Cobalt-Catalyzed Electrophilic Aminations with Anthranils: An Expendient Route to Condensation Quinolines**

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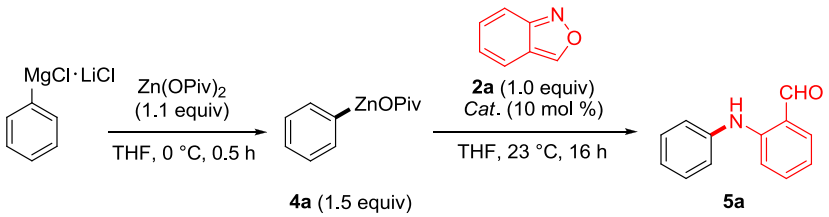
Contents

General Remarks

Unless otherwise indicated, all reactions were carried out with magnetic stirring and in flame-dried glassware under argon. Syringes used to transfer reagents and solvents were purged with N_2 prior to use. The following starting materials were synthesized according to previously described methods: Anthranils **2**.[1] Other chemicals were obtained from commercial sources and were used without further purification. Yields refer to isolated compounds, estimated to be > 95% pure as determined by ^{1}H-NMR and GC-analysis. Reactions were monitored by gas chromatography (GC and GC-MS) or thin layer chromatography (TLC). TLC were performed using aluminum plates covered with SiO_2 (Merck 60, F-254) and visualized by UV detection. Purification *via* column chromatography was performed using Merck silica gel 60 (40–63 mm 230–400 mesh ASTM from Merck). THF was continuously refluxed and freshly distilled from sodium benzophenone ketyl under nitrogen. Melting points were measured using a Büchi B-540 apparatus and are uncorrected. NMR spectra were recorded in $CDCl_3$ and chemical shifts (δ) are reported in parts per million (ppm). Mass spectra and highresolution mass spectra (HR-MS) were recorded using electro ionization (EI) except where otherwise noted. GCs were recorded on machines of the type Hewlett-Packard 6890 (Hewlett Packard, 5% phenylmethylpolysiloxane; length: 15 m, diameter: 0.25 mm; film thickness: 0.25 μm).

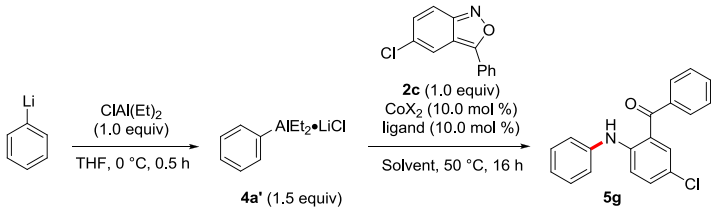
Table S1. Optimization for cobalt-catalyzed amination using anthranils (2a).[a]



entry	[met] (10 mol %)	yield (%)[b]
1	$CoCl_2$	65
2	$MnCl_2$	0
3	$CrCl_2$	0
4	$FeCl_2$	0
5	$Fe(acac)_3$	0
6	--	0
7	$CoCl_2$	0[c]

[a] Reaction conditions: **4a** (0.75 mmol), **2a** (0.50 mmol), [Cat.] (10 mol %), THF (2.0 mL), 23 °C, N_2, 16 h. [b] Isolated yields. [c] PhMgCl (1.5 equiv) instead of PhZnOPiv.

Table S2. Optimization for cobalt-catalyzed amination using organoaluminun reagents.

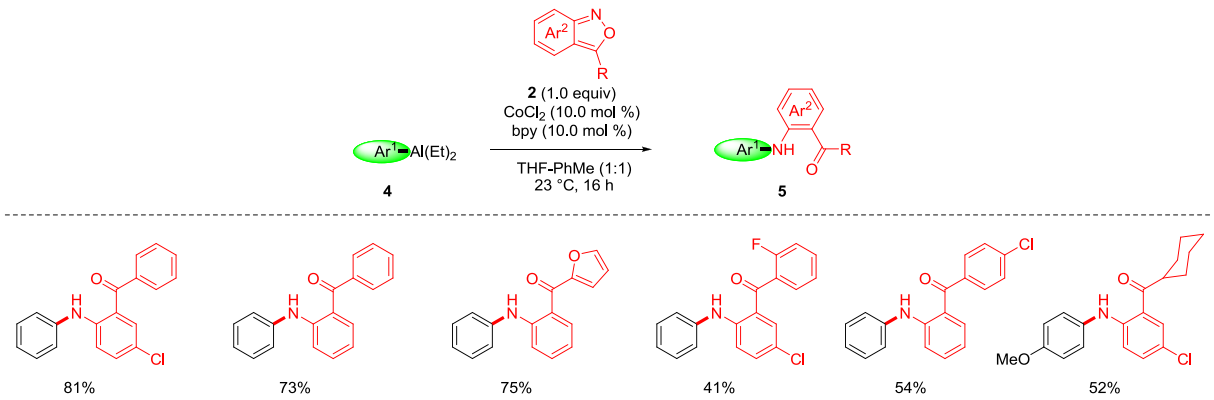


entry	[Co]	ligand (10 mol %)	solvent	yield (%)[b]
1	$CoBr_2$	--	THF-Tol (1:1)	36
2	$CoBr_2$	bpy	THF-Tol (1:1)	75
3	$CoBr_2$	bpy	THF-Tol (1:1)	14 (25 °C)
4	$CoBr_2$	Xantphos	THF-Tol (1:1)	46
5	$CoBr_2$	dppbz	THF-Tol (1:1)	57
6	$CoBr_2$	IMesHCl	THF-Tol (1:1)	54
7	$CoBr_2$	IMesHCl	MeCN-Tol (1:1)	21
8	$CoBr_2$	dttbpy	THF-Tol (1:1)	74
9	$CoCl_2$	bpy	THF-Tol (1:1)	77
10	**$Co(acac)_2$**	**bpy**	**THF-Tol (1:1)**	**81**
11	--	bpy	THF-Tol (1:1)	0
12	$Co(acac)_2$	bpy	THF-Tol (1:1)	34 (40 °C)
13	$Co(acac)_2$	bpy	THF	53
14	$Co(acac)_2$	bpy	THF	51[c]
15	$Co(acac)_2$	bpy	THF	12[d]
16	$CoBr_2$bpy	--	THF-Tol (1:1)	56
17	$Co(acac)_2$	bpy	THF-Tol (1:1)	0[e]
18	$Co(acac)_2$	bpy	THF-Tol (1:1)	23[f]

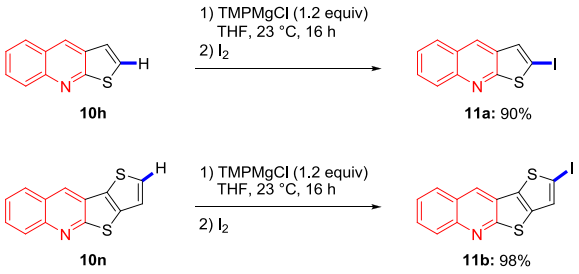
[c]: 5.0 mol % of [Co] and bpy were used. [d]: **1a** was prepared from PhMgCl•LiCl. [e]: 1.5 equiv of $PhAlCl_2$ was used. [f]: 1.5 equiv of PhAlEtCl was used.

Additional Experiments:

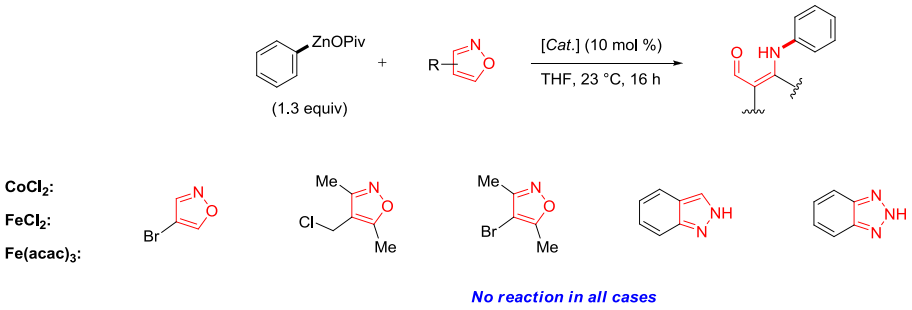
a) Cobalt-catalyzed electrophilic amination using $ArAl(Et)_2$•LiCl:



b) Selective C–H metalation by TMPMgCl:



c) Other aminating reagents:



Representative Procedures

Preparation of $Zn(OPiv)_2$:

Pivalic acid (20.4 g, 22.6 mL, 200 mmol) was placed in a dry and argon-flushed 500 mL three-necked roundbottom flask, equipped with a magnetic stirring bar, a septum and a pressure equalizer, and was dissolved in dry THF (120 mL). The mixture was cooled to 0 °C, and a solution of Et_2Zn (13.0 g, 10.8 mL, 105 mmol) in dry THF (120 mL) was added over a period of 30 min under vigorous stirring. Then, the ice-bath was removed and stirring was continued at 25 °C for one additional hour at which point bubbling was ceased (a thick slurry was formed). The solvent was removed *in vacuo* and the solid residue was dried for at least 4 h longer. $Zn(OPiv)_2$ was obtained in quantitative yield, as a puffy amorphous white solid.

Typical procedure 1 (TP1) for the preparation of organozinc pivalates:

LiCl (1.5 equiv) was dried under high vacuum and allowed to cool to room temperature, then Mg turnings (1.2 equiv) and THF (1 M solution relating to the aryl bromide) were added. The reaction mixture was cooled to 0 °C and the corresponding aryl bromide (1.0 equiv) was then added. The reaction was stirred at room temperature until iodolysis and protolysis of a reaction aliquot indicated full consumption of the starting material. $Zn(OPiv)_2$ (1.1 equiv) is then added to afford a solution of the corresponding zinc reagent.

Typical procedure 2 (TP2) for the preparation of organozinc pivalates:

TMPMgCl·LiCl (1.1 equiv, 1.2 M) is added dropwise to a solution of aromatic substrate in THF at the indicated temperature. The reaction was stirred until iodolysis of a reaction aliquot indicated full consumption of the starting material. $Zn(OPiv)_2$ (1.1 equiv) is then added to afford a solution of the corresponding zinc reagent.

Typical procedure 3 (TP3) for the preparation of organozinc pivalates:

TMPZnCl·$Mg(OPiv)_2$·LiCl (1.1 equiv, 1.2 M) is added dropwise to a solution of aromatic substrate in THF at the indicated temperature. The reaction mixture was stirred until iodolysis of a reaction aliquot indicated full consumption of the starting material.

Typical procedure 4 (TP4) for the preparation of organozinc pivalates:

$Zn(OPiv)_2$ (1.1 equiv) is added to a solution of the corresponding commercial Grignard

reagent.

Typical procedure 5 (TP5) for the preparation of organozinc pivalates:

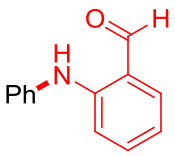
i-PrMgCl.LiCl (1.1 equiv, 1.267 M) was added dropwise to a 1.0 M solution of aryl bromide in THF. The reaction was stirred until iodolysis and protolysis of a reaction aliquot indicated full consumption of the starting material. $Zn(OPiv)_2$ (1.1 equiv) is then added to afford a solution of the corresponding zinc reagent.

Typical procedure 6 (TP6) for the preparation of alkenylzinc pivalates:

Mg turnings (1.2 equiv), catalytic amount of I_2 (10 mol %), THF (1.0 M solution relating to the alkenyl bromide) and the corresponding alkenyl bromide (1.0 equiv) were added. The reaction mixture was refluxed at 80 ℃ for 3–6 h. The reaction was stirred until protolysis of a reaction aliquot indicated full consumption of the starting material. $Zn(OPiv)_2$ (1.1 equiv) is then added to afford a solution of the corresponding zinc reagent.

Typical procedure 7 (TP7) for the cobalt-catalyzed electrophilic amination of organozinc pivalate with anthranil derivatives:

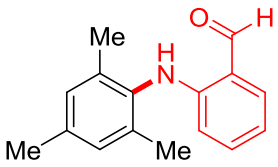
Organozinc pivalates (0.45 mmol, 1.5 equiv) prepared from (**TP1-TP6**) is added to a solution of anthranil **2** (0.3 mmol, 1.0 equiv) and $CoCl_2$ (2.6 mg, 10 mol %) in THF (1.5 mL). The reaction mixture is stirred for 16 h at room temperature. The reaction mixture was quenched with water (2 drops), diluted with ethyl acetate and concentrated under vacuo. The residue was purified by column chromatography using a gradient of 100% *iso*-hexane to 100% ethyl acetate as eluent to yield the title compound.



2-(Phenylamino)benzaldehyde (5a)[2]

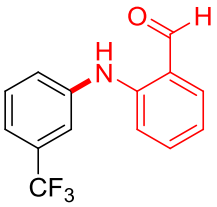
The general procedure **TP7** was followed using benzo[*c*]isoxazole (60 mg, 0.5 mmol) and oxo(phenyl)(pivaloyl)zinc **(**prepared from **TP4**, 0.75 mmol) for 16 h. Purification by column chromatography (*n*-hexane/EtOAc 15:1) yielded **5a** (64 mg, 65%) as a white solid. **M.p.**: 74–76 ℃. **^{1}H-NMR (400 MHz, $CDCl_3$)** δ = 9.94 (s, 1H), 9.83 (s, 1H), 7.49 (dd, *J* = 7.8, 1.8 Hz, 1H), 7.29 (qd, *J* = 8.2, 7.3, 1.8 Hz, 3H), 7.23 – 7.13 (m, 3H), 7.07 (td, *J* = 7.3, 1.3 Hz, 1H), 6.78 – 6.72 (m, 1H). **^{13}C-NMR (100 MHz, $CDCl_3$)** δ = 194.3, 147.8, 139.7, 136.6, 135.6,

129.4, 124.4, 123.2, 119.4, 117.1, 112.9. **IR (Diamond-ATR, neat):** ν / cm = 3279, 2921, 2848, 2835, 2755, 1648, 1589, 1570, 1518, 1492, 1450, 1422, 1397, 1321, 1314, 1245, 1199, 1184, 1154, 1117, 1079, 1041, 1028, 1004, 1004, 940, 898, 821, 808, 750, 697, 662. **MS (EI, 70 eV):** m/z (%) = 197 (41), 196 (51), 179 (57), 178 (17), 169 (13), 168 (100), 167 (47). **HR-MS (EI, 70 eV)** : [$C_{13}H_{10}ON$], [M-H], calcd.: 197.0841; found: 197.0757.



2-(Mesitylamino)benzaldehyde (5b)

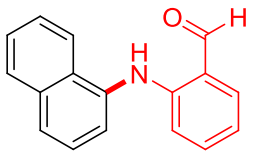
The general procedure **TP7** was followed using benzo[*c*]isoxazole (36 mg, 0.3 mmol) and mesityl(oxo)(pivaloyl)zinc (prepared from **TP1**, 0.45 mmol) for 16 h. Purification by column chromatography (*n*-hexane/EtOAc 15:1) yielded **5b** (51 mg, 71%) as a white solid. **M.p.**: 54–56 °C. **^{1}H-NMR (400 MHz, $CDCl_3$)** δ = 9.99 (s, 1H), 9.53 (s, 1H), 7.58 (dd, *J* = 7.8, 1.7 Hz, 1H), 7.28 (ddd, *J* = 8.6, 7.0, 1.7 Hz, 1H), 7.00 (s, 2H), 6.76 (ddd, *J* = 7.8, 7.1, 1.0 Hz, 1H), 6.27 (d, *J* = 8.6 Hz, 1H), 2.36 (s, 3H), 2.18 (s, 6H). **^{13}C-NMR (100 MHz, $CDCl_3$)** δ = 194.3, 149.9, 136.6, 136.4, 136.3, 135.7, 133.6, 129.2, 118.3, 115.8, 112.3, 21.0, 18.2. **IR (Diamond-ATR, neat):** ν / cm = 3293, 2914, 2853, 2815, 2745, 1654, 1650, 1602, 1566, 1495, 1454, 1395, 1372, 1331, 1322, 1303, 1236, 1216, 1201, 1186, 1154, 1115, 1034, 1011, 888, 854, 800, 750, 712, 658. **MS (EI, 70 eV):** m/z (%) = 240 (17), 239 (100), 238 (19), 224 (42), 222 (15), 211 (10), 210 (34), 209 (10), 208 (18), 196 (51), 195 (17), 194 (27), 193 (11), 181 (42), 180 (32), 179 (11), 134 (16), 120 (11), 119 (33), 91 (12). **HR-MS (EI, 70 eV)** : [$C_{16}H_{17}NO$], calcd: 265.0714; found: 265.0704.



2-{[3-(Trifluoromethyl)phenyl]amino}benzaldehyde (5c)

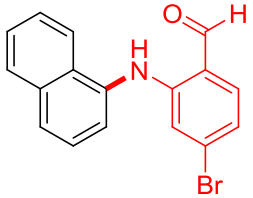
The general procedure **TP7** was followed using benzo[*c*]isoxazole (36 mg, 0.3 mmol) and oxo(pivaloyl)(3-(trifluoromethyl)phenyl)zinc (prepared from **TP5**, 0.45 mmol) for 16 h. Purification by column chromatography (*n*-hexane/EtOAc 15:1) yielded **5c** (48 mg, 56%) as a yellow oil. **^{1}H-NMR (400 MHz, $CDCl_3$)** δ = 10.03 (s, 1H), 9.83 (s, 1H), 7.53 (dd, *J* = 7.7, 1.7 Hz, 1H), 7.45 (m, 1H), 7.41 – 7.25 (m, 4H), 7.17 (m, 1H), 6.86 – 6.80 (m, 1H). **^{13}C-NMR**

(100 MHz, $CDCl_3$) δ = 194.0, 146.6, 140.5, 136.8, 135.7, 131.9 (q, *J* = 32 Hz), 130.0, 125.54, 123.8 (q, *J* = 270 Hz), 120.6 (q, *J* = 4 Hz), 119.94, 119.0 (q, *J* = 4 Hz), 118.25, 112.89. **^{19}F-NMR (376 MHz, $CDCl_3$)** δ = -62.78. **MS (EI, 70 eV):** m/z (%) = 265 (61), 264 (29), 237 (13), 236 (100), 216 (60), 196 (16), 168 (11), 167 (64), 166 (11). **HR-MS (EI, 70 eV)** : [$C_{14}H_{10}F_3NO$], calcd: 265.0714; found: 265.0704.



2-(Naphthalen-1-ylamino)benzaldehyde (5d)

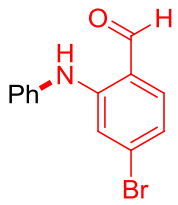
The general procedure **TP7** was followed using benzo[*c*]isoxazole (36 mg, 0.3 mmol) and naphthalen-1-yl(oxo)(pivaloyl)zinc (prepared from **TP1**, 0.45 mmol) for 16 h. Purification by column chromatography (*n*-hexane/EtOAc 15:1) yielded **5d** (57 mg, 77%) as a yellow solid. **M.p.**: 115–117 ℃. **^{1}H-NMR (400 MHz, $CDCl_3$)** δ = 10.44 (s, 1H), 10.06 (s, 1H), 8.18 – 8.12 (m, 1H), 7.96 (dd, *J* = 8.0, 1.7 Hz, 1H), 7.81 (d, *J* = 8.0 Hz, 1H), 7.65 (dd, *J* = 8.0, 1.7 Hz, 1H), 7.62 – 7.51 (m, 4H), 7.32 (ddd, *J* = 8.6, 7.0, 1.7 Hz, 1H), 6.97 (d, *J* = 8.6 Hz, 1H), 6.89 – 6.82 (m, 1H). **^{13}C-NMR** (100 MHz, $CDCl_3$) δ = 194.6, 149.3, 136.5, 135.7, 135.6, 134.8, 129.7, 128.5, 126.5, 126.5, 126.0, 125.8, 122.7, 121.8, 119.3, 117.0, 113.4. **IR (Diamond-ATR, neat):** ν / cm = 3273, 3047, 2833, 2742, 1651, 1626, 1607, 1594, 1572, 1515, 1499, 1455, 1420, 1392, 1314, 1269, 1224, 1197, 1154, 1119, 1082, 1037, 1015, 965, 900, 856, 785, 769, 731, 693, 659. **MS (EI, 70 eV):** m/z (%) = 247 (25), 246 (12), 230 (18), 229 (100), 228 (34), 227 (11), 218 (25), 217 (28), 114 (13). **HR-MS (EI, 70 eV)**: [$C_{17}H_{13}ON$], calcd.: 247.0997; found: 247.0989.



4-Bromo-2-(naphthalen-1-ylamino)benzaldehyde (5e)

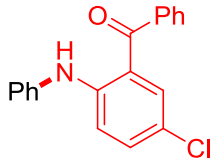
The general procedure **TP7** was followed using 6-bromobenzo[*c*]isoxazole (60 mg, 0.3 mmol) and naphthalen-1-yl(oxo)(pivaloyl)zinc (prepared from **TP1**, 0.45 mmol) for 16 h. Purification by column chromatography (*n*-hexane/EtOAc 15:1) yielded **5e** (81 mg, 81%) as a white solid. **M.p.**: 157–159 ℃. **^{1}H-NMR (400 MHz, $CDCl_3$)** δ = 10.26 (s, 1H), 9.84 (d, *J* = 3.0 Hz, 1H), 7.95 – 7.86 (m, 1H), 7.83 – 7.77 (m, 1H), 7.69 (dt, *J* = 6.9, 3.0 Hz, 1H), 7.42 (m,

4H), 7.33 (dd, *J* = 8.2, 3.0 Hz, 1H), 6.91 (d, *J* = 2.0 Hz, 1H), 6.82 (dt, *J* = 8.5, 2.0 Hz, 1H). **^{13}C-NMR (100 MHz, $CDCl_3$)** δ = 193.7, 150.1, 137.6, 134.8, 134.6, 131.5, 129.7, 128.5, 126.8, 126.7, 126.7, 125.8, 122.5, 122.4, 120.3, 117.9, 116.0. **IR (Diamond-ATR, neat):** ν / cm = 3263, 3050, 2834, 2742, 1648, 1594, 1562, 1492, 1424, 1382, 1324, 1277, 1219, 1187, 1123, 1072, 1016, 915, 871, 861, 851, 829, 788, 727, 685. **MS (EI, 70 eV):** m/z (%) = 309 (87), 307 (91), 228 (57), 226 (63), 217 (100), 114 (44). **HR-MS (EI, 70 eV)**: [$C_{17}H_{12}ONBr$], calcd.: 325.0102; found: 325.0096.



4-Bromo-2-(phenylamino)benzaldehyde (**5f**)

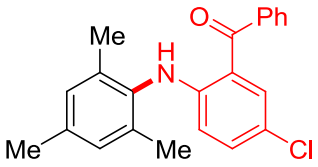
The general procedure **TP7** was followed using 6-bromobenzo[*c*]isoxazole (60 mg, 0.3 mmol) and oxo(phenyl)(pivaloyl)zinc (prepared from **TP4**, 0.45 mmol) for 16 h. Purification by column chromatography (*n*-hexane/EtOAc 15:1) yielded **5f** (64 mg, 78%) as an oil. **^{1}H-NMR (400 MHz, $CDCl_3$)** δ = 10.08 (s, 1H), 9.87 (d, *J* = 0.5 Hz, 1H), 7.47 – 7.40 (m, 3H), 7.35 (d, *J* = 1.5 Hz, 1H), 7.29 (dd, *J* = 5.6, 1.9 Hz, 2H), 7.26 – 7.20 (m, 1H), 6.96 (dd, *J* = 8.3, 1.7 Hz, 1H). **^{13}C-NMR (100 MHz, $CDCl_3$)** δ = 193.4, 148.7, 138.8, 137.7, 131.4, 129.7, 125.3, 123.8, 120.4, 118.0, 115.6. **IR (Diamond-ATR, neat):** ν / cm = 3274, 2835, 1656, 1482, 1241, 1018. **MS (EI, 70 eV):** m/z (%) = 274 (30), 257 (100), 255 (35). **HR-MS (EI, 70 eV)**: [$C_{13}H_{10}BrNO$], calcd.: 274.9946; found: 274.9942.



[5-Chloro-2-(phenylamino)phenyl](phenyl)methanone (5g)

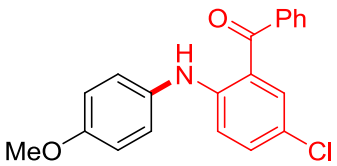
The general procedure **TP7** was followed using 5-chloro-3-phenylbenzo[*c*]isoxazole (69 mg, 0.3 mmol) and oxo(phenyl)(pivaloyl)zinc (prepared from **TP4**, 0.45 mmol) for 16 h. Purification by column chromatography (*n*-hexane/EtOAc 15:1) yielded **5g** (84 mg, 91%) as a yellow oil. **^{1}H-NMR (400 MHz, $CDCl_3$)** δ = 9.92 (s, 1H), 7.64 – 7.59 (m, 2H), 7.52 – 7.47 (m, 1H), 7.45 – 7.38 (m, 3H), 7.28 (m, 2H), 7.22 – 7.15 (m, 4H), 7.03 (t, *J* = 7.3 Hz, 1H). **^{13}C-NMR (100 MHz, $CDCl_3$)** δ = 198.0, 146.6, 140.1, 139.0, 134.1, 133.6, 131.8, 129.5, 129.4, 128.4, 124.0, 122.3, 121.0, 120.5, 116.3. **IR (Diamond-ATR, neat):** ν / cm = 3279, 3059,

2921, 2849, 1626, 1587, 1565, 1500, 1454, 1401, 1304, 1243, 1227, 1153, 1120, 1075, 1026, 847, 897, 812, 802, 773, 738, 670, 655. **MS (EI, 70 eV):** m/z (%) = 308 (31), 307 (26), 306 (100), 271 (17), 254 (13), 195 (11), 167 (15), 166 (14), 77 (12). **HR-MS (EI, 70 eV)**: [$C_{19}H_{13}ONCl$], [M-H], calcd.: 306.0764; found: 306.0681.



[5-Chloro-2-(mesitylamino)phenyl](phenyl)methanone (5h)

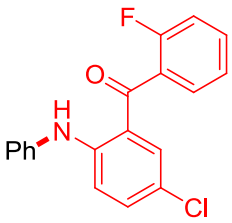
The general procedure **TP7** was followed using 5-chloro-3-phenylbenzo[*c*]isoxazole (69 mg, 0.3 mmol) and mesityl(oxo)(pivaloyl)zinc (prepared from **TP6**, 0.45 mmol) for 16 h. Purification by column chromatography (*n*-hexane/EtOAc 15:1) yielded **5h** (68 mg, 65%) as a colorless oil. **^{1}H-NMR (400 MHz, $CDCl_3$)** δ = 9.59 (s, 1H), 7.64 – 7.59 (m, 2H), 7.48 (m, 1H), 7.45 – 7.40 (m, 3H), 7.07 (dd, *J* = 9.1, 2.5 Hz, 1H), 6.89 (s, 2H), 6.19 (d, *J* = 9.1 Hz, 1H), 2.24 (s, 3H), 2.10 (s, 6H). **^{13}C-NMR** (100 MHz, $CDCl_3$) δ = 198.5, 149.4, 139.6, 136.6, 136.2, 134.7, 133.8, 131.4, 129.4, 129.3, 129.2, 128.4, 119.2, 117.9, 114.8, 21.0, 18.3. **IR (Diamond-ATR, neat):** ν / cm = 3289, 3057, 2916, 2854, 1625, 1561, 1500, 1444, 1430, 1327, 1311, 1298, 1237, 1217, 1177, 1152, 1118, 1098, 1053, 1025, 1011, 999, 947, 928, 906, 850, 808, 803, 770, 737, 730, 699, 679, 664. **MS (EI, 70 eV):** m/z (%) = 351 (15), 350 (11), 350 (32), 349 (52), 348 (100), 208 (12), 207 (11), 105 (13), 77 (15). **HR-MS (EI, 70 eV)**: [$C_{22}H_{19}ONCl$], [M-H], calcd.: 348.1233; found: 348.1147.



{5-Chloro-2-[(4-methoxyphenyl)amino]phenyl}(phenyl)methanone (5i)

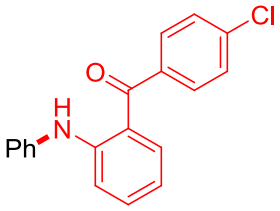
The general procedure **TP7** was followed using 5-chloro-3-phenylbenzo[*c*]isoxazole (69 mg, 0.3 mmol) and (4-methoxyphenyl)(oxo)(pivaloyl)zinc (prepared from **TP5**, 0.45 mmol) for 16 h. Purification by column chromatography (*n*-hexane/EtOAc 10:1) yielded **5i** (80 mg, 81%) as a red solid. **M.p.**: 104–106 °C. **^{1}H-NMR (400 MHz, $CDCl_3$)** δ = 10.04 (s, 1H), 7.74 – 7.70 (m, 2H), 7.60 (t, *J* = 6.7 Hz, 1H), 7.56 – 7.49 (m, 3H), 7.27 – 7.21 (m, 3H), 7.08 (m, 1H), 6.99 – 6.94 (m, 2H), 3.85 (s, 3H). **^{13}C-NMR (100 MHz, $CDCl_3$)** δ = 198.1, 157.0, 148.5, 139.4, 134.4, 133.8, 132.7, 131.6, 129.3, 128.4, 125.7, 120.0, 119.2, 115.6, 114.8, 55.5.

IR (Diamond-ATR, neat): ν / cm = 3258, 3083, 3067, 3002, 2844, 1622, 1588, 1568, 1510, 1444, 1466, 1411, 1496, 1331, 1294, 1250, 1238, 1153, 1098, 1024, 946, 923, 816, 801, 773, 674, 667. **MS (EI, 70 eV):** m/z (%) = 339 (21), 338 (30), 337 (75), 336 (100), 322 (22), 319 (23), 216 (27), 188 (23), 105 (21), 77 (20). **HR-MS (EI, 70 eV)**: [$C_{20}H_{15}O_2NCl$], [M-H], calcd.: 336.0870; found: 336.0764.



[5-Chloro-2-(phenylamino)phenyl](2-fluorophenyl)methanone (**5j**)

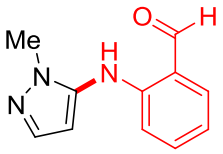
The general procedure **TP7** was followed using 5-chloro-3-(2-fluorophenyl)benzo[*c*]isoxazole (74 mg, 0.3 mmol) and oxo(phenyl)(pivaloyl)zinc (prepared from **TP4**, 0.45 mmol) for 16 h. Purification by column chromatography (*n*-hexane/EtOAc 15:1) yielded **5j** (71 mg, 74%) as a white solid. **M.p.**: 165–167 °C. **^{1}H-NMR (400 MHz, $CDCl_3$)** δ = 10.46 (s, 1H), 7.55 (dddd, *J* = 8.3, 7.3, 5.2, 1.8 Hz, 1H), 7.49 (td, *J* = 7.4, 1.8 Hz, 1H), 7.41 (ddd, *J* = 6.8, 6.1, 2.1 Hz, 3H), 7.36 – 7.29 (m, 3H), 7.28 (dd, *J* = 3.8, 1.4 Hz, 2H), 7.26 – 7.17 (m, 2H). **^{13}C-NMR (100 MHz, $CDCl_3$)** δ = 194.7, 159.2 (d, J_{C-F} = 250.7 Hz), 147.5, 139.6, 135.2, 133.7 (d, J_{C-F} = 1.8 Hz), 132.5 (d, J_{C-F} = 8.2 Hz), 129.9 (d, J_{C-F} = 3.0 Hz), 129.6, 127.8 (d, J_{C-F} = 15.9 Hz), 124.7, 124.4 (d, J_{C-F} = 3.6 Hz), 123.4, 120.9, 119.8, 116.4 (d, J_{C-F} = 21.5 Hz), 115.8. **IR (Diamond-ATR, neat):** ν / cm = 3262, 1635, 1519, 1264, 946. **MS (EI, 70 eV):** m/z (%) = 325 (15), 324 (100), 308 (45), 306 (20). **HR-MS (EI, 70 eV)**: [$C_{19}H_{13}ClFNO$], calcd.: 325.0670; found: 325.0664.



(4-Chlorophenyl)[2-(phenylamino)phenyl]methanone (**5k**)

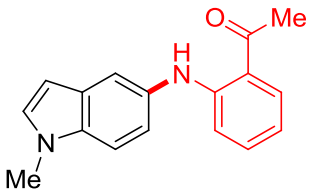
The general procedure **TP7** was followed using 5-chloro-3-(2-fluorophenyl)benzo[*c*]isoxazole (69 mg, 0.3 mmol) and oxo(phenyl)(pivaloyl)zinc (prepared from **TP4**, 0.45 mmol) for 16 h. Purification by column chromatography (*n*-hexane/EtOAc 15:1) yielded **5k** (68 mg, 74%) as a white solid. **M.p.**: 147–149 °C. **^{1}H-NMR (400 MHz, $CDCl_3$)** δ = 10.08 (s, 1H), 7.72 – 7.65 (m, 2H), 7.55 – 7.46 (m, 3H), 7.42 – 7.34 (m, 4H), 7.34 – 7.29 (m, 2H), 7.17 – 7.09 (m, 1H),

6.78 – 6.70 (m, 1H). **^{13}C-NMR (100 MHz, $CDCl_3$)** δ = 197.8, 148.2, 140.4, 138.1, 137.7, 134.7, 134.5, 130.9, 129.4, 128.5, 123.7, 122.3, 119.4, 116.7, 114.8. **IR (Diamond-ATR, neat):** ν / cm = 3258, 1641, 1509, 1247, 946. **MS (EI, 70 eV):** m/z (%) = 307 (10), 306 (45), 290 (100), 288 (40). **HR-MS (EI, 70 eV)**: [$C_{19}H_{14}ClNO$], calcd.: 307.0764; found: 307.0758.



2-[(1-Methyl-1*H*-pyrazol-5-yl)amino]benzaldehyde (5l)

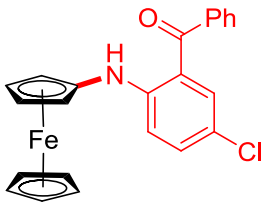
The general procedure **TP7** was followed using benzo[*c*]isoxazole (37 mg, 0.3 mmol) and (1-methyl-1*H*-pyrazol-5-yl)(oxo)(pivaloyl)zinc (prepared from **TP2**, metalation at room temperature, 0.45 mmol) for 16 h. Purification by column chromatography (*n*-hexane/EtOAc 15:1) yielded **5l** (33 mg, 55%) as a yellow oil. **^{1}H-NMR (400 MHz, $CDCl_3$)** δ = 9.96 (s, 1H), 9.77 (s, 1H), 7.64 (dd, *J* = 7.6, 1.6 Hz, 1H), 7.53 (s, 1H), 7.44 (ddd, *J* = 8.6, 7.1, 1.6 Hz, 1H), 6.95 (td, *J* = 7.6, 1.0 Hz, 1H), 6.83 (d, *J* = 8.6 Hz, 1H), 6.20 – 6.14 (m, 1H), 3.77 (s, 3H). **^{13}C-NMR (100 MHz, $CDCl_3$)** δ = 194.8, 147.5, 138.8, 138.0, 136.3, 136.1, 119.5, 118.4, 113.3, 100.0, 35.1. **IR (Diamond-ATR, neat):** ν / cm = 3275, 3071, 2919, 1631, 1601, 1567, 1545, 1491, 1454, 1421, 1318, 1321, 1241, 1161, 1099, 1038, 1009, 951, 880, 848, 791, 745, 715, 700, 665. **MS (EI, 70 eV):** m/z (%) = 201 (14), 184 (11), 183 (96), 182 (100), 173 (14), 155 (13), 129 (25), 128 (20), 117 (11). **HR-MS (EI, 70 eV)**: [$C_{11}H_{11}N_3O$], calcd.: 201.0902; found: 201.0895.



1-{2-[(1-Methyl-1*H*-indol-5-yl)amino]phenyl}ethan-1-one (5m)

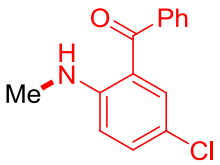
The general procedure **TP7** was followed using methylbenzo[*c*]isoxazole (40 mg, 0.3 mmol) and (1-methyl-1*H*-indol-5-yl)(oxo)(pivaloyl)zinc (prepared from **TP1**, 0.45 mmol) for 16 h. Purification by column chromatography (*n*-hexane/EtOAc 10:1) yielded **5m** (59 mg, 75%) as a colorless liquid. **^{1}H-NMR (400 MHz, $CDCl_3$)** δ = 10.60 (s, 1H), 7.87 – 7.81 (m, 1H), 7.57 (s, 1H), 7.36 (d, *J* = 8.6 Hz, 1H), 7.31 – 7.25 (m, 1H), 7.18 (dd, *J* = 8.6, 1.5 Hz, 1H), 7.12 (d, *J* = 3.0 Hz, 1H), 7.08 (d, *J* = 8.6 Hz, 1H), 6.69 (t, *J* = 7.5 Hz, 1H), 6.51 (d, *J* = 3.0 Hz, 1H), 3.84 (s, 3H), 2.71 (s, 3H). **^{13}C-NMR (100 MHz, $CDCl_3$)** δ = 201.0, 150.5, 134.6, 132.5,

132.0, 129.8, 129.1, 120.4, 117.9, 117.4, 115.2, 113.9, 110.0, 100.9, 33.1, 28.1. **IR (Diamond-ATR, neat):** ν / cm = 3265, 3070, 2919, 1631, 1602, 1566, 1505, 1490, 1444, 1420, 1358, 1321, 1241, 1160, 1079, 1038, 1009, 950, 880, 847, 794, 742, 715, 699, 666. **MS (EI, 70 eV):** m/z (%) = 265 (18), 264 (100), 249 (13), 246 (19), 234 (21), 221 (26), 206 (49), 205 (12), 144 (50), 120 (17). **HR-MS (EI, 70 eV)**: [$C_{17}H_{16}ON_2$], calcd.: 264.1263; found: 264.1259.



[5-Chloro-2-(ferrocenylamino)phenyl](phenyl)methanone (5n)

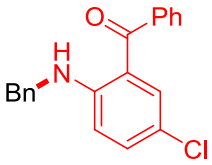
The general procedure **TP7** was followed using 5-chloro-3-phenylbenzo[*c*]isoxazole (69 mg, 0.3 mmol) and oxo(ferrocenyl)(pivaloyl)zinc (prepared from **TP1**, 0.45 mmol) for 16 h. Purification by column chromatography (*n*-hexane/EtOAc 10:1) yielded **5n** (50 mg, 40%) as a orange solid. **M.p.**: 114–116 °C. **^{1}H-NMR (400 MHz, $CDCl_3$)** δ = 9.72 (s, 1H), 7.73 – 7.65 (m, 2H), 7.60 (m, 1H), 7.56 – 7.48 (m, 3H), 7.31 – 7.26 (m, 1H), 7.11 (m, 1H), 4.39 (s, 2H), 4.29 (s, 5H), 4.17 (s, 2H). **^{13}C-NMR (100 MHz, $CDCl_3$)** δ = 198.5, 149.7, 139.5, 134.4, 133.6, 131.5, 129.1, 128.4, 119.6, 118.4, 115.8, 95.5, 69.5, 65.8, 65.1. **IR (Diamond-ATR, neat):** ν / cm = 3299, 3082, 2922, 1622, 1597, 1563, 1497, 1444, 1406, 1324, 1304, 1233, 1204, 1178, 1151, 1104, 1026, 999, 949, 934, 906, 814, 801, 768, 729, 710, 666. **MS (EI, 70 eV):** m/z (%) = 417 (29), 416 (24), 415 (100), 350 (14), 77 (12). **HR-MS (EI, 70 eV):** [$C_{23}H_{18}ClFeNO$], calcd: 415.0426.1052; found: 415.0420.



[5-Chloro-2-(methylamino)phenyl](phenyl)methanone (5o)

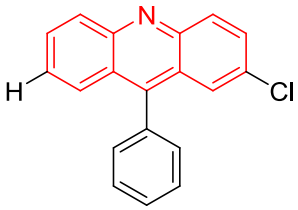
The general procedure **TP7** was followed using 5-chloro-3-phenylbenzo[*c*]isoxazole (69 mg, 0.3 mmol) and methyl(oxo)(pivaloyl)zinc (prepared from **TP4**, 0.45 mmol) for 16 h. Purification by column chromatography (*n*-hexane/EtOAc 15:1) yielded **5o** (58 mg, 79%) as a yellow solid. **M.p.**: 89–91 °C. **^{1}H-NMR (400 MHz, $CDCl_3$)** δ = 8.38 (s, 1H), 7.52 – 7.47 (m, 2H), 7.45 – 7.41 (m, 1H), 7.40 – 7.33 (m, 3H), 7.24 (dd, *J* = 9.0, 2.5 Hz, 1H), 6.61 (d, *J* = 9.0 Hz, 3H). **^{13}C-NMR (100 MHz, $CDCl_3$)** δ = 198.3, 151.2, 139.8, 134.9, 134.1, 131.2, 129.0, 128.3, 118.2, 117.9, 112.8, 29.6. **IR (ATR):** 3328, 1618, 1613, 1561, 1555, 1508, 1503, 1466,

1441, 1397, 1340, 1238, 1170, 1101, 1078, 945, 939, 892, 813, 809, 800, 754, 737, 700, 660. **MS (EI, 70 eV):** m/z (%) = 247 (14), 246 (32), 245 (46), 244 (100), 230 (11), 228 (34), 209 (18), 193 (48), 168 (11), 133 (14), 77 (19). **HR-MS (EI)**: [$C_{14}H_{11}ONCl$], [M-H], calcd.: 245.0607; found: 245.0523.



[2-(Benzylamino)-5-chlorophenyl](phenyl)methanone (5p)

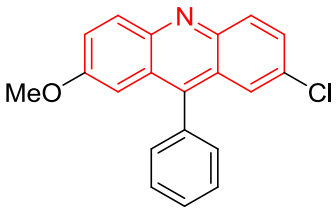
The general procedure **TP7** was followed using 5-chloro-3-phenylbenzo[*c*]isoxazole (69 mg, 0.3 mmol) and benzyl(oxo)(pivaloyl)zinc (prepared from **TP4**, 0.45 mmol) for 16 h. Purification by column chromatography (*n*-hexane/EtOAc 15:1) yielded **5p** (64 mg, 66%) as a yellow solid. **M.p.**: 69–71 ℃. **^{1}H-NMR (400 MHz, $CDCl_3$)** δ = 8.84 (s, 1H), 7.54 – 7.49 (m, 2H), 7.44 (m, 1H), 7.40 – 7.33 (m, 3H), 7.29 – 7.22 (m, 4H), 7.17 (m, 3H), 6.57 (d, *J* = 9.1 Hz, 1H), 4.37 (s, 2H). **^{13}C-NMR (100 MHz, $CDCl_3$)** δ = 198.3, 150.0, 140.6, 138.00, 134.7, 134.0, 131.2, 129.0, 128.7, 128.2, 127.3, 127.0, 118.7, 118.2, 113.6, 47.0. **IR (ATR):** 3356, 3239, 3059, 2921, 2849, 1626, 1587, 1465, 1506, 1454, 1401, 1304, 1243, 1227, 1153, 1130, 1075, 1026, 847, 897, 812, 802, 753, 738, 670, 655. **MS (EI):** m/z (%) = 323 (21), 321 (67), 320 (29), 304 (46), 303 (22), 290 (29), 214 (28), 152 (23), 106 (45), 105 (20), 91 (100), 77 (24). **HR-MS (EI, 70 eV)**: [$C_{20}H_{16}ONCl$], calcd.: 321.0920; found: 321.0914.



2-Chloro-9-phenylacridine (**6a**)

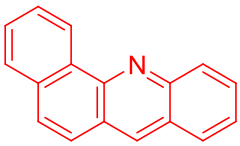
A suspension of compound **5g** (61 mg, 0.2 mmol) in TFA (2.0 mL) was stirred at 80℃ for 12 h under an atmosphere of N_2.[3]. At ambient temperature, the reaction mixture was extracted with DCM (3 × 20 mL) and the combined organic layers were washed with saturated $NaHCO_3$ and brine, and dried over Na_2SO_4. The solvent was evaporated *in vacuo* and the remaining residue was purified by column chromatography on silica gel (*n*-hexane/EtOAc 5:1) to yield product **6a** (54 mg, 94%) as a colorless solid. **M.p.** = 197−200 ℃. **^{1}H-NMR (400 MHz, $CDCl_3$)** δ = 8.82 (d, *J* = 9.3 Hz, 1H), 8.78 (d, *J* = 8.8 Hz, 1H), 8.14 (dd, *J* = 11.2, 4.2 Hz, 1H), 8.07 – 7.98 (m, 1H), 7.95 – 7.88 (m, 1H), 7.86 (d, *J* = 2.2 Hz, 1H), 7.80 – 7.69 (m,

4H), 7.55 – 7.43 (m, 2H). **^{13}C-NMR (100 MHz, $CDCl_3$)** δ = 156.8, 141.2, 139.5, 136.7, 136.2, 134.2, 132.8, 130.4, 129.8, 129.2, 128.4, 127.8, 125.9, 125.8, 125.8, 124.0, 122.3. **IR (Diamond-ATR, neat):** ν / cm = 3325, 1715, 1564, 1252, 927. **MS (EI, 70 eV):** m/z (%) = 289 (35), 254 (100). **HR-MS (EI, 70 eV)**: [$C_{19}H_{12}ClN$], calcd.: 289.0658; found: 289.0653.



2-Chloro-7-methoxy-9-phenylacridine (**6b**)

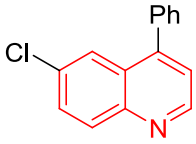
A suspension of compound **5i** (67 mg, 0.2 mmol) in TFA (2.0 mL) was stirred at 80 ℃ for 12 h under an atmosphere of N_2.[3]. At ambient temperature, the reaction mixture was extracted with DCM (3 × 20 mL) and the combined organic layers were washed with saturated $NaHCO_3$ and brine, and dried over Na_2SO_4. The solvent was evaporated *in vacuo* and the remaining residue was purified by column chromatography on silica gel (*n*-hexane/EtOAc 5:1) to yield product **6b** (62 mg, 97%) as a colorless solid. **M.p.** = 221−223 ℃. **^{1}H-NMR (400 MHz, $CDCl_3$)** δ = 8.81 – 8.73 (m, 1H), 8.71 (d, *J* = 9.5 Hz, 1H), 7.90 (dd, *J* = 9.2, 2.1 Hz, 1H), 7.81 – 7.70 (m, 5H), 7.53 – 7.43 (m, 2H), 6.93 (d, *J* = 2.6 Hz, 1H), 3.80 (s, 3H). **^{13}C-NMR (100 MHz, $CDCl_3$)** δ = 158.8, 152.4, 138.8, 138.3, 134.8, 134.0, 133.5, 130.6, 130.1, 129.5, 129.4, 127.4, 126.0, 125.2, 124.5, 124.4, 102.6, 55.7. **IR (Diamond-ATR, neat):** ν / cm = 3319, 1721, 1557, 1248, 1046. **MS (EI, 70 eV):** m/z (%) = 319 (25), 304 (75), 288 (100), 284 (20). **HR-MS (EI, 70 eV)**: [$C_{20}H_{14}ClNO$], calcd.: 319.0764; found: 319.0761.



Benzo[*c*]acridine (**6c**)

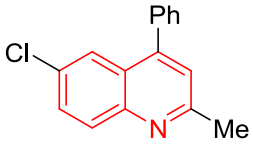
A suspension of compound **5d** (49 mg, 0.2 mmol) in TFA (2.0 mL) was stirred at 80 ℃ for 12 h under an atmosphere of N_2.[3]. At ambient temperature, the reaction mixture was extracted with DCM (3 × 20 mL) and the combined organic layers were washed with saturated $NaHCO_3$ and brine, and dried over Na_2SO_4. The solvent was evaporated *in vacuo* and the remaining residue was purified by column chromatography on silica gel (*n*-hexane/EtOAc 5:1) to yield product **6c** (45 mg, 97%) as a colorless solid. **M.p.** = 179−182 ℃. **^{1}H-NMR (400 MHz, $CDCl_3$)** δ = 9.61 – 9.50 (m, 1H), 8.66 (s, 1H), 8.42 (dd, *J* = 8.7, 0.8 Hz, 1H), 8.09 –

8.01 (m, 1H), 7.90 (dd, *J* = 7.7, 1.4 Hz, 1H), 7.88 – 7.70 (m, 5H), 7.62 (ddd, *J* = 8.0, 6.7, 1.1 Hz, 1H). **^{13}C-NMR (100 MHz, $CDCl_3$)** δ = 147.8, 147.8, 135.0, 134.0, 131.6, 129.8, 129.7, 129.1, 127.9, 127.8, 127.7, 127.3, 127.1, 125.9, 125.8, 125.3, 125.2. **IR (Diamond-ATR, neat):** ν / cm = 3323, 1691, 1536, 1268, 1046. **MS (EI, 70 eV):** m/z (%) = 229 (100). **HR-MS (EI, 70 eV)**: [$C_{17}H_{11}N$], calcd.: 229.0891; found: 229.0893.



6-Chloro-4-phenylquinoline (**8a**)

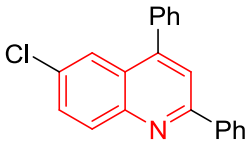
The general procedure **TP7** was followed using 5-chloro-3-phenylbenzo[*c*]isoxazole (69 mg, 0.3 mmol) and oxo(pivaloyl)(vinyl)zinc (prepared from **TP4**, 0.45 mmol) for 16 h. Purification by column chromatography (*n*-hexane/EtOAc 8:1) yielded **8a** (61 mg, 85%) as a white solid. **M.p.**: 134–135 °C. **^{1}H-NMR (400 MHz, $CDCl_3$)** δ = 8.93 (d, *J* = 4.4 Hz, 1H), 8.12 (d, *J* = 9.0 Hz, 1H), 7.90 (d, *J* = 2.3 Hz, 1H), 7.66 (dd, *J* = 9.0, 2.3 Hz, 1H), 7.57 – 7.45 (m, 5H), 7.35 (d, *J* = 4.4 Hz, 1H). **^{13}C-NMR (100 MHz, $CDCl_3$)** δ = 150.2, 147.7, 147.1, 137.3, 132.6, 131.5, 130.3, 129.4, 128.8, 128.7, 127.5, 124.7, 122.1. **IR (Diamond-ATR, neat):** ν / cm = 3054, 3024, 2963, 1601, 1583, 1571, 1561, 1498, 1486, 1449, 1434, 1420, 1353, 1151, 1125, 1074, 1054, 1028, 970, 880, 854, 824, 780, 758, 730, 710, 700, 665. **MS (EI, 70 eV):** m/z (%) = 239 (55), 238 (15), 205 (15), 204 (100), 203 (23), 176 (25), 88 (13). **HR-MS (EI, 70 eV)**: [$C_{15}H_{10}NCl$], calcd: 239.0502; found: 239.0494.



6-Chloro-2-methyl-4-phenylquinoline (**8b**)

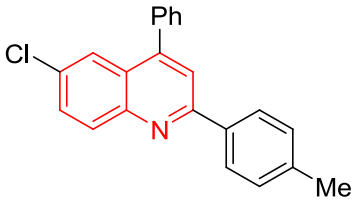
The general procedure **TP7** was followed using 5-chloro-3-phenylbenzo[*c*]isoxazole (69 mg, 0.3 mmol) and oxo(pivaloyl)(prop-1-en-2-yl)zinc (prepared from **TP4**, 0.45 mmol) for 16 h. Purification by column chromatography (*n*-hexane/EtOAc 8:1) yielded **8b** (68 mg, 90%) as a white solid. **M.p.**: 138–140 °C. **^{1}H-NMR (600 MHz, $CDCl_3$)** δ = 8.01 (d, *J* = 9.0 Hz, 1H), 7.82 (d, *J* = 2.3 Hz, 1H), 7.62 (dd, *J* = 9.0, 2.3 Hz, 1H), 7.57 – 7.49 (m, 3H), 7.49 – 7.45 (m, 2H), 7.25 (s, 1H), 2.77 (s, 3H). **^{13}C-NMR (150 MHz, $CDCl_3$)** δ = 158.8, 147.8, 146.8, 137.5, 131.6, 130.6, 130.1, 129.3, 128.7, 128.6, 125.8, 124.5 (d, *J* = 2.7 Hz), 123.0 (d, *J* = 5.8 Hz). **IR (Diamond-ATR, neat):** ν / cm = 3048, 1607, 1578, 1349, 1075, 963. **MS (EI, 70 eV):**

m/z (%) = 253 (45), 252 (15), 238 (55), 218 (100). **HR-MS (EI, 70 eV)**: [$C_{16}H_{12}NCl$], calcd: 253.0658; found: 253.0654.



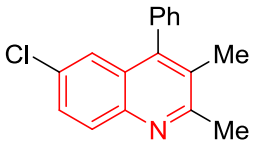
6-Chloro-2,4-diphenylquinoline (**8c**)

The general procedure **TP7** was followed using 5-chloro-3-phenylbenzo[*c*]isoxazole (69 mg, 0.3 mmol) and oxo(1-phenylvinyl)(pivaloyl)zinc (prepared from **TP6**, 0.45 mmol) for 16 h. Purification by column chromatography (*n*-hexane/EtOAc 8:1) yielded **8c** (88 mg, 93%) as a white solid. **M.p.**: 138–140 °C. **^{1}H-NMR (400 MHz, $CDCl_3$)** δ = 8.25 – 8.18 (m, 3H), 7.90 (d, *J* = 2.3 Hz, 1H), 7.87 (s, 1H), 7.69 (dd, *J* = 9.0, 2.3 Hz, 1H), 7.64 – 7.47 (m, 8H). **^{13}C-NMR (100 MHz, $CDCl_3$)** δ = 157.1, 148.5, 147.3, 139.2, 137.8, 132.2, 131.8, 130.5, 129.6, 129.5, 128.9, 128.8, 128.7, 127.6, 126.5, 124.5, 120.1. **IR (Diamond-ATR, neat):** ν / cm = 3051, 1614, 1582, 1354, 1067, 963. **MS (EI, 70 eV):** m/z (%) = 315 (25), 314 (10), 280 (100). **HR-MS (EI, 70 eV)**: [$C_{21}H_{14}NCl$], calcd: 315.0815; found: 315.0819.



