Support Information

Manganese(I)-catalyzed direct nucleophilic addition of C(sp^3)–H bonds to aromatic aldehydes

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Contents

1. General procedures.

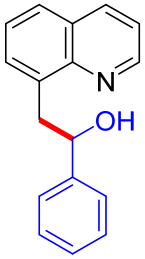
All reactions were carried out under argon atmosphere using standard Schlenk technique. ^{1}H NMR (400 MHz or 600 MHz), ^{13}C NMR (101 MHz or 151 MHz), and ^{19}F (376 M Hz) were recorded on a Bruker AV400 NMR or a Bruker AV600 NMR spectrometer with $CDCl_3$ or DMSO-d_6 as solvent. Chemical shifts of ^{1}H, ^{13}C, and ^{19}F NMR spectra are reported in parts per million (ppm). The residual solvent signals were used as references and the chemical shifts were converted to the TMS scale ($CDCl_3$: δ_H = 7.26 ppm, δ_C = 77.16 ppm; DMSO-d_6: δ_H = 2.50 ppm, δ_C = 39.43 ppm). All coupling constants (J values) were reported in Hertz (Hz). Multiplicities are reported as follows: singlet (s), doublet (d), doublet of doublets (dd), triplet (t), quartet (q), and multiplet (m). Column chromatography was performed on silica gel 200−300 mesh. Analytical thin-layer chromatography (TLC) was performed on pre-coated, glass-backed silica gel plates. Visualization of the developed chromatogram was performed by UV absorbance (254 nm and 365nm). High-resolution mass spectrometry (HRMS) was done on a FTICR-mass spectrometer. Unless otherwise noted below, all other compounds have been reported in the literature or are commercially available without any further purification. **1b, 1e, 1f, 1g, 1j, 1k, 1l, 1o, 1p**, and $[Mn(CO)_4Br]_2$ were synthesized following the literature procedures.[1,2]

1.1 General procedure for the synthesis of derivatives 3. A mixture of **1** (0.2 mmol, 1.0 equiv), **2** (0.4 mmol, 2.0 equiv), $[Mn(CO)_4Br]_2$ (9.9 mg, 0.02 mmol, 10 mol %), Me_2Zn (1 M in toluene, 0.3 mL, 0.3 mmol, 1.5 equiv), and $ZnBr_2$ (26.7 mg, 0.2 mmol, 1.0 equiv) were weighed in a Schlenk tube equipped with a stir bar. Dry 1,4-dioxane (2.0 mL) was added and the mixture was stirred at 120 °C in a pre-heated oil bath for 12 h under Ar atmosphere. After cooling to room temperature, saturated NH_4Cl aqueous solution was added to the system, and then it was extracted three times with ethyl acetate. After removal of solvents under vacuum the purification was performed by flash column chromatography on silica gel (eluent: EtOAc/petroleum ether = 1/5 to 1/2).

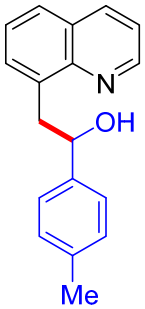
1.2 5.0 mmol of scale for the synthesis of 3aa. A mixture of **1a** (716.0 mg, 5.0 mmol, 1.0 equiv), **2a** (1.0612 g, 10.0 mmol, 2.0 equiv), $[Mn(CO)_4Br]_2$ (246.9 mg, 0.5 mmol, 10 mol %),

Me_2Zn (1 M in toluene, 7.5 mL, 7.5 mmol, 1.5 equiv), and $ZnBr_2$ (1.126 g, 5 mmol, 1.0 equiv) were weighed in a Schlenk tube equipped with a stir bar. Dry 1,4-dioxane (37.5 mL) was added and the mixture was stirred at 120 °C in a pre-heated oil bath for 12 h under Ar atmosphere. After cooling to room temperature, saturated NH_4Cl aqueous solution was added to the system, and then it was extracted three times with ethyl acetate. After removal of solvents under vacuum the purification was performed by flash column chromatography on silica gel (eluent: EtOAc/petroleum ether = 1/5 to 1/2). The product **3aa** (1.0843 g, 87%) was obtained as a white solid.

2. Characterization of the products.

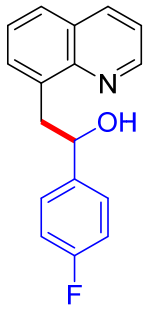


1-Phenyl-2-(quinolin-8-yl)ethan-1-ol ***(3aa)***. The title compound was isolated as a white solid (eluent: EtOAc/petroleum ether = 1/5 to 1/2), 46.8 mg, 94%; mp 65–67 °C. ^{1}H NMR ($CDCl_3$, 600 MHz): δ 8.83 (s, 1H), 8.08 (d, J = 8.1 Hz, 1H), 7.65 – 7.58 (m, 1H), 7.40 (d, J = 7.3 Hz, 2H), 7.37 – 7.31 (m, 3H), 7.28 (t, J = 7.3 Hz, 2H), 7.24 – 7.16 (m, 1H), 6.77 (s, 1H), 5.17 – 5.05 (m, 1H), 3.68 (dd, J = 13.4, 7.8 Hz, 1H), 3.54 (d, J = 13.9 Hz, 1H). ^{13}C{^{1}H} NMR ($CDCl_3$, 151 MHz): δ 149.1, 147.2, 145.4, 137.8, 137.2, 131.4, 128.6, 128.1, 126.8, 126.8, 126.6, 125.7, 121.0, 75.3, 44.0. HRMS (ESI) *m*/*z*: $[M + H]^+$ calcd for $C_{17}H_{16}NO$, 250.1227; found, 250.1225.

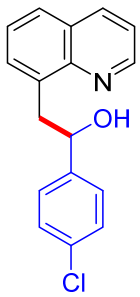


2-(Quinolin-8-yl)-1-(p-tolyl)ethan-1-ol ***(3ab)***. The title compound was isolated as a white solid (eluent: EtOAc/petroleum ether = 1/5 to 1/2), 42.6 mg, 81%; mp 63–67 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.94 (dd, J = 4.2, 1.7 Hz, 1H), 8.23 (dd, J = 8.3, 1.6 Hz, 1H), 7.78 – 7.70 (m, 1H), 7.51 – 7.43 (m, 3H), 7.32 (d, J = 8.0 Hz, 2H), 7.14 (d, J = 7.8 Hz, 2H), 6.72 (br, 1H),

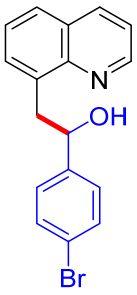
5.09 (dd, J = 8.3, 2.2 Hz, 1H), 3.73 (dd, J = 14.0, 8.4 Hz, 1H), 3.53 (dd, J = 14.0, 2.5 Hz, 1H), 2.34 (s, 3H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 101 MHz): δ 149.3, 147.4, 142.7, 138.2, 137.5, 136.5, 131.7, 129.0, 128.8, 127.0, 126.9, 125.8, 121.2, 75.5, 44.3, 21.3. HRMS (ESI) *m/z*: $[M+H]^+$ calcd for $C_{18}H_{18}NO$, 264.1383; found, 264.1384.



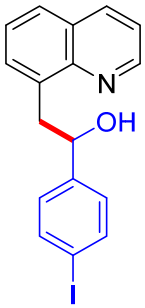
1-(4-Fluorophenyl)-2-(quinolin-8-yl)ethan-1-ol ***(3ac).*** The title compound was isolated as a white solid (eluent: EtOAc/petroleum ether = 1/5 to 1/2), 47.5 mg, 89%; mp 85–90 °C. ^1H NMR (400 MHz, $CDCl_3$): δ 8.93 (d, J = 3.3 Hz, 1H), 8.22 (d, J = 8.2 Hz, 1H), 7.73 (d, J = 7.9 Hz, 1H), 7.52 – 7.31 (m, 5H), 6.98 (t, J = 8.4 Hz, 2H), 6.86 (s, 1H), 5.14 (d, J = 7.2 Hz, 1H), 3.66 (dd, J = 14.0, 7.6 Hz, 1H), 3.58 (d, J = 13.6 Hz, 1H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 101 MHz): δ 162.0 (d, J = 244.0 Hz), 149.4, 147.4, 141.3, 137.8, 137.5, 131.8, 128.8, 127.4 (d, J = 7.9 Hz), 127.0 (d, J = 20.7 Hz), 121.3, 115.1, 114.9, 74.9, 44.2. ^{19}F NMR ($CDCl_3$, 376 MHz) δ -116.4. HRMS (ESI) *m/z*: $[M+H]^+$ calcd for $C_{17}H_{15}FNO$, 268.1132; found, 268.1136.



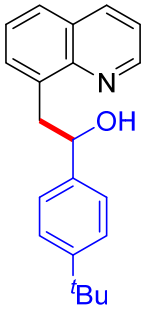
1-(4-Chlorophenyl)-2-(quinolin-8-yl)ethan-1-ol ***(3ad)***. The title compound was isolated as a white solid (eluent: EtOAc/petroleum ether = 1/5 to 1/2), 55.0 mg, 97%; mp 101-105 °C. ^1H NMR ($CDCl_3$, 400 MHz): δ 8.89 (d, J = 3.2 Hz, 1H), 8.19 (d, J = 8.2 Hz, 1H), 7.70 (d, J = 8.0 Hz, 1H), 7.47 – 7.34 (m, 3H), 7.30 (d, J = 8.3 Hz, 2H), 7.24 (d, J = 8.2 Hz, 2H), 7.00 (br, 1H), 5.12 (s, 1H), 3.67 – 3.52 (m, 2H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 101 MHz): δ 149.3, 147.2, 144.0, 137.5, 132.4, 131.7, 128.8, 128.6, 128.3, 127.3, 127.1, 126.8, 121.2, 74.8, 44.0. HRMS (ESI) *m/z*: $[M+H]^+$ calcd for $C_{17}H_{15}ClNO$, 284.0873; found, 284.0832.



1-(4-Bromophenyl)-2-(quinolin-8-yl)ethan-1-ol ***(3ae)***. The title compound was isolated as a white solid (eluent: EtOAc/petroleum ether = 1/5 to 1/2), 60.6 mg, 80%; mp 94-97 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.89 (dd, *J* = 4.1, 1.4 Hz, 1H), 8.20 (dd, *J* = 8.3, 1.3 Hz, 1H), 7.75 – 7.66 (m, 1H), 7.46 – 7.40 (m, 3H), 7.39 (d, *J* = 2.3 Hz, 1H), 7.38 – 7.34 (m, 1H), 7.24 (d, *J* = 8.2 Hz, 2H), 7.02 (br, 1H), 5.10 (dd, *J* = 6.4, 2.6 Hz, 1H), 3.67 – 3.52 (m, 2H). ^{13}C{^{1}H} NMR ($CDCl_3$, 101 MHz): δ 149.3, 147.2, 144.5, 137.5, 131.8, 131.2, 128.8, 128.6, 127.7, 127.1, 126.9, 121.2, 120.6, 74.8, 44.0. HRMS (ESI) *m/z*: $[M+H]^+$ calcd for $C_{17}H_{15}BrNO$, 328.0332; found, 328.0331.

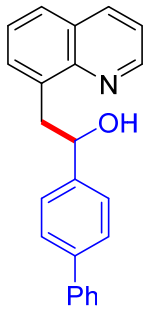


1-(4-Iodophenyl)-2-(quinolin-8-yl)ethan-1-ol ***(3af)***. The title compound was isolated as a white solid (eluent: EtOAc/petroleum ether = 1/5 to 1/2), 66.7 mg, 88%; mp 78-82 °C. ^{1}H NMR ($CDCl_3$, 600 MHz): δ 8.89 (d, *J* = 3.0 Hz, 1H), 8.20 (d, *J* = 8.0 Hz, 1H), 7.71 (d, *J* = 8.0 Hz, 1H), 7.60 (d, *J* = 8.0 Hz, 2H), 7.49 – 7.40 (m, 2H), 7.37 (d, *J* = 6.8 Hz, 1H), 7.12 (d, *J* = 8.0 Hz, 2H), 7.01 (br, 1H), 5.08 (d, *J* = 5.4 Hz, 1H), 3.73 – 3.39 (m, 2H). ^{13}C{^{1}H} NMR ($CDCl_3$, 151 MHz): δ 149.3, 147.2, 145.2, 137.6, 137.5, 137.2, 131.8, 128.82, 128.78, 128.0, 127.1, 126.9, 121.2, 74.9, 44.0. RMS (ESI) *m/z*: $[M+H]^+$ calcd for $C_{17}H_{15}INO$, 376.0193; found, 376.0192.

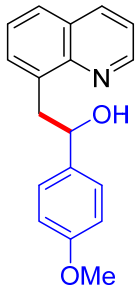


1-(4-(tert-Butyl)phenyl)-2-(quinolin-8-yl)ethan-1-ol ***(3ag)***. The title compound was

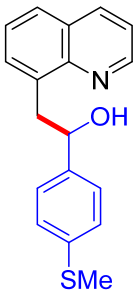
isolated as a colorless oil (eluent: EtOAc/petroleum ether = 1/10), 43.7 mg, 72%. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.91 (d, J = 2.8 Hz, 1H), 8.19 (d, J = 9.3 Hz, 1H), 7.71 (d, J = 7.8 Hz, 1H), 7.51 – 7.33 (m, 7H), 6.60 (br, 1H), 5.07 (d, J = 7.3 Hz, 1H), 3.77 (dd, J = 14.0, 8.8 Hz, 1H), 3.48 (dd, J = 14.0, 1.7 Hz, 1H), 1.32 (s, 9H). ^{13}C{^{1}H} NMR ($CDCl_3$, 101 MHz): δ 149.9, 149.3, 147.4, 142.7, 138.4, 137.3, 131.5, 128.8, 127.0, 126.9, 125.6, 125.2, 121.2, 75.6, 44.2, 34.6, 31.5. HRMS (ESI) *m/z*: $[M+H]^+$ calcd for $C_{21}H_{24}NO$, 306.1853; found, 306.1849.



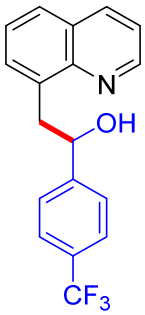
1-([1,1'-Biphenyl]-4-yl)-2-(quinolin-8-yl)ethan-1-ol ***(3ah)***. The title compound was isolated as a white solid (eluent: EtOAc/petroleum ether = 1/5 to 1/2), 51.9 mg, 80%; mp 61-64 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.90 (dd, J = 4.2, 1.6 Hz, 1H), 8.17 (dd, J = 8.3, 1.5 Hz, 1H), 7.69 (dd, J = 7.4, 2.0 Hz, 1H), 7.57 (dd, J = 13.6, 7.8 Hz, 5H), 7.48 (d, J = 8.2 Hz, 2H), 7.43 (s, 2H), 7.41 (d, J = 2.9 Hz, 2H), 7.32 (d, J = 7.3 Hz, 1H), 6.89 (br, 1H), 5.17 (dd, J = 8.1, 2.3 Hz, 1H), 3.75 (dd, J = 14.1, 8.2 Hz, 1H), 3.58 (dd, J = 14.1, 2.5 Hz, 1H). ^{13}C{^{1}H} NMR ($CDCl_3$, 101 MHz): δ 149.3, 147.3, 144.6, 141.2, 139.8, 137.9, 137.5, 131.7, 128.8, 127.5, 127.4, 127.3, 127.1, 127.0, 126.9, 126.3, 121.2, 75.3, 44.1. HRMS (ESI) *m/z*: $[M+H]^+$ calcd for $C_{23}H_{20}NO$, 326.1540; found, 326.1539.



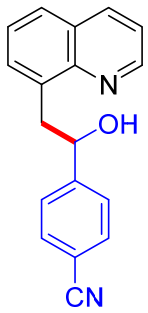
1-(4-Methoxyphenyl)-2-(quinolin-8-yl)ethan-1-ol ***(3ai)***. The title compound was isolated as a colorless oil (eluent: EtOAc/petroleum ether = 1/5 to 1/2), 35.8 mg, 64%. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.93 (d, J = 2.8 Hz, 1H), 8.25 – 8.17 (m, 1H), 7.72 (dd, J = 6.6, 3.0 Hz, 1H), 7.50 – 7.41 (m, 3H), 7.34 (d, J = 8.6 Hz, 2H), 6.87 (d, J = 8.6 Hz, 2H), 6.66 (br, 1H), 5.10 (d, J = 6.6 Hz, 1H), 3.80 (s, 3H), 3.71 (dd, J = 14.0, 8.1 Hz, 1H), 3.54 (dd, J = 14.0, 2.0 Hz, 1H). ^{13}C{^{1}H} NMR ($CDCl_3$, 101 MHz): δ 158.6, 149.2, 147.2, 138.0, 137.7, 137.4, 131.6, 128.7, 127.0, 126.9, 126.8, 121.1, 113.9, 113.6, 55.3, 44.2. HRMS (ESI) *m/z*: $[M+H]^+$ calcd for $C_{18}H_{18}NO_2$, 280.1332; found, 280.1329.



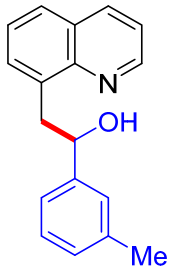
1-(4-(Methylthio)phenyl)-2-(quinolin-8-yl)ethan-1-ol ***(3aj)***. The title compound was isolated as a colorless oil (eluent: EtOAc/petroleum ether = 1/5 to 1/2), 36.2 mg, 61%. ^{1}H NMR ($CDCl_3$, 600 MHz): δ 8.97 – 8.92 (m, 1H), 8.24 (d, *J* = 7.1 Hz, 1H), 7.74 (d, *J* = 7.7 Hz, 1H), 7.52 – 7.38 (m, 3H), 7.33 (d, *J* = 8.0 Hz, 2H), 7.22 (d, *J* = 8.0 Hz, 2H), 6.79 (s, 1H), 5.11 (d, *J* = 6.3 Hz, 1H), 3.69 (dd, *J* = 13.8, 8.1 Hz, 1H), 3.57 (d, *J* = 13.8 Hz, 1H), 2.47 (s, 3H). ^{13}C{^{1}H} NMR ($CDCl_3$, 151 MHz): δ 149.3, 142.7, 137.9, 137.5, 136.6, 131.8, 128.8, 127.7, 127.0, 126.9, 126.8, 126.5, 121.2, 75.1, 44.1, 16.3. HRMS (ESI) *m/z*: $[M+H]^+$ calcd for $C_{18}H_{18}NOS$, 296.1104; found, 296.1106.



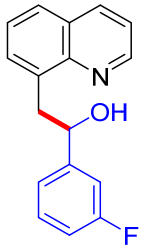
2-(Quinolin-8-yl)-1-(4-(trifluoromethyl)phenyl)ethan-1-ol ***(3ak)***. The title compound was isolated as a white solid (eluent: EtOAc/petroleum ether = 1/5 to 1/2), 75.5 mg, 96%; mp 99–102 °C. ^{1}H NMR ($CDCl_3$, 600 MHz): δ 8.95 – 8.87 (m, 1H), 8.24 (d, *J* = 8.0 Hz, 1H), 7.73 (d, *J* = 8.0 Hz, 1H), 7.63 – 7.59 (m, 1H), 7.55 (d, *J* = 7.8 Hz, 2H), 7.49 (dd, *J* = 7.9, 3.8 Hz, 1H), 7.47 – 7.39 (m, 4H), 7.32 (d, *J* = 6.8 Hz, 1H), 5.21 (d, *J* = 5.6 Hz, 1H), 3.66 (d, *J* = 14.0 Hz, 1H), 3.59 (dd, *J* = 14.0, 7.2 Hz, 1H). ^{13}C{^{1}H} NMR ($CDCl_3$, 101 MHz): δ 149.5, 149.3, 147.2, 137.6, 137.3, 131.8, 129.0, 128.8, 127.3, 126.9, 126.2, 125.2 (q, *J* = 3.7 Hz). 121.3, 74.9, 44.0. ^{19}F NMR ($CDCl_3$, 376 MHz): δ -62.2. HRMS (ESI) *m/z*: $[M+H]^+$ calcd for $C_{18}H_{15}F_3NO$, 318.1100; found, 318.1098.



4-(1-Hydroxy-2-(quinolin-8-yl)ethyl)benzonitrile ***(3al)***. The title compound was isolated as a white solid (eluent: EtOAc/petroleum ether = 1/5 to 1/2), 35.1 mg, 61%; mp 84–86 °C. ^{1}H NMR ($CDCl_3$, 600 MHz): δ 8.93 – 8.89 (m, 1H), 8.23 (d, *J* = 8.1 Hz, 1H), 7.72 (d, *J* = 8.0 Hz, 1H), 7.60 (d, *J* = 7.7 Hz, 1H), 7.55 (d, *J* = 7.9 Hz, 2H), 7.48 (dd, *J* = 8.1, 4.2 Hz, 1H), 7.45 (d, *J* = 8.0 Hz, 2H), 7.40 (d, *J* = 7.7 Hz, 1H), 7.32 (d, *J* = 6.8 Hz, 1H), 5.20 (d, *J* = 5.6 Hz, 1H), 3.65 (d, *J* = 14.0 Hz, 1H), 3.58 (dd, *J* = 14.2, 7.5 Hz, 1H). ^{13}C{^{1}H} NMR ($CDCl_3$, 151 MHz): δ 150.9, 149.3, 147.1, 137.6, 136.9, 132.1, 131.8, 128.8, 127.3, 126.9, 126.6, 121.3, 119.2, 110.5, 74.7, 43.7. HRMS (ESI) *m/z*: $[M+H]^+$ calcd for $C_{18}H_{15}N_2O$, 275.1179; found, 275.1177.

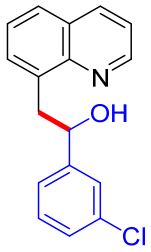


2-(Quinolin-8-yl)-1-(m-tolyl)ethan-1-ol ***(3am)***. The title compound was isolated as a colorless oil (eluent: EtOAc/petroleum ether = 1/5 to 1/2), 42.4 mg, 81%. **^{1}**H NMR (DMSO-d_6, 400 MHz): δ 8.98 (dd, *J* = 4.0, 1.4 Hz, 1H), 8.35 (dd, *J* = 8.3, 1.7 Hz, 1H), 7.82 (d, *J* = 7.4 Hz, 1H), 7.54 (dd, *J* = 8.3, 4.5 Hz, 2H), 7.47 (t, *J* = 7.5 Hz, 1H), 7.22 – 7.11 (m, 3H), 7.02 (d, *J* = 7.0 Hz, 1H), 5.38 (d, *J* = 4.8 Hz, 1H), 5.02 (dt, *J* = 8.9, 4.7 Hz, 1H), 3.61 (dd, *J* = 13.1, 4.7 Hz, 1H), 3.43 (dd, *J* = 13.3, 8.6 Hz, 1H), 2.29 (s, 3H). ^{13}C{^{1}H} NMR (DMSO-d_6, 101 MHz): δ 149.5, 146.5, 146.3, 137.5, 136.8, 136.5, 130.7, 128.0, 127.8, 127.2, 126.5, 126.4, 126.1, 123.0, 121.1, 72.8, 41.8, 21.2. HRMS (ESI) *m/z*: $[M+H]^+$ calcd for $C_{18}H_{18}NO$, 264.1383; found, 264.1379.

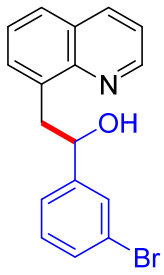


1-(3-Fluorophenyl)-2-(quinolin-8-yl)ethan-1-ol ***(3an)***. The title compound was isolated as

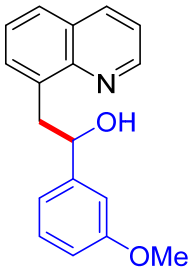
a white solid (eluent: EtOAc/petroleum ether = 1/10), 43.8 mg, 82%; mp 65-69 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.89 (d, *J* = 2.9 Hz, 1H), 8.19 (d, *J* = 7.8 Hz, 1H), 7.69 (dd, *J* = 7.7, 1.7 Hz, 1H), 7.47 – 7.34 (m, 3H), 7.26 – 7.19 (m, 1H), 7.17 – 7.07 (m, 2H), 6.92 – 6.84 (m, 1H), 5.12 (d, *J* = 5.9 Hz, 1H), 3.75 – 3.46 (m, 2H). ^{13}C{^{1}H} NMR ($CDCl_3$, 101 MHz): δ 163.0 (d, *J* = 245.1 Hz), 149.3, 148.3 (d, *J* = 6.5 Hz), 147.2, 137.53, 137.48, 131.8, 129.6 (d, *J* = 8.1 Hz), 128.8, 127.1, 126.9, 121.4 (d, *J* = 2.6 Hz), 121.2, 113.7 (d, *J* = 21.2 Hz), 112.8 (d, *J* = 21.9 Hz), 74.8, 44.0. ^{19}F NMR ($CDCl_3$, 376 MHz): δ -113.6. HRMS (ESI) *m/z*: $[M+H]^+$ calcd for $C_{17}H_{15}FNO$, 268.1132; found, 268.1128.



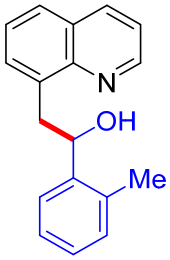
1-(3-Chlorophenyl)-2-(quinolin-8-yl)ethan-1-ol ***(3ao)***. The title compound was isolated as a colorless oil (eluent: EtOAc/petroleum ether = 1/10), 53.4 mg, 94%. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.92 – 8.87 (m, 1H), 8.19 (d, *J* = 8.2 Hz, 1H), 7.70 (dd, *J* = 7.6, 1.8 Hz, 1H), 7.47 – 7.39 (m, 4H), 7.29 – 7.15 (m, 4H), 5.09 (d, *J* = 6.8 Hz, 1H), 3.65 (dd, *J* = 14.0, 7.6 Hz, 1H), 3.54 (d, *J* = 14.0 Hz, 1H). ^{13}C{^{1}H} NMR ($CDCl_3$, 101 MHz): δ 149.2, 147.6, 147.1, 137.5, 137.4, 134.1, 131.7, 129.5, 128.8, 127.14, 127.05, 126.9, 126.1, 124.0, 121.2, 74.9, 44.0. HRMS (ESI) *m/z*: $[M+H]^+$ calcd for $C_{17}H_{15}ClNO$, 284.0837; found, 284.0832.



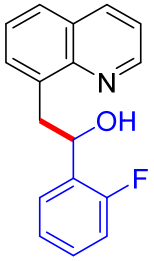
1-(3-Bromophenyl)-2-(quinolin-8-yl)ethan-1-ol ***(3ap)***. The title compound was isolated as a colorless oil (eluent: EtOAc/petroleum ether = 1/10 to 1/2), 58.7 mg, 89%. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.94 – 8.88 (m, 1H), 8.21 (d, *J* = 8.2 Hz, 1H), 7.72 (dd, *J* = 7.5, 1.8 Hz, 1H), 7.59 (s, 1H), 7.49 – 7.41 (m, 3H), 7.38 – 7.27 (m, 2H), 7.17 (t, *J* = 7.7 Hz, 1H), 5.10 (d, *J* = 6.9 Hz, 1H), 3.66 (dd, *J* = 13.9, 7.7 Hz, 1H), 3.55 (d, *J* = 14.0 Hz, 1H). ^{13}C{^{1}H} NMR ($CDCl_3$, 101 MHz): δ 149.3, 147.9, 147.1, 137.5, 137.4, 131.7, 130.0, 129.8, 129.0, 128.8, 127.2, 126.9, 124.5, 122.4, 121.2, 74.8, 44.0. HRMS (ESI) *m/z*: $[M+H]^+$ calcd for $C_{17}H_{15}BrNO$, 328.0332; found, 328.0328.



1-(3-Methoxyphenyl)-2-(quinolin-8-yl)ethan-1-ol ***(3aq)***. The title compound was isolated as a colorless oil (eluent: EtOAc/petroleum ether = 1/2 to 1/1), 25.8 mg, 46%. ^{1}H NMR ($CDCl_3$, 600 MHz): δ 8.99 – 8.87 (m, 1H), 8.23 (d, *J* = 8.0 Hz, 1H), 7.73 (d, *J* = 8.7 Hz, 1H), 7.55 – 7.40 (m, 3H), 7.24 (t, *J* = 7.8 Hz, 1H), 7.00 (d, *J* = 7.9 Hz, 2H), 6.93 (s, 1H), 6.78 (d, *J* = 7.4 Hz, 1H), 5.12 (d, *J* = 7.1 Hz, 1H), 3.77 (s, 3H), 3.72 (dd, *J* = 14.1, 8.2 Hz, 1H), 3.58 (d, *J* = 13.8 Hz, 1H). ^{13}C{^{1}H} NMR ($CDCl_3$, 151 MHz): δ 159.7, 149.2, 147.3, 138.0, 137.6, 131.8, 129.7, 129.3, 128.8, 127.02, 126.97, 121.2, 118.3, 112.8, 111.2, 75.5, 55.3, 44.2. HRMS (ESI) *m*/*z*: $[M+H]^+$ calcd for $C_{18}H_{17}NO_2$, 280.1332; found, 280.1330.

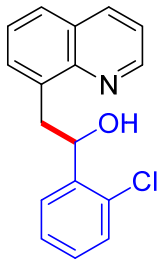


2-(Quinolin-8-yl)-1-(o-tolyl)ethan-1-ol ***(3ar)***. The title compound was isolated as a white solid (eluent: EtOAc/petroleum ether = 1/5 to 1/2), 36.0 mg, 68%; mp 102–104 °C. ^{1}H NMR ($CDCl_3$, 600 MHz): δ 9.11 – 8.89 (m, 1H), 8.23 (d, *J* = 8.1 Hz, 1H), 7.76 – 7.73 (m, 1H), 7.62 (d, *J* = 7.5 Hz, 1H), 7.48 (t, *J* = 5.8 Hz, 3H), 7.23 – 7.19 (m, 1H), 7.18 – 7.15 (m, 2H), 6.68 (s, 1H), 5.41 – 5.27 (m, 1H), 3.70 (dd, *J* = 14.2, 8.5 Hz, 1H), 3.46 (d, *J* = 14.2 Hz, 1H), 2.45 (s, 3H). ^{13}C{^{1}H} NMR ($CDCl_3$, 151 MHz): δ 149.4, 147.4, 143.7, 138.5, 137.4, 134.0, 131.3, 130.2, 128.8, 127.0, 126.9, 126.8, 126.1, 125.5, 121.3, 72.2, 42.9, 19.4. HRMS (ESI) *m*/*z*: $[M+H]^+$ calcd for $C_{18}H_{18}NO$, 264.1383; found, 264.1380.

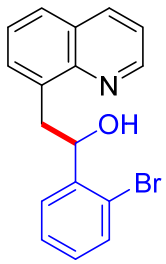


1-(2-Fluorophenyl)-2-(quinolin-8-yl)ethan-1-ol ***(3as)***. The title compound was isolated as a white solid (eluent: EtOAc/petroleum ether = 1/5 to 1/2), 43.8 mg, 82%; mp 88–89 °C. ^{1}H

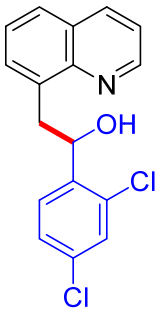
NMR ($CDCl_3$, 600 MHz): δ 8.98 – 8.89 (m, 1H), 8.21 (d, J = 8.0 Hz, 1H), 7.70 (d, J = 7.7 Hz, 1H), 7.51 – 7.38 (m, 4H), 7.17 (q, J = 6.4 Hz, 1H), 7.05 – 6.97 (m, 2H), 5.46 (d, J = 6.6 Hz, 1H), 3.73 (dd, J = 14.2, 7.5 Hz, 1H), 3.66 (d, J = 13.6 Hz, 1H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 151 MHz): δ 159.68 (d, J = 244.6 Hz), 149.2, 147.3, 137.9, 137.5, 132.4 (d, J = 13.1 Hz), 131.8, 128.7, 128.2 (d, J = 8.2 Hz), 127.5 (d, J = 4.5 Hz), 127.0, 126.9, 123.9 (d, J = 2.9 Hz), 121.2, 114.8 (d, J = 21.6 Hz), 69.5, 42.4. ^{19}F NMR ($CDCl_3$, 376 MHz) δ -119.7. δ HRMS (ESI) *m*/*z*: $[M+H]^+$ calcd for $C_{17}H_{15}FNO$, 268.1132; found, 268.1131.



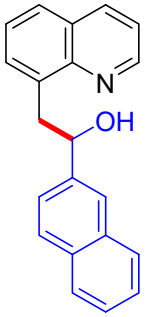
1-(2-Chlorophenyl)-2-(quinolin-8-yl)ethan-1-ol ***(3at)***. The title compound was isolated as a colorless oil (eluent: EtOAc/petroleum ether = 1/5 to 1/2), 51.9 mg, 92%. ^1H NMR ($CDCl_3$, 400 MHz): ^1H NMR (600 MHz, Chloroform-*d*) δ 8.96 – 8.90 (m, 1H), 8.23 (d, J = 8.1 Hz, 1H), 7.72 (d, J = 7.9 Hz, 1H), 7.56 (d, J = 7.0 Hz, 1H), 7.52 – 7.40 (m, 4H), 7.35 (d, J = 7.4 Hz, 1H), 7.16 (dt, J = 15.2, 6.9 Hz, 2H), 5.46 (d, J = 7.0 Hz, 1H), 3.72 (dd, J = 14.2, 7.6 Hz, 1H), 3.61 (d, J = 14.2 Hz, 1H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 151 MHz): δ 149.2, 147.2, 142.7, 138.0, 137.5, 131.6, 131.4, 129.1, 128.7, 127.9, 127.4, 126.93, 126.88, 126.7, 121.1, 72.3, 41.7. HRMS (ESI) *m*/*z*: $[M+H]^+$ calcd for $C_{17}H_{15}ClNO$, 284.0837; found, 284.0837.



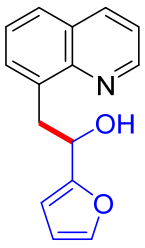
1-(2-Bromophenyl)-2-(quinolin-8-yl)ethan-1-ol ***(3au)***. The title compound was isolated as a white solid (eluent: EtOAc/petroleum ether = 1/5 to 1/2), 58.8 mg, 90%; mp 84–86 °C. ^1H NMR ($CDCl_3$, 600 MHz): δ 8.97 – 8.89 (m, 1H), 8.23 (d, J = 8.0 Hz, 1H), 7.72 (d, J = 8.0 Hz, 1H), 7.58 (d, J = 7.5 Hz, 1H), 7.54 (d, J = 7.7 Hz, 2H), 7.50 – 7.42 (m, 2H), 7.23 (t, J = 7.4 Hz, 1H), 7.08 (t, J = 7.3 Hz, 1H), 5.39 (d, J = 7.3 Hz, 1H), 3.72 (dd, J = 14.3, 7.9 Hz, 1H), 3.59 (d, J = 14.2 Hz, 1H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 151 MHz): δ 149.2, 147.3, 144.2, 138.0, 137.6, 132.5, 131.8, 128.8, 128.4, 127.8, 127.4, 127.04, 126.99, 121.7, 121.2, 74.5, 41.9. HRMS (ESI *m*/*z*: $[M+H]^+$ calcd for $C_{17}H_{15}BrNO$, 328.0332; found, 328.0329.



1-(2,4-Dichlorophenyl)-2-(quinolin-8-yl)ethan-1-ol ***(3av)***. The title compound was isolated as a white solid (eluent: EtOAc/petroleum ether = 1/5 to 1/2), 57.4 mg, 90%; mp 94–97 °C. ^{1}H NMR ($CDCl_3$, 600 MHz): δ 8.97 – 8.90 (m, 1H), 8.24 (d, *J* = 8.0 Hz, 1H), 7.75 – 7.70 (m, 1H), 7.63 (br, 1H), 7.49 (dd, *J* = 8.1, 4.2 Hz, 1H), 7.47 – 7.41 (m, 3H), 7.36 (s, 1H), 7.12 (d, *J* = 7.8 Hz, 1H), 5.41 (d, *J* = 6.0 Hz, 1H), 3.81 – 3.49 (m, 2H). ^{13}C{^{1}H} NMR ($CDCl_3$, 151 MHz): δ 149.2, 147.2, 141.4, 137.7, 137.6, 132.8, 132.0, 131.8, 128.9, 128.8, 128.6, 127.1, 127.1, 127.1, 121.3, 72.0, 41.5. HRMS (ESI) *m/z*: $[M+H]^+$calcd for $C_{17}H_{14}Cl_2NO$, 318.0447; found, 318.0451.

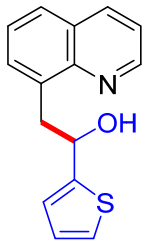


1-(Naphthalen-2-yl)-2-(quinolin-8-yl)ethan-1-ol ***(3aw)***. The title compound was isolated as a white solid (eluent: EtOAc/petroleum ether = 1/5 to 1/2), 48.7 mg, 81%; mp 99–103 °C. ^{1}H NMR ($CDCl_3$, 600 MHz): δ 9.03 – 8.91 (m, 1H), 8.22 (d, *J* = 8.0 Hz, 1H), 7.90 (s, 1H), 7.83 (d, *J* = 7.5 Hz, 3H), 7.72 (d, *J* = 7.7 Hz, 1H), 7.57 (d, *J* = 8.3 Hz, 1H), 7.51 – 7.38 (m, 5H), 7.02 (s, 1H), 5.32 (d, *J* = 7.1 Hz, 1H), 3.81 (dd, *J* = 14.1, 8.2 Hz, 1H), 3.68 (d, *J* = 13.7 Hz, 1H). ^{13}C{^{1}H} NMR ($CDCl_3$, 151 MHz): δ 149.3, 147.4, 143.0, 138.0, 137.5, 133.5, 132.9, 131.7, 128.8, 128.1, 127.9, 127.7, 127.0, 126.9, 125.9, 125.5, 124.5, 124.3, 121.2, 75.7, 44.1. HRMS (ESI) *m/z*: $[M+H]^+$ calcd for $C_{21}H_{18}NO$, 300.1383; found, 300.1386.

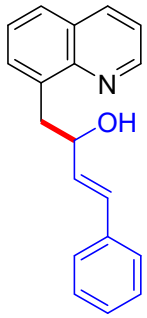


1-(Furan-2-yl)-2-(quinolin-8-yl)ethan-1-ol ***(3ax)***. The title compound was isolated as a

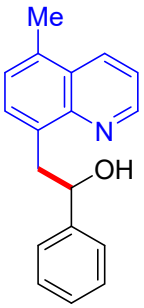
colorless oil (eluent: EtOAc/petroleum ether = 1/5 to 1/2), 34.8 mg, 73%. ^{1}H NMR (DMSO-d_6, 400 MHz): δ 8.94 (dd, J = 4.1, 1.6 Hz, 1H), 8.34 (dd, J = 8.2, 1.8 Hz, 1H), 7.94 – 7.69 (m, 1H), 7.59 – 7.40 (m, 4H), 6.34 (dd, J = 3.0, 1.9 Hz, 1H), 6.23 (d, J = 3.1 Hz, 1H), 5.47 (d, J = 5.0 Hz, 1H), 5.05 (s, 1H), 3.88 – 3.45 (m, 2H). ^{13}C{^{1}H} NMR (DMSO-d_6, 101 MHz): δ 158.0, 149.6, 146.4, 141.5, 136.6, 136.5, 130.7, 127.9, 126.6, 126.1, 121.2, 110.1, 105.5, 66.3, 38.1. HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{15}H_{14}NO_2$, 240.1019; found, 240.1020.



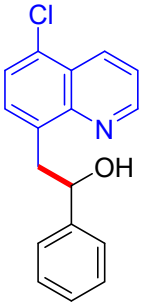
2-(Quinolin-8-yl)-1-(thiophen-2-yl)ethan-1-ol ***(3ay)***. The title compound was isolated as a colorless oil (eluent: EtOAc/petroleum ether = 1/5 to 1/2), 42.5 mg, 79%. ^{1}H NMR ($CDCl_3$, 600 MHz): δ 8.96 – 8.85 (m, 1H), 8.21 (d, J = 8.0 Hz, 1H), 7.73 (d, J = 7.9 Hz, 1H), 7.51 (d, J = 6.7 Hz, 1H), 7.49 – 7.41 (m, 2H), 7.17 (d, J = 4.6 Hz, 1H), 7.02 – 6.90 (m, 2H), 5.39 (d, J = 7.2 Hz, 1H), 3.81 (dd, J = 14.1, 8.2 Hz, 1H), 3.67 (d, J = 13.9 Hz, 1H). ^{13}C{^{1}H} NMR ($CDCl_3$, 151 MHz): δ 150.2, 149.3, 147.2, 137.5, 131.9, 128.8, 127.2, 126.9, 126.6, 123.8, 122.6, 121.2, 71.8, 44.5. HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{15}H_{14}NOS$, 256.0791; found, 256.0795.



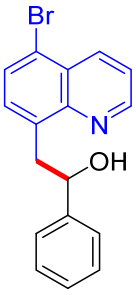
4-Phenyl-1-(quinolin-8-yl)but-3-en-2-ol ***(3az)***. The title compound was isolated as a colorless oil (eluent: EtOAc/petroleum ether = 1/5 to 1/2), 24.7 mg, 45%. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.91 (dd, J = 4.2, 1.6 Hz, 1H), 8.24 – 8.18 (m, 1H), 7.77 – 7.71 (m, 1H), 7.60 (d, J = 6.8 Hz, 1H), 7.51 (d, J = 7.7 Hz, 1H), 7.45 (dd, J = 8.3, 4.3 Hz, 1H), 7.35 (d, J = 7.2 Hz, 2H), 7.29 (t, J = 7.5 Hz, 2H), 7.20 (t, J = 7.2 Hz, 1H), 6.68 (d, J = 15.8 Hz, 1H), 6.33 (dd, J = 15.8, 6.1 Hz, 1H), 4.73 (q, J = 5.3 Hz, 1H), 3.61 – 3.55 (m, 2H). ^{13}C{^{1}H} NMR ($CDCl_3$, 101 MHz): δ 149.3, 147.3, 137.9, 137.4, 137.3, 133.1, 131.7, 129.3, 128.9, 128.6, 127.3, 127.1, 126.9, 126.6, 121.2, 73.6, 42.0. HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{19}H_{18}NO$, 276.1383; found,276.1386.



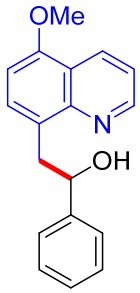
2-(5-Methylquinolin-8-yl)-1-phenylethan-1-ol ***(3ba)***. The title compound was isolated as a colorless oil (eluent: EtOAc/petroleum ether = 1/5 to 1/2), 40.6 mg, 77%. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.95 – 8.89 (m, 1H), 8.36 (d, *J* = 8.4 Hz, 1H), 7.46 (dd, *J* = 8.5, 3.9 Hz, 1H), 7.41 (d, *J* = 7.4 Hz, 2H), 7.34 – 7.28 (m, 3H), 7.26 – 7.21 (m, 2H), 6.97 (br, 1H), 5.11 (d, *J* = 6.4 Hz, 1H), 3.66 (dd, *J* = 13.7, 7.7 Hz, 1H), 3.52 (d, *J* = 13.9 Hz, 1H), 2.64 (s, 3H). ^{13}C{^{1}H} NMR ($CDCl_3$, 101 MHz): δ 148.7, 147.6, 145.7, 136.0, 133.8, 133.6, 131.3, 128.2, 128.1, 127.3, 126.9, 125.9, 120.7, 75.7, 44.2, 18.6. HRMS (ESI) *m*/*z*: $[M+H]^+$ calcd for $C_{18}H_{18}NO$, 264.1383; found, 264.1380.



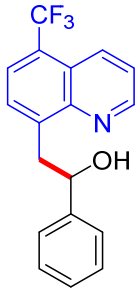
2-(5-Chloroquinolin-8-yl)-1-phenylethan-1-ol ***(3ca)***. The title compound was isolated as a white solid (eluent: EtOAc/petroleum ether = 1/5 to 1/2), 39.1 mg, 69%; mp 70–72 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.94 (d, *J* = 3.0 Hz, 1H), 8.64 – 8.58 (m, 1H), 7.53 (dd, *J* = 8.5, 4.1 Hz, 1H), 7.47 (d, *J* = 7.7 Hz, 1H), 7.36 (d, *J* = 7.3 Hz, 2H), 7.30 (t, *J* = 7.8 Hz, 3H), 7.22 (d, *J* = 7.1 Hz, 1H), 6.13 (br, 1H), 5.16 – 5.07 (m, 1H), 3.71 – 3.48 (m, 2H). ^{13}C{^{1}H} NMR ($CDCl_3$, 101 MHz): δ 149.9, 147.9, 145.1, 137.2, 134.1, 131.2, 130.0, 128.3, 127.1, 126.75, 126.66, 125.8, 121.9, 75.3, 43.6. HRMS (ESI) *m*/*z*: $[M+H]^+$ calcd for $C_{17}H_{15}ClNO$, 284.0837; found, 284.0832.



2-(5-Bromoquinolin-8-yl)-1-phenylethan-1-ol ***(3da)***. The title compound was isolated as a white solid (eluent: EtOAc/petroleum ether = 1/15 to 1/10), 36.2 mg, 55%; mp 78-81 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.93 (d, *J* = 3.0 Hz, 1H), 8.59 (d, *J* = 8.5 Hz, 1H), 7.68 (d, *J* = 7.7 Hz, 1H), 7.54 (dd, *J* = 8.5, 3.8 Hz, 1H), 7.37 (d, *J* = 7.3 Hz, 2H), 7.31 (t, *J* = 7.4 Hz, 2H), 7.24 (dd, *J* = 7.4, 3.6 Hz, 2H), 6.08 (br, 1H), 5.29 – 5.03 (m, 1H), 3.76 – 3.49 (m, 2H). ^{13}C{^{1}H} NMR ($CDCl_3$, 101 MHz): δ 150.0, 148.0, 145.1, 138.0, 136.8, 131.8, 130.5, 128.3, 128.0, 127.1, 125.8, 122.3, 120.4, 76.6, 43.6. HRMS (ESI) *m/z*: $[M+H]^+$ calcd for $C_{17}H_{15}BrNO$,328.0332; found, 328.0333.

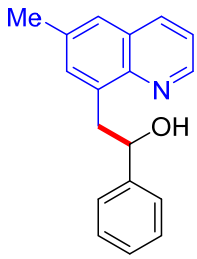


2-(5-Methoxyquinolin-8-yl)-1-phenylethan-1-ol ***(3ea)***. The title compound was isolated as a colorless oil (eluent: EtOAc/petroleum ether = 1/5 to 1/2), 46.1 mg, 8.%. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.89 (d, *J* = 4.0 Hz, 1H), 8.62 (d, *J* = 8.4 Hz, 1H), 7.41 (dd, *J* = 8.3, 3.8 Hz, 3H), 7.35 – 7.27 (m, 3H), 7.22 (d, *J* = 8.2 Hz, 1H), 6.92 (br, 1H), 6.71 (d, *J* = 7.9 Hz, 1H), 5.09 (d, *J* = 6.3 Hz, 1H), 3.94 (s, 3H), 3.59 (dd, *J* = 14.2, 8.0 Hz, 1H), 3.47 (dd, *J* = 14.2, 1.9 Hz, 1H). ^{13}C{^{1}H} NMR ($CDCl_3$, 101 MHz): δ 154.1, 149.5, 147.8, 145.7, 132.1, 131.4, 129.6, 128.2, 126.9, 125.9, 121.2, 120.2, 104.3, 75.7, 55.8, 43.8. HRMS (ESI) *m/z*: $[M+H]^+$ calcd for $C_{18}H_{18}NO_2$, 280.1332; found, 280.1330.

