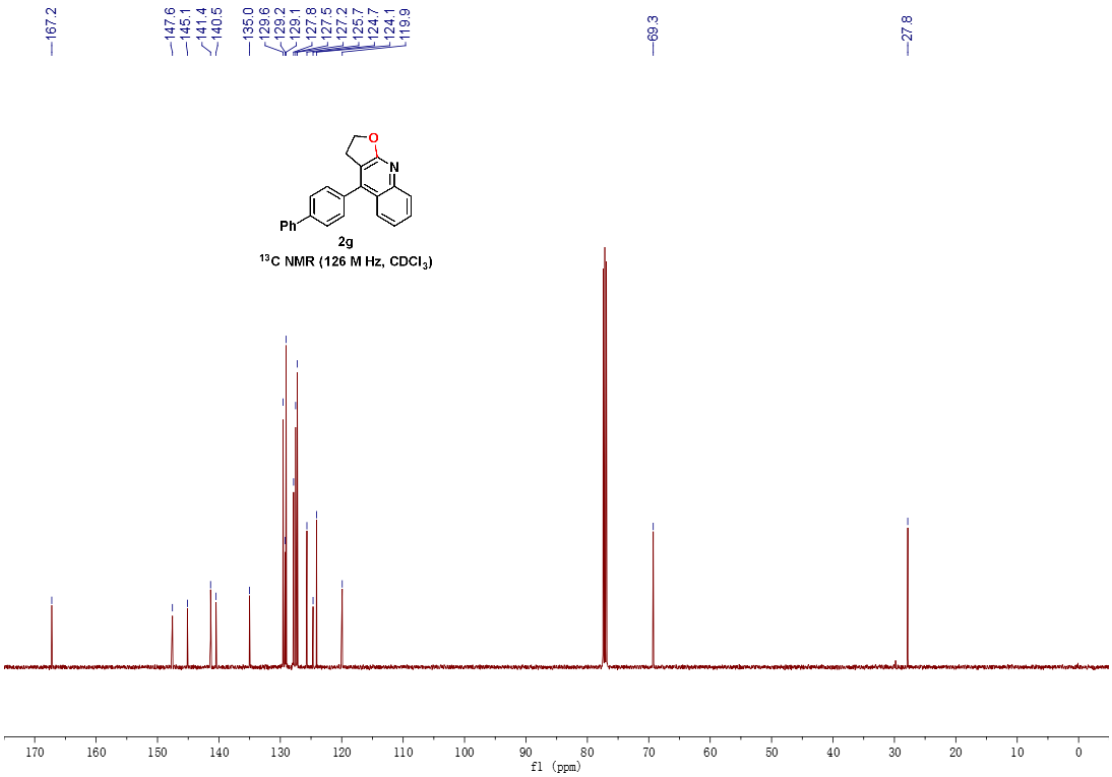


Figure S29. ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of 2g

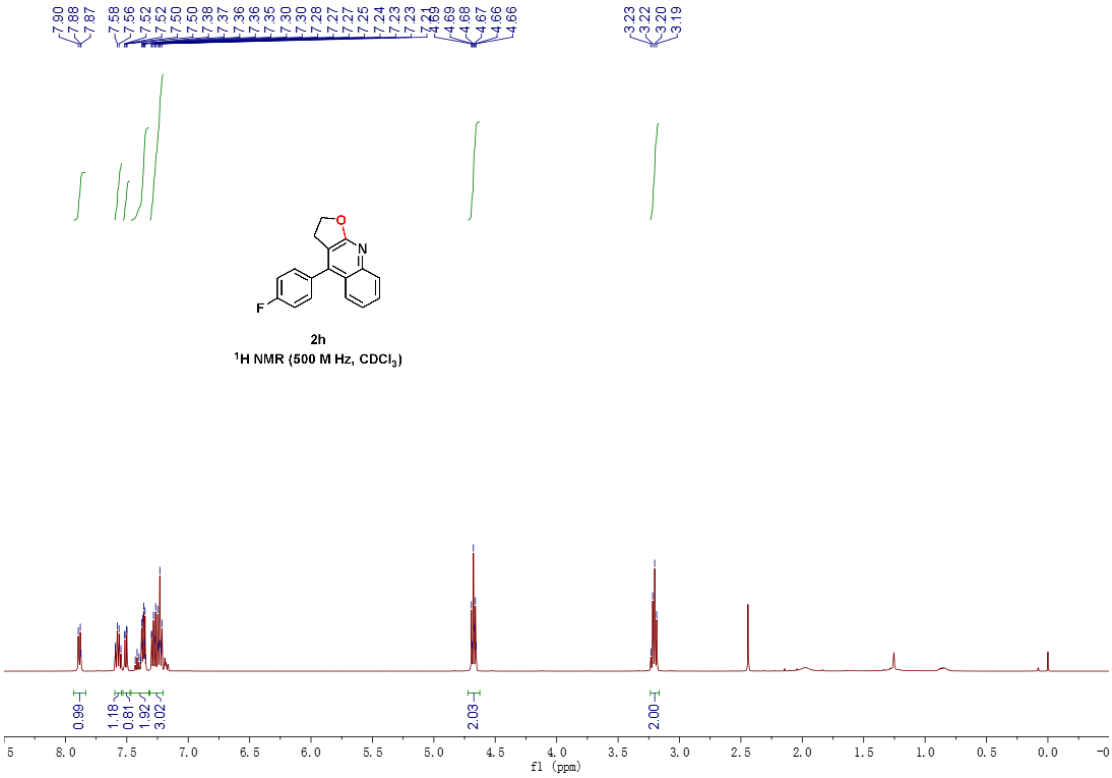


Figure S30. ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of 2h

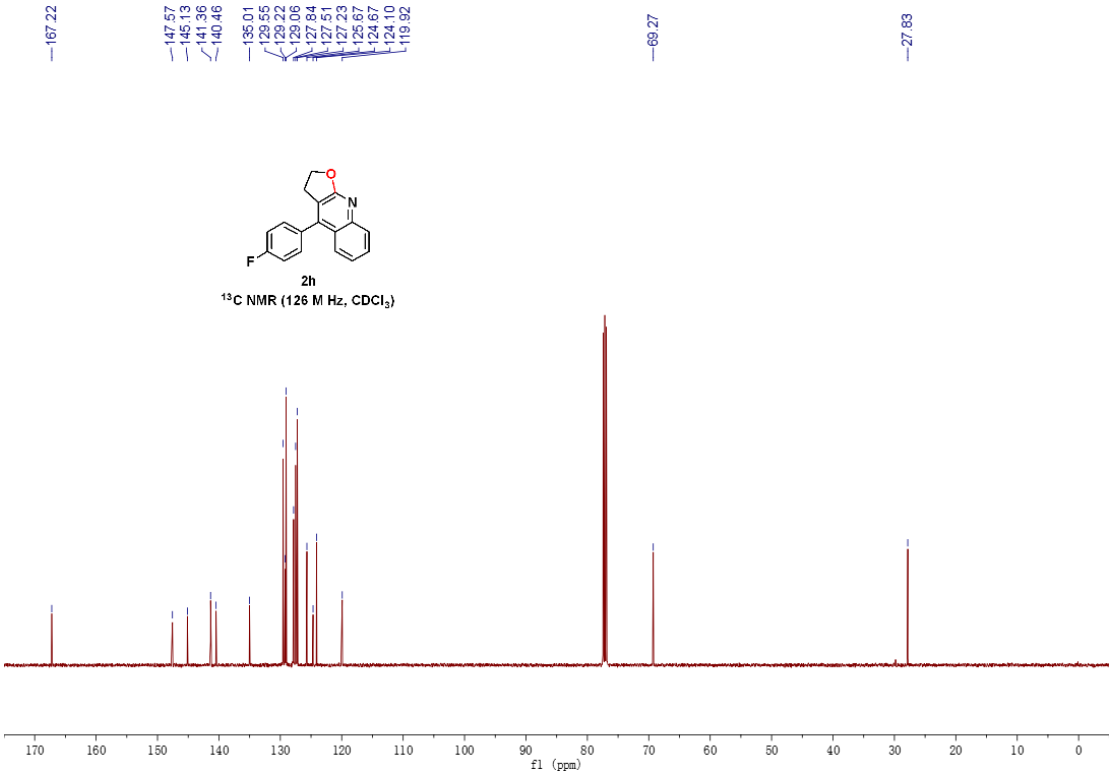


Figure S31. ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of 2h

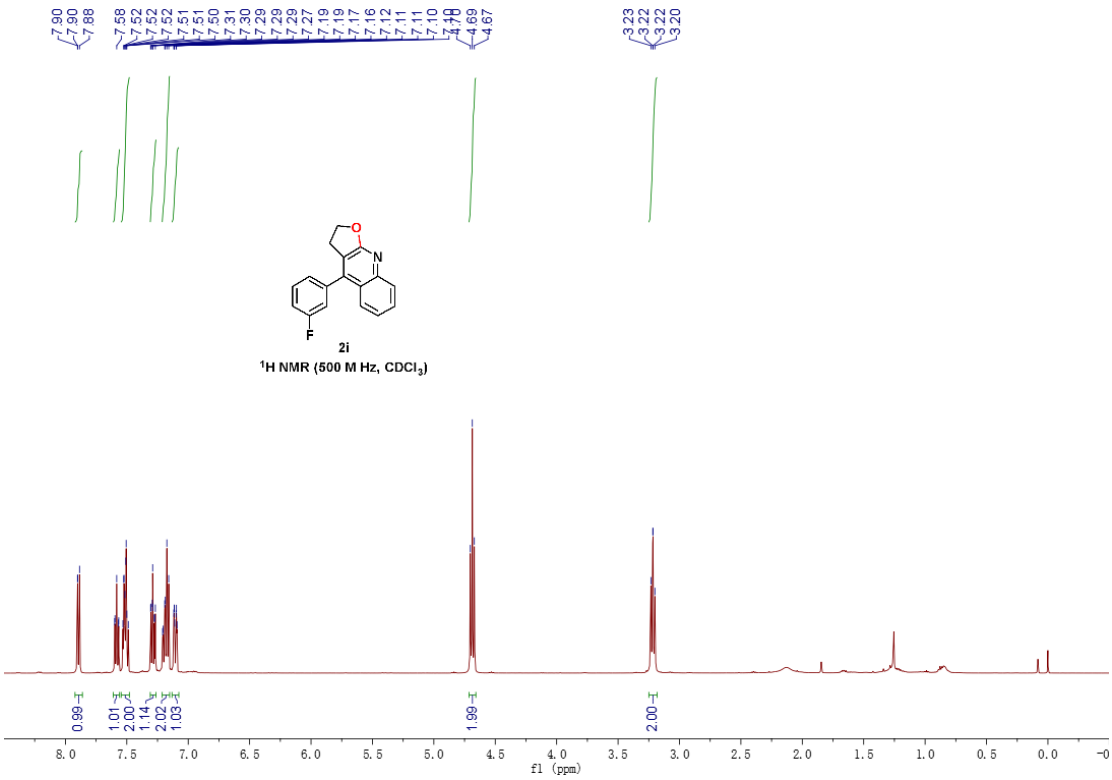


Figure S32. ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of 2i

