

Supporting Information

**Unsymmetrical triazolyl-naphthyridinyl-pyridine bridged high active
copper complexes supported on reduced graphene oxide and the
application in water**

Wenkang Hu,^a Yilin Zhang,^b Haiyan Zhu,^a Dongdong Ye,^a and Dawei Wang*^a

^a The Key Laboratory of Food Colloids and Biotechnology, Ministry of Education, School of Chemical and Material Engineering,
Jiangnan University, Wuxi 214122, China. E-mail: wangdw@jiangnan.edu.cn

^b C. Eugene Bennett Department of Chemistry, West Virginia University, Morgantown, West Virginia 26506, United States.

Table of contents

General methods and materials.....	S2
Preparation of TNP-Cu@rGO.....	S2-S3
Characterization of catalyst TNP-Cu@rGO.....	S4-S8
General procedure for the 3 and 6	S9
Hammett plot and mechanism studies.....	S9
Analytical data of the obtained compounds.....	S9-S25
NMR spectra of obtained compounds.....	S26-S63
Reference.....	S64

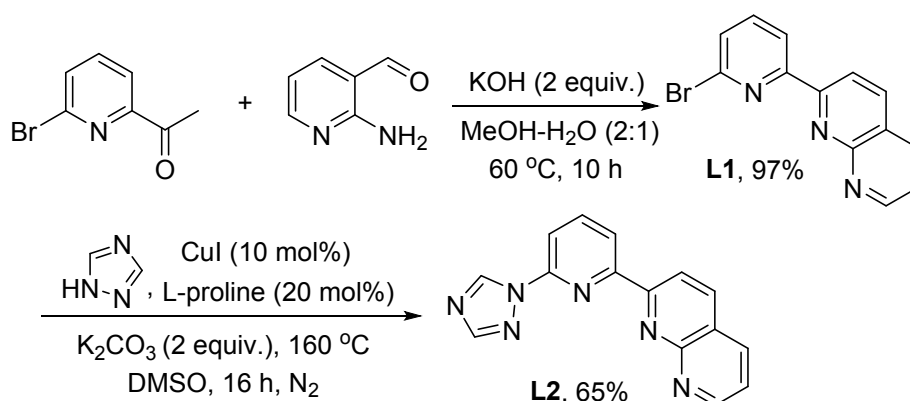
1. General Methods and Materials

All of the reactions dealing with air were carried using standard Schlenk techniques or glovebox techniques. All the obtained products were characterized by ^1H -NMR, ^{13}C -NMR and melting points (m.p), melting points were measured by an Electrothermal WRS X-4A microscopy digital apparatus and without correction. ^1H NMR and ^{13}C NMR spectra were obtained on Bruker Advance III HD 400 MHz spectrometer and referenced to CDCl_3 (7.26 ppm for ^1H , and 77.1 ppm for ^{13}C) or $\text{DMSO}-d_6$ (2.50 ppm for ^1H , and 39.5 ppm for ^{13}C) with tetramethylsilane as internal standard (0 ppm). Chemical shifts were reported in parts per million (ppm δ) downfield from TMS and coupling constants are reported in Hertz. The following abbreviations were used to explain NMR peak multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, p = pentet, m = multiplet, br = broad. TLC was performed using commercially prepared 100-400 mesh silica gel plates (GF254), and visualization was effected at shortwave UV light (254 nm) and KMnO_4 . Flash column chromatography was performed on 230-430 mesh silica gel. Unless otherwise stated, all the reagents were purchased from commercial sources (Acros, J&K Chemic, TCI, SCRC, Energy Chemical), used without further purification.

2. Preparation of Catalyst TNP-Cu@rGO

2.1 Synthesis of Complexes TNP-Cu

2.1.1 Procedure for synthesis of 2-(6-bromopyridin-2-yl)-1,8-naphthyridine ¹



To an oven-dried 100 mL round bottom flask were successively added 2-acetyl-6-bromopyridine (3.000 g, 15 mmol) and 2-amino-3-pyridinecarboxaldehyde (1.221 g, 15 mmol) dissolved in methanol (30 mL) with potassium hydroxide (1.683 g, 30 mmol) dissolved by deionized water (15 mL) under air. The reaction was processed for 10 hours at 60 $^\circ\text{C}$, and then the reaction mixture was quenched by the addition of water (40 mL) and the resulting precipitate was isolated by filtration. The crude product was washed with water, dried in a vacuum oven, and collected (4.147 g, 98%), leading to 2-(6-bromopyridin-2-yl)-1,8-naphthyridine (**L1**). This product was used without further purification.

To an oven-dried 100-mL Schlenk tube were successively added **L1** (2.850 g, 10 mmol), 1,2,4-triazole (0.829 g, 12 mmol), copper (I) iodide (0.190 g, 1 mmol), potassium carbonate (2.764 g, 20 mmol), L-proline (0.230 g, 2 mmol), and dimethylsulfoxide (30 mL) under N_2 atmosphere. Then, the tube was closed and the resulting mixture was stirred at 160 $^\circ\text{C}$ for 16 h and monitored by TLC until complete disappearance of 2-bromopyridine. After cooling down to ambient temperature, the reaction mixture was added water and extracted with ethyl acetate three

times. The combined organic phases were dried over anhydrous MgSO_4 and concentrated by removing the solvent under vacuum. Finally, the residue was purified by flash column chromatography with hexane/ethyl acetate (1:1) to give the desired product: 2-(6-(1H-1,2,4-triazol-1-yl)-pyridin-2-yl)-1,8-naphthyridine (TNP, **L2**) (1.783 g, 65% yield).

Pale-yellow solid; Mp. 235-237 °C; ^1H NMR (400 MHz, Chloroform-*d*) δ 9.33 (s, 1H), 9.19 – 9.13 (m, 1H), 8.86 (d, J = 7.5 Hz, 1H), 8.68 (d, J = 8.5 Hz, 1H), 8.34 (d, J = 8.5 Hz, 1H), 8.24 (dd, J = 8.1, 1.8 Hz, 1H), 8.14 (s, 1H), 8.07 (t, J = 7.9 Hz, 1H), 7.98 (d, J = 7.6 Hz, 1H), 7.52 (dd, J = 8.1, 4.2 Hz, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 157.62, 155.67, 154.29, 152.92, 148.81, 141.41, 140.43, 138.16, 136.97, 123.13, 122.54, 121.67, 119.71, 113.94.

2.1.2 Preparation of triazolyl-naphthyridinyl-pyridine copper complexes²

In an oven-dried 100 mL round bottom flask were successively added $[\text{Cu}(\text{CH}_3\text{CN})_4]\text{PF}_6$ (1.864 g, 5 mmol), **L2** (1.399 g, 5.1 mmol) and methanol (20 mL). The mixture was vigorously stirred under air at room temperature for 16 h. As the reaction finished, the crude products were obtained by filtration, subsequently washed several times with EtOH, dichloromethane and dried by freeze dryer, leading to pale yellow solid $[\{\text{Cu}(\text{CH}_3\text{CN})_2\}(\text{triazolyl-naphthyridinyl-pyridine})](\text{PF}_6)_2$ (**TNP-Cu**, 95% yield).

2.2 Preparation of highly reduced graphene oxide³

GO was synthesized from purified natural graphite (SP-1, J&K Chemic) by the modified Hummers method. H_2SO_4 (75 mL) was added into the 250 mL flask filled with graphite (3.0 g) at room temperature, followed by addition of solid KMnO_4 (10.5 g) slowly at 0 °C (ice bath). After increase of temperature to 40 °C, the mixture was stirred by magnetic stirring bar for 3 h. Excess water was added into the mixture at 0 °C (ice bath) and then H_2O_2 (30 wt% in water from Sigma-Aldrich) was added until there was no gas producing. Filtration with glass filter afforded brown powder (GO) and the GO powder was dried in the vacuum at room temperature for 12 h.

A colloidal suspension of individual graphene oxide powder in purified water (20 mL, 5 mg/mL) was prepared in 4-L batches with 2 h of bath ultrasound (CH-01AM). The graphene oxide suspension in the $\text{H}_2\text{O}/\text{N,N}$ -dimethylformamide (DMF) solvent mixture was obtained by addition of DMF (180 mL) into the aqueous graphene oxide suspensions (thus, volume ratio DMF/ H_2O = 9), producing a homogeneous suspension of the graphene oxide. Hydrazine monohydrate (1 mL for 100 mg of GO) (98%, J&K Chemic) was subsequently added to the suspension (pH = ~6). Additional stirring with a Teflon-coated stirring bar at 80 °C for 12 h yielded a black suspension (pH = ~7) of rGO. The suspension was centrifuged to obtain a high concentration of reduced graphene oxide. A total of 1.3 g of reduced graphene oxide was prepared as repeated the above procedure.

2.3 Preparation of TNP-Cu@rGO

Next, copper complexes (15 mg), reduced graphene oxide (500 mg) and the DMSO (30 mL) were stirred in a Schlenk tube at 160 °C for 24 h. In the progress, PF_6^- was replaced by hydroxyl groups on the surface of rGO. The product TNP-Cu@rGO (TNP-Cu@rGO (3% loading, w/w) was filtered off by centrifuge and washed with EtOH and CH_2Cl_2 , leading to black powders. The powders were kept at -20 °C for 2 h, and dried for 24 h by vacuum refrigeration dryer machine.

3. Characterization of catalyst TNP-Cu@rGO

Fig.S1. showed EDX image of TNP-Cu@rGO (a), and corresponding elemental mapping images of (b) TNP-Cu@rGO, (c) C, (d) N, (e) O, (f) Cu, which revealed Cu complexes was supported on reduced graphene oxide successfully.

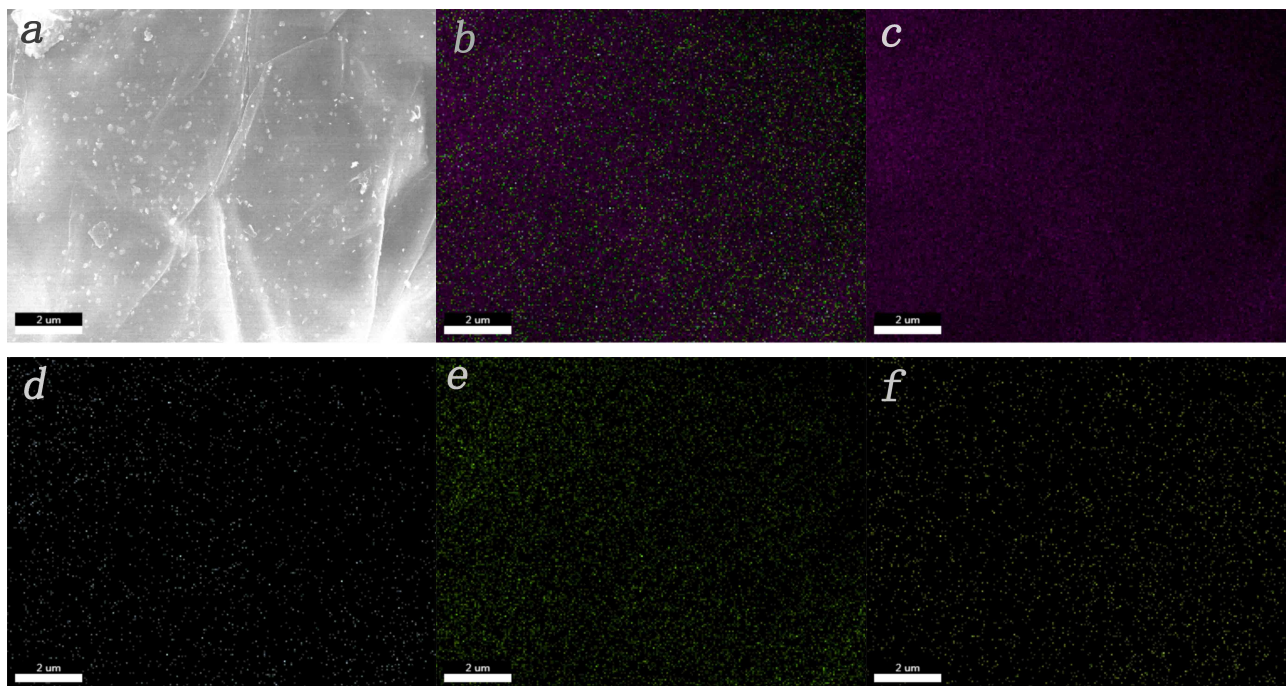
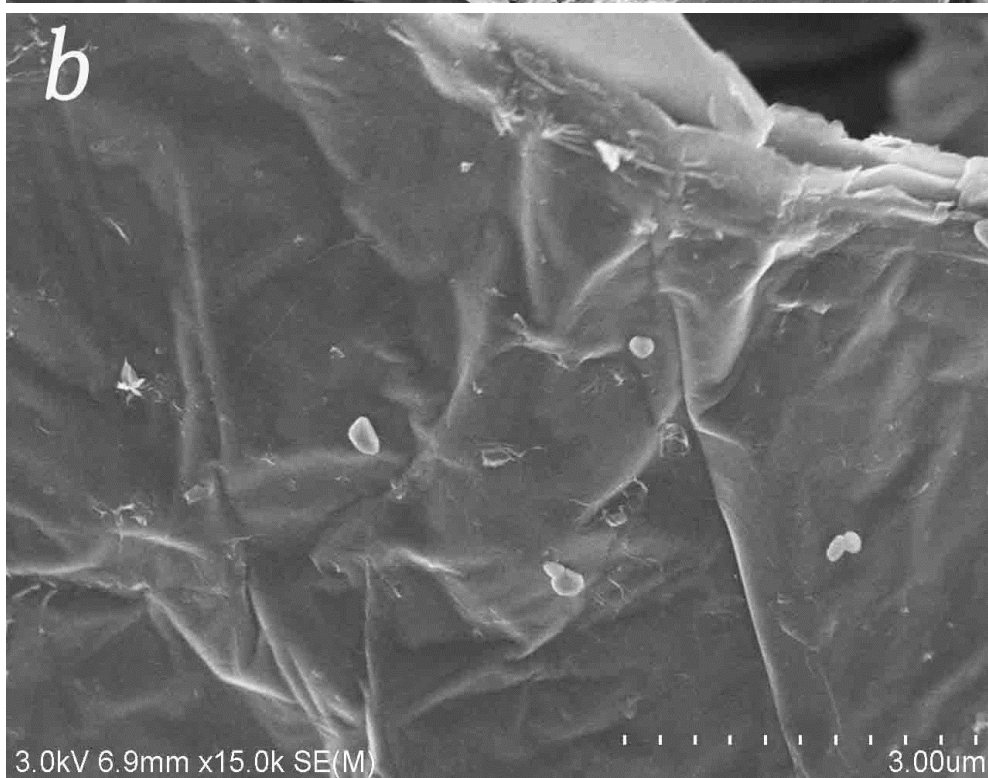
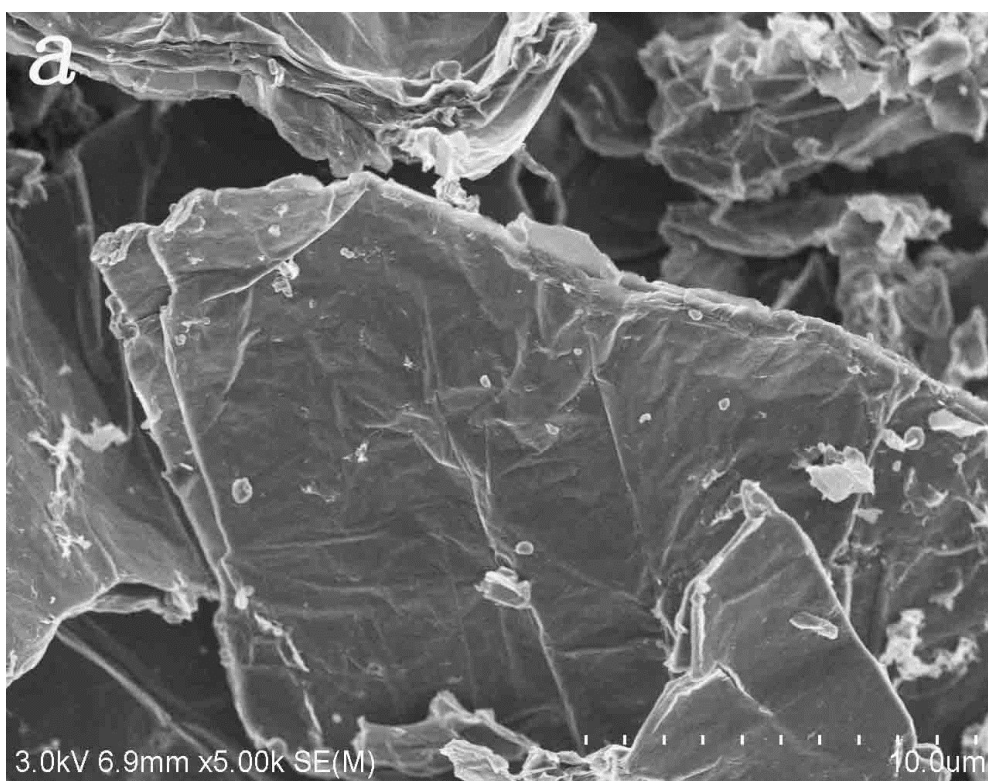
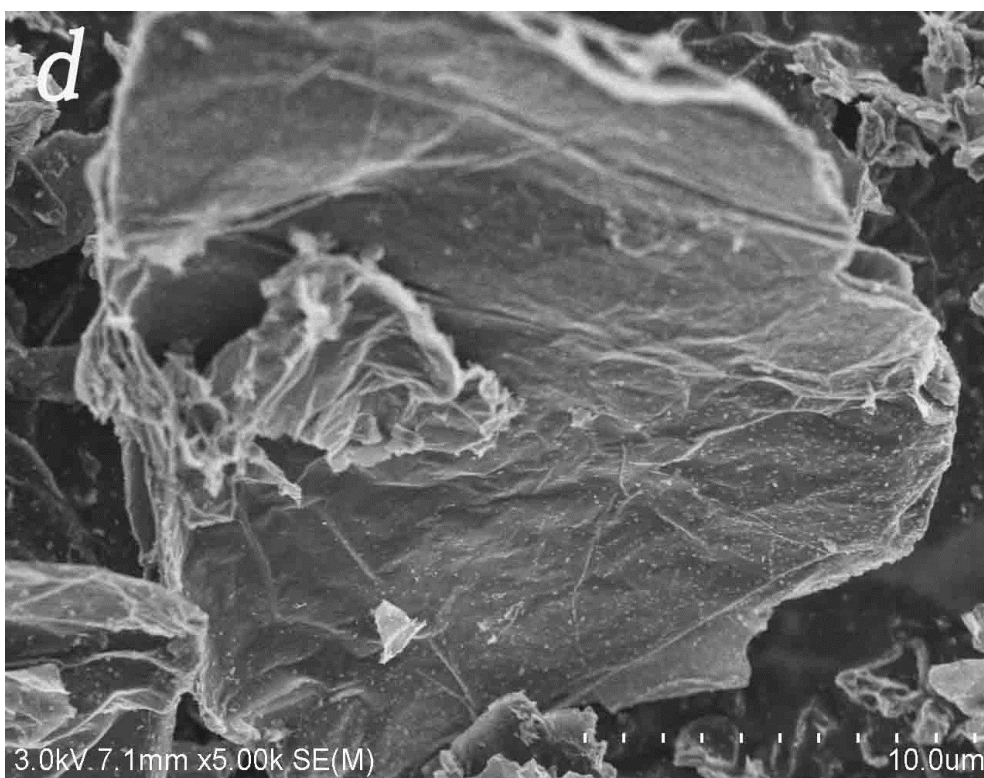
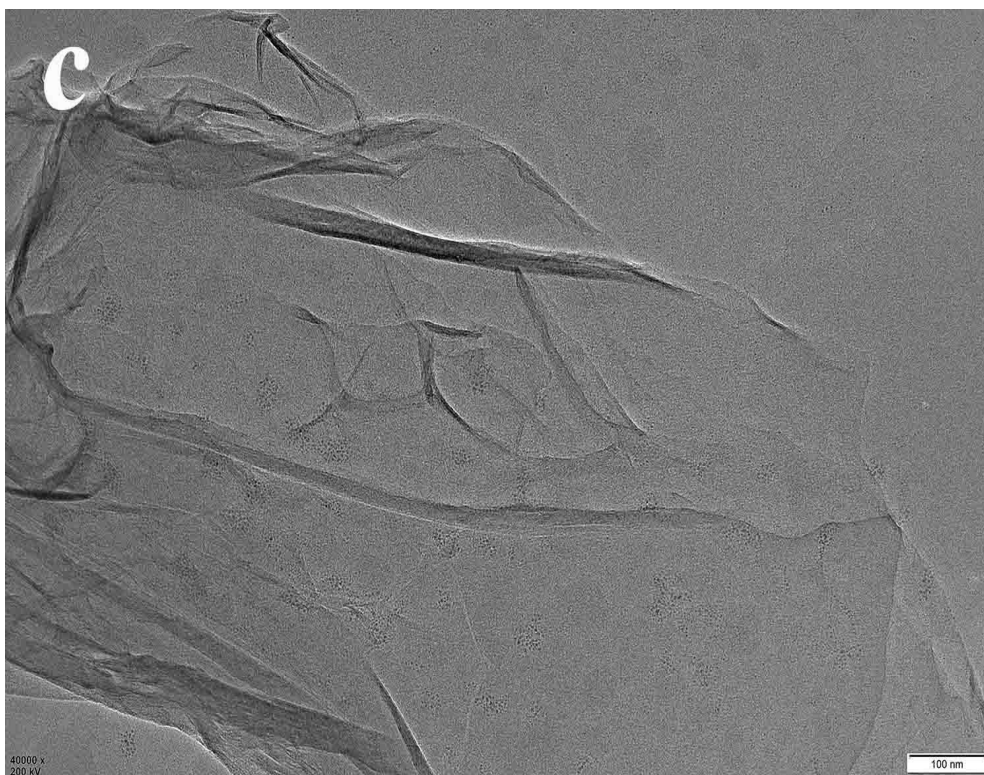


Fig.S1. EDX image of TNP-Cu@rGO (a), and corresponding elemental mapping images of (b)TNP-Cu@rGO, (c) C, (d) N, (e) O, (f) Cu.

Fig.S2. The SEM and TEM images of rGO and TNP-Cu@rGO, which indicated copper complex was supported uniformly on the rGO.





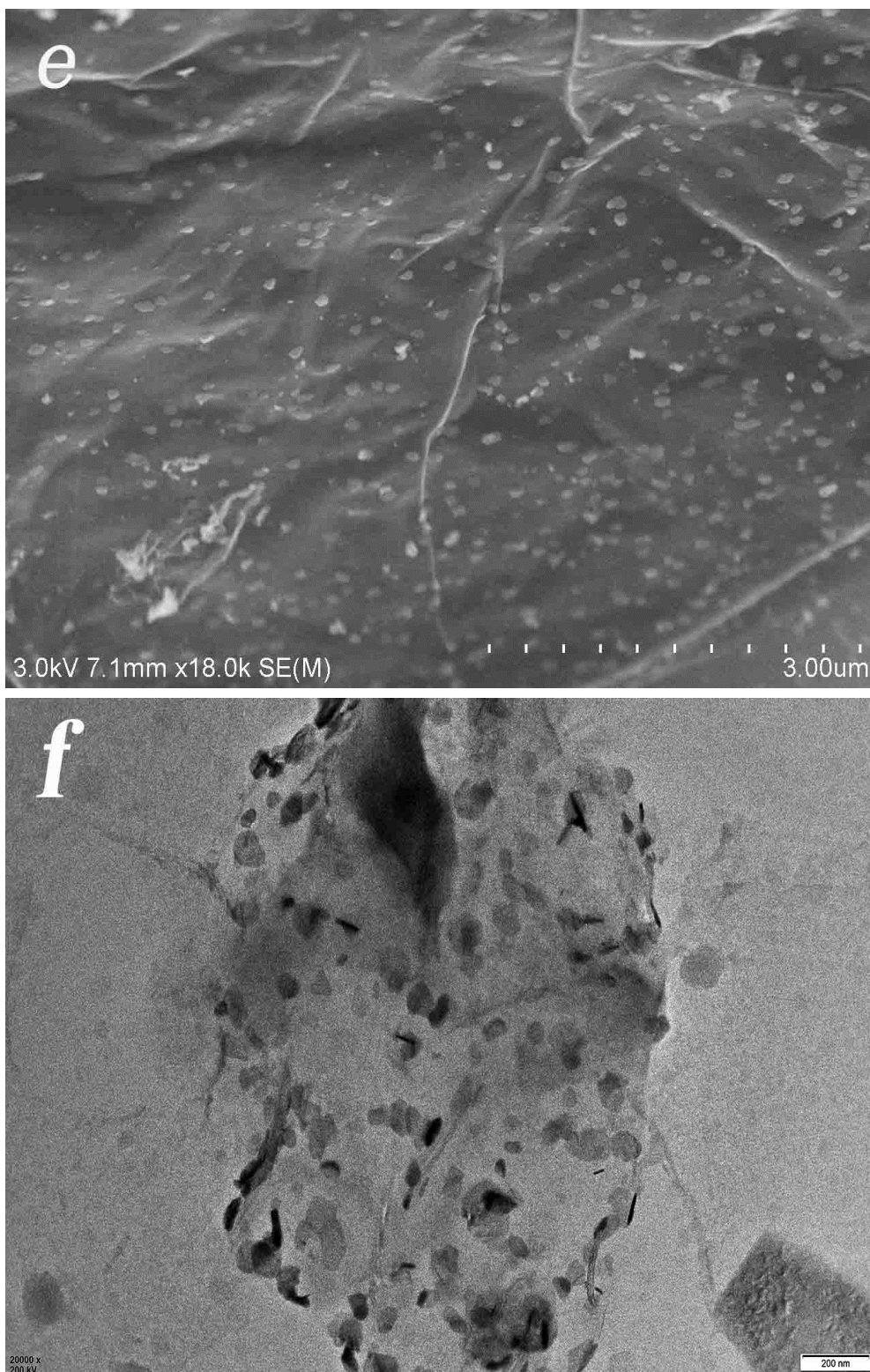


Fig.S2. SEM image of (a and b) rGO, (d and e) TNP-Cu@rGO; TEM images of (c) rGO and (f) TNP-Cu@rGO.

Fig.S4. The XPS pattern of TNP-Cu@rGO. We could find the peaks at 931.1 and 951.1 eV were belonged to Cu^{2+} . From the peak separation of C, N and Cu, it can be clearly seen that the complexes were successfully loaded on rGO, and PF_6^- were replaced by hydroxyl groups on the surface of rGO, and weak adsorption bonds were formed between Cu and C on rGO.

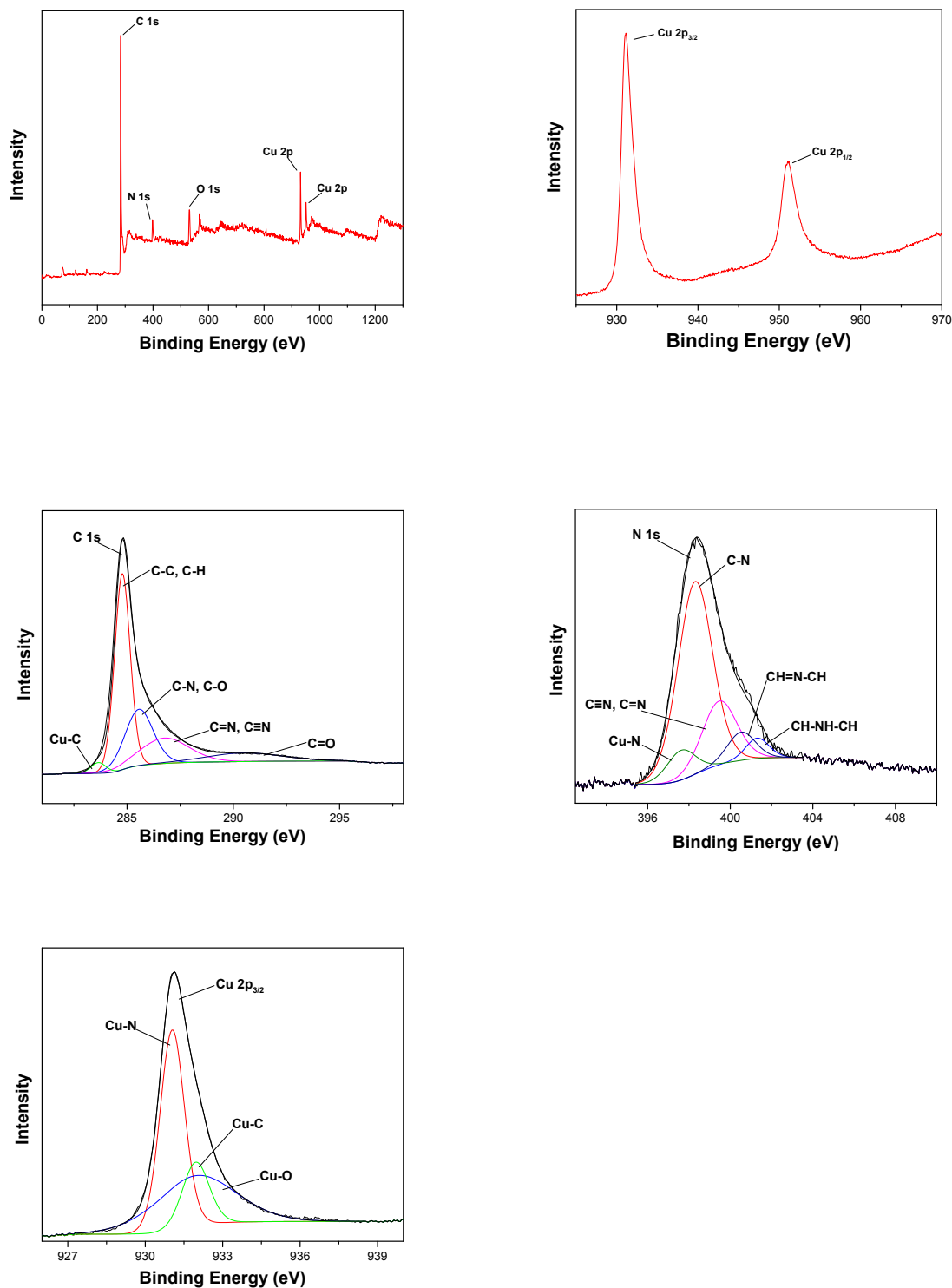


Fig.S4. XPS pattern of TNP-Cu@rGO

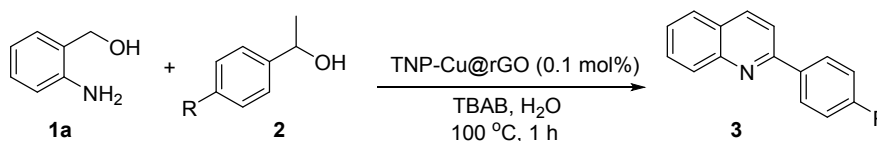
4. General procedure for 3

In a 25 mL round-bottomed flask with a condenser tube were added *o*-aminobenzyl alcohols **1** (1 mmol), **2** (1.2 mmol, 1.2 equiv.), TNP-Cu@rGO (10 mg, 3 wt%, 0.1 mol%), KOH (56 mg, 1 equiv.) and H₂O (2 mL) under air atmosphere. The reaction mixture was heated at 100 °C in an oil bath for 12 h and then cooled to ambient temperature. The reaction mixture was cooled to ambient temperature, concentrated in vacuo, and purified by flash column chromatography with hexane/ethyl acetate to afford the corresponding product **3**.

5. General procedure for 6

To 20 mL Schlenk tube was added TNP-Cu@rGO (10 mg, 3 wt%, 0.1 mol%), water (2.0 mL) and KOH (1.0 eq.). Then **4** (1.0 mmol) and **5** (1.1 mmol) were added and the mixture was stirred at 100 °C for 10 h. Then the mixture was added water and extracted with ethyl acetate. The combined organic phases were washed with dried over anhydrous MgSO₄ (The reaction mixture or concentrated in vacuo). The solvent was removed under reduced pressure carefully and purification of the crude product by flash column chromatography with hexane/ethyl acetate afforded the compound **6**.

6. Hammett plot and mechanism studies.

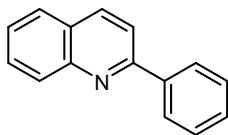


Experimental procedure: Under air, *o*-aminobenzyl alcohols (1.0 mmol), 1-phenylethanol (1.2 mmol), TNP-Cu@rGO (0.1 mol%), KOH (1.0 equiv.), H₂O (2 mL) were introduced in a round-bottomed flask (25 mL) with a condenser tube, successively. Then, the flask tube was opened and the resulting mixture was stirred at 100 °C for 1 h. After cooling down to room temperature, the water mixture was extracted with EtOAc (3 x 10 mL). Next, the yield of product **3** was determined by GC.

R	H	Me	OMe	F	CF ₃
Yield (%)	18	11	9	22	41

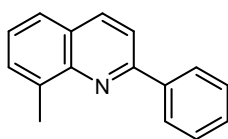
7. Analytical data of the obtained compounds

(1) 2-phenylquinoline (**3a**).⁴



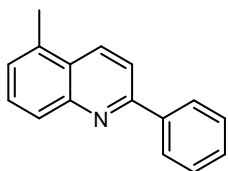
White solid; Mp. 80-82 °C; ^1H NMR (400 MHz, Chloroform-*d*) δ 9.18 (s, 1H), 7.28 – 7.13 (m, 6H), 6.88 (dd, J = 14.1, 7.4 Hz, 2H), 6.73 (d, J = 7.4 Hz, 1H), 3.75 (dd, J = 9.3, 4.5 Hz, 1H), 3.50 (dd, J = 13.7, 4.5 Hz, 1H), 2.93 (dd, J = 13.7, 9.3 Hz, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 180.05, 141.56, 137.81, 129.41, 128.99, 128.33, 127.95, 126.66, 124.79, 121.98, 109.84, 47.60, 36.61.

(2) 8-methyl-2-phenylquinoline (3b).⁴



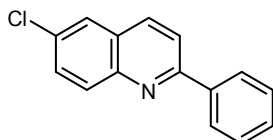
Pale-yellow oil; ^1H NMR (400 MHz, Chloroform-*d*) δ 8.29 – 8.22 (m, 2H), 8.17 (d, J = 8.6 Hz, 1H), 7.89 (d, J = 8.6 Hz, 1H), 7.65 (d, J = 8.1 Hz, 1H), 7.56 (d, J = 6.9 Hz, 1H), 7.52 (t, J = 7.4 Hz, 2H), 7.45 (d, J = 7.3 Hz, 1H), 7.43 – 7.37 (m, 1H), 2.90 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 155.28, 146.93, 139.62, 137.43, 136.65, 129.40, 128.95, 128.50, 127.20, 126.84, 125.75, 125.11, 117.92, 17.61.

(3) 5-methyl-2-phenylquinoline (3c).⁴



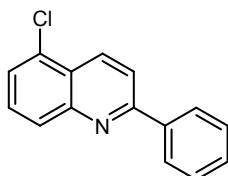
White solid; Mp. 58-60 °C; ^1H NMR (400 MHz, Chloroform-*d*) δ 8.14 (dd, J = 7.9, 4.6 Hz, 3H), 8.09 (d, J = 8.5 Hz, 1H), 7.84 (d, J = 8.6 Hz, 1H), 7.60 – 7.50 (m, 4H), 7.45 (t, J = 7.2 Hz, 1H), 2.55 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 156.51, 146.75, 139.68, 136.24, 132.03, 129.32, 129.20, 128.83, 127.53, 127.23, 126.34, 119.04, 21.61.

(4) 6-chloro-2-phenylquinoline (3d).⁴



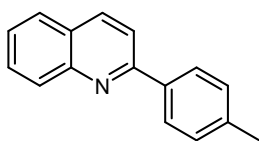
White solid; Mp. 108-110 °C; ^1H NMR (400 MHz, Chloroform-*d*) δ 8.32 – 8.06 (m, 4H), 7.92 (d, J = 8.6 Hz, 1H), 7.83 (s, 1H), 7.68 (d, J = 8.7 Hz, 1H), 7.53 (dt, J = 15.0, 7.2 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 157.58, 146.63, 139.18, 135.91, 131.96, 131.31, 130.62, 129.62, 128.93, 127.75, 127.55, 126.15, 119.84.

(5) 5-chloro-2-phenylquinoline (3e).



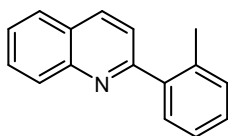
White solid; Mp. 91-93 °C; ^1H NMR (400 MHz, Chloroform-*d*) δ 8.65 (d, J = 8.9 Hz, 1H), 8.23 – 8.19 (m, 2H), 8.14 (d, J = 8.1 Hz, 1H), 8.00 (d, J = 8.9 Hz, 1H), 7.69 – 7.64 (m, 1H), 7.62 (dd, J = 7.5, 1.4 Hz, 1H), 7.60 – 7.55 (m, 2H), 7.54 – 7.49 (m, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 157.96, 148.95, 138.99, 133.71, 131.25, 129.75, 129.38, 128.94, 127.67, 126.29, 125.34, 119.77.

(6) 2-(*p*-tolyl)quinoline (3f).⁴



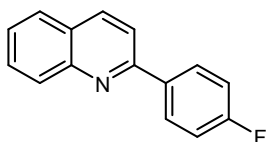
White solid; Mp. 87-89 °C; ^1H NMR (400 MHz, Chloroform-*d*) δ 8.22 (t, J = 9.3 Hz, 2H), 8.10 (d, J = 8.1 Hz, 2H), 7.92 – 7.82 (m, 2H), 7.75 (t, J = 8.2 Hz, 1H), 7.54 (t, J = 7.5 Hz, 1H), 7.37 (d, J = 7.9 Hz, 2H), 2.47 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 157.35, 148.33, 139.41, 136.91, 136.65, 129.70, 129.58, 127.47, 127.44, 127.13, 126.09, 118.85, 21.34.

(7) 2-(*o*-tolyl)quinoline(3g).⁴



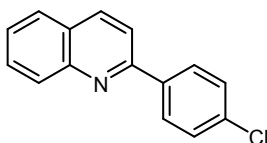
White solid; Mp. 74-75 °C; ^1H NMR (400 MHz, Chloroform-*d*) δ 8.25 (d, J = 8.5 Hz, 1H), 8.20 (d, J = 8.5 Hz, 1H), 7.91 – 7.88 (m, 1H), 7.77 (ddd, J = 8.4, 6.9, 1.4 Hz, 1H), 7.62 – 7.56 (m, 2H), 7.55 – 7.51 (m, 1H), 7.36 (dq, J = 5.4, 2.8, 2.3 Hz, 3H), 2.44 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 160.32, 147.92, 140.76, 136.05, 136.01, 130.87, 129.70, 129.64, 129.61, 128.50, 127.50, 126.75, 126.40, 126.01, 122.38, 20.33.

(8) 2-(4-fluorophenyl)quinoline(3h).⁴



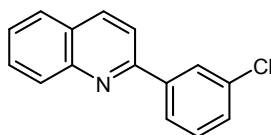
White solid; Mp. 93-95 °C; ^1H NMR (400 MHz, Chloroform-*d*) δ 8.24 (d, J = 8.6 Hz, 1H), 8.22 – 8.16 (m, 3H), 7.86 (d, J = 8.6 Hz, 2H), 7.76 (ddd, J = 8.4, 6.9, 1.4 Hz, 1H), 7.56 (ddd, J = 8.1, 6.9, 1.1 Hz, 1H), 7.27 – 7.21 (m, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 165.08, 162.60, 156.24, 148.22, 136.93, 135.79, 129.72 (d, J = 15.8 Hz), 129.43 (d, J = 8.4 Hz), 127.47, 127.10, 126.36, 118.62, 115.77 (d, J = 21.6 Hz).

