Silver/molybdenum-promoted skeletal reconstructive cyclization of N-quinolinyl indoles and anthranils

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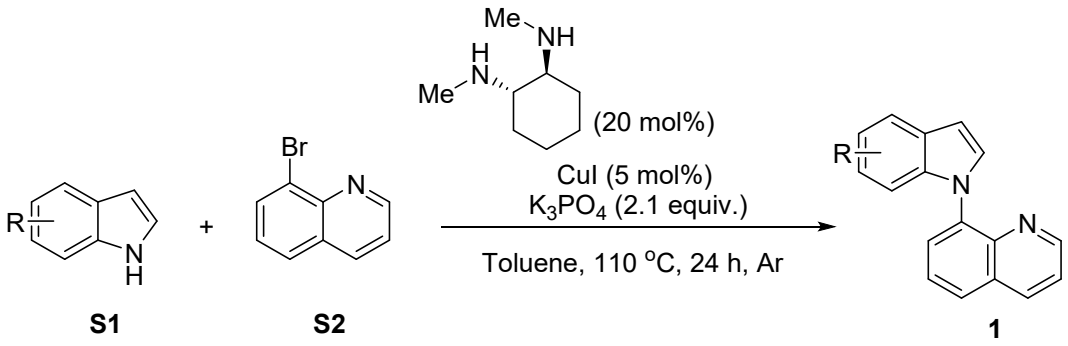
General Information and Procedure

1. General information

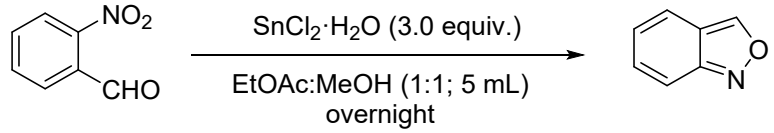
All commercial materials were used as received unless otherwise noted. Commercial reagents were purchased from Alfa Aesar, TCI, Energy Chemical, and used without further purification. ^{1}H NMR spectra were recorded at 400 MHz NMR spectrometers using TMS as an internal standard, ^{13}C NMR spectra were recorded at 100 MHz NMR spectrometers. ^{19}F NMR spectra were recorded at a 376 MHz NMR spectrometer and were fully decoupled by broad band proton decoupling. The multiplicities are reported as follows: singlet (s), doublet (d), doublet of doublets (dd), multiplet (m), triplet (t) and broad resonances (br). Melting points were measured on a hot-stage microscope (XT4-A) and are uncorrected. High resolution mass spectra (HRMS) were obtained on an APEXM Fourier transform mass spectrometry (ESI).

2. General procedure for the preparation of substrates[1]



To a resealable tube was added **S1** indole (2.4 mmol), **S2** 8-bromoquinoline (2 mmol, 1.0 equiv), CuI (5 mol%) and K_3PO_4 (4.2 mmol,). The reaction vessel was evacuated and back-filled with argon and this evacuation/back-fill procedure was repeated two additional times. Trans-N, N'-dimethyl-1,2 cyclohexaneamine (20 mol%) and toluene (1.0 M) were then successively added under a stream of argon. The reaction tube was quickly sealed and the contents were stirred while heating in an oil bath at 110 °C for 24 h. The reaction mixture was cooled to ambient temperature, diluted with ethyl

acetate and concentrated. The resulting residue was purified by column chromatography to provide the desired product[3] **1**. (56-95% yield).

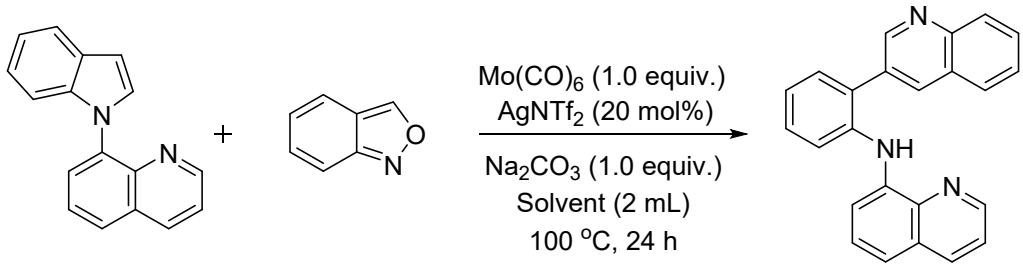


S3 **2a**

A round bottom flask equipped with a magnetic stirrer bar was charged with the **S3** 2-nitroacylbenzene (1.0 mmol) in EtOAc – MeOH (1:1; 5 mL). $SnCl_2 \cdot H_2O$ (3.0 mmol) was added and the reaction stirred at room temperature overnight. The resulting residue was purified by column chromatography to provide the desired product[4] **2a**. (70-85% yield).

3. Optimization of reaction conditions

Screening of Solvent



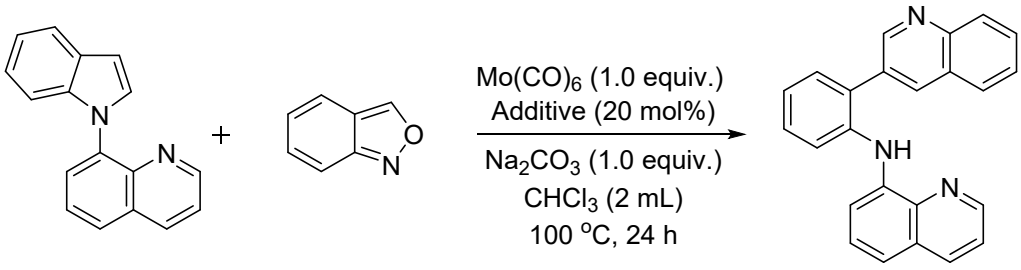
1a **2a** **3a**

Entry	Solvent	Yield/% [b]
1	EA	24
2	DCE	28
3	MeCN	trace
4	DMF	N.D.
5	DCM	31
6	THF	trace
7	toulene	34
8	HFIP	trace
9	$CHCl_3$	44

[a] Unless otherwise noted, the reaction was conducted using **1a** (0.1 mmol), **2a** (0.3 mmol), $Mo(CO)_6$ (0.1 mmol), $AgNTf_2$ (20 mol%), Na_2CO_3（0.1 mmol）in Solvent (2 mL) at 100 °C for 24 h under

Air. [b]Isolated yield by flash column chromatography.

Screening of Additive

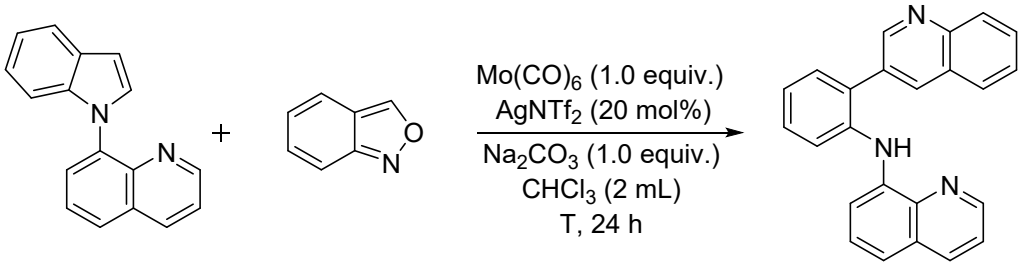


1a **2a** **3a**

Entry	Additive	Yield/% [b]
10	$AgNTf_2$	44
11	$AgSbF_6$	27
12	Ag_3PO_4	trace
13	$AgPF_6$	33
14	AgOTf	36
15	$AgBF_4$	30
16	\	17

[a] Unless otherwise noted, the reaction was conducted using **1a** (0.1 mmol), **2a** (0.3 mmol), $Mo(CO)_6$ (0.1 mmol), Additive (20 mol%), Na_2CO_3（0.1 mmol）in $CHCl_3$ (2 mL) at 100 °C for 24 h under Air. [b]Isolated yield by flash column chromatography.

Screening of Temperatures



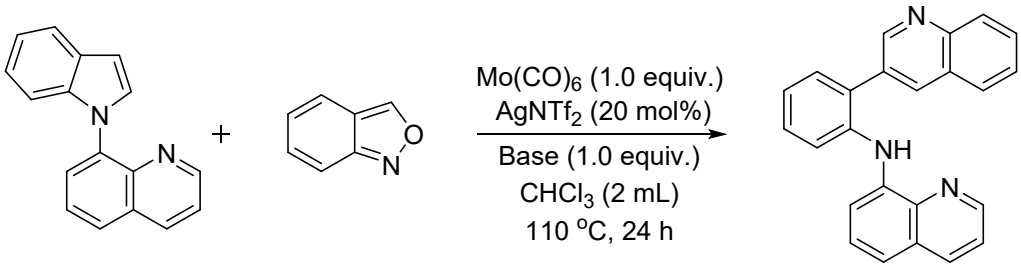
1a **2a** **3a**

Entry	T/ °C	Yield/% [b]
17	100	44
18	110	70
19	120	55

20	130	51

[a] Unless otherwise noted, the reaction was conducted using **1a** (0.1 mmol), **2a** (0.3 mmol), $Mo(CO)_6$ (0.1 mmol), $AgNTf_2$ (20 mol%), Na_2CO_3 (0.1 mmol） in $CHCl_3$ (2 mL) for 24 h under Air. [b]Isolated yield by flash column chromatography.

Screening of Base

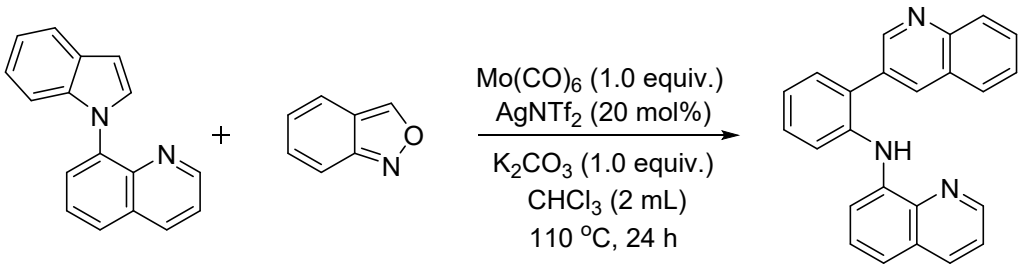


1a **2a** **3a**

Entry	Base	Yield/% [b]
21	K_3PO_4	50
22	K_2HPO_4	44
23	KH_2PO_4	61
24	Li_2CO_3	82
25	Na_2CO_3	70
26	K_2CO_3	90
27	Cs_2CO_3	58
28	$KHCO_3$	53
29	DBU	0
30	Et_3N	15

[a] Unless otherwise noted, the reaction was conducted using **1a** (0.1 mmol), **2a** (0.3 mmol), $Mo(CO)_6$ (0.1 mmol), $AgNTf_2$ (20 mol%), Base (0.1 mmol） in $CHCl_3$ (2 mL) at 110 °C for 24 h under Air. [b]Isolated yield by flash column chromatography.

Screening of Time

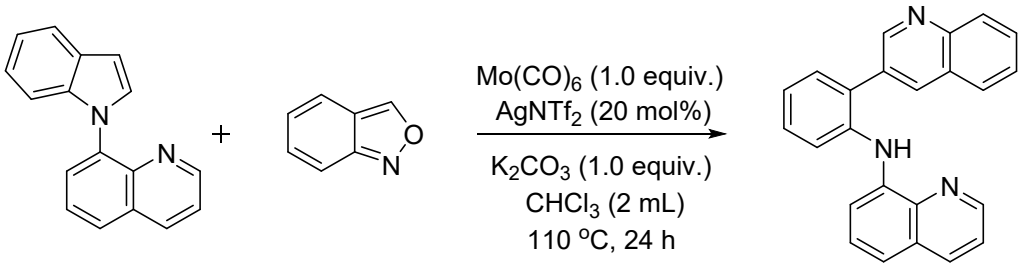


1a **2a** **3a**

Entry	Time/h	Yield/% [b]
31	12	55
32	24	90
33	36	79

[a] Unless otherwise noted, the reaction was conducted using **1a** (0.1 mmol), **2a** (0.3 mmol), $Mo(CO)_6$ (0.1 mmol), $AgNTf_2$ (20 mol%), K_2CO_3 (0.1 mmol） in $CHCl_3$ (2 mL) at 110 °C under Air. [b]Isolated yield by flash column chromatography.

Screening of $Mo(CO)_6$ Loadings

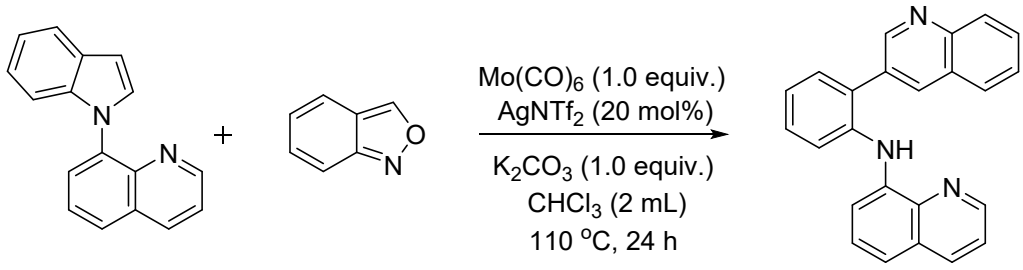


1a **2a** **3a**

Entry[a]	$Mo(CO)_6$	Yield/% [b]
34	0.5	55
35	1.0	90
36	1.5	61
37	2.0	43

[a] Unless otherwise noted, the reaction was conducted using **1a** (0.1 mmol), **2a** (0.3 mmol), $Mo(CO)_6$, $AgNTf_2$ (20 mol%), K_2CO_3 (0.1 mmol） in $CHCl_3$ (2 mL) at 110 °C for 24 h under Air. [b]Isolated yield by flash column chromatography.

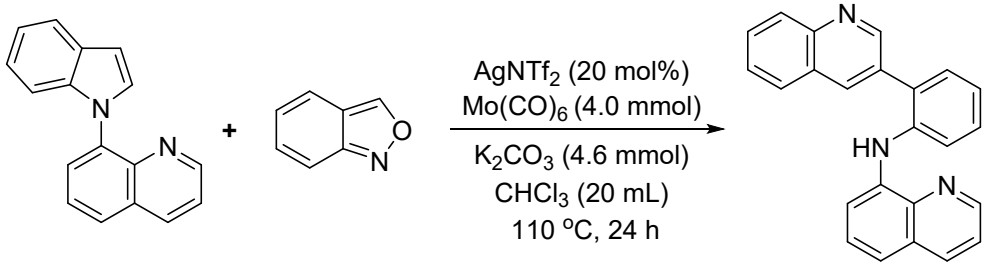
4. General procedure for skeletal reconstructive cyclization of N-quinolinyl indoles and benzisoxazoles



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

To an oven-dried 25 mL Schlenk tube was added substrate **1a** (0.0244 g, 0.10 mmol), **2a** (30 μL, 0.30 mmol), $Mo(CO)_6$ (0.0264 g, 1.0 equiv.), $AgNTf_2$ (0.0078 g, 20 mol%), K_2CO_3 (0.0138 g, 0.1 mmol), in $CHCl_3$ 2 mL. The mixture was stirred for 24 h at 110 °C (oil bath) followed by cooling. The reaction mixture was cooled to ambient temperature and monitored by TLC. The residue was purified by flash column chromatography on silica gel using petroleum ether/EtOAc (15:1) as the eluent to afford the product **3a**.

A Scale-up Experiment of 3a



1a
4.6 mmol

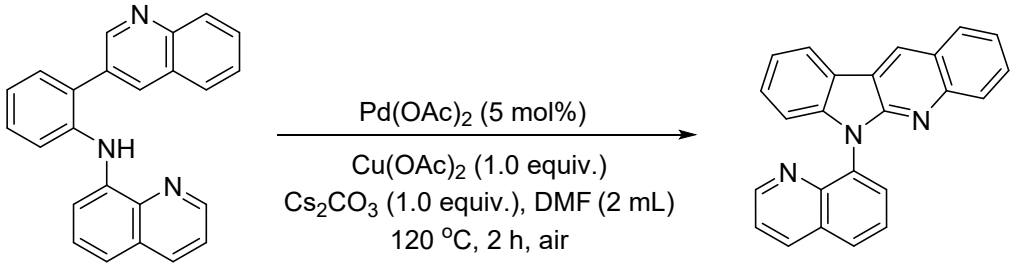
2a
10.0 mmol

3a
1.02 g, 63%
2.9 mmol

To an oven-dried 25 mL Schlenk tube was added substrate **1a** (1.1224 g, 4.6 mmol), **2a** (1.19 g, 10 mmol), $Mo(CO)_6$ (1.2144 g, 4.0 mmol), $AgNTf_2$ (0.3588 g, 0.92 mmol), K_2CO_3 (0.6348 g, 4.6 mmol) in $CHCl_3$ 20 mL. The mixture was stirred for 24 h at 110

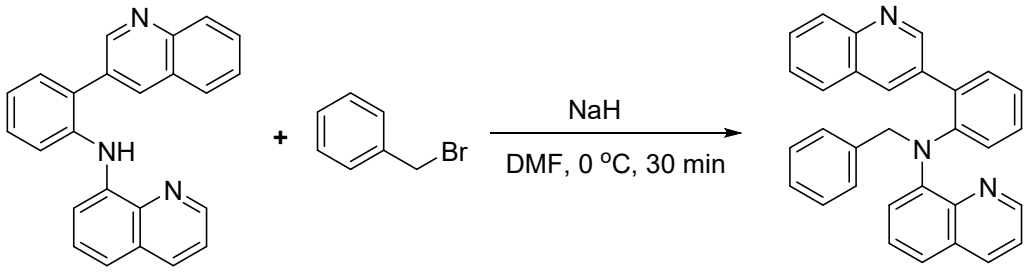
°C (oil bath) followed by cooling. The reaction mixture was cooled to ambient temperature and monitored by TLC. The residue was purified by flash column chromatography on silica gel using petroleum ether/EtOAc (15:1) as the eluent to afford the product **3a (**1.02 g）.

Derivatization of Product 3a



3a **4**, 60%

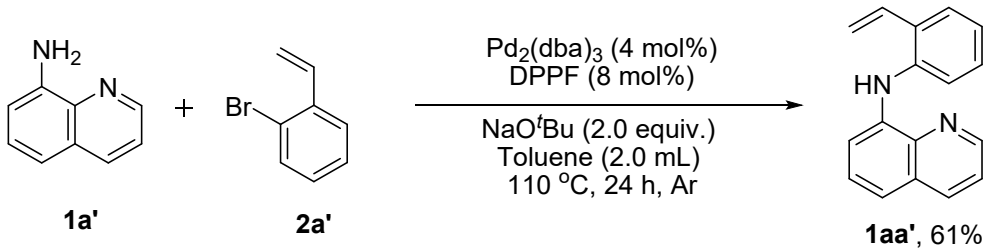
An oven-dried Schlenk tube was charged with **3a** (0.2 mmol), $Pd(OAc)_2$ (5 mol%), $Cu(OAc)_2$ (0.2 mmol), Cs_2CO_3 (0.2 mmol) and DMF (1 mL),mixture was stirred at 120 °C under air for 2 h and then quenched by the addition of a saturated solution of $NaHCO_3$ (10 mL). The aqueous phase was extracted with EA (3 x 30 mL). The combined organic layers were washed with brine (50 mL), dried over Na_2SO_4 and concentrated in vacuo. The organic layer was concentrated under reduced pressure and the residue was purified by chromatography (PE/EA 20:1) to give the cyclization product **4** in good 60% yield.



3a **5**, 85%

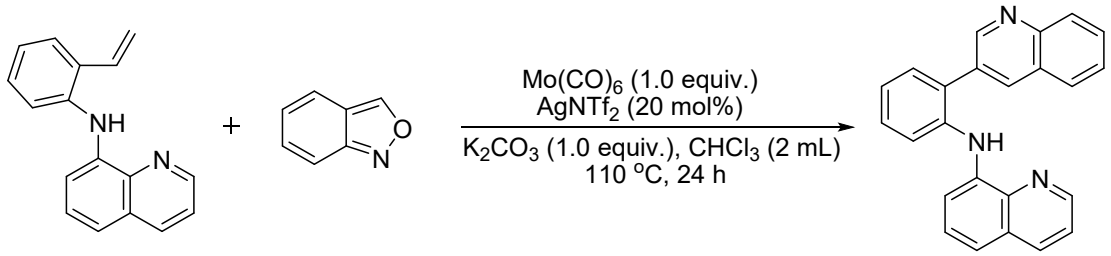
An oven-dried Schlenk tube was charged with substrate **3a** (0.2 mmol), NaH (0.24 mmol, 1.2 equiv) and DMF (2 mL), mixture was stirred at room temperature under air for 5 min then add benzyl bromide (0.24 mmol, 1.2 equiv, 40.8 mg), mixture was stirred at 0 °C under air for 30 min and then quenched by the addition of a saturated solution of $NaHCO_3$ (10 mL). The aqueous phase was extracted with EA (3 x 30 mL). The combined organic layers were washed with brine (50 mL), dried over Na_2SO_4 and concentrated in vacuo. The organic layer was concentrated under reduced pressure and the residue was purified by chromatography (PE/EA 10:1) to give the alkylation product 5 in good 85% yield. [2]

Mechanistic Exploration



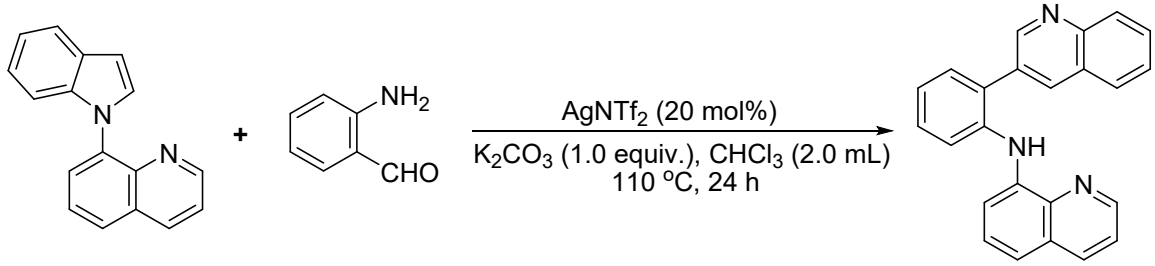
1a' **2a'** **1aa'**, 61%

To an oven-dried 25 mL Schlenk tube was added substrate **1a'** (0.10 mmol), **2a'** (0.12 mmol), $Pd_2(dba)_3$ (4 mol%), DPPF (8 mol%), NaO^{t}Bu (0.20 mmol, Toluene (2.0 mL). After the vessel was evacuated and back-filled with argon. The mixture was stirred for 24 h at 110 °C (oil bath) followed by cooling. The reaction mixture was cooled to ambient temperature and monitored by TLC. The organic layer was concentrated under reduced pressure and the residue was purified by chromatography (PE/EA 5:1) to give the desired product **1aa'** in good 61% yield.



1aa' **2a** **3a,** 0%

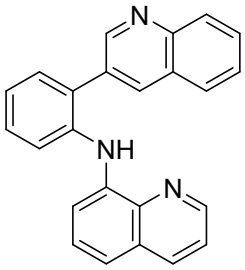
To an oven-dried 25 mL Schlenk tube was added substrate **1aa'** (0.0246 g, 0.10 mmol), **2a** (0.0238 g, 0.20 mmol), $Mo(CO)_6$ (0.0264 g, 1.0 equiv.), $AgNTf_2$ (0.0078 g, 0.02 mmol), K_2CO_3 (0.0138 g, 0.1 mmol), in $CHCl_3$ 2 mL. The mixture was stirred for 24 h at 110 °C (oil bath) followed by cooling. The reaction mixture was cooled to ambient temperature and monitored by TLC.



