Supporting Information

Palladium-Catalyzed Direct Coupling of 2-Vinylanilines and Isocyanides: An Efficient Synthesis of 2-Aminoquinolines

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Experimental Section (Supporting Information)

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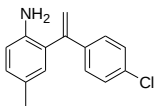
I General Considerations

Unless otherwise noted, all the materials were purchased from commercial suppliers and used as received. Solvents were freshly distilled by standard procedures prior to use. All ^{1}H and $^{13}C\{^{1}H\}$ NMR spectra were recorded on a Bruker 400 MHz spectrometer. The NMR chemical shift values refer to $CDCl_3$ (δ (^{1}H), 7.26 ppm; δ (^{13}C), 77.16 ppm). Mass spectra were obtained on a micrOTOF-Q II mass spectrometer.

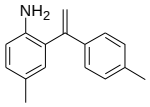
II Procedures for the Preparation of Starting Materials

II.I 2-(1-Phenylvinyl)benzenamines (1a-1i, 1r) were synthesized according to the literature methods:[1] Anilines (10 mmol), phenylacetylenes (1.0 g, 10 mmol), and montmorillonite KSF (1.0 g) were combined in a round-bottomed flask. The flask was stirred and heated in an oil bath to 140 °C, under a reflux condenser (running cold water as the coolant) that was connected at its top to a paraffin bubbler. The reaction was monitored by TLC. After 5 h, the reaction mixture was cooled to room temperature and purified directly by flash chromatography with a gradient of hexane to ethyl acetate/hexane (v/v = 1:20), followed by distillation under high vacuum in 43%-58% yield.



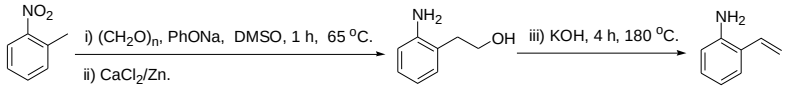
2-(1-(4-chlorophenyl)vinyl)-4-methylbenzenamine, 1h: ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.28-7.33 (m, 4 H), 7.00 (dd, J = 8 Hz, 1.6 Hz,1 H), 6.92 (d, J = 1.2 Hz,

1 H), 6.64 (d, J = 8 Hz, 1 H), 5.79 (d, J = 1.2 Hz, 1 H), 5.37 (d, J = 1.2 Hz, 1 H), 3.36 (br s, 2 H), 2.28 (s, 3 H); ^{13}C NMR (101 MHz, $CDCl_3$) δ ppm 146.3, 141.4, 138.3, 133.9, 131.2, 129.6, 128.8, 128.1, 127.7, 126.9, 116.5, 115.9, 20.5. HRMS (ESI) m/z calcd for $C_{15}H_{14}ClN$ $(M+H)^+$ 244.0888, found 244.0882.



4-methyl-2-(1-p-tolylvinyl)benzenamine, 1i: ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.28-7.30 (m, 2 H), 7.10-7.15 (m, 2 H), 6.95-7.00 (m, 2 H), 6.63 (d, J = 8 Hz, 1 H), 5.76 (d, J = 1.6 Hz, 1 H), 5.30 (d, J = 1.2 Hz, 1 H), 3.42 (br s, 2 H), 2.36 (s, 3 H), 2.28 (s, 3 H); ^{13}C NMR (101 MHz, $CDCl_3$) δ ppm 147.2, 141.5, 138.0, 137.0, 131.3, 129.4, 129.3, 127.8, 127.6, 126.7, 115.8, 115.2, 21.3, 20.6. HRMS (ESI) m/z calcd for $C_{16}H_{17}N$ $(M+H)^+$ 224.1434, found 224.1433.

II.II The preparation of 2-vinylbenzenamine:

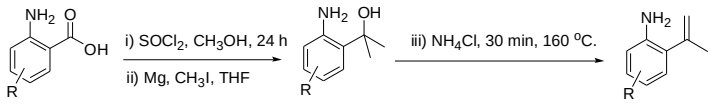


2-Nitrotoluene (36.7 g, 268.0 mmol), sodium phenoxide (0.26 g, 2.2 mmol), paraformaldehyde (3.6 g of 95%), and dimethyl sulfoxide (60 mL) were heated for 1 h at 60-67 °C. The mixture was poured into water and extracted with ether. The combined extracts were washed with saturated aqueous solution of sodium chloride. The organic phase was dried over magnesium sulfate and evaporated. Crude product was purified by flash chromatography using DCM as the eluent to afford the target product as yellow oil in 43% yield.[2] 2-(2-Nitrophenyl)ethanol (3 g, 18 mmol) was added dropwise to a flask containing calcium chloride (1.2 g, 12.0 mmol) and zinc powder (4 g, 180 mmol) in hot water (25 mL). The mixture was heated under reflux

for 30 min. The solid was filtered off, and then sodium carbonate (1.2 g, 12.0 mmol) was added to the filtrate. After filtering off the $CaCO_3$ precipitant and evaporating all the volatiles by a rotary evaporator, a mixture of sodium chloride and oil was obtained. The residue was extracted with ether. The salt was filtered off and the solvent was removed under vacuum. The title compound was obtained as yellow oil, which was pure enough to use in the next step without further purification.[3] The above alcohol was dehydrated with KOH(s) by heating at 180 °C. The reaction was monitored by TLC. After 4 h, the reaction mixture was cooled to room temperature and purified directly by flash chromatography on silica gel with EtOAc as eluant.

II.III 2-(Prop-1-en-2-yl)benzenamine was synthesized according to the literature methods:[4] To a solution of 1-(2-aminophenyl)ethanone (6.7 g, 50 mmol) in THF (100 mL), CH_3MgBr (3 M in diethyl ether, 50 mL, 150 mmol) was added at 0 °C. After being stirred at room temperature for 30 min, the reaction mixture was quenched by saturated aqueous solution of NH_4Cl and filtered through Celite pad. After the filtrate was extracted with EtOAc, the organic layer was washed with brine, and dried over anhydrous $MgSO_4$. After removing the volatiles, the residue was purified with silica gel column chromatography with a gradient of DCM/CH_3OH (v/v = 20:1) to give 2-(2-aminophenyl)propan-2-ol. The above alcohol (2.3 g, 15.2 mmol) was treated with solid NH_4Cl (2.4 g, 45.7 mmol) for 20 min at 180 °C. The reaction mixture was cooled to room temperature and purified directly by silica gel column chromatography with DCM to give 2-(prop-1-en-2-yl)benzenamine (1.6 g, 12 mmol, 80% yield).

II.IV The preparation of 2-(prop-1-en-2-yl)benzenamines (1k-1m):



A solution of the corresponding 2-aminobenzoic acid (1.0 equiv) in MeOH was cooled to 0 °C followed by a dropwise addition of thionyl chloride (2.5 equiv). The mixture was refluxed for 24 h. After evaporation of the solvent and neutralization by addition of a saturated aqueous $NaHCO_3$ solution, the mixture was extracted with EtOAc. The combined organic layers were dried over $MgSO_4$. Removing the solvents afforded the target ester which was pure enough to use in the next step without further purification.[5] To a suspension of magnesium turnings (6.6 g, 0.27 mol) in 40 mL of Et_2O, freshly distilled, was added dropwise under vigorous stirring 40 g (0.28 mol) of CH_3I in 40 mL of Et_2O. The mixture was then refluxed for 2 h. After cooling, the suspension was filtered to give 80 mL of CH_3MgI (3.4 M) in diethyl ether solution.[6] A solution of the above ester (0.05 mmol) in dry THF (100 mL) was slowly added to the CH_3MgI (3.4 M) in diethyl ether solution at -20°C about 30 minutes. The resulting mixture was gradually warmed up to room temperature overnight. Addition of a saturated aqueous $NaHCO_3$ solution (50 mL) produced a suspension mixture, then filtered, and extracted with EtOAc. The organic layer was separated, and the aqueous phase was extracted for another three times. The combined organic phases were dried (Na_2SO_4), filtered, and evaporated. The residue was purified with silica gel column chromatography with a gradient of hexane/EtOAc (v/v = 5:1) to give corresponding alcohol. The above alcohol (1.0 equiv) was treated with solid NH_4Cl (3.0 equiv) for 30 min at 160 °C. The reaction mixture was cooled to room temperature and purified

directly by silica gel column chromatography with a gradient of hexane/EtOAc (v/v = 20:1) to give corresponding alkene.[4]

II.V General process for the preparation of isocyanides (2a-2c): Amine(1.0 equiv) and ethyl formate (1.5 equiv) were added to a pressure bottle, the mixture was heated at 80 °C for 48 h. Evaporating low-boiling point substances, and then through distillation under reduced pressure, a colorless oil was obtained. A solution of formamide (0.1 mol) in dichloromethane (100 ml) was cooled to -10 °C, Et_3N (0.34 mol) was added to. Then phosphorous oxychloride (0.11 mol) was added dropwise. The mixture was stirred at -10 °C for 2 h. After the reaction was completed, an aqueous saturated solution of sodium carbonate was added to quench the reaction. After stirring for 1 h at room temperature, the organic layer was separated, and the aqueous phase was extracted with DCM for another three times, dried with sodium sulfate, and a colorless foul-smelling liquid isocyanide was obtained by distillation in 90% yield.

II.VI 2d was synthesized according to the literature methods: Formic acid (4.0 equiv) was added to aniline (1.0 equiv) and then reaction mixture was heated under stirring for 60 ^oC. Progress of the reaction was monitored by TLC. After completion of reaction, reaction mixture was quenched over ice and extracted with ethyl acetate and washed with $NaHCO_3$. The organic layer dried over Na_2SO_4 and concentrated to yield pure product.[7] A solution of formamide (0.1 mol) in dichloromethane (100 ml) was cooled to 0 °C, Et_3N (0.34 mol) was added to. Then phosphorous oxychloride (0.11 mol) was added dropwise. The mixture was stirred at

0 °C for 1 h. After the reaction was completed, an aqueous saturated solution of sodium carbonate was added to quench the reaction. After stirring for 1 h at room temperature, the organic layer was separated and then the aqueous phase was extracted with DCM for another three times. The combined organic phase was dried with sodium sulfate. A colorless foul-smelling liquid isocyanide was obtained by distillation in 80% yield.

II.VII 2e was synthesized according to the literature methods:[8] a solution of 2,6-diisopropylaniline (10 mL, 53.0 mmol) in toluene (*ca*. 170 mL) was treated with formic acid (30 mL, 795.1 mmol). The resulting mixture was refluxed in a Dean-Stark apparatus for three hours, at which point additional formic acid (11 mL, 291.5 mmol) was added. After 1 hour of further refluxing (4 hours total), the reaction mixture was allowed to cool to room temperature, and was evaporated *in vacuo* to give a white powder, which was then washed with Et_2O (*ca*. 20 mL) and dried *in vacuum* giving N-formyl-2,6-diisopropylaniline. Recrystallization from DCM/hexane yielded the formamide compound as colourless crystals in 75% yield. A colorless solution of N-formyl-2,6-diisopropylaniline (2.00 g, 9.74 mmol) in CH_2Cl_2 (*ca*. 100 mL) was treated with diisopropylamine (4.75 mL, 33.90 mmol), which was then cooled to 0 °C using an ice-water bath. The solution was treated in a dropwise manner with phosphorus(V) oxychloride (1.12 mL, 11.96 mmol) over a period of 20 minutes. The mixture was allowed to warm to room temperature, and stirred at room temperature for 2 hours. At this point, an aqueous solution of Na_2CO_3 (1.5 M, 100 mL, 150 mmol) was added, and the resulting biphasic mixture was allowed to stir for 20 hours. The

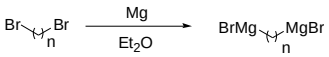
mixture was diluted with H_2O (*ca*. 50 mL), and the organic and aqueous layers were separated, and the latter was extracted with CH_2Cl_2 (100 mL). The combined organic extracts were dried with Na_2SO_4, and filtered over 50 mL of silica gel. The silica gel was extracted with CH_2Cl_2 (*ca*. 100 mL), and the combined filtrates were evaporated *in vacuo* giving 2,6-diisopropylphenylisocyanide as a pale yellow oil in 98% yield.

II.VIII 2f was synthesized according to the literature methods:[9]

2,4,6-trimethylaniline (10 g, 73.9 mmol) was dissolved in ethylformiate (15 ml). The mixture was heated in a heavy sealed flask at 200 °C for 12 h. After this, the precipitant was filtered off and washed with pentane. Recrystallization from acetone yielded the formamide compound as colourless crystals in 45% yield. The formamide (2 g, 12.3 mmol) was dissolved in absolute DCM (50 ml). The solution was cooled to -60 °C in an EtOH/liquid nitrogen bath and $POCl_3$ (3.34 ml, 36.6 mmol) was added dropwise over a period of 10 min. The suspension was stirred for 20 min and NEt_3 (11.14 g, 110.0 mmol) was added dropwise over 10 min. The resulting yellow suspension was stirred overnight. During this time, the cooling bath was allowed to warm up to room temperature. Afterwards, the suspension was poured onto ice and warmed up to room temperature. DCM (30 mL) was added and the layers were separated. The organic layer was washed with a saturated solution of $NaHCO_3$ (3x10 mL). The organic phase was dried with Na_2SO_4 and the solvent was removed under reduced pressure. The crude product was purified by flash chromatography to yield the title compound as colourless crystals (1.5 g, 84%).

II. IX 1O was prepared according to a literature method.[4]

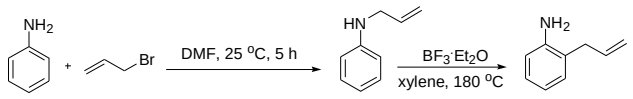
II.X General process for the preparation of 1p, 1r:



n = 4,5

Diethyl ether (15 ml) was added to magnesium turnings (180 mmol, 4.0 eqiuv) without stirring followed by addition of 2-3 ml of a solution of 1,ω-dibromoalkane (45 mmol, 1.0 eqiuv) in diethyl ether (35 ml). The reaction mixture was warmed up gently until moderate clouding and bubble formation were observed. Stirring was continued, the mixture was cooled with a water bath to 20 °C and the remaining solution was added dropwise for 30 min. After complete addition, stirring of the resulting biphasic reaction mixture was continued for 2 h at ambient temperature.[10] The solution of the Digrignard reagents in diethyl ether solution was slowly added to methyl 2-amino-5-methylbenzoate (15 mmol) in dry THF (60 mL) at -78 °C about 30 minutes. The resulting mixture was gradually warmed up to room temperature overnight. Addition of a saturated aqueous $NaHCO_3$ solution (50 mL) produced a suspension mixture, then filtered, and extracted with EtOAc. The organic layer was separated, and the aqueous phase was extracted for another three times. The combined organic phases were dried, filtered, and evaporated. The residue was purified with silica gel column chromatography with a gradient of hexane/EtOAc to give corresponding alcohol in 70-77% yield. The above alcohol (1.0 equiv) was treated with solid NH_4Cl (3.0 equiv) for 30 min at 160 °C. The reaction mixture was cooled to room temperature and purified directly by silica gel column chromatography with a gradient of hexane/EtOAc to give corresponding alkene in 90-94% yield.[4]

II.XI General process for the preparation of 1s:



To a solution of aniline (18.6 g, 0.2 mol) in DMF (200 mL) at room temperature allyl bromide (26.4 g, 0.22 mol) was added. The resulting mixture was stirred at room temperature for 3 h. After the reaction, K_2CO_3 (s), DI water (100 mL) and diethyl ether (100 mL) was added to the mixture to adjust PH > 7, stirred for 5 mins and the layers were separated. The aqueous layer was extracted with diethyl ether (2 x 20 mL). The combined organic layer was washed with DI water (2 x 30 mL) to remove traces of DMF, dried over *anhy.* Na_2SO_4, filtered and the solvent was evaporated under reduced pressure to get the crude product. The crude product was purified by silica gel column chromatography with a gradient of hexane/EtOAc to get the product in 25% yield.[11] $BF_3 \cdot OEt_2$ (4.5 g, 32 mmol) was added to a solution of the above aniline (4.3 g, 32 mmol) in xylene (60 mL). The mixture was heated to 180 ºC in a sealed tube and stirred at this temperature for 21 hours. After cooling, the reaction mixture was poured into 20% NaOH (50 mL) solution, and extracted with EtOAc (3x15 mL). The combined organic extracts were washed with brine (50 mL), dried over Na_2SO_4, and concentrated *in vacuo*. The crude product was purified by column chromatography to get 2-allylaniline in 63% yield as a colorless oil.[12]