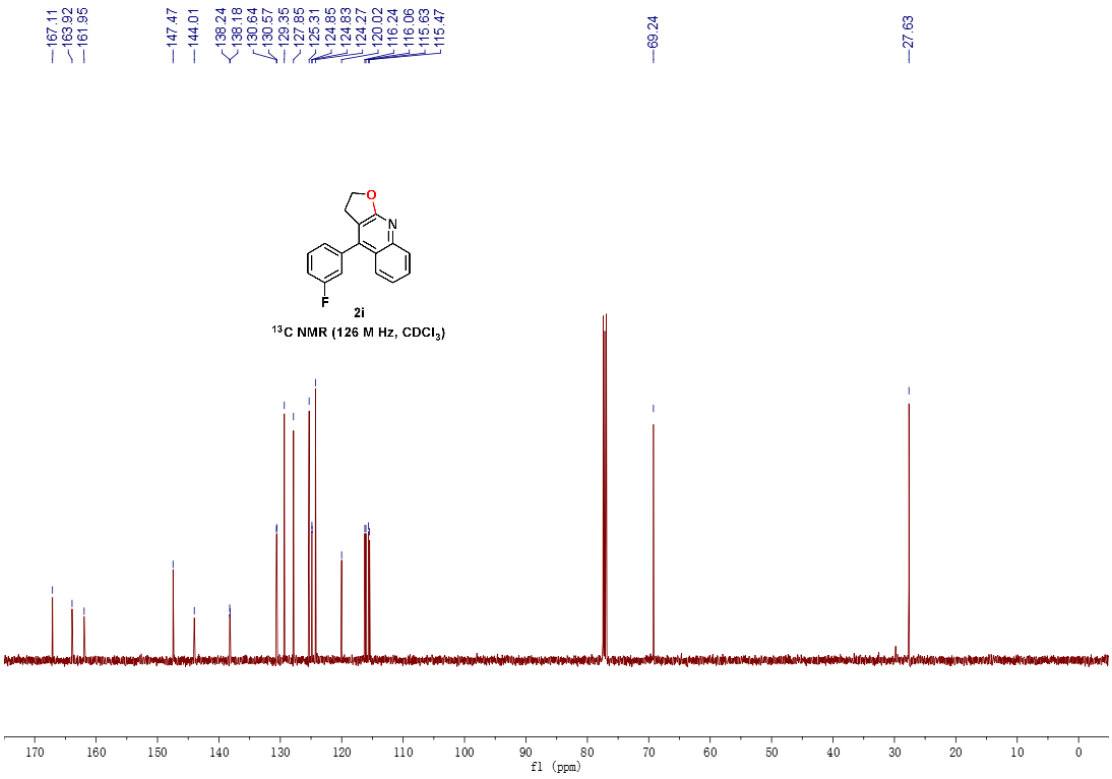


Figure S33. ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of 2i

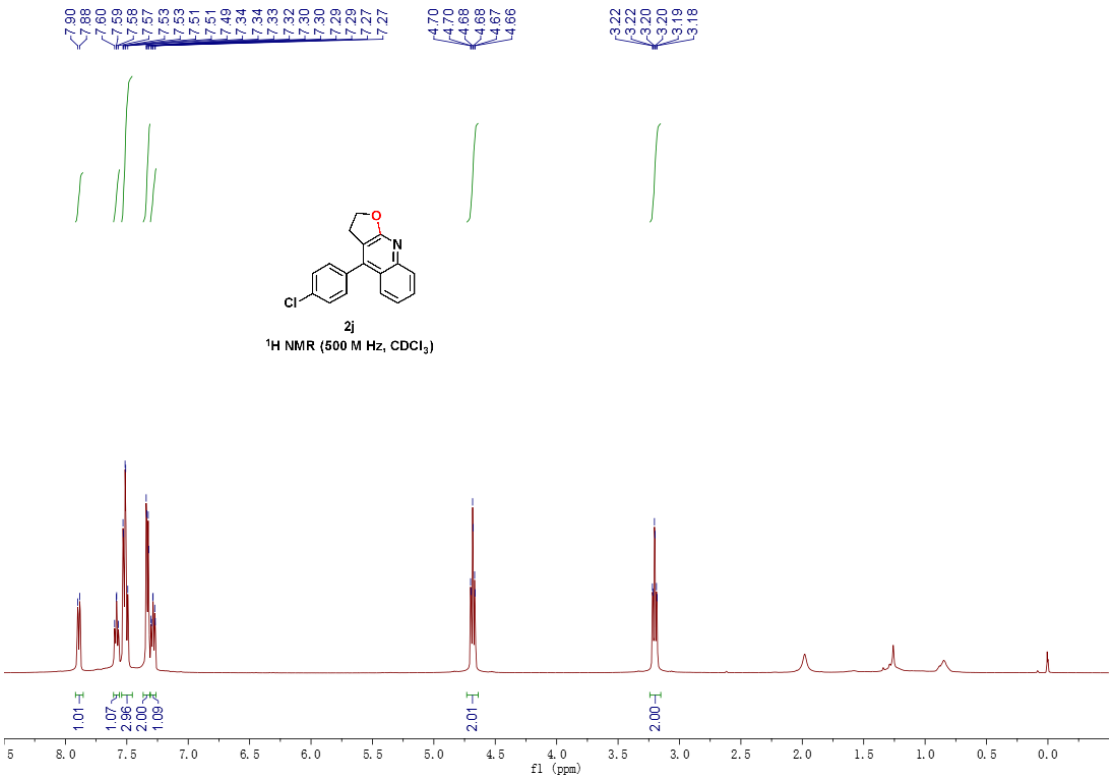


Figure S34. ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of 2j

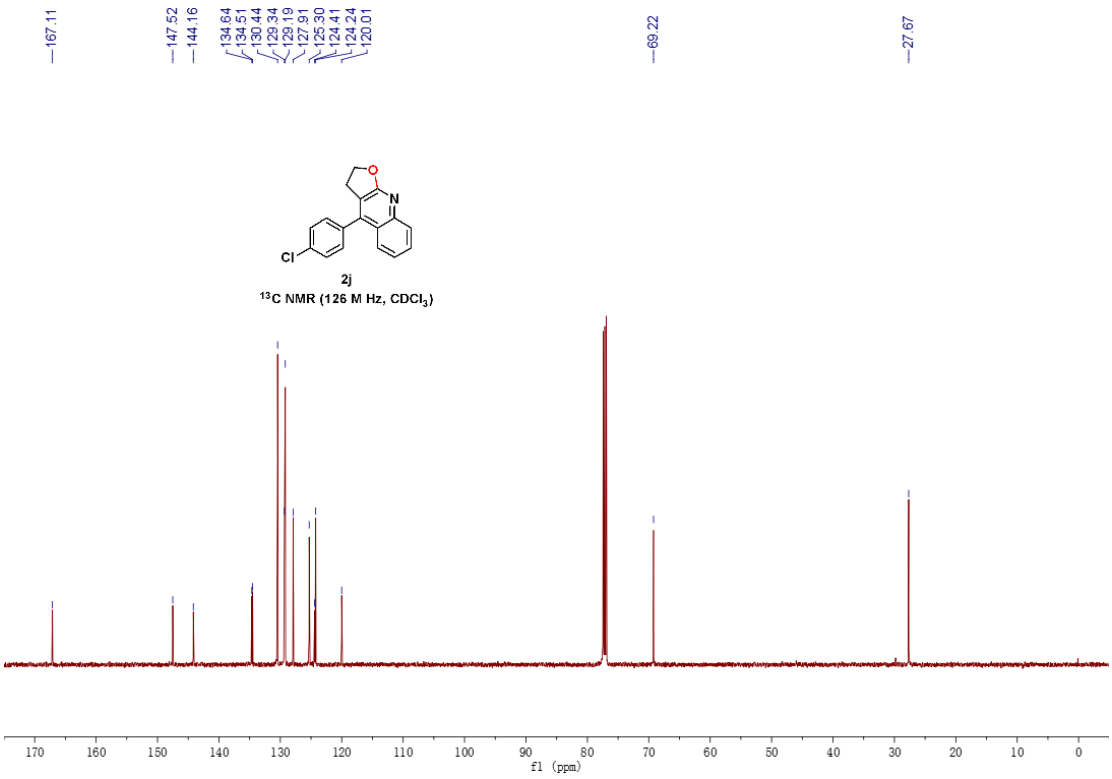


Figure S35. ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of 2j

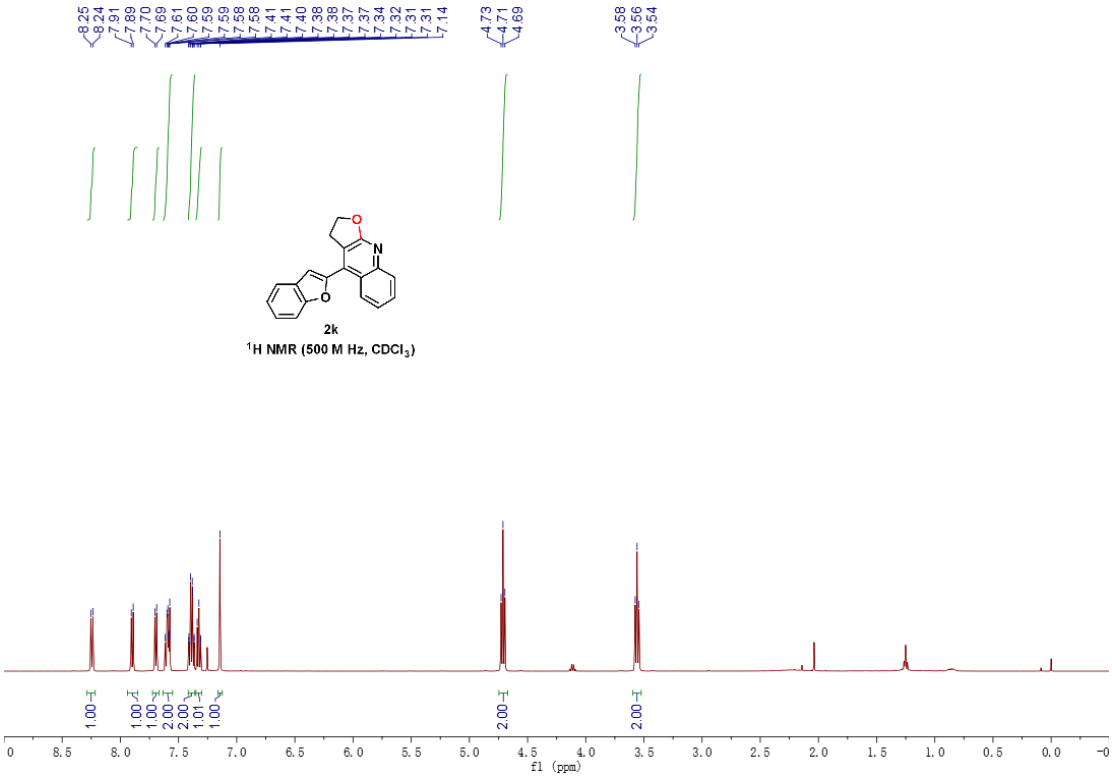