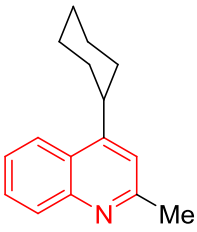
6-Chloro-4-phenyl-2-p-tolylquinoline (**8d**)

The general procedure **TP7** was followed using 5-chloro-3-phenylbenzo[*c*]isoxazole (69 mg, 0.3 mmol) and oxo(pivaloyl)(1-*p*-tolylvinyl)zinc (prepared from **TP6**, 0.45 mmol) for 16 h. Purification by column chromatography (*n*-hexane/EtOAc 10:1) yielded **8d** (61 mg, 62%) as a white solid. **M.p.**: 151–153 °C. **^{1}H-NMR (400 MHz, $CDCl_3$)** δ = 8.18 (d, *J* = 9.0 Hz, 1H), 8.15 – 8.09 (m, 2H), 7.88 (t, *J* = 4.0 Hz, 1H), 7.85 (d, *J* = 4.0 Hz, 1H), 7.72 – 7.65 (m, 1H), 7.64 – 7.53 (m, 5H), 7.35 (t, *J* = 8.8 Hz, 2H), 2.46 (s, 3H). **^{13}C-NMR (100 MHz, $CDCl_3$)** δ = 157.1, 148.3, 147.2, 139.8, 137.8, 136.4, 132.0, 131.7, 130.4, 129.7, 129.5, 128.8, 128.7, 127.4, 126.4, 124.5, 119.9, 21.4. **IR (Diamond-ATR, neat):** ν / cm = 3052, 1621, 1575, 1361, 1066, 967. **MS (EI, 70 eV):** m/z (%) = 329 (20), 328 (5), 314 (35), 294 (100). **HR-MS (EI, 70 eV)**: [$C_{22}H_{16}NCl$], calcd: 329.0971; found: 329.0973.



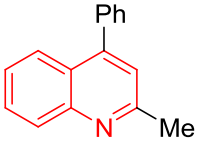
6-Chloro-2,3-dimethyl-4-phenylquinoline (**8e**)

The general procedure **TP7** was followed using 5-chloro-3-phenylbenzo[*c*]isoxazole (69 mg, 0.3 mmol) and but-2-en-2-yl(oxo)(pivaloyl)zinc (prepared from **TP4**, 0.45 mmol) for 16 h. Purification by column chromatography (*n*-hexane/EtOAc 9:1) yielded **8e** (73 mg, 91%) as a white solid. **M.p.**: 127–130 ℃. **^{1}H-NMR (400 MHz, $CDCl_3$)** δ = 7.98 (d, *J* = 8.9 Hz, 1H), 7.60 – 7.48 (m, 4H), 7.30 (d, *J* = 2.3 Hz, 1H), 7.27 – 7.21 (m, 2H), 2.77 (s, 3H), 2.20 (s, 3H). **^{13}C-NMR (100 MHz, $CDCl_3$)** δ = 159.3, 145.6, 144.5, 136.9, 131.3, 130.1, 129.3, 129.1, 128.8, 128.6, 128.1, 127.7, 124.9, 24.5, 17.1. **IR (Diamond-ATR, neat):** ν / cm = 3035, 1619, 1571, 1349, 1062, 952. **MS (EI, 70 eV):** m/z (%) = 267 (20), 252 (45), 232 (100). **HR-MS (EI, 70 eV)**: [$C_{17}H_{14}NCl$], calcd: 267.0815; found: 267.0812.



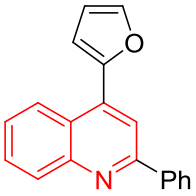
4-Cyclohexyl-2-methylquinoline (**8f**)

The general procedure **TP7** was followed using 3-cyclohexylbenzo[*c*]isoxazole (60 mg, 0.3 mmol) and oxo(pivaloyl)(prop-1-en-2-yl)zinc (prepared from **TP4**, 0.45 mmol) for 16 h. Purification by column chromatography (*n*-hexane/EtOAc 9:1) yielded **8f** (42 mg, 62%) as a yellow oil. **^{1}H-NMR (400 MHz, $CDCl_3$)** δ = 8.05 (d, *J* = 8.9 Hz, 2H), 7.67 (ddd, *J* = 8.4, 6.9, 1.3 Hz, 1H), 7.50 (ddd, *J* = 8.2, 6.9, 1.3 Hz, 1H), 7.19 (s, 1H), 3.31 (ddd, *J* = 11.2, 8.3, 3.1 Hz, 1H), 2.74 (s, 3H), 2.08 – 1.81 (m, 5H), 1.65 – 1.48 (m, 4H), 1.43 – 1.30 (m, 1H). **^{13}C-NMR (125 MHz, $CDCl_3$)** δ = 158.8, 153.3, 148.2, 129.6, 128.8, 125.3, 125.2, 122.8, 118.3, 38.8, 33.6, 27.0, 26.3, 25.6. **IR (Diamond-ATR, neat):** ν / cm = 3021, 1643, 1514, 1354, 1057, 951. **MS (EI, 70 eV):** m/z (%) = 225 (55), 224 (15), 210 (100). **HR-MS (EI, 70 eV)**: [$C_{16}H_{19}N$], calcd: 225.1517; found: 225..1519



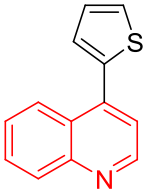
2-Methyl-4-phenylquinoline (**8g**)

The general procedure **TP7** was followed using 3-phenylbenzo[*c*]isoxazole (59 mg, 0.3 mmol) and oxo(pivaloyl)(prop-1-en-2-yl)zinc (prepared from **TP4**, 0.45 mmol) for 16 h. Purification by column chromatography (*n*-hexane/EtOAc 9:1) yielded **8g** (57 mg, 86%) as a white solid. **M.p.**: 121–123 °C. **^{1}H-NMR (400 MHz, $CDCl_3$)** δ = 8.11 (dd, *J* = 8.5, 0.6 Hz, 1H), 7.88 (dd, *J* = 8.4, 1.0 Hz, 1H), 7.71 (ddd, *J* = 8.4, 6.9, 1.4 Hz, 1H), 7.58 – 7.50 (m, 5H), 7.46 (ddd, *J* = 8.2, 6.9, 1.2 Hz, 1H), 7.26 (s, 1H), 2.81 (s, 3H). **^{13}C-NMR (100 MHz, $CDCl_3$)** δ = 158.5, 148.6, 148.4, 138.2, 129.5, 129.3, 129.0, 128.5, 128.3, 125.8, 125.7, 125.1, 122.3, 25.4. **IR (Diamond-ATR, neat):** ν / cm = 3051, 1624, 1601, 1351, 1066, 967. **MS (EI, 70 eV):** m/z (%) = 219 (25), 218 (10), 204 (100). **HR-MS (EI, 70 eV)**: [$C_{16}H_{13}N$], calcd: 219.1048; found: 219.1043.



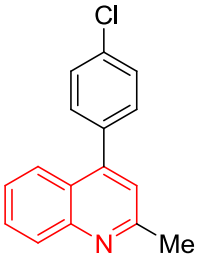
4-(Furan-2-yl)-2-phenylquinoline (**8h**)

The general procedure **TP7** was followed using 3-(furan-2-yl)benzo[*c*]isoxazole (56 mg, 0.3 mmol) and oxo(1-phenylvinyl)(pivaloyl)zinc (prepared from **TP6**, 0.45 mmol) for 16 h. Purification by column chromatography (*n*-hexane/EtOAc 9:1) yielded **8h** (78 mg, 96%) as a slight yellow solid. **M.p.**: 117–119 °C. **^{1}H-NMR (600 MHz, $CDCl_3$)** δ = 8.48 (dd, *J* = 8.5, 0.7 Hz, 1H), 8.25 – 8.19 (m, 3H), 8.12 (s, 1H), 7.75 (qd, *J* = 6.6, 3.1 Hz, 1H), 7.73 – 7.70 (m, 1H), 7.58 (ddd, *J* = 8.2, 6.8, 1.3 Hz, 1H), 7.55 (dd, *J* = 10.3, 4.8 Hz, 2H), 7.51 – 7.46 (m, 1H), 7.04 (dd, *J* = 6.1, 2.9 Hz, 1H), 6.67 (dd, *J* = 3.4, 1.8 Hz, 1H). **^{13}C-NMR (150 MHz, $CDCl_3$)** δ = 157.1, 151.3, 149.2, 143.8, 143.8, 139.6, 136.4, 130.4, 129.5, 129.4 (d, *J* = 2.0 Hz), 128.8, 127.6 (d, *J* = 13.6 Hz), 126.7 (d, *J* = 1.9 Hz), 125.1, 123.5, 116.7 (t, *J* = 6.7 Hz), 112.0 (d, *J* = 2.0 Hz). **IR (Diamond-ATR, neat):** ν / cm = 3031, 1647, 1589, 1344, 1106, 962. **MS (EI, 70 eV):** m/z (%) = 271 (100), 270 (15). **HR-MS (EI, 70 eV)**: [$C_{19}H_{13}NO$], calcd: 271.0997; found: 271.0996.



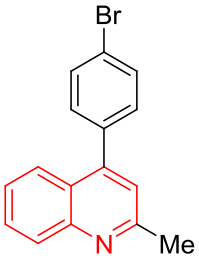
4-(Thiophen-2-yl)quinoline (**8i**)

The general procedure **TP7** was followed using 3-(thiophen-2-yl)benzo[*c*]isoxazole (60 mg, 0.3 mmol) and oxo(pivaloyl)(vinyl)zinc (prepared from **TP4**, 0.45 mmol) for 16 h. Purification by column chromatography (*n*-hexane/EtOAc 9:1) yielded **8i** (57 mg, 90%) as a red solid. **M.p.**: 105–108 °C. **^{1}H-NMR (400 MHz, $CDCl_3$)** δ = 8.94 (d, *J* = 4.5 Hz, 1H), 8.33 (dd, *J* = 8.5, 1.0 Hz, 1H), 8.20 (d, *J* = 8.0 Hz, 1H), 7.78 (ddd, *J* = 8.4, 6.9, 1.4 Hz, 1H), 7.60 (ddd, *J* = 8.3, 6.9, 1.3 Hz, 1H), 7.56 (dt, *J* = 4.4, 2.2 Hz, 1H), 7.49 (dd, *J* = 8.1, 2.9 Hz, 1H), 7.42 (dd, *J* = 3.6, 1.1 Hz, 1H), 7.26 (dd, *J* = 5.1, 3.6 Hz, 1H). **^{13}C-NMR (100 MHz, $CDCl_3$)** δ = 149.9, 148.9, 140.9, 138.9, 130.0, 129.6, 128.6, 127.8, 127.3, 127.0, 126.5, 125.6, 121.7. **IR (Diamond-ATR, neat):** ν / cm = 3029, 1650, 1571, 1341, 1124, 957. **MS (EI, 70 eV):** m/z (%) = 211 (100), 270 (5). **HR-MS (EI, 70 eV)**: [$C_{13}H_9NS$], calcd: 211.0456; found: 211.0461.



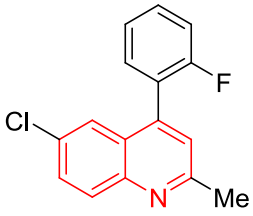
4-(4-Chlorophenyl)-2-methylquinoline (**8j**)

The general procedure **TP7** was followed using 3-(4-chlorophenyl)benzo[*c*]isoxazole (69 mg, 0.3 mmol) and oxo(pivaloyl)(prop-1-en-2-yl)zinc (prepared from **TP4**, 0.45 mmol) for 16 h. Purification by column chromatography (*n*-hexane/EtOAc 9:1) yielded **8j** (69 mg, 91%) as a white solid. **M.p.**: 135–137 °C. **^{1}H-NMR (600 MHz, $CDCl_3$)** δ = 8.11 – 8.07 (m, 1H), 7.82 – 7.77 (m, 1H), 7.69 (ddd, *J* = 8.3, 6.9, 1.3 Hz, 1H), 7.52 – 7.47 (m, 2H), 7.47 – 7.41 (m, 3H), 7.20 (s, 1H), 2.78 (s, 3H). **^{13}C-NMR (150 MHz, $CDCl_3$)** δ = 158.5, 148.3, 147.2, 136.5, 134.4 (d, *J* = 33.7 Hz), 130.8 (dd, *J* = 10.0, 5.5 Hz), 129.5 (d, *J* = 2.6 Hz), 129.1, 128.8 – 128.7 (m), 125.9 (d, *J* = 7.9 Hz), 125.3 – 125.2 (m), 124.8, 122.1 (d, *J* = 9.3 Hz), 25.3 (q, *J* = 6.9 Hz). **IR (Diamond-ATR, neat):** ν / cm = 3027, 1649, 1579, 1343, 1126, 957. **MS (EI, 70 eV):** m/z (%) = 253 (30), 252 (10), 238 (25), 218 (100). **HR-MS (EI, 70 eV)**: [$C_{16}H_{12}ClN$], calcd: 253.0658; found: 253.0655.



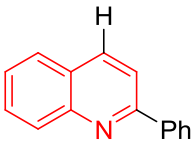
4-(4-Bromophenyl)-2-methylquinoline (8k)

The general procedure **TP7** was followed using 3-(4-bromophenyl)benzo[*c*]isoxazole (82 mg, 0.3 mmol) and oxo(pivaloyl)(prop-1-en-2-yl)zinc (prepared from **TP4**, 0.45 mmol) for 16 h. Purification by column chromatography (*n*-hexane/EtOAc 9:1) yielded **8k** (82 mg, 92%) as a white solid. **M.p.**: 135–137 °C. **^{1}H-NMR (400 MHz, CDCl$_3$)** δ = 8.11 (d, J = 8.4 Hz, 1H), 7.81 (dd, J = 8.4, 1.0 Hz, 1H), 7.75 – 7.69 (m, 1H), 7.69 – 7.64 (m, 2H), 7.50 – 7.44 (m, 1H), 7.43 – 7.36 (m, 2H), 7.22 (s, 1H), 2.80 (s, 3H). **^{13}C-NMR (100 MHz, CDCl$_3$)** δ = 158.5, 148.4, 147.3, 137.0, 131.8, 131.1, 129.5, 129.1, 126.0, 125.3, 124.8, 122.7, 122.1, 25.4. **IR (Diamond-ATR, neat):** ν / cm = 3029, 1653, 1581, 1342, 1131, 943. **MS (EI, 70 eV):** m/z (%) = 299 (45), 297 (45), 284 (30), 282 (30), 218 (100). **HR-MS (EI, 70 eV)**: [$C_{16}H_{12}BrN$], calcd: 297.0153; found: 297.0151.



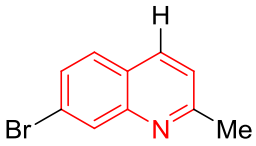
6-Chloro-4-(2-fluorophenyl)-2-methylquinoline (8l)

The general procedure **TP7** was followed using 5-chloro-3-(2-fluorophenyl)benzo[*c*]isoxazole (74 mg, 0.3 mmol) and oxo(pivaloyl)(prop-1-en-2-yl)zinc (prepared from **TP4**, 0.45 mmol) for 16 h. Purification by column chromatography (*n*-hexane/EtOAc 9:1) yielded **8l** (76 mg, 93%) as a white solid. **M.p.**: 136–137 °C. **^{1}H-NMR (400 MHz, CDCl$_3$)** δ = 8.04 (d, J = 8.9 Hz, 1H), 7.65 (dd, J = 8.9, 2.3 Hz, 1H), 7.60 (t, J = 2.1 Hz, 1H), 7.53 (dddd, J = 8.2, 7.2, 5.2, 2.0 Hz, 1H), 7.39 (td, J = 7.4, 2.0 Hz, 1H), 7.36 – 7.25 (m, 3H), 2.80 (s, 3H). **^{13}C-NMR (100 MHz, CDCl$_3$)** δ = 159.6 (d, $J_{C–F}$ = 248.3 Hz), 158.8, 146.6, 141.9, 131.8, 131.6 (d, $J_{C–F}$ = 3.1 Hz), 130.8 (d, $J_{C–F}$ = 8.0 Hz), 130.7, 130.4, 126.0, 124.9 (d, $J_{C–F}$ = 16.0 Hz), 124.5 (d, $J_{C–F}$ = 3.7 Hz), 124.4 (d, $J_{C–F}$ = 1.4 Hz), 123.9, 116.2 (d, $J_{C–F}$ = 21.8 Hz), 25.3. **^{19}F-NMR (376 MHz, CDCl$_3$)** δ = -111.56 – -115.41 (m). **IR (Diamond-ATR, neat):** ν / cm = 3137, 1649, 1573, 1350, 1135, 961. **MS (EI, 70 eV):** m/z (%) = 299 (45), 297 (45), 284 (30), 282 (30), 218 (100). **HR-MS (EI, 70 eV)**: [$C_{16}H_{11}ClFN$], calcd: 271.0564; found: 271.0563.



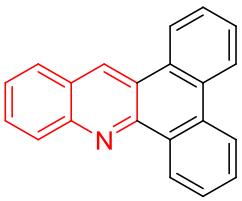
2-Phenylquinoline (8m)

The general procedure **TP7** was followed using benzo[*c*]isoxazole (37 mg, 0.3 mmol) and oxo(1-phenylvinyl)(pivaloyl)zinc (prepared from **TP6**, 0.45 mmol) for 16 h. Purification by column chromatography (*n*-hexane/EtOAc 9:1) yielded **8m** (54 mg, 87%) as a white solid. **M.p.**: 123–124 °C. **^{1}H-NMR (400 MHz, $CDCl_3$)** δ = 8.25 (d, *J* = 8.6 Hz, 1H), 8.23 – 8.15 (m, 3H), 7.91 (d, *J* = 8.6 Hz, 1H), 7.86 (dd, *J* = 8.1, 1.2 Hz, 1H), 7.76 (ddd, *J* = 8.4, 6.9, 1.5 Hz, 1H), 7.56 (tdd, *J* = 3.5, 2.5, 1.4 Hz, 3H), 7.53 – 7.46 (m, 1H). **^{13}C-NMR (125 MHz, $CDCl_3$)** δ = 157.4, 148.3, 139.7, 136.8, 129.8, 129.7, 129.3, 128.9, 127.6, 127.5, 127.2, 126.3, 119.0. **IR (Diamond-ATR, neat):** ν / cm = 3027, 1647, 1570, 1348, 1207, 957. **MS (EI, 70 eV):** m/z (%) = 205 (100). **HR-MS (EI, 70 eV)**: [$C_{15}H_{11}N$], calcd: 205.0891; found: 205.0887.



7-Bromo-2-methylquinoline (**8n**)

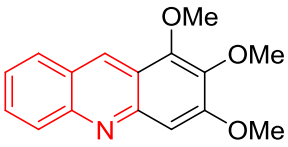
The general procedure **TP7** was followed using 5-bromobenzo[*c*]isoxazole (59 mg, 0.3 mmol) and oxo(pivaloyl)(prop-1-en-2-yl)zinc (prepared from **TP4**, 0.45 mmol) for 16 h. Purification by column chromatography (*n*-hexane/EtOAc 9:1) yielded **8n** (54 mg, 81%) as a colorless oil. **^{1}H-NMR (400 MHz, $CDCl_3$)** δ = 8.22 (d, *J* = 1.7 Hz, 1H), 8.01 (d, *J* = 8.4 Hz, 1H), 7.63 (d, *J* = 8.6 Hz, 1H), 7.56 (dd, *J* = 8.6, 1.9 Hz, 1H), 7.30 (d, *J* = 8.5 Hz, 1H), 2.75 (s, 3H). **^{13}C-NMR (100 MHz, $CDCl_3$)** δ = 160.2, 148.4, 136.0, 131.0, 129.2, 128.7, 125.1, 123.5, 122.4, 25.3. **IR (Diamond-ATR, neat):** ν / cm = 3023, 1658, 1566, 1347, 1212, 947. **MS (EI, 70 eV):** m/z (%) = 223 (25), 221 (25), 208 (100), 206 (100), 142 (40). **HR-MS (EI, 70 eV)**: [$C_{15}H_{11}N$], calcd: 220.9840; found: 220.9847.



Dibenzo[*a*,*c*]acridine (10a)

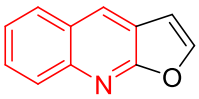
The general procedure **TP7** was followed using benzo[*c*]isoxazole (37 mg, 0.3 mmol) and Oxo(phenanthren-9-yl)(pivaloyl)zinc (prepared from **TP1**, 0.45 mmol) for 16 h. Purification by column chromatography (*n*-hexane/EtOAc 10:1) yielded **10a** (51 mg, 61%) as a white solid. **M.p.**: 204–205 °C. **^{1}H-NMR (400 MHz, $CDCl_3$)** δ = 9.58 – 9.50 (m, 1H), 9.24 (s, 1H), 8.67 – 8.61 (m, 1H), 8.60 – 8.51 (m, 2H), 8.34 (d, *J* = 8.5 Hz, 1H), 8.07 – 8.00 (m, 1H), 7.83

(ddd, *J* = 8.5, 6.7, 1.4 Hz, 1H), 7.79 – 7.74 (m, 2H), 7.70 – 7.58 (m, 3H). **^{13}C-NMR (100 MHz, $CDCl_3$)** δ = 147.6, 147.5, 132.0, 131.1, 130.2, 129.8, 129.6, 129.4, 129.1, 128.1, 128.0, 127.7, 127.6, 127.1, 126.3, 126.2, 123.6, 123.5, 123.4, 122.7. **IR (Diamond-ATR, neat):** ν / cm = 2921, 2849, 1736, 1724, 1710, 1697, 1691, 1596, 1502, 1491, 1466, 1440, 1410, 1379, 1341, 1236, 1127, 1035, 949, 902, 853, 800, 753, 720, 699, 682. **MS (EI, 70 eV):** m/z (%) = 279 (100), 280 (17), 278 (19), 139 (10). **HR-MS (EI, 70 eV):** [$C_{21}H_{13}N$], calcd: 279.1048; found: 279.1047.



1,2,3-Trimethoxyacridine (10b)

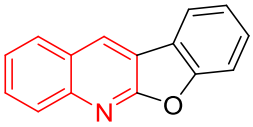
The general procedure **TP7** was followed using benzo[*c*]isoxazole (24 mg, 0.2 mmol) and oxo(pivaloyl)(3,4,5-trimethoxyphenyl)zinc (prepared from **TP6**, 0.40 mmol) for 16 h. Purification by column chromatography (*n*-hexane/EtOAc 7:1) yielded **10b** (30 mg, 55%) as a colorless oil. **^{1}H-NMR (400 MHz, $CDCl_3$)** δ = 8.86 (s, 1H), 8.05 (dd, *J* = 8.7, 1.1 Hz, 1H), 7.91 (dt, *J* = 8.4, 1.1 Hz, 1H), 7.66 (ddd, *J* = 8.7, 6.6, 1.5 Hz, 1H), 7.41 (ddd, *J* = 8.1, 6.6, 1.1 Hz, 1H), 7.23 (s, 1H), 4.09 (s, 3H), 3.99 (s, 3H), 3.95 (s, 3H). **^{13}C-NMR (100 MHz, $CDCl_3$)** δ = 157.5, 148.5, 147.3, 146.1, 140.1, 130.6, 130.1, 128.4, 125.2, 124.8, 119.5, 102.3, 61.6, 61.4, 56.3. **IR (Diamond-ATR, neat):** ν / cm = 2934, 1630, 1612, 1562, 1476, 1462, 1430, 1352, 1314, 1301, 1232, 1208, 1180, 1131, 1094, 1034, 998, 913, 829, 748. **MS (EI, 70 eV):** m/z (%) = 269 (100), 254 (64), 226 (81), 211 (68), 207 (39), 183 (35), 182 (33), 140 (64). **HR-MS (EI, 70 eV):** [$C_{16}H_{15}NO_3$], calcd: 269.1052; found: 269.1048.



Furo[2,3-*b*]quinoline (10c)

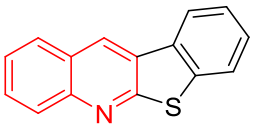
The general procedure **TP7** was followed using benzo[*c*]isoxazole (37 mg, 0.3 mmol) and furan-2-yl(oxo)(pivaloyl)zinc (prepared from **TP2**, metalation at room temperature, 0.45 mmol) for 16 h. Purification by column chromatography (*n*-hexane/EtOAc 10:1) yielded **10c** (31 mg, 61%) as a white solid. **M.p.**: 74–76 °C. **^{1}H-NMR (400 MHz, $CDCl_3$)** δ = 8.22 (d, *J* = 1.9 Hz, 1H), 8.10 (d, *J* = 8.5 Hz, 1H), 7.83 (d, *J* = 8.2 Hz, 1H), 7.71 (d, *J* = 2.6 Hz, 1H), 7.65 (ddd, *J* = 8.5, 6.8, 1.5 Hz, 1H), 7.44 (dd, *J* = 8.5, 6.8 Hz, 1H), 6.76 (t, *J* = 1.9 Hz, 1H). **^{3}C-NMR (100 MHz, $CDCl_3$)** δ = 161.5, 146.9, 144.8, 129.3, 128.9, 128.3, 127.9, 126.2, 124.7,

119.8, 105.7. **IR (Diamond-ATR, neat):** ν / cm = 3103, 1587, 1537, 1504, 1387, 1329, 1244, 1129, 1098, 1014, 912, 907, 774, 764, 754, 745, 730. **MS (EI, 70 eV):** m/z (%) = 170 (12), 169 (100), 141 (34), 140 (36), 114 (26), 113 (12). **HR-MS (EI, 70 eV)**: [$C_{11}H_7NO$], calcd: 169.0528; found: 169.0522.



Benzofuro[2,3-*b*]quinoline (10d)

The general procedure **TP7** was followed using benzo[*c*]isoxazole (37 mg, 0.3 mmol) and benzofuran-2-yl(oxo)(pivaloyl)zinc (prepared from **TP1**, 0.45 mmol) for 16 h. Purification by column chromatography (*n*-hexane/EtOAc 10:1) yielded **10d** (49 mg, 75%) as a white solid. **M.p.**: 190–192 °C. **^{1}H-NMR (400 MHz, $CDCl_3$)** δ = 8.38 (s, 1H), 7.99 (d, *J* = 8.3 Hz, 1H), 7.81 – 7.75 (m, 2H), 7.58 (ddd, *J* = 8.3, 6.7, 1.5 Hz, 1H), 7.43 (d, *J* = 8.3 Hz, 1H), 7.36 (t, *J* = 7.6 Hz, 2H), 7.20 (t, *J* = 7.6 Hz, 1H). **^{13}C-NMR (100 MHz, $CDCl_3$)** δ = 162.5, 155.8, 145.9, 129.6, 129.3, 129.0, 128.4, 128.1, 126.0, 125.0, 123.4, 122.1, 121.7, 117.6, 111.9. **IR (Diamond-ATR, neat):** ν / cm =3048, 1593, 1582, 1508, 1465, 1452, 1388, 1349, 1333, 1198, 1173, 1146, 1119, 1098, 1013, 984, 907, 864, 784, 754, 750, 720, 712, 666. **MS (EI, 70 eV):** m/z (%) = 220 (16), 219 (100), 190 (23). **HR-MS (EI, 70 eV)**: [$C_{15}H_9NO$], calcd: 219.0684; found: 219.0676.

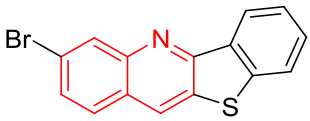


Benzo[4,5]thieno[2,3-*b*]quinoline (10e)

The general procedure **TP7** was followed using benzo[*c*]isoxazole (37 mg, 0.3 mmol) and benzo[*b*]thiophen-2-yl(oxo)(pivaloyl)zinc (prepared from **TP1**, 0.45 mmol) for 16 h. Purification by column chromatography (*n*-hexane/EtOAc 10:1) yielded **10e** (41 mg, 60%) as a white solid. **M.p.**: 140–142 °C. **^{1}H-NMR (400 MHz, $CDCl_3$)** δ = 8.68 (s, 1H), 8.18 – 8.11 (m, 2H), 7.97 (dd, *J* = 8.3, 1.5 Hz, 1H), 7.84 – 7.79 (m, 1H), 7.76 (ddd, *J* = 8.3, 6.8, 1.5 Hz, 1H), 7.59 – 7.43 (m, 3H). **^{13}C-NMR (101 MHz, $CDCl_3$)** δ = 163.2, 147.7, 138.3, 132.4, 129.7, 128.7, 128.4, 128.4, 128.1, 127.8, 125.6, 125.4, 125.0, 123.1, 122.2. **IR (Diamond-ATR, neat):** ν / cm = 3048, 2922, 2849, 1584, 1552, 1490, 1450, 1339, 1132, 1093, 1065, 1020, 954, 908, 862, 779, 760, 752, 740, 700, 689, 666. **MS (EI, 70 eV):** m/z (%) = 236 (15), 235 (100). **HR-MS (EI, 70 eV)**: [$C_{15}H_9NS_2$], calcd: 235.0456; found: 235.0450.

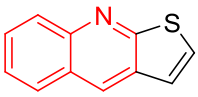
Benzo[4,5]thieno[3,2-*b*]quinoline (10f)

The general procedure **TP7** was followed using benzo[*c*]isoxazole (357 mg, 3 mmol) and benzo[*b*]thiophen-3-yl(oxo)(pivaloyl)zinc (prepared from **TP1**, 4.5 mmol) for 16 h. Purification by column chromatography (*n*-hexane/EtOAc 10:1) yielded **10f** (318 mg, 45%) as a red solid. **M.p.**: 175–177 °C. **^{1}H-NMR (400 MHz, $CDCl_3$)** δ = 8.74 – 8.68 (m, 1H), 8.62 (s, 1H), 8.34 (d, *J* = 8.5 Hz, 1H), 7.94 (dd, *J* = 8.5, 1.4 Hz, 1H), 7.90 – 7.86 (m, 1H), 7.80 (ddd, *J* = 8.5, 6.8, 1.4 Hz, 1H), 7.68 – 7.56 (m, 3H). **^{13}C-NMR (100 MHz, $CDCl_3$)** δ = 154.0, 146.4, 141.3, 134.1, 131.7, 130.0, 129.4, 129.2, 129.0, 127.1, 126.6, 126.3, 125.1, 124.1, 123.1. **IR (Diamond-ATR, neat):** ν / cm = 3103, 1587, 1537, 1504, 1387, 1329, 1244, 1129, 1098, 1014, 912, 907, 774, 764, 754, 745, 730. **MS (EI, 70 eV):** m/z (%) = 281 (13), 236 (16), 235 (100), 207 (60), 191 (14). **HR-MS (EI, 70 eV)**: [$C_{15}H_9NS$], calcd: 235.0456; found: 235.0449.



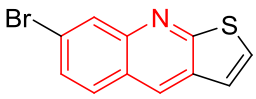
3-Bromobenzo[4,5]thieno[3,2-*b*]quinoline (10g)

The general procedure **TP7** was followed using 5-bromobenzo[*c*]isoxazole (59 mg, 0.3 mmol) and benzo[*b*]thiophen-3-yl(oxo)(pivaloyl)zinc (prepared from **TP1**, 0.45 mmol) for 16 h. Purification by column chromatography (*n*-hexane/EtOAc 10:1) yielded **10g** (39 mg, 40%) as a white solid. **M.p.**: 189–191 °C. **^{1}H-NMR (400 MHz, $CDCl_3$)** δ = 8.67 (d, *J* = 7.9 Hz, 1H), 8.59 (s, 1H), 8.52 (d, *J* = 1.8 Hz, 1H), 7.89 (dt, *J* = 7.9, 1.0 Hz, 1H), 7.81 (d, *J* = 8.8 Hz, 1H), 7.71 – 7.65 (m, 2H), 7.61 (td, *J* = 7.5, 1.0 Hz, 1H). **^{13}C-NMR (100 MHz, $CDCl_3$)** δ = 154.6, 146.9, 141.4, 133.8, 132.0, 131.7, 130.3, 129.7, 129.0, 128.3, 125.3, 125.1, 124.2, 123.1, 122.8. **IR (Diamond-ATR, neat):** ν / cm = 3051, 1603, 1591, 1546, 1476, 1445, 1338, 1168, 1078, 1054, 906, 888, 868, 799, 760, 754, 734, 740, 699, 684, 665. **MS (EI, 70 eV):** m/z (%) = 316 (15), 315 (97), 314 (15), 313 (100), 234 (35), 233 (27), 207 (26), 190 (23), 157 (12), 156 (11), 117 (16), 103 (10). **HR-MS (EI, 70 eV)**: [$C_{15}H_8BrNS$], calcd: 312.9561; found: 312.9556.



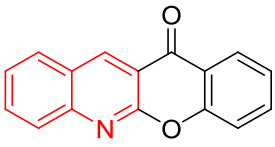
Thieno[2,3-*b*]quinoline (**10h**)

The general procedure **TP7** was followed using benzo[*c*]isoxazole (37 mg, 0.3 mmol) and oxo(pivaloyl)(thiophen-2-yl)zinc (prepared from **TP1**, metalation at room temperature, 0.45 mmol) for 16 h. Purification by column chromatography (*n*-hexane/EtOAc 10:1) yielded **10h** (32 mg, 58%) as a white solid. **M.p.**: 77–79 °C. **^{1}H-NMR (400 MHz, $CDCl_3$)** δ = 8.57 (s, 1H), 8.18 (dd, *J* = 8.6, 0.7 Hz, 1H), 8.03 – 7.96 (m, 1H), 7.77 (ddd, *J* = 8.5, 5.2, 1.4 Hz, 1H), 7.61 (d, *J* = 6.2 Hz, 1H), 7.58 (ddd, *J* = 8.1, 5.6, 1.1 Hz, 1H), 7.39 (d, *J* = 6.2 Hz, 1H). **^{13}C-NMR (100 MHz, $CDCl_3$)** δ = 163.3, 146.7, 131.5, 130.2, 129.3, 128.6, 128.4, 128.3, 125.6, 125.5, 121.2. **IR (Diamond-ATR, neat):** ν / cm = 3047, 1611, 1549, 1443, 1082, 973, 679. **MS (EI, 70 eV):** m/z (%) = 185 (100). **HR-MS (EI, 70 eV)**: [$C_{11}H_7NS$], calcd: 185.0299; found: 185.0293.



7-Bromothieno[2,3-*b*]quinoline (**10i**)

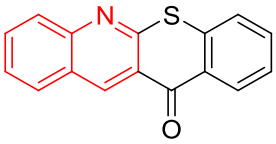
The general procedure **TP7** was followed using 5-bromobenzo[*c*]isoxazole (59 mg, 0.3 mmol) and oxo(pivaloyl)(thiophen-2-yl)zinc (prepared from **TP1**, metalation at room temperature, 0.45 mmol) for 16 h. Purification by column chromatography (*n*-hexane/EtOAc 10:1) yielded **10i** (30 mg, 38%) as a white solid. **M.p.**: 64–67 °C. **^{1}H-NMR (400 MHz, $CDCl_3$)** δ = 8.47 (s, 1H), 8.31 (d, *J* = 1.9 Hz, 1H), 7.80 (d, *J* = 8.8 Hz, 1H), 7.64 – 7.56 (m, 2H), 7.33 (d, *J* = 6.2 Hz, 1H). **^{13}C-NMR (100 MHz, $CDCl_3$)** δ = 164.1, 146.9, 131.6, 130.6, 130.0, 129.4, 129.1, 129.0, 124.0, 123.3, 121.1. **IR (Diamond-ATR, neat):** ν / cm = 3046, 1617, 1553, 1439, 1087, 954, 682. **MS (EI, 70 eV):** m/z (%) = 265 (30), 263 (30), 184 (100). **HR-MS (EI, 70 eV)**: [$C_{11}H_6BrNS$], calcd: 262.9404; found: 262.9401.



12*H*-Chromeno[2,3-*b*]quinolin-12-one (10j)

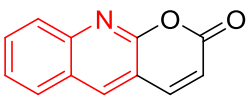
The general procedure **TP7** was followed using benzo[*c*]isoxazole (37 mg, 0.3 mmol) and benzo[*c*]isoxazole and oxo(4-oxo-4*H*-chromen-2-yl)(pivaloyl)zinc (prepared from **TP3**, metalation at -30 °C, 0.45 mmol) for 16 h. Purification by column chromatography (*n*-

hexane/EtOAc 10:1) yielded **10j** (38 mg, 51%) as a white solid. **M.p.**: 240–242 °C. **^{1}H-NMR (400 MHz, $CDCl_3$)** δ = 9.26 (s, 1H), 8.32 (dd, *J* = 7.9, 1.7 Hz, 1H), 8.11 – 8.03 (m, 2H), 7.89 (ddd, *J* = 8.5, 7.0, 1.4 Hz, 1H), 7.79 (ddd, *J* = 8.5, 7.0, 1.7 Hz, 1H), 7.64 – 7.56 (m, 2H), 7.45 – 7.37 (m, 1H). **^{13}C-NMR (100 MHz, $CDCl_3$)** δ = 178.1, 157.4, 156.2, 149.3, 140.0, 136.1, 133.5, 129.6, 128.1, 127.0, 126.4, 126.2, 124.4, 120.9, 118.4, 116.4. **IR (Diamond-ATR, neat):** ν / cm = 1670, 1618, 1599, 1494, 1466, 1414, 1402, 1378, 1331, 1299, 1258, 1215, 1118, 1025, 956, 934, 859, 800, 774, 750, 719, 687, 652. **MS (EI, 70 eV):** m/z (%) = 248 (17), 247 (100), 219 (38), 190 (22). **HR-MS (EI, 70 eV)**: [$C_{16}H_9NO_2$], calcd: 247.0633; found: 247.0628.



12*H*-Thiochromeno[2,3-*b*]quinolin-12-one (**10k**)

The general procedure **TP7** was followed using benzo[*c*]isoxazole (37 mg, 0.3 mmol) and benzo[*c*]isoxazole and oxo(4-oxothiochroman-2-yl)(pivaloyl)zinc (prepared from **TP3**, metalation at -40 °C, with 1.2 equiv of TMPZnOPiv; 0.45 mmol) for 16 h. Purification by column chromatography (*n*-hexane/EtOAc 10:1) yielded **10k** (48 mg, 61%) as a white solid. **M.p.**: 251–252 °C. **^{1}H-NMR (400 MHz, $CDCl_3$)** δ = 9.42 (s, 1H), 8.63 (dd, *J* = 8.0, 0.8 Hz, 1H), 8.11 (d, *J* = 8.7 Hz, 1H), 8.08 (d, *J* = 8.1 Hz, 1H), 7.91 (ddd, *J* = 8.5, 6.9, 1.4 Hz, 1H), 7.75 – 7.59 (m, 3H), 7.53 (ddd, *J* = 8.2, 6.7, 1.6 Hz, 1H). **^{13}C-NMR (100 MHz, $CDCl_3$)** δ = 181.3, 156.8, 149.6, 140.0, 137.7, 133.4, 133.3, 130.2, 129.9, 128.4, 127.9, 126.8, 126.5, 126.4, 126.3, 124.3. **IR (Diamond-ATR, neat):** ν / cm = 3116, 1727, 1549, 1417, 1078, 967, 672. **MS (EI, 70 eV):** m/z (%) = 263 (25), 262 (100). **HR-MS (EI, 70 eV)**: [$C_{16}H_9NOS$], calcd: 263.0405; found: 263.0403.



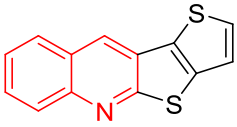
2*H*-Pyrano[2,3-*b*]quinolin-2-one (**10l**)

The general procedure **TP7** was followed using benzo[*c*]isoxazole (37 mg, 0.3 mmol) and oxo(2-oxo-2*H*-pyran-6-yl)(pivaloyl)zinc (prepared from **TP3**, metalation at -40 °C for 15 min, with 1.2 equiv of TMPMgCl and $Zn(OPiv)_2$; 0.45 mmol) for 16 h. Purification by column chromatography (*n*-hexane/EtOAc 10:1) yielded **10l** (32 mg, 55%) as a white solid. **M.p.**: 161–163 °C. **^{1}H-NMR (400 MHz, $CDCl_3$)** δ = 8.40 (s, 1H), 8.10 (d, *J* = 8.6 Hz, 1H), 7.95 (dd,

J = 8.4, 1.0 Hz, 1H), 7.90 – 7.82 (m, 2H), 7.62 (ddd, *J* = 8.1, 6.9, 1.1 Hz, 1H), 6.57 (d, *J* = 9.5 Hz, 1H). **^{13}C-NMR (100 MHz, $CDCl_3$)** δ = 1160.0, 156.2, 147.2, 141.8, 138.0, 132.3, 128.7, 128.1, 126.7, 126.3, 118.4, 114.0. **IR (Diamond-ATR, neat):** ν / cm = 3109, 1723, 1527, 1394, 1082, 958, 668. **MS (EI, 70 eV):** m/z (%) = 198 (20), 197 (100). **HR-MS (EI, 70 eV)**: [$C_{12}H_7NO_2$], calcd: 197.0477; found: 197.0483.

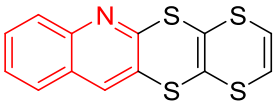
2-(1,3-Dithiol-2-ylidene)-[1,3]dithiolo[4,5-*b*]quinoline (10m)

The general procedure **TP7** was followed using benzo[*c*]isoxazole (37 mg, 0.3 mmol) and TTF-ZnOPiv (prepared from **TP3**, metalation at room temperature for 1 h, with 1.2 equiv of TMPMgCl and $Zn(OPiv)_2$; 0.45 mmol) for 16 h. Purification by column chromatography (*n*-hexane/EtOAc 10:1) yielded **10m** (47 mg, 51%) as a yellow solid. **M.p.**: 147–149 ℃. **^{1}H-NMR (400 MHz, $CDCl_3$)**: δ = 7.88 (d, *J* = 8.0 Hz, 1H), 7.84 (s, 1H), 7.68 – 7.59 (m, 2H), 7.47 (ddd, *J* = 8.1, 7.0, 1.2 Hz, 1H), 6.43 – 6.36 (m, 2H). **^{13}C-NMR (100 MHz, $CDCl_3$)**: δ = 162.7, 146.1, 131.9, 129.3, 127.9, 126.7, 126.6, 125.9, 125.8, 125.8, 118.8, 118.6. **IR (Diamond-ATR, neat):** ν / cm = 3101, 1472, 1399, 1088, 907, 671. **MS (EI, 70 eV):** m/z (%) = 305 (15), 304 (100). **HR-MS (EI, 70 eV)**: [$C_{13}H_7NS_4$], calcd: 304.9461; found: 304.9466.



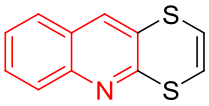
Thieno[2',3':4,5]thieno[2,3-*b*]quinoline (10n)

The general procedure **TP7** was followed using benzo[*c*]isoxazole (37 mg, 0.3 mmol) and oxo(pivaloyl)(thieno[3,2-*b*]thiophen-2-yl)zinc (prepared from **TP2**, metalation at room temperature; 0.9 mmol) for 16 h. Purification by column chromatography (*n*-hexane/EtOAc 10:1) yielded **10n** (38 mg, 53%) as a yellow solid. **M.p.**: 164–166 ℃. **^{1}H-NMR (400 MHz, $CDCl_3$)** δ = 8.44 (s, 1H), 8.06 (d, *J* = 8.5 Hz, 1H), 7.89 (dd, *J* = 8.3, 1.5 Hz, 1H), 7.67 (ddd, *J* = 8.3, 6.9, 1.5 Hz, 1H), 7.55 (d, *J* = 5.1 Hz, 1H), 7.49 (ddd, *J* = 8.3, 6.9, 1.2 Hz, 1H), 7.31 (dd, *J* = 5.1, 0.9 Hz, 1H). **^{13}C-NMR (100 MHz, $CDCl_3$)** δ = 165.8, 146.0, 137.5, 130.5, 129.3, 129.2, 128.3, 128.1, 126.4, 126.2, 125.9, 125.5, 121.3. **IR (Diamond-ATR, neat):** ν / cm = 3108, 3054, 1554, 1477, 1412, 1379, 1330, 1320, 1127, 1074, 904, 898, 778, 753, 720, 715, 666. **MS (EI, 70 eV):** m/z (%) = 242 (13), 241 (100), 196 (11). **HR-MS (EI, 70 eV)** : [$C_{13}H_7NS_2$], calcd: 241.0020; found: 241.0012.



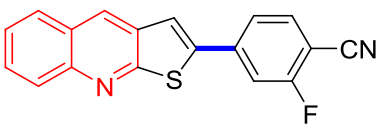
Compound (**10o**)

The general procedure **TP7** was followed using benzo[*c*]isoxazole (37 mg, 0.3 mmol) and [1,4]dithiino[2,3-*b*][1,4]dithiin-2-yl(oxo)(pivaloyl)zinc (prepared from **TP2**, metalation at -40 °C, with 1.2 equiv of TMPZnOPiv; 0.9 mmol) for 16 h. Purification by column chromatography (*n*-hexane/EtOAc 10:1) yielded **10o** (50 mg, 55%) as a yellow solid. **M.p.**: 157–159 °C. **^{1}H-NMR (400 MHz, $CDCl_3$)** δ = 8.04 (s, 1H), 8.02 – 7.95 (m, 1H), 7.76 – 7.68 (m, 2H), 7.59 – 7.50 (m, 1H), 6.54 (s, 2H). **^{13}C-NMR (100 MHz, $CDCl_3$)** δ = 157.4, 146.9, 134.6, 130.6, 128.7, 127.6, 127.2, 126.9, 126.5, 126.4, 126.4, 125.4, 121.0, 119.3. **IR (Diamond-ATR, neat):** ν / cm = 3099, 1475, 1411, 1097, 913, 665. **MS (EI, 70 eV):** m/z (%) = 305 (30), 304 (100). **HR-MS (EI, 70 eV)**: [$C_{13}H_7NS_4$], calcd: 304.9461; found: 304.9466.



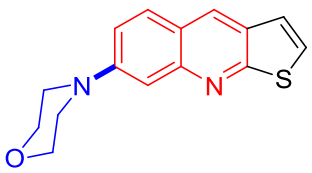
[1,4]Dithiino[2,3-*b*]quinoline (10p)

The general procedure **TP7** was followed using benzo[*c*]isoxazole (37 mg, 0.3 mmol) and [1,4]dithiino[2,3-*b*][1,4]dithiin-2-yl(oxo)(pivaloyl)zinc (prepared from **TP2**, metalation at –30 °C; 0.45 mmol) for 16 h. Purification by column chromatography (*n*-hexane/EtOAc 10:1) yielded **10p** (52 mg, 80%) as a slight yellow solid. **M.p.**: 95–97 °C. **^{1}H-NMR (400 MHz, $CDCl_3$)** δ = 7.82 – 7.77 (m, 1H), 7.70 (s, 1H), 7.55 – 7.47 (m, 2H), 7.37 – 7.29 (m, 1H), 6.40 (d, *J* = 8.1 Hz, 1H), 6.25 (d, *J* = 8.1 Hz, 1H). **^{13}C-NMR (100 MHz, $CDCl_3$)** δ = 155.5, 146.8, 133.2, 130.0, 128.3, 127.3, 126.9, 126.9, 124.7, 122.2, 119.6. **IR (Diamond-ATR, neat):** ν / cm = 3026, 2963, 2921, 2866, 1612, 1577, 1553, 1483, 1377, 1362, 1319, 1295, 1198, 1150, 1135, 1119, 1015, 985, 951, 900, 855, 803, 774, 750, 660. **MS (EI, 70 eV):** m/z (%) = 218 (12), 217 (100), 215 (20), 185 (27), 173 (24), 172 (11), 141 (21), 140 (15). **HR-MS (EI, 70 eV)**: [$C_{11}H_7NS_2$], calcd: 217.0020; found: 217.009.



2-Fluoro-4-(thieno[2,3-*b*]quinolin-2-yl)benzonitrile (**12**)

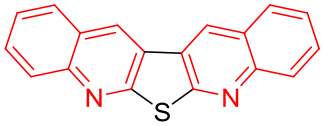
To a suspension of compound **10h** (37 mg, 0.2 mmol) in anhydrous THF (1.0 mL) was added a solution of TMPMgCl·LiCl (1.2 equiv, 1.07 M) at 0℃ under an atmosphere of N_2. The mixture was stirred at the same temperature for 1 h, then $Zn(OPiv)_2$ (64 mg, 0.24 mmol, 1.2 equiv) was added and the mixture stirred for another 15 min. 4-Bromo-2-fluorobenzonitrile (48 mg, 0.24 mmol), $Pd(OAc)_2$ (0.9 mg, 2 mol %) and X-phos (4.0 mg, 4 mol %) were added, and the reaction mixture was stirred at 50℃ for another 12 h.[4] At ambient temperature, the reaction mixture was extracted with DCM (3 × 20 mL) and the combined organic layers were washed with brine, and dried over Na_2SO_4. The solvent was evaporated *in vacuo* and the remaining residue was purified by column chromatography on silica gel (*n*-hexane/EtOAc/DCM 6:1:1) to yield product **12** (46 mg, 75%) as a colorless solid. **M.p.** = 227−229 ℃. **^{1}H-NMR (400 MHz, $CDCl_3$)** δ = 8.58 (s, 1H), 8.17 (d, J = 8.6 Hz, 1H), 8.00 (d, J = 8.2 Hz, 1H), 7.81 (ddd, J = 8.5, 6.8, 1.4 Hz, 1H), 7.77 – 7.70 (m, 2H), 7.67 (dd, J = 8.1, 1.6 Hz, 1H), 7.65 – 7.58 (m, 2H). **^{13}C-NMR (100 MHz, $CDCl_3$)** δ = 163.4 (d, $J_{C–F}$ = 259.6 Hz), 162.6, 147.3, 141.5 (d, $J_{C–F}$ = 2.5 Hz), 140.8 (d, $J_{C–F}$ = 8.4 Hz), 134.1, 132.5, 131.1, 130.2, 128.5, 126.1, 122.8 (d, $J_{C–F}$ = 3.4 Hz), 119.7, 114.2 (d, $J_{C–F}$ = 21.3 Hz), 113.7, 101.2 (d, $J_{C–F}$ = 15.8 Hz). ^{19}F-NMR ($CDCl_3$, 377 MHz): δ = -105.33 (dd, J = 9.8, 6.5 Hz). **IR (Diamond-ATR, neat):** ν / cm = 3119, 1805, 1521, 1433, 1127, 917. **MS (EI, 70 eV):** m/z (%) = 305 (25), 304 (100). **HR-MS (EI, 70 eV)**: [$C_{18}H_9FN_2S$], calcd: 304.0470; found: 304.0474.



4-(Thieno[2,3-*b*]quinolin-7-yl)morpholine (**13**)

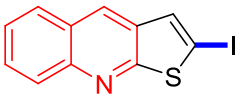
A suspension of compound **10h** (37 mg, 0.2 mmol) and $Pd_2(dba)_3$ (9.2 mg, 5 mol %), Xantphos (11.6 mg, 10 mol %), NaO^{t}Bu (38.4 mg, 2.0 equiv), morpholine (35.0 mg, 2.0 equiv) in anhydrous PhMe (2.0 mL) was stirred at 80℃ for 12 under an atmosphere of N_2.[5]. At ambient temperature, the reaction mixture was extracted with DCM (3 × 20 mL) and the combined organic layers were washed with brine, and dried over Na_2SO_4. The solvent was evaporated *in vacuo* and the remaining residue was purified by column chromatography on silica gel (*n*-hexane/EtOAc 7:1) to yield product **13** (39 mg, 72%) as a colorless solid. **M.p.** = 136−139 ℃. **^{1}H-NMR (400 MHz, $CDCl_3$)** δ = 8.37 (s, 1H), 7.80 (d, J = 9.1 Hz, 1H), 7.41 (d, J = 6.1 Hz, 1H), 7.35 (d, J = 2.1 Hz, 1H), 7.30 (dd, J = 9.2, 2.5 Hz, 1H), 7.27 (d, J = 6.2 Hz, 1H), 3.96 – 3.86 (m, 4H), 3.40 – 3.31 (m, 4H). **^{13}C-NMR (100 MHz, $CDCl_3$)** δ = 163.8, 151.8, 148.4, 129.6, 129.5, 128.9, 126.1, 121.3, 120.5, 118.3, 109.1, 66.7, 48.9. **IR**

(Diamond-ATR, neat): ν / cm = 3312, 1655, 1519, 1439, 1136, 918. **MS (EI, 70 eV):** m/z (%) = 271 (35), 270 (100). **HR-MS (EI, 70 eV)**: [$C_{15}H_{14}N_2OS$], calcd: 270.0827; found: 270.0832.



Compound (**14**)

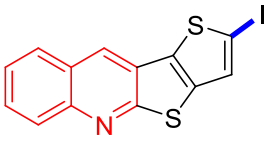
To a suspension of compound **10h** (56 mg, 0.3 mmol) in anhydrous THF (1.0 mL) was added a solution of TMPMgCl·LiCl (1.2 equiv, 1.07 M) at 0 ℃ under an atmosphere of N_2. The mixture was stirred at the same temperature for 1 h, then $Zn(OPiv)_2$ (96 mg, 0.36 mmol, 1.2 equiv) was added and the mixture stirred for another 15 min. Anthranil (24 mg, 0.2 mmol) and $CoCl_2$ (2.6 mg, 10 mol %) were added, and the reaction mixture was stirred at room temperature for another 16 h. At ambient temperature, the reaction mixture was extracted with DCM (3 × 20 mL) and the combined organic layers were washed with brine, and dried over Na_2SO_4. The solvent was evaporated *in vacuo* and the remaining residue was purified by column chromatography on silica gel (*n*-hexane/EtOAc/DCM 15:1:10) to yield product **14** (20 mg, 34%) as a slight yellow solid. **M.p.** = 261−264 ℃. **^{1}H-NMR (400 MHz, $CDCl_3$)** δ = 8.82 (s, 2H), 8.17 (d, *J* = 8.5 Hz, 2H), 8.03 (d, *J* = 8.1 Hz, 2H), 7.81 (ddd, *J* = 8.3, 6.9, 1.4 Hz, 2H), 7.65 – 7.59 (m, 2H). **^{13}C-NMR (100 MHz, $CDCl_3$)** δ = 161.9, 148.3, 130.5, 128.5, 128.4, 128.4, 126.6, 126.2, 125.8. **IR (Diamond-ATR, neat):** ν / cm = 3132, 1541, 1421, 1098, 677. **MS (EI, 70 eV):** m/z (%) = 287 (15), 286 (100). **HR-MS (EI, 70 eV)**: [$C_{18}H_{10}N_2S$], calcd: 286.0565; found: 286.0571.



2-Iodothieno[2,3-*b*]quinoline (**11a**)

To a suspension of compound **10h** (28 mg, 0.15 mmol) in anhydrous THF (1.0 mL) was added a solution of TMPMgCl·LiCl (1.2 equiv, 1.07 M) under an atmosphere of N_2. The mixture was stirred at room temperature for 16 h, then a soultion of I_2 (76 mg, 0.3 mmol, 0.3 M) was added and the mixture stirred for another 30 min. At ambient temperature, the reaction mixture was extracted with DCM (2 × 10 mL) and the combined organic layers were washed with brine, and dried over Na_2SO_4. The solvent was evaporated *in vacuo* and the remaining residue was purified by column chromatography on silica gel (*n*-hexane/EtOAc

15:1) to yield product **11a** (42 mg, 90%) as a slight yellow solid. **M.p.** = 107−109 ℃. **^{1}H-NMR (400 MHz, $CDCl_3$)** δ = 8.44 (s, 1H), 8.12 (dd, *J* = 8.6, 0.7 Hz, 1H), 8.00 – 7.94 (m, 1H), 7.78 (ddd, *J* = 8.5, 6.8, 1.4 Hz, 1H), 7.66 (s, 1H), 7.57 (ddd, *J* = 11.1, 6.1, 2.7 Hz, 1H). **^{13}C-NMR (125 MHz, $CDCl_3$)** δ = 166.5, 146.2, 133.0, 131.1, 129.8, 128.4, 128.3, 126.0, 125.6, 82.7. **R (Diamond-ATR, neat):** ν / cm = 3102, 1569, 1472, 1156, 711. **MS (EI, 70 eV):** m/z (%) = 312 (10), 311 (100), 184 (35). **HR-MS (EI, 70 eV)**: [$C_{11}H_6INS$], calcd: 310.9266; found: 310.9274.