References

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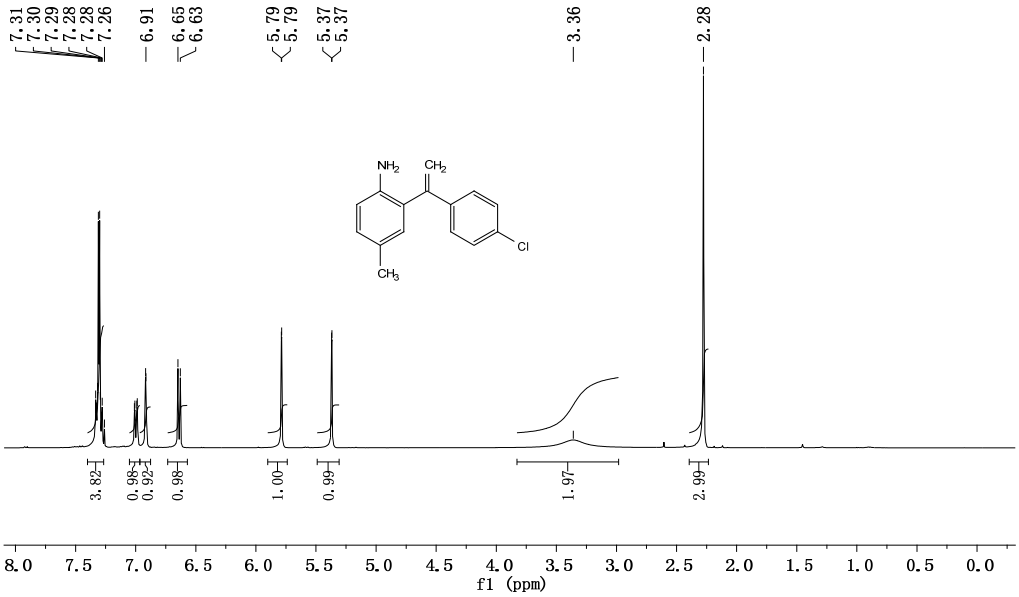
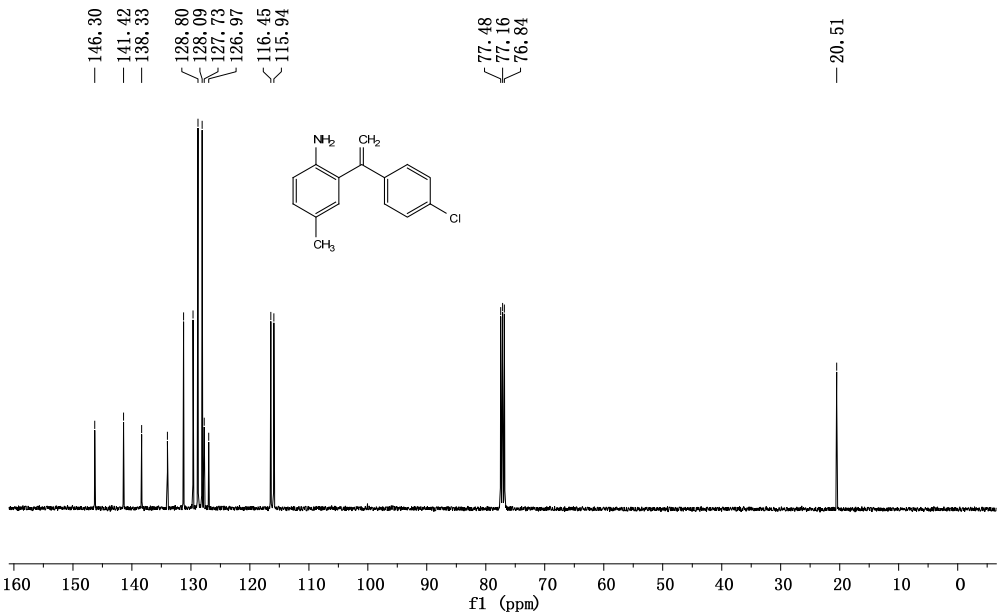
IV ^{1}H and ^{13}C NMR spectra

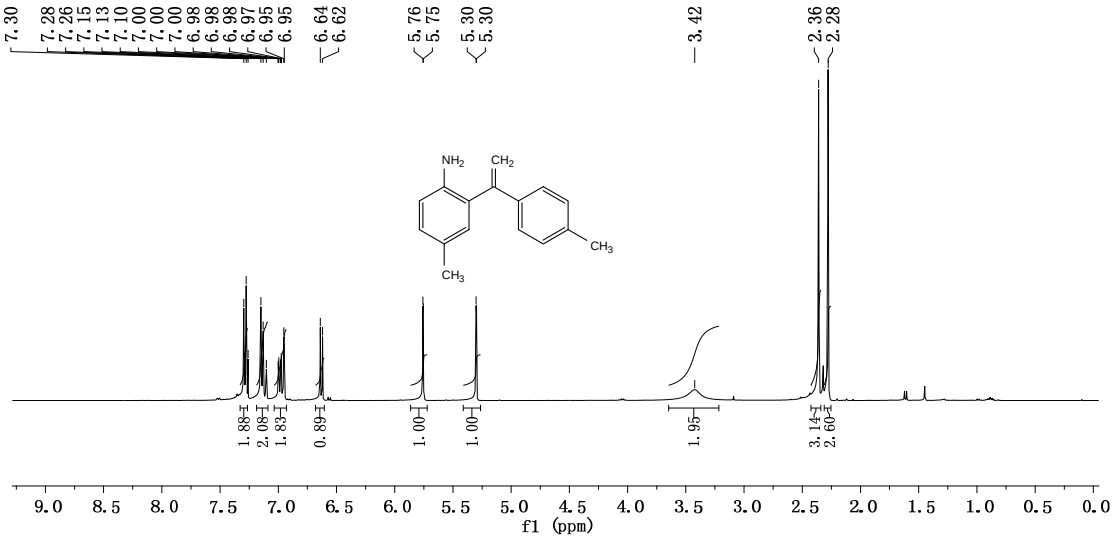
^{1}H NMR spectrum of compound **1h** (400 MHz in $CDCl_3$)



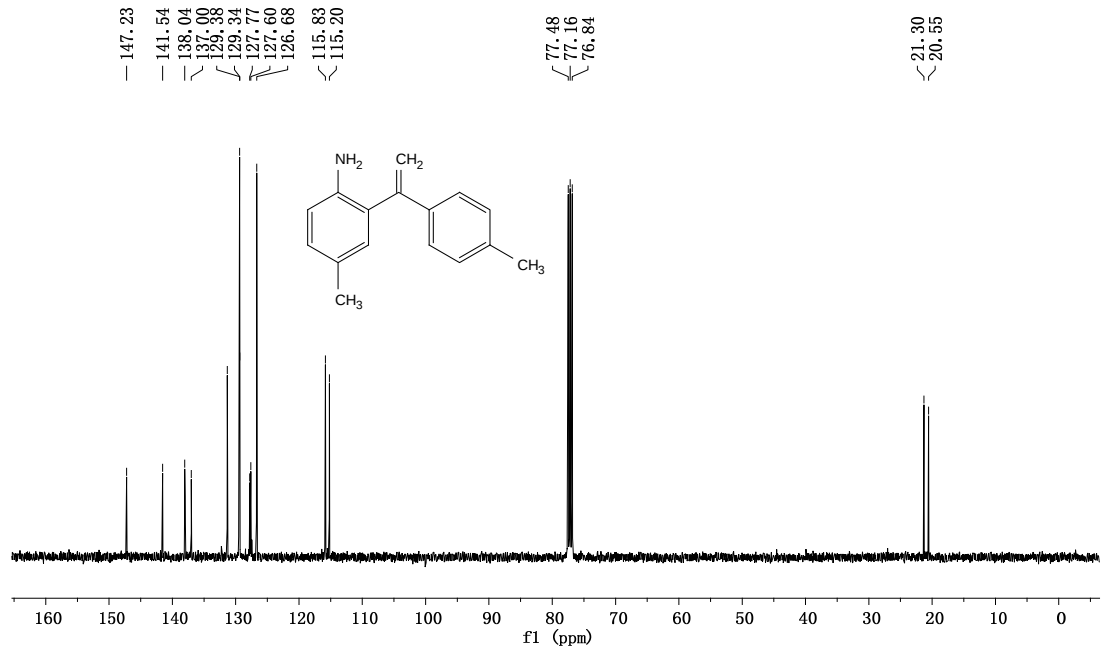
^{13}C NMR spectrum of compound **1h** (101 MHz in $CDCl_3$)



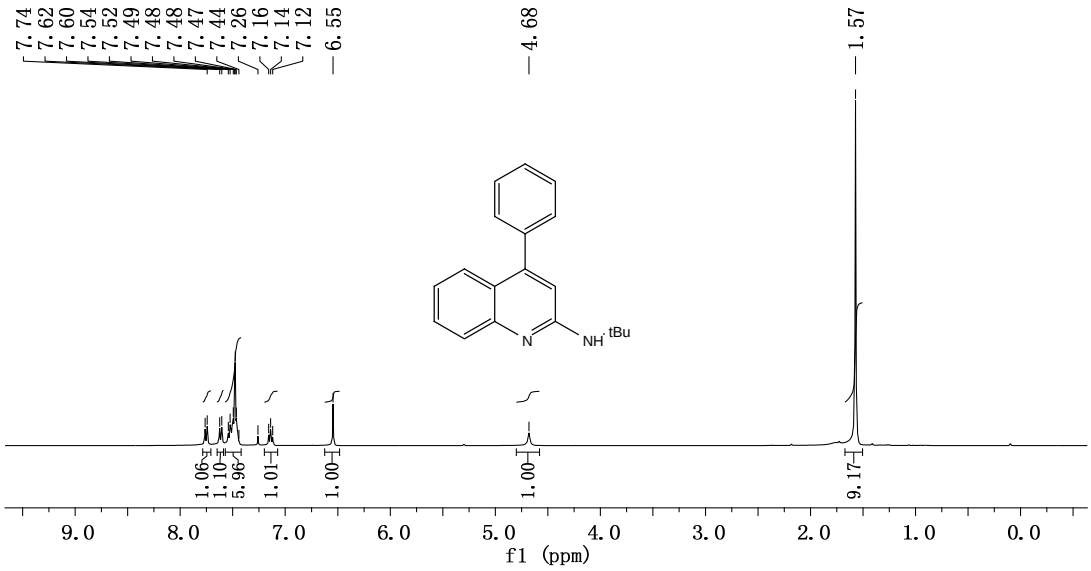
^{1}H NMR spectrum of compound **1i** (400 MHz in $CDCl_3$)



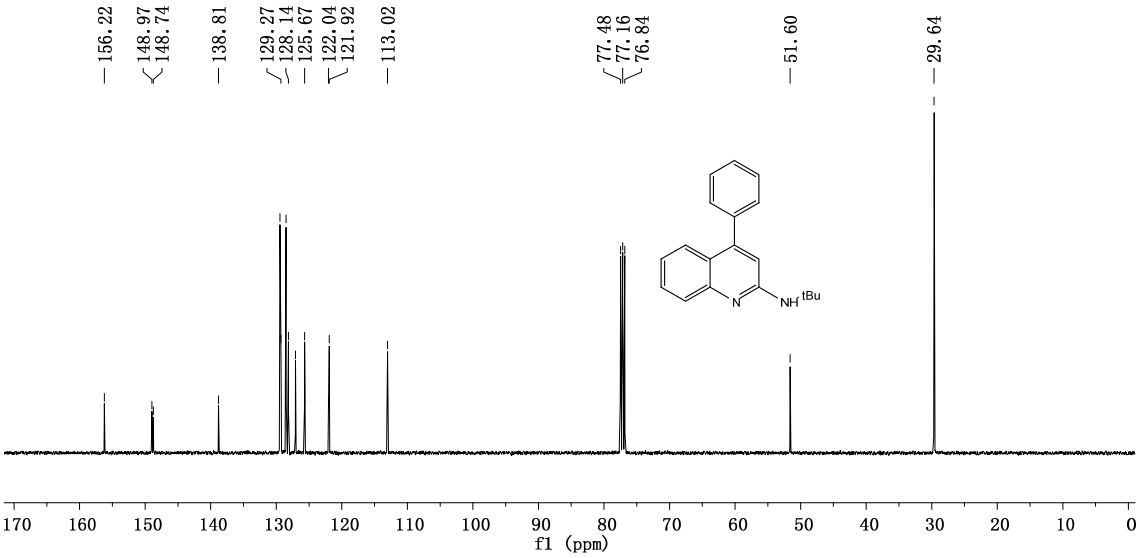
^{13}C NMR spectrum of compound **1i** (101 MHz in $CDCl_3$)



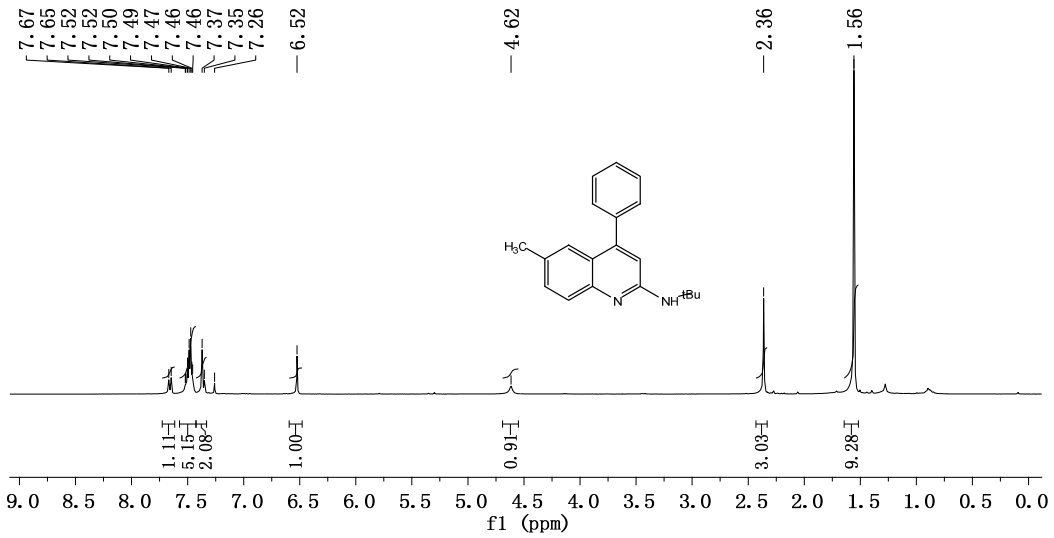
^{1}H NMR spectrum of compound **3aa** (400 MHz in $CDCl_3$)



