Supporting Information

Iron-Catalyzed Radical Intermolecular Addition of Unactivated Alkenes to Alkenyl *N*-heteroarenes

Wen-Dao Chu,* Chun-Mei Wang, Shu Li, Zhi-Hong Dong, Teng Long, Jia-Xi Jiang, Bo Chen, Cheng-Yu He,* Quan-Zhong Liu*

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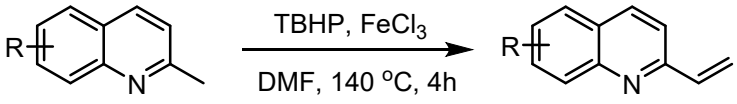
1. General information

All reactions were carried out under an atmosphere of argon using standard Schlenk techniques. All the reagents were obtained from commercial supplier and used as received, without further purification unless otherwise noted. Solvents used in the reactions were distilled from appropriate drying agents prior to use. ^{1}H NMR and ^{13}C NMR spectra were recorded respectively at 400 MHz and 100 MHz on a Bruker AVANCE 400. High resolution mass spectra were obtained on Bruker Daltonics micrOTOF-Q II spectrometer in ESI mode.

2. Preparation of alkenyl *N*-heteroarenes 1 and the alkenes 2

General experimental procedure for the synthesis of alkenyl *N*-heteroarenes 1

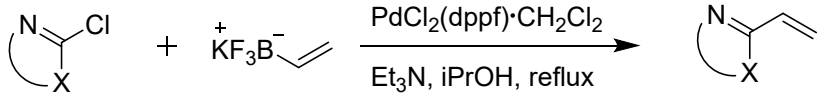
Route 1:



1a-l, 1u

The alkenyl *N*-heteroarenes **1a-l** and **1u** were prepared according to the literature procedures.[1a] To a 25 mL reaction vial equipped with a magnetic stir bar, TBHP (6.0 mmol, 70% aqueous solution) was added to a mixture of $FeCl_3$ (32.0 mg, 0.2 mmol), 2-methylquinoline (286.4 mg, 2 mmol), and *N,N*-dimethylformamide (10 mL). Subsequently, the resulting mixture was placed into a preheated oil bath at 140 ℃ and stirred at this temperature for 4 h under air. The resulting mixture was then cooled to room temperature and poured into H_2O (10 mL). The organic layer was then extracted with CH_2Cl_2 (20 mL × 3). The organic phase was washed with brine (20 mL) and dried over sodium sulfate, and the solvent was evaporated under reduced pressure. The resulting residue was purified by flash chromatography over silica gel (petroleum ether/EtOAc = 20:1) then gave the alkenylation product.

Route 2:



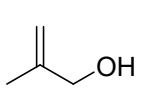
1r-s, 1v-y

The alkenyl *N*-heteroarenes **1r-s** and **1v-y** were prepared according to the literature procedures.[1e] A solution of 2-chloroquinoline (1.64 g, 10.0 mmol), potassium vinyltrifluoroborate (1.61 g, 12.0 mmol), $PdCl_2(dppf)\cdot CH_2Cl_2$ (163 mg,

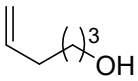
0.20 mmol), and Et_3N (1.39 mL, 10.0 mmol) in *i*-PrOH (156 mL) was heated to reflux for 16 h. The mixture was cooled to room temperature and partitioned between CH_2Cl_2 (100 mL) and H_2O (40 mL). The aqueous layer was separated and extracted with CH_2Cl_2 (2 × 50 mL) and the combined organic layers were washed with brine (100 mL), dried ($MgSO_4$), filtered, and concentrated in vacuo. Purification of the residue by column chromatography (5% EtOAc/hexane) gave the alkenylation product that displayed spectroscopic data consistent with those reported previously.

The alkenyl *N*-heteroarenes **1n-o**[1b], **1p**[1c], **1q**[1d] and **1z**[1f] were prepared according to the reported literature procedures.

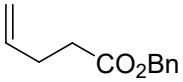
General experimental procedure for the synthesis of the alkenes 2



2a

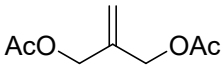


2b

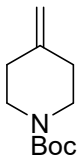


2c

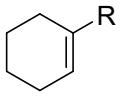
2d



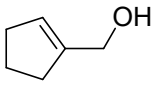
2e



2f

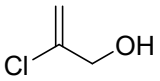


2g, R = CH_3
2h, R = CH_2OH

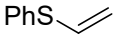


2i

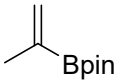
2j



2k



2l

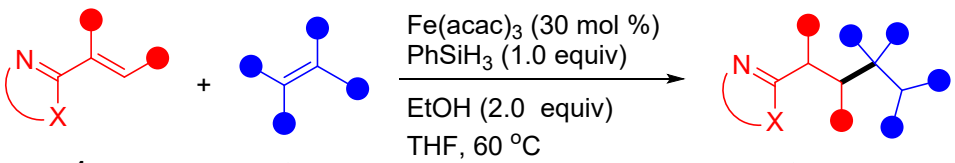


2m

The alkenes **2c**[2a], **2e**[2b] and **2h-i**[2c] were prepared according to the reported literature procedures. The alkenes **2a**, **2b**, **2d**, **2f**, **2g** and **2j-m** were commercial available.

3. Radical Intermolecular Addition to Alkenyl *N*-heteroarenes

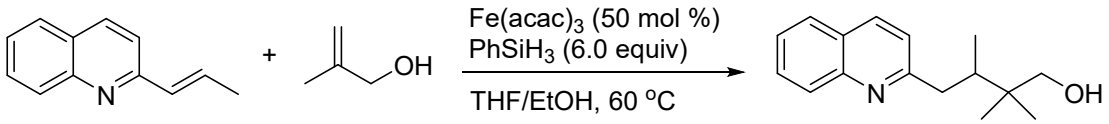
3.1. Typical procedure for Synthesis of 3 or 4



1 **2** **3** or **4**

A Schlenk tube containing $Fe(acac)_3$ (10.5 mg, 30 mol %) was evacuated and purged with argon three times. Afterwards, **1** (0.1 mmom), **2** (0.3 mmol), EtOH (9.2 mg, 0.2 mmol), $PhSiH_3$ (10.8 mg, 0.1 mmol) and 2 mL THF were added via syringe. The solution was kept at 60 °C for 2 h. After the reaction was completed, cooled it to room temperature, filtered and evaporated under reduced pressure. The purification was performed by flash column chromatography on silica gel using ethyl acetate/petroleum ether (v/v, 1:30 to 1:10) as eluent to give **3** or **4**.

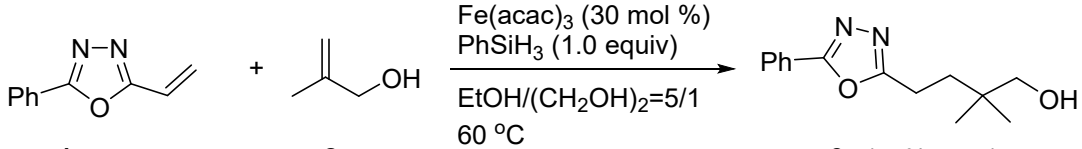
3.2. Typical procedure for Synthesis of 3p



1p **2a** **3p** (50% yield)

A Schlenk tube containing $Fe(acac)_3$ (17.7 mg, 50 mol %) was evacuated and purged with argon three times. Afterwards, **1p** (0.1 mmom), **2a** (0.3 mmol), $PhSiH_3$ (64.9 mg, 0.6 mmol), 0.1 mL EtOH and 2 mL THF were added via syringe. The solution was kept at 60 °C for 14 h. After the reaction was completed, cooled it to room temperature, filtered and evaporated under reduced pressure. The purification was performed by flash column chromatography on silica gel using ethyl acetate/petroleum ether (v/v, 1:30 to 1:10) as eluent to give **3p**.

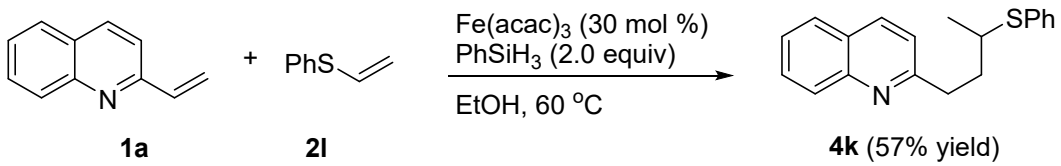
3.3. Typical procedure for Synthesis of 3z



1z **2a** **3z** (50% yield)

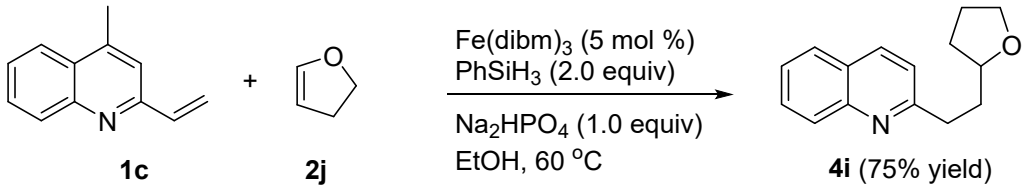
A Schlenk tube containing $Fe(acac)_3$ (10.6 mg, 30 mol %) was evacuated and purged with argon three times. Afterwards, **1z** (0.1 mmom), **2a** (0.3 mmol), $PhSiH_3$ (10.8 mg, 0.1 mmol), 2 mL EtOH and 0.4 mL ethylene glycol were added via syringe. The solution was kept at 60 °C for 2 h. After the reaction was completed, cooled it to room temperature, filtered and evaporated under reduced pressure. The purification was performed by flash column chromatography on silica gel using ethyl acetate/petroleum ether (v/v, 1:30 to 1:10) as eluent to give **3z**.

3.4. Typical procedure for Synthesis of 4k



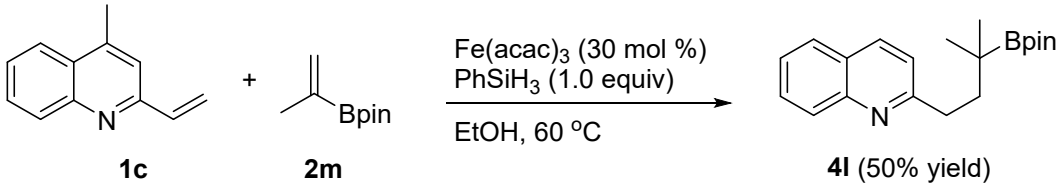
A Schlenk tube containing $Fe(acac)_3$ (10.6 mg, 30 mol %) was evacuated and purged with argon three times. Afterwards, **1a** (0.1 mmom), **2l** (0.3 mmol), $PhSiH_3$ (21.6 mg, 0.2 mmol), 2 mL EtOH were added via syringe. The solution was kept at 60 °C for 4 h. After the reaction was completed, cooled it to room temperature, filtered and evaporated under reduced pressure. The purification was performed by flash column chromatography on silica gel using ethyl acetate/petroleum ether (v/v, 1:50 to 1:20) as eluent to give **4k**.

3.5. Typical procedure for Synthesis of 4i



A Schlenk tube containing $Fe(dibm)_3$ (2.6 mg, 5 mol %), Na_2HPO_4 (14.2 mg, 0.1 mmol) was evacuated and purged with argon three times. Afterwards, **1c** (0.1 mmom), **2j** (0.3 mmol), $PhSiH_3$ (21.6 mg, 0.2 mmol), 2 mL EtOH were added via syringe. The solution was kept at 60 °C for 3 h. After the reaction was completed, cooled it to room temperature, filtered and evaporated under reduced pressure. The purification was performed by flash column chromatography on silica gel using ethyl acetate/petroleum ether (v/v, 1:50 to 1:20) as eluent to give **4i**.

3.6. Typical procedure for Synthesis of 4l

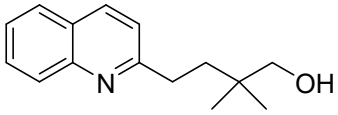


A Schlenk tube containing $Fe(acac)_3$ (10.6 mg, 30 mol %) was evacuated and

purged with argon three times. Afterwards, **1c** (0.1 mmom), **2m** (0.3 mmol), $PhSiH_3$ (10.8 mg, 0.1 mmol), 2 mL EtOH and 0.4 mL Ethylene glycol were added via syringe. The solution was kept at 60 °C for 4 h. After the reaction was completed, cooled it to room temperature, filtered and evaporated under reduced pressure. The purification was performed by flash column chromatography on silica gel using ethyl acetate/petroleum ether (v/v, 1:50 to 1:20) as eluent to give **4l**.

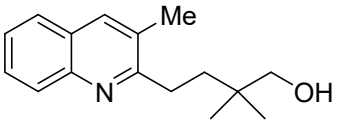
3.7. Characterization data for the products 3 and 4

2,2-dimethyl-4-(quinolin-2-yl)butan-1-ol (3a)



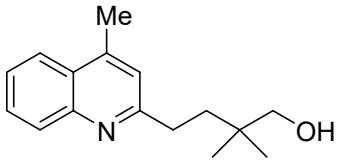
Pale yellow solid, 17.4 mg, yield 76%. R_f = 0.3 (petroleum ether/ethyl acetate = 2:1), mp = 70.6 - 71.8 °C. **^{1}H NMR** (400 MHz, $CDCl_3$, ppm) δ 7.95 (q, *J* = 8.0 Hz, 2H), 7.68 (d, *J* = 8.0 Hz, 1H), 7.58 (t, *J* = 8.0 Hz, 1H), 7.39 (t, *J* = 8.0 Hz, 1H), 7.20 (d, *J* = 8.0 Hz, 1H), 4.38 (s, 1H), 3.30 (s, 2H), 2.89 (t, *J* = 8.0 Hz, 2H), 1.74 (t, *J* = 8.0 Hz, 2H), 0.91 (s, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$, ppm) δ 163.5, 147.5, 136.7, 129.7, 128.4, 127.6, 126.8, 125.9, 121.8, 70.1, 37.2, 35.8, 33.3, 24.7. **IR**: = 3431, 2955, 2927, 2865, 1616, 1560, 1503, 1263, 1054, 1020, 833 cm^{-1}. **HRMS (ESI)**: calcd for $C_{15}H_{19}NO$ $[M+H]^+$ 230.1539, found 230.1552.

2,2-dimethyl-4-(3-methylquinolin-2-yl)butan-1-ol (3b)



White solid, 16.9 mg, yield 70%. R_f = 0.3 (petroleum ether/ethyl acetate = 2:1), mp = 94.3 - 95.6 °C. **^{1}H NMR** (400 MHz, $CDCl_3$, ppm) δ 7.99 (d, *J* = 12.0 Hz, 1H), 7.83 (s, 1H), 7.69 (d, *J* = 8.0 Hz, 1H), 7.60 (t, *J* = 8.0 Hz, 1H), 7.44 (t, *J* = 8.0 Hz, 1H), 4.79 (s, 1H), 3.31 (s, 2H), 2.94 (t, *J* = 8.0 Hz, 2H), 2.46 (s, 3H), 1.85 (t, *J* = 4.0 Hz, 2H), 1.01 (s, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$, ppm) δ 162.6, 146.1, 136.2, 129.8, 128.7, 128.0, 127.4, 126.8, 126.0, 67.0, 35.9, 35.4, 30.0, 24.9, 19.4. **IR**: = 3394, 2961, 2867, 1494, 1469, 1441, 1267, 1097, 1060, 801, 756 cm^{-1}. **HRMS (ESI)**: calcd for $C_{16}H_{21}NO$ $[M+H]^+$ 244.1696, found 244.1714.

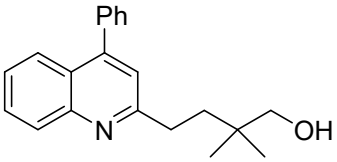
2,2-dimethyl-4-(4-methylquinolin-2-yl)butan-1-ol (3c)



White solid, 20.6 mg, yield 85%. R_f = 0.3 (petroleum ether/ethyl acetate = 2:1), mp = 83.7 - 85.2 °C. **^{1}H NMR** (400 MHz, $CDCl_3$, ppm) δ 8.00 (d, *J* = 8.0 Hz, 1H), 7.91 (d, *J* = 8.0 Hz, 1H), 7.64 (t, *J* = 8.0 Hz, 1H), 7.48 (t, *J* =

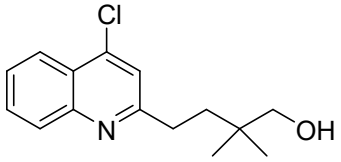
8.0 Hz, 1H), 7.11 (s, 1H), 4.74 (s, 1H), 3.36 (s, 2H), 2.91 (t, *J* = 8.0 Hz 2H), 2.64 (s, 3H), 1.81 (t, *J* = 8.0 Hz, 2H), 0.98 (s, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$, ppm) δ 163.1, 147.3, 144.8, 129.3, 128.9, 126.8, 125.7, 123.7, 122.4, 70.1, 37.0, 35.8, 33.1, 24.7, 18.7. **IR**: =3218, 2962, 2898, 1602, 1565, 1447, 1358, 1261, 1074, 1074, 1018, 802, 758 cm^{-1}. **HRMS (ESI)**: calcd for $C_{16}H_{21}NO$ $[M+H]^+$ 244.1696, found 244.1718.

2,2-dimethyl-4-(4-phenylquinolin-2-yl)butan-1-ol (3d)



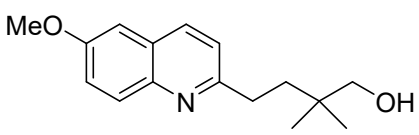
White solid, 25.0 mg, yield 82%. R_f = 0.3 (petroleum ether/ethyl acetate = 2:1), mp = 117.2 - 117.8 °C. **^{1}H NMR** (400 MHz, $CDCl_3$, ppm) δ 8.09 (d, *J* = 8.0 Hz, 1H), 7.85 (d, *J* = 8.0 Hz, 1H), 7.67 (t, *J* = 8.0 Hz, 1H), 7.51-7.49 (m, 5H), 7.42 (t, *J* = 8.0 Hz, 1H), 7.24 (s, 1H), 4.59 (s, 1H), 3.40 (s, 2H), 3.01 (t, *J* = 8.0 Hz, 2H), 1.87 (t, *J* = 8.0 Hz, 2H), 1.01 (s, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$, ppm) δ 163.0, 149.0, 148.1, 138.2, 129.6, 129.5, 128.8, 128.6, 128.5, 126.0, 125.8, 125.39, 121.9, 70.2, 37.2, 35.8, 33.3, 24.7. **IR**: =3343, 3057, 2950, 2858, 1594, 1558, 1489, 1360, 1058, 768, 698 cm^{-1}. **HRMS (ESI)**: calcd for $C_{21}H_{23}NO$ $[M+H]^+$ 306.1852, found 306.1873.

4-(4-chloroquinolin-2-yl)-2,2-dimethylbutan-1-ol (3e)



Pale yellow oil, 17.3 mg, yield 66%. R_f = 0.3 (petroleum ether/ethyl acetate = 2:1). **^{1}H NMR** (400 MHz, $CDCl_3$, ppm) δ 8.16 (d, *J* = 8.0 Hz, 1H), 8.01 (d, *J* = 8.0 Hz, 1H), 7.72 (t, *J* = 8.0 Hz, 1H), 7.57 (t, *J* = 4.0 Hz, 1H), 7.39 (s, 1H), 3.90 (s, 1H), 3.37 (s, 2H), 2.94 (t, *J* = 8.0 Hz, 2H), 1.81 (t, *J* = 8.0, 2H), 0.98 (s, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$, ppm) δ 163.4, 148.4, 143.0, 130.6, 128.8, 126.9, 125.0, 124.1, 121.7, 70.4, 37.1, 35.7, 33.3, 24.6. **IR**: =3390, 2957, 2867, 1590, 1556, 1496, 1410, 1316, 1262, 1055, 762 cm^{-1}. **HRMS (ESI)**: calcd for $C_{15}H_{18}ClNO$ $[M+H]^+$ 264.1150, found 264.1170.

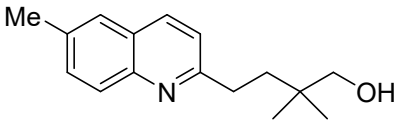
4-(6-methoxyquinolin-2-yl)-2,2-dimethylbutan-1-ol (3f)



Pale yellow solid, 22.0 mg, yield 85%. R_f = 0.2 (petroleum ether/ethyl acetate = 2:1), mp = 53.6 - 53.8 °C. **^{1}H NMR** (400 MHz, $CDCl_3$, ppm) δ 7.94 (q, *J* = 8.0 Hz, 2H), 7.33 (dd, J_1 = 12.0 Hz, J_2 = 4.0 Hz, 1H), 7.24 (d, *J* = 8.0 Hz, 1H),

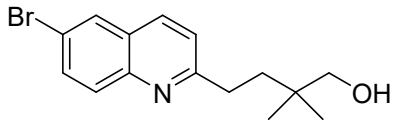
7.04 (d, J = 4.0 Hz, 1H), 3.91 (s, 3H), 3.35 (s, 2H), 2.95 (t, J = 4.0 Hz, 2H), 1.81 (t, J = 8.0 Hz, 2H), 0.98 (s, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$, ppm) δ 160.8, 157.5, 143.4, 135.7, 129.7, 127.7, 122.2, 122.0, 105.4, 70.2, 55.7, 37.2, 35.8, 32.9, 24.7. **IR**: =3147, 2958, 2871, 1624, 1606, 1502, 1382, 1238, 1169, 1060, 1026, 831 cm^{-1}. **HRMS (ESI)**: calcd for $C_{16}H_{21}NO_2$ $[M+H]^+$ 260.1645, found 260.1669.

2,2-dimethyl-4-(6-methylquinolin-2-yl)butan-1-ol (3g)



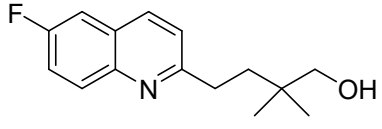
White solid, 17.1 mg, yield 70%. R_f = 0.3 (petroleum ether/ethyl acetate = 2:1), mp = 106.6 - 106.8 °C. **^{1}H NMR** (400 MHz, $CDCl_3$, ppm) δ 7.92 (dd, J_1 = 20.0 Hz, J_2 = 8.0 Hz, 2H), 7.49 (d, J = 12.0 Hz, 2H), 7.22 (d, J = 8.0 Hz, 1H), 4.68 (s, 1H), 3.36 (s, 2H), 2.94 (t, J = 8.0 Hz, 2H), 2.49 (s, 3H), 1.81 (t, J = 8.0 Hz, 2H), 0.98 (s, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$, ppm) δ 162.4, 146.0, 136.0, 135.7, 131.9, 128.1, 126.8, 126.5, 121.7, 70.1, 37.0, 35.8, 33.1, 24.7, 21.6. **IR**: =3262, 2957, 2865, 1600, 1566, 1500, 1380, 1322, 1122, 1060, 838 cm^{-1}. **HRMS (ESI)**: calcd for $C_{16}H_{21}NO$ $[M+H]^+$ 244.1696, found 244.1715.

4-(6-bromoquinolin-2-yl)-2,2-dimethylbutan-1-ol (3h)



White solid, 19.1 mg, yield 62%. R_f = 0.3 (petroleum ether/ethyl acetate = 2:1), mp = 110.9 - 112.4 °C. **^{1}H NMR** (400 MHz, $CDCl_3$, ppm) δ 7.95 (d, J = 8.0 Hz, 1H), 7.91 (d, J = 4.0 Hz, 1H), 7.86 (d, J = 8.0 Hz, 1H), 7.72 (dd, J_1 = 12.0 Hz, J_2 = 4.0 Hz, 1H), 7.29 (d, J = 8.0 Hz, 1H), 3.91 (s, 1H), 3.36 (s, 2H), 2.95 (t, J = 8.0 Hz, 2H), 1.81 (t, J = 8.0 Hz, 2H), 0.98 (s, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$, ppm) δ 164.0, 146.2, 135.6, 133.1, 130.3, 129.6, 127.9, 122.6, 119.7, 70.4, 37.1, 35.8, 33.4, 24.6. **IR**: =3407, 2958, 2861, 1597, 1488, 1311, 1262, 1097, 1058, 828, 803 cm^{-1}. **HRMS (ESI)**: calcd for $C_{15}H_{18}BrNO$ $[M+H]^+$ 308.0645, found 308.0653.

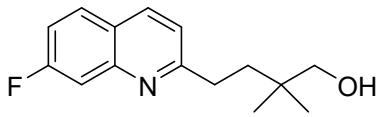
4-(6-fluoroquinolin-2-yl)-2,2-dimethylbutan-1-ol (3i)



Pale yellow solid, 19.0 mg, yield 77%. R_f = 0.3 (petroleum ether/ethyl acetate = 2:1), mp = 61.6 - 61.7 °C. **^{1}H NMR** (400 MHz, $CDCl_3$, ppm) δ 7.99 - 7.97 (m, 2H), 7.44 - 7.34 (m, 2H), 7.29 (d, J = 8.0 Hz, 1H), 4.26 (s, 1H), 3.36 (s, 2H), 2.94 (t, J = 8.0, 2H), 1.79 (t, J = 8.0, 2H), 0.97 (s, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$, ppm)

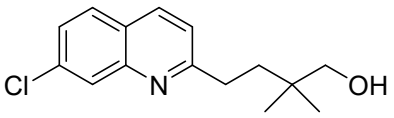
δ 162.8, 158.9, 144.6, 136.0 (d, *J* = 6.0 Hz), 130.8 (d, *J* = 9.0 Hz), 127.3 (d, *J* = 10.0 Hz), 122.5, 119.8 (d, *J* = 26.0 Hz), 110.8 (d, *J* = 22.0 Hz), 70.2, 37.3, 35.7, 33.2, 24.6. **^{19}F NMR** (377 MHz, $CDCl_3$, ppm) δ –114.5 (s). **IR**: =3332, 2958, 2867, 1608, 1565, 1504, 1474, 1225, 1141, 1107, 1149, 828, 732 cm^{-1}. **HRMS (ESI)**: calcd for $C_{15}H_{18}FNO$ $[M+H]^+$ 248.1445, found 248.1463.