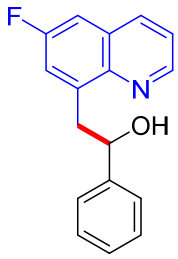


1-Phenyl-2-(5-(trifluoromethyl)quinolin-8-yl)ethan-1-ol ***(3fa)***. The title compound was isolated as a white solid (eluent: EtOAc/petroleum ether = 1/5 to 1/2), 37.1 mg, 50%; mp 118-120 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 9.00 (s, 1H), 8.55 (d, *J* = 8.4 Hz, 1H), 7.79 (d, *J* = 7.4 Hz, 1H), 7.58 (dd, *J* = 8.6, 3.1 Hz, 1H), 7.44 (d, *J* = 7.4 Hz, 1H), 7.39 (d, *J* = 7.4 Hz, 2H), 7.32 (t, *J* = 7.3 Hz, 2H), 7.25 (d, *J* = 6.3 Hz, 1H), 5.95 (br, 1H), 5.17 (s, 1H), 3.80 – 3.58 (m, 2H). ^{13}C{^{1}H} NMR ($CDCl_3$, 151 MHz): δ 149.9, 147.4, 144.8, 143.0, 133.7, 129.8, 128.3, 127.2, 125.7, 125.2 (q, *J* = 5.5 Hz), 125.0, 124.8, δ 124.1 (q, *J* = 273.5 Hz), 122.3, 75.0, 43.7. ^{19}F NMR

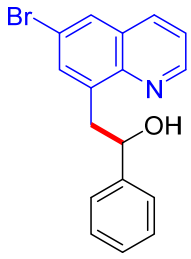
($CDCl_3$, 376 MHz) δ -59.0. HRMS (ESI) *m/z*: $[M+H]^+$ calcd for $C_{18}H_{15}F_3NO$, 318.1100; found, 318.1095.



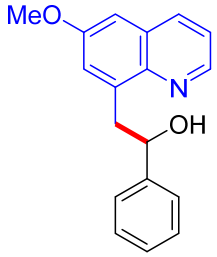
2-(6-Methylquinolin-8-yl)-1-phenylethan-1-ol ***(3ga)***. The title compound was isolated as a colorless oil (eluent: EtOAc/petroleum ether = 1/5 to 1/2), 41.3 mg, 78%. ^1H NMR ($CDCl_3$, 400 MHz): δ 8.93 – 8.78 (m, 1H), 8.09 (d, *J* = 8.1 Hz, 1H), 7.44 (d, *J* = 9.2 Hz, 3H), 7.39 (dd, *J* = 8.2, 4.1 Hz, 1H), 7.32 (t, *J* = 7.3 Hz, 2H), 7.28 (s, 1H), 7.24 (d, *J* = 6.9 Hz, 1H), 6.99 (br, 1H), 5.09 (d, *J* = 7.6 Hz, 1H), 3.69 (dd, *J* = 13.8, 8.5 Hz, 1H), 3.46 (d, *J* = 14.0 Hz, 1H), 2.45 (s, 3H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 101 MHz): δ 148.4, 146.0, 145.7, 137.8, 136.7, 133.9, 128.9, 128.2, 127.0, 125.9, 125.8, 121.2, 75.7, 44.4, 21.6. HRMS (ESI) *m/z*: $[M+H]^+$ calcd for $C_{18}H_{18}NO$, 264.1383; found, 264.1381.



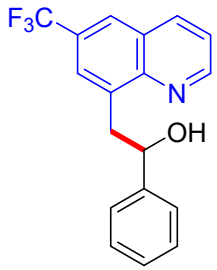
2-(6-Fluoroquinolin-8-yl)-1-phenylethan-1-ol ***(3ha)***. The title compound was isolated as a white solid (eluent: EtOAc/petroleum ether = 1/5 to 1/2), 32.1 mg, 60%; mp 108-112 °C. ^1H NMR ($CDCl_3$, 400 MHz): δ 8.89 (d, *J* = 3.0 Hz, 1H), 8.19 – 8.10 (m, 1H), 7.47 (dd, *J* = 8.3, 4.1 Hz, 1H), 7.41 (d, *J* = 7.3 Hz, 2H), 7.37 – 7.30 (m, 3H), 7.28 – 7.20 (m, 2H), 6.37 (s, 1H), 5.15 (dd, *J* = 8.2, 2.7 Hz, 1H), 3.70 (dd, *J* = 14.0, 8.0 Hz, 1H), 3.58 (dd, *J* = 13.9, 1.9 Hz, 1H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 101 MHz): δ 160.0 (d, *J* = 248.9 Hz), 148.5 (d, *J* = 2.5 Hz), 145.0, 144.5, 141.3 (d, *J* = 8.6 Hz), 136.7 (d, *J* = 5.6 Hz), 129.4 (d, *J* = 10.2 Hz), 128.3, 127.1, 125.7, 121.9, 121.5 (d, *J* = 25.5 Hz), 109.6 (d, *J* = 21.2 Hz), 75.1, 43.8. ^{19}F NMR ($CDCl_3$, 376 MHz) δ -112.8. HRMS (ESI) *m/z*: $[M+H]^+$ calcd for $C_{17}H_{15}FNO$, 268.1132; found, 268.1130.



2-(6-Bromoquinolin-8-yl)-1-phenylethan-1-ol ***(3ia)***. The title compound was isolated as a colorless oil (eluent: EtOAc/petroleum ether = 1/5 to 1/2), 45.1 mg, 69%. ^{1}H NMR ($CDCl_3$, 400 MHz):δ 8.90 (d, *J* = 3.9 Hz, 1H), 8.11 – 8.04 (m, 1H), 7.85 (d, *J* = 2.0 Hz, 1H), 7.53 (d, *J* = 2.0 Hz, 1H), 7.47 – 7.38 (m, 3H), 7.33 (t, *J* = 7.5 Hz, 2H), 7.26 (s, 1H), 6.21 (br, 1H), 5.10 (d, *J* = 7.5 Hz, 1H), 3.66 (dd, *J* = 14.0, 8.3 Hz, 1H), 3.49 (d, *J* = 13.5 Hz, 1H). ^{13}C{^{1}H} NMR ($CDCl_3$, 101 MHz): δ 149.6, 146.0, 145.1, 140.3, 136.3, 134.6, 129.8, 128.8, 128.4, 127.2, 125.8, 122.0, 120.6, 75.3, 43.7. HRMS (ESI) *m/z*: $[M+H]^+$ calcd for $C_{17}H_{15}BrNO$, 328.0332; found, 328.0336.

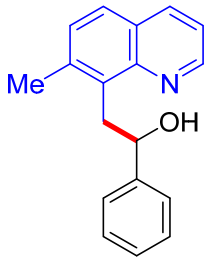


2-(6-Methoxyquinolin-8-yl)-1-phenylethan-1-ol ***(3ja)***. The title compound was isolated as a colorless oil (eluent: EtOAc/petroleum ether = 1/5 to 1/2), 38.0 mg, 68%. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.74 (d, *J* = 3.1 Hz, 1H), 8.06 (d, *J* = 8.1 Hz, 1H), 7.42 (d, *J* = 7.4 Hz, 2H), 7.38 (dd, *J* = 8.2, 4.1 Hz, 1H), 7.32 (t, *J* = 7.4 Hz, 2H), 7.23 (d, *J* = 6.7 Hz, 1H), 7.10 (d, *J* = 2.6 Hz, 1H), 7.00 – 6.87 (d, *J* = 2.6 Hz, 1H), 5.10 (d, *J* = 7.2 Hz, 1H), 3.86 (s, 3H), 3.67 (dd, *J* = 13.8, 8.1 Hz, 1H), 3.46 (d, *J* = 14.0 Hz, 1H). ^{13}C{^{1}H} NMR ($CDCl_3$, 101 MHz): ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.6, 146.7, 145.5, 143.6, 139.8, 136.0, 130.0, 128.3, 127.0, 125.8, 124.2, 121.5, 104.1, 75.4, 55.5, 44.3. HRMS (ESI) *m/z*: $[M+H]^+$ calcd for $C_{18}H_{17}NO_2$, 280.1332; found, 280.1330.

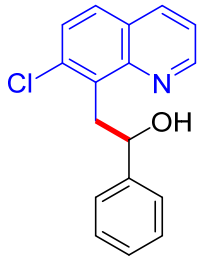


1-Phenyl-2-(6-(trifluoromethyl)quinolin-8-yl)ethan-1-ol ***(3ka)***. The title compound was isolated as a colorless oil (eluent: EtOAc/petroleum ether = 1/5 to 1/2), 50.4 mg, 79%. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 9.02 (d, *J* = 4.0 Hz, 1H), 8.27 (d, *J* = 8.3 Hz, 1H), 8.02 (s, 1H), 7.58 (s, 1H), 7.54 (dd, *J* = 8.3, 4.2 Hz, 1H), 7.40 (d, *J* = 7.5 Hz, 2H), 7.32 (t, *J* = 7.5 Hz, 2H), 7.27 – 7.20 (m, 1H), 5.92 (s, 1H), 5.14 (d, *J* = 6.2 Hz, 1H), 3.73 (dd, *J* = 13.9, 8.2 Hz, 1H), 3.62 (dd, *J* = 13.9, 2.1 Hz, 1H). ^{13}C{^{1}H} NMR ($CDCl_3$, 101 MHz): ^{13}C NMR (101 MHz, $CDCl_3$) δ 151.5, 148.4, 144.9, 139.7, 138.2, 128.7, 128.4, 127.7, 127.3, 126.9 (q, *J* = 2.8 Hz), 125.8, 124.7 (q, *J* = 4.3 Hz), 123.9 (q, *J* = 272.1 Hz), 122.3, 75.2, 43.7. ^{19}F NMR ($CDCl_3$, 376 MHz) δ -62.5. HRMS

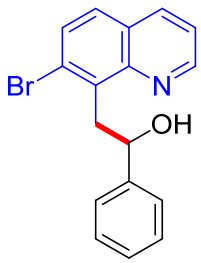
(ESI) *m/z*: $[M+H]^+$ calcd for $C_{18}H_{15}F_3NO$, 318.1100; found, 318.1100.



2-(7-Methylquinolin-8-yl)-1-phenylethan-1-ol ***(3la)***. The title compound was isolated as a colorless oil (eluent: EtOAc/*n*-pentane = 1/5 to 1/2), 39.4 mg, 75%. ^{1}H NMR ($CDCl_3$, 400 MHz): ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.88 (d, *J* = 3.3 Hz, 1H), 8.12 (d, *J* = 8.1 Hz, 1H), 7.60 (d, *J* = 8.3 Hz, 1H), 7.42 (d, *J* = 7.5 Hz, 2H), 7.38 – 7.30 (m, 4H), 7.27 – 7.22 (m, 1H), 6.71 (br, 1H), 5.27 – 4.96 (m, 1H), 3.78 (dd, *J* = 14.1, 8.2 Hz, 1H), 3.57 (d, *J* = 14.0 Hz, 1H), 2.32 (s, 2H). ^{13}C{^{1}H} NMR ($CDCl_3$, 101 MHz): δ 149.3, 147.9, 145.9, 138.7, 137.1, 134.9, 130.4, 128.3, 127.1, 127.0, 126.0, 125.8, 120.3, 75.4, 38.4, 20.5. HRMS (ESI) *m/z*: $[M+H]^+$ calcd for $C_{18}H_{18}NO$, 264.1383; found, 264.1377.

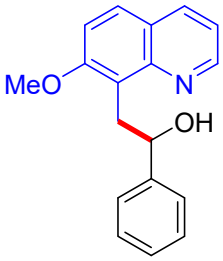


2-(7-Chloroquinolin-8-yl)-1-phenylethan-1-ol ***(3ma)***. The title compound was isolated as a colorless oil (eluent: EtOAc/petroleum ether = 1/10 to 1/5), 23.9 mg, 42%. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.95 (s, 1H), 8.18 (d, *J* = 8.2 Hz, 1H), 7.66 (d, *J* = 11.0 Hz, 1H), 7.55 (d, *J* = 8.5 Hz, 3H), 7.49 – 7.42 (m, 1H), 7.41 – 7.33 (m, 2H), 7.31 – 7.24 (m, 1H), 5.96 (br, 1H), 5.11 (d, *J* = 9.2 Hz, 1H), 3.97 (dd, *J* = 18.5, 4.7 Hz, 1H), 3.73 (d, *J* = 14.0 Hz, 1H). ^{13}C{^{1}H} NMR ($CDCl_3$, 101 MHz): δ 150.4, 148.3, 145.6, 137.2, 136.1, 135.5, 128.8, 128.4, 127.4, 127.3, 127.2, 125.7, 121.3, 74.9, 39.5. HRMS (ESI) *m/z*: $[M+H]^+$ calcd for $C_{17}H_{14}ClNO$, 284.0837; found, 284.0840.

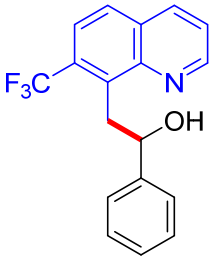


2-(7-Bromoquinolin-8-yl)-1-phenylethan-1-ol ***(3na)***. The title compound was isolated as a

colorless oil (eluent: EtOAc/petroleum ether = 1/10 to 1/5), 25.1 mg, 38%. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 9.03 – 8.87 (m, 1H), 8.20 (d, *J* = 8.2 Hz, 1H), 7.78 – 7.72 (m, 1H), 7.63 – 7.57 (m, 3H), 7.51 – 7.46 (m, 1H), 7.43 – 7.36 (m, 2H), 7.33 – 7.26 (m, 1H), 5.95 (br, 1H), 5.11 (d, *J* = 9.6 Hz, 1H), 4.05 (dd, *J* = 13.9, 9.8 Hz, 1H), 3.70 (d, *J* = 14.0 Hz, 1H). ^{13}C{^{1}H} NMR ($CDCl_3$, 101 MHz): δ 150.2, 148.2, 145.6, 137.5, 137.2, 131.6, 128.3, 127.6, 127.5, 127.11, 127.06, 125.6, 121.4, 74.8, 42.3. HRMS (ESI) *m/z*: $[M+H]^+$ calcd for $C_{17}H_{14}BrNO$, 328.0332; found, 328.0333.



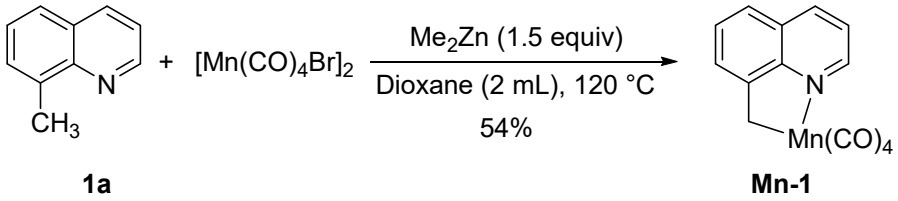
2-(7-Methoxyquinolin-8-yl)-1-phenylethan-1-ol ***(3oa)***. The title compound was isolated as a colorless oil (eluent: EtOAc/petroleum ether = 1/10 to 1/5), 43.8 mg, 79%. ^{1}H NMR ($CDCl_3$, 400 MHz): ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.89 – 8.84 (m, 1H), 8.10 (d, *J* = 8.2 Hz, 1H), 7.69 (d, *J* = 9.0 Hz, 1H), 7.47 (d, *J* = 7.5 Hz, 2H), 7.35 – 7.27 (m, 4H), 7.23 (d, *J* = 7.5 Hz, 1H), 6.51 (br, 1H), 5.07 (dd, *J* = 7.8, 2.8 Hz, 1H), 3.82 (s, 3H), 3.76 – 3.64 (m, 2H). ^{13}C{^{1}H} NMR ($CDCl_3$, 101 MHz): δ 157.9, 150.1, 148.4, 146.2, 137.0, 128.0, 127.5, 126.7, 125.8, 123.7, 122.9, 118.9, 114.2, 75.4, 56.5, 34.6. HRMS (ESI) *m/z*: $[M+H]^+$ calcd for $C_{18}H_{18}NO_2$, 280.1332; found, 280.1331.



1-Phenyl-2-(7-(trifluoromethyl)quinolin-8-yl)ethan-1-ol ***(3pa)***. The title compound was isolated as a colorless oil (eluent: EtOAc/petroleum ether = 1/10 to 1/5), 27.1 mg, 43%. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 9.06 (s, 1H), 8.28 (d, *J* = 8.1 Hz, 1H), 7.87 (s, 2H), 7.64 (d, *J* = 7.5 Hz, 2H), 7.62 – 7.55 (m, 1H), 7.44 (t, *J* = 7.4 Hz, 2H), 7.34 (d, *J* = 7.3 Hz, 1H), 6.42 (br, 1H), 5.10 (d, *J* = 9.1 Hz, 1H), 4.18 – 4.05 (m, 1H), 3.58 (d, *J* = 14.1 Hz, 1H). ^{13}C{^{1}H} NMR ($CDCl_3$, 101 MHz): δ 150.8, 147.7, 146.1, 138.8, 137.5, 130.3, 130.1, 130.0, 128.6, 127.3, 126.0 (q, *J* = 275.7 Hz),125.8, 123.4 (q, *J* = 5.5 Hz). 122.9, 76.0, 38.8. ^{19}F NMR ($CDCl_3$, 376 MHz) δ -57.6. HRMS (ESI) *m/z*: $[M+H]^+$ calcd for $C_{18}H_{15}F_3NO$, 318.1100; found, 318.1105.

3. Mechanistic studies

3.1 Procedure for the preparation of Mn-1

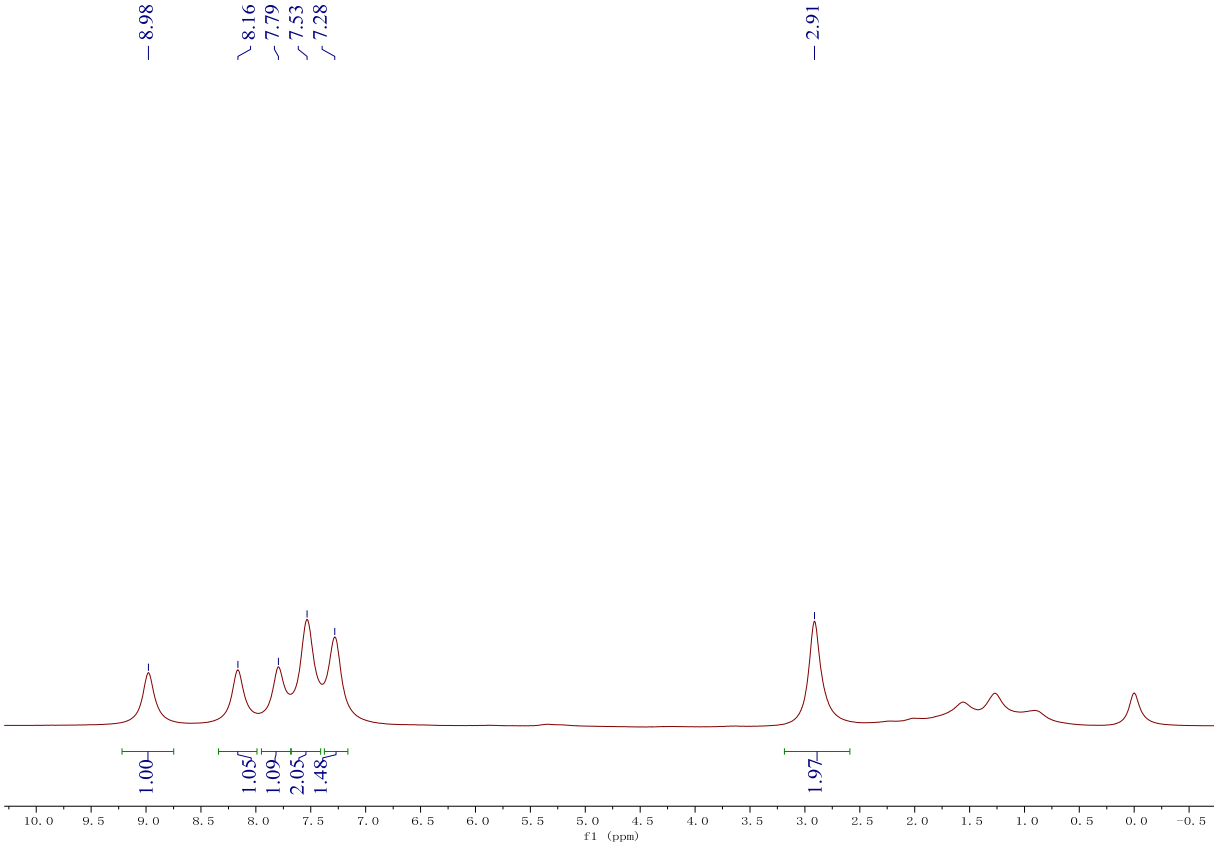


1a **Mn-1**

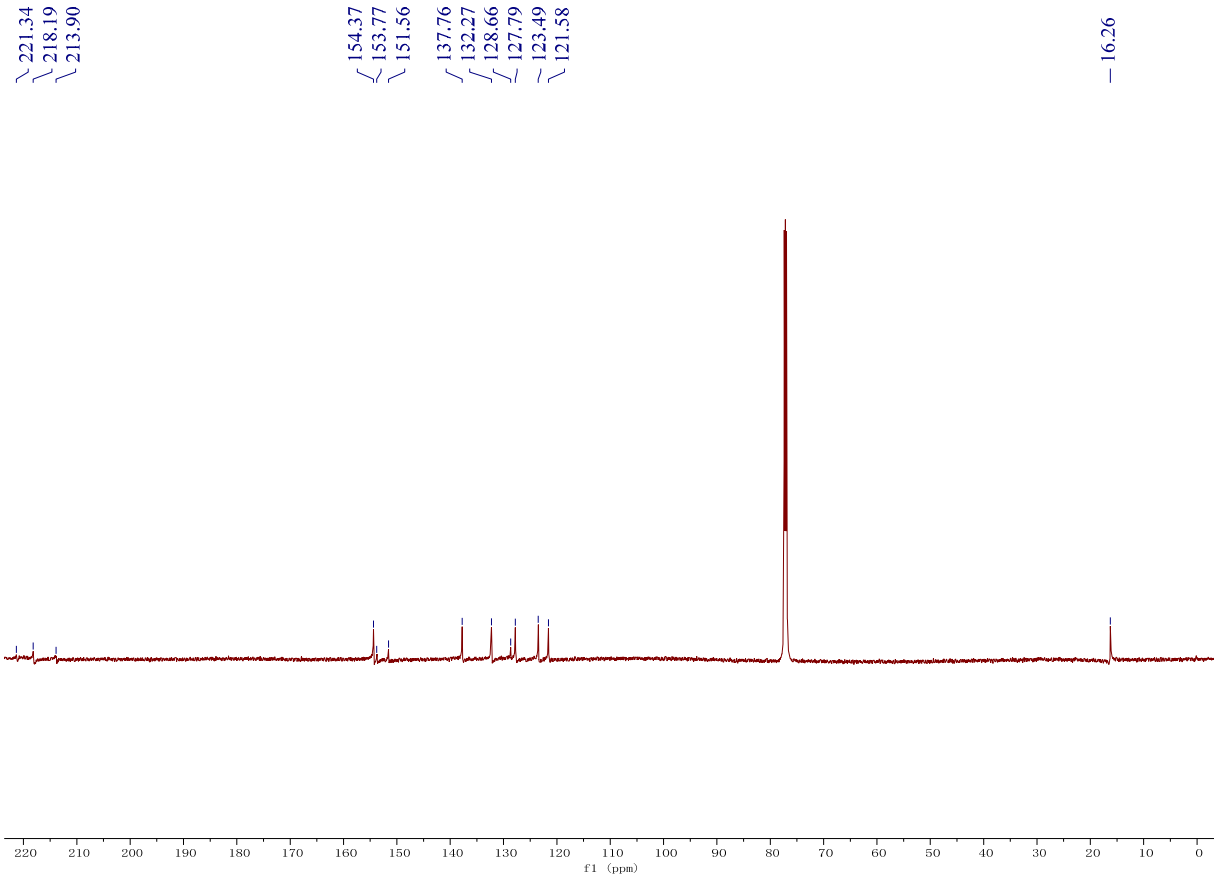
Scheme S3.1

$[Mn(CO)_4Br]_2$ (0.1 mmol, 49 mg) was added into a Schlenk tube under Ar atmosphere. Dry 1,4-dioxane (2.0 mL), 8-methylquinoline **1a** (0.2 mmol, 31 mg), and Me_2Zn (1 M in toluene, 0.3 mL, 0.3 mmol, 1.5 equiv) were then injected into the reaction tube. The reaction mixture was stirred at 120 °C for 24 h. The mixture was diluted with ethyl acetate (20 mL) and filtered through a short pad of silica gel. The solvent was removed by rotary evaporation and the residue was purified by silica gel column chromatography (eluent: EtOAc/petroleum ether = 10/1) to afford the manganacycle **Mn-1**[3] in 54% yield (33.4 mg) (*Note: please as far as possible decrease the time of the reaction mixture or **Mn-1** in the solvent in air*). Mp 106–107 °C. **^{1}H NMR ($CDCl_3$, 400 MHz)**: δ 8.98 (s, 1H), 8.16 (s, 1H), 7.79 (s, 1H), 7.53 (s, 2H), 7.28 (s, 1H), 2.91 (s, 2H). **^{13}C NMR ($CDCl_3$, 101 MHz)**: δ 221.3, 218.2, 213.9, 154.4, 153.8, 151.6, 137.8, 132.3, 128.7, 127.8, 123.5, 121.6, 16.3. Anal. Calcd for $C_{14}H_8MnNO_4$: C, 54.39; H, 2.61; N, 4.53. Found: C, 54.65; H, 2.78; N, 4.27.

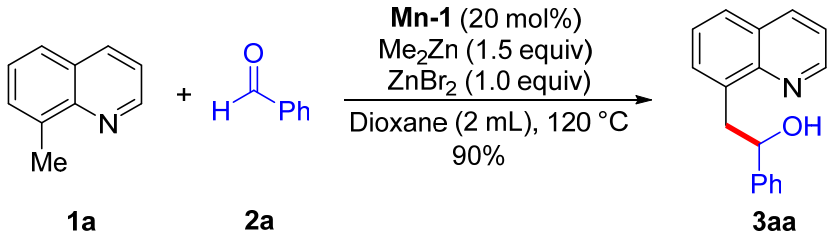
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **Mn-1**



^{13}C NMR (101 MHz, $CDCl_3$) spectrum of **Mn-1**



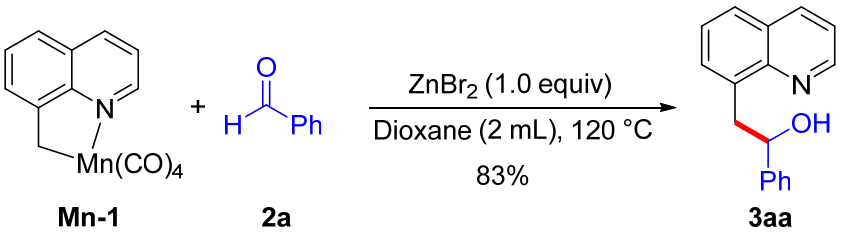
3.2 Procedure for the preparation of 3aa with Mn-1 as catalyst



Scheme S3.2

A mixture of **1a** (0.2 mmol, 28.6 mg 1.0 equiv), **2a** (0.4 mmol, 42.4 mg, 2.0 equiv), **Mn-1** (12.4 mg, 0.04 mmol, 20 mol %), Me_2Zn (1 M in toluene, 0.3 mL, 0.3 mmol, 1.5 equiv) and $ZnBr_2$ (45.1 mg, 0.2 mmol, 1.0 equiv) were weighed in a Schlenk tube equipped with a stir bar. Dry 1,4-dioxane (2.0 mL) was added and the mixture was stirred at 120 °C in a pre-heated oil bath for 24 h under Ar atmosphere. After cooling to room temperature, saturated NH_4Cl aqueous solution was added to the system, and then extracted three times with ethyl acetate. After removal of the solvent under vacuum, the purification was performed by flash column chromatography on silica gel (eluent: EtOAc/petroleum ether = 1/5 to 1/2) to afford **3aa** in 90% yield (44.8 mg).

3.3 Procedure for the preparation of 3aa from Mn-1



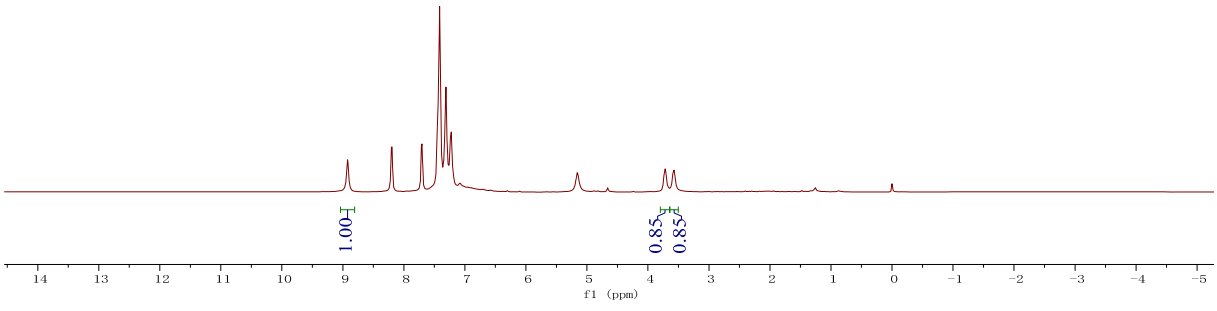
Scheme S3.3

A mixture of **Mn-1** (0.2 mmol, 61.8 mg 1.0 equiv), **2a** (0.4 mmol, 42.4 mg, 2.0 equiv), and $ZnBr_2$ (45.1 mg, 0.2 mmol, 1.0 equiv) were weighed in a Schlenk tube equipped with a stir bar. Dry 1,4-dioxane (2.0 mL) was added and the mixture was stirred at 120 °C in a pre-heated oil bath for 24 h under Ar atmosphere. After cooling to room temperature, saturated NH_4Cl aqueous solution was added to the system, and then extracted three times with ethyl acetate. After removal of the solvent under vacuum, the purification was performed by flash column chromatography on silica gel (eluent: EtOAc/petroleum ether = 1/5 to 1/2) to afford **3ae** in 83% yield (41.4 mg).

3.4 KIE experiments:

Competitive KIE experiment

A mixture of **1a** (0.1 mmol, 0.5 equiv), 8-(methyl-d_3)quinoline **D_3-1a** (0.1 mmol, 0.5 equiv), **2a** (42.4 mg, 0.4 mmol, 2.0 equiv), $[Mn(CO)_4Br]_2$ (9.9 mg, 0.02 mmol, 10 mol %), Me_2Zn (1 M in toluene, 0.3 mL, 0.3 mmol, 1.5 equiv), and $ZnBr_2$ (45.1 mg, 1.2 mmol, 1.0 equiv) were weighed in a Schlenk tube equipped with a stir bar. Dry 1,4-dioxane (2.0 mL) was added and the mixture was stirred at 120 °C in a pre-heated oil bath for 15 min under Ar atmosphere. After cooling to room temperature, saturated NH_4Cl aqueous solution was added to the system, and then extracted three times with ethyl acetate. After removal of the solvent under vacuum, the residue was solved in $CDCl_3$ and analyzed by ^1H NMR. Competitive kinetic isotope effect (KIE) value was measured to be 5.67 [0.85/(1-0.85) = 5.67].



Parallel KIE experiment:

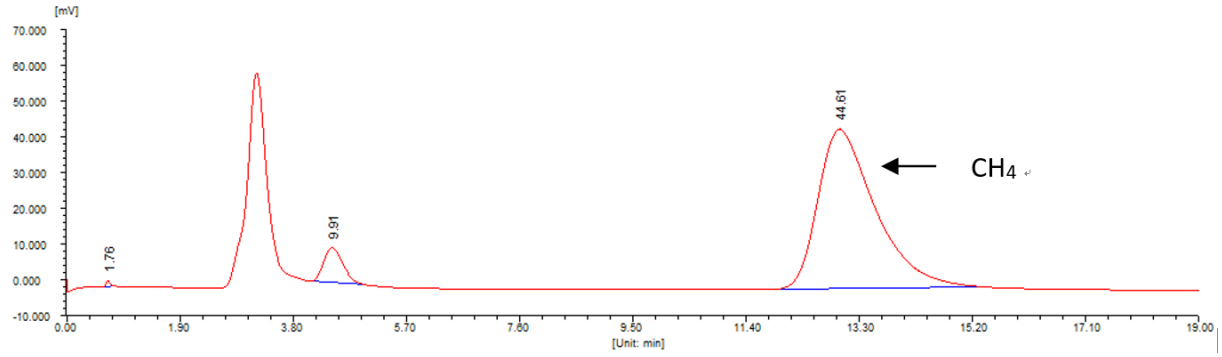
A mixture of **1a** (0.1 mmol, 0.5 equiv) or 8-(methyl-d_3)quinoline **D_3-1a** (0.1 mmol, 0.5 equiv), **2a** (42.4 mg, 0.4 mmol, 2.0 equiv), $[Mn(CO)_4Br]_2$ (9.9 mg, 0.02 mmol, 10 mol %), Me_2Zn (1 M in toluene, 0.3 mL, 0.3 mmol, 1.5 equiv), and $ZnBr_2$ (45.1 mg, 0.2 mmol, 1.0 equiv) were weighed in a Schlenk tube equipped with a stir bar. Dry 1,4-dioxane (2.0 mL) was added and the mixture was stirred at 120 °C in a pre-heated oil bath for 15 min under Ar atmosphere. After cooling to room temperature, saturated NH_4Cl aqueous solution was added to the system, and then extracted three times with ethyl acetate. After removal of the solvent under vacuum, the corresponding yields are 37% and 11%. Parallel kinetic isotope effect (KIE) value was measured to be 3.36 (0.37 / 0.11 = 3.36).

3.5 Experiment to explore the electronic effects of the aldehydes.

A mixture of **1a** (0.2 mmol, 1 equiv), **2i** (54.5 mg, 0.4 mmol, 2.0 equiv), **2k** (69.6 mg, 0.4 mmol, 2.0 equiv), $[Mn(CO)_4Br]_2$ (9.9 mg, 0.02 mmol, 10 mol %), Me_2Zn (1 M in toluene, 0.3 mL, 0.3 mmol, 1.5 equiv), and $ZnBr_2$ (45.1 mg, 0.2 mmol, 1.0 equiv) were weighed in a Schlenk tube equipped with a stir bar. Dry 1,4-dioxane (2.0 mL) was added and the mixture was stirred at 120 °C in a pre-heated oil bath for 24 h under Ar atmosphere. After cooling to room temperature, saturated NH_4Cl aqueous solution was added to the system, and then extracted three times with ethyl acetate. After removal of the solvent under vacuum, the corresponding yields are 12% (**3ai**) and 84% (**3ak**).

3.6 Detection of methane (CH_4) by GC

GC spectrum of the gas of the reaction mixture



4. X-ray crystallography of compounds 3ha and Mn-1

CCDC-2321504 (**3ha**) and 2321505 (**Mn-1**) contain the supplementary crystallographic data. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

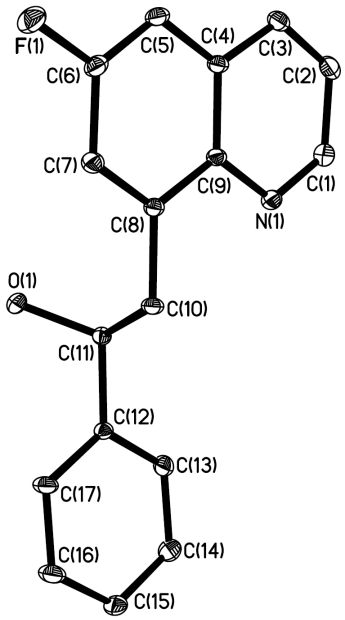


Figure S1. The molecular structure of **3ha**. Thermal ellipsoids are shown at 30% probability level. Hydrogen atoms have been omitted for clarity.

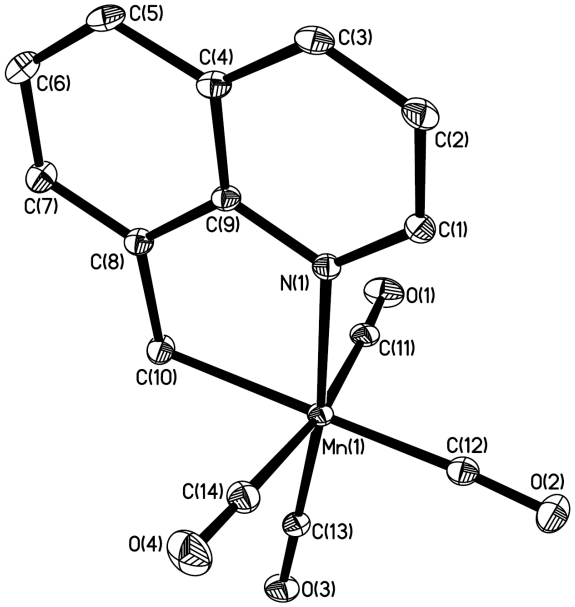


Figure S2. The molecular structure of **Mn-1**. Thermal ellipsoids are shown at 30% probability level. Hydrogen atoms have been omitted for clarity.

5. References:

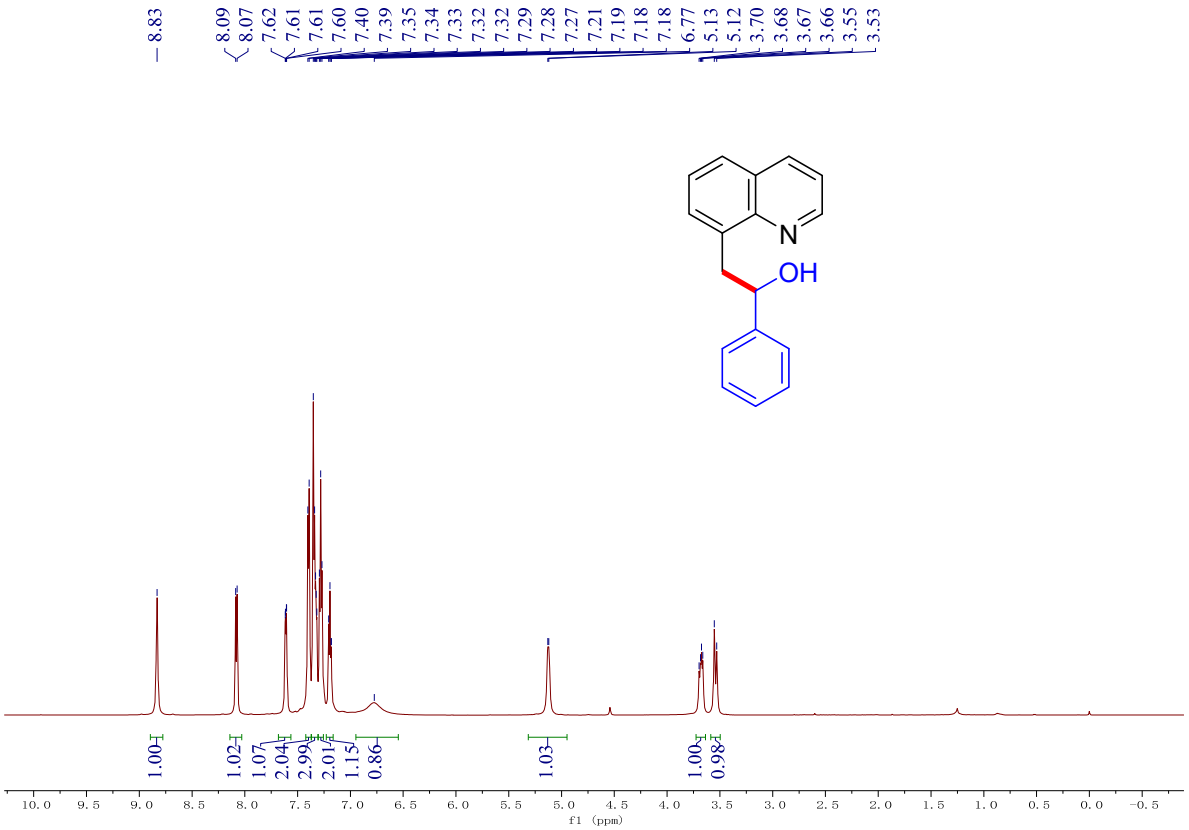
(1) Pang, Y.; Liu, G.; Huang, C.; Yuan, X.; Li, W.; Xie, J. *Angew. Chem., Int. Ed*. **2020**, *59*, 12789–12794.

(2) Wang, N.; Li, R.; Li, L.; Xu, S.; Song, H.; Wang, B. *J. Org. Chem.* **2014**, *79*, 5379−5385.

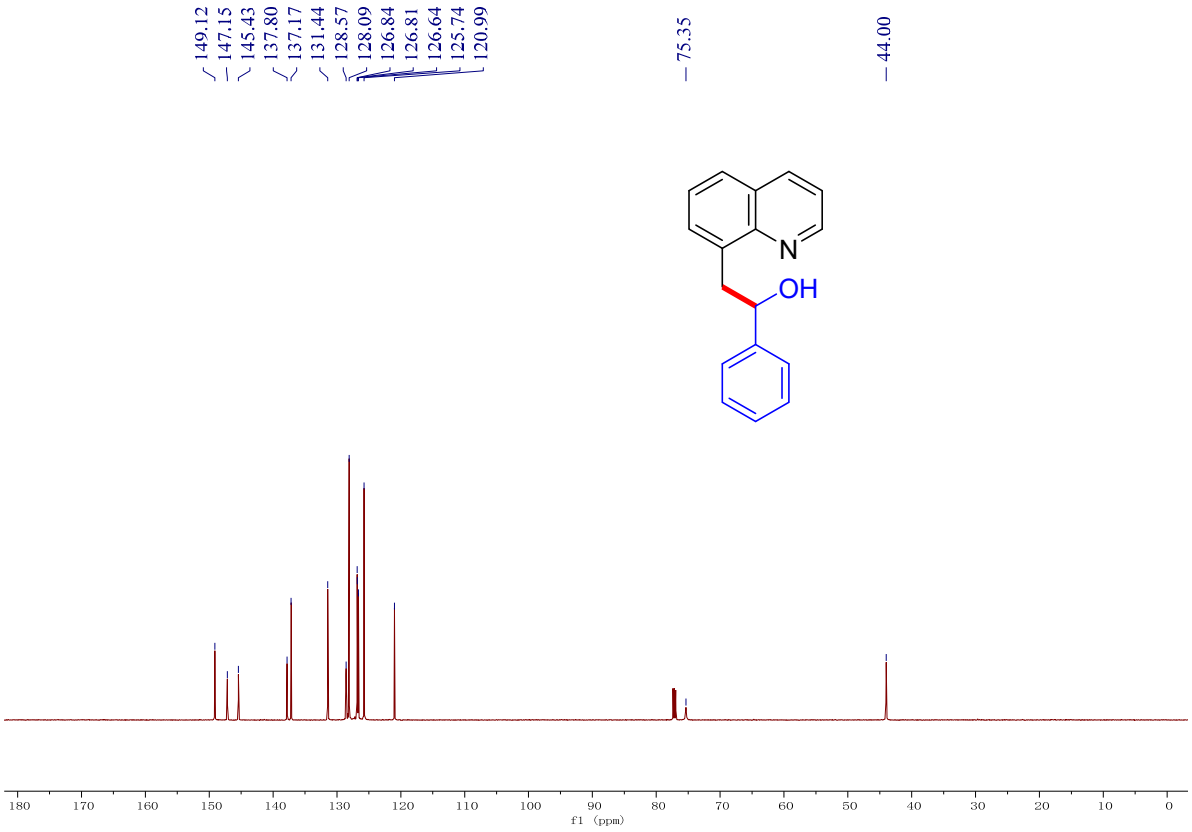
(3) (a) Pfeffer, M.; Urriolabeitia, E. P.; Fischer, J. Effects of Ortho-Substituents in the Synthesis and Stability of Cyclomanganated Benzylamine Derivatives. X-ray Crystal Structure of $Mn\{C_6H_2(OCH_3)_2$-4,6-CH_2NMe_2-2$\}(CO)_4$. *Inorg. Chem*. **1995**, *34*, 643–650. (b) Djukic, J.-P.; Michon, C.; Heiser, D.; Kyritsakas-Gruber, N.; de Cian, A.; Dötz, Karl H.; Pfeffer, M. The Reaction of Diazocyclopentadienyl Compounds with Cyclomanganated Arenes as a Route to Ligand-Appended Cymantrenes. *Eur. J. Inorg. Chem*. **2004**, 2107–2122.