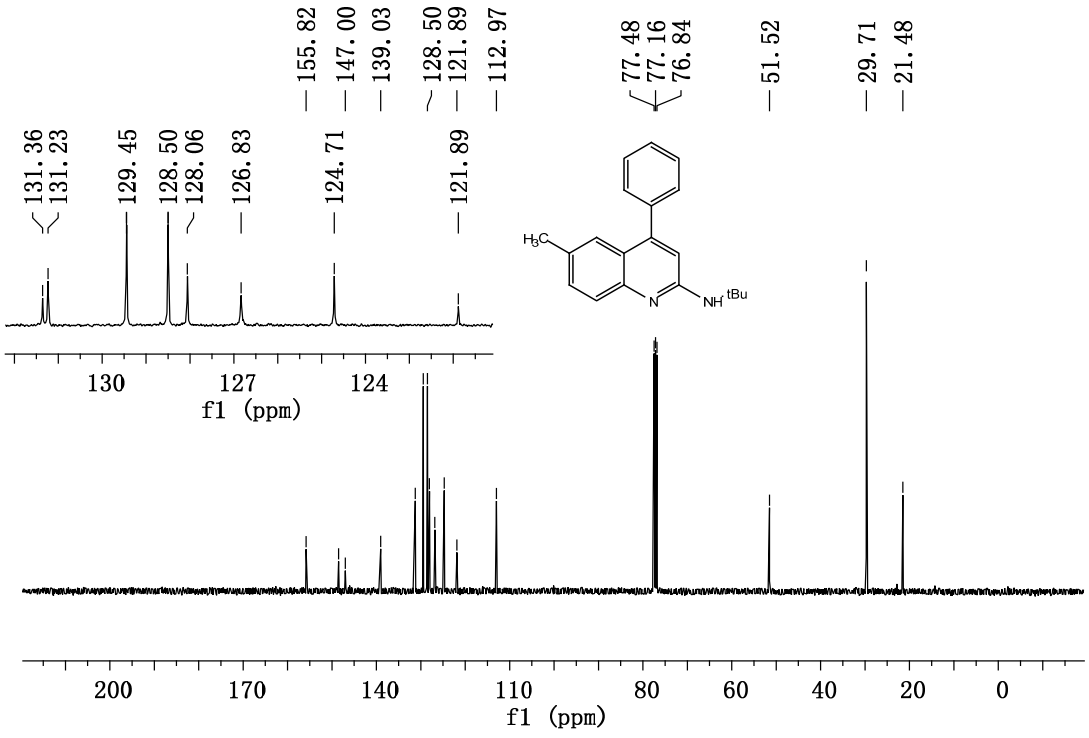
^{13}C NMR spectrum of compound **3aa** (101 MHz in $CDCl_3$)



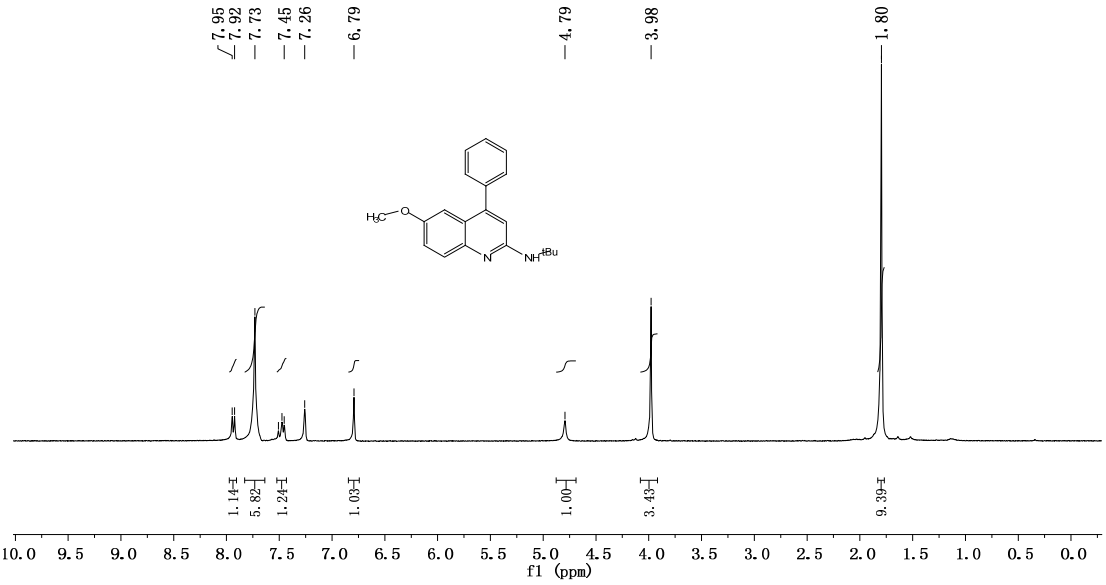
^{1}H NMR spectrum of compound **3ba** (400 MHz in $CDCl_3$)



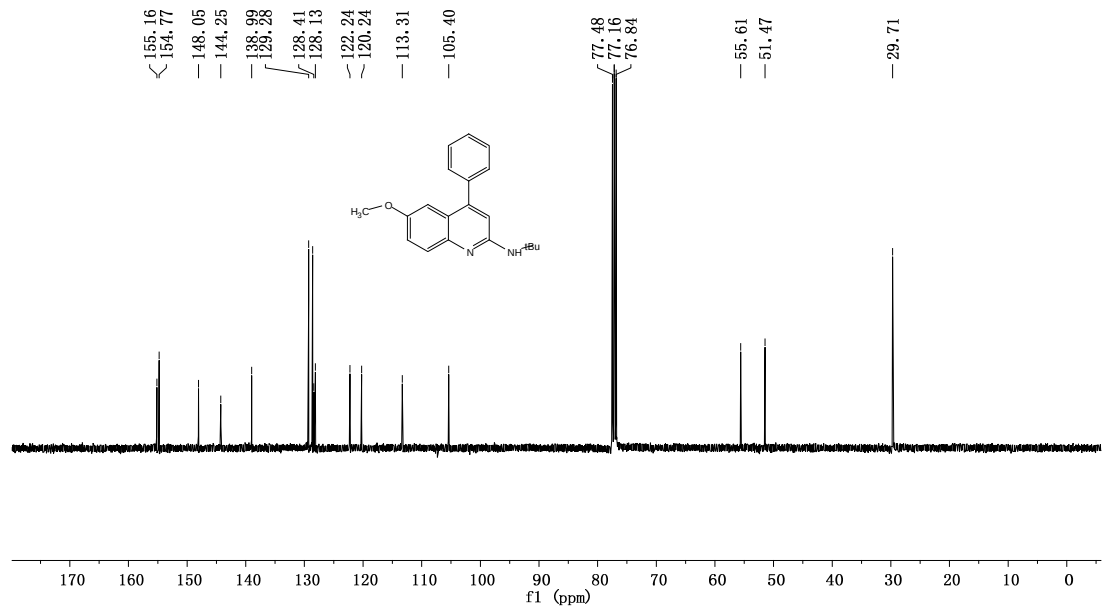
^{13}C NMR spectrum of compound **3ba** (101 MHz in $CDCl_3$)



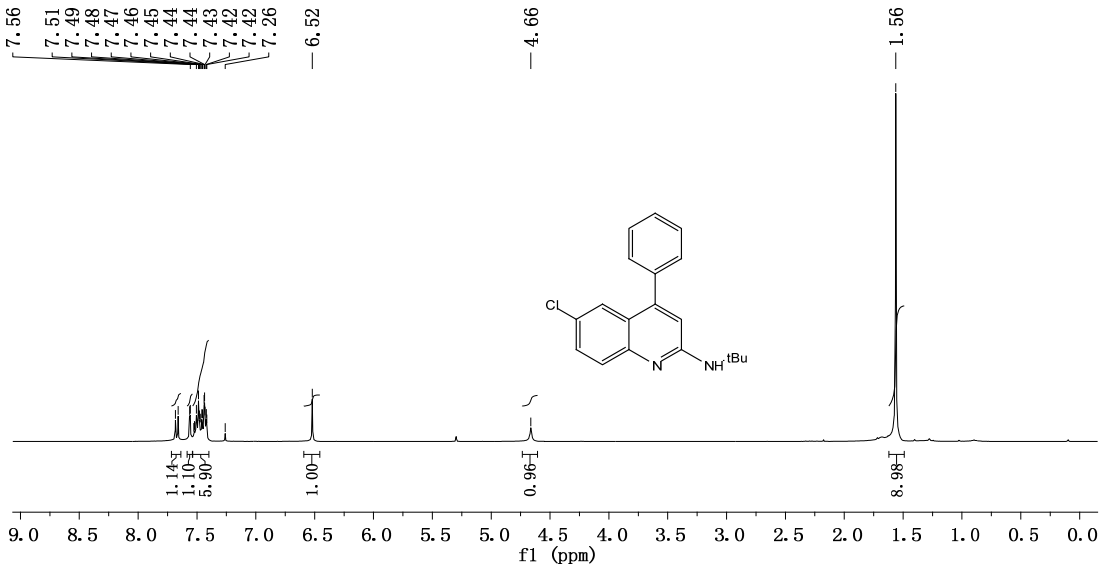
^{1}H NMR spectrum of compound **3ca** (400 MHz in $CDCl_3$)



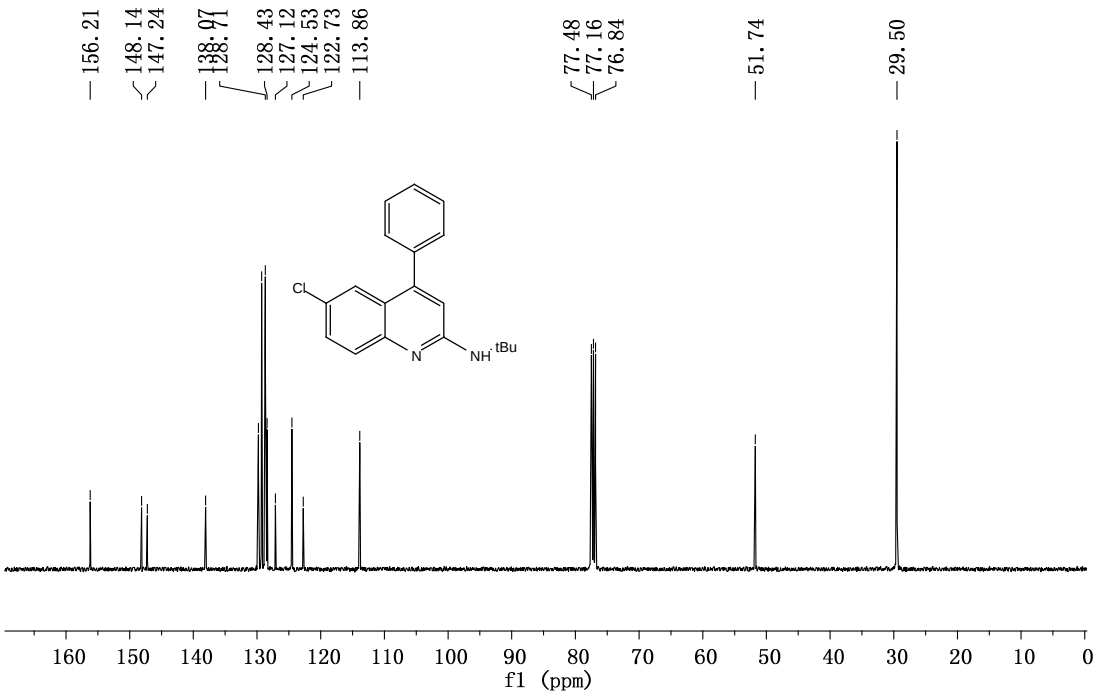
^{13}C NMR spectrum of compound **3ca** (101 MHz in $CDCl_3$)



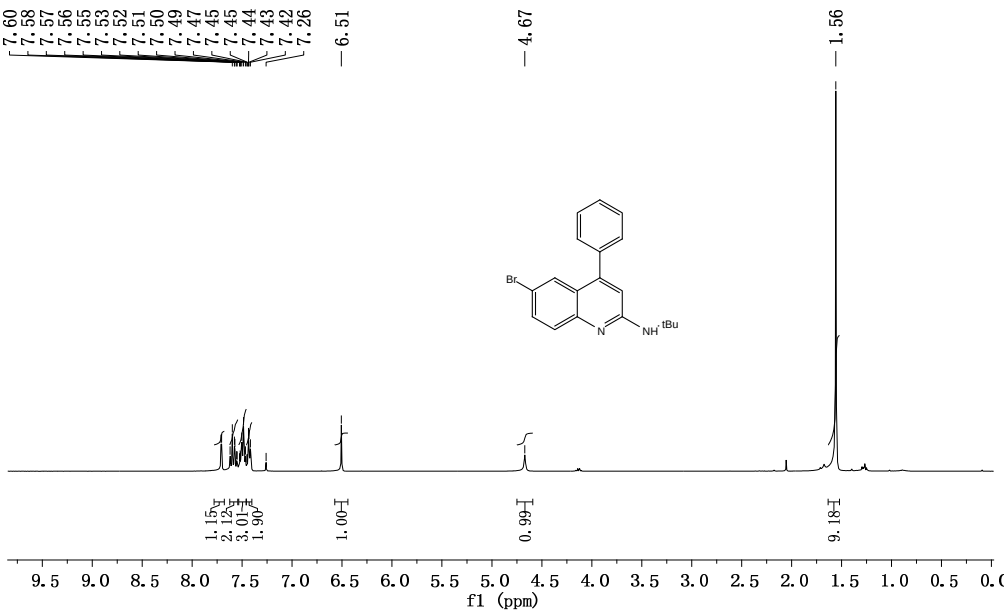
^{1}H NMR spectrum of compound **3da** (400 MHz in $CDCl_3$)



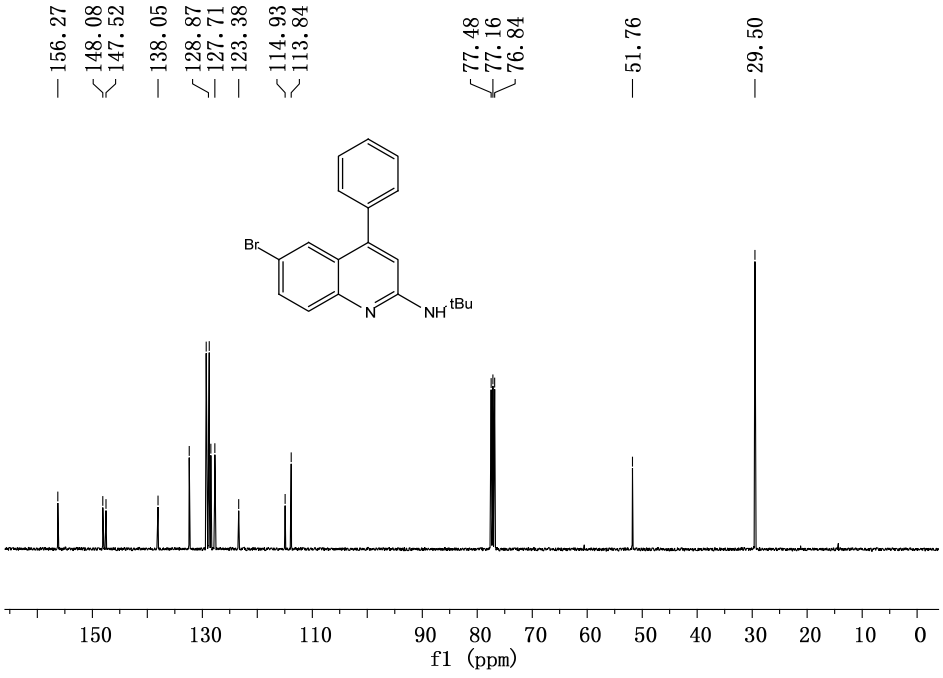
^{13}C NMR spectrum of compound **3da** (101 MHz in $CDCl_3$)