(9) 2-(4-chlorophenyl)quinoline (3i).⁴



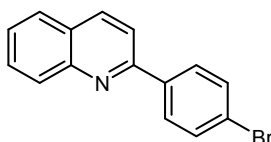
White solid; Mp. 114-115 °C; ^1H NMR (400 MHz, Chloroform-*d*) δ 8.21 (d, J = 8.6 Hz, 1H), 8.16 (d, J = 8.5 Hz, 1H), 8.11 (d, J = 8.3 Hz, 2H), 7.82 (d, J = 8.6 Hz, 2H), 7.73 (t, J = 7.6 Hz, 1H), 7.53 (t, J = 7.6 Hz, 1H), 7.49 (d, J = 8.3 Hz, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 156.01, 148.19, 138.00, 137.04, 135.60, 129.90, 129.67, 129.04, 128.85, 127.50, 127.24, 126.54, 118.59.

(10) 2-(3-chlorophenyl)quinoline (3j).⁴



White solid; Mp. 68-70 °C; ^1H NMR (400 MHz, Chloroform-*d*) δ 8.23 (d, J = 8.6 Hz, 1H), 8.19 (d, J = 8.2 Hz, 2H), 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), 7.50 – 7.39 (m, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) 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.

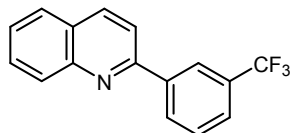
(11) 2-(4-bromophenyl)quinoline (3k).⁴



White solid; Mp. 118-119 °C; ^1H NMR (400 MHz, Chloroform-*d*) δ 8.25 (d, J = 8.6 Hz, 1H), 8.19 (d, J = 8.5 Hz, 1H), 8.11 – 8.06 (m, 2H), 7.86 (dd, J = 8.3, 2.0 Hz, 2H), 7.77 (ddd, J = 8.4, 6.9, 1.4 Hz, 1H), 7.71 – 7.65 (m, 2H),

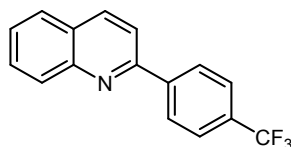
7.60 – 7.54 (m, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 156.04, 148.20, 138.45, 137.04, 131.99, 129.90, 129.69, 129.12, 127.50, 127.27, 126.56, 123.98, 118.51.

(12) 2-(3-(trifluoromethyl)phenyl)quinoline (3l).



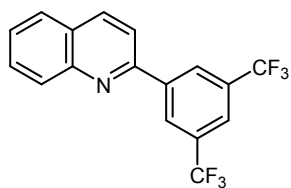
White solid; Mp. 56-58 °C; ^1H NMR (400 MHz, Chloroform-*d*) δ 8.49 (s, 1H), 8.39 (d, J = 7.7 Hz, 1H), 8.30 (d, J = 8.6 Hz, 1H), 8.24 (d, J = 8.5 Hz, 1H), 7.92 (d, J = 8.6 Hz, 1H), 7.90 – 7.86 (m, 1H), 7.79 (ddd, J = 8.4, 6.9, 1.4 Hz, 1H), 7.75 (d, J = 7.8 Hz, 1H), 7.68 (t, J = 7.8 Hz, 1H), 7.60 (ddd, J = 8.1, 7.0, 1.1 Hz, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 155.58, 148.14, 140.25, 137.32, 130.79, 130.09, 129.73, 129.35, 127.54, 127.41, 126.85, 125.96 (q, J = 3.7 Hz), 124.47 (q, J = 3.8 Hz), 118.65.

(13) 2-(4-(trifluoromethyl)phenyl)quinoline (3m).⁴



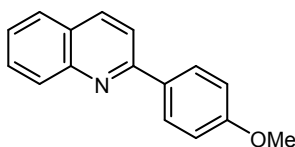
White solid; Mp. 122-124 °C; ^1H NMR (400 MHz, Chloroform-*d*) δ 8.30 (t, J = 8.1 Hz, 3H), 8.24 (d, J = 8.5 Hz, 1H), 7.91 (d, J = 8.6 Hz, 1H), 7.89 – 7.86 (m, 1H), 7.80 (ddd, J = 8.8, 5.3, 3.8 Hz, 3H), 7.60 (ddd, J = 8.1, 7.0, 1.1 Hz, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 155.66, 148.17, 142.83, 137.26, 131.15 (d, J = 32.4 Hz), 130.08, 129.78, 127.90, 127.55, 127.46, 126.92, 125.87 – 125.67 (m), 122.86, 118.82.

(14) 2-(3,5-bis(trifluoromethyl)phenyl)quinoline (3n).⁴



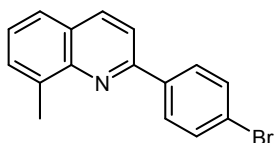
White solid; Mp. 96-98 °C; ^1H NMR (400 MHz, Chloroform-*d*) δ 8.66 (s, 2H), 8.31 (d, J = 8.6 Hz, 1H), 8.21 (d, J = 8.5 Hz, 1H), 7.96 (s, 1H), 7.92 (d, J = 8.6 Hz, 1H), 7.87 (d, J = 8.2 Hz, 1H), 7.79 (t, J = 7.7 Hz, 1H), 7.60 (t, J = 7.5 Hz, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 153.68, 148.22, 141.51, 137.58, 132.19 (q, J = 33.4 Hz), 130.34, 129.91, 127.60 (d, J = 5.2 Hz), 127.53 – 127.44 (m), 127.32, 124.79, 122.75 (dt, J = 7.5, 3.7 Hz), 122.07, 118.14.

(15) 2-(4-methoxyphenyl)quinoline (3o).⁴



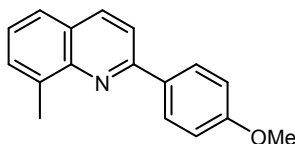
White solid; Mp. 122-124 °C; ^1H NMR (400 MHz, Chloroform-*d*) δ 8.20 – 8.10 (m, 4H), 7.81 (t, 2H), 7.71 (t, 1H), 7.49 (t, $J = 7.4$ Hz, 1H), 7.05 (d, $J = 8.5$ Hz, 1H), 3.88 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 159.81, 155.88, 147.23, 135.63, 131.20, 128.56, 128.47, 127.88, 126.40, 125.88, 124.90, 117.53, 113.21, 54.37.

(16) 2-(4-bromophenyl)-8-methylquinoline (3p).



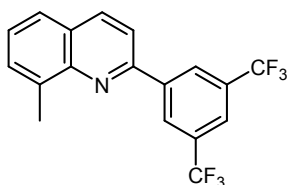
Yellow solid; mp 83-85 °C; ^1H NMR (400 MHz, Chloroform-*d*) δ 8.10 (t, $J = 9.3$ Hz, 3H), 7.78 (d, $J = 8.5$ Hz, 1H), 7.60 (d, $J = 8.0$ Hz, 3H), 7.54 (d, $J = 6.8$ Hz, 1H), 7.38 (t, $J = 7.5$ Hz, 1H), 2.86 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 153.20, 146.05, 137.63, 136.59, 136.07, 130.83, 128.81, 127.92, 126.10, 125.22, 124.35, 122.71, 116.67, 16.83.

(17) 2-(4-methoxyphenyl)-8-methylquinoline (3q).



White solid; Mp. 85-86 °C; ^1H NMR (400 MHz, Chloroform-*d*) δ 8.21 (d, $J = 8.0$ Hz, 2H), 8.11 (d, $J = 8.5$ Hz, 1H), 7.82 (d, $J = 8.5$ Hz, 1H), 7.62 (d, $J = 8.0$ Hz, 1H), 7.54 (d, $J = 6.8$ Hz, 1H), 7.36 (t, $J = 7.4$ Hz, 1H), 7.03 (d, $J = 8.0$ Hz, 2H), 3.87 (s, 3H), 2.88 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 160.80, 155.19, 147.13, 137.41, 136.86, 132.52, 129.66, 128.81, 126.80, 125.67, 125.39, 117.78, 114.18, 55.42, 17.93.

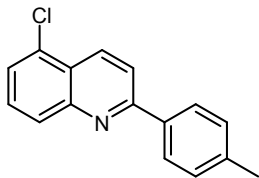
(18) 2-(3,5-bis(trifluoromethyl)phenyl)-8-methylquinoline (3r).



White solid; Mp. 63-65 °C; ^1H NMR (400 MHz, Chloroform-*d*) δ 8.69 (s, 2H), 8.24 (d, $J = 8.5$ Hz, 1H), 7.97 – 7.88 (m, 2H), 7.68 (d, $J = 8.1$ Hz, 1H), 7.61 (d, $J = 6.9$ Hz, 1H), 7.46 (t, $J = 7.5$ Hz, 1H), 2.89 (s, 3H). ^{13}C NMR (101

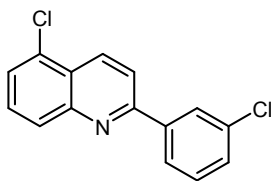
MHz, Chloroform-*d*) δ 152.07, 147.12, 141.80, 137.97, 137.74, 132.12 (q, $J = 33.3$ Hz), 130.33, 127.68 – 127.22 (m), 127.11, 125.47, 124.83, 122.55 (dt, $J = 7.6, 3.8$ Hz), 122.12, 117.53, 17.81.

(19) 5-chloro-2-(*p*-tolyl)quinoline (3s).



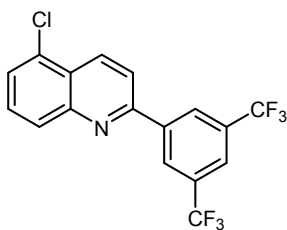
White solid; Mp. 99-101 °C; ^1H NMR (400 MHz, Chloroform-*d*) δ 8.63 (d, $J = 9.2$ Hz, 1H), 8.12 (dd, $J = 8.5, 2.1$ Hz, 3H), 7.99 (d, $J = 8.9$ Hz, 1H), 7.67 – 7.63 (m, 1H), 7.60 (dd, $J = 7.5, 1.3$ Hz, 1H), 7.37 (d, $J = 8.0$ Hz, 2H), 2.47 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 157.90, 148.89, 139.98, 136.10, 133.63, 131.23, 129.68, 129.34, 128.79, 127.57, 126.12, 125.24, 119.62, 21.39.

(20) 5-chloro-2-(3-chlorophenyl)quinoline (3t).



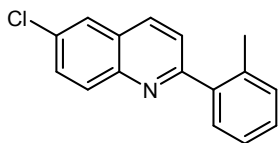
Pale-yellow solid; Mp. 75-77 °C; ^1H NMR (400 MHz, Chloroform-*d*) δ 8.68 – 8.64 (m, 1H), 8.26 – 8.22 (m, 1H), 8.12 (d, $J = 8.1$ Hz, 1H), 8.07 (ddd, $J = 5.6, 3.4, 1.7$ Hz, 1H), 7.96 (d, $J = 8.9$ Hz, 1H), 7.70 – 7.65 (m, 1H), 7.64 (dd, $J = 7.5, 1.4$ Hz, 1H), 7.51 – 7.46 (m, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 156.34, 148.85, 140.71, 135.09, 133.99, 131.28, 130.13, 129.72, 129.61, 128.97, 127.81, 126.63, 125.68, 125.52, 119.44.

(21) 2-(3,5-bis(trifluoromethyl)phenyl)-5-chloroquinoline (3u).



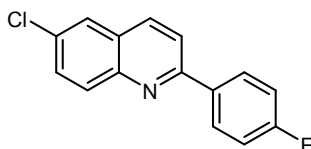
White solid; Mp. 108-109 °C; ^1H NMR (400 MHz, Chloroform-*d*) δ 8.74 – 8.71 (m, 1H), 8.69 (s, 2H), 8.17 – 8.13 (m, 1H), 8.03 (d, $J = 8.9$ Hz, 2H), 7.74 – 7.70 (m, 1H), 7.68 (dd, $J = 7.5, 1.5$ Hz, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 154.26, 148.83, 140.82, 134.54, 132.31 (q, $J = 33.5$ Hz), 131.36, 130.01, 129.09, 127.80 – 127.46 (m), 127.24, 125.80, 124.72, 123.13 (dt, $J = 7.5, 3.7$ Hz), 122.00, 118.84.

(22) 6-chloro-2-(*o*-tolyl)quinoline (3v).



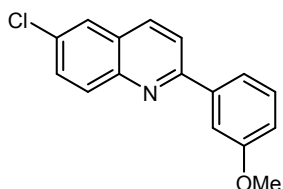
White solid; Mp. 101-103 °C; ¹H NMR (400 MHz, Chloroform-*d*) δ 8.09 (d, *J* = 2.4 Hz, 1H), 8.07 (d, *J* = 3.0 Hz, 1H), 7.81 (d, *J* = 2.3 Hz, 1H), 7.65 (dd, *J* = 9.0, 2.3 Hz, 1H), 7.54 (d, *J* = 8.5 Hz, 1H), 7.50 – 7.47 (m, 1H), 7.32 (dq, *J* = 5.4, 3.3, 2.4 Hz, 3H), 2.40 (s, 3H). ¹³C NMR (101 MHz, Chloroform-*d*) δ 160.56, 146.30, 140.31, 136.03, 135.17, 132.10, 131.26, 131.01, 130.55, 129.70, 128.74, 127.32, 126.19, 126.12, 123.24, 20.39.

(23) 6-chloro-2-(4-fluorophenyl)quinoline (3w).



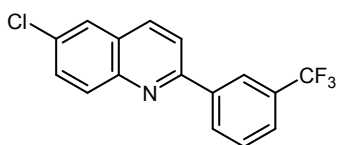
White solid; Mp. 123-124 °C; ¹H NMR (400 MHz, Chloroform-*d*) δ 8.17 – 8.06 (m, 4H), 7.86 – 7.79 (m, 2H), 7.66 (dd, *J* = 9.0, 2.3 Hz, 1H), 7.21 (t, *J* = 8.7 Hz, 2H). ¹³C NMR (101 MHz, Chloroform-*d*) δ 165.19, 162.71, 156.43, 146.61, 135.99, 135.33, 132.01, 131.24, 130.72, 129.40 (d, *J* = 8.5 Hz), 127.63, 126.16, 119.42, 115.88 (d, *J* = 21.7 Hz).

(24) 6-chloro-2-(3-methoxyphenyl)quinoline (3x).



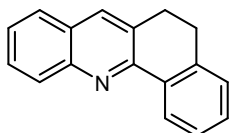
White solid; Mp. 135-137 °C; ¹H NMR (400 MHz, Chloroform-*d*) δ 8.10 (dd, *J* = 8.7, 3.5 Hz, 2H), 7.87 (d, *J* = 8.7 Hz, 1H), 7.79 (d, *J* = 2.3 Hz, 1H), 7.77 – 7.73 (m, 1H), 7.70 – 7.67 (m, 1H), 7.65 (dd, *J* = 9.0, 2.3 Hz, 1H), 7.43 (t, *J* = 7.9 Hz, 1H), 7.04 – 7.00 (m, 1H), 3.92 (s, 3H). ¹³C NMR (101 MHz, Chloroform-*d*) δ 160.20, 157.34, 146.60, 140.68, 135.84, 131.98, 131.36, 130.59, 129.90, 127.83, 126.15, 119.96, 119.91, 115.61, 112.72, 55.45.

(25) 6-chloro-2-(3-(trifluoromethyl)phenyl)quinoline (3y).



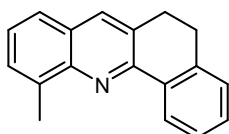
Yellow solid ; Mp.84-86 °C; ^1H NMR (400 MHz, Chloroform-*d*) δ 8.44 (s, 1H), 8.32 (d, J = 7.7 Hz, 1H), 8.12 (dd, J = 16.5, 8.8 Hz, 2H), 7.89 (d, J = 8.6 Hz, 1H), 7.83 – 7.77 (m, 1H), 7.72 (d, J = 7.7 Hz, 1H), 7.69 – 7.61 (m, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 155.73, 146.60, 139.87, 136.22, 132.50, 131.54, 131.40, 131.21, 130.93, 130.67 – 130.57 (m), 129.38, 127.92, 126.19, 126.13 (d, J = 3.8 Hz), 124.37 (q, J = 3.9 Hz), 119.36.

(26) 5,6-dihydrobenzo[*c*]acridine (3z).⁴



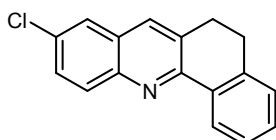
White solid; Mp. 65-67 °C; ^1H NMR (400 MHz, Chloroform-*d*) δ 8.68 – 8.58 (m, 1H), 8.20 (d, J = 8.4 Hz, 1H), 7.92 (s, 1H), 7.76 (d, J = 8.1 Hz, 1H), 7.69 (ddd, J = 8.3, 7.0, 1.3 Hz, 1H), 7.53 – 7.46 (m, 2H), 7.42 (td, J = 7.4, 1.4 Hz, 1H), 7.31 (d, J = 7.4 Hz, 1H), 3.13 (q, J = 5.8, 5.2 Hz, 2H), 3.03 (dd, J = 8.3, 5.4 Hz, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 153.42, 147.66, 139.47, 134.75, 133.76, 130.62, 129.74, 129.44, 128.70, 128.00, 127.92, 127.37, 126.99, 126.14, 126.10, 28.86, 28.44.

(27) 11-methyl-5,6-dihydrobenzo[*c*]acridine (3aa).



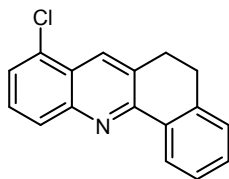
Pale-yellow oil; ^1H NMR (400 MHz, Chloroform-*d*) δ 8.68 (d, J = 7.6 Hz, 1H), 7.91 (s, 1H), 7.62 (d, J = 8.0 Hz, 1H), 7.53 (d, J = 6.9 Hz, 1H), 7.49 – 7.44 (m, 1H), 7.40 (td, J = 7.5, 1.5 Hz, 2H), 7.30 (d, J = 7.4 Hz, 1H), 3.16 (dd, J = 8.0, 5.8 Hz, 2H), 3.05 (dd, J = 8.3, 5.5 Hz, 2H), 2.94 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 151.98, 146.53, 139.33, 137.38, 135.22, 133.91, 130.10, 129.51, 128.76, 127.94, 127.79, 127.26, 126.09, 125.87, 124.92, 28.67, 28.46, 17.95.

(28) 9-chloro-5,6-dihydrobenzo[*c*]acridine (3ab).



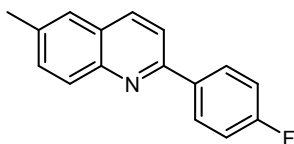
White solid; Mp. 101-102 °C; ^1H NMR (400 MHz, Chloroform-*d*) δ 8.62 – 8.52 (m, 1H), 8.08 (d, J = 9.0 Hz, 1H), 7.78 (s, 1H), 7.70 (d, J = 2.3 Hz, 1H), 7.59 (dd, J = 9.0, 2.3 Hz, 1H), 7.48 – 7.43 (m, 1H), 7.40 (td, J = 7.4, 1.5 Hz, 1H), 7.29 (d, J = 6.5 Hz, 1H), 3.10 (dd, J = 7.7, 5.4 Hz, 2H), 3.01 (dd, J = 8.1, 5.2 Hz, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 153.68, 145.97, 139.40, 134.36, 132.73, 131.63, 131.60, 130.99, 129.96, 129.52, 128.41, 128.04, 127.41, 126.08, 125.63, 28.81, 28.23.

(29) 8-chloro-5,6-dihydrobenzo[c]acridine (3ac).



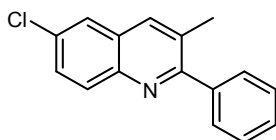
White solid; Mp. 83-85 °C; ^1H NMR (400 MHz, Chloroform-*d*) δ 8.60 (dd, $J = 7.5, 1.3$ Hz, 1H), 8.36 – 8.34 (m, 1H), 8.09 (dd, $J = 5.9, 3.5$ Hz, 1H), 7.58 (d, $J = 2.7$ Hz, 1H), 7.57 (s, 1H), 7.47 – 7.40 (m, 2H), 7.33 – 7.30 (m, 1H), 3.21 (dd, $J = 8.7, 5.5$ Hz, 2H), 3.06 (dd, $J = 8.2, 5.7$ Hz, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 154.05, 148.21, 139.61, 134.13, 131.70, 130.57, 130.14, 128.61, 128.32, 128.06, 127.41, 126.26, 126.04, 125.86, 28.97, 28.25.

(30) 2-(4-fluorophenyl)-6-methylquinoline (3ad).



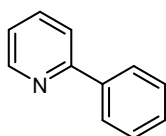
White solid; Mp. 77-79 °C; ^1H NMR (400 MHz, Chloroform-*d*) δ 8.16 (ddd, $J = 8.9, 5.6, 2.8$ Hz, 3H), 8.08 (d, $J = 8.5$ Hz, 1H), 7.81 (d, $J = 8.6$ Hz, 1H), 7.59 (dd, $J = 10.8, 2.0$ Hz, 2H), 7.26 – 7.19 (m, 2H), 2.57 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 162.49, 155.40, 146.72, 136.33, 136.31, 135.85 (d, $J = 3.0$ Hz), 129.33 (d, $J = 8.4$ Hz), 129.24, 127.11, 126.36, 118.65, 115.85, 115.64, 21.61.

(31) 6-chloro-3-methyl-2-phenylquinoline (3ae).



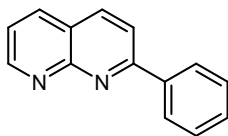
Yellow solid ; Mp. 78-79 °C; ^1H NMR (400 MHz, Chloroform-*d*) δ 8.11 (d, $J = 9.0$ Hz, 1H), 7.97 (s, 1H), 7.79 (d, $J = 2.3$ Hz, 1H), 7.64 – 7.59 (m, 3H), 7.55 – 7.47 (m, 3H), 2.50 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 160.72, 144.81, 140.20, 135.99, 132.17, 130.80, 130.42, 129.81, 128.84, 128.50, 128.40, 128.19, 125.37, 20.67.

(32) 2-phenylpyridine (3af).



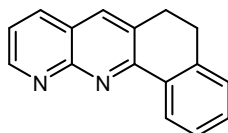
Colorless oil; ^1H NMR (400 MHz, Chloroform-*d*) δ 8.73 (d, $J = 4.8$ Hz, 1H), 8.03 (t, $J = 1.7$ Hz, 1H), 8.01 (d, $J = 3.2$ Hz, 1H), 7.82 – 7.74 (m, 2H), 7.54 – 7.48 (m, 2H), 7.48 – 7.41 (m, 1H), 7.29 – 7.25 (m, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 157.42, 149.55, 139.23, 136.93, 129.05, 128.79, 126.97, 122.15, 120.67.

(33) 2-phenyl-1,8-naphthyridine (3ag).



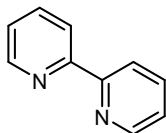
Yellow soild; Mp. 118-120 °C; ^1H NMR (400 MHz, Chloroform-*d*) δ 9.14 (dd, $J = 3.9, 1.6$ Hz, 1H), 8.35 – 8.31 (m, 2H), 8.25 (d, $J = 8.5$ Hz, 1H), 8.19 (d, $J = 8.1$ Hz, 1H), 8.01 (d, $J = 8.5$ Hz, 1H), 7.57 – 7.49 (m, 3H), 7.47 (dd, $J = 8.0, 4.2$ Hz, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 160.31, 156.14, 153.83, 138.51, 137.77, 136.77, 130.13, 128.82, 127.93, 121.78, 121.71, 119.72.

(34) 5,6-dihydronaphtho[1,2-b][1,8]naphthyridine (3ah).



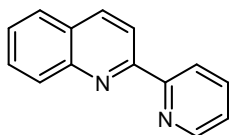
Yellow soild; Mp. 90-91 °C; ^1H NMR (400 MHz, Chloroform-*d*) δ 9.01 (dd, $J = 4.2, 1.9$ Hz, 1H), 8.73 (dd, $J = 7.6, 1.4$ Hz, 1H), 8.07 – 8.04 (m, 1H), 7.87 (s, 1H), 7.42 (dd, $J = 8.9, 1.5$ Hz, 1H), 7.39 (dd, $J = 4.5, 2.6$ Hz, 1H), 7.37 – 7.34 (m, 1H), 7.27 – 7.22 (m, 1H), 3.10 (t, $J = 4.8$ Hz, 2H), 2.98 (dd, $J = 8.2, 5.6$ Hz, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 156.47, 155.64, 152.70, 139.50, 136.15, 134.56, 134.03, 131.88, 130.46, 127.90, 127.36, 127.03, 122.26, 121.49, 28.49, 28.10.

(35) 2,2'-bipyridine (3ai).



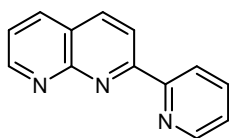
White soild; Mp. 72-73°C; ^1H NMR (400 MHz, Chloroform-*d*) δ 8.69 (ddd, $J = 4.8, 1.7, 0.9$ Hz, 2H), 8.41 (dt, $J = 8.0, 1.0$ Hz, 2H), 7.82 (td, $J = 7.8, 1.8$ Hz, 2H), 7.31 (ddd, $J = 7.5, 4.8, 1.2$ Hz, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 156.14, 149.18, 136.94, 123.72, 121.10.

(36) 2-(pyridin-2-yl)quinoline (3aj).⁴



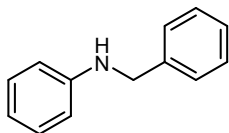
Pale-yellow solid; Mp. 97-99 °C; ^1H NMR (400 MHz, Chloroform-*d*) δ 8.76 (ddd, $J = 4.8, 1.8, 0.9$ Hz, 1H), 8.68 (dt, $J = 8.0, 1.0$ Hz, 1H), 8.59 (d, $J = 8.6$ Hz, 1H), 8.29 (d, $J = 8.6$ Hz, 1H), 8.21 (d, $J = 8.5$ Hz, 1H), 7.90 – 7.85 (m, 2H), 7.75 (ddd, $J = 8.4, 6.9, 1.5$ Hz, 1H), 7.56 (ddd, $J = 8.1, 6.9, 1.2$ Hz, 1H), 7.36 (ddd, $J = 7.5, 4.8, 1.2$ Hz, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) 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.

(37) 2-(pyridin-2-yl)-1,8-naphthyridine (3ak).



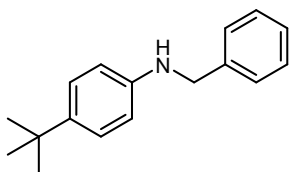
Pale-yellow solid; Mp. 148-149 °C; ^1H NMR (400 MHz, DMSO-*d*₆) δ 9.14 (dd, $J = 4.2, 2.0$ Hz, 1H), 8.78 (d, $J = 4.7$ Hz, 1H), 8.64 (dd, $J = 17.8, 8.7$ Hz, 3H), 8.51 (dd, $J = 8.1, 1.9$ Hz, 1H), 8.05 (td, $J = 7.8, 1.7$ Hz, 1H), 7.65 (dd, $J = 8.1, 4.2$ Hz, 1H), 7.55 (ddd, $J = 7.4, 4.8, 1.0$ Hz, 1H). ^{13}C NMR (101 MHz, DMSO-*d*₆) δ 158.72, 155.67, 155.28, 154.53, 149.85, 139.25, 137.99, 137.90, 125.51, 123.18, 123.03, 122.07, 119.75.

(38) N-benzylaniline (6a).



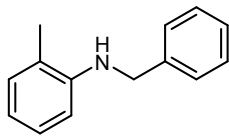
White solid; ^1H NMR (400 MHz, Chloroform-*d*) δ 7.45 – 7.34 (m, 4H), 7.37 – 7.29 (m, 1H), 7.31 – 7.23 (m, 2H), 6.78 (t, $J = 7.3$ Hz, 1H), 6.68 (d, $J = 7.7$ Hz, 2H), 4.25 (s, 2H), 4.13 (s, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 148.25, 139.49, 129.33, 128.72, 127.58, 127.32, 117.65, 112.93, 48.41.

(39) N-benzyl-4-(tert-butyl)aniline (6b).



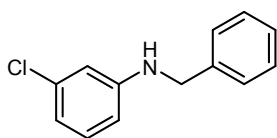
Colorless liquid; ^1H NMR (400 MHz, Chloroform-*d*) δ 7.41 (dt, $J = 14.7, 7.5$ Hz, 4H), 7.32 (d, $J = 6.9$ Hz, 1H), 7.28 (d, $J = 8.6$ Hz, 2H), 6.59 (d, $J = 8.6$ Hz, 2H), 4.34 (s, 2H), 1.29 (s, 9H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 145.47, 140.74, 139.53, 128.62, 127.71, 127.23, 126.03, 112.88, 48.90, 33.91, 31.56.

(40) N-benzyl-2-methylaniline (6c).



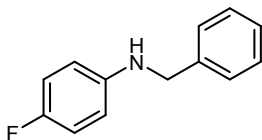
White solid; ^1H NMR (400 MHz, Chloroform-*d*) δ 7.42 (m, 4H), 7.40 – 7.30 (m, 1H), 7.16 (dd, J = 12.7, 7.1 Hz, 2H), 6.78 (t, J = 7.4 Hz, 1H), 6.75 (d, J = 8.0 Hz, 1H), 4.53 (s, 2H), 4.01 (s, 1H), 2.26 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 146.14, 139.58, 130.23, 129.03, 127.62, 127.39, 127.23, 122.05, 117.29, 110.17, 48.41, 17.57.

(41) N-benzyl-3-chloroaniline (6d)



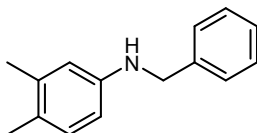
Yellow liquid; ^1H NMR (400 MHz, Chloroform-*d*) δ 7.44 – 7.35 (m, 4H), 7.33 (m, 1H), 7.10 (t, J = 8.0 Hz, 1H), 6.75 (dd, J = 7.9, 1.1 Hz, 1H), 6.63 (t, J = 2.1 Hz, 1H), 6.52 (dd, J = 8.0, 1.9 Hz, 1H), 4.37 (s, 2H), 4.17 (s, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 149.31, 138.79, 135.08, 130.27, 128.79, 127.54, 127.47, 117.48, 112.58, 111.24, 48.19.

(42) N-benzyl-4-fluoroaniline (6e).



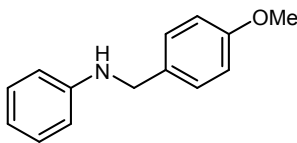
Yellow solid; ^1H NMR (400 MHz, Chloroform-*d*) δ 7.28 - 7.19 (m, 4H), 7.17 - 7.12 (m, 1H), 6.79 - 6.70 (m, 2H), 6.41 (dt, J = 6.4, 4.0 Hz, 2H), 4.17 (s, 2H), 4.08 - 3.65 (m, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 157.48 (d, J = 236.3 Hz), 144.61, 139.42, 128.77, 127.41 (d, J = 1.8 Hz), 115.78 (d, J = 21.8 Hz), 113.75, 48.82.

(43) N-benzyl-3,4-dimethylaniline (6f)



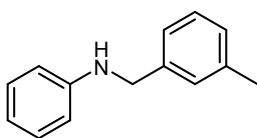
Colorless liquid; ^1H NMR (400 MHz, Chloroform-*d*) δ 7.45 – 7.36 (m, 4H), 7.31 (m, 1H), 6.98 (d, J = 8.1 Hz, 1H), 6.54 (d, J = 2.1 Hz, 1H), 6.46 (dd, J = 8.0, 2.4 Hz, 1H), 4.35 (s, 2H), 3.86 (s, 1H), 2.24 (s, 3H), 2.20 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 146.36, 139.78, 137.34, 130.33, 128.61, 127.56, 127.15, 125.66, 114.82, 110.35, 48.73, 20.06, 18.71

(44) N-(4-methoxybenzyl)aniline (6g)



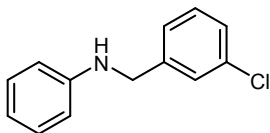
White solid; ^1H NMR (400 MHz, Chloroform-*d*) δ 7.43 (t, J = 7.2 Hz, 2H), 7.35 (t, J = 7.6 Hz, 2H), 7.04 (d, J = 8.2 Hz, 2H), 6.90 (t, J = 7.2 Hz, 1H), 6.79 (d, J = 8.0 Hz, 2H), 4.39 (s, 2H), 4.18 - 3.99 (m, 1H), 3.86 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 159.12, 148.43, 131.65, 129.46, 128.95, 117.63, 114.24, 113.05, 55.42, 47.88.

(45) N-(3-methylbenzyl)aniline (6h)



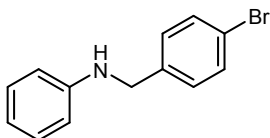
White solid; ^1H NMR (400 MHz, Chloroform-*d*) δ 7.31 (t, J = 7.4 Hz, 1H), 7.30 – 7.21 (m, 4H), 7.19 (d, J = 7.3 Hz, 1H), 6.82 (t, J = 7.3 Hz, 1H), 6.74 – 6.68 (m, 2H), 4.37 (s, 2H), 4.09 (s, 1H), 2.41 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 148.37, 139.42, 138.36, 129.32, 128.58, 128.41, 128.03, 124.71, 117.65, 113.01, 48.43, 21.51.

(46) N-(3-chlorobenzyl)aniline (6i)



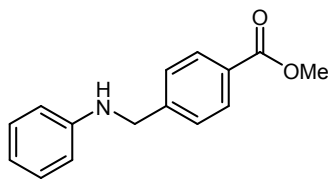
Yellow liquid; ^1H NMR (400 MHz, Chloroform-*d*) δ 7.34 (s, 1H), 7.27 – 7.11 (m, 5H), 6.73 (t, J = 7.3 Hz, 1H), 6.63 (dd, J = 8.5, 0.9 Hz, 2H), 4.25 (s, 2H), 4.12 (s, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 148.15, 141.97, 134.65, 130.12, 129.52, 127.51, 127.47, 125.53, 117.95, 113.08, 47.85.

(47) N-(4-bromobenzyl)aniline (6j)



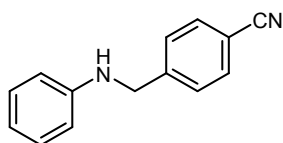
Yellow liquid; ^1H NMR (400 MHz, Chloroform-*d*) δ 7.41 (d, J = 8.3 Hz, 2H), 7.32 – 7.27 (m, 2H), 7.17 (dd, J = 8.3, 7.5 Hz, 2H), 6.75 (t, J = 7.3 Hz, 1H), 6.61 (d, J = 7.8 Hz, 2H), 4.29 (s, 2H), 4.12 (s, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 147.73, 138.50, 131.69, 129.27, 129.03, 120.92, 117.89, 112.95, 47.69.

(48) Methyl 4-((phenylamino)methyl)benzoate (6k)



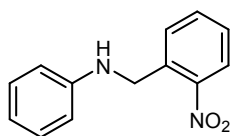
Colorless liquid; ^1H NMR (400 MHz, Chloroform-*d*) δ 8.01 (d, J = 8.3 Hz, 2H), 7.43 (d, J = 8.4 Hz, 2H), 7.22 – 7.14 (m, 2H), 6.75 (t, J = 7.3 Hz, 1H), 6.61 (dd, J = 8.5, 0.9 Hz, 2H), 4.39 (s, 2H), 3.92 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 166.96, 147.79, 145.03, 129.95, 129.30, 129.09, 127.16, 117.87, 112.93, 52.02, 47.98.

(49) 4-((phenylamino)methyl)benzonitrile (6l)



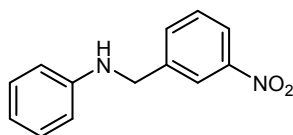
Colorless liquid; ^1H NMR (400 MHz, Chloroform-*d*) δ 7.74 (d, J = 8.3 Hz, 2H), 7.61 (d, J = 8.4 Hz, 2H), 7.34 – 7.25 (m, 2H), 6.87 (t, J = 7.3 Hz, 1H), 6.70 (dd, J = 8.5, 0.9 Hz, 2H), 4.54 (s, 2H), 4.36 (s, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 147.57, 145.58, 132.54, 129.51, 127.86, 119.01, 118.23, 11.02, 111.03, 47.90.

(50) N-(2-nitrobenzyl)aniline (6m)



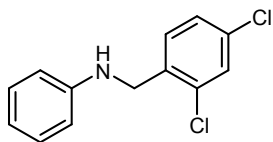
Colorless liquid; ^1H NMR (400 MHz, Chloroform-*d*) δ 8.03 (dd, J = 8.1, 1.1 Hz, 1H), 7.62 (d, J = 7.6 Hz, 1H), 7.54 (td, J = 7.6, 1.1 Hz, 1H), 7.47 – 7.38 (m, 1H), 7.12 (dd, J = 8.5, 7.4 Hz, 2H), 6.70 (t, J = 7.3 Hz, 1H), 6.56 (d, J = 7.7 Hz, 2H), 4.71 (s, 2H), 4.31 (s, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 148.33, 147.36, 135.62, 133.61, 129.78, 129.36, 127.99, 125.23, 118.11, 112.89, 45.73.

(51) N-(3-nitrobenzyl)aniline (6n)



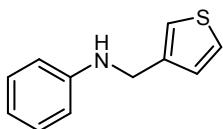
Colorless liquid; ^1H NMR (400 MHz, Chloroform-*d*) δ 8.32 (s, 1H), 8.21 (dd, J = 8.2, 1.3 Hz, 1H), 7.81 (dd, J = 7.6, 0.7 Hz, 1H), 7.58 (t, J = 7.9 Hz, 1H), 7.29 – 7.16 (m, 2H), 6.87 – 6.76 (m, 1H), 6.69 (dd, J = 8.6, 1.0 Hz, 2H), 4.54 (s, 2H), 4.36 (s, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 148.69, 147.39, 142.11, 133.30, 129.65, 129.47, 122.23, 122.02, 118.35, 113.07, 47.68.

(52) N-(2,4-dichlorobenzyl)aniline (6o)



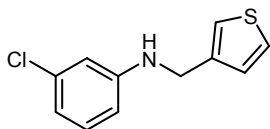
White solid; ^1H NMR (400 MHz, Chloroform-*d*) δ = 7.36 (d, J = 8.1 Hz, 2H), 7.30 – 7.16 (m, 3H), 6.83 – 6.75 (m, 3H), 4.62 (s, 2H), 4.06 (s, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ = 147.80, 136.13, 134.64, 129.41, 129.19, 128.58, 118.16, 113.53, 44.36.

(53) N-(thiophen-3-ylmethyl)aniline (6p)



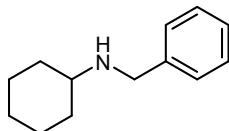
Yellow solid; ^1H NMR (400 MHz, Chloroform-*d*) δ 7.40 (dd, J = 4.9, 3.0 Hz, 1H), 7.35 – 7.26 (m, 3H), 7.18 (dd, J = 4.9, 1.1 Hz, 1H), 6.84 (t, J = 7.3 Hz, 1H), 6.77 (d, J = 7.7 Hz, 2H), 4.43 (s, 2H), 4.05 (s, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 148.08, 140.52, 129.34, 127.21, 126.21, 121.79, 117.78, 113.01, 43.85.

(54) 3-chloro-N-(thiophen-2-ylmethyl)aniline (6q)



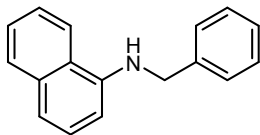
Pale-yellow liquid; ^1H NMR (400 MHz, Chloroform-*d*) δ = 7.27 (d, J = 5.0, 1H), 7.13 (t, J = 8.0 Hz, 1H), 7.05 – 7.01 (m, 2H), 6.80 – 6.72 (m, 1H), 6.67 (t, J = 2.0 Hz, 1H), 6.54 (dd, J = 8.1, 2.2 Hz, 1H), 4.52 (s, 2H), 4.12 (s, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ = 148.72, 142.16, 135.10, 130.28, 127.04, 125.32, 124.83, 118.03, 112.87, 111.42, 43.31.

(55) N-(cyclohexylmethyl)aniline (6r)



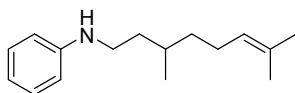
Colorless liquid; ^1H NMR (400 MHz, Chloroform-*d*) δ 7.21 (dd, J = 8.3, 7.5 Hz, 2H), 6.74 (t, J = 7.3 Hz, 1H), 6.66 (d, J = 7.7 Hz, 2H), 3.71 (s, 1H), 3.02 (d, J = 6.7 Hz, 2H), 1.88 (d, J = 13.0 Hz, 2H), 1.85 – 1.71 (m, 3H), 1.39 – 1.22 (m, 4H), 1.09 – 0.96 (m, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 148.81, 129.35, 117.06, 112.81, 50.73, 37.69, 31.42, 26.67, 26.02.