6. Copies of ^{1}H, ^{13}C, and ^{19}F NMR spectra for compounds

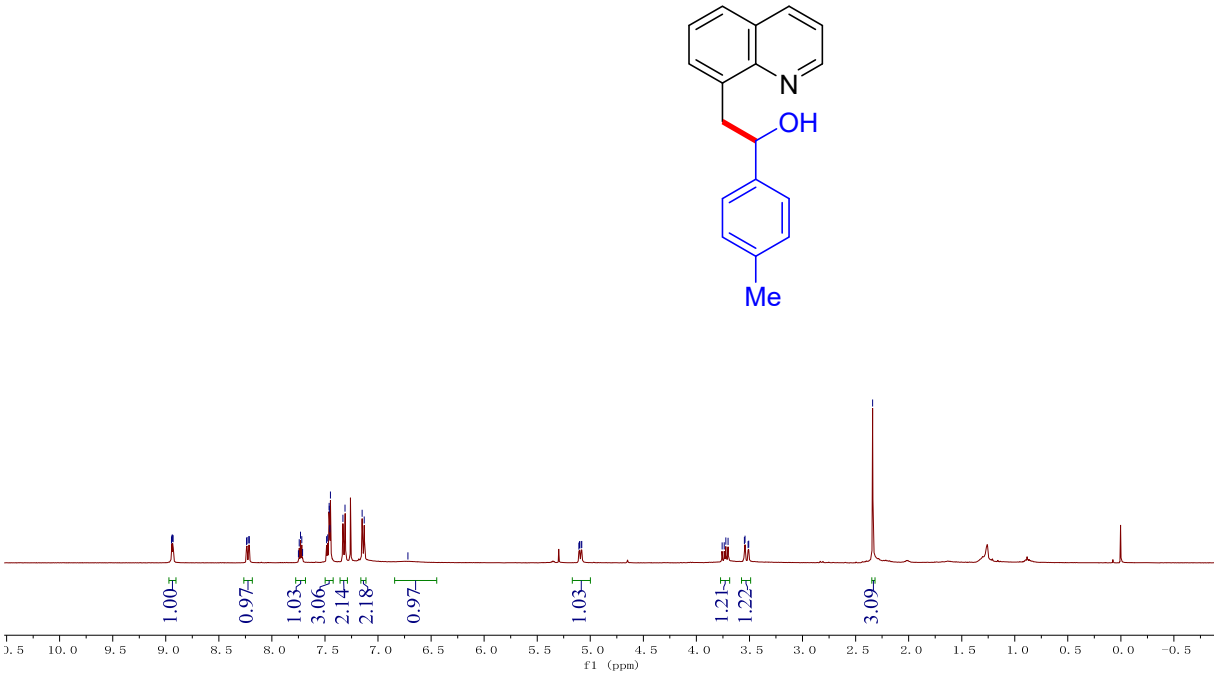
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **3aa**



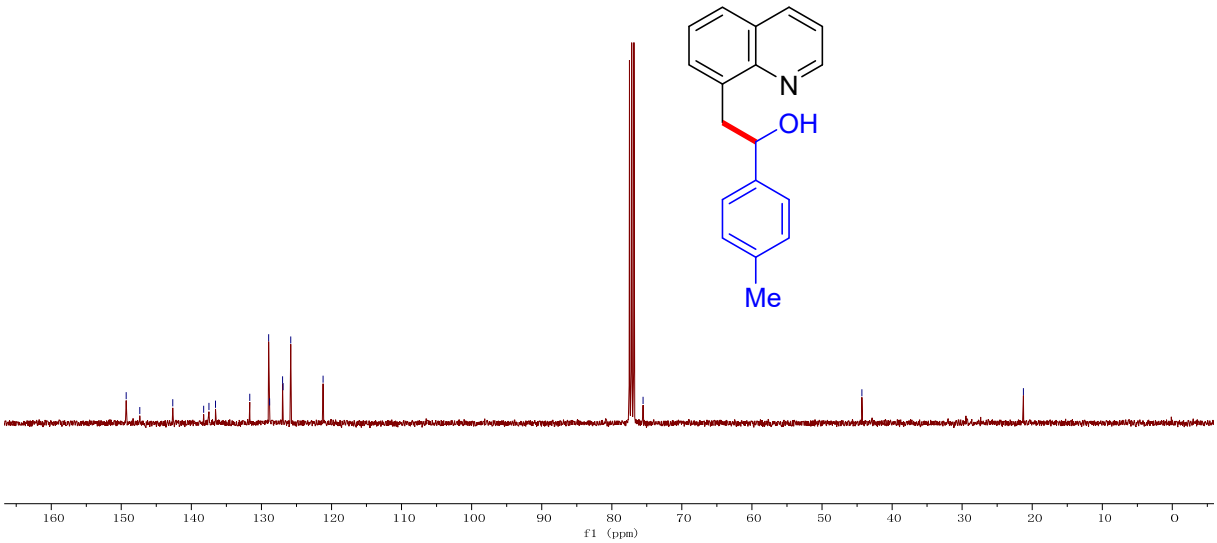
$^{13}C\{^{1}H\}$ NMR (151 MHz, $CDCl_3$) spectrum of **3aa**



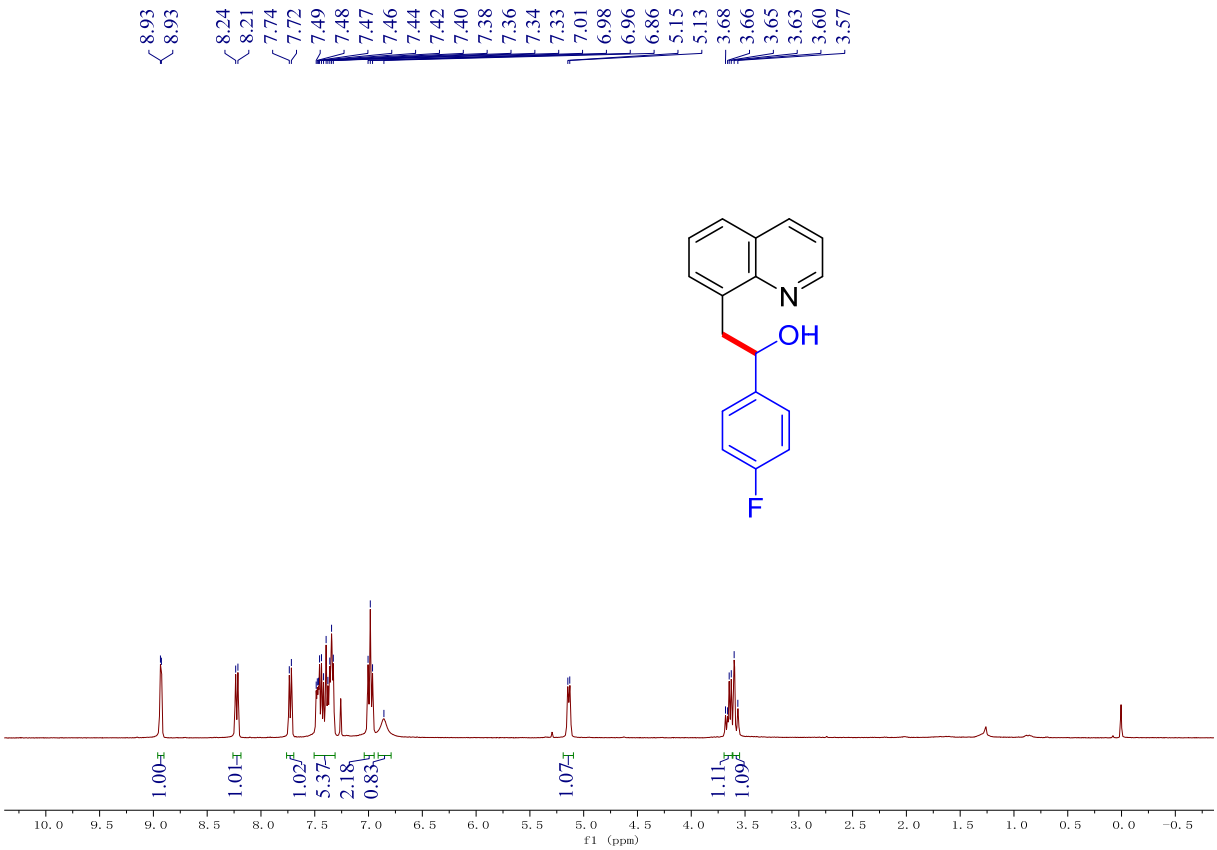
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3ab**



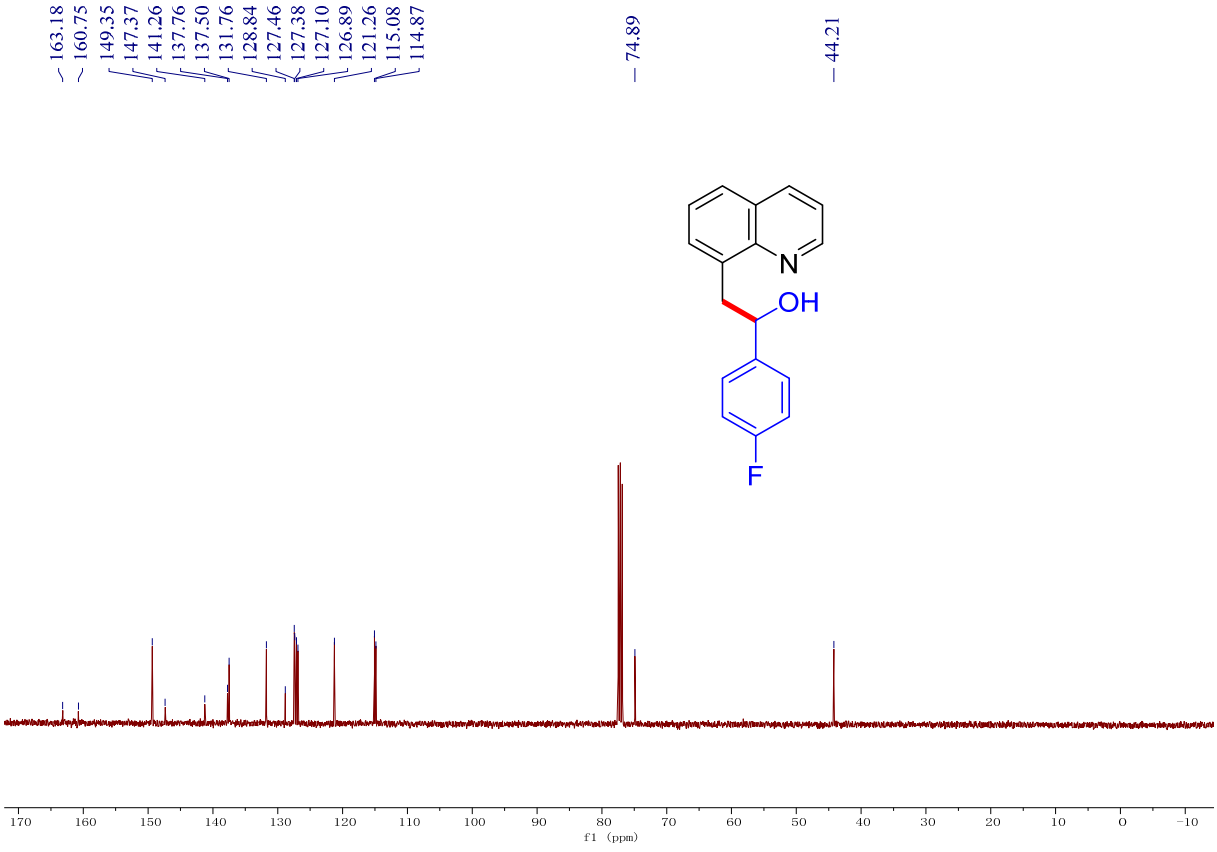
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) spectrum of **3ab**



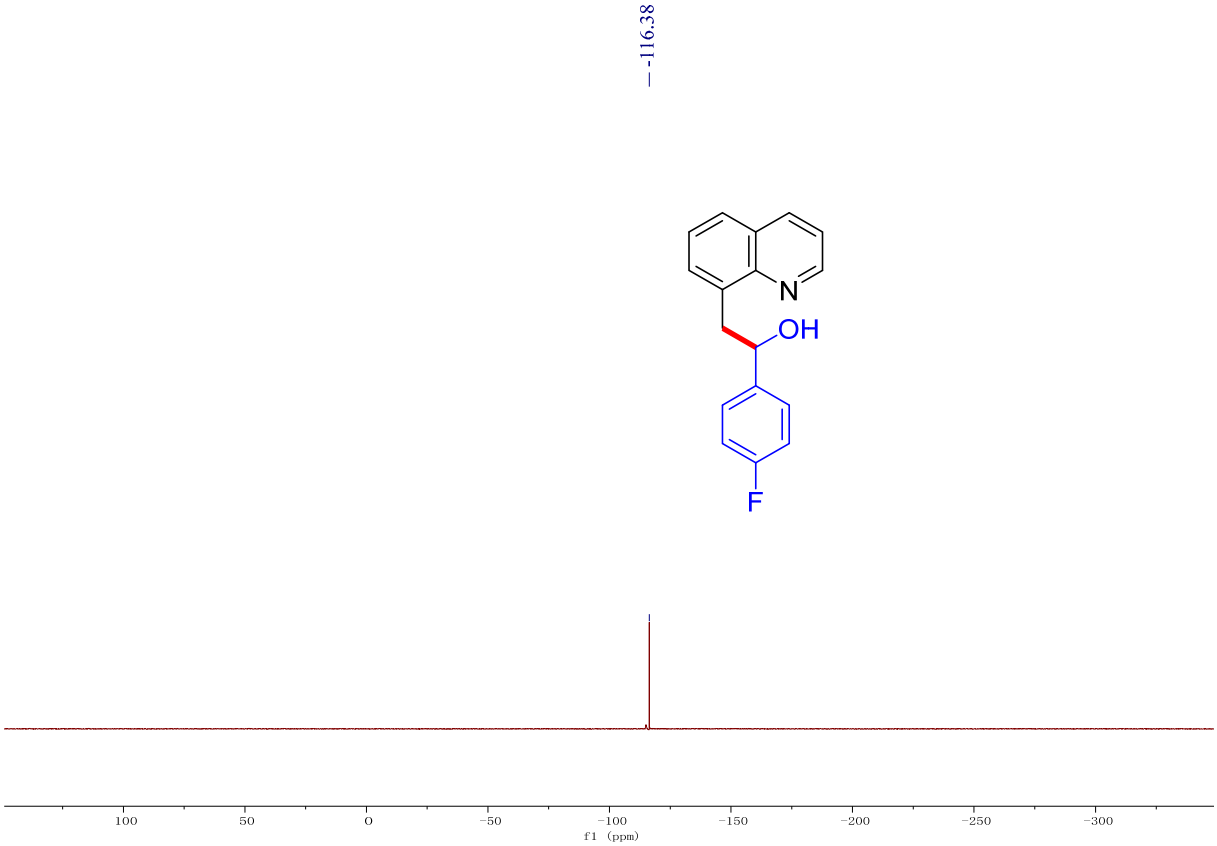
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3ac**



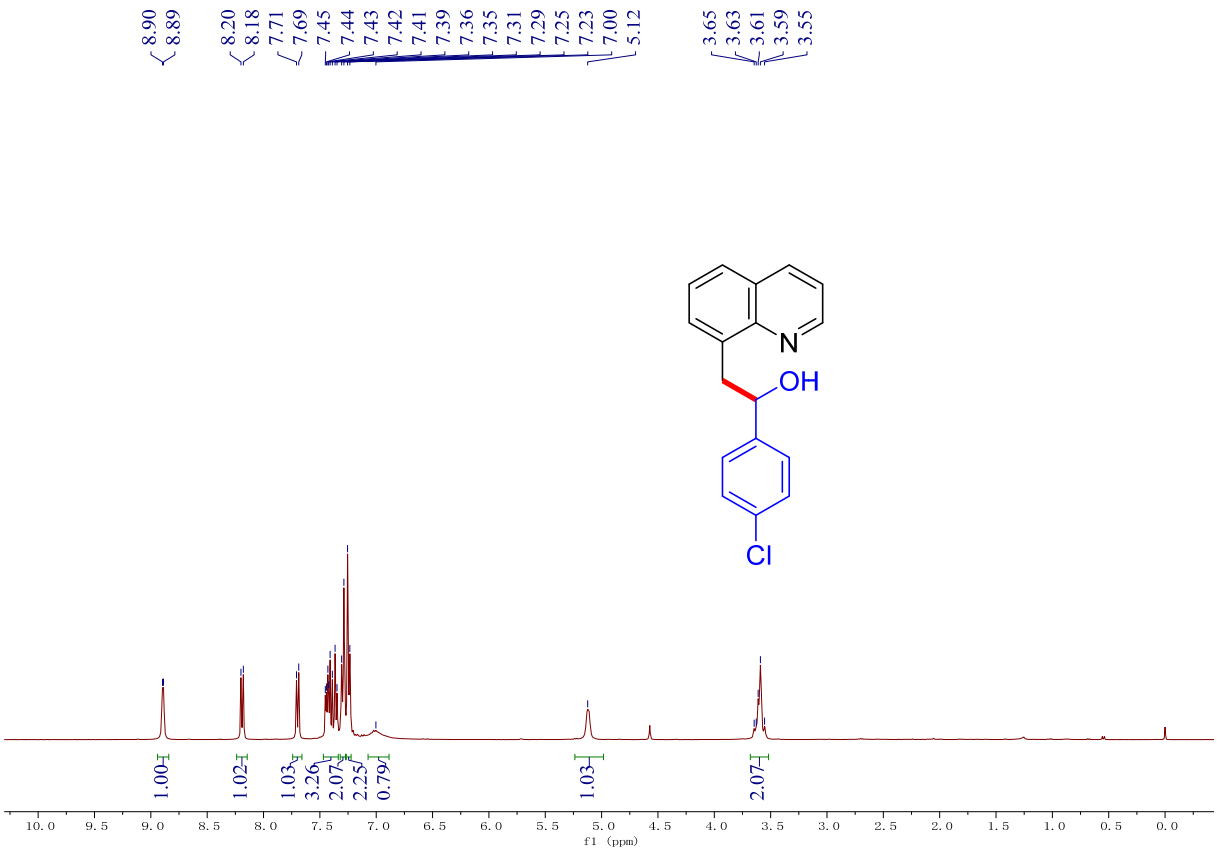
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) spectrum of **3ac**



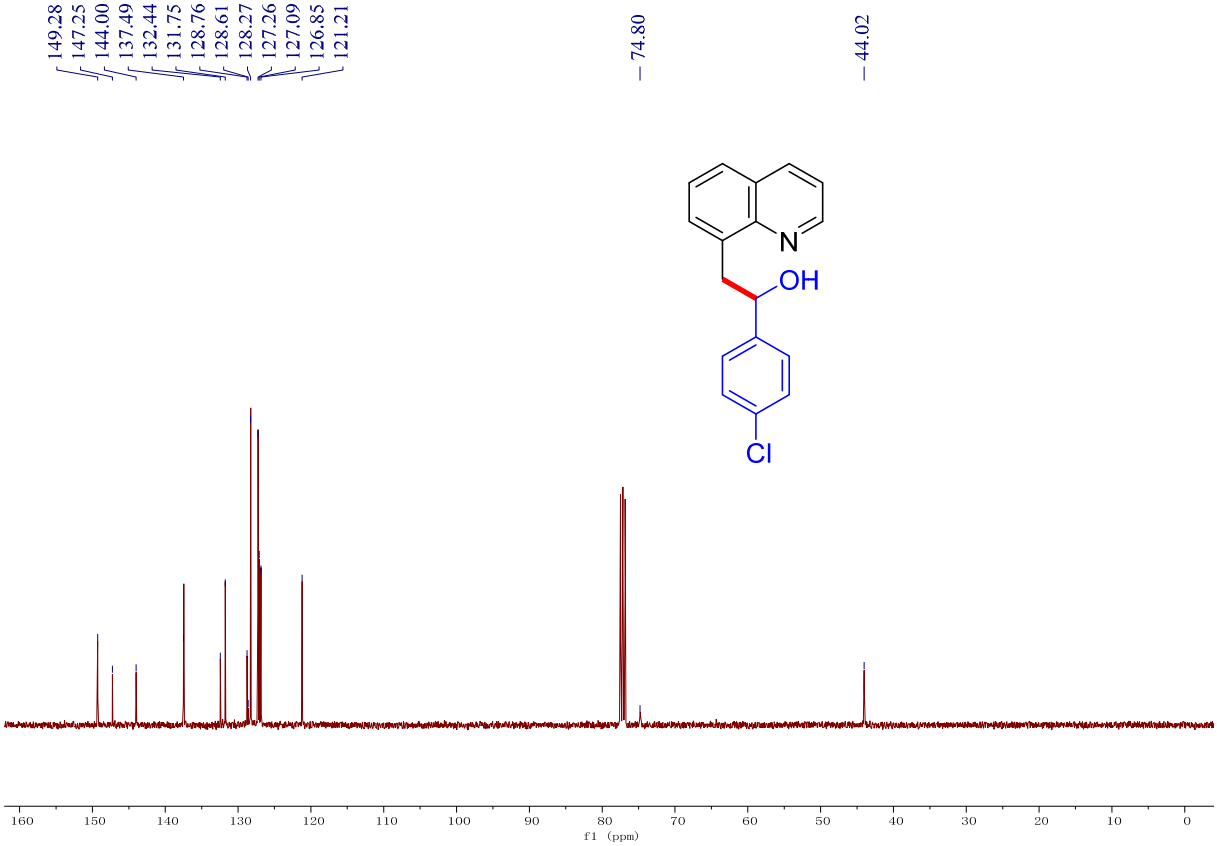
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of **3ac**



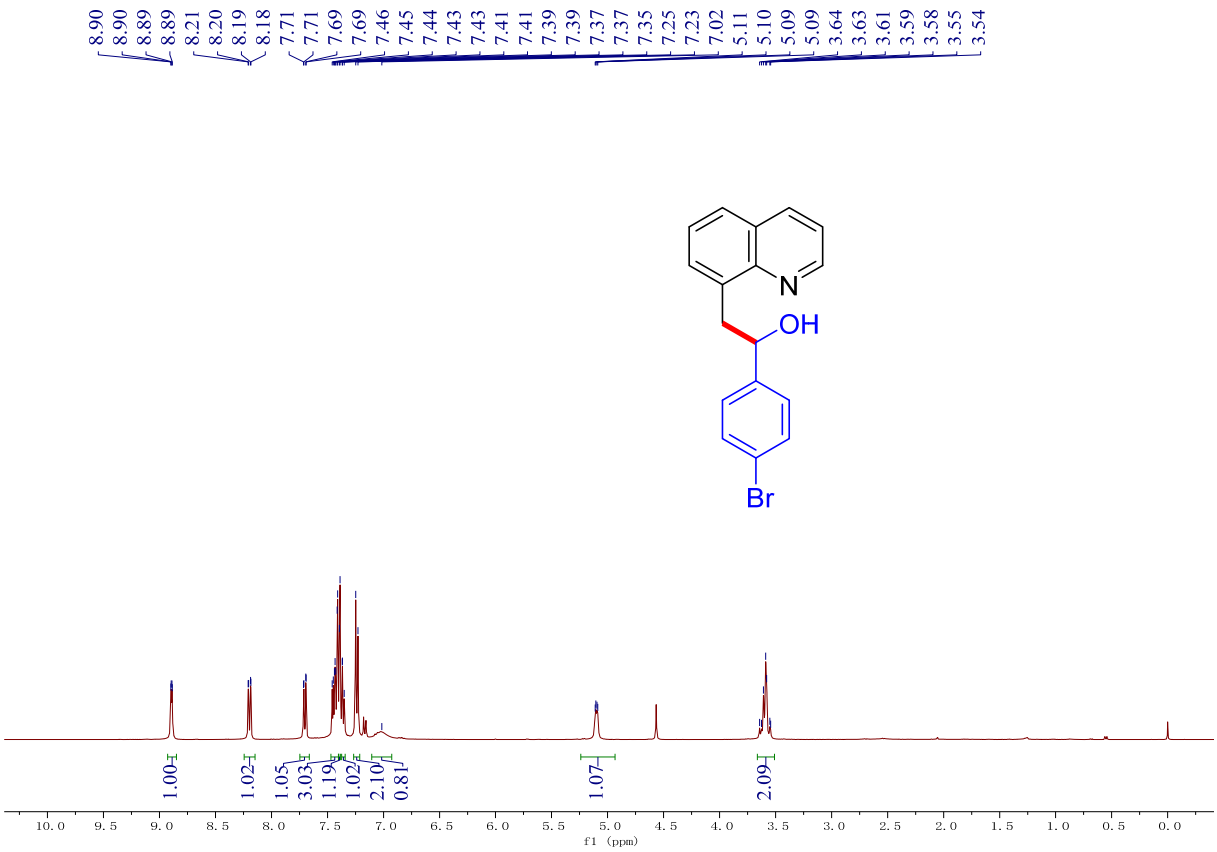
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3ad**



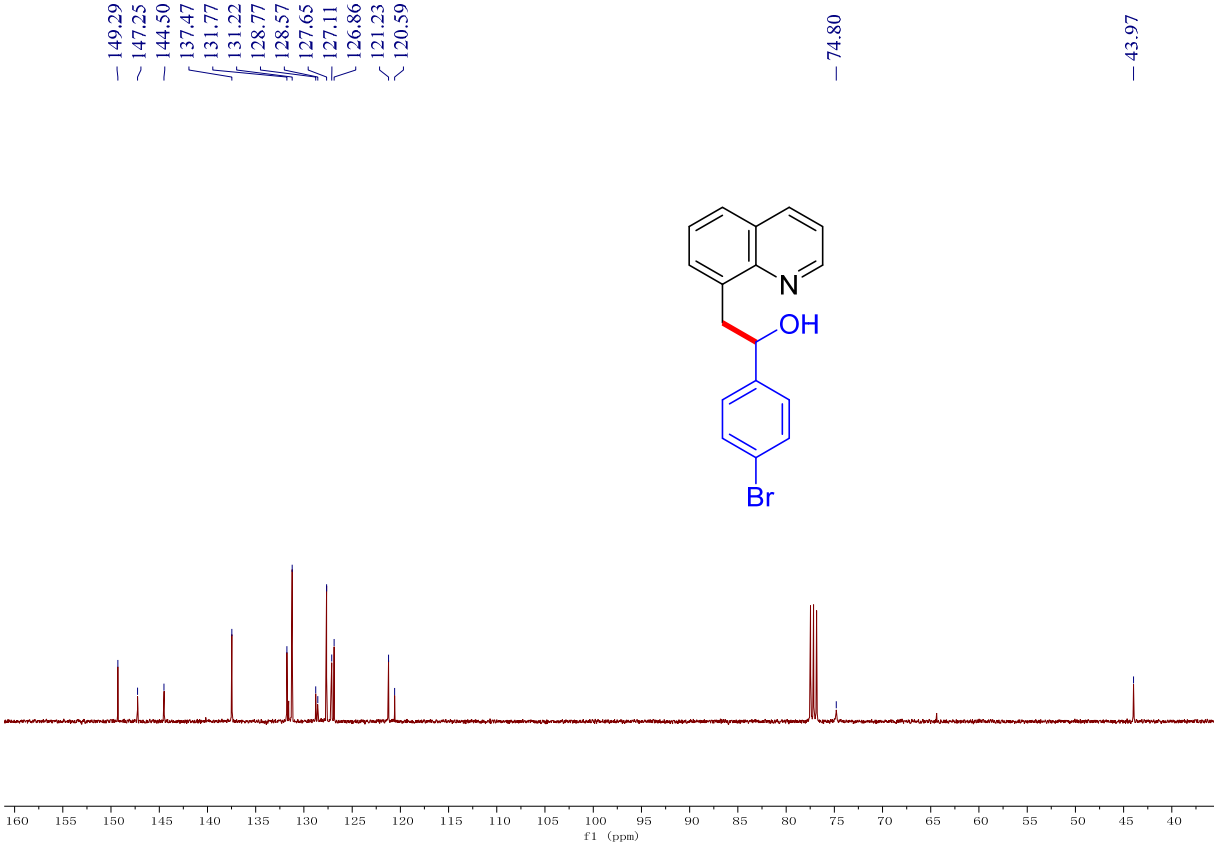
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) spectrum of **3ad**



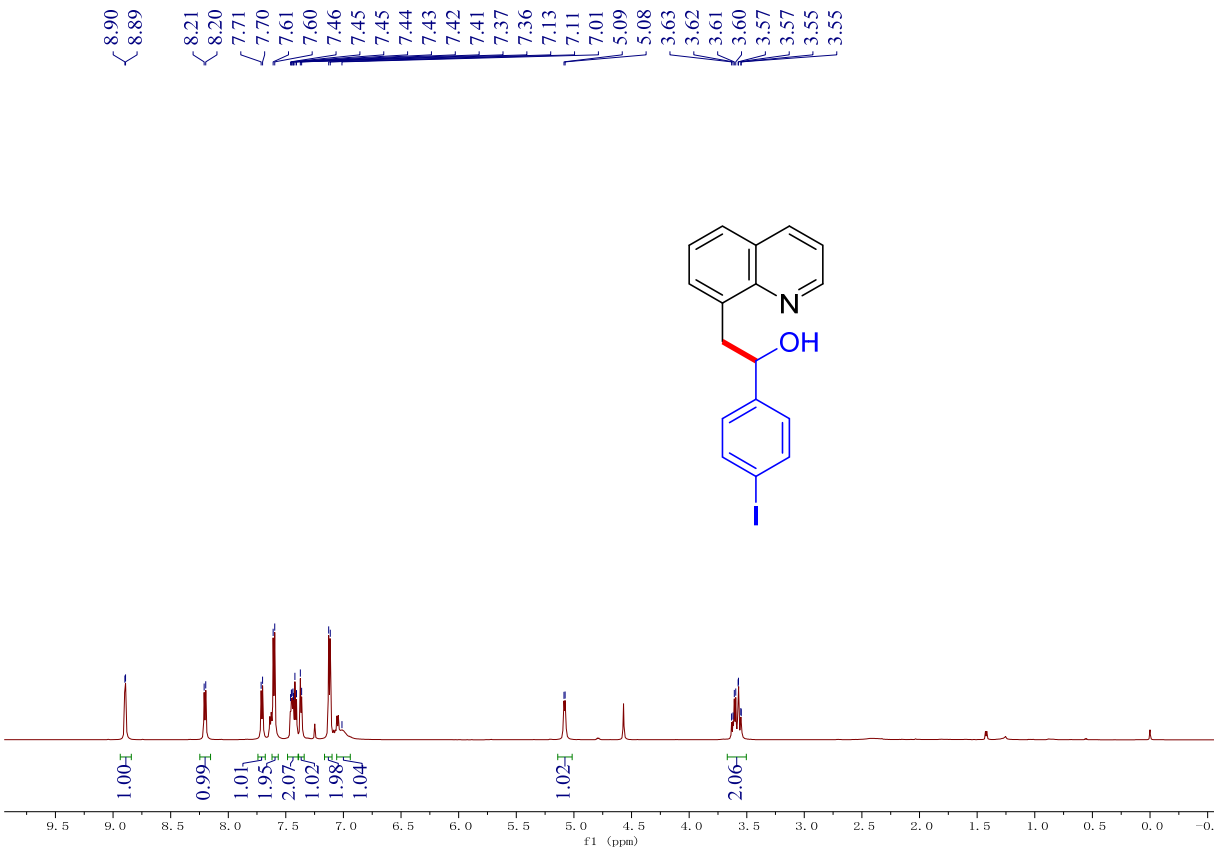
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3ae**



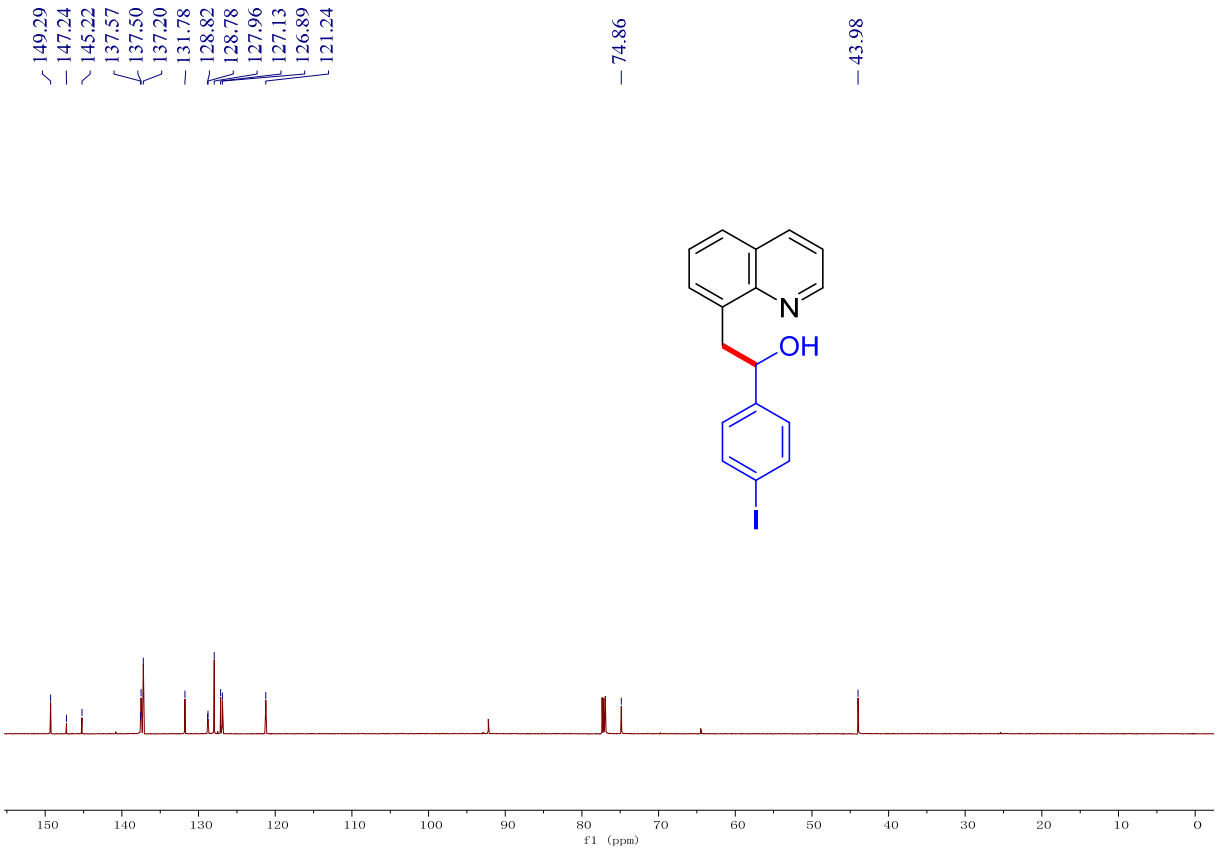
$^{13}C\{^{1}H\}$ NMR (151 MHz, $CDCl_3$) spectrum of **3ae**



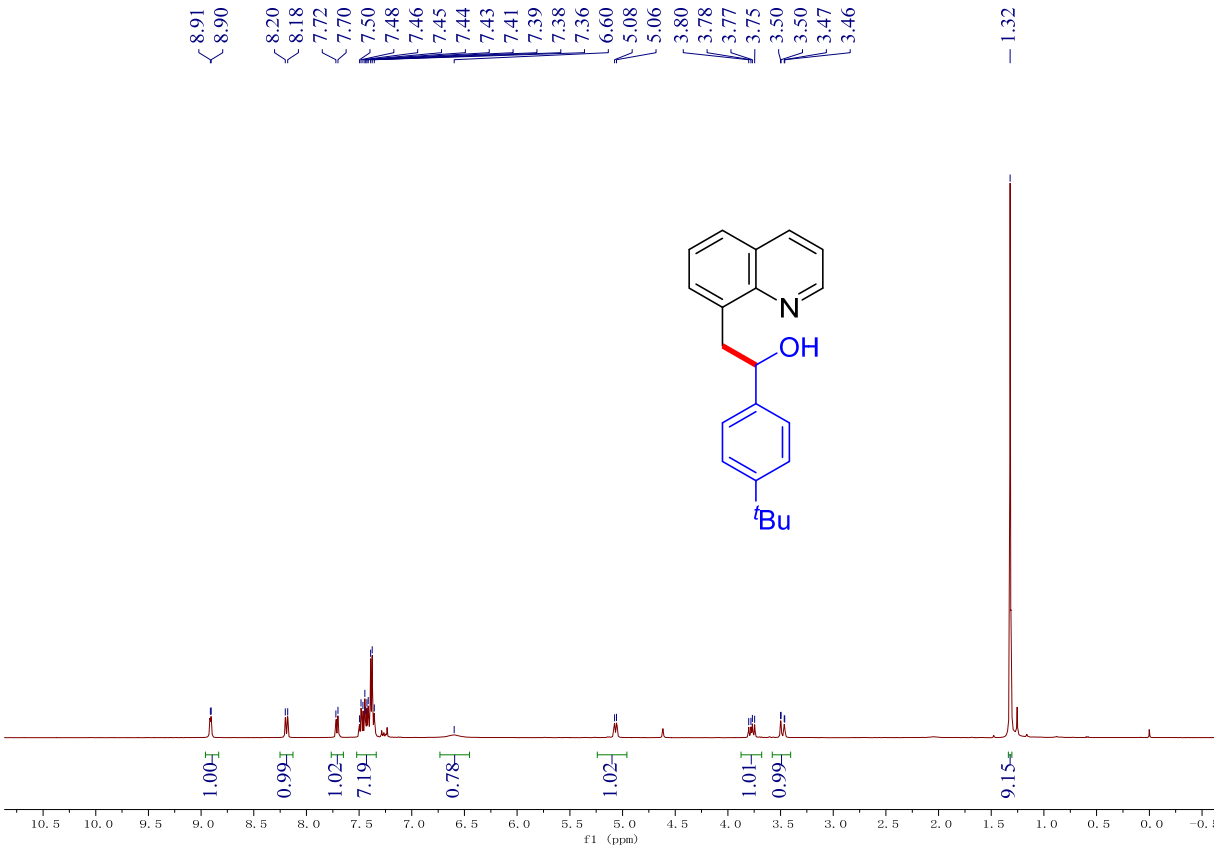
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **3af**



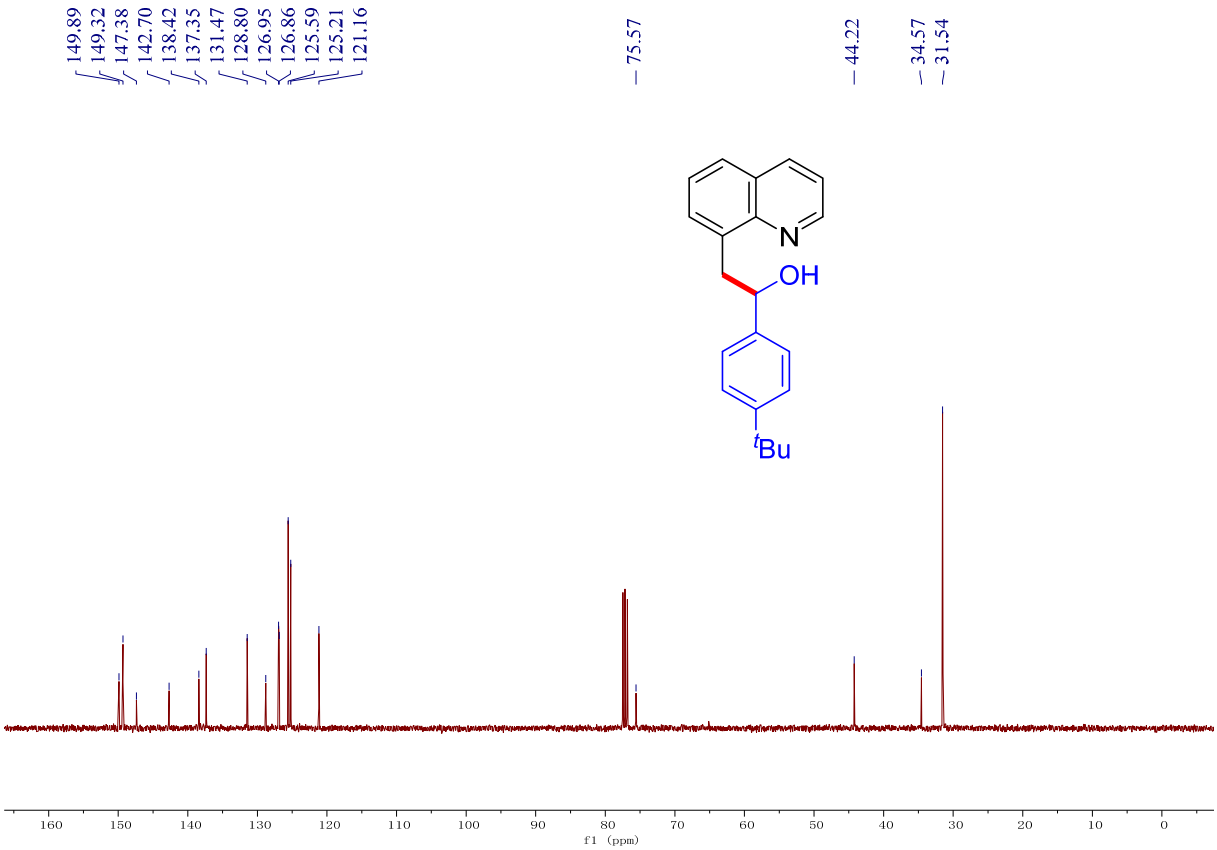
$^{13}C\{^{1}H\}$ NMR (151 MHz, $CDCl_3$) spectrum of **3af**



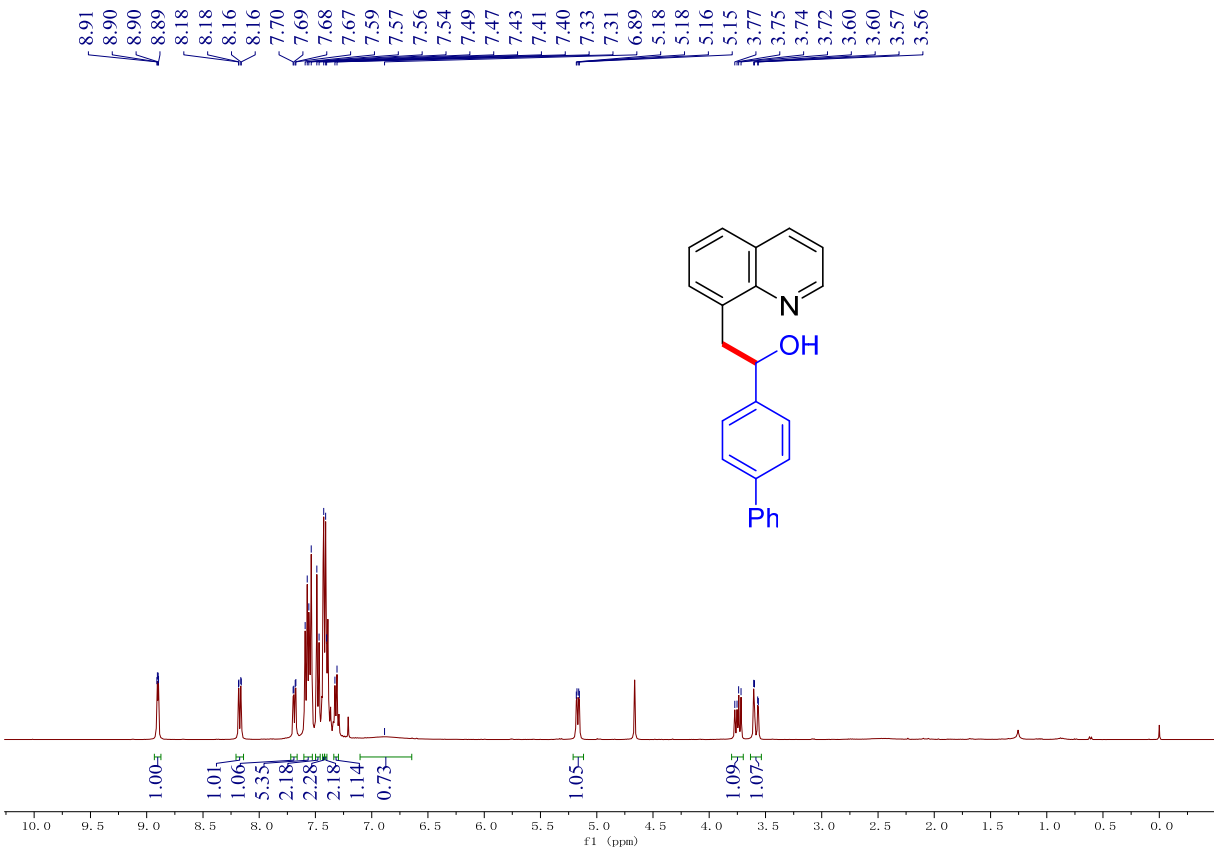
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3ag**



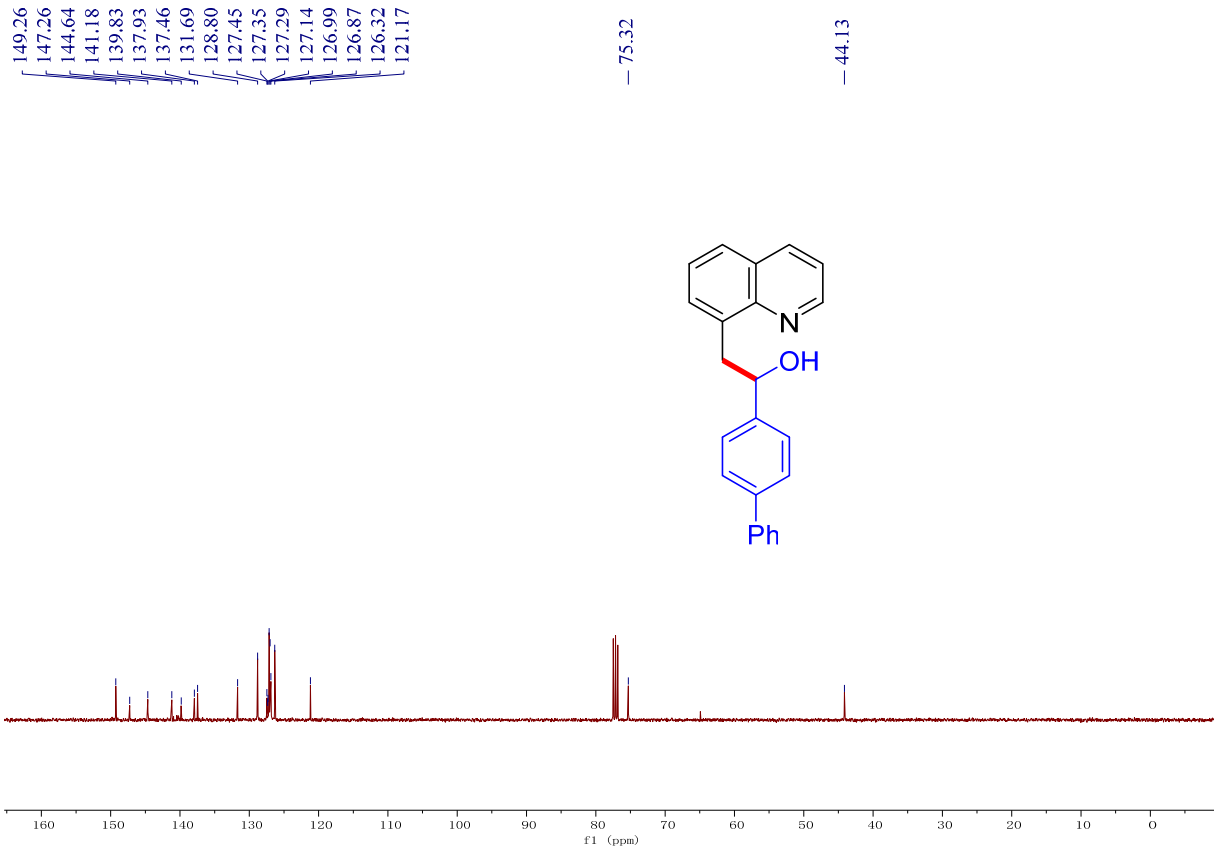
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) spectrum of **3ag**