1a **2b** **3a,** 81%

To an oven-dried 25 mL Schlenk tube was added substrate **1a** (0.0244 g, 0.10 mmol), **2b** (0.0274 g, 0.20 mmol), $AgNTf_2$ (0.0078 g, 20 mol%), K_2CO_3 (0.0138 g, 0.1 mmol), in $CHCl_3$ 2 mL. The mixture was stirred for 24 h at 110 °C (oil bath) followed by cooling. The reaction mixture was cooled to ambient temperature and monitored by TLC. The residue was purified by flash column chromatography on silica gel using petroleum ether/EtOAc (15:1) as the eluent to afford the product **3a** in good 81% yield.

Analytic Data of Products



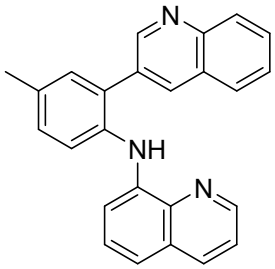
(3a) N-(2-(quinolin-3-yl)phenyl)quinolin-8-amine

This compound was purified by column chromatography (PE: EA =15:1) to afford a yellow solid (31.6 mg, 91% yield); m.p. 212-213 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.05 (d, J = 2.2 Hz, 1H), 8.50 (dd, J = 4.2, 1.6 Hz, 1H), 8.29 (d, J = 2.1 Hz, 1H), 8.11–8.04 (m, 3H), 7.79 – 7.75 (m, 2H), 7.72 – 7.68 (m, 1H), 7.55 – 7.48 (m, 2H), 7.47 – 7.41 (m, 2H), 7.38 (t, J = 7.8 Hz, 1H), 7.31 (dd, J = 8.4, 4.2 Hz, 1H), 7.24 (td, J = 7.5, 1.0 Hz, 1H), 7.20 (dd, J = 7.9, 1.3 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 151.6, 147.5, 147.2, 140.6, 139.5, 138.6, 136.0, 135.7, 132.4, 131.5, 131.5, 129.4, 129.2, 128.9, 128.0, 128.0, 127.2, 126.8, 123.6, 121.9, 121.6, 116.9, 108.0.

HRMS (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{24}H_{18}N_3$ 348.1495; Found 348.1495.



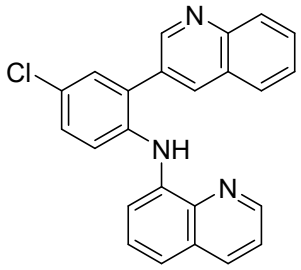
(3b) N-(4-methyl-2-(quinolin-3-yl)phenyl)quinolin-8-amine

(This compound was purified by column chromatography (PE: EA =15:1) to afford a yellow solid (27.5 mg, 76% yield); m.p. 140-141 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.03 (d, J = 2.2 Hz, 1H), 8.52 (dd, J = 4.2, 1.6 Hz, 1H), 8.25 (d, J = 2.0 Hz, 1H), 8.07 (d, J = 8.4 Hz, 1H), 8.04 (dd, J = 8.3, 1.6 Hz, 1H), 7.94 (s, 1H), 7.73 (d, J = 8.1 Hz, 1H), 7.70 – 7.66 (m, 1H), 7.63 (d, J = 8.1 Hz, 1H), 7.53 – 7.49 (m, 1H), 7.38 – 7.32 (m, 2H), 7.32 – 7.26 (m, 3H), 7.16 (dd, J = 7.9, 1.2 Hz, 1H), 2.45 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 151.6, 147.4, 147.1, 141.4, 138.5, 136.8, 136.0, 135.5, 133.7, 132.6, 132.2, 132.0, 129.9, 129.3, 129.2, 128.8, 128.0, 127.9, 127.3, 126.7, 123.3, 121.6, 116.3, 107.4, 21.0.

HRMS (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{25}H_{20}N_3$ 362.1652; Found 362.1652 .



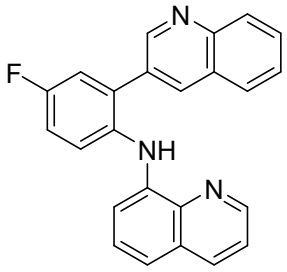
(3c) N-(4-chloro-2-(quinolin-3-yl)phenyl)quinolin-8-amine

This compound was purified by column chromatography (PE: EA =15:1) to afford a yellow solid (17.2 mg, 45% yield); m.p. 165-166 ^oC.

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.00 (d, J = 2.2 Hz, 1H), 8.52 (dd, J = 4.2, 1.7 Hz, 1H), 8.28 (d, J = 2.0 Hz, 1H), 8.09 (d, J = 8.6 Hz, 1H), 8.06 (dd, J = 8.3, 1.7 Hz, 1H), 8.01 (s, 1H), 7.79 (dd, J = 8.2, 1.0 Hz, 1H), 7.75 – 7.69 (m, 2H), 7.58 – 7.53 (m, 1H), 7.47 (d, J = 2.5 Hz, 1H), 7.42 – 7.37 (m, 3H), 7.33 (dd, J = 8.3, 4.2 Hz, 1H), 7.23 (dd, J = 6.7, 2.7 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 151.1, 147.6, 140.2, 138.6, 138.3, 136.1, 135.8, 132.9, 131.2, 131.2, 129.8, 129.3, 129.1, 128.8, 128.2, 128.0, 127.9, 127.1, 127.0, 122.9, 121.7, 117.3, 108.2.

HRMS (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{24}H_{17}ClN_3$ 382.1106; Found 382.1104 .



(3d) N-(4-fluoro-2-(quinolin-3-yl)phenyl)quinolin-8-amine

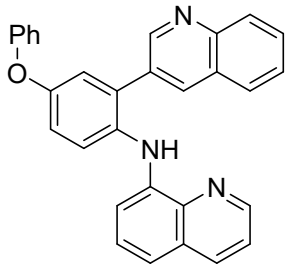
This compound was purified by column chromatography (PE: EA =15:1) to afford a yellow solid (18.7 mg, 51% yield); m.p. 142-143 ^oC.

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.00 (d, J = 2.2 Hz, 1H), 8.53 (dd, J = 4.2, 1.6 Hz, 1H), 8.25 (d, J = 2.1 Hz, 1H), 8.08 – 8.04 (m, 2H), 7.85 (s, 1H), 7.74 (d, J = 8.1 Hz, 1H), 7.72 – 7.65 (m, 2H), 7.53 (ddd, J = 8.0, 6.9, 1.0 Hz, 1H), 7.38 – 7.31 (m, 2H), 7.26 – 7.20 (m, 2H), 7.17 (ddd, J = 8.6, 6.6, 1.9 Hz, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 159.4 (d, $J_{F\text{-}C}$ = 241.5 Hz), 151.0, 147.4 ($J_{F\text{-}C}$ = 16.0 Hz), 141.5, 138.4, 136.1, 135.6, 135.5 ($J_{F\text{-}C}$ = 2.8 Hz), 134.4 ($J_{F\text{-}C}$ = 7.3 Hz), 131.5 ($J_{F\text{-}C}$ = 1.7 Hz), 129.7, 129.2, 128.8, 128.0, 127.9, 127.2, 126.9, 125.5 ($J_{F\text{-}C}$ = 8.4 Hz), 121.7, 117.82 ($J_{F\text{-}C}$ = 22.7 Hz), 116.7, 116.1 ($J_{F\text{-}C}$ = 22.2 Hz), 107.3.

^{19}F NMR (376 MHz, $CDCl_3$) δ -118.4.

HRMS (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{24}H_{17}FN_3$ 366.1401; Found 366.1399 .



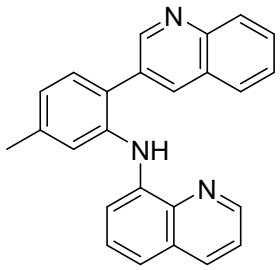
(3e) N-(4-phenoxy-2-(quinolin-3-yl)phenyl)quinolin-8-amine

This compound was purified by column chromatography (PE: EA =15:1) to afford a yellow solid (29.5 mg, 67% yield); m.p. 189-192 ^{o}C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.00 (d, J = 2.2 Hz, 1H), 8.53 (dd, J = 4.2, 1.6 Hz, 1H), 8.24 (d, J = 1.9 Hz, 1H), 8.08 – 8.05 (m, 1H), 8.05 – 8.04 (m, 1H), 7.89 (s, 1H), 7.72 (d, J = 8.2 Hz, 1H), 7.71 – 7.66 (m, 2H), 7.53 – 7.49 (m, 1H), 7.41 – 7.35 (m, 3H), 7.33 (dd, J = 8.3, 4.2 Hz, 1H), 7.28 (d, J = 1.0 Hz, 1H), 7.20 (d, J = 2.8 Hz, 1H), 7.18 (dd, J = 8.1, 0.9 Hz, 1H), 7.15 – 7.11 (m, 4H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 157.4, 153.6, 151.3, 147.4, 147.2, 141.6, 138.4, 136.0, 135.5, 134.8, 134.1, 131.9, 129.9, 129.5, 129.2, 128.8, 128.0, 127.9, 127.3, 126.8, 125.2, 123.4, 121.6, 121.6, 119.7, 118.7, 116.5, 107.3.

HRMS (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{30}H_{22}N_3O$ 440.1757; Found 440.1755 .



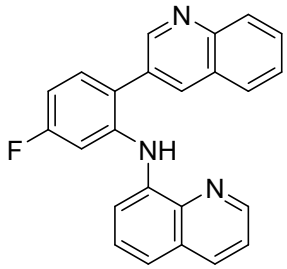
(3f) N-(5-methyl-2-(quinolin-3-yl)phenyl)quinolin-8-amine

This compound was purified by column chromatography (PE: EA =15:1) to afford a yellow solid (27.5 mg, 76% yield); m.p. 227-228 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.04 (d, J = 2.2 Hz, 1H), 8.52 (dd, J = 4.2, 1.7 Hz, 1H), 8.26 (d, J = 2.0 Hz, 1H), 8.09 – 8.03 (m, 3H), 7.74 (dd, J = 8.1, 1.0 Hz, 1H), 7.71 – 7.66 (m, 1H), 7.59 (s, 1H), 7.53 – 7.49 (m, 1H), 7.42 – 7.26 (m, 3H), 7.31 (dd, J = 8.3, 4.2 Hz, 1H), 7.19 (dd, J = 7.3, 2.1 Hz, 1H), 7.07 (dd, J = 7.8, 0.9 Hz, 1H), 2.45 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 151.8, 147.5, 147.1, 140.8, 139.3, 139.3, 138.6, 136.0, 135.5, 132.5, 131.3, 129.3, 129.2, 128.8, 128.8, 128.1, 127.9, 127.2, 126.7, 124.6, 122.7, 121.6, 116.7, 108.0, 21.5.

HRMS (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{25}H_{20}N_3$ 362.1652; Found 362.1647 .



(3g) N-(5-fluoro-2-(quinolin-3-yl)phenyl)quinolin-8-amine

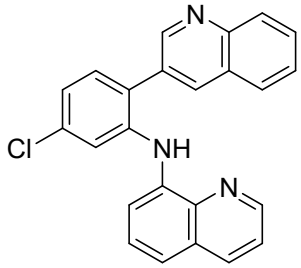
This compound was purified by column chromatography (PE: EA =15:1) to afford a yellow solid (22.0 mg, 60% yield); m.p. 160-161 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.03 (d, J = 2.3 Hz, 1H), 8.49 (dd, J = 4.2, 1.7 Hz, 1H), 8.29 (d, J = 2.0 Hz, 1H), 8.24 (s, 1H), 8.12 (d, J = 8.4 Hz, 1H), 8.06 (dd, J = 8.3, 1.7 Hz, 1H), 7.80 (dd, J = 8.2, 1.4 Hz, 1H), 7.75 – 7.71 (m, 1H), 7.58 – 7.51 (m, 3H), 7.44 (t, J = 7.9 Hz, 1H), 7.40 (dd, J = 8.5, 6.5 Hz, 1H), 7.32 (dd, J = 8.3, 4.2 Hz, 1H), 7.29 – 7.26 (m, 1H), 6.91 – 6.86 (m, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 163.4 (d, J_{F-C} = 243.9 Hz), 151.6, 147.8, 147.3, 141.4 (J_{F-C} = 10.5 Hz), 139.2, 138.9, 136.0 (J_{F-C} = 18.1 Hz), 132.7 (J_{F-C} = 9.8 Hz), 131.6, 129.6, 129.3, 128.8, 128.0, 127.9, 127.1, 126.9, 126.1 (J_{F-C} = 3.0 Hz), 121.7, 118.0, 109.5 (J_{F-C} = 21.6 Hz), 109.2, 106.5 (J_{F-C} = 25.0 Hz).

^{19}F NMR (376 MHz, $CDCl_3$) δ -111.6.

HRMS (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{24}H_{17}FN_3$ 366.1401; Found 366.1404 .



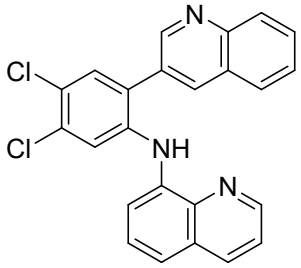
(3h) N-(5-chloro-2-(quinolin-3-yl)phenyl)quinolin-8-amine

This compound was purified by column chromatography (PE: EA =15:1) to afford a yellow solid (19.1 mg, 50% yield); m.p. 197-198 ^{o}C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.02 (d, J = 2.2 Hz, 1H), 8.52 – 8.49 (m, 1H), 8.30 (d, J = 2.0 Hz, 1H), 8.17 (s, 1H), 8.11 (d, J = 8.5 Hz, 1H), 8.07 (dd, J = 8.3, 1.6 Hz, 1H), 7.81 – 7.78 (m, 2H), 7.75 – 7.71 (m, 1H), 7.58 – 7.54 (m, 1H), 7.54 – 7.51 (m, 1H), 7.45 (t, J = 7.9 Hz, 1H), 7.39 (d, J = 8.2 Hz, 1H), 7.33 (dd, J = 8.3, 4.2 Hz, 1H), 7.29 – 7.26 (m, 1H), 7.17 (dd, J = 8.2, 2.0 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 151.4, 147.7, 147.3, 140.9, 139.4, 138.8, 136.1, 135.8, 134.9, 132.4, 131.4, 129.7, 129.3, 128.9, 128.8, 128.0, 127.1, 127.0, 122.9, 121.7, 120.0, 117.9, 109.0.

HRMS (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{24}H_{17}ClN_3$ 382.1106; Found 382.1106 .



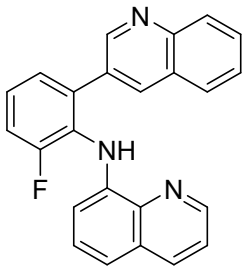
(3i) N-(4,5-dichloro-2-(quinolin-3-yl)phenyl)quinolin-8-amine

This compound was purified by column chromatography (PE: EA =15:1) to afford a yellow solid (22.5 mg, 54% yield); m.p. 224-225 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.00 (d, J = 2.3 Hz, 1H), 8.50 (dd, J = 4.2, 1.7 Hz, 1H), 8.30 (d, J = 2.2 Hz, 1H), 8.12 (d, J = 8.7 Hz, 2H), 8.08 (dd, J = 8.3, 1.7 Hz, 1H), 7.87 (s, 1H), 7.82 (dd, J = 8.2, 1.4 Hz, 1H), 7.77 – 7.73 (m, 1H), 7.60 – 7.56 (m, J = 8.1, 6.9, 1.2 Hz, 1H), 7.53 (s, 1H), 7.49 – 7.43 (m, 2H), 7.34 (dd, J = 8.3, 4.2 Hz, 1H), 7.29 (dd, J = 7.6, 1.8 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 150.9, 147.8, 147.5, 139.4, 139.1, 138.8, 136.2, 136.0, 132.89, 132.5, 130.5, 130.2, 130.0, 129.4, 128.8, 128.0, 127.8, 127.2, 127.1, 125.7, 121.8, 121.4, 118.3, 109.1.

HRMS (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{24}H_{16}Cl_2N_3$ 416.0716; Found 416.0712 .



(3*J*) N-(2-fluoro-6-(quinolin-3-yl)phenyl)quinolin-8-amine

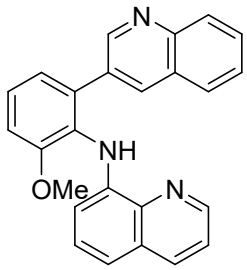
This compound was purified by column chromatography (PE: EA =15:1) to afford a yellow solid (23.1 mg, 65% yield); m.p. 116-117 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.98 (d, J = 2.2 Hz, 1H), 8.60 (dd, J = 4.2, 1.7 Hz, 1H), 8.21 (d, J = 2.2 Hz, 1H), 8.05 (dd, J = 8.3, 1.7 Hz, 1H), 8.03 – 7.99 (m, 1H), 7.73 (s, 1H), 7.69 – 7.64 (m, 2H), 7.47 (t, J = 6.9 Hz, 1H), 7.39 – 7.26 (m, 5H), 7.15 (dd, J = 8.3, 1.2 Hz, 1H), 6.72 (ddd, J = 7.7, 3.4, 1.2 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 168.3, 153.8, 150.6, 144.7 (d, $J_{F\text{-}C}$ = 328.6 Hz), 139.9, 137.1, 135.8, 135.4, 133.8, 130.0, 126.8 ($J_{F\text{-}C}$ = 15.9 Hz), 126.0 ($J_{F\text{-}C}$ = 11.3 Hz), 124.9, 123.9, 123.4, 122.1 ($J_{F\text{-}C}$ = 13.4 Hz), 121.6 ($J_{F\text{-}C}$ = 4.0 Hz), 121.5, 120.4, 120.0 ($J_{F\text{-}C}$ = 3.6 Hz), 118.8, 116.3, 111.7, 101.8.

^{19}F NMR (376 MHz, $CDCl_3$) δ -117.4.

HRMS (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{24}H_{17}FN_3$ 366.1401; Found 366.1396 .



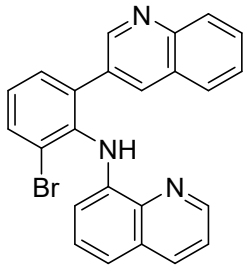
(3k) N-(2-methoxy-6-(quinolin-3-yl)phenyl)quinolin-8-amine

This compound was purified by column chromatography (PE: EA =15:1) to afford a yellow solid (23.4 mg, 62% yield); m.p. 181-182 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.05 (d, J = 2.3 Hz, 1H), 8.66 (dd, J = 4.2, 1.7 Hz, 1H), 8.25 (dd, J = 2.3, 0.8 Hz, 1H), 7.99 (dd, J = 8.3, 1.7 Hz, 1H), 7.96 (dd, J = 8.4, 1.0 Hz, 1H), 7.81 (s, 1H), 7.64 – 7.58 (m, 2H), 7.45 – 7.41 (m, 1H), 7.37 (t, J = 8.0 Hz, 1H), 7.31 (dd, J = 8.3, 4.2 Hz, 1H), 7.17 (dd, J = 7.8, 1.3 Hz, 1H), 7.14 – 7.08 (m, 2H), 7.01 (dd, J = 8.2, 1.3 Hz, 1H), 6.51 (dd, J = 7.6, 1.2 Hz, 1H), 3.87 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 155.4, 151.0, 147.3, 147.0, 141.6, 138.3, 135.9, 134.8, 133.0, 129.2, 129.0, 128.6, 128.3, 127.9, 127.0, 126.5, 126.3, 123.0, 121.2, 116.0, 111.5, 107.8, 56.0.

HRMS (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{25}H_{20}N_3O$ 378.1601; Found 378.1596 .



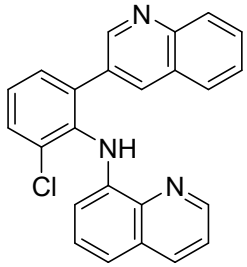
(3l) N-(2-bromo-6-(quinolin-3-yl)phenyl)quinolin-8-amine

This compound was purified by column chromatography (PE: EA =15:1) to afford a yellow solid (19.2 mg, 45% yield); m.p. 163-164 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.02 (d, J = 2.25 Hz, 1H), 8.50 (dd, J = 4.22, 1.70 Hz, 1H), 8.30 (dd, J = 2.33, 0.80 Hz, 1H), 8.15 (s, 1H), 8.11 (dd, J = 8.46, 1.02 Hz, 1H), 8.07 (dd, J = 8.30, 1.67 Hz, 1H), 7.93 (d, J = 1.10 Hz, 1H), 7.80 (dd, J = 8.09, 1.44 Hz, 1H), 7.73 (ddd, J = 8.41, 6.92, 1.50 Hz, 1H), 7.58 – 7.54 (m, 1H), 7.51 (dd, J = 7.73, 1.35 Hz, 1H), 7.45 (t, J = 7.88 Hz, 1H), 7.35 – 7.31 (m, 3H), 7.29 – 7.26 (m, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 151.3, 147.7, 147.3, 141.1, 139.4, 138.8, 136.1, 135.8, 132.7, 131.4, 129.7, 129.4, 129.3, 128.8, 128.0, 127.1, 127.0, 125.9, 123.0, 122.9, 121.7, 117.9, 109.0.

HRMS (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{24}H_{17}BrlN_3$ 426.0600; 426.0604 .



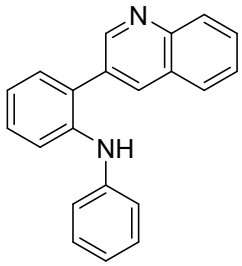
(3m) N-(2-chloro-6-(quinolin-3-yl)phenyl)quinolin-8-amine

This compound was purified by column chromatography (PE: EA =15:1) to afford a yellow solid (30.9 mg, 81% yield); m.p. 143-145 ^{o}C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.00 (d, J = 2.2 Hz, 1H), 8.67 (dd, J = 4.2, 1.7 Hz, 1H), 8.21 (dd, J = 2.3, 0.8 Hz, 1H), 7.99 (dd, J = 8.3, 1.7 Hz, 1H), 7.97 – 7.93 (m, 2H), 7.63 – 7.59 (m, 3H), 7.46 (dd, J = 7.7, 1.6 Hz, 1H), 7.45 – 7.40 (m, 1H), 7.37 – 7.33 (m, 1H), 7.32 (dd, J = 7.9, 3.8 Hz, 1H), 7.15 (t, J = 7.9 Hz, 1H), 7.05 (dd, J = 8.2, 1.2 Hz, 1H), 6.50 (dd, J = 7.6, 1.2 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 150.6, 147.5, 147.1, 140.8, 138.0, 137.7, 136.7, 136.0, 134.9, 133.3, 132.4, 130.4, 129.9, 129.5, 129.0, 128.6, 127.9, 127.7, 126.9, 126.7, 121.4, 116.8, 108.0.

HRMS (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{24}H_{17}ClN_3$ 382.1106; Found 382.1102 .



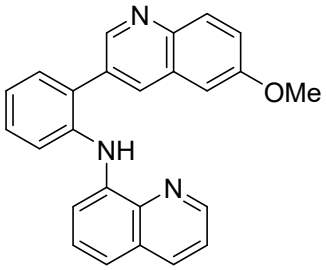
(3q) N-phenyl-2-(quinolin-3-yl)aniline

This compound was purified by column chromatography (PE: EA = 20:1) to afford a yellow solid (8.3 mg, 28% yield); m.p. 93-94 ^{o}C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.01 (d, J = 2.0 Hz, 1H), 8.25 (d, J = 2.0 Hz, 1H), 8.13 (d, J = 8.4 Hz, 1H), 7.84 – 7.82 (m, 1H), 7.76 – 7.72 (m, 1H), 7.60 – 7.56 (m, 1H), 7.45 – 7.43 (m, 1H), 7.37 – 7.32 (m, 2H), 7.27 – 7.22 (m, 2H), 7.11 – 7.08 (m, 1H), 7.03 – 7.00 (m, 2H), 6.95 – 6.91 (m, 1H), 5.51 (s, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 151.7, 147.3, 143.0, 140.9, 135.8, 132.2, 131.3, 129.7, 129.4, 129.3, 128.3, 128.0, 127.9, 127.1, 121.8, 121.4, 118.4, 118.3.

