Supporting Information

Metal-Free Photoinduced-Radical Hydrocyclization of 2-Isocyanides: A Unified Synthetic Approach to Facilely Assemble Diverse α-Unsubstituted *N*-Heteroarenes

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A. General information:

All reactions were carried out under nitrogen atmosphere and involving air- or moisture-sensitive reagents or intermediates were carried out in pre-heated glassware using standard Schlenk techniques. All reagents were used as received unless otherwise noted. DCM and MeCN were dried over CaH_2. THF were dried over sodium.

Thin layer chromatography (TLC) was performed with 0.25 m coated commercial silica gel plates (TLC Silica Gel 60 F254) and visualized by fluorescence quenching under UV light (254 nm and 365 nm). Flash chromatography was performed with silica gel (300-400 mesh).

Proton nuclear magnetic resonance (^{1}H NMR) data were acquired on Bruker Ascend 400 (400 MHz) spectrometer. Chemical shifts are reported in delta (δ) units, in parts per million (ppm) downfield from tetramethylsilane. Splitting patterns are designated as s, singlet; d, doublet; dd, quartet; t, triplet; q, quartet; m, multiple; dd, double doublet. Coupling constants J is quoted in Hz. Carbon-13 nuclear magnetic resonance (^{13}C NMR) data were acquired at 100 MHz on Bruker Ascend 400 spectrometer. Chemical shifts are reported in ppm relative to the center line of a triplet at 77.0 ppm for chloroform-d. Fluorine nuclear magnetic resonance (^{19}F NMR) data were acquired at 376 MHz on a JEOL ECZ 400 spectrometer.

Mass spectra were acquired on a Bruker Daltonics MicroTof-Q II mass spectrometer.

UV-Vis spectra were determined on a Hitachi U-2900 spectrometer. Fluorescence spectra were acquired on a Hitachi F-4600 fluorescence spectrometer with a 10-mm quartz cuvette.

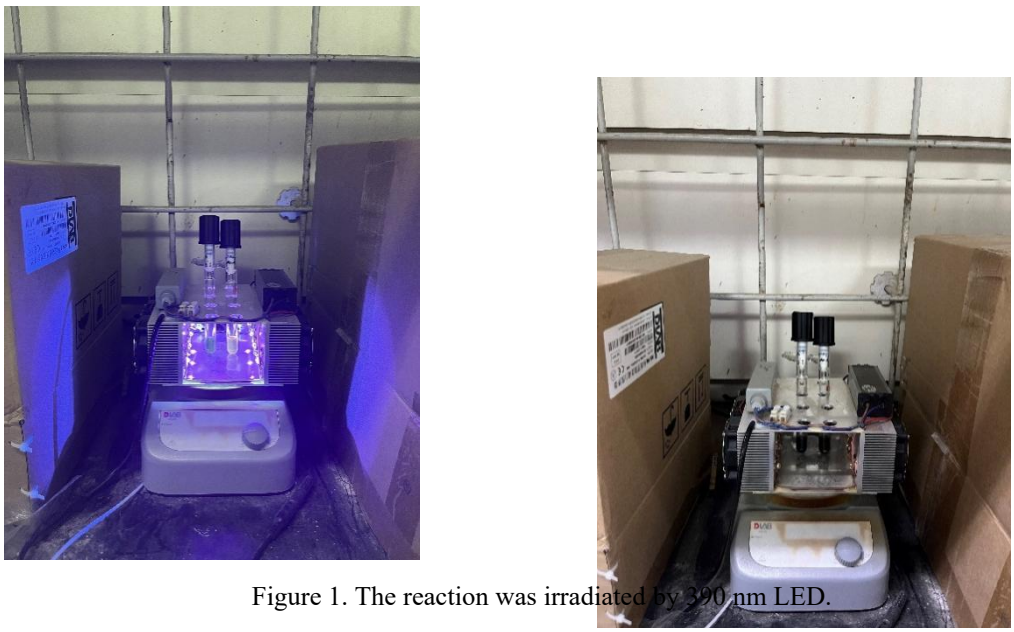
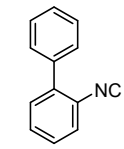


Figure 1. The reaction was irradiated by 390 nm LED.

B. Preparation of the starting materials

Substrates Preparation:



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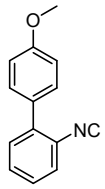

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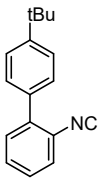

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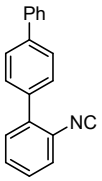

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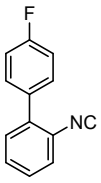

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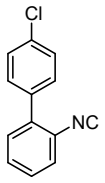

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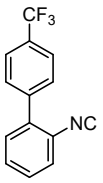

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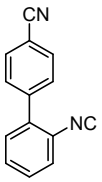

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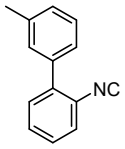

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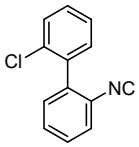

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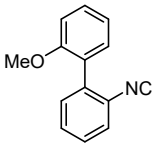

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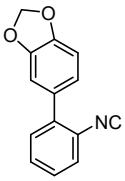

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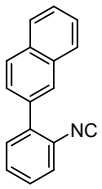

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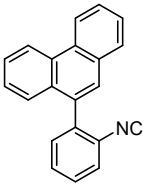

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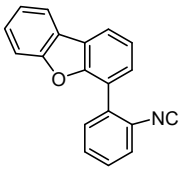

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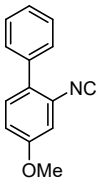

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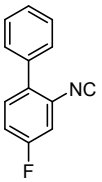

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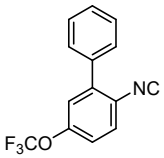

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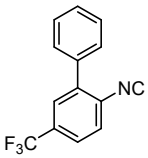

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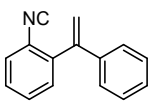

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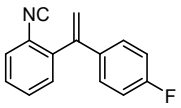

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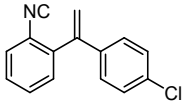

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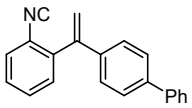

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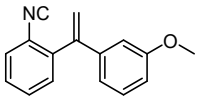

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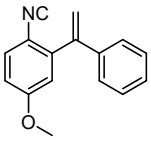

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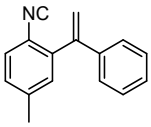

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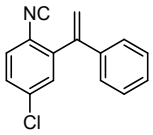

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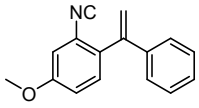

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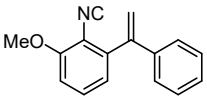

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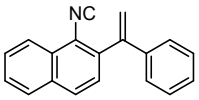

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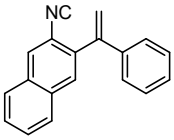

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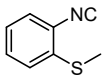

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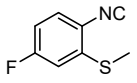

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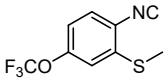

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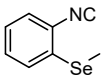

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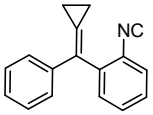

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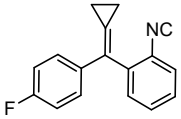

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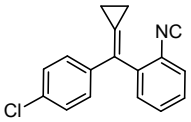

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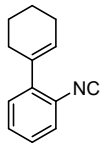

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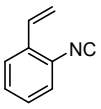

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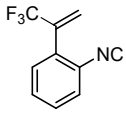

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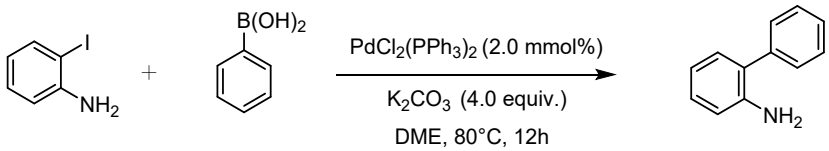
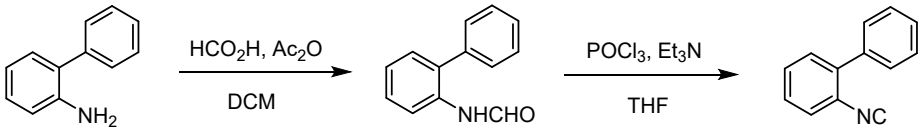
The general procedure A for the synthesis of 2-Aminodiphenyls: [1]



2-iodoaniline (10.0 mmol，1.0 equiv.), phenylboronic acid (12.0 mmol, 1.2 equiv.) were added to a dry Schlenk flask. The flask was evacuated and backfilled with pure N_2 for 3 times. DME (10 mL) and aqueous solution of K_2CO_3 (2 M, 20 mL) were added with syringe and the mixture was stirred for 30 min at room temperature under N_2 atmosphere. To the stirred mixture, $PdCl_2(PPh_3)_2$ (0.2 mmol, 140.0 mg, 0.02 equiv.) in DME (10 mL) was added with syringe at room temperature and the mixture was

stirred and heated by an oil bath at 80 °C for 12 h under N_2 atmosphere. After the reaction was complete, the mixture was then cooled to room temperature and diluted with ethyl acetate (20 mL). The aqueous layer was extracted with ethyl acetate for 3 times (20 ml × 3). Then the organic phase was combined and dried over anhydrous $MgSO_4$. The solvent was removed under reduced pressure and the residue was purified by column chromatography on silica gel by using a mixture of petroleum ether/ethyl acetate as an eluent to provide amine.

The general procedure B for the synthesis of 2-isocyanobiphenyls:

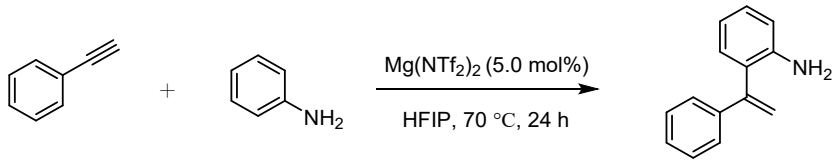


Step 1: a dry Schlenk flask was evacuated and backfilled with pure N_2 for 3 times. Amine (5.0 mmol, 1.0 equiv.) in DCM (10 mL) was added with syringe. Then the mixture was cooled to 0 °C. Acetic formic anhydride (7.5mmol, 1.5 equiv.) was added dropwise with syringe to the stirring solution at 0 °C. The mixture was stirred at 0 °C to room temperature for 2 h. After the reaction was complete, the mixture was quenched and neutralized by saturated aqueous solution of $NaHCO_3$. The aqueous layer was extracted with ethyl acetate for 3 times (20 mL × 3). Then the organic phase was combined and dried over anhydrous $MgSO_4$. The solvent was removed under reduced pressure and the residue formamide was used for the subsequent dehydration without further purification.

(NOTE: Acetic formic anhydride, which was prepared from the reaction of acetic anhydride (47 mL) with formic acid (21 mL) at 50 °C for 2 h under N_2 atmosphere in a dry Schlenk flask.)

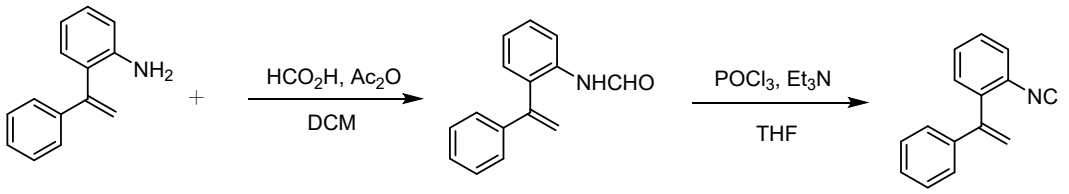
Step 2: a dry Schlenk flask was evacuated and backfilled with pure N_2 for 3 times. Formamide (2 mmol, 1.0 equiv.) in THF (5 mL) and Et_3N (8.0 mmol, 4.0 equiv.) were added with syringe. Then the mixture was cooled to 0 °C. $POCl_3$ (4.0 mmol, 0.4 mL, 2.0 equiv.) was added dropwise with syringe to the stirring solution at 0 °C in 2 h. The mixture was stirred at 0 °C for 2 h and at room temperature overnight. After the reaction was complete, the mixture was quenched and neutralized by saturated aqueous solution of $NaHCO_3$. The aqueous layer was extracted with CH_2Cl_2 for 3 times (20 mL × 3). Then the organic phase was combined and dried over anhydrous $MgSO_4$. The solvent was removed under reduced pressure and the residue was purified by column chromatography on silica gel by using a mixture of petroleum ether/ethyl acetate as an eluent to provide isocyanide.

The general procedure C for the synthesis of 2-(1-phenylvinyl)aniline:[2]



A dry Schlenk flask was charged with corresponding alkyne (10.0 mmol, 1.0 equiv.), aniline (30.0 mmol, 3.0 equiv.) in HFIP (30 mL) was added. Then, $Mg(NTf_2)_2$ (5.0 mol%) was added to the reaction at room temperature and the reaction mixture was stirred at the optimal temperature until the reaction was completed. After completion, the solvent was evaporated to obtain the crude reaction. The corresponding products were obtained after column chromatography (hexane/ethyl acetate = 40:1).

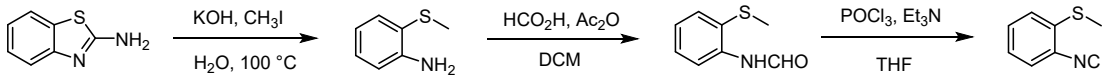
The general procedure D for the synthesis of 1-isocyano-2-(1-phenylvinyl)benzenes:[3]



Step 1: To a stirring solution of 2-(1-phenylvinyl)aniline (5.0 mmol) in DCM (10 mL) was added dropwise acetic formic anhydride (7.5 mmol, 1.5 equiv.) at 0 °C. The mixture was stirred for 2 h at room temperature. Then, the mixture was quenched with saturated Na_2CO_3 solution and extracted with DCM for three times. The organic layers were combined, dried over anhydrous Na_2SO_4 and concentrated under reduced pressure to give the crude formamides. The crude product was used for next dehydration without further purification.

Step 2: a dry Schlenk flask was evacuated and backfilled with pure N_2 for 3 times. Formamide (2.0 mmol,1.0 equiv.) in THF (5 mL) and Et_3N (8.0 mmol, 4.0 equiv.) were added with syringe. Then the mixture was cooled to 0 °C. $POCl_3$ (4.0 mmol, 0.4 mL, 2.0 equiv.) was added dropwise with syringe to the stirring solution at 0 °C in 2 h. The mixture was stirred at 0 °C for 2 h and at room temperature overnight. After the reaction was complete, the mixture was quenched and neutralized by saturated aqueous solution of $NaHCO_3$. The aqueous layer was extracted with CH_2Cl_2 for 3 times (20 mL × 3). Then the organic phase was combined and dried over anhydrous $MgSO_4$. The solvent was removed under reduced pressure and the residue was purified by column chromatography on silica gel by using a mixture of petroleum ether/ethyl acetate as an eluent to provide isocyanide.

The general procedure E for the synthesis of (2-isocyanophenyl)(methyl)sulfanes:[4]



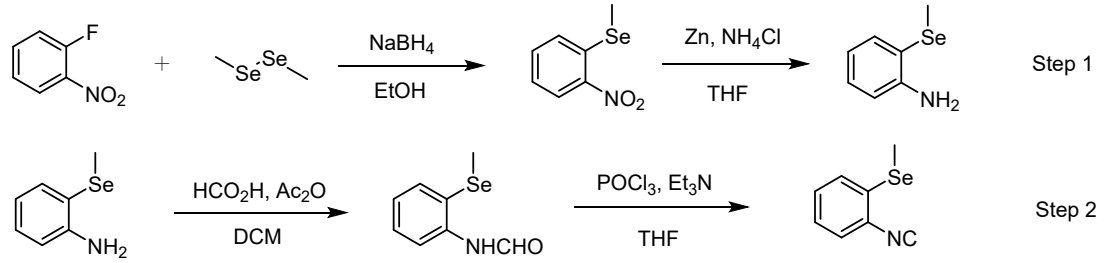
Step 1: Synthesis of 2-(methylthio)aniline. An aqueous solution (35 mL) of benzo[d]thiazol-2-amine (5.0 mmol) and KOH (0.18 mol) was refluxed for 24 h. After being cooled down to room temperature, MeI (5.0 mmol) was added dropwise and the mixture was stirred for another 1 hour. The resulting solution was extracted with diethyl ether (3 × 20 mL) and the combined organic layers were dried over anhydrous $MgSO_4$ and concentrated in vacuum. The final residue was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 10/1) to afford aniline.

Step 2: Synthesis of N-(2-(methylthio)phenyl)formamide. Acetic formic anhydride (7.5 mmol, 1.5 equiv.) was added dropwise to a stirring solution of 2-(methylthio)aniline (5.0 mmol) at 0 °C in dichloromethane (10 mL). The mixture was stirred for 2 h at room temperature. Then the mixture was quenched with saturated aqueous solution of Na_2CO_3 and extracted with dichloromethane for three times. The organic layers were dried over $MgSO_4$ and concentrated under vacuum to give N-(2-(methylthio)phenyl)formamide. This material was used directly for the subsequent dehydration without further purification.

Step 3: Synthesis of (2-isocyanophenyl)(methyl)sulfane. a dry Schlenk flask was evacuated and backfilled with pure N_2 for 3 times. N-(2-(methylthio)phenyl)formamide (2.0 mmol,1.0 equiv.) in THF (5 mL) and Et_3N (8.0 mmol, 4.0 equiv.) were added with syringe. Then the mixture was cooled to 0 °C. $POCl_3$ (4.0 mmol, 0.4 mL, 2 equiv.) was added dropwise with syringe to the stirring solution at 0 °C in 2 h. The mixture was stirred at 0 °C for 2 h and at room temperature overnight. After the reaction was complete, the mixture was quenched and neutralized by saturated aqueous solution of $NaHCO_3$. The aqueous layer was extracted with CH_2Cl_2 for 3 times (20 mL × 3). Then the organic phase was combined and dried over anhydrous $MgSO_4$. The solvent was removed under reduced pressure and the residue was

purified by column chromatography on silica gel by using a mixture of petroleum (ether/ethyl＝20/1) acetate as an eluent to provide (2-isocyanophenyl)(methyl)sulfane.

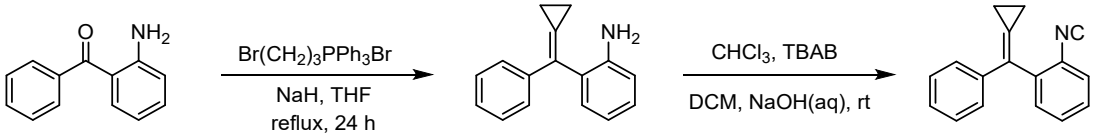
The general procedure F for the synthesis of (2-isocyanophenyl)(methyl)selane:[5]



Step 1: To a solution of dimethyl diselenide (5.0 mmol, 0.47 mL) in 25 mL of ethanol was added $NaBH_4$ (10.9 mmol, 0.41 g). The solution was stirred until the color disappeared, and then 0.97 mL (9.2 mmol) of 2-fluoronitrobenzene was added. The solution was stirred for 12 h at room temperature. After that, the solvent was removed, water (20 mL) was added, and the mixture was extracted with DCM. The organic layers were combined, dried over anhydrous $MgSO_4$, and concentrated under reduced pressure to give crude product for next step without further purification. A suspension of methylseleno-2-nitrobenzene (8.0 mmol, 1.5 g), zinc powder (75.0 mmol, 4.9 g), and ammonium chloride (48.0 mmol, 2.6 g) in THF (70 mL) was reflux for 20 h under N_2 atmosphere. The resulting suspension was filtered and the solid was washed with dichloromethane. The organic layer was then dried over $MgSO_4$, concentrated under reduced pressure to give crude product. The crude product was purified through silica gel column chromatography using petroleum ether/ethyl acetate as eluent to give pure 2-methylselenoaniline.

Step 2: Acetic formic anhydride (11.3 mmol, 0.89 mL) was added dropwise to a stirring solution of 2-methylselenoaniline (4.3 mmol) at 0 °C in DCM (8.0 mL). The mixture was stirred for 2 h at room temperature. Then, the mixture was quenched with saturated aqueous solution of Na_2CO_3 and extracted with DCM for three times. The organic phase was dried over $MgSO_4$ and concentrated under reduced pressure to give N-(2-(methylselanyl)phenyl)formamide. The crude product was used for the subsequent dehydration without further purification. THF (8 mL) and Et_3N (4.3 mL) were added to a flask containing the formamide obtained above under nitrogen atmosphere. $POCl_3$ (7.5 mmol, 0.7 mL) in 2 mL of THF was added slowly via syringe for a period of 1 h at 0 °C, and the mixture was stirred for another 2 h at 0 °C. After then, the reaction mixture was diluted with 15 mL ethyl acetate at 0 °C and slowly quenched with saturated aqueous solution of Na_2CO_3 with stirring for 30 min. The crude compound was purified by column chromatography using petroleum ether/ethyl acetate as eluent to give (2-isocyanophenyl)(methyl)selane.

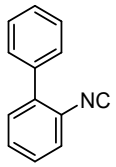
The general procedure G for the synthesis of 1-(cyclopropylidene(phenyl)methyl)-2-isocyanobenzene:[6],[7]



Step 1: To a solution of 3-bromopropyltriphenylphosphonium bromide (11 g, 24 mmol) NaH (1.15 g, 48 mmol) in THF (20 mL) was added, then the resulting reaction mixture was stirred at 70 °C for 12 h. Afterwards (2-aminophenyl)(phenyl)methanone (20 mmol) in THF (10 mL) was added and the reaction solution was stirred at 70 °C for another 12 h. Then the solvent was removed under reduced pressure and

the residue was purified by silica gel flash chromatography (eluent: petroleum ether / ethyl acetate = 50 / 1) to afford the product in moderate yield.

Step 2: To a round-bottom flask was added compound 2-(cyclopropylidene(phenyl)methyl)aniline (3.1 g, 14.0 mmol), which was diluted with 62 mL of DCM. Then 31 mL of 50 wt.% aqueous NaOH and 1.0 mol% tetrabutylammonium bromide were added. To the DCM/NaOH solution was added 1.7 mL (1.5 equiv., 21.0 mmol) of $CHCl_3$. The reaction mixture was stirred overnight, and diluted with 120 mL of H_2O. The mixture was transferred to a separatory flask. The organic layer was separated and washed twice with 60 mL of H_2O and then once with 60 mL of saturated aqueous NaCl. The organic layer was dried over anhydrous Na_2SO_4, filtered, and concentrated in vacuo at room temperature. The residue was purified by silica gel column flash chromatography (eluent: petroleum ether: dichloromethane = 6:1 to 2:1) to give the corresponding compound in moderate yield.

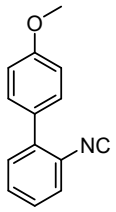


2-isocyano-1,1'-biphenyl (1a)

The product **1a** was prepared by general procedure B as green oil (304.4 mg, 85% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.56-7.35 (m, 9H).

The ^{1}H NMR data was in accordance with previously reported literature.[1]

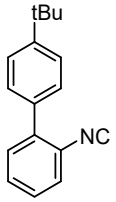


2-isocyano-4'-methoxy-1,1'-biphenyl (1b)

The product **1b** was prepared by general procedure B as yellow solid (271.8 mg, 65% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.48-7.40 (m, 5H), 7.36-7.30 (m, 1H), 7.01 (d, J = 8.7 Hz, 2H), 3.87 (s, 3H).

The ^{1}H NMR data was in accordance with previously reported literature. [1]

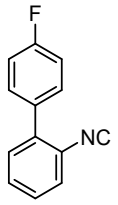


4'-(tert-butyl)-2-isocyano-1,1'-biphenyl (1c)

The product **1c** was prepared by general procedure B as green oil (376.2 mg, 80% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.57-7.42 (m, 7H), 7.40-7.32 (m, 1H), 1.41 (s, 9H).

The ^{1}H NMR data was in accordance with previously reported literature.[1]

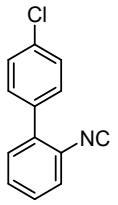


4'-fluoro-2-isocyano-1,1'-biphenyl (1d)

The product **1d** was prepared by general procedure B as green solid (236.5 mg, 60% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.51-7.44 (m, 4H), 7.41-7.35 (m, 2H), 7.17 (t, *J* = 8.6 Hz, 2H).

The ^{1}H NMR data was in accordance with previously reported literature. [1]

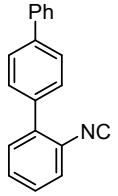


4'-chloro-2-isocyano-1,1'-biphenyl (1e)

The product **1e** was prepared by general procedure B as white solid (255.6 mg, 60% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.51-7.36 (m, 8H).

The ^{1}H NMR data was in accordance with previously reported literature. [1]

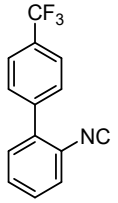


methyl 2'-isocyano-[1,1'-biphenyl]-4-carboxylate (1f)

The product **1f** was prepared by general procedure B as pale-yellow solid (244.9 mg, 48% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ 9.38 (s, 1H), 8.68 (d, *J* = 8.6 Hz, 1H), 8.61 (d, J = 8.0 Hz, 1H), 8.30-8.22 (m, 2H), 8.13 (dd, *J* = 8.6, 1.9 Hz, 1H), 7.89-7.76 (m, 3H), 7.76-7.69 (m, 1H), 7.57 (t, *J* = 7.5 Hz, 2H), 7.48 (t, *J* = 7.4 Hz, 1H).

The ^{1}H NMR data was in accordance with previously reported literature.[8]

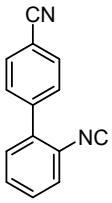


2-isocyano-4'-(trifluoromethyl)-1,1'-biphenyl (1g)

The product **1g** was prepared by general procedure B as white solid (345.9 mg, 70% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.75 (d, *J* = 8.1 Hz, 2H), 7.63 (d, *J* = 8.1 Hz, 2H), 7.54-7.42 (m, 4H).

The ^{1}H NMR data was in accordance with previously reported literature. [1]

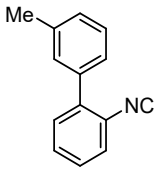


2'-isocyano-[1,1'-biphenyl]-4-carbonitrile (1h)

The product **1h** was prepared by general procedure B as green solid (277.5 mg, 68% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.82 – 7.76 (m, 2H), 7.73 – 7.60 (m, 2H), 7.58 – 7.38 (m, 4H).

The ^{1}H NMR data was in accordance with previously reported literature.[9]

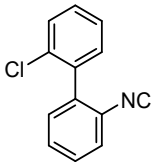


2-isocyano-3'-methyl-1,1'-biphenyl (1i)

The product **1i** was prepared by general procedure B as green oil (239.4 mg, 62% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.50-7.33 (m, 7H), 7.25 (d, J = 6.8 Hz, 1H), 2.44 (s, 3H).

The ^{1}H NMR data was in accordance with previously reported literature. [1]

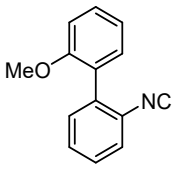


2-chloro-2'-isocyano-1,1'-biphenyl (1j)

The product **1j** was prepared by general procedure B as green solid (255.6 mg, 60% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.54-7.42 (m, 4H), 7.41-7.30 (m, 4H).

The ^{1}H NMR data was in accordance with previously reported literature. [1]

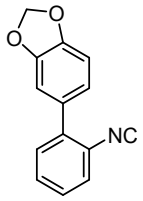


2-isocyano-2'-methoxy-1,1'-biphenyl (1k)

The product **1k** was prepared by general procedure B as white solid (334.5 mg, 80% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.47-7.34 (m, 5H), 7.24-7.20 (m, 1H), 7.08-7.00 (m, 2H), 3.84 (s, 3H).

The ^{1}H NMR data was in accordance with previously reported literature. [1]

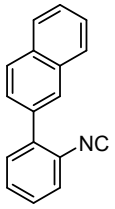


5-(2-isocyanophenyl)benzo[d][1,3]dioxole (1l)

The product **1l** was prepared by general procedure B as green solid (312.3 mg, 70% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.48-7.31 (m, 4H), 6.98-6.90 (m, 3H), 6.03 (s, 2H).

The ^{1}H NMR data was in accordance with previously reported literature. [1]

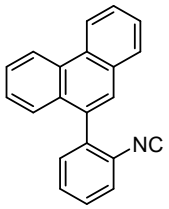


2-(2-isocyanophenyl)naphthalene (1m)

The product **1m** was prepared by general procedure B as grey solid (229.1 mg, 50% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.99-7.90 (m, 4H), 7.66 (dd, *J* = 8.5, 1.5 Hz, 1H), 7.57-7.48 (m, 5H), 7.43-7.38 (m, 1H).

The ^{1}H NMR data was in accordance with previously reported literature. [1]

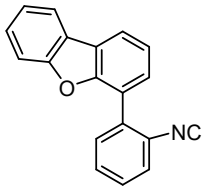


9-(2-isocyanophenyl)phenanthrene (1n)

The product **1n** was prepared by general procedure B as white solid (435.4 mg, 78% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.81 (d, J = 8.3 Hz, 1H), 8.76 (d, *J* = 8.3 Hz, 1H), 7.93 (d, *J* = 7.8 Hz, 1H), 7.74-7.65 (m, 3H), 7.65-7.61 (m, 1H), 7.60-7.45 (m, 6H).

The ^{1}H NMR data was in accordance with previously reported literature.[10]

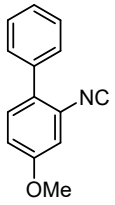


4-(2-isocyanophenyl)dibenzo[b,d]furan (1o)

The product **1o** was prepared by general procedure B as white solid (484.4 mg, 90% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.03 (d, *J* = 7.5 Hz, 1H), 7.99 (d, *J* = 29.7 Hz, 1H), 7.65 (d, *J* = 7.9 Hz, 1H), 7.59–7.51 (m, 4H), 7.48 (dd, *J* = 3.9 Hz, *J* = 0.8 Hz, 1H), 7.47–7.44 (m, 2H), 7.36 (t, *J* = 7.9 Hz, 1H).

The ^{1}H NMR data was in accordance with previously reported literature.[11]

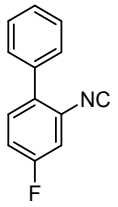


2-isocyano-4-methoxy-1,1'-biphenyl (1p)

The product **1p** was prepared by general procedure B as green solid (355.4 mg, 85% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.53-7.45 (m, 4H), 7.40 (tt, *J* = 6.9, 2.6 Hz, 1H), 7.34 (d, *J* = 8.4 Hz, 1H), 7.05-6.99 (m, 2H), 3.85 (s, 3H).

The ^{1}H NMR data was in accordance with previously reported literature.[9]

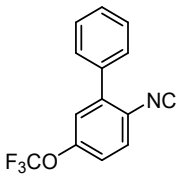


4-fluoro-2-isocyano-1,1'-biphenyl (1q)

The product **1q** was prepared by general procedure B as green solid (283.8 mg, 72% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.51–7.39 (m, 6H), 7.23–7.18 (m, 2H).

The ^{1}H NMR data was in accordance with previously reported literature.[11]

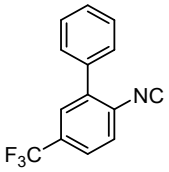


2-isocyano-5-(trifluoromethoxy)-1,1'-biphenyl (1r)

The product **1r** was prepared by general procedure B as green solid (394.6 mg, 75% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.57 – 7.42 (m, 6H), 7.31 – 7.20 (m, 2H).

The ^{1}H NMR data was in accordance with previously reported literature.[12]

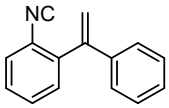


2-isocyano-5-(trifluoromethyl)-1,1'-biphenyl (1s)

The product **1s** was prepared by general procedure B as green oil (385.4 mg, 78% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.71 (s, 1H), 7.67 – 7.60 (m, 2H), 7.54 – 7.45 (m, 5H).

The ^{1}H NMR data was in accordance with previously reported literature. [1]

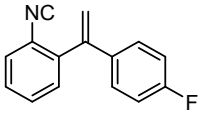


1-isocyano-2-(1-phenylvinyl)benzene (1t)

The product **1t** was prepared by general procedure D as yellow oil (254.3 mg, 62% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.44 – 7.26 (m, 9H), 5.89 (s, 1H), 5.41 (s, 1H).

The ^{1}H NMR data was in accordance with previously reported literature.[3]

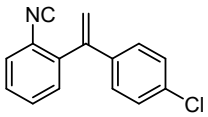


1-(1-(4-fluorophenyl)vinyl)-2-isocyanobenzene (1u)

The product **1u** was prepared by general procedure D as yellow oil (241.1 mg, 50% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.50 – 7.33 (m, 4H), 7.32 – 7.18 (m, 2H), 7.02 (t, J = 8.7 Hz, 2H), 5.82 (s, 1H), 5.39 (s, 1H).

The ^{1}H NMR data was in accordance with previously reported literature.[3]

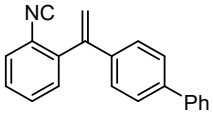


1-(1-(4-chlorophenyl)vinyl)-2-isocyanobenzene (1v)

The product **1v** was prepared by general procedure D as green solid (233.1 mg, 50% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ 6.79 – 6.68 (m, 3H), 6.65 (ddd, *J* = 7.0, 1.8, 0.9 Hz, 1H), 6.66 – 6.51 (m, 2H), 6.55 – 6.45 (m, 2H), 5.16 (s, 1H), 4.72 (s, 1H).

The ^{1}H NMR data was in accordance with previously reported literature.[13]



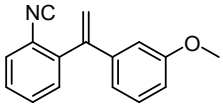
4-(1-(2-isocyanophenyl)vinyl)-1,1'-biphenyl (1w)

The product **1w** was prepared by general procedure D as yellow solid (258.6 mg, 46% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.63 – 7.51 (m, 4H), 7.48 – 7.31 (m, 9H), 5.95 (s, 1H), 5.43 (s, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 166.8, 157.2, 145.2, 141.0, 140.7, 139.3, 138.4, 131.0, 129.4, 128.9, 128.7, 127.5, 127.3, 127.3, 127.2.

HRMS (ESI) m/z: [M+H$^+$] Calcd for $C_{21}H_{16}N$ 282.1277; found: 282.1271.

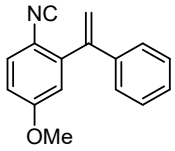


1-isocyano-2-(1-(3-methoxyphenyl)vinyl)benzene (1x)

The product **1x** was prepared by general procedure D as yellow solid (216.3 mg, 46% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.45 – 7.31 (m, 4H), 7.25 (d, *J* = 8.1 Hz, 1H), 6.85 (dd, *J* = 7.9, 2.0 Hz, 2H), 6.80 (t, *J* = 2.1 Hz, 1H), 5.88 (s, 1H), 5.40 (s, 1H), 3.78 (s, 3H).

The ^{1}H NMR data was in accordance with previously reported literature.[14]

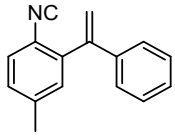


1-isocyano-4-methoxy-2-(1-phenylvinyl)benzene (1y)

The product **1y** was prepared by general procedure D as yellow solid (282.1 mg, 60% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.40 – 7.30 (m, 6H), 6.94 – 6.85 (m, 2H), 5.91 (s, 1H), 5.44 (s, 1H), 3.86 (s, 3H).

The ^{1}H NMR data was in accordance with previously reported literature.[3]

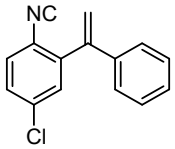


1-isocyano-4-methyl-2-(1-phenylvinyl)benzene (1z)

The product **1z** was prepared by general procedure D as yellow solid (376.8 mg, 86% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.40 – 7.21 (m, 6H), 7.17 (dd, *J* = 6.0, 2.6 Hz, 2H), 5.86 (s, 1H), 5.39 (s, 1H), 2.39 (s, 3H).

The ^{1}H NMR data was in accordance with previously reported literature.[3]

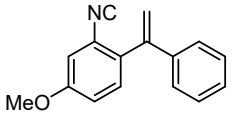


4-chloro-1-isocyano-2-(1-phenylvinyl)benzene (1aa)

The product **1aa** was prepared by general procedure D as yellow solid (368.1 mg, 77% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.40 – 7.29 (m, 6H), 7.29 – 7.22 (m, 2H), 5.90 (s, 1H), 5.42 (s, 1H).

The ^{1}H NMR data was in accordance with previously reported literature.[3]

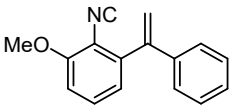


2-isocyano-4-methoxy-1-(1-phenylvinyl)benzene(1ab)

The product **1ab** was prepared by general procedure D as yellow solid (362.1 mg, 77% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.39 – 7.28 (m, 6H), 7.11 (dd, *J* = 8.1, 1.1 Hz, 1H), 7.01 (dd, *J* = 8.4, 1.1 Hz, 1H), 6.08 (s, 1H), 5.36 (s, 1H), 3.76 (s, 3H).

The ^{1}H NMR data was in accordance with previously reported literature.[13]

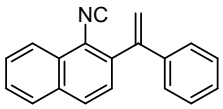


2-isocyano-1-methoxy-3-(1-phenylvinyl)benzene(1ac)

The product **1ac** was prepared by general procedure D as yellow solid (404.4 mg, 86% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.39 – 7.26 (m, 6H), 6.94 (ddd, *J* = 12.0, 8.1, 1.2 Hz, 2H), 5.87 (s, 1H), 5.41 (s, 1H), 3.94 (s, 3H).

The ^{1}H NMR data was in accordance with previously reported literature.[15]

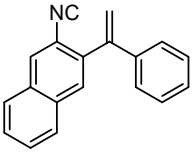


1-isocyano-2-(1-phenylvinyl)naphthalene (1ad)

The product **1ad** was prepared by general procedure D as yellow oil (265.3 mg, 52% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.28 (d, *J* = 8.4 Hz, 1H), 8.02 – 7.88 (m, 2H), 7.80 – 7.61 (m, 2H), 7.48 – 7.32 (m, 6H), 6.08 (s, 1H), 5.59 (s, 1H).

The ^{1}H NMR data was in accordance with previously reported literature.[3]

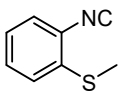


2-isocyano-3-(1-phenylvinyl)naphthalene (1ae)

The product **1ae** was prepared by general procedure D as yellow solid (285.7 mg, 56% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.94 – 7.84 (m, 3H), 7.56 (ddd, *J* = 8.1, 6.9, 1.4 Hz, 1H), 7.53 – 7.44 (m, 2H), 7.28 (s, 5H), 6.28 (s, 1H), 5.43 (s, 1H).

The ^{1}H NMR data was in accordance with previously reported literature.[16]

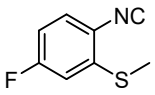


(2-isocyanophenyl)(methyl)sulfane (1af)

The product **1af** was prepared by general procedure E as yellow oil (166.9 mg, 56% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.34 – 7.24 (m, 2H), 7.18 (d, *J* = 8.0 Hz, 1H), 7.09 (t, *J* = 7.6 Hz, 1H), 2.46 (s, 3H).

The ^{1}H NMR data was in accordance with previously reported literature.[17]

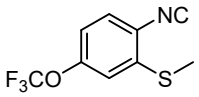


(5-fluoro-2-isocyanophenyl)(methyl)sulfane (1ag)

The product **1ag** was prepared by general procedure E as white solid (290.6 mg, 87% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.33 (dd, *J* = 8.4, 5.2 Hz, 1H), 6.91 (dd, *J* = 9.2, 2.8 Hz, 1H), 6.83 (td, *J* = 8.0, 2.8 Hz, 1H), 2.52 (s, 3H).

The ^{1}H NMR data was in accordance with previously reported literature.[17]

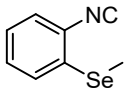


(2-isocyano-5-(trifluoromethoxy)phenyl)(methyl)sulfane (1ah)

The product **1ah** was prepared by general procedure E as yellow solid (405.4 mg, 87% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.38 (d, *J* = 8.6 Hz, 1H), 7.02 (s, *J* = 2.9 Hz, 1H), 7.00 (d, *J* = 8.6, 2.5, 1.2 Hz, 1H), 2.53 (s, 3H).

The ^{1}H NMR data was in accordance with previously reported literature.[4]

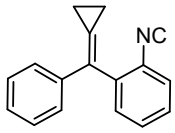


(2-isocyanophenyl)(methyl)selane (1ai)

The product **1ai** was prepared by general procedure F as yellow solid (512.1 mg, 52% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.38 – 7.27 (m, 3H), 7.24 – 7.16 (m, 1H), 2.38 (s, 3H).

The ^{1}H NMR data was in accordance with previously reported literature.[5]

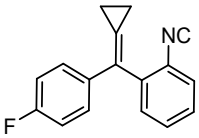


1-(cyclopropylidene(phenyl)methyl)-2-isocyanobenzene (1aj)

The product **1aj** was prepared by general procedure G as yellow oil (924.4 mg, 20% yield)

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.48 – 7.30 (m, 9H), 1.75 – 1.59 (m, 2H), 1.30 – 1.21 (m, 2H).

The ^{1}H NMR data was in accordance with previously reported literature. [29]

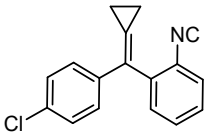


1-(cyclopropylidene(4-fluorophenyl)methyl)-2-isocyanobenzene (1ak)

The product **1ak** was prepared by general procedure G as yellow oil (1.1 g, 22% yield)

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.52 – 7.31 (m, 6H), 7.08 – 6.95 (m, 2H), 1.73 – 1.52 (m, 2H), 1.28 – 1.17 (m, 2H).

The ^{1}H NMR data was in accordance with previously reported literature. [29]



1-((4-chlorophenyl)(cyclopropylidene)methyl)-2-isocyanobenzene (1al)

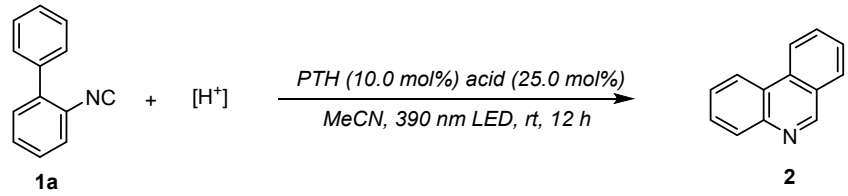
The product **1al** was prepared by general procedure G as yellow oil (1.3 g, 25% yield)

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.36-7.46 (m, 3H), 7.31-7.34 (m, 3H), 7.25-7.29 (m, 2H), 1.61-1.65 (m, 2H), 1.24-1.28 (m, 2H).

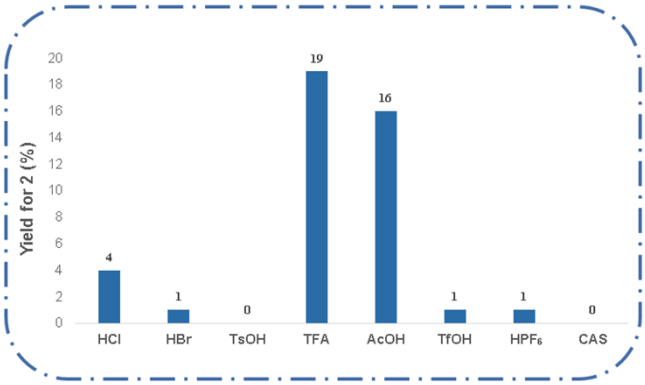
The ^{1}H NMR data was in accordance with previously reported literature. [29]

C. Optimization of the reaction conditions:

(a) Figure 2. Optimization of H^+ source

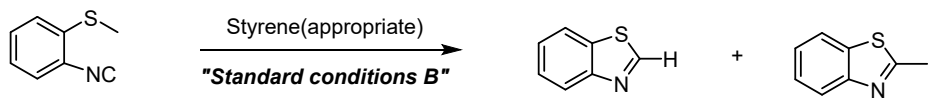


Enter	PC	Acid	Yield
1	PTH	HCl	4%
2	PTH	HBr	1%
3	PTH	TsOH	n.d.
4	PTH	TFA	19%
5	PTH	AcOH	16%
6	PTH	TfOH	1%
7	PTH	HPF_6	1%
8	PTH	CAS	n.d.



