Supporting Information

1,5-Hydrogen Atom Transfer of *α*-Iminyl Radical Cations: A New Platform for Relay Annulation towards Pyridine Derivatives and Axially Chiral Heterobiaryls

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General Information

Methods. All reactions dealing with air- and moisture-sensitive compounds were carried out in dry reaction vessels under a nitrogen atmosphere. Flash column chromatography was performed using 200-300 mesh silica gels. Thin layer chromatography was used for product detection using silica gel-coated plates, with visualization effected via exposure to UV Light at 254 nm or staining and heating with 2,4-Dinitrophenylhydrazine (DNP) or 1,2,3-Indantrione Monohydrate.

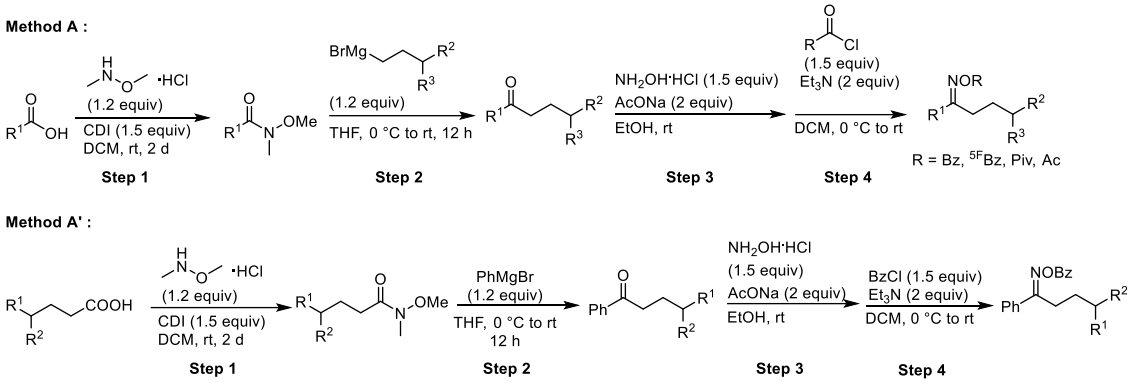
Instrumentation. ^{1}H NMR, ^{13}C NMR and ^{19}F NMR spectra were obtained on a Bruker Ascend 400 at 400 MHz (^{1}H NMR at 400 MHz, ^{13}C NMR at 101 MHz, ^{19}F NMR at 376 MHz) and Bruker Ascend 600 at 600 MHz (^{1}H NMR at 600 MHz, ^{13}C NMR at 151 MHz, ^{19}F NMR at 565 MHz) at ambient temperature with chloroform-d as the deuterated solvent unless stated otherwise. All chemical shifts δ are reported in parts per million (ppm), and the residual solvent peak was used as an internal reference: proton (chloroform δ 7.26), carbon (chloroform δ 77.0), or tetramethylsilane (TMS δ 0.00) was used as a reference. Coupling constants (J) were reported in Hertz (Hz) and referred to apparent peak multiplications. Data for ^{1}H NMR spectra were reported as follows: chemical shift (ppm), multiplicity (given as s(singlet), d (doublet), t (triplet), q (quartet), m (multiplet), br (broad) or a combination of them), coupling constants (Hz) and integration. ^{13}C NMR was only reported as chemical shifts. High-resolution mass spectra (HRMS) were recorded on a Bruker Impact II Q-TOF mass spectrometer (ESI). The enantiomeric ratios of products were determined by chiral phase HPLC analysis (Chiralpak AD-H, IE, ID columns were purchased from Daicel Chemical Industries, LTD). Optical rotations were determined at λ = 589 nm (sodium D line) at 25 ℃ by using a Rudolph-API automatic polarimeter. Gas chromatography (GC) analysis was performed on Shimadzu GC-2014. Single crystal X-ray data were recorded in a diffractometer with Mo Kα radiation. Melting points were determined using a capillary melting point apparatus and were uncorrected.

Materials. Unless stated otherwise, materials were purchased from commercial suppliers and used without additional purification. Anhydrous 1,4-dioxane, toluene, and other solvents were dried and degassed by standard methods and stored under N_2 atmosphere. Ammonium and iminium salts were prepared according to the literature procedure.[1]

Preparation of Starting Materials

General Procedures for the Synthesis of Oxime Esters

All oximes were synthesized according to general procedures (Methods A, B, C, D, and A') reported in the literature.[2-10] The characterization data of newly synthesized substrates were summarization below. ^{1}H, ^{13}C NMR and ^{19}F NMR spectra data for the rest of known ones were in agreement with the literature data.



Method A and Method A'

Step 1

A 100 mL flask was fitted with a stirring bar, and carboxylic acid (10 mmol) and DCM (0.25 M) were added. The acid dissolved in DCM to give a solution. Subsequently, N, N'-Carbonyldiimidazole (15 mmol, 1.5 equiv) was slowly added in several portions. The reaction mixture was stirred at room temperature for 1 h, then N, O-dimethylhydroxylamine hydrochloride (12 mmol, 1.2 equiv) was slowly added and the flask was sealed with a rubber septum equipped with a deflated balloon. The mixture was stirred at room temperature for 1-2 days and monitored by TLC. The reaction was quenched with an aqueous solution of saturated $NaHCO_3$. Then the aqueous layers were extracted with ethyl acetate. The combined organic layers were washed with brine and dried over Na_2SO_4. Then the solution was filtered, and concentrated to give the crude Weinreb amide which was used in the next step without further purification.

Step 2

To a 100 mL flask was added the crude Weinreb amide (10 mmol). The flask was backfilled with nitrogen (3 times). Dry THF (0.5 M) was added, then the solution was cooled to 0 ℃, and Grignard reagent (12 mmol, 1.2 equiv) was added dropwise. The reaction was warmed to room temperature and stirred for 12 h. The reaction was quenched with an aqueous solution of saturated NH_4Cl. The aqueous layers were extracted with ethyl acetate. The combined organic layers were dried over Na_2SO_4. Then the solution was filtered, and concentrated to give the crude ketone, which was purified by flash chromatography to be used in the next step.

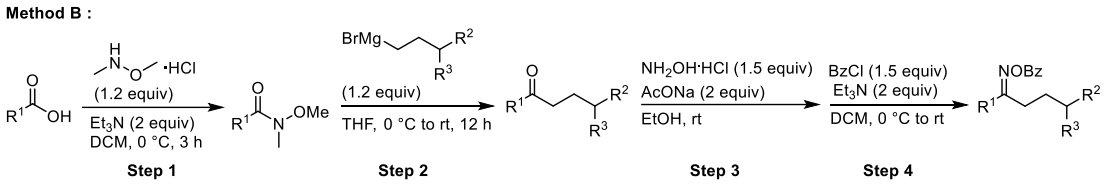
Step 3

A mixture of ketone (5 mmol), hydroxylamine hydrochloride (7.5 mmol, 1.5 equiv), and NaOAc (10 mmol, 2 equiv) was dissolved in $EtOH/H_2O$ (25 mL/25 mL). The mixture was stirred at room temperature for 3-4 h. Then EtOH was removed by concentration, and the residue was diluted

with 1N HCl and ethyl acetate. The organic layer was separated and the aqueous layer was extracted with ethyl acetate. The combined organic layers were washed with saturated $NaHCO_3$ solution, and brine, and dried over Na_2SO_4. The combined organic solution was concentrated by rotary evaporation to give the crude hydroxyl oxime, which was used in the next step without further purification.

Step 4

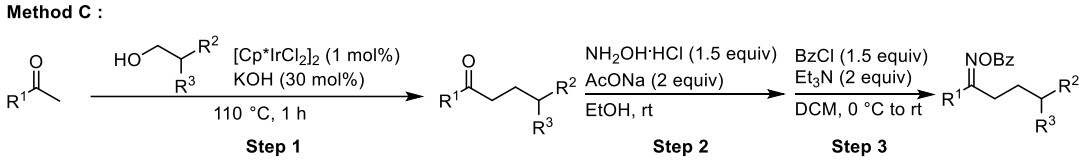
To a mixture of hydroxyl oxime (~5 mmol, 1 equiv), triethylamine (10 mmol, 2 equiv), and DCM (0.5 M) was added Acyl chloride (7.5 mmol, 1.5 equiv) at 0 ℃. Then, the reaction mixture was stirred at room temperature for 0.5 h under a nitrogen atmosphere. The reaction was quenched with an aqueous solution of saturated $NaHCO_3$. The aqueous layer was extracted with DCM. The combined organic layers were washed with brine and dried over Na_2SO_4. The crude product was purified by flash chromatography on silica gel to give the final oxime ester.



Method B

Step 1

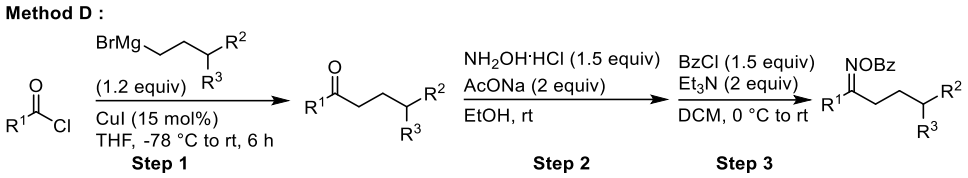
A 100 mL three-necked flask was charged with *N*, *O*-dimethylhydroxylamine hydrochloride (12 mmol, 1.2 equiv), and the flask was evacuated and backfilled with nitrogen (3 times). Dry DCM (0.25 M) was added, and after cooling to 0 ℃, triethylamine (20 mmol, 2 equiv) was subsequently added followed by the dropwise addition of carboxylic acid (10 mmol). The mixture was then slowly warmed to room temperature and stirred for 3 h before being quenched with saturated $NaHCO_3$. The aqueous layers were extracted with ethyl acetate. The combined organic layers were washed with brine and dried over Na_2SO_4. Then the solution was filtered, and concentrated to give the crude Weinreb amide, which was used in the next step without further purification. The final oxime ester was prepared according to steps 2-4 of Method A.



Method C

Step 1

A mixture of ketone (10 mmol), primary alcohol (15 mmol, 1.5 equiv), $[Cp^*IrCl_2]_2$ (1 mol%) and KOH (3 mmol) was placed in a 50 mL screw-capped flask under nitrogen. The reaction mixture was allowed to react at 110 ℃ for 1 h. The reaction was quenched by adding water and the aqueous phase was extracted with ethyl acetate. The combined organic layers were washed with 1N HCl and brine, and then dried over Na_2SO_4. The crude product was purified by flash chromatography to give the ketone. The final oxime ester was prepared according to steps 3-4 of Method A.



Method D

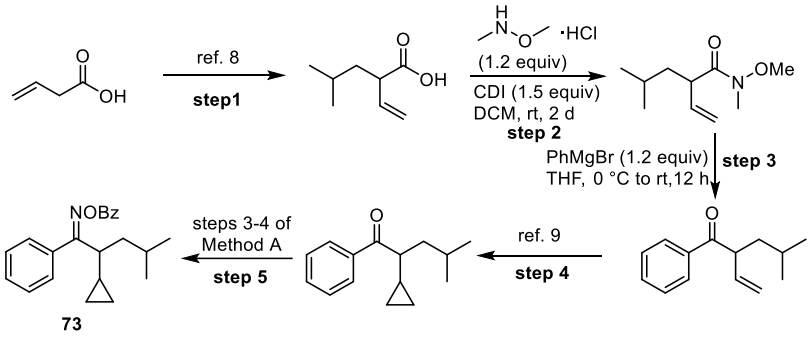
Step 1

To a 100 mL three-necked flask was added CuI (1.5 mmol, 15 mol%), and the flask was evacuated and backfilled with nitrogen (3 times). Dry THF (0.5 M) and acid chloride (10 mmol) were added. The solution was cooled to -78 ℃ and Grignard reagent (12 mmol, 1.2 equiv) was added dropwise. Then the mixture was warmed to room temperature and stirred for 6 h. The reaction was quenched with an aqueous solution of saturated NH_4Cl. The aqueous layer was extracted with ethyl acetate. The combined organic layer was washed with brine and dried over Na_2SO_4. Subsequently, the solution was filtered, and concentrated to give the crude ketone, which was used in the next step without further purification. The final oxime ester was prepared according to steps 3-4 of Method A.

Oxime Esters

Substrates (**1**, **95**, **S4, S5, S9, S12, S14-16, S24, S25, S98, S99, S104, S121, S122)** were prepared according to Method A reported in the literature,[4,6] substrates (**S6-8, S10, S11, S13, S17, S18, S28, S29, S100-103**) were prepared according to Method B reported in the literature,[3] substrates (**87, S21, S22, S106**) were prepared according to Method C reported in the literature,[3,7] substrates (**S19, S20, S105)** were prepared according to Method D reported in the literature,[2,3,5,10] substrates (**S23, S26, S27**) were prepared according to Method A' reported in the literature.[4,6]

73 was synthesized according to the literature with some variations.[8,9]



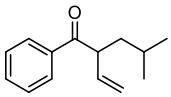
Step 1. A solution of commercial LDA (2 M in THF, 11.8 mL, 23.5 mmol, 2 equiv) was cooled to ice-water temperature, and a solution of 3-butenoic acid (1 mL, 11.77 mmol) in 10 mL of THF was added slowly over 15 min. The resulting mixture was stirred at the same temperature for 45 min to obtain a deep yellow solution. A total of the alkylating agent (12.9 mmol, 1.1 equiv) was added, whereupon the reaction mixture immediately turned colorless. After stirring for 30 min at the same temperature and 1 h at room temperature, the pH of the solution was adjusted to 2.5 with 10% HCl. The organic phase was separated. The aqueous layer was saturated with solid NaCl and

the mixture was extracted with ethyl acetate. The combined organic layers were dried over anhydrous Na_2SO_4 and filtered. Removal of solvents under reduced pressure followed by chromatography on silica gel produced the targeted 4-methyl-2-vinylpentanoic acid.

Steps 2-3 were performed according to steps 1-2 of Method A' to afford 4-methyl-1-phenyl-2-vinylpentan-1-one.

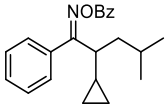
Step 4. A dried 100 mL round bottom flask was charged with a stir bar, and DCM (10 mL) under nitrogen atmosphere was added and cooled to –40 ℃. $ZnEt_2$ (1.0 M, 4 mL, 4 mmol, 2 equiv) was added followed by a solution of TFA (3.3 mL, 4 mmol, 2.0 equiv) in DCM (10 mL). The reaction mixture was stirred at this temperature for 1 h followed by warming to –10 ℃. Next, CH_2I_2 (4 mmol, 2.0 equiv) was dropwise into the reaction mixture and the resulting solution was allowed to stir at –10 ℃ for another 1 h. A solution of 4-methyl-1-phenyl-2-vinylpentan-1-one (2 mmol, 1.0 equiv) in DCM (5 mL) was then added, and the reaction mixture was allowed to warmed to room temperature and stirred for 16 h. The reaction was quenched by saturated NH_4Cl (3 mL) and extracted with DCM (5 mL× 3). The combined organic layers were washed with aqueous $NaHCO_3$ and brine, dried over Na_2SO_4, filtered, concentrated, and purified by flash chromatography (Petroleum ether/Ethyl acetate = 100:1) to afford 2-cyclopropyl-4-methyl-1-phenylpentan-1-one.

Step 5 was performed according to steps 3-4 of Method A to give the final oxime ester **73**.



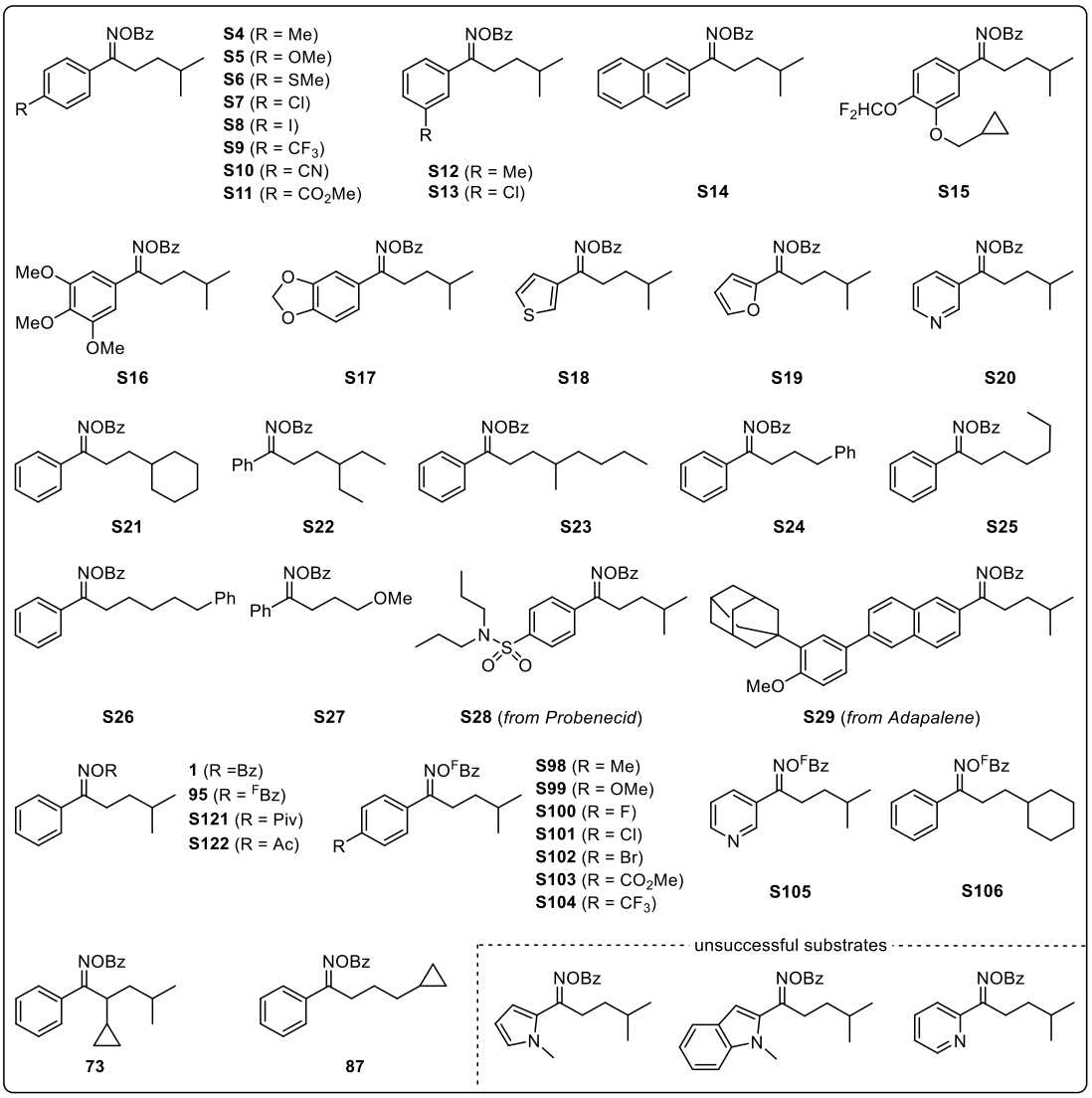
4-methyl-1-phenyl-2-vinylpentan-1-one:

Colorless oil (1.07 g, 5.3 mmol, 45% yield over steps 1-3; R_f = 0.7 (Petroleum ether/Ethyl acetate = 10:1); **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.00 – 7.96 (m, 2H), 7.55 (t, *J* = 7.4 Hz, 1H), 7.46 (t, *J* = 7.7 Hz, 2H), 5.88 (ddd, *J* = 17.3, 10.1, 8.8 Hz, 1H), 5.16 (d, *J* = 17.5 Hz, 1H), 5.13 (d, *J* = 10.2 Hz, 1H), 4.18 – 4.12 (m, 1H), 1.78 – 1.72 (m, 1H), 1.67 – 1.61 (m, 1H), 1.56 – 1.50 (m, 1H), 0.93 (d, *J* = 6.5 Hz, 3H), 0.90 (d, *J* = 6.6 Hz, 3H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 201.1, 137.4, 136.9, 132.9, 128.6, 128.4, 117.3, 49.8, 41.1, 25.6, 23.0, 22.2; **HRMS** (ESI) m/z: $[M + Na]^+$ calcd. for $C_{14}H_{18}NaO$ 225.1250; found 225.1251.



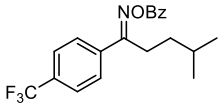
2-cyclopropyl-4-methyl-1-phenylpentan-1-one O-benzoyl oxime (73):

Colorless oil (203.0 mg, 0.6 mmol, 30% yield over steps 4-5; R_f = 0.5 (Petroleum ether/Ethyl acetate = 10:1); **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.07 (d, *J* = 7.6 Hz, 2H), 7.64 – 7.56 (m, 3H), 7.50 (t, *J* = 7.5 Hz, 2H), 7.45–7.37 (m, 3H), 2.90 – 2.77 (m, 1H), 1.80 – 1.71 (m, 2H), 1.66 – 1.60 (m, 1H), 1.00 – 0.93 (m, 1H), 0.90 (d, *J* = 5.8 Hz, 6H), 0.71 – 0.71 (m, 1H), 0.54 – 0.46 (m, 1H), 0.37 – 0.24 (m, 2H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 171.6, 163.9, 133.3, 129.6, 129.5, 129.3, 128.6, 128.4, 128.3, 42.1, 26.0, 23.0, 22.6, 14.1, 6.9, 3.9; **HRMS** (ESI) m/z: $[M + Na]^+$ calcd. for $C_{22}H_{25}NNaO_2$ 358.1778; found 358.1778.



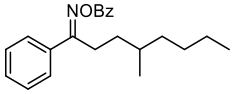
Scheme S1. Oxime ester substrates used in the reactions.

The Characterization Data for Oxime Esters



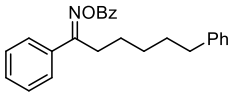
4-methyl-1-(4-(trifluoromethyl)phenyl)pentan-1-one O-benzoyl oxime (S9):

White solid (1.20 g, 66% yield over steps 3-4); R_f = 0.5 (Petroleum ether/Ethyl acetate = 10:1); Mp = 45 – 46 ℃; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.13 (d, *J* = 7.6 Hz, 2H), 7.91 (d, *J* = 8.1 Hz, 2H), 7.70 (d, *J* = 8.1 Hz, 2H), 7.63 (t, *J* = 7.4 Hz, 1H), 7.51 (t, *J* = 7.5 Hz, 2H), 3.01 – 2.96 (m, 2H), 1.75 – 1.67 (m, 1H), 1.57 – 1.52 (m, 2H), 0.98 (d, *J* = 6.6 Hz, 6H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 166.5, 163.7, 137.7, 133.5, 132.4 (q, $^2J_{C\text{-}F}$ = 32.8 Hz), 129.6, 128.7, 127.8, 125.7 (q, $^3J_{C\text{-}F}$ = 3.8 Hz), 124.74, 123.8 (q, $^1J_{C\text{-}F}$ = 272.6 Hz), 28.5, 26.8, 22.3; **^{19}F NMR** (565 MHz, $CDCl_3$) δ -62.90; **HRMS** (ESI) m/z: $[M + H]^+$ calcd. for $C_{20}H_{21}F_3NO_2$ 364.1519; found 364.1520.



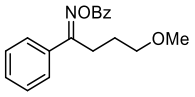
4-methyl-1-phenyloctan-1-one O-benzoyl oxime (S23):

White solid (1.18 g, 70% yield over steps 3-4); R_f = 0.5 (Petroleum ether/Ethyl acetate = 10:1); Mp = 35 – 36 ℃; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.13 (d, *J* = 7.5 Hz, 2H), 7.79 (d, *J* = 7.0 Hz, 2H), 7.62 (t, *J* = 7.4 Hz, 1H), 7.50 (t, *J* = 7.7 Hz, 2H), 7.47 – 7.41 (m, 3H), 3.01 – 2.91 (m, 2H), 1.70 – 1.63 (m, 1H), 1.57 – 1.45 (m, 2H), 1.39 – 1.32 (m, 1H), 1.32 – 1.23 (m, 4H), 1.21 – 1.18 (m, 1H), 0.97 (d, *J* = 6.5 Hz, 3H), 0.85 (t, *J* = 6.8 Hz, 3H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 167.9, 163.9, 134.2, 133.3, 130.6, 129.6, 128.7, 128.6, 127.4, 36.3, 33.8, 33.3, 29.2, 26.6, 22.9, 19.5, 14.1; **HRMS** (ESI) m/z: $[M + H]^+$ calcd. for $C_{22}H_{28}NO_2$ 338.2115; found 338.2115.



1,6-diphenylhexan-1-one O-benzoyl oxime (S26):

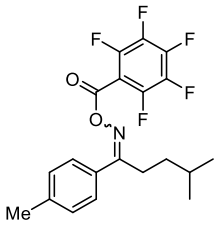
Colorless oil (1.45 g, 78% yield over steps 3-4); R_f = 0.4 (Petroleum ether/Ethyl acetate = 10:1); **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.10 (d, *J* = 7.7 Hz, 2H), 7.78 (d, *J* = 7.3 Hz, 2H), 7.61 (t, *J* = 7.4 Hz, 1H), 7.49 – 7.45 (m, 3H), 7.43 (t, *J* = 7.3 Hz, 2H), 7.25 – 7.22 (m, 2H), 7.16 (t, *J* = 7.2 Hz, 1H), 7.11 (d, *J* = 7.4 Hz, 2H), 2.97 (m, t, *J* = 7.8 Hz, 2H), 2.58 (t, *J* = 7.6 Hz, 2H), 1.73 – 1.63 (m, 4H), 1.51 – 1.44 (m, 2H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 167.5, 163.9, 142.3, 134.1, 133.3, 130.6, 129.6, 128.7, 128.6, 128.4, 128.3, 127.4, 125.7, 35.7, 31.1, 29.3, 28.6, 26.7; **HRMS** (ESI) m/z: $[M + H]^+$ calcd. for $C_{25}H_{26}NO_2$ 372.1958; found 372.1957.



4-methoxy-1-phenylbutan-1-one O-benzoyl oxime (S27):

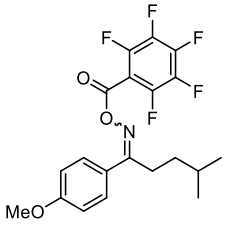
Yellow oil (1.07 g, 72% yield over steps 3-4); R_f = 0.33 (Petroleum ether/Ethyl acetate = 10:1); **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.16 (d, *J* = 7.3 Hz, 2H), 7.83 (d, *J* = 6.9 Hz, 2H), 7.61 (t, *J* = 7.4 Hz, 1H), 7.50 (t, *J* = 7.7 Hz, 2H), 7.47 – 7.40 (m, 3H), 3.43 (t, *J* = 5.9 Hz, 2H), 3.29 (s, 3H), 3.10 (t, *J* = 7.8 Hz, 2H), 1.98 – 1.91 (m, 2H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 167.10, 163.82, 133.99, 133.30, 130.65, 129.71, 129.22, 128.67, 128.60, 127.42, 77.27, 77.06, 76.85, 71.54, 58.62, 27.10,

25.40; **HRMS** (ESI) m/z: $[M + H]^+$ calcd. for $C_{18}H_{20}NO_3$ 298.1438; found 298.1439.



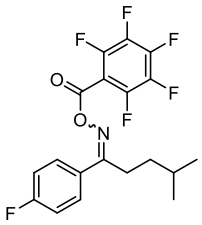
4-methyl-1-(p-tolyl)pentan-1-one O-perfluorobenzoyl oxime (**S98**)

White solid (1.28 g, 64% yield over steps 3-4); R_f = 0.67 (Petroleum ether/Ethyl acetate = 10:1); Mp = 62 – 63 ℃; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.64 (d, *J* = 7.5 Hz, 2H), 7.24 (d, *J* = 7.6 Hz, 2H), 2.90 – 2.81 (m, 2H), 2.40 (s, 3H), 1.67 – 1.60 (m, 1H), 1.48 – 1.42 (m, 2H), 0.91 (d, *J* = 6.2 Hz, 6H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 169.1, 156.7, 146.3 (m), 142.5 (m), 141.5, 137.0 (m), 130.3, 129.5, 127.3, 107.3 (m), 35.7, 28.4, 26.9, 22.1, 21.4; **^{19}F NMR** (565 MHz, $CDCl_3$) δ -137.2 (m, 2F), -147.8 (m, F), -159.9 (m, 2F); **HRMS** (ESI) m/z: $[M + H]^+$ calcd. for $C_{20}H_{19}F_5NO_2$ 400.1330; found 400.1330.



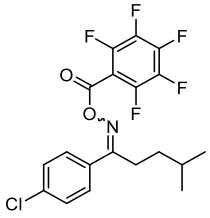
1-(4-methoxyphenyl)-4-methylpentan-1-one O-perfluorobenzoyl oxime (S99):

White solid (1.47 g, 71% yield over steps 3-4); R_f = 0.5 (Petroleum ether/Ethyl acetate = 10:1); Mp = 67 – 69 ℃; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.72 (d, *J* = 8.4 Hz, 2H), 6.95 (d, *J* = 8.4 Hz, 2H), 3.86 (s, 3H), 2.89 – 2.81 (m, 2H), 1.66 – 1.60 (m, 1H), 1.49 – 1.42 (m, 2H), 0.92 (d, *J* = 6.3 Hz, 6H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 168.5, 162.0, 156.7, 146.3 (m), 142.6 (m), 137.0 (m), 127.0, 125.3, 114.2, 107.3 (m), 55.4, 35.8, 28.5, 26.7, 22.1; **^{19}F NMR** (565 MHz, $CDCl_3$) δ -137.3 (m, 2F), -147.9 (m, 1F), -160.0 (m, 2F); **HRMS** (ESI) m/z: $[M + H]^+$ calcd. for $C_{20}H_{19}F_5NO_3$ 416.1280; found 416.1277.



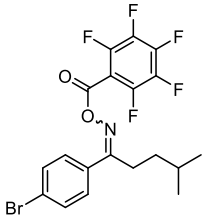
1-(4-fluorophenyl)-4-methylpentan-1-one O-perfluorobenzoyl oxime (S100):

White solid (1.67 g, 83% yield over steps 3-4); R_f = 0.67 (Petroleum ether/Ethyl acetate = 10:1); Mp = 41 – 42 ℃; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.80 – 7.72 (m, 2H), 7.17 – 7.10 (m, 2H), 2.90 – 2.82 (m, 2H), 1.68 – 1.60 (m, 1H), 1.49 – 1.42 (m, 2H), 0.92 (d, *J* = 6.6 Hz, 6H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 168.1, 164.5 (d, $^1J_{C\text{-}F}$ = 252.0 Hz), 156.5, 137.0 (m), 129.5 (d, $^3J_{C\text{-}F}$ = 8.7 Hz), 129.3, 116.0 (d, $^2J_{C\text{-}F}$ = 21.8 Hz), 107.0 (m), 35.5, 28.4, 27.0, 22.1; **^{19}F NMR** (565 MHz, $CDCl_3$) δ -108.8 (s, 1F), -137.1 (m, 2F), -147.4 (m, 1F), -159.8 (m, 2F); **HRMS** (ESI) m/z: $[M + H]^+$ calcd. for $C_{19}H_{16}F_6NO_2$ 404.1080; found 404.1079.



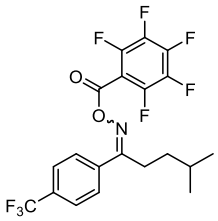
1-(4-chlorophenyl)-4-methylpentan-1-one O-perfluorobenzoyl oxime (S101):

White solid (1.57 g, 75% yield over steps 3-4); R_f = 0.67 (Petroleum ether/Ethyl acetate = 10:1); Mp = 50 – 51 ℃; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.70 (d, *J* = 8.3 Hz, 2H), 7.42 (d, *J* = 8.2 Hz, 2H), 2.90 – 2.81 (m, 2H), 1.67 – 1.60 (m, 1H), 1.48 – 1.41 (m, 2H), 0.92 (d, *J* = 6.5 Hz, 6H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 168.1, 156.5, 146.4 (m), 137.3, 131.7, 129.1, 128.7, 107.0 (m), 35.5, 28.4, 26.8, 22.1; **^{19}F NMR** (565 MHz, $CDCl_3$) δ -137.08 (m, 2F), -147.3 (m, 1F), -159.7 (m, 2F); **HRMS** (ESI) m/z: $[M + H]^+$ calcd. for $C_{19}H_{16}ClF_5NO_2$ 420.0784; found 420.0784.



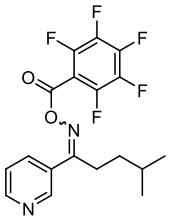
1-(4-bromophenyl)-4-methylpentan-1-one O-perfluorobenzoyl oxime (S102):

White solid (1.51 g, 65% yield over steps 3-4); R_f = 0.67 (Petroleum ether/Ethyl acetate = 10:1); Mp = 66 – 67 ℃; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.63 (d, *J* = 7.9 Hz, 2H), 7.58 (d, *J* = 7.5 Hz, 2H), 2.89 – 2.81 (m, 2H), 1.68 – 1.60 (m, 1H), 1.48 – 1.40 (m, 2H), 0.92 (d, *J* = 6.3 Hz, 6H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 168.2, 156.5, 146.4 (m), 142.7 (m), 137.0 (m), 132.1, 132.1, 128.9, 125.7, 107.0 (m), 35.5, 28.4, 26.8, 22.1; **^{19}F NMR** (565 MHz, $CDCl_3$) δ -137.1 (m,2F), -147.3 (m,1F), -159.7 (m,2F); **HRMS** (ESI) m/z: $[M + H]^+$ calcd. for $C_{19}H_{16}BrF_5NO_2$ 464.0279; found 464.0278.



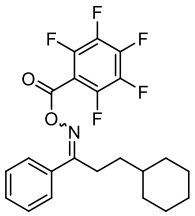
4-methyl-1-(4-(trifluoromethyl)phenyl)pentan-1-one O-perfluorobenzoyl oxime (S104):

White solid (1.63 g, 72% yield over steps 3-4); R_f = 0.67 (Petroleum ether/Ethyl acetate = 10:1); Mp = 50 – 51 ℃; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.87 (d, *J* = 7.6 Hz, 2H), 7.71 (d, *J* = 7.6 Hz, 2H), 2.94 – 2.86 (m, 2H), 1.68 – 1.60 (m, 1H), 1.49 – 1.42 (m, 2H), 0.93 (d, *J* = 6.1 Hz, 6H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 168.0, 156.4, 146.5 (m), 136.8, 132.8 (q, $^2J_{C\text{-}F}$ = 32.8 Hz), 127.8, 125.8 (q, $^3J_{C\text{-}F}$ = 3.8 Hz), 123.7 (q, $^1J_{C\text{-}F}$ = 272.7 Hz), 35.4, 28.4, 27.0, 22.1; **^{19}F NMR** (565 MHz, $CDCl_3$) δ -63.00 (s, 3F), -136.97 (m, 2F), -147.05 (m, 1F), -159.6 (m, 2F); **HRMS** (ESI) m/z: $[M + Na]^+$ calcd. for $C_{20}H_{15}F_8NNaO_2$ 476.0867; found 476.0867.



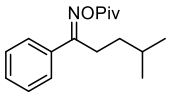
4-methyl-1-(pyridin-3-yl)pentan-1-one O-perfluorobenzoyl oxime (S105):

White solid (1.14 g, 59% yield over steps 3-4); R_f = 0.3 (Petroleum ether/Ethyl acetate = 10:1); Mp = 38 – 39 ℃; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.96 (s, 1H), 8.74 (d, *J* = 4.1 Hz, 1H), 8.14 (d, *J* = 7.0 Hz, 1H), 7.46 – 7.37 (m, 1H), 2.96 – 2.86 (m, 2H), 1.70 – 1.60 (m, 1H), 1.53 – 1.41 (m, 2H), 0.93 (d, *J* = 6.3 Hz, 6H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 166.9, 156.4, 151.6, 148.1, 146.5 (m), 142.8 (m), 137.0 (m), 135.2, 129.5, 123.8, 106.7 (m), 35.3, 28.4, 26.8, 22.1; **^{19}F NMR** (565 MHz, $CDCl_3$) δ -137.0 (m, 2F), -147.0 (m, 1F), -159.6 (m, 2F); **HRMS** (ESI) m/z: $[M + H]^+$ calcd. for $C_{18}H_{16}F_5N_2O_2$ 387.1126; found 387.1125.



3-cyclohexyl-1-phenylpropan-1-one O-perfluorobenzoyl oxime (S106):

White solid (1.66 g, 78% yield over steps 3-4); R_f = 0.67 (Petroleum ether/Ethyl acetate = 10:1); Mp = 93 – 95 ℃; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.74 (d, *J* = 7.4 Hz, 2H), 7.51 – 7.46 (m, 1H), 7.44 (t, *J* = 7.1 Hz, 2H), 2.92 – 2.84 (m, 2H), 1.75 – 1.60 (m, 5H), 1.50 – 1.40 (m, 2H), 1.35 – 1.25 (s, 1H), 1.25 – 1.07 (m, 3H), 0.95 – 0.85 (m, 2H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 169.3, 156.7, 146.3 (m), 142.6 (m), 137.0 (m), 133.3, 131.0, 128.8, 127.4, 107.3 (m), 38.0, 34.1, 32.9, 26.6, 26.5, 26.2; **^{19}F NMR** (565 MHz, $CDCl_3$) δ -137.15 (m, 2F), -147.72 (m, 1F), -159.87 (m, 2F); **HRMS** (ESI) m/z: $[M + H]^+$ calcd. for $C_{22}H_{21}F_5NO_2$ 426.1487; found 426.1485.

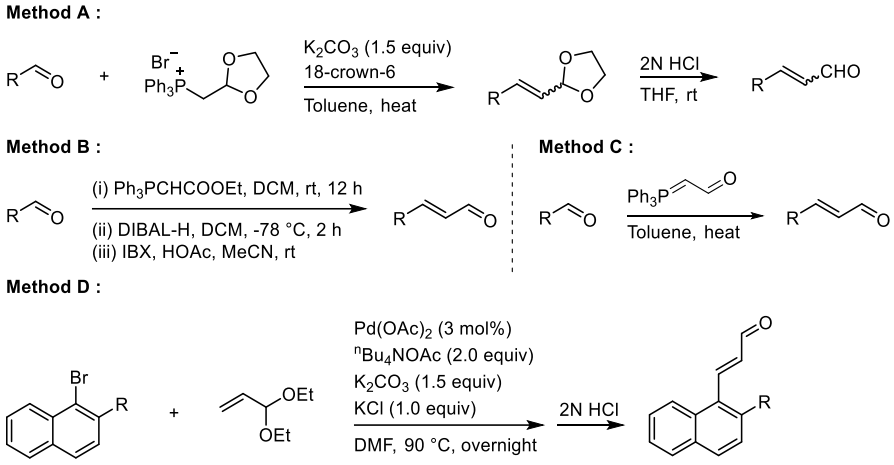


4-methyl-1-phenylpentan-1-one O-pivaloyl oxime (S121):

White solid (1.10 g, 80% yield over steps 3-4); R_f = 0.7 (Petroleum ether/Ethyl acetate = 10:1); Mp = 48 – 49 ℃; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.73 (d, *J* = 7.5 Hz, 2H), 7.45 – 7.39 (m, 3H), 2.85 – 2.80 (m, 2H), 1.70 – 1.62 (m, 1H), 1.50 – 1.44 (m, 2H), 1.34 (s, 9H), 0.95 (d, *J* = 6.6 Hz, 6H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 175.1, 167.2, 134.3, 130.4, 128.6, 127.3, 38.8, 35.6, 28.6, 27.3, 26.7, 22.3; **HRMS** (ESI) m/z: $[M + H]^+$ calcd. for $C_{17}H_{26}NO_2$ 276.1958; found 276.1960.

General Procedures for the Synthesis of Enals

All enals were synthesized according to general procedures (Methods A, B, C, D) reported in the literature[11-18] with sight modifications. The characterization data of newly synthesized substrates were summarization below. ^{1}H, ^{13}C NMR and ^{19}F NMR spectra data for the rest of known ones were in agreement with the literature data. Some substrates of them were synthesized according to additional procedures given in the Supporting Information.



Method A

According to the procedures reported in the literature[11], a 100 mL round bottom flask was charged with carbonyl compound (5 mmol, 1.0 equiv), 18-crown-6 (2 mol%), (1,3-dioxolan-2-ylmethyl)triphenylphosphnium bromide (7.5 mmol, 1.5 equiv), K_2CO_3 (7.5 mmol, 1.5 equiv), and toluene (20 mL). Then the reaction mixture was heated at 100 ºC with stirring for 18 h. After cooling to room temperature, the solvent was evaporated in vacuo. The reaction mixture was then diluted with deionized water, followed by extraction with ethyl acetate (2 × 20 mL). The combined organic phases were dried over Na_2SO_4, then concentrated in vacuo to give the crude acetal product, which was used in the next step without any further purification. The crude acetal was added to tetrahydrofuran (20 mL), followed by 2N HCl. The reaction was stirred at room temperature for 6 h. Then, the solvent was evaporated in vacuo. The reaction mixture was diluted with deionized water, followed by extraction with ethyl acetate (2 × 20 mL). The combined organic phases were dried over Na_2SO_4, and concentrated in vacuo. The residue was then purified by flash chromatography on silica gel to give the desired cinnamaldehyde product.

Method B

According to the procedures reported in the literature[12,13] with slight modification, to a stirred solution of the appropriate aldehyde (5 mmol, 1.0 equiv) in DCM (0.5 M) was added ethyl (triphenylphosphoranylidene)acetate (5.5 mmol, 1.1 equiv) by portions. The resulting solution was stirred at room temperature for 12 hours. The volatiles were removed under vacuum and a mixture of petroleum ether/Et_2O (4/1, 25 mL) was added to the solid obtained. The white solid (Ph_3PO) was filtered off and washed thoroughly with petroleum ether/Et_2O (1/1). The solvents were removed under vacuum and the crude residue was washed on a short pad of SiO_2 eluting with petroleum ether/Et_2O (4/1). The α,β-unsaturated ester was used in the next step without further

purification.

The α,β-unsaturated ester (~ 5 mmol) was dissolved in DCM (0.5 M) and the resulting solution was cooled down to −78 ℃. DIBAL-H solution (1.0 M in hexanes, 11 mmol, 2.2 equiv) was added dropwise over 15 min. The reaction was stirred at the same temperature for 2 h at which point water (5 mL) was added. The solution was allowed to warm up to room temperature then a NaOH solution (10% in water, 20 mL) was added followed by water (10 mL). The suspension was stirred vigorously for 1 h, diluted with water. Then the aqueous layers were extracted with DCM. The combined organic layers were washed with brine, dried over Na_2SO_4, filtered, and concentrated to give the crude allylic alcohol which was used in the next step without further purification.

A suspension of the allylic alcohol (1 equiv), IBX (1.2 equiv), and acetic acid (1.2 equiv) in acetonitrile (20 mL) was stirred vigorously at room temperature. The reaction progress was monitored by a TLC plate. After completion of the reaction, excess sodium bicarbonate was added to the mixture. The resulting mixture was passed through a short path of silica gel using ethyl acetate as the eluent. After the removal of the solvent, the residue was purified by flash chromatography on silica gel to afford the desired enal.

Method C

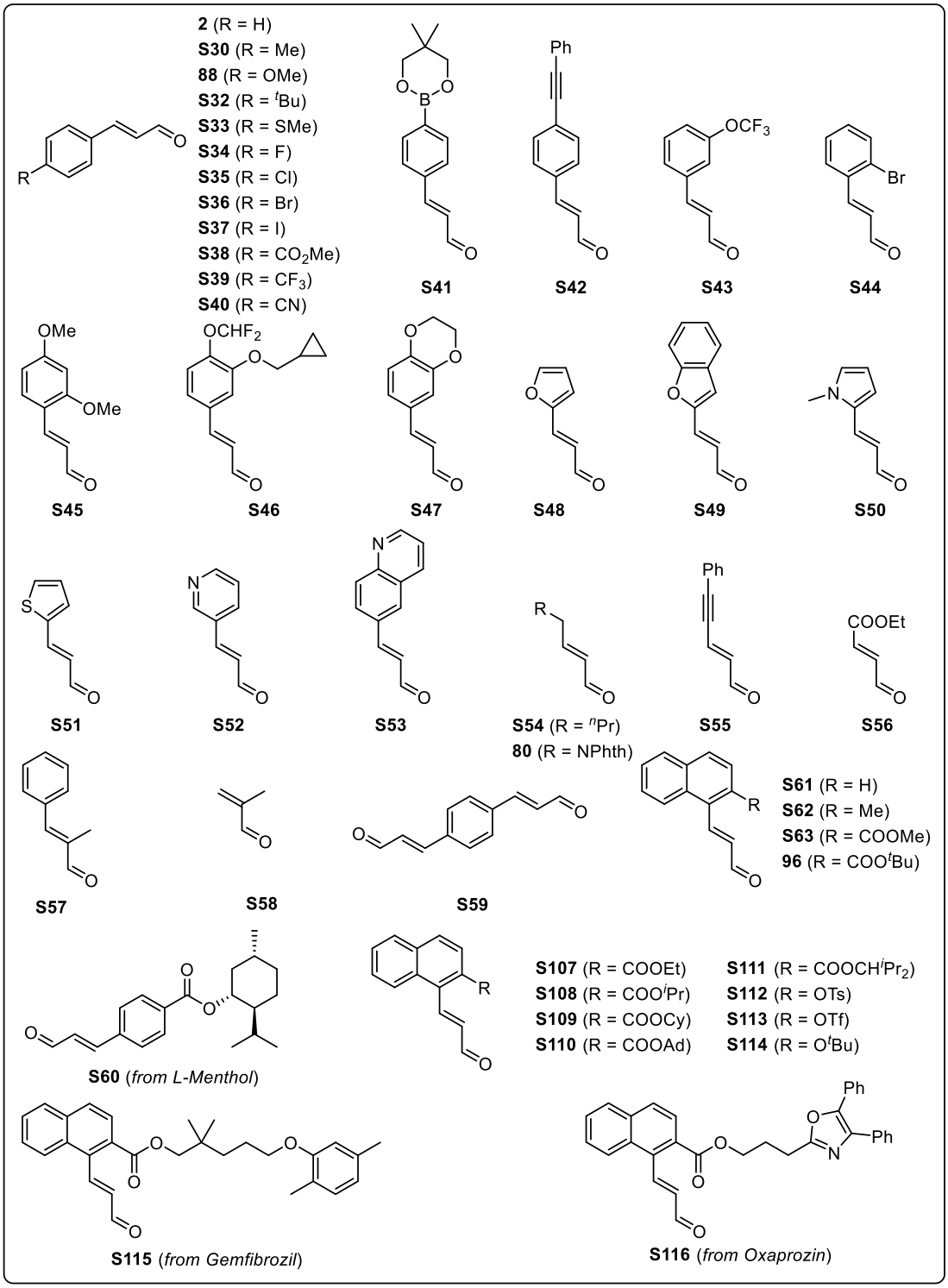
According to the procedures reported in the literature[14], to a suspension of aldehyde (5 mmol, 1.0 equiv) in toluene (20.0 mL) was added 2- (triphenylphosphoranylidene)acetaldehyde (5.5 mmol, 1.1 equiv), the reaction mixture was heated to 120 ℃ (oil bath) and stirred for 4 h. Then the mixture was concentrated directly in vacuum and the residue was purified by silica gel chromatography to give the desired enal.

Method D

According to the procedures reported in the literature[15], to a stirred solution of aryl bromide (5 mmol, 1 equiv) in 20 mL of DMF were added acrolein diethyl acetal (2.29 mL, 15 mmol), $^{n}Bu_4NOAc$ (3.02 g, 10 mmol), K_2CO_3 (1.04 g, 7.5 mmol), KCl (0.37 g, 5 mmol), and $Pd(OAc)_2$ (0.03 g, 0.15 mmol). The mixture was stirred for 6 h at 90 ℃. After cooling, 2N HCl was slowly added and the reaction mixture was stirred at room temperature for 20 min. Then, it was diluted with ethyl acetate and washed with water. The organic layer was dried over Na_2SO_4 and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel to afford the desired cinnamaldehyde.

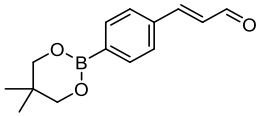
Enals

Substrates (**2**, **88**, **S30, S34, S36, S39, S48, S54, S56-58)** were purchased from commercial sources and used as received. Substrates (**S32, S33, S35, S37, S38, S40-47, S49-53, S59-62, S112)** were prepared according to Method A. Substrate **S113** was prepared according to Method B. Substrates **(80, S55)** were prepared according to Method C. Substrates **(96, S63, S107-111, S114-116)** were prepared according to Method D.



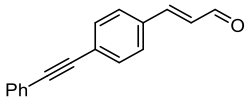
Scheme S2. Enal substrates used in the reactions.

The Characterization Data for Enals



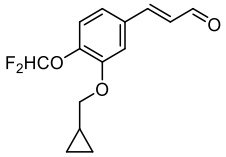
(*E*)-3-(4-(5,5-dimethyl-1,3,2-dioxaborinan-2-yl)phenyl)acrylaldehyde (S41):

White solid (0.55 g, 45% yield); R_f = 0.3 (Petroleum ether/Ethyl acetate = 10:1); Mp = 93 – 95 ℃; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 9.64 (d, *J* = 7.7 Hz, 1H), 7.78 (d, *J* = 7.7 Hz, 2H), 7.47 (d, *J* = 7.7 Hz, 2H), 7.41 (d, *J* = 15.9 Hz, 1H), 6.68 (dd, *J* = 15.9, 7.7 Hz, 1H), 3.71 (s, 4H), 0.96 (s, 6H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 192.7, 151.8, 134.8, 133.5, 127.9, 126.5, 71.4, 30.9, 20.9; **HRMS** (ESI) m/z: $[M + Na]^+$ calcd. for $C_{14}H_{17}BNaO_3$ 267.1163; found 267.1167.



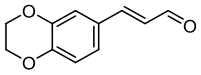
(*E*)-3-(4-(phenylethynyl)phenyl)acrylaldehyde (S42):

White solid (0.72 g, 62% yield); R_f = 0.5 (Petroleum ether/Ethyl acetate = 10:1); Mp = 131 – 133 ℃; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 9.72 (d, *J* = 7.6 Hz, 1H), 7.58 (d, *J* = 8.0 Hz, 2H), 7.57 – 7.53 (m, 4H), 7.46 (d, *J* = 16.0 Hz, 1H), 7.39 – 7.34 (m, 3H), 6.73 (dd, *J* = 15.9, 7.6 Hz, 1H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 193.4, 151.6, 133.7, 132.2, 131.7, 129.0, 128.8, 128.5, 128.4, 126.3, 122.8, 92.3, 88.9; **HRMS** (ESI) m/z: $[M + H]^+$ calcd. for $C_{17}H_{13}O$ 233.0961; found 233.0962.



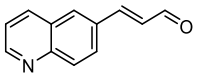
(*E*)-3-(3-(cyclopropylmethoxy)-4-(difluoromethoxy)phenyl)acrylaldehyde (S46):

White solid (0.54 g, 40% yield); R_f = 0.3 (Petroleum ether/Ethyl acetate = 10:1); Mp = 60 – 61 ℃; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 9.69 (d, *J* = 7.5 Hz, 1H), 7.41 (d, *J* = 15.9 Hz, 1H), 7.21 (d, *J* = 8.0 Hz, 1H), 7.14 (d, *J* = 9.7 Hz, 2H), 6.69 (t, *J* = 75.0 Hz, 1H), 6.65 (dd, *J* = 15.9, 7.6 Hz, 1H), 3.92 (d, *J* = 6.9 Hz, 2H), 1.35 – 1.26 (m, 1H), 0.71 – 0.64 (m, 2H), 0.41 – 0.35 (m, 2H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 193.28, 151.4, 150.8, 142.7, 132.5, 128.8, 122.8, 122.2, 115.8 (t, $^1J_{C\text{-}F}$ = 261.1 Hz), 113.4, 74.1, 10.1, 3.3; **^{19}F NMR** (565 MHz, $CDCl_3$) δ -81.84; **HRMS** (ESI) m/z: $[M + H]^+$ calcd. for $C_{14}H_{15}F_2O_3$ 269.0984; found 269.0985.



(*E*)-3-(2,3-dihydrobenzo[*b*][1,4]dioxin-6-yl)acrylaldehyde (S47):

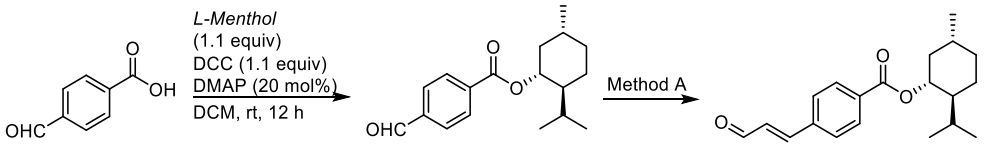
White solid (0.74 g, 78% yield); R_f = 0.3 (Petroleum ether/Ethyl acetate = 10:1); Mp = 80 – 82 ℃; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 9.64 (d, *J* = 7.7 Hz, 1H), 7.35 (d, *J* = 15.8 Hz, 1H), 7.10 (s, 1H), 7.09 – 7.06 (m, 1H), 6.91 (d, *J* = 8.3 Hz, 1H), 6.58 (dd, *J* = 15.8, 7.7 Hz, 1H), 4.33 – 4.31 (m, 2H), 4.30 – 4.27 (m, 2H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 193.6, 152.6, 146.6, 143.9, 127.7, 127.1, 122.7, 118.0, 117.2, 64.6, 64.2; **HRMS** (ESI) m/z: $[M + H]^+$ calcd. for $C_{11}H_{11}O_3$ 191.0703; found 191.0701.



(*E*)-3-(quinolin-6-yl)acrylaldehyde (S53):

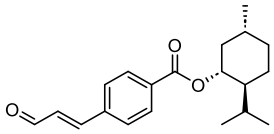
White solid (0.48 g, 52% yield); R_f = 0.1 (Petroleum ether/Ethyl acetate = 5:1); Mp = 159 –

160 °C; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 9.80 – 9.76 (m, 1H), 8.98 – 8.94 (m, 1H), 8.21 (d, *J* = 7.8 Hz, 1H), 8.15 (d, *J* = 7.2 Hz, 1H), 7.99 (s, 1H), 7.93 (d, *J* = 8.4 Hz, 1H), 7.65 (d, *J* = 15.9 Hz, 1H), 7.49 – 7.44 (m, 1H), 6.88 – 6.81 (m, 1H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 193.4, 151.9, 151.4, 149.4, 136.6, 132.3, 130.6, 129.9, 129.6, 128.2, 127.4, 122.1; **HRMS** (ESI) m/z: $[M + H]^+$ calcd. for $C_{12}H_{10}NO$ 184.0757; found 184.0756.

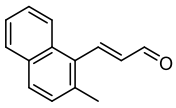


S60

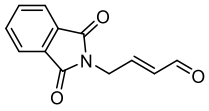
According to the procedure reported in the literature[16], A 50 mL round bottom flask was fitted with a stirring bar, 4-formylbenzoic acid (5 mmol, 1.0 equiv), DCC (5.5 mmol, 1.1 equiv), and DMAP (20 mol%) was added. Then DCM (20 mL) and *L*-Menthol (5.5 mmol, 1.1 equiv) were added sequentially. The reaction mixture was stirred at room temperature for 12 h. The reaction was filtered through a Celite pad and concentrated in vacuo. The crude residue was purified by flash silica gel chromatography (Petroleum ether/Ethyl acetate 30:1 to 10:1) to afford the desired ester product. The final ester substituted cinnamaldehyde was prepared according to Method A in General procedures for the Synthesis of Enals.



(1R,2S,5R)-2-isopropyl-5-methylcyclohexyl 4-((*E*)-3-oxoprop-1-en-1-yl)benzoate (S60):
Colorless oil (1.12 g, 71% yield); R_f = 0.35 (Petroleum ether/Ethyl acetate = 10:1); **^{1}H NMR** (600 MHz, $CDCl_3$) δ 9.75 (d, *J* = 7.6 Hz, 1H), 8.10 (d, *J* = 8.3 Hz, 2H), 7.63 (d, *J* = 8.3 Hz, 2H), 7.51 (d, *J* = 16.0 Hz, 1H), 6.78 (dd, *J* = 16.0, 7.6 Hz, 1H), 4.95 (td, *J* = 10.9, 4.4 Hz, 1H), 2.17 – 2.10 (m, 1H), 1.99 – 1.91 (m, 1H), 1.77 – 1.71 (m, 2H), 1.60 – 1.53 (m, 2H), 1.19 – 1.08 (m, 2H), 0.93 (t, *J* = 7.0 Hz, 7H), 0.80 (d, *J* = 6.9 Hz, 3H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 193.3, 165.3, 151.0, 137.9, 133.0, 130.3, 130.2, 128.3, 75.4, 47.3, 41.0, 34.3, 31.5, 26.6, 23.7, 22.0, 20.8, 16.6; **HRMS** (ESI) m/z: $[M + H]^+$ calcd. for $C_{20}H_{27}O_3$ 315.1955; found 315.1961.



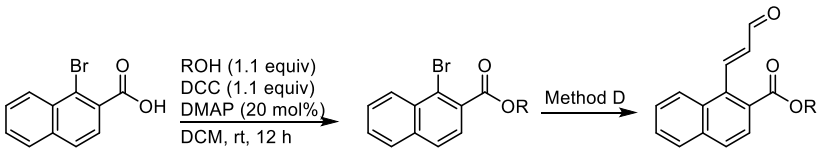
(*E*)-3-(2-methylnaphthalen-1-yl)acrylaldehyde (S62):
White solid (0.64 g, 65% yield); R_f = 0.55 (Petroleum ether/Ethyl acetate = 10:1); Mp = 87 – 88 °C; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 9.88 (d, *J* = 7.8 Hz, 1H), 8.06 – 7.99 (m, 2H), 7.84 (d, *J* = 8.0 Hz, 1H), 7.79 (d, *J* = 8.4 Hz, 1H), 7.52 (t, *J* = 7.4 Hz, 1H), 7.48 (t, *J* = 7.3 Hz, 1H), 7.38 (d, *J* = 8.4 Hz, 1H), 6.57 (dd, *J* = 16.3, 7.8 Hz, 1H), 2.54 (s, 3H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 193.8, 150.6, 136.0, 134.6, 132.2, 131.1, 130.0, 129.6, 129.0, 128.6, 127.0, 125.5, 124.2, 21.2; **HRMS** (ESI) m/z: $[M + H]^+$ calcd. for $C_{14}H_{13}O$ 197.0961; found 197.0962.



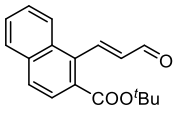
(*E*)-4-(1,3-dioxoisoindolin-2-yl)but-2-enal (80):

White solid (0.43 g, 40% yield, E/Z = 7/1); R_f = 0.2 (Petroleum ether/Ethyl acetate = 4:1); Mp = 117 – 118 ℃; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 9.57 (d, *J* = 7.6 Hz, 1H), 7.91 – 7.87 (m, 2H), 7.78 – 7.75 (m, 2H), 6.82 (dt, *J* = 15.8, 5.0 Hz, 1H), 6.15 (dd, *J* = 15.8, 7.6 Hz, 1H), 4.59 – 4.53 (m, 2H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 192.5, 167.5, 149.0, 134.4, 133.2, 131.9, 123.7, 38.4; **HRMS** (ESI) m/z: $[M + H]^+$ calcd. for $C_{12}H_{10}NO_3$ 216.0655; found 216.0658.

General procedures for the Synthesis of ester-substituted enals

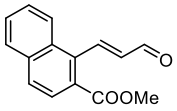


According to the procedure reported in the literature[16], A 50 mL round bottom flask was fitted with a stirring bar, naphthoic acid (5 mmol, 1.0 equiv), DCC (5.5 mmol, 1.1 equiv), and DMAP (20 mol%) were added. Then DCM (20 mL) and alcohol (5.5 mmol, 1.1 equiv) were added sequentially. The reaction mixture was stirred at room temperature for 12 h. The reaction was filtered through a Celite pad and concentrated in vacuo. The crude residue was purified by flash silica gel chromatography (Petroleum ether/Ethyl acetate 40:1 to 5:1) to afford the desired ester product. The final ester substituted cinnamaldehyde was prepared according to Method D in General Procedures for the Synthesis of Enals.



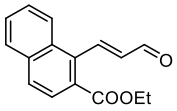
tert-butyl (E)-1-(3-oxoprop-1-en-1-yl)-2-naphthoate (96):

White solid (0.44 g, 31% yield); R_f = 0.5 (Petroleum ether/Ethyl acetate = 10:1); Mp = 72 – 74 ℃; **^{1}H NMR** (600 MHz, CDCl3) δ 9.93 (d, J = 7.8 Hz, 1H), 8.35 (d, J = 16.3 Hz, 1H), 8.10 (d, J = 8.4 Hz, 1H), 7.95 (d, J = 8.6 Hz, 1H), 7.92 – 7.87 (m, 2H), 7.60 (t, J = 7.0 Hz, 1H), 7.56 (dd, J = 11.2, 3.9 Hz, 1H), 6.39 (dd, J = 16.3, 7.8 Hz, 1H), 1.61 (s, 9H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 193.5, 166.4, 152.0, 135.2, 135.0, 134.7, 130.4, 129.2, 128.5, 128.4, 127.9, 127.3, 126.3, 125.8, 82.4, 28.3; **HRMS** (ESI) m/z: $[M + H]^+$ calcd. for $C_{18}H_{19}O_3$ 283.1329; found 283.1329.



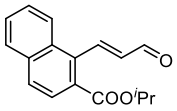
methyl (*E*)-1-(3-oxoprop-1-en-1-yl)-2-naphthoate (S63):

White solid (0.46 g, 38% yield); R_f = 0.5 (Petroleum ether/Ethyl acetate = 10:1); Mp = 92 – 93 ℃; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 9.94 (d, *J* = 7.8 Hz, 1H), 8.38 (d, *J* = 16.3 Hz, 1H), 8.13 (d, *J* = 8.5 Hz, 1H), 8.02 (d, *J* = 8.7 Hz, 1H), 7.91 (d, *J* = 8.7 Hz, 2H), 7.63 (t, *J* = 7.4 Hz, 1H), 7.57 (t, *J* = 7.6 Hz, 1H), 6.38 (dd, *J* = 16.3, 7.8 Hz, 1H), 3.95 (s, 3H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 193.5, 167.4, 151.7, 136.0, 135.5, 135.3, 130.4, 129.3, 128.5, 128.3, 127.5, 126.5, 126.2 125.6, 52.5; **HRMS** (ESI) m/z: $[M + H]^+$ calcd. for $C_{15}H_{13}O_3$ 241.0859; found 241.0860.



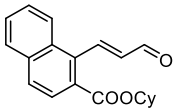
ethyl (*E*)-1-(3-oxoprop-1-en-1-yl)-2-naphthoate (S107):

White solid (0.46 g, 36% yield); R_f = 0.5 (Petroleum ether/Ethyl acetate = 10:1); Mp = 83 – 84 ℃; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 9.93 (d, *J* = 7.8 Hz, 1H), 8.38 (d, *J* = 16.2 Hz, 1H), 8.13 (d, *J* = 8.4 Hz, 1H), 8.03 (d, *J* = 8.5 Hz, 1H), 7.91 (d, *J* = 8.4 Hz, 2H), 7.62 (t, *J* = 7.3 Hz, 1H), 7.57 (t, *J* = 7.5 Hz, 1H), 6.38 (dd, *J* = 16.2, 7.8 Hz, 1H), 4.45 – 4.37 (m, 2H), 1.42 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 193.5, 167.0, 151.8, 135.7, 135.4, 135.3, 130.3, 129.2, 128.5, 128.2, 127.4, 126.6, 126.5, 125.7, 61.6, 14.3; **HRMS** (ESI) m/z: $[M + H]^+$ calcd. for $C_{16}H_{15}O_3$ 255.1016; found 255.1015.



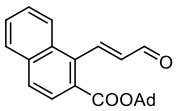
isopropyl (*E*)-1-(3-oxoprop-1-en-1-yl)-2-naphthoate (S108):

White solid (0.41 g, 30% yield); R_f = 0.5 (Petroleum ether/Ethyl acetate = 10:1); Mp = 63 – 64 ℃; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 9.93 (d, *J* = 7.8 Hz, 1H), 8.37 (d, *J* = 16.3 Hz, 1H), 8.12 (d, *J* = 8.4 Hz, 1H), 8.00 (d, *J* = 8.6 Hz, 1H), 7.91 (d, *J* = 8.4 Hz, 2H), 7.64 – 7.58 (m, 1H), 7.58 – 7.53 (m, 1H), 6.39 (dd, *J* = 16.3, 7.8 Hz, 1H), 5.31 – 5.24 (m, 1H), 1.39 (d, *J* = 6.3 Hz, 6H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 193.5, 166.6, 151.8, 135.4, 135.3, 135.2, 130.3, 129.2, 128.4, 128.1, 127.4, 127.1, 126.4, 125.7, 69.3, 22.0; **HRMS** (ESI) m/z: $[M + H]^+$ calcd. for $C_{17}H_{17}O_3$ 269.1172; found 269.1173.



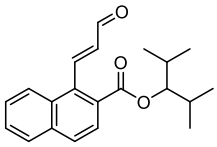
cyclohexyl (*E*)-1-(3-oxoprop-1-en-1-yl)-2-naphthoate (S109):

White solid (0.54 g, 35% yield); R_f = 0.5 (Petroleum ether/Ethyl acetate = 10:1); Mp = 68 – 70 ℃; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 9.93 (d, *J* = 7.8 Hz, 1H), 8.38 (d, *J* = 16.3 Hz, 1H), 8.13 (d, *J* = 8.4 Hz, 1H), 8.02 (d, *J* = 8.6 Hz, 1H), 7.91 (d, *J* = 8.3 Hz, 2H), 7.62 (t, *J* = 7.3 Hz, 1H), 7.59 – 7.53 (m, 1H), 6.39 (dd, *J* = 16.2, 7.8 Hz, 1H), 5.09 – 5.01 (m, 1H), 2.05 – 1.95 (m, 2H), 1.85 – 1.75 (m, 2H), 1.63 – 1.57 (m, 3H), 1.51 – 1.38 (m, 2H), 1.39 – 1.30 (m, 1H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 193.5, 166.5, 151.9, 135.4, 135.3, 135.2, 130.4, 129.2, 128.4, 128.1, 127.4, 127.2, 126.4, 125.7, 74.2, 31.7, 25.4, 23.8; **HRMS** (ESI) m/z: $[M + H]^+$ calcd. for $C_{20}H_{21}O_3$ 309.1485; found 309.1484.



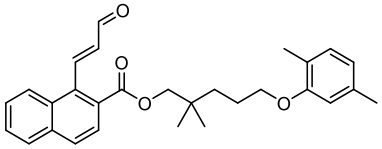
(*3r*)-adamantan-1-yl 1-((*E*)-3-oxoprop-1-en-1-yl)-2-naphthoate (S110):

White solid (0.40 g, 22% yield); R_f = 0.5 (Petroleum ether/Ethyl acetate = 10:1); Mp = 119 – 120 ℃; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 9.93 (d, *J* = 7.8 Hz, 1H), 8.34 (d, *J* = 16.3 Hz, 1H), 8.10 (d, *J* = 8.4 Hz, 1H), 7.95 (d, *J* = 8.6 Hz, 1H), 7.92 – 7.87 (m, 2H), 7.60 (t, *J* = 7.4 Hz, 1H), 7.55 (t, *J* = 7.6 Hz, 1H), 6.39 (dd, *J* = 16.3, 7.8 Hz, 1H), 2.30 – 2.25 (m, 6H), 2.25 – 2.21 (m, 3H), 1.76 – 1.68 (m, 6H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 193.6, 166.1, 152.1, 135.1, 135.0, 134.6, 130.4, 129.1, 128.6, 128.4, 127.9, 127.3, 126.3, 125.9, 82.7, 41.6, 36.2, 31.0; **HRMS** (ESI) m/z: $[M + H]^+$ calcd. for $C_{24}H_{25}O_3$ 361.1798; found 361.1796.



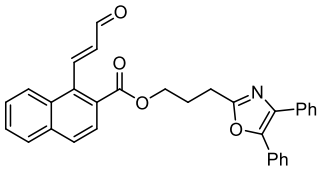
2,4-dimethylpentan-3-yl (*E*)-1-(3-oxoprop-1-en-1-yl)-2-naphthoate (S111):

White solid (0.44 g, 27% yield); R_f = 0.5 (Petroleum ether/Ethyl acetate = 10:1); Mp = 70 – 72 ℃; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 9.93 (d, *J* = 7.9 Hz, 1H), 8.39 (d, *J* = 16.3 Hz, 1H), 8.14 (d, *J* = 8.5 Hz, 1H), 8.07 (d, *J* = 8.7 Hz, 1H), 7.95 – 7.90 (m, 2H), 7.62 (t, *J* = 7.1 Hz, 1H), 7.57 (t, *J* = 7.2 Hz, 1H), 6.39 (dd, *J* = 16.3, 7.9 Hz, 1H), 4.90 (t, *J* = 6.1 Hz, 1H), 2.10 – 2.01 (m, 2H), 0.97 (dd, *J* = 6.7, 1.5 Hz, 12H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 193.6, 166.9, 152.1, 135.9, 135.3, 135.3, 130.4, 129.2, 128.4, 128.2, 127.4, 126.6, 125.6, 84.4, 29.6, 19.7, 17.5; **HRMS** (ESI) m/z: $[M + Na]^+$ calcd. for $C_{21}H_{24}NaO_3$ 347.1618; found 347.1619.



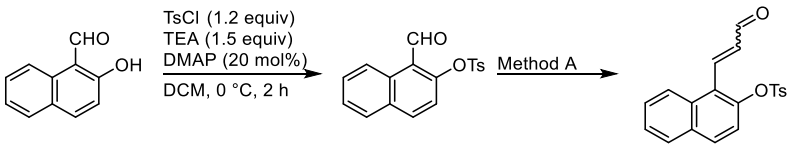
5-(2,5-dimethylphenoxy)-2,2-dimethylpentyl (*E*)-1-(3-oxoprop-1-en-1-yl)-2-naphthoate (S115)

Yellow oil (0.77 g, 35% yield); R_f = 0.45 (Petroleum ether/Ethyl acetate = 10:1); **^{1}H NMR** (600 MHz, $CDCl_3$) δ 9.92 (d, *J* = 7.6 Hz, 1H), 8.38 (d, *J* = 16.2 Hz, 1H), 8.13 (d, *J* = 8.2 Hz, 1H), 8.03 (d, *J* = 8.3 Hz, 1H), 7.95 – 7.85 (m, 2H), 7.66 – 7.59 (m, 1H), 7.59 – 7.52 (m, 1H), 6.97 (d, *J* = 6.9 Hz, 1H), 6.63 (d, *J* = 7.0 Hz, 1H), 6.61 (s, 1H), 6.38 (dd, *J* = 16.1, 7.7 Hz, 1H), 4.12 (s, 2H), 3.98 – 3.90 (m, 2H), 2.29 (s, 3H), 2.13 (s, 3H), 1.88 – 1.76 (m, 2H), 1.61 – 1.53 (m, 2H), 1.07 (s, 6H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 193.5, 167.0, 157.0, 151.7, 136.5, 136.0, 135.5, 135.3, 130.4, 130.3, 129.3, 128.5, 128.3, 127.5, 126.5, 126.5, 125.5, 123.5, 120.8, 112.0, 73.5, 68.2, 35.7, 33.9, 24.5, 24.2, 21.4, 15.8; **HRMS** (ESI) m/z: $[M + H]^+$ calcd. for $C_{29}H_{33}O_4$ 445.2373; found 445.2372.



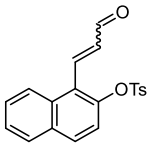
3-(4,5-diphenyloxazol-2-yl)propyl (*E*)-1-(3-oxoprop-1-en-1-yl)-2-naphthoate (S116):

Yellow oil (0.56 g, 23% yield); R_f = 0.2 (Petroleum ether/Ethyl acetate = 5:1); **^{1}H NMR** (600 MHz, $CDCl_3$) δ 9.91 (d, *J* = 7.7 Hz, 1H), 8.32 (d, *J* = 16.3 Hz, 1H), 8.07 (d, *J* = 8.3 Hz, 1H), 7.98 (d, *J* = 8.6 Hz, 1H), 7.84 (d, *J* = 7.8 Hz, 1H), 7.79 (d, *J* = 8.5 Hz, 1H), 7.62 – 7.55 (m, 3H), 7.54 – 7.46 (m, 3H), 7.35 – 7.26 (m, 6H), 6.32 (dd, *J* = 16.2, 7.8 Hz, 1H), 4.51 (t, *J* = 5.7 Hz, 2H), 3.05 (t, *J* = 7.0 Hz, 2H), 2.44 – 2.32 (m, 2H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 193.5, 166.7, 162.4, 151.7, 145.4, 136.2, 135.4, 135.2, 132.4, 130.3, 129.2, 128.9, 128.6, 128.5, 128.4, 128.3, 128.1, 127.9, 127.4, 126.5, 126.4, 126.0, 125.6, 64.7, 26.2, 25.3; **HRMS** (ESI) m/z: $[M + H]^+$ calcd. for $C_{32}H_{26}NO_4$ 488.1856; found 488.1857.



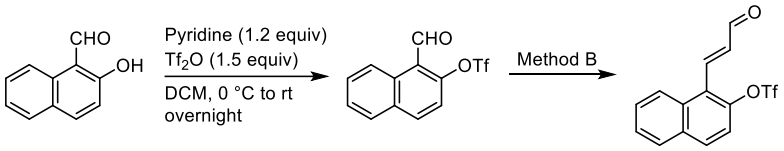
Prepared according to literature[17]. To round bottom flask equipped with a stirring bar, 2-hydroxy-1-naphthaldehyde (5 mmol, 1 equiv), TEA (7.5 mmol, 1.5 equiv), DMAP (20 mol%), and DCM were added. The reaction was cooled to 0 °C and TsCl (6 mmol, 1.2 equiv) in DCM was added

dropwise and left to stir for 2 hours. The reaction was quenched with DCM (3 × 25 mL) and the combined organic layers were washed with brine (3 × 25 mL) and dried over magnesium sulfate. The solvent was evaporated to give the crude product. The crude product was purified by flash column chromatography to afford 1-formylnaphthalen-2-yl 4-methylbenzenesulfonate. Then, the desired cinnamaldehyde was prepared according to Method A in General Procedures for the Synthesis of Enals.

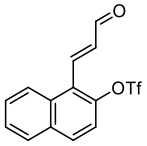


1-(3-oxoprop-1-en-1-yl)naphthalen-2-yl 4-methylbenzenesulfonate (S112):

White solid (0.52 g, 29% yield); R_f = 0.2 (Petroleum ether/Ethyl acetate = 10:1); Mp = 92 – 94 °C; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 9.50 – 9.36 (m, 1H), 8.04 – 7.82 (m, 3H), 7.72 – 7.41 (m, 6H), 7.32 – 7.17 (m, 2H), 6.45 – 6.28 (m, 1H), 2.46 – 2.33 (m, 3H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 193.1, 146.3, 145.5, 144.3, 135.9, 132.4, 131.8, 131.0, 130.1, 128.9, 128.6, 128.0, 126.8, 124.6, 124.5, 122.0, 21.7; **HRMS** (ESI) m/z: $[M + H]^+$ calcd. for $C_{20}H_{17}O_4S$ 353.0842; found 353.0841.

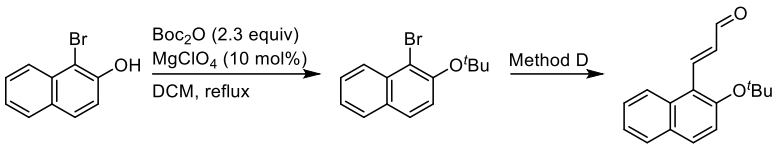


Prepared according to literature[17]. To round bottom flask equipped with a stirring bar, 2-hydroxy-1-naphthaldehyde (5 mmol, 1 equiv), pyridine (6 mmol, 1.2 equiv), and dry DCM were added. The flask was cooled to 0 °C and Tf_2O (7.5 mmol, 1.5 equiv) was added dropwise. The reaction was warmed to room temperature and left to stir overnight. The reaction was saturated with $NaHCO_3$ (25 mL). The aqueous phase was washed with DCM (3 × 25 mL) and dried over magnesium sulfate. The solvent was evaporated to give the crude product. The crude product was purified by flash column chromatography to afford 1-formylnaphthalen-2-yl trifluoromethanesulfonate. Then, the desired cinnamaldehyde was prepared according to Method B in General Procedures for the Synthesis of Enals.

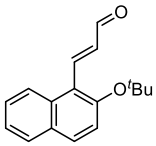


(*E*)-1-(3-oxoprop-1-en-1-yl)naphthalen-2-yl trifluoromethanesulfonate (S113):

White solid (0.81 g, 49% yield); R_f = 0.35 (Petroleum ether/Ethyl acetate = 10:1); Mp = 42 – 44 °C; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 9.89 (d, *J* = 7.5 Hz, 1H), 8.10 (d, *J* = 8.4 Hz, 1H), 7.99 (d, *J* = 9.1 Hz, 1H), 7.97 – 7.92 (m, 2H), 7.70 – 7.62 (m, 2H), 7.48 (d, *J* = 9.0 Hz, 1H), 6.79 (dd, *J* = 16.4, 7.5 Hz, 1H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 192.7, 144.4, 143.0, 138.0, 132.6, 132.2, 131.2, 128.9, 128.6, 127.5, 124.9, 124.8, 119.6, 118.6 (q, $^1J_{C\text{-}F}$ = 320.6 Hz); **^{19}F NMR** (565 MHz, $CDCl_3$) δ -73.5; **HRMS** (ESI) m/z: $[M + Na]^+$ calcd. for $C_{14}H_9F_3NaO_4S$ 353.0066; found 353.0064.



According to the procedure reported in the literature[18], in a 100 mL three-necked flask equipped with a magnetic stirring bar and a condenser coil, $Mg(ClO_4)_2$ (0.5 mmol, 10 mol%) and the alcohol (5.0 mmol) were dissolved in 10 mL of DCM. Then Boc_2O (11.5 mmol, 2.3 equiv) was added and bubbling was immediately observed. The mixture was stirred at reflux until the TLC analysis revealed the presence of Boc_2O. The crude reaction mixture was diluted with water and extracted with DCM. The organic layer was separated, dried over Na_2SO_4, filtered, and removed by rotary evaporation. The tert-butyl ether was purified by flash chromatography on silica gel with a mixture of petroleum ether/Ethyl acetate =40:1. The final tert-butoxy substituted cinnamaldehyde was prepared according to Method D in General Procedures for the Synthesis of Enals.

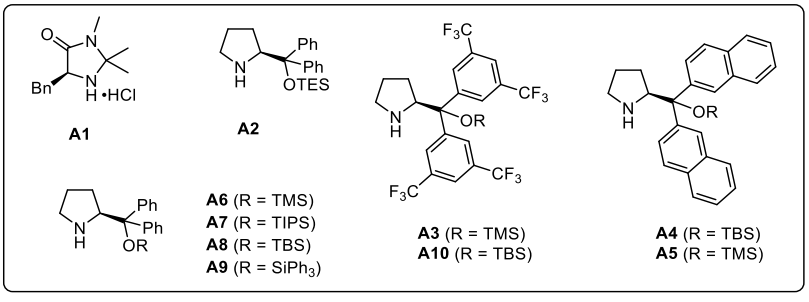


(*E*)-3-(2-(tert-butoxy)naphthalen-1-yl)acrylaldehyde (S114):

White solid (0.38 g, 30% yield); R_f = 0.5 (Petroleum ether/Ethyl acetate = 10:1); Mp = 116 – 117 °C; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 9.83 (d, *J* = 7.8 Hz, 1H), 8.19 – 8.10 (m, 2H), 7.82 (t, *J* = 7.4 Hz, 2H), 7.54 (t, *J* = 7.6 Hz, 1H), 7.44 (t, *J* = 7.3 Hz, 1H), 7.35 (d, *J* = 8.9 Hz, 1H), 7.00 (dd, *J* = 16.2, 7.8 Hz, 1H), 1.47 (s, 9H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 194.8, 154.0, 148.5, 134.5, 132.1, 131.4, 130.2, 128.7, 127.5, 124.8, 123.7, 123.0, 122.3, 81.7, 29.6; **HRMS** (ESI) m/z: $[M + Na]^+$ calcd. for $C_{17}H_{18}NaO_2$ 277.1199; found 277.1201.

Chiral Secondary Amines

A1 was purchased from commercial sources and used as received. **A2**,[19a] **A3**,[19b] **A4**,[19c] **A5**,[19d] **A6**,[19e] **A7**,[19f] **A8**,[19g] **A9**,[19a] and **A10**[19b] were prepared according to the procedures reported in the literature.



Scheme S3. Chiral secondary amines used in the reactions.

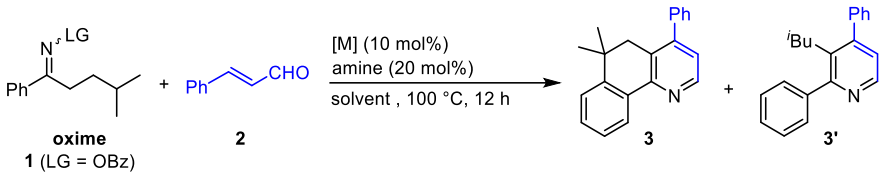
Optimization of the Reaction Conditions

General Procedures:

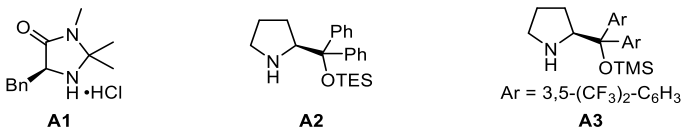
For the conditions toward achiral pyridine, an oven-dried Schlenk tube (10 mL) containing a stirring bar was charged with oxime (0.3 mmol, 3 equiv) and **2** (0.1 mmol, 1 equiv). The Schlenk tube was then introduced into a glove box, where it was charged with [Fe] (10 mol%) and amine (20 mol%). The tube was fitted with a rubber septum and removed from the glove box. Then solvent (1 mL) was added to the Schlenk tube through the rubber septum using syringes, and then the septum was replaced by a Teflon screwcap under nitrogen flow. The reaction mixture was stirred at the set temperature for 12 h. Then, the mixture was cooled to room temperature and diluted with ethyl acetate (3 mL). Then, n-tridecane (0.1 mmol) was added to the tube as an internal standard, and the yield of the desired product was determined by GC analysis. As for the isolated yield of the desired product, the reaction mixture was diluted with ethyl acetate (5 mL) and filtered through a pad of silica gel with additional ethyl acetate (20 mL) as the eluent. The filtrate was concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel to afford the desired product.

For the conditions toward axially chiral heterobiaryls, an oven-dried Schlenk tube (10 mL) containing a stirring bar was charged with the oxime (0.3 mmol, 3 equiv) and enal **96** (0.1 mmol, 1 equiv). The Schlenk tube was then introduced into a glove box, where it was charged with $Fe(acac)_2$ (10 mol%) and chiral amine (20 mol%). The tube was fitted with a rubber septum and removed from the glove box. Then solvent (1 mL) was added to the Schlenk tube through the rubber septum using syringes, and then the septum was replaced by a Teflon screwcap under nitrogen flow. The reaction mixture was stirred at the set temperature for a set length of time. Upon cooling to room temperature, the reaction mixture was diluted with 5 mL of ethyl acetate and filtered through a pad of silica gel with additional ethyl acetate (20 mL) as the eluent. The filtrate was concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel to afford the desired product.

Table S1. Optimization of the Reaction Conditions Toward Pyridines[a]

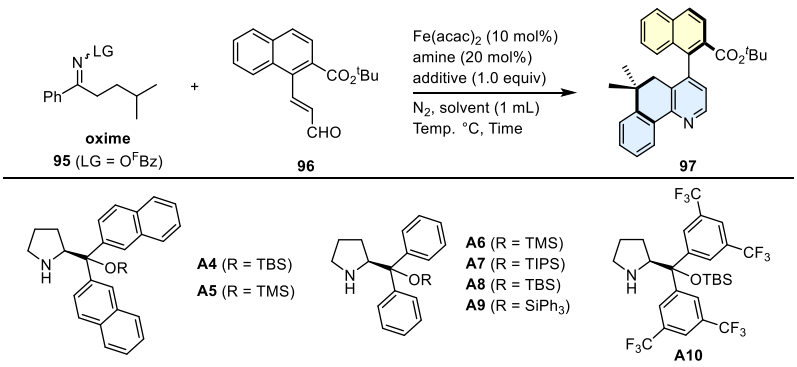


Entry	[M]	LG	Solvent	Amine	3 (%)[b]	3' (%)[b]
1	FeS	OBz	1,4-dioxane	pyrrolidine·$HClO_4$	42	13
2	$Fe(OTf)_2$	OBz	1,4-dioxane	pyrrolidine·$HClO_4$	48	21
3	$FeCl_3$	OBz	1,4-dioxane	pyrrolidine·$HClO_4$	31	20
4	CuI	OBz	1,4-dioxane	pyrrolidine·$HClO_4$	0	56
5	$Fe(acac)_2$	OBz	1,4-dioxane	pyrrolidine·$HClO_4$	59 (55[h], 47[i])	13
6	$Fe(acac)_2$	OAc	1,4-dioxane	pyrrolidine·$HClO_4$	40	27
7	$Fe(acac)_2$	OPiv	1,4-dioxane	pyrrolidine·$HClO_4$	58	16
8	$Fe(acac)_2$	O^{F}Bz	1,4-dioxane	pyrrolidine·$HClO_4$	57	5
9	$Fe(acac)_2$	OBz	toluene	pyrrolidine·$HClO_4$	47	4
10	$Fe(acac)_2$	OBz	THF	pyrrolidine·$HClO_4$	50	17
11	$Fe(acac)_2$	OBz	MeCN	pyrrolidine·$HClO_4$	56	11
12	$Fe(acac)_2$	OBz	DMSO	pyrrolidine·$HClO_4$	46	22
13	$Fe(acac)_2$	OBz	1,4-dioxane	piperidine·$HClO_4$	51	15
14	$Fe(acac)_2$	OBz	1,4-dioxane	morpholine·$HClO_4$	55	12
15	$Fe(acac)_2$	OBz	1,4-dioxane	^{i}Pr$_2$NH·$HClO_4$	34	7
16	$Fe(acac)_2$	OBz	1,4-dioxane	**A1**	0	0
17	$Fe(acac)_2$	OBz	1,4-dioxane	**A2**	18	18
18	$Fe(acac)_2$	OBz	1,4-dioxane	**A3**	17	7
19	$Fe(acac)_2$	OBz	1,4-dioxane	pyrrolidine·HOTf	55	15
20[c]	$Fe(acac)_2$	OBz	1,4-dioxane	pyrrolidine·$HClO_4$	51	10
21[c]	$Fe(acac)_2$	OBz	1,4-dioxane	none	0	0
22[c]	none	OBz	1,4-dioxane	pyrrolidine·$HClO_4$	0	0
23[d]	**$Fe(acac)_2$**	**OBz**	**1,4-dioxane**	**pyrrolidine·$HClO_4$**	**72 (70[e])**	**12(7[e])**
24[d,f]	$Fe(acac)_2$	OBz	1,4-dioxane	pyrrolidine·$HClO_4$	N.D.	N.D.
25[d,g]	$Fe(acac)_2$	OBz	1,4-dioxane	pyrrolidine·$HClO_4$	26	19



[a] Reaction conditions: oxime (0.3 mmol), **2** (0.1 mmol), [Fe] (10 mol%), amine (20 mol%), 1,4-dioxane (1 mL), 100 °C, 12 h, under N_2. [b] Yield determined by GC using n-tridecane as an internal standard. [c] Reaction was run at 60 °C. [d] Reaction was run at 120 °C. [e] Isolated yield. [f] **1** (0.15 mmol, 1.5 equiv), DDQ (0.2 mmol, 2 equiv) as an extrinsic oxidant. [g] **1** (0.15 mmol, 1.5 equiv), $PhNO_2$ (0.2 mmol, 2 equiv) as an extrinsic oxidant. [h] The amount of oxime was 0.2 mmol. [i] The amount of oxime was 0.15 mmol. Abbreviation: LG = Leaving group. Bz = Benzoyl. Ac = Acetyl. Piv = pivaloyl. ^{F}Bz = Pentafluorobenzoyl. TES = Triethylsilyl. TMS = Trimethylsilyl. DDQ = 2,3-Dichloro-5,6-dicyano-1,4-benzoquinone. N.D. = Not detected.

Table S2. Optimization of the Reaction Conditions Toward Axially Chiral Heterobiaryls[a]



Entry	LG	Additive	Temp. (°C)	Amine	Solvent	Time(h)	3 (%)[b]	er (%)[c]
1	OBz	PhCOOH	60	**A4**	1,4-dioxane	12	N.D.	-
2	OAc	PhCOOH	60	**A4**	1,4-dioxane	12	N.D.	-
3	OPiv	PhCOOH	60	**A4**	1,4-dioxane	12	N.D.	-
4	O^FBz	PhCOOH	60	**A4**	1,4-dioxane	12	47	90:10
5	O^FBz	*m*-MeBzOH	60	**A4**	1,4-dioxane	12	34	89.5:10.5
6	O^FBz	*p*-OMeBzOH	60	**A4**	1,4-dioxane	12	31	88:12
7	O^FBz	*p*-NO_2BzOH	60	**A4**	1,4-dioxane	12	35	88.5:11.5
8	O^FBz	KH_2PO_4	60	**A4**	1,4-dioxane	12	33	92:8
9	O^FBz	PhCOOH	50	**A4**	1,4-dioxane	12	43	90:10
10	O^FBz	PhCOOH	70	**A4**	1,4-dioxane	12	44	87.5:12.5
11	O^FBz	none	60	**A4**	1,4-dioxane (0.5 mL)	12	36	92:8
12	O^FBz	none	60	**A4**	1,4-dioxane (2.0 mL)	12	34	92:8
13	O^FBz	none	60	**A4**	1,4-dioxane	12	35	93:7
14	O^FBz	none	60	**A5**	1,4-dioxane	12	13	85:15
15	O^FBz	none	60	**A6**	1,4-dioxane	12	trace	-
16	O^FBz	none	60	**A7**	1,4-dioxane	12	19	91.5:8.5
17	O^FBz	none	60	**A8**	1,4-dioxane	12	40	91.5:8.5
18	O^FBz	none	60	**A9**	1,4-dioxane	12	20	90.5:9.5
19	O^FBz	none	60	**A10**	1,4-dioxane	12	17	90:10
20	O^FBz	none	40	**A4**	1,4-dioxane	72	40	93.5:7.5
21	O^FBz	none	50	**A4**	1,4-dioxane	48	39	93:7
22	O^FBz	none	50	**A4**	THF	48	N.D.	-
23	O^FBz	none	50	**A4**	MeCN	48	N.D.	-
24	O^FBz	none	50	**A4**	DMSO	48	N.D.	-
25	O^FBz	none	50	**A4**	Toluene	48	50	90:10
26	O^FBz	none	50	**A4**	$PhCF_3$	48	35	85:15
27	O^FBz	none	50	**A4**	*p*-xylene	48	42	85:15
28	**O^FBz**	**none**	**50**	**A4**	**Toluene / 1,4-dioxane (0.5mL/0.5mL)**	**48**	**53(0[d])**	**93:7**

[a] Reaction conditions: **oxime** (0.3 mmol), **96** (0.1 mmol), $Fe(acac)_2$ (10 mol%), amine (20 mol%), solvent (1 mL), additive (0 or 1 equiv), at a set temperature for the set reaction time, under N_2. [b] Isolated yield. [c] Determined by chiral HPLC analysis. [d] In absence of $Fe(acac)_2$ or amine.

Abbreviation: LG = Leaving group. Bz = Benzoyl. Ac = Acetyl. Piv = pivaloyl. ^{F}Bz = Pentafluorobenzoyl. TBS = Tert-butyldimethylsilyl. TIPS = Triisopropylsilyl. TMS = Trimethylsilyl. N.D. = Not detected. er = enantiomeric ratio.

Construction of Fused Pyridines and Axially Chiral Heterobiaryls

General Procedures Toward Fused Pyridines:

An oven-dried Schlenk tube (10 mL) containing a stirring bar was charged with the oxime (0.6 mmol, 3 equiv) and enal (0.2 mmol, 1 equiv). The Schlenk tube was then introduced into a glove box, where it was charged with $Fe(acac)_2$ (10 mol%, 5.0 mg) and pyrrolidine·$HClO_4$ (20 mol%, 6.8 mg). The tube was fitted with a rubber septum and removed from the glove box. Then 1,4-dioxane (2 mL) was added to the Schlenk tube through the rubber septum using syringes, and then the septum was replaced by a Teflon screwcap under nitrogen flow. The reaction mixture was stirred at 120 ℃ for 12 h. Upon cooling to room temperature, the reaction mixture was diluted with ethyl acetate (5 mL) and filtered through a pad of silica gel with additional ethyl acetate (20 mL) as the eluent. The filtrate was concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel to afford the desired product.

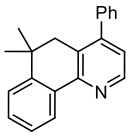
General Procedures Toward Axially Chiral Heterobiaryls:

An oven-dried Schlenk tube (10 mL) containing a stirring bar was charged with the oxime (0.6 mmol, 3 equiv) and enal (0.2 mmol, 1 equiv). The Schlenk tube was then introduced into a glove box, where it was charged with $Fe(acac)_2$ (10 mol%, 5.0 mg) and chiral amine **A4** (20 mol%, 18.7 mg). The tube was fitted with a rubber septum and taken out from the glove box. Then solvent (1,4-dioxane (1 mL) and toluene (1 mL)) was added to the Schlenk tube through the rubber septum using syringes, and then the septum was replaced by a Teflon screwcap under nitrogen flow. The reaction mixture was stirred at 50 ℃ for 48 h. Upon cooling to room temperature, the reaction mixture was diluted with 5 mL of ethyl acetate and filtered through a pad of silica gel with additional ethyl acetate (20 mL) as the eluent. The filtrate was concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel to afford the desired axially chiral heterobiaryls. The racemic heterobiaryls were prepared according to the general procedures toward pyridines.

Note:

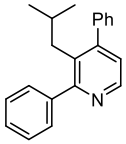
All the axially chiral aza-biaryl compounds obtained in this work are stable when they are stored under air, and their enantiopurity remains unchanged.

Characterization Data for Products



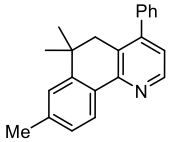
6,6-dimethyl-4-phenyl-5,6-dihydrobenzo[h]quinoline (3):

According to the general procedure, a mixture consisting of oxime (0.6 mmol, 177.2 mg), enal (0.2 mmol, 26.4 mg), $Fe(acac)_2$ (0.02 mmol, 5.0 mg), pyrrolidine·$HClO_4$ (0.04 mmol, 6.8 mg) and 1,4-dioxane (2 mL) under a N_2 atmosphere was stirred at 120 ℃ for 12 h to afford **3**. White solid (40.1 mg, 70% yield); R_f = 0.6 (Petroleum ether/Ethyl acetate = 10:1); Mp = 93-94 ℃; **^{1}H NMR** (600 MHz, $CDCl_3$): δ 8.57 (d, *J* = 4.8 Hz, 1H), 8.44 – 8.40 (m, 1H), 7.47 (t, *J* = 7.4 Hz, 2H), 7.43 (t, *J* = 7.3 Hz, 1H), 7.39 – 7.36 (m, 3H), 7.34 (d, *J* = 7.1 Hz, 2H), 7.11 (d, *J* = 4.8 Hz, 1H), 2.80 (s, 2H), 1.22 (s, 6H); **^{13}C NMR** (151 MHz, $CDCl_3$): δ 152.8, 149.1, 147.1, 146.3, 139.0, 133.6, 129.6, 128.8, 128.5, 128.1, 127.9, 126.7, 125.9, 123.7, 123.3, 40.1, 33.8, 28.1; **HRMS** (ESI) m/z: $[M + H]^+$ calcd. for $C_{21}H_{20}N$ 286.1590; found 286.1587.



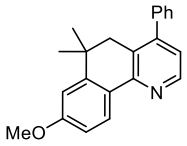
3-isobutyl-2,4-diphenylpyridine (Side product 3'):

White solid (4.0 mg, 7% yield); R_f = 0.3 (Petroleum ether/Ethyl acetate = 10:1); Mp = 113-114 ℃; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.52 (d, *J* = 4.8 Hz, 1H), 7.51 (d, *J* = 7.3 Hz, 2H), 7.47 – 7.42 (m, 4H), 7.41 – 7.37 (m, 2H), 7.36 (d, *J* = 7.1 Hz, 2H), 7.10 (d, *J* = 4.8 Hz, 1H), 2.69 (d, *J* = 7.2 Hz, 2H), 1.24 – 1.19 (m, 1H), 0.40 (d, *J* = 6.6 Hz, 6H); **^{13}C NMR** (151 MHz, DMSO) δ 160.7, 151.4, 146.5, 142.0, 140.6, 132.6, 129.3, 129.0, 128.5, 128.3, 127.8, 127.8, 123.9, 37.7, 28.9, 28.8, 22.3; **HRMS** (ESI) m/z: $[M + H]^+$ calcd. for $C_{21}H_{22}N$ 288.1747; found 288.1748.



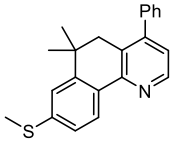
6,6,8-trimethyl-4-phenyl-5,6-dihydrobenzo[h]quinoline (4):

According to the general procedure, a mixture consisting of oxime (0.6 mmol, 185.6 mg), enal (0.2 mmol, 26.4 mg), $Fe(acac)_2$ (0.02 mmol, 5.0 mg), pyrrolidine·$HClO_4$ (0.04 mmol, 6.8 mg) and 1,4-dioxane (2 mL) under a N_2 atmosphere was stirred at 120 ℃ for 12 h to afford **4**. White solid (19.0 mg, 31% yield); R_f = 0.6 (Petroleum ether/Ethyl acetate = 10:1); Mp = 107-108 ℃; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.54 (d, *J* = 4.9 Hz, 1H), 8.30 (d, *J* = 7.8 Hz, 1H), 7.47 (t, *J* = 7.3 Hz, 2H), 7.42 (t, *J* = 7.3 Hz, 1H), 7.33 (d, *J* = 7.0 Hz, 2H), 7.22 – 7.15 (m, 2H), 7.08 (d, *J* = 4.9 Hz, 1H), 2.78 (s, 2H), 2.41 (s, 3H), 1.20 (s, 6H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 153.0, 148.9, 147.0, 146.2, 139.5, 139.1, 131.0, 128.8, 128.4, 127.9, 127.7, 127.5, 125.9, 124.4, 123.0, 40.2, 33.8, 28.2, 21.7; **HRMS** (ESI) m/z: $[M + H]^+$ calcd. for $C_{22}H_{22}N$ 300.1747; found 300.1749.



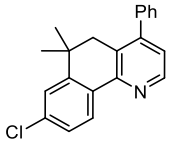
8-methoxy-6,6-dimethyl-4-phenyl-5,6-dihydrobenzo[h]quinoline (5):

According to the general procedure, a mixture consisting of oxime (0.6 mmol, 195.2 mg), enal (0.2 mmol, 26.4 mg), $Fe(acac)_2$ (0.02 mmol, 5.0 mg), pyrrolidine·$HClO_4$ (0.04 mmol, 6.8 mg) and 1,4-dioxane (2 mL) under a N_2 atmosphere was stirred at 120 ℃ for 12 h to afford **5** White solid (40.4 mg, 64% yield); R_f = 0.5 (Petroleum ether/Ethyl acetate = 10:1); Mp = 128–129 ℃; **^{1}H NMR** (600 MHz, $CDCl_3$): δ 8.52 (d, *J* = 4.9 Hz, 1H), 8.40-8.34 (m, 1H), 7.47 (t, *J* = 7.3 Hz, 2H), 7.42 (t, *J* = 7.3 Hz, 1H), 7.36 – 7.31 (m, 2H), 7.05 (d, *J* = 4.9 Hz, 1H), 6.93 – 6.88 (m, 2H), 3.88 (s, 3H), 2.78 (s, 2H), 1.20 (s, 6H); **^{13}C NMR** (151 MHz, $CDCl_3$): δ 161.0, 152.8, 148.9, 148.2, 146.9, 139.1, 128.7, 128.4, 127.8, 127.6, 127.0, 126.7, 122.6, 111.3, 110.1, 55.3, 40.1, 34.0, 28.1; **HRMS** (ESI) m/z: $[M + H]^+$ calcd. for $C_{22}H_{22}NO$ 316.1696; found 316.1692.



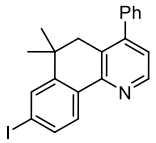
6,6-dimethyl-8-(methylthio)-4-phenyl-5,6-dihydrobenzo[h]quinoline (6):

According to the general procedure, a mixture consisting of oxime (0.6 mmol, 204.9 mg), enal (0.2 mmol, 26.4 mg), $Fe(acac)_2$ (0.02 mmol, 5.0 mg), pyrrolidine·$HClO_4$ (0.04 mmol, 6.8 mg) and 1,4-dioxane (2 mL) under a N_2 atmosphere was stirred at 120 ℃ for 12 h to afford **6**. White solid (34.0 mg, 51% yield); R_f = 0.5 (Petroleum ether/Ethyl acetate = 10:1); Mp = 141–142 ℃; **^{1}H NMR** (600 MHz, $CDCl_3$): δ 8.54 (d, *J* = 4.9 Hz, 1H), 8.35 (d, *J* = 8.1 Hz, 1H), 7.49-7.44 (m, 2H), 7.44 – 7.40 (m, 1H), 7.34 – 7.31 (m, 2H), 7.26 – 7.23 (m, 2H), 7.08 (d, *J* = 4.9 Hz, 1H), 2.78 (s, 2H), 2.54 (s, 3H), 1.21 (s, 6H); **^{13}C NMR** (151 MHz, $CDCl_3$): δ 152.5, 149.0, 147.1, 146.7, 140.2, 138.9, 130.7, 128.7, 128.5, 127.9, 127.6, 126.5, 124.3, 123.1, 121.9, 40.1, 34.0, 28.1, 15.7; **HRMS** (ESI) m/z: $[M + H]^+$ calcd. for $C_{22}H_{22}NS$ 332.1467; found 332.1464.



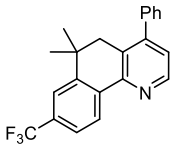
8-chloro-6,6-dimethyl-4-phenyl-5,6-dihydrobenzo[h]quinoline (7):

According to the general procedure, a mixture consisting of oxime (0.6 mmol, 197.9 mg), enal (0.2 mmol, 26.4 mg), $Fe(acac)_2$ (0.02 mmol, 5.0 mg), pyrrolidine·$HClO_4$ (0.04 mmol, 6.8 mg) and 1,4-dioxane (2 mL) under a N_2 atmosphere was stirred at 120 ℃ for 12 h to afford **7**. White solid (33.9 mg, 53% yield); R_f = 0.6 (Petroleum ether/Ethyl acetate = 10:1); Mp = 108–110 ℃; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.55 (d, *J* = 4.8 Hz, 1H), 8.36 (d, *J* = 8.9 Hz, 1H), 7.48 (t, *J* = 7.2 Hz, 2H), 7.44 (t, *J* = 7.2 Hz, 1H), 7.36 – 7.30 (m, 4H), 7.12 (d, *J* = 4.8 Hz, 1H), 2.80 (s, 2H), 1.21 (s, 6H); **^{13}C NMR** (151 MHz, DMSO) δ 147.2, 144.5, 143.3, 142.4, 134.0, 130.8, 127.4, 123.9, 123.7, 123.3, 123.1, 122.7, 122.2, 119.4, 118.8, 35.2, 29.3, 23.2; **HRMS** (ESI) m/z: $[M + H]^+$ calcd. for $C_{21}H_{19}ClN$ 320.1201; found 320.1196.



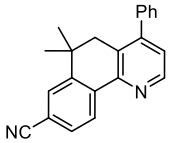
8-iodo-6,6-dimethyl-4-phenyl-5,6-dihydrobenzo[h]quinoline (8):

According to the general procedure, a mixture consisting of oxime (0.6 mmol, 252.7 mg), enal (0.2 mmol, 26.4 mg), $Fe(acac)_2$ (0.02 mmol, 5.0 mg), pyrrolidine·$HClO_4$ (0.04 mmol, 6.8 mg) and 1,4-dioxane (2 mL) under a N_2 atmosphere was stirred at 120 ℃ for 12 h to afford **8**. White solid (28.0 mg, 34% yield); R_f = 0.6 (Petroleum ether/Ethyl acetate = 10:1); Mp = 119–121 ℃; **^{1}H NMR** (600 MHz, $CDCl_3$): δ 8.55 (d, *J* = 4.9 Hz, 1H), 8.13 (d, *J* = 8.2 Hz, 1H), 7.71 (d, *J* = 8.3 Hz, 1H), 7.69 (s, 1H), 7.48 (t, *J* = 7.3 Hz, 2H), 7.44 (t, *J* = 7.3 Hz, 1H), 7.32 (d, *J* = 7.2 Hz, 2H), 7.13 (d, *J* = 4.9 Hz, 1H), 2.78 (s, 2H), 1.20 (s, 6H); **^{13}C NMR** (151 MHz, $CDCl_3$): δ 152.1, 149.3, 148.4, 147.2, 138.7, 136.0, 133.2, 133.1, 128.7, 128.5, 128.1, 128.0, 127.8, 123.8, 96.3, 39.95, 33.9, 28.0; **HRMS** (ESI) m/z: $[M + H]^+$ calcd. for $C_{21}H_{19}IN$ 412.0557; found 412.0551.



6,6-dimethyl-4-phenyl-8-(trifluoromethyl)-5,6-dihydrobenzo[h]quinoline (9):

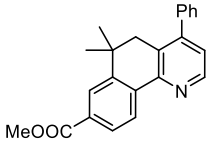
According to the general procedure, a mixture consisting of oxime (0.6 mmol, 218.0 mg), enal (0.2 mmol, 26.4 mg), $Fe(acac)_2$ (0.02 mmol, 5.0 mg), pyrrolidine·$HClO_4$ (0.04 mmol, 6.8 mg) and 1,4-dioxane (2 mL) under a N_2 atmosphere was stirred at 120 ℃ for 12 h to afford **9**. White solid (35.3 mg, 50% yield); R_f = 0.6 (Petroleum ether/Ethyl acetate = 10:1); Mp = 130–132 ℃; **^{1}H NMR** (600 MHz, $CDCl_3$): δ 8.60 (d, *J* = 4.9 Hz, 1H), 8.54 (d, *J* = 8.1 Hz, 1H), 7.63 (d, *J* = 8.5 Hz, 1H), 7.61 (s, 1H), 7.50 (t, *J* = 7.2 Hz, 2H), 7.45 (t, *J* = 7.3 Hz, 1H), 7.36 – 7.32 (m, 2H), 7.18 (d, *J* = 4.9 Hz, 1H), 2.84 (s, 2H), 1.25 (s, 6H); **^{13}C NMR** (151 MHz, $CDCl_3$): δ 151.5, 149.4, 147.4, 146.8, 138.6, 136.9, 131.2 (q, $^2J_{C\text{-}F}$ = 32.0 Hz), 128.7, 128.6, 128.1, 126.4, 124.4 (q, $^1J_{C\text{-}F}$ = 272.4 Hz), 124.2, 123.6 (q, $^3J_{C\text{-}F}$ = 3.8 Hz), 120.8 (q, $^3J_{C\text{-}F}$ = 3.8 Hz,), 39.80, 34.03, 27.94; **^{19}F NMR** (565 MHz, $CDCl_3$): δ -62.48; **HRMS** (ESI) m/z: $[M + H]^+$ calcd. for $C_{22}H_{19}F_3N$ 354.1464; found 354.1463.



6,6-dimethyl-4-phenyl-5,6-dihydrobenzo[h]quinoline-8-carbonitrile (10):

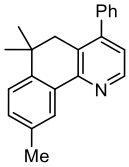
According to the general procedure, a mixture consisting of oxime (0.6 mmol, 192.2 mg), enal (0.2 mmol, 26.4 mg), $Fe(acac)_2$ (0.02 mmol, 5.0 mg), pyrrolidine·$HClO_4$ (0.04 mmol, 6.8 mg) and 1,4-dioxane (2 mL) under a N_2 atmosphere was stirred at 120 ℃ for 12 h to afford **10**. White solid (33.5 mg, 54% yield); R_f = 0.4 (Petroleum ether/Ethyl acetate = 40:1); Mp = 201–202 ℃; **^{1}H NMR** (600 MHz, $CDCl_3$): δ 8.61 (d, *J* = 4.9 Hz, 1H), 8.54 – 8.51 (m, 1H), 7.67-7.62 (m, 2H), 7.52-7.47 (m, 2H), 7.47 – 7.43 (m, 1H), 7.35 – 7.29 (m, 2H), 7.20 (d, *J* = 4.9 Hz, 1H), 2.84 (s, 2H), 1.23 (s, 6H); **^{13}C NMR** (151 MHz, $CDCl_3$): δ 150.9, 149.6, 147.5, 147.1, 138.3, 137.8, 130.4, 128.8, 128.6, 128.6, 128.2, 127.9, 126.6, 124.5, 119.2, 112.8, 39.6, 34.0, 27.8; **HRMS** (ESI) m/z:

$[M + H]^+$ calcd. for $C_{22}H_{19}N_2$ 311.1543; found 311.1537.



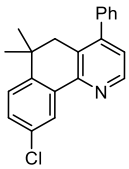
methyl 6,6-dimethyl-4-phenyl-5,6-dihydrobenzo[h]quinoline-8-carboxylate (11):

According to the general procedure, a mixture consisting of oxime (0.6 mmol, 212.0 mg), enal (0.2 mmol, 26.4 mg), $Fe(acac)_2$ (0.02 mmol, 5.0 mg), pyrrolidine·$HClO_4$ (0.04 mmol, 6.8 mg) and 1,4-dioxane (2 mL) under a N_2 atmosphere was stirred at 120 ℃ for 12 h to afford **11**. White solid (26.3 mg, 38% yield); R_f = 0.4 (Petroleum ether/Ethyl acetate = 10:1); Mp = 148–149 ℃; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.60 (d, *J* = 4.8 Hz, 1H), 8.49 (d, *J* = 8.1 Hz, 1H), 8.06 (s, 1H), 8.03 (d, *J* = 8.1 Hz, 1H), 7.48 (t, *J* = 7.2 Hz, 2H), 7.44 (t, *J* = 7.2 Hz, 1H), 7.33 (d, *J* = 6.9 Hz, 2H), 7.16 (d, *J* = 4.8 Hz, 1H), 3.94 (s, 3H), 2.83 (s, 2H), 1.25 (s, 6H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 167.2, 151.8, 149.4, 147.3, 146.3, 138.7, 137.8, 130.8, 128.9, 128.7, 128.5, 128.1, 127.9, 126.0, 125.3, 124.1, 52.0, 40.0, 34.0, 28.0; **HRMS** (ESI) m/z: $[M + H]^+$ calcd. for $C_{23}H_{22}NO_2$ 344.1645; found 344.1644.



6,6,9-trimethyl-4-phenyl-5,6-dihydrobenzo[h]quinoline (12):

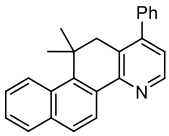
According to the general procedure, a mixture consisting of oxime (0.6 mmol, 185.6 mg), enal (0.2 mmol, 26.4 mg), $Fe(acac)_2$ (0.02 mmol, 5.0 mg), pyrrolidine·$HClO_4$ (0.04 mmol, 6.8 mg) and 1,4-dioxane (2 mL) under a N_2 atmosphere was stirred at 120 ℃ for 12 h to afford **12**. White solid (26.0 mg, 43% yield); R_f = 0.6 (Petroleum ether/Ethyl acetate = 10:1); Mp = 120–121 ℃; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.57 (d, *J* = 4.8 Hz, 1H), 8.24 (s, 1H), 7.48 (t, *J* = 7.2 Hz, 2H), 7.43 (t, *J* = 7.3 Hz, 1H), 7.34 (d, *J* = 7.1 Hz, 2H), 7.27 (d, *J* = 7.9 Hz, 1H), 7.21 (d, *J* = 7.7 Hz, 1H), 7.11 (d, *J* = 4.8 Hz, 1H), 2.79 (s, 2H), 2.43 (s, 3H), 1.20 (s, 6H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 152.9, 149.2, 147.0, 143.5, 139.0, 136.3, 133.3, 130.4, 128.7, 128.4, 128.2, 127.9, 126.3, 123.7, 123.2, 40.3, 33.5, 28.2, 21.1; **HRMS** (ESI) m/z: $[M + H]^+$ calcd. for $C_{22}H_{22}N$ 300.1747; found 300.1750.



9-chloro-6,6-dimethyl-4-phenyl-5,6-dihydrobenzo[h]quinoline (13):

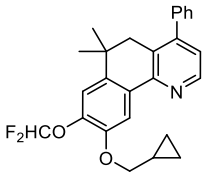
According to the general procedure, a mixture consisting of oxime (0.6 mmol, 197.9 mg), enal (0.2 mmol, 26.4 mg), $Fe(acac)_2$ (0.02 mmol, 5.0 mg), pyrrolidine·$HClO_4$ (0.04 mmol, 6.8 mg) and 1,4-dioxane (2 mL) under a N_2 atmosphere was stirred at 120 ℃ for 12 h to afford **13**. White solid (45.4 mg, 71% yield); R_f = 0.6 (Petroleum ether/Ethyl acetate = 10:1); Mp = 137–138 ℃; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.57 (d, *J* = 4.8 Hz, 1H), 8.41 (d, *J* = 1.8 Hz, 1H), 7.52 – 7.46 (m, 2H), 7.46 – 7.41 (m, 1H), 7.35-7.32 (m, 3H), 7.30 (d, *J* = 8.3 Hz, 1H), 7.14 (d, *J* = 4.8 Hz, 1H), 2.80 (s, 2H), 1.20 (s, 6H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 151.6, 149.3, 147.2, 144.5, 138.7, 135.3, 132.9,

129.4, 128.7, 128.5, 128.3, 128.0, 125.8, 125.4, 123.9, 39.9, 33.7, 28.1; **HRMS** (ESI) m/z: [M + H]$^+$ calcd. for $C_{21}H_{19}ClN$ 320.1201; found 320.1205.



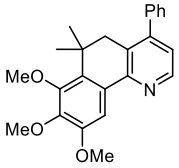
11,11-dimethyl-1-phenyl-11,12-dihydronaphtho[1,2-h]quinoline (14):

According to the general procedure, a mixture consisting of oxime (0.6 mmol, 207.2 mg), enal (0.2 mmol, 26.4 mg), $Fe(acac)_2$ (0.02 mmol, 5.0 mg), pyrrolidine·$HClO_4$ (0.04 mmol, 6.8 mg) and 1,4-dioxane (2 mL) under a N_2 atmosphere was stirred at 120 ℃ for 12 h to afford **14**. White solid (27.0 mg, 40% yield); R_f = 0.6 (Petroleum ether/Ethyl acetate = 10:1); Mp = 170–171 ℃; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.60 (d, *J* = 4.8 Hz, 1H), 8.56 (d, *J* = 8.4 Hz, 1H), 8.41 – 8.36 (m, 1H), 7.89-7.86 (m, 1H), 7.85 (d, *J* = 8.4 Hz, 1H), 7.50 (t, *J* = 7.2 Hz, 2H), 7.47 – 7.42 (m, 3H), 7.41 – 7.37 (m, 2H), 7.13 (d, *J* = 4.8 Hz, 1H), 2.94 (s, 2H), 1.59 (s, 7H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 153.4, 148.5, 147.3, 142.79, 138.8, 135.6, 132.4, 131.3, 129.3, 128.9, 128.5, 128.0, 127.9, 127.2, 126.6, 125.5, 124.8, 124.0, 123.2, 43.8, 36.1, 28.8; **HRMS** (ESI) m/z: [M + H]$^+$ calcd. for $C_{25}H_{22}N$ 336.1747; found 336.1741.



9-(cyclopropylmethoxy)-8-(difluoromethoxy)-6,6-dimethyl-4-phenyl-5,6-dihydrobenzo[h]quinoline (15):

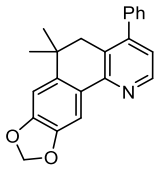
According to the general procedure, a mixture consisting of oxime (0.6 mmol, 258.9 mg), enal (0.2 mmol, 26.4 mg), $Fe(acac)_2$ (0.02 mmol, 5.0 mg), pyrrolidine·$HClO_4$ (0.04 mmol, 6.8 mg) and 1,4-dioxane (2 mL) under a N_2 atmosphere was stirred at 120 ℃ for 12 h to afford **15**. White solid (61.8 mg, 73% yield); R_f = 0.45 (Petroleum ether/Ethyl acetate = 10:1); Mp = 87–89 ℃; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.54 (d, *J* = 4.9 Hz, 1H), 8.04 (s, 1H), 7.48 (t, *J* = 7.3 Hz, 2H), 7.43 (t, *J* = 7.3 Hz, 1H), 7.34 – 7.30 (m, 2H), 7.14 (s, 1H), 7.11 (d, *J* = 4.9 Hz, 1H), 6.74 (t, *J* = 75.9 Hz, 1H), 4.03 (d, *J* = 6.9 Hz, 2H), 2.78 (s, 2H), 1.37 – 1.31 (m, 1H), 1.18 (s, 6H), 0.68 – 0.63 (m, 2H), 0.41-0.36 (m, 2H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 151.9, 149.3, 149.1, 147.0, 141.5, 139.8, 138.8, 132.0, 128.7, 128.5, 128.1, 128.0, 123.5, 118.5, 116.4 (t, $^1J_{C\text{-}F}$ = 259.2 Hz), 111.7, 74.0, 40.1, 33.4, 28.1, 10.3, 3.1. **^{19}F NMR** (565 MHz, $CDCl_3$) δ -81.45; **HRMS** (ESI) m/z: [M + H]$^+$ calcd. for $C_{26}H_{26}F_2NO_2$ 422.1926; found 422.1923.



7,8,9-trimethoxy-6,6-dimethyl-4-phenyl-5,6-dihydrobenzo[h]quinoline (16):

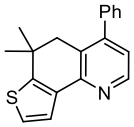
According to the general procedure, a mixture consisting of oxime (0.6 mmol, 231.2 mg), enal (0.2 mmol, 26.4 mg), $Fe(acac)_2$ (0.02 mmol, 5.0 mg), pyrrolidine·$HClO_4$ (0.04 mmol, 6.8 mg) and 1,4-dioxane (2 mL) under a N_2 atmosphere was stirred at 120 ℃ for 12 h to afford **16**. White solid

(42.0 mg, 56% yield); R_f = 0.4 (Petroleum ether/Ethyl acetate = 10:1); Mp = 155–157 ℃; **^{1}H NMR** (600 MHz, $CDCl_3$): δ 8.52 (d, *J* = 4.9 Hz, 1H), 7.90 (s, 1H), 7.47 (t, *J* = 7.3 Hz, 2H), 7.44-7.40 (m, 1H), 7.36-7.31 (m, 2H), 7.07 (d, *J* = 4.9 Hz, 1H), 4.00 (s, 3H), 3.91 (s, 3H), 3.90 (s, 3H), 2.76 (s, 2H), 1.32 (s, 6H); **^{13}C NMR** (151 MHz, $CDCl_3$): δ 152.5, 152.3, 152.2, 148.7, 146.8, 144.3, 138.9, 132.1, 130.1, 128.7, 128.4, 127.9, 127.4, 123.0, 105.2, 60.8, 60.5, 56.0, 42.3, 34.4, 28.3; **HRMS** (ESI) m/z: $[M + H]^+$ calcd. for $C_{24}H_{26}NO_3$ 376.1907; found 376.1900.



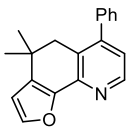
6,6-dimethyl-4-phenyl-5,6-dihydro-[1,3]dioxolo[4',5':4,5]benzo[1,2-h]quinoline (17):

According to the general procedure, a mixture consisting of oxime (0.6 mmol, 203.6 mg), enal (0.2 mmol, 26.4 mg), $Fe(acac)_2$ (0.02 mmol, 5.0 mg), pyrrolidine·$HClO_4$ (0.04 mmol, 6.8 mg) and 1,4-dioxane (2 mL) under a N_2 atmosphere was stirred at 120 ℃ for 12 h to afford **17**. White solid (45.5 mg, 69% yield); R_f = 0.45 (Petroleum ether/Ethyl acetate = 10:1); Mp = 160–161 ℃; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.51 (d, *J* = 4.8 Hz, 1H), 7.93 (s, 1H), 7.47 (t, *J* = 7.2 Hz, 2H), 7.42 (t, *J* = 7.3 Hz, 1H), 7.34 – 7.30 (m, 2H), 7.05 (d, *J* = 4.8 Hz, 1H), 6.86 (s, 1H), 5.98 (s, 2H), 2.76 (s, 2H), 1.17 (s, 6H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 152.7, 149.0, 148.9, 146.9, 146.6, 141.5, 139.1, 128.8, 128.5, 128.1, 127.9, 127.2, 122.8, 106.2, 104.3, 101.1, 40.2, 34.0, 28.3; **HRMS** (ESI) m/z: $[M + H]^+$ calcd. for $C_{22}H_{20}NO_2$ 330.1489; found 330.1492.



6,6-dimethyl-4-phenyl-5,6-dihydrothieno[2,3-h]quinoline (18):

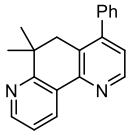
According to the general procedure, a mixture consisting of oxime (0.6 mmol, 180.8 mg), enal (0.2 mmol, 26.4 mg), $Fe(acac)_2$ (0.02 mmol, 5.0 mg), pyrrolidine·$HClO_4$ (0.04 mmol, 6.8 mg) and 1,4-dioxane (2 mL) under a N_2 atmosphere was stirred at 120 ℃ for 12 h to afford **18**. White solid (33.8 mg, 58% yield); R_f = 0.5 (Petroleum ether/Ethyl acetate = 10:1); Mp = 103–105 ℃; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.46 (d, *J* = 5.0 Hz, 1H), 7.71 (d, *J* = 5.1 Hz, 1H), 7.47 (t, *J* = 7.3 Hz, 2H), 7.42 (t, *J* = 7.3 Hz, 1H), 7.32 (d, *J* = 7.0 Hz, 2H), 7.18 (d, *J* = 5.1 Hz, 1H), 7.02 (d, *J* = 5.0 Hz, 1H), 2.88 (s, 2H), 1.27 (s, 6H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 152.5, 151.1, 149.1, 146.8, 139.3, 135.8, 128.6, 128.5, 127.9, 126.8, 125.1, 122.8, 122.6, 41.2, 34.1, 29.0; **HRMS** (ESI) m/z: $[M + H]^+$ calcd. for $C_{19}H_{18}NS$ 292.1154; found 292.1150.



4,4-dimethyl-6-phenyl-4,5-dihydrofuro[3,2-h]quinoline (19):

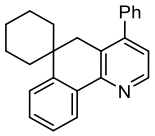
According to the general procedure, a mixture consisting of oxime (0.6 mmol, 171.2 mg), enal (0.2 mmol, 26.4 mg), $Fe(acac)_2$ (0.02 mmol, 5.0 mg), pyrrolidine·$HClO_4$ (0.04 mmol, 6.8 mg) and 1,4-dioxane (2 mL) under a N_2 atmosphere was stirred at 120 ℃ for 12 h to afford **19**. White solid (14.4 mg, 26% yield); R_f = 0.2 (Petroleum ether/Ethyl acetate = 20:1); Mp = 125–127 ℃; **^{1}H**

NMR (600 MHz, $CDCl_3$) δ 8.43 (d, *J* = 4.9 Hz, 1H), 7.50 (d, *J* = 1.4 Hz, 1H), 7.47 (t, *J* = 7.3 Hz, 2H), 7.42 (t, *J* = 7.2 Hz, 1H), 7.31 (d, *J* = 7.0 Hz, 2H), 6.98 (d, *J* = 5.0 Hz, 1H), 6.42 (d, *J* = 1.4 Hz, 1H), 2.82 (s, 2H), 1.19 (s, 6H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 149.0, 147.5, 146.8, 146.5, 144., 139.1, 133.8, 128.6, 128.5, 127.9, 126.8, 122.4, 108.3, 41.1, 31.6, 27.8; **HRMS** (ESI) m/z: $[M + H]^+$ calcd. for $C_{19}H_{18}NO$ 276.1383; found 276.1379.



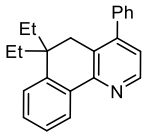
6,6-dimethyl-4-phenyl-5,6-dihydro-1,7-phenanthroline (20):

According to the general procedure, a mixture consisting of oxime (0.6 mmol, 177.8 mg), enal (0.2 mmol, 26.4 mg), $Fe(acac)_2$ (0.02 mmol, 5.0 mg), pyrrolidine·$HClO_4$ (0.04 mmol, 6.8 mg) and 1,4-dioxane (2 mL) under a N_2 atmosphere was stirred at 120 ℃ for 12 h to afford **20**. White solid (43.1 mg, 75% yield); R_f = 0.5 (Petroleum ether/Ethyl acetate = 10:1); Mp = 80–81 ℃; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.66 (dd, *J* = 7.8, 1.2 Hz 1H), 8.58 (dd, *J* = 4.8, 1.4 Hz, 1H), 8.57 (d, *J* = 4.9 Hz, 1H), 7.49 (t, *J* = 7.2 Hz, 2H), 7.45 (t, *J* = 7.3 Hz, 1H), 7.35 (d, *J* = 7.9 Hz, 2H), 7.29 (dd, *J* = 7.7, 4.8 Hz, 1H), 7.16 (d, *J* = 4.9 Hz, 1H), 2.92 (s, 2H), 1.28 (s, 6H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 164.3, 151.6, 149.7, 149.4, 147.4, 138.6, 133.1, 128.8, 128.7, 128.5, 128.1, 128.1, 123.9, 122.1, 39.7, 36.3, 26.8; **HRMS** (ESI) m/z: $[M + H]^+$ calcd. for $C_{20}H_{19}N_2$ 287.1543; found 287.1542.



4-phenyl-5*H*-spiro[benzo[h]quinoline-6,1'-cyclohexane] (21):

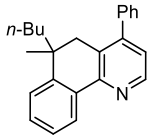
According to the general procedure, a mixture consisting of oxime (0.6 mmol, 201.3 mg), enal (0.2 mmol, 26.4 mg), $Fe(acac)_2$ (0.02 mmol, 5.0 mg), pyrrolidine·$HClO_4$ (0.04 mmol, 6.8 mg) and 1,4-dioxane (2 mL) under a N_2 atmosphere was stirred at 120 ℃ for 12 h to afford **21**. White solid (32.6 mg, 50% yield); R_f = 0.6 (Petroleum ether/Ethyl acetate = 50:1); Mp = 134–135 ℃; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.56 (d, *J* = 4.7 Hz, 1H), 8.41 (d, *J* = 7.0 Hz, 1H), 7.48 (t, *J* = 7.1 Hz, 2H), 7.45-7.43 (m, 2H), 7.42 – 7.33 (m, 4H), 7.12 (d, *J* = 4.8 Hz, 1H), 2.92 (s, 2H), 1.68 – 1.61 (m, 2H), 1.57-1.50 (m, 3H), 1.50-1.43 (m, 2H), 1.23 – 1.10 (m, 3H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 153.2, 149.1, 147.1, 147.0, 138.9, 134.0, 129.6, 128.6, 128.4, 128.0, 127.6, 126.6, 126.1, 123.2, 123.1, 36.5, 35.0, 32.5, 25.9, 22.1; **HRMS** (ESI) m/z: $[M + H]^+$ calcd. for $C_{24}H_{24}N$ 326.1903; found 326.1892.



6,6-diethyl-4-phenyl-5,6-dihydrobenzo[h]quinoline (22):

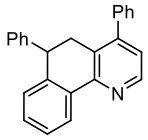
According to the general procedure, a mixture consisting of oxime (0.6 mmol, 194.1 mg), enal (0.2 mmol, 26.4 mg), $Fe(acac)_2$ (0.02 mmol, 5.0 mg), pyrrolidine·$HClO_4$ (0.04 mmol, 6.8 mg) and 1,4-dioxane (2 mL) under a N_2 atmosphere was stirred at 120 ℃ for 12 h to afford **22**. White solid (27.6 mg, 44% yield); R_f = 0.6 (Petroleum ether/Ethyl acetate = 10:1); Mp = 106–108 ℃; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.55 (d, *J* = 4.9 Hz, 1H), 8.47-8.43 (m, 1H), 7.47 (t, *J* = 7.3 Hz, 2H),

7.43 (t, *J* = 7.4 Hz, 1H), 7.39 – 7.32 (m, 4H), 7.26-7.24 (m, 1H), 7.09 (d, *J* = 4.9 Hz, 1H), 2.82 (s, 2H), 1.62-1.57 (m, 2H), 1.56-1.49 (m, 2H), 0.70 (t, *J* = 7.4 Hz, 6H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 152.7, 149.1, 146.9, 142.9, 139.1, 134.6, 128.9, 128.7, 128.4, 128.0, 127.9, 126.5, 126.1, 125.8, 123.3, 40.1, 34.3, 29.6, 8.5; **HRMS** (ESI) m/z: $[M + H]^+$ calcd. for $C_{23}H_{24}N$ 314.1903; found 314.1896.



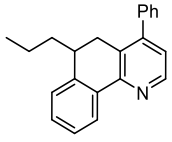
6-butyl-6-methyl-4-phenyl-5,6-dihydrobenzo[h]quinoline (23):

According to the general procedure, a mixture consisting of oxime (0.6 mmol, 202.5 mg), enal (0.2 mmol, 26.4 mg), $Fe(acac)_2$ (0.02 mmol, 5.0 mg), pyrrolidine·$HClO_4$ (0.04 mmol, 6.8 mg) and 1,4-dioxane (2 mL) under a N_2 atmosphere was stirred at 120 ℃ for 12 h to afford **23**. Colorless oil (40.5 mg, 61% yield); R_f = 0.6 (Petroleum ether/Ethyl acetate = 10:1); **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.56 (d, *J* = 4.8 Hz, 1H), 8.43-8.39 (m, 1H), 7.47 (t, *J* = 7.3 Hz, 2H), 7.42 (t, *J* = 7.3 Hz, 1H), 7.39 – 7.35 (m, 2H), 7.35-7.32 (m, 2H), 7.32 – 7.29 (m, 1H), 7.10 (d, *J* = 4.8 Hz, 1H), 2.83 (d, *J* = 15.7 Hz, 1H), 2.77 (d, *J* = 15.7 Hz, 1H), 1.39-1.31 (m, 2H), 1.28 (s, 3H), 1.10 – 1.00 (m, 3H), 0.99-0.91 (m, 1H), 0.72 (t, *J* = 7.0 Hz, 3H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 153.0, 149.0, 147.0, 145.4, 139.0, 133.9, 129.3, 128.7, 128.4, 128.0, 127.9, 126.6, 125.9, 124.7, 123.3, 39.5, 38.0, 36.8, 26.8, 25.5, 23.1, 13.9; **HRMS** (ESI) m/z: $[M + H]^+$ calcd. for $C_{24}H_{26}N$ 328.2060; found 328.2057.



4,6-diphenyl-5,6-dihydrobenzo[h]quinoline (24):

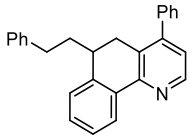
According to the general procedure, a mixture consisting of oxime (0.6 mmol, 206.1 mg), enal (0.2 mmol, 26.4 mg), $Fe(acac)_2$ (0.02 mmol, 5.0 mg), pyrrolidine·$HClO_4$ (0.04 mmol, 6.8 mg) and 1,4-dioxane (2 mL) under a N_2 atmosphere was stirred at 120 ℃ for 12 h to afford **24**. White solid (16.8 mg, 25% yield); R_f = 0.6 (Petroleum ether/Ethyl acetate = 10:1); Mp = 141–143 ℃; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.57 (d, *J* = 4.8 Hz, 1H), 8.46 (d, *J* = 7.8 Hz, 1H), 7.45-7.33 (m, 4H), 7.29 (t, *J* = 7.4 Hz, 1H), 7.24 (d, *J* = 7.8 Hz, 2H), 7.20 (t, *J* = 7.4 Hz, 3H), 7.10 (d, *J* = 7.4 Hz, 2H), 7.08 (d, *J* = 4.8 Hz, 1H), 6.92 (d, *J* = 7.6 Hz, 1H), 4.17 (dd, *J* = 8.9, 5.8 Hz, 1H), 3.25 (dd, *J* = 15.5, 9.3 Hz, 1H), 3.18 (dd, *J* = 15.5, 5.6 Hz, 1H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 153.0, 149.0, 147.4, 142.9, 140.5, 138.8, 135.0, 129.4, 128.7, 128.5, 128.5, 128.4, 128.0, 127.8, 127.5, 126.7, 125.7, 123.5, 44.0, 33.3; **HRMS** (ESI) m/z: $[M + H]^+$ calcd. for $C_{25}H_{20}N$ 334.1590; found 334.1596.



4-phenyl-6-propyl-5,6-dihydrobenzo[*h*]quinoline (25):

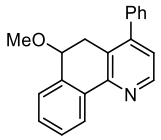
According to the general procedure, a mixture consisting of oxime (0.6 mmol, 185.6 mg), enal (0.2 mmol, 26.4 mg), $Fe(acac)_2$ (0.02 mmol, 5.0 mg), pyrrolidine·$HClO_4$ (0.04 mmol, 6.8 mg) and 1,4-dioxane (2 mL) under a N_2 atmosphere was stirred at 120 ℃ for 12 h to afford **25**. Colorless oil (13.9 mg, 23% yield); R_f = 0.6 (Petroleum ether/Ethyl acetate = 50:1); **^{1}H NMR** (600 MHz,

$CDCl_3$) δ 8.57 (d, *J* = 4.9 Hz, 1H), 8.37 (d, *J* = 7.6 Hz, 1H), 7.48 (t, *J* = 7.3 Hz, 2H), 7.43 (t, *J* = 7.3 Hz, 1H), 7.39 (t, *J* = 7.5 Hz, 1H), 7.36 – 7.30 (m, 3H), 7.19 (d, *J* = 7.4 Hz, 1H), 7.12 (d, *J* = 4.9 Hz, 1H), 3.03 (dd, *J* = 15.7, 5.5 Hz, 1H), 2.89 (dd, *J* = 15.7, 3.1 Hz, 1H), 2.85 – 2.79 (m, 1H), 1.41 – 1.34 (m, 1H), 1.32 – 1.27 (m, 1H), 1.22 – 1.17 (m, 1H), 1.16 – 1.08 (m, 1H), 0.78 (t, *J* = 7.3 Hz, 3H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 152.8, 149.4, 147.0, 142.2, 139.0, 133.9, 129.0, 128.7, 128.4, 128.0, 127.9, 127.6, 127.1, 125.7, 123.4, 37.6, 36.3, 30.4, 20.6, 14.0; **HRMS** (ESI) m/z: $[M + H]^+$ calcd. for $C_{25}H_{20}N$ 334.1590; found 334.1596.



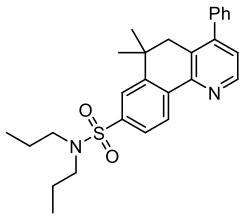
6-phenethyl-4-phenyl-5,6-dihydrobenzo[h]quinoline (26):

According to the general procedure, a mixture consisting of oxime (0.6 mmol, 222.9 mg), enal (0.2 mmol, 26.4 mg), $Fe(acac)_2$ (0.02 mmol, 5.0 mg), pyrrolidine·$HClO_4$ (0.04 mmol, 6.8 mg) and 1,4-dioxane (2 mL) under a N_2 atmosphere was stirred at 120 ℃ for 12 h to afford **26**. Colorless oil (16.0 mg, 22% yield); R_f = 0.55 (Petroleum ether/Ethyl acetate = 10:1); **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.56 (d, *J* = 4.9 Hz, 1H), 8.39 (d, *J* = 7.7 Hz, 1H), 7.47 (t, *J* = 7.4 Hz, 2H), 7.43 (t, *J* = 7.2 Hz, 1H), 7.40 (t, *J* = 7.5 Hz, 1H), 7.36-7.32 (m, 3H), 7.21 – 7.16 (m, 3H), 7.13-7.09 (m, 2H), 6.99 (d, *J* = 7.6 Hz, 2H), 3.05 (dd, *J* = 15.8, 5.5 Hz, 1H), 2.95 (dd, *J* = 15.8, 3.1 Hz, 1H), 2.87 – 2.82 (m, 1H), 2.52 – 2.45 (m, 1H), 2.43 – 2.36 (m, 1H), 1.77-1.69 (m, 1H), 1.66 – 1.62 (m, 1H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 152.8, 149.4, 147.1, 141.9, 141.7, 139.0, 134.0, 129.1, 128.7, 128.5, 128.2, 128.3, 128.0, 127.6, 127.6, 127.3, 125.9, 125.8, 123.4, 37.4, 35.7, 33.7, 30.3; **HRMS** (ESI) m/z: $[M + H]^+$ calcd. for $C_{27}H_{24}N$ 362.1903; found 362.1895.



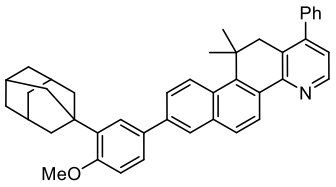
6-methoxy-4-phenyl-5,6-dihydrobenzo[h]quinoline (27):

According to the general procedure, a mixture consisting of oxime (0.6 mmol, 178.4 mg), enal (0.2 mmol, 26.4 mg), $Fe(acac)_2$ (0.02 mmol, 5.0 mg), pyrrolidine·$HClO_4$ (0.04 mmol, 6.8 mg) and 1,4-dioxane (2 mL) under a N_2 atmosphere was stirred at 120 ℃ for 12 h to afford **27**. White solid (18.0 mg, 31% yield); R_f = 0.5 (Petroleum ether/Ethyl acetate = 10:1); Mp = 128–130 ℃; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.58 (d, *J* = 4.8 Hz, 1H), 8.46 (d, *J* = 7.8 Hz, 1H), 7.51 (t, *J* = 7.3 Hz, 1H), 7.47 (t, *J* = 7.3 Hz, 2H), 7.45 – 7.36 (m, 5H), 7.14 (d, *J* = 4.8 Hz, 1H), 4.32 (t, *J* = 4.3 Hz, 1H), 3.26 (dd, *J* = 16.2, 4.9 Hz, 1H), 3.20 (s, 3H), 3.04 (dd, *J* = 16.2, 3.8 Hz, 1H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 152.04, 149.49, 147.29, 138.82, 135.90, 134.42, 129.04, 128.83, 128.78, 128.47, 128.03, 127.81, 126.38, 126.01, 123.58, 75.82, 56.11, 31.38; **HRMS** (ESI) m/z: $[M + H]^+$ calcd. for $C_{20}H_{18}NO$ 288.1383; found 288.1379.



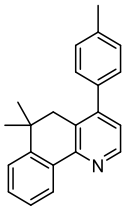
6,6-dimethyl-4-phenyl-N,N-dipropyl-5,6-dihydrobenzo[h]quinoline-8-sulfonamide (28):

According to the general procedure, a mixture consisting of oxime (0.6 mmol, 275.2 mg), enal (0.2 mmol, 26.4 mg), $Fe(acac)_2$ (0.02 mmol, 5.0 mg), pyrrolidine·$HClO_4$ (0.04 mmol, 6.8 mg) and 1,4-dioxane (2 mL) under a N_2 atmosphere was stirred at 120 ℃ for 12 h to afford **28**. White solid (71.0 mg, 79% yield); R_f = 0.45 (Petroleum ether/Ethyl acetate = 10:1); Mp = 99–101 ℃; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.60 (d, *J* = 4.9 Hz, 1H), 8.54 (d, *J* = 8.1 Hz, 1H), 7.80 (s, 1H), 7.79 (d, *J* = 8.2 Hz, 1H), 7.49 (t, *J* = 7.3 Hz, 2H), 7.45 (t, *J* = 7.3 Hz, 1H), 7.33 (d, *J* = 7.0 Hz, 2H), 7.18 (d, *J* = 4.9 Hz, 1H), 3.16 – 3.10 (m, 4H), 2.85 (s, 2H), 1.60 – 1.52 (m, 4H), 1.25 (s, 6H), 0.88 (t, *J* = 7.4 Hz, 6H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 151.3, 149.5, 147.5, 147.1, 140.8, 138.5, 137.2, 128.7, 128.7, 128.6, 128.2, 126.6, 125.3, 124.3, 122.8, 77.2, 77.0, 76.8, 49.8, 39.8, 34.1, 28.0, 21.8, 11.2; **HRMS** (ESI) m/z: $[M + H]^+$ calcd. for $C_{27}H_{33}N_2O_2S$ 449.2257; found 449.2258.



8-(3-(adamantan-1-yl)-4-methoxyphenyl)-11,11-dimethyl-1-phenyl-11,12-dihydronaphtho[1,2-h]quinoline (29):

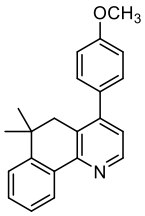
According to the general procedure, a mixture consisting of oxime (0.6 mmol, 351.4 mg), enal (0.2 mmol, 26.4 mg), $Fe(acac)_2$ (0.02 mmol, 5.0 mg), pyrrolidine·$HClO_4$ (0.04 mmol, 6.8 mg) and 1,4-dioxane (2 mL) under a N_2 atmosphere was stirred at 120 ℃ for 12 h to afford **29**. White solid (46.2 mg, 40% yield); R_f = 0.55 (Petroleum ether/Ethyl acetate = 10:1); Mp = 237–238 ℃; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.60 (d, *J* = 4.8 Hz, 1H), 8.57 (d, *J* = 8.5 Hz, 1H), 8.42 (d, *J* = 8.9 Hz, 1H), 8.02 (s, 1H), 7.89 (d, *J* = 8.5 Hz, 1H), 7.70 (d, *J* = 8.4 Hz, 1H), 7.62 (s, 1H), 7.55 (d, *J* = 7.2 Hz, 1H), 7.50 (t, *J* = 6.9 Hz, 2H), 7.45 (t, *J* = 6.9 Hz, 1H), 7.39 (d, *J* = 6.9 Hz, 2H), 7.12 (d, *J* = 4.6 Hz, 1H), 6.99 (d, *J* = 8.3 Hz, 1H), 3.90 (s, 3H), 2.95 (s, 2H), 2.20 (s, 6H), 2.10 (s, 3H), 1.81 (s, 6H), 1.61 (s, 6H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 158.7, 153.4, 148.4, 147.2, 142.7, 139.0, 138.8, 138.4, 136.1, 132.7, 132.0, 130.0, 128.8, 128.5, 128.0, 127.9, 127.1, 126.9, 126.1, 125.8, 125.4, 124.4, 124.3, 123.0, 112.2, 55.2, 43.7, 40.7, 37.3, 37.2, 36.0, 29.2, 28.9; **HRMS** (ESI) m/z: $[M + H]^+$ calcd. for $C_{42}H_{42}NO$ 576.3261; found 576.3260.



6,6-dimethyl-4-(p-tolyl)-5,6-dihydrobenzo[h]quinoline (30):

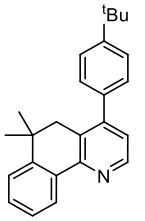
According to the general procedure, a mixture consisting of oxime (0.6 mmol, 177.2 mg), enal (0.2 mmol, 29.2 mg), $Fe(acac)_2$ (0.02 mmol, 5.0 mg), pyrrolidine·$HClO_4$ (0.04 mmol, 6.8 mg) and 1,4-dioxane (2 mL) under a N_2 atmosphere was stirred at 120 ℃ for 12 h to afford **30**. White solid (40.0 mg, 66% yield); R_f = 0.6 (Petroleum ether/Ethyl acetate = 10:1); Mp = 115–116 ℃; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.55 (d, *J* = 4.7 Hz, 1H), 8.44-8.38 (m, 1H), 7.40-7.34 (m, 3H), 7.28 (d, *J* = 7.6 Hz, 2H), 7.23 (d, *J* = 7.7 Hz, 2H), 7.10 (d, *J* = 4.8 Hz, 1H), 2.82 (s, 2H), 2.44 (s, 3H), 1.21 (s, 6H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 152.8, 149.1, 147.0, 146.3, 137.8, 136.0, 133.7, 129.6, 129.2, 128.7, 128.1, 126.7, 125.9, 123.7, 123.4, 40.1, 33.8, 28.1, 21.2; **HRMS** (ESI) m/z:

[M + H]$^+$ calcd. for $C_{22}H_{22}N$ 300.1747; Found 300.1751.



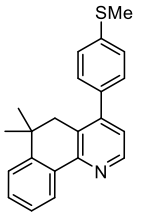
4-(4-methoxyphenyl)-6,6-dimethyl-5,6-dihydrobenzo[h]quinoline (31):

According to the general procedure, a mixture consisting of oxime (0.6 mmol, 177.2 mg), enal (0.2 mmol, 32.4 mg), $Fe(acac)_2$ (0.02 mmol, 5.0 mg), pyrrolidine·$HClO_4$ (0.04 mmol, 6.8 mg) and 1,4-dioxane (2 mL) under a N_2 atmosphere was stirred at 120 ℃ for 12 h to afford **31**. White solid (50.2 mg, 79% yield); R_f = 0.5 (Petroleum ether/Ethyl acetate = 10:1); Mp = 101–102 ℃; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.55 (d, *J* = 4.9 Hz, 1H), 8.44-8.38 (m, 1H), 7.39 – 7.35 (m, 3H), 7.28 (d, *J* = 8.4 Hz, 2H), 7.10 (d, *J* = 4.9 Hz, 1H), 7.01 (d, *J* = 8.4 Hz, 2H), 3.88 (s, 3H), 2.83 (s, 2H), 1.22 (s, 6H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 159.5, 152.8, 148.7, 147.0, 146.2, 133.7, 131.3, 130.0, 129.6, 128.1, 126.7, 125.9, 123.6, 123.4, 113.9, 55.3, 40.2, 33.9, 28.1; **HRMS** (ESI) m/z: [M + H]$^+$ calcd. for $C_{22}H_{22}NO$ 316.1696; Found 316.1699.



