Supporting Information

The Prepartion of Co@C_3N_4 Catalyst and Applications on Synthesis of Quinolines from 2-Aminobenzyl Alcohols with Ketones†

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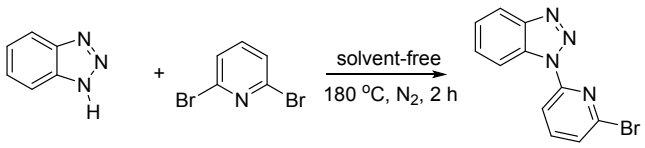
Contents

1. General methods and materials

All commercial reagents and solvents were obtained from the commercial provider and used without further purification. ^{1}H NMR, ^{13}C NMR and ^{31}P NMR spectra were recorded on Varian 400, 101 or 162 MHz spectrometers. Chemical shifts were reported relative to internal tetramethylsilane (0.00 ppm) or $CDCl_3$ (7.26 ppm), DMSO (2.50 ppm) for ^{1}H NMR and $CDCl_3$ (77.0 ppm), DMSO (40.35 ppm) for ^{13}C NMR. Flash column chromatography was performed on 230-430 mesh silica gel. IR spectra were recorded on total reflection Fourier infrared spectrometer (NICOLET 6700). The heterogeneous catalyst was characterized with powder X-ray diffraction (XRD) on a Bruker D8 Advance X-ray diffractometer. SEM image and EDX spectra was performed on a HITACHI S-4800 field-emission scanning electron microscope. XPS data were recorded with electron energy analyzer (ESCALAB 250Xi, Thermo Fisher Co, USA).

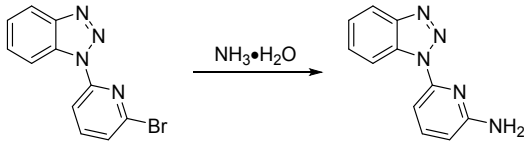
2. Synthesis of catalyst NNP-Co and Co@C_3N_4

2.1 Procedure for synthesis of 1-(6-Bromo-2-pyridinyl)-1H-benzotriazole



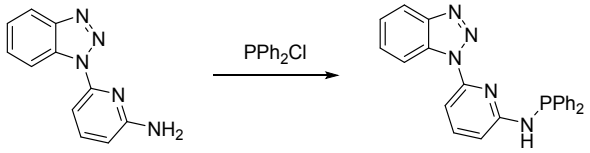
Under nitrogen atmosphere, a mixture of 2,6-dibromopyridine (4.74 g, 20.0 mmol) and 1H-benzotriazole (3.57 g, 30.0 mmol) was stirred at 180 °C for 2 h. After the reaction mixture was cooled to ambient temperature, dichloromethane (100 mL) was added and the solution was filtered to separate the insoluble substances, all the volatiles were removed under reduced pressure to give a crude product which was subjected to purification by silica gel column chromatography (eluent petroleum ether/ethyl acetate: 20/1, v/v) to afford the desired product as white solid (3.891 g, 71% yield). Mp: 80.1−82.6 °C.

2.2 Procedure for synthesis of 6-(1H-benzo[d][1,2,3] triazol-1-yl) pyridin-2-amine



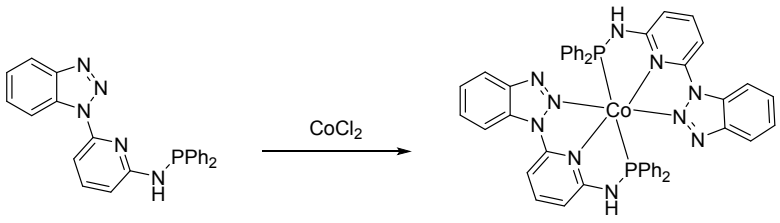
1-(6-Bromo-2-pyridinyl)-1H-benzotriazole (550 mg, 2.0 mmol), $NH_3 \cdot H_2O$ (4.0 mL), Cu_2O (43 mg, 0.3 mmol), DMEDA (54 mg, 0.6 mmol) and K_2CO_3 (84 mg, 0.6 mmol) in glycol (4.0 mL) was combined under nitrogen atmosphere. The reaction mixture was stirred 110 °C for 12 h. The reaction mixture was then added to deionized water (10 mL), and the resulting solution was extracted with dichloromethane (3×10 mL). The resulting solution was directly purified by column chromatography with petroleum ether/ethyl acetate (10/1) as eluent to give the ligand **2**. White solid (367 mg, 87% yield), Mp: 146.7-148.1 °C.

2.3 Procedure for synthesis of 6-(1H-benzo[d][1,2,3]triazol-1-yl)-N-(diphenylphosphanyl)-pyridin -2-amine (**1a**)



To a suspension of 6-(1H-benzo[d][1,2,3]triazol-1-yl)pyridin-2-amine (**L2**) (211 mg, 1.0 mmol) in dry THF (2.0 mL) was added dry NEt_3 (101 mg, 1.0 mmol), upon further cooling to 0 °C, then Ph_2PCl (220 mg, 1.0 mmol) was slowly added under nitrogen atmosphere. The solution was allowed to reach room temperature, the reaction mixture was stirred 70 °C for 6 h. After this time, the ammonium salt was separated by filtration and the solvent was removed under vaccum. The oily residue obtained, then resulting solution was directly purified by column chromatography with petroleum ether/ethyl acetate (10/1) as eluent to give the **1a**. White solid (42% yield, 166 mg), Mp: 155.1-157.6 °C.

2.4 Procedure for synthesis of NNP-Co complex **1b**



Under N_2 atmosphere, to a suspension of $CoCl_2$ (16 mg, 0.125 mmol) in THF (1.0 mL) was slowly added a solution of ligand **1a** (39 mg, 0.1 mmol) in THF (1.0 mL) was stirred at room temperature for 24 h. Then diethyl ether (5.0 mL) was added to precipitate the product. The

collected solid was washed with hexane to afford the crude product. Then the crude product by column chromatography with CH_2Cl_2/MeOH (9/1) as eluent to give the metal complex (67% yield, 85 mg). Mp: 225.8-226.6 ºC. The product peak in the MS does not match the calculated value very well (847.1775 vs. 847.1938).

2.5 Preparation of Co@C_3N_4 catalyst **1c**

Firstly, the commercially available urea was dried at 70 ºC for 12 h, then the NNP-Co complex (200 mg) was grinded with the urea (2.0 g), and the mixture was heated in an alumina crucible at 500 ºC for 2 h under N_2 to generate crude Co@g-C_3N_4. Then crude product was washed with water and ethanol three times respectively. After filtration, the target product was obtained as a brown solid. Finally, after ultrasonic washing and drying, the desired solid Co@g-C_3N_4 was attained.

3. Characterization of catalyst NNP-Co and Co@C_3N_4

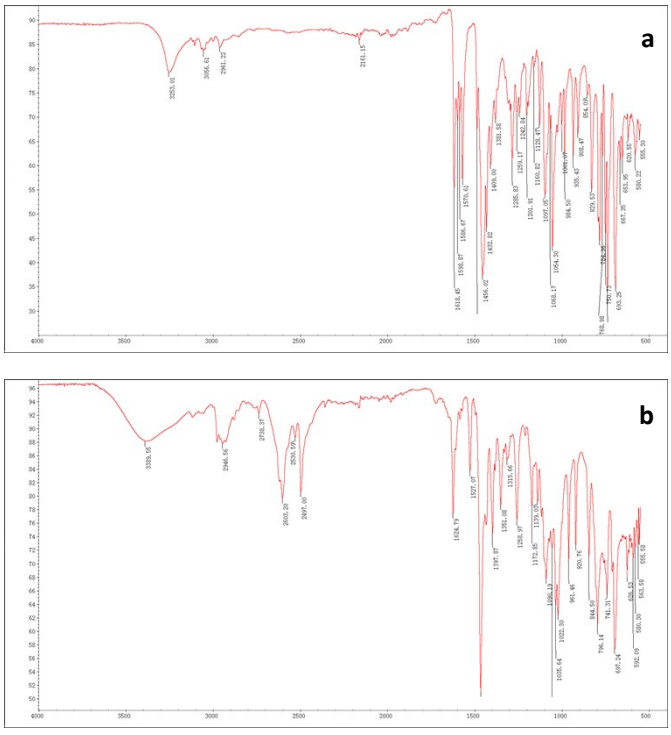


Fig. S1. IR images of NNP and NNP-Co.

The images of (a) and (b) were infrared spectroscopy (IR) of NNP and NNP-Co (Figure 1). Firstly, P-N bond infrared absorption in the range of 1110-930, 770-680. It can also be seen from the comparison of Fig S1 (a) and (b). The characteristic absorption peaks of

cobalt chloride overlap with the characteristic absorption peaks of the ligand NNP, and it is not certain whether there is a Co-Cl bond of complex. What's important is that we preliminarily judged that there is an NNP skeleton in the complex through IR.

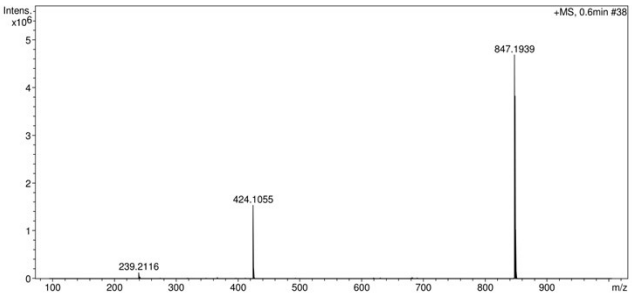


Fig. S2. MS image of NNP-Co

From the mass spectrum, the highest molecular ion peak can also be detected as 847.1938, this result is exactly the result of the interaction between two molecules of ligand and one molecule of metal precursor. According to the data, it is speculated and analyzed that the two ligands lose one proton respectively, then two anion forms are formed.

4. General procedure for 4

Under air atmosphere, 2-aminobenzyl alcohol (1.0 mmol), ketones (1.0 mmol), Co@C_3N_4 catalyst (50 mg), NaOH (0.5 equiv.) and toluene (2.0 mL) were introduced in a Schlenk tube, successively. The Schlenk tube was then closed and the resulting mixture was stirred at 135 °C for 24 h. After cooling down to room temperature, water was added to quench the reaction and extracted with ethyl acetate, the organic phase was concentrated by removing the solvent under vacuum. Finally, the residue was purified by column chromatography with petroleum ether/ethyl acetate as eluent to give the desired product.

5. Compounds characterization

6-(1H-benzo[d][1,2,3] triazol-1-yl)pyridin-2-amine L2[1]

White solid. Mp.146.7-148.1 °C, (367 mg, 87% yield) ^{1}H NMR (400 MHz, DMSO) δ 8.76 (d, *J* = 8.4 Hz, 1H), 8.15 (d, *J* = 8.3 Hz, 1H), 7.66 (td, *J* = 7.7, 3.4 Hz, 2H), 7.51 (t, *J* = 7.6 Hz, 1H), 7.29 (d, *J* = 7.6 Hz, 1H), 6.66 – 6.46 (m, 3H). ^{13}C NMR (101 MHz, DMSO) δ 159.75, 150.06, 146.37, 140.44, 131.43, 129.04, 125.39, 119.79, 115.81, 107.00, 100.68.

6-(1H-benzo[d][1,2,3] triazol-1-yl)-N-(diphenylphosphanyl)pyridin-2-amine (1a)

White solid. Mp.155.1-157.6 °C. (166 mg, 42% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.55 (d, *J* = 8.1 Hz, 1H), 8.08 (d, *J* = 8.2 Hz, 1H), 7.79 – 7.68 (m, 2H), 7.66 – 7.52 (m, 4H), 7.51 – 7.36 (m, 8H), 6.89 (d, *J* = 7.3 Hz, 1H), 5.27 (d, *J* = 7.7 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.82 – 156.72 (m), 150.38 (d, *J* = 7.9 Hz), 146.66 (d, *J* = 7.3 Hz), 140.28 (d, *J* = 5.7 Hz), 139.03 (d, *J* = 13.1 Hz), 131.87 – 131.03 (m), 130.75 (d, *J* = 11.3 Hz), 129.58, 128.85 (dd, *J* = 16.1, 9.8 Hz), 128.44 (dd, *J* = 14.2, 9.0 Hz), 124.59, 119.66 (d, *J* = 19.8 Hz), 115.15 (d, *J* = 4.0 Hz), 114.79, 107.55 (d, *J* = 9.1 Hz), 106.55, 104.63, 103.95. ^{31}P NMR (162 MHz, $CDCl_3$) δ 28.45 (s). HRMS Calculated for $C_{23}H_{19}N_5P$ $[M+H]^+$ 396.1378, found 396.1376.

1b, Red solid. Mp: 225.8-226.6 °C. (85 mg, 67% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08-7.95 (m, 4H), 7.2-7.04 (m, 24H), 6.67-6.52 (m, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.95 (s), 146.38 (s), 145.49 (s), 142.14 (s), 133.06 (s), 132.80 (s), 132.52 (s), 131.84 (s), 130.78 (s), 130.57 (s), 129.81 – 129.43 (m), 128.96 (d, *J* = 3.8 Hz), 128.60 (t, *J* = 5.5 Hz), 127.73 (t, *J* = 5.3 Hz), 126.62 (s), 120.18 (s), 113.61 (t, *J* = 11.0 Hz), 111.79 (s), 98.48 (s). ^{31}P NMR (162 MHz, $CDCl_3$) δ -20.00 (s). MS Calculated for $C_{46}H_{36}CoN_{10}P_2$ $[M-2H]^+$ 847.1775, found 847.1938.