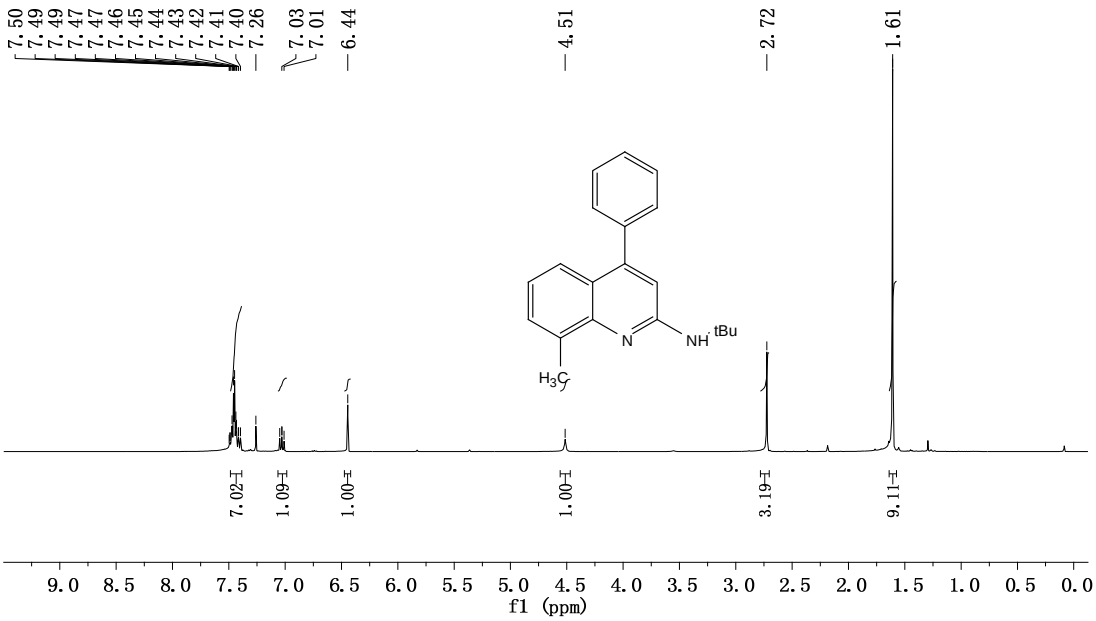
^{1}H NMR spectrum of compound **3ea** (400 MHz in $CDCl_3$)



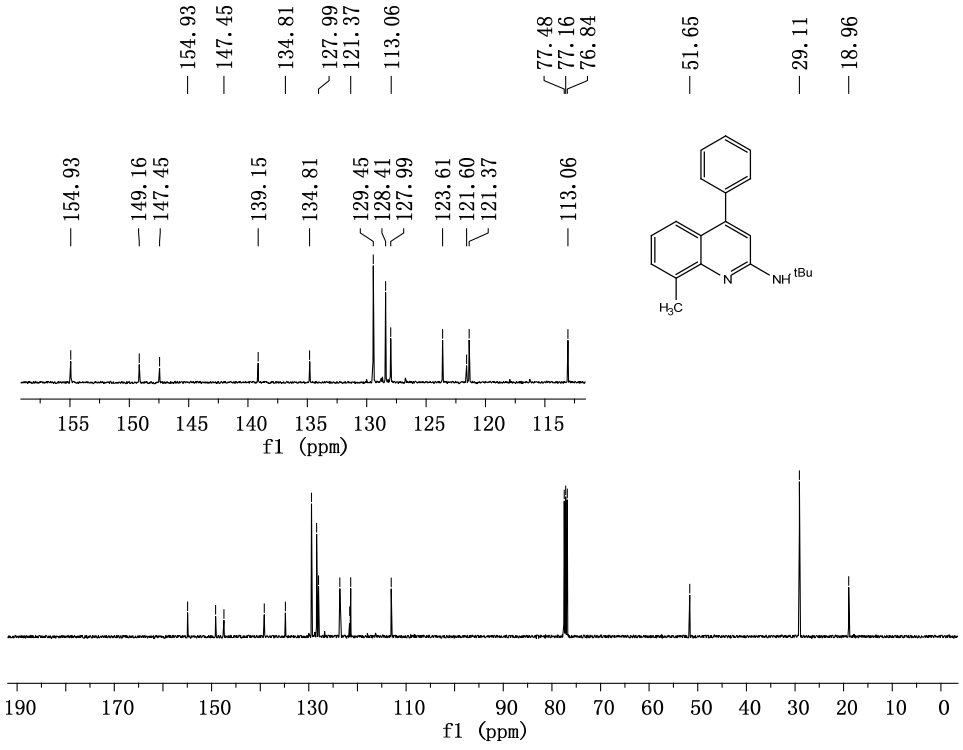
^{13}C NMR spectrum of compound **3ea** (101 MHz in $CDCl_3$)



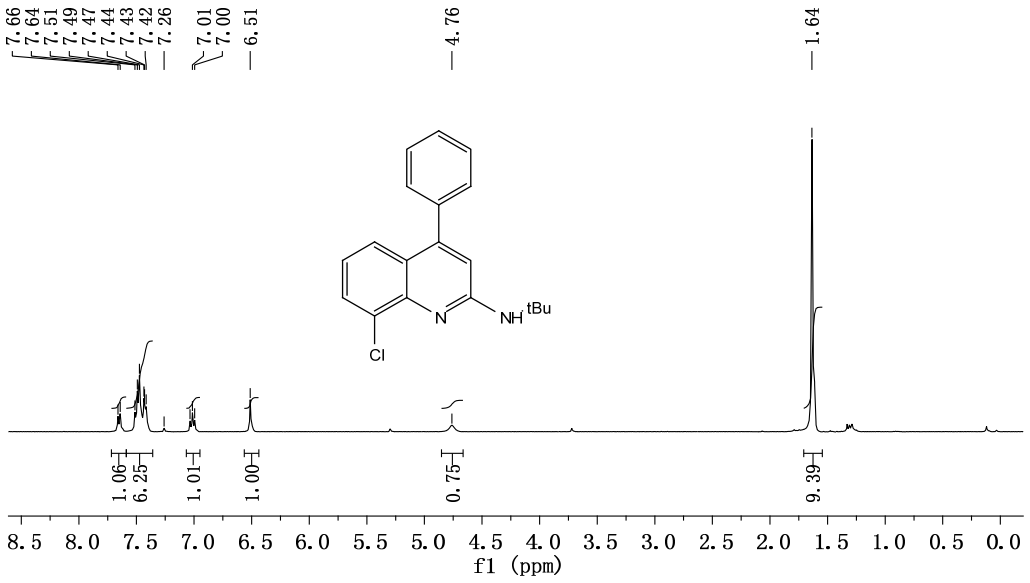
^{1}H NMR spectrum of compound **3fa** (400 MHz in $CDCl_3$)



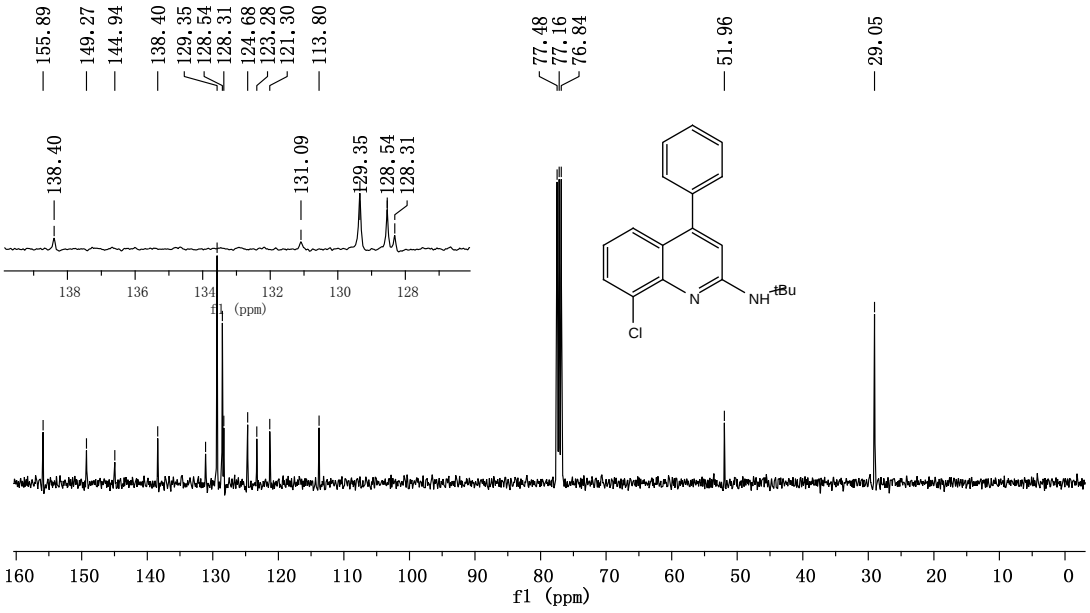
^{13}C NMR spectrum of compound **3fa** (101 MHz in $CDCl_3$)



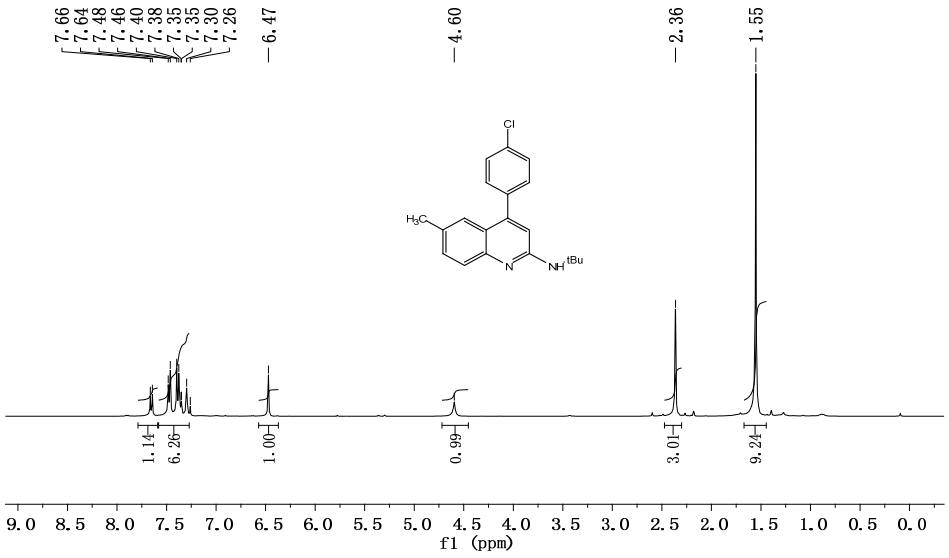
^{1}H NMR spectrum of compound **3ga** (400 MHz in $CDCl_3$)



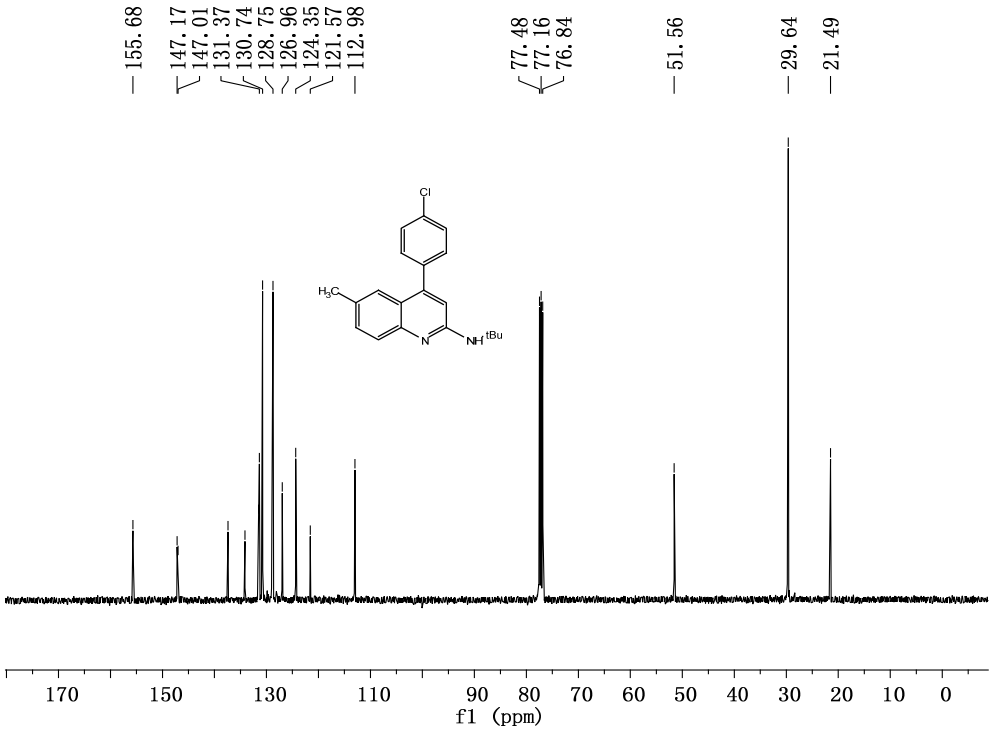
^{13}C NMR spectrum of compound **3ga** (101 MHz in $CDCl_3$)



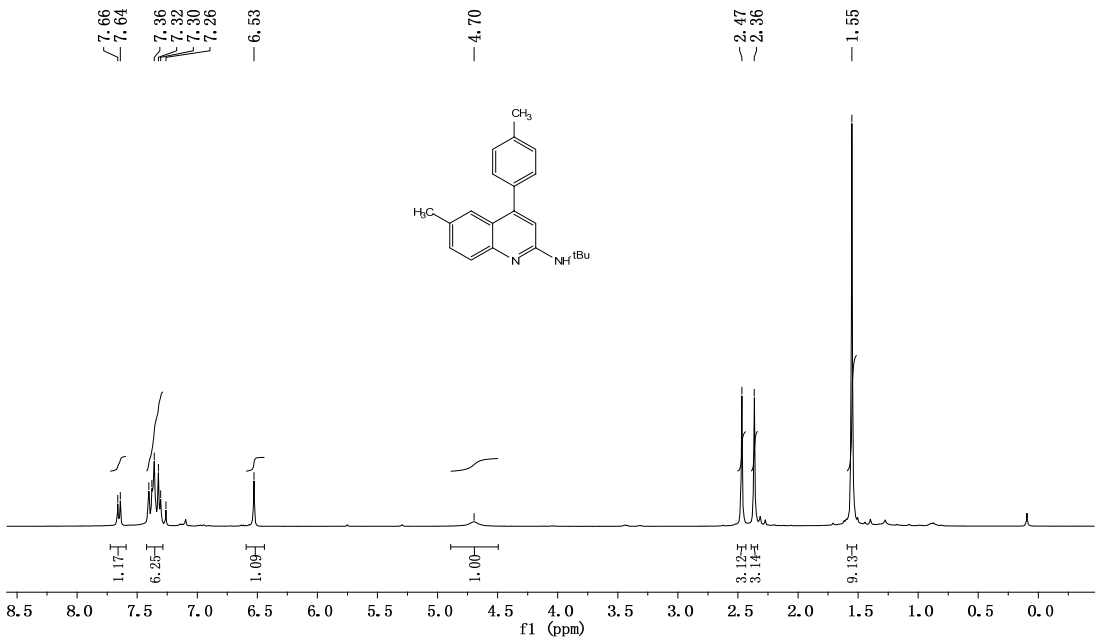
^{1}H NMR spectrum of compound **3ha** (400 MHz in $CDCl_3$)



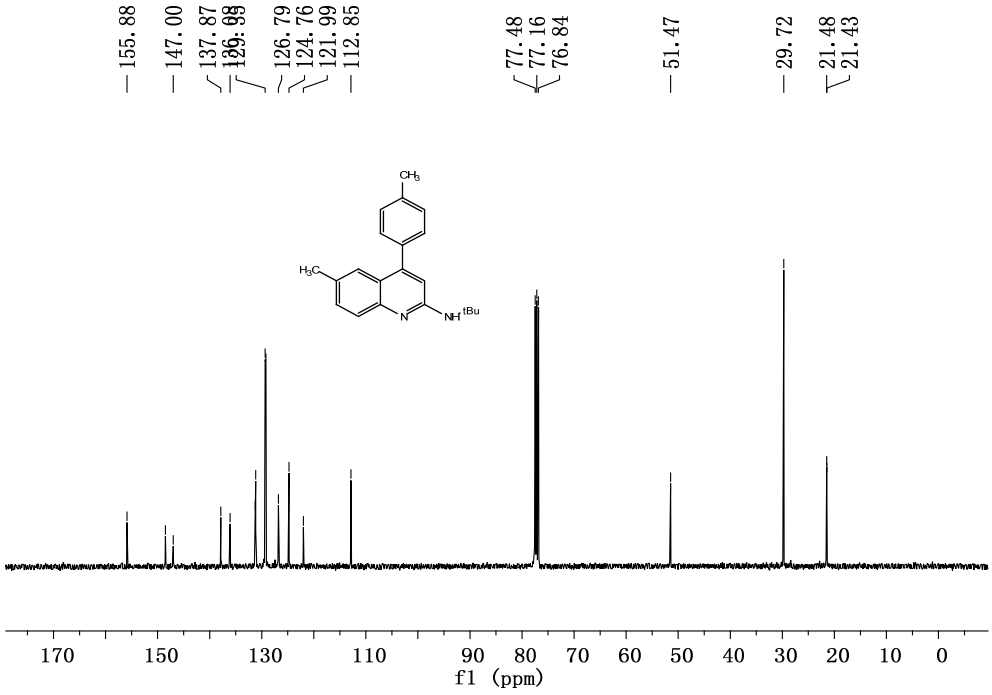
^{13}C NMR spectrum of compound **3ha** (101 MHz in $CDCl_3$)