4-(7-fluoroquinolin-2-yl)-2,2-dimethylbutan-1-ol (3j)



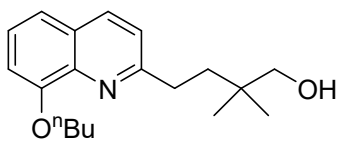
Pale yellow solid, 13.1 mg, yield 53%. R_f = 0.3 (petroleum ether/ethyl acetate = 2:1), mp = 70.1 - 70.8 °C. **^{1}H NMR** (400 MHz, $CDCl_3$, ppm) δ 8.04 (d, *J* = 8.0 Hz, 1H), 7.74 (q, *J* = 2.0 Hz, 1H), 7.63 (d, *J* = 12.0 Hz, 1H), 7.27 - 7.25 (m, 2H), 4.23 (s, 1H), 3.38 (s, 2H), 2.95 (t, *J* = 8.0 Hz, 2H), 1.80 (t, *J* = 8.0 Hz, 2H), 0.99 (s, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$, ppm) δ 164.7 (d, *J* = 20.0 Hz), 162.0, 148.6 (d, *J* = 13.0 Hz), 136.5, 129.6 (d, *J* = 10.0 Hz), 123.8, 121.1 (d, *J* = 2.0 Hz), 116.4 (d, *J* = 26.0 Hz), 112.3 (d, *J* = 21.0 Hz), 70.2, 37.4, 35.7, 33.4, 24.6. **^{19}F NMR** (377 MHz, $CDCl_3$, ppm) δ –109.5 (s). **IR**: =3262, 2957, 2865, 1627, 1512, 1257, 1209, 1171, 1058, 870, 846 cm^{-1}. **HRMS (ESI)**: calcd for $C_{15}H_{18}FNO$ $[M+H]^+$ 248.1445, found 248.1463.

4-(7-chloroquinolin-2-yl)-2,2-dimethylbutan-1-ol(3k)



White solid, 14.9 mg, yield 57%. R_f = 0.3 (petroleum ether/ethyl acetate = 2:1), mp = 71.0 - 71.9 °C. **^{1}H NMR** (400 MHz, $CDCl_3$, ppm) δ 8.02 (d, *J* = 8.0 Hz, 2H), 7.69 (d, *J* = 8.0 Hz, 1H), 7.42 (d, *J* = 8.0 Hz, 1H), 7.29 (d, *J* = 12.0 Hz, 1H), 4.11 (s, 1H), 3.37 (s, 2H), 2.96 (t, *J* = 8.0 Hz, 2H), 1.81 (t, *J* = 8.0 Hz, 2H), 0.99 (s, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$, ppm) δ 164.7, 147.9, 136.4, 135.5, 128.8, 127.6, 127.0, 125.1, 122.0, 70.3, 37.1, 35.8, 33.4, 24.6. **IR**: =3337, 2960, 2872, 1607, 1496, 1415, 1136, 1063, 881, 849 cm^{-1}. **HRMS (ESI)**: calcd for $C_{15}H_{18}ClNO$ $[M+H]^+$ 264.1150, found 264.1163.

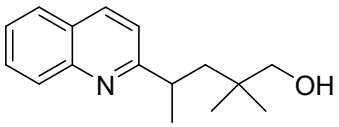
4-(8-butoxyquinolin-2-yl)-2,2-dimethylbutan-1-ol (3l)



Pale yellow solid, 17.5 mg, yield 58%. R_f = 0.3 (petroleum ether/ethyl acetate = 2:1), mp = 81.9 - 83.6 °C. **^{1}H NMR** (400 MHz, $CDCl_3$, ppm) δ 7.98 (d, *J* = 8.0 Hz, 1H), 7.36 (t, *J* = 8.0 Hz, 1H), 7.30 (d, *J* = 8.0 Hz, 1H), 7.26 (d, *J* = 8.0 Hz, 1H), 7.01

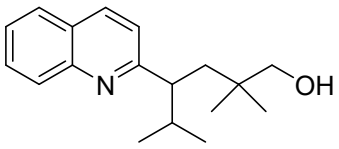
(d, J = 8.0 Hz, 1H), 4.66 (s, 1H), 4.18 (t, J = 8.0 Hz, 2H), 3.19 (s, 2H), 3.02 (t, J = 4.0 Hz, 2H), 2.04 - 1.97 (m, 2H), 1.92 (t, J = 8.0 Hz, 2H), 1.64 - 1.55 (m, 2H), 1.03 (t, J = 4.0 Hz, 3H), 0.97 (s, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$, ppm) δ 161.8, 154.4, 139.5, 136.3, 127.9, 126.0, 122.3, 119.1, 109.0, 69.2, 68.8, 35.8, 34.8, 32.9, 31.1, 25.1 19.4, 14.0. **IR**: =3329, 2964, 2868, 1601, 1565, 1505, 1465, 1326, 1260, 1104, 1059, 847, 746 cm^{-1}. **HRMS (ESI)**: calcd for $C_{19}H_{27}NO_2$ $[M+H]^+$ 302.2115, found 302.2131.

2,2-dimethyl-4-(quinolin-2-yl)pentan-1-ol (3m)



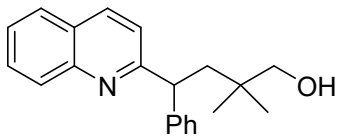
Pale yellow oil, 15.5 mg, yield 64%. R_f = 0.3 (petroleum ether/ethyl acetate = 2:1). **^{1}H NMR** (400 MHz, $CDCl_3$, ppm) δ 8.10 (d, J = 8.0 Hz, 1H), 8.02 (d, J = 8.0 Hz, 1H), 7.77 (d, J = 8.0 Hz, 1H), 7.68 (t, J = 8.0 Hz, 1H), 7.48 (t, J = 8.0 Hz, 1H), 7.35 (d, J = 8.0 Hz, 1H), 4.57 (s, 1H), 3.22 (t, J = 8.0 Hz, 1H), 2.98 (q, J = 12.0 Hz, 2H), 2.50 - 2.44 (m, 1H), 1.34 (d, J = 4.0 Hz, 3H), 1.28 (d, J = 20.0 Hz, 1H), 0.98 (s, 3H), 0.85 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$, ppm) δ 167.3, 147.3, 137.1, 129.9, 128.6, 127.6, 127.1, 126.2, 120.5, 69.9, 43.6, 38.0, 36.2, 27.4, 24.7, 23.7. **IR**: =3334, 2959, 2925, 2868, 1600, 1503, 1427, 1263, 1045, 830, 755 cm^{-1}. **HRMS (ESI)**: calcd for $C_{16}H_{21}NO$ $[M+H]^+$ 244.1696, found 244.1702.

2,2,5-trimethyl-4-(quinolin-2-yl)hexan-1-ol (3n)



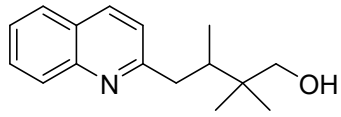
Pale yellow oil, 11.7 mg, yield 43%. R_f = 0.3 (petroleum ether/ethyl acetate = 2:1). **^{1}H NMR** (400 MHz, $CDCl_3$, ppm) δ 8.06 (dd, J_1 = 20.0 Hz, J_2 = 12.0 Hz, 2H), 7.77 (d, J = 8.0 Hz, 1H), 7.70 - 7.66 (m, 1H), 7.49 (t, J = 7.2 Hz, 1H), 7.32 (d, J = 12.0 Hz, 1H), 3.83 (s, 1H), 2.93 - 2.86 (m, 2H), 2.65 (d, J = 8.0 Hz, 1H), 2.48 (dd, J_1 = 16.0 Hz, J_2 = 12.0 Hz, 1H), 2.06 - 1.93 (m, 1H), 1.39 (d, J = 16.0 Hz, 1H), 0.98 (s, 3H), 0.89 (d, J = 4.0 Hz, 3H), 0.84 (d, J = 8.0 Hz, 3H), 0.79 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$, ppm) δ 165.5, 147.1, 136.5, 129.8, 128.8, 127.6, 127.1, 126.2, 122.5, 70.0, 49.7, 36.0, 35.7, 35.1, 27.7, 23.7, 21.1, 19.1. **IR**: =3305, 3060, 2958, 2924, 1721, 1600,1564, 1504, 1427, 1377, 1041, 823 cm^{-1}. **HRMS (ESI)**: calcd for $C_{18}H_{25}NO$ $[M+H]^+$ 272.2009, found 272.2027.

2,2-dimethyl-4-phenyl-4-(quinolin-2-yl)butan-1-ol (3o)



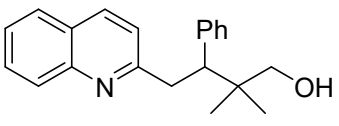
Colorless oil, 15.2 mg, yield 50%. R_f = 0.3 (petroleum ether/ethyl acetate = 2:1).**^{1}H NMR** (400 MHz, $CDCl_3$, ppm) δ 8.11 (d, *J* = 8.0 Hz, 1H), 7.97 (d, *J* = 8.0 Hz, 1H), 7.75 - 7.70 (m, 2H), 7.52 - 7.48 (m, 1H), 7.28 - 7.15 (m, 6H), 5.08 (s, 1H), 4.33 (dd, J_1 = 12.0 Hz, J_2 = 4.0 Hz, 1H), 3.10 (q, *J* = 8.0 Hz, 1H), 3.01 (s, 2H), 1.59 (dd, *J* = 16.0 Hz, J_2 = 4.0 Hz, 1H), 1.06 (s, 3H), 0.93 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$, ppm) δ 163.8, 146.9, 146.3, 136.9, 130.1, 128.9, 128.6, 128.1, 127.6, 127.1, 126.5, 126.4, 122.6, 69.3, 49.9, 42.4, 36.5, 27.6, 23.7. **IR**: =3340, 3059, 2955, 1598, 1499, 1425, 1263, 1113, 1044, 818, 750, 700 cm^{-1}. **HRMS (ESI)**: calcd for $C_{21}H_{23}NOO$ $[M+H]^+$ 306.1852, found 306.1867.

2,2,3-trimethyl-4-(quinolin-2-yl)butan-1-ol (3p)



Pale yellow oil, 12.2 mg, yield 50%. R_f = 0.3 (petroleum ether/ethyl acetate = 2:1). **^{1}H NMR** (400 MHz, $CDCl_3$, ppm) δ 8.04 (dd, J_1 = 16.0 Hz, J_2 = 8.0 Hz, 2H), 7.77 (d, *J* = 8.0 Hz, 1H), 7.67 (t, *J* = 8.0 Hz, 1H), 7.48 (t, *J* = 8.0 Hz, 1H), 7.28 (d, *J* = 8.0 Hz, 1H), 3.65 (d, *J* = 12.0 Hz, 1H), 3.33 (d, *J* = 12.0 Hz, 1H), 3.24 (dd, J_1 = 12.0 Hz, J_2 = 4.0 Hz, 1H), 2.53 (dd, J_1 = 12.0 Hz, J_2 = 8.0 Hz, 1H), 2.31 - 2.21 (m, 1H), 1.02 (s, 3H), 0.89 (d, *J* = 8.0 Hz, 3H), 0.87 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$, ppm) δ 163.4, 147.5, 136.6, 129.8, 128.4, 127.6, 126.8, 126.0, 122.3, 70.8, 41.0, 38.4, 38.1, 23.6, 19.7, 15.4. **IR**: =3302, 3060, 2958, 2924, 1599, 1504, 1427, 1380, 312, 1041, 823, 767 cm^{-1}. **HRMS (ESI)**: calcd for $C_{16}H_{21}NO$ $[M+H]^+$ 244.1696, found 244.1713.

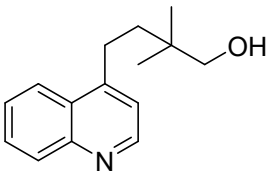
2,2-dimethyl-3-phenyl-4-(quinolin-2-yl)butan-1-ol (3q)



Pale yellow oil, 12.8 mg, yield 42%. R_f = 0.3 (petroleum ether/ethyl acetate = 2:1). **^{1}H NMR** (400 MHz, $CDCl_3$, ppm) δ 8.01 (d, *J* = 8.0 Hz, 1H), 7.89 (d, *J* = 8.0 Hz, 1H), 7.71 - 7.64 (m, 2H), 7.45 (t, *J* = 8.0 Hz, 1H), 7.23 - 7.21 (m, 4H), 7.17 - 7.14 (m, 1H), 7.03 (d, *J* = 8.0 Hz, 1H), 5.15 (s, 1H), 3.74 (d, *J* = 12.0 Hz, 1H), 3.59 (dd, J_1 = 20.0 Hz, J_2 = 4.0 Hz, 1H), 3.52 (q, *J* = 4.0 Hz, 1H), 3.30 (dd, J_1 = 12.0 Hz, J_2 = 8.0 Hz, 2H), 0.98 (s, 3H), 0.88 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$, ppm) δ 162.6, 147.5, 143.0, 136.4, 130.0, 129.7, 128.3, 127.8, 127.6, 126.7, 126.2, 126.0, 122.2, 70.6, 50.1,

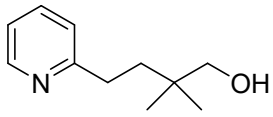
39.7, 39.5, 24.4, 20.6. **IR**: =3383, 2968, 2871, 1600, 1500, 1454, 1427, 1055, 755, 705 cm^{-1}. **HRMS (ESI)**: calcd for $C_{21}H_{23}NO$ $[M+H]^+$ 306.1852, found 306.1869.

2,2-dimethyl-4-(quinolin-4-yl)butan-1-ol (3r)



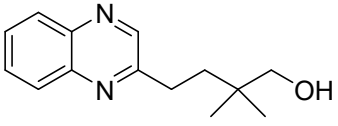
White solid, 11.5 mg, yield 50%. R_f = 0.3 (petroleum ether/ethyl acetate = 2:1), mp = 89.8 - 91.6 °C. **^{1}H NMR** (400 MHz, $CDCl_3$, ppm) δ 8.74 (d, *J* = 4.0 Hz, 1H), 8.09 (d, *J* = 8.0 Hz, 1H), 8.03 (d, *J* = 8.0 Hz, 1H), 7.68 - 7.64 (m, 1H), 7.54 - 7.50 (m, 1H), 7.19 (d, *J* = 8.0 Hz, 1H), 3.47 (s, 2H), 3.04 - 3.00 (m, 2H), 2.49 (s, 1H), 1.70 - 1.66 (m, 2H), 1.04 (s, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$, ppm) δ 150.2, 149.6, 148.2, 130.1, 129.2, 127.7 126.5, 123.6, 120.8, 71.5, 39.5, 35.7, 27.1, 24.1. **IR**: =3253, 2925, 2849, 2708, 1595, 1511, 1469, 1385, 1059, 837, 780 cm^{-1}. **HRMS (ESI)**: calcd for $C_{15}H_{19}NO$ $[M+H]^+$ 230.1539, found 230.1553.

2,2-dimethyl-4-(pyridin-2-yl)butan-1-ol (3t)



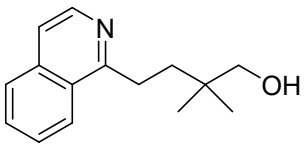
Pale yellow oil, 8.8 mg, yield 49%. R_f = 0.3 (petroleum ether/ethyl acetate = 2:1). **^{1}H NMR** (400 MHz, $CDCl_3$, ppm) δ 8.48 (d, *J* = 4.0 Hz, 1H), 7.60 - 7.56 (m, 1H), 7.15 (d, *J* = 8.0 Hz, 1H), 7.11 - 7.08 (m, 1H), 3.35 (s, 2H), 2.77 (t, *J* = 8.0 Hz, 2H), 1.72 - 1.68 (m, 2H), 0.95 (s, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$, ppm) δ 163.0, 149.1, 136.8, 123.1, 121.1, 70.5, 37.9, 35.7, 32.6, 24.5. **IR**: =331, 2953, 2865, 1673, 1594, 1569, 1474, 1434, 1153, 1052, 752 cm^{-1}. **HRMS (ESI)**: calcd for $C_{11}H_{17}NO$ $[M+H]^+$ 180.1383, found 180.1390.

2,2-dimethyl-4-(quinoxalin-2-yl)butan-1-ol (3u)



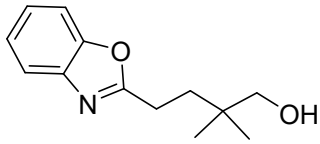
Pale yellow oil, 11.1 mg, yield 48%. R_f = 0.3 (petroleum ether/ethyl acetate = 2:1). **^{1}H NMR** (400 MHz, $CDCl_3$, ppm) δ 8.74 (s, 1H), 8.06 (d, *J* = 8.0 Hz, 1 H), 8.01 (d, *J* = 8.0 Hz, 1H), 7.75 - 7.67 (m, 2H), 3.39 (s, 2H), 3.01 (t, *J* = 8.0 Hz, 2H), 2.76 (s, 1H), 1.83 (t, *J* = 8.0 Hz, 2H), 1.00 (s, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$, ppm) δ 158.0, 146.1, 141.9, 141.3, 130.2, 129.3, 129.2, 128.7, 70.8, 37.3, 35.7, 31.0, 24.4. **IR**: =3351, 2957, 2868, 1560, 1492, 1364, 1263, 1110, 1048, 985, 759 cm^{-1}. **HRMS (ESI)**: calcd for $C_{14}H_{18}N_2O$ $[M+H]^+$ 231.1492, found 241.1503.

4-(isoquinolin-1-yl)-2,2-dimethylbutan-1-ol (3v)



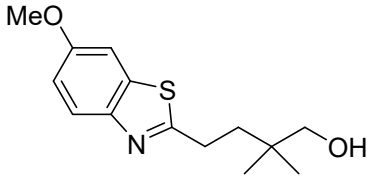
Yellow oil, 13.1 mg, yield 57%. R_f = 0.3 (petroleum ether/ethyl acetate = 2:1). **^{1}H NMR** (400 MHz, $CDCl_3$, ppm) δ 8.37 (d, *J* = 4.0 Hz, 1H), 8.17 (d, *J* = 8.0 Hz, 1H), 7.79 (d, *J* = 8.0 Hz, 1H), 7.68 - 7.64 (m, 1H), 7.60 - 7.56 (m, 1H), 7.49 (d, *J* = 4.0 Hz, 1H), 4.01 (s, 1H), 3.40 (s, 2H), 3.32 - 3.28 (m, 2H), 1.87 - 1.83 (m, 2H), 1.03 (s, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$, ppm) δ 162.7, 141.5, 136.4, 130.1, 127.5, 127.3, 127.0, 125.4, 119.5, 70.4, 37.3, 35.8, 29.5, 24.7. **IR**: =3335, 2953, 2866, 1622, 1562, 1503, 1469, 1387, 1359, 1050, 822, 746 cm^{-1}. **HRMS (ESI)**: calcd for $C_{15}H_{19}NO$ $[M+H]^+$ 230.1539, found 230.1555.

4-(benzo[d]oxazol-2-yl)-2,2-dimethylbutan-1-ol (3w)



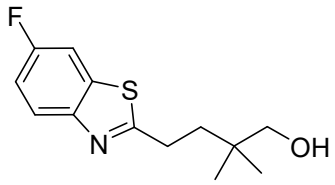
Pale yellow oil, 13.8 mg, yield 63%. R_f = 0.3 (petroleum ether/ethyl acetate = 2:1). **^{1}H NMR** (400 MHz, $CDCl_3$, ppm) δ 7.57 - 7.55 (m, 1H), 7.38 - 7.35 (m, 1H), 7.22 - 7.17 (m, 2H), 3.27 (s, 2H), 3.11 (s, 1H), 2.85 (t, *J* = 8.0 Hz, 2H), 1.82 (t, *J* = 8.0 Hz, 2H), 0.89 (s, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$, ppm) δ 168.1, 150.8, 141.1, 124.6, 124.2, 119.5, 110.3, 70.6, 35.36, 34.8, 24.1, 23.6. **IR**: =3376, 2954, 2869, 1613, 1570, 1456, 1242, 1164, 1052, 843, 744 cm^{-1}. **HRMS (ESI)**: calcd for $C_{13}H_{17}NO_2$ $[M+H]^+$ 220.1332, found 220.1338.

4-(6-methoxybenzo[d]thiazol-2-yl)-2,2-dimethylbutan-1-ol (3x)



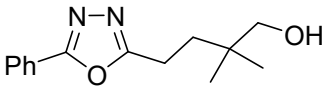
White solid, 19.7 mg, yield 74%. R_f = 0.2 (petroleum ether/ethyl acetate = 2:1), mp = 50.3 - 52.2 °C. **^{1}H NMR** (400 MHz, $CDCl_3$, ppm) δ 7.81 (d, *J* = 8.0 Hz, 1H), 7.28 (d, *J* = 4.0 Hz, 1H), 7.03 (dd, J_1 = 8.0 Hz, J_2 = 4.0 Hz, 1H), 3.85 (s, 3H), 3.36 (s, 2H), 3.06 (t, *J* = 8.0 Hz,2H), 1.86 (t, *J* = 8.0 Hz, 2H), 0.97 (s, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$, ppm) δ 170.5, 157.5, 147.5, 136.3, 122.9, 115.1, 104.4, 70.7, 55.9, 37.6, 35.6, 29.1, 24.2. **IR**: =3337, 2955, 1604, 1559, 1524, 1468, 1270, 1215, 1060, 843, 808 cm^{-1}. **HRMS (ESI)**: calcd for $C_{14}H_{19}NO_2S$ $[M+H]^+$ 266.1209, found 266.1215.

4-(6-fluorobenzo[d]thiazol-2-yl)-2,2-dimethylbutan-1-ol (3y)



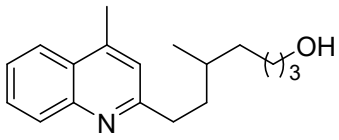
White solid, 20.1 mg, yield 79%. R_f = 0.3 (petroleum ether/ethyl acetate = 2:1), mp = 50.1 - 51.7 °C. **^{1}H NMR** (400 MHz, $CDCl_3$, ppm) δ 7.86 (dd, J_1 = 12.0 Hz, J_2 = 8.0 Hz, 1H), 7.49 (dd, J_1 = 8.0 Hz, J_2 = 4.0 Hz, 1H), 7.16 (td, J_1 = 8.0 Hz, J_2 = 4.0 Hz, 1H), 3.36 (s, 2H), 3.08 (t, J = 8.0 Hz2H), 2.80 (s, 1H), 1.87 (t, J = 8.0 Hz, 2H), 0.97 (s, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 172.8 (d, J = 3.0 Hz), 159.1, 149.7, 136.1 (d, J = 11.0 Hz), 123.4 (d, J = 10.0 Hz), 114.7 (d, J = 24.0 Hz), 108.0 (d, J = 27.0 Hz), 70.8, 37.6, 35.6, 29.3, 24.2. **^{19}F NMR** (377 MHz, $CDCl_3$, ppm) δ –116.8 (s). **IR**: =3455, 2961, 2866, 1605, 1568, 1521, 1458, 1258, 1091, 1049, 834 cm^{-1}. **HRMS (ESI)**: calcd for $C_{13}H_{16}FNOS$ $[M+H]^+$ 254.1009, found 254.1026.

2,2-dimethyl-4-(5-phenyl-1,3,4-oxadiazol-2-yl)butan-1-ol (3z)



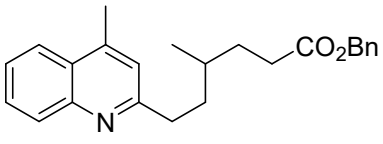
Pale yellow solid, 12.4 mg, yield 50%. R_f = 0.3 (petroleum ether/ethyl acetate = 2:1), mp = 53.9 – 55.0 °C. **^{1}H NMR** (400 MHz, $CDCl_3$,ppm) δ 8.02 (d, J = 8.0 Hz, 2H), 7.53 - 7.47 (m, 3H), 3.38 (s, 2H), 2.93 (t, J = 8.0 Hz, 2H), 2.33 (s, 1H), 1.86 (t, J = 8.0 Hz, 2H), 0.97 (s, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$, ppm) δ 167.7, 164.9, 131.7, 129.1, 126.9, 124.1, 71.0, 35.3, 34.8, 23.9, 20.8. **IR**: =3430, 2956, 2925, 2869, 1635, 1573, 1450, 1387, 1063, 780, 705 cm^{-1}. **HRMS (ESI)**: calcd for $C_{14}H_{18}N_2O_2$ $[M+H]^+$ 247.1441, found 247.1447.

5-methyl-7-(4-methylquinolin-2-yl)heptan-1-ol (4a)



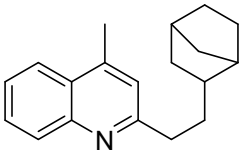
Orange oil, 10.8 mg, yield 40%. R_f = 0.4 (petroleum ether/ethyl acetate = 2:1). **^{1}H NMR** (400 MHz, $CDCl_3$, ppm) δ 8.04 (d, J = 8.0 Hz, 1H), 7.92 (d, J = 8.0 Hz, 1H), 7.67 - 7.63 (m, 1H), 7.49 (t, J = 8.0 Hz, 1H), 7.13 (s, 1H), 3.64 (t, J = 8.0 Hz, 2H), 2.99 - 2.84 (m, 2H), 2.67 (s, 3H), 2.05 (s, 1H), 1.84 - 1.78 (m, 1H), 1.61 – 1.22 (m, 8H), 0.97 (d, J = 8.0 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$, ppm) δ 163.1, 147.8, 144.4, 129.3, 129.1, 126.9, 125.5, 123.7, 122.1, 62.9, 37.2, 36.9, 36.6, 33.2, 32.9, 23.2, 19.7, 18.8. **IR**: =3319, 2925, 2858, 1603, 1562, 1509, 1448, 1142, 1052, 866, 74 cm^{-1}. **HRMS (ESI)**: calcd for $C_{18}H_{25}NO$ $[M+H]^+$ 272.2009, found 272.2037.

benzyl 4-methyl-6-(4-methylquinolin-2-yl)hexanoate (4b)



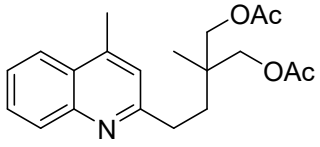
Orange oil, 15.5 mg, yield 43%. R_f = 0.5 (petroleum ether/ethyl acetate = 5:1). **^{1}H NMR** (400 MHz, $CDCl_3$, ppm) δ 8.04 (d, *J* = 8.0 Hz, 1H), 7.94 (d, *J* = 8.0 Hz, 1H), 7.69 - 7.64 (m, 1H), 7.52 - 7.48 (m, 1H), 7.38 - 7.30 (m, 5H), 7.12 (s, 1H), 5.10 (s, 2H), 3.00 - 2.84 (m, 2H), 2.67 (s, 3H), 2.42 - 2.37 (m, 2H), 1.88 - 1.77 (m, 2H), 1.69 - 1.54 (m, 3H), 1.00 (d, *J* = 4.0 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$, ppm) δ 173.9, 162.7, 147.9, 144.3, 136.2, 129.5, 129.1, 128.6, 128.29, 128.27, 126.9, 125.5, 123.7, 122.1, 66.2, 36.84, 36.82, 32.7, 32.2, 31.9, 19.3, 18.8. **IR**: =2957, 2923, 1732, 1603, 1505, 1450 1380, 1262, 1157, 1093, 756 cm^{-1}. **HRMS (ESI)**: calcd for $C_{24}H_{27}NO_2$ $[M+H]^+$ 362.2115, found 362.2140.