HRMS (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{21}H_{17}N_2$ 297.1386; Found 297.1383.



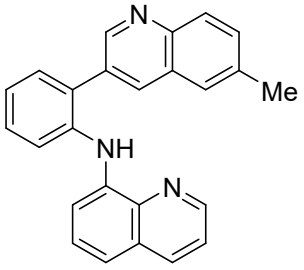
(3r) N-(2-(6-methoxyquinolin-3-yl)phenyl)quinolin-8-amine

This compound was purified by column chromatography (PE: EA =15:1) to afford a yellow solid (15.1 mg, 40% yield); m.p. 108-109 ^{o}C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.88 (d, J = 2.1 Hz, 1H), 8.52 (dd, J = 4.2, 1.6 Hz, 1H), 8.17 (d, J = 1.9 Hz, 1H), 8.08 – 8.04 (m, 2H), 7.98 (d, J = 9.2 Hz, 1H), 7.77 (d, J = 8.0 Hz, 1H), 7.49 – 7.43 (m, 3H), 7.40 (d, J = 7.9 Hz, 1H), 7.36 – 7.30 (m, 2H), 7.25 – 7.19 (m, 2H), 6.99 (d, J = 2.8 Hz, 1H), 3.89 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 158.0, 149.1, 147.5, 143.3, 140.6, 139.5, 138.7, 136.0, 134.5, 132.6, 131.5, 130.6, 129.1, 129.0, 128.9, 127.2, 123.5, 122.2, 121.7, 121.6, 116.8, 108.0, 105.3, 55.6.

HRMS (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{25}H_{20}N_3O$ 378.1601; Found 378.1599 .



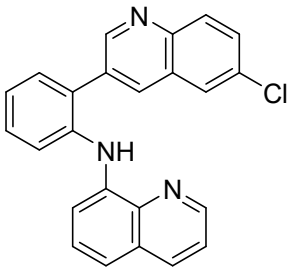
(3s) N-(2-(6-methylquinolin-3-yl)phenyl)quinolin-8-amine

This compound was purified by column chromatography (PE: EA =15:1) to afford a yellow solid (20.6 mg, 57% yield); m.p. 140-141 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.97 (d, J = 2.2 Hz, 1H), 8.51 (dd, J = 4.2, 1.7 Hz, 1H), 8.21 – 8.18 (m, 1H), 8.09 – 8.02 (m, 2H), 7.98 (d, J = 8.4 Hz, 1H), 7.77 (d, J = 8.0 Hz, 1H), 7.54 – 7.43 (m, 5H), 7.38 (t, J = 7.9 Hz, 1H), 7.31 (dd, J = 8.3, 4.2 Hz, 1H), 7.26 – 7.19 (m, 2H), 2.52 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 150.7, 147.5, 145.8, 140.6, 139.5, 138.7, 136.7, 136.0, 135.0, 132.4, 131.7, 131.6, 131.6, 129.1, 128.9, 128.9, 128.1, 127.2, 126.8, 123.5, 121.8, 121.6, 116.8, 108.0, 21.6.

HRMS (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{25}H_{20}N_3$ 362.1652; Found 362.1656 .



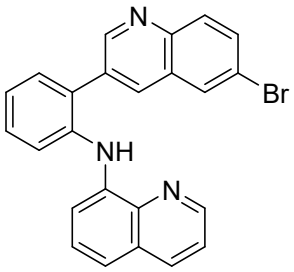
(3t) N-(2-(6-chloroquinolin-3-yl)phenyl)quinolin-8-amine

This compound was purified by column chromatography (PE: EA =15:1) to afford a yellow solid (26.7 mg, 70% yield); m.p. 186-187 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.02 (d, J = 2.2 Hz, 1H), 8.53 (dd, J = 4.2, 1.7 Hz, 1H), 8.19 (d, J = 2.0 Hz, 1H), 8.08 – 8.03 (m, 2H), 8.01 (d, J = 9.0 Hz, 1H), 7.78 – 7.75 (m, 1H), 7.72 (d, J = 2.3 Hz, 1H), 7.62 (dd, J = 9.0, 2.3 Hz, 1H), 7.47 (dd, J = 7.5, 1.6 Hz, 2H), 7.40 – 7.35 (m, 2H), 7.33 (dd, J = 8.3, 4.2 Hz, 1H), 7.24 (dd, J = 7.4, 0.9 Hz, 1H), 7.20 (dd, J = 6.5, 2.8 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 151.9, 147.5, 145.5, 140.5, 139.6, 138.6, 136.1, 134.6, 133.4, 132.5, 131.4, 131.1, 130.8, 130.3, 129.5, 128.8, 128.6, 127.2, 126.5, 123.8, 122.2, 121.7, 117.0, 108.0.

HRMS (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{24}H_{17}ClN_3$ 382.1106; Found 382.1107 .



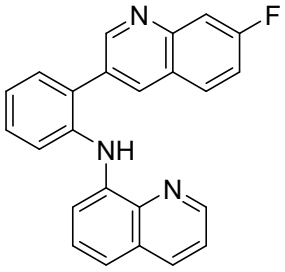
(3u) N-(2-(6-bromo-3,4-dihydroquinolin-3-yl)phenyl)quinolin-8-amine

This compound was purified by column chromatography (PE: EA =15:1) to afford a yellow solid (29.4 mg, 69% yield); m.p. 205-206 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.03 (d, J = 2.2 Hz, 1H), 8.53 (dd, J = 4.2, 1.7 Hz, 1H), 8.19 (d, J = 2.1 Hz, 1H), 8.07 (dd, J = 8.3, 1.6 Hz, 1H), 8.03 (s, 1H), 7.94 (d, J = 8.9 Hz, 1H), 7.90 (d, J = 2.1 Hz, 1H), 7.77 – 7.73 (m, 2H), 7.49 – 7.45 (m, 2H), 7.39 – 7.37 (m, 2H), 7.35 – 7.32 (m, 1H), 7.24 (dd, J = 7.5, 1.0 Hz, 1H), 7.20 (dd, J = 6.1, 3.2 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 152.04, 147.54, 145.72, 140.53, 139.55, 138.58, 136.09, 134.48, 133.36, 132.81, 131.45, 131.10, 130.97, 129.88, 129.52, 129.16, 128.84, 127.14, 123.77, 122.18, 121.66, 120.67, 116.98, 108.02.

HRMS (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{24}H_{17}BrlN_3$ 426.0600; 426.0600 .



(3v) N-(2-(7-fluoroquinolin-3-yl)phenyl)quinolin-8-amine

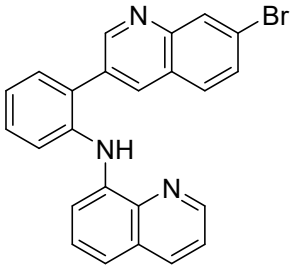
This compound was purified by column chromatography (PE: EA =15:1) to afford a yellow solid (26.7 mg, 73% yield); m.p. 144-145 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.04 (d, J = 2.1 Hz, 1H), 8.52 (dd, J = 4.2, 1.7 Hz, 1H), 8.27 (d, J = 2.1 Hz, 1H), 8.06 (dd, J = 8.3, 1.7 Hz, 2H), 7.74 (dt, J = 13.4, 7.7 Hz, 3H), 7.49 – 7.44 (m, 2H), 7.42 – 7.37 (m, 2H), 7.36 – 7.29 (m, 2H), 7.26 – 7.23 (m, 1H), 7.20 (dd, J = 7.4, 2.0 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 163.0 (d, $J_{F\text{-}C}$ = 247.5 Hz), 161.8, 152.6, 148.0 ($J_{F\text{-}C}$ = 12.4 Hz), 147.5, 140.6, 139.5, 138.6, 136.1, 135.6, 131.8 ($J_{F\text{-}C}$ = 2.8 Hz), 131.4, 131.3, 130.0, 130.0, 129.3, 128.8, 127.2, 125.0, 123.7, 122.1, 121.6, 117.3 ($J_{F\text{-}C}$ = 25.2 Hz), 116.9, 112.9 ($J_{F\text{-}C}$ = 20.1 Hz), 107.9.

^{19}F NMR (376 MHz, $CDCl_3$) δ -109.5.

HRMS (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{24}H_{17}FN_3$ 366.1401; Found 366.1402 .



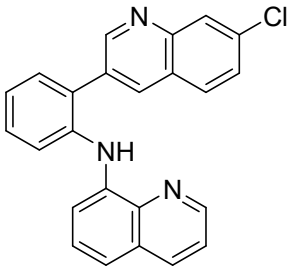
(3w) N-(2-(7-bromoquinolin-3-yl)phenyl)quinolin-8-amine

This compound was purified by column chromatography (PE: EA =15:1) to afford a yellow solid (20.4 mg, 48% yield); m.p. 210-211 ^{o}C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.03 (d, J = 2.1 Hz, 1H), 8.51 (dd, J = 4.1, 1.5 Hz, 1H), 8.27 – 8.23 (m, 2H), 8.06 (dd, J = 8.2, 1.3 Hz, 2H), 7.76 (d, J = 7.9 Hz, 1H), 7.61 – 7.59 (m, 2H), 7.47 (t, J = 7.6 Hz, 2H), 7.40 – 7.35 (m, 2H), 7.32 (dd, J = 8.3, 4.2 Hz, 1H), 7.24 (d, J = 7.0 Hz, 1H), 7.20 (dd, J = 7.0, 2.3 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 152.6, 147.7, 147.5, 140.5, 139.5, 138.6, 136.1, 135.4, 132.8, 131.6, 131.4, 131.2, 130.3, 129.4, 129.2, 128.8, 127.2, 126.6, 123.7, 123.4, 122.2, 121.6, 116.9, 107.9.

HRMS (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{24}H_{17}BrlN_3$ 426.0600; Found 426.0605 .



(3x) N-(2-(7-chloroquinolin-3-yl)phenyl)quinolin-8-amine

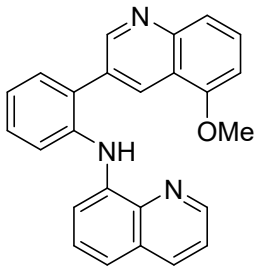
This compound was purified by column chromatography (PE: EA =15:1) to afford a

yellow solid (24.1 mg, 63% yield); m.p. 186-187 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.04 (d, J = 2.0 Hz, 1H), 8.51 (dd, J = 4.2, 1.3 Hz, 1H), 8.27 – 8.24 (m, 1H), 8.06 (d, J = 8.6 Hz, 3H), 7.76 (d, J = 8.0 Hz, 1H), 7.68 (d, J = 8.7 Hz, 1H), 7.47 (dd, J = 8.0, 2.5 Hz, 3H), 7.38 (d, J = 7.4 Hz, 2H), 7.32 (dd, J = 8.3, 4.2 Hz, 1H), 7.24 (d, J = 7.5 Hz, 1H), 7.20 (dd, J = 7.0, 2.2 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 152.6, 147.5, 147.5, 140.6, 139.5, 138.6, 136.1, 135.4, 135.2, 132.7, 131.4, 131.2, 129.4, 129.1, 128.8, 128.3, 127.9, 127.15, 126.4, 123.7, 122.2, 121.6, 116.9, 107.9.

HRMS (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{24}H_{17}ClN_3$ 382.1106; Found 382.1109 .



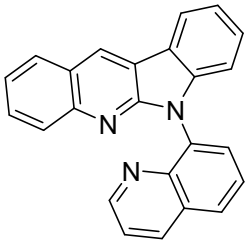
(3y) N-(2-(5-methoxyquinolin-3-yl)phenyl)quinolin-8-amine

This compound was purified by column chromatography (PE: EA =15:1) to afford a yellow solid (14.4 mg, 38% yield); m.p. 44-45 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.02 (d, J = 2.2 Hz, 1H), 8.68 (d, J = 1.9 Hz, 1H), 8.51 (dd, J = 4.1, 1.5 Hz, 1H), 8.07 – 8.01 (m, 2H), 7.76 (d, J = 8.0 Hz, 1H), 7.66 (d, J = 8.5 Hz, 1H), 7.59 (t, J = 8.1 Hz, 1H), 7.50 (dd, J = 7.6, 1.2 Hz, 1H), 7.47 – 7.43 (m, 1H), 7.42 – 7.35 (m, 2H), 7.31 (dd, J = 8.2, 4.2 Hz, 1H), 7.26 – 7.22 (m, 1H), 7.19 (dd, J = 7.6, 1.5 Hz, 1H), 3.92 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 155.3, 151.8, 147.9, 147.4, 140.8, 139.5, 138.6, 136.0, 132.0, 131.7, 131.6, 130.6, 129.3, 129.1, 128.8, 127.2, 123.7, 122.2, 121.5, 121.3, 120.6, 116.8, 107.9, 104.5, 55.7.

HRMS (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{25}H_{20}N_3O$ 378.1601; Found 378.1605 .



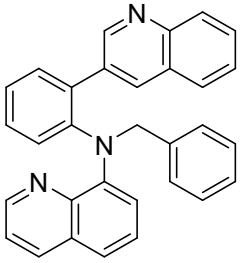
(4) 6-(quinolin-8-yl)-6H-indolo[2,3-b]quinoline

This compound was purified by column chromatography (PE: EA =15:1) to afford a yellow solid (20.8 mg, 60% yield); m.p. 95-96 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.85 (s, 1H), 8.77 (dd, J = 4.2, 1.7 Hz, 1H), 8.32 (dd, J = 8.3, 1.7 Hz, 1H), 8.25 (d, J = 8.2 Hz, 1H), 8.08 – 8.02 (m, 3H), 7.94 (d, J = 8.6 Hz, 1H), 7.82 (dd, J = 8.3, 7.2 Hz, 1H), 7.64 – 7.60 (m, 1H), 7.48 – 7.38 (m, 3H), 7.33 (td, J = 7.4, 1.1 Hz, 1H), 6.89 (d, J = 8.1 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 154.1, 150.8, 146.9, 145.0, 144.1, 136.4, 134.1, 130.8, 129.8, 128.9, 128.5, 128.4, 128.1, 127.9, 127.5, 126.8 124.8, 123.2, 121.8, 121.4, 120.8, 120.6, 119.0, 111.1.

HRMS (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{24}H_{16}N_3$ 346.1339; Found 346.1337 .



(5) N-benzyl-N-(2-(quinolin-3-yl)phenyl)quinolin-8-amine

This compound was purified by column chromatography (PE: EA =15:1) to afford a yellow solid (37.2 mg, 85% yield); m.p. 59-60 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.02 (d, J = 2.1 Hz, 1H), 8.71 (dd, J = 4.1, 1.7 Hz, 1H), 8.15 (d, J = 1.8 Hz, 1H), 7.81 (d, J = 8.7 Hz, 1H), 7.73 (dd, J = 8.3, 1.7 Hz, 1H), 7.51 (q, J = 7.1 Hz, 4H), 7.34 (t, J = 7.4 Hz, 1H), 7.28 – 7.24 (m, 3H), 7.20 (t, J = 7.5 Hz, 2H), 7.14 – 7.06 (m, 6H), 5.07 (s, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 151.9, 149.3, 148.2, 146.6, 146.2, 143.1, 139.2, 135.6, 135.1, 133.8, 132.6, 131.7, 129.3, 128.7, 128.7, 128.5, 128.2, 128.0, 127.7, 127.2, 126.7, 126.0, 125.9, 123.1, 123.1, 123.0, 122.5, 120.8, 57.5.

HRMS (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{31}H_{24}N_3$ 438.1965; Found 438.1960 .

References

[1] X. Liu, H. Sheng, Y. Zhou and Q. Song, *Chem. Commun.*, 2020, **56**, 1665−1668.

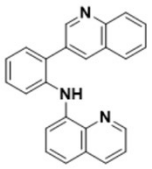
[2] D. Toullec, P. Pianetti, H. Coste, P. Bellevergue, T. Grand-Perret, M. A*J*akane, V. Baudet, P. Boissin, E. Boursier, F. Loriolle, L. Duhamel, D. Charon, *J*. Kirilovsky, *J. Biol. Chem*., 1991, **266**, 15771−15781.

[3] H. A. El-Aal; A. A. Khalaf, *Aust. J. Chem.,* 2013, **66**, 635−645.

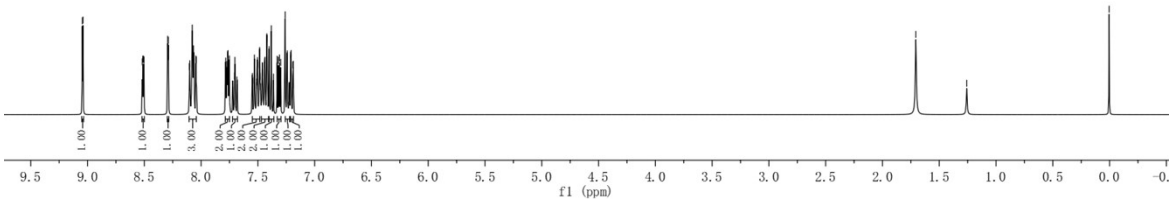
[4] L. Marti, L. M. Sanchez, M. *J*. Climent, A. Corma, S. Iborra, G. P. Romanelli, P. Concepcion, *ACS Catal.*, 2017, **7**, 8255−8262.