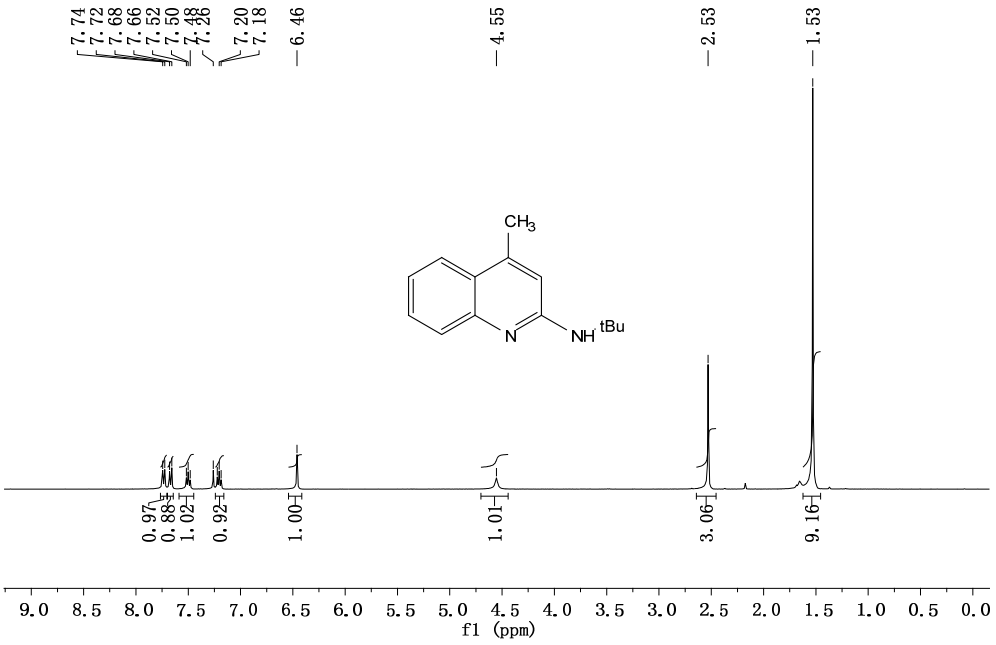
^{1}H NMR spectrum of compound **3ia** (400 MHz in $CDCl_3$)



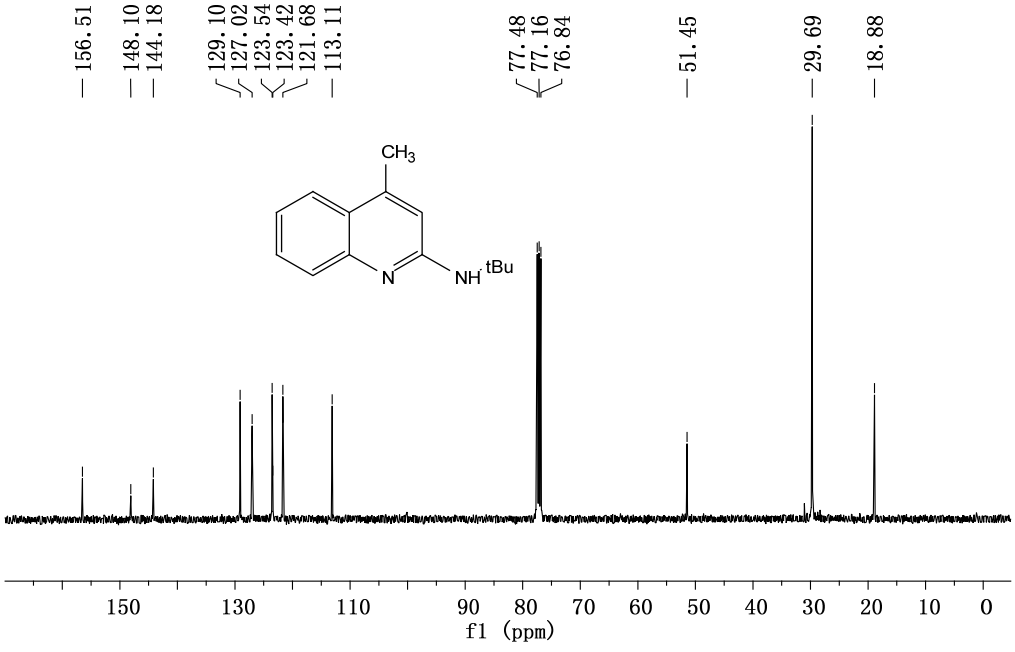
^{13}C NMR spectrum of compound **3ia** (101 MHz in $CDCl_3$)



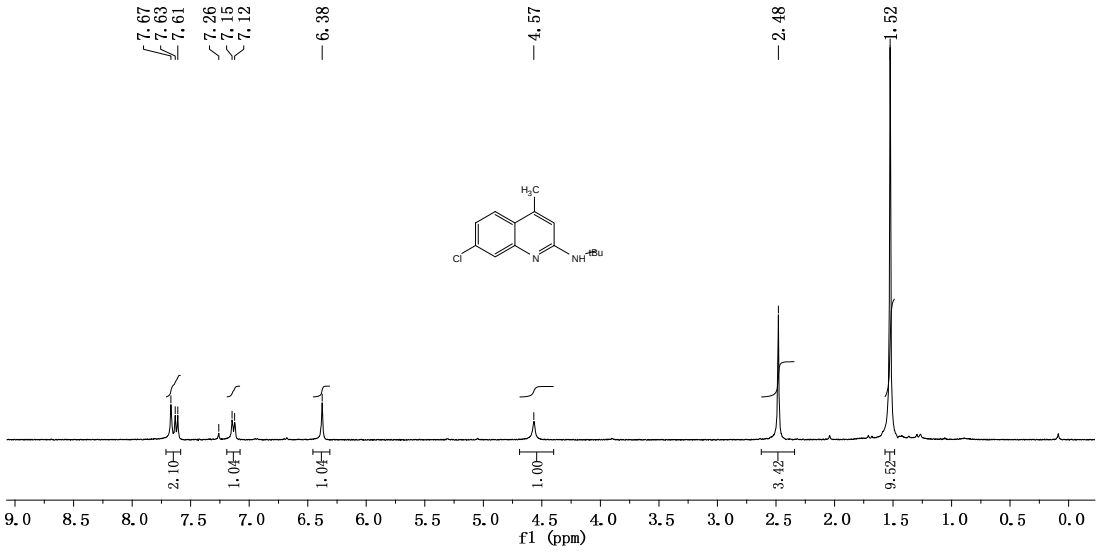
^{1}H NMR spectrum of compound **3ja** (400 MHz in $CDCl_3$)



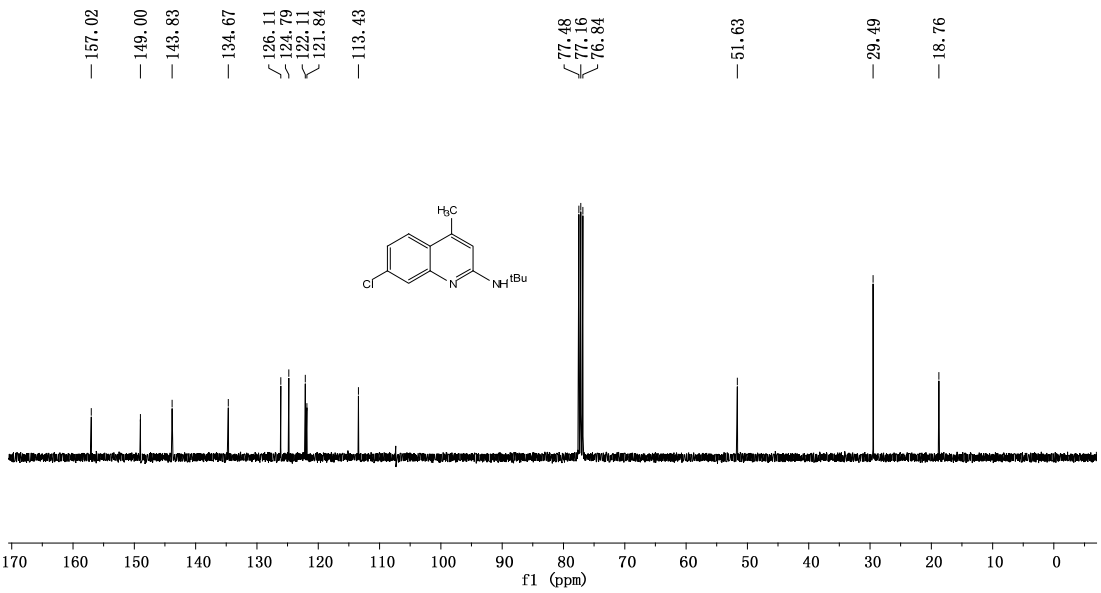
^{13}C NMR spectrum of compound **3ja** (101 MHz in $CDCl_3$)



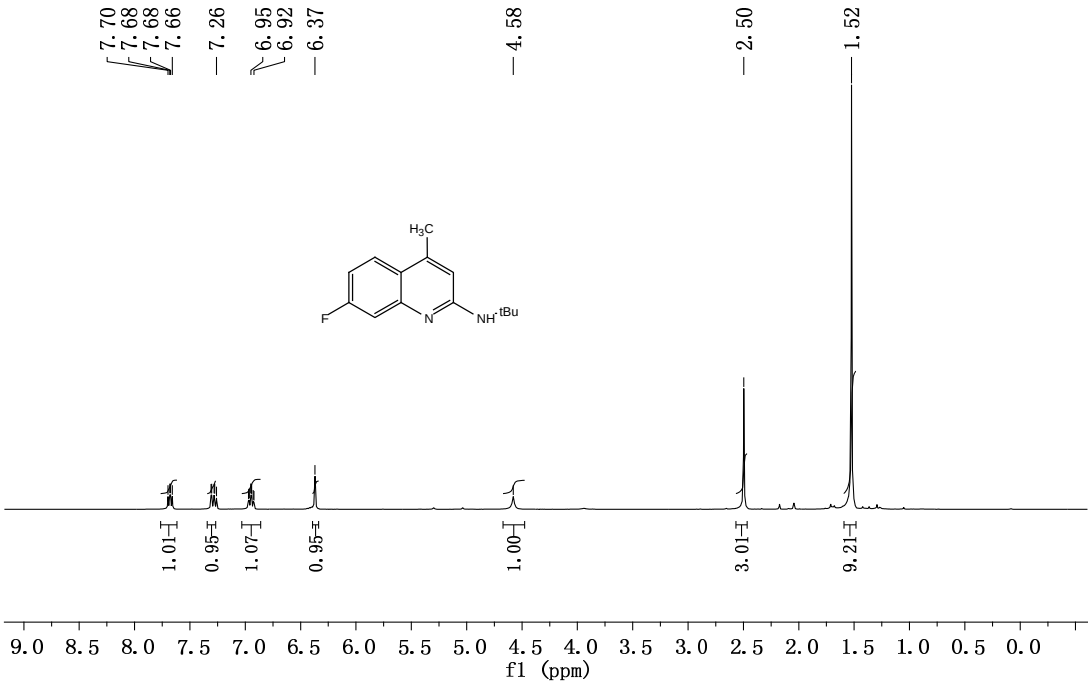
^{1}H NMR spectrum of compound **3ka** (400 MHz in $CDCl_3$)



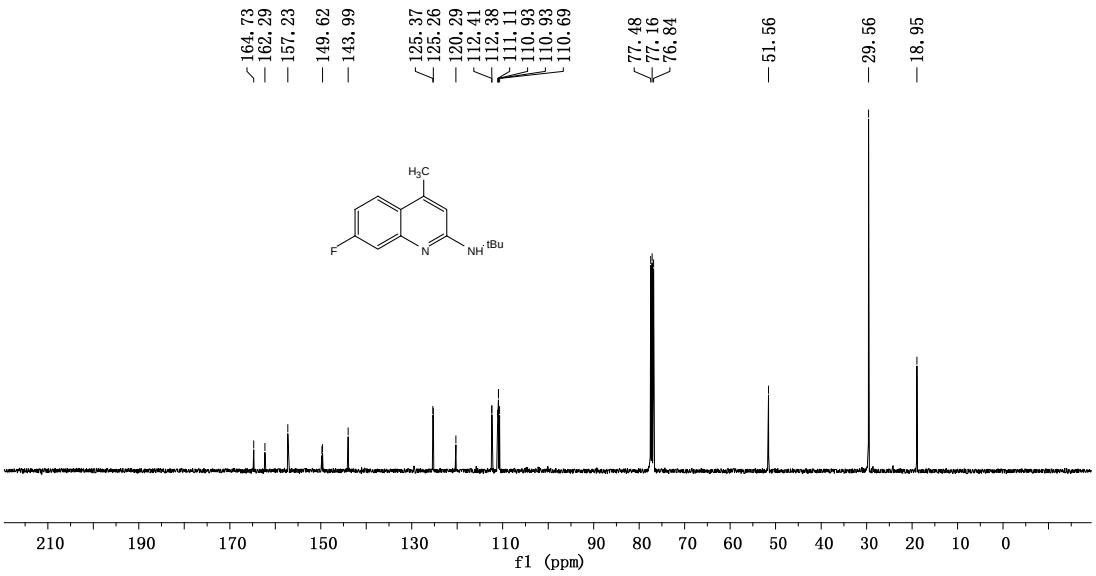
^{13}C NMR spectrum of compound **3ka** (101 MHz in $CDCl_3$)



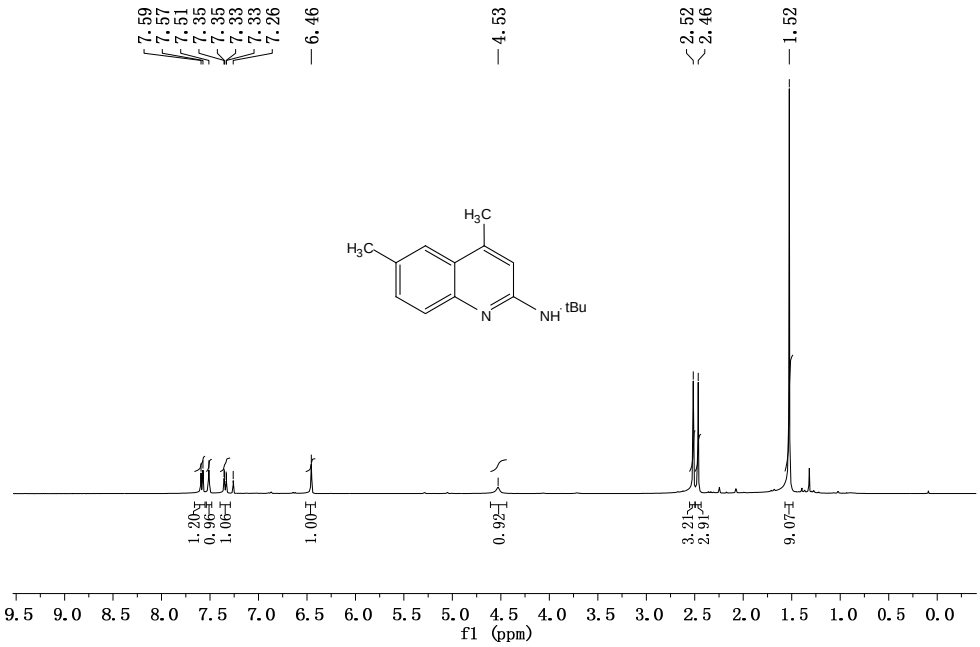
^{1}H NMR spectrum of compound **3la** (400 MHz in $CDCl_3$)