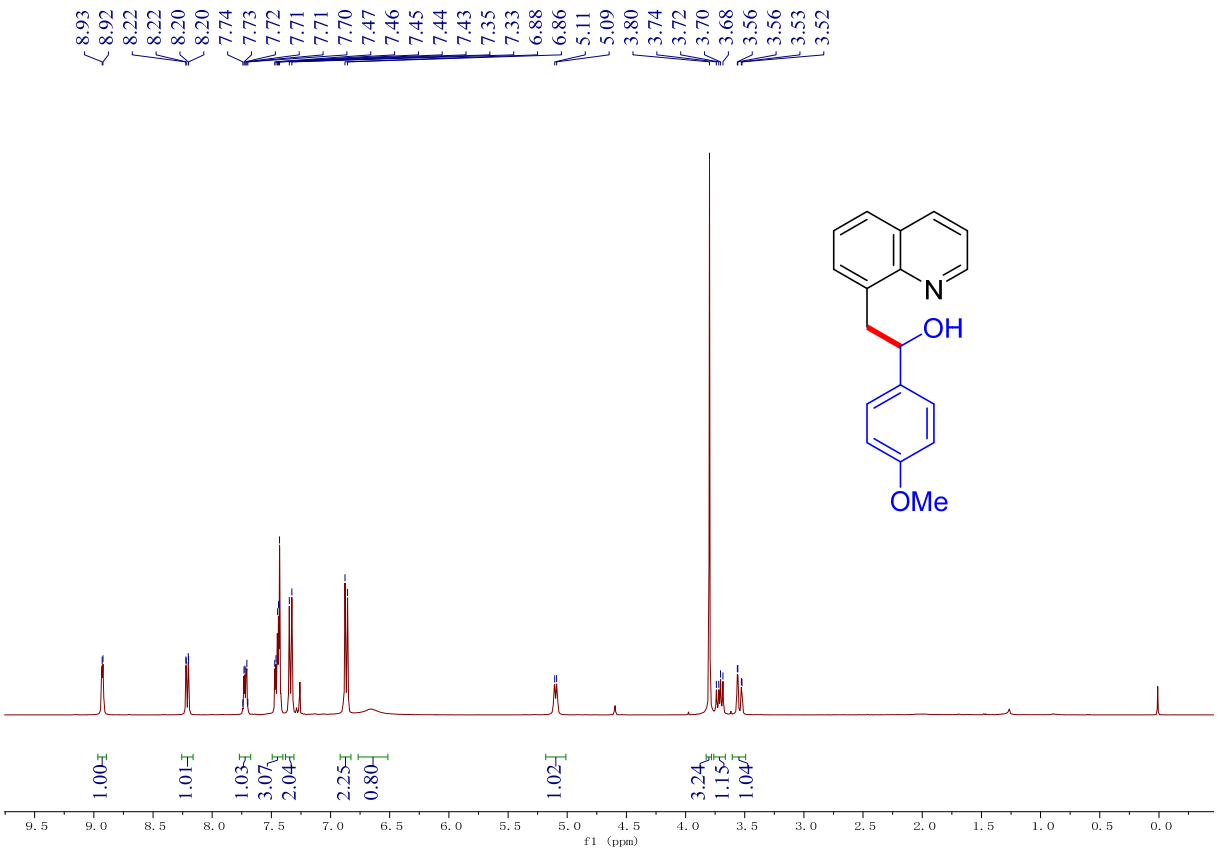
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3ah**



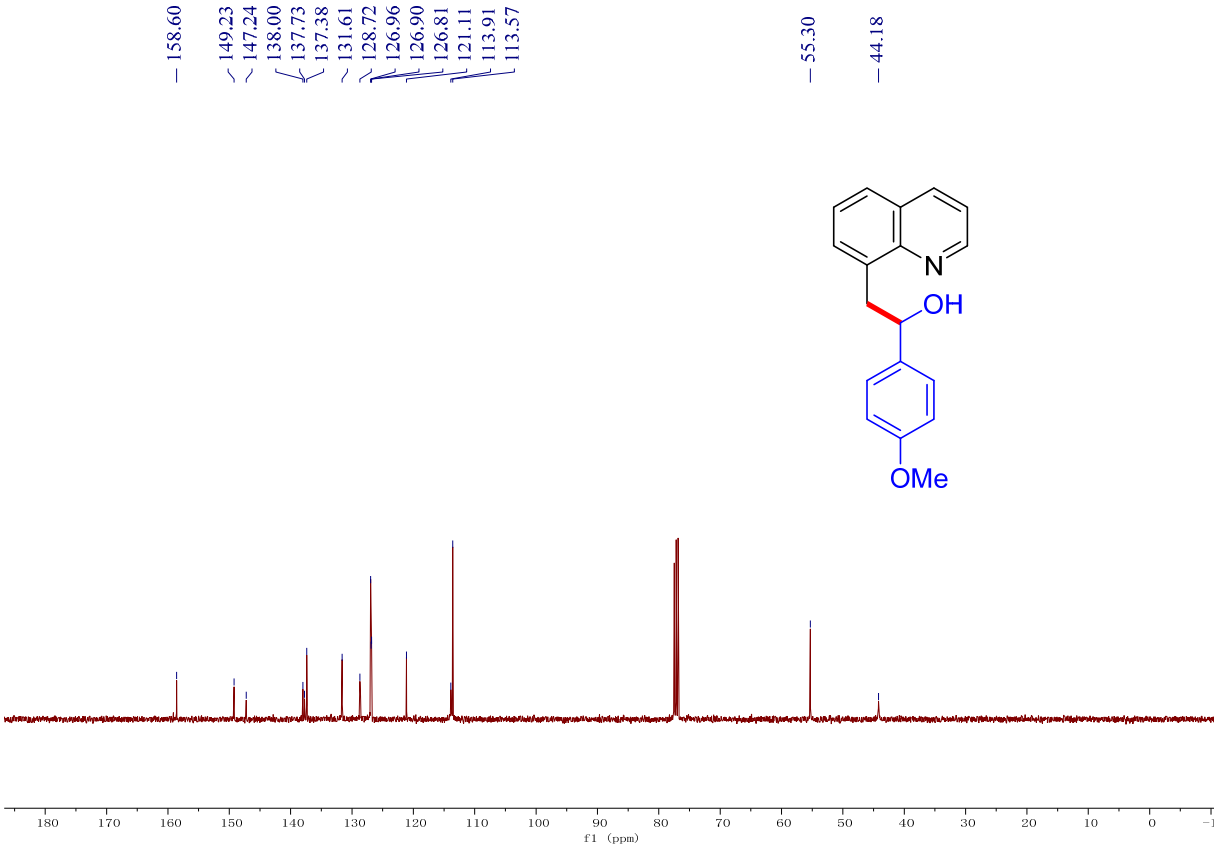
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) spectrum of **3ah**



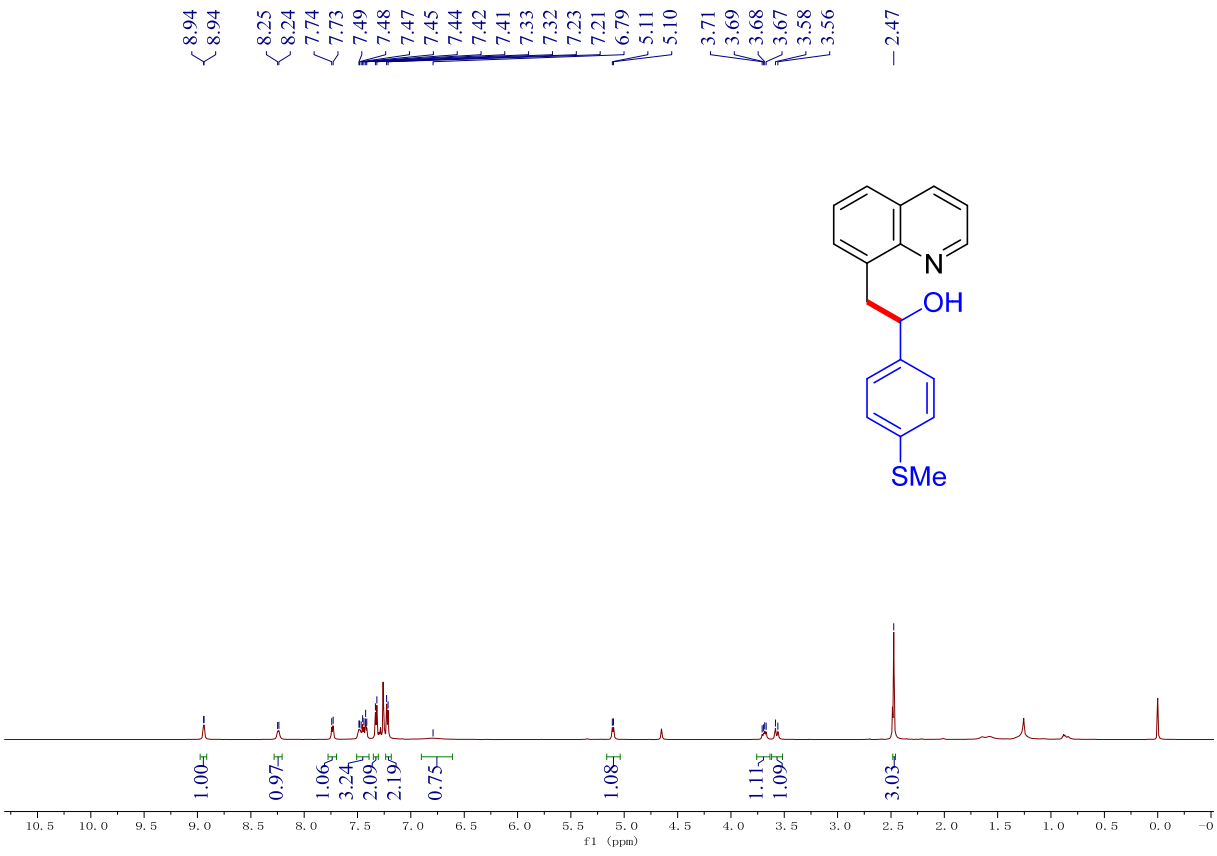
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3ai**



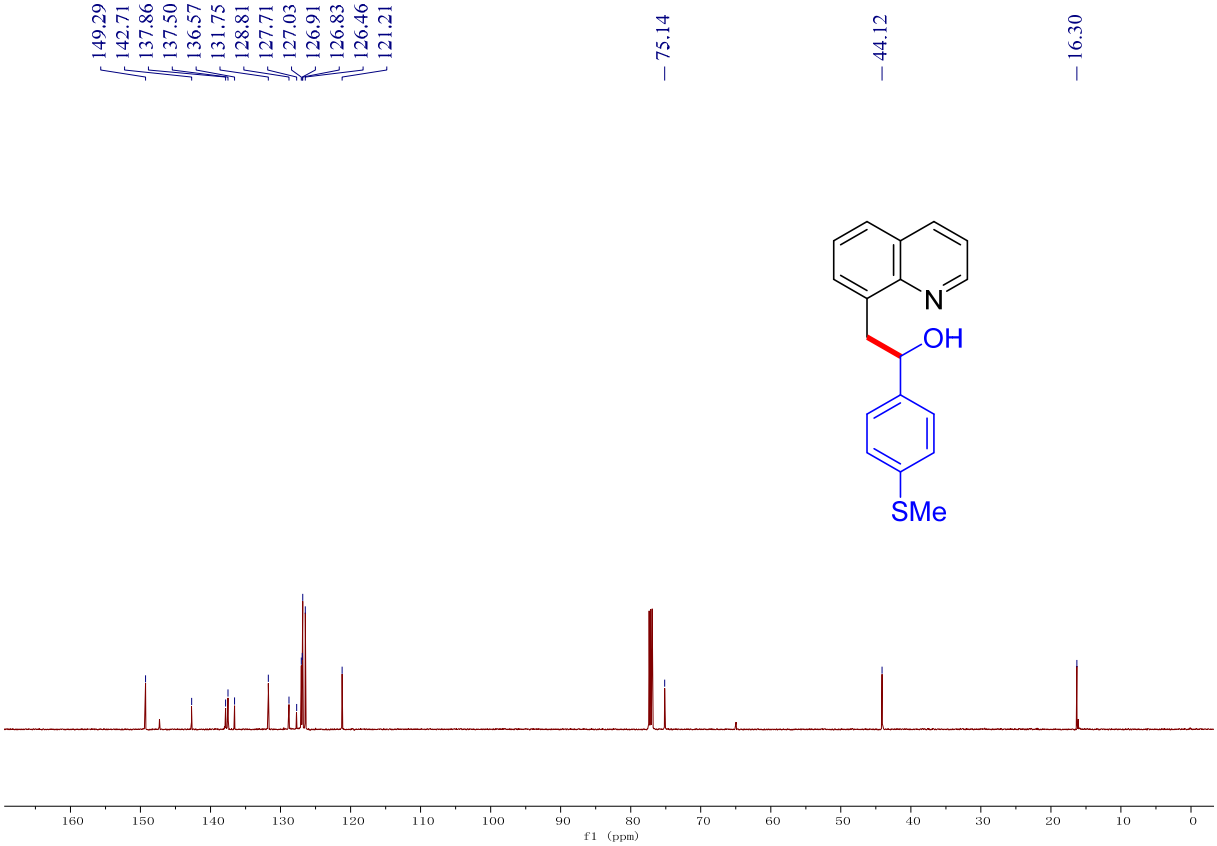
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) spectrum of **3ai**



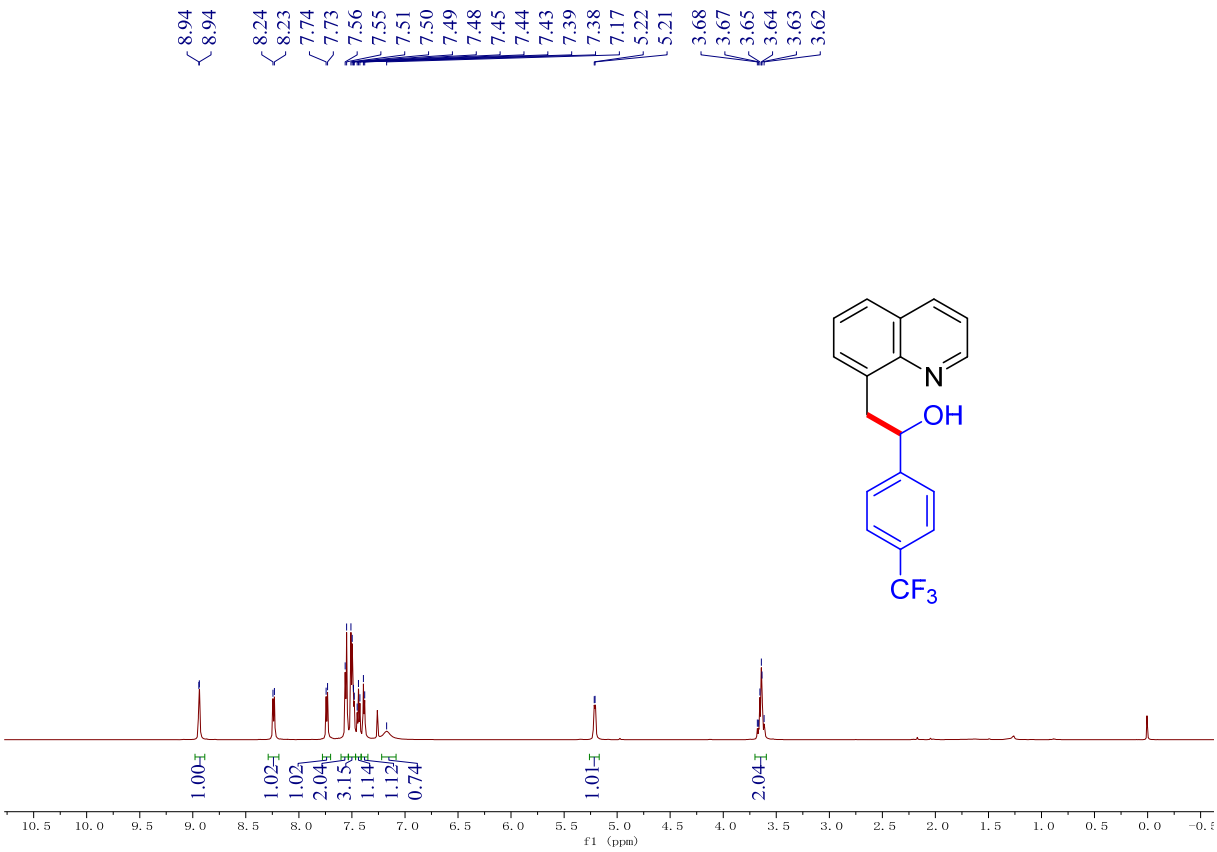
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **3aj**



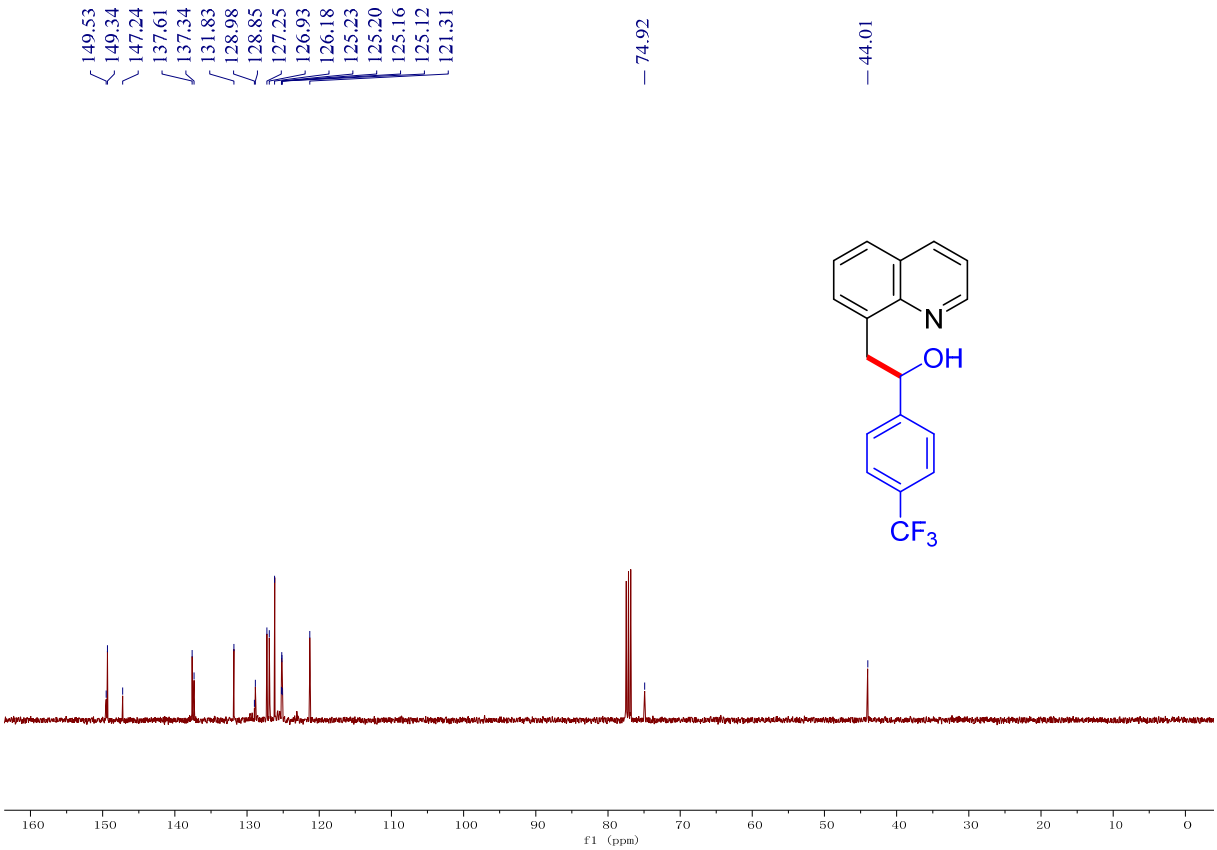
$^{13}C\{^{1}H\}$ NMR (151 MHz, $CDCl_3$) spectrum of **3aj**



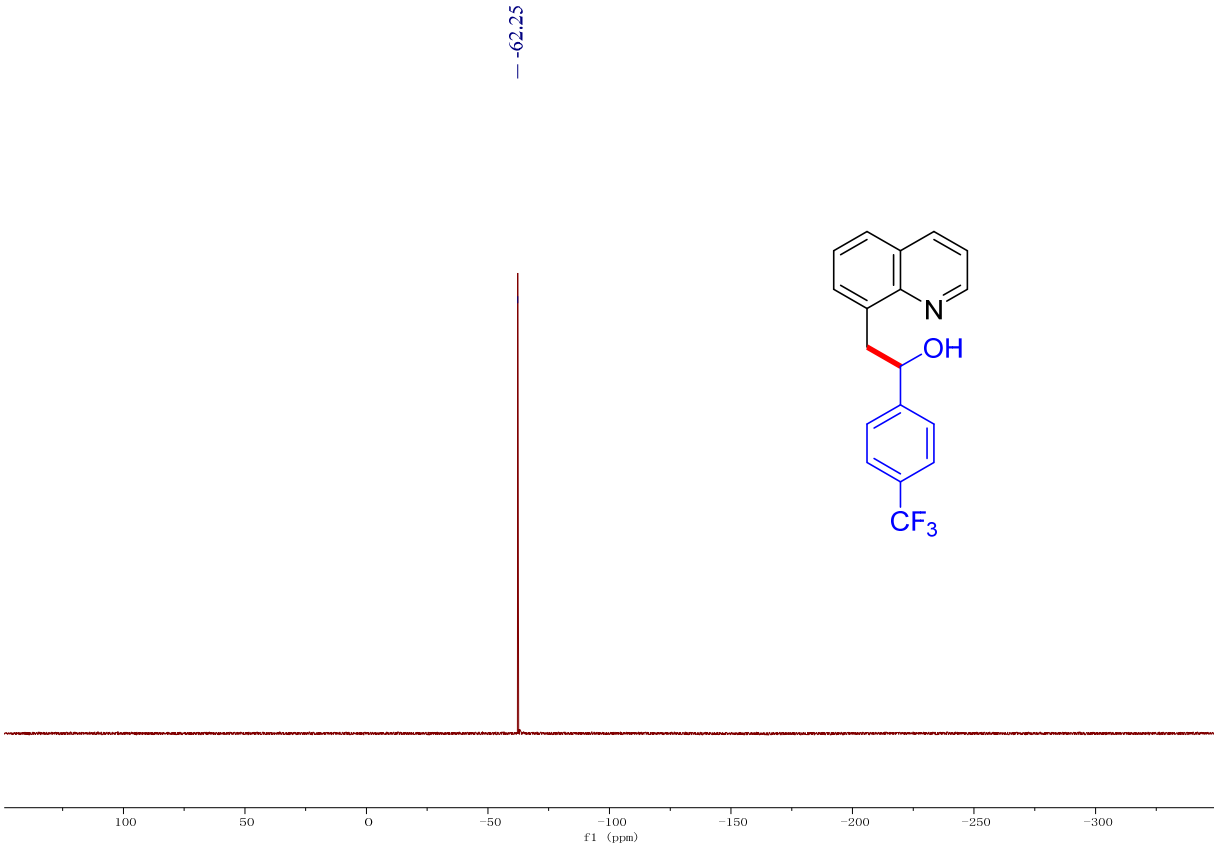
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **3ak**



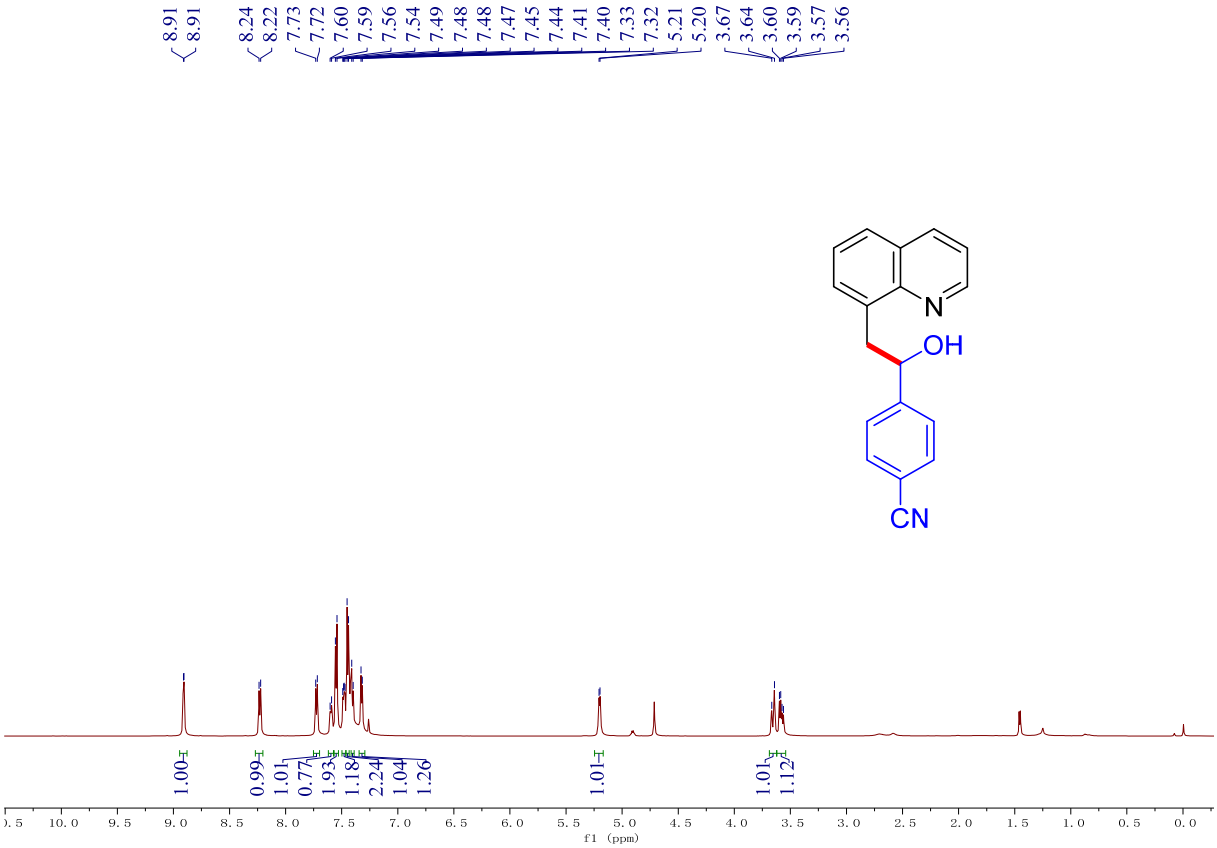
$^{13}C\{^{1}H\}$ NMR (151 MHz, $CDCl_3$) spectrum of **3ak**



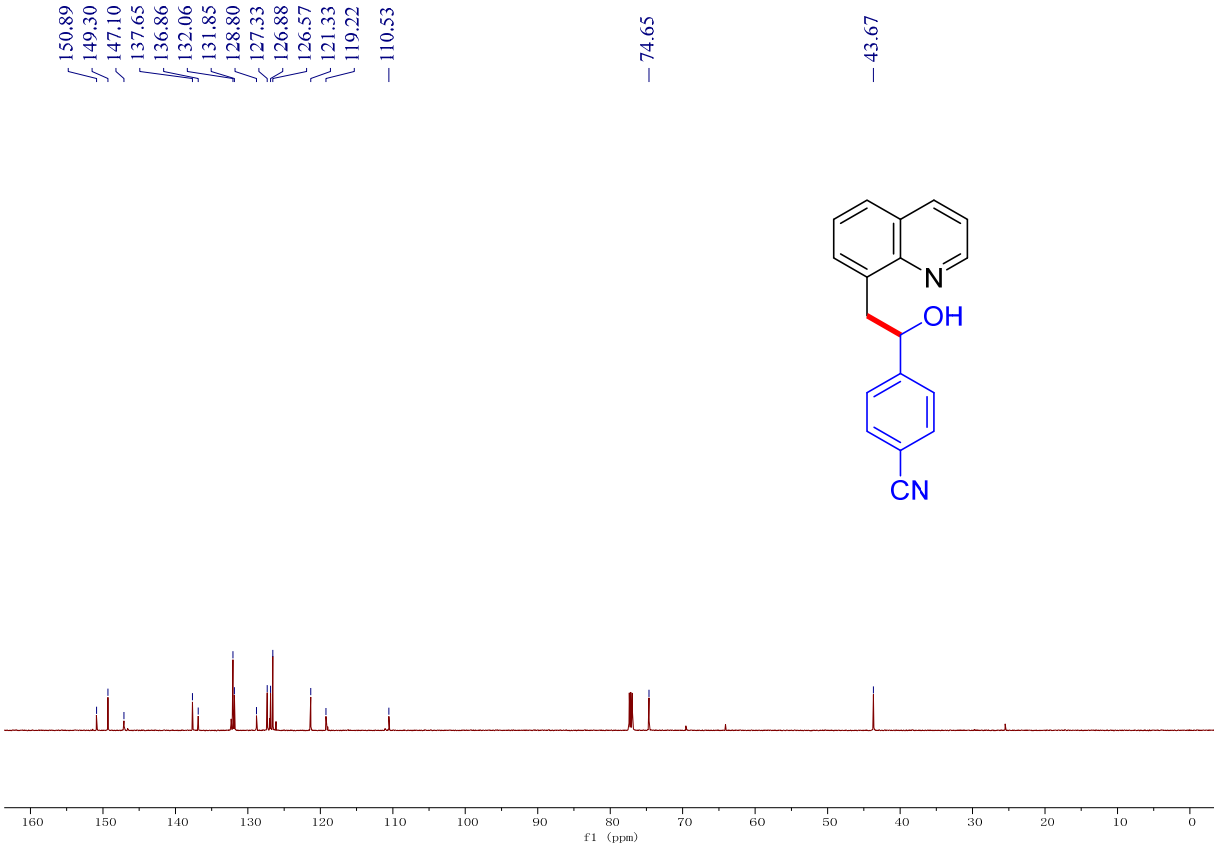
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of **3ak**



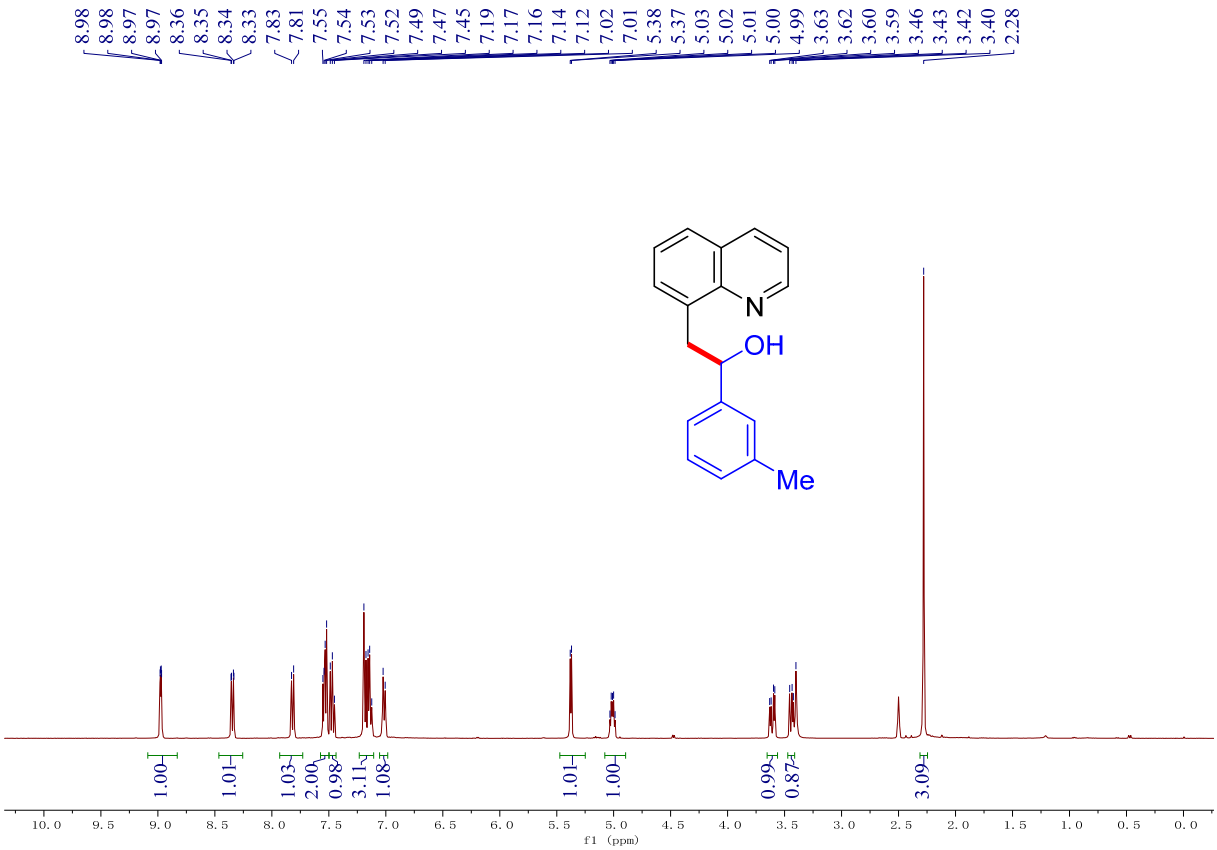
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **3al**



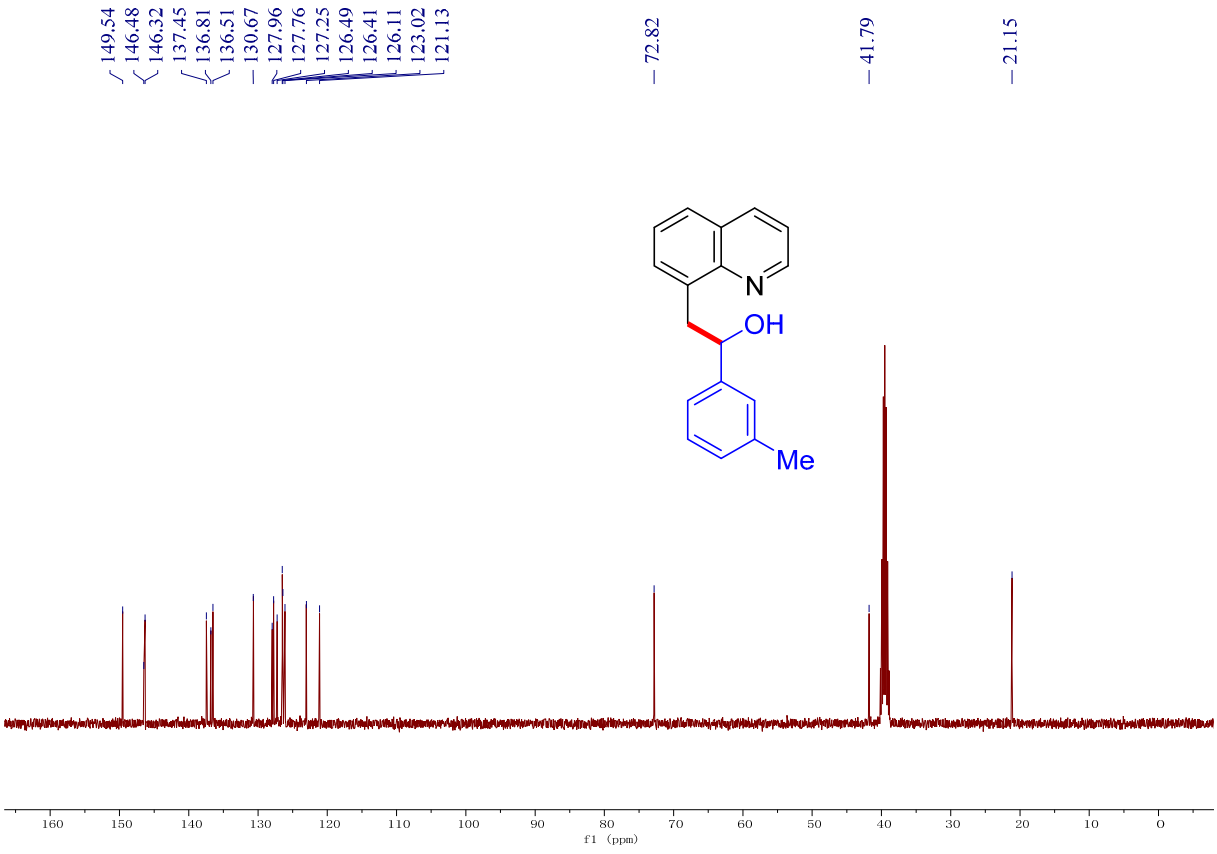
^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) spectrum of **3al**



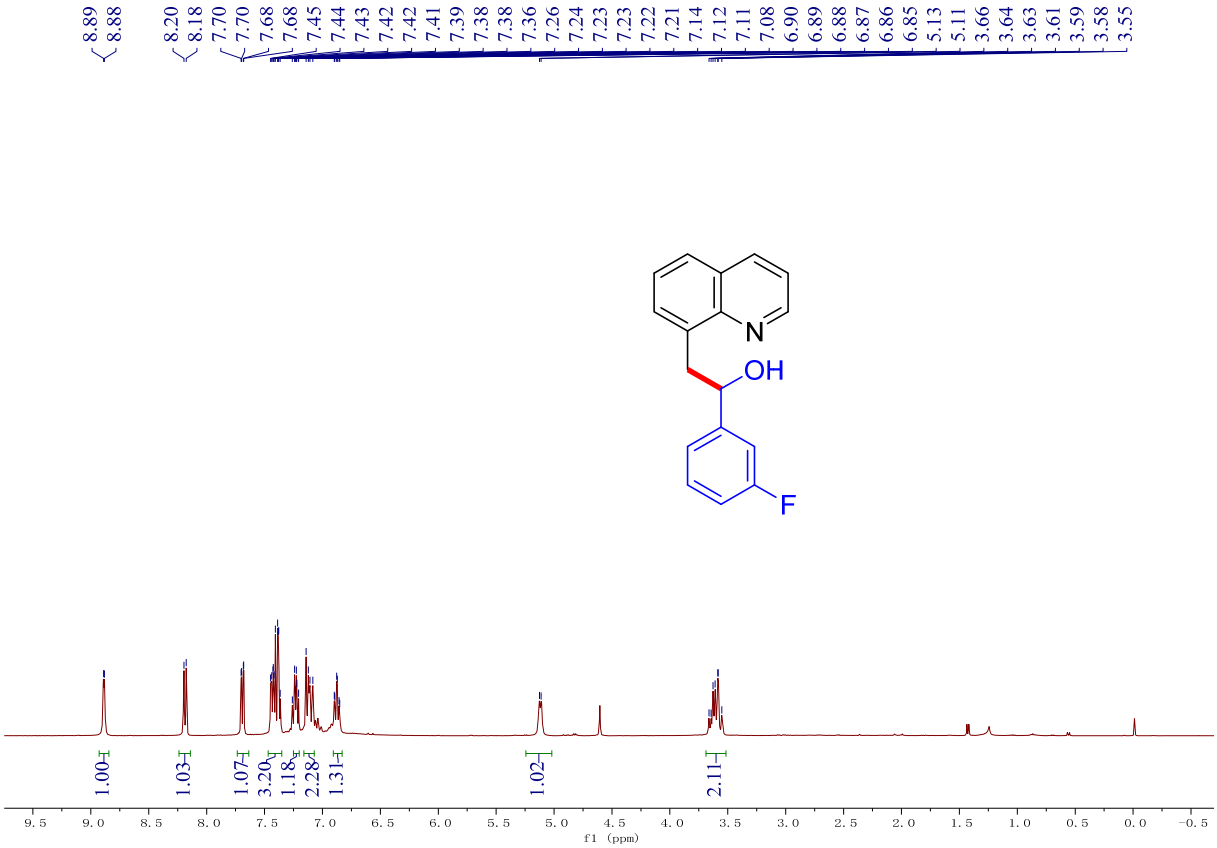
^{1}H NMR (400 MHz, DMSO-d_6) spectrum of **3am**



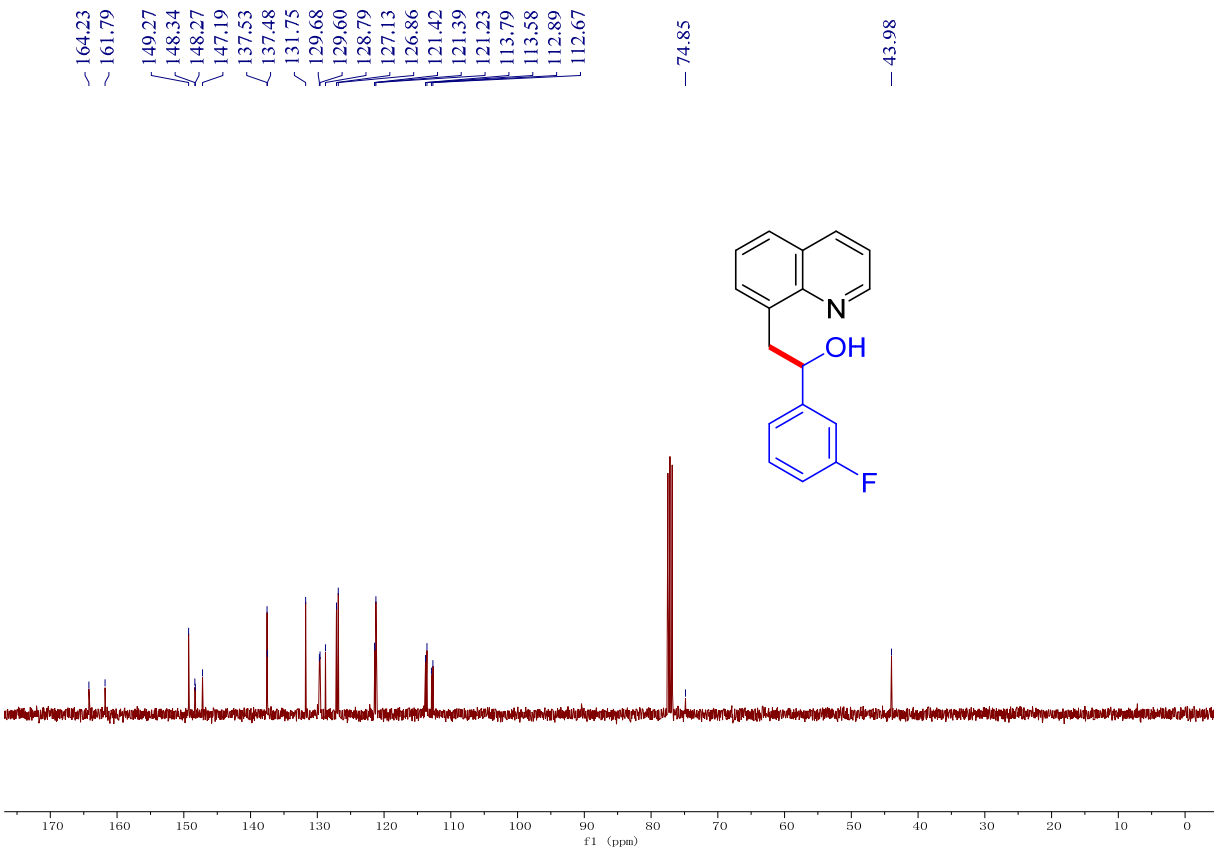
^{13}C{^{1}H} NMR (101 MHz, DMSO-d_6) spectrum of **3am**



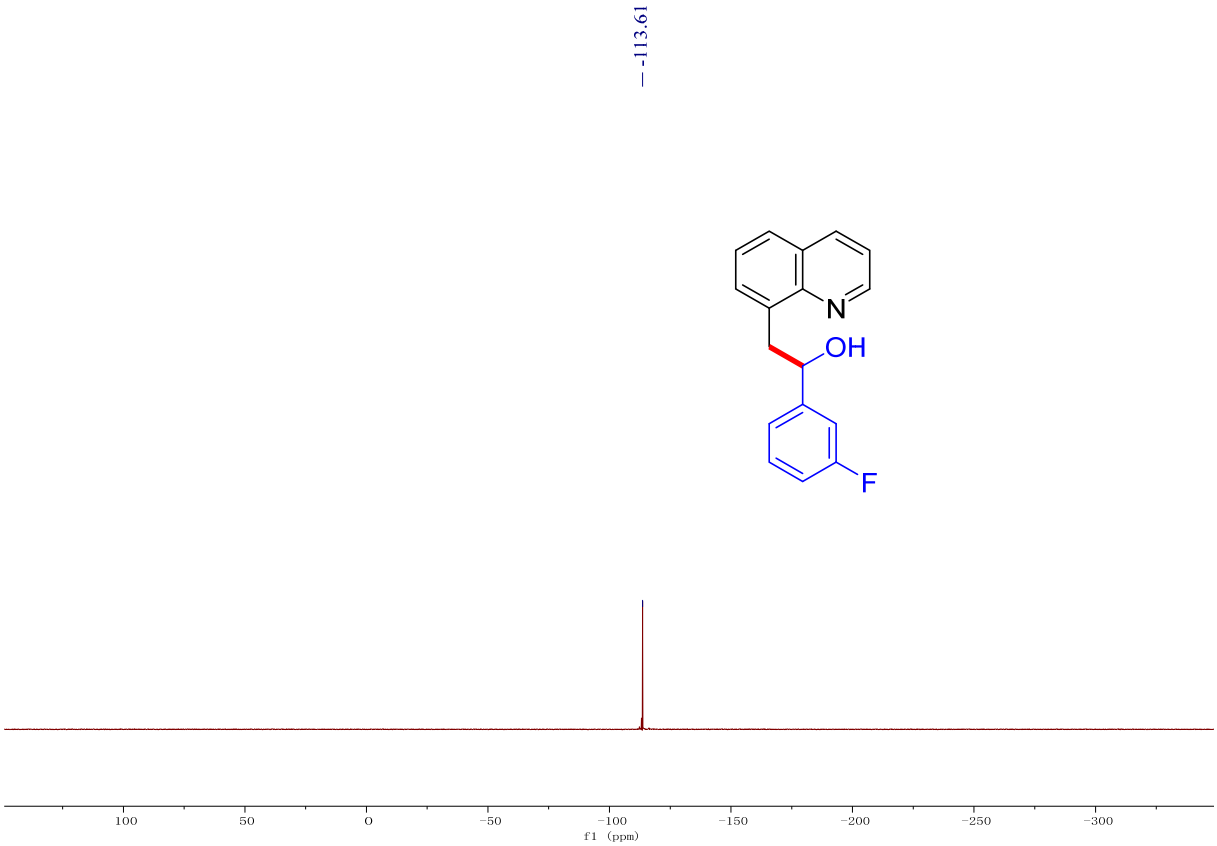
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3an**