2-(2-(bicyclo[2.2.1]heptan-2-yl)ethyl)-4-methylquinoline (4c)



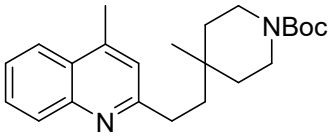
Yellow oil, 10.6 mg, yield 40%. R_f = 0.5 (petroleum ether/ethyl acetate = 5:1). **^{1}H NMR** (400 MHz, $CDCl_3$, ppm) δ 8.04 (d, *J* = 8.0 Hz, 1H), 7.93 (d, *J* = 8.0 Hz, 1H), 7.68 - 7.64 (m, 1H), 7.51 - 7.47 (m, 1H), 7.12 (s, 1H), 2.89 (t, *J* = 8.0 Hz, 2H), 2.66 (s, 3H), 2.20 (s, 1H), 2.06 (s, 1H), 1.83 - 1.74 (m, 1H), 1.61 – 1.43 (m, 5H), 1.36 - 1.34 (m, 1H), 1.18 - 1.07 (m, 4H). **^{13}C NMR** (100 MHz, $CDCl_3$, ppm) δ 163.0, 147.8, 144.2, 129.4, 129.1, 126.9, 125.5, 123.7, 122.2, 42.5, 41.2, 38.3, 37.8, 37.3, 36.7, 35.5, 30.2, 28.9, 18.8. **IR**: =3354, 2945, 2865, 1698, 1602, 1561, 1508, 1447, 1095, 863, 756 cm^{-1}. **HRMS (ESI)**: calcd for $C_{19}H_{23}N$ $[M+H]^+$ 266.1903, found 266.1930.

2-methyl-2-(2-(4-methylquinolin-2-yl)ethyl)propane-1,3-diyl diacetate (4d)



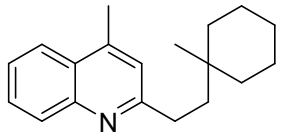
Pale yellow oil, 15.4 mg, yield 45%. R_f = 0.3 (petroleum ether/ethyl acetate = 5:1). **^{1}H NMR** (400 MHz, $CDCl_3$, ppm) δ 8.02 (d, *J* = 8.0 Hz, 1H), 7.94 (d, *J* = 8.0 Hz, 1H), 7.68 - 7.64 (m, 1H), 7.49 (t, *J* = 8.0 Hz, 1H), 7.10 (s, 1H), 4.01 (s, 4H), 2.93 - 2.89 (m, 2H), 2.67 (s, 3H), 2.06 (s, 6H), 1.89 - 1.84 (m, 2H), 1.06 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$, ppm) δ 171.1, 162.0, 147.8, 144.6, 129.4, 129.3, 126.9, 125.7, 123.7, 122.0, 68.0, 37.4, 34.5, 33.2, 21.0, 19.2, 18.8. **IR**: =3347, 2964, 2731, 1735, 1603, 1563, 1508, 1376, 1227, 1037, 755 cm^{-1}. **HRMS (ESI)**: calcd for $C_{20}H_{25}NO_4$ $[M+H]^+$ 344.1856, found 344.1875.

tert-butyl 4-methyl-4-(2-(4-methylquinolin-2-yl)ethyl)piperidine-1-carboxylate (4e)



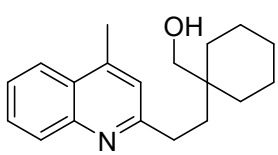
Orange oil, 19.9 mg, yield 54%. R_f = 0.5 (petroleum ether/ethyl acetate = 5:1). **^{1}H NMR** (400 MHz, $CDCl_3$, ppm) δ 8.02 (d, *J* = 8.0 Hz, 1H), 7.92 (d, *J* = 8.0 Hz, 1H), 7.65 (t, *J* = 4.0 Hz, 1H), 7.48 (t, *J* = 8.0 Hz, 1H), 7.11 (s, 1H), 3.61 - 3.58 (m, 2H), 3.25 - 3.19 (m, 2H), 2.89 - 2.85 (m, 2H), 2.65 (s, 3H), 1.77 - 1.72 (m, 2H), 1.52 – 1.37 (m, 5H), 1.45 (s, 9 H), 1.05 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$, ppm) δ 162.9, 155.1, 147.8, 144.4, 129.4, 129.2, 126.8, 125.6, 123.7, 122.0, 79.3, 41.9, 40.0, 36.9, 33.3, 31.7, 28.6, 28.5, 23.4, 18.7. **IR**: =3368, 2969, 2962, 1687, 1603, 1562, 1419, 1362, 1247, 1158, 759, 731 cm^{-1}. **HRMS (ESI)**: calcd for $C_{23}H_{32}N_2O_2$ $[M+H]^+$ 369.2537, found 369.2549.

4-methyl-2-(2-(1-methylcyclohexyl)ethyl)quinoline (4f)



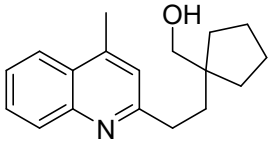
Pale yellow oil, 13.4 mg, yield 50%. R_f = 0.5 (petroleum ether/ethyl acetate = 5:1). **^{1}H NMR** (400 MHz, $CDCl_3$, ppm) δ 8.05 (d, *J* = 8.0 Hz, 1H), 7.93 (d, *J* = 8.0 Hz, 1H), 7.68 - 7.64 (m, 1H), 7.50 - 7.46 (m, 1H), 7.14 (s, 1H), 2.89 - 2.85 (m, 2H), 2.66 (s, 3H), 1.73 - 1.68 (m, 2H), 1.54 - 1.45 (m, 5H), 1.40 - 1.35 (m, 5H), 1.00 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$, ppm) δ 163.7, 147.9, 144.2, 129.4, 129.1, 126.8, 125.4, 123.7, 122.1, 42.5, 37.9, 33.6, 33.0, 26.7, 25.0, 22.2, 18.8. **IR**: =3348, 2921, 2848, 1603, 1561, 1507, 1447, 1263, 1098, 865, 756 cm^{-1}. **HRMS (ESI)**: calcd for $C_{19}H_{25}N$ $[M+H]^+$ 268.2060, found 268.2085.

(1-(2-(4-methylquinolin-2-yl)ethyl)cyclohexyl)methanol (4g)



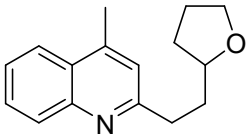
Pale yellow oil, 17.8 mg, yield 63%. R_f = 0.3 (petroleum ether/ethyl acetate = 2:1). **^{1}H NMR** (400 MHz, $CDCl_3$, ppm) δ 8.00 (d, *J* = 8.0 Hz, 1H), 7.91 (d, *J* = 8.0 Hz, 1H), 7.64 (t, *J* = 8.0 Hz, 1H), 7.48 (t, *J* = 4.0 Hz, 1H), 7.11 (s, 1H), 5.00 (s, 1H), 3.46 (s, 2H), 2.89 (t, *J* = 8.0 Hz, 2H), 2.64 (s, 3H), 1.89 (t, *J* = 8.0 Hz, 2H), 1.48 - 1.35 (m, 10H). **^{13}C NMR** (100 MHz, $CDCl_3$, ppm) δ 163.3, 147.3, 144.8, 129.4, 128.8, 126.8, 125.7, 123.7, 122.5, 67.1, 37.8, 33.4, 33.1, 31.9, 26.7, 21.7, 18.7. **IR**: =3329, 2922, 2850, 1603, 1563, 1508, 1447, 1350, 1264, 1045, 753 cm^{-1}. **HRMS (ESI)**: calcd for $C_{19}H_{25}NO$ $[M+H]^+$ 284.2009, found 284.2028.

(1-(2-(4-methylquinolin-2-yl)ethyl)cyclopentyl)methanol (4h)



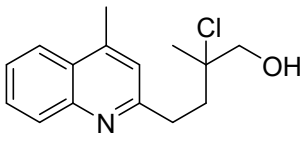
Pale yellow oil, 18.5 mg, yield 69%. R_f = 0.3 (petroleum ether/ethyl acetate = 2:1). **^{1}H NMR** (400 MHz, $CDCl_3$, ppm) δ 8.00 (d, *J* = 8.0 Hz, 1H), 7.90 (d, *J* = 8.0 Hz, 1H), 7.65 - 7.61 (m, 1H), 7.49 - 7.45 (m, 1H), 7.10 (s, 1H), 5.20 (s, 1H), 3.41 (s, 2H), 2.93 (t, *J* = 8.0 Hz, 2H), 2.63 (s, 3H), 1.95 (t, *J* = 8.0 Hz, 2H), 1.63 - 1.55 (m, 6H), 1.43 - 1.40 (m, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$, ppm) δ 163.0, 147.2, 144.8, 129.4, 128.8, 126.9, 125.7, 123.7, 122.5, 67.3, 48.1, 35.4, 35.1, 33.8, 25.3, 18.7. **IR**: =3339, 2942, 2861, 1603, 1563, 1508, 1446, 1351, 1263, 1099, 756 cm^{-1}. **HRMS (ESI)**: calcd for $C_{18}H_{23}NO$ $[M+H]^+$ 270.1852, found 270.1866.

4-methyl-2-(2-(tetrahydrofuran-2-yl)ethyl)quinoline (4i)



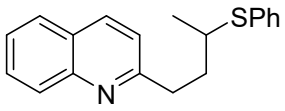
Yellow oil, 18.0 mg, yield 75%. R_f = 0.5 (petroleum ether/ethyl acetate = 5:1). **^{1}H NMR** (400 MHz, $CDCl_3$, ppm) δ 8.03 (d, *J* = 12.0 Hz, 1H), 7.92 (d, *J* = 4.0 Hz, 1H), 7.66 - 7.62 (m, 1H), 7.49 - 7.45 (m, 1H), 7.15 (s, 1H), 3.92 - 3.85 (m, 2H), 3.73 (q, *J* = 8.0 Hz, 1H), 3.07 - 2.94 (m, 2H), 2.64 (s, 3H), 2.08 - 1.95 (m, 3H), 1.93 - 1.7 (m, 2H), 1.56 - 1.47 (m, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$, ppm) δ 162.2, 147.8, 144.3, 129.4, 129.1, 126.9, 125.5, 123.6, 122.2, 78.9, 67.8, 35.9, 35.7, 31.4, 25.9, 18.7. **IR**: =3381, 2963, 2924, 2861, 1602, 1561, 1508, 1446, 1098, 1062, 757 cm^{-1}. **HRMS (ESI)**: calcd for $C_{16}H_{19}NO$ $[M+H]^+$ 242.1539, found 242.1560.

2-chloro-2-methyl-4-(4-methylquinolin-2-yl)butan-1-ol (4j)



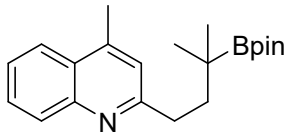
Pale yellow solid, 17.2 mg, yield 65%. R_f = 0.3 (petroleum ether/ethyl acetate = 2:1), mp = 49.4 - 50.9 °C. **^{1}H NMR** (400 MHz, $CDCl_3$, ppm) δ 7.97 (dd, J_1 = 12.0 Hz, J_2 = 8.0 Hz, 2H), 7.69 - 7.65 (m, 1H), 7.54 - 7.49 (m, 1H), 7.14 (s, 1H), 5.76 (s, 1H), 3.72 (d, *J* = 12.0 Hz, 1H), 3.57 (d, *J* = 12.0 Hz, 1H), 3.25 - 3.19 (m, 1H), 3.13 - 3.07 (m, 1H), 2.67 (s, 3H), 2.60 - 2.53 (m, 1H), 2.25 - 2.18 (m, 1H), 1.70 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$, ppm) δ 161.5, 147.1, 145.3, 129.6, 128.6, 127.0, 126.0, 123.8, 122.6, 74.1, 68.9, 37.5, 33.0, 28.2, 18.7. **IR**: =3173, 2927, 2852, 1605, 1567, 1510, 1447, 1378, 1062, 872, 758 cm^{-1}. **HRMS (ESI)**: calcd for $C_{15}H_{18}ClNO$ $[M+H]^+$ 264.1150, found 264.1160.

2-(3-(phenylthio)butyl)quinoline (4k)



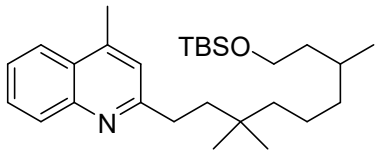
Pale yellow solid, 16.7 mg, yield 57%. R_f = 0.5 (petroleum ether/ethyl acetate = 5:1), mp = 37.5 - 37.9 °C. **^{1}H NMR** (400 MHz, $CDCl_3$, ppm) δ 8.04 (t, *J* = 8.0 Hz, 2H), 7.77 (d, *J* = 8.0 Hz, 1H), 7.70 - 7.66 (m, 1H), 7.50 - 7.46 (m, 1H), 7.41 - 7.38 (m, 2H), 7.30 - 7.17 (m, 4H), 3.35 - 3.26 (m, 1H), 3.19 - 3.10 (m, 2H), 2.19 - 2.02 (m, 2H), 1.37 (d, *J* = 8.0 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$, ppm) δ 162.1, 148.1, 136.4, 135.3, 132.2, 129.5, 129.0, 128.9, 127.6, 126.9, 125.9, 121.6, 43.2, 36.6, 36.5, 21.4. **IR**: =3395, 3053, 2921, 1598, 1502, 1476, 1430, 1374, 1308, 825, 742, 693 cm^{-1}. **HRMS (ESI)**: calcd for $C_{19}H_{19}NS$ $[M+H]^+$ 294.1311, found 294.1323.

4-methyl-2-(3-methyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butyl)quinoline (4l)



White solid, 17.0 mg, yield 50%. R_f = 0.5 (petroleum ether/ethyl acetate = 5:1), mp = 83.5 - 84.3 °C. **^{1}H NMR** (400 MHz, $CDCl_3$, ppm) δ 8.03 (d, *J* = 8.0 Hz, 1H), 7.92 (d, *J* = 8.0 Hz, 1H), 7.66 - 7.62 (m, 1H), 7.47 (t, *J* = 8.0 Hz, 1H), 7.17 (s, 1H), 2.92 - 2.87 (m, 2H), 2.66 (s, 3H), 1.79 - 1.75 (m, 2H), 1.26 (s, 12H), 1.05 (s, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$, ppm) δ 163.5, 147.8, 144.2, 129.4, 129.0, 126.9, 125.4, 123.6, 122.2, 83.2, 41.1, 36.3, 24.9, 24.8, 18.8. **IR**: =2975, 2950, 2863, 1605, 1562, 1508, 1473, 1363, 1303, 1134, 965, 852, 763 cm^{-1}. **HRMS (ESI)**: calcd for $C_{21}H_{30}BNO_2$ $[M+H]^+$ 340.2442, found 340.2465.

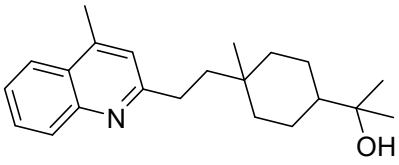
2-(9-((tert-butyldimethylsilyl)oxy)-3,3,7-trimethylnonyl)-4-methylquinoline (4m)



Pale yellow oil, 17.7 mg, yield 40%. R_f = 0.4 (petroleum ether/ethyl acetate = 5:1). **^{1}H NMR** (400 MHz, $CDCl_3$, ppm) δ 8.04 (d, *J* = 8.0 Hz, 1H), 7.93 (d, *J* = 8.0 Hz, 1H), 7.68 - 7.64 (m, 1H), 7.48 (t, *J* = 8.0 Hz, 1H), 7.13 (s, 1H), 3.69 - 3.59 (m, 2H), 2.89 - 2.85 (m, 2H), 2.67 (s, 3H), 1.70 - 1.65 (m, 2H), 1.61 - 1.52 (m, 2H), 1.35 - 1.24 (m, 6H), 1.16 - 1.11 (m, 1H), 0.97 (s, 6H), 0.88 (d, J = 4.0 Hz, 3H), 0.05 (s, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$, ppm) δ 163.6, 147.8, 144.3, 129.4, 129.1, 126.9, 125.5, 123.7, 122.1, 61.7, 42.5, 42.3, 40.1, 38.2, 34.4, 33.2, 29.6, 27.2, 26.1, 21.5, 19.9, 18.8, 18.5, -5.1. **IR**: =3348, 2954,

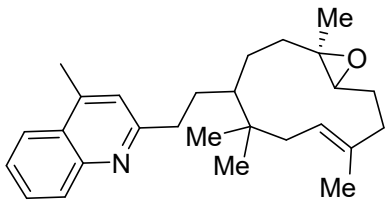
2929, 2857, 1604, 1562, 1467, 1254, 1093, 833, 756 cm^{-1}. **HRMS (ESI)**: calcd for $C_{28}H_{47}NOSi$ $[M+H]^+$ 442.3500, found 442.3526.

2-(4-methyl-4-(2-(4-methylquinolin-2-yl)ethyl)cyclohexyl)propan-2-ol (4n)



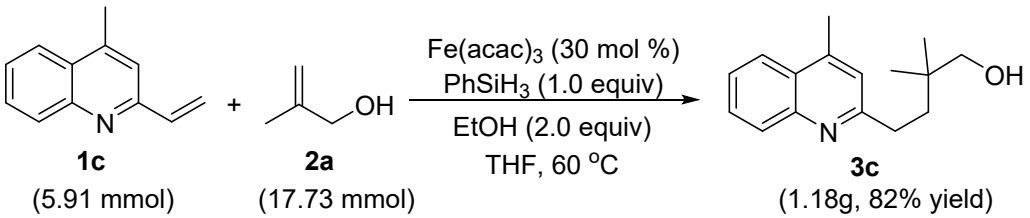
White solid, 16.2 mg, yield 50%. R_f = 0.3 (petroleum ether/ethyl acetate = 2:1), 2.5:1 dr, mp = 104.1 - 104.9 °C. **^{1}H NMR** (400 MHz, $CDCl_3$, ppm) δ 8.04 (d, *J* = 8.0 Hz, 1H), 7.94 (d, *J* = 8.0 Hz, 1H), 7.66 (t, *J* = 8.0 Hz, 1H), 7.49 (t, *J* = 8.0 Hz, 1H), 7.13 (s, 1H), 2.85 - 2.80 (m, 2H), 2.67 (s, 3H), 2.22 (s, 1H), 1.70 - 1.59 (m, 2H), 1.70 - 1.59 (m, 4H), 1.30 - 1.21 (m, 4H), 1.17 (s, 6H), 0.99 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$, ppm) δ 163.5, 147.8, 144.4, 129.4, 129.2, 126.9, 125.5, 123.7, 122.1, 73.0, 49.1, 37.9, 35.8, 33.8, 32.5, 29.6, 27.3, 22.8, 18.8. **IR**: =3446, 2962, 2865, 1605, 1567, 1521, 1457, 1260, 1092, 1049, 825 cm^{-1}. **HRMS (ESI)**: calcd for $C_{22}H_{31}NO$ $[M+H]^+$ 326.2478, found 326.2492.

4-methyl-2-(2-((1R,E)-1,5,5,8-tetramethyl-12-oxabicyclo[9.1.0]dodec-7-en-4-yl)ethyl)quinoline (4o)



Orange oil, 21.5 mg, yield 55%. R_f = 0.3 (petroleum ether/ethyl acetate = 5:1), 2.6:1 dr. **^{1}H NMR** (400 MHz, $CDCl_3$, ppm) δ 8.04 (d, *J* = 8.0 Hz, 1H), 7.94 (d, *J* = 12.0 Hz, 1H), 7.66 (t, *J* = 8.0 Hz, 1H), 7.49 (t, *J* = 8.0 Hz, 1H), 7.10 (s, 1H), 5.18 (d, *J* = 8.0 Hz, 1H), 2.93 (t, *J* = 8.0 Hz, 2H), 2.67 (s, 3H), 2.44 (d, *J* = 8.0 Hz, 1H), 2.29 - 2.08 (m, 4H), 2.04 - 1.95 (m, 1H), 1.86 - 1.83 (m, 1H), 1.73 (d, *J* = 16.0 Hz, 1H), 1.55 (s, 3H), 1.45 - 1.37 (m, 2H), 1.19 - 1.18 (m, 2H), 1.14 (s, 3H), 1.09 (s, 3H), 0.93 - 0.87 (m, 1H), 0.81 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$, ppm) δ 162.8, 147.9, 144.5, 133.5, 129.5, 129.1, 126.9, 125.6, 123.7, 122.8, 122.2, 64.2, 62.6, 45.0, 40.6, 40.2, 38.5, 37.3, 36.6, 32.4, 28.0, 25.3, 24.6, 23.8, 18.8, 17.5, 15.9. **IR**: =3349, 2956, 2924, 1603, 1561, 1508, 1447, 1384, 1261, 1097, 757 cm^{-1}. **HRMS (ESI)**: calcd for $C_{27}H_{37}NO$ $[M+H]^+$ 392.2948, found 392.2968.

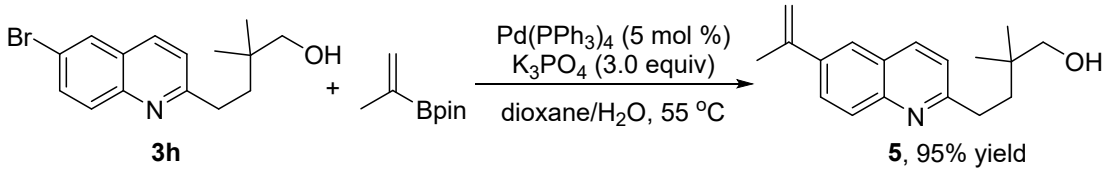
4. Experimental Procedure for the Gram-Scale Reaction



1c (5.91 mmol) + **2a** (17.73 mmol) → **3c** (1.18g, 82% yield)

A Schlenk tube containing $Fe(acac)_3$ (610.0 mg, 30 mol %) was evacuated and purged with Argon three times. Afterwards, **1c** (1.00 g, 5.91 mmol), **2a** (1.28 g, 17.73 mmol), EtOH (545.0 mg, 11.82 mmol), $PhSiH_3$ (640.0 mg, 5.91 mmol) and 80 mL THF were added via syringe. The solution was kept at 60 °C for 2 h. After the reaction was completed, cooled it to room temperature, filtered and evaporated under reduced pressure. The purification was performed by flash column chromatography on silica gel using ethyl acetate/petroleum ether (v/v, 1:30 to 1:10) as eluent to give **3c** (1.18 g, 82% yield).

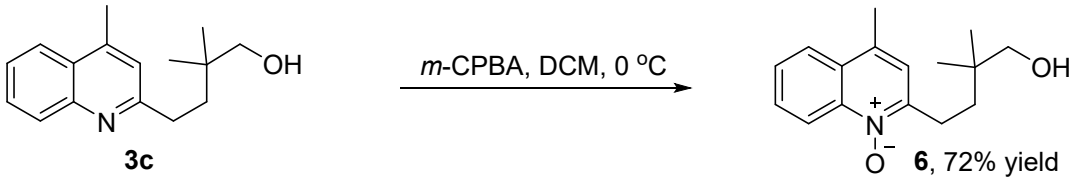
5. Further derivatization



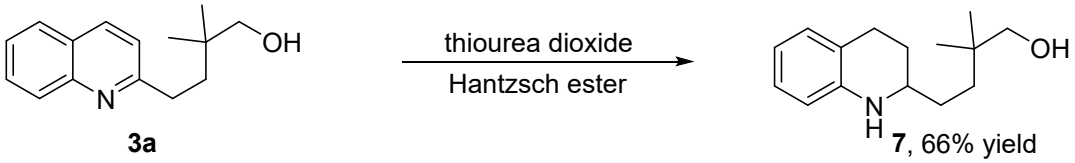
3h → **5**, 95% yield

5 was prepared according to a previously reported literature procedures.[3] To a solution of compound **3h** (36.8 mg, 0.12 mmol, 1.0 equiv), K_3PO_4 (76.4 mg, 0.36 mmol, 3.0 equiv) and $Pd(PPh_3)_4$ (6.9 mg, 0.006 mmol, 0.05 equiv) in dioxane (1 mL) and H_2O (0.2 mL) was added isopropenylboronic acid pinacol ester (45 μL, 0.24 mmol, 2.0 equiv) at room temperature. Then the reaction was heated at 55 °C for 17 h before being cooled to room temperature and quenched with H_2O (5 mL). The resulting mixture was extracted with EtOAc (3 × 5 mL), the combined organic layers were dried over Na_2SO_4, filtered and concentrated under reduced pressure. The residue was purified by flash column chromatography (silica gel, 1:20 to 1:10 EtOAc/petroleum ether) to give compound **5** (25.6 mg, 95% yield) as white solid. Mp = 57.4 - 59.3 °C. **^{1}H NMR** (400 MHz, $CDCl_3$, ppm) δ 8.02 (d, J = 8.0 Hz, 1H), 7.95 (d, J = 8.0, 1H), 7.85 (dd, J_1 = 8.8 Hz, J_2 = 2.0 Hz, 1H), 7.75 (d, J = 1.6 Hz, 1H), 7.26 (d, J = 8.0 Hz, 1H), 5.52 (s, 1H), 5.20 (s, 1H), 4.20 (s, 1H), 3.36 (s, 2H), 2.96 (t, J = 8.0 Hz, 2H), 2.24 (s, 3H), 1.83 (t, J = 8.0 Hz, 2H), 0.99 (s, 6H). **^{13}C NMR** (100 MHz,

$CDCl_3$, ppm) δ 163.3, 147.2, 142.5, 138.6, 136.8, 128.2, 127.8, 126.6, 123.8, 122.0, 113.7, 70.3, 37.1, 35.8 33.3, 24.7, 21.9. **IR**: =3214, 2952, 2929, 2858, 1627, 1592, 1460, 1379, 1191, 1132, 1064, 887, 837 cm^{-1}. **HRMS (ESI)**: calcd for $C_{18}H_{23}NO$ $[M+H]^+$ 270.1852, found 270.1870.