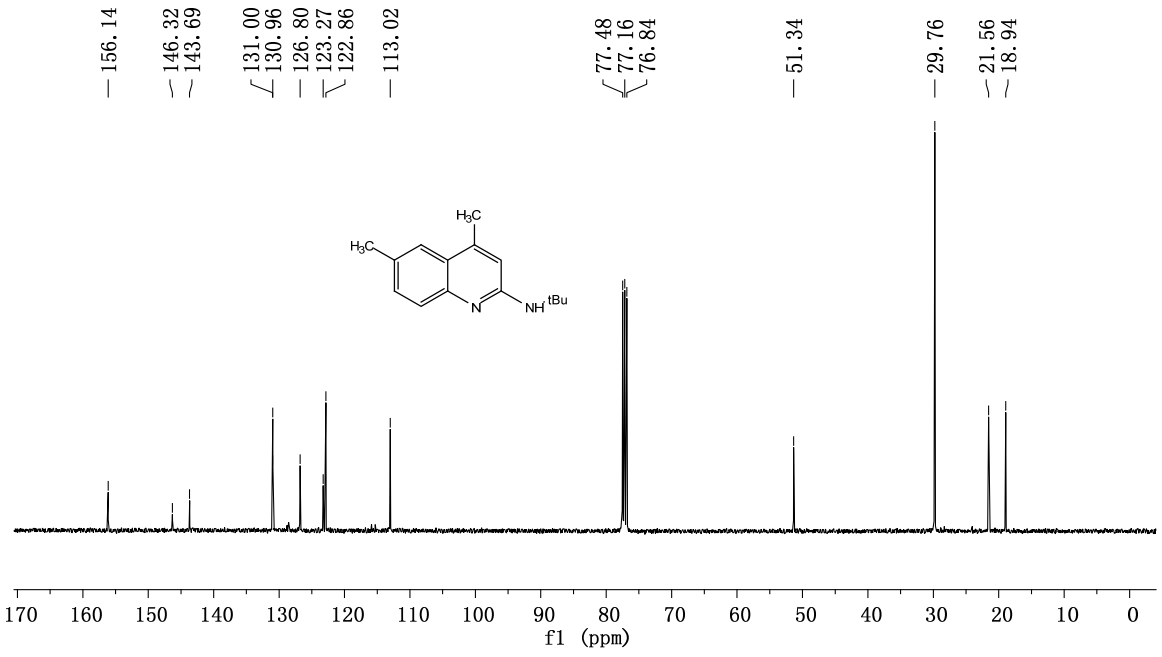
^{13}C NMR spectrum of compound **3la** (101 MHz in $CDCl_3$)



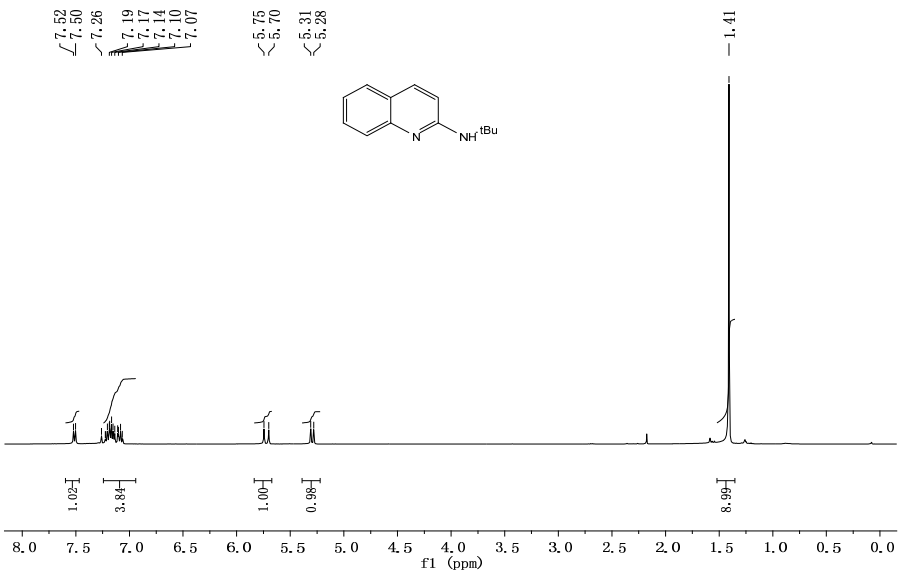
^{1}H NMR spectrum of compound **3ma** (400 MHz in $CDCl_3$)



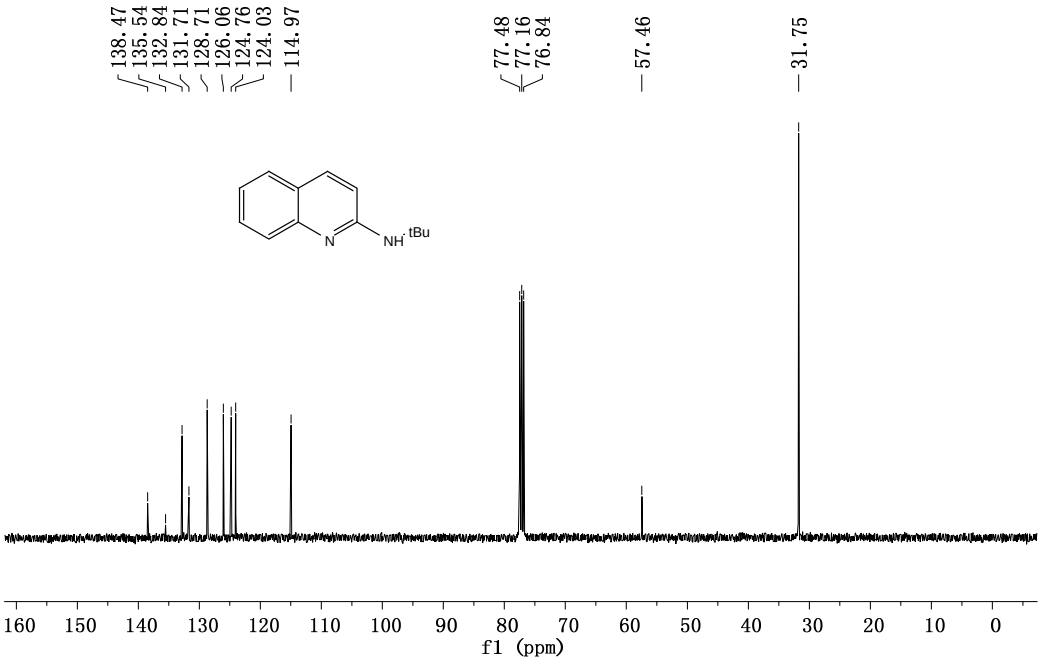
^{13}C NMR spectrum of compound **3ma** (101 MHz in $CDCl_3$)



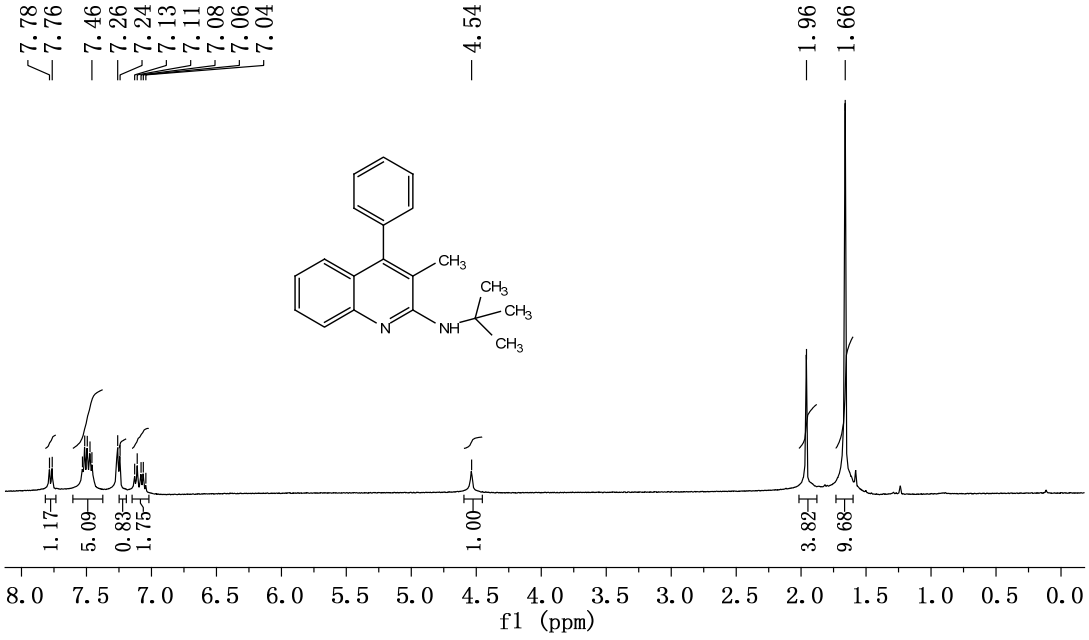
^{1}H NMR spectrum of compound **3na** (400 MHz in $CDCl_3$)



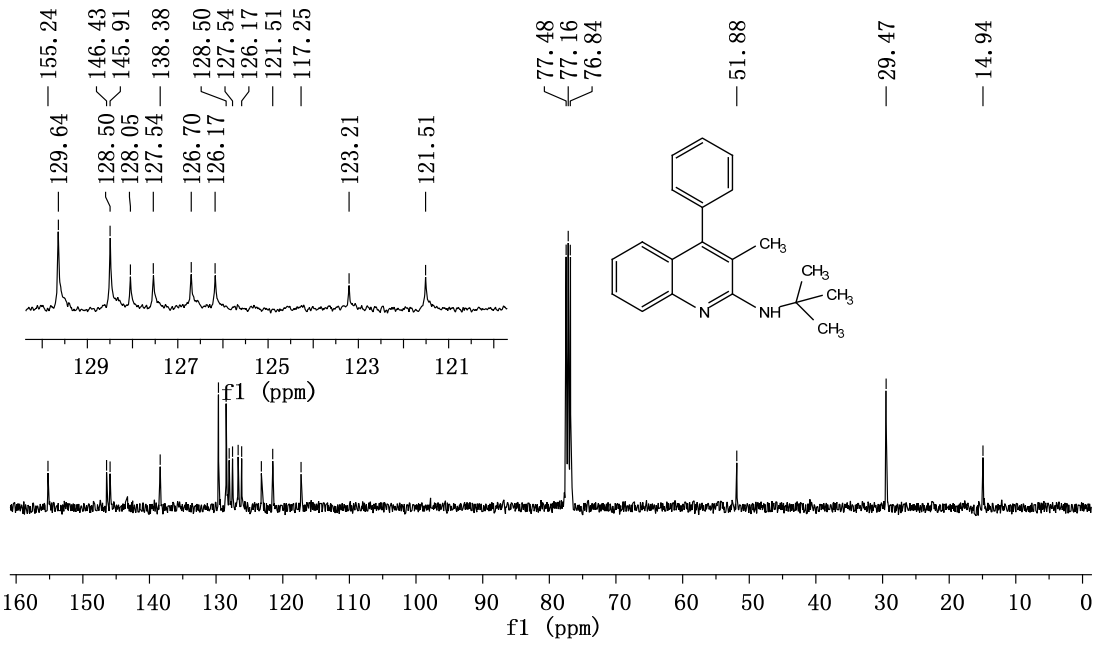
^{13}C NMR spectrum of compound **3na** (101 MHz in $CDCl_3$)



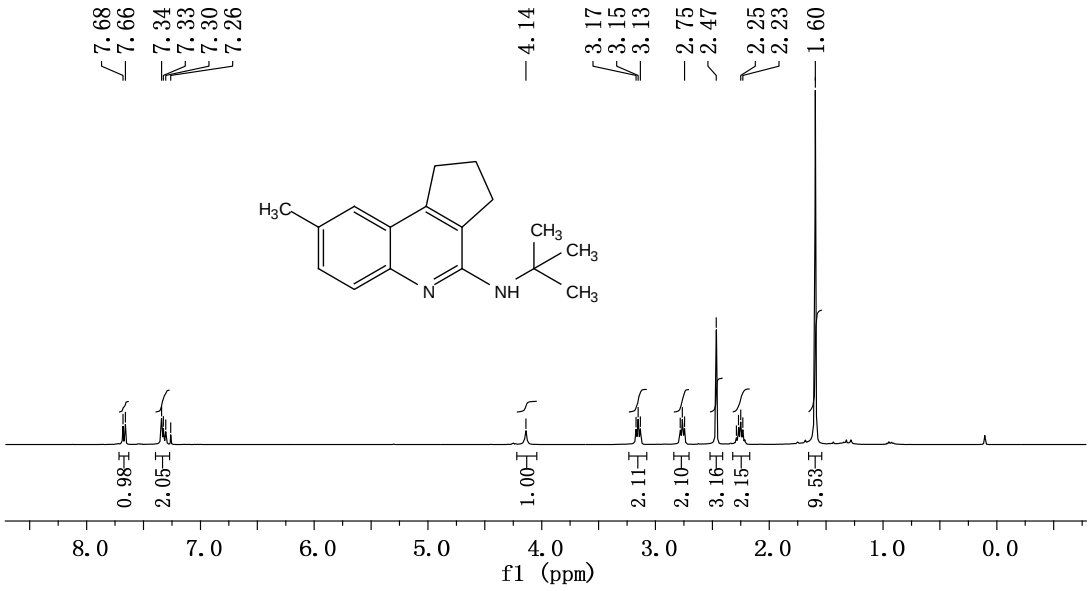
^{1}H NMR spectrum of compound **3oa** (400 MHz in $CDCl_3$)



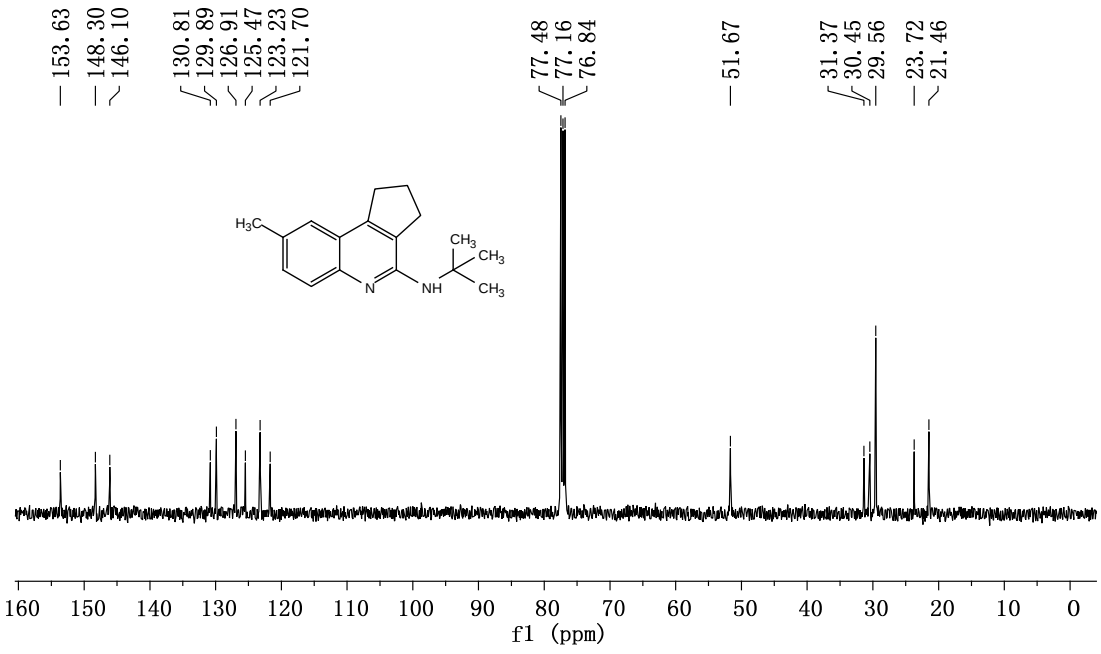
^{13}C NMR spectrum of compound **3oa** (101 MHz in $CDCl_3$)