2-phenylquinoline 4a[2]

White solid. Mp.85.1-86.5°C. (174 mg, 85% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.31 – 8.08 (m, 2H), 8.20 (dd, *J* = 5.3, 3.3 Hz, 2H), 7.92 (d, *J* = 8.6 Hz, 1H), 7.87 (dd, *J* = 8.1, 0.9 Hz, 1H), 7.81 – 7.73 (m, 1H), 7.61 – 7.53 (m, 3H), 7.50 (ddd, *J* = 7.3, 3.6, 1.2 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.35, 139.44, 137.04, 129.83, 129.58, 129.46, 128.89, 127.67, 127.49, 127.21, 126.41, 119.10.

2-(*p*-tolyl) quinoline 4b[2]

Yellow solid, Mp.81.5-82.8°C. (190 mg, 87% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.22 (t, *J* = 9.3 Hz, 2H), 8.10 (d, *J* = 8.1 Hz, 2H), 7.87 (dd, *J* = 18.5, 8.3 Hz, 2H), 7.80 – 7.69 (m, 1H), 7.54 (t, *J* = 7.5 Hz, 2H), 7.37 (d, *J* = 7.9 Hz, 1H), 2.47 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.35, 148.33, 139.41, 136.91, 136.65, 129.70, 129.58, 127.47, 127.44, 127.13, 126.09, 118.85, 21.34.

2-(4-methoxyphenyl) quinoline 4c[2]

White solid. Mp.125.4-126.7 °C. (186 mg, 79% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 (t, *J* = 9.3 Hz, 4H), 7.87 – 7.75 (m, 2H), 7.71 (t, *J* = 7.6 Hz, 1H), 7.49 (t, *J* = 7.4 Hz, 1H), 7.05 (d, *J* = 8.4 Hz, 2H),

3.88 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.81, 155.88, 147.23, 135.63, 131.20, 128.56, 128.47, 127.88, 126.40, 125.88, 124.90, 117.53, 113.21, 54.37.

2-(4-bromophenyl) quinoline 4d[2]

White solid. Mp.116.8-118.2 °C. (221 mg, 78% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19 (d, *J* = 8.5 Hz, 2H), 8.13 – 8.01 (m, 2H), 7.90 – 7.72 (m, 3H), 7.71 – 7.62 (m, 2H), 7.61 – 7.51 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.98, 148.24, 138.46, 136.99, 131.99, 129.89, 129.72, 129.12, 127.54, 127.26, 126.55, 123.97, 118.48.

2-(4-chlorophenyl) quinoline 4e[2]

White solid. Mp.111.5-112.3 °C. (179 mg, 75% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21 (d, *J* = 8.6 Hz, 1H), 8.16 (d, *J* = 8.5 Hz, 1H), 8.11 (d, *J* = 8.3 Hz, 2H), 7.82 (d, *J* = 8.5 Hz, 2H), 7.73 (t, *J* = 7.6 Hz, 1H), 7.57 – 7.43 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.01, 148.19, 138.00, 137.04, 135.60, 129.90, 129.67, 129.04, 128.85, 127.50, 127.24, 126.54, 118.59.

2-(4-(trifluoromethyl) phenyl) quinoline 4f[2]

White solid. Mp.124.4-126.1 °C. (147 mg, 54% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.30 (t, *J* = 8.1 Hz, 3H), 8.24 (d, *J* = 8.5 Hz, 1H), 7.94 – 7.85 (m, 2H), 7.80 (ddd, *J* = 8.5, 5.2, 1.7 Hz, 3H), 7.60 (ddd, *J* = 8.1, 7.0, 1.1 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.66, 148.17, 142.83, 137.26, 131.31, 130.99, 130.08, 129.78, 127.90, 127.50 (d, *J* = 8.6 Hz), 126.92, 125.77 (q, *J* = 3.8 Hz), 125.57, 122.86, 118.82.

2-(*m*-tolyl) quinoline 4g[3]

Yellow oil. (188 mg, 86% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.23 (dd, *J* = 8.5, 2.1 Hz, 2H), 8.06 (s, 1H), 7.97 (d, *J* = 7.7 Hz, 1H), 7.87 (dd, *J* = 18.4, 8.4 Hz, 2H), 7.80 – 7.72 (m, 1H), 7.55 (t, *J* = 7.5 Hz, 1H), 7.50 – 7.49 (m, 1H), 7.32 (d, *J* = 7.5 Hz, 1H), 2.52 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.52, 147.23, 138.61, 137.45, 135.64, 129.06, 128.66, 128.56, 127.68, 127.22, 126.40, 126.12, 125.15, 123.66, 118.10, 20.54.

2-(3-bromophenyl) quinoline 4h[4]

White solid. Mp.63.7-65.0 °C. (212 mg, 75% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.38 (t, *J* = 1.8 Hz, 1H), 8.26 (d, *J* = 8.6 Hz, 1H), 8.19 (d, *J* = 8.5 Hz, 1H), 8.10 (dd, *J* = 7.8, 1.0 Hz, 1H), 7.86 (d, *J* = 8.6 Hz, 2H), 7.77 (ddd, *J* = 8.4, 6.9, 1.4 Hz, 1H), 7.64 – 7.55 (m, 2H), 7.42 (t, *J* = 7.9 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.66, 148.23, 141.70, 137.05, 132.24, 130.66, 130.34, 129.92, 129.81, 127.50, 127.37, 126.68, 126.08, 123.17, 118.71.

2-(3-chlorophenyl) quinoline 4i[5]

White solid. Mp.64.5-66.2 °C. (172 mg, 72% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21 (dd, *J* = 19.2, 8.4 Hz, 3H), 8.03 (d, *J* = 6.6 Hz, 1H), 7.83 (d, *J* = 8.5 Hz, 2H), 7.75 (t, *J* = 7.7 Hz, 1H), 7.55 (t, *J* = 7.5 Hz, 1H), 7.49 – 7.40 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.75, 148.15, 141.36, 137.13, 134.98, 130.08, 129.96, 129.74, 129.36, 127.76, 127.51, 127.38, 126.70, 125.65, 118.74.

2-(*o*-tolyl) quinoline 4j[2]

White solid, Mp. 75.2-75.4 °C. (179 mg, 82% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.24 (dd, *J* = 16.1, 8.5 Hz, 2H), 7.88 (d, *J* = 8.1 Hz, 1H), 7.78 (ddd, *J* = 8.4, 7.0, 1.3 Hz, 1H), 7.58 (ddd, *J* = 8.3, 6.0, 2.0 Hz, 3H), 7.45 – 7.32 (m, 3H), 2.48 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.31, 147.95, 140.78, 136.15, 136.06, 130.95, 129.79, 129.69, 129.64, 128.59, 127.58, 126.79, 126.46, 126.09, 122.42, 20.46.

2-(2-methoxyphenyl) quinoline 4k[4]

Yellow oil. (178 mg, 76% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.24 (d, *J* = 8.5 Hz, 1H), 8.16 (d, *J* = 8.6 Hz, 1H), 7.97 – 7.89 (m, 2H), 7.85 (d, *J* = 8.1 Hz, 1H), 7.79 – 7.69 (m, 1H), 7.55 (t, *J* = 7.5 Hz, 1H), 7.46 (td, *J* = 8.3, 1.6 Hz, 1H), 7.18 (t, *J* = 7.5 Hz, 1H), 7.06 (d, *J* = 8.3 Hz, 1H), 3.88 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.28, 157.19, 148.39, 135.14, 131.56, 130.40, 129.79, 129.68, 129.27, 127.46, 127.10, 126.23, 123.52, 121.32, 111.52, 55.68.

2-(2-chlorophenyl) quinoline 4l[4]

White solid, Mp. 79.0-79.4 °C. (177 mg, 74% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.22 (dd, *J* = 12.9, 8.6 Hz, 2H), 7.86 (d, *J* = 8.1 Hz, 1H), 7.82 – 7.70 (m, 3H), 7.63 – 7.49 (m, 2H), 7.48 – 7.33 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.45, 148.13, 139.70, 135.75, 132.42, 131.80, 130.16, 129.95, 129.76, 129.71, 127.63, 127.24, 127.19, 126.84, 122.82.

2-(2-bromophenyl) quinoline 4m[3]

Yellow solid, Mp. 71.1-72.9 °C. (201 mg, 71% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.28 – 8.16 (m, 2H), 7.90 (d, *J* = 8.2 Hz, 1H), 7.82 – 7.71 (m, 3H), 7.67 (dd, *J* = 7.6, 1.6 Hz, 1H), 7.61 (t, *J* = 7.5 Hz, 1H), 7.48 (td, *J* = 7.5, 1.0 Hz, 1H), 7.32 (td, *J* = 8.0, 1.7 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.76, 147.96, 141.70, 135.69, 133.29, 131.60, 130.01, 129.74, 129.70, 127.72, 127.60, 127.16, 126.82, 122.74, 121.88.

6-chloro-2-(*p*-tolyl) quinoline 4n[6]

Pale yellow solid. Mp.157.9-159.7 °C. (197 mg, 78% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 – 8.00 (m, 4H), 7.88 (d, *J* = 8.7 Hz, 1H), 7.79 (d, *J* = 2.2 Hz, 1H), 7.67 (dd, *J* = 9.0, 2.3 Hz, 1H), 7.36 (d, *J* =

8.0 Hz, 2H), 2.46 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.50, 146.63, 139.77, 136.36, 135.76, 131.69, 131.23, 130.50, 129.66, 127.64, 127.41, 126.14, 119.64, 21.39.

2-(pyridin-2-yl) quinoline 4o[7]

white solid. Mp.97.5-98.2 °C. (171 mg, 83% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.76 (ddd, *J* = 4.8, 1.8, 0.9 Hz, 1H), 8.68 (dt, *J* = 8.0, 1.0 Hz, 1H), 8.59 (d, *J* = 8.6 Hz, 1H), 8.29 (d, *J* = 8.6 Hz, 1H), 8.25 – 8.18 (m, 1H), 7.91 – 7.82 (m, 2H), 7.75 (ddd, *J* = 8.4, 6.9, 1.5 Hz, 1H), 7.56 (ddd, *J* = 8.1, 6.9, 1.2 Hz, 1H), 7.36 (ddd, *J* = 7.5, 4.8, 1.2 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.35, 156.16, 149.18, 147.94, 136.96, 136.83, 129.84, 129.58, 128.27, 127.64, 126.77, 124.04, 121.86, 118.98.

2-(3,5-bis(trifluoromethyl)phenyl) quinoline 4p[8]

White solid. Mp.95.7-98.3 °C. (174 mg, 51% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.66 (s, 2H), 8.31 (d, *J* = 8.6 Hz, 1H), 8.21 (d, *J* = 8.5 Hz, 1H), 8.02 – 7.90 (m, 2H), 7.87 (d, *J* = 8.1 Hz, 1H), 7.79 (t, *J* = 7.7 Hz, 1H), 7.60 (t, *J* = 7.5 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.68 (s), 148.22 (s), 141.51 (s), 137.58 (s), 132.69 (s), 132.36 (s), 132.02 (s), 131.69 (s), 130.34 (s), 129.91 (s), 127.57 (t, *J* = 5.1 Hz), 127.32 (s), 124.79 (s), 122.75 (dt, *J* = 7.5, 3.8 Hz), 122.07 (s), 119.36 (s), 118.14 (s).

2-(thiophen-3-yl) quinoline 4q[4]

White solid. Mp.127.1-129.9 °C. (171 mg, 81% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 (dd, *J* = 11.6, 8.6 Hz, 2H), 8.09 – 8.04 (m, 1H), 7.92 (dd, *J* = 5.0, 1.0 Hz, 1H), 7.83 – 7.69 (m, 3H), 7.52 (t, *J* = 7.2 Hz, 1H), 7.46 (dd, *J* = 5.0, 3.0 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 152.18, 147.16, 141.58, 135.58, 128.59, 128.38, 126.40, 126.01, 125.77, 125.29, 124.99, 123.58, 117.95.

2-(naphthalen-2-yl) quinoline 4r[9]

White solid. Mp.155.7-157.8 °C. (145 mg, 57% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.65 (s, 1H), 8.41 (dd, *J* = 8.6, 1.6 Hz, 1H), 8.27 (dd, *J* = 8.3, 5.6 Hz, 2H), 8.11 – 7.99 (m, 3H), 7.97 – 7.90 (m, 1H), 7.87 (d, *J* = 8.1 Hz, 1H), 7.79 (dd, *J* = 11.2, 4.2 Hz, 1H), 7.62 – 7.52 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.20, 148.41, 137.00, 136.83, 133.90, 133.54, 129.78, 129.75, 128.86, 128.61, 127.76, 127.53, 127.26, 127.18, 126.74, 126.36, 125.10, 119.18.

2-(3,4-dichlorophenyl) quinoline 4s[10]

White solid. Mp.91.4-92.5 °C. (155 mg, 57% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.30 (d, *J* = 2.1 Hz, 1H), 8.17 (dd, *J* = 8.3, 2.1 Hz, 2H), 7.96 (dd, *J* = 8.4, 2.1 Hz, 1H), 7.83 – 7.78 (m, 1H), 7.75 (ddd, *J* = 8.3, 6.8, 1.3 Hz, 2H), 7.59 – 7.51 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.43, 148.12, 139.39, 137.13, 133.53, 133.12, 130.69, 130.03, 129.72, 129.36, 127.53, 127.35, 126.81, 126.52, 118.19.