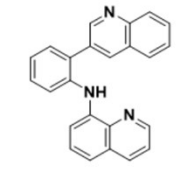
NMR Spectra

(3a) N-(2-(quinolin-3-yl)phenyl)quinolin-8-amine

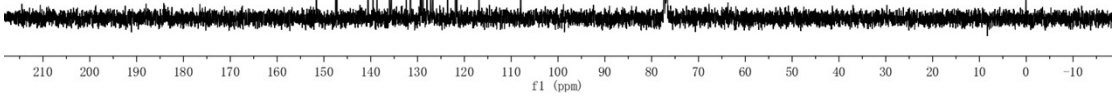


^{1}H NMR 400MHz, $CDCl_3$

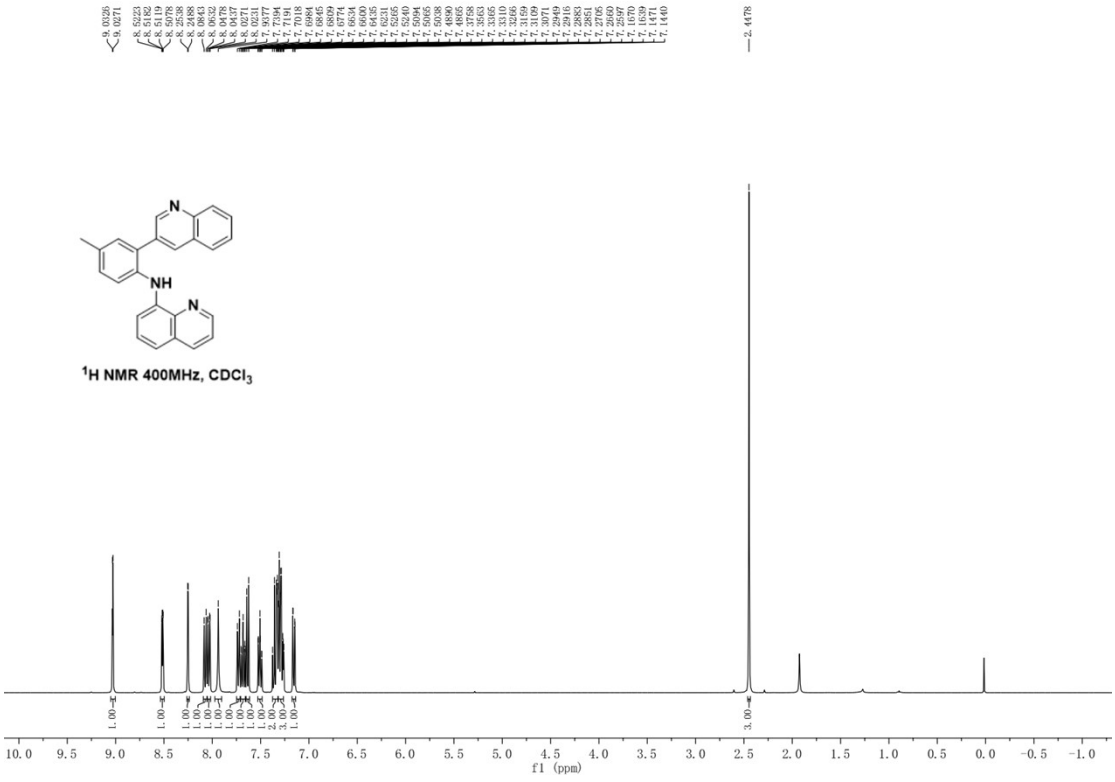


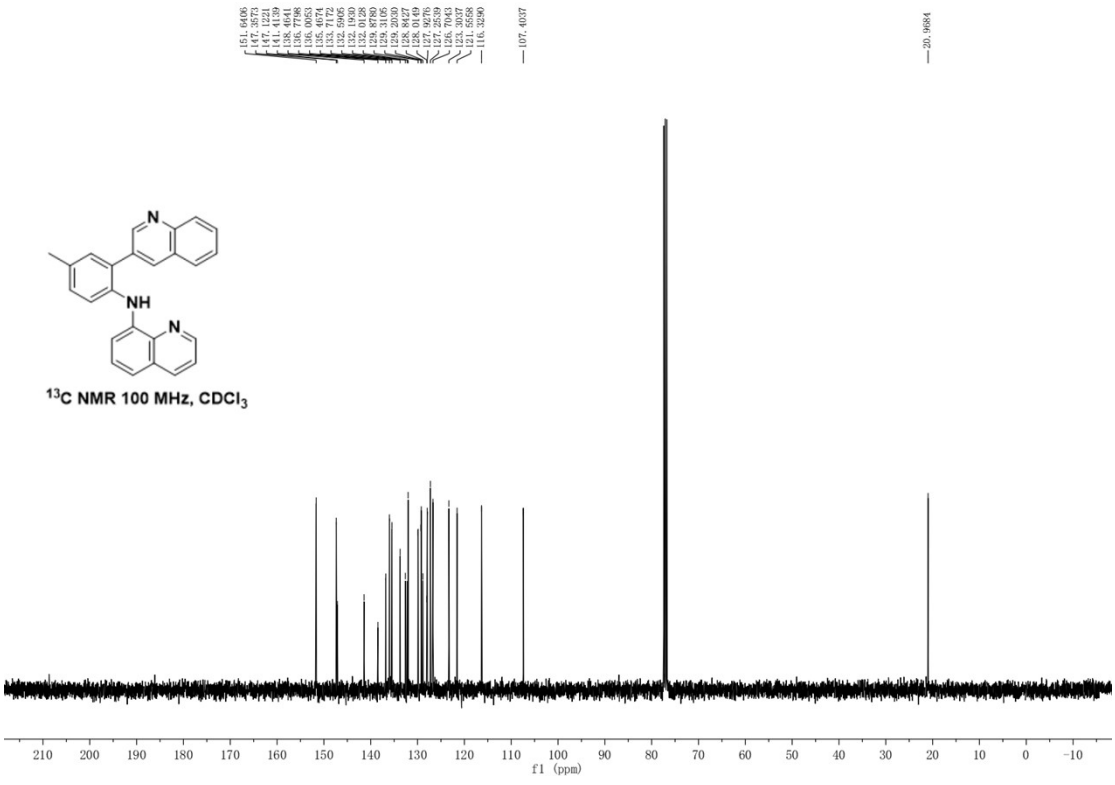


^{13}C NMR 100 MHz, $CDCl_3$

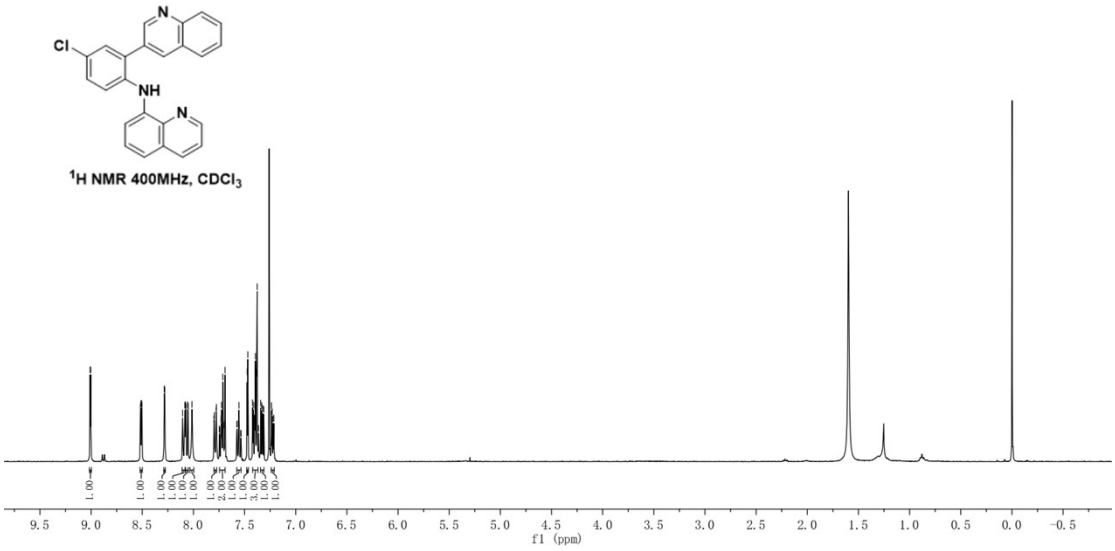


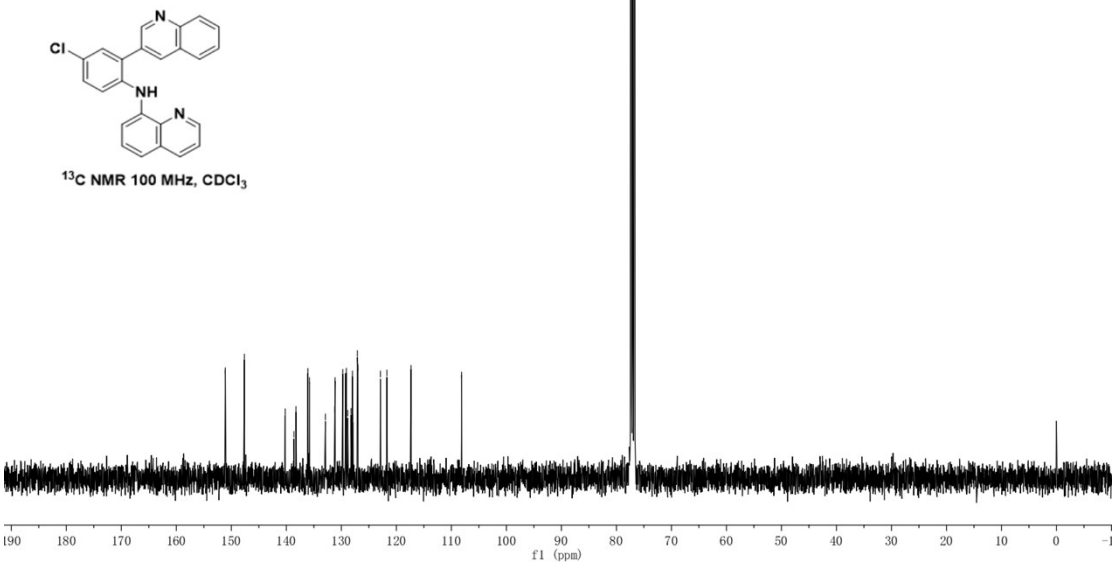
(3b) N-(4-methyl-2-(quinolin-3-yl)phenyl)quinolin-8-amine



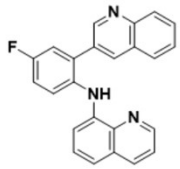


(3c) N-(4-chloro-2-(quinolin-3-yl)phenyl)quinolin-8-amine

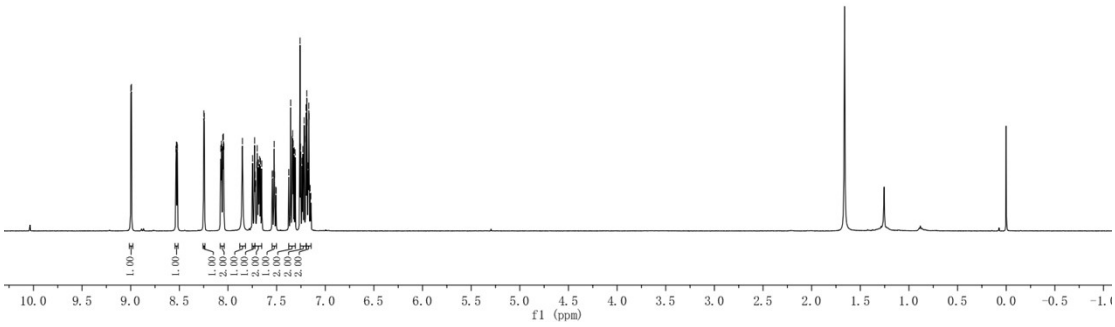


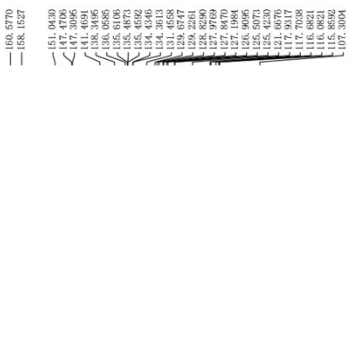


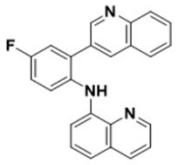
(3d) N-(4-fluoro-2-(quinolin-3-yl)phenyl)quinolin-8-amine



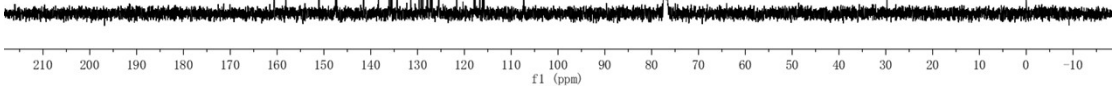
^{1}H NMR 400MHz, $CDCl_3$



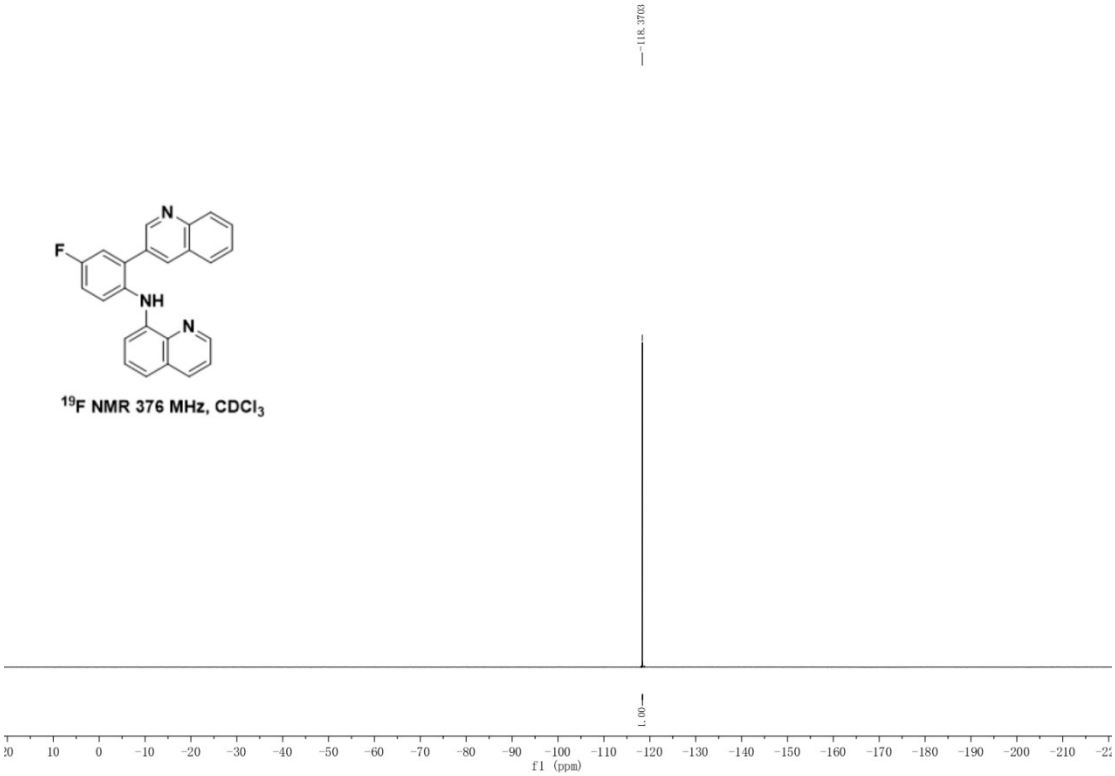




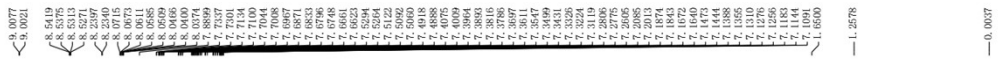
^{13}C NMR 100 MHz, $CDCl_3$

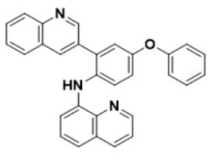


^{19}F NMR 376 MHz, $CDCl_3$

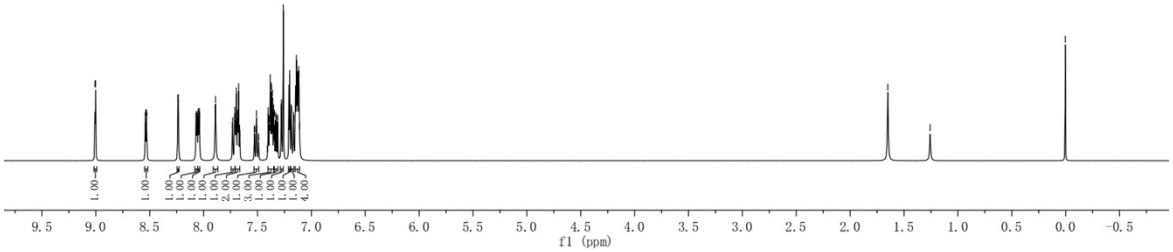


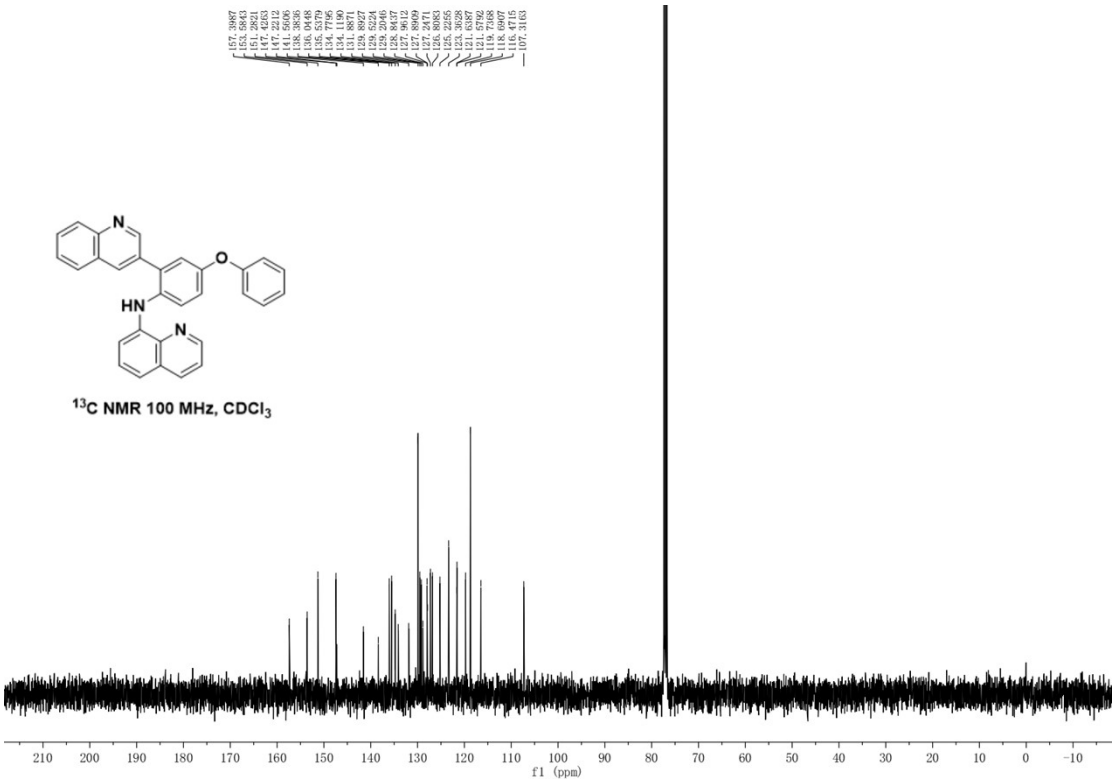
(3e) N-(4-phenoxy-2-(quinolin-3-yl)phenyl)quinolin-8-amine



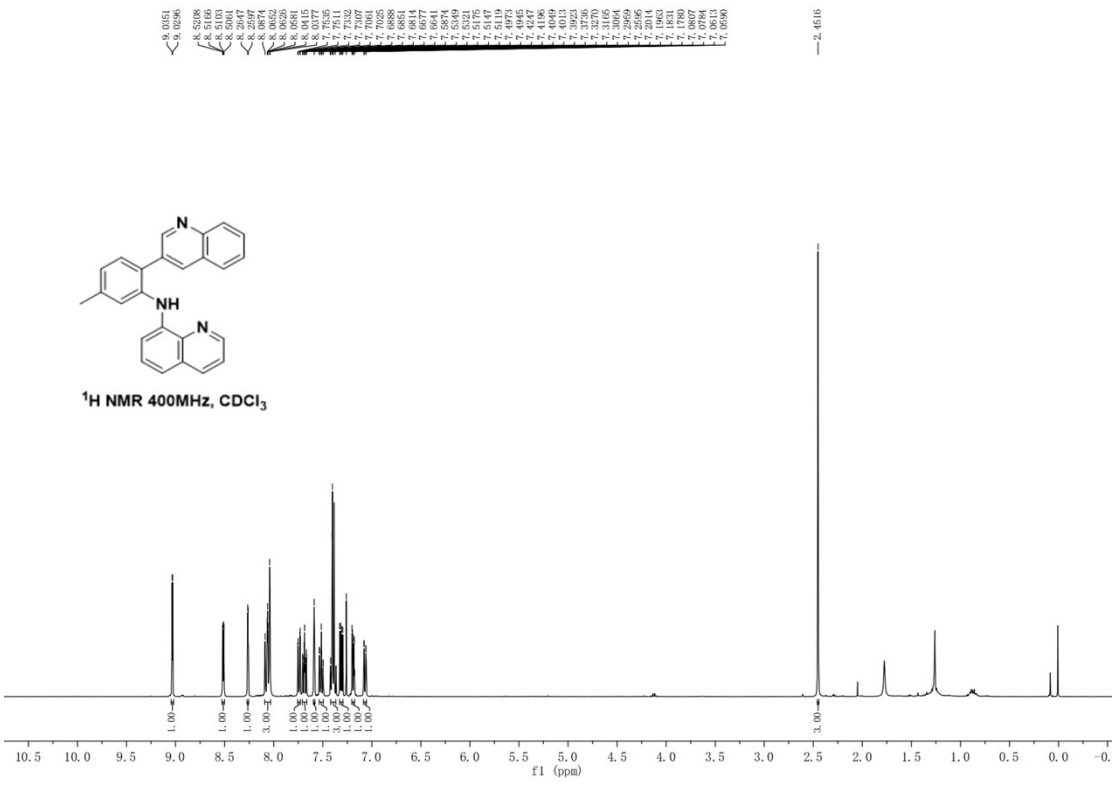


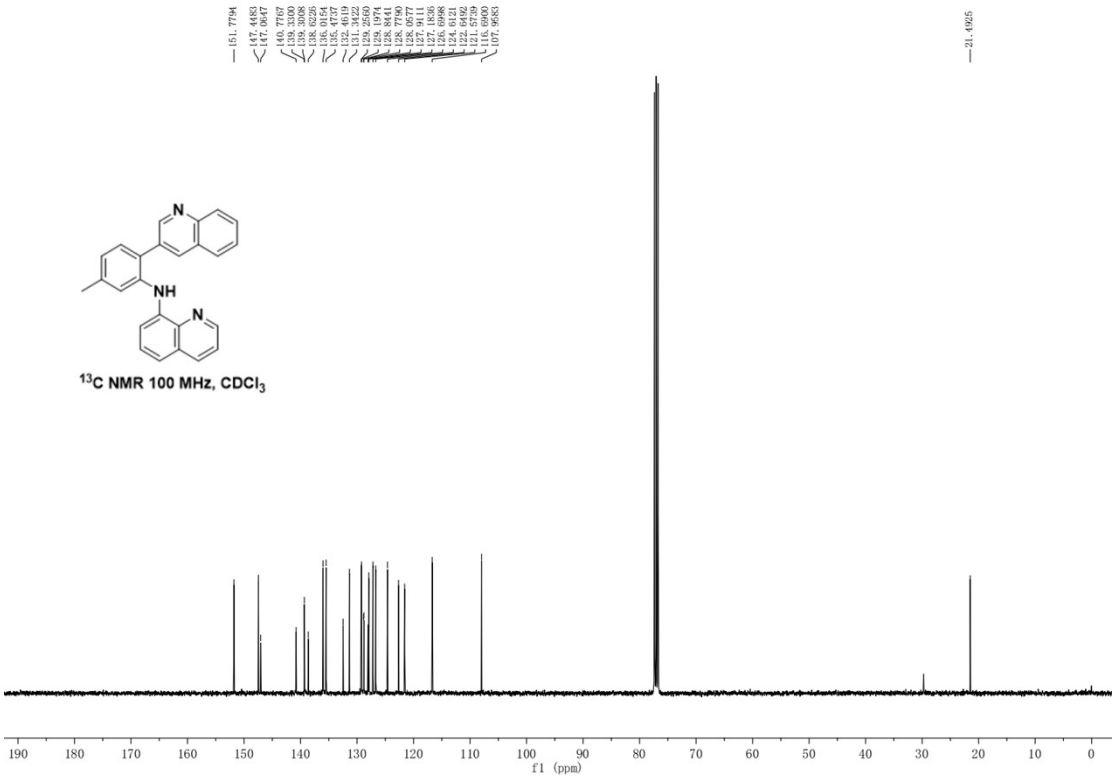
^{1}H NMR 400MHz, $CDCl_3$



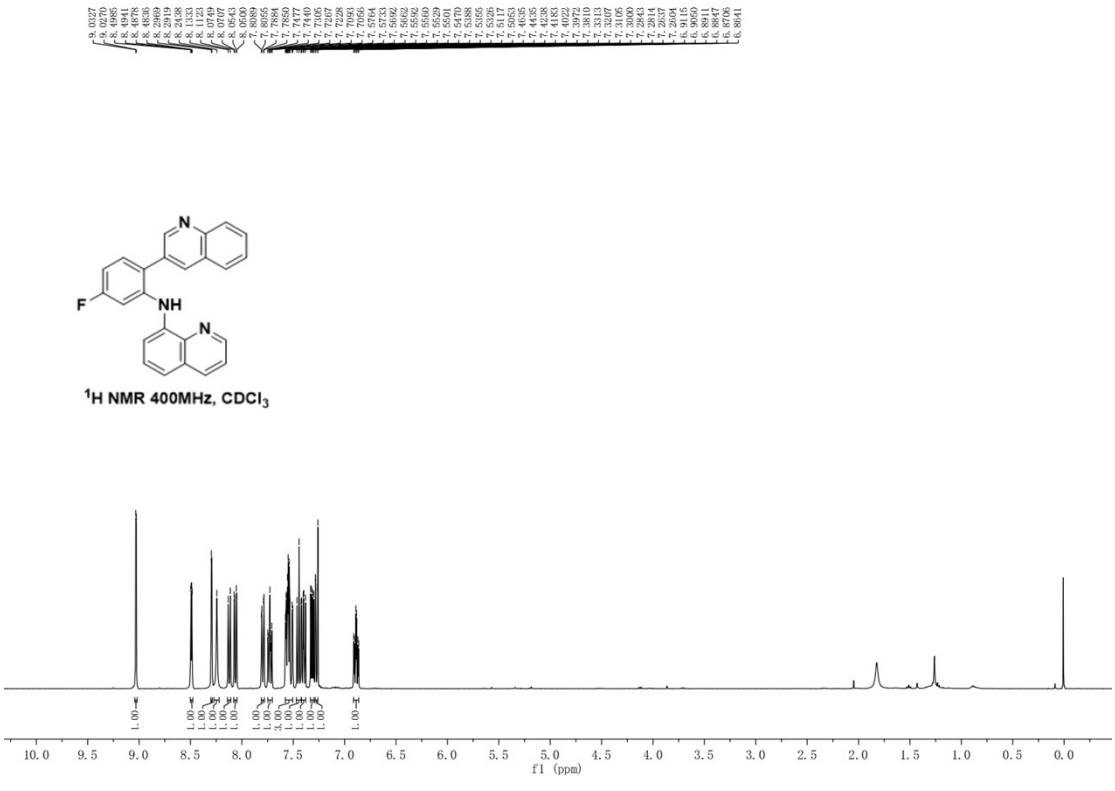


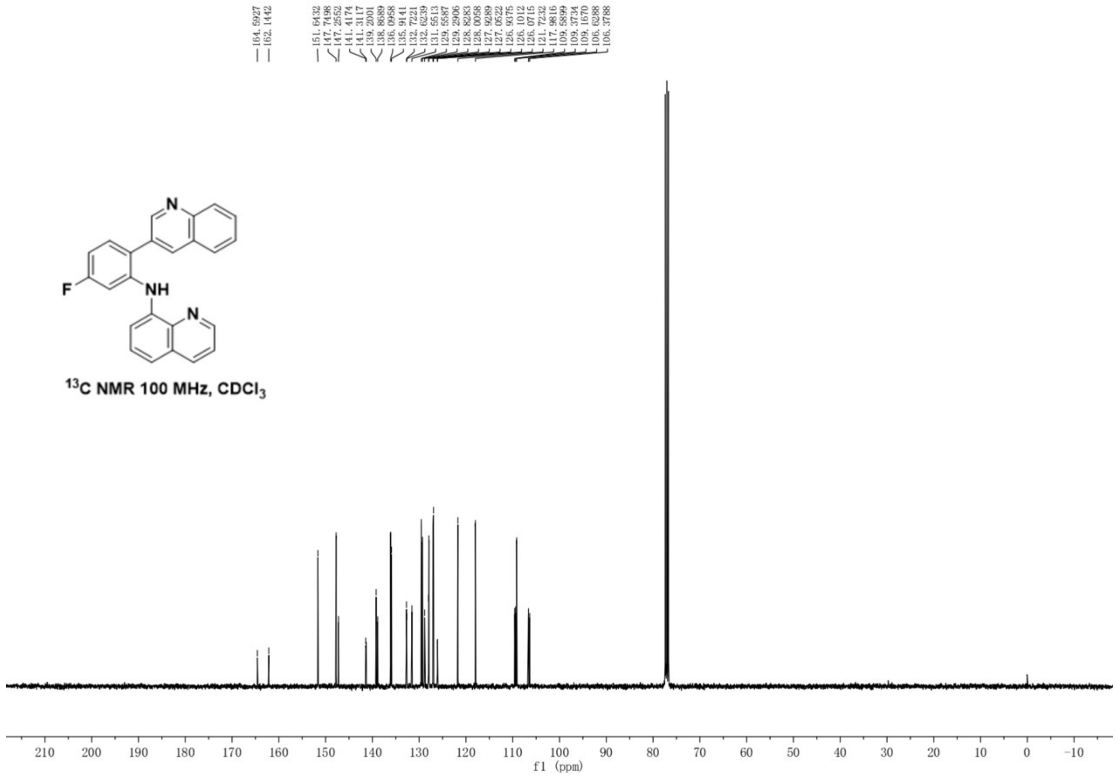
(3f) N-(5-methyl-2-(quinolin-3-yl)phenyl)quinolin-8-amine