Reaction conditions: **1** (0.1 mmol), **PC** (10.0 mol %), **Acid** (25.0 mol %) in solvent MeCN (1.0 mL) at room temperature under irradiation of 390 nm LED for 12 h. (NOTE: TFA = Trifluoroacetic acid, CAS = Camphorsulfonic acid)

(b) Figure 3. Optimization of the reaction conditions for the synthesis of 33



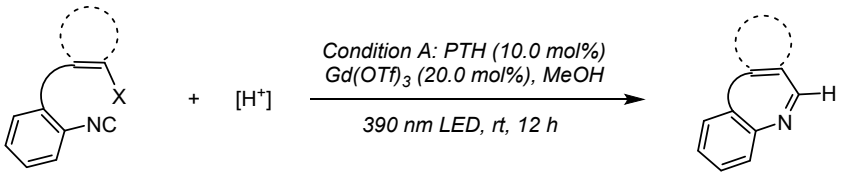
1af **33** **33'**

entry	Styrene	Yield of **33**	Yield of **33'**
1	0 equiv.	26%	45%
2	1.0 equiv.	53%	18%
3	5.0 equiv.	64%	8%
4	10.0 equiv.	66%	4%

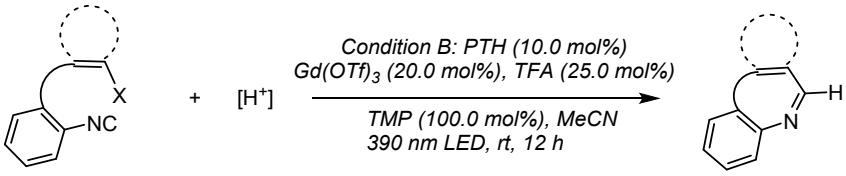
5	20.0 equiv.	68%	2%

Reaction conditions: **1af** (0.1 mmol), **PC** (10.0 mol %), **Gd(OTf)$_3$** (20.0 mol %), **TMP** (100.0 mol %), **TFA** (25.0 mol %) and **Styrene** (appropriate) in solvent MeCN (1.0 mL) at room temperature under irradiation of 390 nm LED for 12 h.

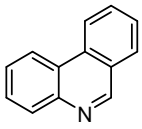
D. Catalytic results:



Condition A: To an oven-dried 5 mL Schlenk tube equipped with a stir bar, were added Gd(OTf)$_3$ (24.2 mg, 20.0 mol%.), photocatalyst PTH (5.5 mg, 10.0 mol%). Then the reaction was evacuated and backfilled with argon for three times. After isocyanide (0.2 mmol, 1.0 equiv.) and anhydrous MeOH (2.0 ml) were added. The reaction mixture was irradiated under 390 nm LED at room temperature for 12 h. The residue was purified by silica gel chromatography to afford the desired product.



Condition B: To an oven-dried 5 mL Schlenk tube equipped with a stir bar, were added Gd(OTf)$_3$ (24.2 mg, 20.0 mol%.), photocatalyst PTH (5.5 mg, 10.0 mol%). Then the reaction was evacuated and backfilled with argon for three times. After isocyanide (0.2 mmol, 1.0 equiv.), TMP (0.2 mmol 1.0 equiv.), TFA (5.7mg 25.0 mol%) and anhydrous MeCN (2.0 ml) were added. The reaction mixture was irradiated under 390 nm LED at room temperature for 12 h. The residue was purified by silica gel chromatography to afford the desired product.



Phenanthridine (2)

Purified by flash silica column chromatography (hexane/ethyl acetate = 10:1)

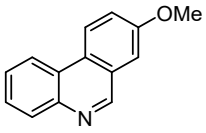
White solid (29.7 mg, 83% yield)

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.31 (s, 1H), 8.65 – 8.55 (m, 2H), 8.23 (d, *J* = 8.0 Hz, 1H), 8.06 (d, *J* = 8.0 Hz, 1H), 7.88 (t, *J* = 7.7 Hz, 1H), 7.81 – 7.66 (m, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 153.4, 144.2, 132.6, 131.1, 130.0, 128.8, 128.7, 127.5, 127.2, 126.3, 124.1, 122.2, 121.9.

HRMS (ESI) m/z: [M+H$^+$] Calcd for $C_{13}H_{10}N$ 180.0808; found: 180.0800.

The NMR data was in accordance with previously reported literature.[18]



Phenanthridine, 8-methoxy- (3)

Purified by flash silica column chromatography (hexane/ethyl acetate = 10:1)

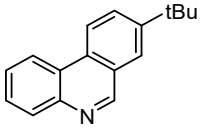
White solid (30.1 mg, 72% yield)

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.19 (s, 1H), 8.50 – 8.41 (m, 2H), 8.15 (d, *J* = 9.3 Hz, 1H), 7.71 – 7.58 (m, 2H), 7.44 (dd, *J* = 9.0, 2.7 Hz, 1H), 7.33 (d, *J* = 2.7 Hz, 1H), 3.95 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 159.0, 152.8, 143.5, 130.0, 127.8, 127.8, 127.3, 127.1, 124.4, 123.7, 122.2, 121.8, 108.1, 55.7.

HRMS (ESI) m/z: [M+Na^+] Calcd for $C_{14}H_{11}NONa$ 232.0733; found: 232.0730.

The NMR data was in accordance with previously reported literature.[18]



Phenanthridine, 8-(1,1-dimethylethyl)- (4)

Purified by flash silica column chromatography (hexane/ethyl acetate = 10:1)

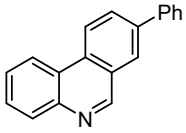
Brown oil (31.5 mg, 67% yield)

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.29 (s, 1H), 8.58 – 8.50 (m, 2H), 8.20 (dd, *J* = 8.0, 1.6 Hz, 1H), 8.00 (d, *J* = 2.0 Hz, 1H), 7.95 (dd, *J* = 8.7, 2.1 Hz, 1H), 7.75 – 7.65 (m, 2H), 1.47 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 153.1, 150.0, 143.5, 129.8, 129.3, 128.8, 127.6, 126.3, 125.7, 123.6, 123.4, 121.4, 121.0, 34.3, 30.6.

HRMS (ESI) m/z: [M+H^+] Calcd for $C_{17}H_{18}N$ 236.1434; found: 236.1430.

The NMR data was in accordance with previously reported literature.[18]



8-phenylphenanthridine (5)

Purified by flash silica column chromatography (hexane/ethyl acetate = 10:1)

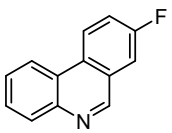
White solid (18.4 mg, 36% yield)

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.33 (s, 1H), 8.62 (d, *J* = 8.7 Hz, 1H), 8.56 (d, *J* = 7.8 Hz, 1H), 8.24 – 8.19 (m, 2H), 8.08 (d, *J* = 8.6 Hz, 1H), 7.74 (d, *J* = 7.5 Hz, 3H), 7.68 (t, *J* = 7.0 Hz, 1H), 7.52 (t, *J* = 7.6 Hz, 2H), 7.43 (t, *J* = 7.3 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 152.7, 142.9, 139.9, 139.1, 131.1, 130.0, 129.0, 128.4, 128.2, 127.4, 126.8, 126.7, 126.1, 125.9, 123.4, 121.9, 121.6.

HRMS (ESI) m/z: [M+H^+] Calcd for $C_{19}H_{14}N$ 256.1121 256.1110

The NMR data was in accordance with previously reported literature.[8]



8-Fluorophenanthridine (6)

Purified by flash silica column chromatography (hexane/ethyl acetate = 10:1)

White solid (20.5 mg, 52% yield)

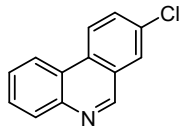
^{1}H NMR (400 MHz, $CDCl_3$) δ 9.22 (s, 1H), 8.58 (dd, *J* = 9.1, 5.0 Hz, 1H), 8.49 (d, *J* = 8.0 Hz, 1H), 8.20 (d, *J* = 8.4 Hz, 1H), 7.80 – 7.63 (m, 3H), 7.63 – 7.54 (m, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 161.6 (d, *J* = 249.0 Hz), 152.3 (d, *J* = 3.9 Hz), 143.8, 130.1, 129.4, 128.8, 127.7, 127.5 (d, *J* = 8.2 Hz), 124.7 (d, *J* = 8.2 Hz), 123.8, 122.1, 120.5 (d, *J* = 23.6 Hz), 112.9 (d, *J* = 20.2 Hz).

^{19}FNMR (376 MHz, $CDCl_3$) δ -112.99.

HRMS (ESI) m/z: [M+H$^+$] Calcd for $C_{13}H_9FN$ 198.0714; found: 198.0711.

The NMR data was in accordance with previously reported literature.[18]



8-chlorophenanthridine (7)

Purified by flash silica column chromatography (hexane/ethyl acetate = 10:1)

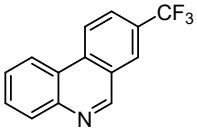
White solid (21.7 mg, 54% yield)

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.22 (s, 1H), 8.57 – 8.49 (m, 2H), 8.22 (dd, *J* = 8.1, 1.5 Hz, 1H), 8.03 (d, *J* = 2.3 Hz, 1H), 7.87 – 7.65 (m, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 151.4, 143.5, 132.7, 130.9, 130.2, 129.5, 128.4, 127.0, 126.9, 126.4, 123.0, 121.4.

HRMS (ESI) m/z: [M+H$^+$] Calcd for $C_{13}H_9ClN$ 214.0418; found: 214.0413.

The NMR data was in accordance with previously reported literature.[18]



Phenanthridine, 8-(trifluoromethyl)- (8)

Purified by flash silica column chromatography (hexane/ethyl acetate = 10:1)

White solid (32.1 mg, 65% yield)

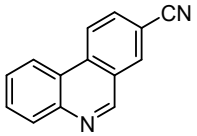
^{1}H NMR (400 MHz, $CDCl_3$) δ 9.32 (s, 1H), 8.68 (d, *J* = 8.7 Hz, 1H), 8.56 (d, *J* = 8.2 Hz, 1H), 8.32 (s, 1H), 8.23 (d, *J* = 8.1 Hz, 1H), 8.03 (d, *J* = 8.6 Hz, 1H), 7.82 (t, *J* = 7.6 Hz, 1H), 7.73 (t, *J* = 7.8 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 153.0, 144.9, 134.8, 130.3, 130.1, 129.7 (d, *J* =30.0 Hz), 127.9, 127.0 (q, *J* =3.3 Hz), 126.4 (q, *J* = 4.2 Hz), 125.5, 125.3, 123.3, 123.1, 122.7.

19FNMR (376 MHz, $CDCl_3$) δ -62.75

HRMS (ESI) m/z: [M+H$^+$] Calcd for $C_{14}H_9F_3N$ 248.0682; found: 248.0677.

The NMR data was in accordance with previously reported literature.[18]



Phenanthridine-8-carbonitrile (9)

Purified by flash silica column chromatography (hexane/ethyl acetate = 5:1)

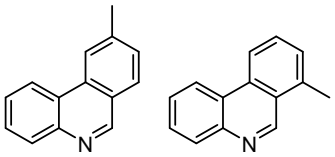
Yellow solid (30.2 mg, 74% yield)

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.31 (s, 1H), 8.70 (d, *J* = 8.6 Hz, 1H), 8.58 (d, *J* = 8.1 Hz, 1H), 8.41 (s, 1H), 8.25 (d, *J* = 8.1 Hz, 1H), 8.03 (d, *J* = 6.7 Hz, 1H), 7.87 (t, *J* = 6.9 Hz, 1H), 7.77 (t, *J* = 6.9 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 151.9, 144.8, 134.6, 133.5, 131.8, 130.1, 130.0, 127.6, 125.1, 122.9, 122.3, 177.8, 110.6.

HRMS (ESI) m/z: [M+H$^+$] Calcd for $C_{14}H_9N_2$ 205.0760; found: 205.0755.

The NMR data was in accordance with previously reported literature.[18]



9-methylphenanthridine/7-methylphenanthridine (10)

Purified by flash silica column chromatography (hexane/ethyl acetate = 10:1) as inseparable regioisomer (rr = 1 : 2.74)

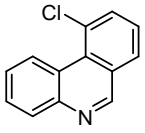
White solid (31.6 mg, 82% yield)

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.55 (s, 1H), 9.22 (s, 0.38H), 8.63 – 8.54 (m, 1H), 8.53 (s, 0.12H), 8.46 (d, *J* = 8.5 Hz, 1H), 8.36 (s, 0.4H), 8.21 (dd, *J* = 8.1, 1.5 Hz, 1H), 8.17 (s, 0.13H), 7.92 (dd, *J* = 8.1, 1.6 Hz, 0.37H), 7.78 – 7.66 (m, 3H), 7.65 (dq, *J* = 2.7, 1.4 Hz, 0.36H), 7.51 (dd, *J* = 8.1, 1.7 Hz, 0.31H), 7.48 (dq, *J* = 7.2, 1.0 Hz, 1H), 2.85 (s, 3H), 2.64 (s, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 153.0, 149.9, 144.1, 143.5, 141.7, 136.6, 132.8, 132.6, 130.9, 129.7, 129.6, 129.2, 128.8, 128.6, 128.6, 127.1, 126.8, 124.7, 124.4, 124.2, 123.9, 122.3, 122.1, 121.4, 119.9, 22.4, 18.8.

HRMS (ESI) m/z: [M+H$^+$] Calcd for $C_{14}H_{12}N$ 194.0964; found: 194.0961.

The NMR data was in accordance with previously reported literature.[18]



10-chlorophenanthridine (11)

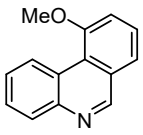
Purified by flash silica column chromatography (hexane/ethyl acetate = 10:1)

White solid (26.0 mg, 61% yield)

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.84 (dd, *J* = 8.6, 1.4 Hz, 1H), 9.25 (s, 1H), 8.25 (dd, *J* = 8.1, 1.6 Hz, 1H), 8.00 (dd, *J* = 7.8, 1.4 Hz, 1H), 7.95 (dd, *J* = 7.7, 1.4 Hz, 1H), 7.81 (t, *J* = 8.2 Hz, 1H), 7.72 (t, *J* = 8.6, 7.0 Hz, 1H), 7.63 (t, *J* = 7.7 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 153.2, 144.9, 134.7, 131.1, 129.9, 129.3, 129.0, 128.6, 127.3, 126.8, 126.1, 123.2.

HRMS (ESI) m/z: [M+H$^+$] Calcd for $C_{13}H_9ClN$ 214.0418; found: 214.0423.



10-Methoxyphenanthridine (12)

Purified by flash silica column chromatography (hexane/ethyl acetate = 5:1)

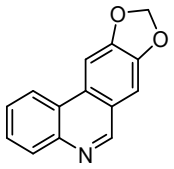
Yellow solid (30.1 mg, 72% yield)

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.48 (dd, *J* = 8.5, 1.6 Hz, 1H), 9.23 (s, 1H), 8.21 (dd, *J* = 8.0, 1.7 Hz, 1H), 7.74 (ddd, *J* = 8.3, 7.0, 1.5 Hz, 1H), 7.70 – 7.63 (m, 3H), 7.32 (dd, *J* = 6.1, 3.1 Hz, 1H), 4.14 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 157.7, 153.2, 144.5, 129.4, 128.3, 127.9, 127.8, 127.6, 126.8, 123.9, 122.6, 121.1, 111.7, 55.6.

HRMS (ESI) m/z: [M+H$^+$] Calcd for $C_{14}H_{12}NO$ 210.0913; found: 210.0915.

The NMR data was in accordance with previously reported literature.[19]



Trisphaeridine (13)

Purified by flash silica column chromatography (hexane/ethyl acetate = 10:1)

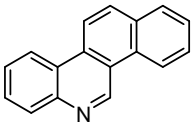
Yellow solid (22.8 mg, 51% yield)

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.07 (s, 1H), 8.36 (d, *J* = 8.1 Hz, 1H), 8.15 (d, *J* = 8.2 Hz, 1H), 7.87 (s, 1H), δ 7.68 (t, *J* = 8.3 Hz, 1H), 7.62 (t, *J* = 8.3 Hz, 1H), 7.30 (s, 1H), 6.15 (s, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 151.8, 151.6, 148.3, 144.0, 130.4, 130.0, 128.1, 126.8, 124.4, 123.1, 122.1, 105.6, 102.0, 100.0.

HRMS (ESI) m/z: [M+H$^+$] Calcd for $C_{14}H_{10}NO_2$ 224.0706; found: 224.0696.

The NMR data was in accordance with previously reported literature.[18]



Benzo[*i*]phenanthridine (14)

Purified by flash silica column chromatography (hexane/ethyl acetate = 10:1)

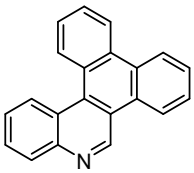
Yellow solid (23.4 mg, 52% yield)

^{1}H NMR (400 MHz, $CDCl_3$) δ 10.13 (s, 1H), 8.80 (d, *J* = 8.4 Hz, 1H), 8.55 (d, *J* = 7.6 Hz, 1H), 8.45 (d, *J* = 9.0 Hz, 1H), 8.25 (d, *J* = 8.2 Hz, 1H), 8.06 (d, *J* = 9.0 Hz, 1H), 7.93 (d, *J* = 7.9 Hz, 1H), 7.69 (m, *J* = 36.9, 14.6, 7.6 Hz, 4H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 147.0, 144.3, 131.4, 129.2, 128.2, 128.1, 127.3, 126.4, 126.4, 123.5, 121.9, 121.3, 120.9, 119.0.

HRMS (ESI) m/z: [M+H$^+$] Calcd for $C_{17}H_{12}N$ 230.0964; found: 230.0958.

The NMR data was in accordance with previously reported literature.[20]



Dibenzo[i,k]phenanthridine (15)

Purified by flash silica column chromatography (hexane/ethyl acetate = 10:1)

Pale yellow solid (34.1 mg, 61% yield)

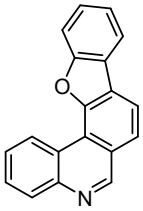
^{1}H NMR (400 MHz, $CDCl_3$) δ 10.00 (s, 1H), 8.78 (ddd, *J* = 20.2, 8.4, 1.4 Hz, 2H), 8.69 – 8.54 (m, 3H),

8.28 (dd, *J* = 8.3, 1.4 Hz, 1H), 7.80 – 7.59 (m, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 146.3, 132.0, 131.9, 129.6, 129.2, 129.1, 128.3, 128.2, 127.7, 127.6, 127.5, 127.2, 127.1, 126.4, 126.3, 123.7, 123.3, 122.9, 122.4, 121.5.

HRMS (ESI) m/z: [M+H$^+$] Calcd for $C_{21}H_{14}N$ 280.1121; found: 280.1129

The NMR data was in accordance with previously reported literature.[8]



Benzofuro[3,2-k]phenanthridine (16)

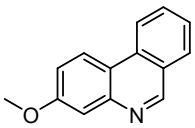
Purified by flash silica column chromatography (hexane/ethyl acetate = 10:1)

Pale yellow solid (48.5 mg, 90% yield)

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.18 (dd, *J* = 8.1, 1.5 Hz, 1H), 9.13 (s, 1H), 8.14 (d, *J* = 8.0 Hz, 1H), 7.88 – 7.79 (m, 2H), 7.71 (td, *J* = 8.2, 7.6, 1.6 Hz, 1H), 7.65 (t, *J* = 7.8 Hz, 2H), 7.58 (d, *J* = 8.2 Hz, 1H), 7.46 (td, *J* = 8.3, 7.8, 1.3 Hz, 1H), 7.32 (td, *J* = 7.5, 1.0 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 156.2, 152.6, 151.0, 144.3, 129.2, 128.4, 127.5, 126.9, 126.8, 125.4, 125.1, 123.1, 123.0, 122.9, 121.6, 120.5, 119.3, 119.2, 111.6.

HRMS (ESI) m/z: [M+H$^+$] Calcd for $C_{19}H_{12}NO$ 270.0913; found: 270.0924.



3-Methoxyphenanthridine (17)

Purified by flash silica column chromatography (hexane/ethyl acetate = 5:1)

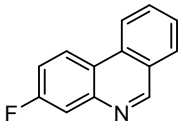
Yellow solid (28.8 mg, 69% yield)

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.23 (s, 1H), 8.45 (dd, *J* = 16.4, 8.7 Hz, 2H), 7.99 (d, *J* = 7.9 Hz, 1H), 7.84 – 7.76 (m, 1H), 7.65 – 7.57 (m, 2H), 7.30 (dd, *J* = 9.0, 2.7 Hz, 1H), 3.98 (s,3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 159.4, 153.1, 145.2, 132.0, 130.4, 128.1, 125.7, 124.8, 122.6, 120.6, 117.4, 109.1, 54.8.

HRMS (ESI) m/z: [M+H$^+$] Calcd for $C_{14}H_{12}NO$ 210.0913; found: 210.0910.

The NMR data was in accordance with previously reported literature.[18]



3-Fluorophenanthridine (18)

Purified by flash silica column chromatography (hexane/ethyl acetate = 10:1)

Yellow solid (23.3mg, 59% yield)

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.29 (s, 1H), 8.58 – 8.49 (m, 2H), 8.05 (dd, *J* = 8.0, 1.8 Hz, 1H), 7.91 – 7.81 (m, 2H), 7.70 (ddd, *J* = 8.1, 7.1, 1.1 Hz, 1H), 7.44 (ddd, *J* = 9.0, 7.9, 2.7 Hz, 1H).

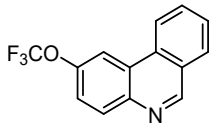
^{13}C NMR (100 MHz, $CDCl_3$) δ 161.5 (d, *J* = 248.5 Hz), 154.6, 145.4, 132.5, 131.8, 129.2, 127.6, 125.9,

124.2 (d, J = 9.2 Hz), 121.8, 120.9, 116.3 (d, J = 24.1 Hz), 114.4 (d, J = 20.7 Hz).

^{19}F NMR (376 MHz, $CDCl_3$) δ -111.29.

HRMS (ESI) m/z: [M+H$^+$] Calcd for $C_{13}H_9FN$ 198.0714; found: 198.0706.

The NMR data was in accordance with previously reported literature.[18]



2-(Trifluoromethoxy)phenanthridine (19)

Purified by flash silica column chromatography (hexane/ethyl acetate = 10:1)

Yellow solid (35.3 mg, 67% yield)

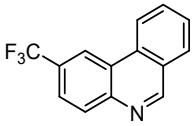
^{1}H NMR (400 MHz, $CDCl_3$) δ 9.23 (s, 1H), 8.44 (d, J = 8.3 Hz, 1H), 8.29 (s, 1H), 8.18 (d, J = 9.0 Hz, 1H), 8.00 (d, J = 7.9 Hz, 1H), 7.83 (t, J = 7.8 Hz, 1H), 7.71 (t, J = 7.5 Hz, 1H), 7.57 (d, J = 8.6 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 153.2, 146.9, 141.9, 131.3, 131.1, 130.6, 128.1, 127.5, 125.6, 124.3, 121.2, 121.1, 118.6, 113.1.

^{19}F NMR (376 MHz, $CDCl_3$) δ -58.09.

HRMS (ESI) m/z: [M+H$^+$] Calcd for $C_{14}H_9F_3NO$ 264.0631; found: 264.0636.

The NMR data was in accordance with previously reported literature.[21]



2-(Trifluoromethyl)phenanthridine (20)

Purified by flash silica column chromatography (hexane/ethyl acetate = 10:1)

Yellow solid (26.2 mg, 53% yield)

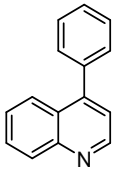
^{1}H NMR (400 MHz, $CDCl_3$) δ 9.27 (s, 1H), 8.72 (s, 1H), 8.50 (d, J = 8.3 Hz, 1H), 8.21 (d, J = 8.6 Hz, 1H), 8.00 (d, J = 7.8 Hz, 1H), 7.91 – 7.80 (m, 2H), 7.71 (t, J = 7.2 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 154.8, 144.9, 131.2, 130.8, 130.2, 128.2, 128.0, 127.5, 125.6, 123.8 (d, J = 3.3 Hz), 121.0, 119.2 (d, J = 4.3 Hz).

^{19}F NMR (376 MHz, $CDCl_3$) δ -62.47.

HRMS (ESI) m/z: [M+H$^+$] Calcd for $C_{14}H_9F_3N$ 248.0682; found: 248.0683.

The NMR data was in accordance with previously reported literature.[8]



4-Phenylquinoline (21)

Purified by flash silica column chromatography (hexane/ethyl acetate = 10:1)

Colourless oil (38.6 mg, 94% yield)

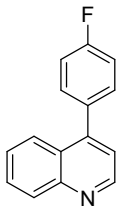
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.95 (d, J = 4.4 Hz, 1H), 8.20 (dd, 1H), 7.93 (dd, J = 8.5, 1.4 Hz, 1H), 7.73 (ddd, J = 8.4, 6.8, 1.4 Hz, 1H), 7.61 – 7.45 (m, 6H), 7.34 (d, J = 4.4 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 150.0, 148.7, 148.7, 138.0, 129.9, 129.7, 129.5, 128.7, 128.6, 126.9,

126.8, 126.0, 121.5.

HRMS (ESI) m/z: [M+H$^+$] Calcd for $C_{15}H_{12}N$ 206.0964; found: 206.0953.

The NMR data was in accordance with previously reported literature.[22]



4-(4-fluorophenyl)quinoline (22)

Purified by flash silica column chromatography (hexane/ethyl acetate = 10:1)

Yellow solid (40.6 mg, 91% yield)

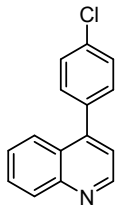
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.93 (d, *J* = 4.4 Hz, 1H), 8.19 (d, *J* = 9.0 Hz, 1H), 7.88 (d, *J* = 8.4 Hz, 1H), 7.74 (t, *J* = 7.8 Hz, 1H), 7.55 – 7.43 (m, 3H), 7.31 (d, *J* = 4.3 Hz, 1H), 7.22 (t, *J* = 8.6 Hz, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 162.5 (d, *J* = 248.5 Hz), 149.2, 147.6 (d, *J* = 58.8 Hz), 133.3, 130.8, 130.8, 129.2, 129.1, 126.5, 126.3, 125.2, 120.9, 115.3 (d, *J* = 21.2 Hz).

^{19}FNMR (376 MHz, $CDCl_3$) δ -113.33.

HRMS (ESI) m/z: [M+H$^+$] Calcd for $C_{15}H_{11}FN$ 224.0870; found: 224.0868.

The NMR data was in accordance with previously reported literature.[23]



4-(4-chlorophenyl)quinoline (23)

Purified by flash silica column chromatography (hexane/ethyl acetate = 10:1)

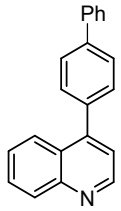
Yellow solid (43.0 mg, 90% yield)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.95 (d, *J* = 4.4 Hz, 1H), 8.22 (d, *J* = 8.4 Hz, 1H), 7.87 (d, *J* = 8.3 Hz, 1H), 7.80 – 7.71 (m, 1H), 7.57 – 7.48 (m, 3H), 7.48 – 7.41 (m, 2H), 7.33 (d, *J* = 4.4 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 149.7, 148.3, 147.7, 136.3, 134.9, 130.9, 129.8, 129.7, 129.0, 127.1, 126.6, 125.6, 121.4.

HRMS (ESI) m/z: [M+H$^+$] Calcd for $C_{15}H_{11}ClN$ 240.0575; found: 240.0572.

The NMR data was in accordance with previously reported literature.[24]



4-([1,1'-biphenyl]-4-yl)quinoline (24)

Purified by flash silica column chromatography (hexane/ethyl acetate = 10:1)

Yellow solid (52.8 mg, 94% yield)

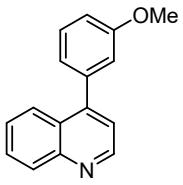
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.97 (d, *J* = 4.4 Hz, 1H), 8.24 (d, *J* = 8.4 Hz, 1H), 8.03 (d, *J* = 8.3 Hz,

1H), 7.77 (d, *J* = 7.9 Hz, 3H), 7.69 (d, *J* = 7.5 Hz, 2H), 7.60 (d, *J* = 8.0 Hz, 2H), 7.52 (dt, *J* = 14.9, 8.0 Hz, 3H), 7.41 (dd, *J* = 11.1, 5.8 Hz, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 149.2, 147.9, 147.8, 140.8, 139.8, 136.2, 129.5, 129.1, 129.0, 128.4, 127.1, 126.7, 126.6, 126.2, 126.1, 125.3, 120.7.

HRMS (ESI) m/z: [M+H$^+$] Calcd for $C_{21}H_{16}N$ 282.1277; found: 282.1277.

The NMR data was in accordance with previously reported literature.[25]



4-(3-methoxyphenyl)quinoline (25)

Purified by flash silica column chromatography (hexane/ethyl acetate = 10:1)

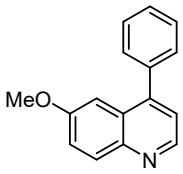
Yellow oil (44.7 mg, 95% yield)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.94 (d, *J* = 4.4 Hz, 1H), 8.19 (d, *J* = 8.4 Hz, 1H), 7.95 (d, *J* = 8.4 Hz, 1H), 7.77 – 7.68 (m, 1H), 7.50 (t, *J* = 7.7 Hz, 1H), 7.47 – 7.39 (m, 1H), 7.34 (d, *J* = 4.4 Hz, 1H), 7.07 (dt, *J* = 7.4, 1.2 Hz, 1H), 7.05 – 7.00 (m, 2H), 3.85 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 159.0, 149.2, 148.0, 147.9, 138.7, 129.1, 128.9, 126.1, 125.4, 121.4, 120.6, 114.6, 113.3, 54.8.

HRMS (ESI) m/z: [M+H$^+$] Calcd for $C_{16}H_{14}NO$ 236.1070; found: 236.1069.

The NMR data was in accordance with previously reported literature.[26]



6-methoxy-4-phenylquinoline (26)

Purified by flash silica column chromatography (hexane/ethyl acetate = 10:1)

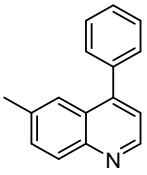
Yellow oil (36.2 mg, 77% yield)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.80 (d, *J* = 4.5 Hz, 1H), 8.11 (d, *J* = 9.2 Hz, 1H), 7.58 – 7.45 (m, 5H), 7.40 (dd, *J* = 9.2, 2.8 Hz, 1H), 7.30 (d, *J* = 4.4 Hz, 1H), 7.20 (d, *J* = 2.8 Hz, 1H), 3.79 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 157.5, 147.0, 146.6, 143.8, 137.7, 130.4, 128.8, 128.2, 128.0, 127.3, 121.5, 121.2, 103.2, 55.0.

HRMS (ESI) m/z: [M+H$^+$] Calcd for $C_{16}H_{14}NO$ 236.1070; found: 236.1066.

The NMR data was in accordance with previously reported literature.[27]



6-Methyl-4-phenylquinoline (27)

Purified by flash silica column chromatography (hexane/ethyl acetate = 10:1)

Yellow solid (36.4 mg, 83% yield)

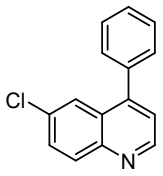
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.87 (d, *J* = 4.4 Hz, 1H), 8.09 (d, *J* = 8.6 Hz, 1H), 7.67 (s, 1H), 7.60 –

7.45 (m, 6H), 7.29 (d, *J* = 4.4 Hz, 1H), 2.46 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 148.5, 147.4, 146.6, 137.7, 136.2, 131.2, 129.0, 129.0, 128.1, 127.9, 126.2, 124.1, 120.9, 21.4.

HRMS (ESI) m/z: [M+H$^+$] Calcd for $C_{16}H_{14}N$ 220.1121; found: 220.1110.

The NMR data was in accordance with previously reported literature.[27]



6-chloro-4-phenylquinoline (28)

Purified by flash silica column chromatography (hexane/ethyl acetate = 10:1)

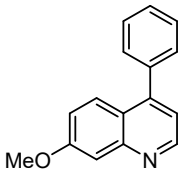
Yellow solid (48.4 mg, 89% yield)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.93 (d, *J* = 4.4 Hz, 1H), 8.11 (d, *J* = 9.0 Hz, 1H), 7.88 (d, *J* = 2.4 Hz, 1H), 7.66 (dd, *J* = 9.0, 2.4 Hz, 1H), 7.59 – 7.45 (m, 5H), 7.35 (d, *J* = 4.4 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 149.7, 147.4, 146.6, 136.8, 132.2, 131.0, 129.9, 129.0, 128.4, 128.3, 127.0, 124.2, 121.6.

HRMS (ESI) m/z: [M+H$^+$] Calcd for $C_{15}H_{11}ClN$ 240.0575; found: 240.0571.

The NMR data was in accordance with previously reported literature.[27]



7-Methoxy-4-phenylquinoline (29)

Purified by flash silica column chromatography (hexane/ethyl acetate = 5:1)

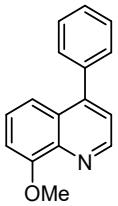
Yellow solid (40.0 mg, 85% yield)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.86 (d, *J* = 4.4 Hz, 1H), 7.81 (d, *J* = 8.2 Hz, 1H), 7.68 – 7.60 (m, 1H), 7.46 – 7.34 (m, 3H), 7.31 (dd, *J* = 7.2, 2.3 Hz, 2H), 7.19 (d, *J* = 4.4 Hz, 1H), 6.83 (d, *J* = 6.8 Hz, 1H), 3.52 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 155.9, 149.3, 148.8, 147.7, 142.1, 129.1, 127.6, 126.5, 126.4, 122.6, 121.7, 118.4, 105.7, 54.8.

HRMS (ESI) m/z: [M+H$^+$] Calcd for $C_{16}H_{14}NO$ 236.1070; found: 236.1069.

The NMR data was in accordance with previously reported literature.[27]



8-Methoxy-4-phenylquinoline (30)

Purified by flash silica column chromatography (hexane/ethyl acetate = 5:1)

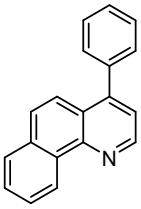
Yellow solid (42.8 mg, 91% yield)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.85 (d, *J* = 4.3 Hz, 1H), 7.43 – 7.31 (m, 6H), 7.29 (d, *J* = 7.9 Hz, 1H), 7.23 (d, *J* = 4.4 Hz, 1H), 6.94 (d, *J* = 7.6 Hz, 1H), 4.00 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 155.0, 148.1, 147.7, 140.0, 137.6, 128.9, 127.9, 127.7, 127.2, 126.0, 121.4, 117.0, 106.7, 55.4.

HRMS (ESI) m/z: [M+H$^+$] Calcd for $C_{16}H_{14}NO$ 236.1070; found: 236.1060.

The NMR data was in accordance with previously reported literature.[26]



4-phenylbenzo[h]quinoline (31)

Purified by flash silica column chromatography (hexane/ethyl acetate = 10:1)

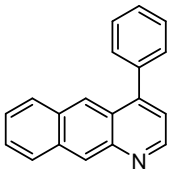
Yellow oil (49.0 mg,96% yield)

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.40 (d, *J* = 8.1 Hz, 1H), 9.04 (d, *J* = 4.6 Hz, 1H), 7.91 (d, *J* = 7.8 Hz, 1H), 7.85 – 7.68 (m, 4H), 7.60 – 7.50 (m, 5H), 7.48 (d, *J* = 4.6 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 147.5, 137.8, 132.9, 130.9, 129.2, 128.1, 128.0, 127.9, 127.3, 127.2, 126.7, 124.4, 124.0, 122.5, 121.9.

HRMS (ESI) m/z: [M+H$^+$] Calcd for $C_{19}H_{14}N$ 256.1121; found: 256.1120.

The NMR data was in accordance with previously reported literature.[27]



4-phenylbenzo[*g*]quinoline (32)

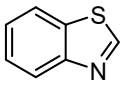
Purified by flash silica column chromatography (hexane/ethyl acetate = 10:1)

Yellow solid (48.4 mg, 95% yield)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.91 (d, *J* = 4.6 Hz, 1H), 8.06 (d, *J* = 9.0 Hz, 1H), 7.97 (d, *J* = 9.0 Hz, 1H), 7.86 (d, *J* = 7.2 Hz, 1H), 7.68 (d, *J* = 8.6 Hz, 1H), 7.53 – 7.45 (m, 4H), 7.43 – 7.36 (m, 2H), 7.33 (d, *J* = 4.5 Hz, 1H), 7.16 (t, *J* = 8.0 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 149.0, 148.0, 147.7, 142.0, 132.4, 130.9, 129.1, 128.7, 128.1, 128.0, 127.7, 127.6, 126.1, 125.0, 123.8, 123.4.

HRMS (ESI) m/z: [M+H$^+$] Calcd for $C_{19}H_{14}N$ 256.1121; found: 256.1120.



Benzothiazole (33)

Purified by flash silica column chromatography (hexane/ethyl acetate = 10:1)

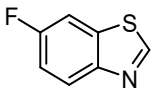
Yellow solid (18.4 mg,68% yield)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.95 (s, 1H), 8.13 (d, *J* = 8.2 Hz, 1H), 7.91 (dt, *J* = 8.0, 0.8 Hz, 1H), 7.52 – 7.44 (m, 1H), 7.44 – 7.35 (m, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 153.5, 152.7, 133.2, 125.7, 125.0, 123.1, 121.4.

HRMS (ESI) m/z: [M+H$^+$] Calcd for C_7H_6NS 136.0215; found: 136.0209.

The NMR data was in accordance with previously reported literature.[28]



6-fluorobenzo[d]thiazole (34)

Purified by flash silica column chromatography (hexane/ethyl acetate = 10:1)

Yellow solid (17.7 mg, 58% yield)

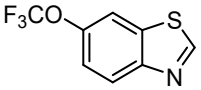
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.94 (s, 1H), 8.07 (dd, *J* = 9.0, 4.8 Hz, 1H), 7.63 (dd, *J* = 8.1, 2.6 Hz, 1H), 7.31 – 7.21 (m, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 160.8 (d, *J* = 246.1 Hz), 153.6 (d, *J* = 3.3 Hz), 149.9, 134.8 (d, *J* = 11.4 Hz), 124.6 (d, *J* = 9.5 Hz), 115.1 (d, *J* = 24.9 Hz), 108.0 (d, *J* = 26.8 Hz).

^{19}F NMR (376 MHz, $CDCl_3$) δ -116.03.

HRMS (ESI) m/z: [M+H$^+$] Calcd for C_7H_5FNS 154.0121; found: 154.0121.

The NMR data was in accordance with previously reported literature.[28]



6-fluorobenzo[d]thiazole (35)

Purified by flash silica column chromatography (hexane/ethyl acetate = 10:1)

Yellow solid (27.6 mg, 63% yield)

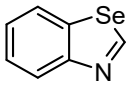
^{1}H NMR (400 MHz, $CDCl_3$) δ 9.04 (s, 1H), 8.15 (d, *J* = 8.9 Hz, 1H), 7.84 (s, 1H), 7.41 (d, *J* = 8.9 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 154.6, 151.3, 146.4, 134.2, 127.5, 124.1, 113.9.

^{19}FNMR (376 MHz, $CDCl_3$) δ -58.41.

HRMS (ESI) m/z: [M+H$^+$] Calcd for $C_8H_5F_3NOS$ 220.0038; found: 220.0040.

The NMR data was in accordance with previously reported literature.[28]



Benzo[*d*][1,3]selenazole (36)

Purified by flash silica column chromatography (hexane/ethyl acetate = 10:1)

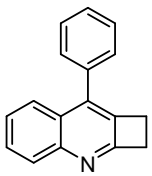
Yellow solid (27.1 mg, 74% yield)

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.91 (s, 1H), 8.20 (d, *J* = 8.2 Hz, 1H), 8.00 (d, *J* = 8.0 Hz, 1H), 7.51 (t, *J* = 7.0 Hz, 1H), 7.37 (t, *J* = 7.6 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 158.1, 154.9, 137.2, 126.3, 125.7, 125.3, 125.2.

HRMS (ESI) m/z: [M+H$^+$] Calcd for C_7H_6NSe 183.9660; found: 183.9657.

The NMR data was in accordance with previously reported literature.[32]



8-phenyl-1,2-dihydrocyclobuta[b]quinoline (37)

Purified by flash silica column chromatography (hexane/ethyl acetate = 10:1)

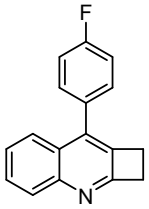
Yellow solid (33.3 mg, 72% yield)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 (d, *J* = 8.4, 1.3 Hz, 1H), 7.97 (d, *J* = 8.5, 1.6 Hz, 1H), 7.63 (t, *J* = 8.5, 6.9, 1.6 Hz, 1H), 7.52 (d, *J* = 4.5 Hz, 4H), 7.51 – 7.38 (m, 2H), 3.62 – 3.55 (t, 2H), 3.28 – 3.21 (t, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 165.9, 149.9, 140.0, 136.9, 134.7, 129.7, 129.4, 128.8, 128.5, 128.1, 127.9, 125.8, 125.3, 34.7, 26.3.

HRMS (ESI) m/z: [M+H$^+$] Calcd for $C_{17}H_{14}N$ 232.1121; found: 232.1121.

The NMR data was in accordance with previously reported literature.[29]



8-(4-fluorophenyl)-1,2-dihydrocyclobuta[b]quinoline (38)

Purified by flash silica column chromatography (hexane/ethyl acetate = 10:1)

Yellow solid (27.9 mg, 56% yield)

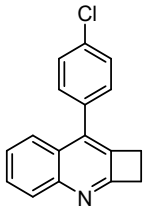
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 (d, *J* = 8.4 Hz, 1H), 7.87 (d, *J* = 8.4 Hz, 1H), 7.62 (t, *J* = 7.6 Hz, 1H), 7.49 – 7.37 (m, 3H), 7.21 – 7.13 (m, 2H), 3.58 (t, *J* = 5.3 Hz, 2H), 3.21 (t, *J* = 5.3 Hz, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 165.8, 164.1, 150.0, 138.9, 136.9, 131.4 (d, *J* = 8.2 Hz), 129.5, 128.1, 127.9, 125.5, 125.4, 115.9 (d, *J* = 21.7 Hz), 34.7, 26.2.

^{19}F NMR (376 MHz, $CDCl_3$) δ -112.24.

HRMS (ESI) m/z: [M+H$^+$] Calcd for $C_{17}H_{13}FN$ 250.1027; found: 250.1030.

The NMR data was in accordance with previously reported literature.[29]



8-(4-chlorophenyl)-1,2-dihydrocyclobuta[b]quinoline (39)

Purified by flash silica column chromatography (hexane/ethyl acetate = 10:1)

Yellow solid (34.5 mg, 65% yield)

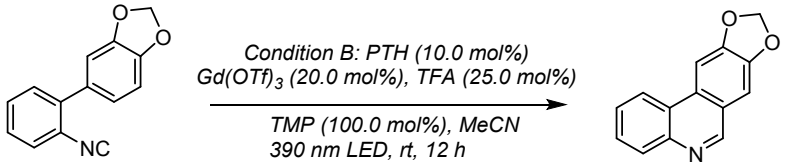
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (d, *J* = 8.5 Hz, 1H), 7.88 (d, *J* = 8.5 Hz, 1H), 7.70 – 7.59 (m, 1H), 7.55 – 7.32 (m, 5H), 3.60 – 3.53 (m, 2H), 3.24 – 3.17 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 165.8, 150.0, 138.6, 136.9, 134.7, 133.1, 131.0, 129.5, 129.1, 128.2, 127.6, 125.5, 125.4, 34.8, 26.2.