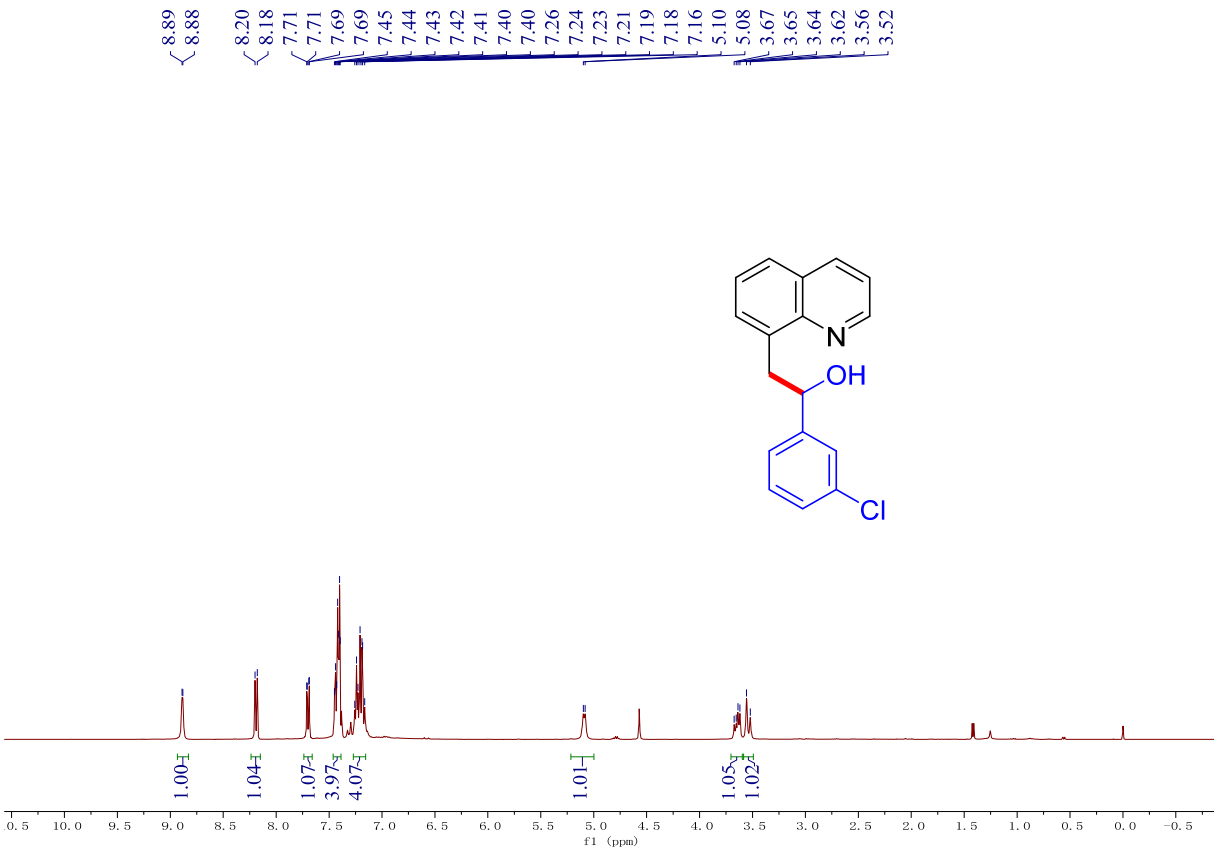
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) spectrum of **3an**



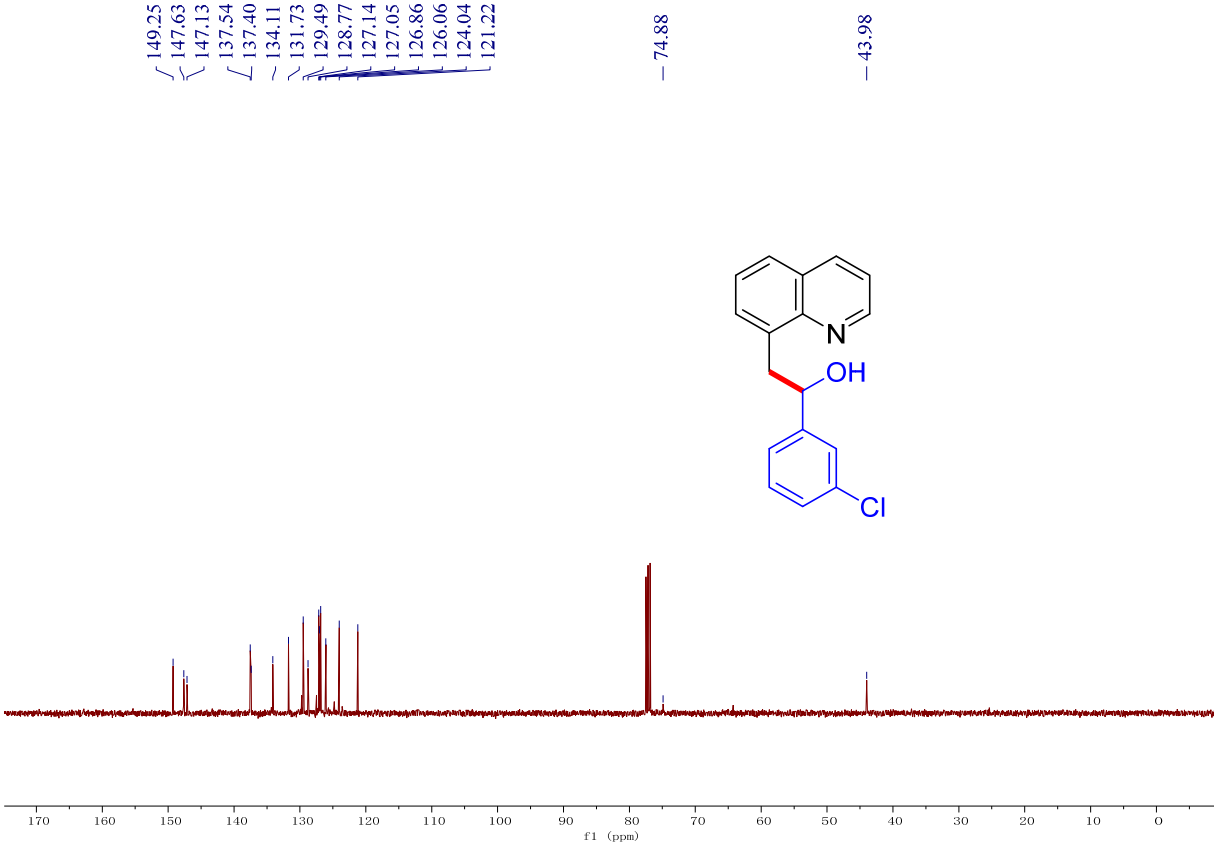
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of **3an**



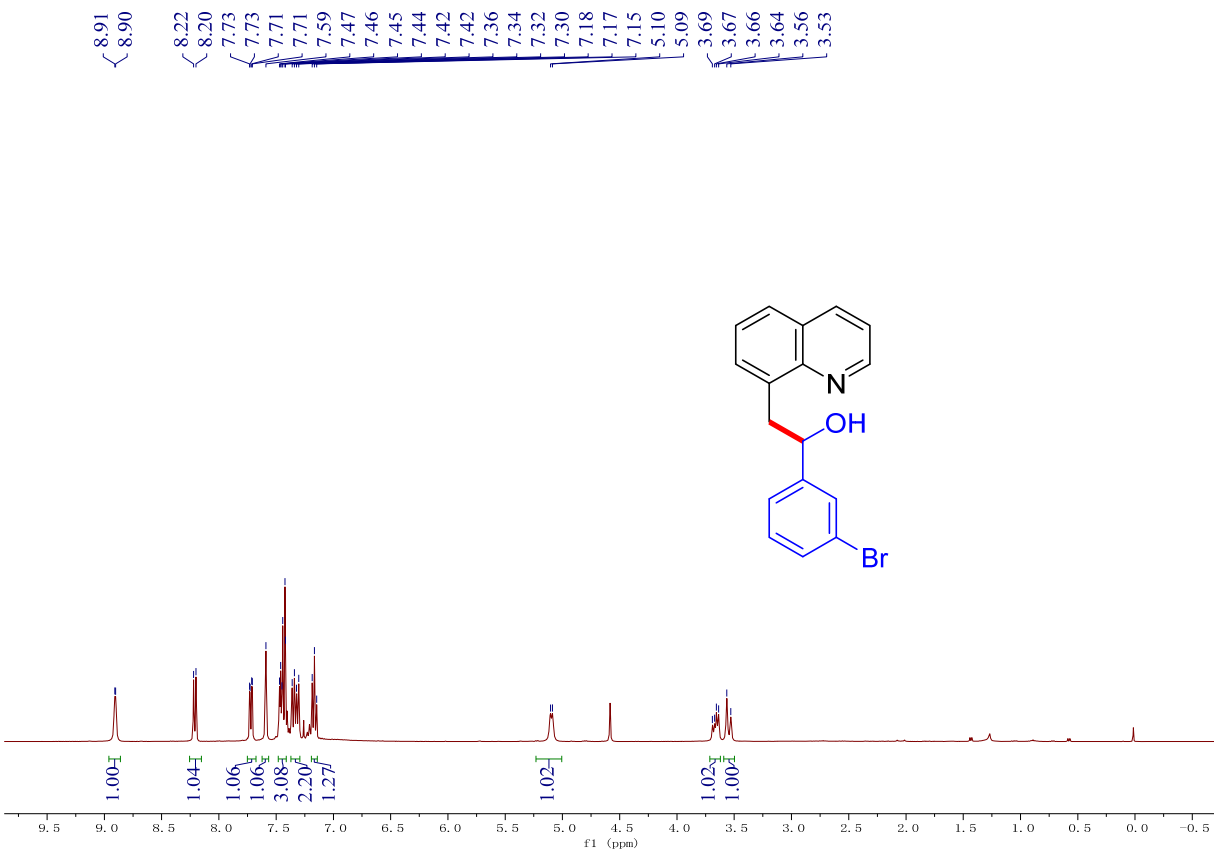
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3ao**



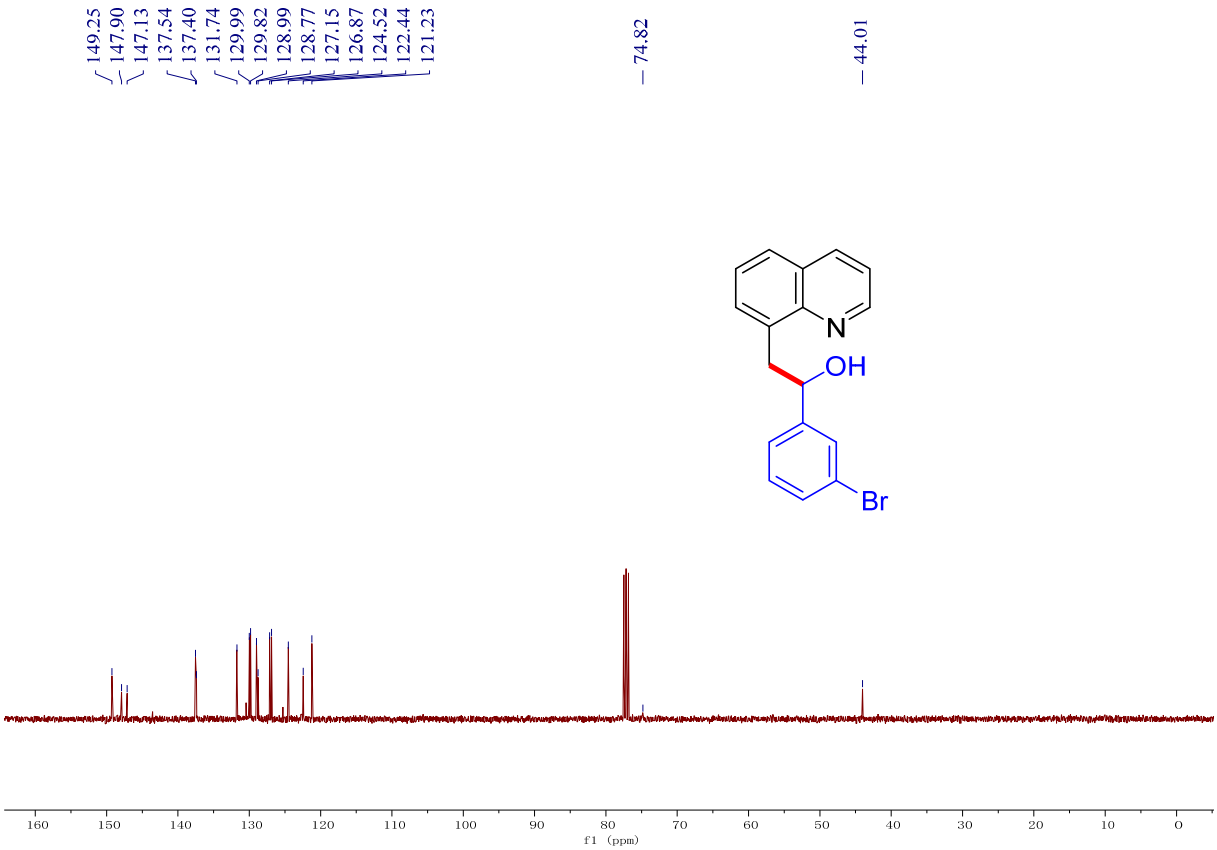
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) spectrum of **3ao**



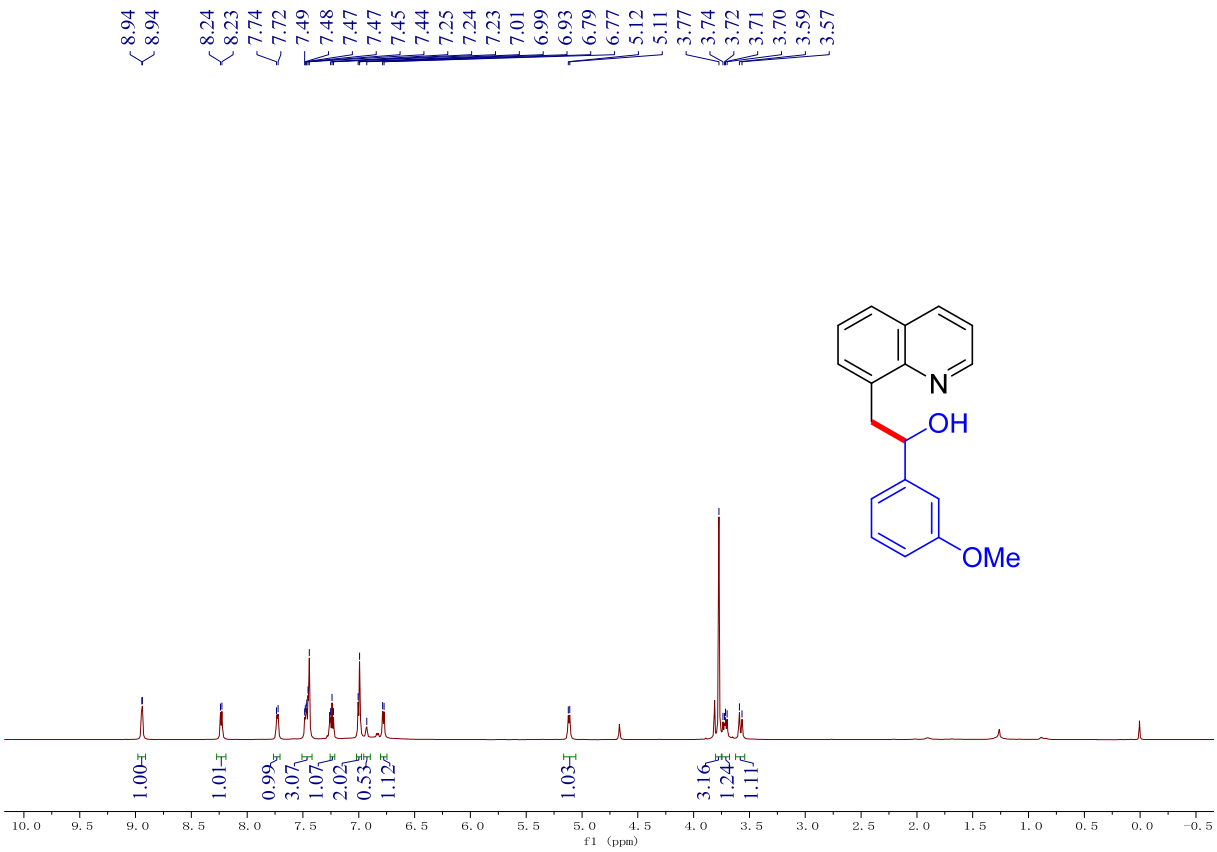
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3ap**



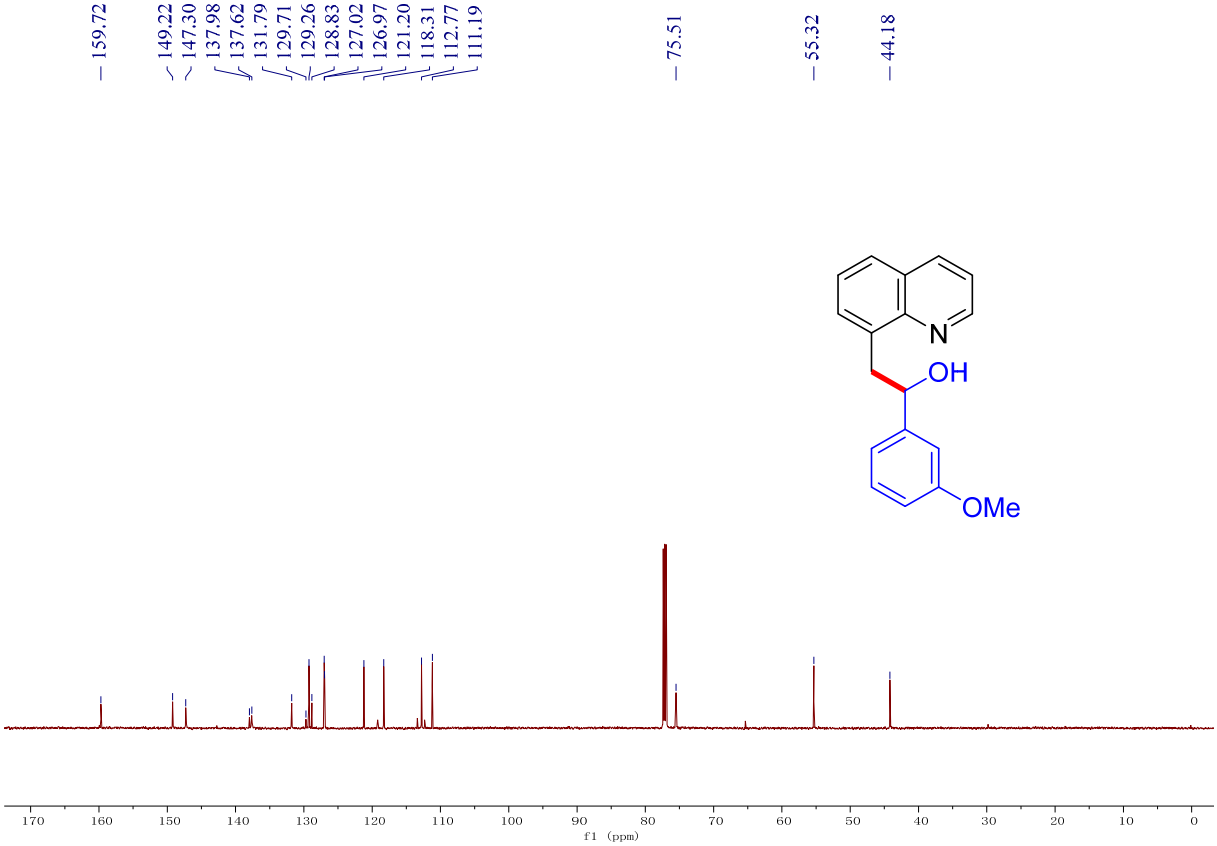
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) spectrum of **3ap**



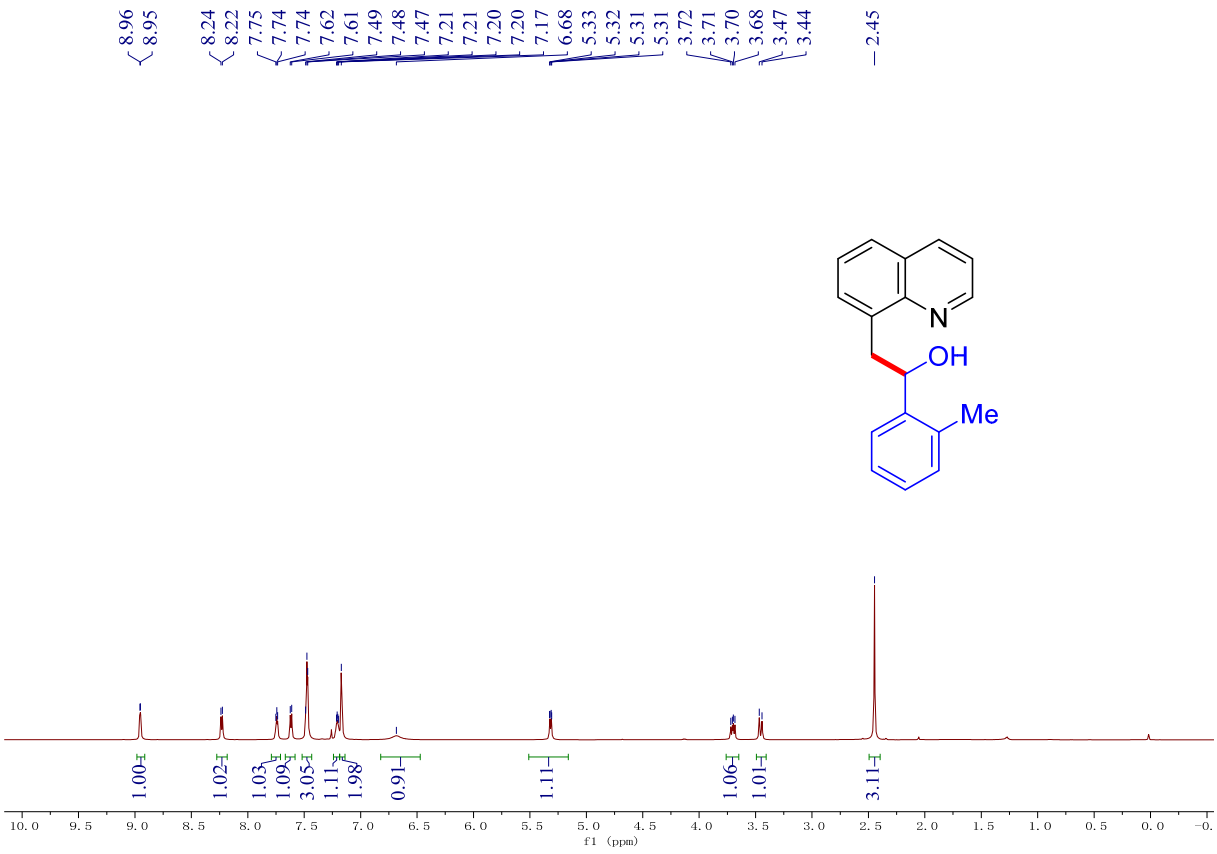
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **3aq**



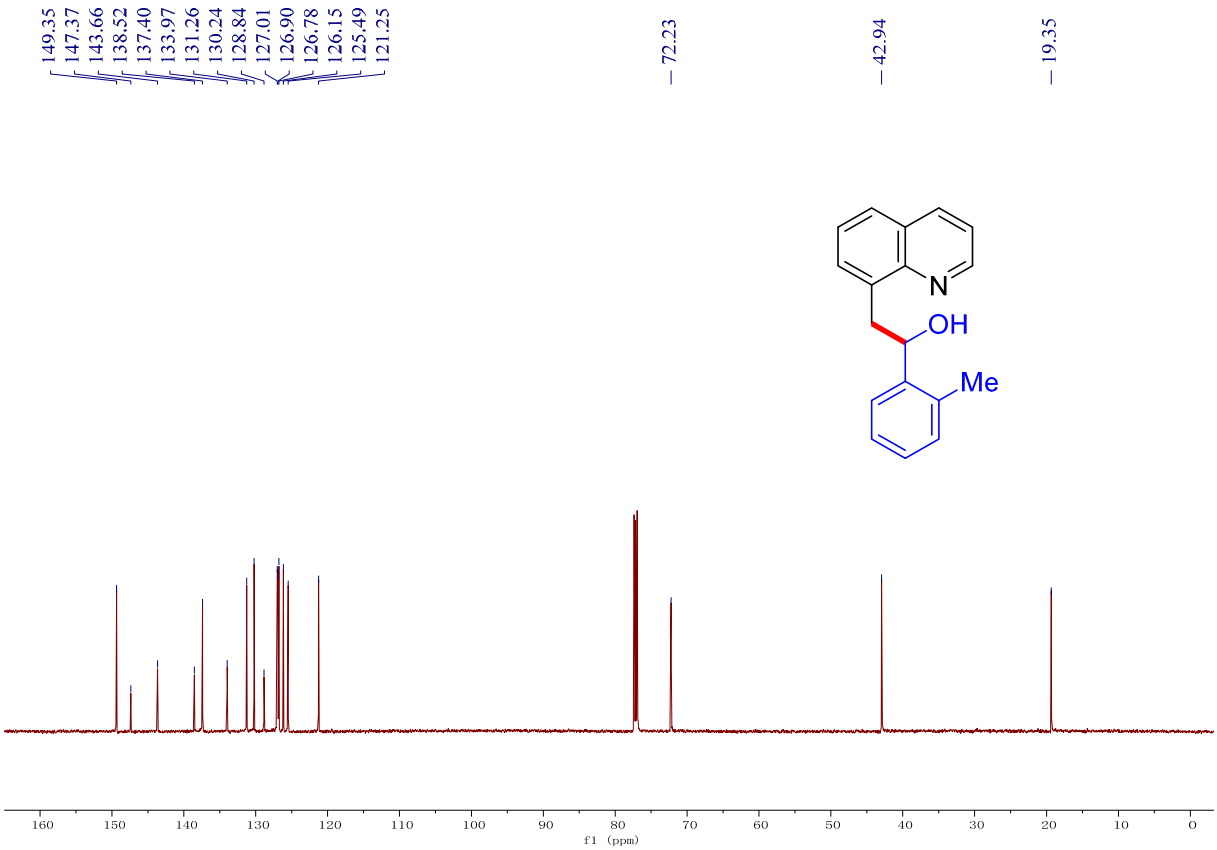
$^{13}C\{^{1}H\}$ NMR (151 MHz, $CDCl_3$) spectrum of **3aq**



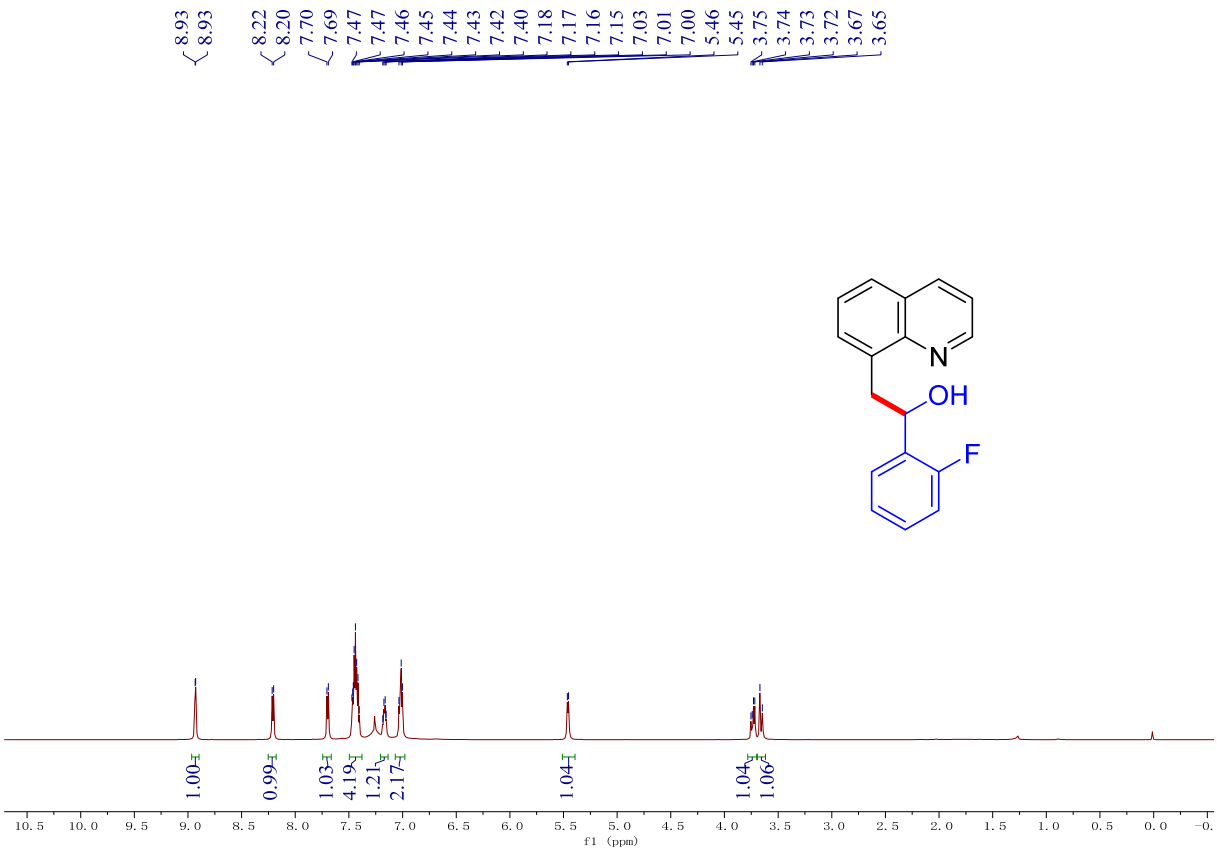
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **3ar**



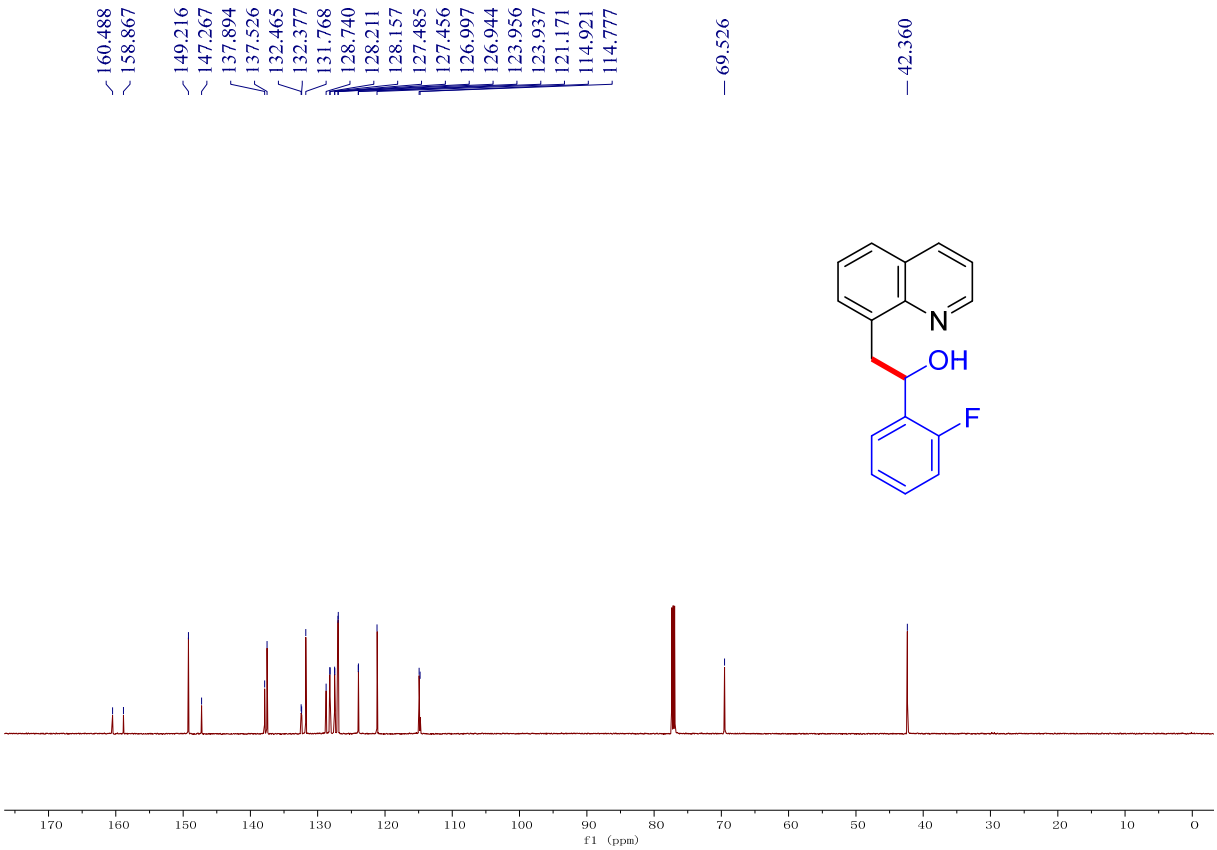
$^{13}C\{^{1}H\}$ NMR (151 MHz, $CDCl_3$) spectrum of **3ar**



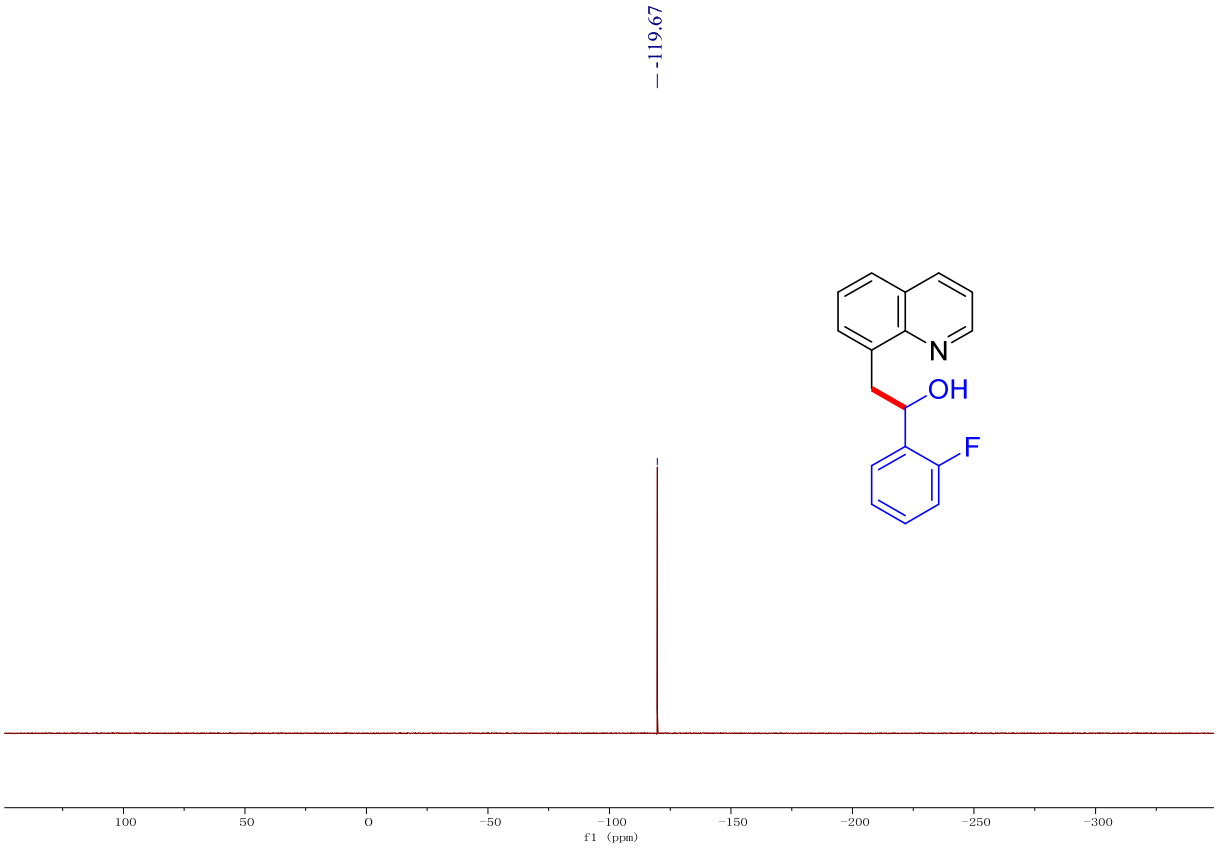
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **3as**



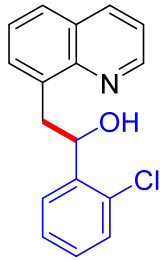
$^{13}C\{^{1}H\}$ NMR (151 MHz, $CDCl_3$) spectrum of **3as**

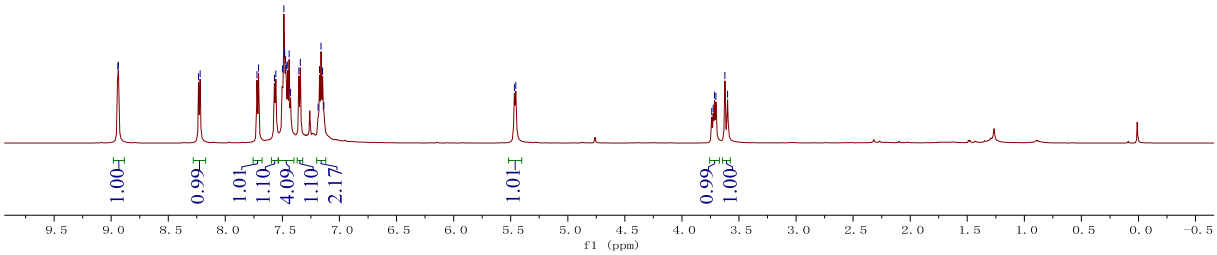


^{19}F NMR (376 MHz, $CDCl_3$) spectrum of **3as**

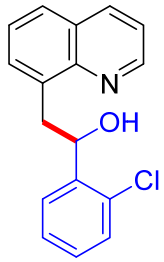


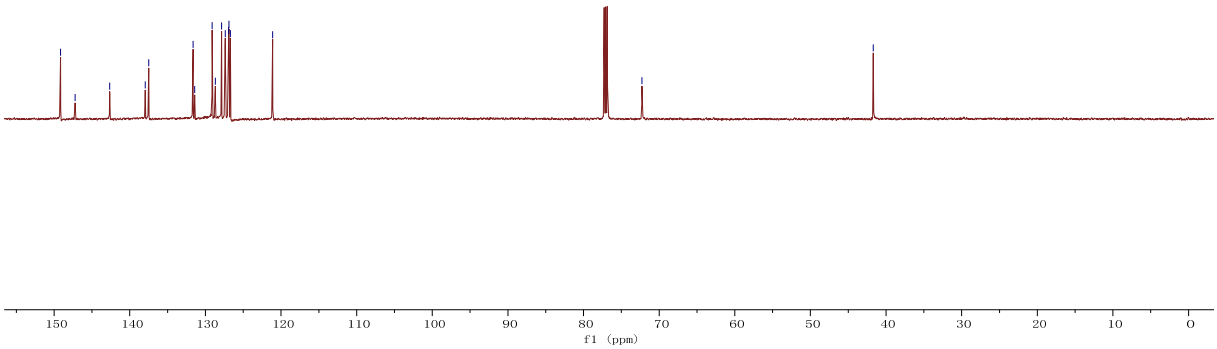
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **3at**



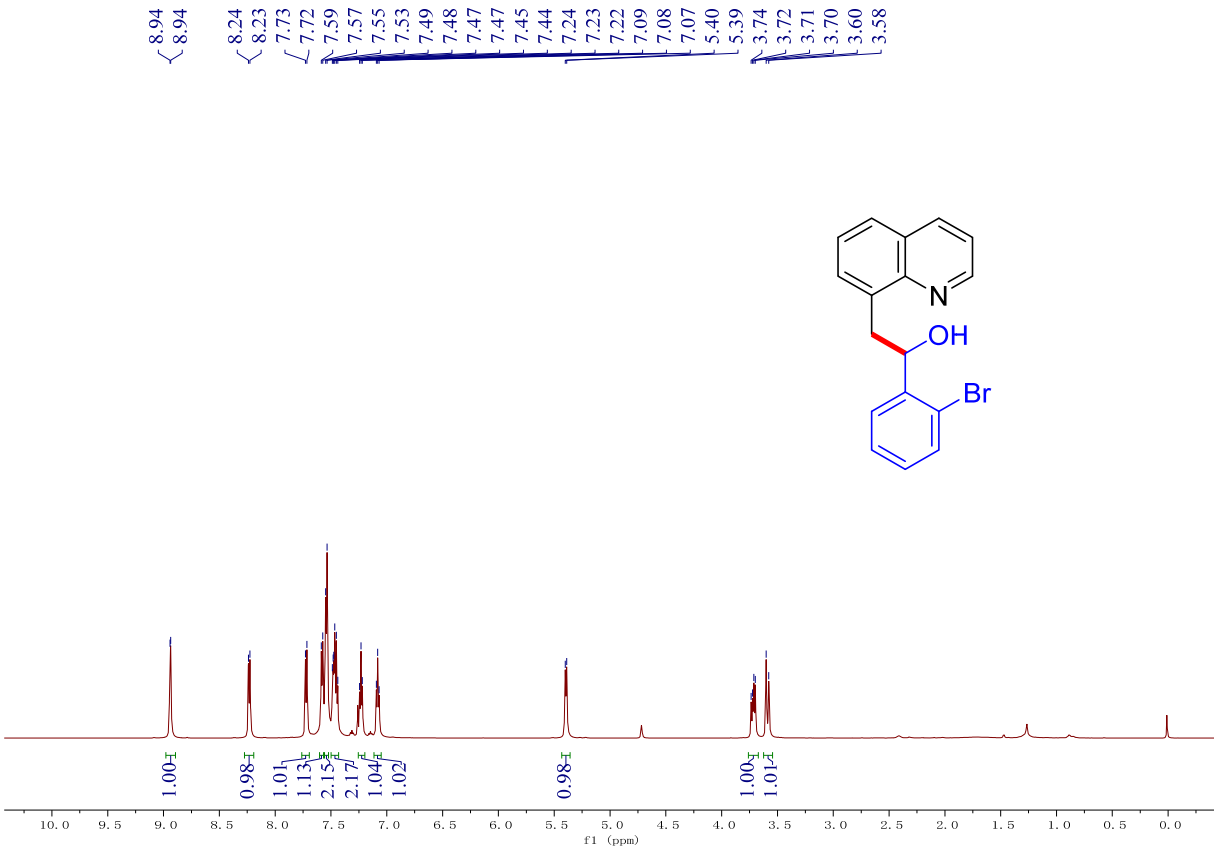


^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) spectrum of **3at**

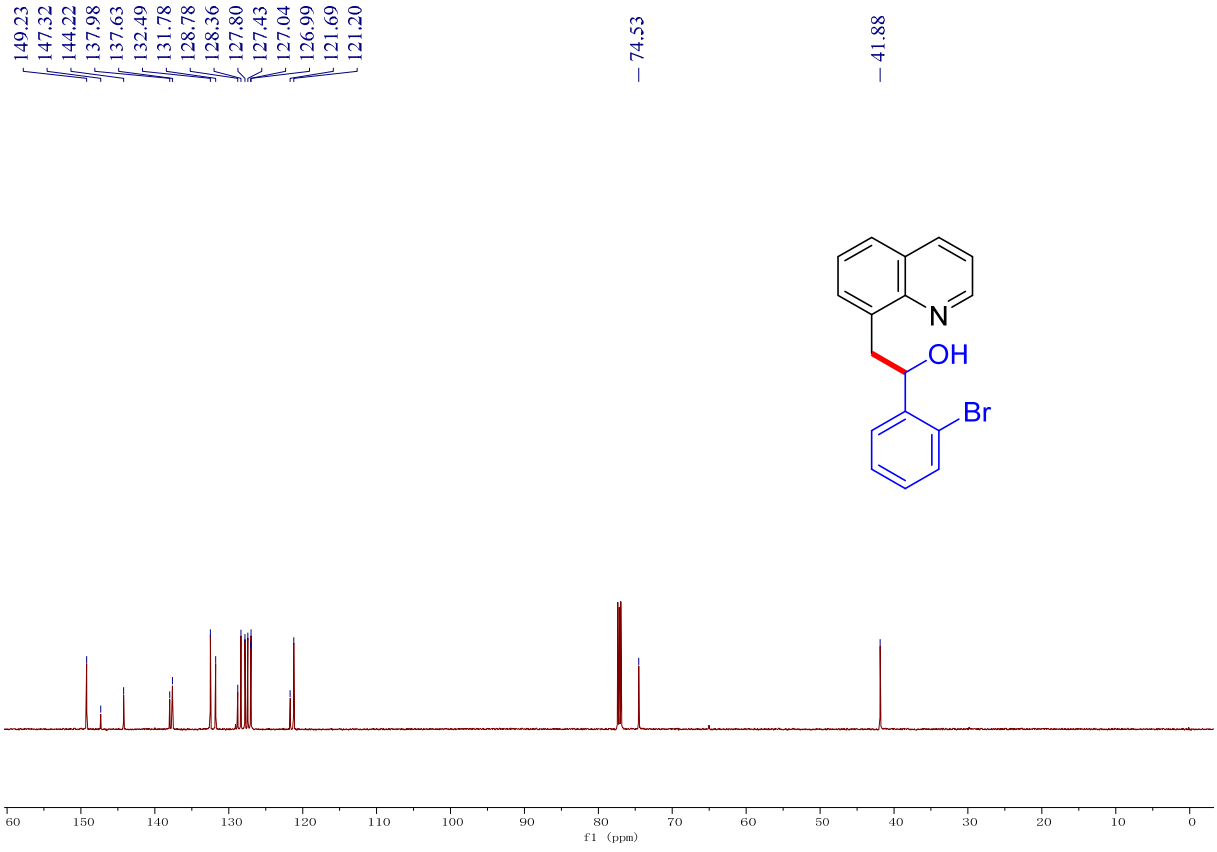




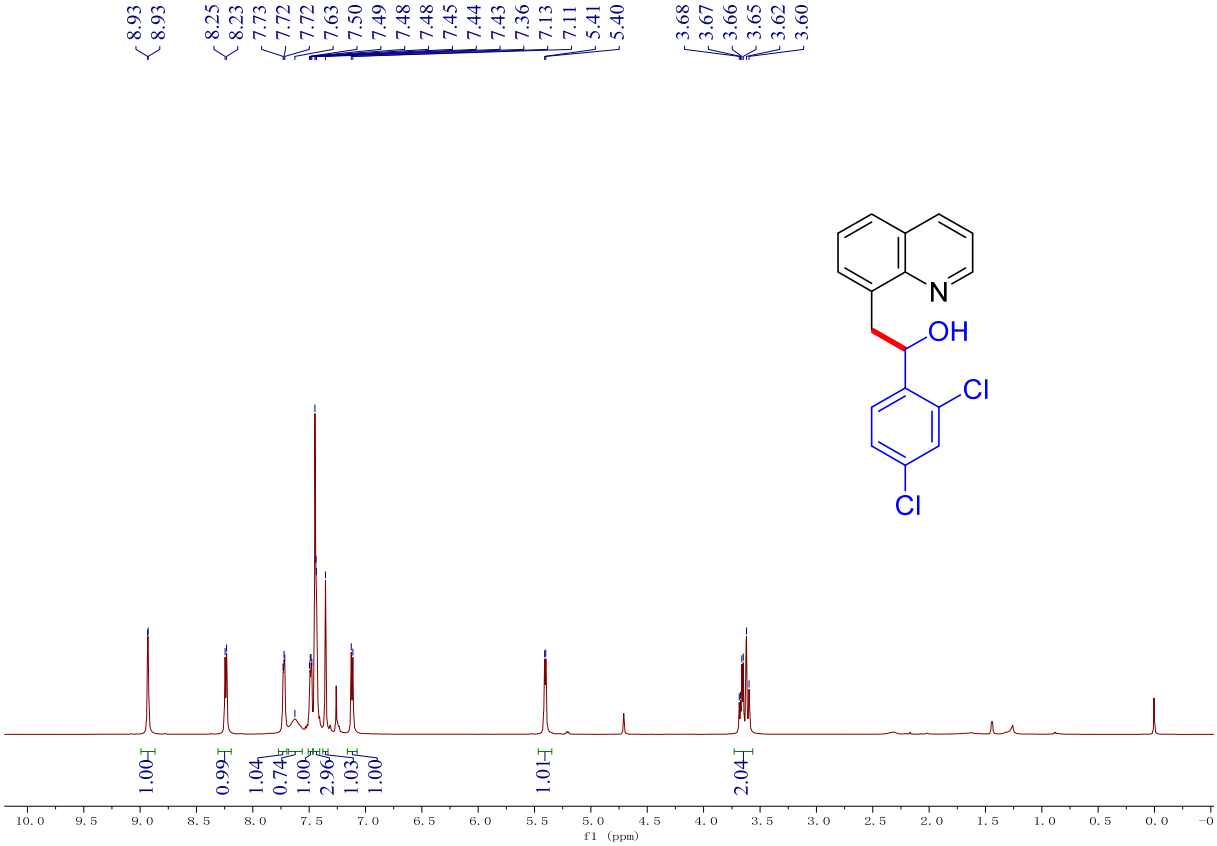
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **3au**