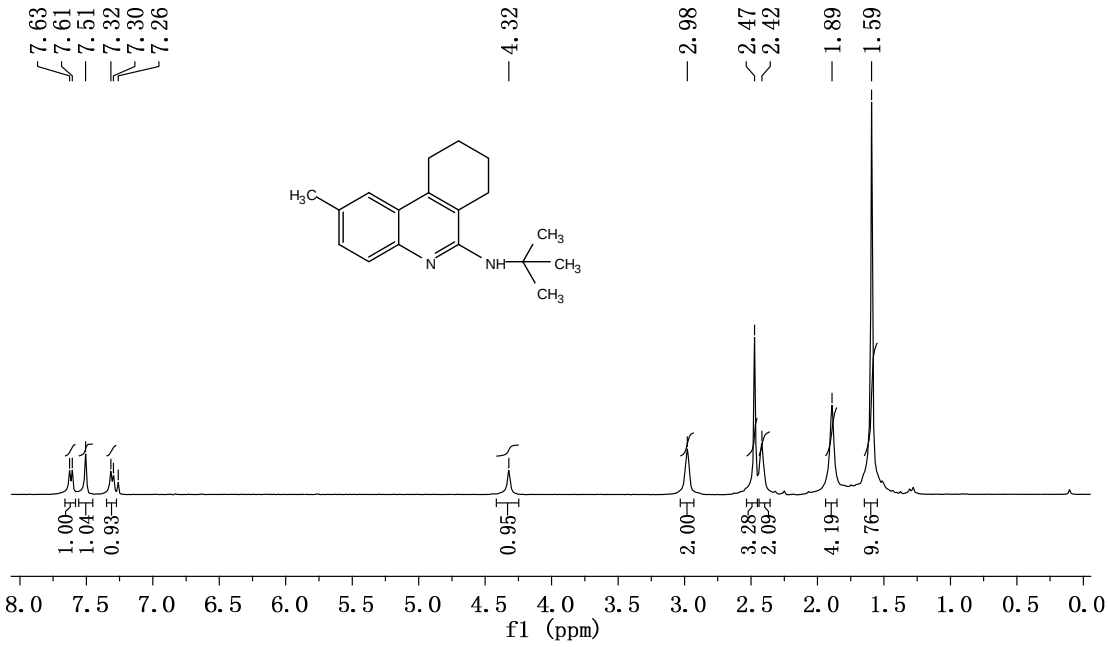
^{1}H NMR spectrum of compound **3pa** (400 MHz in $CDCl_3$)



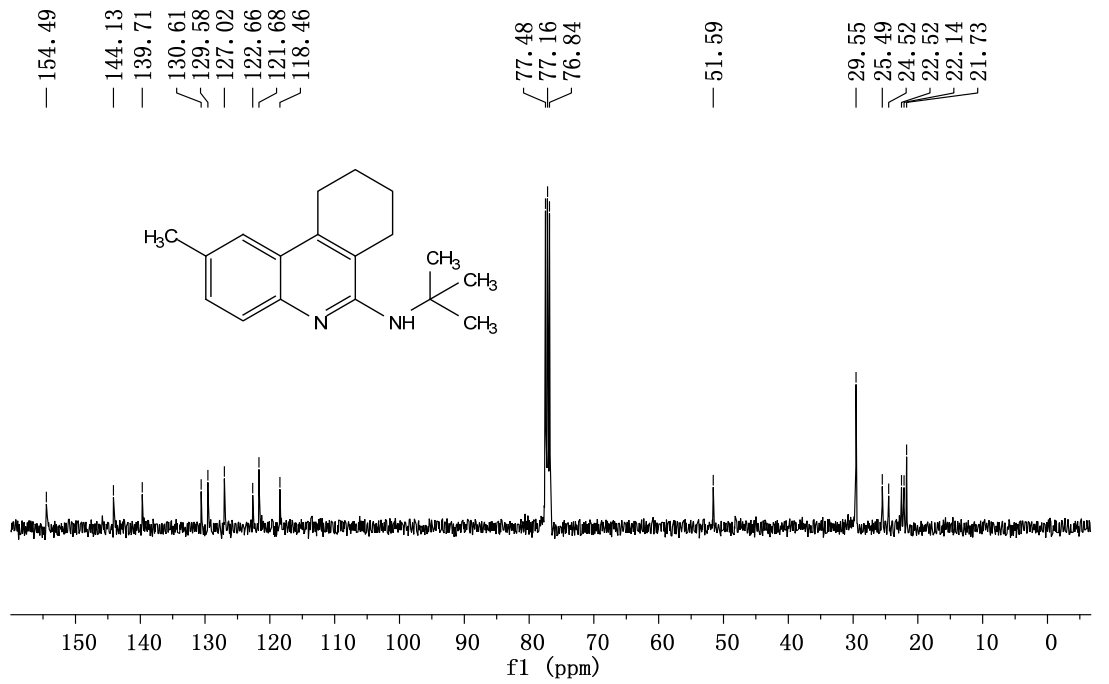
^{13}C NMR spectrum of compound **3pa** (101 MHz in $CDCl_3$)



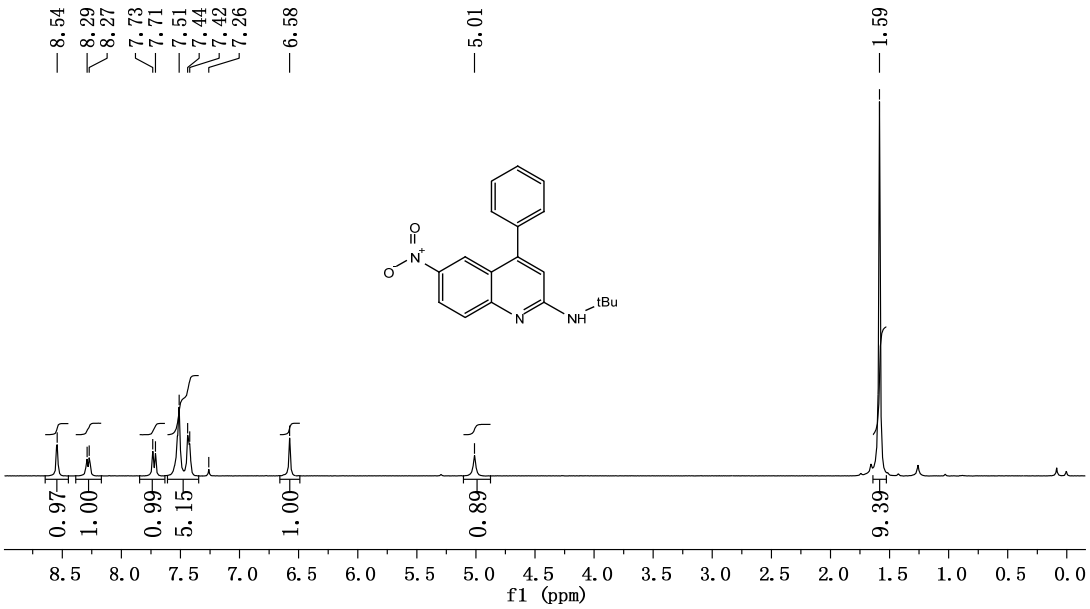
^{1}H NMR spectrum of compound **3qa** (400 MHz in $CDCl_3$)



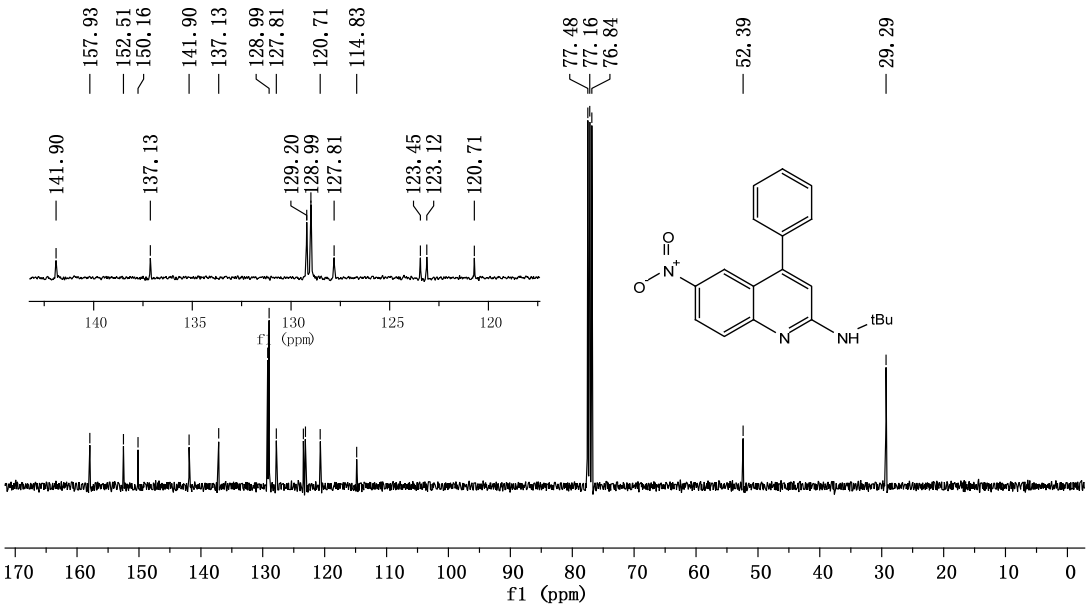
^{13}C NMR spectrum of compound **3qa** (101 MHz in $CDCl_3$)



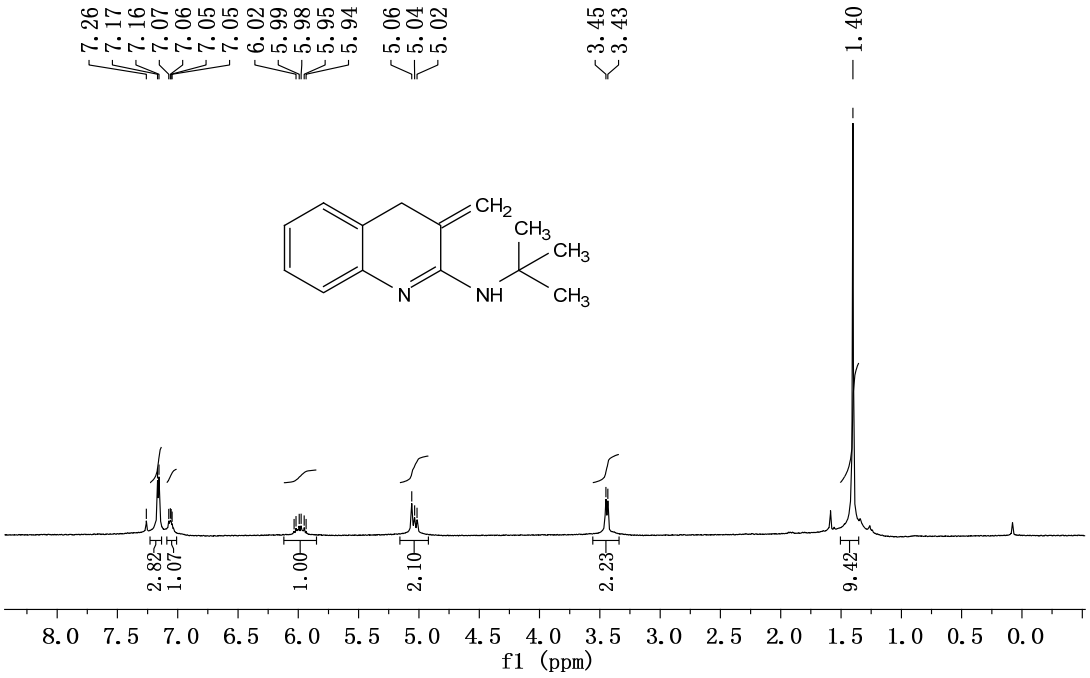
^{1}H NMR spectrum of compound **3ra** (400 MHz in $CDCl_3$)



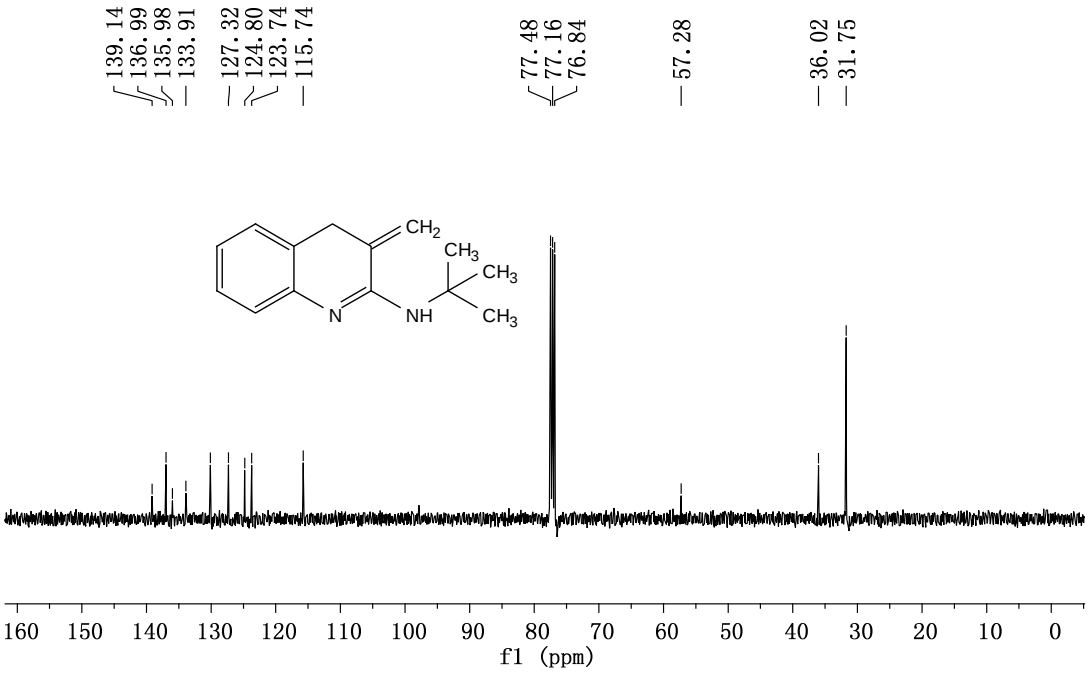
^{13}C NMR spectrum of compound **3ra** (101 MHz in $CDCl_3$)



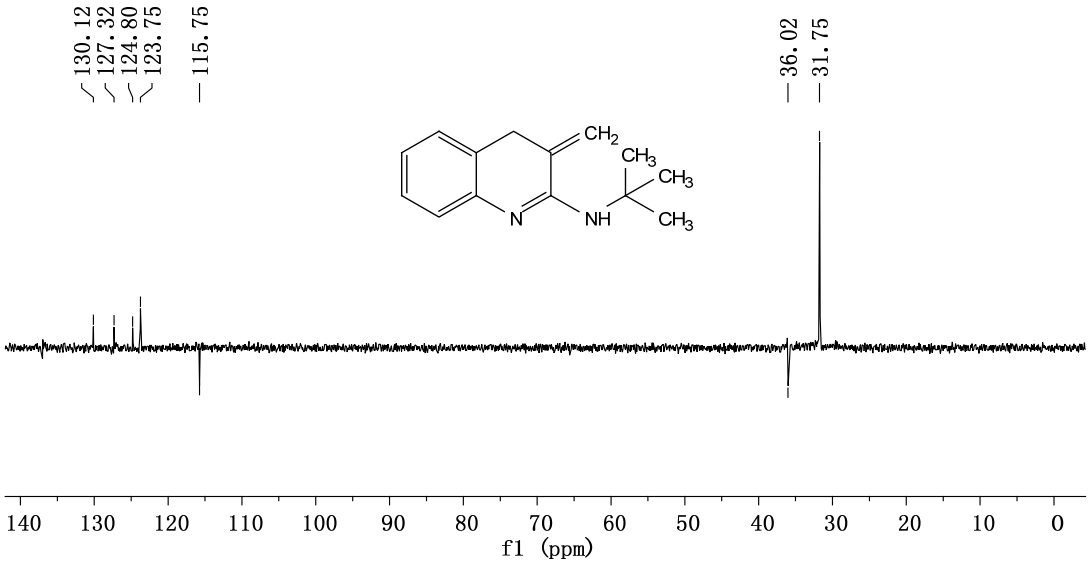
^{1}H NMR spectrum of compound **3sa** (400 MHz in $CDCl_3$)