Figure S36. ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of 2k

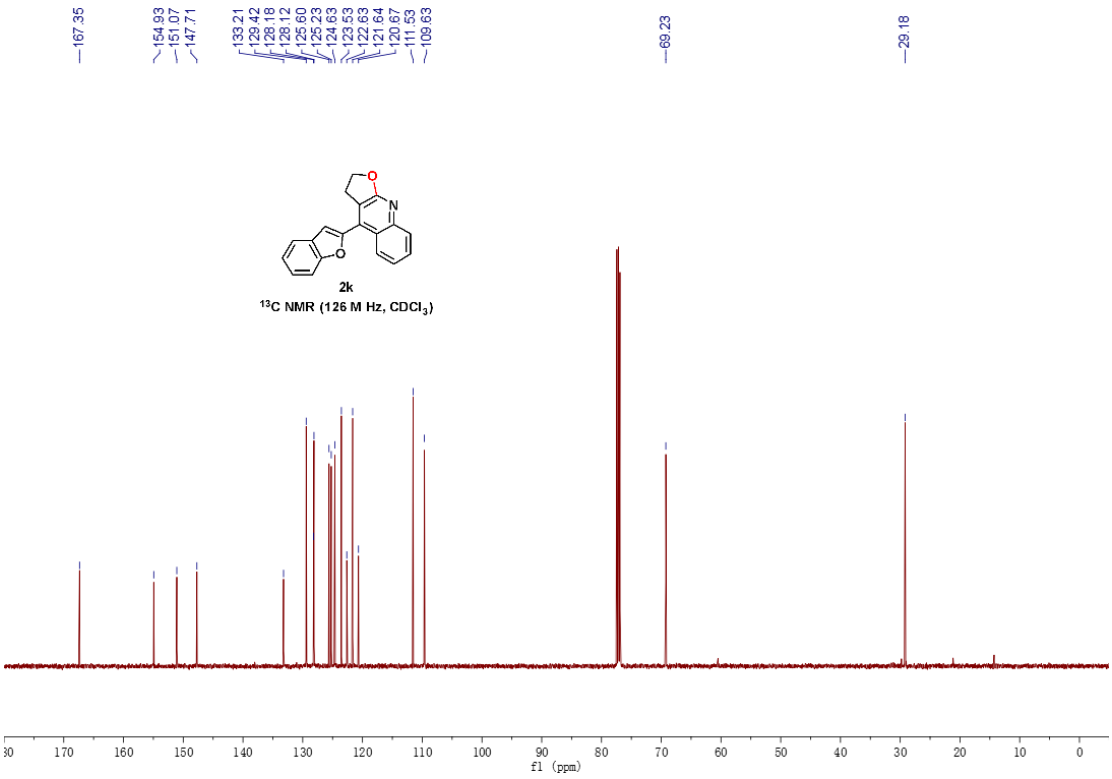


Figure S37. ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of 2k

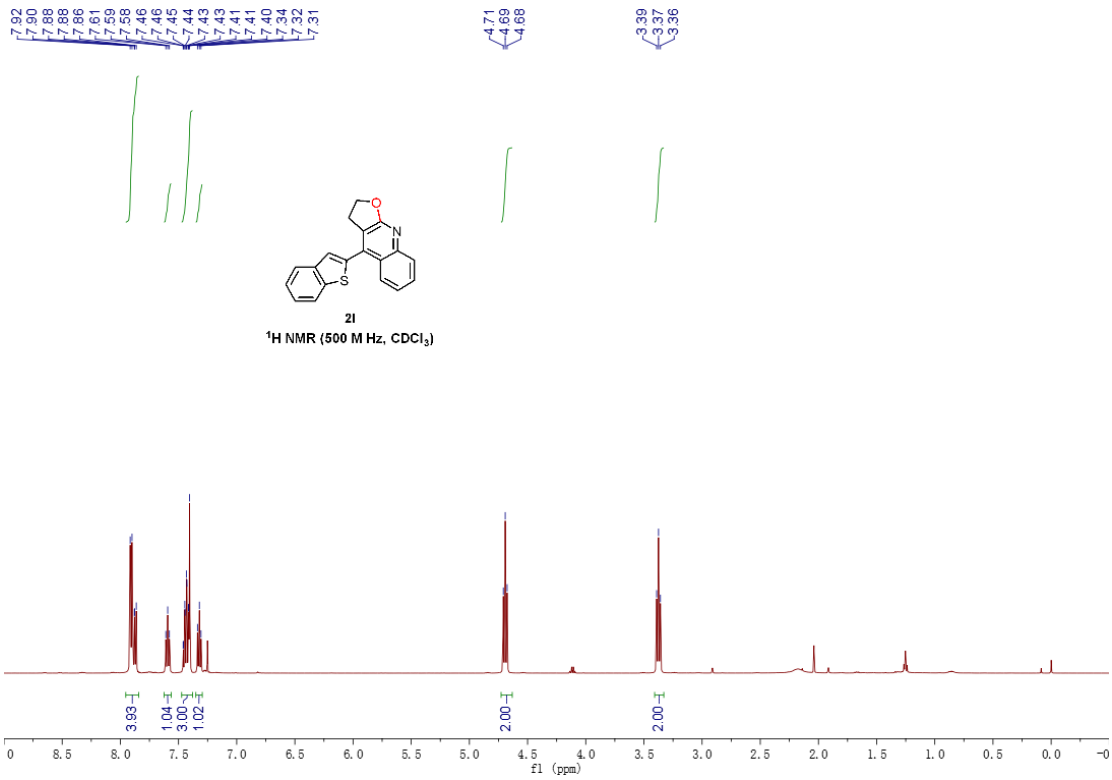


Figure S38. ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of 2l

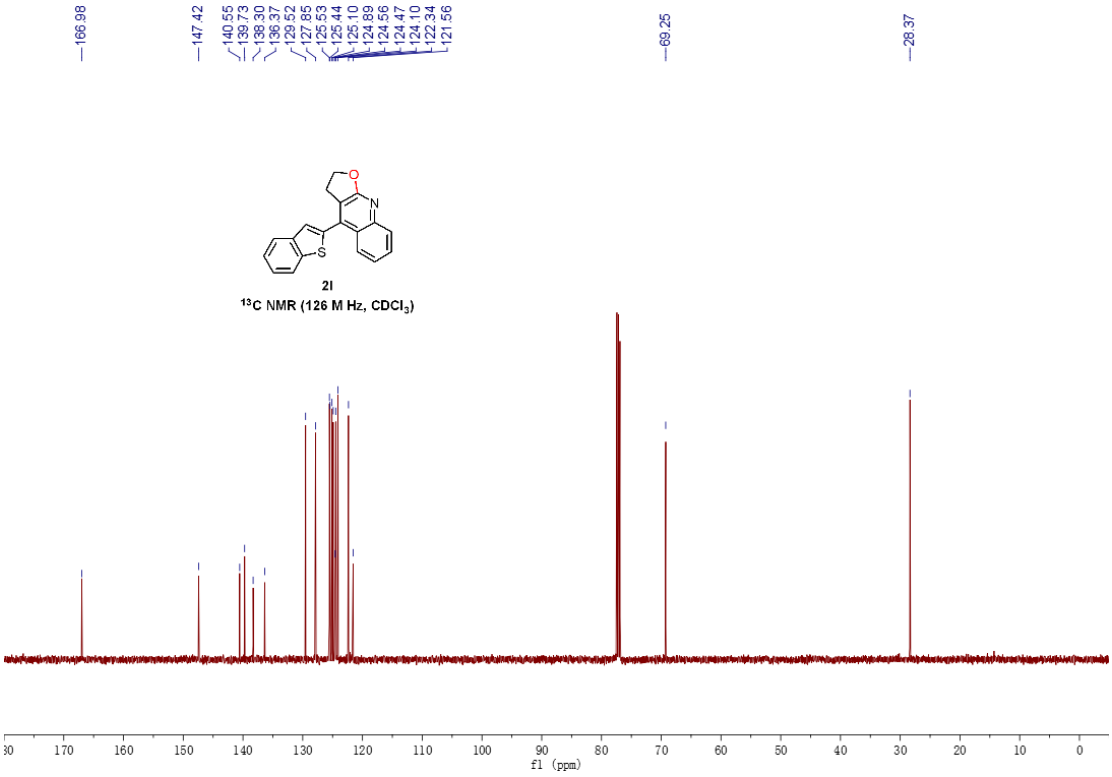


Figure S39. ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of 2l

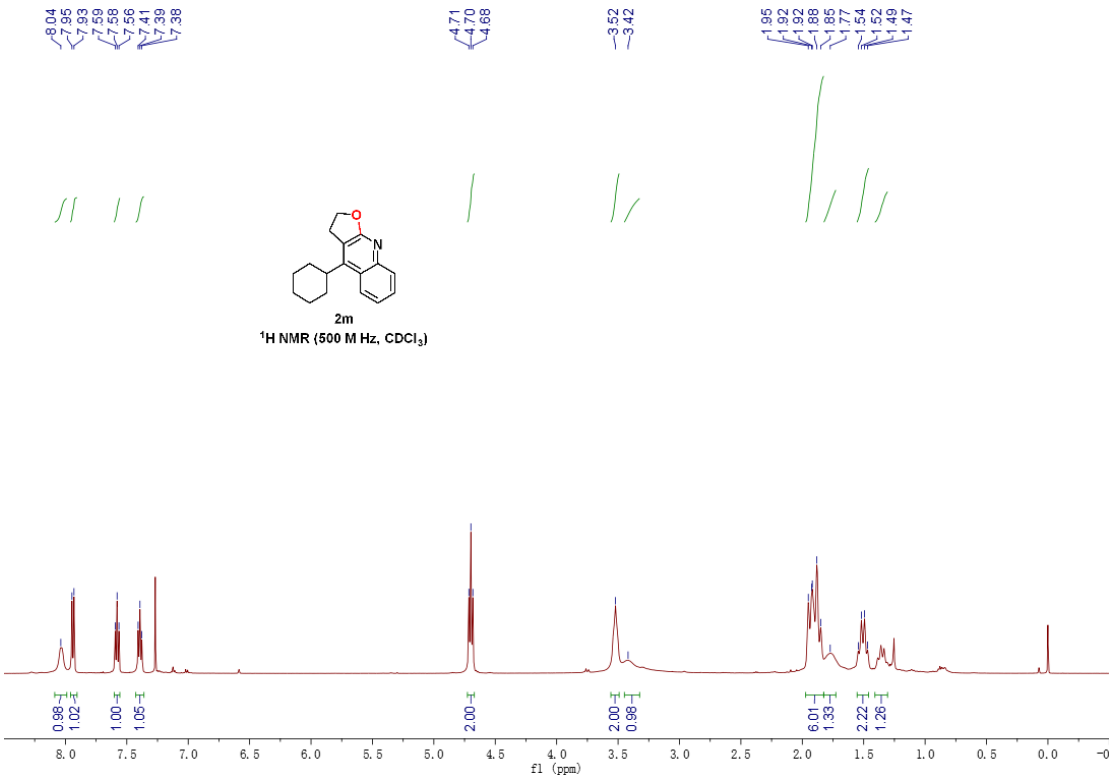