Compound (**11b**)

To a suspension of compound **10n** (35 mg, 0.15 mmol) in anhydrous THF (1.0 mL) was added a solution of TMPMgCl·LiCl (1.2 equiv, 1.07 M) under an atmosphere of N_2. The mixture was stirred at room temperature for 16 h, then a soultion of I_2 (76 mg, 0.3 mmol, 0.3 M) was added and the mixture stirred for another 30 min. At ambient temperature, the reaction mixture was extracted with DCM (2 × 10 mL) and the combined organic layers were washed with brine, and dried over Na_2SO_4. The solvent was evaporated *in vacuo* and the remaining residue was purified by column chromatography on silica gel (*n*-hexane/EtOAc 15:1) to yield product **11b** (54 mg, 98%) as a slight yellow solid. **M.p.** = 128−130 ℃. **^{1}H-NMR (400 MHz, $CDCl_3$)** δ = 8.44 (s, 1H), 8.13 (d, *J* = 8.6 Hz, 1H), 7.96 (d, *J* = 8.3 Hz, 1H), 7.75 (dd, *J* = 11.3, 4.1 Hz, 1H), 7.62 – 7.55 (m, 1H), 7.53 (s, 1H). **^{13}C-NMR (100 MHz, $CDCl_3$)** δ = 164.9, 146.0, 137.8, 135.6, 130.3, 129.5, 128.3, 128.1, 126.7, 126.1, 125.4, 125.4. **IR (Diamond-ATR, neat):** ν / cm = 3092, 1572, 1419, 1106, 692. **MS (EI, 70 eV):** m/z (%) = 368 (15), 367 (100), 240 (60). **HR-MS (EI, 70 eV)**: [$C_{13}H_6INS_2$], calcd: 366.8986; found: 366.8995.

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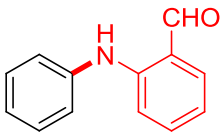
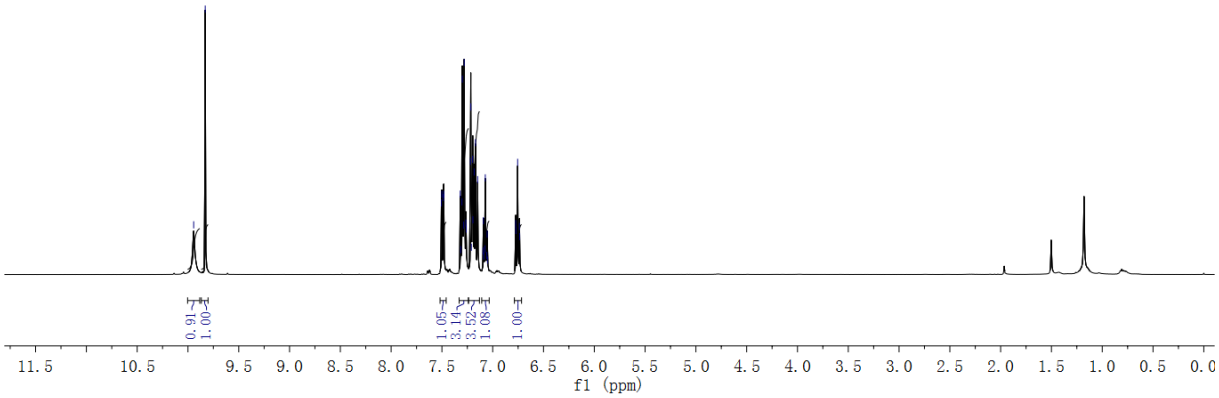
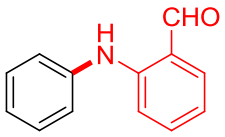
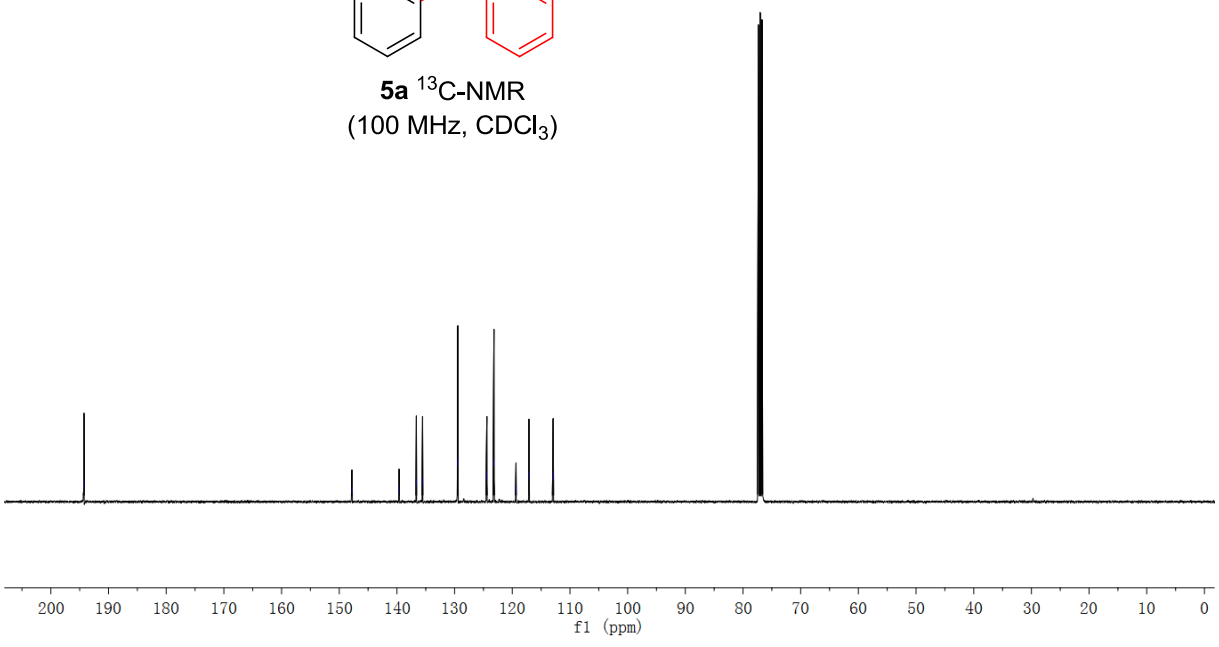


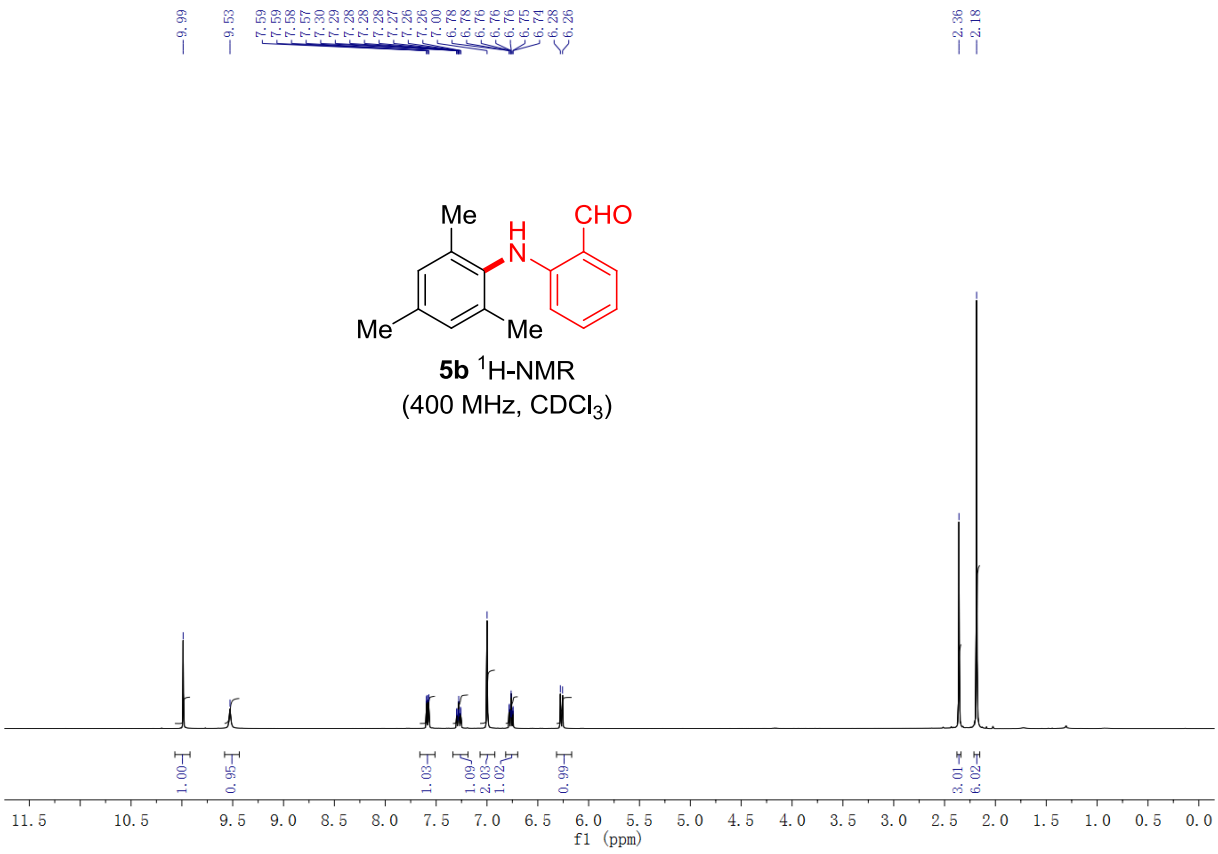
5a ^{1}H-NMR
(400 MHz, $CDCl_3$)



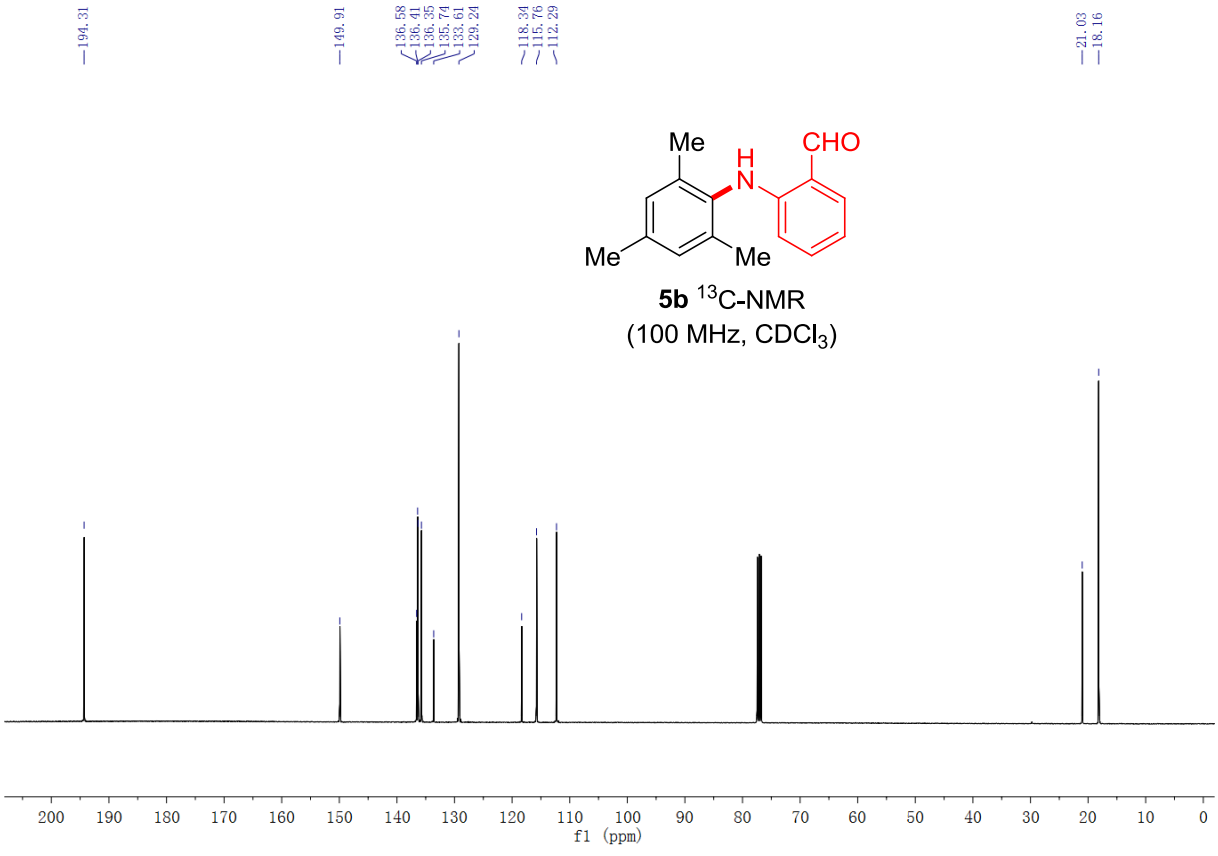


5a ^{13}C-NMR
(100 MHz, $CDCl_3$)

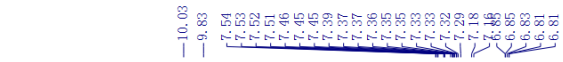


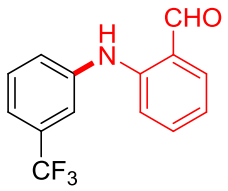


5b ^{1}H-NMR
(400 MHz, $CDCl_3$)

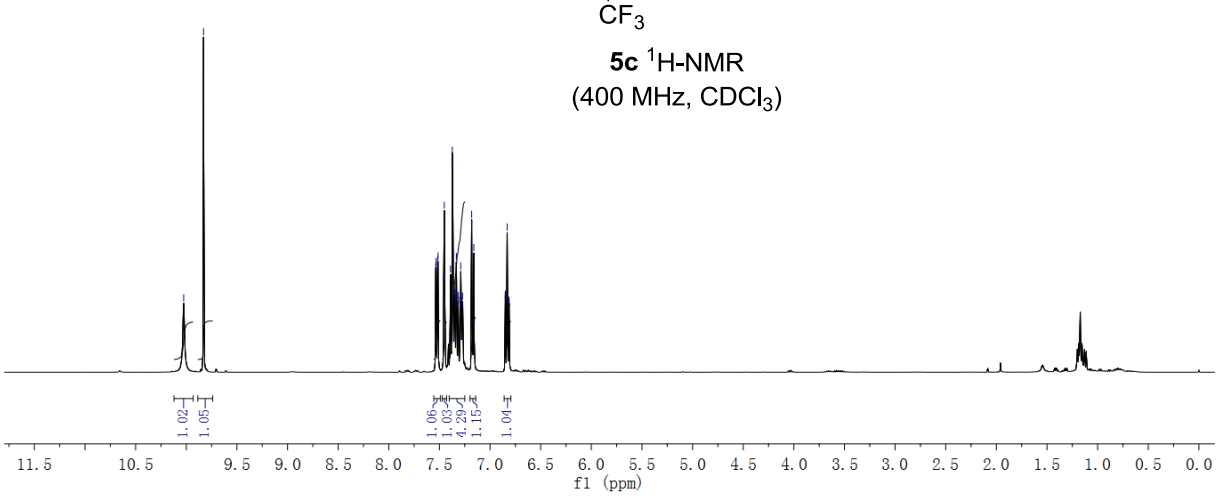


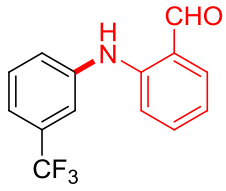
5b ^{13}C-NMR
(100 MHz, $CDCl_3$)



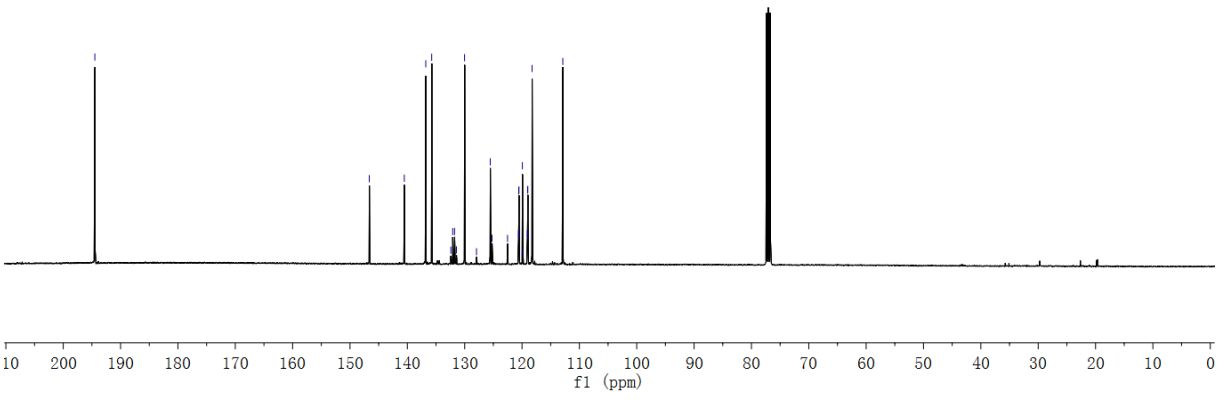


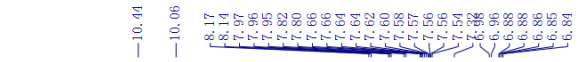
5c ^{1}H-NMR
(400 MHz, $CDCl_3$)

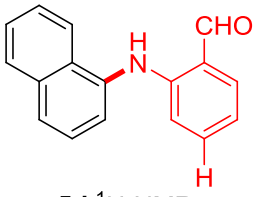




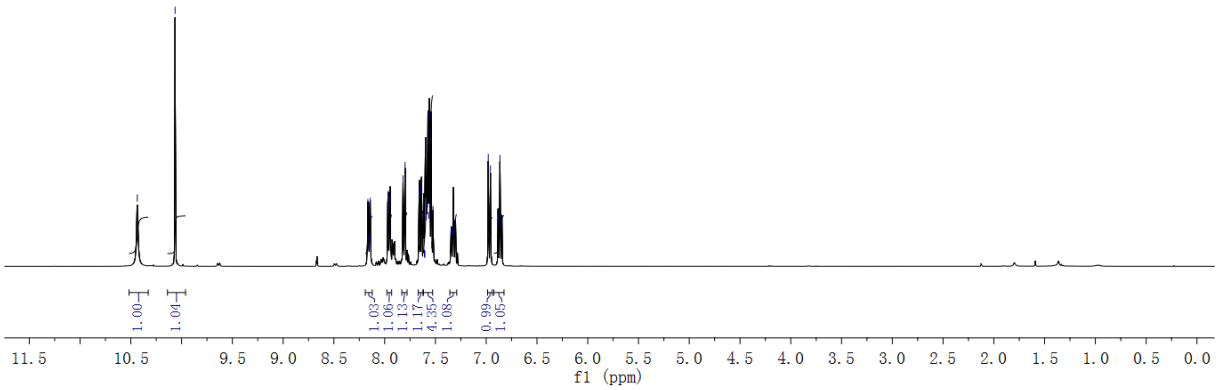
5c ^{13}C-NMR
(100 MHz, $CDCl_3$)

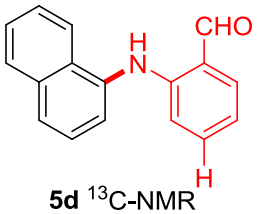




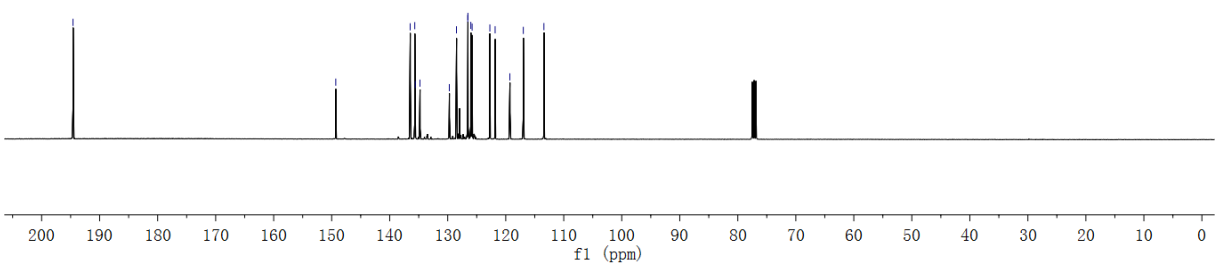


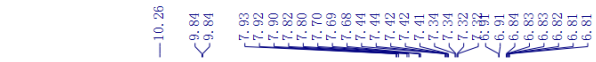
5d ^{1}H-NMR
(400 MHz, $CDCl_3$)

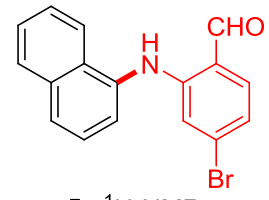




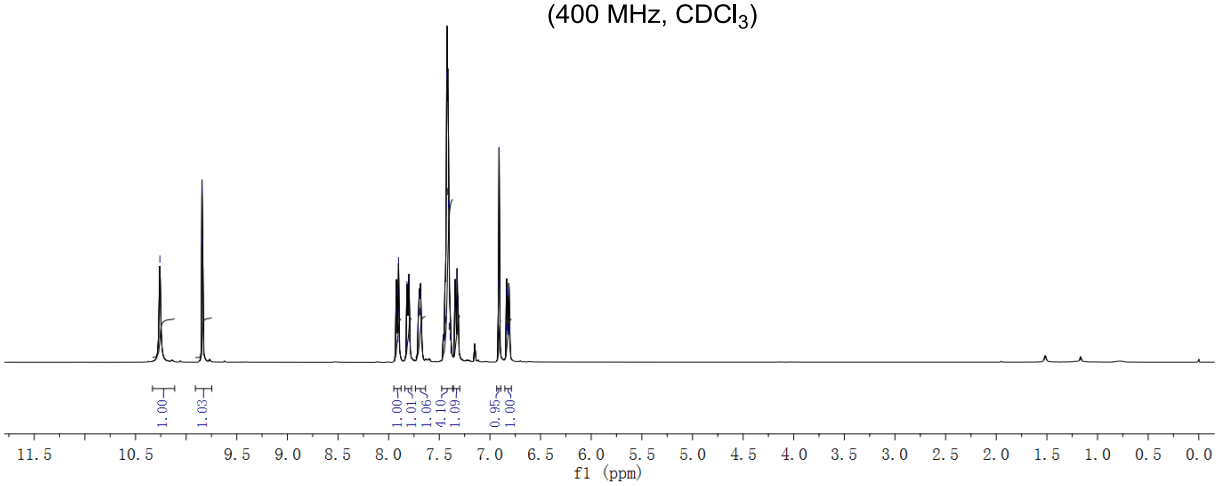
5d ^{13}C-NMR
(100 MHz, $CDCl_3$)

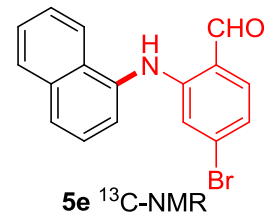




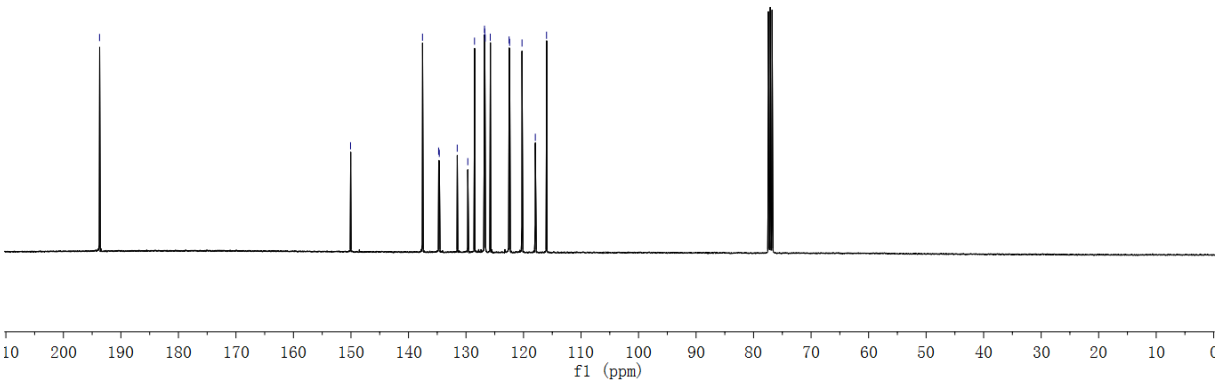


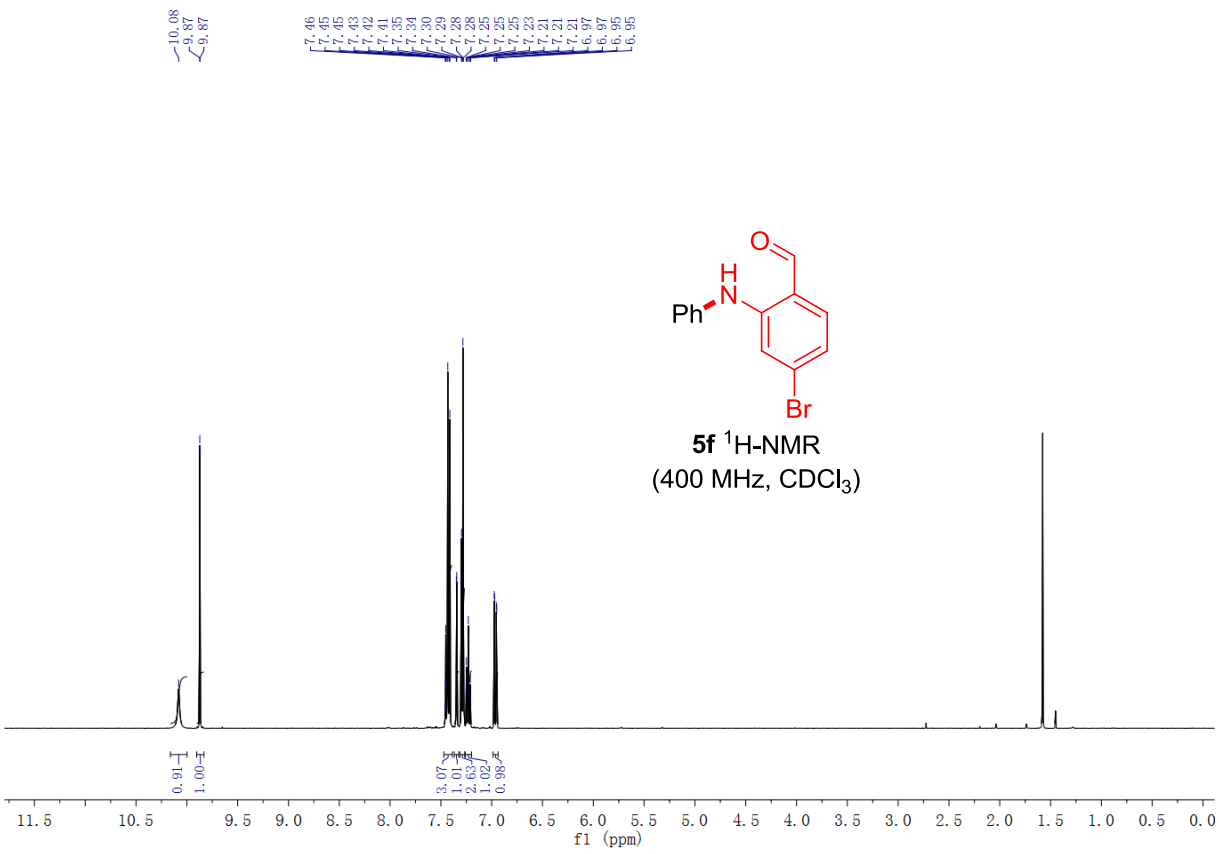
5e ^{1}H-NMR
(400 MHz, $CDCl_3$)



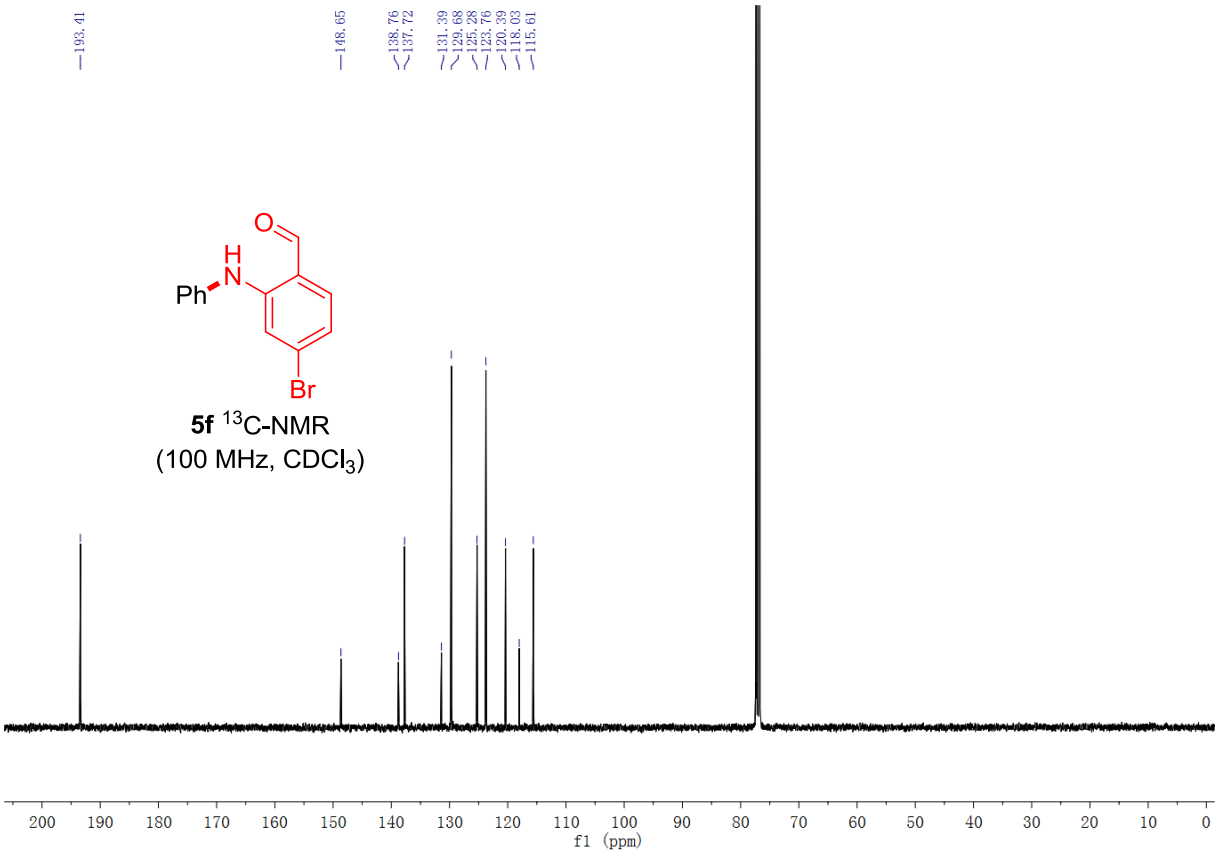


5e ^{13}C-NMR
(100 MHz, $CDCl_3$)

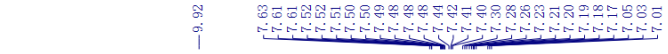


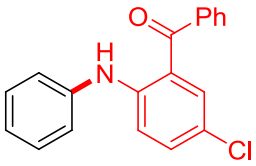


5f ^{1}H-NMR
(400 MHz, $CDCl_3$)

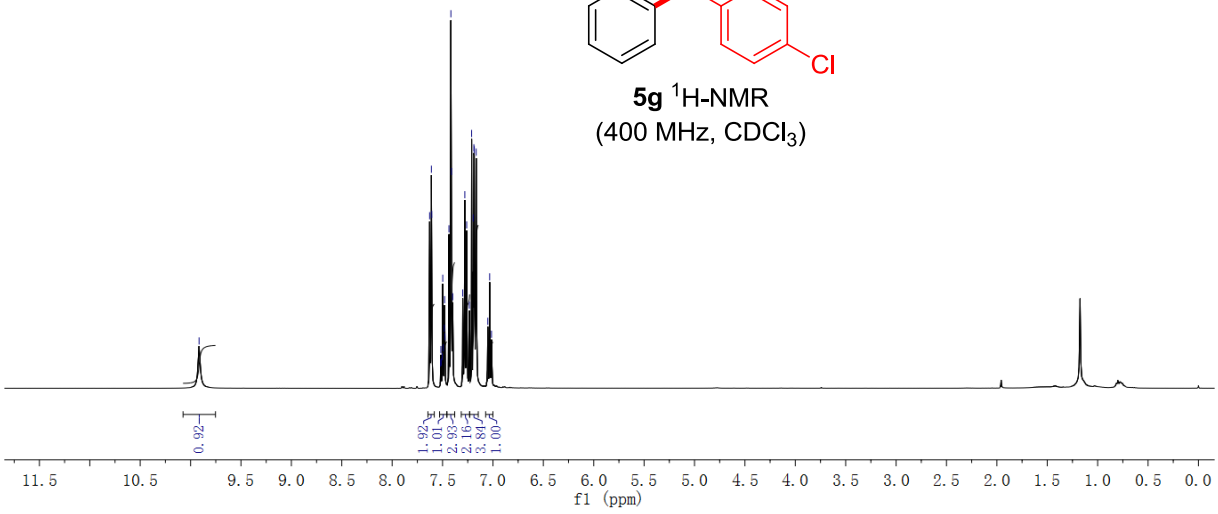


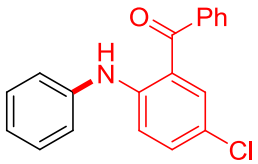
5f ^{13}C-NMR
(100 MHz, $CDCl_3$)



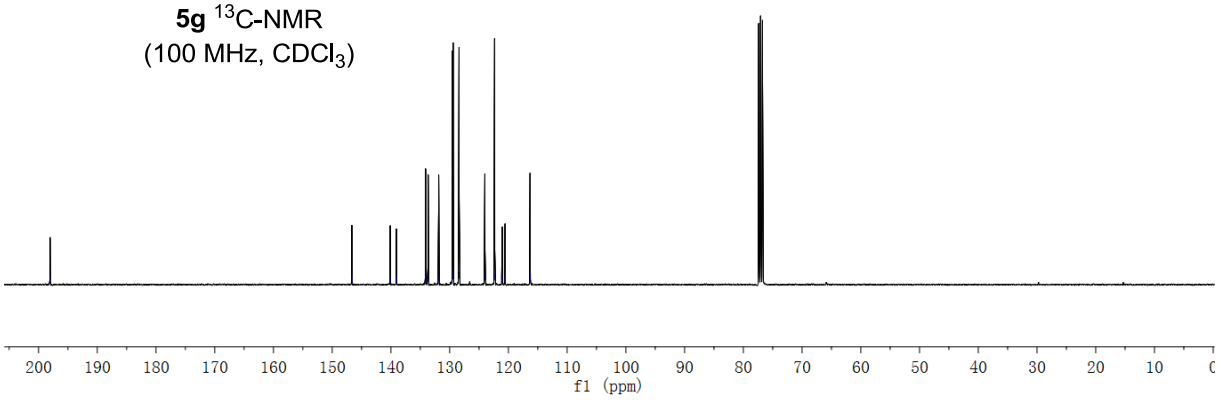


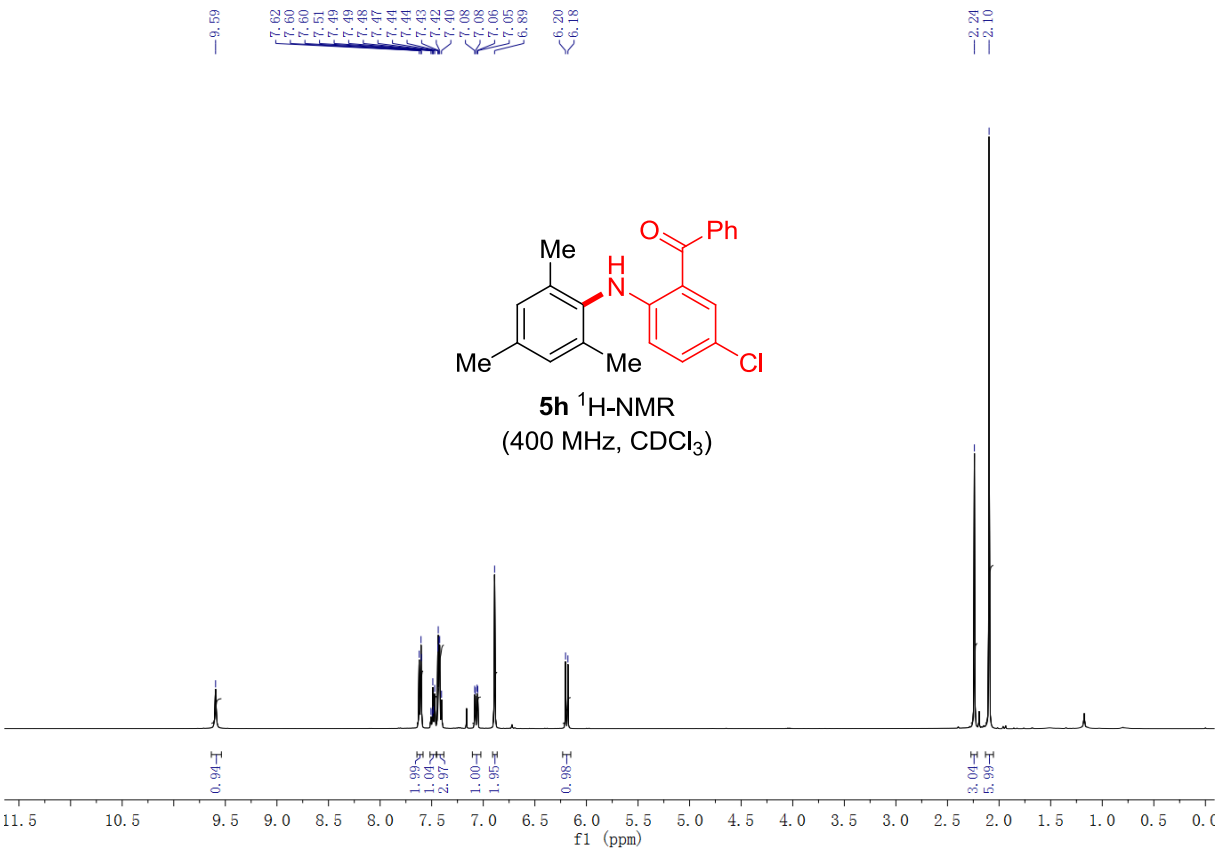
5g ^{1}H-NMR
(400 MHz, $CDCl_3$)



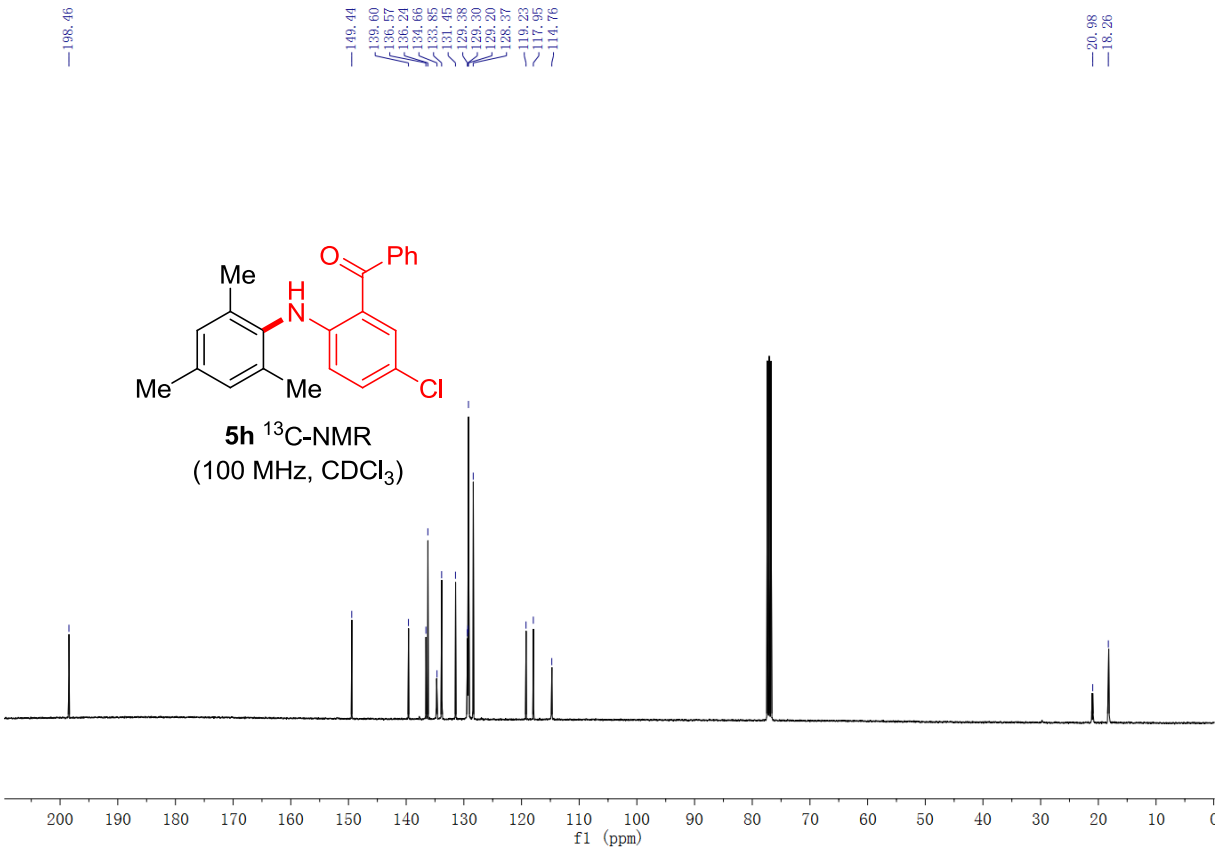


5g ^{13}C-NMR
(100 MHz, $CDCl_3$)

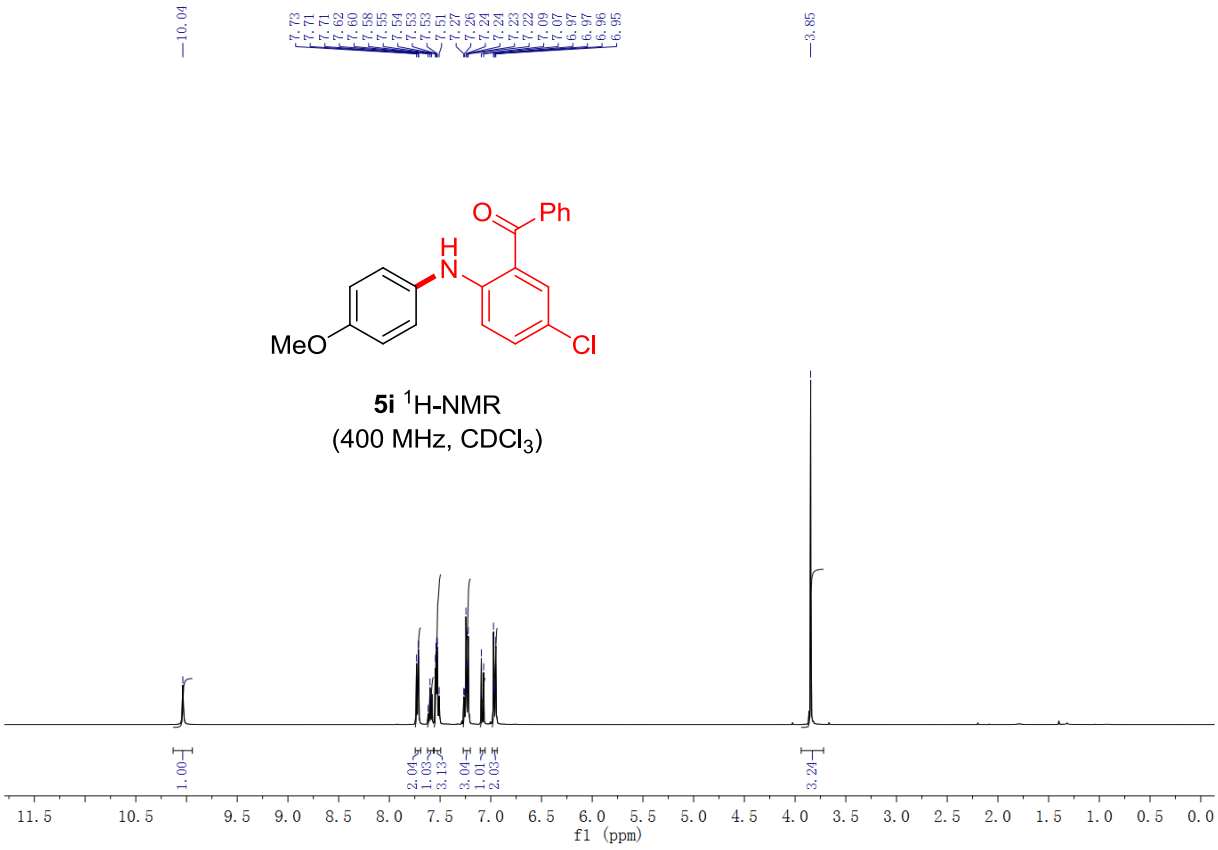




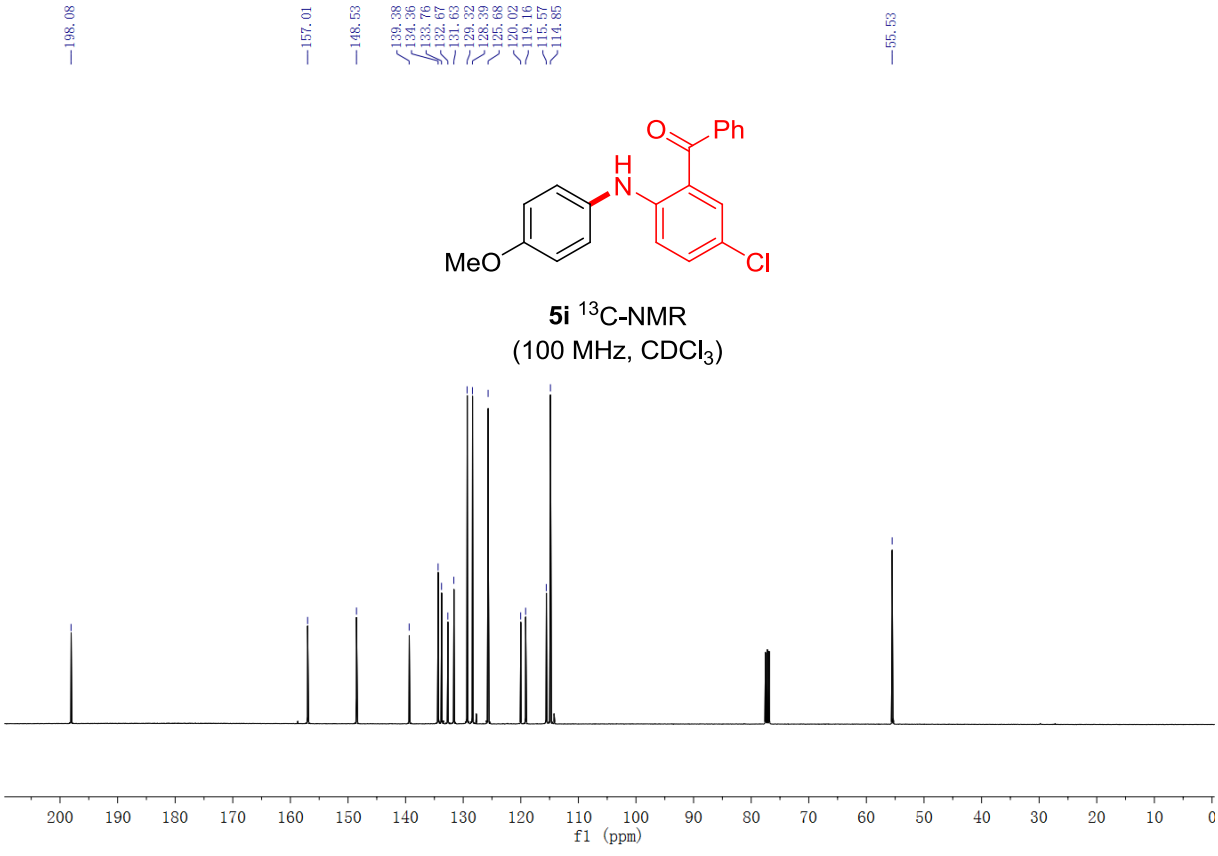
5h ^{1}H-NMR
(400 MHz, $CDCl_3$)



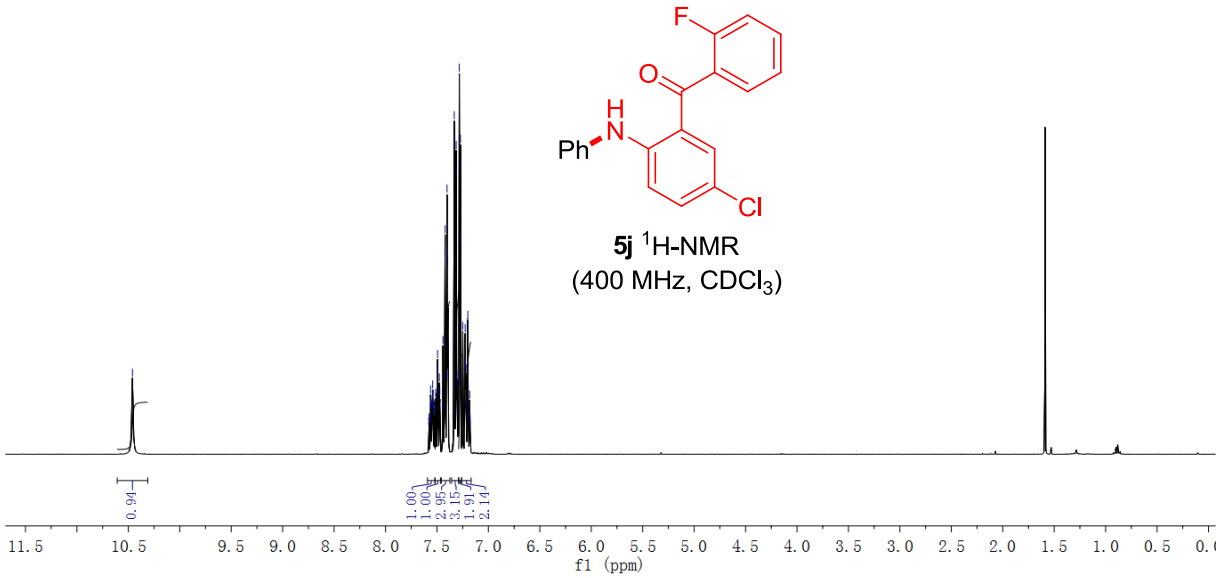
5h ^{13}C-NMR
(100 MHz, $CDCl_3$)



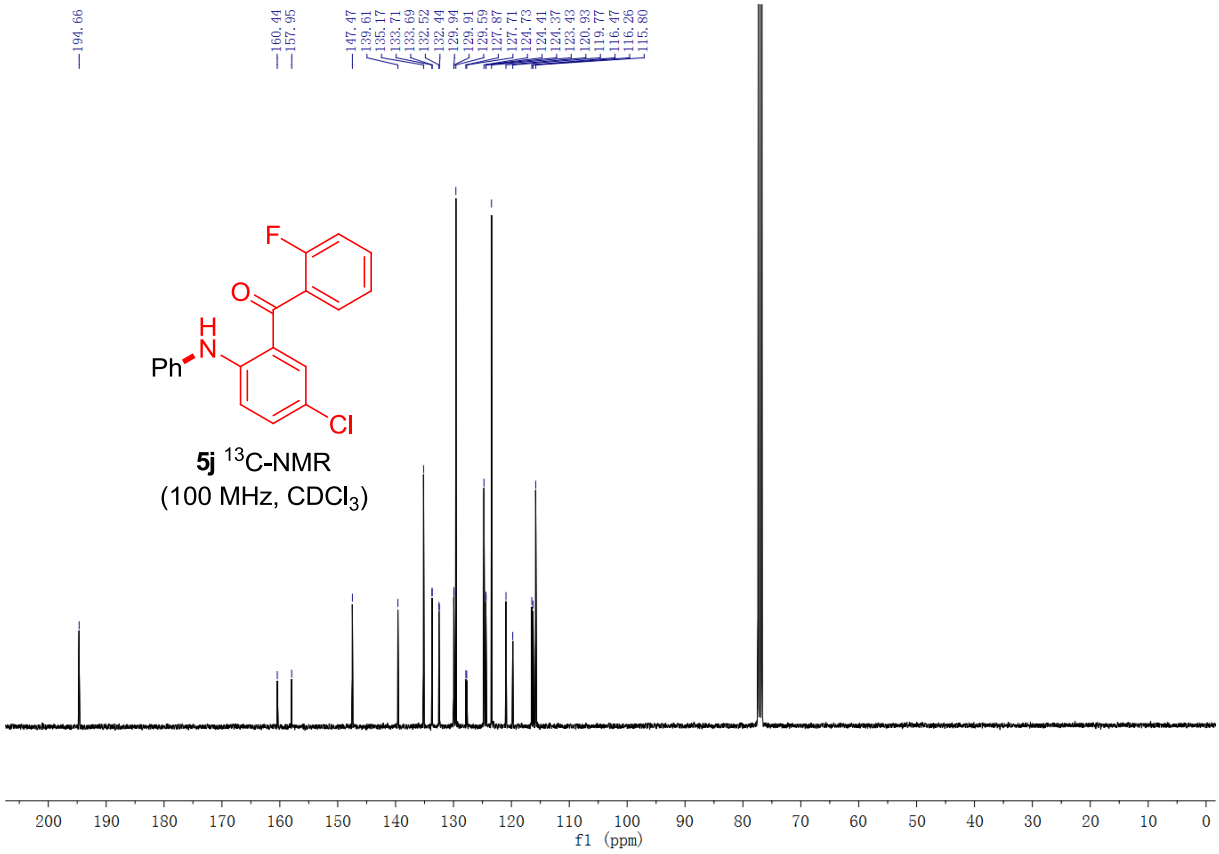
5i ^{1}H-NMR
(400 MHz, $CDCl_3$)



5i ^{13}C-NMR
(100 MHz, $CDCl_3$)



5j ^{1}H-NMR
(400 MHz, $CDCl_3$)