4-(4-(tert-butyl)phenyl)-6,6-dimethyl-5,6-dihydrobenzo[h]quinoline (32):

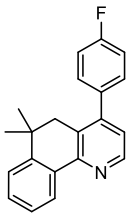
According to the general procedure, a mixture consisting of oxime (0.6 mmol, 177.2 mg), enal (0.2 mmol, 37.6 mg), $Fe(acac)_2$ (0.02 mmol, 5.0 mg), pyrrolidine·$HClO_4$ (0.04 mmol, 6.8 mg) and 1,4-dioxane (2 mL) under a N_2 atmosphere was stirred at 120 ℃ for 12 h to afford **32**. White solid (48.5 mg, 71% yield); R_f = 0.6 (Petroleum ether/Ethyl acetate = 10:1); Mp = 155–157 ℃; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.55 (d, *J* = 4.9 Hz, 1H), 8.43 – 8.39 (m, 1H), 7.49 (d, *J* = 8.3 Hz, 2H), 7.39 – 7.35 (m, 3H), 7.28 (d, *J* = 8.3 Hz, 2H), 7.11 (d, *J* = 4.9 Hz, 1H), 2.84 (s, 2H), 1.39 (s, 9H), 1.23 (s, 6H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 152.8, 151.0, 149.1, 147.0, 146.3, 136.0, 133.7, 129.6, 128.5, 128.2, 126.7, 125.9, 125.4, 123.7, 123.5, 40.2, 34.71, 33.9, 31.4, 28.2; **HRMS** (ESI) m/z: [M + H]$^+$ calcd. for $C_{25}H_{28}N$ 342.2216; Found 342.2215.



6,6-dimethyl-4-(4-(methylthio)phenyl)-5,6-dihydrobenzo[h]quinoline (33):

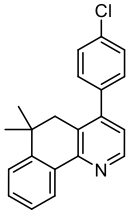
According to the general procedure, a mixture consisting of oxime (0.6 mmol, 177.2 mg), enal (0.2 mmol, 35.6 mg), $Fe(acac)_2$ (0.02 mmol, 5.0 mg), pyrrolidine·$HClO_4$ (0.04 mmol, 6.8 mg) and 1,4-dioxane (2 mL) under a N_2 atmosphere was stirred at 120 ℃ for 12 h to afford **33**. White solid (47.2 mg, 71% yield); R_f = 0.55 (Petroleum ether/Ethyl acetate = 10:1); Mp = 99–100 ℃; **^{1}H**

NMR (600 MHz, $CDCl_3$) δ 8.56 (d, *J* = 4.9 Hz, 1H), 8.42 – 8.39 (m, 1H), 7.41 – 7.37 (m, 3H), 7.35 (d, *J* = 8.3 Hz, 2H), 7.27 (d, *J* = 8.3 Hz, 2H), 7.09 (d, *J* = 4.9 Hz, 1H), 2.81 (s, 2H), 2.55 (s, 3H), 1.22 (s, 6H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 152.9, 148.4, 147.1, 146.2, 138.7, 135.6, 133.6, 129.6, 129.2, 128.0, 126.7, 126.3, 125.9, 123.7, 123.2, 40.2, 33.8, 28.1, 15.6; **HRMS** (ESI) m/z: $[M + H]^+$ calcd. for $C_{22}H_{22}NS$ 332.1467; Found 332.1467.



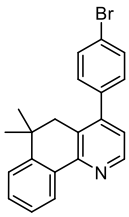
4-(4-fluorophenyl)-6,6-dimethyl-5,6-dihydrobenzo[h]quinoline (34):

According to the general procedure, a mixture consisting of oxime (0.6 mmol, 177.2 mg), enal (0.2 mmol, 30.0 mg), $Fe(acac)_2$ (0.02 mmol, 5.0 mg), pyrrolidine·$HClO_4$ (0.04 mmol, 6.8 mg) and 1,4-dioxane (2 mL) under a N_2 atmosphere was stirred at 120 ℃ for 12 h to afford **34**. White solid (26.4 mg, 43% yield); R_f = 0.6 (Petroleum ether/Ethyl acetate = 10:1); Mp = 129–130 ℃; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.56 (d, *J* = 4.8 Hz, 1H), 8.44 – 8.38 (m, 1H), 7.40 – 7.35 (m, 3H), 7.33 – 7.28 (m, 2H), 7.17 (t, *J* = 8.2 Hz, 2H), 7.08 (d, *J* = 4.6 Hz, 1H), 2.77 (s, 2H), 1.22 (s, 6H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 162.6 (d, $^1J_{C\text{-}F}$ = 247.9 Hz), 152.9, 148.0, 147.1, 146.2, 134.9, 133.5, 130.4 (d, $^3J_{C\text{-}F}$ = 8.2 Hz), 129.7, 128.1, 126.8, 125.9, 123.7, 123.2, 115.5 (d, $^2J_{C\text{-}F}$ = 21.6 Hz), 40.2, 33.8, 28.1; **^{19}F NMR** (565 MHz, $CDCl_3$) δ -113.95; **HRMS** (ESI) m/z: $[M + H]^+$ calcd. for $C_{21}H_{19}FN$ 304.1496; Found 304.1495.



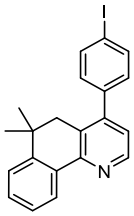
4-(4-chlorophenyl)-6,6-dimethyl-5,6-dihydrobenzo[h]quinoline (35):

According to the general procedure, a mixture consisting of oxime (0.6 mmol, 177.2 mg), enal (0.2 mmol, 33.3 mg), $Fe(acac)_2$ (0.02 mmol, 5.0 mg), pyrrolidine·$HClO_4$ (0.04 mmol, 6.8 mg) and 1,4-dioxane (2 mL) under a N_2 atmosphere was stirred at 120 ℃ for 12 h to afford **35**. White solid (39.0 mg, 60% yield); R_f = 0.6 (Petroleum ether/Ethyl acetate = 10:1); Mp = 137–139 ℃; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.57 (d, *J* = 4.8 Hz, 1H), 8.43 – 8.39 (m, 1H), 7.46 (d, *J* = 8.2 Hz, 2H), 7.41 – 7.35 (m, 3H), 7.27 (d, *J* = 8.3 Hz, 2H), 7.07 (d, *J* = 4.8 Hz, 1H), 2.77 (s, 2H), 1.22 (s, 6H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 153.0, 147.8, 147.2, 146.2, 137.4, 134.2, 133.4, 130.1, 129.8, 128.7, 127.9, 126.8, 125.9, 123.7, 123.0, 40.1, 33.8, 28.1; **HRMS** (ESI) m/z: $[M + H]^+$ calcd. for $C_{21}H_{19}ClN$ 320.1201; Found 320.1200.



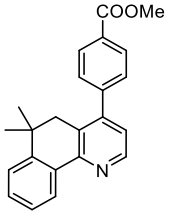
4-(4-bromophenyl)-6,6-dimethyl-5,6-dihydrobenzo[h]quinoline (36):

According to the general procedure, a mixture consisting of oxime (0.6 mmol, 177.2 mg), enal (0.2 mmol, 42.2 mg), $Fe(acac)_2$ (0.02 mmol, 5.0 mg), pyrrolidine·$HClO_4$ (0.04 mmol, 6.8 mg) and 1,4-dioxane (2 mL) under a N_2 atmosphere was stirred at 120 ℃ for 12 h to afford **36**. White solid (49.7 mg, 68% yield); R_f = 0.6 (Petroleum ether/Ethyl acetate = 10:1); Mp = 132–133 ℃; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.57 (d, *J* = 4.9 Hz, 1H), 8.43-8.39 (m, 1H), 7.61 (d, *J* = 8.2 Hz, 2H), 7.41 – 7.35 (m, 3H), 7.21 (d, *J* = 8.2 Hz, 2H), 7.07 (d, *J* = 4.9 Hz, 1H), 2.77 (s, 2H), 1.21 (s, 6H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 153.0, 147.9, 147.2, 146.2, 137.8, 133.4, 131.7, 130.4, 129.8, 127.9, 126.8, 126.0, 123.8, 123.0, 122.3, 40.2, 33.9, 28.2; **HRMS** (ESI) m/z: $[M + H]^+$ calcd. for $C_{21}H_{19}BrN$ 364.0695; Found 364.0695.



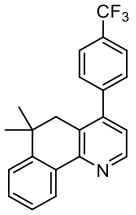
4-(4-iodophenyl)-6,6-dimethyl-5,6-dihydrobenzo[h]quinoline (37):

According to the general procedure, a mixture consisting of oxime (0.6 mmol, 177.2 mg), enal (0.2 mmol, 51.6 mg), $Fe(acac)_2$ (0.02 mmol, 5.0 mg), pyrrolidine·$HClO_4$ (0.04 mmol, 6.8 mg) and 1,4-dioxane (2 mL) under a N_2 atmosphere was stirred at 120 ℃ for 12 h to afford **37**. White solid (49.5 mg, 60% yield); R_f = 0.6 (Petroleum ether/Ethyl acetate = 10:1); Mp = 67–69 ℃; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.56 (d, *J* = 4.9 Hz, 1H), 8.42 – 8.39 (m, 1H), 7.81 (d, *J* = 8.3 Hz, 2H), 7.39 – 7.35 (m, 3H), 7.08 (d, *J* = 8.3 Hz, 2H), 7.06 (d, *J* = 5.0 Hz, 1H), 2.76 (s, 2H), 1.21 (s, 6H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 153.0, 147.9, 147.2, 146.2, 138.5, 137.7, 133.4, 130.6, 129.8, 127.8, 126.8, 126.0, 123.7, 122.9, 93.9, 40.1, 33.8, 28.2; **HRMS** (ESI) m/z: $[M + H]^+$ calcd. for $C_{21}H_{19}IN$ 412.0557; Found 412.0555.



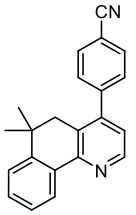
methyl 4-(6,6-dimethyl-5,6-dihydrobenzo[h]quinolin-4-yl)benzoate (38):

According to the general procedure, a mixture consisting of oxime (0.6 mmol, 177.2 mg), enal (0.2 mmol, 38.0 mg), $Fe(acac)_2$ (0.02 mmol, 5.0 mg), pyrrolidine·$HClO_4$ (0.04 mmol, 6.8 mg) and 1,4-dioxane (2 mL) under a N_2 atmosphere was stirred at 120 ℃ for 12 h to afford **38**. White solid (47.0 mg, 68% yield); R_f = 0.45 (Petroleum ether/Ethyl acetate = 10:1); Mp = 146–148 ℃; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.59 (d, *J* = 4.9 Hz, 1H), 8.44-8.40 (m, 1H), 8.15 (d, *J* = 8.2 Hz, 2H), 7.42 (d, *J* = 8.1 Hz, 2H), 7.40 – 7.35 (m, 3H), 7.10 (d, *J* = 4.9 Hz, 1H), 3.97 (s, 3H), 2.76 (s, 2H), 1.21 (s, 6H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 166.7, 153.0, 148.0, 147.2, 146.2, 143.6, 133.3, 129.9, 129.8, 129.8, 128.8, 127.8, 126.8, 126.0, 123.7, 122.8, 52.2, 40.1, 33.8, 28.1; **HRMS** (ESI) m/z: $[M + H]^+$ calcd. for $C_{23}H_{22}NO_2$ 344.1645; Found 344.1641.



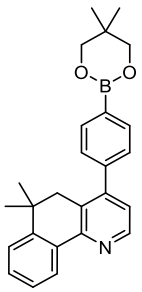
6,6-dimethyl-4-(4-(trifluoromethyl)phenyl)-5,6-dihydrobenzo[h]quinoline (39):

According to the general procedure, a mixture consisting of oxime (0.6 mmol, 177.2 mg), enal (0.2 mmol, 40.0 mg), $Fe(acac)_2$ (0.02 mmol, 5.0 mg), pyrrolidine·$HClO_4$ (0.04 mmol, 6.8 mg) and 1,4-dioxane (2 mL) under a N_2 atmosphere was stirred at 120 ℃ for 12 h to afford **39**. White solid (45.2 mg, 64% yield); R_f = 0.6 (Petroleum ether/Ethyl acetate = 10:1); Mp = 150–152 ℃; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.60 (d, *J* = 4.9 Hz, 1H), 8.42 (d, *J* = 7.7 Hz, 1H), 7.75 (d, *J* = 8.0 Hz, 2H), 7.46 (d, *J* = 7.9 Hz, 2H), 7.42 – 7.36 (m, 3H), 7.09 (d, *J* = 4.9 Hz, 1H), 2.76 (s, 2H), 1.22 (s, 6H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 153.09, 147.59, 147.26, 146.14, 142.62, 133.27, 130.3 (q, $^2J_{C\text{-}F}$ = 32.6 Hz), 129.89, 129.14, 127.85, 126.83, 125.98, 125.5 (q, $^3J_{C\text{-}F}$ = 3.8 Hz), 124.1 (q, $^1J_{C\text{-}F}$ = 272.2 Hz), 123.74, 122.88, 40.11, 33.82, 28.13; **^{19}F NMR** (565 MHz, $CDCl_3$) δ -62.57; **HRMS** (ESI) m/z: $[M + H]^+$ calcd. for $C_{22}H_{19}F_3N$ 354.1464; Found 354.1459.



4-(6,6-dimethyl-5,6-dihydrobenzo[h]quinolin-4-yl)benzonitrile (40):

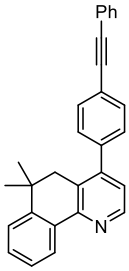
According to the general procedure, a mixture consisting of oxime (0.6 mmol, 177.2 mg), enal (0.2 mmol, 31.4 mg), $Fe(acac)_2$ (0.02 mmol, 5.0 mg), pyrrolidine·$HClO_4$ (0.04 mmol, 6.8 mg) and 1,4-dioxane (2 mL) under a N_2 atmosphere was stirred at 120 ℃ for 12 h to afford **40**. White solid (38.0 mg, 61% yield); R_f = 0.3 (Petroleum ether/Ethyl acetate = 10:1); Mp = 183–184 ℃; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.60 (d, *J* = 4.9 Hz, 1H), 8.43-8.40 (m, 1H), 7.78 (d, *J* = 8.1 Hz, 2H), 7.45 (d, *J* = 8.1 Hz, 2H), 7.42 – 7.35 (m, 3H), 7.07 (d, *J* = 4.9 Hz, 1H), 2.73 (s, 2H), 1.22 (s, 6H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 153.2, 147.4, 147.0, 146.1, 143.7, 133.1, 132.3, 130.0, 129.6, 127.6, 126.9, 126.0, 123.8, 122.6, 118.4, 112.6, 40.1, 33.8, 28.2; **HRMS** (ESI) m/z: $[M + H]^+$ calcd. for $C_{22}H_{19}N_2$ 311.1543; Found 311.1542.



4-(4-(5,5-dimethyl-1,3,2-dioxaborinan-2-yl)phenyl)-6,6-dimethyl-5,6-dihydrobenzo[h]quinoline (41):

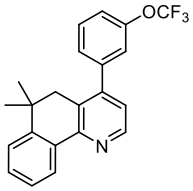
According to the general procedure, a mixture consisting of oxime (0.6 mmol, 177.2 mg), enal

(0.2 mmol, 48.8 mg), $Fe(acac)_2$ (0.02 mmol, 5.0 mg), pyrrolidine·$HClO_4$ (0.04 mmol, 6.8 mg) and 1,4-dioxane (2 mL) under a N_2 atmosphere was stirred at 120 ℃ for 12 h to afford **41**. White solid (47.7 mg, 60% yield); R_f = 0.2 (Petroleum ether/Ethyl acetate = 10:1); Mp = 137–138 ℃; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.56 (d, *J* = 4.9 Hz, 1H), 8.43-8.39 (m, 1H), 7.91 (d, *J* = 7.9 Hz, 2H), 7.39-7.35 (m, 3H), 7.33 (d, *J* = 8.0 Hz, 2H), 7.12 (d, *J* = 4.9 Hz, 1H), 3.81 (s, 4H), 2.80 (s, 2H), 1.20 (s, 6H), 1.05 (s, 6H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 152.8, 149.2, 147.0, 146.3, 141.1, 133.9, 133.6, 129.6, 128.1, 128.0, 126.7, 125.9, 123.7, 123.2, 72.4, 40.1, 33.8, 31.9, 28.1, 21.9; **HRMS** (ESI) m/z: $[M + H]^+$ calcd. for $C_{26}H_{29}BNO_2$ 398.2286; Found 398.2289.



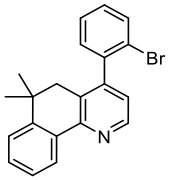
6,6-dimethyl-4-(4-(phenylethynyl)phenyl)-5,6-dihydrobenzo[h]quinoline (42):

According to the general procedure, a mixture consisting of oxime (0.6 mmol, 177.2 mg), enal (0.2 mmol, 46.4 mg), $Fe(acac)_2$ (0.02 mmol, 5.0 mg), pyrrolidine·$HClO_4$ (0.04 mmol, 6.8 mg) and 1,4-dioxane (2 mL) under a N_2 atmosphere was stirred at 120 ℃ for 12 h to afford **42**. White solid (41.8 mg, 54% yield); R_f = 0.6 (Petroleum ether/Ethyl acetate = 10:1); Mp = 165–166 ℃; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.58 (d, *J* = 4.8 Hz, 1H), 8.45 – 8.40 (m, 1H), 7.64 (d, *J* = 7.9 Hz, 2H), 7.59 – 7.53 (m, 2H), 7.42 – 7.34 (m, 6H), 7.33 (d, *J* = 8.0 Hz, 2H), 7.11 (d, *J* = 4.9 Hz, 1H), 2.80 (s, 2H), 1.22 (s, 6H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 153.0, 148.4, 147.2, 146.2, 138.8, 133.5, 131.7, 129.7, 128.8, 128.5, 128.4, 127.9, 126.8, 125.9, 123.7, 123.2, 123.0, 90.4, 88.9, 40.2, 33.9, 28.2; **HRMS** (ESI) m/z: $[M + H]^+$ calcd. for $C_{29}H_{24}N$ 386.1903; Found 386.1902.



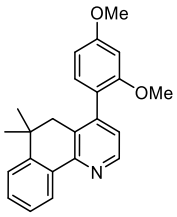
6,6-dimethyl-4-(3-(trifluoromethoxy)phenyl)-5,6-dihydrobenzo[h]quinoline (43):

According to the general procedure, a mixture consisting of oxime (0.6 mmol, 177.2 mg), enal (0.2 mmol, 43.2 mg), $Fe(acac)_2$ (0.02 mmol, 5.0 mg), pyrrolidine·$HClO_4$ (0.04 mmol, 6.8 mg) and 1,4-dioxane (2 mL) under a N_2 atmosphere was stirred at 120 ℃ for 12 h to afford **43**. White solid (35.5 mg, 48% yield); R_f = 0.5 (Petroleum ether/Ethyl acetate = 10:1); Mp = 55–57 ℃; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.59 (d, *J* = 4.9 Hz, 1H), 8.44 – 8.40 (m, 1H), 7.51 (t, *J* = 7.9 Hz, 1H), 7.42 – 7.35 (m, 3H), 7.28 (t, *J* = 9.5 Hz, 2H), 7.21 (s, 1H), 7.09 (d, *J* = 4.9 Hz, 1H), 2.77 (s, 2H), 1.23 (s, 6H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 153.1, 149.3, 147.4, 147.3, 146.2, 141.0, 133.3, 130.0, 129.8, 127.9, 127.1, 126.8, 126.0, 123.7, 122.9, 121.3, 120.5 (q, $^1J_{C\text{-}F}$ = 257.7 Hz), 120.3, 40.0, 33.8, 28.1; **^{19}F NMR** (565 MHz, $CDCl_3$) δ -57.79; **HRMS** (ESI) m/z: $[M + H]^+$ calcd. for $C_{22}H_{19}F_3NO$ 370.1413; Found 370.1411.



4-(2-bromophenyl)-6,6-dimethyl-5,6-dihydrobenzo[h]quinoline (44):

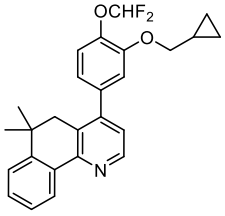
According to the general procedure, a mixture consisting of oxime (0.6 mmol, 177.2 mg), enal (0.2 mmol, 42.2 mg), $Fe(acac)_2$ (0.02 mmol, 5.0 mg), pyrrolidine·$HClO_4$ (0.04 mmol, 6.8 mg) and 1,4-dioxane (2 mL) under a N_2 atmosphere was stirred at 120 ℃ for 12 h to afford **44**. White solid (40.8 mg, 56% yield); R_f = 0.6 (Petroleum ether/Ethyl acetate = 10:1); Mp = 144–145 ℃; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.59 (d, *J* = 4.9 Hz, 1H), 8.46 – 8.41 (m, 1H), 7.70 (d, *J* = 8.0 Hz, 1H), 7.43 – 7.35 (m, 4H), 7.32 – 7.27 (m, 1H), 7.18 (dd, *J* = 7.5, 1.3 Hz, 1H), 7.01 (d, *J* = 4.9 Hz, 1H), 2.61 (d, *J* = 15.7 Hz, 1H), 2.50 (d, *J* = 15.7 Hz, 1H), 1.25 (s, 3H), 1.20 (s, 3H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 152.7, 148.4, 147.0, 146.3, 139.9, 133.3, 132.9, 130.2, 129.7, 129.5, 128.8, 127.4, 126.7, 125.8, 123.8, 123.1, 122.7, 39.8, 33.7, 28.5, 28.2; **HRMS** (ESI) m/z: $[M + H]^+$ calcd. for $C_{21}H_{19}BrN$ 364.0695; Found 364.0693.



4-(2,4-dimethoxyphenyl)-6,6-dimethyl-5,6-dihydrobenzo[h]quinoline (45):

According to the general procedure, a mixture consisting of oxime (0.6 mmol, 177.2 mg), enal (0.2 mmol, 38.4 mg), $Fe(acac)_2$ (0.02 mmol, 5.0 mg), pyrrolidine·$HClO_4$ (0.04 mmol, 6.8 mg) and 1,4-dioxane (2 mL) under a N_2 atmosphere was stirred at 120 ℃ for 12 h to afford **45**. White solid (48.0 mg, 69% yield); R_f = 0.4 (Petroleum ether/Ethyl acetate = 10:1); Mp = 107–109 ℃; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.53 (d, *J* = 4.9 Hz, 1H), 8.42 – 8.39 (m, 1H), 7.38 – 7.34 (m, 3H), 7.08 (d, *J* = 8.2 Hz, 1H), 7.04 (d, *J* = 4.9 Hz, 1H), 6.59 (dd, *J* = 8.2, 2.3 Hz, 1H), 6.57 (d, *J* = 2.2 Hz, 1H), 3.88 (s, 3H), 3.73 (s, 3H), 2.71 (d, *J* = 15.5 Hz, 1H), 2.53 (d, *J* = 15.5 Hz, 1H), 1.26 (s, 3H), 1.14 (s, 3H);

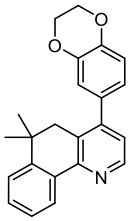
^{13}C NMR (151 MHz, $CDCl_3$) δ 161.1, 157.5, 152.1, 146.8, 146.4, 146.3, 133.8, 130.9, 130.1, 129.4, 126.6, 125.8, 124.3, 123.7, 120.8, 104.6, 98.8, 55.4, 55.4, 40.0, 33.7, 28.3; **HRMS** (ESI) m/z: $[M + H]^+$ calcd. for $C_{23}H_{24}NO_2$ 346.1802; Found 346.1800.



4-(3-(cyclopropylmethoxy)-4-(difluoromethoxy)phenyl)-6,6-dimethyl-5,6-dihydrobenzo[h]quinoline (46):

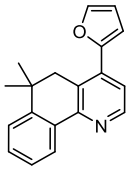
According to the general procedure, a mixture consisting of oxime (0.6 mmol, 177.2 mg), enal (0.2 mmol, 53.6 mg), $Fe(acac)_2$ (0.02 mmol, 5.0 mg), pyrrolidine·$HClO_4$ (0.04 mmol, 6.8 mg) and

1,4-dioxane (2 mL) under a N_2 atmosphere was stirred at 120 ℃ for 12 h to afford **46**. White solid (46.1 mg, 54% yield); R_f = 0.5 (Petroleum ether/Ethyl acetate = 10:1); Mp = 104–105 ℃; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.56 (d, *J* = 4.9 Hz, 1H), 8.43 – 8.38 (m, 1H), 7.41 – 7.35 (m, 3H), 7.25 (d, *J* = 7.8 Hz, 1H), 7.08 (d, *J* = 4.9 Hz, 1H), 6.90 (s, 1H), 6.89 – 6.86 (m, 1H), 6.71 (t, *J* = 75.4 Hz, 1H), 3.90 (d, *J* = 6.8 Hz, 2H), 2.78 (s, 2H), 1.34 – 1.27 (m, 1H), 1.23 (s, 6H), 0.66 (q, *J* = 5.7 Hz, 2H), 0.37 (q, *J* = 5.0 Hz, 2H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 153.0, 150.5, 148.2, 147.2, 146.2, 140.3, 137.5, 133.5, 129.8, 128.0, 126.8, 126.0, 123.8, 123.1, 122.7, 121.6, 116.3 (t, $^1J_{C\text{-}F}$ = 260.2 Hz), 115.3, 74.2, 40.2, 33.9, 28.2, 10.2, 3.2; **^{19}F NMR** (565 MHz, $CDCl_3$) δ -81.53; **HRMS** (ESI) m/z: $[M + H]^+$ calcd. for $C_{26}H_{26}F_2NO_2$ 422.1926; Found 422.1924.



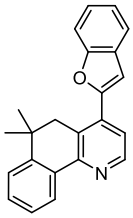
4-(2,3-dihydrobenzo[b][1,4]dioxin-6-yl)-6,6-dimethyl-5,6-dihydrobenzo[h]quinoline (47):

According to the general procedure, a mixture consisting of oxime (0.6 mmol, 177.2 mg), enal (0.2 mmol, 38.0 mg), $Fe(acac)_2$ (0.02 mmol, 5.0 mg), pyrrolidine·$HClO_4$ (0.04 mmol, 6.8 mg) and 1,4-dioxane (2 mL) under a N_2 atmosphere was stirred at 120 ℃ for 12 h to afford **47**. White solid (48.5 mg, 70% yield); R_f = 0.4 (Petroleum ether/Ethyl acetate = 10:1); Mp = 144–146 ℃; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.53 (d, *J* = 4.9 Hz, 1H), 8.42 – 8.37 (m, 1H), 7.39 – 7.34 (m, 3H), 7.08 (d, *J* = 4.9 Hz, 1H), 6.96 (d, *J* = 8.2 Hz, 1H), 6.86 (d, *J* = 2.0 Hz, 1H), 6.81 (dd, *J* = 8.2, 2.1 Hz, 1H), 4.32 (s, 4H), 2.84 (s, 2H), 1.22 (s, 6H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 152.8, 148.5, 147.0, 146.3, 143.5, 143.4, 133.7, 132.2, 129.6, 128.1, 126.7, 125.9, 123.6, 123.3, 122.0, 117.7, 117.3, 64.5, 64.4, 40.2, 33.9, 28.1; **HRMS** (ESI) m/z: $[M + H]^+$ calcd. for $C_{23}H_{22}NO_2$ 344.1645; Found 344.1645.



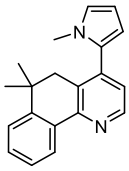
4-(furan-2-yl)-6,6-dimethyl-5,6-dihydrobenzo[h]quinoline (48):

According to the general procedure, a mixture consisting of oxime (0.6 mmol, 177.2 mg), enal (0.2 mmol, 24.4 mg), $Fe(acac)_2$ (0.02 mmol, 5.0 mg), pyrrolidine·$HClO_4$ (0.04 mmol, 6.8 mg) and 1,4-dioxane (2 mL) under a N_2 atmosphere was stirred at 120 ℃ for 12 h to afford **48**. Yellow oil (28.8 mg, 52% yield); R_f = 0.55 (Petroleum ether/Ethyl acetate = 10:1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.56 (d, *J* = 5.1 Hz, 1H), 8.39 – 8.33 (m, 1H), 7.62-7.58 (m, 1H), 7.46 (d, *J* = 5.1 Hz, 1H), 7.42 – 7.33 (m, 3H), 6.70 (d, *J* = 3.3 Hz, 1H), 6.59-6.55 (m, 1H), 3.07 (s, 2H), 1.29 (s, 6H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 153.2, 151.0, 147.2, 145.9, 143.3, 136.9, 133.4, 129.7, 126.7, 126.4, 126.0, 123.6, 120.0, 111.7, 111.6, 40.4, 33.6, 28.6; **HRMS** (ESI) m/z: $[M + H]^+$ calcd. for $C_{19}H_{18}NO$ 276.1383; Found 276.1382.



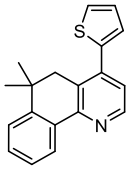
4-(benzofuran-2-yl)-6,6-dimethyl-5,6-dihydrobenzo[h]quinoline (49):

According to the general procedure, a mixture consisting of oxime (0.6 mmol, 177.2 mg), enal (0.2 mmol, 34.4 mg), $Fe(acac)_2$ (0.02 mmol, 5.0 mg), pyrrolidine·$HClO_4$ (0.04 mmol, 6.8 mg) and 1,4-dioxane (2 mL) under a N_2 atmosphere was stirred at 120 ℃ for 12 h to afford **49**. White solid (28.7 mg, 44% yield); R_f = 0.55 (Petroleum ether/Ethyl acetate = 10:1); Mp = 153–154 ℃; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.64 (d, *J* = 5.0 Hz, 1H), 8.40 (d, *J* = 7.4 Hz, 1H), 7.67 (d, *J* = 7.7 Hz, 1H), 7.61 (d, *J* = 5.0 Hz, 1H), 7.59 (d, *J* = 8.3 Hz, 1H), 7.44 – 7.35 (m, 4H), 7.30 (t, *J* = 7.4 Hz, 1H), 7.03 (s, 1H), 3.16 (s, 2H), 1.30 (s, 6H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 155.0, 153.4, 152.9, 147.5, 146.0, 137.0, 133.4, 129.8, 128.7, 127.6, 126.8, 126.1, 125.4, 123.7, 123.3, 121.5, 120.9, 111.5, 108.0, 40.6, 33.8, 28.6; **HRMS** (ESI) m/z: $[M + H]^+$ calcd. for $C_{23}H_{20}NO$ 326.1539; Found 326.1538.



6,6-dimethyl-4-(1-methyl-1H-pyrrol-2-yl)-5,6-dihydrobenzo[h]quinoline (50):

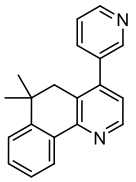
According to the general procedure, a mixture consisting of oxime (0.6 mmol, 177.2 mg), enal (0.2 mmol, 27.0 mg), $Fe(acac)_2$ (0.02 mmol, 5.0 mg), pyrrolidine·$HClO_4$ (0.04 mmol, 6.8 mg) and 1,4-dioxane (2 mL) under a N_2 atmosphere was stirred at 120 ℃ for 12 h to afford **50**. Yellow oil (27.7 mg, 48% yield); R_f = 0.5 (Petroleum ether/Ethyl acetate = 10:1); **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.55 (d, *J* = 4.7 Hz, 1H), 8.43-8.38 (m, 1H), 7.39 – 7.34 (m, 3H), 7.09 (d, *J* = 4.7 Hz, 1H), 6.78-6.75 (m, 1H), 6.27-6.23 (m, 1H), 6.16-6.12 (m, 1H), 3.48 (s, 3H), 2.76 (s, 2H), 1.22 (s, 6H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 153.0, 146.9, 146.4, 140.7, 133.5, 130.4, 130.1, 129.7, 126.8, 125.9, 124.3, 123.8, 123.3, 110.1, 108.0, 40.2, 34.5, 33.8, 28.2; **HRMS** (ESI) m/z: $[M + H]^+$ calcd. for $C_{20}H_{21}N_2$ 289.1699; Found 289.1695.



6,6-dimethyl-4-(thiophen-2-yl)-5,6-dihydrobenzo[h]quinoline (51):

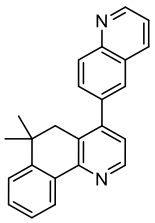
According to the general procedure, a mixture consisting of oxime (0.6 mmol, 177.2 mg), enal (0.2 mmol, 27.6 mg), $Fe(acac)_2$ (0.02 mmol, 5.0 mg), pyrrolidine·$HClO_4$ (0.04 mmol, 6.8 mg) and 1,4-dioxane (2 mL) under a N_2 atmosphere was stirred at 120 ℃ for 12 h to afford **51**. Yellow oil (36.8 mg, 63% yield); R_f = 0.5 (Petroleum ether/Ethyl acetate = 10:1); **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.54 (d, *J* = 4.9 Hz, 1H), 8.39 (d, *J* = 6.8 Hz, 1H), 7.44 (d, *J* = 4.6 Hz, 1H), 7.41 – 7.34 (m, 3H), 7.24 (d, *J* = 4.9 Hz, 1H), 7.17 – 7.13 (m, 2H), 3.00 (s, 2H), 1.25 (s, 6H); **^{13}C NMR** (151

MHz, $CDCl_3$) δ 153.2, 147.1, 146.2, 141.6, 139.9, 133.5, 129.7, 128.3, 127.8, 127.5, 126.7, 126.7, 126.0, 123.7, 123.5, 40.3, 33.8, 28.3; **HRMS** (ESI) m/z: $[M + H]^+$ calcd. for $C_{19}H_{18}NS$ 292.1154; Found 292.1153.



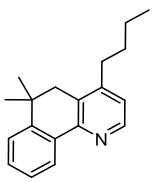
6,6-dimethyl-4-(pyridin-3-yl)-5,6-dihydrobenzo[h]quinoline (52):

According to the general procedure, a mixture consisting of oxime (0.6 mmol, 177.2 mg), enal (0.2 mmol, 26.6 mg), $Fe(acac)_2$ (0.02 mmol, 5.0 mg), pyrrolidine·$HClO_4$ (0.04 mmol, 6.8 mg) and 1,4-dioxane (2 mL) under a N_2 atmosphere was stirred at 120 ℃ for 12 h to afford **52**. Yellow oil (43.0 mg, 75% yield); R_f = 0.3 (Petroleum ether/Ethyl acetate = 10:1); **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.71-8.68 (m, 1H), 8.64 (s, 1H), 8.61 (d, *J* = 4.8 Hz, 1H), 8.44-8.40 (m, 1H), 7.68 (d, *J* = 7.7 Hz, 1H), 7.43 (dd, *J* = 7.3, 5.3 Hz, 1H), 7.41-7.36 (m, 3H), 7.11 (d, *J* = 4.8 Hz, 1H), 2.79 (s, 2H), 1.23 (s, 6H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 153.2, 149.5, 149.3, 147.4, 146.1, 145.3, 136.1, 134.6, 133.2, 129.9, 128.2, 126.8, 126.0, 123.7, 123.3, 123.1, 40.1, 33.8, 28.2; **HRMS** (ESI) m/z: $[M + H]^+$ calcd. for $C_{20}H_{19}N_2$ 287.1543; Found 287.1543.



6,6-dimethyl-4-(quinolin-6-yl)-5,6-dihydrobenzo[h]quinoline (53):

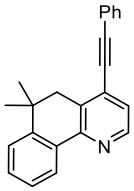
According to the general procedure, a mixture consisting of oxime (0.6 mmol, 177.2 mg), enal (0.2 mmol, 36.6 mg), $Fe(acac)_2$ (0.02 mmol, 5.0 mg), pyrrolidine·$HClO_4$ (0.04 mmol, 6.8 mg) and 1,4-dioxane (2 mL) under a N_2 atmosphere was stirred at 120 ℃ for 12 h to afford **53**. White solid (54.0 mg, 80% yield); R_f = 0.4 (Petroleum ether/Ethyl acetate = 10:1); Mp = 148–149 ℃; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 9.00 (d, *J* = 4.0 Hz, 1H), 8.63 (d, *J* = 4.9 Hz, 1H), 8.46-8.43 (m, 1H), 8.24-8.21 (m, 2H), 7.80 (s, 1H), 7.70 (dd, *J* = 8.6, 1.5 Hz, 1H), 7.49 (dd, *J* = 8.2, 4.2 Hz, 1H), 7.42 – 7.38 (m, 3H), 7.21 (d, *J* = 4.9 Hz, 1H), 2.84 (s, 2H), 1.22 (s, 6H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 153.1, 151.0, 148.3, 147.8, 147.3, 146.2, 137.4, 136.2, 133.5, 130.4, 129.9, 129.7, 128.2, 128.2, 127.7, 126.9, 126.0, 123.8, 123.4, 121.8, 40.3, 33.9, 28.2; **HRMS** (ESI) m/z: $[M + H]^+$ calcd. for $C_{24}H_{21}N_2$ 337.1699; Found 337.1690.



4-butyl-6,6-dimethyl-5,6-dihydrobenzo[h]quinoline (54):

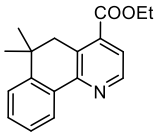
According to the general procedure, a mixture consisting of oxime (0.6 mmol, 177.2 mg), enal (0.2 mmol, 22.4 mg), $Fe(acac)_2$ (0.02 mmol, 5.0 mg), pyrrolidine·$HClO_4$ (0.04 mmol, 6.8 mg) and 1,4-dioxane (2 mL) under a N_2 atmosphere was stirred at 120 ℃ for 12 h to afford **54**. Colorless

oil (18.3 mg, 34% yield); R_f = 0.6 (Petroleum ether/Ethyl acetate = 10:1); **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.42 (d, *J* = 4.9 Hz, 1H), 8.37 – 8.34 (m, 1H), 7.40 – 7.32 (m, 3H), 7.00 (d, *J* = 4.9 Hz, 1H), 2.81 (s, 2H), 2.65 (t, *J* = 7.8 Hz, 2H), 1.61 – 1.54 (m, 2H), 1.45 – 1.38 (m, 2H), 1.30 (s, 6H), 0.96 (t, *J* = 7.3 Hz, 3H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 152.0, 149.2, 147.0, 145.9, 133.7, 129.3, 128.9, 126.7, 125.8, 123.6, 123.2, 38.8, 33.7, 32.2, 32.0, 28.4, 22.5, 13.9; **HRMS** (ESI) m/z: $[M + H]^+$ calcd. for $C_{19}H_{24}N$ 266.1903; Found 266.1900.



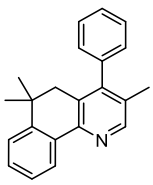
6,6-dimethyl-4-(phenylethynyl)-5,6-dihydrobenzo[h]quinoline (55):

According to the general procedure, a mixture consisting of oxime (0.6 mmol, 177.2 mg), enal (0.2 mmol, 31.2 mg), $Fe(acac)_2$ (0.02 mmol, 5.0 mg), pyrrolidine·$HClO_4$ (0.04 mmol, 6.8 mg) and 1,4-dioxane (2 mL) under a N_2 atmosphere was stirred at 120 ℃ for 12 h to afford **55**. White solid (30.0 mg, 48% yield); R_f = 0.6 (Petroleum ether/Ethyl acetate = 10:1); Mp = 142–144 ℃; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.52 (d, *J* = 4.9 Hz, 1H), 8.37 (d, *J* = 7.4 Hz, 1H), 7.62 – 7.57 (m, 2H), 7.44 – 7.38 (m, 5H), 7.38 – 7.34 (m, 1H), 7.29 (d, *J* = 4.9 Hz, 1H), 3.09 (s, 2H), 1.34 (s, 6H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 152.6, 147.1, 146.4, 133.0, 131.9, 131.7, 130.7, 129.9, 129.1, 128.6, 126.8, 125.7, 124.5, 124.0, 122.6, 97.2, 85.7, 40.9, 33.8, 28.6; **HRMS** (ESI) m/z: $[M + H]^+$ calcd. for $C_{23}H_{20}N$ 310.1590; Found 310.1585.



ethyl 6,6-dimethyl-5,6-dihydrobenzo[h]quinoline-4-carboxylate (56):

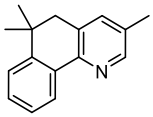
According to the general procedure, a mixture consisting of oxime (0.6 mmol, 177.2 mg), enal (0.2 mmol, 25.6 mg), $Fe(acac)_2$ (0.02 mmol, 5.0 mg), pyrrolidine·$HClO_4$ (0.04 mmol, 6.8 mg) and 1,4-dioxane (2 mL) under a N_2 atmosphere was stirred at 120 ℃ for 12 h to afford **56**. Colorless oil (23.5 mg, 41% yield); R_f = 0.5 (Petroleum ether/Ethyl acetate = 10:1); **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.62 (d, *J* = 5.0 Hz, 1H), 8.36 (d, *J* = 7.5 Hz, 1H), 7.54 (d, *J* = 5.0 Hz, 1H), 7.42 – 7.39 (m, 2H), 7.38 – 7.35 (m, 1H), 4.42 (q, *J* = 7.1 Hz, 2H), 3.20 (s, 2H), 1.43 (t, *J* = 7.1 Hz, 3H), 1.29 (s, 6H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 166.6, 154.0, 147.4, 146.4, 137.6, 132.8, 130.5, 130.0, 126.7, 126.0, 123.8, 121.8, 61.5, 39.7, 33.4, 28.4, 14.2; **HRMS** (ESI) m/z: $[M + H]^+$ calcd. for $C_{18}H_{20}NO_2$ 282.1489; Found 282.1487.



3,6,6-trimethyl-4-phenyl-5,6-dihydrobenzo[h]quinoline (57):

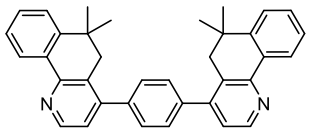
According to the general procedure, a mixture consisting of oxime (0.6 mmol, 177.2 mg), enal (0.2 mmol, 29.2 mg), $Fe(acac)_2$ (0.02 mmol, 5.0 mg), pyrrolidine·$HClO_4$ (0.04 mmol, 6.8 mg) and 1,4-dioxane (2 mL) under a N_2 atmosphere was stirred at 120 ℃ for 12 h to afford **57**. White solid

(17.5 mg, 29% yield); R_f = 0.6 (Petroleum ether/Ethyl acetate = 10:1); Mp = 110–112 ℃; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.45 (s, 1H), 8.41 – 8.37 (m, 1H), 7.48 (t, *J* = 7.4 Hz, 2H), 7.41 (t, *J* = 7.4 Hz, 1H), 7.38 – 7.33 (m, 3H), 7.14 (d, *J* = 7.2 Hz, 2H), 2.51 (s, 2H), 2.06 (s, 3H), 1.19 (s, 6H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 150.3, 148.9, 148.2, 145.9, 138.0, 133.6, 130.0, 129.2, 128.7, 128.4, 128.2, 127.5, 126.7, 125.4, 123.7, 40.4, 33.8, 28.1, 17.5; **HRMS** (ESI) m/z: $[M + H]^+$ calcd. for $C_{22}H_{22}N$ 300.1747; Found 300.1747.



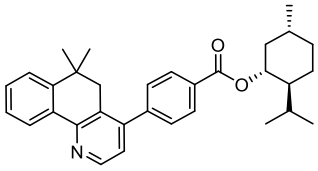
3,6,6-trimethyl-5,6-dihydrobenzo[h]quinoline (58):

According to the general procedure, a mixture consisting of oxime (0.6 mmol, 177.2 mg), enal (0.2 mmol, 14.1 mg), $Fe(acac)_2$ (0.02 mmol, 5.0 mg), pyrrolidine·$HClO_4$ (0.04 mmol, 6.8 mg) and 1,4-dioxane (2 mL) under a N_2 atmosphere was stirred at 120 ℃ for 12 h to afford **58**. White solid (12.7 mg, 28% yield); R_f = 0.6 (Petroleum ether/Ethyl acetate = 10:1); Mp = 66–68 ℃; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.36 (s, 1H), 8.34 – 8.31 (m, 1H), 7.40 – 7.36 (m, 1H), 7.36 – 7.31 (m, 2H), 7.28 (s, 1H), 2.79 (s, 2H), 2.34 (s, 3H), 1.28 (s, 6H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 149.8, 148.2, 146.0, 136.6, 133.3, 131.8, 130.1, 129.2, 126.7, 125.1, 123.9, 77.2, 77.0, 76.8, 43.1, 33.9, 28.3, 18.2; **HRMS** (ESI) m/z: $[M + H]^+$ calcd. for $C_{16}H_{18}N$ 224.1434; Found 224.1435.



1,4-bis(6,6-dimethyl-5,6-dihydrobenzo[h]quinolin-4-yl)benzene (59):

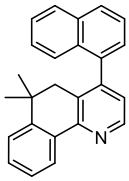
According to the general procedure, a mixture consisting of oxime (1.2 mmol, 354.4 mg), enal (0.2 mmol, 37.2 mg), $Fe(acac)_2$ (0.04 mmol, 10.2 mg), pyrrolidine·$HClO_4$ (0.08 mmol, 13.7 mg) and 1,4-dioxane (4 mL) under a N_2 atmosphere was stirred at 120 ℃ for 12 h to afford **59**. White solid (35.5 mg, 46% yield); R_f = 0.4 (Petroleum ether/Ethyl acetate = 10:1); Mp = 284–285 ℃; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.61 (d, *J* = 4.8 Hz, 2H), 8.46-8.42 (m, 2H), 7.46 (s, 4H), 7.42 – 7.37 (m, 6H), 7.19 (d, *J* = 4.8 Hz, 2H), 2.90 (s, 4H), 1.28 (s, 12H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 153.0, 148.4, 147.2, 146.2, 138.6, 133.5, 129.8, 128.9, 128.0, 126.8, 126.0, 123.7, 123.3, 40.2, 33.9, 28.2; **HRMS** (ESI) m/z: $[M + H]^+$ calcd. for $C_{36}H_{33}N_2$ 493.2638; Found 493.2637.



(1R,2S,5R)-2-isopropyl-5-methylcyclohexyl 4-(6,6-dimethyl-5,6-dihydrobenzo[h]quinolin-4-yl)benzoate (60):

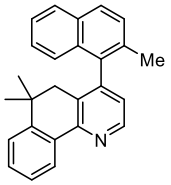
According to the general procedure, a mixture consisting of oxime (0.6 mmol, 177.2 mg), enal (0.2 mmol, 62.8 mg), $Fe(acac)_2$ (0.02 mmol, 5.0 mg), pyrrolidine·$HClO_4$ (0.04 mmol, 6.8 mg) and 1,4-dioxane (2 mL) under a N_2 atmosphere was stirred at 120 ℃ for 12 h to afford **60**. Colorless oil (43.4 mg, 46% yield); R_f = 0.5 (Petroleum ether/Ethyl acetate = 10:1); **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.59 (d, *J* = 4.9 Hz, 1H), 8.45 – 8.39 (m, 1H), 8.16 (d, *J* = 8.2 Hz, 2H), 7.42 (d, *J* = 8.2

Hz, 2H), 7.40 – 7.36 (m, 3H), 7.10 (d, *J* = 4.9 Hz, 1H), 4.99 (td, *J* = 10.9, 4.3 Hz, 1H), 2.78 (s, 2H), 2.19 – 2.14 (m, 1H), 2.06 – 1.97 (m, 1H), 1.79 – 1.72 (m, 2H), 1.63 – 1.55 (m, 2H), 1.22 (d, *J* = 3.2 Hz, 6H), 1.18 – 1.10 (m, 2H), 0.95 (d, *J* = 6.8 Hz, 7H), 0.84 (d, *J* = 6.9 Hz, 3H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 165.8, 153.0, 148.1, 147.2, 146.2, 143.3, 133.3, 130.5, 129.8, 129.7, 128.8, 127.9, 126.8, 125.9, 123.8, 122.9, 75.1, 47.3, 41.0, 40.1, 34.3, 33.8, 31.5, 28.1, 26.6, 23.7, 22.1, 20.8, 16.6; **HRMS** (ESI) m/z: $[M + H]^+$ calcd. for $C_{32}H_{38}NO_2$ 468.2897; Found 468.2893.



6,6-dimethyl-4-(naphthalen-1-yl)-5,6-dihydrobenzo[h]quinoline (61):

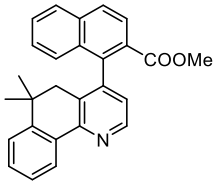
According to the general procedure, a mixture consisting of oxime (0.6 mmol, 177.2 mg), enal (0.2 mmol, 36.4 mg), $Fe(acac)_2$ (0.02 mmol, 5.0 mg), pyrrolidine·$HClO_4$ (0.04 mmol, 6.8 mg) and 1,4-dioxane (2 mL) under a N_2 atmosphere was stirred at 120 ℃ for 12 h to afford **61**. Colorless oil (30.2 mg, 45% yield); R_f = 0.65 (Petroleum ether/Ethyl acetate = 10:1); **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.63 (d, *J* = 4.8 Hz, 1H), 8.50-8.47 (m, 1H), 7.94 (d, *J* = 3.4 Hz, 1H), 7.93 (d, *J* = 3.5 Hz, 1H), 7.56 (t, *J* = 7.2 Hz, 1H), 7.51 (t, *J* = 7.4 Hz, 1H), 7.45 (d, *J* = 8.3 Hz, 1H), 7.41-7.33 (m, 4H), 7.32 (d, *J* = 6.9 Hz, 1H), 7.14 (d, *J* = 4.8 Hz, 1H), 2.51 (d, *J* = 15.8 Hz, 1H), 2.46 (d, *J* = 15.8 Hz, 1H), 1.14 (s, 3H), 1.13 (s, 3H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 152.6, 148.0, 147.0, 146.4, 136.7, 133.6, 133.5, 131.4, 129.7, 129.7, 128.4, 128.3, 126.8, 126.4, 126.2, 126.2, 125.9, 125.7, 125.3, 124.2, 123.8, 39.9, 33.7, 28.2, 28.0; **HRMS** (ESI) m/z: $[M + H]^+$ calcd. for $C_{25}H_{22}N$ 336.1747; Found 336.1746.



(ZYQ-2-189)ok

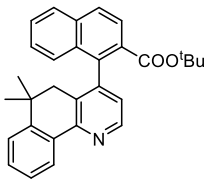
6,6-dimethyl-4-(2-methylnaphthalen-1-yl)-5,6-dihydrobenzo[h]quinoline (62):

According to the general procedure, a mixture consisting of oxime (0.6 mmol, 177.2 mg), enal (0.2 mmol, 39.3 mg), $Fe(acac)_2$ (0.02 mmol, 5.0 mg), pyrrolidine·$HClO_4$ (0.04 mmol, 6.8 mg) and 1,4-dioxane (2 mL) under a N_2 atmosphere was stirred at 120 ℃ for 12 h to afford **62**. White solid (26.6 mg, 38% yield); R_f = 0.65 (Petroleum ether/Ethyl acetate = 10:1); Mp = 188–189 ℃; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.66 (d, *J* = 4.7 Hz, 1H), 8.52 – 8.48 (m, 1H), 7.88 (d, *J* = 8.2 Hz, 1H), 7.85 (d, *J* = 8.4 Hz, 1H), 7.47 – 7.34 (m, 5H), 7.32 (t, *J* = 7.3 Hz, 1H), 7.21 (d, *J* = 8.5 Hz, 1H), 7.04 (d, *J* = 4.8 Hz, 1H), 2.39 (d, *J* = 15.9 Hz, 1H), 2.35 (d, *J* = 15.8 Hz, 1H), 2.19 (s, 3H), 1.15 (s, 3H), 1.11 (s, 3H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 152.8, 147.5, 147.3, 146.4, 134.4, 133.4, 132.8, 131.9, 131.8, 130.1, 129.7, 128.5, 128.0, 127.9, 126.8, 126.3, 125.8, 125.4, 125.2, 124.2, 123.9, 39.5, 33.6, 28.4, 28.3, 20.3; **HRMS** (ESI) m/z: $[M + H]^+$ calcd. for $C_{26}H_{24}N$ 350.1903; Found 350.1905.



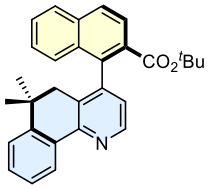
methyl 1-(6,6-dimethyl-5,6-dihydrobenzo[h]quinolin-4-yl)-2-naphthoate (63):

According to the general procedure, a mixture consisting of oxime (0.6 mmol, 177.2 mg), enal (0.2 mmol, 48.0 mg), $Fe(acac)_2$ (0.02 mmol, 5.0 mg), pyrrolidine·$HClO_4$ (0.04 mmol, 6.8 mg) and 1,4-dioxane (2 mL) under a N_2 atmosphere was stirred at 120 ℃ for 12 h to afford **63**. White solid (30.0 mg, 38% yield); R_f = 0.5 (Petroleum ether/Ethyl acetate = 10:1); Mp = 189–190 ℃; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.64 (d, *J* = 4.8 Hz, 1H), 8.51 (dd, *J* = 7.3, 1.6 Hz, 1H), 8.07 (d, *J* = 8.7 Hz, 1H), 7.99 (d, *J* = 8.7 Hz, 1H), 7.95 (d, *J* = 8.2 Hz, 1H), 7.58 (t, *J* = 7.4 Hz, 1H), 7.42-7.37 (m, 3H), 7.35 (d, *J* = 8.4 Hz, 2H), 7.03 (d, *J* = 4.8 Hz, 1H), 3.61 (s, 3H), 2.41 (d, *J* = 15.8 Hz, 1H), 2.31 (d, *J* = 15.8 Hz, 1H), 1.12 (s, 3H), 1.11 (s, 3H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 167.6, 152.1, 147.0, 146.9, 146.3, 138.3, 134.9, 133.4, 131.5, 129.7, 129.6, 128.5, 128.2, 128.0, 127.3, 127.2, 127.1, 126.7, 125.9, 125.8, 123.8, 123.4, 52.0, 39.9, 33.6, 28.4, 28.3; **HRMS** (ESI) m/z: $[M + H]^+$ calcd. for $C_{27}H_{24}NO_2$ 394.1802; Found 394.1804.



tert-butyl 1-(6,6-dimethyl-5,6-dihydrobenzo[h]quinolin-4-yl)-2-naphthoate (64):

According to the general procedure, a mixture consisting of oxime (0.6 mmol, 177.2 mg), enal (0.2 mmol, 56.4 mg), $Fe(acac)_2$ (0.02 mmol, 5.0 mg), pyrrolidine·$HClO_4$ (0.04 mmol, 6.8 mg) and 1,4-dioxane (2 mL) under a N_2 atmosphere was stirred at 120 ℃ for 12 h to afford **64**. White solid (38.4 mg, 44% yield); R_f = 0.5 (Petroleum ether/Ethyl acetate = 10:1); Mp = 131–133 ℃; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.64 (d, *J* = 4.7 Hz, 1H), 8.51-8.47 (m, 1H), 8.02 (d, *J* = 8.6 Hz, 1H), 7.97 (d, *J* = 8.7 Hz, 1H), 7.94 (d, J = 8.2 Hz, 1H), 7.57 (t, J = 7.3 Hz, 1H), 7.43 – 7.33 (m, 5H), 7.07 (d, J = 4.8 Hz, 1H), 2.51 (d, J = 15.9 Hz, 1H), 2.19 (d, J = 15.9 Hz, 1H), 1.21 (s, 3H), 1.20 (s, 9H), 1.02 (s, 3H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 165.8, 151.3, 146.3, 145.8, 145.4, 135.9, 133.7, 132.2, 130.3, 129.0, 128.7, 128.5, 127.4, 127.1, 126.7, 126.1, 125.9, 125.7, 125.1, 124.8, 122.9, 122.8, 80.8, 39.0, 32.6, 27.8, 27.2, 26.7; **HRMS** (ESI) m/z: $[M + H]^+$ calcd. for $C_{30}H_{30}NO_2$ 436.2271; Found 436.2273.



tert-butyl (*S*)-1-(6,6-dimethyl-5,6-dihydrobenzo[*h*]quinolin-4-yl)-2-naphthoate (97):

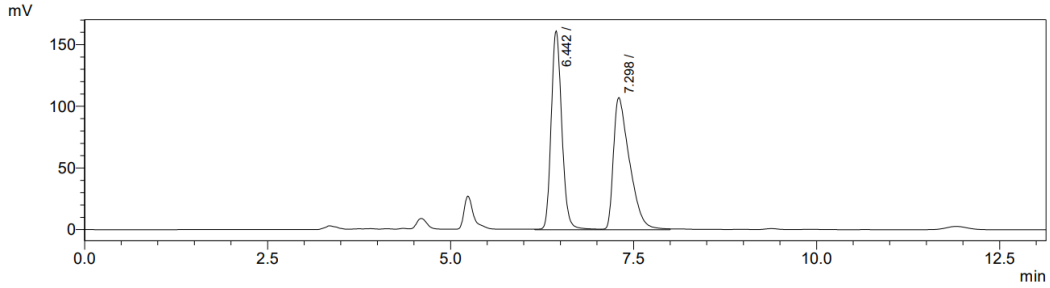
According to the general procedure, a mixture consisting of oxime (0.6 mmol, 231.2 mg), enal (0.2 mmol, 56.4 mg), $Fe(acac)_2$ (0.02 mmol, 5.0 mg), amine A4 (0.04 mmol, 18.7 mg) and 1,4-dioxane (1 mL)/toluene (1 mL) under a N_2 atmosphere was stirred at 50 ℃ for 48 h to afford **97.** Colorless oil (46.5 mg, 53% yield, 93:7 er); R_f = 0.5 (Petroleum ether/Ethyl acetate = 10:1); **^{1}H,**

^{13}C NMR and **HRMS** spectra data for **97** were in agreement with the racemic **64**.

HPLC analysis: DAICEL CHIRALPAK IE, n-hexane/isopropanol = 90/10, flow rate = 1.0 mL/min, λ = 254 nm, t_R (major) = 6.4 min, t_R (minor) = 7.3 min, er = 93:7.

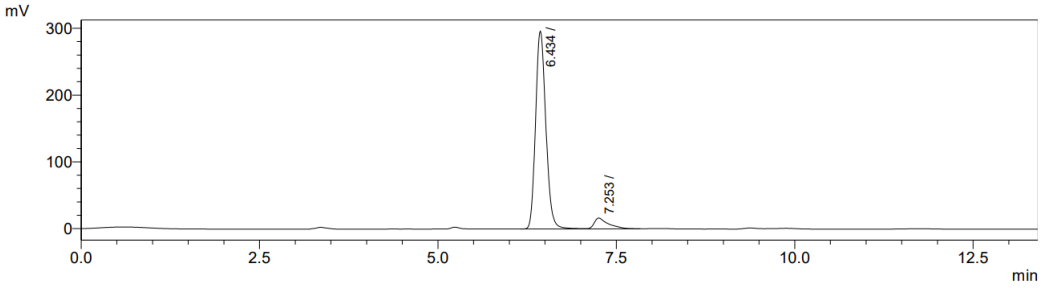
[α]$^{25}_D$ = -61.39 (c = 0.32, $CHCl_3$).

Chiral HPLC spectrum of (*rac*)-**97**:

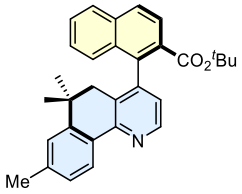


Peak#	Ret. Time	Area	Height	Conc.	Area%
1	6.442	1626600	161215	49.811	49.811
2	7.298	1638935	107164	50.189	50.189

Chiral HPLC spectrum of (*S*)-**97**:



Peak#	Ret. Time	Area	Height	Conc.	Area%
1	6.434	2971529	296380	93.039	93.039
2	7.253	222311	16176	6.961	6.961



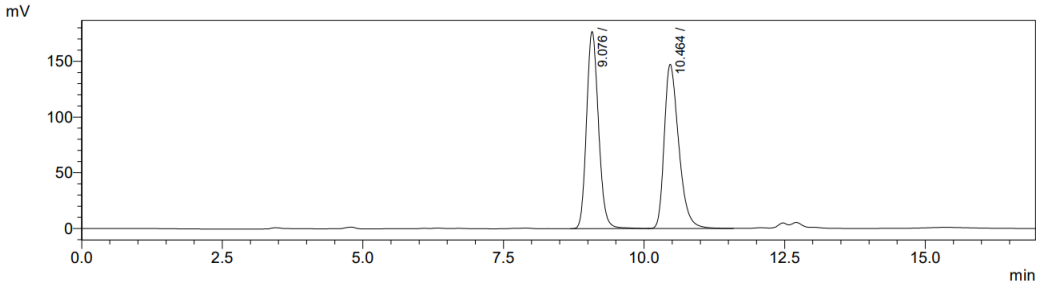
tert-butyl (*S*)-1-(6,6,8-trimethyl-5,6-dihydrobenzo[h]quinolin-4-yl)-2-naphthoate (98):

According to the general procedure, a mixture consisting of oxime (0.6 mmol, 239.6 mg), enal (0.2 mmol, 56.4 mg), $Fe(acac)_2$ (0.02 mmol, 5.0 mg), amine A4 (0.04 mmol, 18.7 mg) and 1,4-dioxane (1 mL)/toluene (1 mL) under a N_2 atmosphere was stirred at 50 ℃ for 48 h to afford **98**. Colorless oil (43.2 mg, 48% yield, 93:7 er); R_f = 0.5 (Petroleum ether/Ethyl acetate = 10:1); **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.61 (d, *J* = 4.2 Hz, 1H), 8.37 (d, *J* = 7.7 Hz, 1H), 8.02 (d, *J* = 8.5 Hz, 1H), 7.96 (d, *J* = 8.5 Hz, 1H), 7.94 (d, *J* = 8.0 Hz, 1H), 7.57 (t, *J* = 6.8 Hz, 1H), 7.42 – 7.35 (m, 2H), 7.21 (d, *J* = 7.7 Hz, 1H), 7.15 (s, 1H), 7.04 (d, *J* = 4.4 Hz, 1H), 2.49 (d, *J* = 15.8 Hz, 1H), 2.40 (s, 3H), 2.16 (d, *J* = 15.8 Hz, 1H), 1.20 (s, 12H), 1.00 (s, 3H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 166.9, 152.4, 147.3, 146.7, 146.3, 139.6, 137.0, 134.7, 131.3, 130.5, 129.7, 129.4, 128.4, 128.2, 127.7, 127.6, 127.2, 126.9, 126.1, 125.8, 124.6, 123.6, 81.8, 40.1, 33.5, 28.8, 28.2, 27.7, 21.7; **HRMS** (ESI) m/z: $[M + H]^+$ calcd. for $C_{31}H_{32}NO_2$ 450.2428; Found 450.2425.

HPLC analysis: DAICEL CHIRALPAK IE, n-hexane/isopropanol = 95/5, flow rate = 1.0 mL/min, λ = 254 nm, t_R (major) = 9.1 min, t_R (minor) = 10.6 min, er = 93:7.

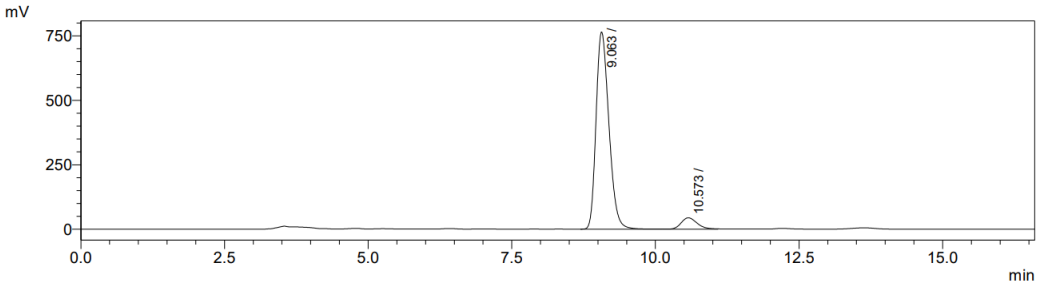
[α]$^{25}_D$ = -70.31 (c = 0.43, $CHCl_3$).

Chiral HPLC spectrum of (*rac*)-**98**:

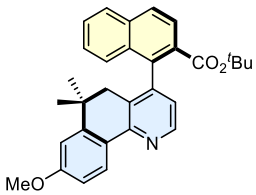


Peak#	Ret. Time	Area	Height	Conc.	Area%
1	9.076	2614590	177064	49.790	49.790
2	10.464	2636683	147460	50.210	50.210

Chiral HPLC spectrum of (*S*)-**98**:



Peak#	Ret. Time	Area	Height	Conc.	Area%
1	9.063	11890950	764916	93.202	93.202
2	10.573	867285	44293	6.798	6.798



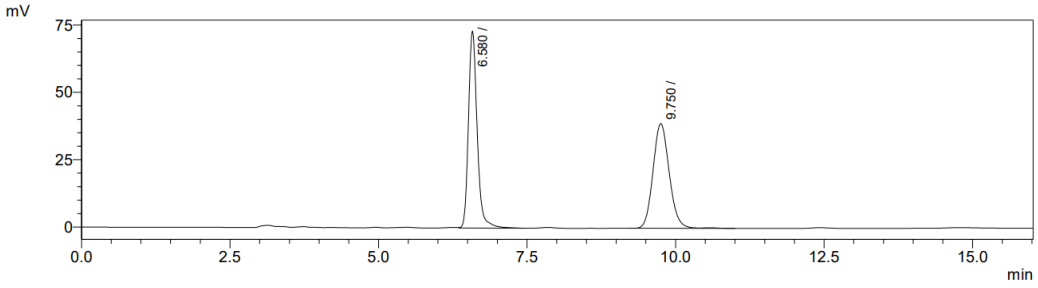
tert-butyl (*S*)-1-(8-methoxy-6,6-dimethyl-5,6-dihydrobenzo[h]quinolin-4-yl)-2-naphthoate (99):

According to the general procedure, a mixture consisting of oxime (0.6 mmol, 249.2 mg), enal (0.2 mmol, 56.4 mg), $Fe(acac)_2$ (0.02 mmol, 5.0 mg), amine A4 (0.04 mmol, 18.7 mg) and 1,4-dioxane (1 mL)/toluene (1 mL) under a N_2 atmosphere was stirred at 50 ℃ for 48 h to afford **99**. White solid (63.1 mg, 67% yield, 90:10 er); R_f = 0.4 (Petroleum ether/Ethyl acetate = 10:1); Mp = 153–154 ℃; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.59 (d, *J* = 4.9 Hz, 1H), 8.44 (d, *J* = 8.6 Hz, 1H), 8.01 (d, *J* = 8.6 Hz, 1H), 7.96 (d, *J* = 8.7 Hz, 1H), 7.93 (d, *J* = 8.2 Hz, 1H), 7.59 – 7.54 (m, 1H), 7.42 – 7.36 (m, 2H), 7.01 (d, *J* = 4.9 Hz, 1H), 6.92 (dd, *J* = 8.7, 2.5 Hz, 1H), 6.88 (d, *J* = 2.5 Hz, 1H), 3.87 (s, 3H), 2.48 (d, *J* = 15.8 Hz, 1H), 2.16 (d, *J* = 15.8 Hz, 1H), 1.20 (s, 9H), 1.19 (s, 3H), 1.00 (s, 3H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 166.9, 161.0, 152.2, 148.4, 147.2, 146.6, 134.7, 131.3, 129.4, 129.0, 128.3, 128.1, 127.7, 127.5, 127.1, 126.9, 126.4, 126.0, 123.2, 111.3, 110.2, 81.8, 55.3, 40.0, 33.8, 28.7, 28.1, 27.7; **HRMS** (ESI) m/z: $[M + H]^+$ calcd. for $C_{31}H_{32}NO_3$ 466.2377; Found 466.2371.

HPLC analysis: DAICEL CHIRALPAK AD-H, n-hexane/isopropanol = 90/10, flow rate = 1.0 mL/min, λ = 254 nm, t_R (major) = 9.7 min, t_R (minor) = 6.5 min, er = 90:10.

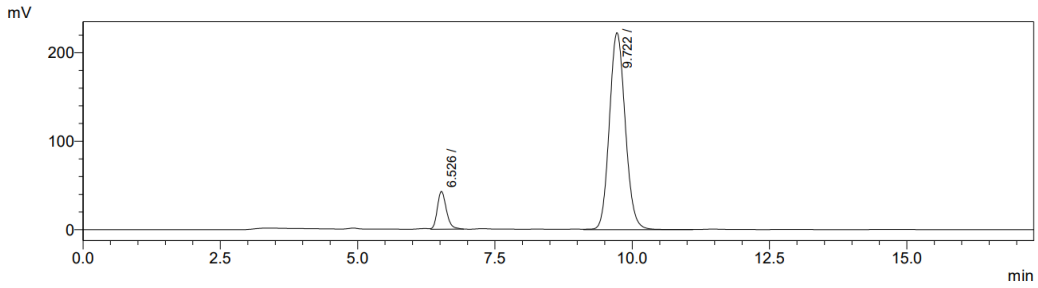
$[\alpha]^{25}_D$ = -70.31 (c = 0.63, $CHCl_3$).

Chiral HPLC spectrum of (*rac*)-**99**:

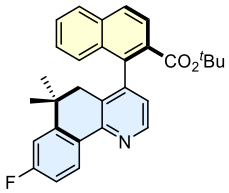


Peak#	Ret. Time	Area	Height	Conc.	Area%
1	6.580	744715	73070	50.228	50.228
2	9.750	737959	38842	49.772	49.772

Chiral HPLC spectrum of (*S*)-**99**:



Peak#	Ret. Time	Area	Height	Conc.	Area%
1	6.526	489318	42716	9.851	9.851
2	9.722	4477854	222547	90.149	90.149

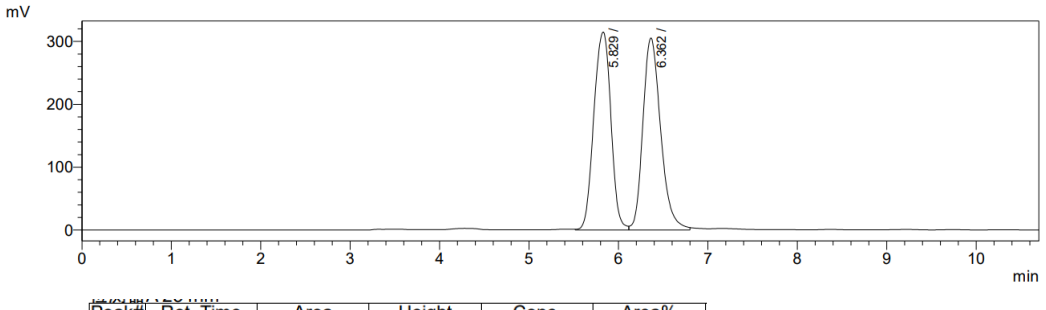


tert-butyl (*S*)-1-(8-fluoro-6,6-dimethyl-5,6-dihydrobenzo[*h*]quinolin-4-yl)-2-naphthoate (100): According to the general procedure, a mixture consisting of oxime (0.6 mmol, 242.0 mg), enal (0.2 mmol, 56.4 mg), $Fe(acac)_2$ (0.02 mmol, 5.0 mg), amine A4 (0.04 mmol, 18.7 mg) and 1,4-dioxane (1 mL)/toluene (1 mL) under a N_2 atmosphere was stirred at 50 °C for 48 h to afford **100**. White solid (52.2 mg, 57% yield, 92:8 er); R_f = 0.5 (Petroleum ether/Ethyl acetate = 10:1); Mp = 150–152 °C; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.61 (d, *J* = 4.8 Hz, 1H), 8.49 (dd, *J* = 8.5, 6.3 Hz, 1H), 8.02 (d, *J* = 8.7 Hz, 1H), 7.97 (d, *J* = 8.7 Hz, 1H), 7.94 (d, *J* = 8.2 Hz, 1H), 7.57 (t, *J* = 7.1 Hz, 1H), 7.41 (t, *J* = 7.2 Hz, 1H), 7.35 (d, *J* = 8.5 Hz, 1H), 7.09 – 7.04 (m, 2H), 7.03 (dd, *J* = 10.2, 2.4 Hz, 1H), 2.50 (d, *J* = 15.9 Hz, 1H), 2.18 (d, *J* = 15.9 Hz, 1H), 1.21 (s, 9H), 1.19 (s, 3H), 1.00 (s, 3H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 166.7, 164.1 (d, $^1J_{C\text{-}F}$ = 248.4 Hz), 151.5, 149.1, 149.1, 147.5, 146.8, 136.7, 134.7, 131.2, 129.5, 129.4, 128.4, 128.2, 128.0 (d, $^3J_{C\text{-}F}$ = 8.5 Hz), 127.7, 127.0, 126.9, 126.0, 123.8, 113.6 (d, $^2J_{C\text{-}F}$ = 21.4 Hz), 111.0 (d, $^2J_{C\text{-}F}$ = 22.3 Hz), 81.8, 39.8, 33.8, 28.5, 28.0, 27.7; **^{19}F NMR** (565 MHz, $CDCl_3$) δ -111.42; **HRMS** (ESI) m/z: $[M + H]^+$ calcd. for $C_{30}H_{29}FNO_2$ 454.2177; Found 454.2169.

HPLC analysis: DAICEL CHIRALPAK IE, n-hexane/isopropanol = 90/10, flow rate = 1.0 mL/min, λ = 254 nm, t_R (major) = 5.8 min, t_R (minor) = 6.4 min, er = 92:8.

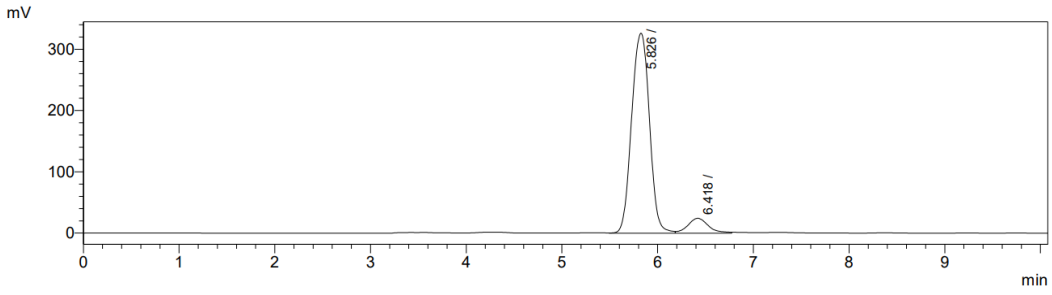
$[\alpha]^{25}_D$ = -52.89 (c = 0.23, $CHCl_3$).

Chiral HPLC spectrum of (*rac*)-**100**:

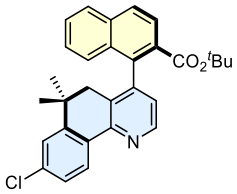


Peak#	Ret. Time	Area	Height	Conc.	Area%
1	5.829	4180006	314899	49.733	49.733
2	6.362	4224917	305342	50.267	50.267

Chiral HPLC spectrum of (*S*)-**100**:



Peak#	Ret. Time	Area	Height	Conc.	Area%
1	5.826	4229604	326623	92.023	92.023
2	6.418	366664	24450	7.977	7.977



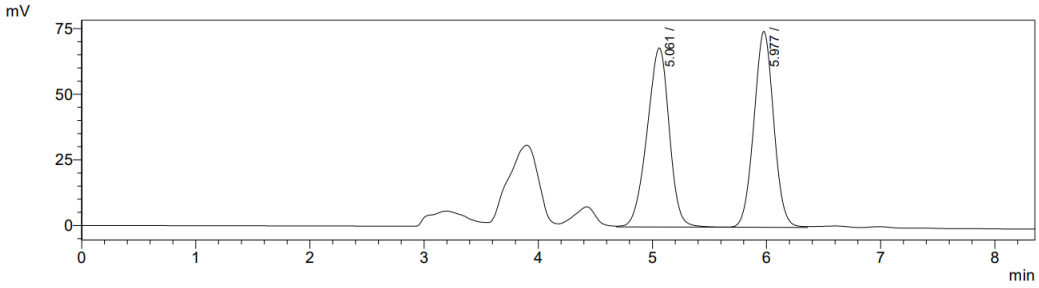
tert-butyl (*S*)-1-(8-chloro-6,6-dimethyl-5,6-dihydrobenzo[*h*]quinolin-4-yl)-2-naphthoate (101):

According to the general procedure, a mixture consisting of oxime (0.6 mmol, 251.8 mg), enal (0.2 mmol, 56.4 mg), $Fe(acac)_2$ (0.02 mmol, 5.0 mg), amine A4 (0.04 mmol, 18.7 mg) and 1,4-dioxane (1 mL)/toluene (1 mL) under a N_2 atmosphere was stirred at 50 ℃ for 48 h to afford **101**. White solid (50.4 mg, 53% yield, 94:6 er); R_f = 0.5 (Petroleum ether/Ethyl acetate = 10:1); Mp = 113–114 ℃; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.63 (d, *J* = 4.8 Hz, 1H), 8.45 (d, *J* = 8.1 Hz, 1H), 8.02 (d, *J* = 8.6 Hz, 1H), 7.98 (d, *J* = 8.7 Hz, 1H), 7.95 (d, *J* = 8.2 Hz, 1H), 7.58 (t, *J* = 7.5 Hz, 1H), 7.41 (t, *J* = 7.6 Hz, 1H), 7.38 – 7.35 (m, 1H), 7.34 (d, *J* = 8.6 Hz, 1H), 7.31 (d, *J* = 1.8 Hz, 1H), 7.08 (d, *J* = 4.5 Hz, 1H), 2.50 (d, *J* = 16.0 Hz, 1H), 2.18 (d, *J* = 16.0 Hz, 1H), 1.20 (s, 9H), 1.20 (s, 3H), 1.01 (s, 3H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 166.7, 151.2, 148.2, 146.8, 136.6, 135.6, 134.7, 131.2, 129.9, 129.4, 128.5, 128.2, 127.8, 127.4, 127.1, 127.0, 126.9, 126.1, 124.3, 124.2, 81.8, 39.8, 33.8, 28.6, 27.9, 27.7; **HRMS** (ESI) m/z: $[M + H]^+$ calcd. for $C_{30}H_{29}ClNO_2$ 470.1881; Found 470.1887.

HPLC analysis: DAICEL CHIRALPAK AD-H, n-hexane/isopropanol = 90/10, flow rate = 1.0 mL/min, λ = 254 nm, t_R (major) = 6.1 min, t_R (minor) = 5.1 min, er = 94:6.

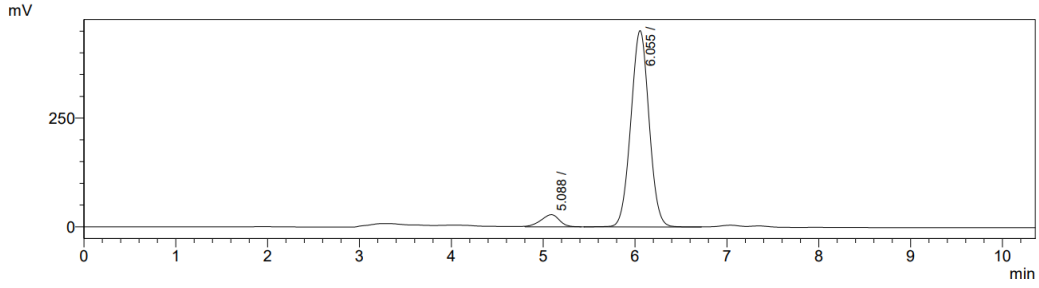
$[\alpha]^{25}_D$ = -75.99 (c = 0.50, $CHCl_3$).

Chiral HPLC spectrum of (*rac*)-**101**:

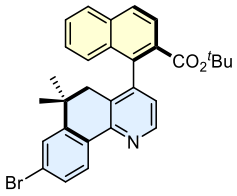


Peak#	Ret. Time	Area	Height	Conc.	Area%
1	5.061	920772	68176	50.557	50.557
2	5.977	900485	74664	49.443	49.443

Chiral HPLC spectrum of (*S*)-**101**:



Peak#	Ret. Time	Area	Height	Conc.	Area%
1	5.088	395458	27996	5.967	5.967
2	6.055	6232189	451854	94.033	94.033



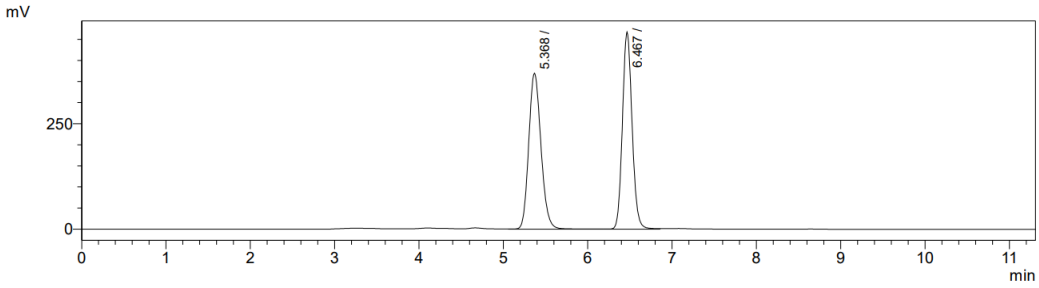
tert-butyl (*S*)-1-(8-bromo-6,6-dimethyl-5,6-dihydrobenzo[h]quinolin-4-yl)-2-naphthoate (102):

According to the general procedure, a mixture consisting of oxime (0.6 mmol, 278.5 mg), enal (0.2 mmol, 56.4 mg), $Fe(acac)_2$ (0.02 mmol, 5.0 mg), amine A4 (0.04 mmol, 18.7 mg) and 1,4-dioxane (1 mL)/toluene (1 mL) under a N_2 atmosphere was stirred at 50 ℃ for 48 h to afford **102**. Colorless oil (49.0 mg, 47% yield, 93:7 er); R_f = 0.5 (Petroleum ether/Ethyl acetate = 10:1); **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.62 (d, *J* = 4.6 Hz, 1H), 8.36 (d, *J* = 8.3 Hz, 1H), 8.02 (d, *J* = 8.6 Hz, 1H), 7.98 (d, *J* = 8.7 Hz, 1H), 7.95 (d, *J* = 8.1 Hz, 1H), 7.58 (t, *J* = 7.3 Hz, 1H), 7.52 (d, *J* = 8.3 Hz, 1H), 7.47 (s, 1H), 7.41 (t, *J* = 7.5 Hz, 1H), 7.34 (d, *J* = 8.5 Hz, 1H), 7.08 (d, *J* = 4.5 Hz, 1H), 2.50 (d, *J* = 16.0 Hz, 1H), 2.17 (d, *J* = 16.0 Hz, 1H), 1.20 (s, 12H), 1.01 (s, 3H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 166.7, 151.3, 148.4, 147.6, 146.9, 136.6, 134.7, 132.2, 131.2, 129.9, 129.9, 129.4, 128.5, 128.2, 127.8, 127.6, 127.3, 127.0, 126.9, 126.1, 124.2, 124.1, 81.8, 39.8, 33.8, 28.6, 27.9, 27.7; **HRMS** (ESI) m/z: $[M + H]^+$ calcd. for $C_{30}H_{29}BrNO_2$ 514.1376; Found 514.1375.

HPLC analysis: DAICEL CHIRALPAK IE, n-hexane/isopropanol = 90/10, flow rate = 1.0 mL/min, λ = 254 nm, t_R (major) = 6.5 min, t_R (minor) = 5.4 min, er = 93:7.

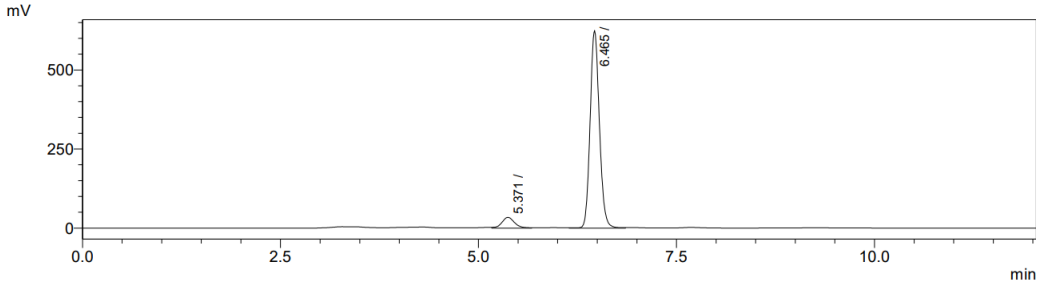
$[\alpha]^{25}_D$ = -71.74 (c = 0.46, $CHCl_3$).

Chiral HPLC spectrum of (*rac*)-**102**:

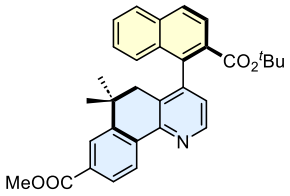


Peak#	Ret. Time	Area	Height	Conc.	Area%
1	5.368	3743244	370029	50.056	50.056
2	6.467	3734825	467638	49.944	49.944

Chiral HPLC spectrum of (*S*)-**102**:



Peak#	Ret. Time	Area	Height	Conc.	Area%
1	5.371	380561	33973	6.955	6.955
2	6.465	5091340	623824	93.045	93.045



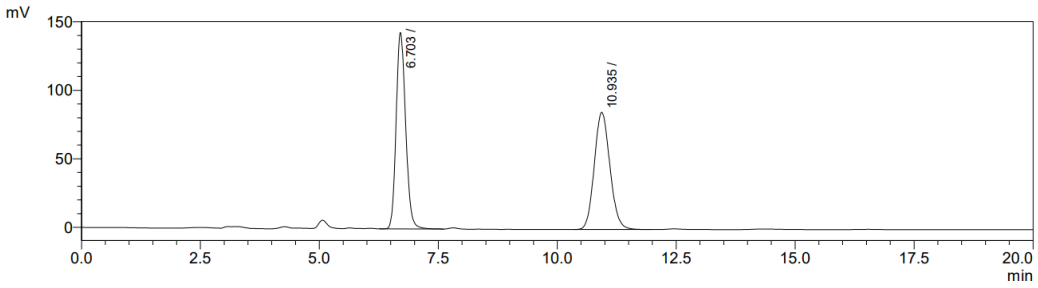
methyl (*S*)-4-(2-(tert-butoxycarbonyl)naphthalen-1-yl)-6,6-dimethyl-5,6-dihydrobenzo[h]quinoline-8-carboxylate (103):

According to the general procedure, a mixture consisting of oxime (0.6 mmol, 266.6 mg), enal (0.2 mmol, 56.4 mg), $Fe(acac)_2$ (0.02 mmol, 5.0 mg), amine A4 (0.04 mmol, 18.7 mg) and 1,4-dioxane (1 mL)/toluene (1 mL) under a N_2 atmosphere was stirred at 50 ℃ for 48 h to afford **103**. Colorless oil (40.5 mg, 41% yield, 93:7 er); R_f = 0.3 (Petroleum ether/Ethyl acetate = 10:1); **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.67 (d, *J* = 4.8 Hz, 1H), 8.57 (d, *J* = 8.1 Hz, 1H), 8.08 – 8.05 (m, 1H), 8.03 – 8.01 (m, 2H), 7.98 (d, *J* = 8.7 Hz, 1H), 7.95 (d, *J* = 8.2 Hz, 1H), 7.58 (t, *J* = 7.3 Hz, 1H), 7.41 (t, *J* = 7.4 Hz, 1H), 7.35 (d, *J* = 8.5 Hz, 1H), 7.12 (d, *J* = 4.8 Hz, 1H), 3.94 (s, 3H), 2.54 (d, *J* = 16.0 Hz, 1H), 2.22 (d, *J* = 16.0 Hz, 1H), 1.26 (s, 3H), 1.20 (s, 9H), 1.05 (s, 3H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 167.2, 166.7, 151.2, 147.8, 147.1, 146.4, 137.4, 136.5, 134.7, 131.2, 130.9, 130.8, 129.4, 128.5, 128.2, 128.0, 127.8, 127.1, 126.9, 126.1, 125.9, 125.5, 124.7, 81.8, 52.1, 39.8, 33.7, 28.7, 28.1, 27.7; **HRMS** (ESI) m/z: $[M + H]^+$ calcd. for $C_{32}H_{32}NO_4$ 494.2326; Found 494.2323.

HPLC analysis: DAICEL CHIRALPAK AD-H, n-hexane/isopropanol = 90/10, flow rate = 1.0 mL/min, λ = 254 nm, t_R (major) = 10.9 min, t_R (minor) = 6.7 min, er = 93:7.

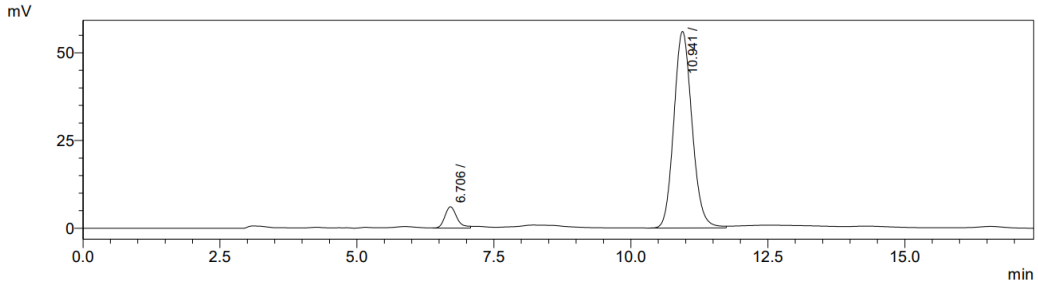
$[\alpha]^{25}_D$ = -77.43 (c = 0.41, $CHCl_3$).

Chiral HPLC spectrum of (*rac*)-**103**:

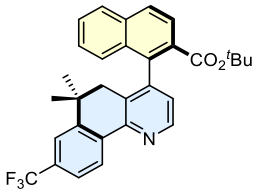


Peak#	Ret. Time	Area	Height	Conc.	Area%
1	6.703	1993815	143233	50.551	50.551
2	10.935	1950312	85408	49.449	49.449

Chiral HPLC spectrum of (*S*)-**103**:



Peak#	Ret. Time	Area	Height	Conc.	Area%
1	6.706	93258	6076	6.722	6.722
2	10.941	1293992	56038	93.278	93.278



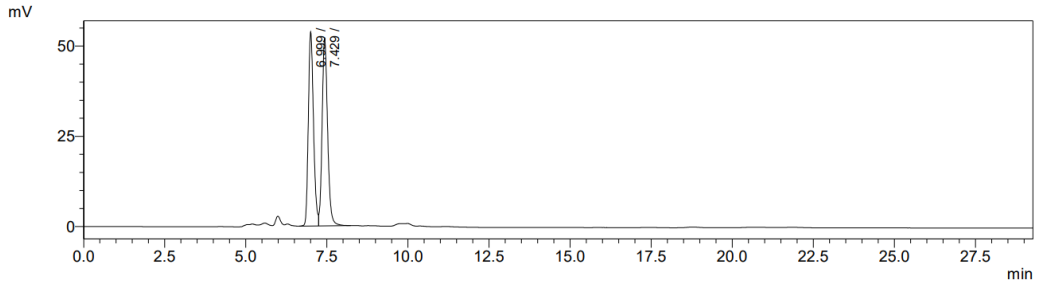
tert-butyl (*S*)-1-(6,6-dimethyl-8-(trifluoromethyl)-5,6-dihydrobenzo[h]quinolin-4-yl)-2-naphthoate (104):

According to the general procedure, a mixture consisting of oxime (0.6 mmol, 272.0 mg), enal (0.2 mmol, 56.4 mg), $Fe(acac)_2$ (0.02 mmol, 5.0 mg), amine A4 (0.04 mmol, 18.7 mg) and 1,4-dioxane (1 mL)/toluene (1 mL) under a N_2 atmosphere was stirred at 50 °C for 48 h to afford **104**. Colorless oil (54.4 mg, 54% yield, 94:6 er); R_f = 0.5 (Petroleum ether/Ethyl acetate = 10:1); **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.67 (d, *J* = 4.2 Hz, 1H), 8.61 (d, *J* = 8.0 Hz, 1H), 8.04 (d, *J* = 8.5 Hz, 1H), 7.99 (d, *J* = 8.6 Hz, 1H), 7.96 (d, *J* = 8.1 Hz, 1H), 7.64 (d, *J* = 8.1 Hz, 1H), 7.61 – 7.56 (m, 2H), 7.42 (t, *J* = 7.5 Hz, 1H), 7.33 (d, *J* = 8.4 Hz, 1H), 7.13 (d, *J* = 4.0 Hz, 1H), 2.54 (d, *J* = 16.0 Hz, 1H), 2.22 (d, *J* = 16.0 Hz, 1H), 1.25 (s, 3H), 1.21 (s, 9H), 1.04 (s, 3H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 166.6, 150.8, 147.9, 147.1, 146.9, 136.5, 134.7, 131.2 (q, $^2J_{C\text{-}F}$ = 31.8 Hz), 131.1, 130.6, 129.4, 128.6, 128.3, 127.83, 127.1, 126.9, 126.2, 126.1, 125.3 (q, $^1J_{C\text{-}F}$ = 272.2 Hz), 124.8, 123.6 (q, $^3J_{C\text{-}F}$ = 3.6 Hz), 121.0 (q, $^3J_{C\text{-}F}$ = 3.8 Hz), 81.9, 39.6, 33.8, 28.6, 27.9, 27.7; **^{19}F NMR** (565 MHz, $CDCl_3$) δ -62.46; **HRMS** (ESI) m/z: $[M + H]^+$ calcd. for $C_{31}H_{29}F_3NO_2$ 504.2145; Found 504.2143.

HPLC analysis: DAICEL CHIRALPAK AD-H, n-hexane/isopropanol = 88/12, flow rate = 0.6 mL/min, λ = 254 nm, t_R (major) = 7.4 min, t_R (minor) = 7.0 min, er = 94:6.

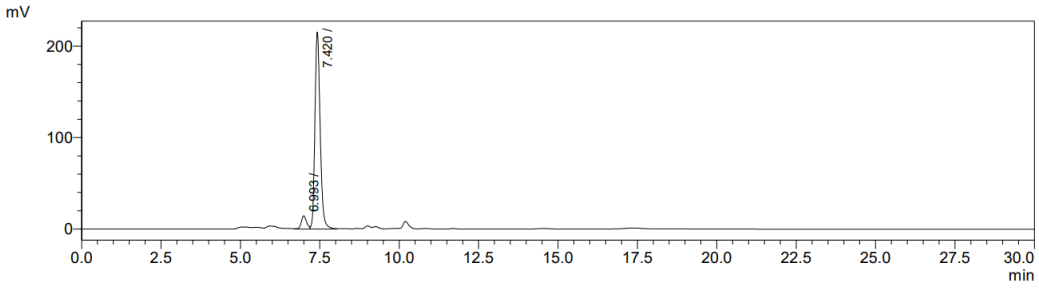
$[\alpha]^{25}_D$ = -62.56 (c = 0.39, $CHCl_3$).

Chiral HPLC spectrum of (*rac*)-**104**:

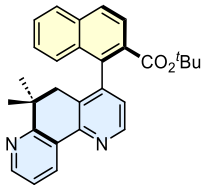


Peak#	Ret. Time	Area	Height	Conc.	Area%
1	6.999	596276	53823	49.360	49.360
2	7.429	611745	51932	50.640	50.640

Chiral HPLC spectrum of (*S*)-**104**:



Peak#	Ret. Time	Area	Height	Conc.	Area%
1	6.993	172046	14605	6.477	6.477
2	7.420	2484271	215394	93.523	93.523



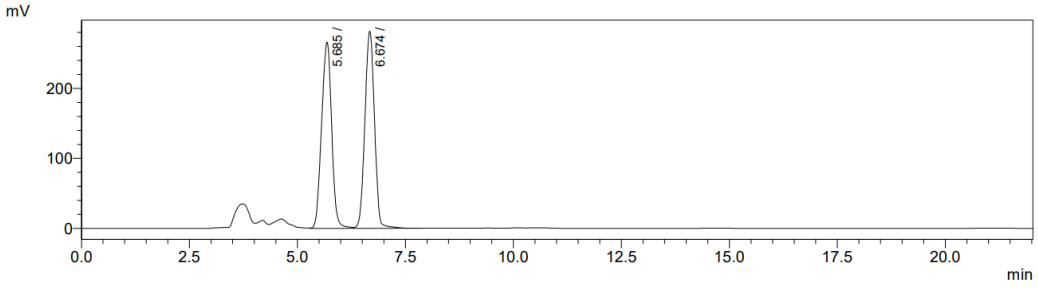
tert-butyl (*S*)-1-(6,6-dimethyl-5,6-dihydro-1,7-phenanthrolin-4-yl)-2-naphthoate (105):

According to the general procedure, a mixture consisting of oxime (0.6 mmol, 231.8 mg), enal (0.2 mmol, 56.4 mg), $Fe(acac)_2$ (0.02 mmol, 5.0 mg), amine A4 (0.04 mmol, 18.7 mg) and 1,4-dioxane (1 mL)/toluene (1 mL) under a N_2 atmosphere was stirred at 50 ℃ for 48 h to afford **105**. Colorless oil (27.6 mg, 31% yield, 93:7 er); R_f = 0.5 (Petroleum ether/Ethyl acetate = 10:1); **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.74 (dd, *J* = 7.9, 1.7 Hz, 1H), 8.64 (d, *J* = 4.8 Hz, 1H), 8.59 (dd, *J* = 4.8, 1.7 Hz, 1H), 8.04 (d, *J* = 8.7 Hz, 1H), 7.99 (d, *J* = 8.7 Hz, 1H), 7.96 (d, *J* = 8.2 Hz, 1H), 7.61 – 7.57 (m, 1H), 7.44 – 7.40 (m, 1H), 7.35 (d, *J* = 8.5 Hz, 1H), 7.32 (dd, *J* = 7.8, 4.8 Hz, 1H), 7.11 (d, *J* = 4.8 Hz, 1H), 2.63 (d, *J* = 16.2 Hz, 1H), 2.31 (d, *J* = 16.2 Hz, 1H), 1.28 (s, 3H), 1.22 (s, 9H), 1.07 (s, 3H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 166.6, 164.4, 150.9, 149.7, 147.8, 147.1, 136.6, 134.7, 133.0, 131.1, 130.0, 129.3, 128.5, 128.5, 128.3, 127.8, 127.1, 126.9, 126.1, 124.5, 122.2, 81.8, 39.6, 36.1, 27.7, 27.4, 26.9; **HRMS** (ESI) m/z: $[M + H]^+$ calcd. for $C_{29}H_{29}N_2O_2$ 437.2224; Found 437.2223.

HPLC analysis: DAICEL CHIRALPAK AD-H, n-hexane/isopropanol = 90/10, flow rate = 1.0 mL/min, λ = 254 nm, t_R (major) = 6.7 min, t_R (minor) = 5.7 min, er = 93:7.

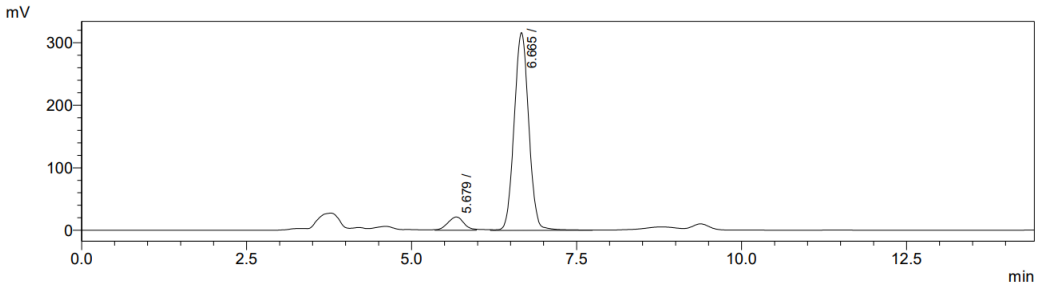
$[\alpha]^{25}_D$ = -73.14 (c = 0.24, $CHCl_3$).

Chiral HPLC spectrum of (*rac*)-**105**:

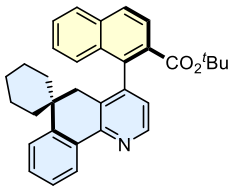


Peak#	Ret. Time	Area	Height	Conc.	Area%
1	5.685	4311201	265839	49.837	49.837
2	6.674	4339391	281533	50.163	50.163

Chiral HPLC spectrum of (*S*)-**105**:



Peak#	Ret. Time	Area	Height	Conc.	Area%
1	5.679	361663	21235	6.917	6.917
2	6.665	4866965	316571	93.083	93.083



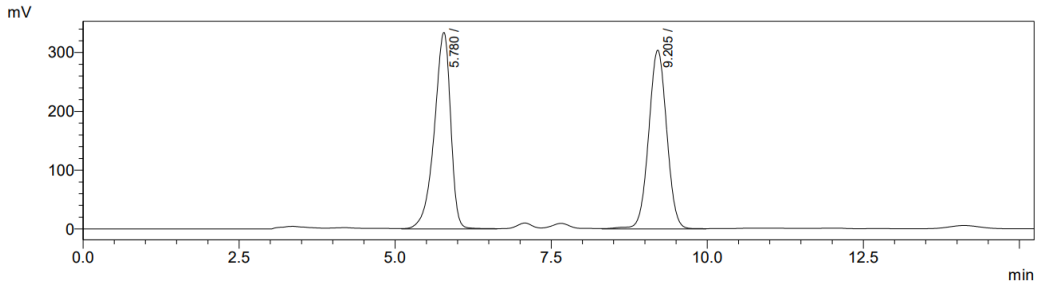
tert-butyl (*S*)-1-(5H-spiro[benzo[*h*]quinoline-6,1'-cyclohexan]-4-yl)-2-naphthoate (106):

According to the general procedure, a mixture consisting of oxime (0.6 mmol, 255.2 mg), enal (0.2 mmol, 56.4 mg), $Fe(acac)_2$ (0.02 mmol, 5.0 mg), amine A4 (0.04 mmol, 18.7 mg) and 1,4-dioxane (1 mL)/toluene (1 mL) under a N_2 atmosphere was stirred at 50 ℃ for 48 h to afford **106**. White solid (43.0 mg, 36% yield, 93:7 er); R_f = 0.5 (Petroleum ether/Ethyl acetate = 10:1); Mp = 127–129 ℃; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.63 (d, *J* = 4.8 Hz, 1H), 8.54 – 8.49 (m, 1H), 8.08 (d, *J* = 8.7 Hz, 1H), 7.98 (d, *J* = 8.7 Hz, 1H), 7.94 (d, *J* = 8.2 Hz, 1H), 7.58 – 7.54 (m, 1H), 7.47 – 7.43 (m, 1H), 7.41 –7.38 (m, 2H), 7.38 –7.34 (m, 2H), 7.08 (d, *J* = 4.9 Hz, 1H), 2.52 (d, *J* = 16.1 Hz, 1H), 2.45 (d, *J* = 16.1 Hz, 1H), 1.76 (td, *J* = 12.6, 3.7 Hz, 1H), 1.56 (d, *J* = 13.3 Hz, 1H), 1.51 (d, *J* = 13.3 Hz, 1H), 1.45 – 1.38 (m, 2H), 1.32 – 1.27 (m, 1H), 1.20 (s, 9H), 1.13 – 1.01 (m, 3H), 0.60 – 0.50 (m, 1H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 166.7, 152.5, 147.5, 147.1, 146.6, 137.1, 134.7, 133.7, 131.5, 129.7, 129.3, 129.1, 128.4, 128.1, 127.7, 127.2, 126.9, 126.6, 126.2, 125.9, 124.0, 123.5, 81.8, 36.4, 35.4, 35.3, 32.7, 27.7, 25.8, 22.1, 21.9; **HRMS** (ESI) m/z: $[M + H]^+$ calcd. for $C_{33}H_{33}NO_2$ 476.2584; Found 476.2583.

HPLC analysis: DAICEL CHIRALPAK AD-H, n-hexane/isopropanol = 95/5, flow rate = 1.0 mL/min, λ = 254 nm, t_R (major) = 9.2 min, t_R (minor) = 5.6 min, er = 93:7.

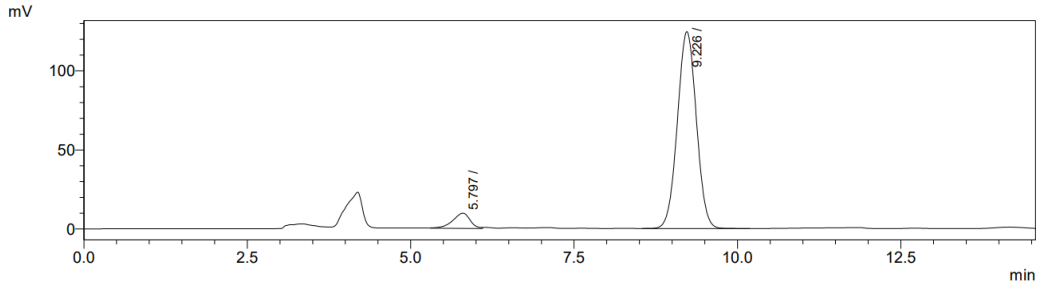
$[\alpha]^{25}_D$ = -73.14 (c = 0.24, $CHCl_3$).

Chiral HPLC spectrum of (*rac*)-**106**:

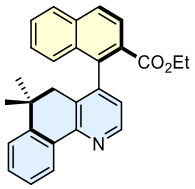


Peak#	Ret. Time	Area	Height	Conc.	Area%
1	5.780	6098677	334310	49.932	49.932
2	9.205	6115202	303737	50.068	50.068

Chiral HPLC spectrum of (*S*)-**106**:



Peak#	Ret. Time	Area	Height	Conc.	Area%
1	5.797	178059	9609	6.608	6.608
2	9.226	2516672	124613	93.392	93.392



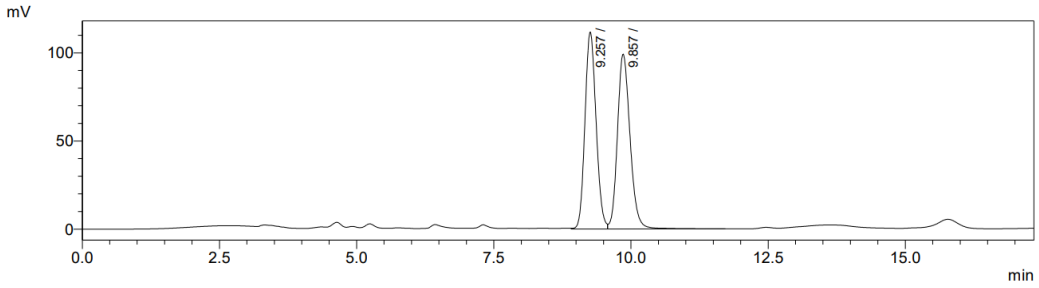
ethyl (*S*)-1-(6,6-dimethyl-5,6-dihydrobenzo[h]quinolin-4-yl)-2-naphthoate (107):

According to the general procedure, a mixture consisting of oxime (0.6 mmol, 231.2 mg), enal (0.2 mmol, 50.8 mg), $Fe(acac)_2$ (0.02 mmol, 5.0 mg), amine A4 (0.04 mmol, 18.7 mg) and 1,4-dioxane (1 mL)/toluene (1 mL) under a N_2 atmosphere was stirred at 50 ℃ for 48 h to afford **107**. Colorless oil (36.7 mg, 45% yield, 93:7 er); R_f = 0.5 (Petroleum ether/Ethyl acetate = 10:1); **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.63 (d, *J* = 4.8 Hz, 1H), 8.53 – 8.48 (m, 1H), 8.09 (d, *J* = 8.7 Hz, 1H), 7.99 (d, *J* = 8.7 Hz, 1H), 7.95 (d, *J* = 8.2 Hz, 1H), 7.58 (t, *J* = 7.4 Hz, 1H), 7.43 – 7.33 (m, 5H), 7.05 (d, *J* = 4.8 Hz, 1H), 4.12 (dq, *J* = 10.9, 7.1 Hz, 1H), 4.02 (dq, *J* = 10.9, 7.1 Hz, 1H), 2.44 (d, *J* = 15.8 Hz, 1H), 2.28 (d, *J* = 15.8 Hz, 1H), 1.15 (s, 3H), 1.09 (s, 3H), 0.97 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 167.3, 152.1, 147.2, 146.8, 146.3, 138.0, 134.9, 133.3, 131.4, 129.8, 129.7, 128.5, 128.2, 128.0, 127.6, 127.2, 127.1, 126.8, 126.0, 125.9, 123.9, 123.7, 61.1, 39.9, 33.6, 28.4, 28.3, 13.7; **HRMS** (ESI) m/z: $[M + H]^+$ calcd. for $C_{28}H_{26}NO_2$ 408.1958; Found 408.1958.

HPLC analysis: DAICEL CHIRALPAK IE, n-hexane/isopropanol = 90/10, flow rate = 1.0 mL/min, λ = 254 nm, t_R (major) = 9.2 min, t_R (minor) = 9.8 min, er = 90:10.

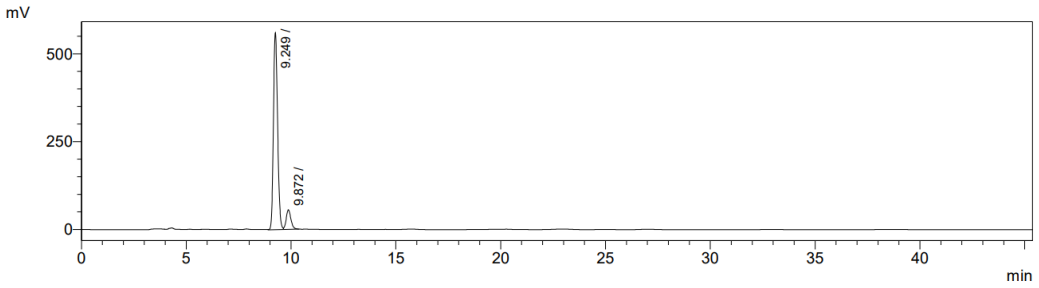
$[\alpha]^{25}_D$ = -94.95 (c = 0.28, $CHCl_3$).

Chiral HPLC spectrum of (*rac*)-**107**:

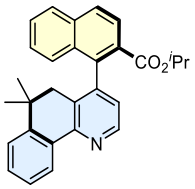


Peak#	Ret. Time	Area	Height	Conc.	Area%
1	9.257	1571193	111764	49.734	49.734
2	9.857	1588006	99218	50.266	50.266

Chiral HPLC spectrum of (*S*)-**107**:



Peak#	Ret. Time	Area	Height	Conc.	Area%
1	9.249	7741136	560569	89.964	89.964
2	9.872	863604	55602	10.036	10.036



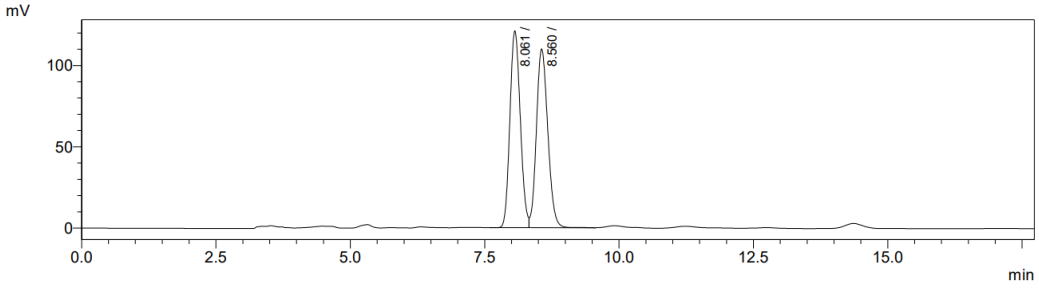
isopropyl (*S*)-1-(6,6-dimethyl-5,6-dihydrobenzo[h]quinolin-4-yl)-2-naphthoate (108):

According to the general procedure, a mixture consisting of oxime (0.6 mmol, 231.2 mg), enal (0.2 mmol, 53.6 mg), $Fe(acac)_2$ (0.02 mmol, 5.0 mg), amine A4 (0.04 mmol, 18.7 mg) and 1,4-dioxane (1 mL)/toluene (1 mL) under a N_2 atmosphere was stirred at 50 ℃ for 48 h to afford **108**. Colorless oil (35.5 mg, 42% yield, 92:8 er); R_f = 0.5 (Petroleum ether/Ethyl acetate = 10:1); **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.63 (d, *J* = 4.8 Hz, 1H), 8.51 – 8.47 (m, 1H), 8.06 (d, *J* = 8.7 Hz, 1H), 7.98 (d, *J* = 8.7 Hz, 1H), 7.95 (d, *J* = 8.2 Hz, 1H), 7.60 – 7.55 (m, 1H), 7.43 – 7.33 (m, 5H), 7.06 (d, *J* = 4.8 Hz, 1H), 5.01 – 4.93 (m, 1H), 2.47 (d, *J* = 15.9 Hz, 1H), 2.23 (d, *J* = 15.8 Hz, 1H), 1.18 (s, 3H), 1.05 (s, 3H), 0.97 (s, 3H), 0.96 (s, 3H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 167.0, 152.1, 147.2, 146.8, 146.3, 137.6, 134.8, 133.2, 131.3, 130.0, 129.7, 128.4, 128.2, 128.1, 127.9, 127.1, 127.0, 126.8, 126.1, 125.8, 123.9, 123.8, 68.8, 40.0, 33.6, 28.6, 28.3, 21.4, 21.3; **HRMS** (ESI) m/z: $[M + H]^+$ calcd. for $C_{29}H_{28}NO_2$ 422.2115; Found 422.2114.

HPLC analysis: DAICEL CHIRALPAK IE, n-hexane/isopropanol = 90/10, flow rate = 1.0 mL/min, λ = 254 nm, t_R (major) = 8.1 min, t_R (minor) = 8.6 min, er = 92:8.

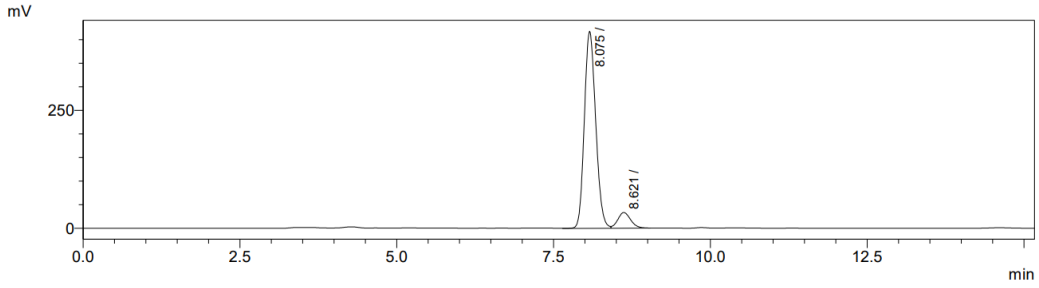
$[\alpha]^{25}_D$ = -82.81 (c = 0.32, $CHCl_3$).

Chiral HPLC spectrum of (*rac*)-**108**:

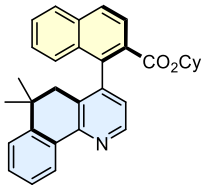


Peak#	Ret. Time	Area	Height	Conc.	Area%
1	8.061	1632456	121077	50.094	50.094
2	8.560	1626306	109983	49.906	49.906

Chiral HPLC spectrum of (*S*)-**108**:



Peak#	Ret. Time	Area	Height	Conc.	Area%
1	8.075	5250684	417612	91.817	91.817
2	8.621	467964	33192	8.183	8.183



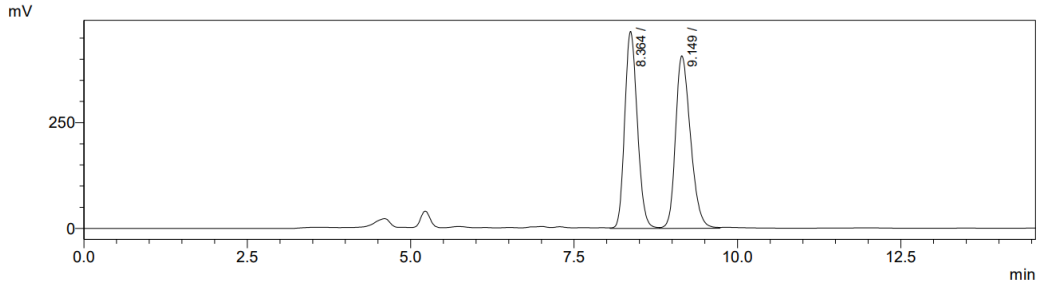
cyclohexyl (*S*)-1-(6,6-dimethyl-5,6-dihydrobenzo[h]quinolin-4-yl)-2-naphthoate (109):

According to the general procedure, a mixture consisting of oxime (0.6 mmol, 231.2 mg), enal (0.2 mmol, 61.7 mg), $Fe(acac)_2$ (0.02 mmol, 5.0 mg), amine A4 (0.04 mmol, 18.7 mg) and 1,4-dioxane (1 mL)/toluene (1 mL) under a N_2 atmosphere was stirred at 50 ℃ for 48 h to afford **109**. White solid (46.3 mg, 50% yield, 90:10 er); R_f = 0.5 (Petroleum ether/Ethyl acetate = 10:1); Mp = 151–152 ℃; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.63 (d, *J* = 4.4 Hz, 1H), 8.48 (d, *J* = 7.0 Hz, 1H), 8.07 (d, *J* = 8.6 Hz, 1H), 7.98 (d, *J* = 8.6 Hz, 1H), 7.95 (d, *J* = 8.1 Hz, 1H), 7.58 (t, *J* = 7.2 Hz, 1H), 7.44 – 7.31 (m, 5H), 7.06 (d, *J* = 4.5 Hz, 1H), 4.77 – 4.68 (m, 1H), 2.46 (d, *J* = 15.8 Hz, 1H), 2.23 (d, *J* = 15.8 Hz, 1H), 1.70 – 1.62 (m, 2H), 1.60 – 1.50 (m, 2H), 1.48 – 1.40 (m, 1H), 1.28 – 1.19 (m, 2H), 1.18 (s, 3H), 1.05 (s, 6H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 166.9, 152.2, 147.2, 146.8, 146.3, 137.6, 134.8, 133.3, 131.3, 123.0, 129.7, 128.4, 128.2, 127.9, 127.1, 127.0, 126.8, 126.1, 125.8, 123.8, 74.0, 40.0, 33.6, 31.3, 31.2, 28.5, 28.3, 25.2, 23.8; **HRMS** (ESI) m/z: $[M + H]^+$ calcd. for $C_{32}H_{32}NO_2$ 462.2428; Found 462.2430.

HPLC analysis: DAICEL CHIRALPAK IE, n-hexane/isopropanol = 90/10, flow rate = 1.0 mL/min, λ = 254 nm, t_R (major) = 8.4 min, t_R (minor) = 9.3 min, er = 90:10.

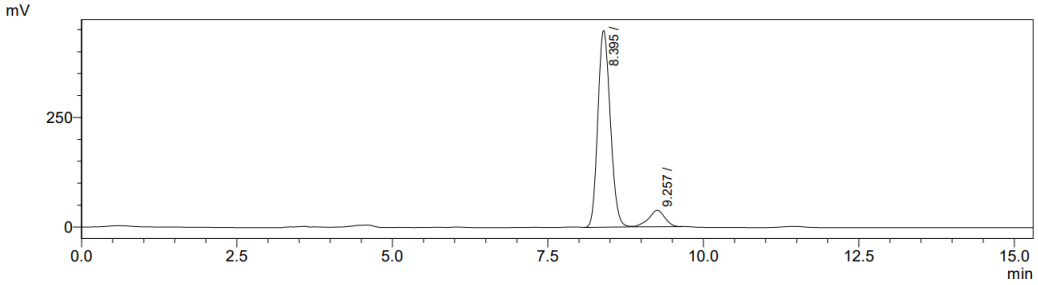
$[\alpha]^{25}_D$ = -50.11 (c = 0.44, $CHCl_3$).

Chiral HPLC spectrum of (*rac*)-**109**:

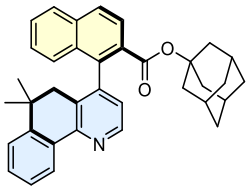


Peak#	Ret. Time	Area	Height	Conc.	Area%
1	8.364	6248055	465805	49.008	49.008
2	9.149	6500913	407972	50.992	50.992

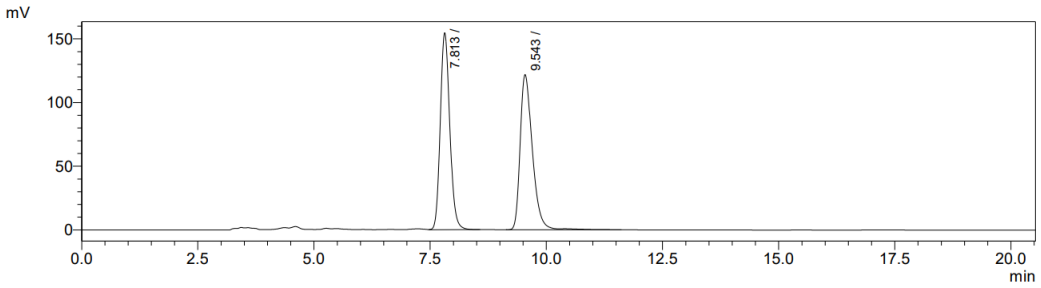
Chiral HPLC spectrum of (*S*)-**109**:



Peak#	Ret. Time	Area	Height	Conc.	Area%
1	8.395	6257117	448481	90.131	90.131
2	9.257	685134	37405	9.869	9.869

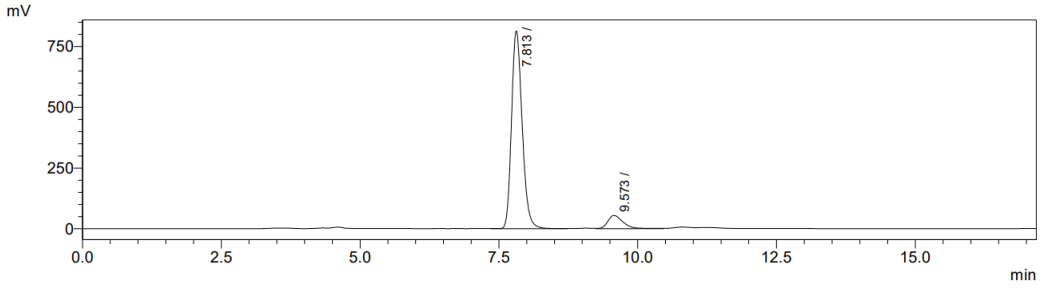


adamantan-1-yl (*S*)-1-(6,6-dimethyl-5,6-dihydrobenzo[h]quinolin-4-yl)-2-naphthoate (110):
According to the general procedure, a mixture consisting of oxime (0.6 mmol, 231.2 mg), enal (0.2 mmol, 72.1 mg), $Fe(acac)_2$ (0.02 mmol, 5.0 mg), amine A4 (0.04 mmol, 18.7 mg) and 1,4-dioxane (1 mL)/toluene (1 mL) under a N_2 atmosphere was stirred at 50 °C for 48 h to afford **110**. Colorless oil (51.4 mg, 50% yield, 91:9 er); R_f = 0.5 (Petroleum ether/Ethyl acetate = 10:1); **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.64 (d, *J* = 4.8 Hz, 1H), 8.50 – 8.44 (m, 1H), 8.01 (d, *J* = 8.6 Hz, 1H), 7.96 (d, *J* = 8.7 Hz, 1H), 7.93 (d, *J* = 8.2 Hz, 1H), 7.59 – 7.54 (m, 1H), 7.42 – 7.34 (m, 5H), 7.07 (d, *J* = 4.9 Hz, 1H), 2.51 (d, *J* = 15.9 Hz, 1H), 2.18 (d, *J* = 15.9 Hz, 1H), 2.03 – 1.98 (m, 3H), 1.84 – 1.79 (m, 6H), 1.54 – 1.50 (m, 6H), 1.21 (s, 3H), 1.02 (s, 3H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 166.5, 152.3, 147.3, 146.8, 146.4, 136.8, 134.6, 133.3, 131.2, 130.2, 129.7, 129.6, 128.4, 128.2, 127.7, 127.1, 126.9, 126.8, 126.1, 125.7, 124.0, 123.9, 82.1, 40.9, 40.0, 36.0, 33.6, 30.8, 28.7, 28.2; **HRMS** (ESI) m/z: $[M + H]^+$ calcd. for $C_{36}H_{36}NO_2$ 514.2741; Found 514.2735.
HPLC analysis: DAICEL CHIRALPAK IE, n-hexane/isopropanol = 90/10, flow rate = 1.0 mL/min, λ = 254 nm, t_R (major) = 7.8 min, t_R (minor) = 9.6 min, er = 91:9.
$[\alpha]^{25}_D$ = -31.83 (c = 0.51, $CHCl_3$).
Chiral HPLC spectrum of (*rac*)-**110**:

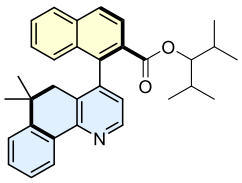


Peak#	Ret. Time	Area	Height	Conc.	Area%
1	7.813	2204625	154585	49.667	49.667
2	9.543	2234192	121877	50.333	50.333

Chiral HPLC spectrum of (*S*)-**110**:



Peak#	Ret. Time	Area	Height	Conc.	Area%
1	7.813	10872740	813763	91.055	91.055
2	9.573	1068160	54696	8.945	8.945



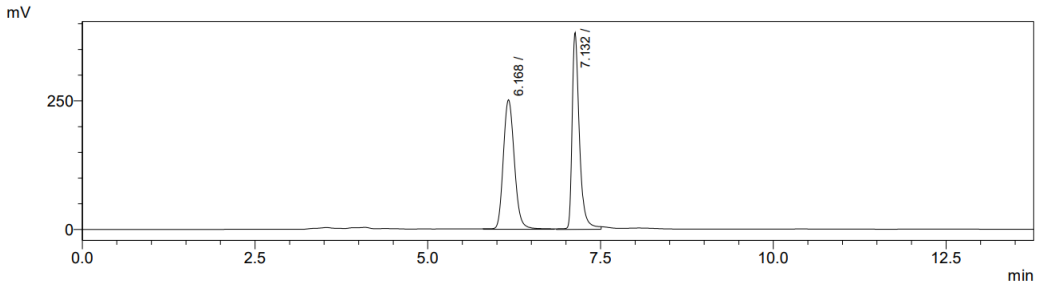
2,4-dimethylpentan-3-yl (*S*)-1-(6,6-dimethyl-5,6-dihydrobenzo[h]quinolin-4-yl)-2-naphthoate (111):

According to the general procedure, a mixture consisting of oxime (0.6 mmol, 231.2 mg), enal (0.2 mmol, 64.9 mg), $Fe(acac)_2$ (0.02 mmol, 5.0 mg), amine A4 (0.04 mmol, 18.7 mg) and 1,4-dioxane (1 mL)/toluene (1 mL) under a N_2 atmosphere was stirred at 50 ℃ for 48 h to afford **111**. Colorless oil (35.7 mg, 37% yield, 93:7 er); R_f = 0.5 (Petroleum ether/Ethyl acetate = 10:1); **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.62 (d, *J* = 4.8 Hz, 1H), 8.51 – 8.44 (m, 1H), 8.09 (d, *J* = 8.7 Hz, 1H), 7.99 (d, *J* = 8.7 Hz, 1H), 7.95 (d, *J* = 8.2 Hz, 1H), 7.58 (t, *J* = 7.3 Hz, 1H), 7.43 – 7.32 (m, 5H), 7.04 (d, *J* = 4.8 Hz, 1H), 4.68 (t, *J* = 6.1 Hz, 1H), 2.55 (d, *J* = 15.9 Hz, 1H), 2.19 (d, *J* = 15.9 Hz, 1H), 1.89 – 1.77 (m, 2H), 1.18 (s, 3H), 1.01 (s, 3H), 0.83 (d, *J* = 6.8 Hz, 3H), 0.81 – 0.78 (m, 6H), 0.72 (d, *J* = 6.7 Hz, 3H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 166.9, 152.2, 147.1, 146.8, 146.3, 138.1, 134.7, 133.3, 131.5, 130.0, 129.6, 128.4, 128.1, 128.0, 127.9, 127.2, 127.0, 126.7, 125.9, 123.8, 123.7, 83.9, 40.0, 33.5, 29.5, 28.8, 28.2, 19.6, 19.4, 17.4, 17.3; **HRMS** (ESI) m/z: $[M + H]^+$ calcd. for $C_{33}H_{36}NO_2$ 478.2741; Found 478.2737.

HPLC analysis: DAICEL CHIRALPAK IE, n-hexane/isopropanol = 90/10, flow rate = 1.0 mL/min, λ = 254 nm, t_R (major) = 6.2 min, t_R (minor) = 7.2 min, er = 93:7.

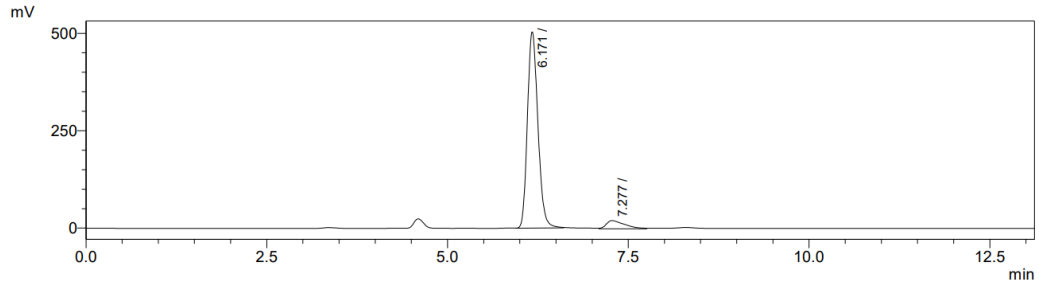
$[\alpha]^{25}_D$ = -66.37 (c = 0.35, $CHCl_3$).

Chiral HPLC spectrum of (*rac*)-**111**:

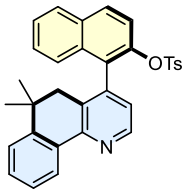


Peak#	Ret. Time	Area	Height	Conc.	Area%
1	6.168	2831133	252342	50.232	50.232
2	7.132	2805037	383131	49.768	49.768

Chiral HPLC spectrum of (*S*)-**111**:



Peak#	Ret. Time	Area	Height	Conc.	Area%
1	6.171	5089533	503272	93.166	93.166
2	7.277	373329	21357	6.834	6.834



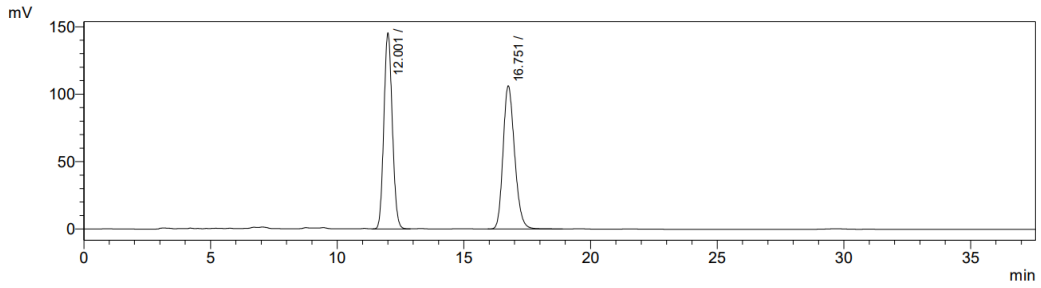
(*S*)-1-(6,6-dimethyl-5,6-dihydrobenzo[h]quinolin-4-yl)naphthalen-2-yl 4-methylbenzenesulfonate (112):

According to the general procedure, a mixture consisting of oxime (0.6 mmol, 231.2 mg), enal (0.2 mmol, 70.4 mg), $Fe(acac)_2$ (0.02 mmol, 5.0 mg), amine A4 (0.04 mmol, 18.7 mg) and 1,4-dioxane (1 mL)/toluene (1 mL) under a N_2 atmosphere was stirred at 50 ℃ for 48 h to afford **112**. Colorless oil (41.9 mg, 41% yield, 89:11 er); R_f = 0.2 (Petroleum ether/Ethyl acetate = 10:1); **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.44 (d, *J* = 7.5 Hz, 1H), 8.42 (d, *J* = 4.5 Hz, 1H), 7.99 (d, *J* = 9.0 Hz, 1H), 7.94 (d, *J* = 8.1 Hz, 1H), 7.74 (d, *J* = 9.0 Hz, 1H), 7.52 (t, *J* = 7.4 Hz, 1H), 7.44 – 7.37 (m, 3H), 7.36 – 7.30 (m, 4H), 7.08 (d, *J* = 7.8 Hz, 2H), 6.69 (d, *J* = 4.5 Hz, 1H), 2.34 (d, *J* = 15.9 Hz, 1H), 2.30 (s, 3H), 2.19 (d, *J* = 15.8 Hz, 1H), 1.13 (s, 3H), 1.03 (s, 3H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 152.5, 146.5, 146.5, 145.3, 144.1, 142.1, 133.1, 133.0, 132.1, 132.1, 130.7, 130.2, 129.8, 129.7, 128.3, 127.9, 127.3, 126.8, 126.5, 125.8, 125.7, 124.7, 123.9, 121.5, 39.4, 33.5, 28.3, 28.0, 21.6; **HRMS** (ESI) m/z: $[M + H]^+$ calcd. for $C_{32}H_{28}NO_3S$ 506.1784; Found 506.1783.

HPLC analysis: DAICEL CHIRALPAK AD-H, n-hexane/isopropanol = 90/10, flow rate = 1.0 mL/min, λ = 254 nm, t_R (major) = 16.7 min, t_R (minor) = 12.0 min, er = 89:11.

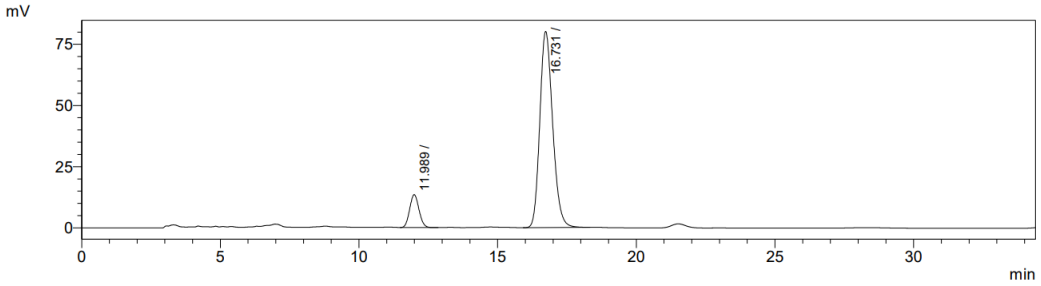
$[\alpha]^{25}_D$ = 9.65 (c = 0.31, $CHCl_3$).

Chiral HPLC spectrum of (*rac*)-**112**:

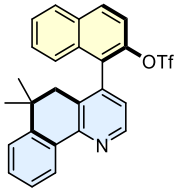


Peak#	Ret. Time	Area	Height	Conc.	Area%
1	12.001	3354614	145567	49.974	49.974
2	16.751	3358140	106232	50.026	50.026

Chiral HPLC spectrum of (*S*)-**112**:



Peak#	Ret. Time	Area	Height	Conc.	Area%
1	11.989	313851	13445	10.860	10.860
2	16.731	2576004	80194	89.140	89.140



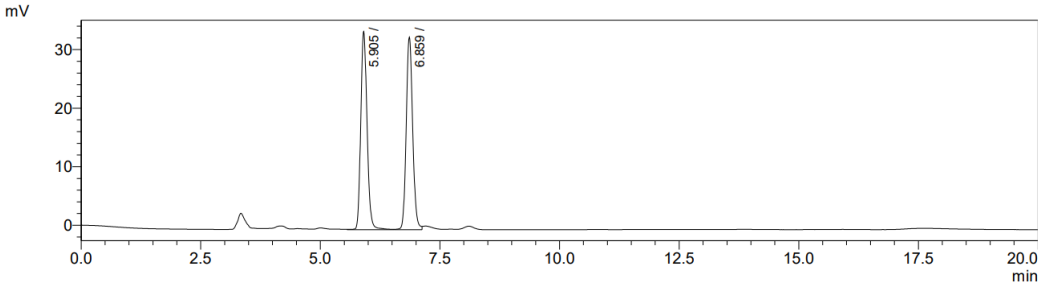
(*S*)-1-(6,6-dimethyl-5,6-dihydrobenzo[h]quinolin-4-yl)naphthalen-2-yl trifluoromethanesulfonate (113) :

According to the general procedure, a mixture consisting of oxime (0.6 mmol, 231.2 mg), enal (0.2 mmol, 66.0 mg), $Fe(acac)_2$ (0.02 mmol, 5.0 mg), amine A4 (0.04 mmol, 18.7 mg) and 1,4-dioxane (1 mL)/toluene (1 mL) under a N_2 atmosphere was stirred at 50 ℃ for 48 h to afford **113**. White solid (39.7 mg, 41% yield, 87:13 er); R_f = 0.5 (Petroleum ether/Ethyl acetate = 10:1); Mp = 123–125 ℃; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.70 (d, *J* = 4.8 Hz, 1H), 8.52 – 8.48 (m, 1H), 8.04 (d, *J* = 9.1 Hz, 1H), 7.99 (d, *J* = 8.2 Hz, 1H), 7.60 (t, *J* = 7.4 Hz, 1H), 7.55 (d, *J* = 9.1 Hz, 1H), 7.49 (t, *J* = 7.6 Hz, 1H), 7.43 – 7.38 (m, 3H), 7.38 – 7.35 (m, 1H), 7.16 (d, *J* = 4.9 Hz, 1H), 2.52 (d, *J* = 15.8 Hz, 1H), 2.34 (d, *J* = 15.8 Hz, 1H), 1.19 (s, 3H), 1.12 (s, 3H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 153.0, 147.3, 146.4, 143.7, 140.7, 133.1, 132.5, 132.3, 131.0, 130.3, 123.0, 128.9, 128.5, 128.0, 127.4, 126.9, 126.1, 126.0, 124.6, 123.9, 119.4, 118.3 (q, $^1J_{C\text{-}F}$ = 320.6 Hz), 39.8, 33.6, 28.3, 28.2; **^{19}F NMR** (565 MHz, $CDCl_3$) δ -74.13; **HRMS** (ESI) m/z: $[M + H]^+$ calcd. for $C_{26}H_{21}F_3NO_3S$ 484.1189; Found 484.1186.

HPLC analysis: DAICEL CHIRALPAK IE, n-hexane/isopropanol = 90/10, flow rate = 1.0 mL/min, λ = 254 nm, t_R (major) = 5.9 min, t_R (minor) = 6.8 min, er = 87:13.

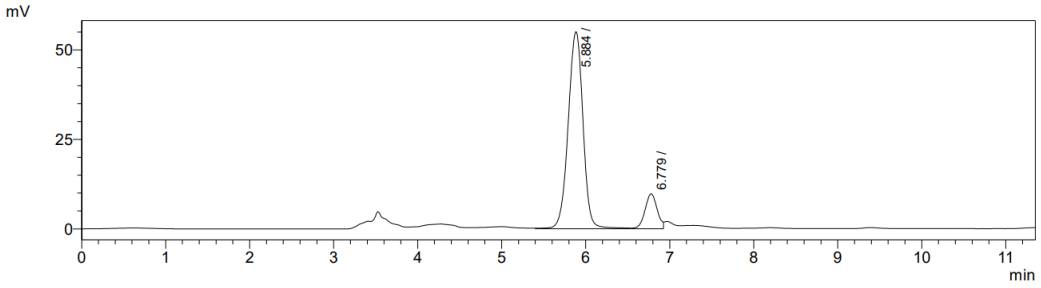
$[\alpha]^{25}_D$ = -46.59 (c = 0.78, $CHCl_3$).

Chiral HPLC spectrum of (*rac*)-**113**:

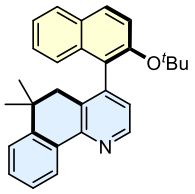


Peak#	Ret. Time	Area	Height	Conc.	Area%
1	5.905	311454	33864	50.300	50.300
2	6.859	307741	32879	49.700	49.700

Chiral HPLC spectrum of (*S*)-**113**:



Peak#	Ret. Time	Area	Height	Conc.	Area%
1	5.884	675181	55090	87.336	87.336
2	6.779	97902	9759	12.664	12.664



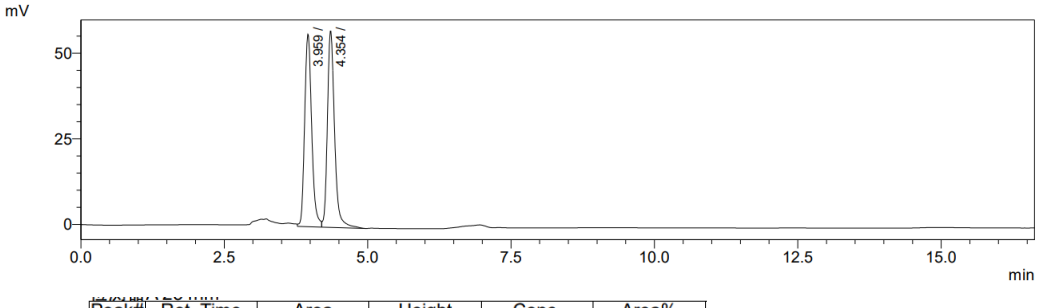
(*S*)-4-(2-(tert-butoxy)naphthalen-1-yl)-6,6-dimethyl-5,6-dihydrobenzo[h]quinoline (114):

According to the general procedure, a mixture consisting of oxime (0.6 mmol, 231.2 mg), enal (0.2 mmol, 50.8 mg), $Fe(acac)_2$ (0.02 mmol, 5.0 mg), amine A4 (0.04 mmol, 18.7 mg) and 1,4-dioxane (1 mL)/toluene (1 mL) under a N_2 atmosphere was stirred at 50 °C for 48 h to afford **114**. Colorless oil (50.0 mg, 61% yield, 80:20 er); R_f = 0.6 (Petroleum ether/Ethyl acetate = 10:1); **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.62 (d, *J* = 4.4 Hz, 1H), 8.53 – 8.46 (m, 1H), 7.86 (t, *J* = 7.7 Hz, 2H), 7.45 – 7.35 (m, 5H), 7.35 – 7.28 (m, 2H), 7.10 (d, *J* = 4.5 Hz, 1H), 2.66 (d, *J* = 15.8 Hz, 1H), 2.37 (d, *J* = 15.8 Hz, 1H), 1.23 (s, 3H), 1.20 (s, 9H), 1.08 (s, 3H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 152.4, 151.1, 146.8, 146.4, 145.6, 133.6, 132.9, 131.3, 130.1, 129.6, 128.9, 128.0, 127.5, 126.7, 126.5, 125.7, 125.6, 125.3, 124.5, 123.9, 122.9, 79.9, 39.8, 33.7, 29.7, 28.5, 28.3; **HRMS** (ESI) m/z: $[M + H]^+$ calcd. for $C_{29}H_{30}NO$ 408.2322; Found 408.2320.

HPLC analysis: DAICEL CHIRALPAK AD-H, n-hexane/isopropanol = 90/10, flow rate = 1.0 mL/min, λ = 254 nm, t_R (major) = 4.4 min, t_R (minor) = 4.0 min, er = 80:20.

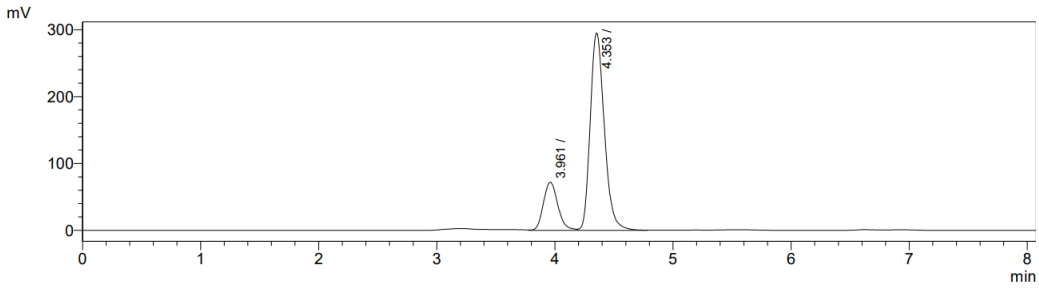
$[\alpha]^{25}_D$ = 32.46 (c = 0.50, $CHCl_3$).