Figure S40. ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of 2m

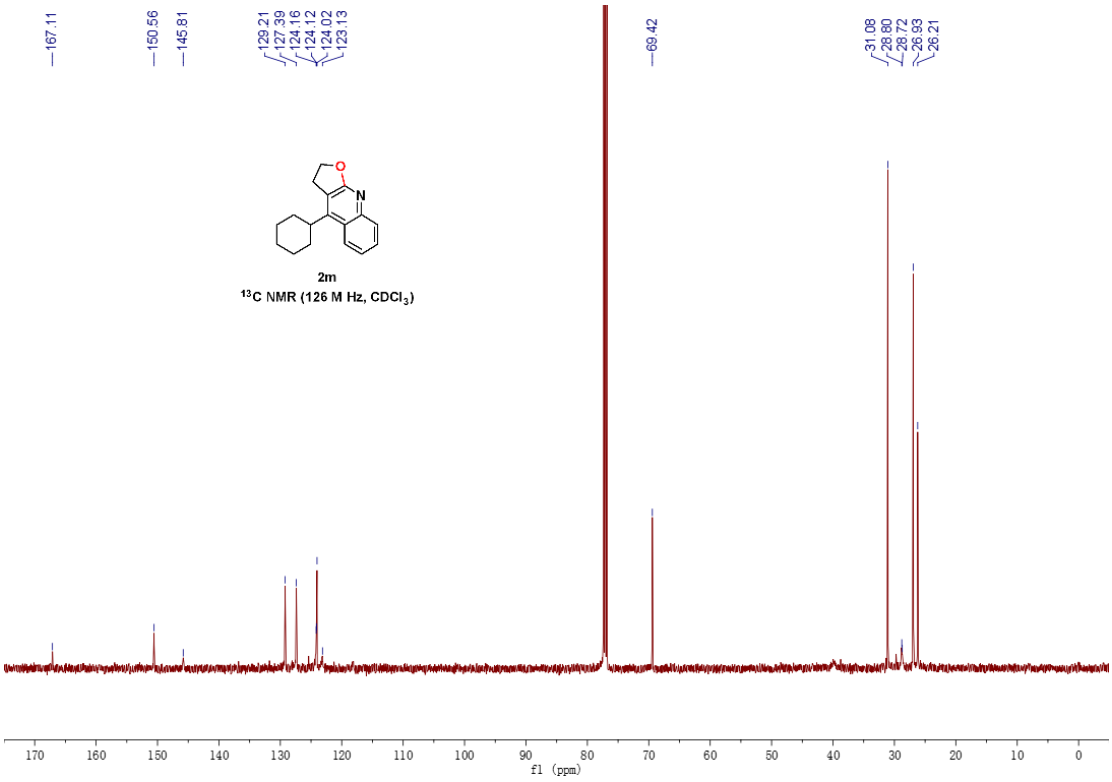


Figure S41. ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of 2m

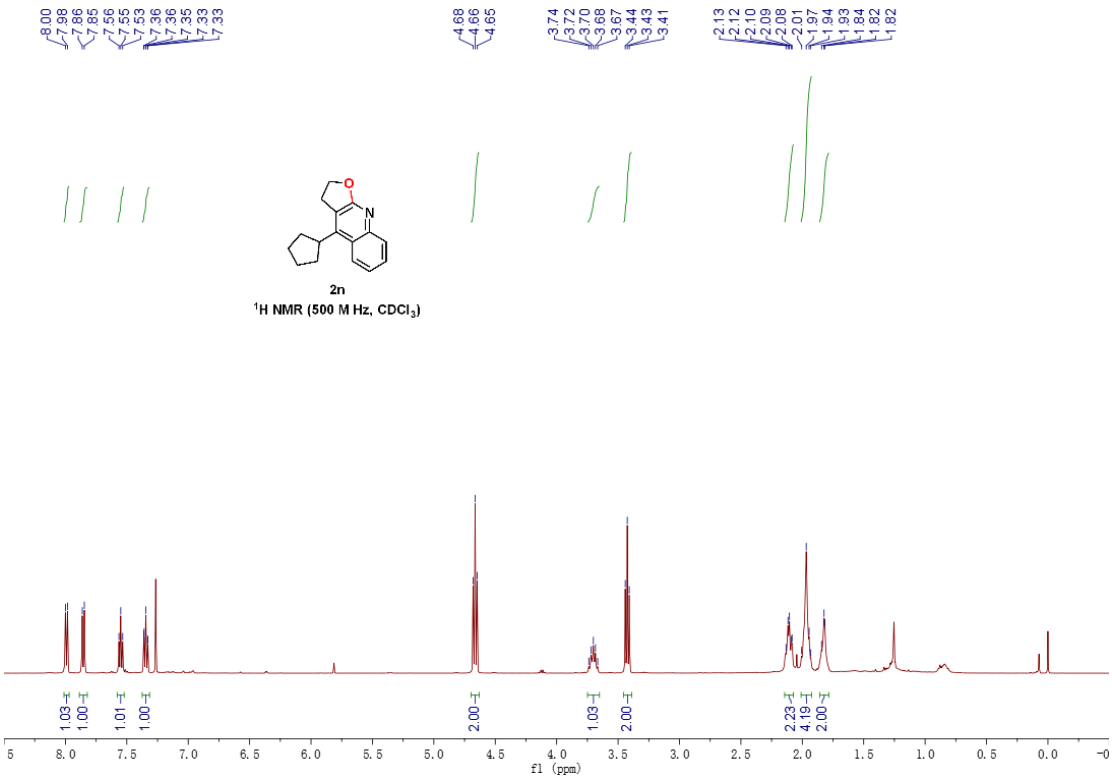


Figure S42. ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of 2n

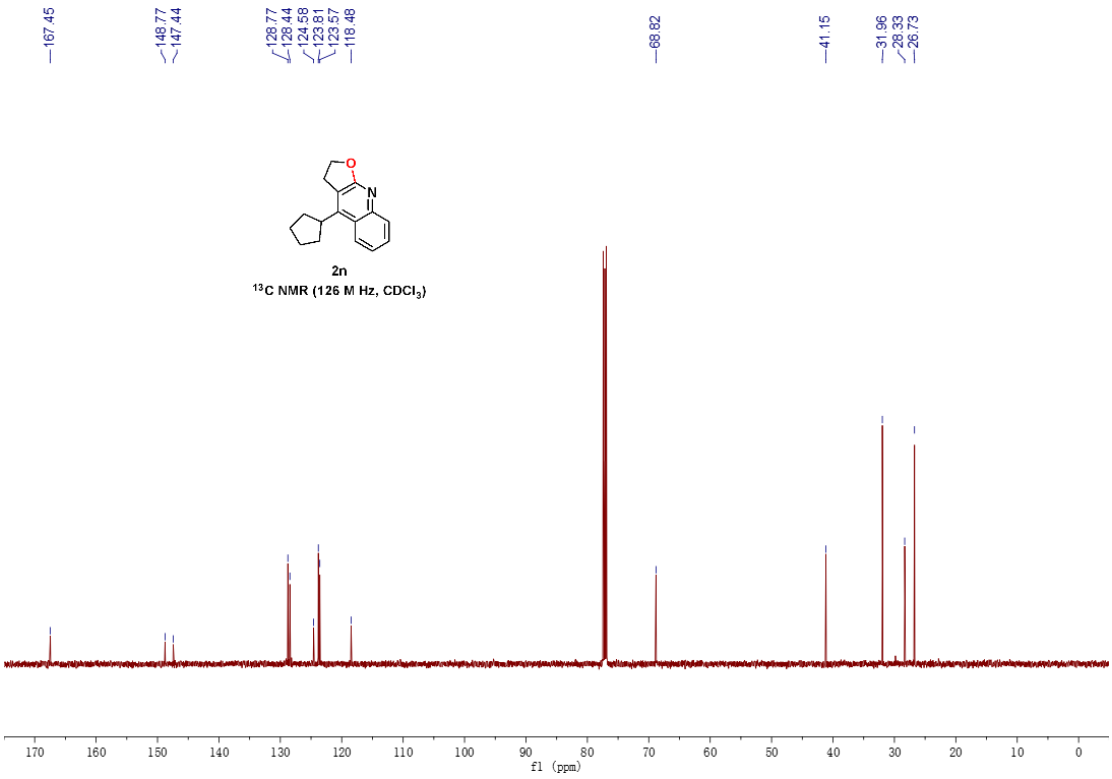


Figure S43. ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of 2n

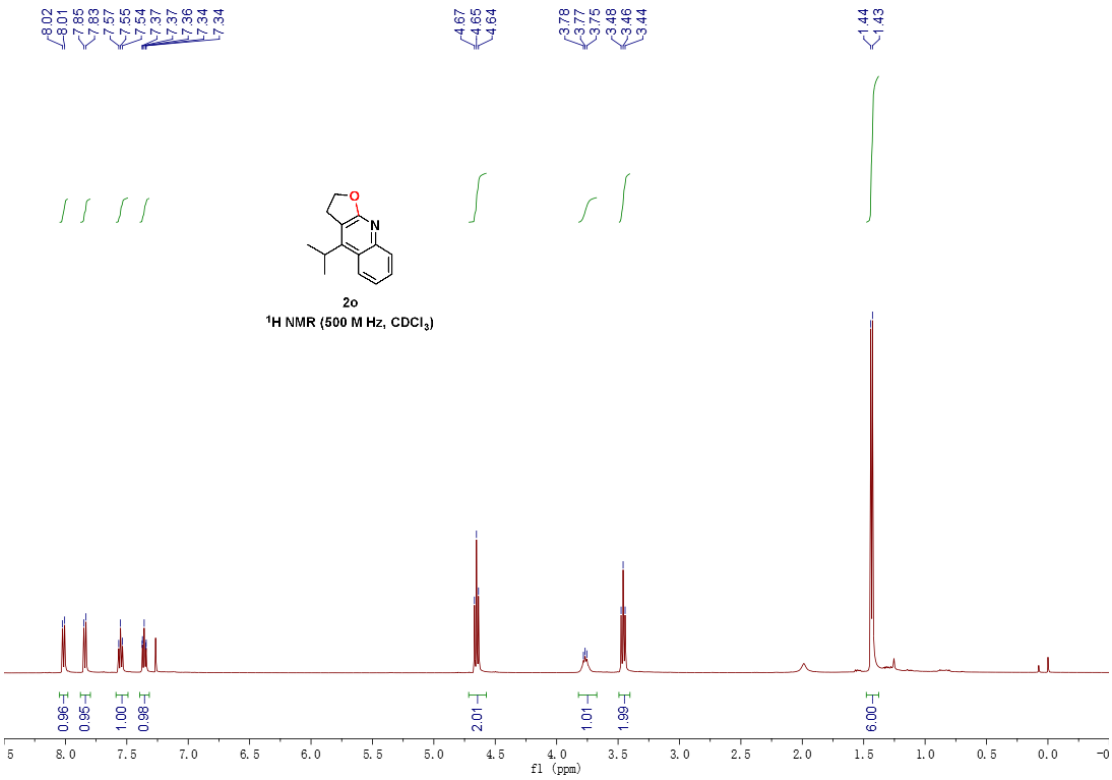


