Supplementary Information

Carbonannulation of *ortho*-Vinylanilines with Dimethyl Sulfoxide to Access 4-Aryl Quinolines

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1. General Considerations

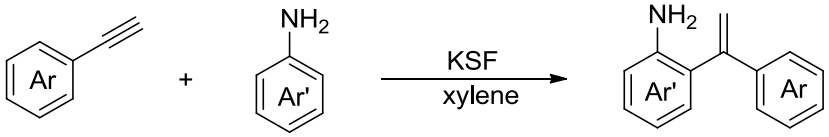
Unless otherwise noted, all chemicals were purchased from commercial suppliers and used without further purification. ^{1}H NMR、^{13}C NMR spectra were recorded at ambient temperature on a 300 or 400 MHz NMR spectrometer (75 or 100 MHz for ^{13}C). NMR experiments are reported in δ units, parts per million (ppm), and were referenced to $CDCl_3$ (δ 7.26 or 77.0 ppm) as the internal standard. The coupling constants J are given in Hz. High-resolution mass spectra (HRMS) were obtained using a Bruker micro-TOF II focus spectrometer (ESI). IR spectra were recorded on a spectrometer using KBr discs. Column chromatography was performed using EM Silica gel 60 (300-400 mesh). All melting points were uncorrected.

2. Synthesis and Reaction

2-(1-Substituted vinyl) anilines were synthesized according to the reported methods.

Substrates 1a-1h, 1l, 1n-1o were sy,1s-1v nthesized according to Mothed A:[1]

Method A:

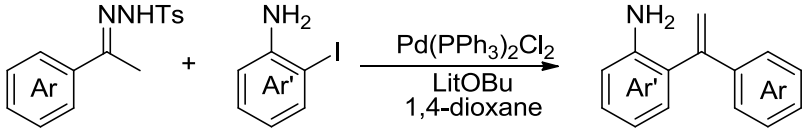


Under air, anilines (9.0 mmol), phenylacetylenes (18.0 mmol) and 1.7 g of montmorillonite KSF were added to 150 mL of xylene in a round-bottomed flask. The flask was stirred and heated in an oil bath to 140 ℃, under a reflux condenser (running cold water as the coolant) that was connected at its top to a paraffin bubbler. After 18 h, the reaction mixture was cooled to room temperature and purified directly by flash chromatography with a gradient of hexane to hexane/ethyl acetate (V_1/V_2 =

60/1), followed by distillation under vacuum to afford corresponding 2-(1-arylvinyl) anilines.

Substrates 1i-1k, 1p were synthesized according to Method B: [2]

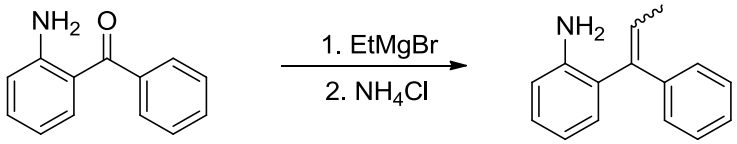
Method B:



Under N_2, a well stirred mixture of tosylhydrazone (7.5 mmol), 2-iodoaniline (5 mmol), $Pd(PPh_3)_2Cl_2$ (2.5 mol%) in 1,4-dioxane (56 mL) was heated at 100 ℃. To this hot clear solution was added *t*-BuOLi (1.6 g, 20 mmol), and the reaction was stirred at 100 ℃ for 3 h. Then, the reaction mixture was cooled to room temperature and diluted with EtOAc (60 mL) and passed through a short Celite pad; the solvent was evaporated under reduced pressure, and purified on a silica gel column (hexane/EtOAc, 90:1) to afford corresponding products.

Substrate 1m were synthesized according to Mothed C:[3]

Method C:

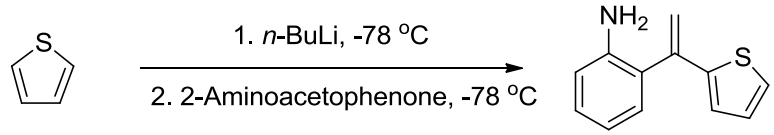


To a solution of 2-aminobenzophenone (1.97 g, 10 mmol) in THF (50 mL), EtMgBr (0.87 M in THF, 31 mmol) was added at -78 ^{o}C. After being stirred at room temperature for 30 min, the reaction mixture was quenched by saturated aqueous solution of NH_4Cl and filtered through Celite pad. After the filtrate was extracted with EtOAc (50 mL×3), the organic layer was washed with brine, dried over anhydrous $MgSO_4$, and evaporated. The residue was purified with silica gel column

chromatography (hexane/EtOAc=10:1) to give 1-(2-aminophenyl)-1-phenyl-1-propanol (2.01 g, 8.8 mmol, 88% yield) as yellow crystals. The above carbinol (1.93 g, 8.5 mmol) was treated with solid NH_4Cl (1.36 g, 25.5 mmol) for 20 min at 180 ^oC. The reaction mixture was cooled to ambient temperature and purified with silica gel column chromatography (hexane/EtOAc=40:1) to give the *E/Z* mixture of 2-(1-phenyl-1-propenyl)aniline (1.30 g, 6.2 mmol, 73% yield, *E*/*Z*=1:1). The *E/Z* mixture was separated by MPLC (hexane/EtOAc=20:1) to give (*Z*)-**1e** (593 mg, 2.83 mmol) as the less polar isomer and (*E*)-**1e** (599 mg, 2.86 mmol) as the more polar isomer.

Substrate 1q were synthesized according to Mothed D:[4]

Method D:

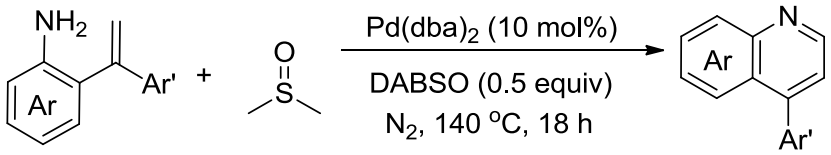


To a solution of thiophene (1.0 mL, 13.2 mmol) in THF (20 mL) was added *n*-BuLi (5.5 mL, 2.4 M in hexanes, 13.5 mmol) dropwise at −78 °C, and the mixture was stirred at −78 ℃ for 20 min and at 0 ℃ for 2h. Then the mixture was cooled to −78 ℃, and 2-Aminoacetophenone (0.36 mL, 3.0 mmol) in THF (4 mL) was added dropwise. After 15 min, the cooling bath was removed, and the mixture was stirred overnight. Subsequently, a saturated NH_4Cl solution was added, and the aqueous layer was extracted with EtOAc (2×10 mL).The combined extracts were washed with saturated NaCl solution, dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The residue was purified by column chromatography on SiO_2 to give 1-(2-aminophenyl)-1- (thiophen-2-yl)ethanol. **1q** was prepared following the general procedure as a brown oil (223 mg, 37% yield). R_f = 0.36 (20% EtOAc/petroleum ether).

Preparation of bis(sulphur dioxide) 1,4-diazabicyclo[2.2.2]octane, (DABCO) $(SO_2)_2$:[5]

According to method reported by Santos and Mello, a 50 mL of round bottom flask was fitted with a condenser, attached to a Dreschel bottle bubbler system and flushed with argon for 10 min. 1,4-Diazabicyclo[2.2.2]octane (DABCO) (2.00 g, 16.4 mmol) was added to the flask and the system flushed with argon for a further 5 min. Sulfur dioxide gas was introduced into the system (approx.1 bubble/sec) for 5 min. The reaction flask was cooled to -20 ^oC and the condenser to -78 ^oC and the sulfur dioxide was allowed to condense dropwise onto the DABCO with stirring until the solid was completely covered with liquid sulfur dioxide (approx. 20 mL). The sulfur dioxide flow was stopped and the flask allowed to warm up to -10 ^oC and left stirring at reflux for 1 h. The condenser and bubbler were removed and the excess liquid sulfur dioxide allowed to evaporating at room temperature under a flow of argon to reveal the complex as a white solid (4.20 g, 98%).

Annulation of 2-(1-Substituted vinyl) Anilines

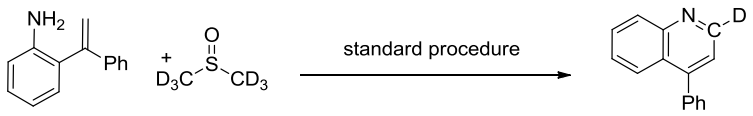


Scheme 1. Annulation of 2-(1-Substituted vinyl) Anilines

Under N_2, a 20 mL of Schlenk tube equipped with a stir bar was charged with 2-(1-arylvinyl) anilines (0.1 mmol), DABSO (0.5 mmol), $Pd(dba)_2$ (0.01 mmol), DMSO (2.0 mL). The tube was sealed with a Teflon lined cap. The reaction mixture was stirred at 140 ℃ for 18 h in oil bath. After the completion of the reaction, 6 mL of saturated brines was added to the mixture, and extracted with ethyl acetate (8 mL × 3) with ethyl acetate. The combined organic extracts were dried over anhydrous Na_2SO_4. Subsequently, the solvent was filtered and evaporated under reduced

pressure, and the residue was purified by flash column chromatography on silica gel with petroleum ether-EtOAc (V_1/V_2, 5:1) as the eluent to give the desired products.

3. Mechanism Studies



Under N_2, a 20 mL of Schlenk tube equipped with a stir bar was charged with 2-(1-arylvinyl) anilines (0.1 mmol), DABSO (0.5 mmol), $Pd(dba)_2$ (0.01 mmol), D_6-DMSO (2.0 mL). The tube was sealed with a Teflon lined cap. The reaction mixture was stirred at 140 ℃ for 18 h in oil bath. After the completion of the reaction, 6 mL of saturated brines was added to the mixture, and extracted with ethyl acetate (8 mL × 3) with ethyl acetate. The combined organic extracts were dried over anhydrous Na_2SO_4. Subsequently, the solvent was filtered and evaporated under reduced pressure, and the residue was purified by flash column chromatography on silica gel with petroleum ether-EtOAc (V_1/V_2, 5:1) as the eluent to give the desired product. The product was analyzed using GC-MS spectrometer (Figure S1) and ^{1}H NMR (Figure S2)

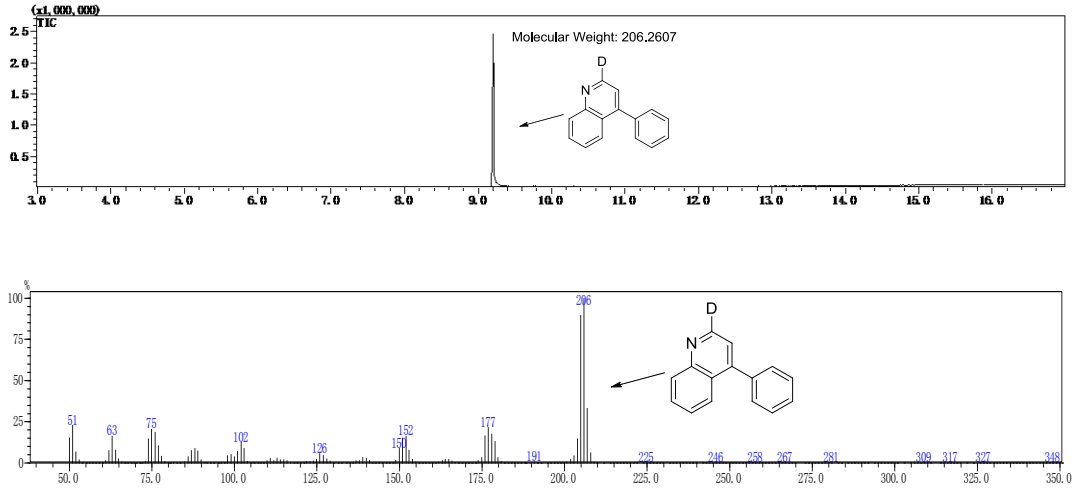


Fig S1 Detection of 2-D-4-phenyl quinoline by GC-MS

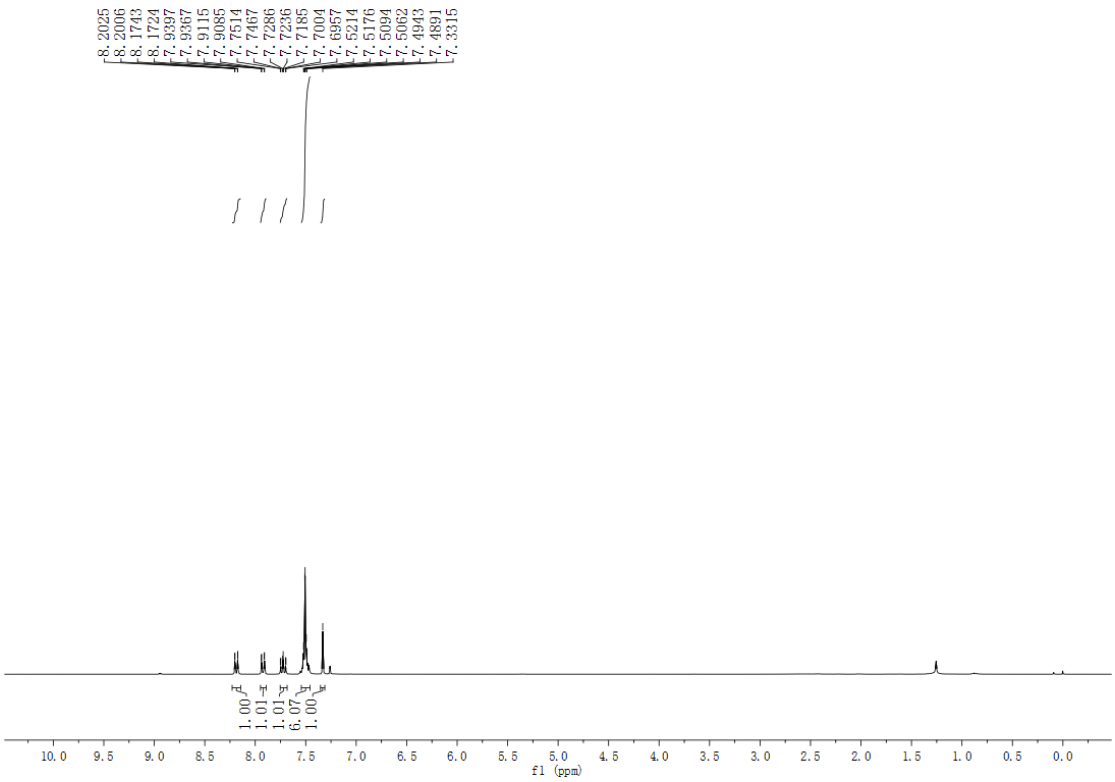
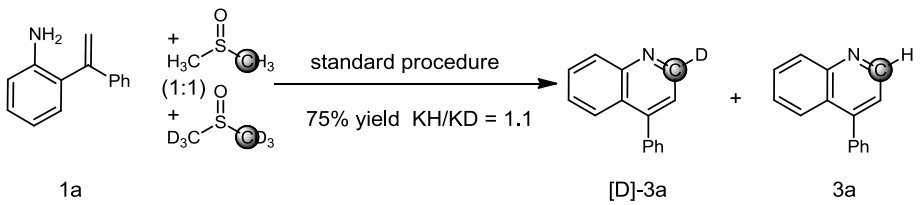


Fig S2 ^{1}H NMR spectra of 2-D-4-phenyl quinoline

The KIE Experiment

Under N_2, a 20 mL of Schlenk tube equipped with a stir bar was charged with 2-(1-phenylvinyl) anilines (0.1 mmol), DABSO (0.5 mmol), $Pd(dba)_2$ (0.01 mmol), DMSO (1.0 mL), D_6-DMSO (1.0 mL). The tube was sealed with a Teflon lined cap. The reaction mixture was stirred at 140 ℃ for 18 h in oil bath. The mixture of the product was analyzed by ^{1}H NMR (Figure S3). The result was listed (Scheme S1).