2-(4-(tert-butyl) phenyl) quinoline 4t[10]

White solid. Mp.65.9-67.2 °C. (232 mg, 89% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.30 – 8.11 (m, 4H), 7.88 (d, *J* = 8.6 Hz, 1H), 7.83 (d, *J* = 8.1 Hz, 1H), 7.76 (ddd, *J* = 8.4, 6.9, 1.4 Hz, 1H), 7.61 (dd, *J* = 8.7, 2.1 Hz, 2H), 7.58 – 7.51 (m, 1H), 1.44 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.27, 151.43, 147.25, 135.85, 135.54, 128.62, 128.46, 126.36, 126.22, 126.01, 124.98, 124.73, 117.83, 33.65, 30.23.

2-(2,6-dichloro-3-fluorophenyl) quinoline 4u

Pale yellow oil, (177 mg, 61% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.33 (d, *J* = 8.4 Hz, 1H), 8.20 (d, *J* = 8.5 Hz, 1H), 7.93 (d, *J* = 8.2 Hz, 1H), 7.85 – 7.76 (m, 1H), 7.65 (t, *J* = 7.5 Hz, 1H), 7.47 – 7.40 (m, 2H), 7.23 (t, *J* = 8.6 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.57 (s), 156.09 (s), 154.82 (d, *J* = 2.3 Hz), 147.99 (s), 140.32 (s), 136.83 (s), 130.03 (s), 129.74 (s), 129.30 (d, *J* = 3.8 Hz), 128.85 (d, *J* = 7.5 Hz), 127.74 (s), 127.43 (s), 127.33 (s), 122.25 (s), 117.14 (s), 116.92 (s). HRMS Calculated for $C_{15}H_9Cl_2FN$ $[M+H]^+$ 292.0096, found 292.0093.

2-(4-cyclopropylphenyl) quinoline 4v[4]

Pale yellow oil, (171 mg, 70% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (dd, *J* = 10.7, 8.9 Hz, 2H), 7.75 (d, *J* = 8.1 Hz, 1H), 7.66 (ddd, *J* = 8.4, 6.9, 1.4 Hz, 1H), 7.45 (ddd, *J* = 8.0, 7.0, 1.1 Hz, 1H), 7.18 (d, *J* = 8.5 Hz, 1H), 2.26 (tt, *J* = 8.2, 4.9 Hz, 1H), 1.21 – 1.16 (m, 2H), 1.15 – 1.08 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.43, 148.00, 135.83, 129.28, 128.67, 127.46, 126.75, 125.18, 119.32, 18.12, 10.27.

2-(4-pentylphenyl) quinoline 4w[11]

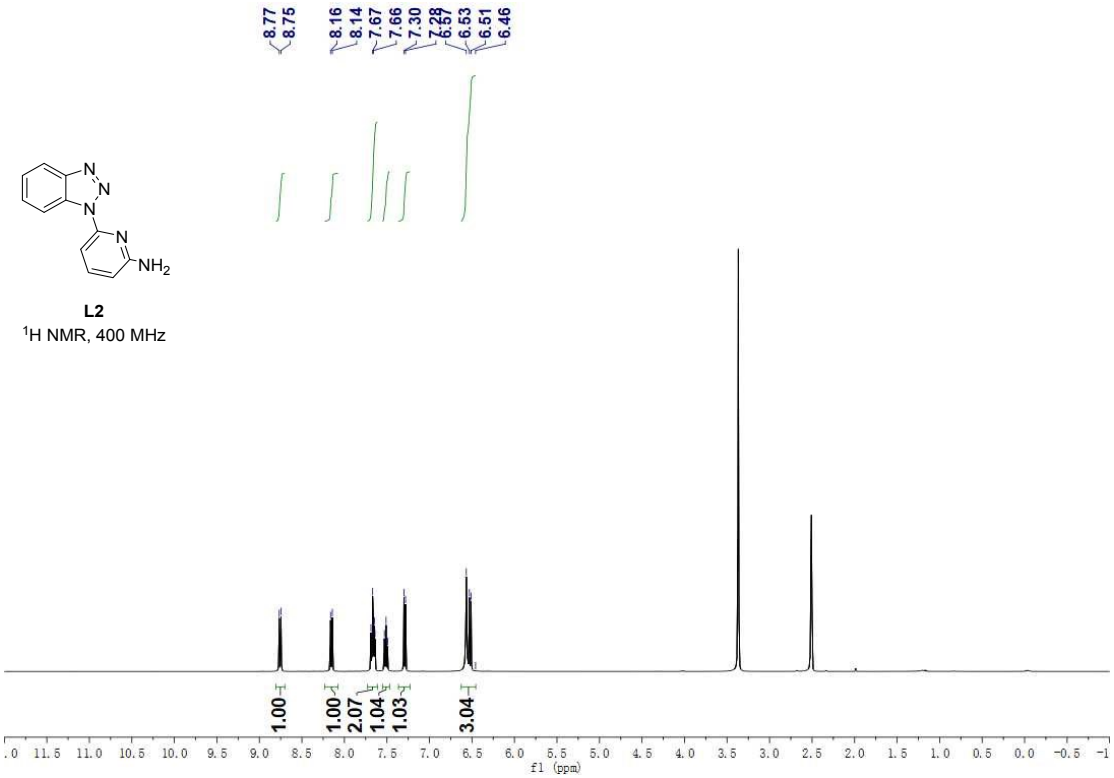
Pale yellow oil, (181 mg, 66% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (dd, *J* = 8.4, 5.3 Hz, 2H), 7.79 (d, *J* = 8.1 Hz, 1H), 7.70 (ddd, *J* = 8.4, 6.9, 1.4 Hz, 1H), 7.50 (ddd, *J* = 8.1, 6.9, 1.1 Hz, 1H), 7.32 (d, *J* = 8.4 Hz, 1H), 3.05 – 2.94 (m, 2H), 1.93 – 1.76 (m, 2H), 1.46 – 1.34 (m, 4H), 0.92 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.16, 147.92, 136.18, 129.32, 128.84, 127.49, 126.73, 125.63, 121.39, 39.38, 31.78, 29.79, 22.59, 14.04.

2-(4-heptylphenyl) quinoline 4x[12]

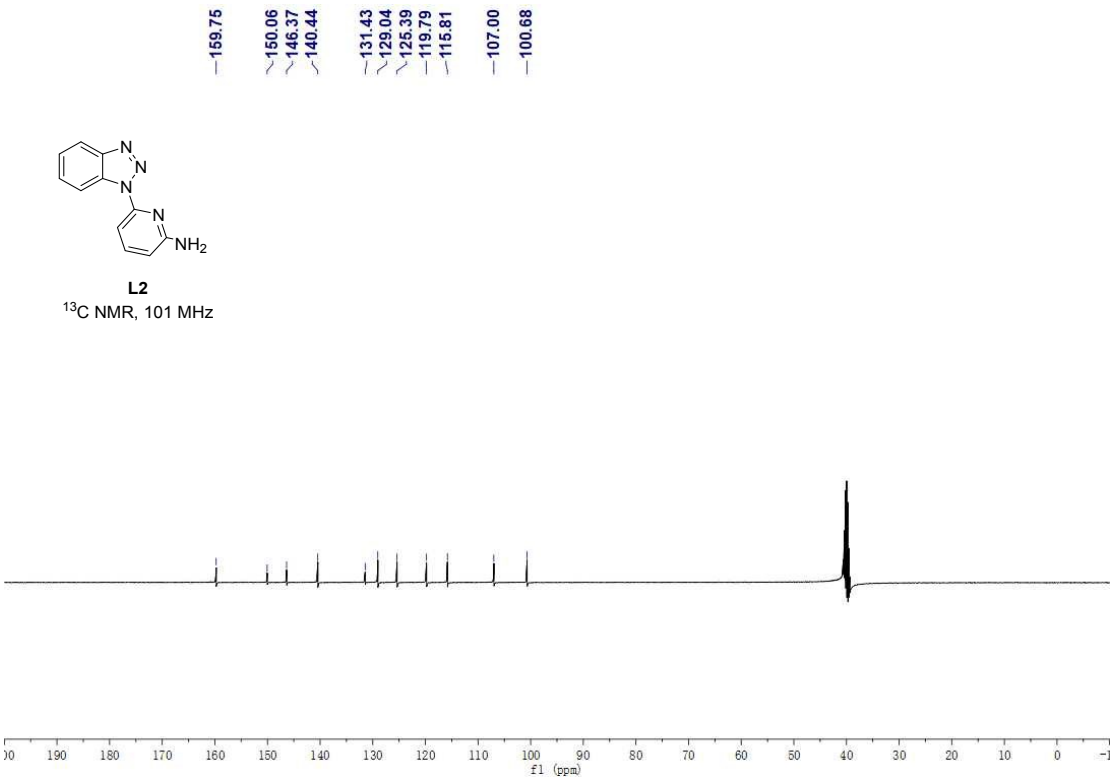
Pale yellow oil, (188 mg, 62% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 – 8.03 (m, 2H), 7.79 (d, *J* = 8.1 Hz, 1H), 7.70 (t, *J* = 7.7 Hz, 1H), 7.50 (t, *J* = 7.5 Hz, 1H), 7.32 (d, *J* = 8.4 Hz, 1H), 3.05 – 2.90 (m, 2H), 1.83 (dt, *J* = 15.6, 7.8 Hz, 2H), 1.48 – 1.34 (m, 4H), 1.33 – 1.26 (m, 4H), 0.90 (t, *J* = 6.8 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 163.16, 147.92, 136.18, 129.32, 128.84, 127.48, 126.72, 125.63, 121.38, 39.42, 31.79, 30.12, 29.56, 29.22, 22.66, 14.10.