Figure S44. ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of 2o

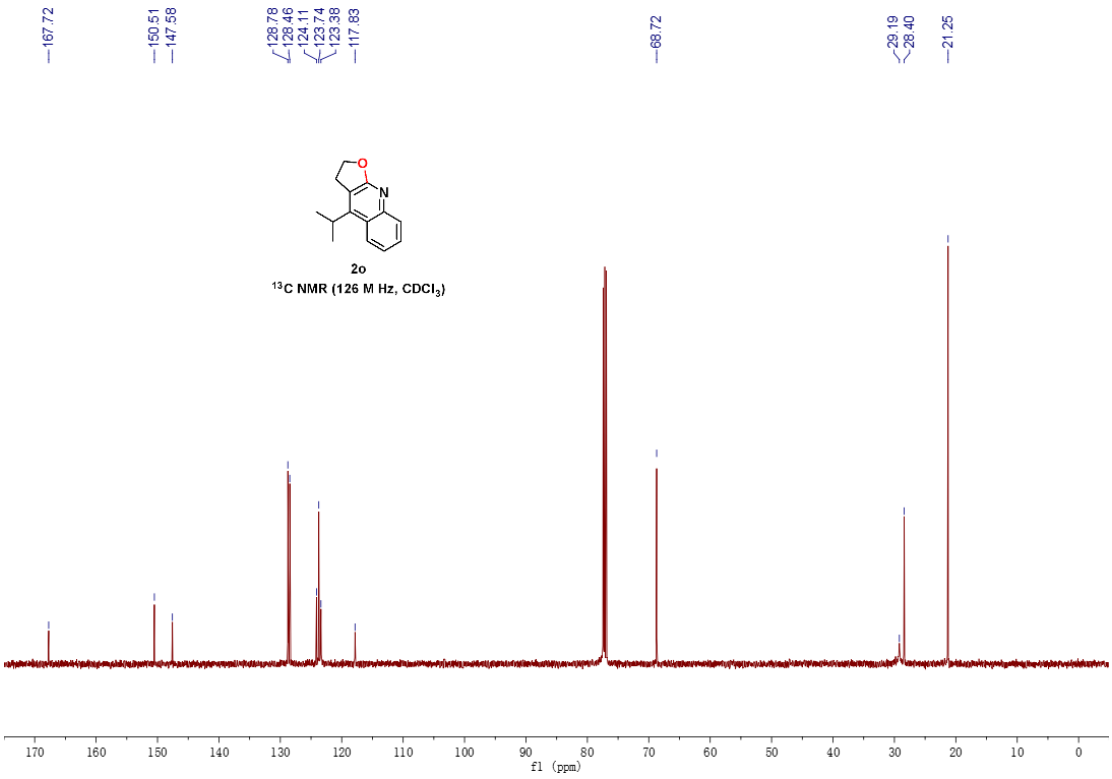


Figure S45. ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of 2o

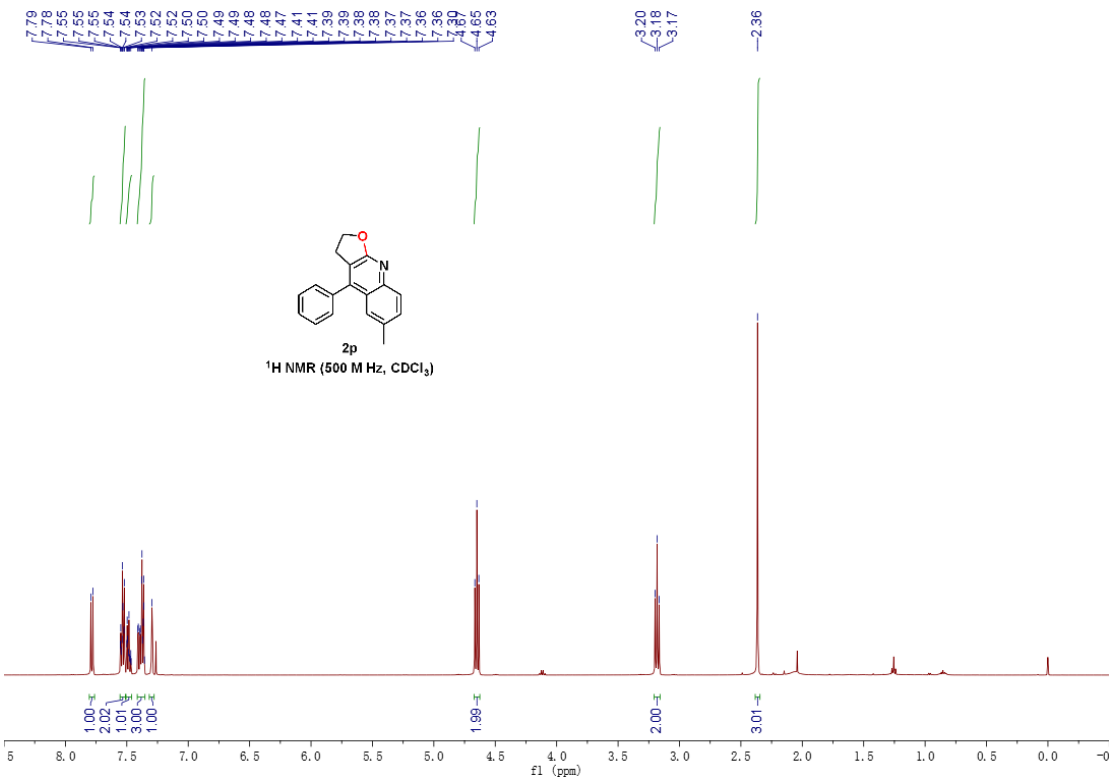


Figure S46 ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of 2p

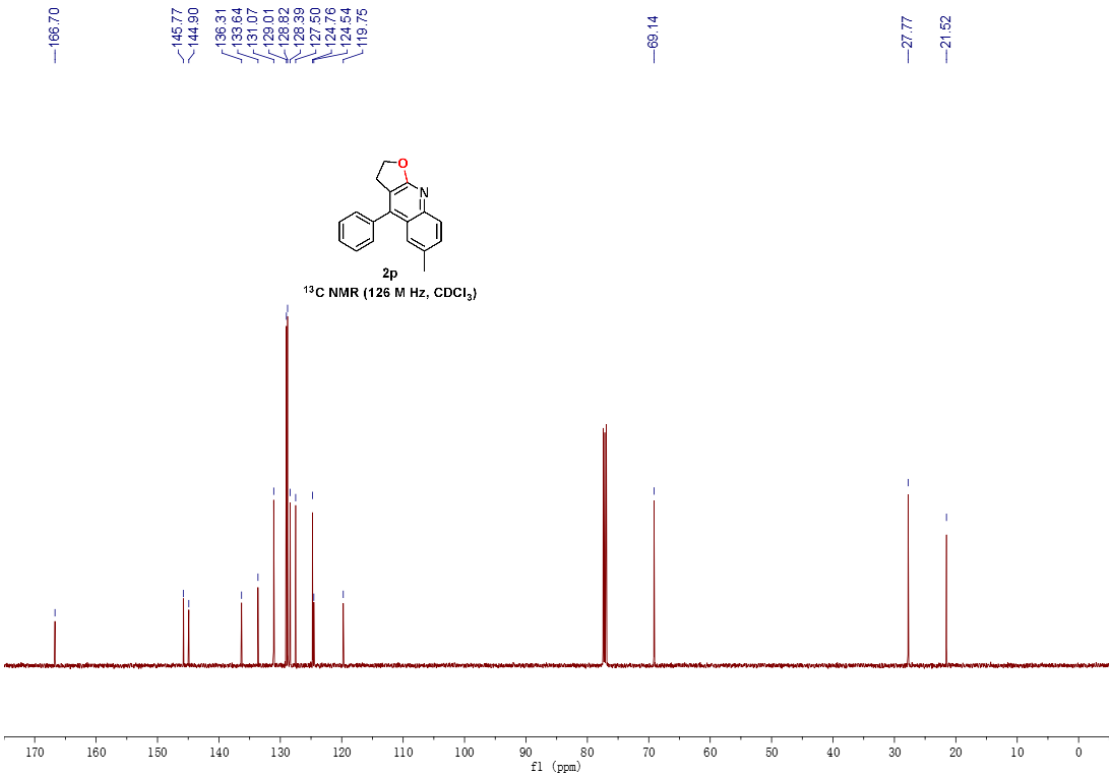


Figure S47. ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of 2p

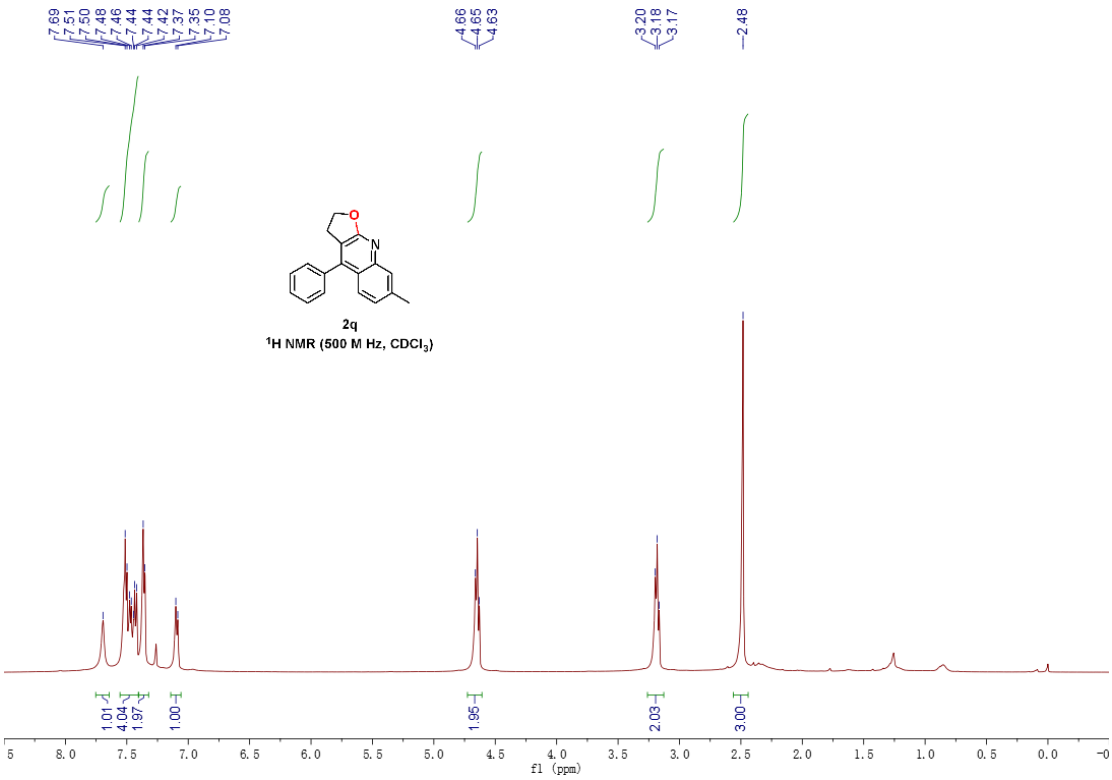