Chiral HPLC spectrum of (*rac*)-**114**:

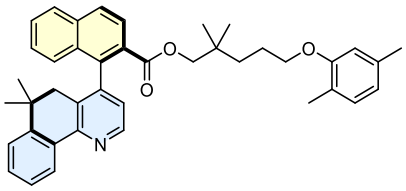


Peak#	Ret. Time	Area	Height	Conc.	Area%
1	3.959	483902	56179	49.300	49.300
2	4.354	497636	57335	50.700	50.700

Chiral HPLC spectrum of (*S*)-**114**:



Peak#	Ret. Time	Area	Height	Conc.	Area%
1	3.961	611941	71967	19.988	19.988
2	4.353	2449581	295019	80.012	80.012



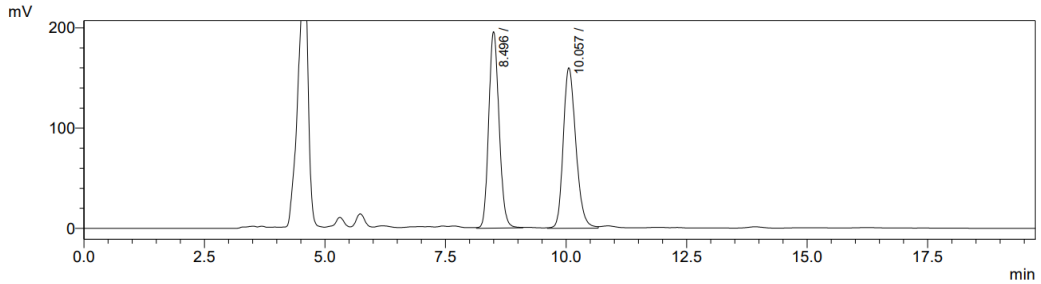
5-(2,5-dimethylphenoxy)-2,2-dimethylpentyl (*S*)-1-(6,6-dimethyl-5,6-dihydrobenzo[*h*]quinolin-4-yl)-2-naphthoate (115)

According to the general procedure, a mixture consisting of oxime (0.6 mmol, 231.2 mg), enal (0.2 mmol, 88.9 mg), $Fe(acac)_2$ (0.02 mmol, 5.0 mg), amine A4 (0.04 mmol, 18.7 mg) and 1,4-dioxane (1 mL)/toluene (1 mL) under a N_2 atmosphere was stirred at 50 ℃ for 48 h to afford **115**. Colorless oil (56.7 mg, 47% yield, 92:8 er); R_f = 0.5 (Petroleum ether/Ethyl acetate = 10:1); **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.64 (d, *J* = 4.6 Hz, 1H), 8.51 – 8.45 (m, 1H), 8.09 (d, *J* = 8.6 Hz, 1H), 7.98 (d, *J* = 8.7 Hz, 1H), 7.95 (d, *J* = 8.2 Hz, 1H), 7.59 (t, *J* = 7.4 Hz, 1H), 7.43 – 7.39 (m, 1H), 7.38 – 7.31 (m, 4H), 7.06 (d, *J* = 4.5 Hz, 1H), 6.97 (d, *J* = 7.3 Hz, 1H), 6.64 (d, *J* = 7.2 Hz, 1H), 6.58 (s, 1H), 3.92 (d, *J* = 10.3 Hz, 1H), 3.85 – 3.80 (m, 3H), 2.49 (d, *J* = 15.8 Hz, 1H), 2.30 (s, 3H), 2.22 (d, *J* = 15.8 Hz, 1H), 2.12 (s, 3H), 1.73 – 1.66 (m, 2H), 1.37 – 1.31 (m, 2H), 1.16 (s, 3H), 1.04 (s, 3H), 0.86 (s, 3H), 0.85 (s, 3H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 167.1, 157.0, 152.3, 147.0, 146.9, 146.3, 138.2, 136.4, 134.9, 133.3, 131.5, 130.3, 129.8, 129.7, 128.5, 128.2, 128.1, 127.4, 127.2, 127.1, 126.8, 125.9, 123.8, 123.7, 123.5, 120.7, 112.0, 73.5, 68.2, 39.8, 35.3, 33.7, 33.6, 28.6, 28.2, 24.2 24.1, 24.1, 21.4, 15.8; **HRMS** (ESI) m/z: $[M + H]^+$ calcd. for $C_{41}H_{44}NO_3$ 598.3316; Found 598.3322.

HPLC analysis: DAICEL CHIRALPAK IE, n-hexane/isopropanol = 90/10, flow rate = 1.0 mL/min, λ = 254 nm, t_R (major) = 8.5 min, t_R (minor) = 10.1 min, er = 92:8.

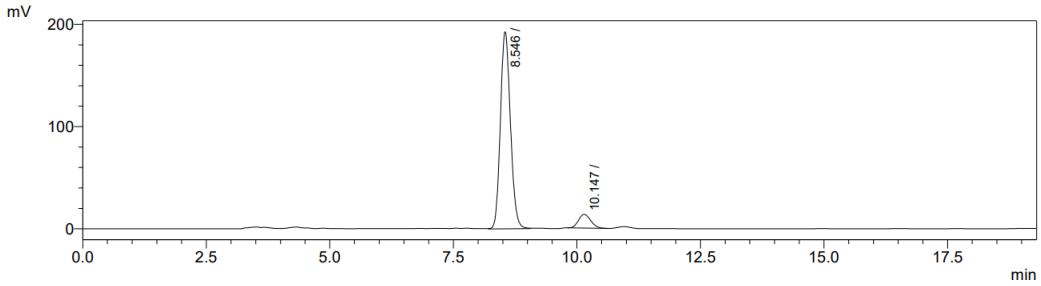
$[\alpha]^{25}_D$ = -31.53 (c = 0.41, $CHCl_3$).

Chiral HPLC spectrum of (*rac*)-**115**:

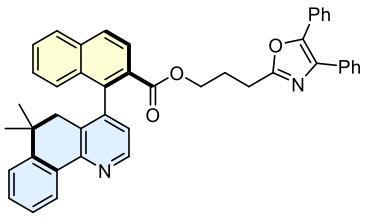


Peak#	Ret. Time	Area	Height	Conc.	Area%
1	8.496	2933111	195997	50.166	50.166
2	10.057	2913752	160159	49.834	49.834

Chiral HPLC spectrum of (*S*)-**115**:



Peak#	Ret. Time	Area	Height	Conc.	Area%
1	8.546	2716491	192713	92.090	92.090
2	10.147	233321	13490	7.910	7.910



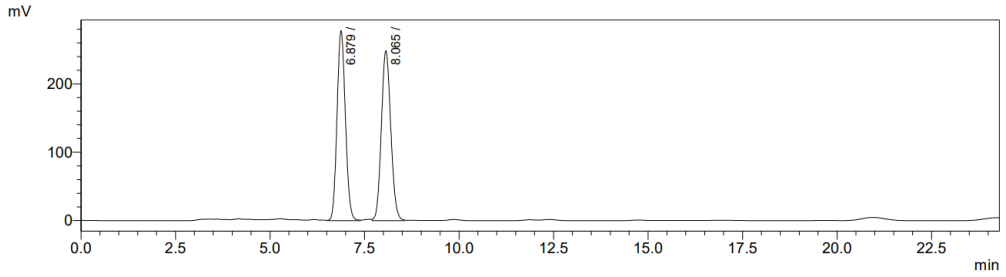
3-(4,5-diphenyloxazol-2-yl)propyl (*S*)-1-(6,6-dimethyl-5,6-dihydrobenzo[h]quinolin-4-yl)-2-naphthoate (116)

According to the general procedure, a mixture consisting of oxime (0.6 mmol, 231.2 mg), enal (0.2 mmol, 97.5 mg), $Fe(acac)_2$ (0.02 mmol, 5.0 mg), amine A4 (0.04 mmol, 18.7 mg) and 1,4-dioxane (1 mL)/toluene (1 mL) under a N_2 atmosphere was stirred at 50 ℃ for 48 h to afford **116**. Yellow oil (57.7 mg, 45% yield, 91:9 er); R_f = 0.5 (Petroleum ether/Ethyl acetate = 10:1); **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.64 (d, *J* = 4.8 Hz, 1H), 8.50 – 8.44 (m, 1H), 8.07 (d, *J* = 8.7 Hz, 1H), 7.93 (d, *J* = 8.5 Hz, 2H), 7.61 – 7.56 (m, 3H), 7.55 – 7.50 (m, 2H), 7.40 (t, *J* = 7.6 Hz, 1H), 7.36 – 7.29 (m, 10H), 7.03 (d, *J* = 4.8 Hz, 1H), 4.28 – 4.23 (m, 1H), 4.20 – 4.15 (m, 1H), 2.76 (t, *J* = 7.4 Hz, 2H), 2.46 (d, *J* = 15.8 Hz, 1H), 2.24 (d, *J* = 15.8 Hz, 1H), 2.06 – 1.94 (m, 2H), 1.14 (s, 3H), 1.05 (s, 3H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 167.0, 162.3, 152.2, 146.9, 146.3, 145.3, 138.3, 135.1, 135.0, 133.2, 132.5, 131.4, 129.8, 129.7, 129.0, 128.6, 128.5, 128.4, 128.2, 128.1, 128.0, 127.9, 127.2, 127.1, 127.1, 126.8, 126.5, 126.0, 125.9, 123.8, 123.6, 64.4, 39.9, 33.6, 28.5, 28.2, 25.8, 25.0; **HRMS** (ESI) m/z: $[M + Na]^+$ calcd. for $C_{44}H_{36}N_2NaO_3$ 663.2618; Found 663.2624.

HPLC analysis: DAICEL CHIRALPAK AD-H, n-hexane/isopropanol = 80/20, flow rate = 1.0 mL/min, λ = 254 nm, t_R (major) = 7.9 min, t_R (minor) = 6.7 min, er = 91:9.

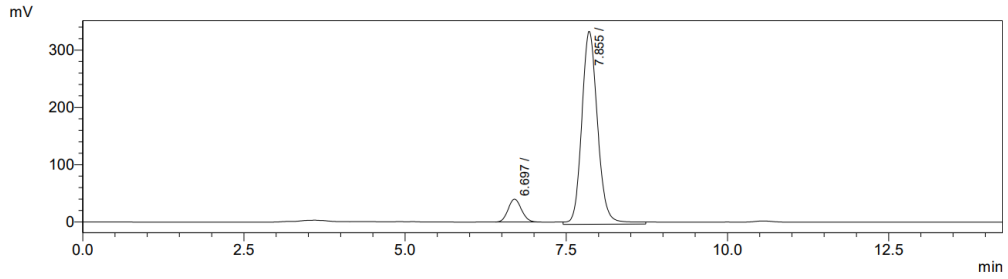
$[\alpha]^{25}_D$ = -17.68 (c = 0.58, $CHCl_3$).

Chiral HPLC spectrum of (*rac*)-**116**:



Peak#	Ret. Time	Area	Height	Conc.	Area%
1	6.879	4286681	278272	49.800	49.800
2	8.065	4321043	248793	50.200	50.200

Chiral HPLC spectrum of (*S*)-**116**:

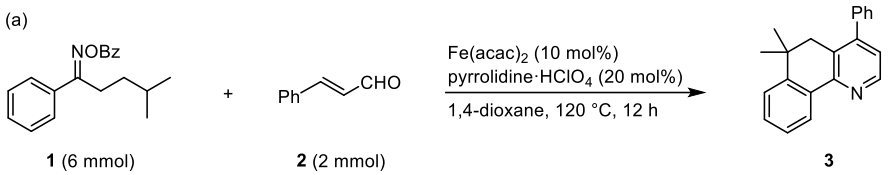


Peak#	Ret. Time	Area	Height	Conc.	Area%
1	6.697	574816	39985	9.032	9.032
2	7.855	5789316	336822	90.968	90.968

Synthetic Transformations

Scale-up Reaction

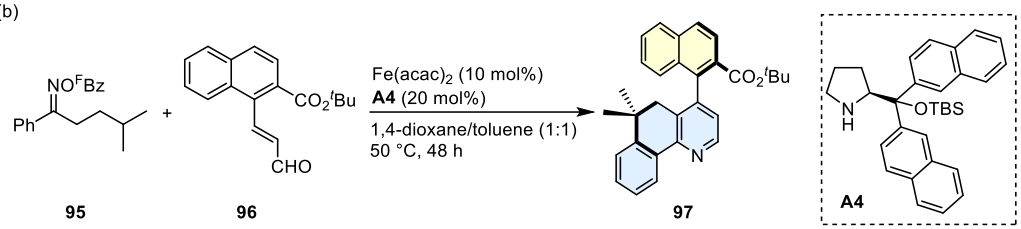
(a)



1 (6 mmol) **2** (2 mmol) **3**

To an oven-dried 100 mL Schlenk tube equipped with a magnetic stir bar was added **1** (6.0 mmol, 3 equiv), **2** (2.0 mmol, 1.0 equiv). The tube was introduced in a nitrogen-filled glove box, and $Fe(acac)_2$ (10 mol%) and pyrrolidine·$HClO_4$ (20 mol%) were added. The tube was then sealed with a Teflon-lined screw cap and taken out from the glove box. Then anhydrous 1,4-dioxane (20 mL) was added to the Schlenk tube through the rubber septum using syringes, and then the septum was replaced by a Teflon screwcap under nitrogen flow. Then the reaction mixture was stirred at 120 °C for 12 h. After the reaction was complete, the reaction was quenched with an aqueous solution of saturated $NaHCO_3$. Then the mixture was extracted with ethyl acetate. The combined organic layers were washed with brine and dried over Na_2SO_4. Then the organic layers were filtered, and concentrated in vacuo. The residue was purified by flash silica gel chromatography (eluent: Petroleum ether /Ethyl acetate = 60:1) to afford the desired product **3** as a white solid in 61% yield (347.7 mg).

(b)

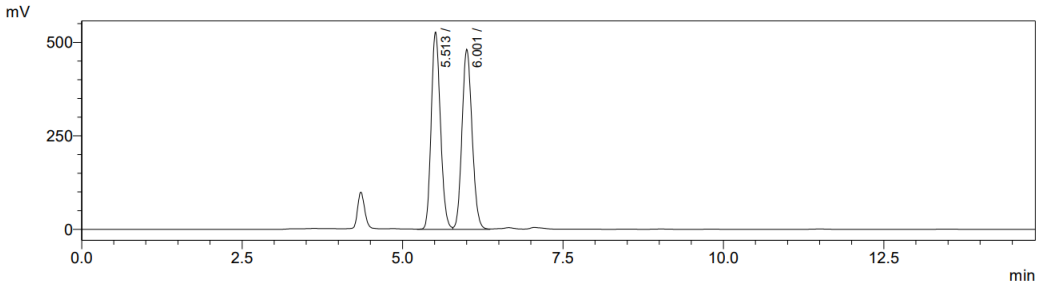


95 **96** **97**

To an oven-dried 100 mL Schlenk tube equipped with a magnetic stir bar was added **95** (6.0 mmol, 3 equiv), **96** (2.0 mmol, 1.0 equiv). The tube was introduced in a nitrogen-filled glove box, and $Fe(acac)_2$ (10 mol%) and **A4** (20 mol%) were added. The tube was then sealed with a Teflon-lined screw cap and taken out from the glove box. Anhydrous 1,4-dioxane (10 mL) and Toluene (10 mL) were added to the Schlenk tube through the rubber septum using syringes, and then the septum was replaced by a Teflon screwcap under nitrogen flow. Then the reaction mixture was stirred at 50 °C for 48 h. After the reaction was complete, the reaction was quenched with an aqueous solution of saturated $NaHCO_3$. Then the mixture was extracted with ethyl acetate. The combined organic layers were washed with brine and dried over anhydrous Na_2SO_4. Then the organic layers were filtered, and concentrated in vacuo. The residue was purified by flash silica gel chromatography (eluent: Petroleum ether /Ethyl acetate = 40:1) to afford the desired product **97** as a colorless oil in 51% yield (444.3 mg) with 93:7 er.

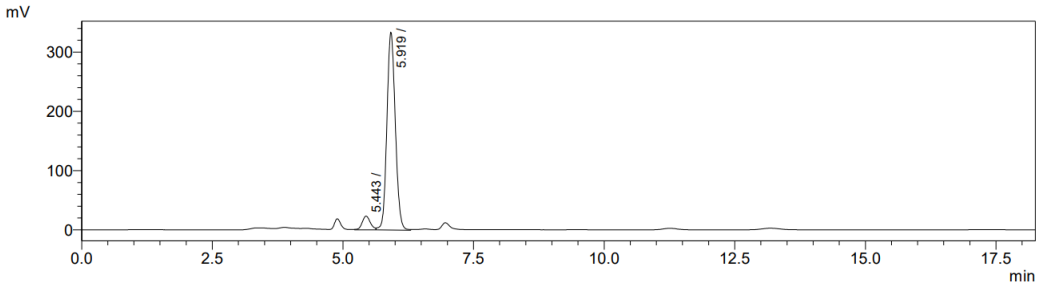
HPLC analysis: DAICEL CHIRALPAK AD-H, n-hexane/isopropanol = 90/10, flow rate = 1.0 mL/min, λ = 254 nm, t_R (major) = 5.9 min, t_R (minor) = 5.4 min, er = 93:7.

Chiral HPLC spectrum of (*rac*)-**97** (scale-up reaction):



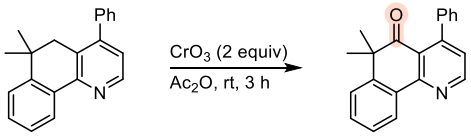
Peak#	Ret. Time	Area	Height	Conc.	Area%
1	5.513	5287502	527709	50.041	50.041
2	6.001	5278885	481878	49.959	49.959

Chiral HPLC spectrum of (*S*)-**97** (scale-up reaction):



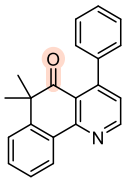
Peak#	Ret. Time	Area	Height	Conc.	Area%
1	5.443	253502	23334	6.358	6.358
2	5.919	3733580	333794	93.642	93.642

Synthetic Transformations of pyridines



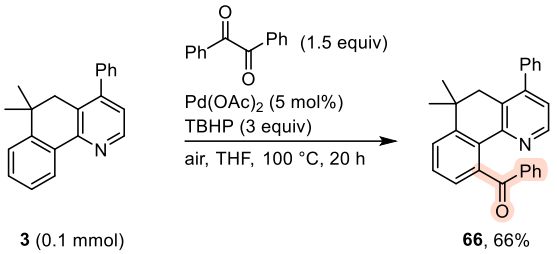
3 (0.4 mmol) **65**, 67%

A 10 mL oven-dried Schlenk tube was charged with **3** (114.1mg, 0.4 mmol), CrO_3 (80.0 mg, 0.8 mmol, 2 equiv), and 3 mL Ac_2O. Then the mixture was stirred for 3 h at room temperature. After completion, the reaction was quenched with an aqueous solution of saturated $NaHCO_3$. Then the aqueous layers were extracted with ethyl acetate. The combined organic layers were washed with brine, dried over Na_2SO_4, filtered, and concentrated. The residue was isolated by flash silica gel chromatography to give the product **65** in 67 % yield (80.5 mg).[20]

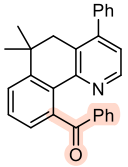


6,6-dimethyl-4-phenylbenzo[h]quinolin-5(6H)-one (65):

White solid (80.5 mg, 67% yield); R_f = 0.5 (Petroleum ether/Ethyl acetate = 10:1); Mp = 176 – 177 °C; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.80 (d, *J* = 4.9 Hz, 1H), 8.69 – 8.65 (m, 1H), 7.50 – 7.41 (m, 6H), 7.30 – 7.26 (m, 2H), 7.21 (d, *J* = 4.9 Hz, 1H), 1.57 (s, 6H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 203.5, 155.0, 152.4, 151.4, 144.4, 139.3, 130.9, 130.7, 128.4, 128.1, 127.5, 127.3, 126.6, 125.4, 125.1, 124.2, 48.8, 25.5; **HRMS** (ESI) m/z: $[M + H]^+$ calcd. for $C_{21}H_{18}NO$ 300.1383; Found 300.1382.

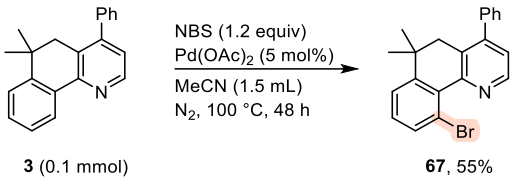


Under air atmosphere, a sealable reaction tube (10 mL) equipped with a magnetic stirrer bar was charged with **3** (28.5 mg, 0.1 mmol), $Pd(OAc)_2$ (1.1 mg, 5 mol%), α-diphenylketone (31.5 mg, 0.15 mmol, 1.5 equiv), TBHP (27.0 mg, 0.3 mmol, 3 equiv) and THF (1.0 mL). The rubber septum was then replaced by a Teflon-coated screw cap, and the reaction vessel was placed in an oil bath at 100 °C for 20 h. After the reaction was completed, it was cooled to room temperature and diluted with ethyl acetate. The resulting solution was directly filtered through a pad of silica gel using a sintered glass funnel, and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel to afford **66** in 66% yield (26.0 mg).[21]

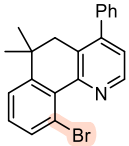


(6,6-dimethyl-4-phenyl-5,6-dihydrobenzo[h]quinolin-10-yl)(phenyl)methanone (66):

White solid (26.0 mg, 66% yield); R_f = 0.5 (Petroleum ether/Ethyl acetate = 10:1); Mp = 179 – 180 °C; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.08 (d, *J* = 4.9 Hz, 1H), 7.80 – 7.76 (m, 2H), 7.51 (dd, *J* = 7.7, 1.0 Hz, 1H), 7.48 – 7.43 (m, 3H), 7.43 – 7.38 (m, 2H), 7.34 – 7.29 (m, 3H), 7.29 – 7.26 (m, 2H), 6.89 (d, *J* = 4.9 Hz, 1H), 2.85 (s, 2H), 1.25 (s, 6H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 198.6, 150.6, 148.6, 147.0, 145.6, 139.4, 138.9, 138.6, 132.5, 131.6, 129.2, 128.9, 128.8, 128.4, 128.4, 128.0, 126.5, 125.0, 123.1, 39.7, 34.5, 28.1; **HRMS** (ESI) m/z: $[M + H]^+$ calcd. for $C_{28}H_{24}NO$ 390.1852; Found 390.1851.

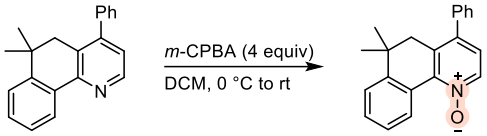


3 (28.5mg, 0.1 mmol), $Pd(OAc)_2$ (1.1 mg, 5 mol%), and NBS (21.2 mg, 0.12 mmol, 1.2 equiv) were dissolved in MeCN (1.5 mL) in a 10 mL tube. The tube was evacuated and backfilled with nitrogen (3 times) and sealed with a Teflon screw cap. The mixture was heated at 100 °C for 48 h. After cooling to room temperature, the solvent was evaporated and the residue was purified by flash chromatography on silica gel to afford **67** in 55% yield (20.2 mg).[22]



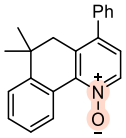
10-bromo-6,6-dimethyl-4-phenyl-5,6-dihydrobenzo[h]quinoline (67):

Colorless oil (20.2 mg, 55% yield); R_f = 0.6 (Petroleum ether/Ethyl acetate = 10:1); **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.66 (d, *J* = 4.9 Hz, 1H), 7.65 (d, *J* = 7.9 Hz, 1H), 7.48 (t, *J* = 7.3 Hz, 2H), 7.44 (t, *J* = 7.3 Hz, 1H), 7.36 (d, *J* = 7.0 Hz, 2H), 7.32 (d, *J* = 7.6 Hz, 1H), 7.20 – 7.15 (m, 2H), 2.74 (s, 2H), 1.11 (s, 6H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 152.4, 150.0, 148.6, 146.0, 138.7, 133.8, 133.0, 129.9, 129.8, 129.0, 128.6, 128.1, 123.4, 123.1, 121.1, 40.4, 35.3, 27.5; **HRMS** (ESI) m/z: $[M + H]^+$ calcd. for $C_{21}H_{19}BrN$ 364.0695; Found 364.0693.



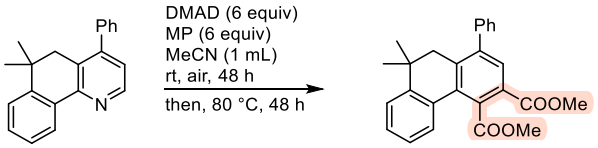
3 (0.1 mmol) **68**, 80%

To a solution of **3** (28.5 mg, 0.1 mmol) in DCM (2.0 mL) was added *m*-chloroperoxybenzoic acid (69.0 mg, 0.4 mmol, 4 equiv) at 0 ℃. The reaction mixture was stirred at 25 ℃ for 12 hours. After the reaction was complete (monitored by TLC), the reaction mixture was then quenched with saturated Na_2CO_3 aqueous solution and extracted with DCM. The combined organic layers were washed with brine, dried over Na_2SO_4, and filtrated. The solvent was removed under reduced pressure and the residue was purified by flash chromatography on silica gel (DCM/MeOH = 60:1) to afford **68** in 80% yield (24.2 mg).[23]



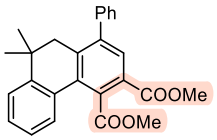
6,6-dimethyl-4-phenyl-5,6-dihydrobenzo[h]quinoline 1-oxide (68):

White solid (24.2 mg, 80% yield); R_f = 0.5 (DCM/MeOH = 30:1); Mp = 139 – 140 ℃; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 9.44 (d, *J* = 7.7 Hz, 1H), 8.29 (d, *J* = 6.6 Hz, 1H), 7.49 (dd, *J* = 10.6, 3.9 Hz, 2H), 7.46 – 7.36 (m, 4H), 7.31 (d, *J* = 7.0 Hz, 2H), 7.08 (d, *J* = 6.7 Hz, 1H), 2.71 (s, 2H), 1.19 (s, 6H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 146.9, 143.1, 139.0, 138.9, 137.9, 133.5, 130.5, 128.9, 128.8, 128.7, 128.2, 126.7, 125.8, 124.2, 123.2, 41.3, 33.9, 27.5; **HRMS** (ESI) m/z: $[M + H]^+$ calcd. for $C_{21}H_{20}NO$ 302.1539; Found 302.1537.



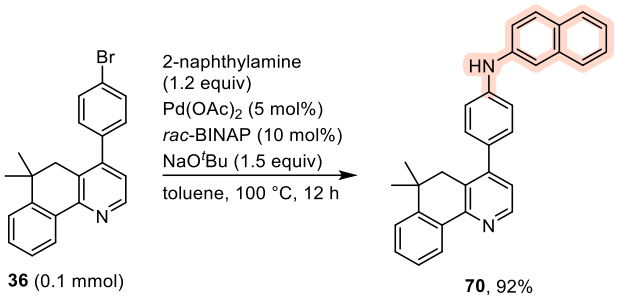
3 (0.15 mmol) **69**, 71%

A 10 mL oven-dried Schlenk tube equipped with a magnetic stirring bar was charged with a pyridine substrate (28.5 mg, 0.15 mmol), methyl pyruvate (91.8 mg, 0.9 mmol, 6 equiv) and MeCN (1 mL, 0.15 M). Dimethyl acetylenedicarboxylate (127.9 mg, 0.9 mmol, 6 equiv) was then added to the stirred reaction mixture. The reaction mixture was allowed to stir at room temperature for 48 h. The reaction mixture was then stirred at 80 ℃ for 48 h under an air atmosphere. After the reaction was complete, as monitored by TLC, the solvent was removed in a rotary evaporator under reduced pressure and the residue was subjected to flash column chromatography over silica gel to give the corresponding product **69** in 71% yield (42.8 mg).[24]



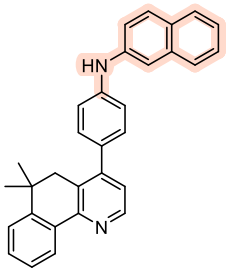
dimethyl 9,9-dimethyl-1-phenyl-9,10-dihydrophenanthrene-3,4-dicarboxylate (69):

White solid (42.8 mg, 71% yield); R_f = 0.4 (Petroleum ether/Ethyl acetate = 10:1); Mp = 185 – 186 °C; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.86 (s, 1H), 7.67 (d, *J* = 7.8 Hz, 1H), 7.46 (t, *J* = 7.3 Hz, 2H), 7.44 – 7.37 (m, 2H), 7.35 – 7.30 (m, 3H), 7.28 – 7.24 (m, 1H), 3.91 (s, 3H), 3.88 (s, 3H), 2.67 (s, 2H), 1.14 (s, 6H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 170.8, 166.8, 146.5, 142.5, 140.5, 139.9, 134.2, 132.2, 131.3, 130.2, 129.2, 128.7, 128.5, 127.7, 127.4, 126.7, 126.2, 123.7, 52.6, 52.6, 42.4, 34.0, 27.0. **HRMS** (ESI) m/z: $[M + H]^+$ calcd. for $C_{26}H_{25}O_4$ 401.1747; Found 401.1747.



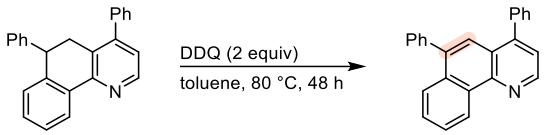
36 (0.1 mmol) **70**, 92%

To a 10 mL Schlenk tube, **36** (36.4 mg, 0.1 mmol), $Pd(OAc)_2$ (1.1 mg, 5 mol%), *rac*-BINAP (6.2 mg, 10 mol%), NaO^tBu (14.4 mg, 0.15 mmol, 1.5 equiv), 2-naphthylamine (17.2 mg, 0.12 mmol, 1.2 equiv), and toluene (1 mL) were added. The tube was charged with nitrogen and the mixture was then heated at 100 °C for 12 h. After cooling to room temperature, the reaction mixture was diluted with ethyl acetate and filtered through a short pad of silica. The final product was purified by flash chromatography to afford **70** in 92% yield (39.3 mg).[25]



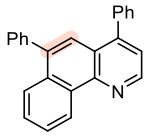
***N*-(4-(6,6-dimethyl-5,6-dihydrobenzo[h]quinolin-4-yl)phenyl)naphthalen-2-amine (70) :**

White solid (39.3 mg, 92% yield); R_f = 0.5 (Petroleum ether/Ethyl acetate = 5:1); Mp = 132 – 133°C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.57 (d, *J* = 4.9 Hz, 1H), 8.43 (d, *J* = 3.7 Hz, 1H), 7.79 (t, *J* = 8.6 Hz, 2H), 7.71 (d, *J* = 8.2 Hz, 1H), 7.56 (d, *J* = 1.7 Hz, 1H), 7.44 (t, *J* = 7.5 Hz, 1H), 7.41 – 7.37 (m, 3H), 7.36 (d, *J* = 7.5 Hz, 1H), 7.34 – 7.27 (m, 3H), 7.24 (d, *J* = 8.5 Hz, 2H), 7.15 (d, *J* = 5.0 Hz, 1H), 6.07 (s, 1H), 2.90 (s, 2H), 1.25 (s, 6H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 152.8, 148.9, 147.0, 146.3, 143.2, 140.0, 134.6, 133.6, 131.2, 130.1, 129.6, 129.3, 128.1, 127.7, 126.8, 126.6, 126.6, 125.9, 123.9, 123.7, 123.4, 120.5, 117.0, 113.1, 40.3, 33.9, 28.2; **HRMS** (ESI) m/z: $[M + H]^+$ calcd. for $C_{31}H_{27}N_2$ 427.2169; Found 427.2168.



24 (0.1 mmol) **71**, 73%

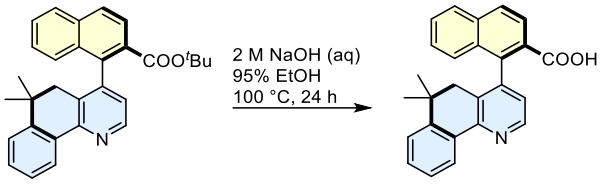
A 10 mL oven-dried reaction tube was charged with **24** (33.3 mg, 0.1 mmol), DDQ (45.4 mg, 0.2 mmol, 2 equiv) and 1 mL toluene. Then the mixture was stirred at 80 ℃ for 48 h. The reaction mixture was purified by silica gel column chromatography to afford **71** in 73 % yield (24.3 mg).[20]



4,6-diphenylbenzo[*h*]quinoline (71) :

White solid (24.3 mg, 73% yield); R_f = 0.6 (Petroleum ether/Ethyl acetate = 10:1); Mp = 173 – 174 ℃; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.50 (d, *J* = 8.2 Hz, 1H), 9.03 (d, *J* = 4.5 Hz, 1H), 7.88 (d, *J* = 8.2 Hz, 1H), 7.80 – 7.72 (m, 2H), 7.64 (t, *J* = 7.2 Hz, 1H), 7.58 – 7.42 (m, 11H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 148.4, 148.2, 146.6, 140.5, 139.8, 138.4, 132.4, 132.0, 130.0, 129.6, 128.7, 128.3, 128.3, 128.2, 127.5, 127.0, 126.2, 125.2, 124.0, 123.4, 122.7; **HRMS** (ESI) m/z: $[M + H]^+$ calcd. for $C_{25}H_{18}N$ 332.1434; Found 332.1432.

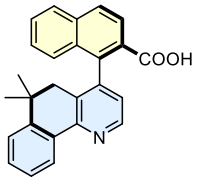
Synthetic Transformations of Axially Chiral Heterobiaryls



97, 0.1 mmol, 93:7 er

117, 98%, 94:6 er
62%, > 99% ee, (recrystallization)

A 50 mL round-bottomed flask, equipped with a magnetic stirring bar, is charged with 10 mL 95% ethanol and NaOH (800 mg, 2 M) and **97** (87.0 mg, 0.2 mmol, 93:7 er). The flask is fitted with a reflux condenser, and the mixture was heated at 100 ℃ for 24 h. After the reaction was complete (monitored by TLC), the reaction mixture was then quenched with saturated NH_4Cl aqueous solution and extracted with ethyl acetate. The organic layers were combined, dried over Na_2SO_4, and filtered. Then the solvent was removed under reduced pressure and the residue was purified by flash chromatography on silica gel (eluent: DCM/MeOH = 30/1) to afford **117** in 98% yield with 94:6 er, or recrystallized from ethyl acetate to afford **117** in 62% yield with > 99% ee.



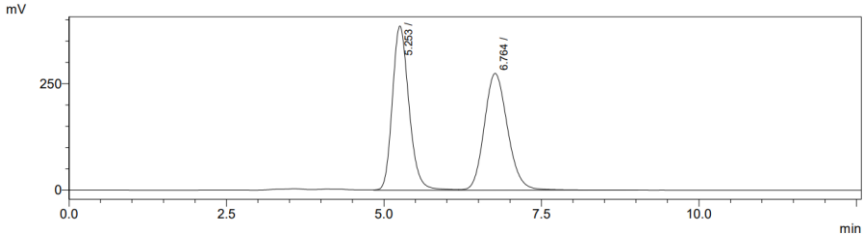
(*S*)-1-(6,6-dimethyl-5,6-dihydrobenzo[h]quinolin-4-yl)-2-naphthoic acid (117) :

White solid (74.4 mg, 98% yield, 94:6 er; 47.3 mg, 62% yield after recrystallization from ethyl acetate, > 99% ee); R_f = 0.3 (DCM/MeOH = 20:1); Mp = 179 – 181 ℃; **^{1}H NMR** (600 MHz, DMSO) δ 12.88 (s, 1H), 8.60 (d, *J* = 4.5 Hz, 1H), 8.42 (d, *J* = 6.9 Hz, 1H), 8.12 (d, *J* = 8.6 Hz, 1H), 8.09 (d, *J* = 8.1 Hz, 1H), 8.04 (d, *J* = 8.6 Hz, 1H), 7.64 (t, *J* = 7.3 Hz, 1H), 7.49 (t, *J* = 7.5 Hz, 1H), 7.43 – 7.35 (m, 3H), 7.27 (d, *J* = 8.4 Hz, 1H), 7.11 (d, *J* = 4.6 Hz, 1H), 2.39 (d, *J* = 15.7 Hz, 1H), 2.21 (d, *J* = 15.8 Hz, 1H), 1.08 (s, 3H), 1.03 (s, 3H); **^{13}C NMR** (151 MHz, DMSO) δ 168.4, 151.3, 147.4, 147.3, 146.4, 137.5, 134.7, 133.3, 131.3, 130.1, 129.5, 128.9, 128.8, 128.4, 127.8, 127.0, 126.8, 126.3, 125.7, 124.5, 124.2, 33.6, 28.7, 28.7; **HRMS** (ESI) m/z: $[M + H]^+$ calcd. for $C_{26}H_{22}NO_2$ 380.1645; Found 380.1646.

HPLC analysis: DAICEL CHIRALPAK AD-H, n-hexane/isopropanol = 60/40, flow rate = 1.0 mL/min, λ = 254 nm, t_R (major) = 5.2 min, t_R (minor) = 6.7 min, er = 94:6; DAICEL CHIRALPAK AD-H, n-hexane/isopropanol = 60/40, flow rate = 1.0 mL/min, λ = 254 nm, t_R (major) = 5.3 min, t_R (minor) = 6.8 min, ee ＞ 99%.

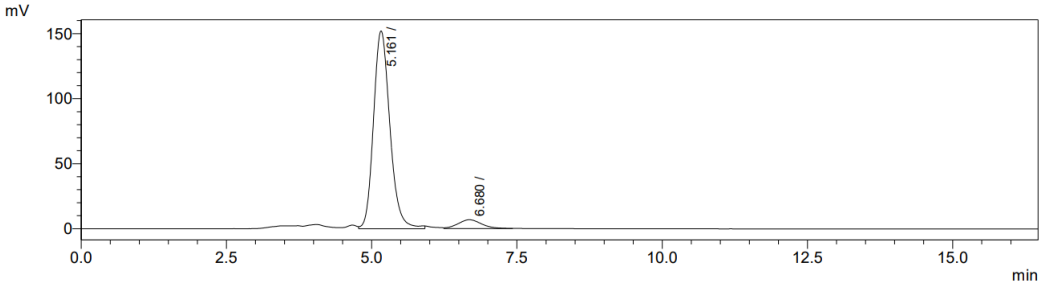
$[\alpha]^{25}_D$ = -102.11 (c = 0.47, DMF, ee ＞ 99%).

Chiral HPLC spectrum of (*rac*)-**117**:



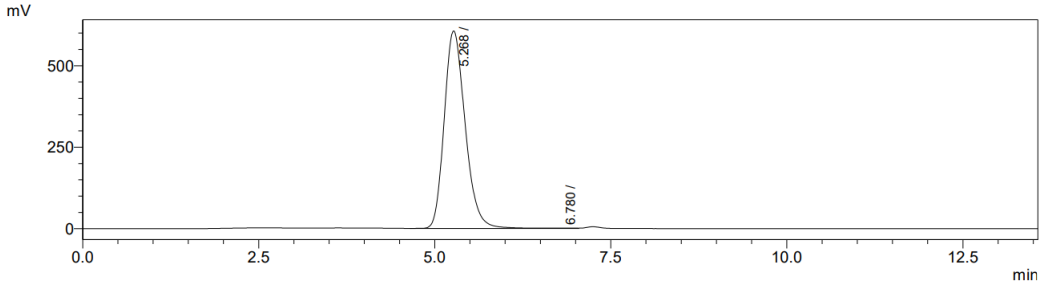
Peak#	Ret. Time	Area	Height	Conc.	Area%
1	5.253	7068403	386044	50.023	50.023
2	6.764	7061916	274493	49.977	49.977

Chiral HPLC spectrum of (*S*)-**117**:

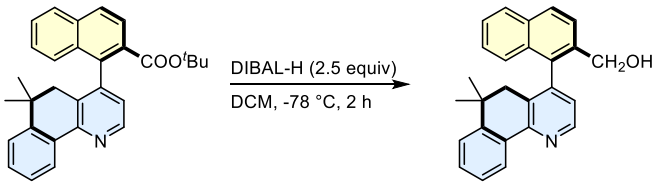


Peak#	Ret. Time	Area	Height	Conc.	Area%
1	5.161	2987437	152069	93.830	93.830
2	6.680	196454	6850	6.170	6.170

Chiral HPLC spectrum of (*S*)-**117** after recrystallization:

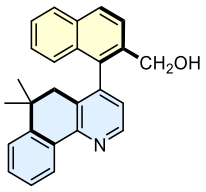


Peak#	Ret. Time	Area	Height	Conc.	Area%
1	5.268	12556751	606078	99.696	99.696
2	6.780	38310	1410	0.304	0.304



97, 0.2 mmol, 93:7 er **118**, 90%, 94:6 er

The axially chiral ester **97** (87.0 mg, 0.2 mmol) was dissolved in anhydrous DCM (5 mL) in a 50 mL flask. Then, the resulting solution was cooled down to −78 °C. DIBAL-H solution (1.0 M in hexanes, 0.5 mL, 0.5 mmol, 2.5 equiv) was added dropwise. The reaction was stirred at the same temperature for 2 h. After the reaction was complete (monitored by TLC), and then point water (2 mL) was added. The solution was allowed to warm up to room temperature and a NaOH solution (10% in water, 2 mL) was added followed by water (10 mL). The mixture was stirred vigorously for an hour until the aqueous phase changed clear, and extracted with DCM (10 mL × 3). The organic layers were combined, dried over Na_2SO_4, and filtered. Then the solvent was removed under reduced pressure and the residue was purified by flash chromatography on silica gel (eluent: petroleum ether/Ethyl acetate = 5/1) to afford **118** in 90% yield with 94:6 er.[12]



(*S*)-(1-(6,6-dimethyl-5,6-dihydrobenzo[h]quinolin-4-yl)naphthalen-2-yl)methanol (118) :

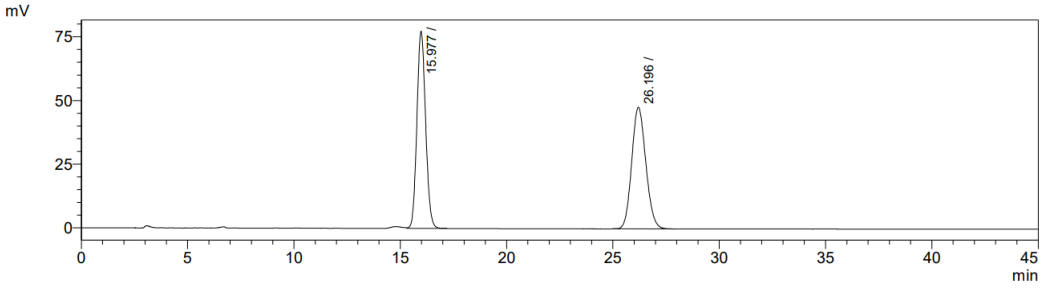
Colorless oil (65.8 mg, 90% yield, 94:6 er); R_f = 0.2 (Petroleum ether/Ethyl acetate = 3:1); **^{1}H**

NMR (600 MHz, $CDCl_3$) δ 8.66 (d, *J* = 4.5 Hz, 1H), 8.51 – 8.47 (m, 1H), 7.99 (d, *J* = 8.5 Hz, 1H), 7.93 (d, *J* = 8.2 Hz, 1H), 7.77 (d, *J* = 8.5 Hz, 1H), 7.50 (t, *J* = 7.4 Hz, 1H), 7.43 – 7.33 (m, 4H), 7.25 – 7.23 (m, 1H), 7.07 (d, *J* = 4.5 Hz, 1H), 4.57 – 4.49 (m, 2H), 2.40 (d, *J* = 15.9 Hz, 1H), 2.33 (d, *J* = 15.7 Hz, 1H), 1.71 (s, 1H), 1.14 (s, 3H), 1.10 (s, 3H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 152.8, 147.4, 146.4, 146.0, 135.4, 133.8, 133.1, 132.9, 131.4, 130.2, 129.9, 128.7, 128.2, 126.9, 126.6, 126.1, 125.9, 125.8, 125.6, 124.2, 123.9, 62.9, 39.7, 33.6, 28.2; **HRMS** (ESI) m/z: $[M + H]^+$ calcd. for $C_{26}H_{24}NO$ 366.1852; Found 366.1857.

HPLC analysis: DAICEL CHIRALPAK AD-H, n-hexane/isopropanol = 90/10, flow rate = 1.0 mL/min, λ = 254 nm, t_R (major) = 26.1 min, t_R (minor) = 16.0 min, er = 94:6.

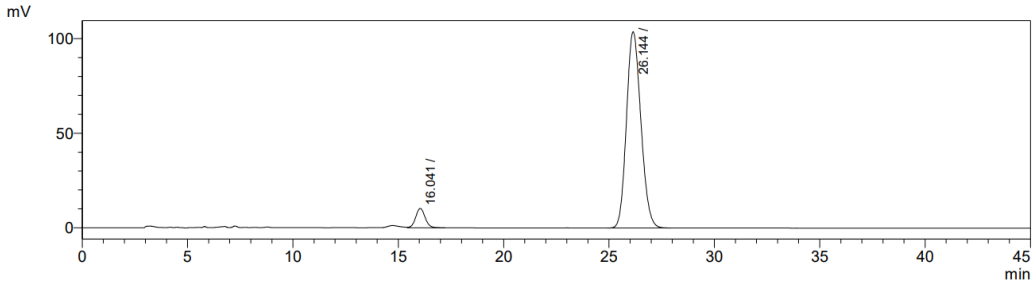
$[\alpha]^{25}_D$ = -157.81 (c = 0.19, $CHCl_3$).

Chiral HPLC spectrum of (*rac*)-**118**:

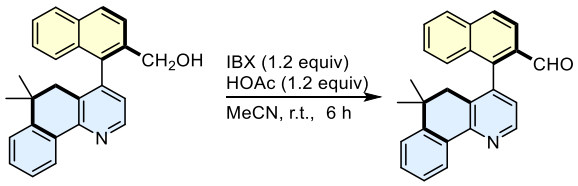


Peak#	Ret. Time	Area	Height	Conc.	Area%
1	15.977	2203295	77520	50.021	50.021
2	26.196	2201436	47727	49.979	49.979

Chiral HPLC spectrum of (*S*)-**118**:



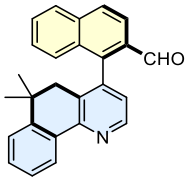
Peak#	Ret. Time	Area	Height	Conc.	Area%
1	16.041	319263	10251	6.079	6.079
2	26.144	4932392	103788	93.921	93.921



118, 0.1 mmol, 94:6 er

119, 83%, 93:7 er

A suspension of the axially chiral alcohol **118** (36.5 mg, 0.1 mmol), IBX (33.6 mg, 0.12 mmol, 1.2 equiv), and acetic acid (7.2 mg, 0.12 mmol, 1.2 equiv) in acetonitrile (2 mL) was stirred at room temperature for 6 h. The reaction progress was monitored by a TLC plate. After completion of the reaction, excess sodium bicarbonate was added to the mixture. The resulting mixture was passed through a short path of silica gel using ethyl acetate as the eluent. Then the solvent was removed under reduced pressure and the residue was purified by flash chromatography on silica gel (eluent: petroleum ether/Ethyl acetate = 30/1) to afford **119** in 83% yield with 93:7 er.[13]



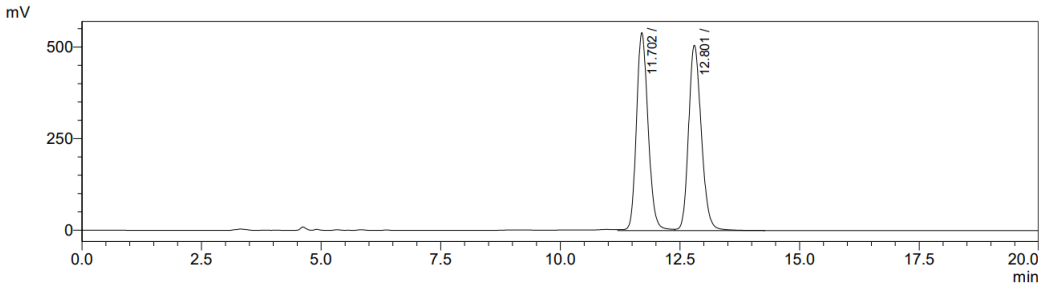
(*S*)-1-(6,6-dimethyl-5,6-dihydrobenzo[h]quinolin-4-yl)-2-naphthaldehyde (119) :

White solid (30.2 mg, 83% yield, 93:7 er); R_f = 0.5 (Petroleum ether/Ethyl acetate = 10:1); Mp = 217 – 218 °C; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 9.88 (s, 1H), 8.71 (d, *J* = 4.8 Hz, 1H), 8.54 – 8.48 (m, 1H), 8.12 (d, *J* = 8.6 Hz, 1H), 8.03 (d, *J* = 8.7 Hz, 1H), 7.99 (d, *J* = 8.2 Hz, 1H), 7.69 – 7.64 (m, 1H), 7.50 – 7.44 (m, 2H), 7.44 – 7.39 (m, 2H), 7.38 – 7.33 (m, 1H), 7.17 (d, *J* = 4.8 Hz, 1H), 2.41 (d, *J* = 15.8 Hz, 1H), 2.35 (d, *J* = 15.8 Hz, 1H), 1.12 (d, *J* = 8.1 Hz, 6H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 191.3, 152.9, 147.2, 146.2, 143.2, 142.7, 136.2, 132.9, 131.3, 130.8, 130.4, 130.2, 129.3, 129.2, 128.6, 127.5, 127.0, 126.9, 126.0, 124.5, 124.0, 122.2, 40.1, 33.7, 28.2, 28.1; **HRMS** (ESI) m/z: $[M + H]^+$ calcd. for $C_{26}H_{22}NO$ 364.1696; Found 364.1694.

HPLC analysis: DAICEL CHIRALPAK IE, n-hexane/isopropanol = 80/20, flow rate = 1.0 mL/min, λ = 254 nm, t_R (major) = 12.8 min, t_R (minor) = 11.8 min, er = 93:7.

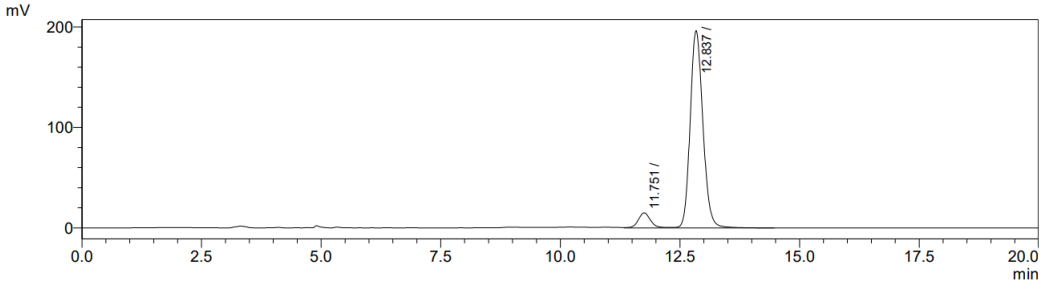
$[\alpha]^{25}_D$ = -102.65 (c = 0.28, $CHCl_3$).

Chiral HPLC spectrum of (*rac*)-**119**:

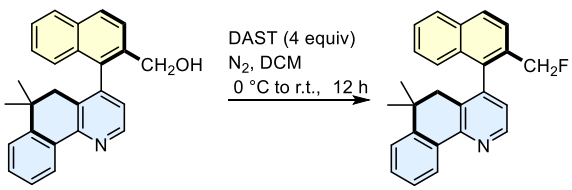


Peak#	Ret. Time	Area	Height	Conc.	Area%
1	11.702	9166930	540571	49.417	49.417
2	12.801	9383193	505888	50.583	50.583

Chiral HPLC spectrum of (*S*)-**119**:



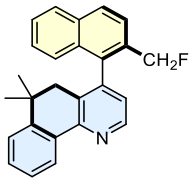
Peak#	Ret. Time	Area	Height	Conc.	Area%
1	11.751	270799	14983	6.942	6.942
2	12.837	3629799	196470	93.058	93.058



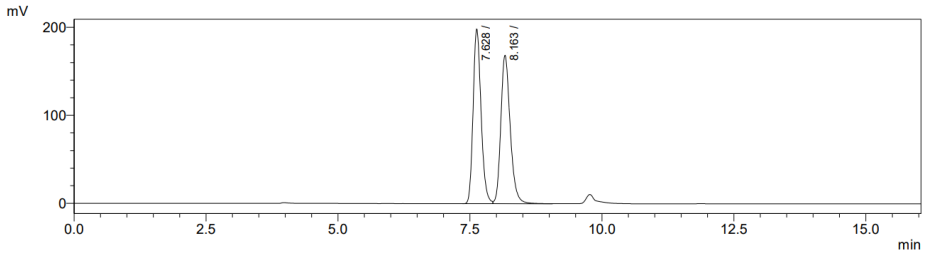
118, 0.1 mmol, 94:6 er **120**, 68%, 93:7 er

A 50 mL round-bottom flask was charged with **118** (36.5 mg, 0.1 mmol), purged with nitrogen,

and dry DCM (5 mL) was added. The solution was cooled to 0 °C and DAST (52 μL, 0.4 mmol, 4 equiv) was added dropwise. The reaction was gradually warmed to room temperature for 12 h, then quenched with saturated aqueous $NaHCO_3$ (10 mL) and extracted with DCM (5 mL × 3). The combined organic phases were dried over Na_2SO_4 and concentrated in vacuum. The residue was purified by silica gel column chromatography to afford **120** in 68 yield with 93:7 er.[26]

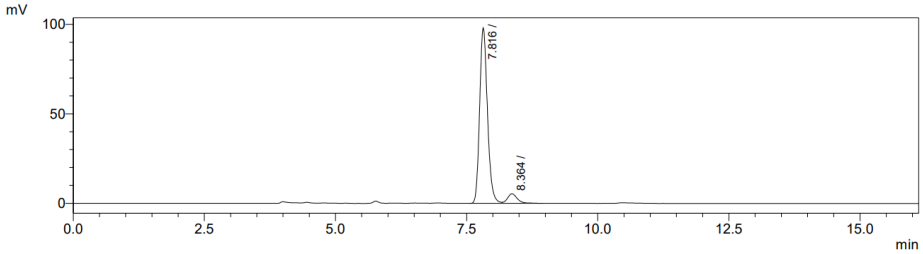


(*S*)-4-(2-(fluoromethyl)naphthalen-1-yl)-6,6-dimethyl-5,6-dihydrobenzo[h]quinoline (120):
White solid (25.0 mg, 68% yield, 93:7 er); R_f = 0.6 (Petroleum ether/Ethyl acetate = 10:1); Mp = 216 – 217 °C; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.67 (d, *J* = 4.7 Hz, 1H), 8.53 – 8.48 (m, 1H), 8.00 (d, *J* = 8.5 Hz, 1H), 7.94 (d, *J* = 8.2 Hz, 1H), 7.71 (d, *J* = 8.5 Hz, 1H), 7.53 (t, *J* = 7.4 Hz, 1H), 7.44 – 7.37 (m, 3H), 7.37 – 7.34 (m, 1H), 7.29 (d, *J* = 8.5 Hz, 1H), 7.07 (d, *J* = 4.7 Hz, 1H), 5.27 (q, *J* = 10.9 Hz, 1H), 5.19 (q, *J* = 11.0 Hz, 1H), 2.39 (d, *J* = 15.9 Hz, 1H), 2.33 (d, *J* = 15.9 Hz, 1H), 1.13 (s, 3H), 1.11 (s, 3H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 152.9, 147.4, 146.4, 145.2, 135.3 (d, $^3J_{C\text{-}F}$ = 5.9 Hz), 133.4, 133.1, 131.3, 131.0 (d, $^2J_{C\text{-}F}$ = 16.5 Hz), 130.2, 130.0, 128.8, 128.3, 126.9, 126.8, 126.1, 125.9, 125.8 (d, $^3J_{C\text{-}F}$ = 5.9 Hz), 124.1, 123.9, 82.5 (d, $^1J_{C\text{-}F}$ = 166.4 Hz), 39.6, 33.6, 28.2; **^{19}F NMR** (565 MHz, $CDCl_3$) δ -206.76; **HRMS** (ESI) m/z: $[M + H]^+$ calcd. for $C_{26}H_{23}FN$ 368.1809; Found 368.1807.
HPLC analysis: DAICEL CHIRALPAK ID, n-hexane/isopropanol = 92/8, flow rate = 0.8 mL/min, λ = 254 nm, t_R (major) = 7.8 min, t_R (minor) = 8.4 min, er = 93:7.
$[\alpha]^{25}_D$ = -213.70 (c = 0.27, $CHCl_3$).
Chiral HPLC spectrum of (*rac*)-**120**:



Peak#	Ret. Time	Area	Height	Conc.	Area%
1	7.628	2083185	198679	49.776	49.776
2	8.163	2101929	168817	50.224	50.224

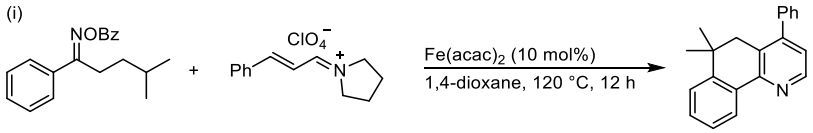
Chiral HPLC spectrum of (*S*)-**120**:



Peak#	Ret. Time	Area	Height	Conc.	Area%
1	7.816	1012377	98176	93.632	93.632
2	8.364	68850	5349	6.368	6.368

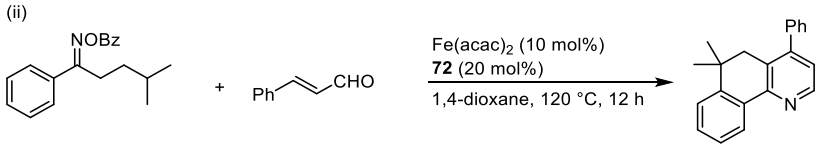
Mechanistic Studies

(a) Role of the Secondary Amine



1, 0.6 mmol **72**, 0.2 mmol **3**, 74%

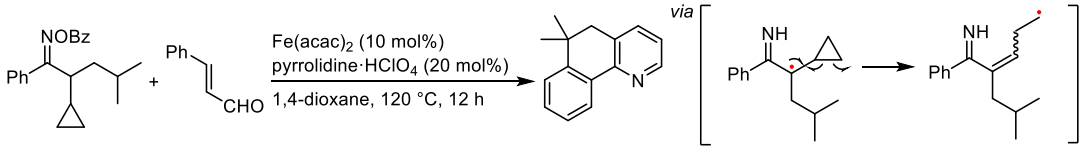
According to the general procedure toward pyridines, a reaction tube charged with **1** (177.2 mg, 0.6 mmol), **72** (57.1 mg, 0.2 mmol), $Fe(acac)_2$ (5.0 mg, 10 mol%), and 1,4-dioxane (2 mL) under a nitrogen atmosphere was stirred at 120 °C for 12 h to afford **3** in 74% yield (42.0 mg).



1, 0.6 mmol **2**, 0.2 mmol **3**, 70%

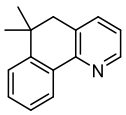
According to the general procedure toward pyridines, a reaction tube charged with **1** (177.2 mg, 0.6 mmol, 3 equiv), **2** (26.4 mg, 0.2 mmol), **72** (11.4 mg, 20 mol%), $Fe(acac)_2$ (5.0 mg, 10 mol%) and 1,4-dioxane (2 mL) under a nitrogen atmosphere was stirred at 120 °C for 12 h to afford **3** in 70% yield (39.9 mg).

(b) Experimental Evidence for the α-Carbon Radical



73 **2** **74**, 10% **75** **76**

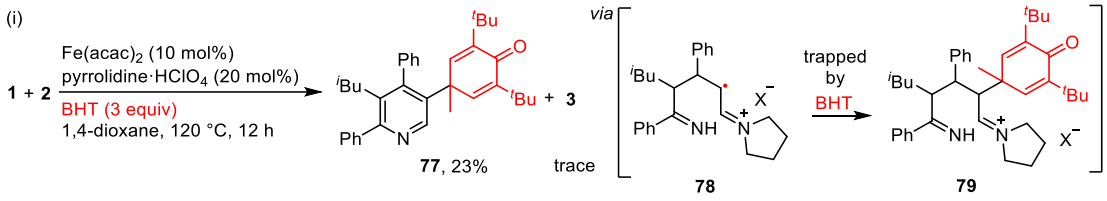
According to the general procedure toward pyridines, a reaction tube charged with **73** (100.6 mg, 0.3 mmol, 3 equiv), **2** (13.2 mg, 0.1 mmol), $Fe(acac)_2$ (2.5 mg, 10 mol%), pyrrolidine·$HClO_4$ (3.4 mg, 20 mol%) and 1,4-dioxane (1 mL) under a nitrogen atmosphere was stirred at 120 °C for 12 h to afford **74** in 10% yield (6.2 mg).



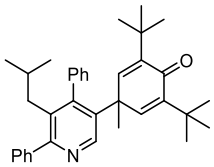
6,6-dimethyl-5,6-dihydrobenzo[h]quinoline (74):

Colorless oil (6.2 mg, 10% yield); R_f = 0.6 (Petroleum ether/Ethyl acetate = 10:1); **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.54 (d, *J* = 4.0 Hz, 1H), 8.38 – 8.35 (m, 1H), 7.48 (d, *J* = 7.4 Hz, 1H), 7.42 – 7.33 (m, 3H), 7.14 (dd, *J* = 7.4, 4.8 Hz, 1H), 2.84 (s, 2H), 1.30 (s, 6H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 152.4, 147.7, 146.3, 136.1, 133.2, 130.7, 129.7, 126.8, 125.4, 124.0, 122.3, 43.1, 33.9, 28.3; **HRMS** (ESI) m/z: $[M + H]^+$ calcd. for $C_{15}H_{16}N$ 210.1277; Found 210.1277.

(c) Experimental Evidence for the α-Iminyl Radical Cation

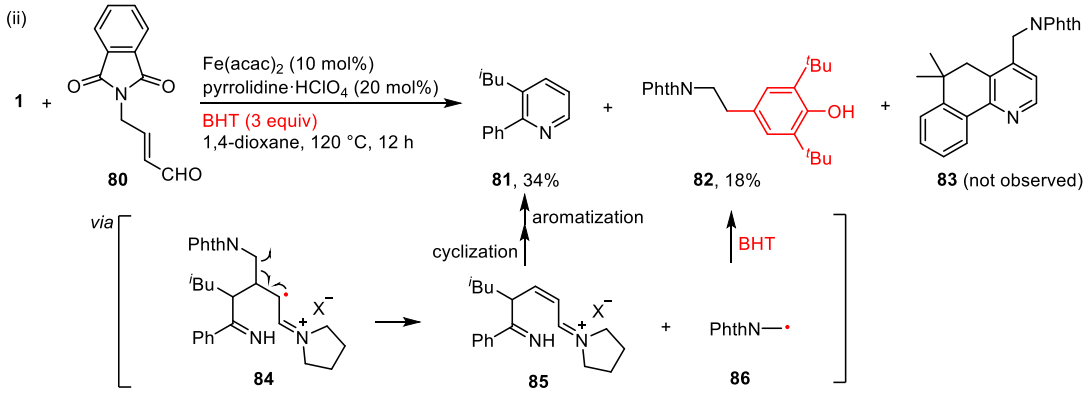


According to the general procedure toward pyridines, a reaction tube charged with **1** (177.2 mg, 0.6 mmol, 3 equiv), **2** (26.4 mg, 0.2 mmol), $Fe(acac)_2$ (5.0 mg, 10 mol%), pyrrolidine·$HClO_4$ (6.8 mg, 20 mol%), BHT (132.2 mg, 0.6 mmol, 3 equiv) and 1,4-dioxane (2 mL) under a nitrogen atmosphere was stirred at 120 °C for 12 h to afford **77** in 23% yield (23.2 mg) and a trace amount of **3**.

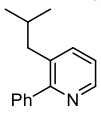


2,6-di-tert-butyl-4-(5-isobutyl-4,6-diphenylpyridin-3-yl)-4-methylcyclohexa-2,5-dien-1-one (77):

Colorless oil (23.2 mg, 23% yield); R_f = 0.45 (Petroleum ether/Ethyl acetate = 10:1); **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.77 (s, 1H), 7.50 (d, *J* = 6.9 Hz, 2H), 7.44 (t, *J* = 7.1 Hz, 2H), 7.38 (t, *J* = 7.2 Hz, 1H), 7.29 (t, *J* = 7.2 Hz, 1H), 7.22 (t, *J* = 7.3 Hz, 2H), 7.02 (d, *J* = 7.1 Hz, 2H), 6.64 (s, 2H), 2.30 (d, *J* = 6.7 Hz, 2H), 1.60 (s, 3H), 1.19 – 1.14 (m, 1H), 1.11 (s, 18H), 0.33 (d, *J* = 6.5 Hz, 6H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 185.1, 159.2, 151.9, 147.2, 144.9, 143.8, 141.5, 137.1, 135.0, 134.0, 130.1, 129.1, 128.4, 128.2, 127.8, 127.4, 43.5, 37.7, 34.5, 30.9, 29.2, 28.8, 22.3; **HRMS** (ESI) m/z: $[M + H]^+$ calcd. for $C_{36}H_{44}NO$ 506.3417; Found 506.3413.



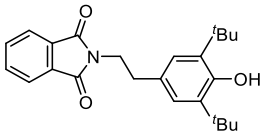
According to the general procedure toward pyridines, a reaction tube charged with **1** (177.2 mg, 0.6 mmol, 3 equiv), **80** (43.0 mg, 0.2 mmol), $Fe(acac)_2$ (5.0 mg, 10 mol%), pyrrolidine·$HClO_4$ (6.8 mg, 20 mol%), BHT (132.2 mg, 0.6 mmol, 3 equiv) and 1,4-dioxane (2 mL) under a nitrogen atmosphere was stirred at 120 °C for 12 h to afford **81** in 34% yield (14.4 mg) and **82** in 18% yield (13.7 mg). The compound **83** was not observed.



3-isobutyl-2-phenylpyridine (81):

Colorless oil (14.4 mg, 34% yield); R_f = 0.45 (Petroleum ether/Ethyl acetate = 10:1); **^{1}H NMR**

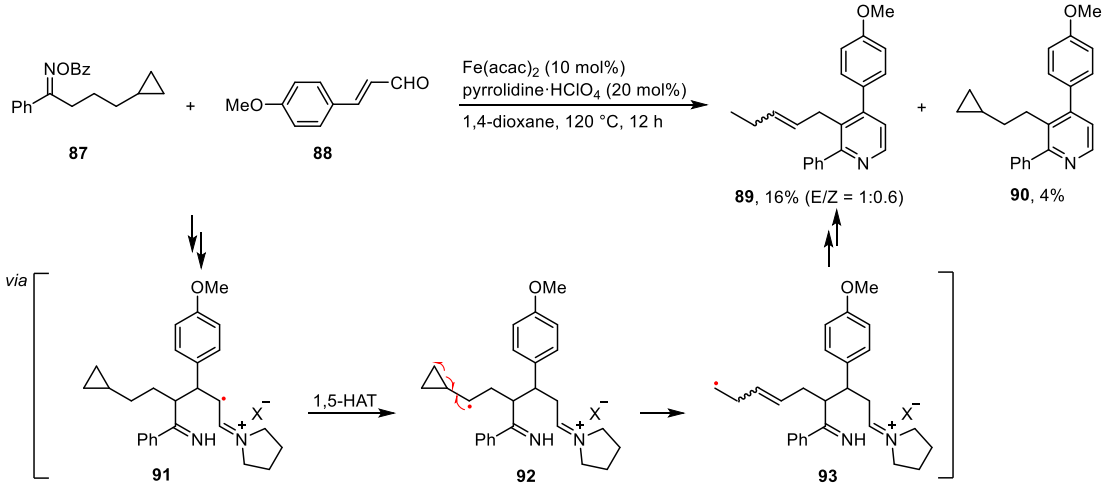
(600 MHz, $CDCl_3$) δ 8.52 (d, *J* = 4.4 Hz, 1H), 7.58 (d, *J* = 7.7 Hz, 1H), 7.47 – 7.41 (m, 4H), 7.40 – 7.35 (m, 1H), 7.21 (dd, *J* = 7.2, 4.8 Hz, 1H), 2.56 (d, *J* = 7.2 Hz, 2H), 1.75 – 1.71 (m, 1H), 0.76 (d, *J* = 6.5 Hz, 6H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 159.4, 146.8, 140.9, 138.0, 134.6, 129.0, 128.1, 127.7, 122.0, 41.4, 29.4, 22.3; **HRMS** (ESI) m/z: $[M + H]^+$ calcd. for $C_{15}H_{18}N$ 212.1434; Found 212.1432.



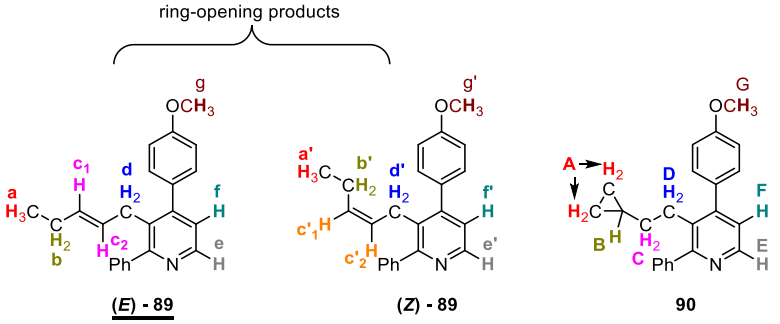
2-(3,5-di-tert-butyl-4-hydroxyphenethyl)isoindoline-1,3-dione (82) :

White solid (13.7 mg, 18% yield); R_f = 0.50 (Petroleum ether/Ethyl acetate = 10:1); Mp = 132 – 133 °C; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.84 – 7.79 (m, 2H), 7.72 – 7,67 (m, 2H), 6.99 (s, 2H), 5.05 (s, 1H), 3.92 – 3.86 (m, 2H), 2.93 – 2.86 (m, 2H), 1.38 (s, 18H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 168.2, 152.5, 136.0, 133.8, 132.2, 128.6, 125.4, 123.1, 39.6, 34.3, 34.2, 30.3; **HRMS** (ESI) m/z: $[M + Na]^+$ calcd. for $C_{24}H_{29}NNaO_3$ 402.2040; Found 402.2039.

(d) Experimental Evidence for the α-Iminyl Radical Cation-Triggered 1,5-HAT



According to the general procedure toward pyridines, a reaction tube charged with **87** (276.6 mg, 0.9 mmol, 3 equiv), **88** (48.7 mg, 0.3 mmol), $Fe(acac)_2$ (7.6 mg, 10 mol%), pyrrolidine·$HClO_4$ (10.3 mg, 20 mol%) and 1,4-dioxane (3 mL) under a nitrogen atmosphere was stirred at 120 °C for 12 h to afford a mixture of **89** and **90** in 20% total yield (20.0 mg). Based on ^{1}H NMR spectra data of the mixture, it can be concluded that the yield of **89** was *ca.* 16% and the E/Z was 1:0.6.

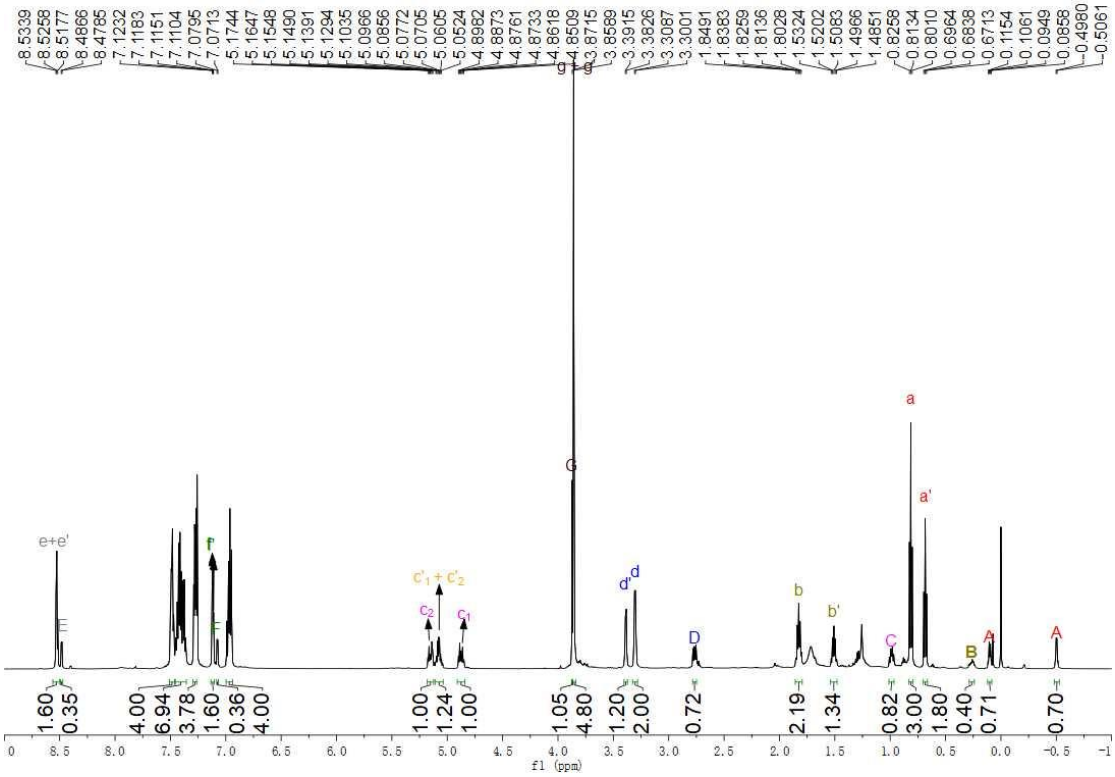


The mixture ((*E*) - **89** : (*Z*) - **89** : **90** = **1: 0.6 : 0.35**)

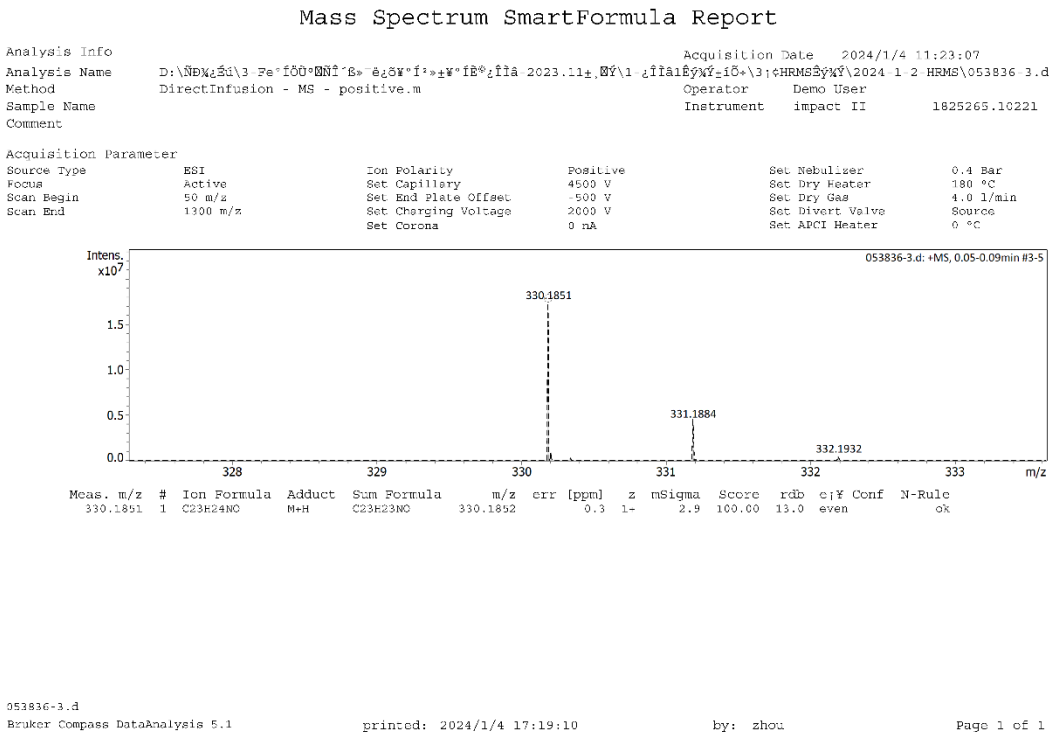
89 or **90**, $[M+H]^+$: calcd. 330.1852, found 330.1851

The mixture was given as a colorless oil (20.0 mg, 20% yield); R_f = 0.25 (Petroleum ether/Ethyl acetate = 10:1); ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.53 (d, *J* = 4.9 Hz, 0.98H (**e**)), δ 8.52 (d, *J* = 4.9 Hz, 0.62H (**e'**)), 8.48 (d, *J* = 4.9 Hz, 0.35H, **E**), 7.49 – 7.46 (m, 4.00H), 7.45 – 7.35 (m, 6.94H), 7.30 – 7.26 (m, 3.78H), 7.12 (d, *J* = 4.8 Hz, 1H (**f**), 0.6H (**f'**)), 7.08 (d, *J* = 4.9 Hz, 0.36H, **F**), 7.00 – 6.94 (m, 4.00H), 5.15 (dt, *J* = 15.3, 5.8 Hz, 1.00H, **c_2**), 5.11 – 5.03 (m, 1.24H, **c'_1 & c'_2**), 4.87 (dt, *J* = 15.3, 6.5 Hz, 1.00H, **c_1**), 3.87 (s, 1.05H, **G**, **OCH_3**), 3.86 (s, 3.00H(**g**), 1.80H (**g'**), **OCH_3**) , 3.39 (d, *J* = 5.4 Hz, 1.20H, **d'**), 3.30 (d, *J* = 5.2 Hz, 2.00H, **d**), 2.78 – 2.75 (m, 0.72H, **D**), 1.86 – 1.80 (m, 2.19H, **b**), 1.54 – 1.48 (m, 1.34H, **b'**), 1.01 – 0.97 (m, 0.82H, **C**), 0.81 (t, *J* = 7.4 Hz, 3.00H, **a**), 0.68 (t, *J* = 7.5 Hz, 1.80H, **a'**), 0.29 – 0.24 (m, 0.40H, **B**), 0.12 – 0.08 (m, 0.71H, **A**), -0.48 – -0.53 (m, 0.70H, **A**); **HRMS** (ESI) m/z: $[M + H]^+$ calcd. for $C_{23}H_{24}NO$ 330.1852; Found 330.1851.

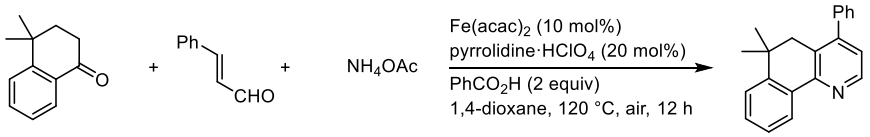
^{1}H NMR Spectrum for the mixture of 89 and 90 (600 MHz, $CDCl_3$) :



HRMS (ESI) analysis for the mixture of 89 and 90 :



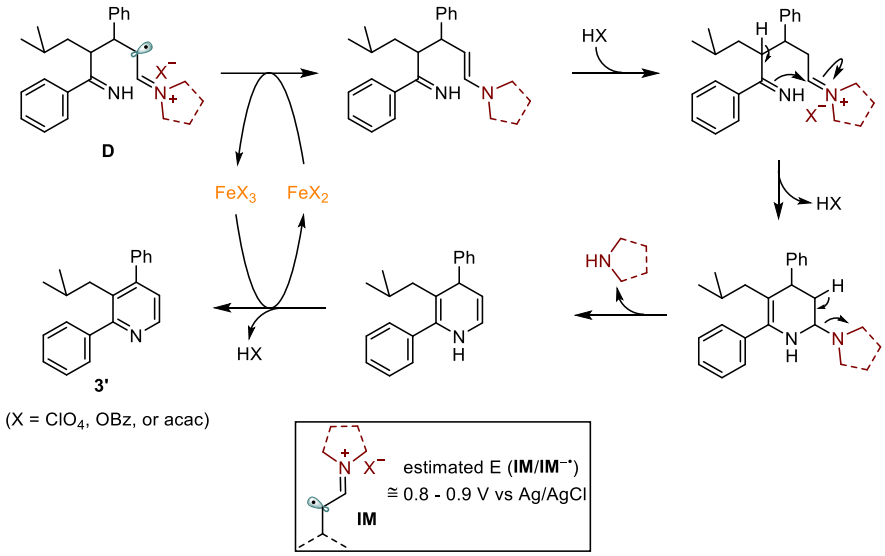
(e) Exclusion of A Route to the Pyridine via A Condensation of A Ketone, An Enal and An Ammonia.



94 **2** **3**, trace

A reaction tube charged with **94** (52.2 mg, 0.3 mmol, 3 equiv), **2** (13.2 mg, 0.1 mmol), $Fe(acac)_2$ (2.5 mg, 10 mol%), pyrrolidine·$HClO_4$ (3.4 mg, 20 mol%), NH_4OAc (46.2 mg, 0.6 mmol, 6 equiv), PhCOOH (24.4 mg, 2 equiv) and 1,4-dioxane (1 mL) under air atmosphere was stirred at 120 °C for 12 h. Only a trace amount of **3** was observed.

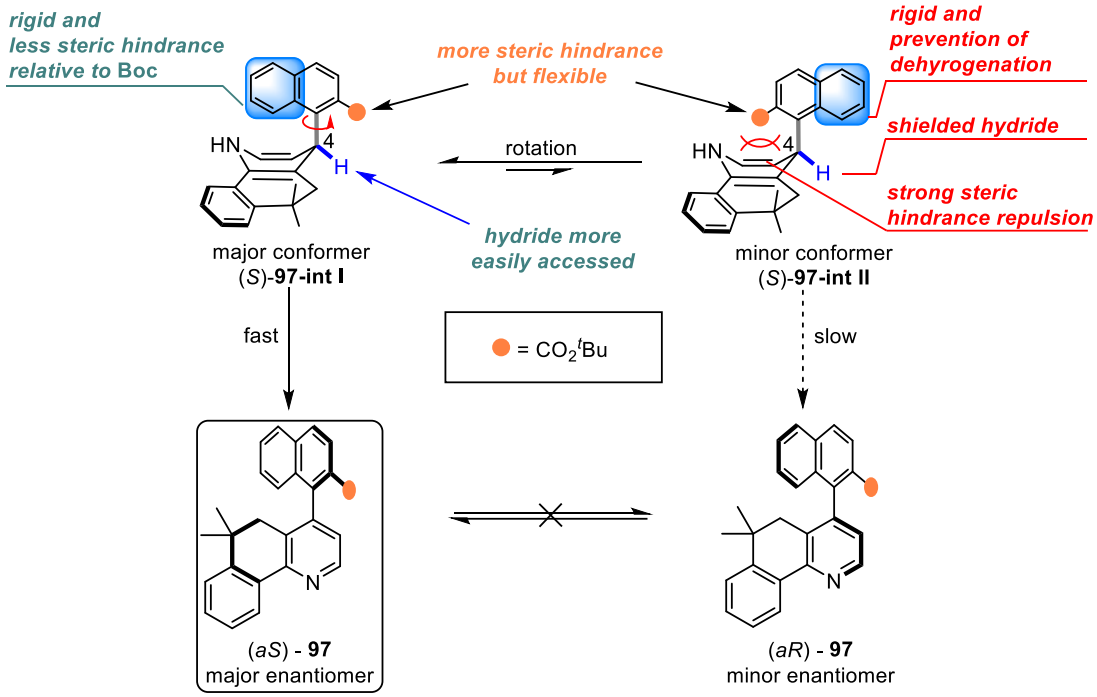
Proposed Mechanism for the Formation of 3’



Scheme S4. Proposed mechanism for the formation of **3’**.

The estimated E ($IM/IM^{-\bullet}$) of α-iminyl radical cation **IM** that has a similar structure as **D** was reported in 0.8-0.9 V vs Ag/AgCl.[27] Thus, a SET event from reductive Fe(II) ($E(Fe^{3+}/Fe^{2+}) \approx 0.55$ V vs Ag/AgCl) to the α-iminyl radical cation **D** might occur to afford the side product **3’** via the following pathway (Scheme S4).

Proposed Model for the Central-to-Axial Chirality Conversion



Scheme S5. Proposed model for the central-to-axial chirality conversion.

1,4-Dihydropyridines bearing sterically bulky substituents on C4 site in the pseudo-axial position are known to exist predominantly as boat conformers.[28] In the case of compound **(*S*)-97-int I**, the sterically bulky group around this bond in the axial orientation slows down its rotation. This rotation was accelerated at a higher temperature (70 °C), resulting in a significant decrease in the enantiomeric ratio value of **97** (entry 10, Table S2). Moreover, the installation of relatively less sterically bulky group (e.g., OTs, OTf, and O^{t}Bu groups) at the β position of the naphthyl ring significantly reduced the stereoselectivities at 50 °C (the axially chiral biaryls **112-114**). These results indicated that an equilibrium between the two rotamers, **(*S*)-97-int I** and **(*S*)-97-int II**, would be slowed down by the sterically bulky groups around the pseudo-axial position. In addition, the two rotamers can undergo oxidation to afford axially chiral pyridines, **(*aS*)-97** and **(*aR*)-97**, respectively. Our observations point towards a scenario where the two conformers are in a slow equilibrium, and the central-to-axial chirality conversion depends on the stability of the two conformers and the ability of the oxidant to efficiently discriminate between the two conformers. The absolute configuration of **97** indicates that oxidation preferentially occurs from the more stable conformer **(*S*)-97-int I** to afford the desired enantioenriched **(*aS*)-97** with efficient central-to-axial chirality conversion. It can be attributed to the fact that the sterically bulky tert-butoxycarbonyl group is positioned away from the crowded dihydropyridine ring, which resulted in a weak repulsion between the polycyclic dihydropyridine skeleton and the rigid aromatic ring. As such, the conformer **(*S*)-97-int I** is more stable. Moreover, the hydride on C4 site is more easily accessed by the oxidant than one in the conformer **(*S*)-97-int II**, because the tert-butoxycarbonyl group is flexible so that the hydride transfer would not be efficiently hampered (Scheme S5).

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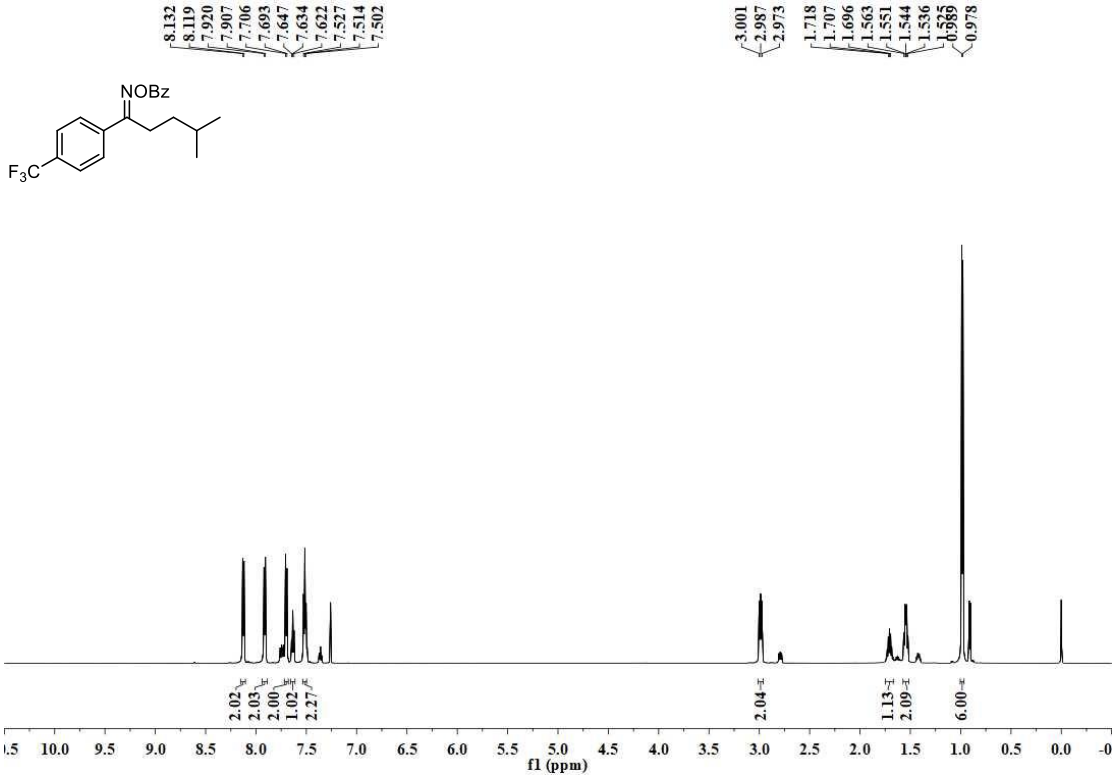
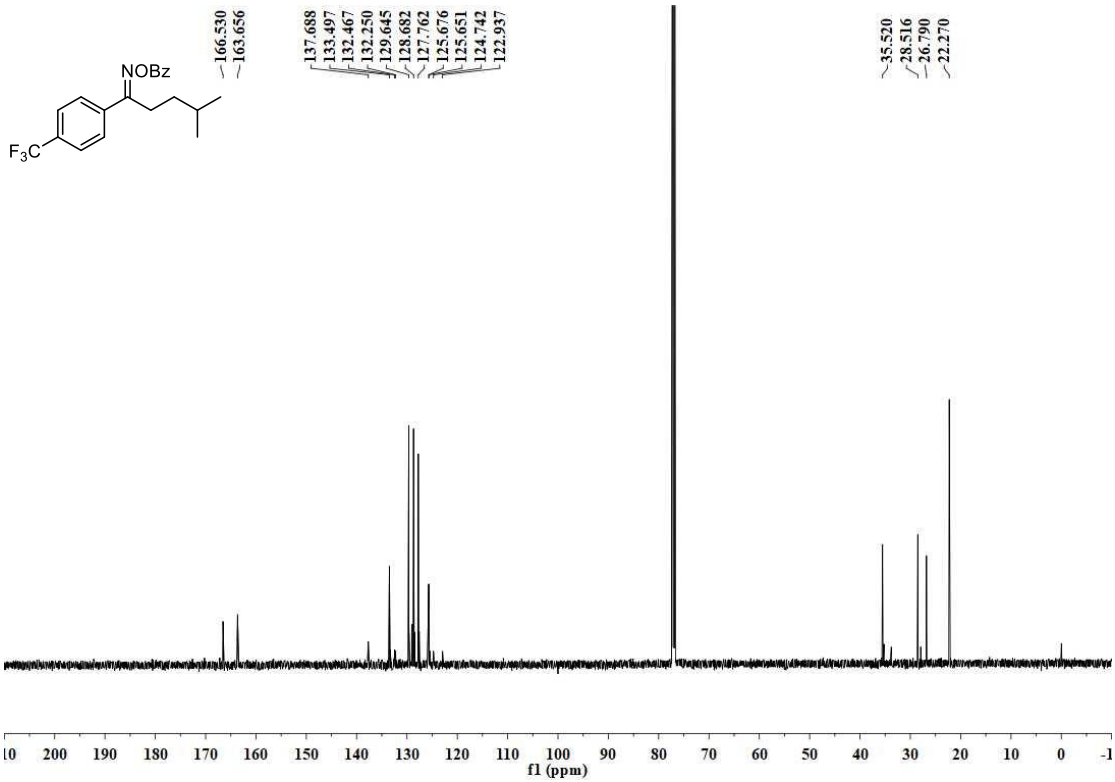
NMR Spectra of the New Compounds

^{1}H NMR Spectrum of S9 (600 MHz, $CDCl_3$)

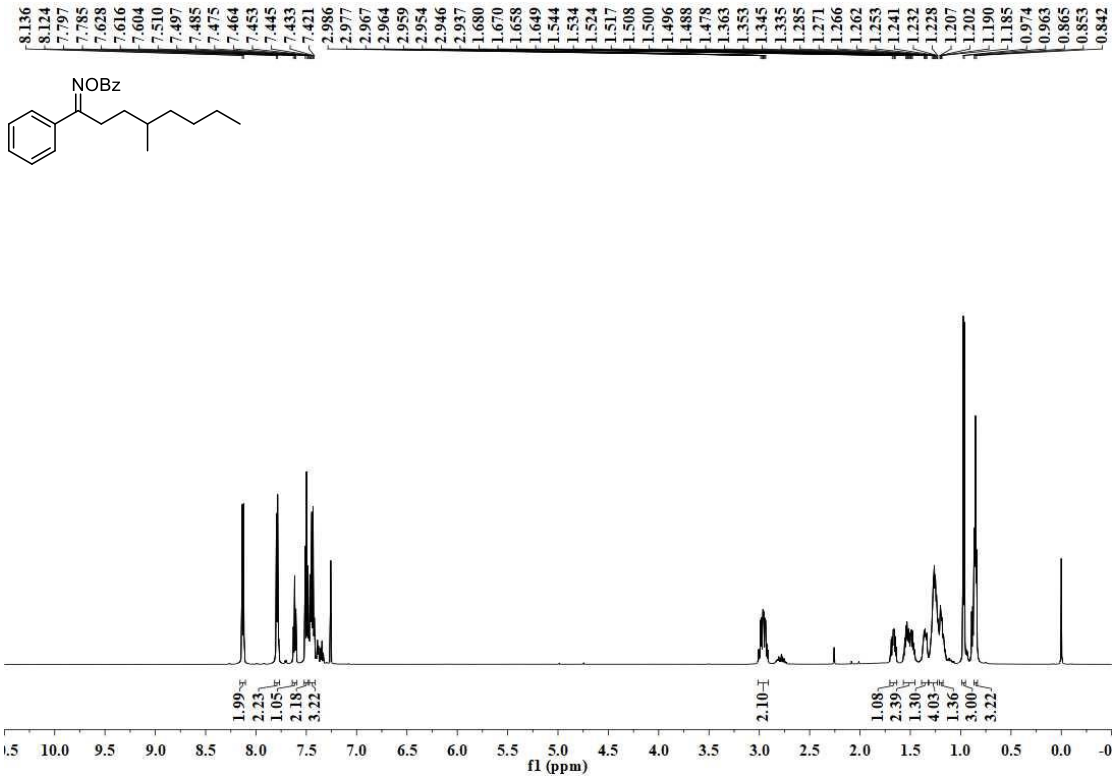


^{13}C NMR Spectrum of S9 (151 MHz, $CDCl_3$)

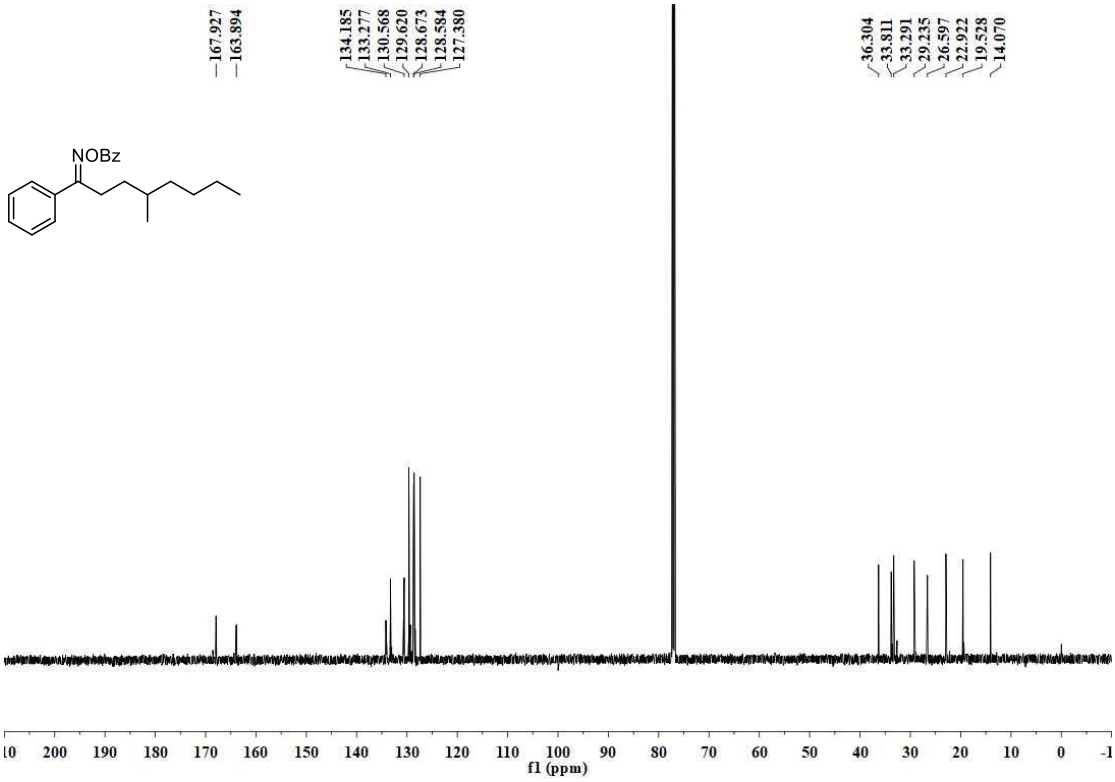


^{19}F NMR Spectrum of S9 (565 MHz, $CDCl_3$)

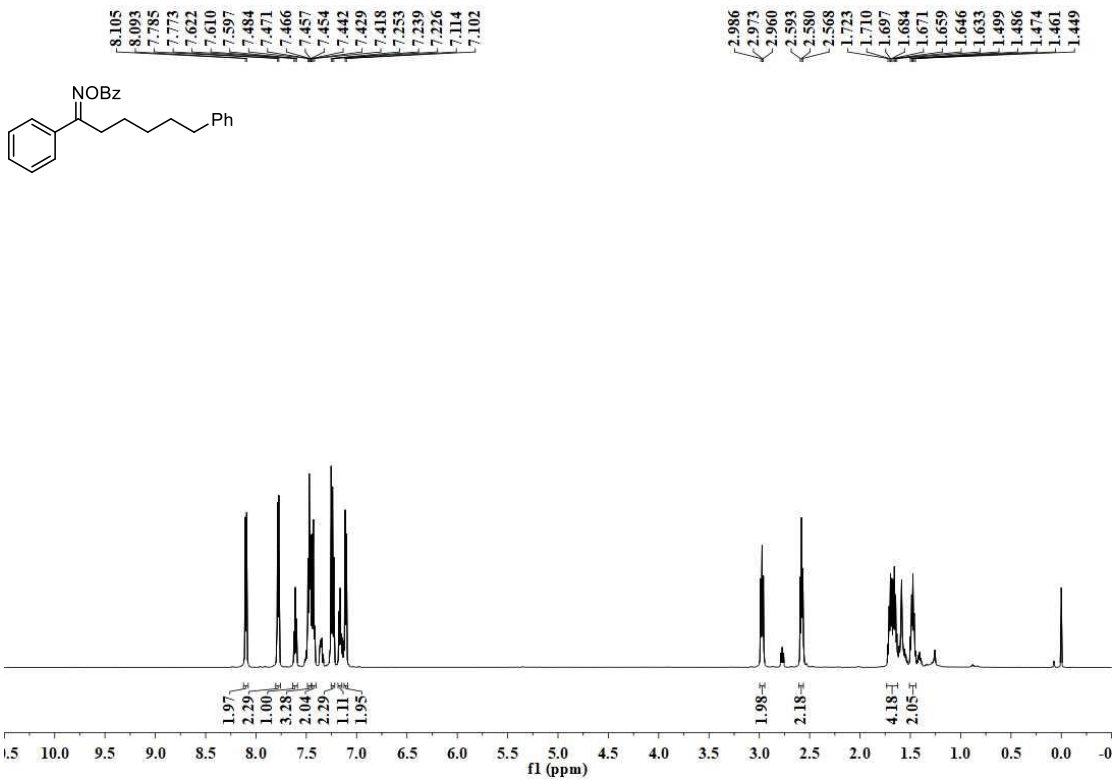
^{1}H NMR Spectrum of S23 (600 MHz, $CDCl_3$)



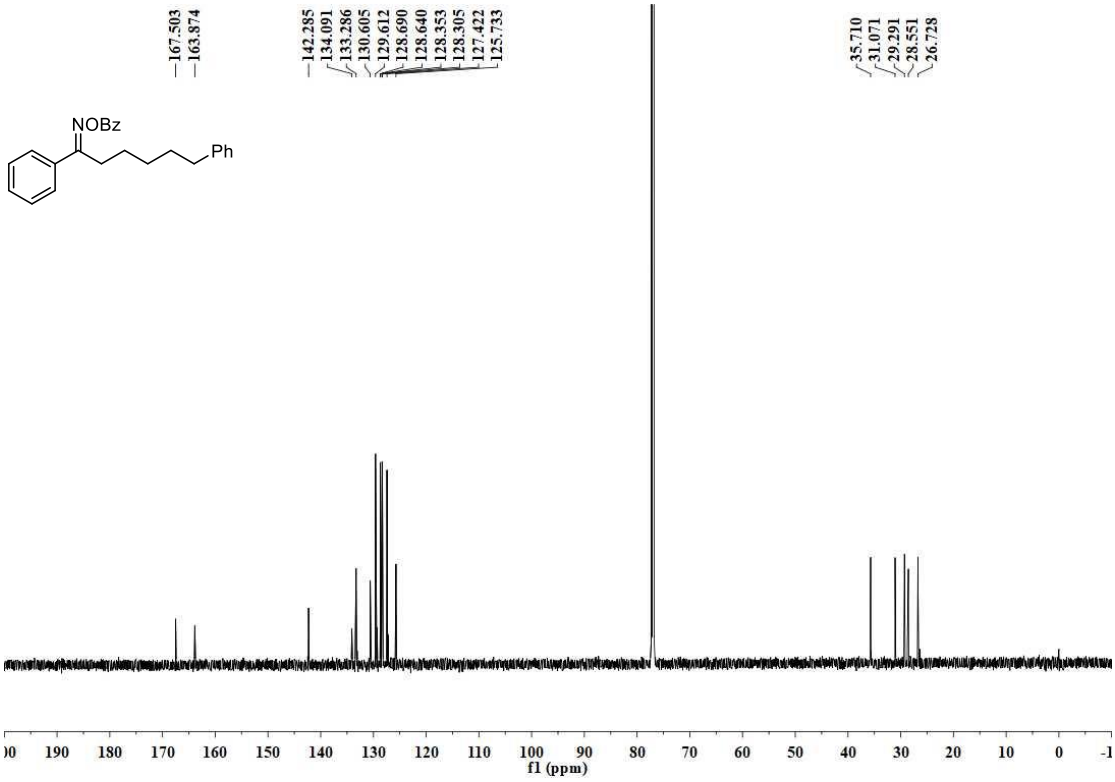
^{13}C NMR Spectrum of S23 (151 MHz, $CDCl_3$)



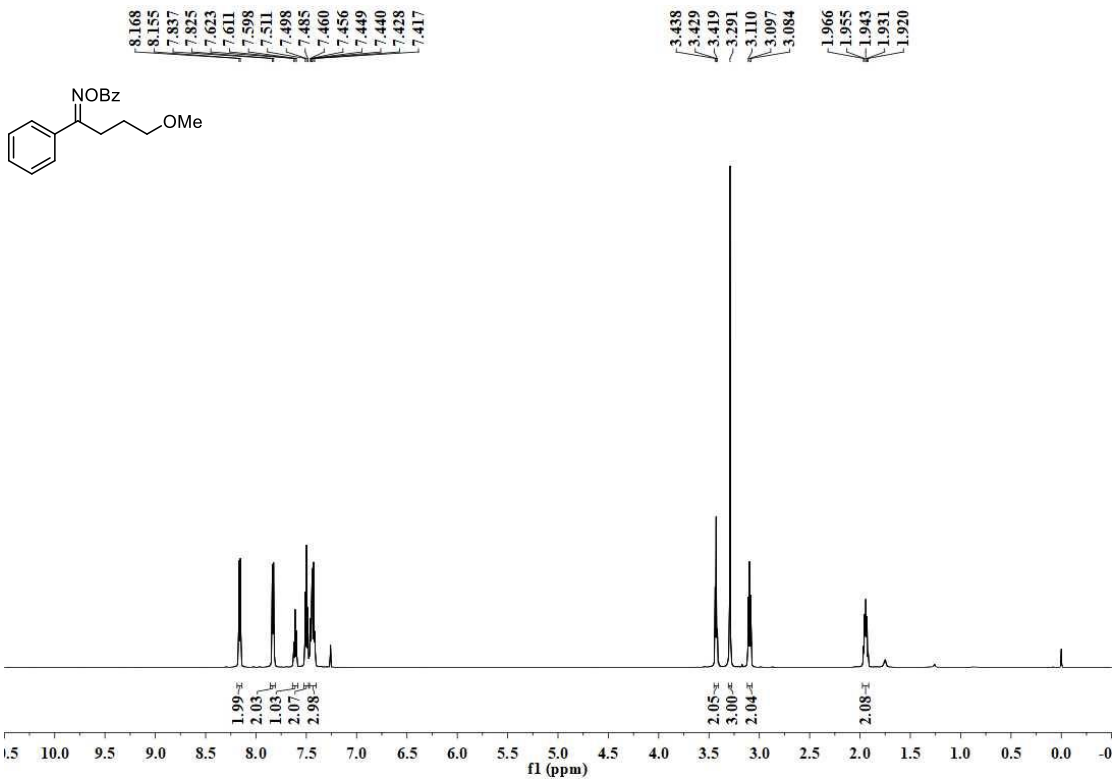
^{1}H NMR Spectrum of S26 (600 MHz, $CDCl_3$)



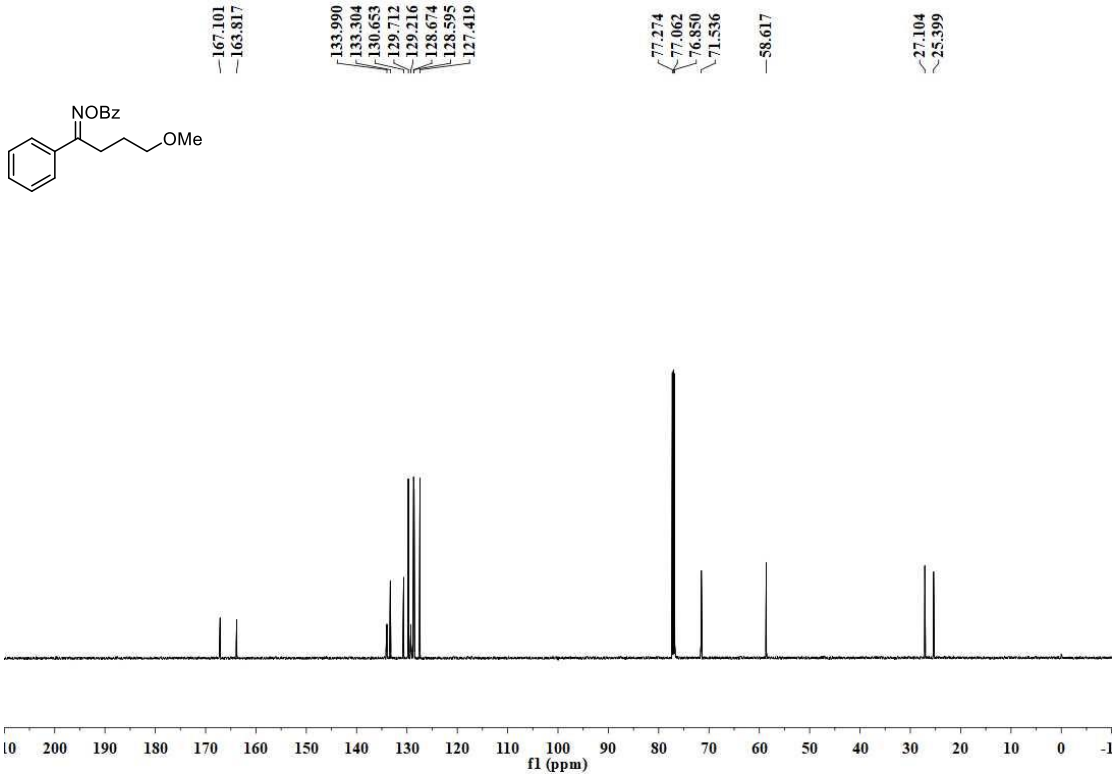
^{13}C NMR Spectrum of S26 (151 MHz, $CDCl_3$)



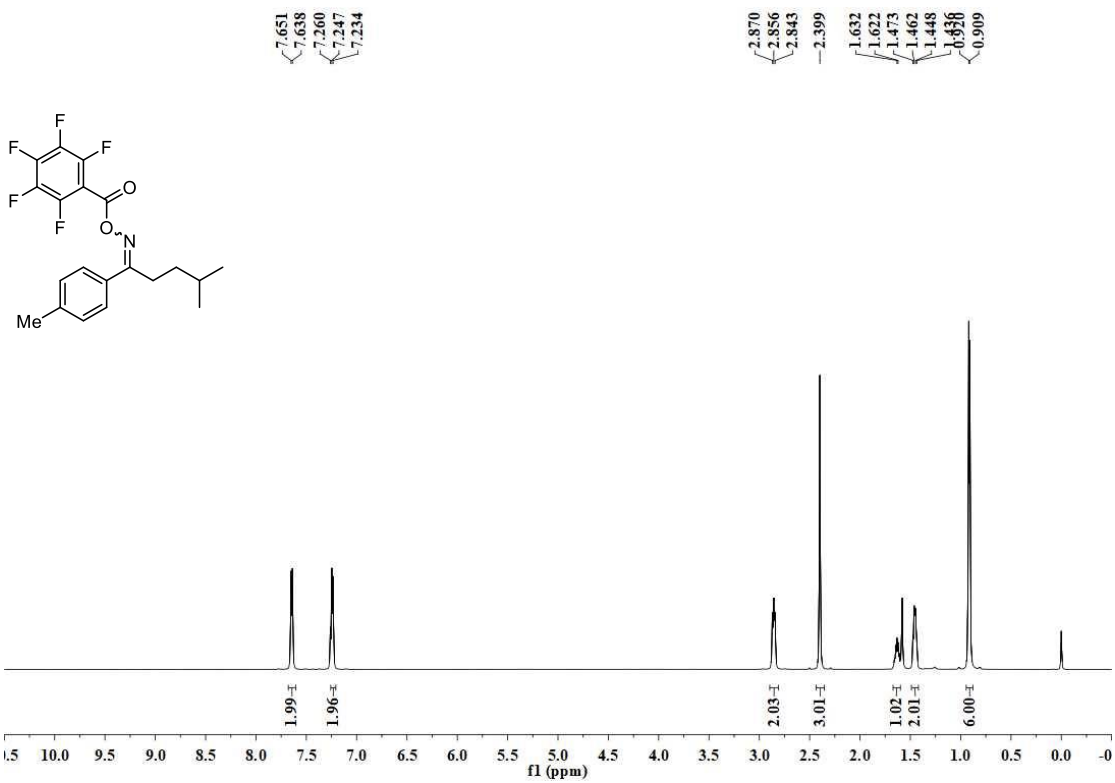
^{1}H NMR Spectrum of S27 (600 MHz, $CDCl_3$)



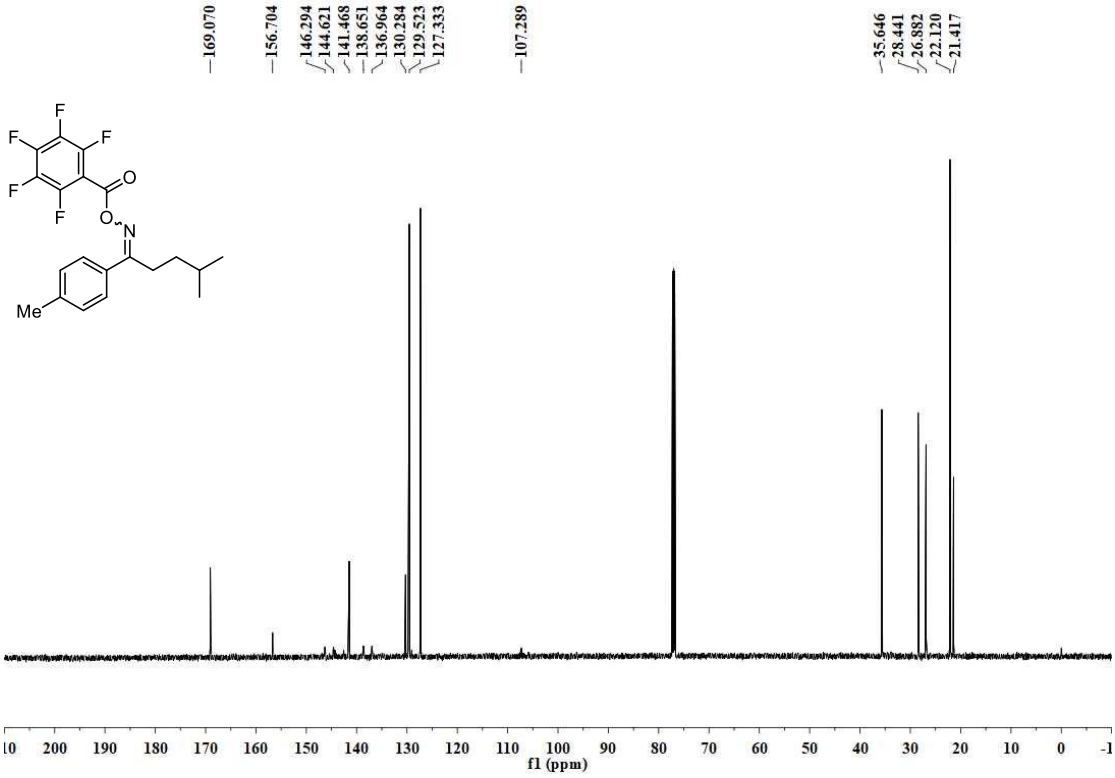
^{13}C NMR Spectrum of S27 (151 MHz, $CDCl_3$)



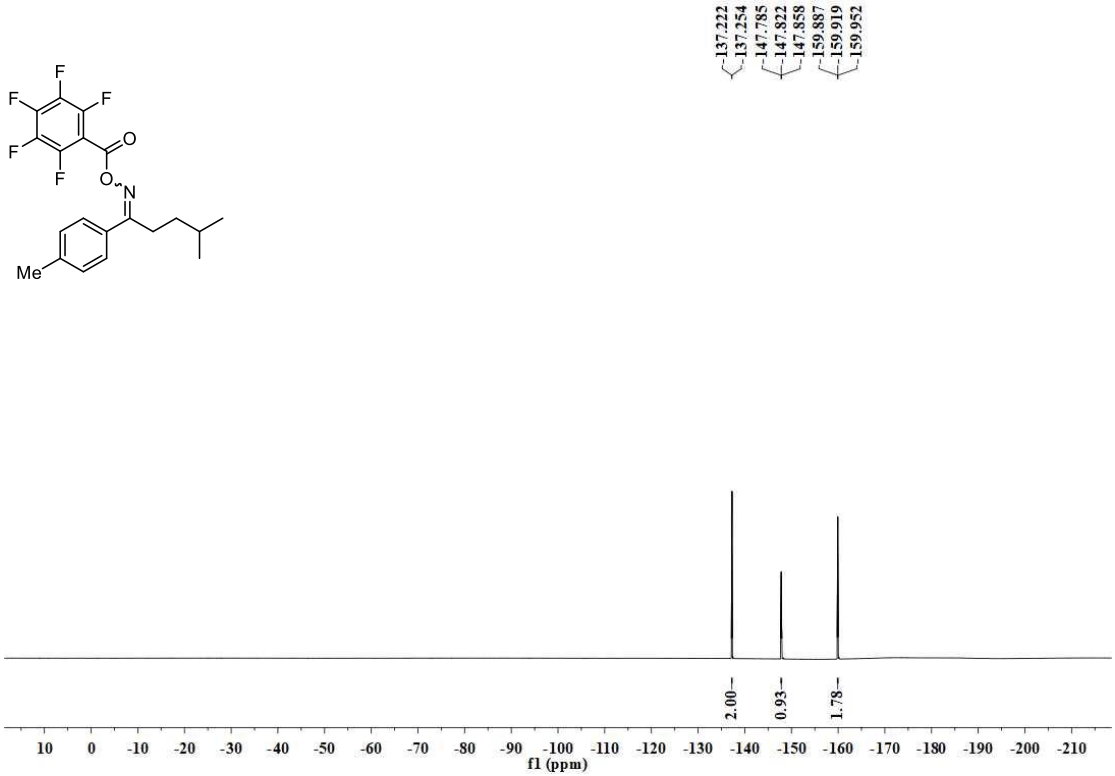
^{1}H NMR Spectrum of S98 (600 MHz, $CDCl_3$)



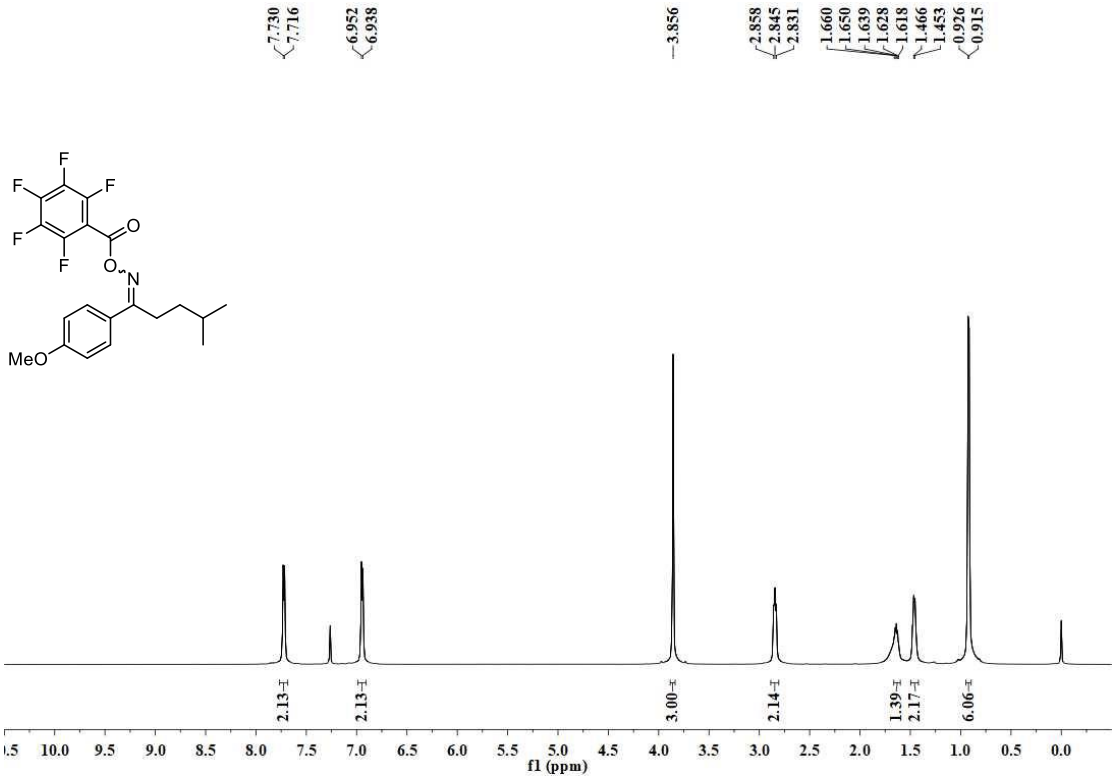
^{13}C NMR Spectrum of S98 (151 MHz, $CDCl_3$)



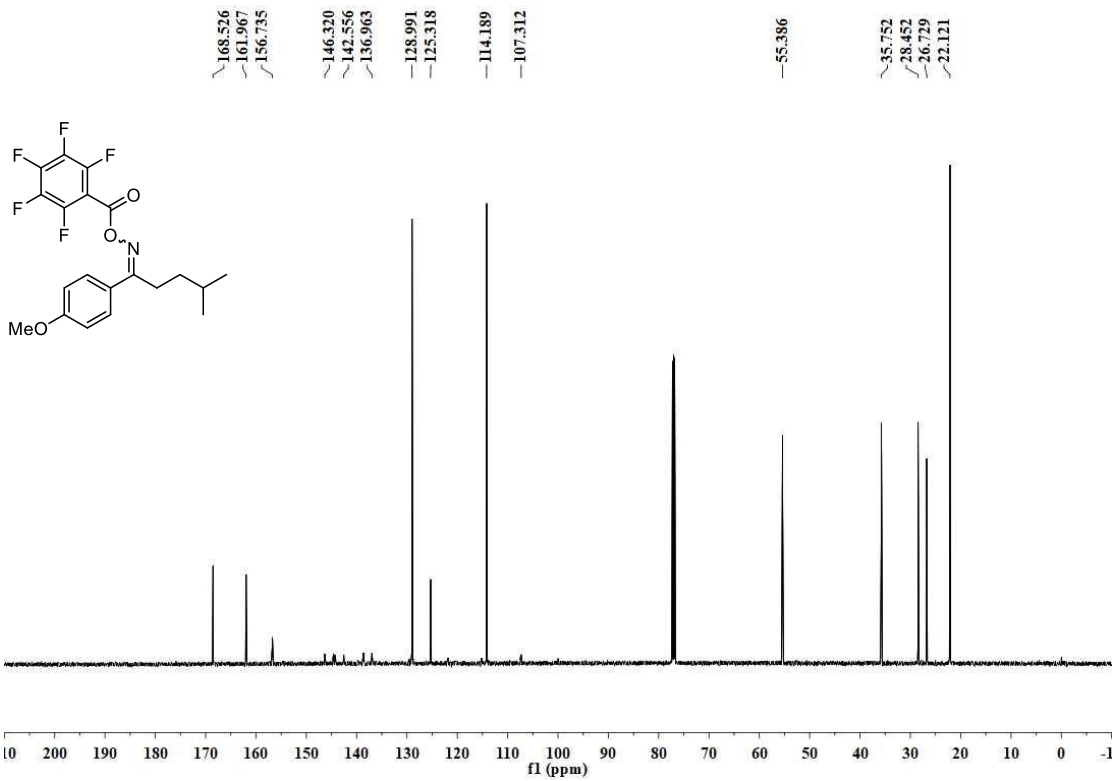
^{19}F NMR Spectrum of S98 (565 MHz, $CDCl_3$)



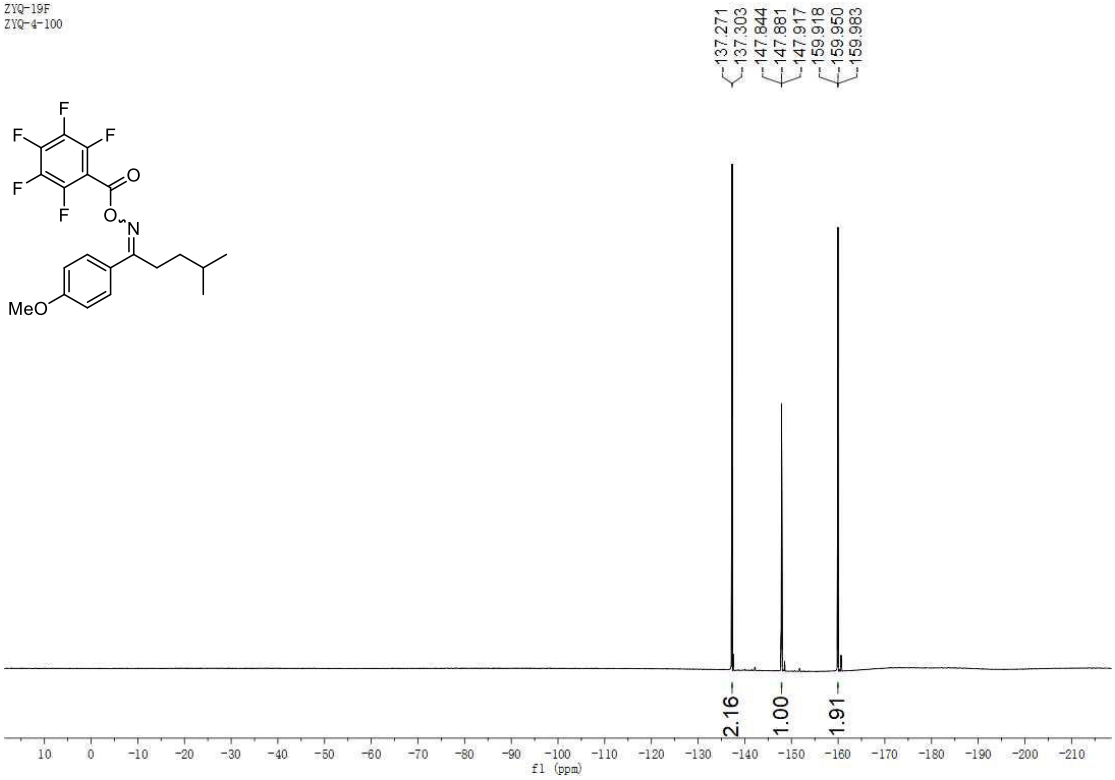
^{1}H NMR Spectrum of S99 (600 MHz, $CDCl_3$)



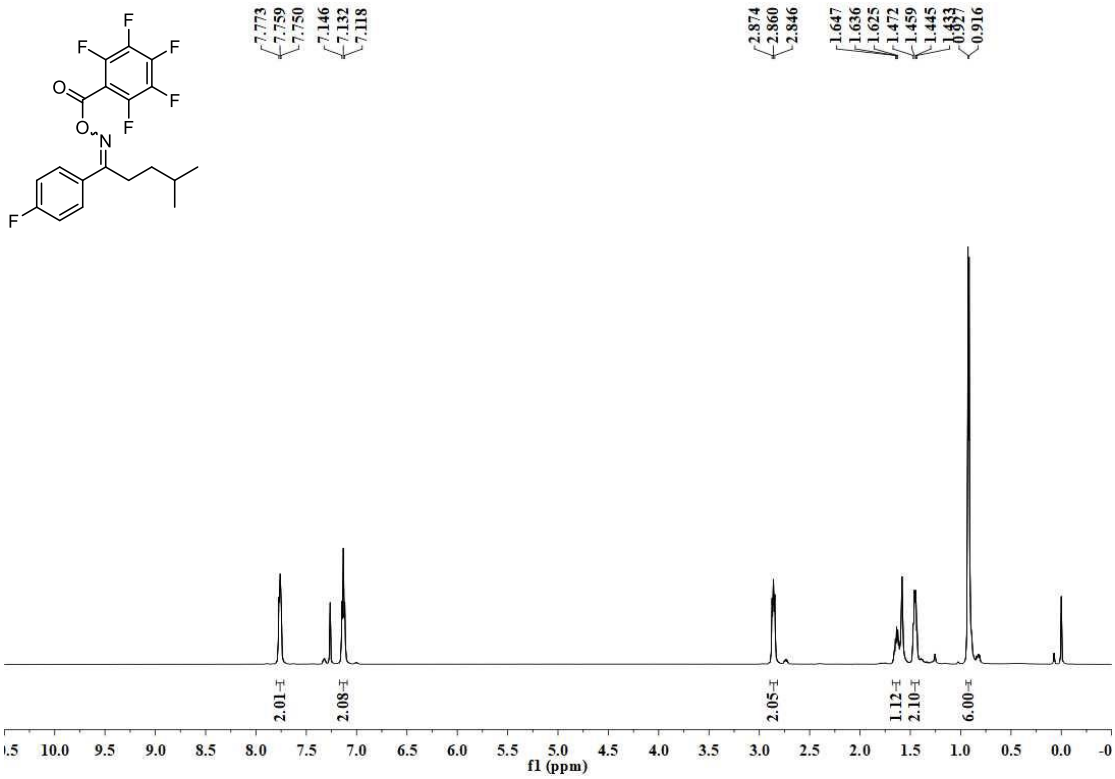
^{13}C NMR Spectrum of S99 (151 MHz, $CDCl_3$)



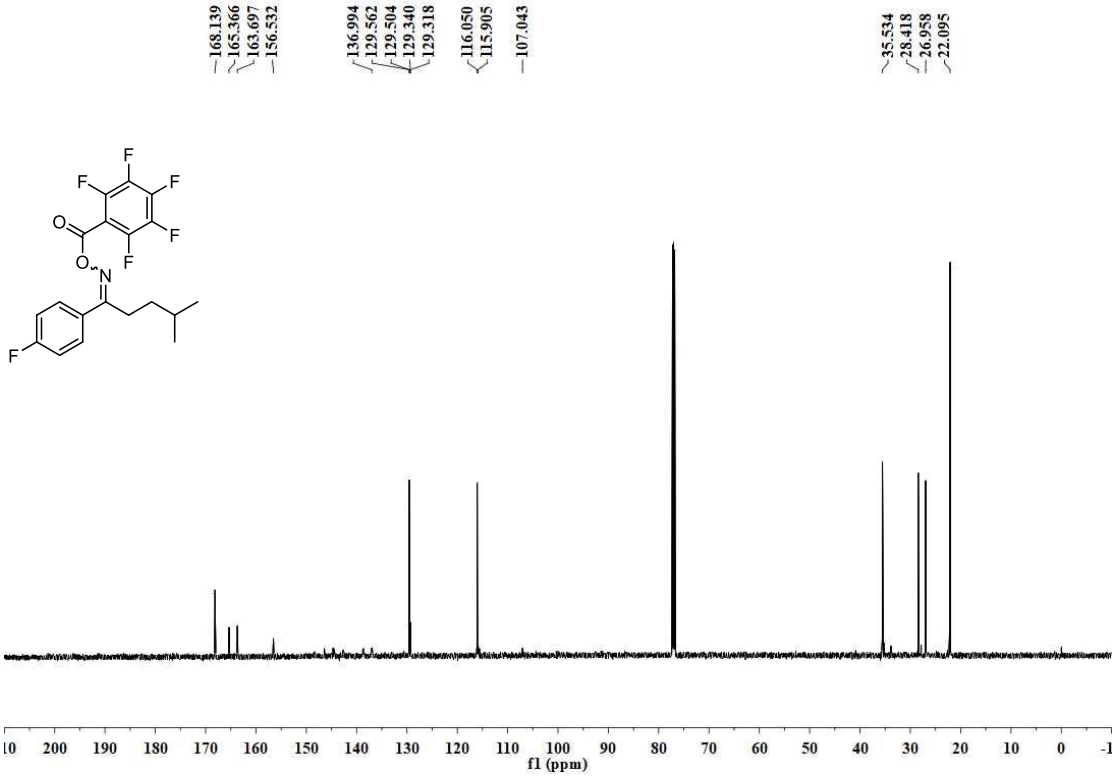
^{19}F NMR Spectrum of S99 (565 MHz, $CDCl_3$)



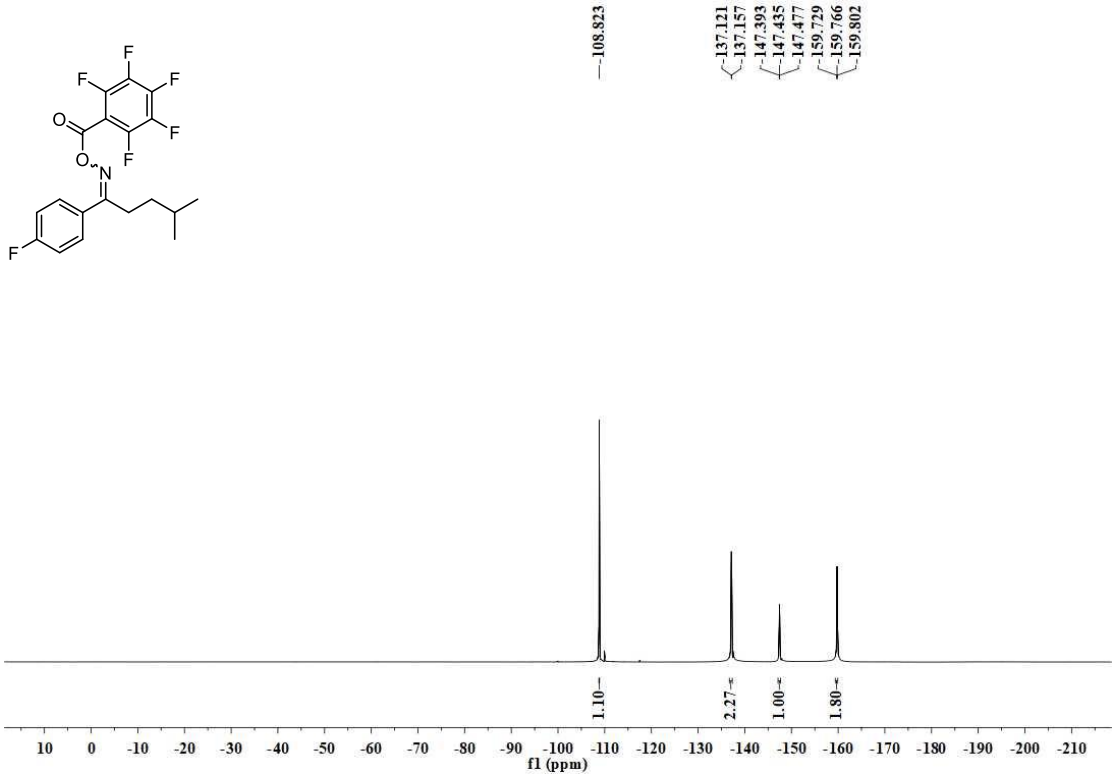
^{1}H NMR Spectrum of S100 (600 MHz, $CDCl_3$)



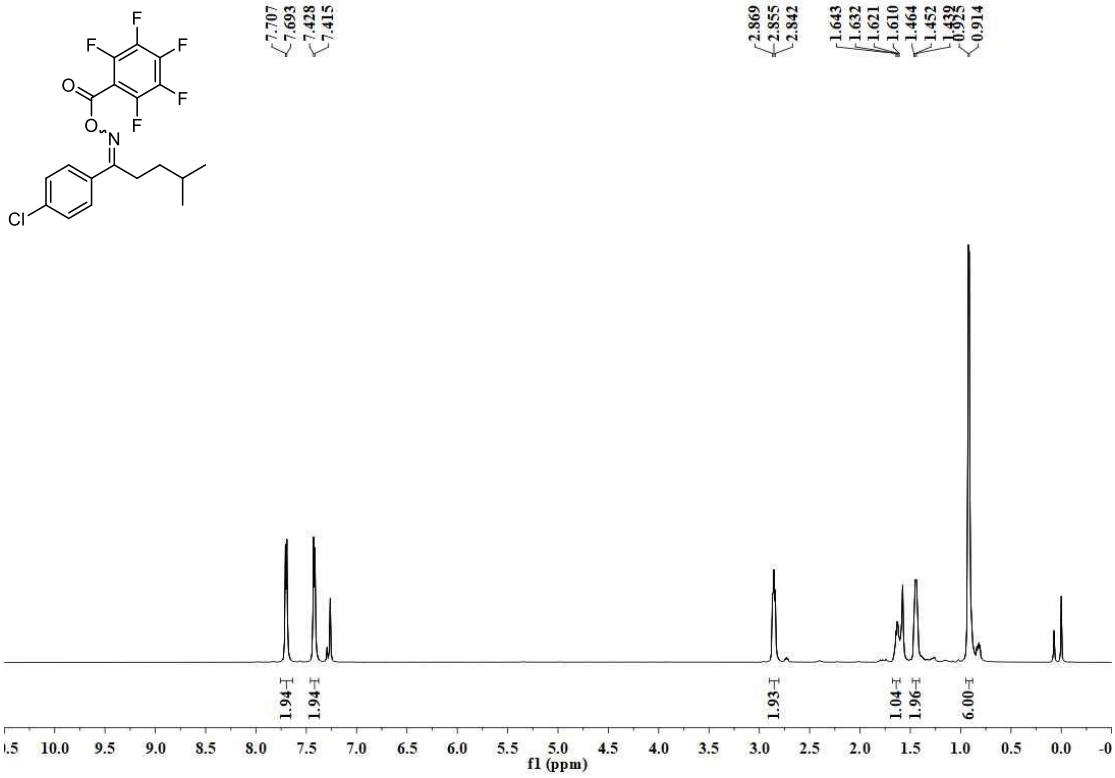
^{13}C NMR Spectrum of S100 (151 MHz, $CDCl_3$)



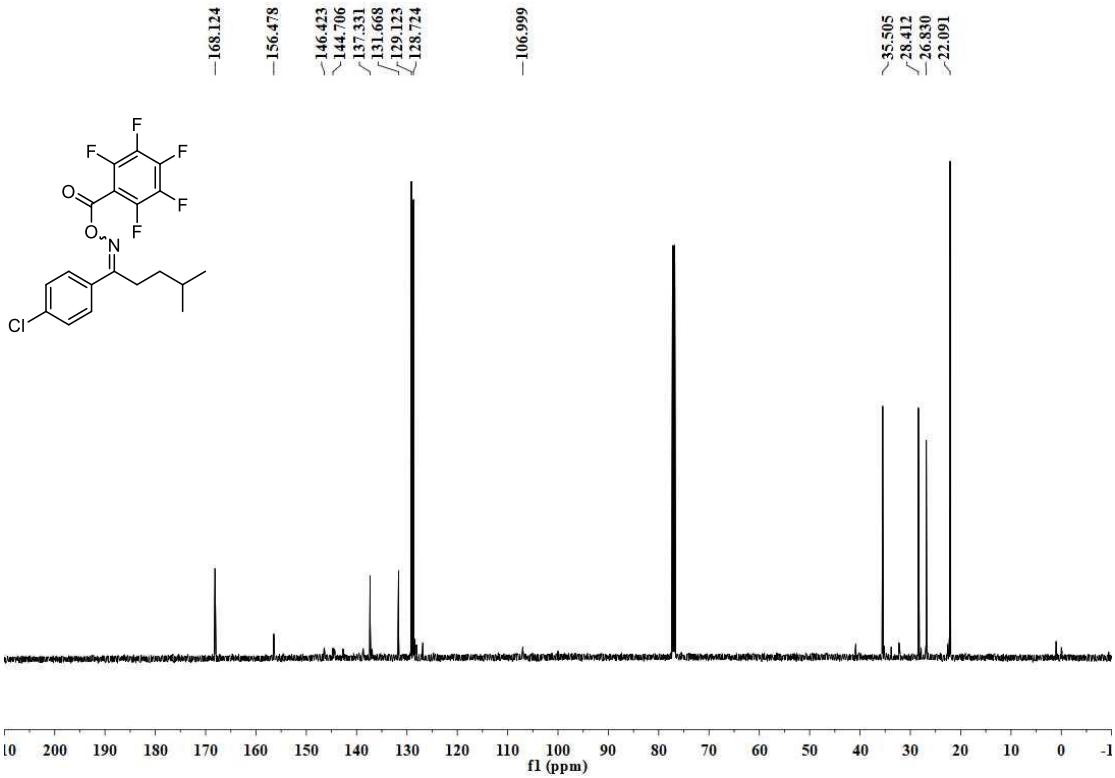
^{19}F NMR Spectrum of S100 (565 MHz, $CDCl_3$)



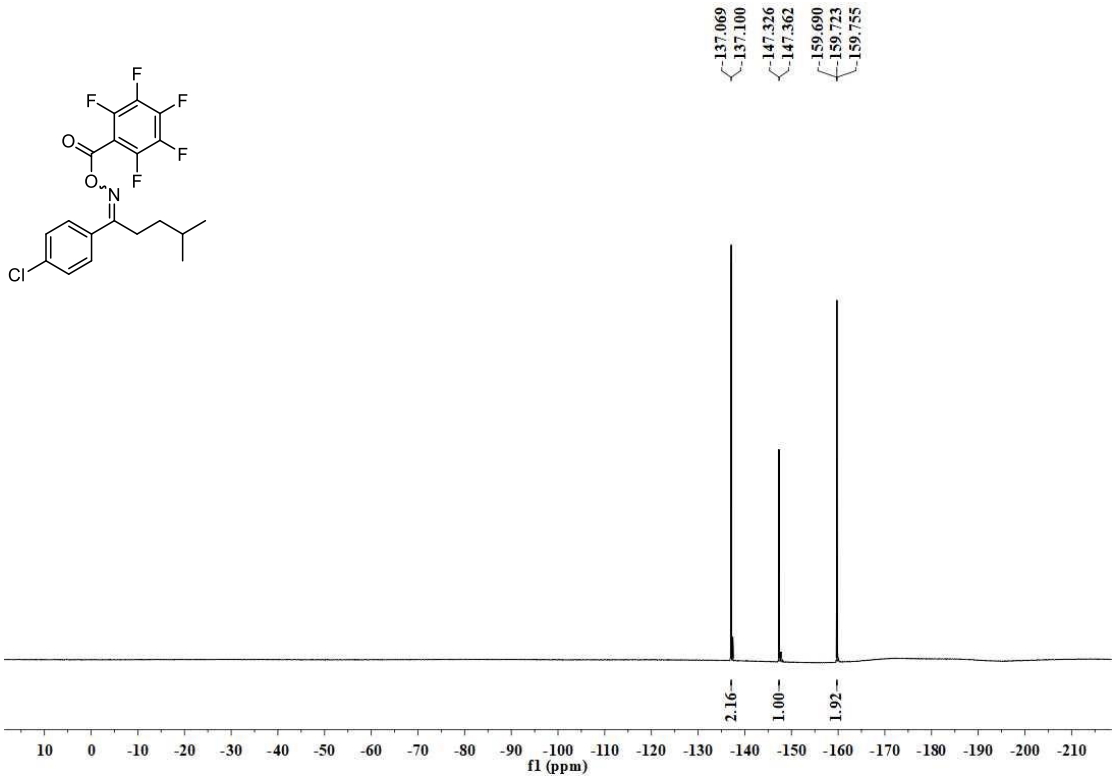
^{1}H NMR Spectrum of S101 (600 MHz, $CDCl_3$)



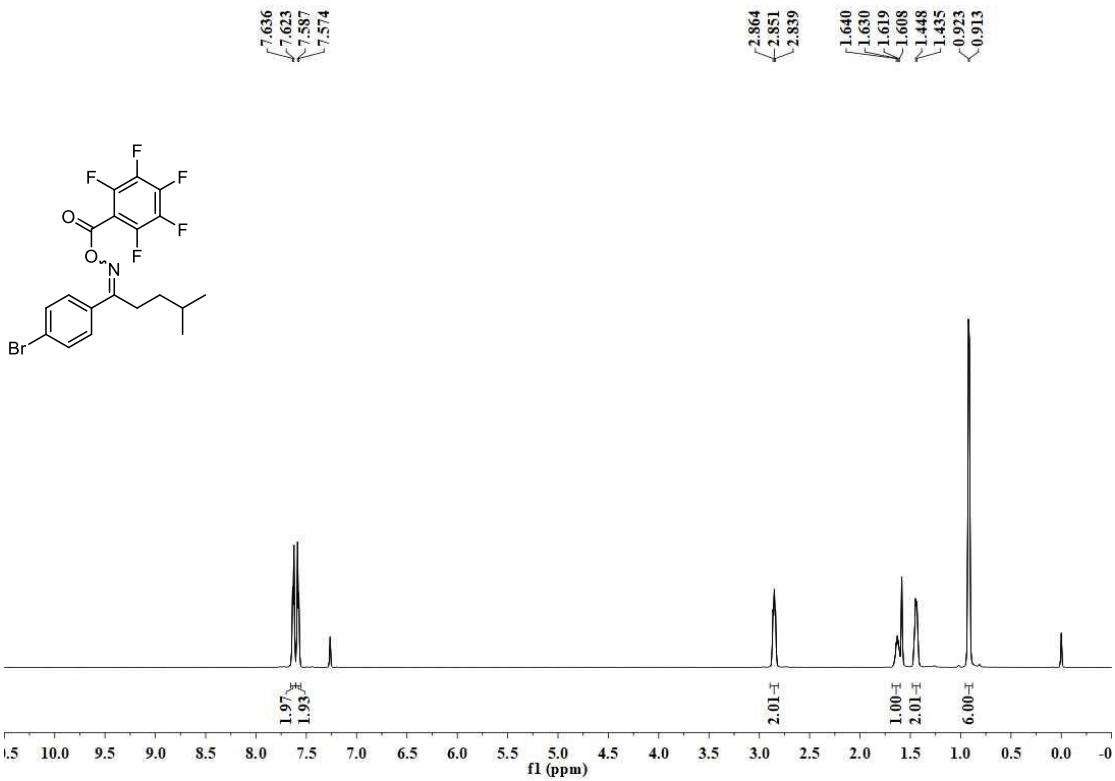
^{13}C NMR Spectrum of S101 (151 MHz, $CDCl_3$)



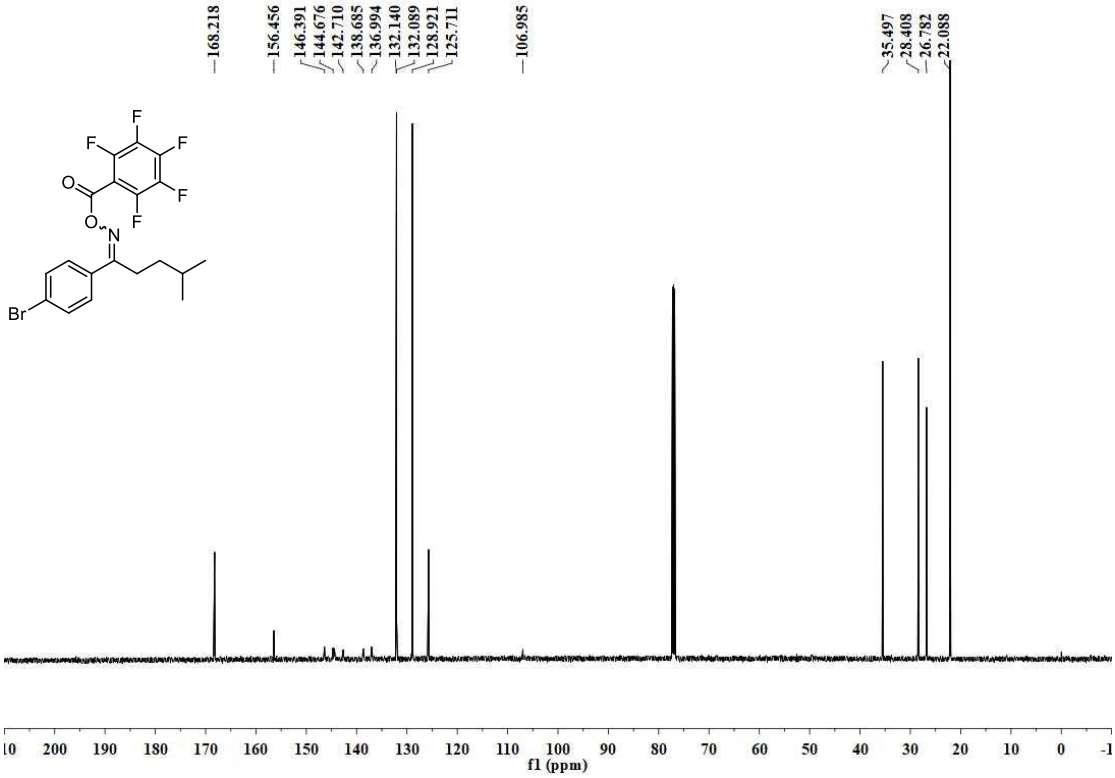
^{19}F NMR Spectrum of S101 (565 MHz, $CDCl_3$)