HRMS (ESI) m/z: [M+H$^+$] Calcd for $C_{17}H_{13}ClN$ 266.0731; found: 266.0731.

The NMR data was in accordance with previously reported literature.[29]

E. Procedure for large-scale synthesis of Trisphaeridine 13:

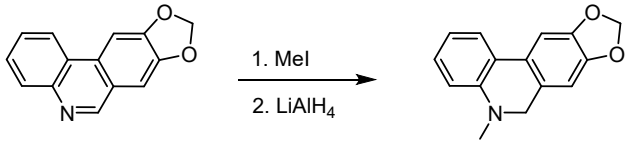


13

To an oven-dried 50 mL Schlenk tube equipped with a stir bar, were added $Gd(OTf)_3$ (241.8mg, 20.0 mol%.), photocatalyst PTH (55.1 mg, 10.0 mol%). Then the reaction was evacuated and backfilled with argon for three times. After isocyanide (2.0 mmol, 1.0 equiv.), TMP (2.0 mmol 1.0 equiv.), TFA (57.0mg 25.0 mol%) and anhydrous MeCN (10 ml) were added. The reaction mixture was irradiated under 390 nm LED at room temperature for 12 h. The residue was purified by silica gel chromatography to afford the desired product. The residue was purified by silica gel chromatography (hexane/ethyl acetate = 10:1) to afford the desired product **13** as yellow solid (214.1 mg, 48% yield).

F. Derivatization reactions:

Synthetic transformation of products:[8]



13 **5,6-Dihydrobicolorine**

Step 1: A 50 mL reaction flask was charged with **13 (Trisphaeridine)** (223.2 mg, 1.0 mmol), MeI (methyliodide, 2838.8 mg, 20.0 mmol) and toluene (20.0 mL). The reaction mixture was stirred at room temperature for 18 h, then filtered by funnel, and the solid residue was washed by CH_2Cl_2 to afford 5-methyl-[1,3]dioxolo[4,5-j]phenanthridin-5-ium iodide as a yellow solid.

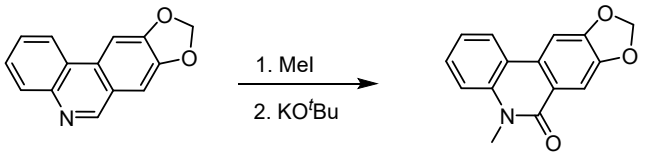
Step 2: A pressure tube was charged with 5-methyl-[1,3]dioxolo[4,5-j]phenanthridin-5-ium iodide (292.0 mg, 0.8 mmol) and THF (8.0 mL), $LiAlH_4$ (121.6 mg, 3.2 mmol) was then slowly added into the solution. The reaction mixture was stirred at room temperature for 1 h, then added ethyl acetate to quench the excess $LiAlH_4$, filtered through a thin Celite pad, and concentrated under reduced pressure to yield the crude product, which was further purified by silica gel chromatography to afford the desired product **40 (5,6-Dihydrobicolorine)** as a yellow solid (138.7 mg, 58% yield).

^1H NMR (400 MHz, $CDCl_3$) δ 7.55 (d, J = 7.8, 1.6 Hz, 1H), 7.30 – 7.13 (m, 2H), 6.87 (t, J = 7.5, 1.2 Hz, 1H), 6.74 (d, J = 8.1, 1.3 Hz, 1H), 6.63 (s, 1H), 5.97 (s, 2H), 4.08 (s, 2H), 2.90 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 147.6, 146.9, 146.6, 128.5, 127.3, 126.3, 123.7, 123.1, 118.8, 112.3, 106.2, 103.3, 101.1, 55.2, 38.7.

HRMS (ESI) m/z: [M+H$^+$] Calcd for $C_{15}H_{13}NO_2$ 240.1019; found: 240.1019.

The NMR data was in accordance with previously reported literature.[8]



13 **N-Methylcrisanidine**

Step 1: A 50 mL reaction flask was charged with **13 (Trisphaeridine)** (223.2 mg, 1.0 mmol), MeI (methyliodide, 2838.8 mg, 20.0 mmol) and toluene (20.0 mL). The reaction mixture was stirred at room temperature for 18 h, then filtered by funnel, and the solid residue was washed by CH_2Cl_2 to afford 5-methyl-[1,3]dioxolo[4,5-j]phenanthridin-5-ium iodide as a yellow solid.

Step 2: A 50 ml reaction flask was charged with 5-methyl-[1,3]dioxolo[4,5-j]phenanthridin-5-ium iodide (292.0 mg, 0.8 mmol), *t*-BuOK (179.6 mg, 1.6 mmol) and DMSO (4.0 mL). The reaction mixture was stirred at room temperature for 38 h under air. Then it was diluted with EtOAc (10.0 mL) and water (10.0 mL) and extracted with EtOAc (10 mL × 3). The combined organic extracts were dried over anhydrous $MgSO_4$, filtered and concentrated under reduced pressure to yield the crude product, which was further purified by silica gel chromatography to afford the desired product as **41 (N-Methylcrisanidine)** a white solid (169.6 mg, 67% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (dd, J = 8.2, 1.5 Hz, 1H), 7.88 (s, 1H), 7.58 (s, 1H), 7.50 (t, *J* = 8.6, 7.1, 1.5 Hz, 1H), 7.37 (d, *J* = 8.4, 1.2 Hz, 1H), 7.32 – 7.24 (t, 1H), 6.11 (s, 2H), 3.78 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 161.1, 152.2, 148.5, 130.5, 129.0, 123.0, 122.4, 121.3, 119.3, 115.1, 107.0, 102.0, 100.5, 30.1.

HRMS (ESI) m/z: [M+H$^+$] Calcd for $C_{15}H_{11}NO_2$ 254.0812; found: 254.0812.

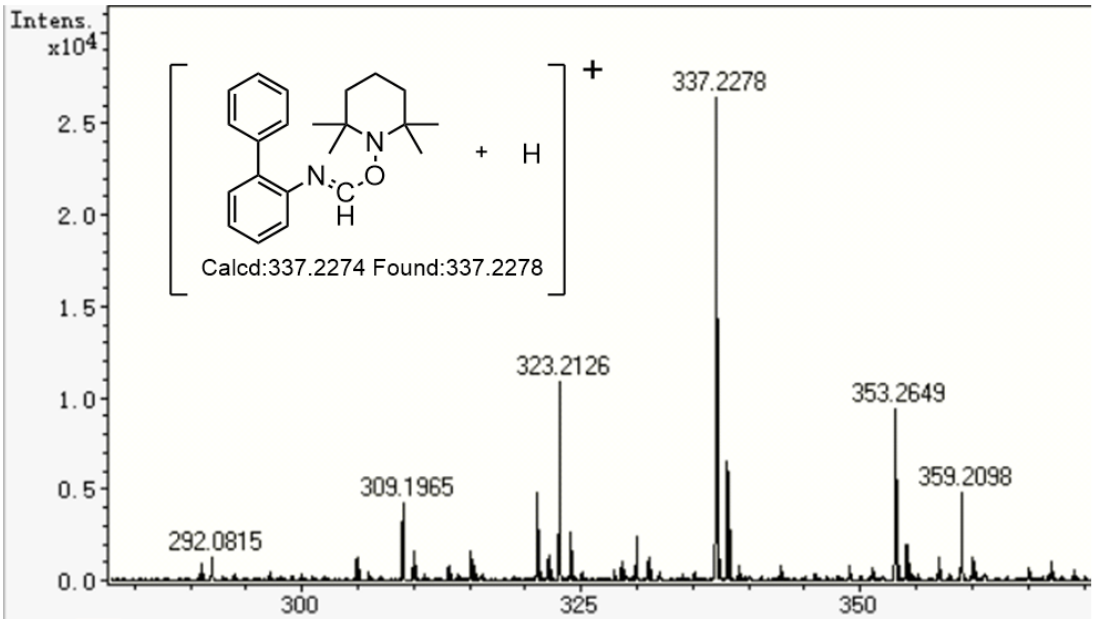
The NMR data was in accordance with previously reported literature.[8]

G. Mechanistic studies:

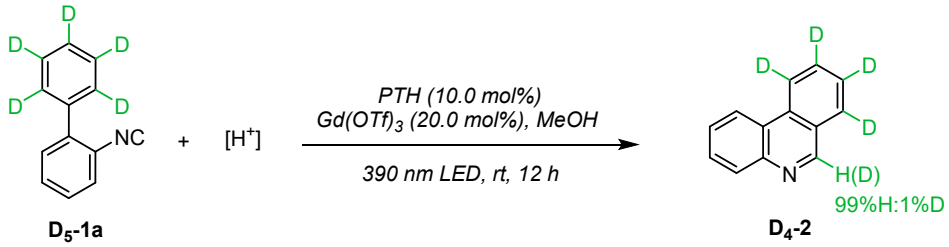
(a) Radical trapping experiment:

1a

To an oven-dried 5 mL Schlenk tube equipped with a stir bar, were added $Gd(OTf)_3$ (12.1 mg, 20.0 mol%.), photocatalyst PTH (2.75 mg, 10.0 mol%) and (2,2,6,6-Tetramethylpiperidin-1-yl)oxyl (TEMPO) (31.7 mg, 0.2 mmol, 2.0 equiv.). Then the reaction was evacuated and backfilled with argon for three times. After isocyanide (0.1 mmol, 1.0 equiv.) and anhydrous MeOH (1.0 ml) were added. The reaction mixture was irradiated under 390 nm LED at room temperature for 12 h. The mixture was detected by HRMS (see below).

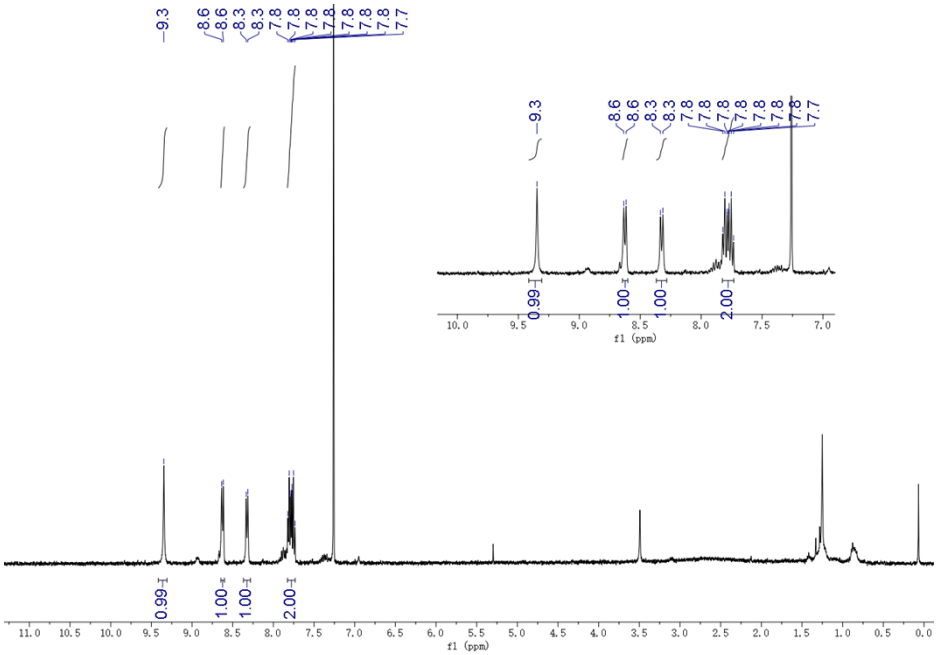


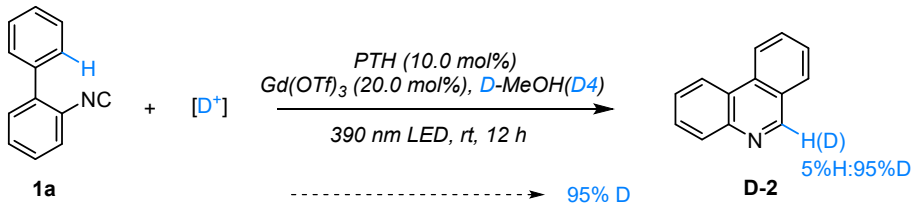
(c) Deuterium control experiment:



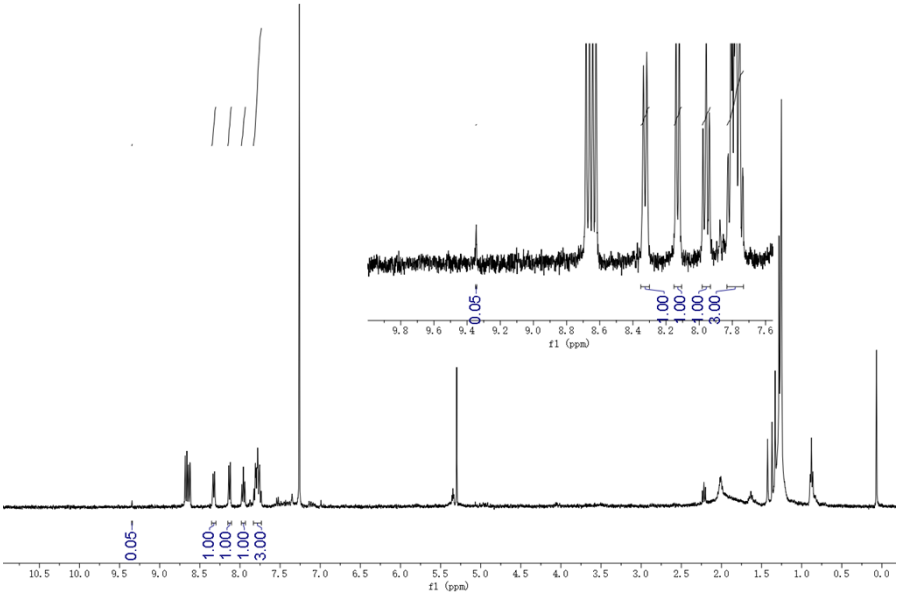
D_5-1a **D_4-2**

To an oven-dried 5 mL Schlenk tube equipped with a stir bar, were added $Gd(OTf)_3$ (12.1mg, 20 mol%.), photocatalyst PTH (2.75 mg, 10 mol%). Then the reaction was evacuated and backfilled with argon for three times. After **D_5-1a** (0.1 mmol, 1.0 equiv.) and anhydrous MeOH (1.0 ml) were added. The reaction mixture was irradiated under 390 nm LED at room temperature for 12 h to afford the desired product **D_4-2**.





To an oven-dried 5 mL Schlenk tube equipped with a stir bar, were added Gd $(OTf)_3$ (12.1mg, 20 mol%.), photocatalyst PTH (2.75 mg, 10 mol%). Then the reaction was evacuated and backfilled with argon for three times. After **1a** (0.1 mmol, 1.0 equiv.) and anhydrous CD_3OD (1.0 ml) were added. The reaction mixture was irradiated under 390 nm LED at room temperature for 12 h to afford the desired product **D-2**.



(d) Stern-Volmer quenching studies:

Emission intensities were recorded using a spectrofluorometer at ambient temperature. All PTH solutions were excited at 320 nm and the emission intensity was recorded at 390 nm. Firstly, the emission spectrum of a 5 x 10^{-5} M solution of PTH in MeCN (10 mL) was collected. Then, an appropriate amount of quencher was added to the measured solution, and the emission spectrum of the sample was collected. The Stern-Volmer emission quenching studies tell that the isocyanide **1a** are easier than TMP, TFA and Lewis acid $Gd(OTf)_3$ to quench the excited photosensitizer.

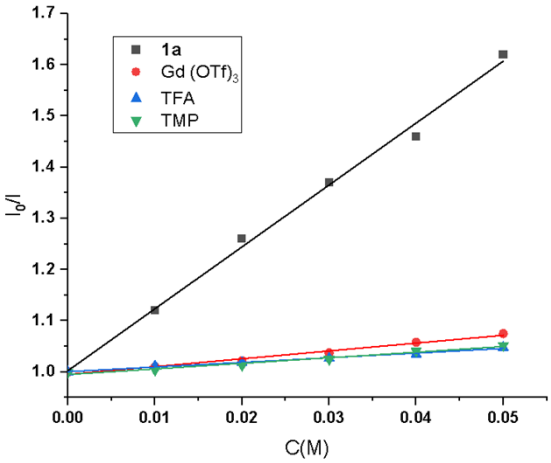


Figure **S4**. Stern-Volmer quenching studies

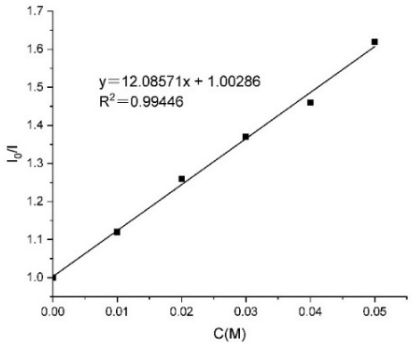


Figure **S5**. PTH emission quenching by **1a**

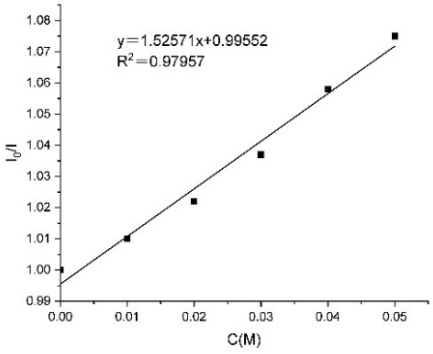


Figure **S6**. PTH emission quenching by $Gd(OTf)_3$

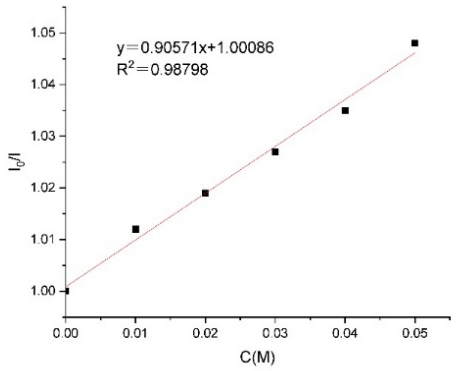


Figure **S7**. PTH emission quenching by TFA

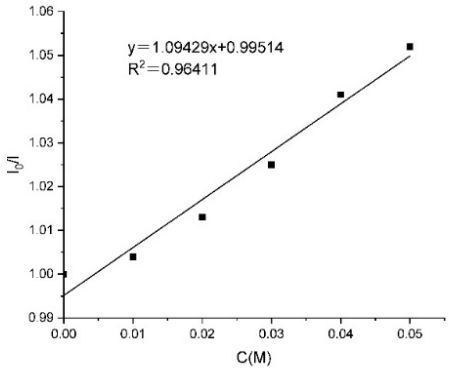


Figure **S8**. PTH emission quenching by TMP

(e) Light on-off experiment:

To an oven-dried 5 mL Schlenk tube equipped with a stir bar, were added $Gd(OTf)_3$ (12.1 mg, 20.0 mol%.), photocatalyst PTH (2.75 mg, 10.0 mol%). Then the reaction was evacuated and backfilled with argon for three times. After isocyanide **1a** (0.1 mmol, 1.0 equiv.) and anhydrous MeOH (1 ml) were added. Then the reaction mixture was irradiated with 390 nm LED and kept in the dark in 2 h intervals at room temperature. Yields of the **2** was determined by ^1H NMR monitors by using the dibromomethane as internal standard. The reaction proceeded well under the irradiation of visible light, but no further transformation was observed without the light irradiation, indicating the continuous irradiation of visible light is essential for this catalytic reaction.

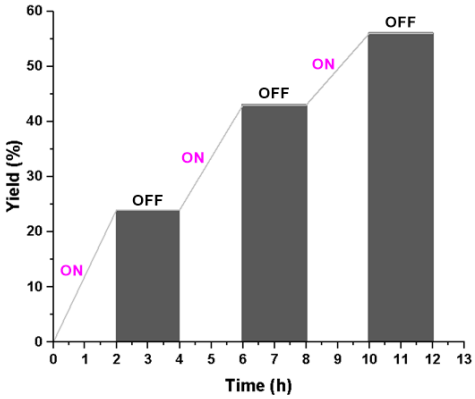


Figure **S9**. Light on-off Experiment

(f) Determination of the reaction quantum yield (Φ) of product 2

Following a modified procedure reported by Yoon[30], ferrioxalate actinometer solution was prepared and stored in the dark. The actinometer solution measures the photodecomposition of ferric oxalate anions to ferrous oxalate anions, which are then reacted with 1,10-phenanthroline to form $Fe(Phen)_3^{2+}$. Its concentration is then estimated by UV/Vis absorbance at 510 nm. The number of moles of $Fe(Phen)_3^{2+}$ complex formed is related to the numbers of photons absorbed by the actinometer solution. Preparation of the solutions used for the studies:

1. Potassium ferrioxalate solution: Potassium ferrioxalate trihydrate (118.0 mg) and 95-98% H_2SO_4 (56.0 μ L) were added to a 20 mL volumetric flask and filled to the mark with distilled water.
2. Buffer solution: Sodium acetate (0.988 g) and 95-98% H_2SO_4 (0.2 mL) were added to a 20 mL volumetric flask and filled to the mark with distilled water.

The actinometry measurements:

a) 1 mL of the actinometer solution was taken in a quartz cuvette (l = 1 cm). The cuvette of actinometer solution was placed at a distance of 7 cm away from a 390 nm LED and irradiated for 90 s.

b) After irradiation, the actinometer solution was transferred to a 10 mL volumetric flask containing 1.0 mg of 1,10-phenanthroline in 2 ml of buffer solution. The flask was filled to the mark with distilled water. The solution was then allowed to rest for 1 h to allow the ferrous ions to completely coordinate to the phenanthroline. In a similar manner, a blank solution (10 mL) was also prepared using the actinometer solution stored in dark.

c) Absorbance of the actinometer solution after complexation with 1,10-phenanthroline at λ = 510 nm was measured by UV/Vis spectrophotometry.

d) According to Beer's law, the number of moles of Fe^{2+} formed (x) for each sample was determined by equation 1:

$$mol\ Fe^{2+} = \frac{v1 * v3 * \Delta A}{1000 * v2 * 1 * \varepsilon} \qquad (1)$$

Where:

v1 = Irradiated volume (1 mL).

v2 = The aliquot of the irradiated solution taken for the estimation of Fe+ ions (1 mL).

v3 = Final volume of the solution after complexation with 1,10-phenanthroline (10 mL). ε (510 nm) =Molar extinction coefficient of $[Fe(Phen)_3]^{2+}$ complex (11100 L mol^{-1} cm^{-1}).

l = Optical path-length of the cuvette (1 cm).

ΔA (510 nm) = Difference in absorbance between the irradiated solution and the solution stored in dark (blank).

Sample calculation:

A0 = 0.034 A90S = 1.496 Δ A90S = 1.462

mol Fe^{2+} (90 S) = (1 mL × 10 mL × 1.462)/ (1000 × 1 mL × 1 cm × 11100 L mol^{-1} cm^{-1}) = 1.406× 10^{-6} mol

Moles of $[Fe(Phen)_3]^{2+}$ per unit of time formed due to decomposition of the actinometer solution at 390 nm LED irradiation by using following equation 2

$$photon\ flux = \frac{mol\ Fe^{2+}}{\Phi * t * f} \qquad (2)$$

Φ(λ) = The quantum yield for Fe^{2+} formation at 406 nm is 1.18[31].

f = 1-10^{-A}, A (390nm) = Absorbance of the ferrioxalate actinometer solution at a wavelength of 390 nm,

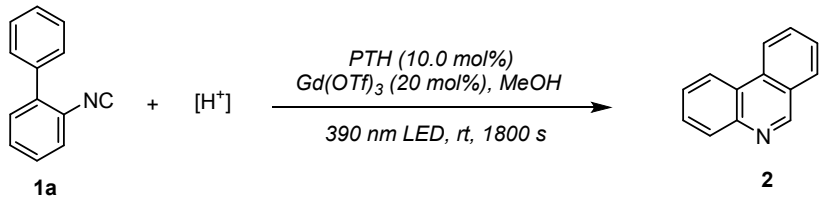
which was measured placing 1 mL of the solution in a cuvette of pathlength 1 cm by UV/Vis spectrophotometry.

Sample calculation:

A(390nm) = 0.118 f = 1-10$^{-0.118}$ = 0.238

photon flux = 1.406 × 10^{-6}/ (1.18 × 90 × 0.238) = 5.5627× 10^{-8} einsteins s^{-1}

Determination of the Reaction Quantum Yield



1a **2**

In the glovebox, to a 5 mL quartz cuvette with two sides taped over with electrical tape **1a** (17.9 mg, 0.1 mmol, 1.0 equiv.), Gd(OTf)$_3$ (12.1 mg, 20% mol), photocatalyst PTH (2.75 mg, 10.0 mol%), and MeOH (1.0 ml, 1M) were introduced in sequence and then the quartz cuvette was capped. The sample was stirred and irradiated for 1800 s (30 min) at λ_{max} = 390 nm at rt. After irradiation, the yield of product **2** was determined to be 5% (1.0 × 10^{-5} mol of **2**) by **^{1}H NMR** with dibromomethane as internal standard. The reaction quantum yield (Φ) was determined using the equation 3 where the photon flux is 5.5627× 10^{-8} einstein s^{-1}. t is the reaction time (1800 s). Essentially all incident light (f > 0.995, vide infra) is absorbed by the PTH at the reaction conditions described above (A (390nm) = 2.328)

$$\Phi = \frac{mol\ of\ product\ formed}{photon\ flux * t * f} \qquad (3)$$

Quantum yield calculation using above equation (3):

Φ = 1.0×10^{-5} mol/(5.5627× 10^{-8} einsteins s^{-1} × 1800 s×0.995) = 0.10

The reaction quantum yield (Φ) was thus determined to be 0.10.

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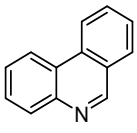
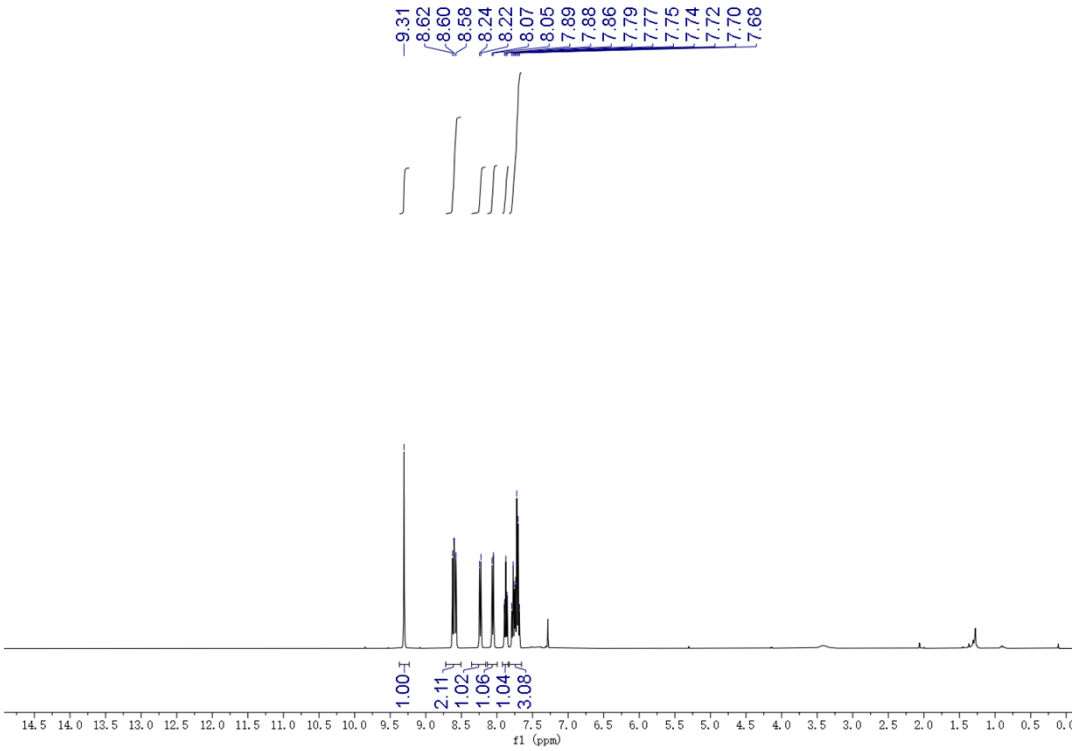
I. NMR spectrum:



(2)

400 MHz in $CDCl_3$



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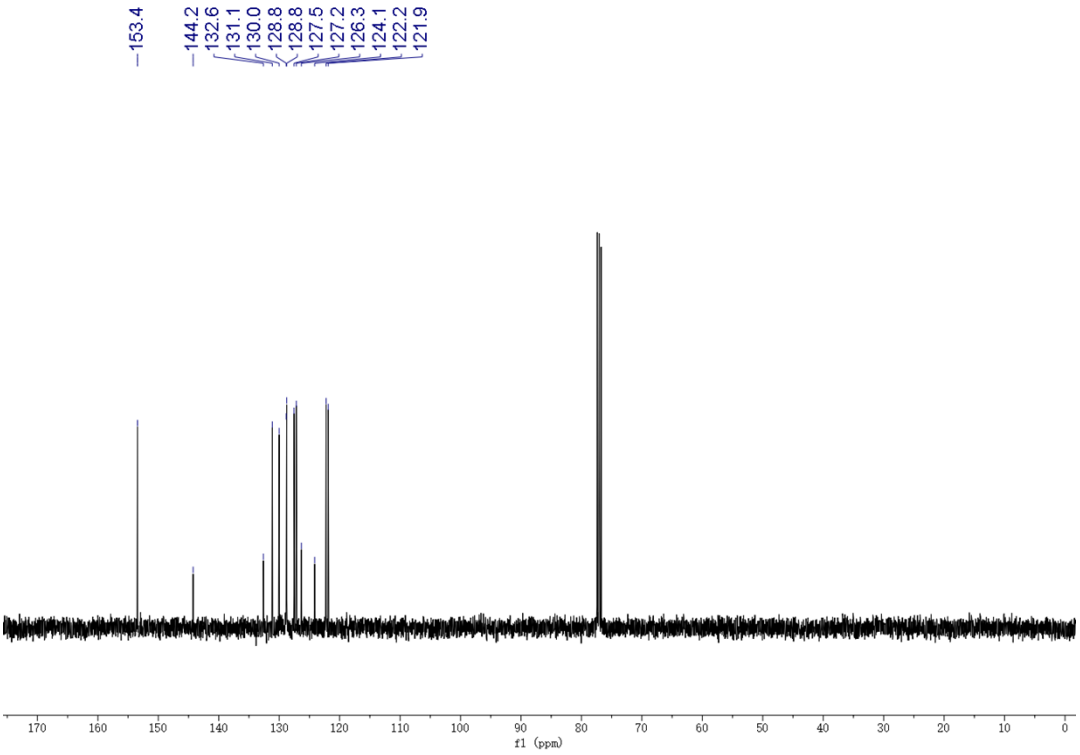

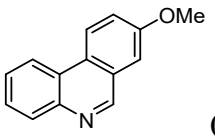

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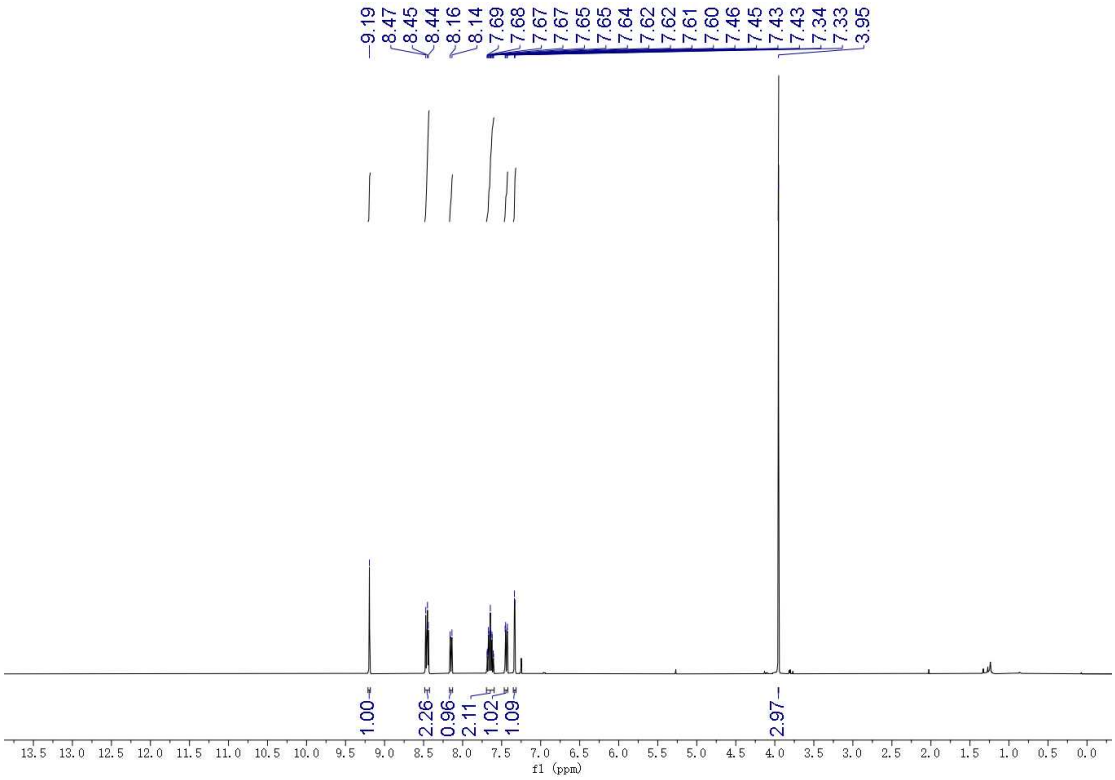
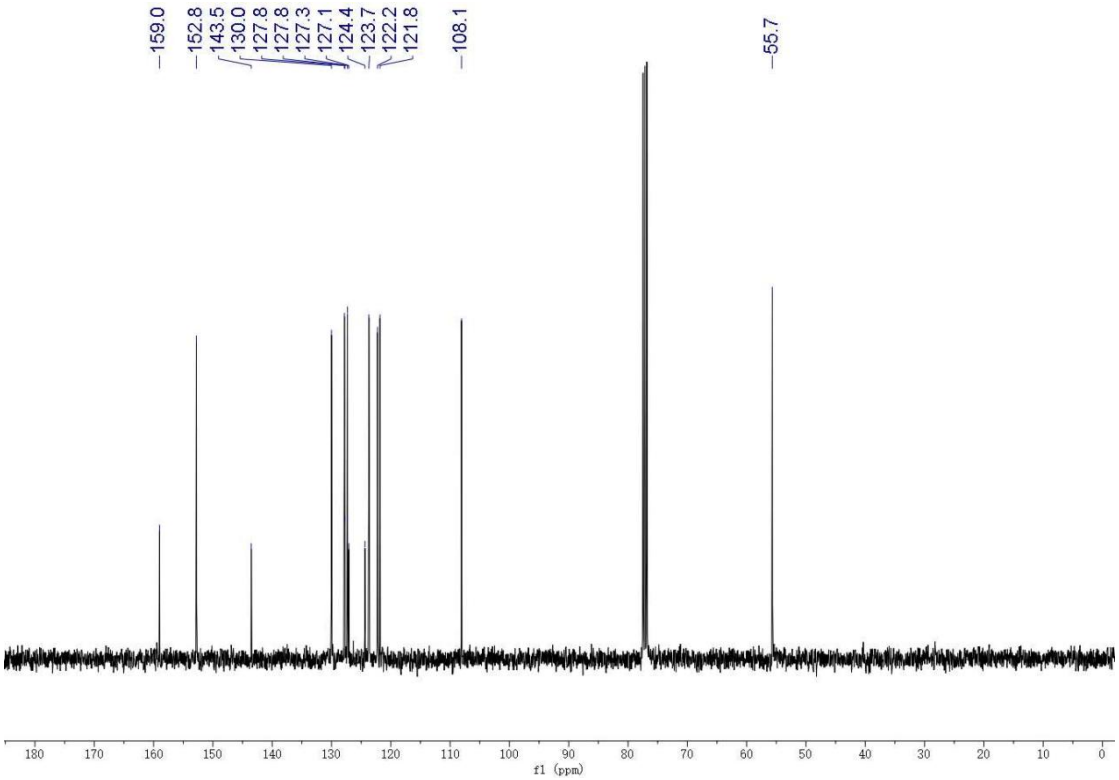
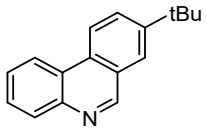


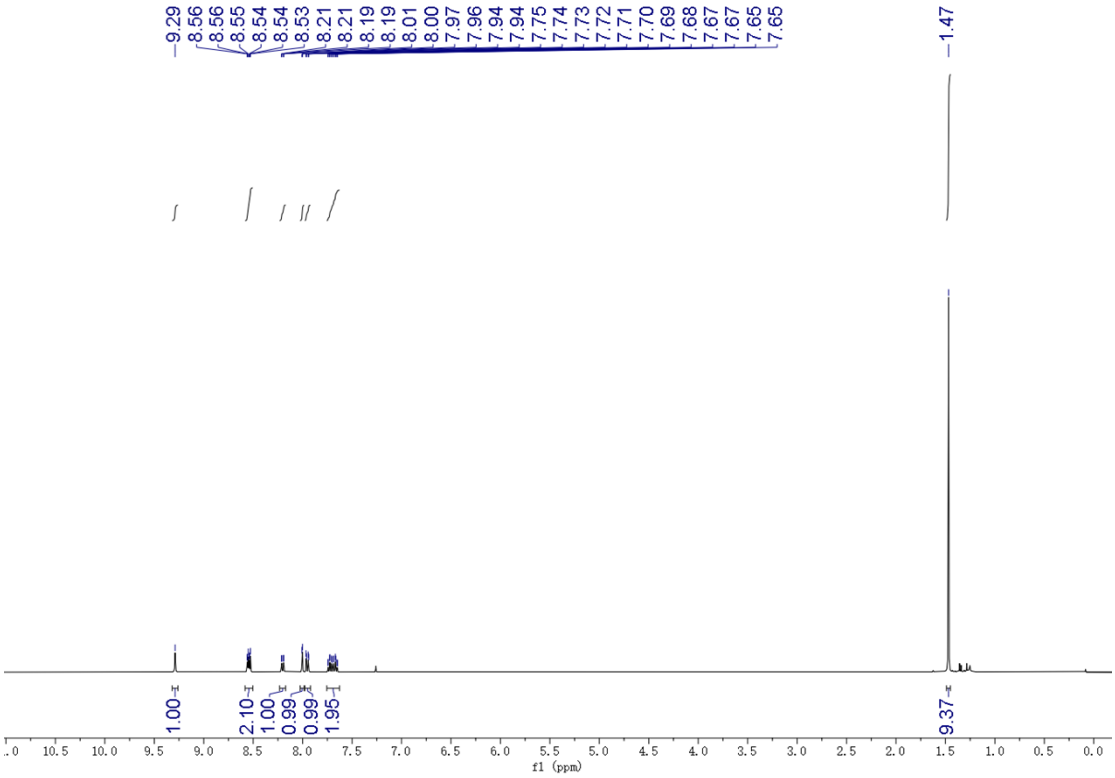
100 MHz in $CDCl_3$



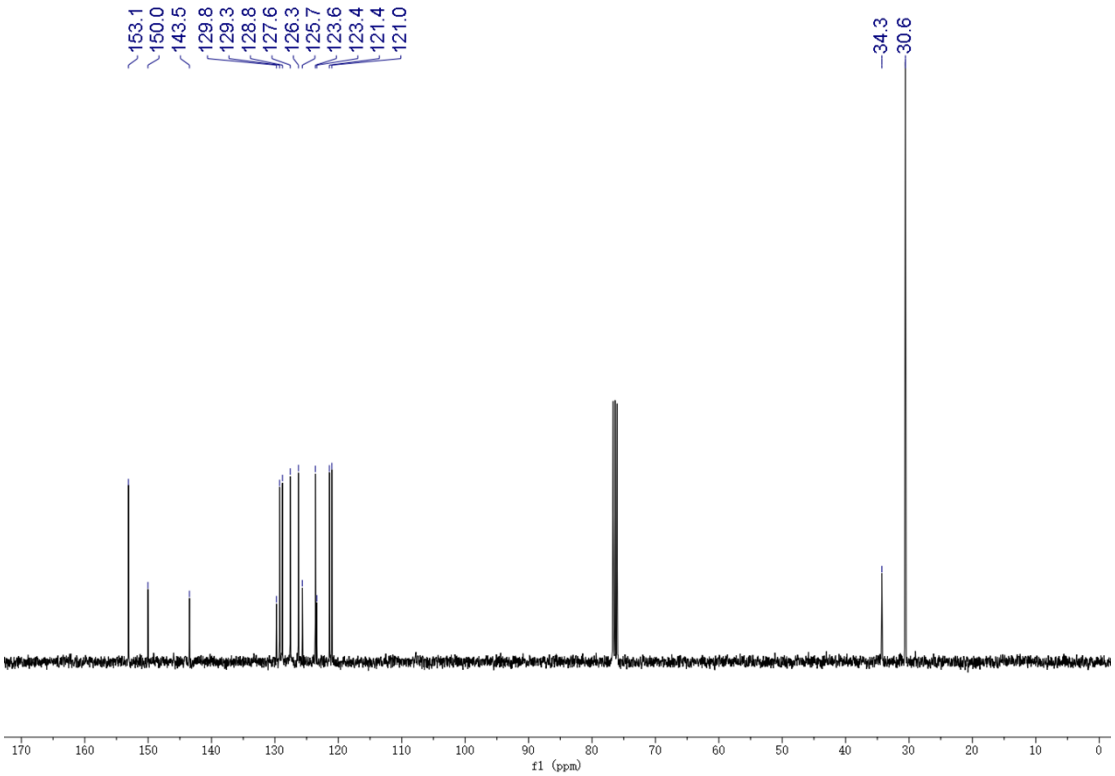


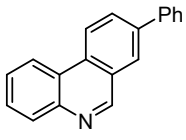
(4)