(56) N-benzyl-naphthalen-1-amine (6s)



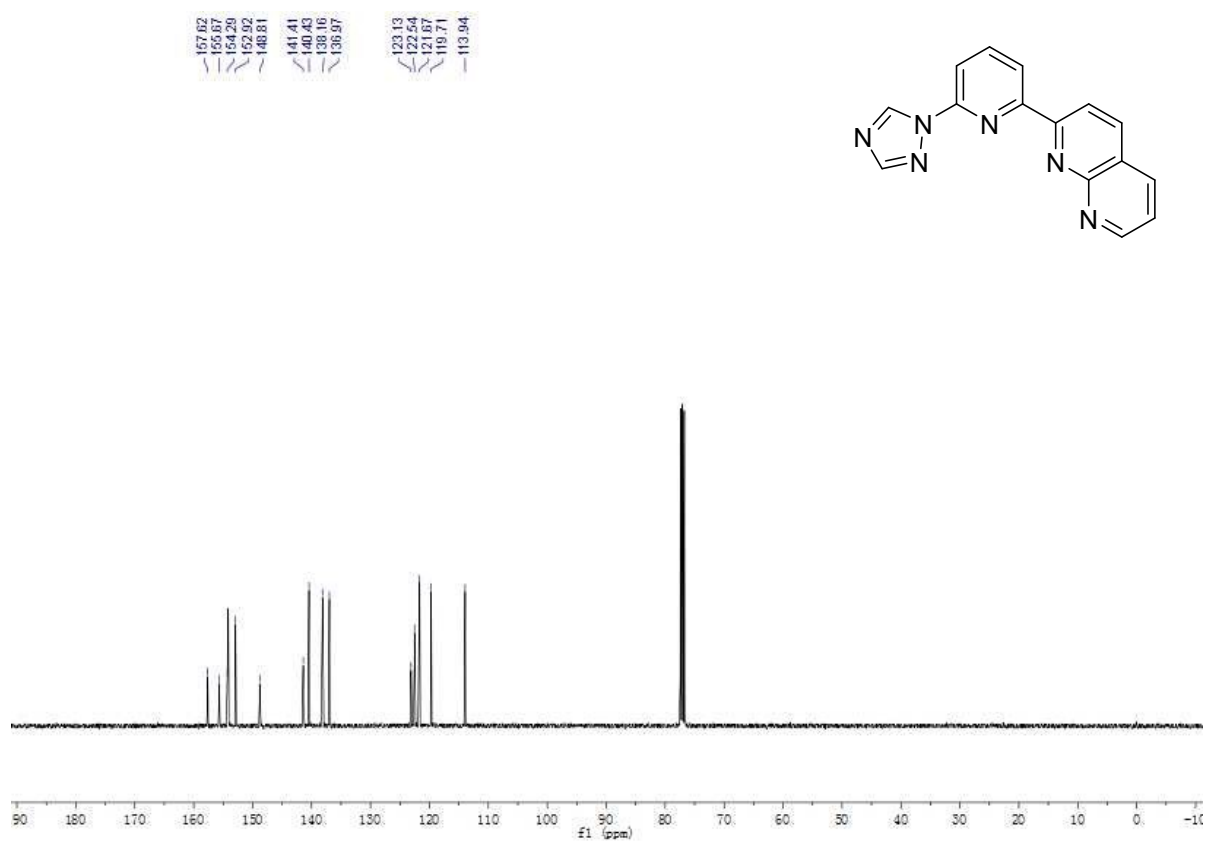
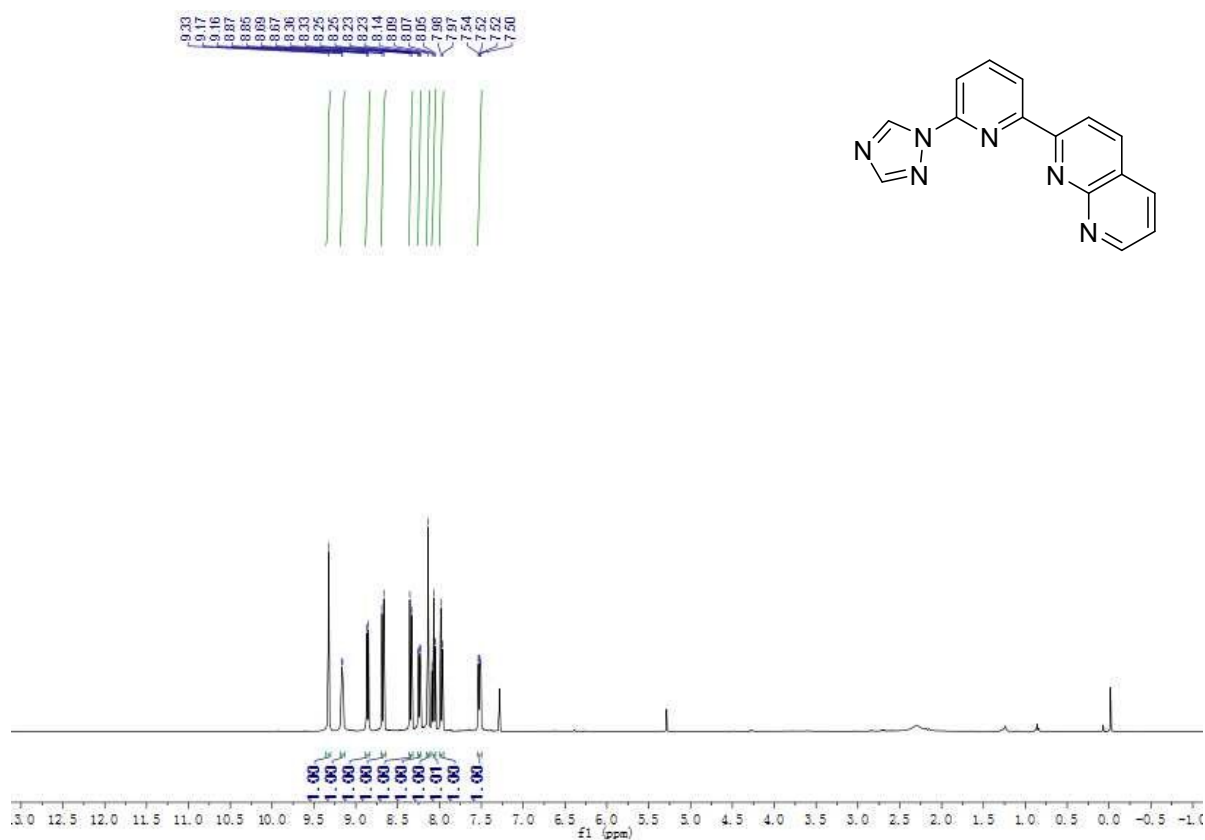
White solid; ^1H NMR (400 MHz, Chloroform-*d*) δ = 7.88 – 7.83 (m, 2H), 7.60 – 7.21 (m, 9H), 6.68 (d, J = 7.5 Hz, 1H), 4.81 (s, 1H), 4.50 (s, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ = 143.21, 139.14, 134.36, 128.73, 127.79, 127.43, 126.67, 125.83, 124.78, 123.50, 119.95, 117.81, 104.90, 48.73.

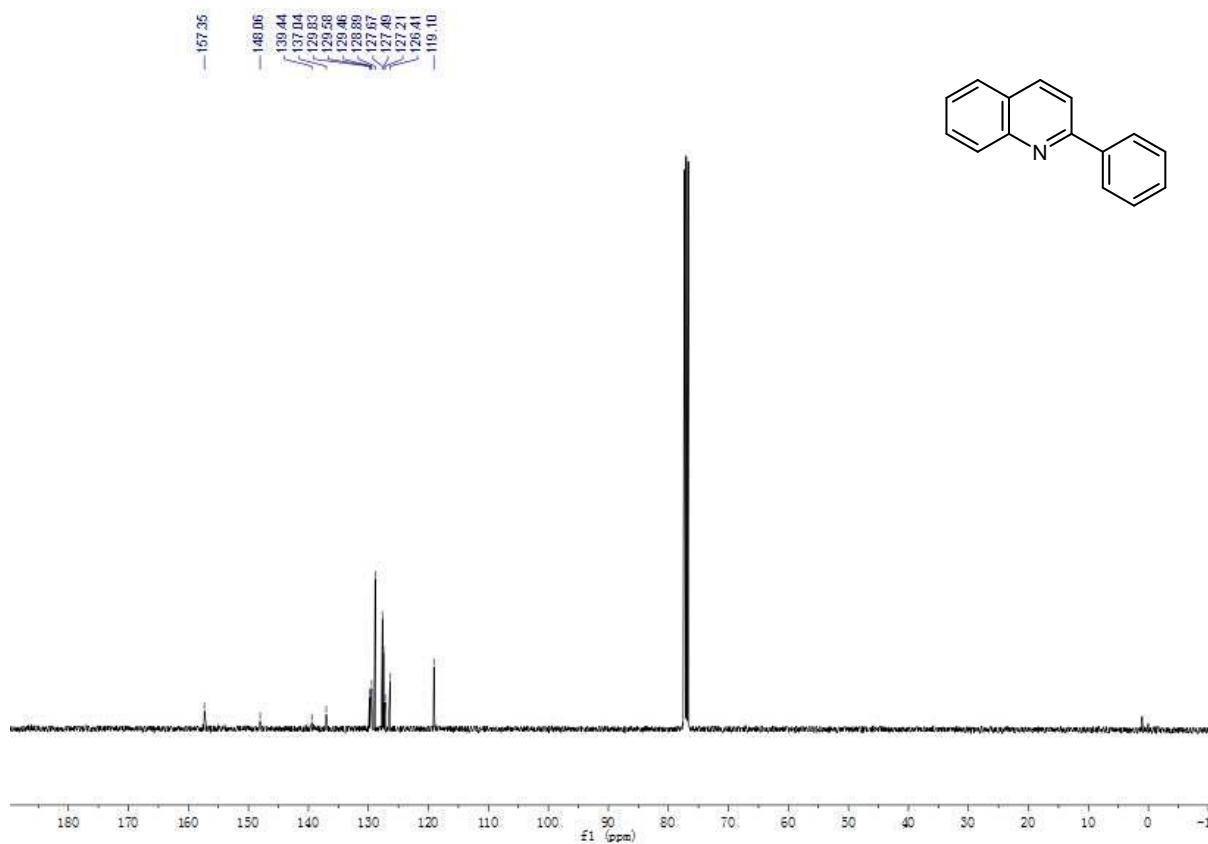
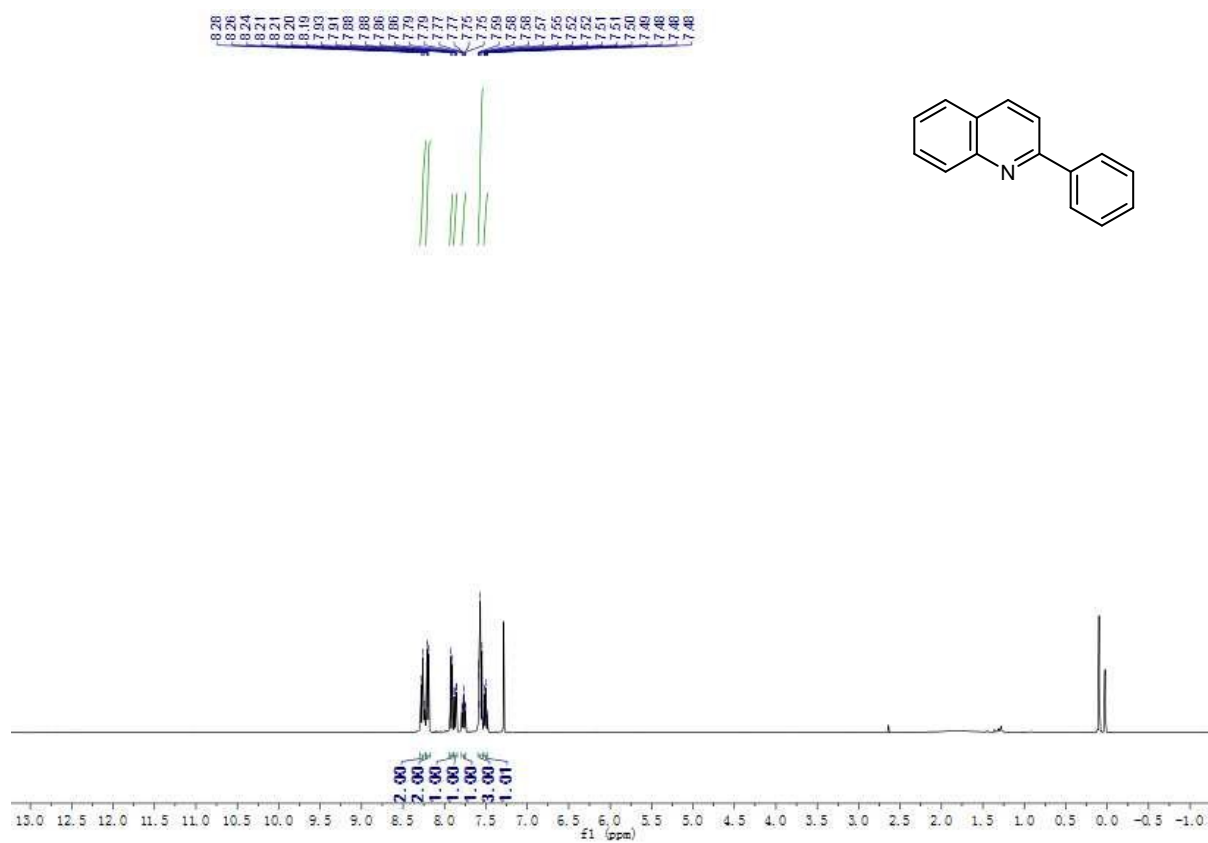
(57) N-(3,7-dimethyloct-6-en-1-yl)aniline (6t)

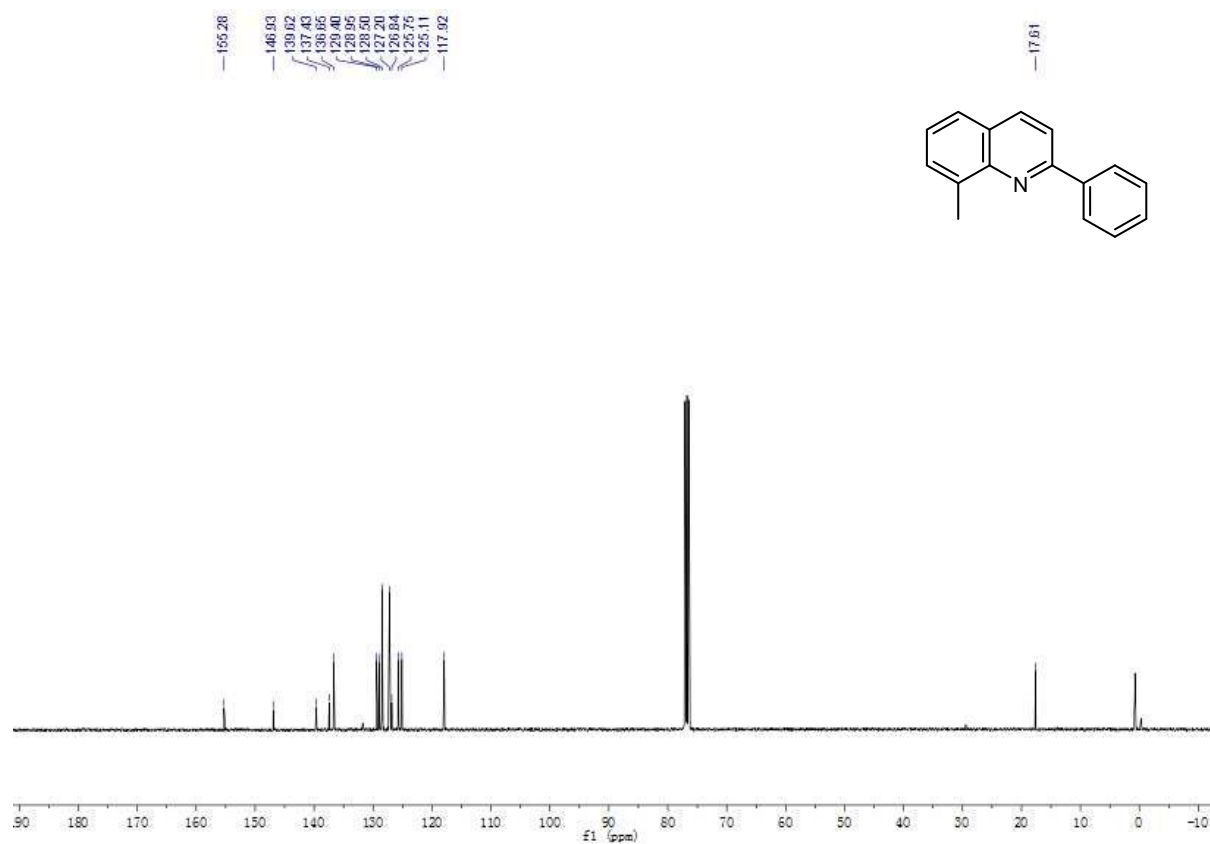
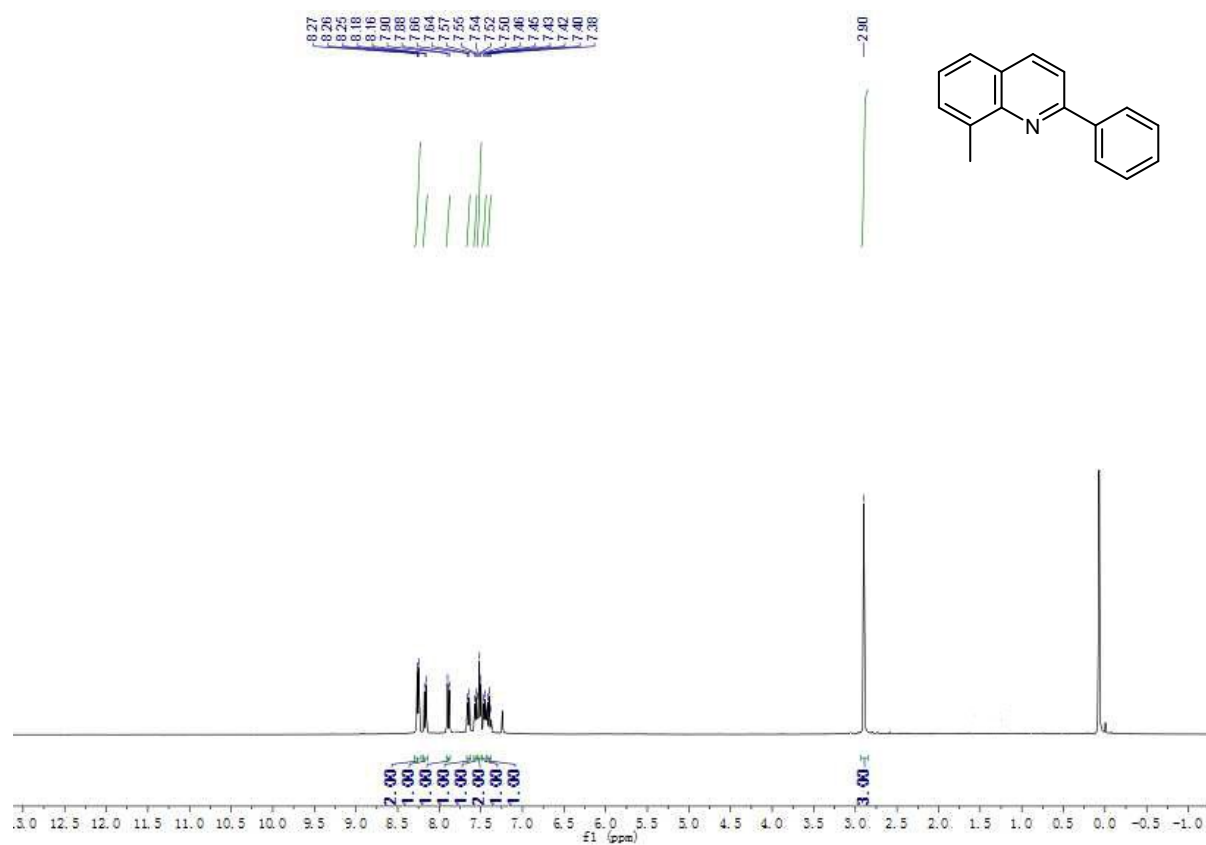


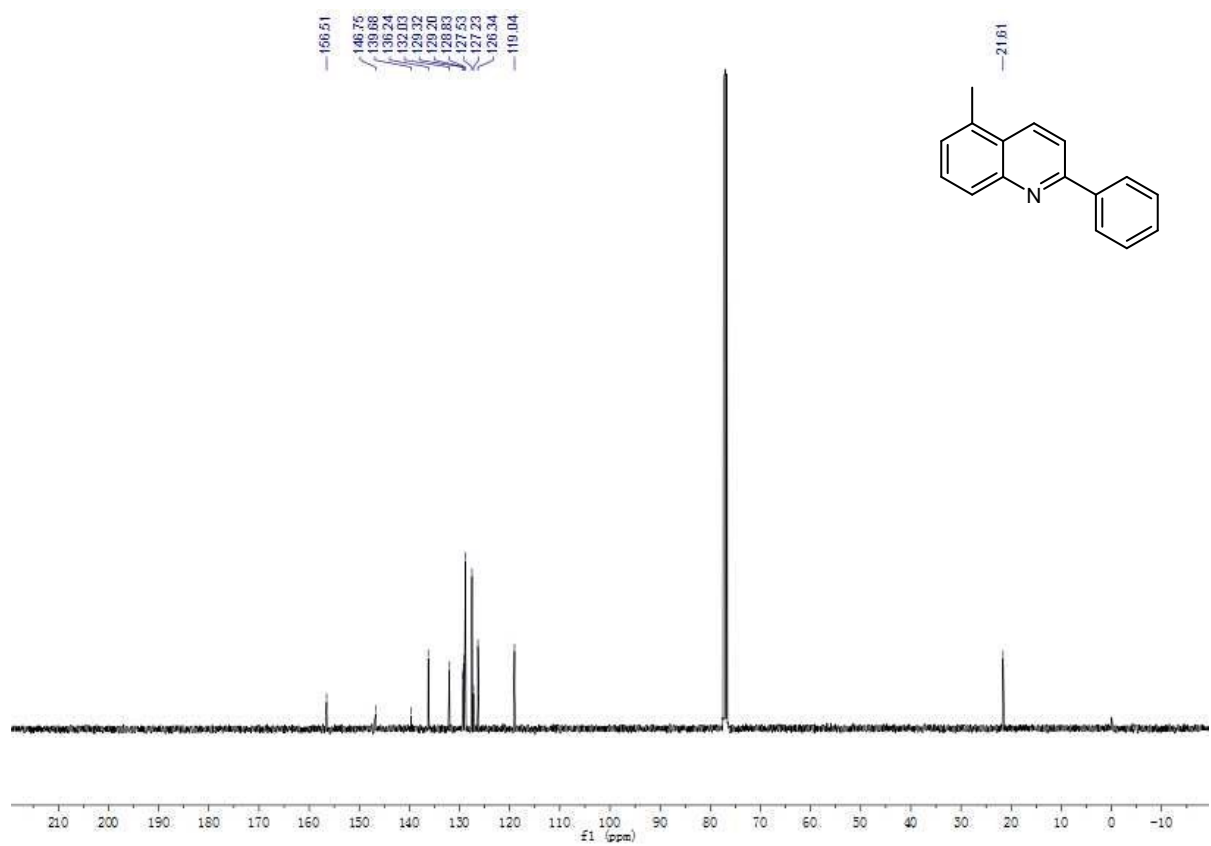
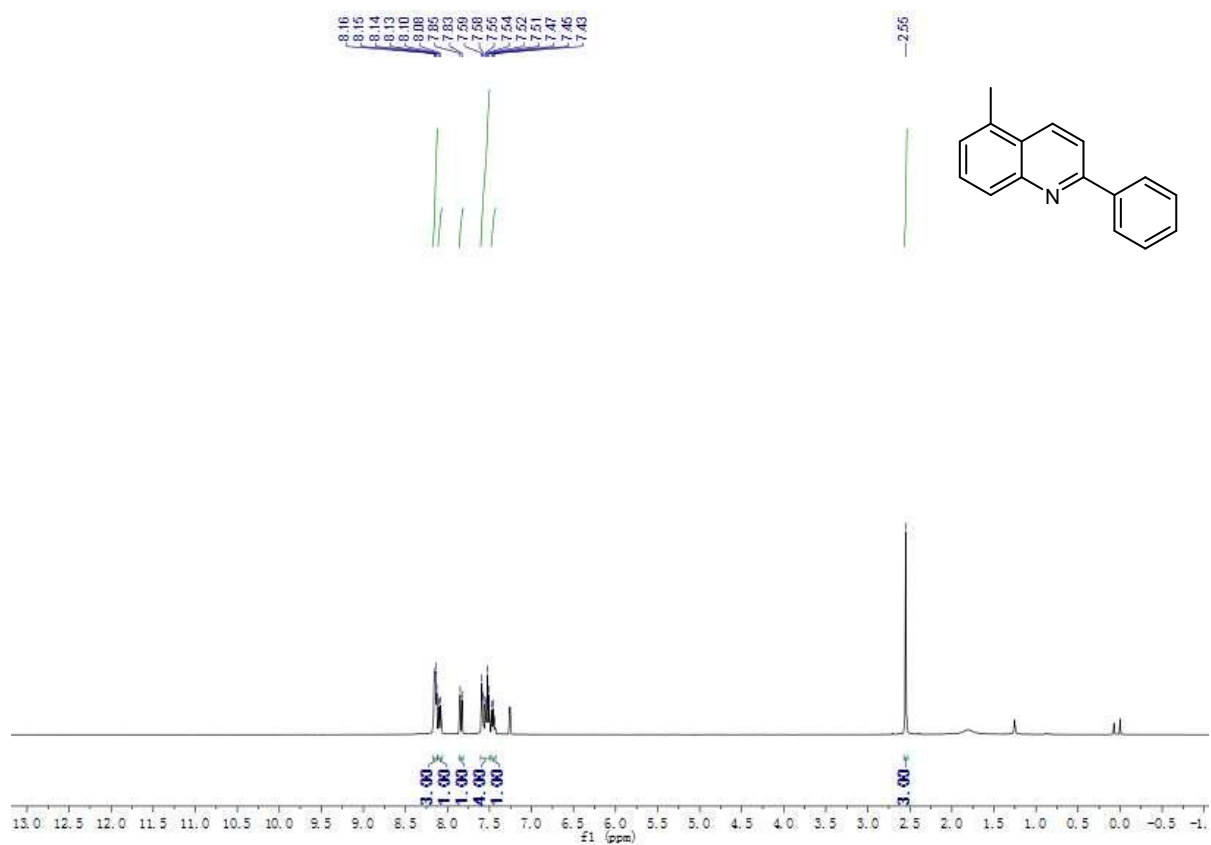
Colorless liquid; ^1H NMR (400 MHz, Chloroform-*d*) δ 7.43 – 7.33 (m, 2H), 6.81 (t, J = 7.3 Hz, 1H), 6.74 (dd, J = 8.5, 0.9 Hz, 2H), 5.44 – 5.27 (m, 1H), 3.63 (s, 1H), 3.26 (m, 2H), 2.32 – 2.08 (m, 2H), 1.91 (s, 3H), 1.86 – 1.73 (m, 5H), 1.64 – 1.51 (m, 2H), 1.53 – 1.38 (m, 1H), 1.17 (d, J = 6.6 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 148.68, 131.30, 129.29, 125.04, 117.17, 112.85, 42.12, 37.31, 36.91, 30.65, 26.01, 25.72, 19.81, 17.87.

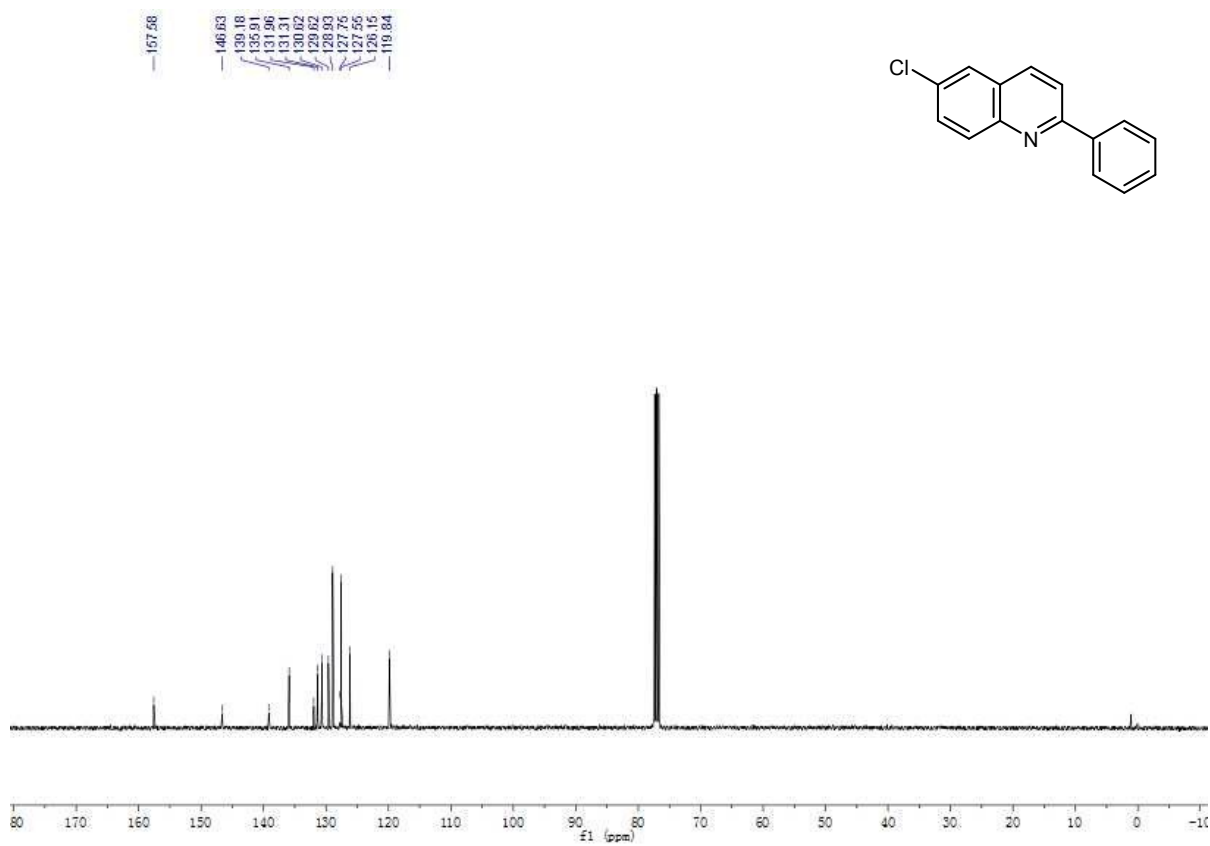
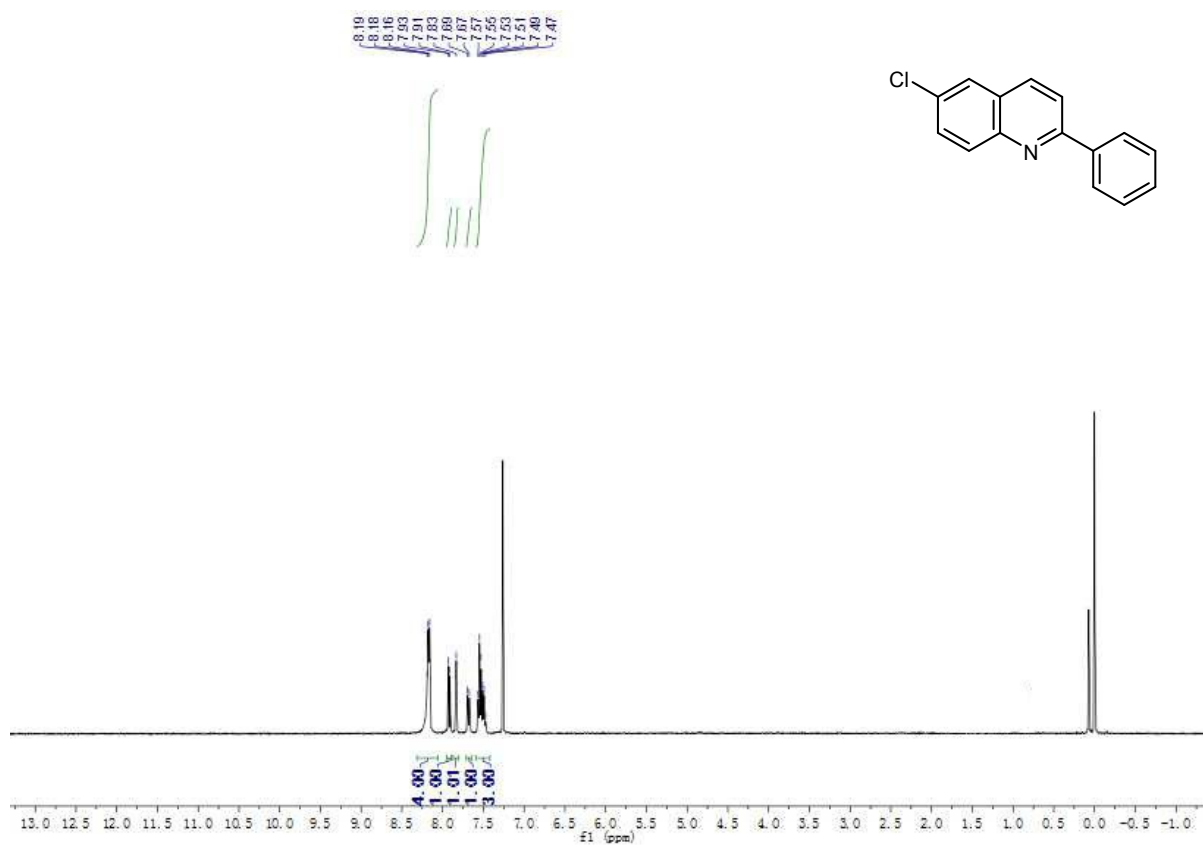
8. NMR spectra of obtained compounds

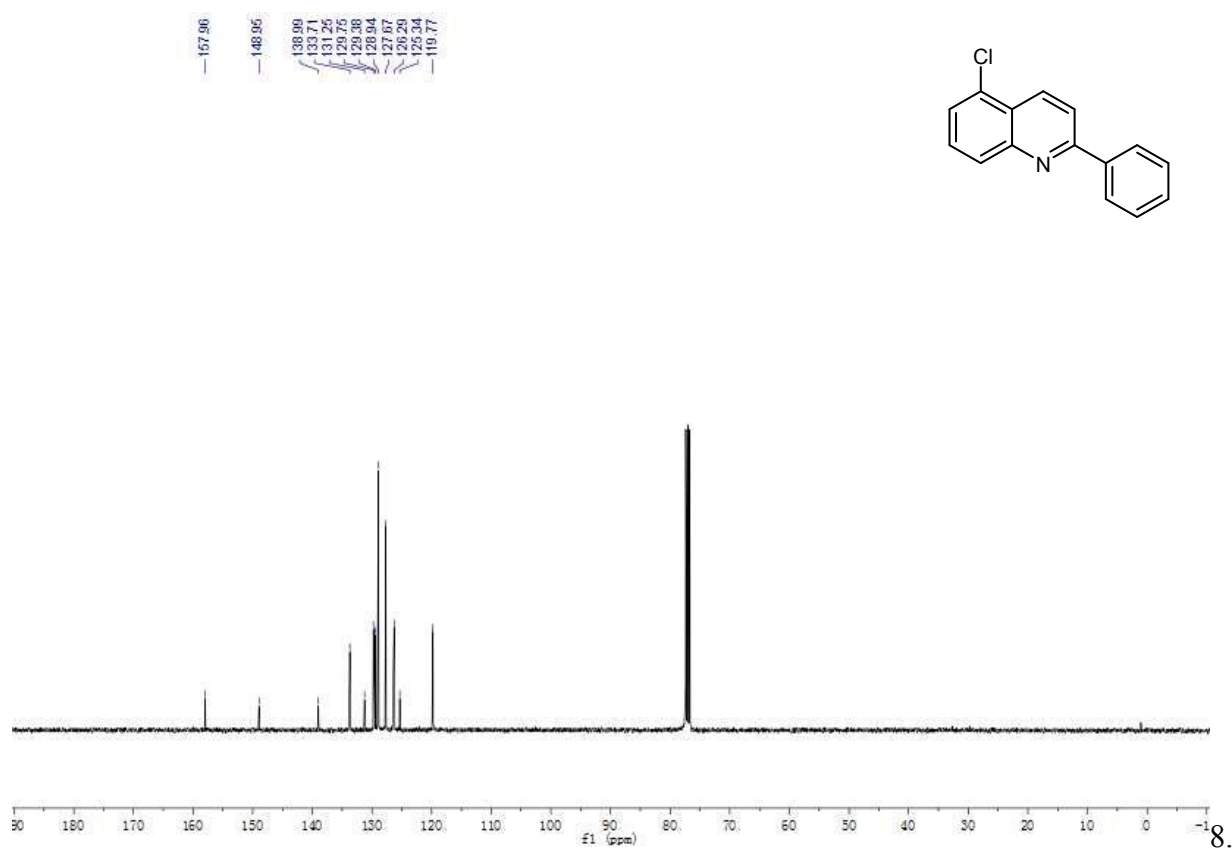
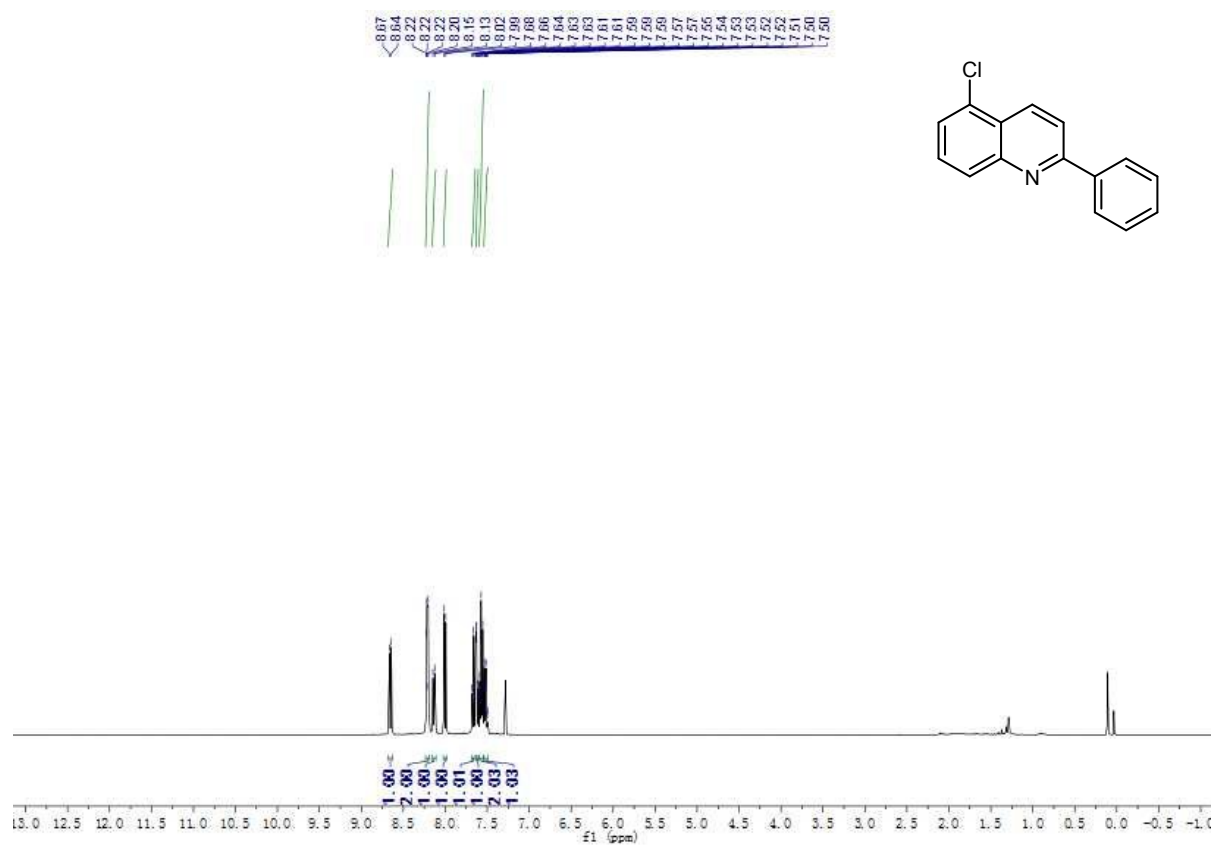