(3g) N-(5-fluoro-2-(quinolin-3-yl)phenyl)quinolin-8-amine

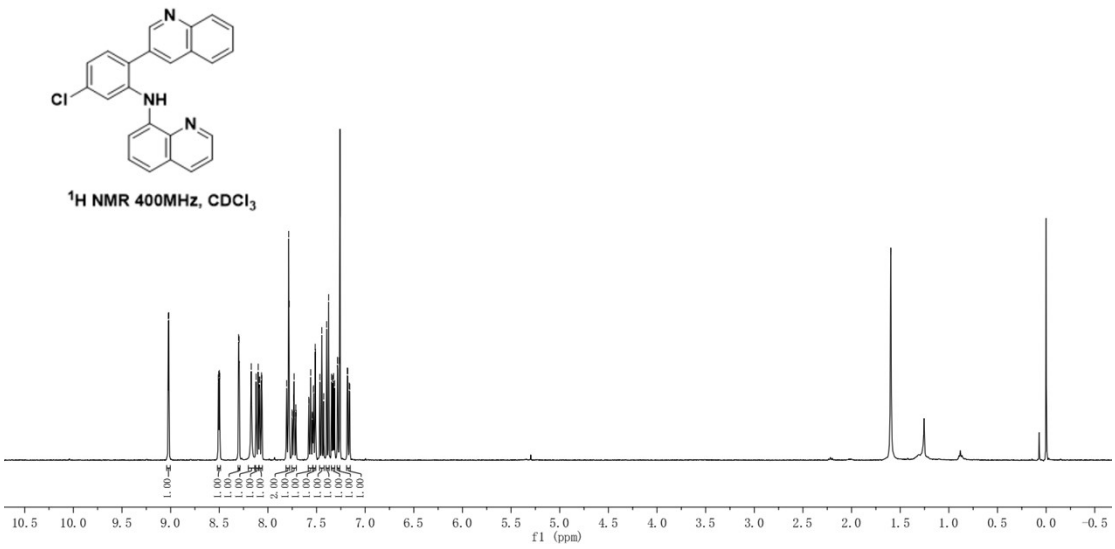


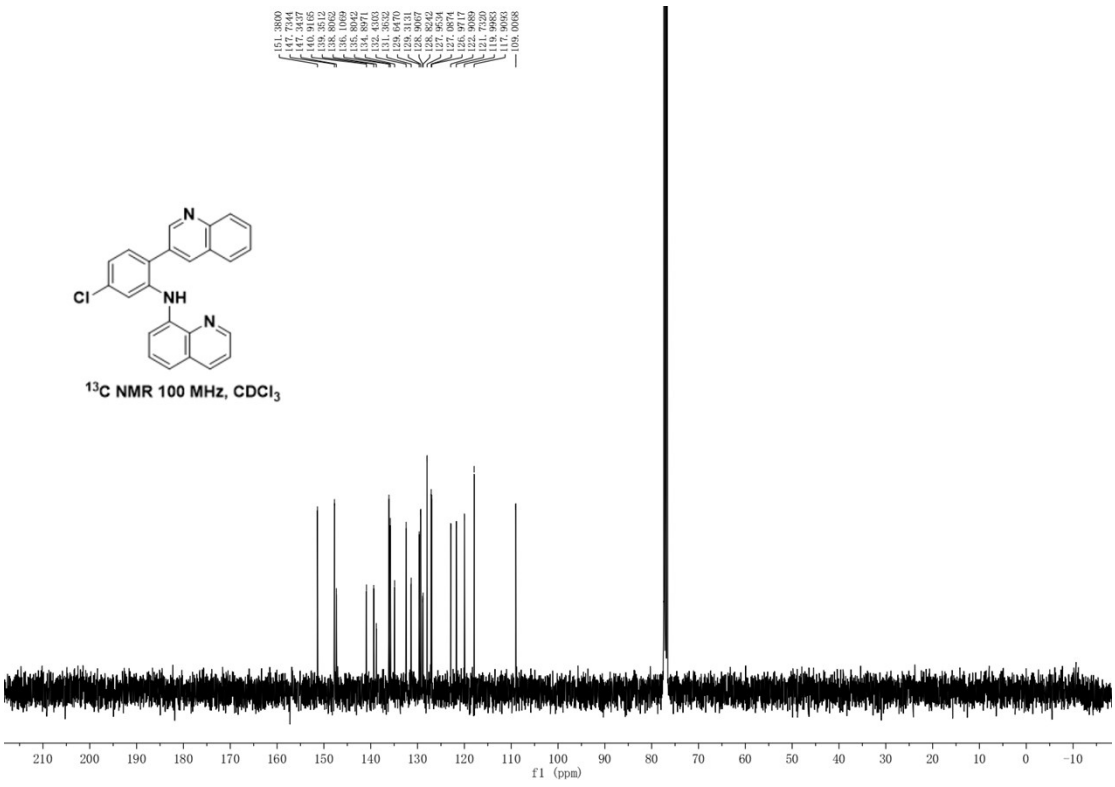


^{13}C NMR 100 MHz, CDCl$_3$
f1 (ppm)

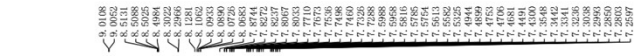
^{19}F NMR 376 MHz, CDCl$_3$
-111.6277
f1 (ppm)

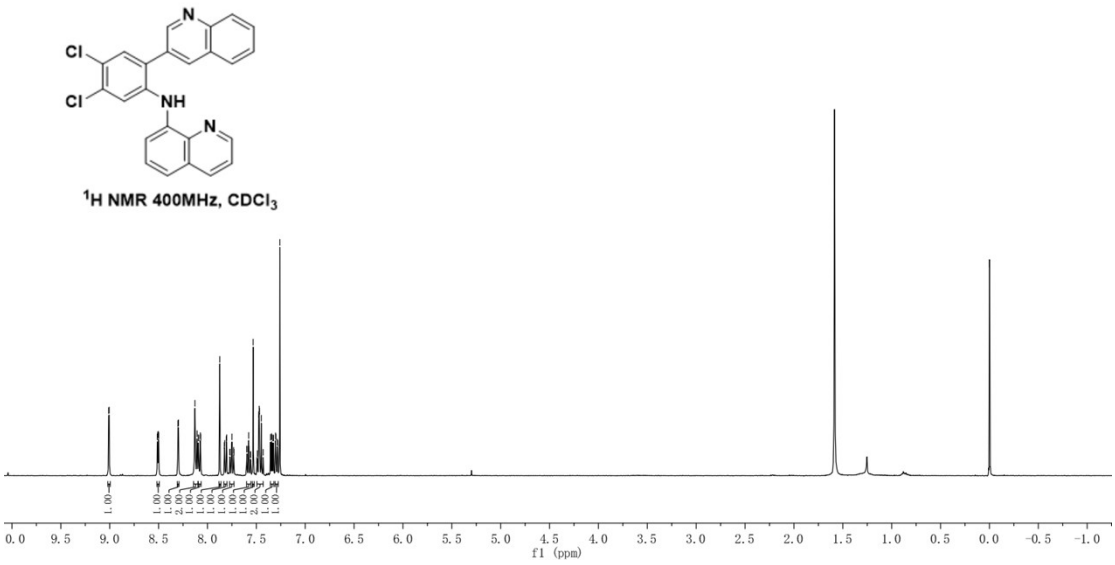
(3h) N-(5-chloro-2-(quinolin-3-yl)phenyl)quinolin-8-amine

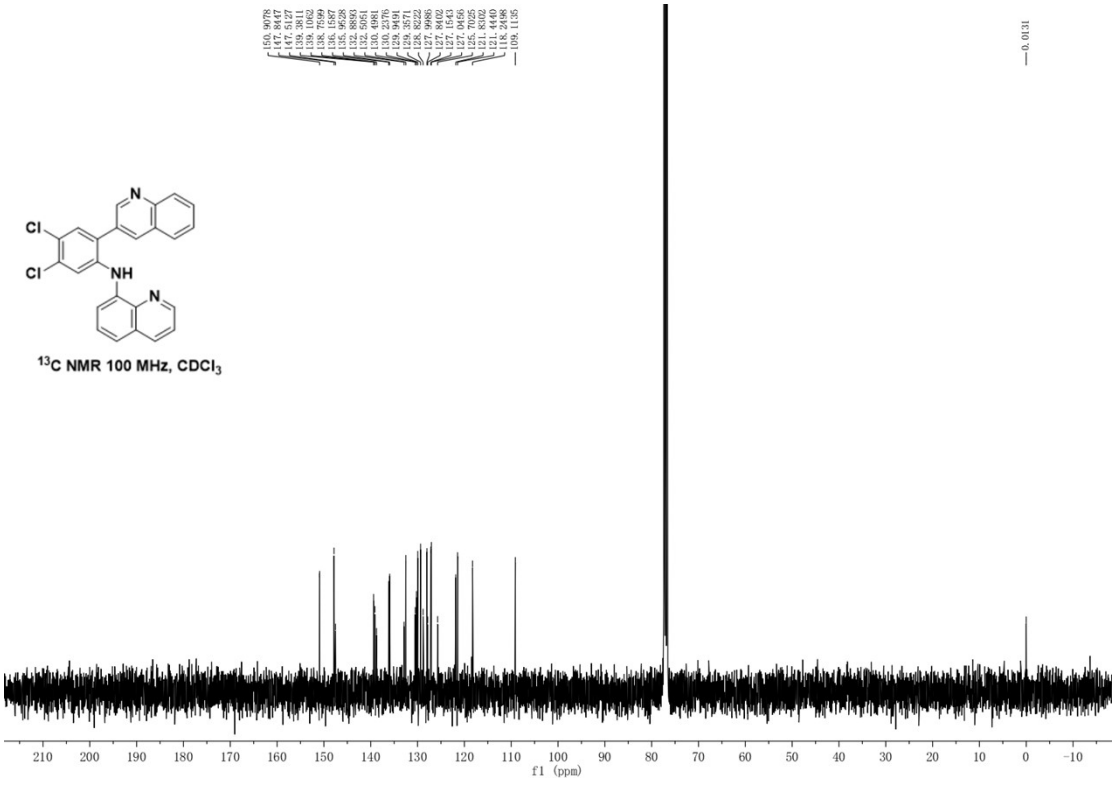




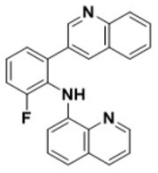
(3i) N-(4,5-dichloro-2-(quinolin-3-yl)phenyl)quinolin-8-amine



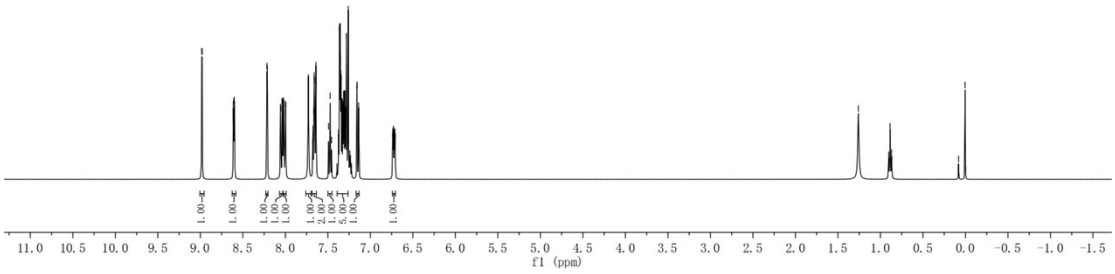


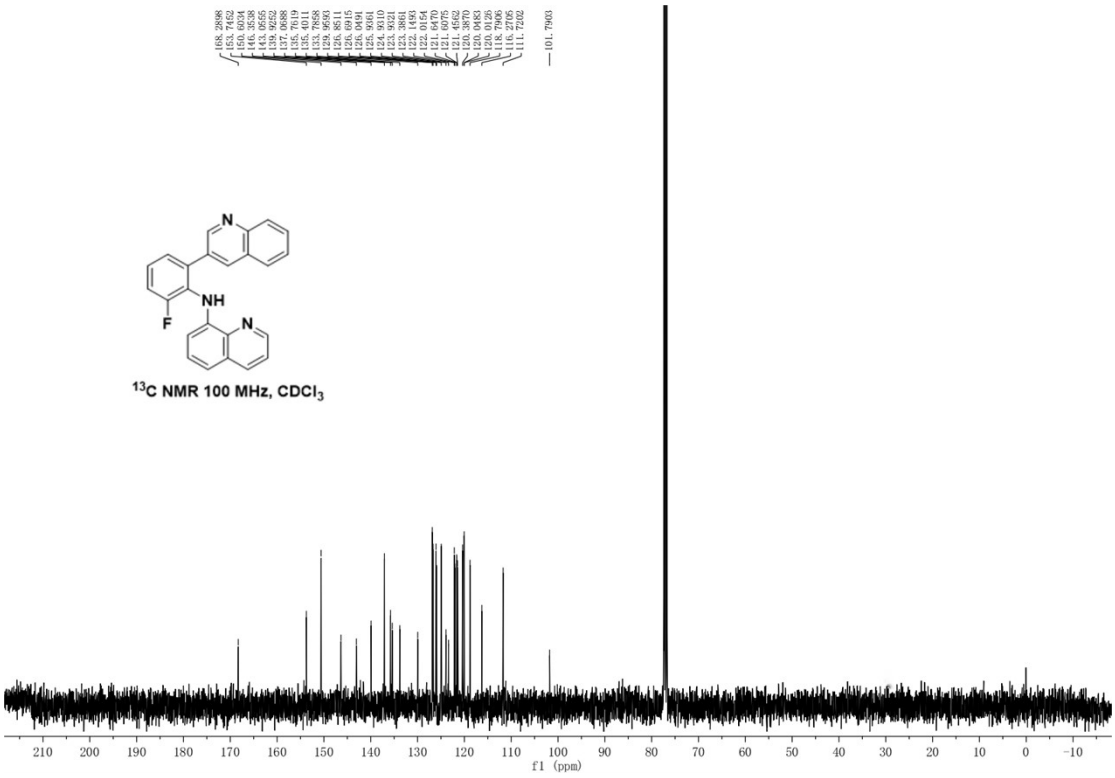


(3*J*) N-(2-fluoro-6-(quinolin-3-yl)phenyl)quinolin-8-amine

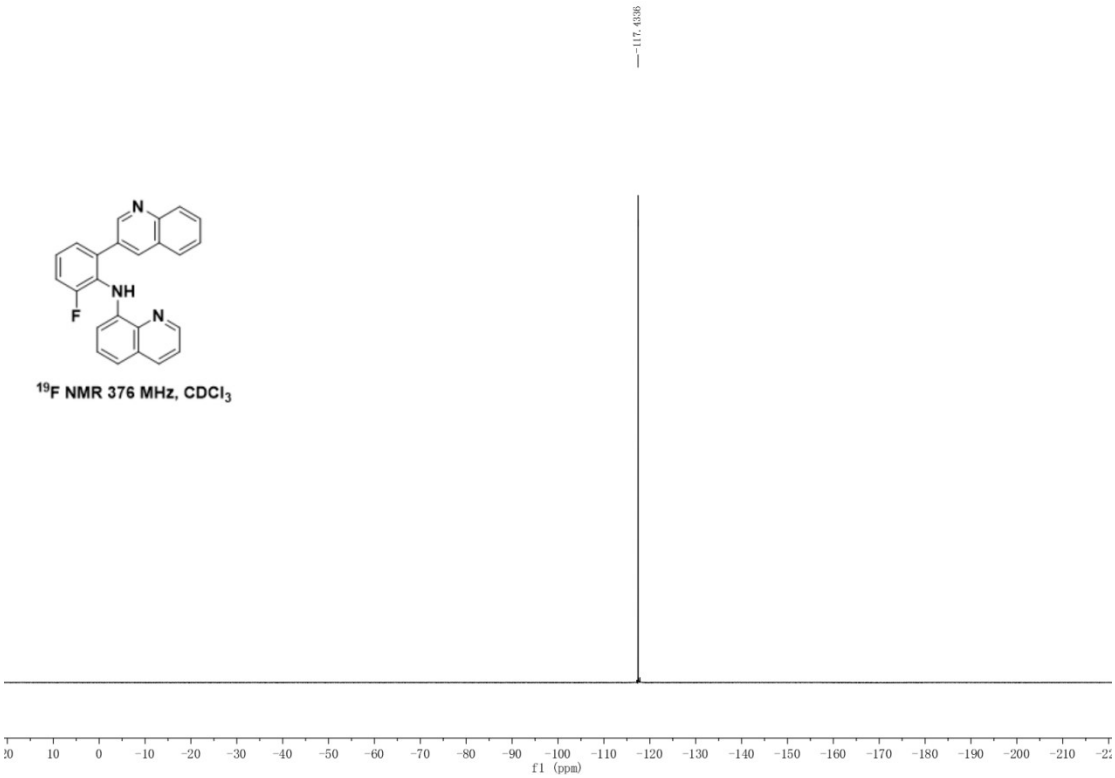


^{1}H NMR 400MHz, $CDCl_3$



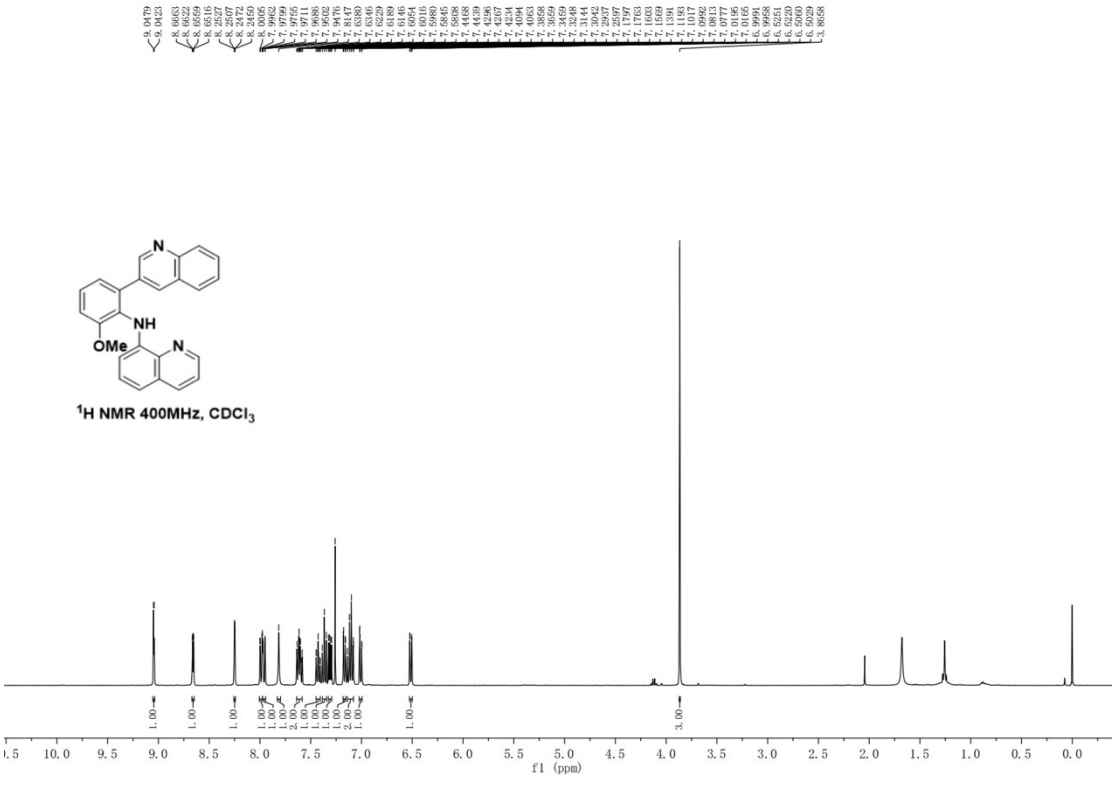


^{13}C NMR 100 MHz, $CDCl_3$

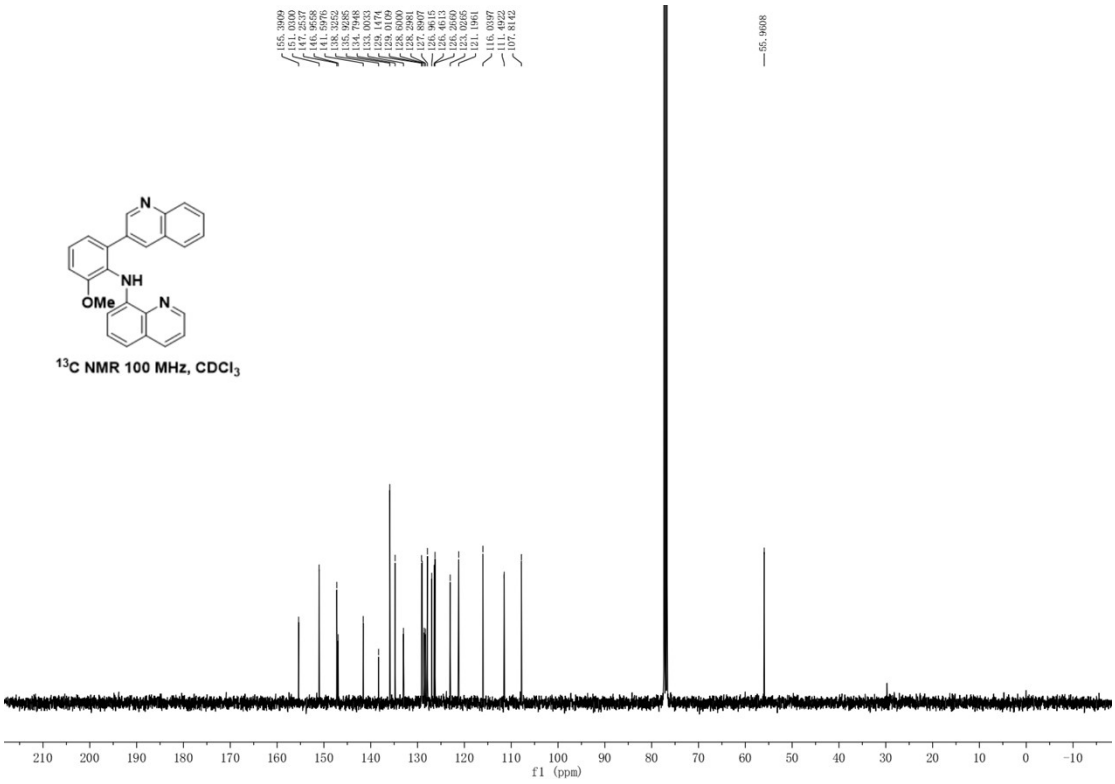


^{19}F NMR 376 MHz, $CDCl_3$

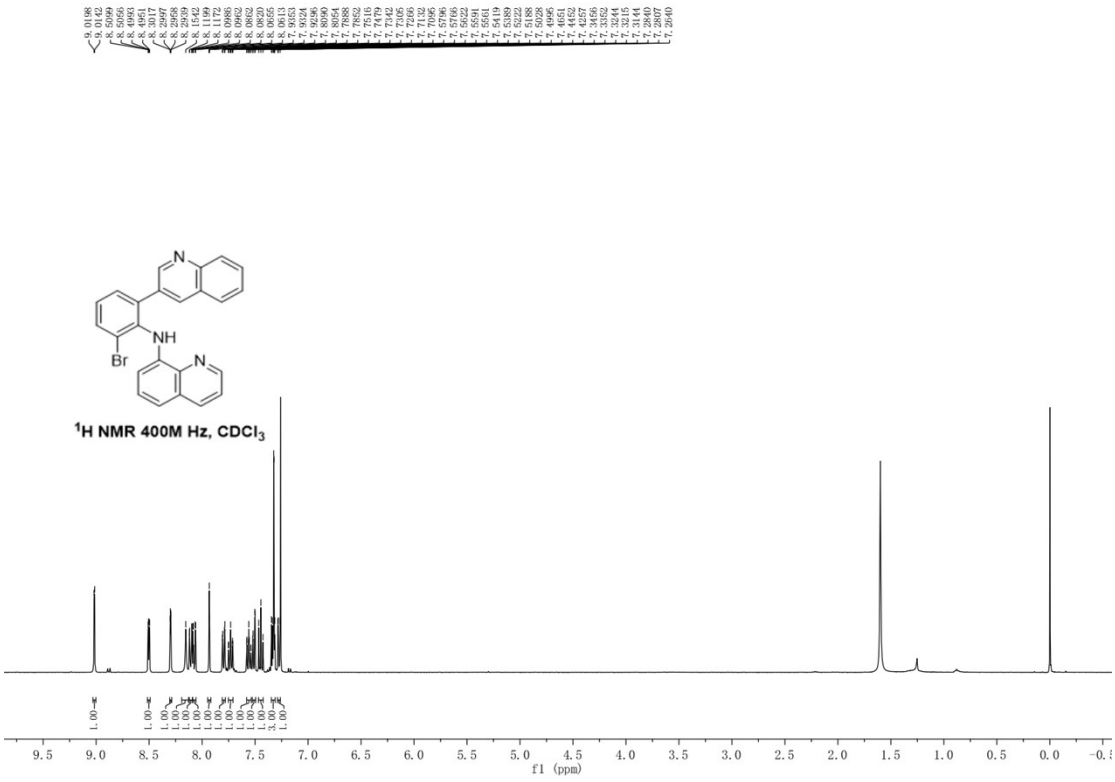
(3k) N-(2-methoxy-6-(quinolin-3-yl)phenyl)quinolin-8-amine