400 MHz in $CDCl_3$



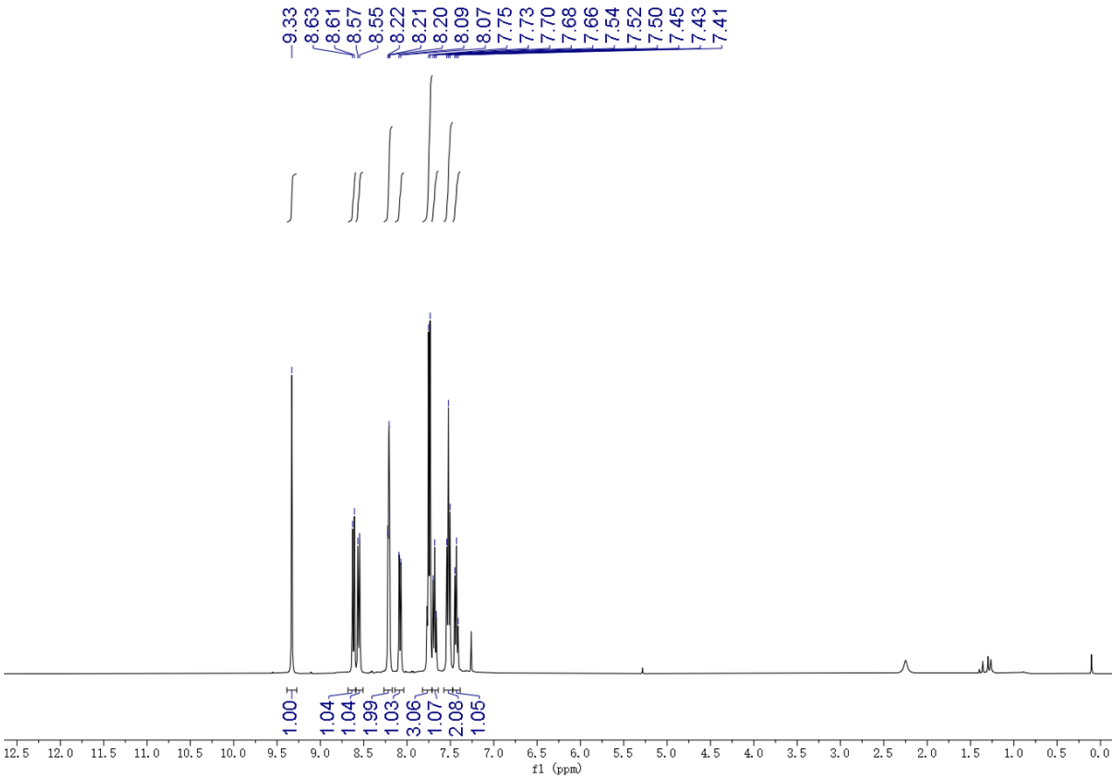
100 MHz in $CDCl_3$



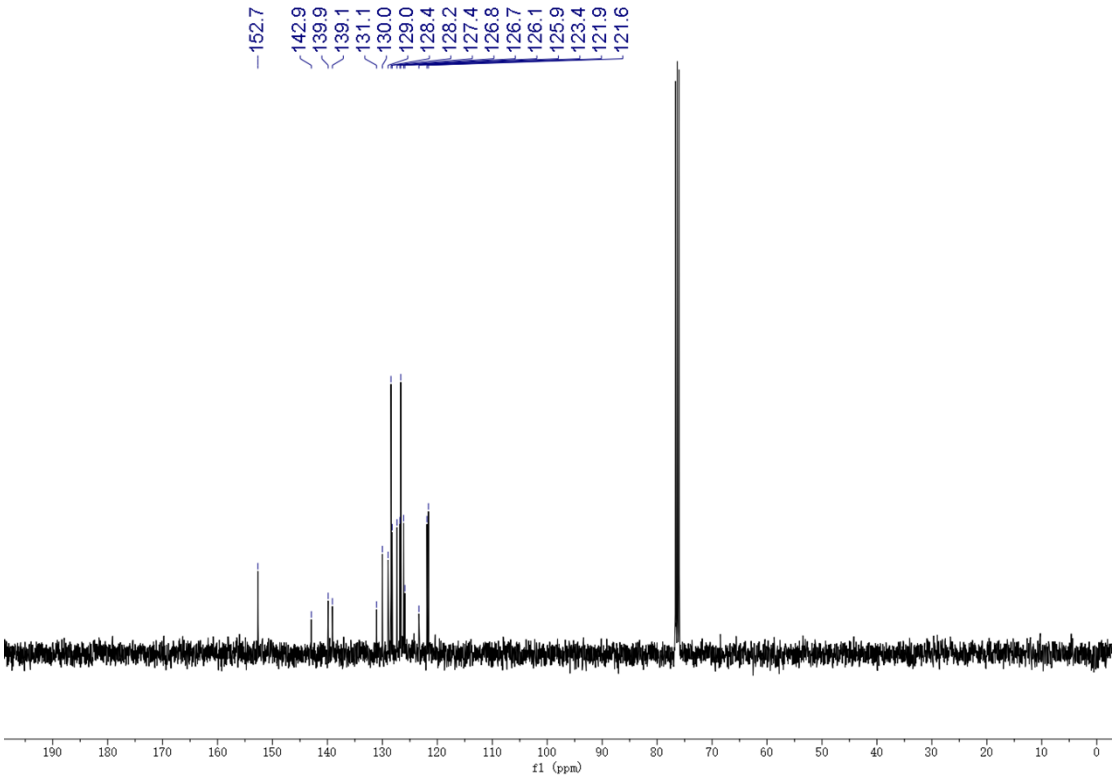


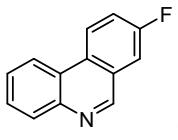
(5)

400 MHz in $CDCl_3$



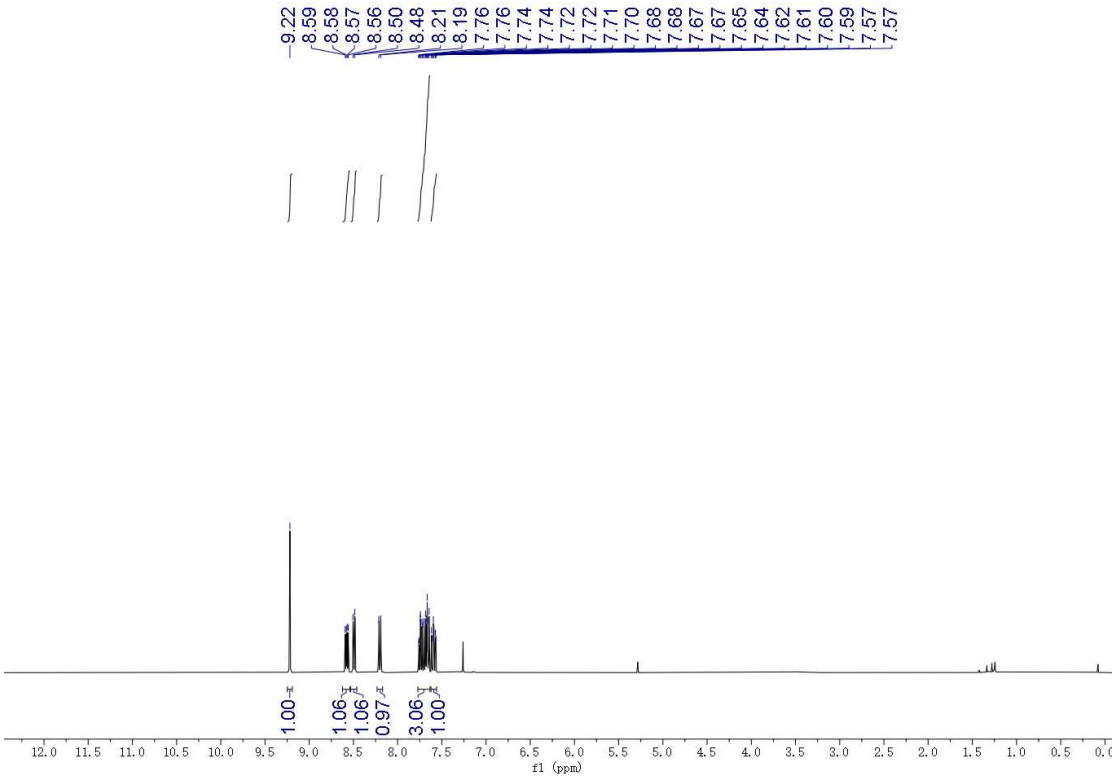
100 MHz in $CDCl_3$



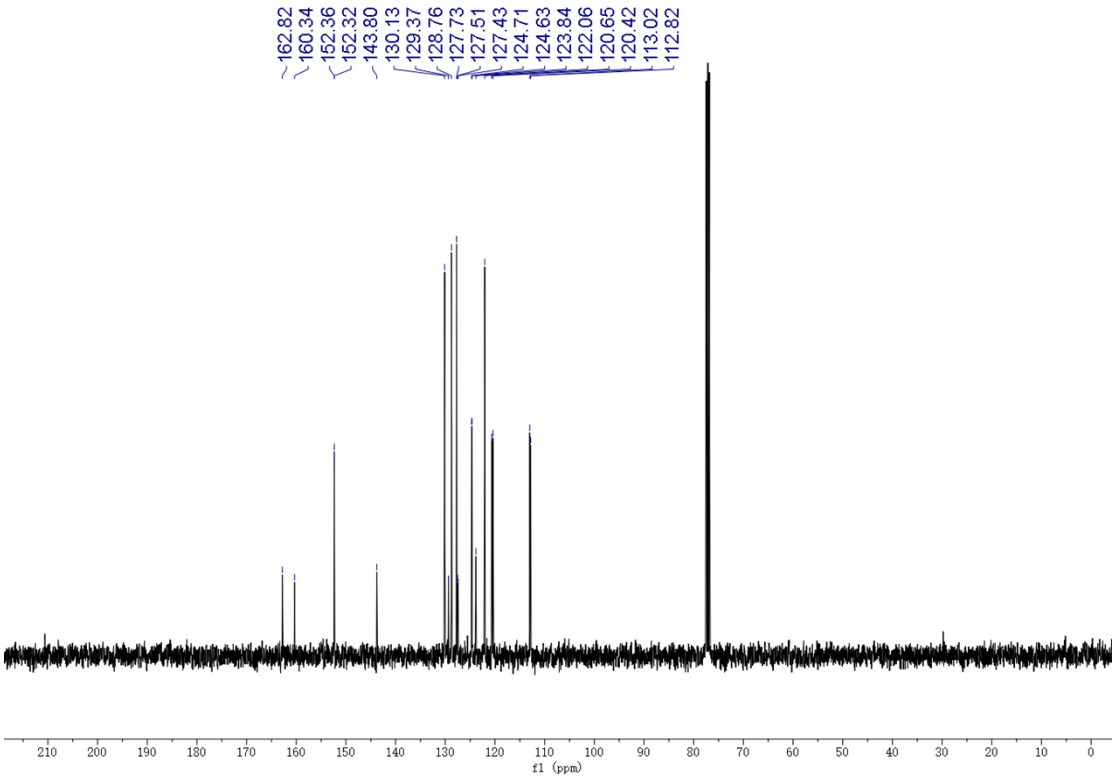


(6)

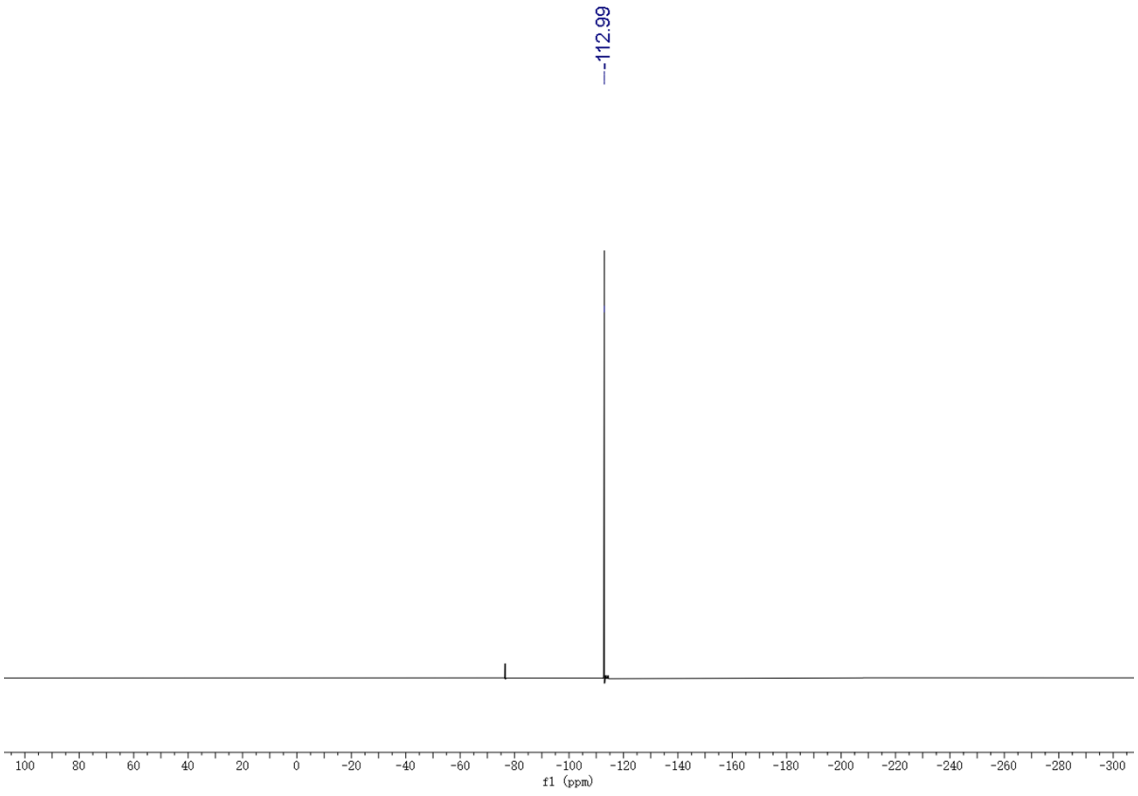
400 MHz in $CDCl_3$

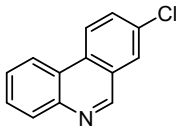


100 MHz in $CDCl_3$



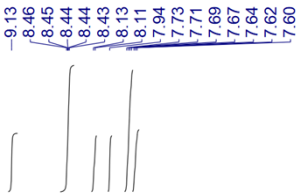
376 MHz in $CDCl_3$

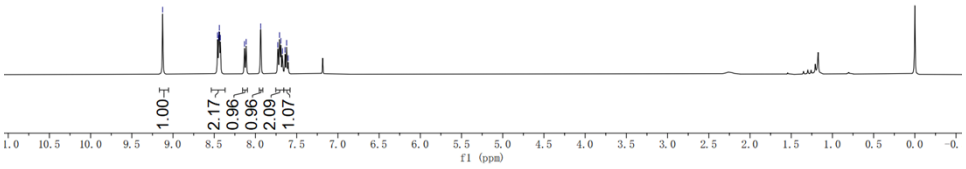




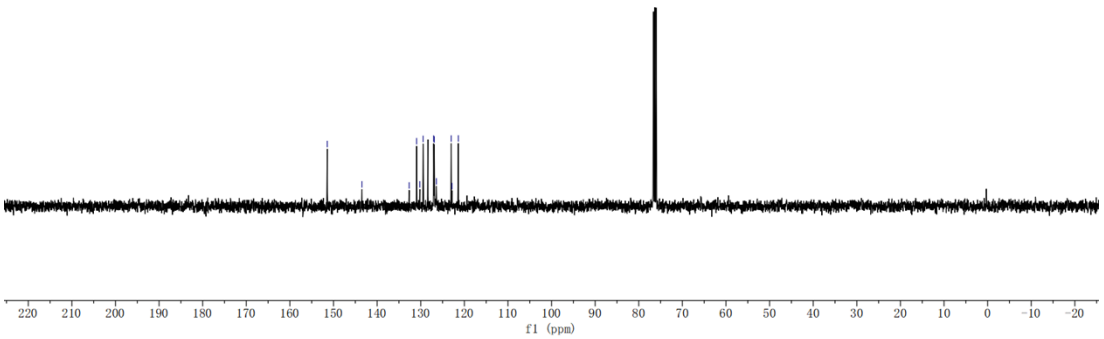
(7)

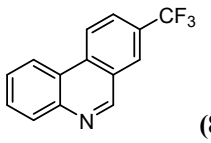
400 MHz in $CDCl_3$





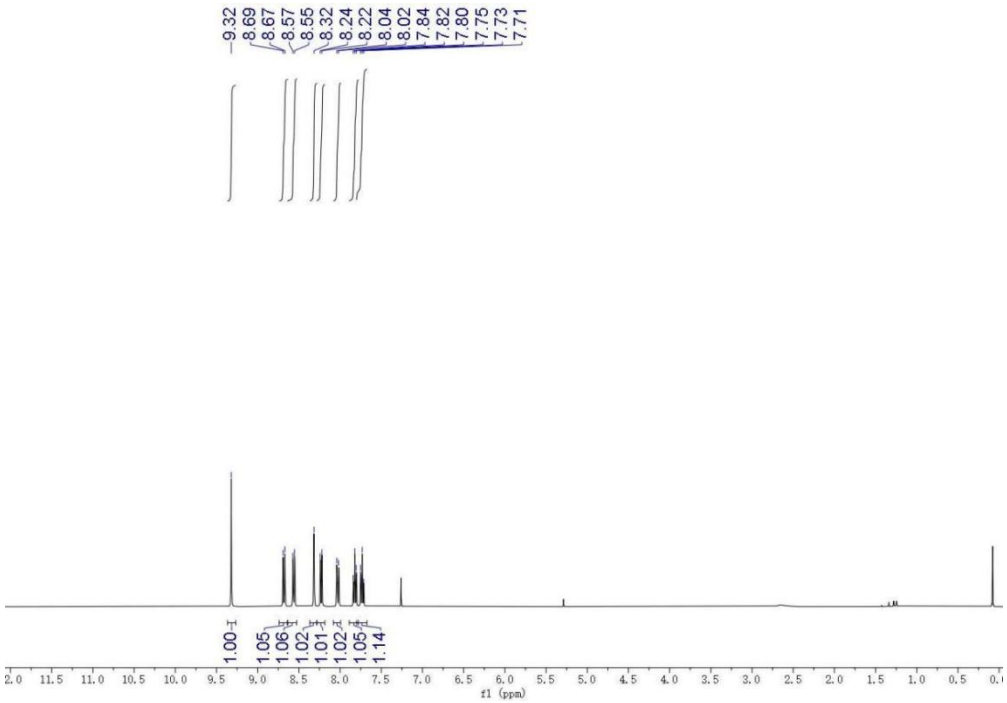
100 MHz in $CDCl_3$



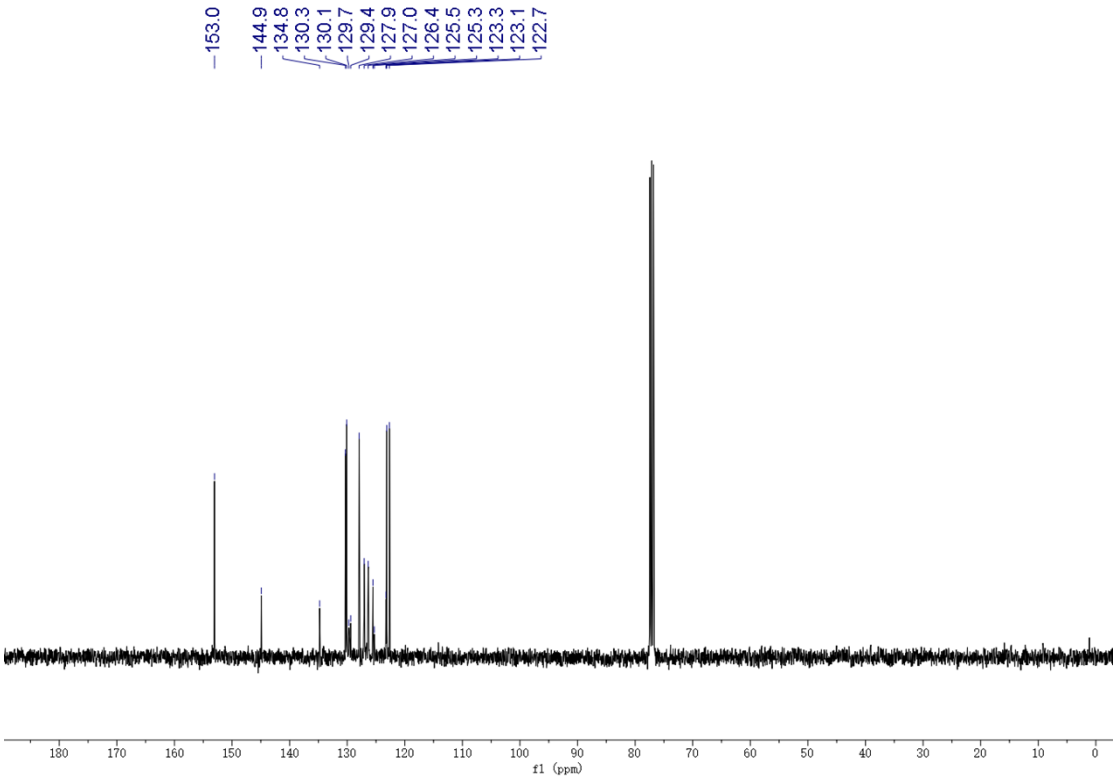


(8)

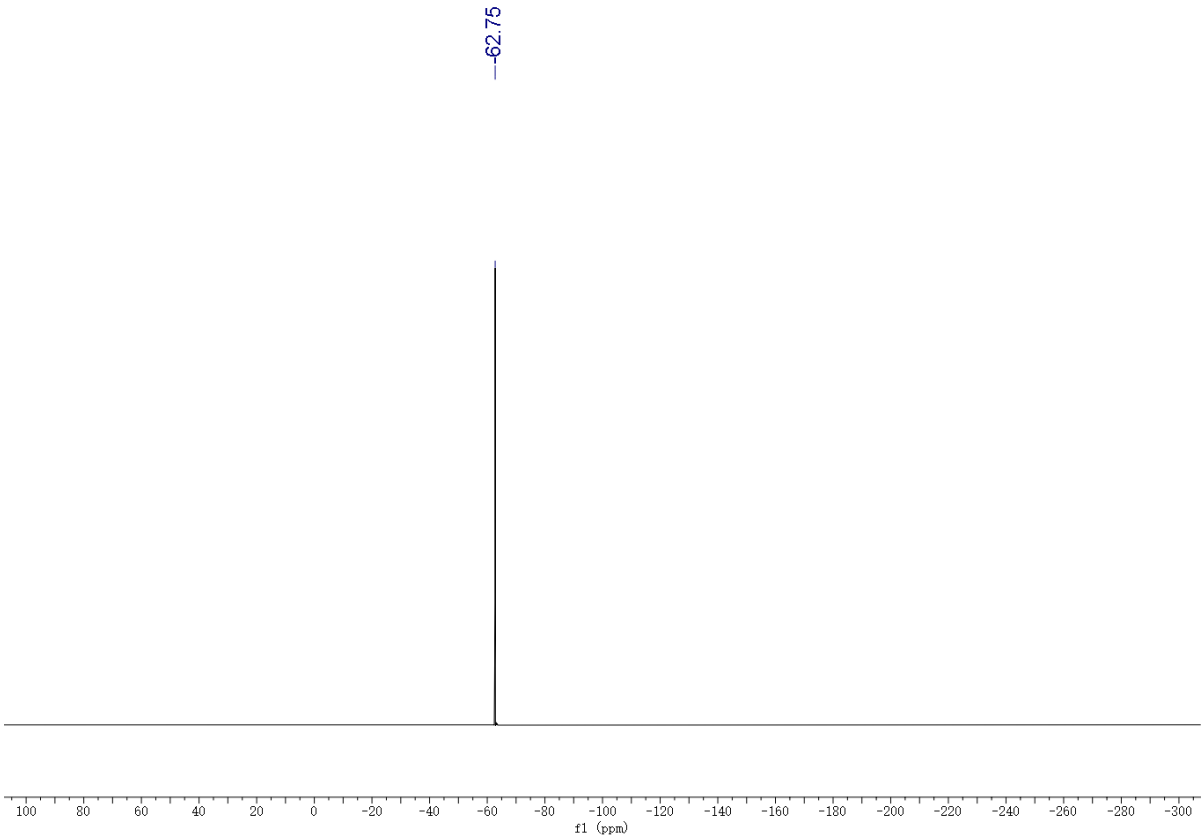
400 MHz in $CDCl_3$

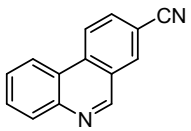


100 MHz in $CDCl_3$



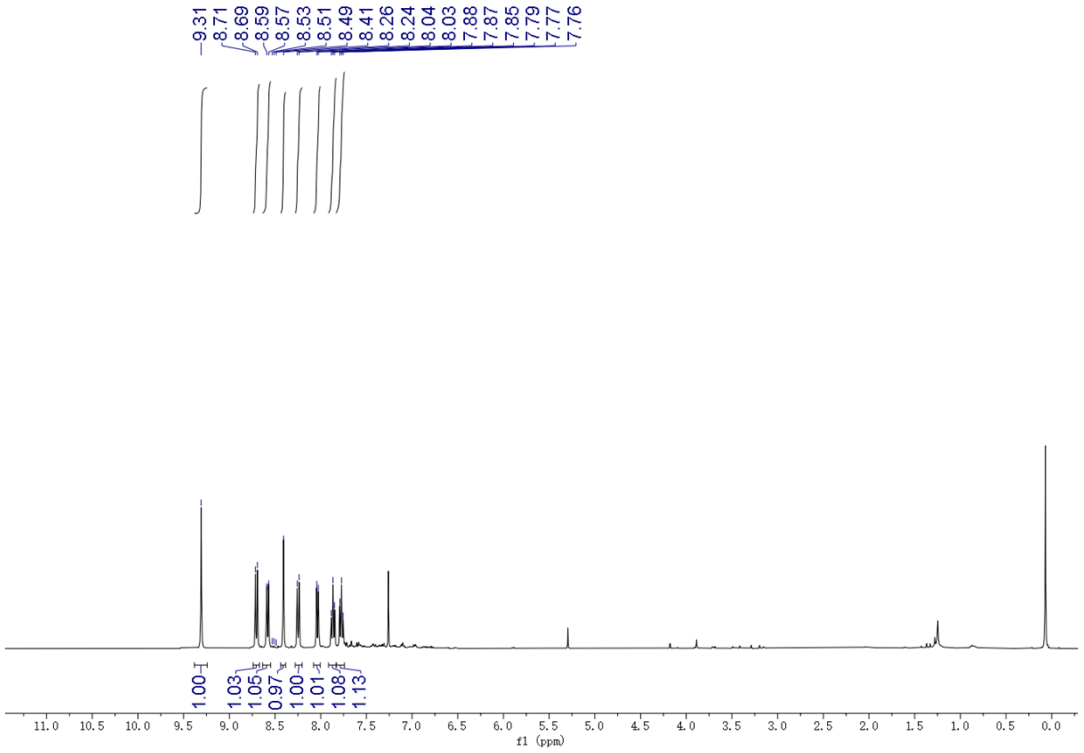
376 MHz in $CDCl_3$



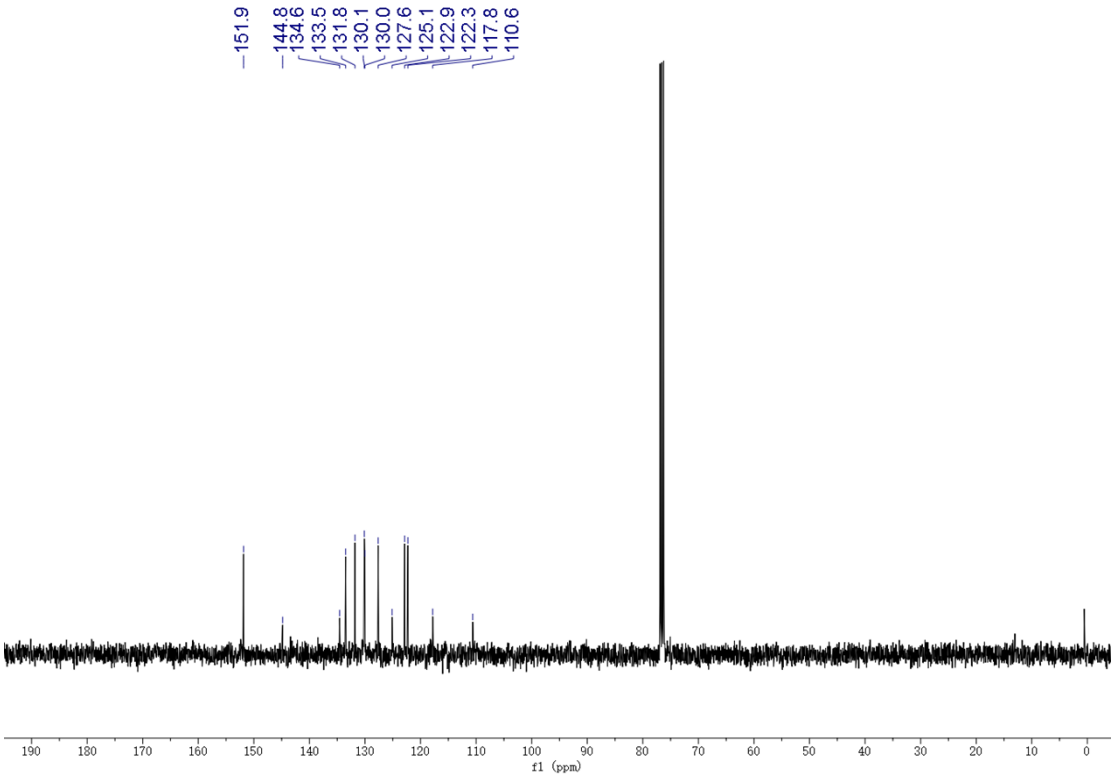


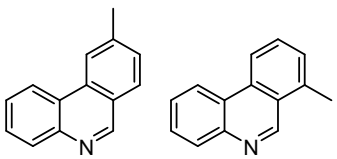
(9)

400 MHz in $CDCl_3$



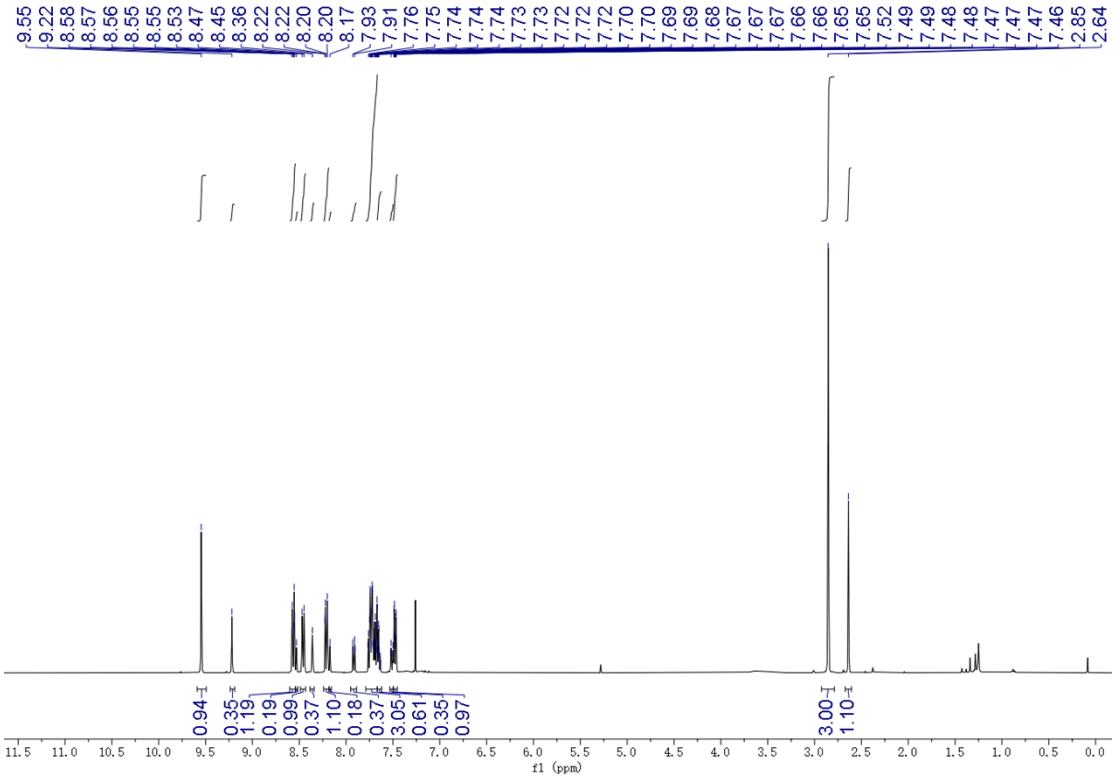
100 MHz in $CDCl_3$



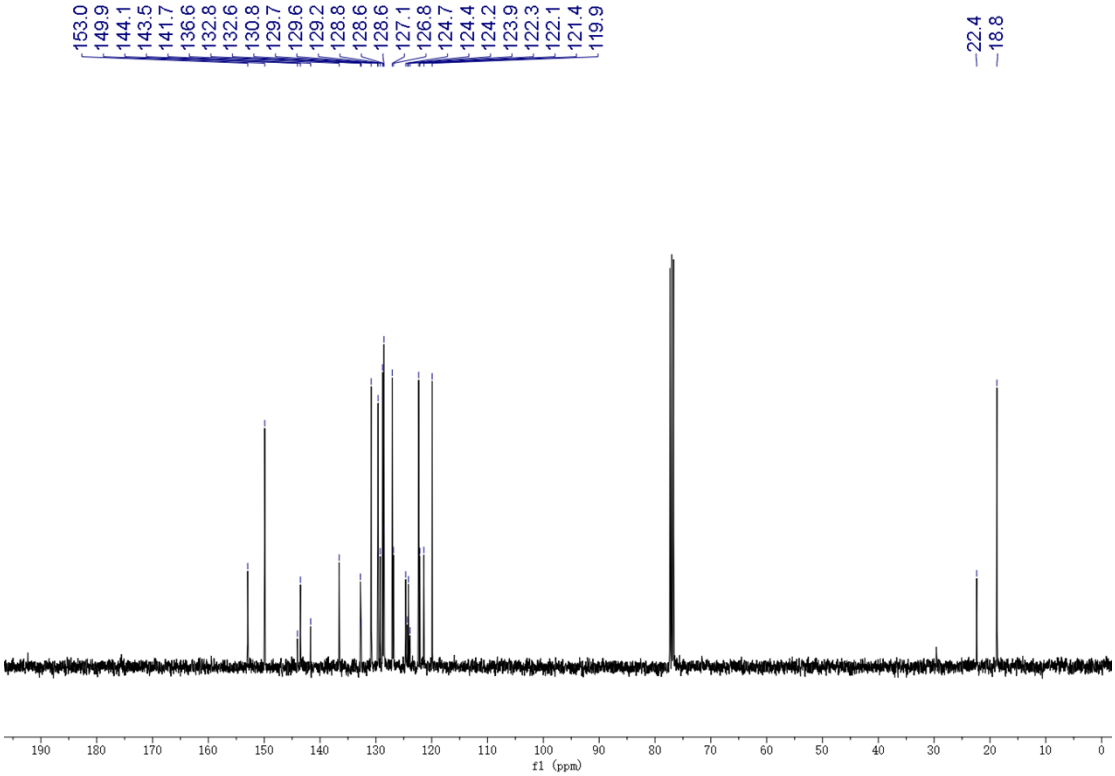


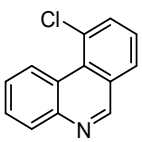
(10)

400 MHz in $CDCl_3$



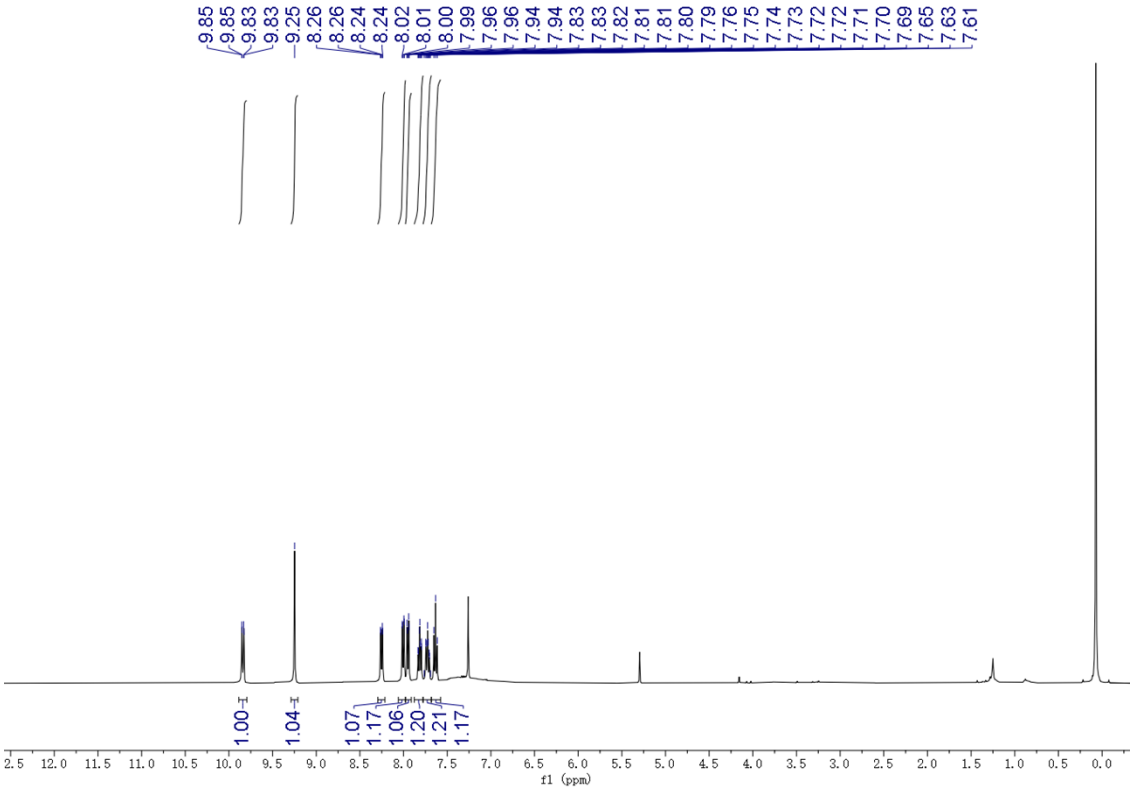
100 MHz in $CDCl_3$



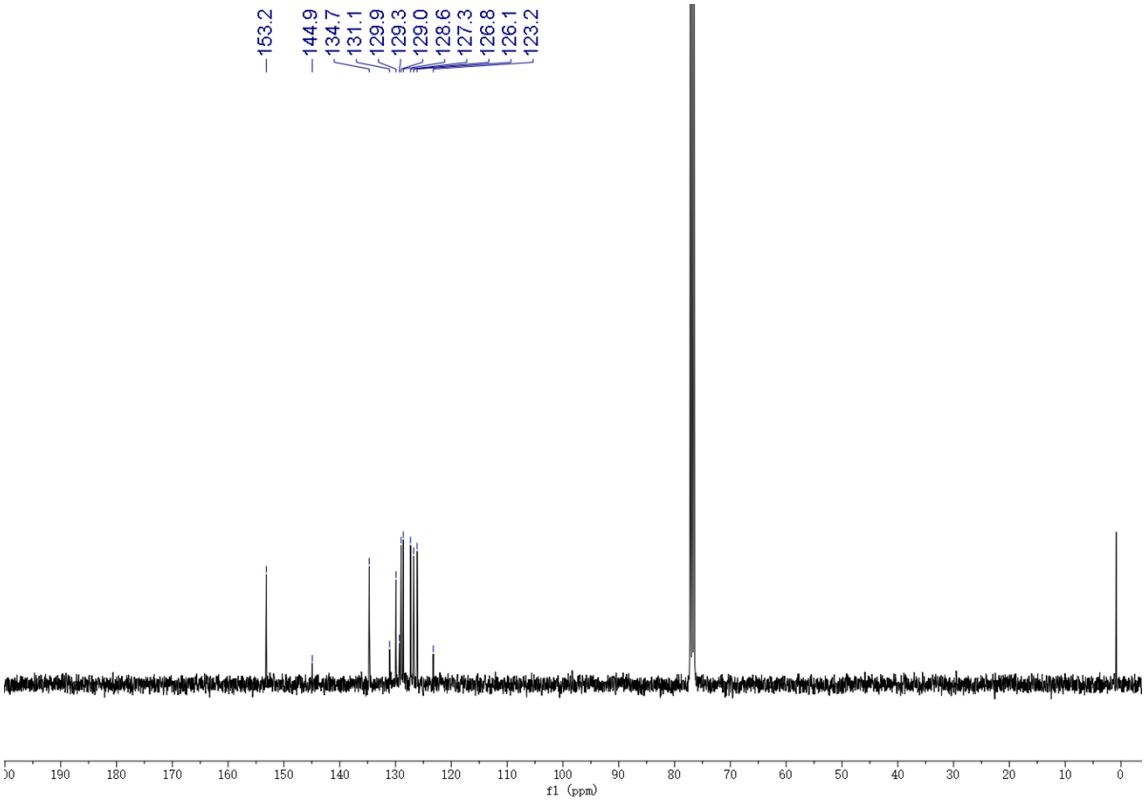


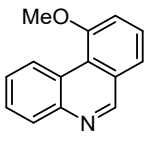
(11)

400 MHz in $CDCl_3$



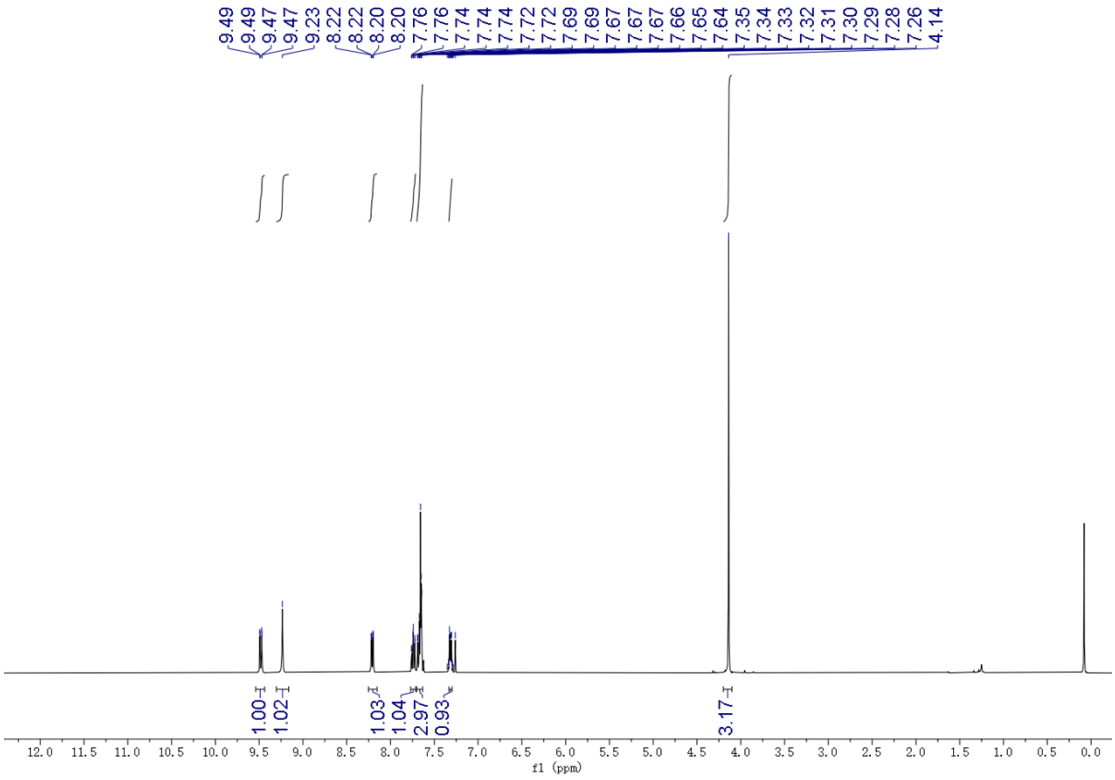
100 MHz in $CDCl_3$



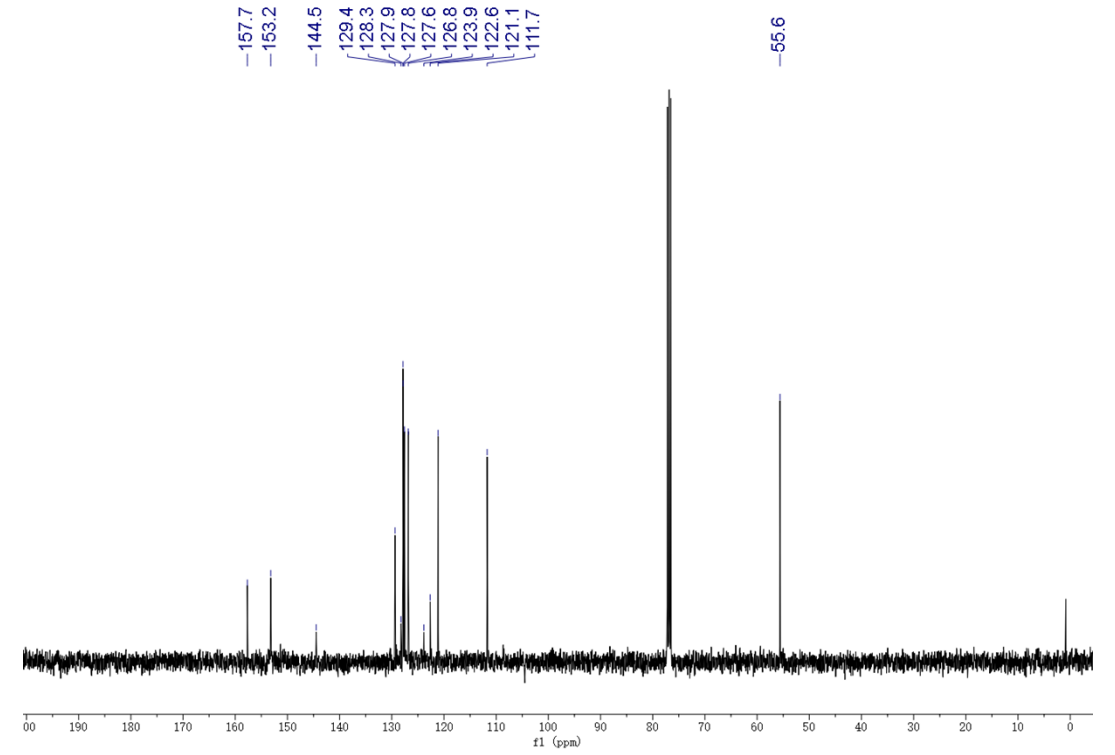


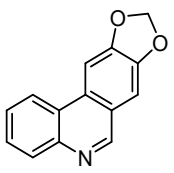
(12)