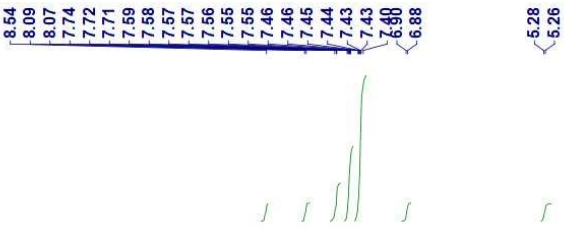
6. ^{1}H NMR and ^{13}C NMR Data

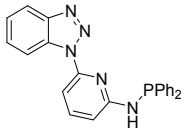


L2
^{1}H NMR, 400 MHz



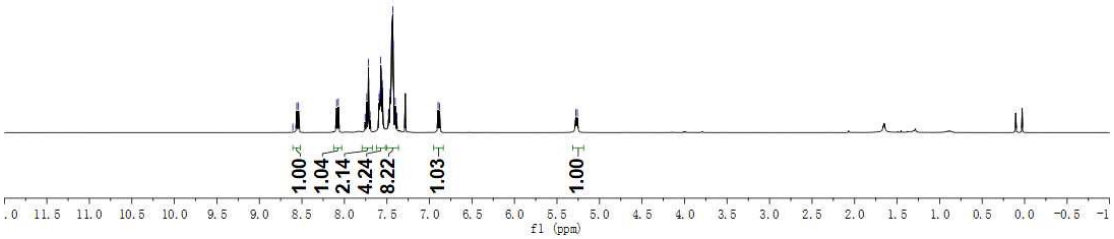
L2
^{13}C NMR, 101 MHz

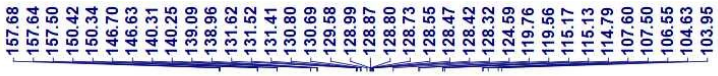


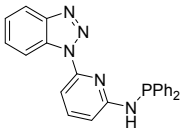


1a

^{1}H NMR, 400 MHz

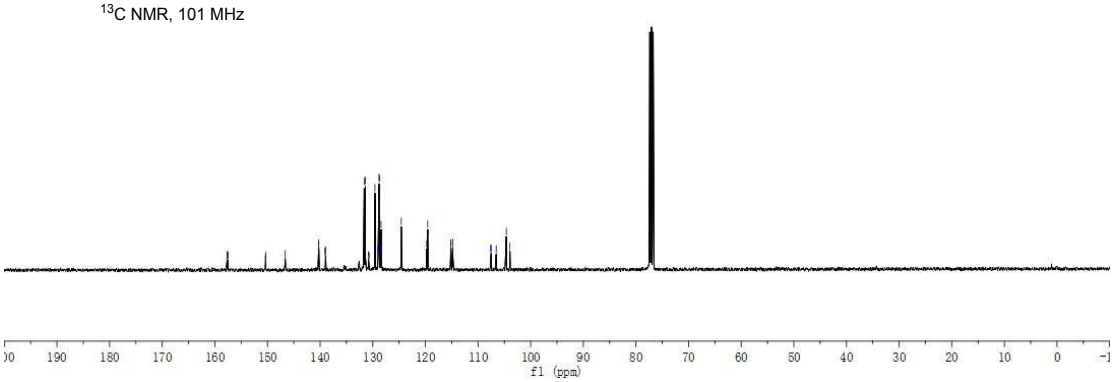




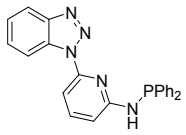


1a

^{13}C NMR, 101 MHz

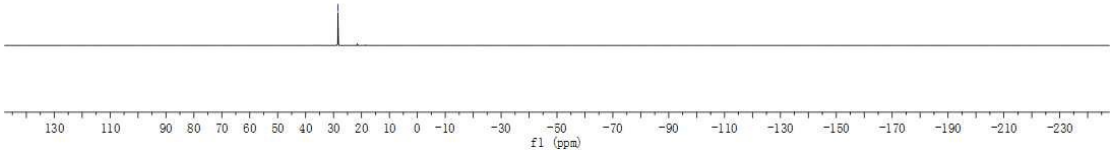


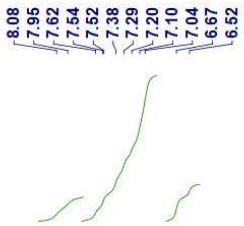
28.45

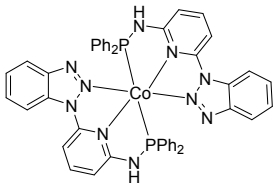


1a

^{31}P NMR, 162 MHz

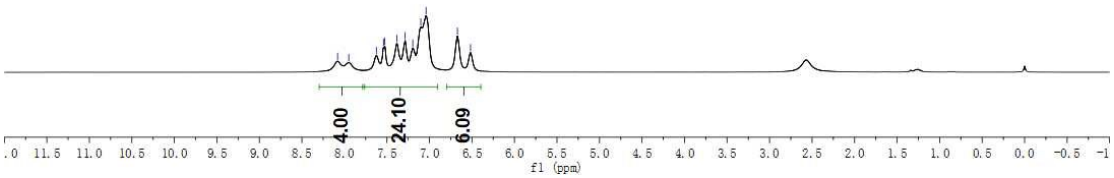


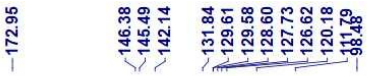


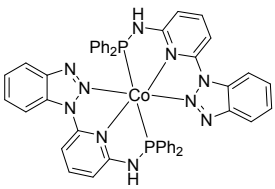


1b

^{1}H NMR, 400 MHz

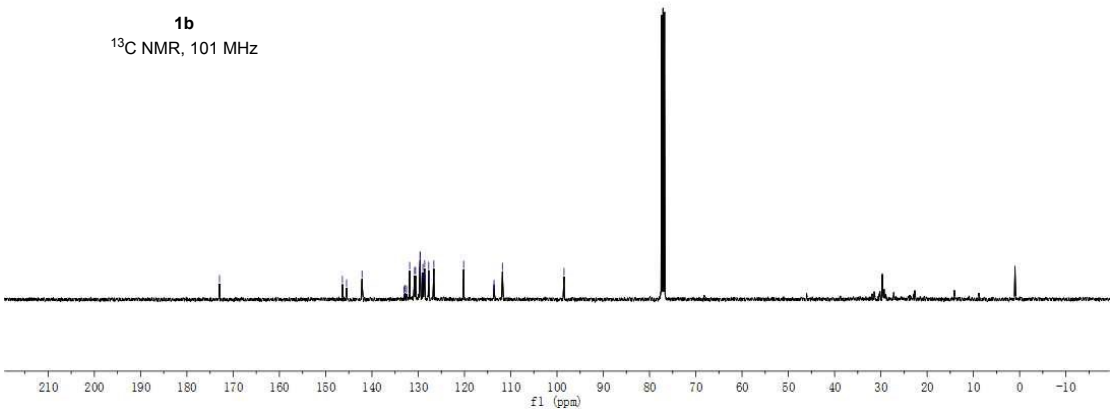


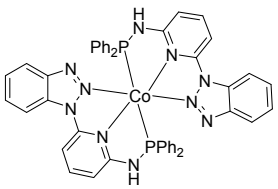




1b

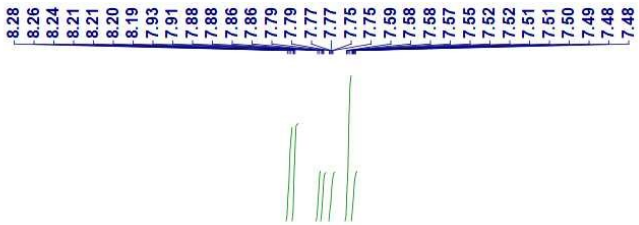
^{13}C NMR, 101 MHz

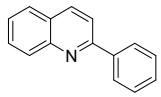




1b

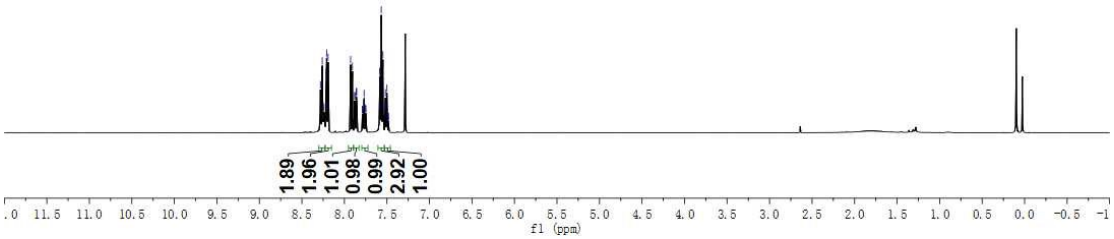
^{31}P NMR, 162 MHz

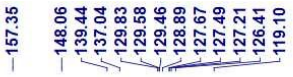


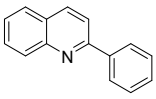


4a

^{1}H NMR, 400 MHz

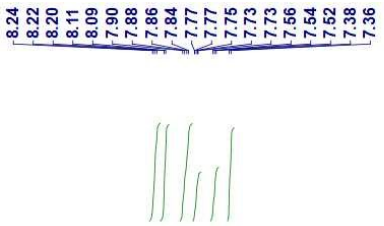


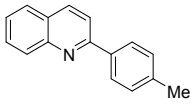