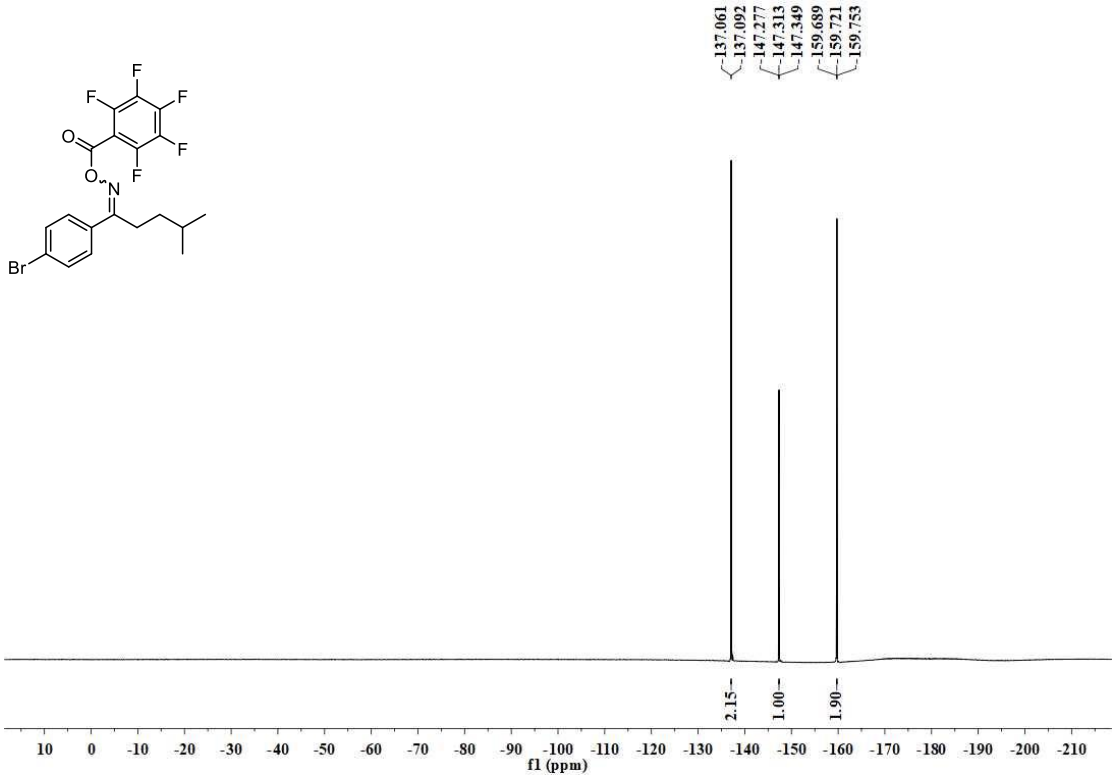
^{1}H NMR Spectrum of S102 (600 MHz, $CDCl_3$)



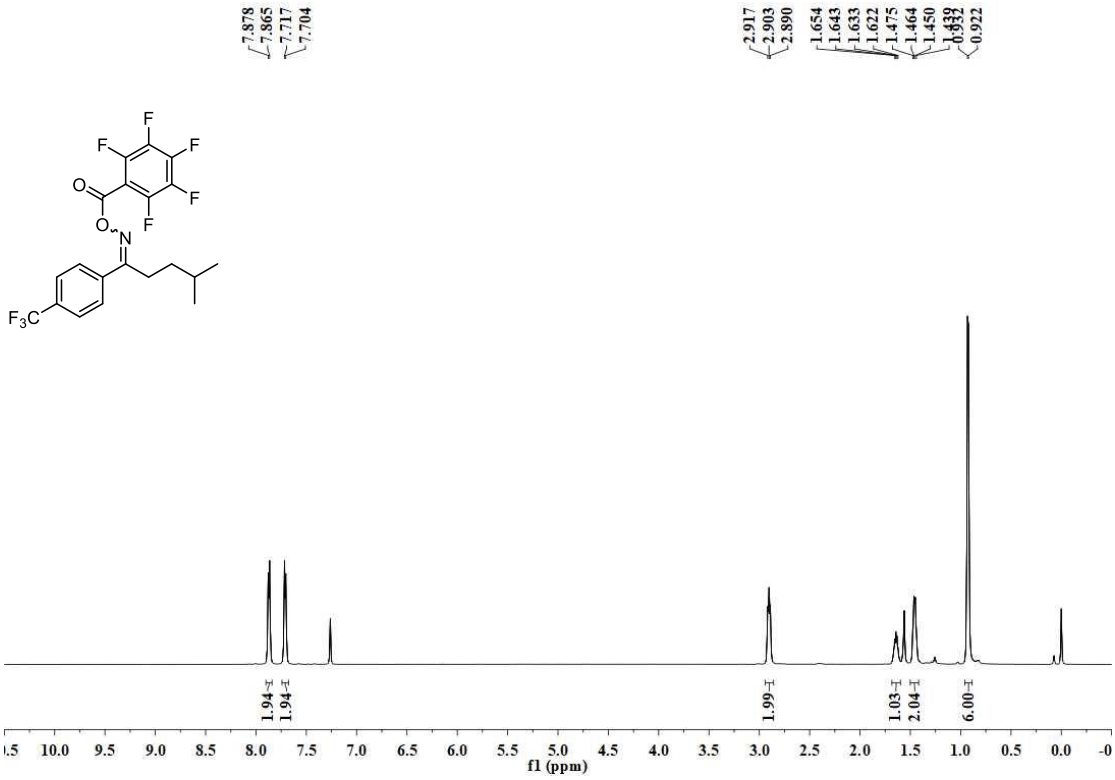
^{13}C NMR Spectrum of S102 (151 MHz, $CDCl_3$)



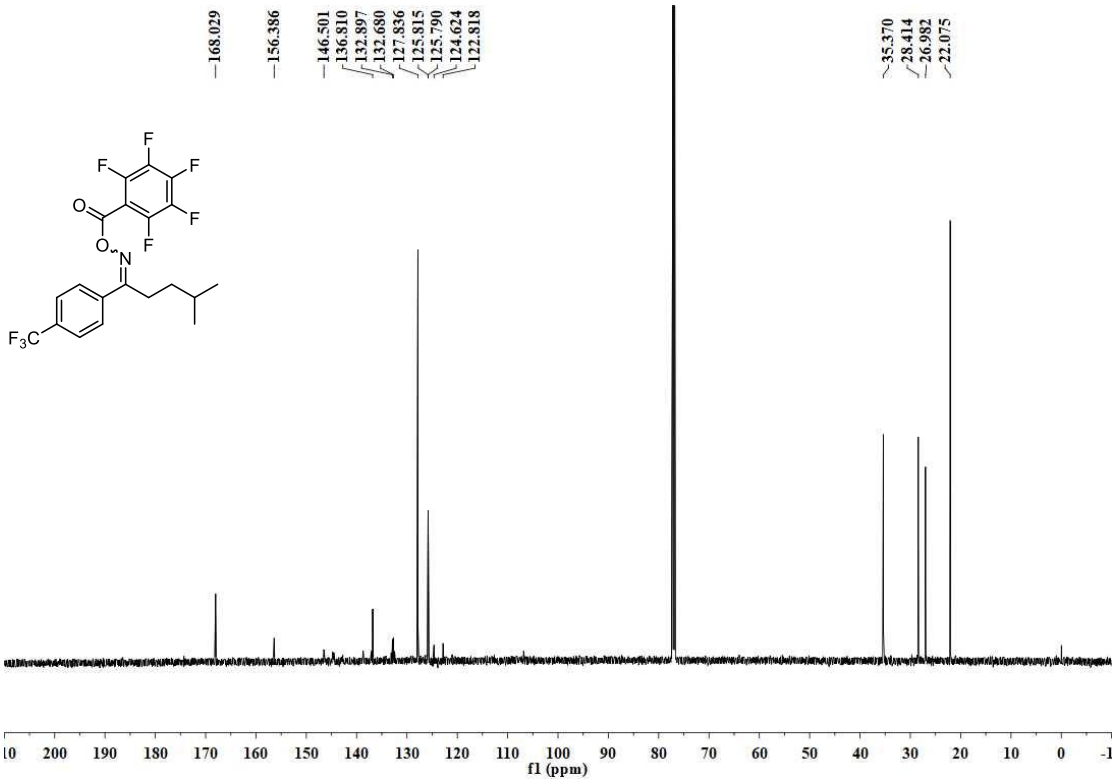
^{19}F NMR Spectrum of S102 (565 MHz, $CDCl_3$)



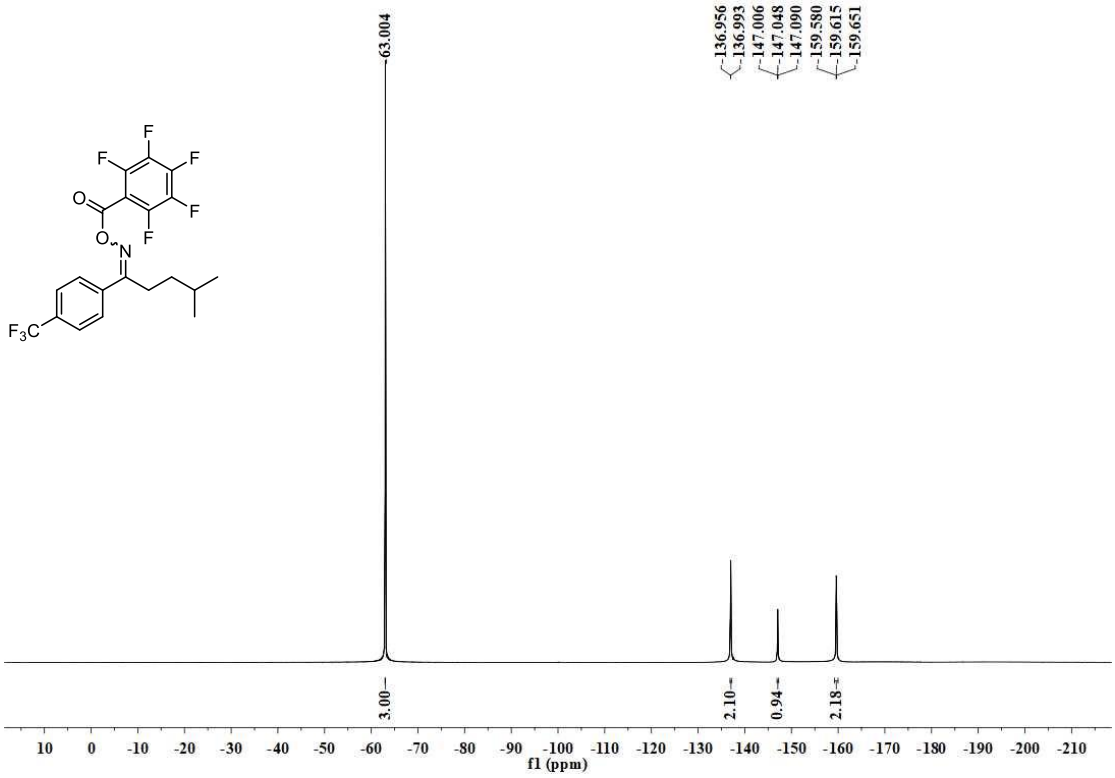
^{1}H NMR Spectrum of S104 (600 MHz, $CDCl_3$)



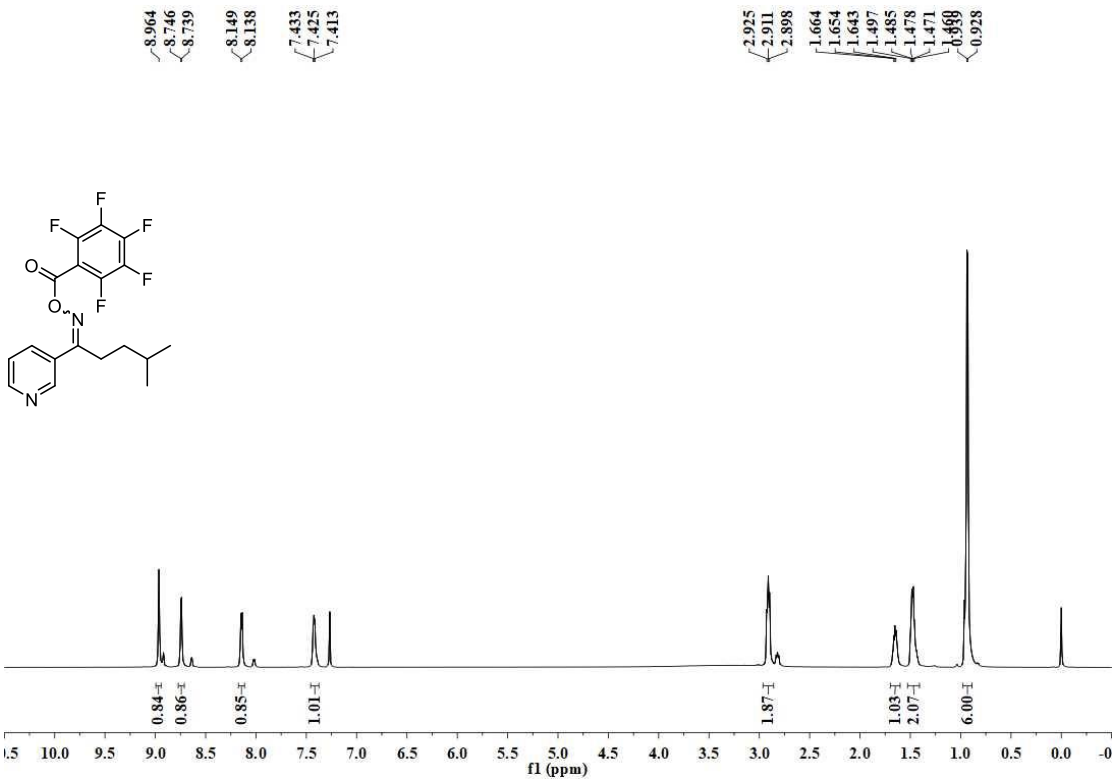
^{13}C NMR Spectrum of S104 (151 MHz, $CDCl_3$)



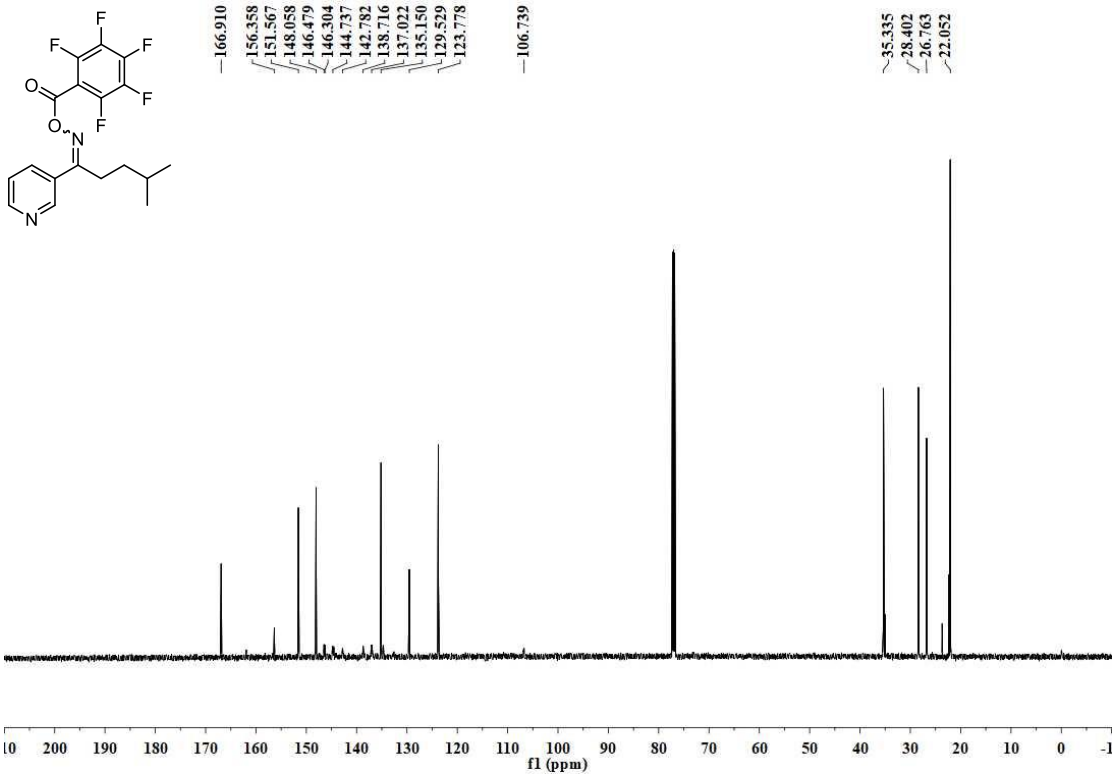
^{19}F NMR Spectrum of S104 (565 MHz, $CDCl_3$)



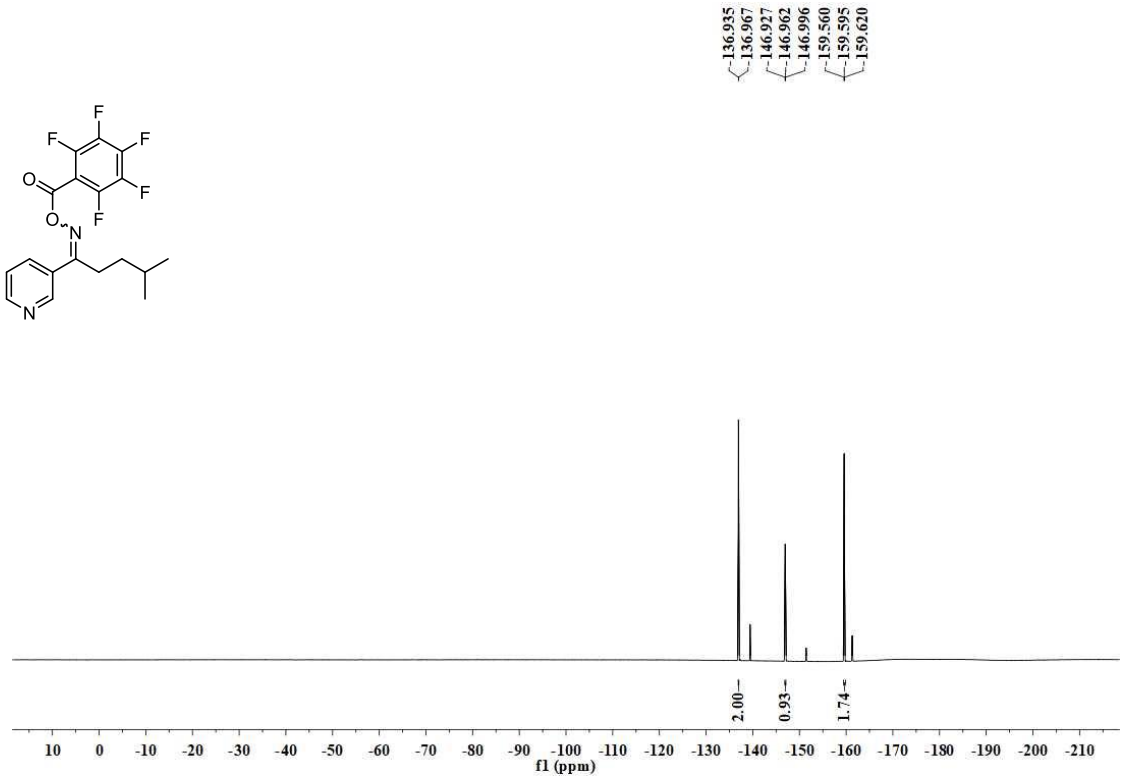
^{1}H NMR Spectrum of S105 (600 MHz, $CDCl_3$)



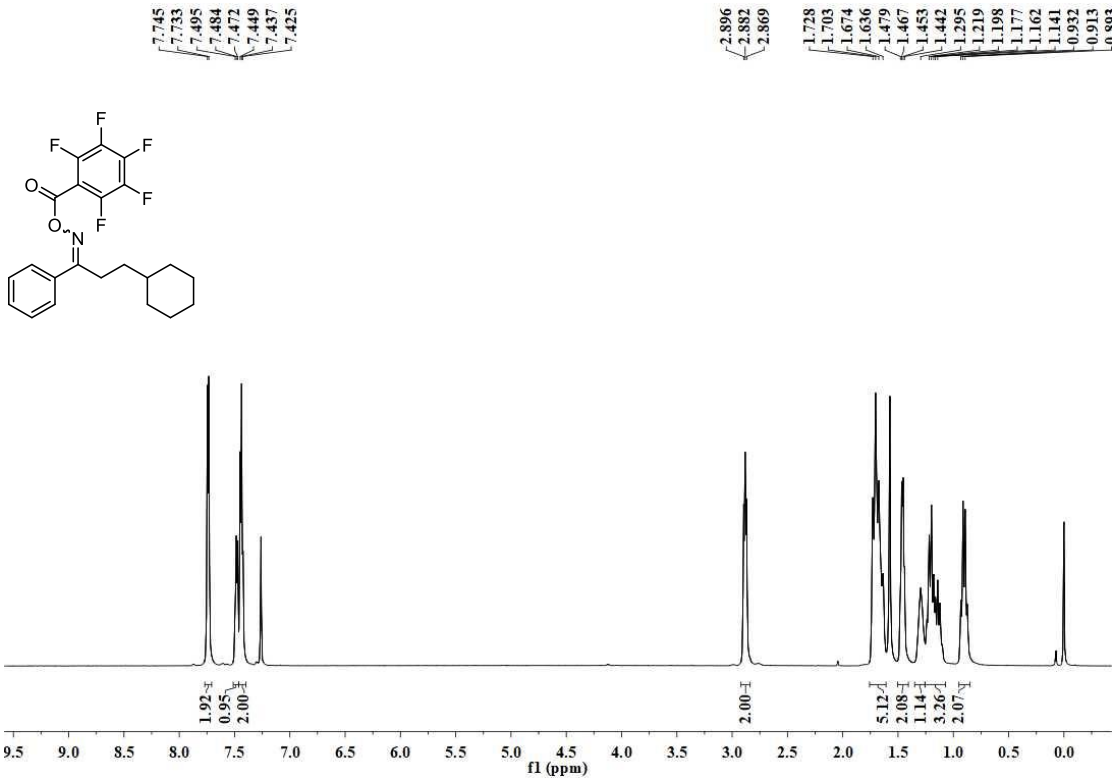
^{13}C NMR Spectrum of S105 (151 MHz, $CDCl_3$)



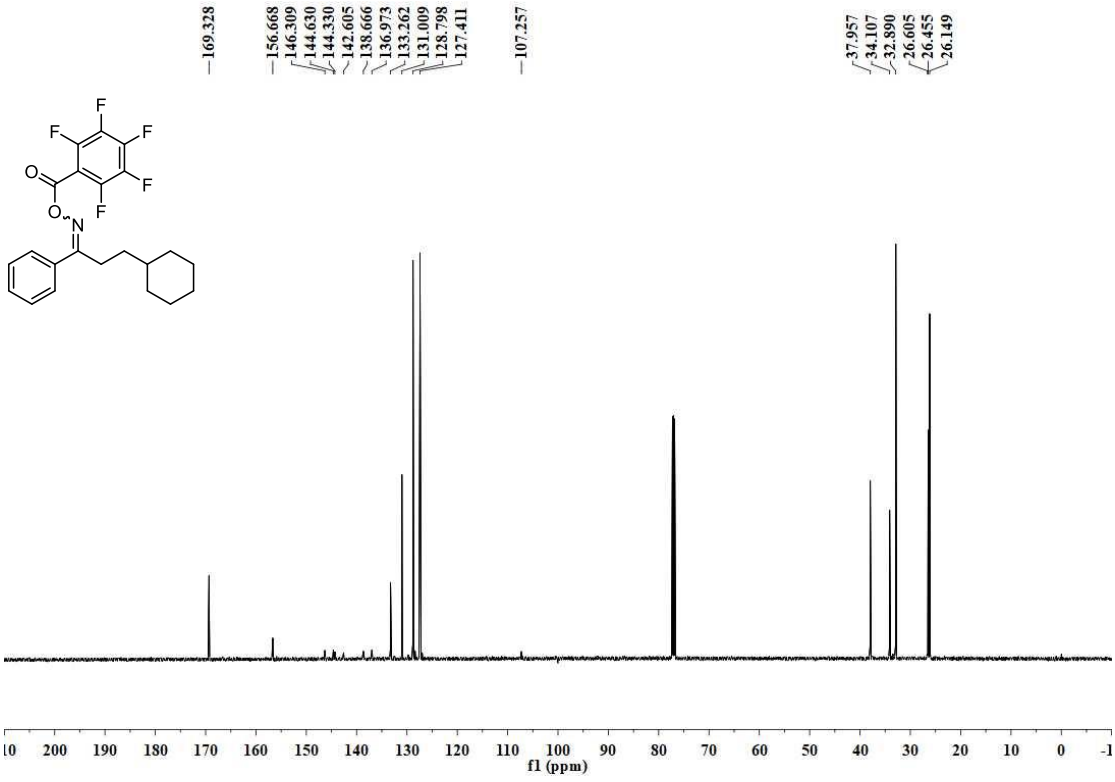
^{19}F NMR Spectrum of S105 (565 MHz, $CDCl_3$)



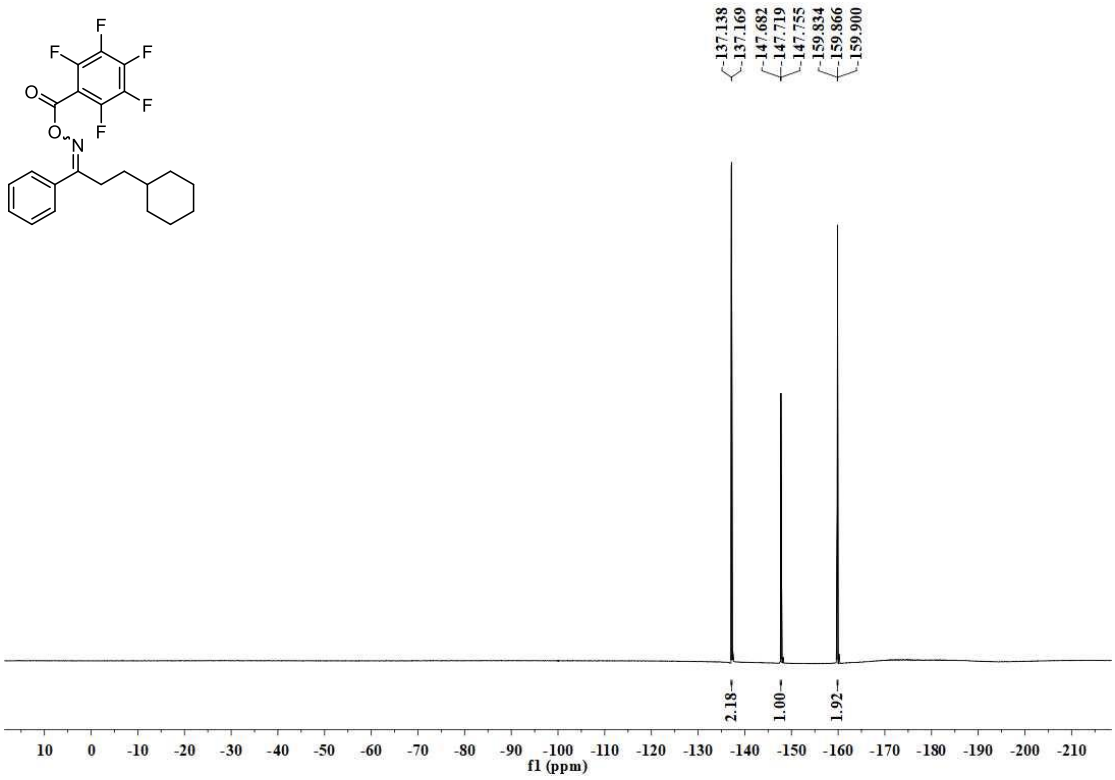
^{1}H NMR Spectrum of S106 (600 MHz, $CDCl_3$)



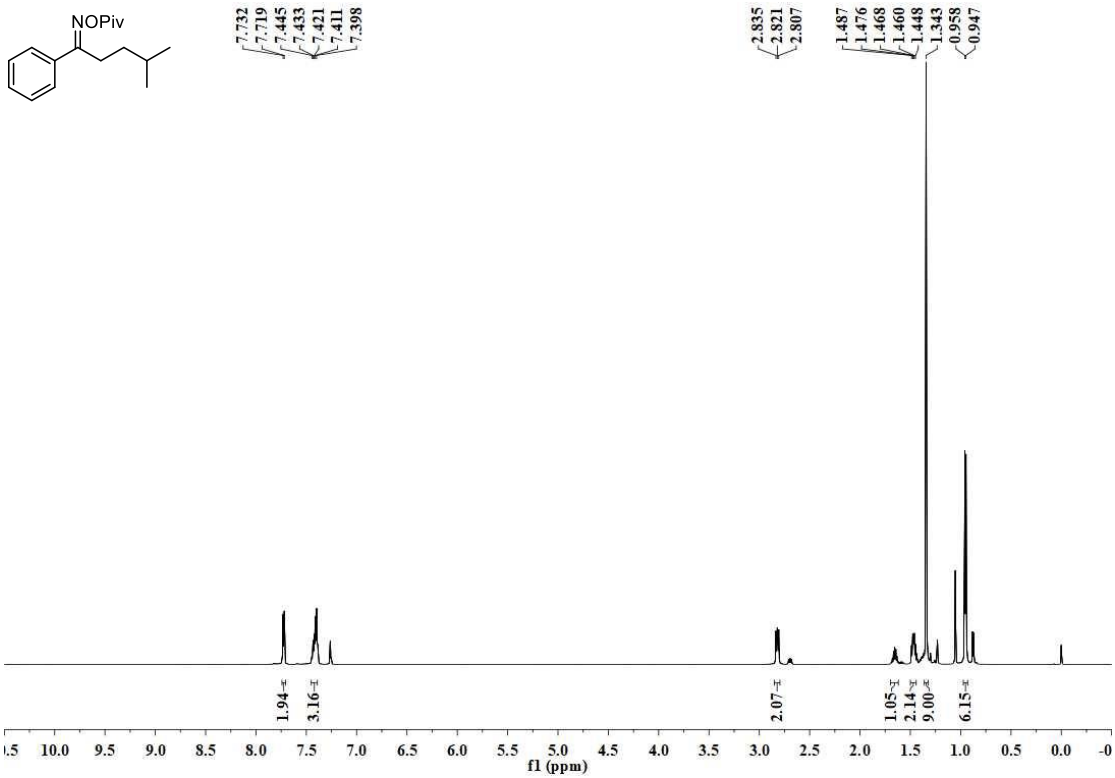
^{13}C NMR Spectrum of S106 (151 MHz, $CDCl_3$)



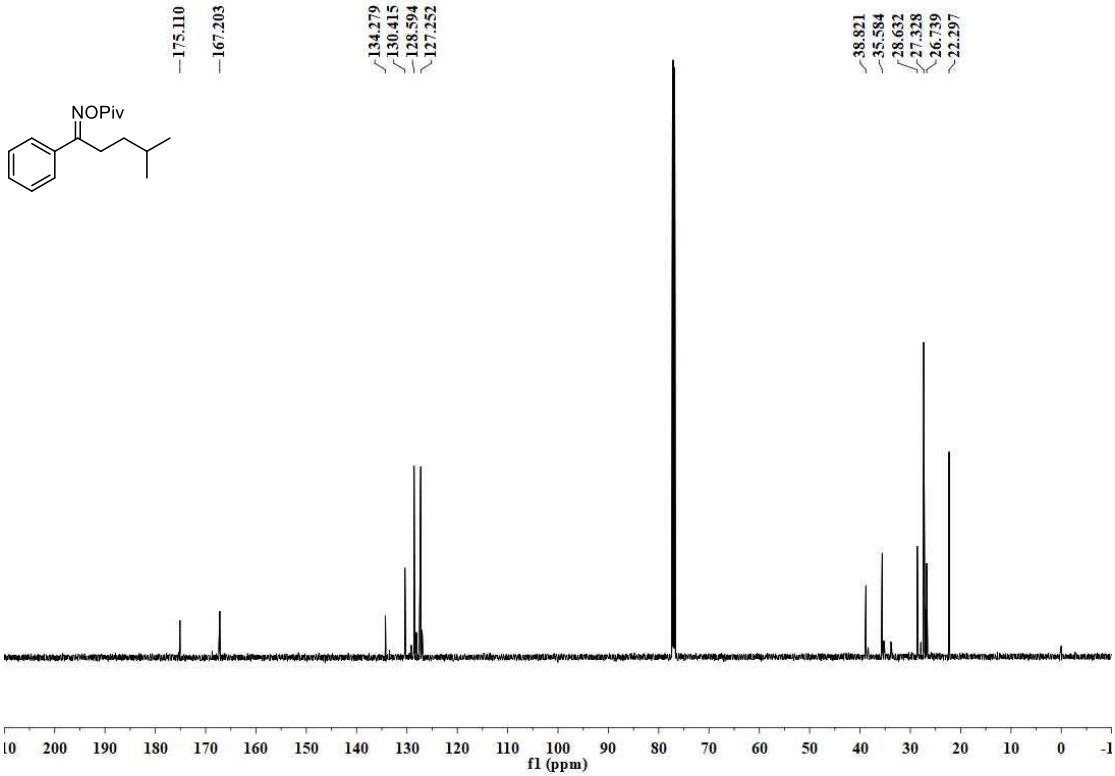
^{19}F NMR Spectrum of S106 (565 MHz, $CDCl_3$)



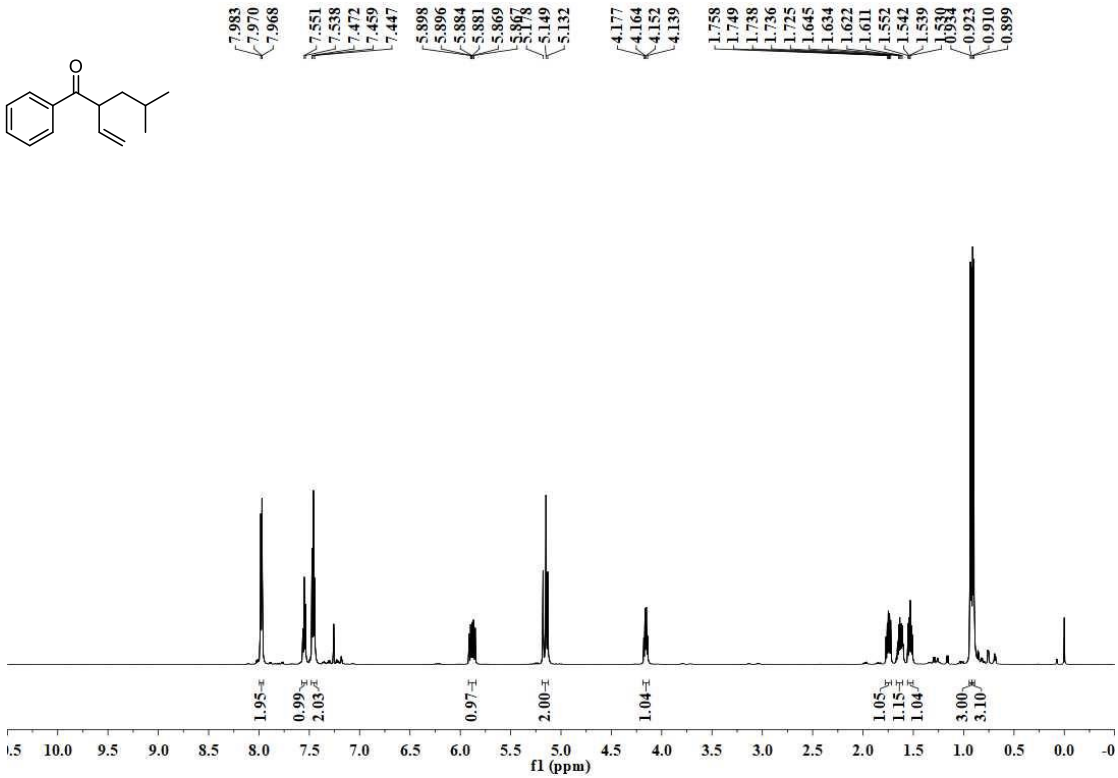
^{1}H NMR Spectrum of S121 (600 MHz, $CDCl_3$)



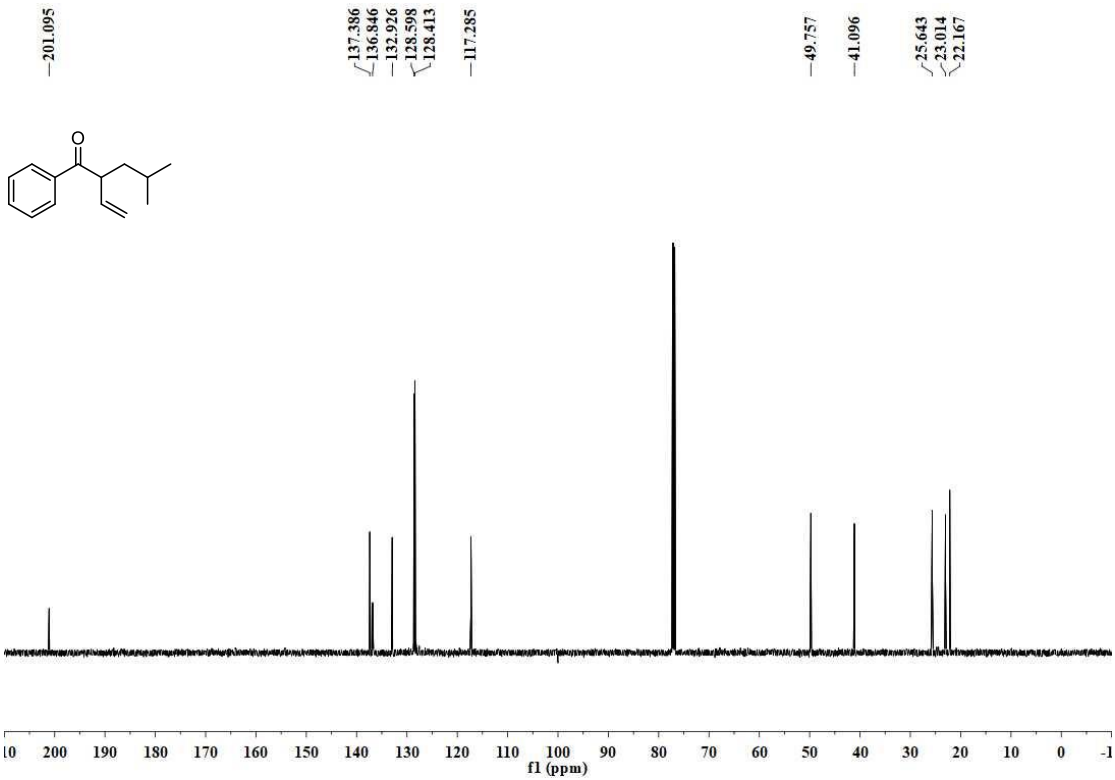
^{13}C NMR Spectrum of S121 (151 MHz, $CDCl_3$)



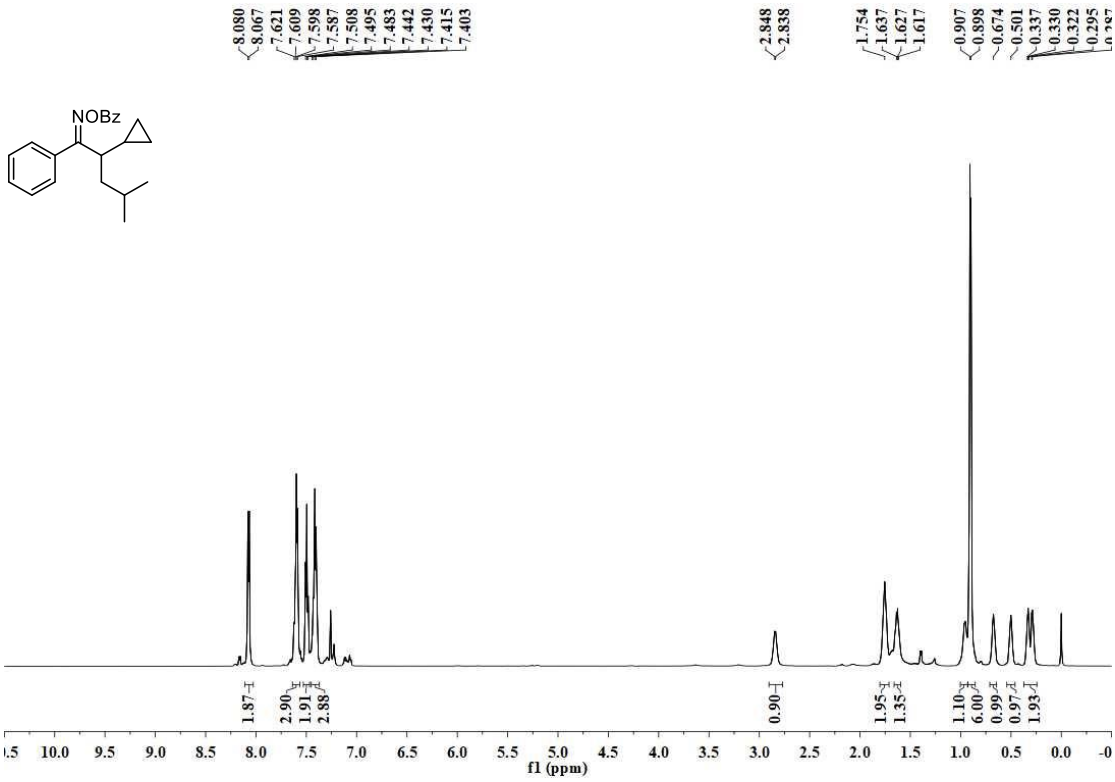
^{1}H NMR Spectrum of 4-methyl-1-phenyl-2-vinylpentan-1-one (600 MHz, $CDCl_3$)



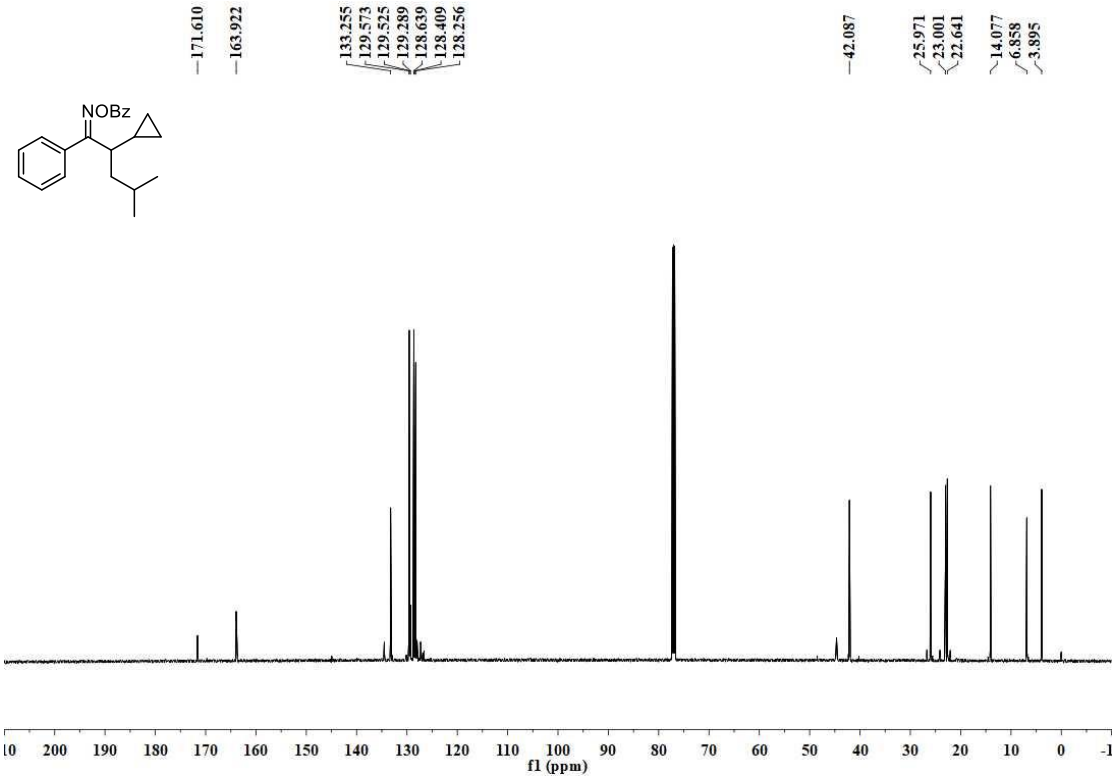
^{13}C NMR Spectrum of 4-methyl-1-phenyl-2-vinylpentan-1-one (151 MHz, $CDCl_3$)



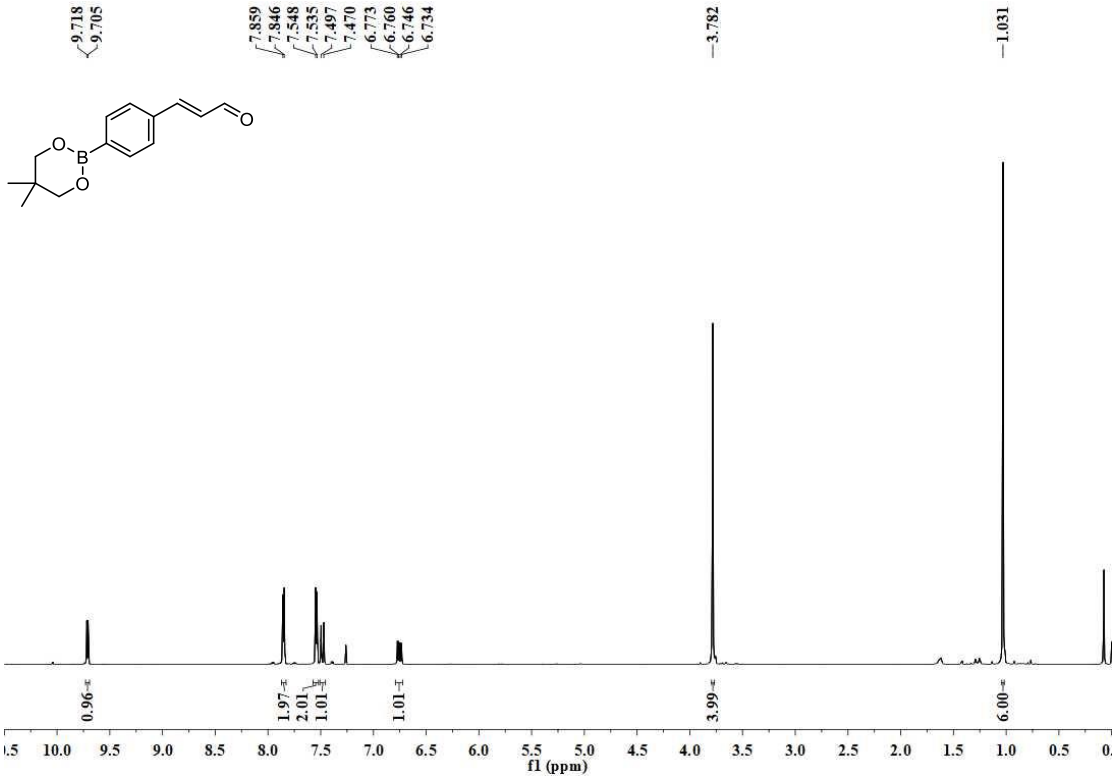
^{1}H NMR Spectrum of 73 (600 MHz, $CDCl_3$)



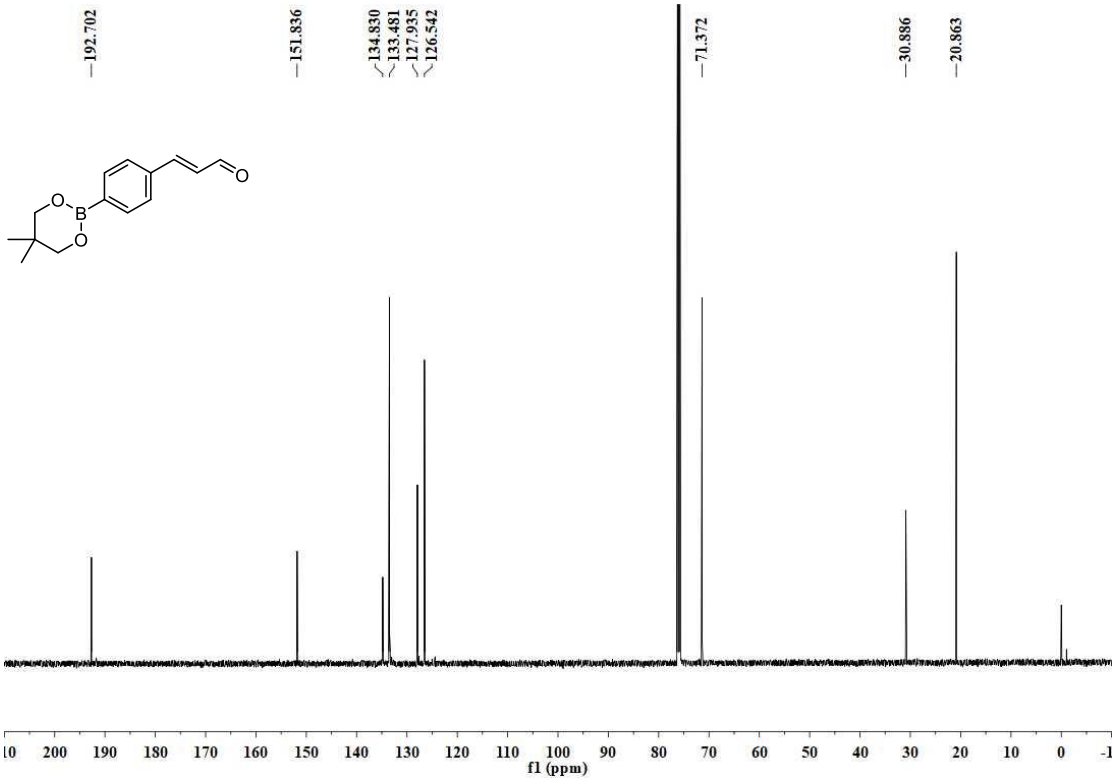
^{13}C NMR Spectrum of 73 (151 MHz, $CDCl_3$)



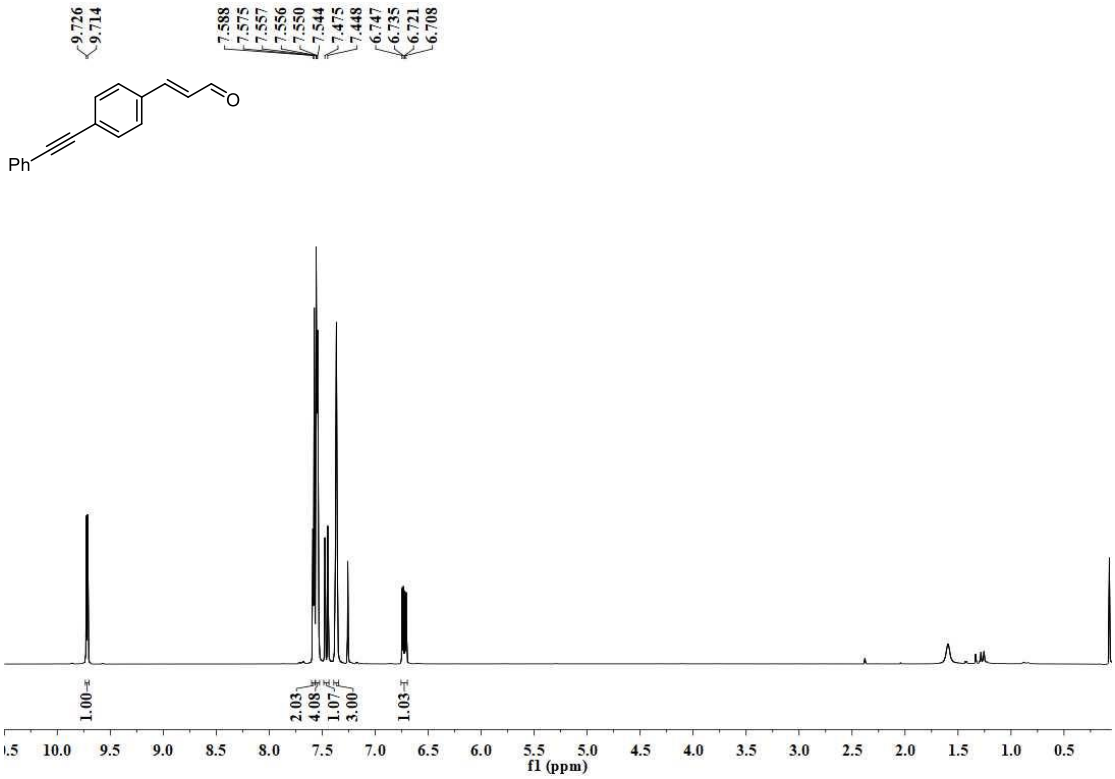
^{1}H NMR Spectrum of S41 (600 MHz, $CDCl_3$)



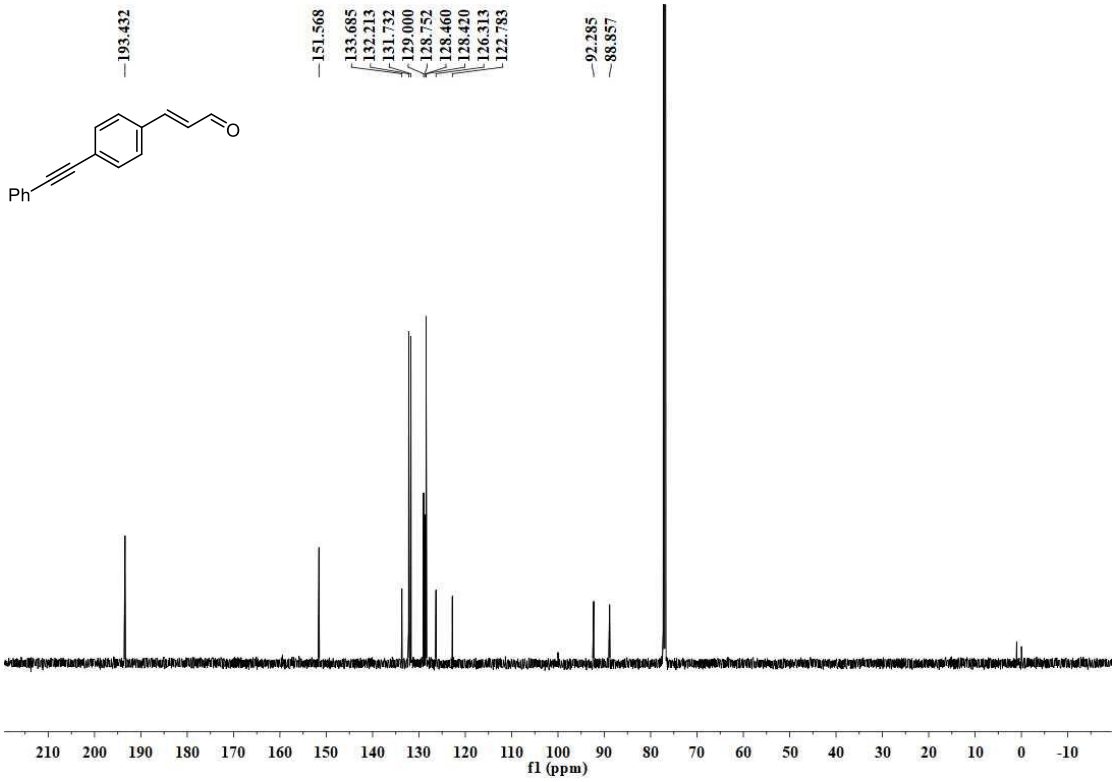
^{13}C NMR Spectrum of S41 (151 MHz, $CDCl_3$)



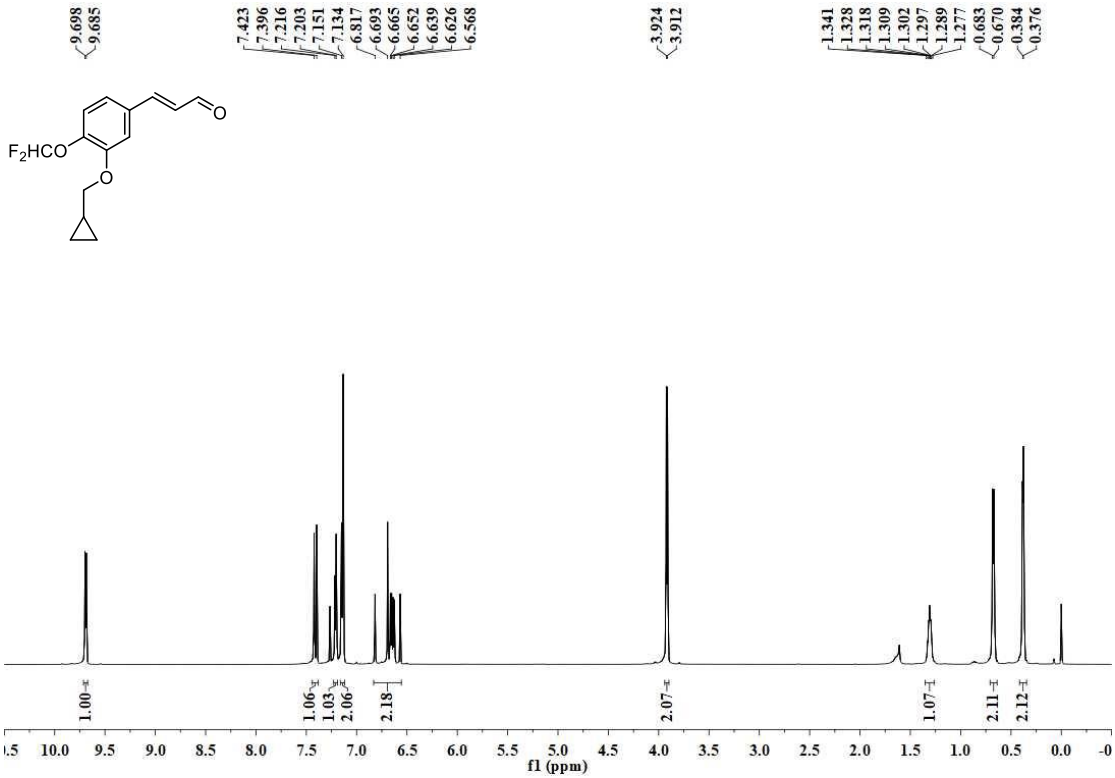
^{1}H NMR Spectrum of S42 (600 MHz, $CDCl_3$)



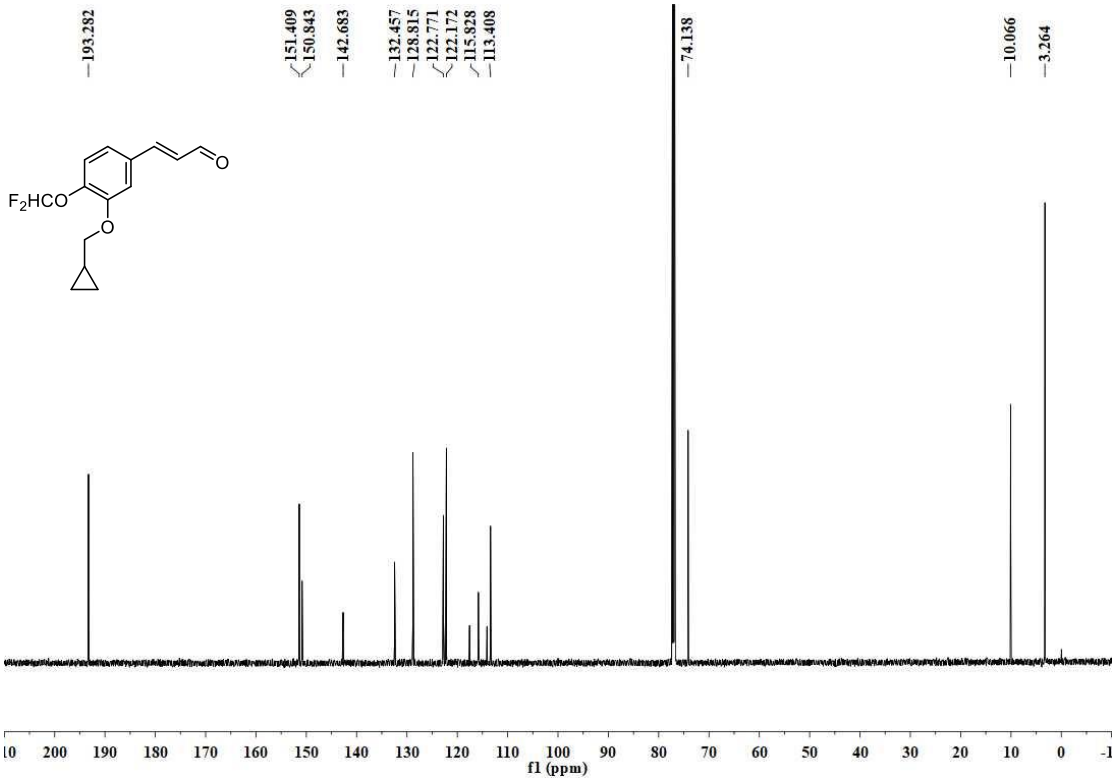
^{13}C NMR Spectrum of S42 (151 MHz, $CDCl_3$)



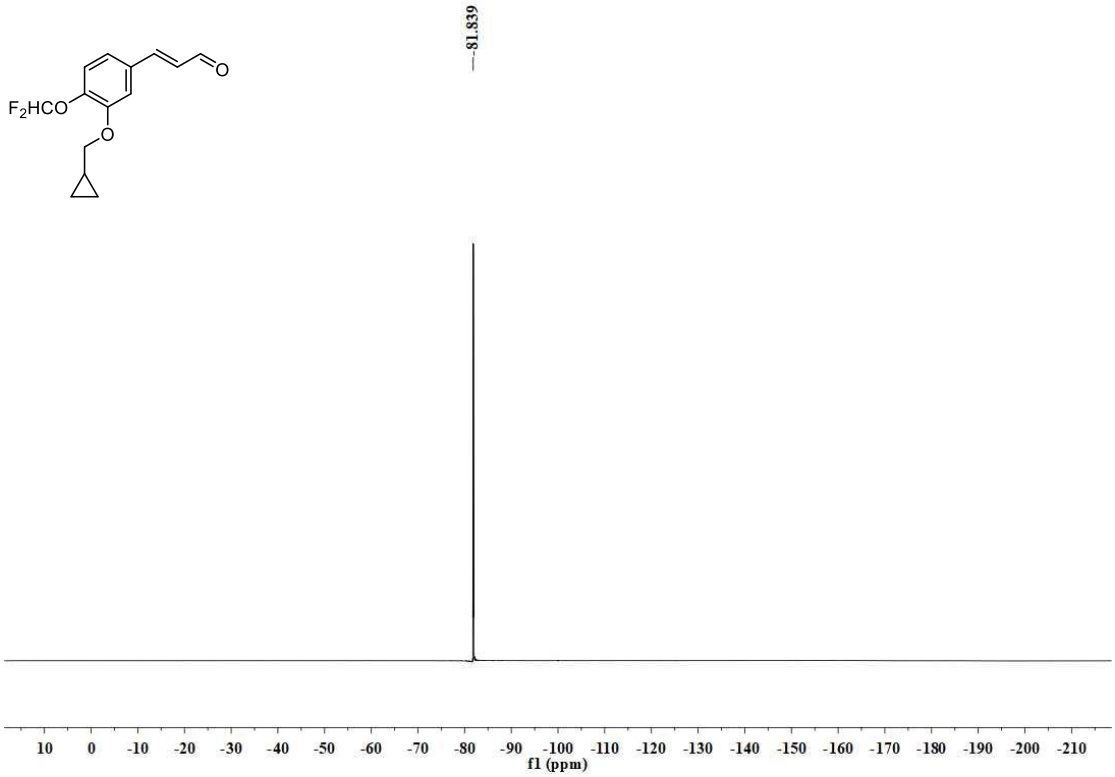
^{1}H NMR Spectrum of S46 (600 MHz, $CDCl_3$)



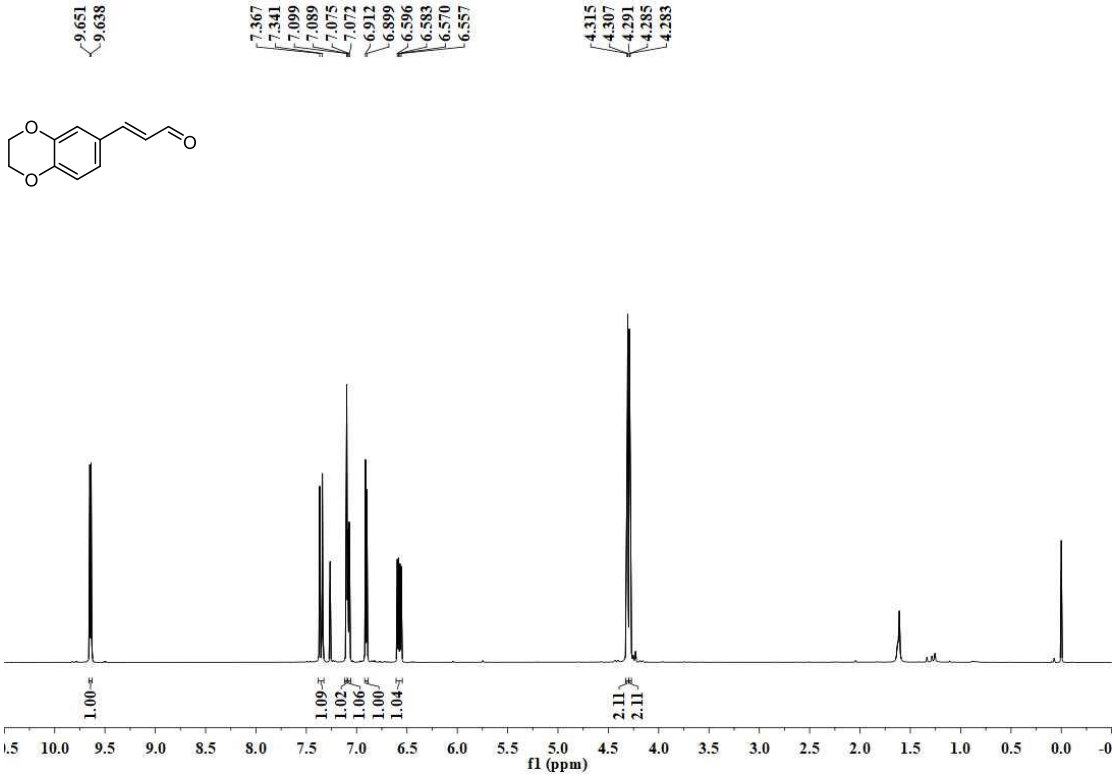
^{13}C NMR Spectrum of S46 (151 MHz, $CDCl_3$)



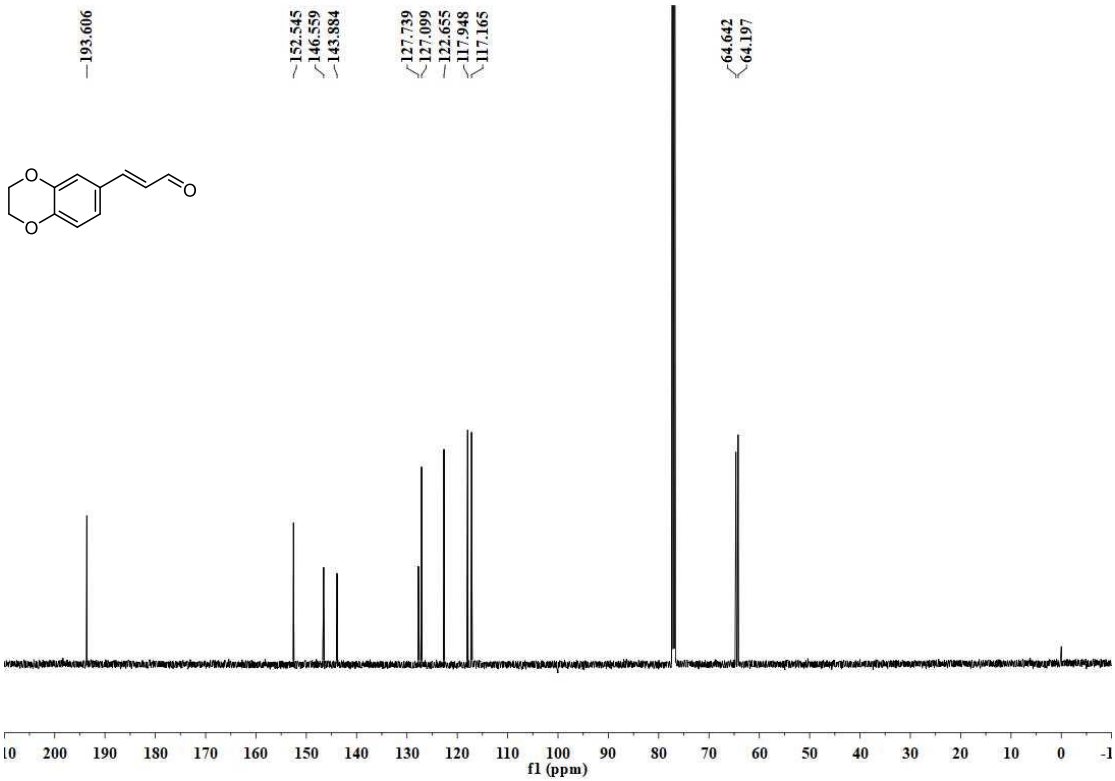
^{19}F NMR Spectrum of S46 (565 MHz, $CDCl_3$)



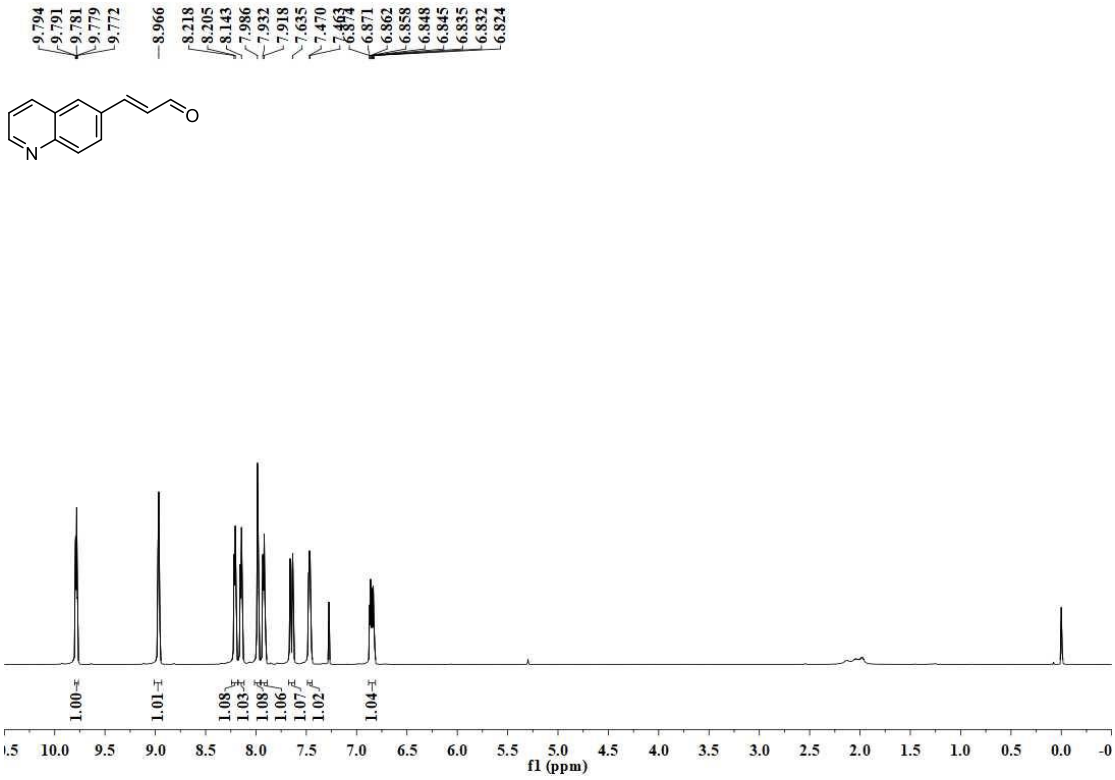
^{1}H NMR Spectrum of S47 (600 MHz, $CDCl_3$)



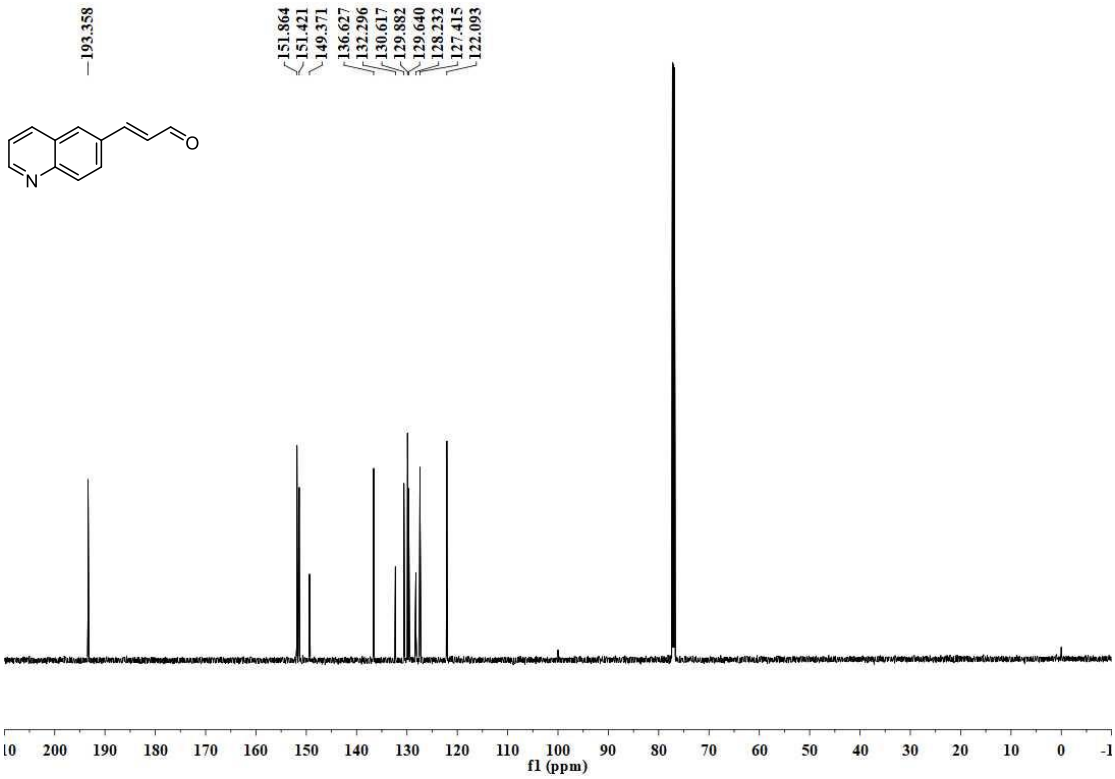
^{13}C NMR Spectrum of S47 (151 MHz, $CDCl_3$)



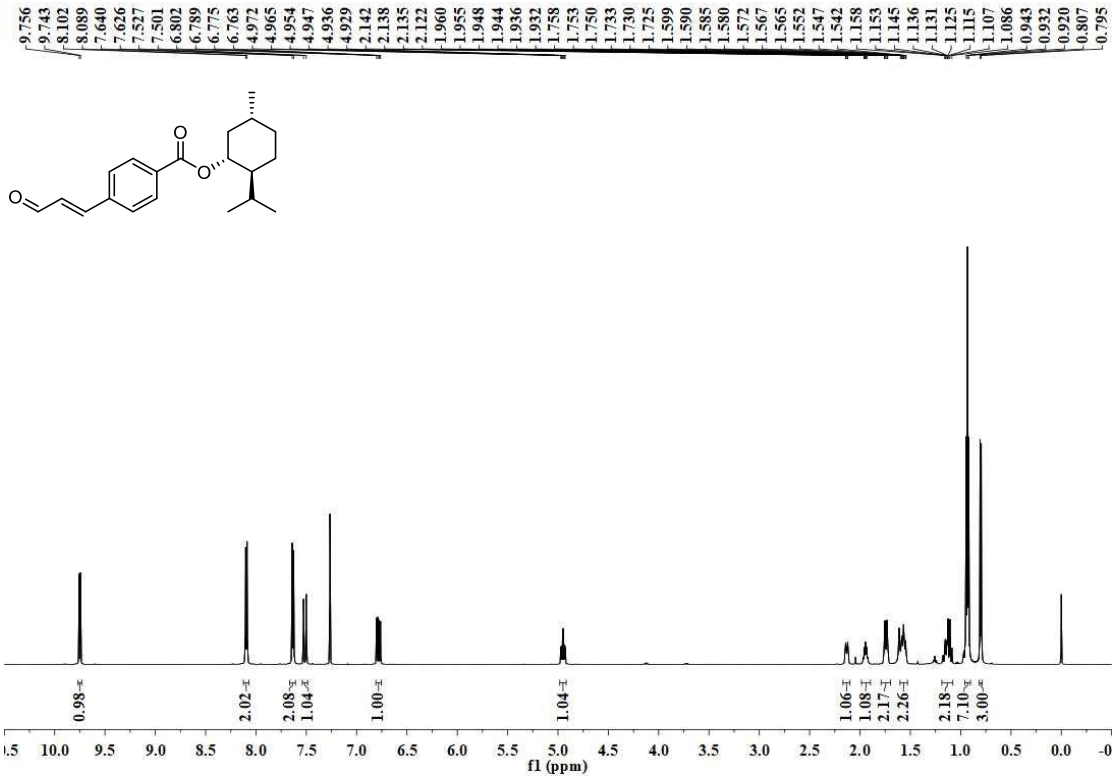
^{1}H NMR Spectrum of S53 (600 MHz, $CDCl_3$)



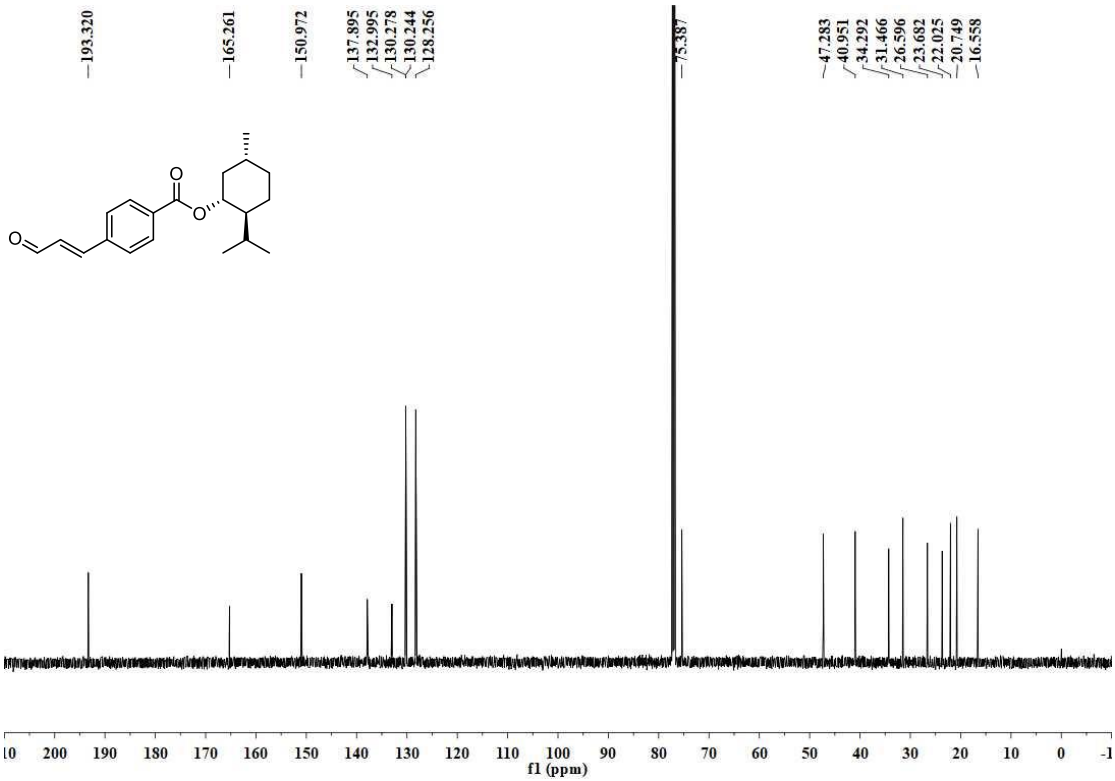
^{13}C NMR Spectrum of S53 (151 MHz, $CDCl_3$)



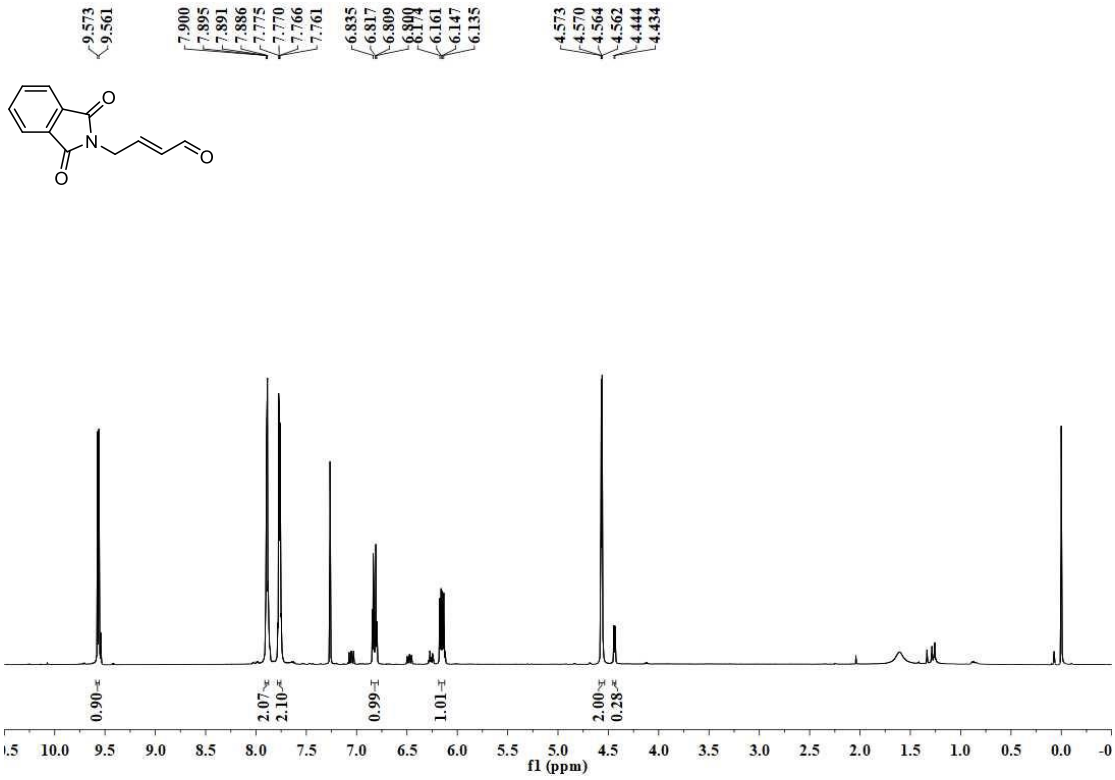
^{1}H NMR Spectrum of S60 (600 MHz, $CDCl_3$)



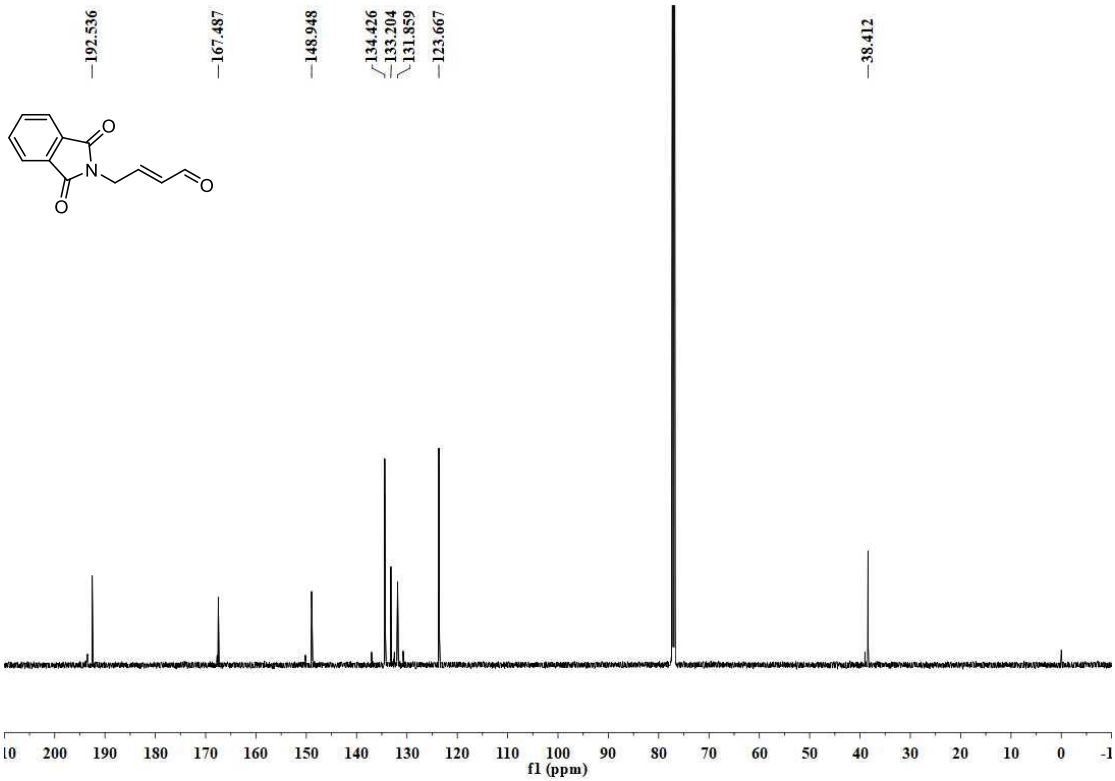
^{13}C NMR Spectrum of S60 (151 MHz, $CDCl_3$)



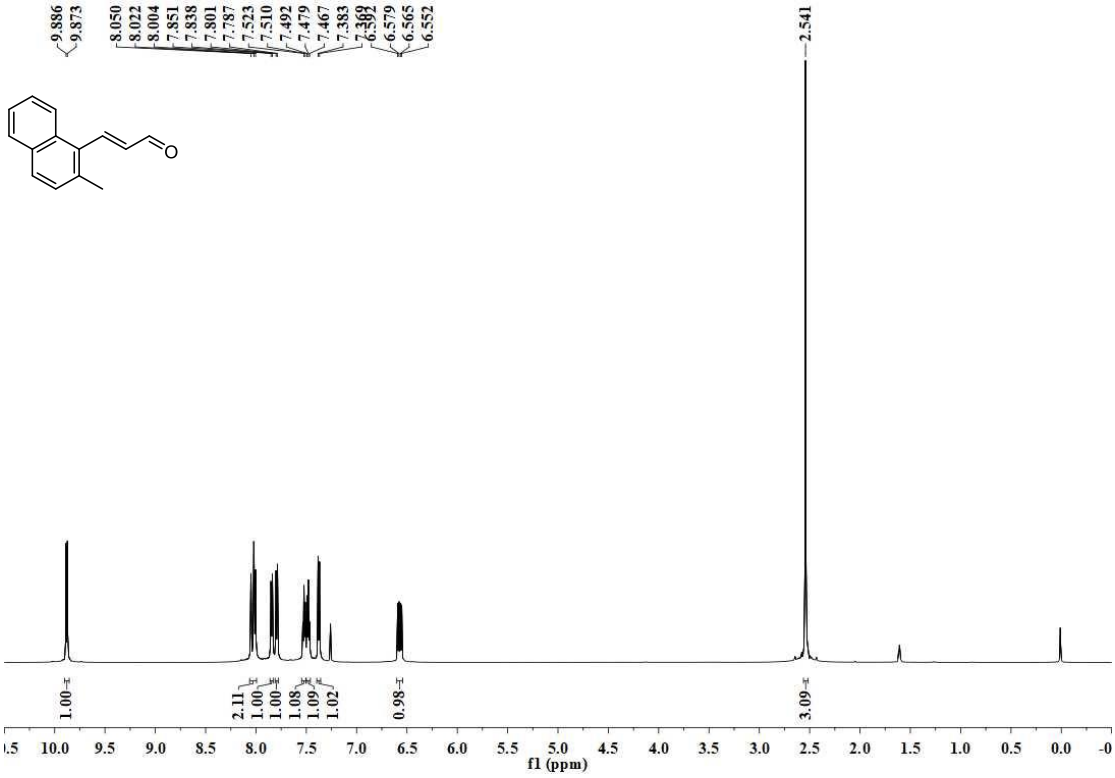
^{1}H NMR Spectrum of 80 (600 MHz, $CDCl_3$)



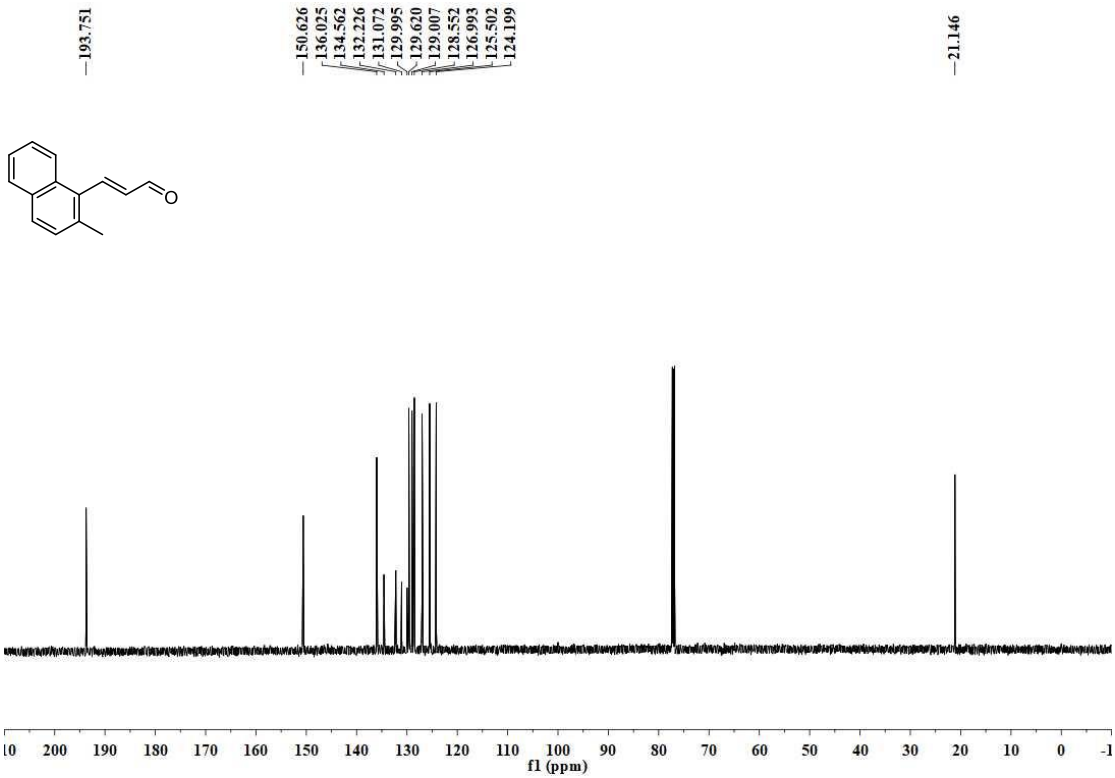
^{13}C NMR Spectrum of 80 (151 MHz, $CDCl_3$)



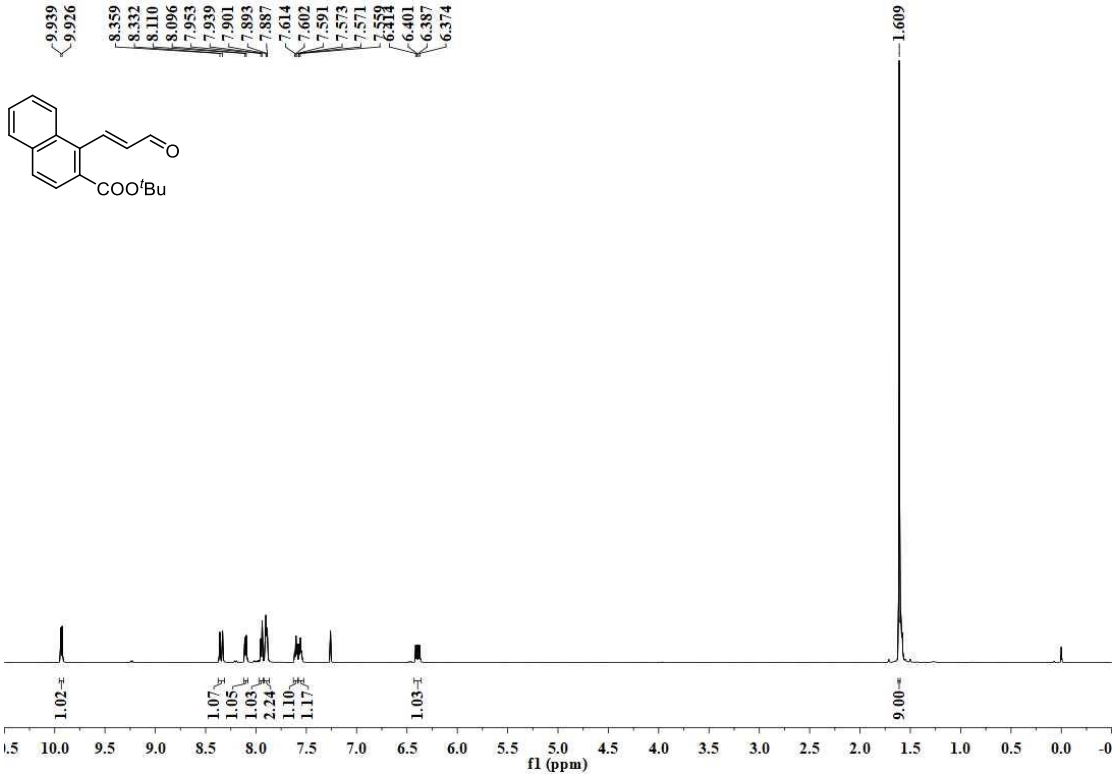
^{1}H NMR Spectrum of S62 (600 MHz, $CDCl_3$)



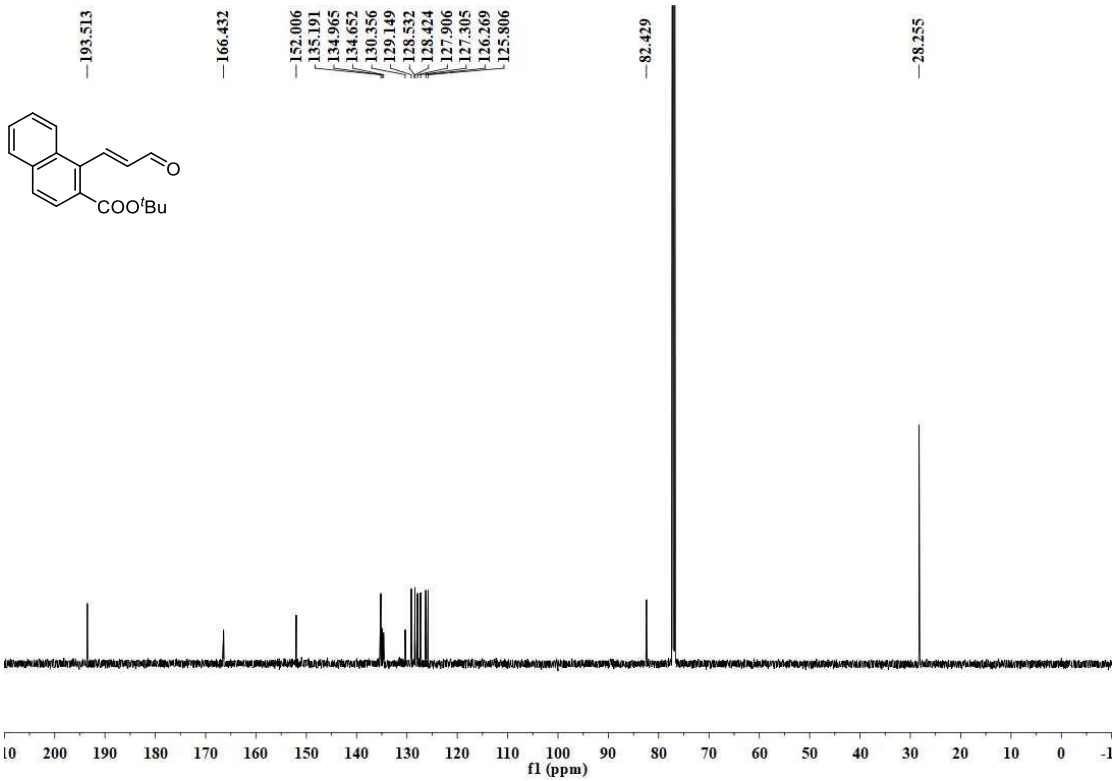
^{13}C NMR Spectrum of S62 (151 MHz, $CDCl_3$)



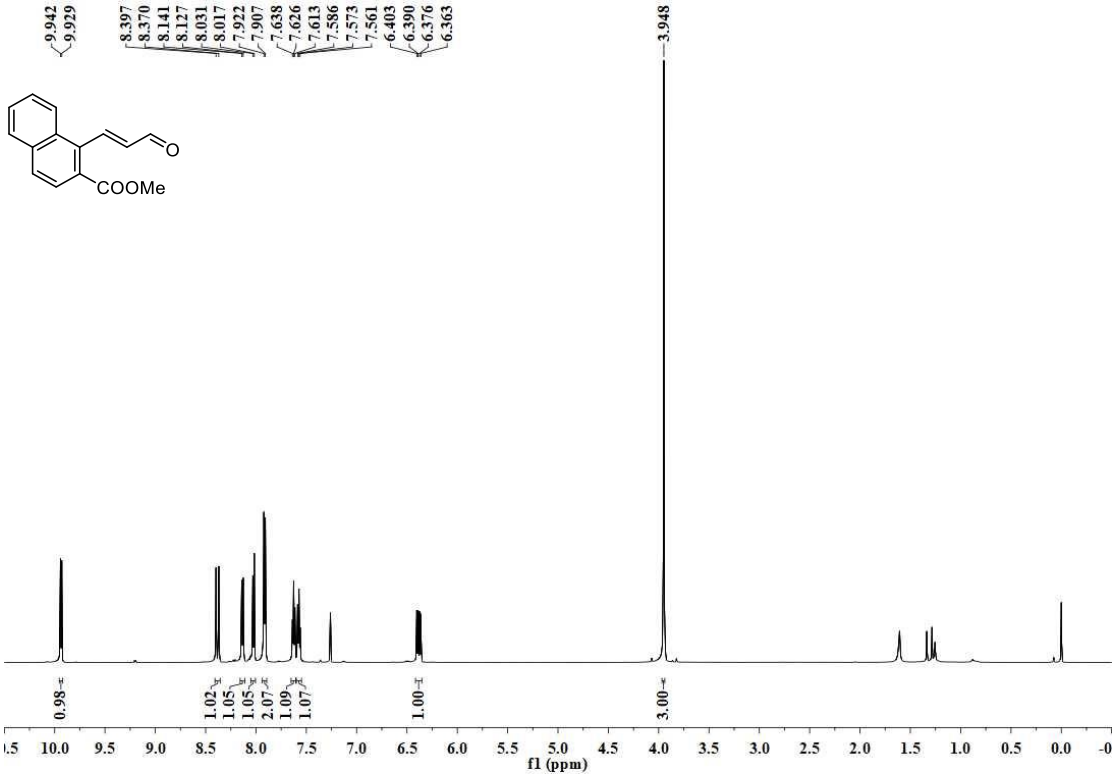
^{1}H NMR Spectrum of 96 (600 MHz, $CDCl_3$)



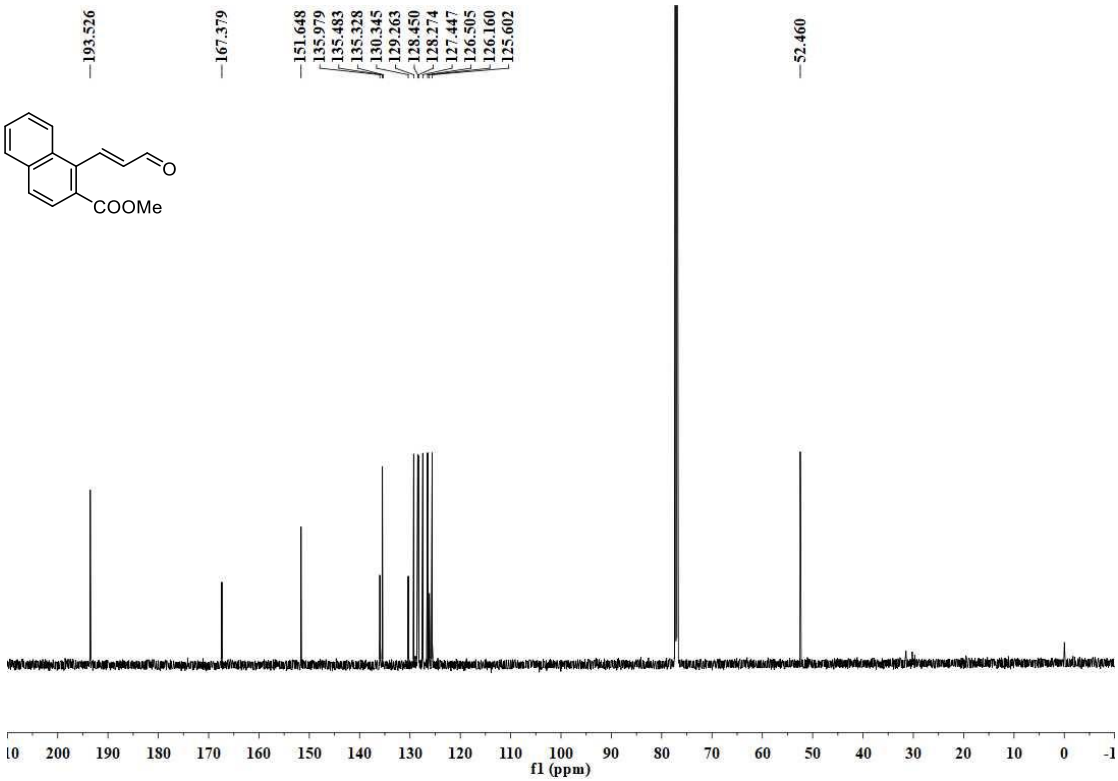
^{13}C NMR Spectrum of 96 (151 MHz, $CDCl_3$)



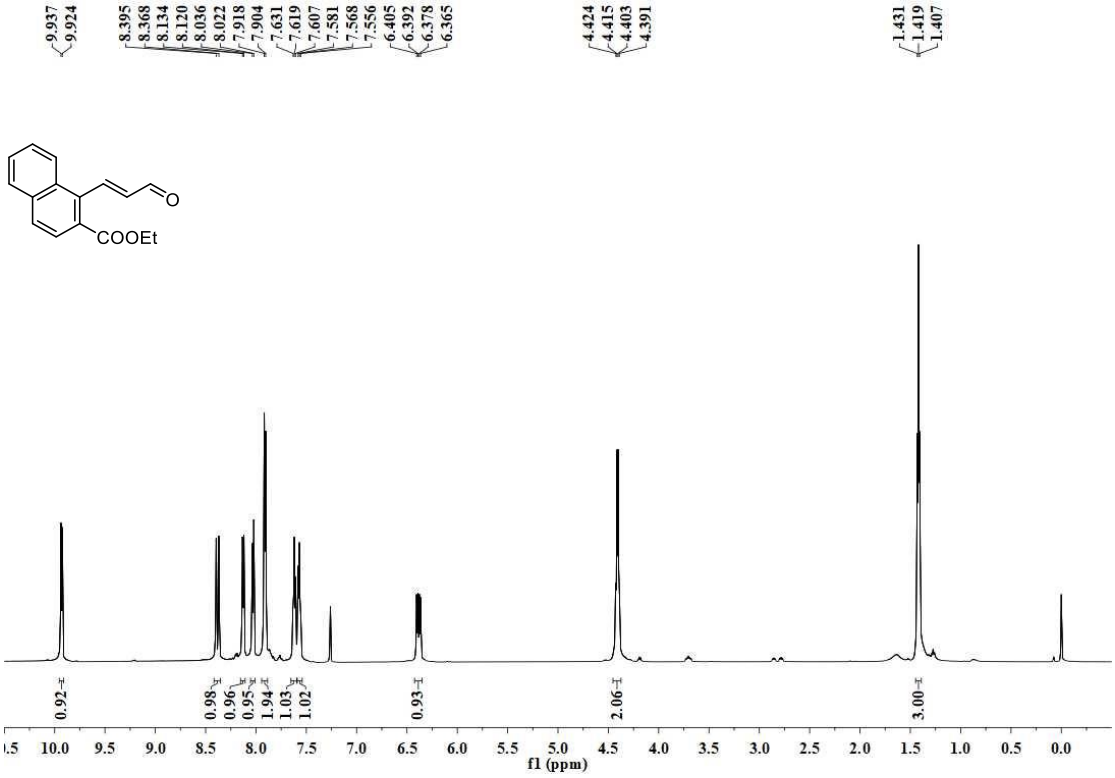
^{1}H NMR Spectrum of S63 (600 MHz, $CDCl_3$)



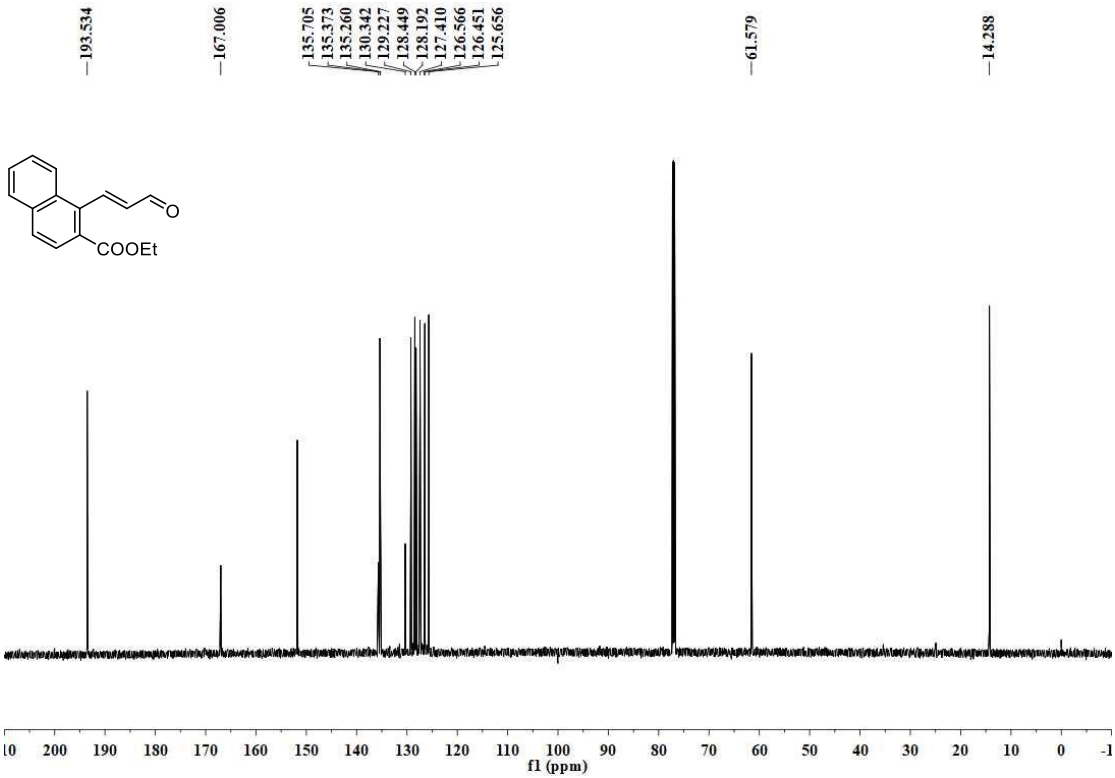
^{13}C NMR Spectrum of S63 (151 MHz, $CDCl_3$)



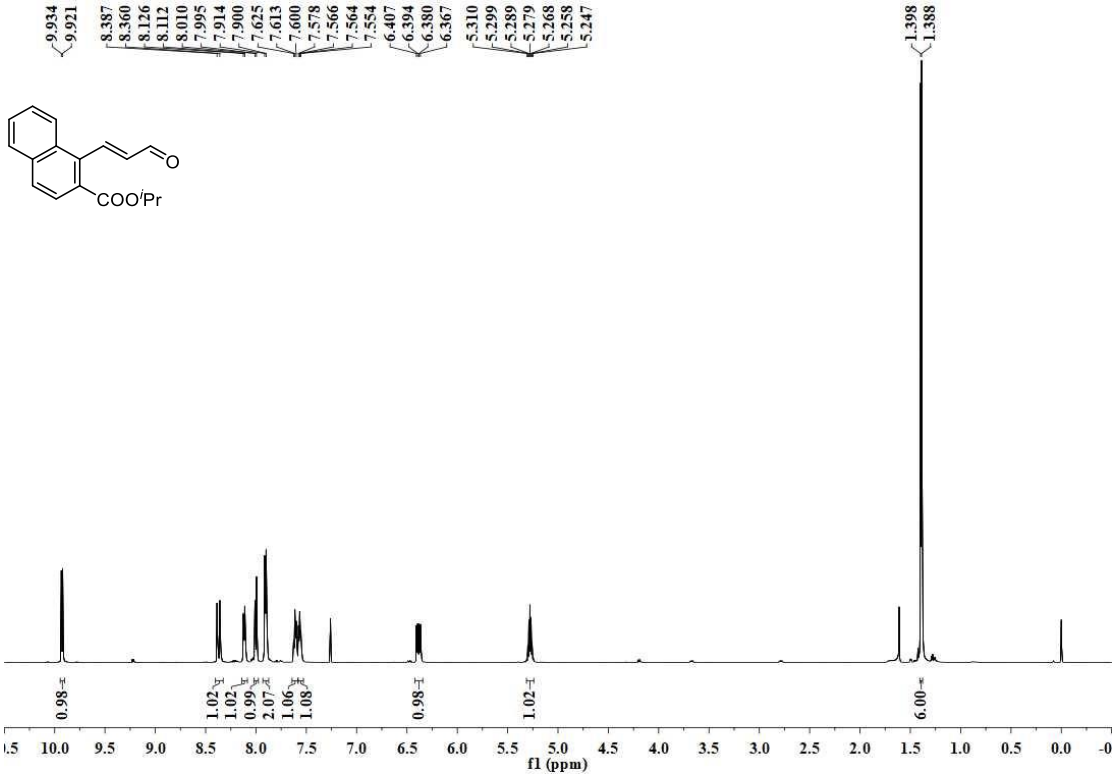
^{1}H NMR Spectrum of S107 (600 MHz, $CDCl_3$)



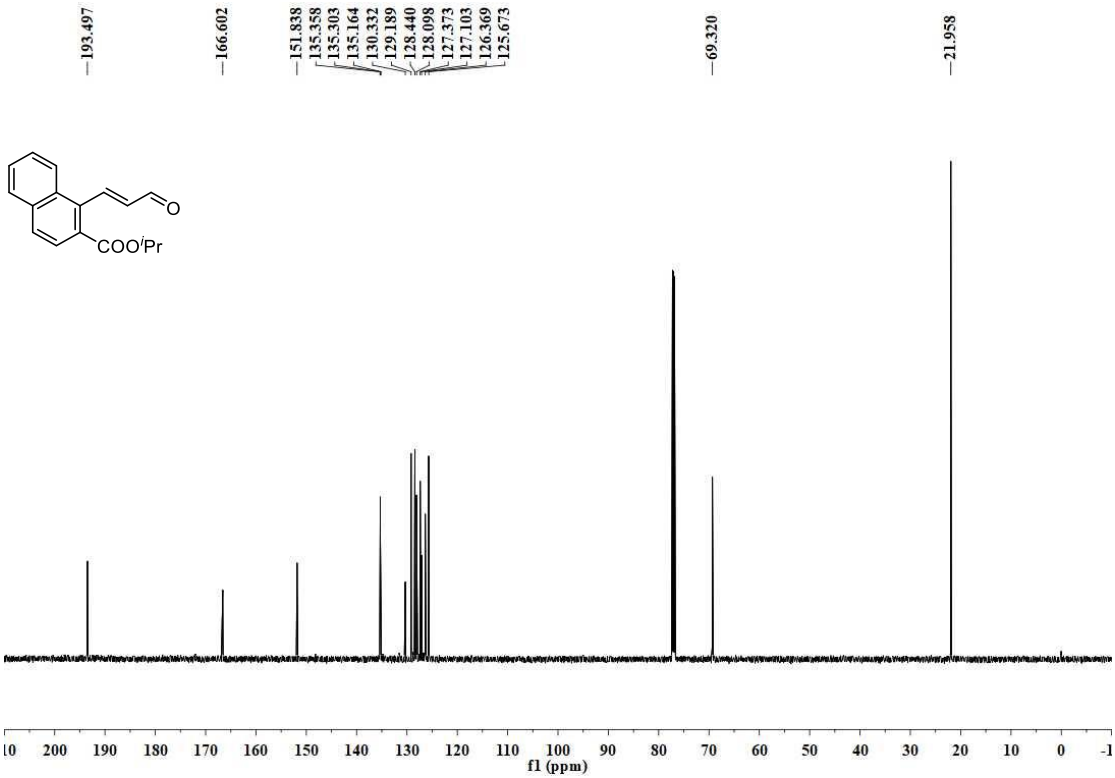
^{13}C NMR Spectrum of S107 (151 MHz, $CDCl_3$)



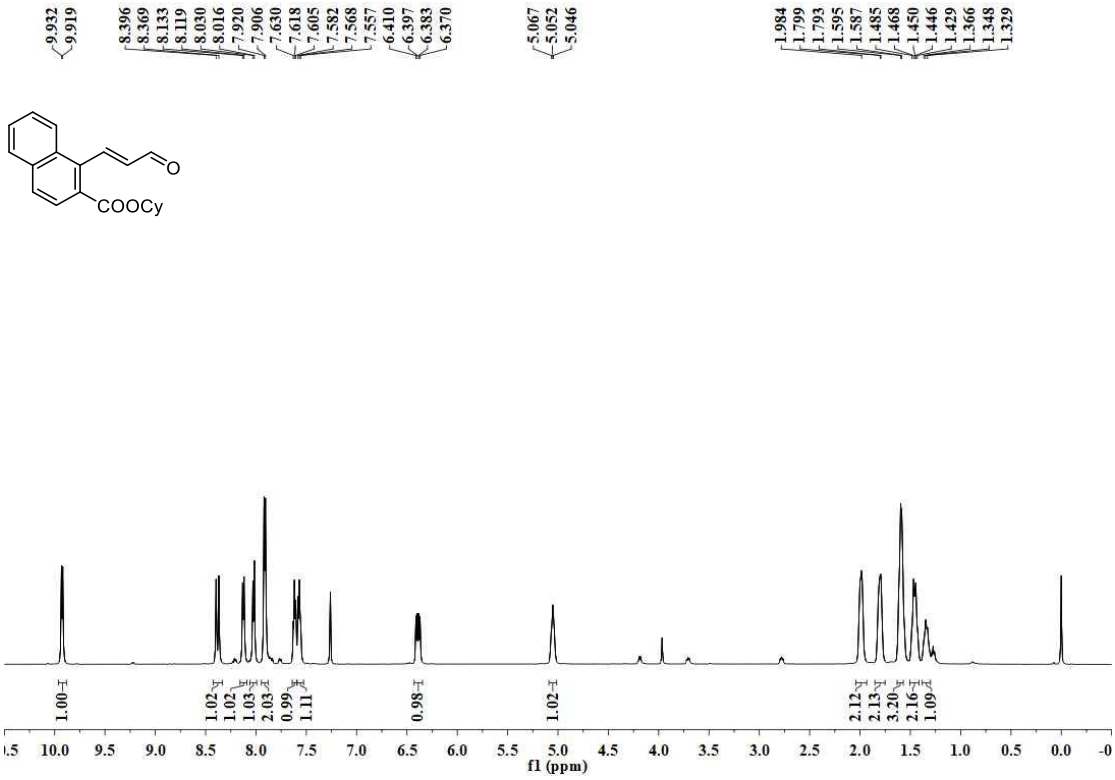
^{1}H NMR Spectrum of S108 (600 MHz, $CDCl_3$)



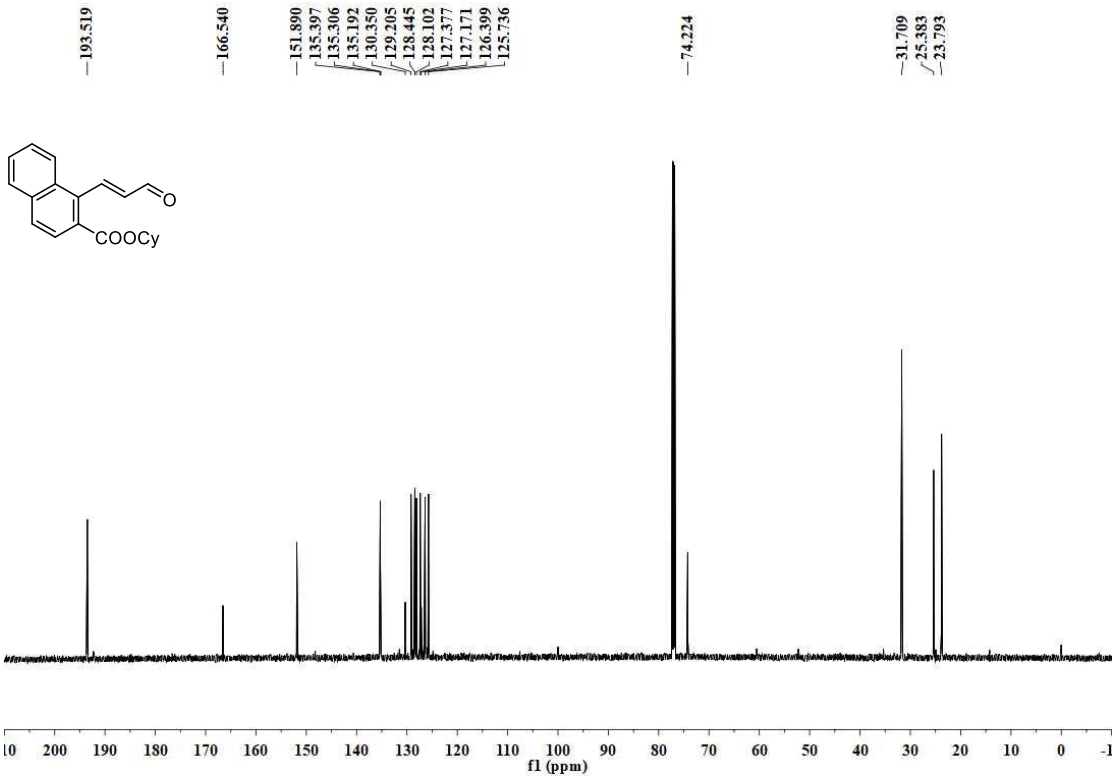
^{13}C NMR Spectrum of S108 (151 MHz, $CDCl_3$)



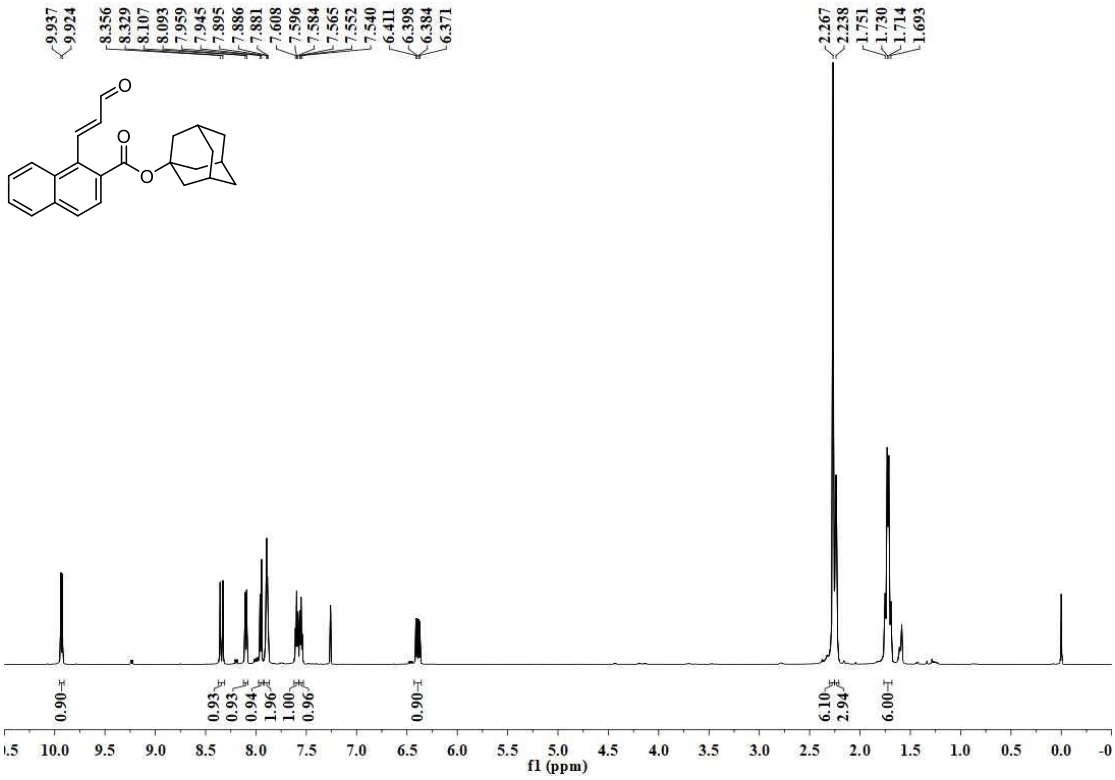
^{1}H NMR Spectrum of S109 (600 MHz, $CDCl_3$)



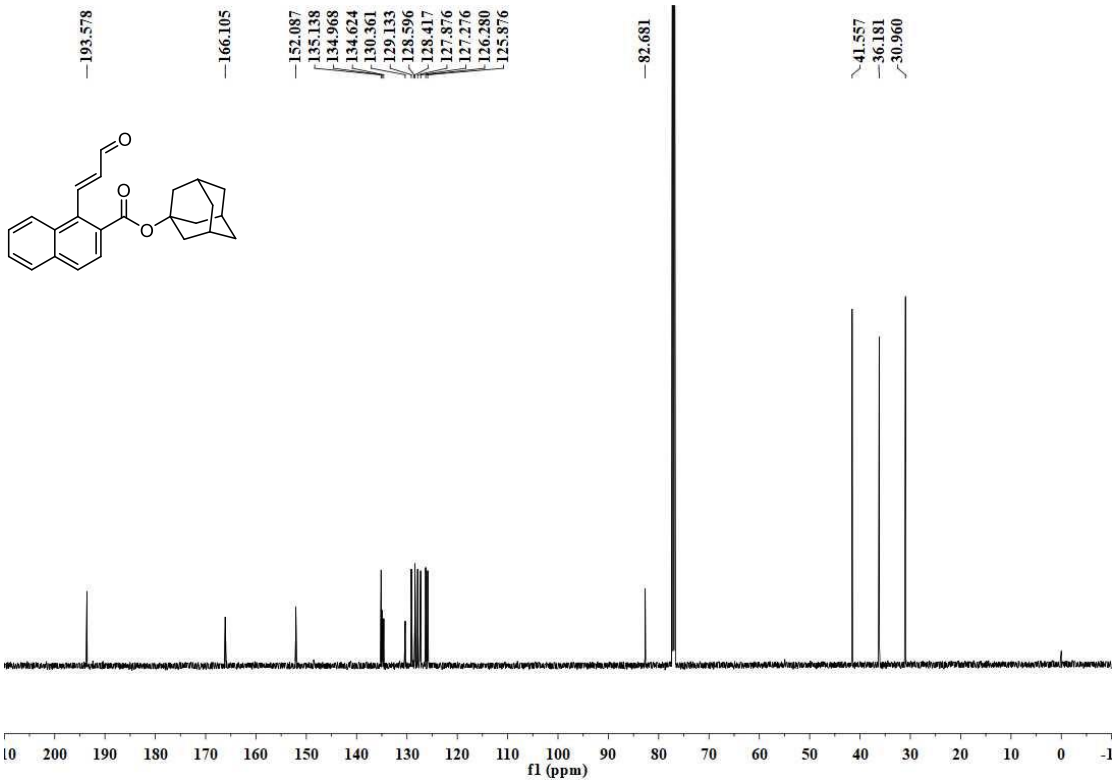
^{13}C NMR Spectrum of S109 (151 MHz, $CDCl_3$)



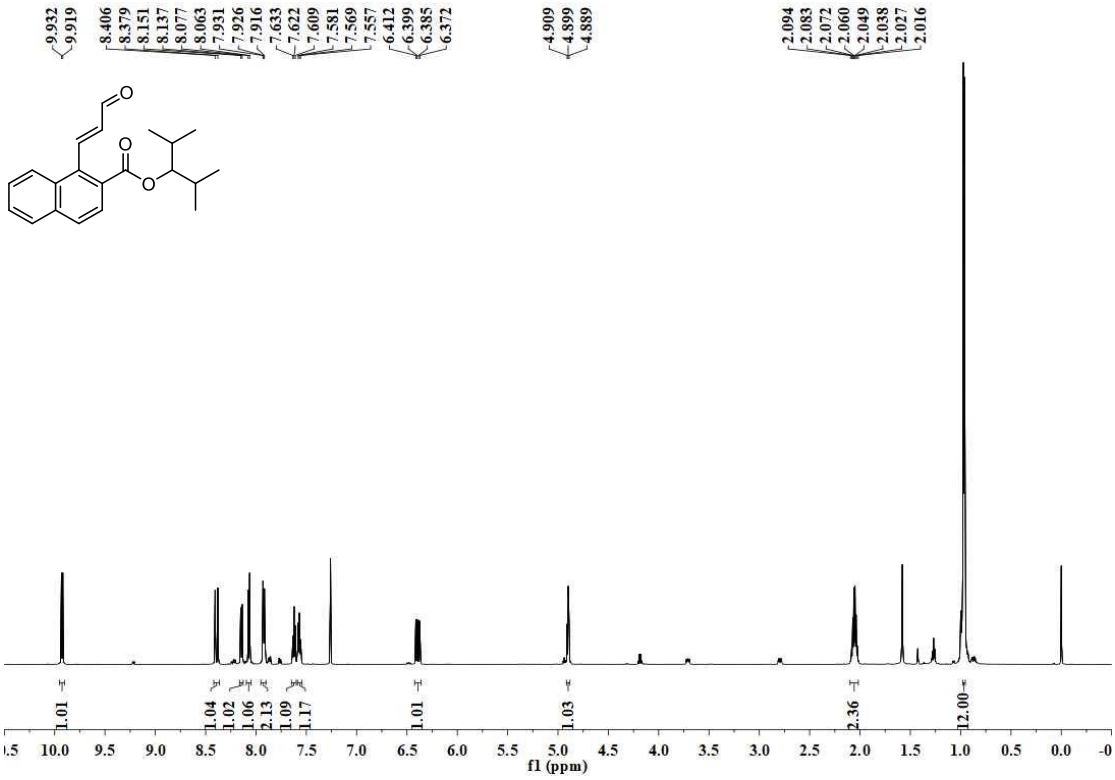
^{1}H NMR Spectrum of S110 (600 MHz, $CDCl_3$)



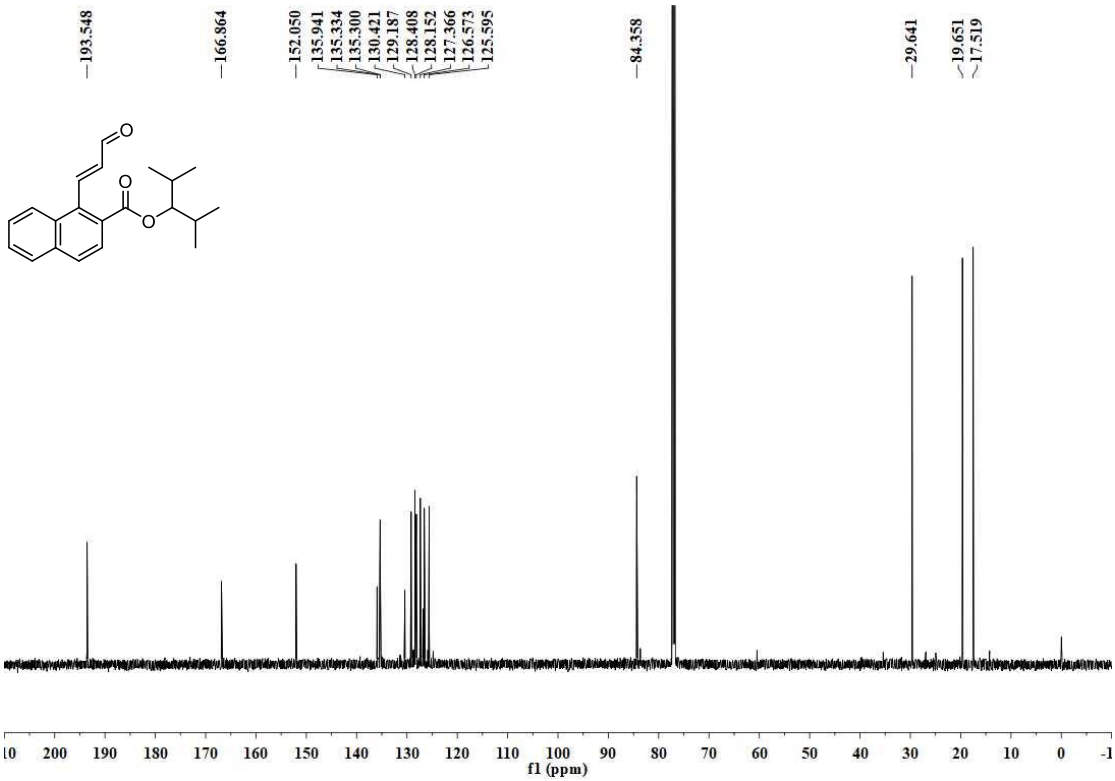
^{13}C NMR Spectrum of S110 (151 MHz, $CDCl_3$)



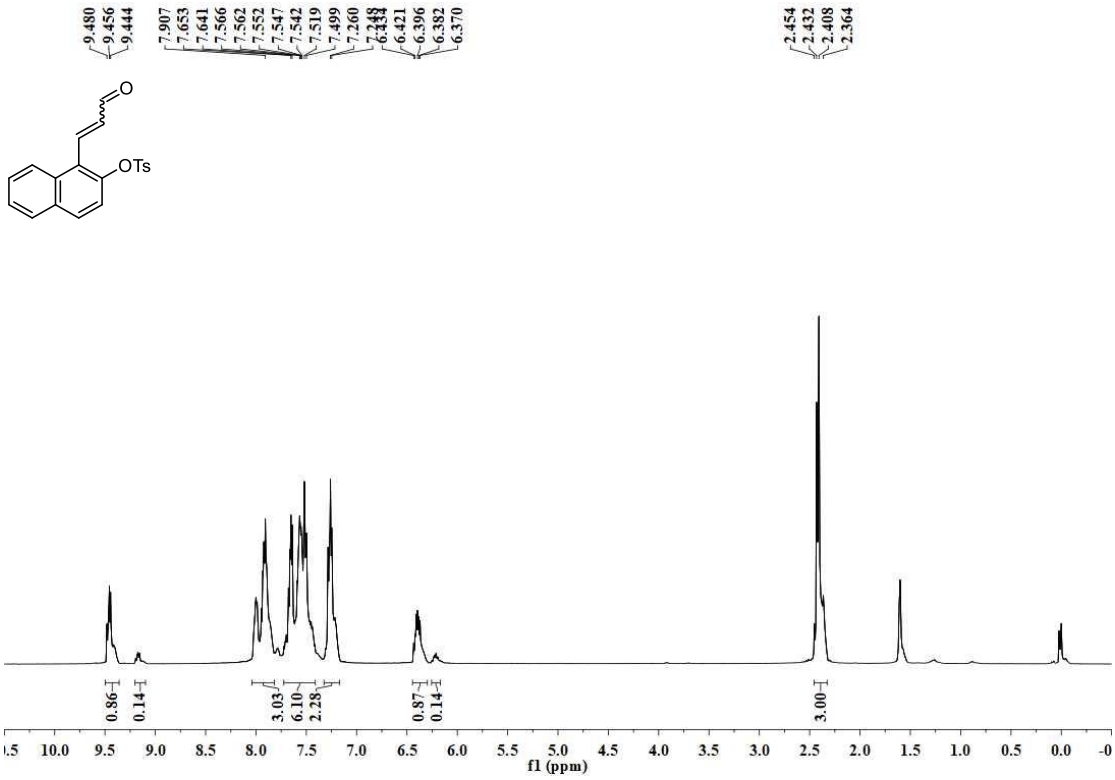
^{1}H NMR Spectrum of S111 (600 MHz, $CDCl_3$)



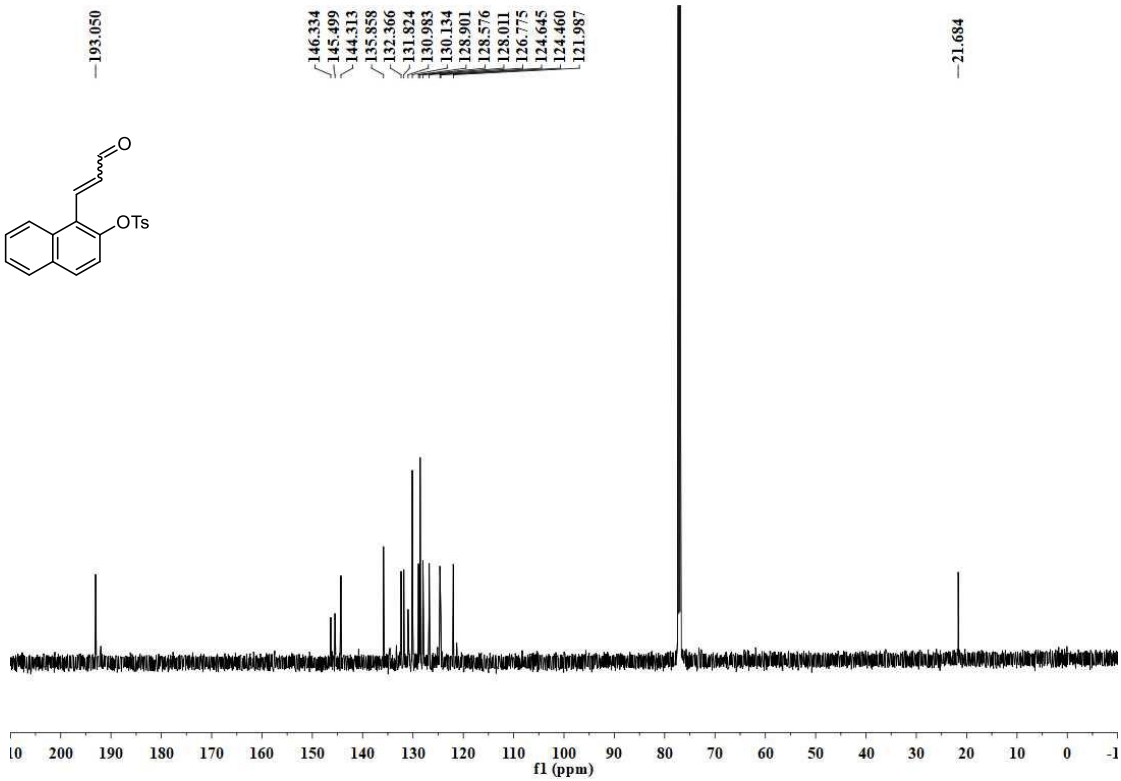
^{13}C NMR Spectrum of S111 (151 MHz, $CDCl_3$)



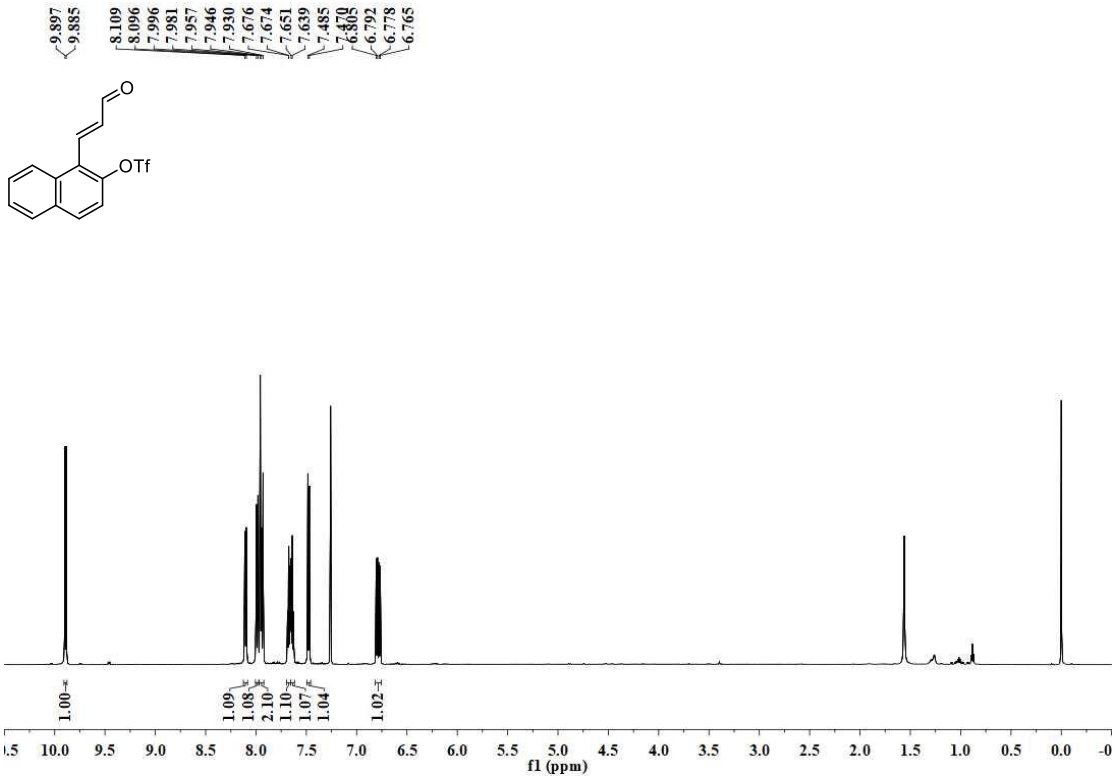
^{1}H NMR Spectrum of S112 (600 MHz, $CDCl_3$)



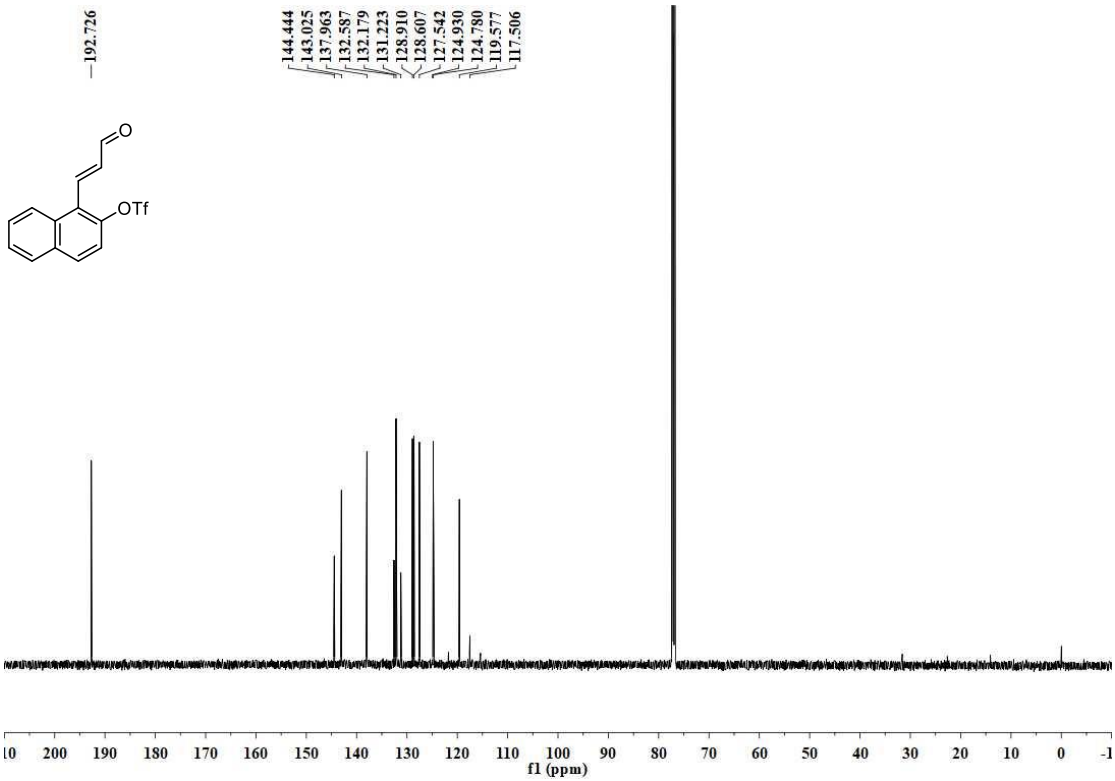
^{13}C NMR Spectrum of S112 (151 MHz, $CDCl_3$)



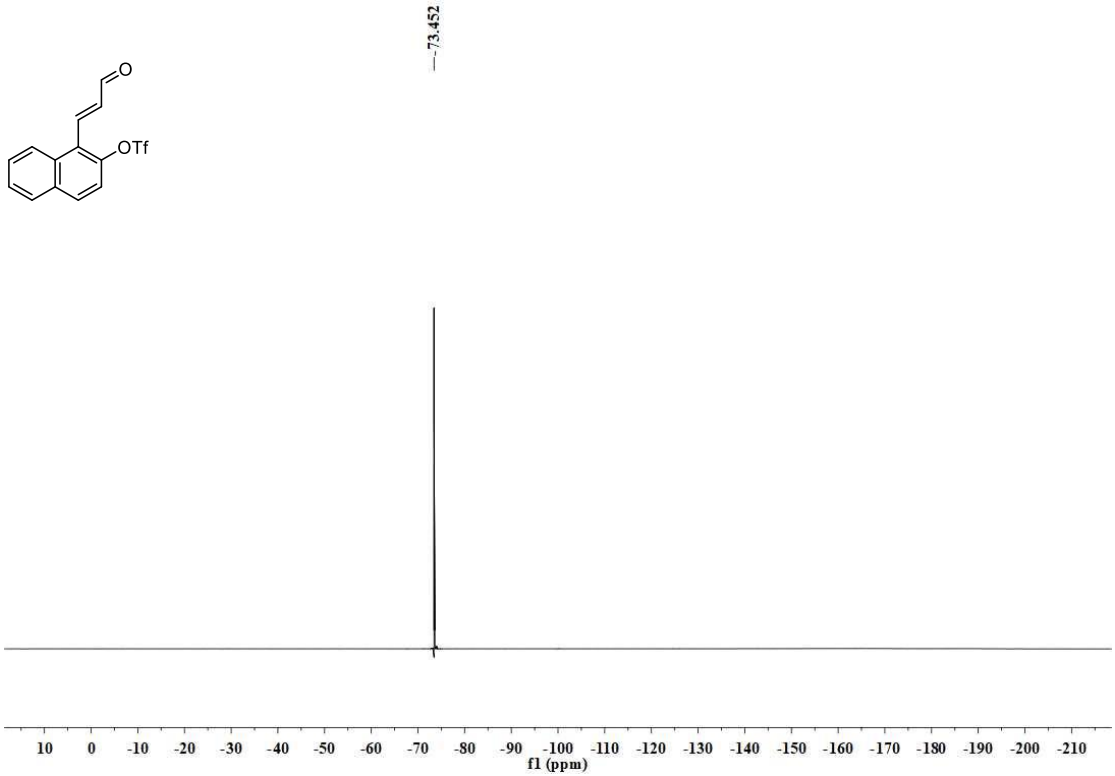
^{1}H NMR Spectrum of S113 (600 MHz, $CDCl_3$)