400 MHz in $CDCl_3$



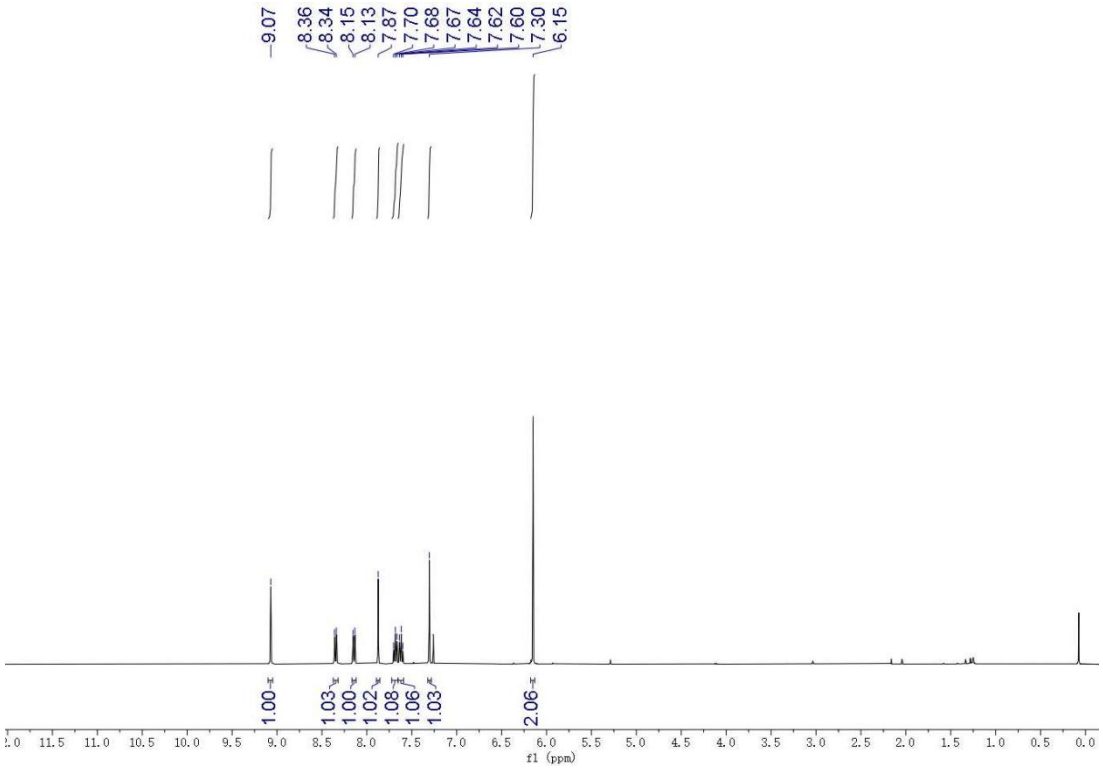
100 MHz in $CDCl_3$



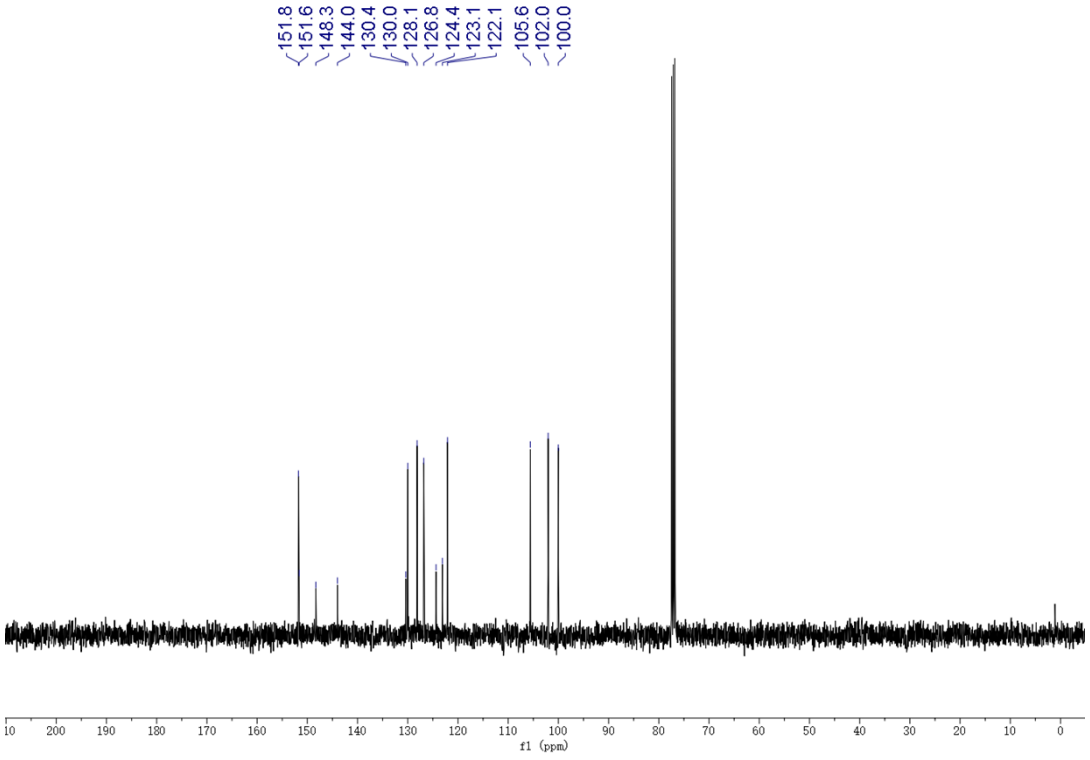


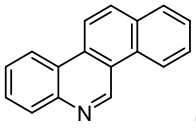
(13)

400 MHz in $CDCl_3$



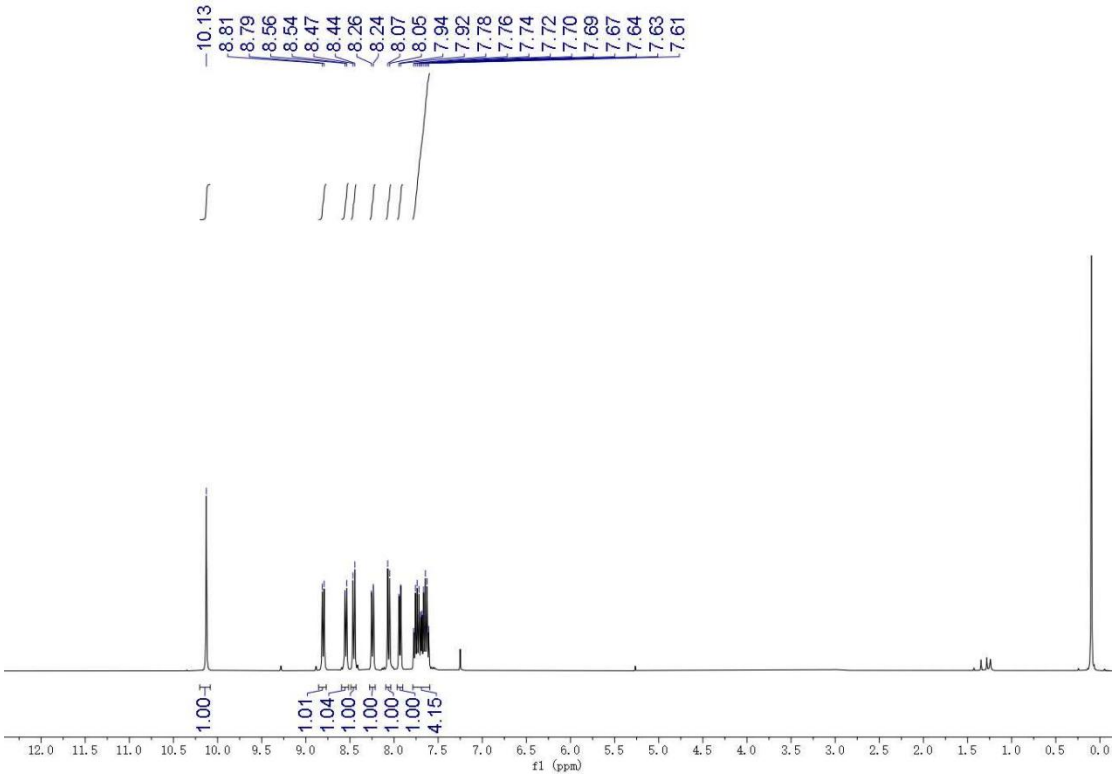
100 MHz in $CDCl_3$



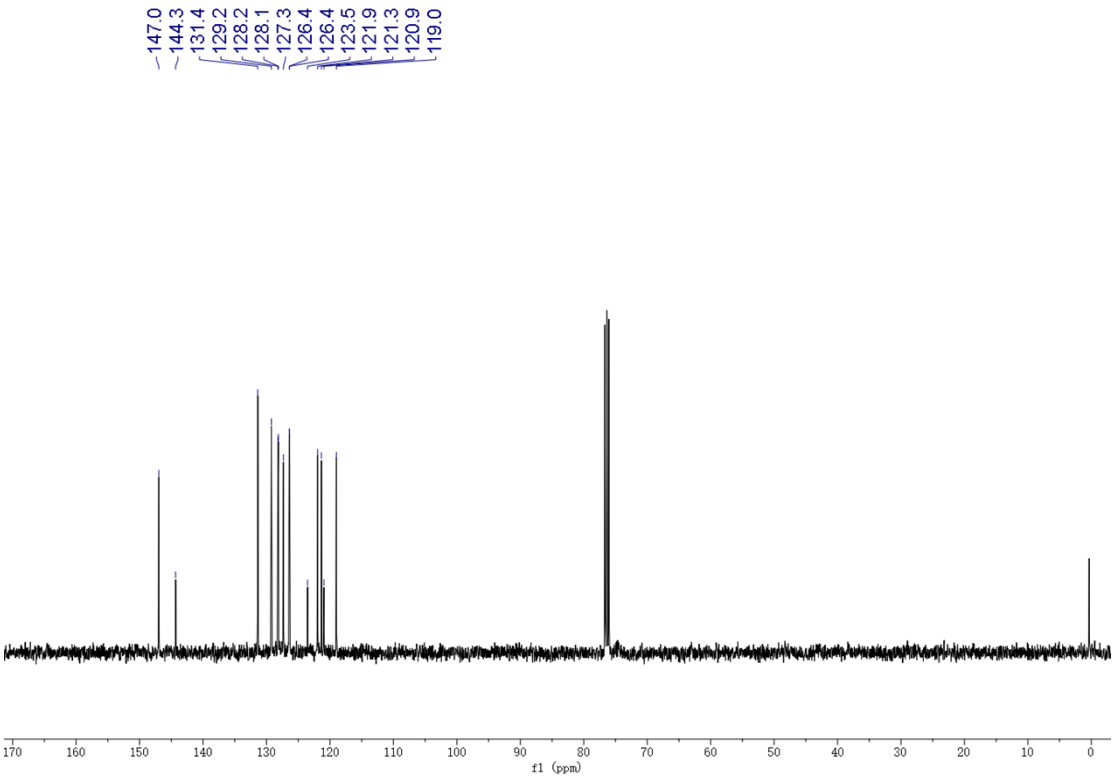


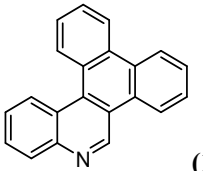
(14)

400 MHz in $CDCl_3$



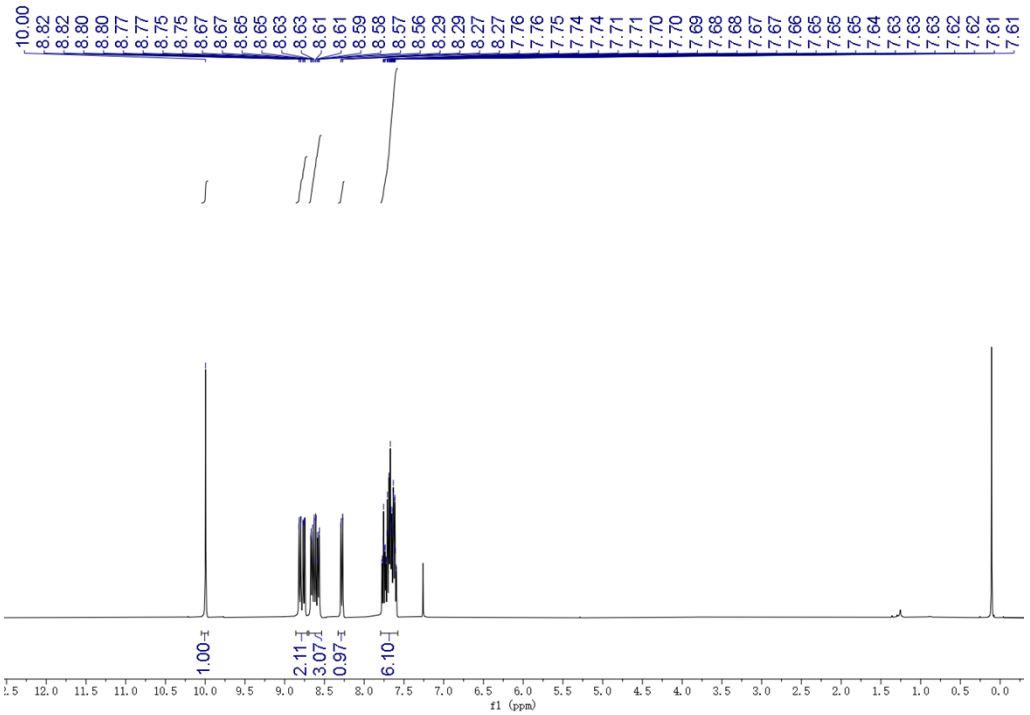
100 MHz in $CDCl_3$



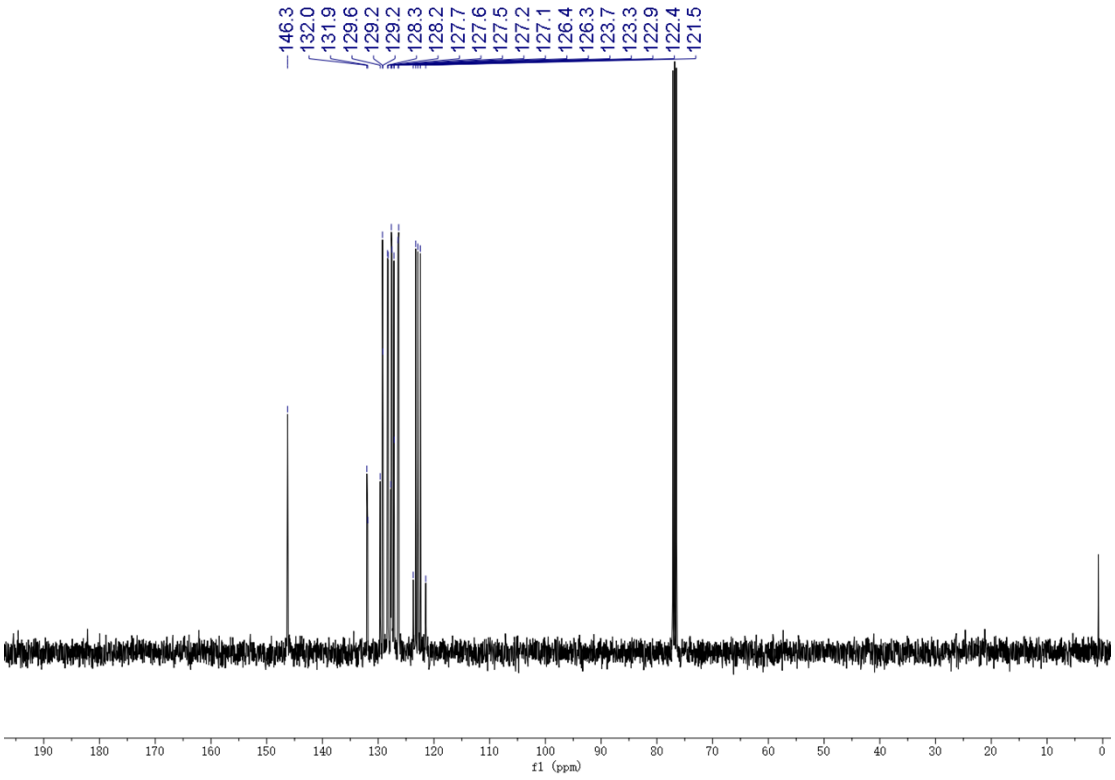


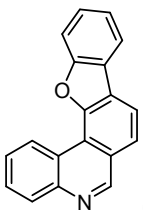
(15)

400 MHz in $CDCl_3$



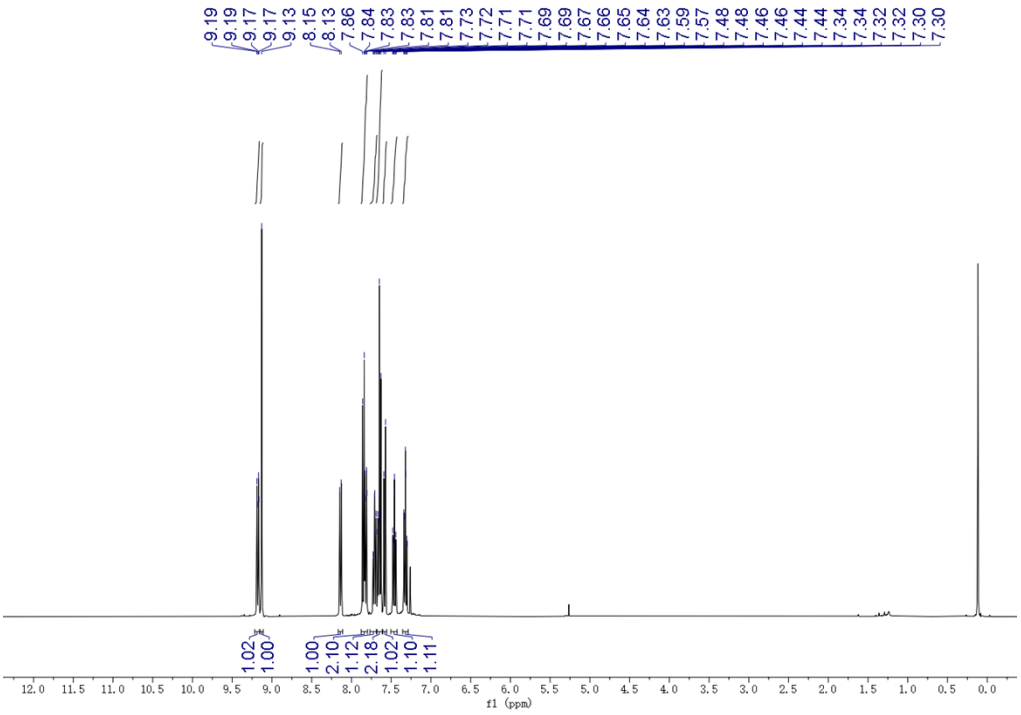
100 MHz in $CDCl_3$



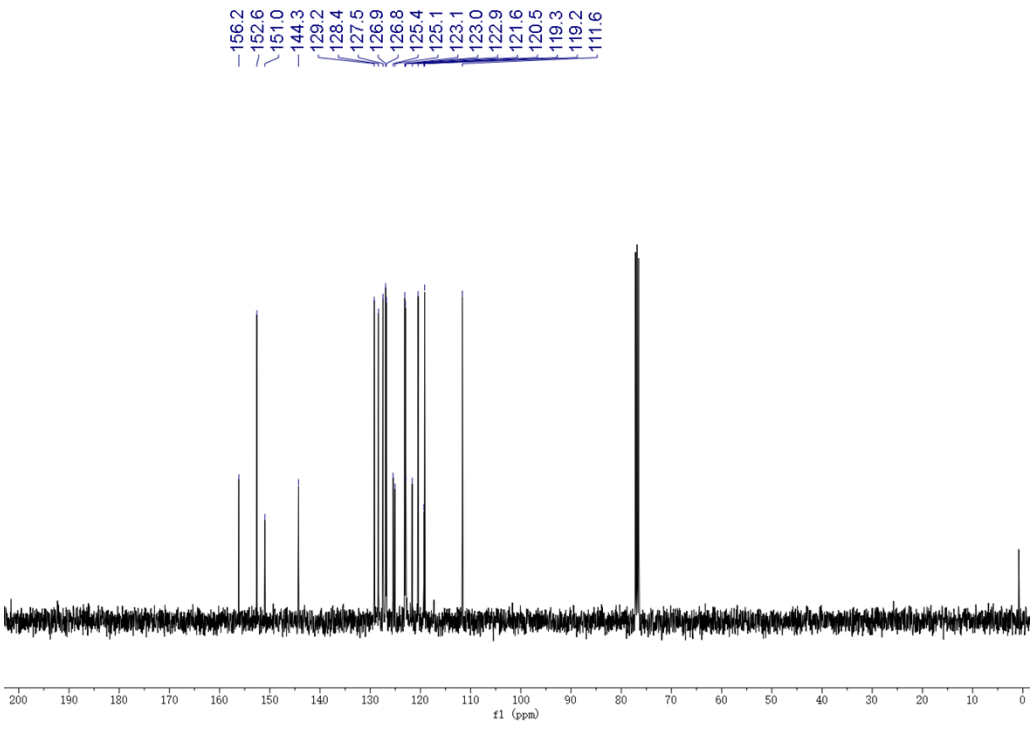


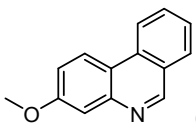
(16)

400 MHz in $CDCl_3$



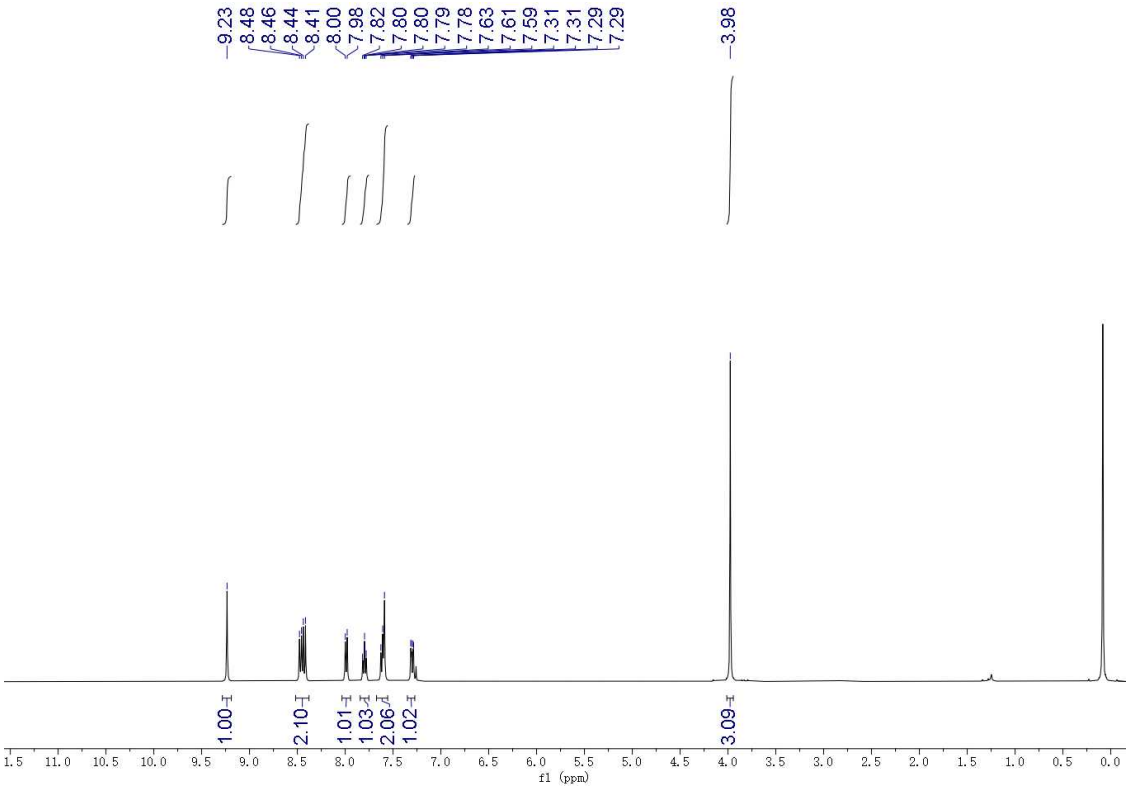
100 MHz in $CDCl_3$



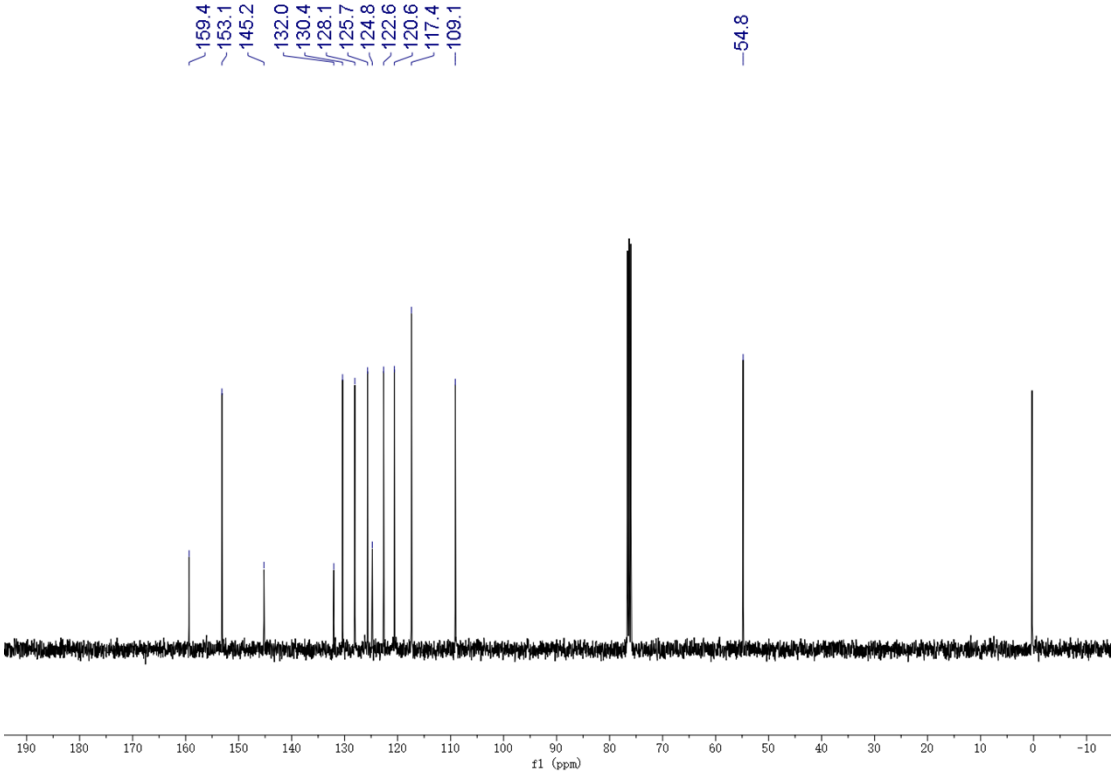


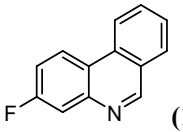
(17)

400 MHz in $CDCl_3$



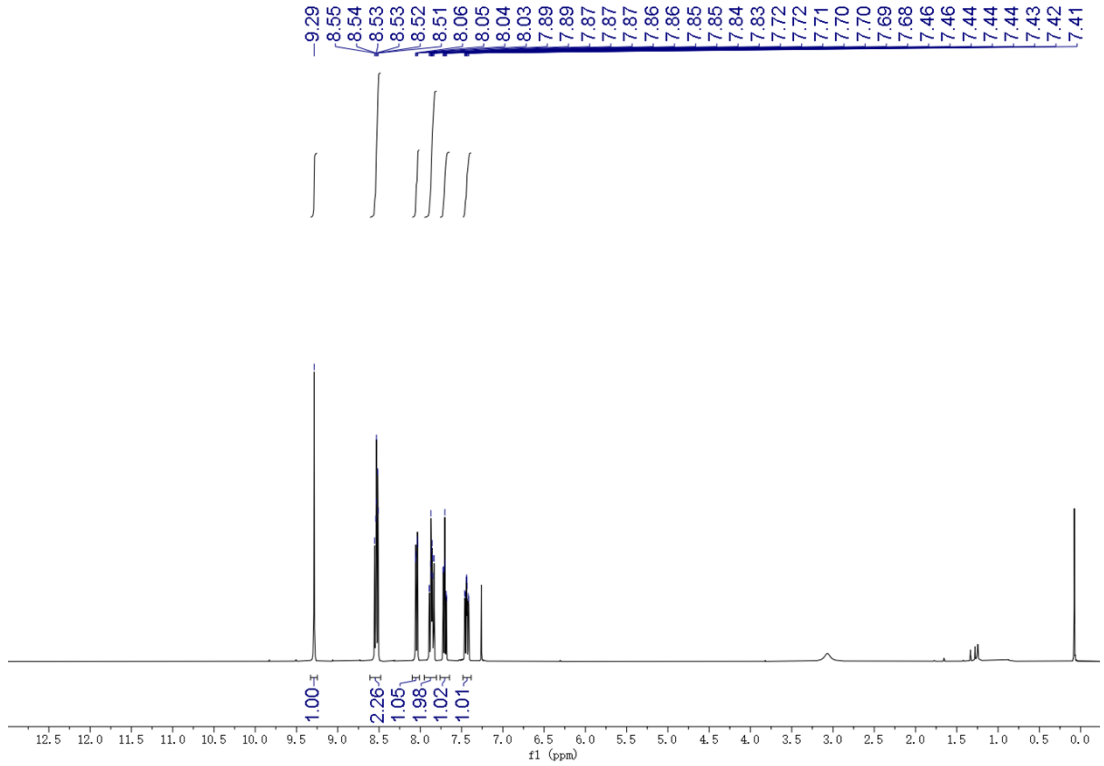
100 MHz in $CDCl_3$



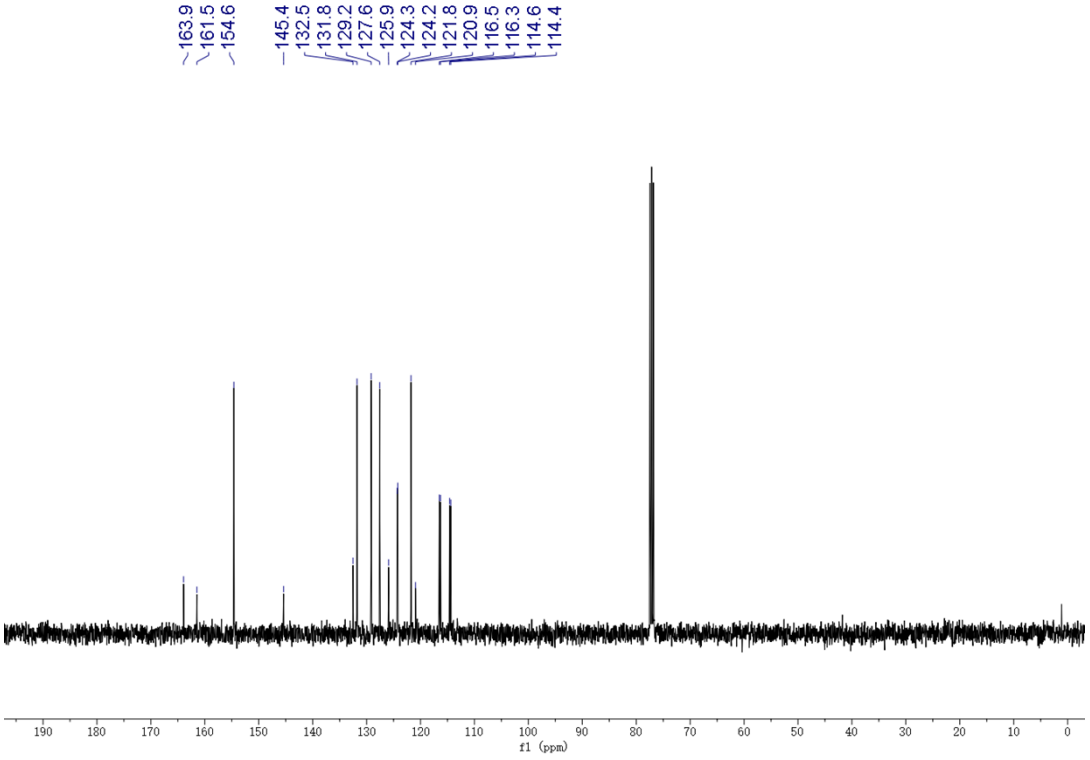


(18)

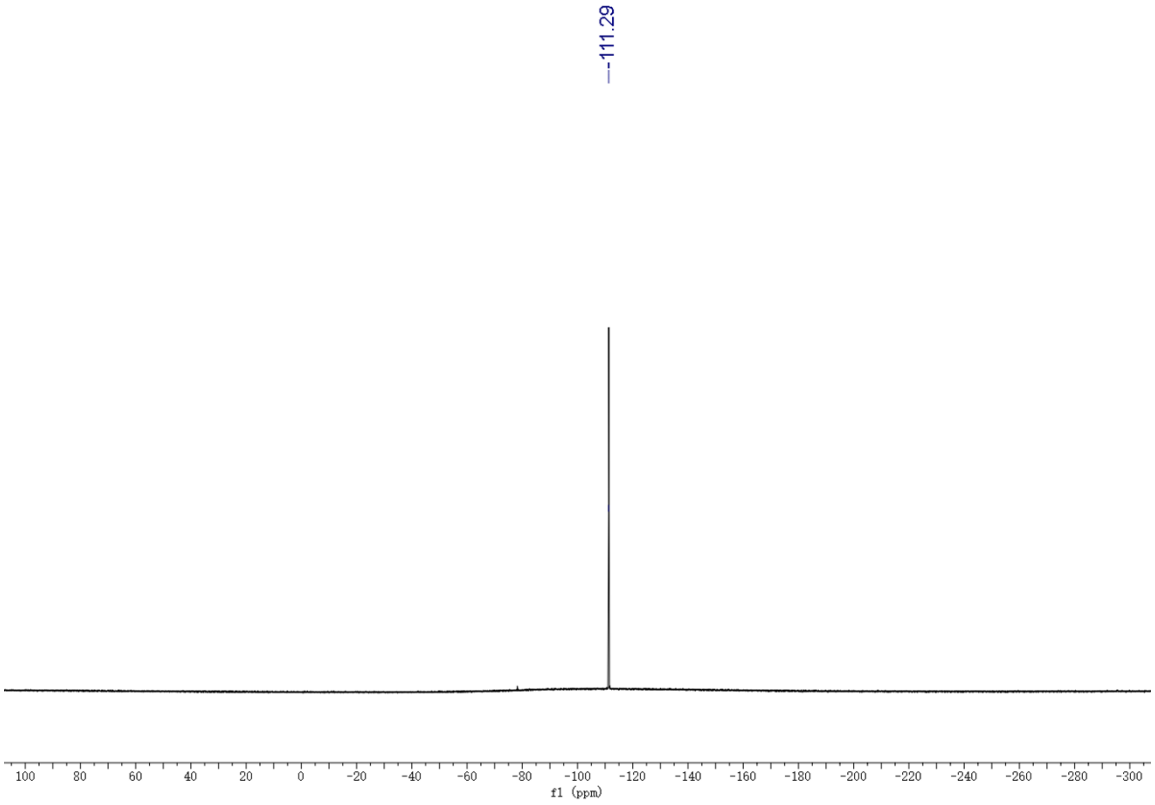
400 MHz in $CDCl_3$

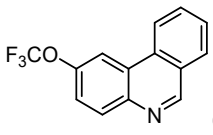


100 MHz in $CDCl_3$



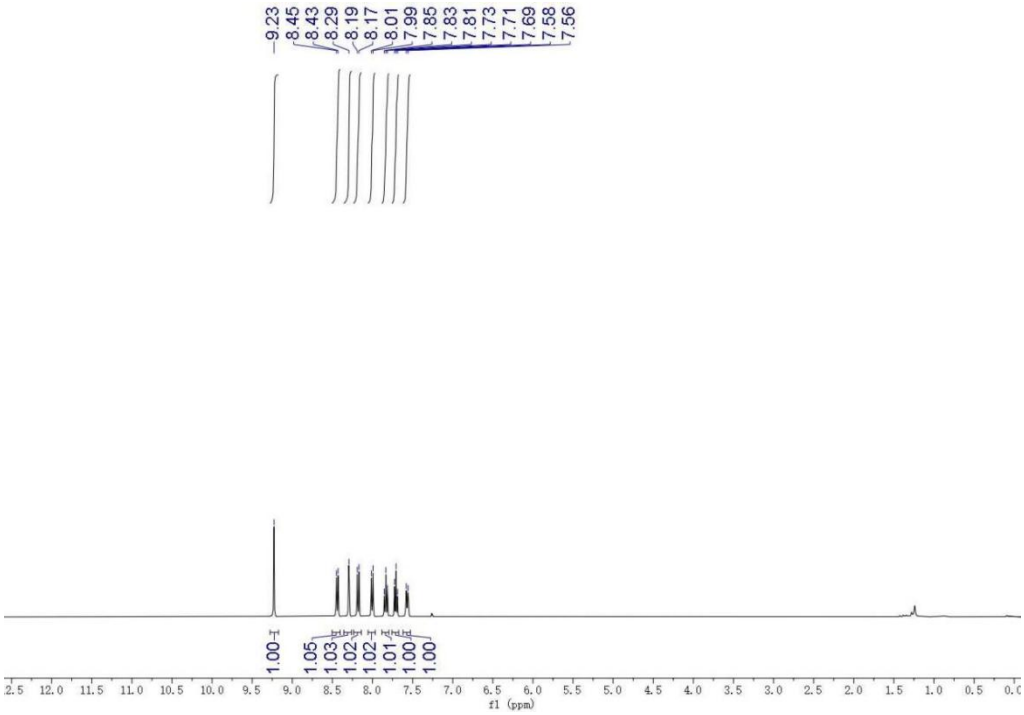
376 MHz in $CDCl_3$


-111.29
100 80 60 40 20 0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200 -220 -240 -260 -280 -300
f1 (ppm)

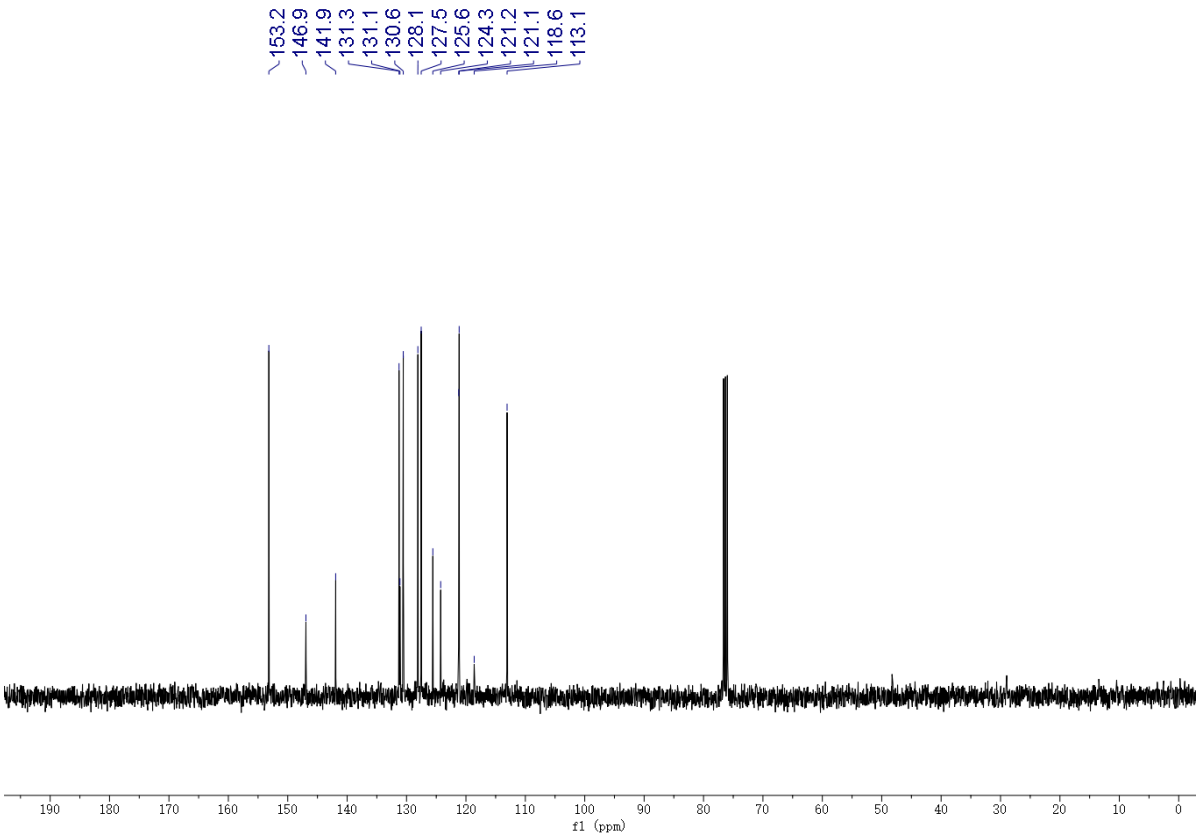

F3CO
N

(19)