Scheme S1 The KIE Experiment



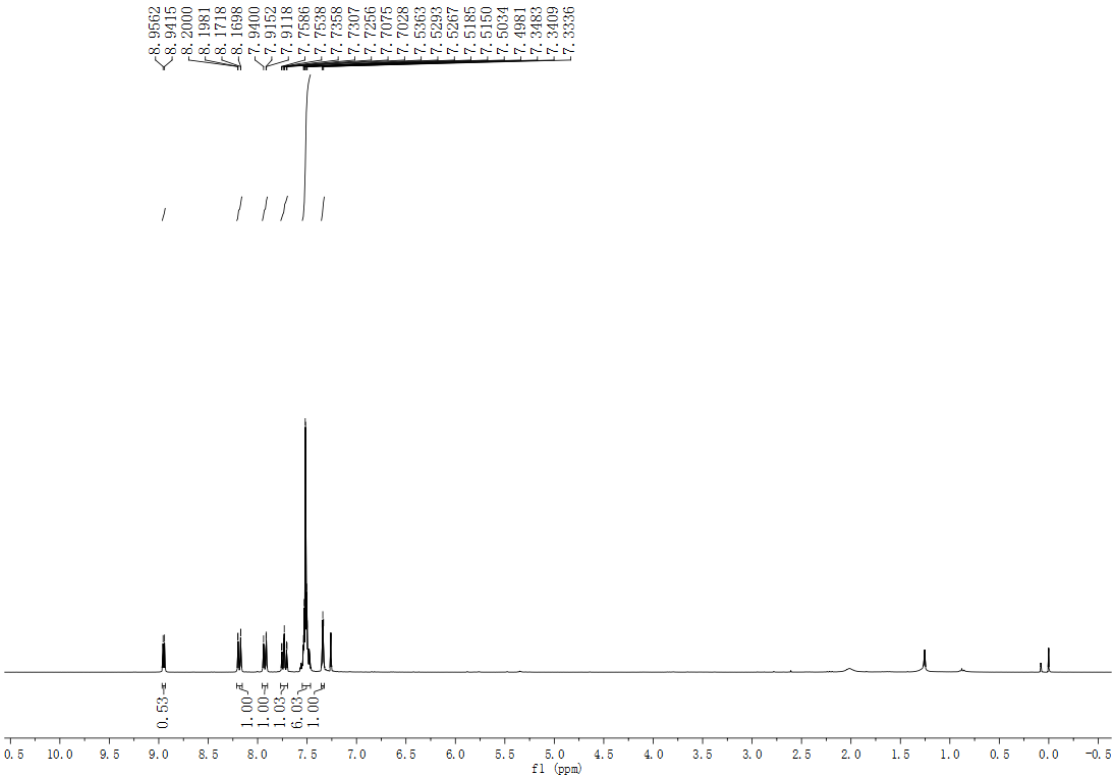


Fig S2 ^{1}H NMR spectra of 3a and [D]-3a

Detection of $CH_3SCH_2SCH_3$

As shown in Fig S3, $CH_3SCH_2SCH_3$ was detected by GC-MS.

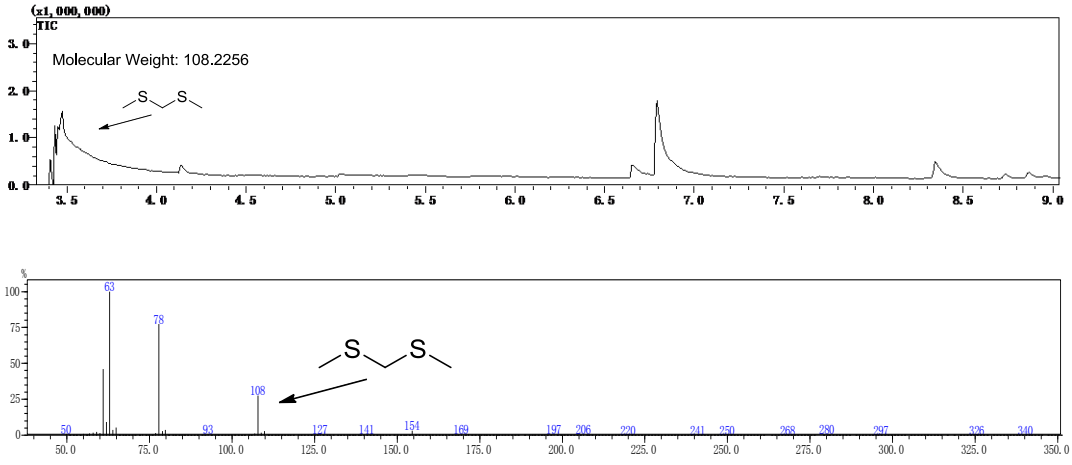
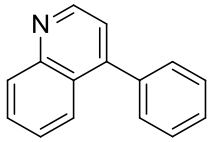


Fig S3 Detection of $CH_3SCH_2SCH_3$ by GC-MS

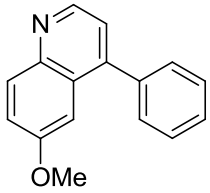
4. Characterization Data for the Products

4-phenylquinoline (3a):[6, 7]



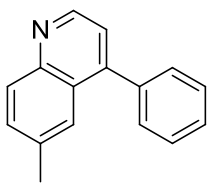
Preparative TLC (ethyl acetate: petroleum ether, 1: 5) give **3a** (16.3 mg, 80% yield) as a yellow oil. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 8.94 (d, J = 4.4 Hz, 1H), 8.20-8.17 (m, 1H), 7.94-7.91 (m, 1H), 7.76-7.70 (m, 1H), 7.56-7.47 (m, 6H), 7.34 (d, J = 4.4 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 149.9, 148.6, 148.5, 138.0, 129.8, 129.5, 129.3, 128.6, 128.4, 126.8, 126.6, 125.9, 121.3. MS (*m/z*): 205.2 $[M]^+$

6-methoxy-4-phenylquinoline (3b):[7]



Preparative TLC (ethyl acetate: petroleum ether, 1: 5) give **3b** (14.8 mg, 63% yield) as a yellow oil. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 8.79 (d, J = 4.4 Hz, 1H), 8.08 (d, J = 9.2 Hz, 1H), 7.54-7.49 (m, 5H), 7.40-7.36 (m, 1H), 7.28 (d, J = 4.4 Hz, 1H), 7.19 (d, J = 2.8 Hz, 1H), 3.78 (s, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 157.8, 147.4, 147.1, 144.7, 138.3, 131.1, 129.3, 128.6, 128.3, 127.7, 121.8, 121.7, 103.6, 55.4. MS (*m/z*): 235.2 $[M]^+$

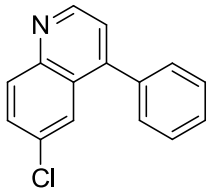
6-methyl-4-phenylquinoline (3c):[7]



Preparative TLC (ethyl acetate: petroleum ether, 1: 5) give **3c** (14.7 mg, 67% yield) as a yellow oil. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 8.87 (d, J = 4.4 Hz, 1H), 8.07 (d, J = 8.6

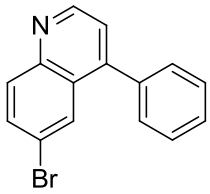
Hz, 1H), 7.66 (t, *J* = 0.8 Hz, 1H), 7.58-7.48 (m, 6H), 7.29 (d, *J* = 4.4 Hz, 1H), 2.47 (s, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 149.0, 147.7, 147.2, 138.1, 136.5, 131.5, 129.4, 128.5, 128.2, 126.6, 124.5, 121.3, 21.8. MS (*m/z*): 219.2 $[M]^+$

6-chloro-4-phenylquinoline (3d):[6]



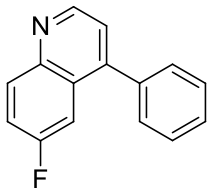
Preparative TLC (ethyl acetate: petroleum ether, 1: 5) give **3d** (17.6 mg, 74% yield) as a yellow solid. m.p. 71-72 ^{o}C; ^{1}H NMR ($CDCl_3$, 300 MHz): *δ* 8.92 (d, *J* = 4.4 Hz, 1H), 8.10 (d, *J* = 9.0 Hz, 1H), 7.88 (d, *J* = 2.3 Hz, 1H), 7.66-7.63 (m, 1H), 7.57-7.45 (m, 5H), 7.34 (d, *J* = 4.4 Hz, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 150.0, 147.7, 147.0, 137.2, 132.6, 131.4, 130.2, 129.3, 128.7, 128.7, 127.4, 124.6, 122.0. MS (*m/z*): 239.6 $[M]^+$

6-bromo-4-phenylquinoline (3e):[8]



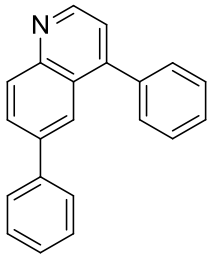
Preparative TLC (ethyl acetate: petroleum ether, 1: 5) give **3e** (21.3 mg, 75% yield) as a brown solid. m.p. 76-77 ^{o}C; ^{1}H NMR ($CDCl_3$, 300 MHz): *δ* 8.94 (d, *J* = 4.4 Hz, 1H), 8.05 (t, *J* = 4.6 Hz, 2H), 7.81-7.77 (m, 1H), 7.56-7.46 (m, 5H), 7.35 (d, *J* = 4.4 Hz, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 150.2, 147.7, 147.2, 137.2, 132.8, 131.6, 129.4, 128.8, 128.7, 128.0, 122.0, 120.8. MS (*m/z*): 284.1 $[M]^+$

6-fluoro-4-phenylquinoline (3f):[7]



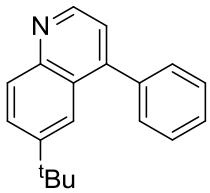
Preparative TLC (ethyl acetate: petroleum ether, 1: 5) give **3f** (17.2 mg, 77% yield) as a yellow oil. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 8.91 (d, J = 4.4 Hz, 1H), 8.20-8.15 (m, 1H), 7.54-7.47 (m, 7H), 7.36-7.34 (m, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 160.6 (d, $J_{C\text{-}F}$ = 246 Hz), 149.2 (d, $J_{C\text{-}F}$ = 3 Hz), 148.0 (d, $J_{C\text{-}F}$ = 6 Hz), 145.8, 137.5, 132.3 (d, $J_{C\text{-}F}$ = 9 Hz), 129.3, 128.7, 128.6, 127.5 (d, $J_{C\text{-}F}$ = 10 Hz), 121.8, 119.5 (d, $J_{C\text{-}F}$ = 26 Hz), 109.2 (d, $J_{C\text{-}F}$ = 23 Hz). MS (*m/z*): 223.2 $[M]^+$

4,6-diphenylquinoline (3g):[9]



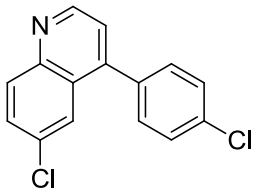
Preparative TLC (ethyl acetate: petroleum ether, 1: 5) give **3g** (20.9 mg, 74% yield) as a yellow solid. m.p. 144-146 ^{o}C; ^{1}H NMR ($CDCl_3$, 300 MHz): δ 8.95 (d, J = 4.4 Hz, 1H), 8.28 (d, J = 8.7 Hz, 1H), 8.14 (d, J = 2.0 Hz, 1H), 8.02-7.98 (m, 1H), 7.63-.7.60 (m, 2H), 7.56-7.50 (m, 5H), 7.47-7.42 (m, 2H), 7.39-7.34 (m, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 149.8, 148.5, 148.0, 140.4, 139.3, 137.8, 130. 2, 129.4, 129.0, 128.8, 128.6, 128.4, 127.6, 127.4, 126.8, 123.5, 121.7. MS (*m/z*): 281.3 $[M]^+$

6-(*tert*-butyl)-4-phenylquinoline (3h)



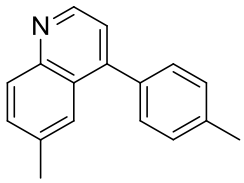
Preparative TLC (ethyl acetate: petroleum ether, 1: 5) give **3h** (21.0 mg, 81% yield) as a yellow oil. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 8.88 (d, J = 4.4 Hz, 1H), 8.13 (d, J = 8.9 Hz, 1H), 7.89 (d, J = 2.1 Hz, 1H), 7.85-7.81 (m, 1H), 7.54-7.50 (m, 5H), 7.30 (d, J = 4.4 Hz, 1H), 1.34 (s, 9H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 149.3, 149.3, 148.2, 147.2, 147.2, 138.1, 129.4, 129.3, 128.5, 128.3, 128.2, 121.3, 120.6, 35.0, 31.1; HRMS (ESI) *m/z* calcd for $C_{19}H_{20}N$ $(M+H)^+$ 262.1590, found 262.1592; IR (KBr) 3022, 2950, 2924, 1655, 1594, 1582, 1488, 1352, 833, 819 cm^{-1}.

6-chloro-4-(4-chlorophenyl)quinoline (3i)



Preparative TLC (ethyl acetate: petroleum ether, 1: 5) give **3i** (17.2 mg, 64% yield) as a white solid. m.p. 124-125 ^{o}C; ^{1}H NMR ($CDCl_3$, 300 MHz): δ 8.92 (d, J = 4.4 Hz, 1H), 8.10 (d, J = 9.0 Hz, 1H), 7.81 (d, J = 2.3 Hz, 1H), 7.68-7.64 (m, 1H), 7.53-7.50 (m, 2H), 7.42-7.39 (m, 2H), 7.31 (d, J = 4.4 Hz, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 150.1, 147.0, 146.4, 135.6, 135.0, 132.9, 131.6, 130.7, 130.4, 129.1, 127.2, 124.3, 122.0; HRMS (ESI) *m/z* calcd for $C_{15}H_{10}Cl_2N$ $(M+H)^+$ 274.9185, found 274.9183; IR (KBr) 3020, 2922, 2851, 1655, 1594, 1582, 1488, 1352, 830, 819 cm^{-1}.

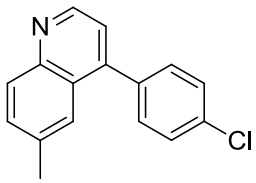
6-methyl-4-(*p*-tolyl)quinoline (3j)



Preparative TLC (ethyl acetate: petroleum ether, 1: 5) give **3j** (15.5 mg, 67% yield) as a yellow oil. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 8.86 (d, J = 4.4 Hz, 1H), 8.07 (d, J = 8.6 Hz, 1H), 7.70 (s, 1H), 7.57-7.53 (m, 1H), 7.42-7.33 (m, 4H), 7.28 (d, J = 4.4 Hz, 1H), 2.47 (d, J = 1.8 Hz, 6H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 149.0, 147.9, 147.2, 138.2,

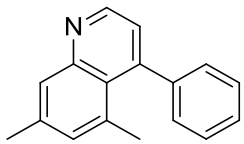
136.5, 135.3, 131.6, 129.4, 129.4, 129.3, 126.8, 124.6, 121.4, 21.8, 21.3; HRMS (ESI) *m/z* calcd for $C_{17}H_{16}N$ $(M+H)^+$ 234.1277, found 234.1278; IR (KBr) 3023, 2920, 2851, 1686, 1584, 1502, 1379, 1364, 819 cm^{-1}.

4-(4-chlorophenyl)-6-methylquinoline (3k)



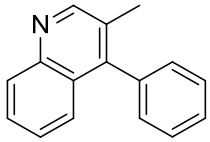
Preparative TLC (ethyl acetate: petroleum ether, 1: 5) give **3k** (17.9 mg, 71% yield) as a yellow solid. m.p. 122-124 ^oC; ^1H NMR ($CDCl_3$, 300 MHz): δ 8.86 (d, J = 4.4 Hz, 1H), 8.07 (d, J = 8.5 Hz, 1H), 7.59-7.50 (m, 4H), 7.44-7.41 (m, 2H), 7.25 (d, J = 4.5 Hz, 1H), 2.47 (s, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 148.9, 147.1, 146.5, 136.8, 136.5, 134.5, 131.7, 130.8, 129.5, 128.8, 126.4, 124.2, 121.3, 21.8; HRMS (ESI) *m/z* calcd for $C_{16}H_{13}ClN$ $(M+H)^+$ 254.0731, found 254.0729; IR (KBr) 3030, 2920, 1654, 1570, 1508, 1378, 1091, 821 cm^{-1}.