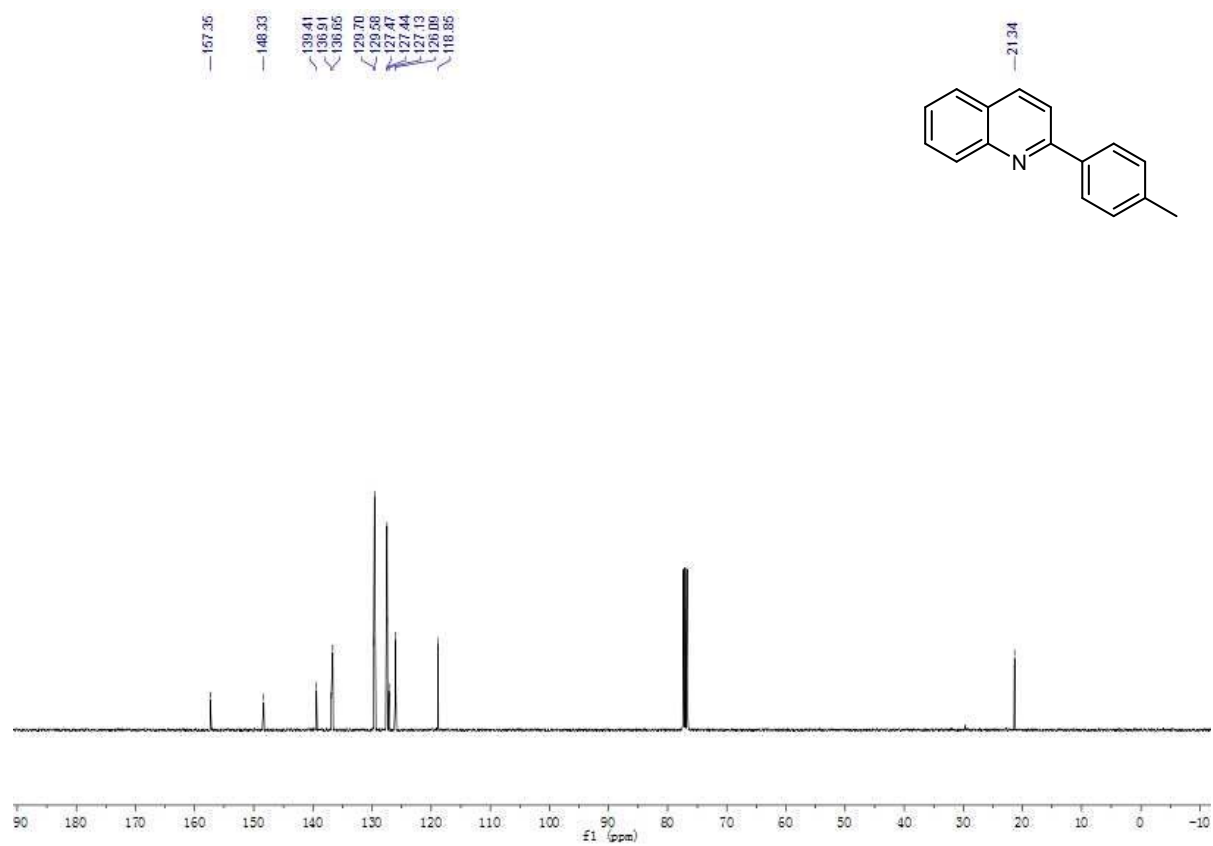
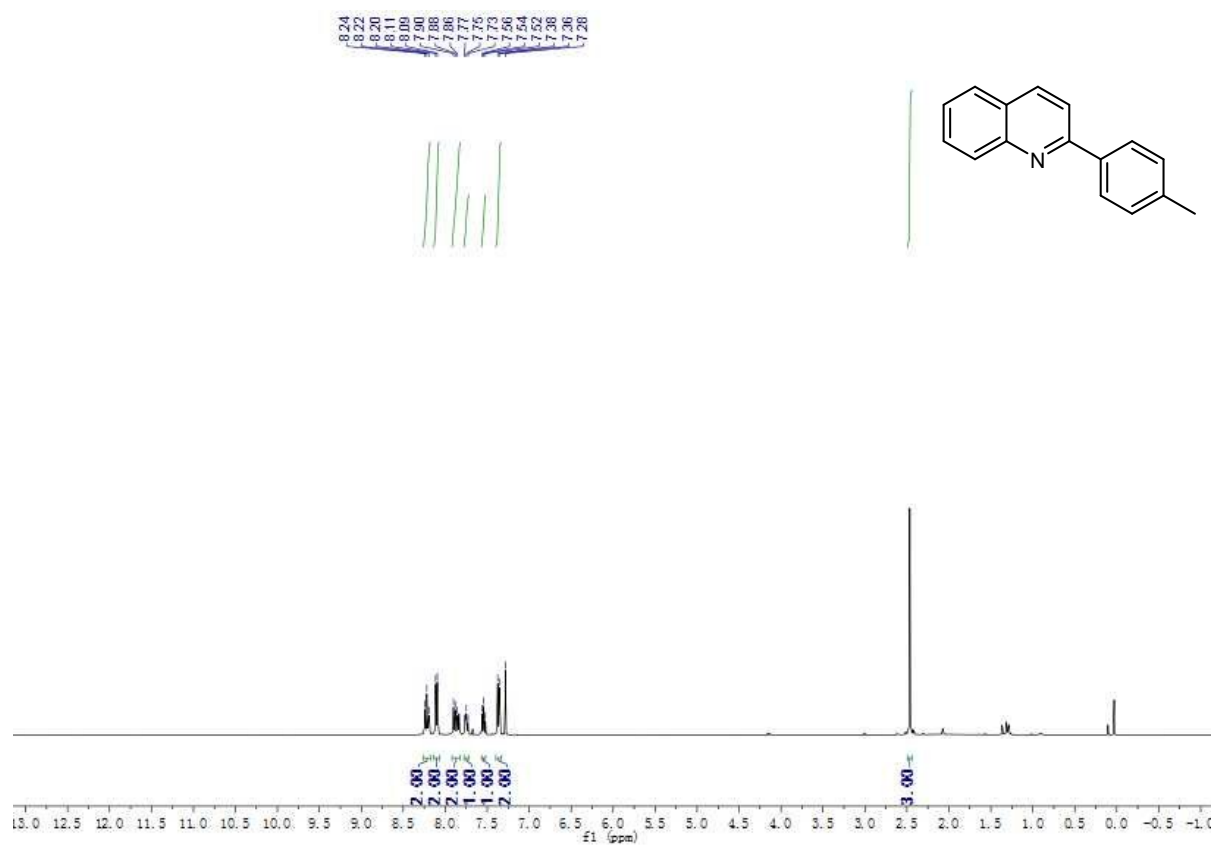


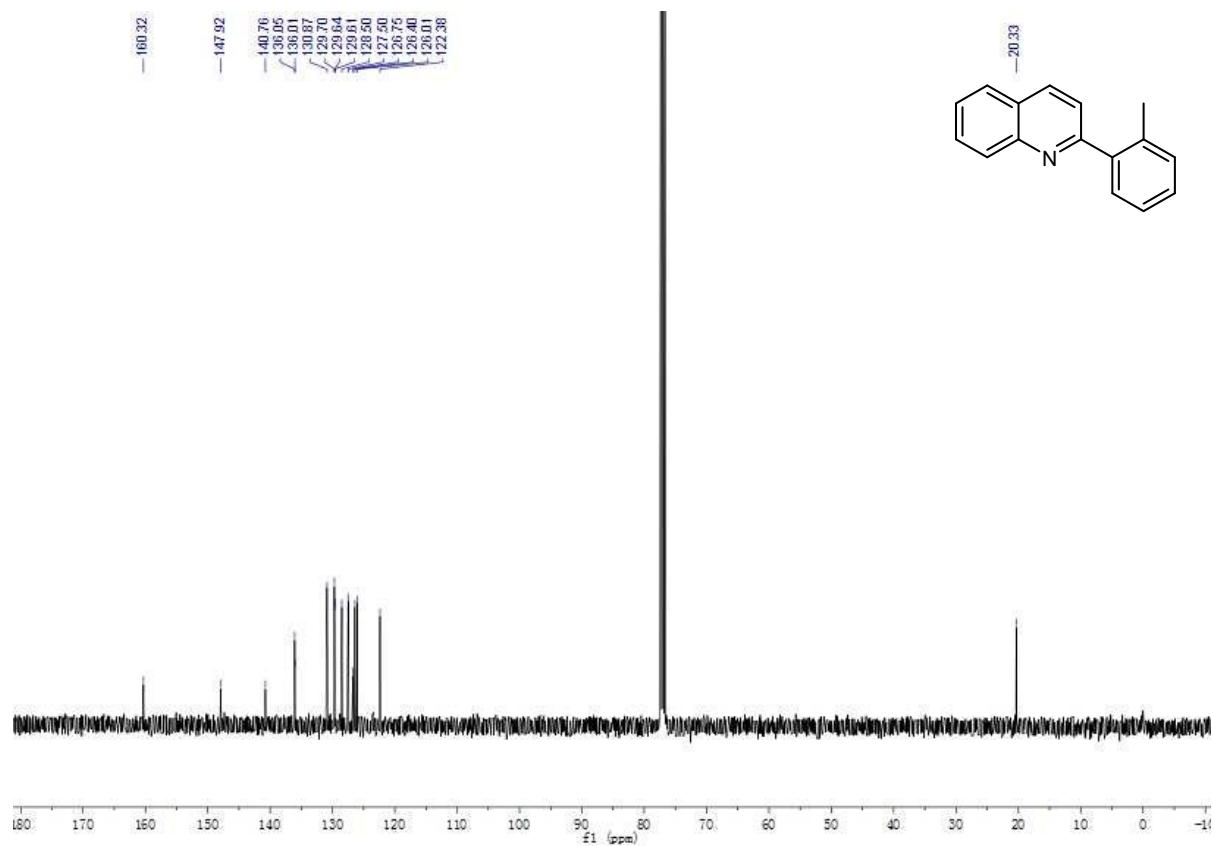
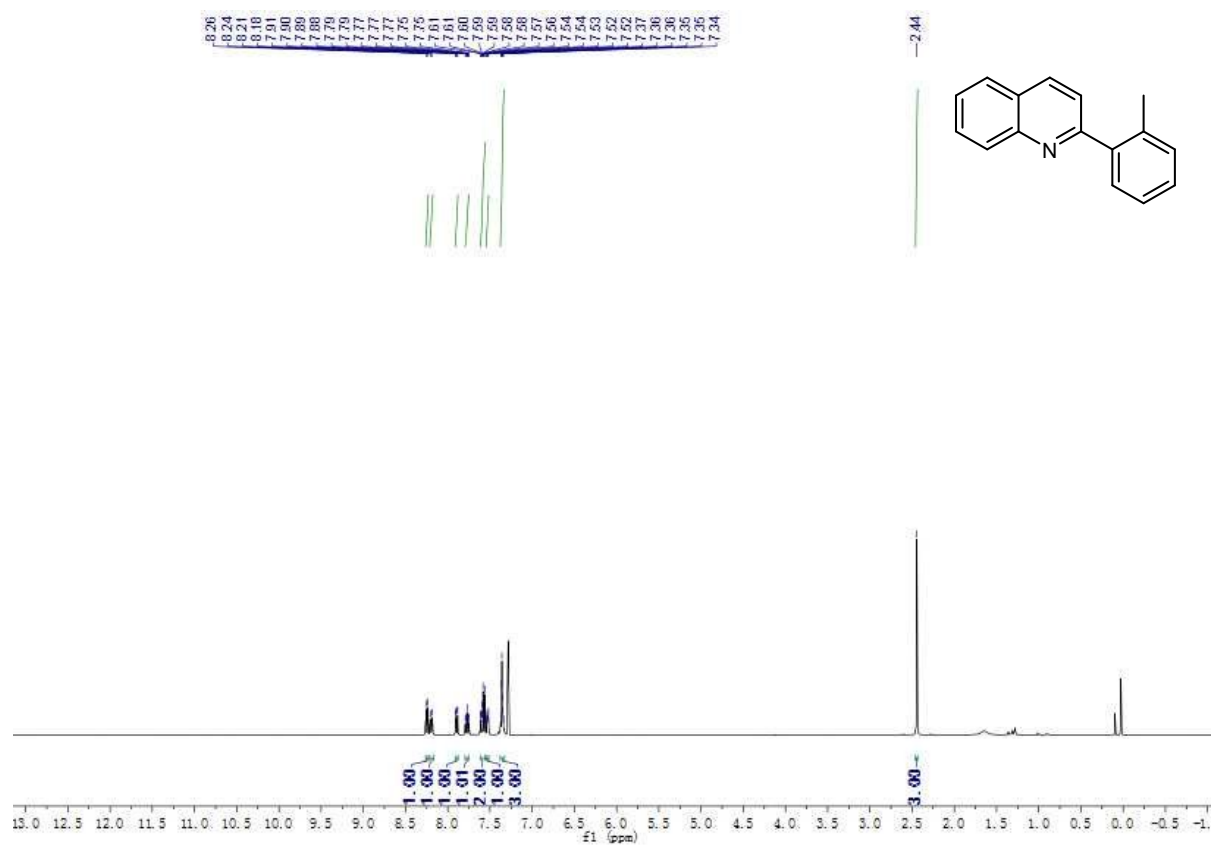


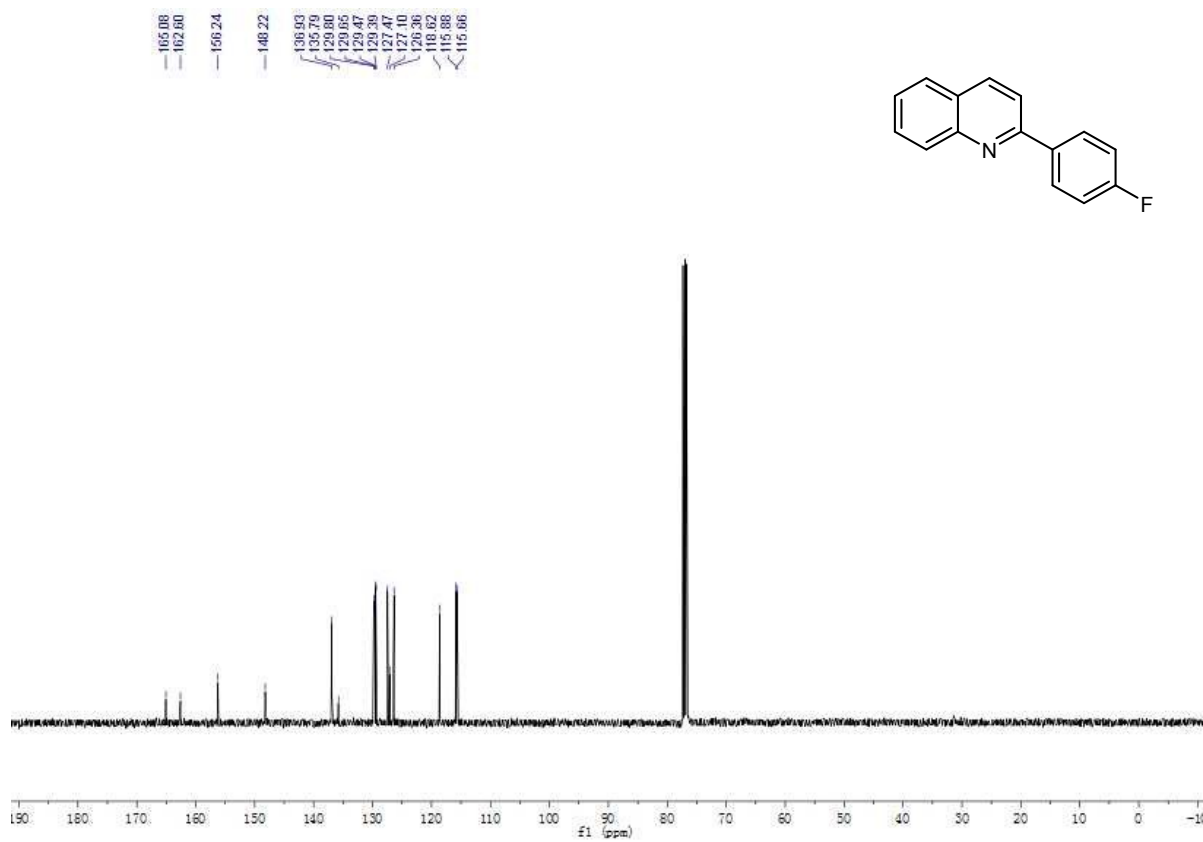
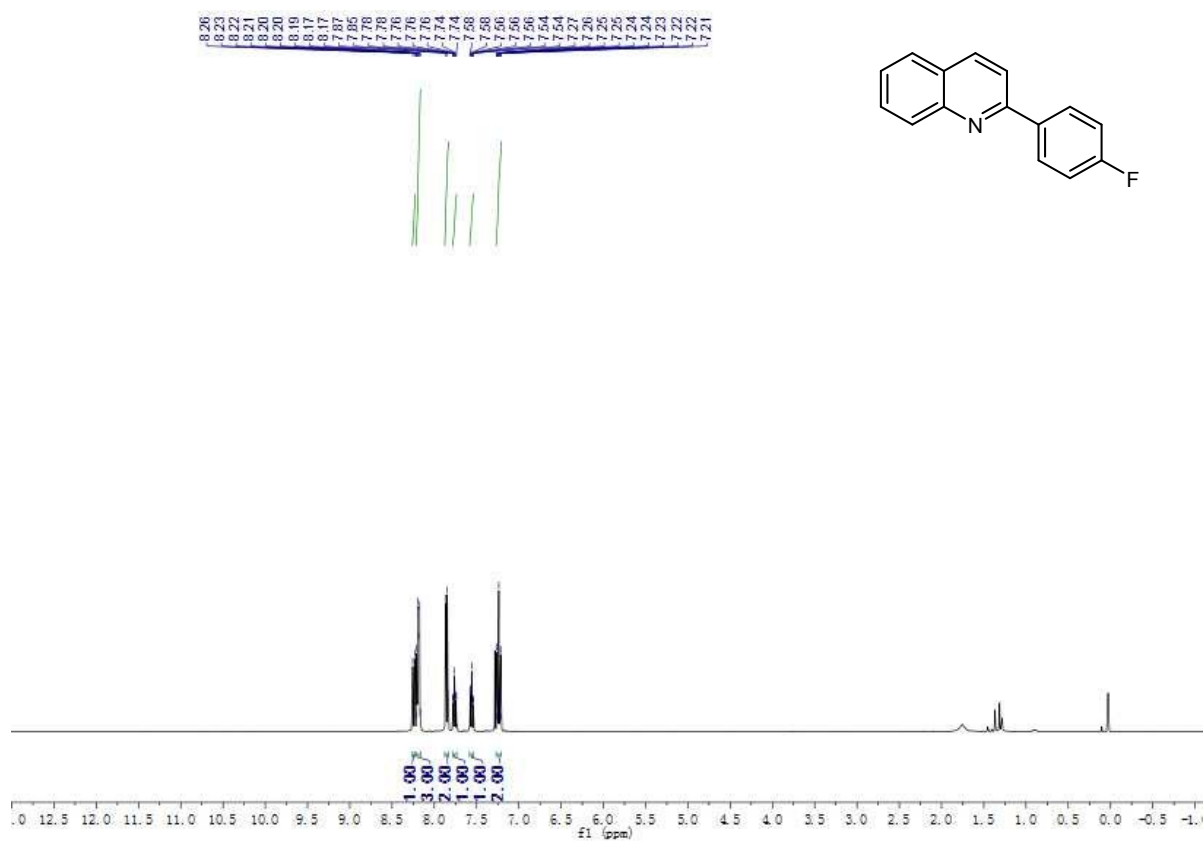


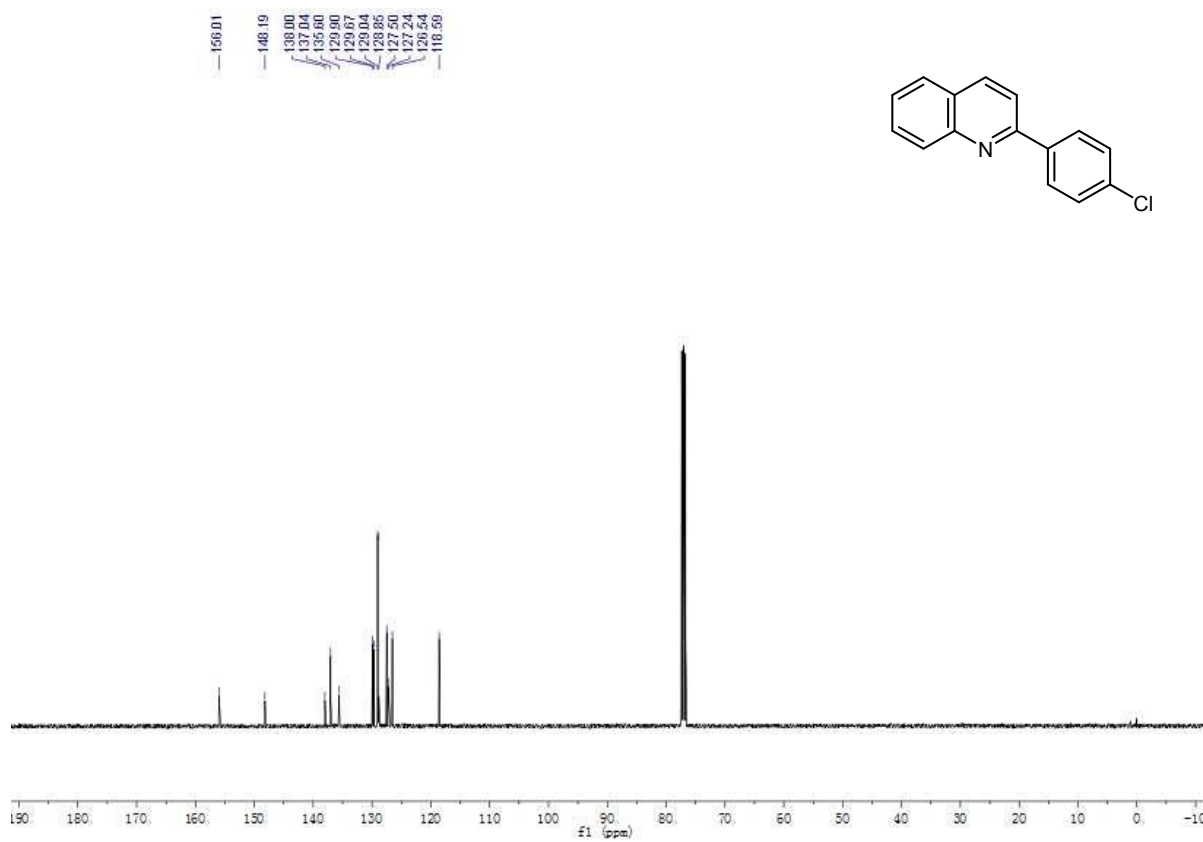
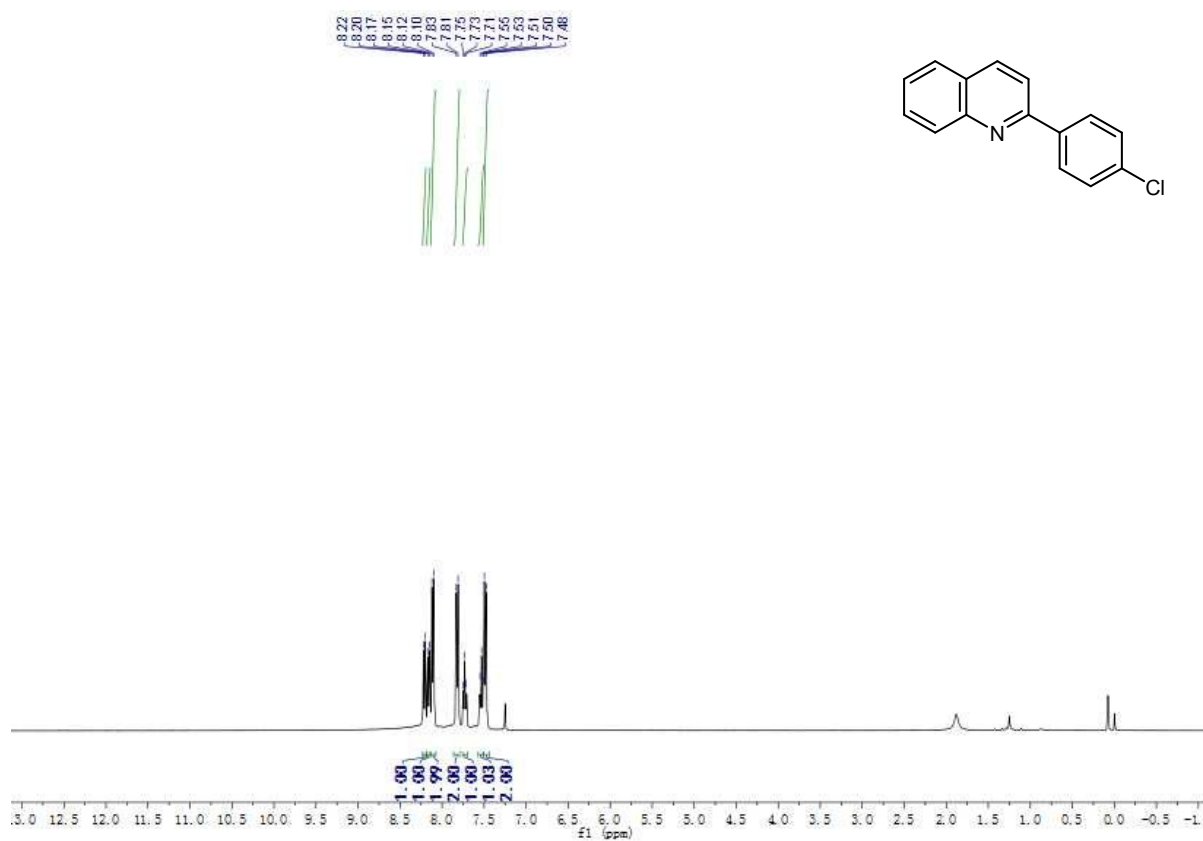


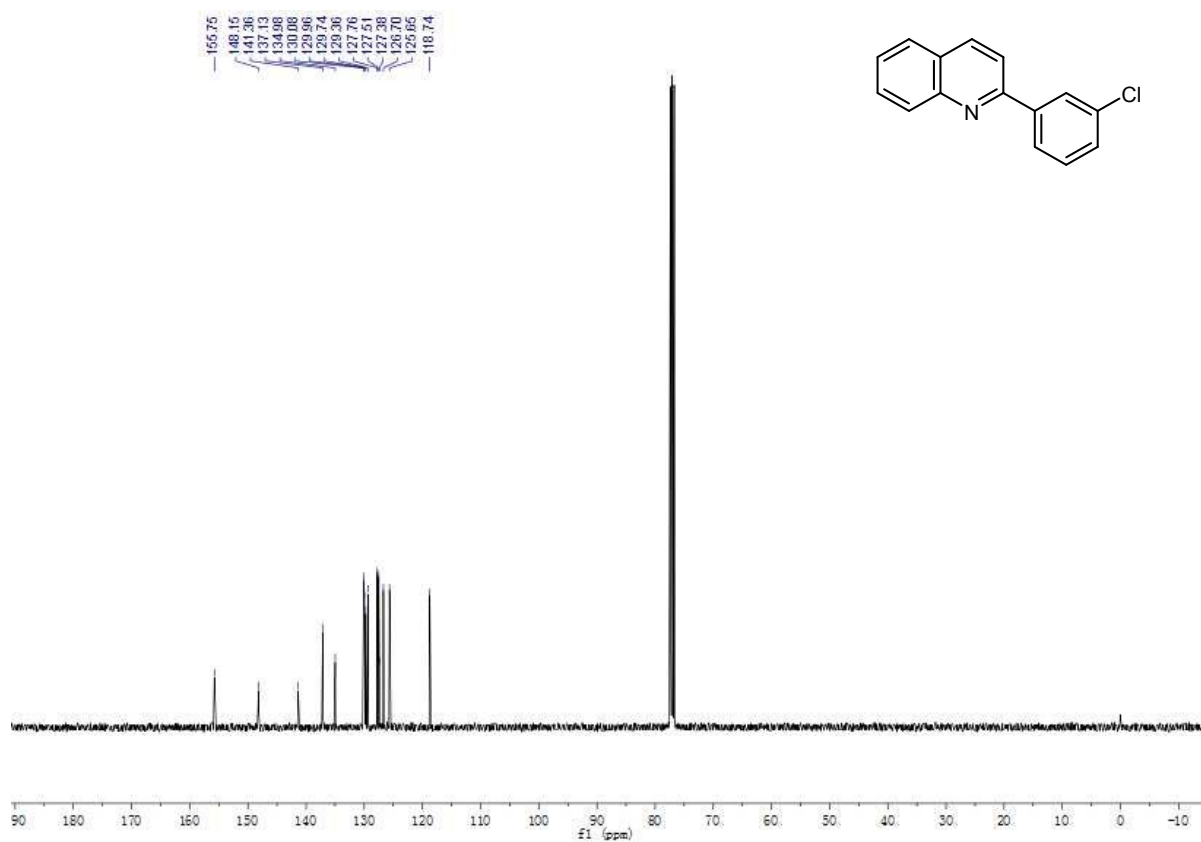
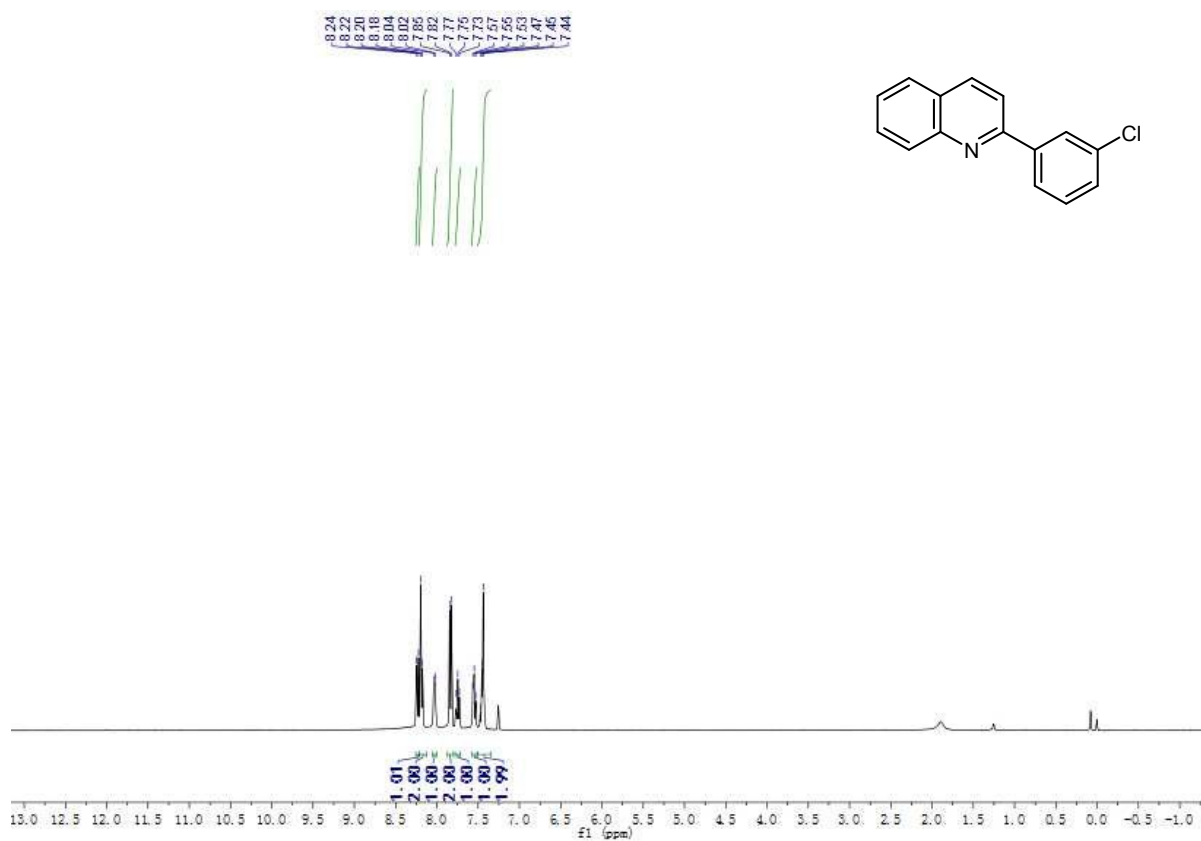


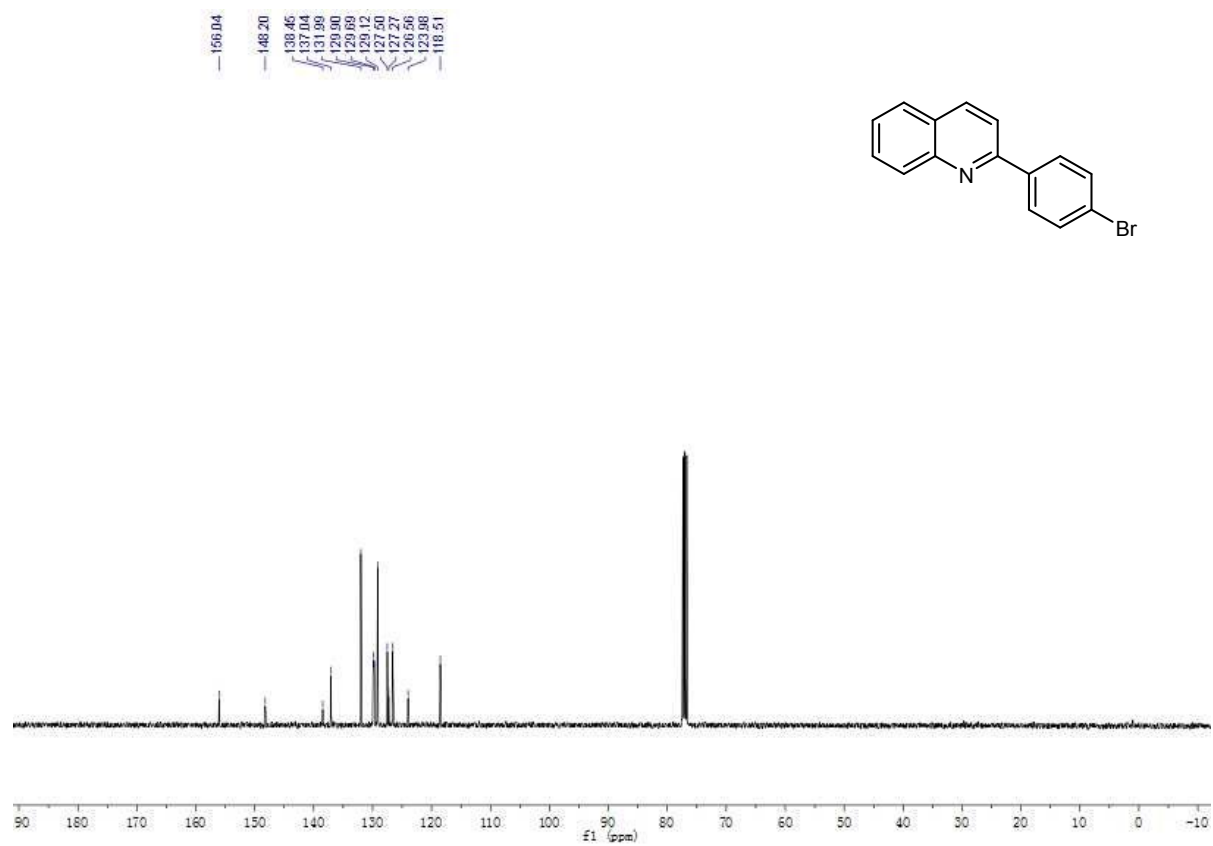
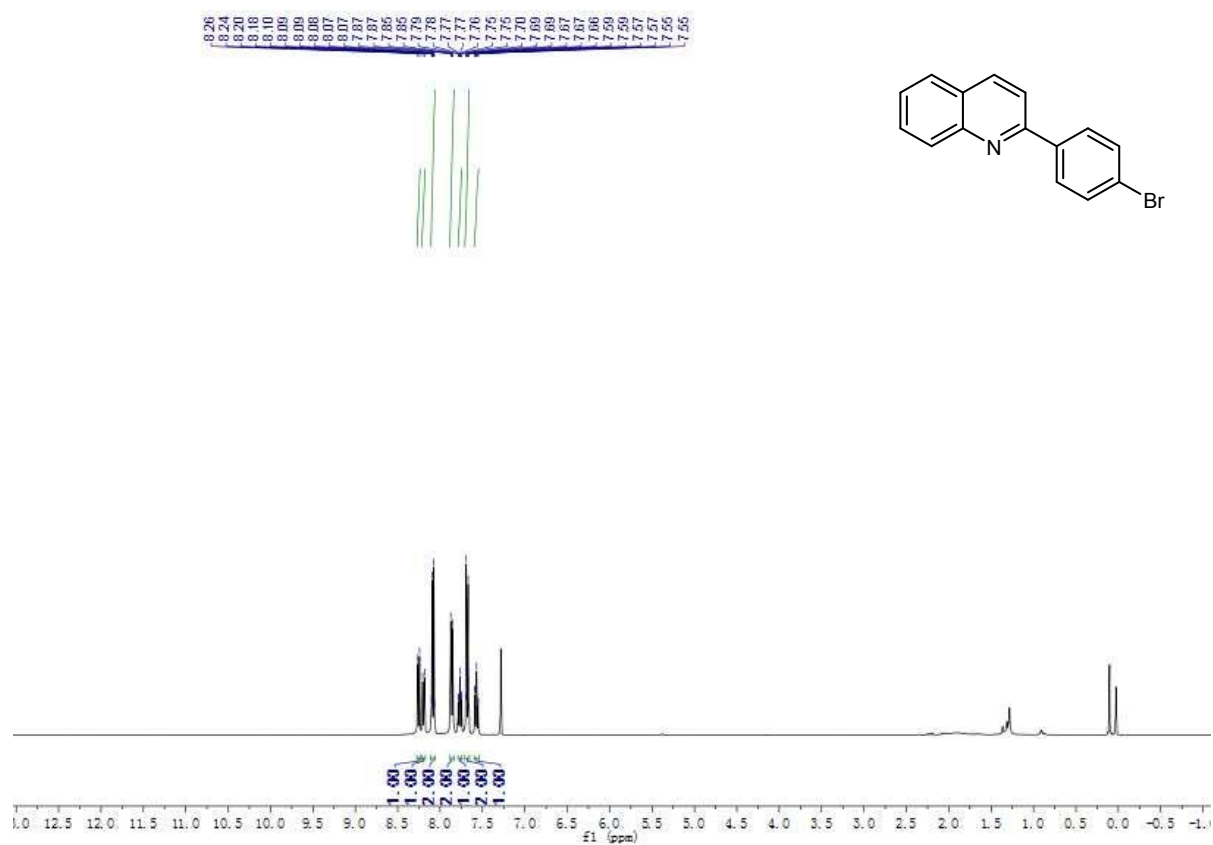