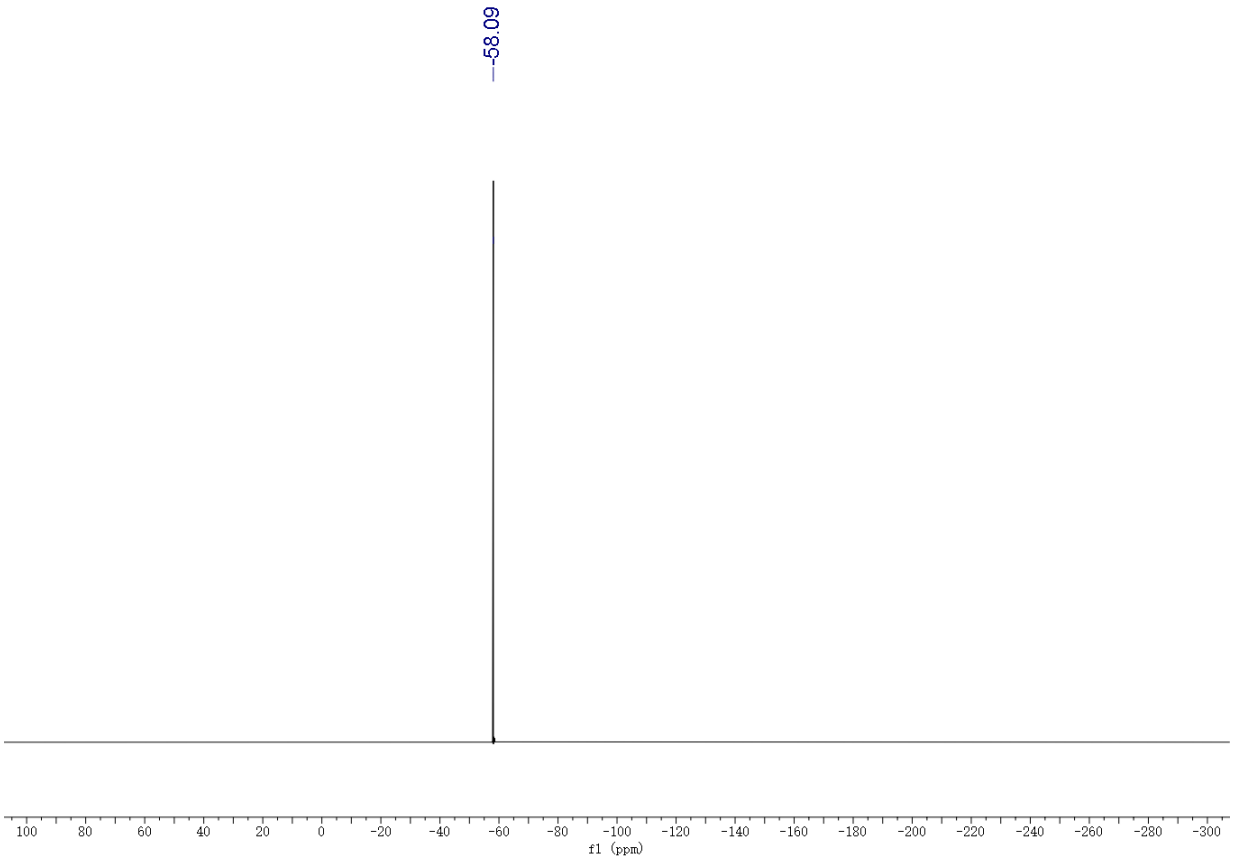
400 MHz in $CDCl_3$



100 MHz in $CDCl_3$



376 MHz in $CDCl_3$


-58.09
100
80
60
40
20
0
-20
-40
-60
-80
-100
-120
-140
-160
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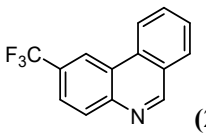
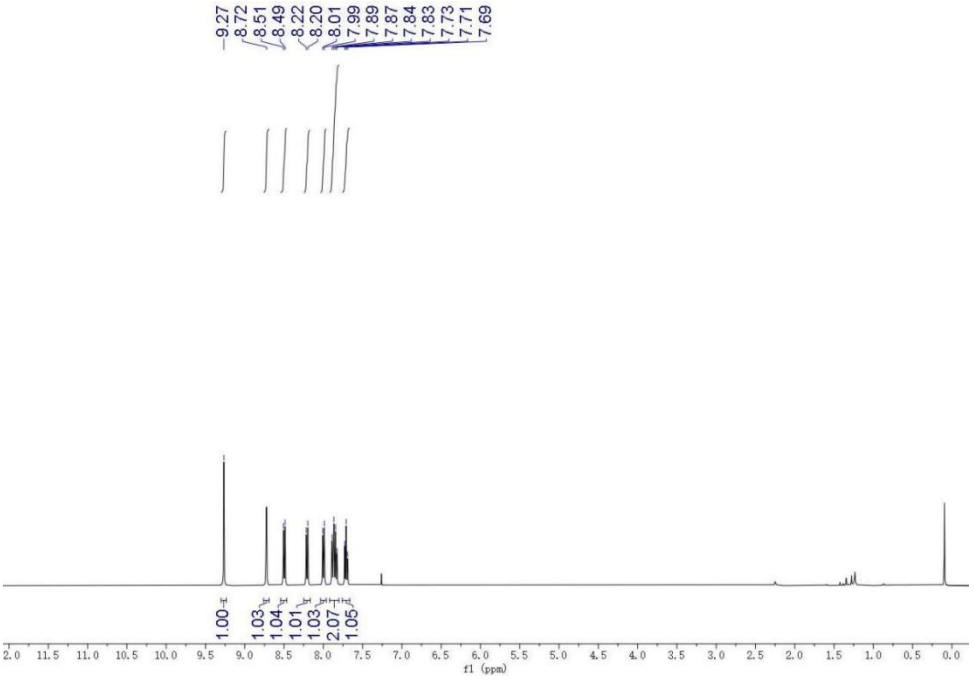
-220
-240
-260
-280
-300
f1 (ppm)

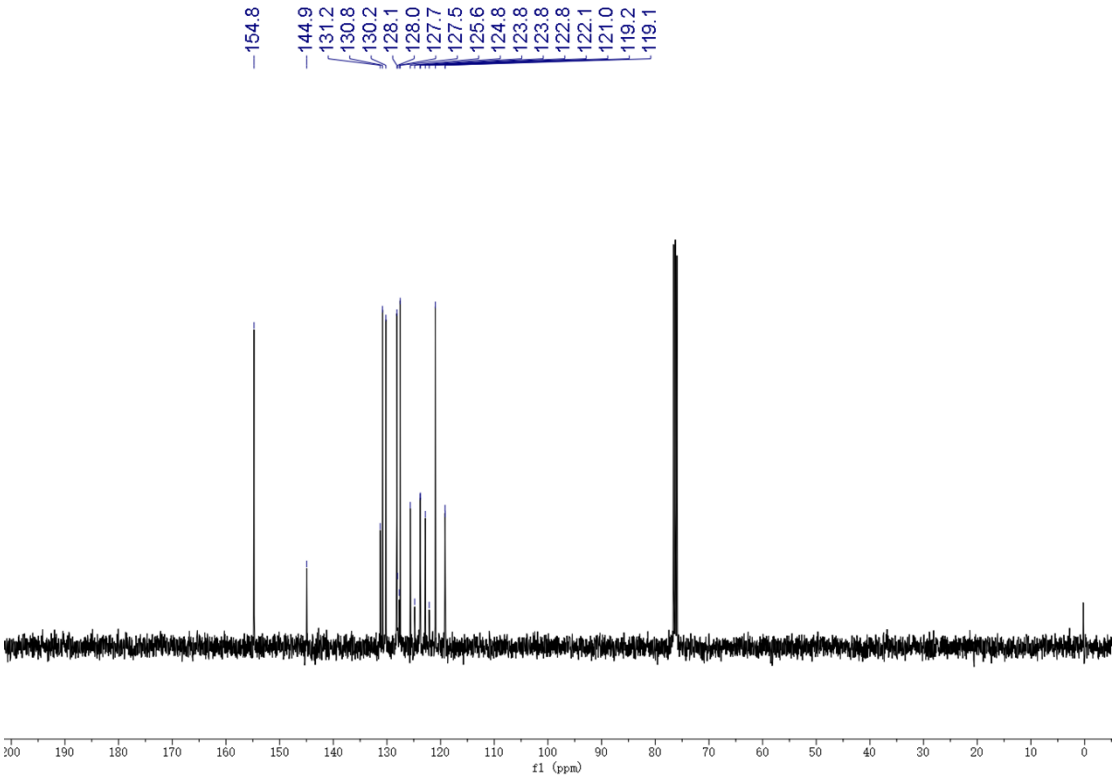


(20)

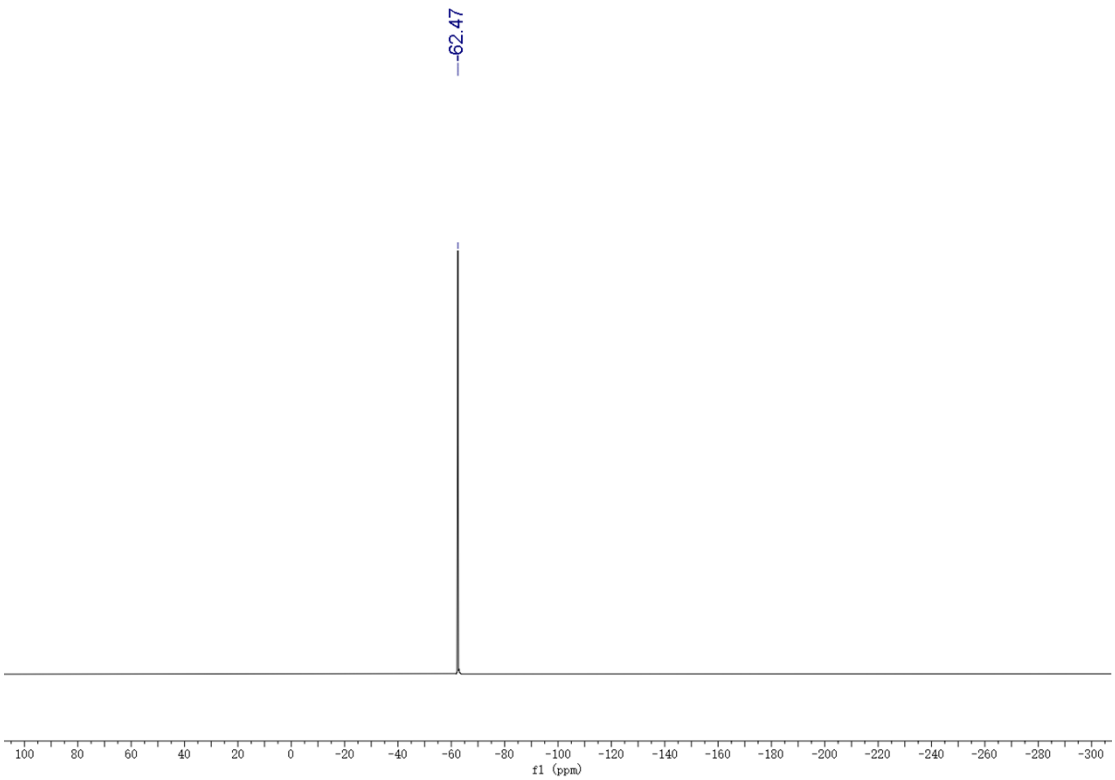
400 MHz in $CDCl_3$

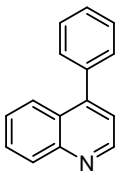


100 MHz in $CDCl_3$



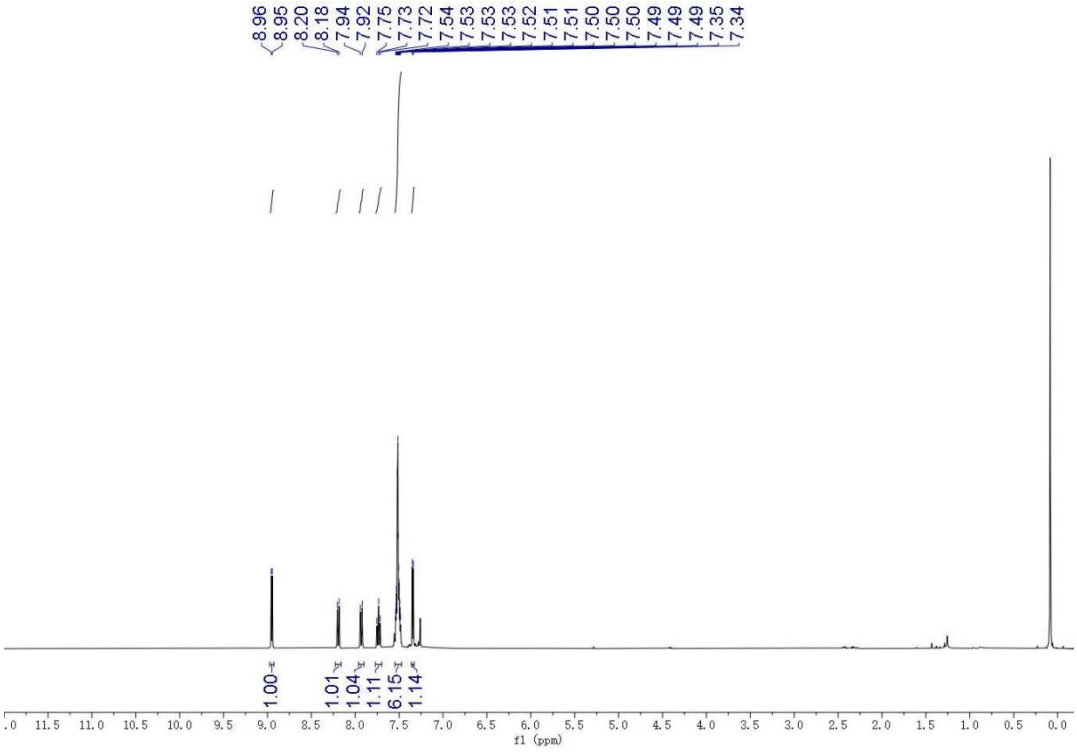
376 MHz in $CDCl_3$


-62.47
100 80 60 40 20 0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200 -220 -240 -260 -280 -300
f1 (ppm)

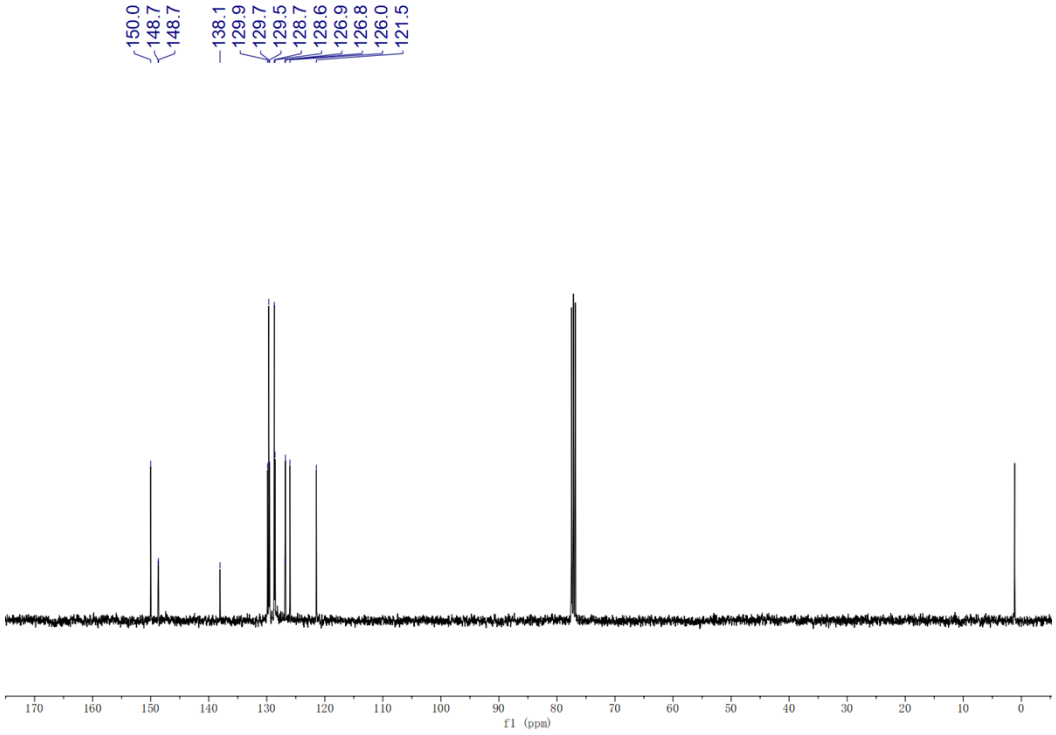

N

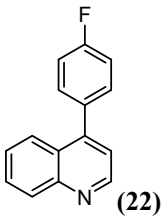
(21)

400 MHz in $CDCl_3$



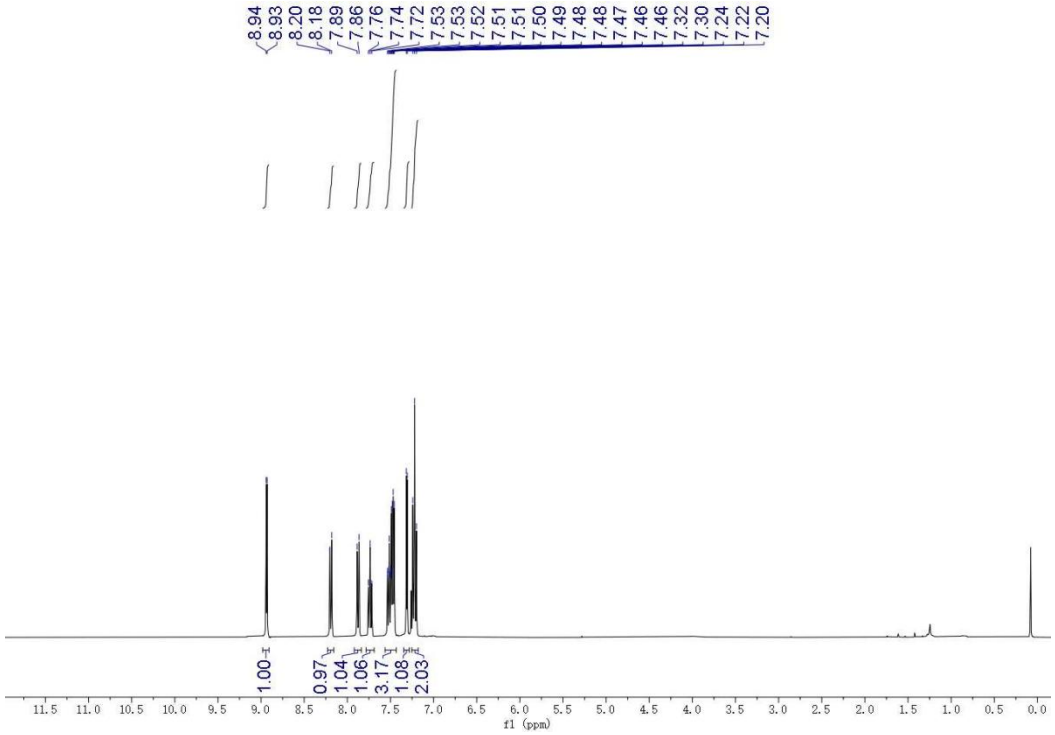
100 MHz in $CDCl_3$



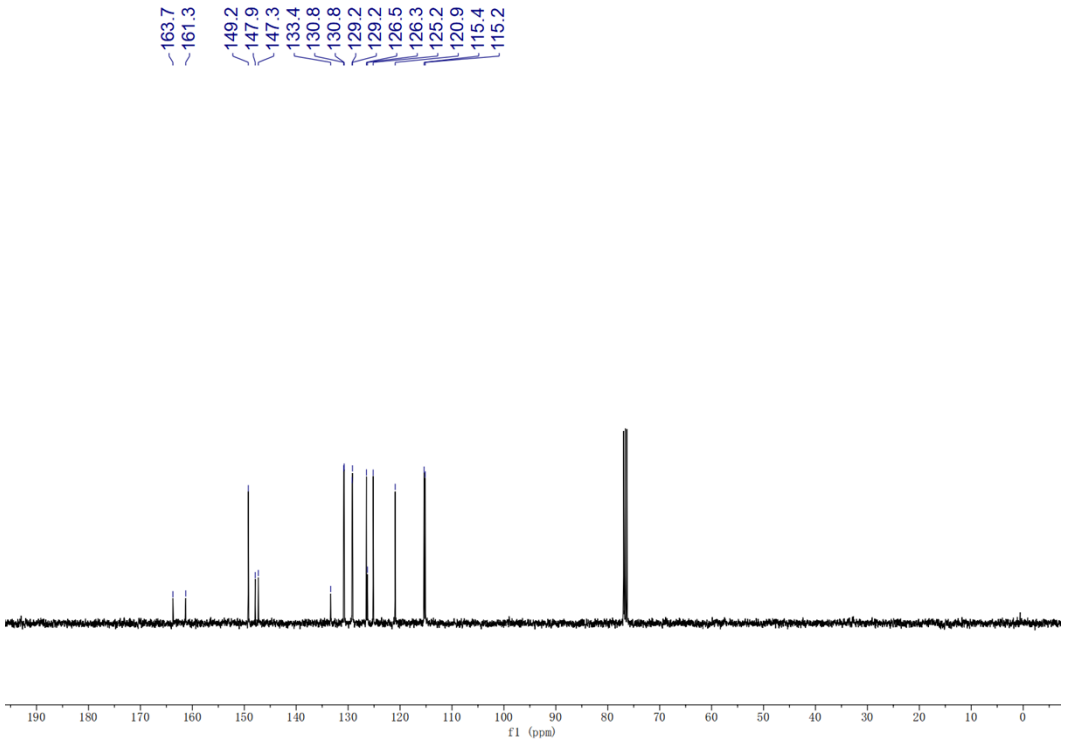


(22)

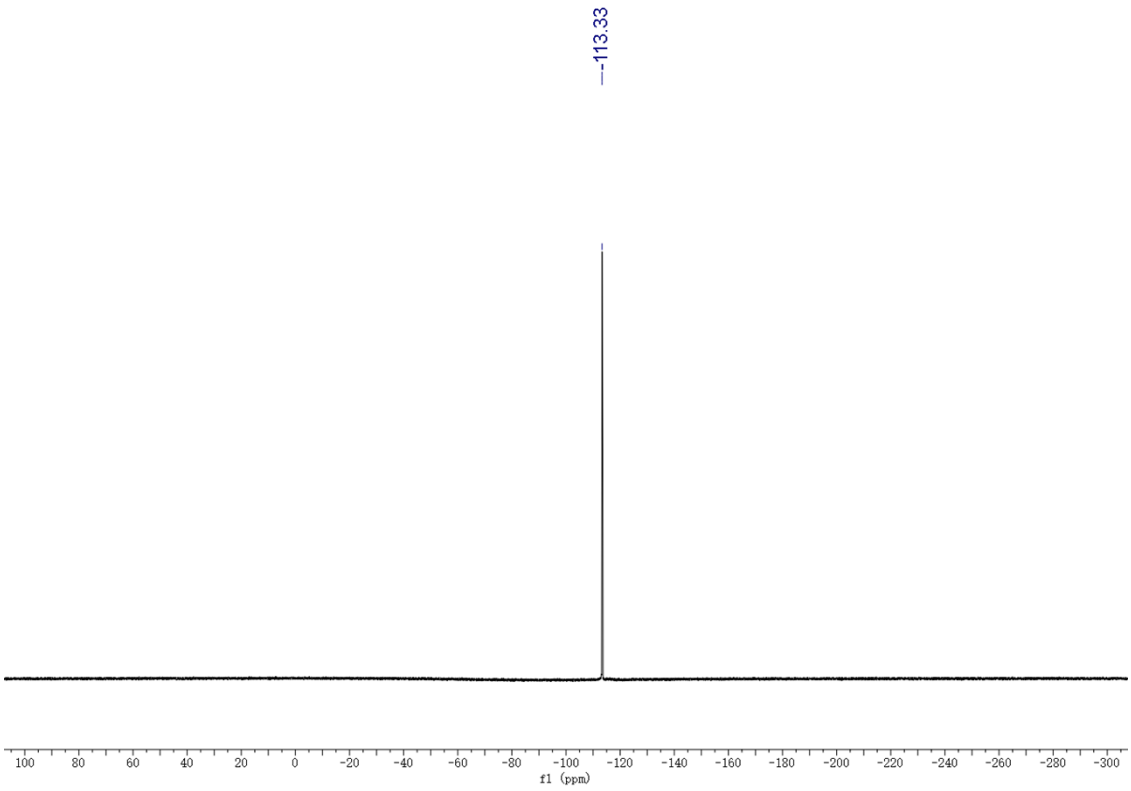
400 MHz in $CDCl_3$



100 MHz in $CDCl_3$



376 MHz in $CDCl_3$


-113.33
100
80
60
40
20
0
-20
-40
-60
-80
-100
-120
-140
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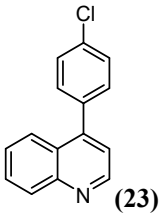
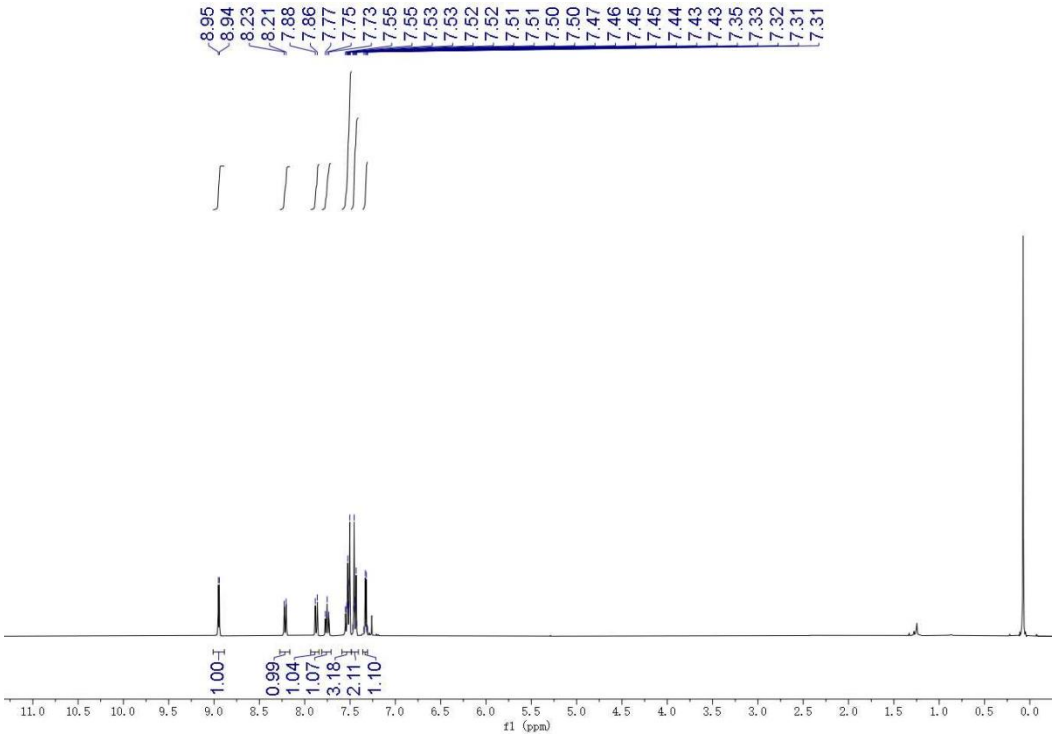
-220
-240
-260
-280
-300
f1 (ppm)

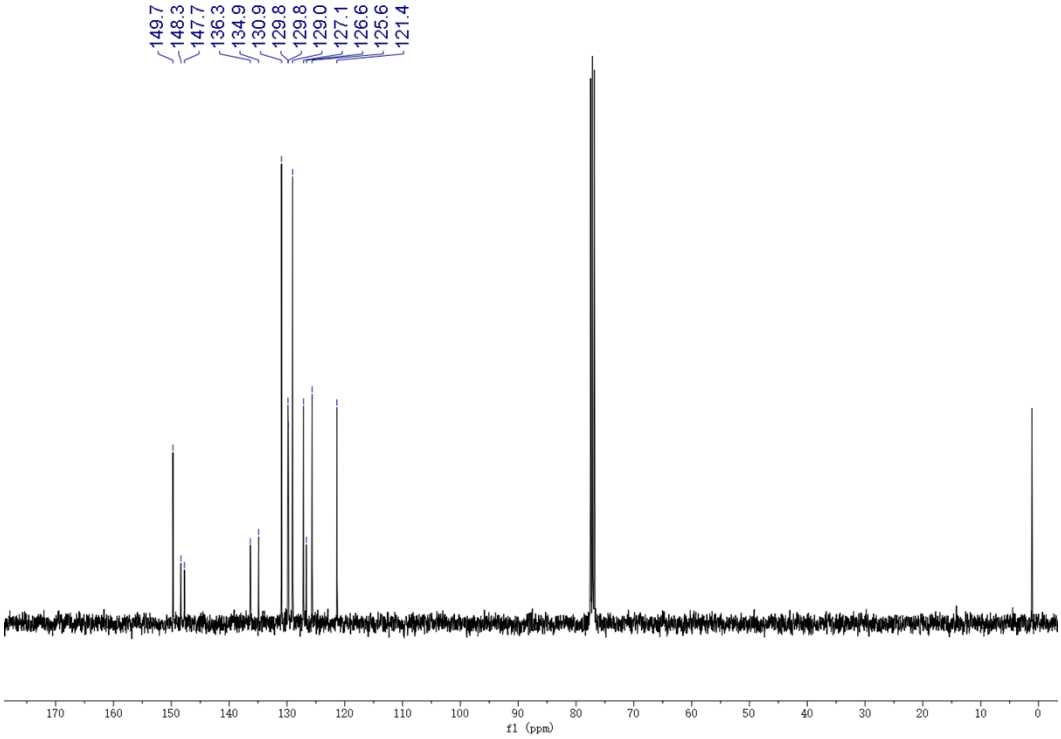


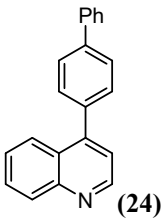
(23)

400 MHz in $CDCl_3$



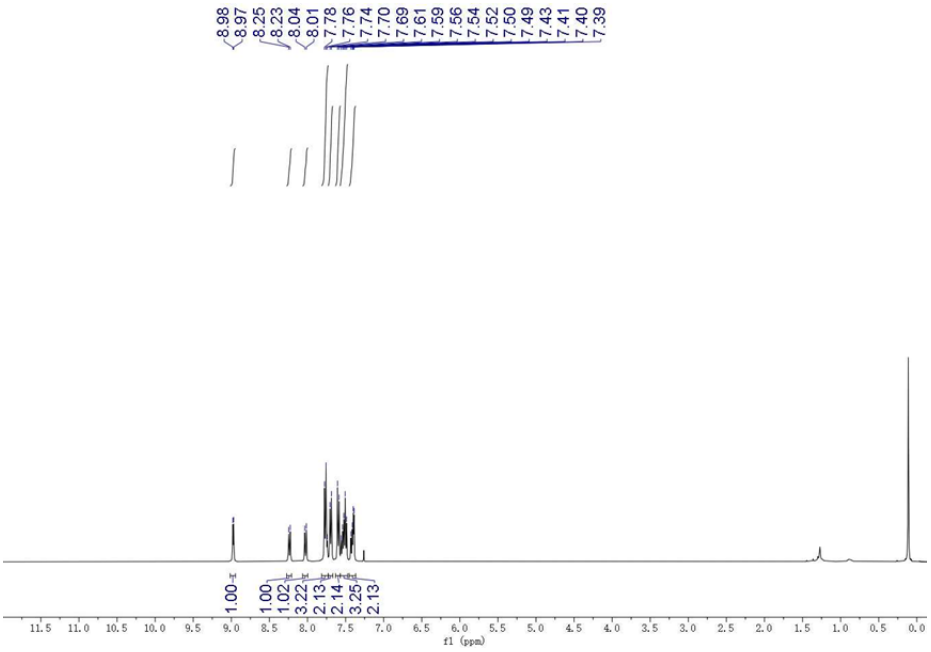
100 MHz in $CDCl_3$



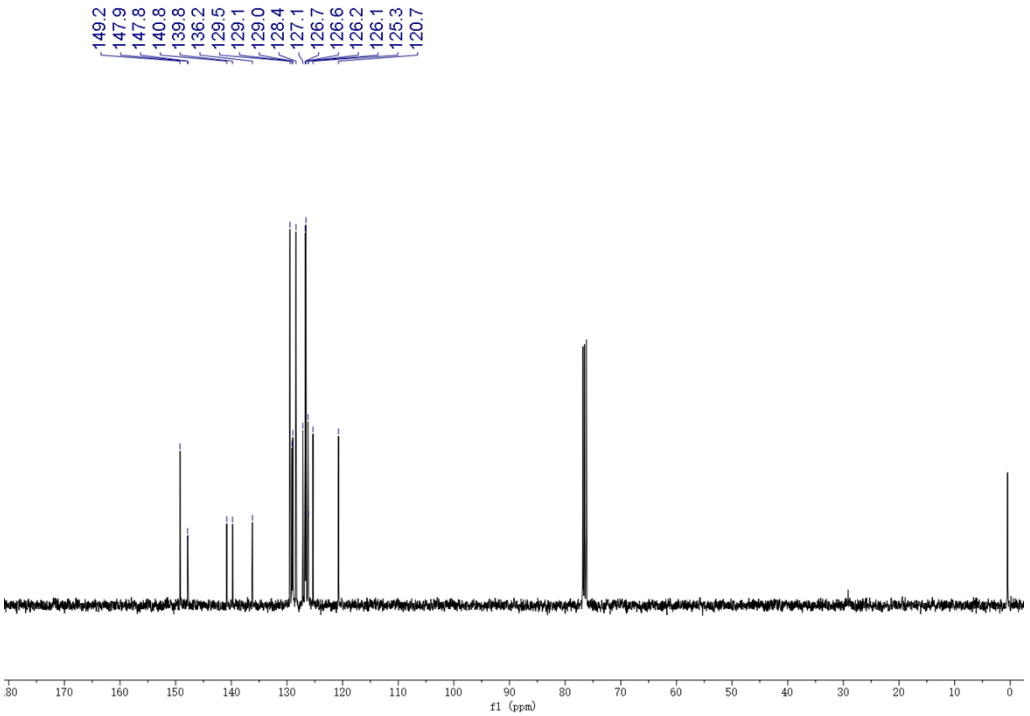


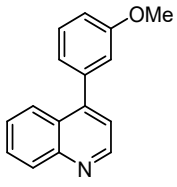
(24)

400 MHz in $CDCl_3$



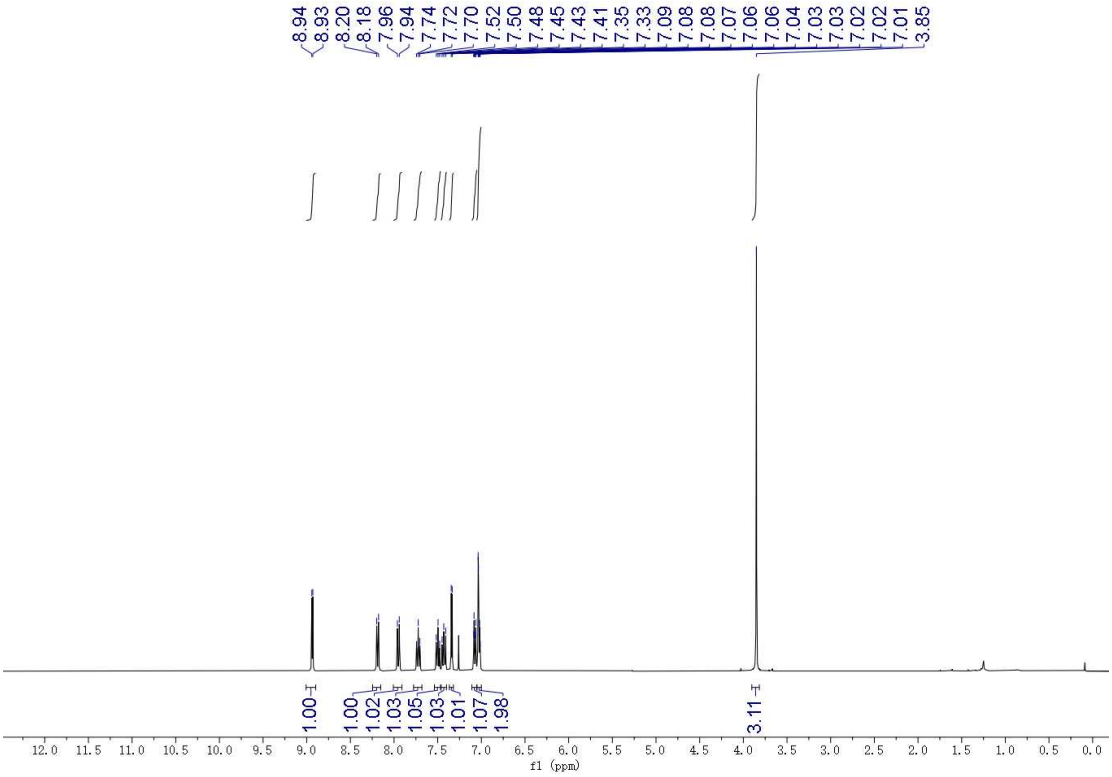
100 MHz in $CDCl_3$



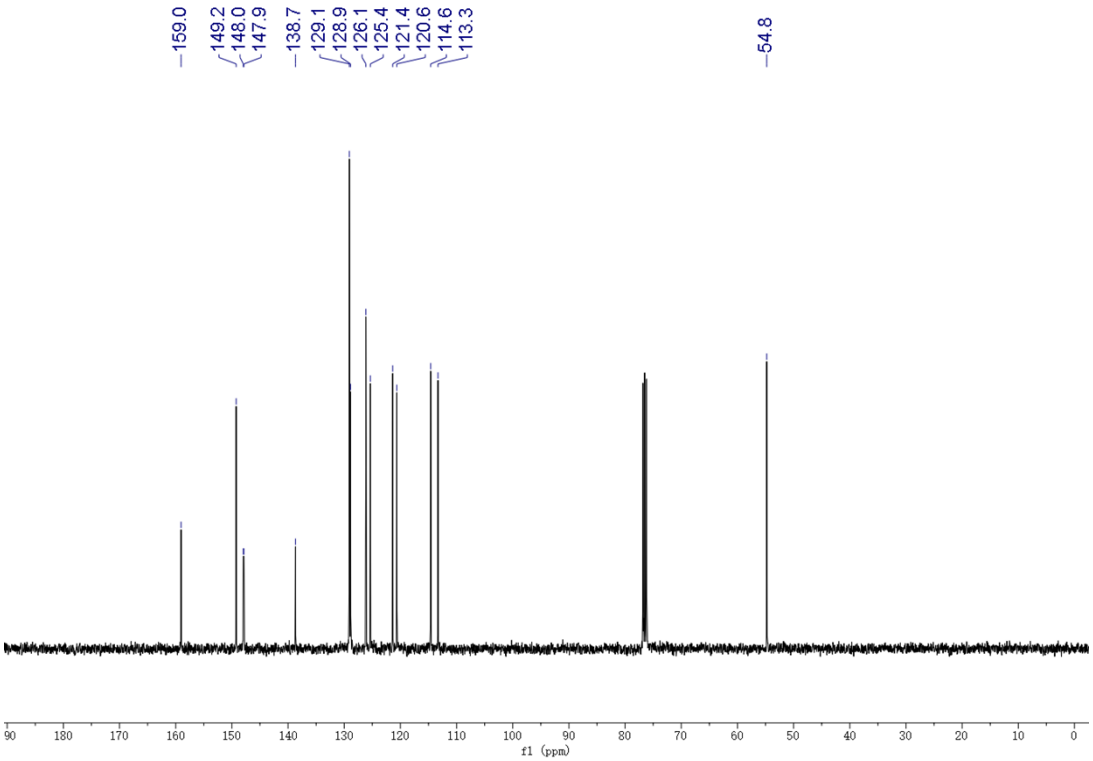


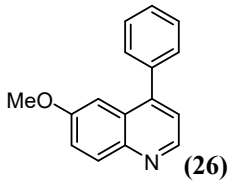
(25)

400 MHz in $CDCl_3$



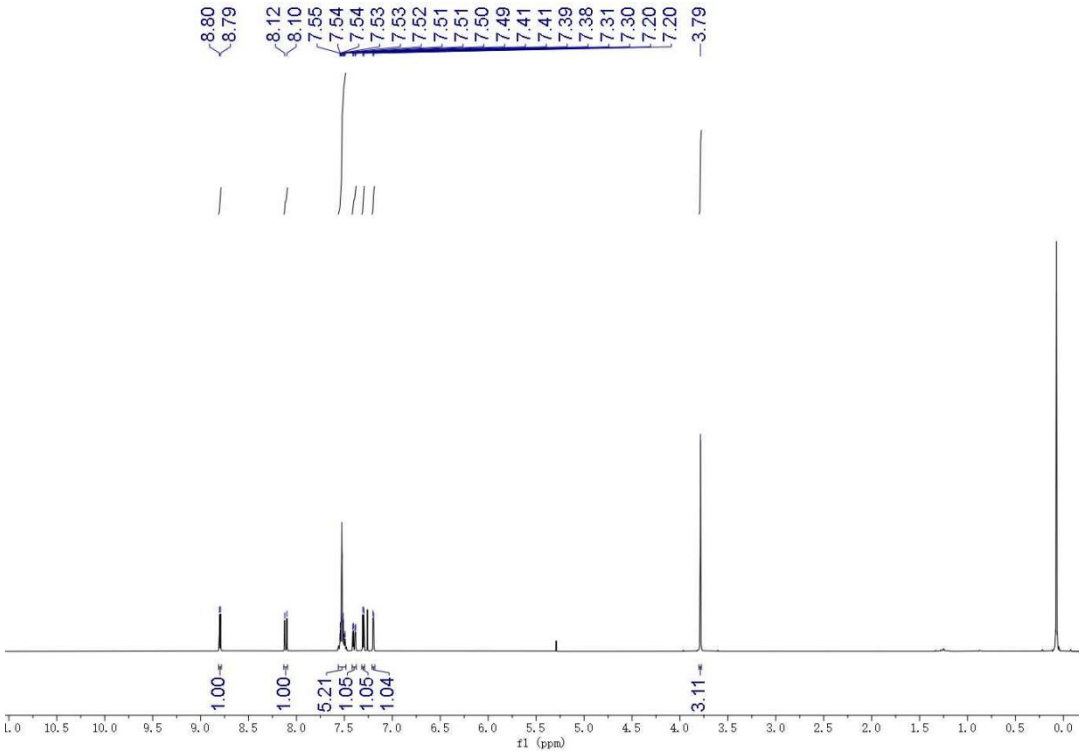
100 MHz in $CDCl_3$



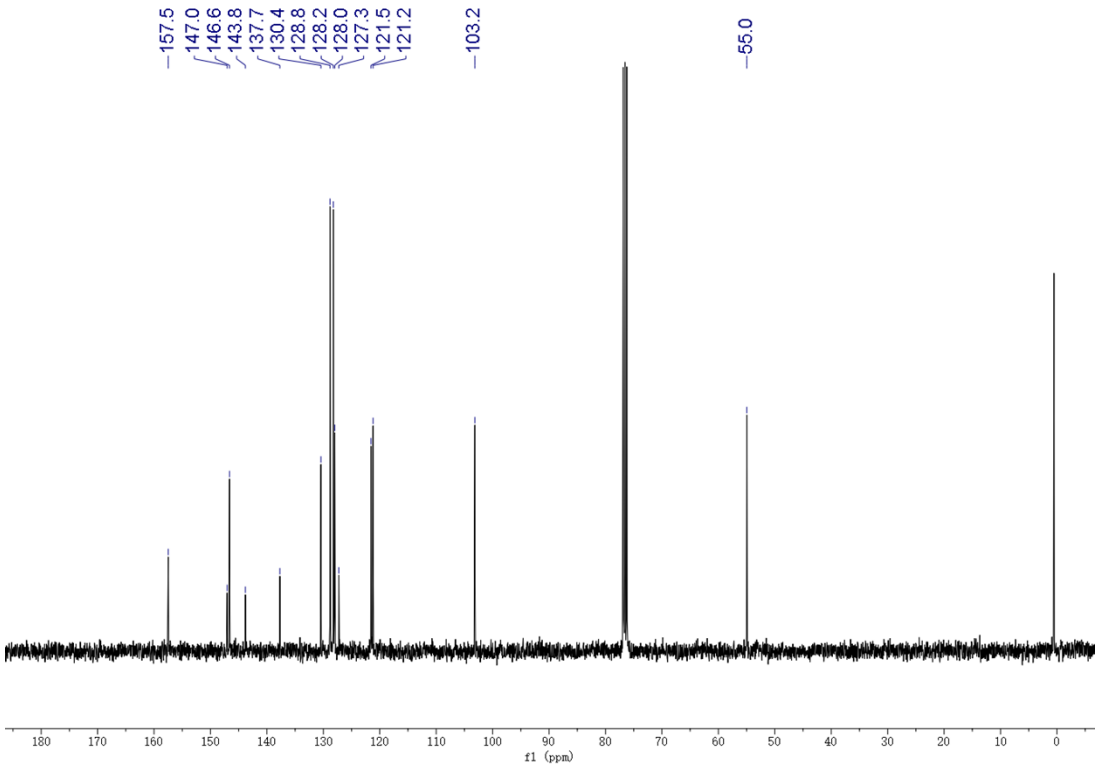


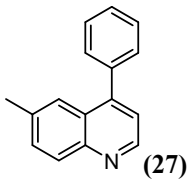
(26)