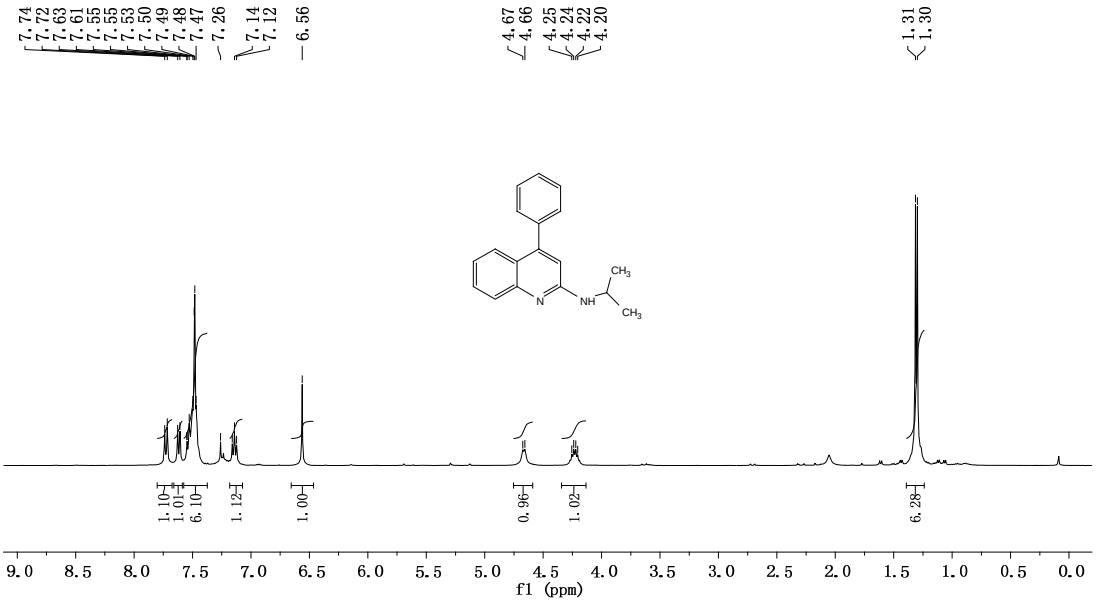
^{13}C NMR spectrum of compound **3sa** (101 MHz in $CDCl_3$)



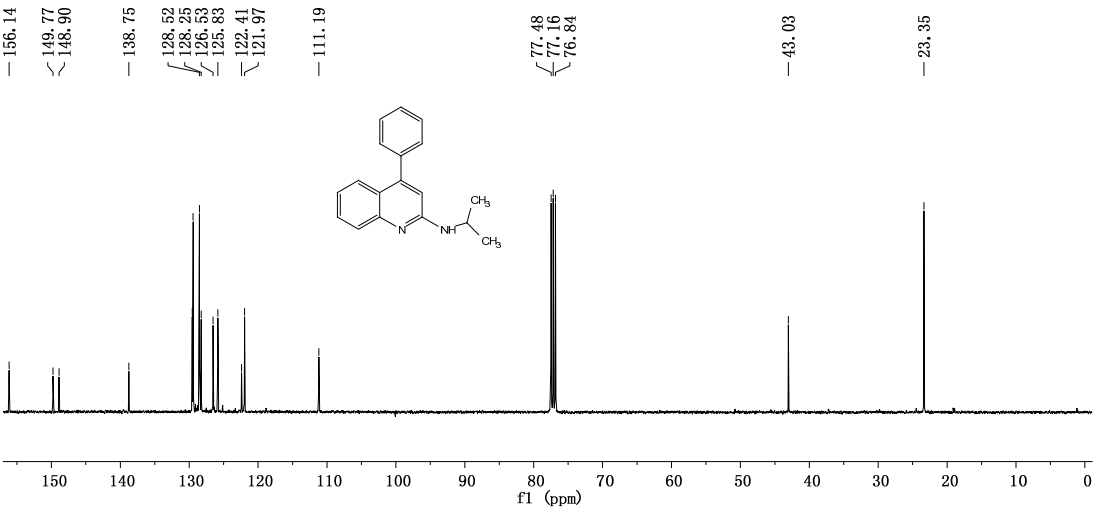
DEPT 135° spectrum of compound **3sa** (101 MHz in $CDCl_3$)



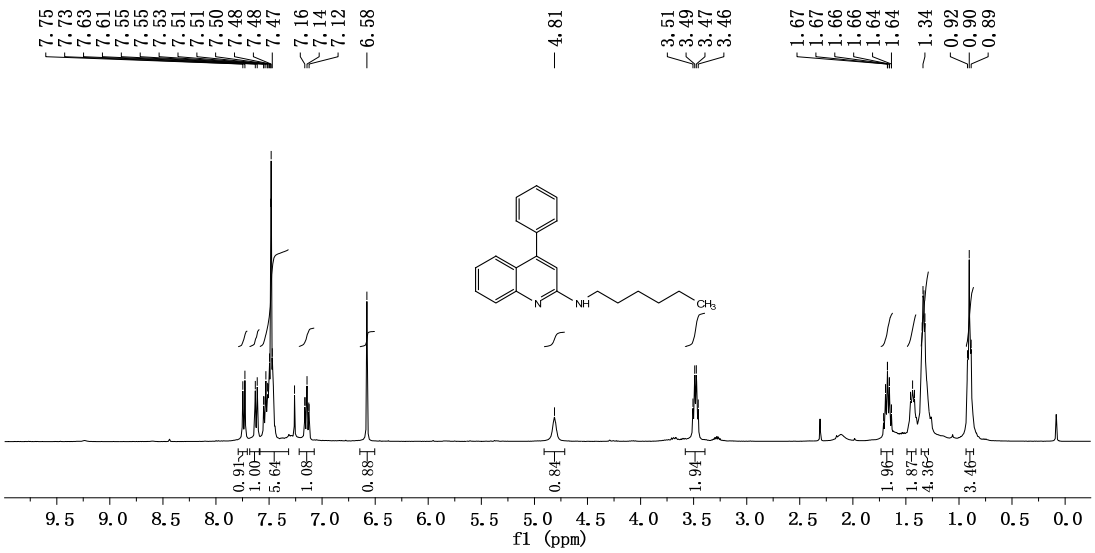
^{1}H NMR spectrum of compound **3ab** (400 MHz in $CDCl_3$)



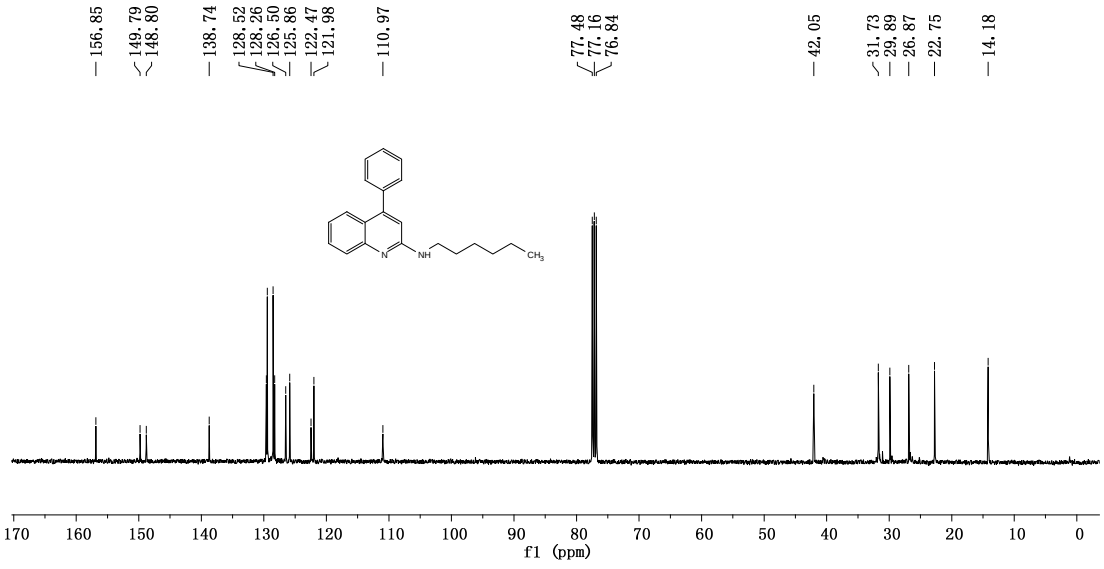
^{13}C NMR spectrum of compound **3ab** (101 MHz in $CDCl_3$)



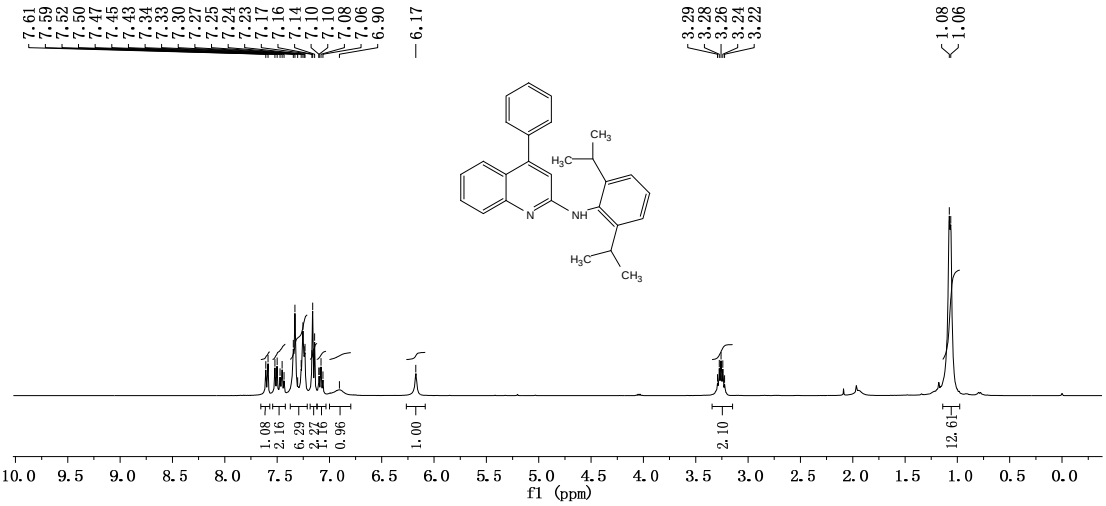
^{1}H NMR spectrum of compound **3ac** (400 MHz in $CDCl_3$)



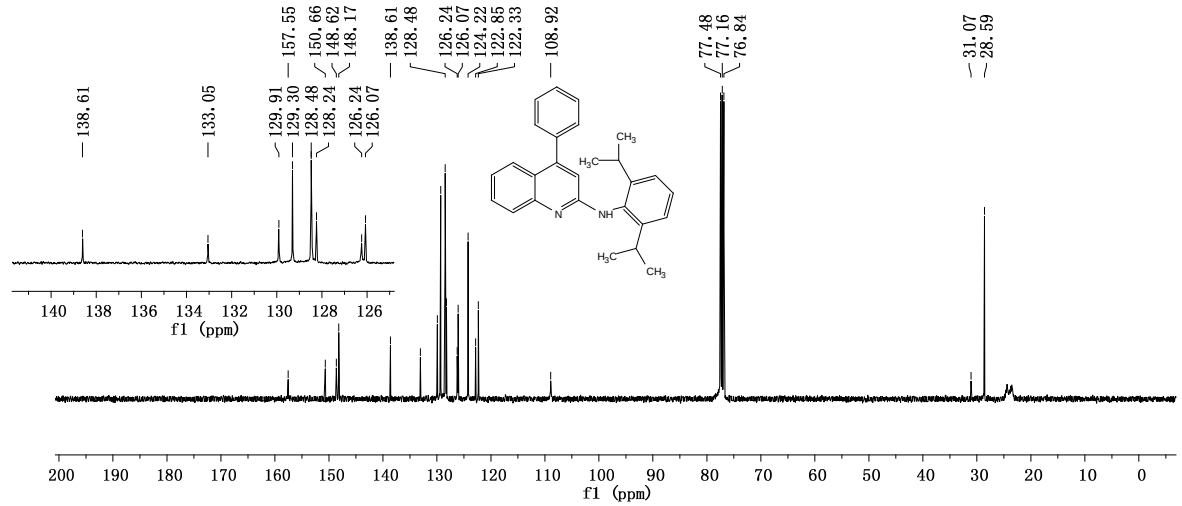
^{13}C NMR spectrum of compound **3ac** (101 MHz in $CDCl_3$)



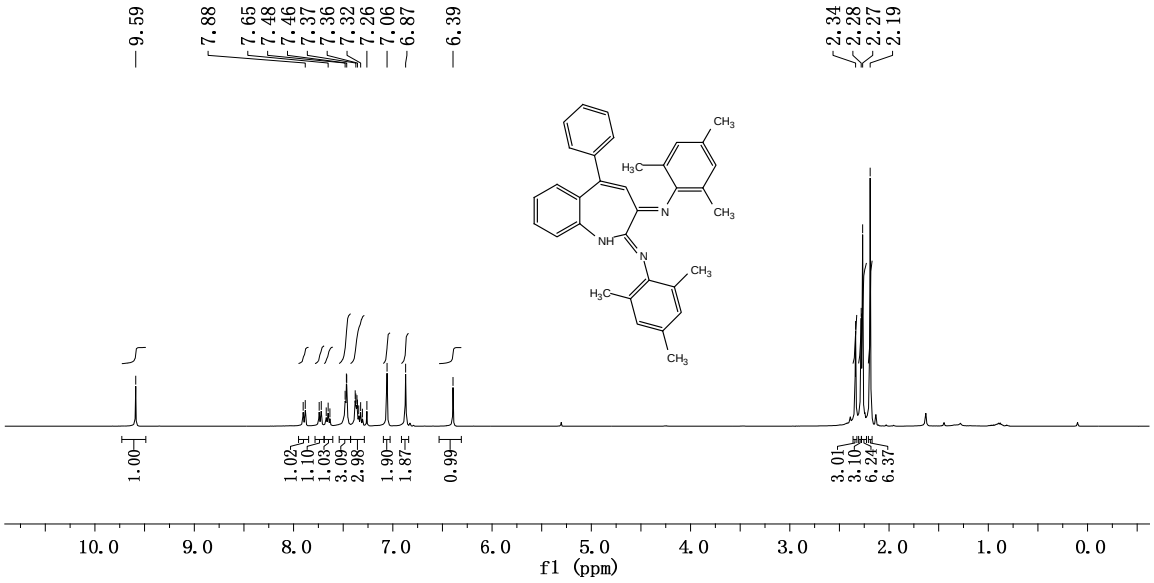
^{1}H NMR spectrum of compound **3ae** (400 MHz in $CDCl_3$)



^{13}C NMR spectrum of compound **3ae** (101 MHz in $CDCl_3$)



^{1}H NMR spectrum of compound **3af** (400 MHz in $CDCl_3$)



^{13}C NMR spectrum of compound **3af** (101 MHz in $CDCl_3$)