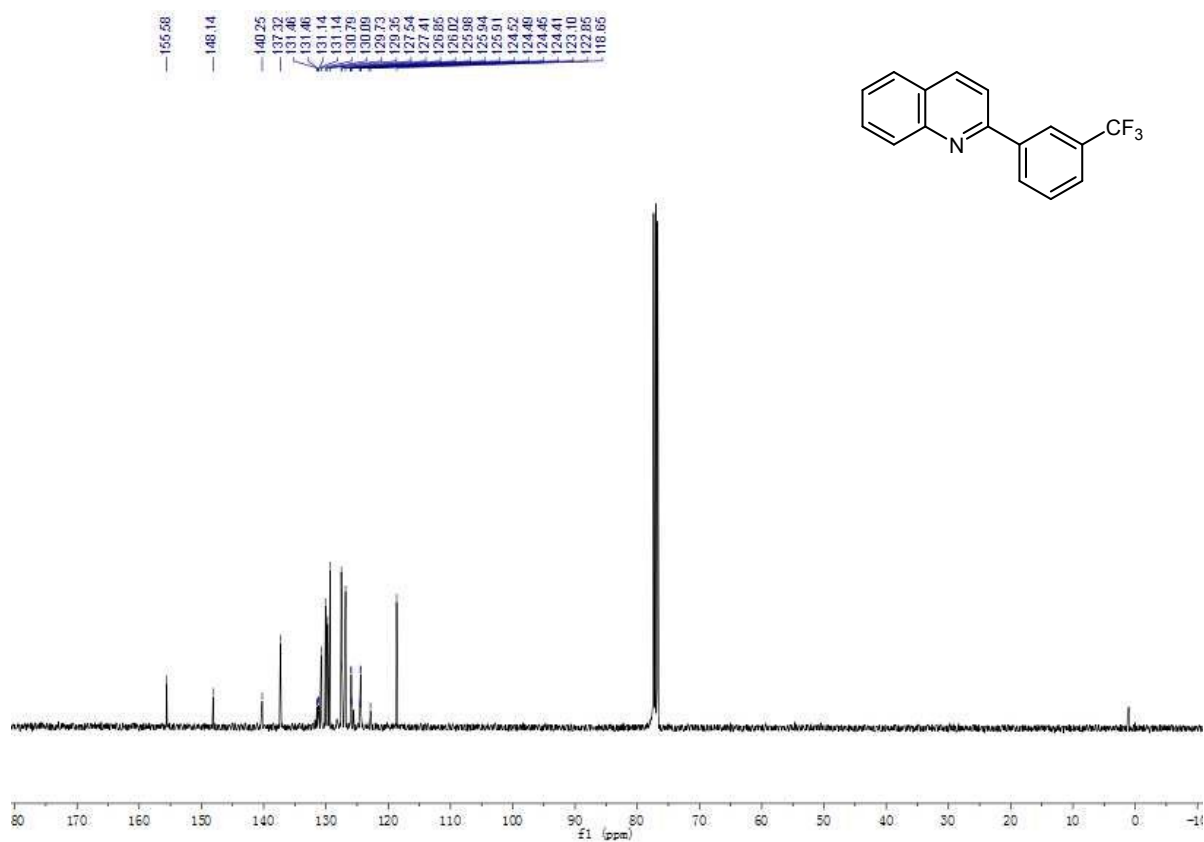
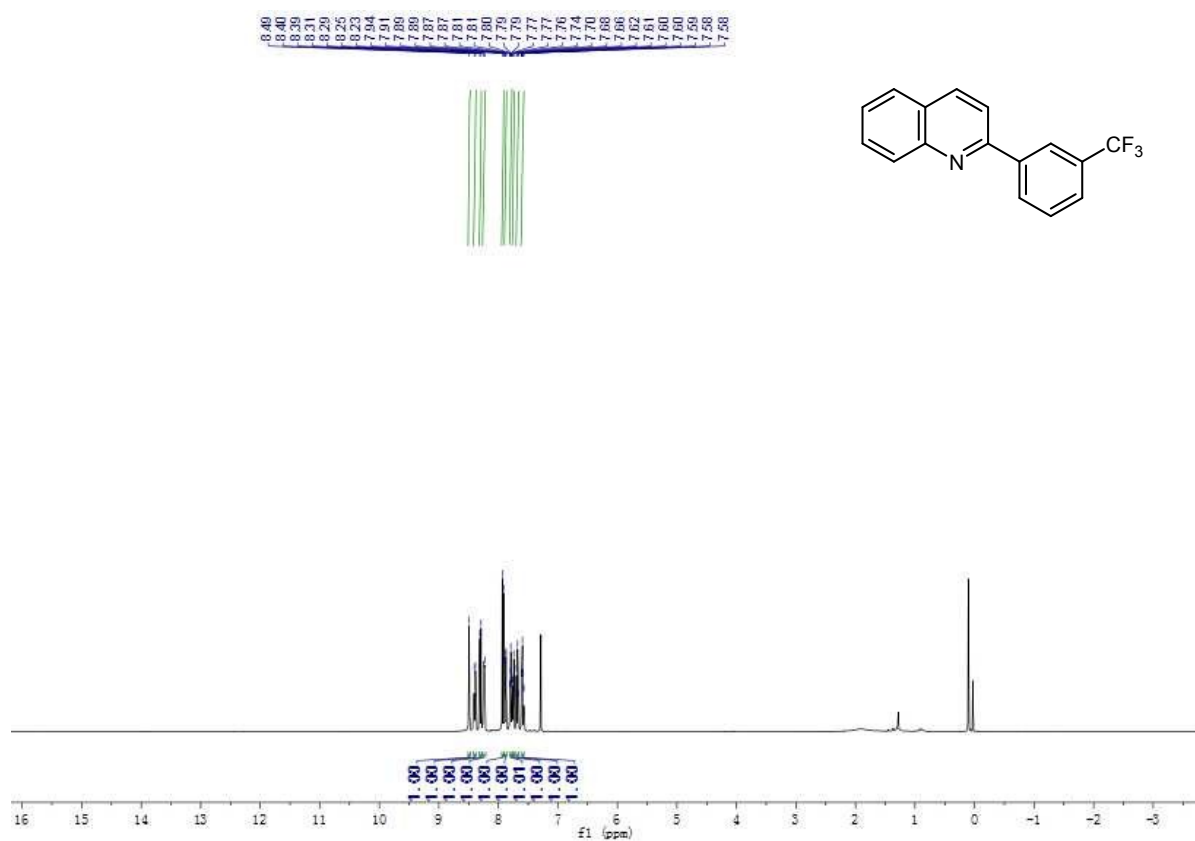


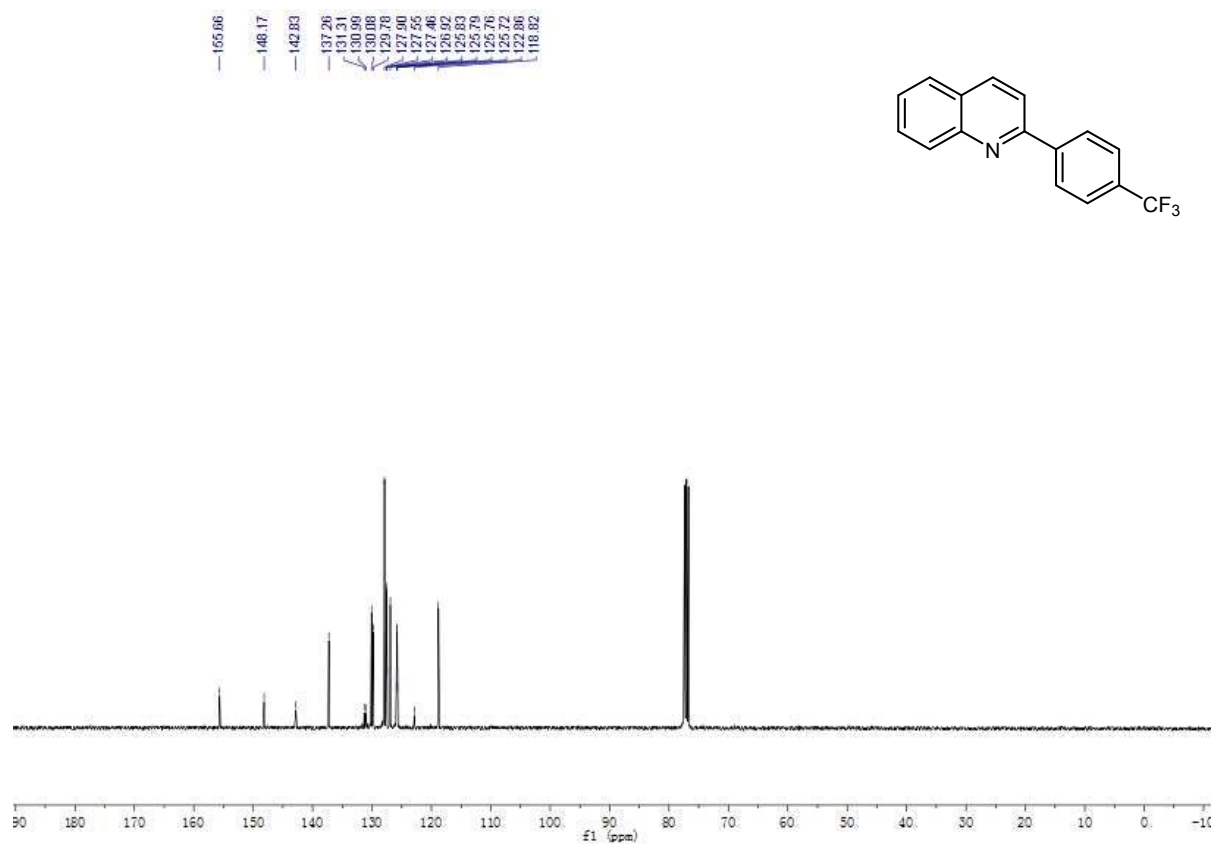
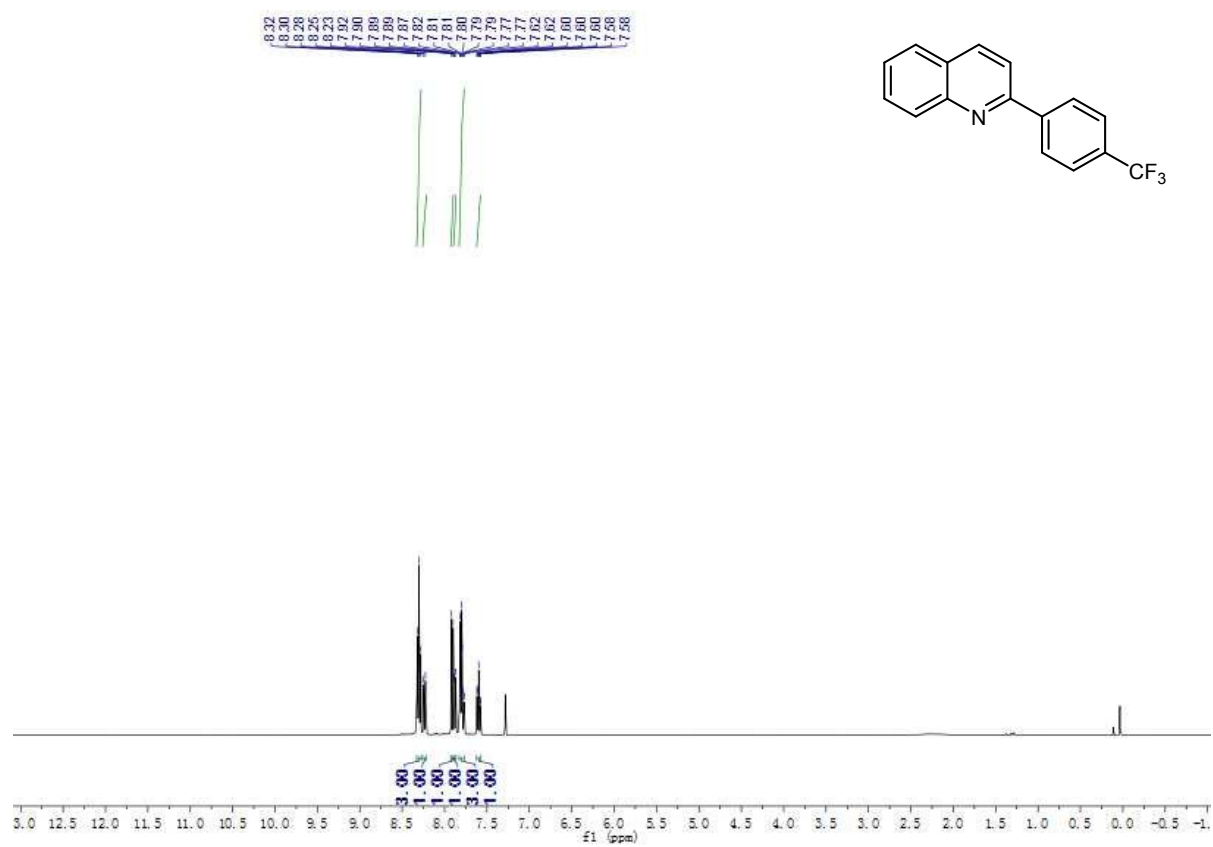


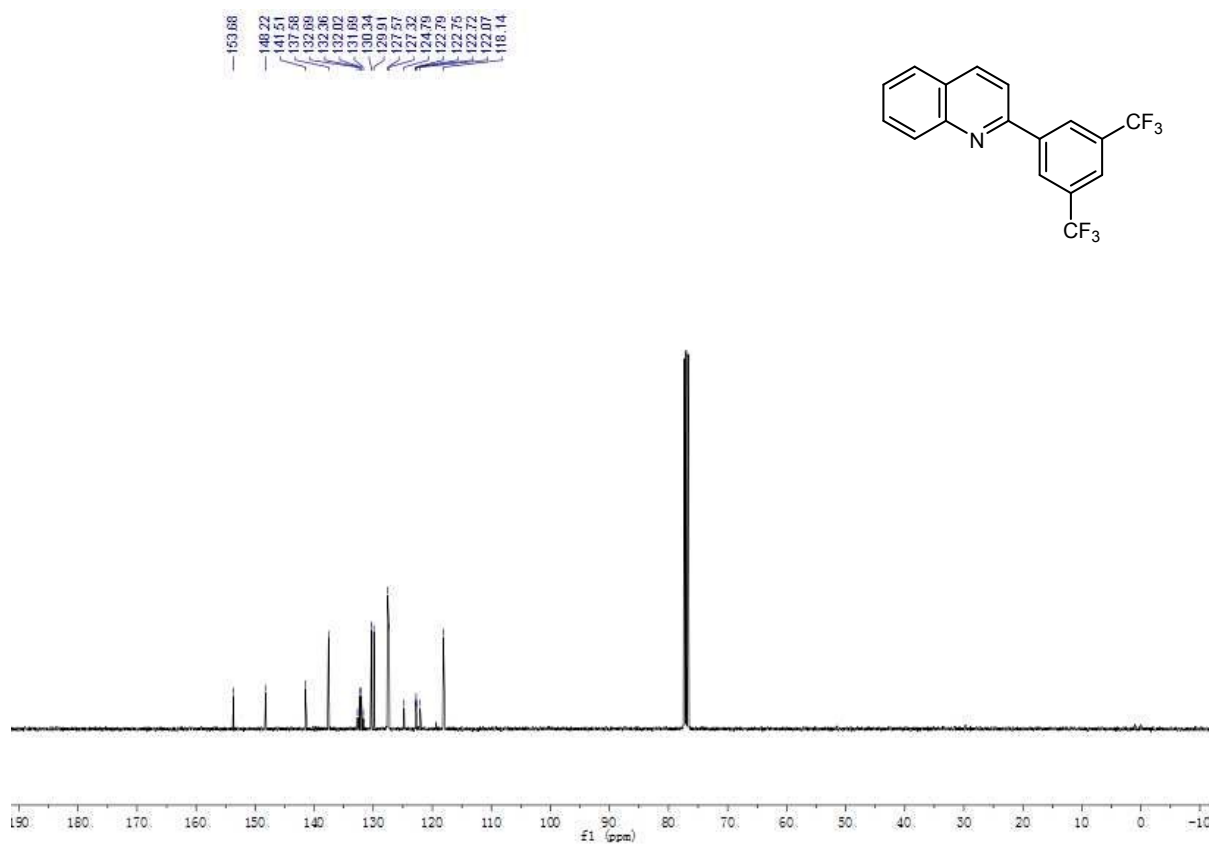
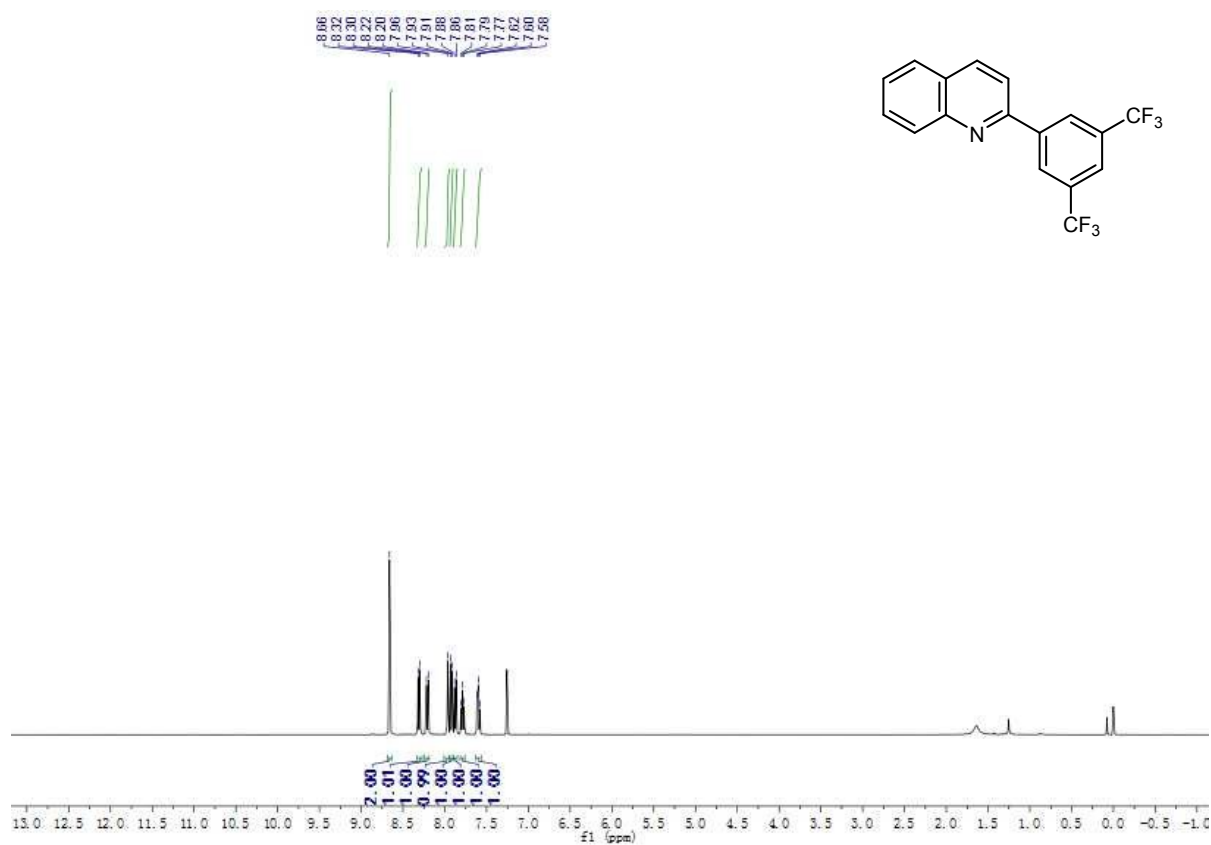


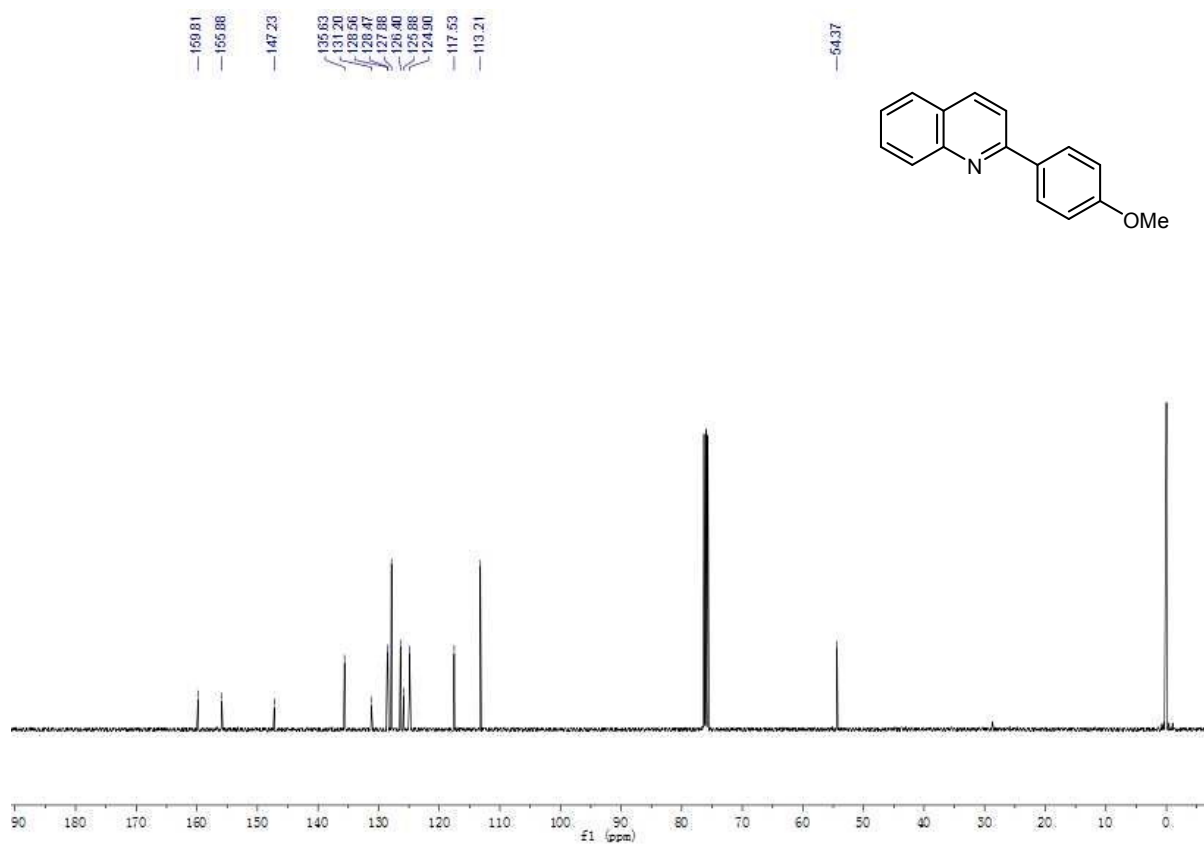
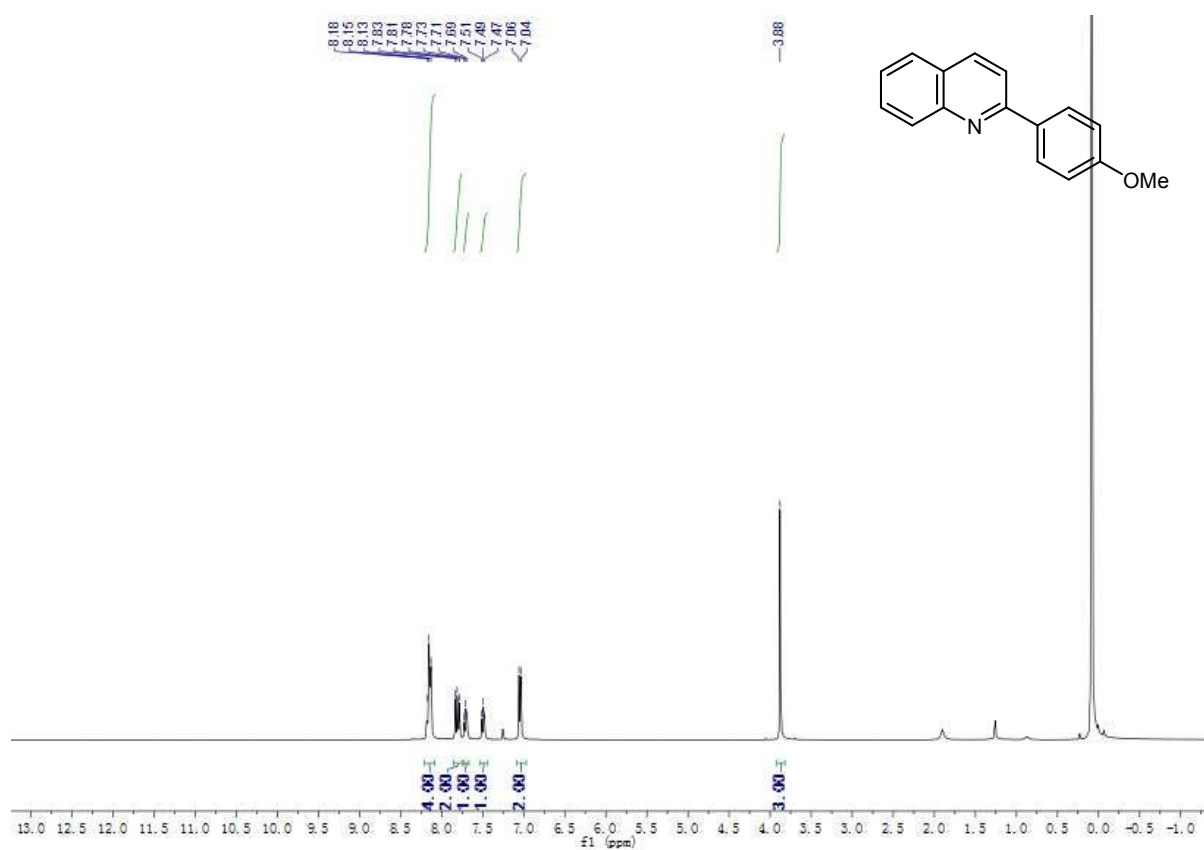


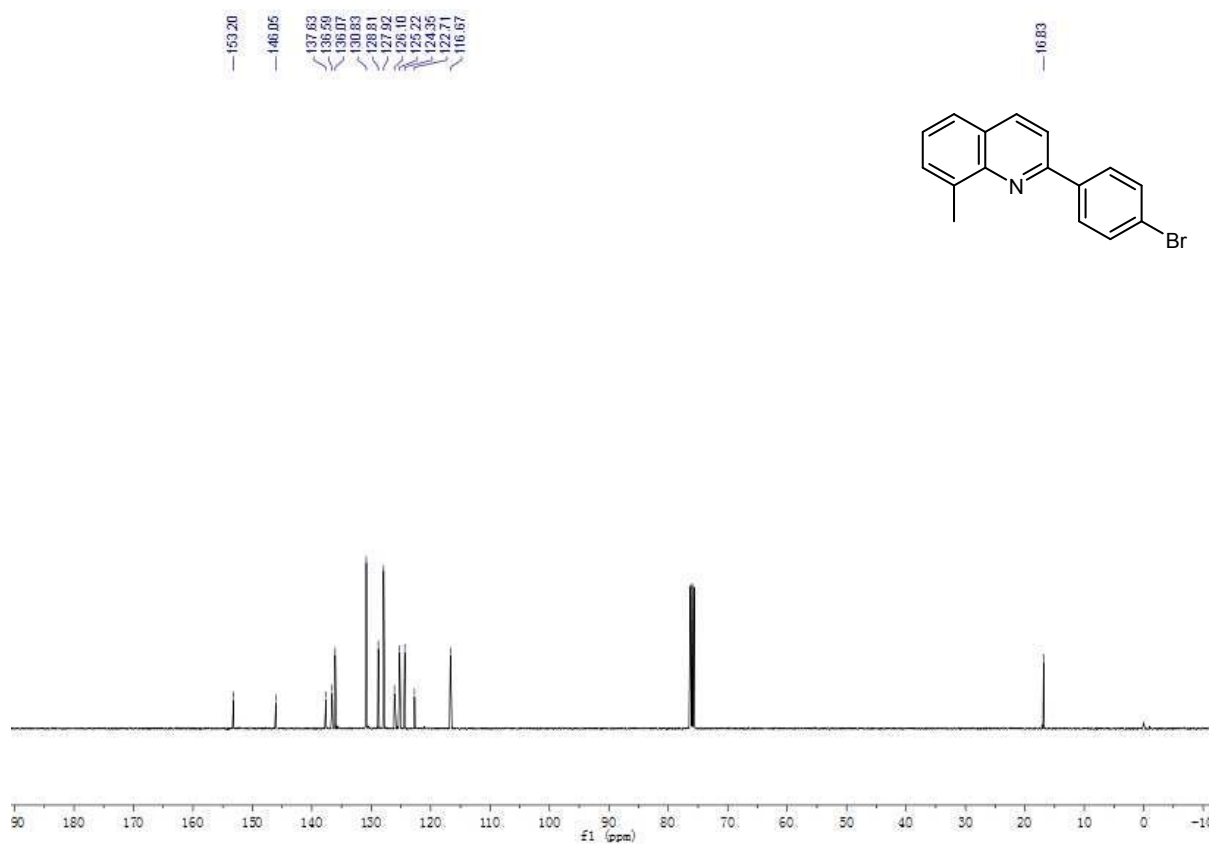
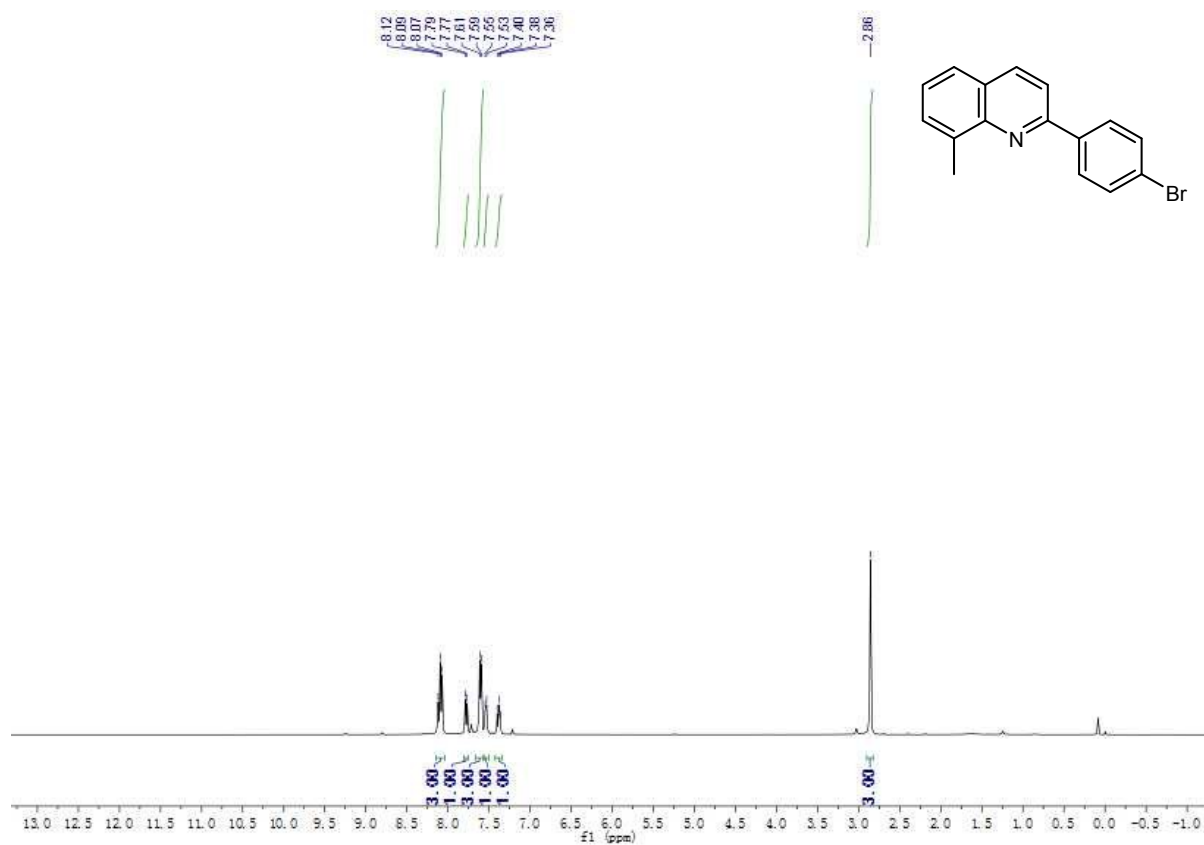


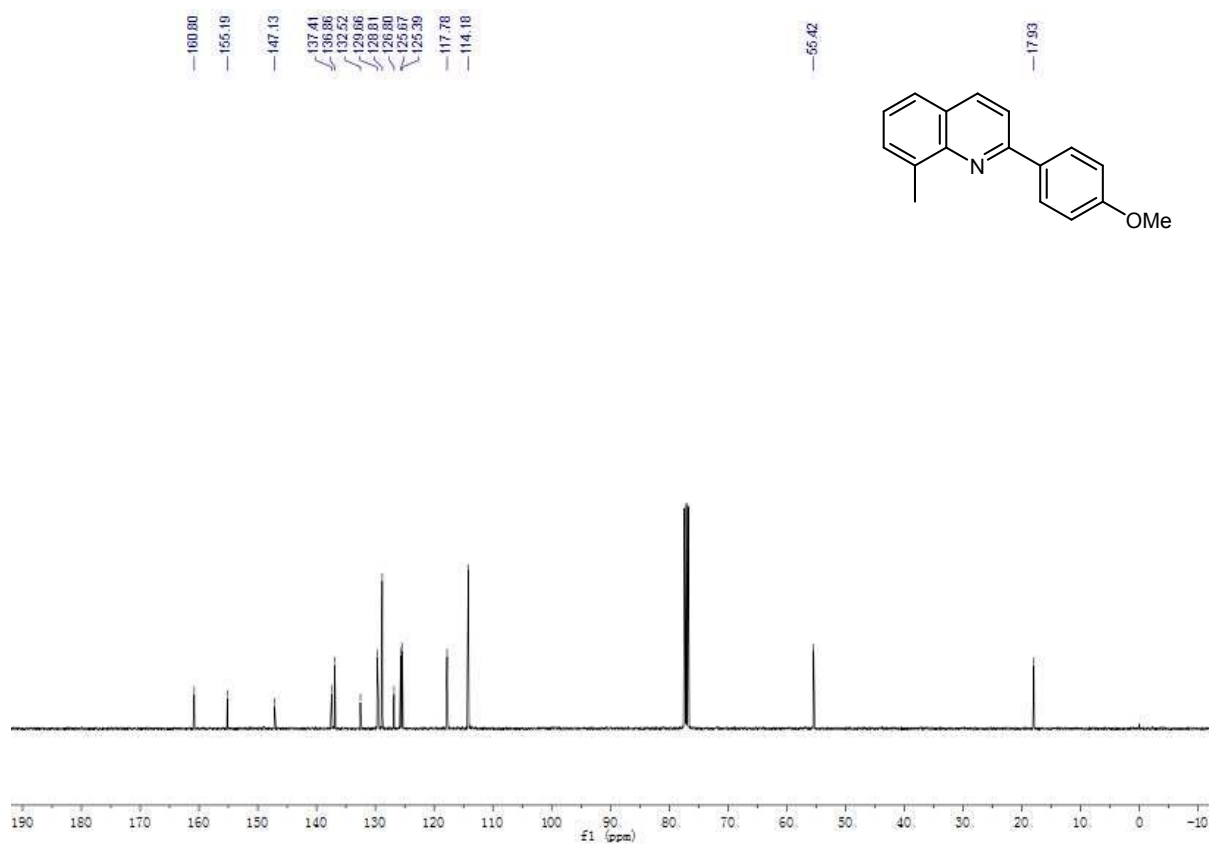
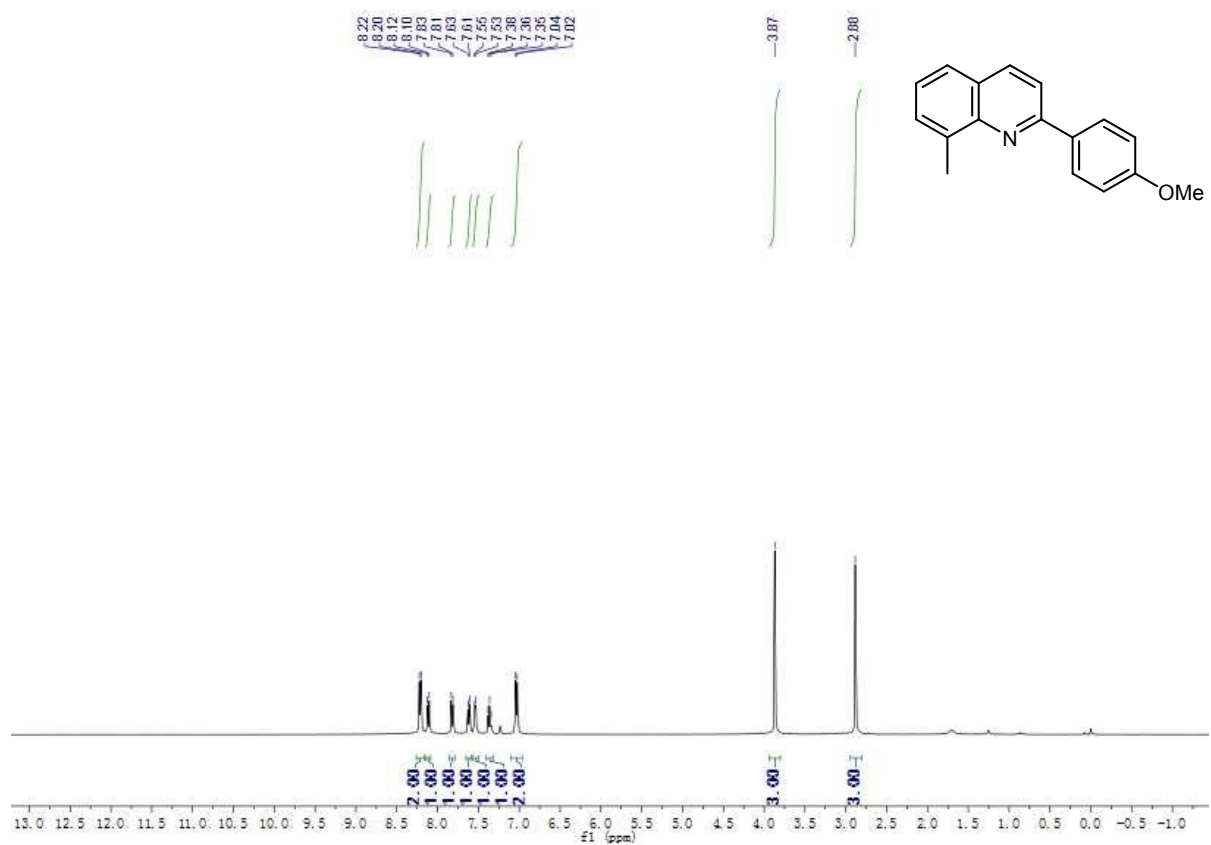