Figure S48. ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of 2q

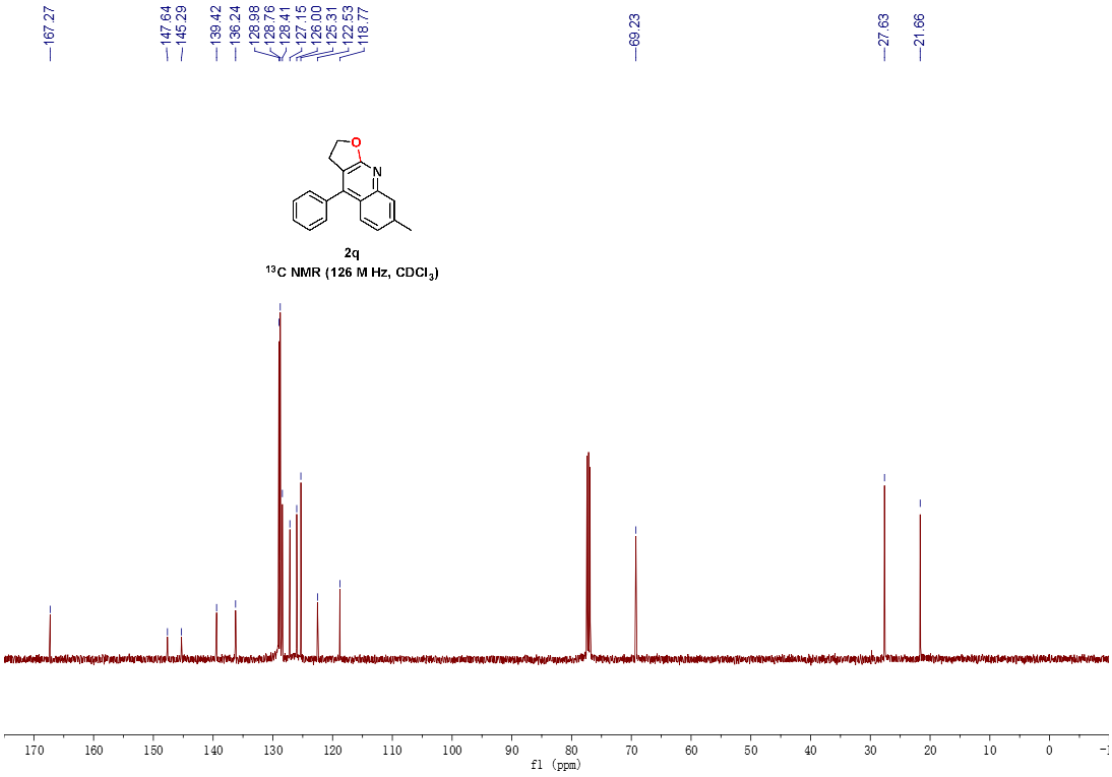


Figure S49. ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of 2q

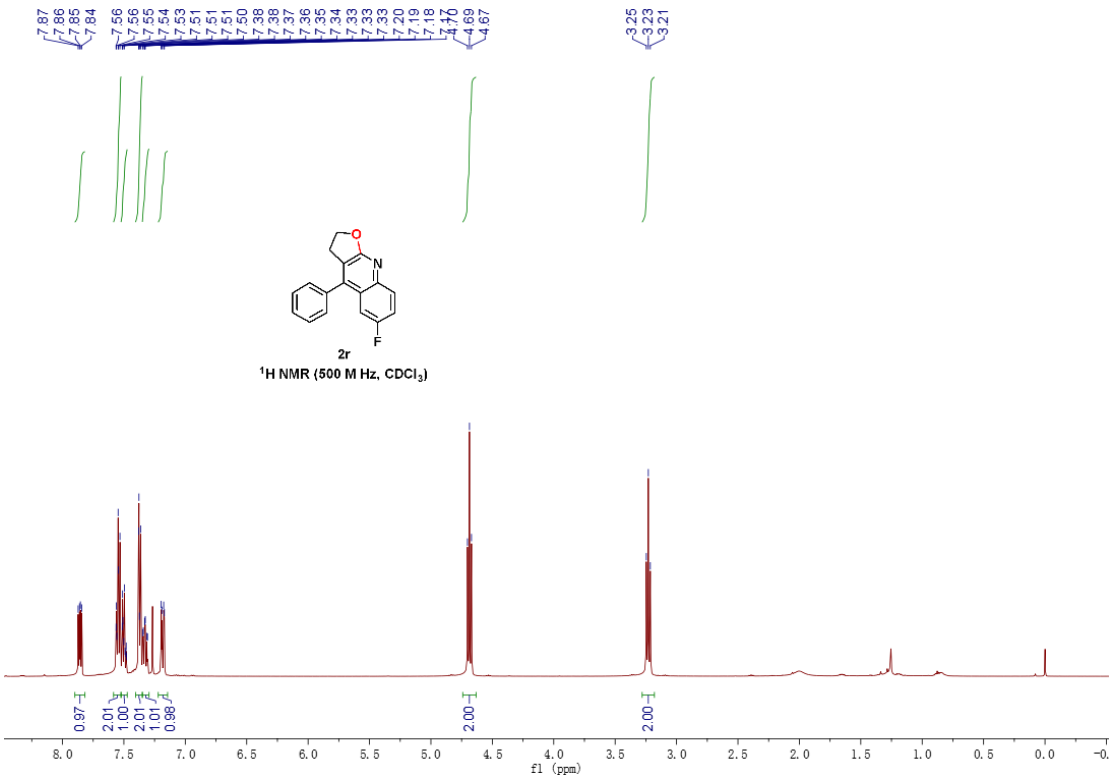


Figure S50. ^{1}H NMR (500 MHz, CDCl$_3$) spectrum of 2r

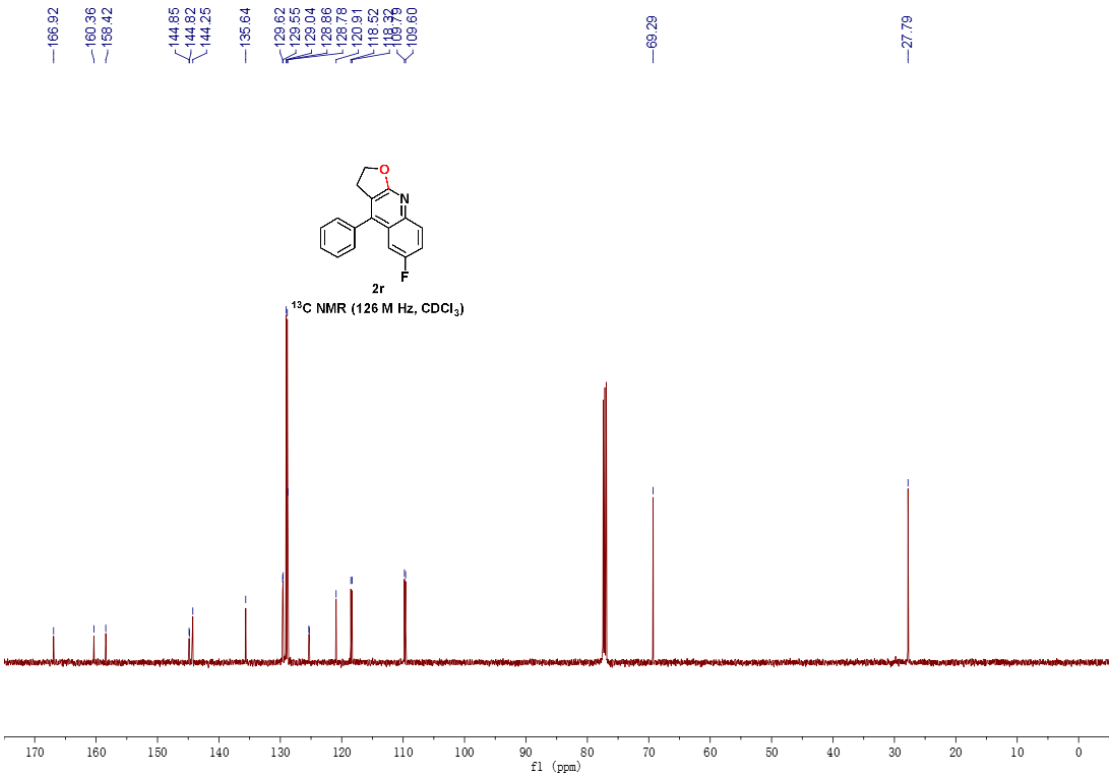


Figure S51. ^{13}C NMR (126 MHz, CDCl$_3$) spectrum of 2r

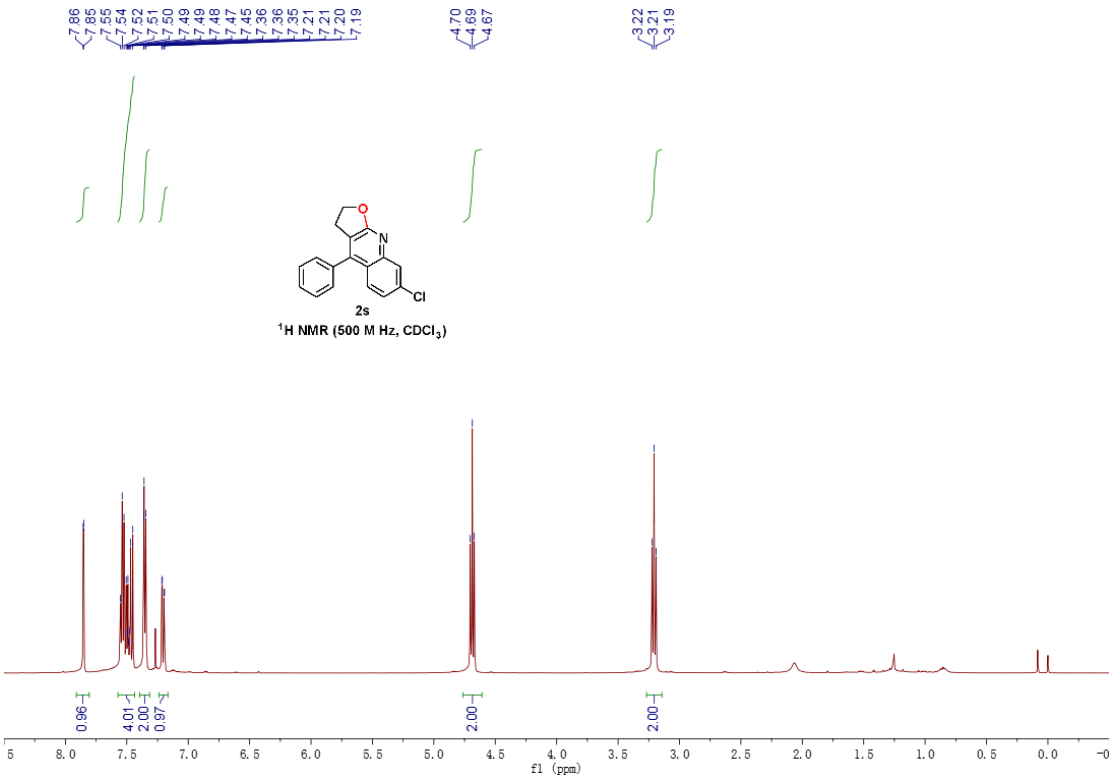