4a

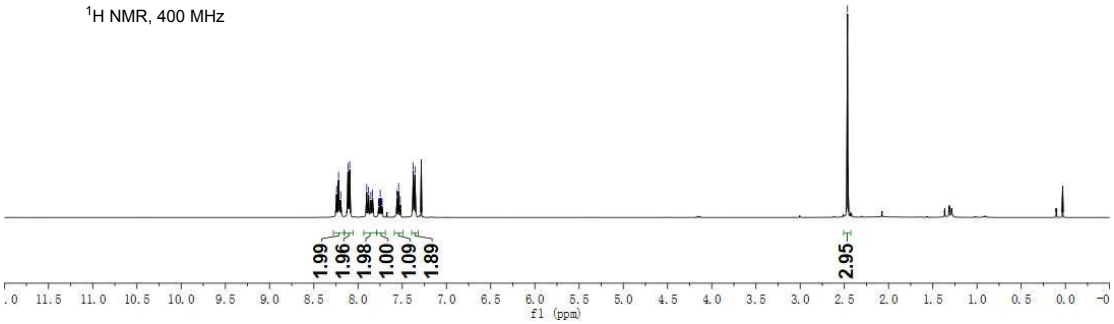
^{13}C NMR, 101 MHz

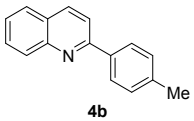




4b

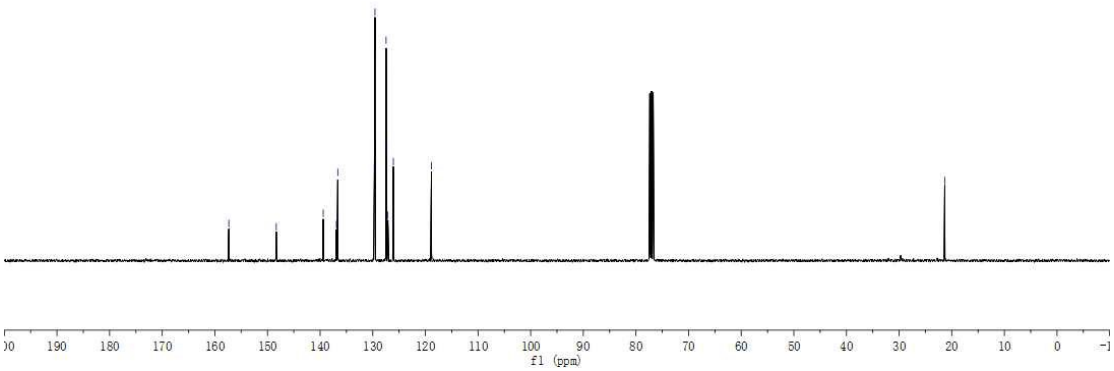
^{1}H NMR, 400 MHz

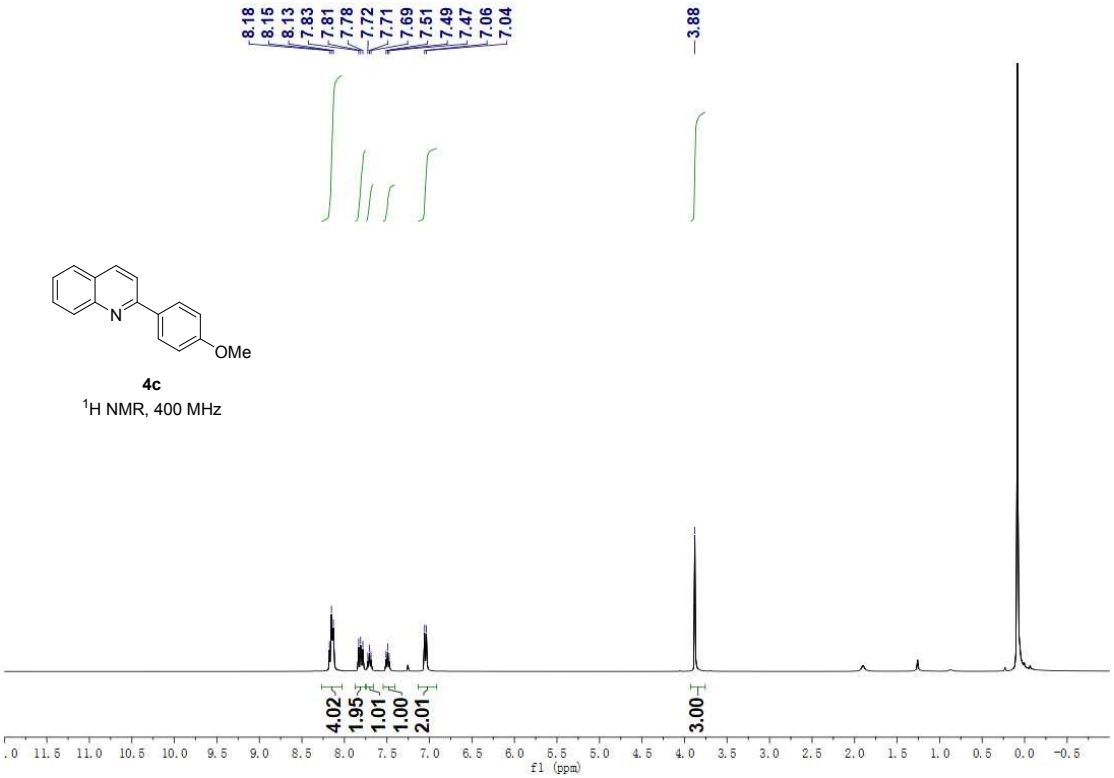




4b

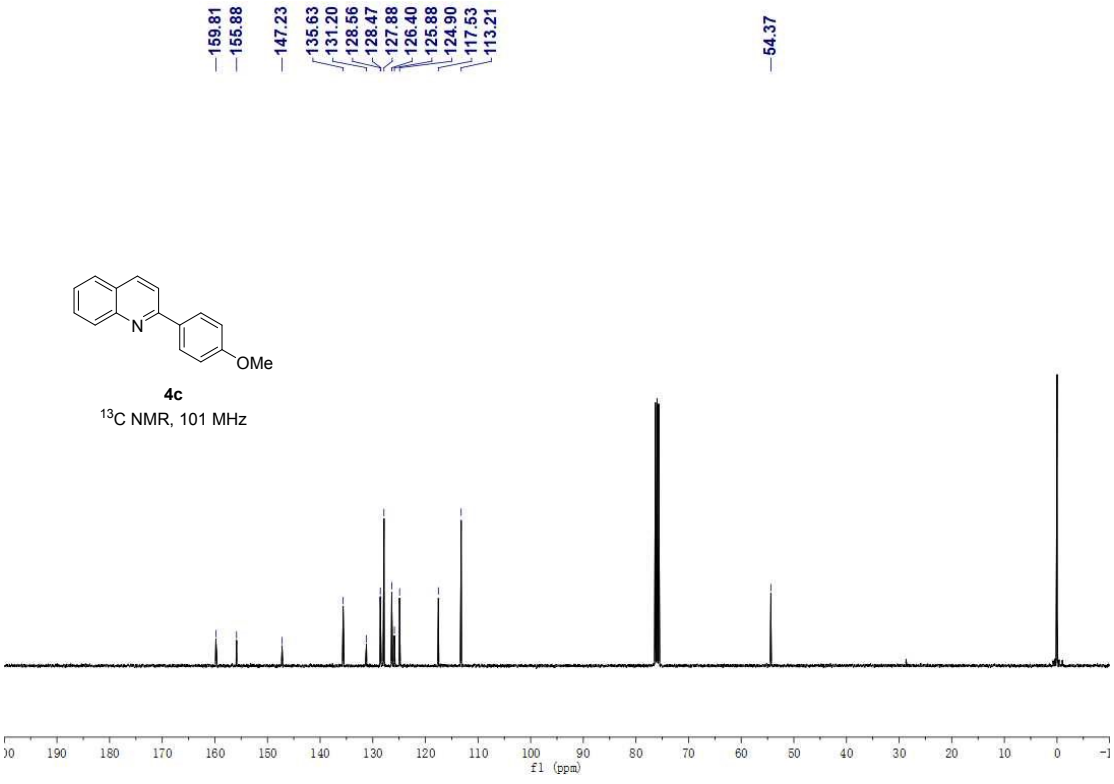
^{13}C NMR, 101 MHz





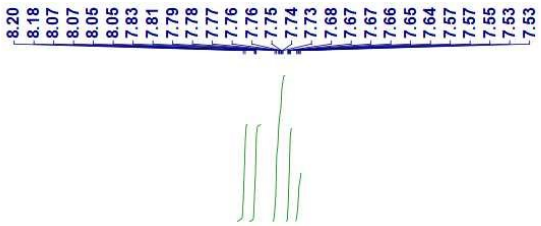
4c

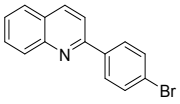
^{1}H NMR, 400 MHz



4c

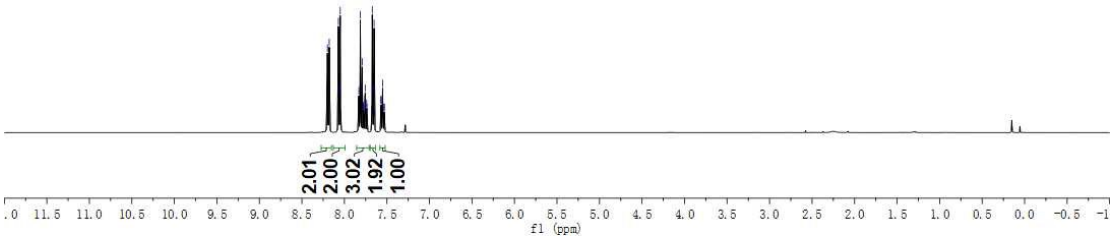
^{13}C NMR, 101 MHz

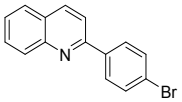




4d

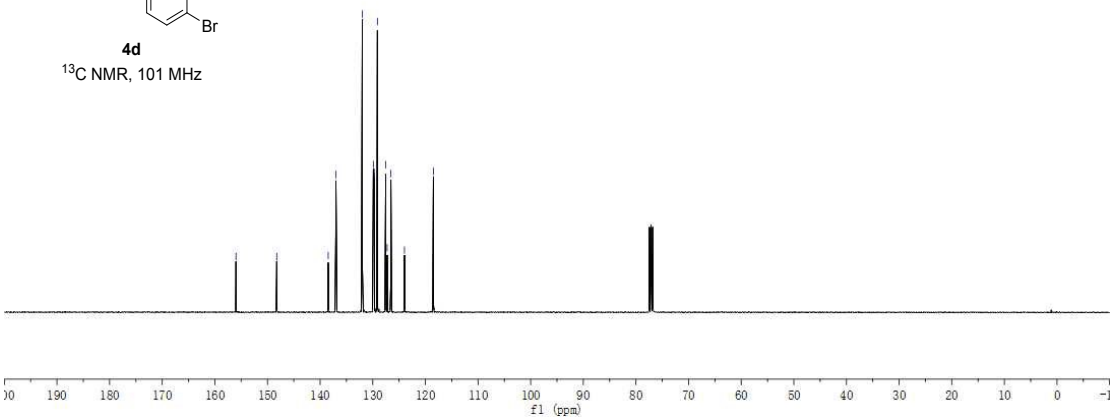
^{1}H NMR, 400 MHz

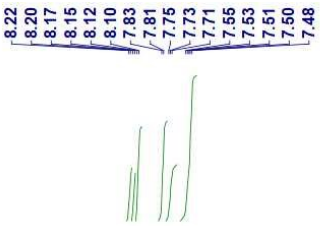


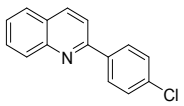


4d

^{13}C NMR, 101 MHz

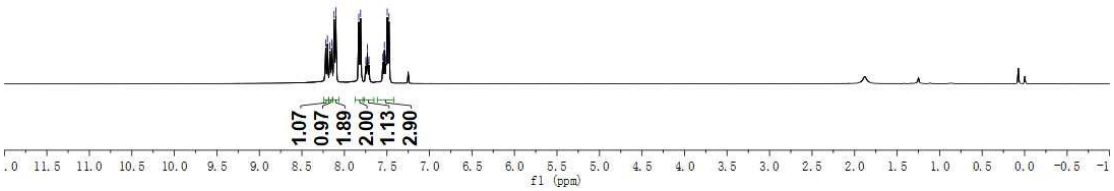


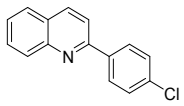




4e

^{1}H NMR, 400 MHz





4e

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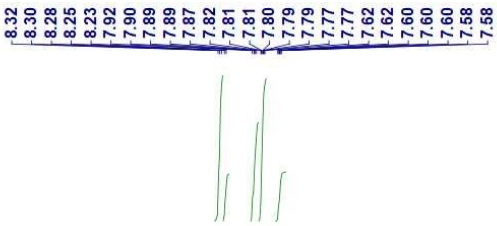

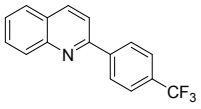

4f

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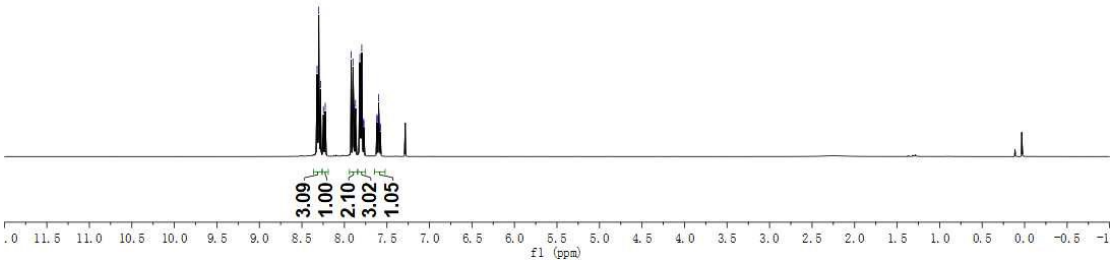
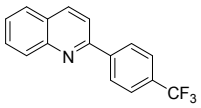
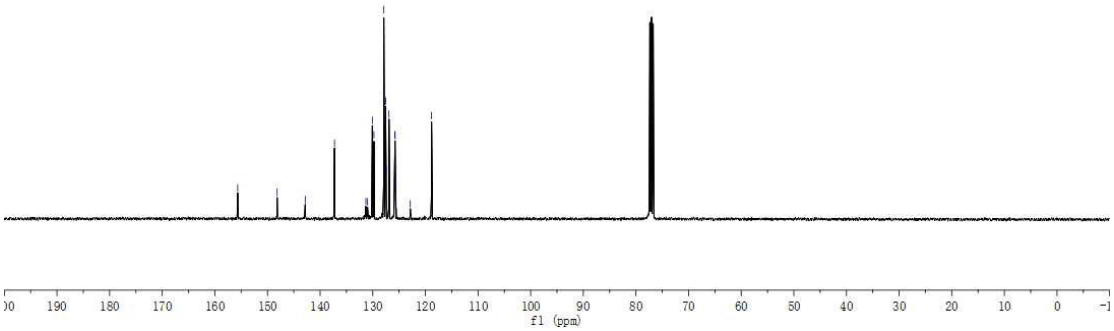
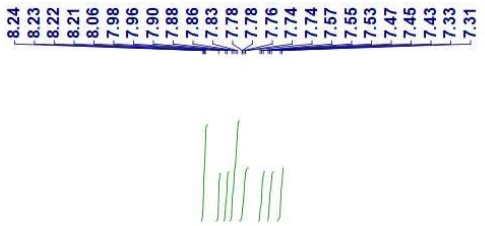