5,7-dimethyl-4-phenylquinoline (3l):[10]



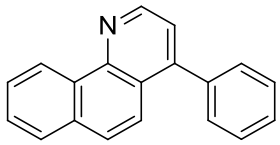
Preparative TLC (ethyl acetate: petroleum ether, 1: 5) give **3l** (7.7 mg, 36% yield) as a yellow oil. ^1H NMR ($CDCl_3$, 300 MHz): δ 8.80 (d, J = 4.4 Hz, 1H), 7.83 (s, 1H), 7.42 (t, J = 3.2 Hz ,3H), 7.32-7.29 (m, 2H), 7.13 (d, J = 4.2 Hz, 2H), 2.51 (s,3H), 1.98 (s, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 150.0, 148.7, 148.6, 142.5, 138.9, 135.2, 132.1, 128.7, 127.8, 127.6, 127.6, 124.2, 122.7, 24.3, 21.4. MS (*m/z*): 233.3 $[M]^+$

3-methyl-4-phenylquinoline (3m):[6]



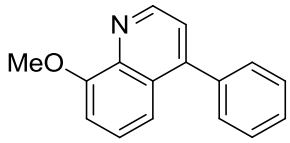
Preparative TLC (ethyl acetate: petroleum ether, 1: 5) give **3m** (6.6 mg, 30% yield) as a pale yellow solid. m.p. 87-88 ^{o}C; ^{1}H NMR ($CDCl_3$, 300 MHz): δ 8.85 (s, 1H), 8.12 (d, J = 8.4 Hz, 1H), 7.66-7.61 (m, 1H), 7.56-7.37 (m, 5H), 7.28-7.25 (m, 2H), 2.27 (s, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 152.6, 146.8, 146.2, 136.8, 129.3, 129.2, 128.6, 128.2, 128.0, 127.9, 127.5, 126.4, 125.8, 17.6. MS (*m/z*): 219.2 $[M]^+$

4-phenylbenzo[h]quinoline (3n):[11]



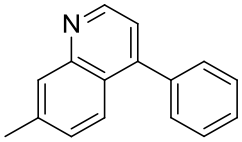
Preparative TLC (ethyl acetate: petroleum ether, 1: 5) give **3n** (23.5 mg, 92% yield) as a purple oil. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 9.40-9.36 (m, 1H), 9.03 (d, J = 4.6 Hz, 1H), 7.92-7.89 (m, 1H), 7.83-7.69 (m, 4H), 7.57-7.46 (m, 5H), 7.47 (d, J = 10.2 Hz, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 148.3, 148.2, 146.9, 138.4, 133.3, 131.6, 129.6, 128.5, 128.3, 128.3, 127.6, 127.6, 127.1, 124.8, 124.4, 123.0, 122.3. MS (*m/z*): 255.3 $[M]^+$

8-methoxy-4-phenylquinoline (3o):[12]



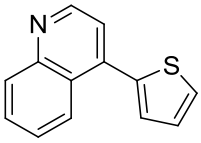
Preparative TLC (ethyl acetate: petroleum ether, 1: 5) give **3o** (22.1 mg, 94% yield) as a yellow solid. m.p. 104-105 ^{o}C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.94 (d, J = 4.2 Hz, 1H), 7.52-7.34 (m, 8H), 7.05 (d, J = 7.5 Hz, 1H), 4.10 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ155.5, 148.6, 148.3, 140.6, 138.2, 129.4, 128.4, 128.3, 127.8, 126.5, 121.9, 117.5, 107.3 , 56.0. MS (*m/z*): 235.2 $[M]^+$

7-methyl-4-phenylquinoline (3p):[7]



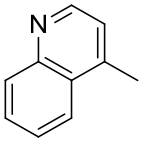
Preparative TLC (ethyl acetate: petroleum ether, 1: 5) give **3p** (11.5 mg, 53% yield) as a yellow oil. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.90 (d, *J* = 4.1 Hz, 1H), 7.95 (s, 1H), 7.81 (d, *J* = 8.6 Hz, 1H), 7.54-7.47 (m, 5H), 7.33 (d, *J* = 8.6 Hz, 1H), 7.28 (s, 1H), 2.58 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 149.9, 148.8, 148.2, 139.6, 138.1, 129.5, 128.86, 128.7, 128.5, 128.3, 125.5, 124.7, 120.6 , 21.7. MS (*m/z*): 219.2 $[M]^+$

4-(thiophen-2-yl)quinoline (3q):[13]



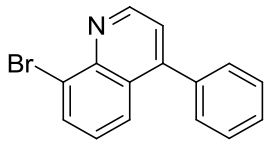
Preparative TLC (ethyl acetate: petroleum ether, 1: 5) give **3q** (12.5 mg, 59% yield) as a brown oil. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.93 (d, *J* = 3.0 Hz, 1H), 8.32 (d, *J* = 8.4 Hz, 1H), 8.19 (d, *J* = 8.4 Hz, 1H), 7.77 (t, *J* = 7.5 Hz, 1H), 7.62-7.55 (m, 2H), 7.48 (d, *J* = 2.9 Hz, 1H), 7.42 (s, 1H), 7.28 (s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ149.8, 148.8, 140.8, 138.8, 123.0, 129.5, 128.6, 127.8, 127.3, 127.0, 126.4, 125.5, 121.7. MS (*m/z*): 211.2 $[M]^+$

4-methylquinoline (3r):[14]



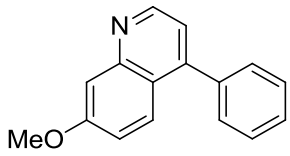
Preparative TLC (ethyl acetate: petroleum ether, 1: 5) give **3r** (4.1 mg, 28% yield) as a colorless oil. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 8.74 (d, *J* = 4.4 Hz, 1H), 8.10-8.07 (m, 1H), 7.94 (d, *J* = 8.4 Hz, 1H), 7.70-7.64 (m, 1H), 7.52 (t, *J* = 7.6 Hz, 1H), 7.18 (d, *J* = 4.4 Hz, 1H), 2.65 (s, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ150.0, 147.8, 144.2, 129.8, 129.0, 128.1, 126.2, 123.7, 121.7, 18.5. MS (*m/z*): 143.1 $[M]^+$

8-bromo-4-phenylquinoline (3s):[15]



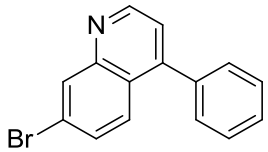
Preparative TLC (ethyl acetate: petroleum ether, 1: 5) give **3s** (20.2 mg, 71% yield) as a brown oil. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 8.92 (d, *J* = 4.4 Hz, 1H), 8.35 (d, *J* = 2.0 Hz, 1H), 7.78 (d, *J* = 9.0 Hz, 1H), 7.58-7.45 (m, 6H), 7.34 (d, *J* = 4.4 Hz, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 150.9, 149.3, 148.6, 137.3, 132.0, 130.0, 129.4, 128.7, 127.3, 125.4, 123.5, 121.5. MS (*m/z*): 284.1 $[M]^+$

7-methoxy-4-phenylquinoline (3t):[10]



Preparative TLC (ethyl acetate: petroleum ether, 1: 5) give **3t** (14.3 mg, 61% yield) as a yellow oil. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.85 (d, *J* = 4.2 Hz, 1H), 7.81 (d, *J* = 9.2 Hz, 1H), 7.54-7.48 (m, 6H), 7.21 (d, *J* = 4.4 Hz, 1H), 7.17-7.14 (m, 1H), 3.98 (s, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ160.5, 150.4, 150.2, 148.4, 138.2, 129.5, 128.5, 128.4, 127.0, 121.8, 119.7, 119.4, 107.6, 55.5. MS (*m/z*): 235.2 $[M]^+$

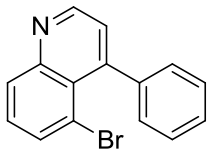
7-bromo-4-phenylquinoline (3u):



Preparative TLC (ethyl acetate: petroleum ether, 1: 5) give **3u** (20.5 mg, 73% yield) as a yellow oil. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 8.90 (d, *J* = 4.4 Hz, 1H), 8.19-8.16 (m, 1H), 7.83-7.80 (m, 1H), 7.56-7.50 (m, 1H), 7.45-7.40 (m, 3H), 7.34-7.30 (m, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ150.0, 149.4, 149.0, 140.1, 133.9, 130.4, 129.4, 129.3,

127.9, 127.7, 125.6, 124.8, 119.1; HRMS (ESI) *m/z* calcd for $C_{15}H_{11}BrN$ $(M+H)^+$ 284.0069, found 284.0066; IR (KBr) 3021, 2928, 2854, 1655, 1594, 1582, 1473, 1348, 1037 cm^{-1}.

5-bromo-4-phenylquinoline (3v):[10]



Preparative TLC (ethyl acetate: petroleum ether, 1: 5) give **3v** (24.7 mg, 87% yield) as a yellow oil. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 8.93 (d, *J* = 4.4 Hz, 1H), 8.35 (d, *J* = 2.0 Hz, 1H), 7.78 (d, *J* = 9.0 Hz, 1H), 7.59-7.46 (m, 6H), 7.35(d, *J* = 4.4 Hz, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ150.9, 149.3, 148.6, 137.4, 132.0, 130.1, 129.4, 128.7 (2), 127.4, 125.4, 123.5, 121.6. MS (*m/z*): 284.1 $[M]^+$

5. Reference

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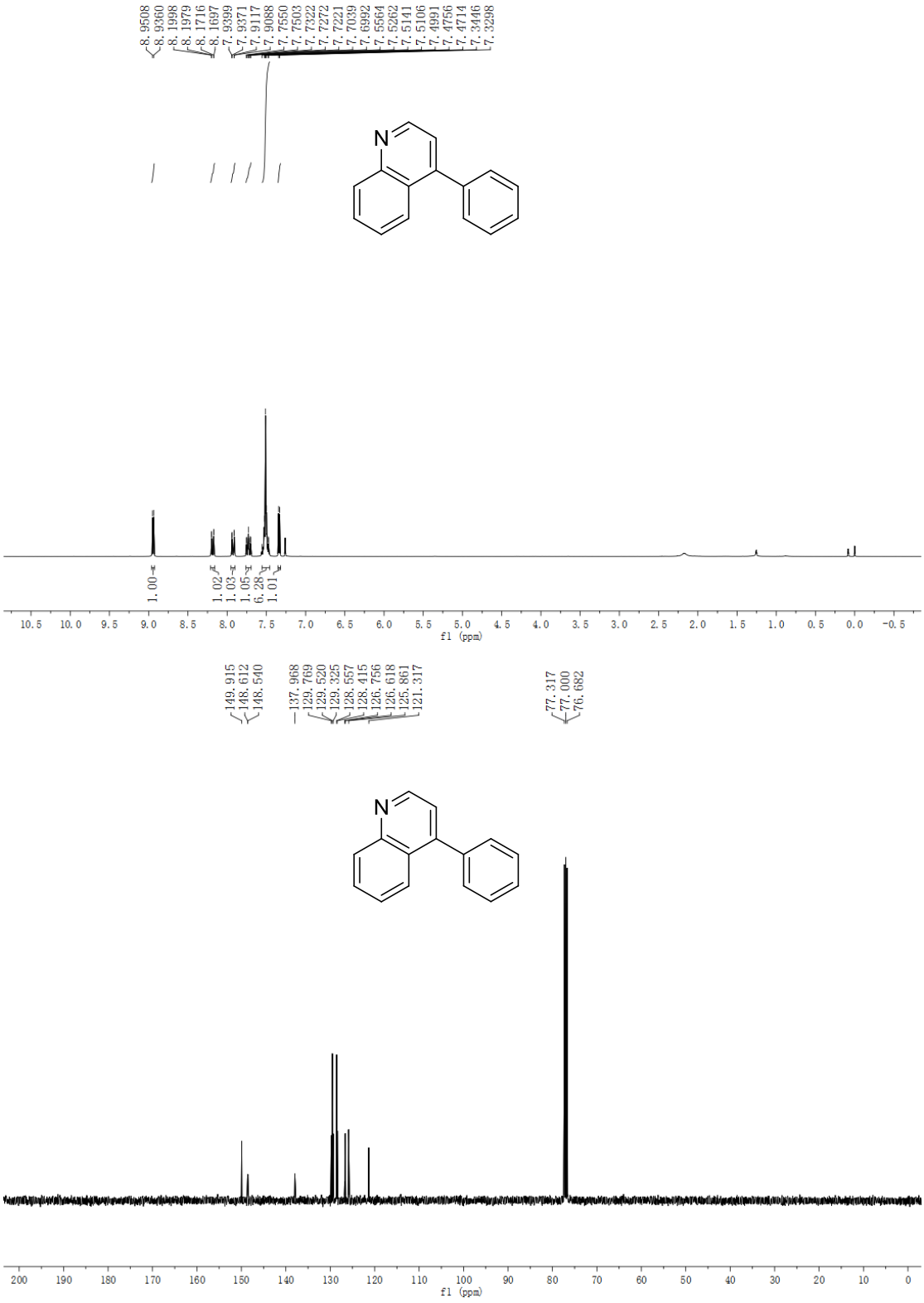
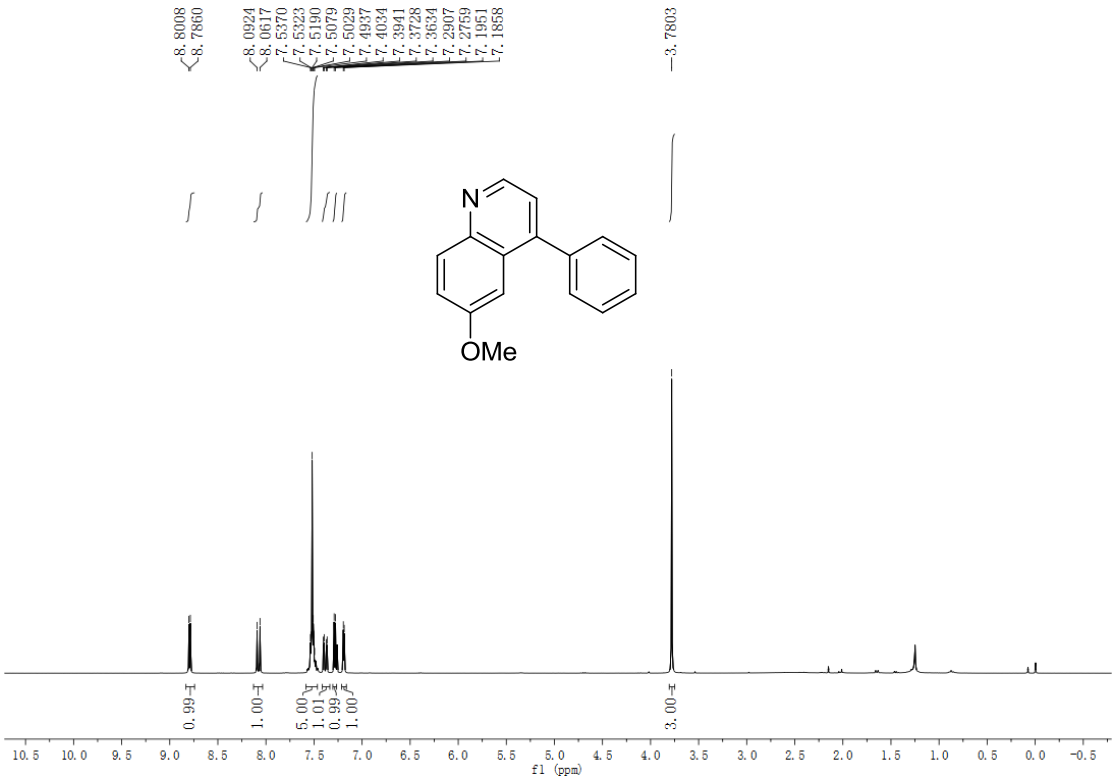
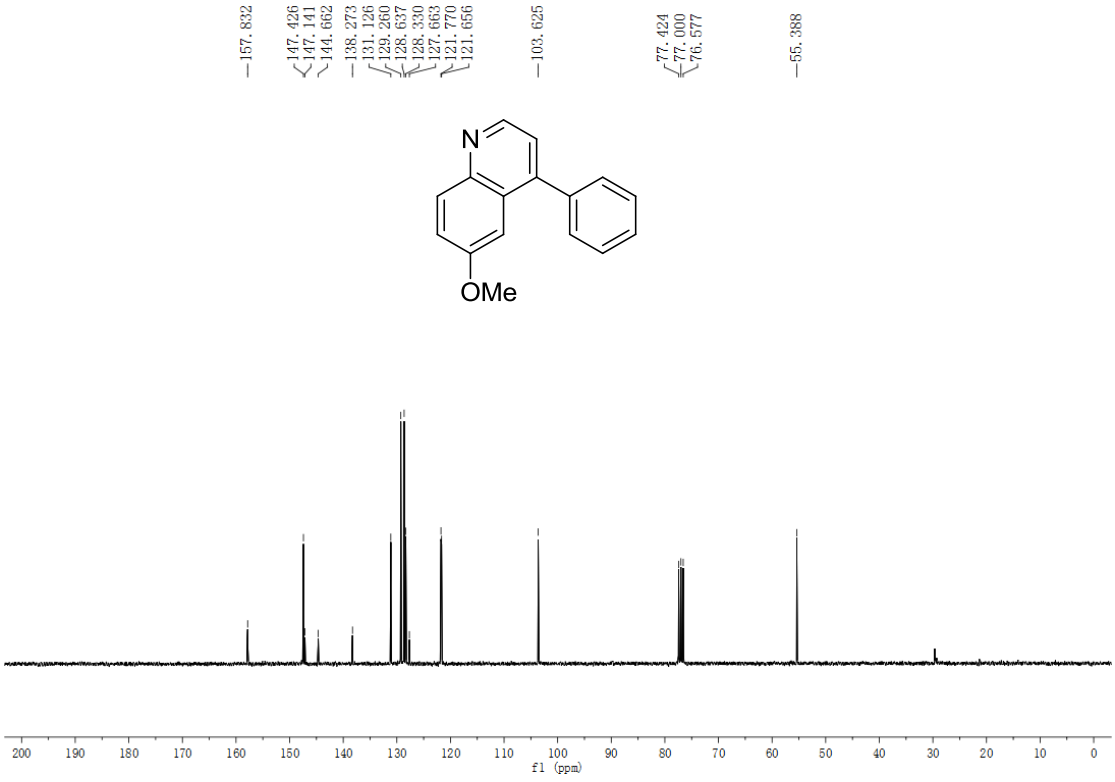
6. Copies of the ^{1}H NMR, ^{13}C NMR Spectra