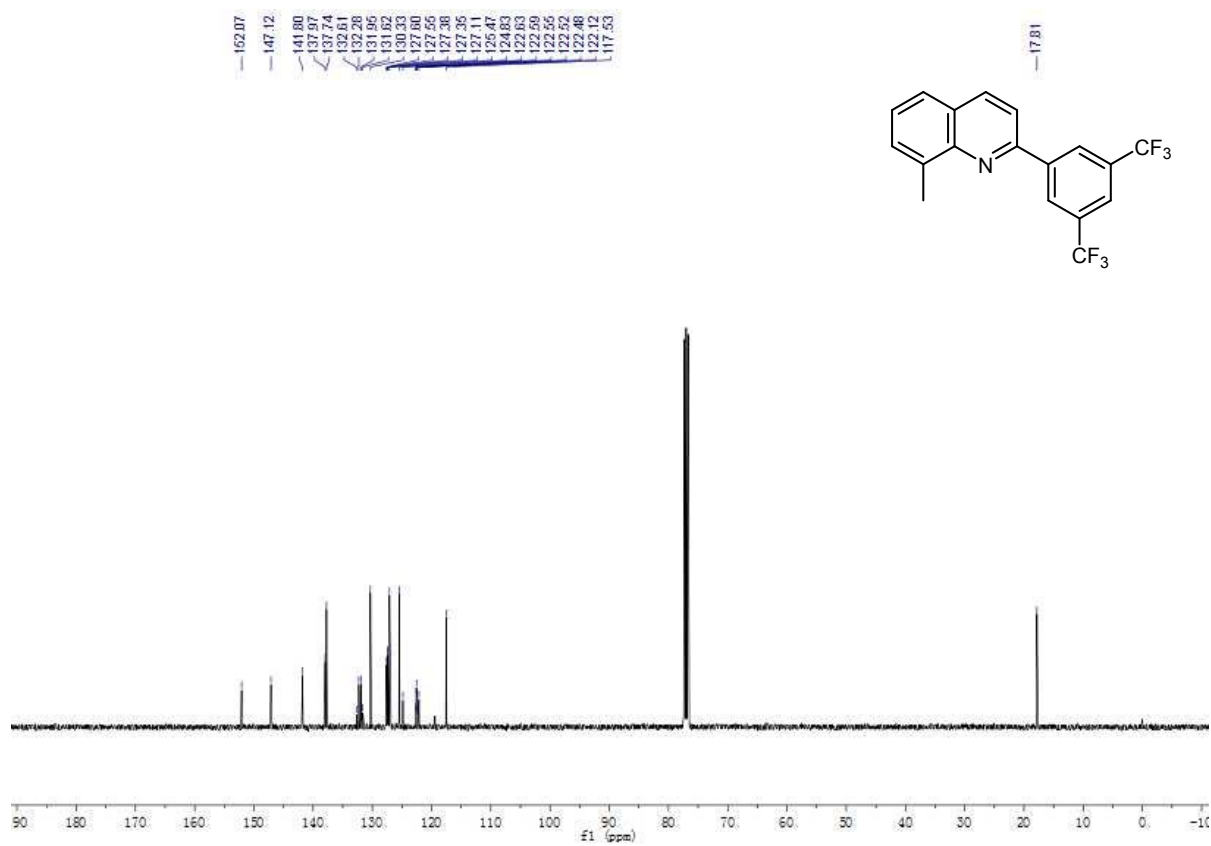
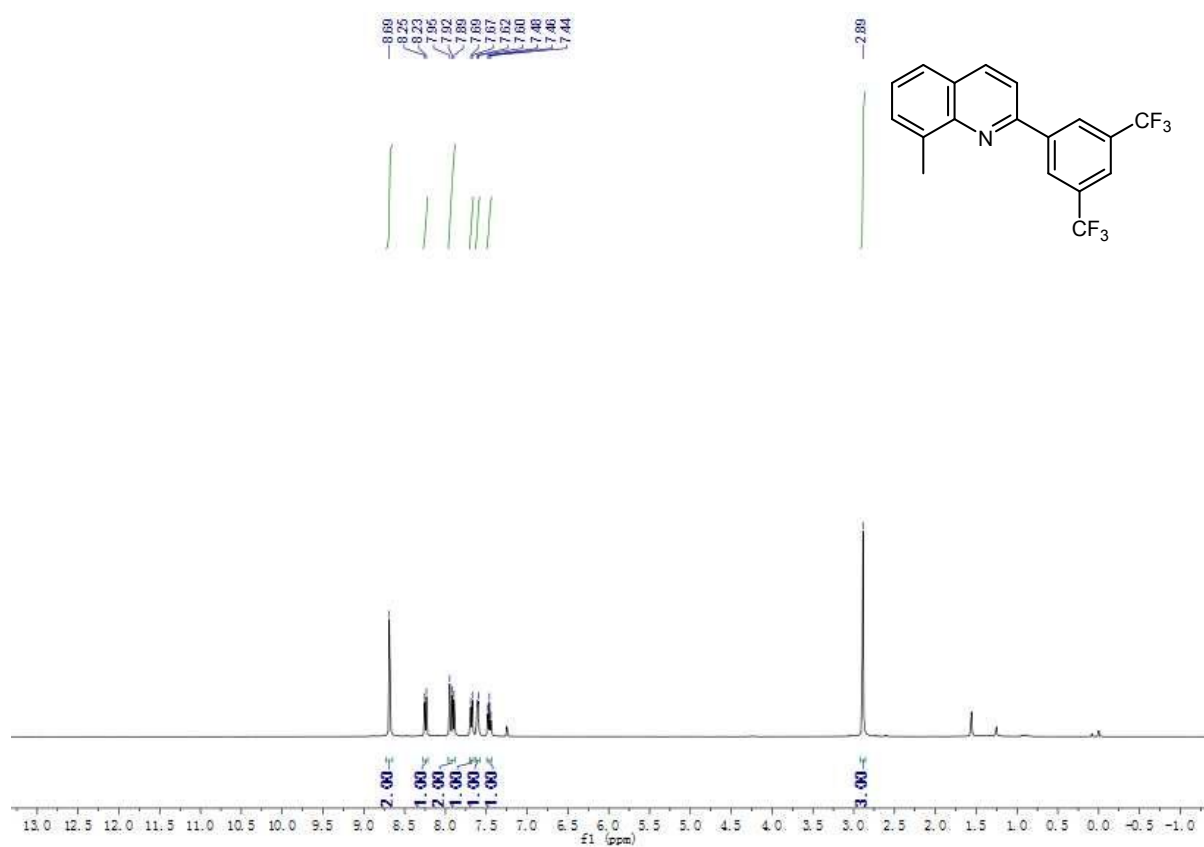


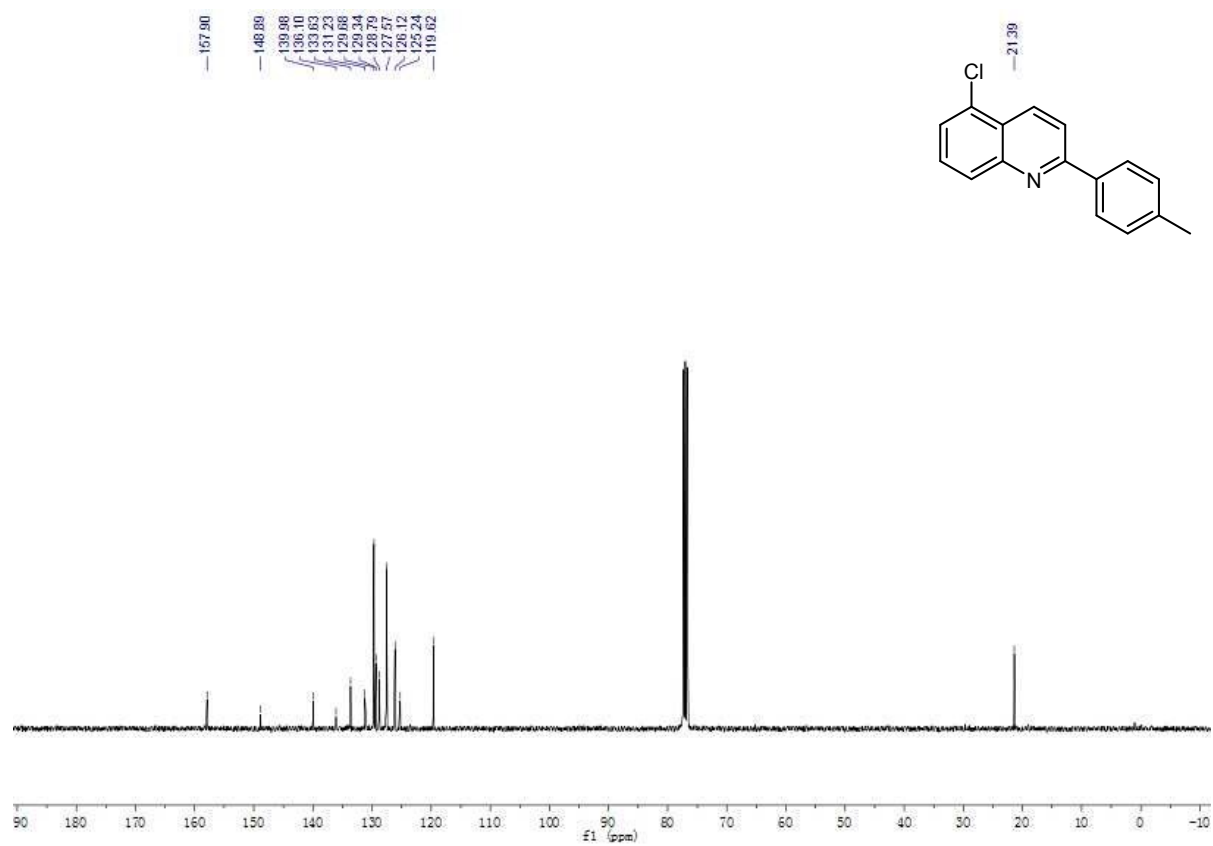
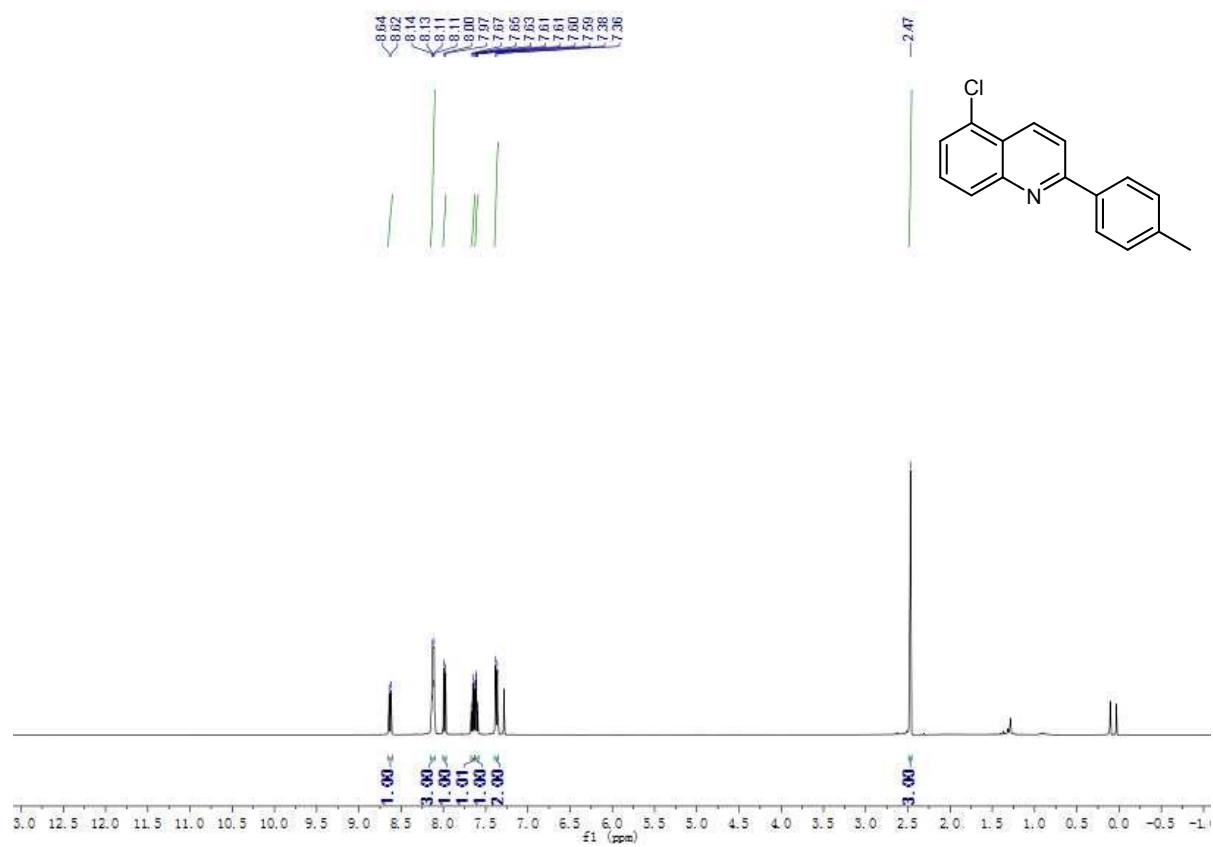


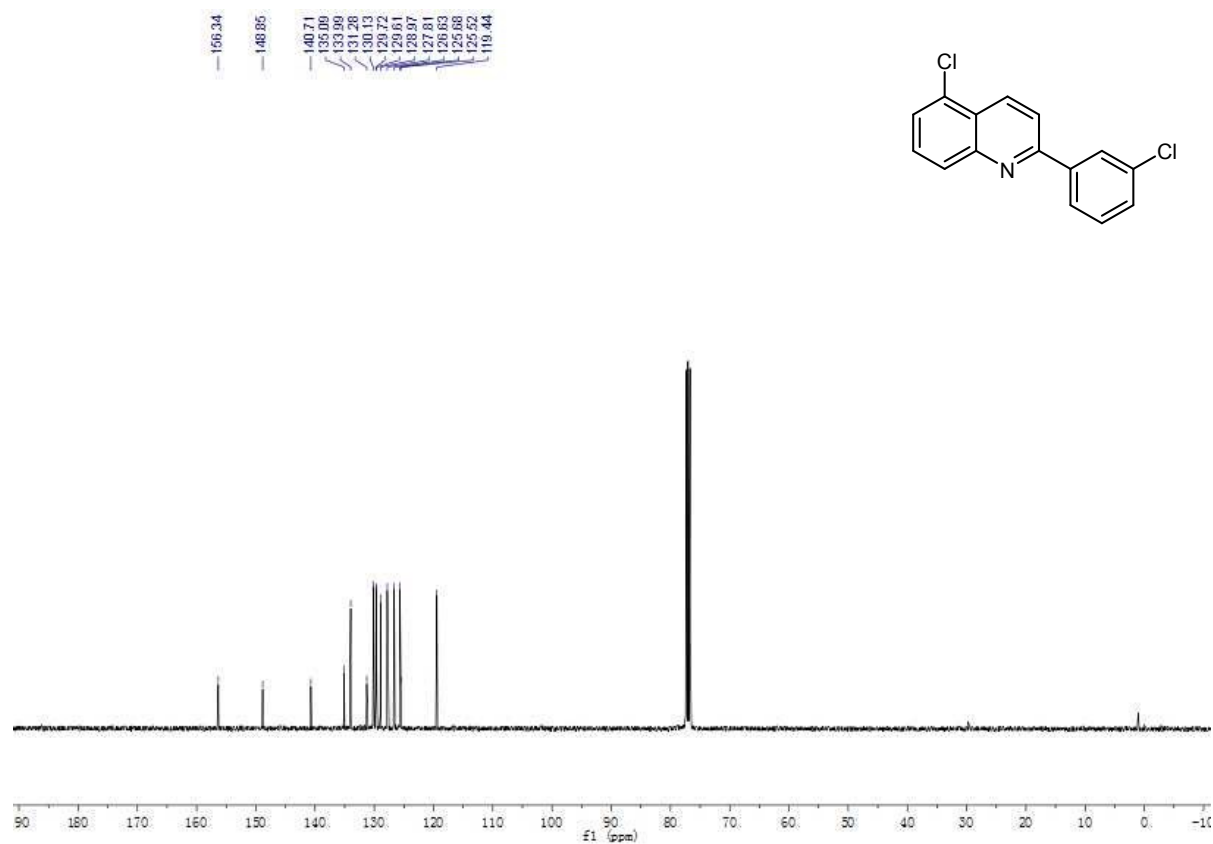
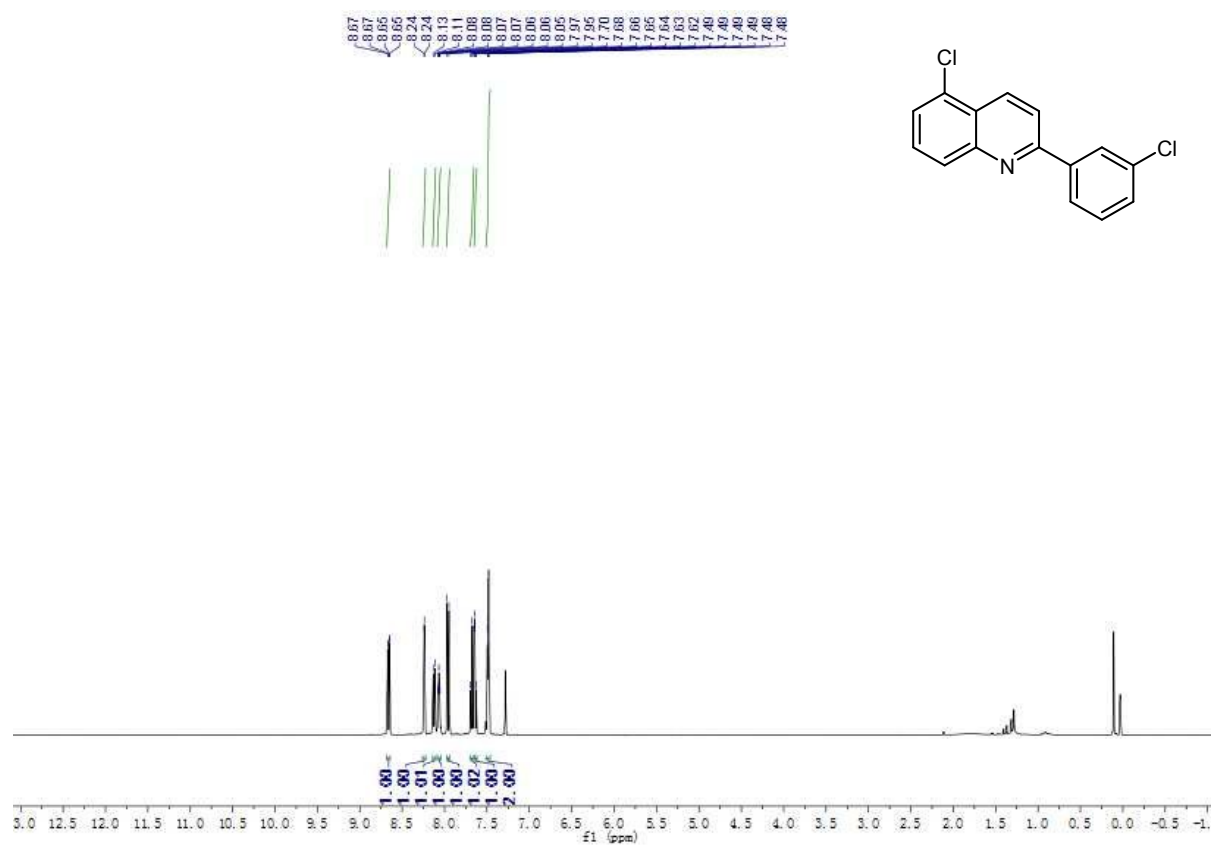


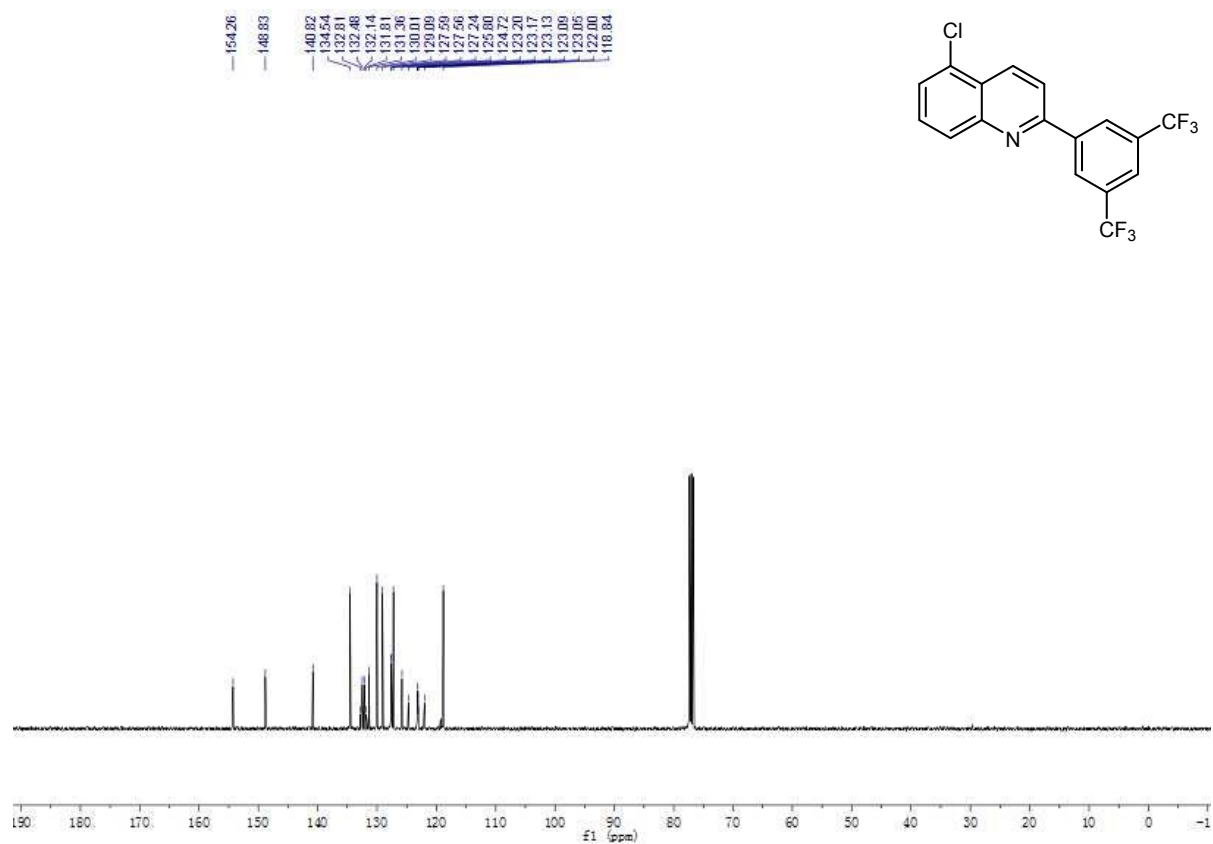
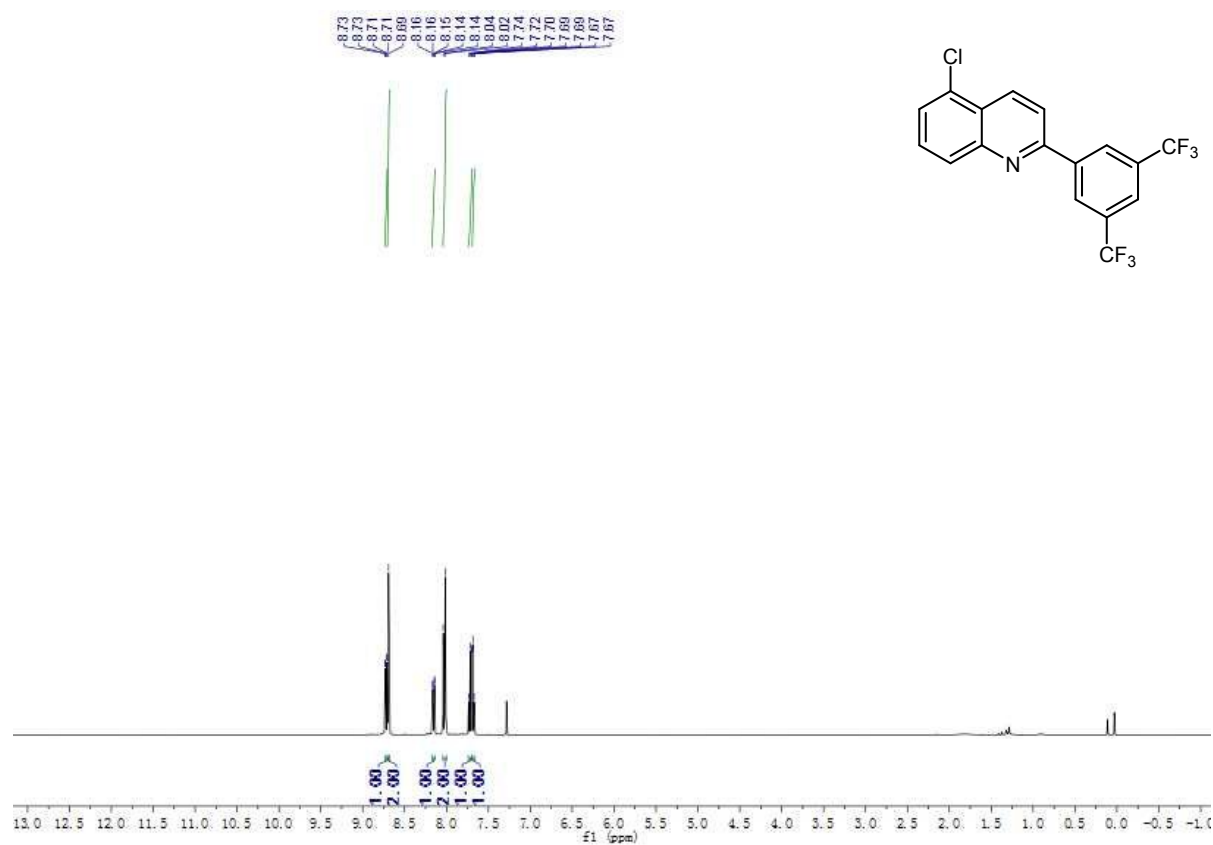


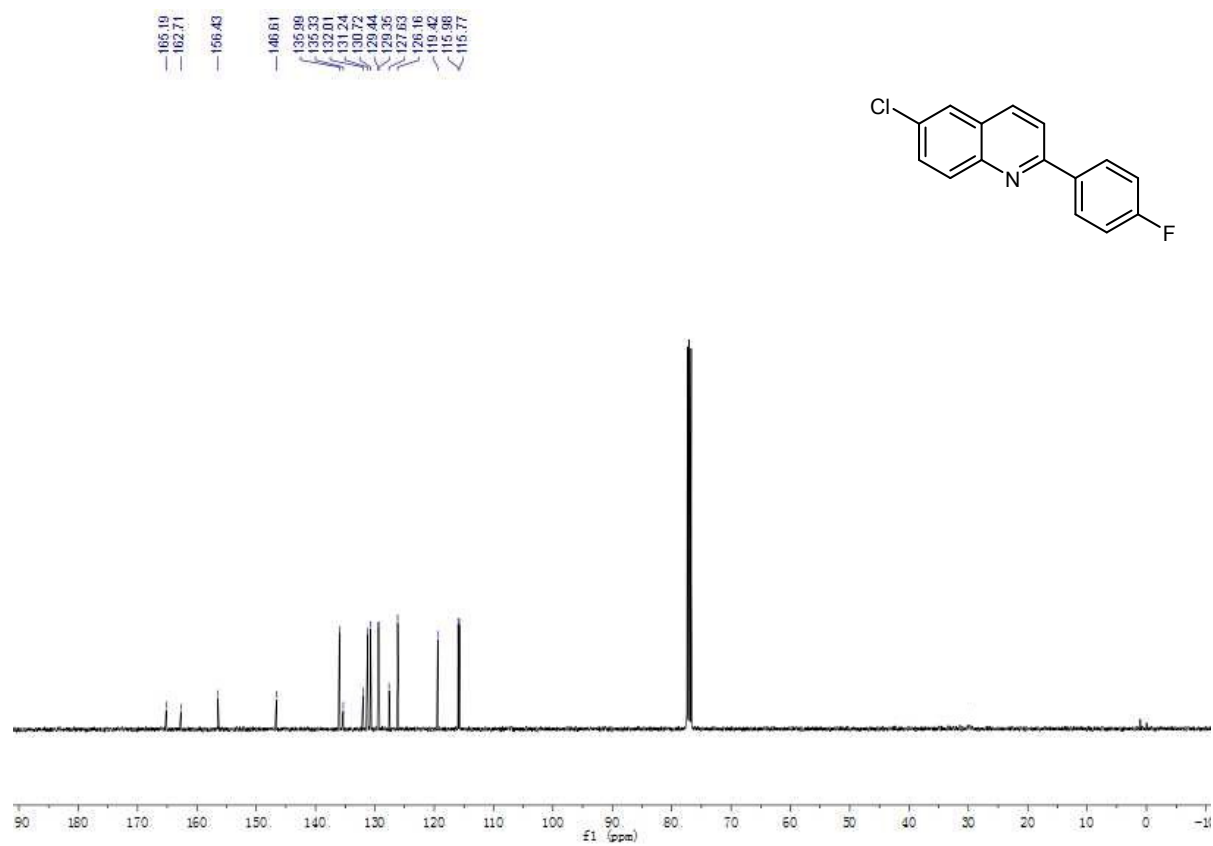
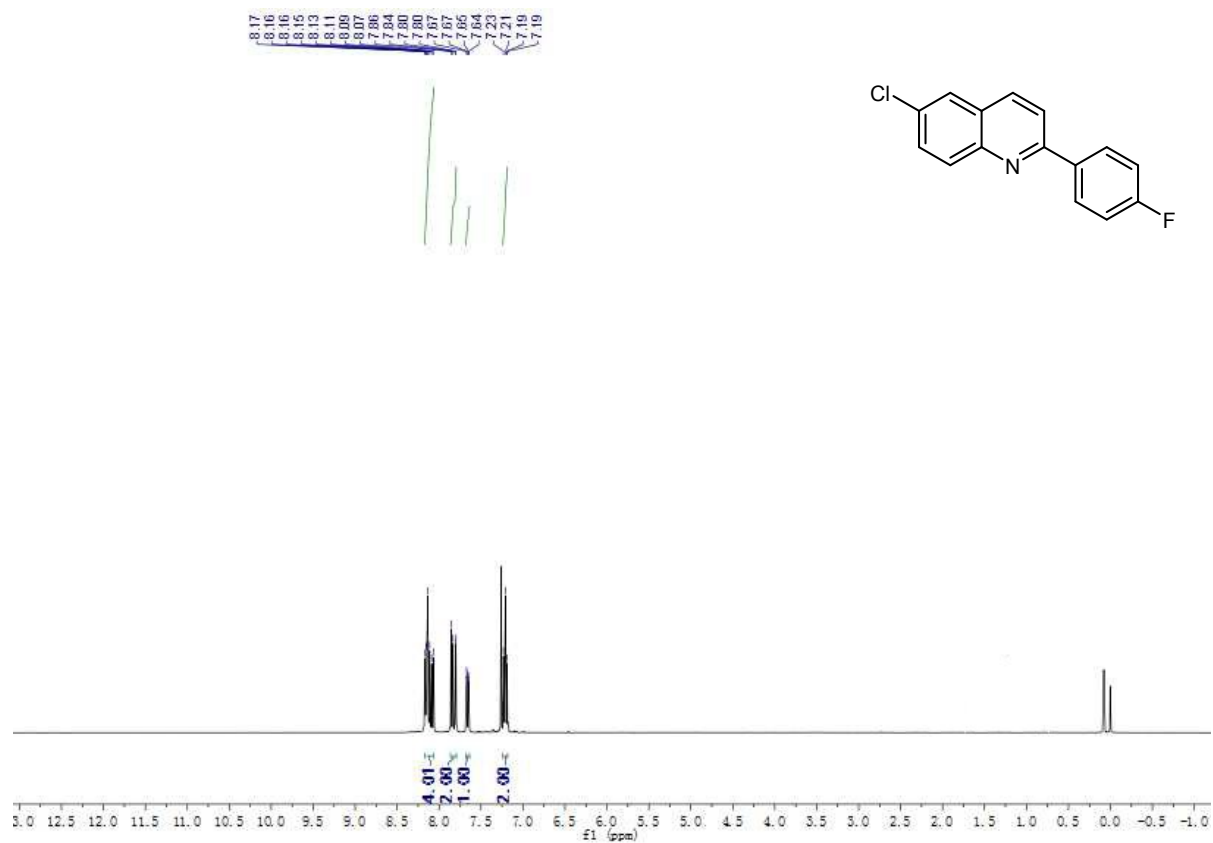


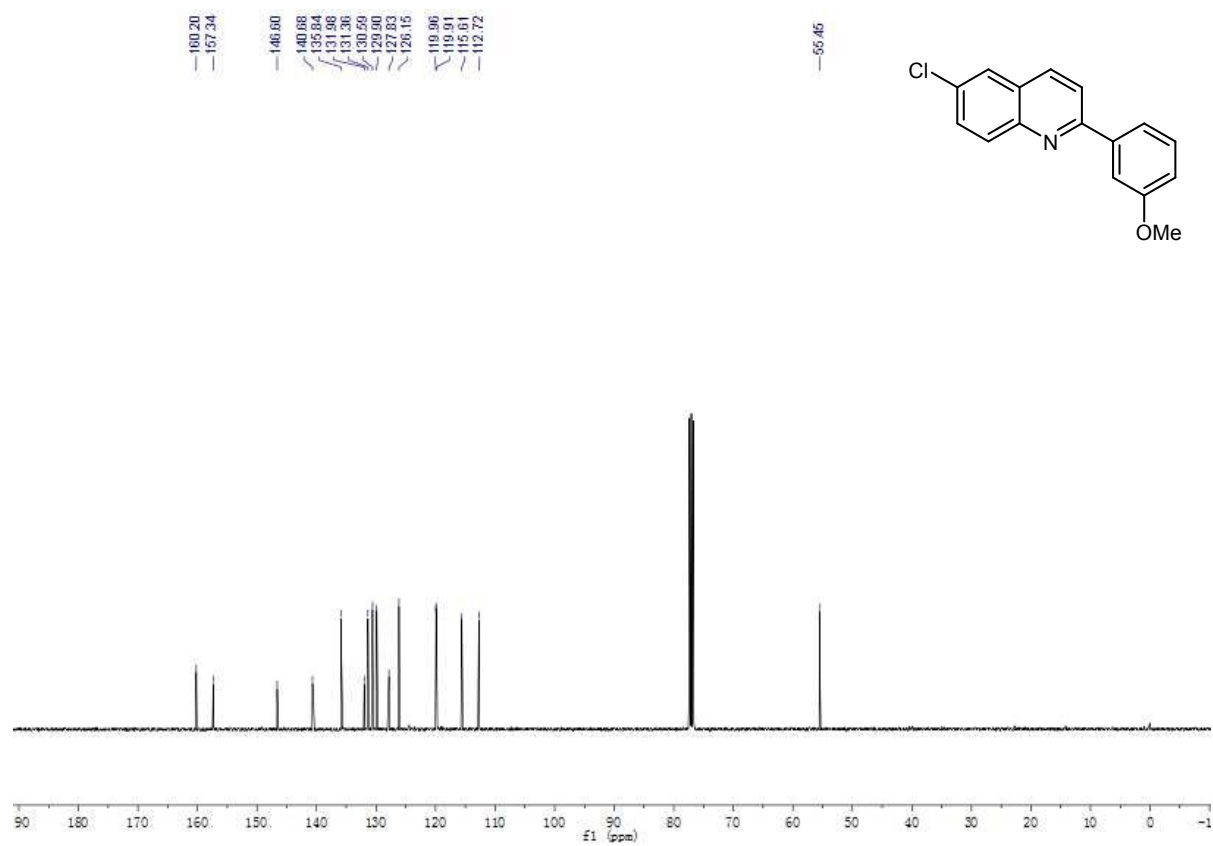
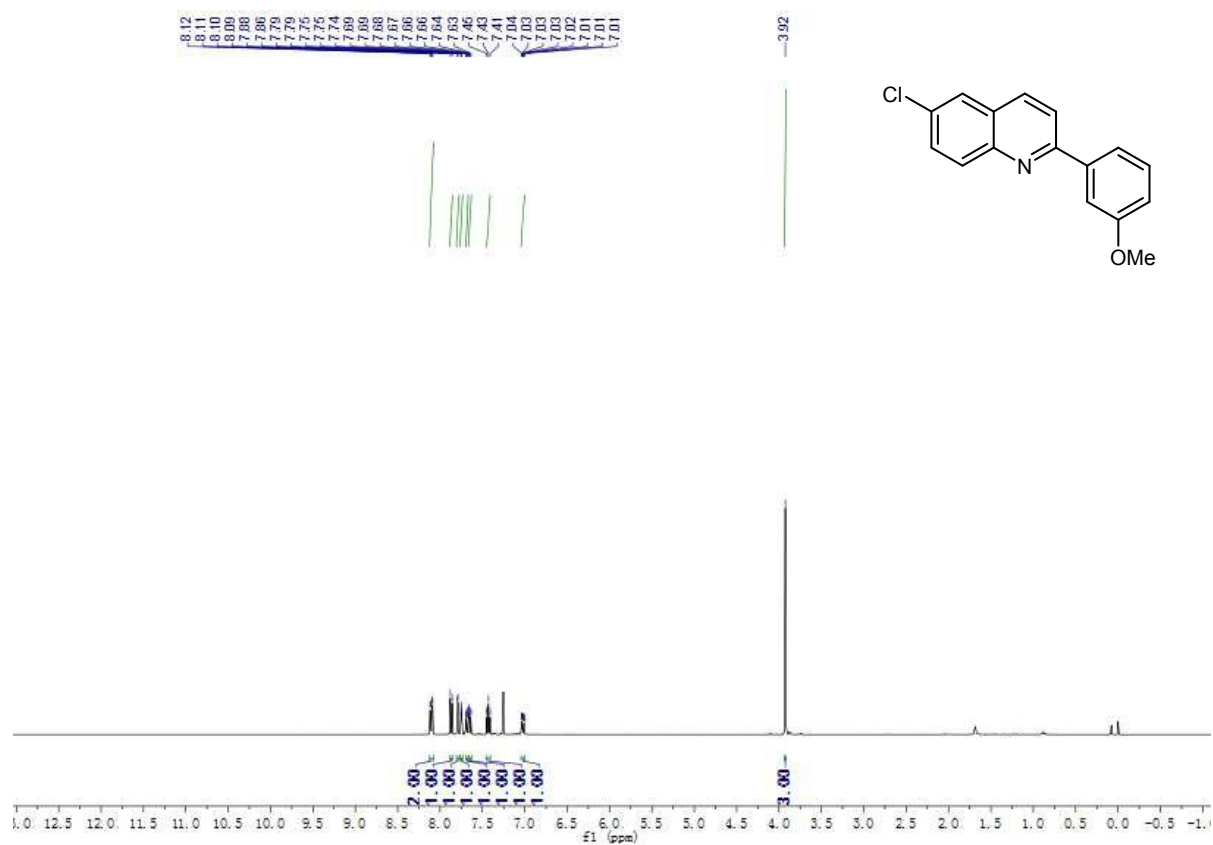