5j ^{13}C-NMR
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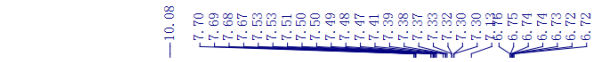
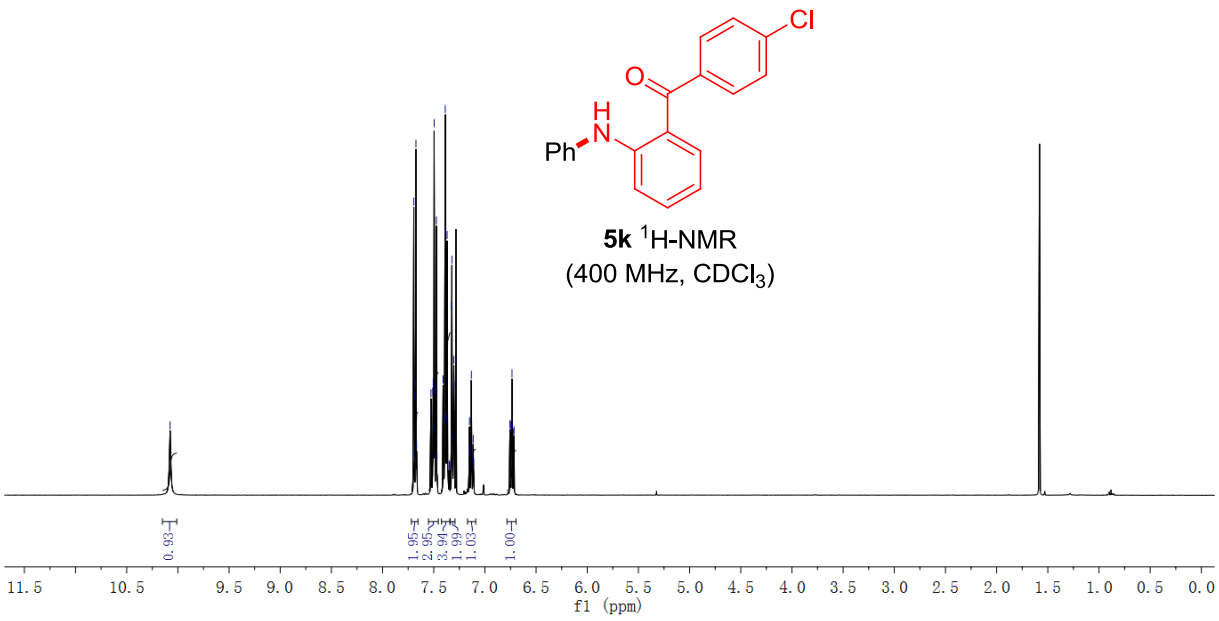
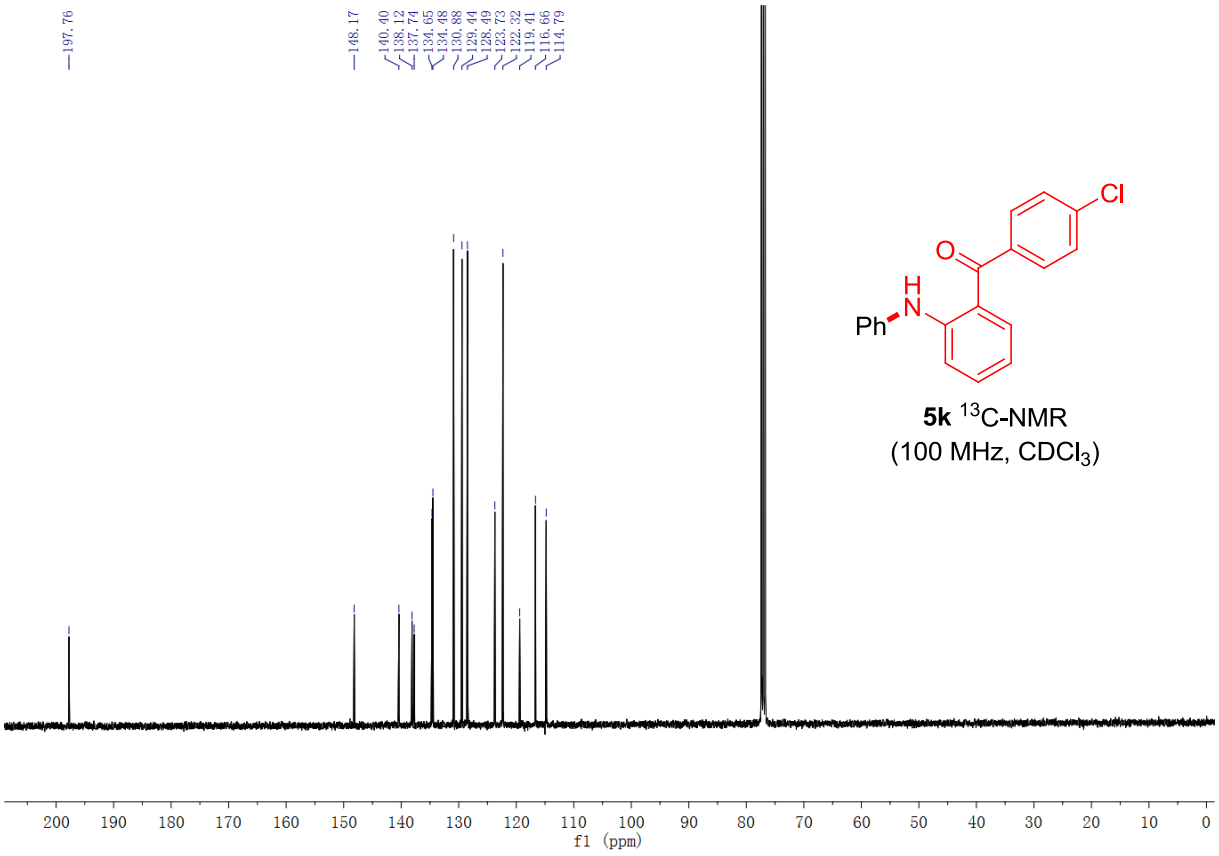
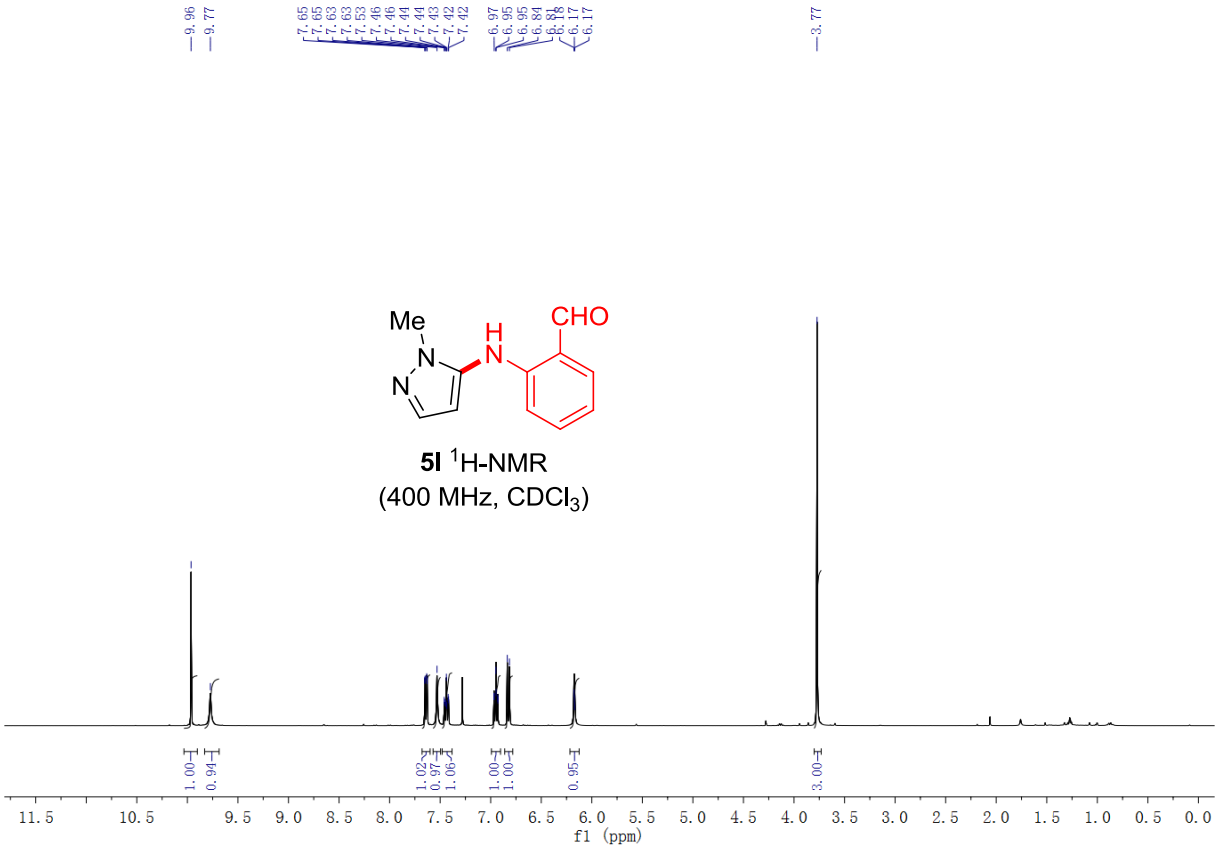




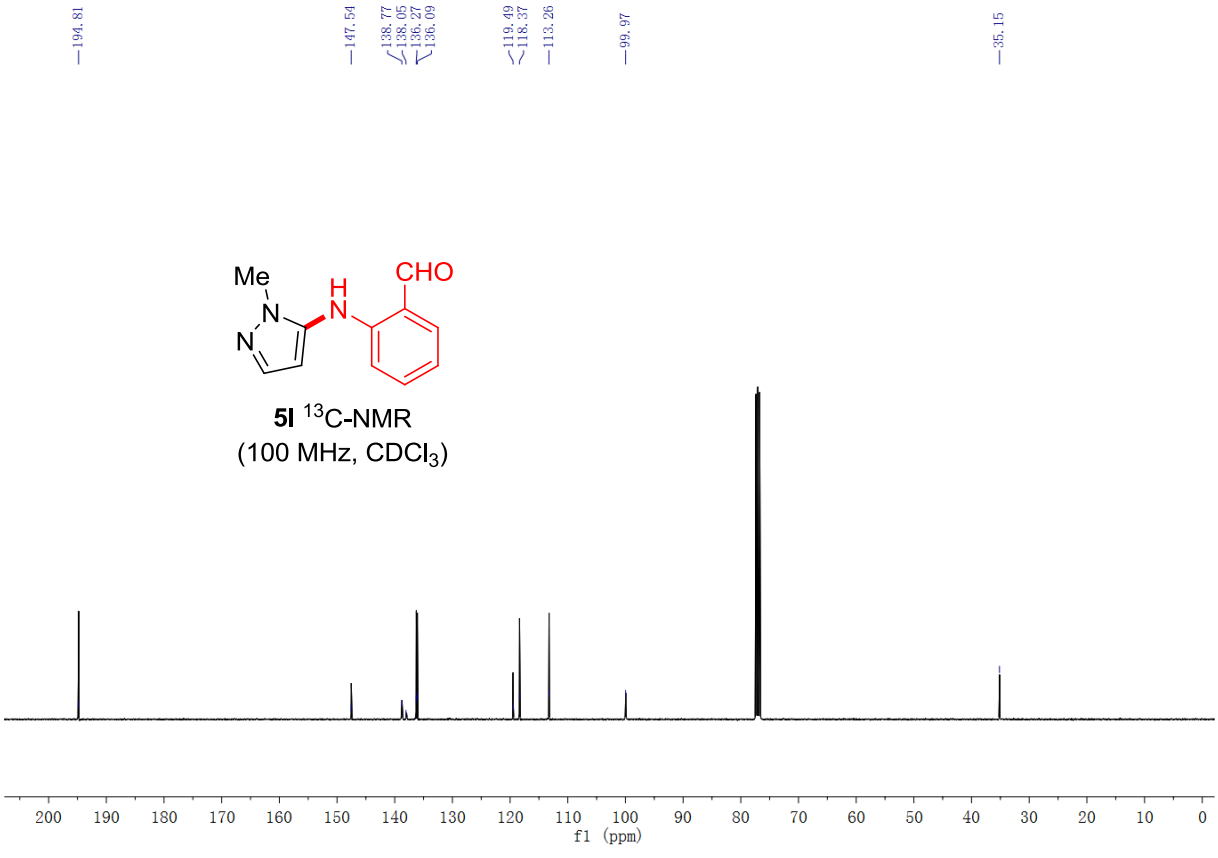
5k ^{1}H-NMR
(400 MHz, $CDCl_3$)



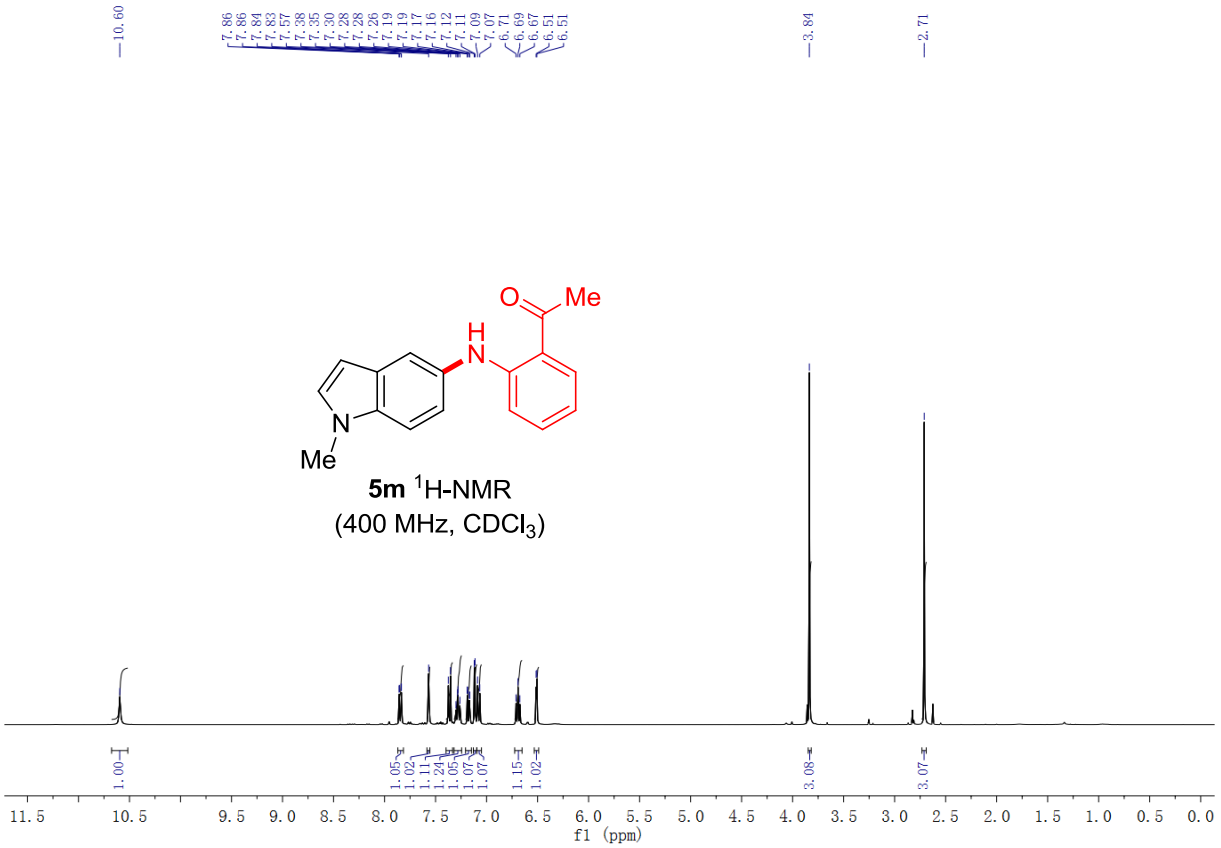
5k ^{13}C-NMR
(100 MHz, $CDCl_3$)



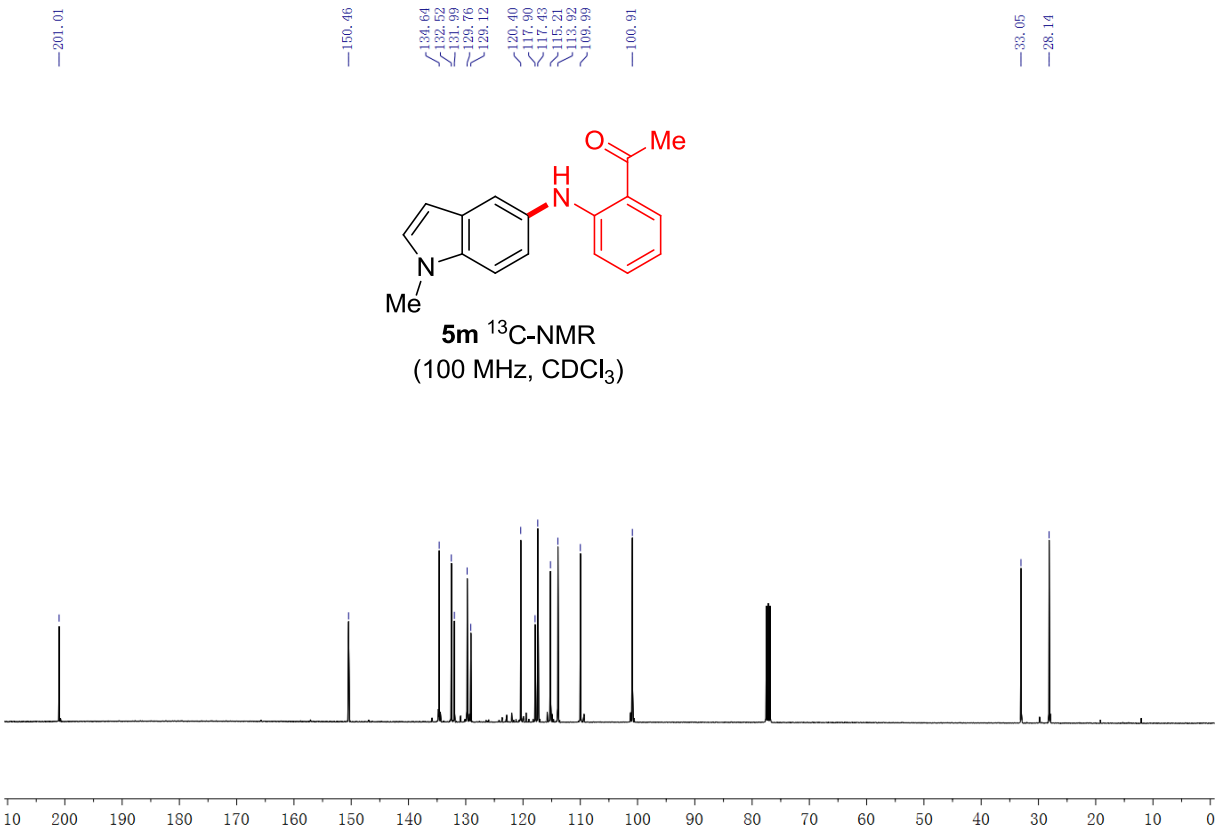
5l ^{1}H-NMR
(400 MHz, $CDCl_3$)



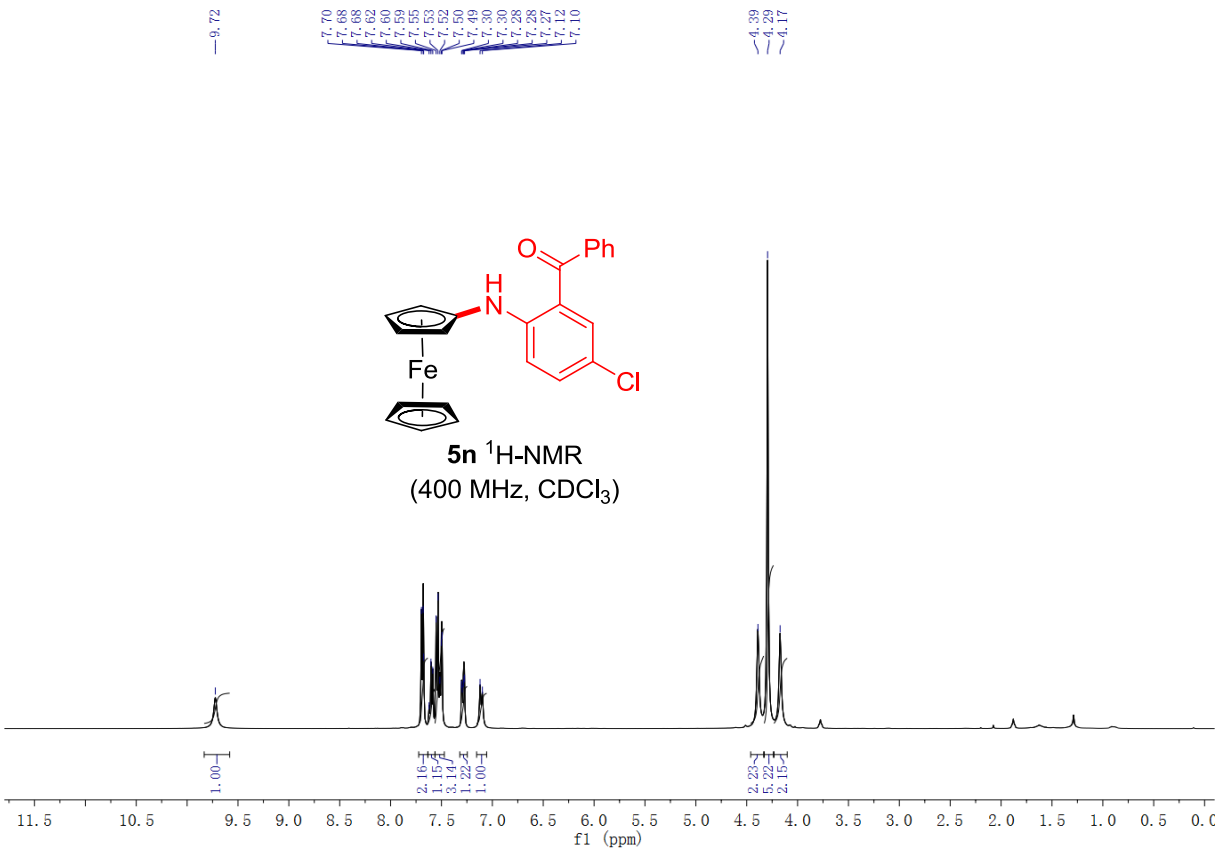
5l ^{13}C-NMR
(100 MHz, $CDCl_3$)



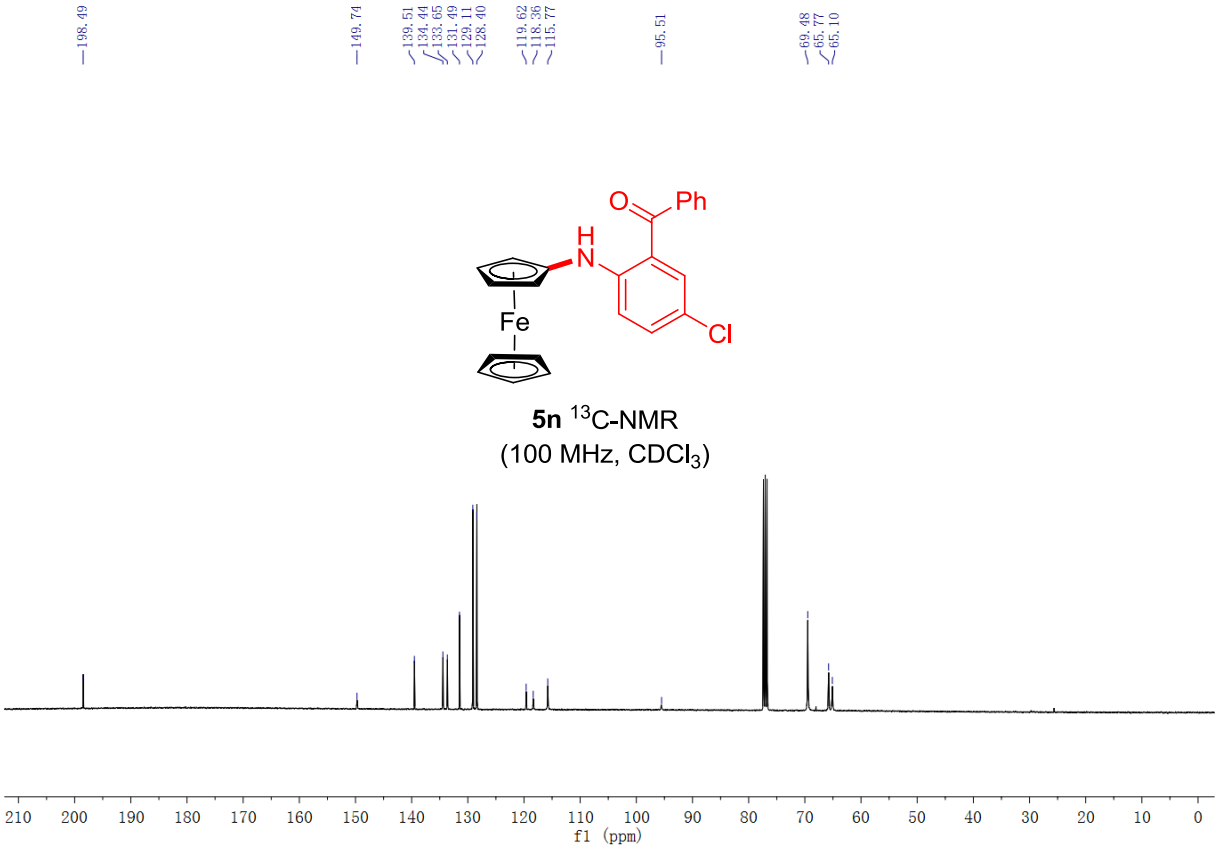
5m ^{1}H-NMR
(400 MHz, $CDCl_3$)



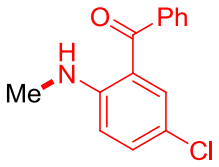
5m ^{13}C-NMR
(100 MHz, $CDCl_3$)



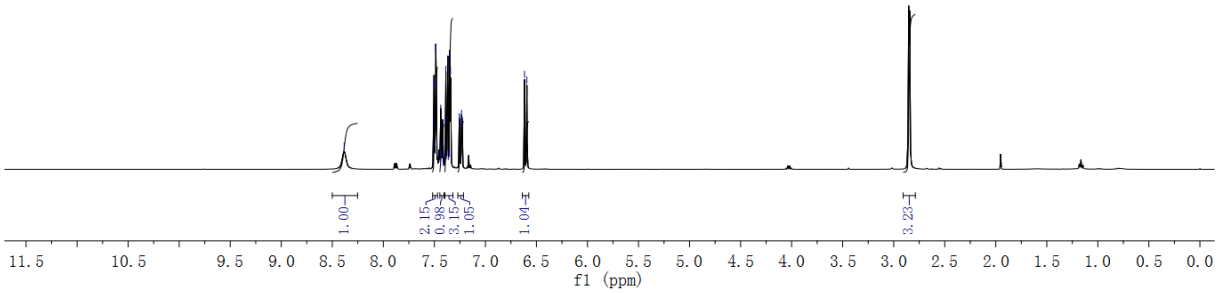
5n ^{1}H-NMR
(400 MHz, $CDCl_3$)

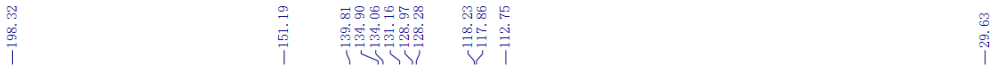


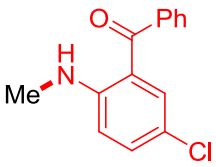
5n ^{13}C-NMR
(100 MHz, $CDCl_3$)



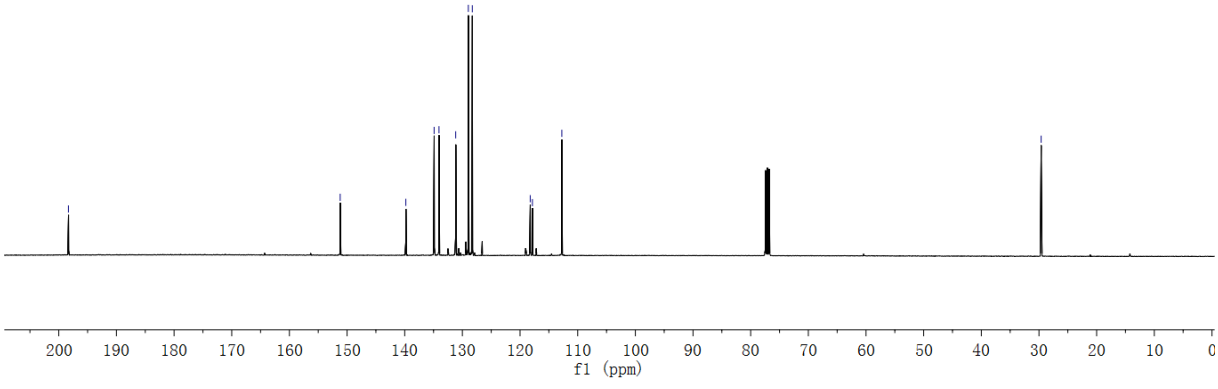
5p ^{1}H-NMR
(400 MHz, $CDCl_3$)

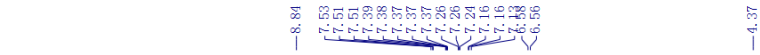


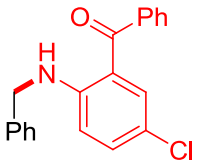




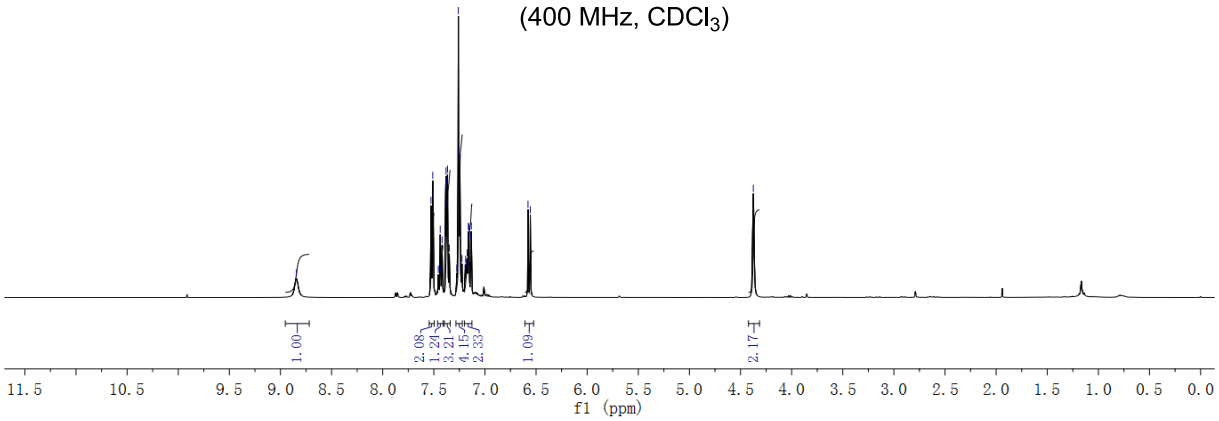
5o ^{13}C-NMR
(100 MHz, $CDCl_3$)

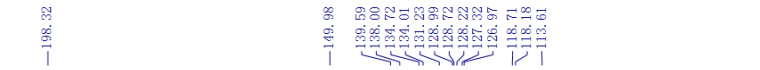


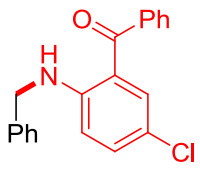




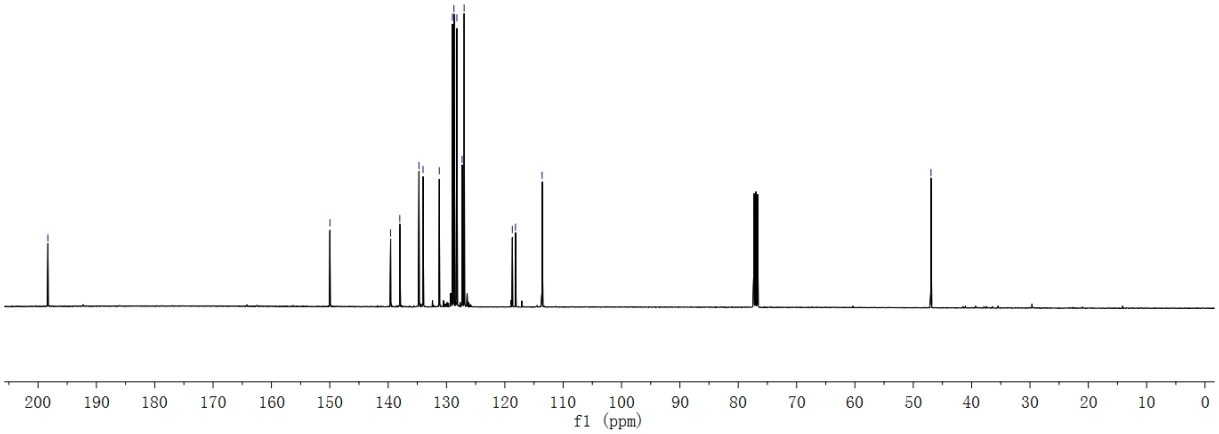
5p ^{1}H-NMR
(400 MHz, $CDCl_3$)

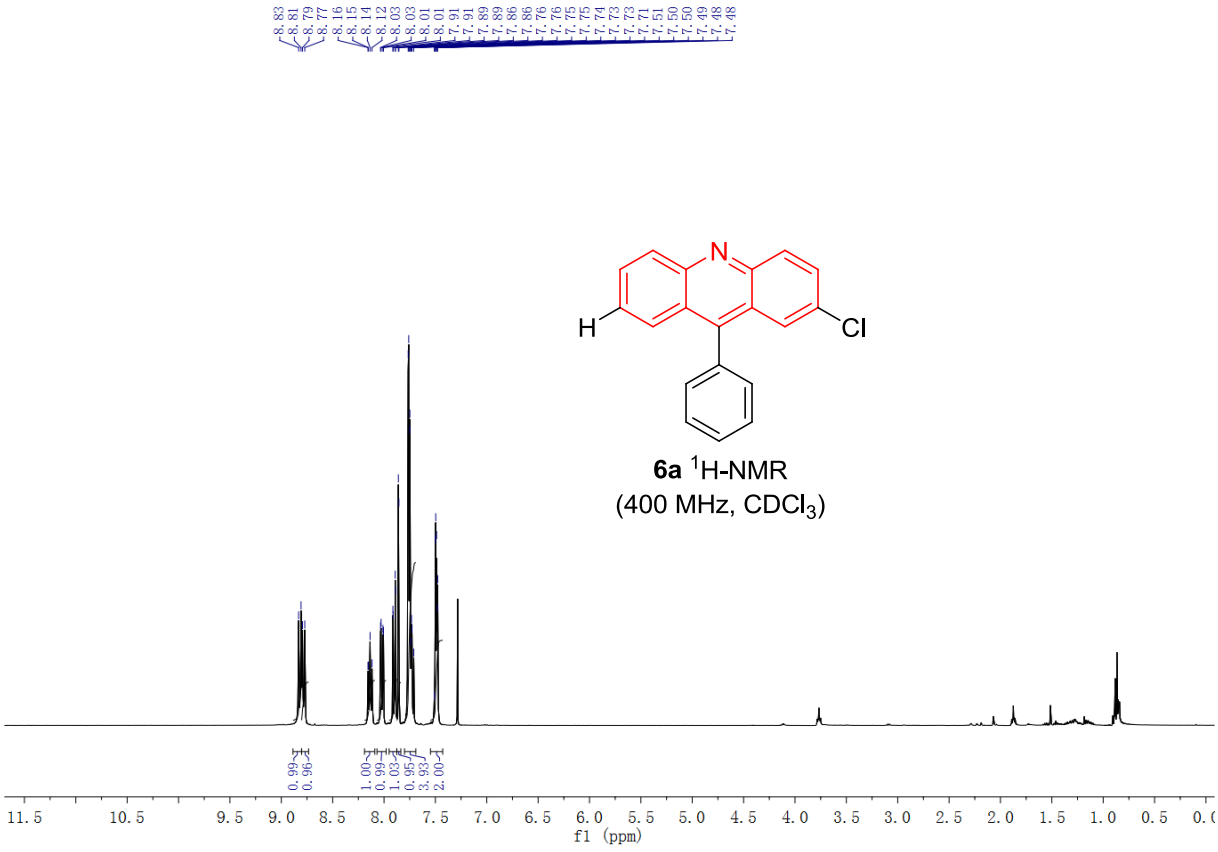




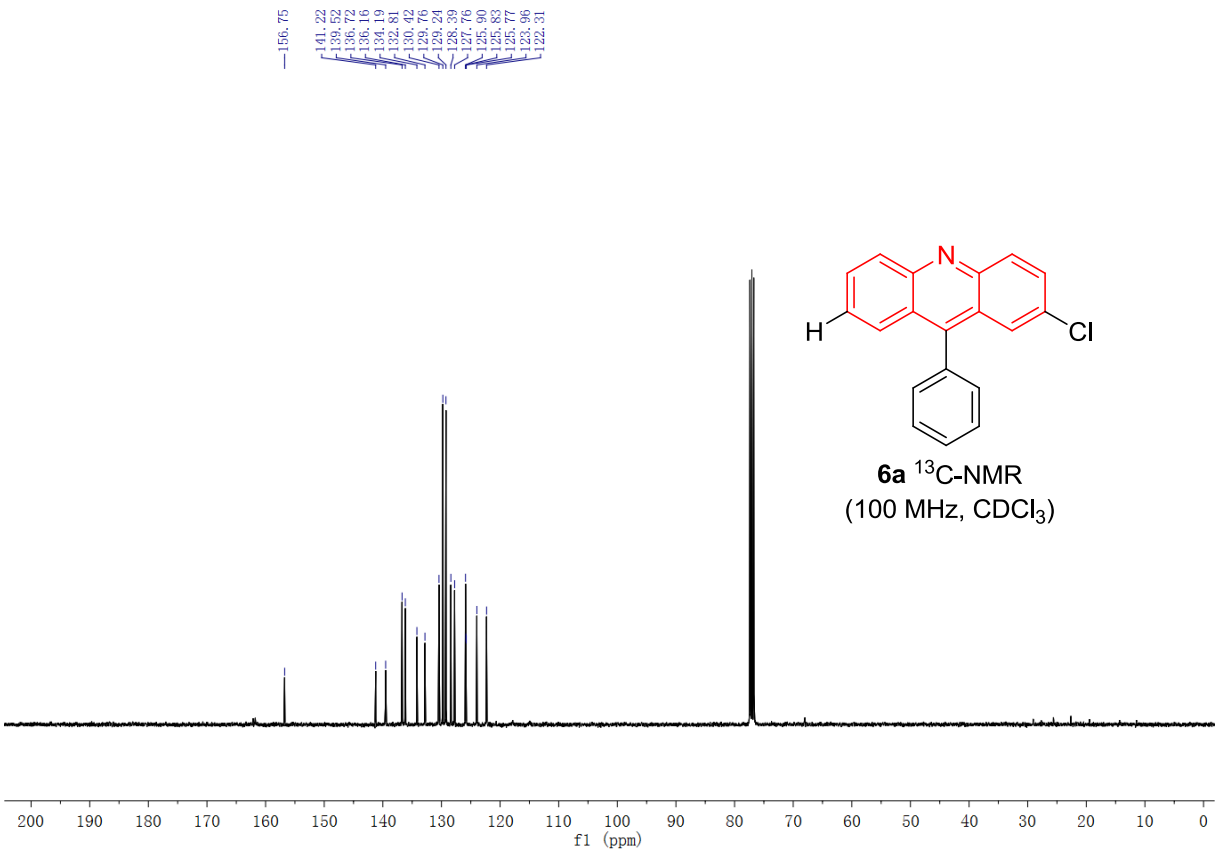


5p ^{13}C-NMR
(100 MHz, $CDCl_3$)

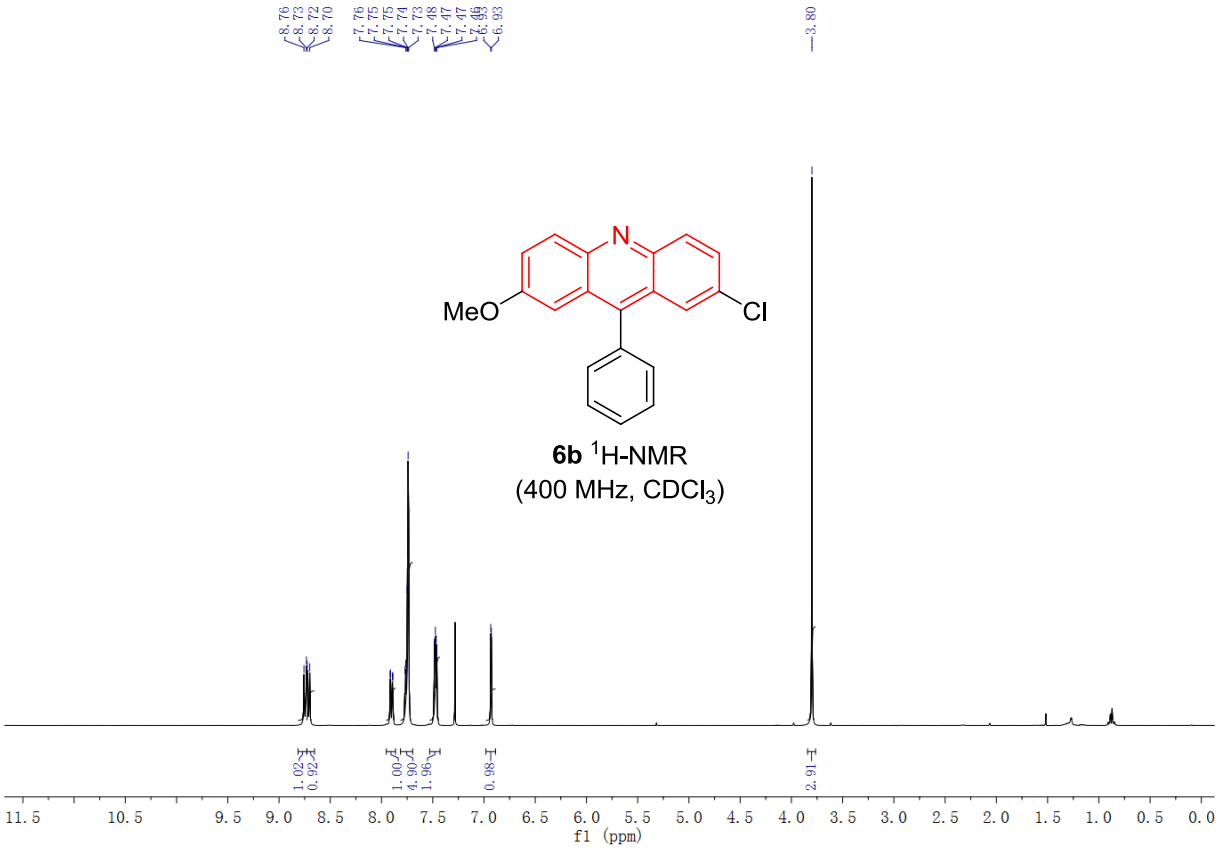




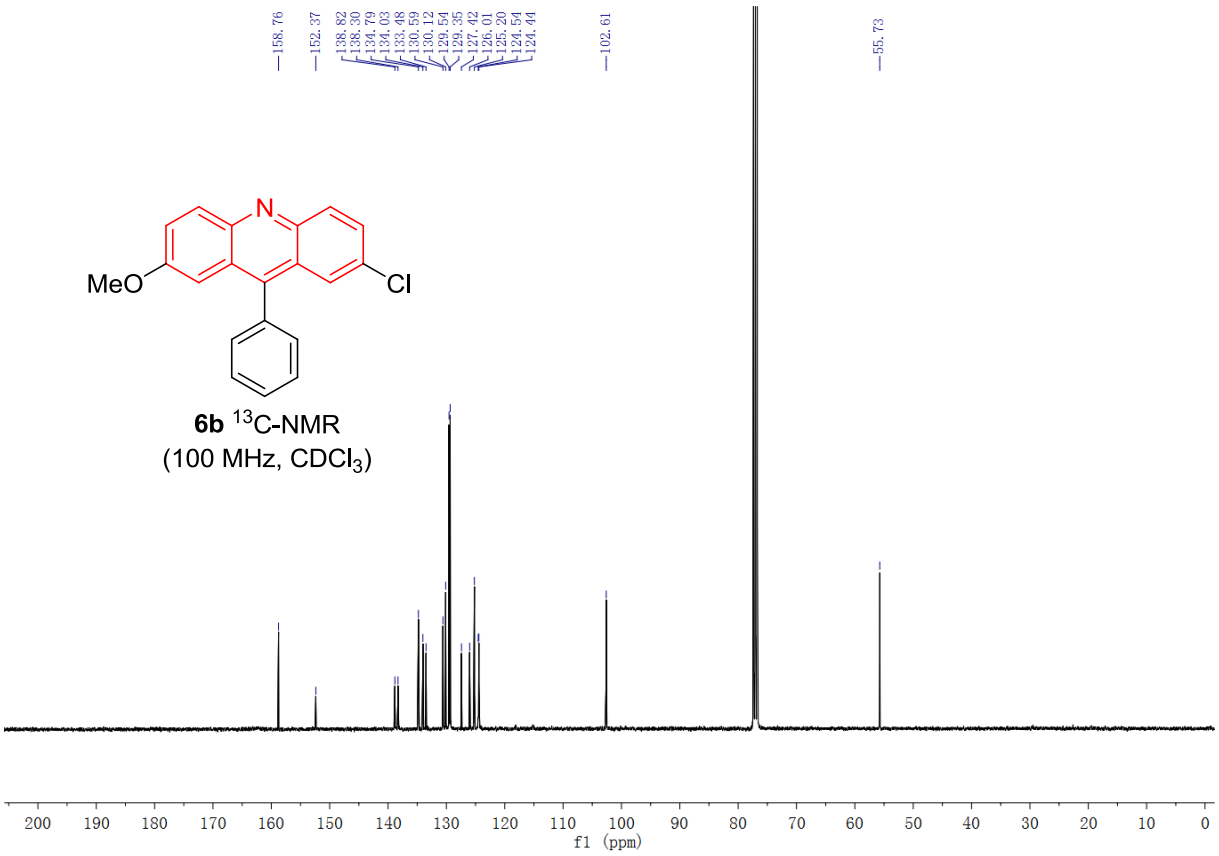
6a ^{1}H-NMR
(400 MHz, $CDCl_3$)



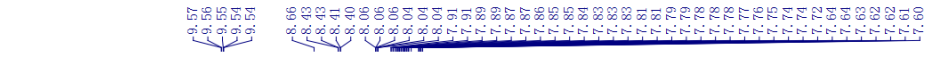
6a ^{13}C-NMR
(100 MHz, $CDCl_3$)

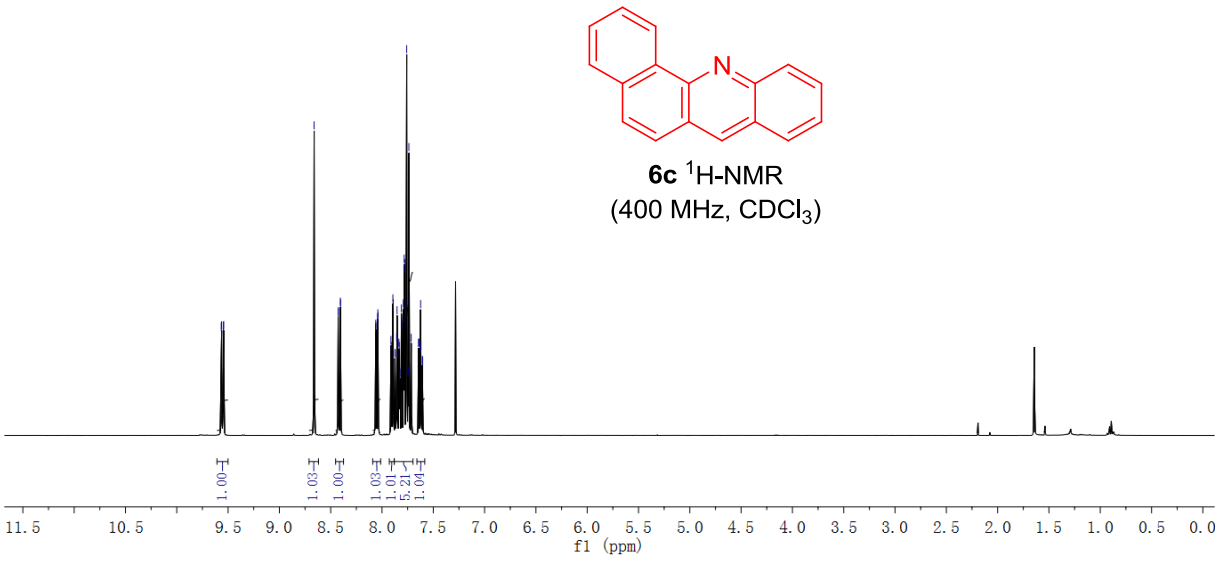


6b ^{1}H-NMR
(400 MHz, $CDCl_3$)

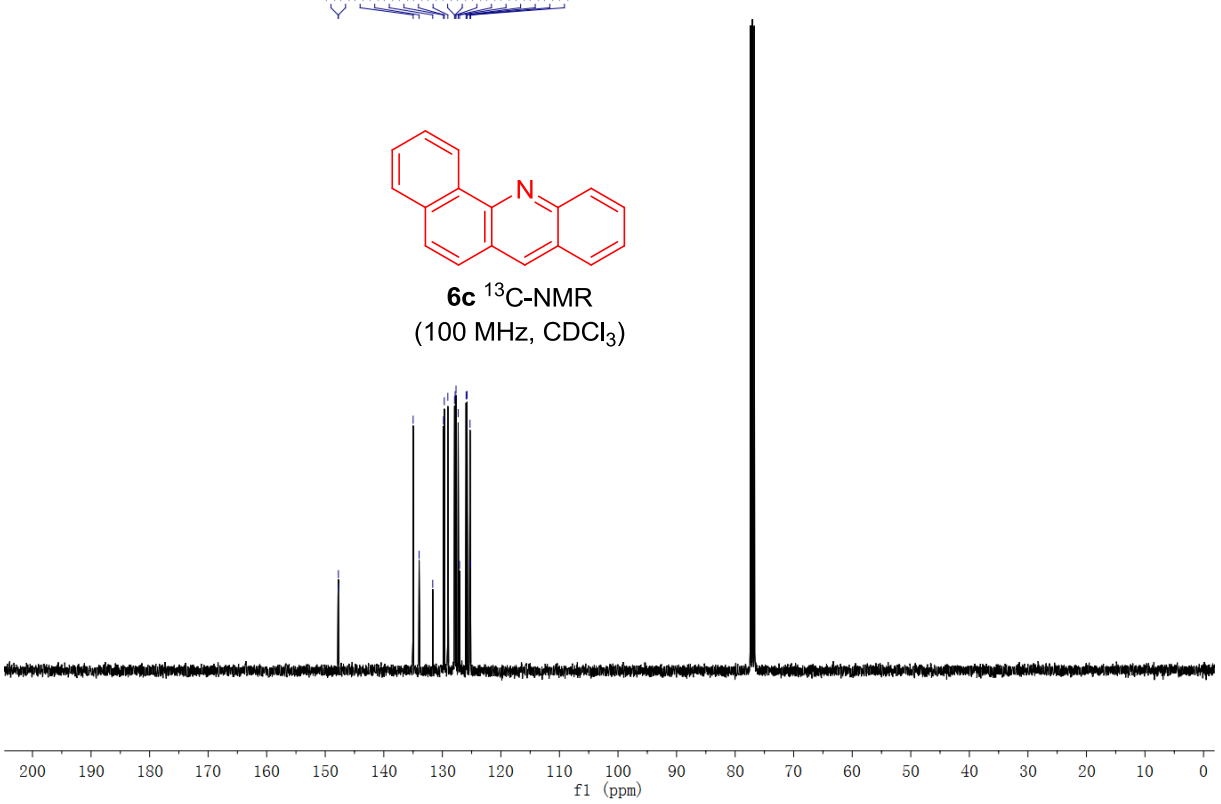


6b ^{13}C-NMR
(100 MHz, $CDCl_3$)

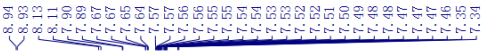


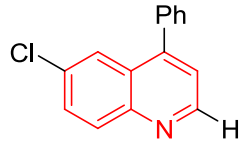


6c ^{1}H-NMR
(400 MHz, $CDCl_3$)

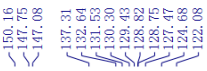


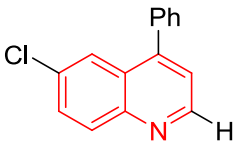
6c ^{13}C-NMR
(100 MHz, $CDCl_3$)