4-phenylquinoline (3a)

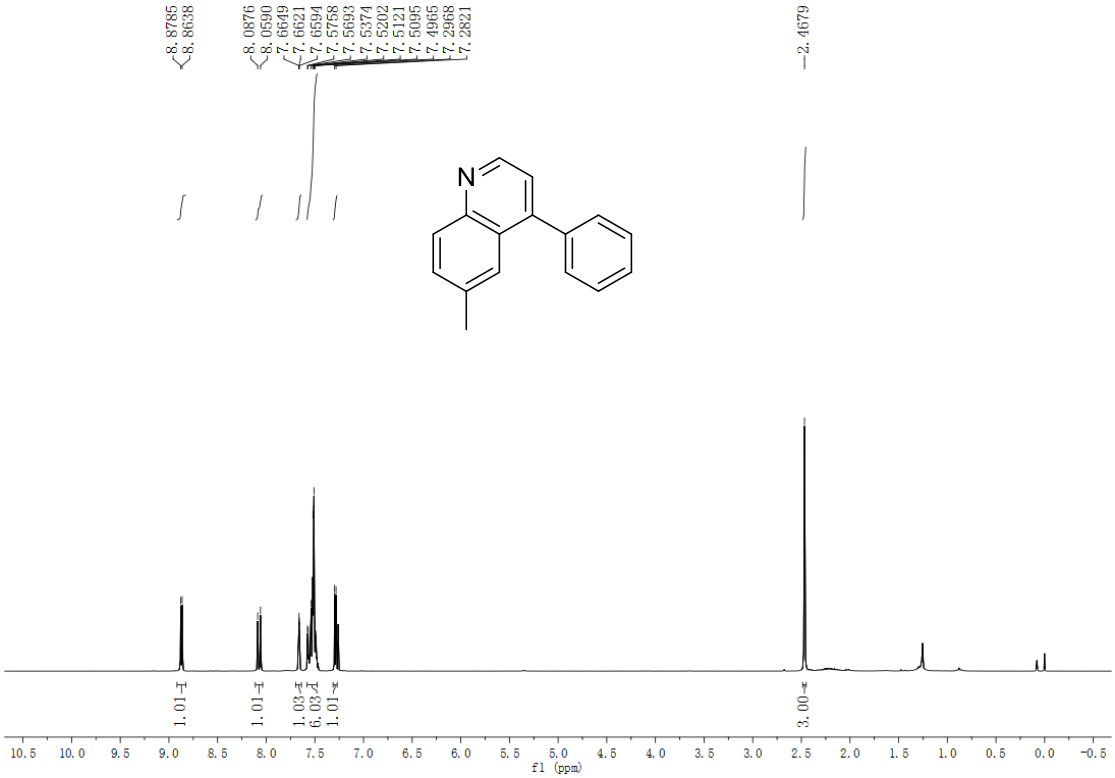


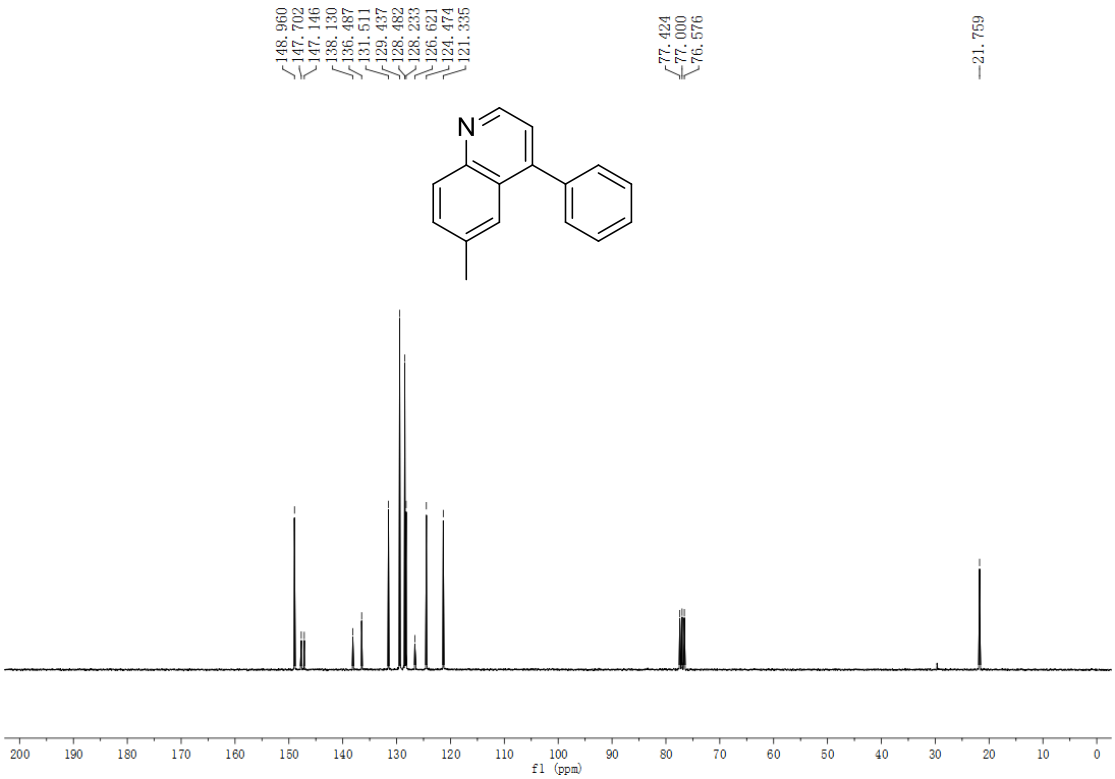
6-methoxy-4-phenylquinoline (3b)



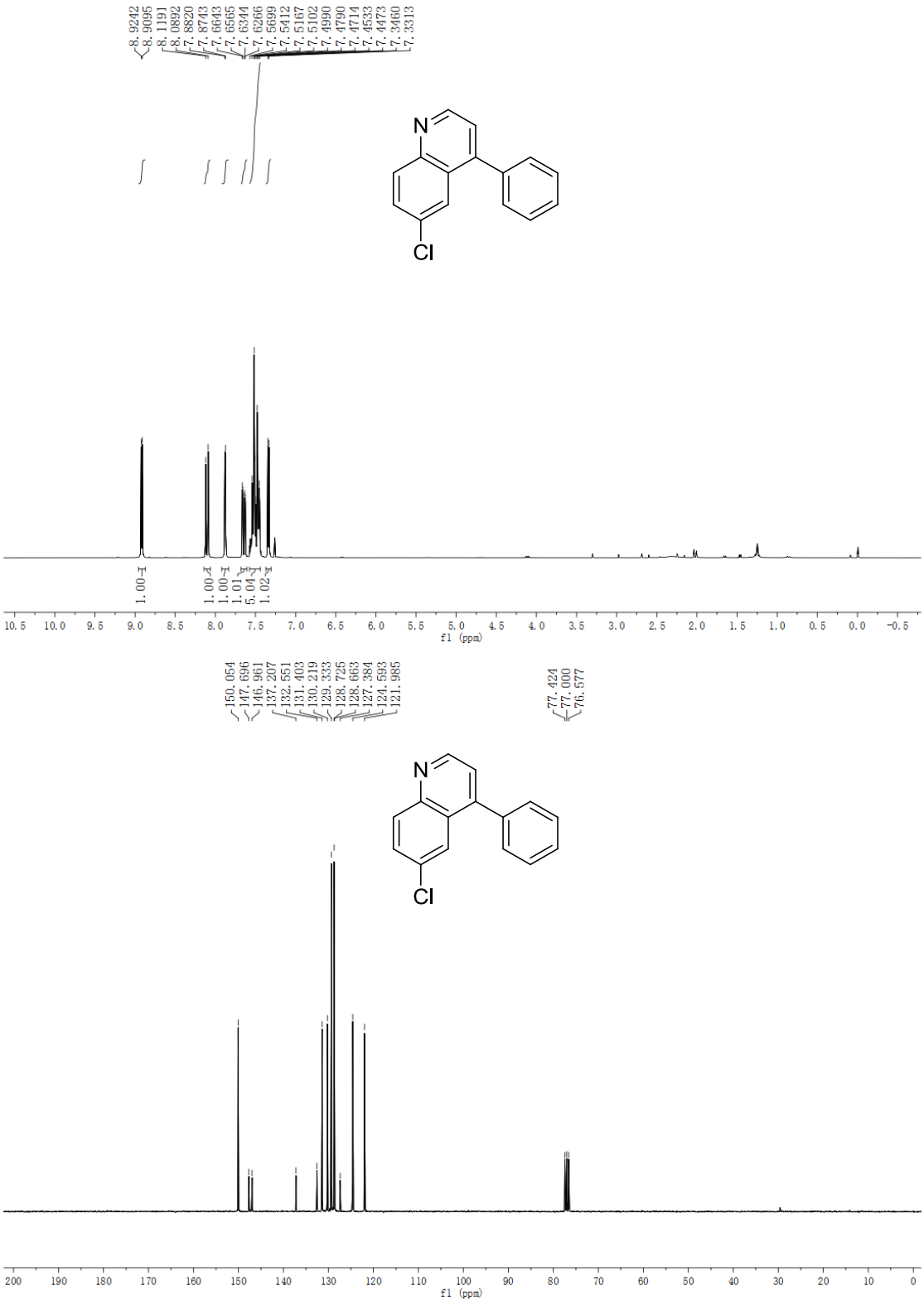


6-methyl-4-phenylquinoline (3c)

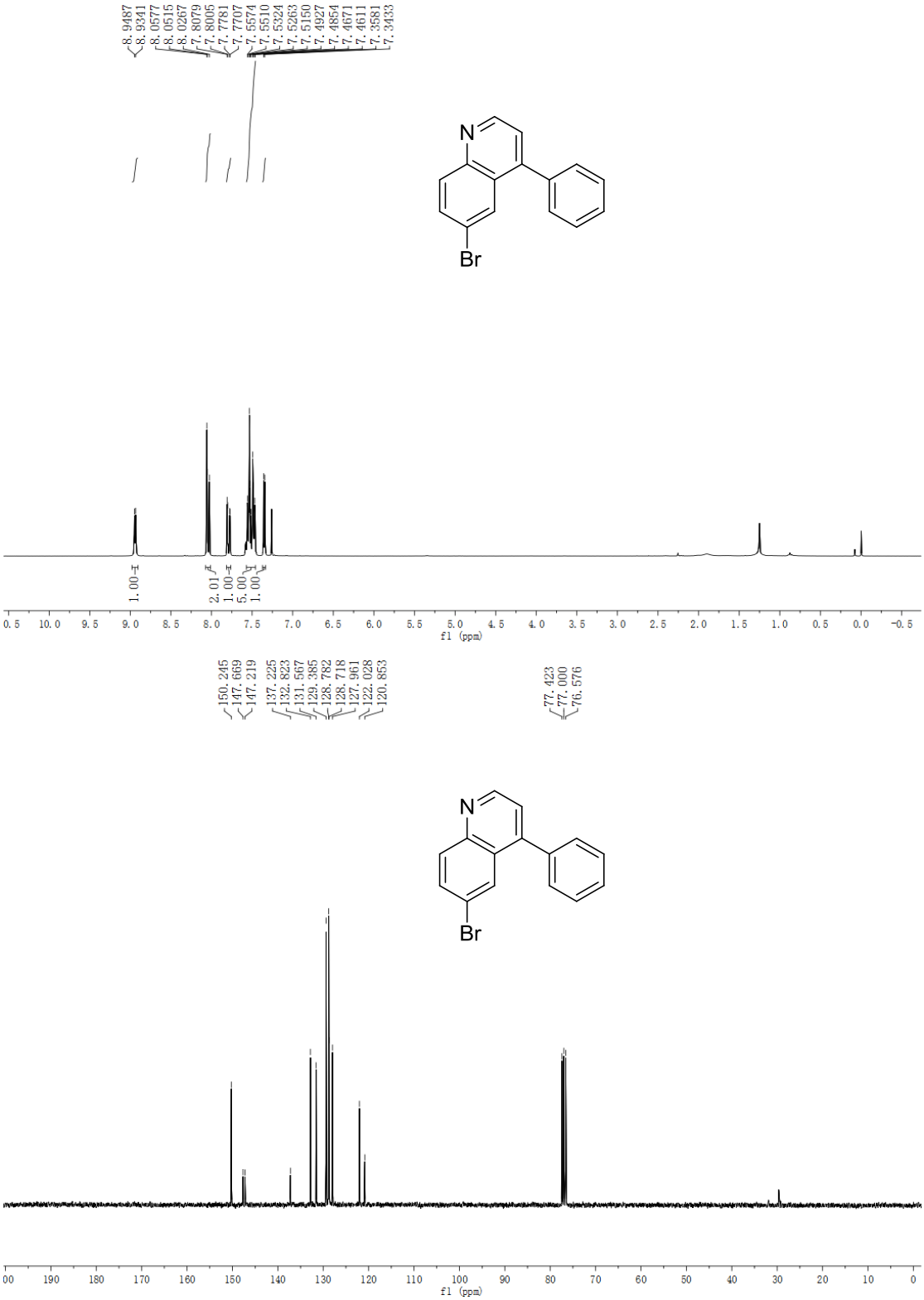




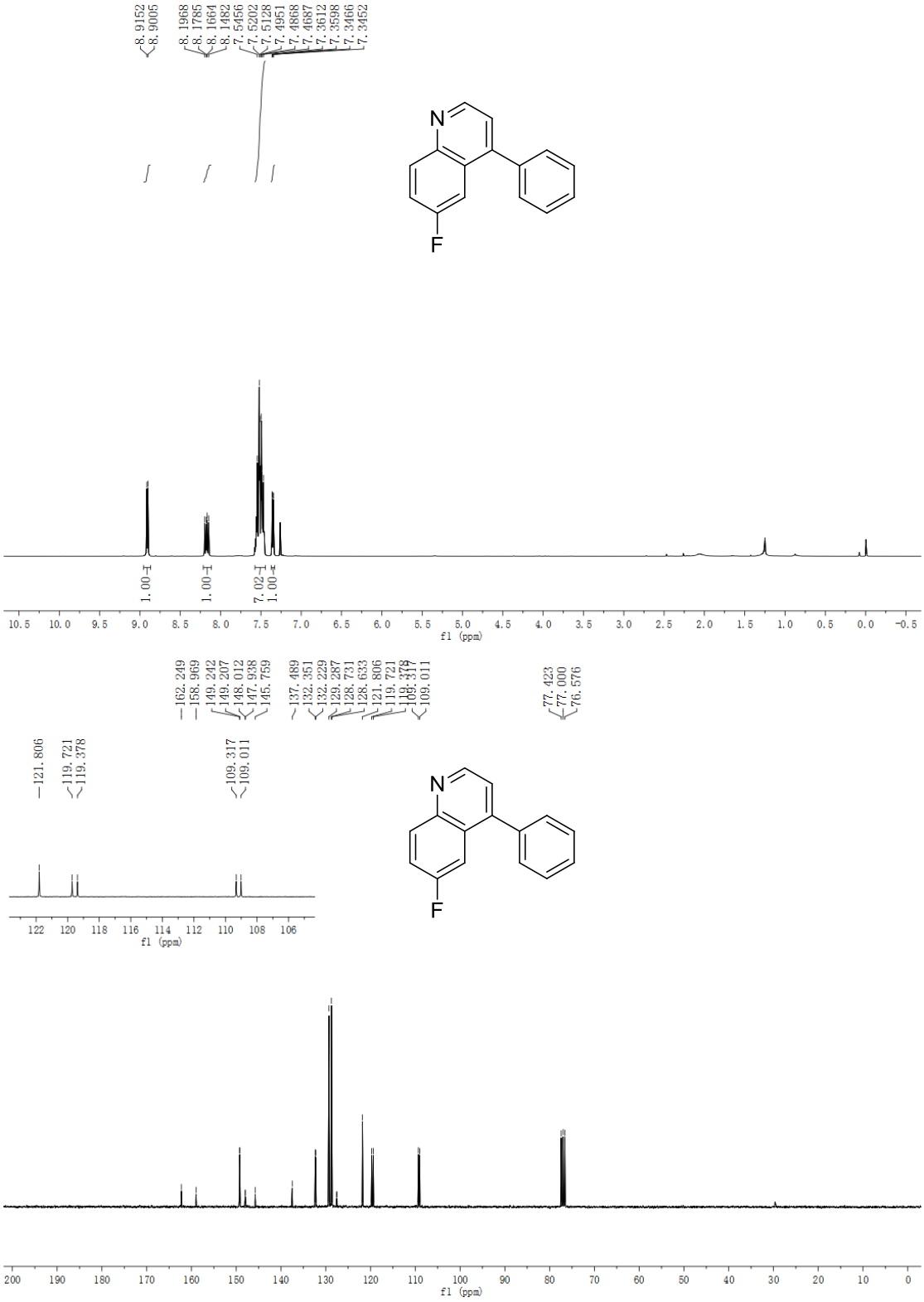
6-chloro-4-phenylquinoline (3d)