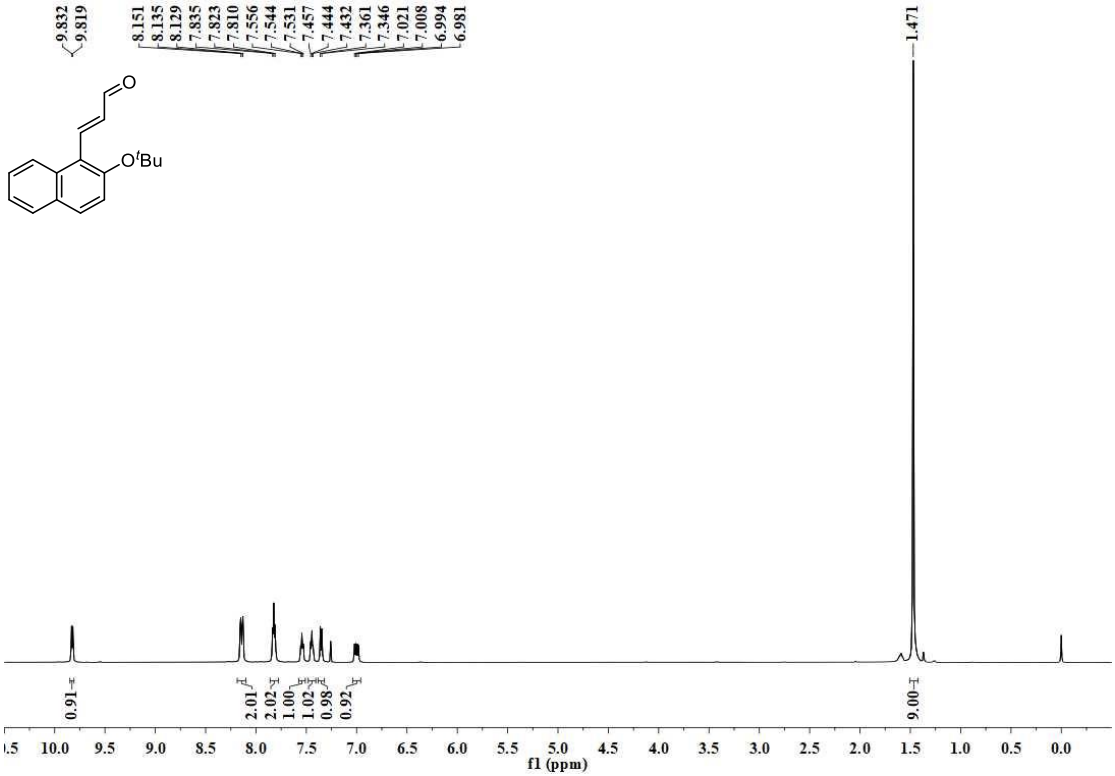
^{13}C NMR Spectrum of S112 (151 MHz, $CDCl_3$)



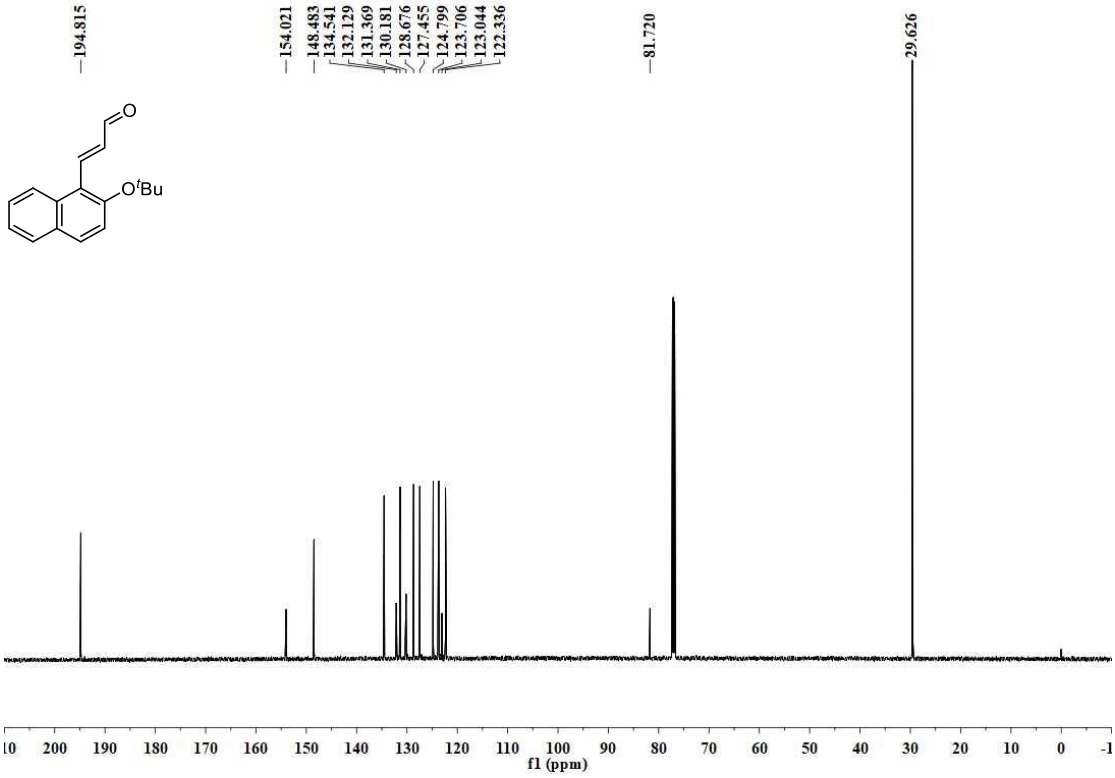
^{19}F NMR Spectrum of S113 (565 MHz, $CDCl_3$)



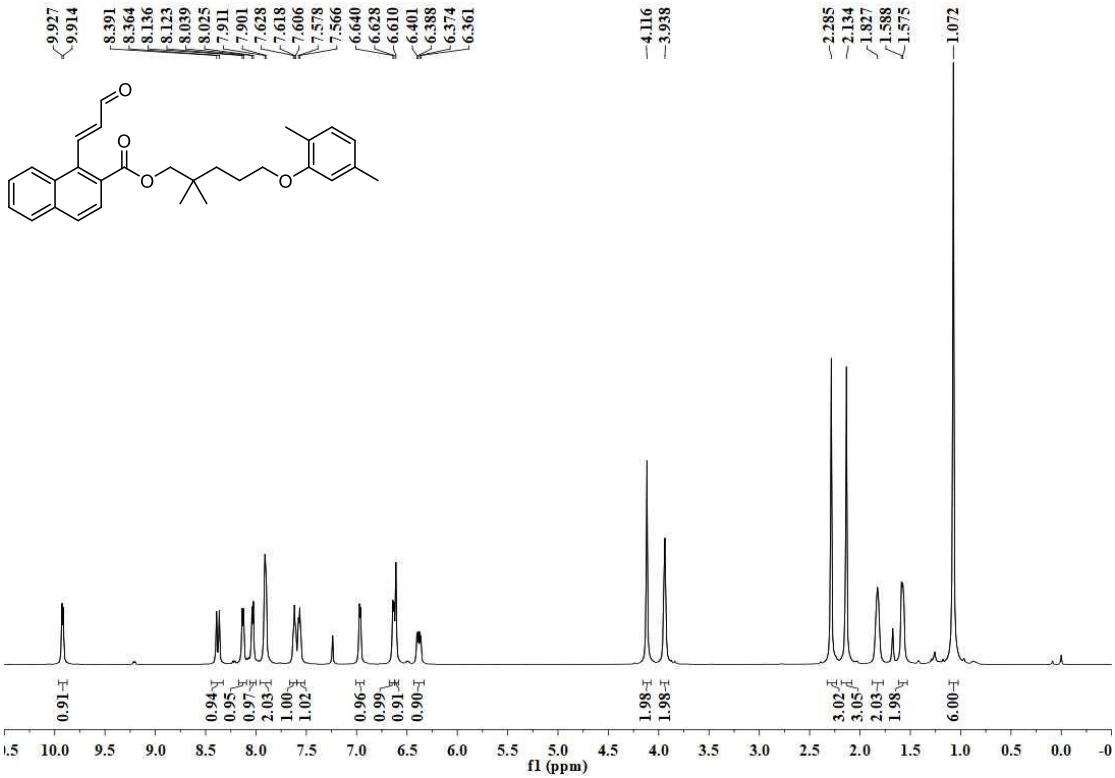
^{1}H NMR Spectrum of S114 (600 MHz, $CDCl_3$)



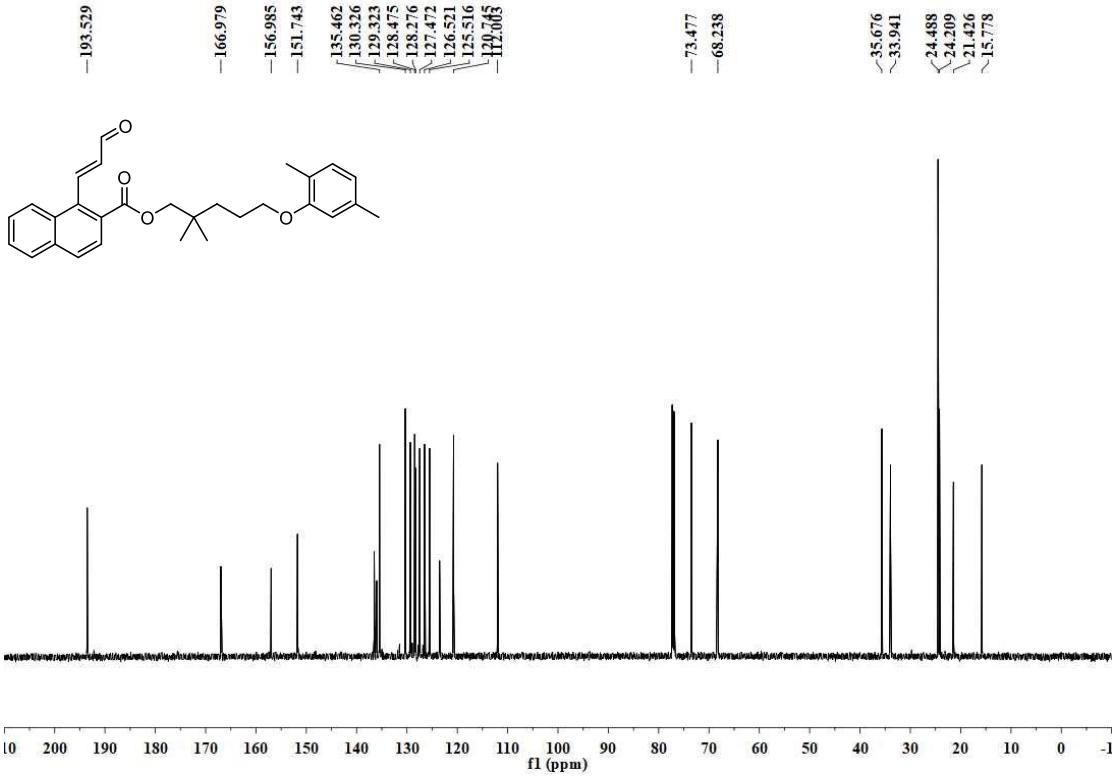
^{13}C NMR Spectrum of S114 (151 MHz, $CDCl_3$)



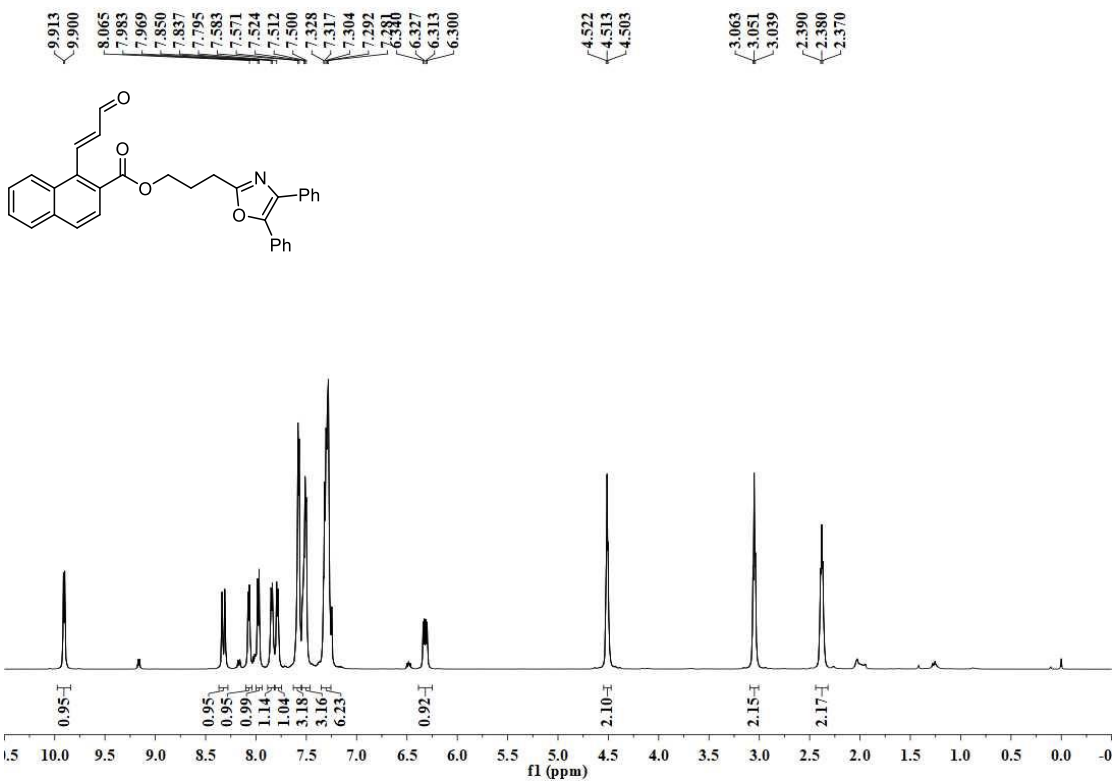
^{1}H NMR Spectrum of S115 (600 MHz, $CDCl_3$)



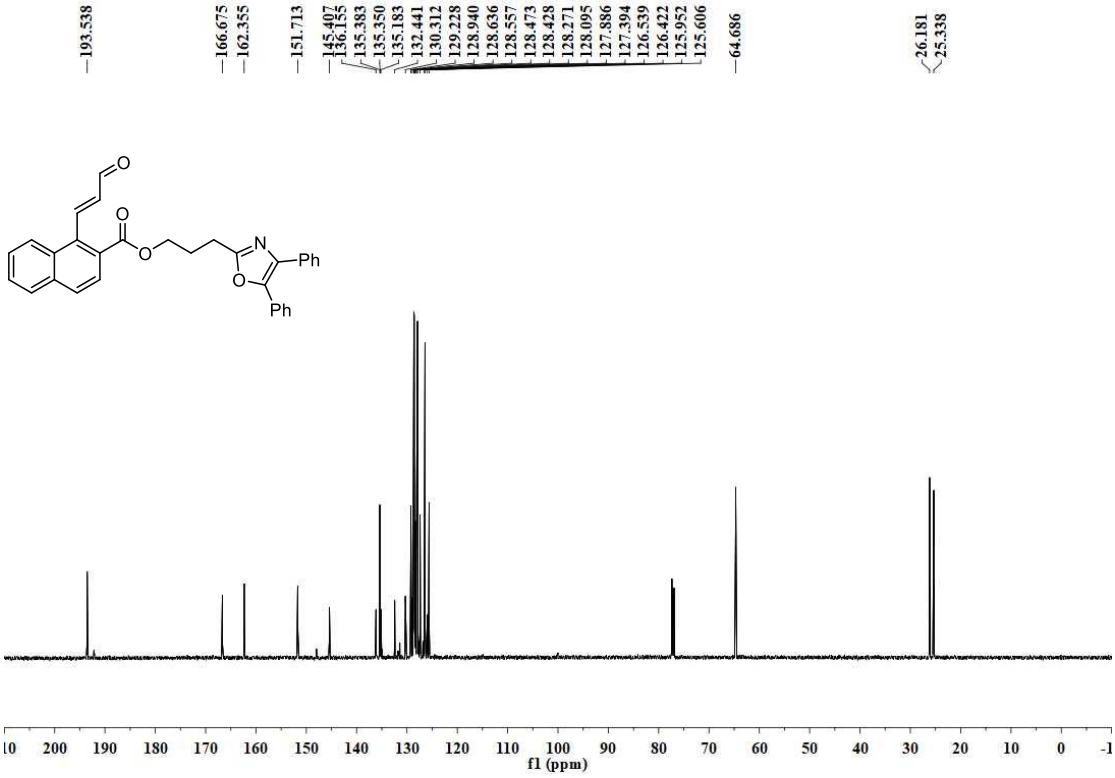
^{13}C NMR Spectrum of S115 (151 MHz, $CDCl_3$)



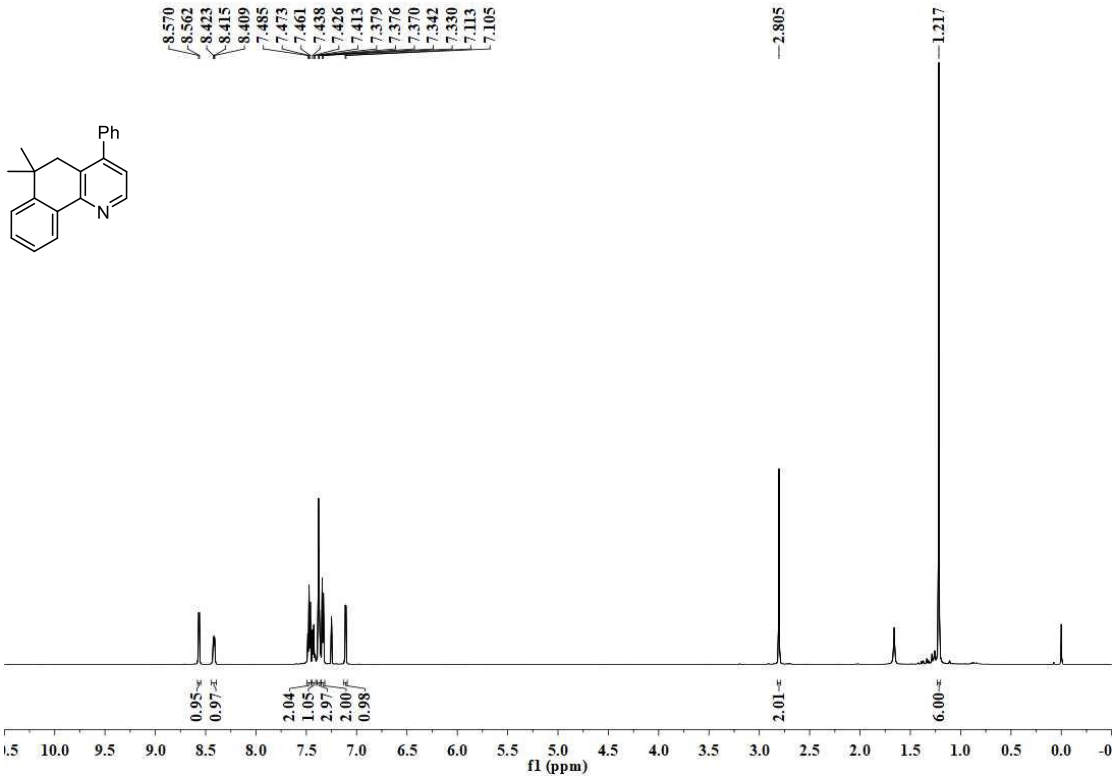
^{1}H NMR Spectrum of S116 (600 MHz, $CDCl_3$)



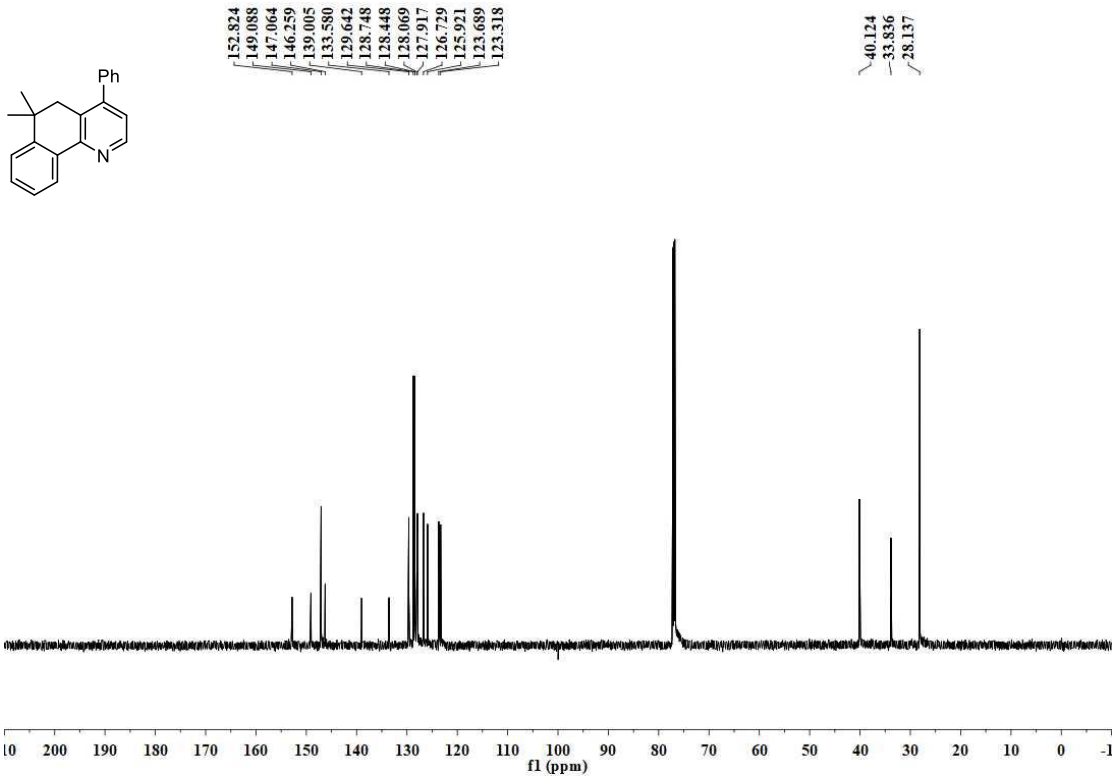
^{13}C NMR Spectrum of S116 (151 MHz, $CDCl_3$)



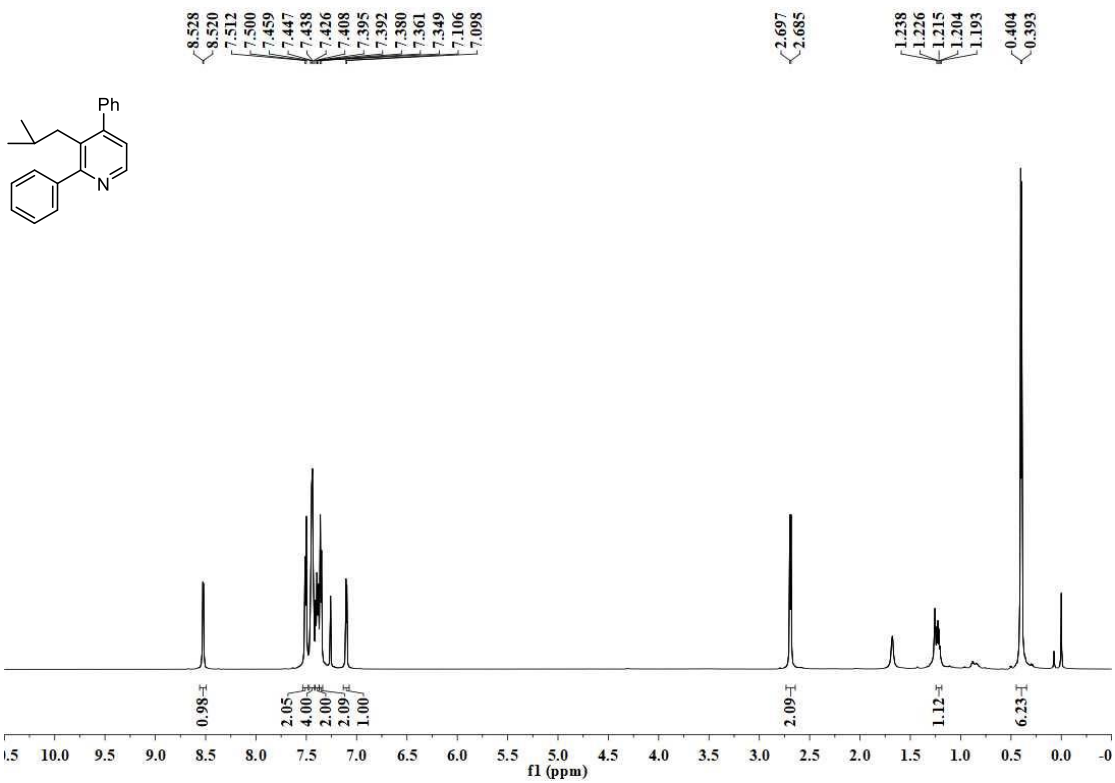
^{1}H NMR Spectrum of 3 (600 MHz, $CDCl_3$)



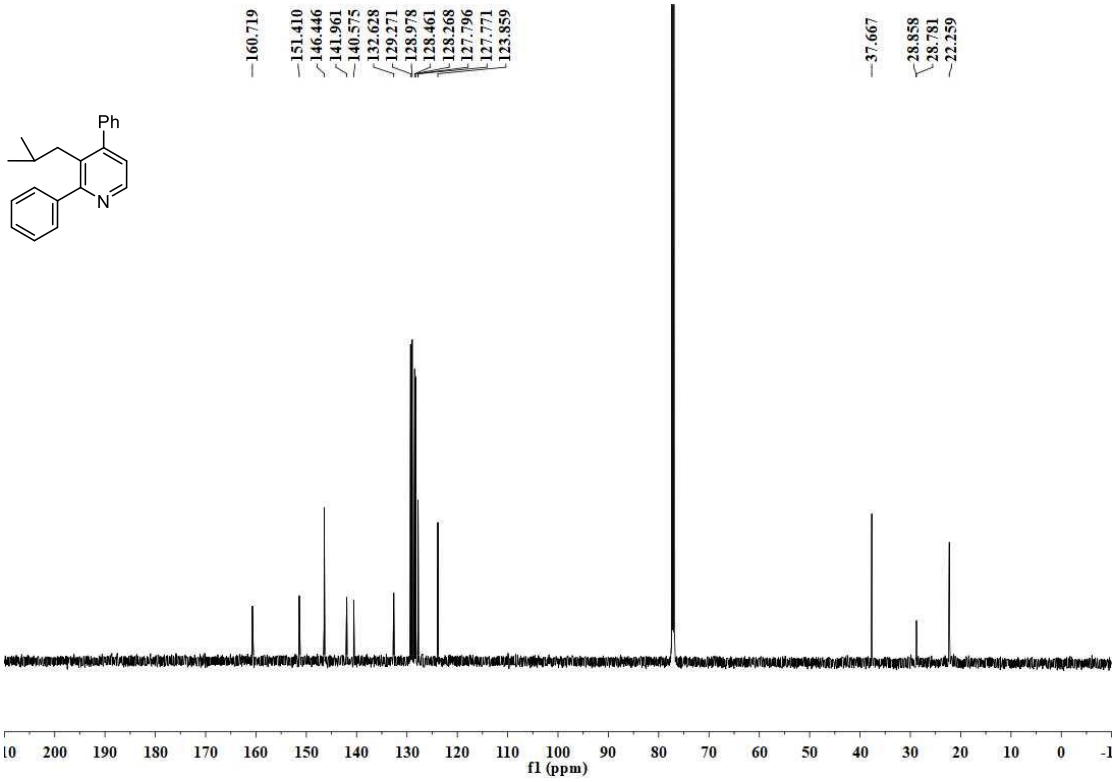
^{13}C NMR Spectrum of 3 (151 MHz, $CDCl_3$)



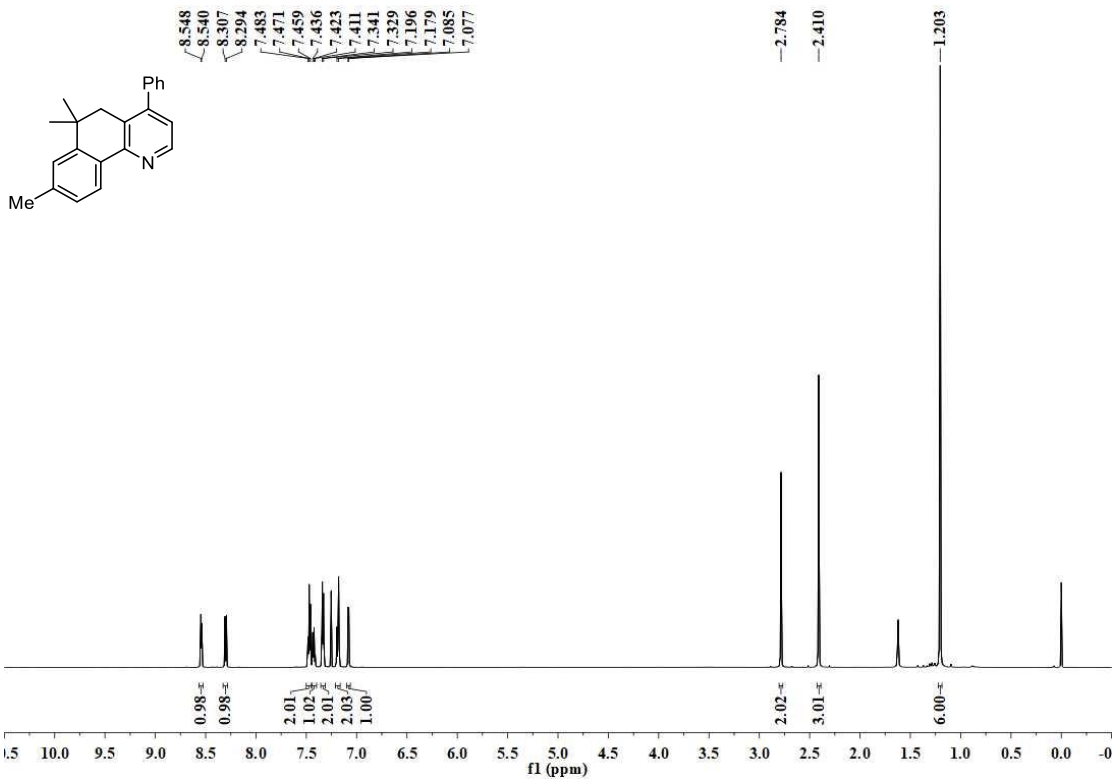
^{1}H NMR Spectrum of 3' (600 MHz, $CDCl_3$)



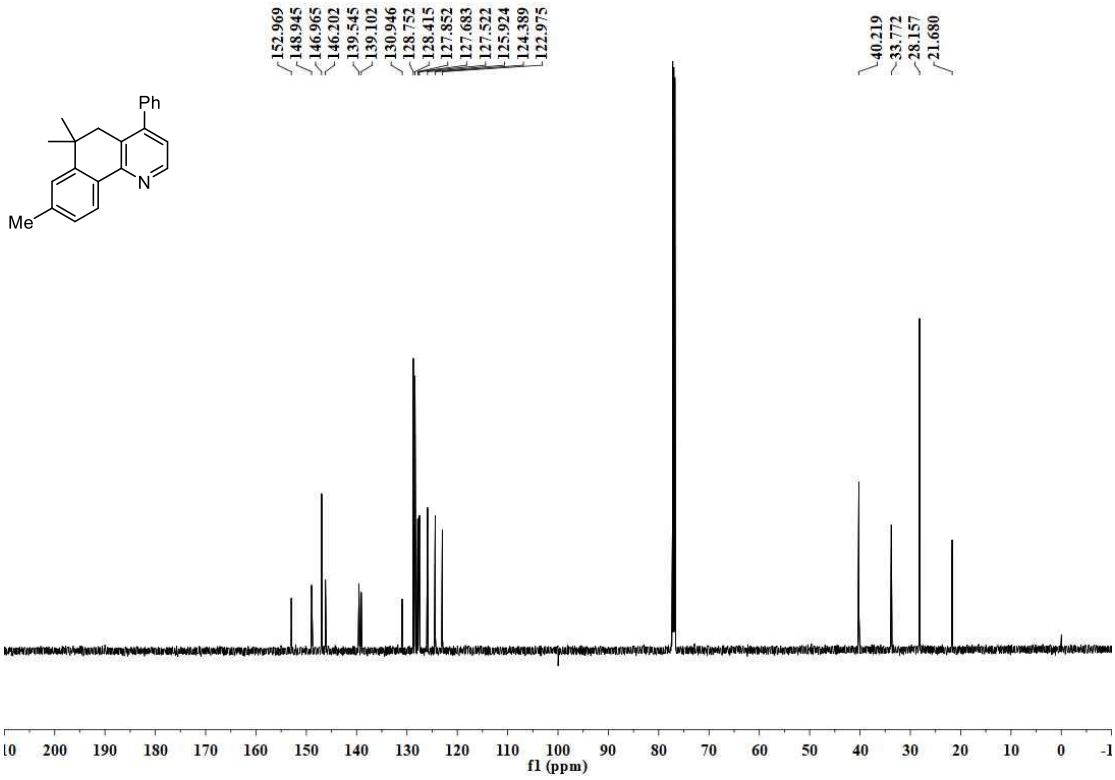
^{13}C NMR Spectrum of 3' (151 MHz, $CDCl_3$)



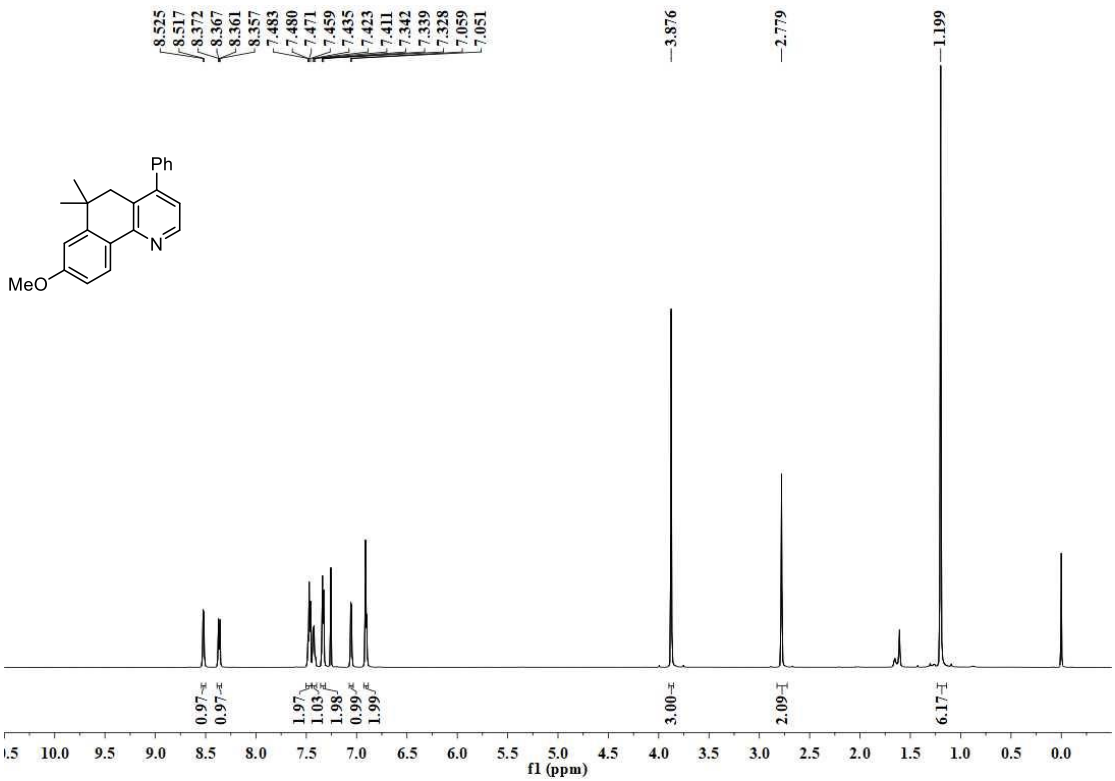
^{1}H NMR Spectrum of 4 (600 MHz, $CDCl_3$)



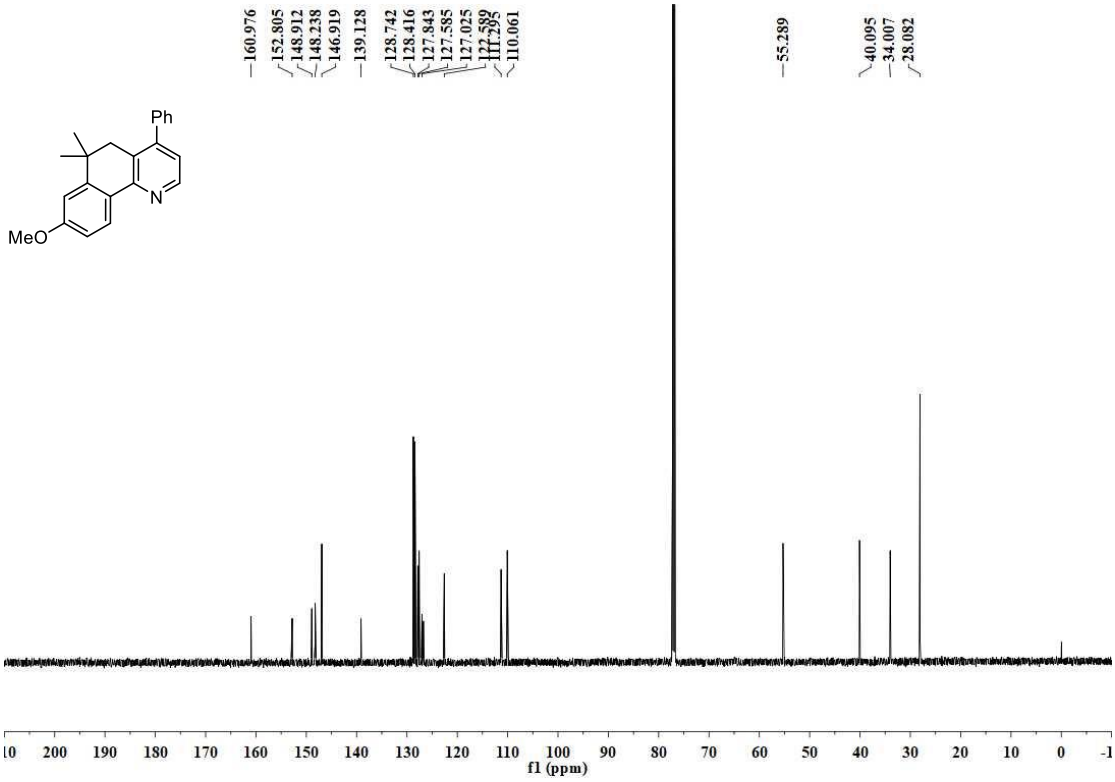
^{13}C NMR Spectrum of 4 (151 MHz, $CDCl_3$)



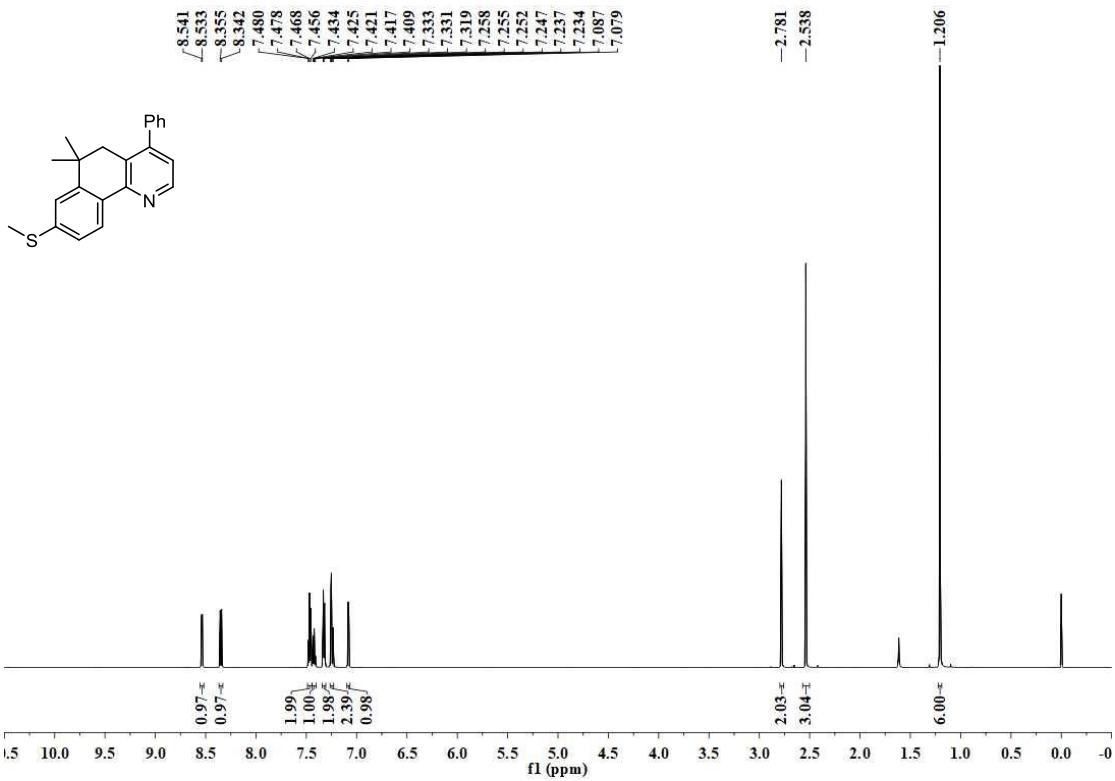
^{1}H NMR Spectrum of 5 (600 MHz, $CDCl_3$)



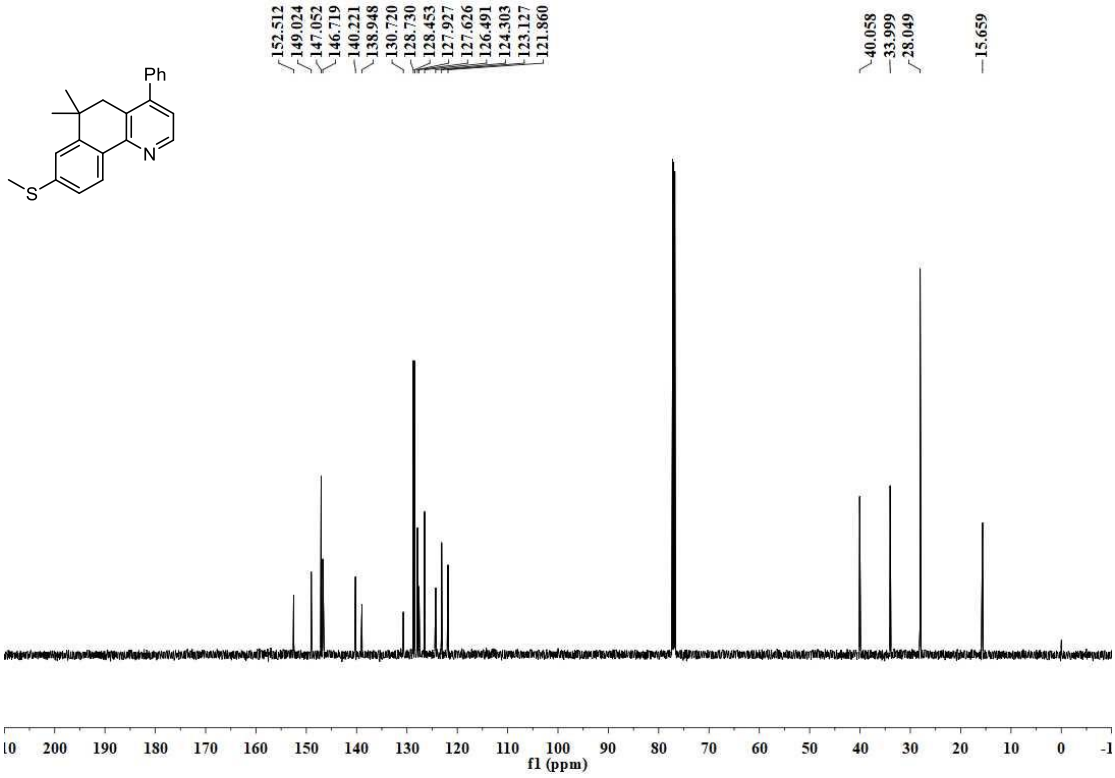
^{13}C NMR Spectrum of 5 (151 MHz, $CDCl_3$)



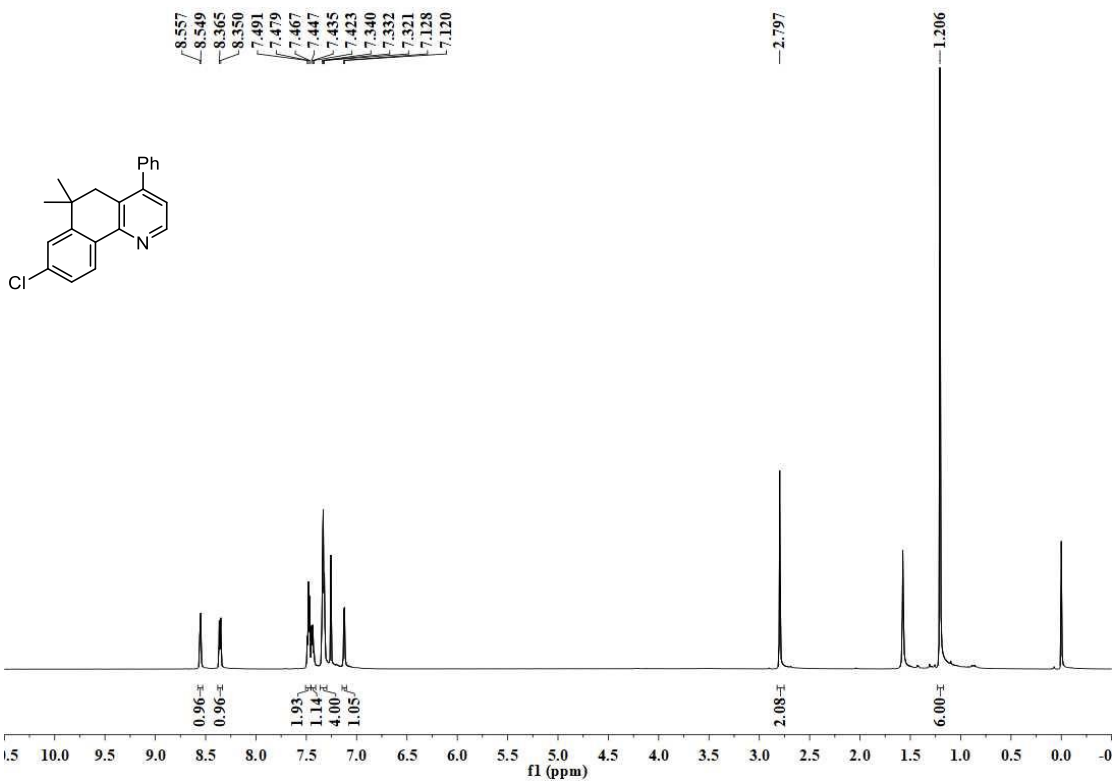
^{1}H NMR Spectrum of 6 (600 MHz, $CDCl_3$)



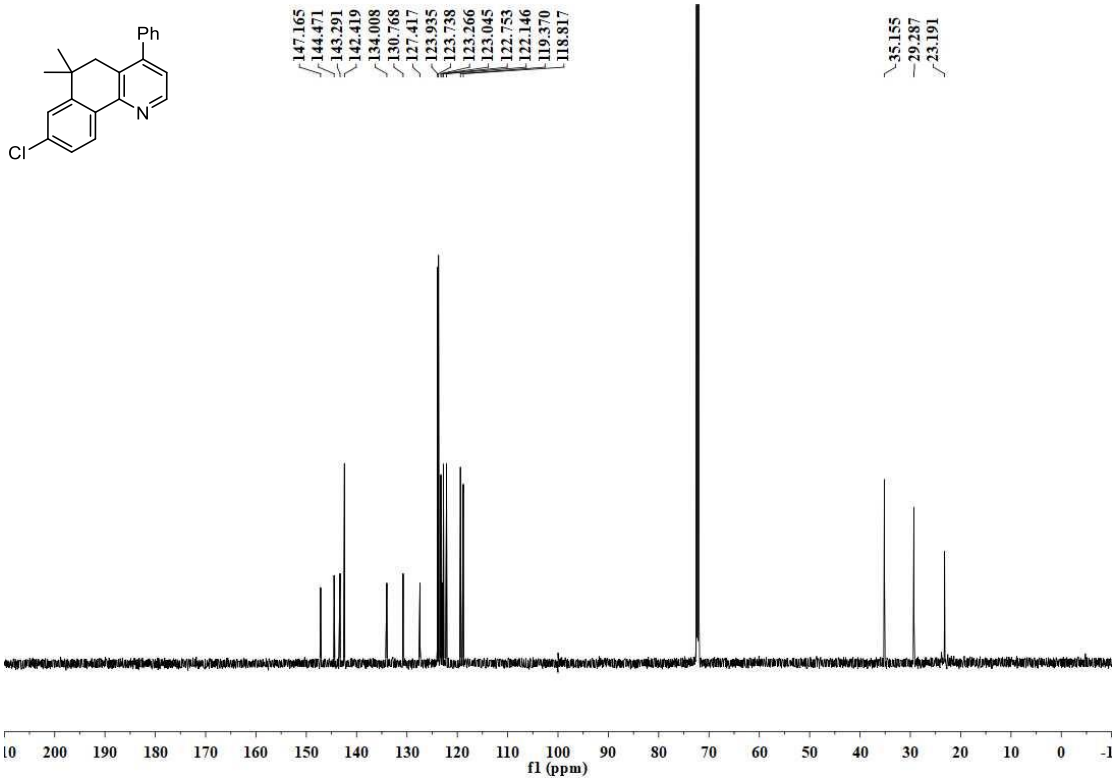
^{13}C NMR Spectrum of 6 (151 MHz, $CDCl_3$)



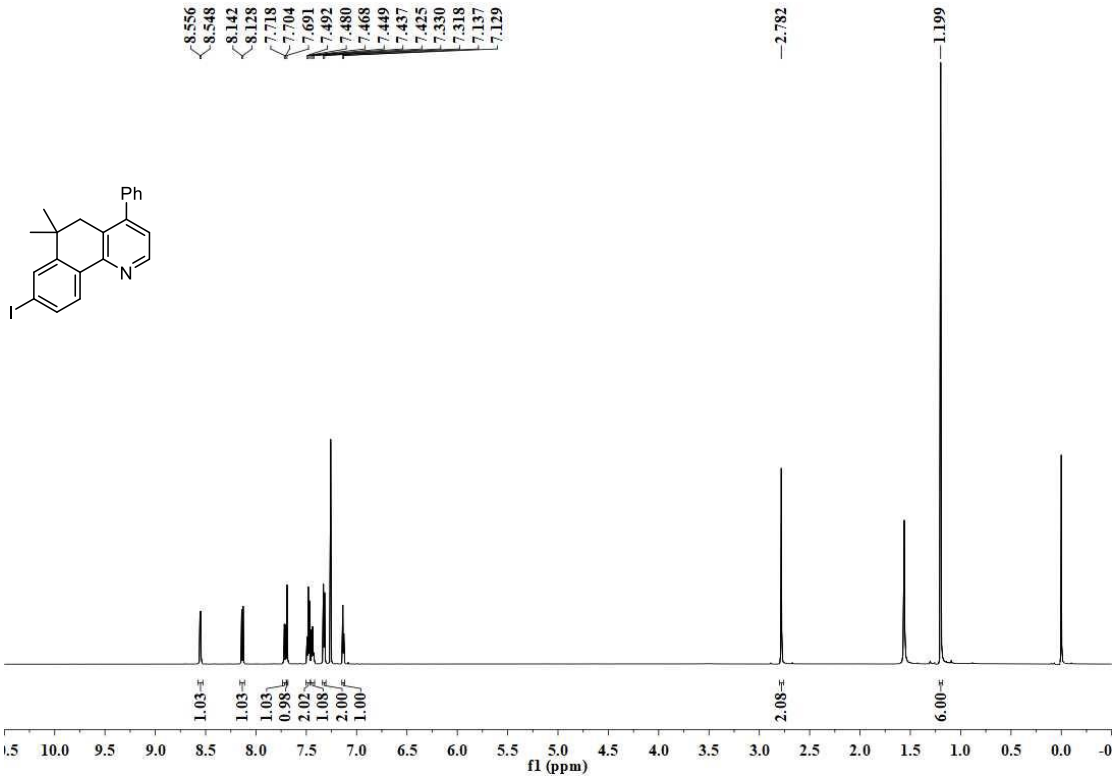
^{1}H NMR Spectrum of 7 (600 MHz, $CDCl_3$)



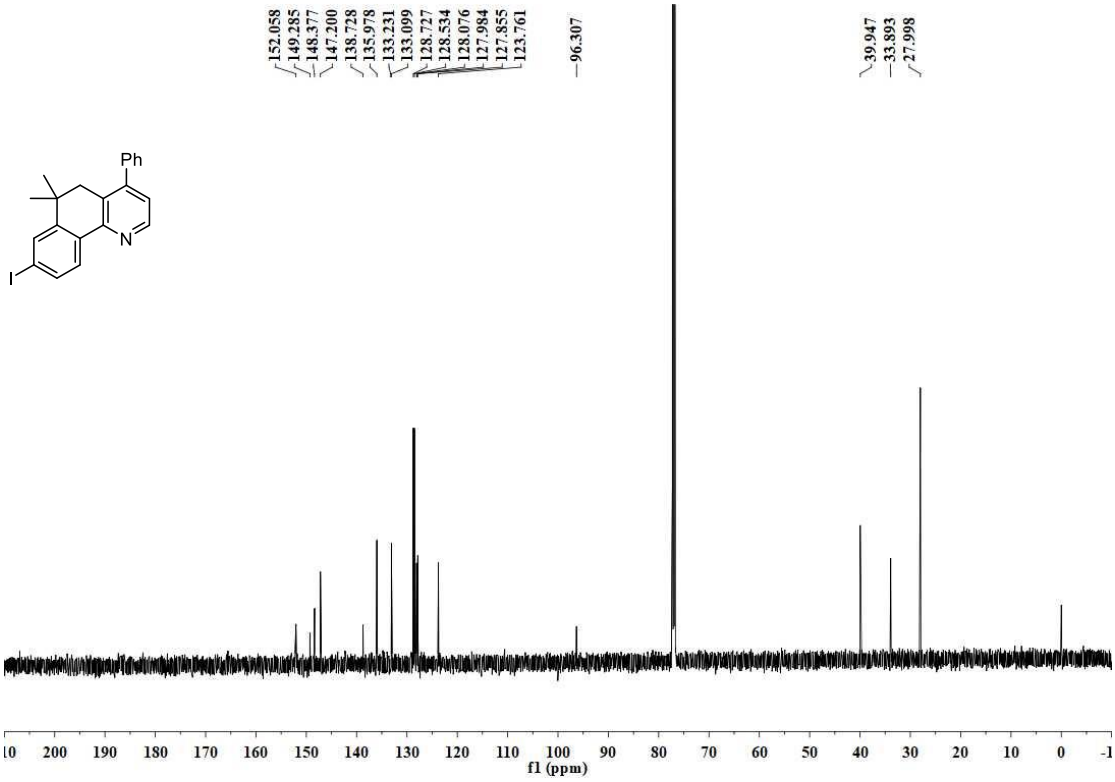
^{13}C NMR Spectrum of 7 (151 MHz, $CDCl_3$)



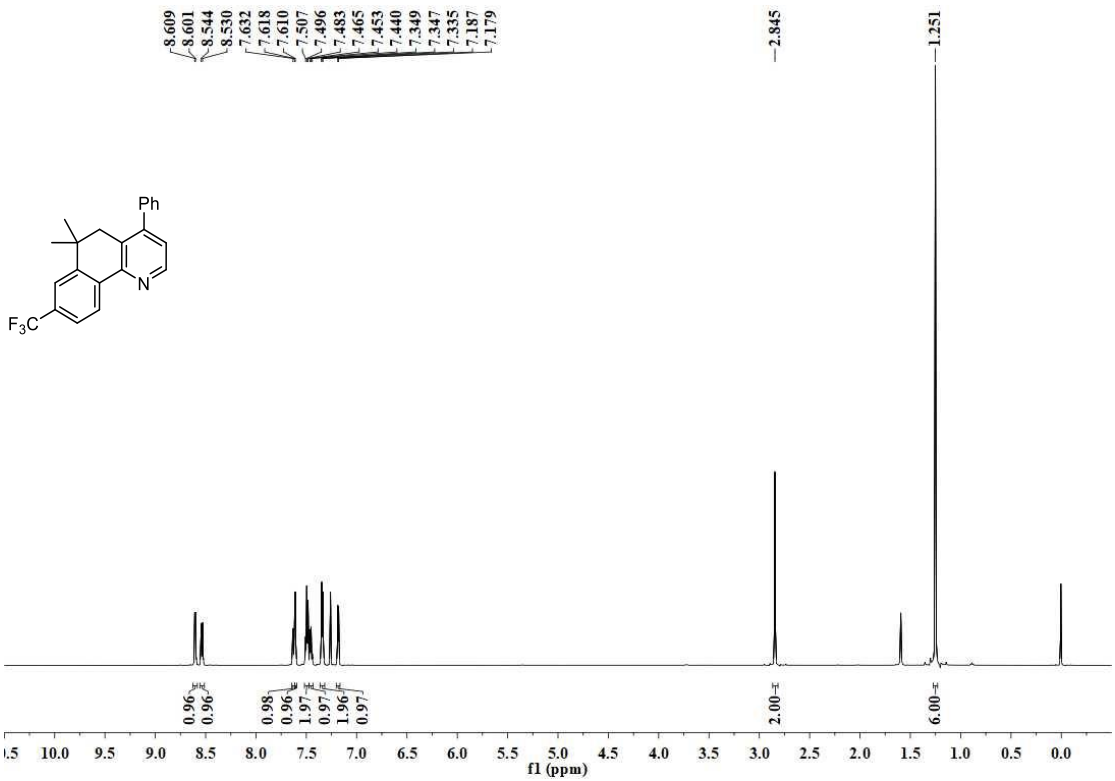
^{1}H NMR Spectrum of 8 (600 MHz, $CDCl_3$)



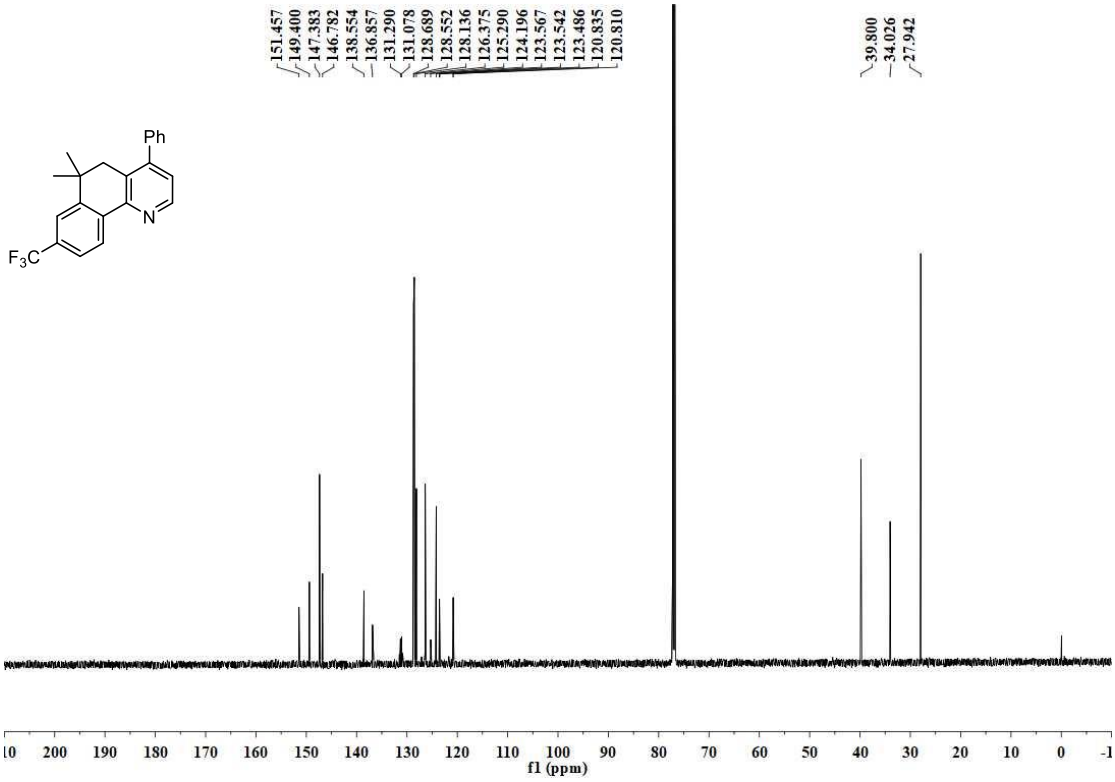
^{13}C NMR Spectrum of 8 (151 MHz, $CDCl_3$)



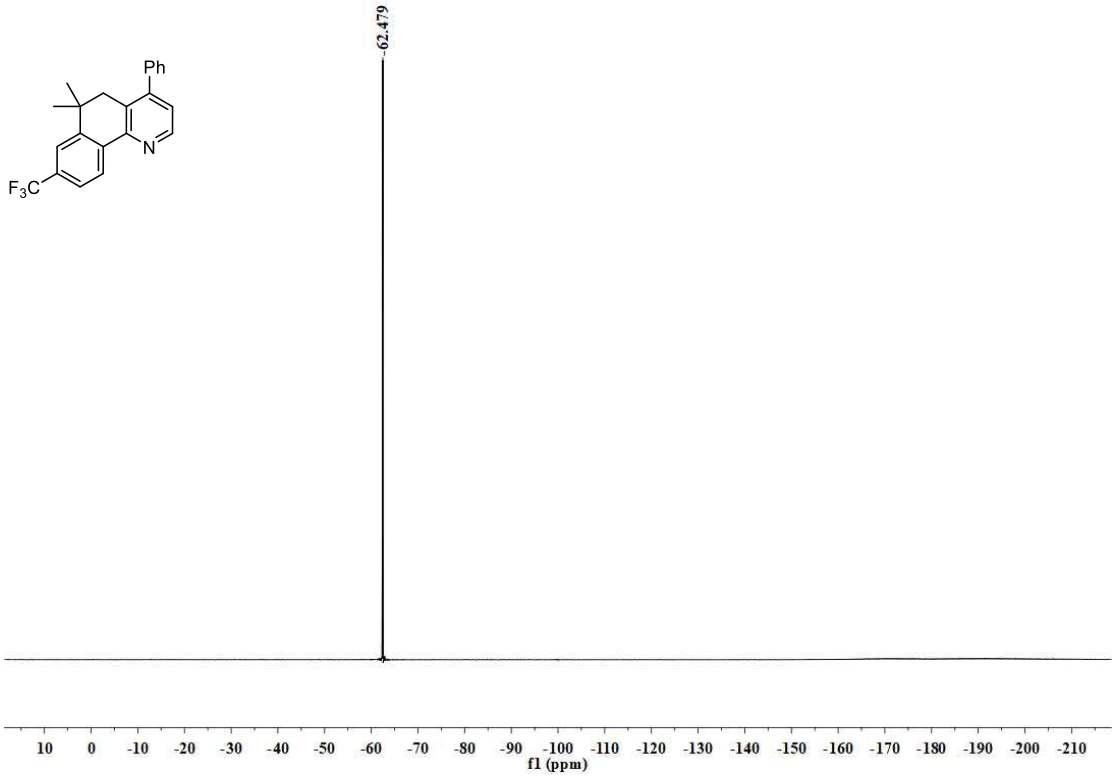
^{1}H NMR Spectrum of 9 (600 MHz, $CDCl_3$)



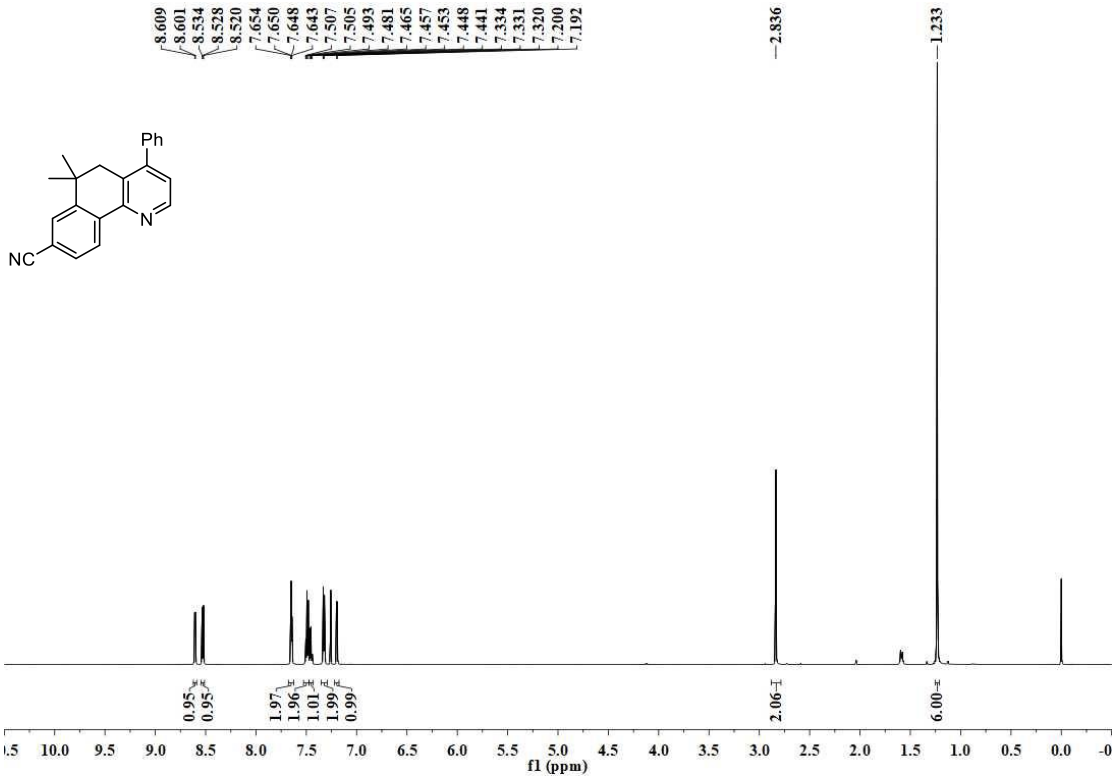
^{13}C NMR Spectrum of 9 (151 MHz, $CDCl_3$)



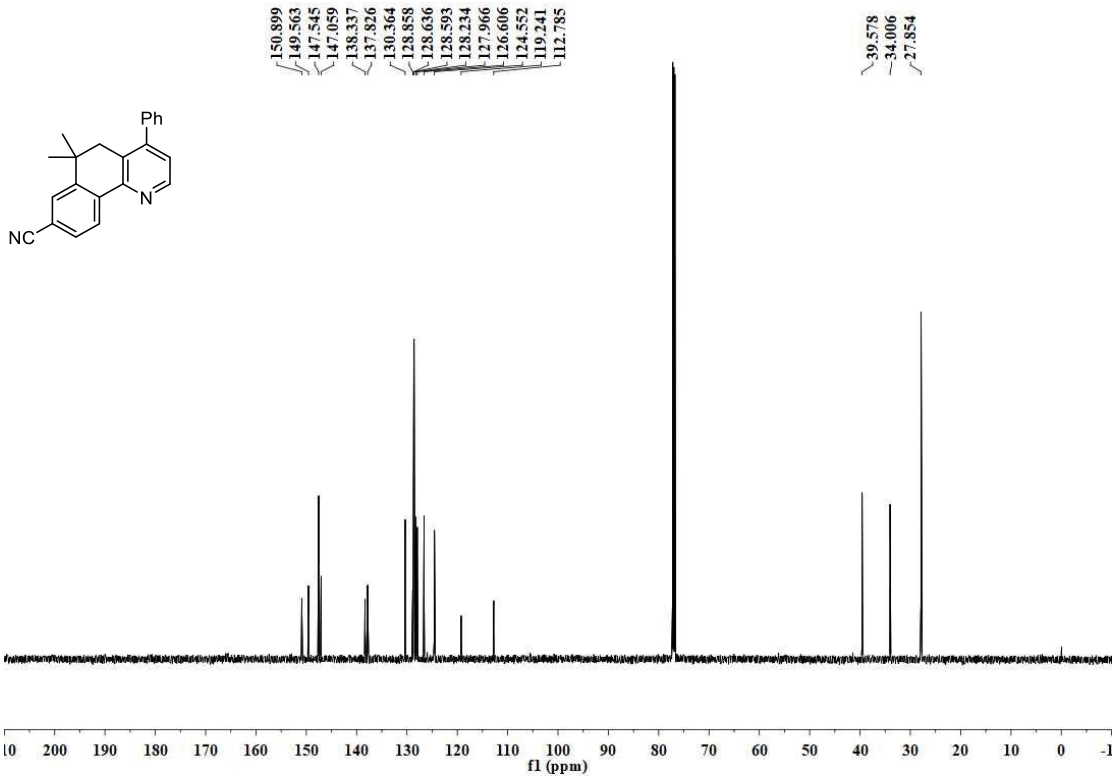
^{19}F NMR Spectrum of 9 (565 MHz, $CDCl_3$)



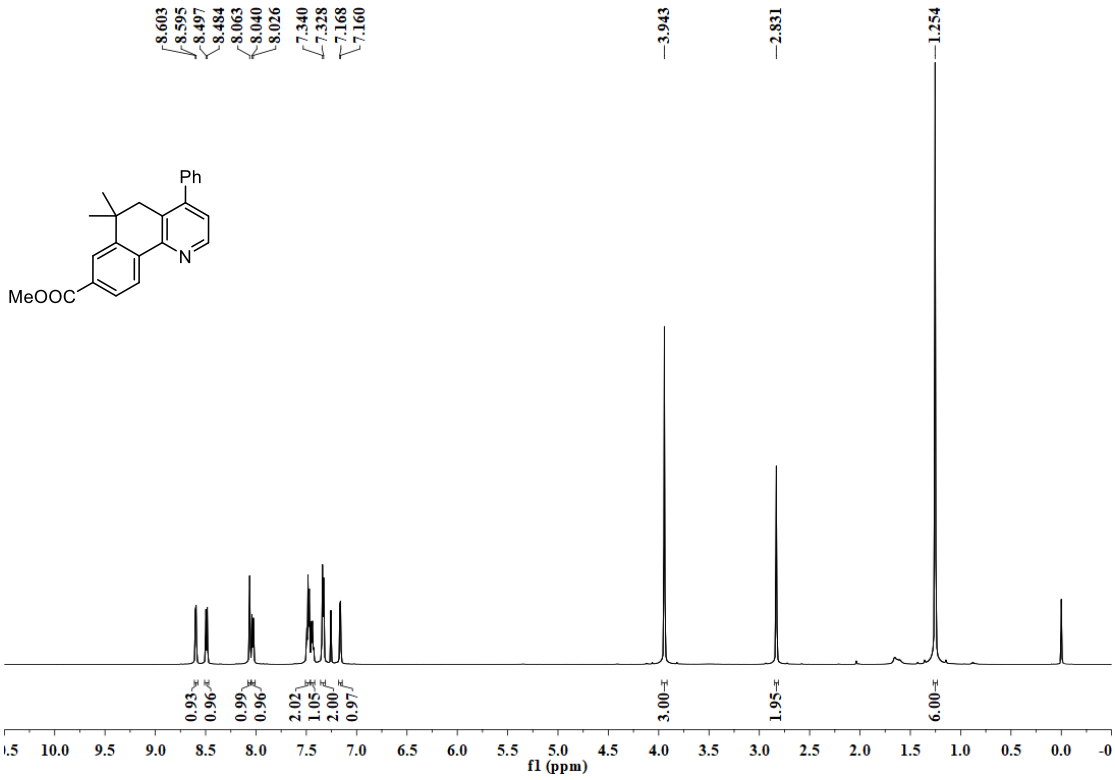
^{1}H NMR Spectrum of 10 (600 MHz, $CDCl_3$)



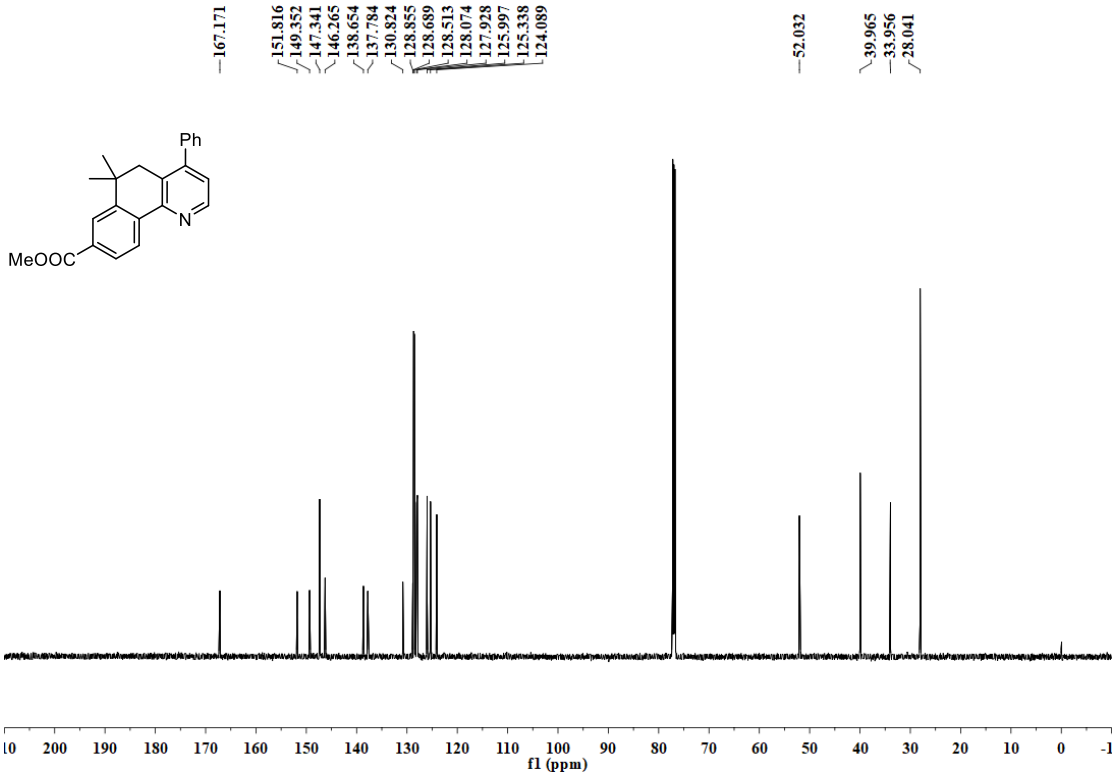
^{13}C NMR Spectrum of 10 (151 MHz, $CDCl_3$)



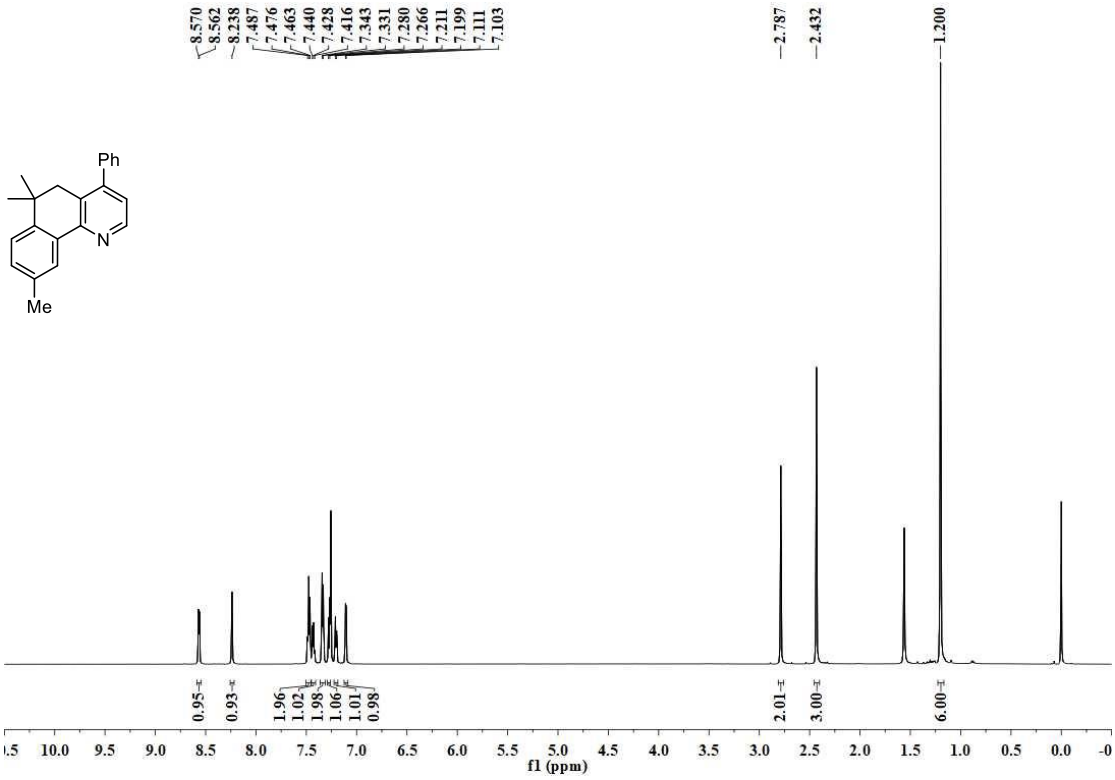
^{1}H NMR Spectrum of 11 (600 MHz, $CDCl_3$)



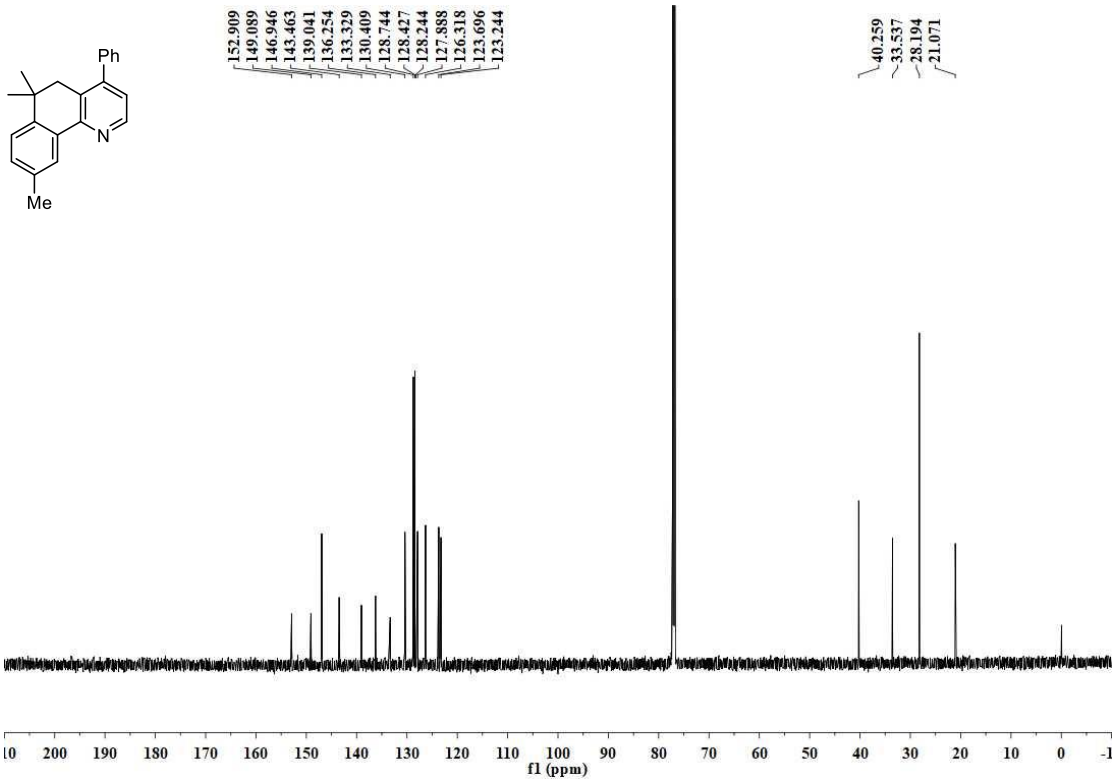
^{13}C NMR Spectrum of 11 (151 MHz, $CDCl_3$)



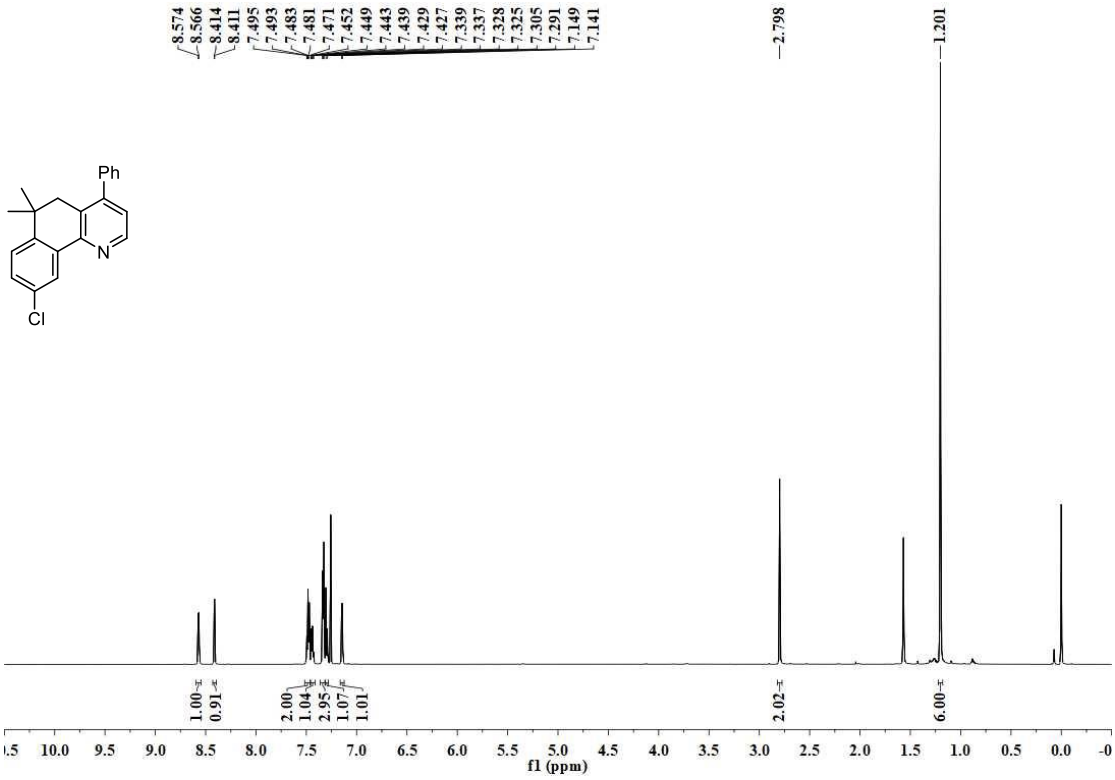
^{1}H NMR Spectrum of 12 (600 MHz, $CDCl_3$)



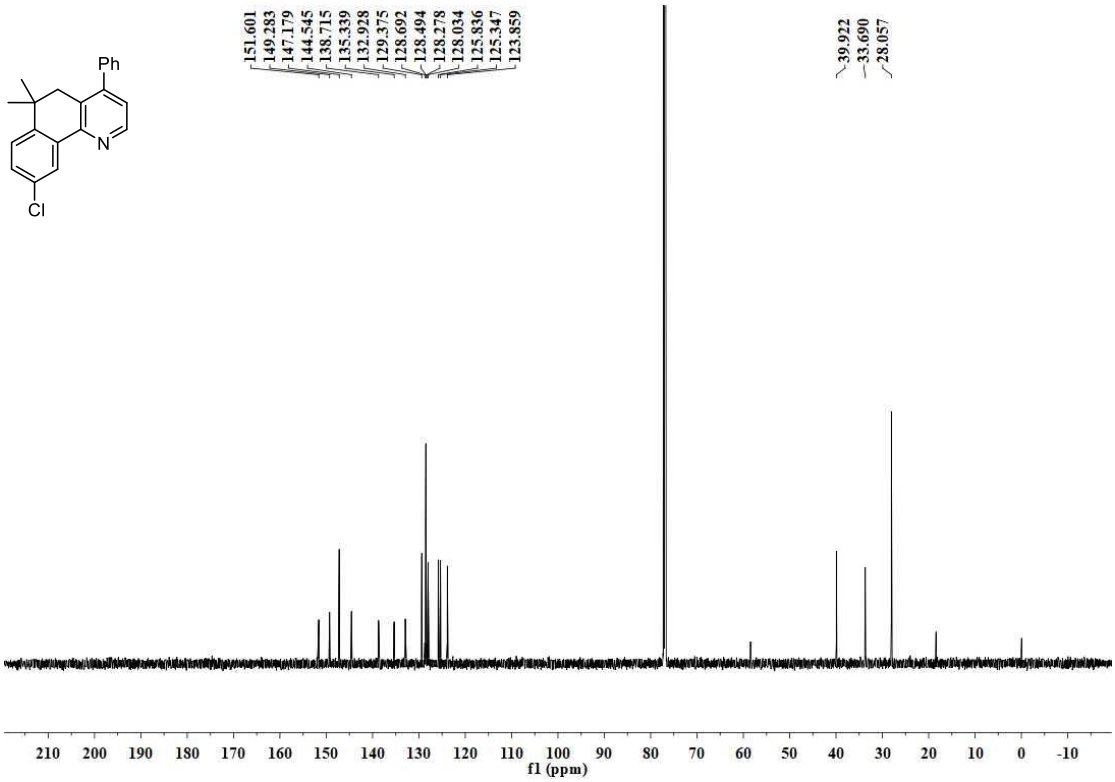
^{13}C NMR Spectrum of 12 (151 MHz, $CDCl_3$)



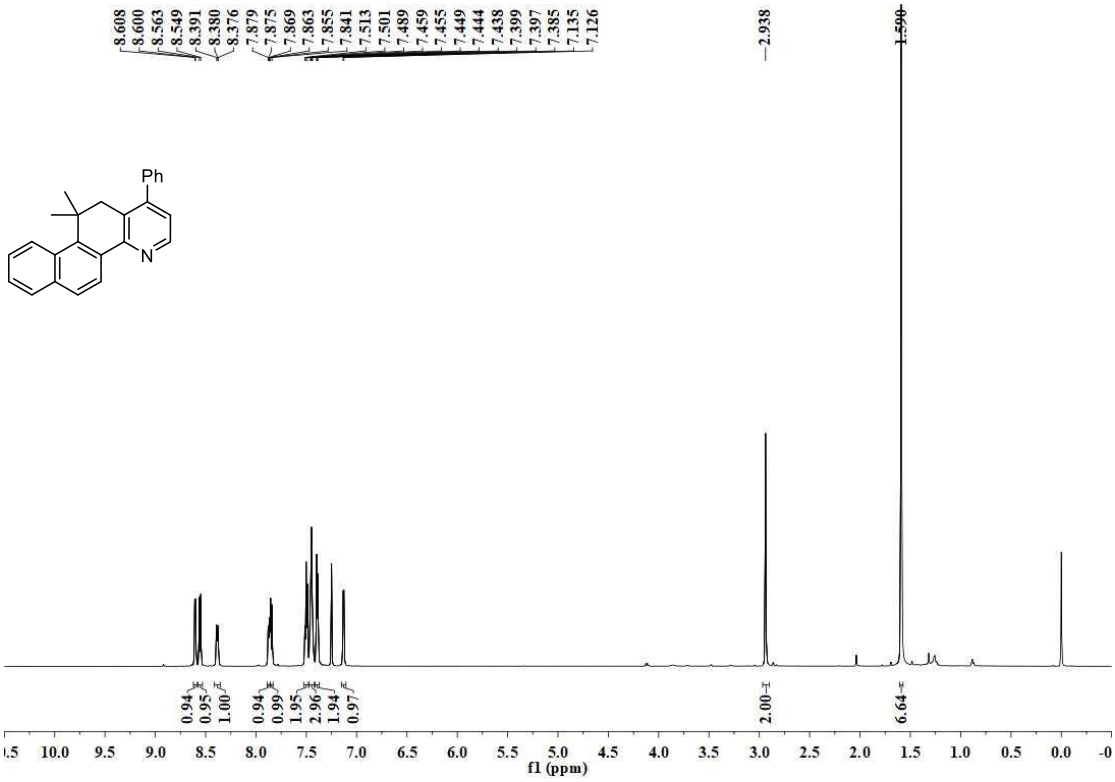
^{1}H NMR Spectrum of 13 (600 MHz, $CDCl_3$)



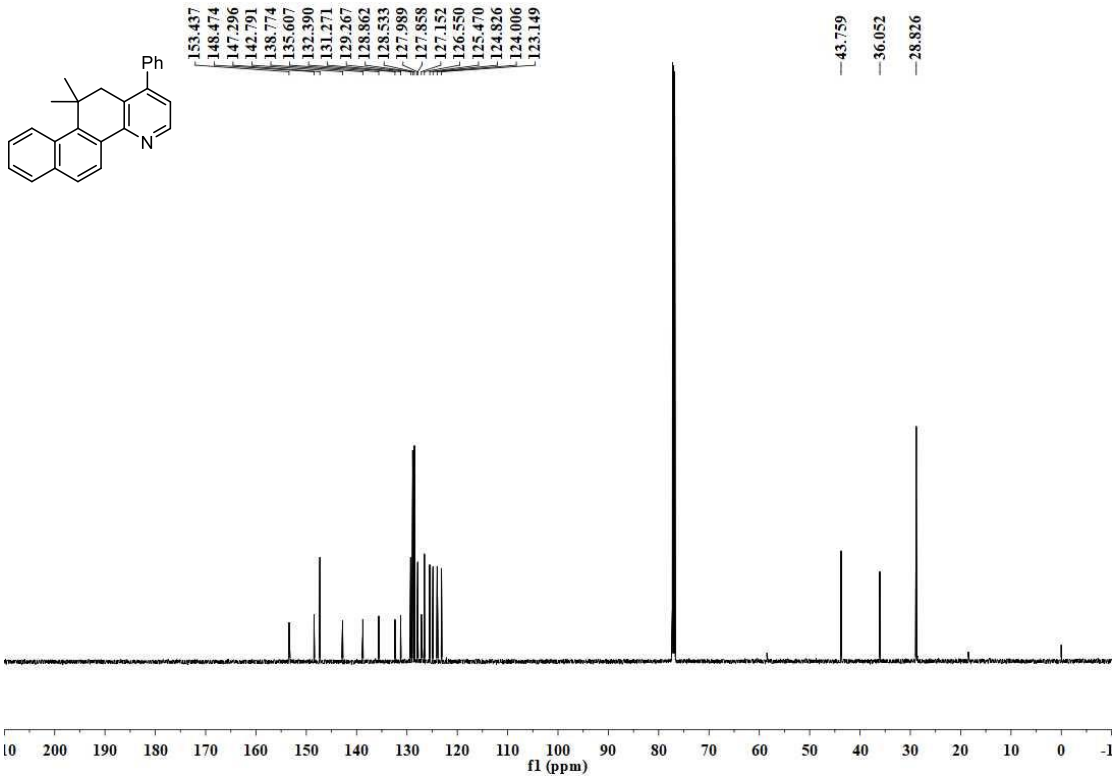
^{13}C NMR Spectrum of 13 (151 MHz, $CDCl_3$)



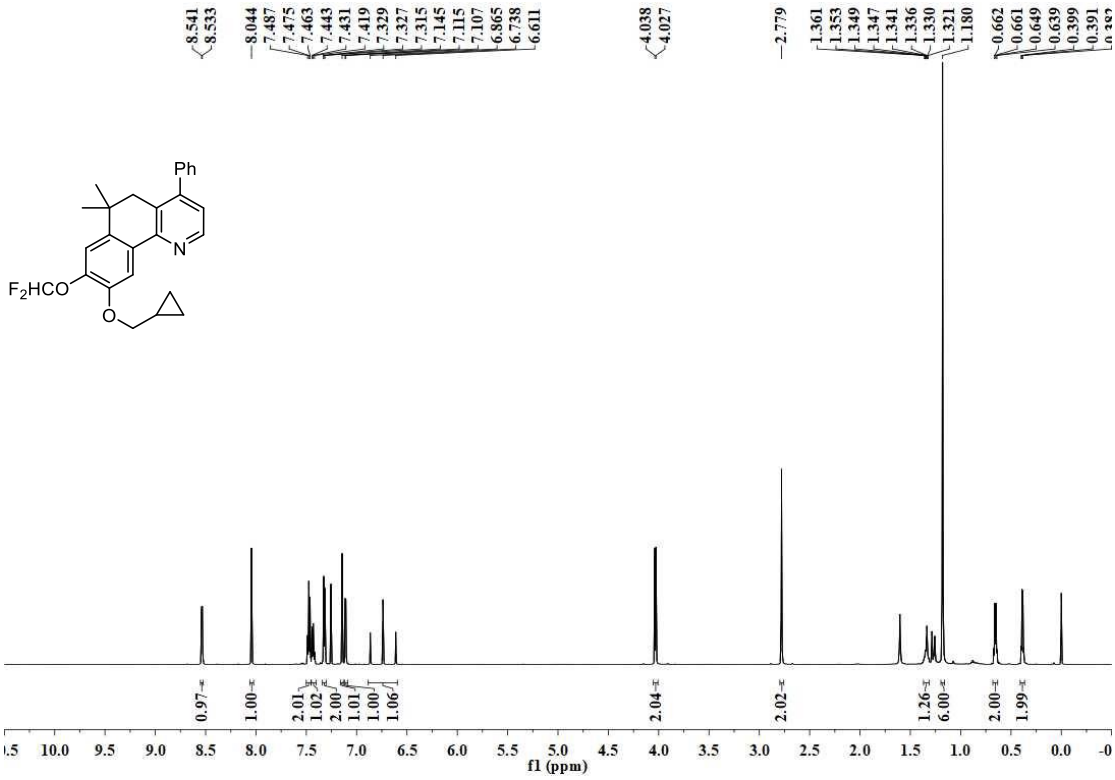
^{1}H NMR Spectrum of 14 (600 MHz, $CDCl_3$)



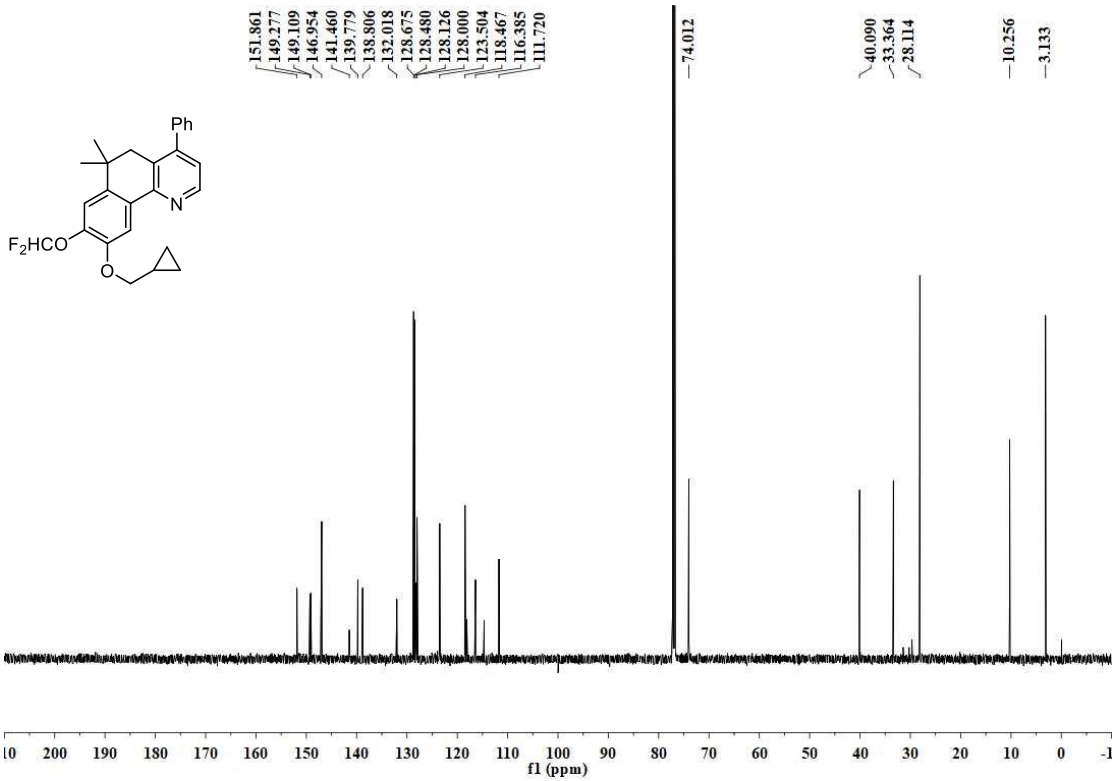
^{13}C NMR Spectrum of 14 (151 MHz, $CDCl_3$)



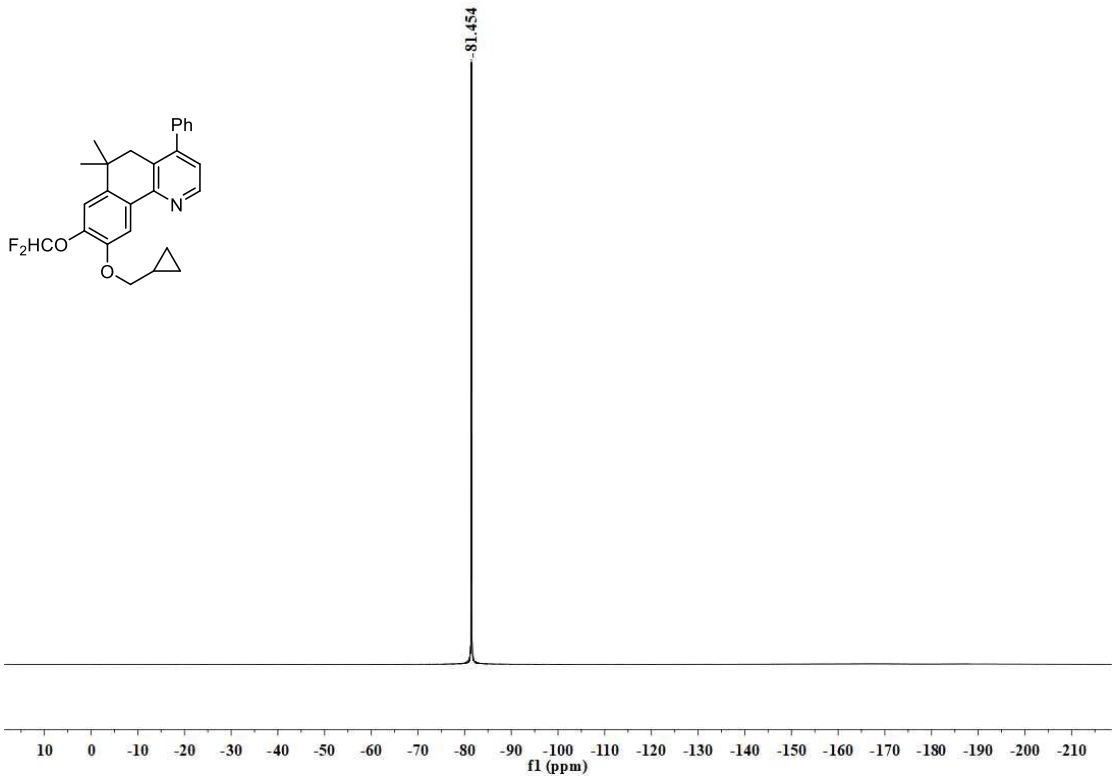
^{1}H NMR Spectrum of 15 (600 MHz, $CDCl_3$)



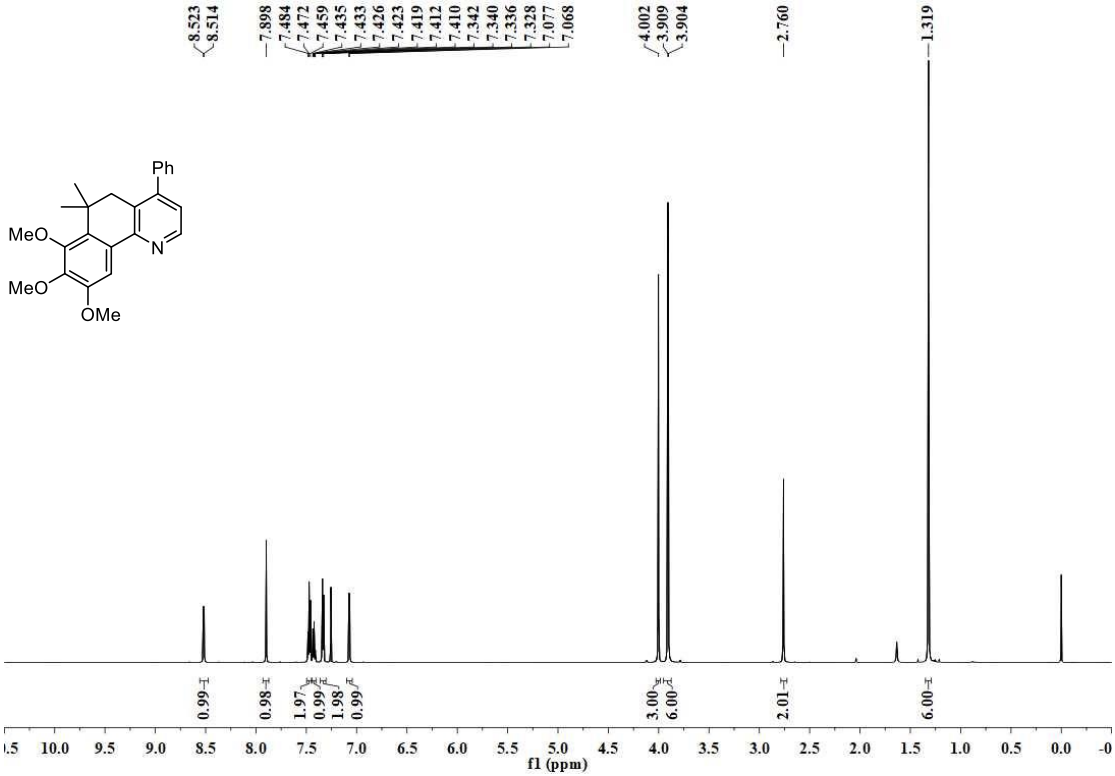
^{13}C NMR Spectrum of 15 (151 MHz, $CDCl_3$)



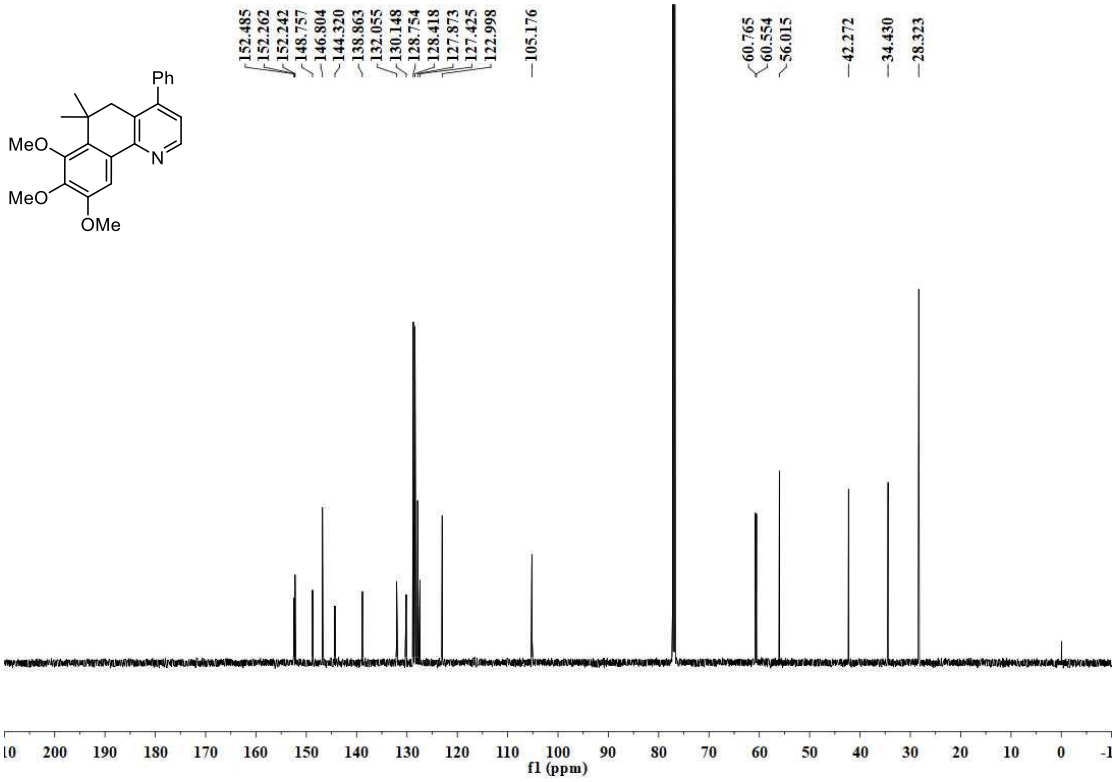
^{19}F NMR Spectrum of 15 (565 MHz, $CDCl_3$)



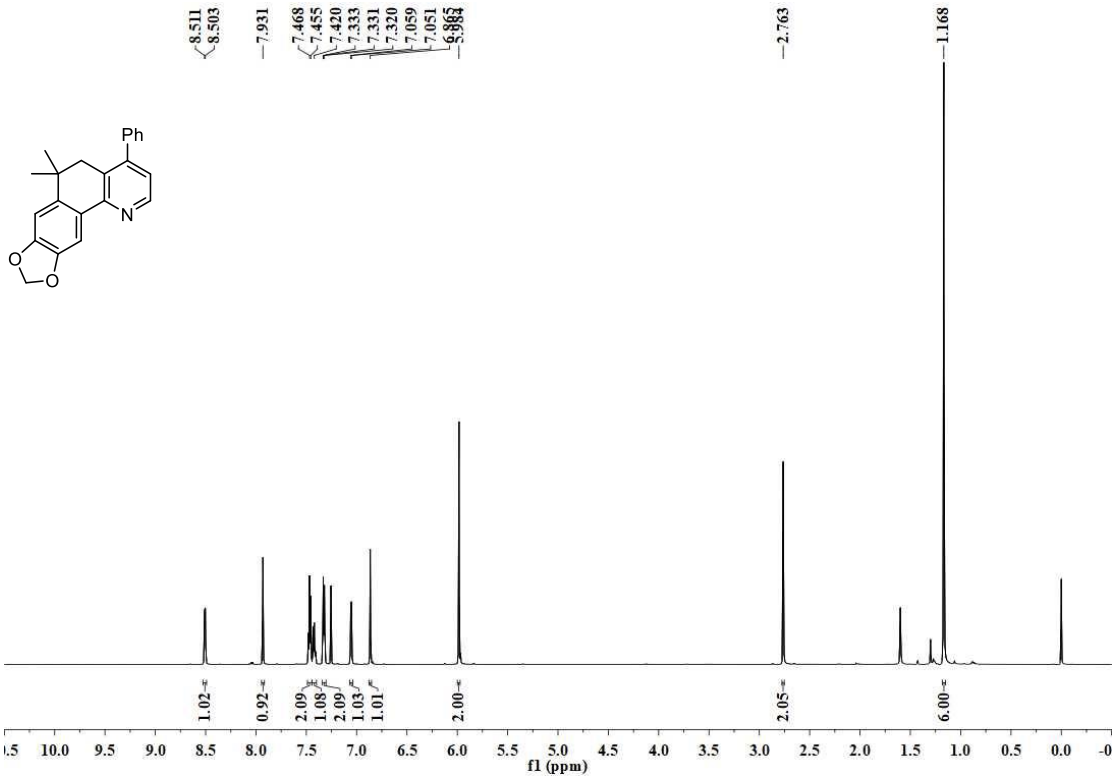
^{1}H NMR Spectrum of 16 (600 MHz, $CDCl_3$)



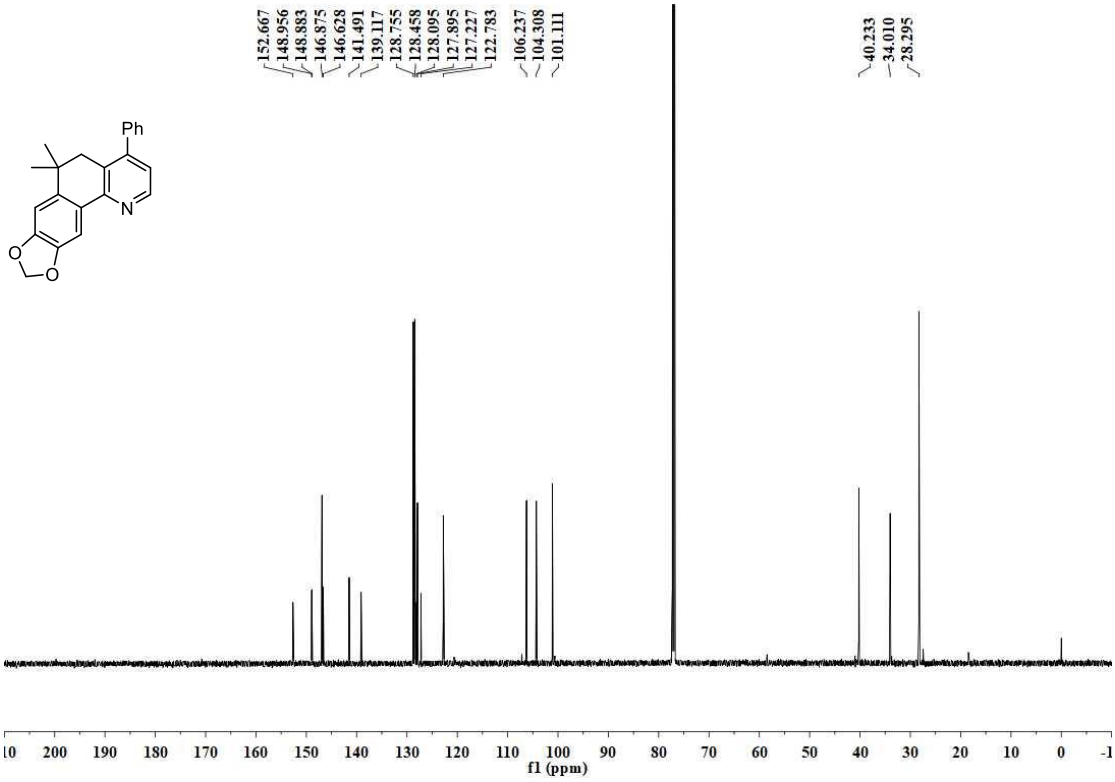
^{13}C NMR Spectrum of 16 (151 MHz, $CDCl_3$)



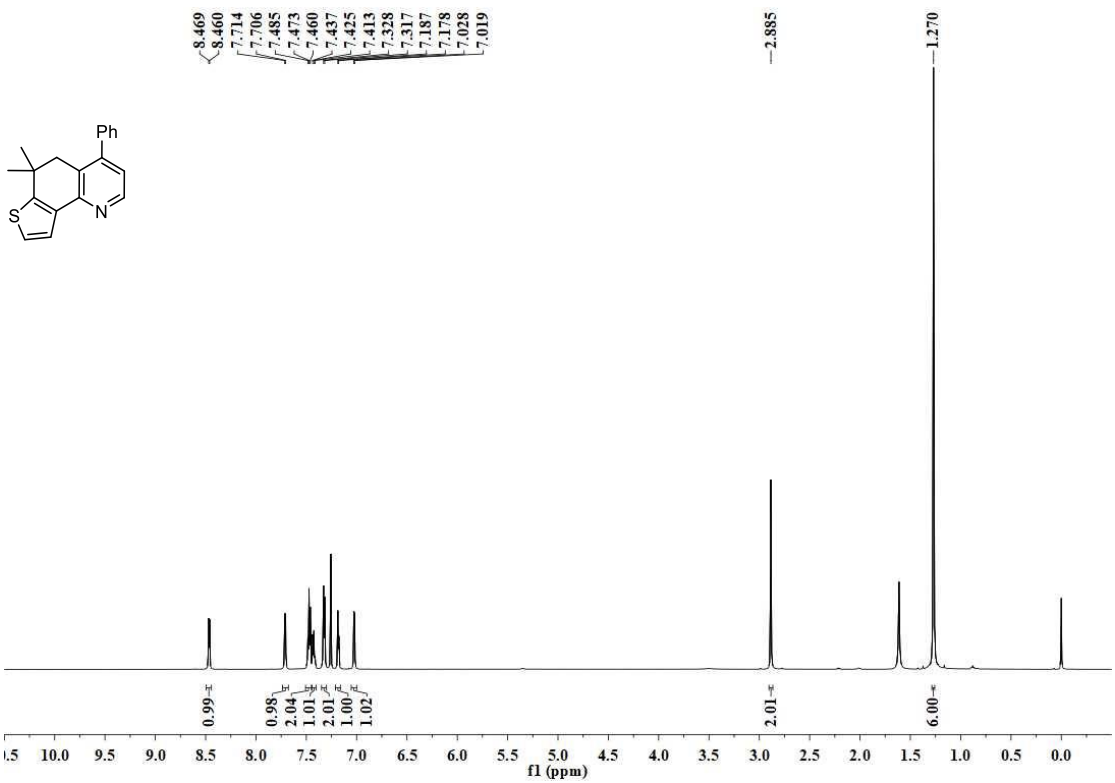
^{1}H NMR Spectrum of 17 (600 MHz, $CDCl_3$)



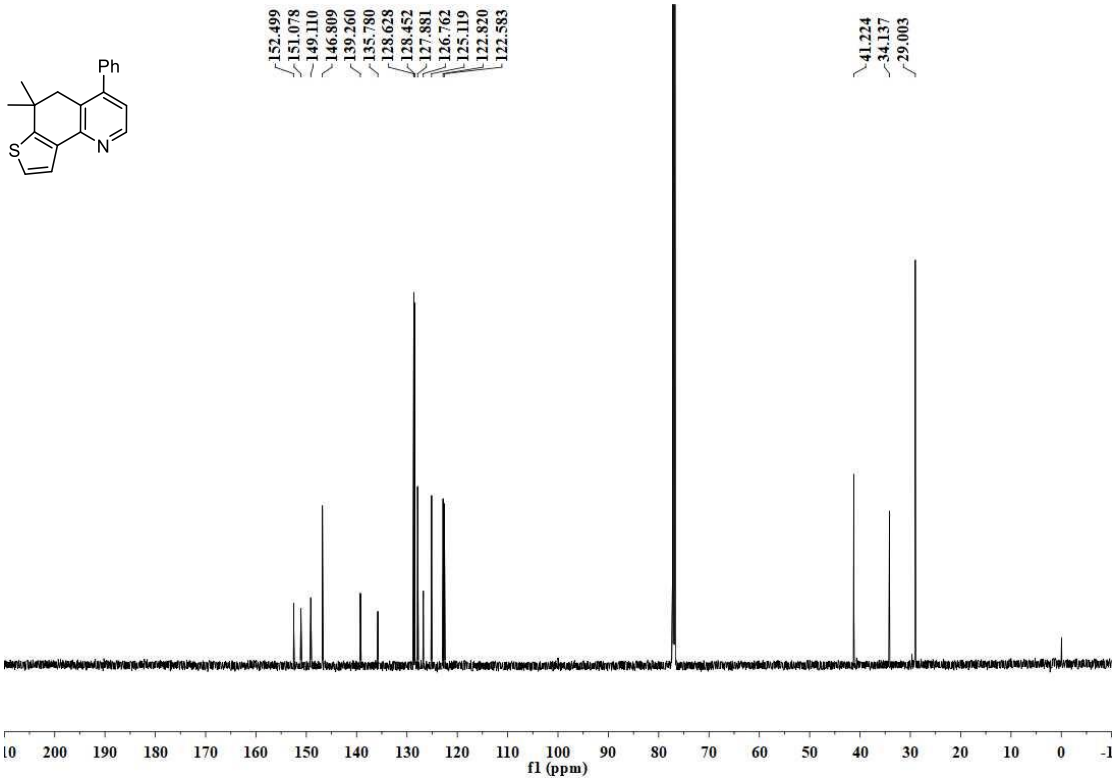
^{13}C NMR Spectrum of 17 (151 MHz, $CDCl_3$)



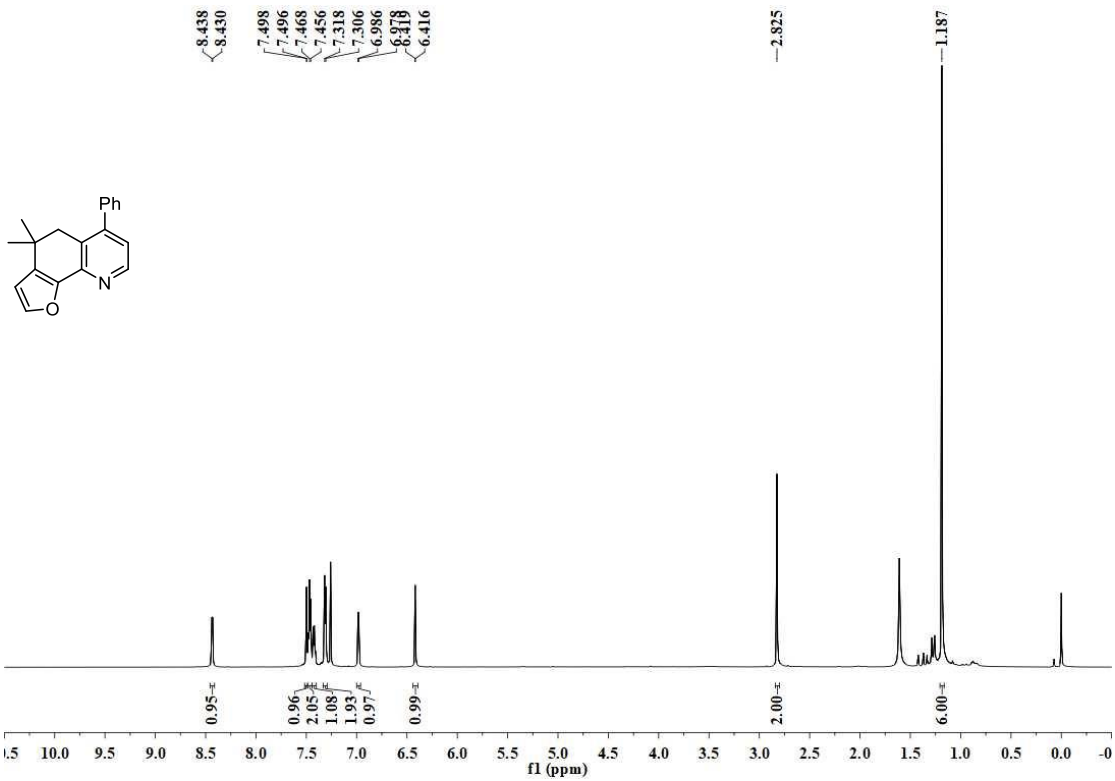
^{1}H NMR Spectrum of 18 (600 MHz, $CDCl_3$)



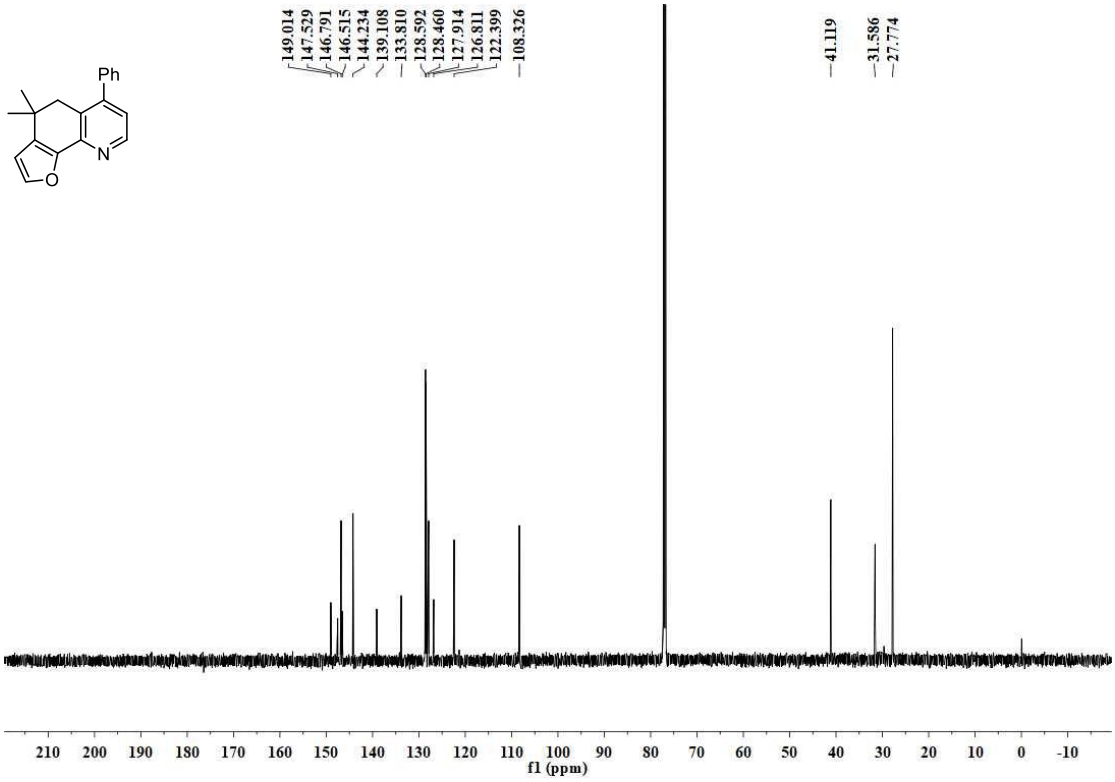
^{13}C NMR Spectrum of 18 (151 MHz, $CDCl_3$)



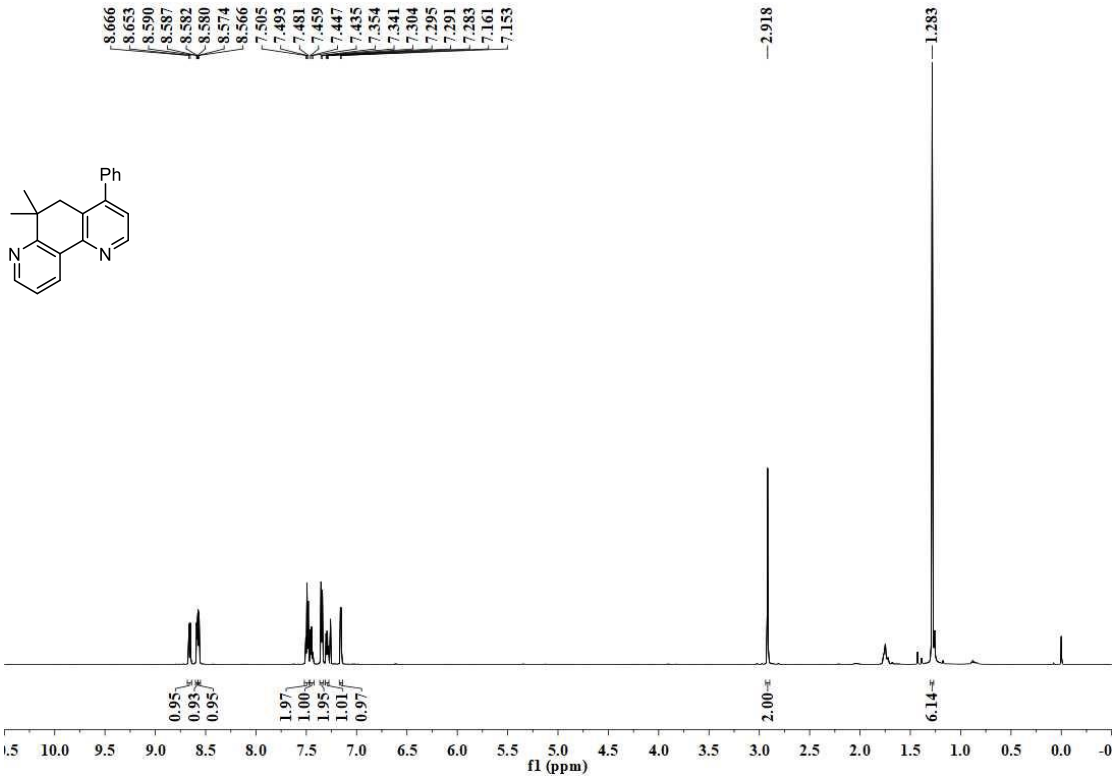
^{1}H NMR Spectrum of 19 (600 MHz, $CDCl_3$)



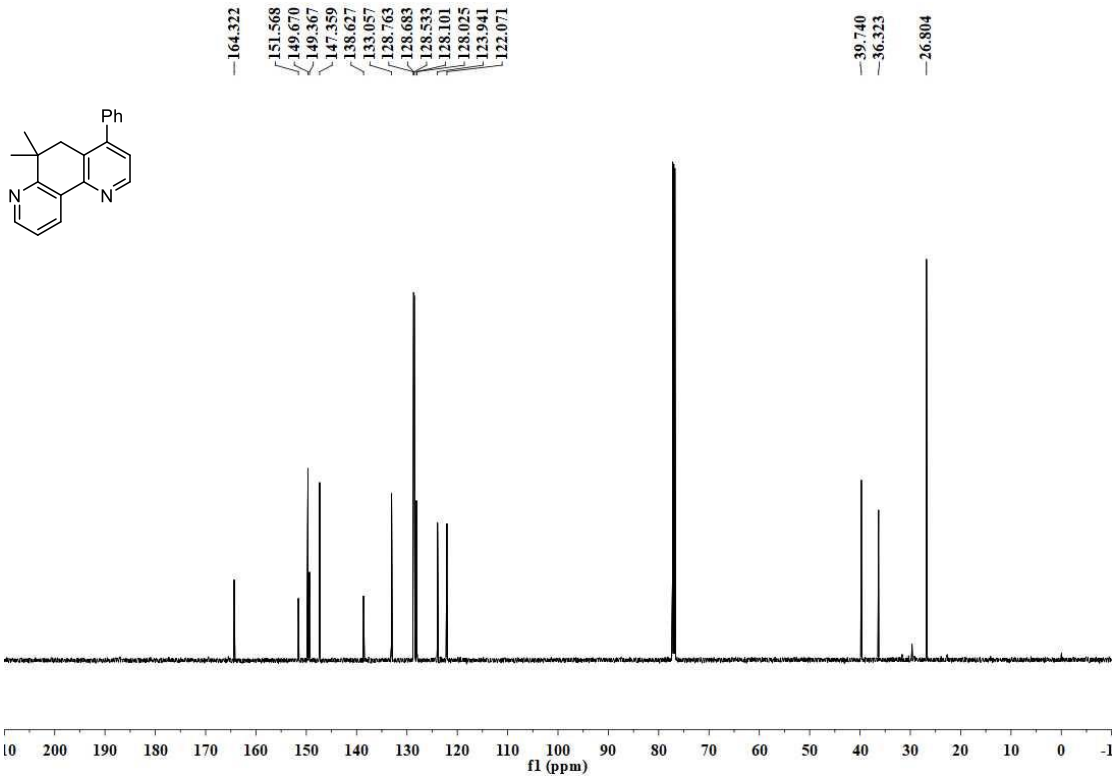
^{13}C NMR Spectrum of 19 (151 MHz, $CDCl_3$)



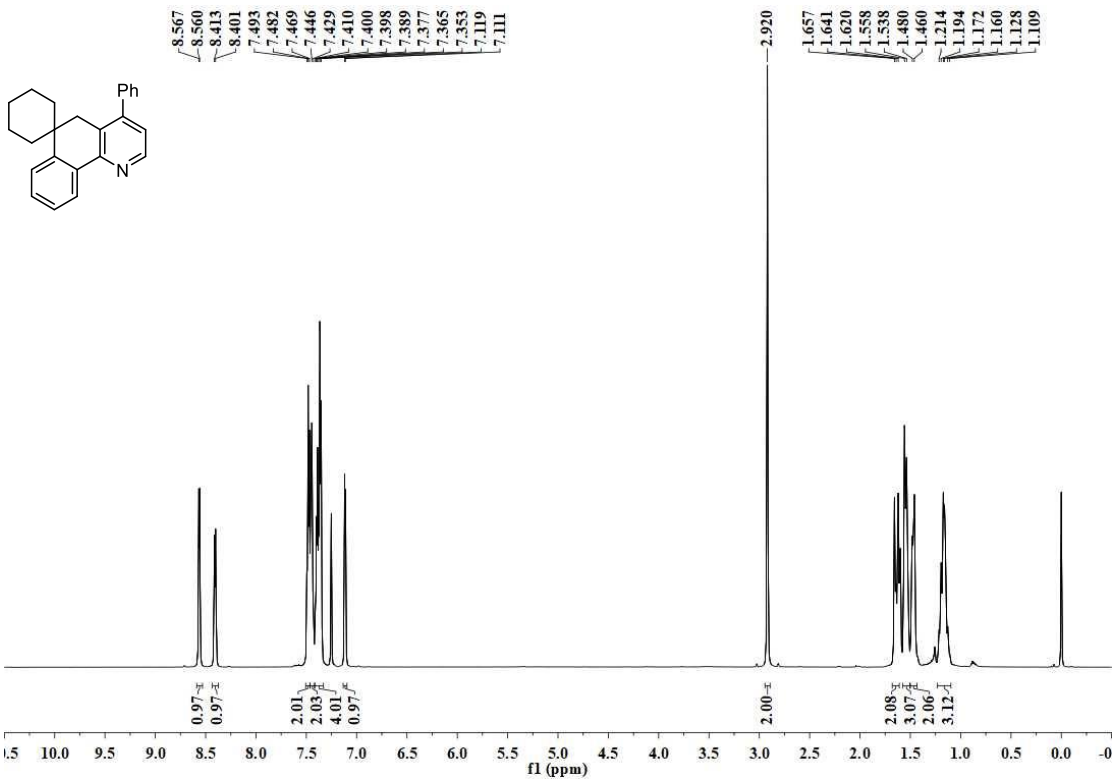
^{1}H NMR Spectrum of 20 (600 MHz, $CDCl_3$)



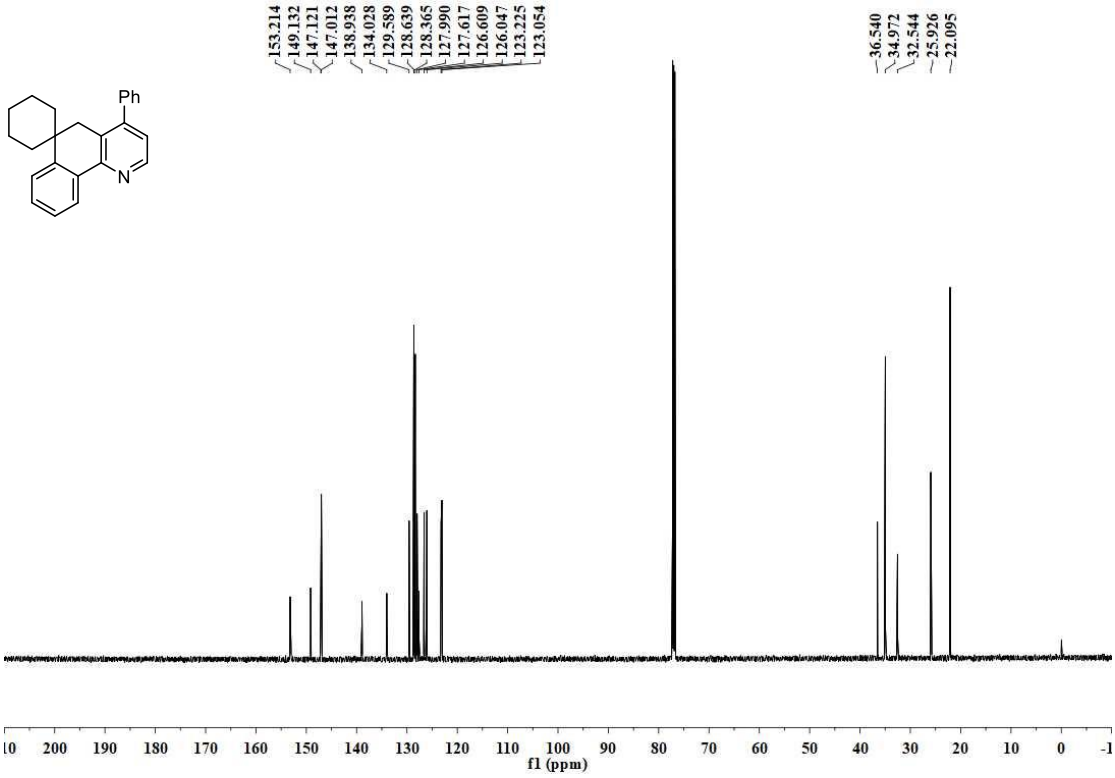
^{13}C NMR Spectrum of 20 (151 MHz, $CDCl_3$)



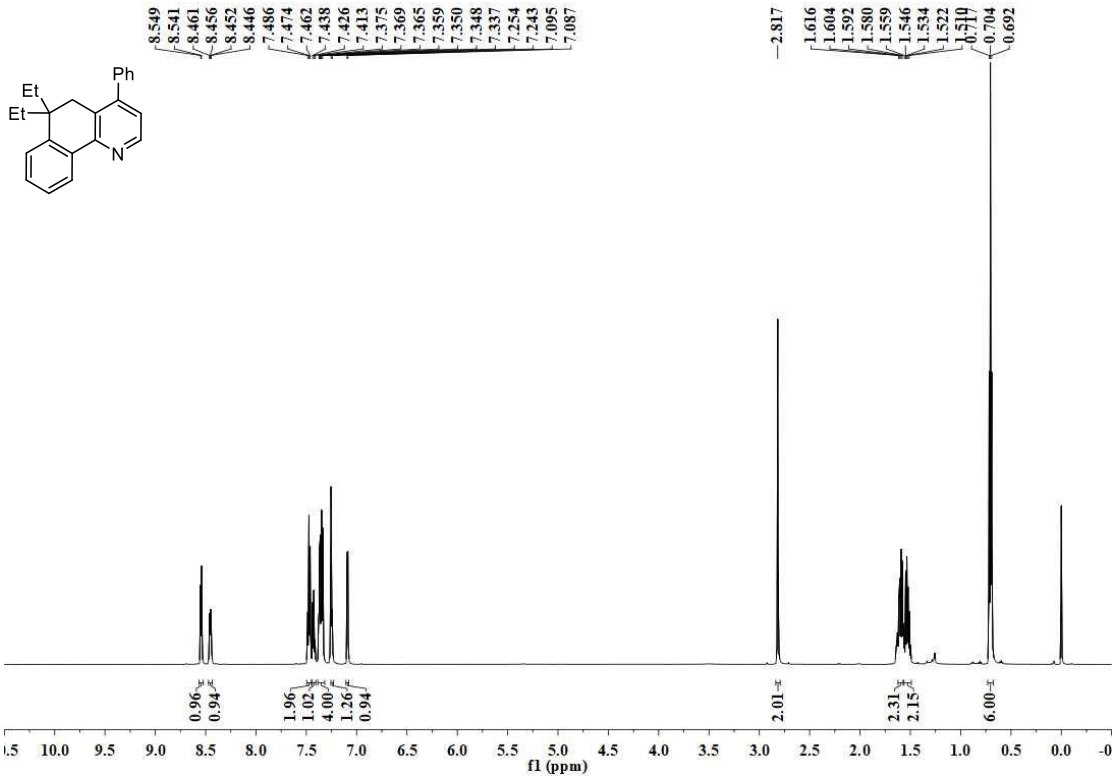
^{1}H NMR Spectrum of 21 (600 MHz, $CDCl_3$)



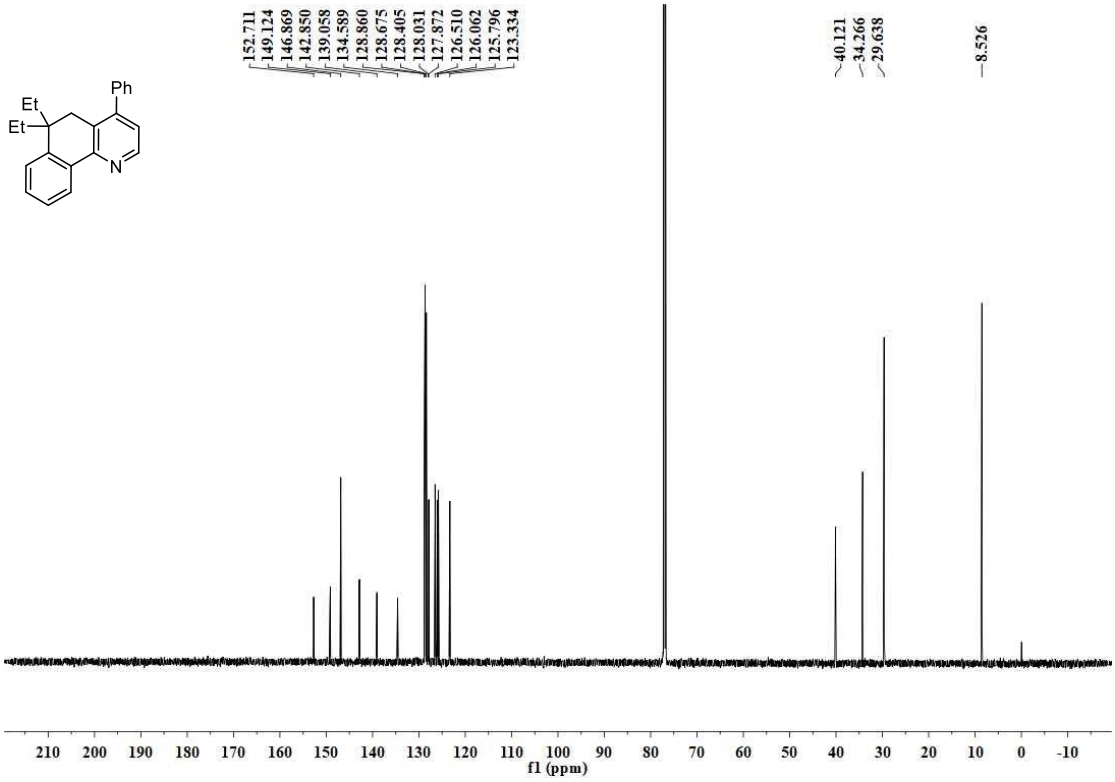
^{13}C NMR Spectrum of 21 (151 MHz, $CDCl_3$)



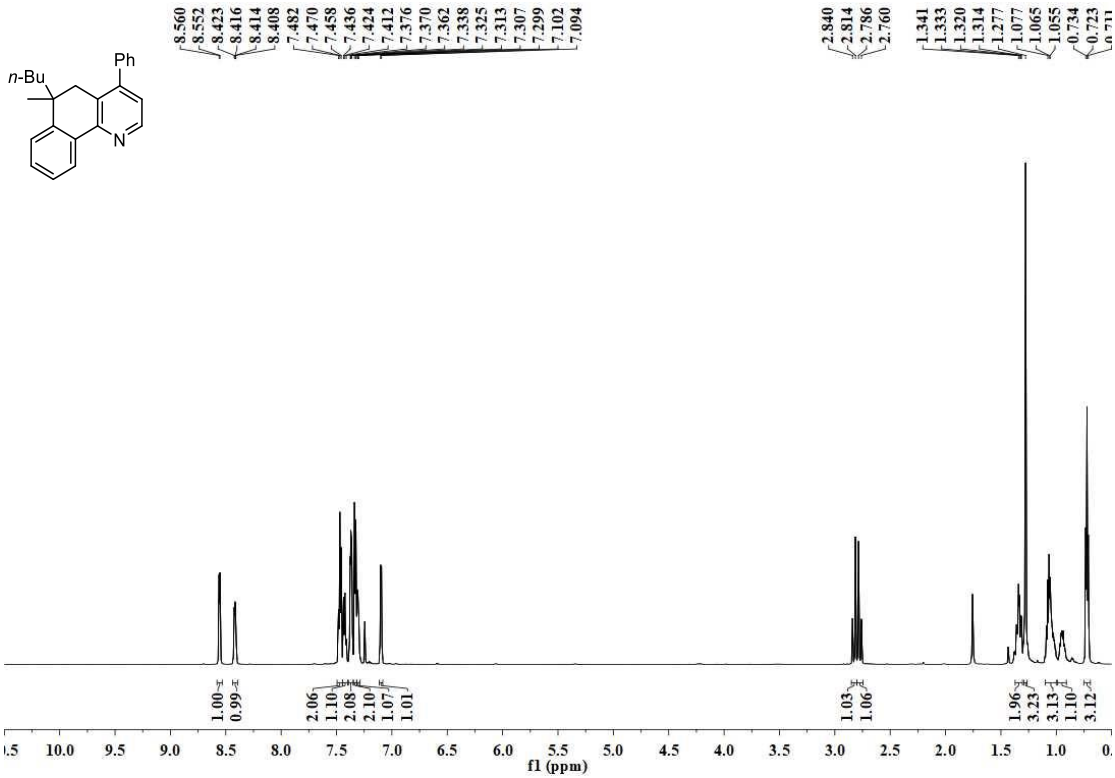
^{1}H NMR Spectrum of 22 (600 MHz, $CDCl_3$)



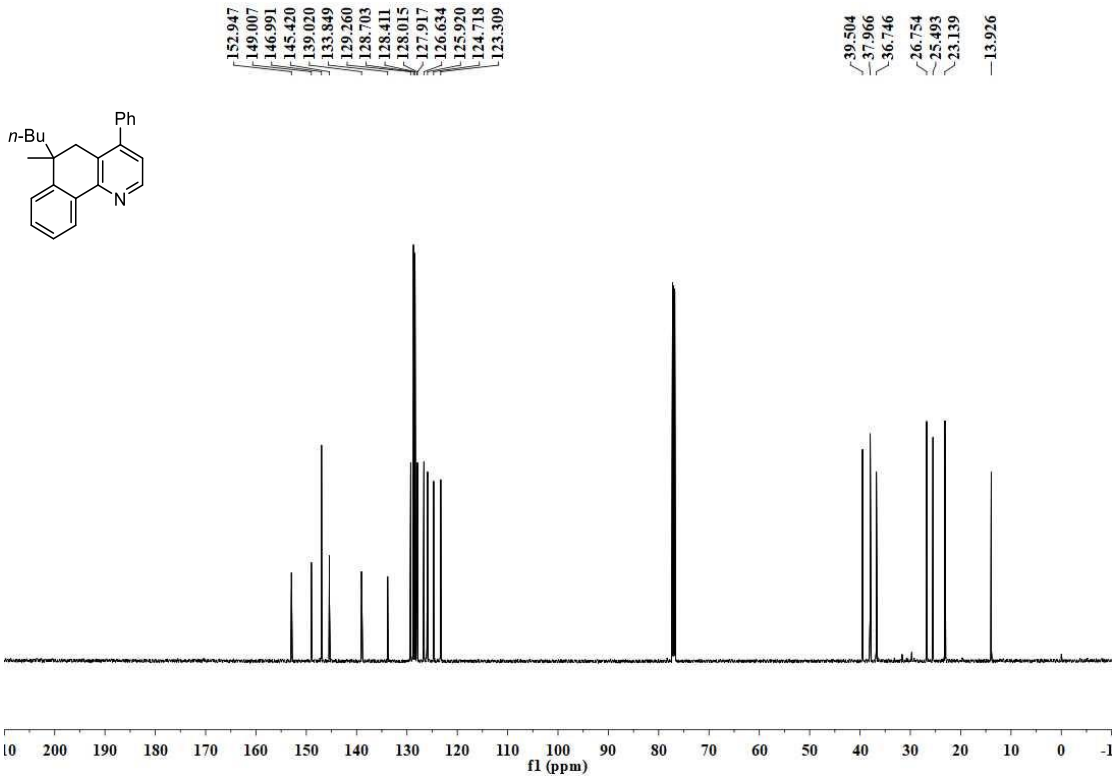
^{13}C NMR Spectrum of 22 (151 MHz, $CDCl_3$)



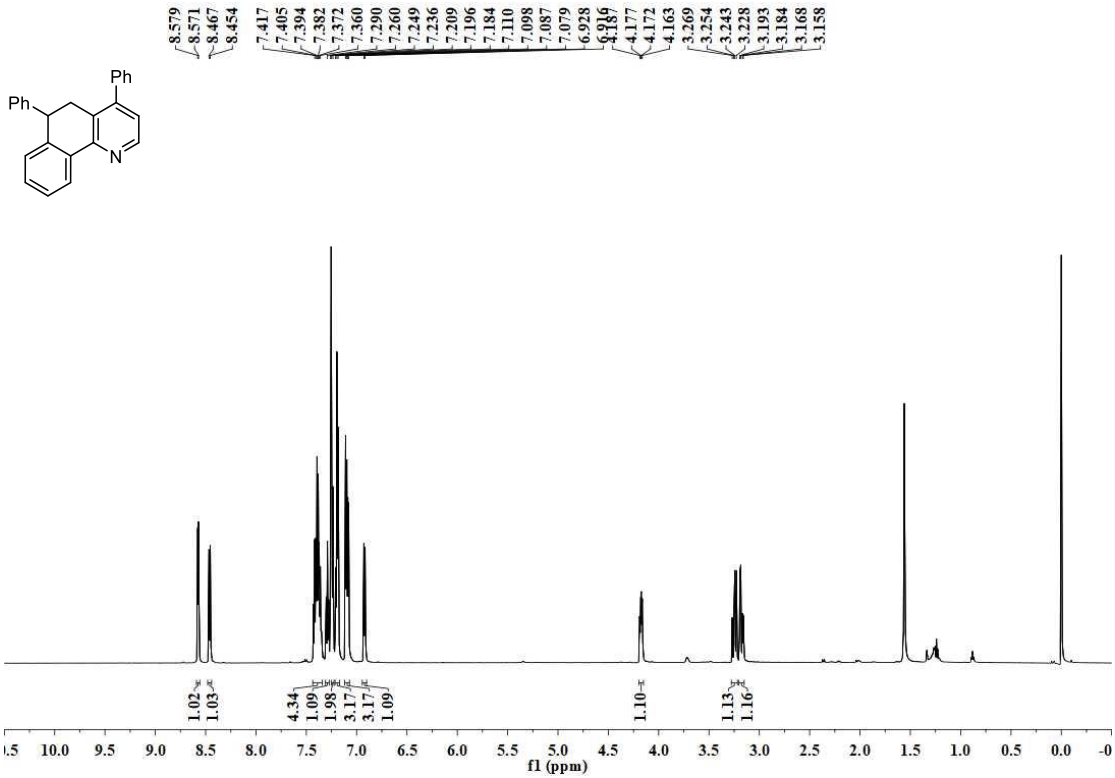
^{1}H NMR Spectrum of 23 (600 MHz, $CDCl_3$)