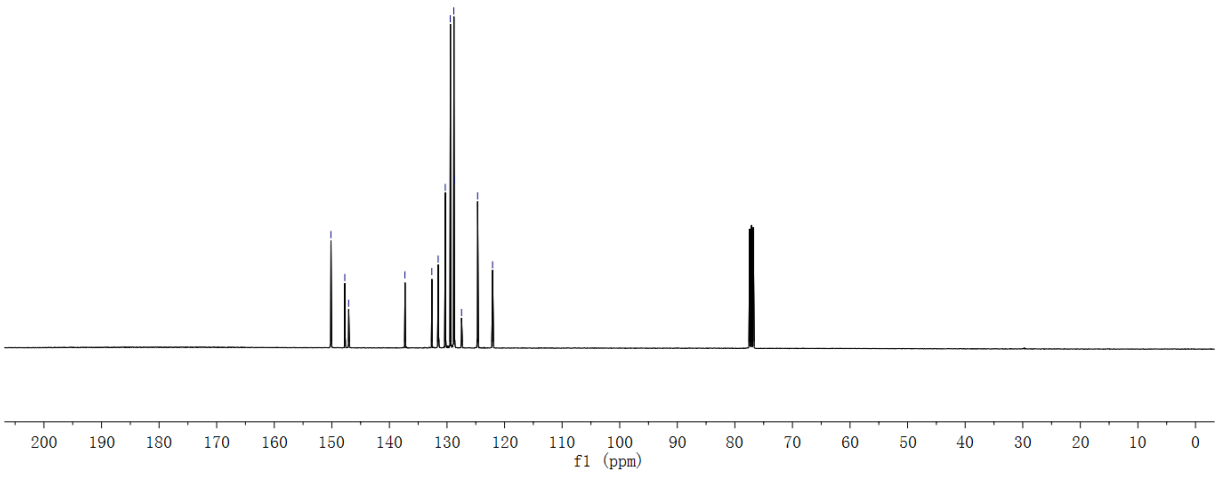


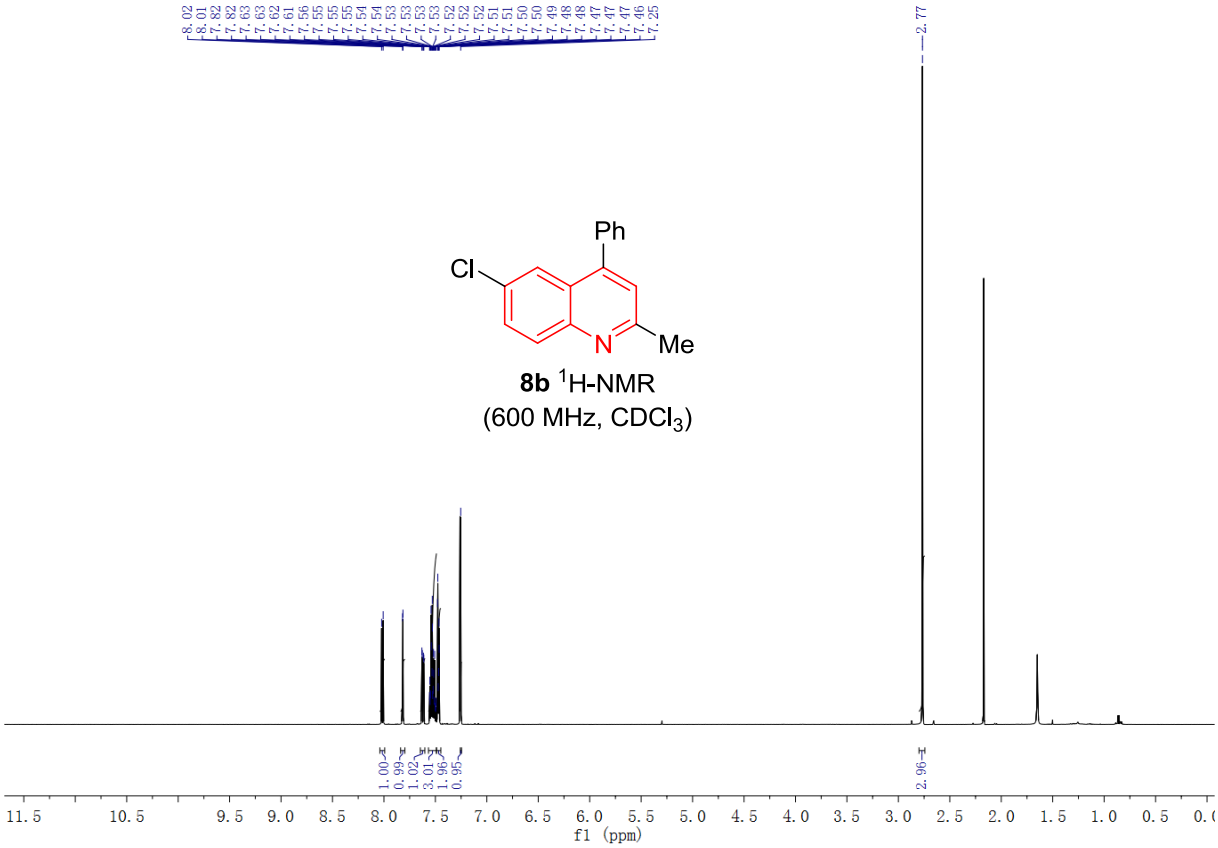
8a ^{1}H-NMR
(400 MHz, $CDCl_3$)

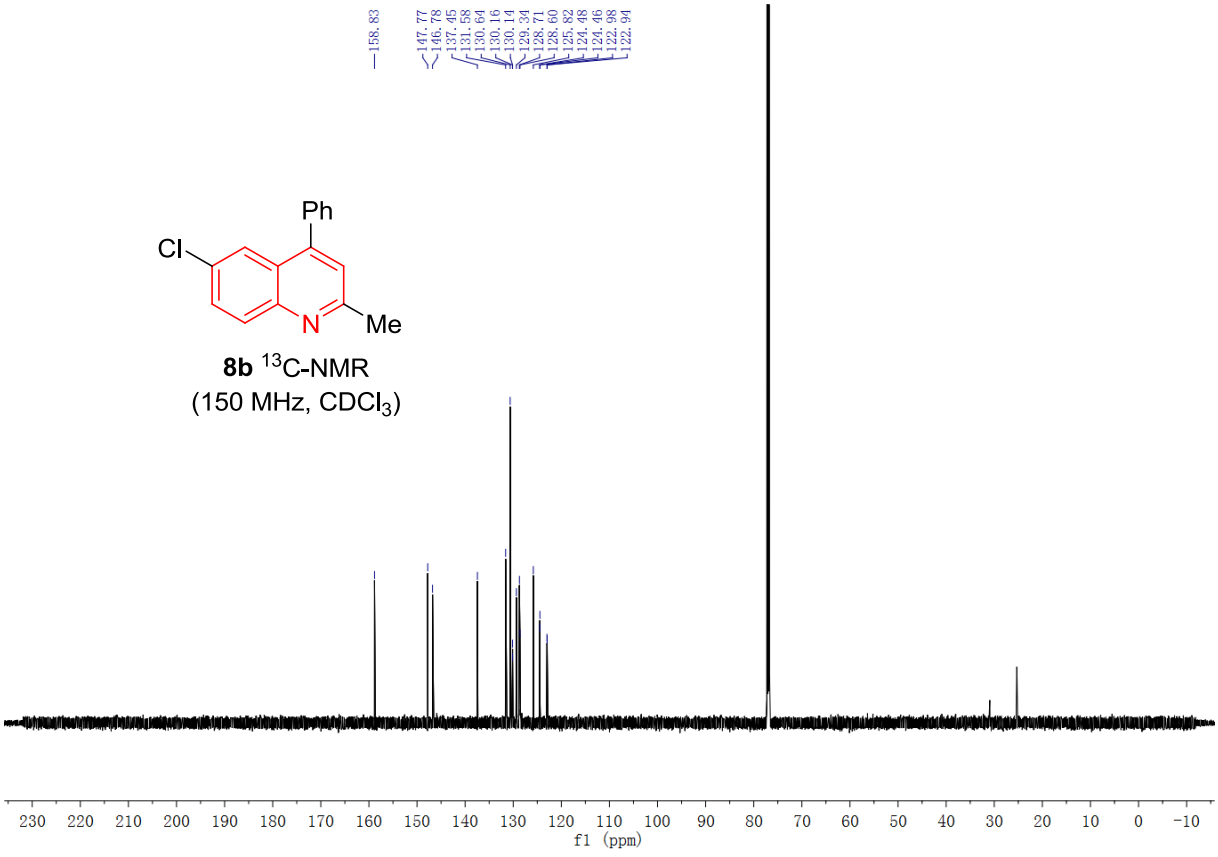


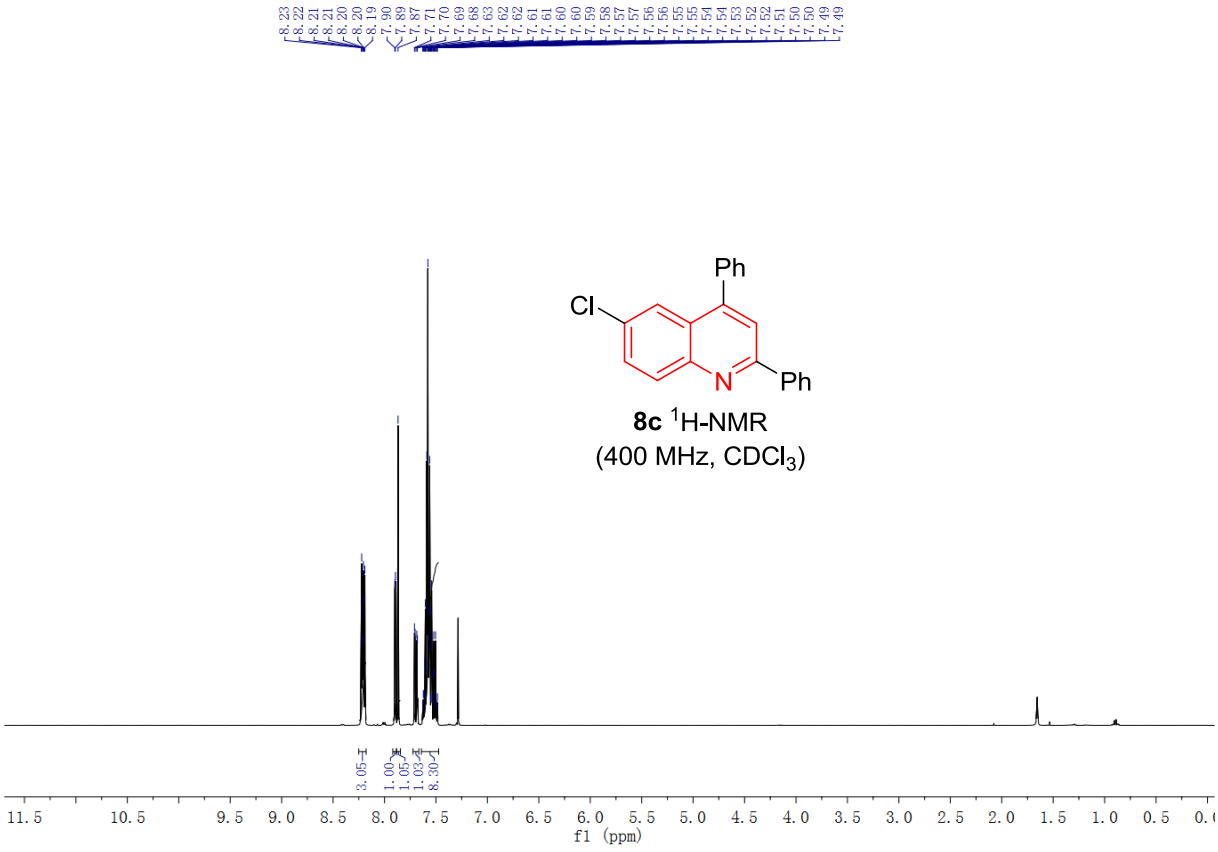


8a ^{13}C-NMR
(100 MHz, $CDCl_3$)

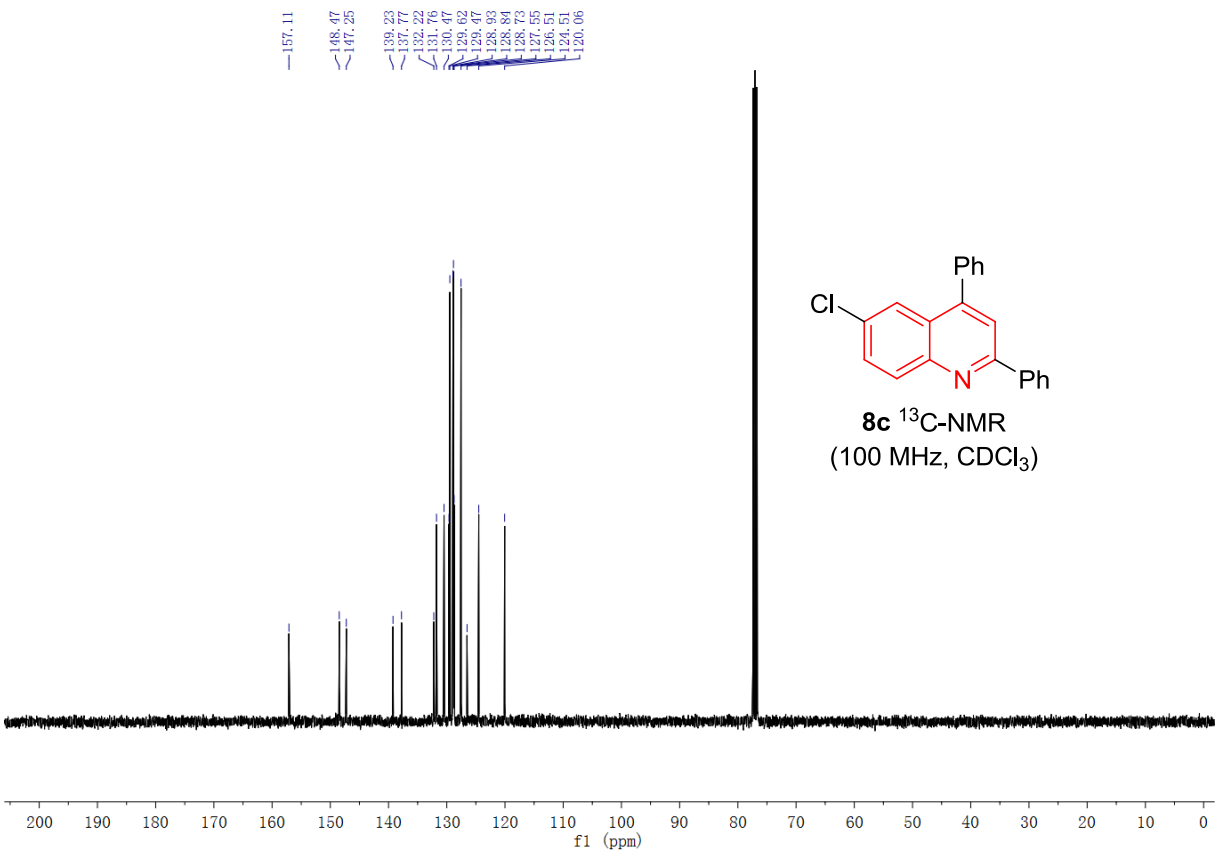



Ph
Cl
N
Me
8b ^{1}H-NMR
(600 MHz, $CDCl_3$)
f1 (ppm)

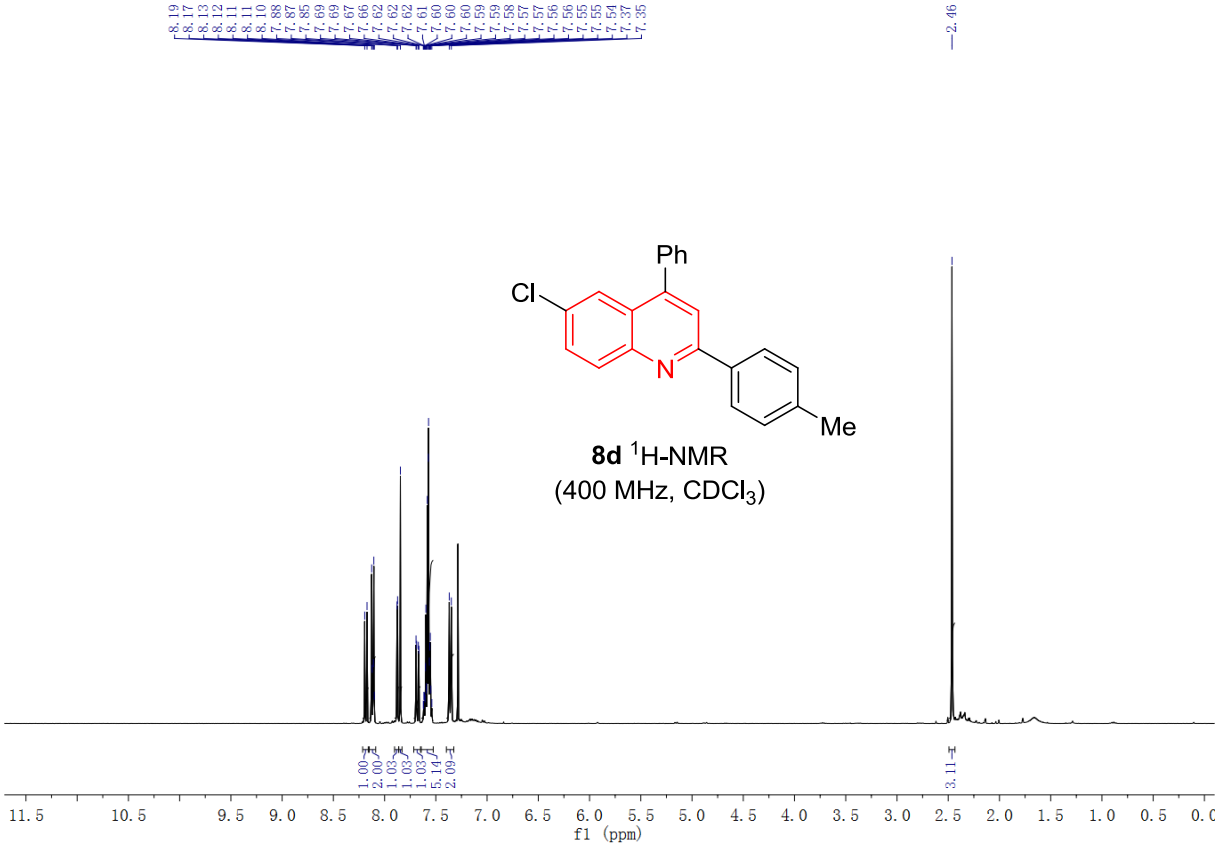

Ph
Cl
N
Me
8b ^{13}C-NMR
(150 MHz, $CDCl_3$)
f1 (ppm)

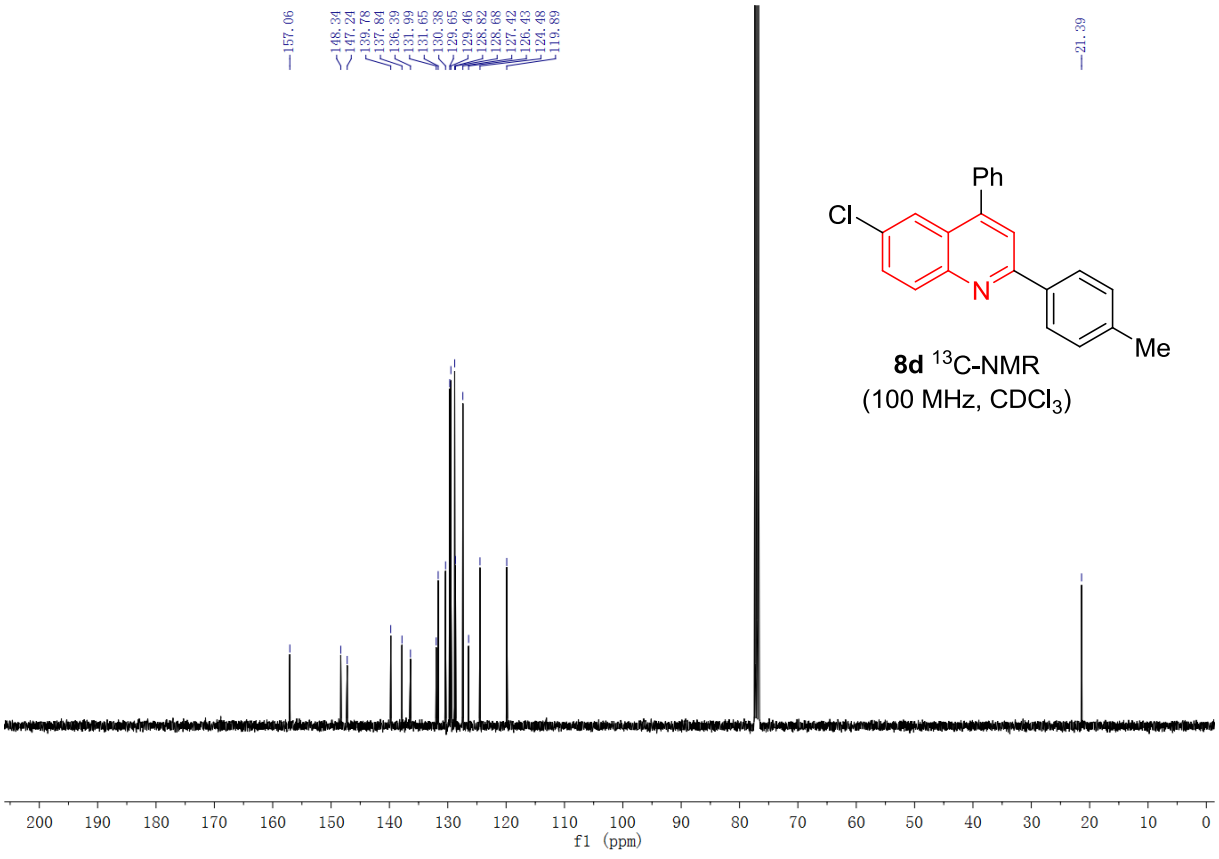


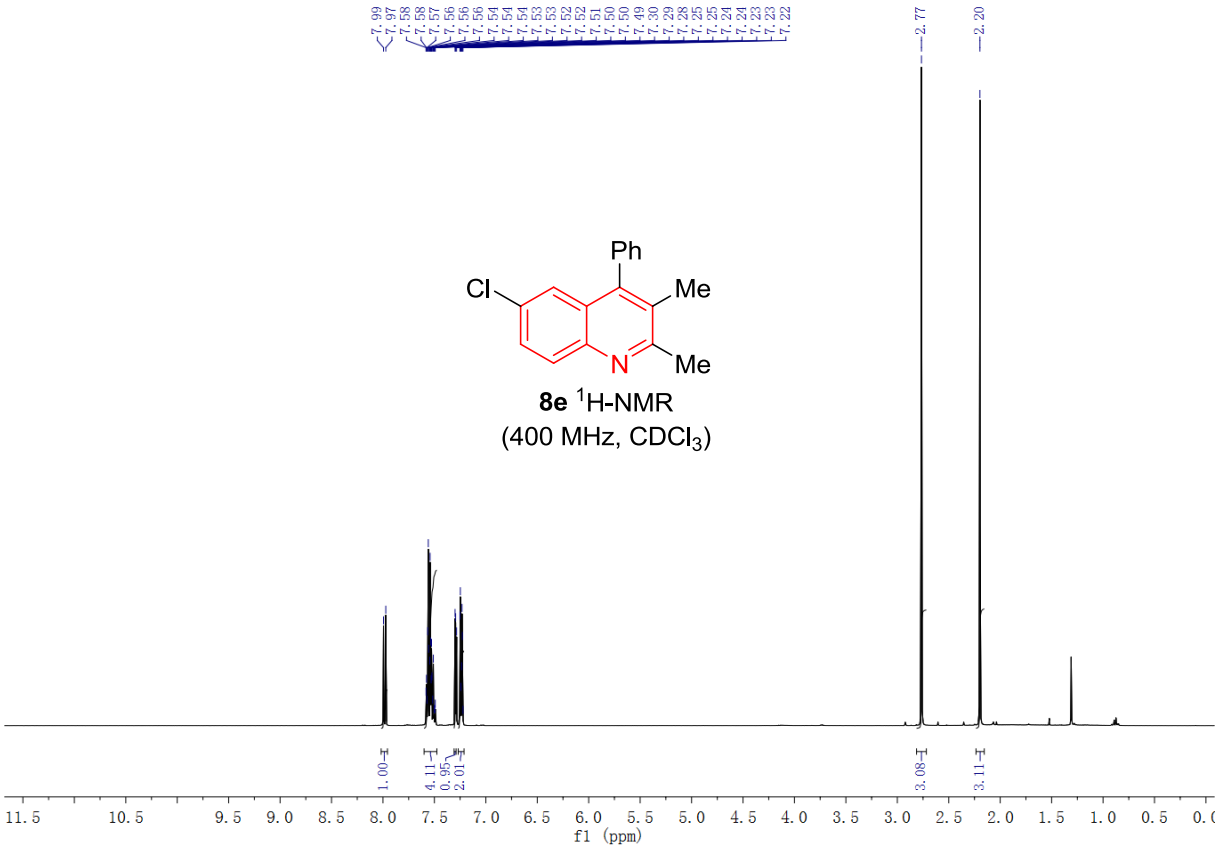
8c ^{1}H-NMR
(400 MHz, $CDCl_3$)

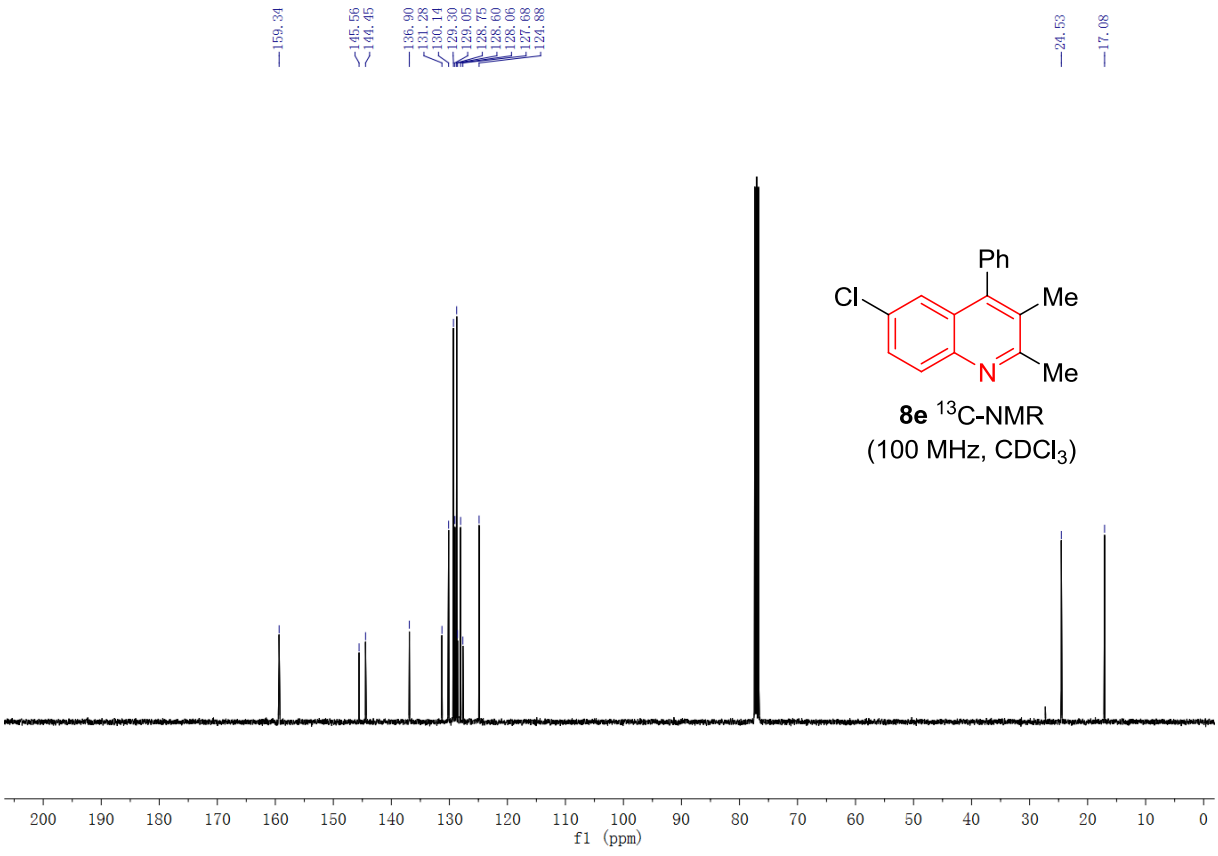


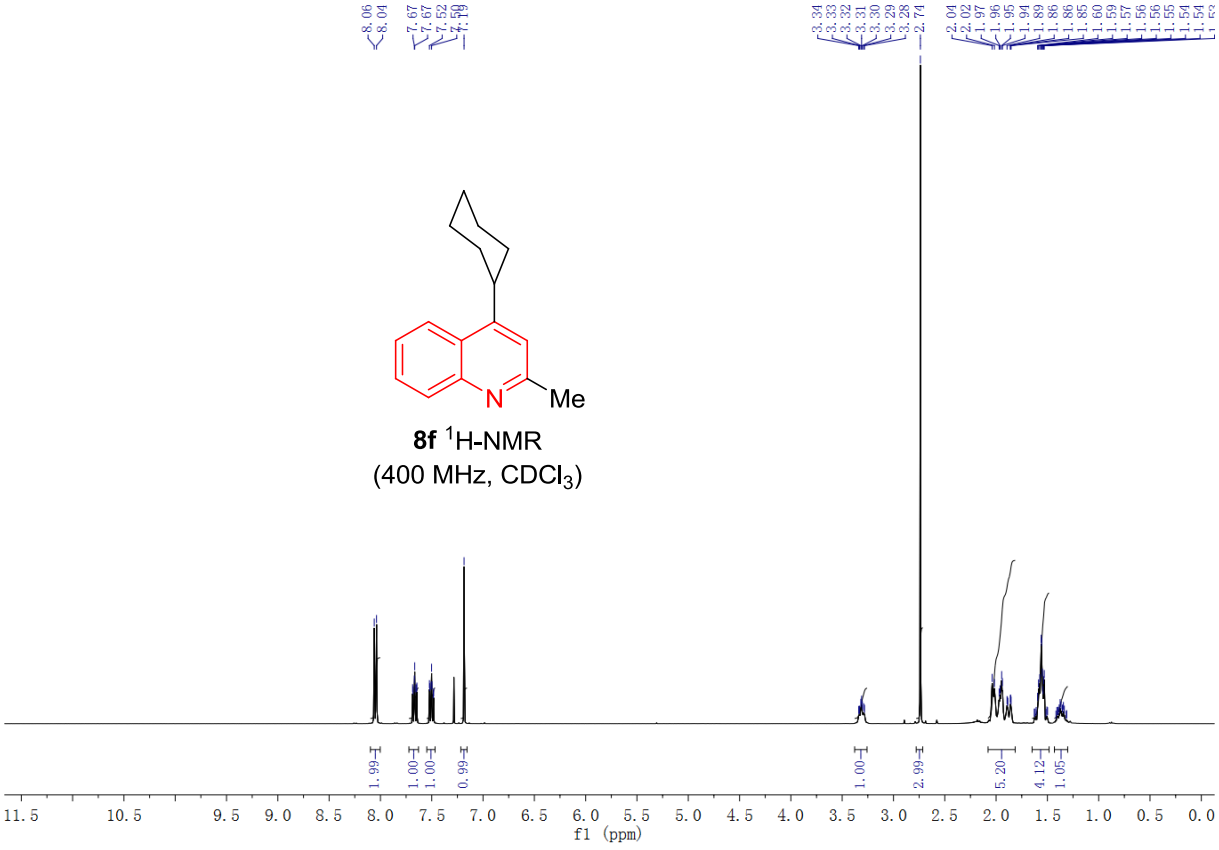
8c ^{13}C-NMR
(100 MHz, $CDCl_3$)


Ph
Cl
N
Me
8d 1H-NMR
(400 MHz, CDCl3)
f1 (ppm)

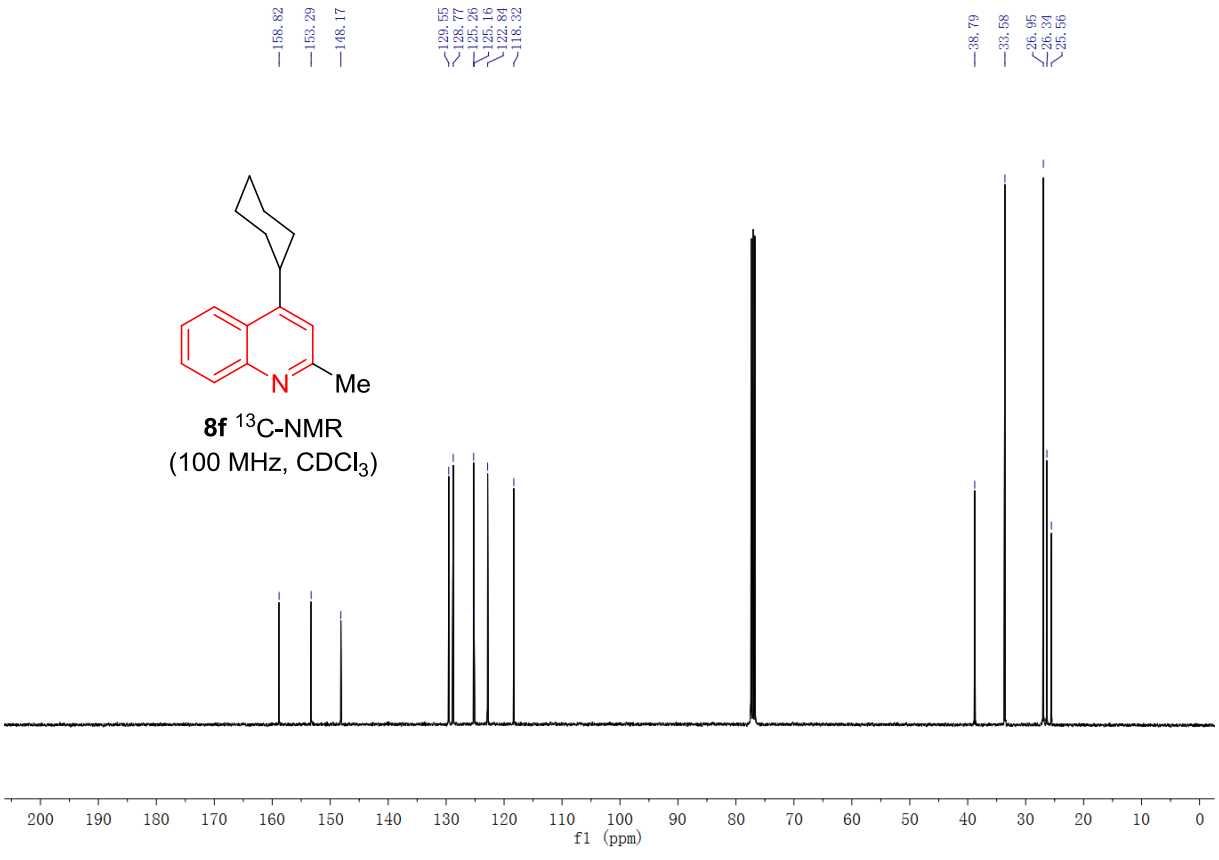

Ph
Cl
N
Me
8d 13C-NMR
(100 MHz, CDCl3)
f1 (ppm)


Ph
Cl
Me
N
Me
8e 1H-NMR
(400 MHz, CDCl3)
f1 (ppm)

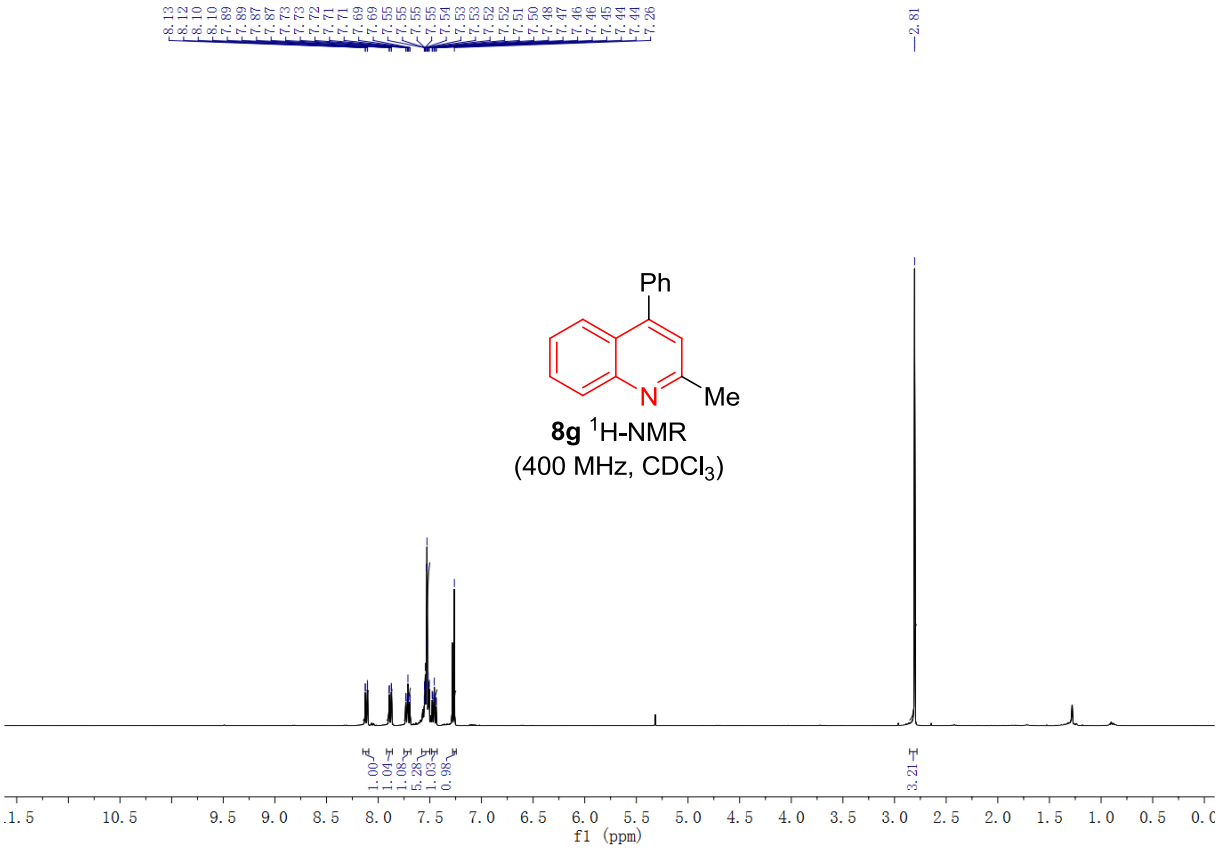

Ph
Cl
Me
N
Me
8e 13C-NMR
(100 MHz, CDCl3)
f1 (ppm)

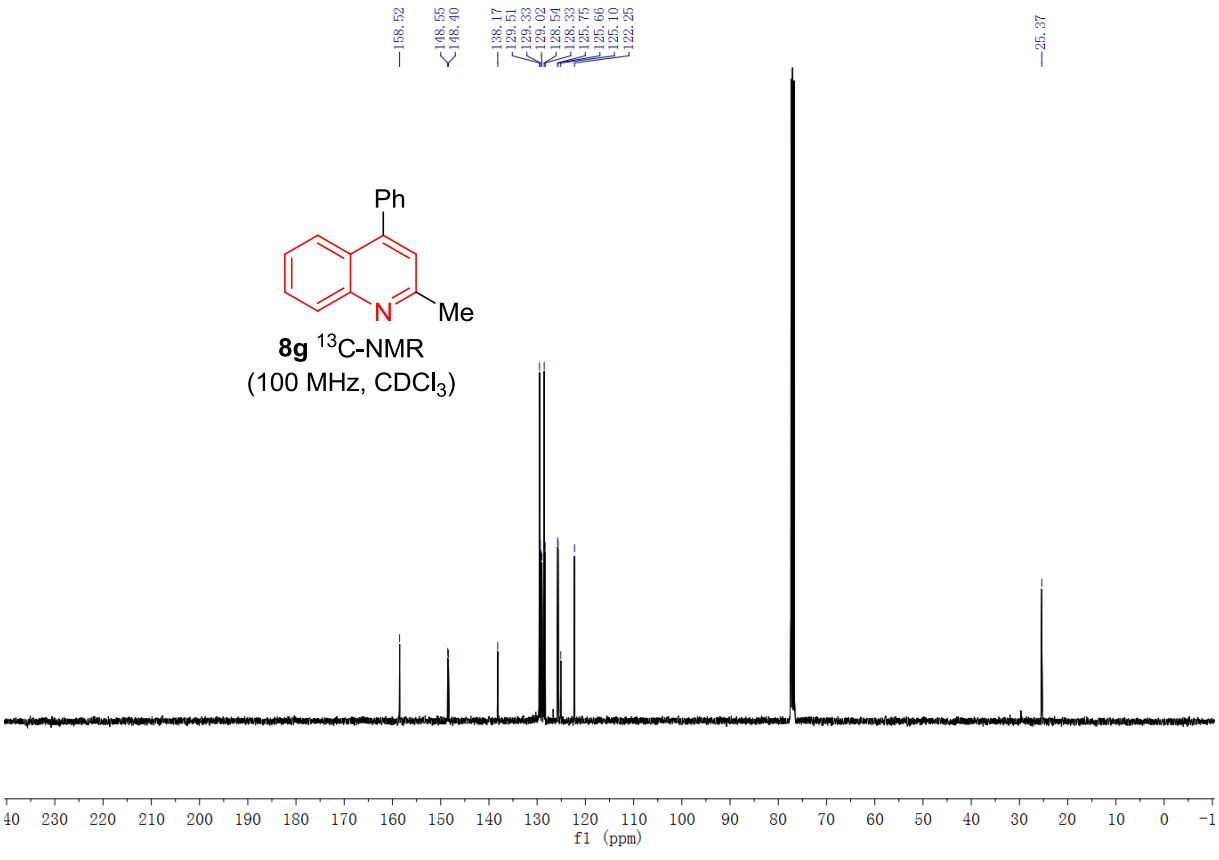


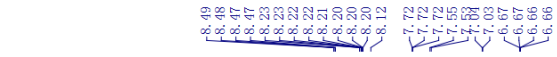
8f ^{1}H-NMR
(400 MHz, $CDCl_3$)

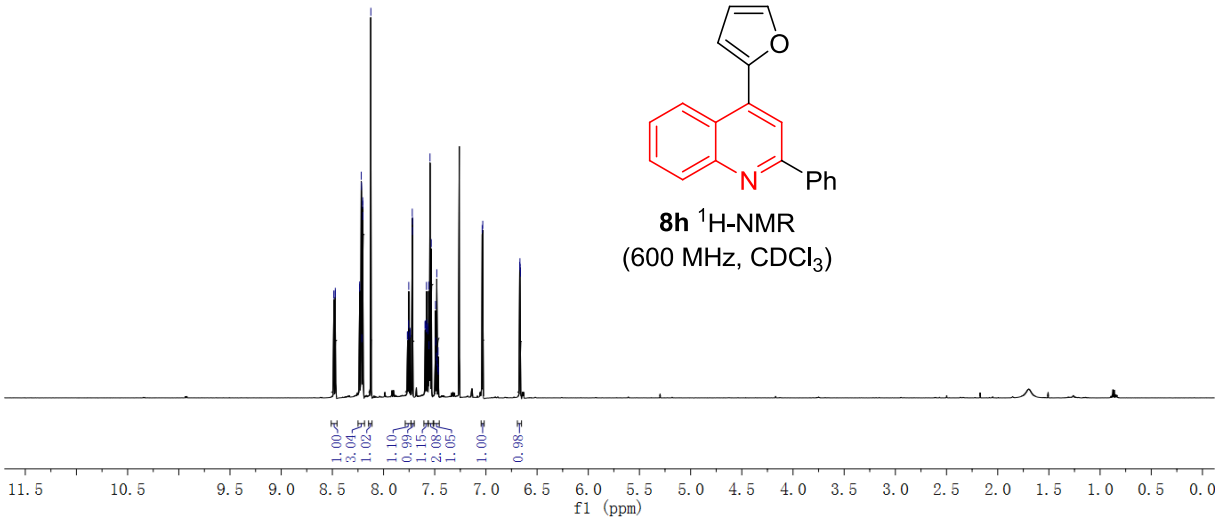


8f ^{13}C-NMR
(100 MHz, $CDCl_3$)

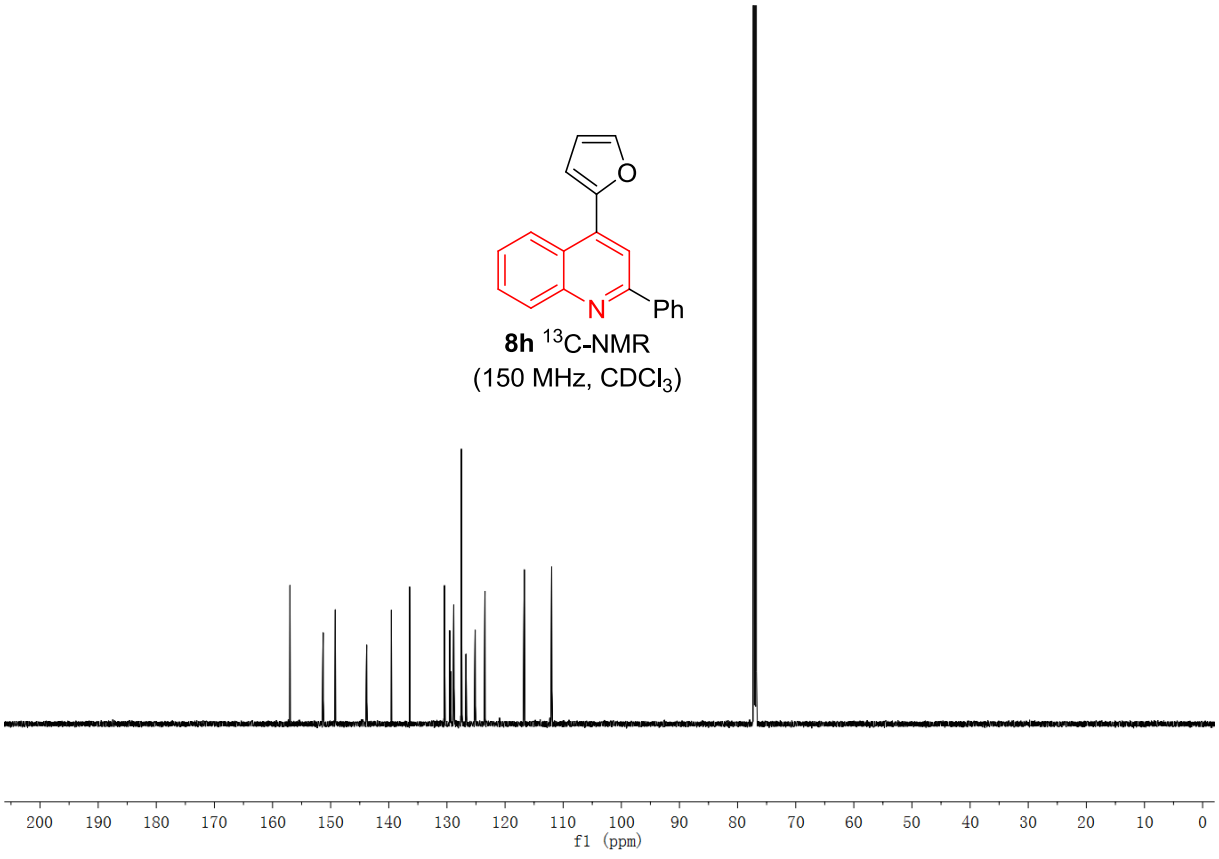

8.13
8.12
8.10
8.10
7.89
7.89
7.87
7.87
7.73
7.73
7.72
7.71
7.71
7.69
7.69
7.55
7.55
7.55
7.54
7.53
7.53
7.52
7.52
7.51
7.50
7.48
7.47
7.46
7.46
7.45
7.44
7.44
7.26
2.81
Ph
N
Me
8g 1H-NMR
(400 MHz, CDCl3)
1.00
1.04
1.08
5.28
1.03
0.98
3.21
f1 (ppm)


158.52
148.55
148.40
138.17
129.51
129.33
129.02
128.54
128.33
125.75
125.66
125.10
122.25
25.37
Ph
N
Me
8g 13C-NMR
(100 MHz, CDCl3)
f1 (ppm)

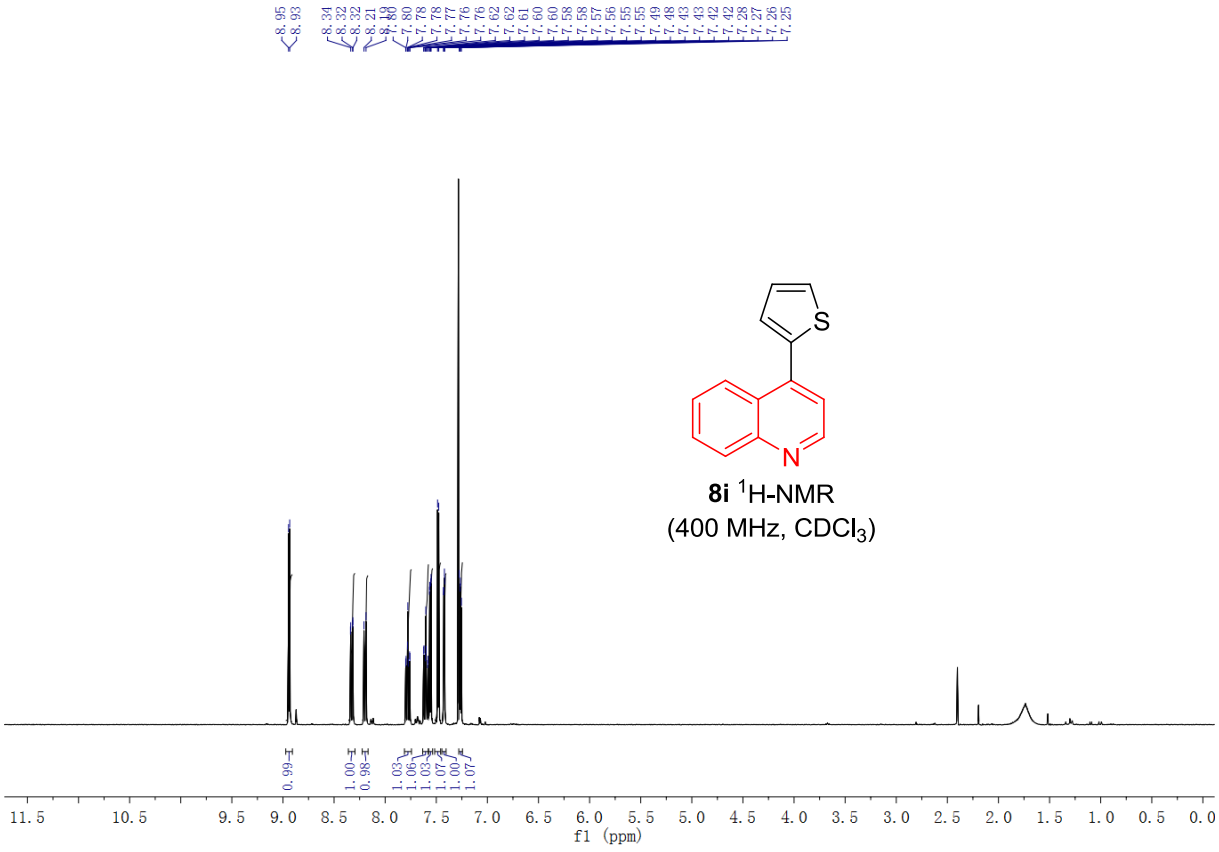




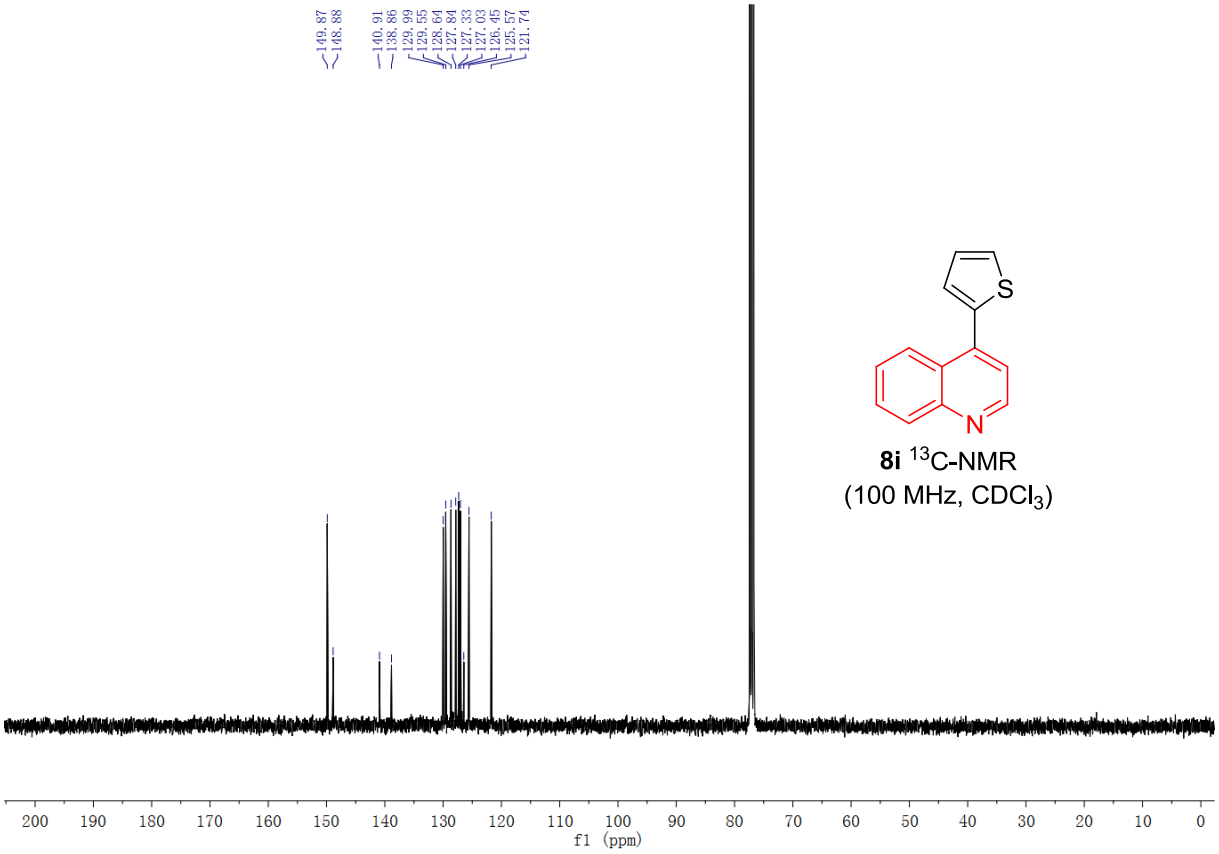
8h ^{1}H-NMR
(600 MHz, $CDCl_3$)