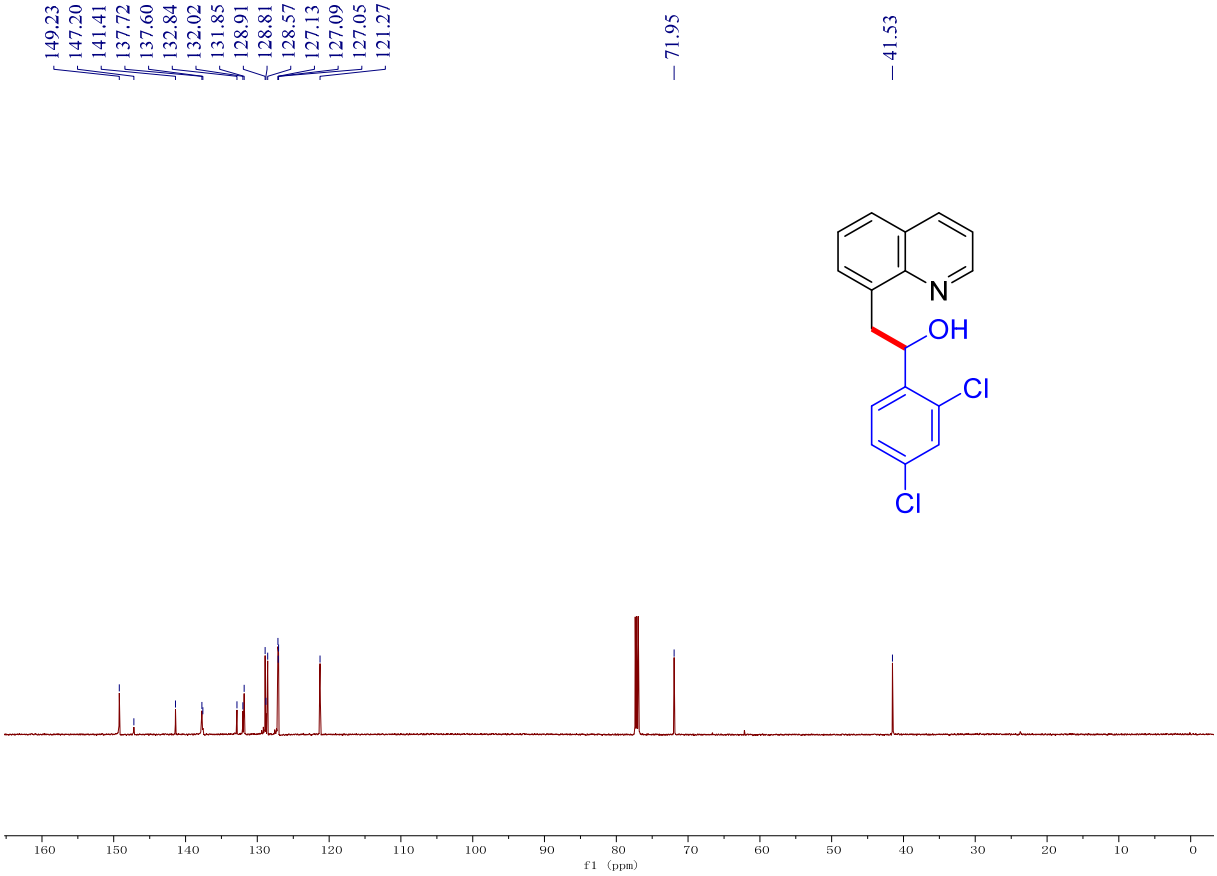
^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) spectrum of **3au**



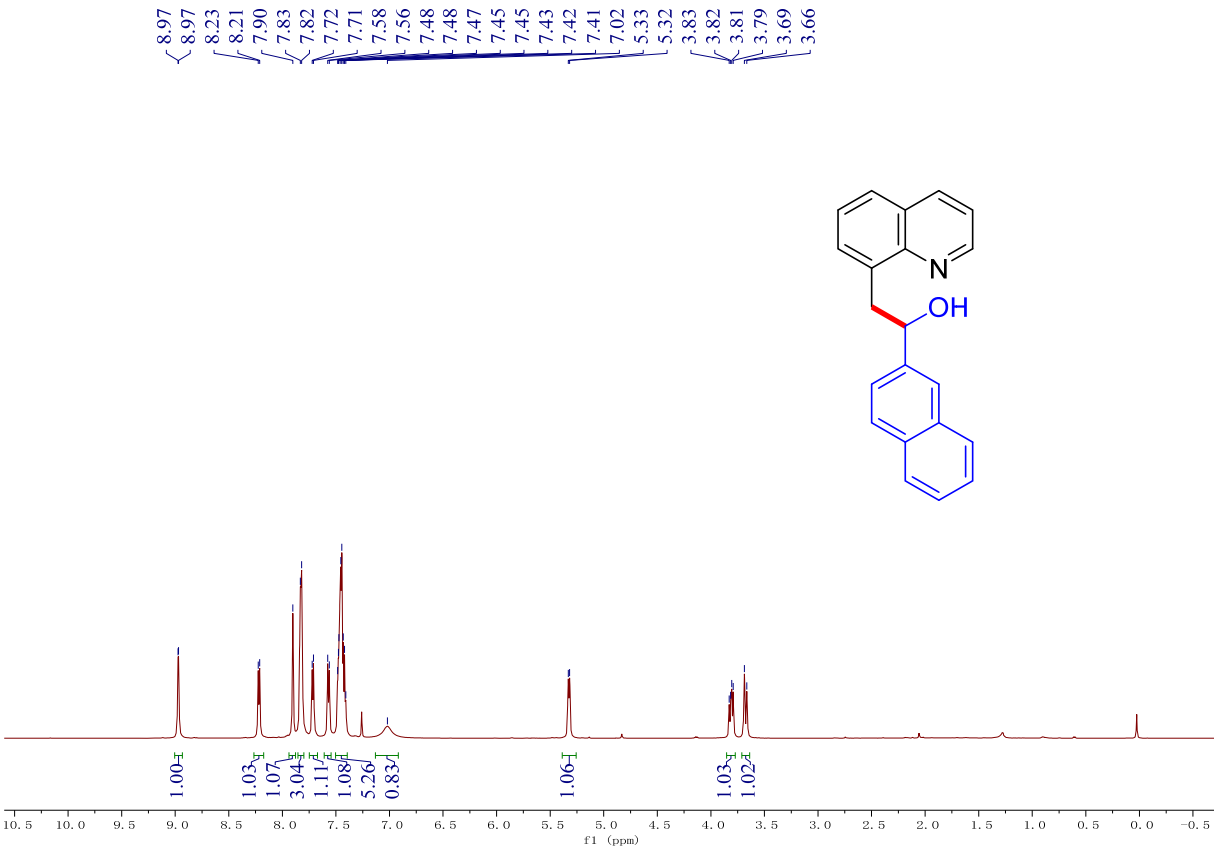
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **3av**



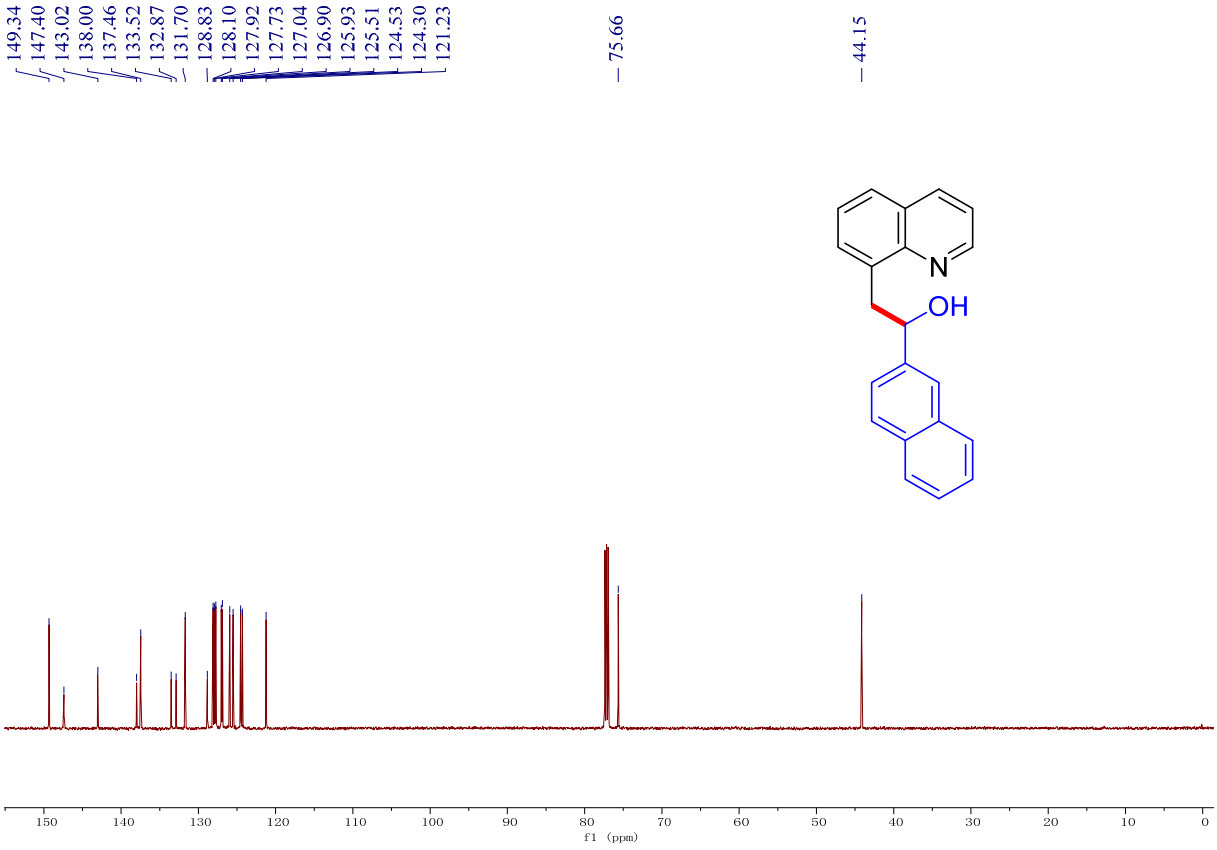
^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) spectrum of **3av**



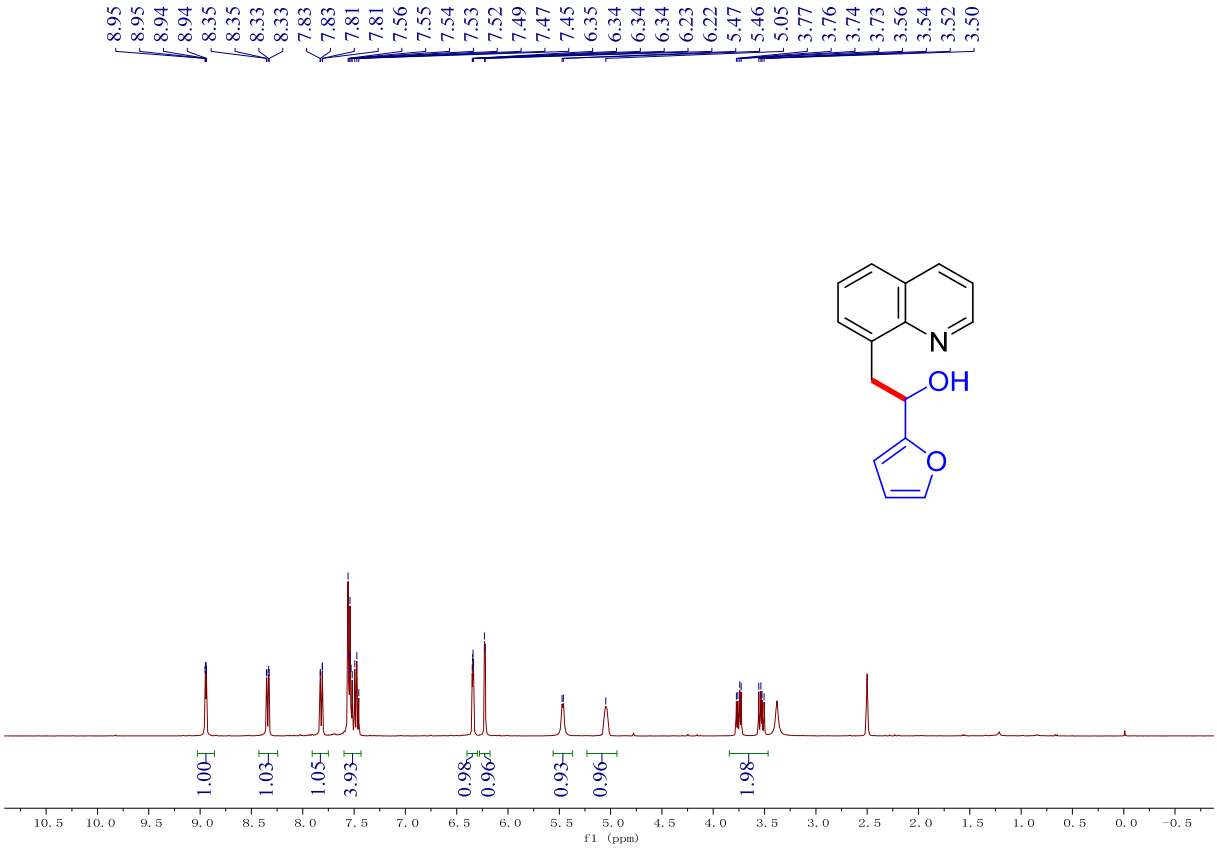
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **3aw**



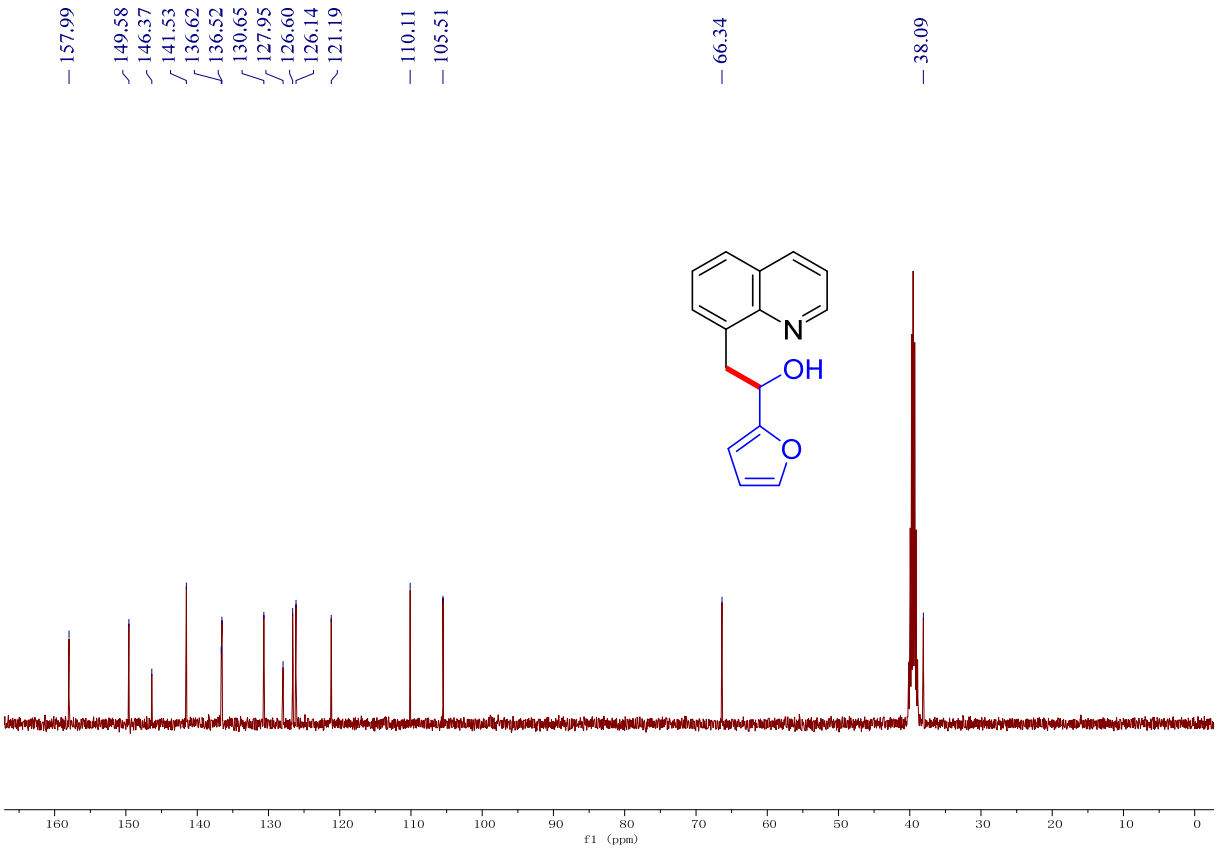
^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) spectrum of **3aw**



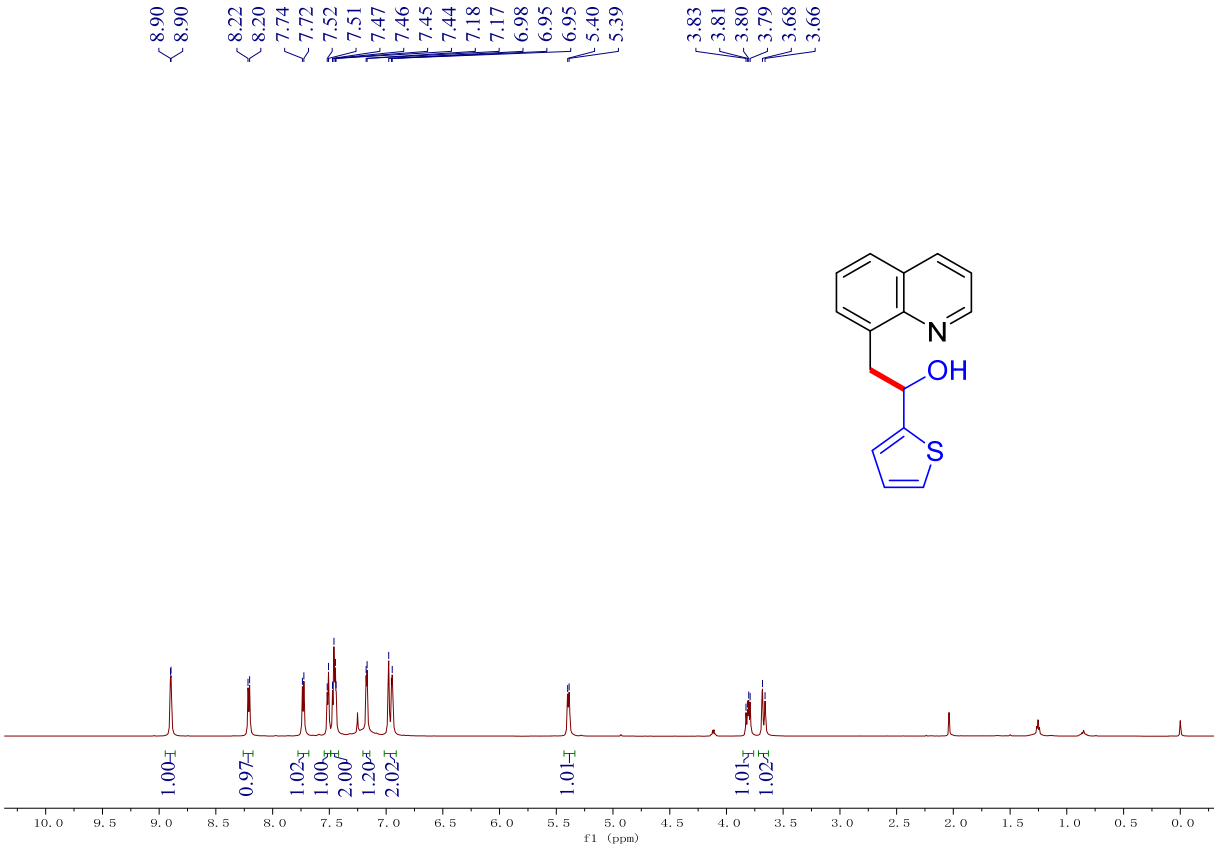
^{1}H NMR (400 MHz, DMSO-d_6) spectrum of **3ax**



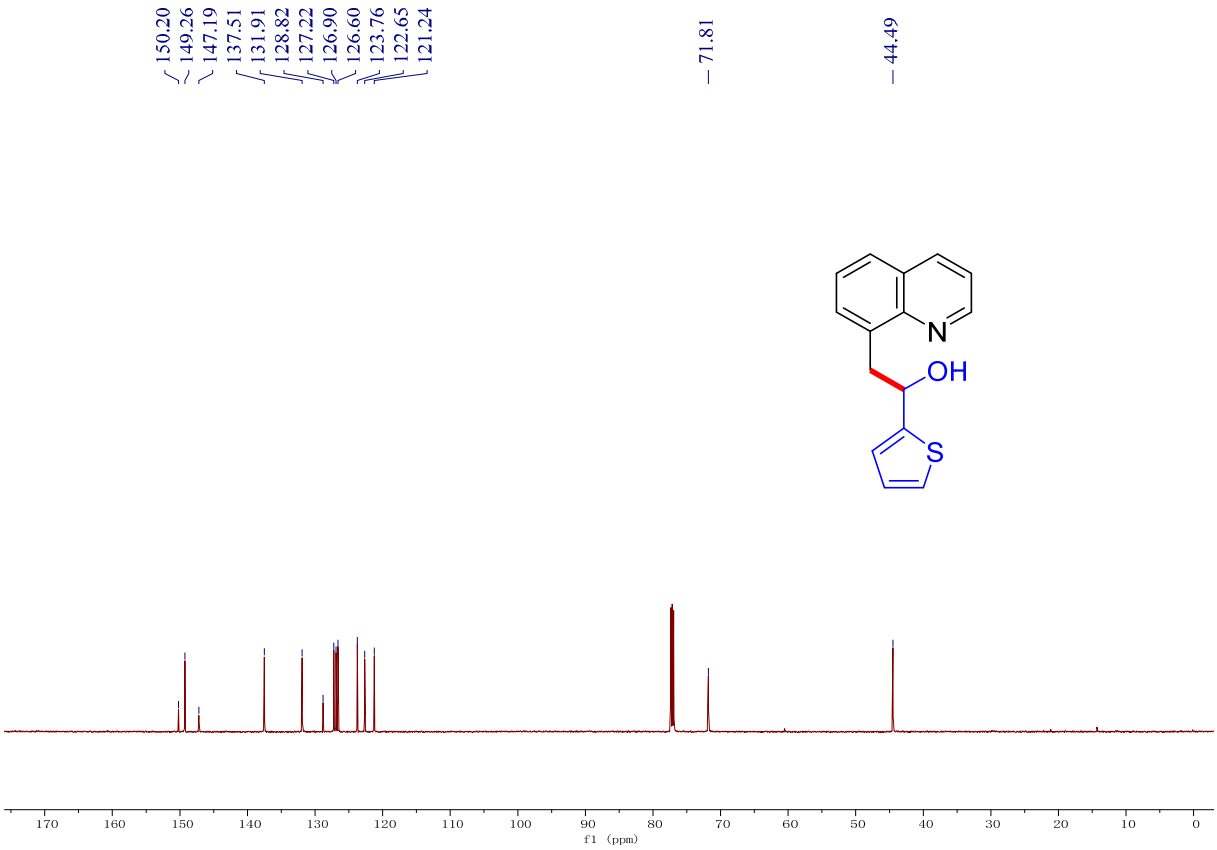
^{13}C{^{1}H} NMR (101 MHz, DMSO-d_6) spectrum of **3ax**



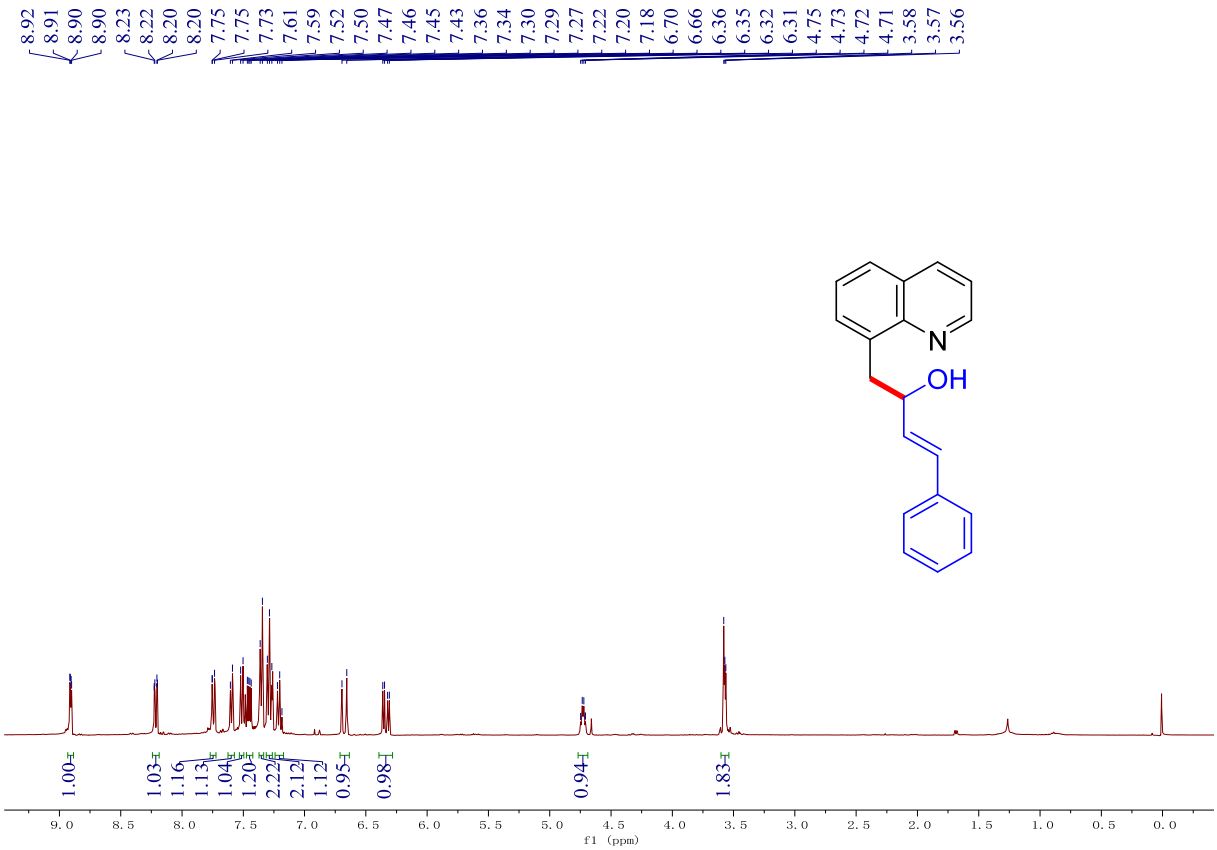
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **3ay**



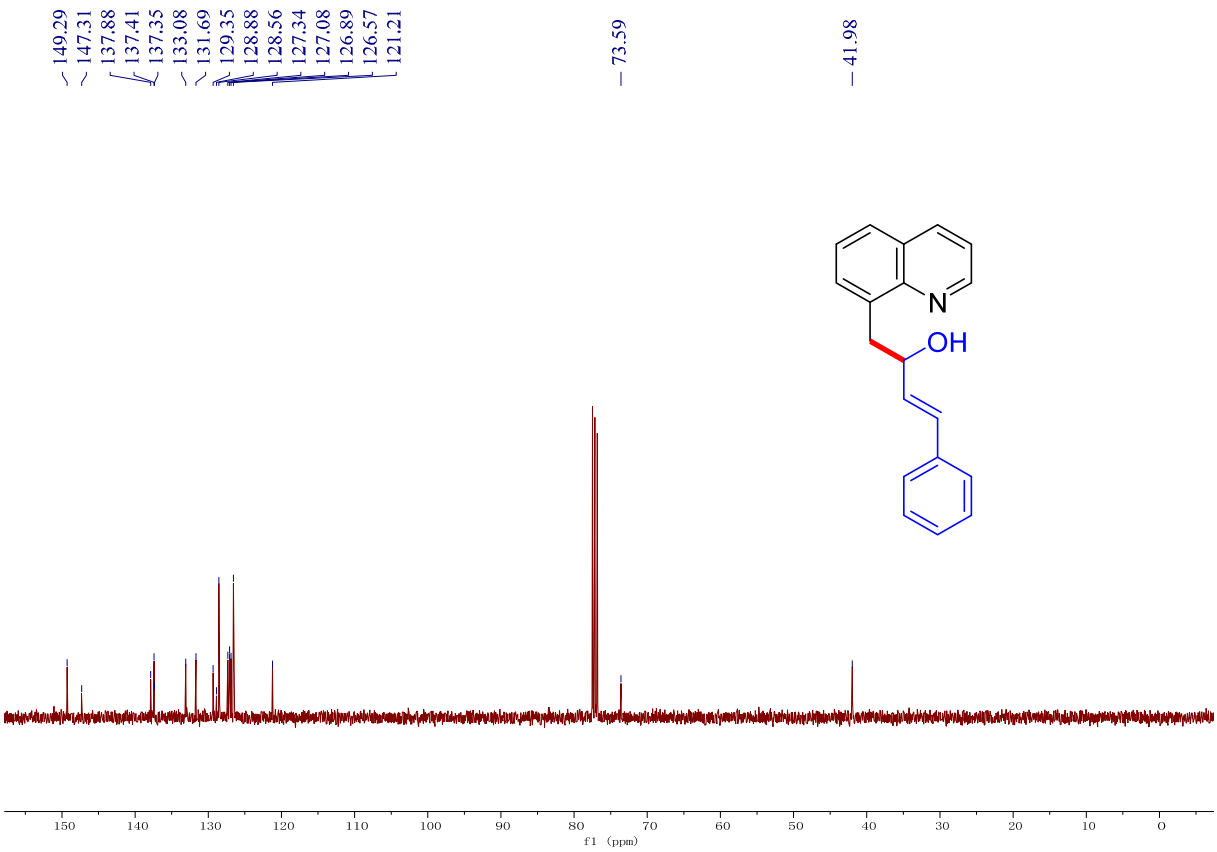
^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) spectrum of **3ay**



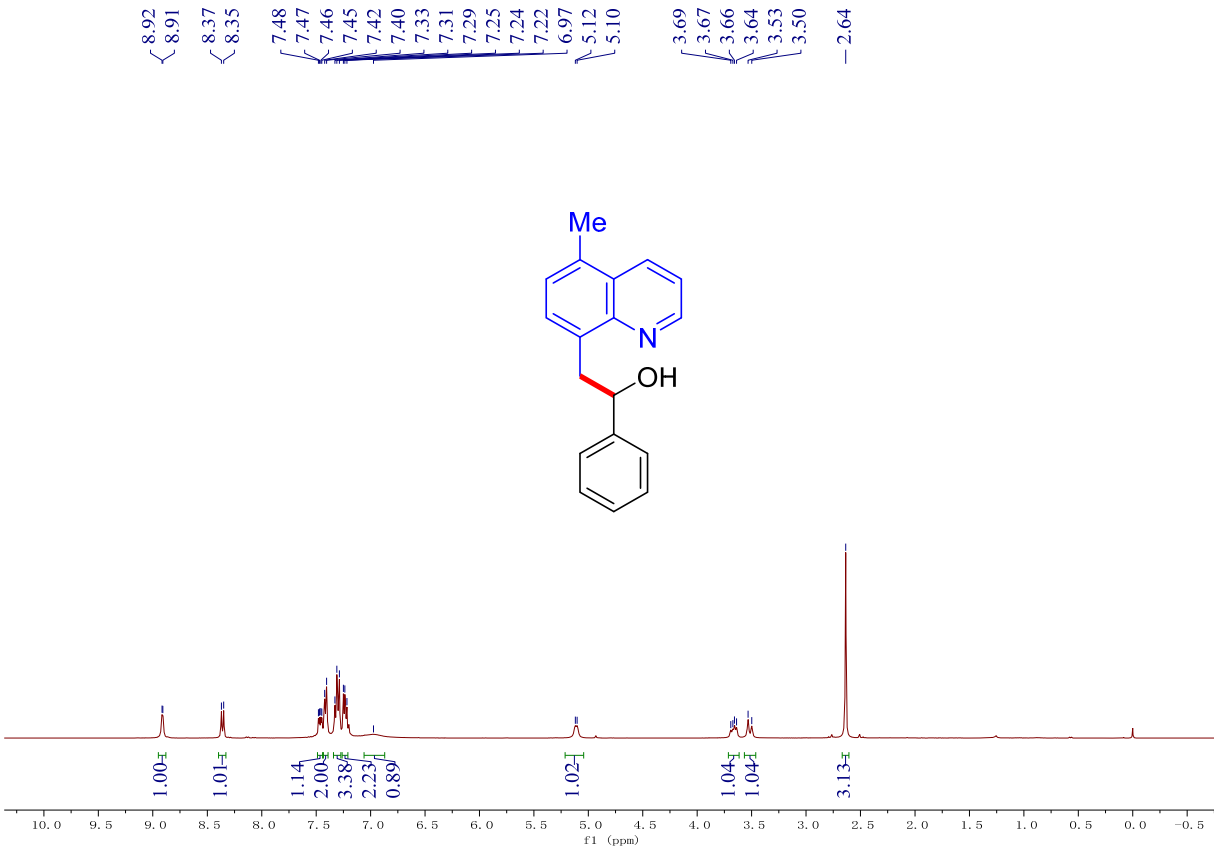
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3az**



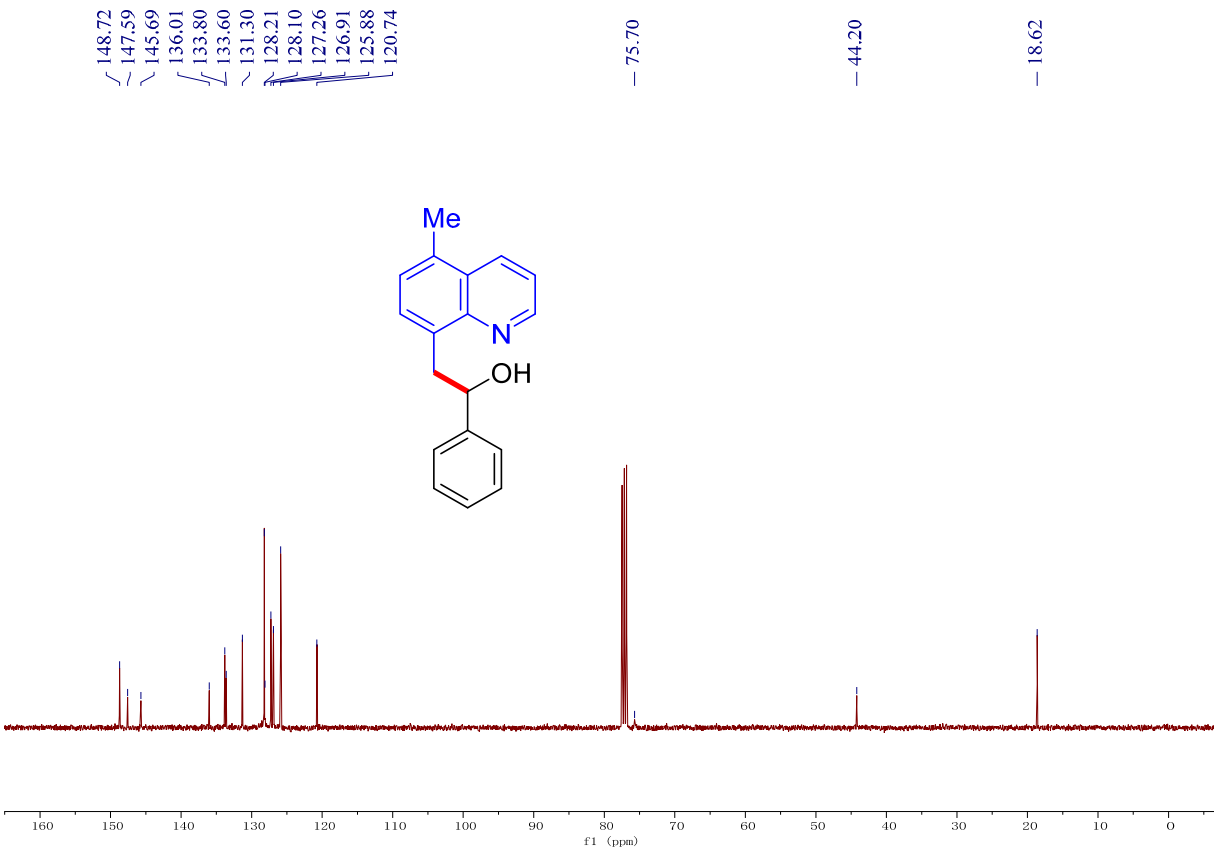
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) spectrum of **3az**



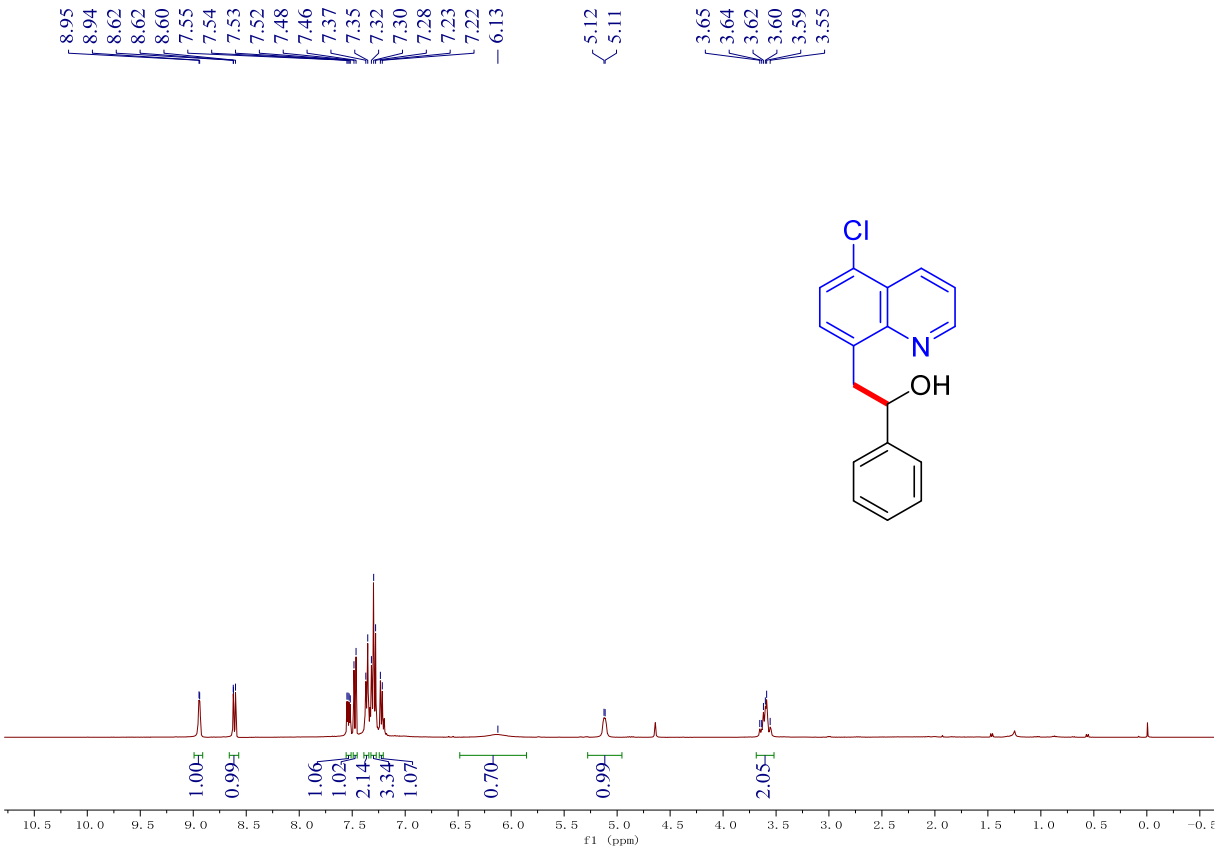
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3ba**



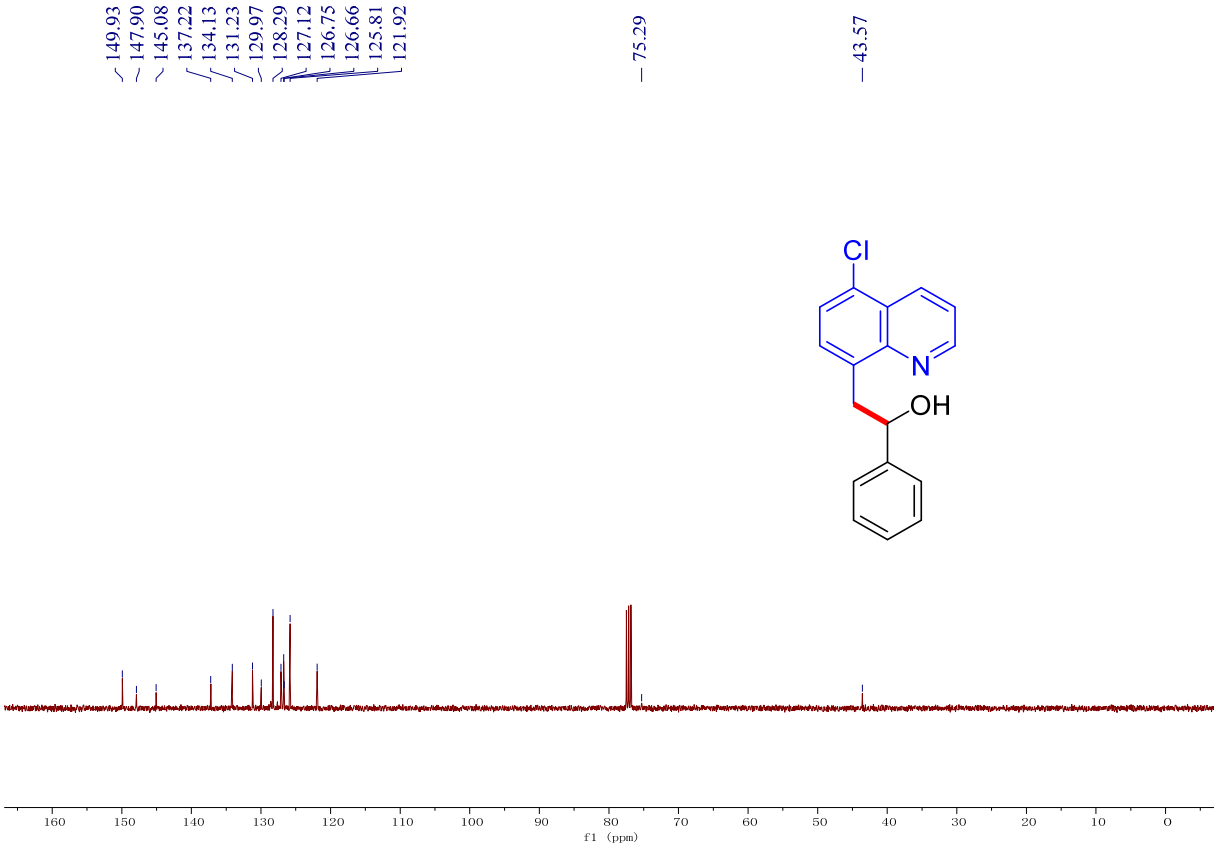
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) spectrum of **3ba**



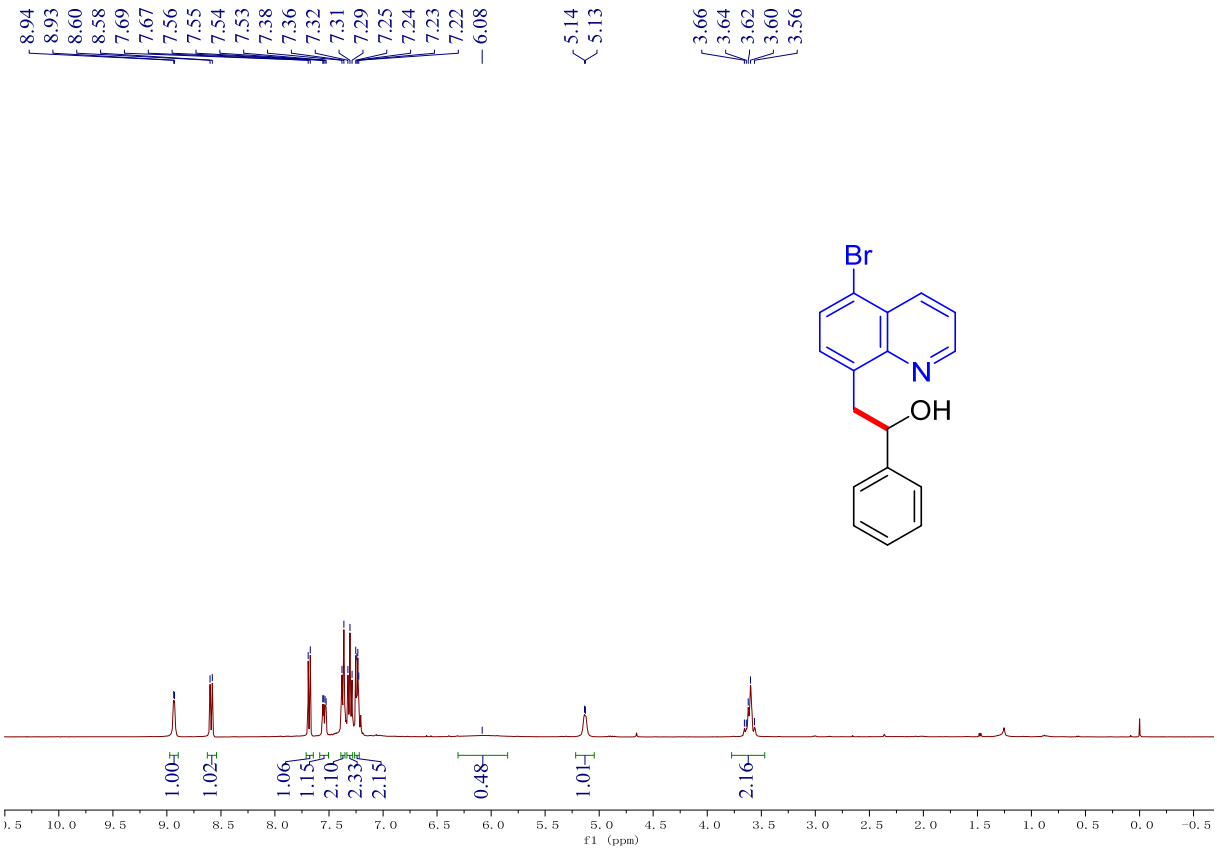
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3ca**