6 was prepared according to a previously reported literature procedures.[4] To a solution of **3c** (24.3 mg, 0.1 mmol) in dry DCM (2 mL) was added *m*-CPBA (85%, 20.3 mg, 0.1 mmol) at 0 °C. The mixture was transferred to room temperature. The solution was kept at room temperature 16 h. After the reaction was completed, the mixture was directly purified via flash chromatography (EtOAc/petroleum ether 1:5) to afford *N*-oxide **6** (18.6 mg, 72% yield) as a white solid. Mp = 129.9 - 130.7 °C. **^{1}H NMR** (400 MHz, $CDCl_3$, ppm) δ 8.79 (d, *J* = 8.0 Hz, 1H), 7.91 (d, *J* = 8.0 Hz, 1H), 7.73 (t, *J* = 8.0 Hz, 1H), 7.60 (t, *J* = 4.0 Hz, 1H), 7.13 (s, 1H), 4.35 (s, 1H), 3.52 (s, 2H), 3.03 - 2.99 (m, 2H), 2.62 (s, 3H), 1.68 - 1.63 (m, 2H), 0.95 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 149.4, 141.0, 135.0, 130.3, 128.7, 127.7, 124.6, 122.9, 120.2, 70.2, 35.4, 34.4, 26.7, 24.6, 18.3. **IR**: =3373, 2952, 2862, 1668, 1609, 1569, 1510, 1390, 1216, 1147, 1101, 1055, 787, 766, 728 cm^{-1}. **HRMS (ESI)**: calcd for $C_{16}H_{21}NO_2$ $[M+H]^+$ 260.1645, found 260.1656.



7 was prepared according to a previously reported literature procedures.[5] An oven-dried flask was fitted with magnetic stirring bar and charged with **3a** (0.10 mmol), thiourea dioxide (10 mol %), Hantzsch dihydropyridine (1.3 equiv) and chloroform (2 mL). The resulting mixture was stirred at 60°C for 70 h. The solvent was removed under reduced pressure and the residue was purified by column chromatography on silica gel using hexane/ EtOAc (5:1) as eluent to yield the corresponding products **7** (15.5 mg, 66% yield). **^{1}H NMR** (400 MHz, $CDCl_3$, ppm) δ 6.96 (t, *J* = 8.0 Hz, 2H), 6.61 (t, *J* = 4.0 Hz, 1H), 6.49 (d, *J* = 8.0 Hz, 1H), 3.35 (s, 2H), 3.22 - 3.16 (m, 1H), 2.81 - 2.71 (m, 2H), 1.99 - 1.94 (m, 1H), 1.70 - 1.57 (m, 1H),

1.51 - 1.31 (m, 4H), 0.90 (s, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$, ppm) δ 144.8, 129.3, 126.8, 121.6, 117.1, 114.3, 71.8, 52.4, 35.0, 34.4, 31.1, 28.2, 26.5, 24.0, 23.9. **IR**: =3346, 3052, 2927, 1605, 1586, 1480, 1357, 1308, 1265, 1104, 1035, 745 cm^{-1}. **HRMS (ESI)**: calcd for $C_{15}H_{23}NO$ $[M+H]^+$ 234.1852, found 234.1860.

6. References

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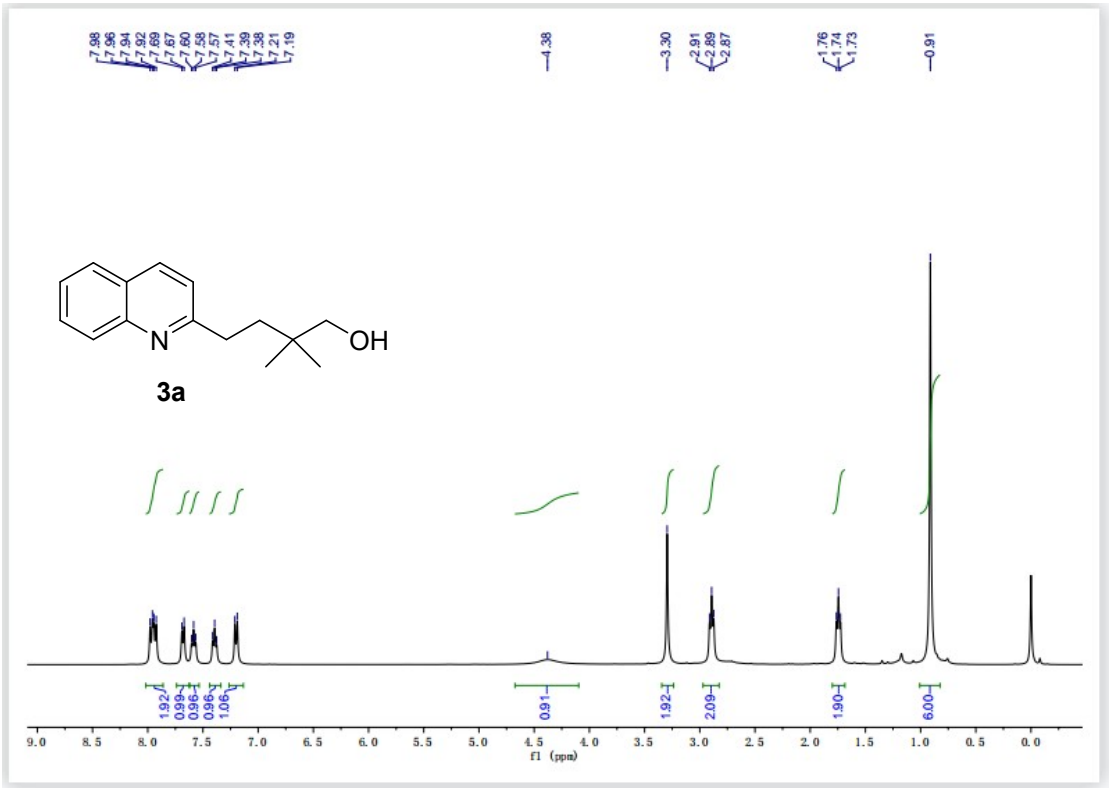
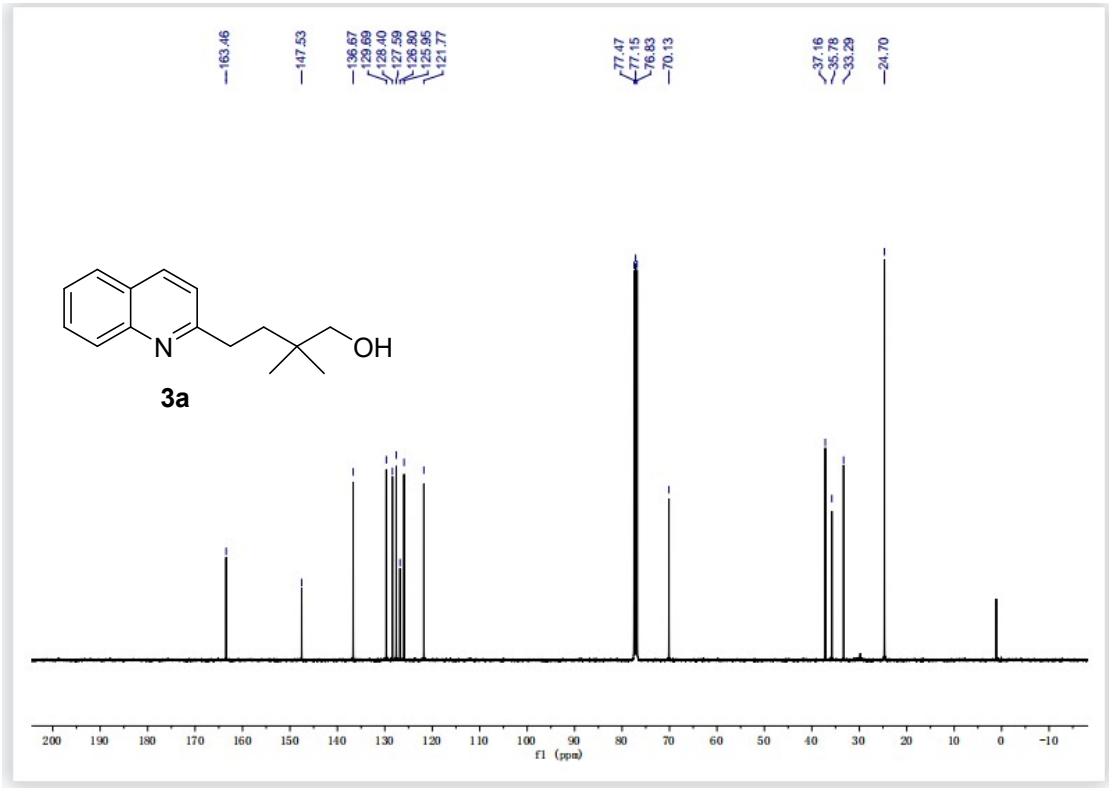
7. NMR spectra of the products

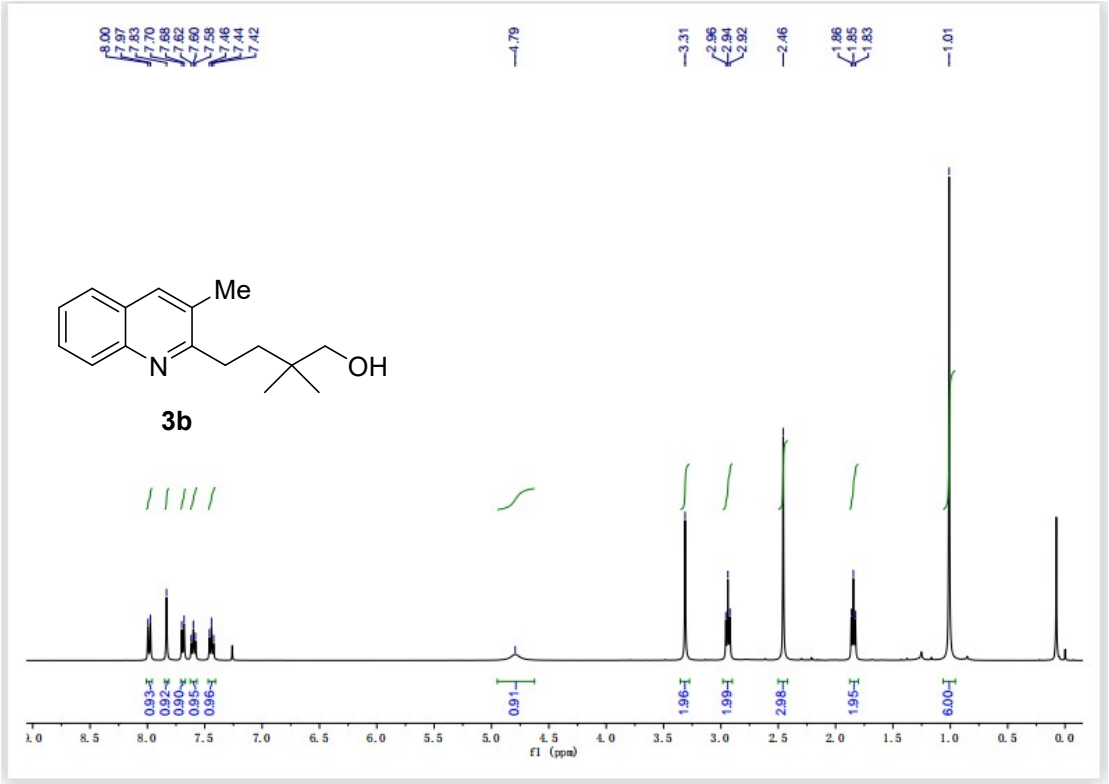
^{1}H NMR (400 MHz, $CDCl_3$) of **3a**



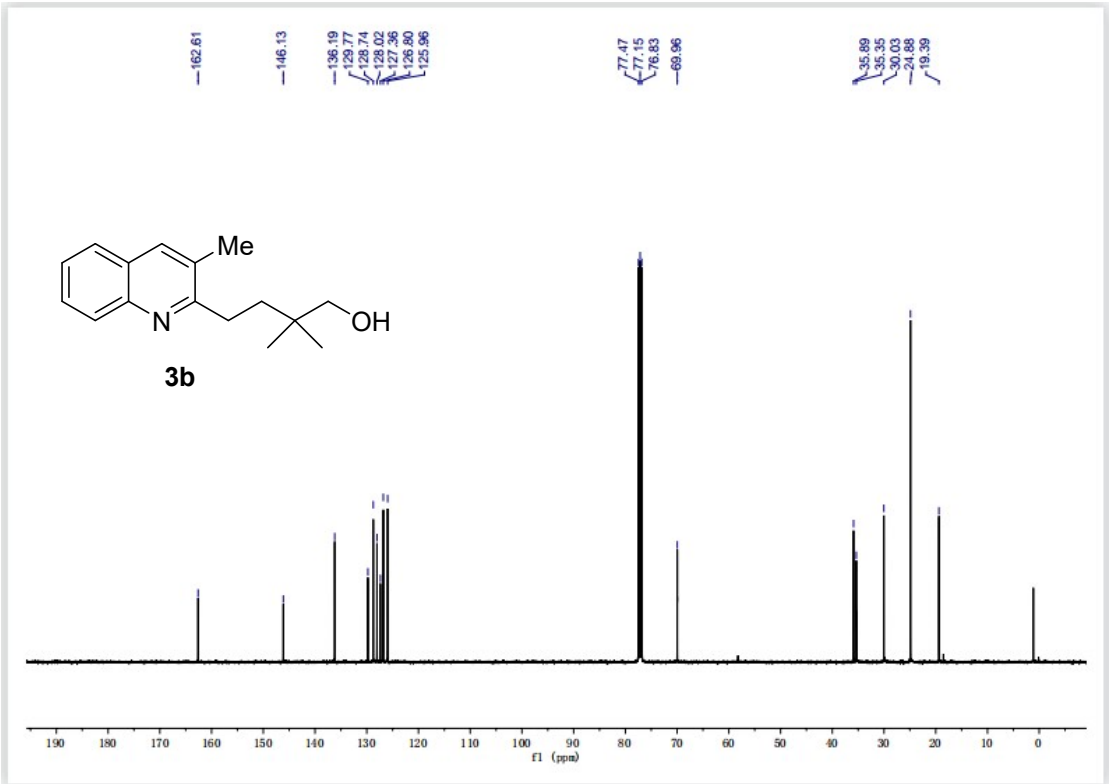
^{13}C NMR (100 MHz, CDCl3) of **3a**



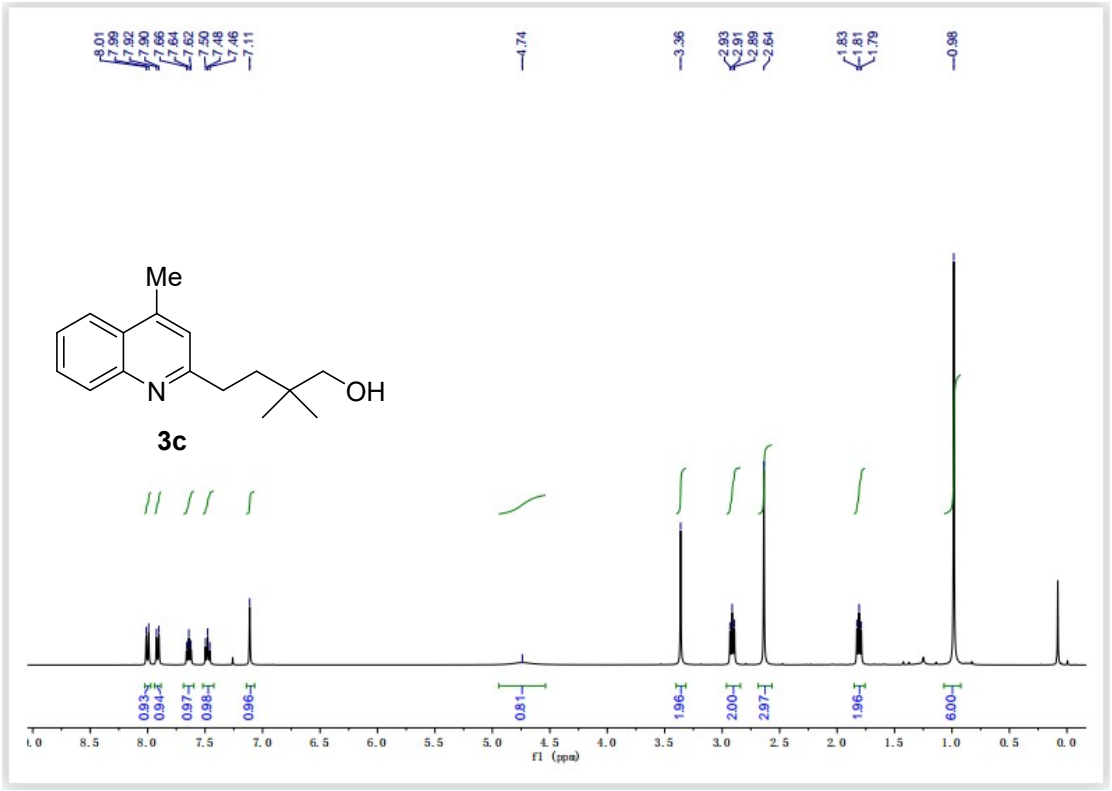
^{1}H NMR (400 MHz, $CDCl_3$) of **3b**



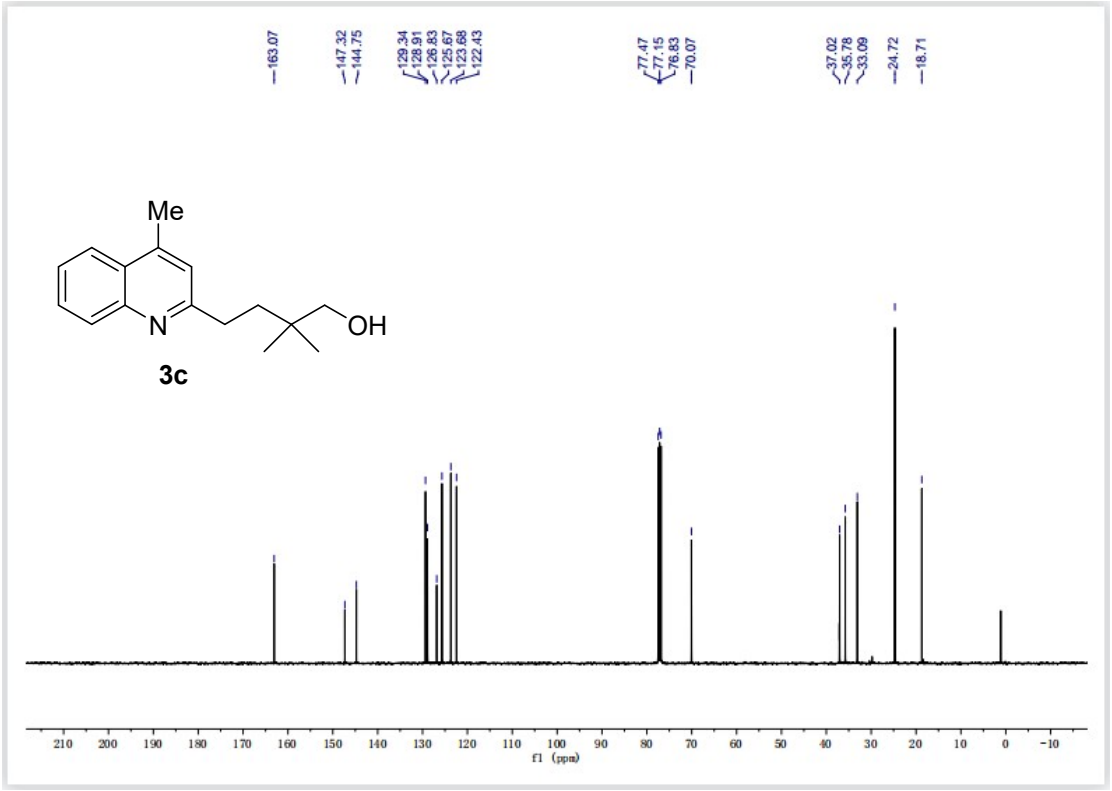
^{13}C NMR (100 MHz, $CDCl_3$) of **3b**



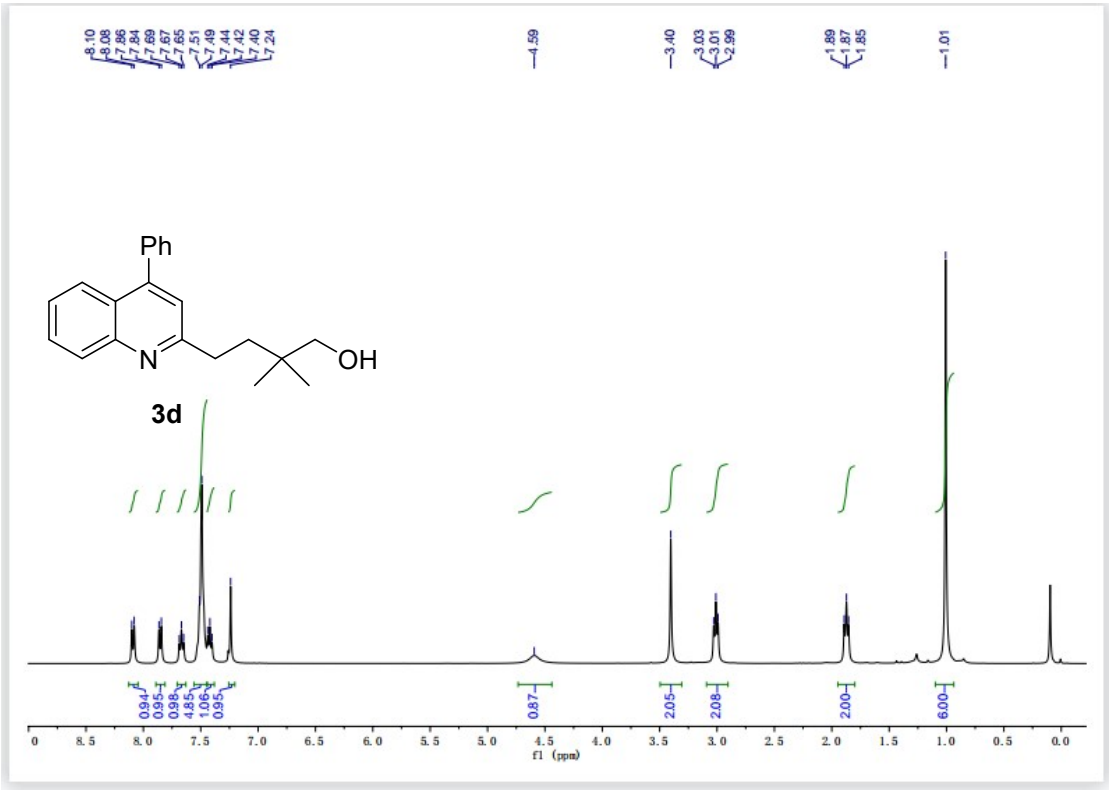
^{1}H NMR (400 MHz, $CDCl_3$) of **3c**



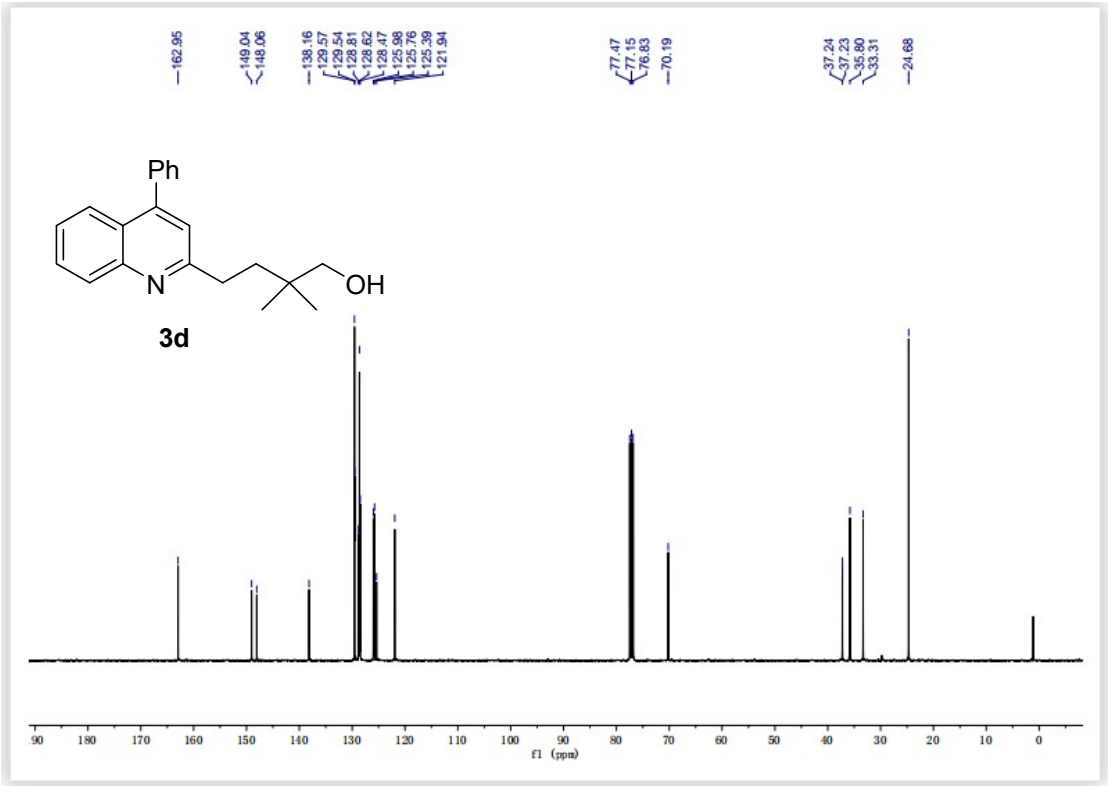
^{13}C NMR (100 MHz, $CDCl_3$) of **3c**