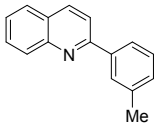


4f

^{13}C NMR, 101 MHz

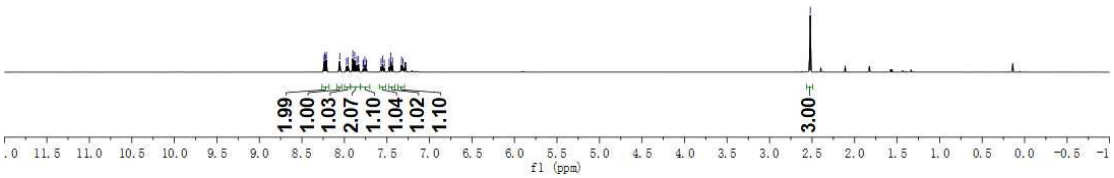


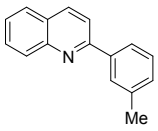




4g

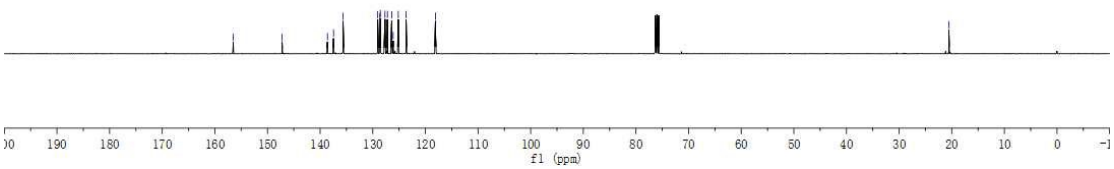
^{1}H NMR, 400 MHz

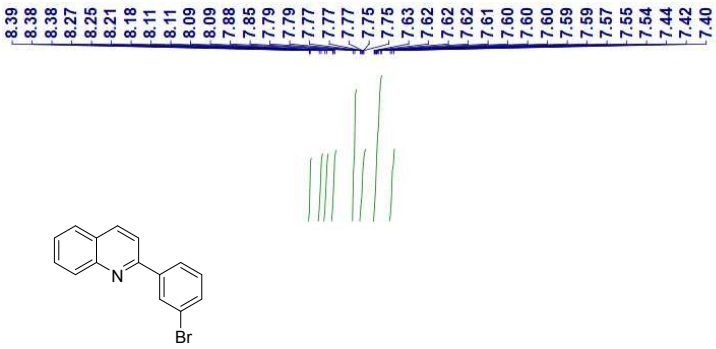




4g

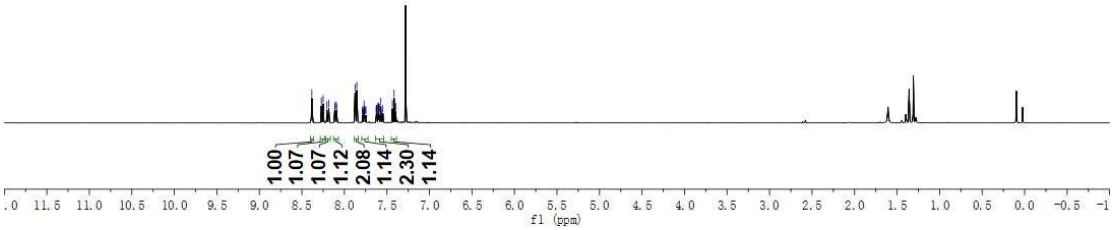
^{13}C NMR, 101 MHz

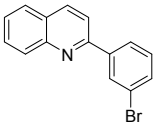




4h

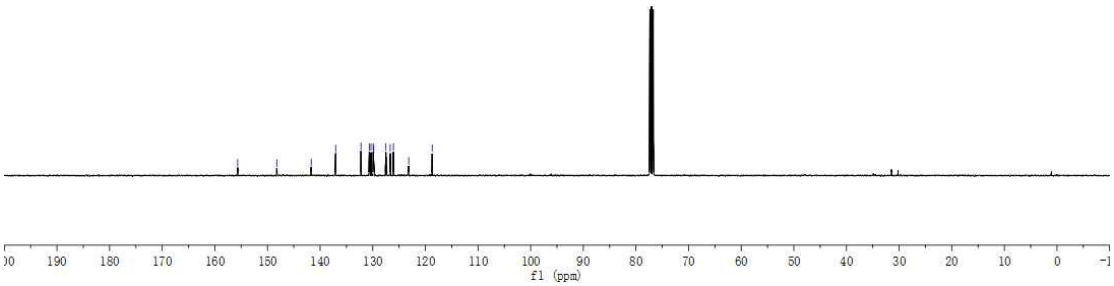
^{1}H NMR, 400 MHz

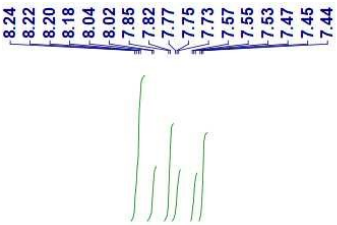


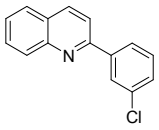


4h

^{13}C NMR, 101 MHz

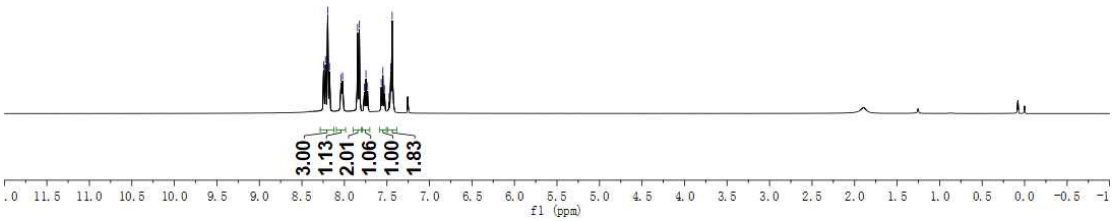


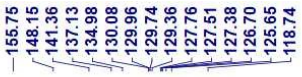


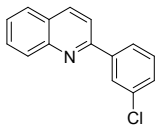


4i

^{1}H NMR, 400 MHz

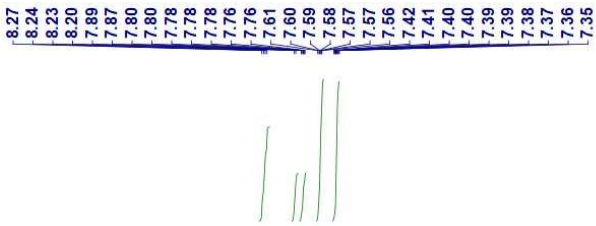


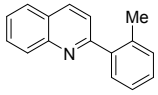




4i

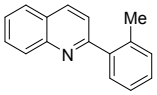
^{13}C NMR, 101 MHz





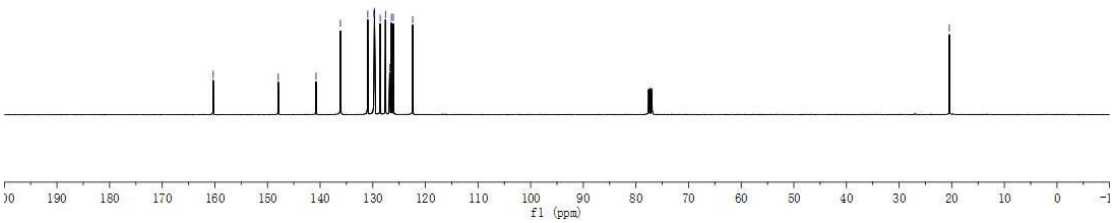
4j

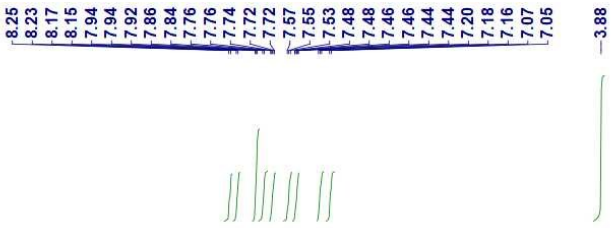
^{1}H NMR, 400 MHz

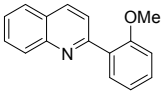


4j

^{13}C NMR, 101 MHz

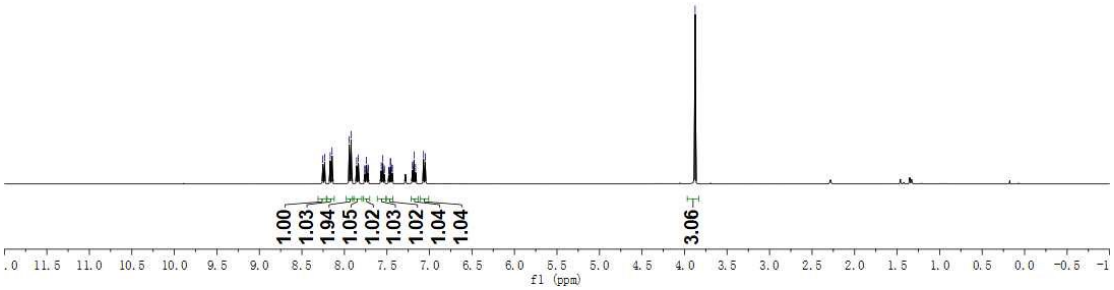