Figure S52. ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of 2s

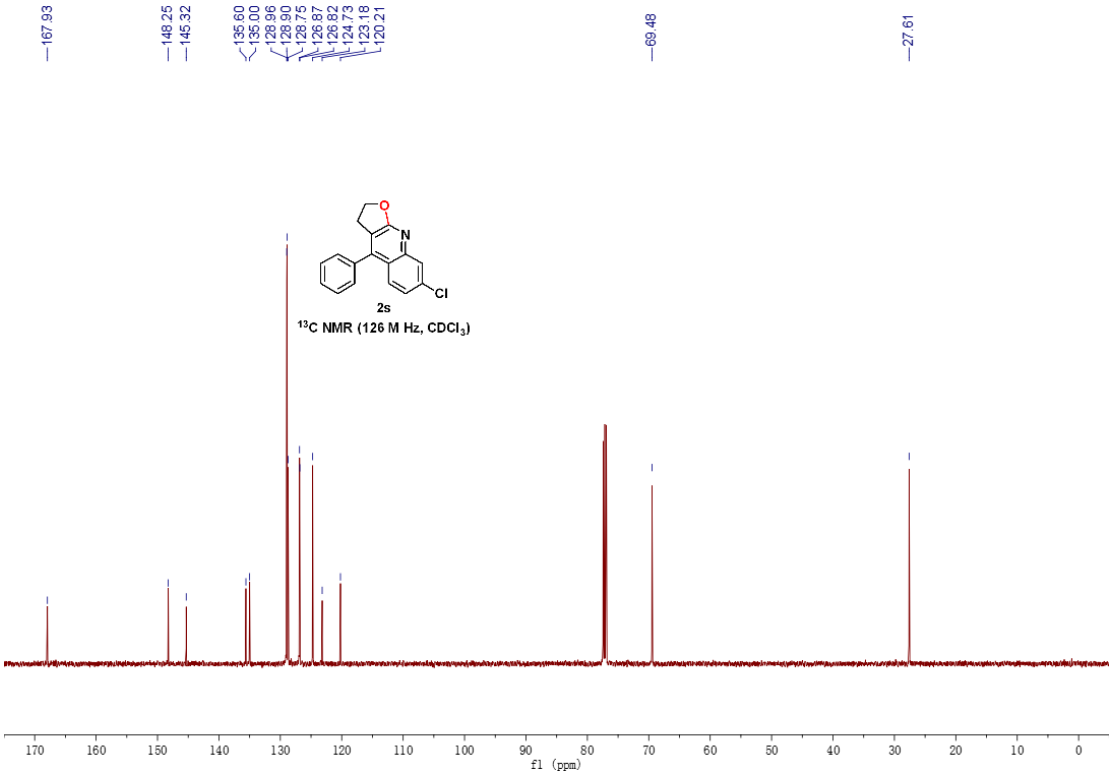


Figure S53. ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of 2s

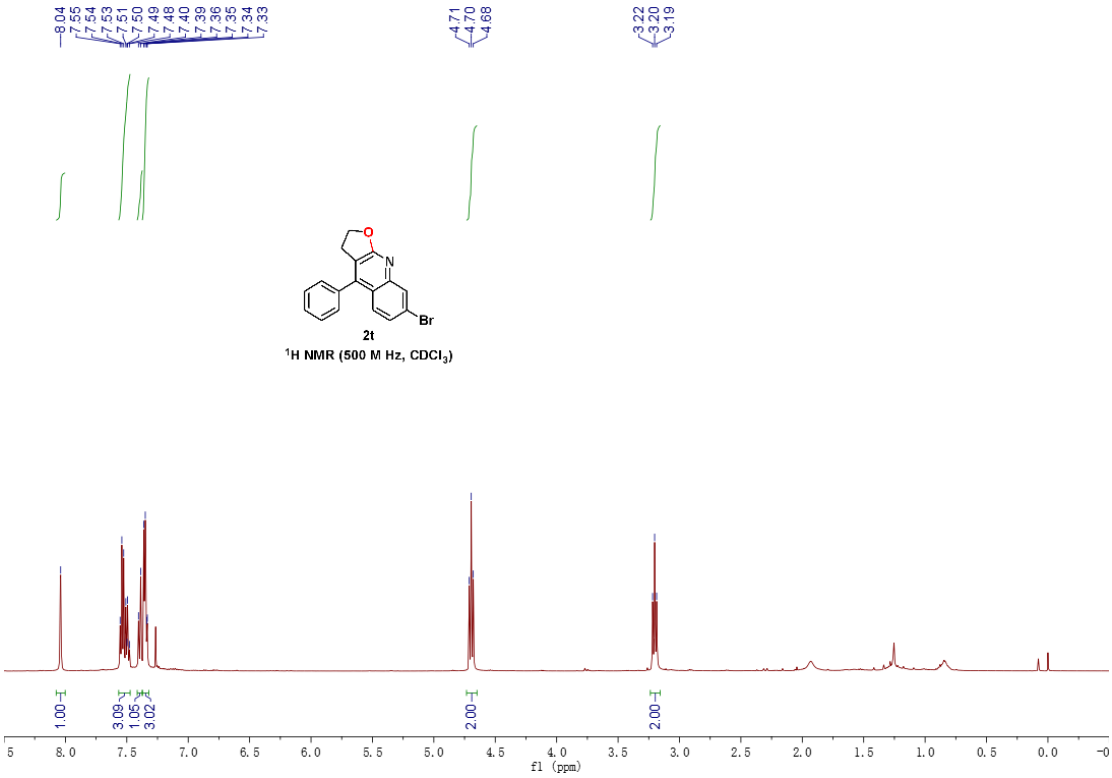


Figure S54. ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of 2t

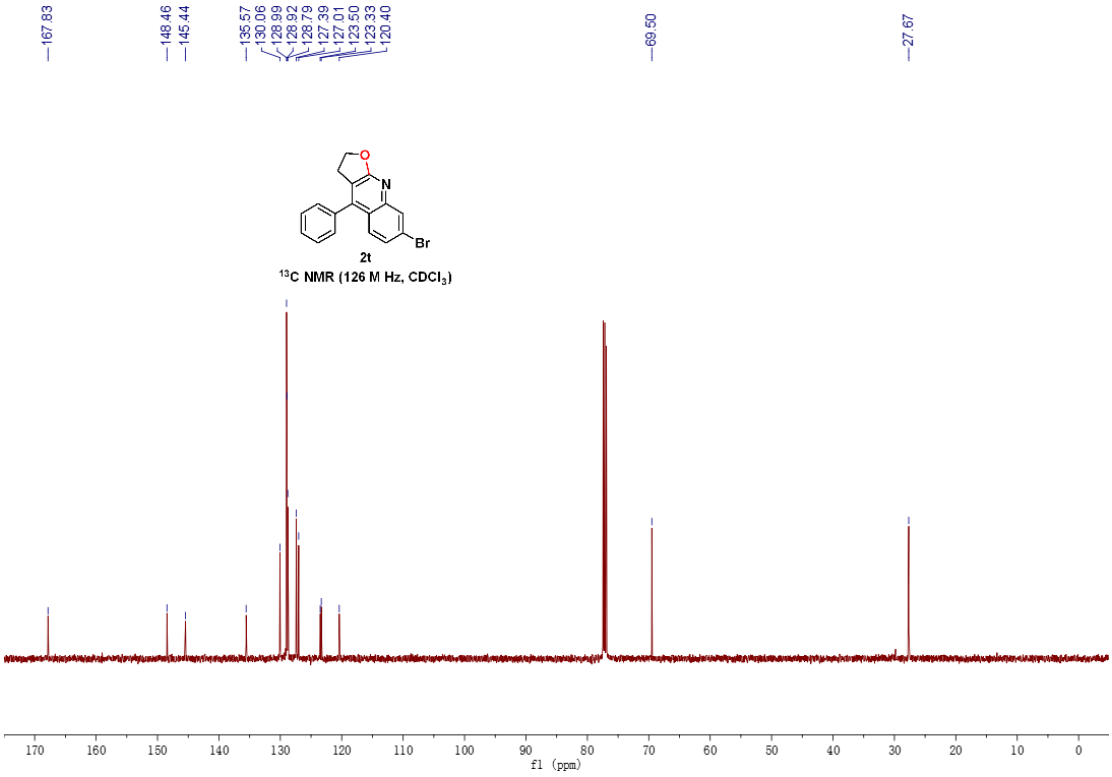


Figure S55. ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of 2t