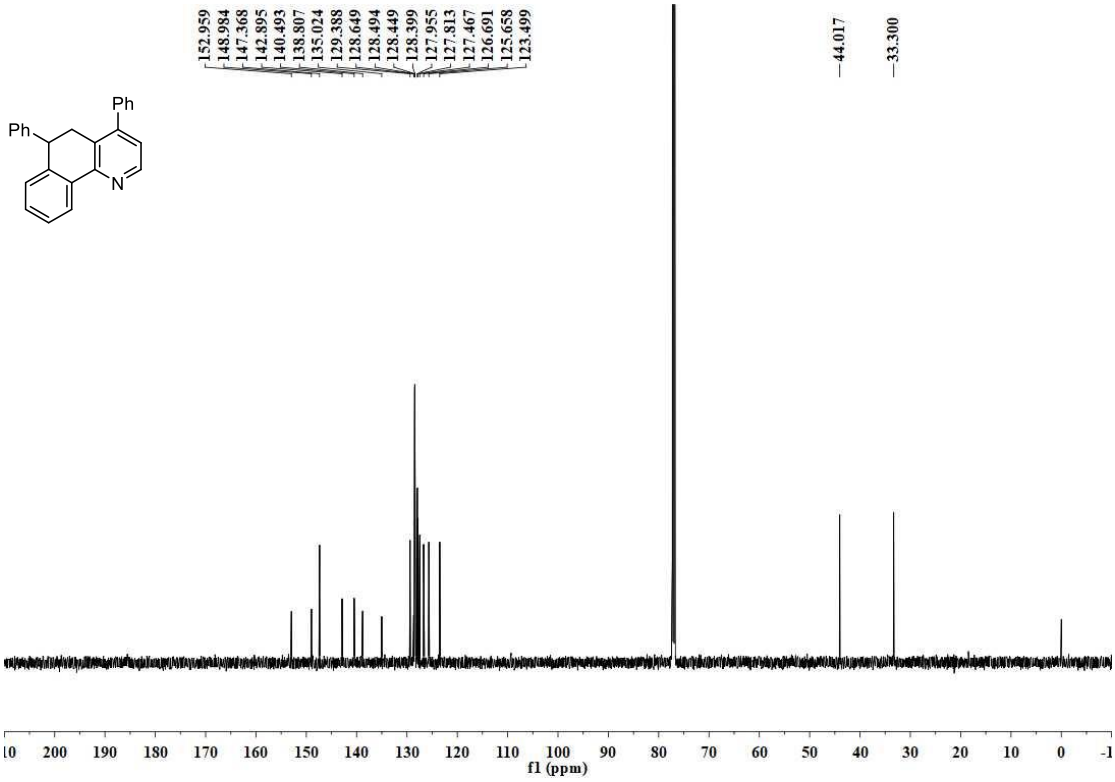
^{13}C NMR Spectrum of 23 (151 MHz, $CDCl_3$)



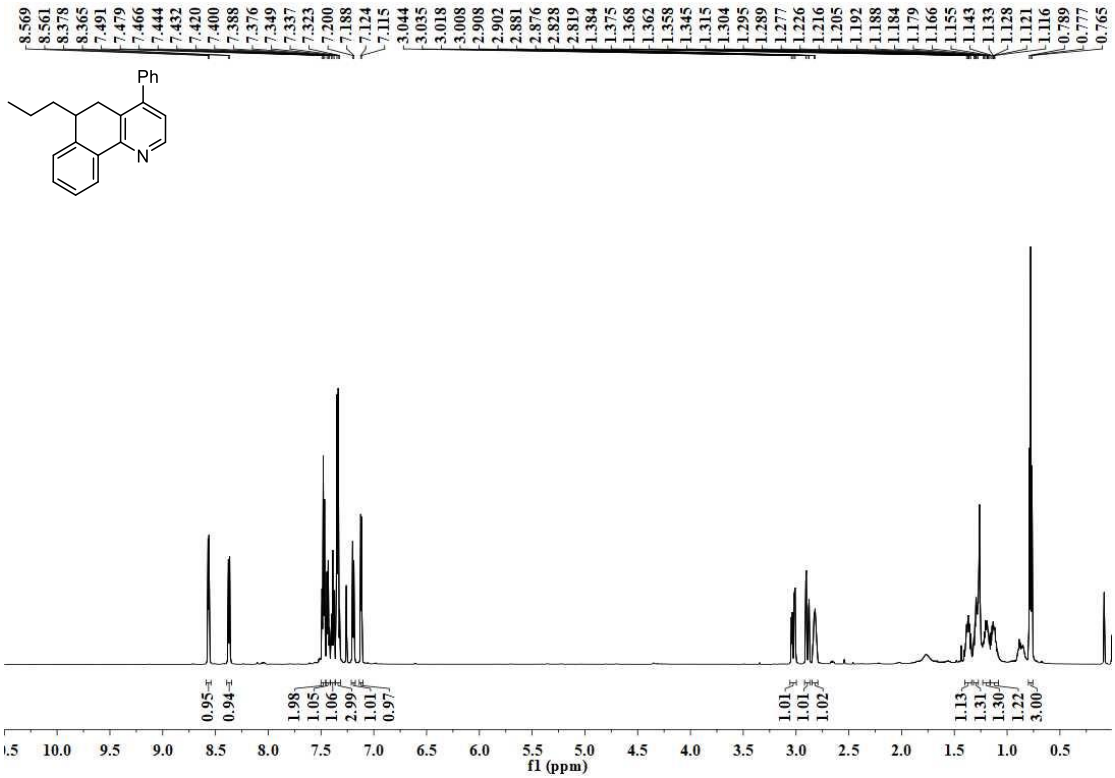
^{1}H NMR Spectrum of 24 (600 MHz, $CDCl_3$)



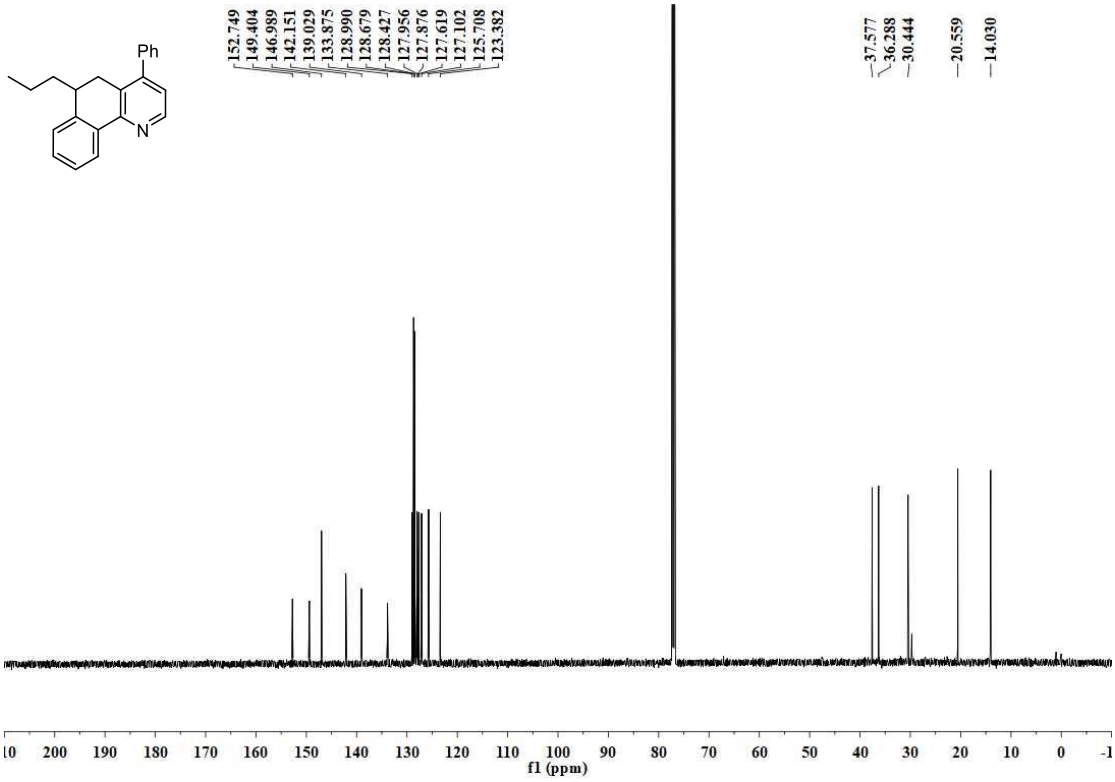
^{13}C NMR Spectrum of 24 (151 MHz, $CDCl_3$)



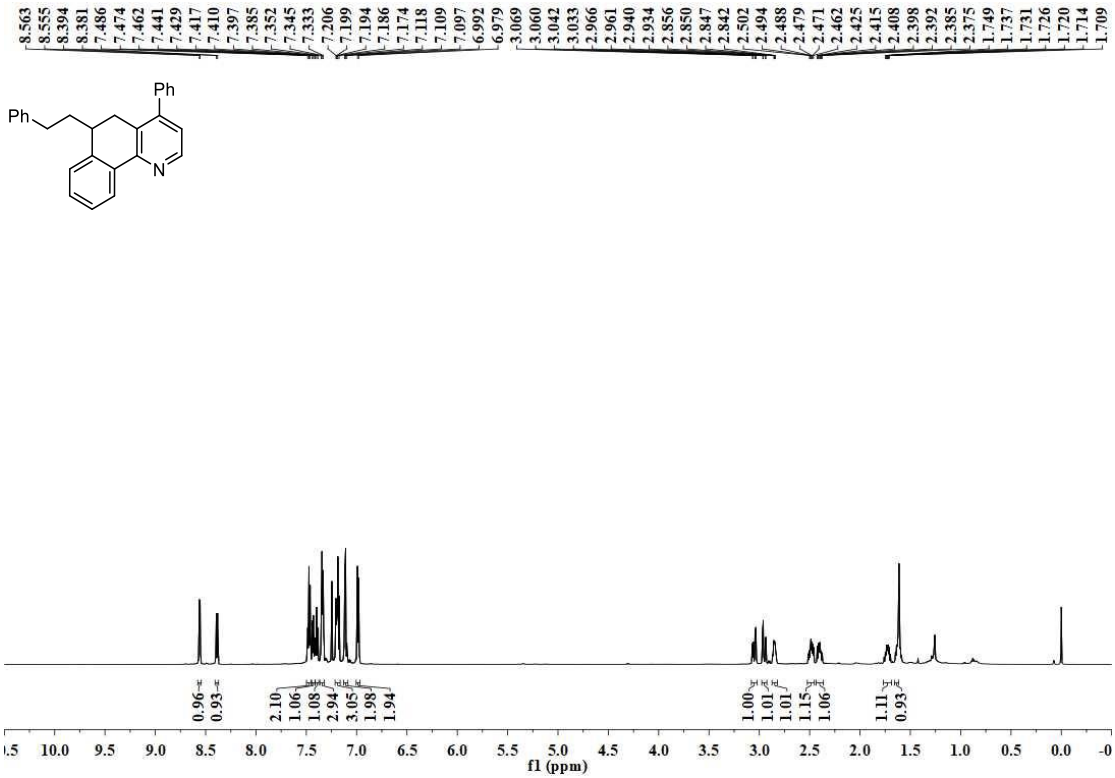
^{1}H NMR Spectrum of 25 (600 MHz, $CDCl_3$)



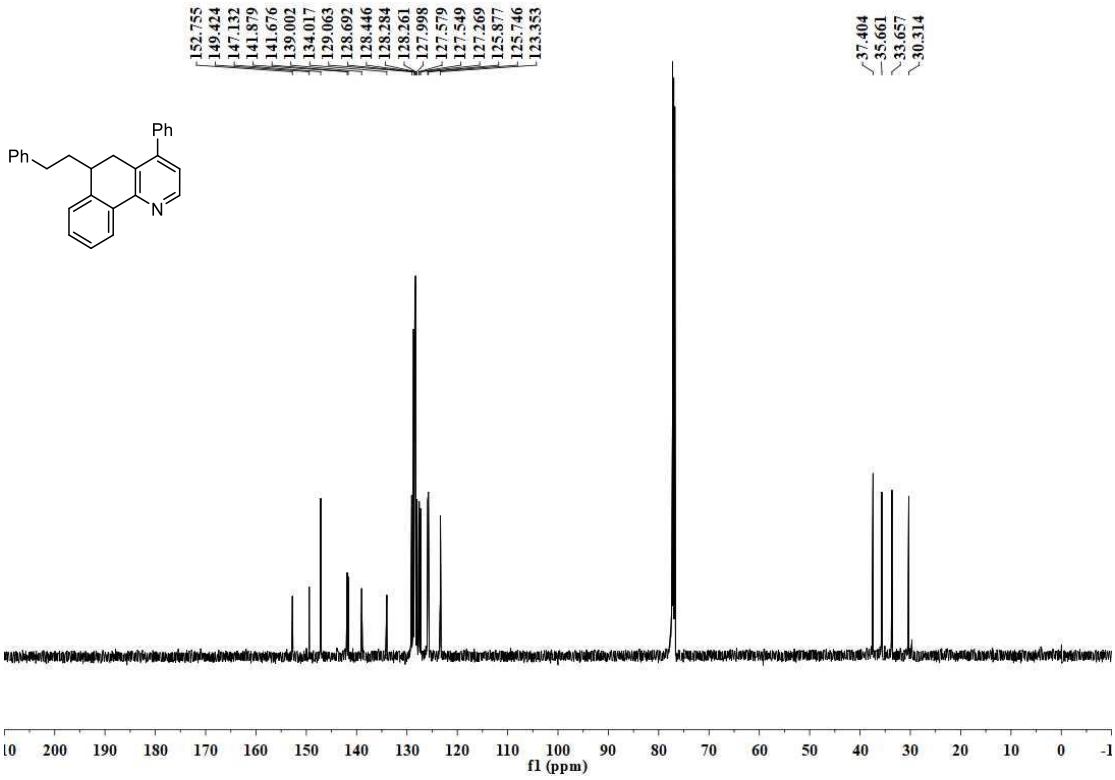
^{13}C NMR Spectrum of 25 (151 MHz, $CDCl_3$)



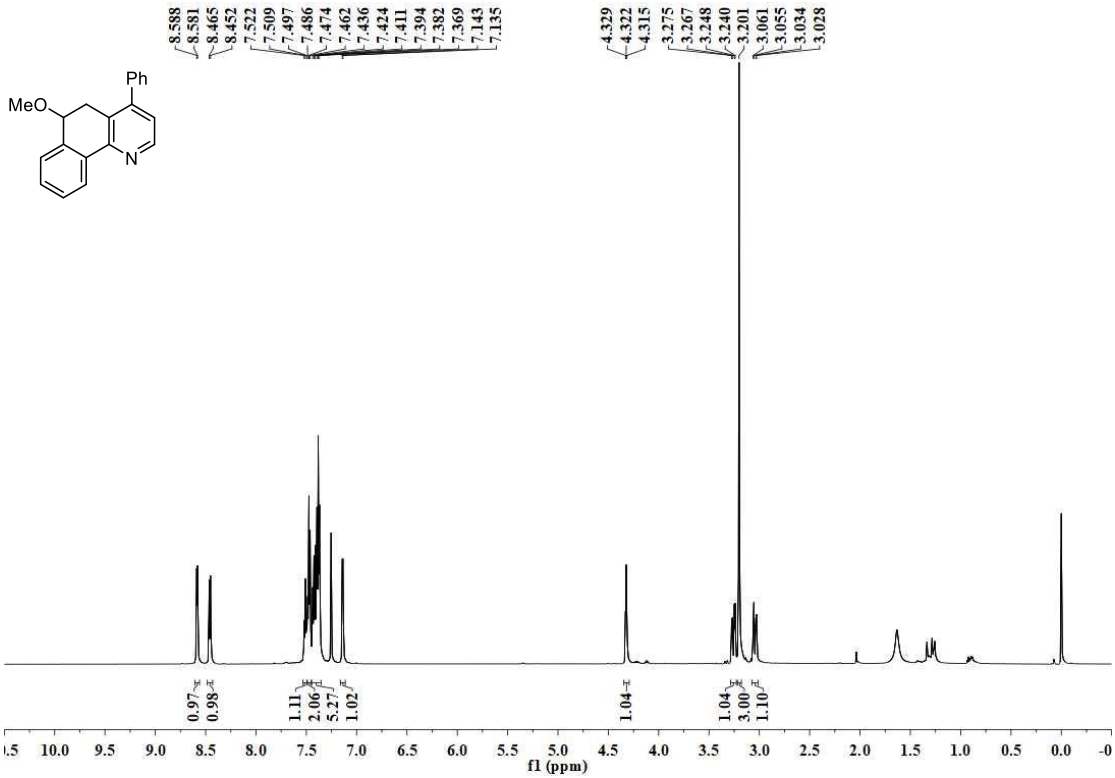
^{1}H NMR Spectrum of 26 (600 MHz, $CDCl_3$)



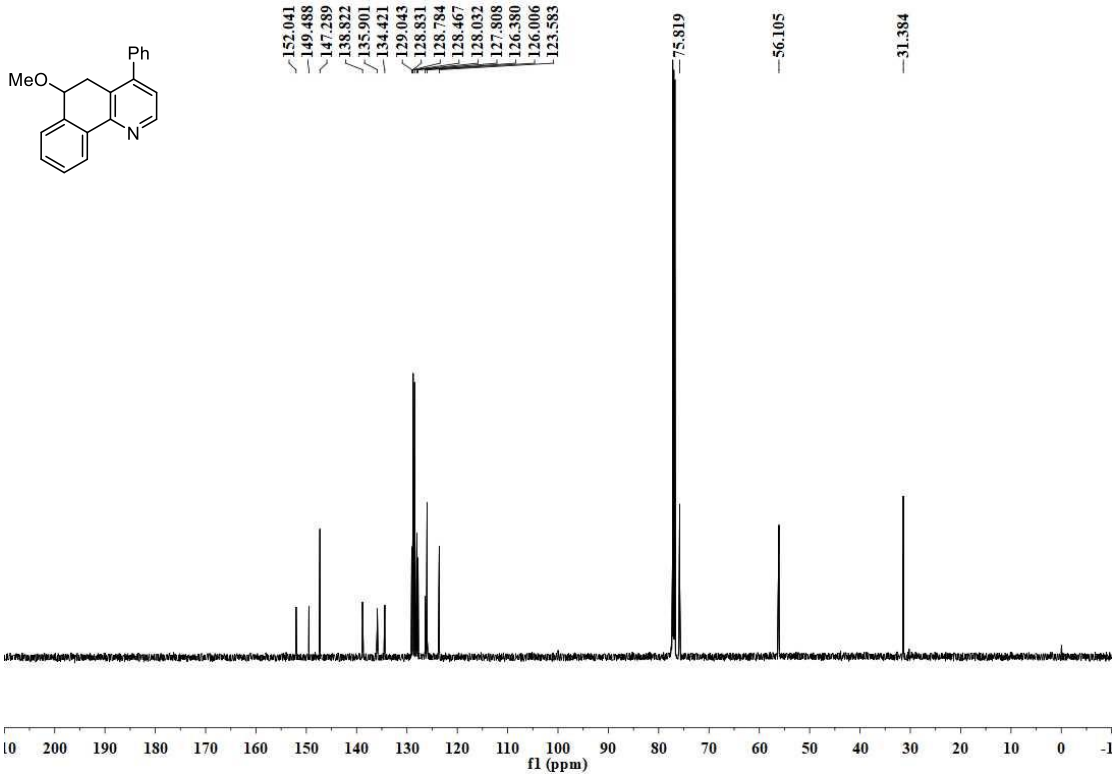
^{13}C NMR Spectrum of 26 (151 MHz, $CDCl_3$)



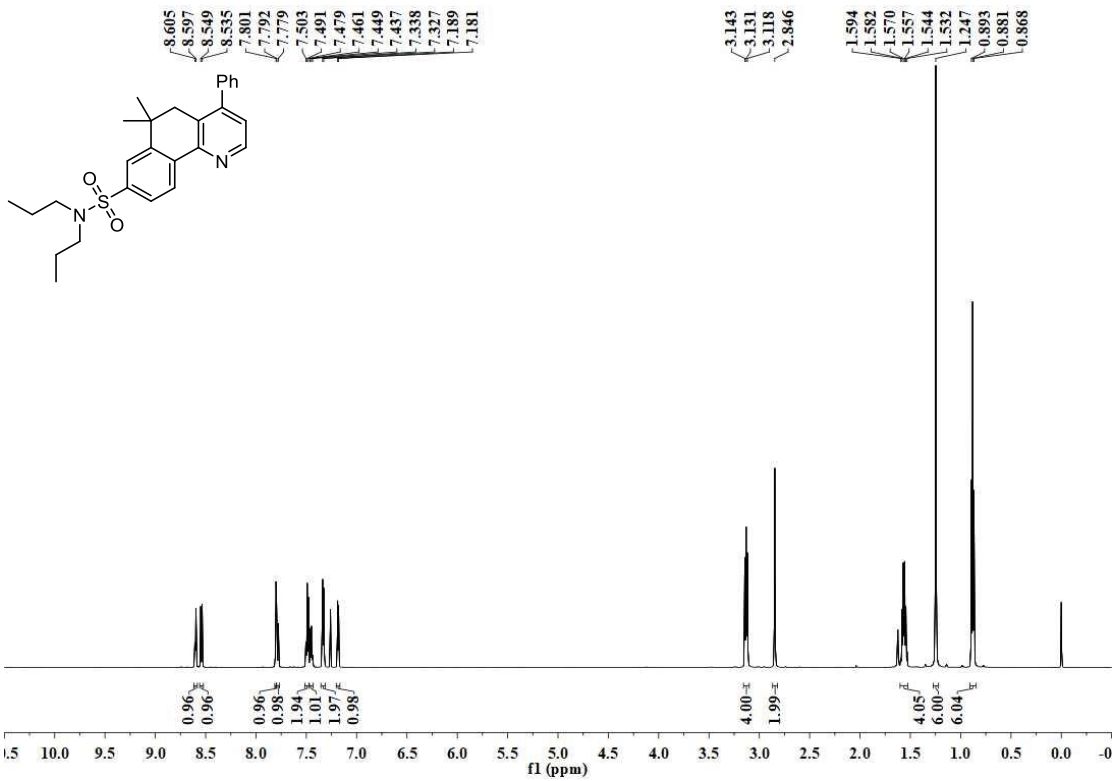
^{1}H NMR Spectrum of 27 (600 MHz, $CDCl_3$)



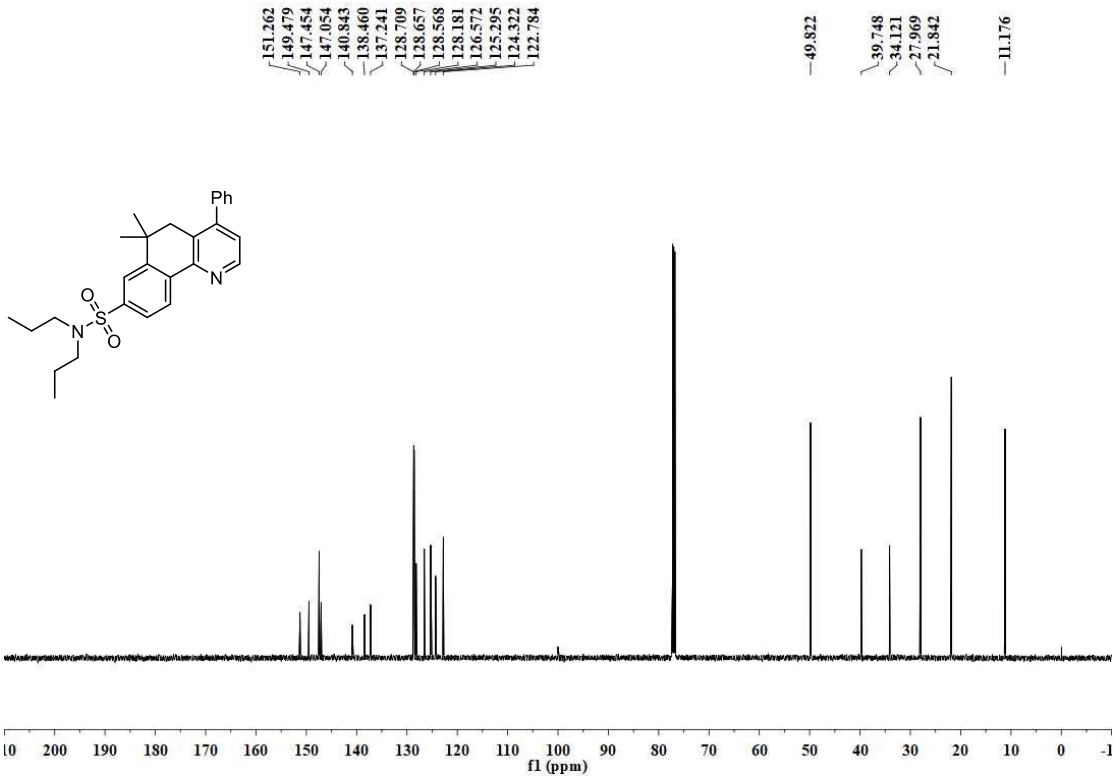
^{13}C NMR Spectrum of 27 (151 MHz, $CDCl_3$)



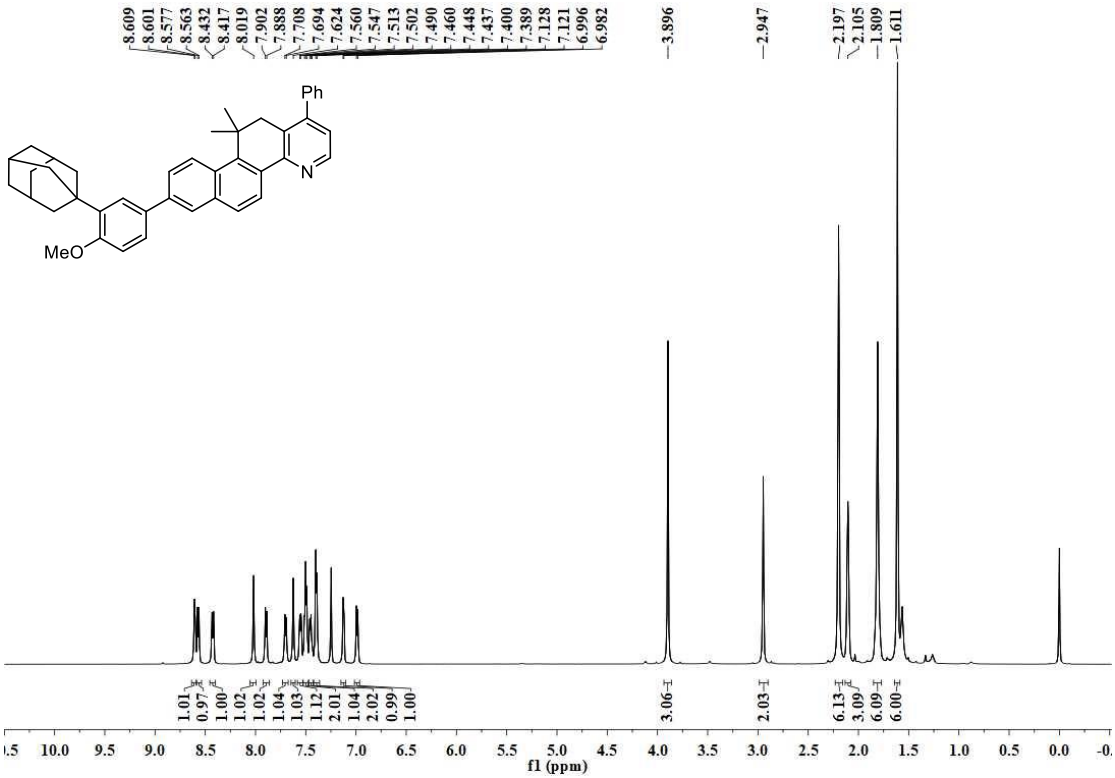
^{1}H NMR Spectrum of 28 (600 MHz, $CDCl_3$)



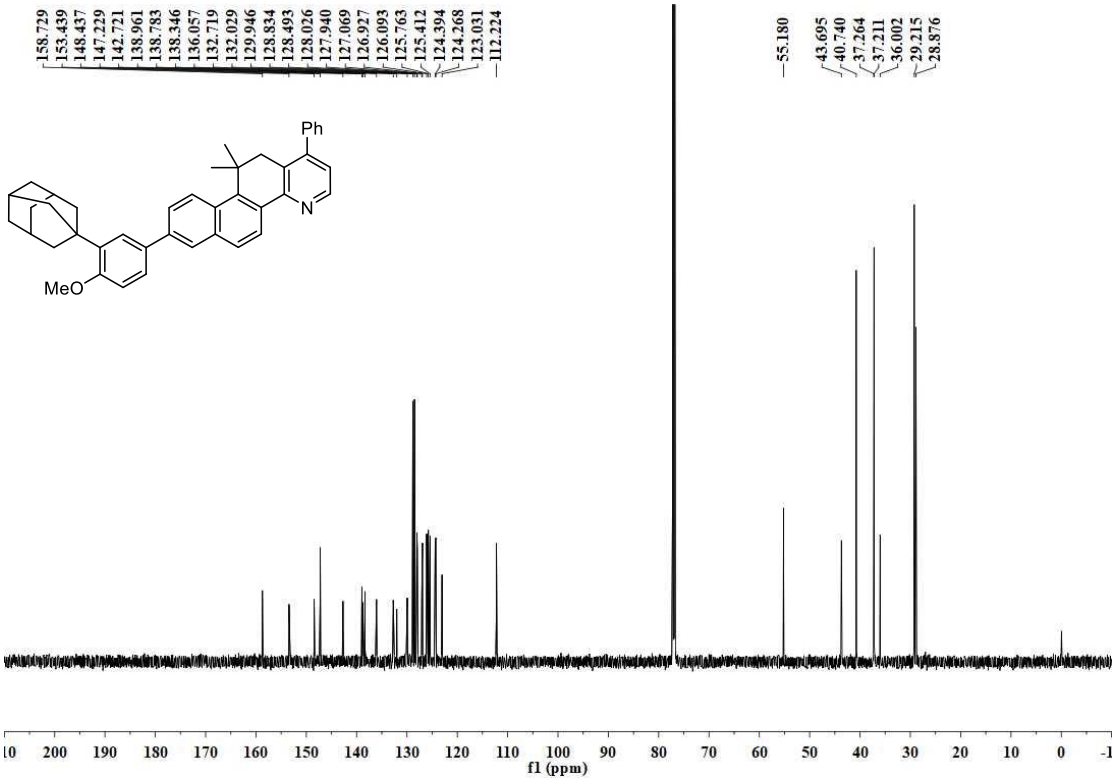
^{13}C NMR Spectrum of 28 (151 MHz, $CDCl_3$)



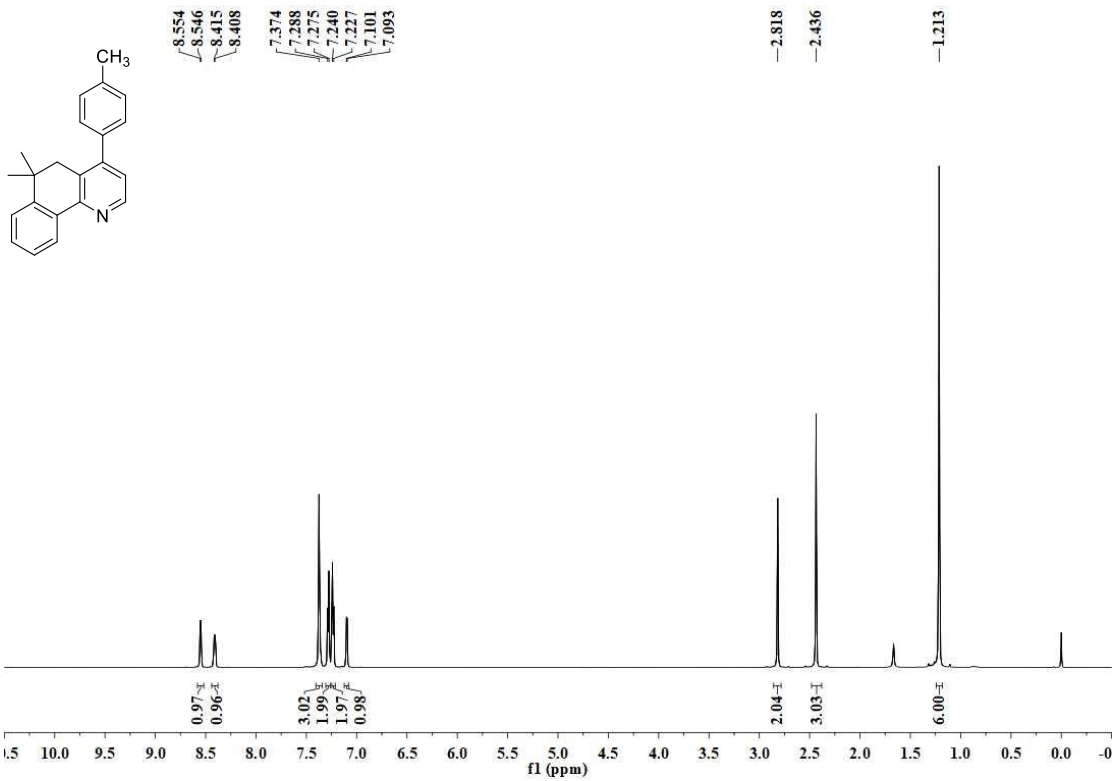
^{1}H NMR Spectrum of 29 (600 MHz, $CDCl_3$)



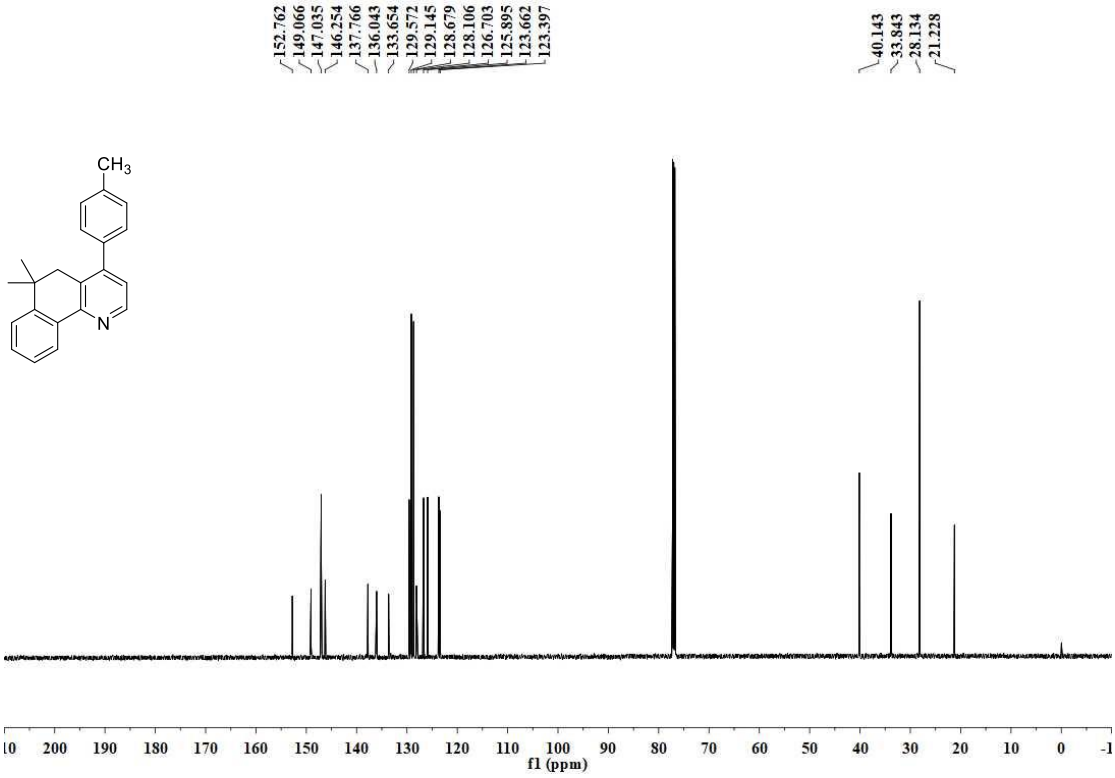
^{13}C NMR Spectrum of 29 (151 MHz, $CDCl_3$)



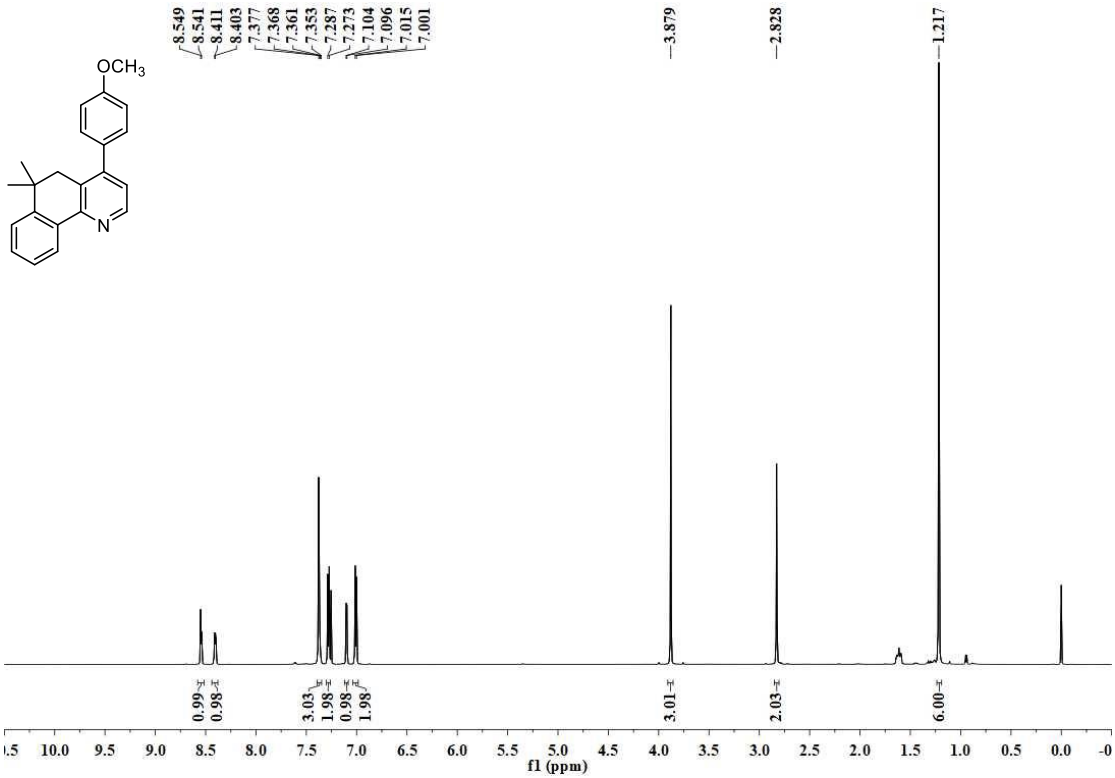
^{1}H NMR Spectrum of 30 (600 MHz, $CDCl_3$)



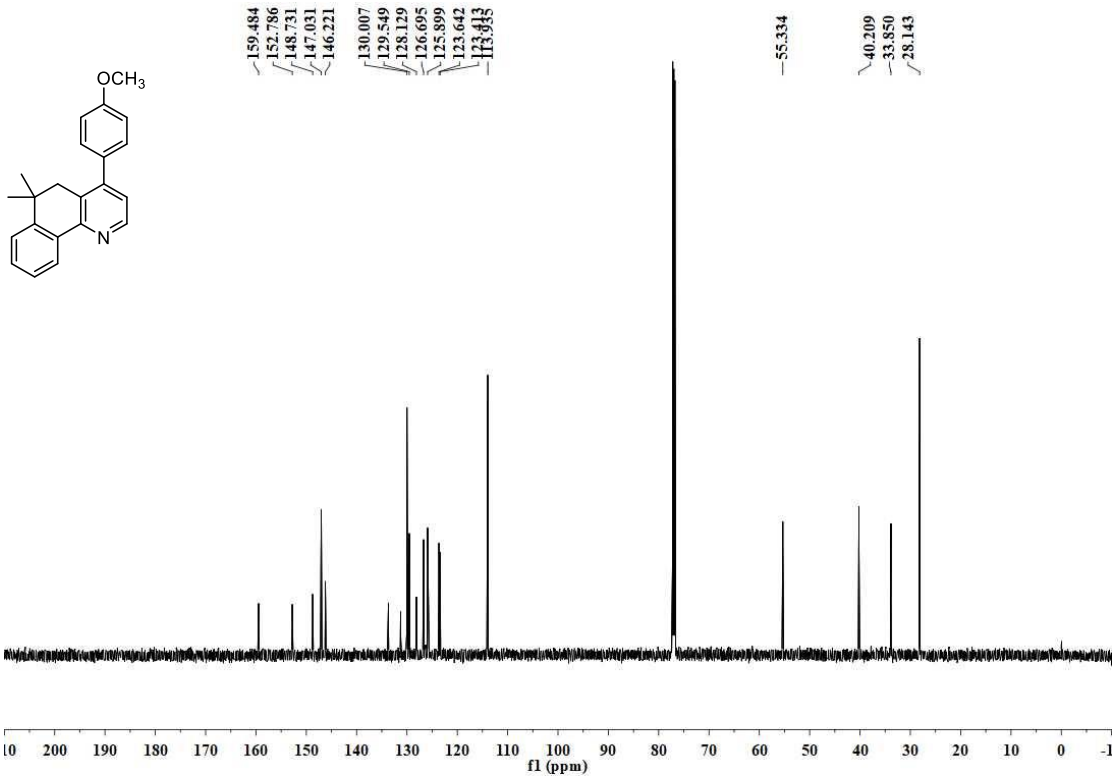
^{13}C NMR Spectrum of 30 (151 MHz, $CDCl_3$)



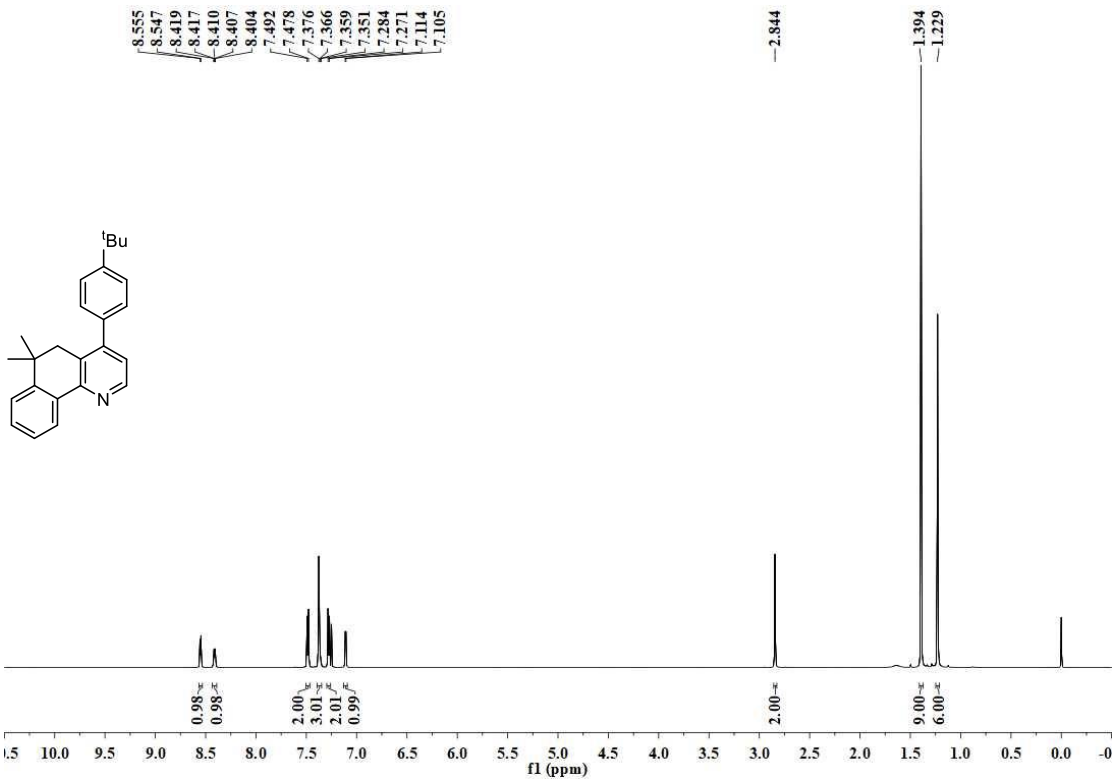
^{1}H NMR Spectrum of 31 (600 MHz, $CDCl_3$)



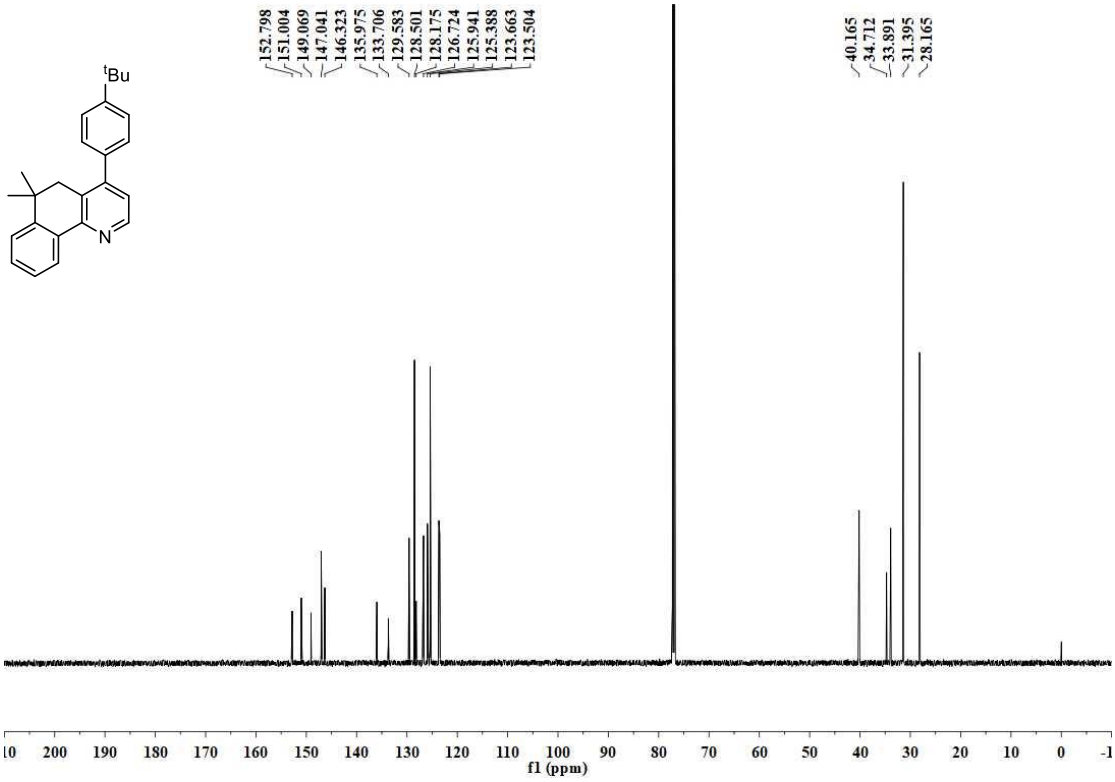
^{13}C NMR Spectrum of 31 (151 MHz, $CDCl_3$)



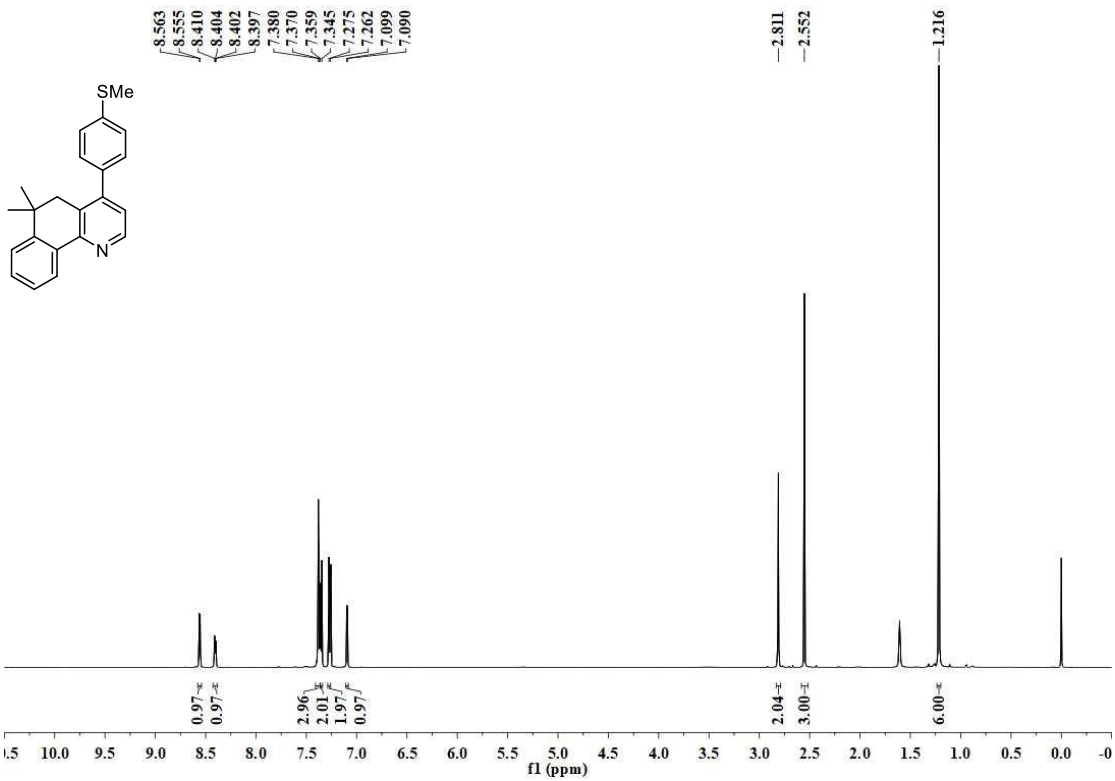
^{1}H NMR Spectrum of 32 (600 MHz, $CDCl_3$)



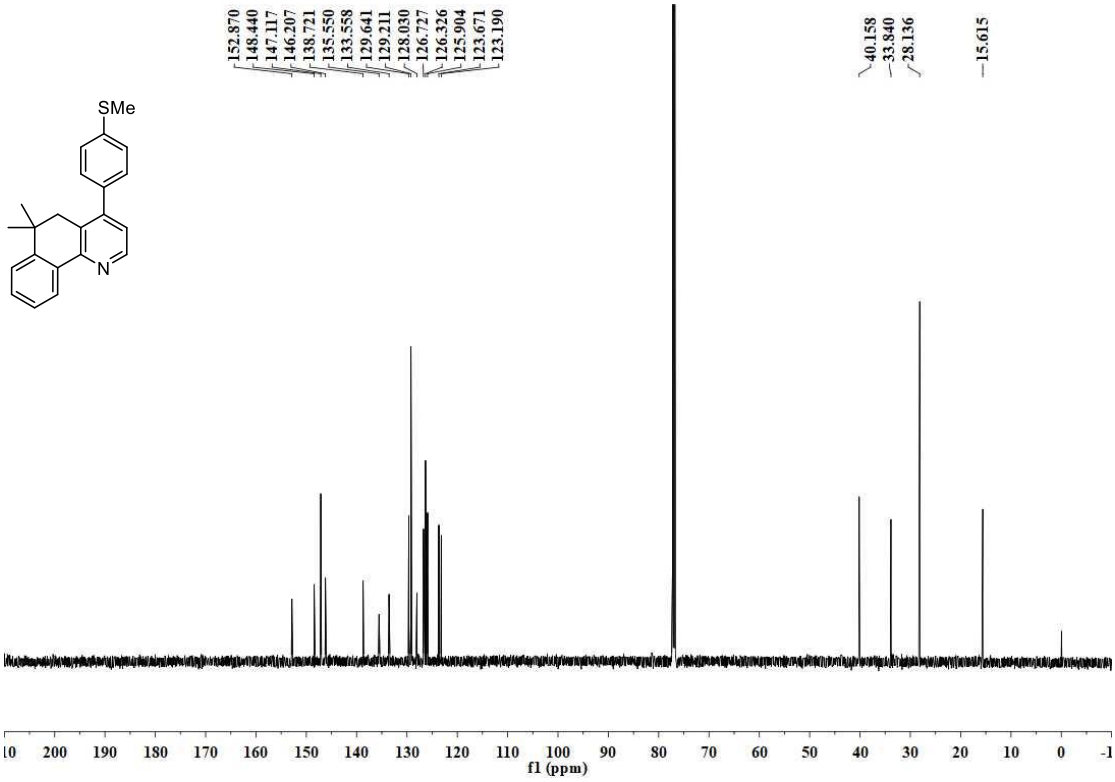
^{13}C NMR Spectrum of 32 (151 MHz, $CDCl_3$)



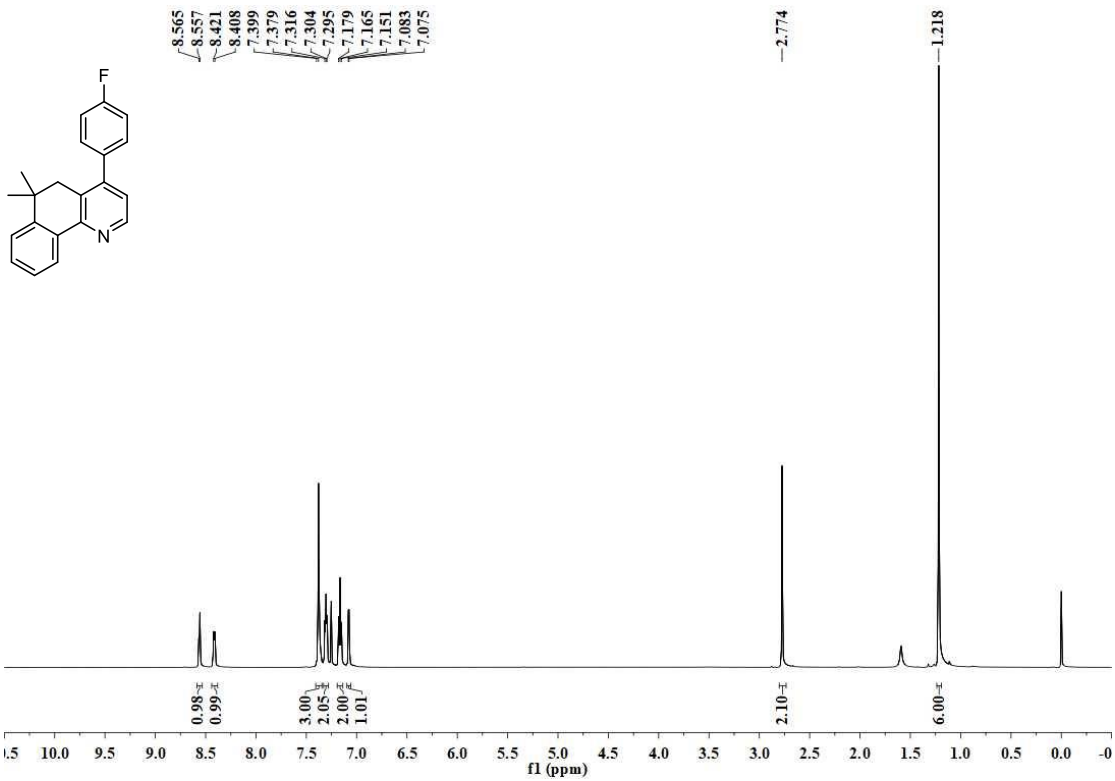
^{1}H NMR Spectrum of 33 (600 MHz, $CDCl_3$)



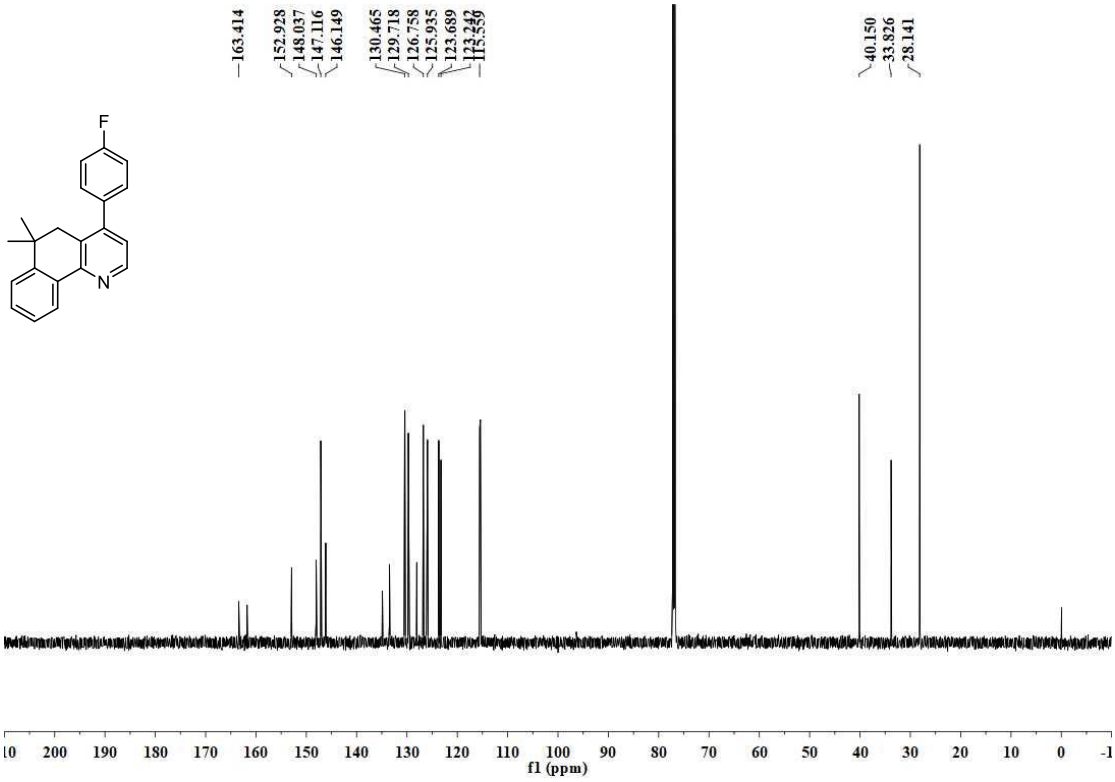
^{13}C NMR Spectrum of 33 (151 MHz, $CDCl_3$)



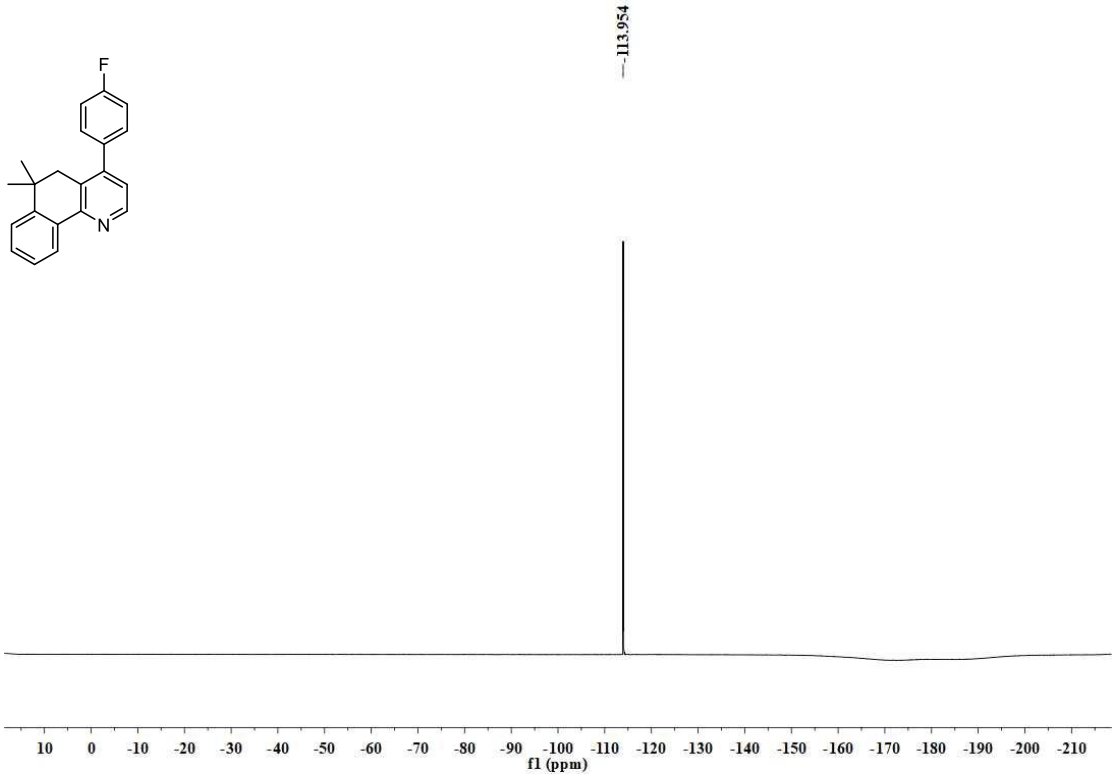
^{1}H NMR Spectrum of 34 (600 MHz, $CDCl_3$)



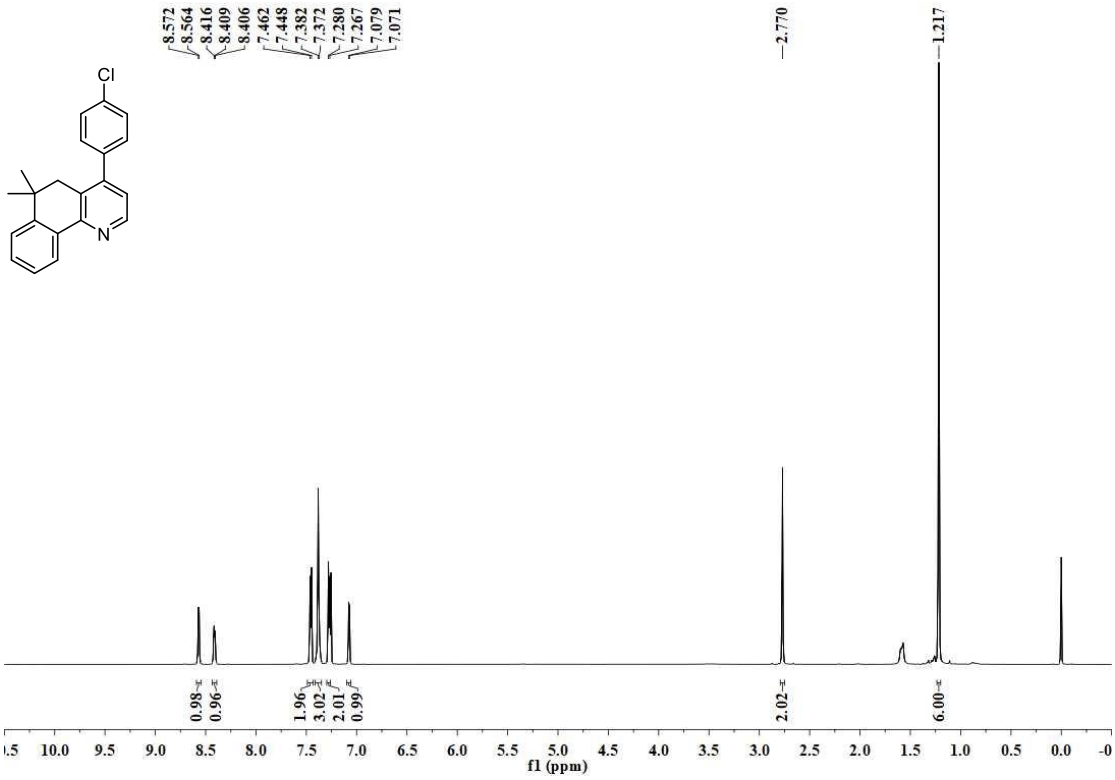
^{13}C NMR Spectrum of 34 (151 MHz, $CDCl_3$)



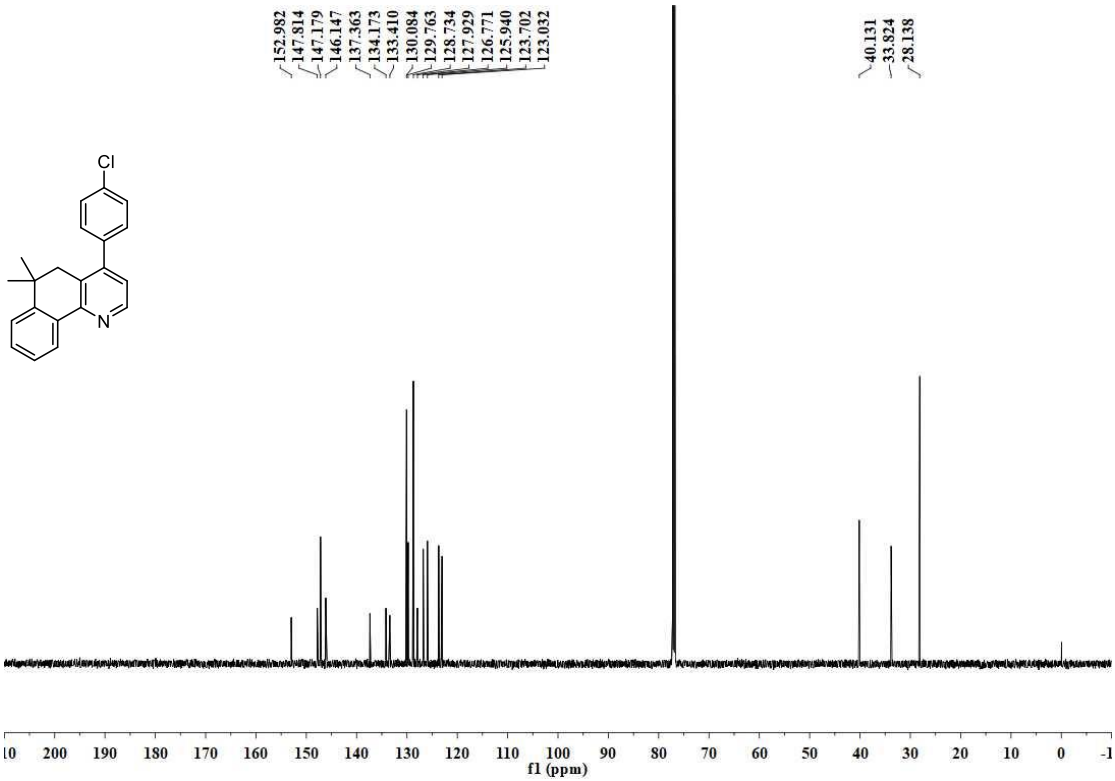
^{19}F NMR Spectrum of 34 (565 MHz, $CDCl_3$)



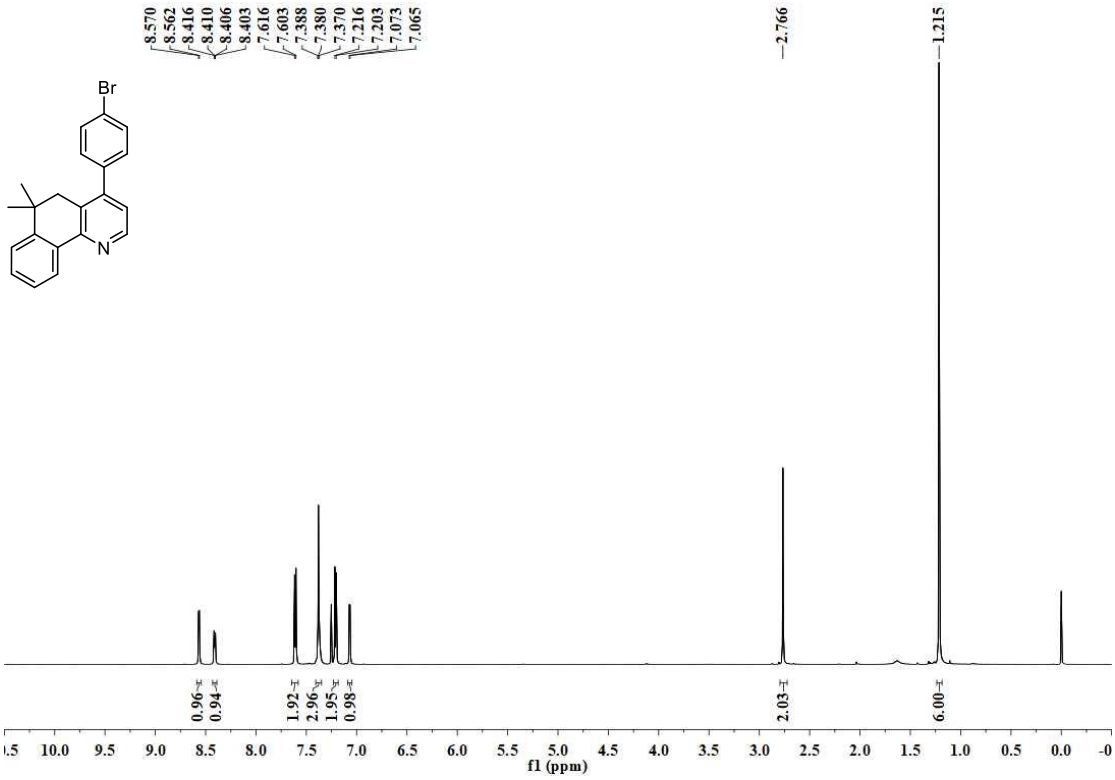
^{1}H NMR Spectrum of 35 (600 MHz, $CDCl_3$)



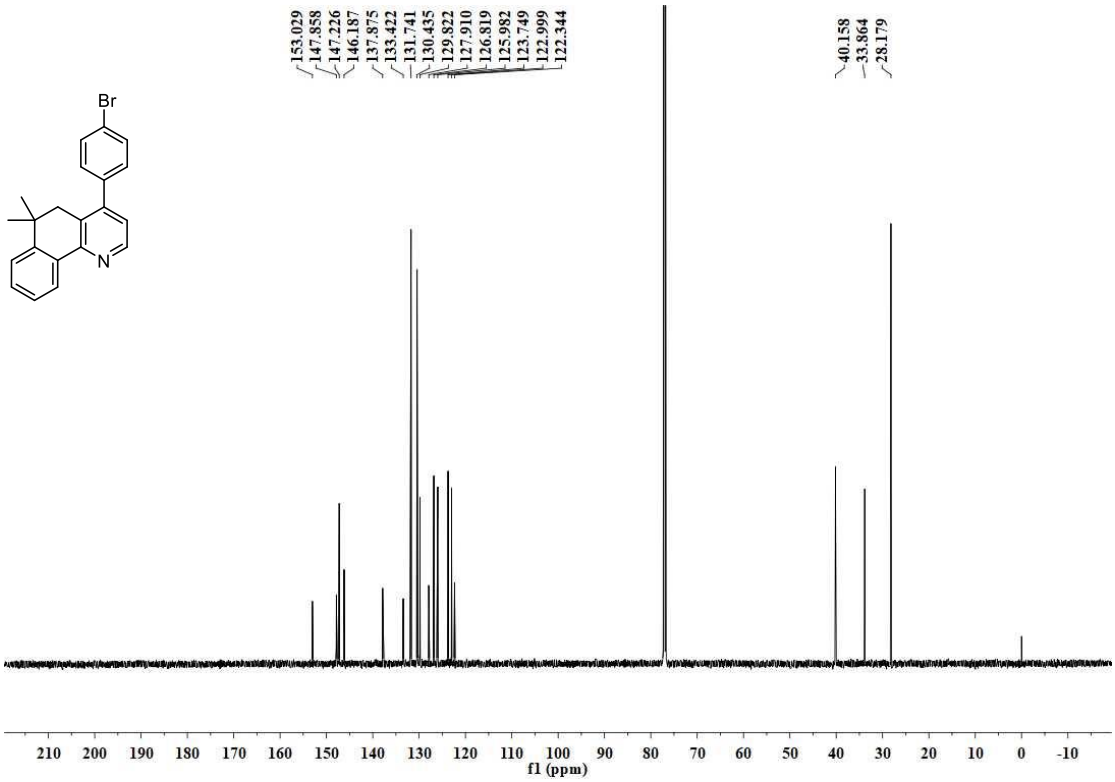
^{13}C NMR Spectrum of 35 (151 MHz, $CDCl_3$)



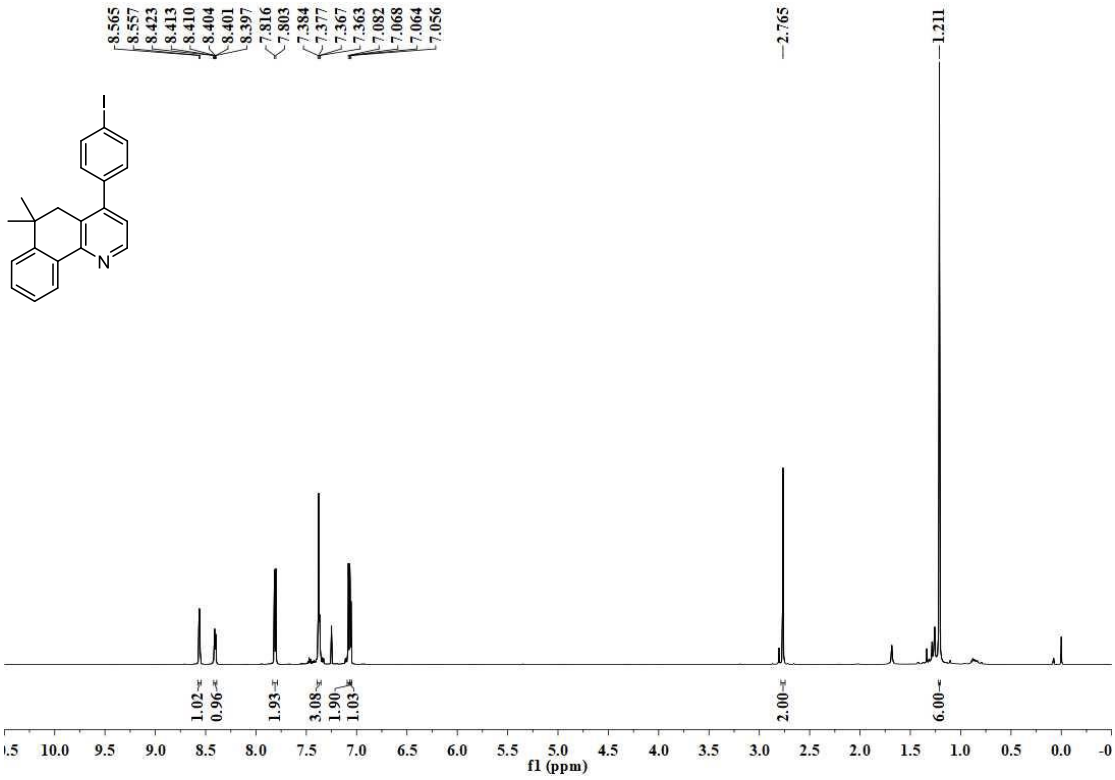
^{1}H NMR Spectrum of 36 (600 MHz, $CDCl_3$)



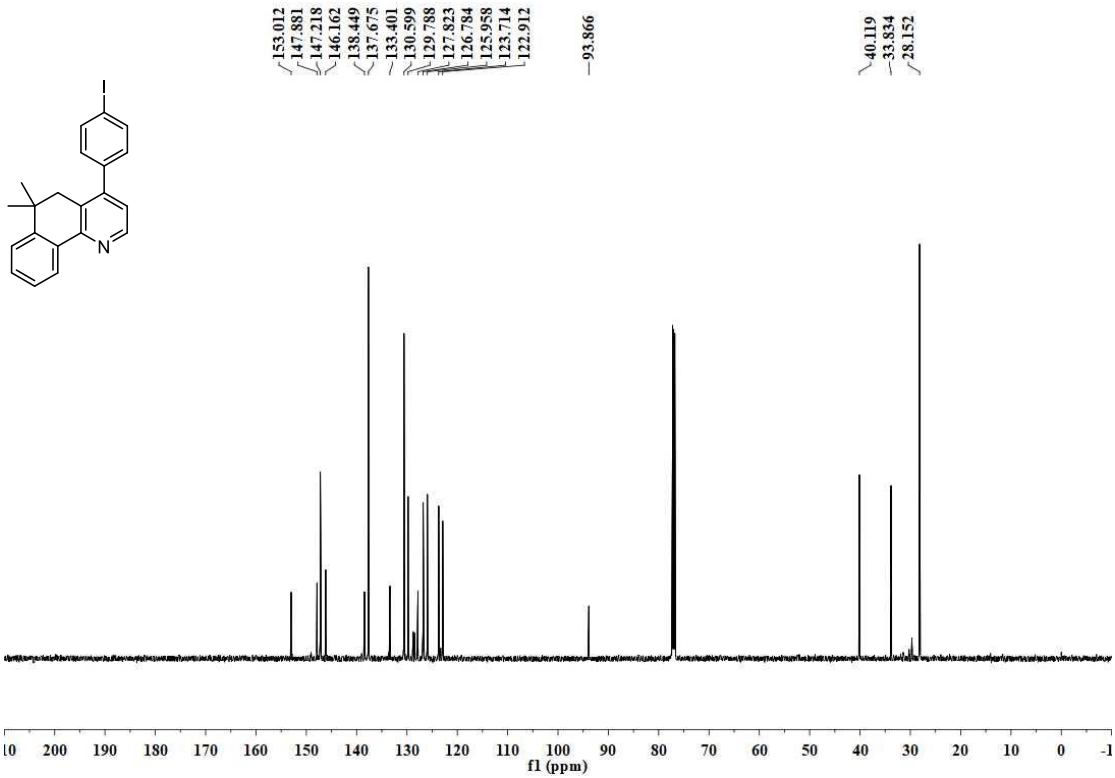
^{13}C NMR Spectrum of 36 (151 MHz, $CDCl_3$)



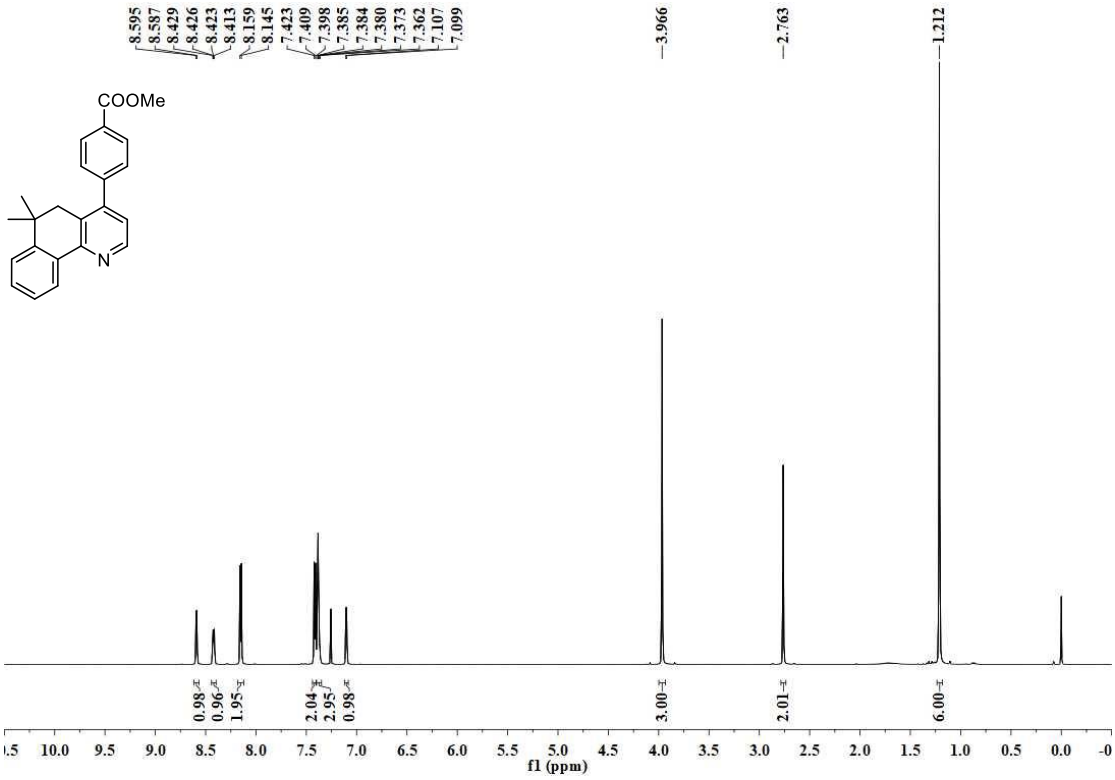
^{1}H NMR Spectrum of 37 (600 MHz, $CDCl_3$)



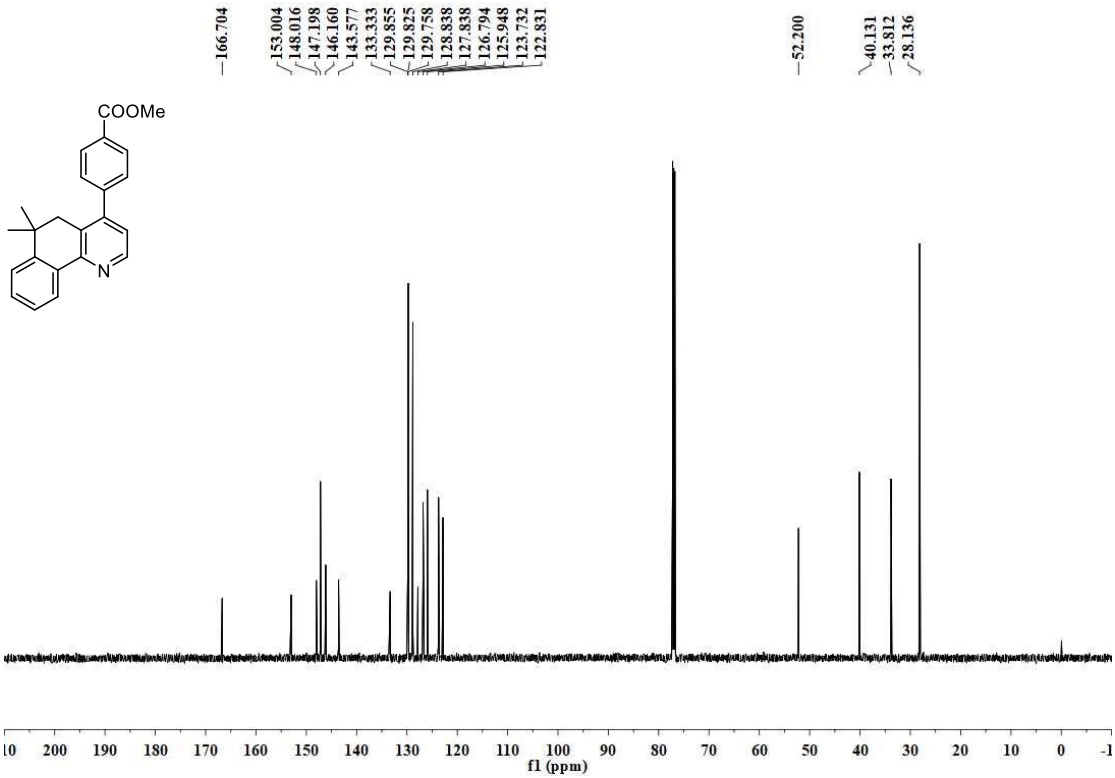
^{13}C NMR Spectrum of 37 (151 MHz, $CDCl_3$)



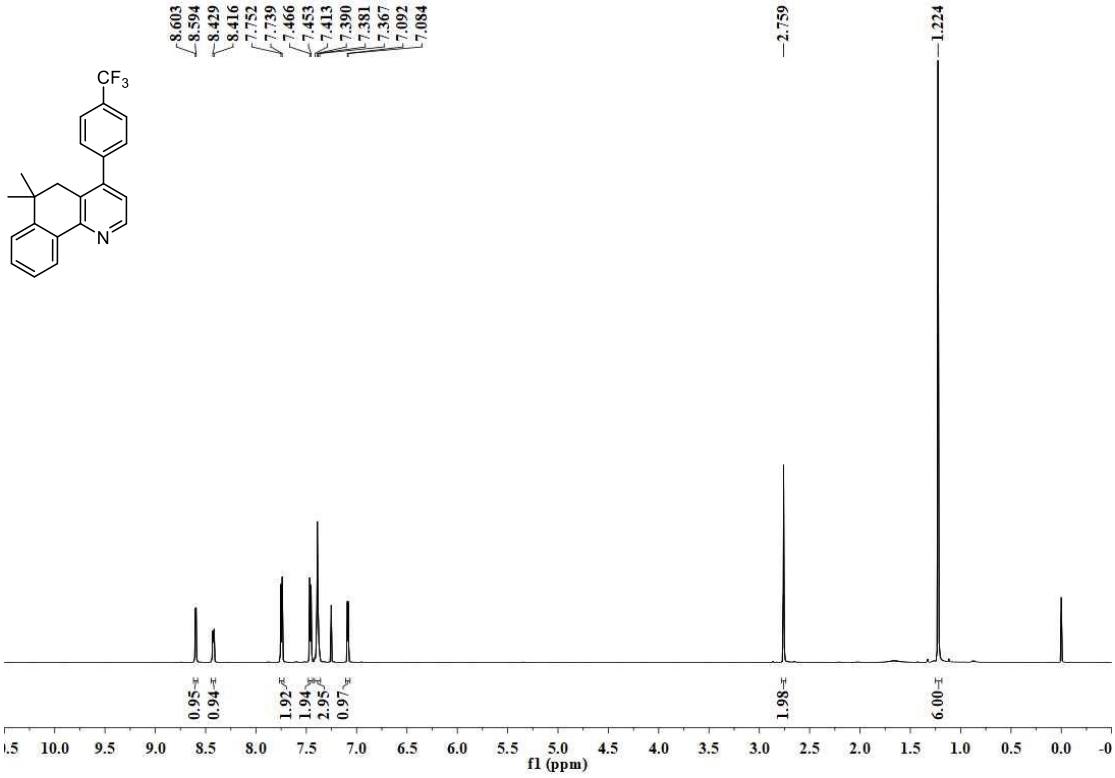
^{1}H NMR Spectrum of 38 (600 MHz, $CDCl_3$)



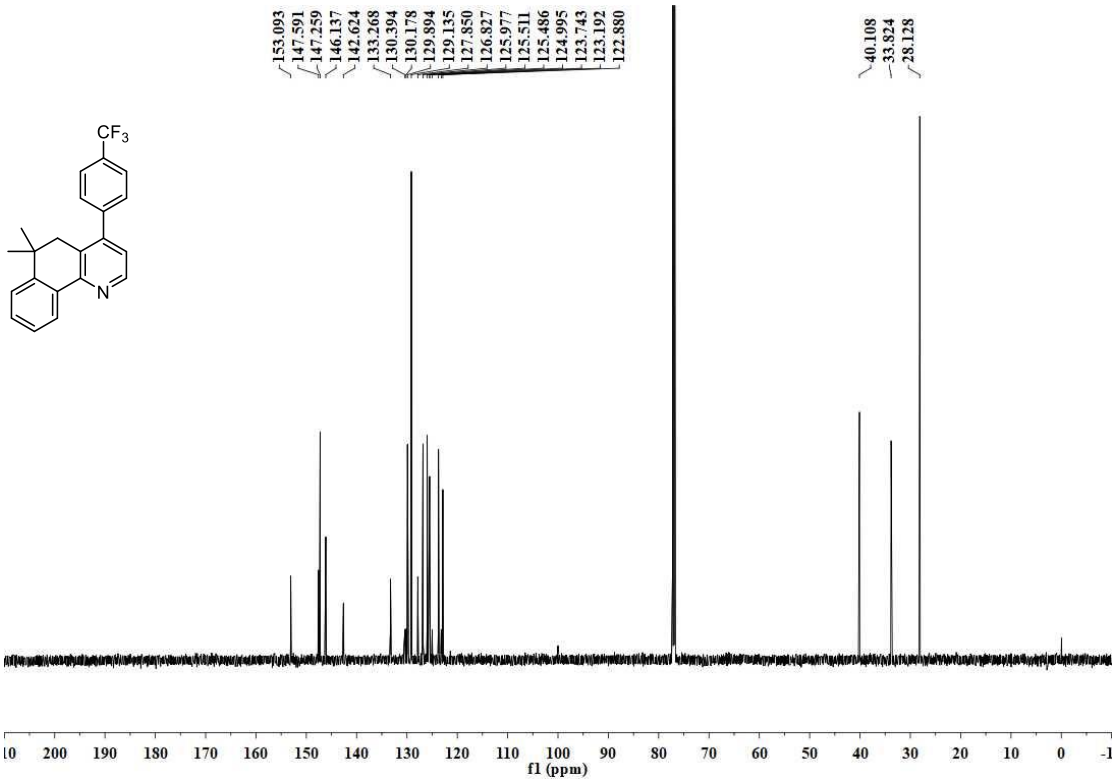
^{13}C NMR Spectrum of 38 (151 MHz, $CDCl_3$)



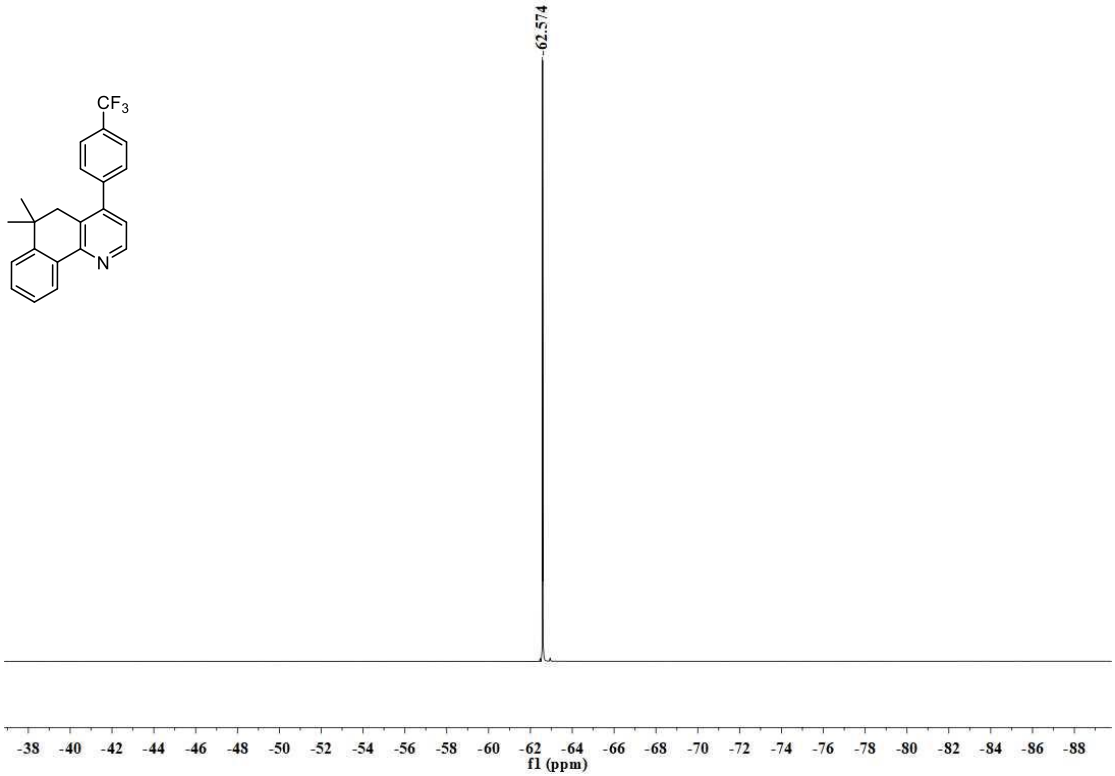
^{1}H NMR Spectrum of 39 (600 MHz, $CDCl_3$)



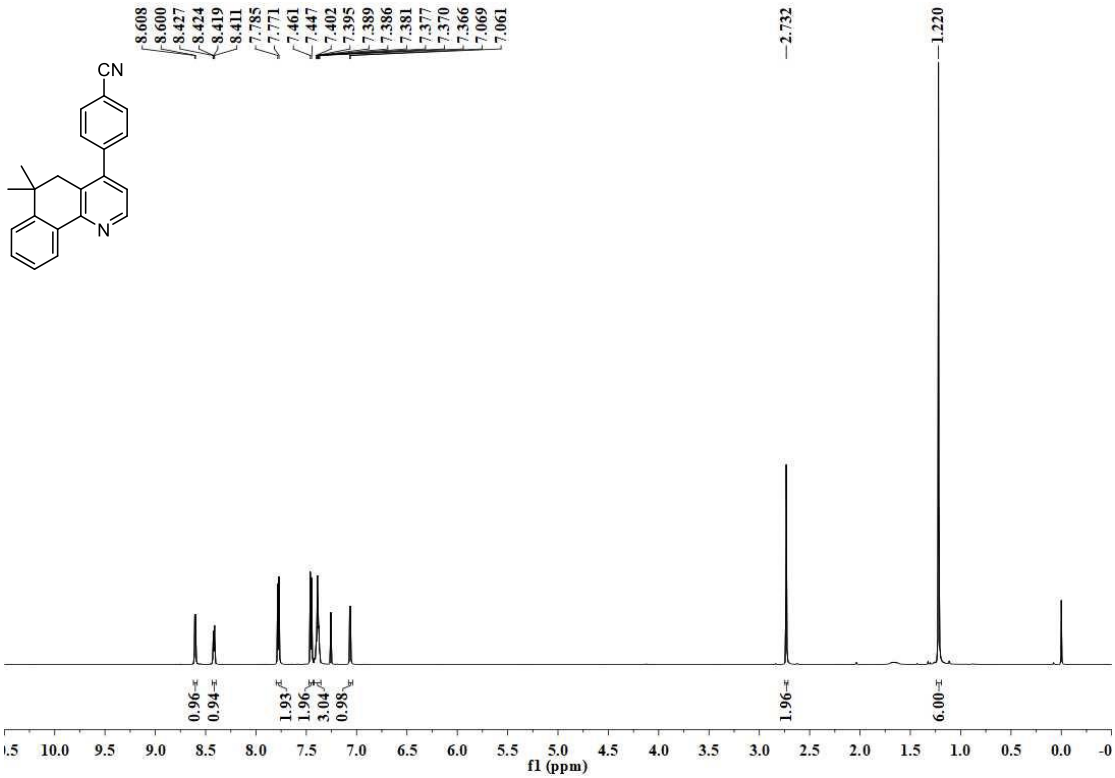
^{13}C NMR Spectrum of 39 (151 MHz, $CDCl_3$)



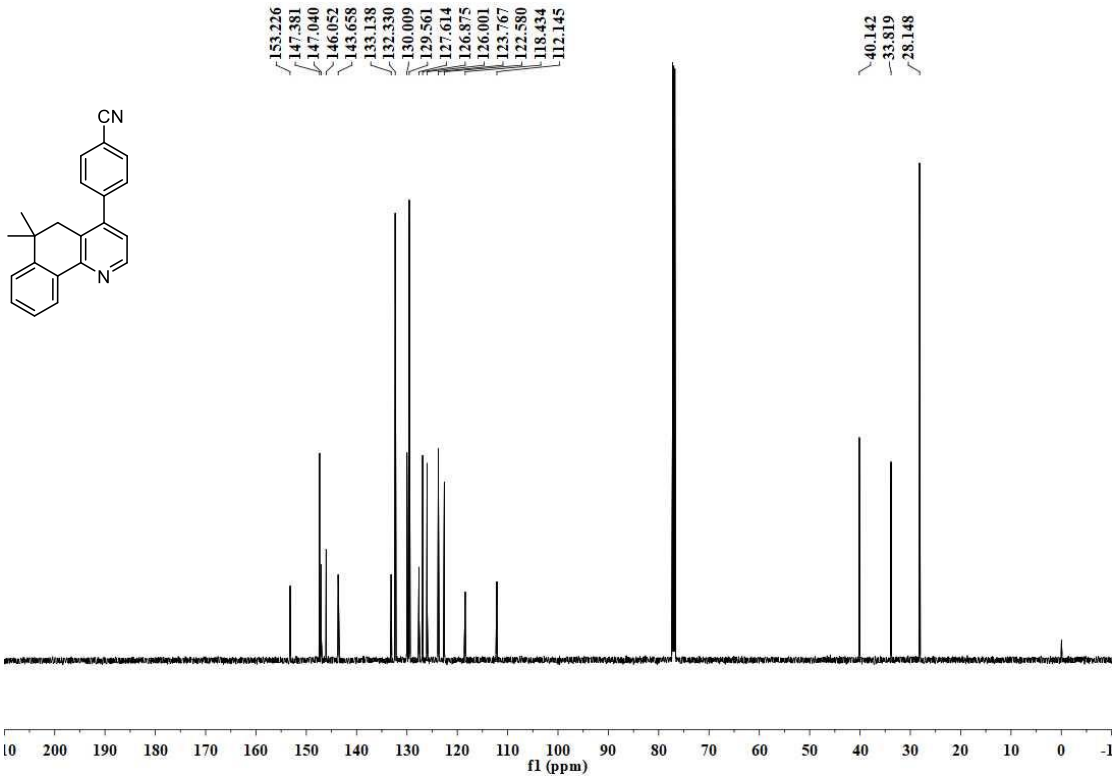
^{19}F NMR Spectrum of 39 (565 MHz, $CDCl_3$)



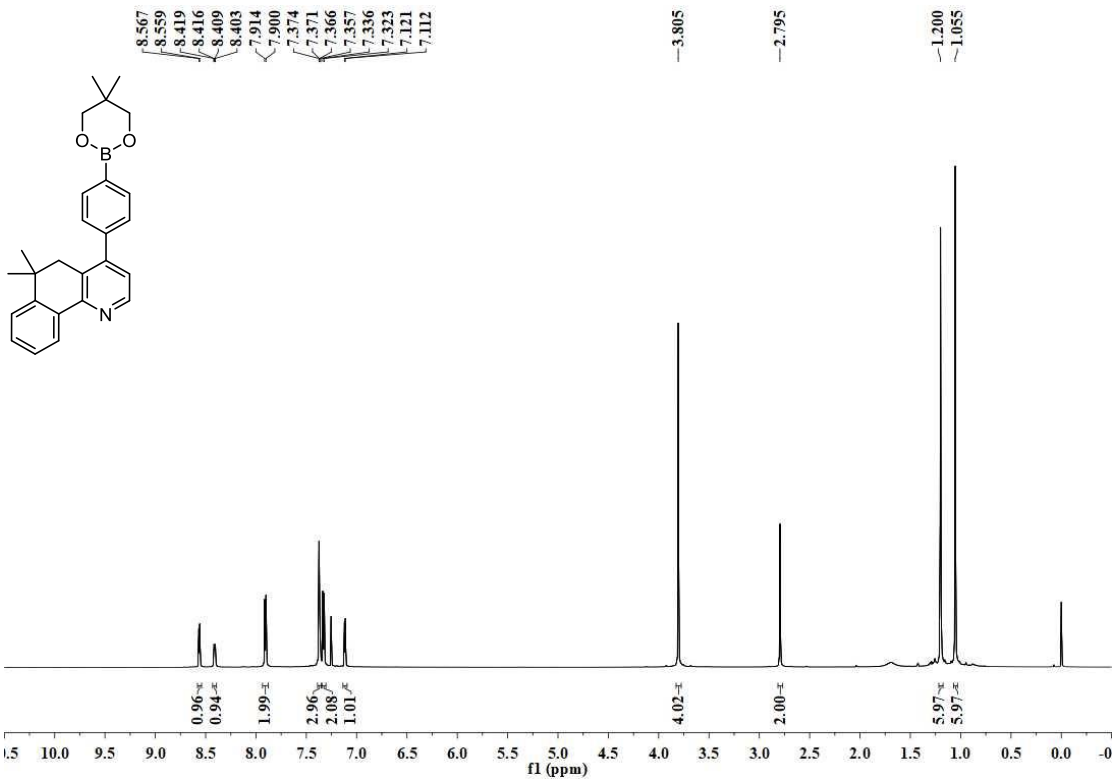
^{1}H NMR Spectrum of 40 (600 MHz, $CDCl_3$)



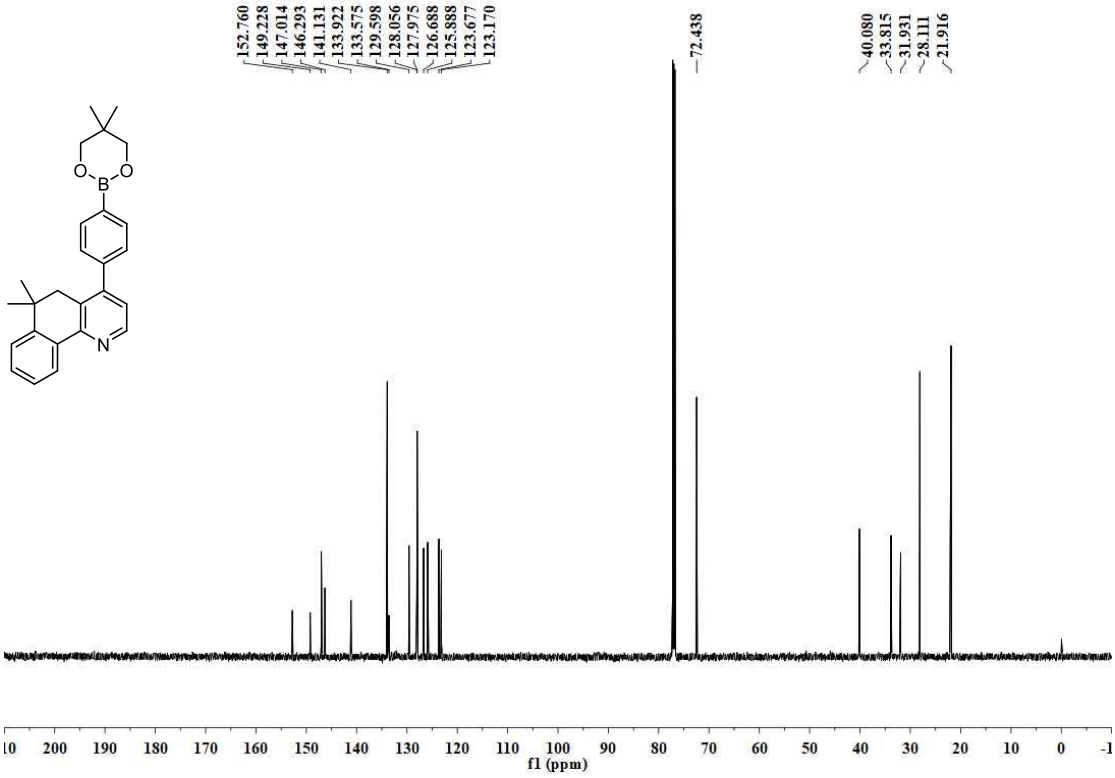
^{13}C NMR Spectrum of 40 (151 MHz, $CDCl_3$)



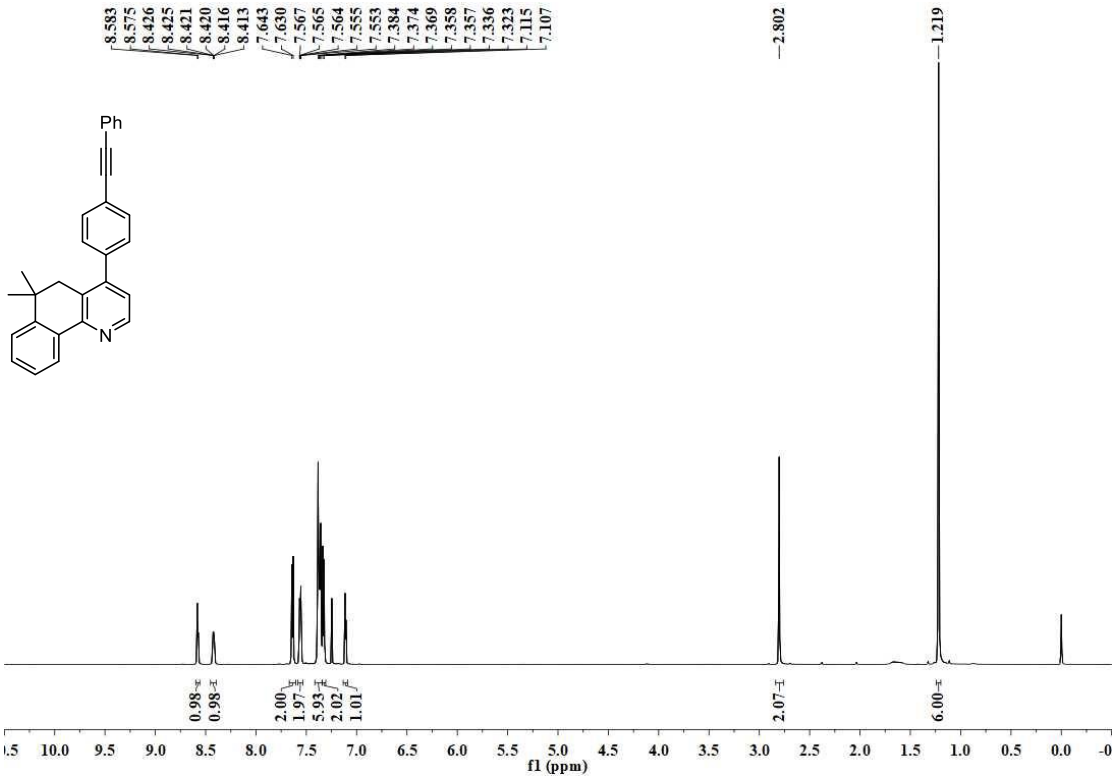
^{1}H NMR Spectrum of 41 (600 MHz, $CDCl_3$)



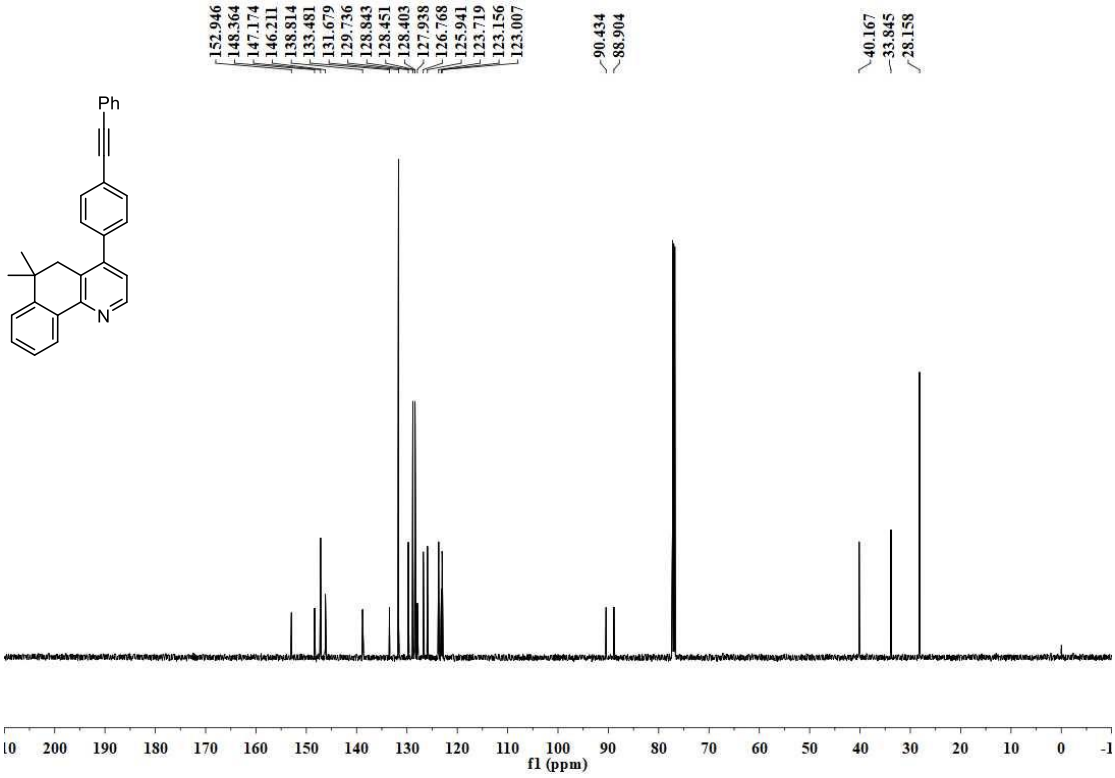
^{13}C NMR Spectrum of 41 (151 MHz, $CDCl_3$)



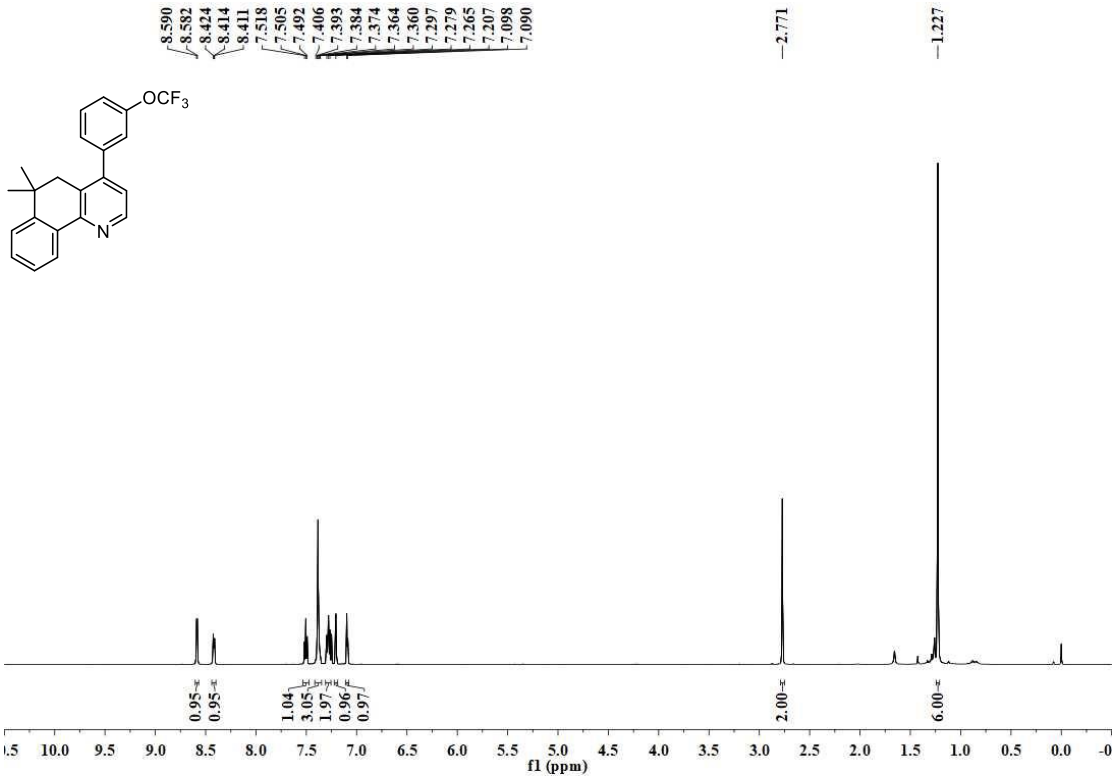
^{1}H NMR Spectrum of 42 (600 MHz, $CDCl_3$)



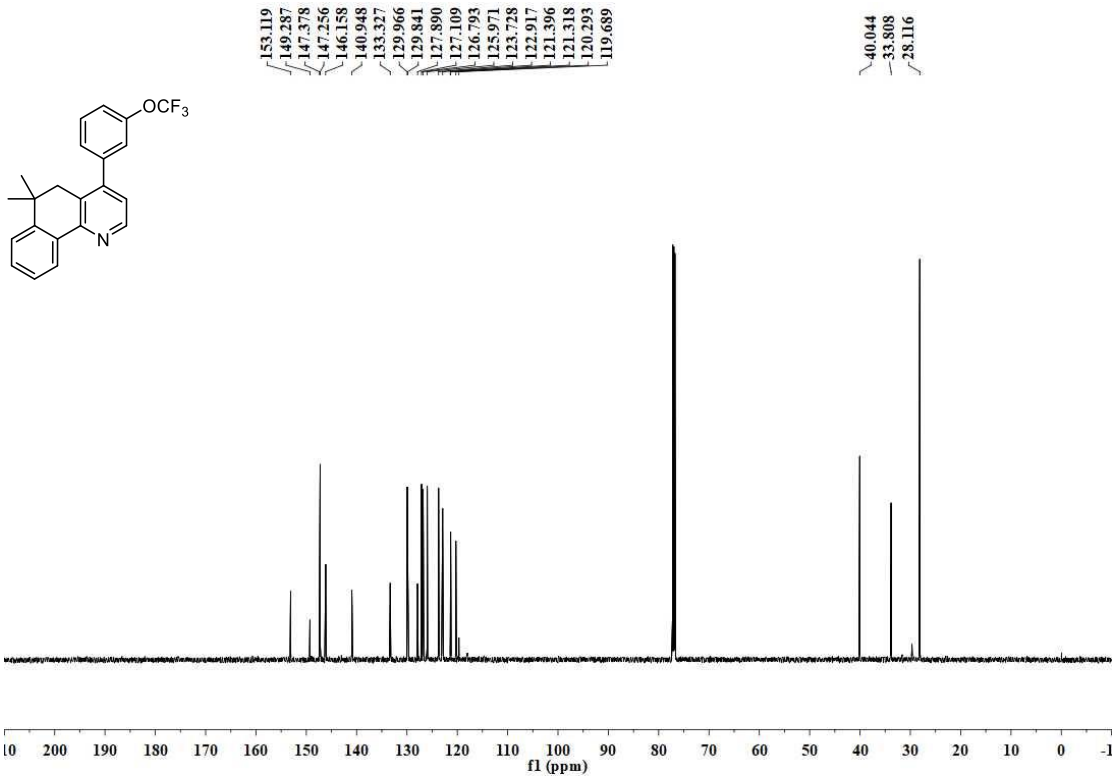
^{13}C NMR Spectrum of 42 (151 MHz, $CDCl_3$)



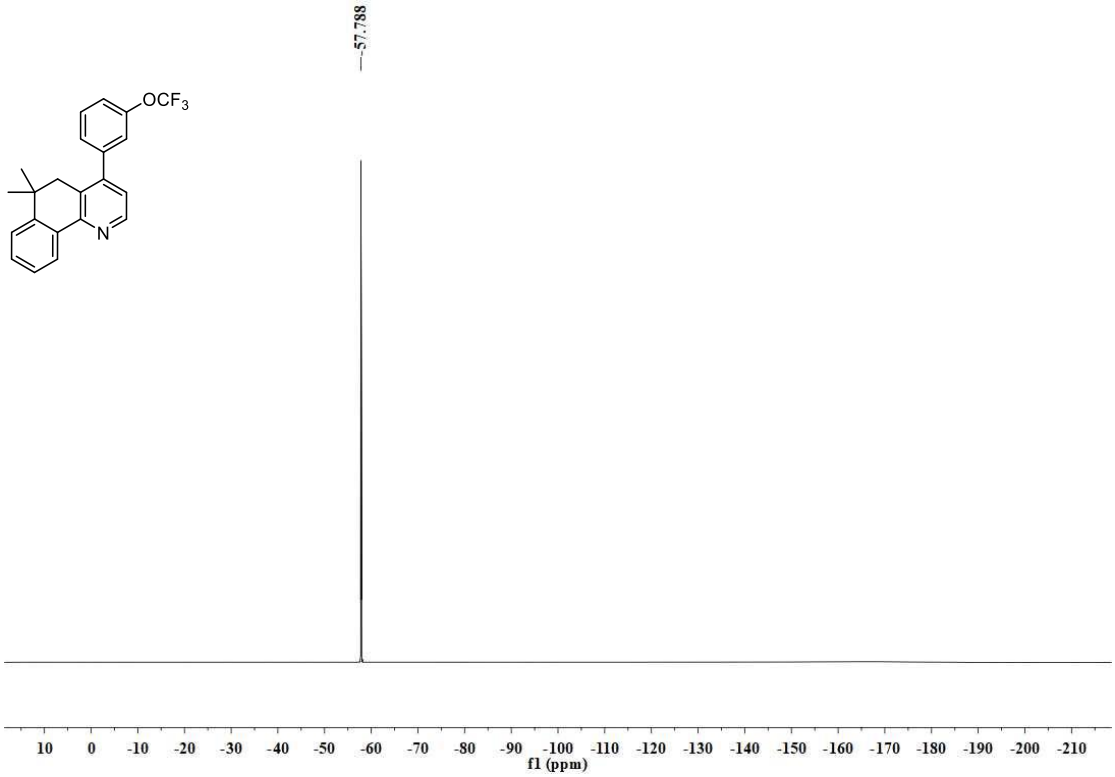
^{1}H NMR Spectrum of 43 (600 MHz, $CDCl_3$)



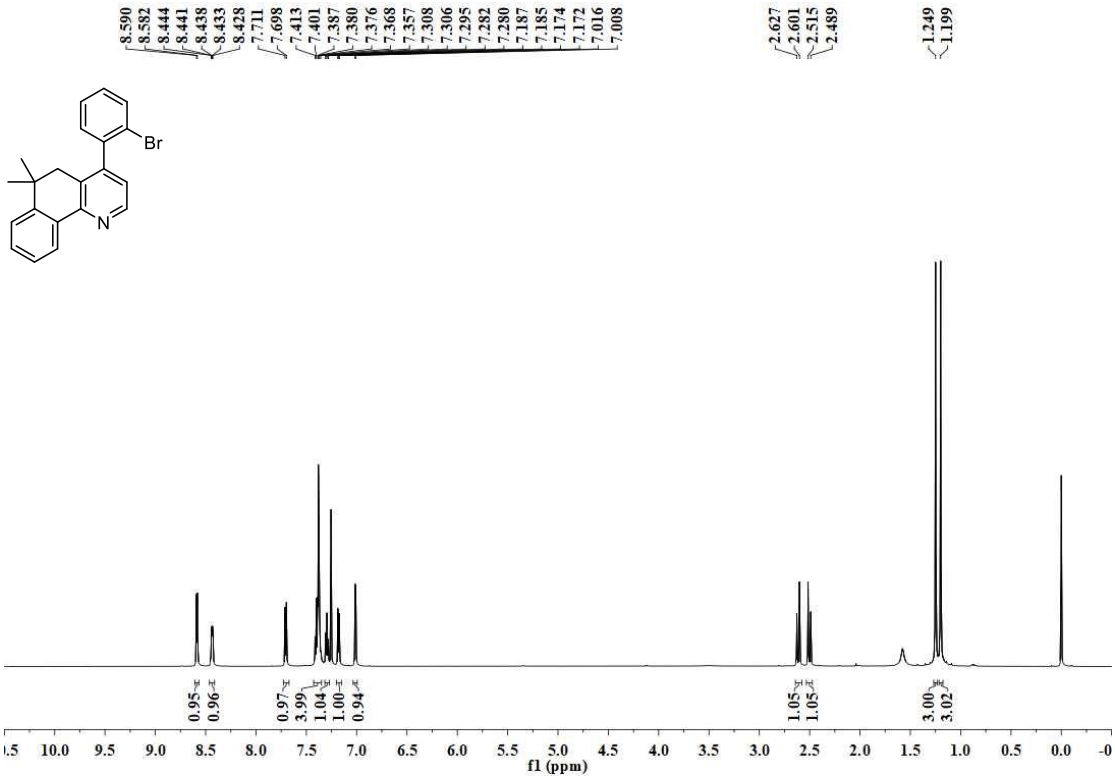
^{13}C NMR Spectrum of 43 (151 MHz, $CDCl_3$)



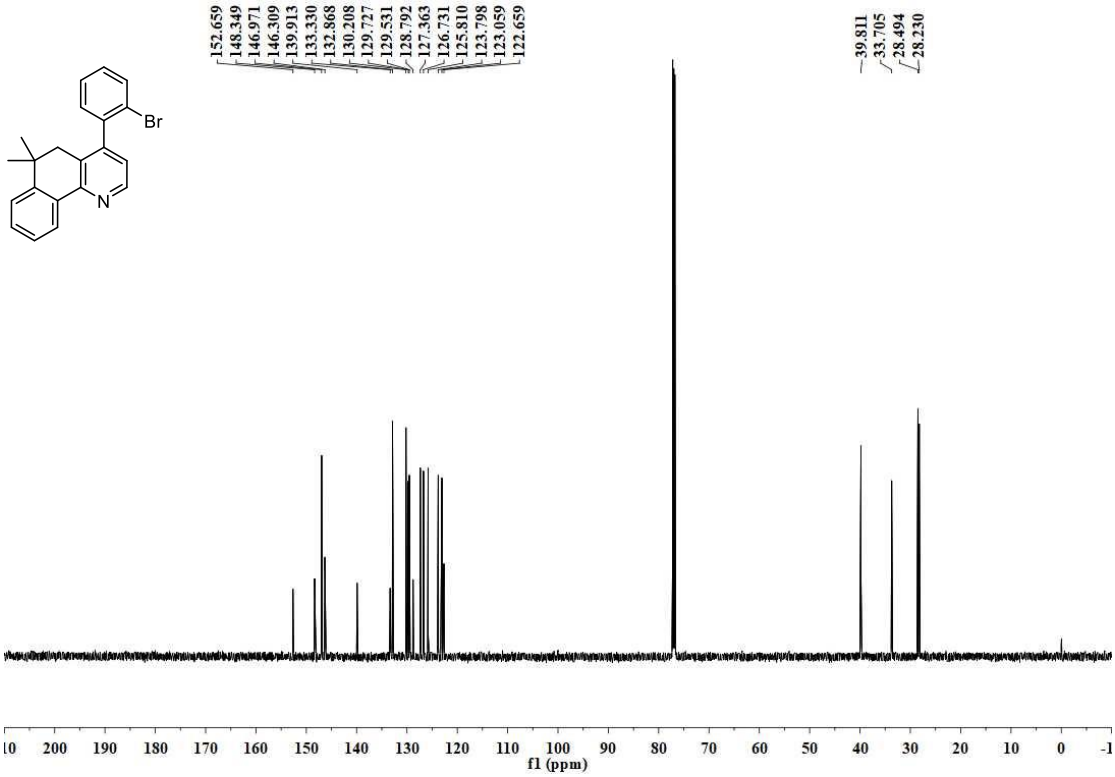
^{19}F NMR Spectrum of 43 (565 MHz, $CDCl_3$)



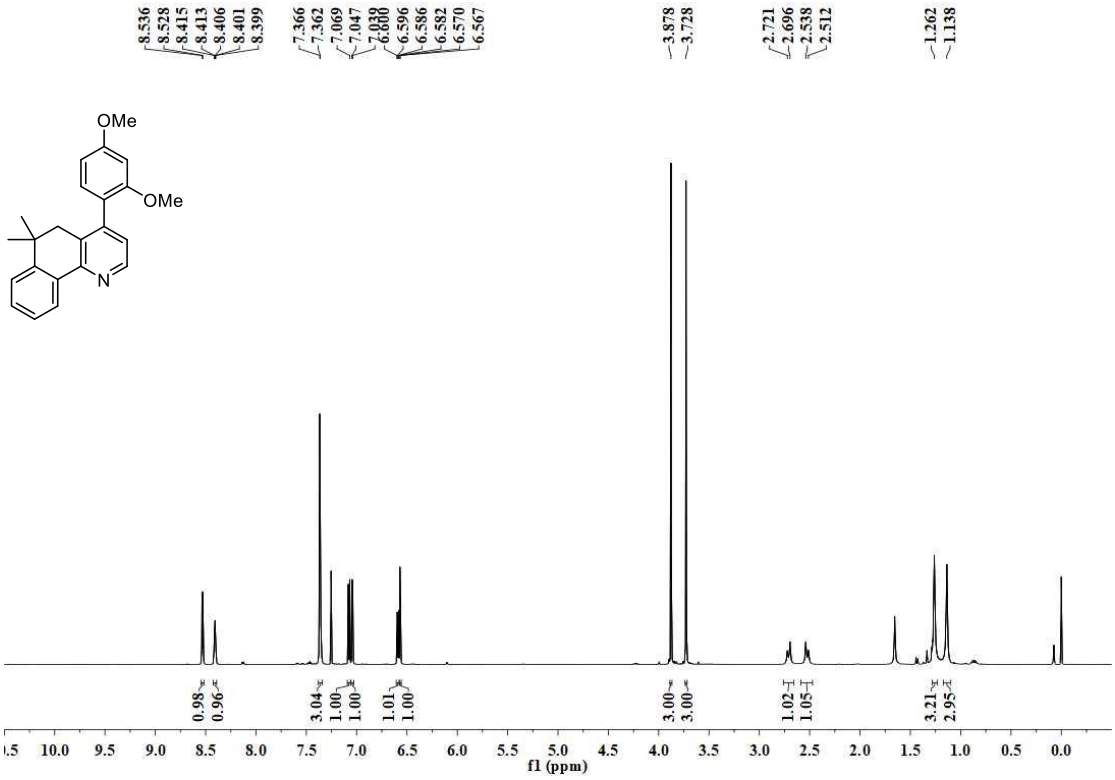
^{1}H NMR Spectrum of 44 (600 MHz, $CDCl_3$)



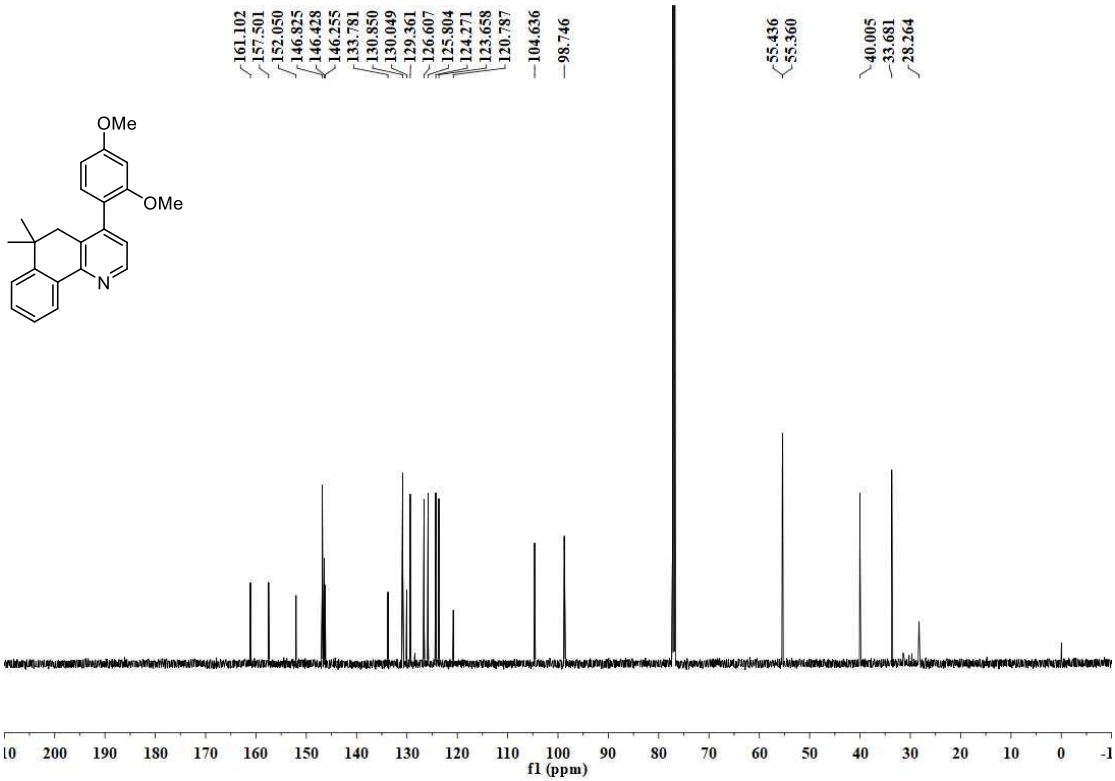
^{13}C NMR Spectrum of 44 (151 MHz, $CDCl_3$)



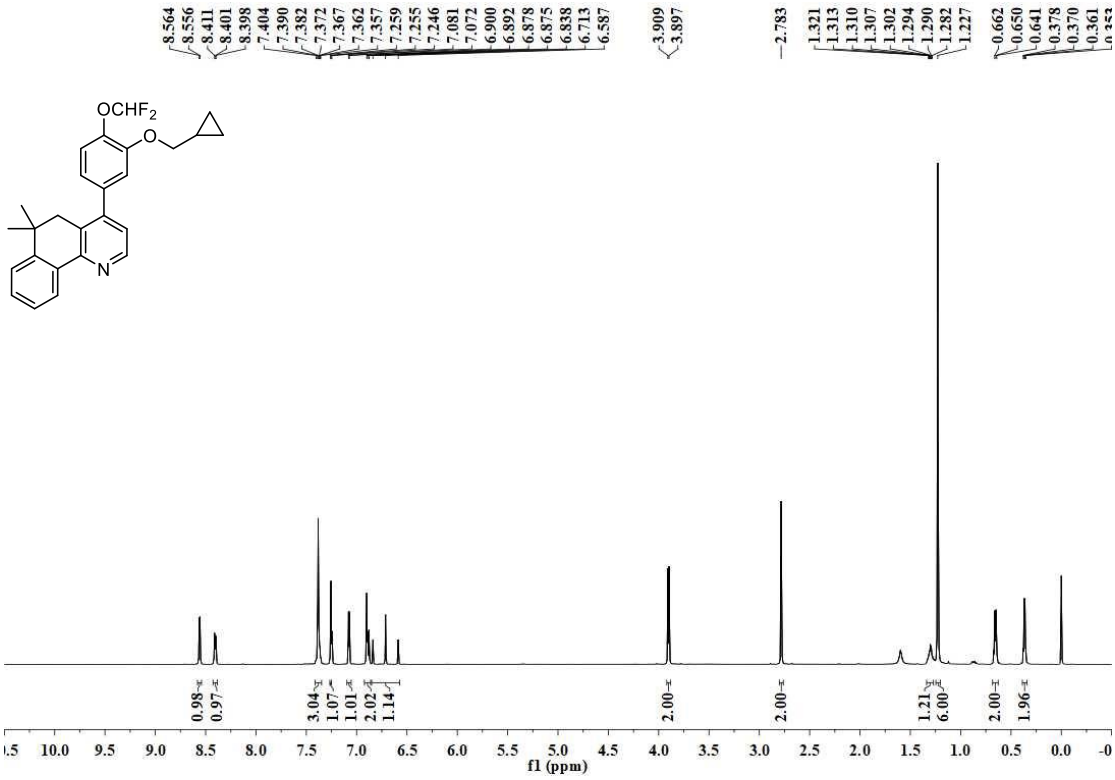
^{1}H NMR Spectrum of 45 (600 MHz, $CDCl_3$)



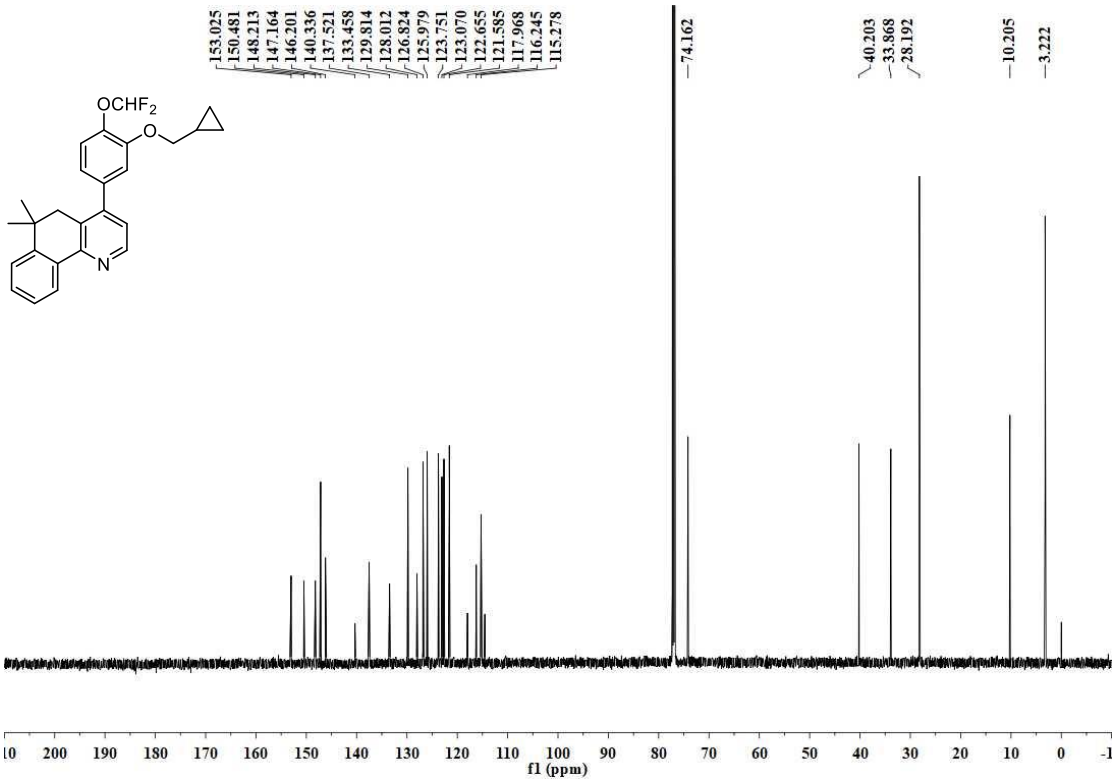
^{13}C NMR Spectrum of 45 (151 MHz, $CDCl_3$)



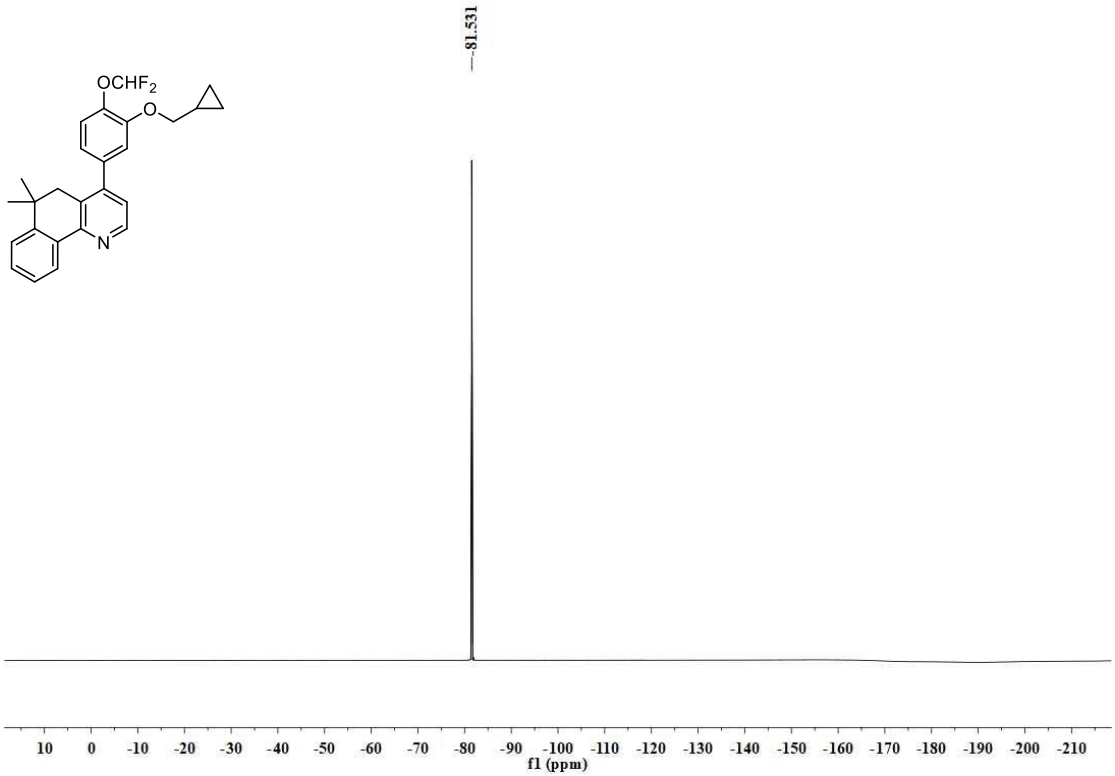
^{1}H NMR Spectrum of 46 (600 MHz, $CDCl_3$)



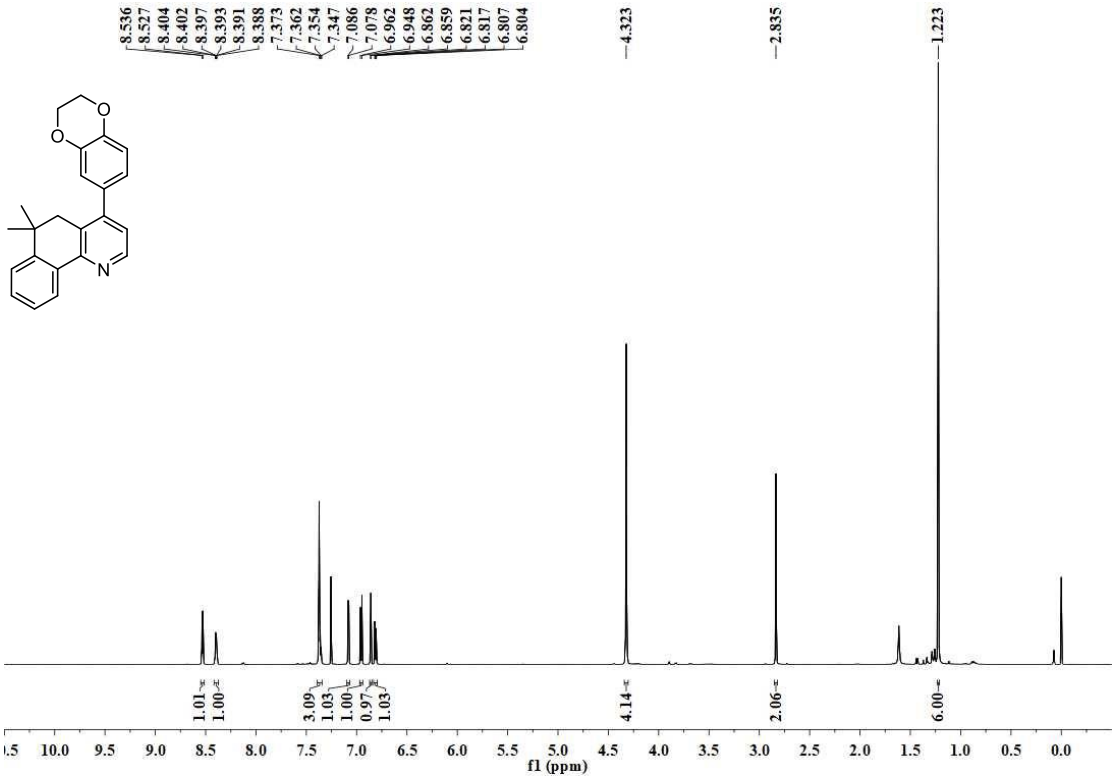
^{13}C NMR Spectrum of 46 (151 MHz, $CDCl_3$)



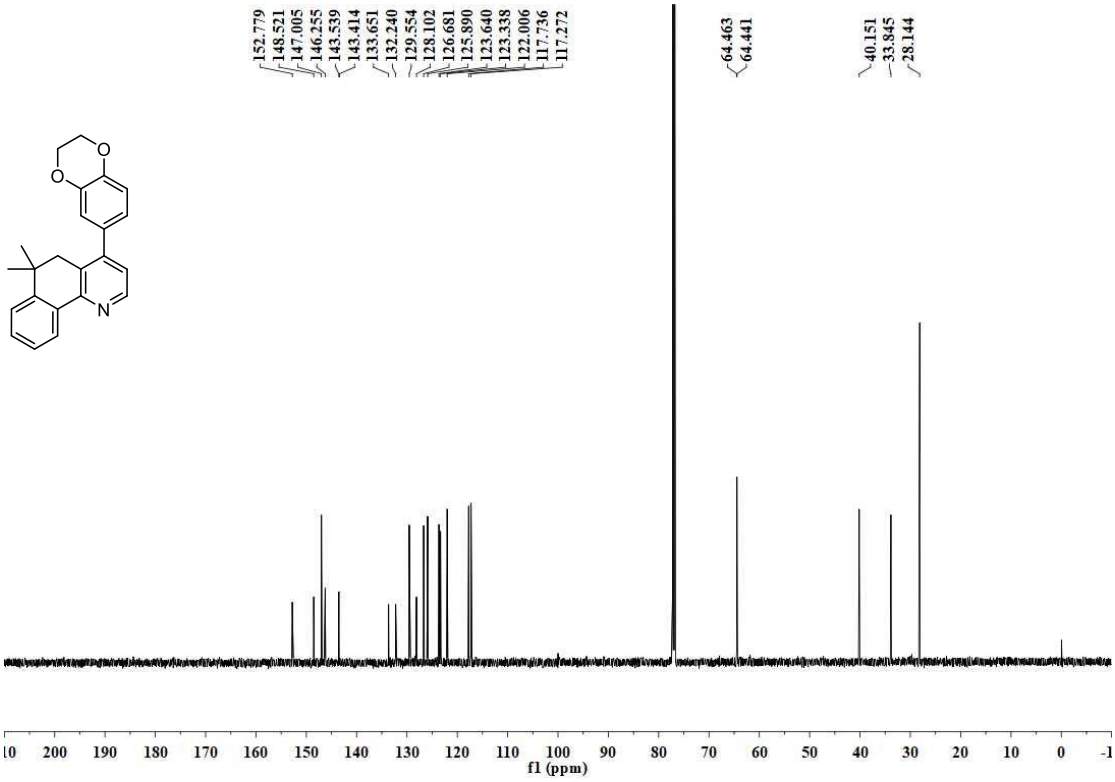
^{19}F NMR Spectrum of 46 (565 MHz, $CDCl_3$)



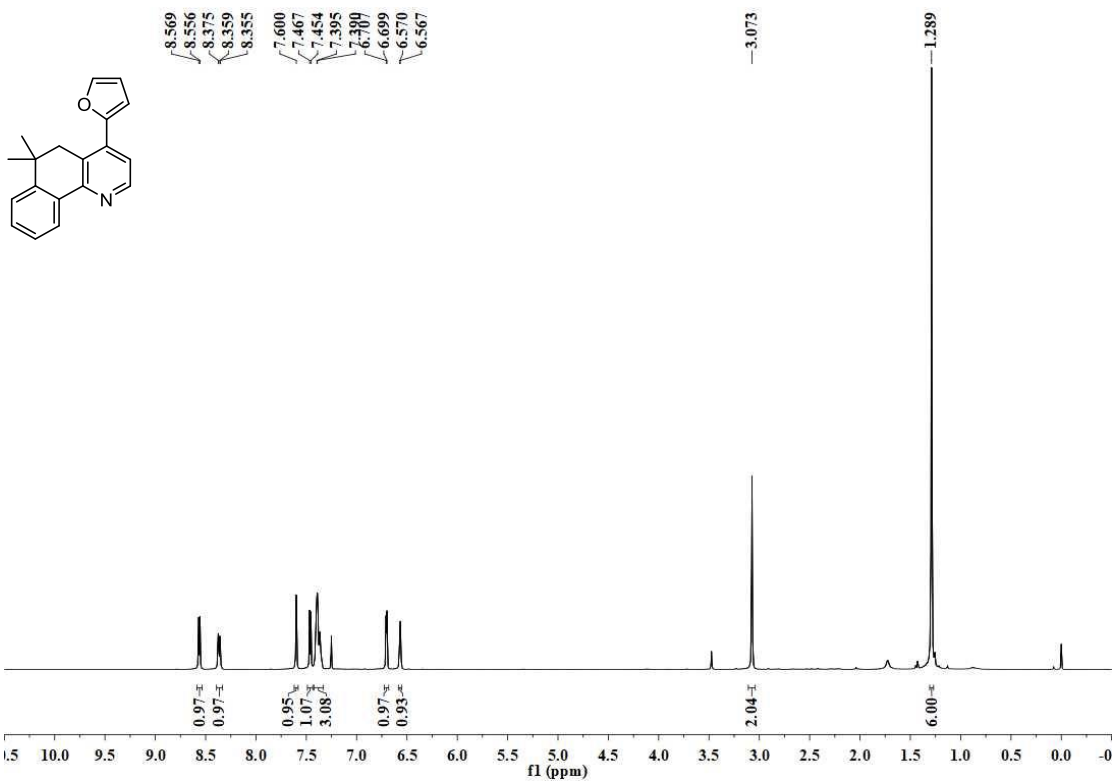
^{1}H NMR Spectrum of 47 (600 MHz, $CDCl_3$)