400 MHz in $CDCl_3$



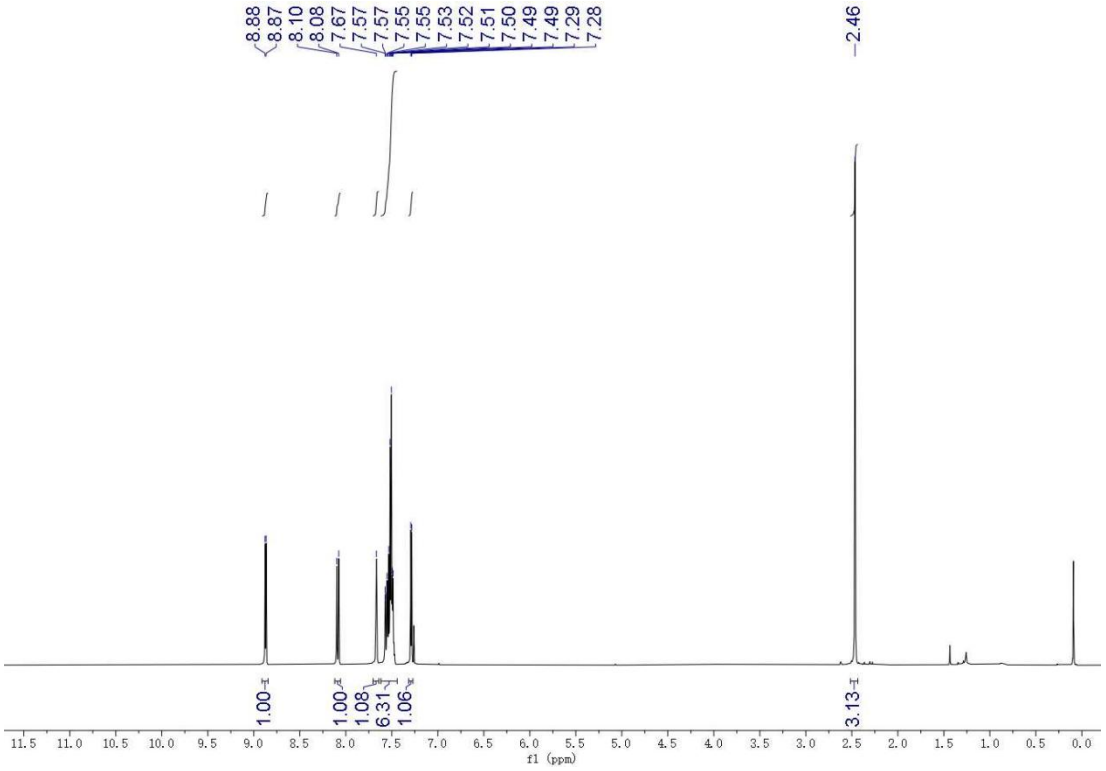
100 MHz in $CDCl_3$



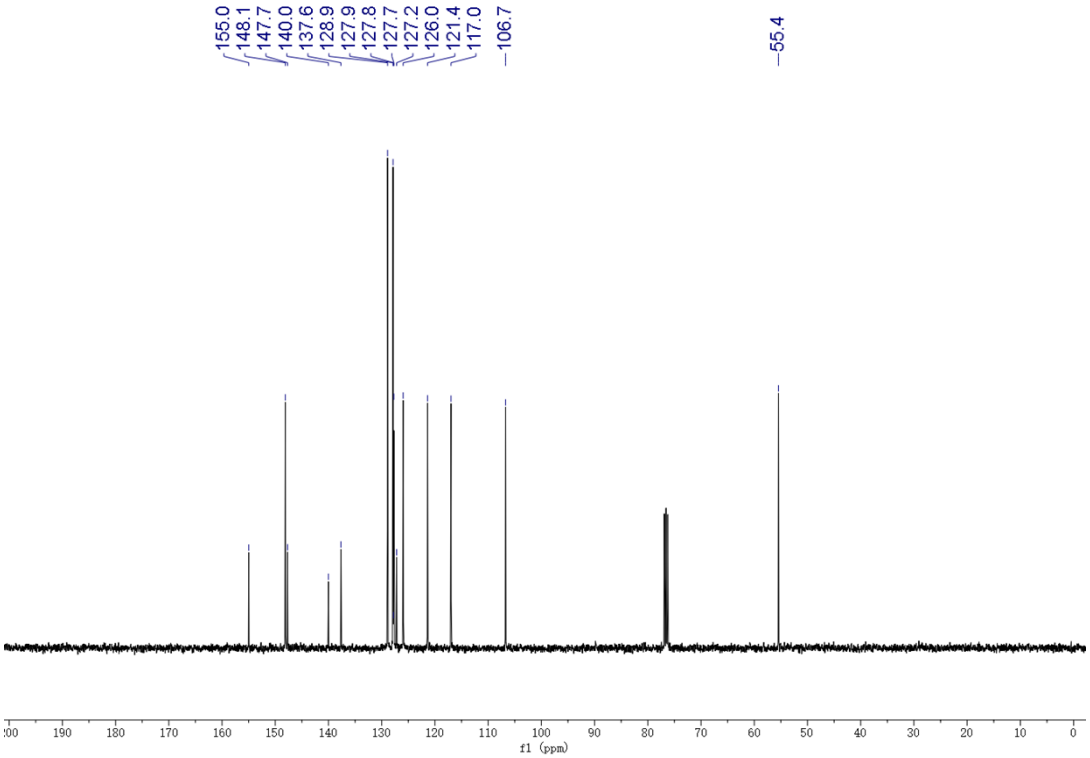


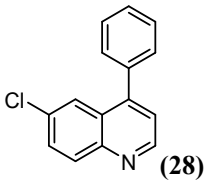
(27)

400 MHz in $CDCl_3$



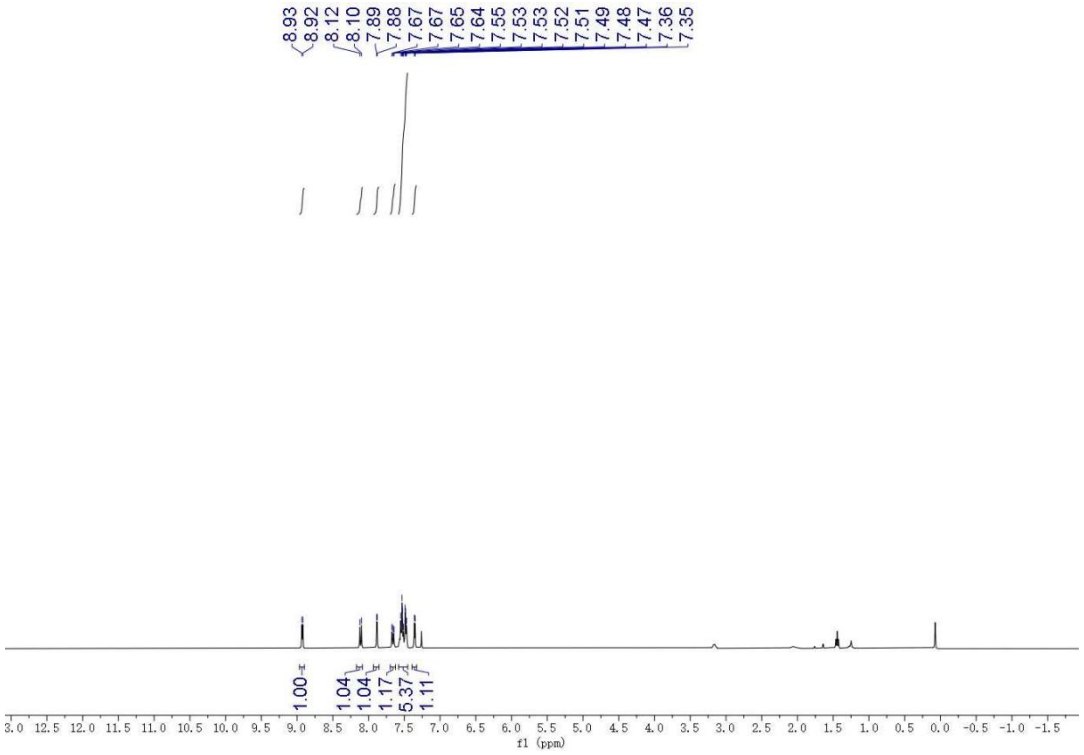
100 MHz in $CDCl_3$



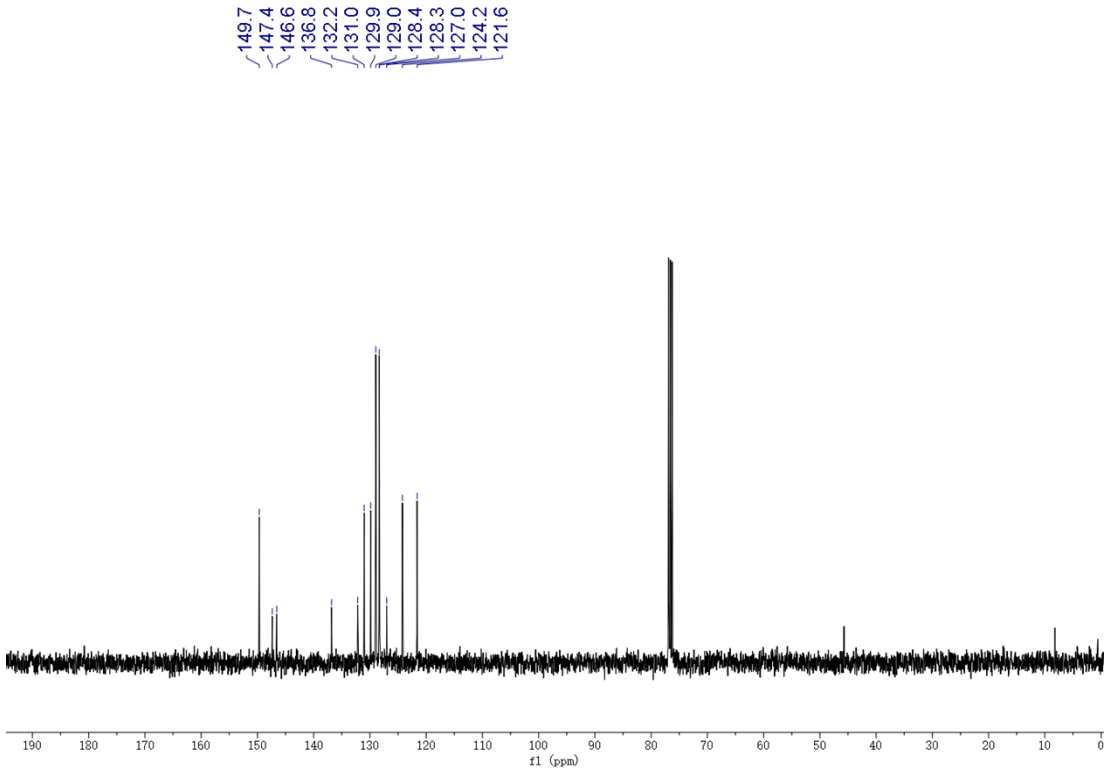


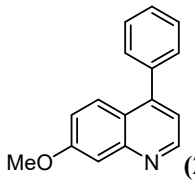
(28)

400 MHz in $CDCl_3$



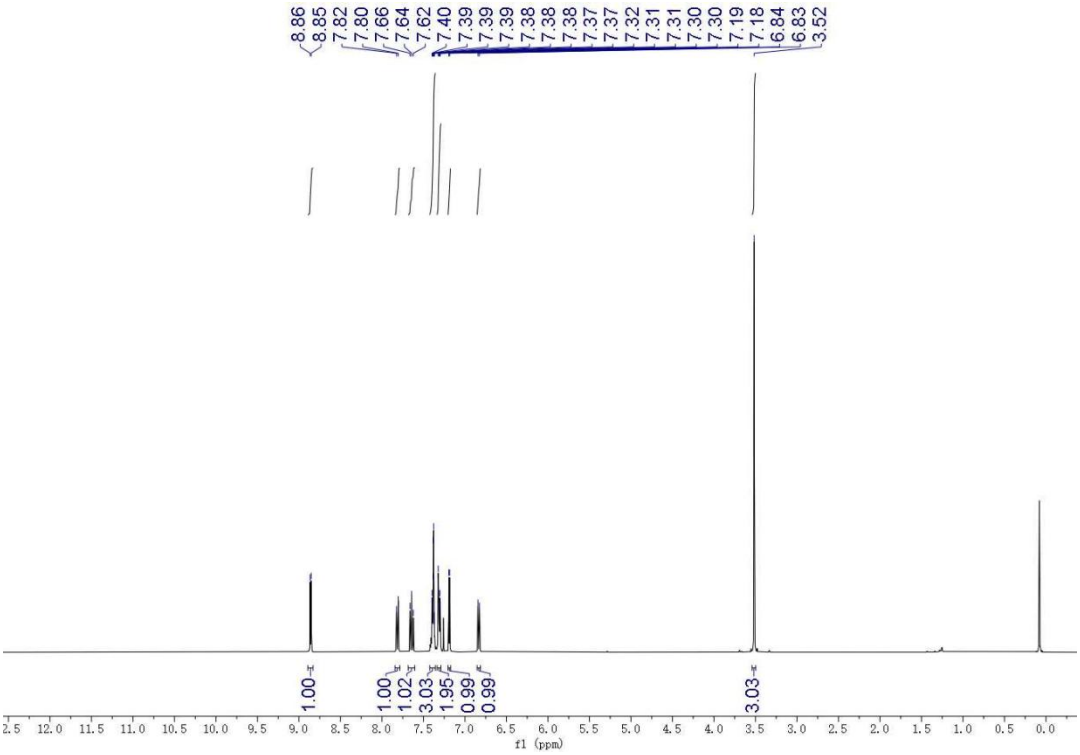
100 MHz in $CDCl_3$



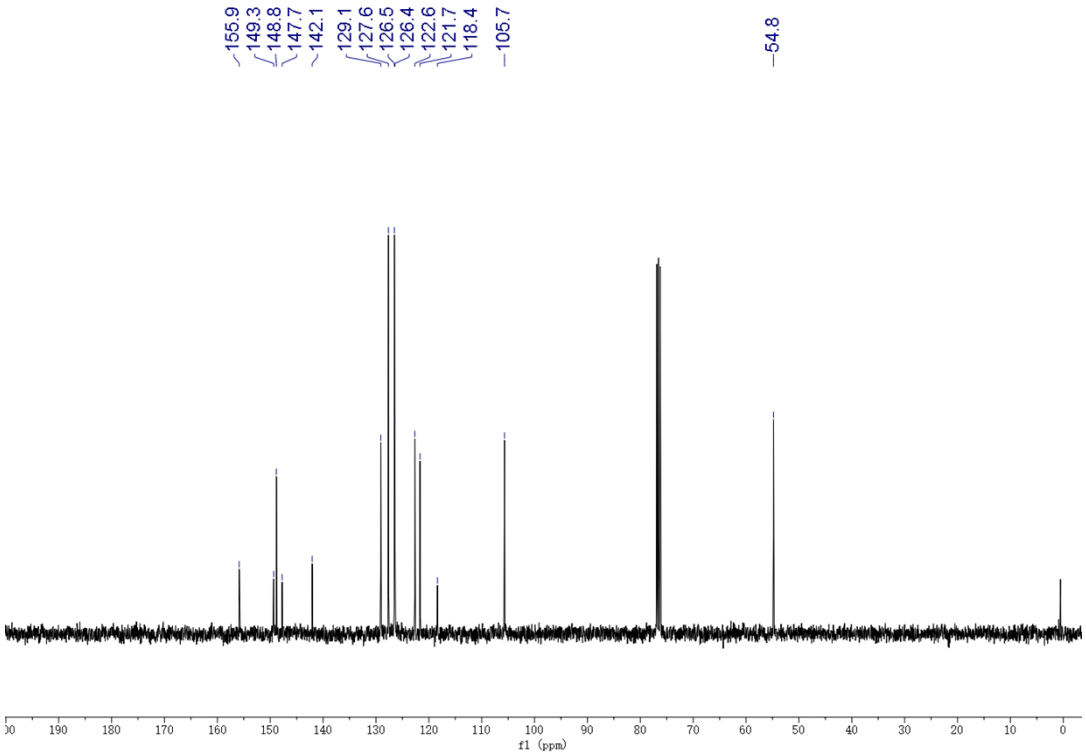


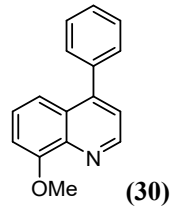
(29)

400 MHz in $CDCl_3$



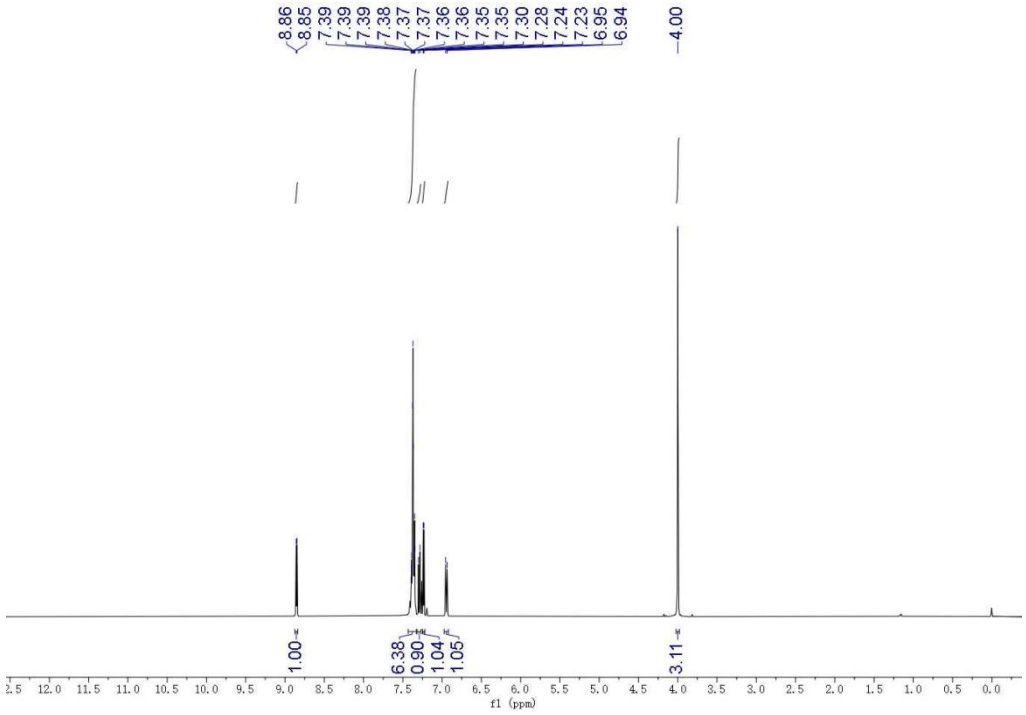
100 MHz in $CDCl_3$



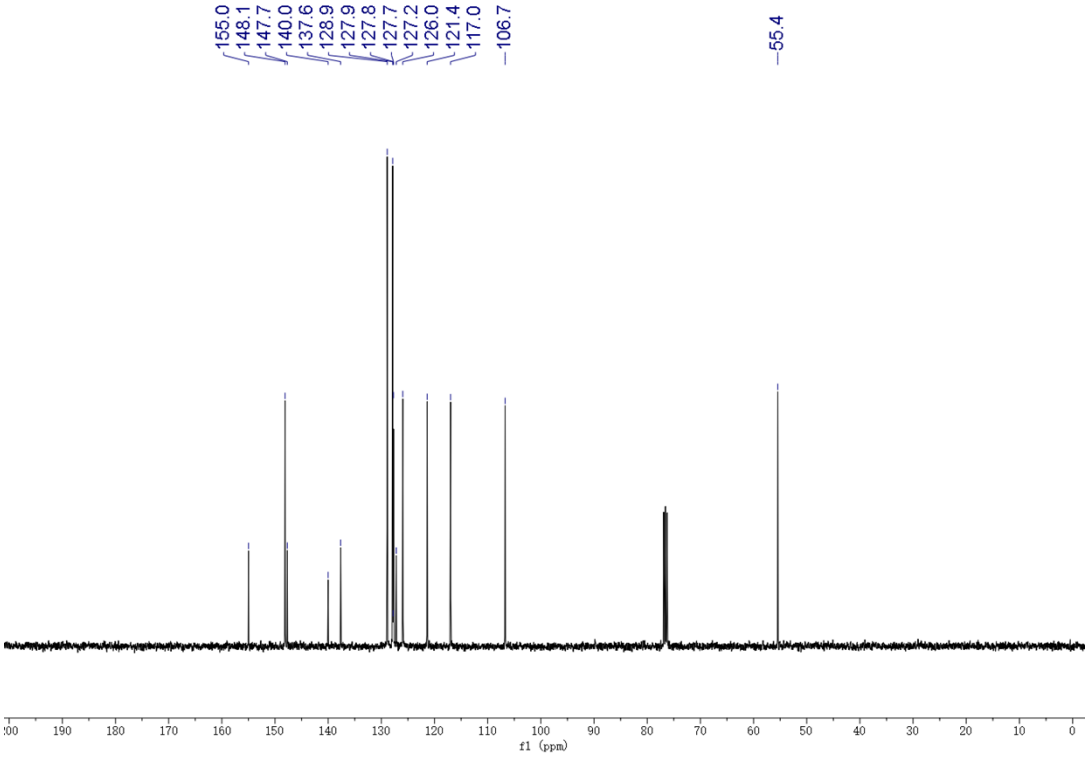


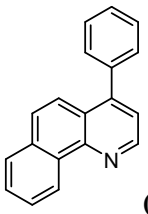
(30)

400 MHz in $CDCl_3$



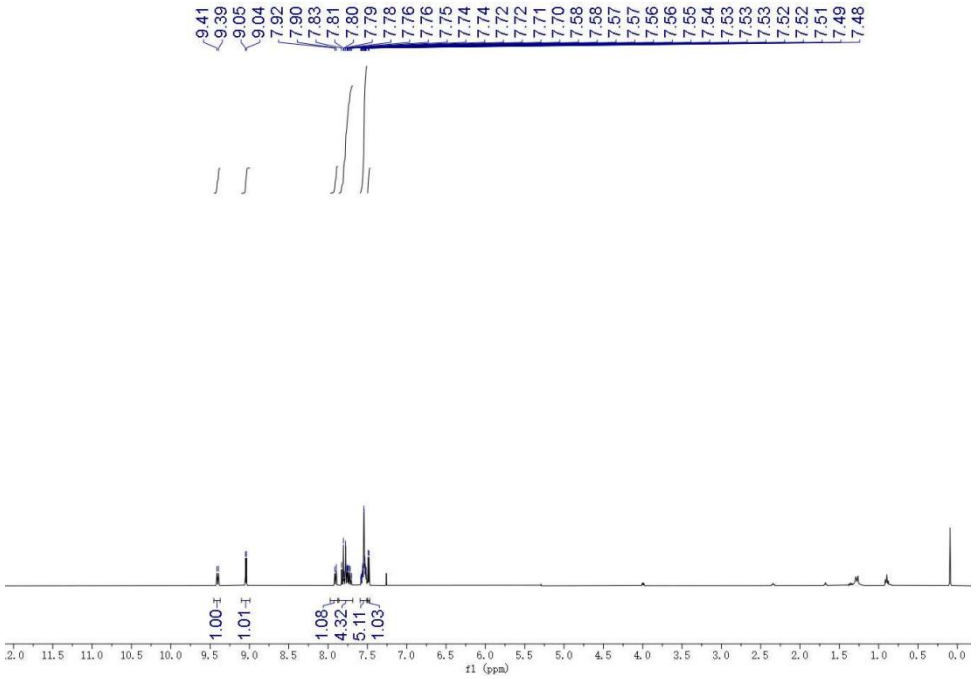
100 MHz in $CDCl_3$



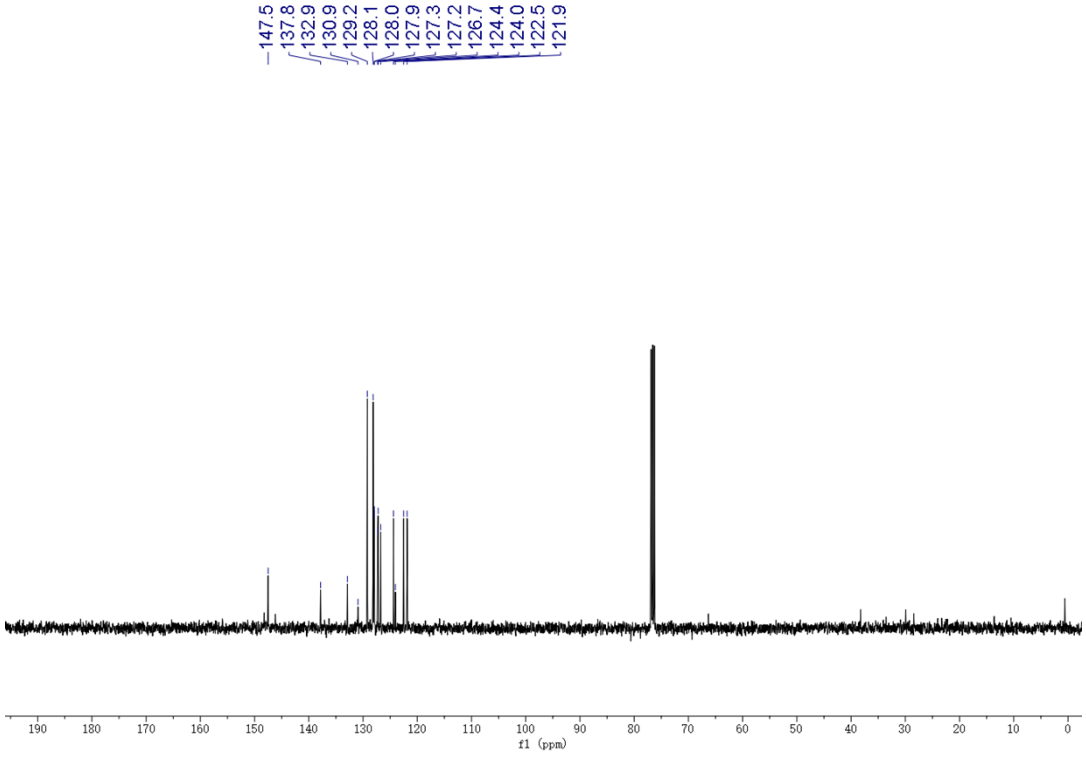


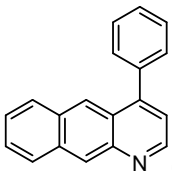
(31)

400 MHz in $CDCl_3$



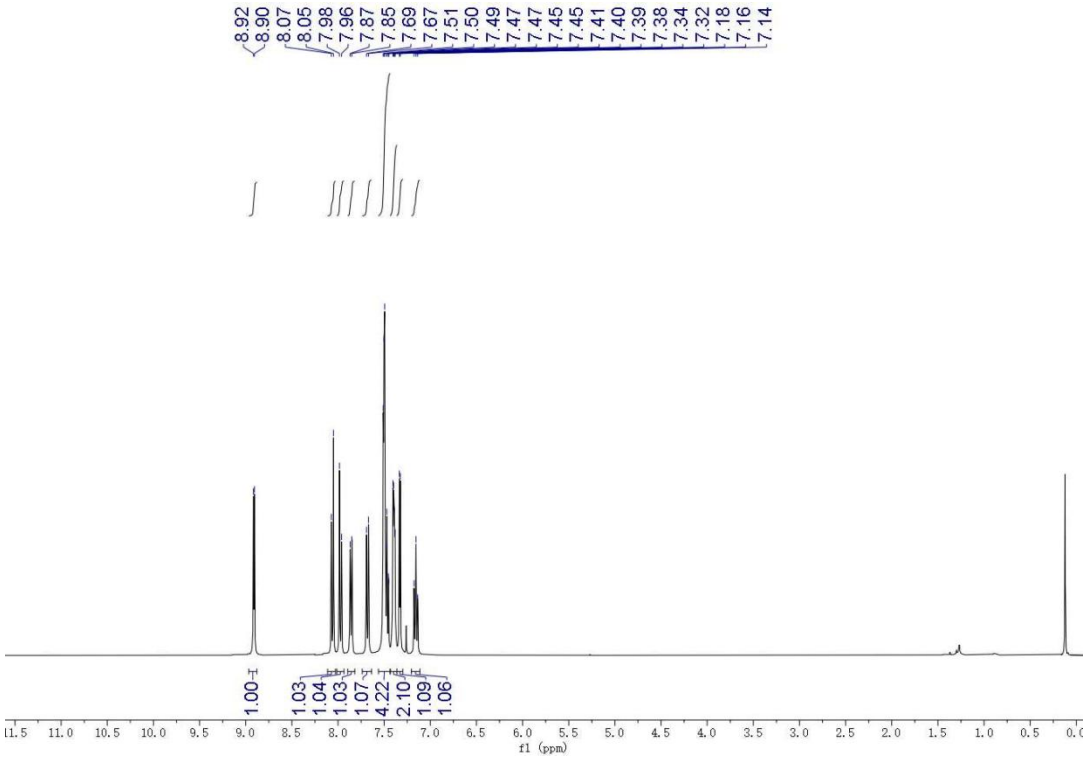
100 MHz in $CDCl_3$



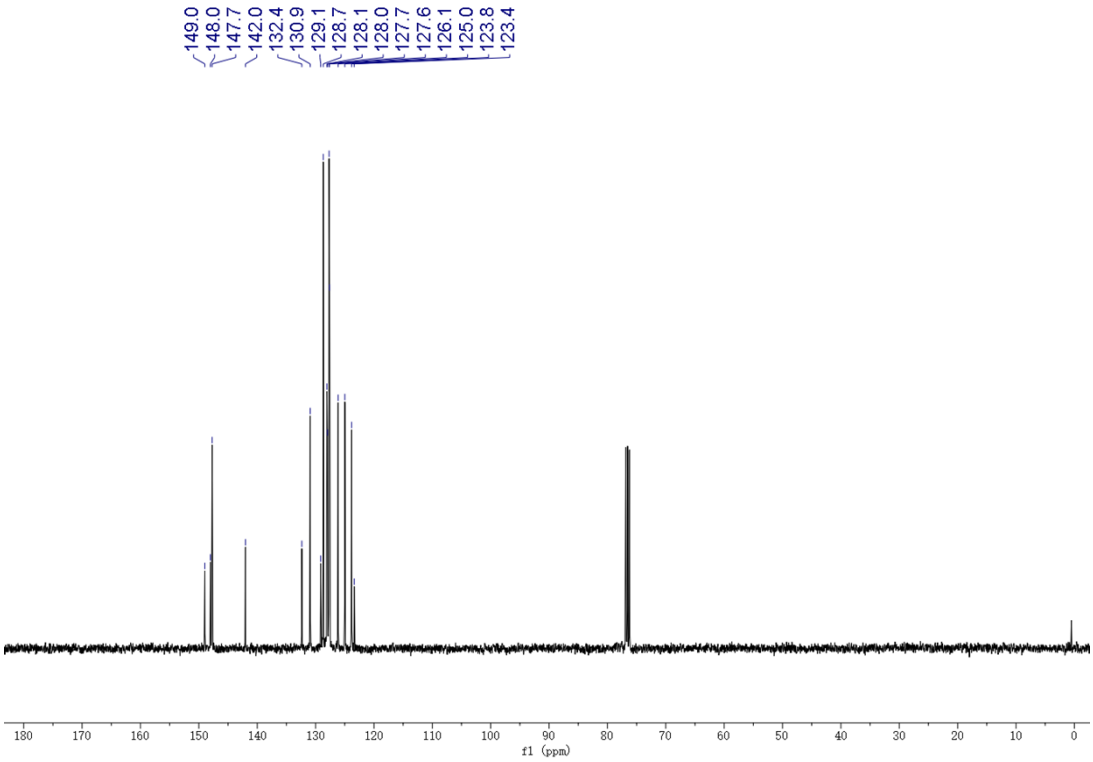


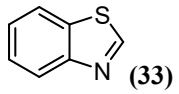
(32)

400 MHz in $CDCl_3$



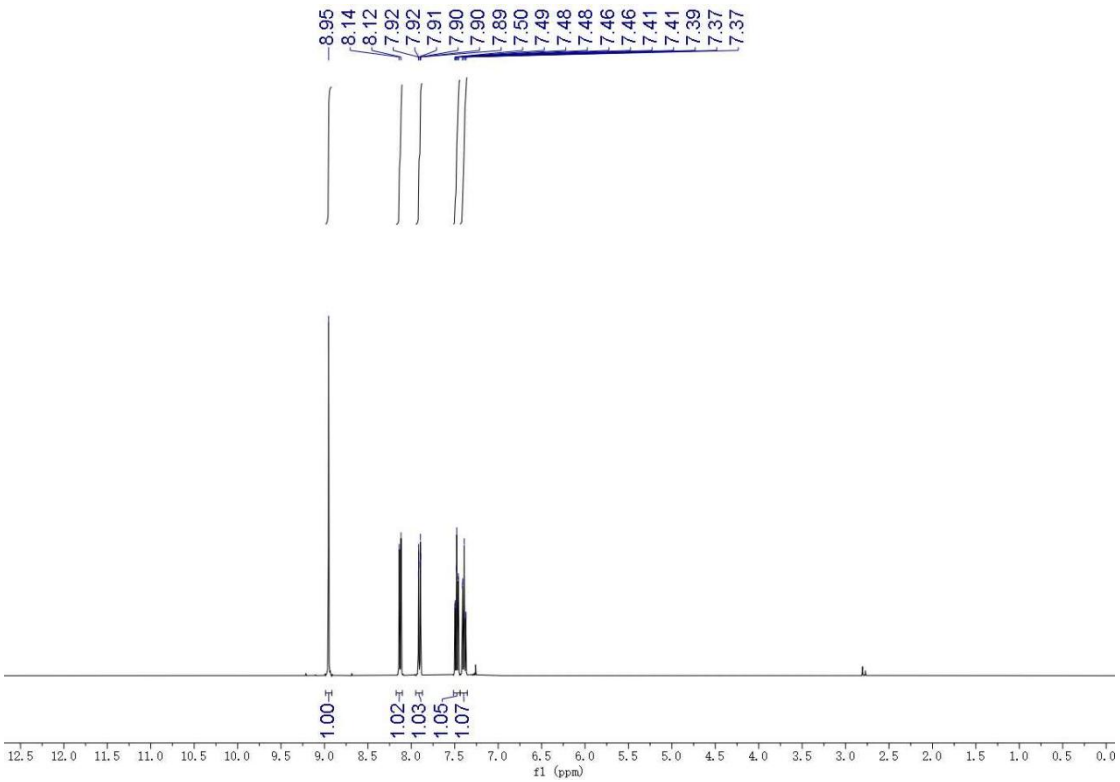
100 MHz in $CDCl_3$



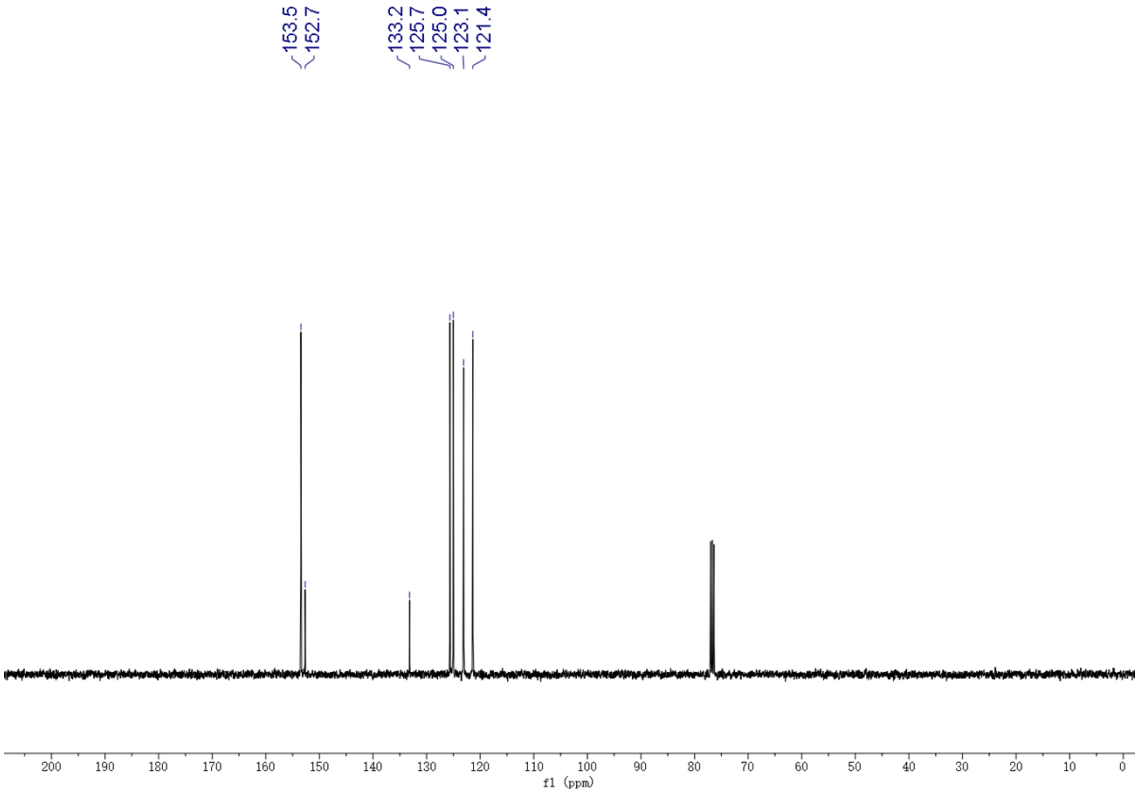


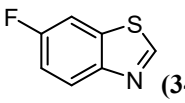
(33)

400 MHz in $CDCl_3$



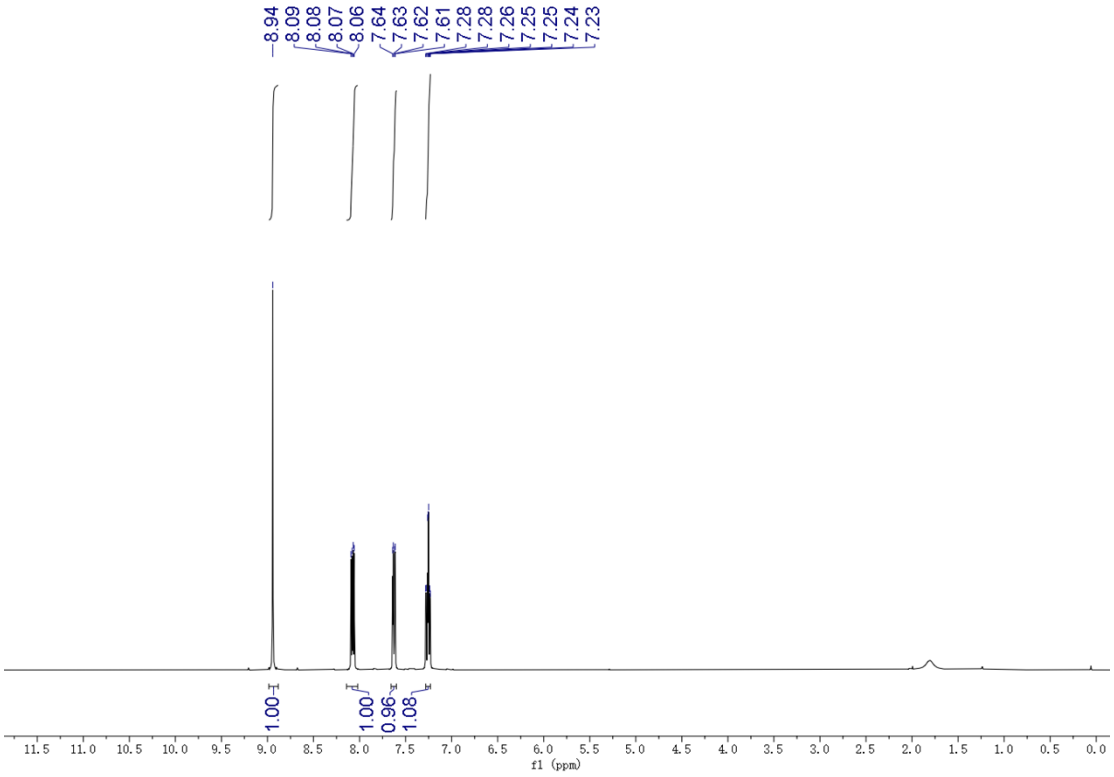
100 MHz in $CDCl_3$



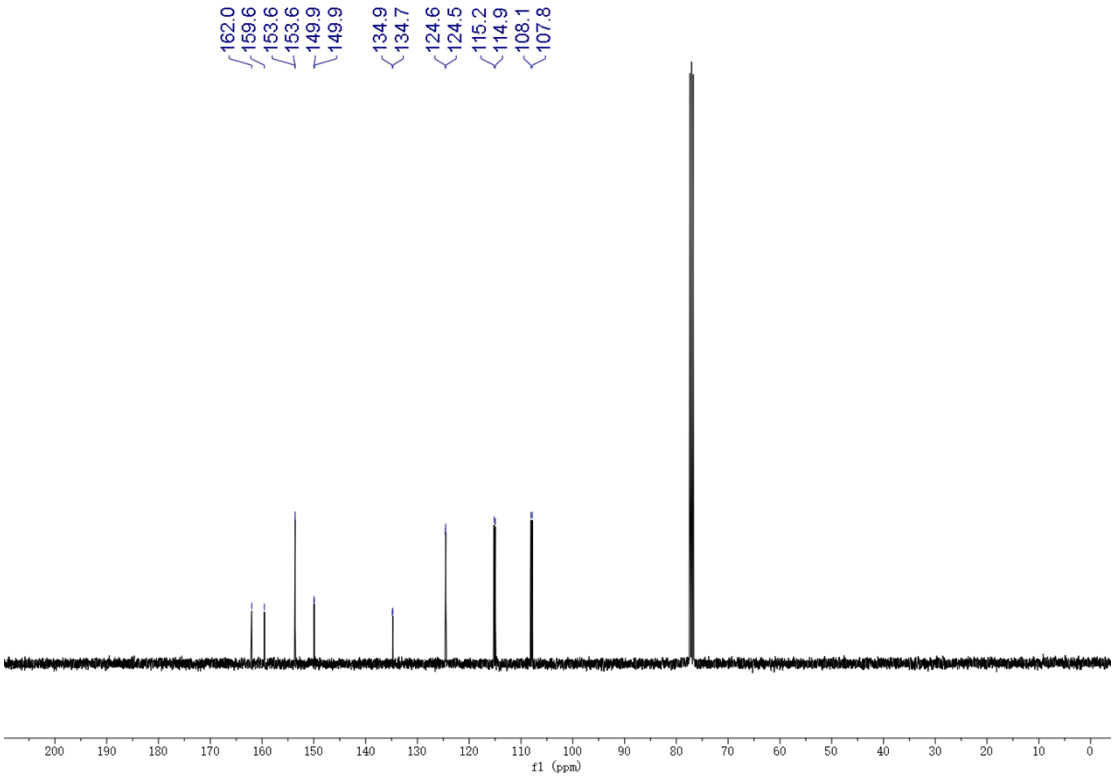


(34)