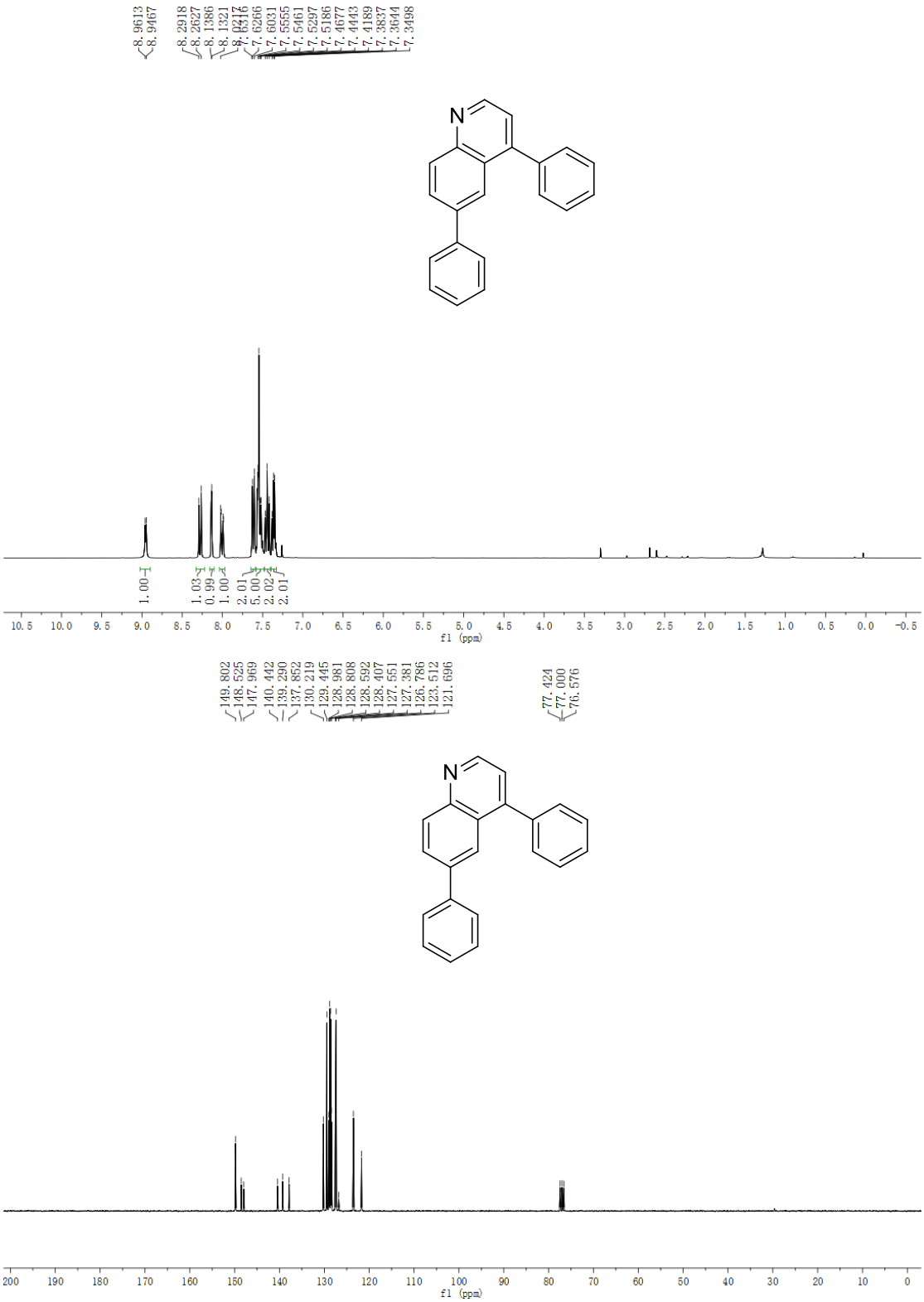
6-bromo-4-phenylquinoline (3e)



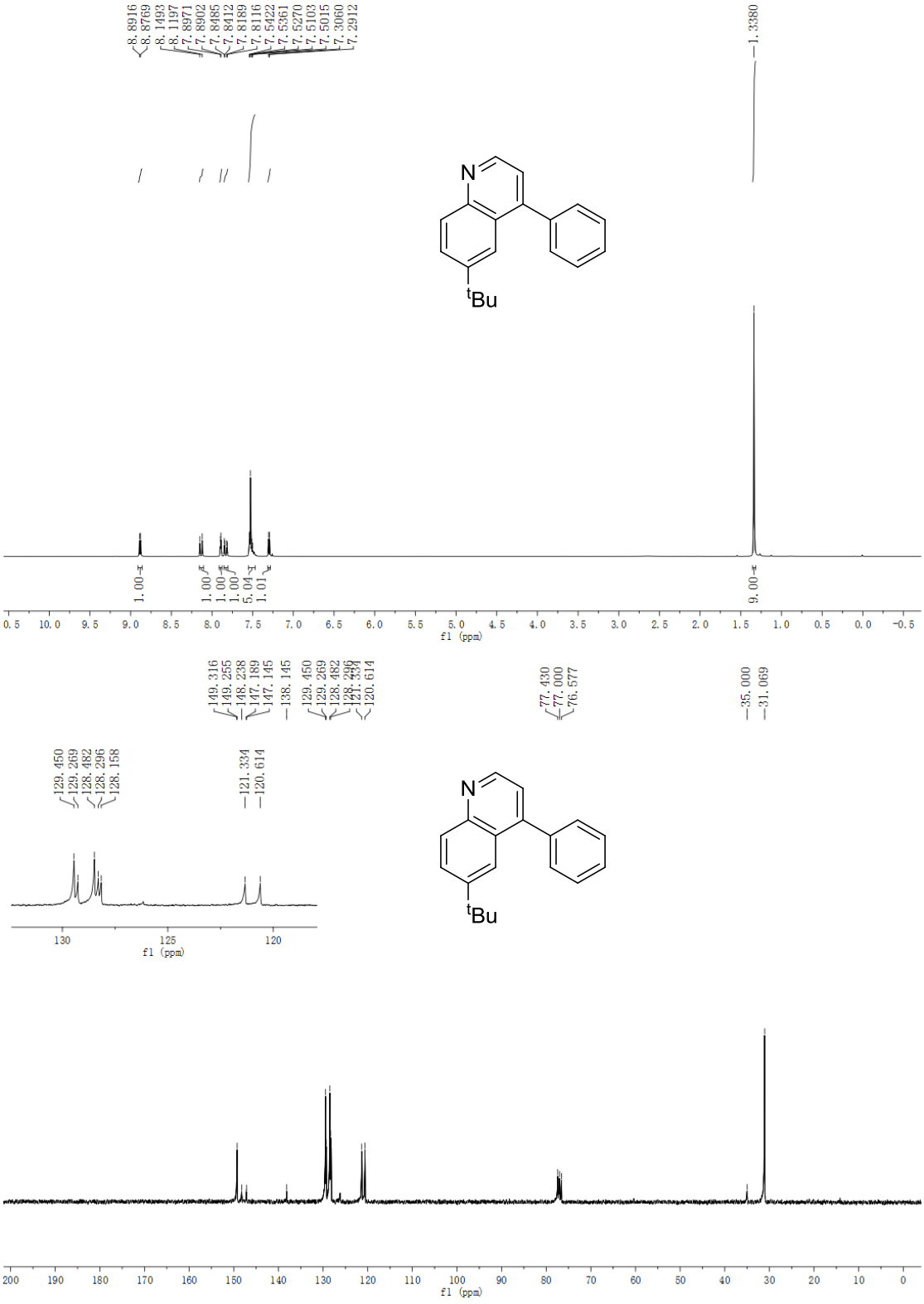
6-fluoro-4-phenylquinoline (3f)



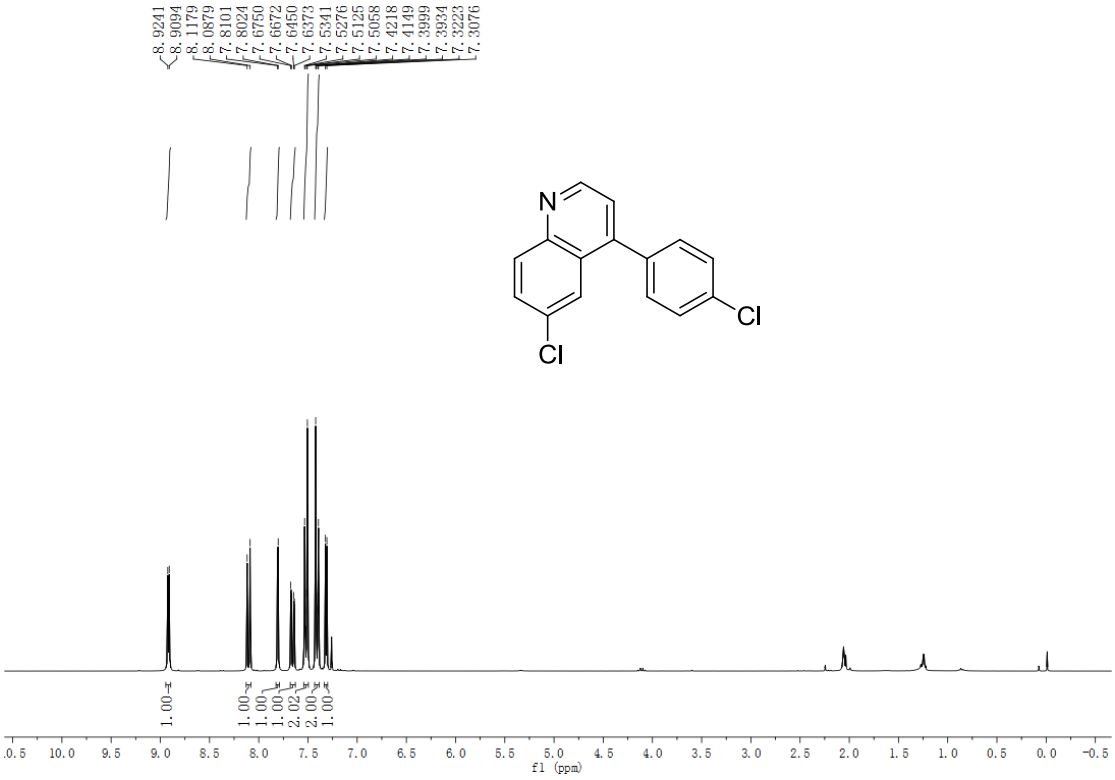
4,6-diphenylquinoline (3g)

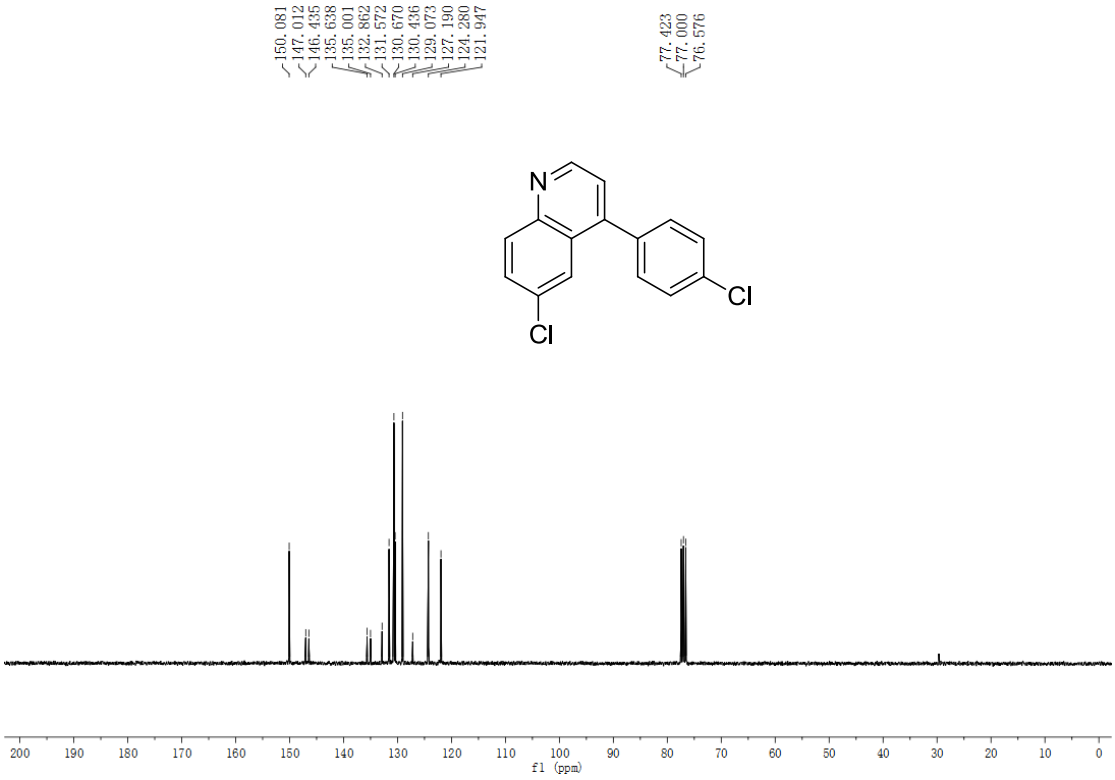


6-(tert-butyl)-4-phenylquinoline (3h)