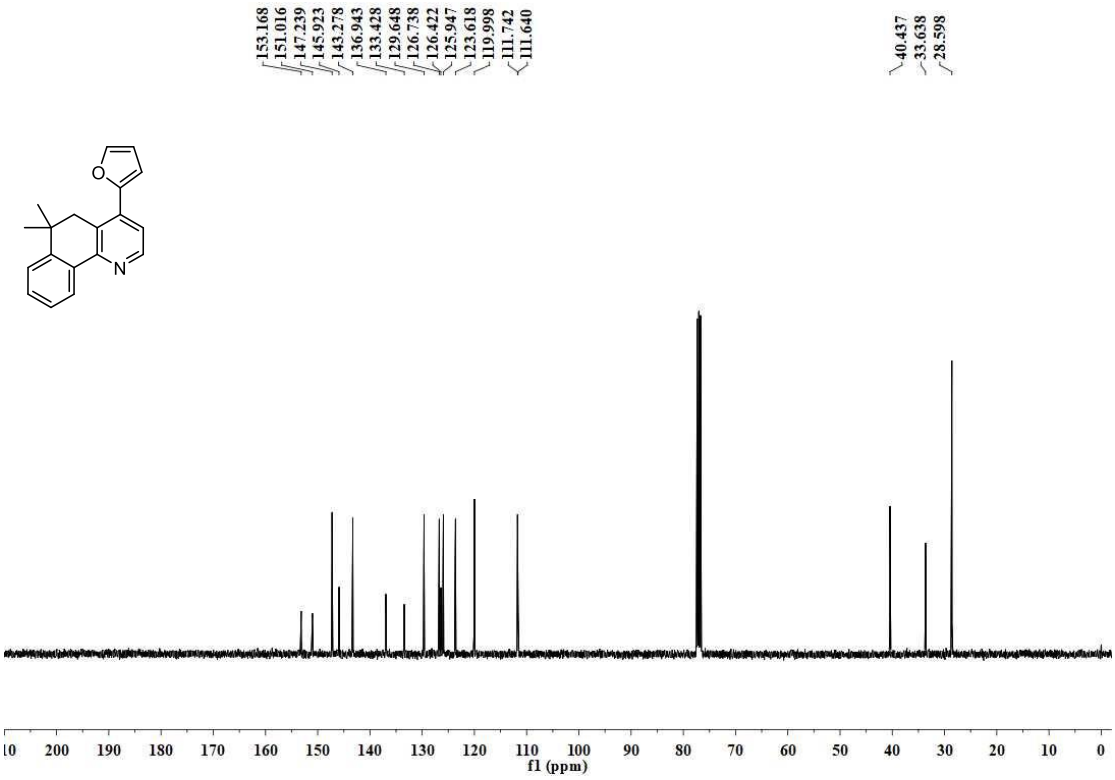
^{13}C NMR Spectrum of 47 (151 MHz, $CDCl_3$)



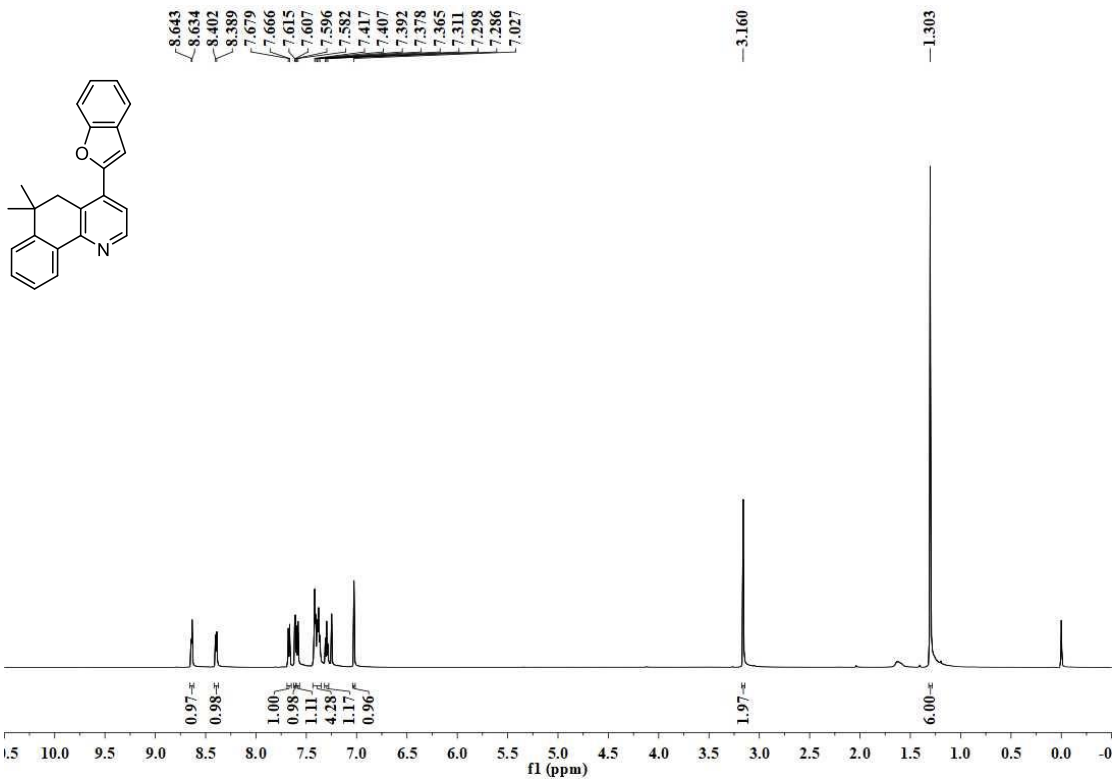
^{1}H NMR Spectrum of 48 (400 MHz, $CDCl_3$)



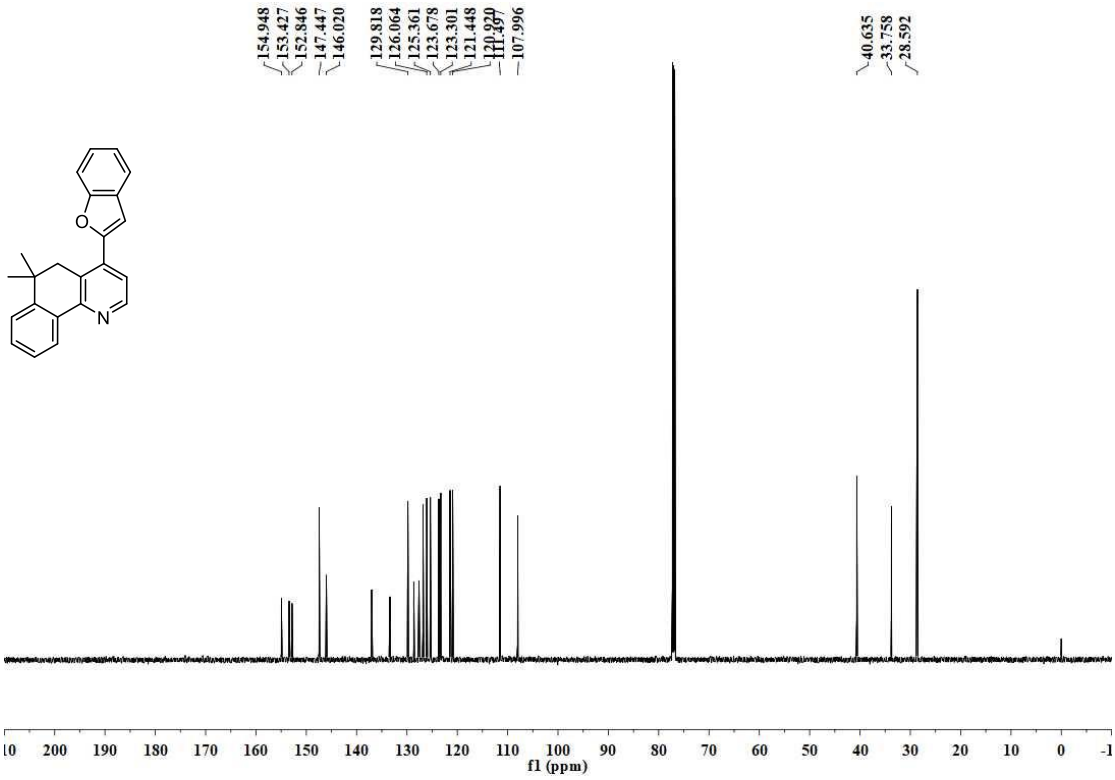
^{13}C NMR Spectrum of 48 (101 MHz, $CDCl_3$)



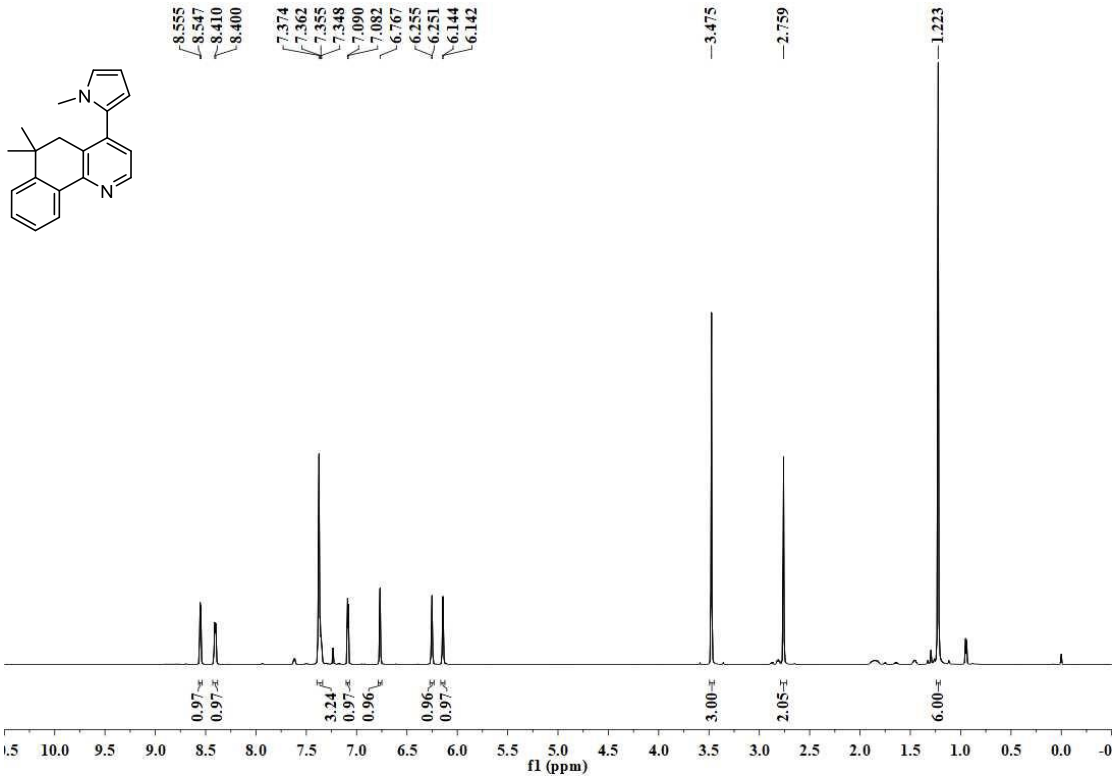
^{1}H NMR Spectrum of 49 (600 MHz, $CDCl_3$)



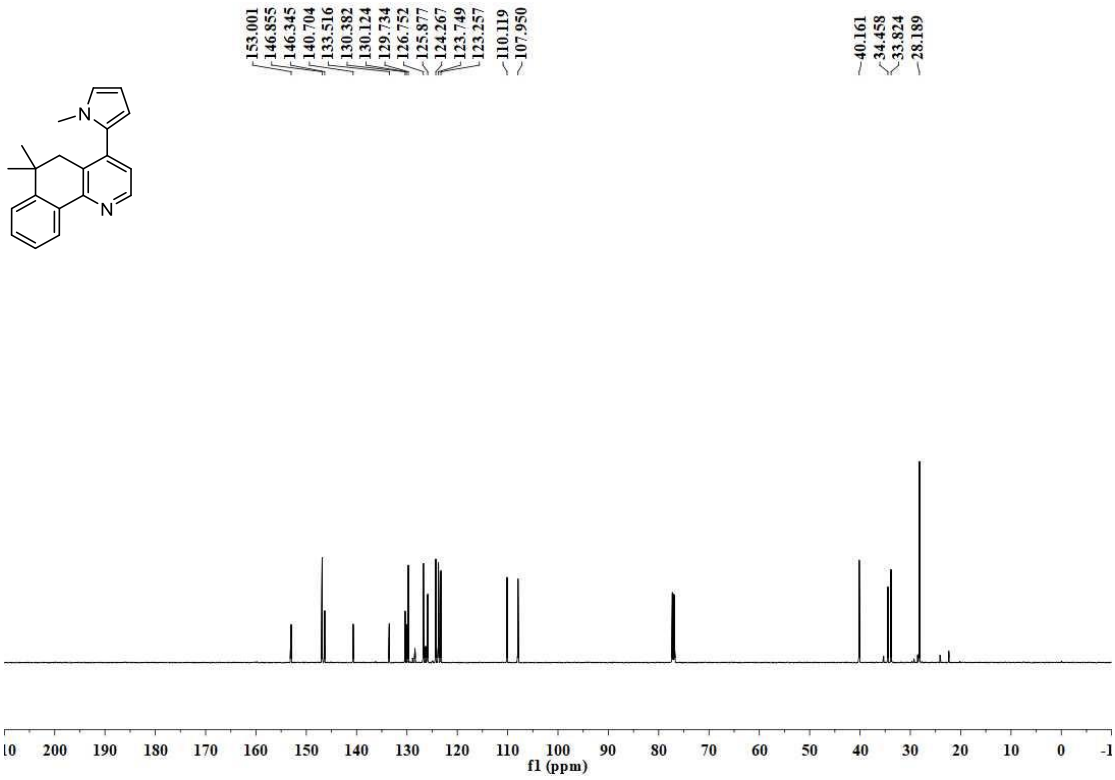
^{13}C NMR Spectrum of 49 (151 MHz, $CDCl_3$)



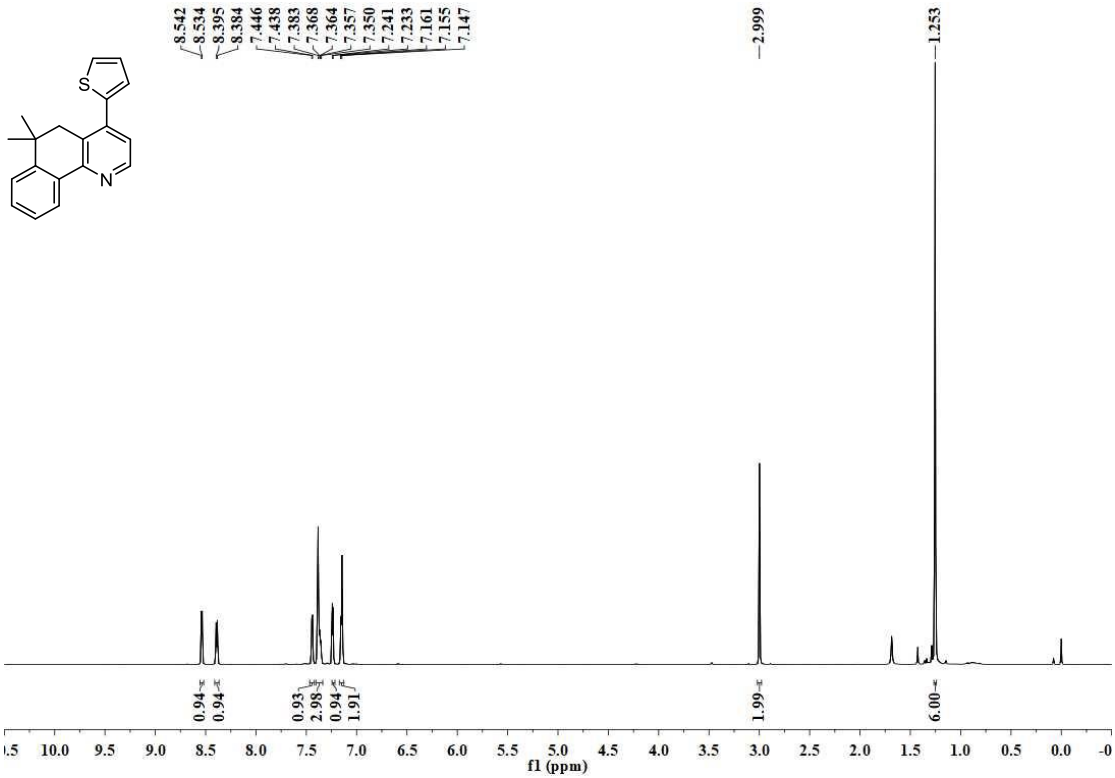
^{1}H NMR Spectrum of 50 (600 MHz, $CDCl_3$)



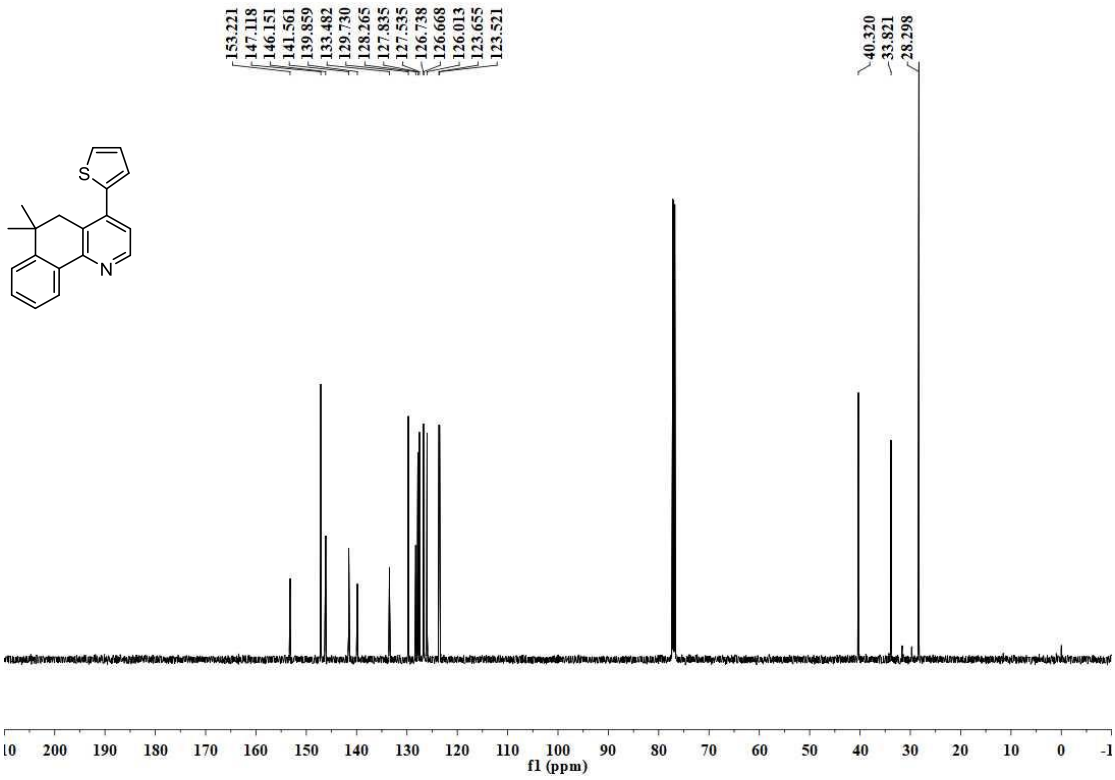
^{13}C NMR Spectrum of 50 (151 MHz, $CDCl_3$)



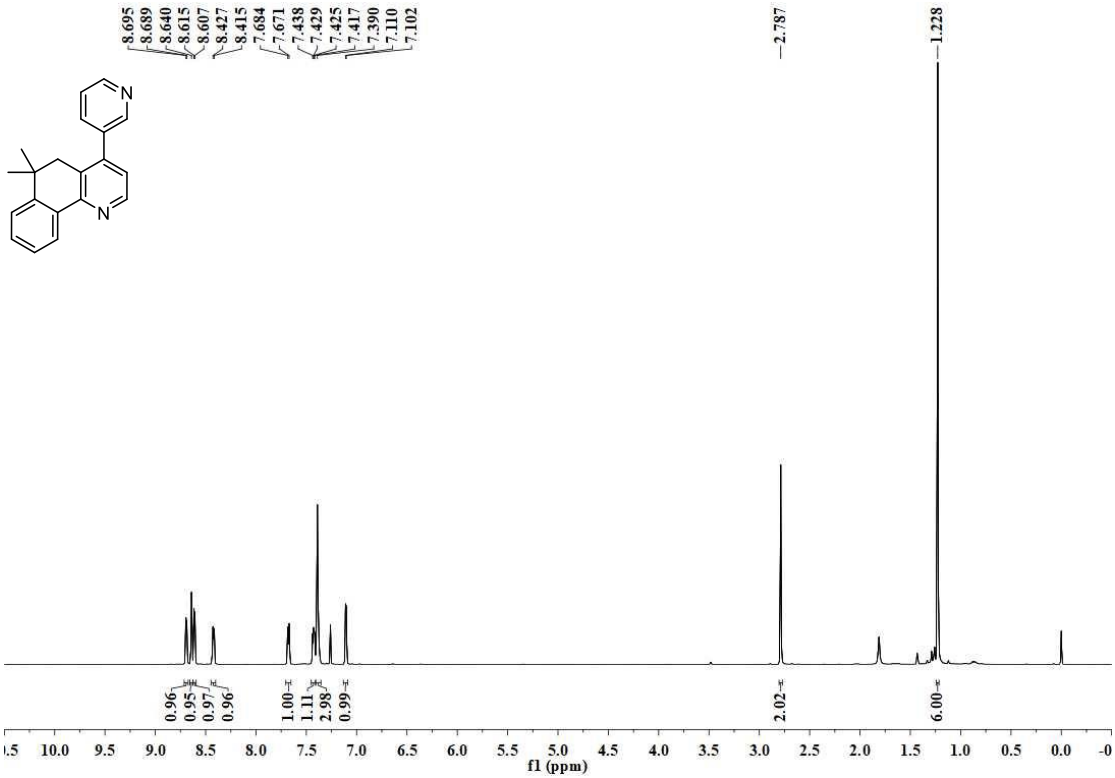
^{1}H NMR Spectrum of 51 (600 MHz, $CDCl_3$)



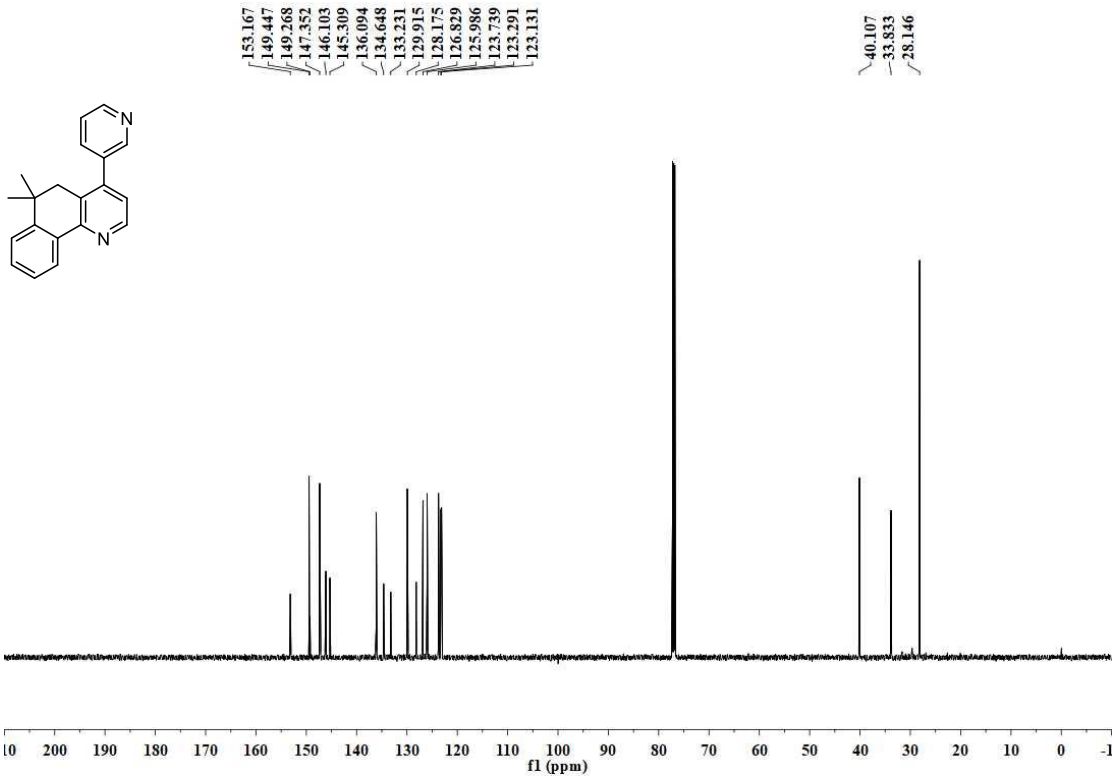
^{13}C NMR Spectrum of 51 (151 MHz, $CDCl_3$)



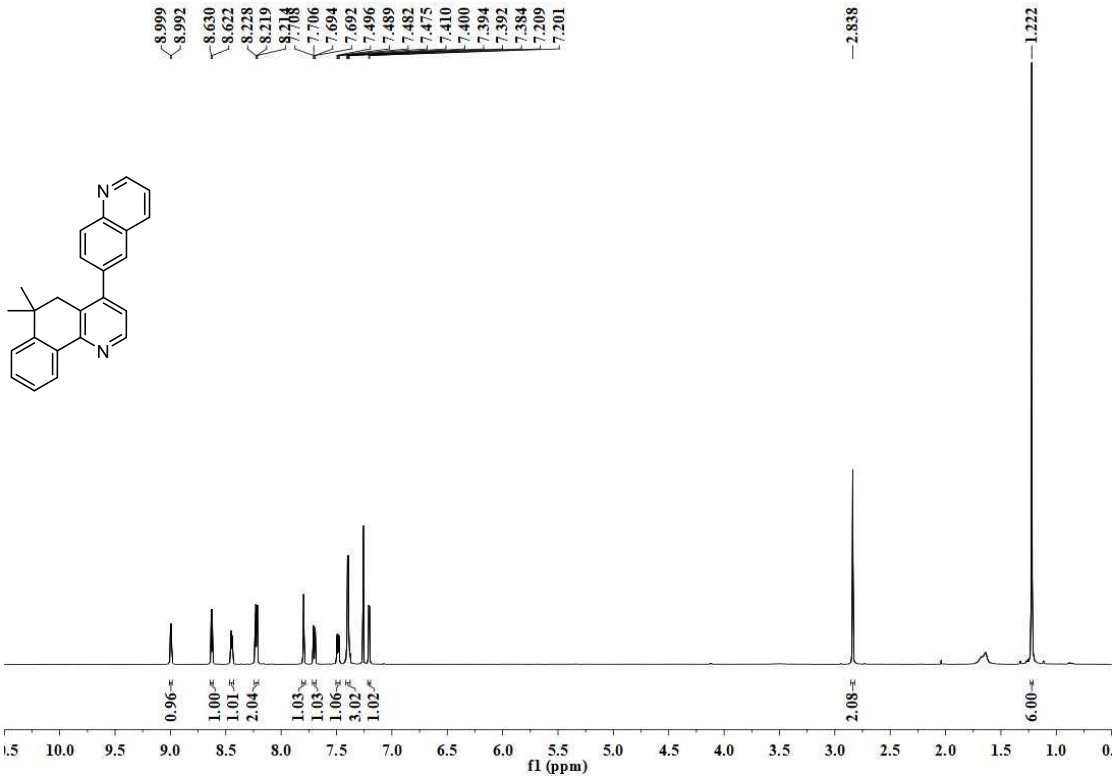
^{1}H NMR Spectrum of 52 (600 MHz, $CDCl_3$)



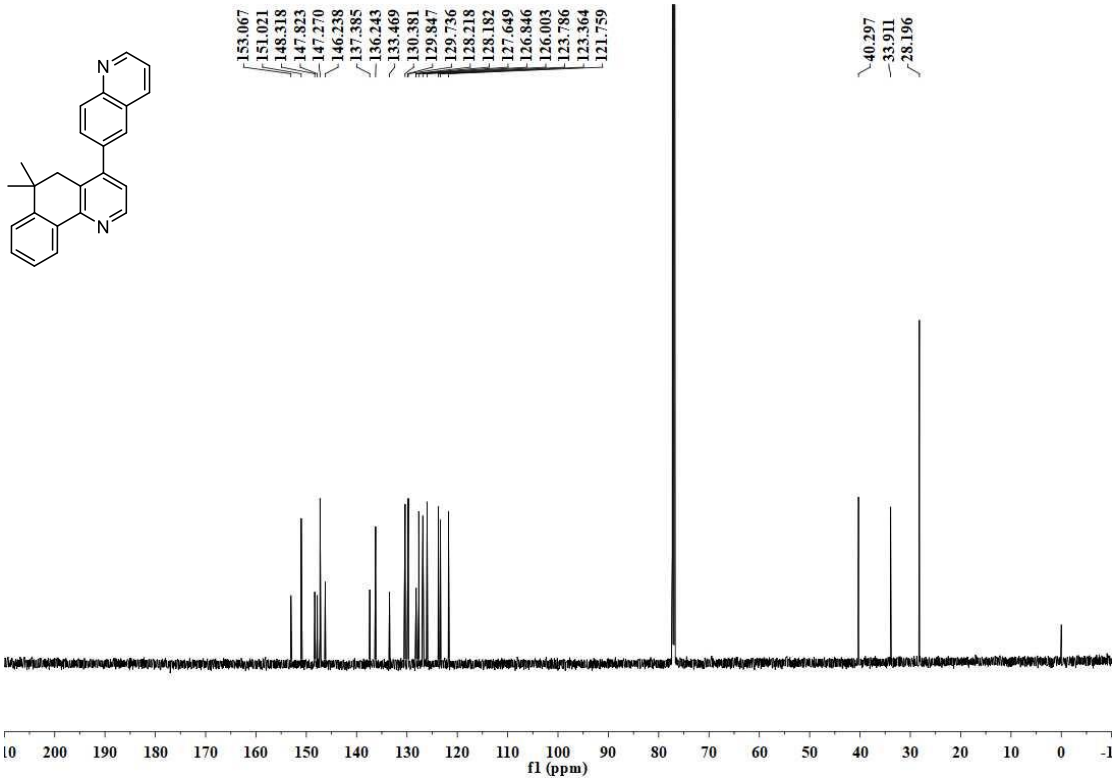
^{13}C NMR Spectrum of 52 (151 MHz, $CDCl_3$)



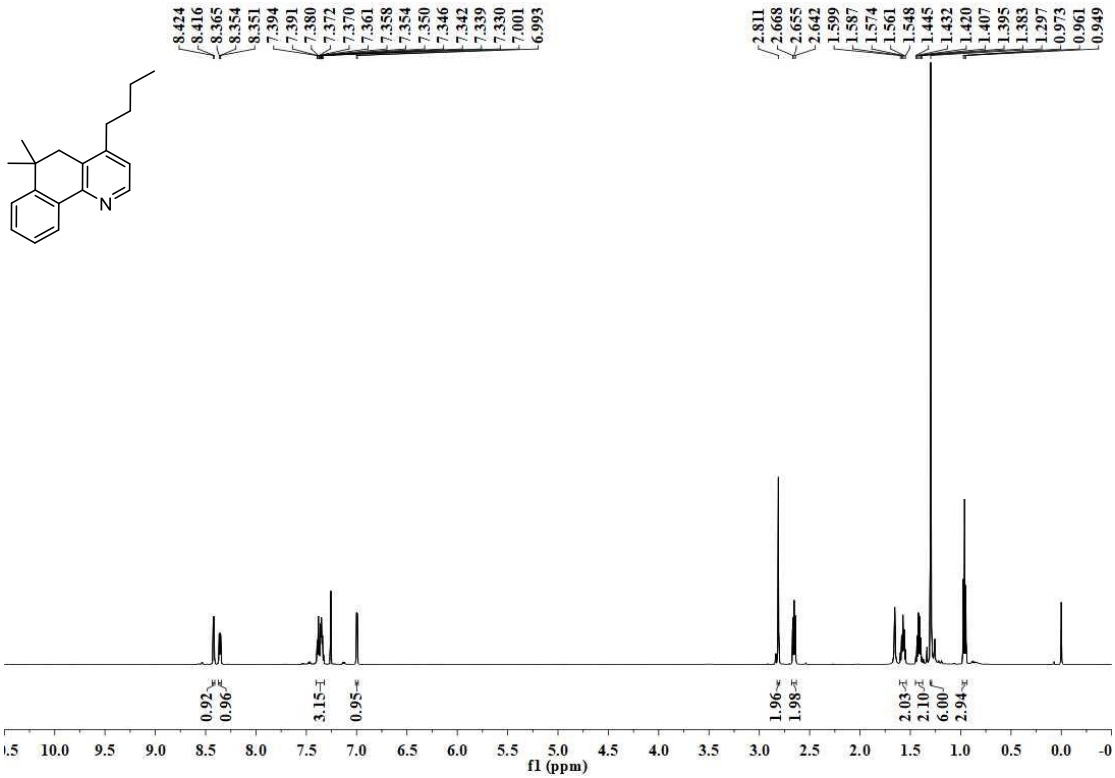
^{1}H NMR Spectrum of 53 (600 MHz, $CDCl_3$)



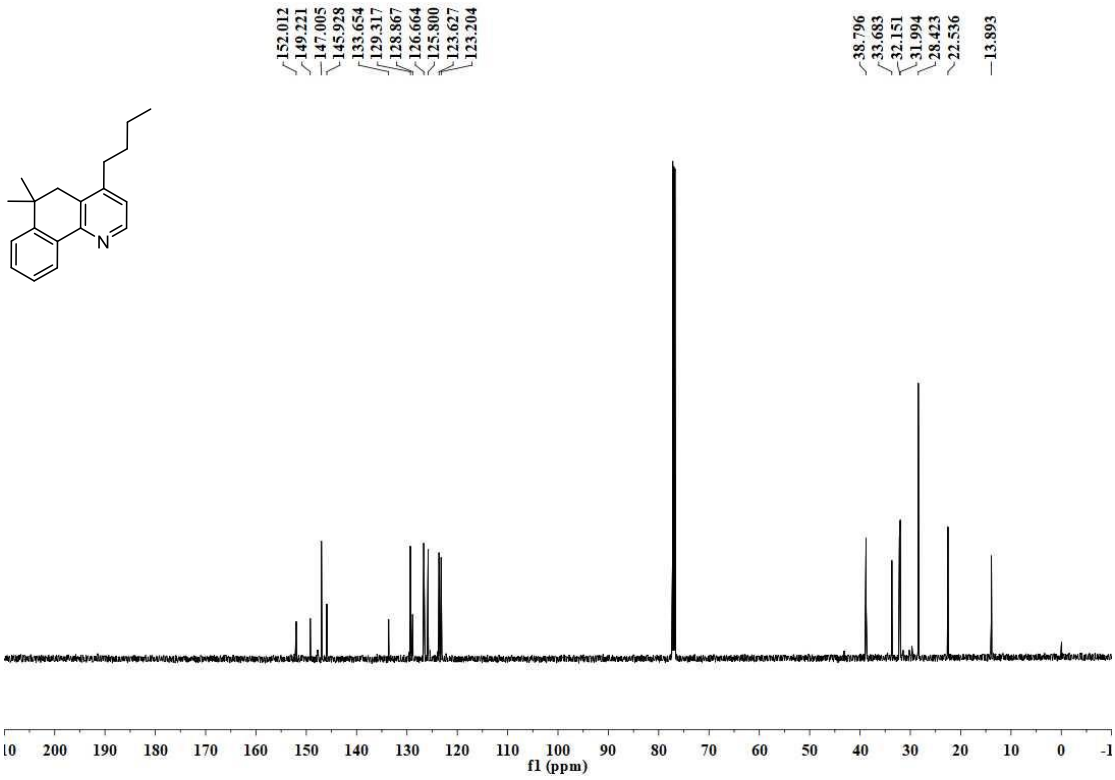
^{13}C NMR Spectrum of 53 (151 MHz, $CDCl_3$)



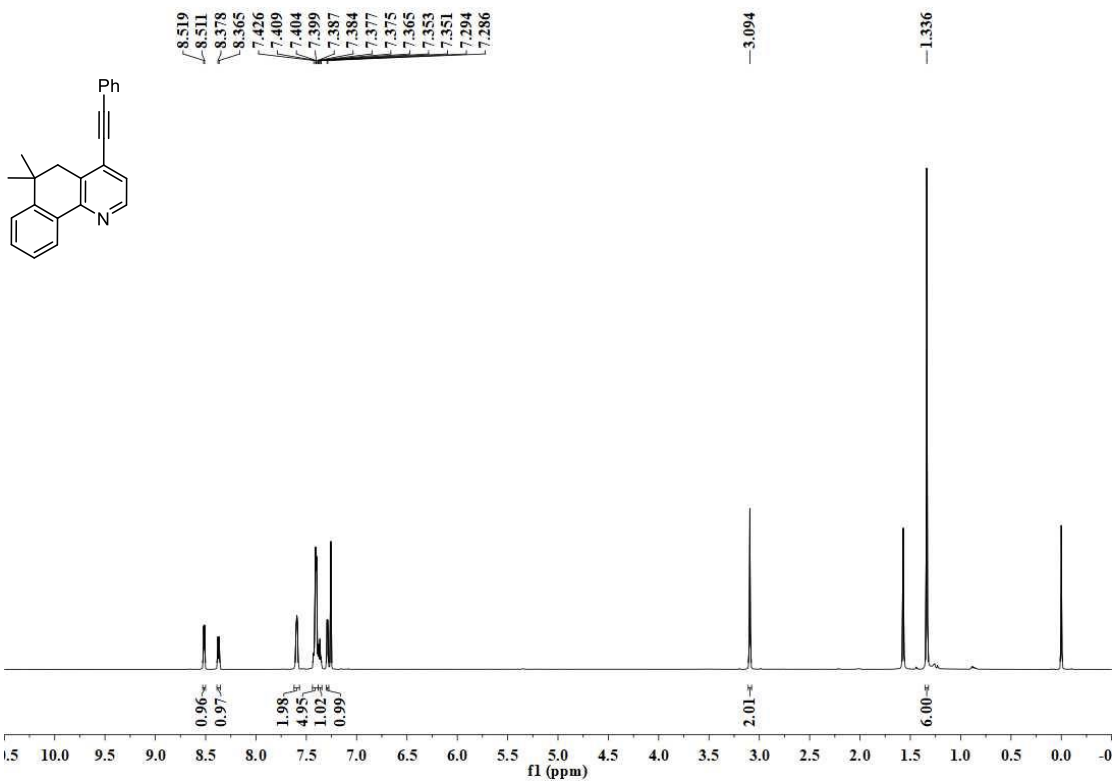
^{1}H NMR Spectrum of 54 (600 MHz, $CDCl_3$)



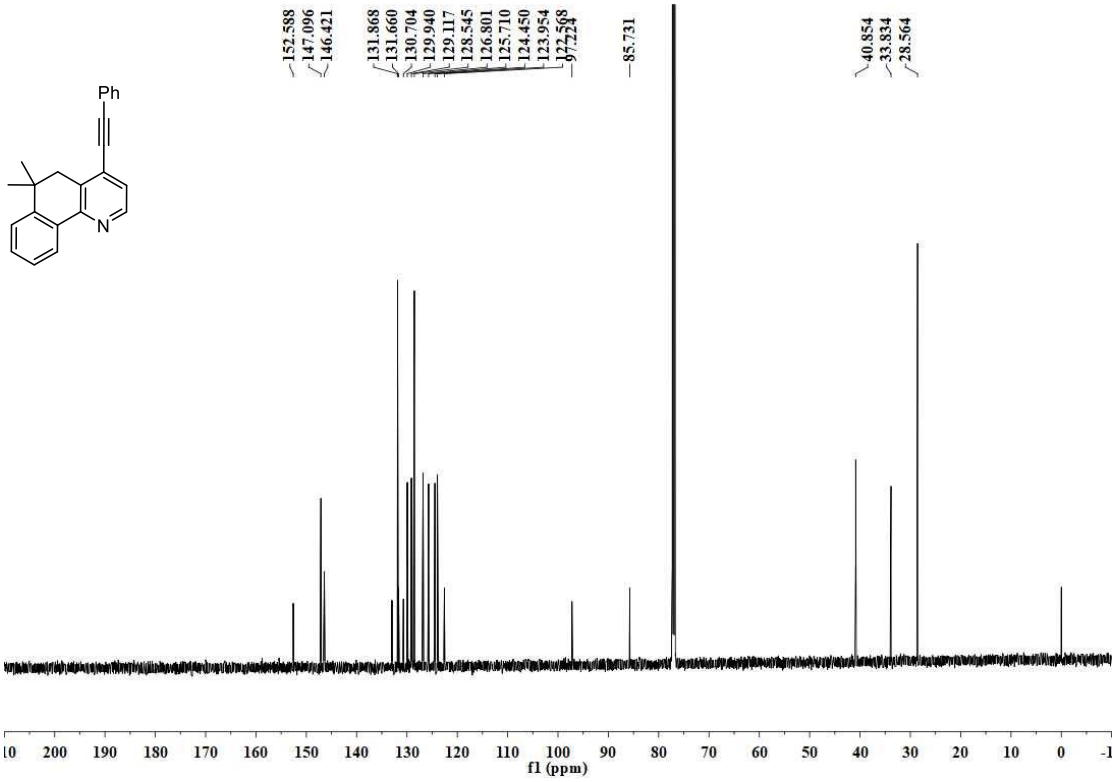
^{13}C NMR Spectrum of 54 (151 MHz, $CDCl_3$)



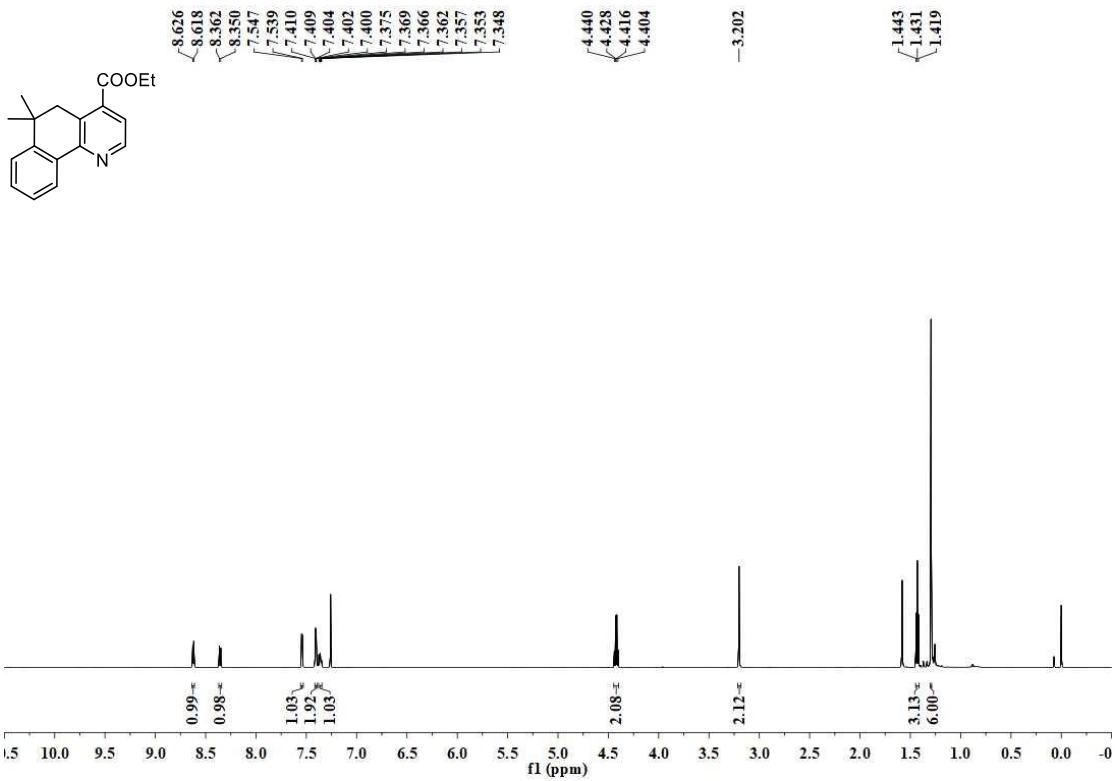
^{1}H NMR Spectrum of 55 (600 MHz, $CDCl_3$)



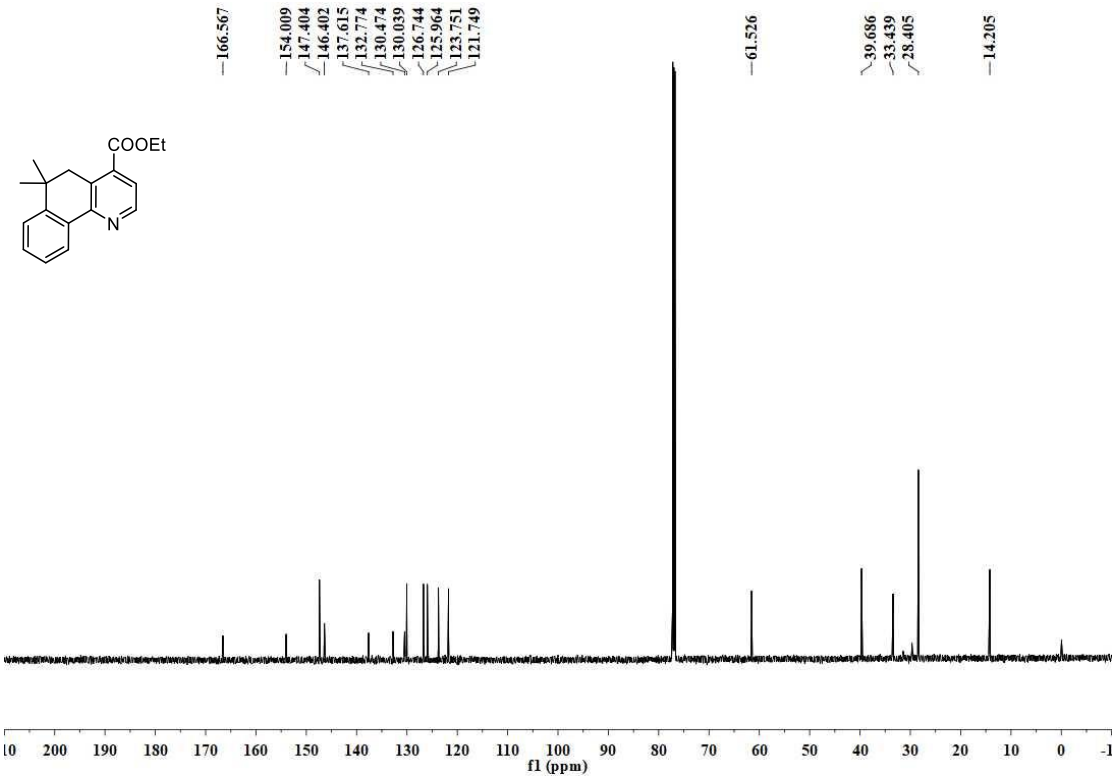
^{13}C NMR Spectrum of 55 (151 MHz, $CDCl_3$)



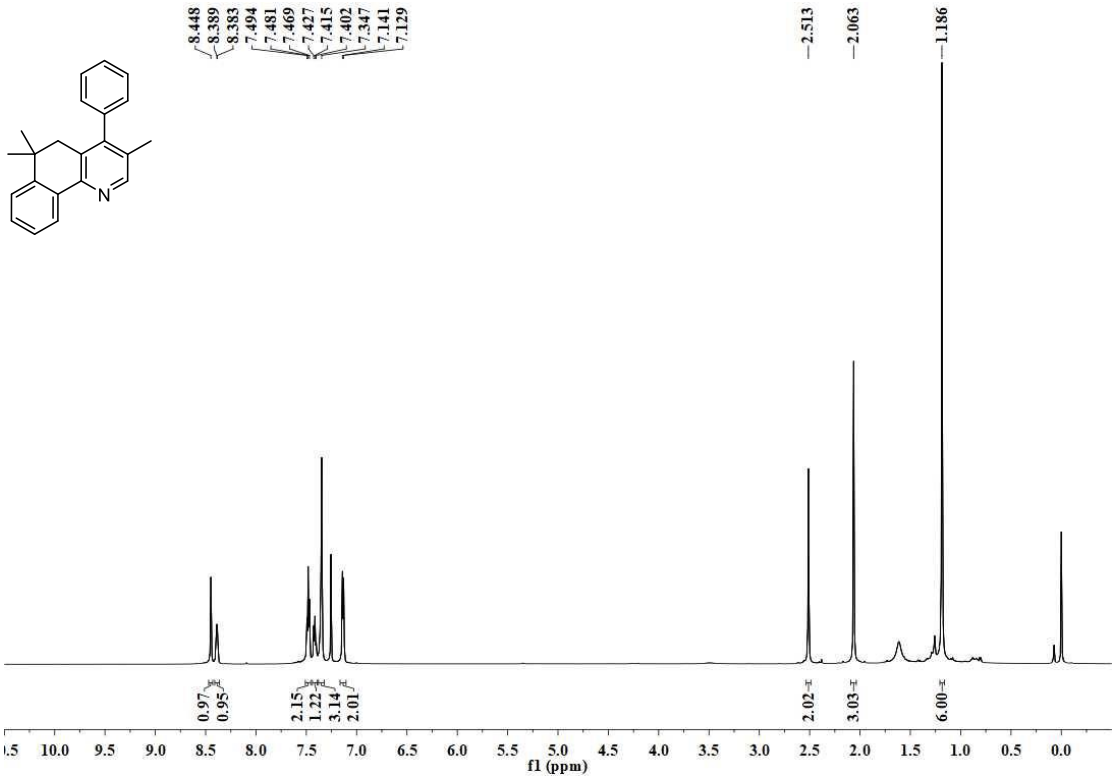
^{1}H NMR Spectrum of 56 (600 MHz, $CDCl_3$)



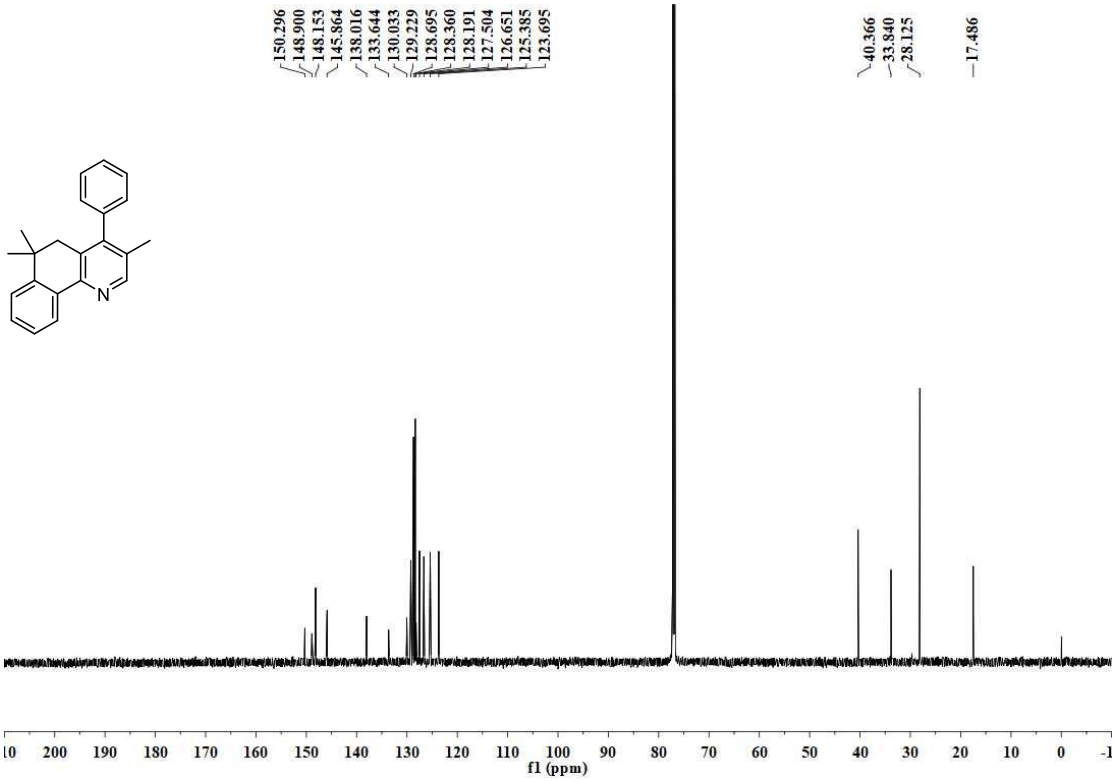
^{13}C NMR Spectrum of 56 (151 MHz, $CDCl_3$)



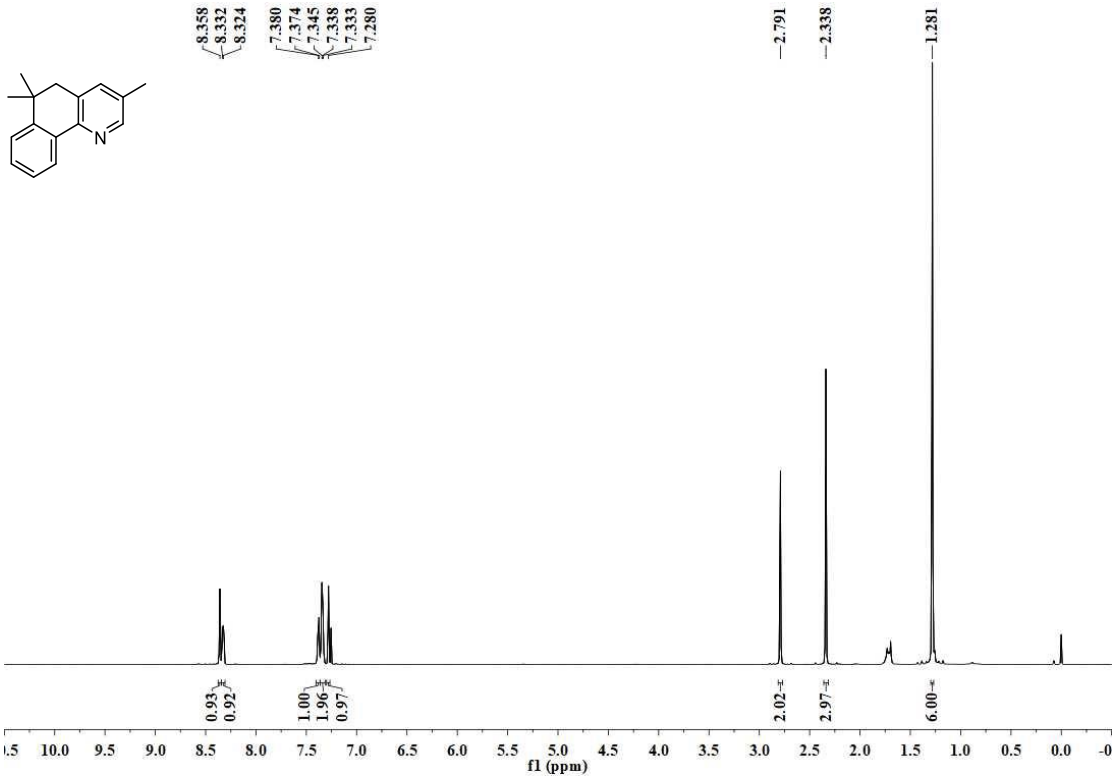
^{1}H NMR Spectrum of 57 (600 MHz, $CDCl_3$)



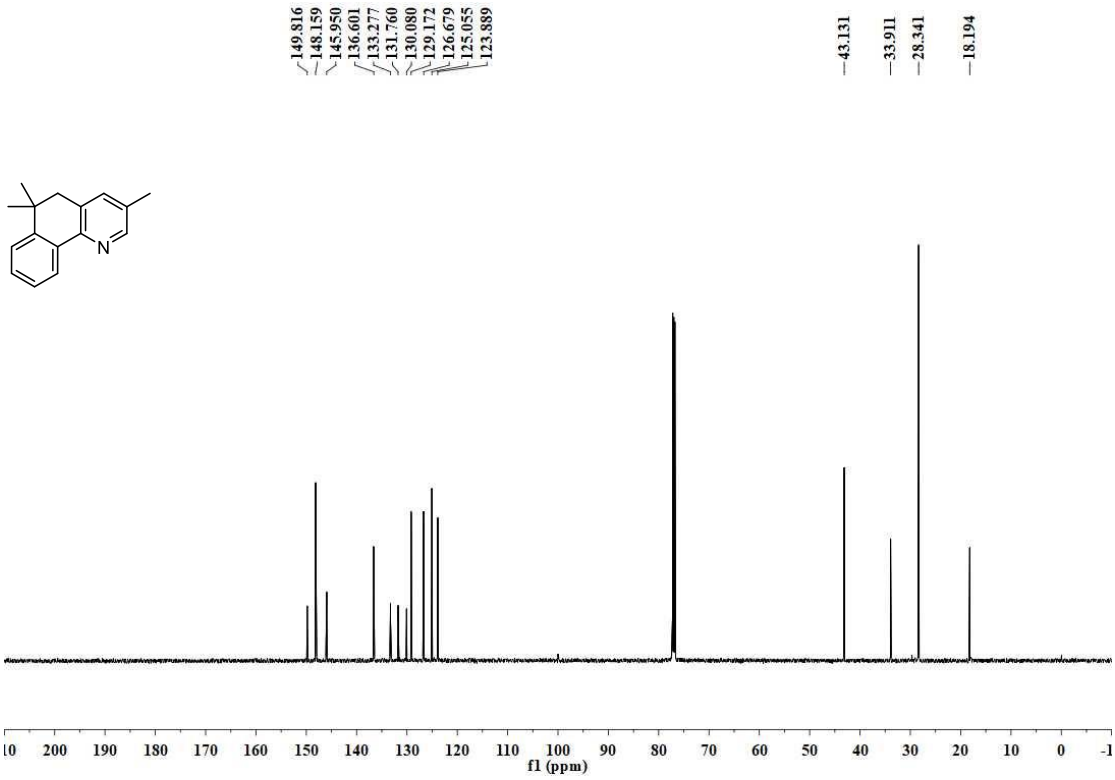
^{13}C NMR Spectrum of 57 (151 MHz, $CDCl_3$)



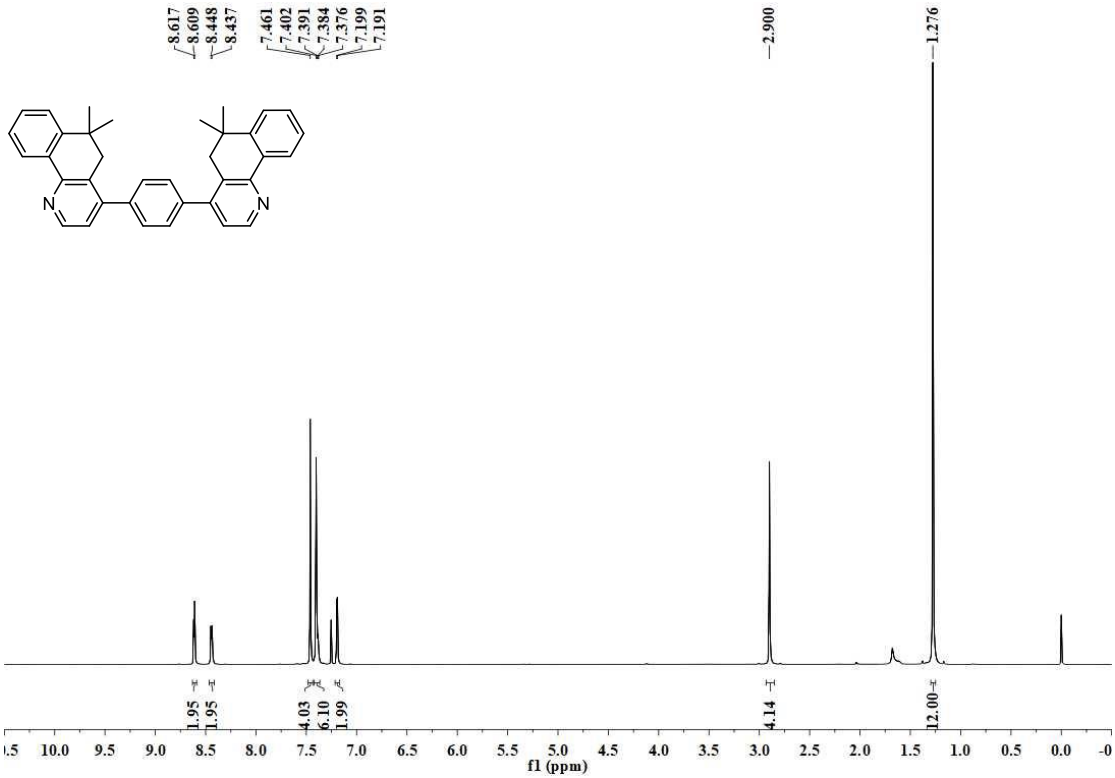
^{1}H NMR Spectrum of 58 (600 MHz, $CDCl_3$)



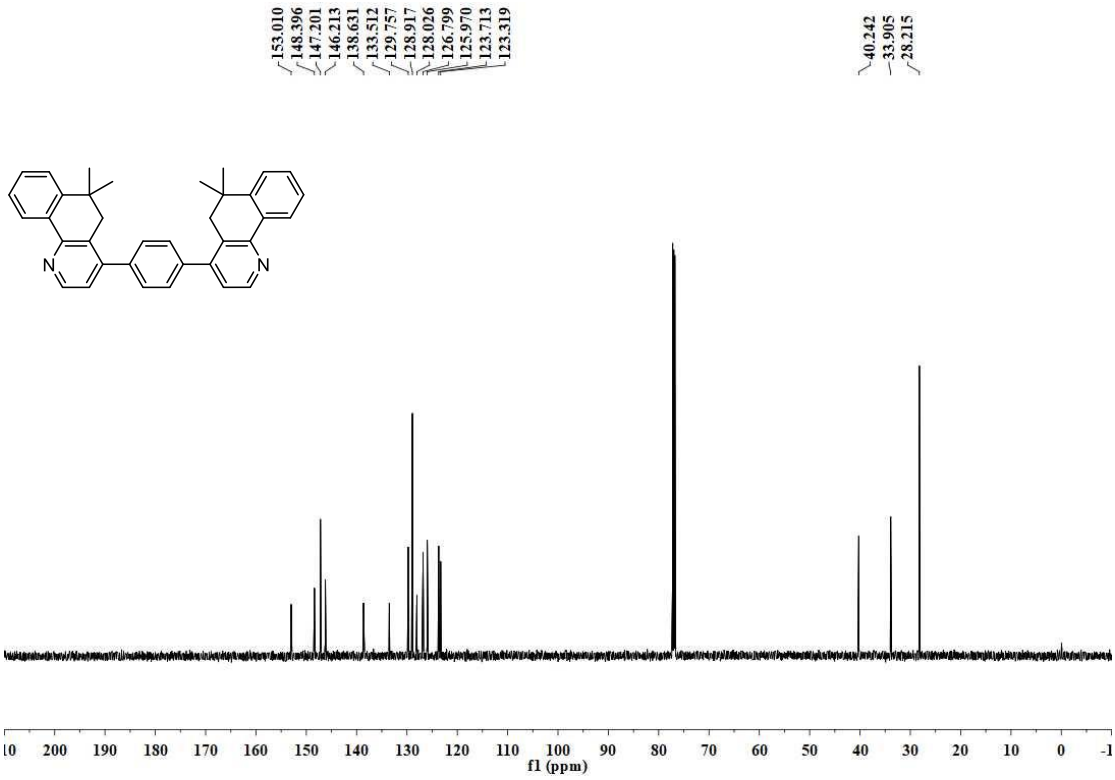
^{13}C NMR Spectrum of 58 (151 MHz, $CDCl_3$)



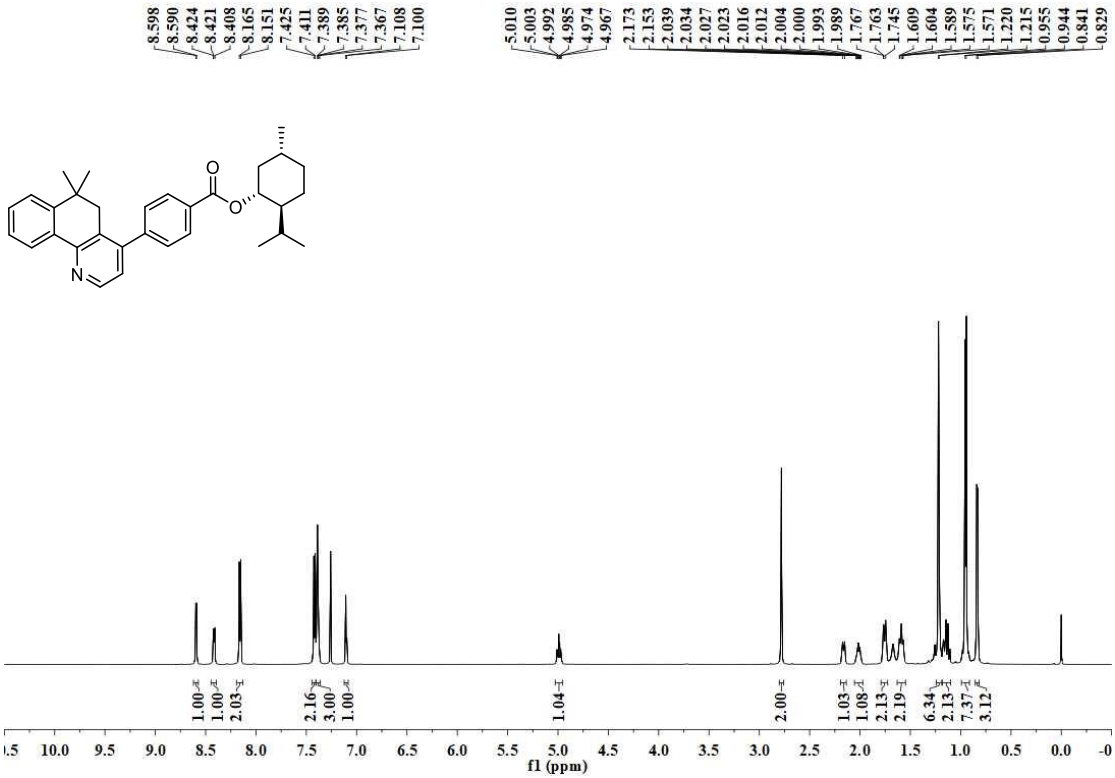
^{1}H NMR Spectrum of 59 (600 MHz, $CDCl_3$)



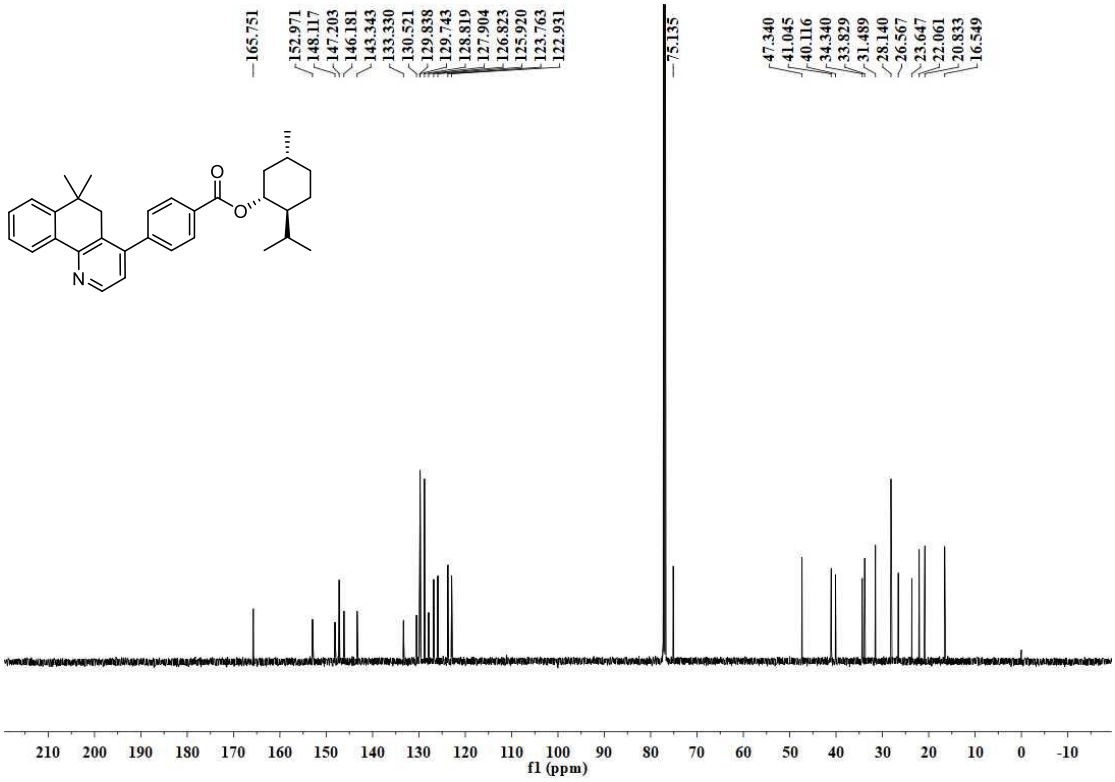
^{13}C NMR Spectrum of 59 (151 MHz, $CDCl_3$)



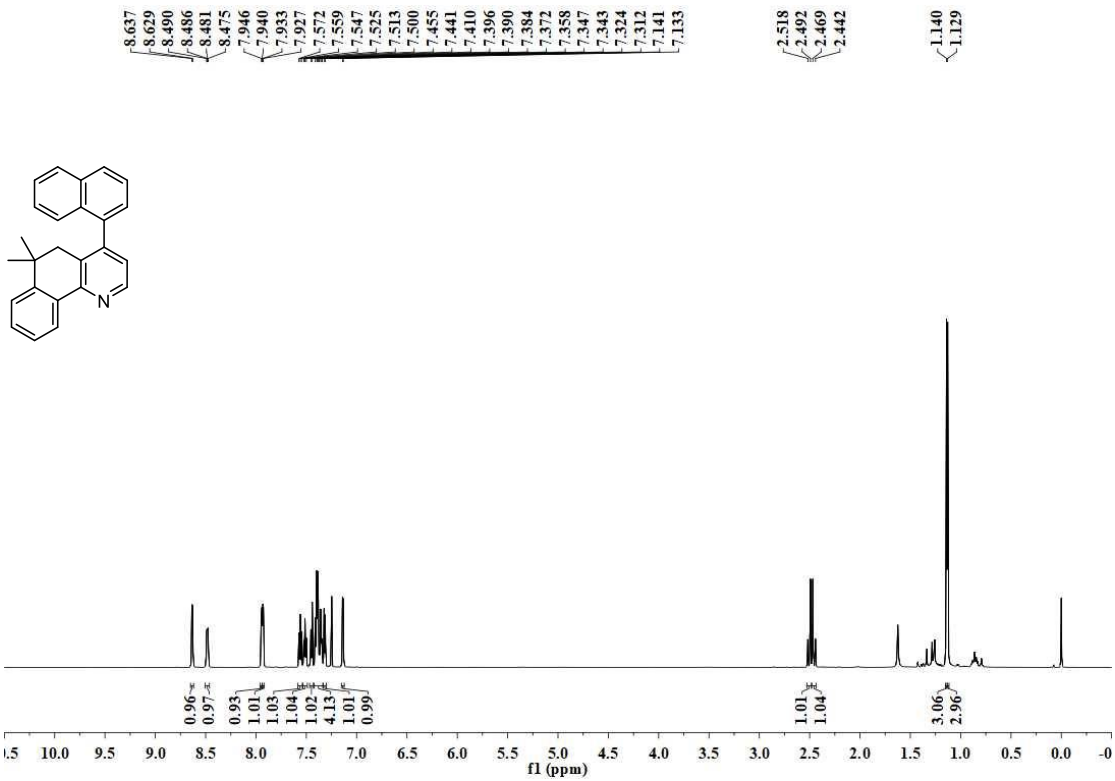
^{1}H NMR Spectrum of 60 (600 MHz, $CDCl_3$)



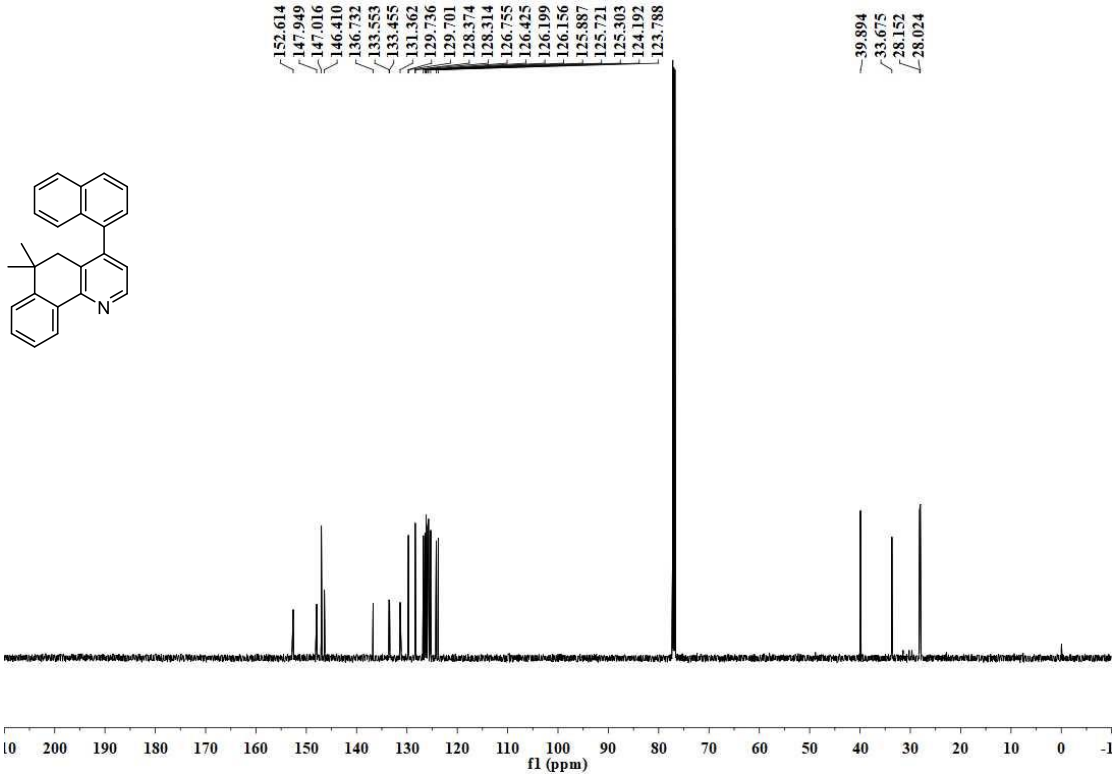
^{13}C NMR Spectrum of 60 (151 MHz, $CDCl_3$)



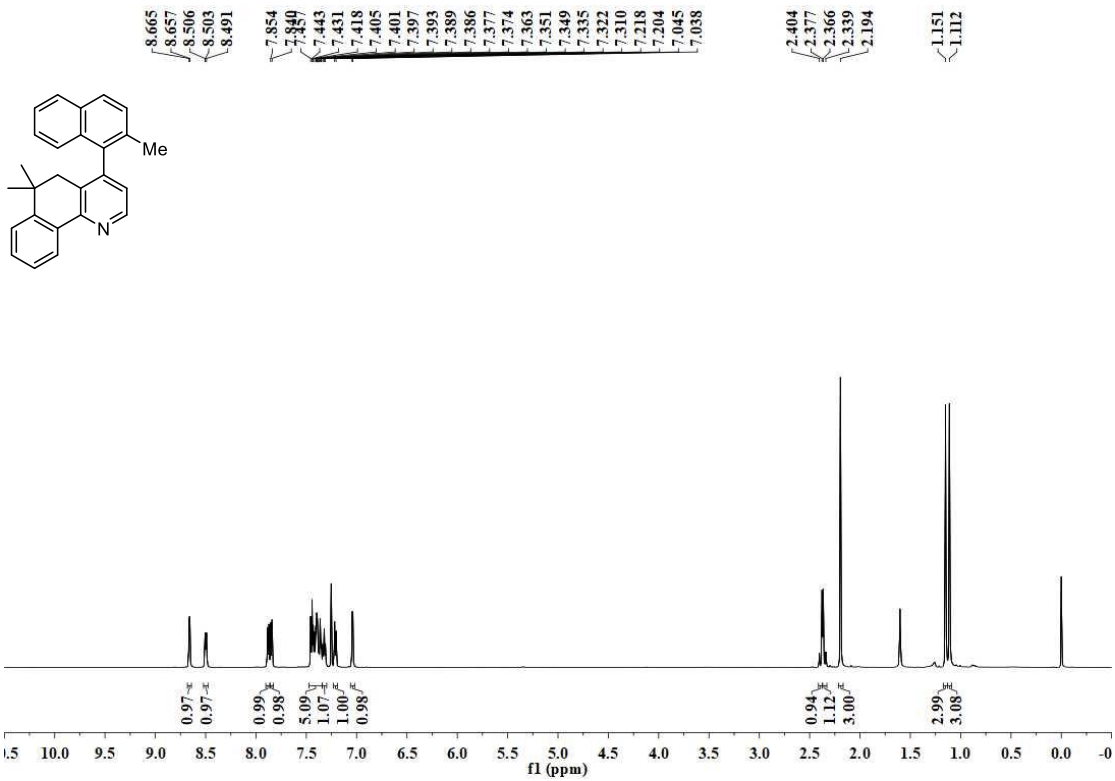
^{1}H NMR Spectrum of 61 (600 MHz, $CDCl_3$)



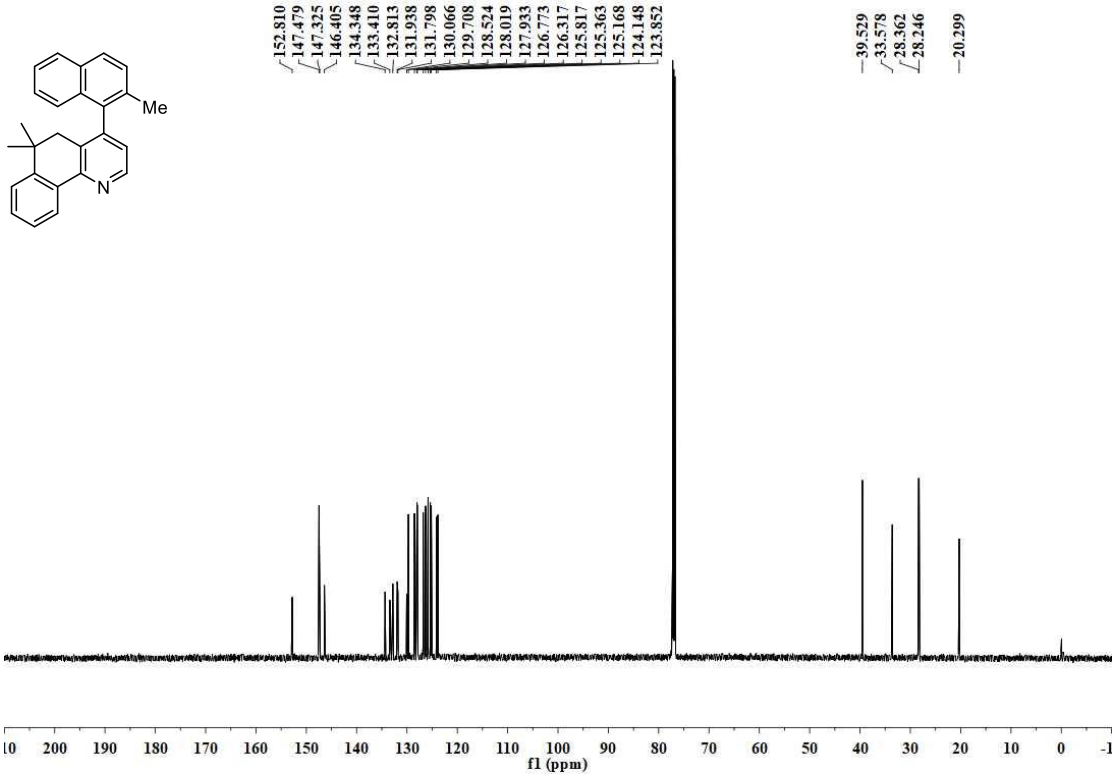
^{13}C NMR Spectrum of 61 (151 MHz, $CDCl_3$)



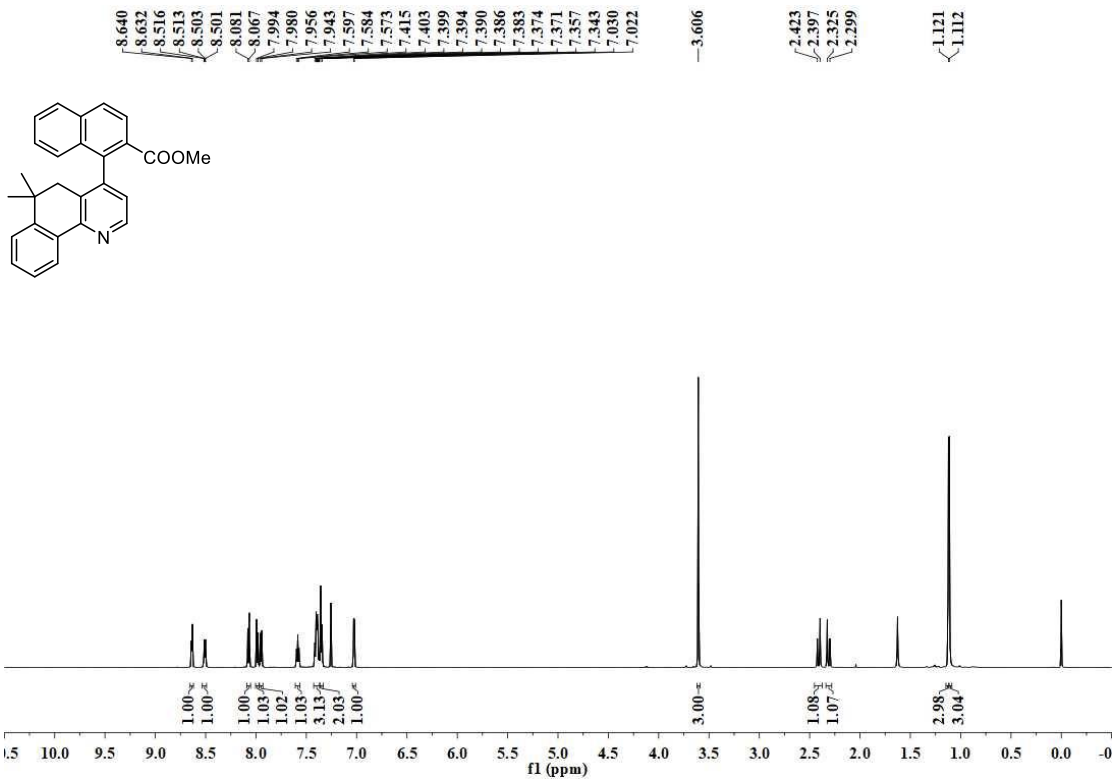
^{1}H NMR Spectrum of 62 (600 MHz, $CDCl_3$)



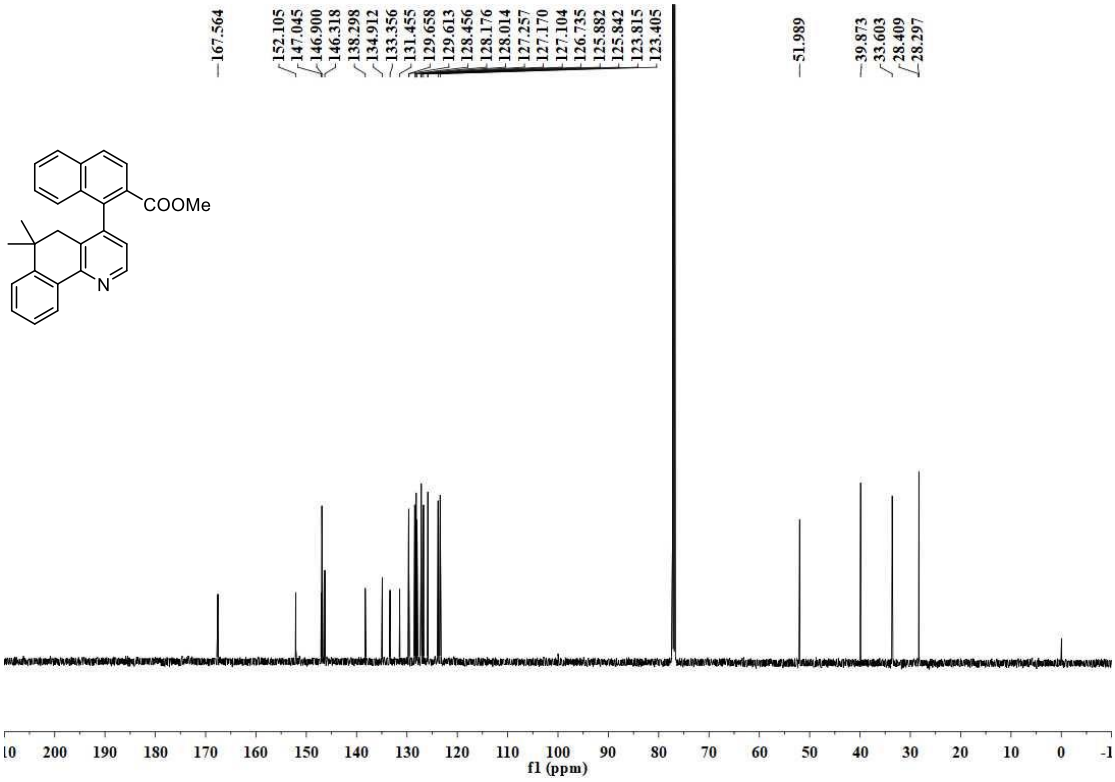
^{13}C NMR Spectrum of 62 (151 MHz, $CDCl_3$)



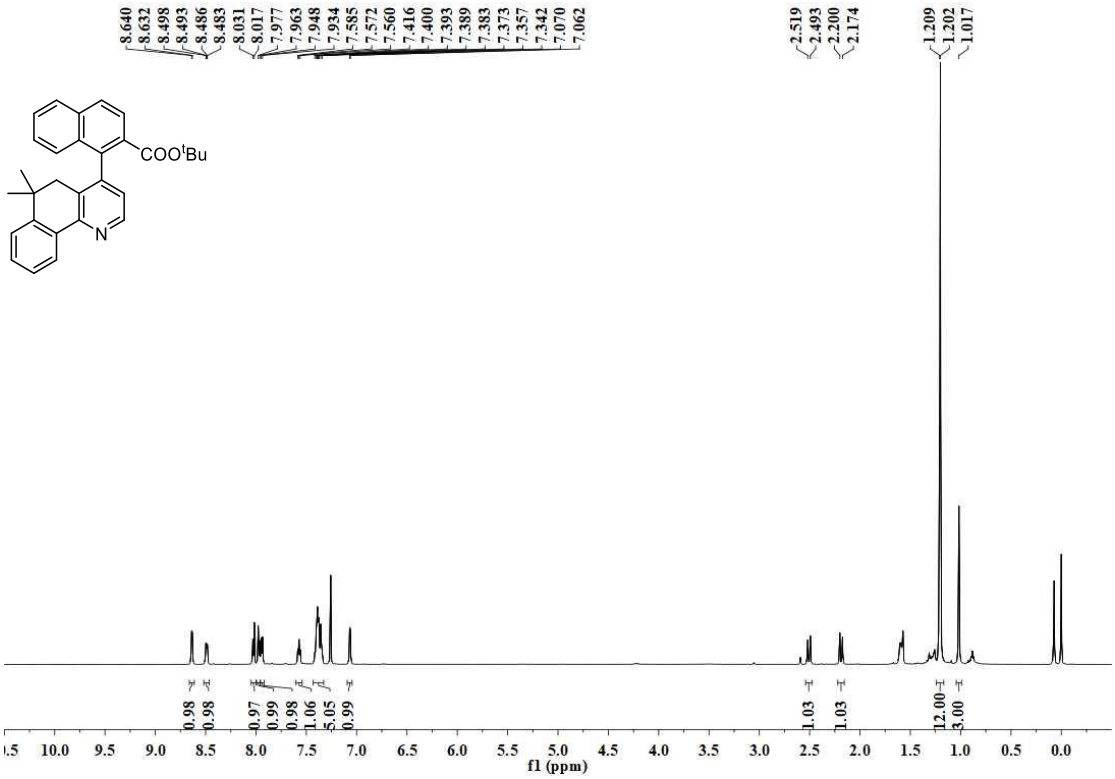
^{1}H NMR Spectrum of 63 (600 MHz, $CDCl_3$)



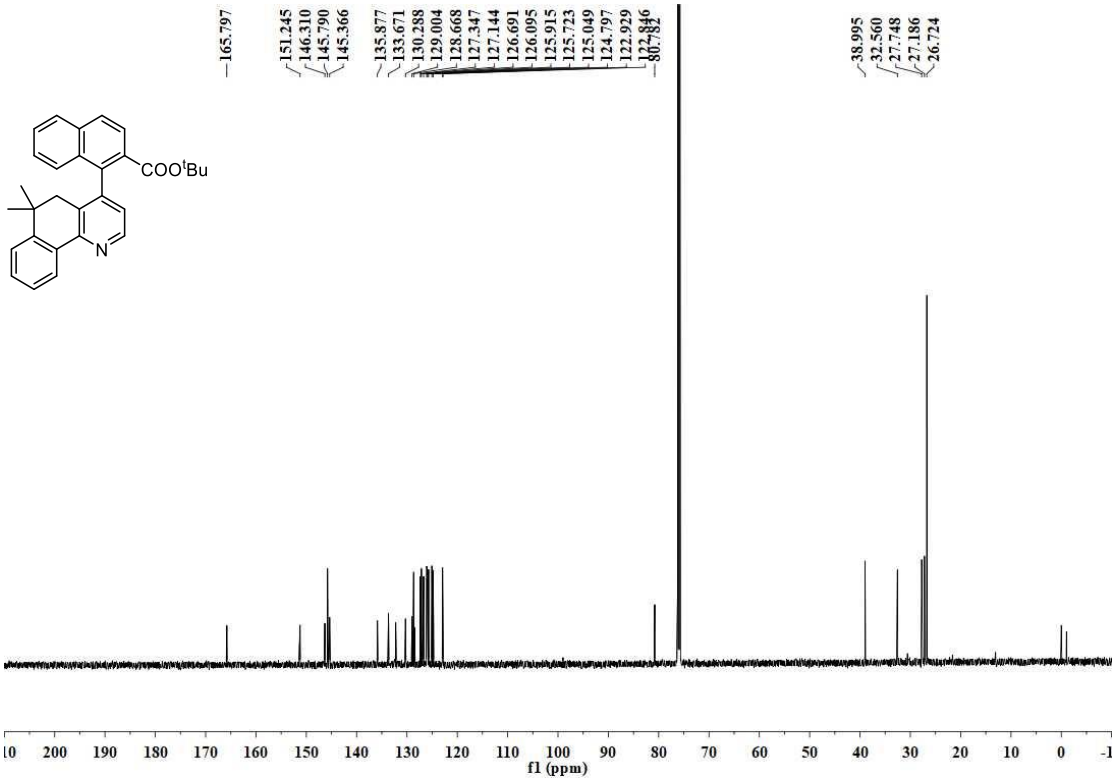
^{13}C NMR Spectrum of 63 (151 MHz, $CDCl_3$)



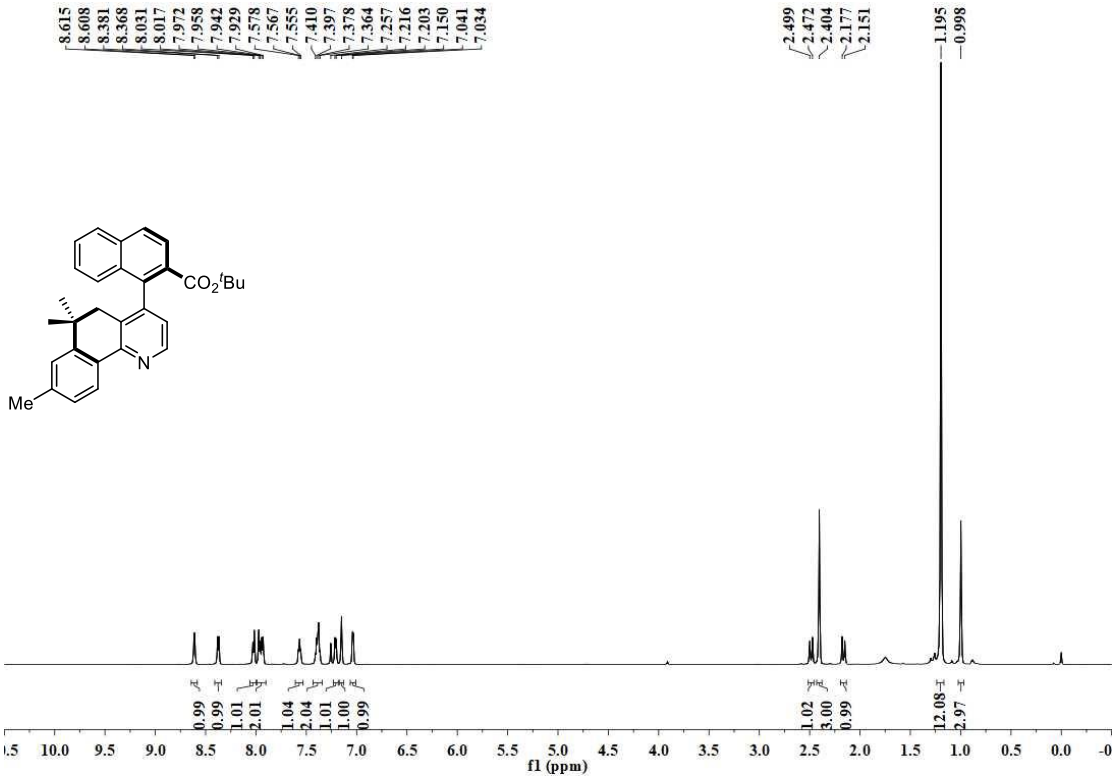
^{1}H NMR Spectrum of 64 (600 MHz, $CDCl_3$)



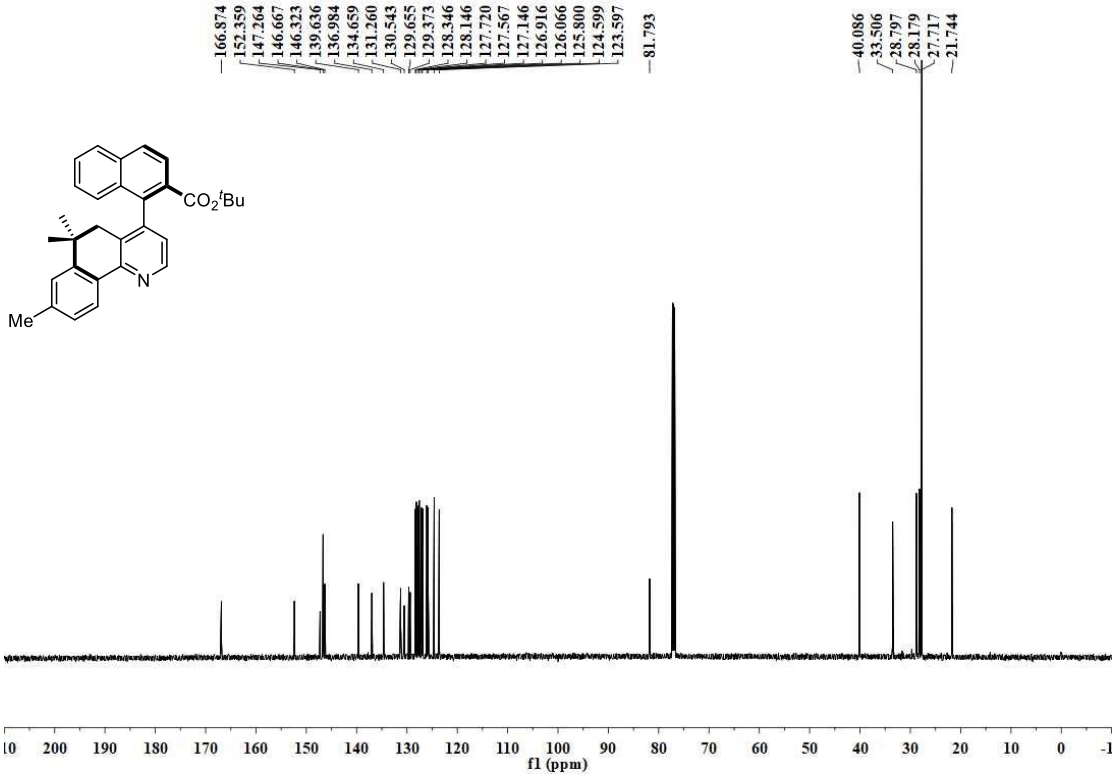
^{13}C NMR Spectrum of 64 (151 MHz, $CDCl_3$)



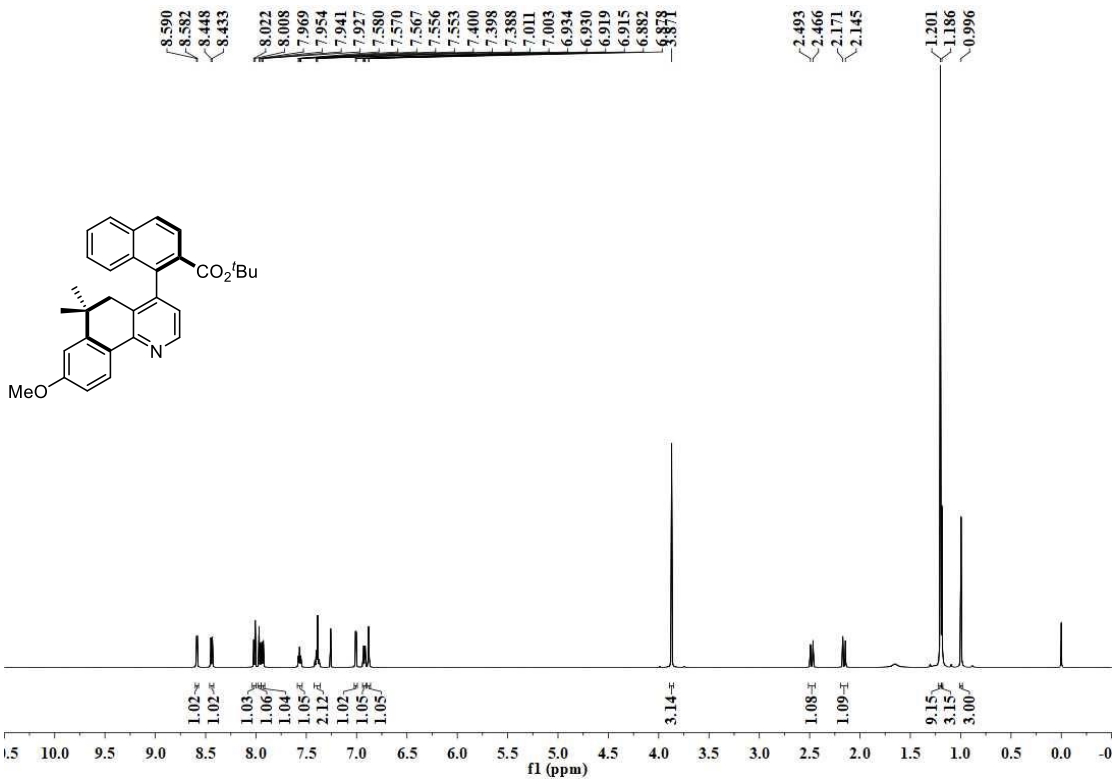
^{1}H NMR Spectrum of 98 (600 MHz, $CDCl_3$)



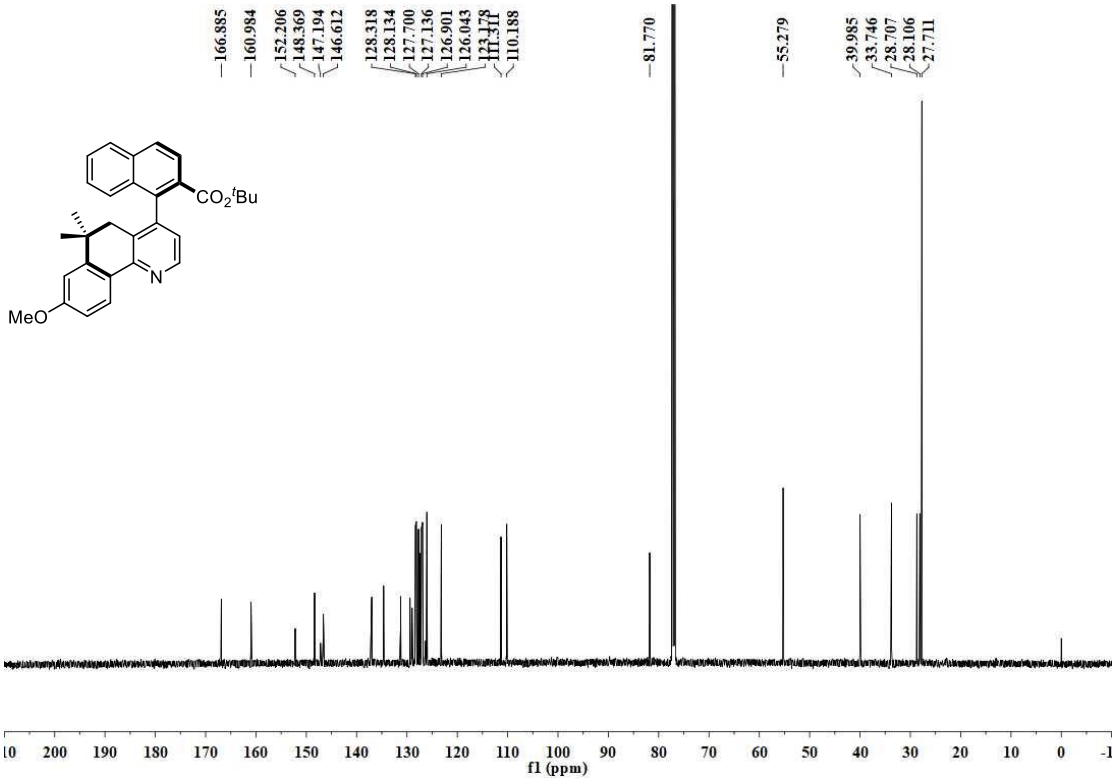
^{13}C NMR Spectrum of 98 (151 MHz, $CDCl_3$)



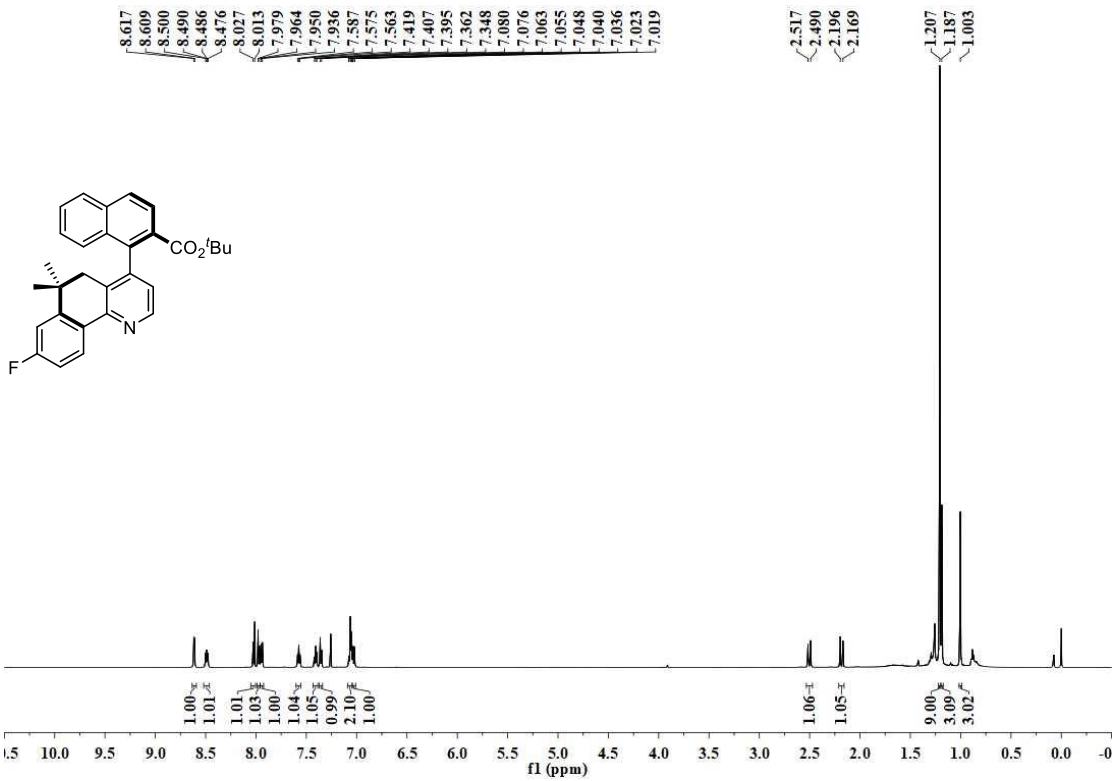
^{1}H NMR Spectrum of 99 (600 MHz, $CDCl_3$)



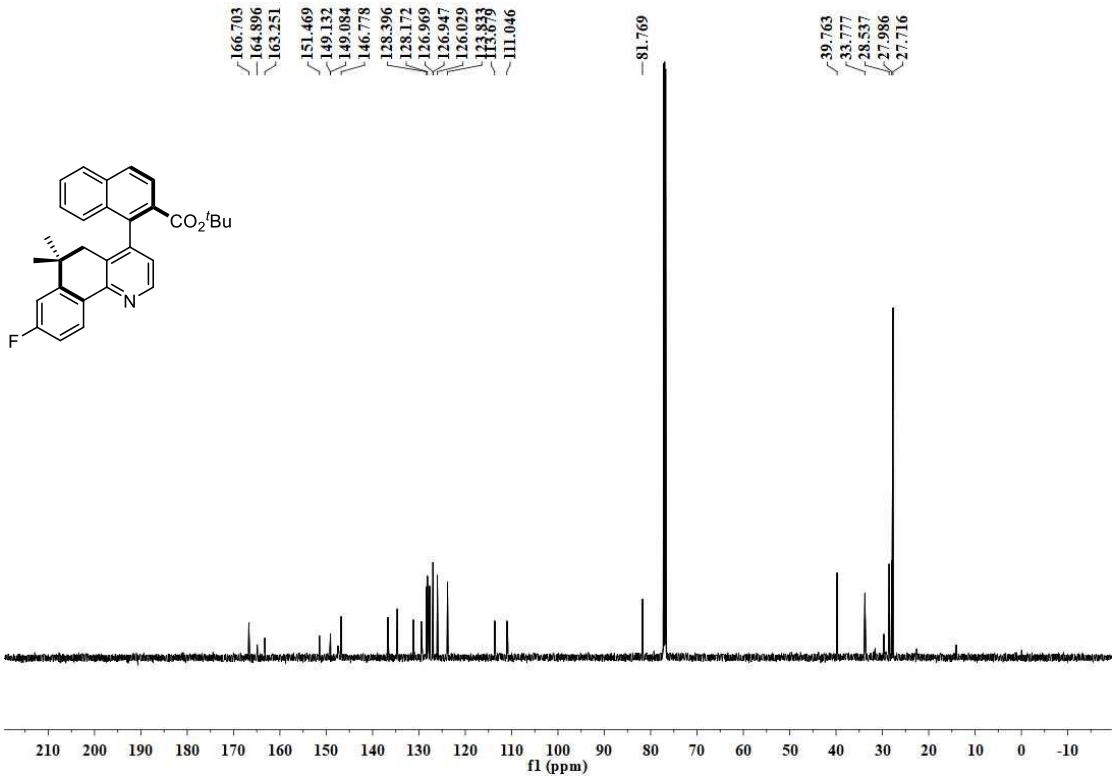
^{13}C NMR Spectrum of 99 (151 MHz, $CDCl_3$)



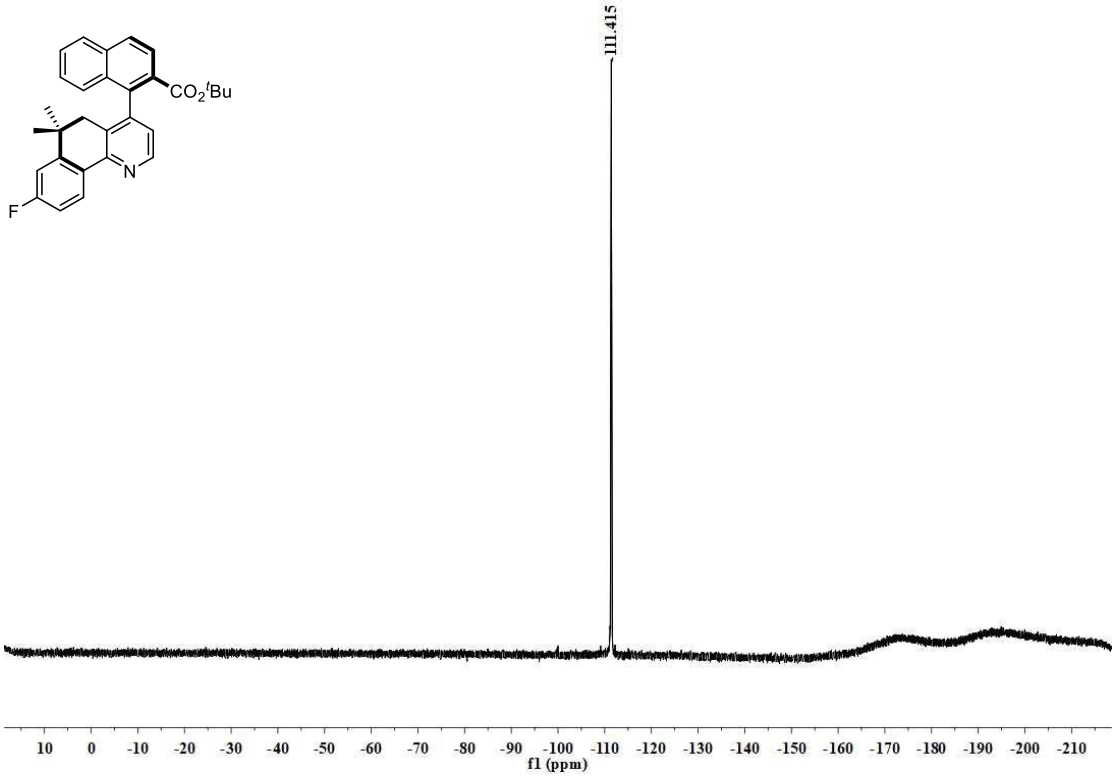
^{1}H NMR Spectrum of 100 (600 MHz, $CDCl_3$)



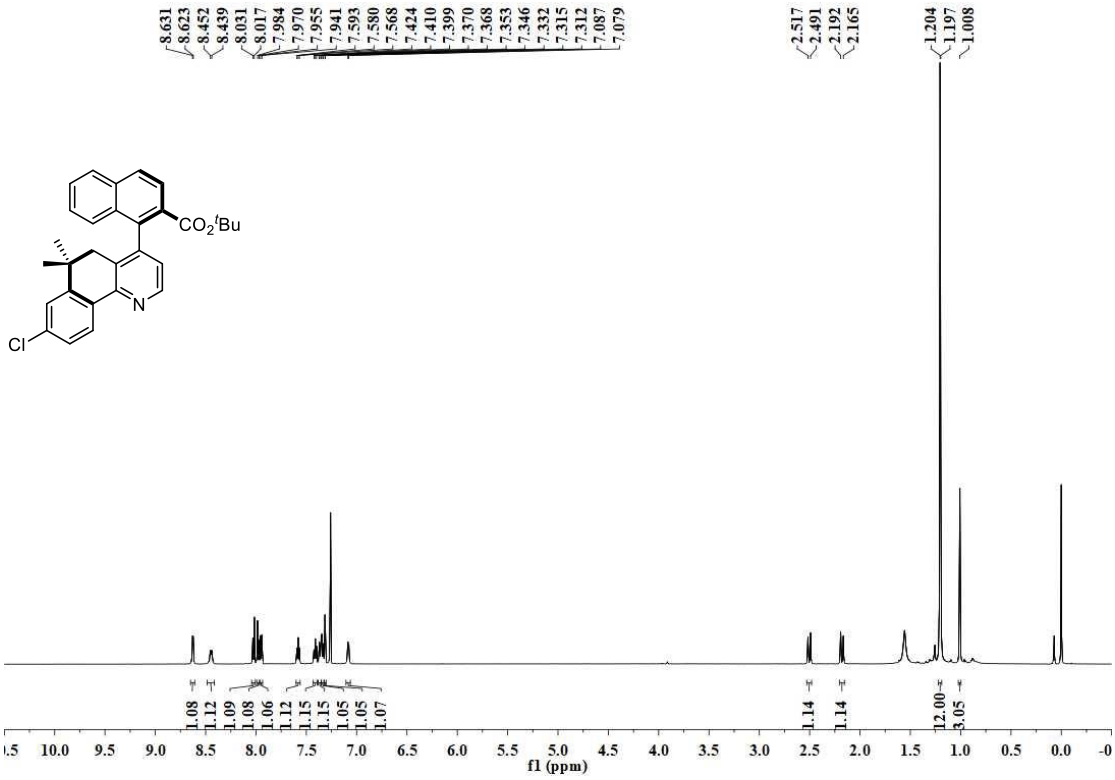
^{13}C NMR Spectrum of 100 (151 MHz, $CDCl_3$)



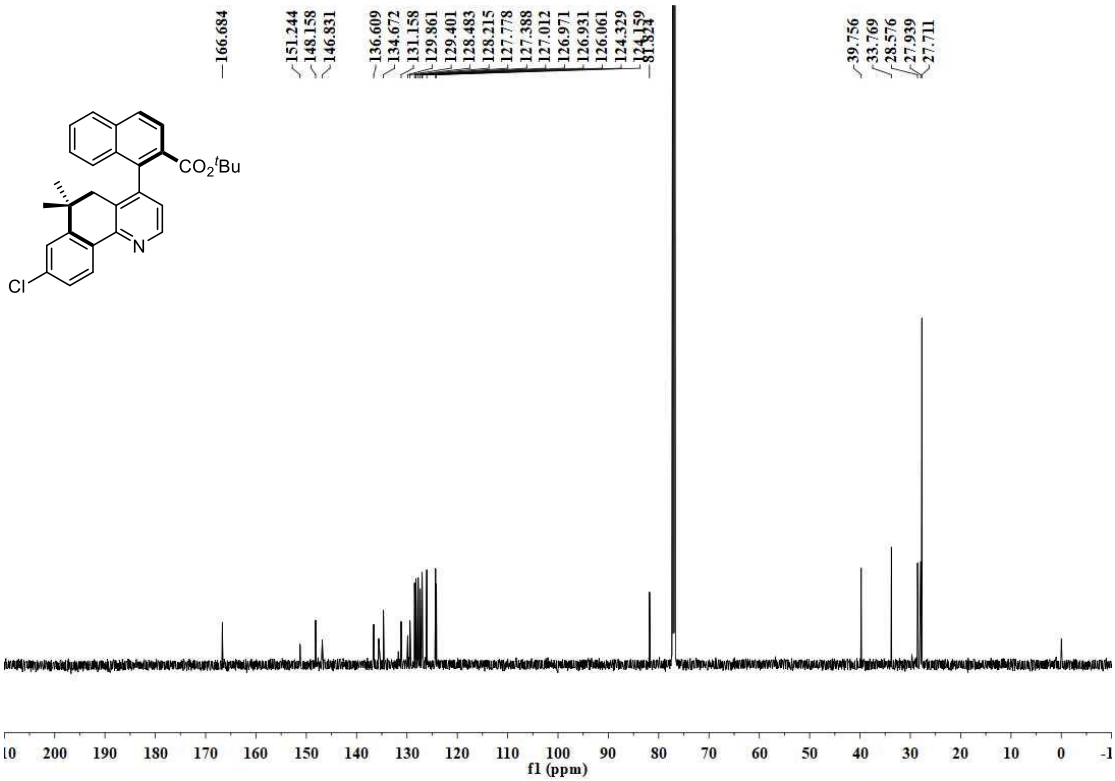
^{19}F NMR Spectrum of 100 (565 MHz, $CDCl_3$)



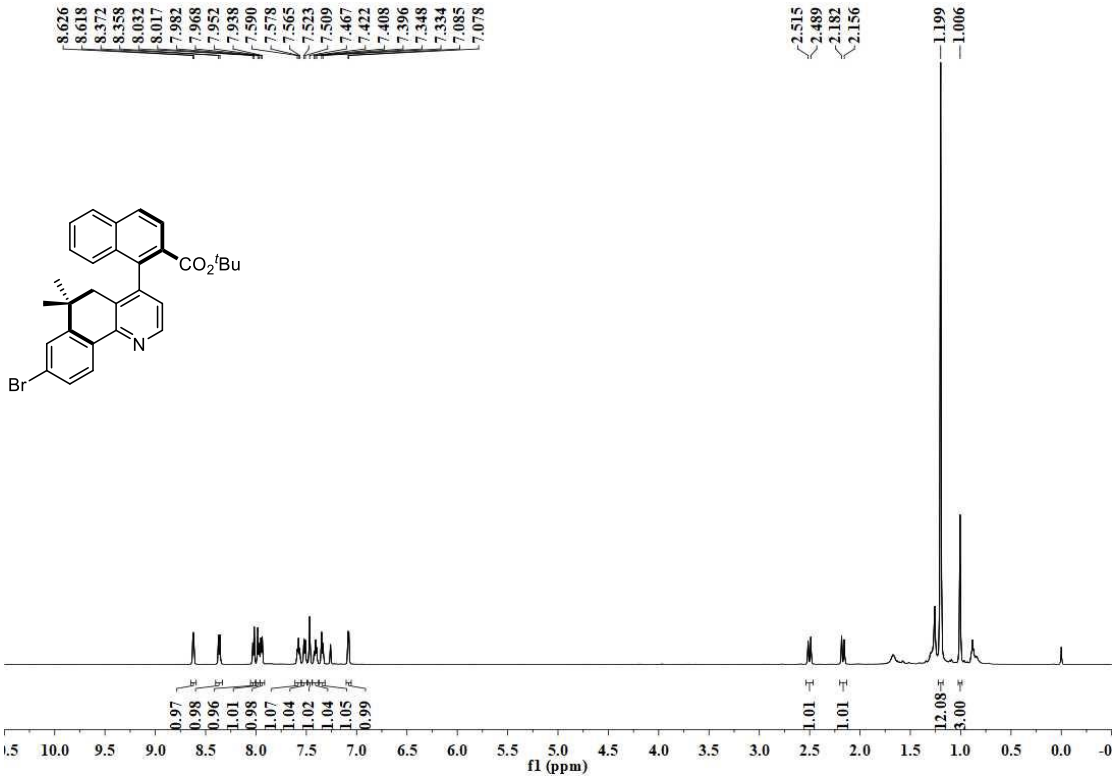
^{1}H NMR Spectrum of 101 (600 MHz, $CDCl_3$)



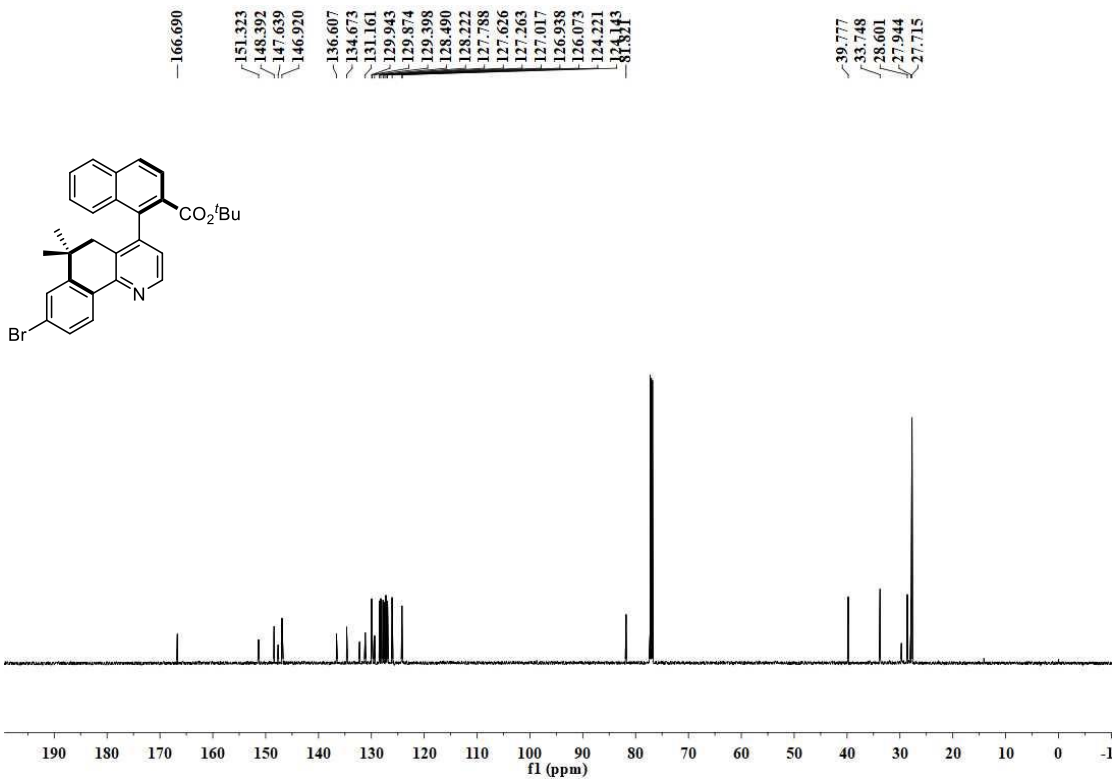
^{13}C NMR Spectrum of 101 (151 MHz, $CDCl_3$)



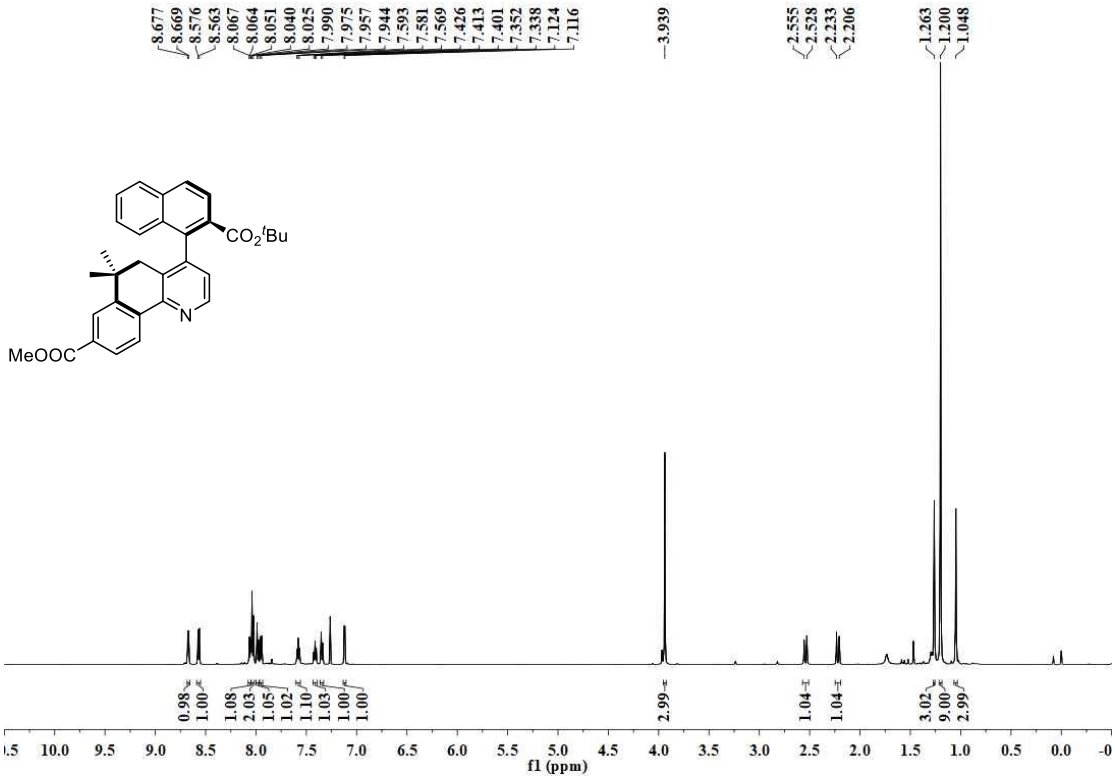
^{1}H NMR Spectrum of 102 (600 MHz, $CDCl_3$)



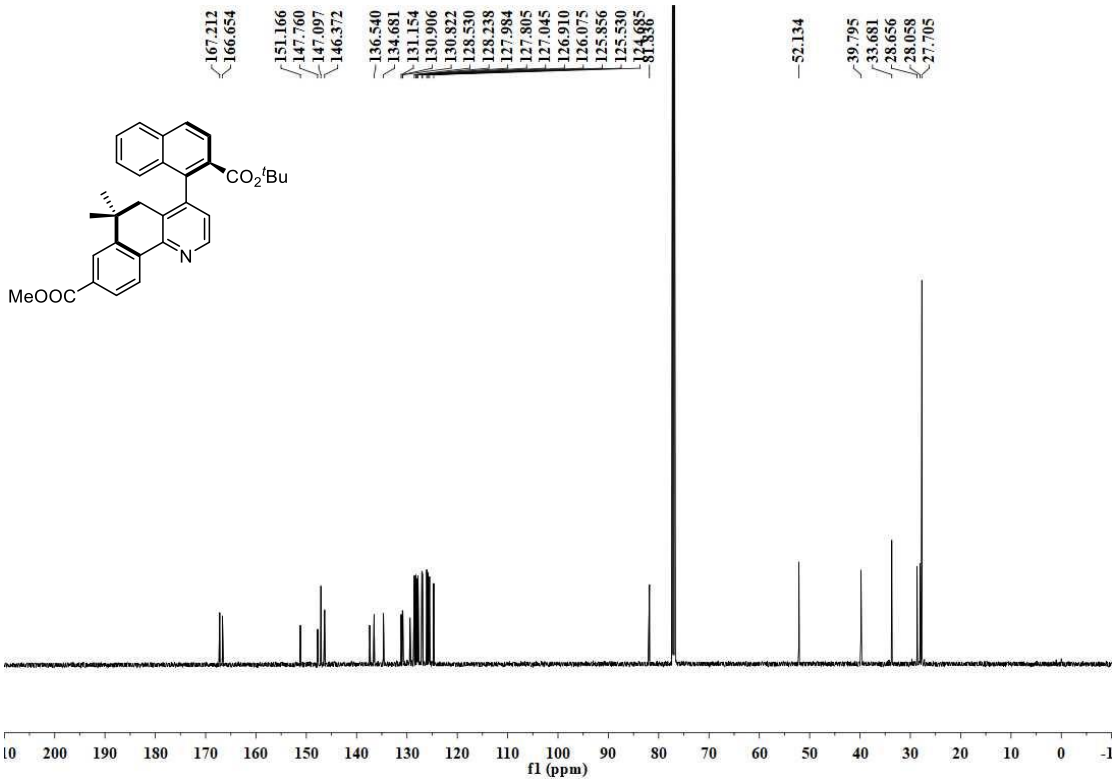
^{13}C NMR Spectrum of 102 (151 MHz, $CDCl_3$)



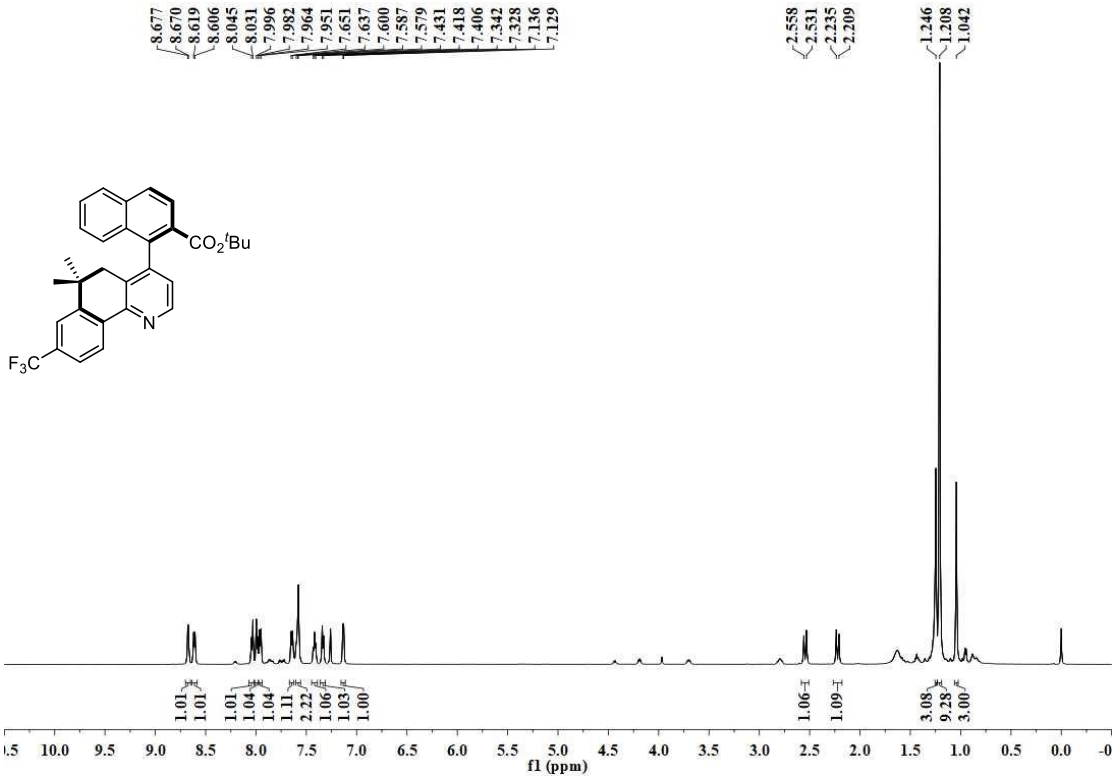
^{1}H NMR Spectrum of 103 (600 MHz, $CDCl_3$)



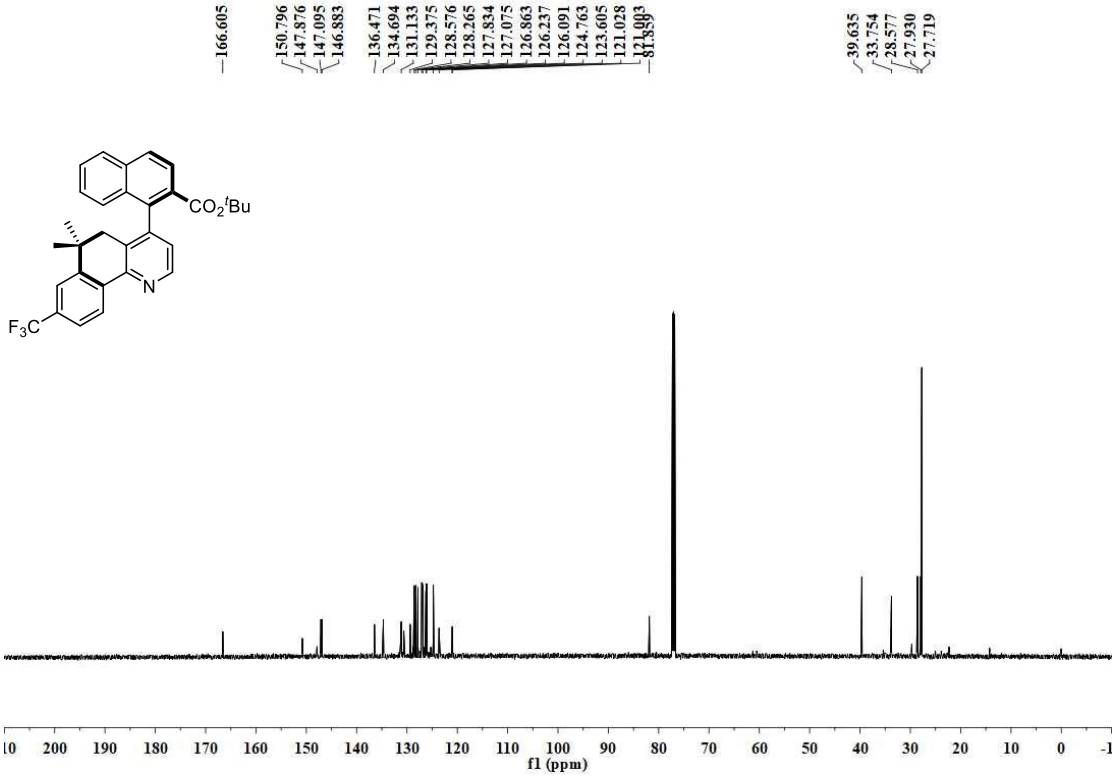
^{13}C NMR Spectrum of 103 (151 MHz, $CDCl_3$)



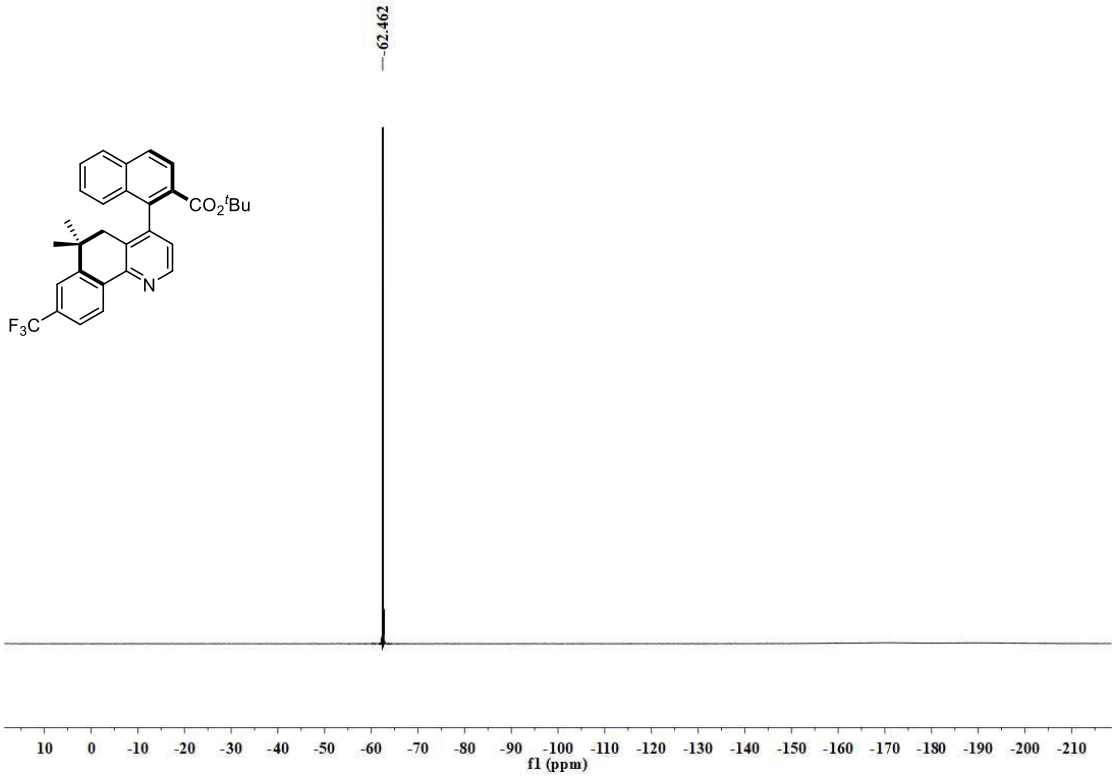
^{1}H NMR Spectrum of 104 (600 MHz, $CDCl_3$)



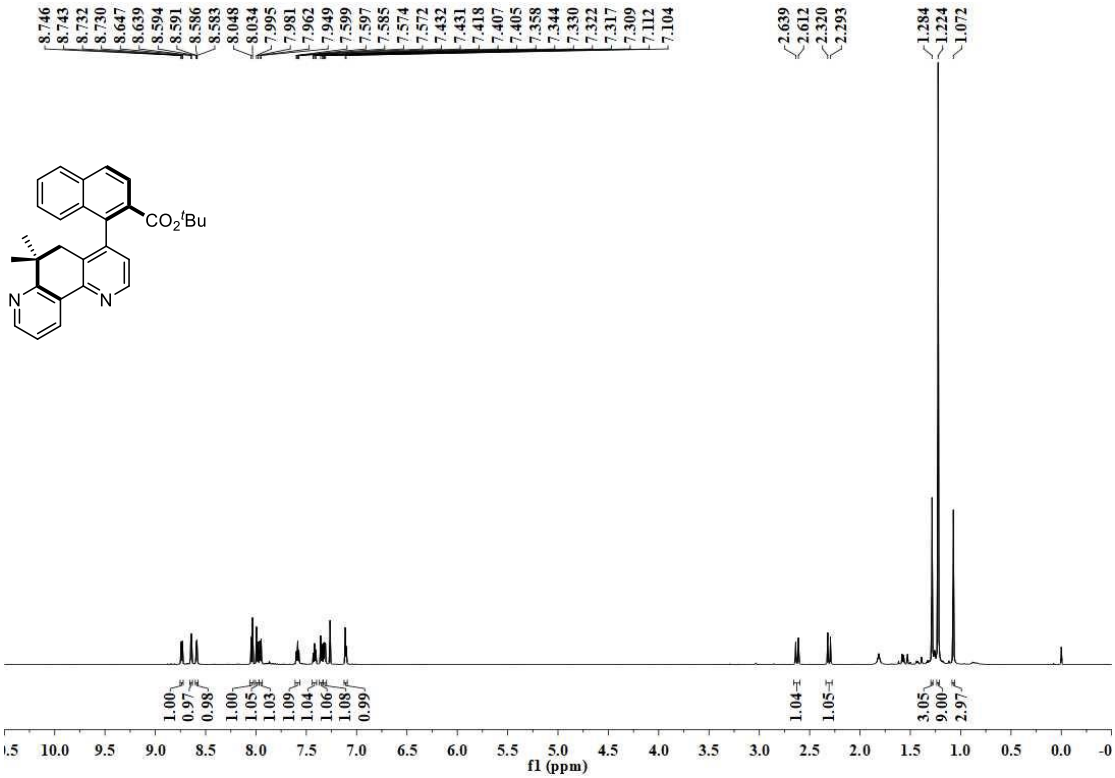
^{13}C NMR Spectrum of 104 (151 MHz, $CDCl_3$)



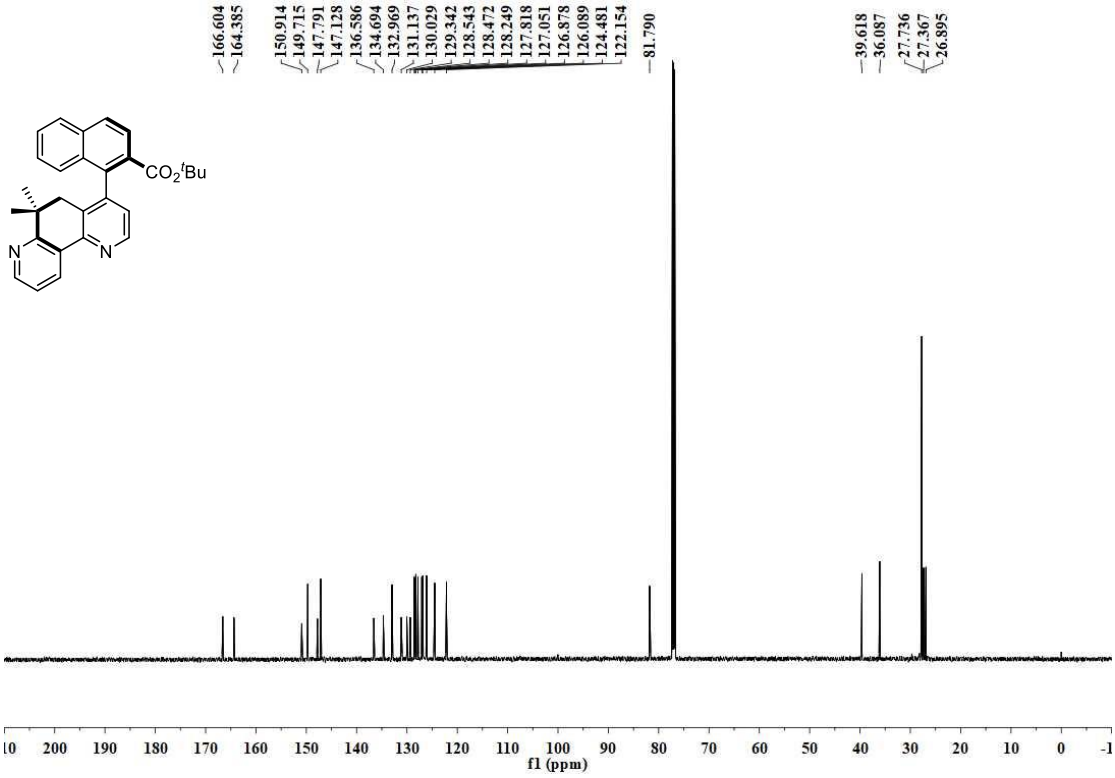
^{19}F NMR Spectrum of 104 (565 MHz, $CDCl_3$)



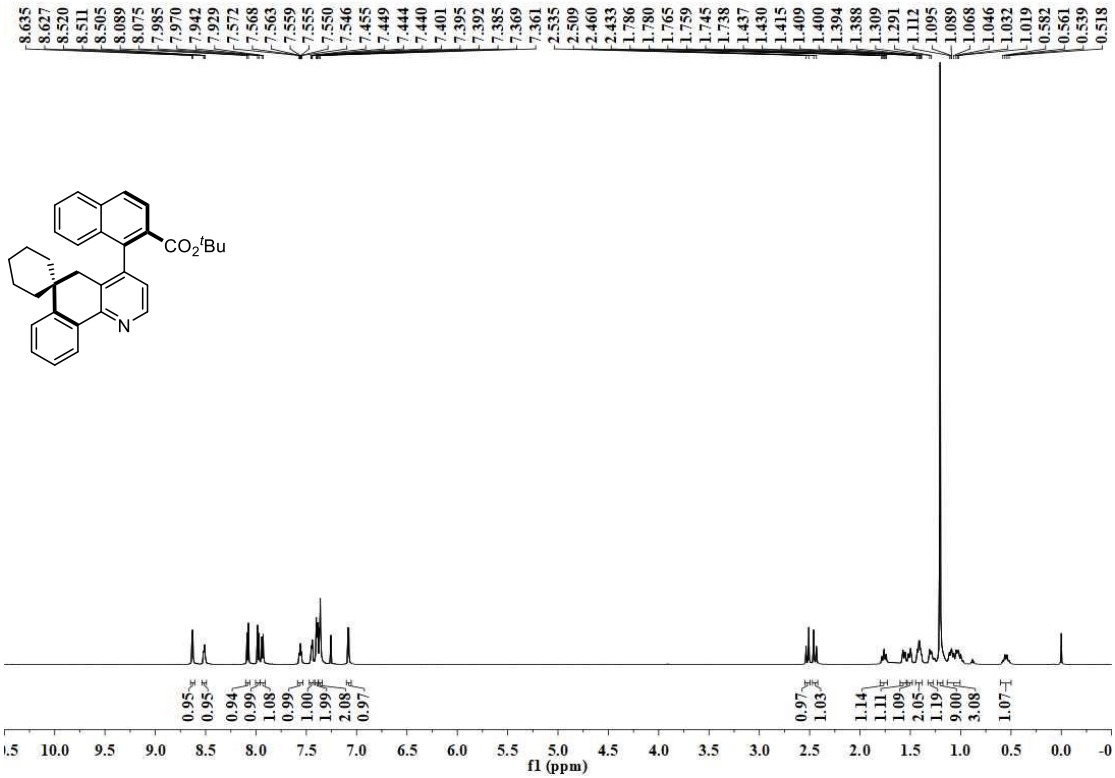
^{1}H NMR Spectrum of 105 (600 MHz, $CDCl_3$)



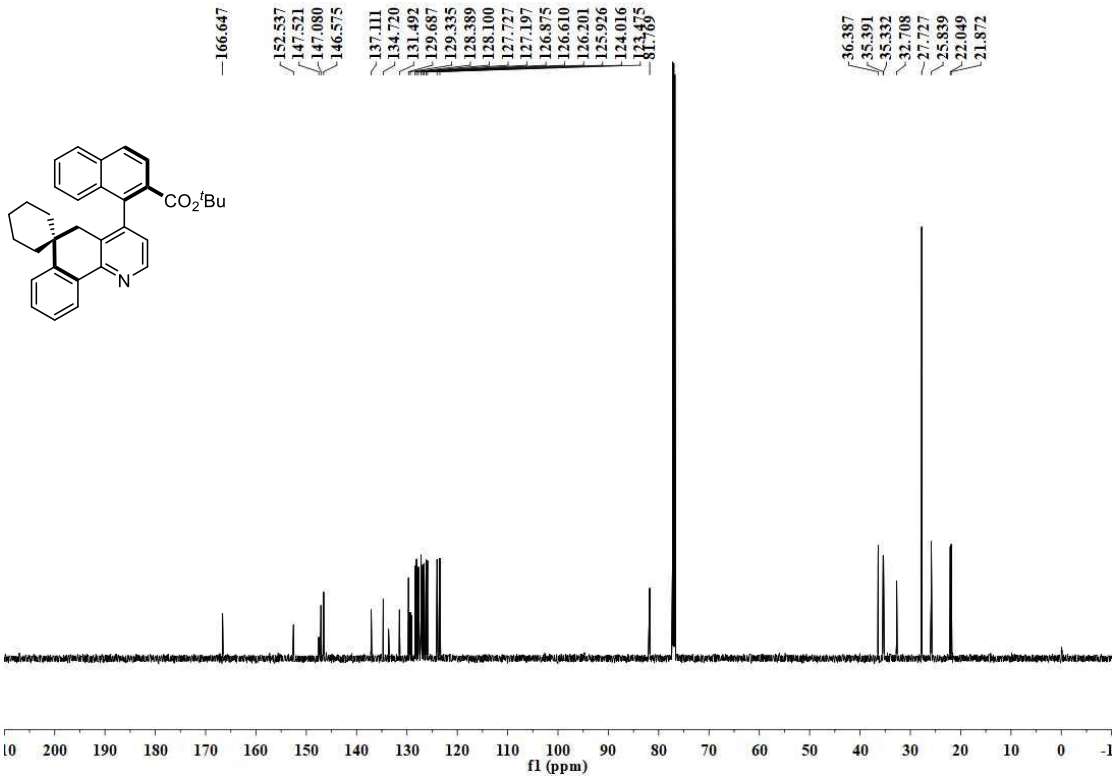
^{13}C NMR Spectrum of 105 (151 MHz, $CDCl_3$)