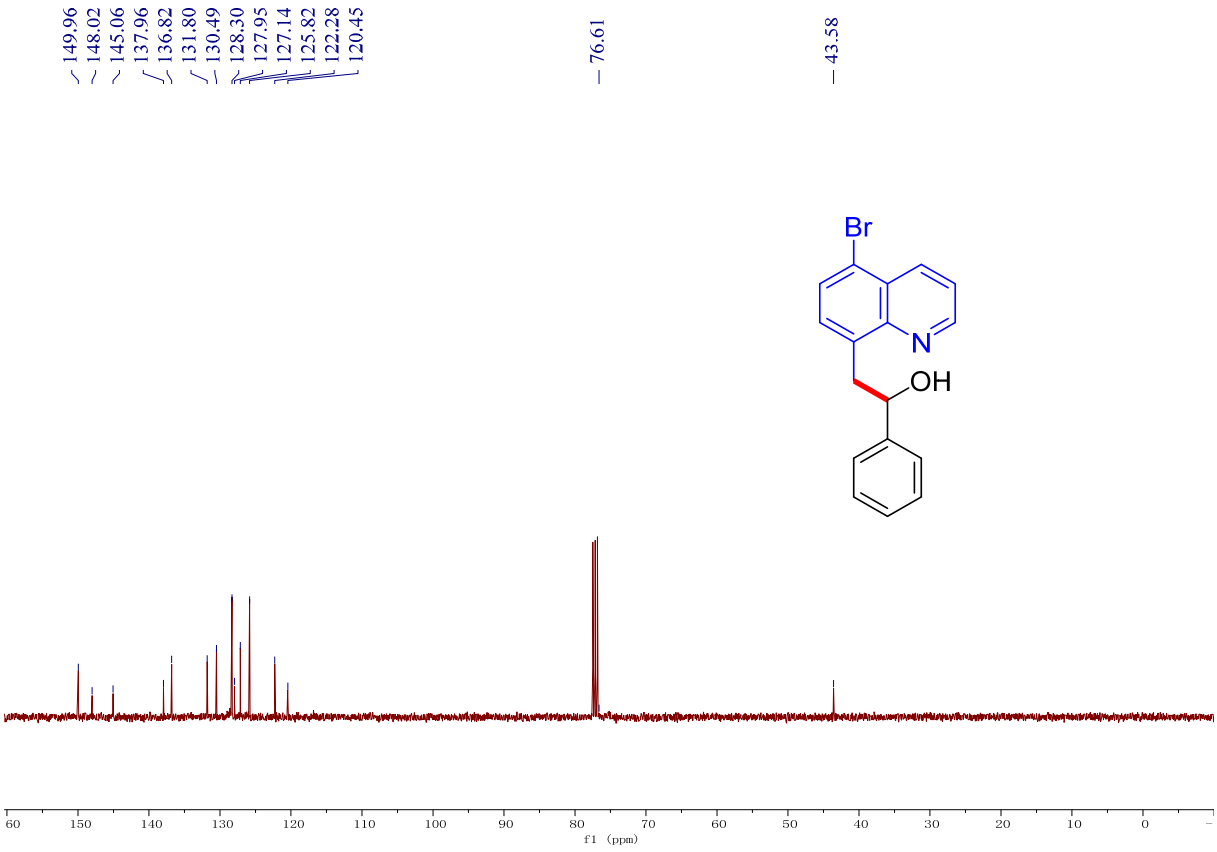
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) spectrum of **3ca**



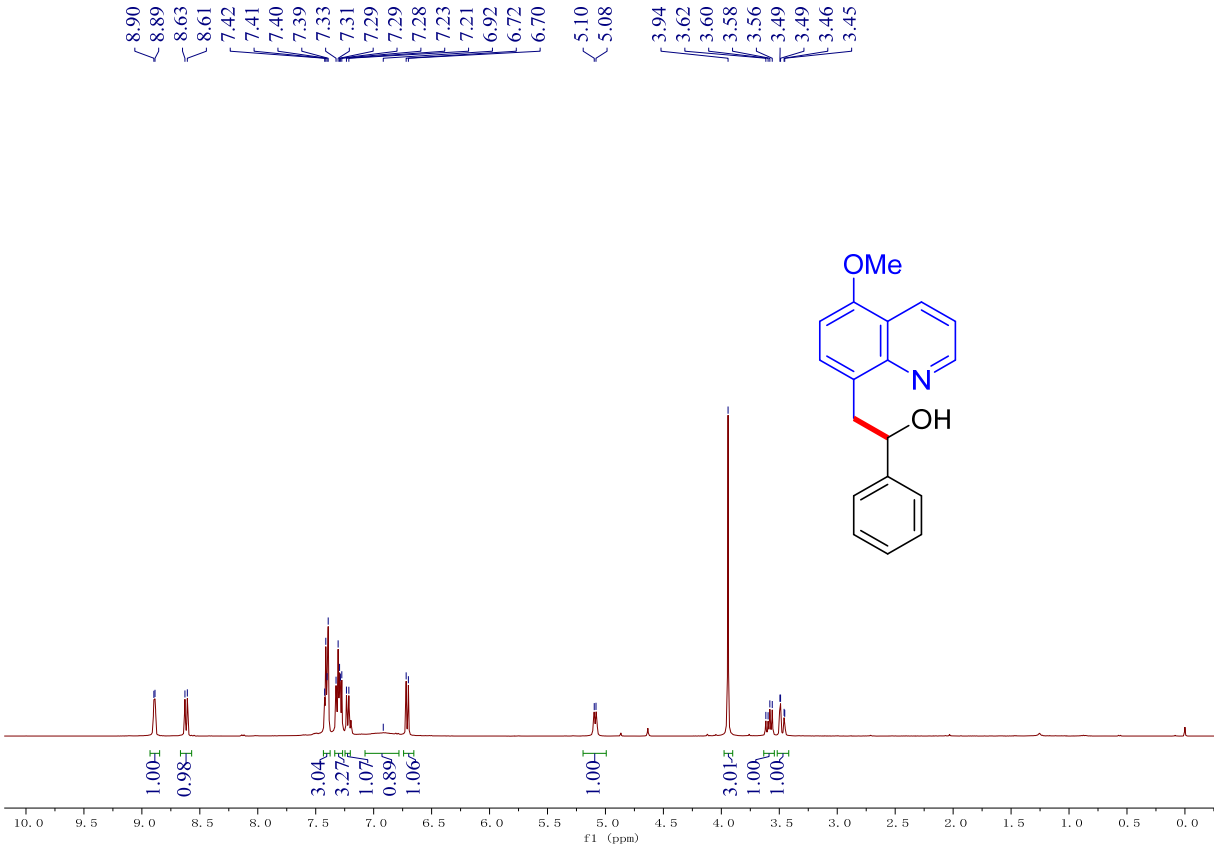
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3da**



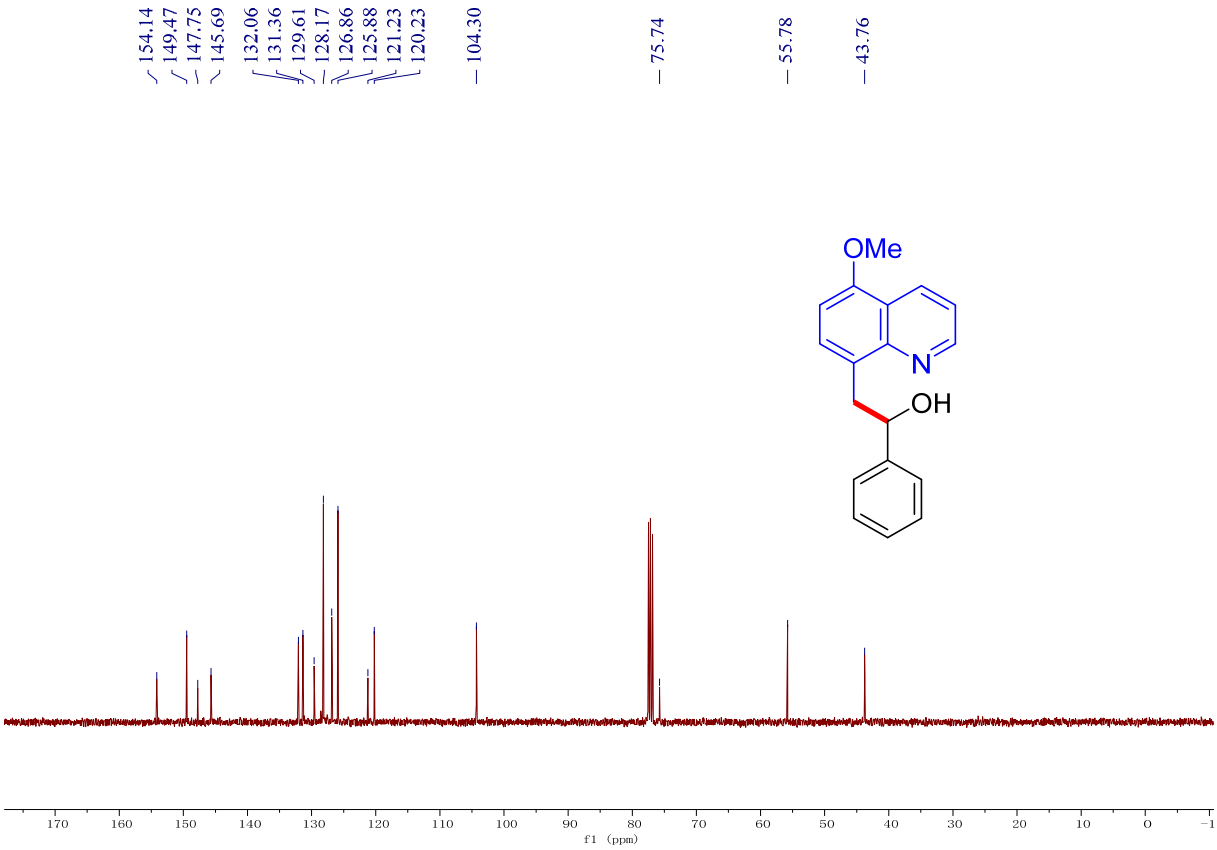
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) spectrum of **3da**



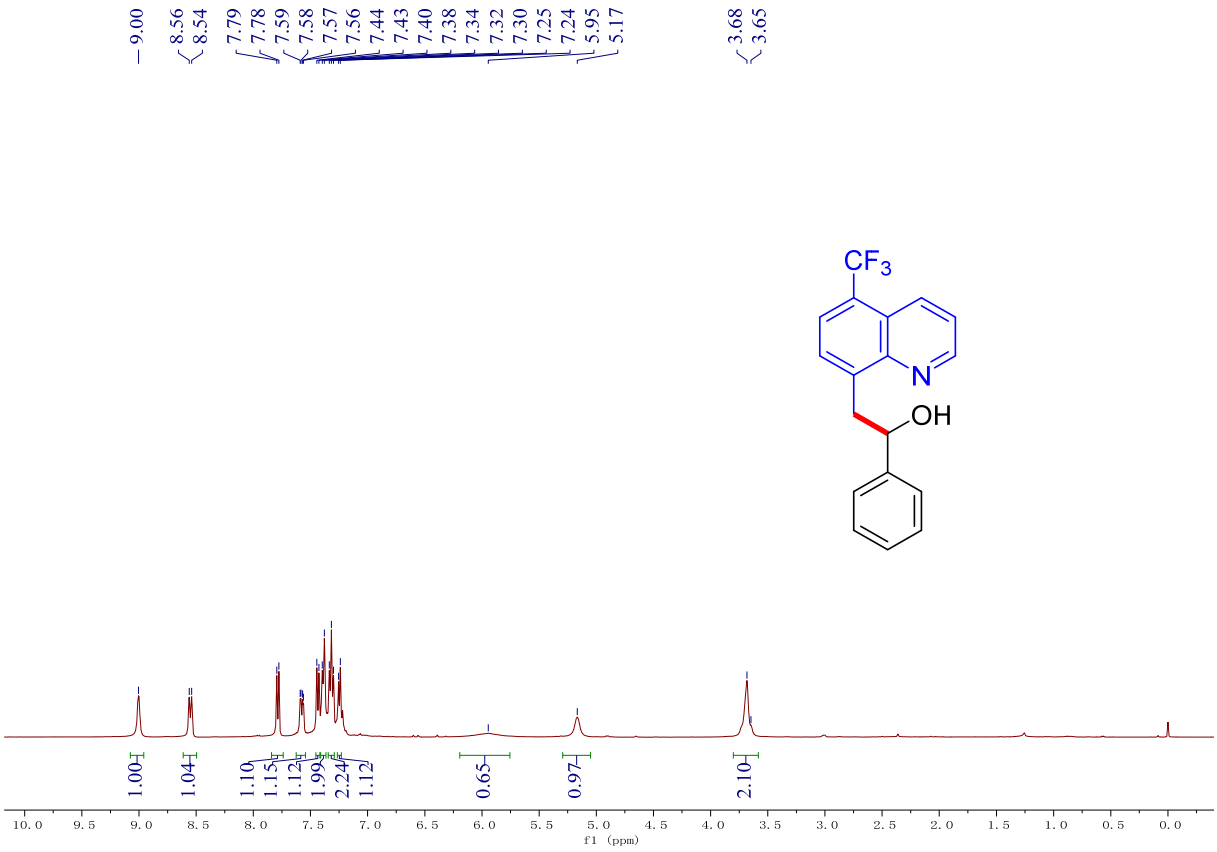
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3ea**



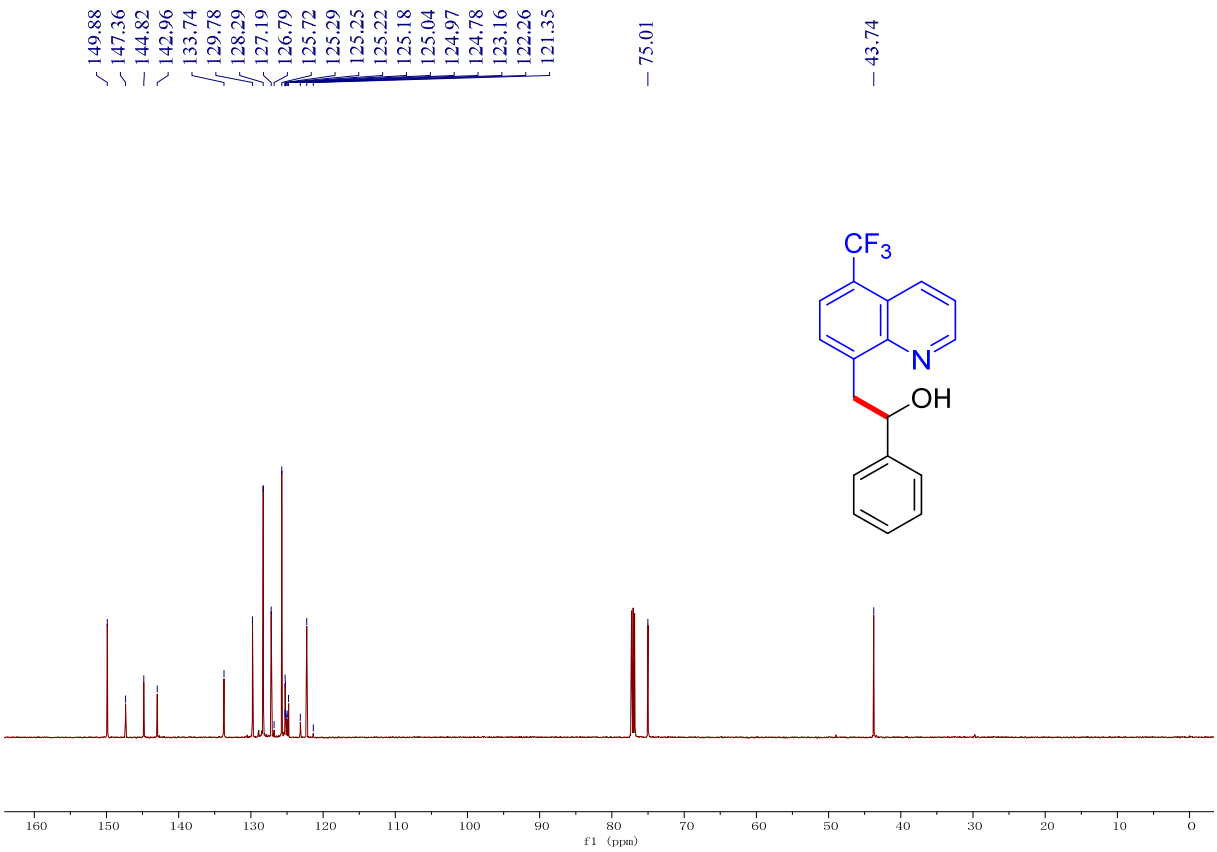
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) spectrum of **3ea**



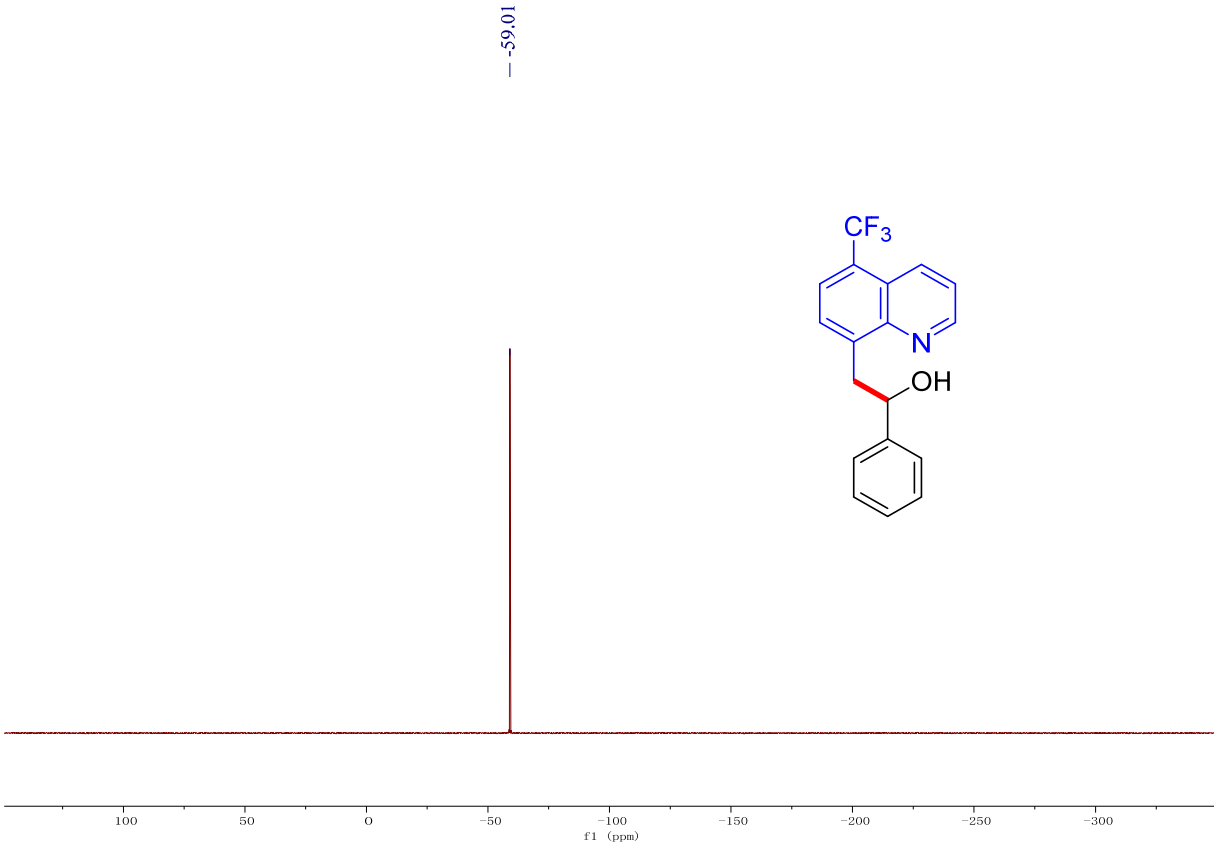
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3fa**



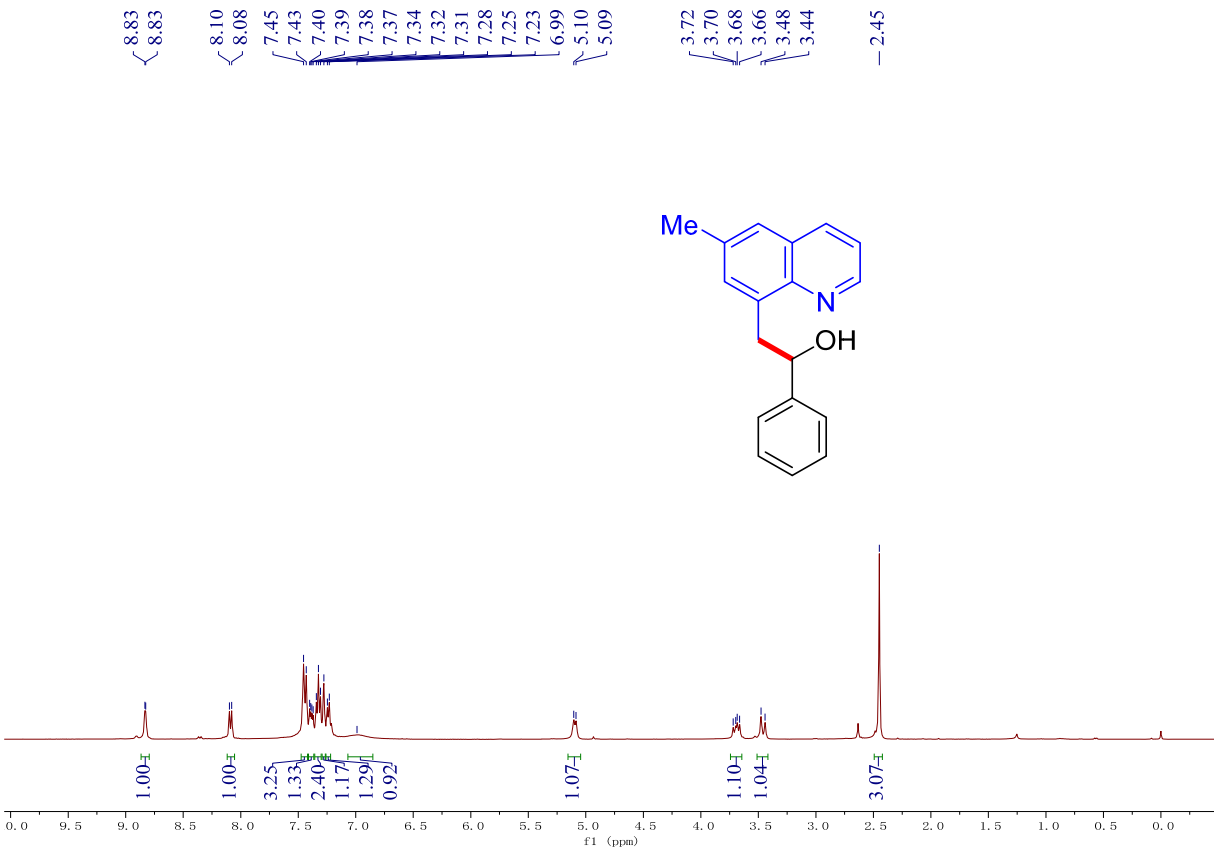
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) spectrum of **3fa**



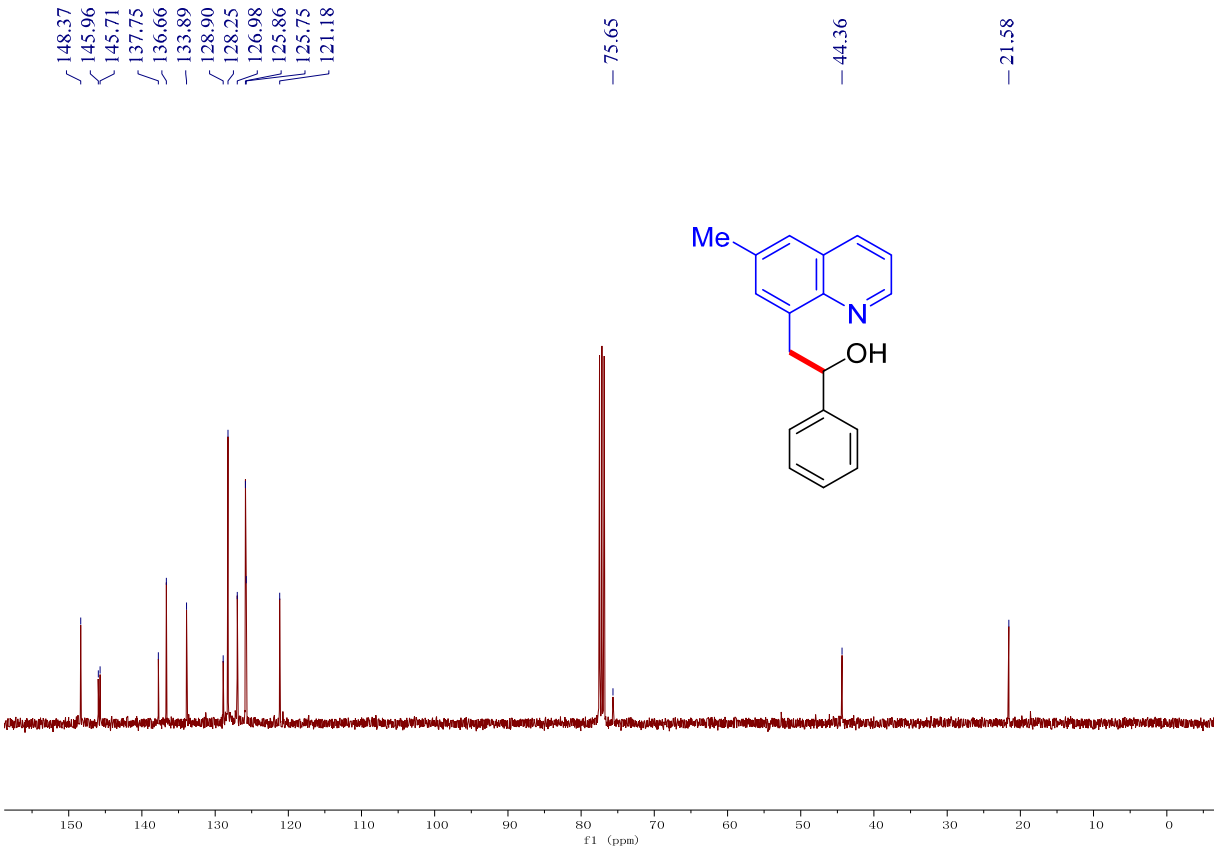
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of **3fa**



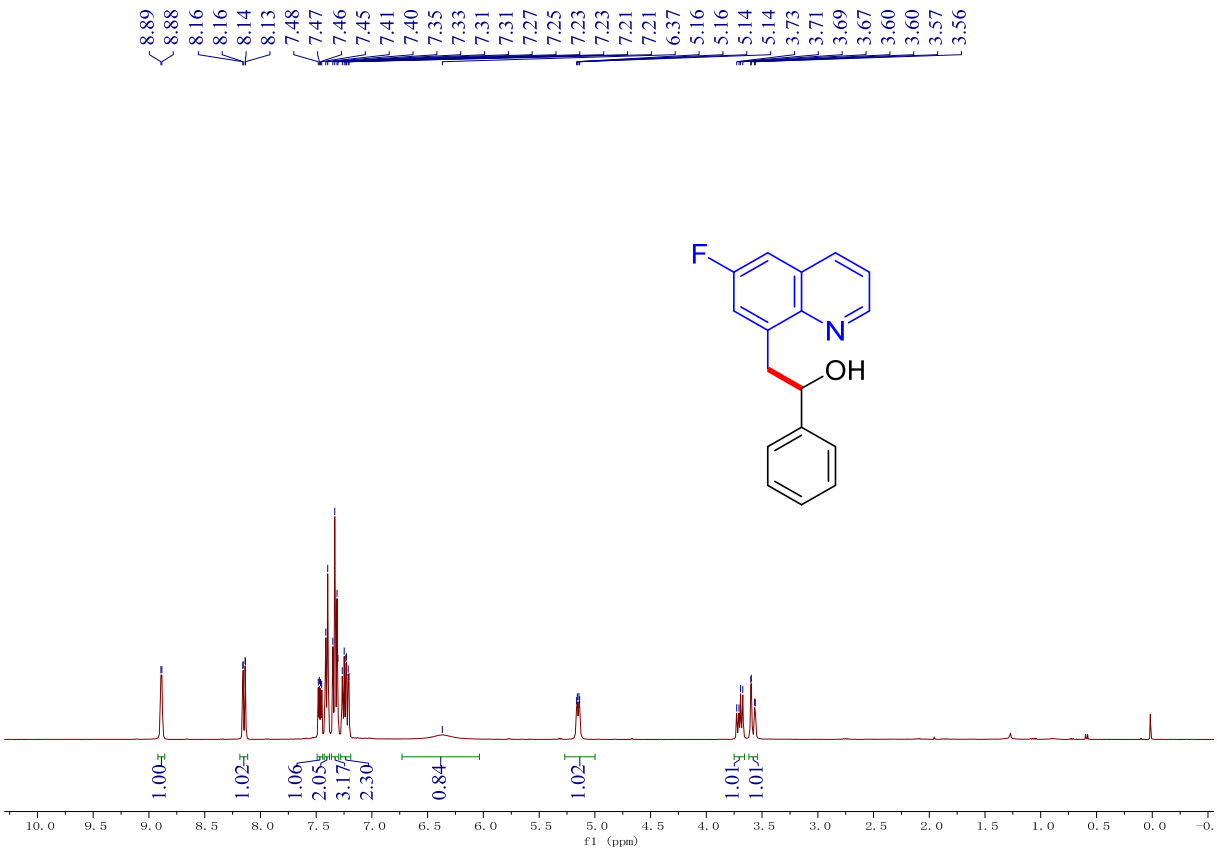
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3ga**



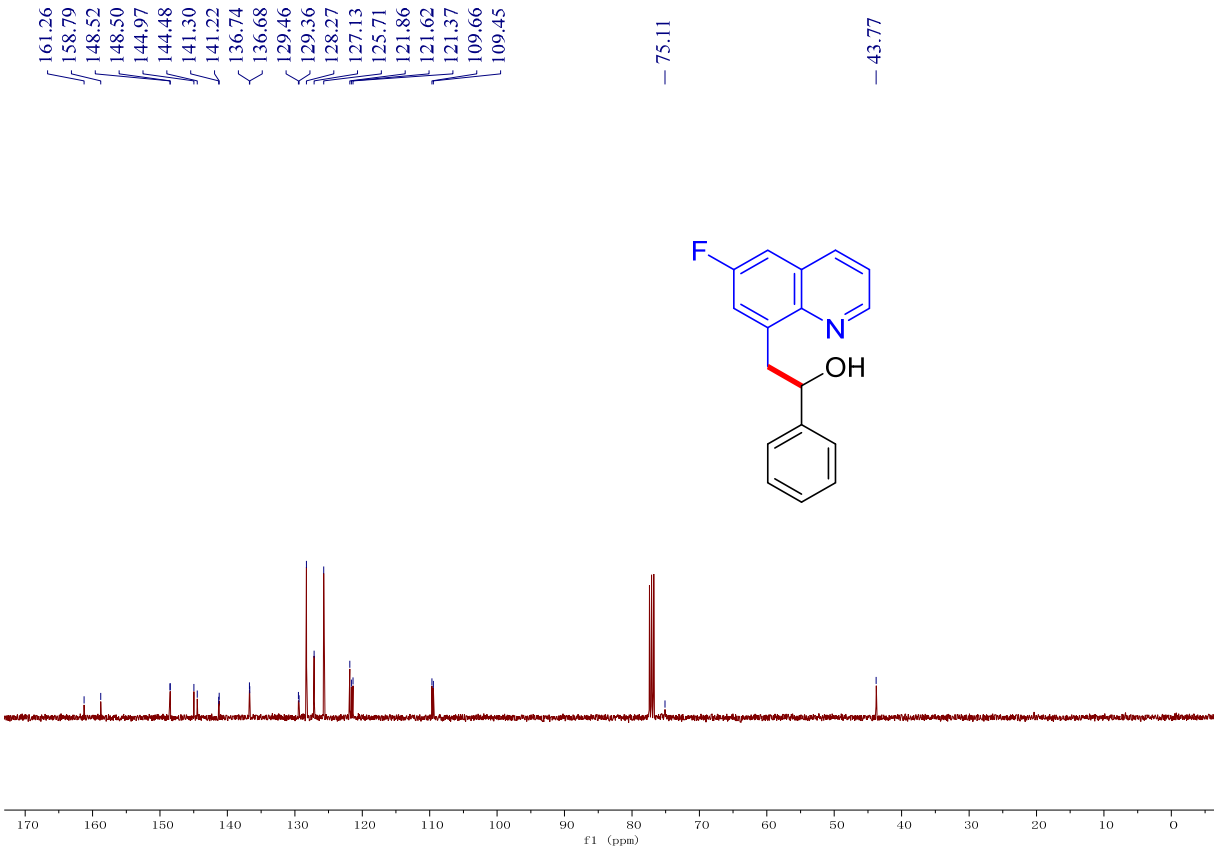
$^{13}C\{^{1}H\}$ NMR (151 MHz, $CDCl_3$) spectrum of **3ga**



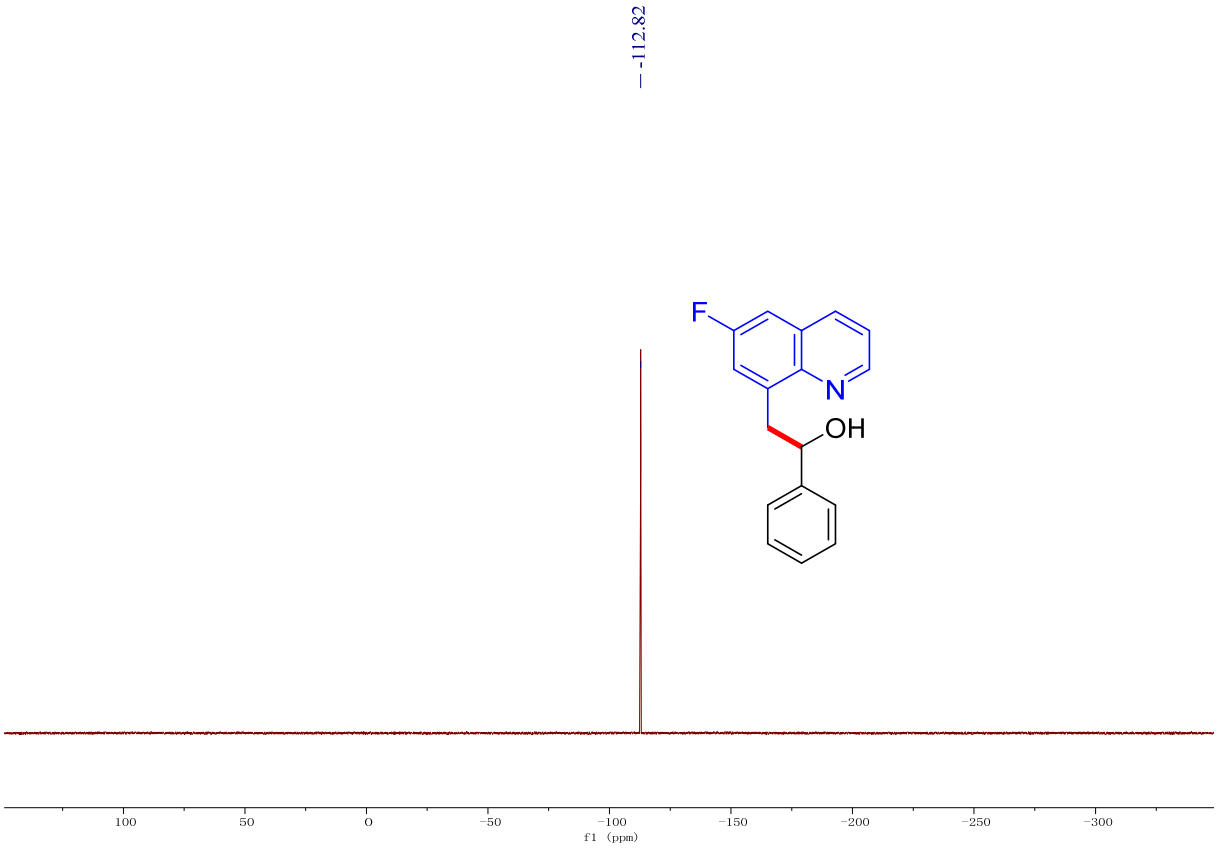
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3ha**



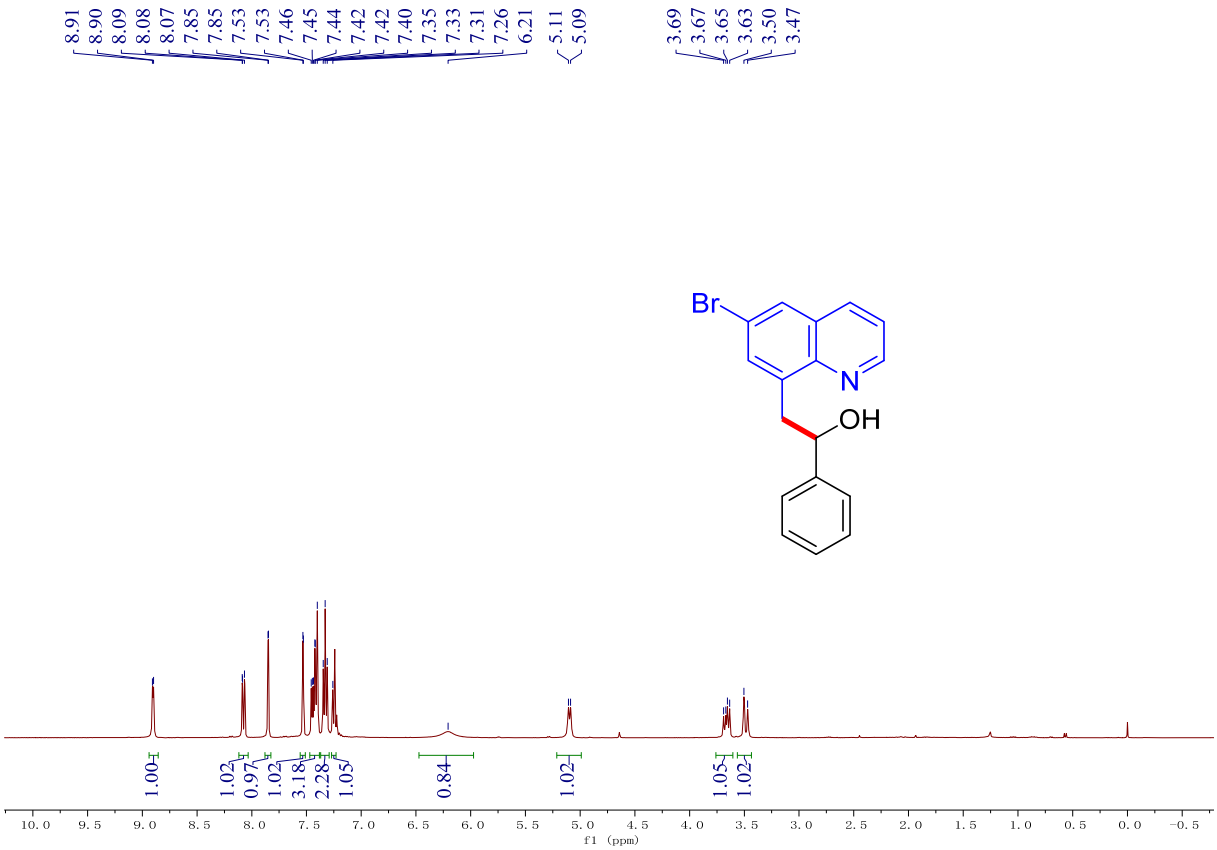
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) spectrum of **3ha**



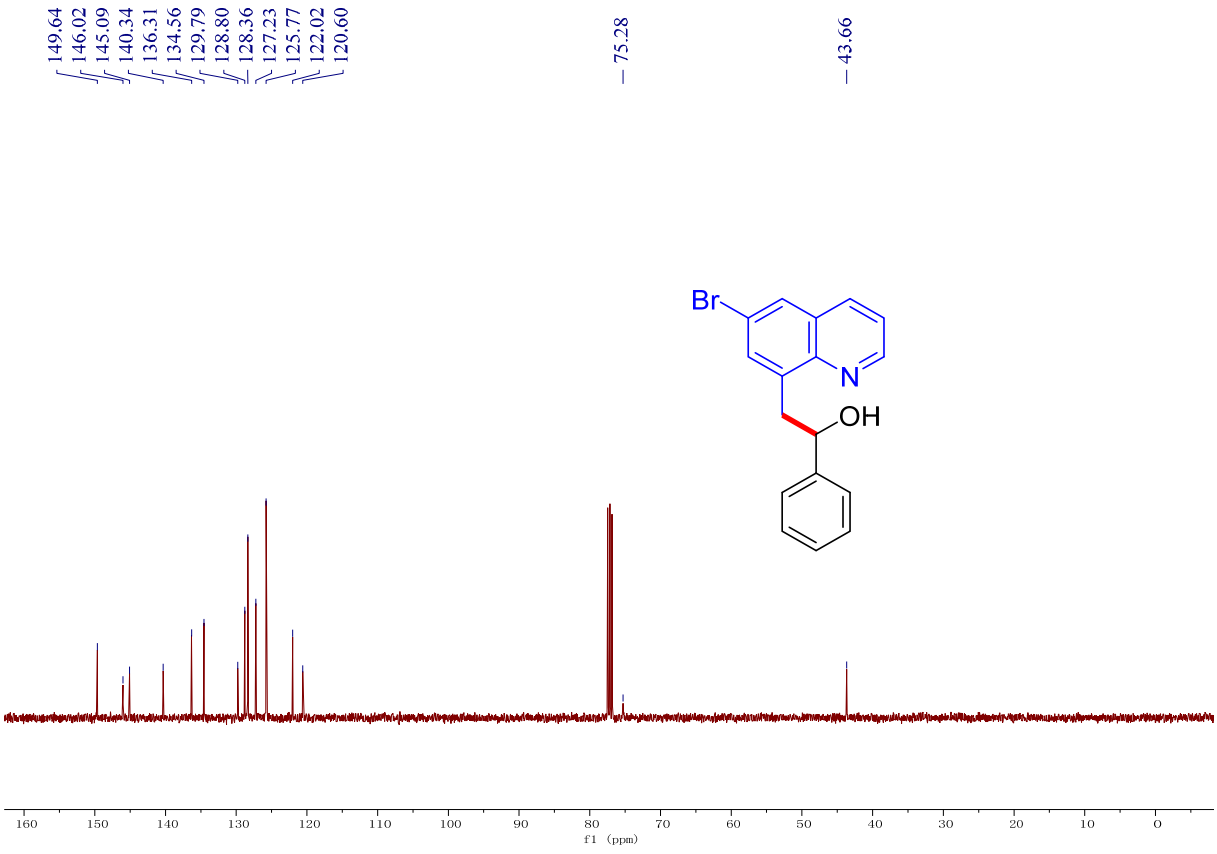
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of **3ha**



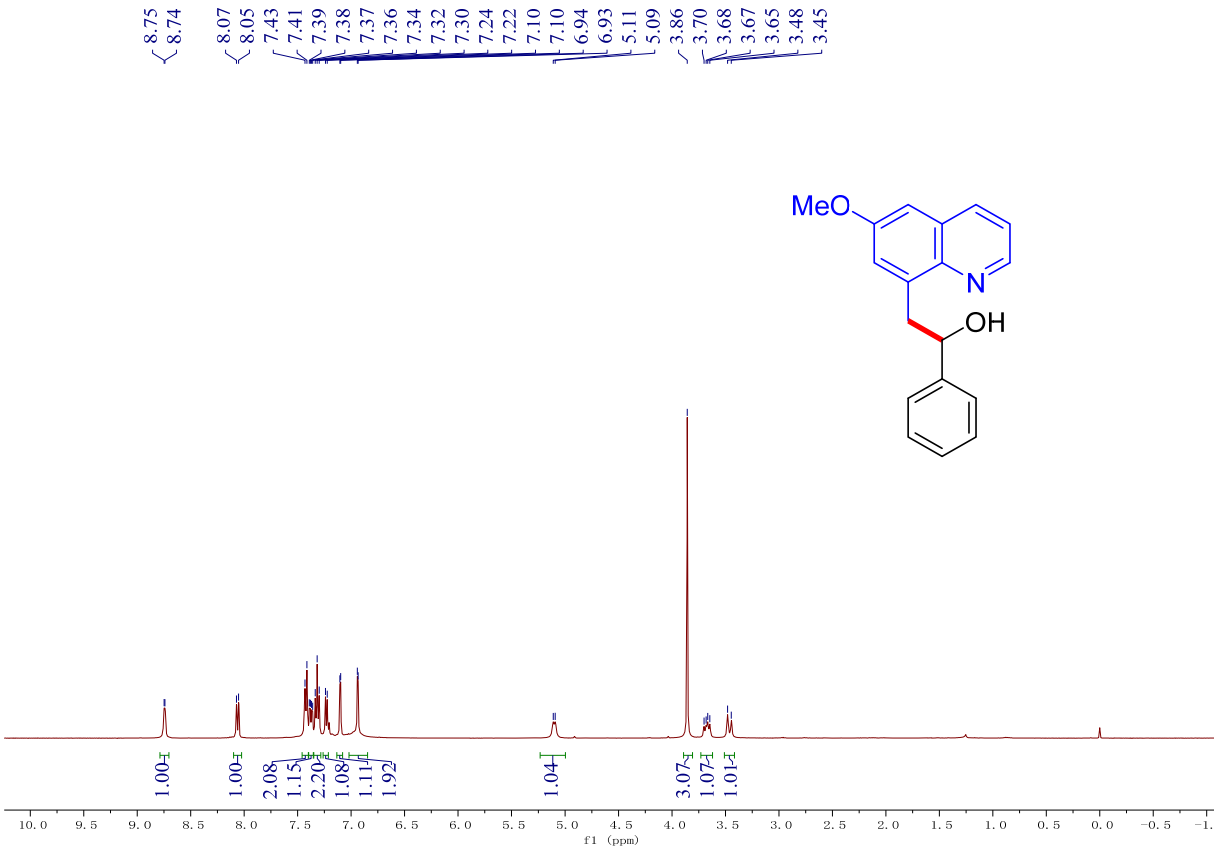
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3ia**