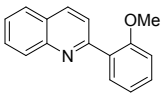




4k

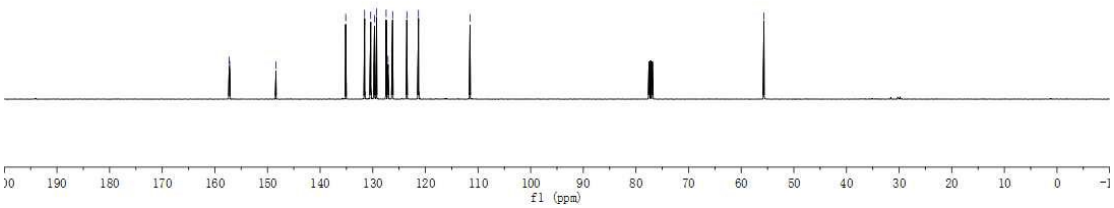
^{1}H NMR, 400 MHz

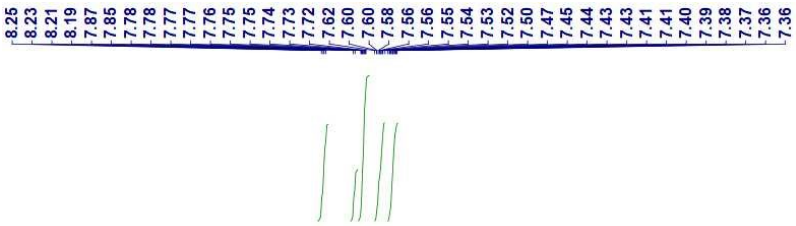


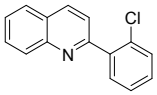


4k

^{13}C NMR, 101 MHz

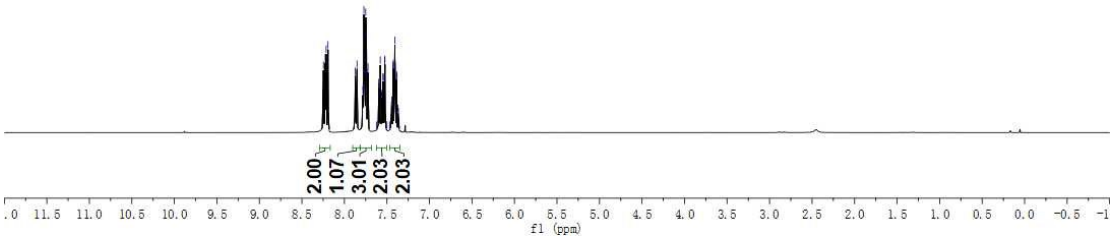


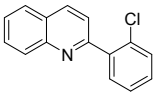




4l

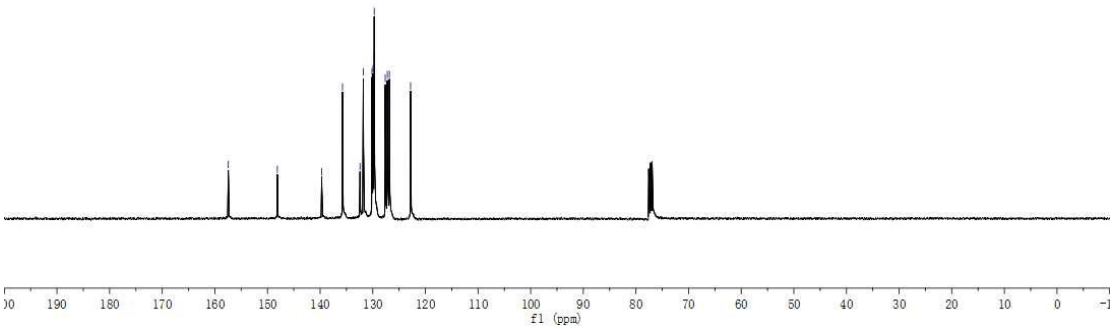
^{1}H NMR, 400 MHz

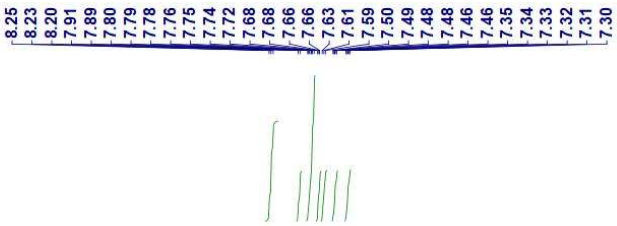


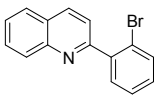


4l

^{13}C NMR, 101 MHz

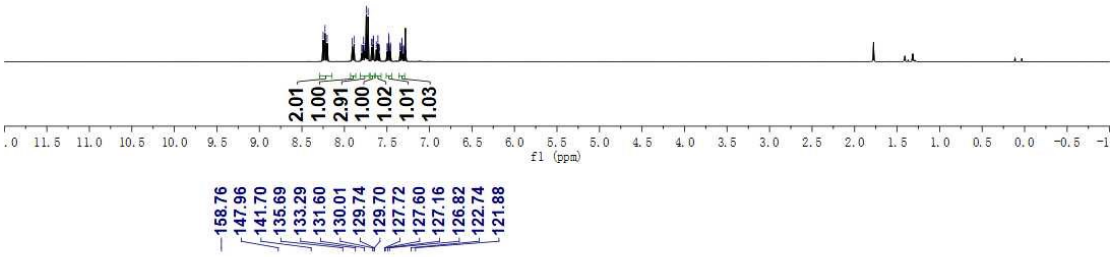


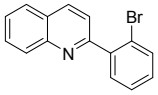




4m

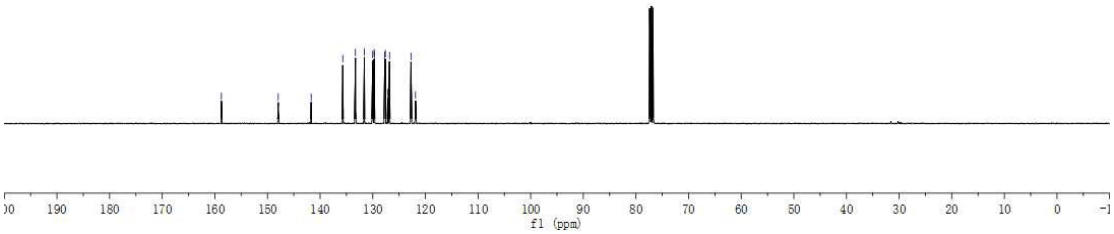
^{1}H NMR, 400 MHz

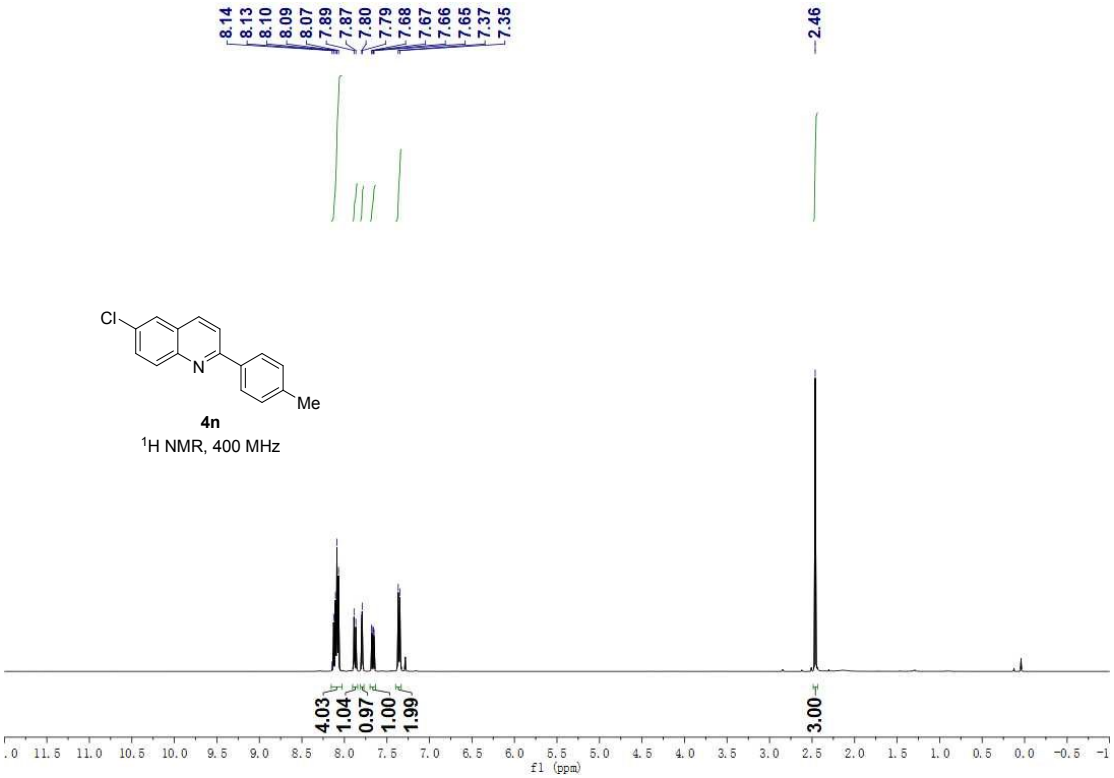




4m

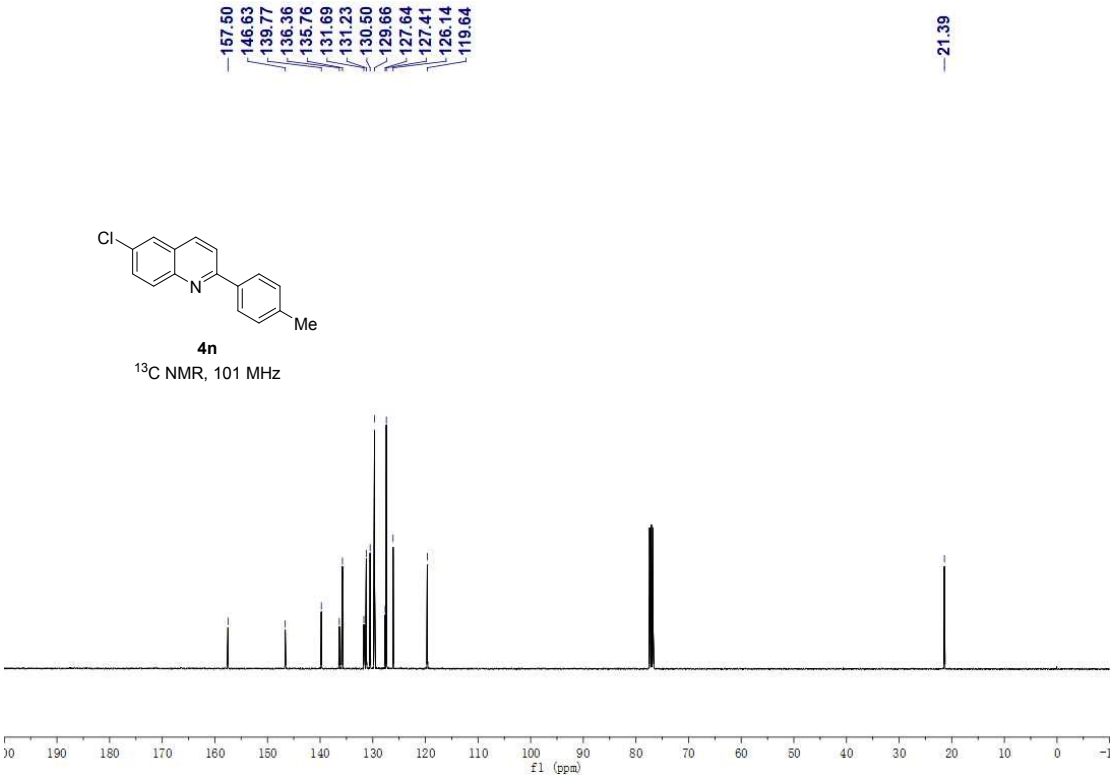
^{13}C NMR, 101 MHz





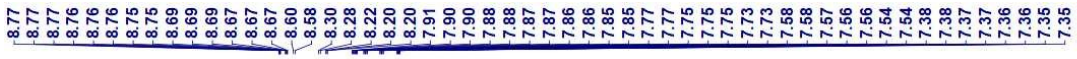
4n

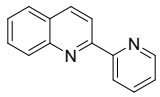
^{1}H NMR, 400 MHz



4n

^{13}C NMR, 101 MHz





4o

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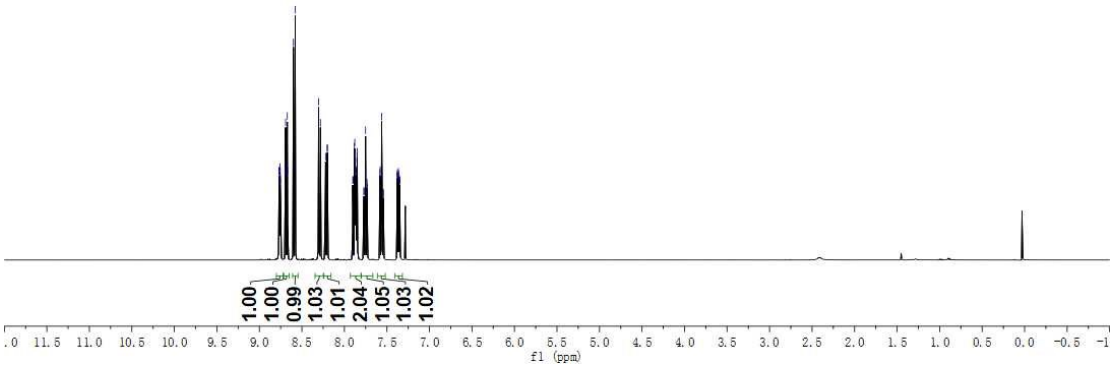
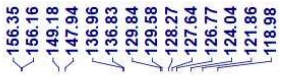
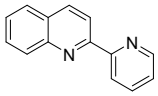
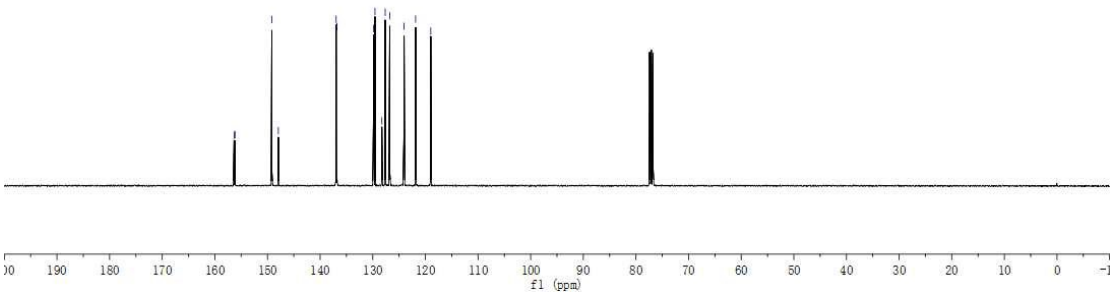