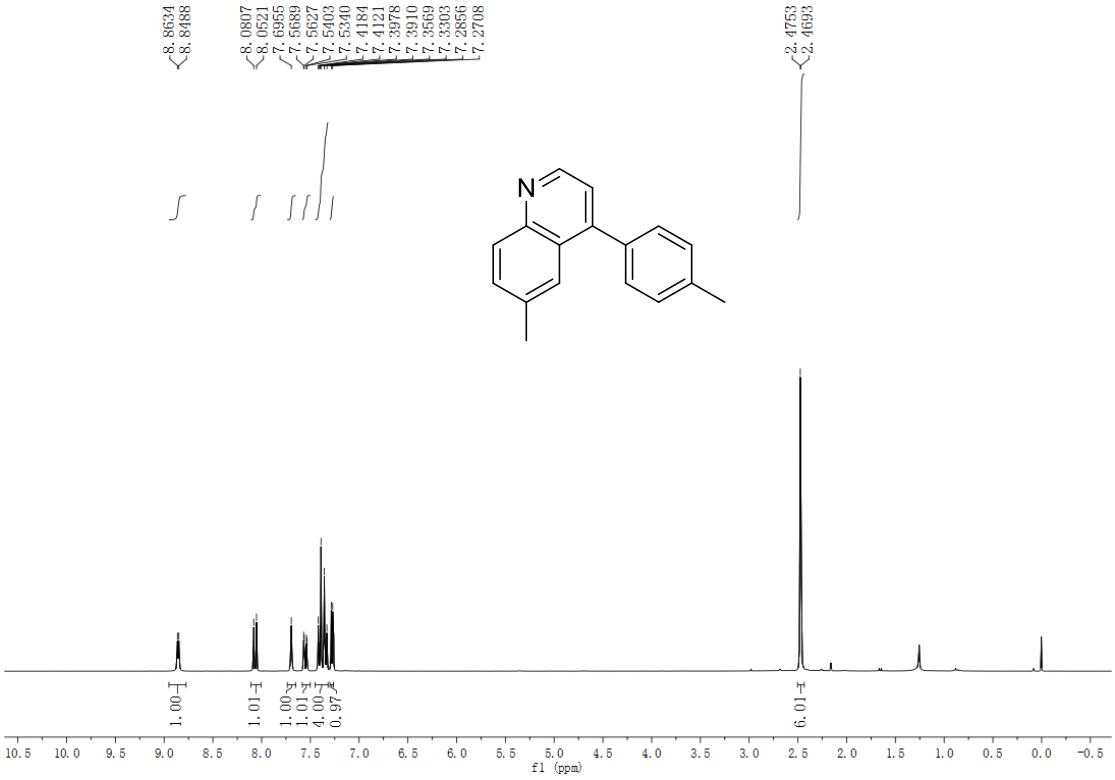


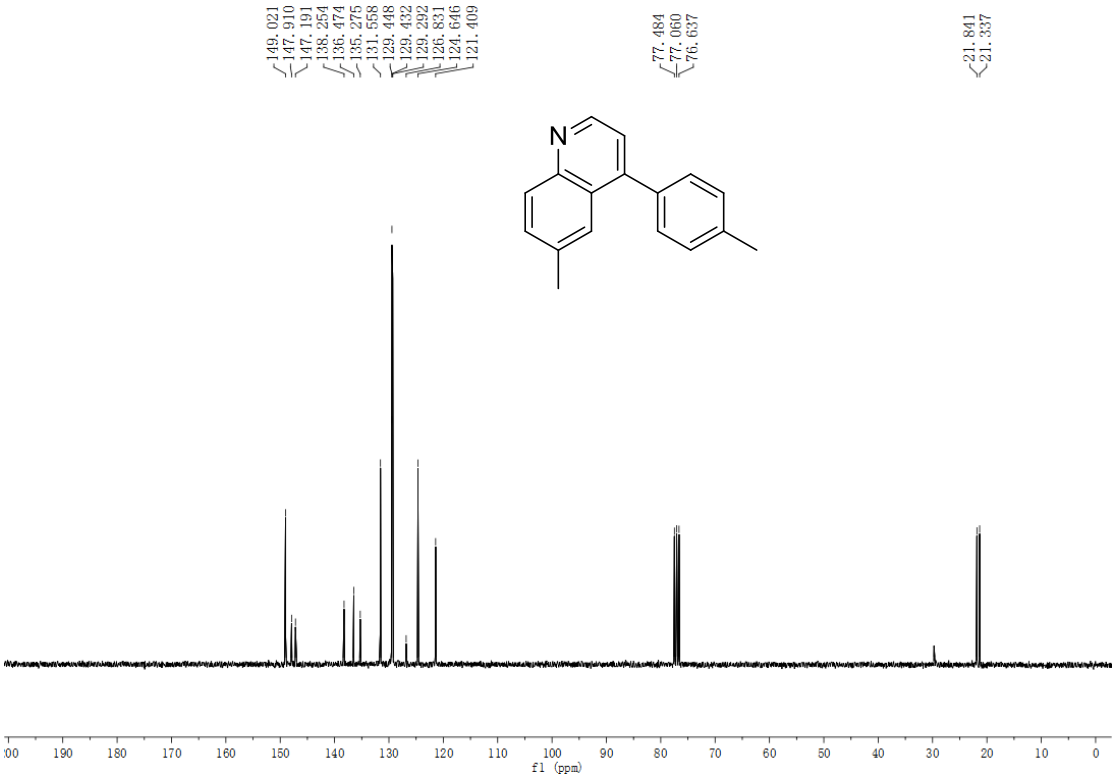
6-chloro-4-(4-chlorophenyl)quinoline (3i)



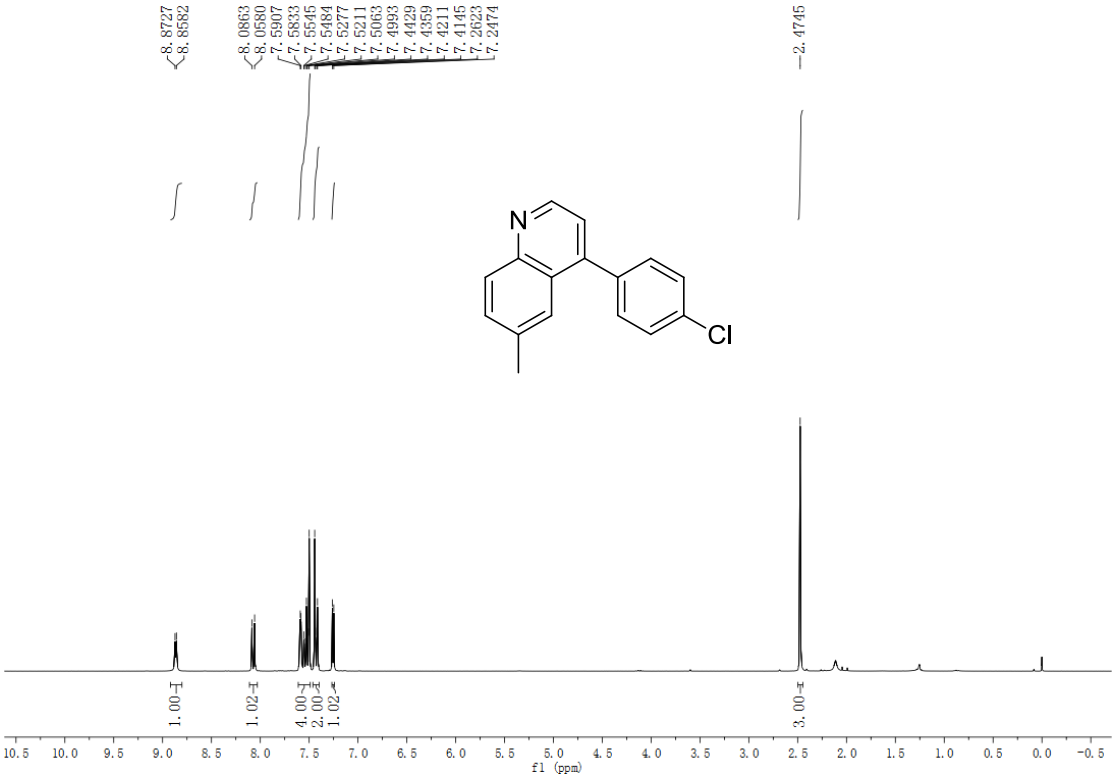


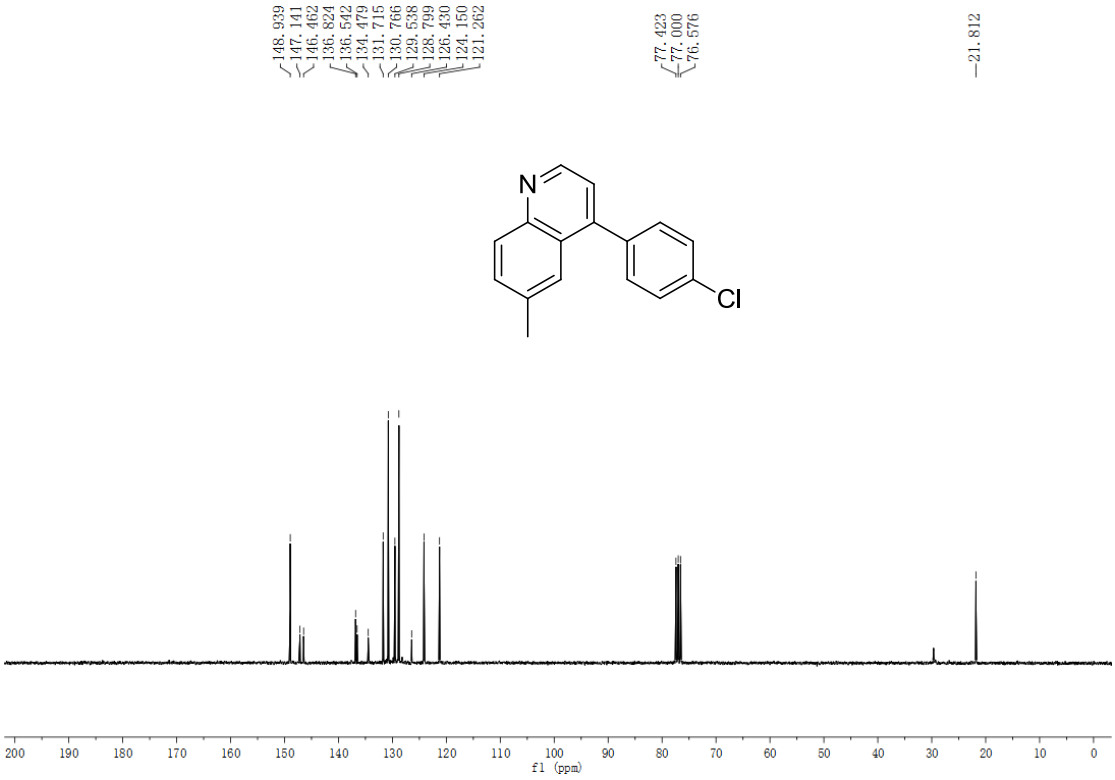
6-methyl-4-(p-tolyl)quinoline (3j)



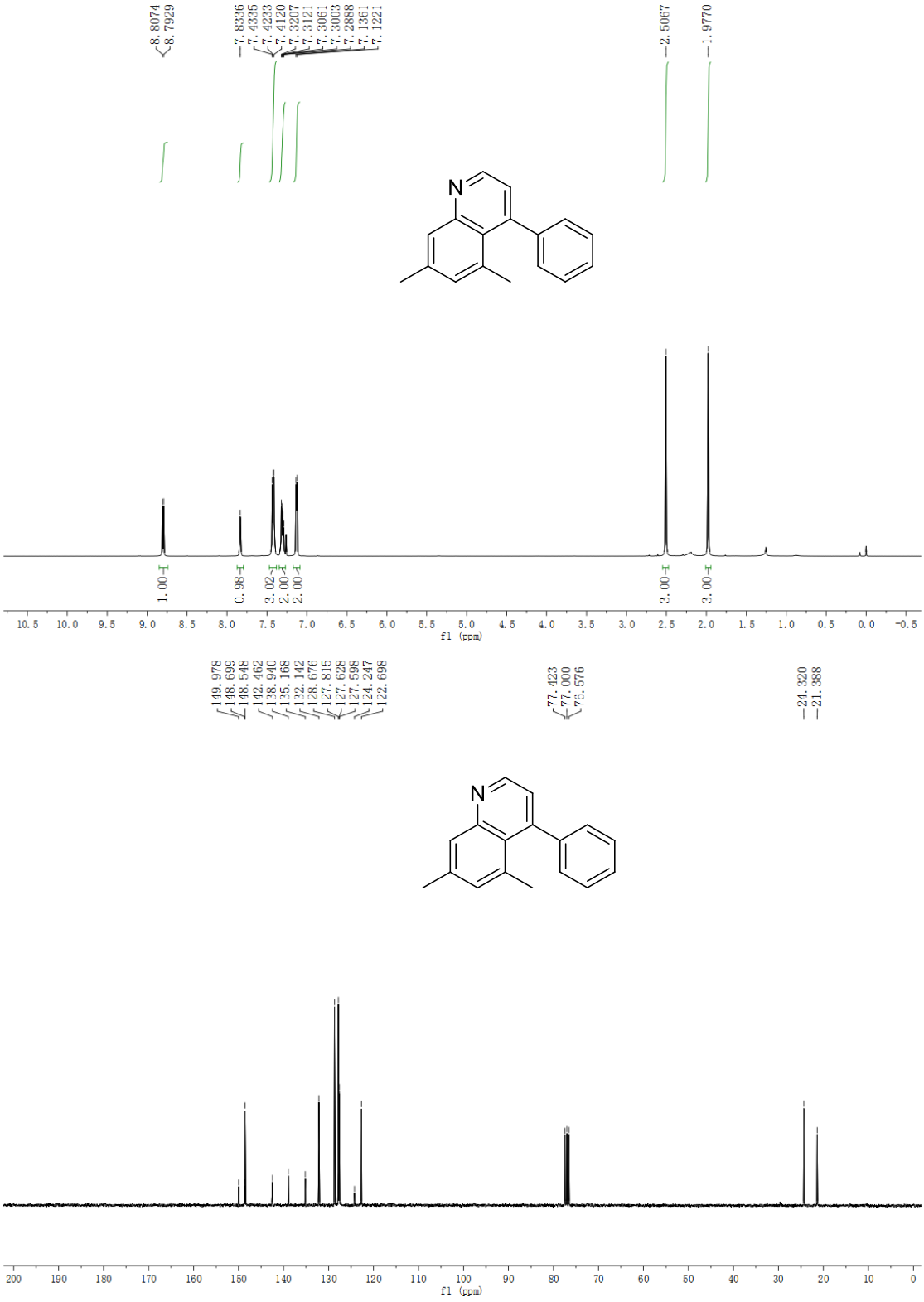


4-(4-chlorophenyl)-6-methylquinoline (3k)