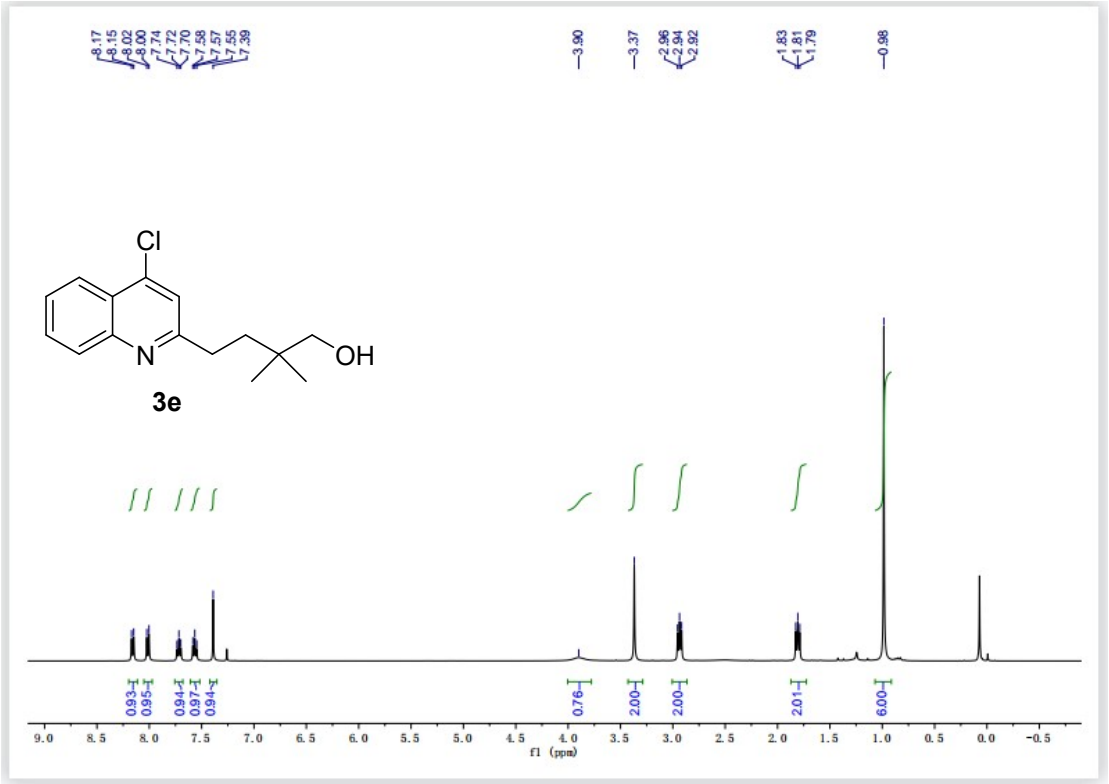
^{1}H NMR (400 MHz, $CDCl_3$) of **3d**



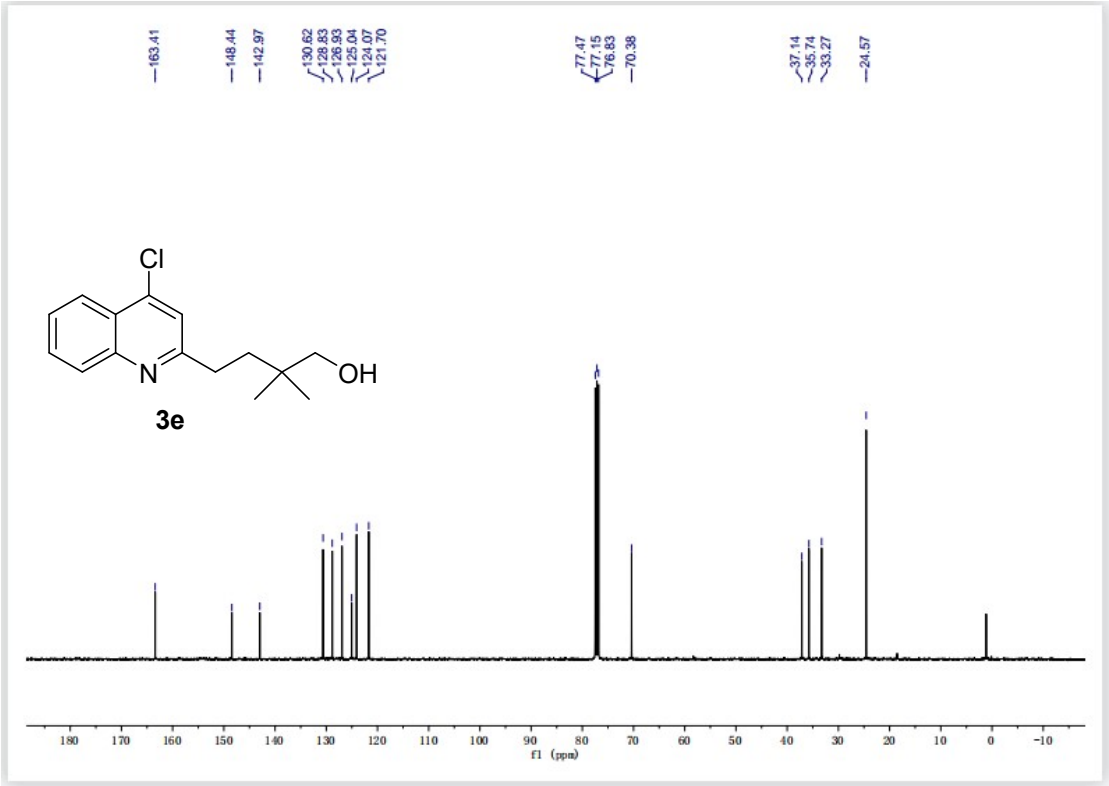
^{13}C NMR (100 MHz, $CDCl_3$) of **3d**



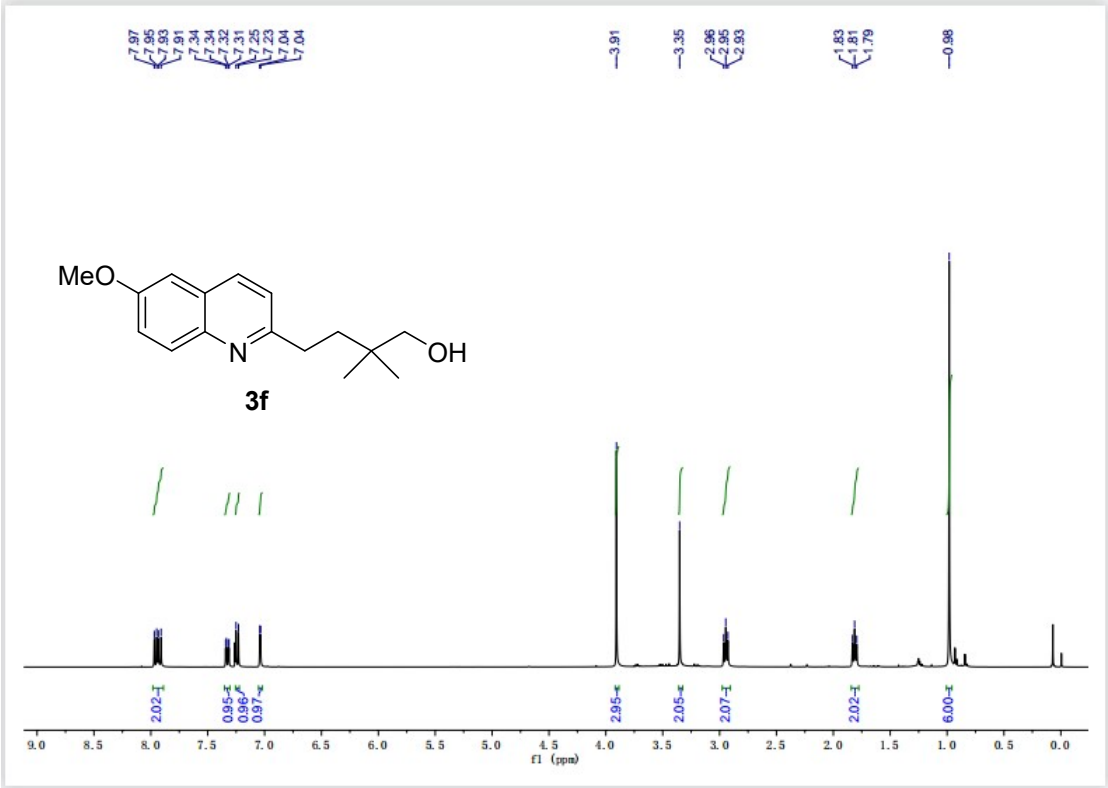
^{1}H NMR (400 MHz, $CDCl_3$) of **3e**



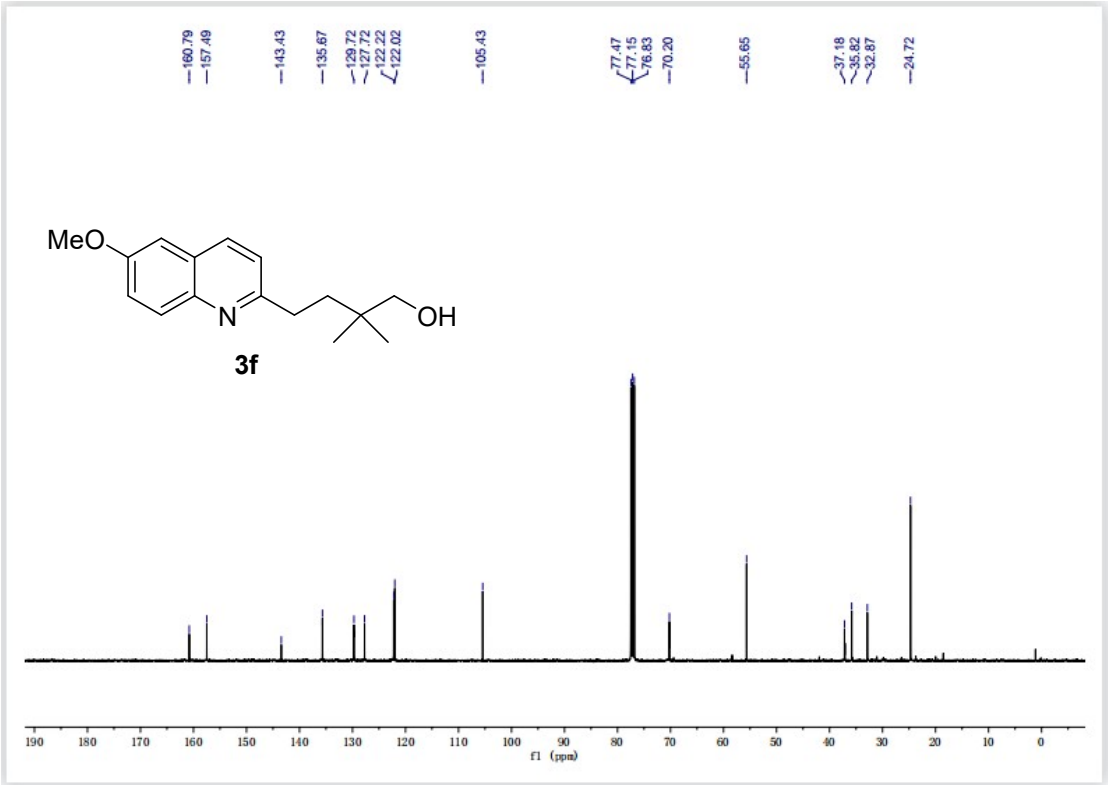
^{13}C NMR (100 MHz, $CDCl_3$) of **3e**



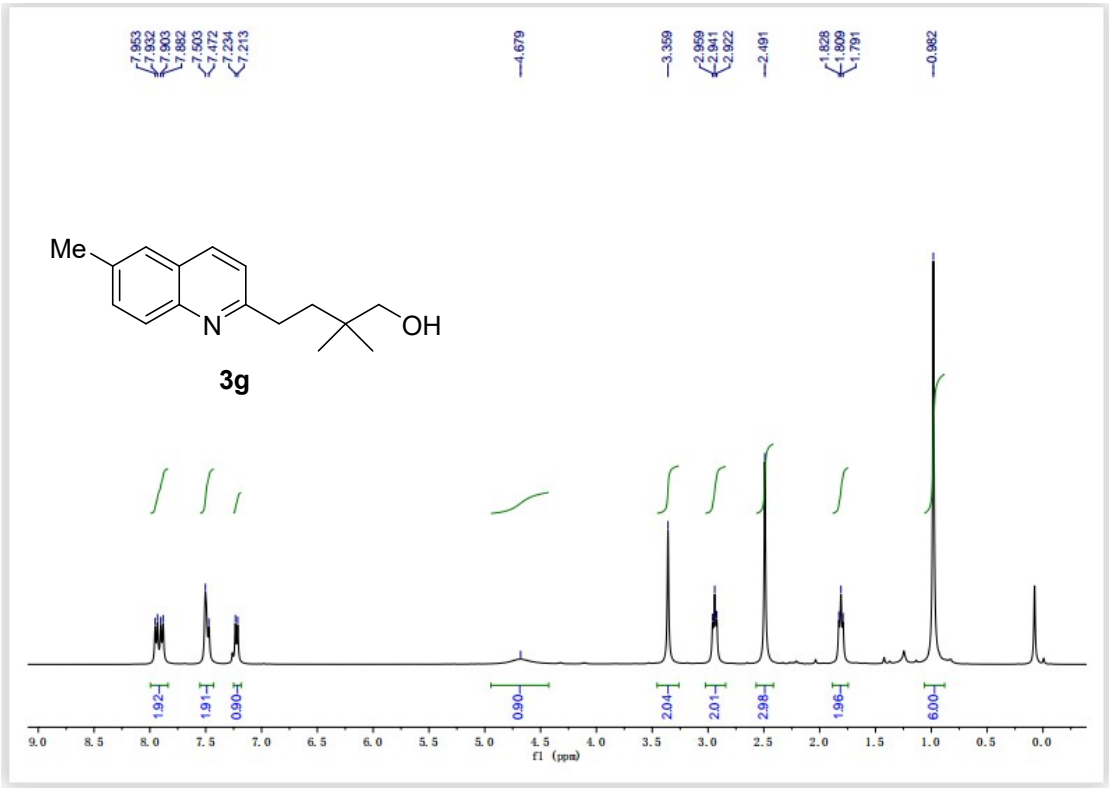
^{1}H NMR (400 MHz, $CDCl_3$) of **3f**



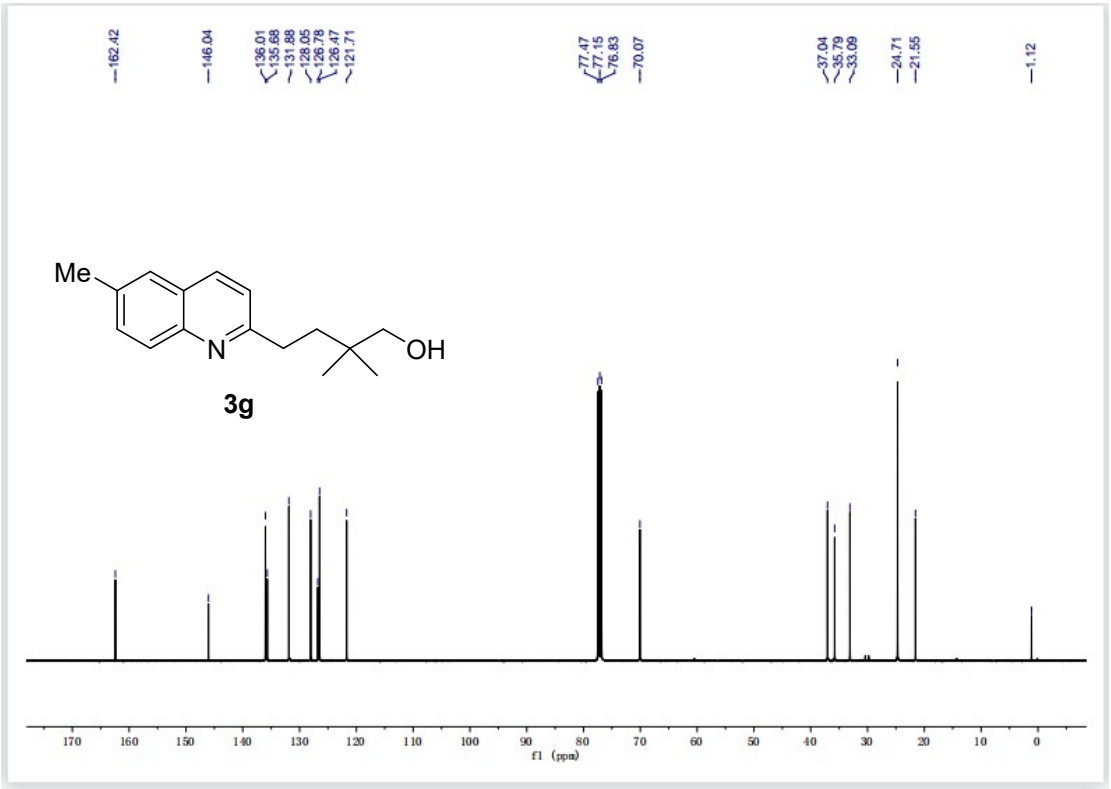
^{13}C NMR (100 MHz, $CDCl_3$) of **3f**



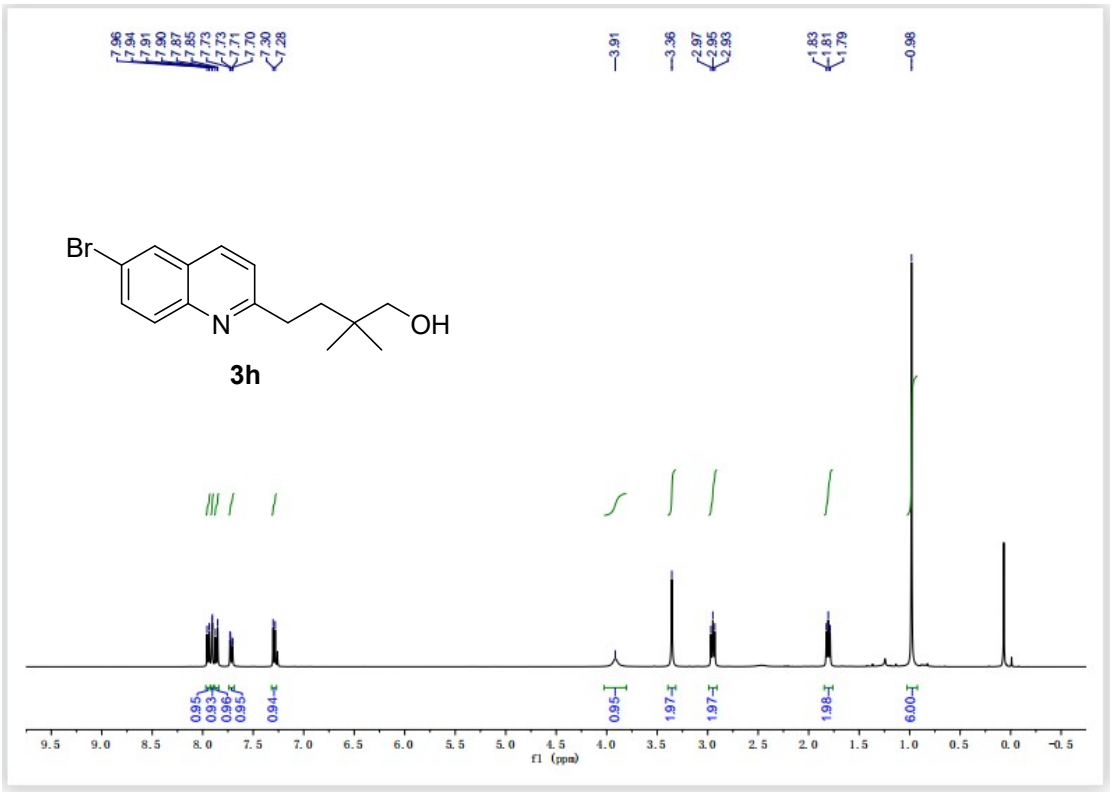
^{1}H NMR (400 MHz, $CDCl_3$) of **3g**



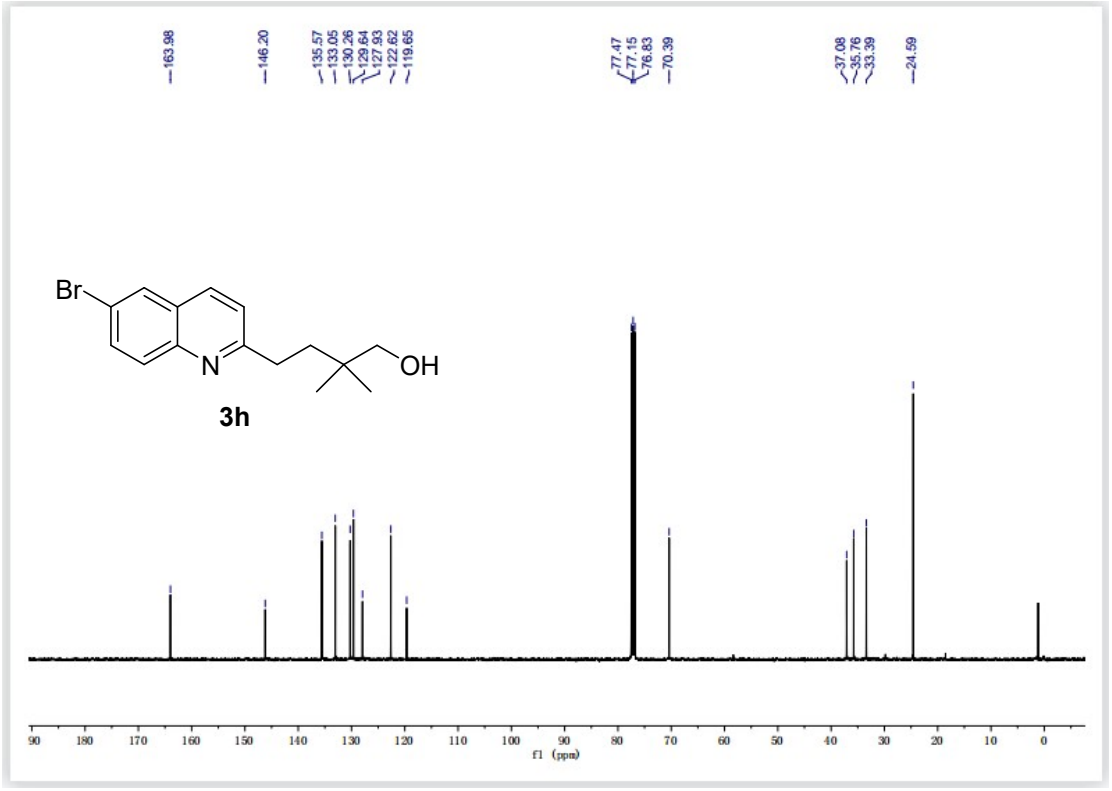
^{13}C NMR (100 MHz, $CDCl_3$) of **3g**