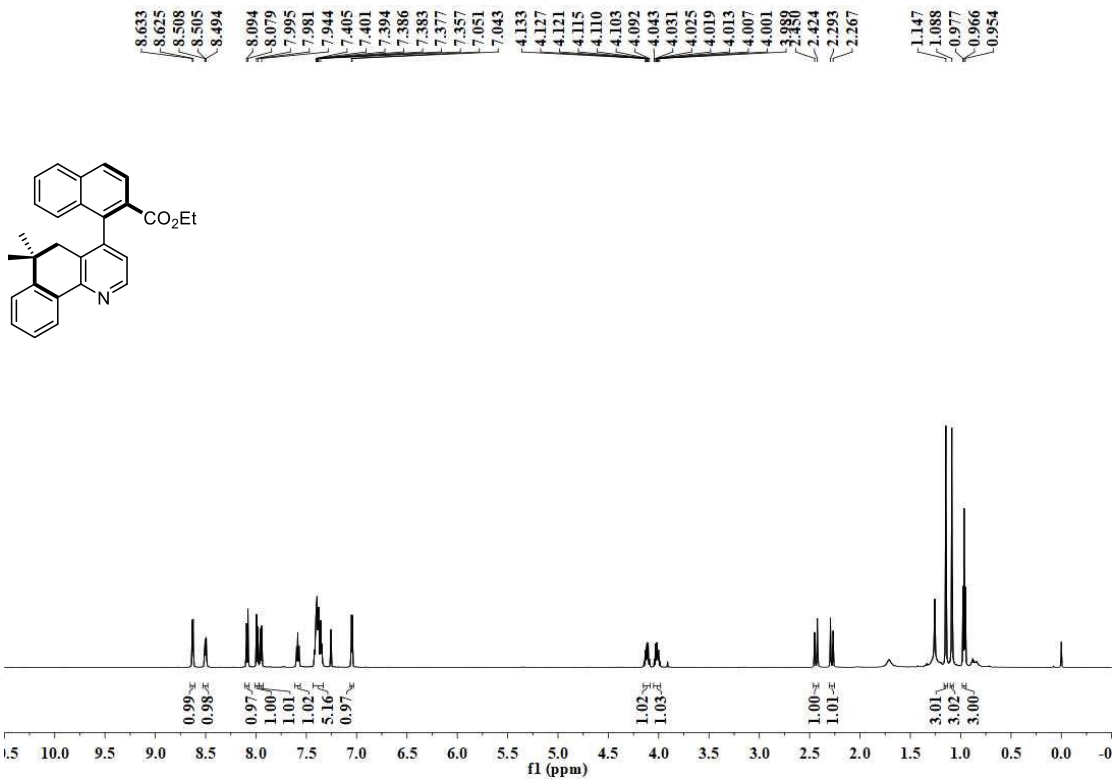
^{1}H NMR Spectrum of 106 (600 MHz, $CDCl_3$)



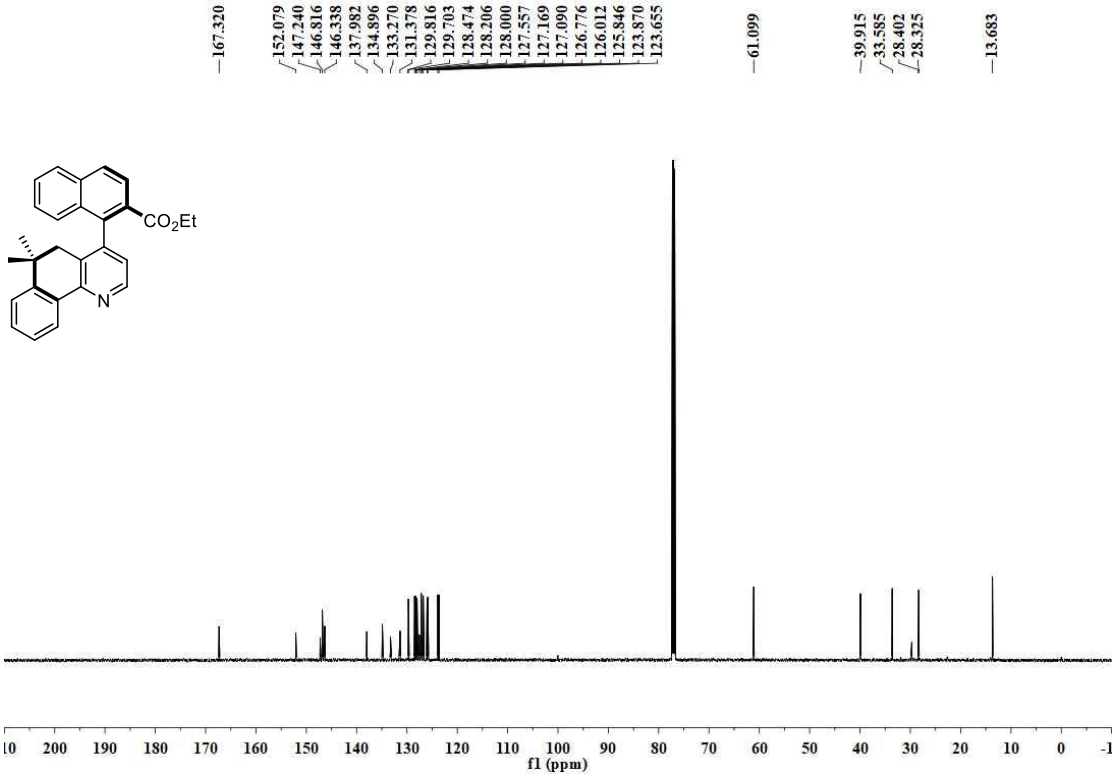
^{13}C NMR Spectrum of 106 (151 MHz, $CDCl_3$)



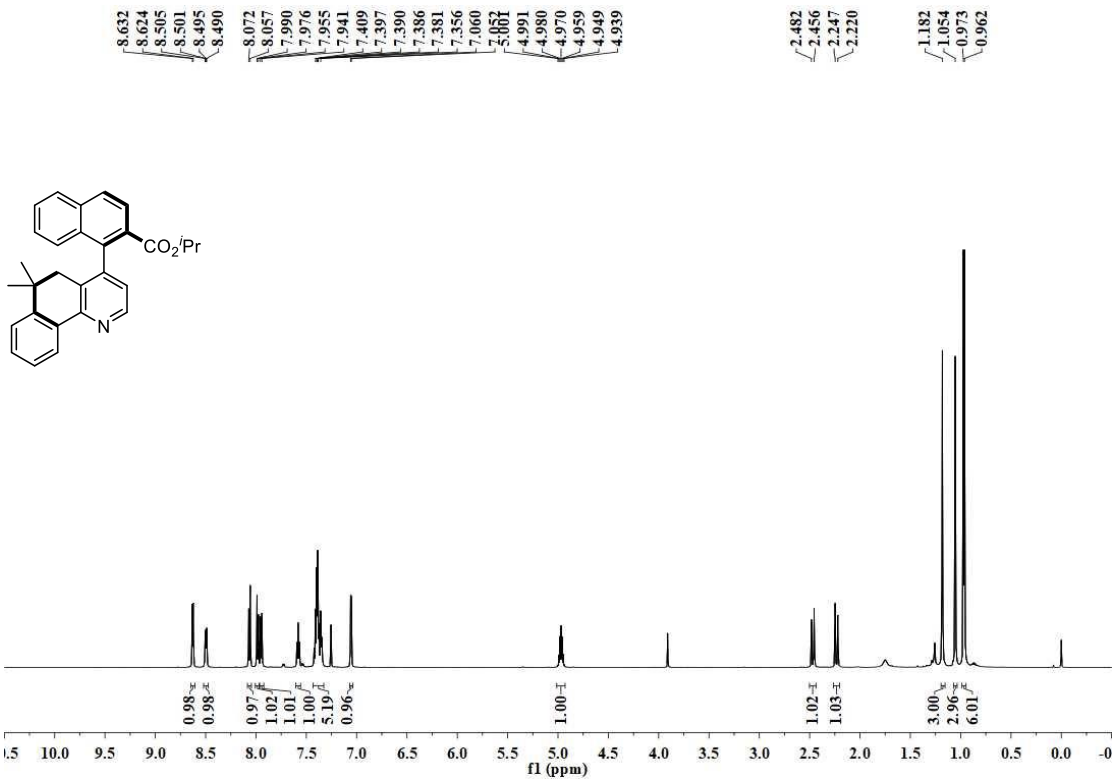
^{1}H NMR Spectrum of 107 (600 MHz, $CDCl_3$)



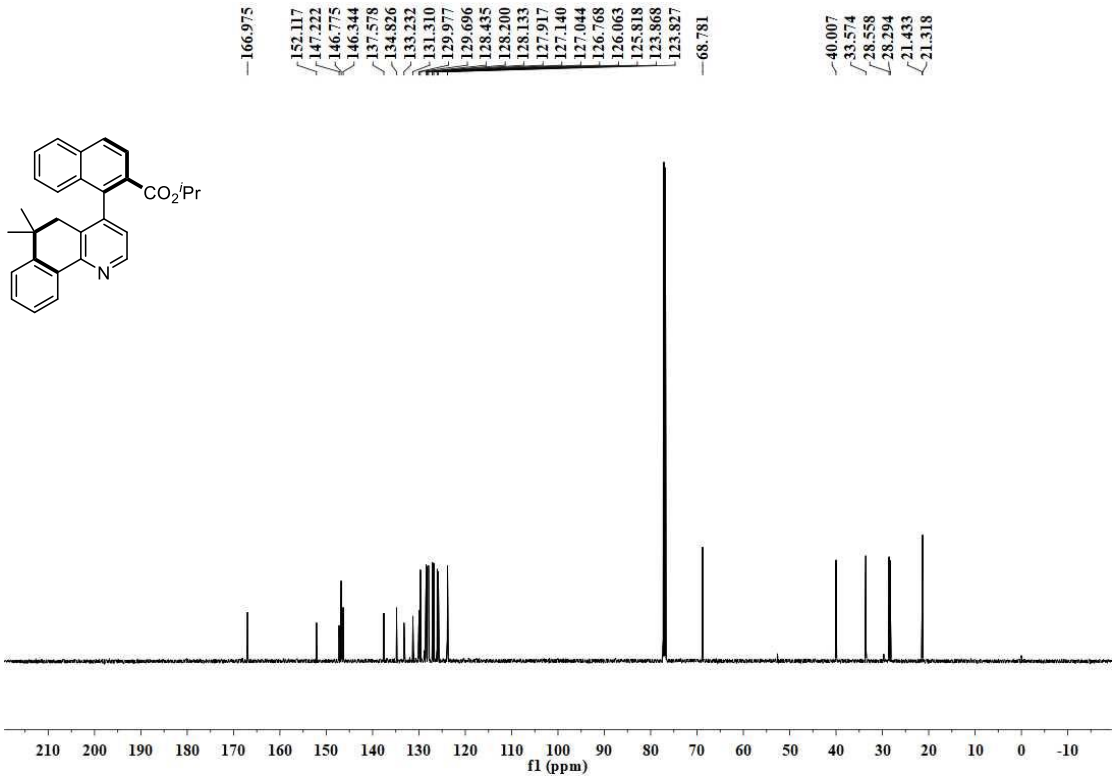
^{13}C NMR Spectrum of 107 (151 MHz, $CDCl_3$)



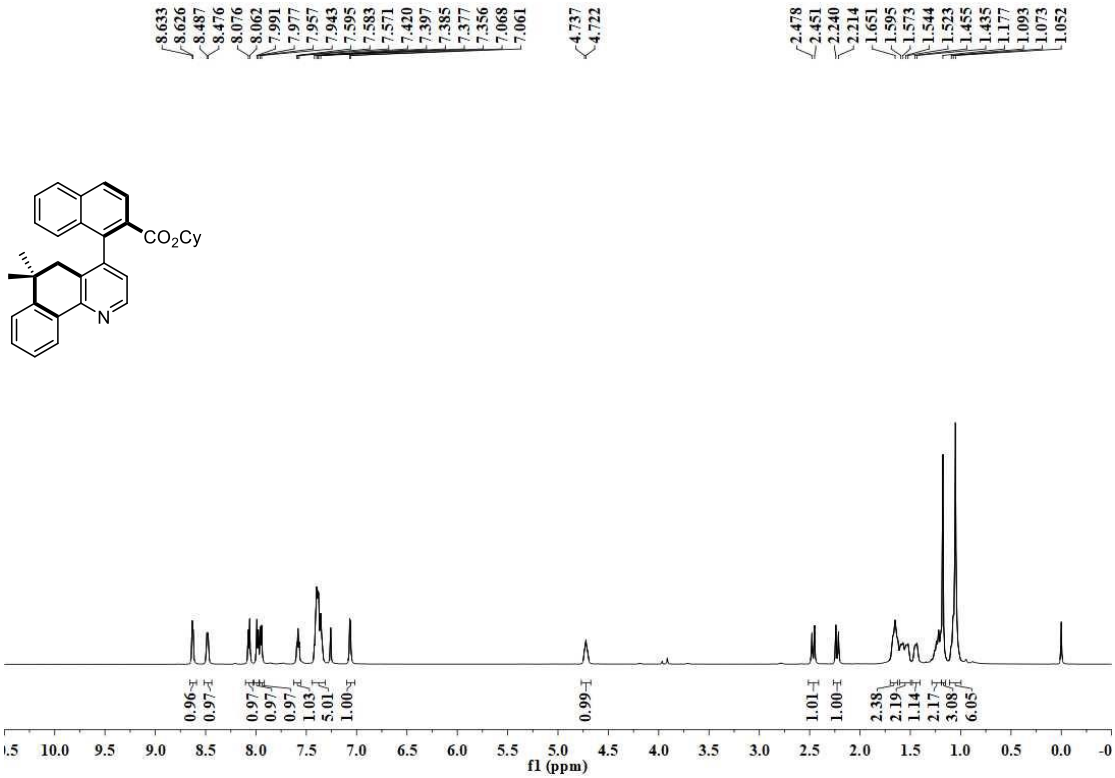
^{1}H NMR Spectrum of 108 (600 MHz, $CDCl_3$)



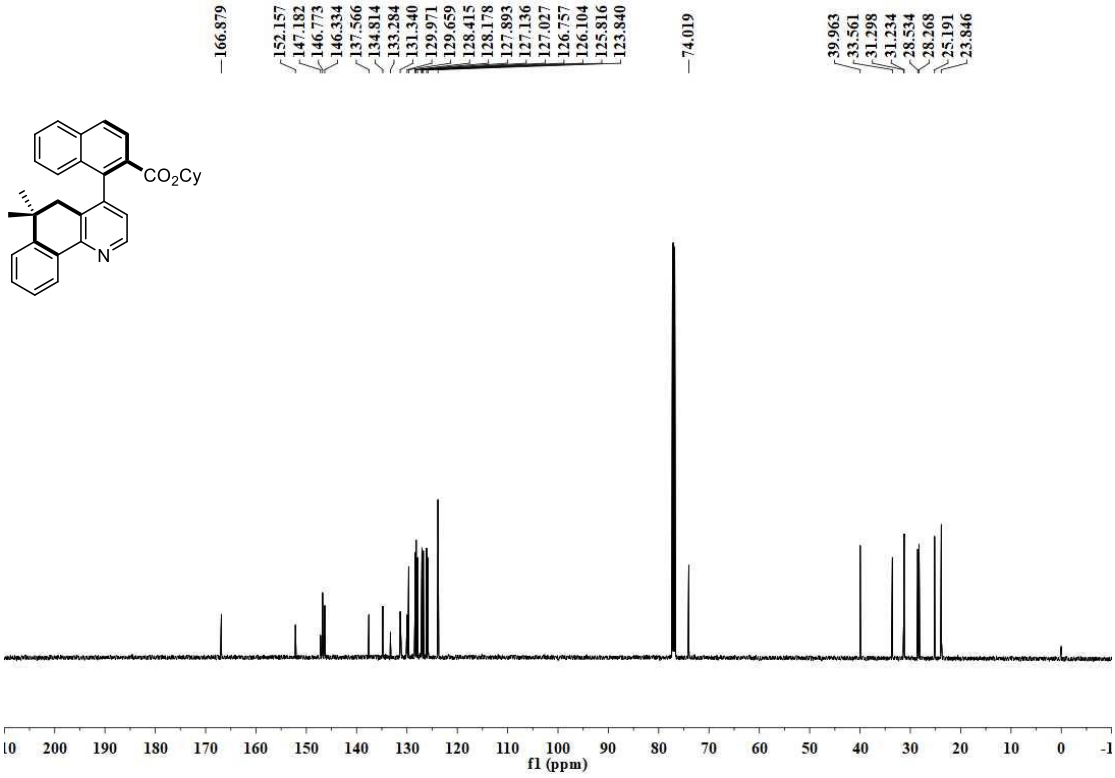
^{13}C NMR Spectrum of 108 (151 MHz, $CDCl_3$)



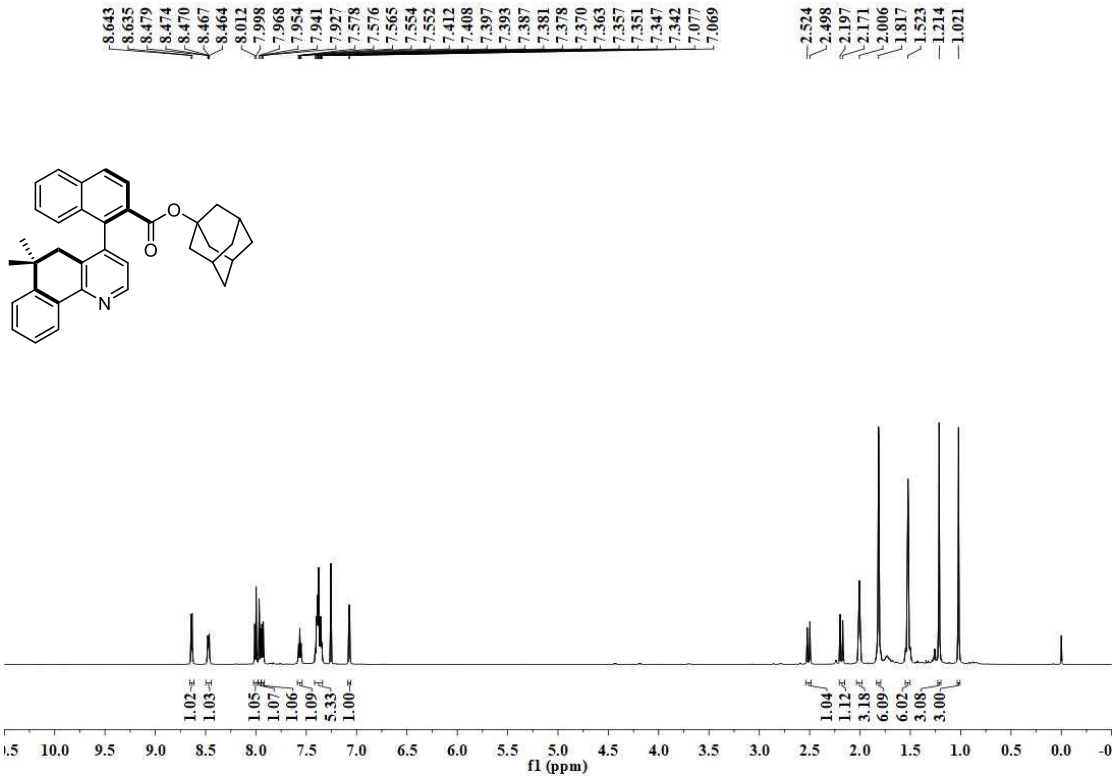
^{1}H NMR Spectrum of 109 (600 MHz, $CDCl_3$)



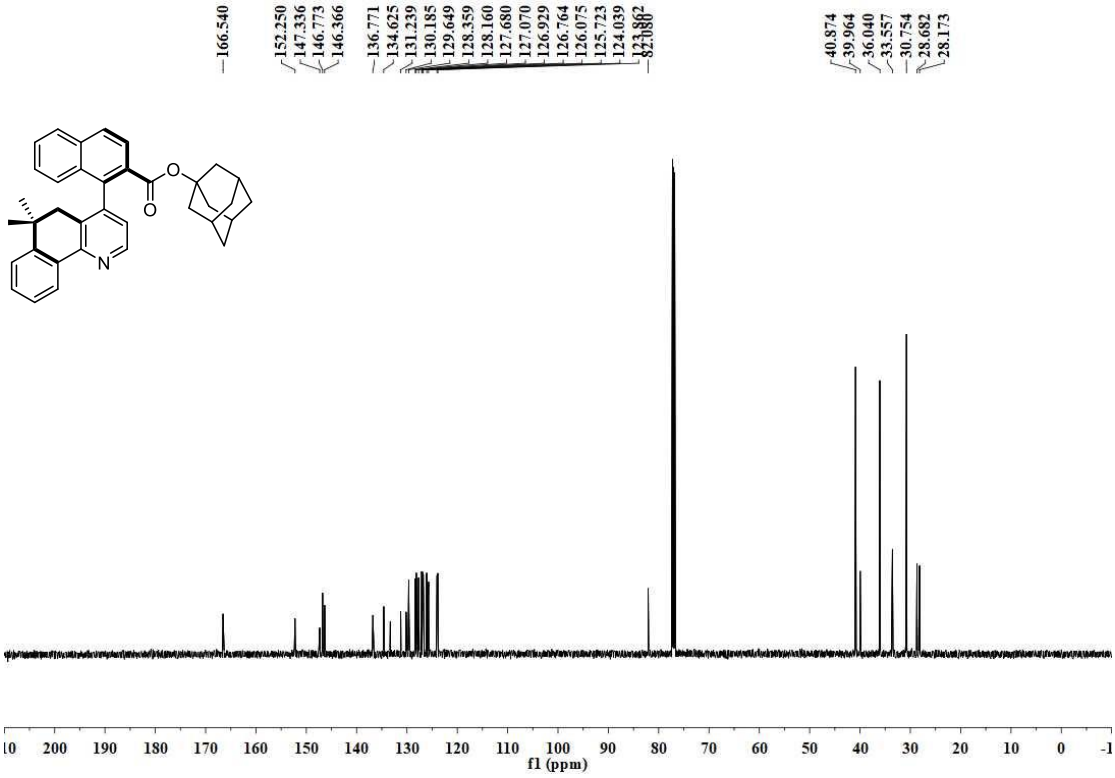
^{13}C NMR Spectrum of 109 (151 MHz, $CDCl_3$)



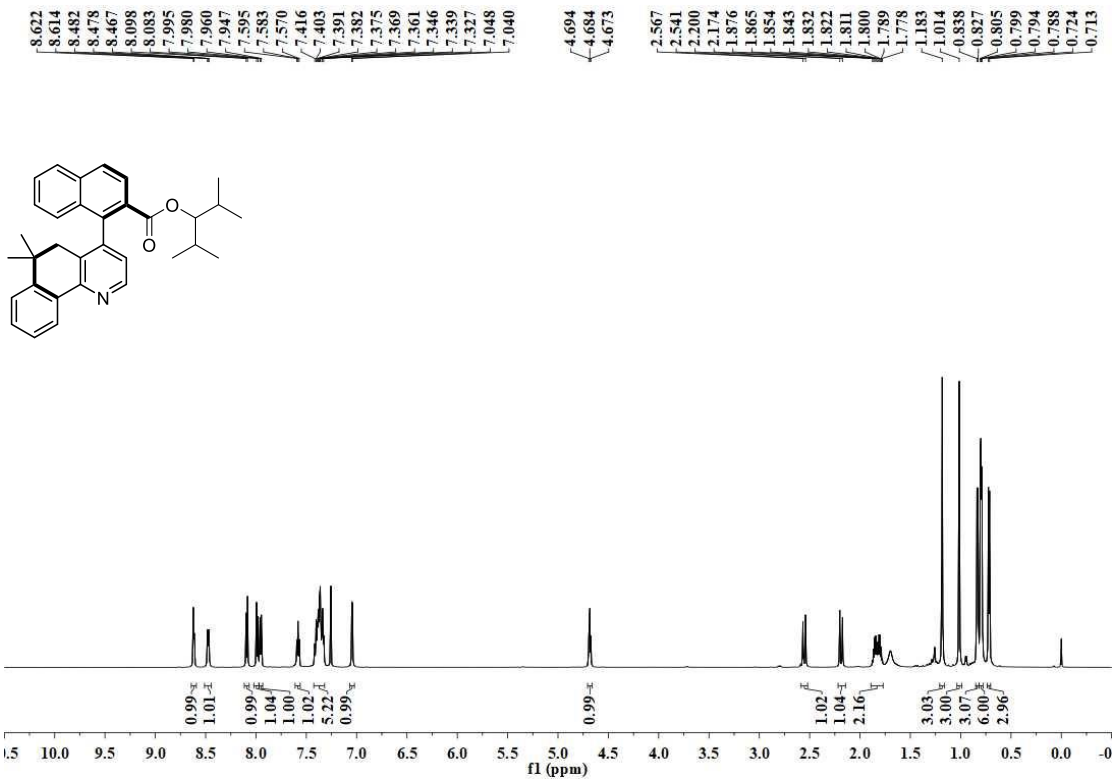
^{1}H NMR Spectrum of 110 (600 MHz, $CDCl_3$)



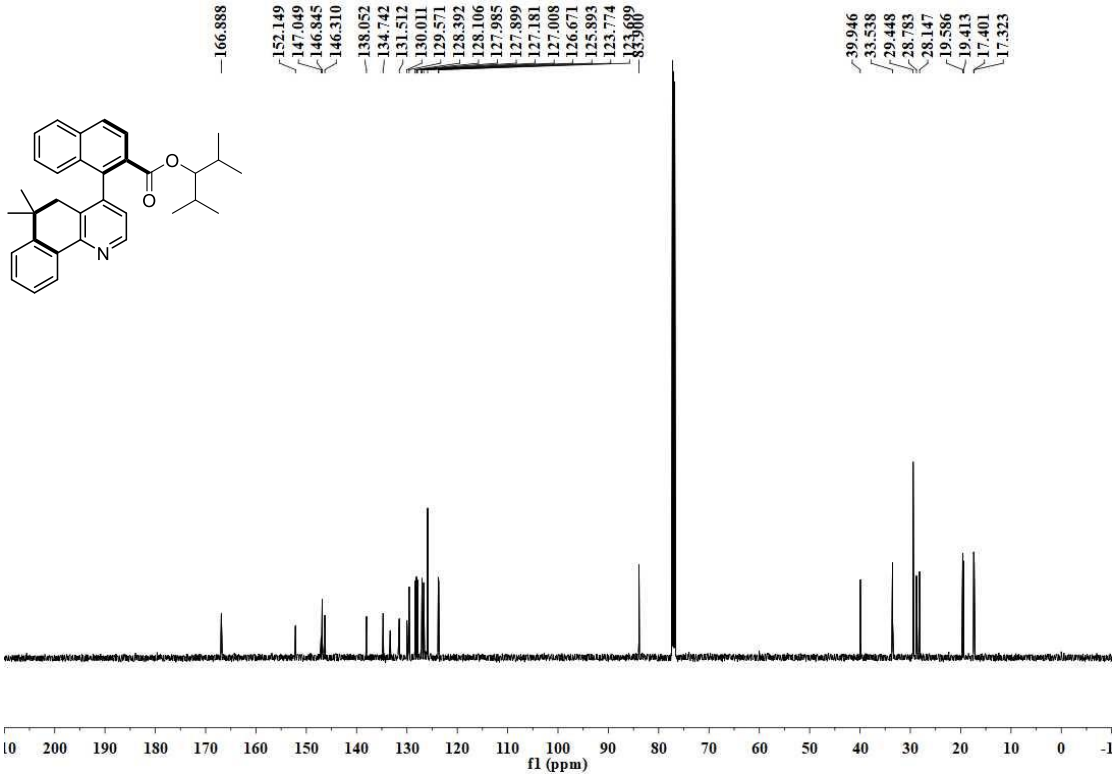
^{13}C NMR Spectrum of 110 (151 MHz, $CDCl_3$)



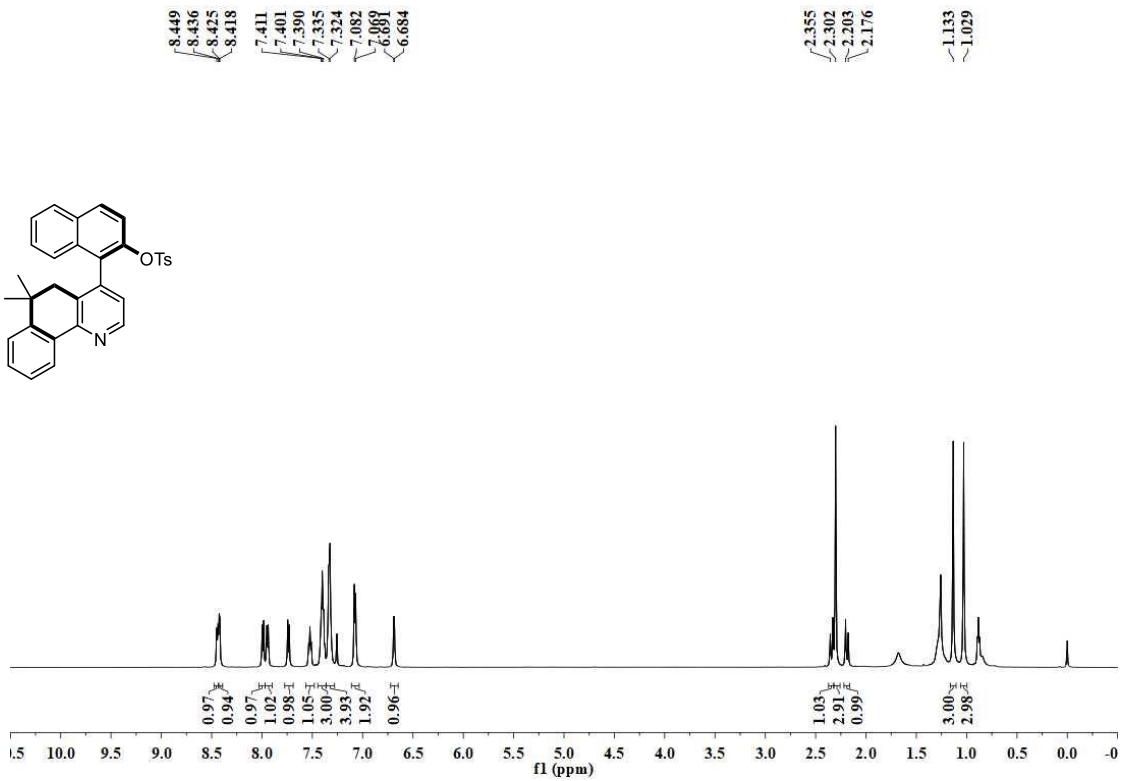
^{1}H NMR Spectrum of 111 (600 MHz, $CDCl_3$)



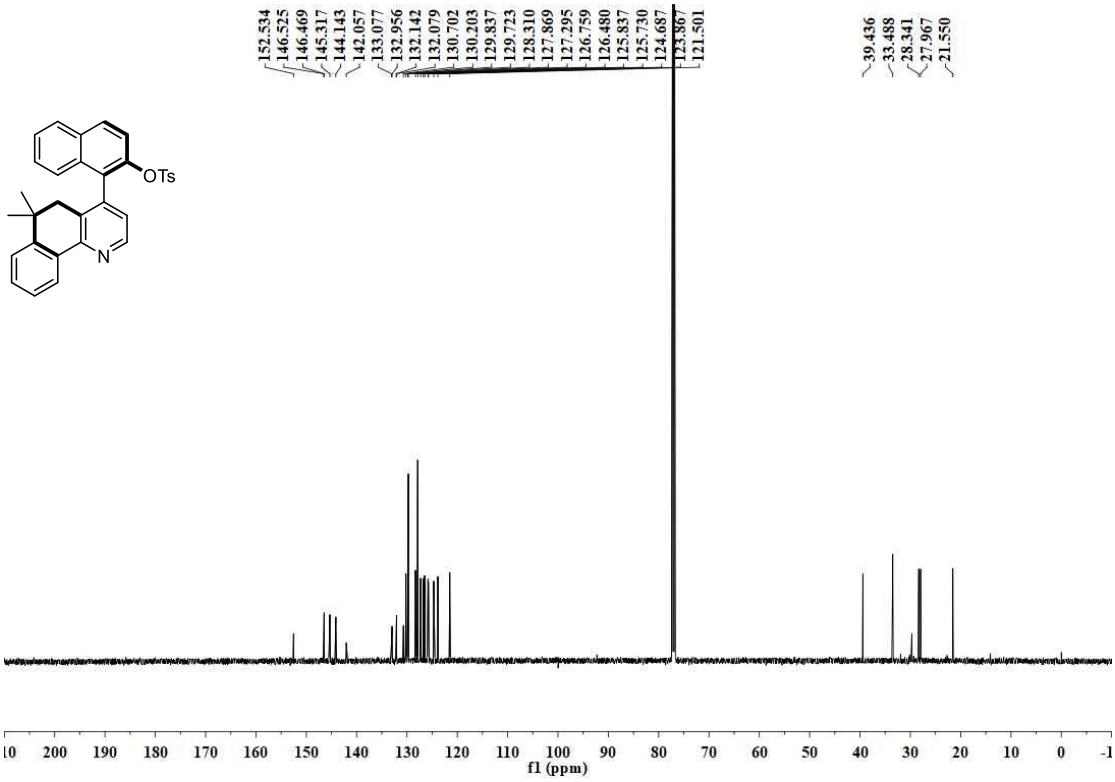
^{13}C NMR Spectrum of 111 (151 MHz, $CDCl_3$)



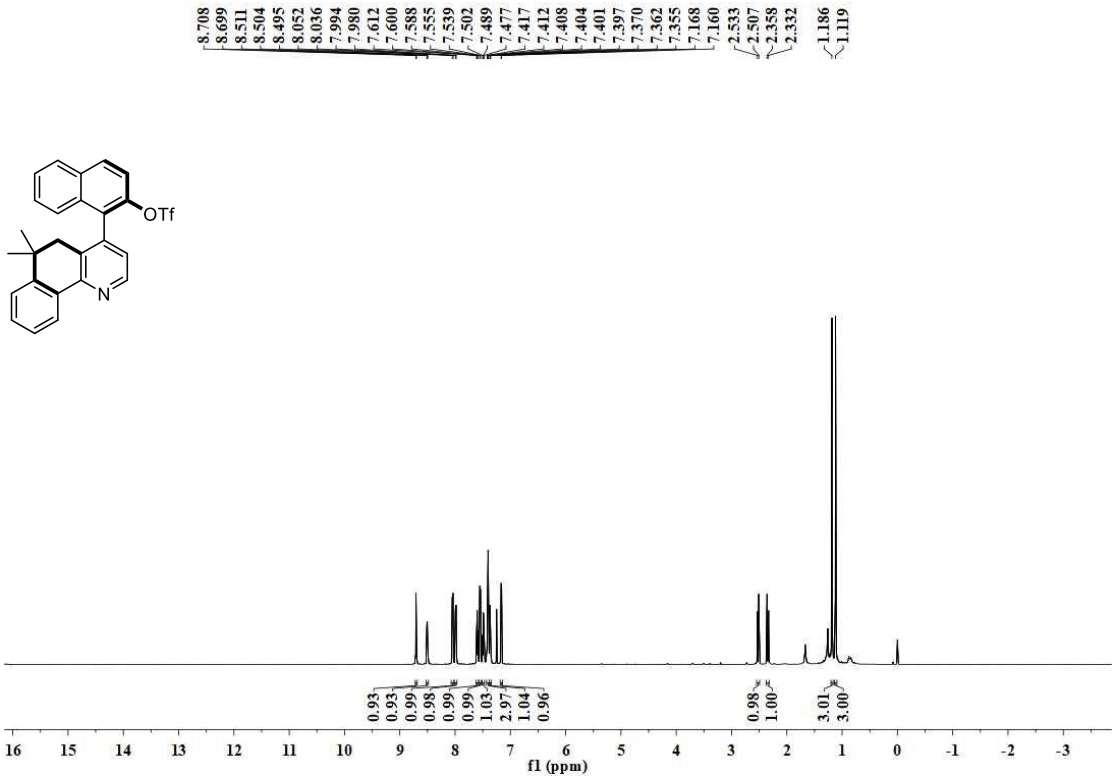
^{1}H NMR Spectrum of 112 (600 MHz, $CDCl_3$)



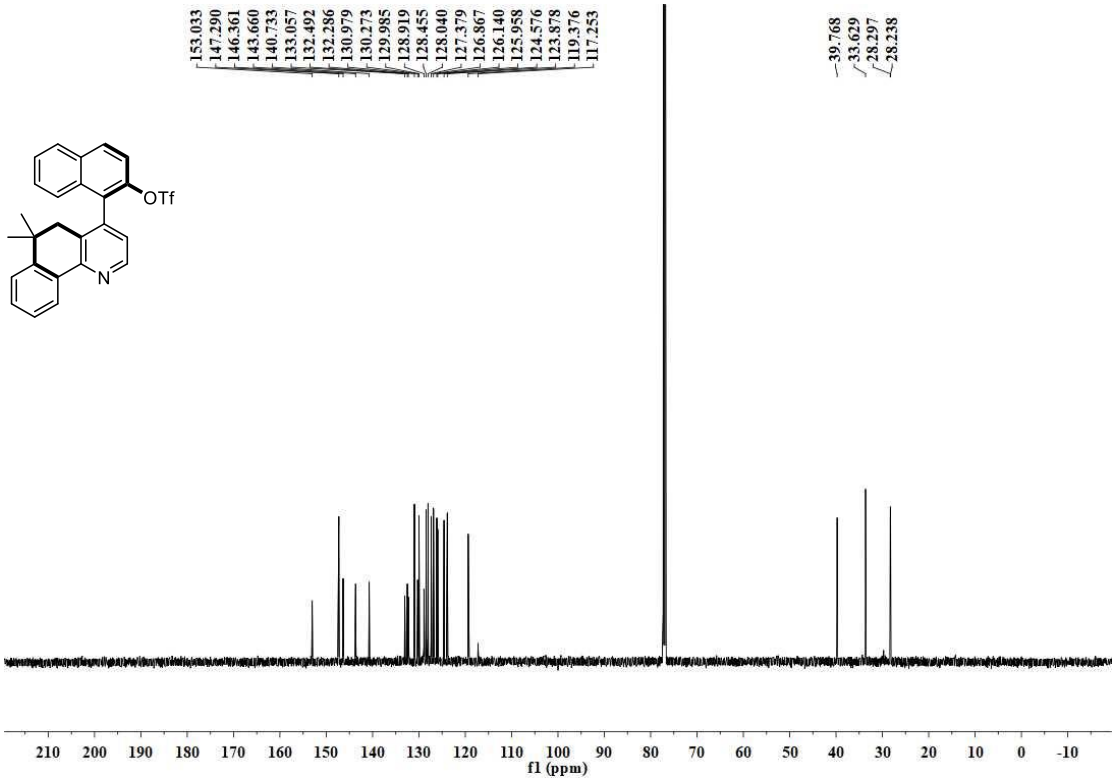
^{13}C NMR Spectrum of 112 (151 MHz, $CDCl_3$)



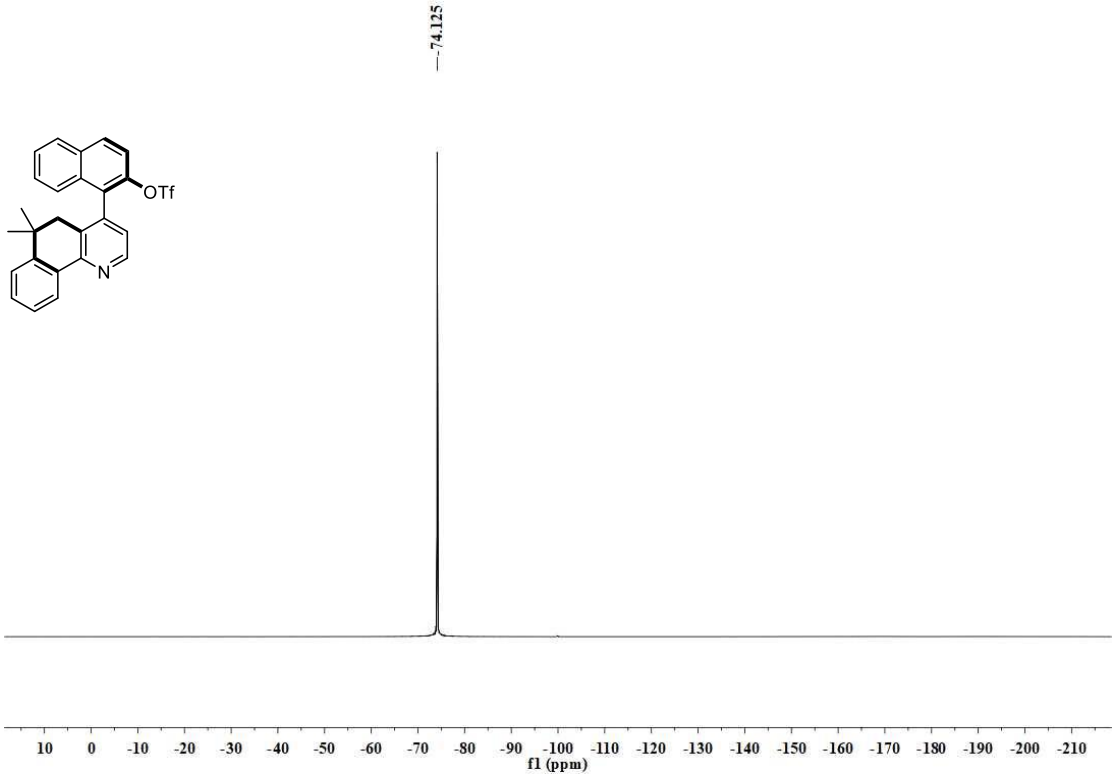
^{1}H NMR Spectrum of 113 (600 MHz, $CDCl_3$)



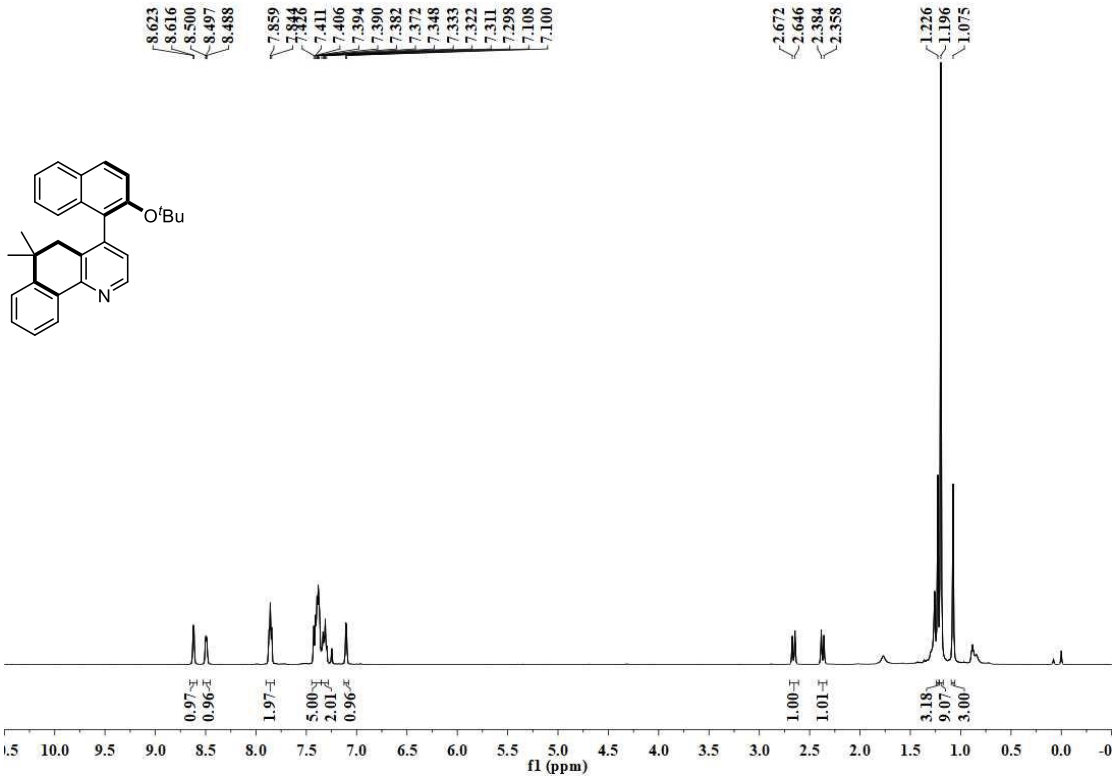
^{13}C NMR Spectrum of 113 (151 MHz, $CDCl_3$)



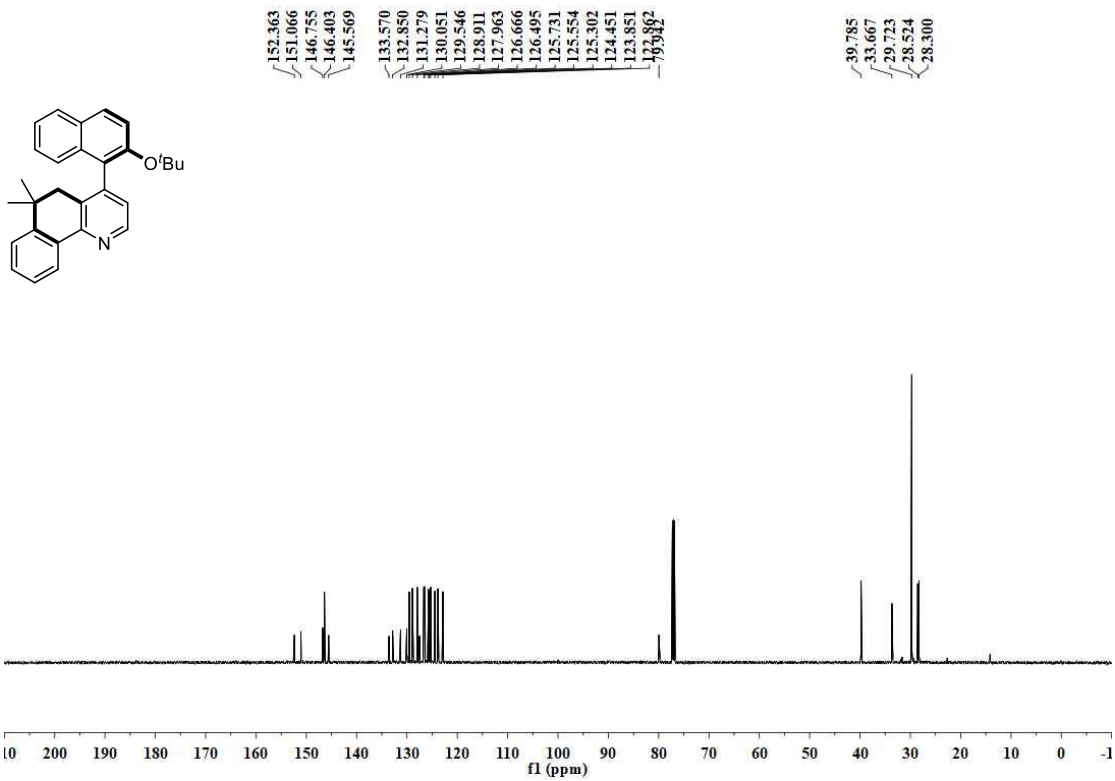
^{19}F NMR Spectrum of 113 (565 MHz, $CDCl_3$)



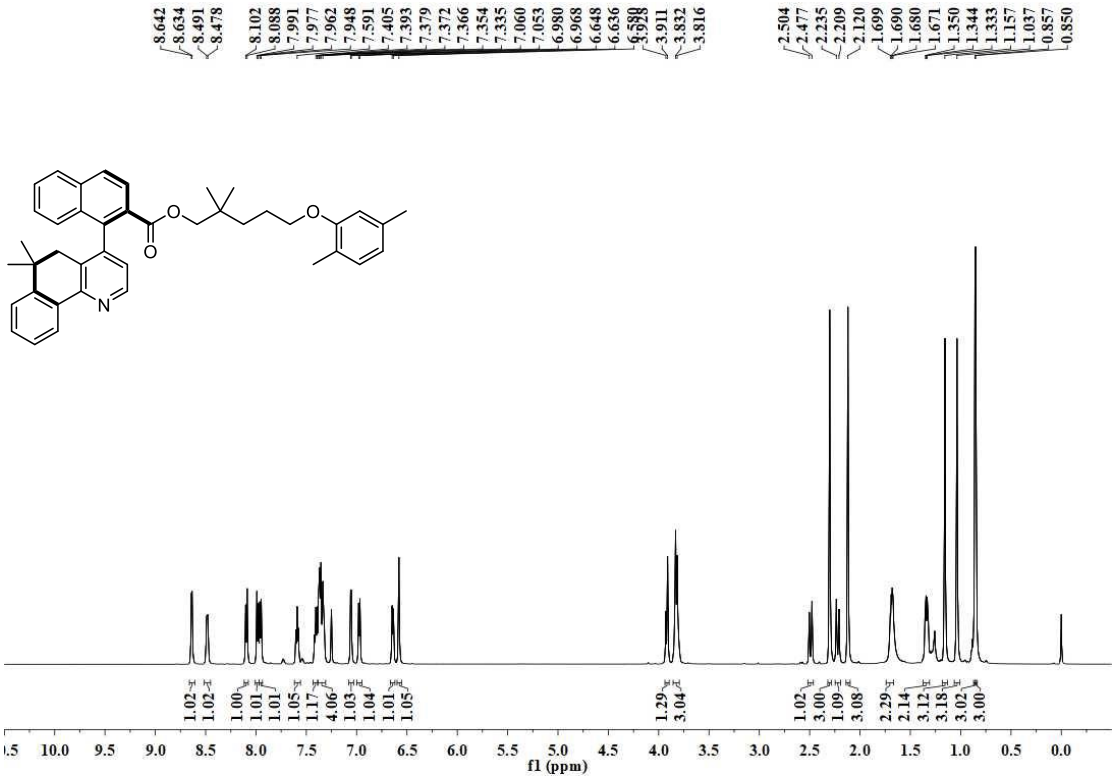
^{1}H NMR Spectrum of 114 (600 MHz, $CDCl_3$)



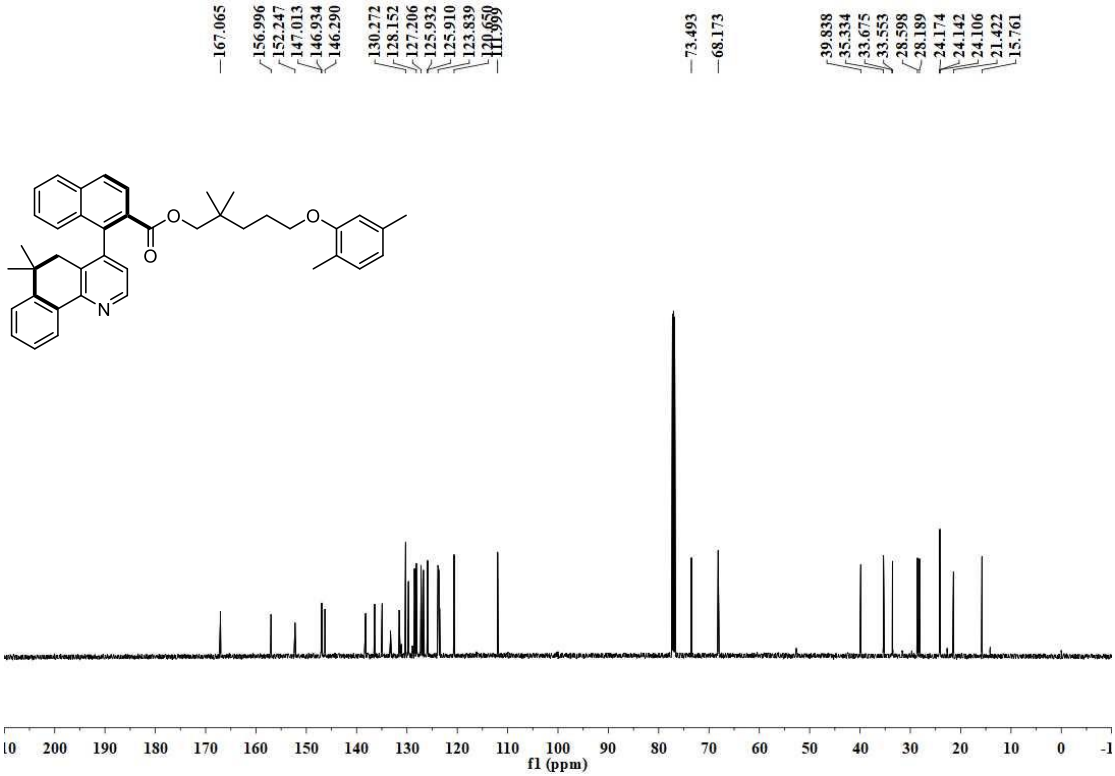
^{13}C NMR Spectrum of 114 (151 MHz, $CDCl_3$)



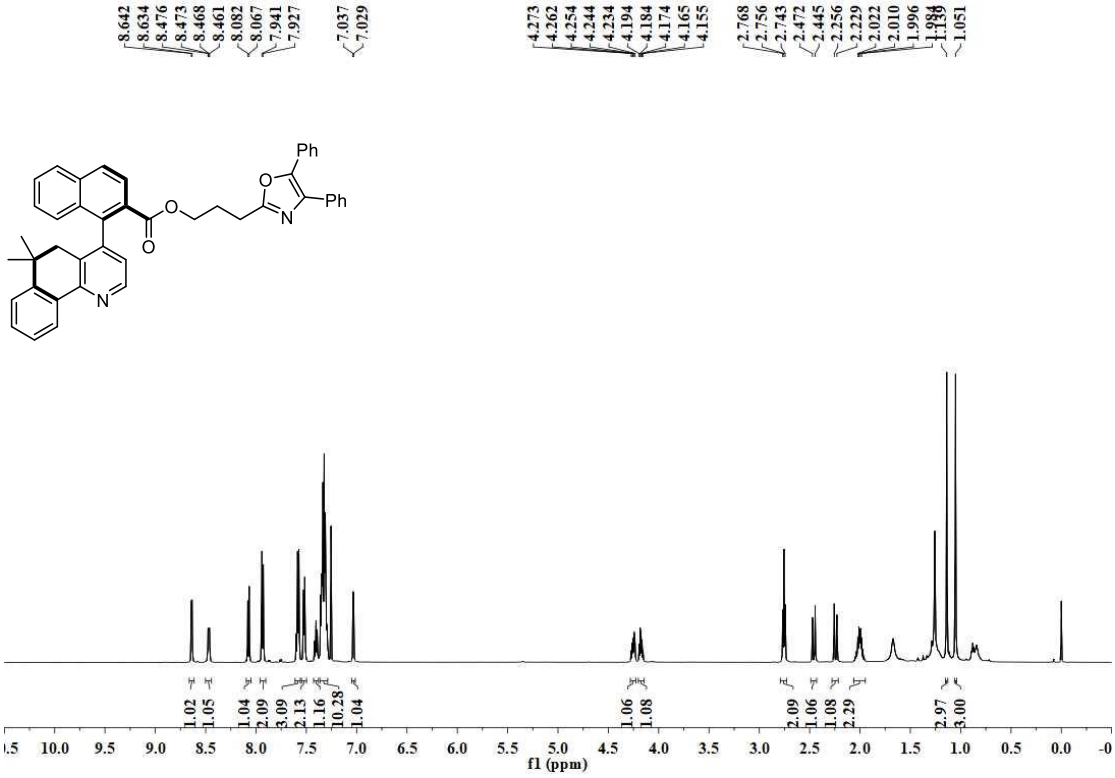
^{1}H NMR Spectrum of 115 (600 MHz, $CDCl_3$)



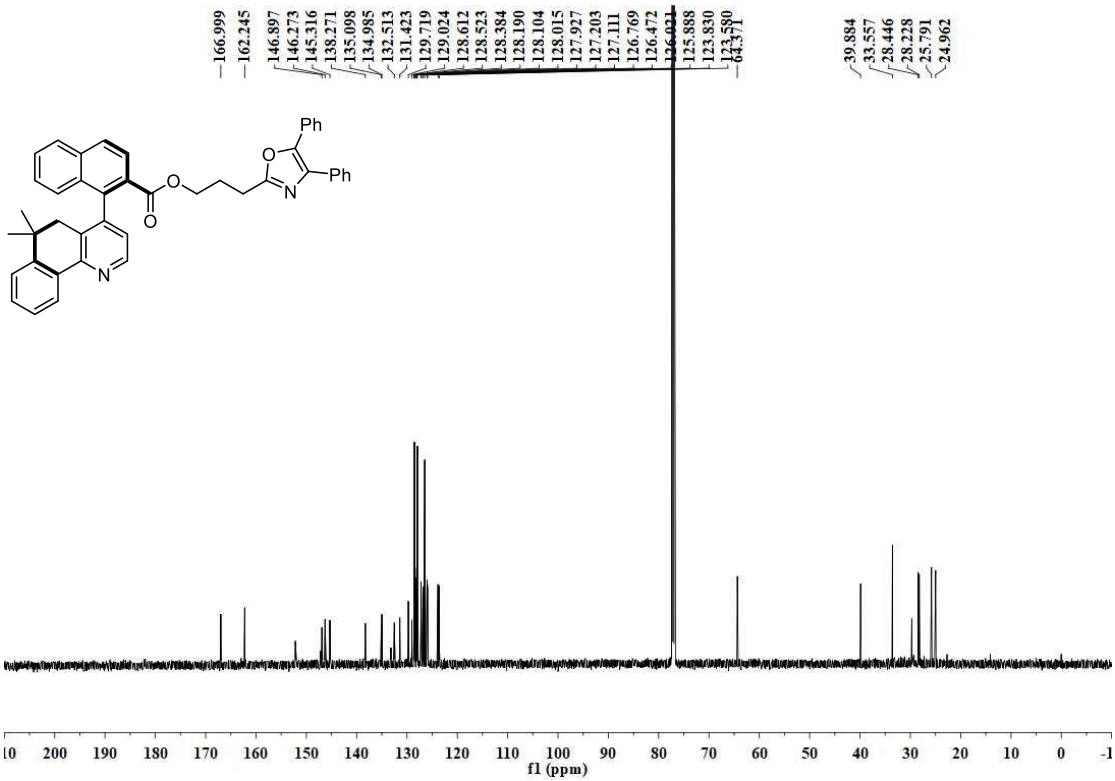
^{13}C NMR Spectrum of 115 (151 MHz, $CDCl_3$)



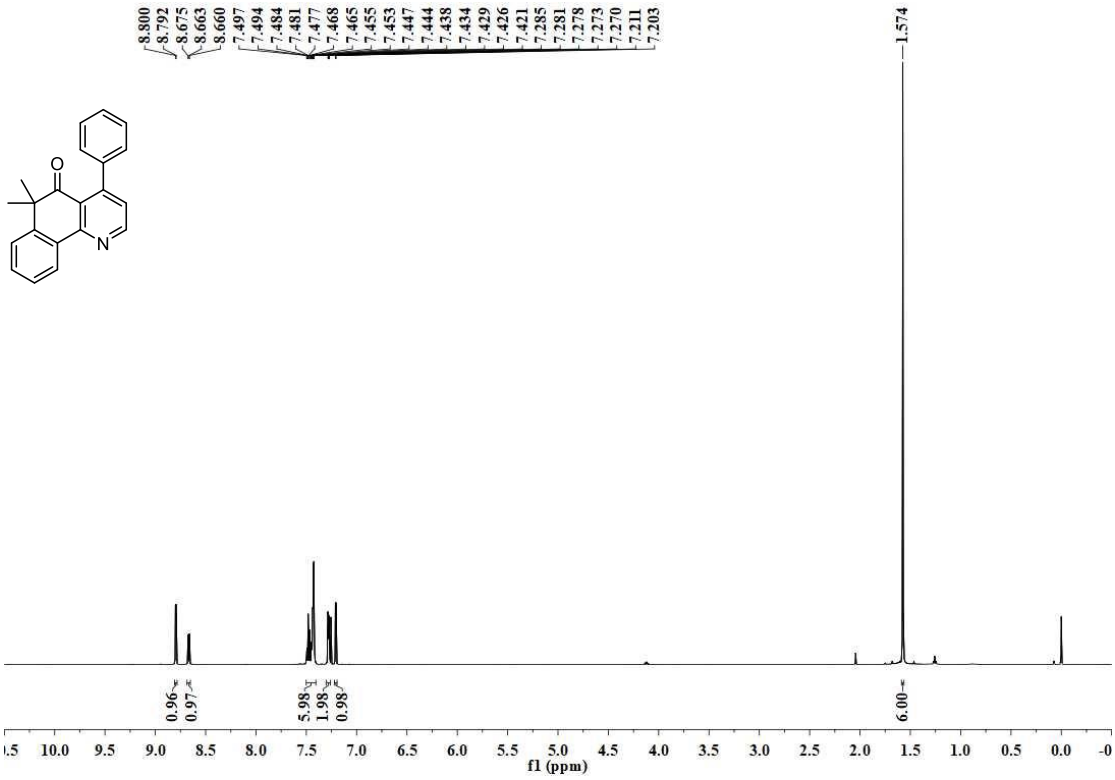
^{1}H NMR Spectrum of 116 (600 MHz, $CDCl_3$)



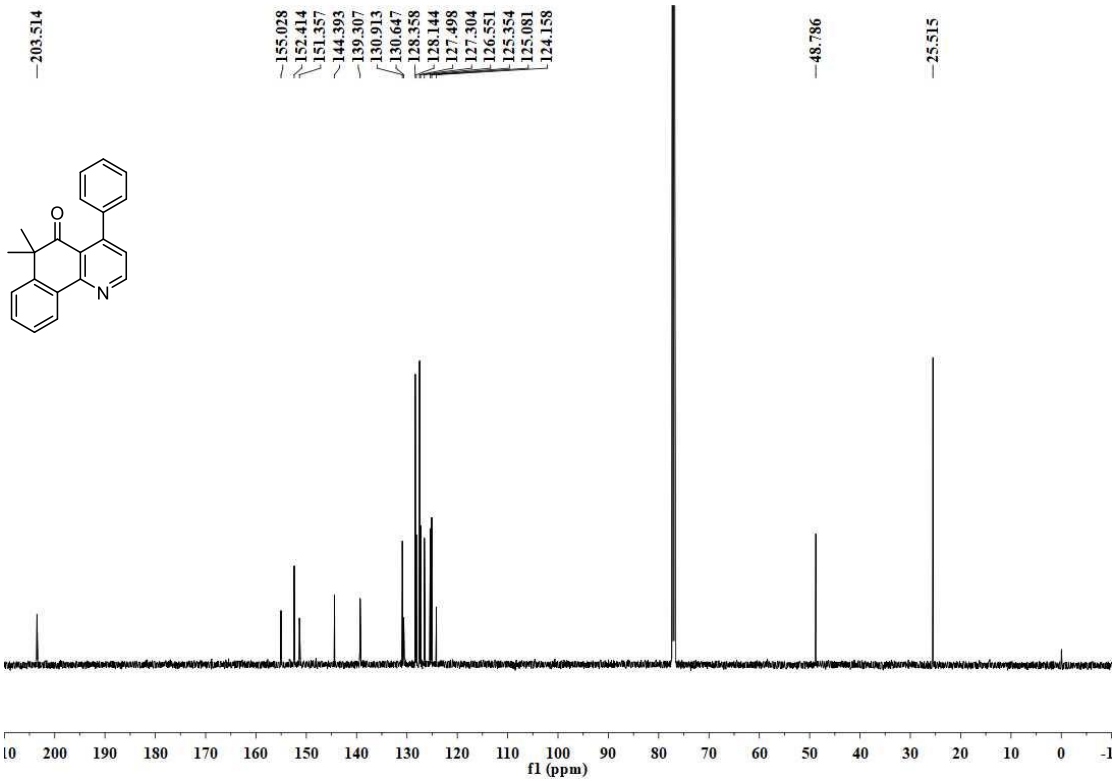
^{13}C NMR Spectrum of 116 (151 MHz, $CDCl_3$)



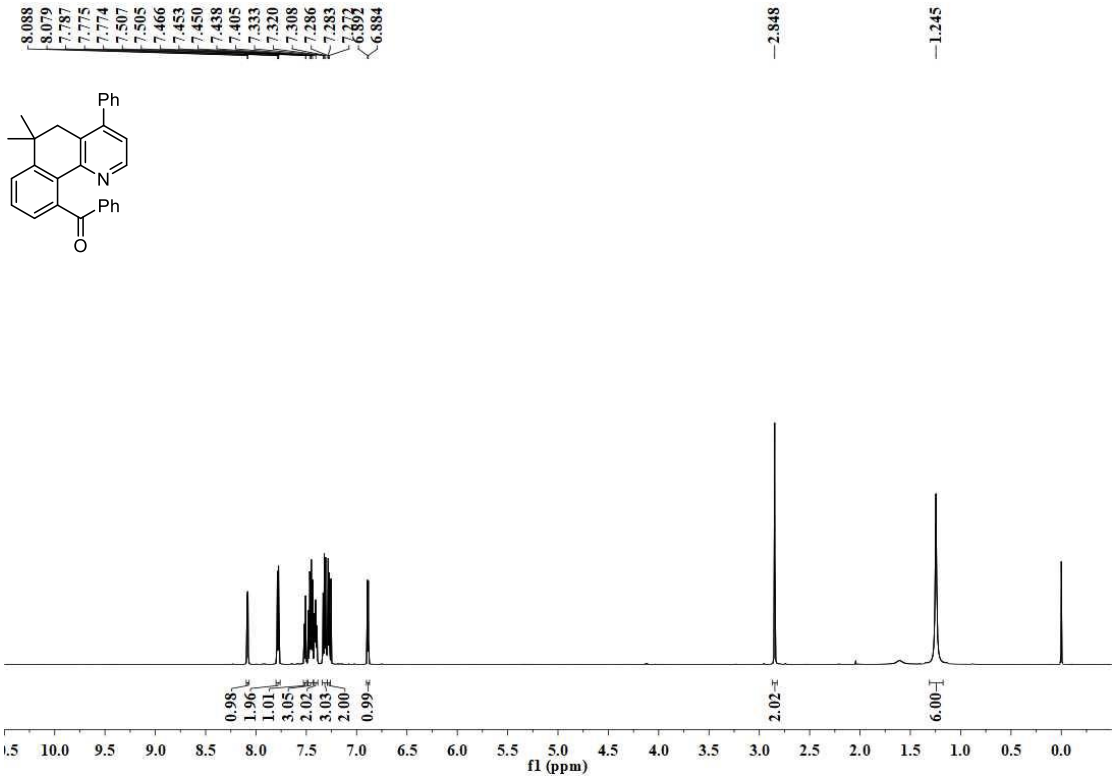
^{1}H NMR Spectrum of 65 (600 MHz, $CDCl_3$)



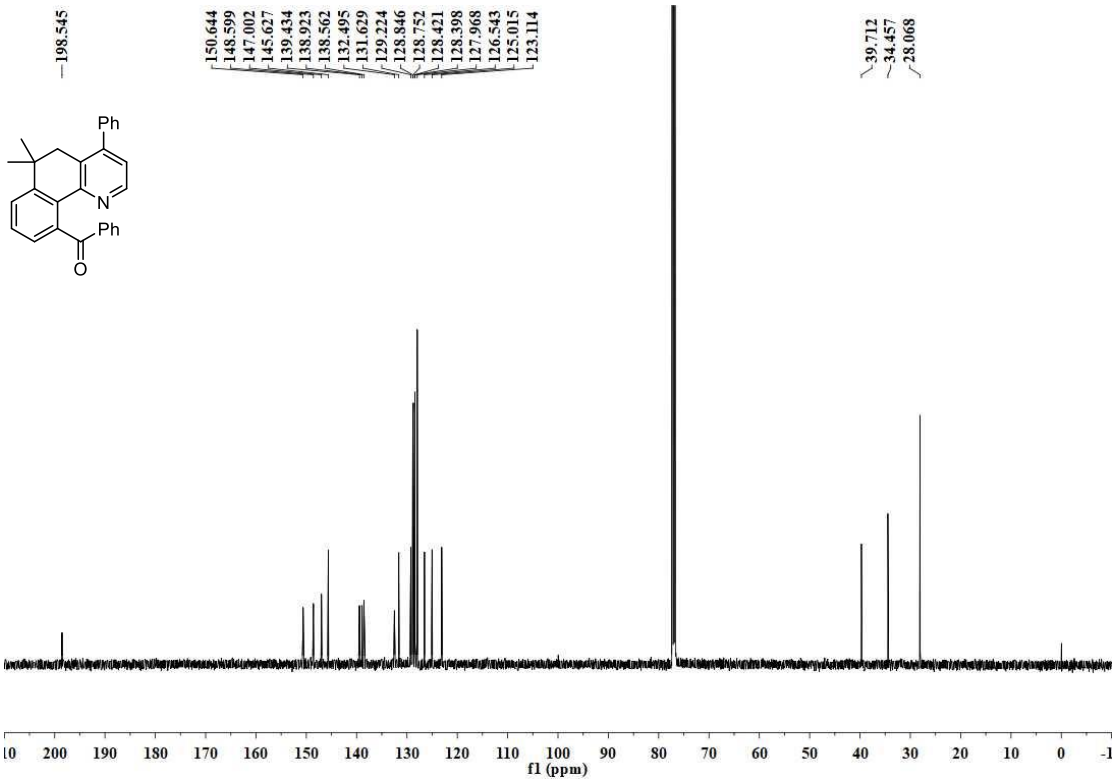
^{13}C NMR Spectrum of 65 (151 MHz, $CDCl_3$)



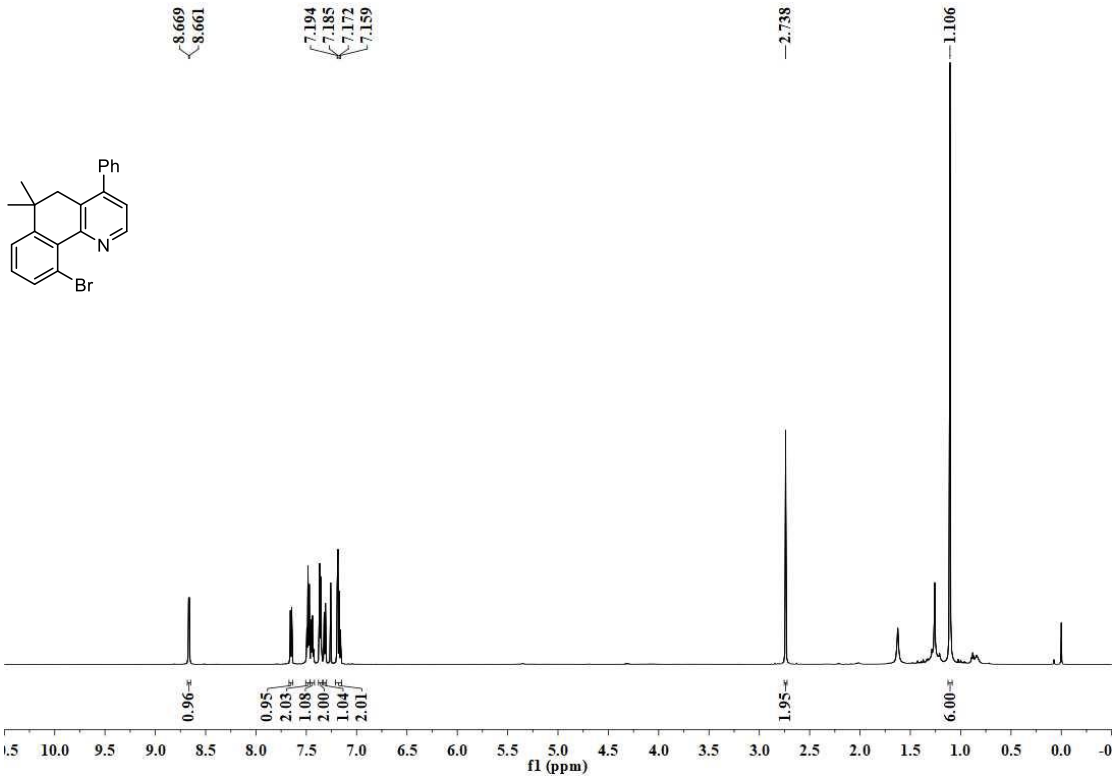
^{1}H NMR Spectrum of 66 (600 MHz, $CDCl_3$)



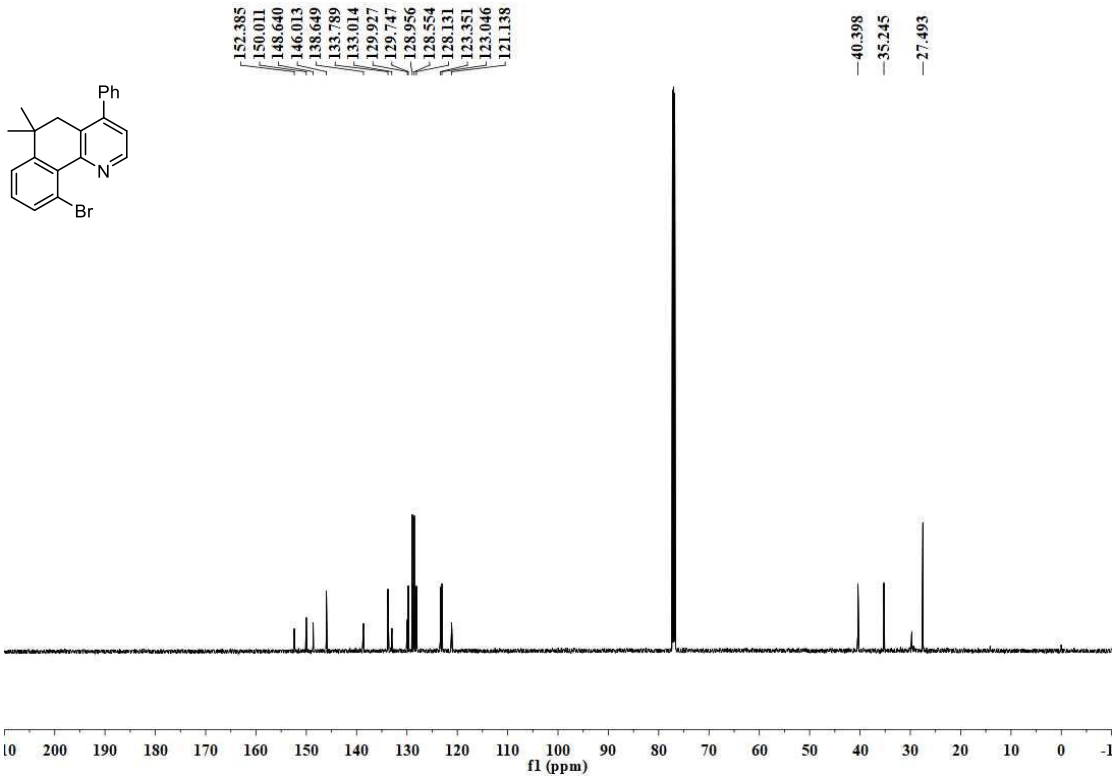
^{13}C NMR Spectrum of 66 (151 MHz, $CDCl_3$)



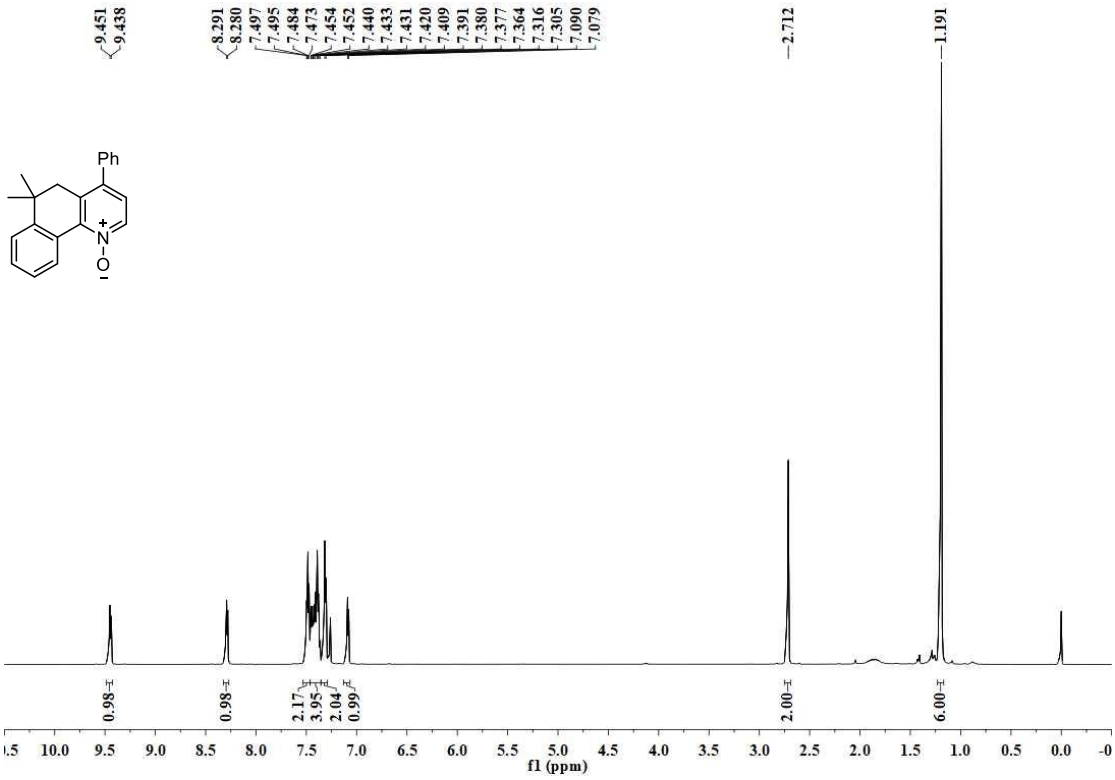
^{1}H NMR Spectrum of 67 (600 MHz, $CDCl_3$)



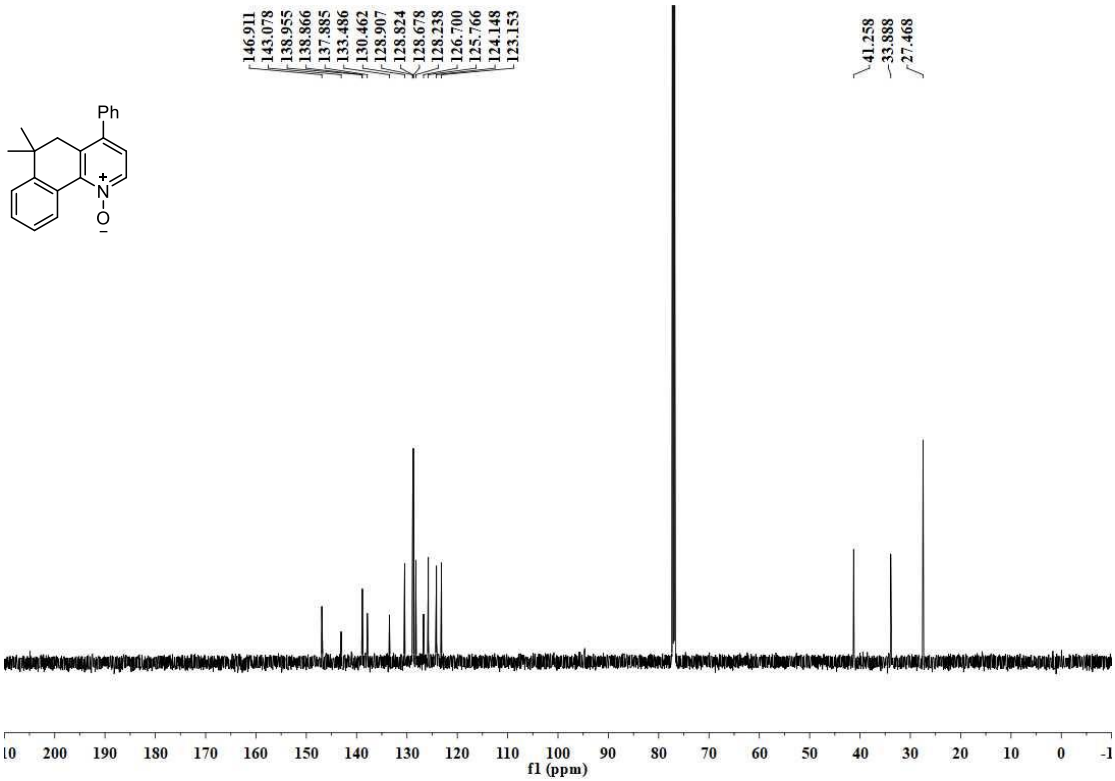
^{13}C NMR Spectrum of 67 (151 MHz, $CDCl_3$)



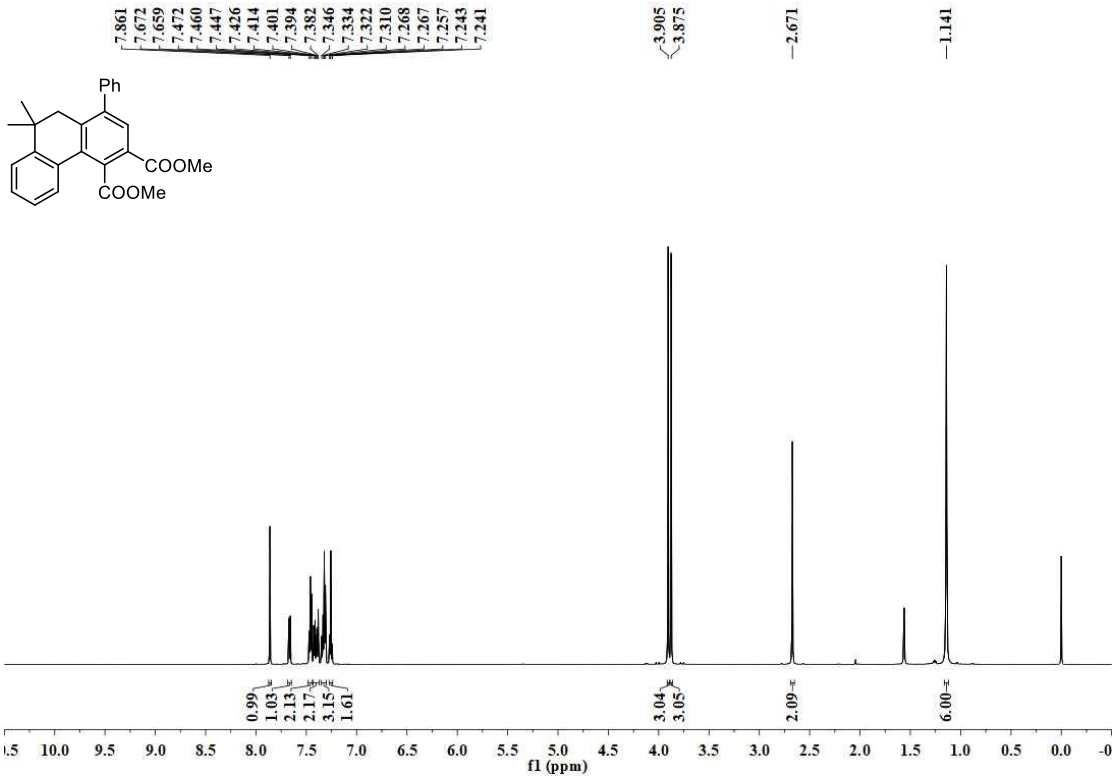
^{1}H NMR Spectrum of 68 (600 MHz, $CDCl_3$)



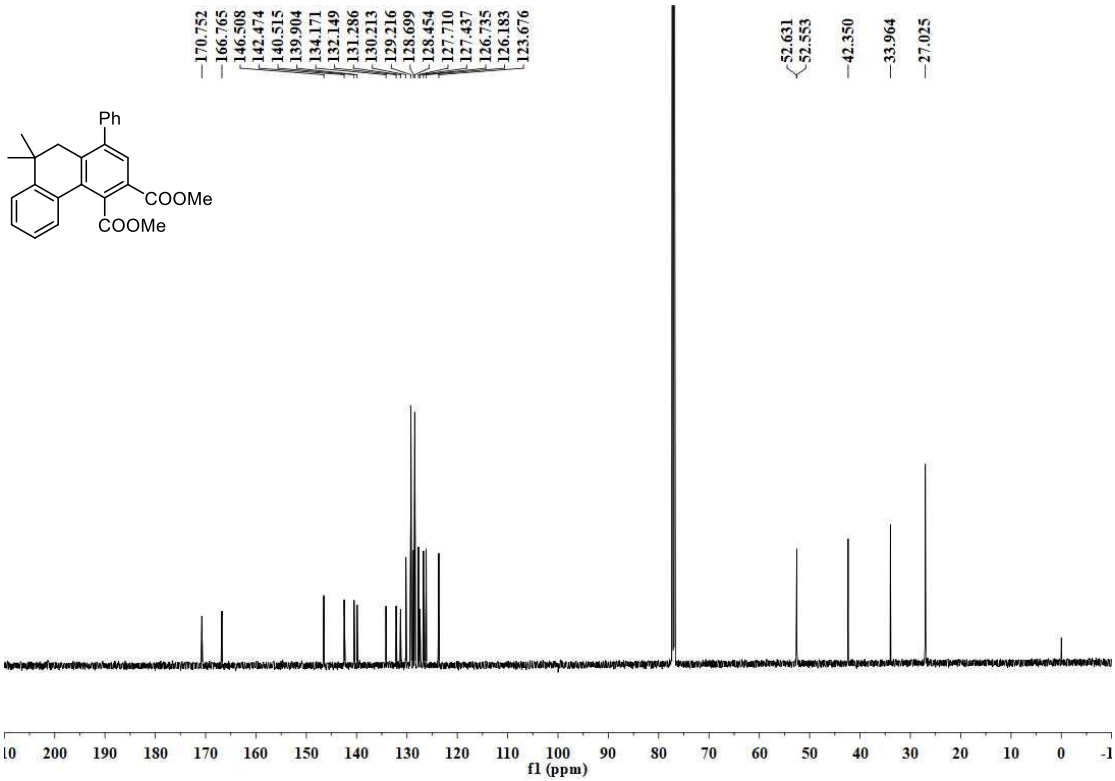
^{13}C NMR Spectrum of 68 (151 MHz, $CDCl_3$)



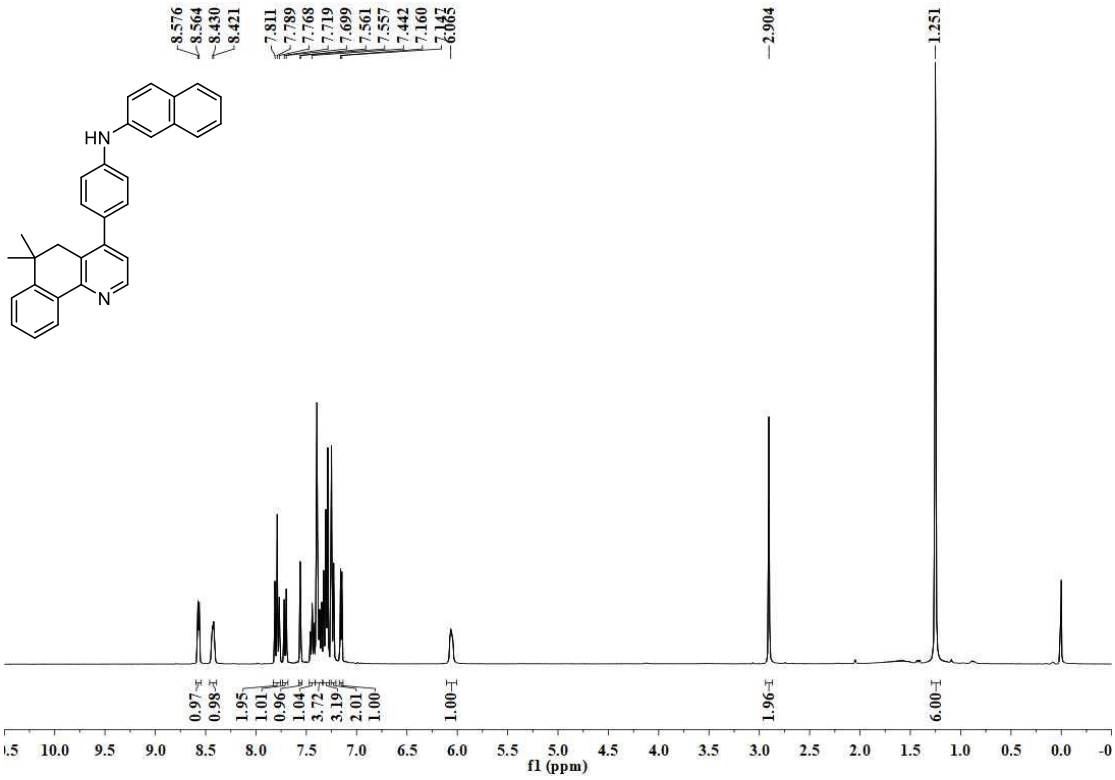
^{1}H NMR Spectrum of 69 (600 MHz, $CDCl_3$)



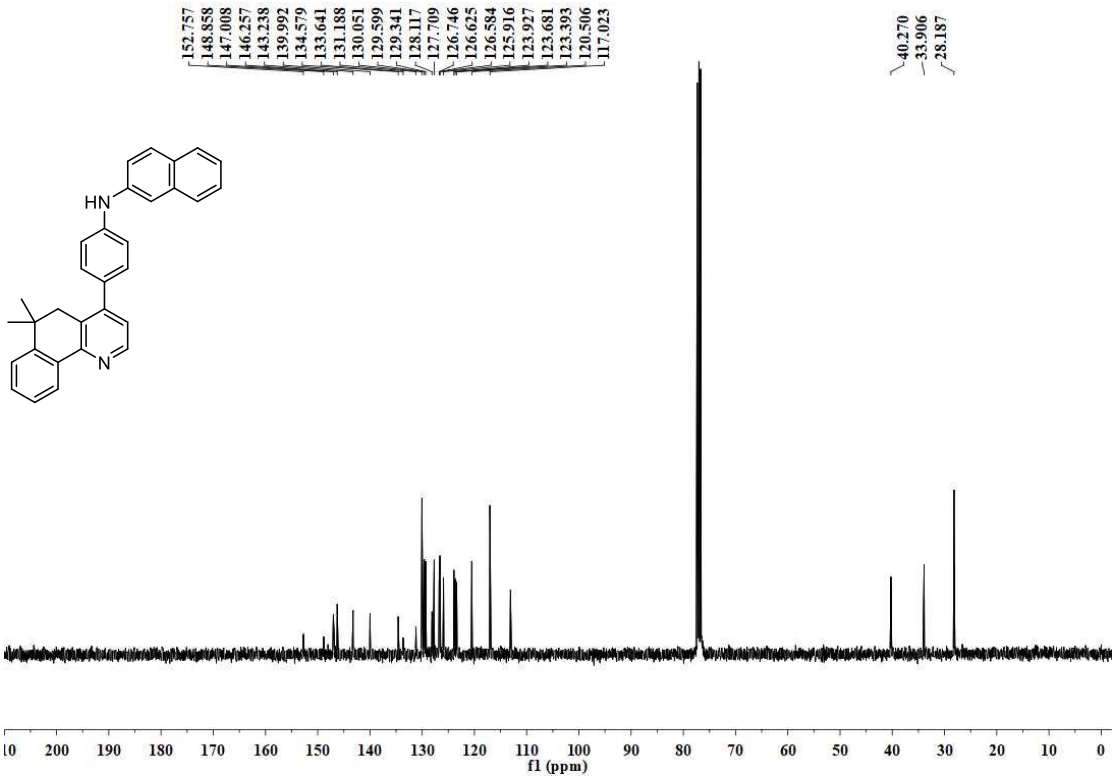
^{13}C NMR Spectrum of 69 (151 MHz, $CDCl_3$)



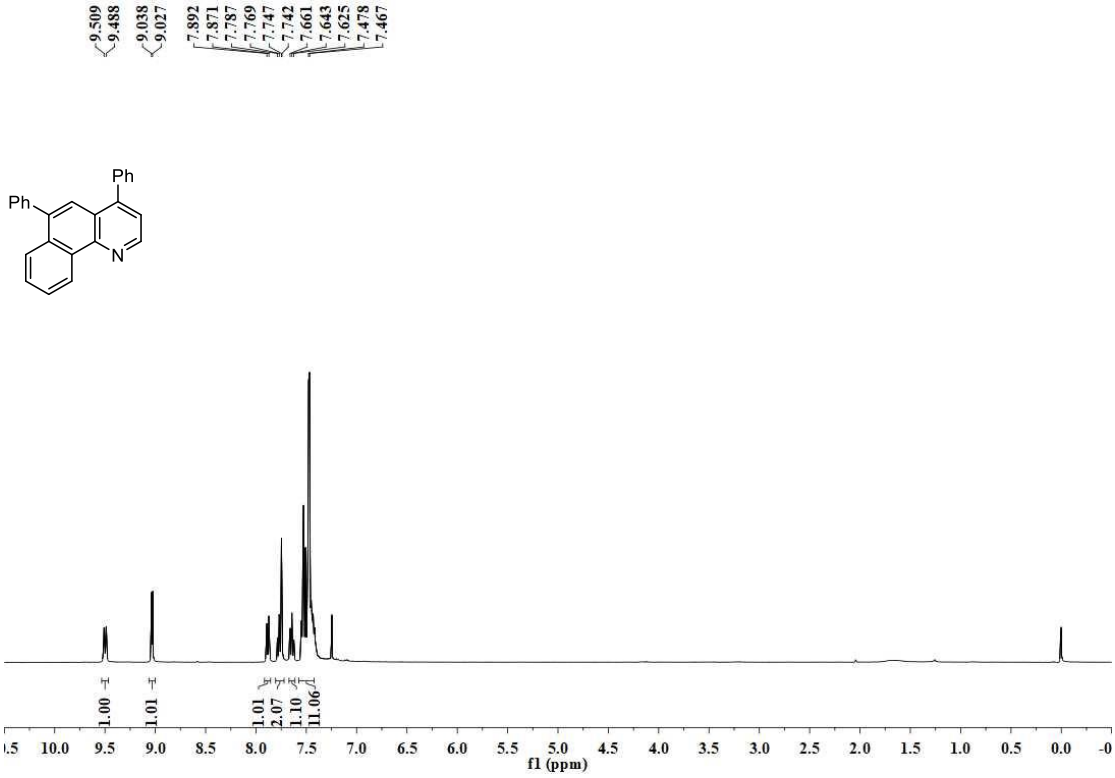
^{1}H NMR Spectrum of 70 (600 MHz, $CDCl_3$)



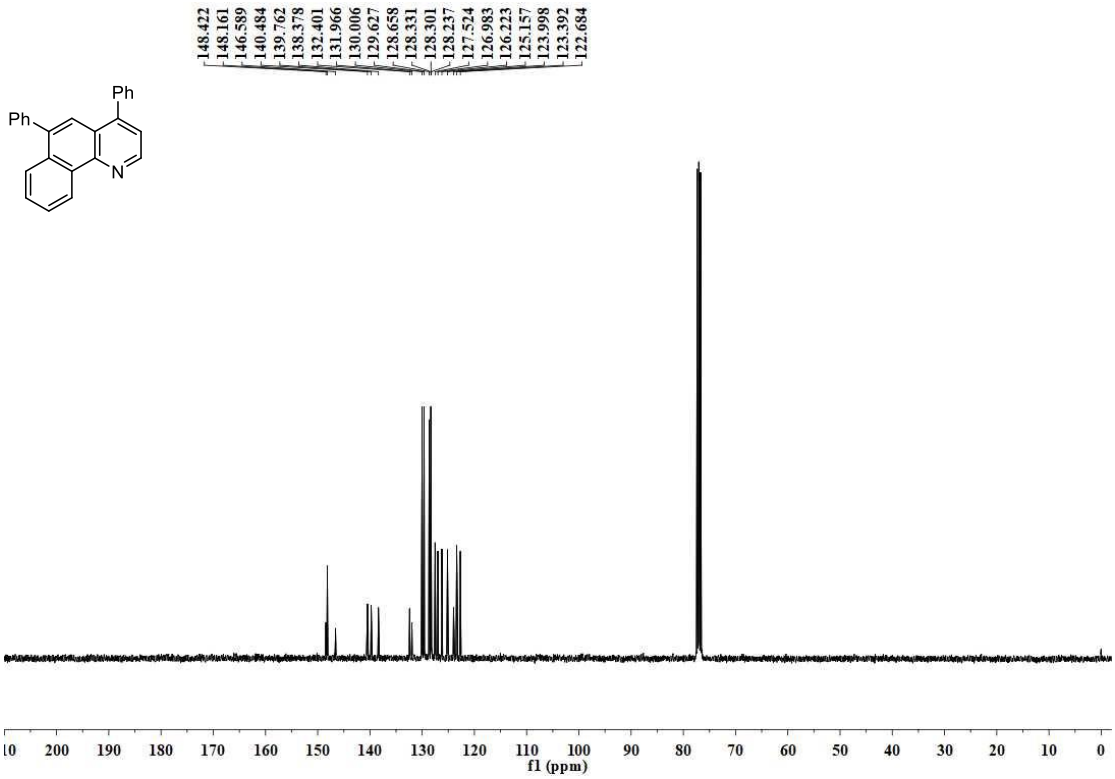
^{13}C NMR Spectrum of 70 (151 MHz, $CDCl_3$)



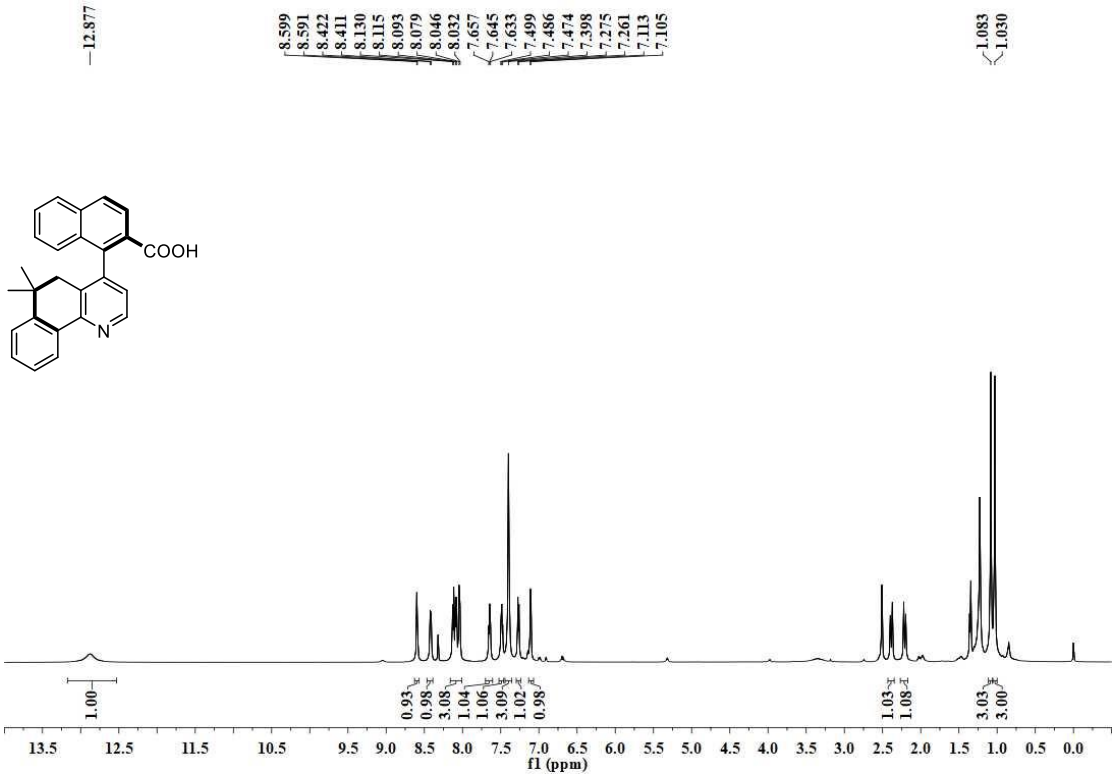
^{1}H NMR Spectrum of 71 (600 MHz, $CDCl_3$)



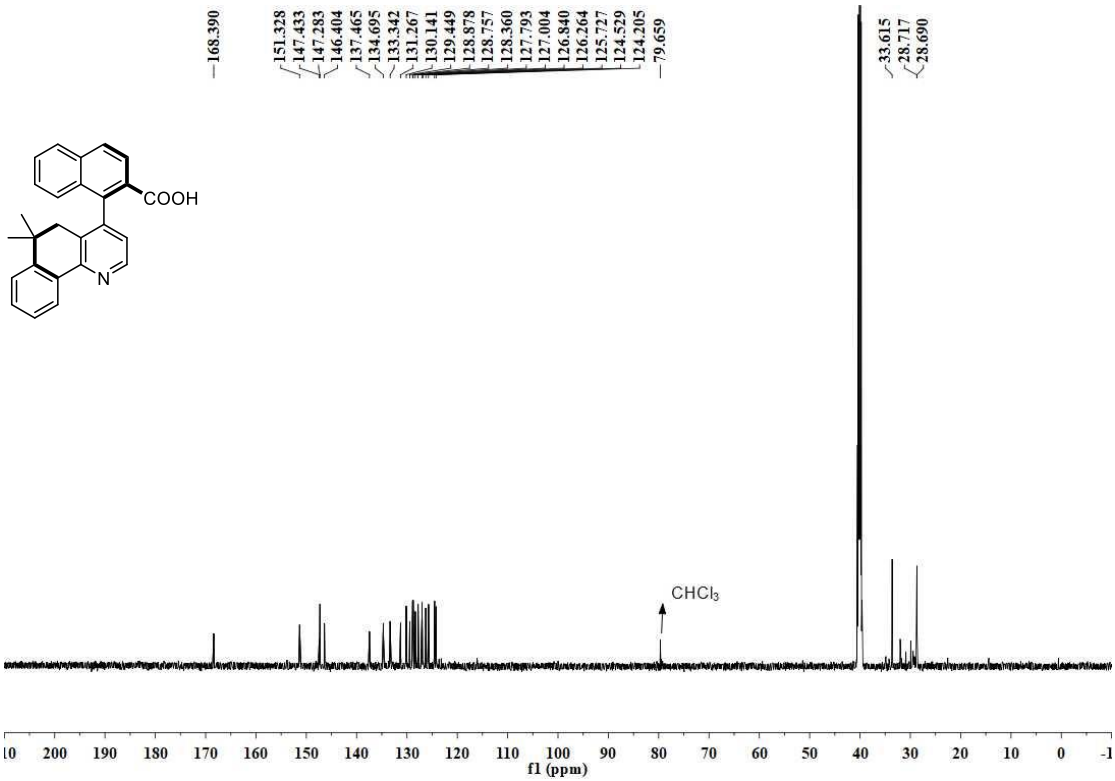
^{13}C NMR Spectrum of 71 (151 MHz, $CDCl_3$)



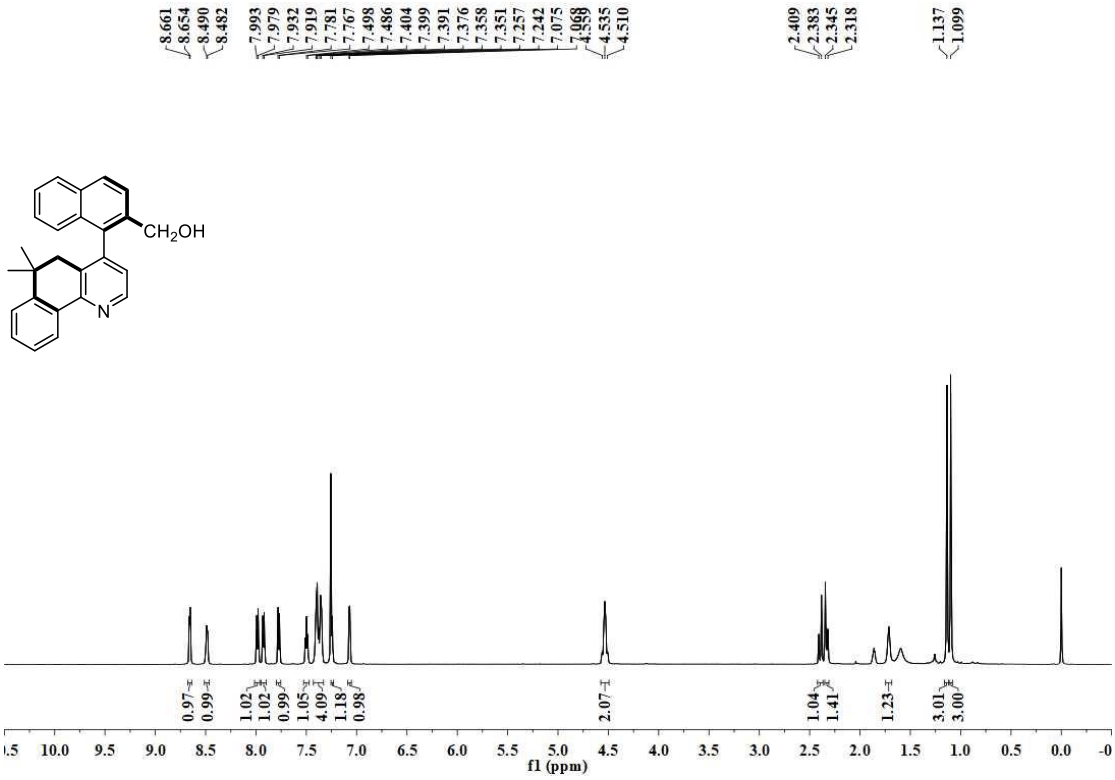
^{1}H NMR Spectrum of 117 (600 MHz, DMSO)



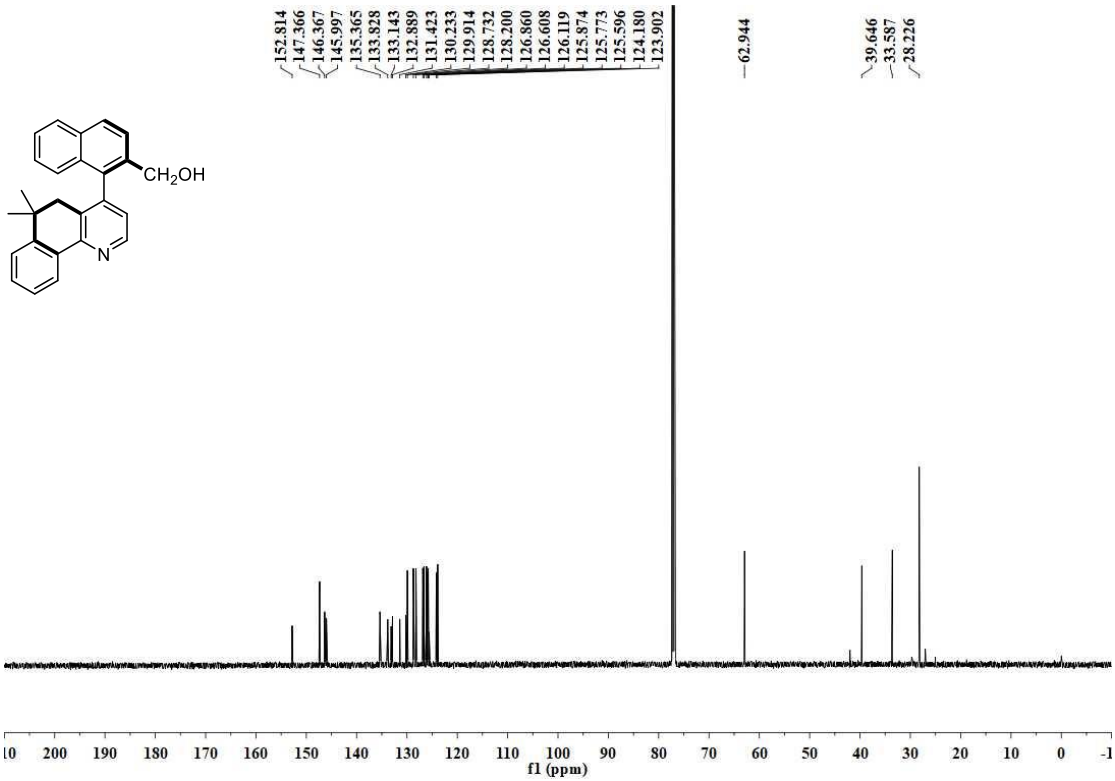
^{13}C NMR Spectrum of 117 (151 MHz, DMSO)



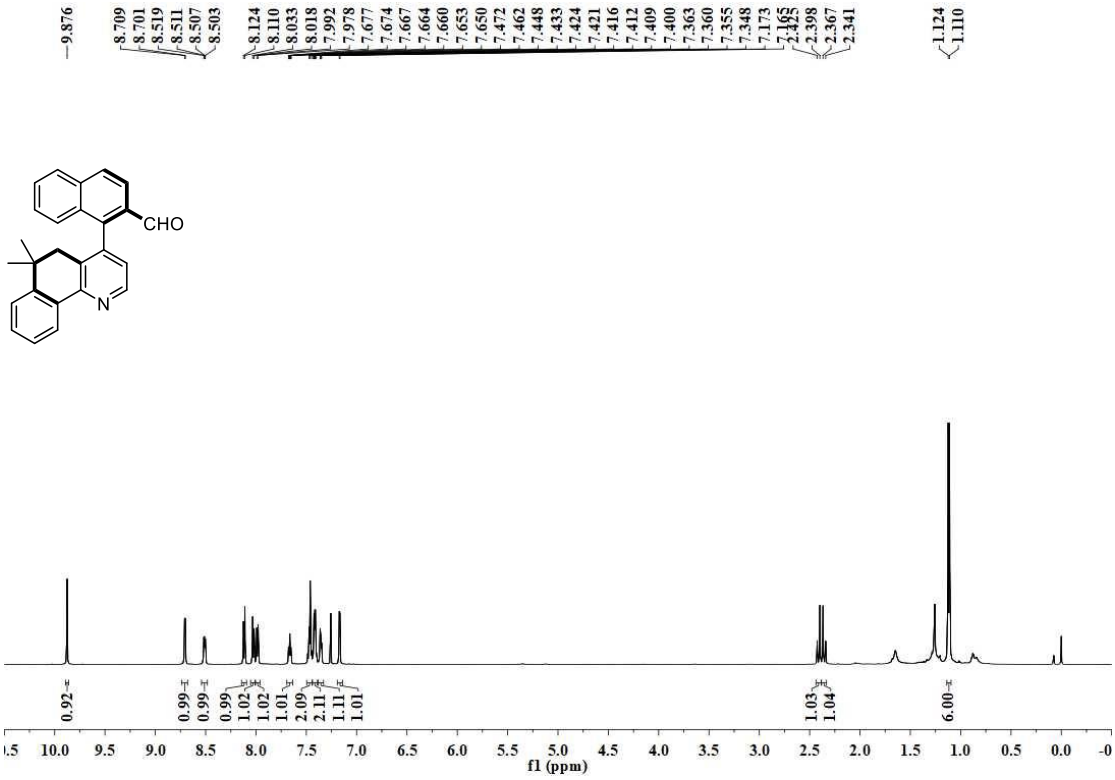
^{1}H NMR Spectrum of 118 (600 MHz, $CHCl_3$)



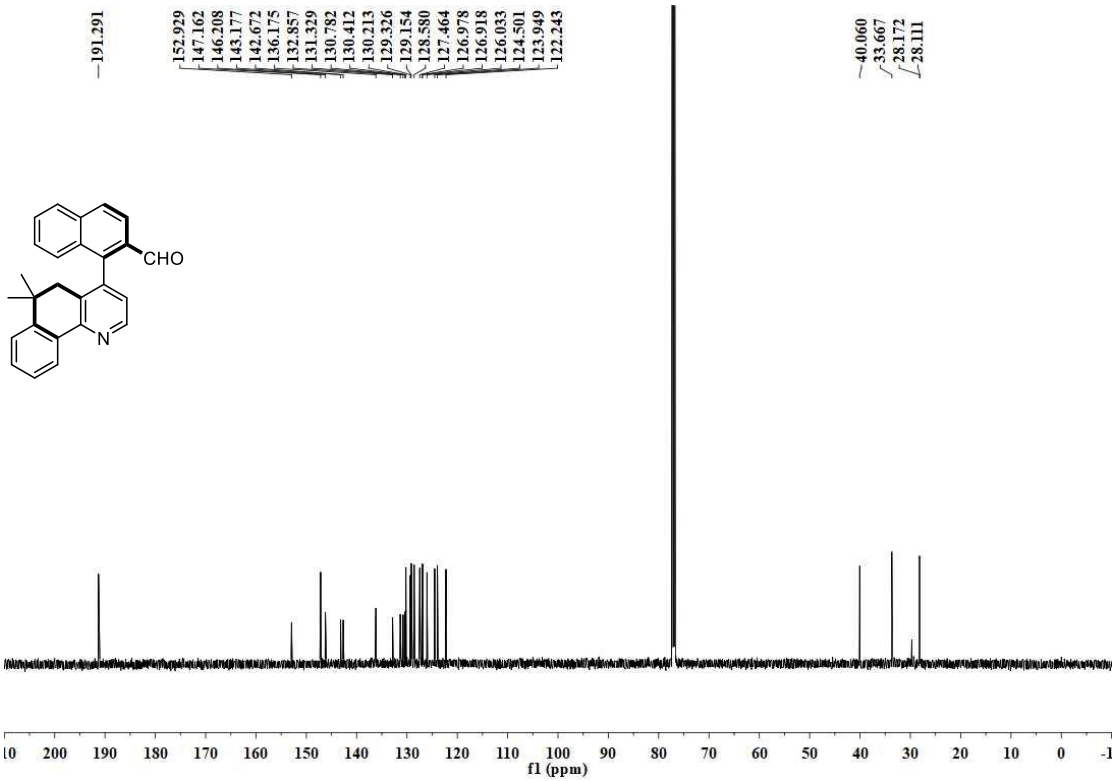
^{13}C NMR Spectrum of 118 (151 MHz, $CHCl_3$)



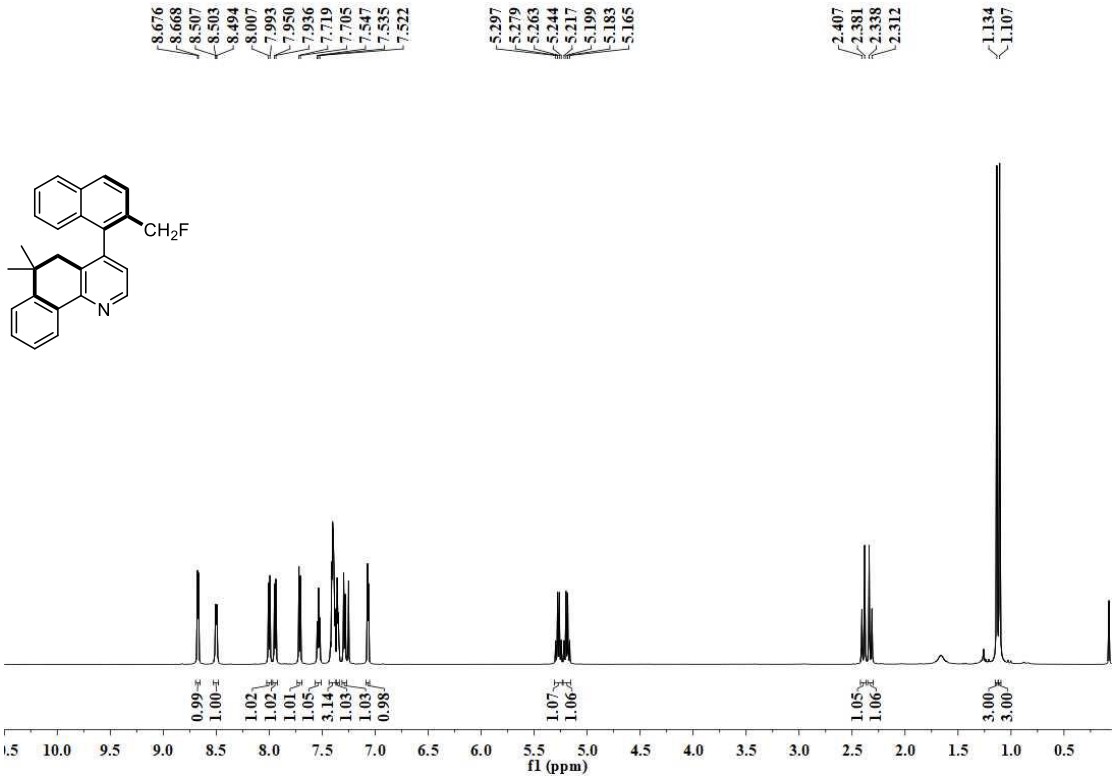
^{1}H NMR Spectrum of 119 (600 MHz, $CDCl_3$)



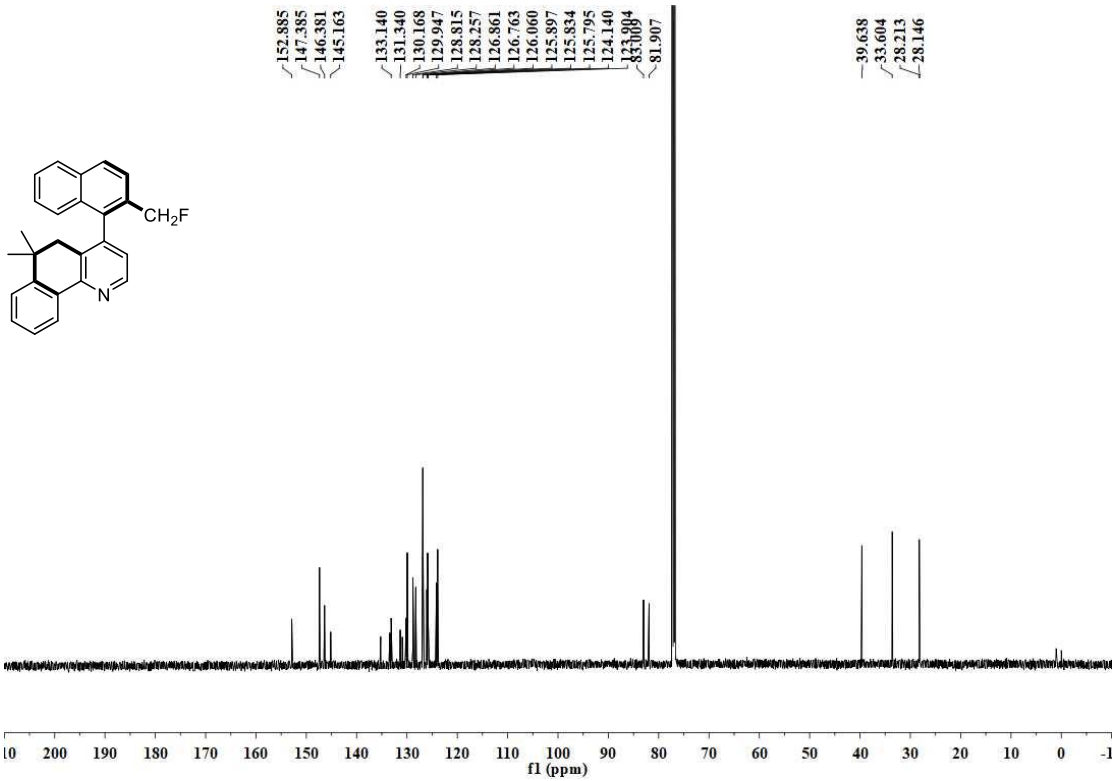
^{13}C NMR Spectrum of 119 (151 MHz, $CDCl_3$)



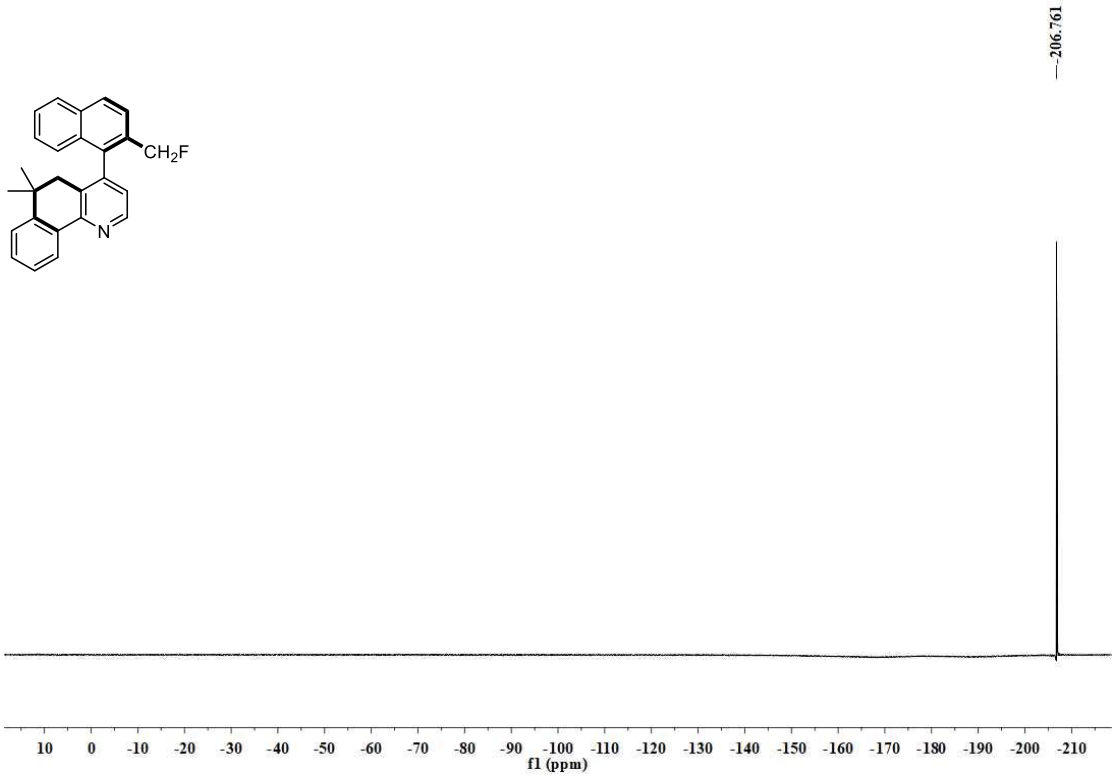
^{1}H NMR Spectrum of 120 (600 MHz, $CDCl_3$)



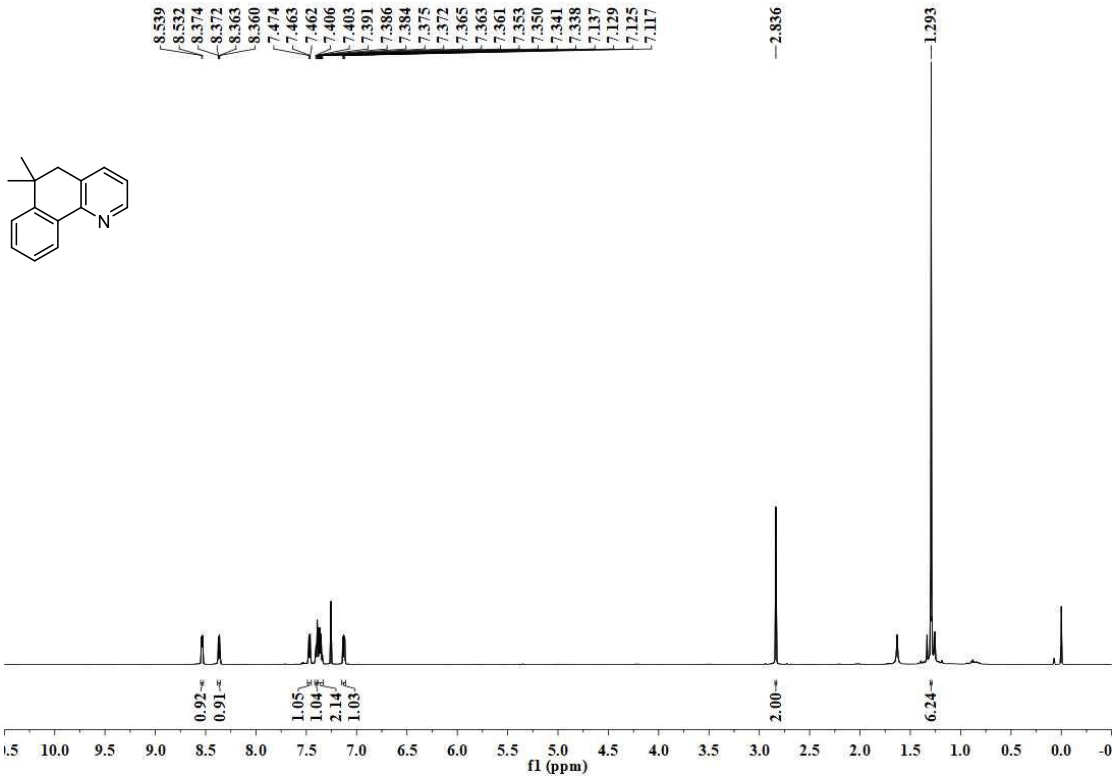
^{13}C NMR Spectrum of 120 (151 MHz, $CDCl_3$)



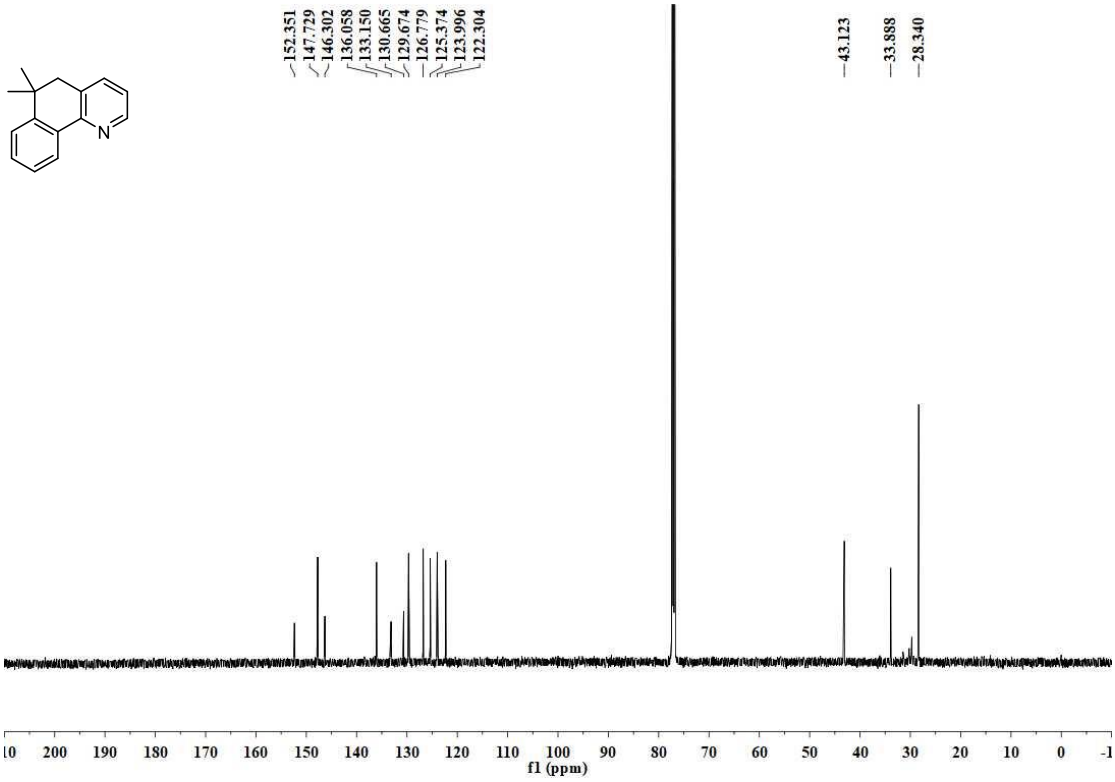
^{19}F NMR Spectrum of 120 (565 MHz, $CDCl_3$)



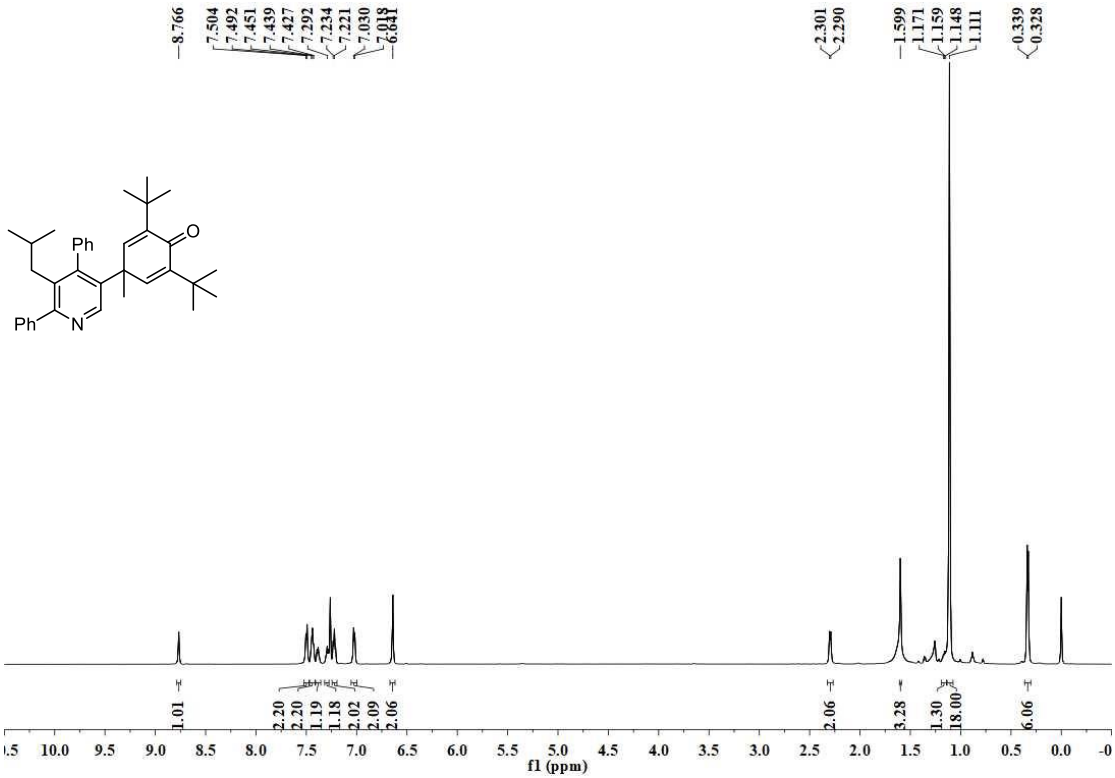
^{1}H NMR Spectrum of 74 (600 MHz, $CDCl_3$)



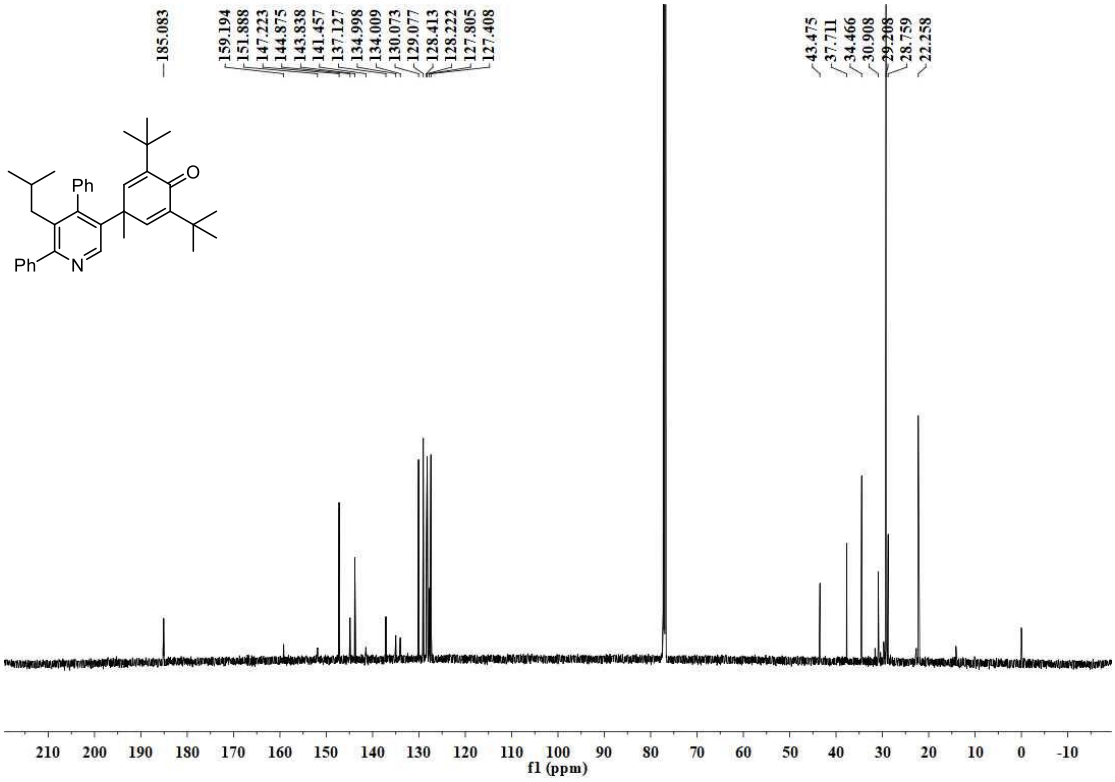
^{13}C NMR Spectrum of 74 (151 MHz, $CDCl_3$)



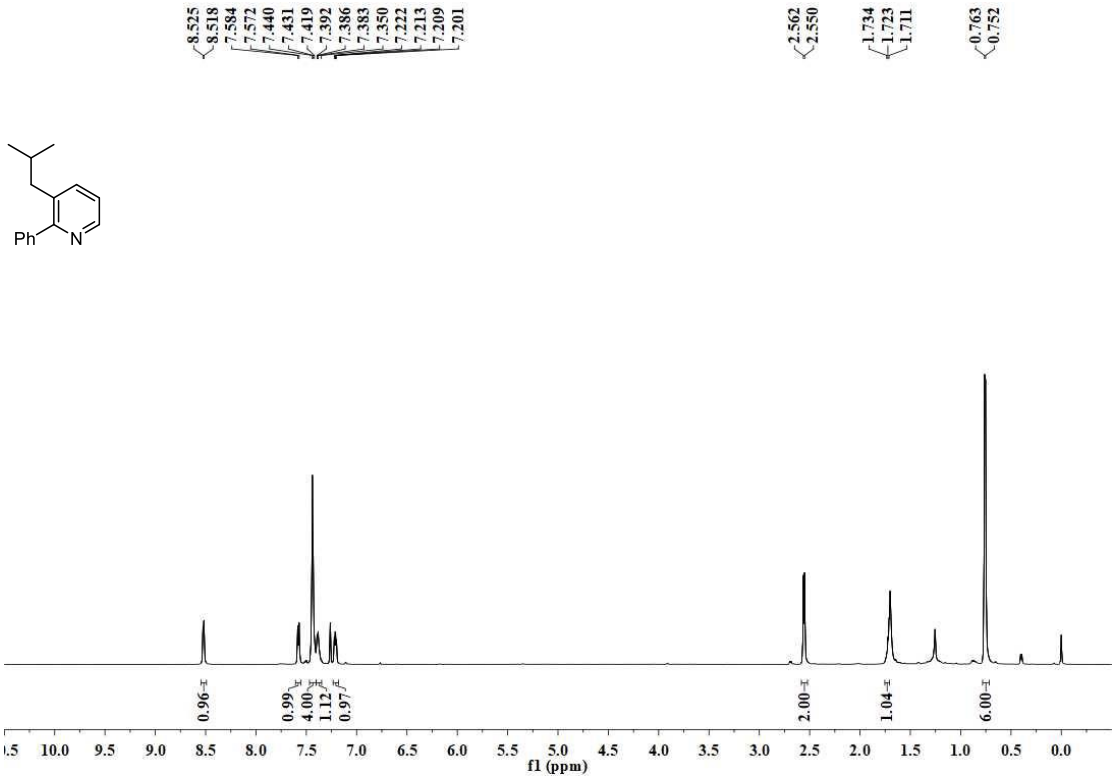
^{1}H NMR Spectrum of 77 (600 MHz, $CDCl_3$)



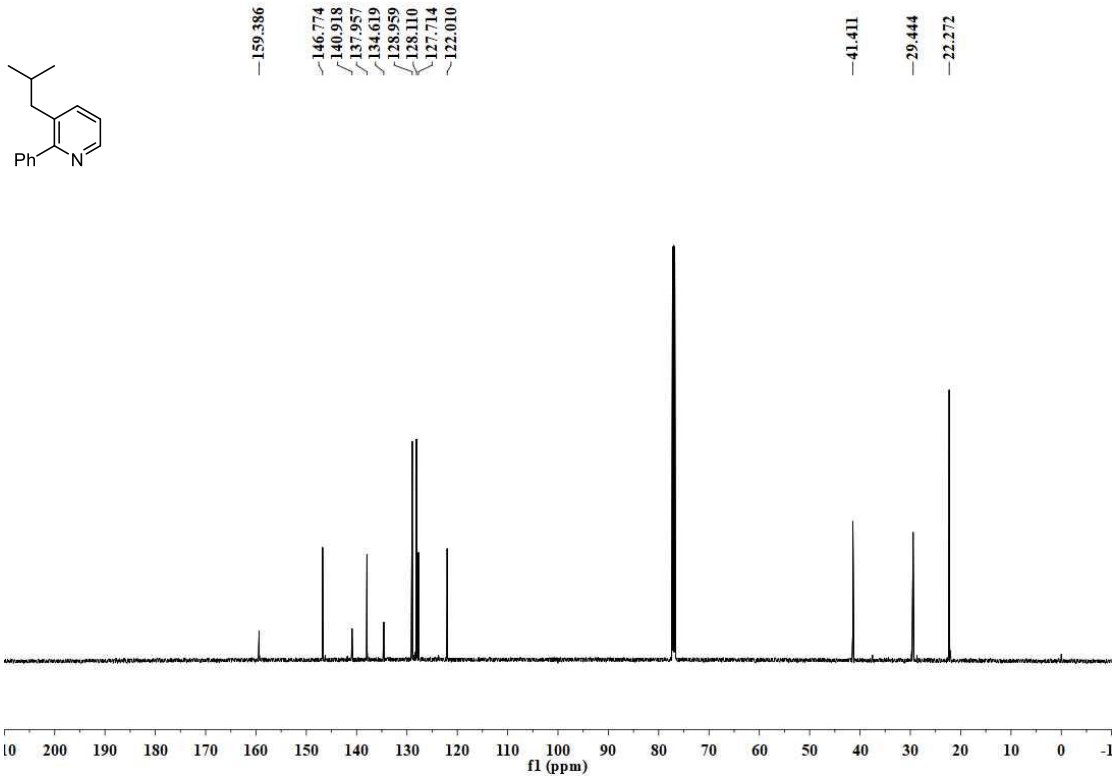
^{13}C NMR Spectrum of 77 (151 MHz, $CDCl_3$)



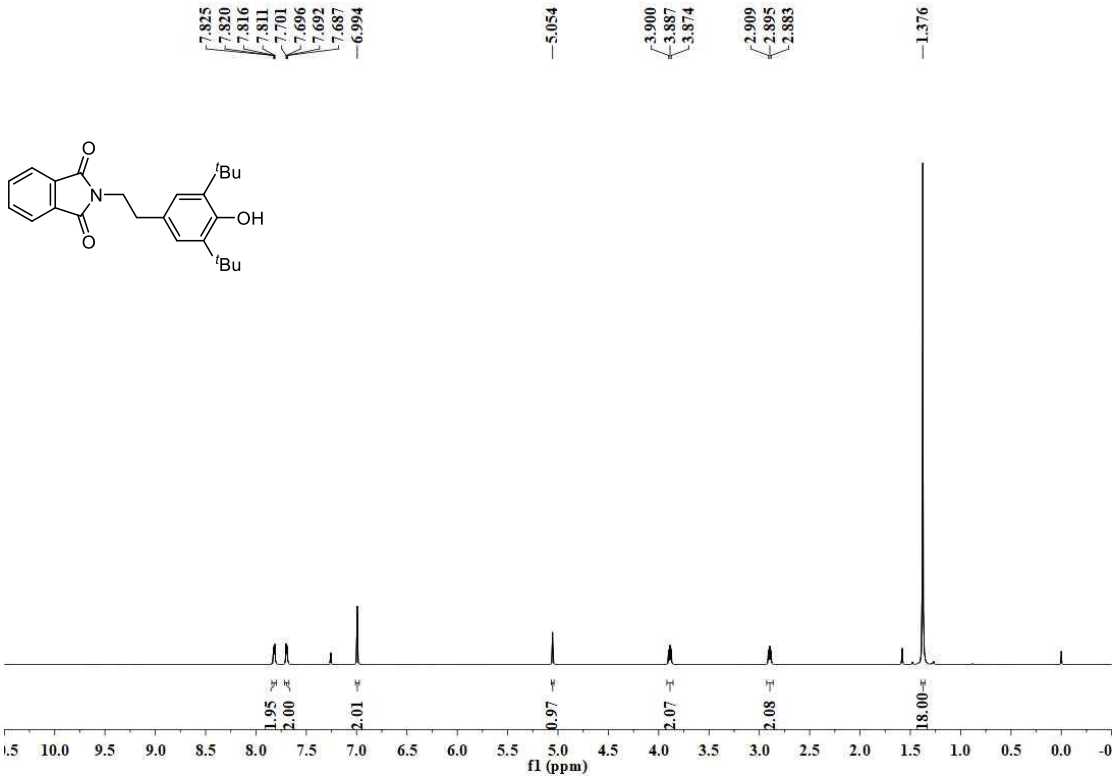
^{1}H NMR Spectrum of 81 (600 MHz, $CDCl_3$)



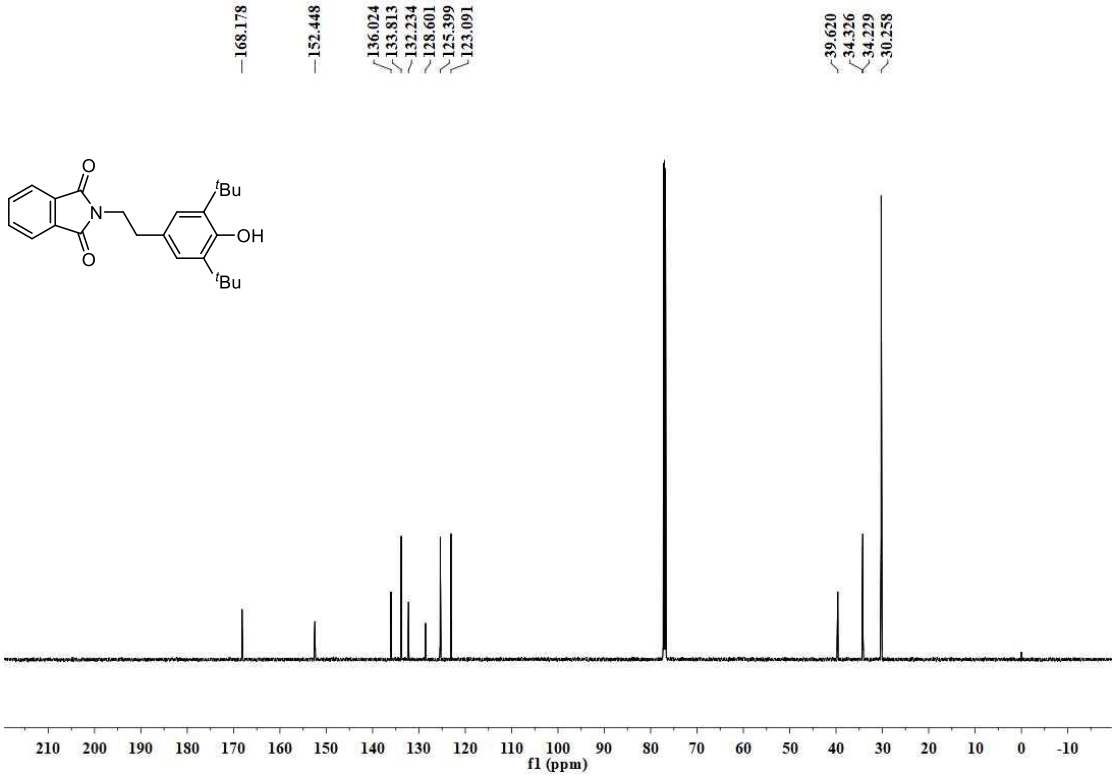
^{13}C NMR Spectrum of 81 (151 MHz, $CDCl_3$)



^{1}H NMR Spectrum of 82 (600 MHz, $CDCl_3$)



^{13}C NMR Spectrum of 82 (151 MHz, $CDCl_3$)



^{1}H NMR Spectrum for the mixture of 89 and 90 (600 MHz, $CDCl_3$)