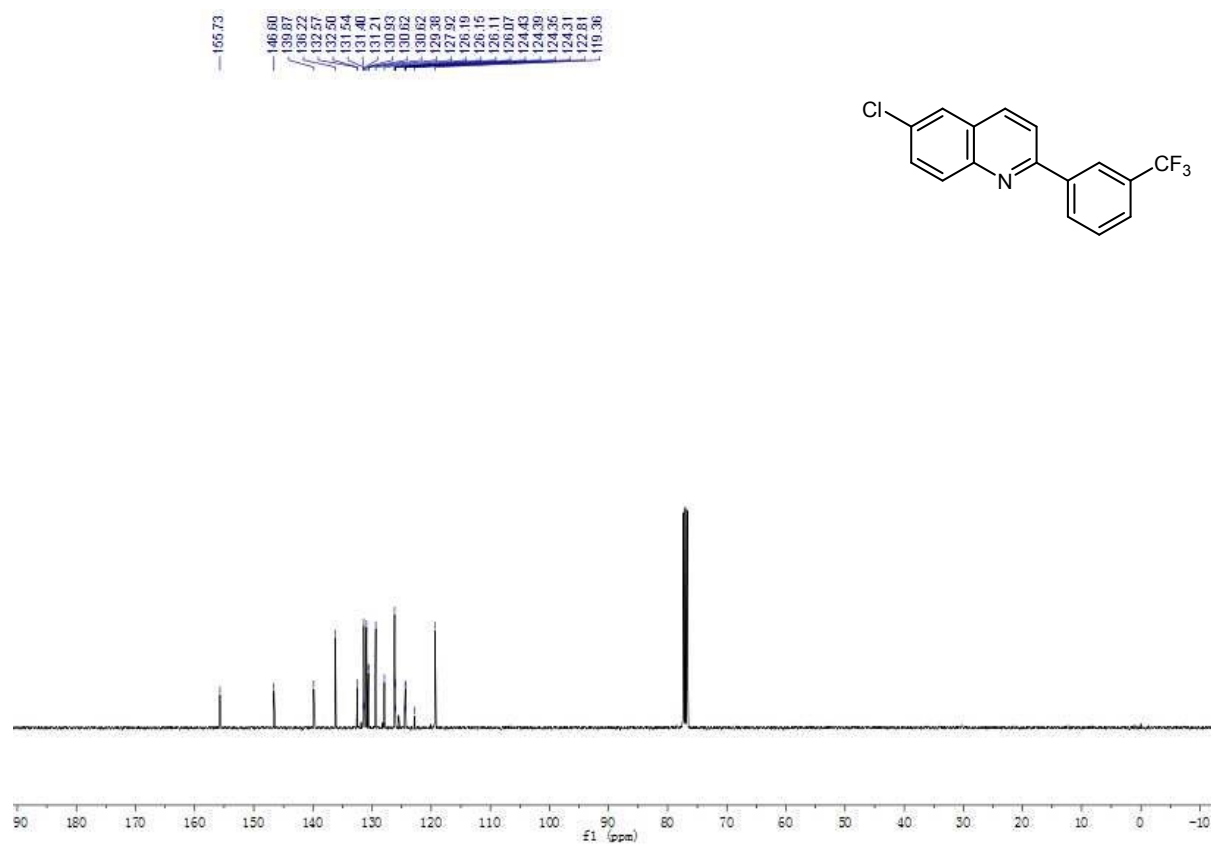
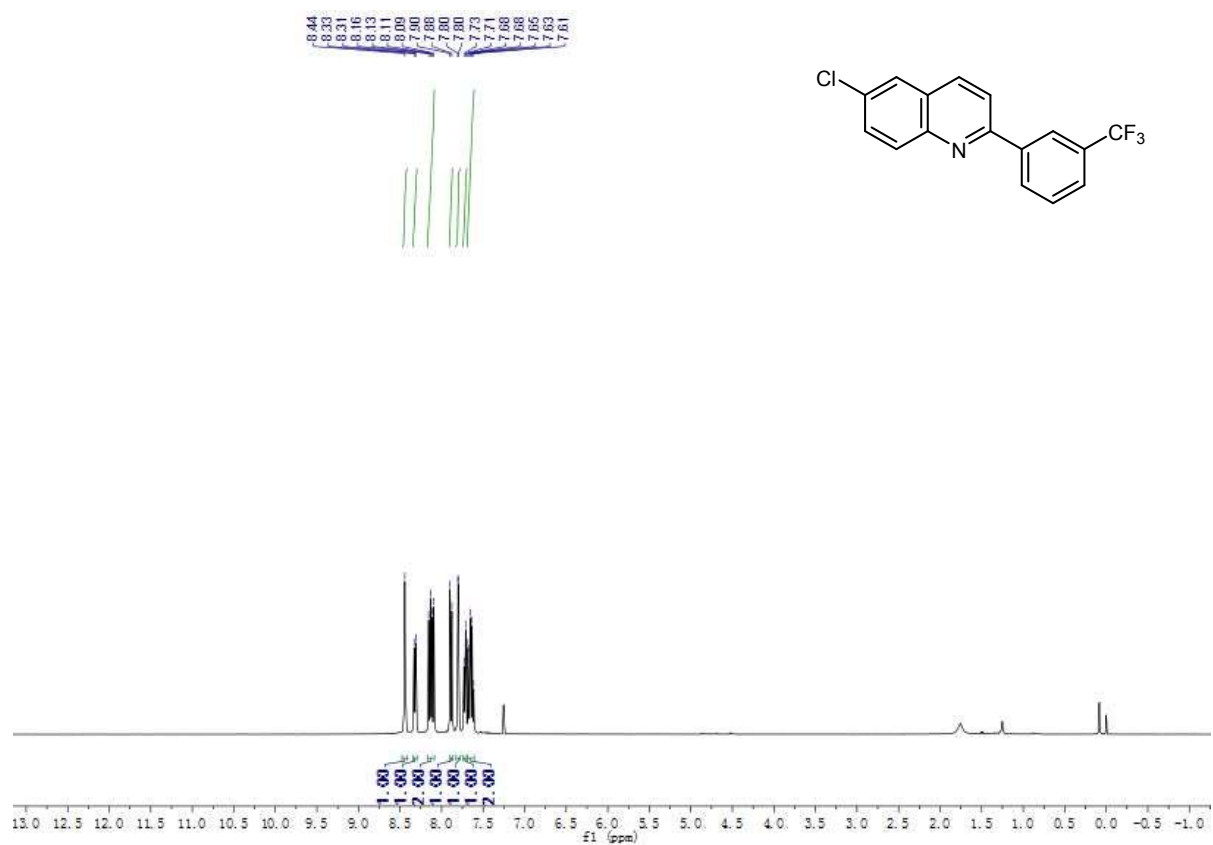


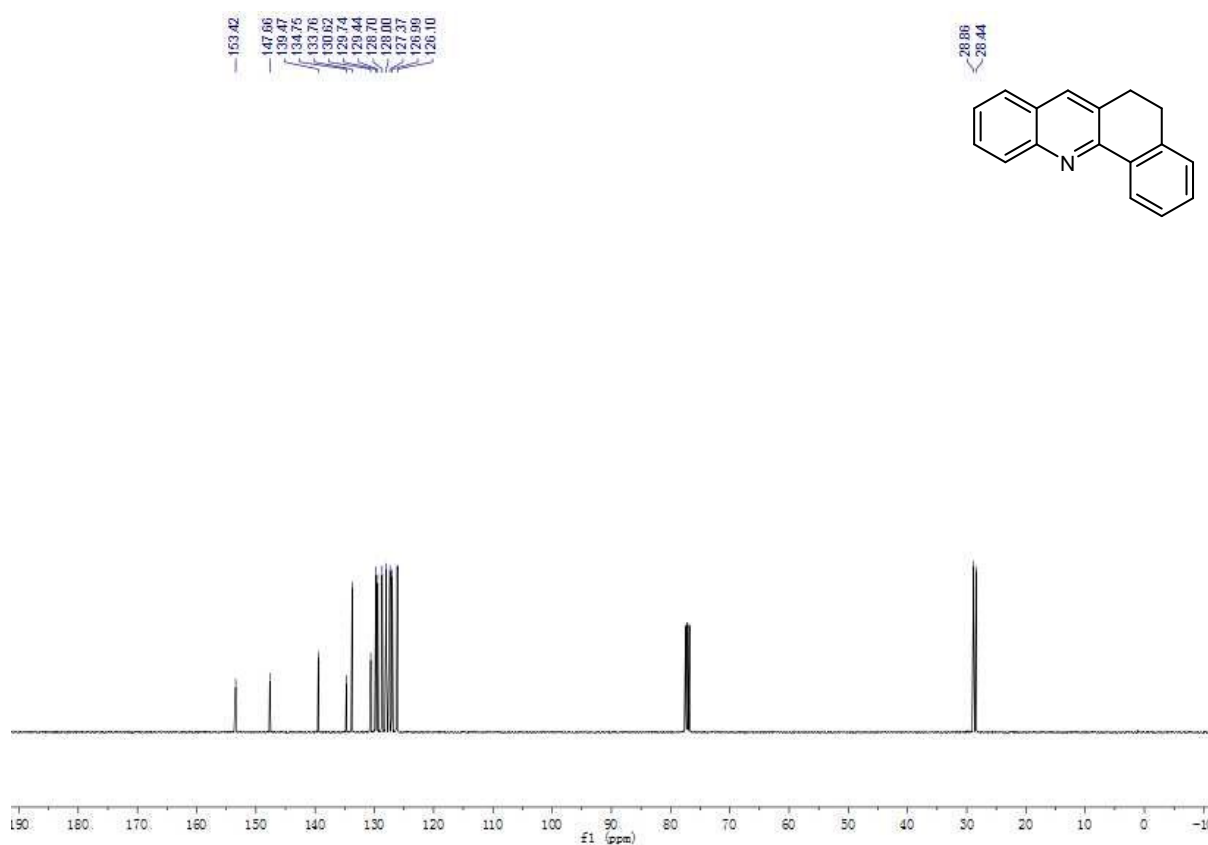
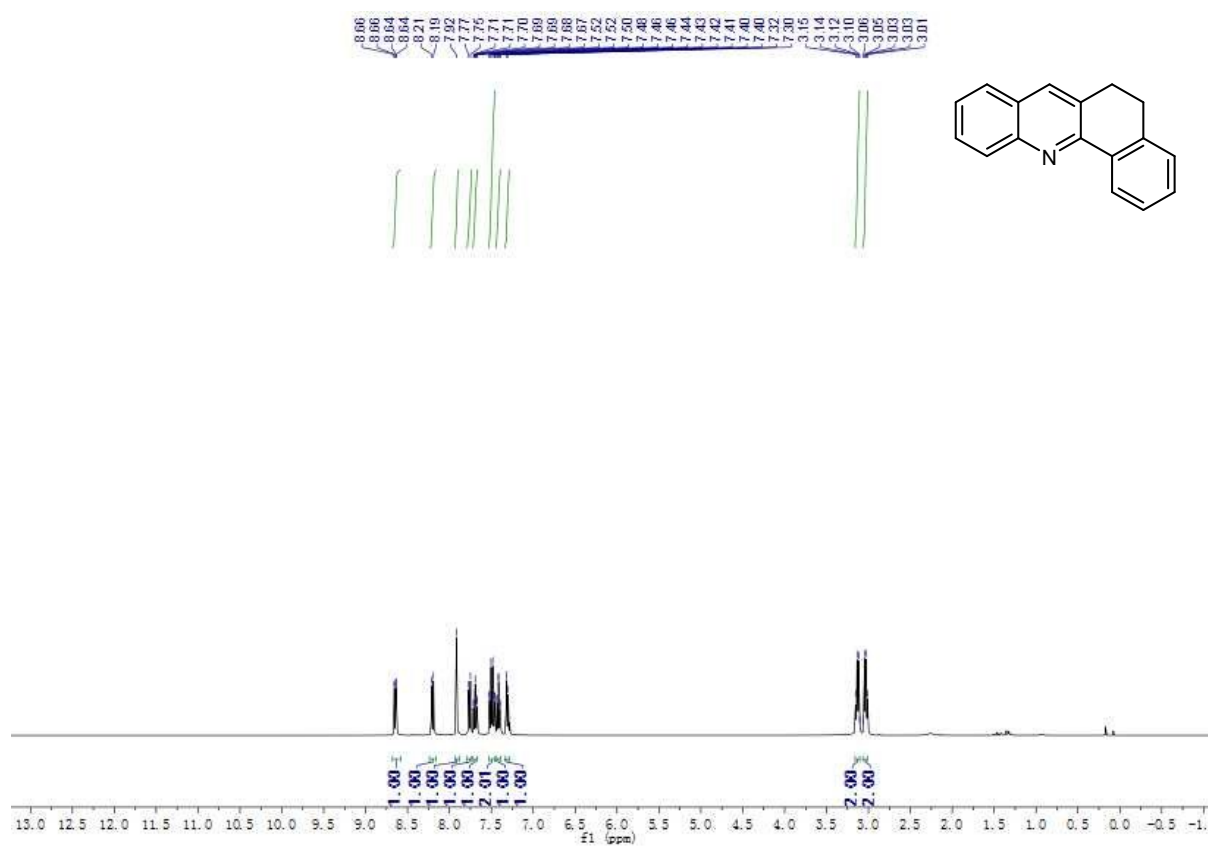


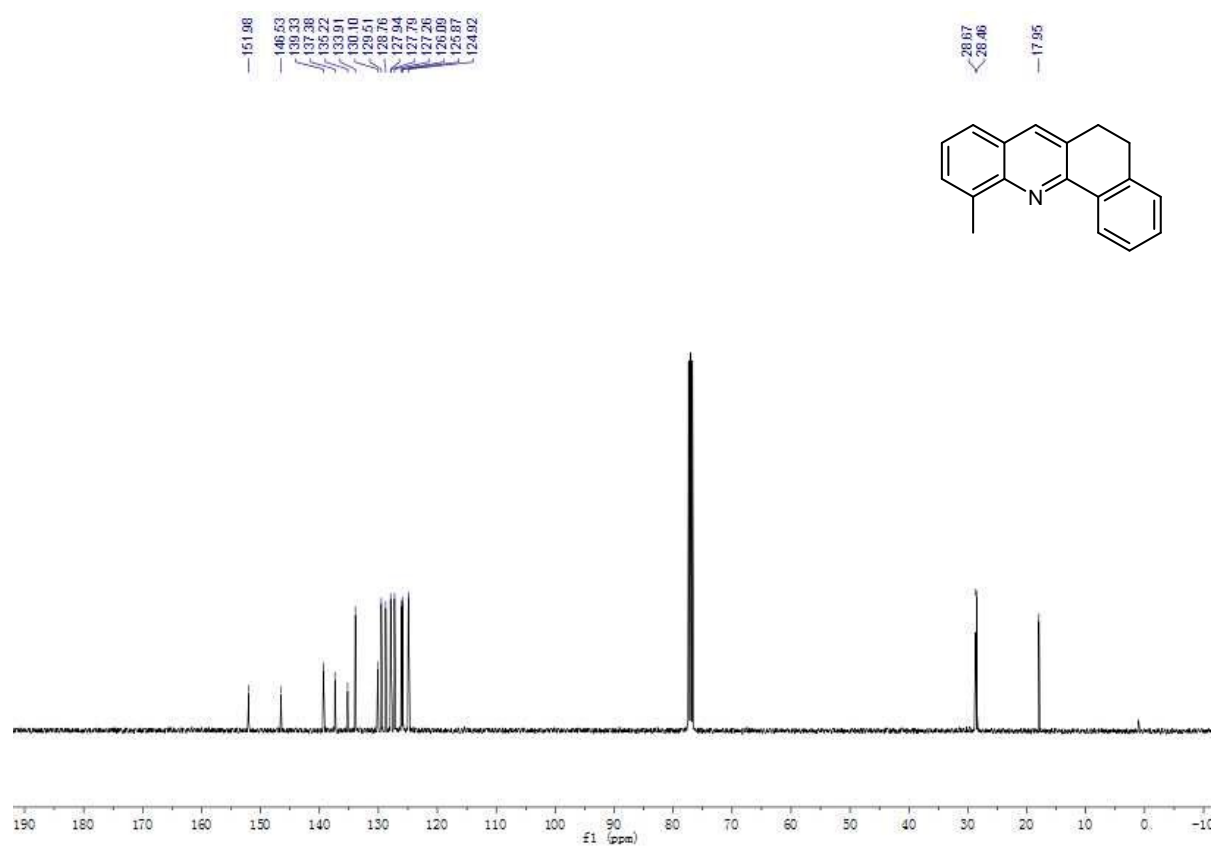
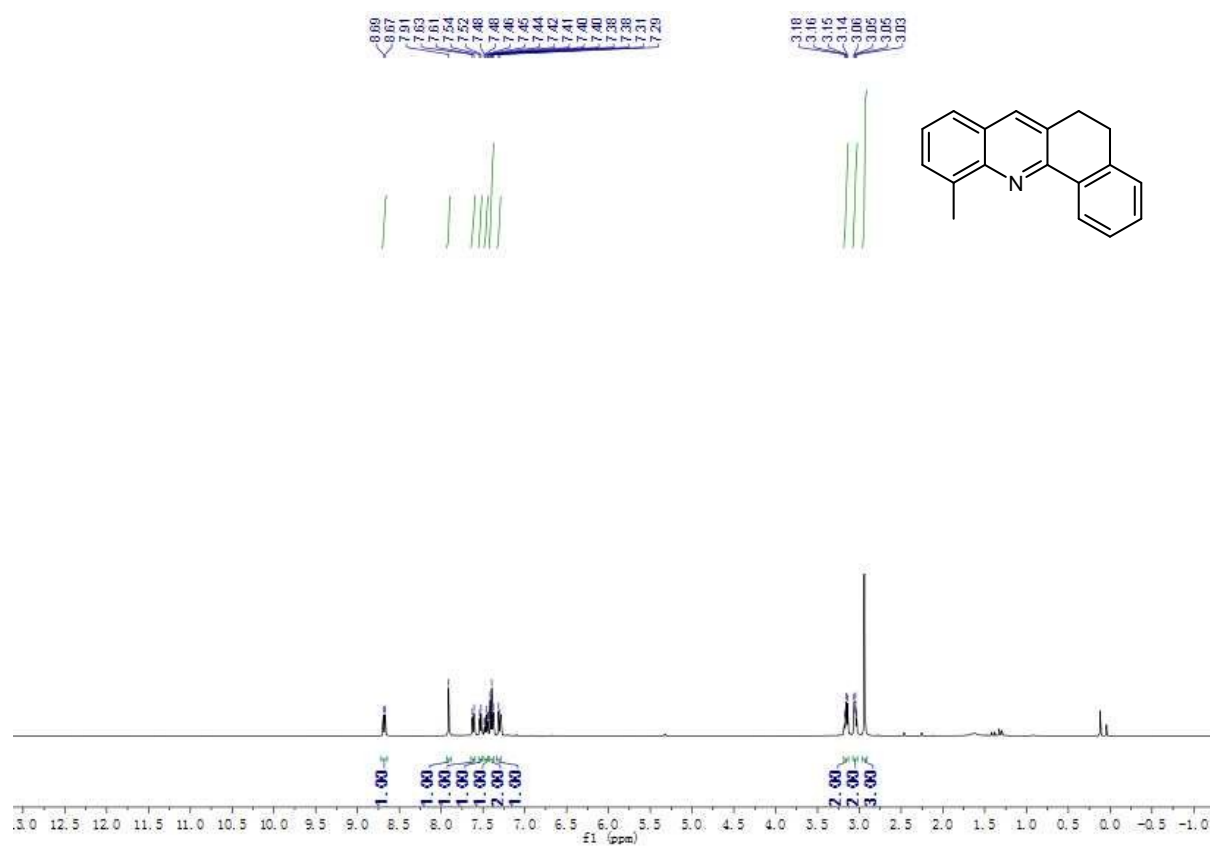


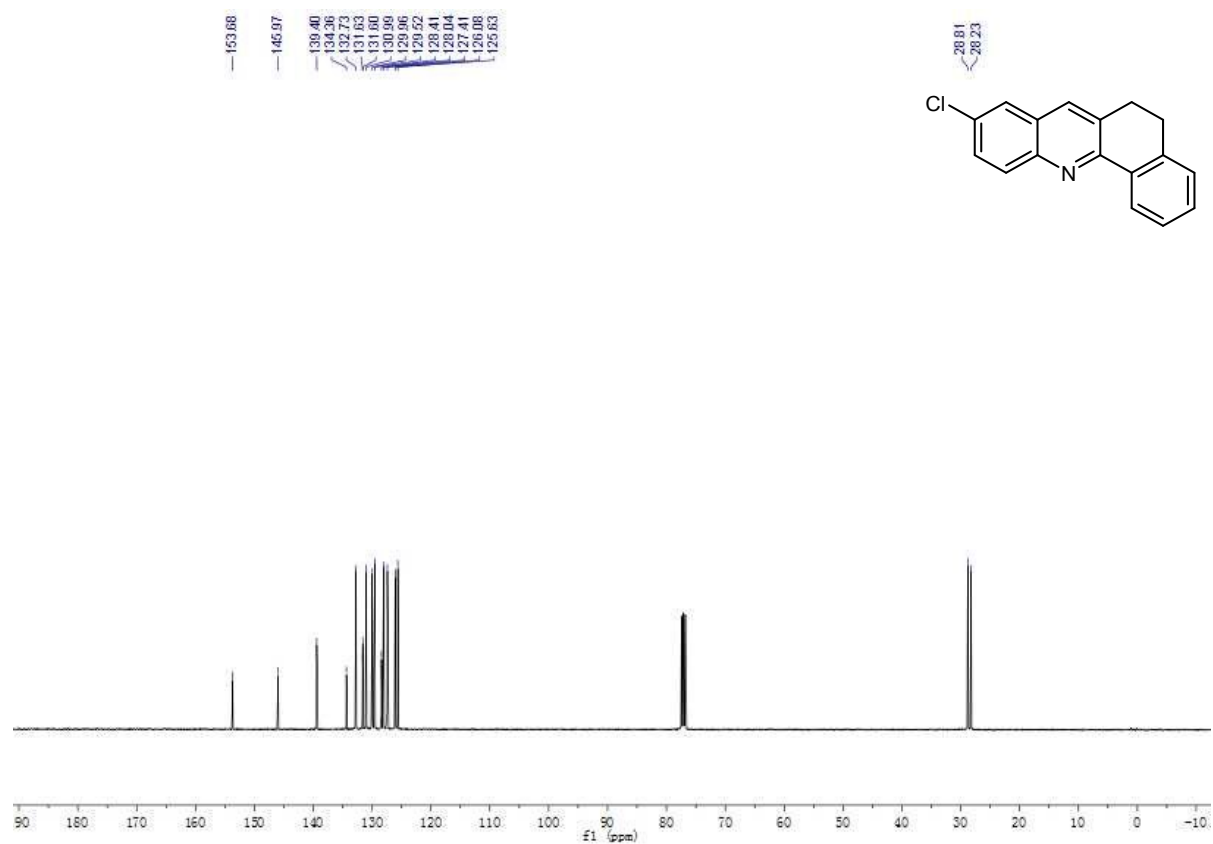
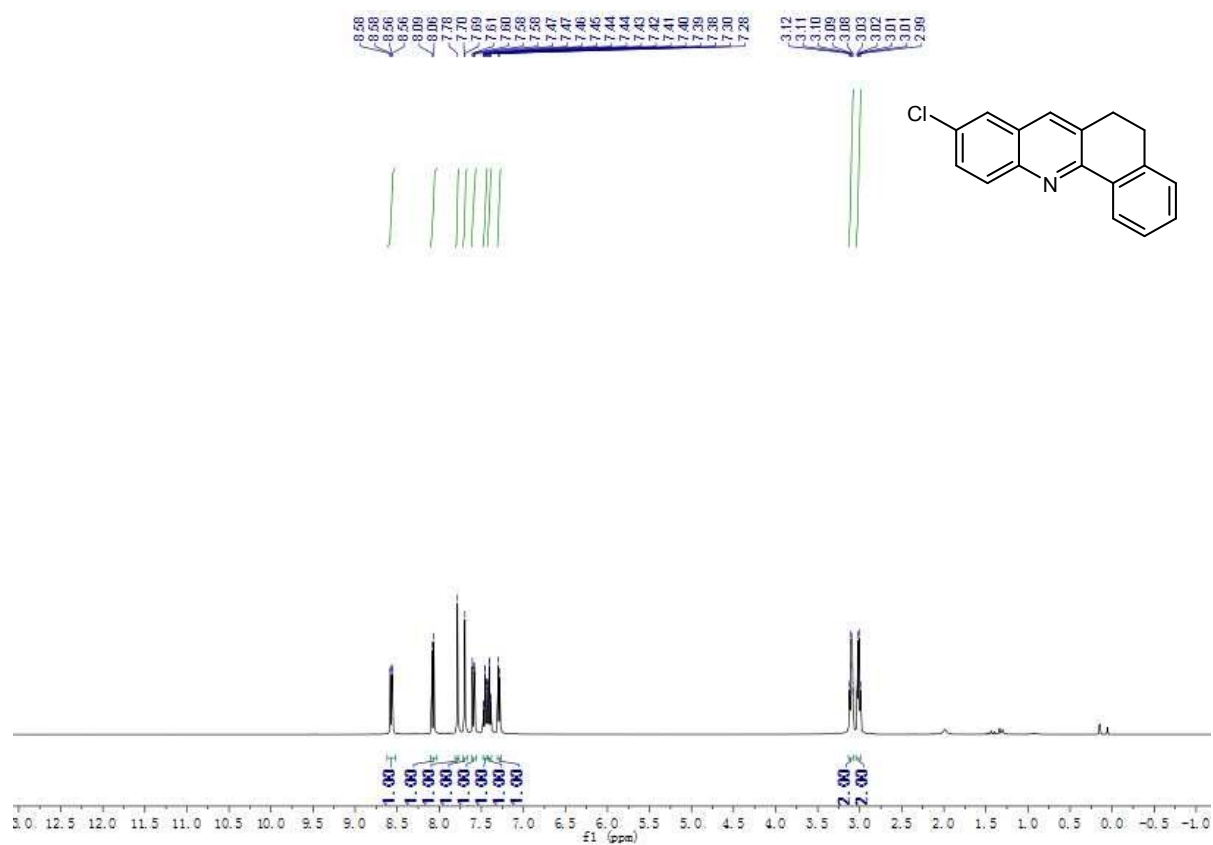


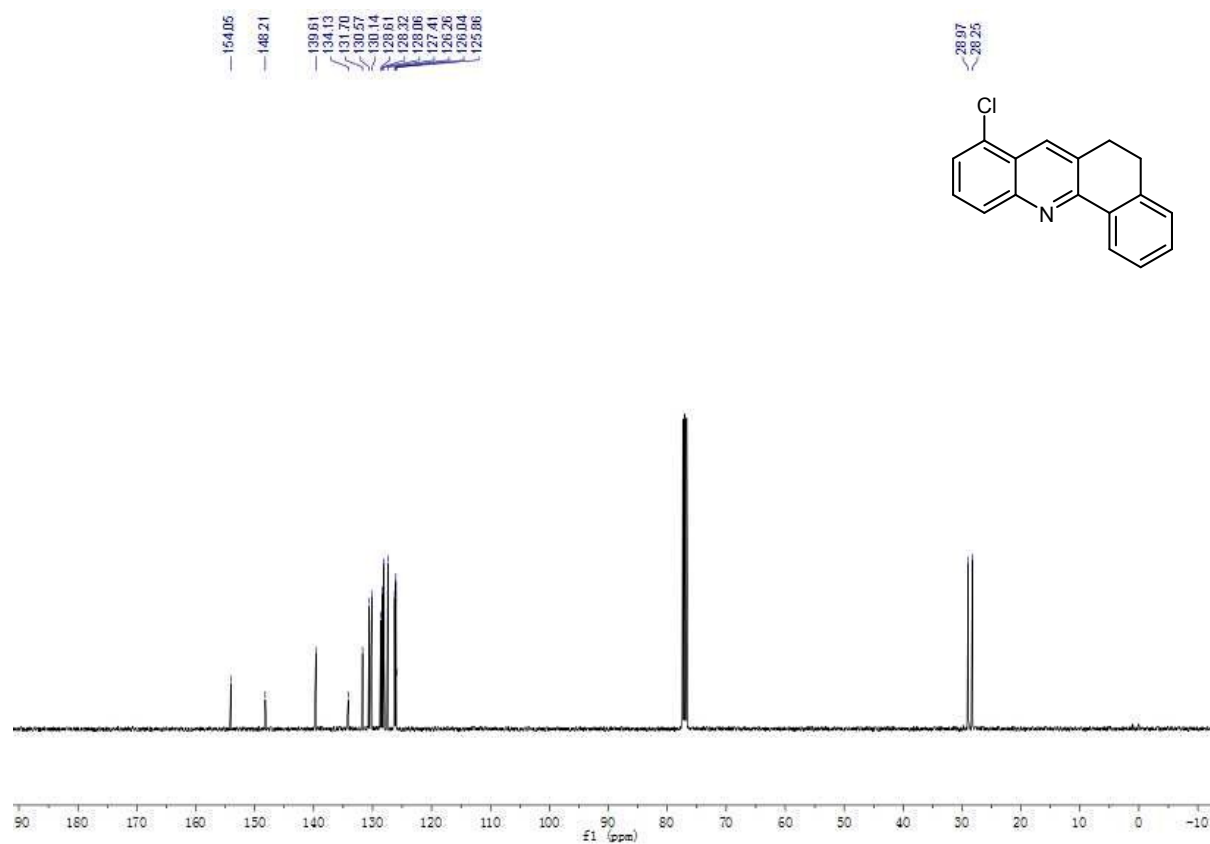
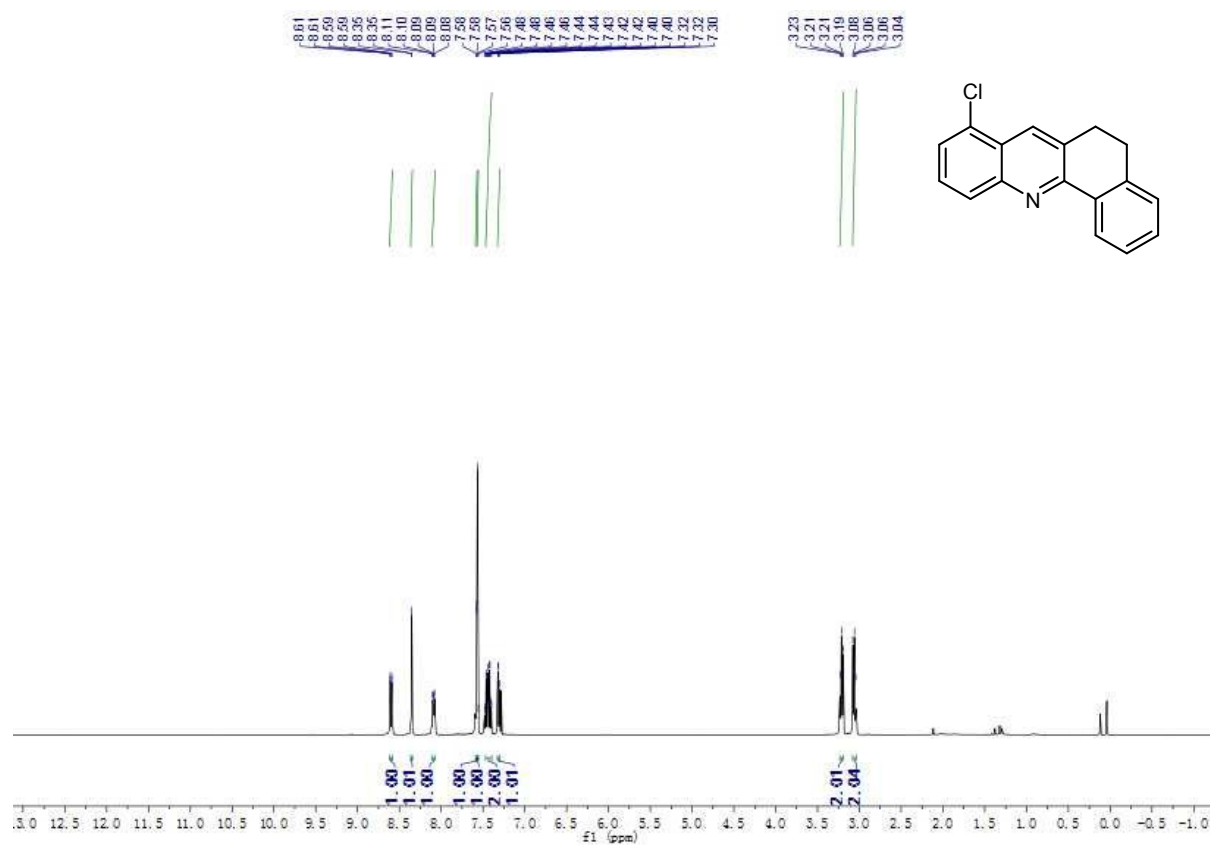


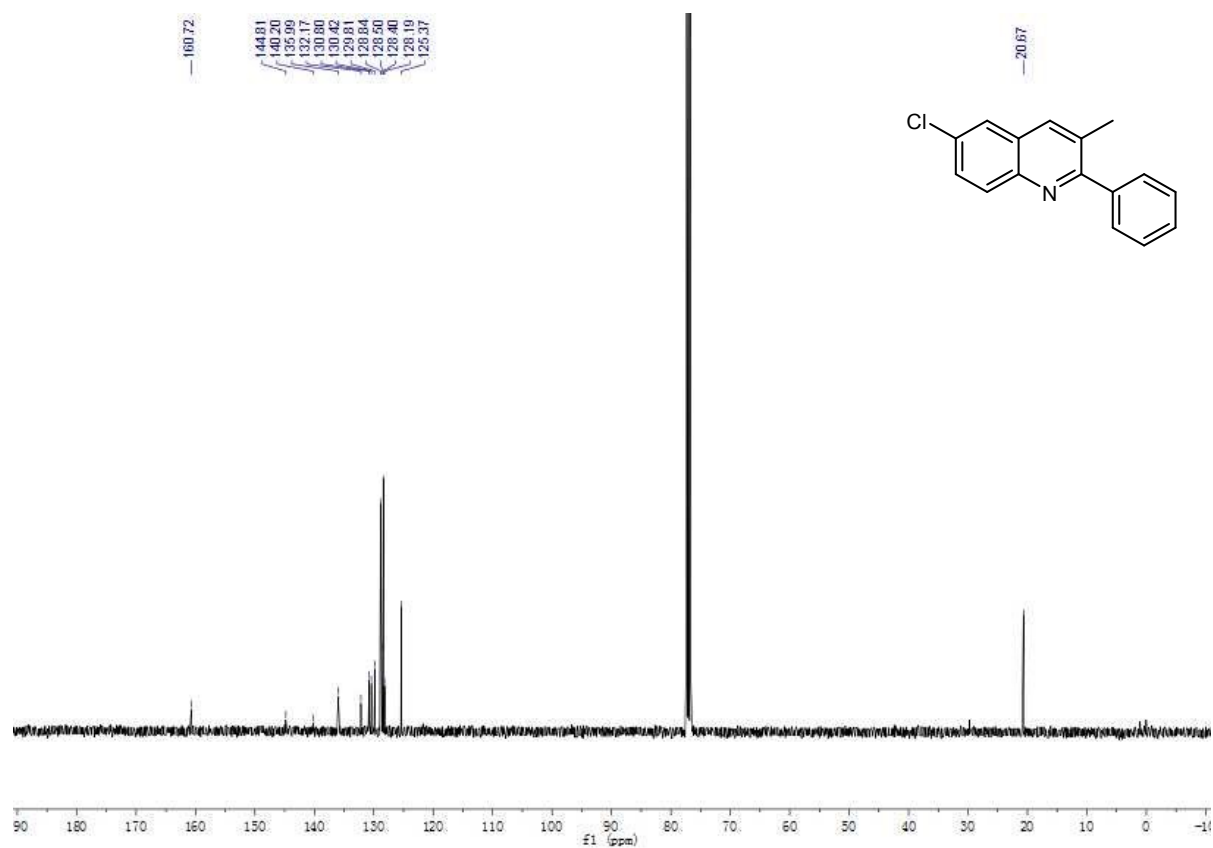
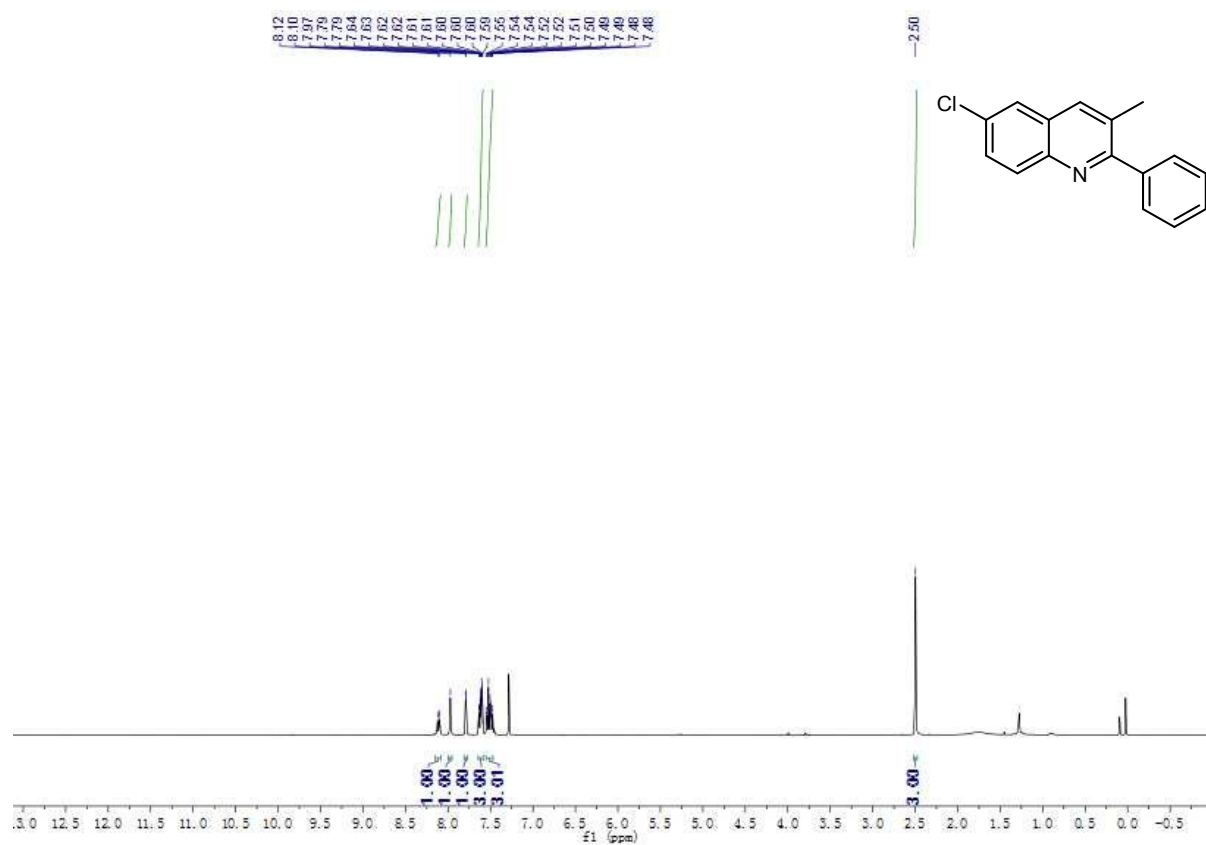