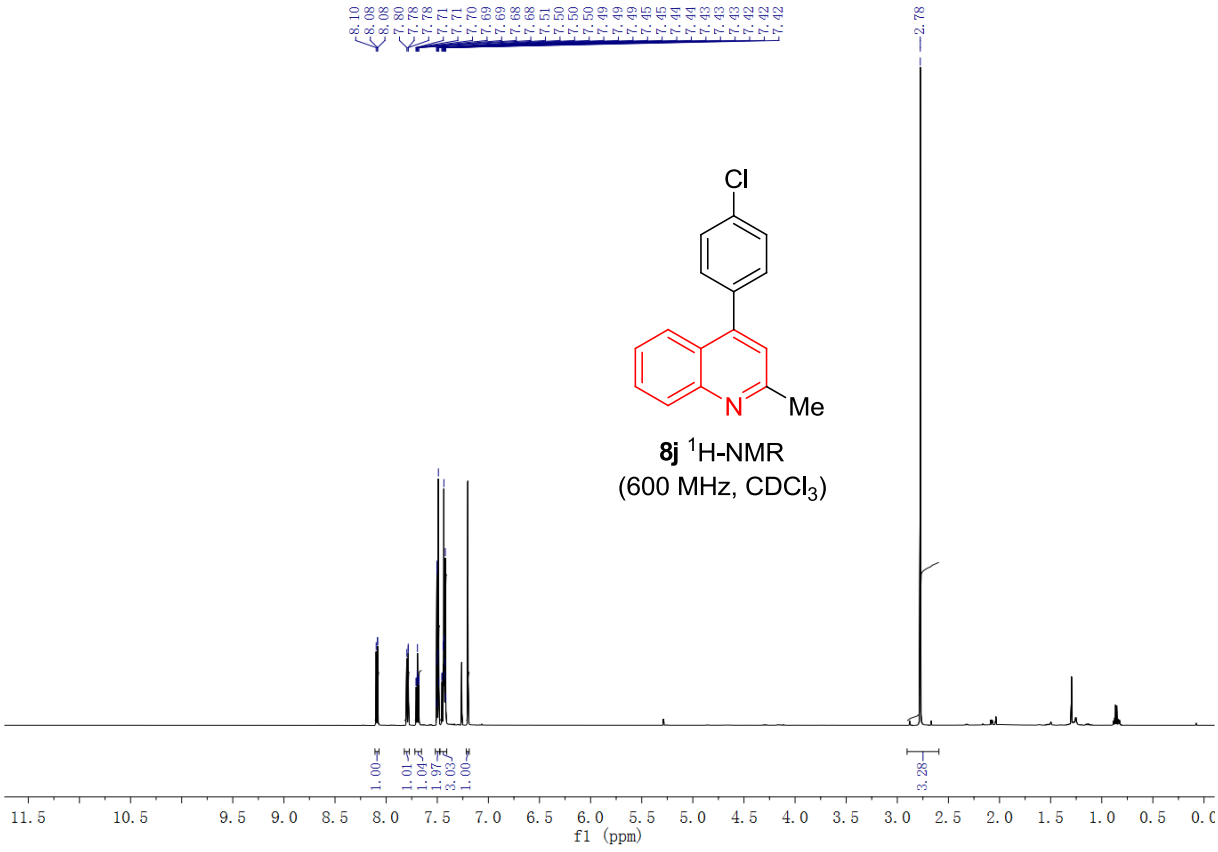
8h ^{13}C-NMR
(150 MHz, $CDCl_3$)

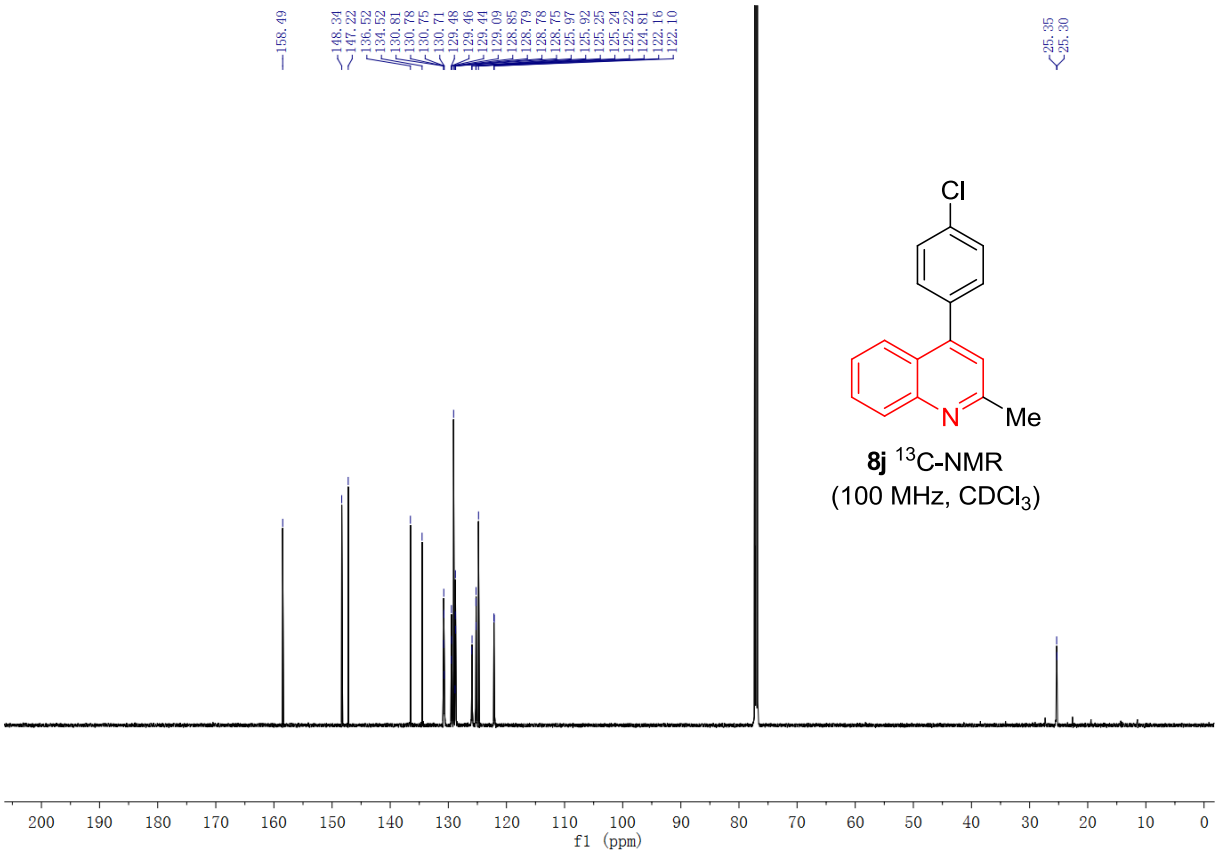


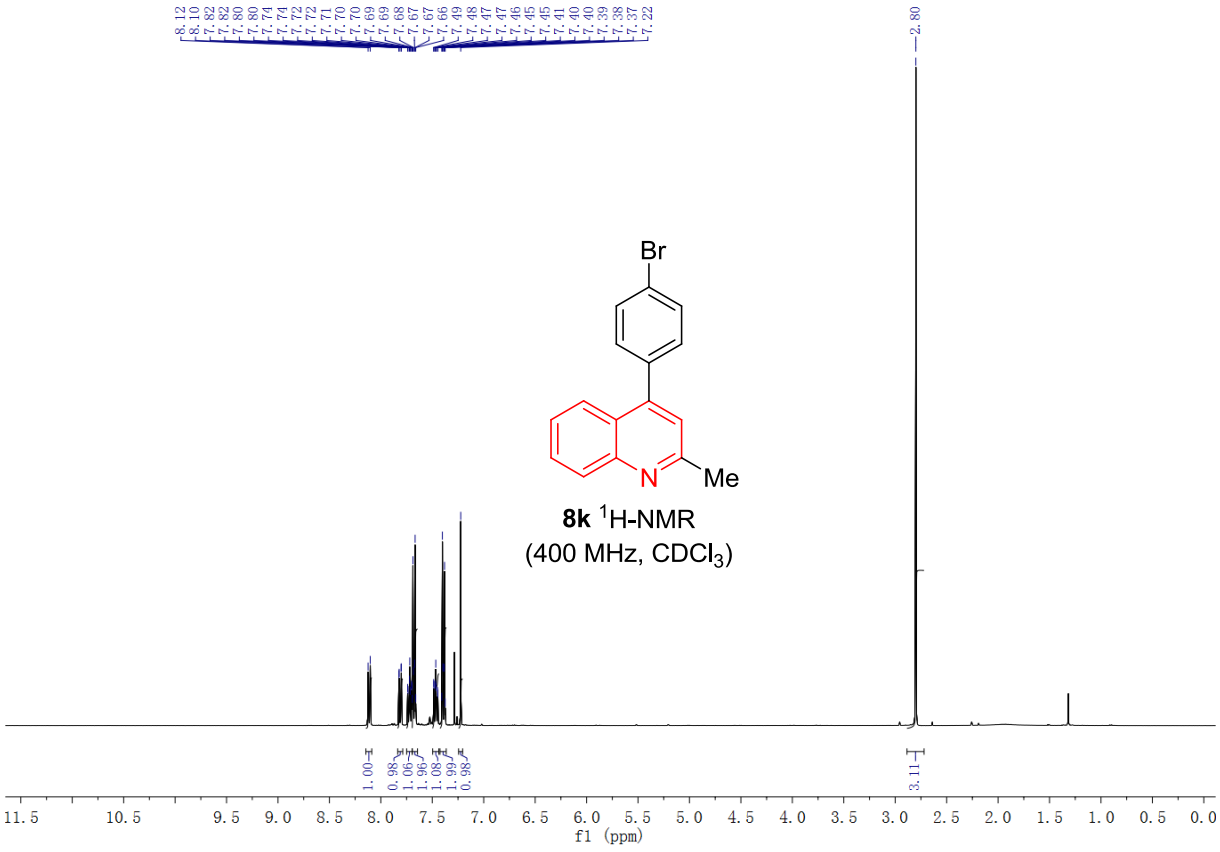
8i ^{1}H-NMR
(400 MHz, $CDCl_3$)

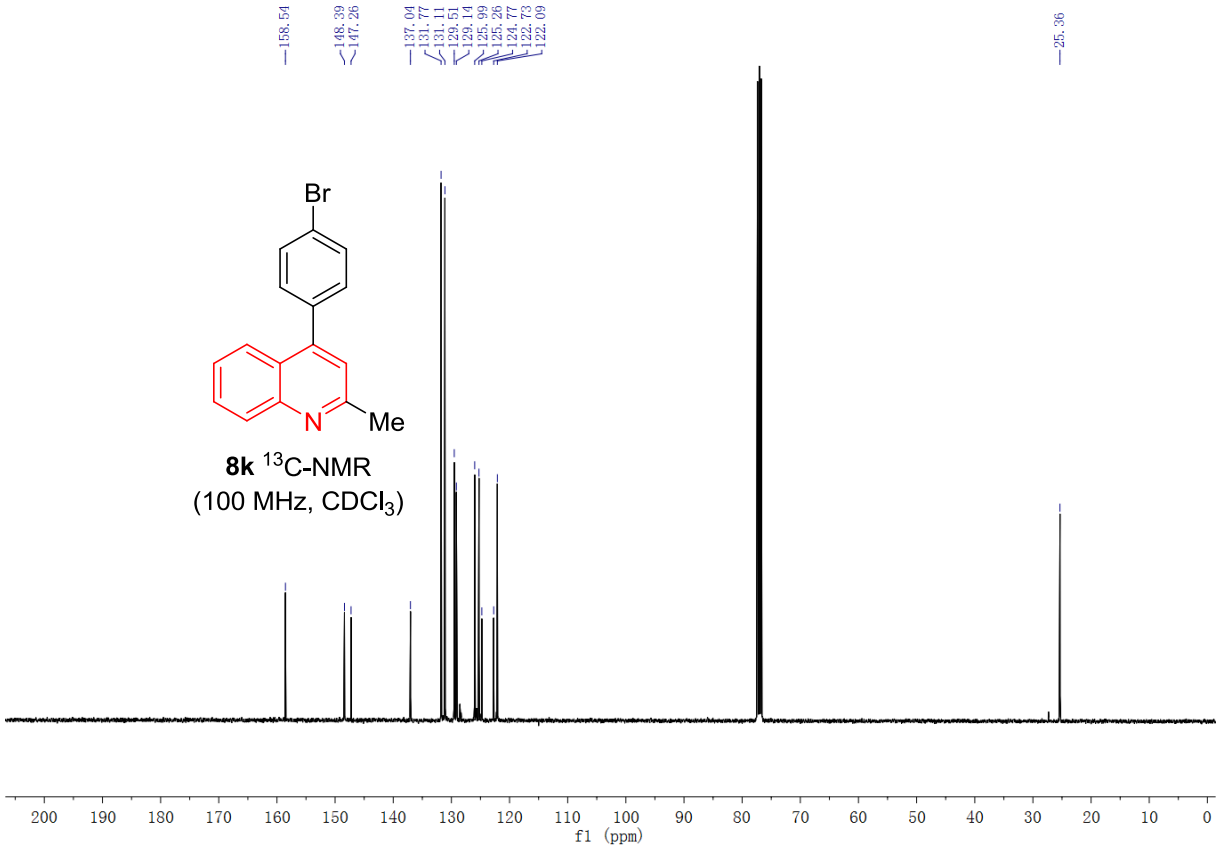


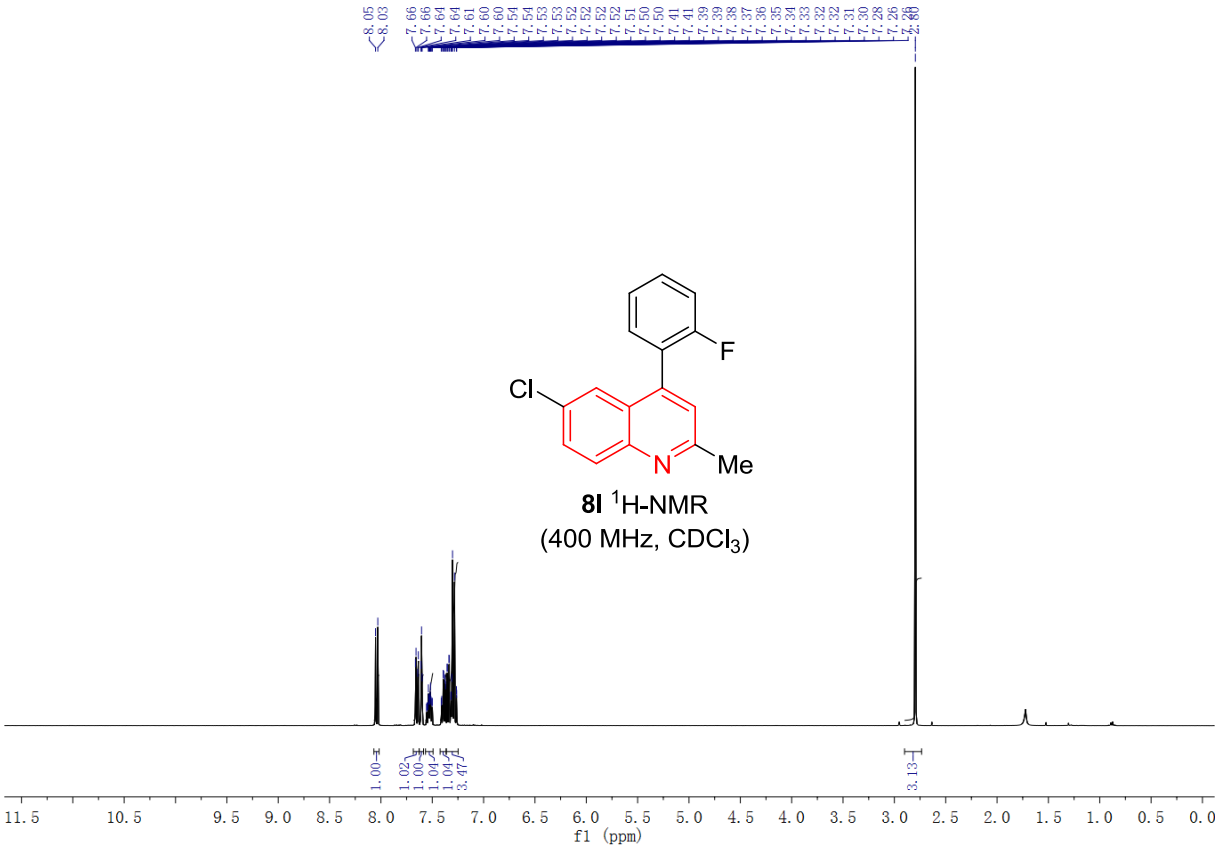
8i ^{13}C-NMR
(100 MHz, $CDCl_3$)

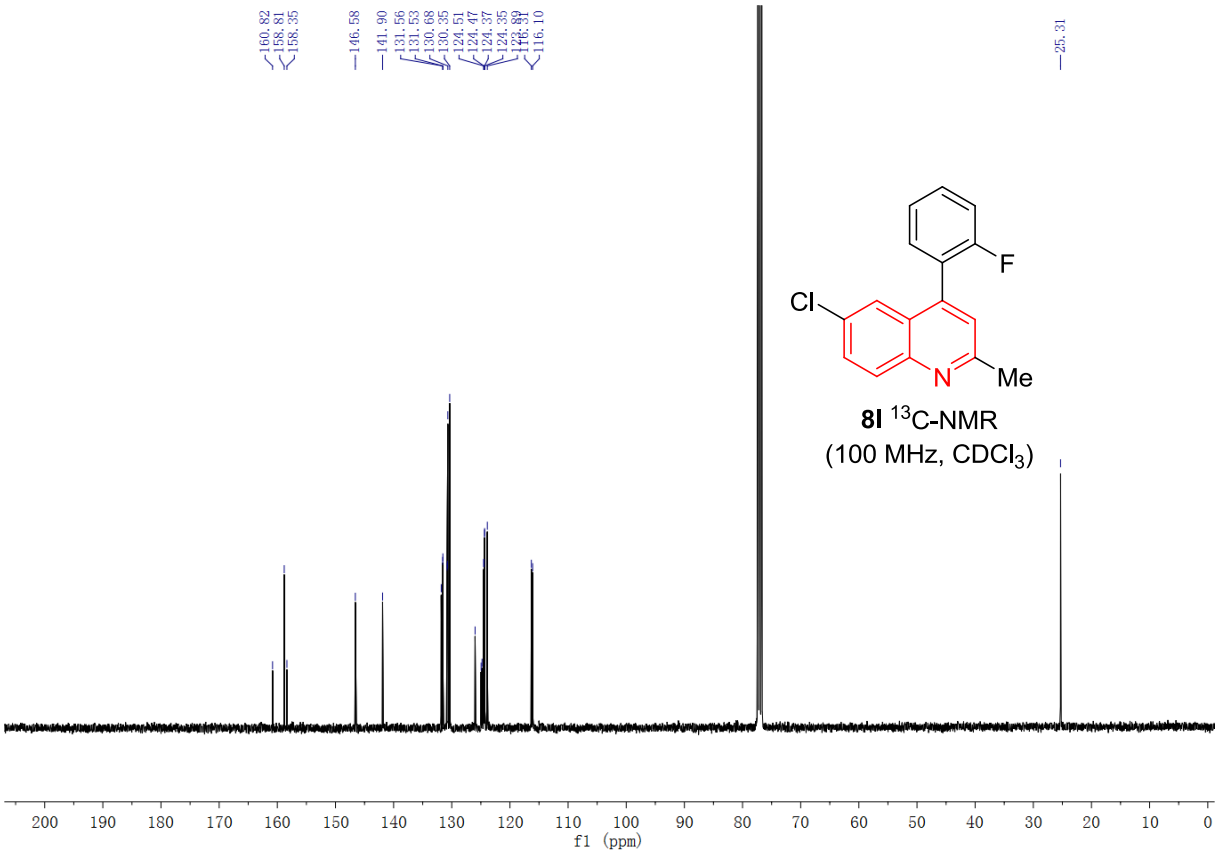

Cl
N
Me
8j ^{1}H-NMR
(600 MHz, $CDCl_3$)
f1 (ppm)

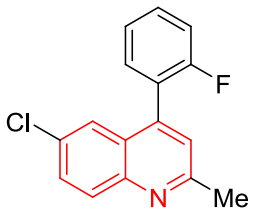

Cl
N
Me
8j ^{13}C-NMR
(100 MHz, $CDCl_3$)
f1 (ppm)


Br
N
Me
8k 1H-NMR
(400 MHz, CDCl3)
f1 (ppm)

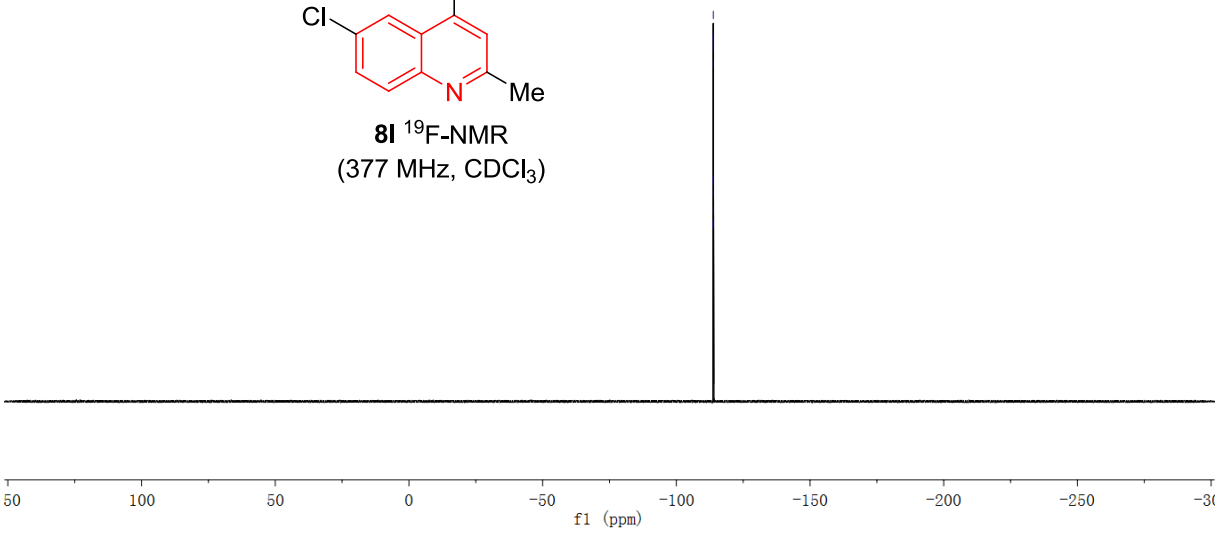

Br
N
Me
8k 13C-NMR
(100 MHz, CDCl3)
f1 (ppm)

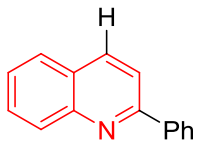

F
Cl
N
Me
8l ^{1}H-NMR
(400 MHz, $CDCl_3$)
f1 (ppm)


F
Cl
N
Me
8l ^{13}C-NMR
(100 MHz, $CDCl_3$)
f1 (ppm)

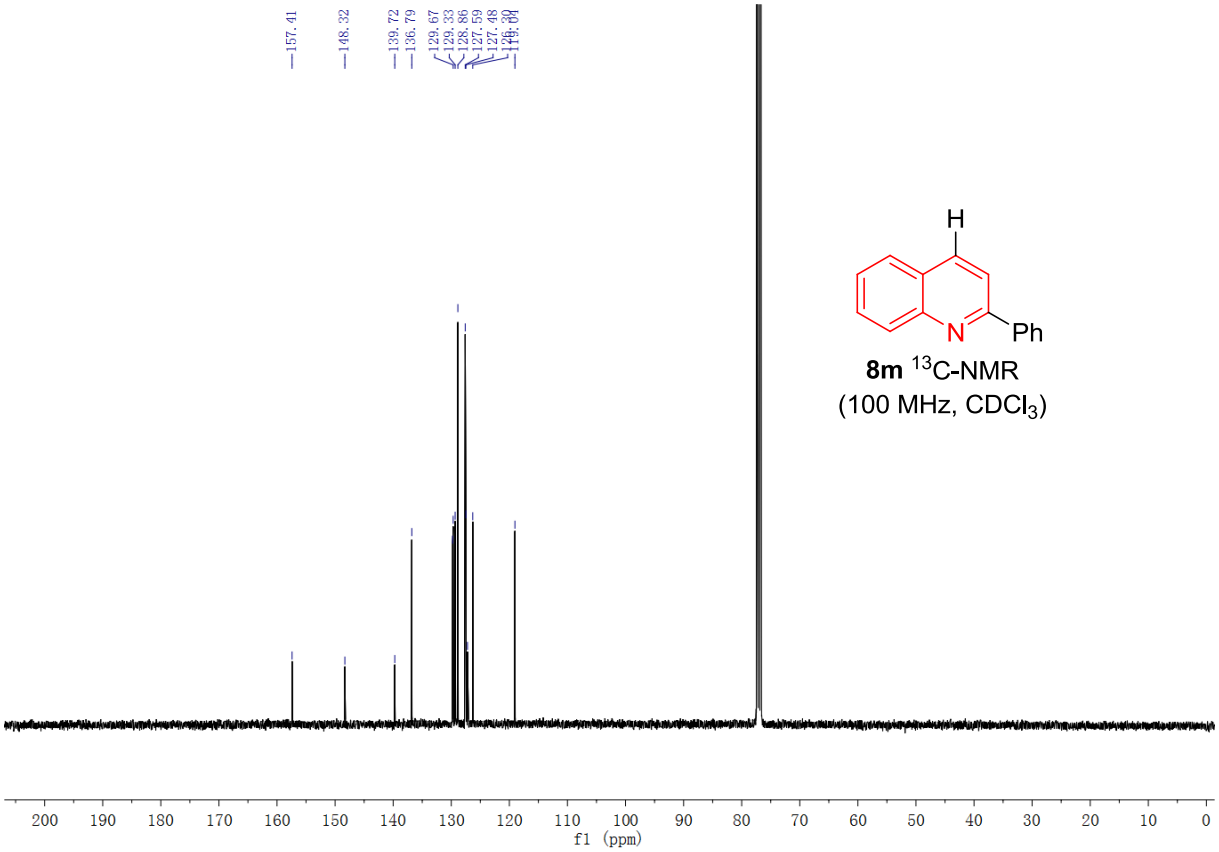


8l ^{19}F-NMR
(377 MHz, $CDCl_3$)

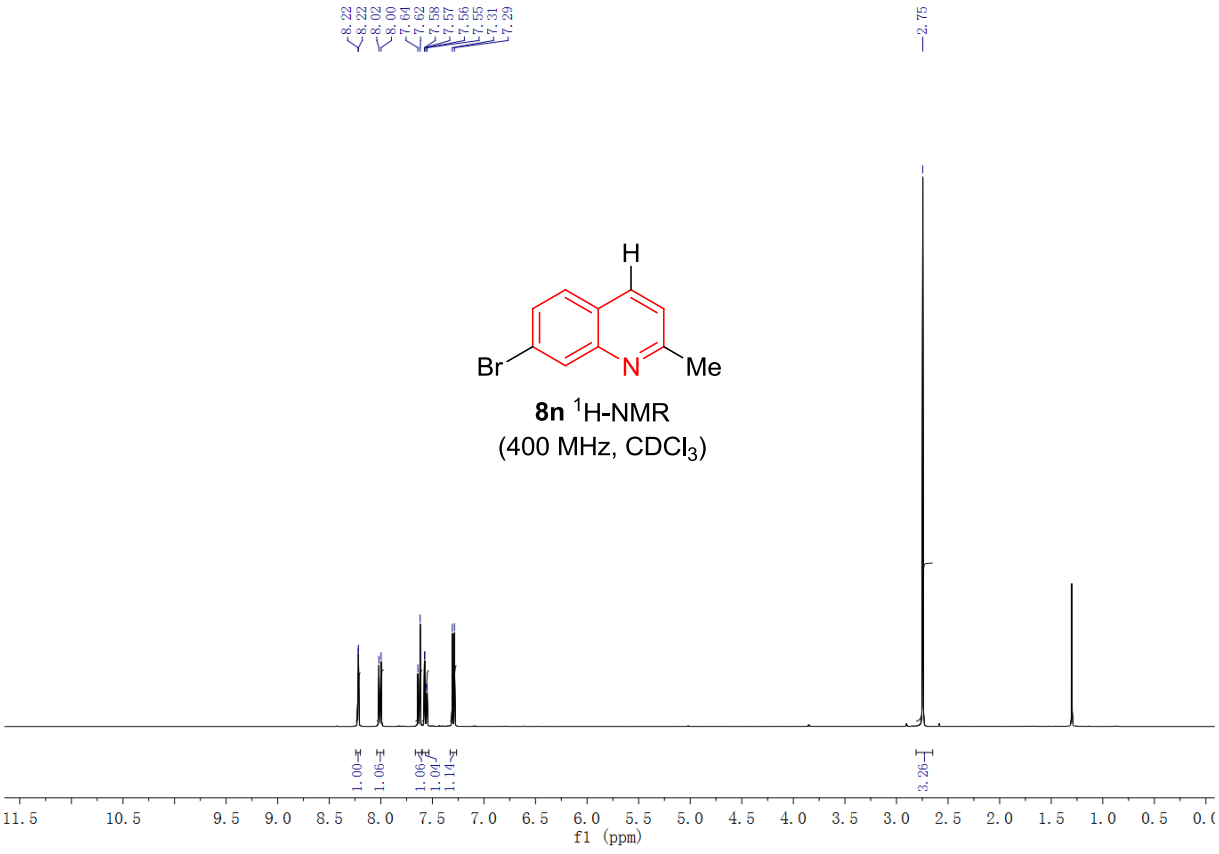




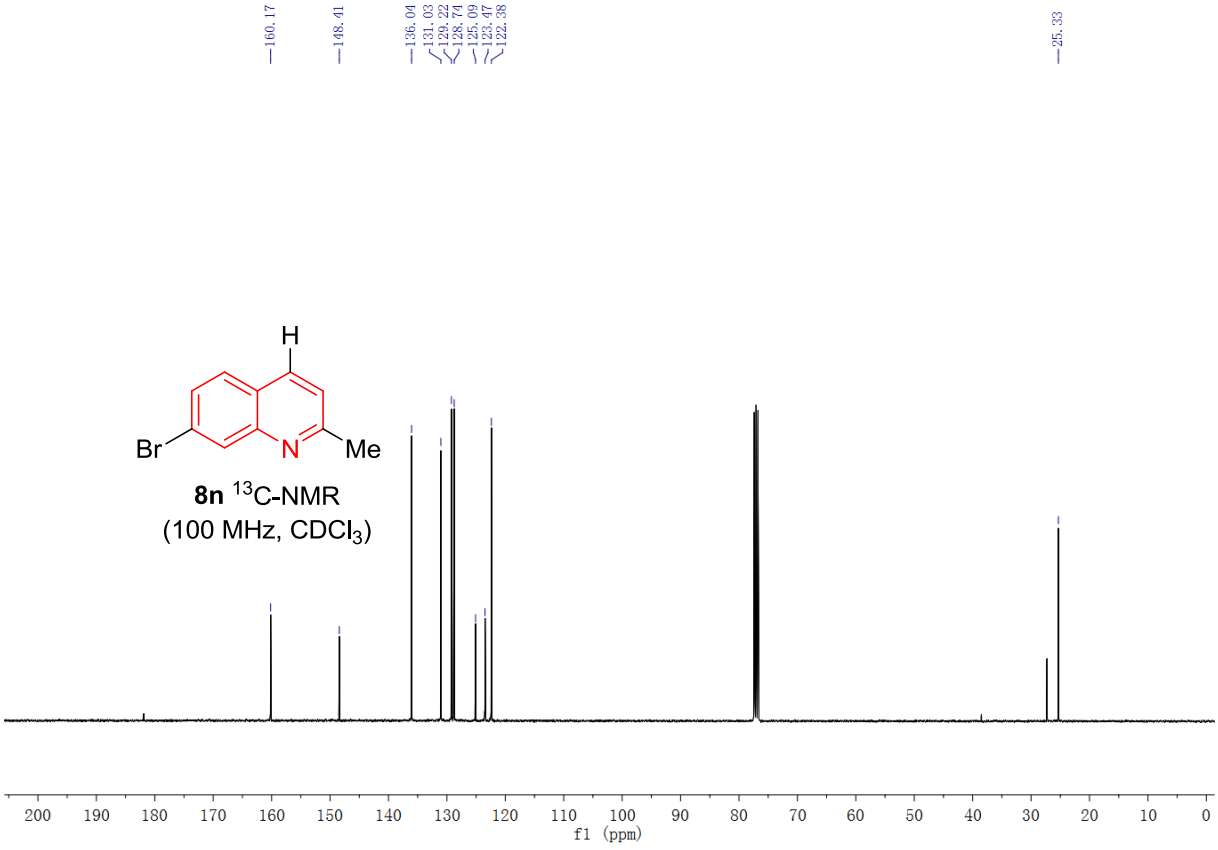
8m ^{1}H-NMR
(400 MHz, $CDCl_3$)



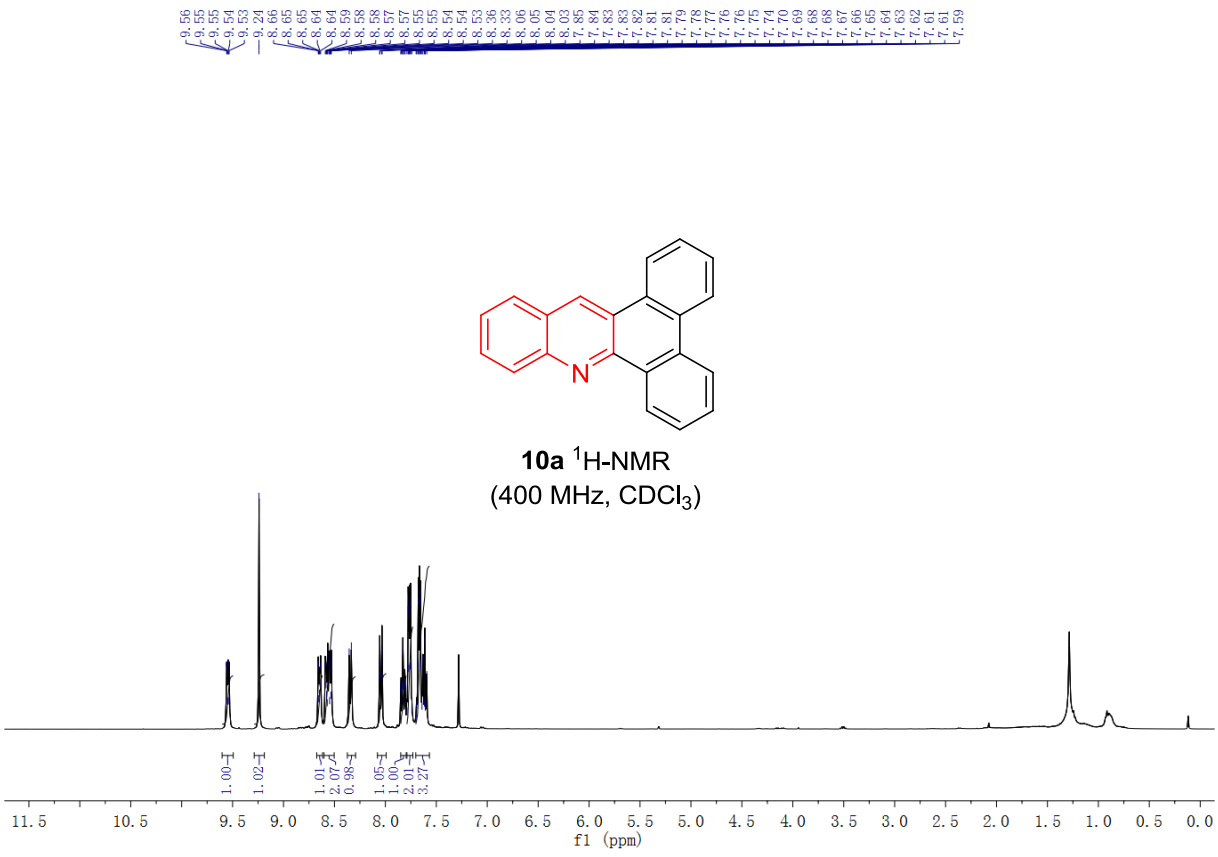
8m ^{13}C-NMR
(100 MHz, $CDCl_3$)



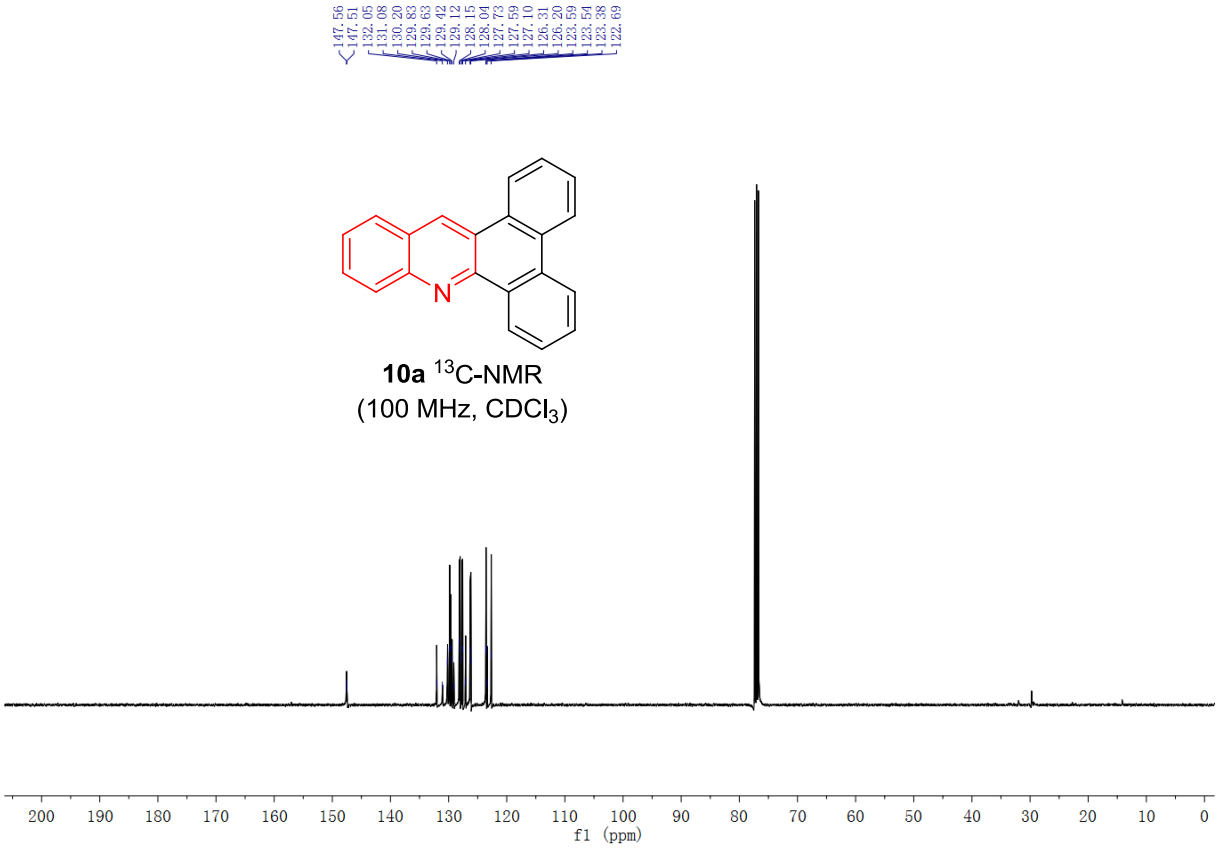
8n ^{1}H-NMR
(400 MHz, $CDCl_3$)



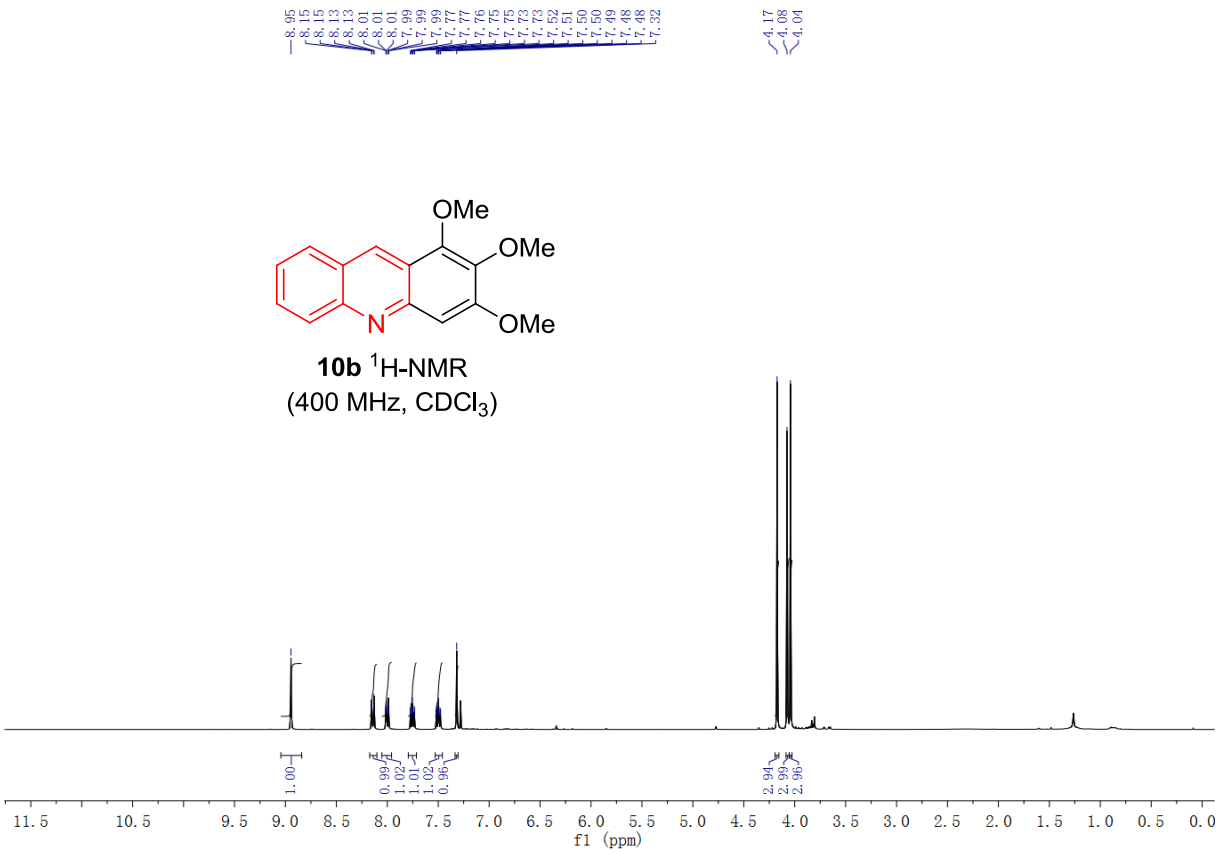
8n ^{13}C-NMR
(100 MHz, $CDCl_3$)



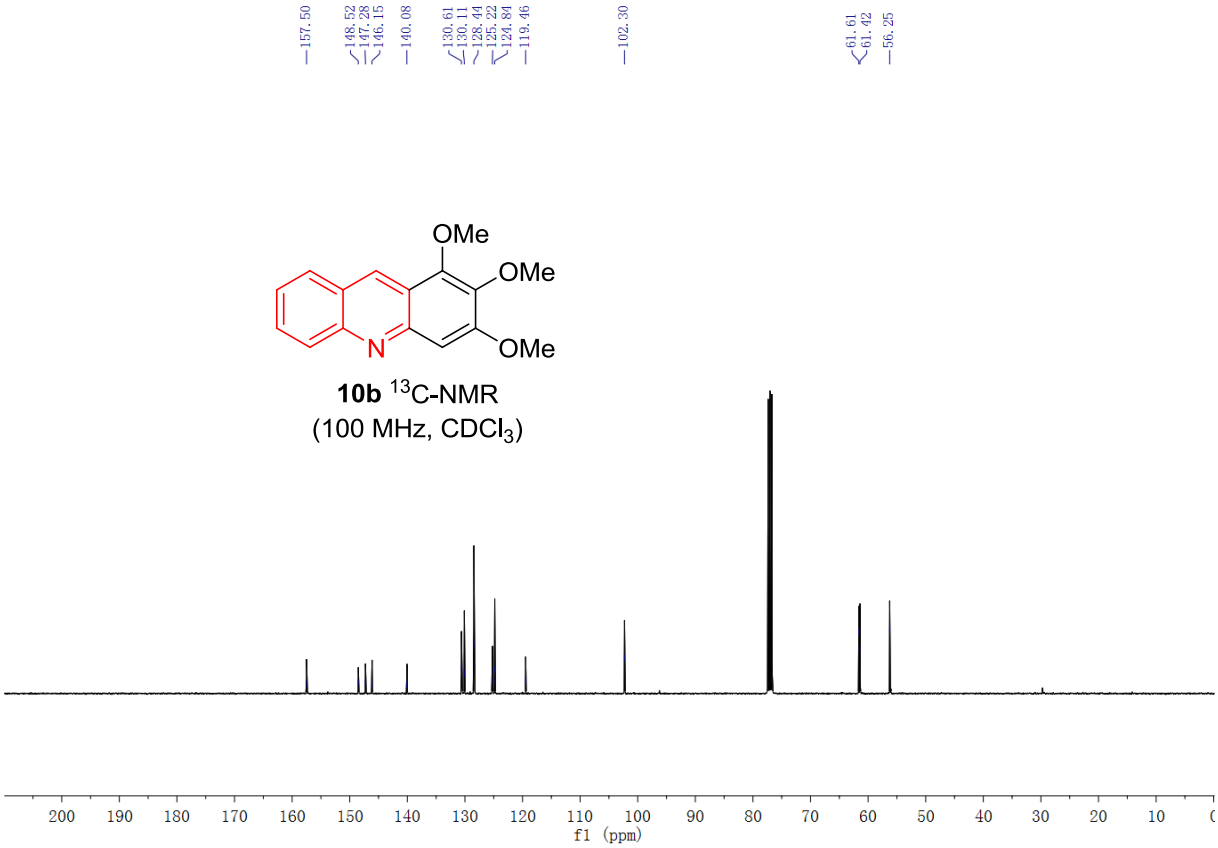
10a ^{1}H-NMR
(400 MHz, $CDCl_3$)



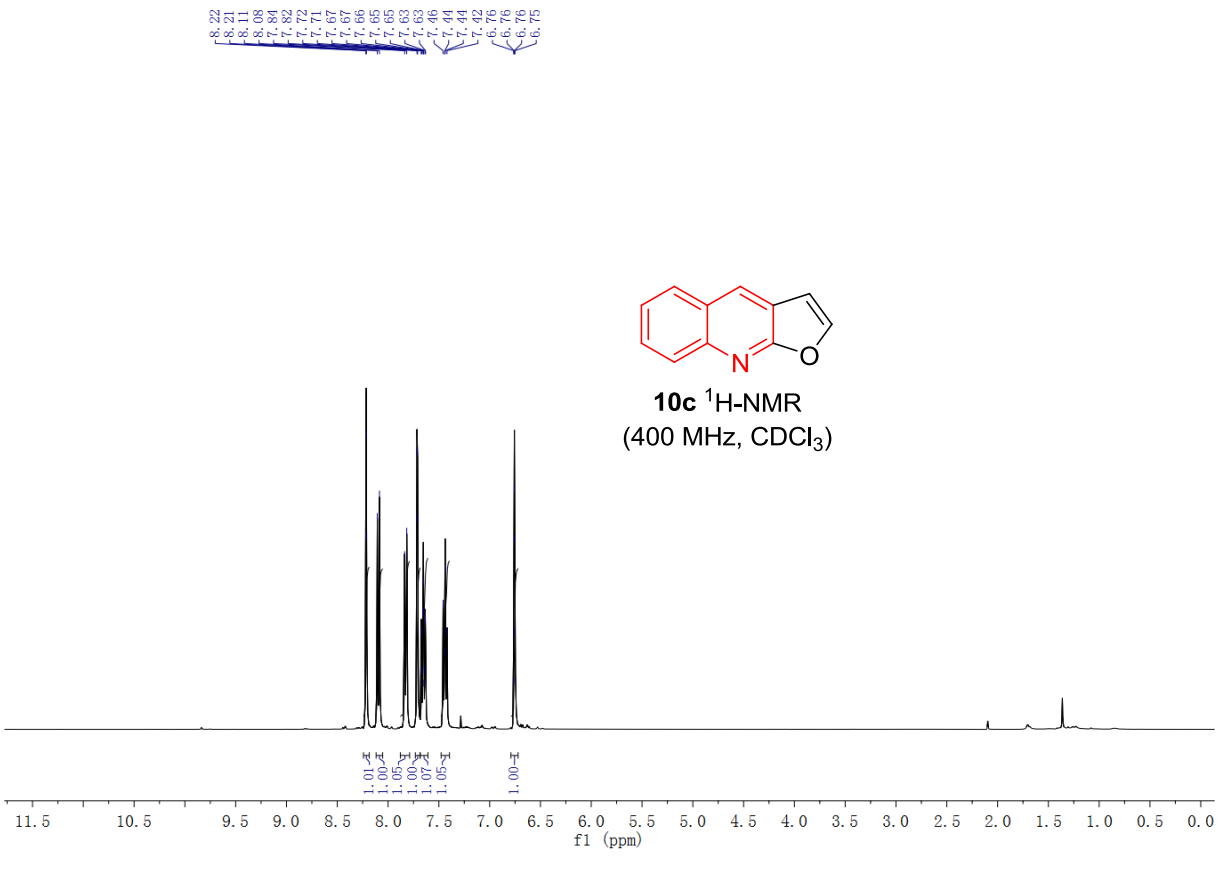
10a ^{13}C-NMR
(100 MHz, $CDCl_3$)



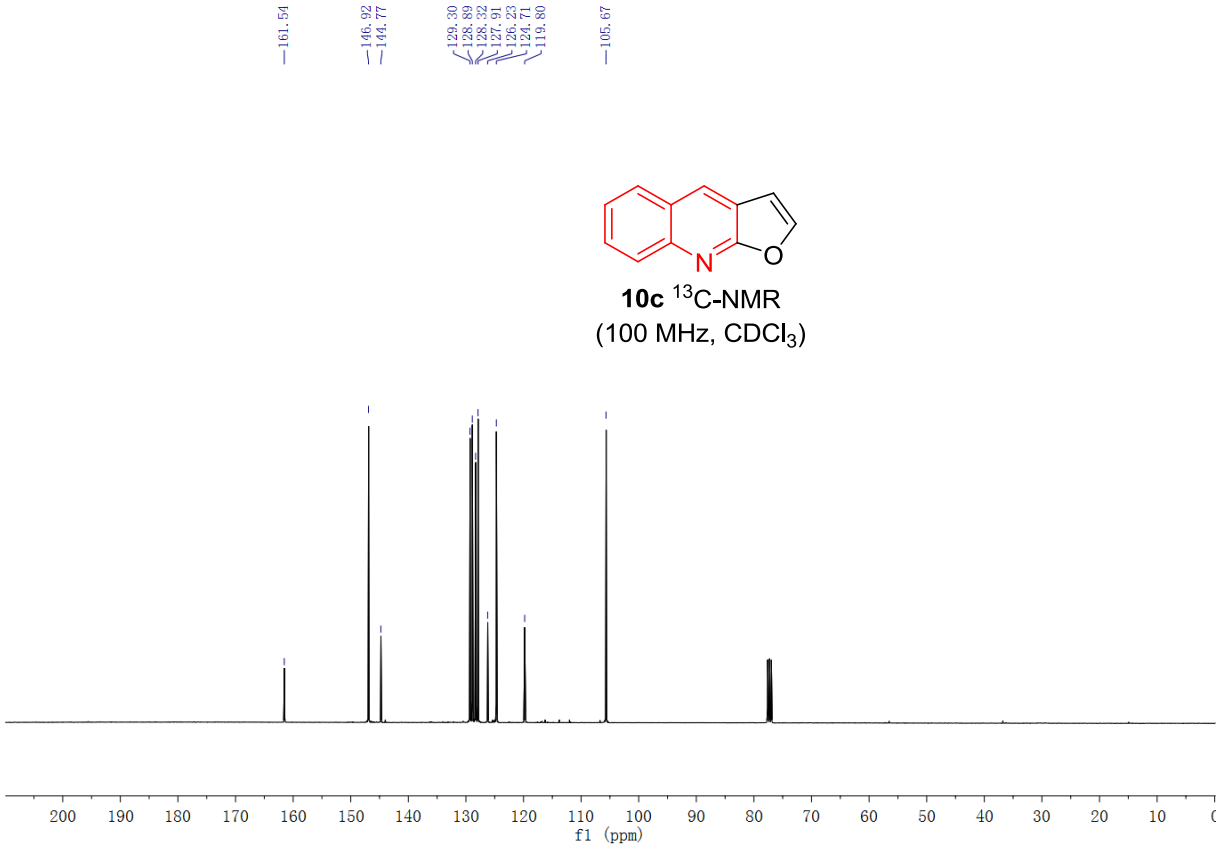
10b ^{1}H-NMR
(400 MHz, $CDCl_3$)



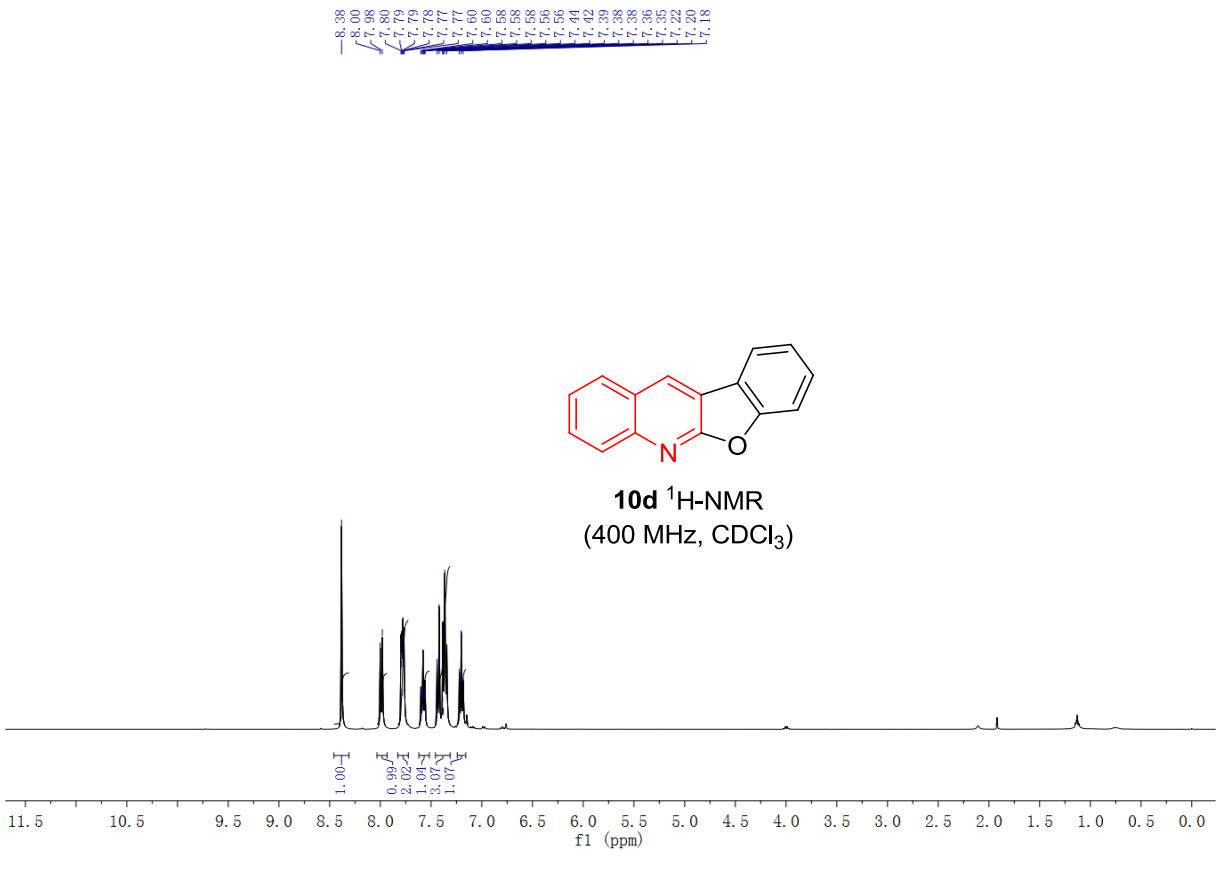
10b ^{13}C-NMR
(100 MHz, $CDCl_3$)