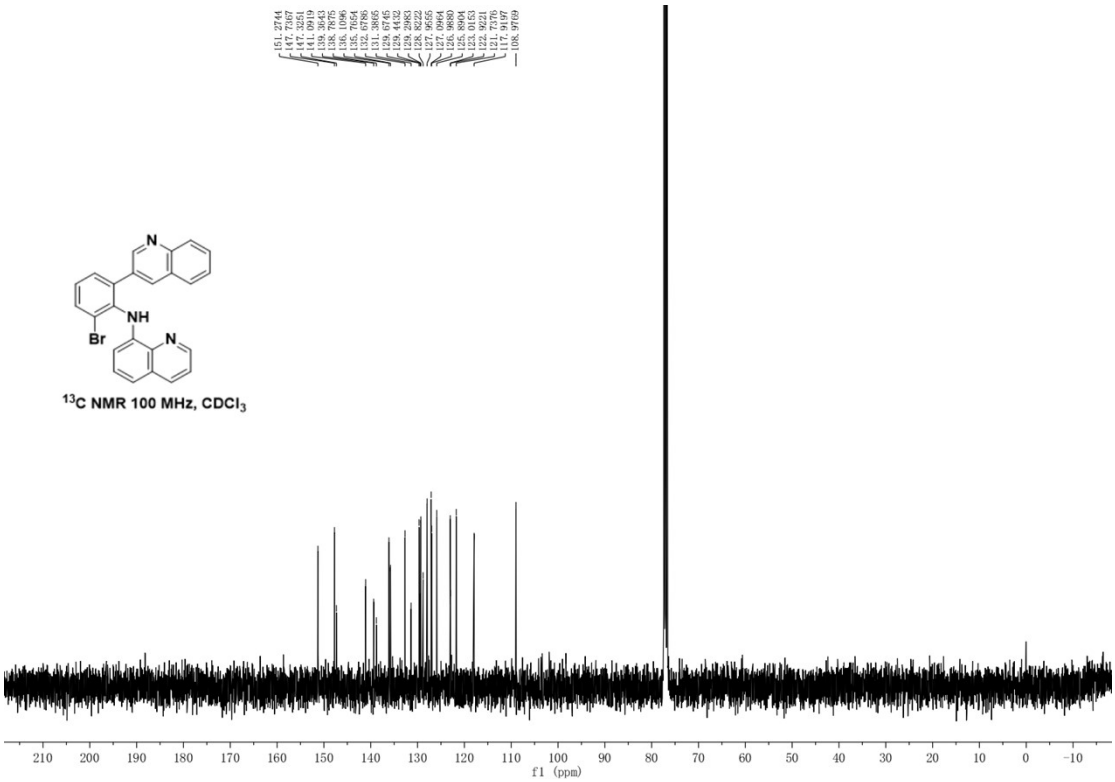


^{1}H NMR 400MHz, $CDCl_3$

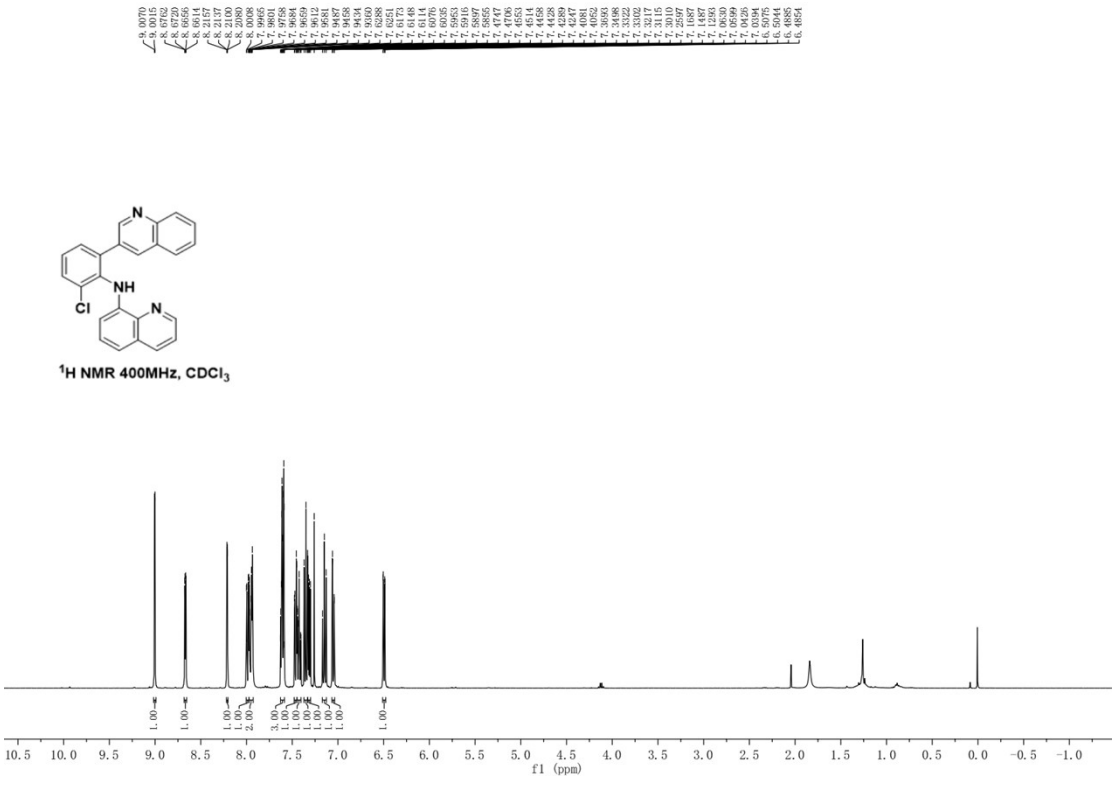


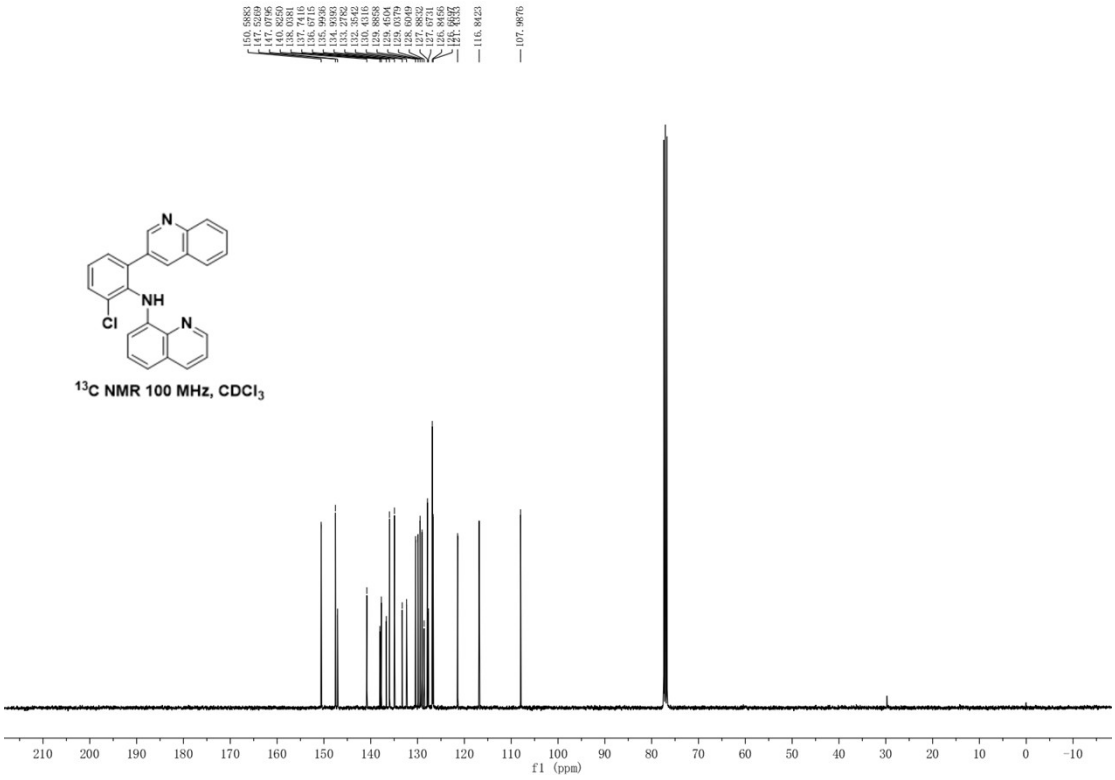
(3l) N-(2-bromo-6-(quinolin-3-yl)phenyl)quinolin-8-amine



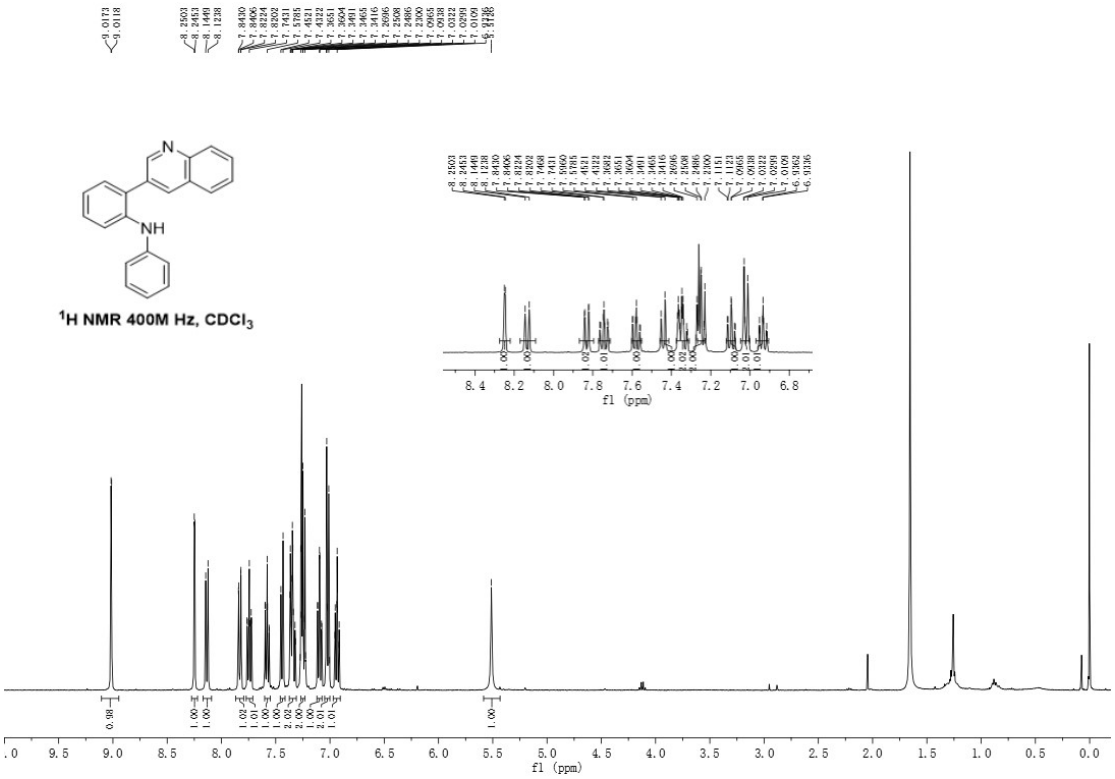


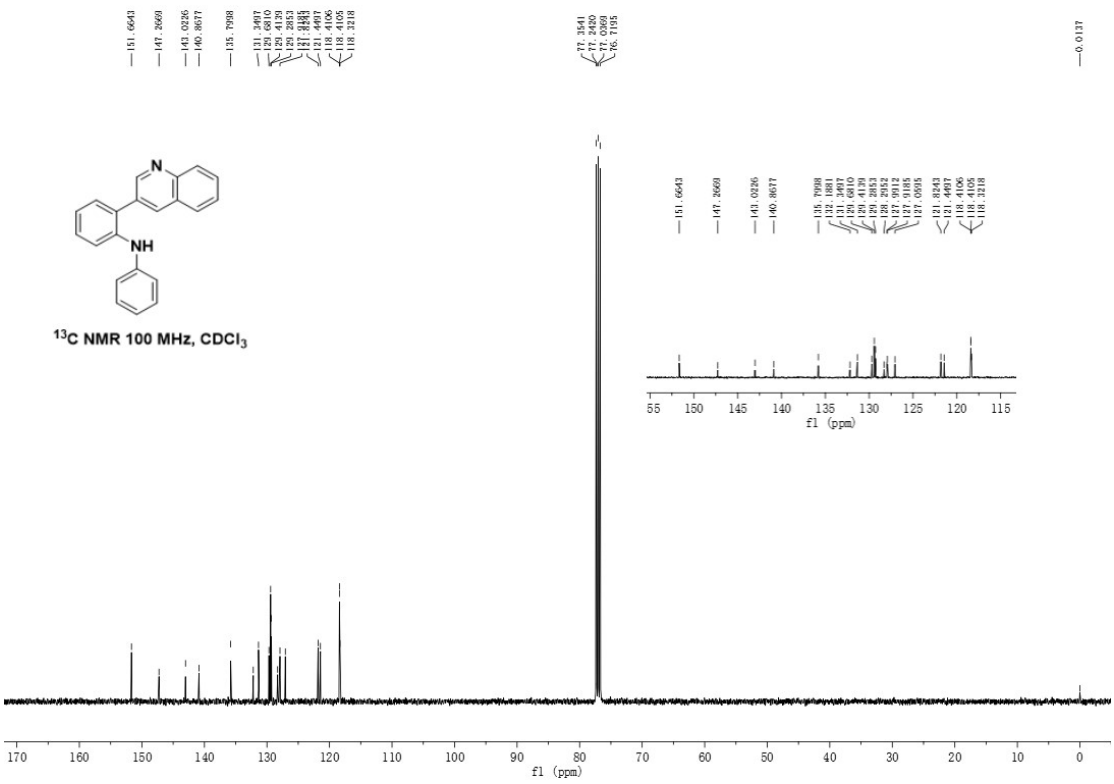
(3m) N-(2-chloro-6-(quinolin-3-yl)phenyl)quinolin-8-amine