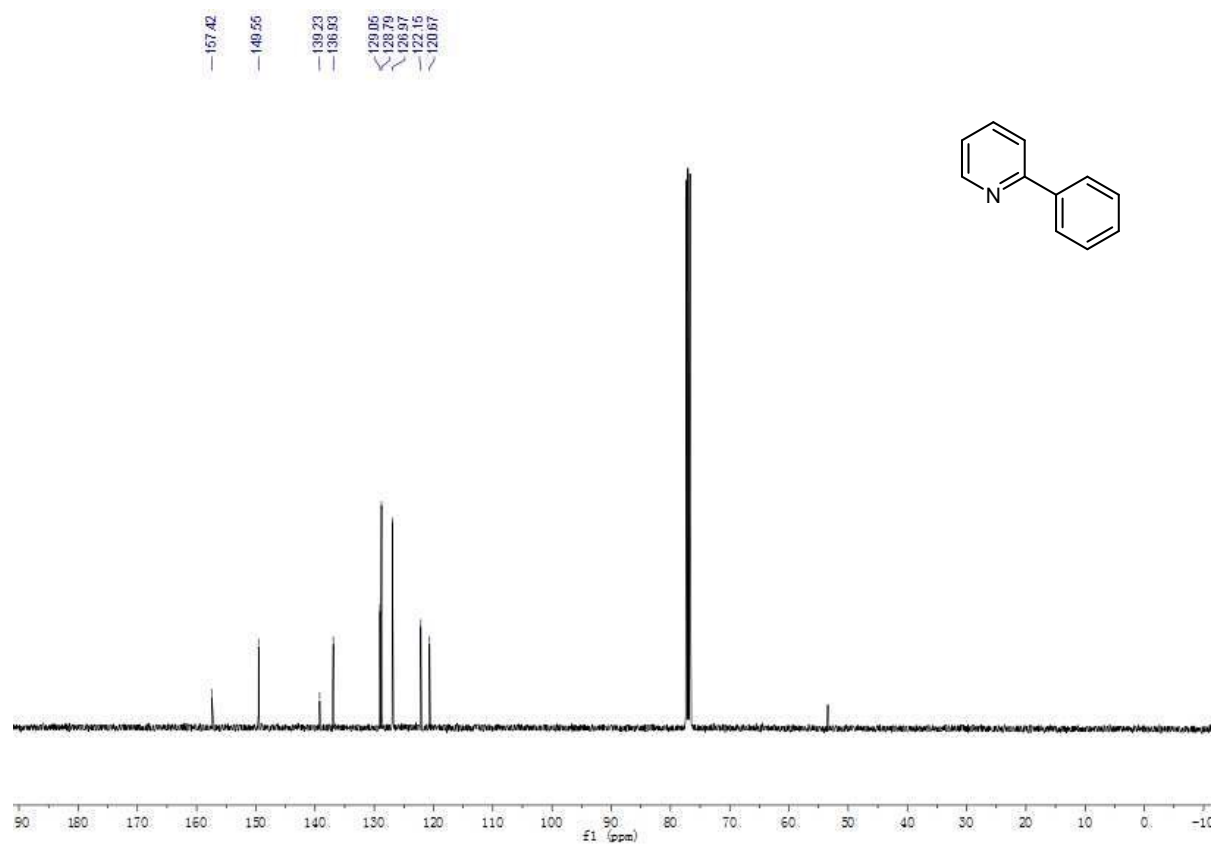
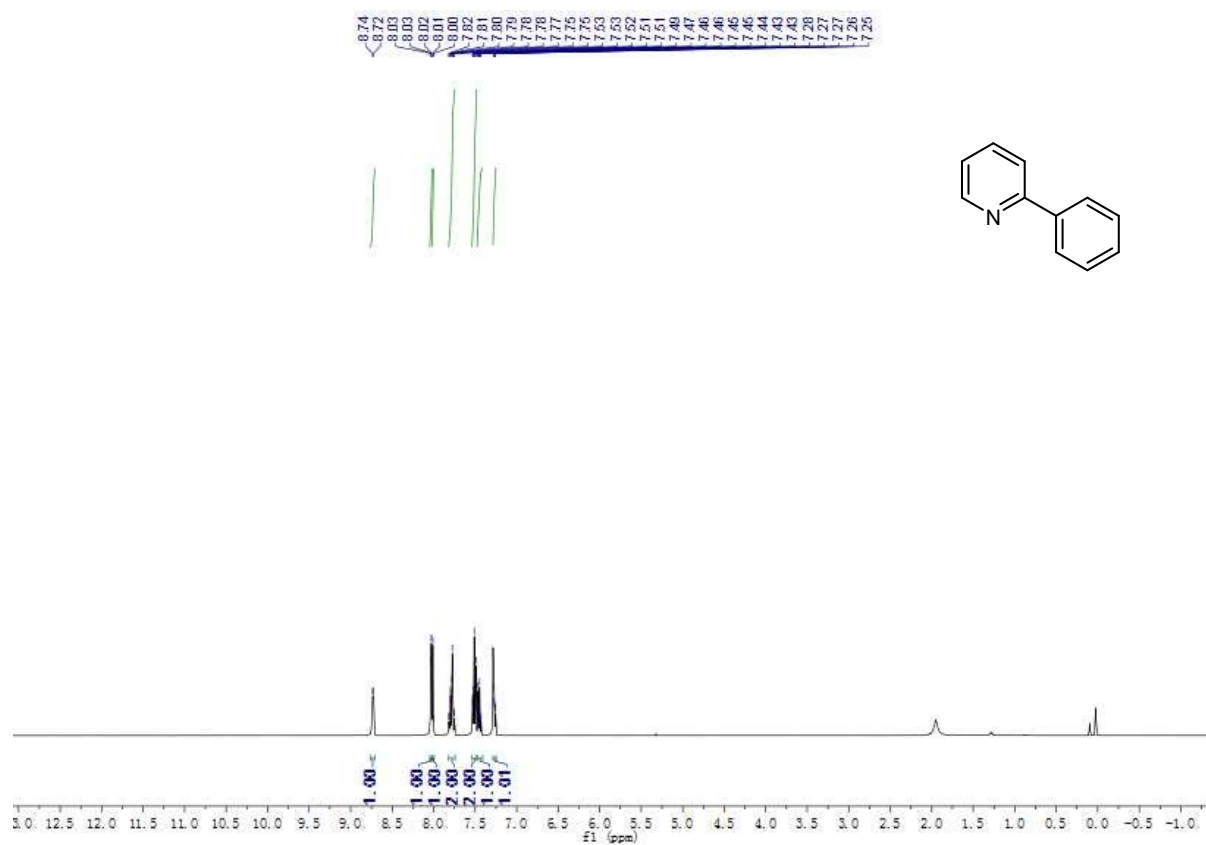


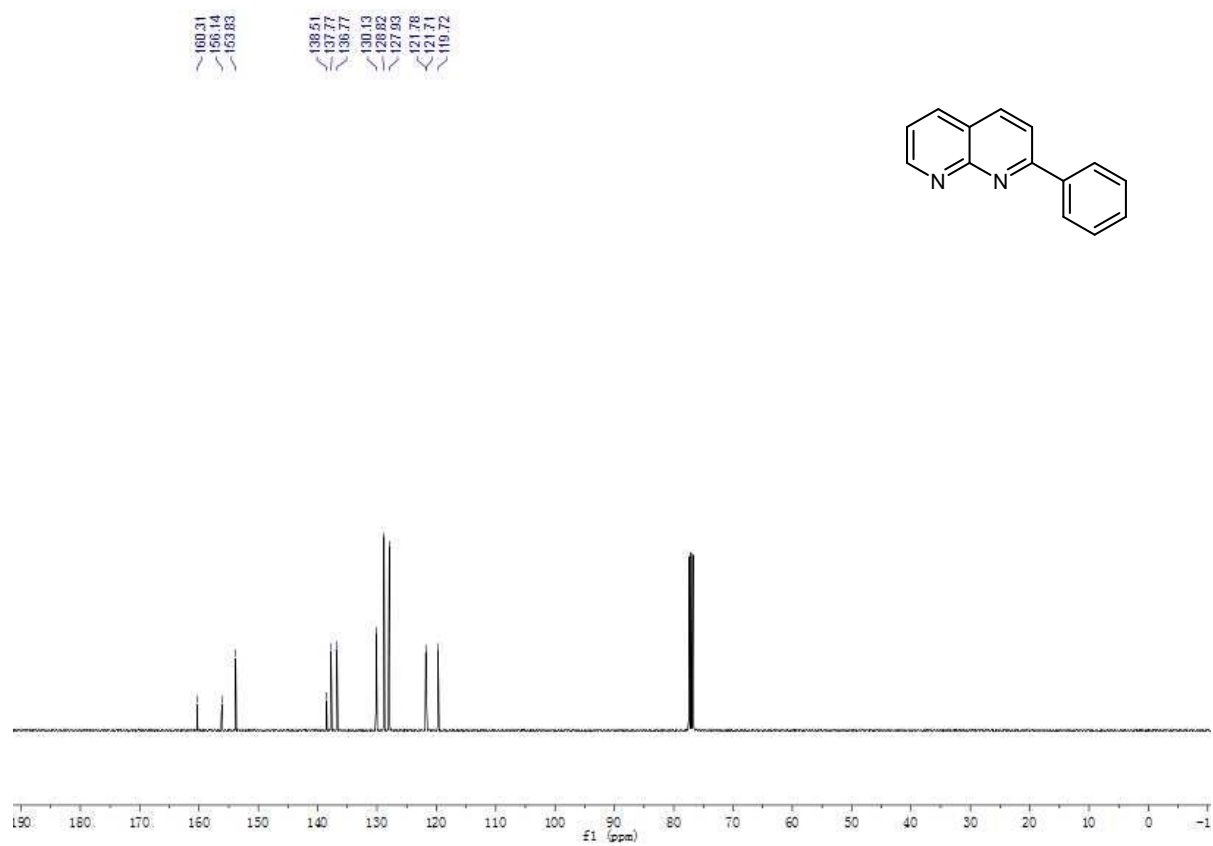
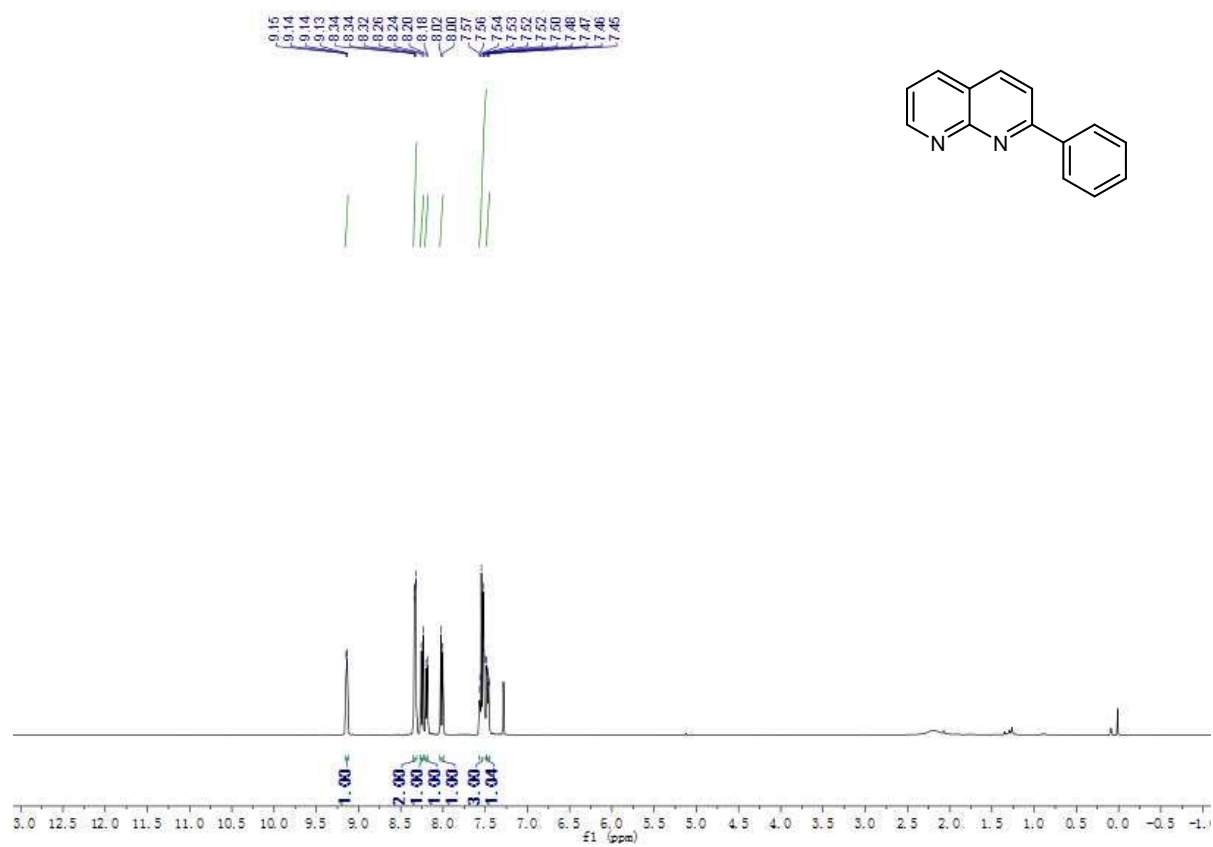


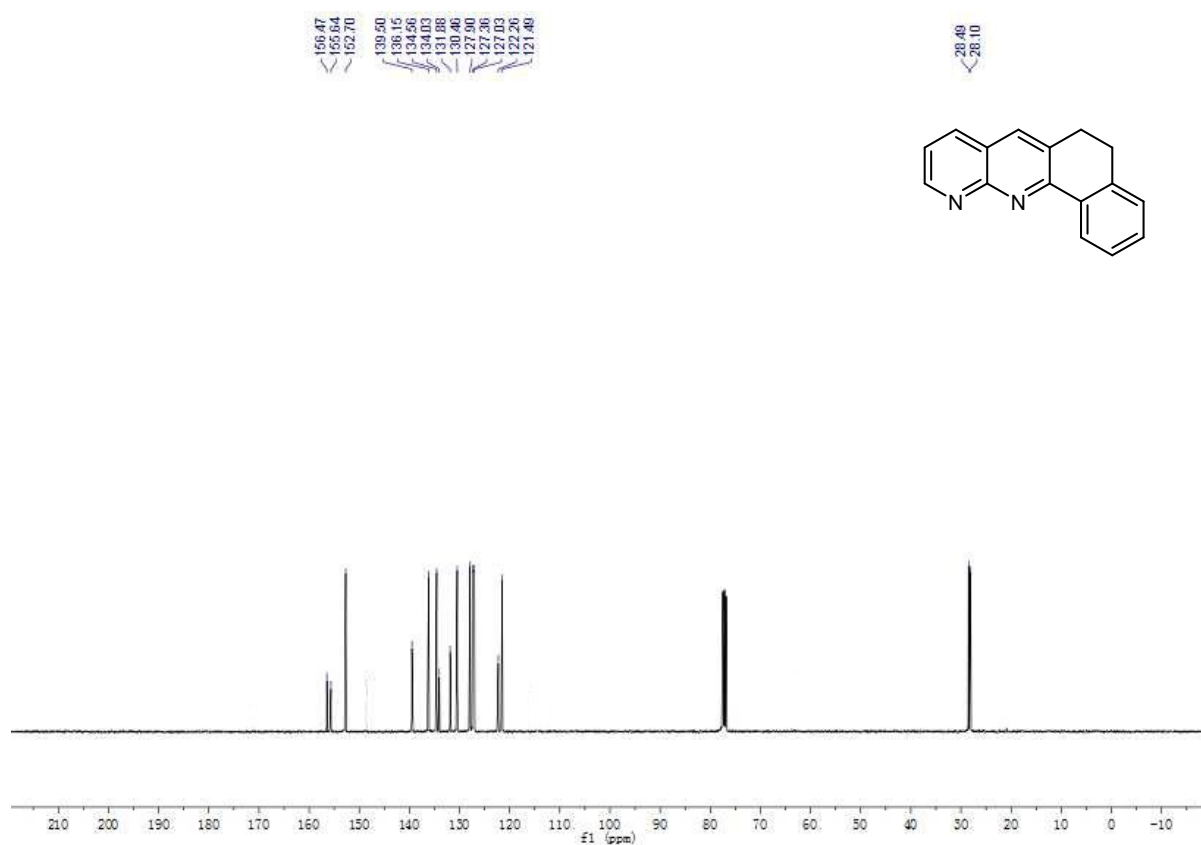
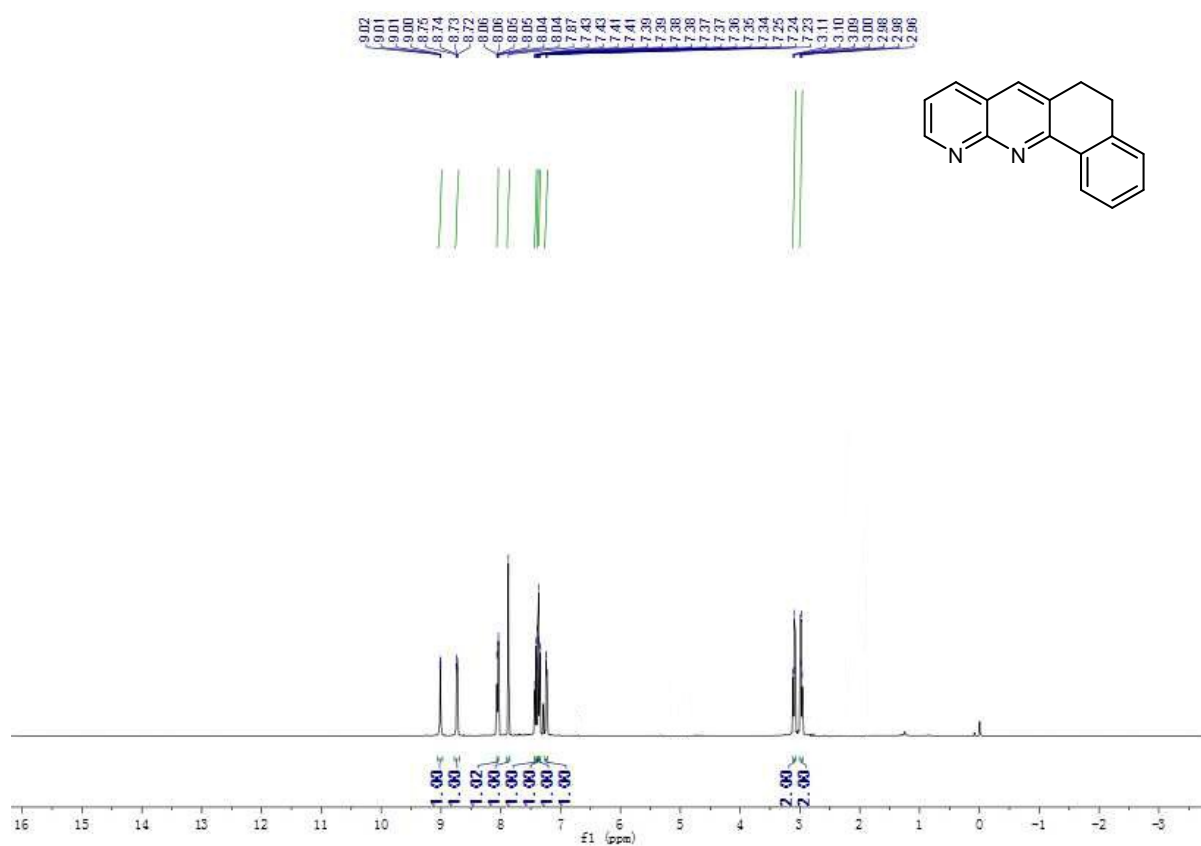


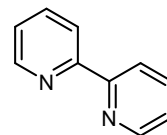
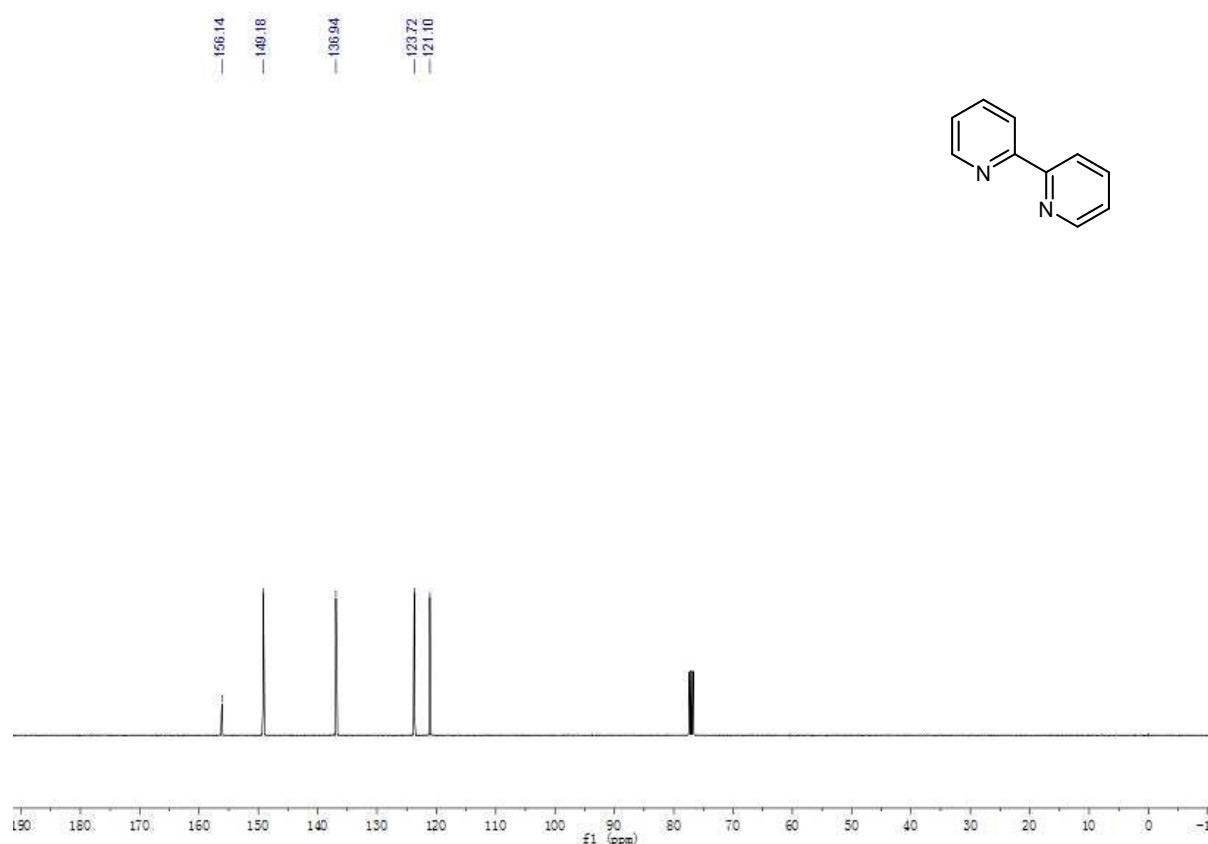
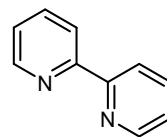
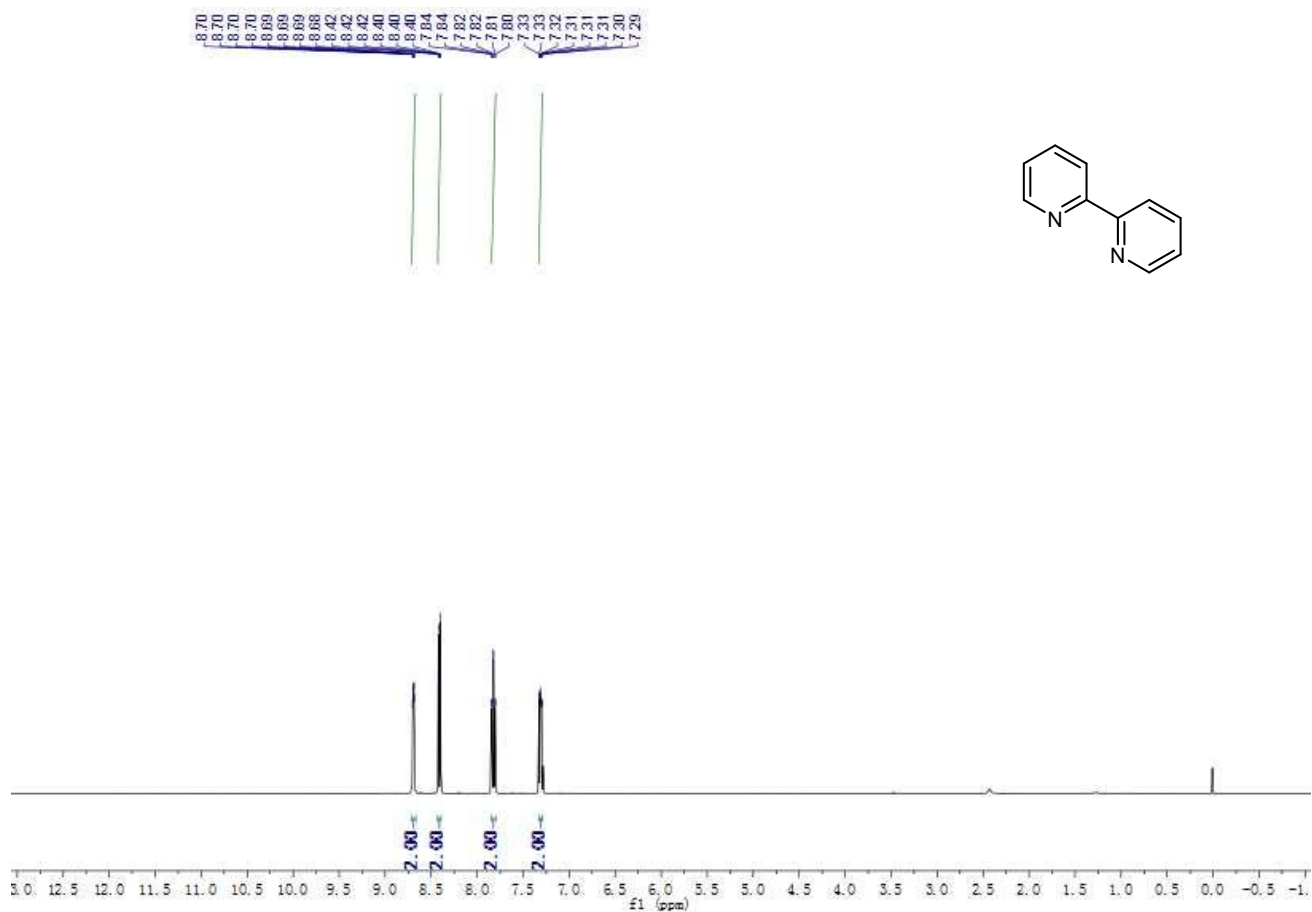


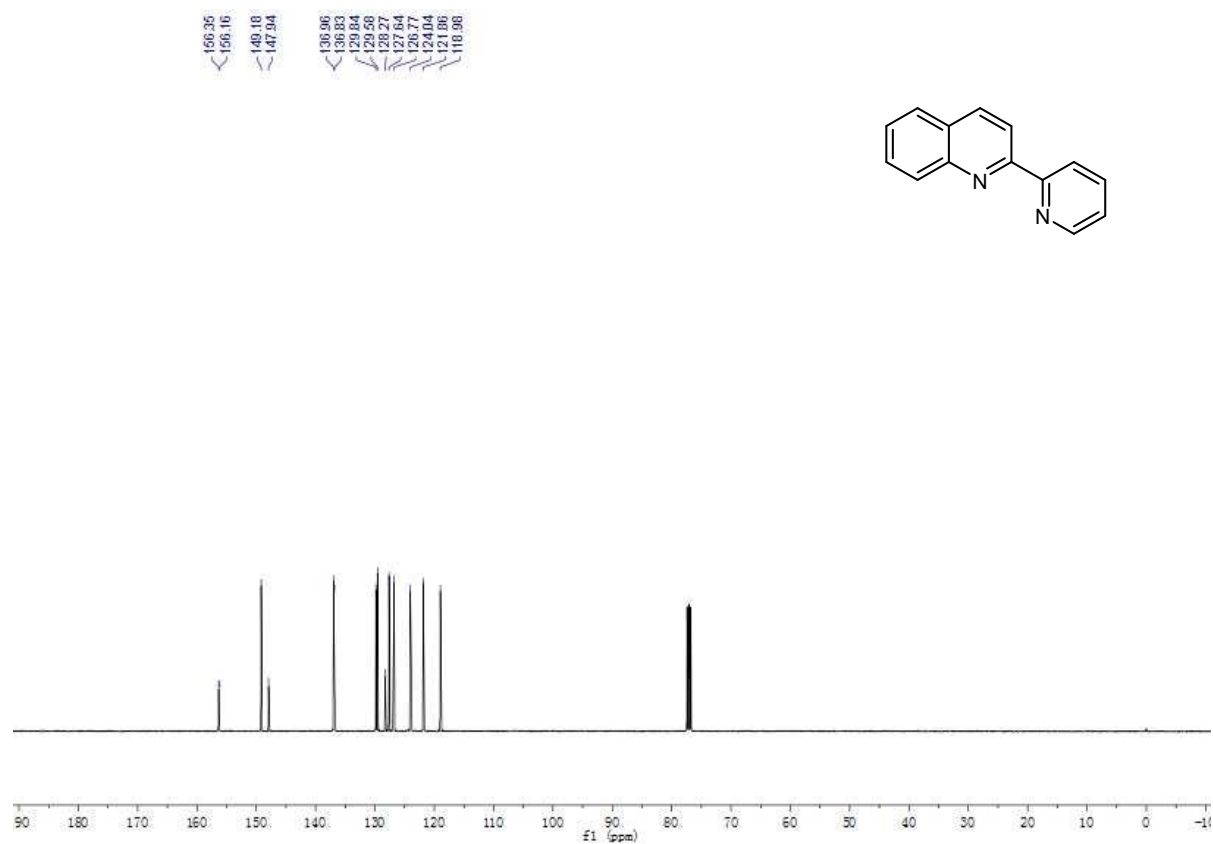
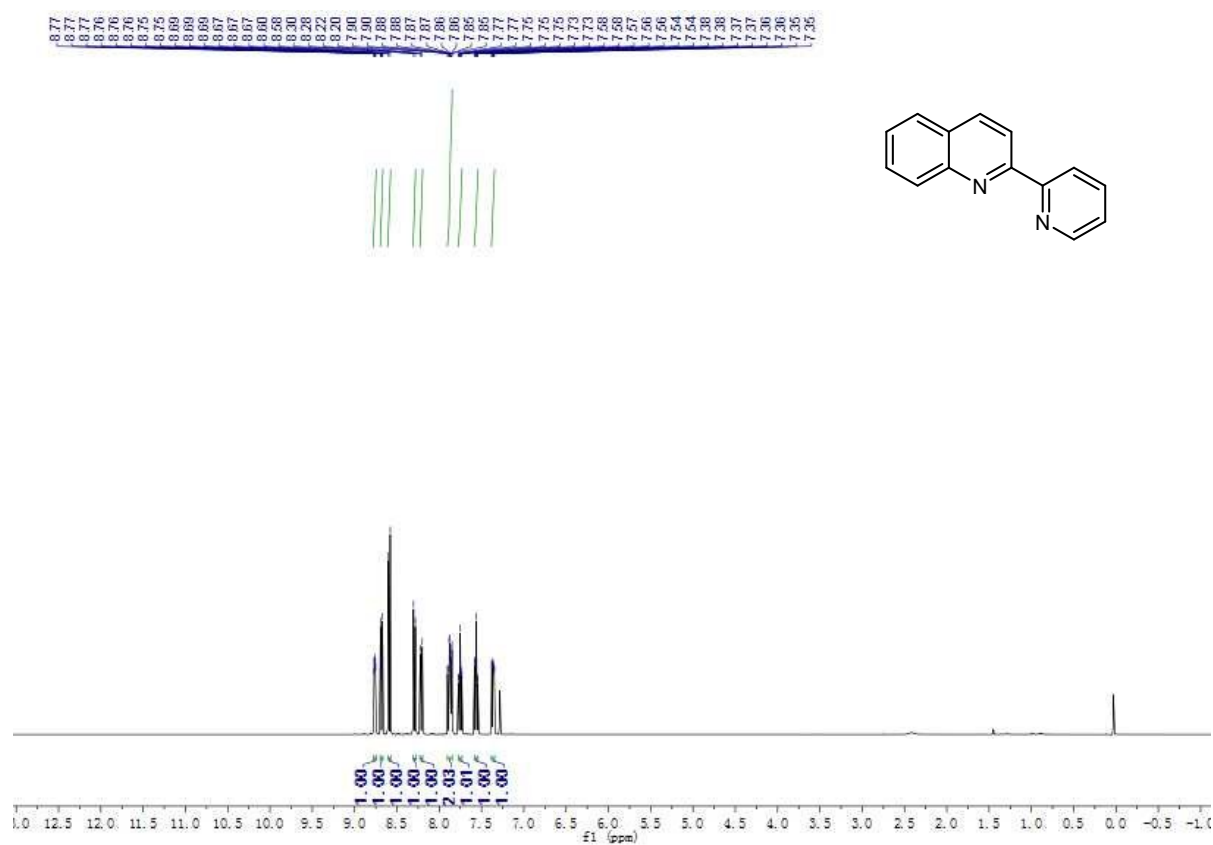


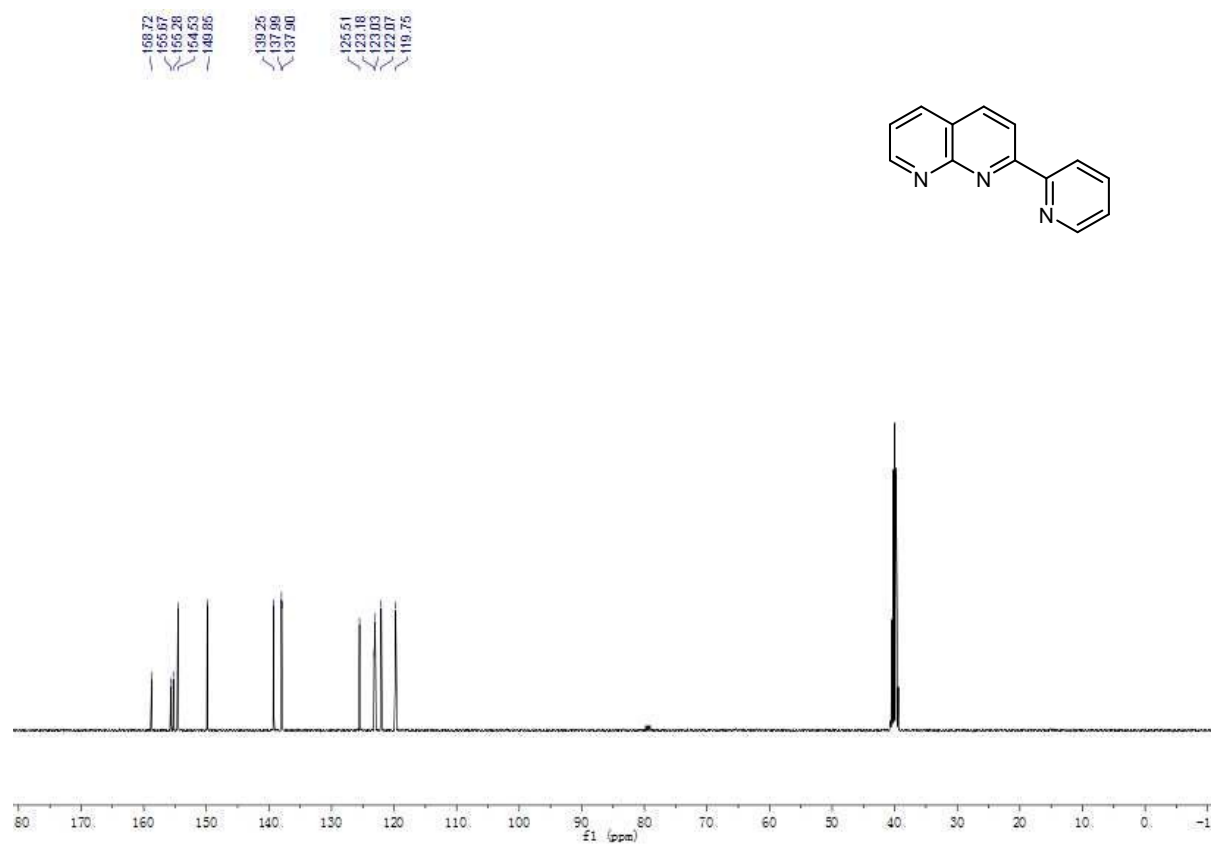
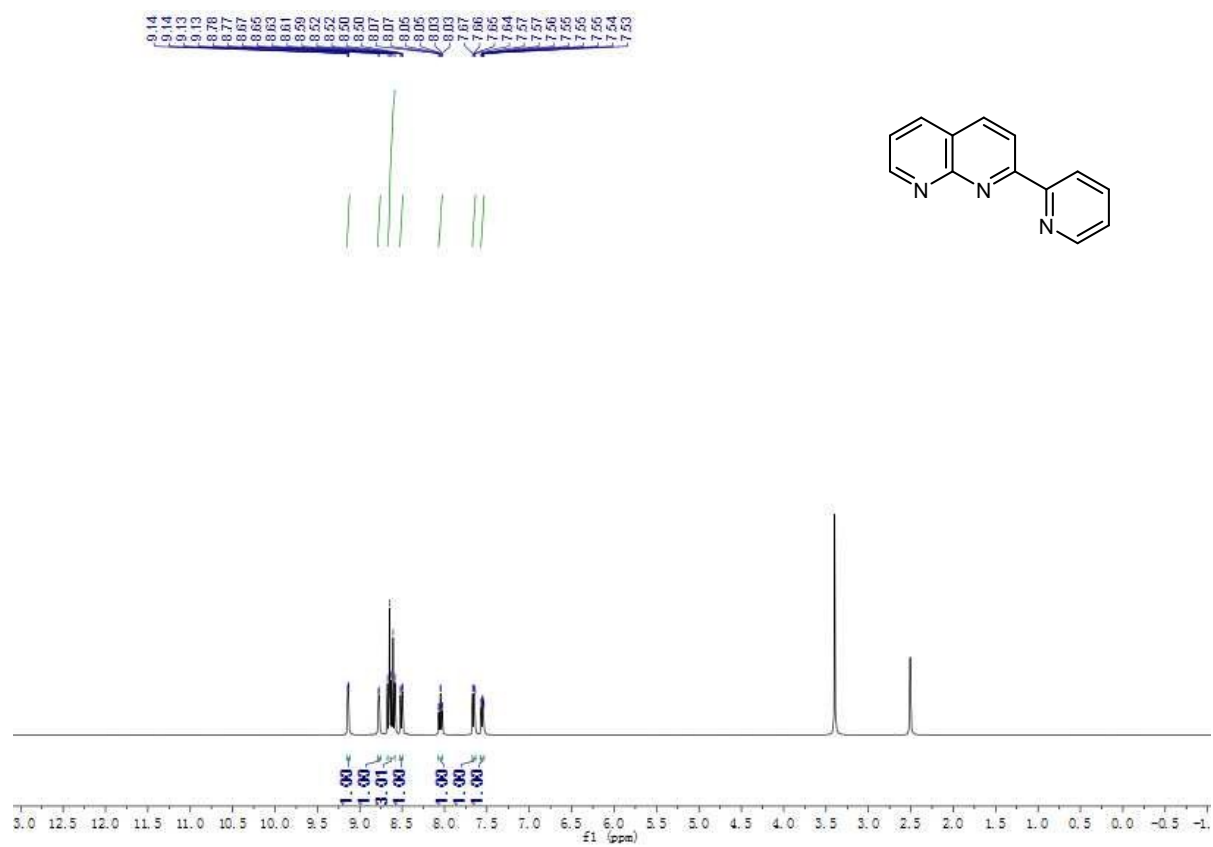












8. Reference

1. a) J. L. Bolliger, M. Oberholzer, and C. M. Frech, *Adv. Synth. Catal.*, 2011, **353**, 945. d) C. Ge, X. Sang, W. Yao, L. Zhang and D. Wang, *Green Chem.*, 2018, **20**, 1805. b) C. Ge, X. Sang, W. Yao, L. Zhang and D. Wang, *Green Chem.*, 2018, **20**, 1805.
2. W. Ye, X. Xiao, L. Wang, S. Hou and C. Hu. *Organometallics*, 2017, **36**, 2116.
3. a) S. Park, J. An, R. D. Piner, I. Jung, D. Yang, A. Velamakanni, S. T. Nguyen, R. S. Ruoff, *Chem. Mater.*, 2008, **20**, 6592. b) Y. Shao, J. Wang, M. Engelhard, *J. Matter. Chem.*, 2010, **24**, 743. c) S. Park, J. An, I. Jung, R. D. Piner, S. J. An, X. Li, A. Velamakanni and R. S. Ruoff, *Nano Lett.*, 2009, **9**, 1593.
4. a) N. Anand, S. Koley, B. J. Ramulu and M. S. Singh, *Org. Biomol. Chem.*, 2015, **13**, 9570. b) R. Wang, H. Fan, W. Zhao and F. Li, *Org. Lett.*, 2016, **18**, 3558. c) Y.-F. Liang, X.-F. Zhou, S.-Y. Tang, Y.-B. Huang, Y.-S. Feng and H.-J. Xu, *RSC Adv.*, 2013, **3**, 7739. d) Y. Zhu and C. Cai, *RSC Adv.*, 2014, **4**, 52911. e) M. K. Barman, A. Jana and B. Maji, *Adv. Synth. Catal.*, 2018, **360**, 3233. f) G. Chakraborty, R. Sikari, S. Das, R. Mondal, S. Sinha, S. Banerjee and N. D. Paul, *J. Org. Chem.*, 2019, **84**, 2626.