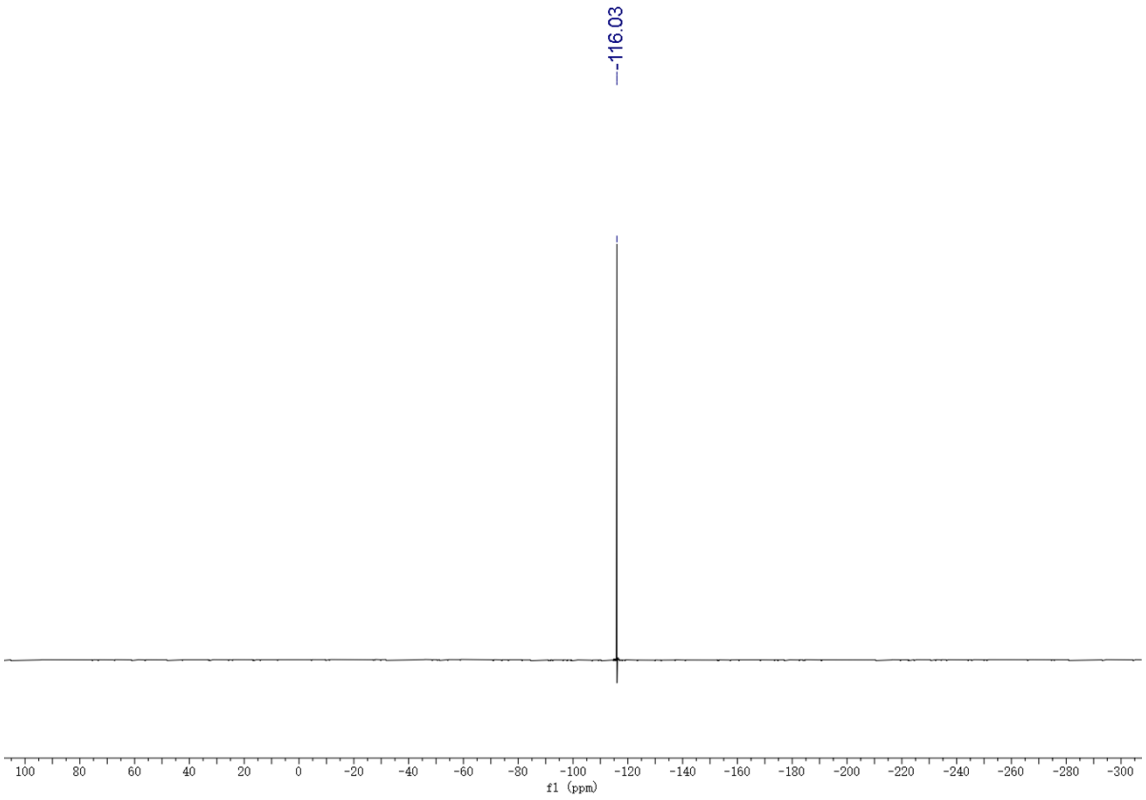
400 MHz in $CDCl_3$

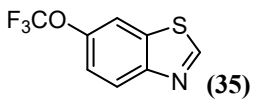


100 MHz in $CDCl_3$



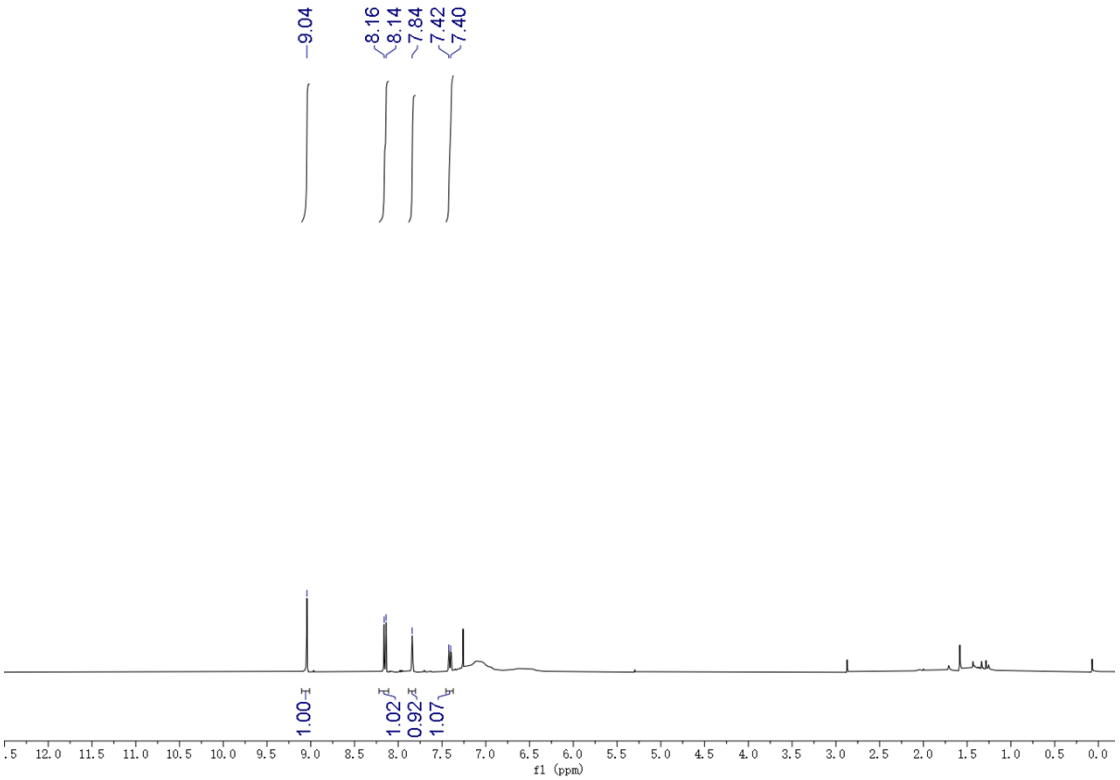
376 MHz in $CDCl_3$



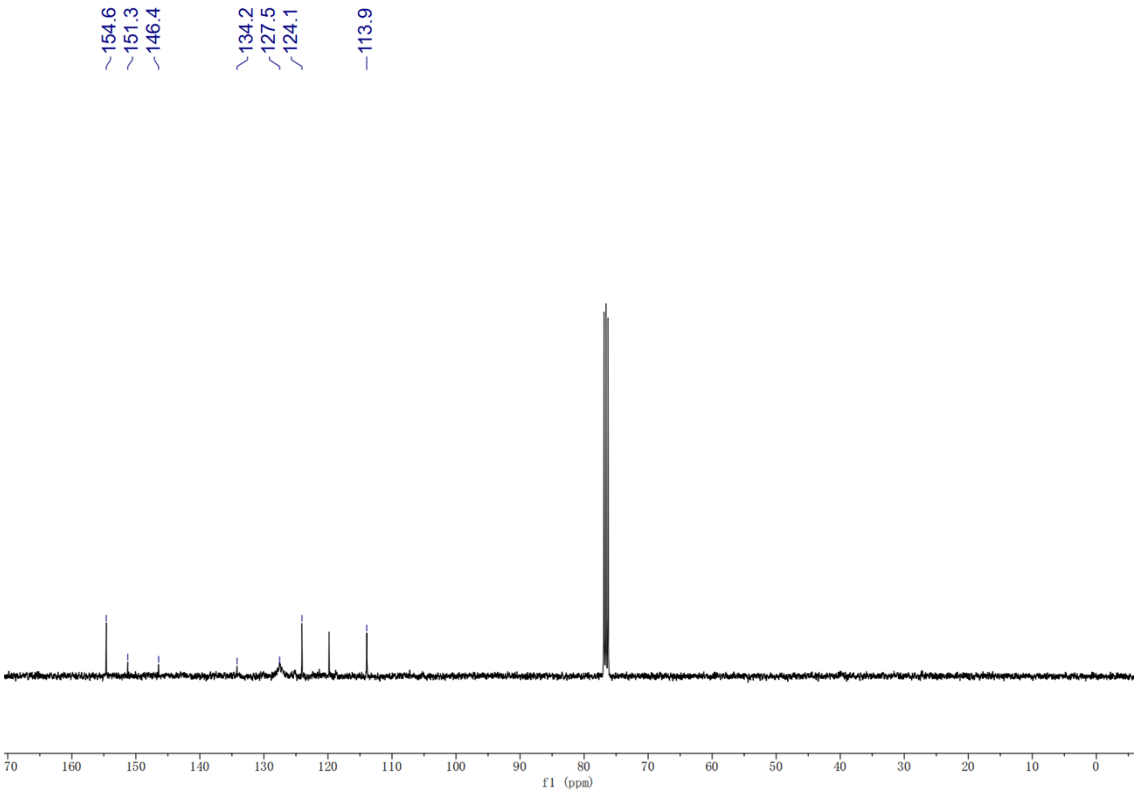


(35)

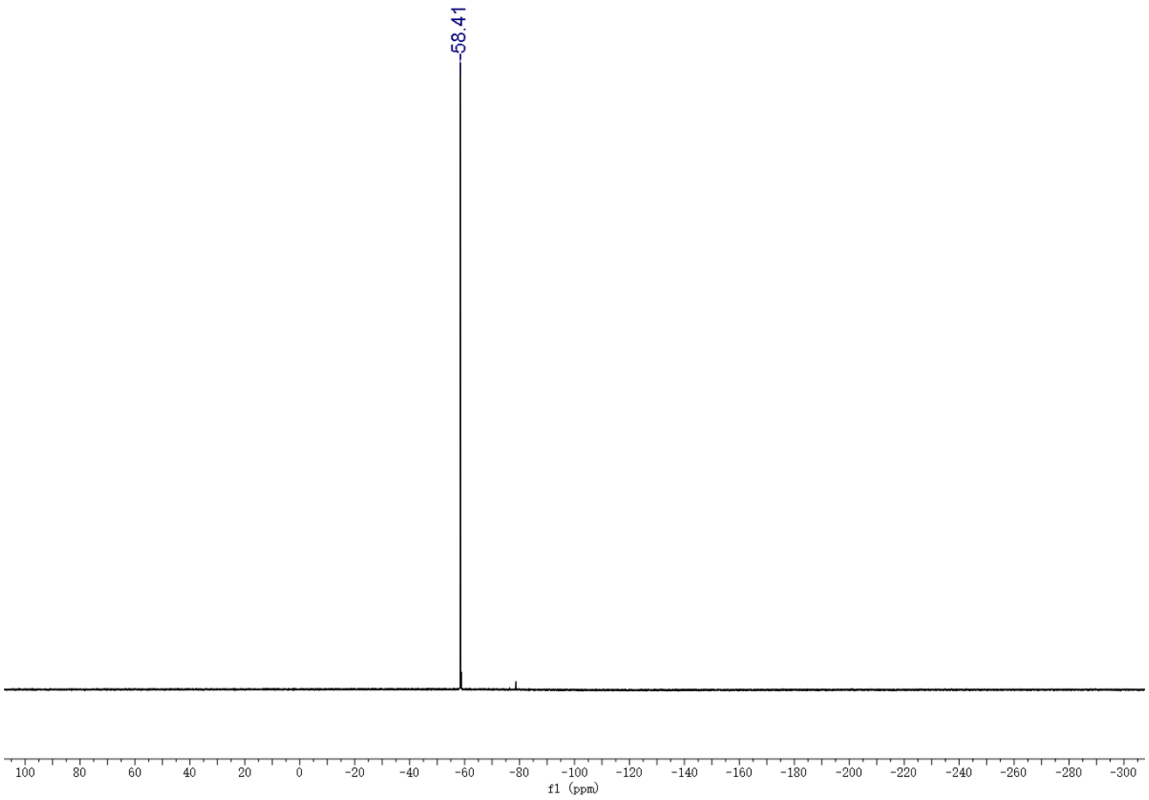
400 MHz in $CDCl_3$

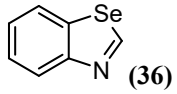


100 MHz in $CDCl_3$



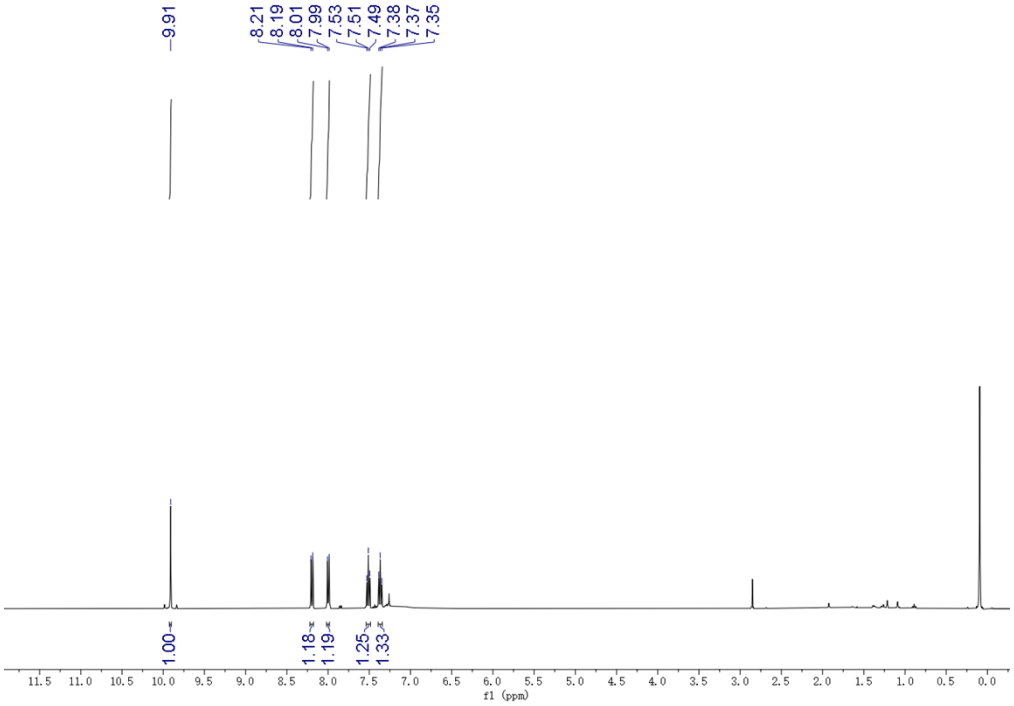
376 MHz in $CDCl_3$



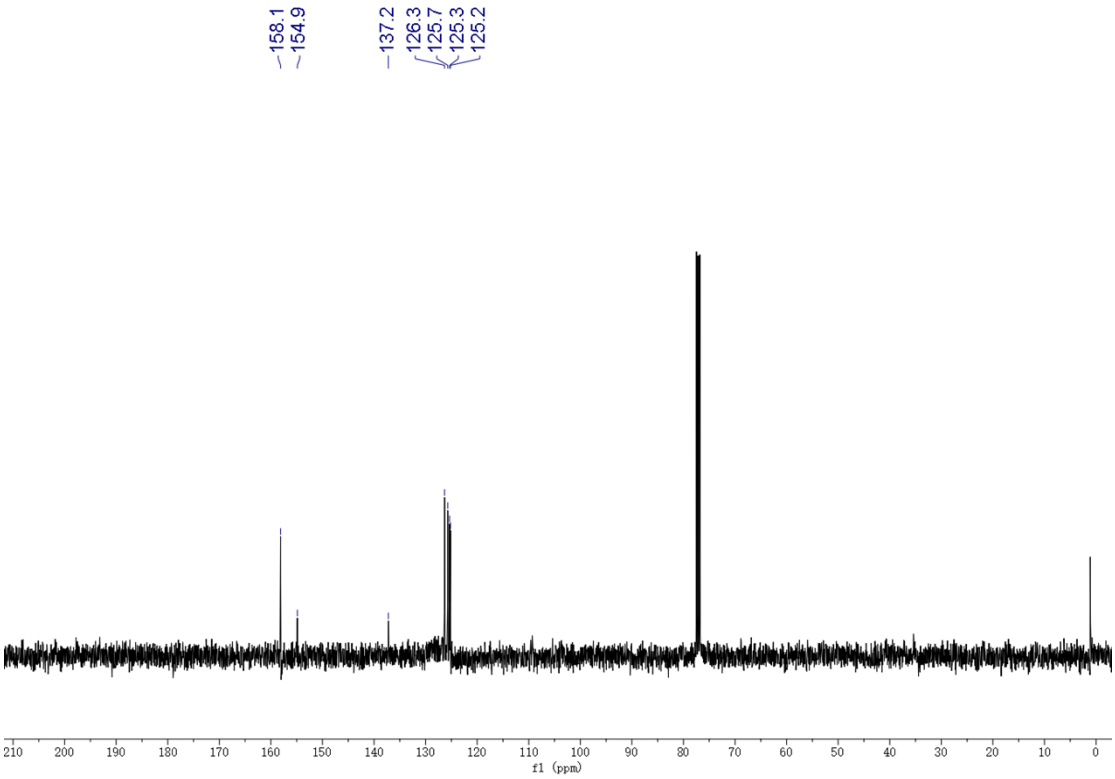


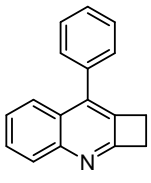
(36)

400 MHz in $CDCl_3$



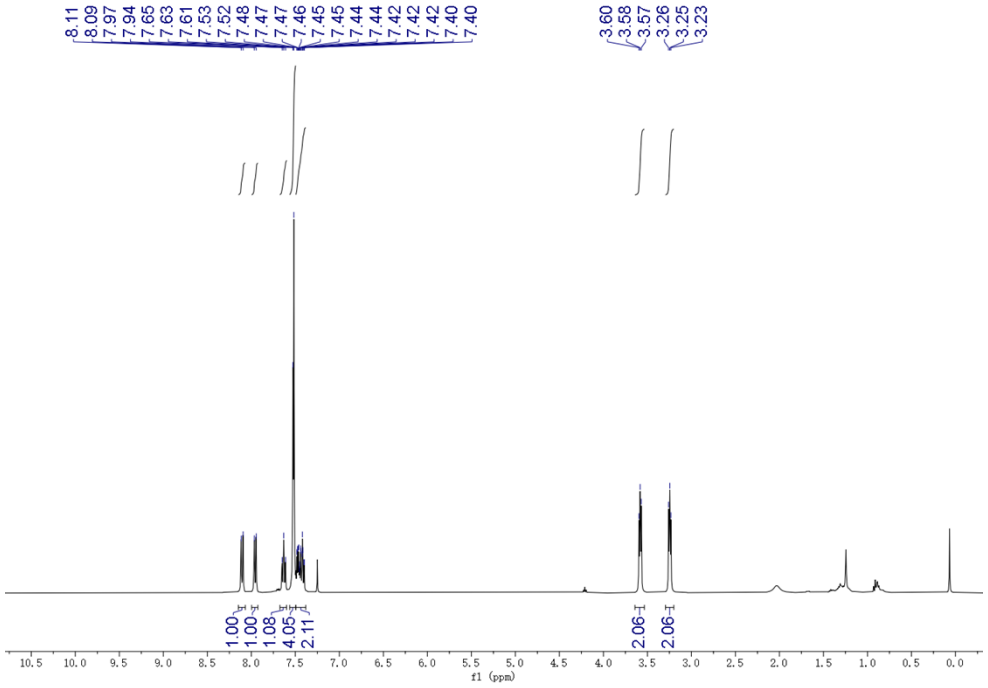
100 MHz in $CDCl_3$



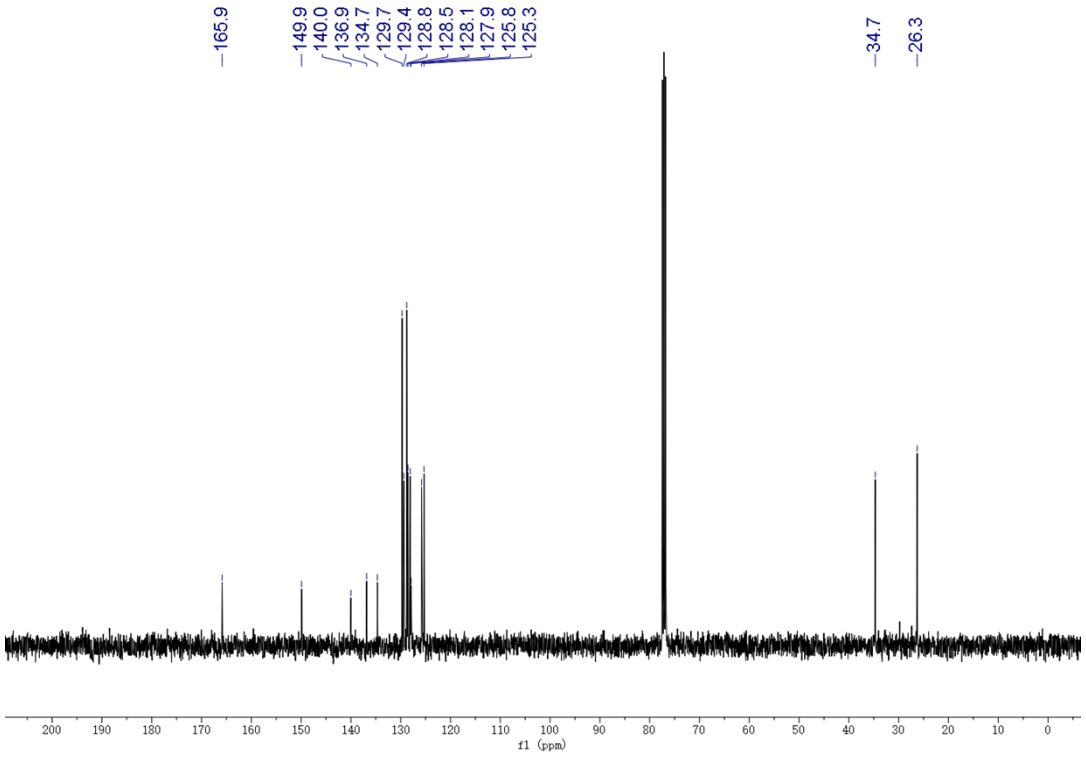


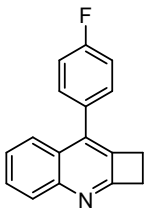
(37)

400 MHz in $CDCl_3$



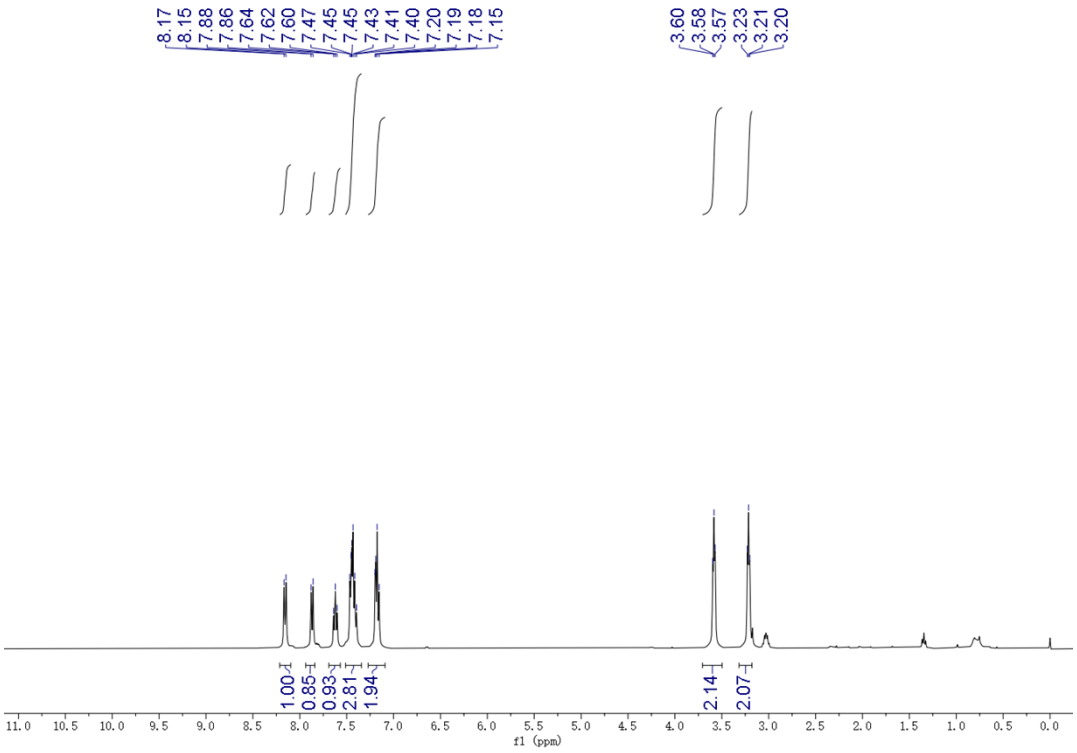
100 MHz in $CDCl_3$



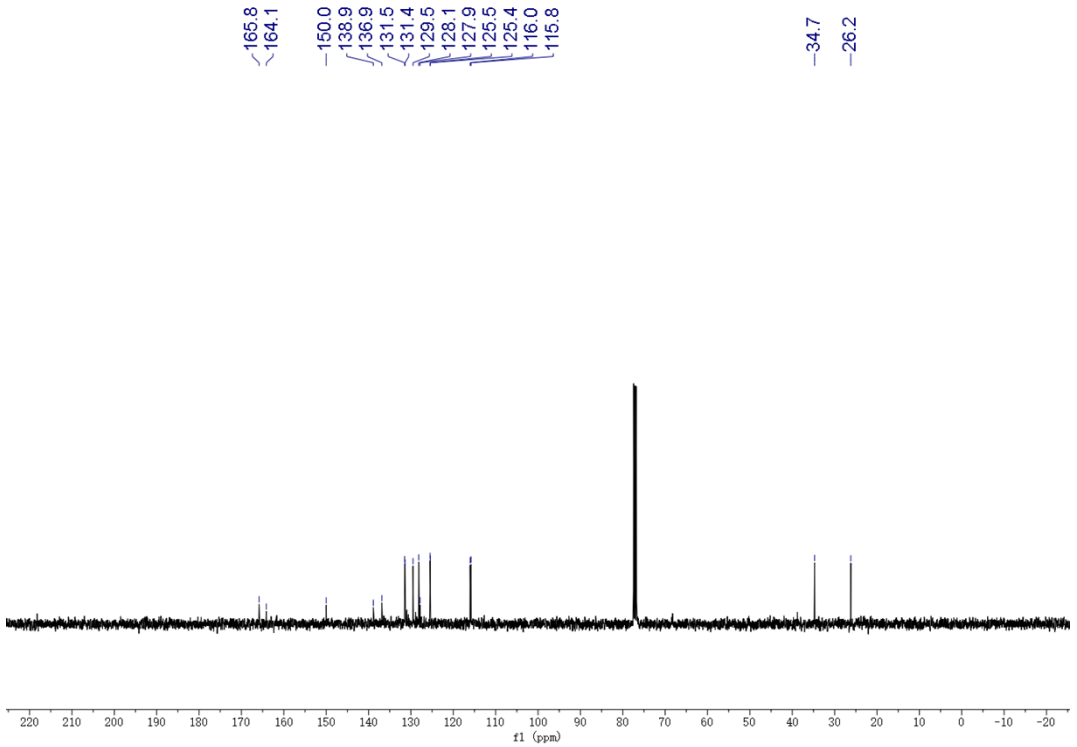


(38)

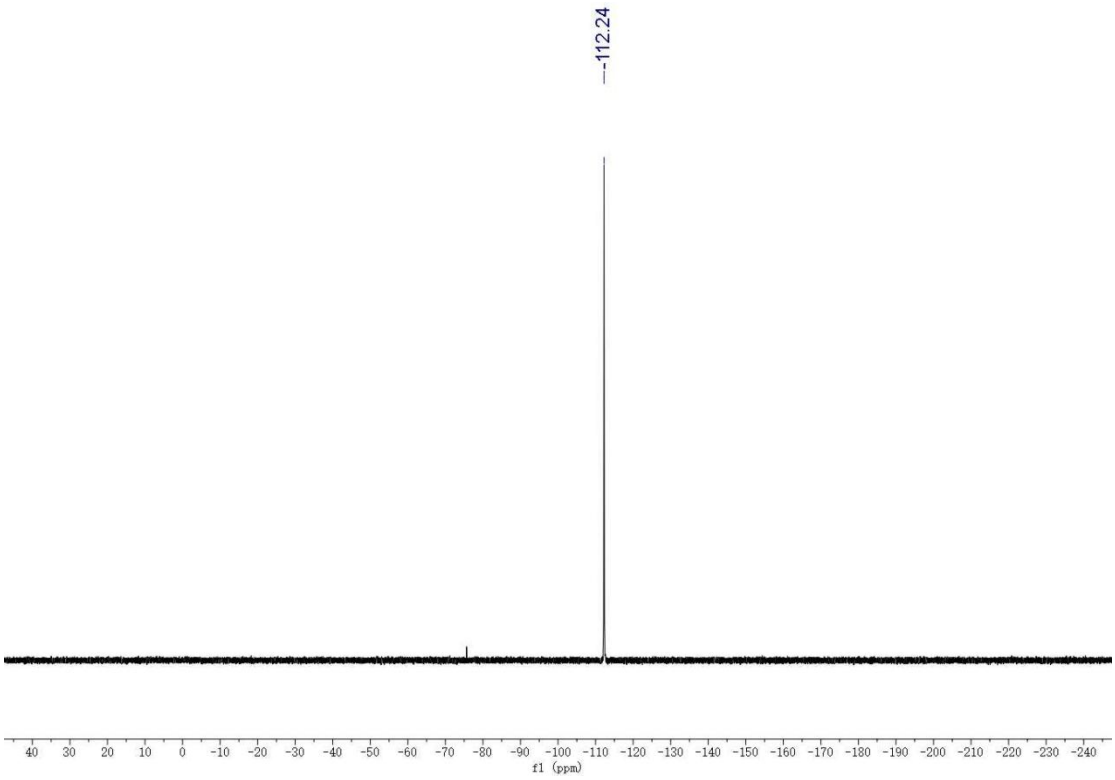
400 MHz in $CDCl_3$

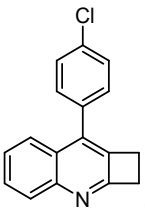


100 MHz in $CDCl_3$



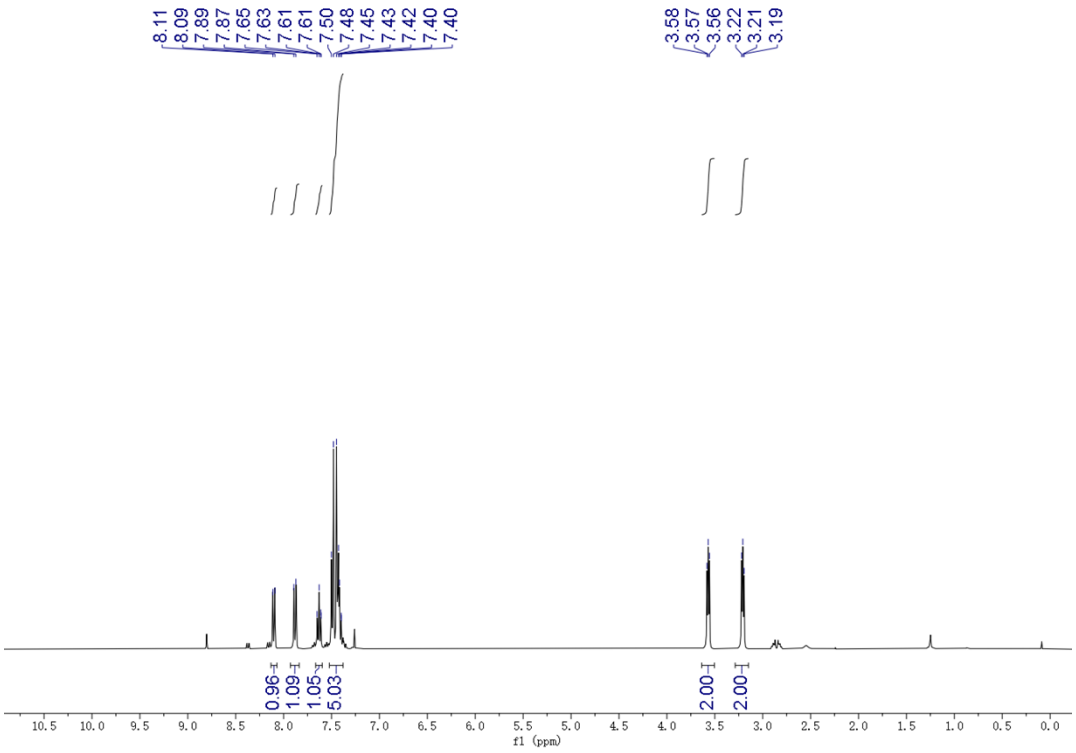
376 MHz in $CDCl_3$



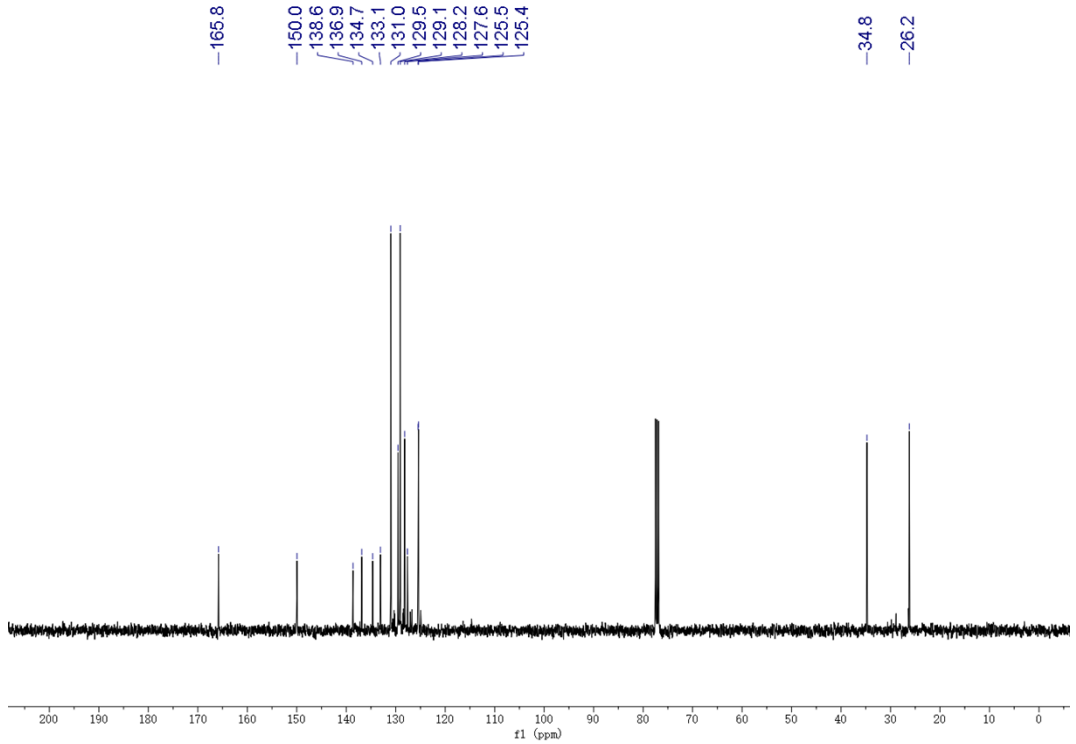


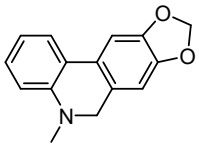
(39)

400 MHz in $CDCl_3$



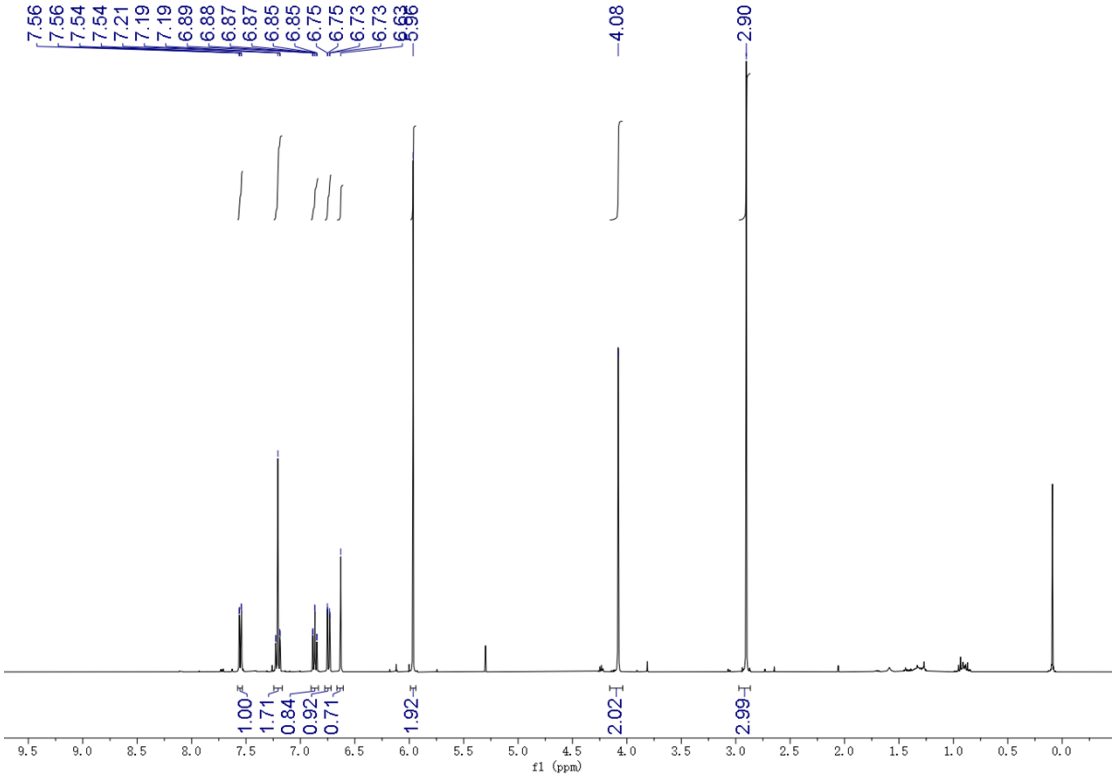
100 MHz in $CDCl_3$



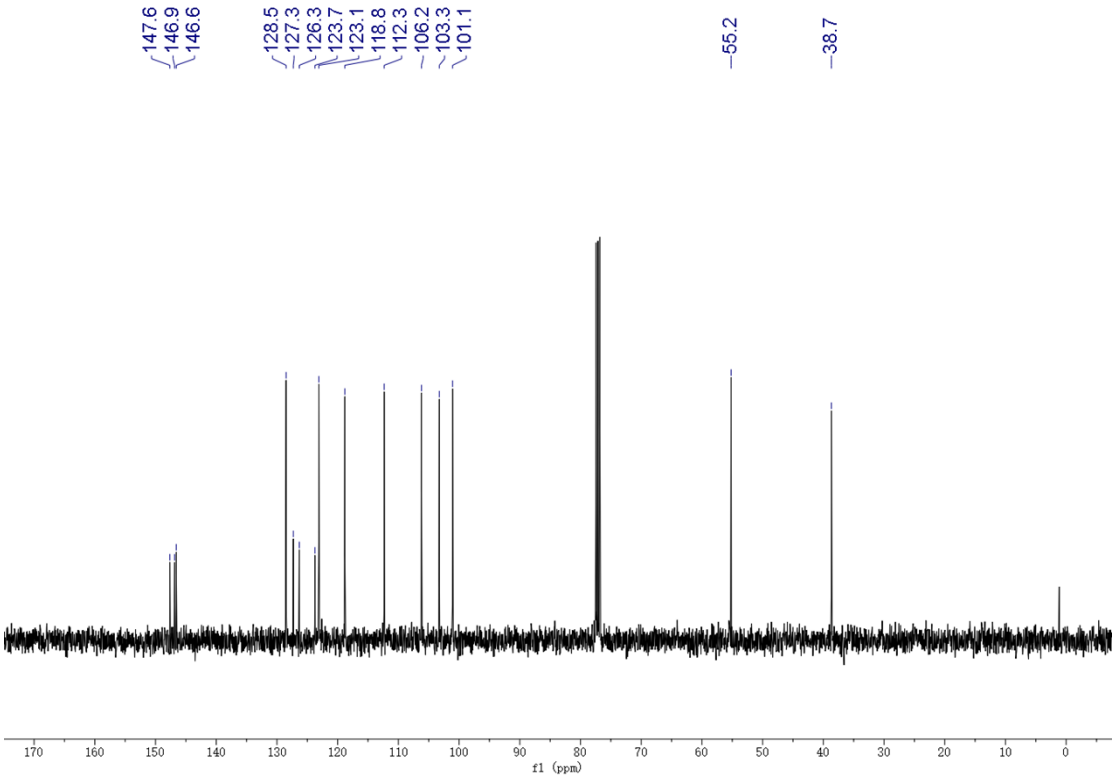


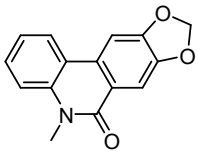
(40)

400 MHz in $CDCl_3$



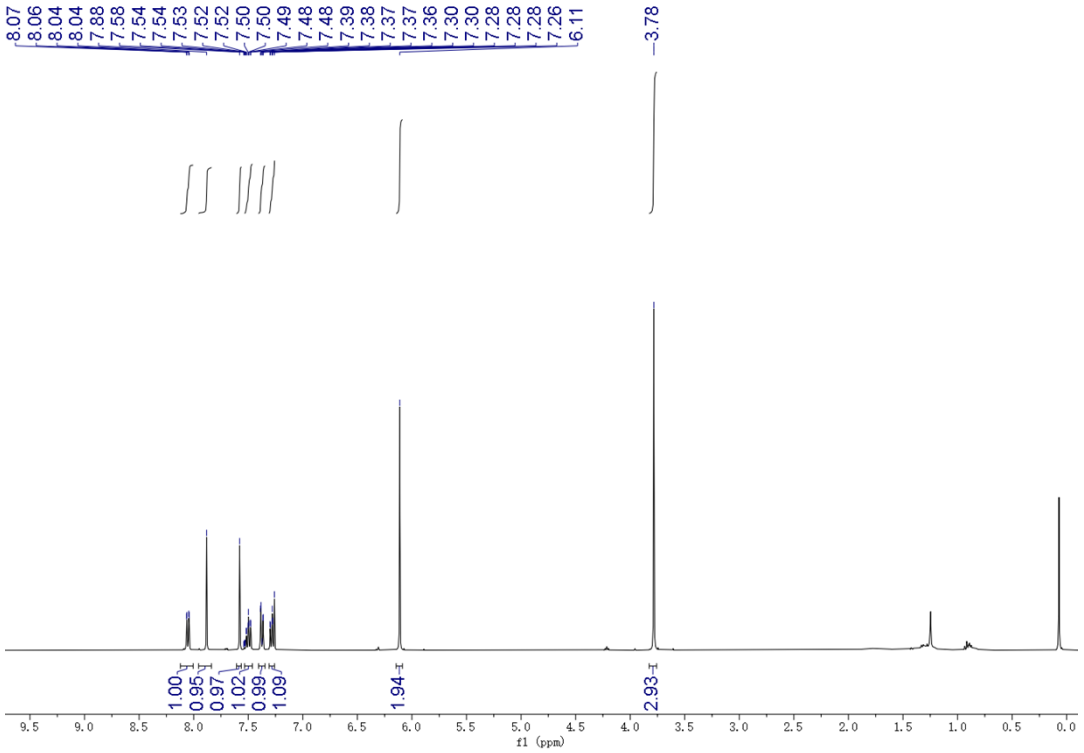
100 MHz in $CDCl_3$





(41)

400 MHz in $CDCl_3$



100 MHz in $CDCl_3$