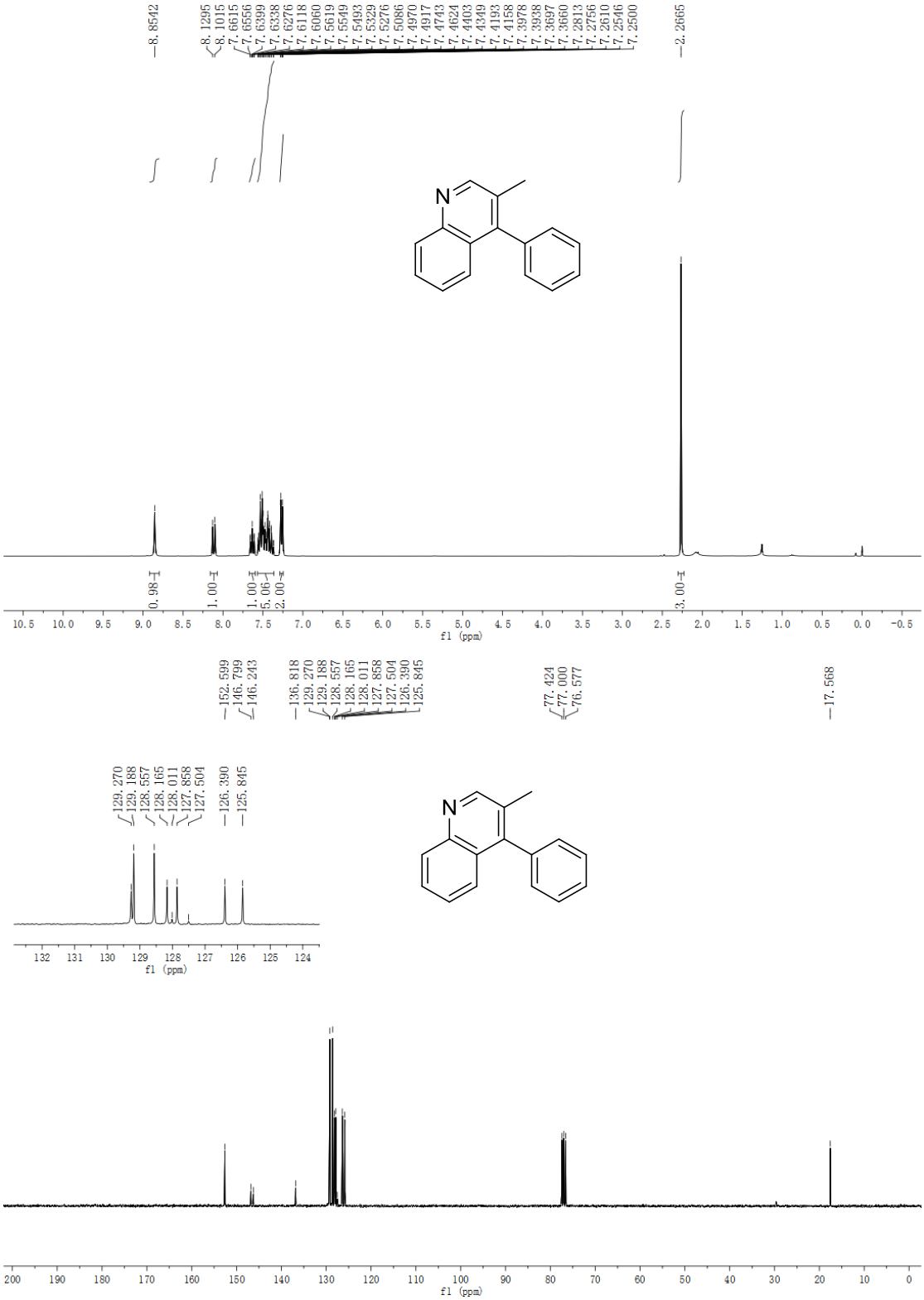




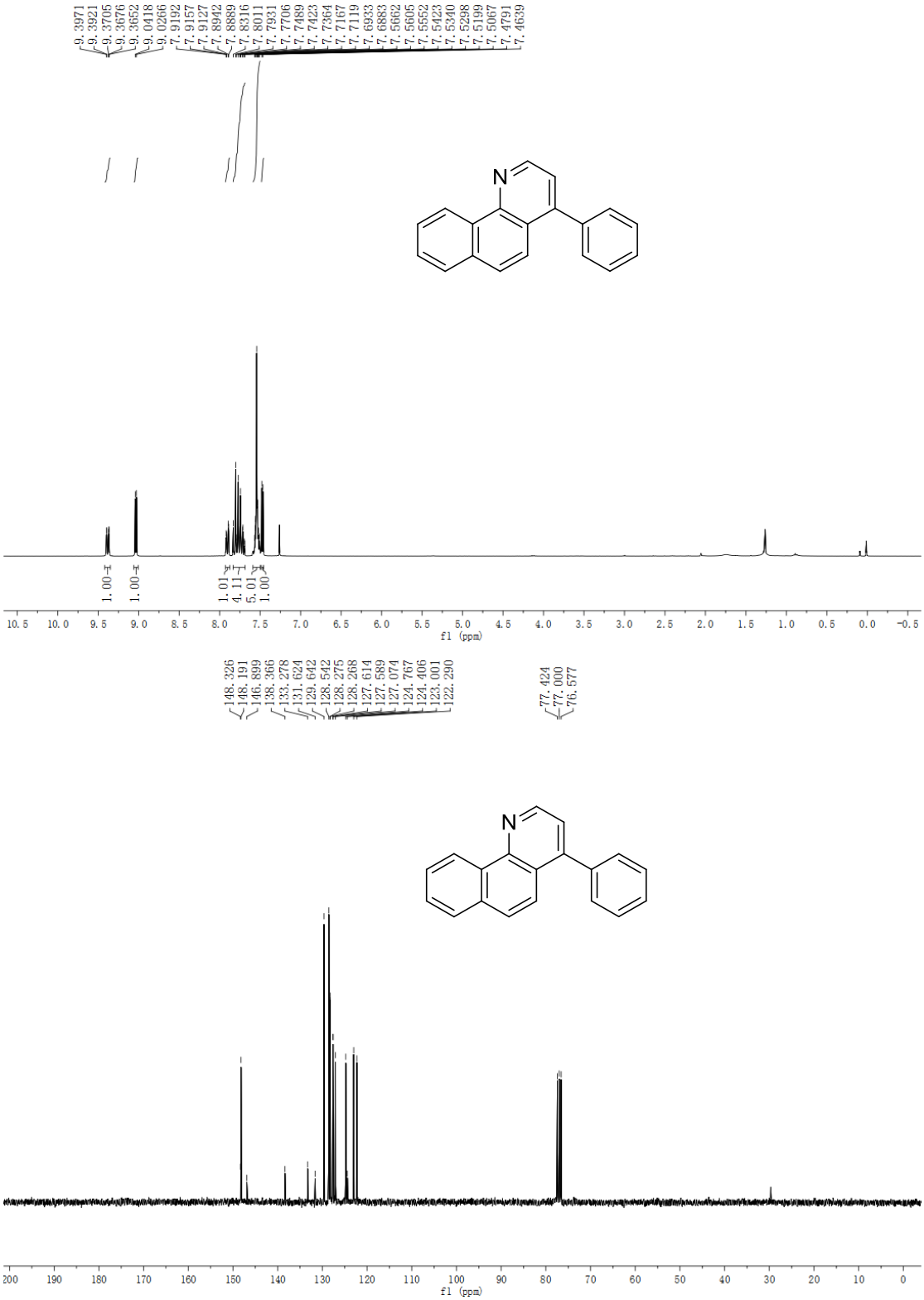
5,7-dimethyl-4-phenylquinoline (3l)



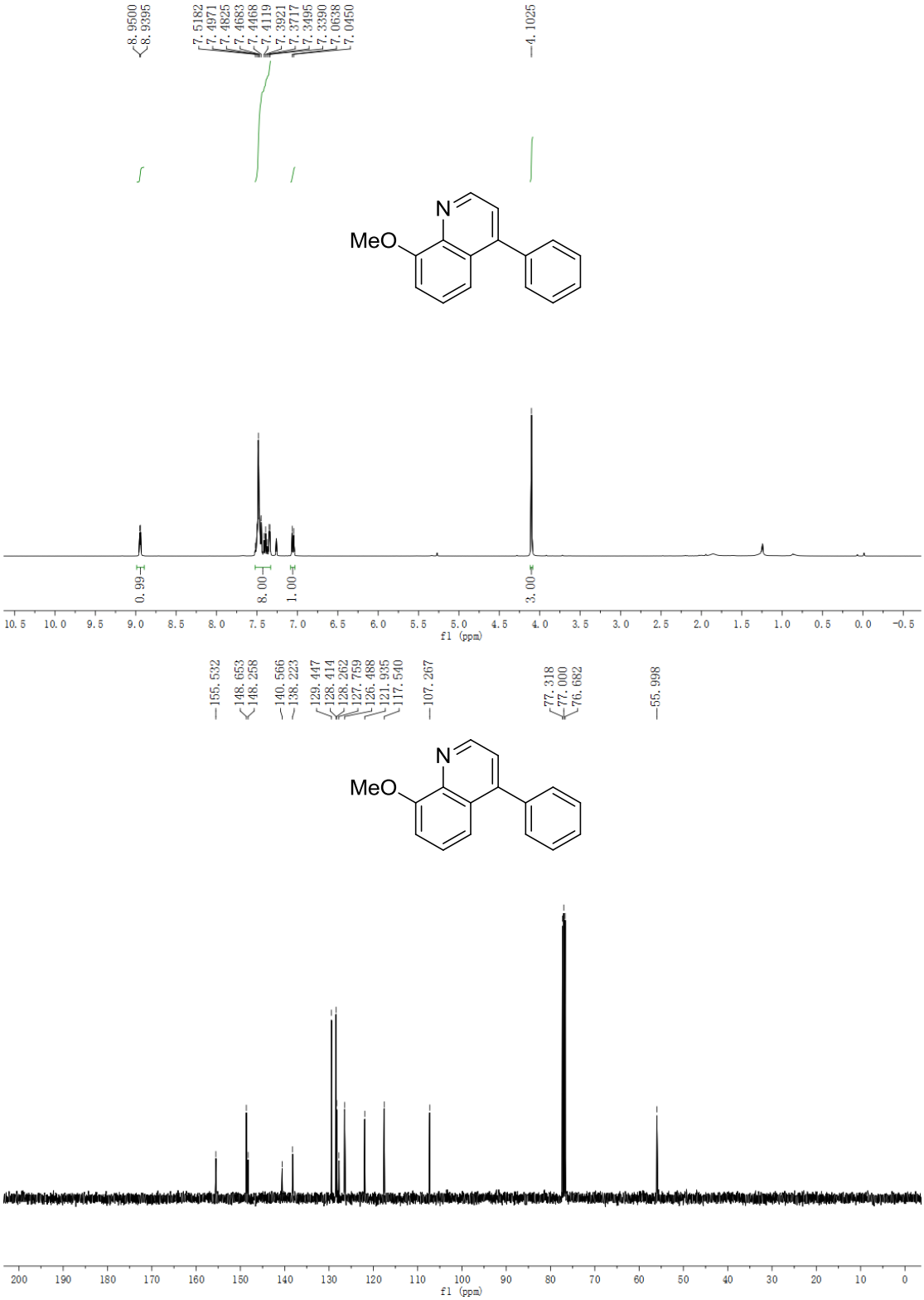
3-methyl-4-phenylquinoline (3m)



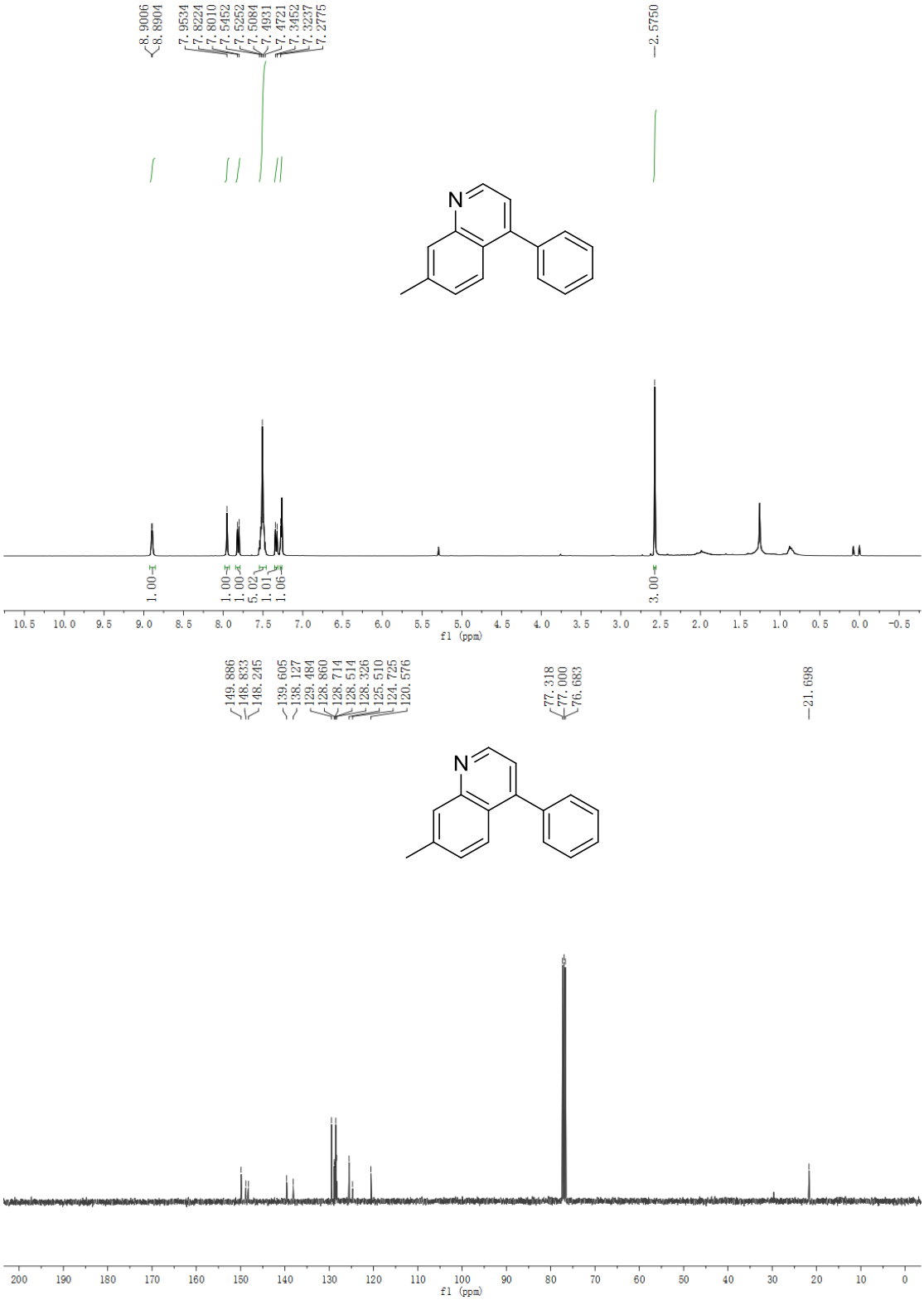
4-phenylbenzo[h]quinoline (3n)



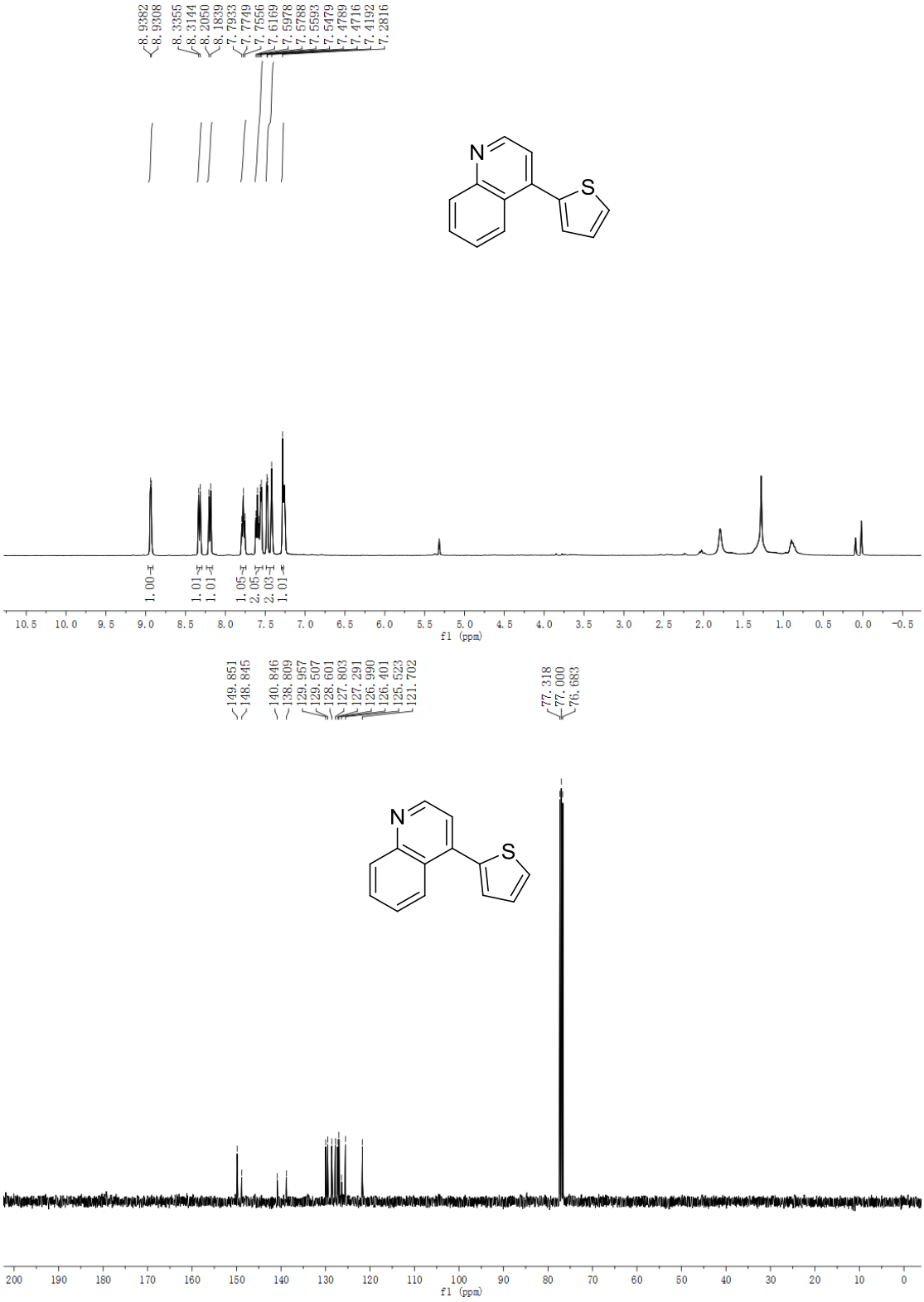
8-methoxy-4-phenylquinoline (3o)



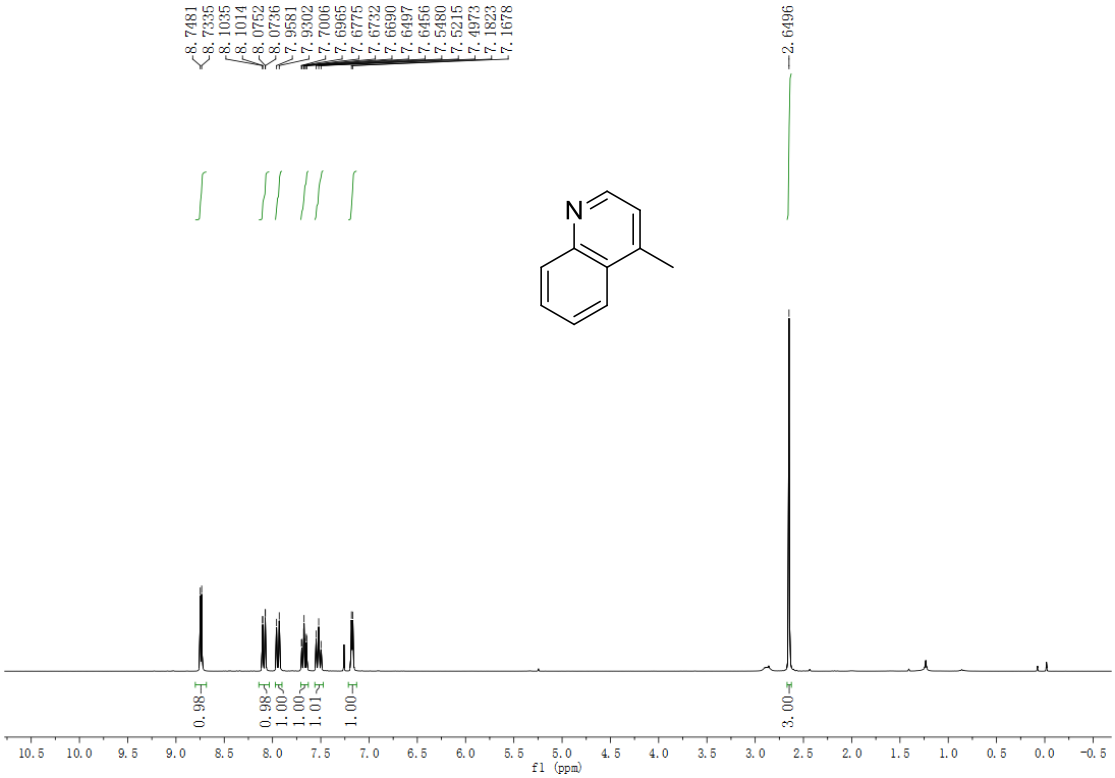
7-methyl-4-phenylquinoline (3p)