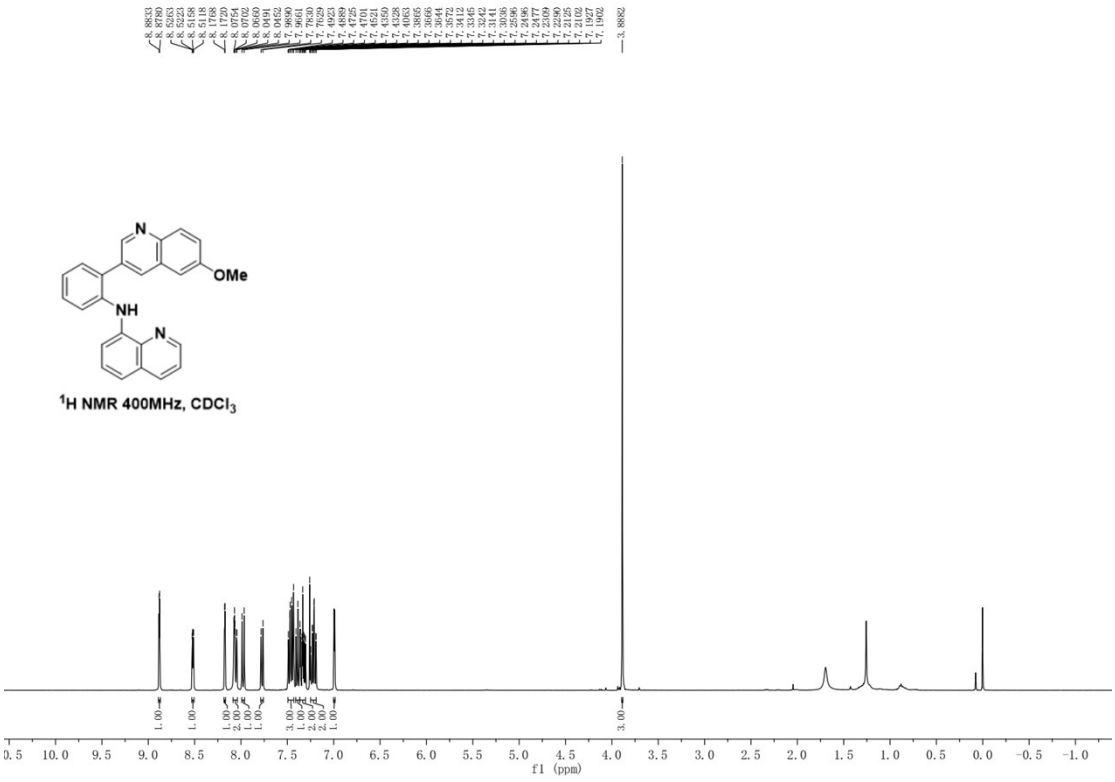


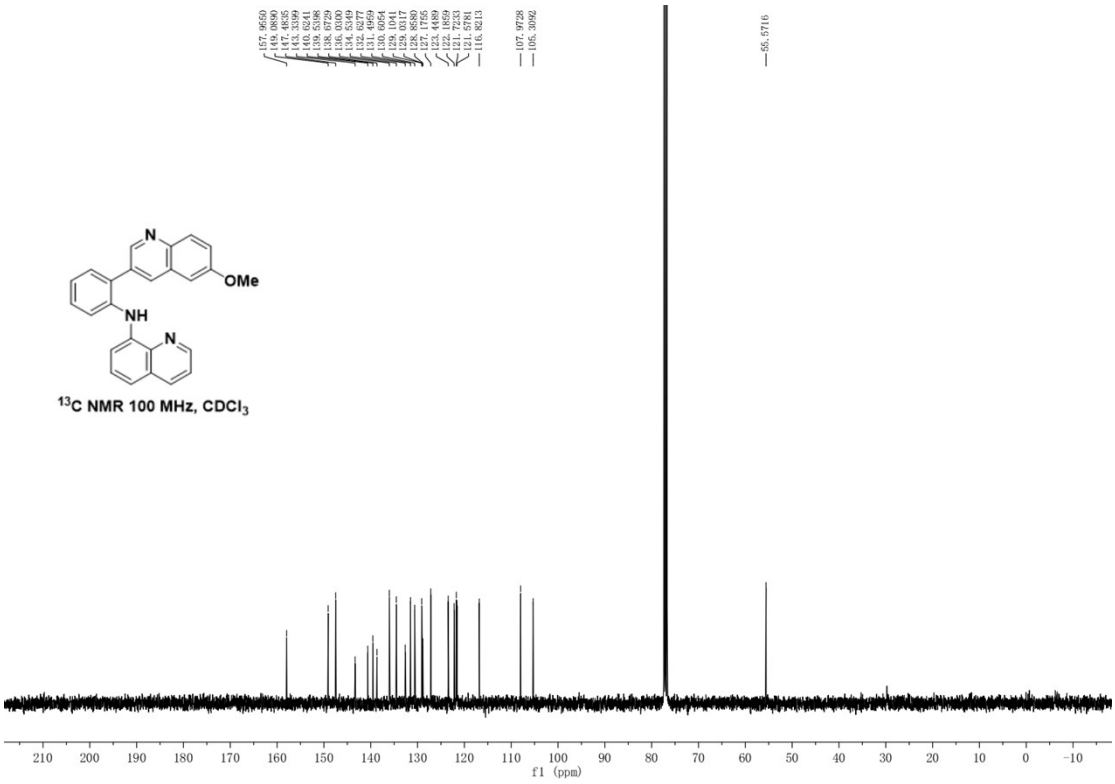
(3q) N-phenyl-2-(quinolin-3-yl)aniline



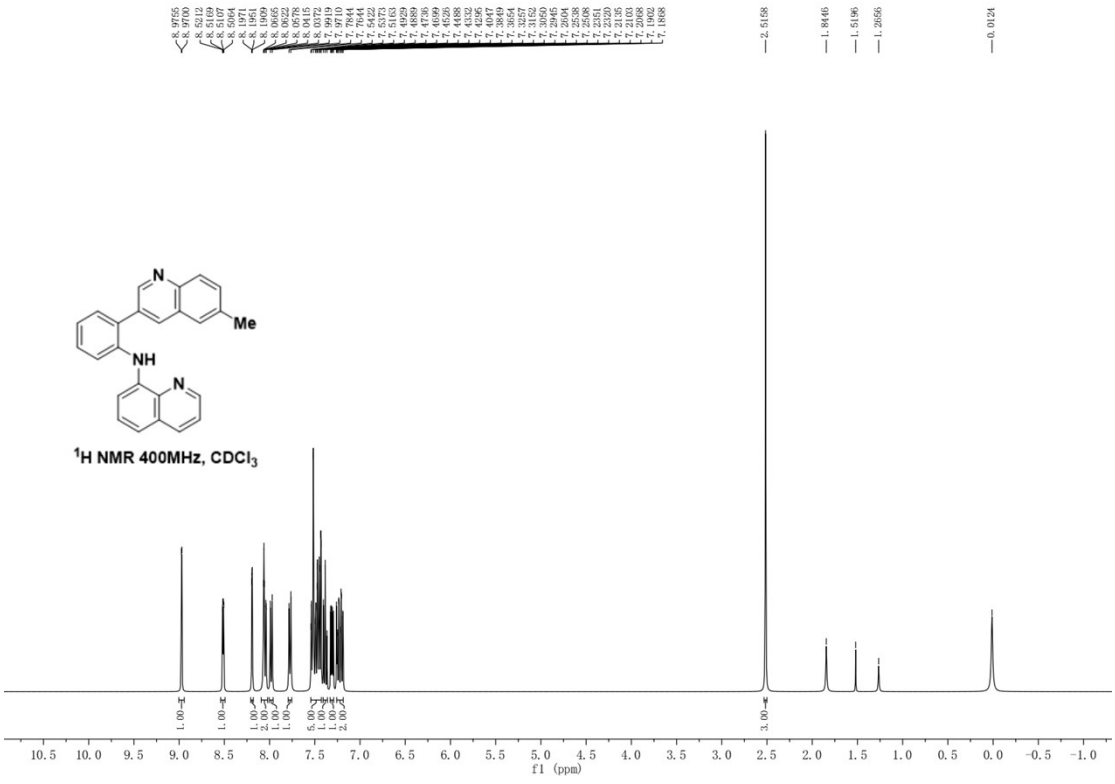


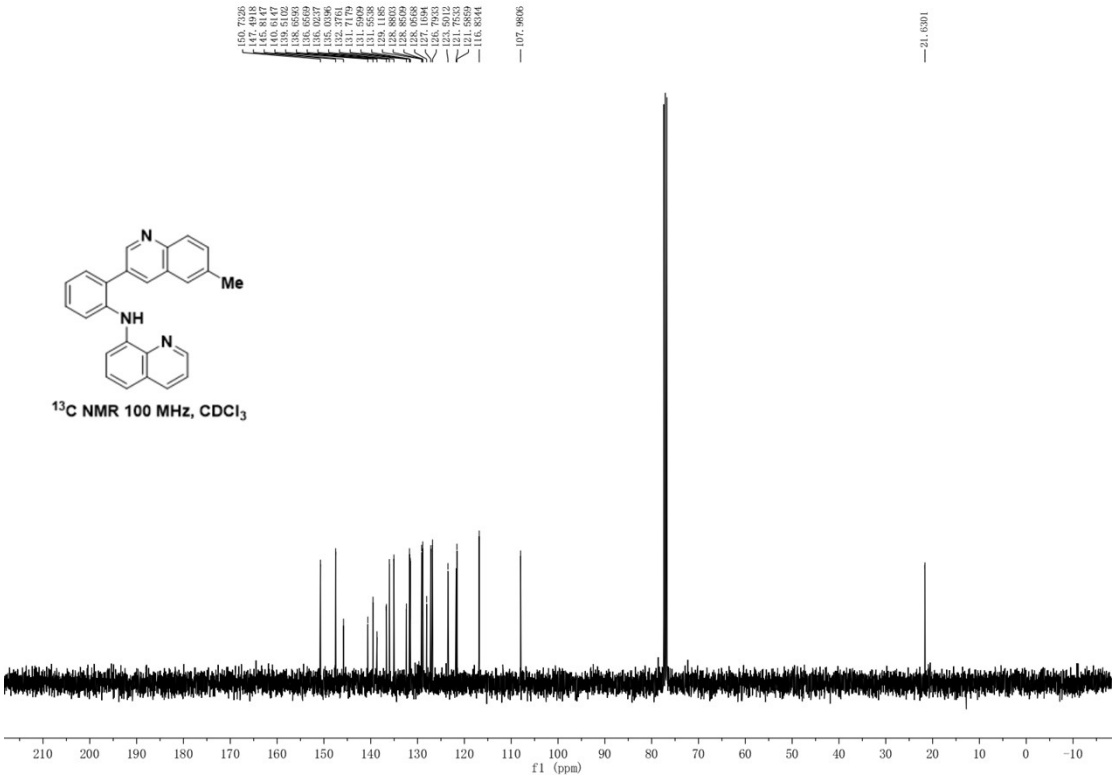
(3r) N-(2-(6-methoxyquinolin-3-yl)phenyl)quinolin-8-amine



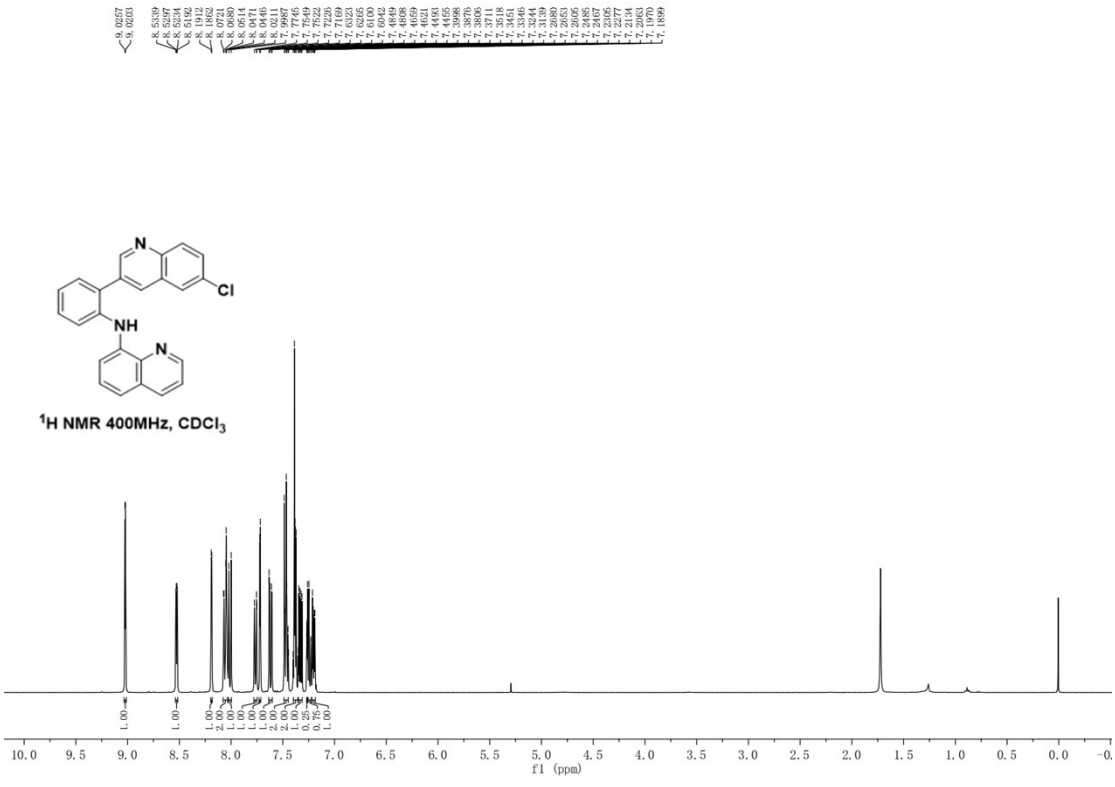


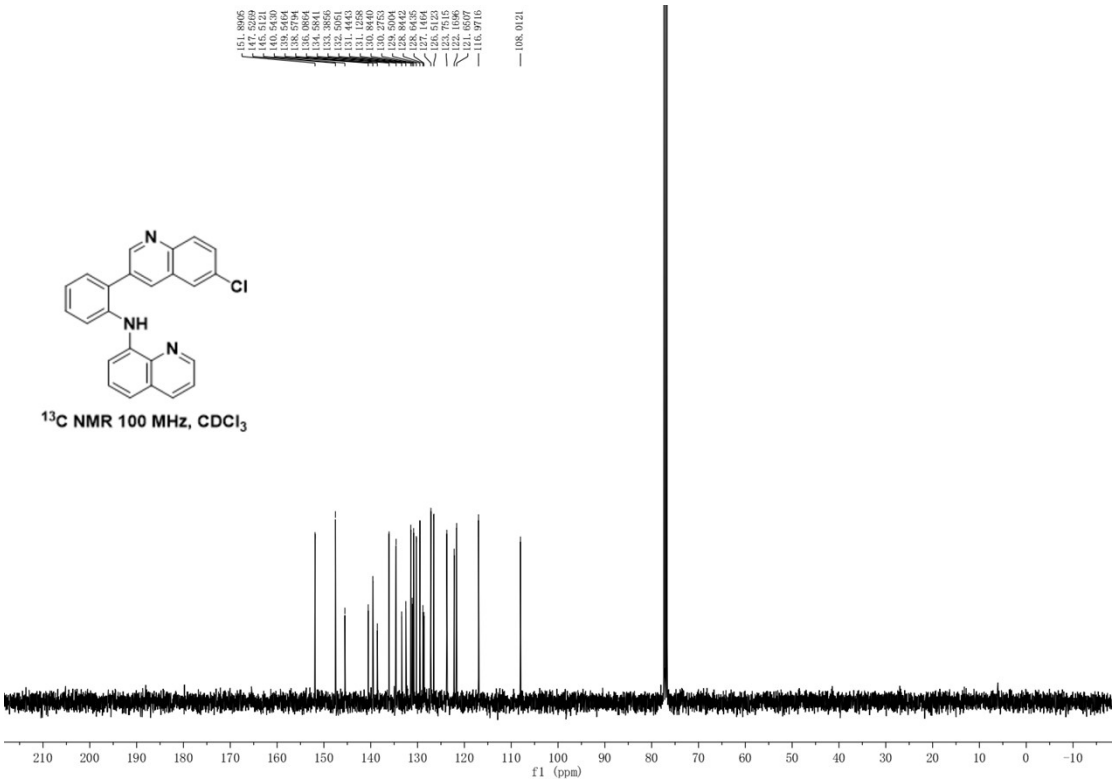
(3s) N-(2-(6-methylquinolin-3-yl)phenyl)quinolin-8-amine



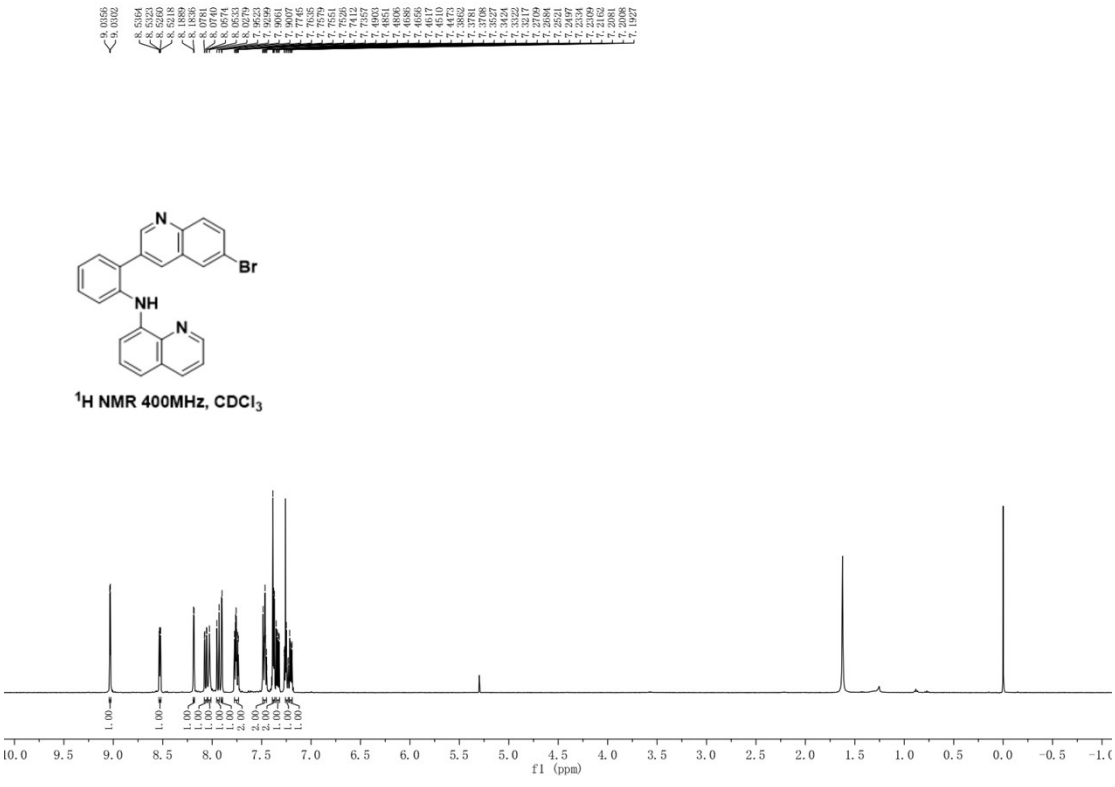


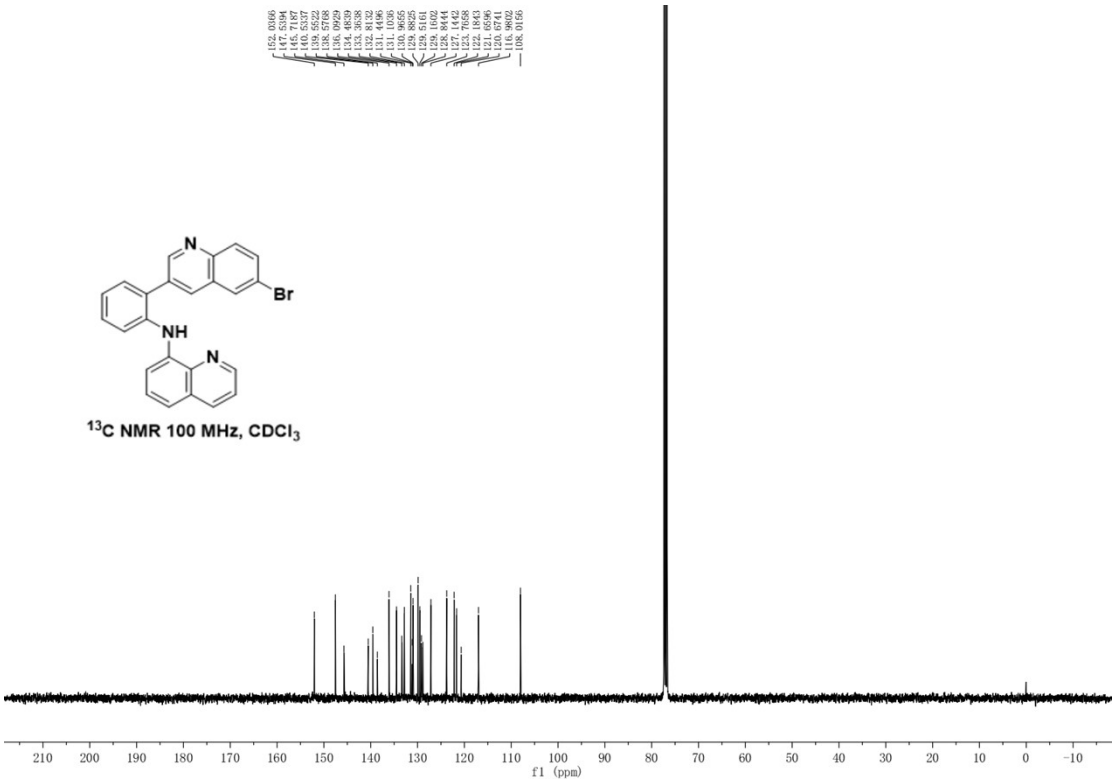
(3t) N-(2-(6-chloroquinolin-3-yl)phenyl)quinolin-8-amine



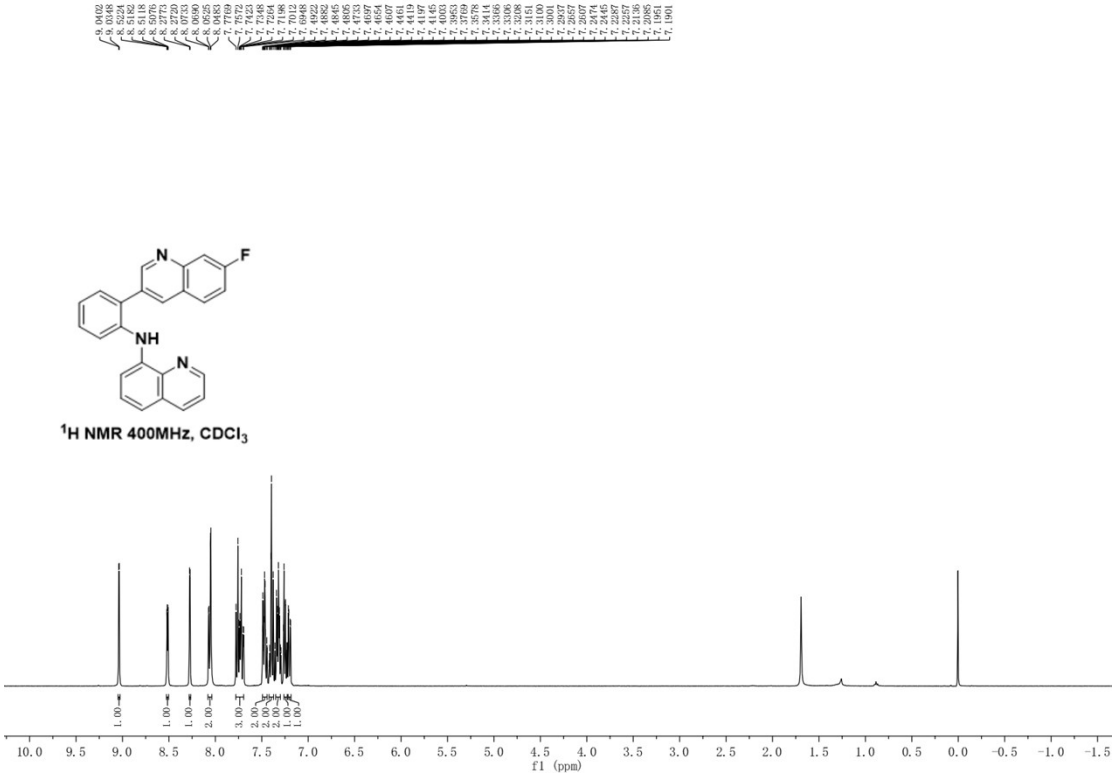


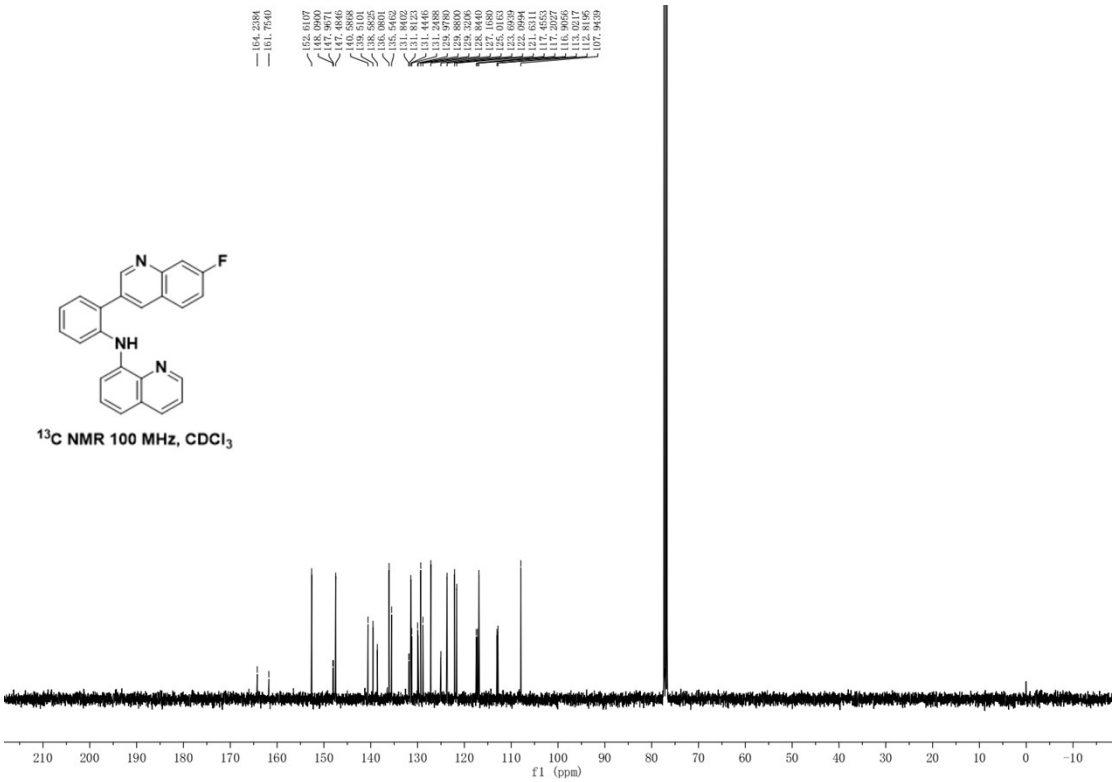
(3u) N-(2-(6-bromo-3,4-dihydroquinolin-3-yl)phenyl)quinolin-8-amine