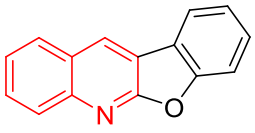
10c ^{1}H-NMR
(400 MHz, $CDCl_3$)



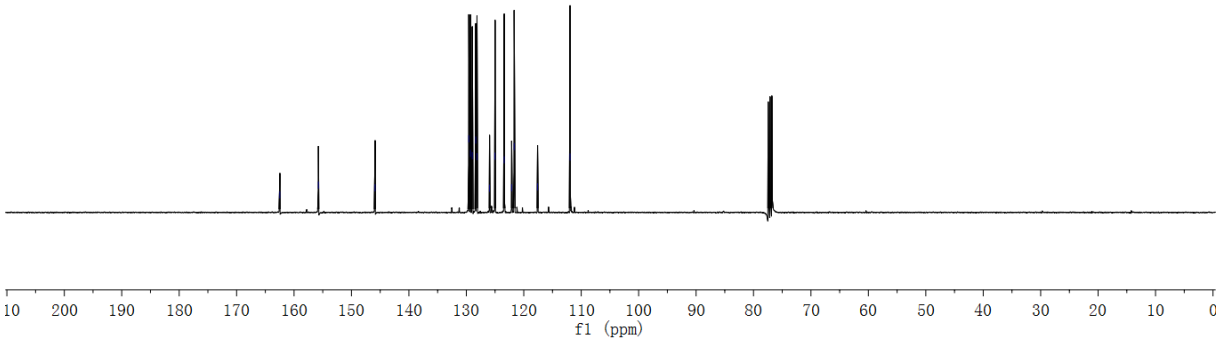
10c ^{13}C-NMR
(100 MHz, $CDCl_3$)

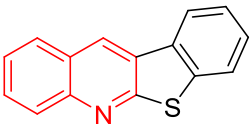


10d ^{1}H-NMR
(400 MHz, $CDCl_3$)

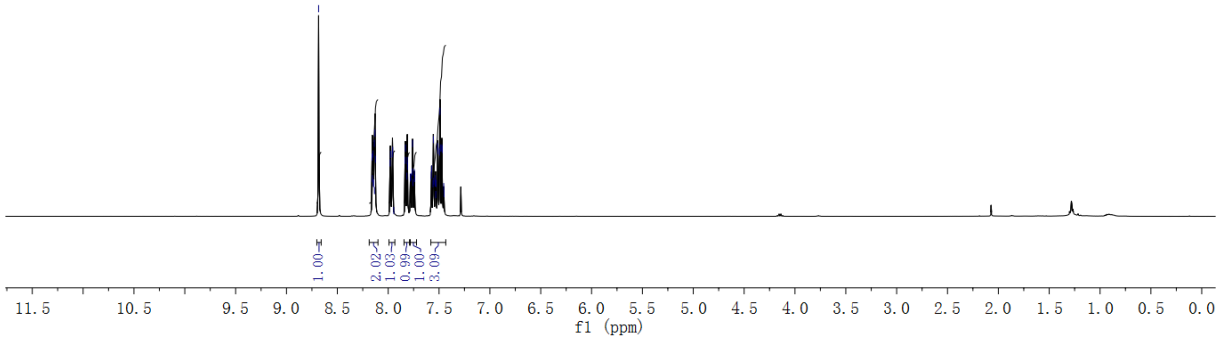


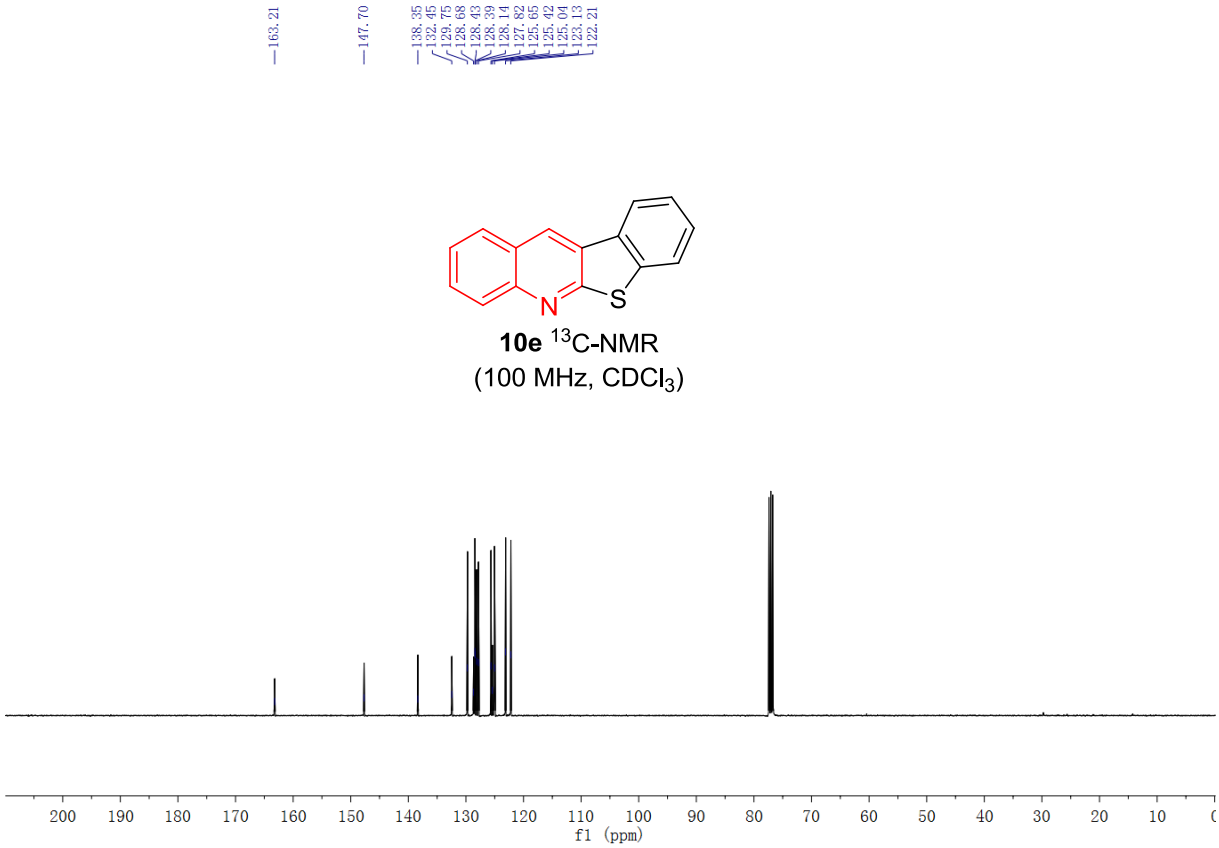
10d ^{13}C-NMR
(100 MHz, $CDCl_3$)



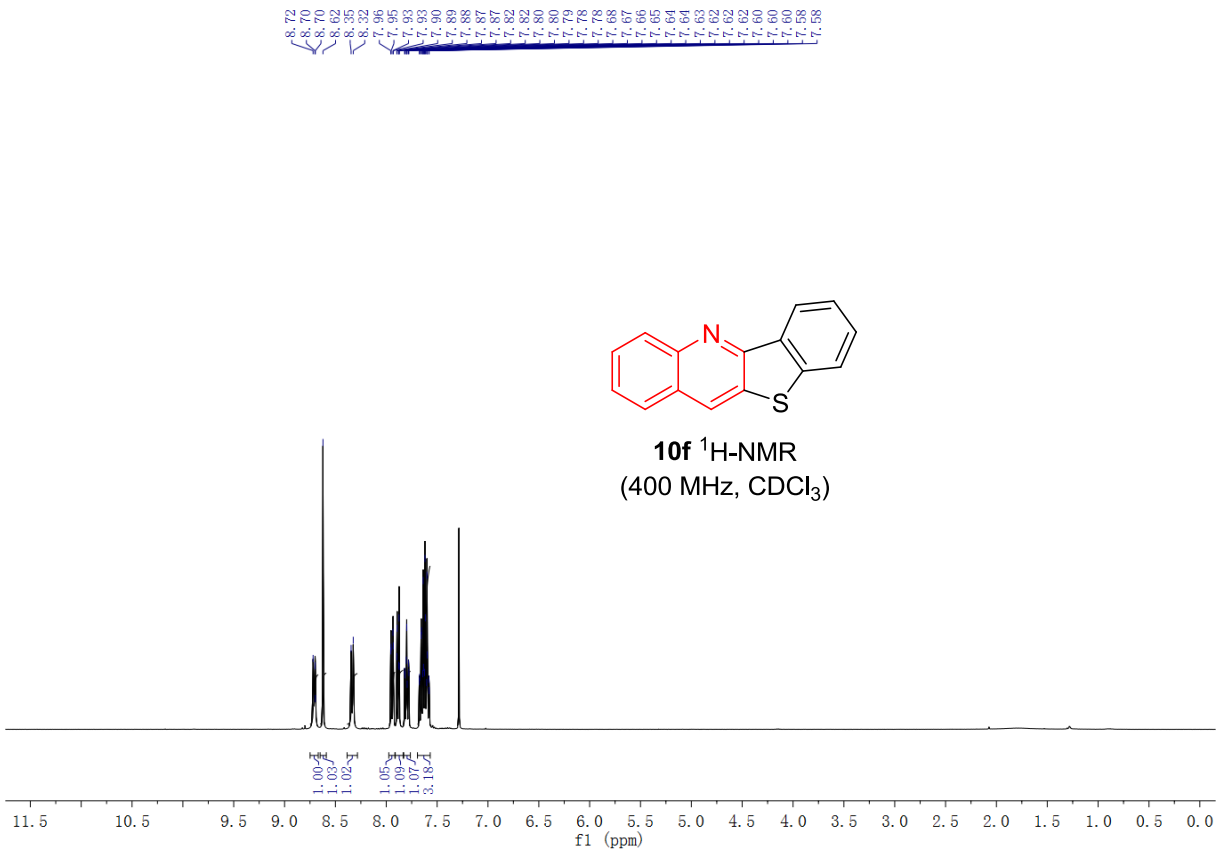


10e ^{1}H-NMR
(400 MHz, $CDCl_3$)

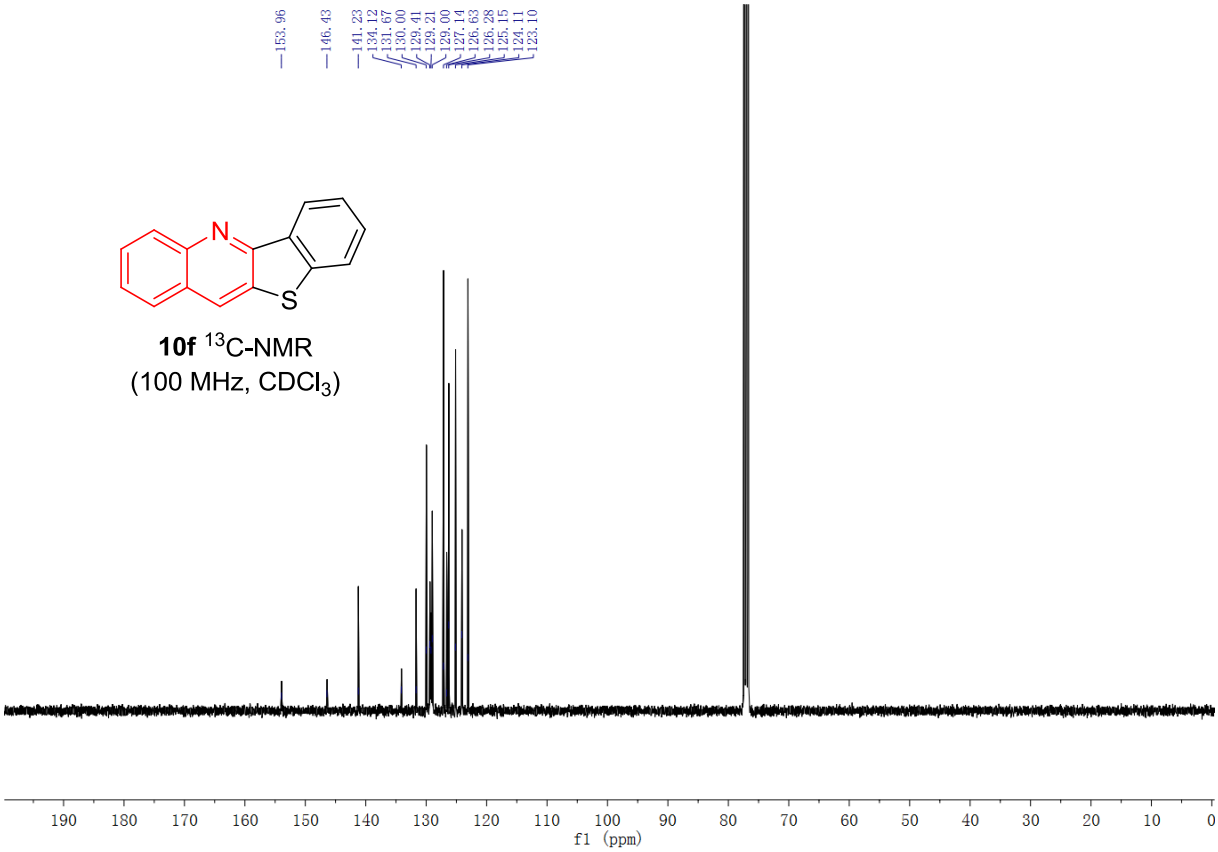




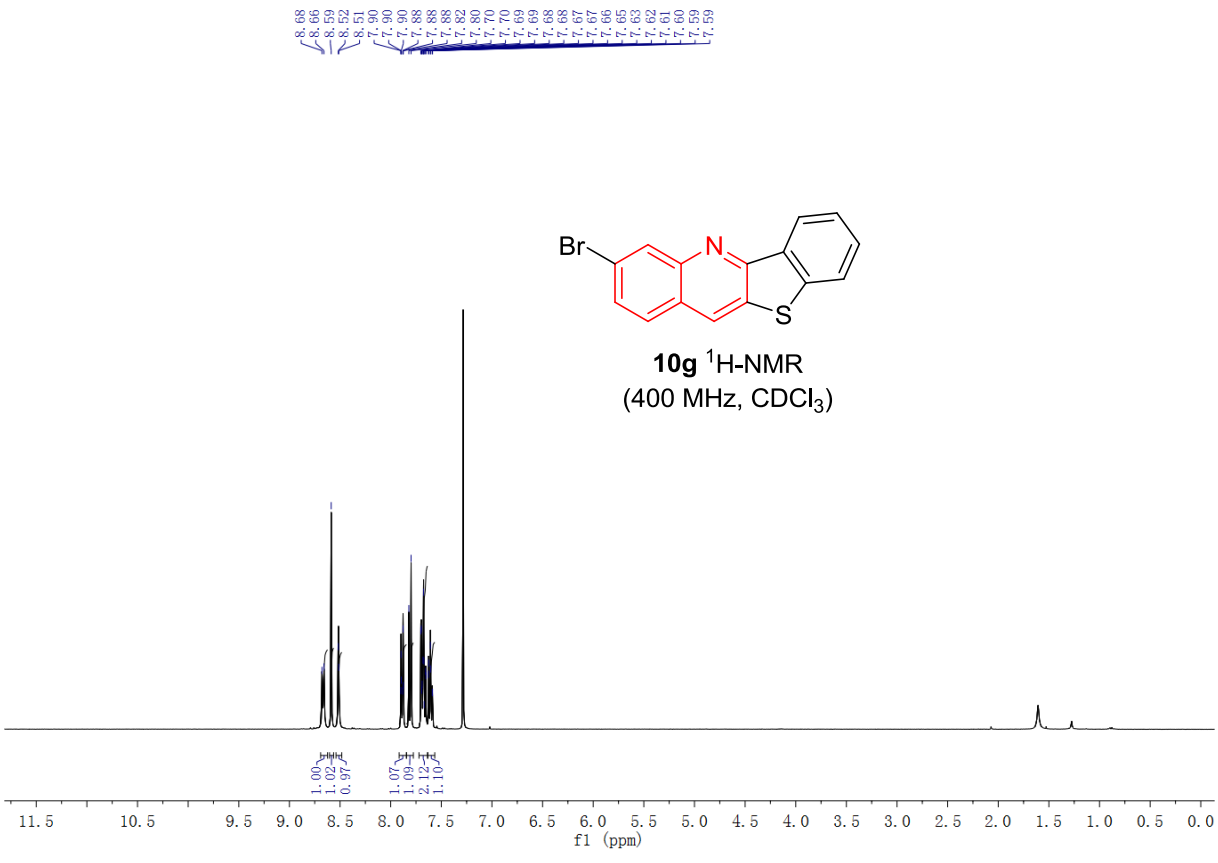
10e ^{13}C-NMR
(100 MHz, $CDCl_3$)



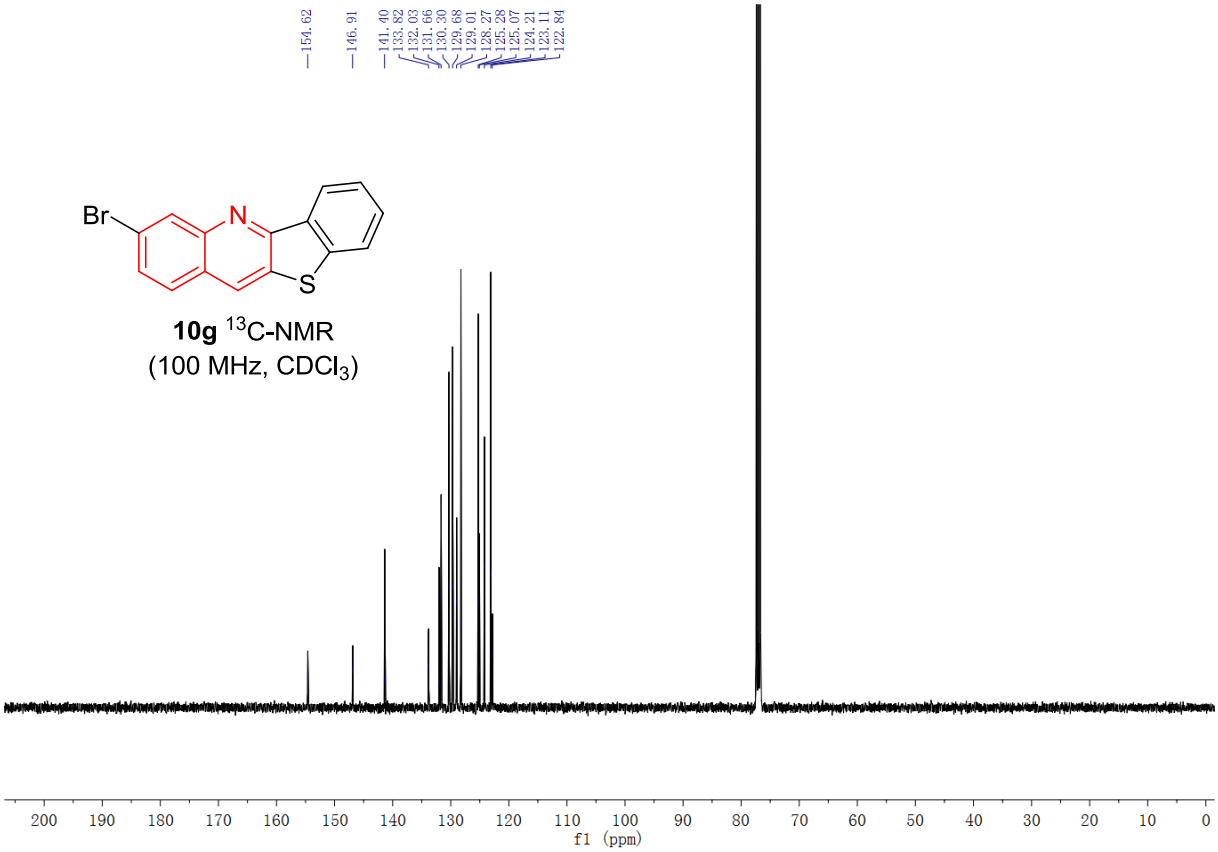
10f ^{1}H-NMR
(400 MHz, $CDCl_3$)



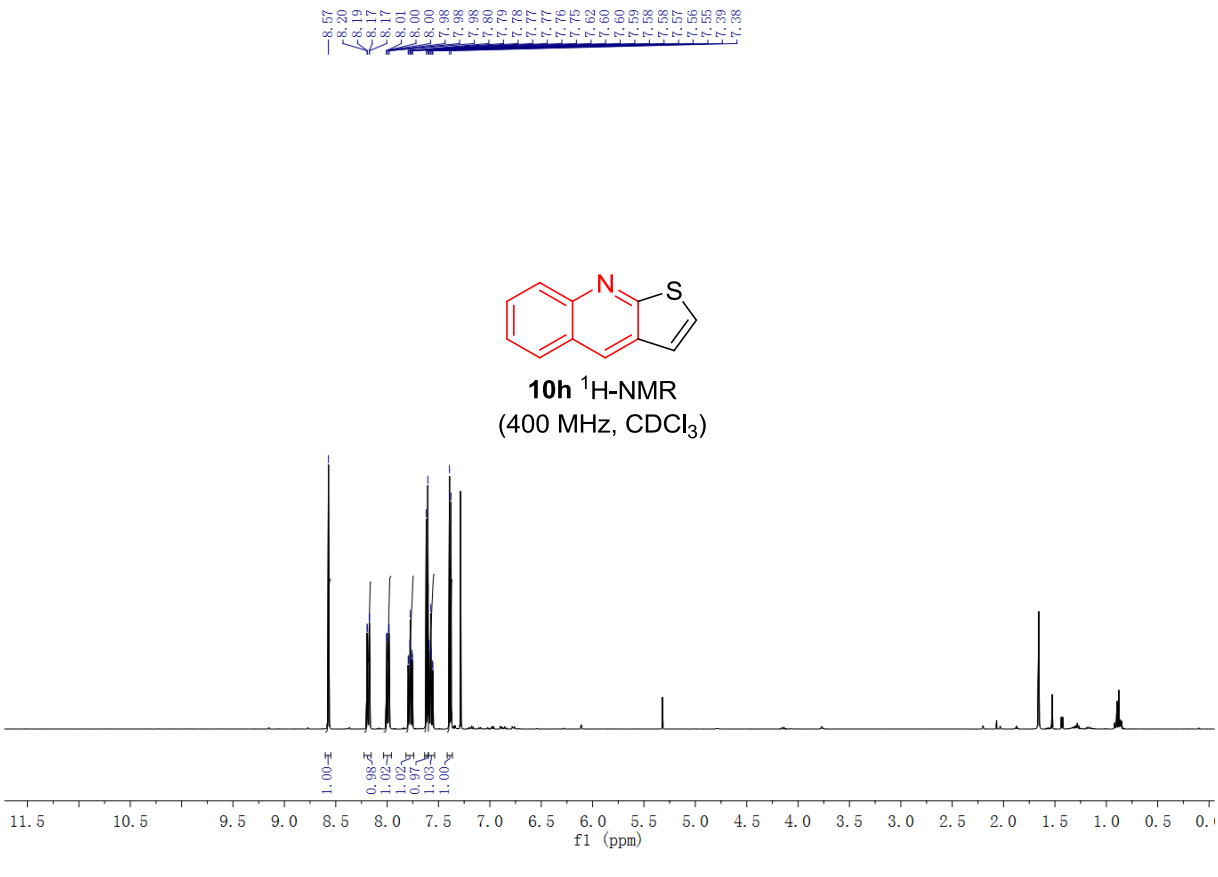
10f ^{13}C-NMR
(100 MHz, $CDCl_3$)



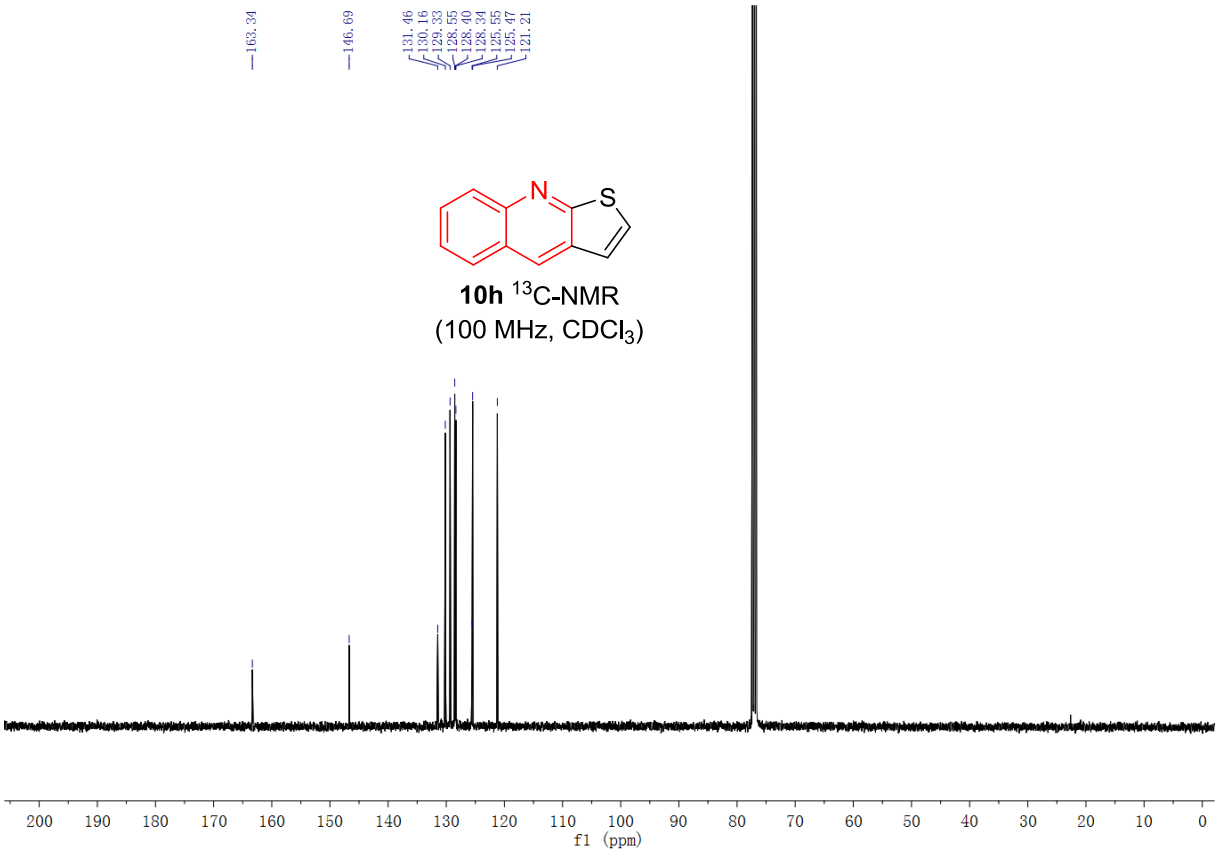
10g ^{1}H-NMR
(400 MHz, $CDCl_3$)



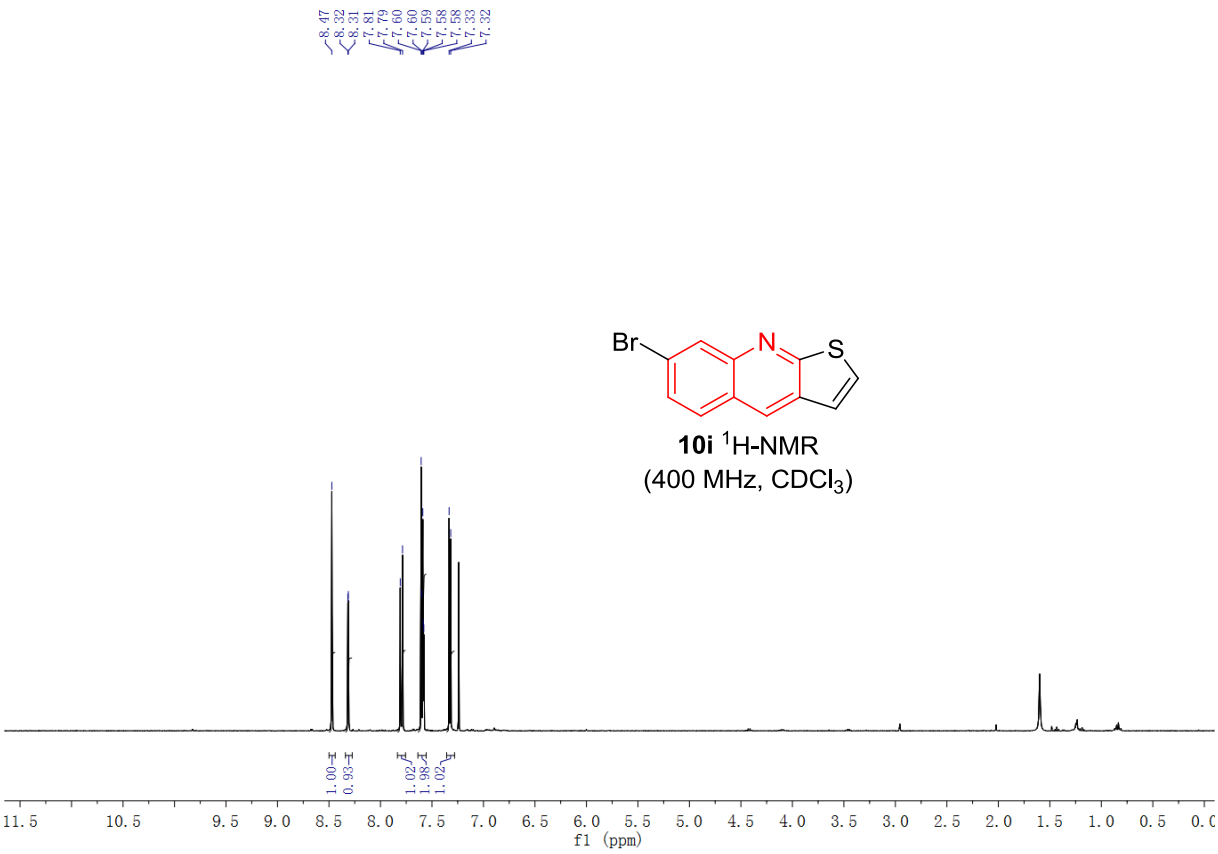
10g ^{13}C-NMR
(100 MHz, $CDCl_3$)



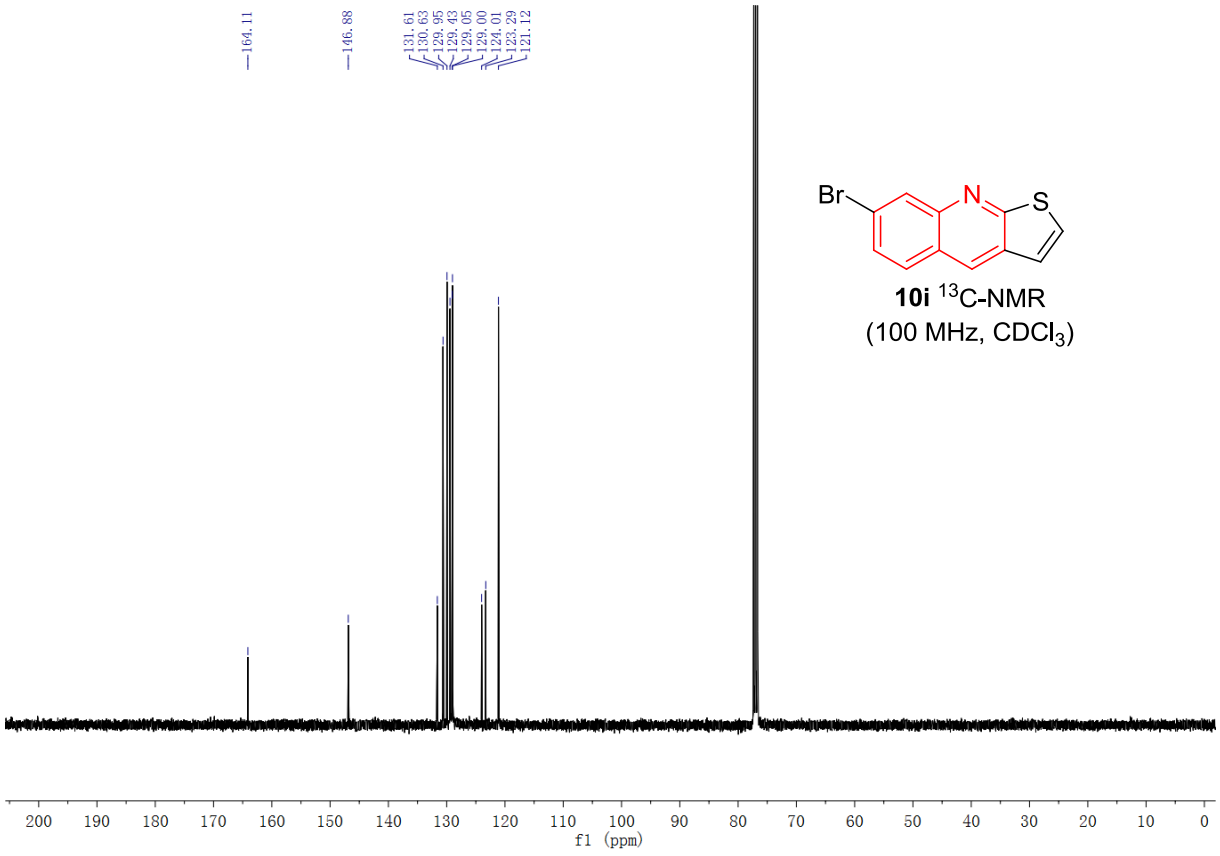
10h ^{1}H-NMR
(400 MHz, $CDCl_3$)



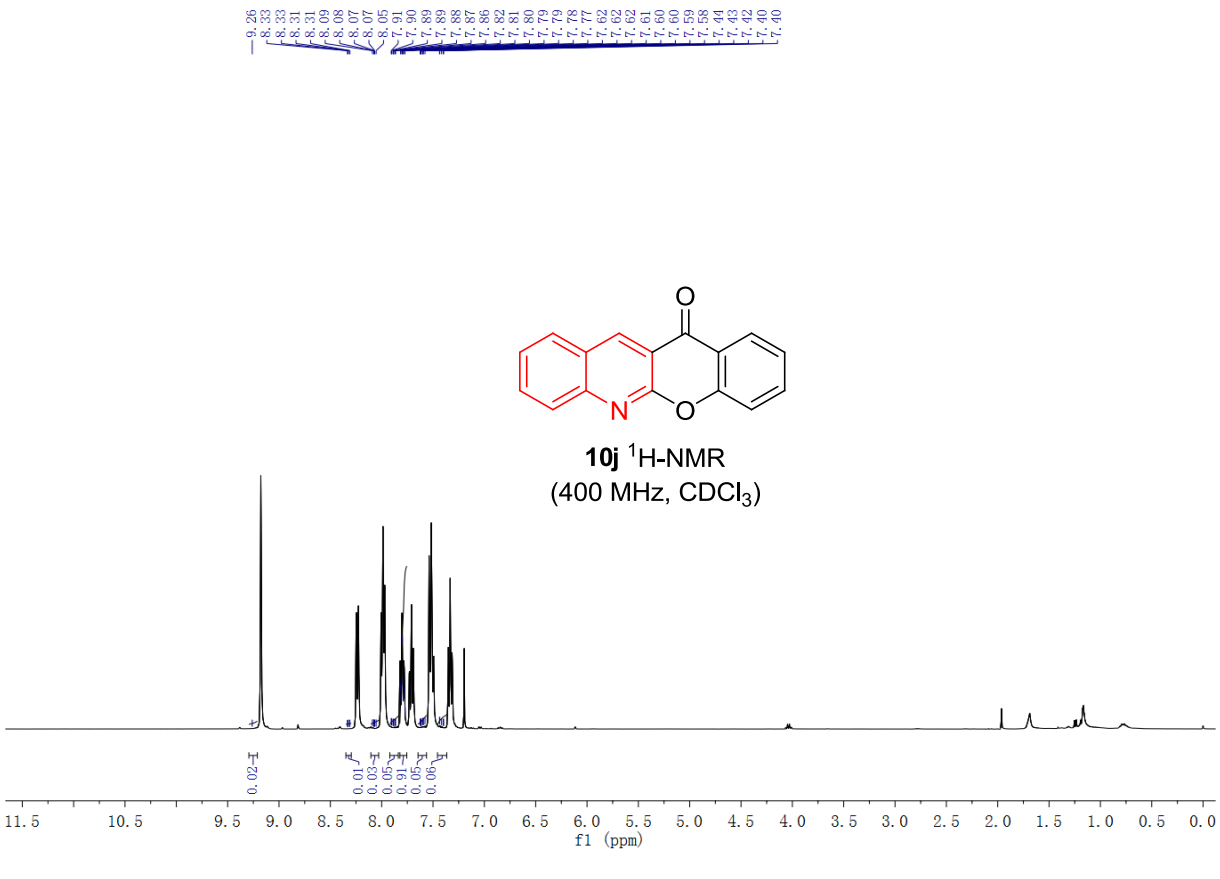
10h ^{13}C-NMR
(100 MHz, $CDCl_3$)



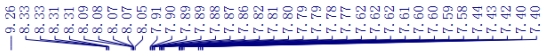
10i ^{1}H-NMR
(400 MHz, $CDCl_3$)

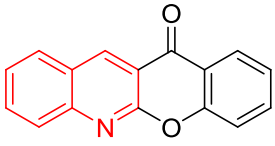


10i ^{13}C-NMR
(100 MHz, $CDCl_3$)

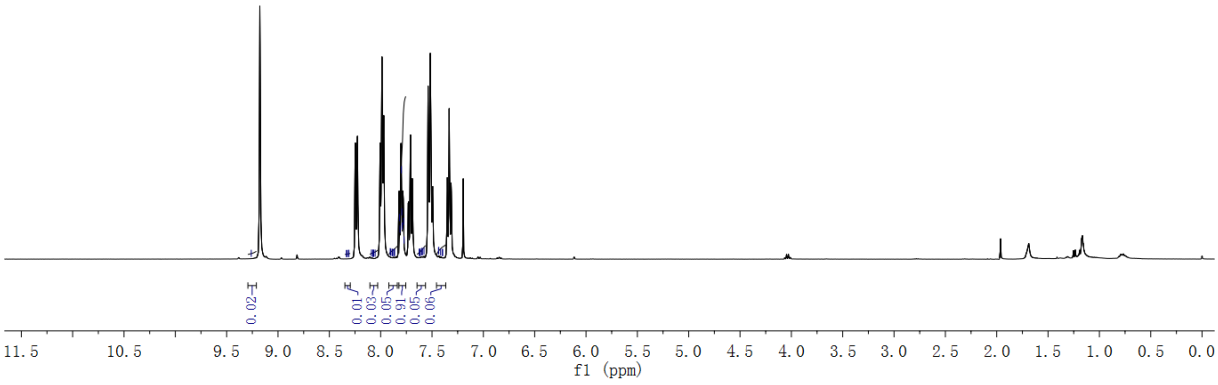


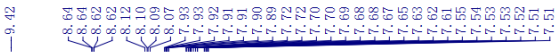
10j ^{1}H-NMR
(400 MHz, $CDCl_3$)

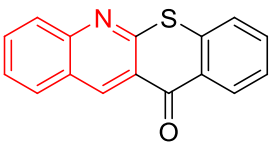




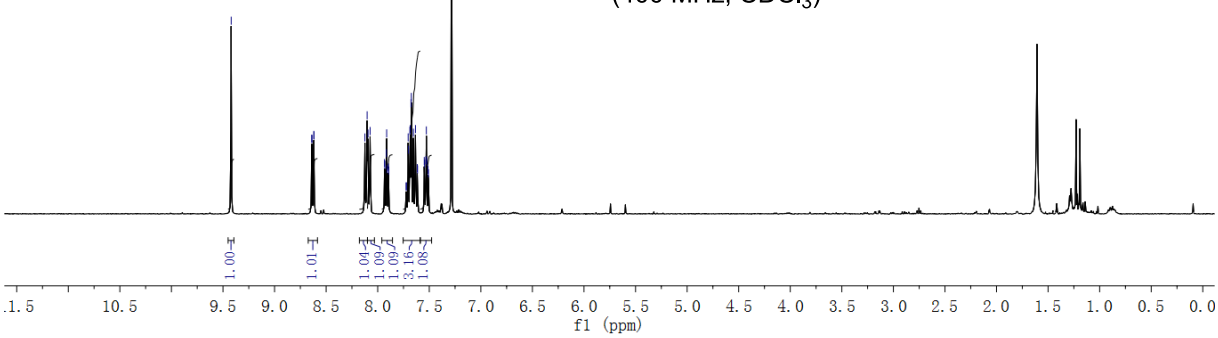
10j ^{13}C-NMR
(100 MHz, $CDCl_3$)

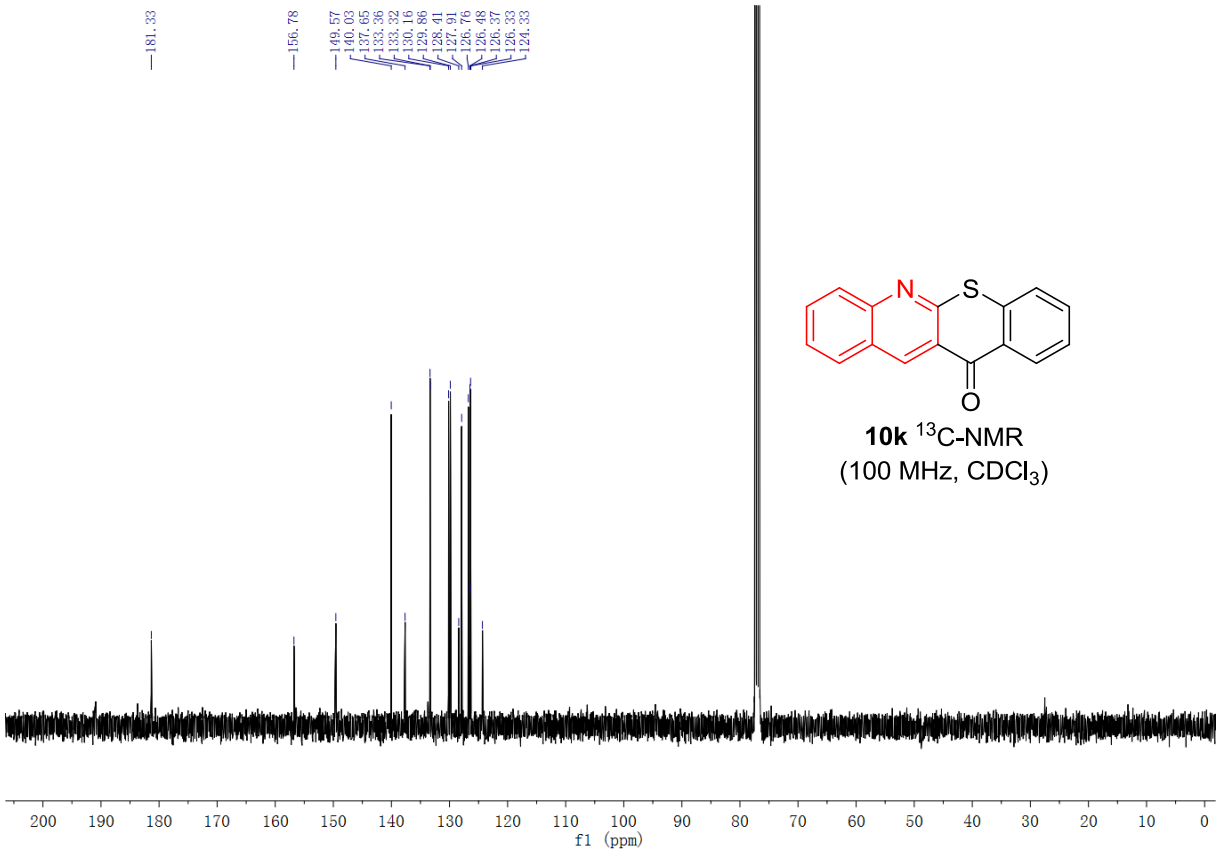




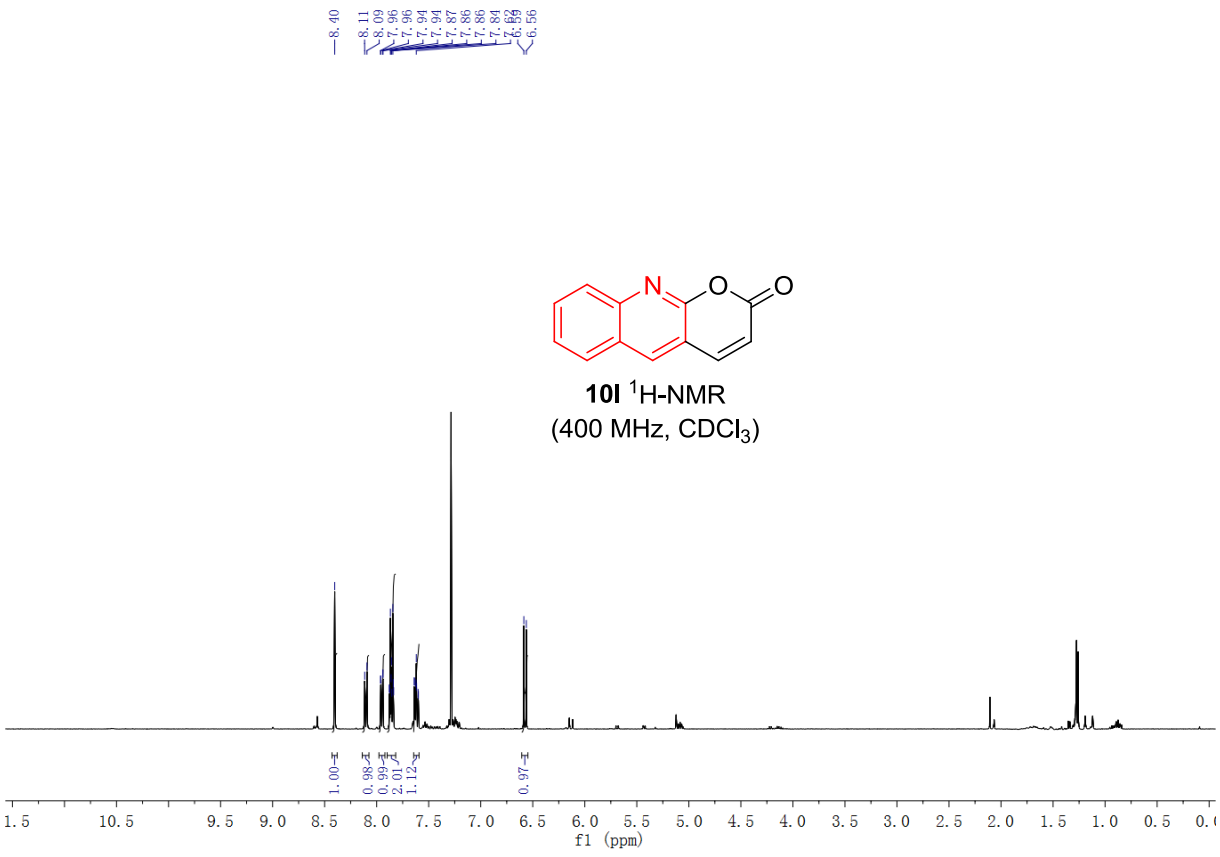


10k ^{1}H-NMR
(400 MHz, $CDCl_3$)

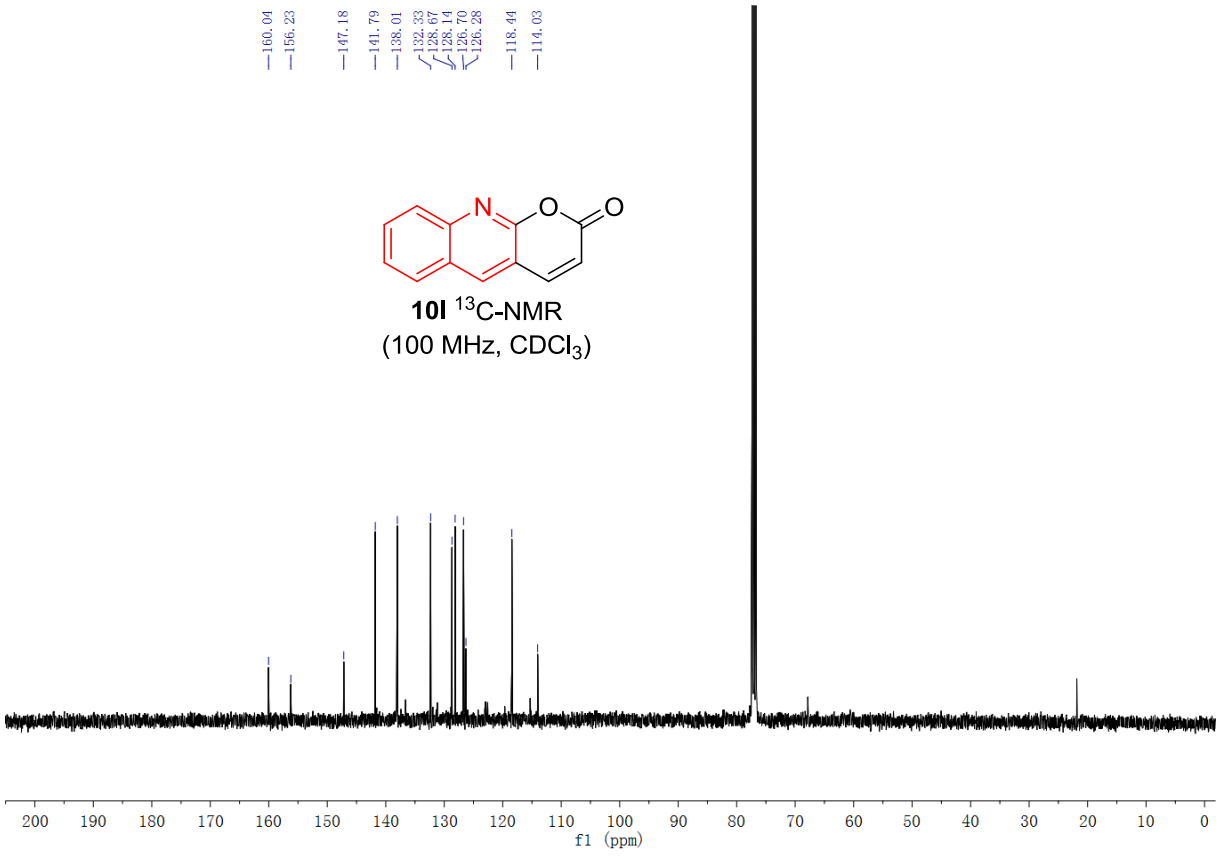




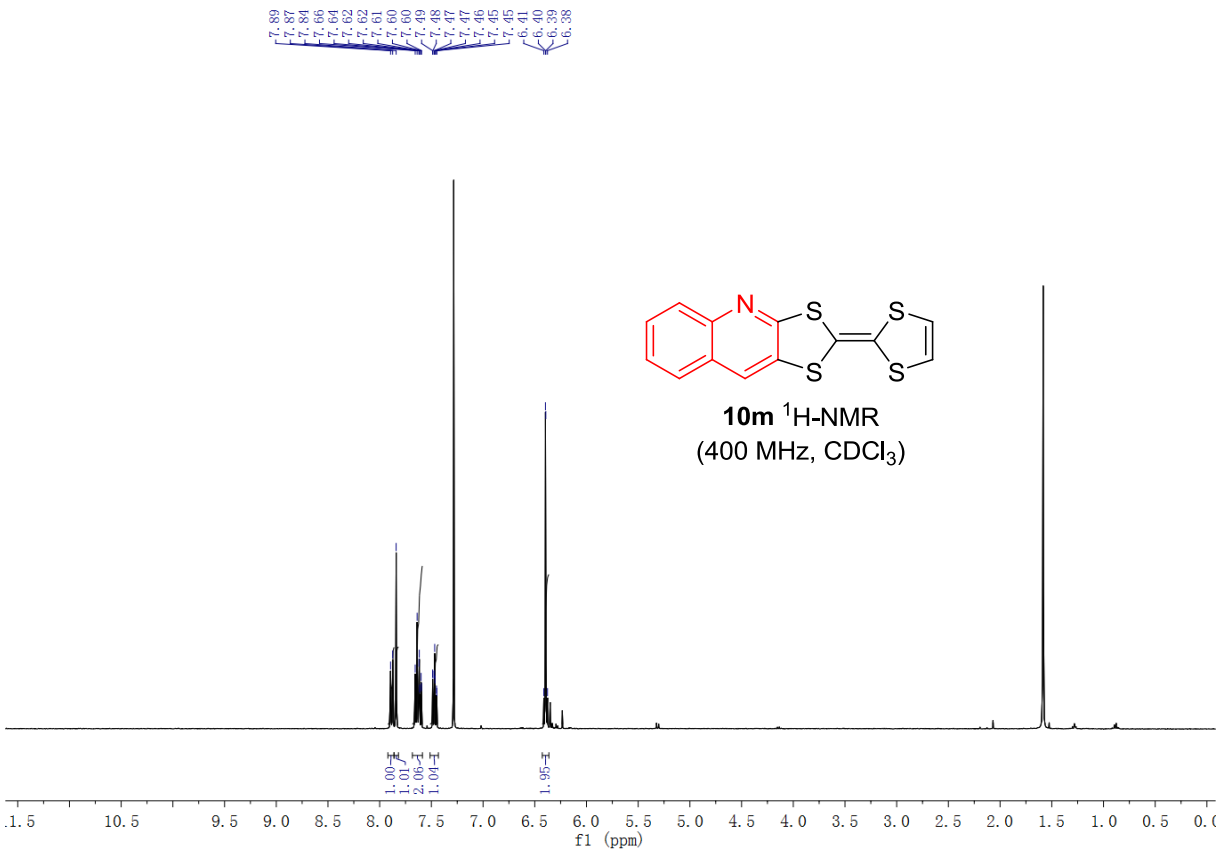
10k ^{13}C-NMR
(100 MHz, $CDCl_3$)