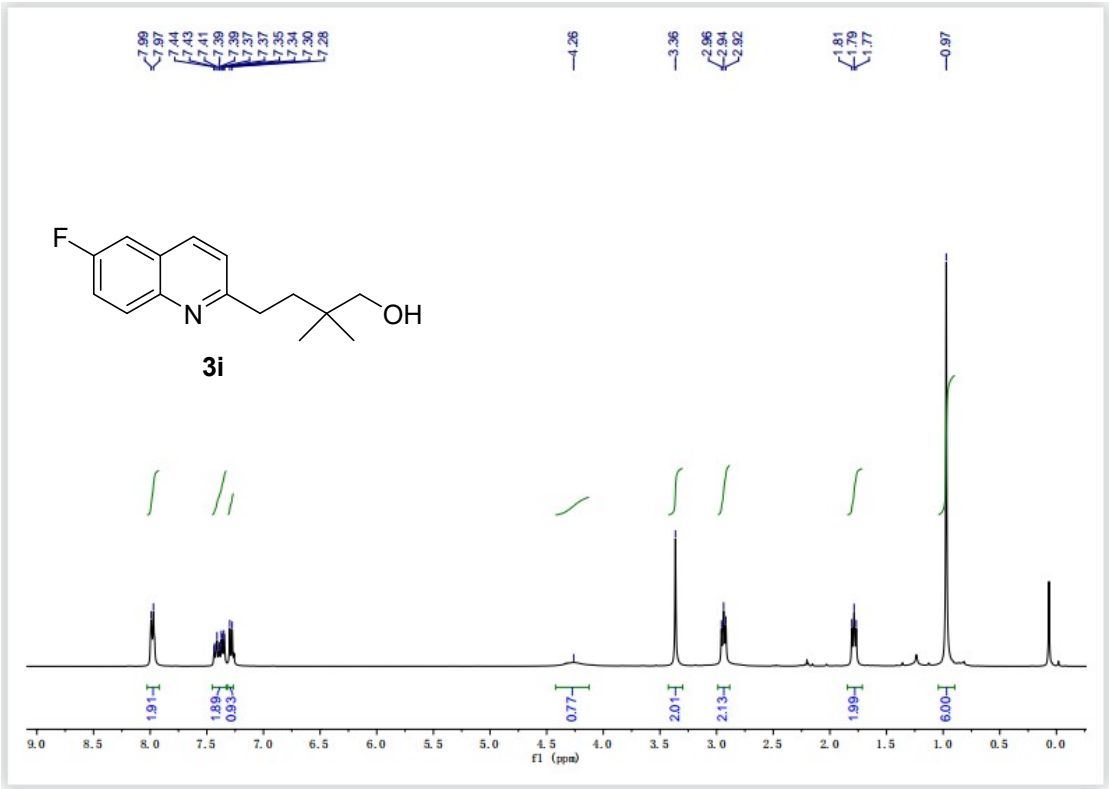
^{1}H NMR (400 MHz, $CDCl_3$) of **3h**



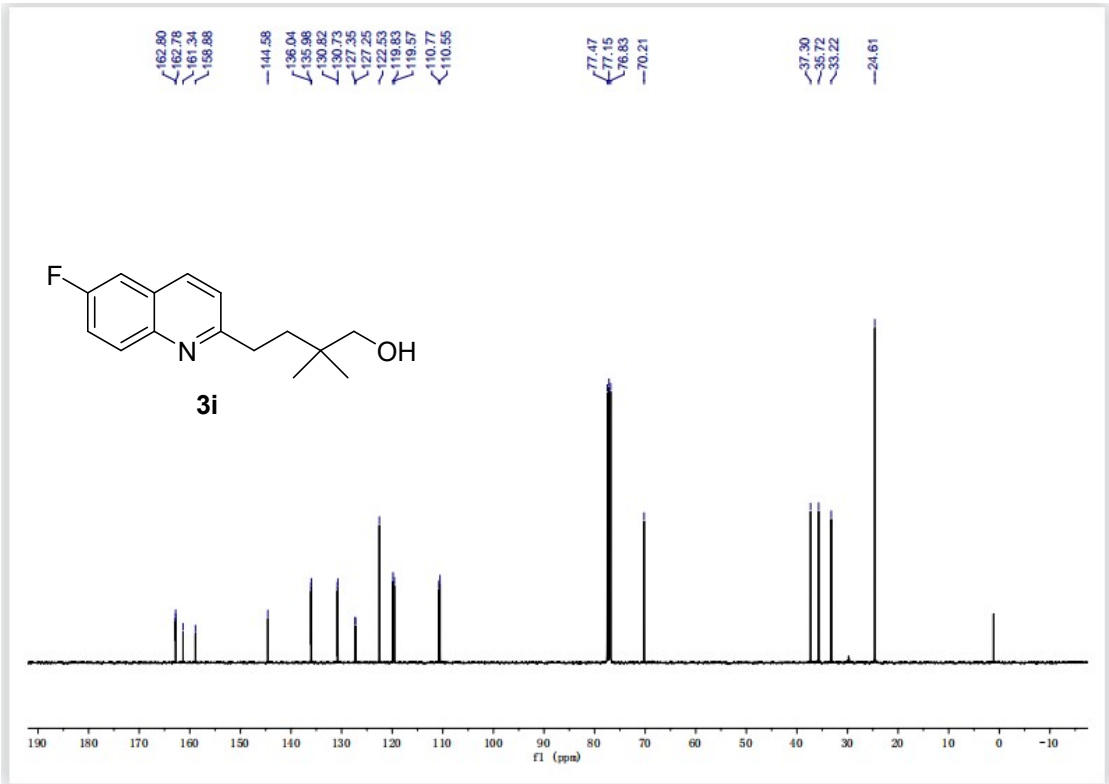
^{13}C NMR (100 MHz, $CDCl_3$) of **3h**



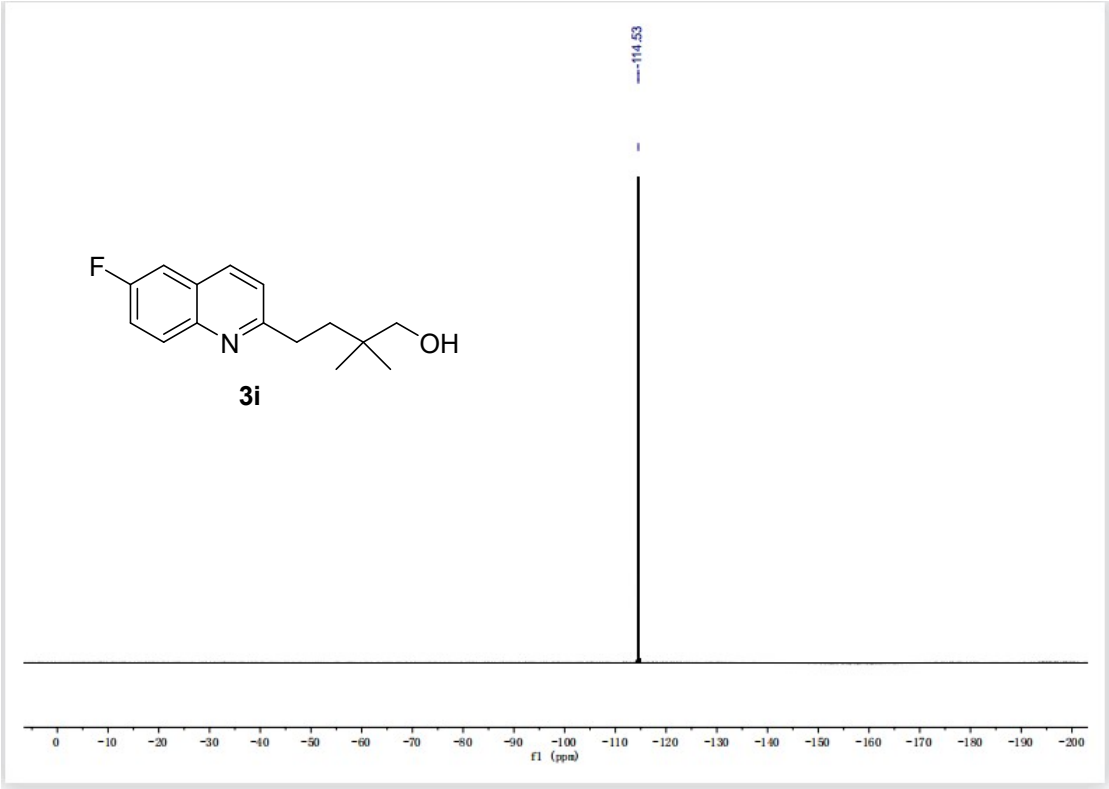
^{1}H NMR (400 MHz, $CDCl_3$) of **3i**



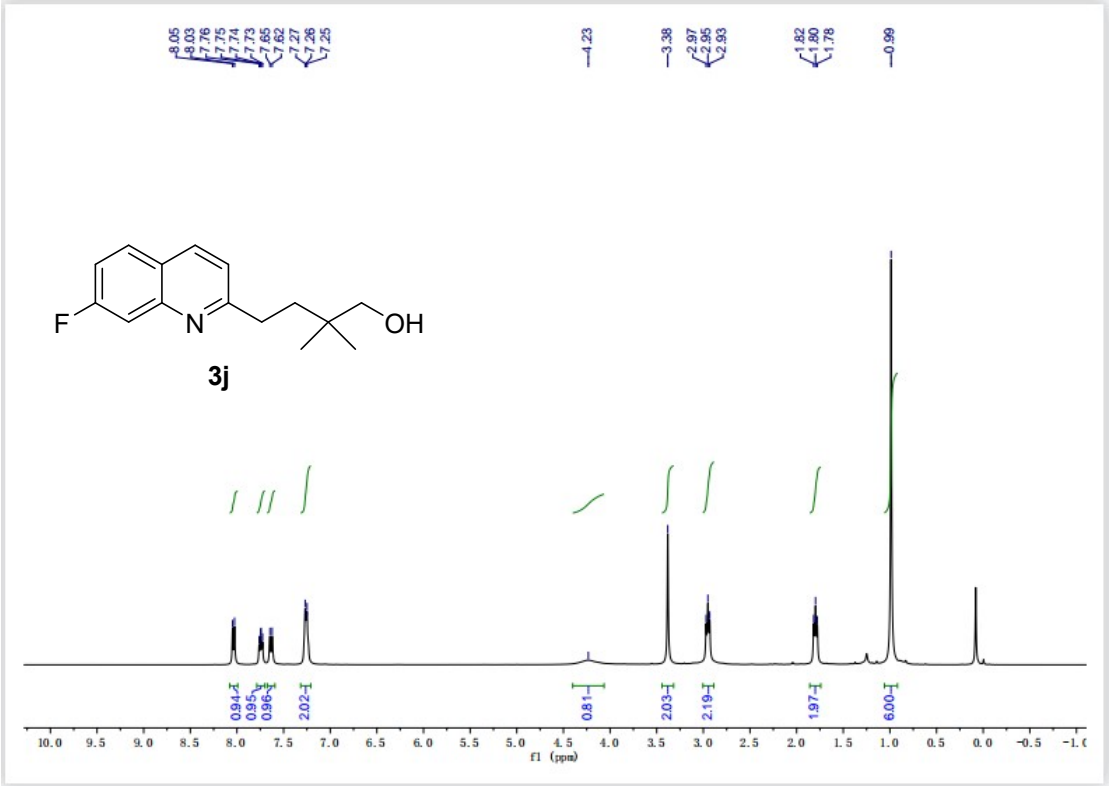
^{13}C NMR (100 MHz, $CDCl_3$) of **3i**



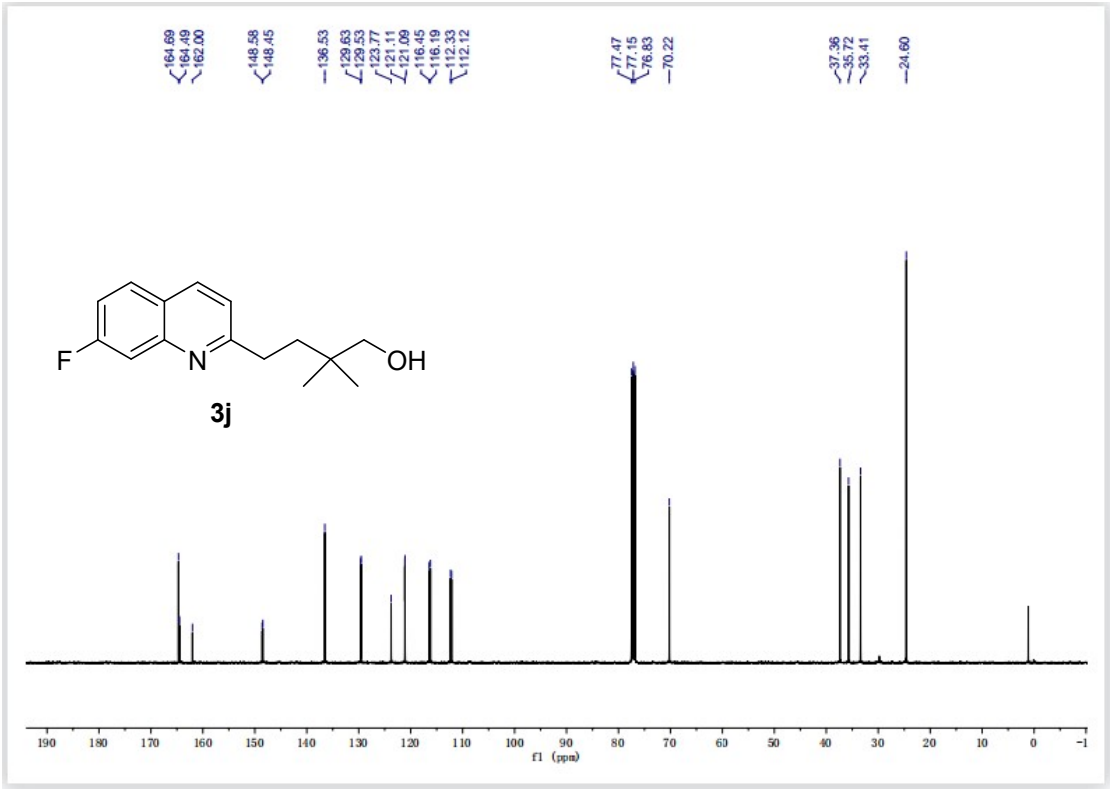
^{19}F NMR (377 MHz, $CDCl_3$, ppm) of **3i**



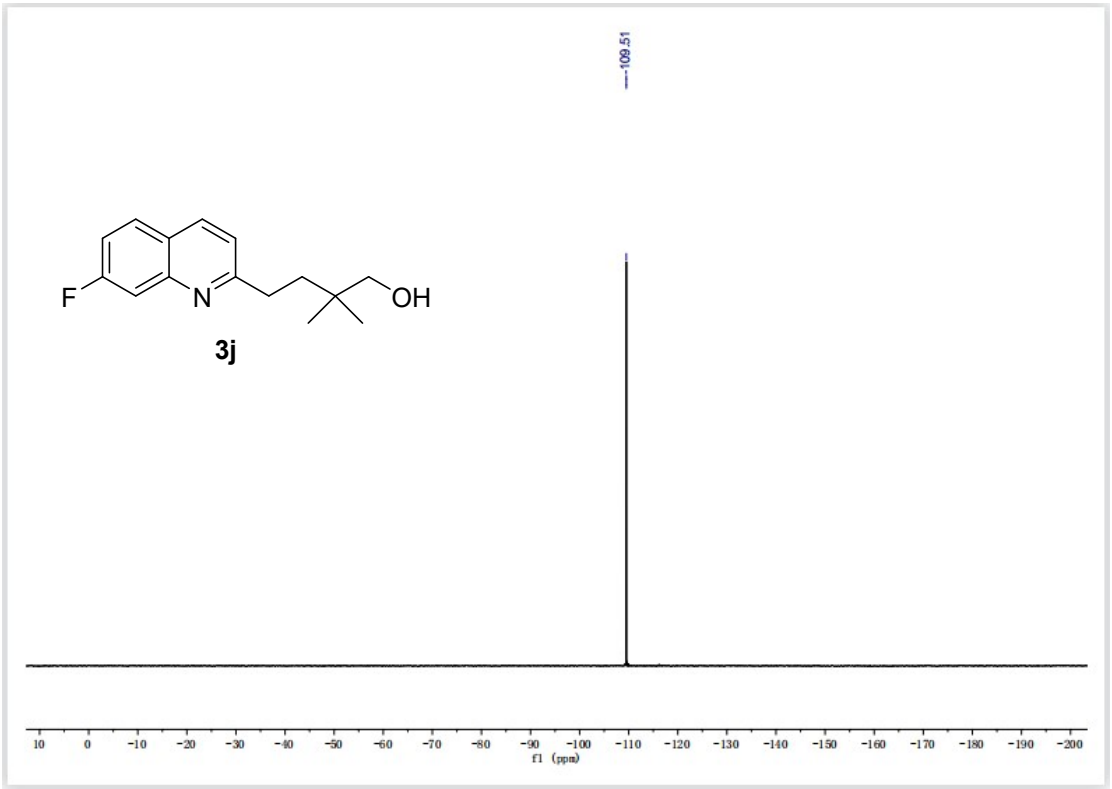
^{1}H NMR (400 MHz, $CDCl_3$) of **3j**



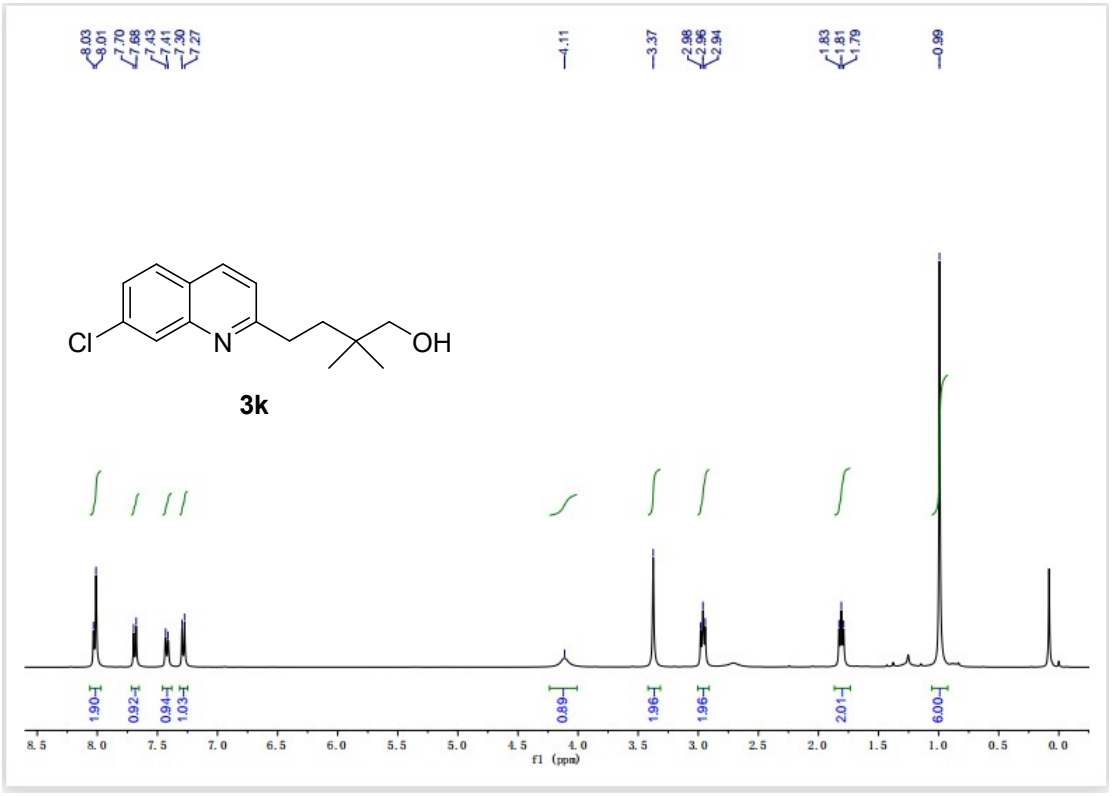
^{13}C NMR (100 MHz, $CDCl_3$) of **3j**



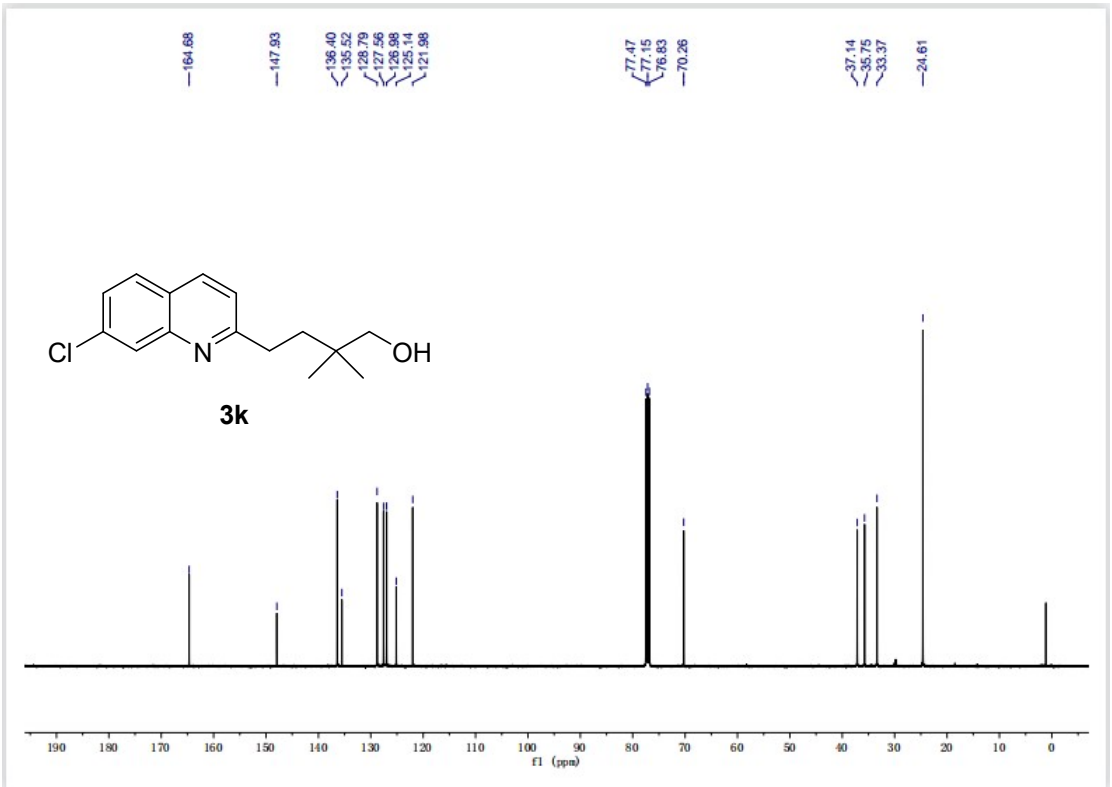
^{19}F NMR (377 MHz, $CDCl_3$, ppm) of **3j**



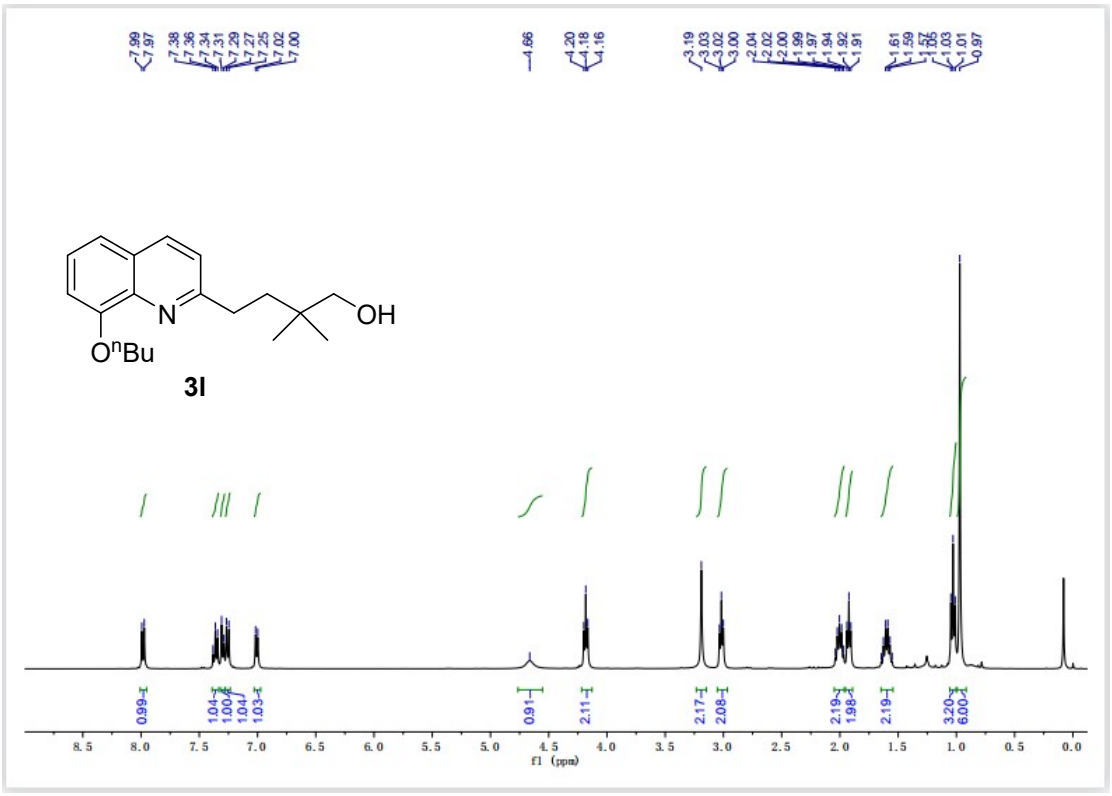
^{1}H NMR (400 MHz, $CDCl_3$) of **3k**



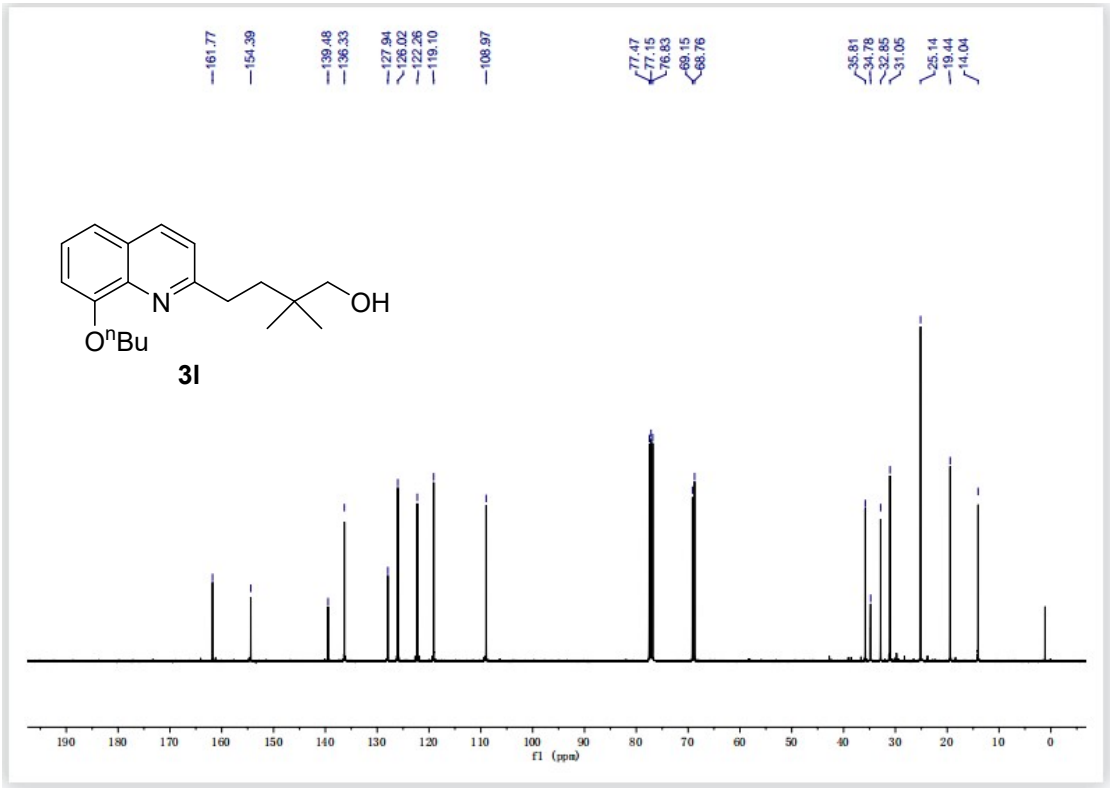
^{13}C NMR (100 MHz, $CDCl_3$) of **3k**