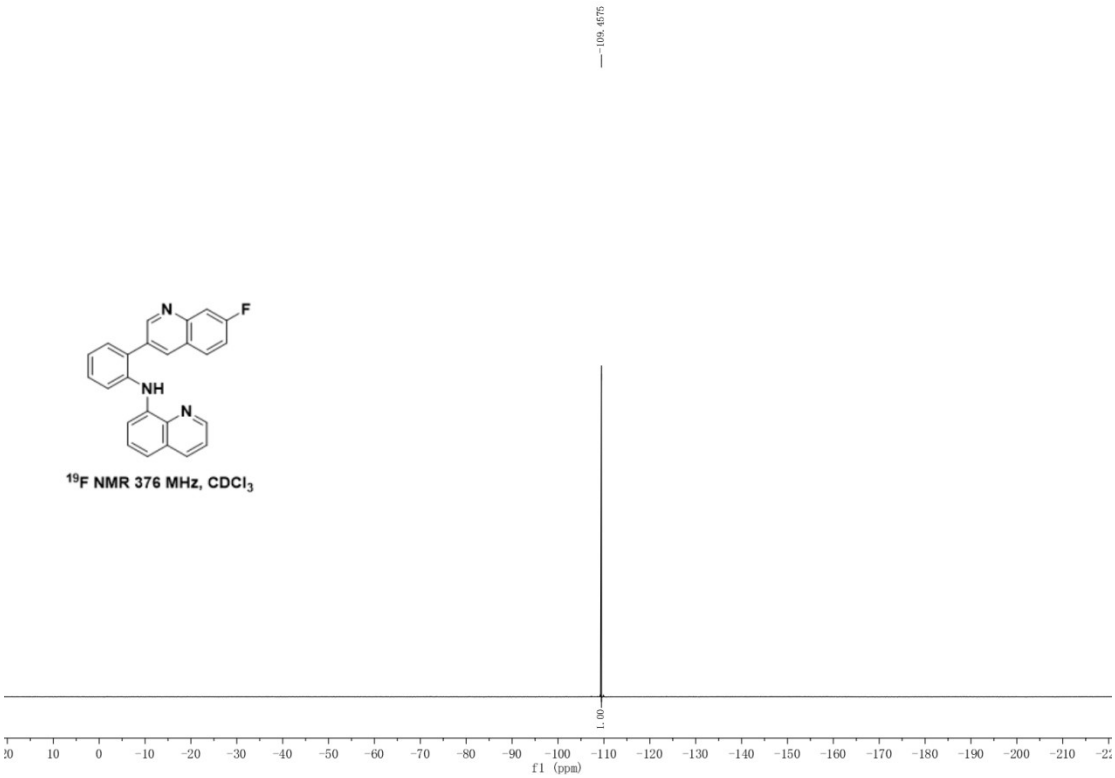


(3v) N-(2-(7-fluoroquinolin-3-yl)phenyl)quinolin-8-amine



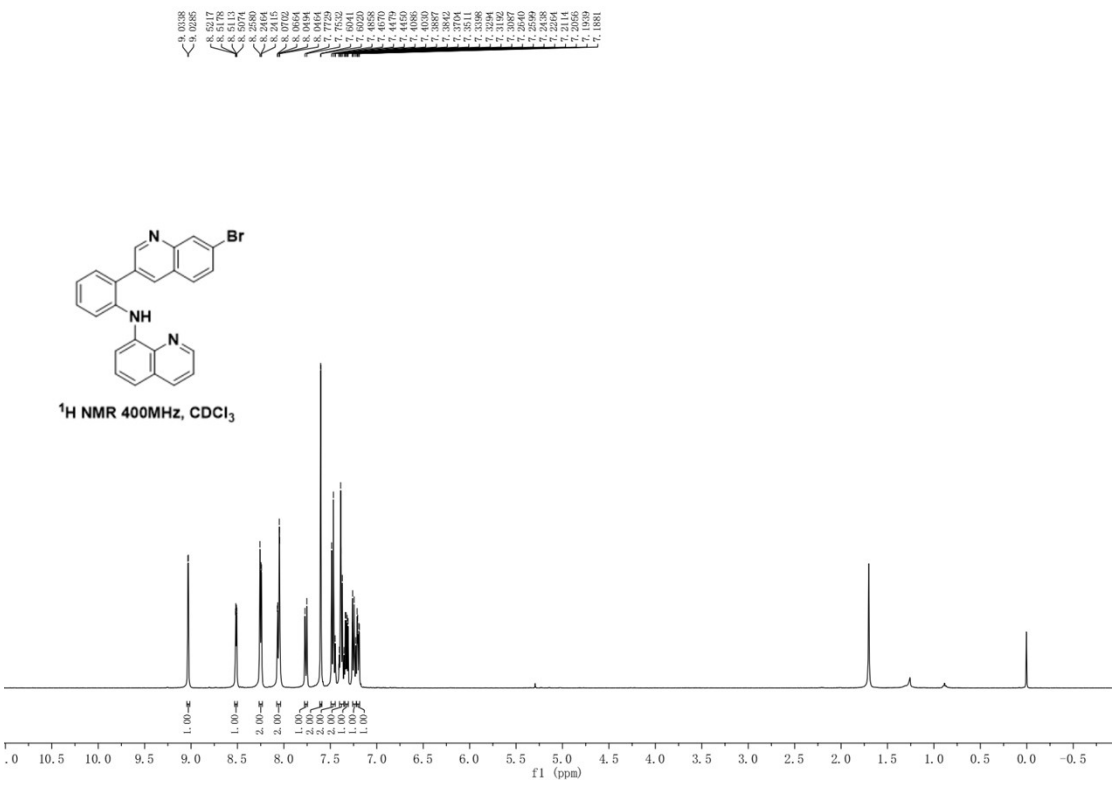


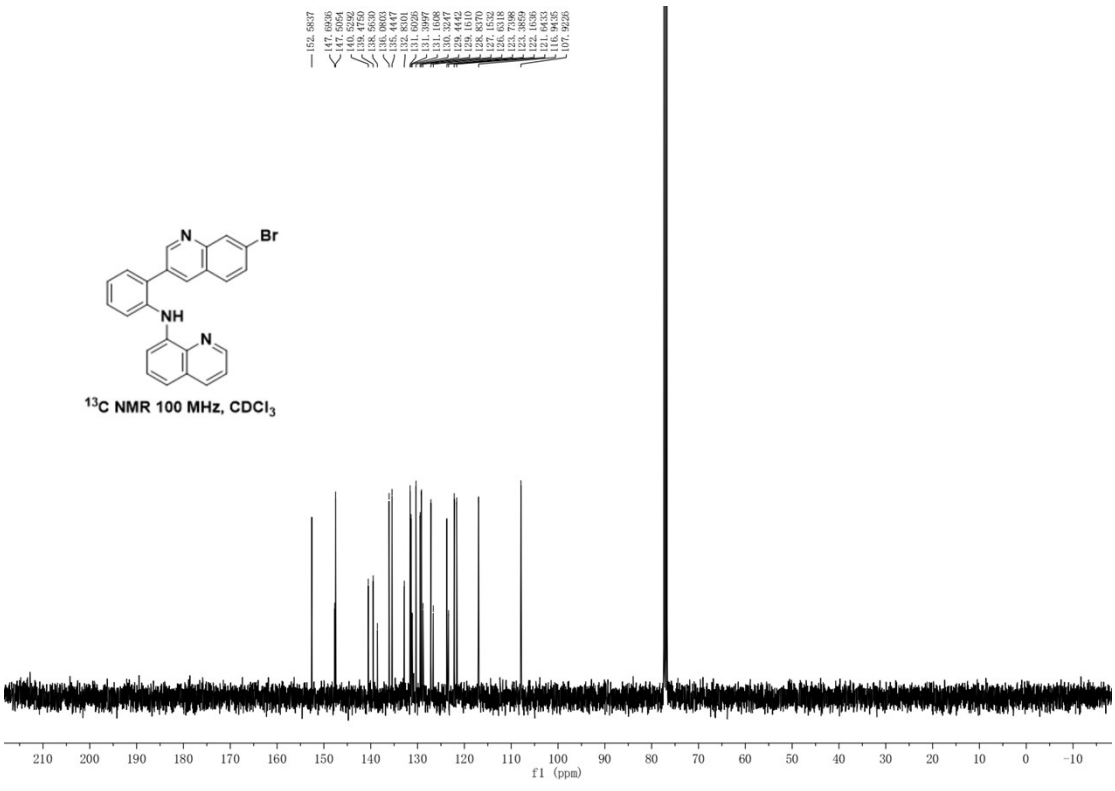
^{13}C NMR 100 MHz, $CDCl_3$



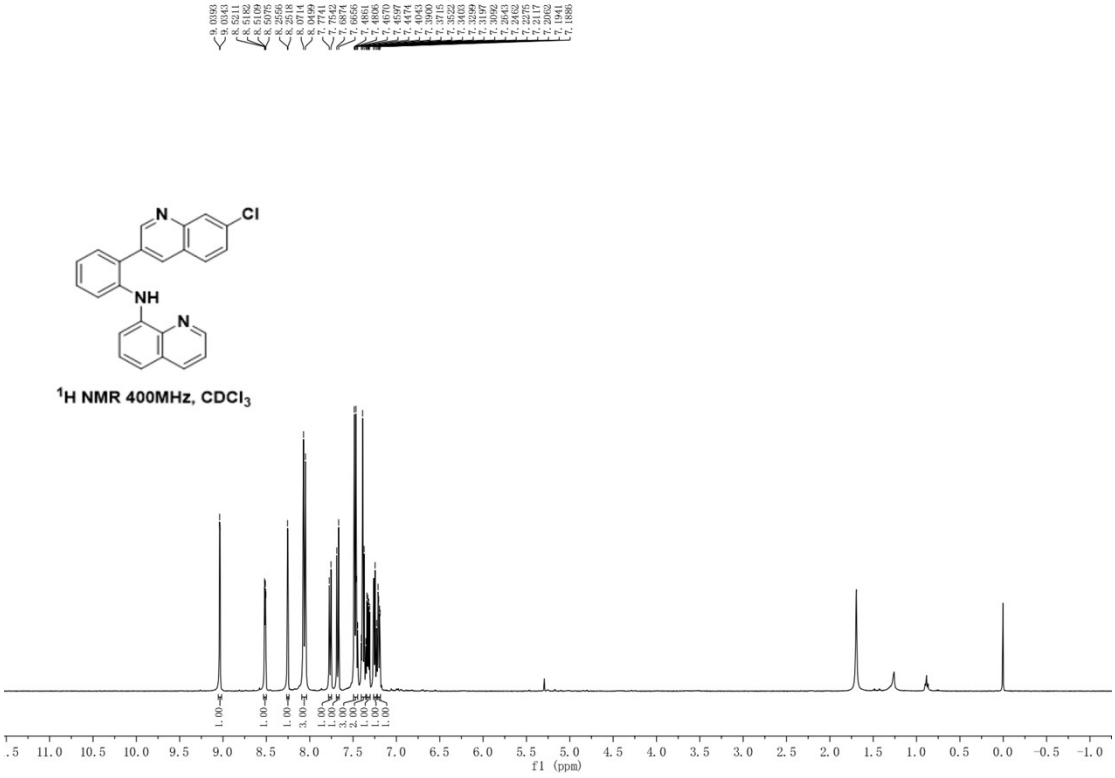
^{19}F NMR 376 MHz, $CDCl_3$

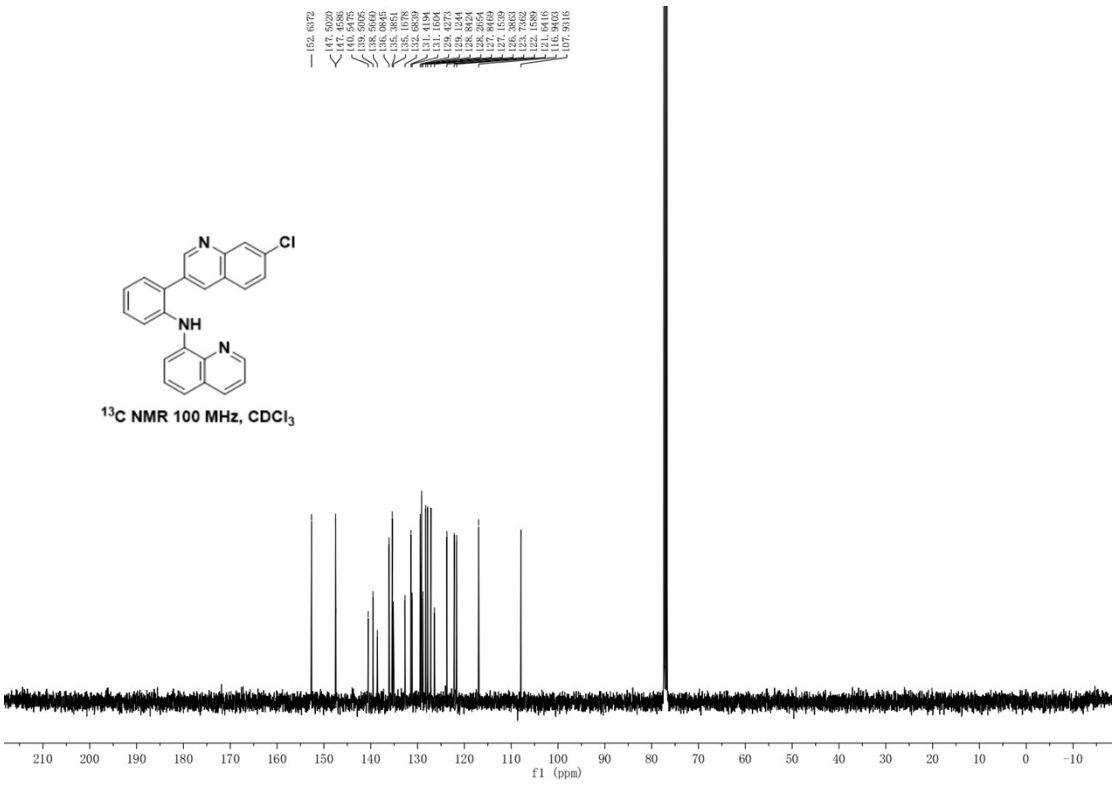
(3w) N-(2-(7-bromoquinolin-3-yl)phenyl)quinolin-8-amine



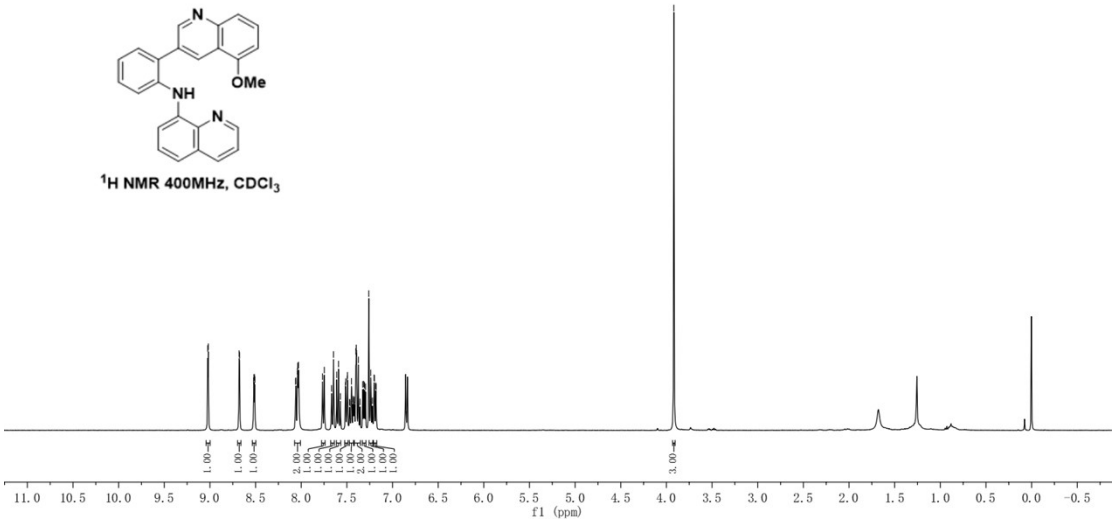


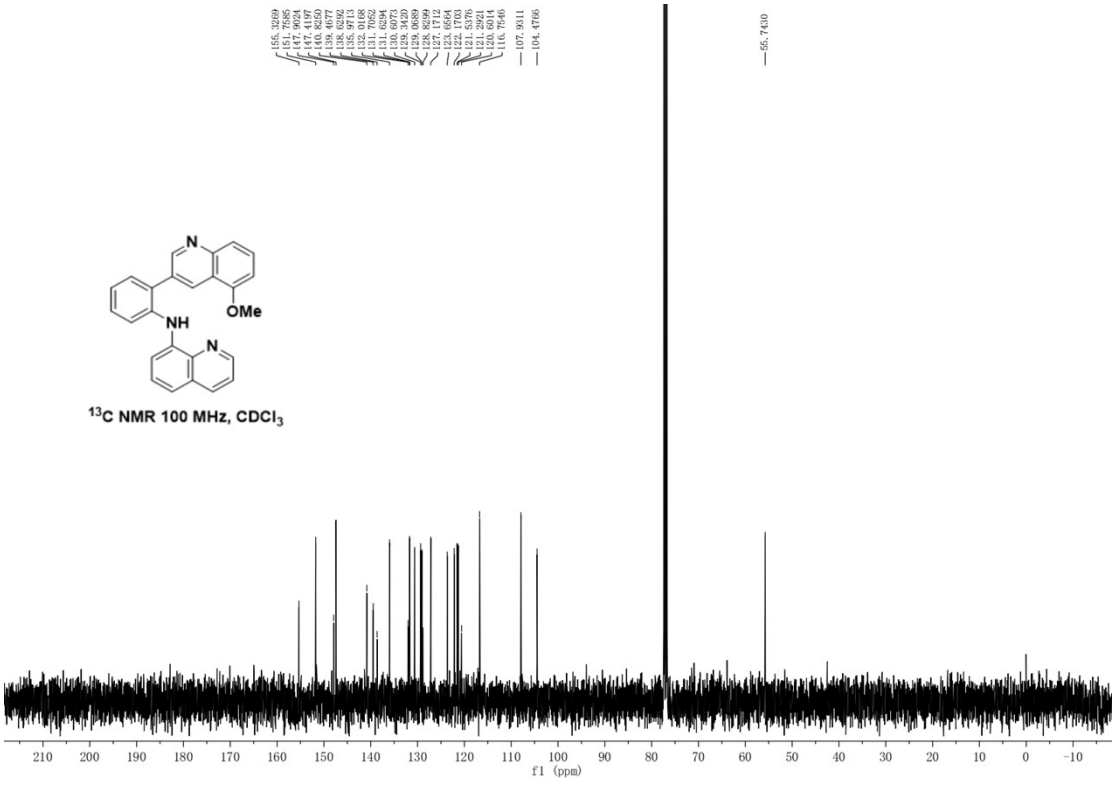
(3x) N-(2-(7-chloroquinolin-3-yl)phenyl)quinolin-8-amine



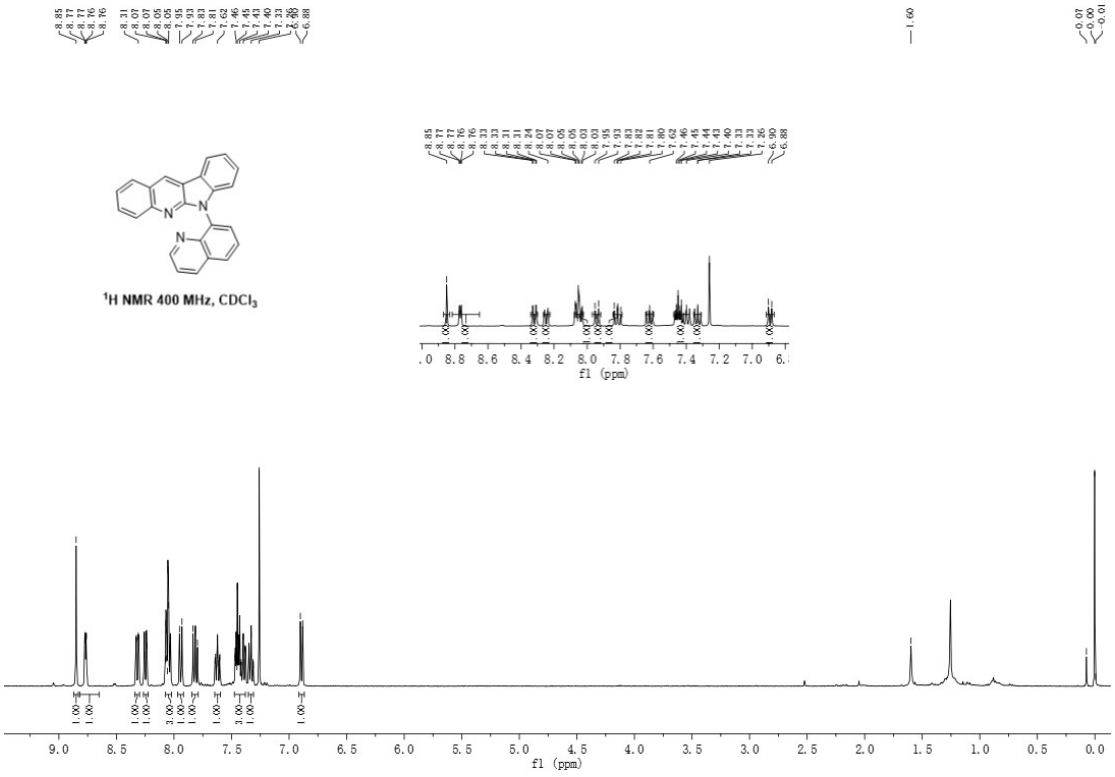


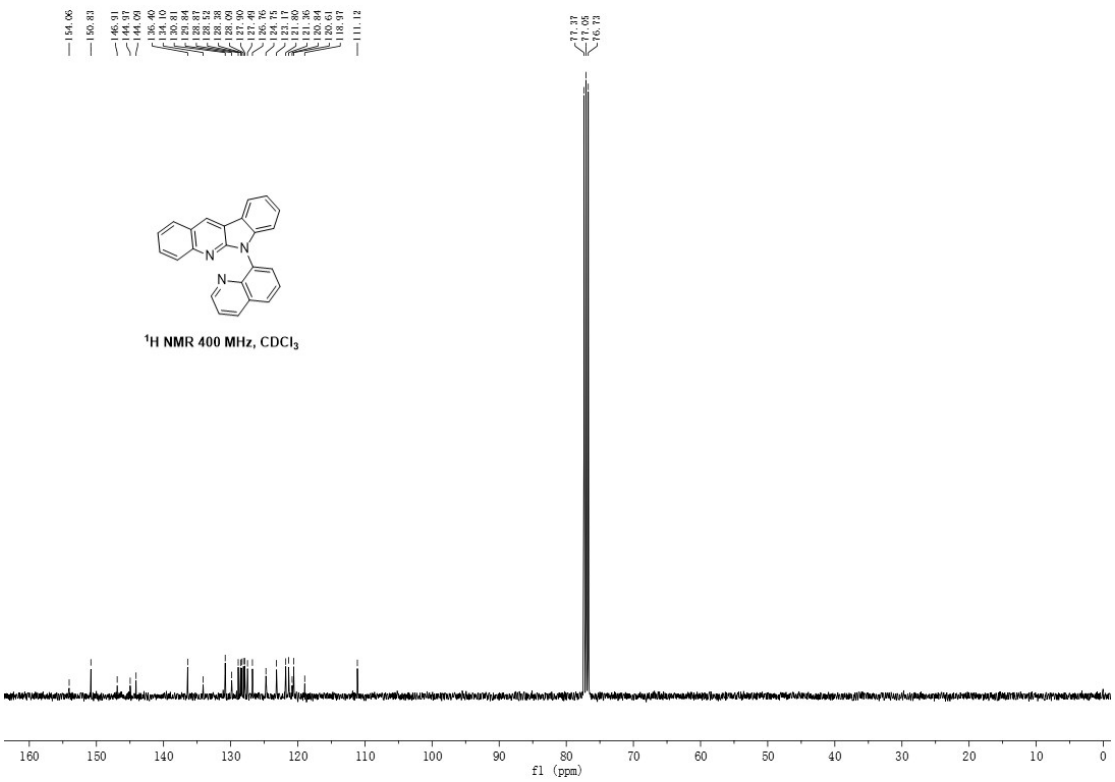
(3y) N-(2-(5-methoxyquinolin-3-yl)phenyl)quinolin-8-amine



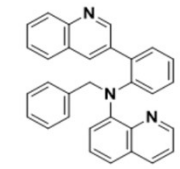


(4) 6-(quinolin-8-yl)-6H-indolo[2,3-b]quinoline

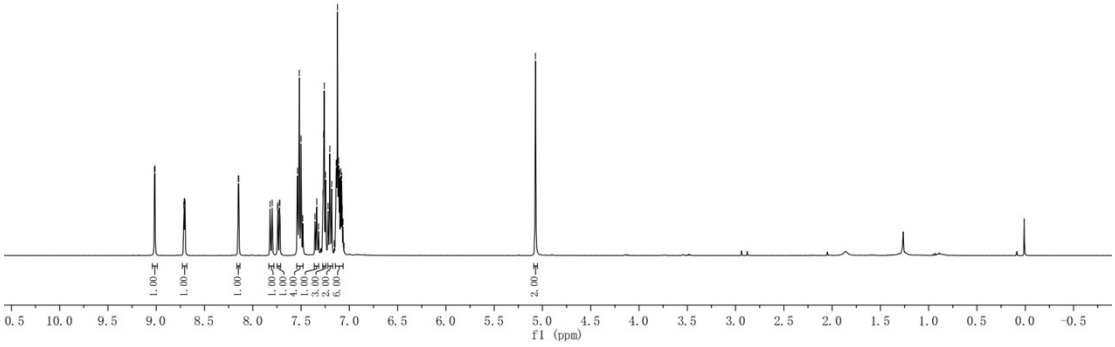


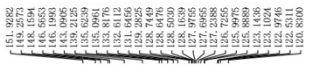


(5) N-benzyl-N-(2-(quinolin-3-yl)phenyl)quinolin-8-amine



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





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