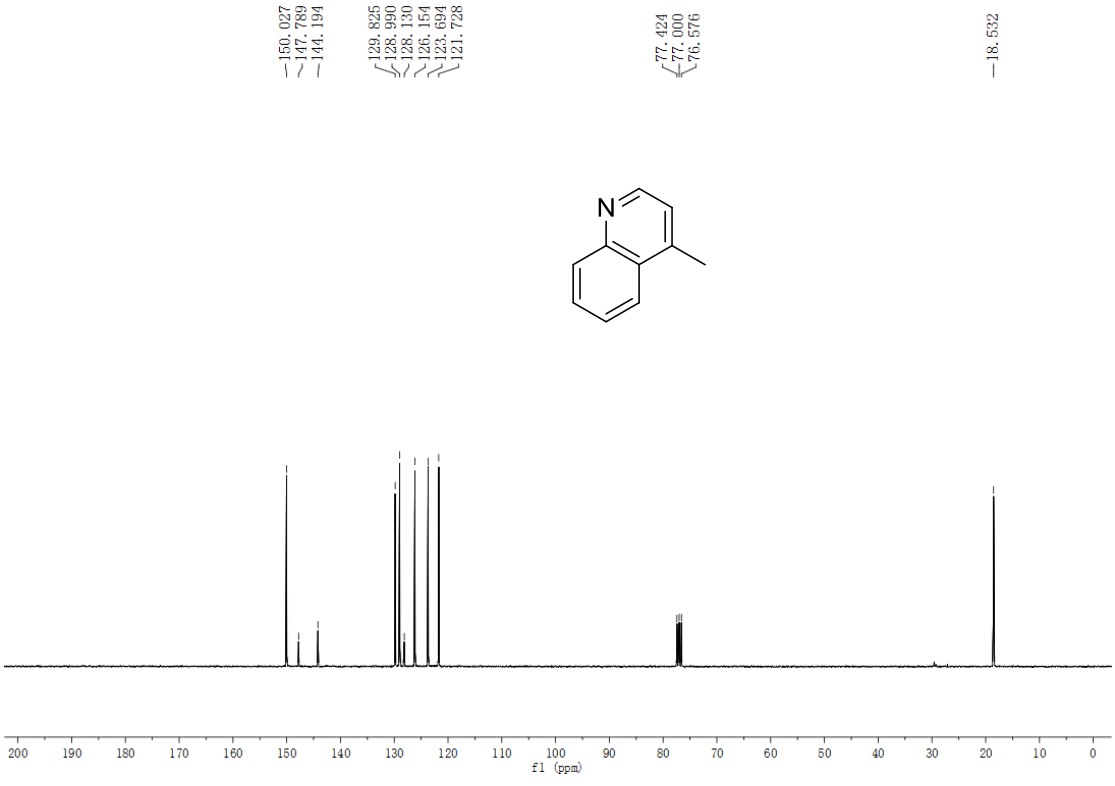


4-(thiophen-2-yl)quinoline (3q)

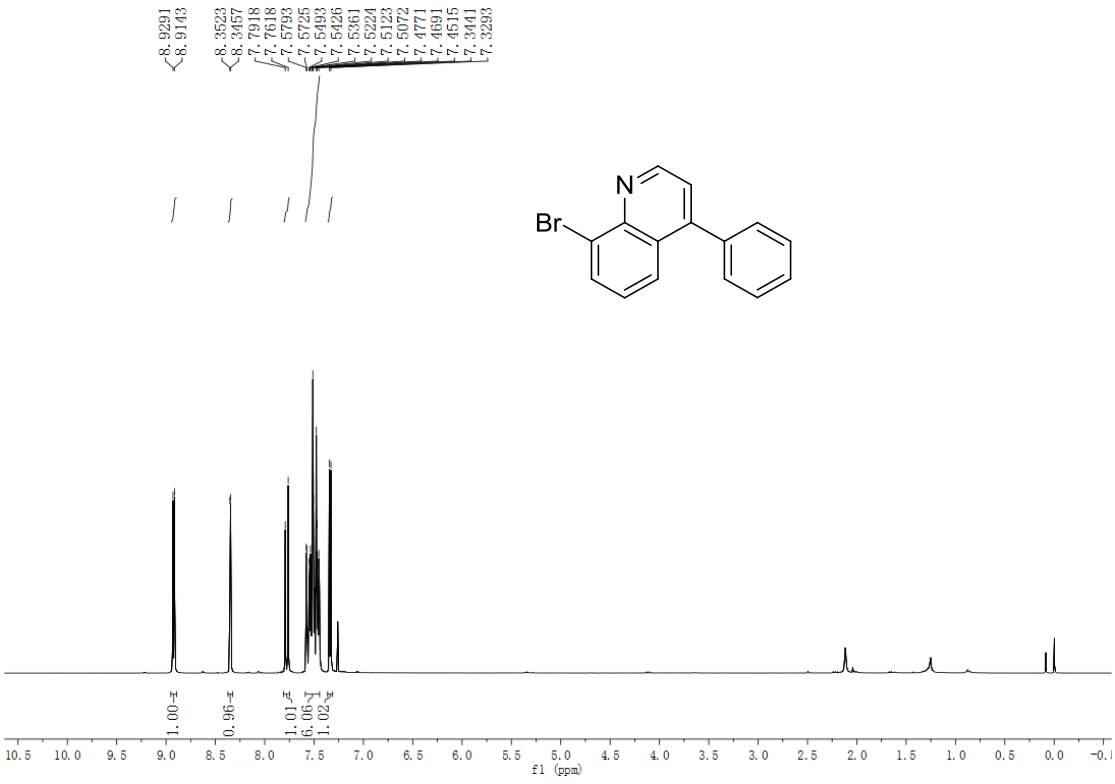


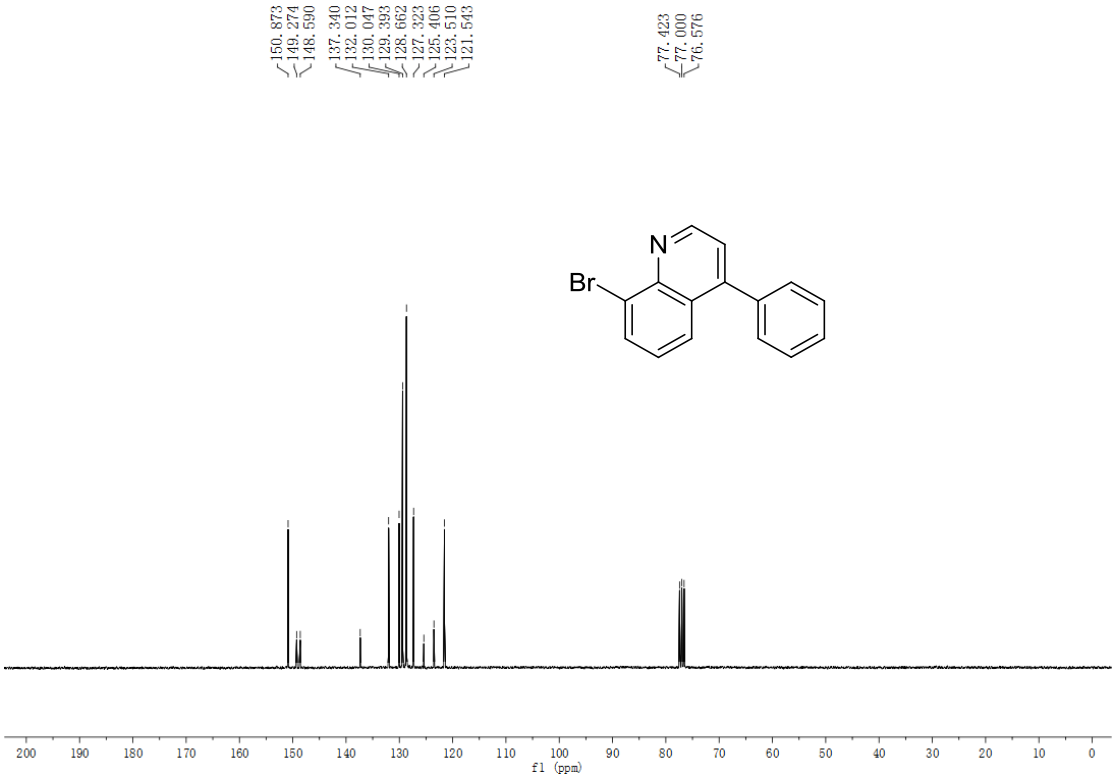
4-methylquinoline (3r)



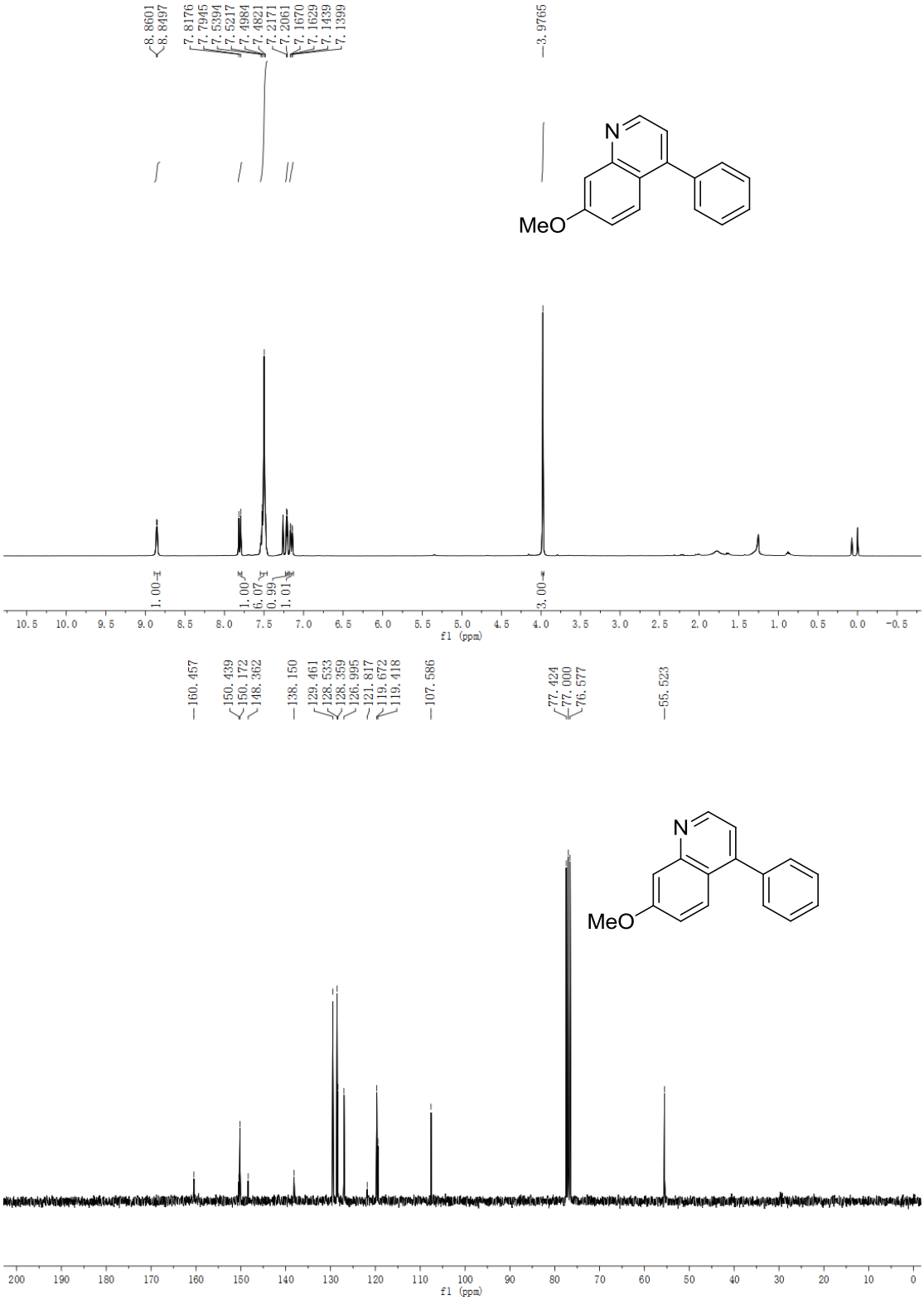


8-bromo-4-phenylquinoline (3s)

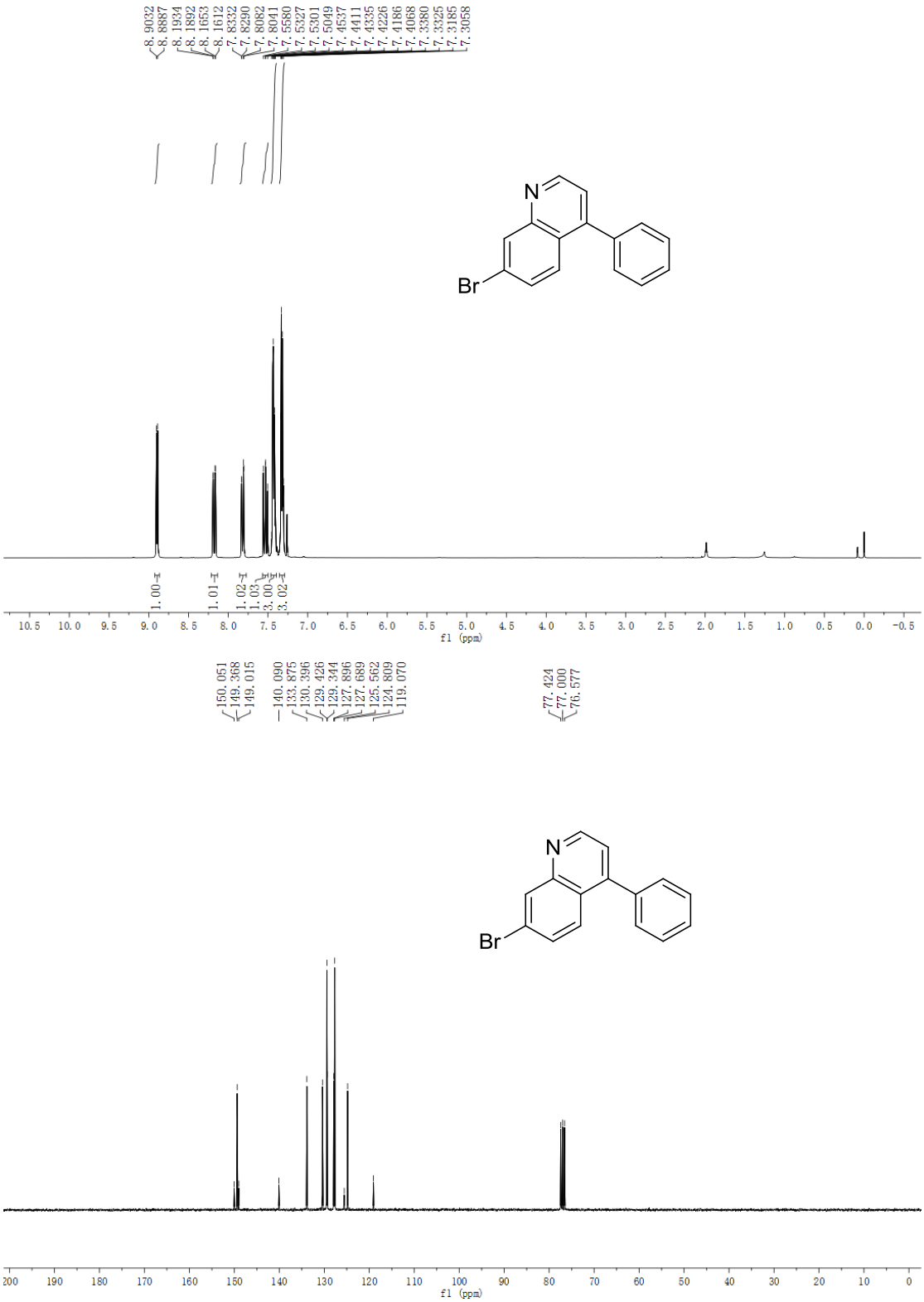




7-methoxy-4-phenylquinoline (3t)



7-bromo-4-phenylquinoline (3u)



5-bromo-4-phenylquinoline (3v)