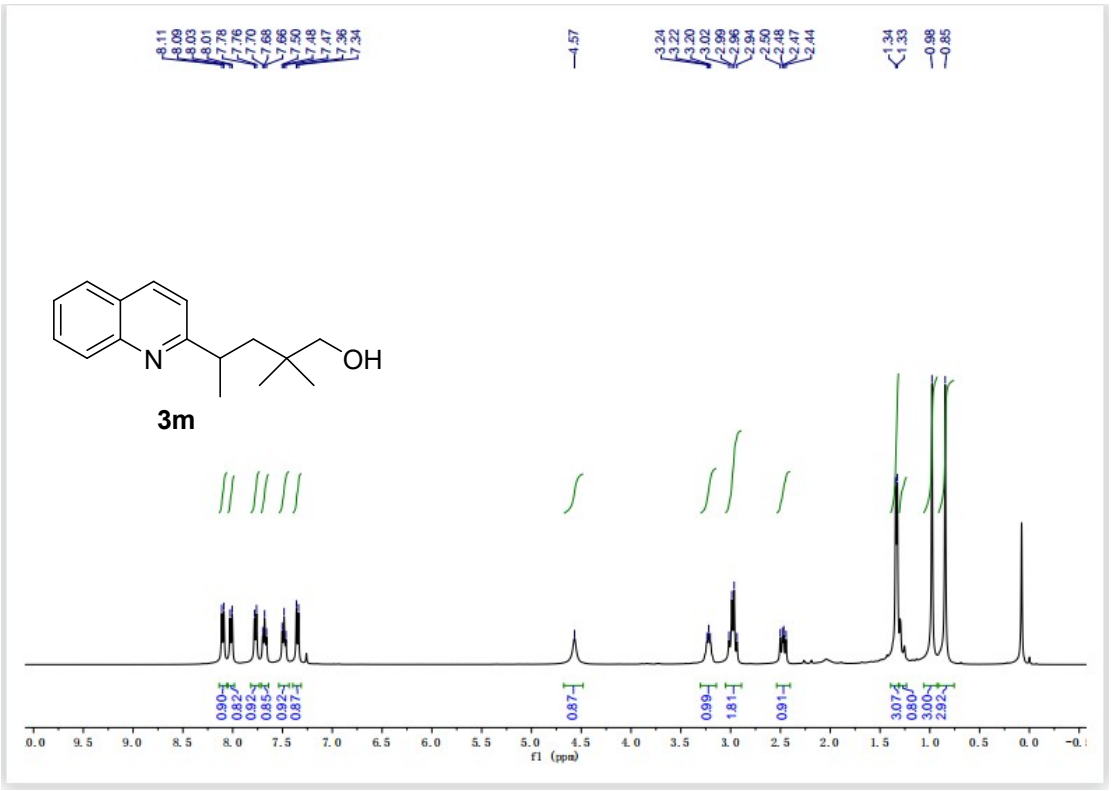
^{1}H NMR (400 MHz, $CDCl_3$) of **3l**



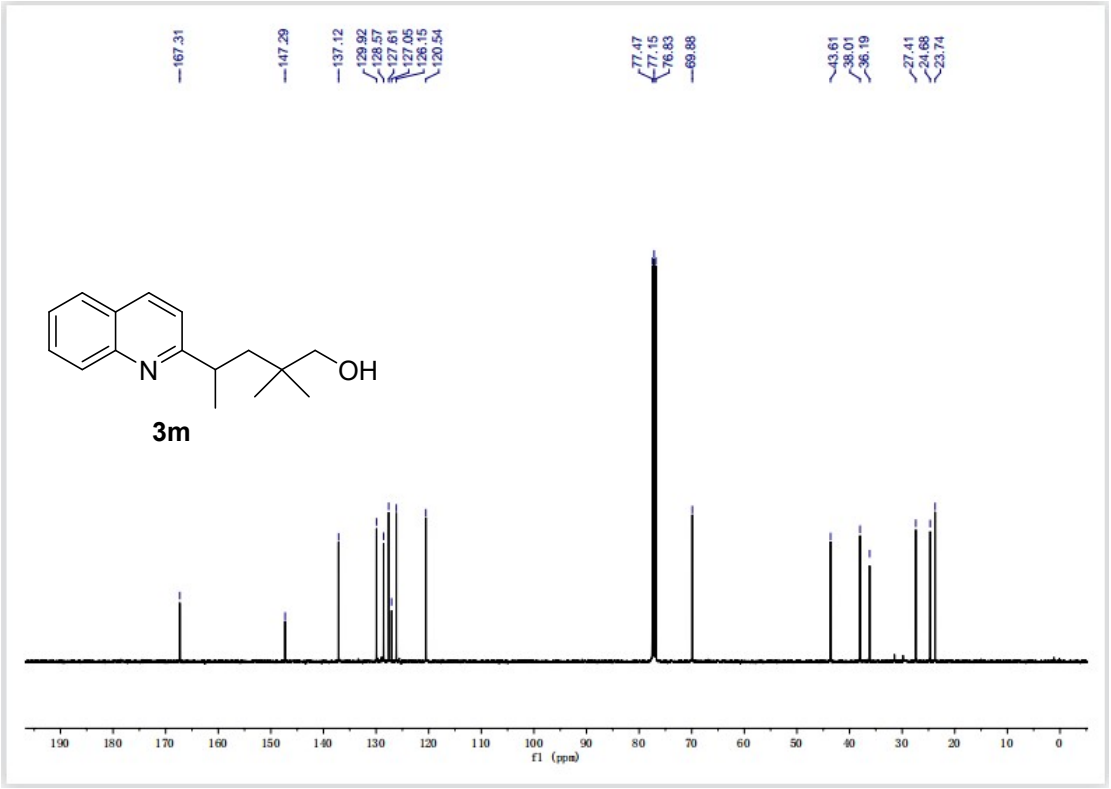
^{13}C NMR (100 MHz, $CDCl_3$) of **3l**



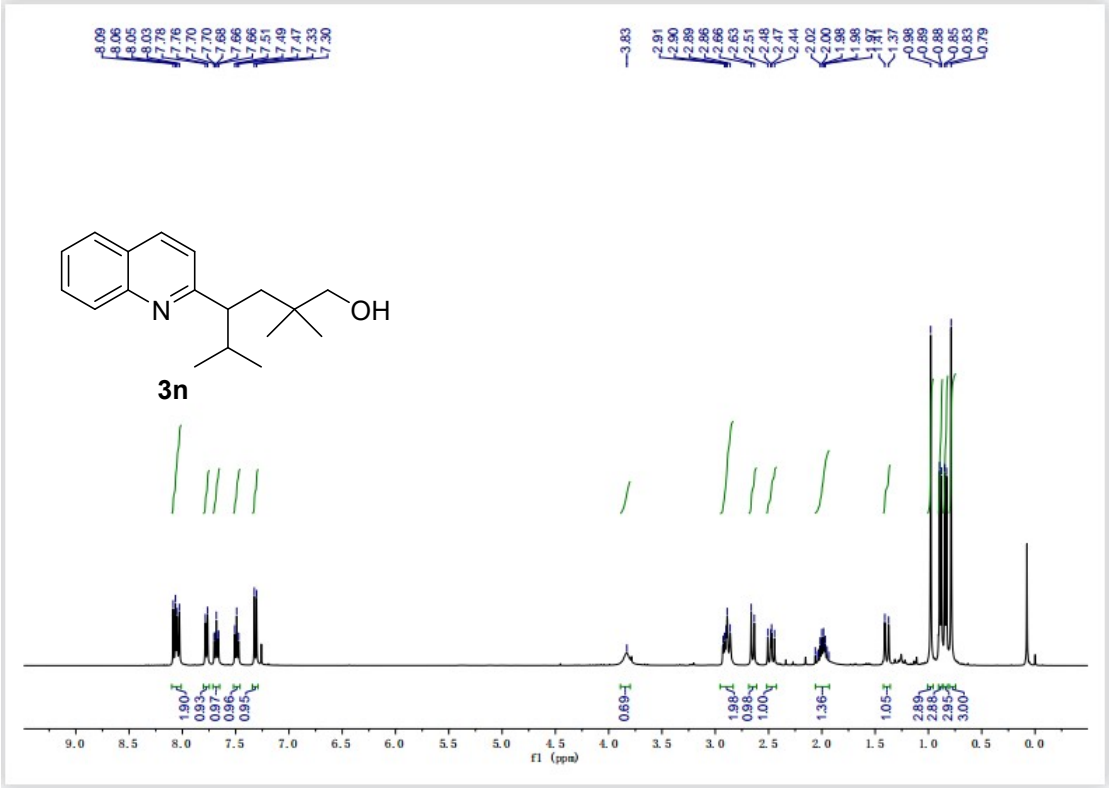
^{1}H NMR (400 MHz, $CDCl_3$) of **3m**



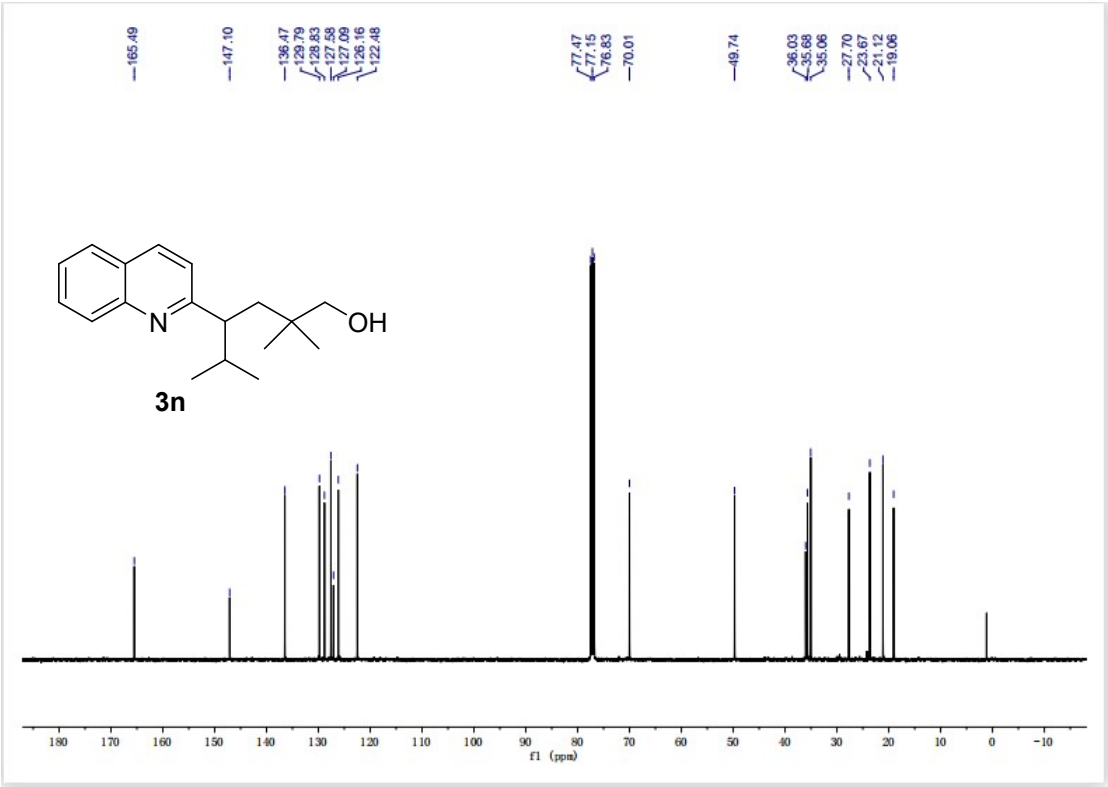
^{13}C NMR (100 MHz, $CDCl_3$) of **3m**



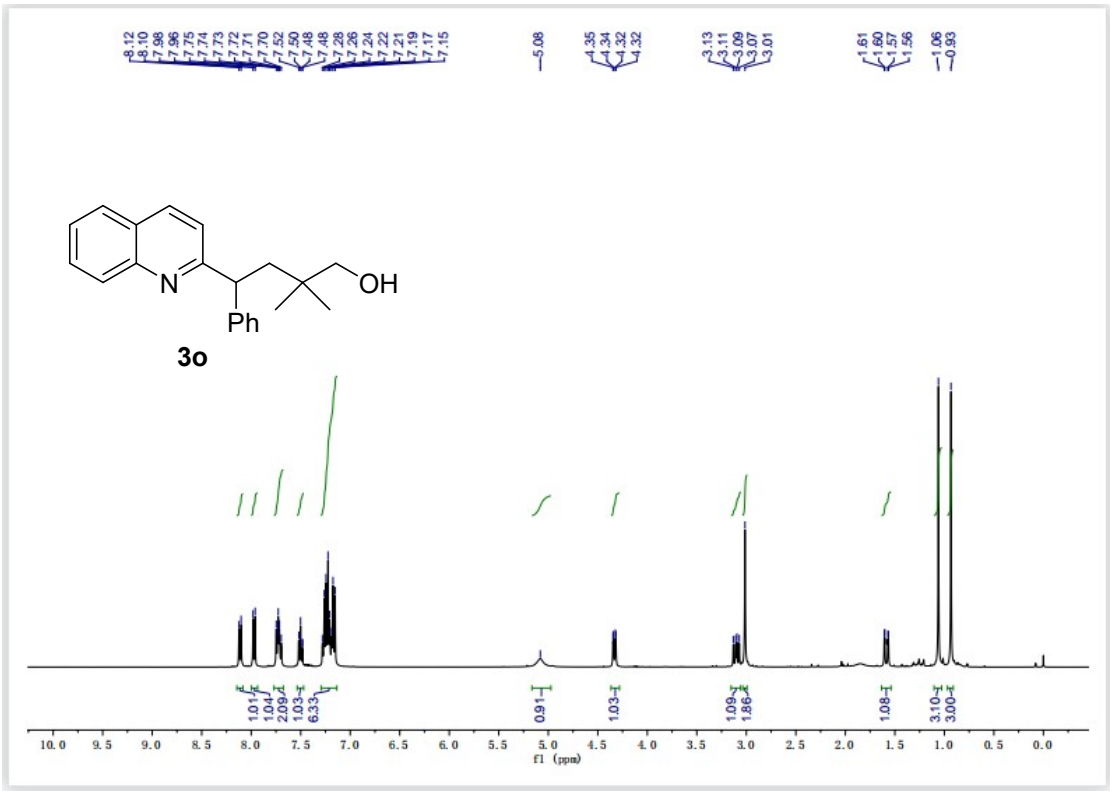
^{1}H NMR (400 MHz, $CDCl_3$) of **3n**



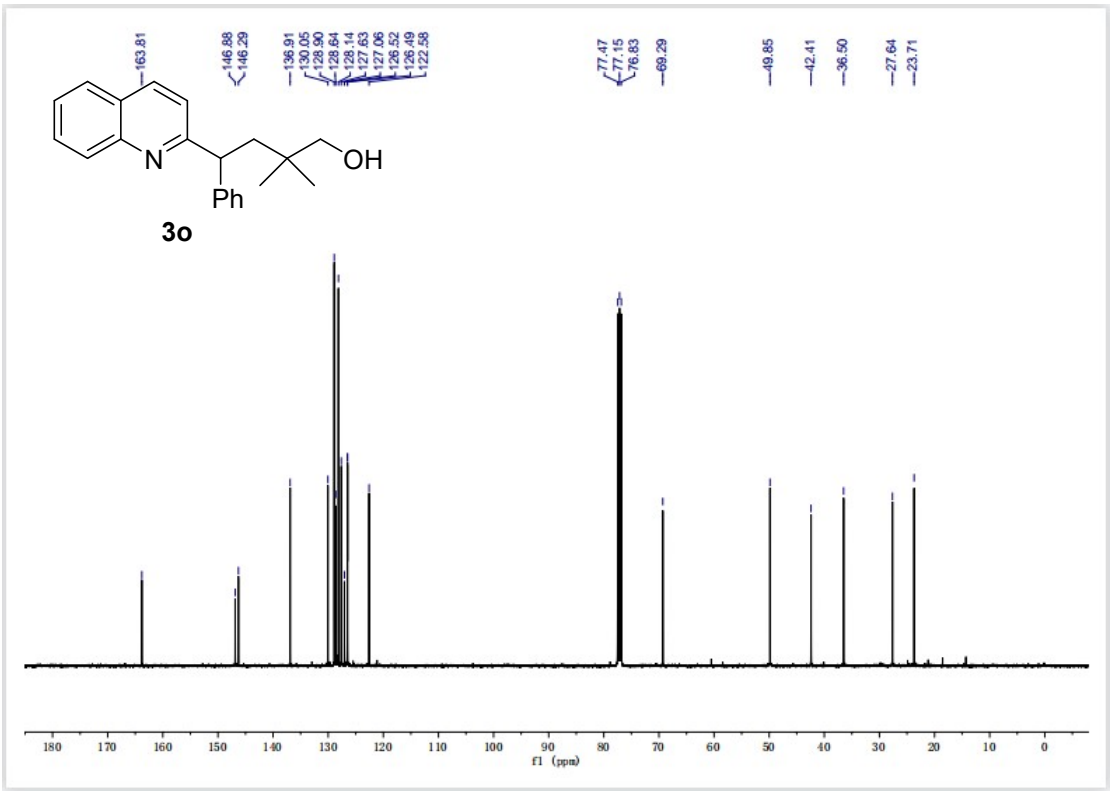
^{13}C NMR (100 MHz, $CDCl_3$) of **3n**



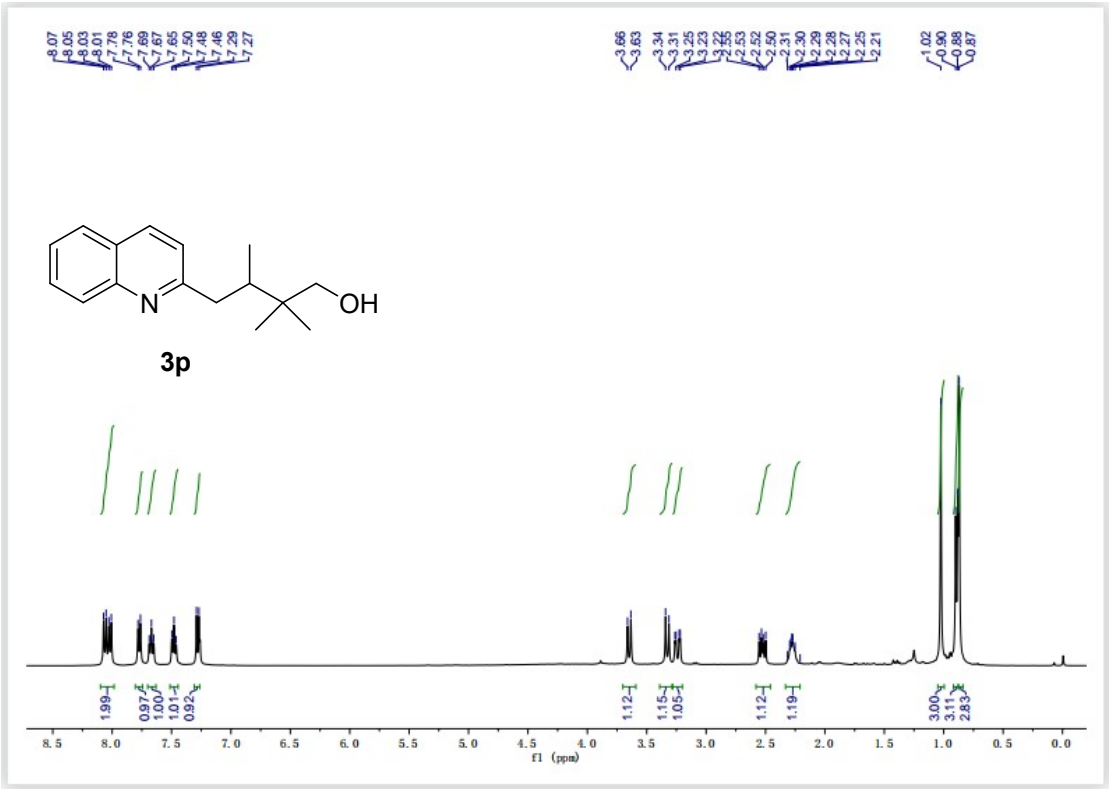
^{1}H NMR (400 MHz, $CDCl_3$) of **3o**



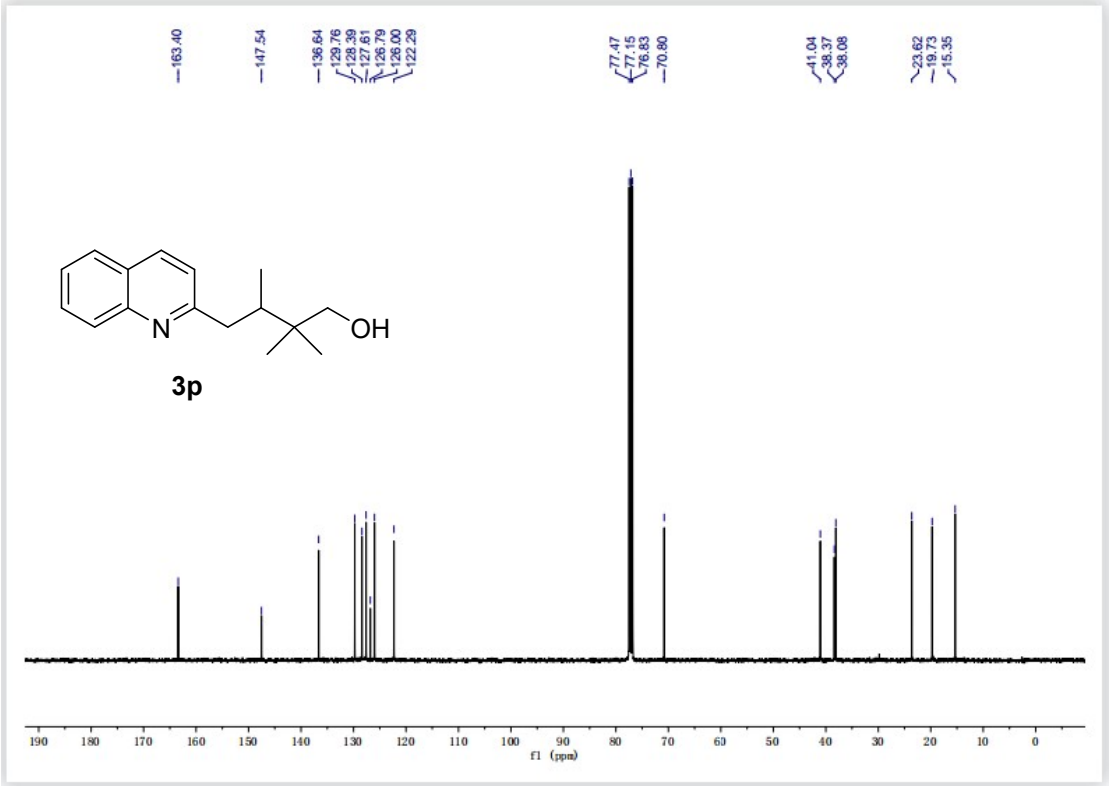
^{13}C NMR (100 MHz, $CDCl_3$) of **3o**