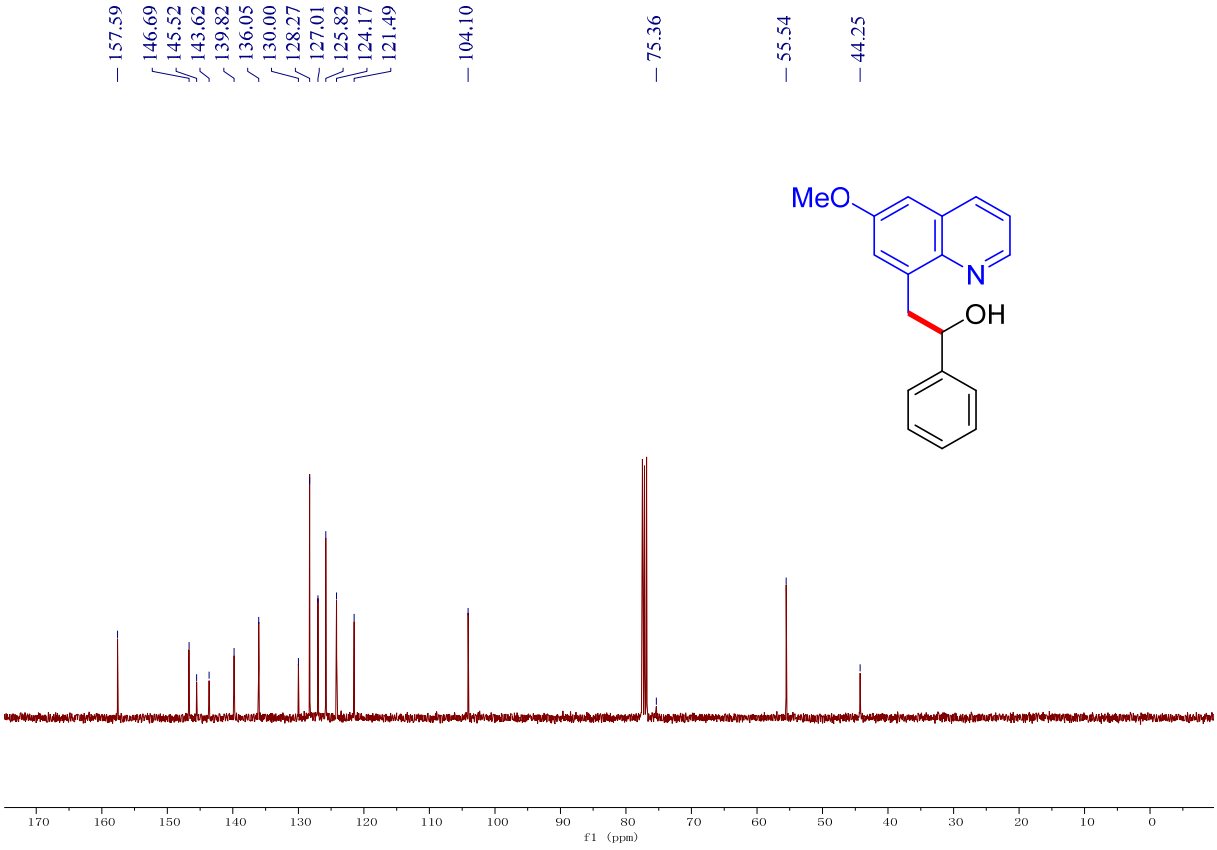
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) spectrum of **3ia**



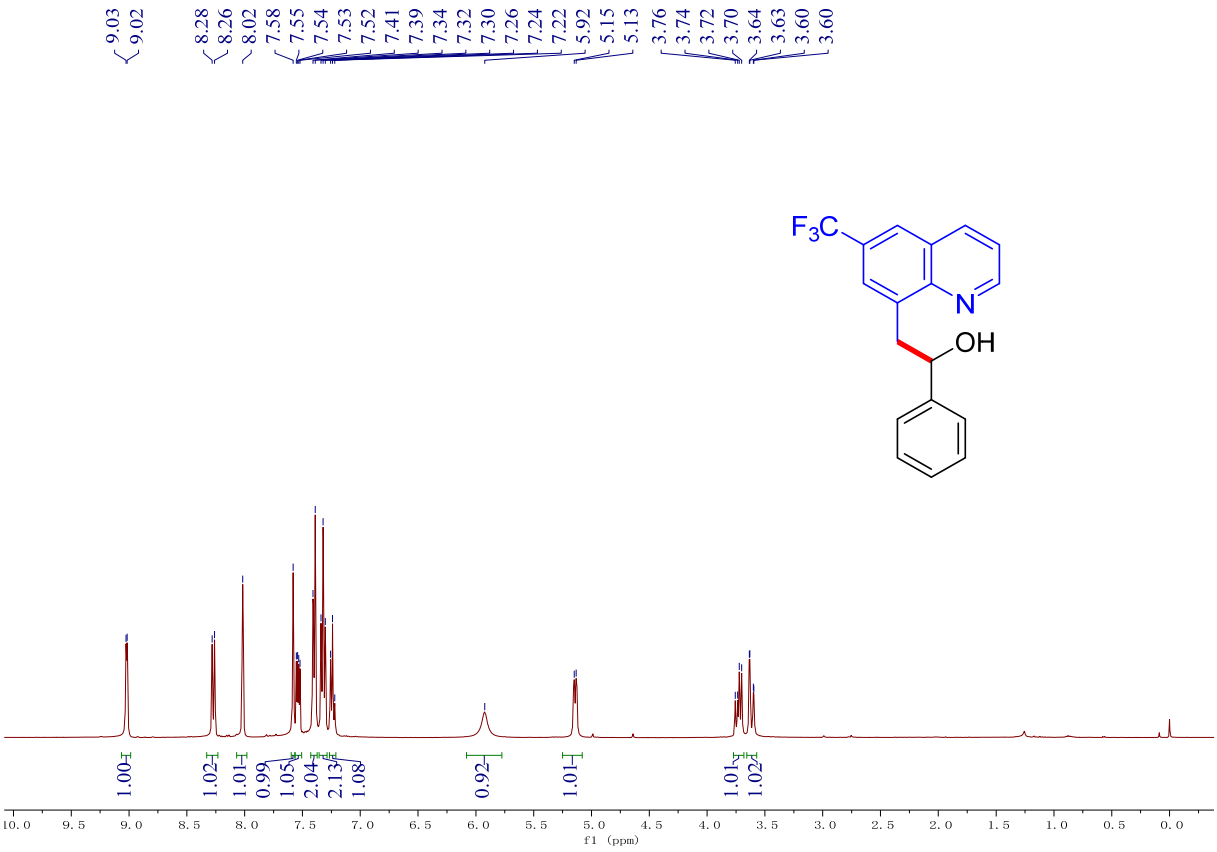
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3ja**



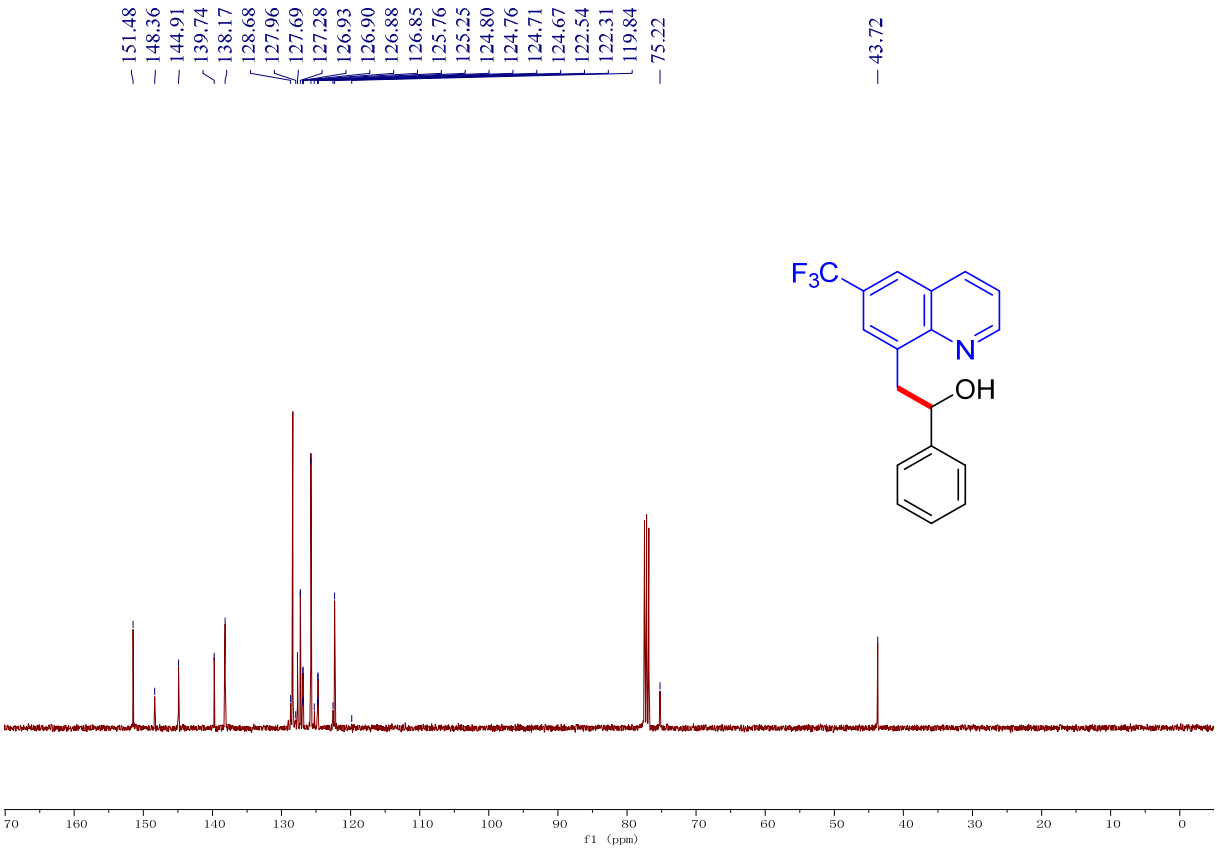
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) spectrum of **3ja**



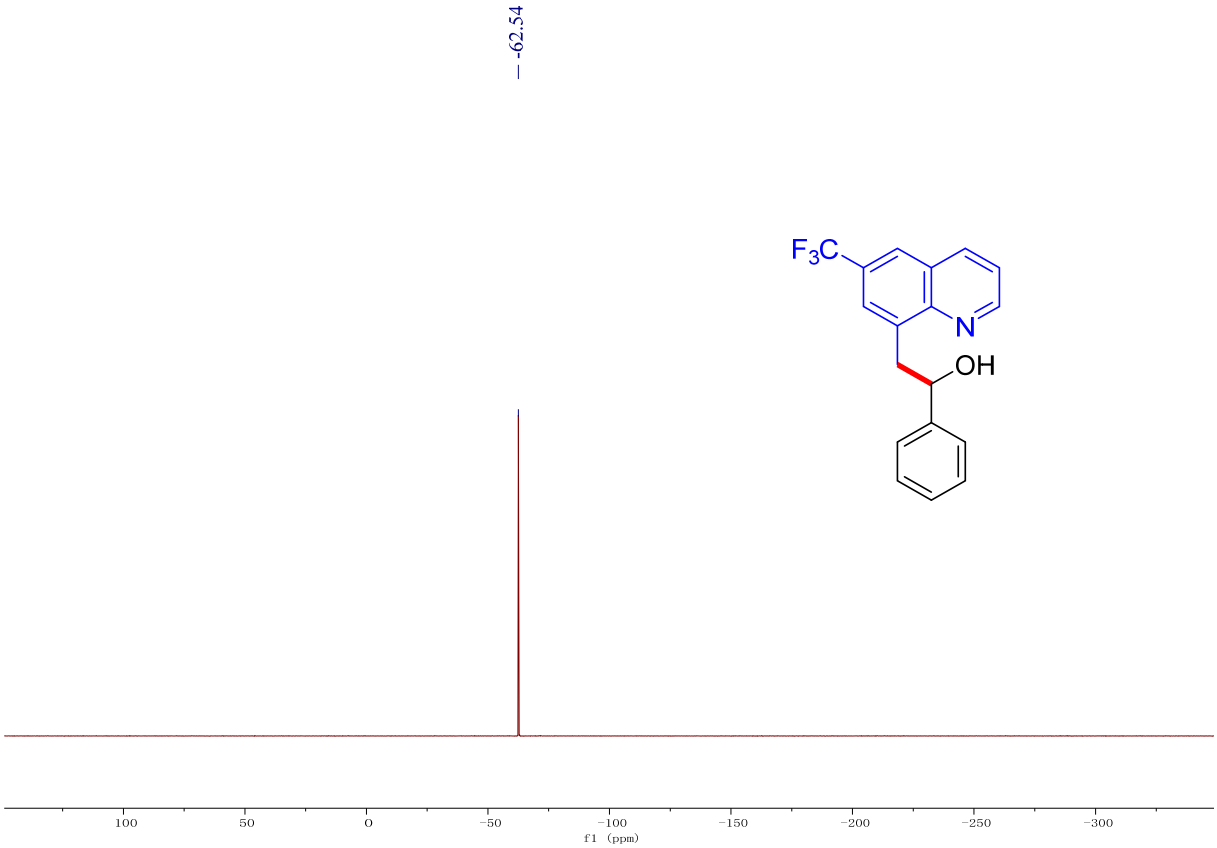
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3ka**



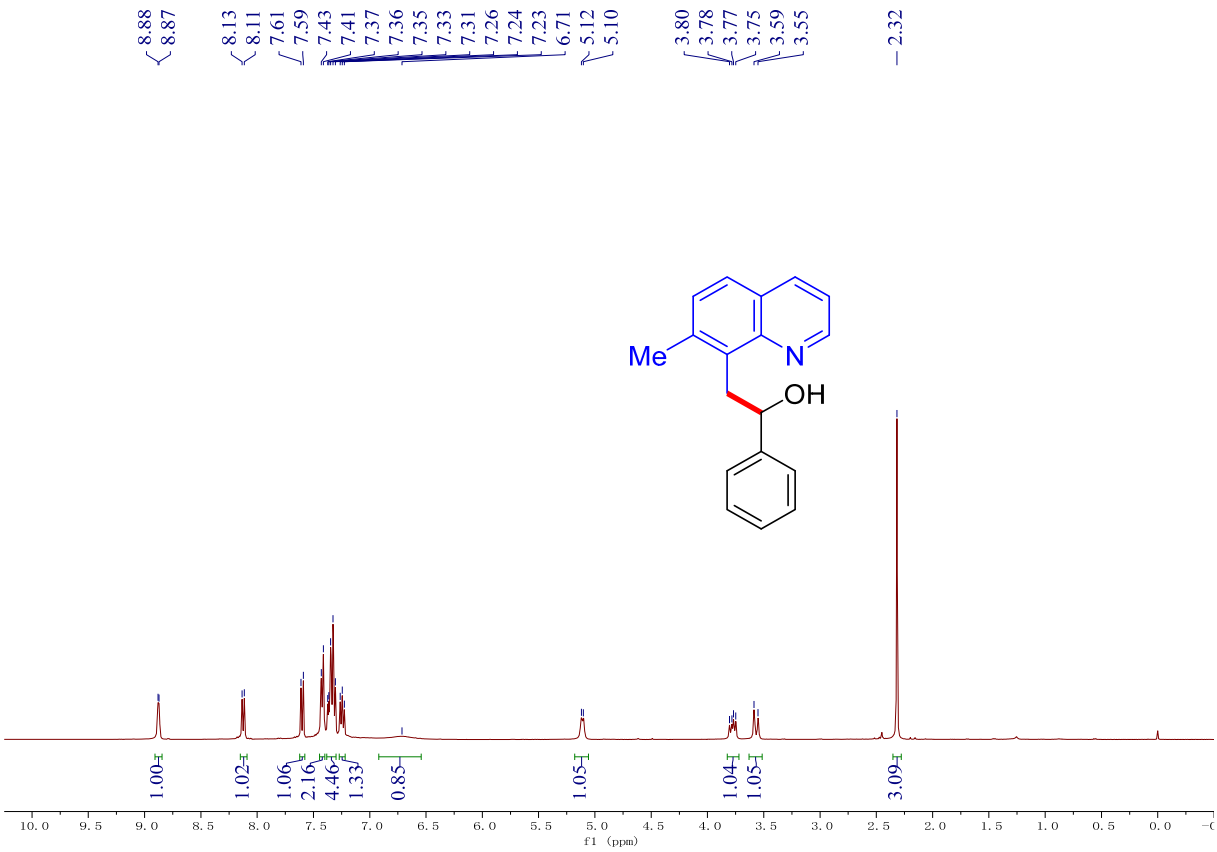
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) spectrum of **3ka**



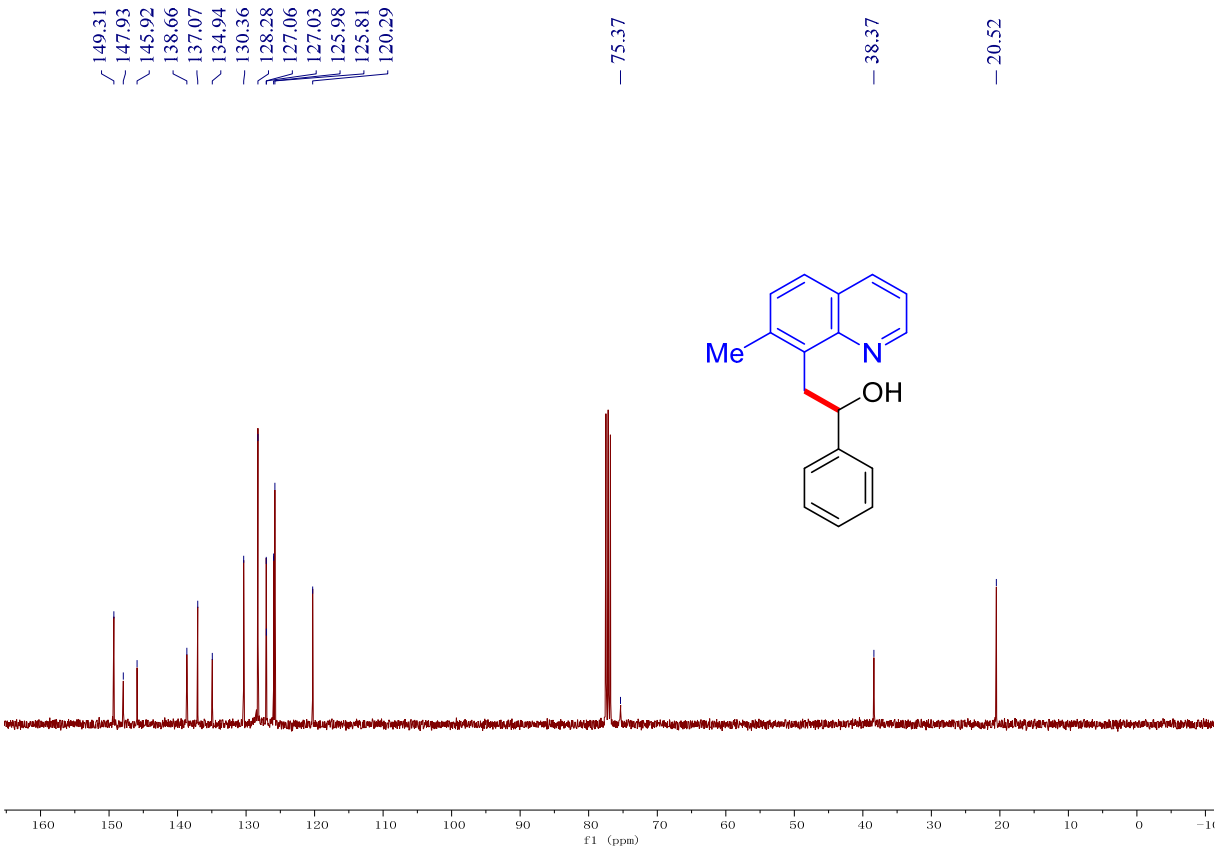
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of **3ka**



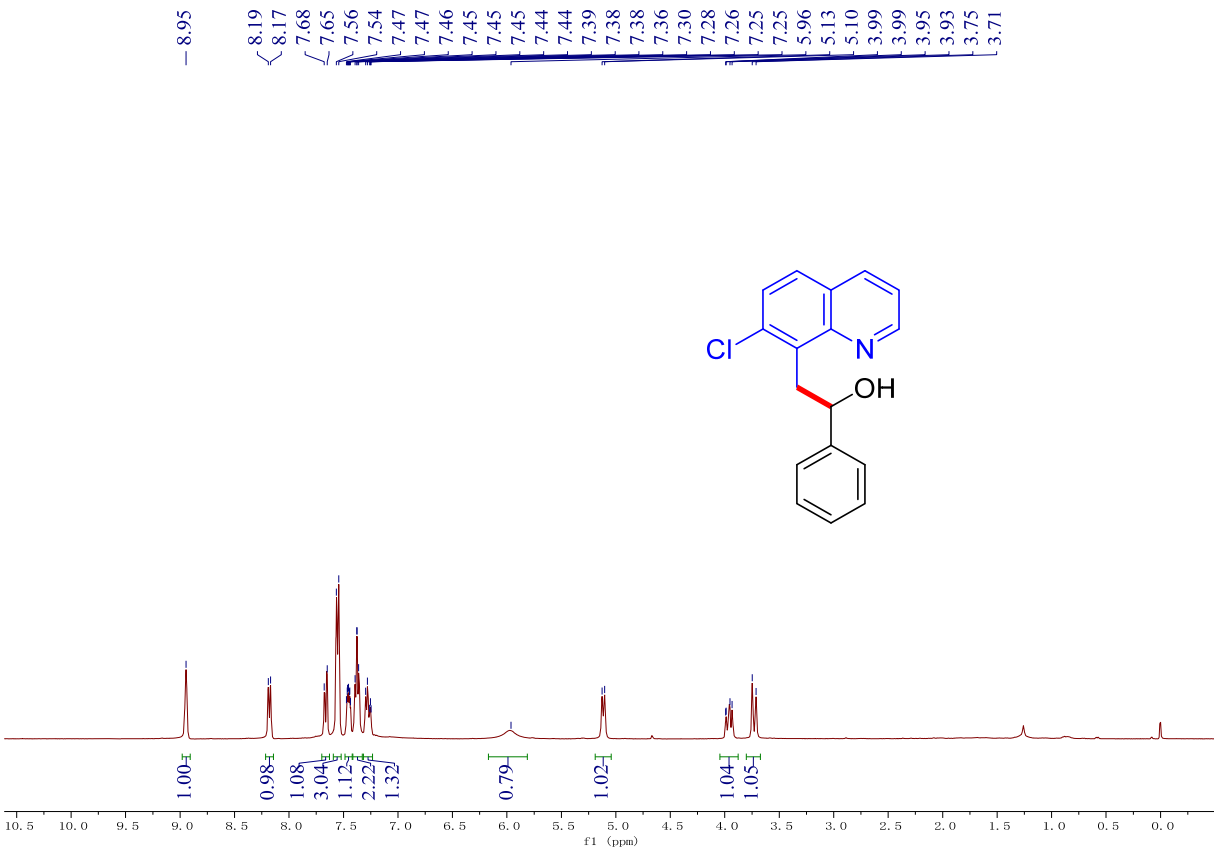
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3la**



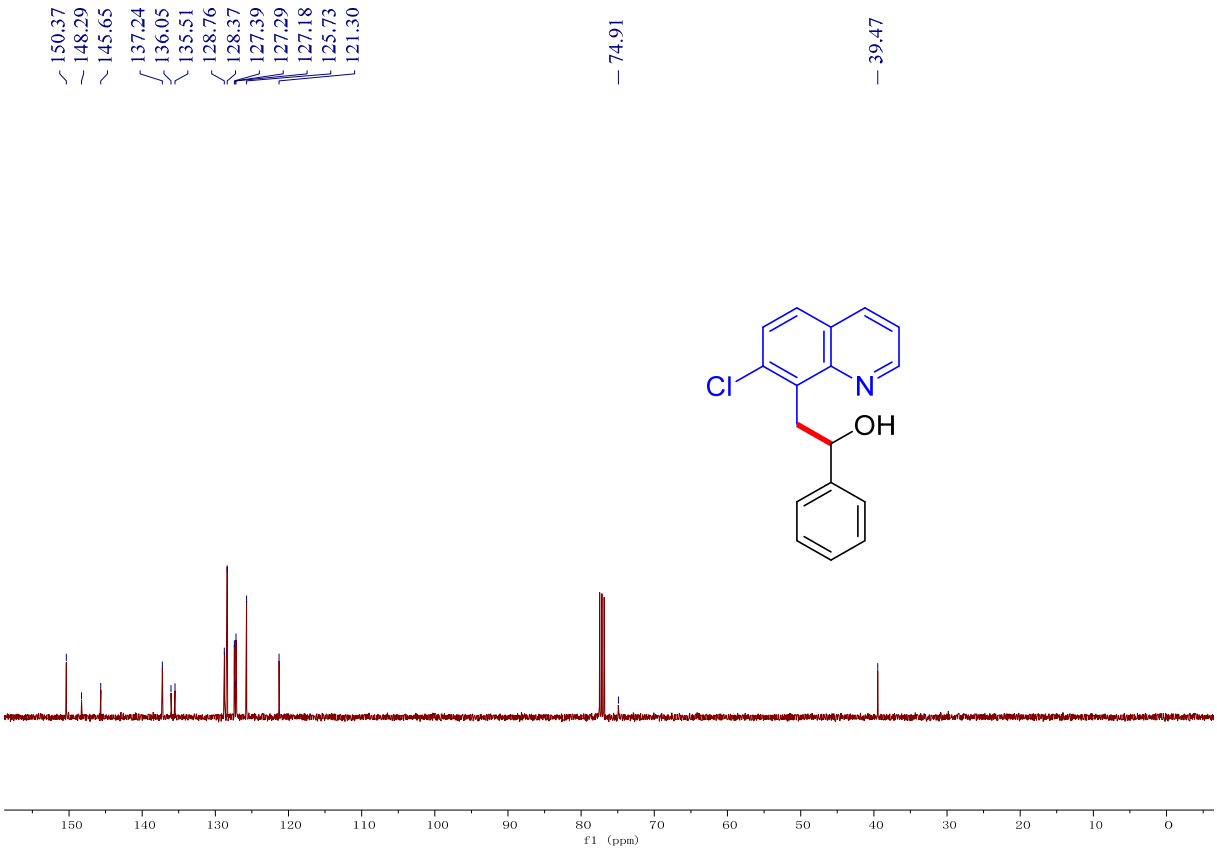
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) spectrum of **3la**



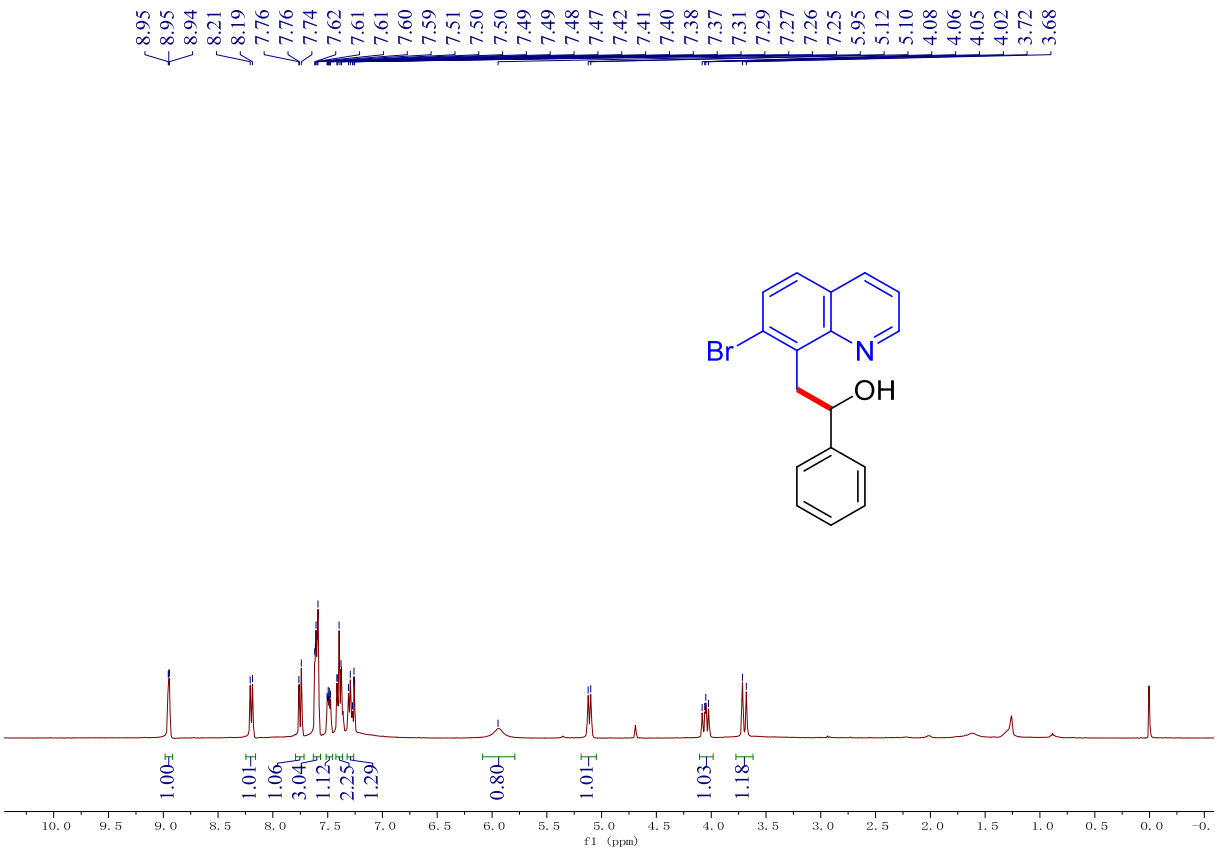
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **3ma**



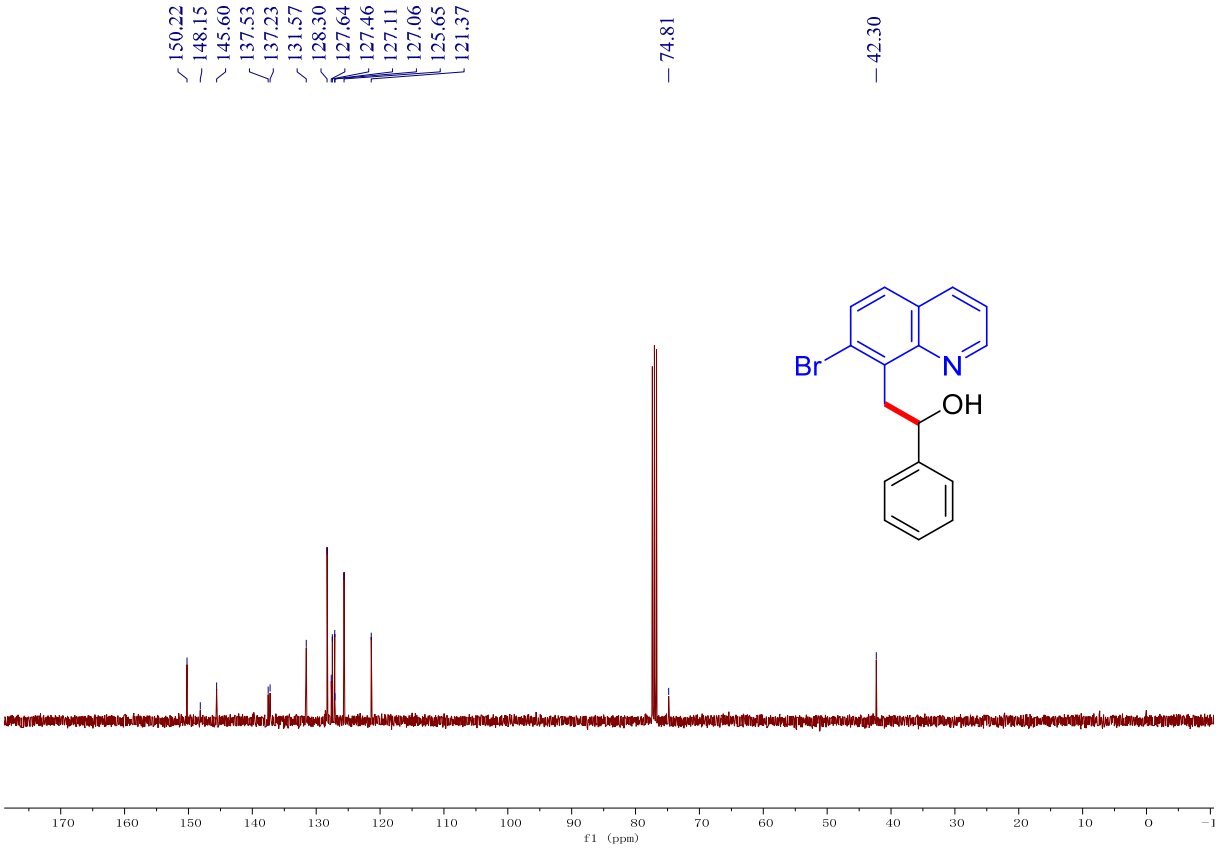
$^{13}C\{^{1}H\}$ NMR (151 MHz, $CDCl_3$) spectrum of **3ma**



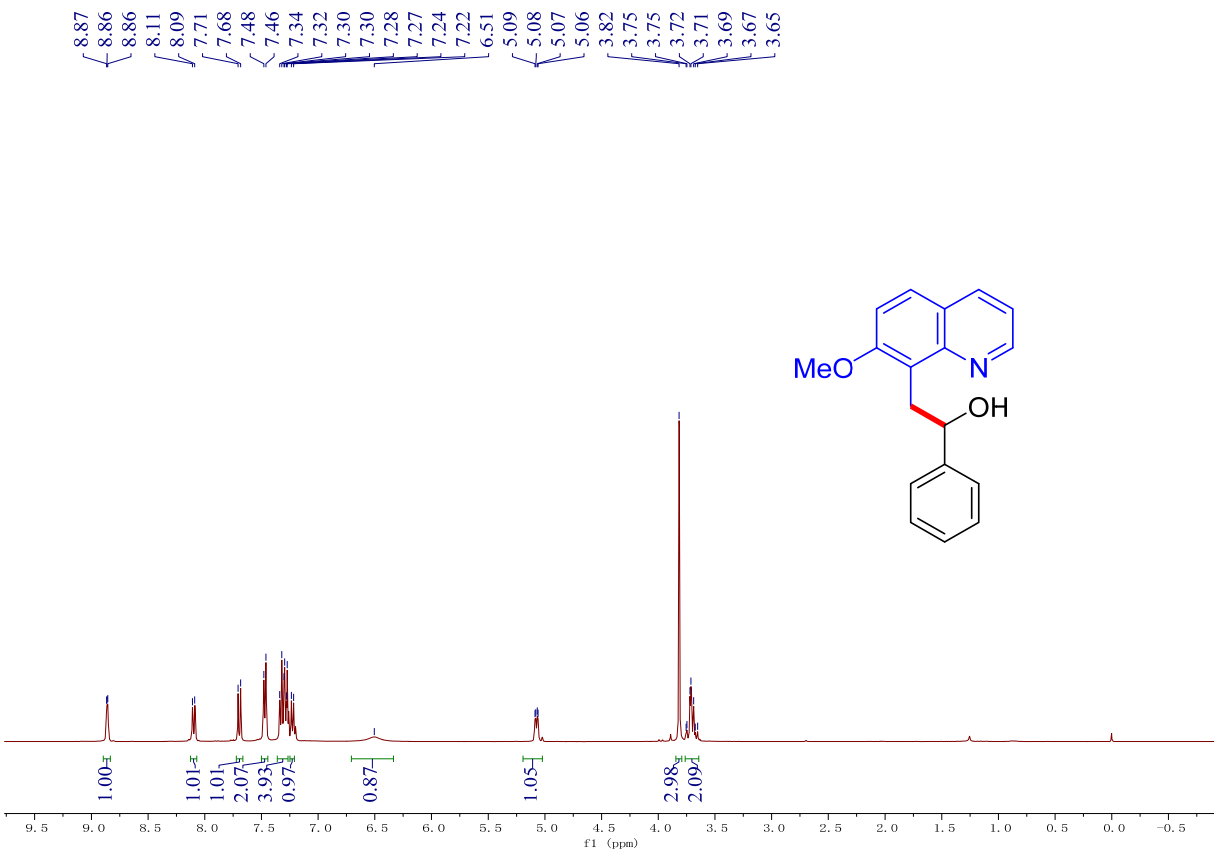
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3na**



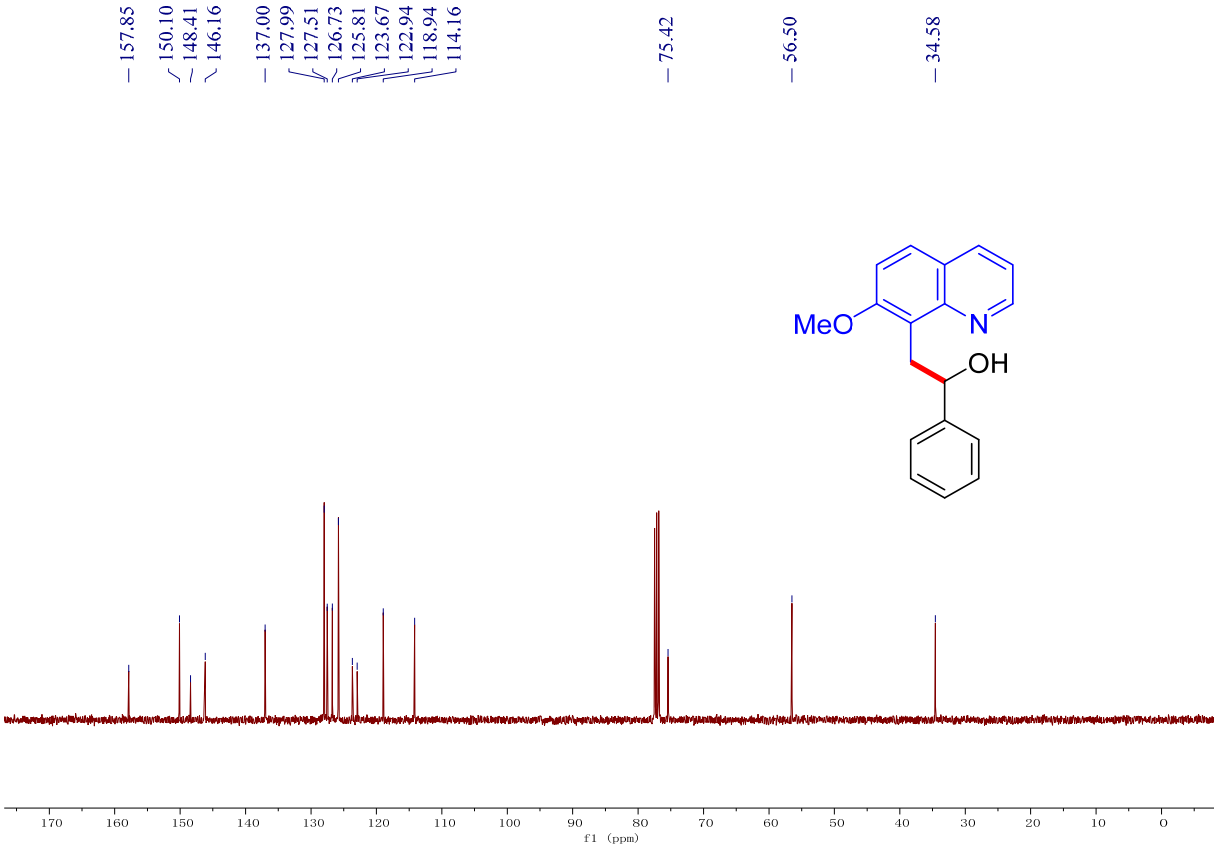
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) spectrum of **3na**



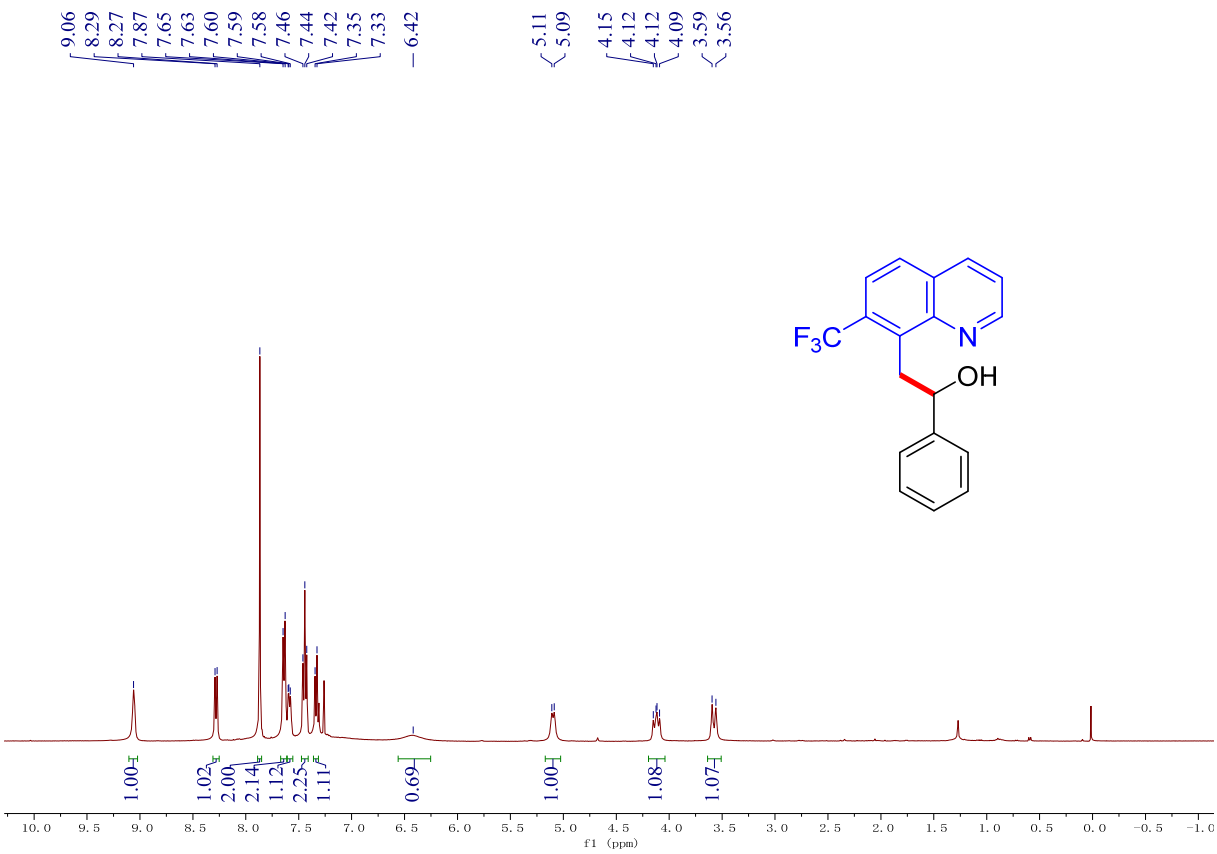
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3oa**



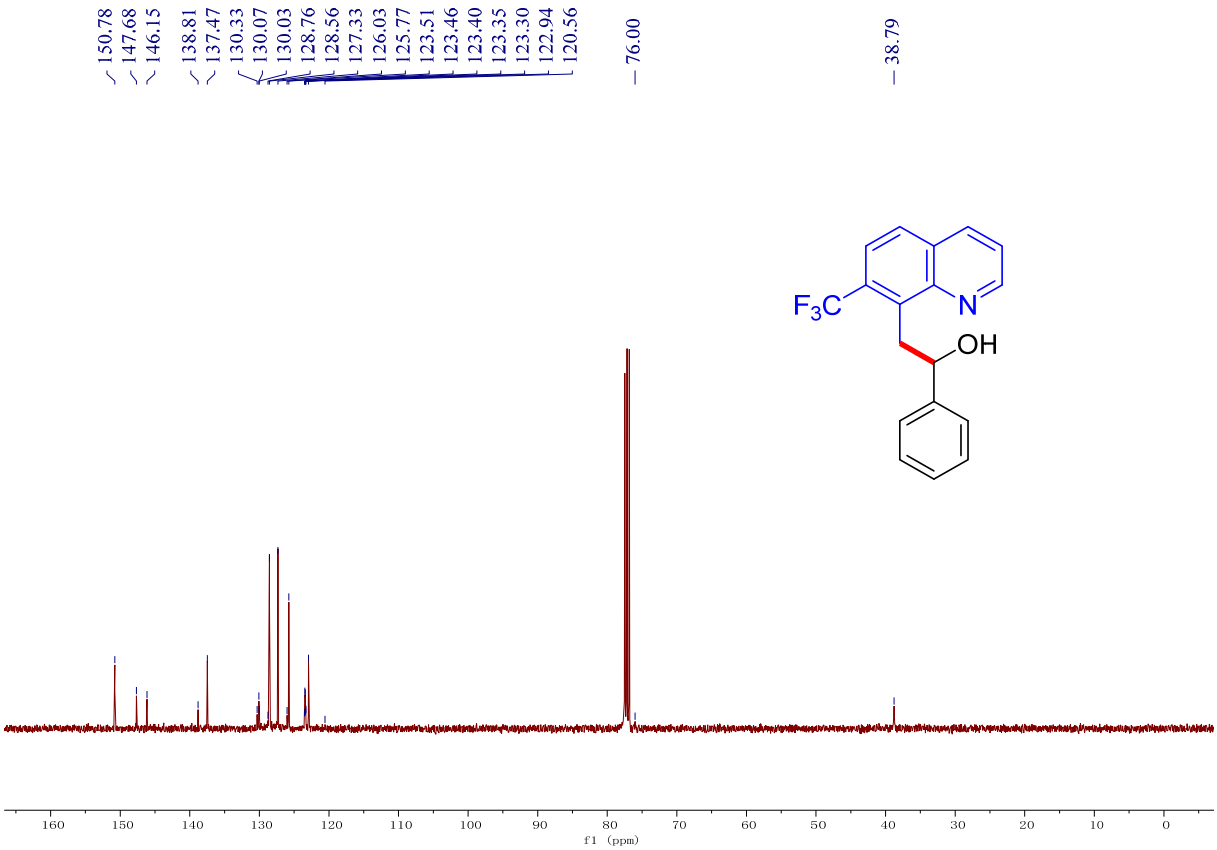
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) spectrum of **3oa**



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



$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) spectrum of **3pa**



^{19}F NMR (376 MHz, $CDCl_3$) spectrum of **3pa**