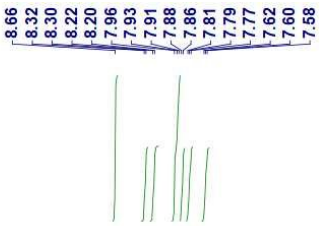


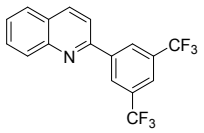


4o

^{13}C NMR, 101 MHz

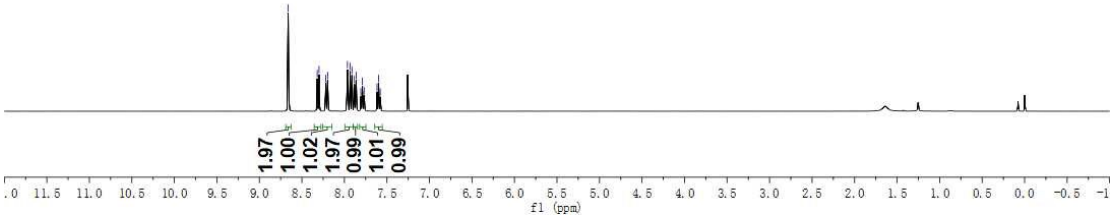


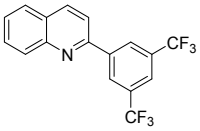




4p

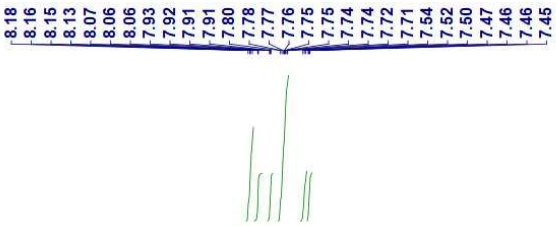
^{1}H NMR, 400 MHz

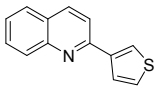




4p

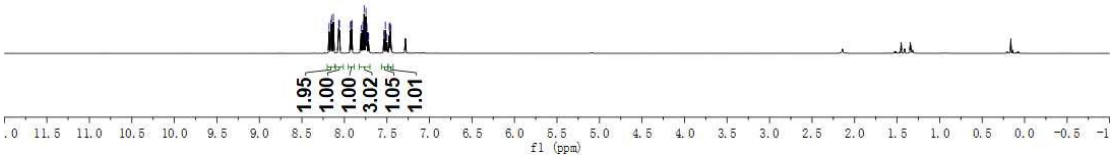
^{13}C NMR, 101 MHz

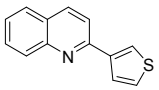




4q

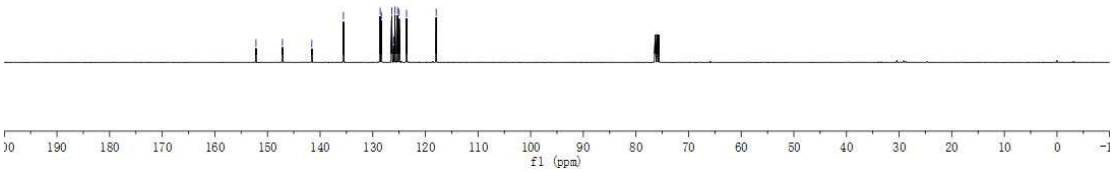
^{1}H NMR, 400 MHz

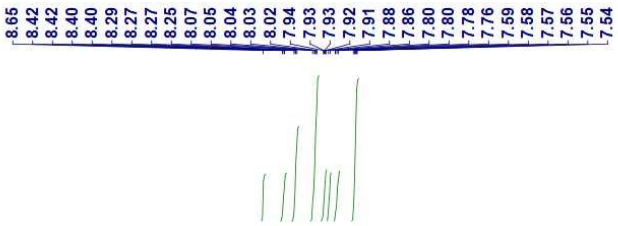


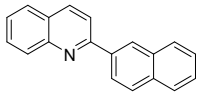


4q

^{13}C NMR, 101 MHz

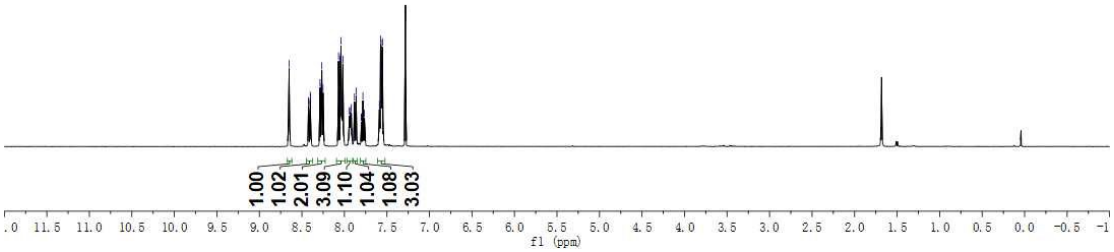


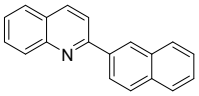




4r

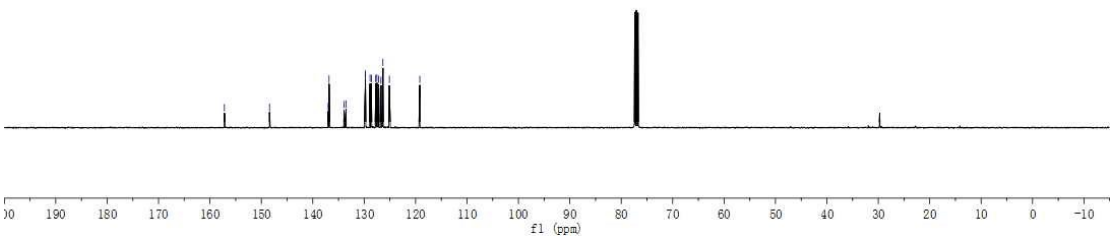
^{1}H NMR, 400 MHz

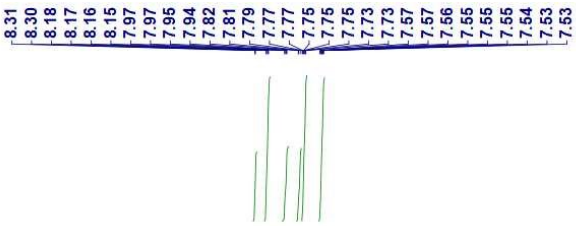


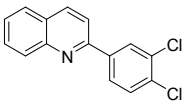


4r

^{13}C NMR, 101 MHz

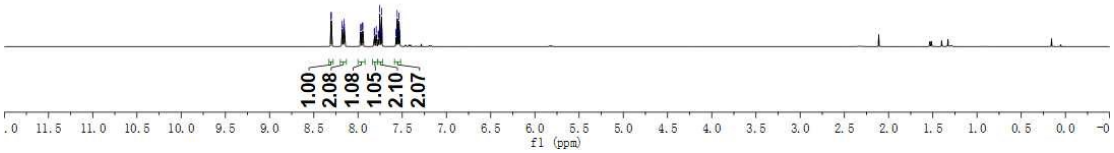


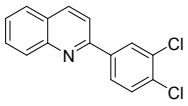




4s

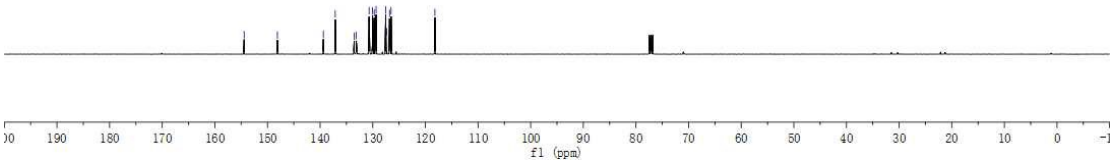
^{1}H NMR, 400 MHz

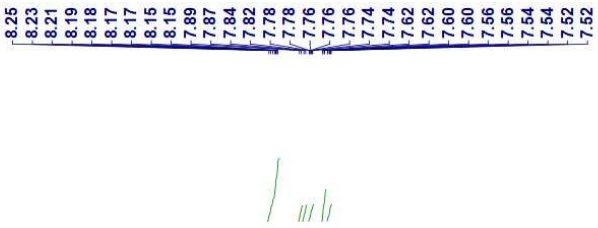


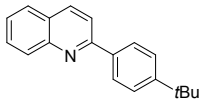


4s

^{13}C NMR, 101 MHz

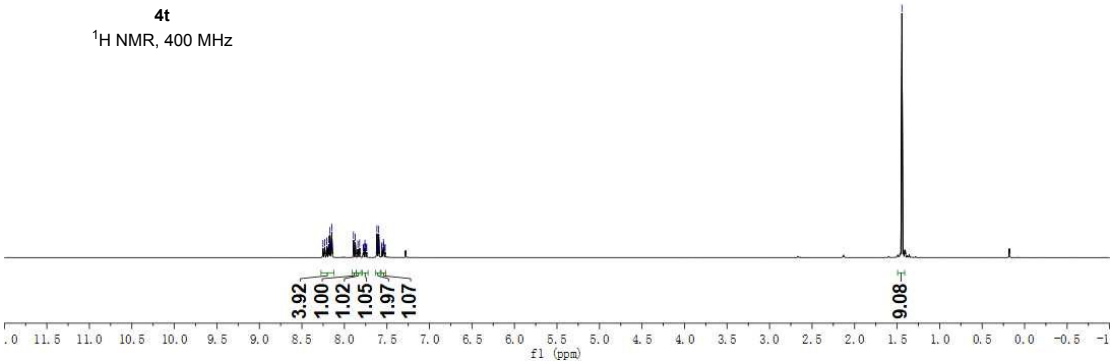


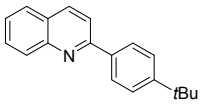




4t

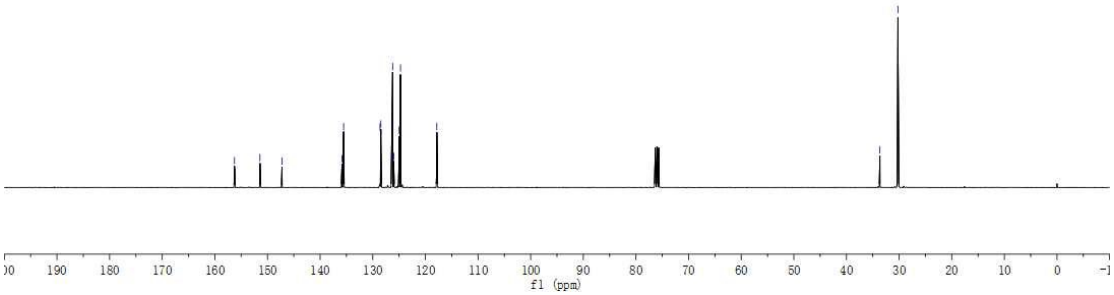
^{1}H NMR, 400 MHz

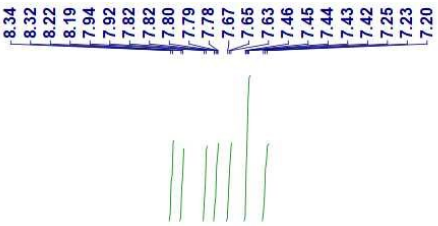


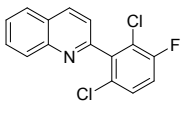


4t

^{13}C NMR, 101 MHz

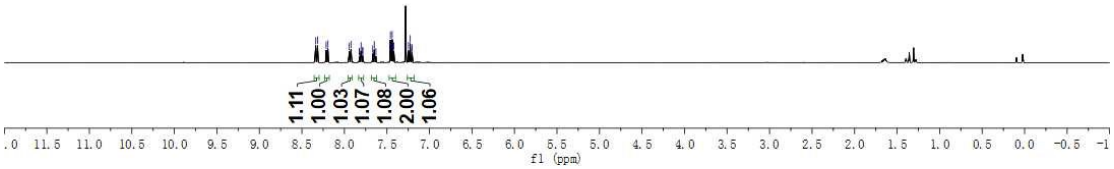


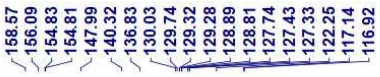


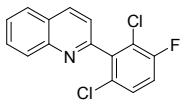


4u

^{1}H NMR, 400 MHz

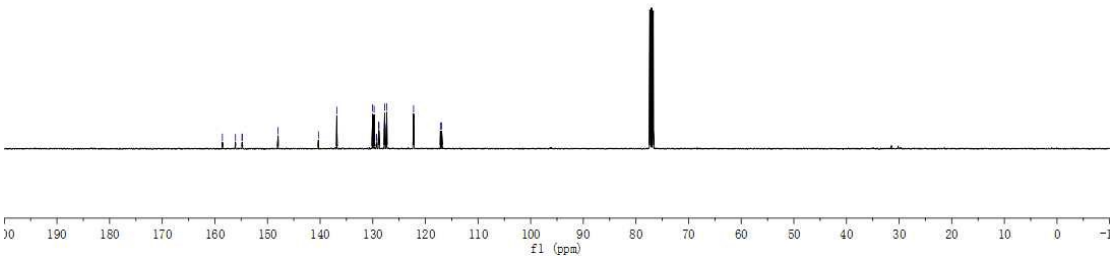


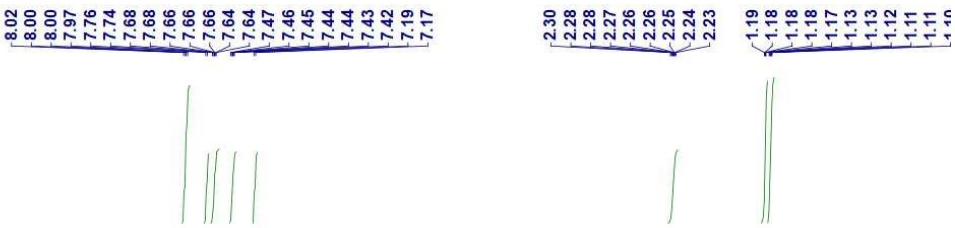


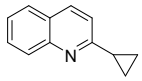


4u

^{13}C NMR, 101 MHz

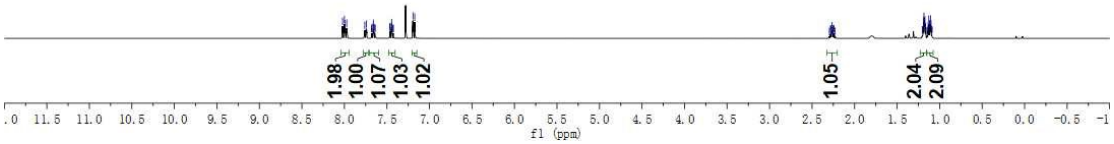


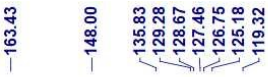


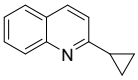


4v

^{1}H NMR, 400 MHz

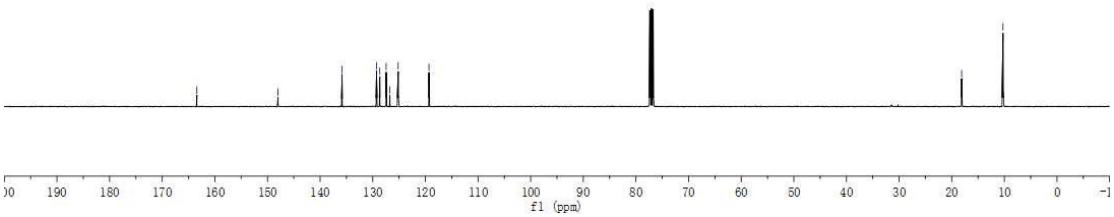


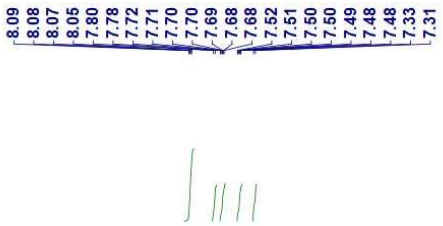


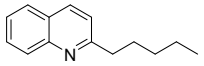


4v

^{13}C NMR, 101 MHz

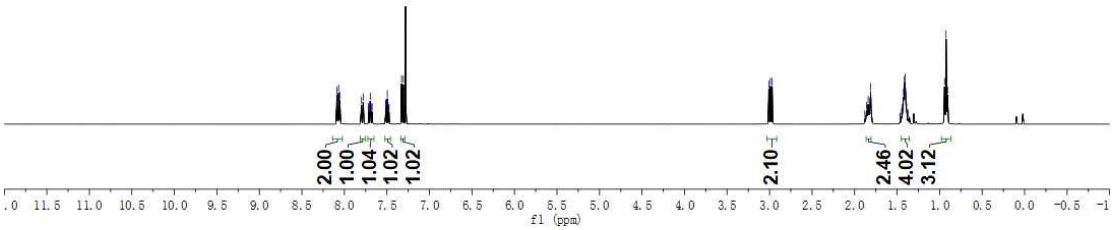


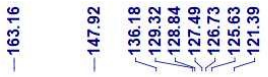


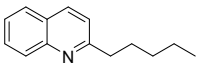


4w

^{1}H NMR, 400 MHz

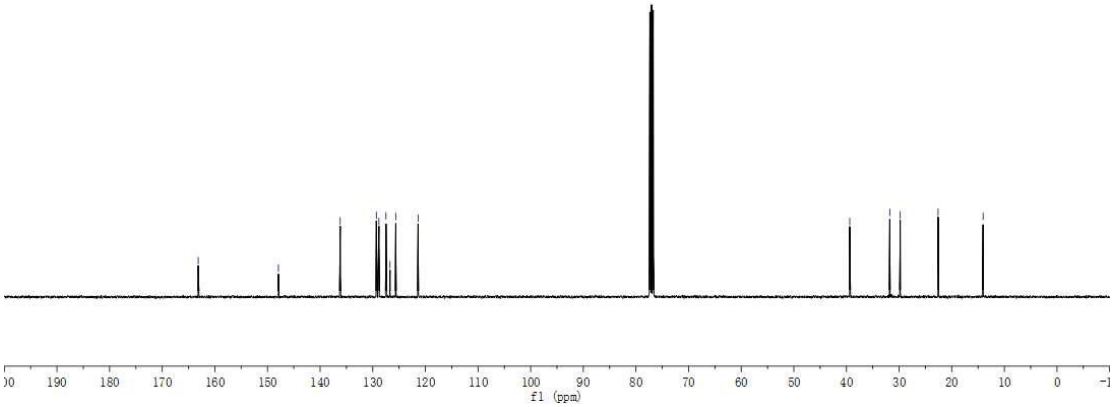


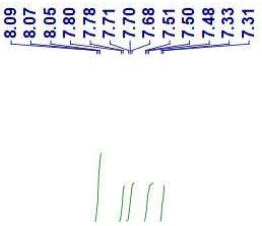


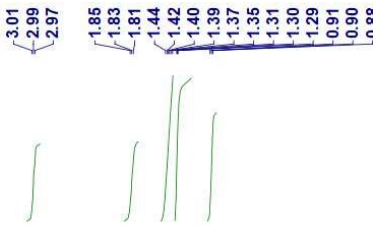


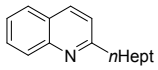
4w

^{13}C NMR, 101 MHz



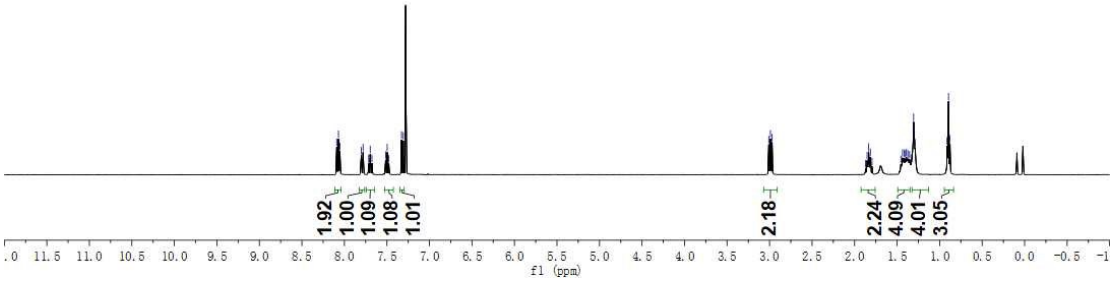


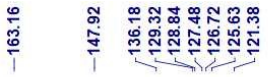


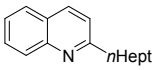


4x

^{1}H NMR, 400 MHz

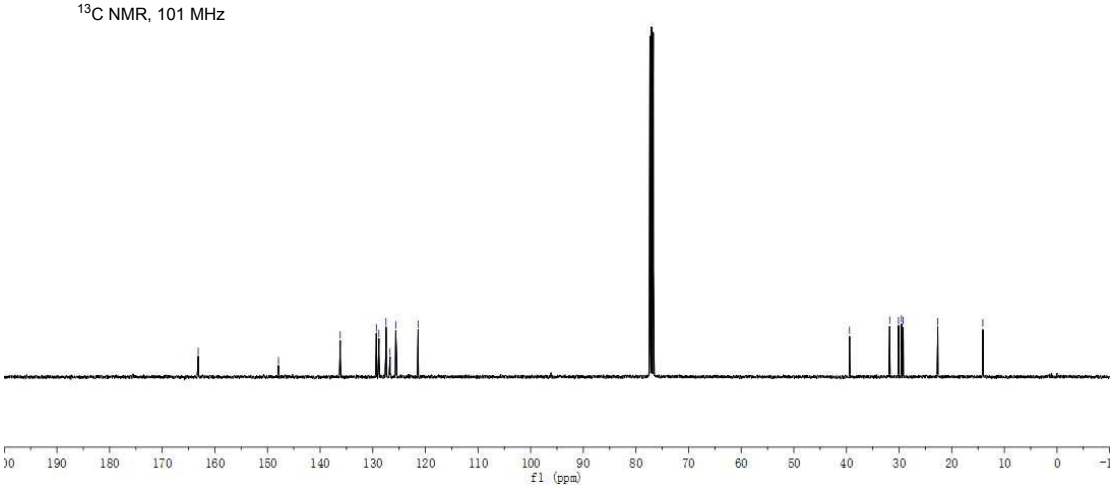






4x

^{13}C NMR, 101 MHz



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