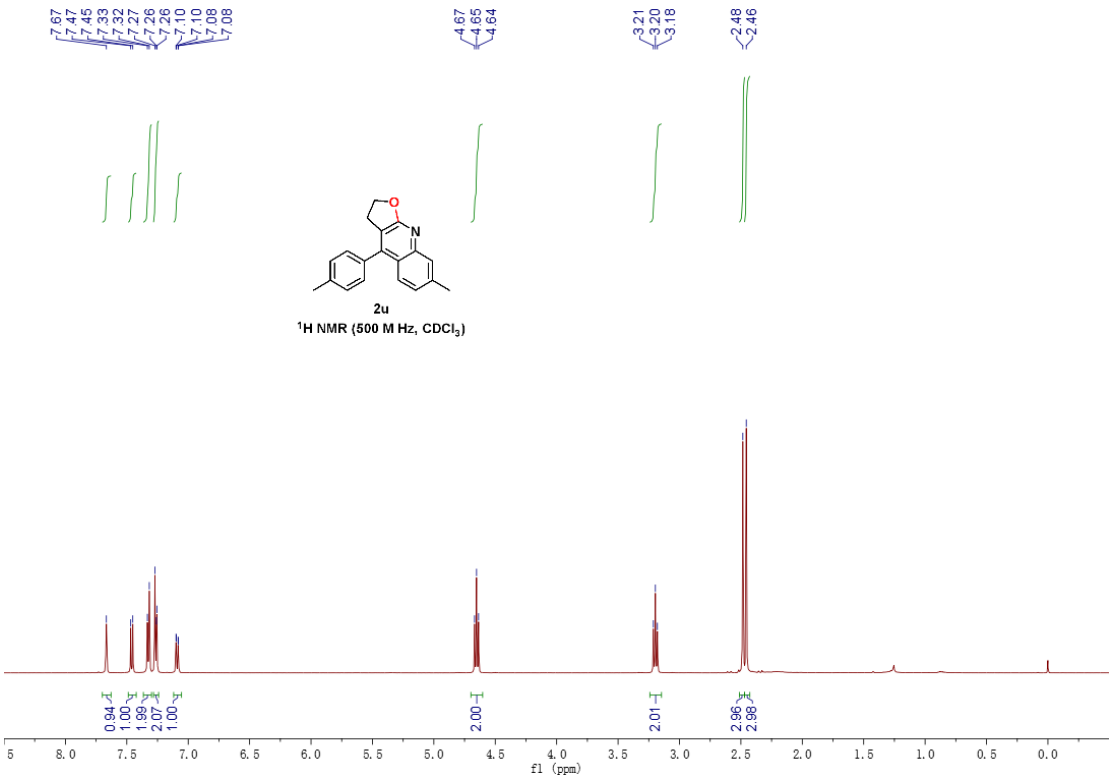


Figure S56. ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of 2u

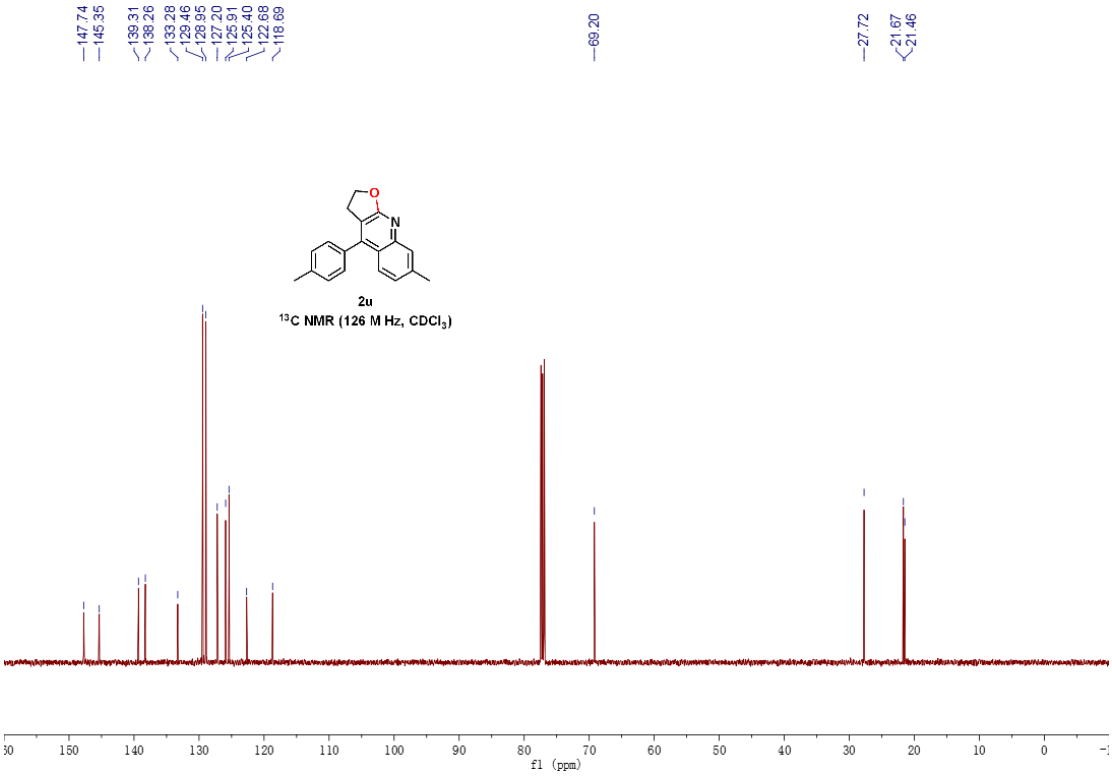


Figure S57. ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of 2u

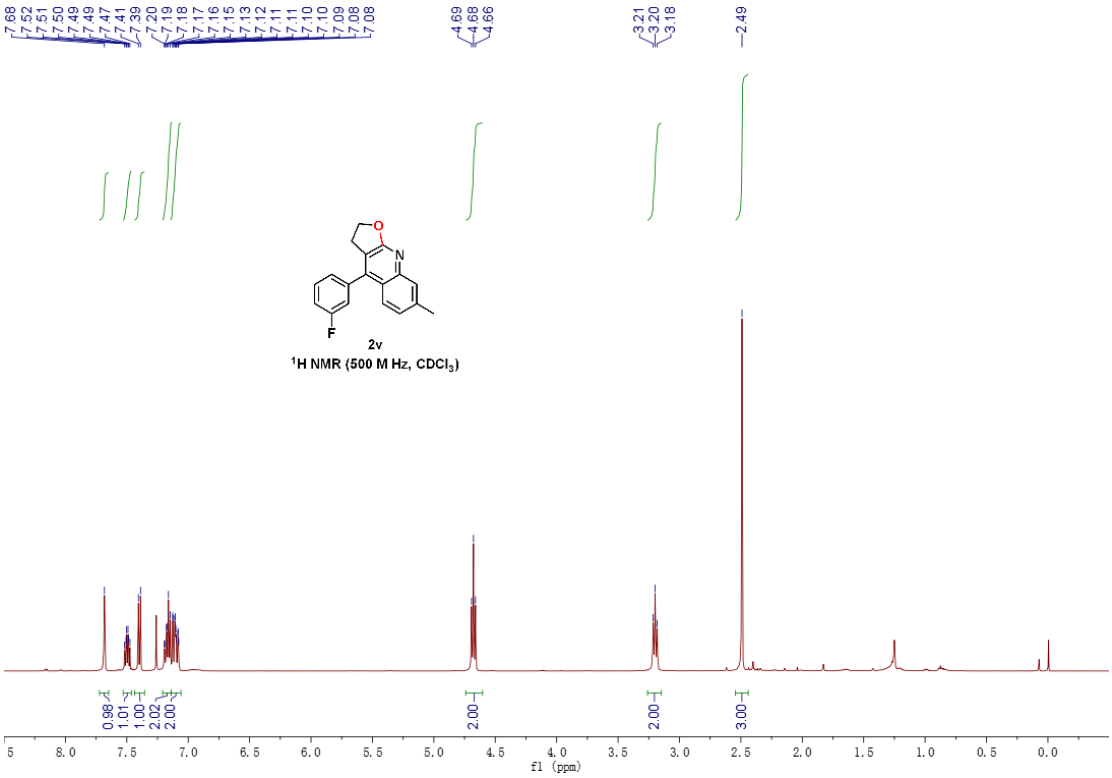


Figure S58. ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of 2v

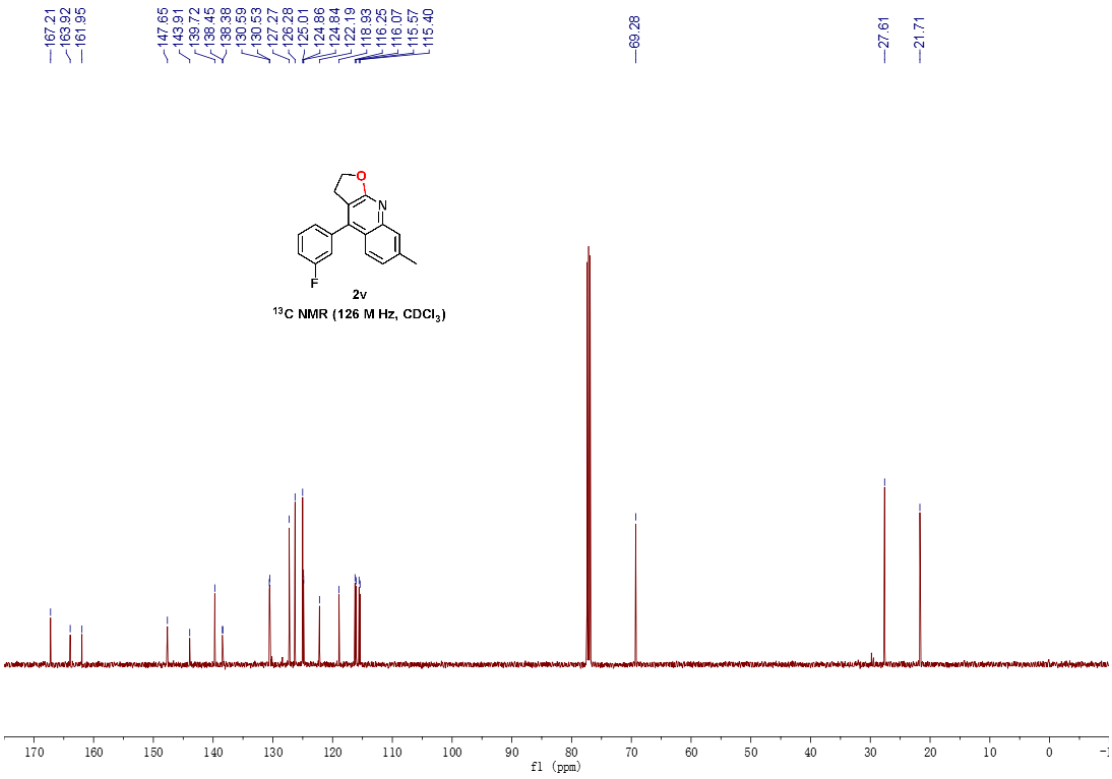


Figure S59. ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of 2v