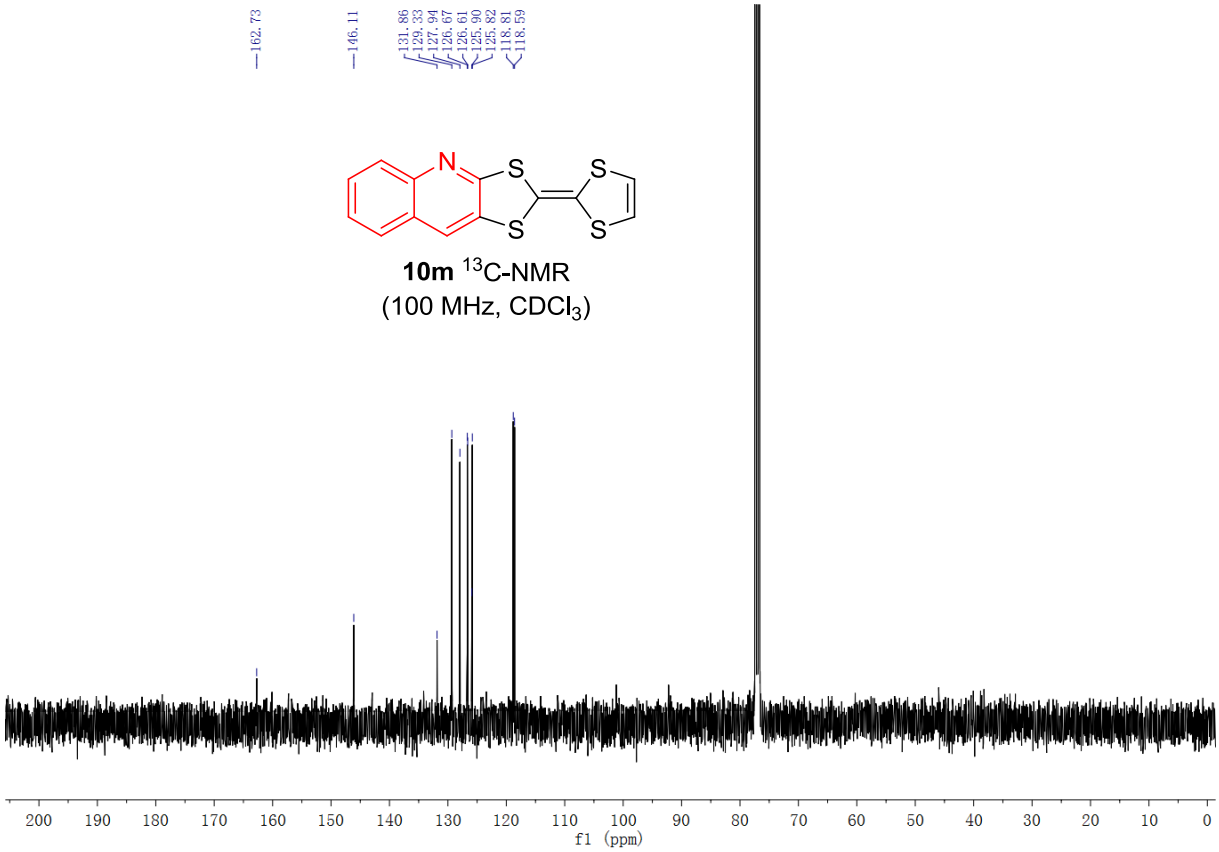
10l ^{1}H-NMR
(400 MHz, $CDCl_3$)



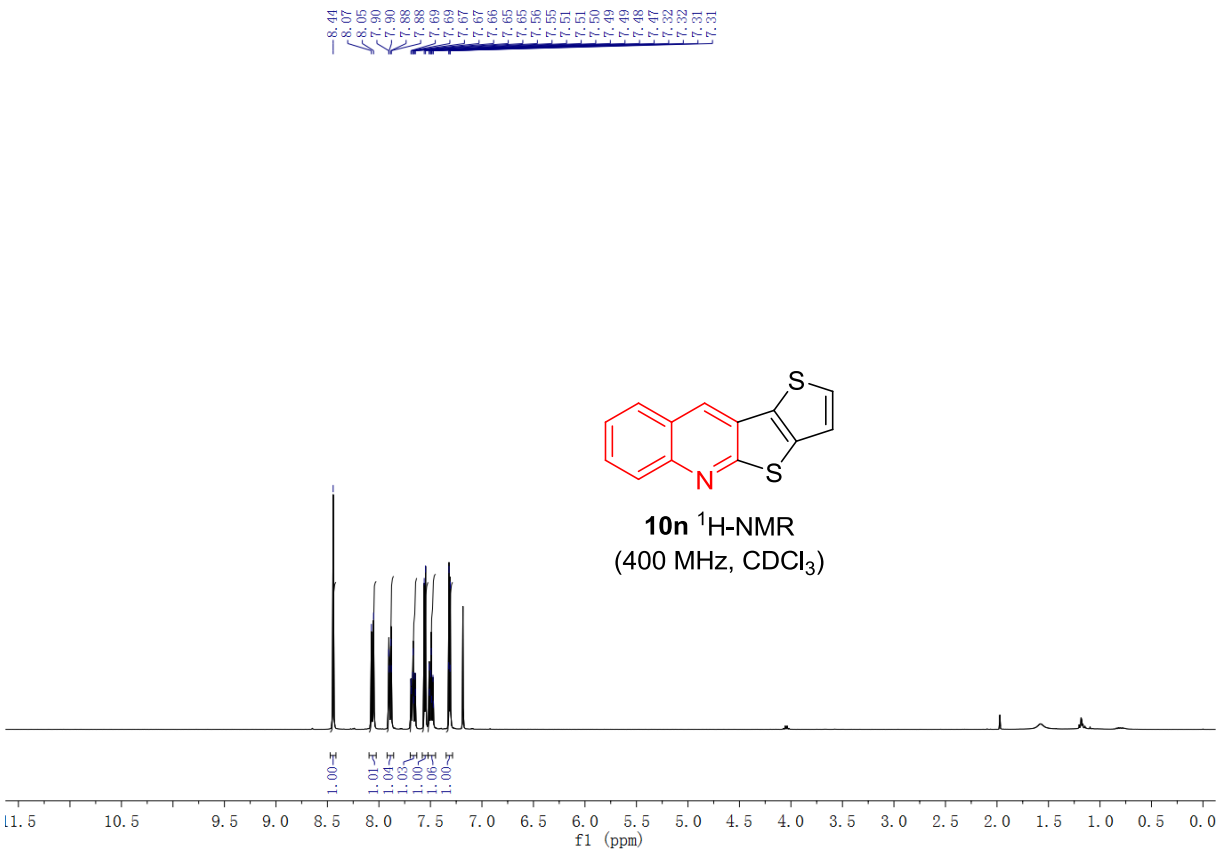
10l ^{13}C-NMR
(100 MHz, $CDCl_3$)



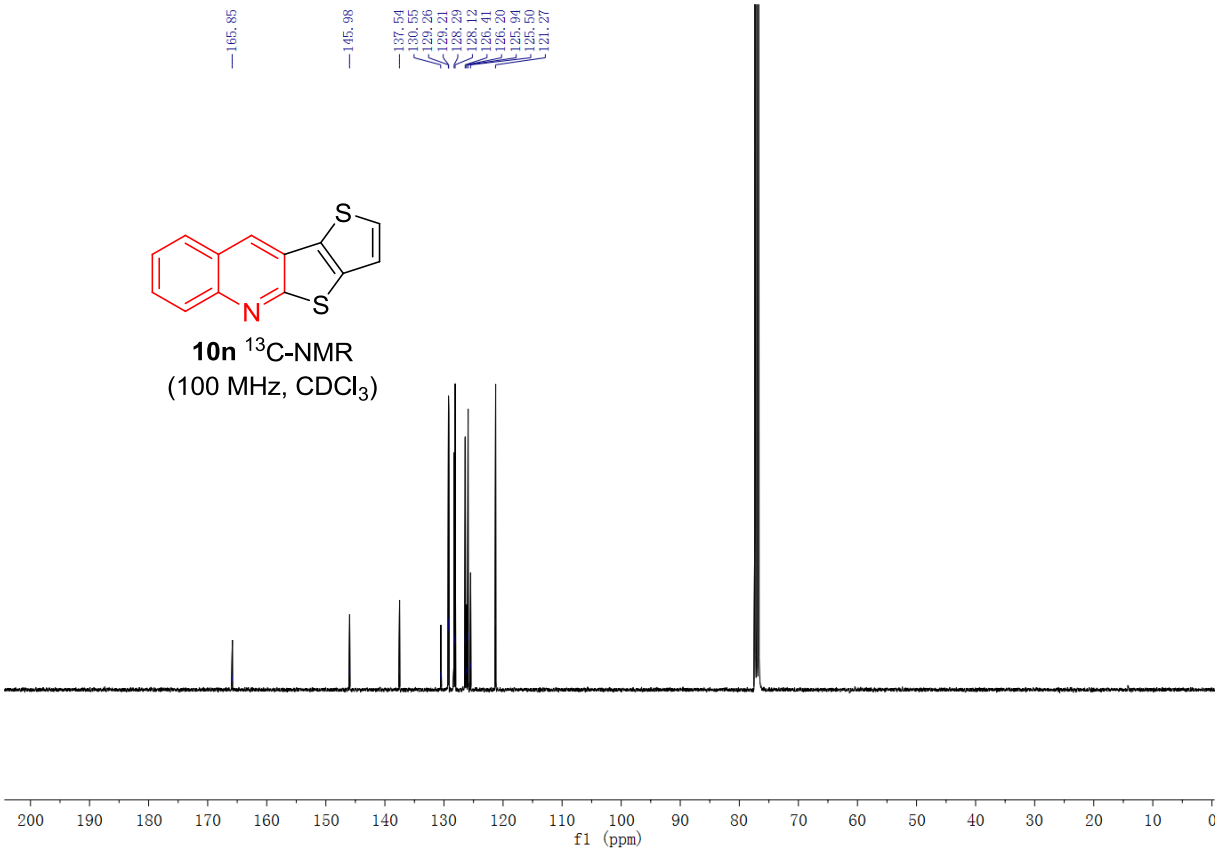
10m ^{1}H-NMR
(400 MHz, $CDCl_3$)



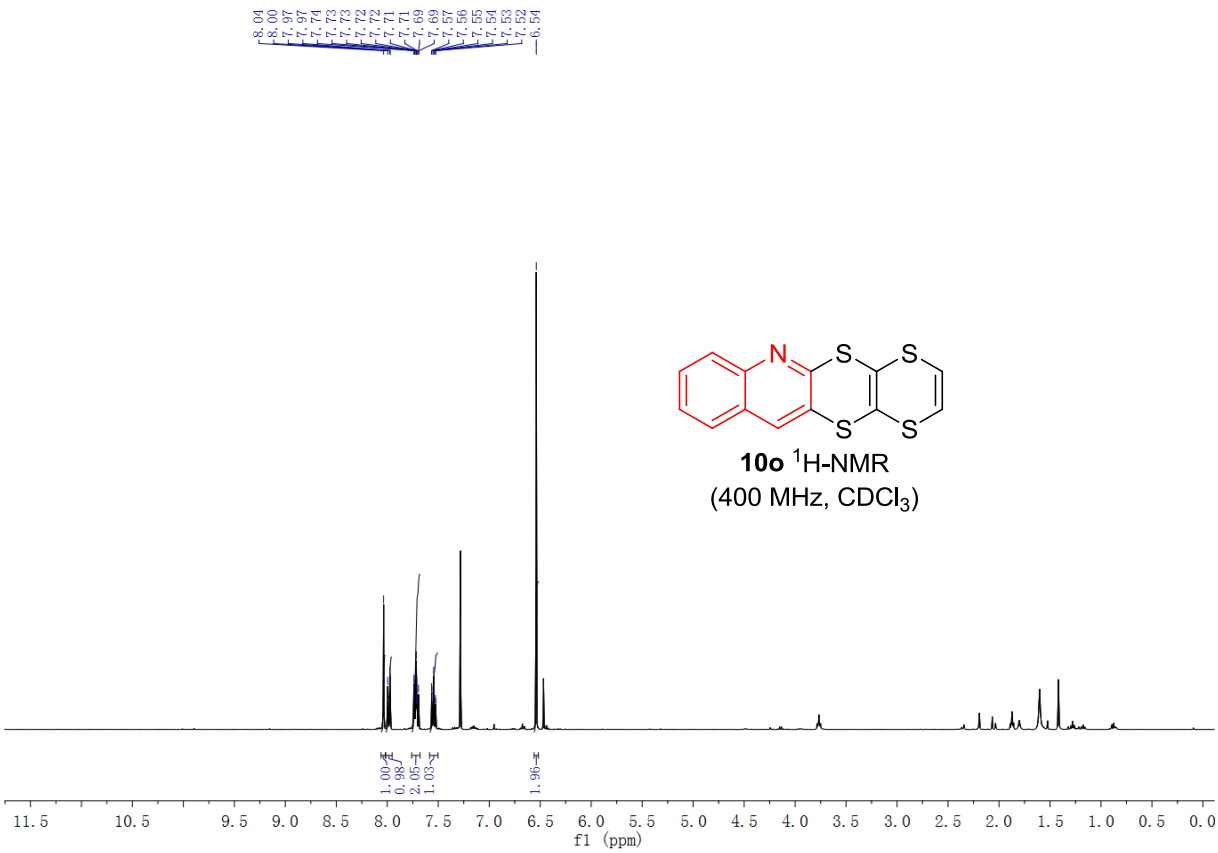
10m ^{13}C-NMR
(100 MHz, $CDCl_3$)



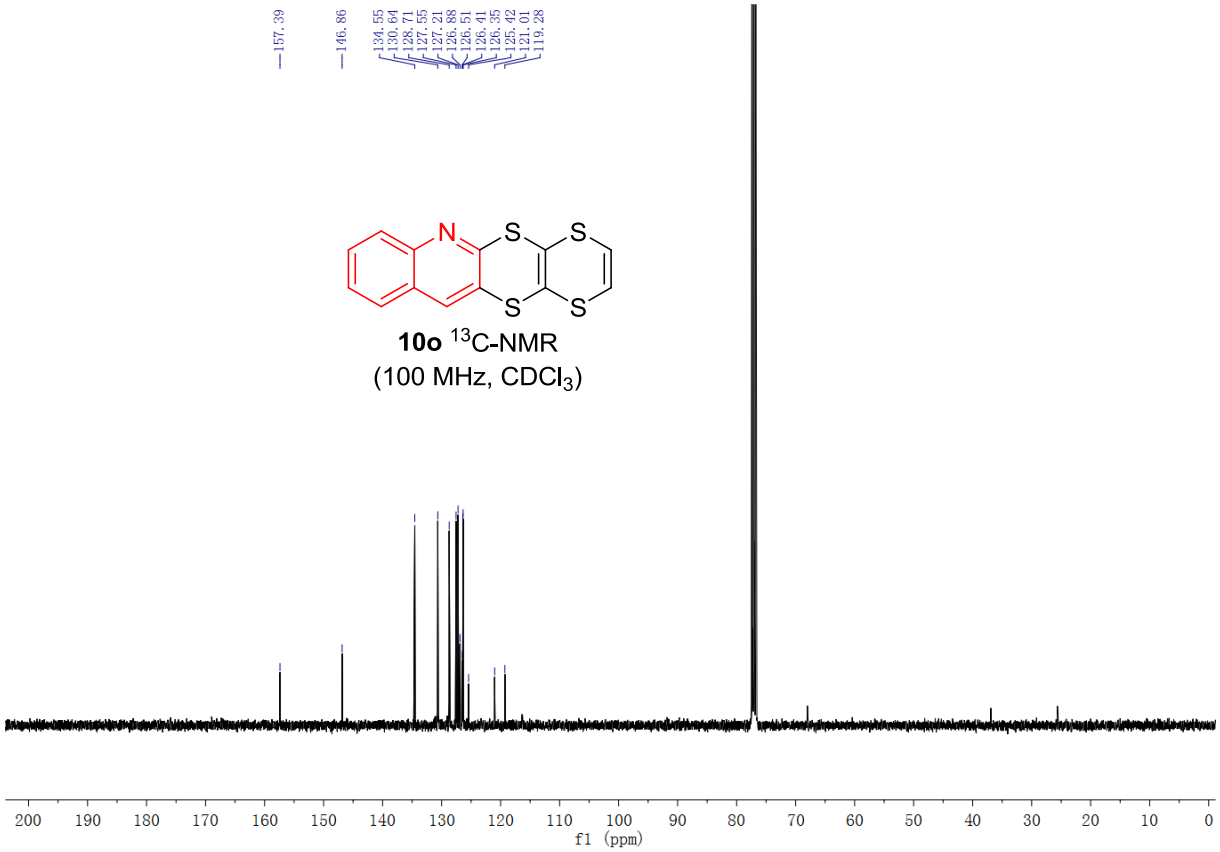
10n ^{1}H-NMR
(400 MHz, $CDCl_3$)



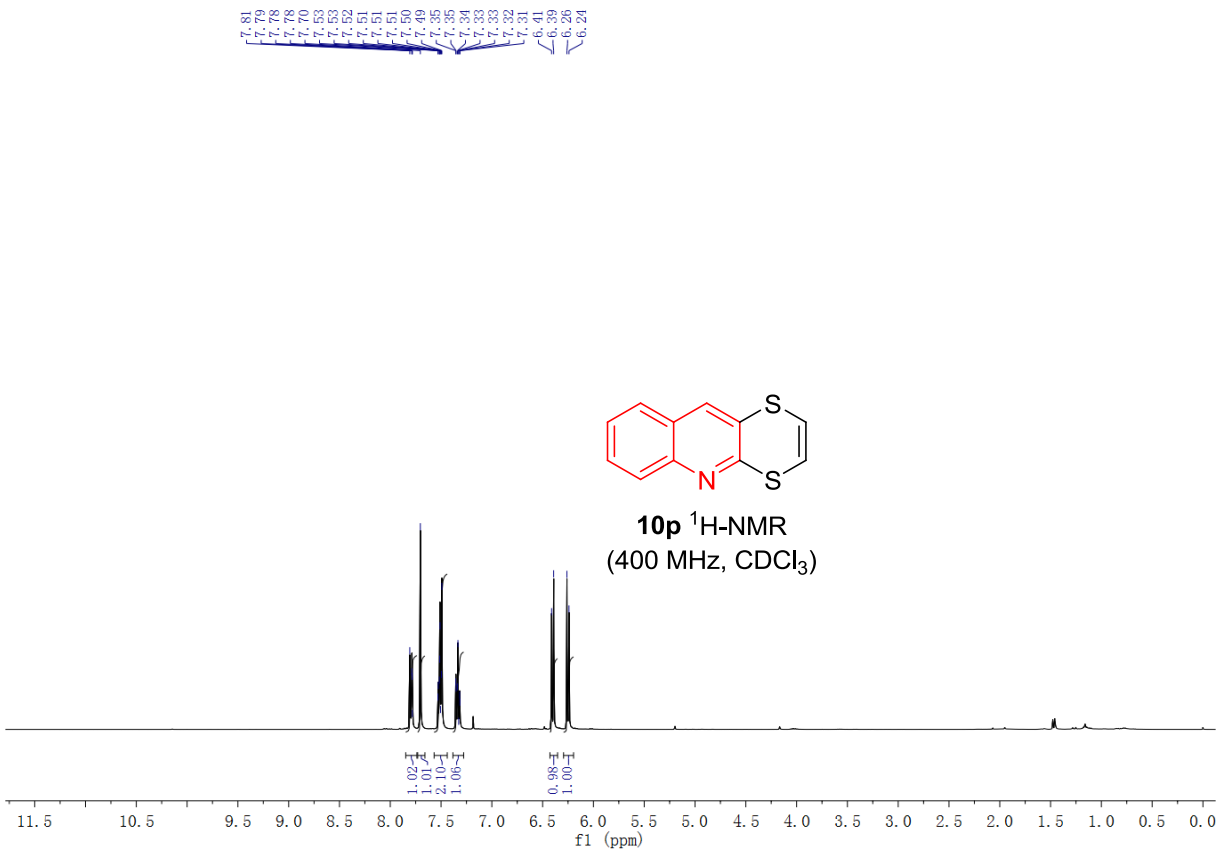
10n ^{13}C-NMR
(100 MHz, $CDCl_3$)



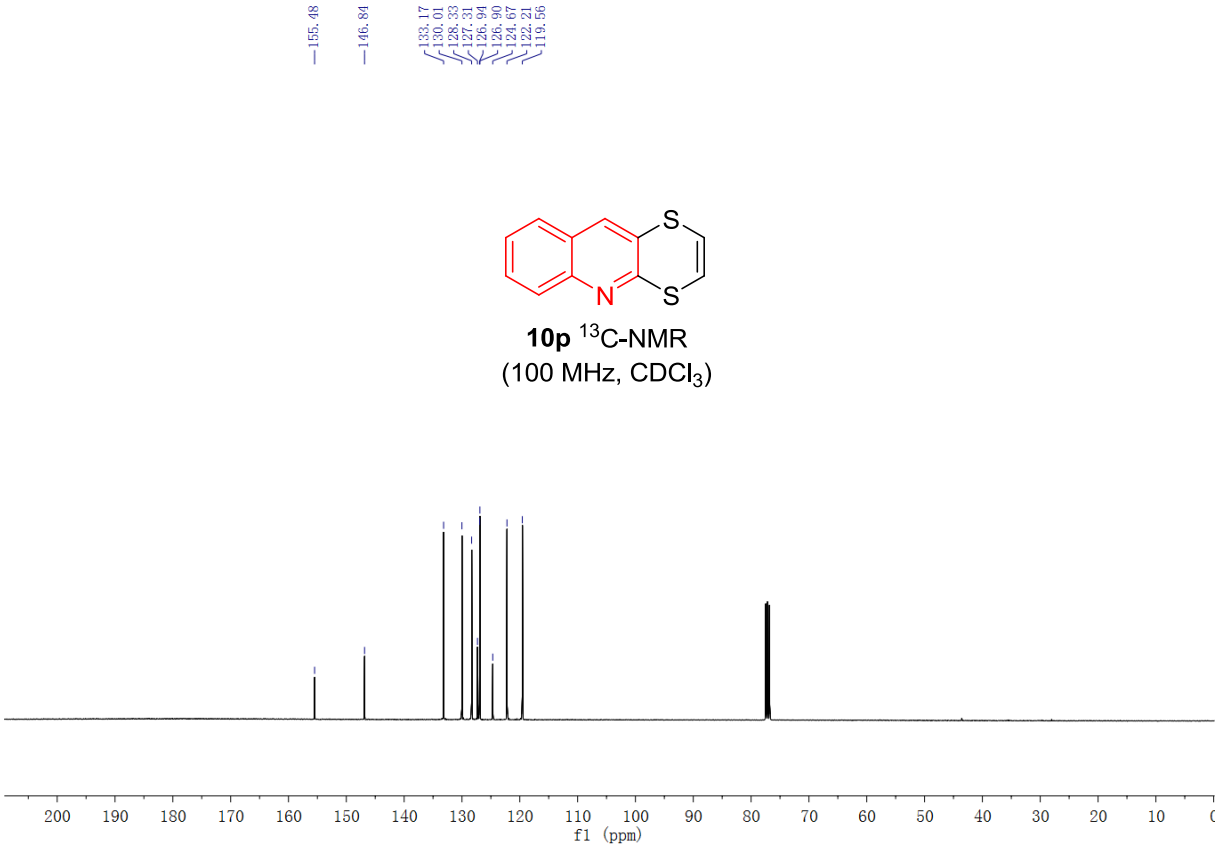
10o ^{1}H-NMR
(400 MHz, $CDCl_3$)



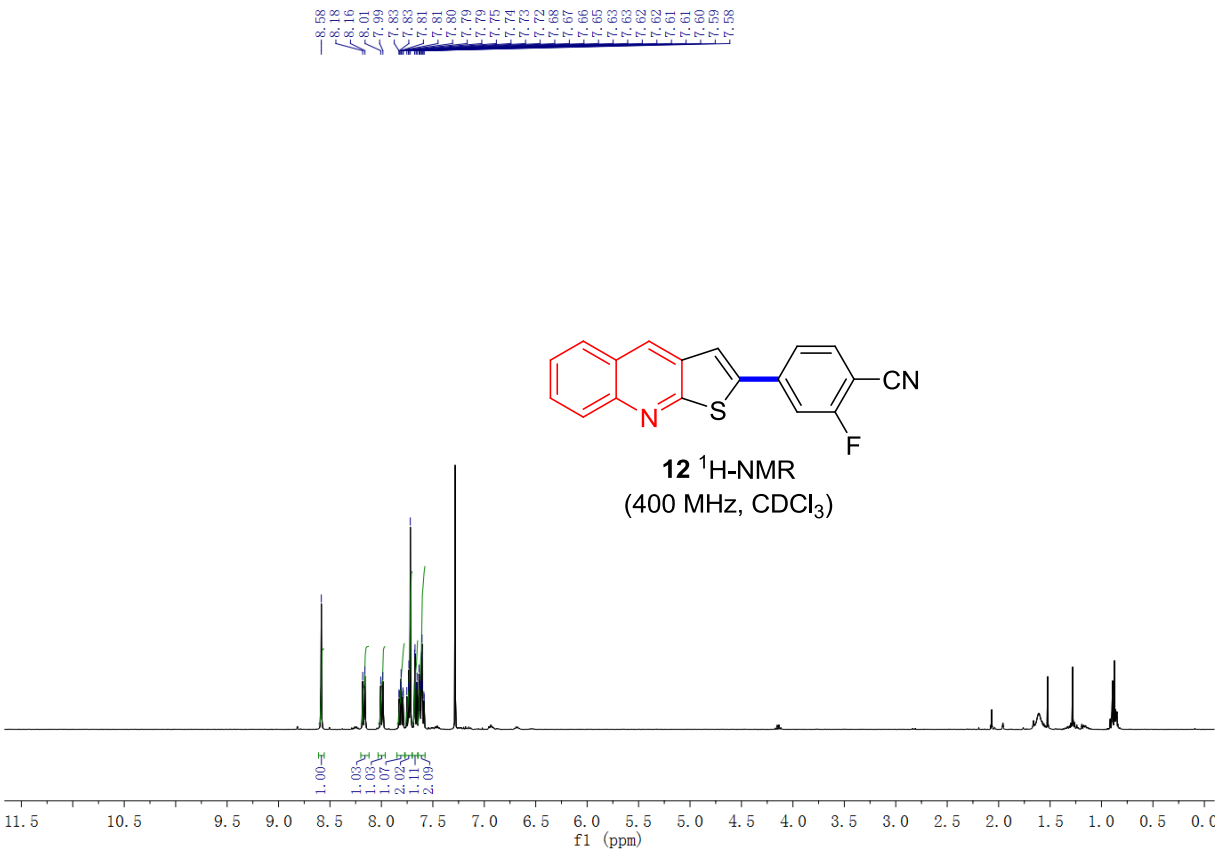
10o ^{13}C-NMR
(100 MHz, $CDCl_3$)



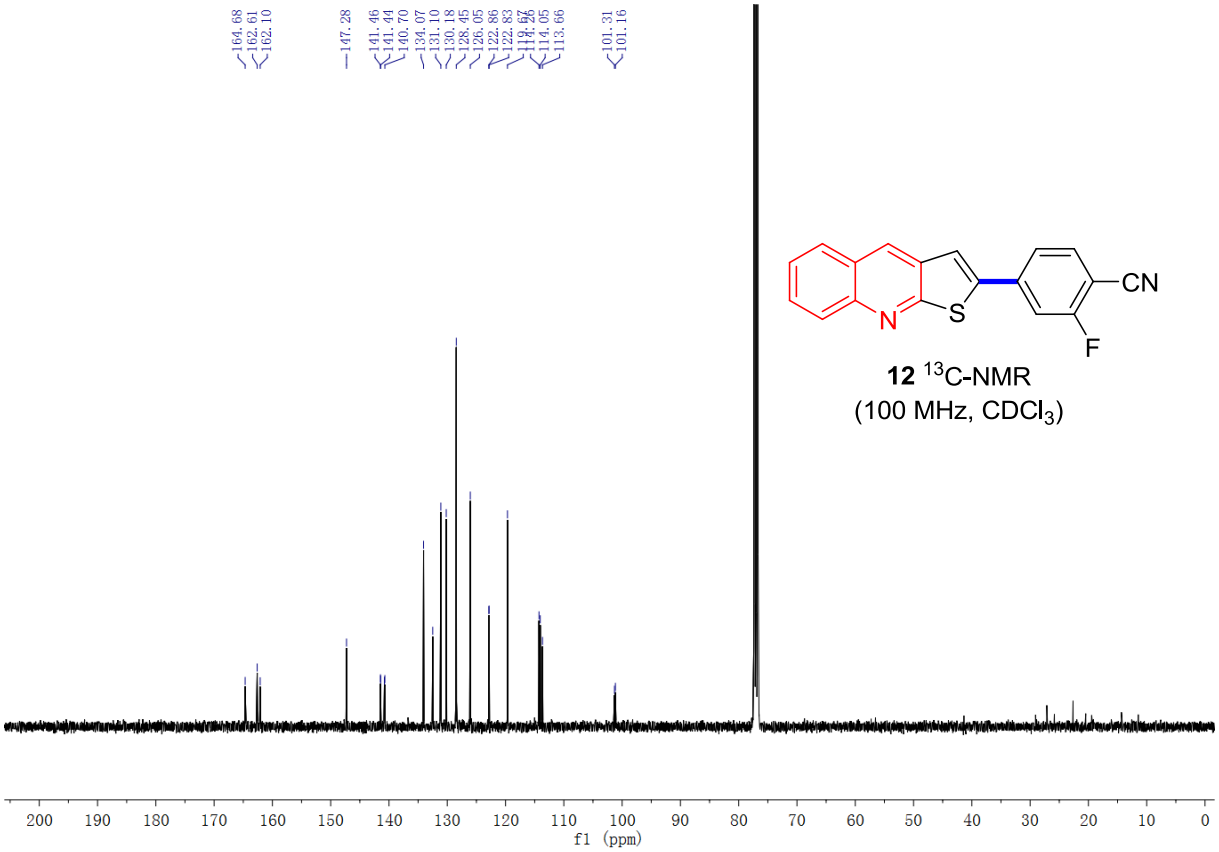
10p ^{1}H-NMR
(400 MHz, $CDCl_3$)



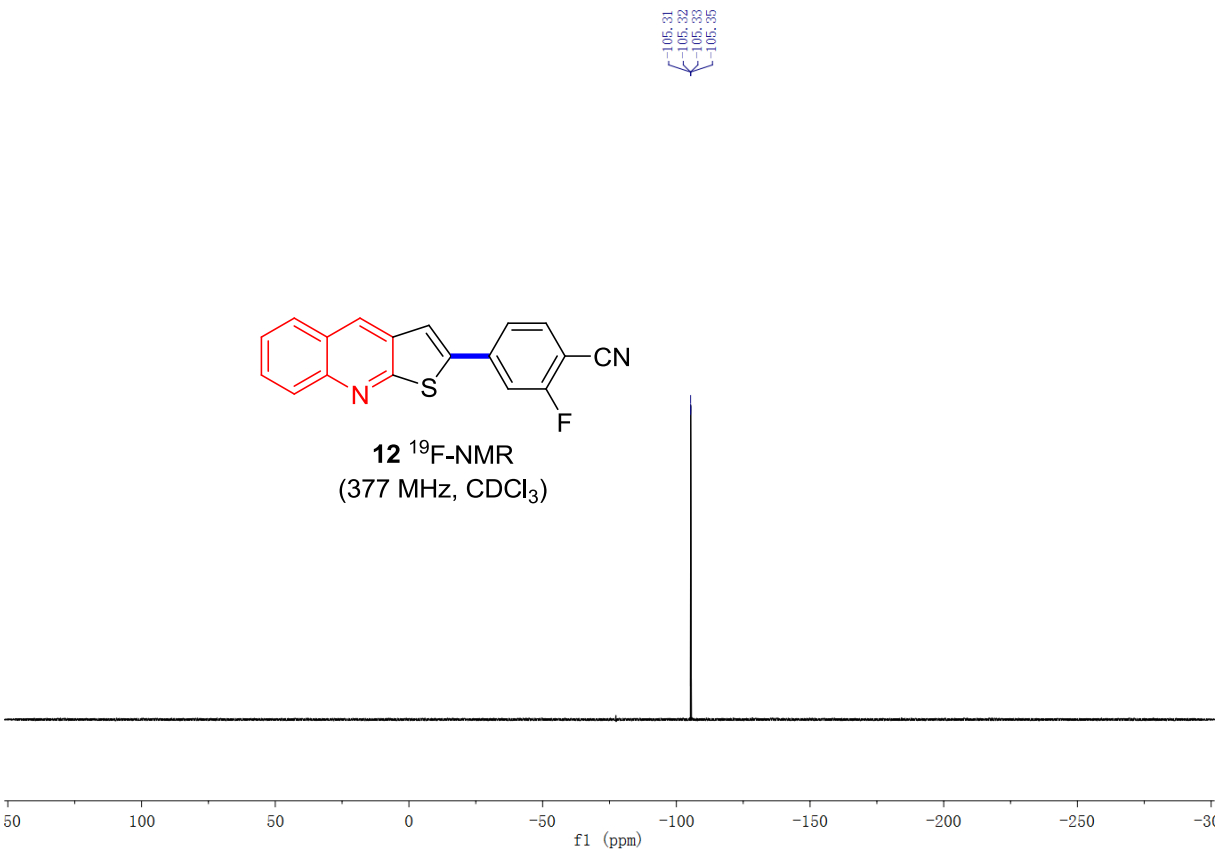
10p ^{13}C-NMR
(100 MHz, $CDCl_3$)



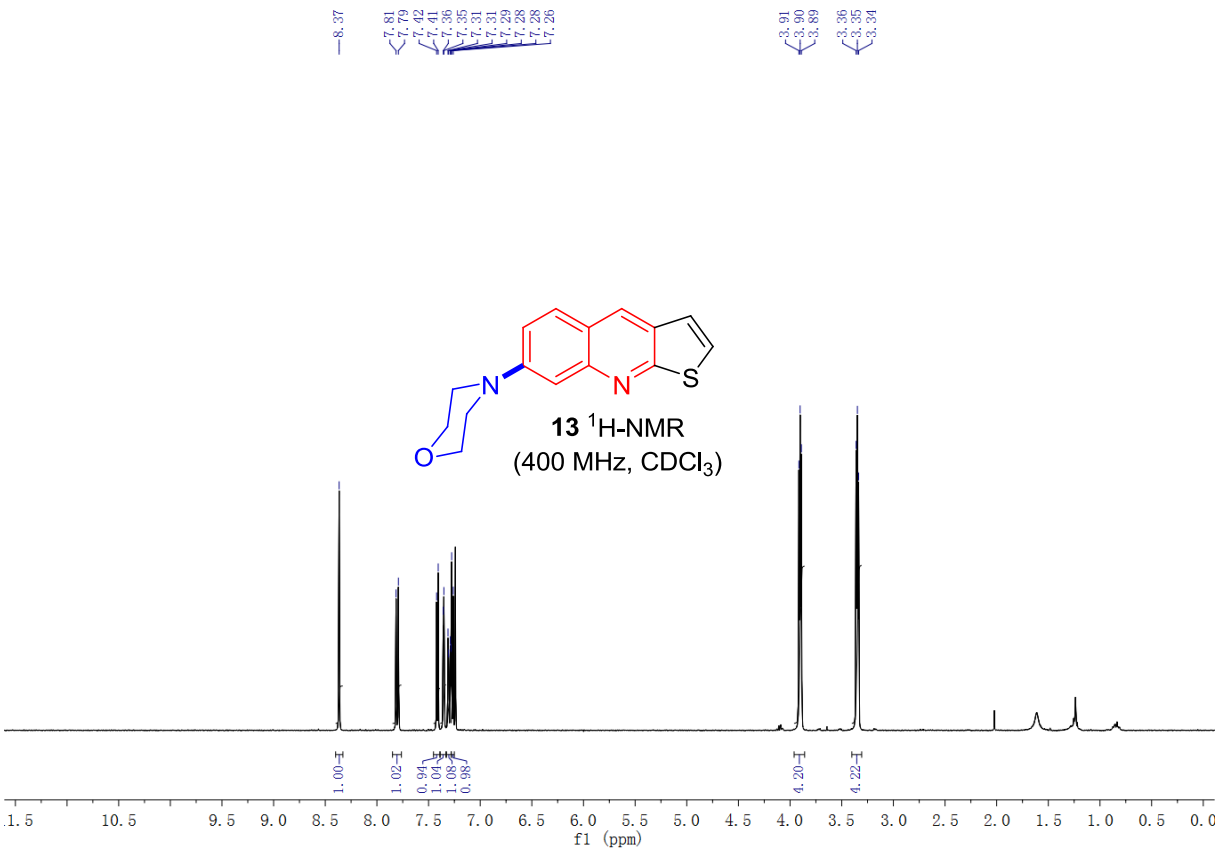
12 ^{1}H-NMR
(400 MHz, $CDCl_3$)

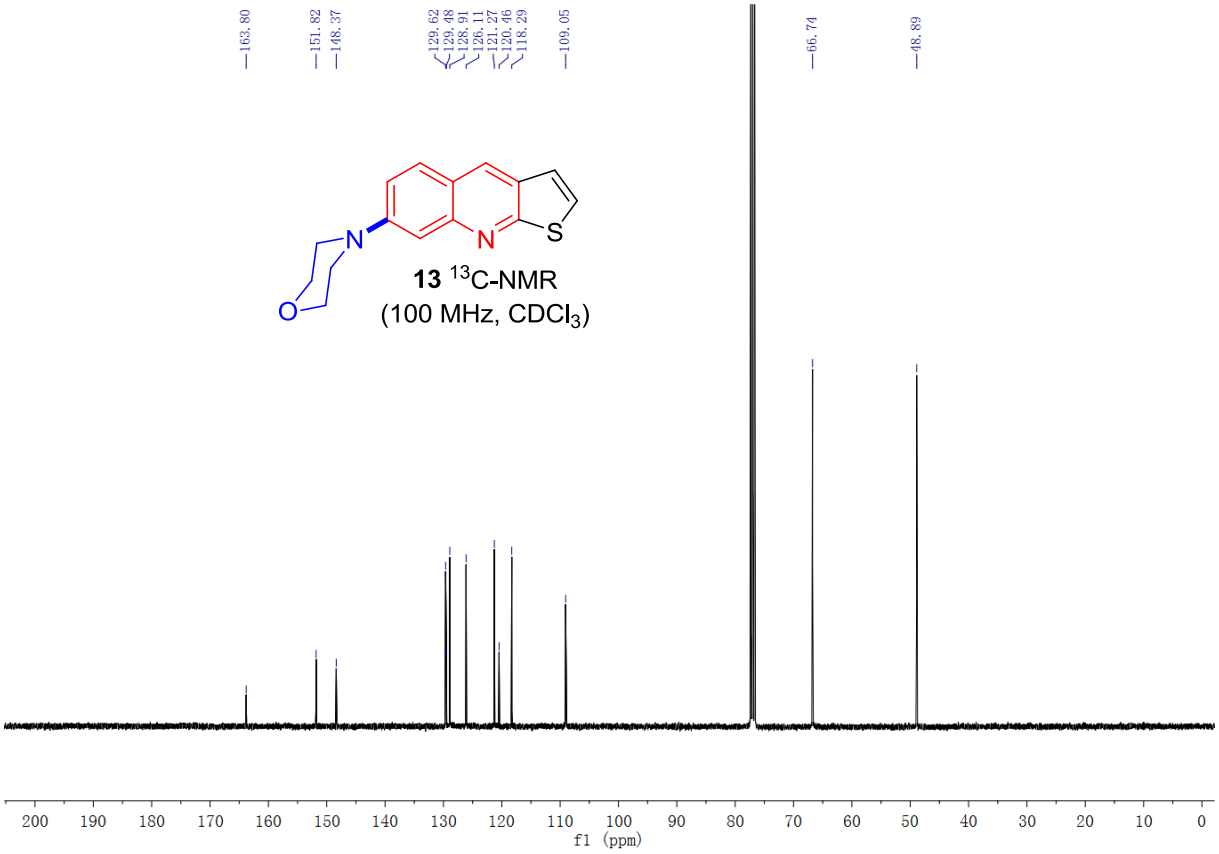


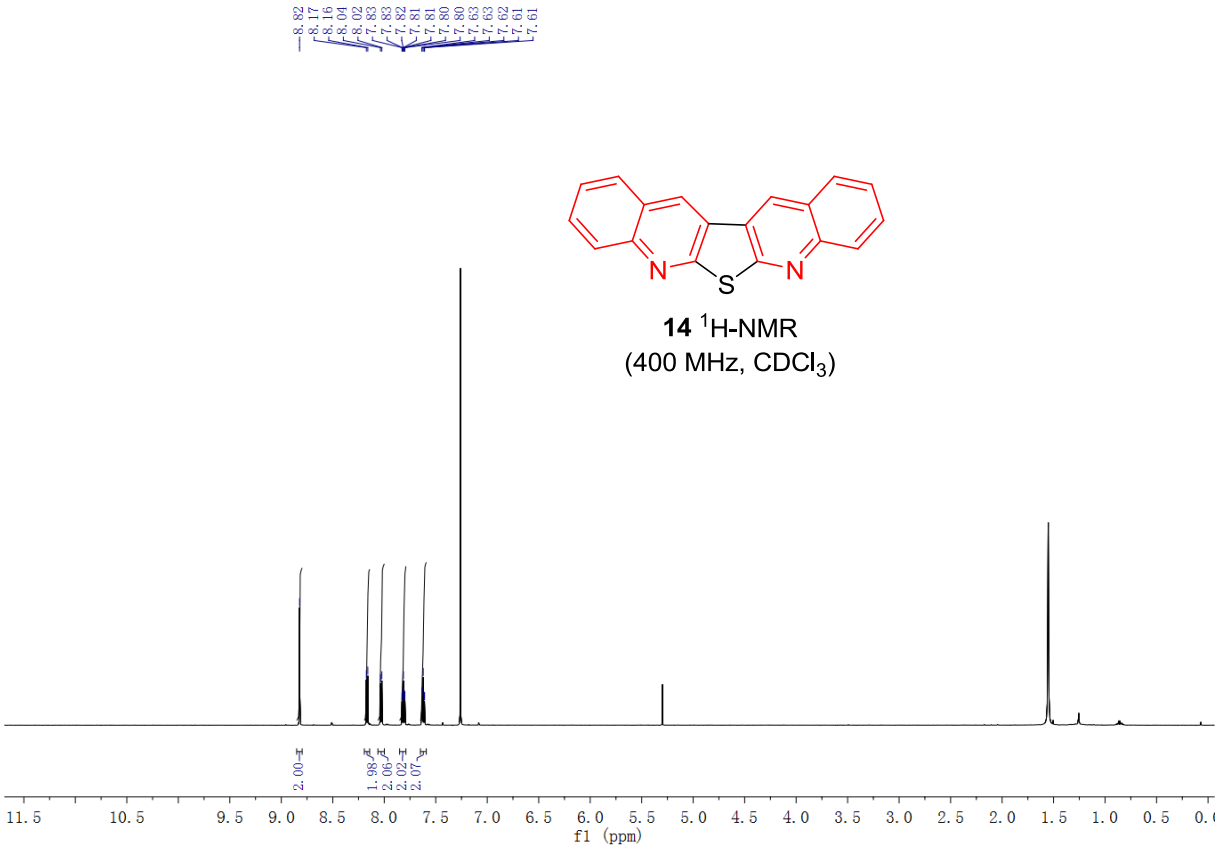
12 ^{13}C-NMR
(100 MHz, $CDCl_3$)



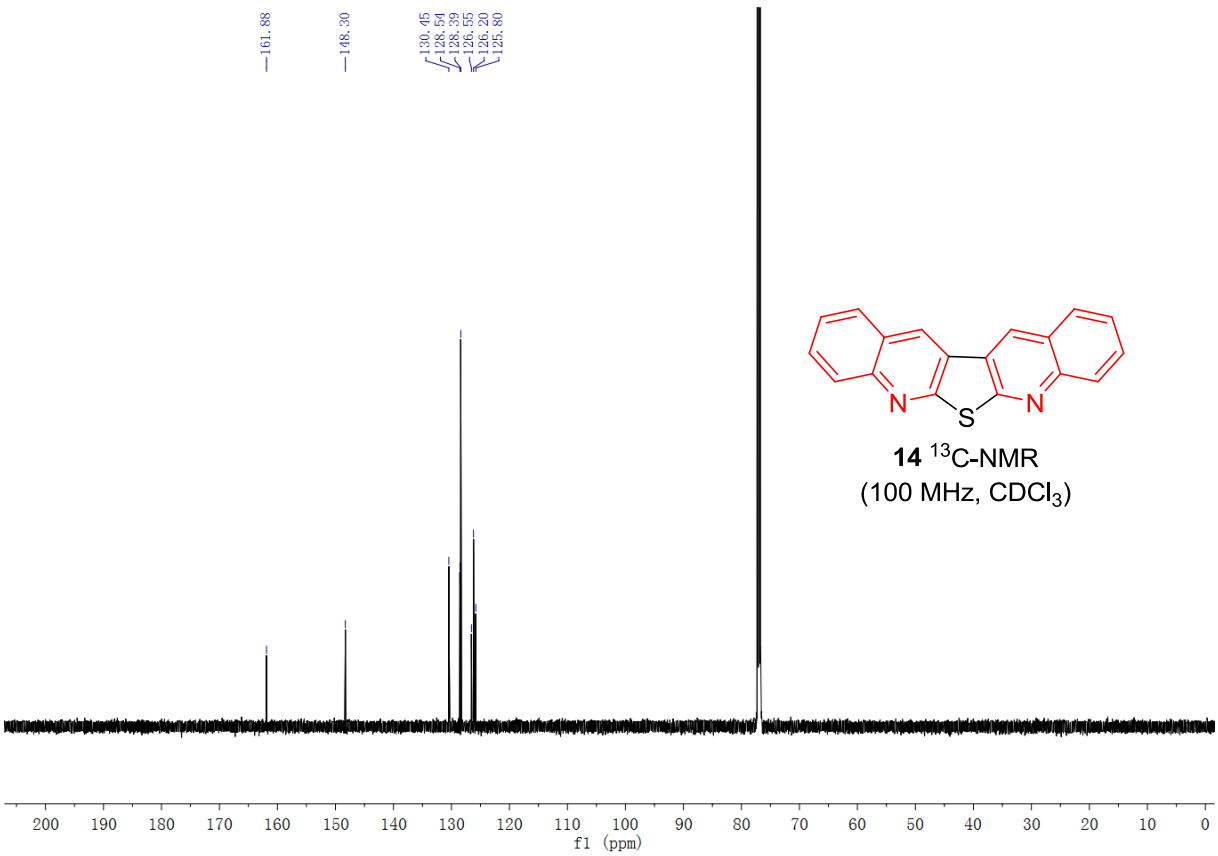
12 ^{19}F-NMR
(377 MHz, $CDCl_3$)


8.37
7.81
7.79
7.42
7.41
7.36
7.35
7.31
7.31
7.29
7.28
7.28
7.26
3.91
3.90
3.89
3.36
3.35
3.34
N
S
N
O
13 1H-NMR
(400 MHz, CDCl3)
1.00
1.02
0.94
1.04
1.08
0.98
4.20
4.22
f1 (ppm)

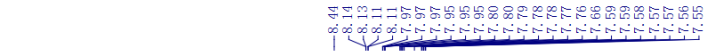

163.80
151.82
148.37
129.62
129.48
128.91
126.11
121.27
120.46
118.29
109.05
66.74
48.89
N
S
N
O
13 13C-NMR
(100 MHz, CDCl3)
f1 (ppm)

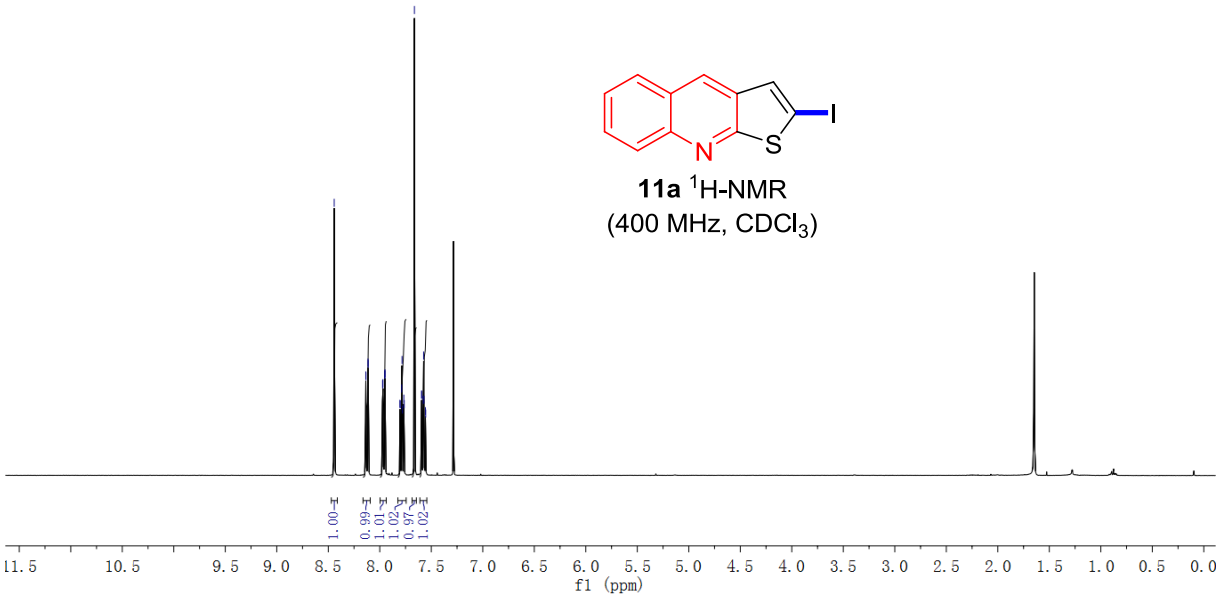


14 ^{1}H-NMR
(400 MHz, $CDCl_3$)

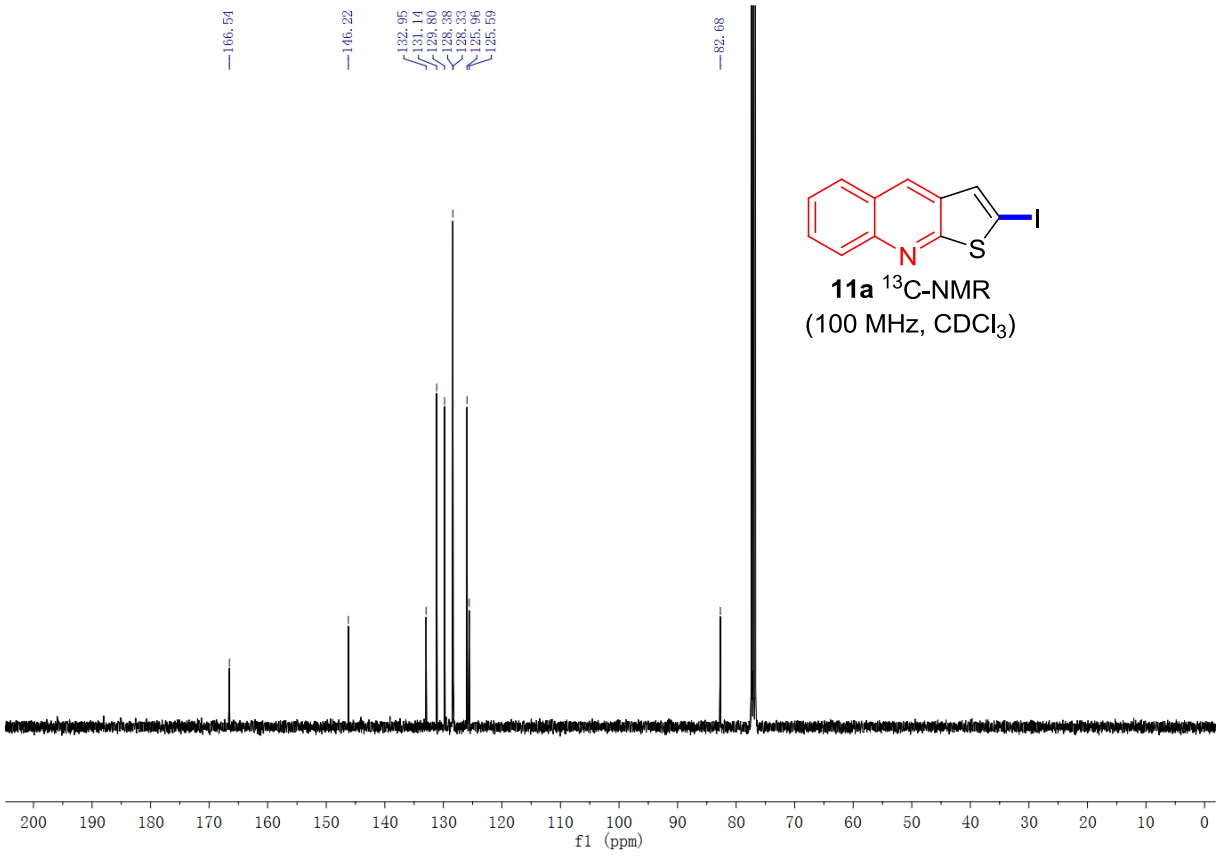


14 ^{13}C-NMR
(100 MHz, $CDCl_3$)

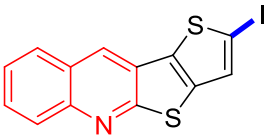




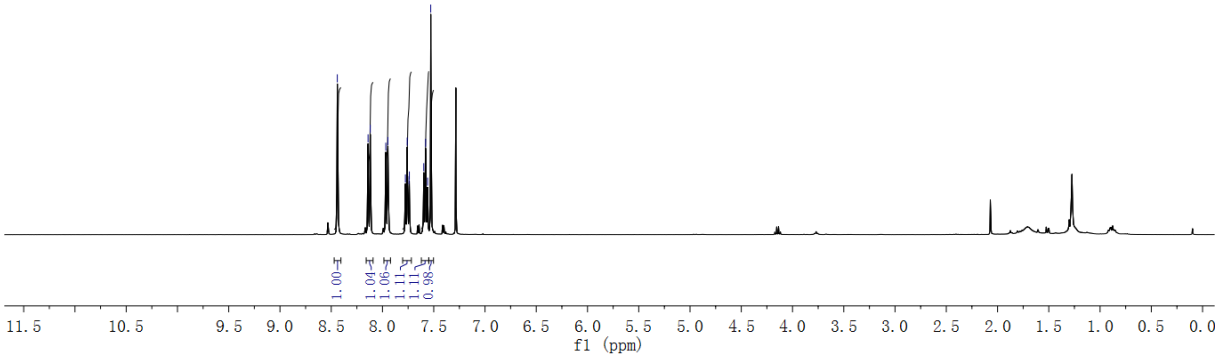
11a ^{1}H-NMR
(400 MHz, $CDCl_3$)

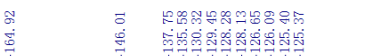


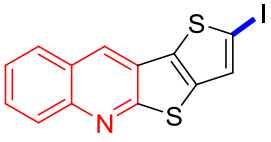
11a ^{13}C-NMR
(100 MHz, $CDCl_3$)



11b ^{1}H-NMR
(400 MHz, $CDCl_3$)







11b ^{13}C-NMR
(100 MHz, $CDCl_3$)