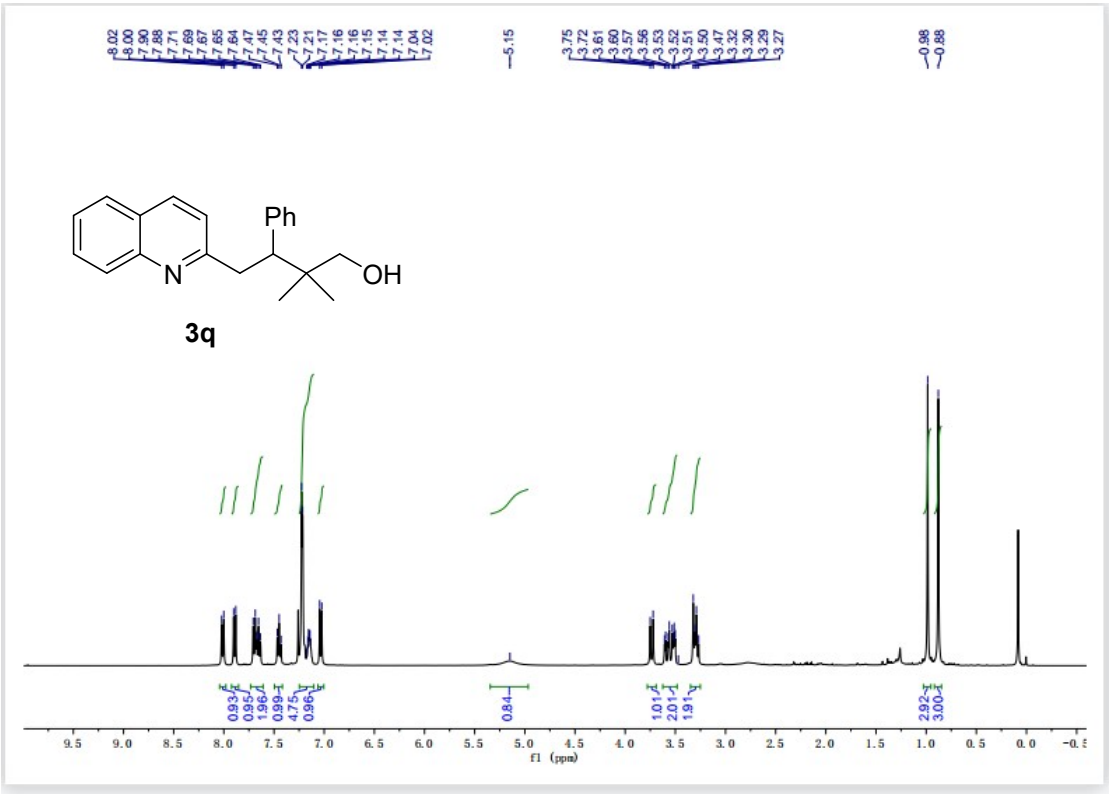
^{1}H NMR (400 MHz, $CDCl_3$) of **3p**



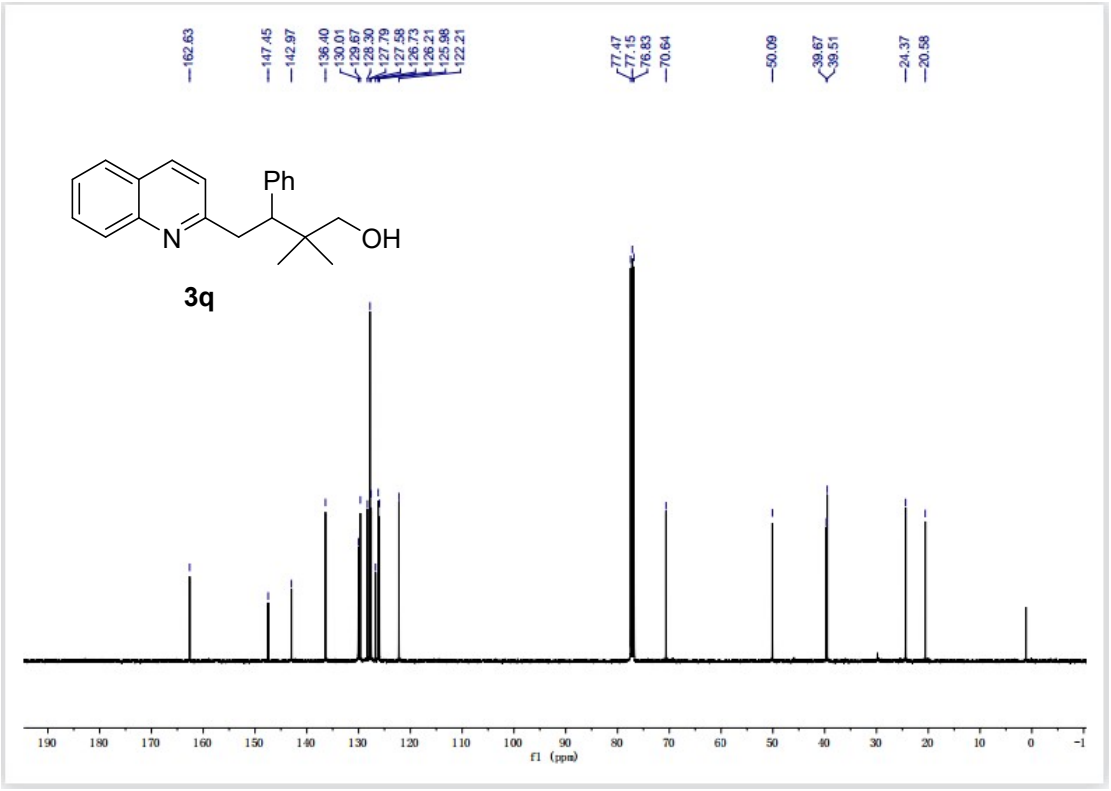
^{13}C NMR (100 MHz, $CDCl_3$) of **3p**



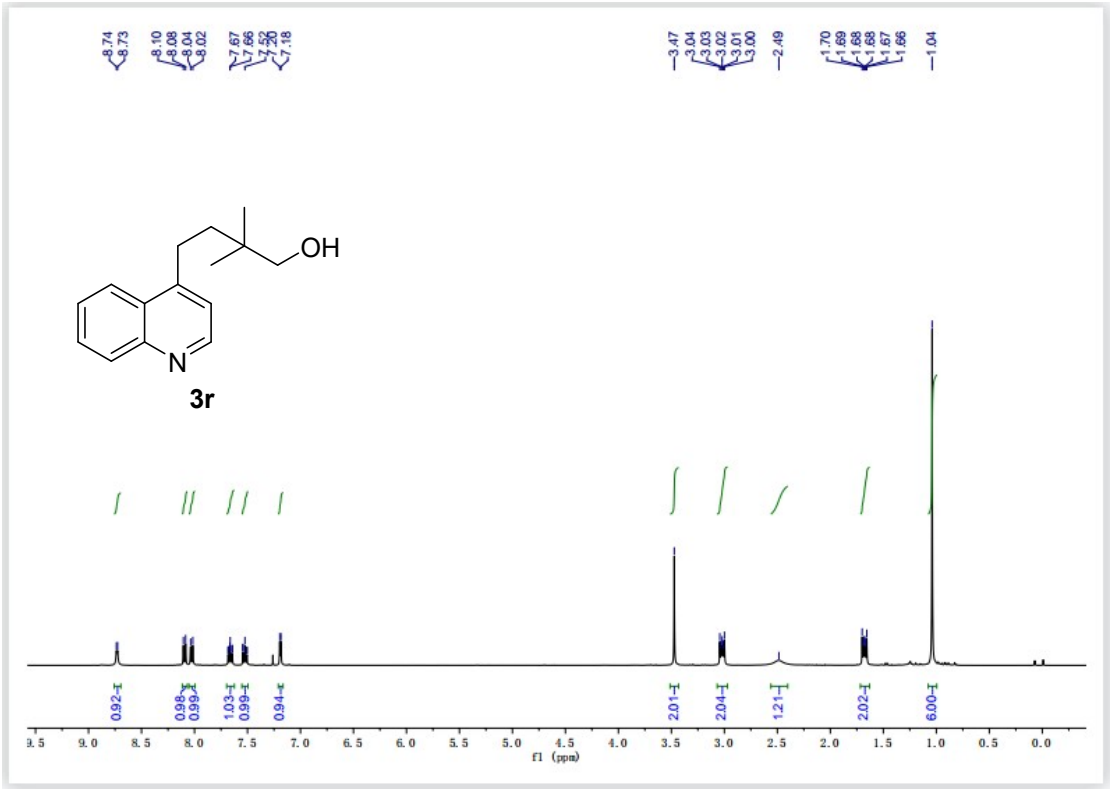
^{1}H NMR (400 MHz, $CDCl_3$) of **3q**



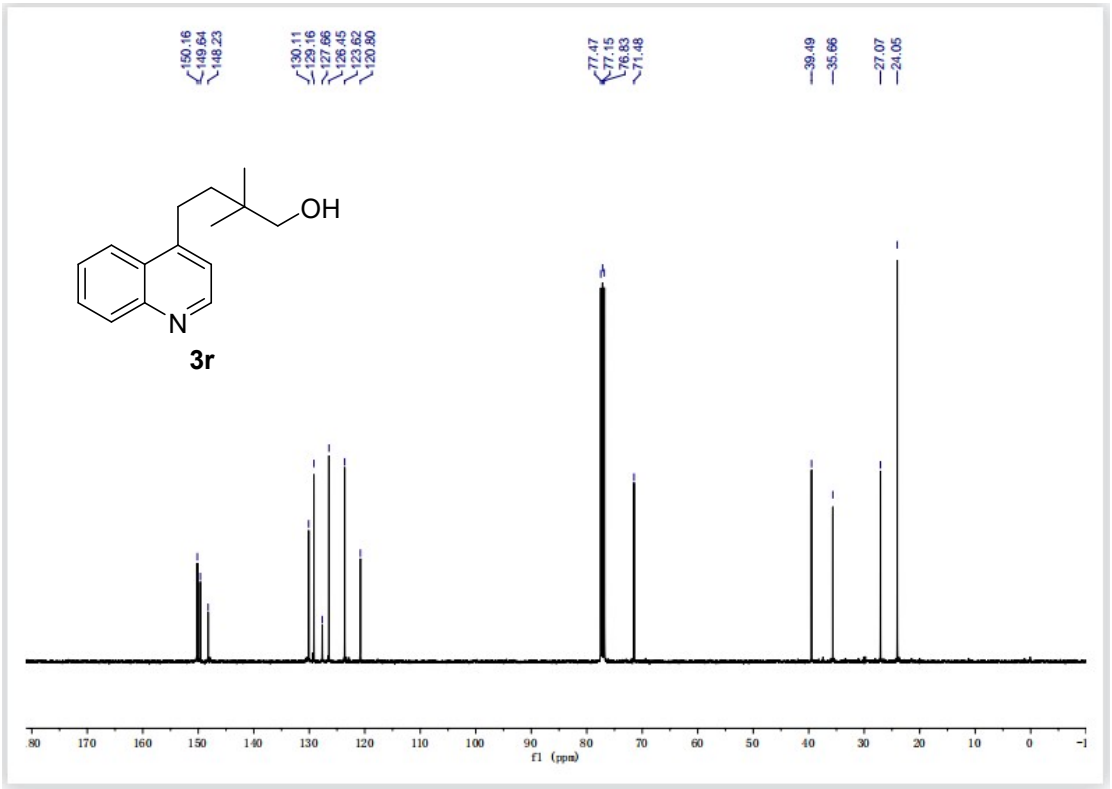
^{13}C NMR (100 MHz, $CDCl_3$) of **3q**



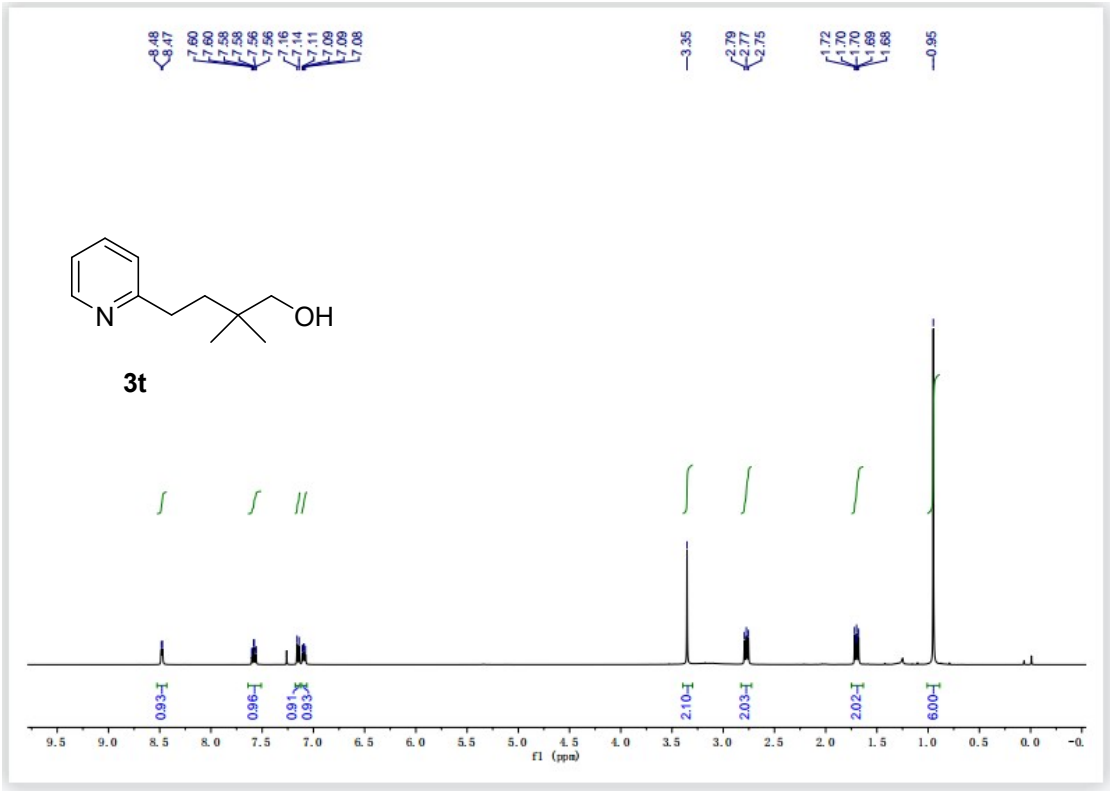
^{1}H NMR (400 MHz, $CDCl_3$) of **3r**



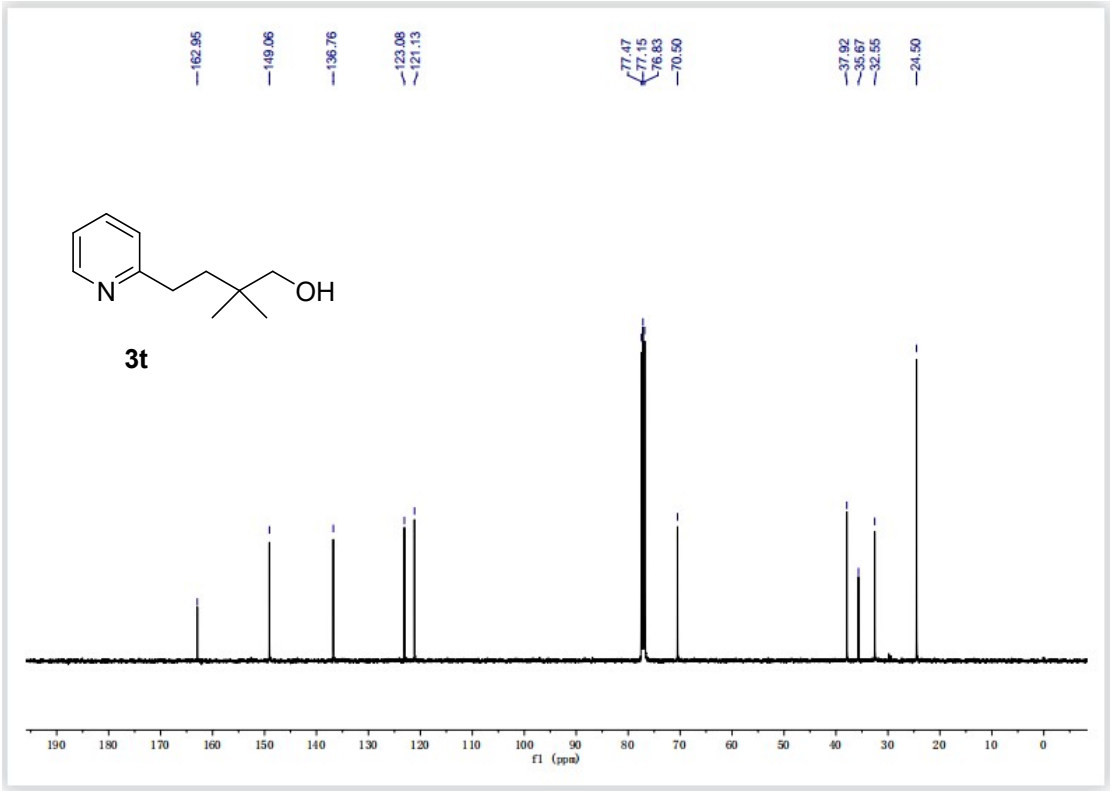
^{13}C NMR (100 MHz, $CDCl_3$) of **3r**



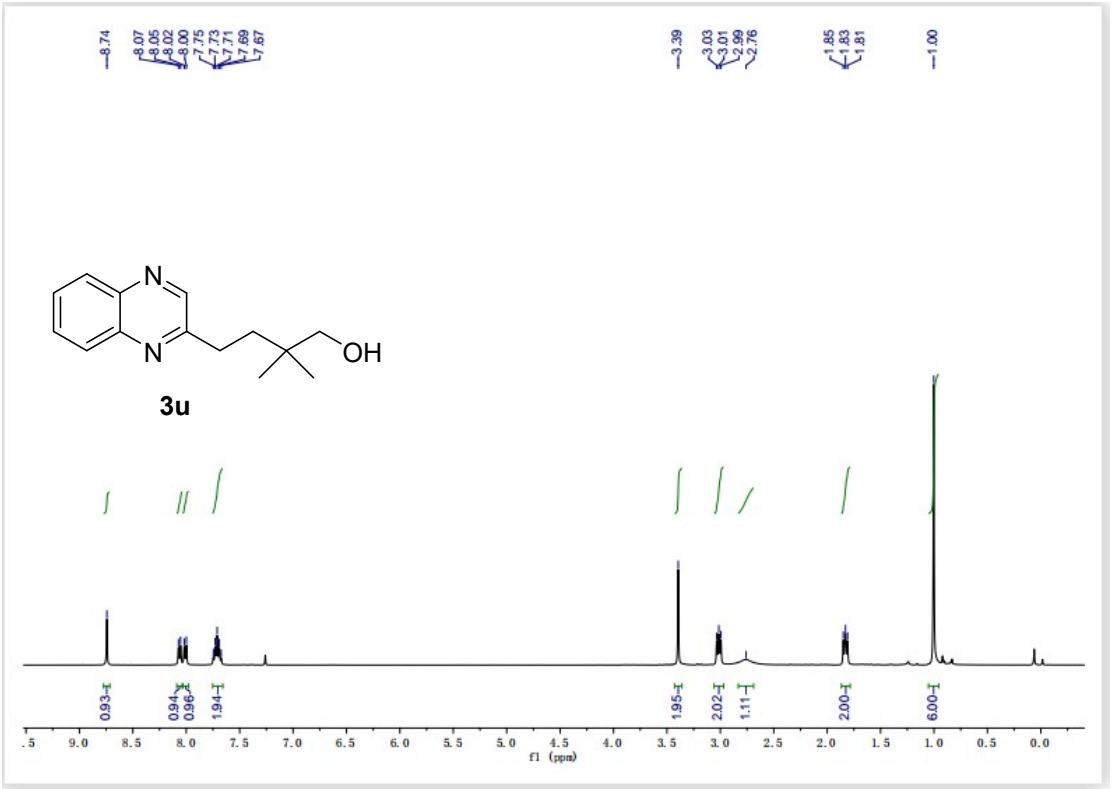
^{1}H NMR (400 MHz, $CDCl_3$) of **3t**



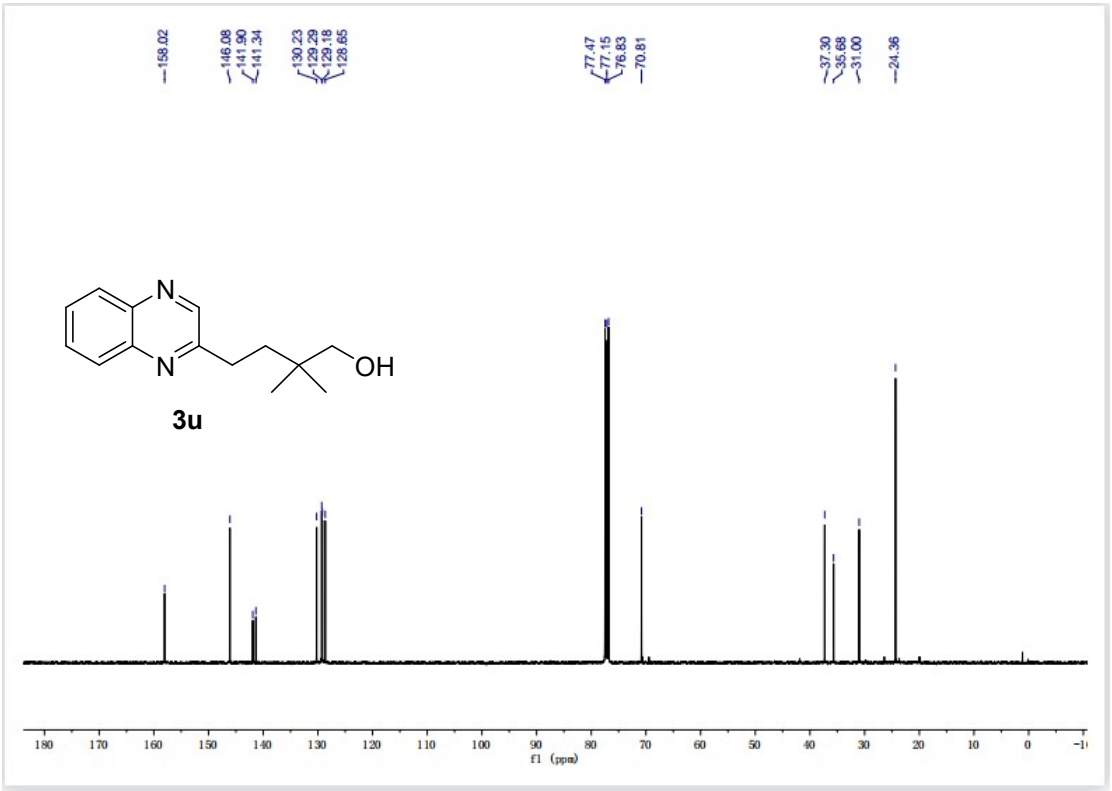
^{13}C NMR (100 MHz, $CDCl_3$) of **3t**



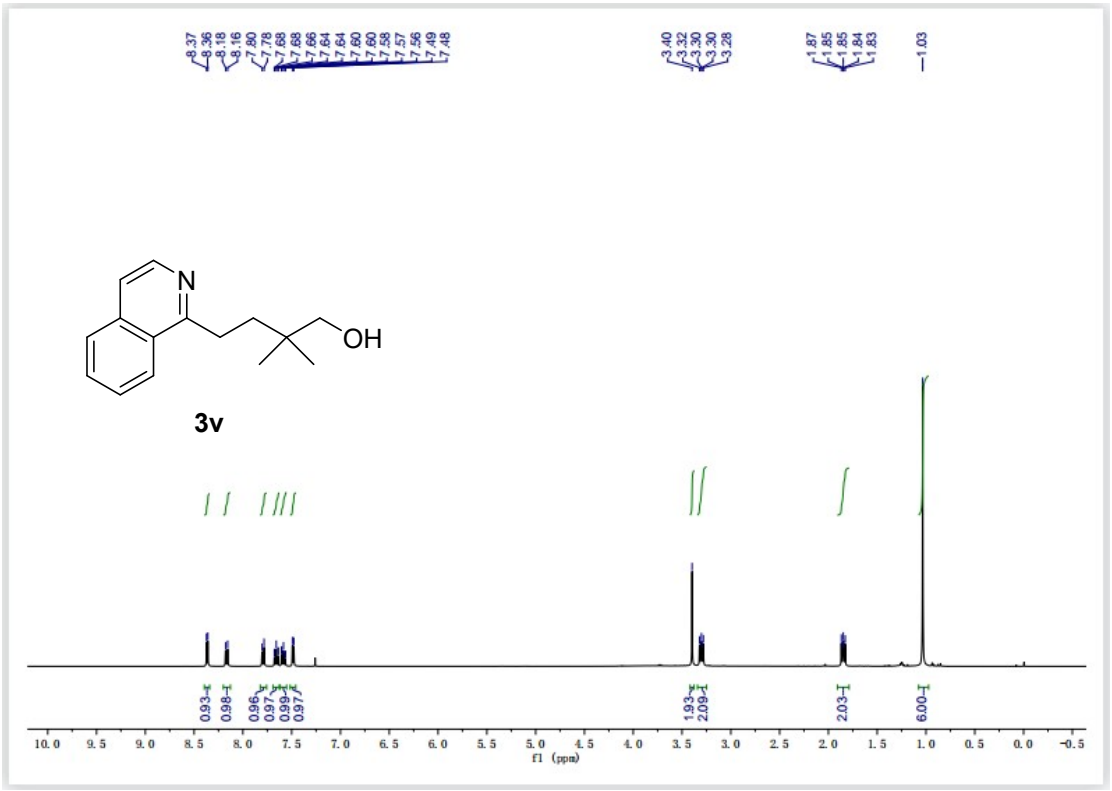
^{1}H NMR (400 MHz, $CDCl_3$) of **3u**



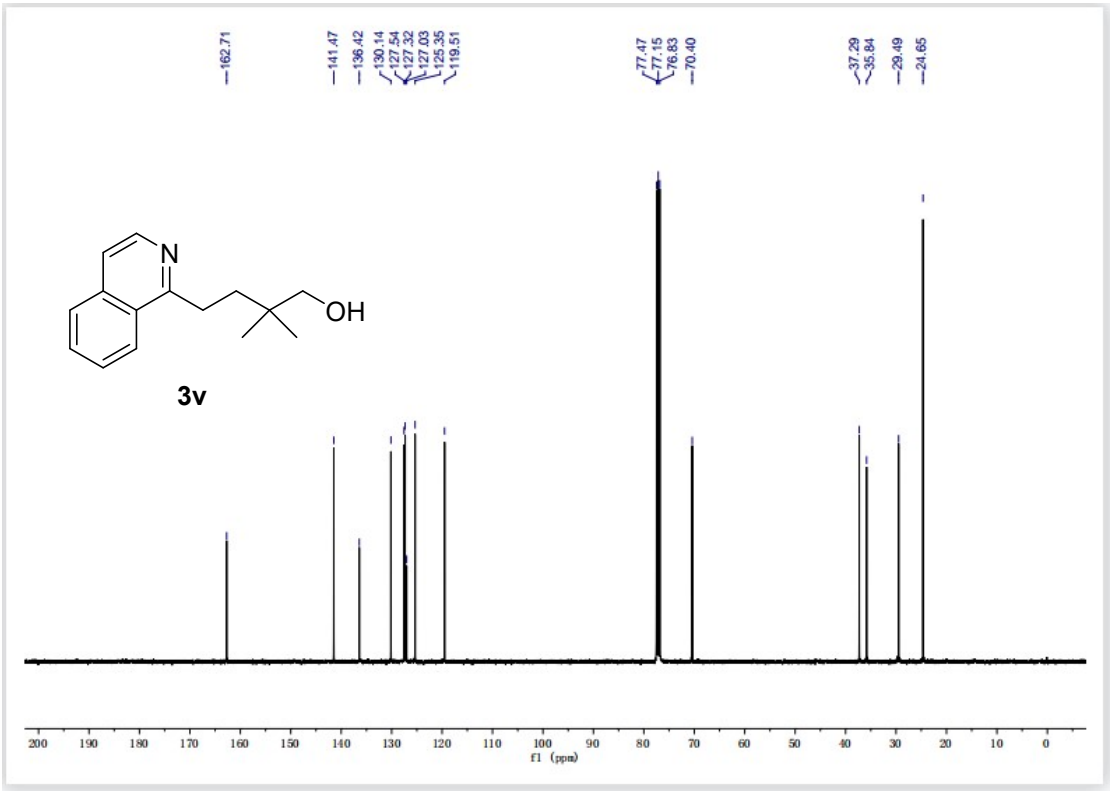
^{13}C NMR (100 MHz, $CDCl_3$) of **3u**



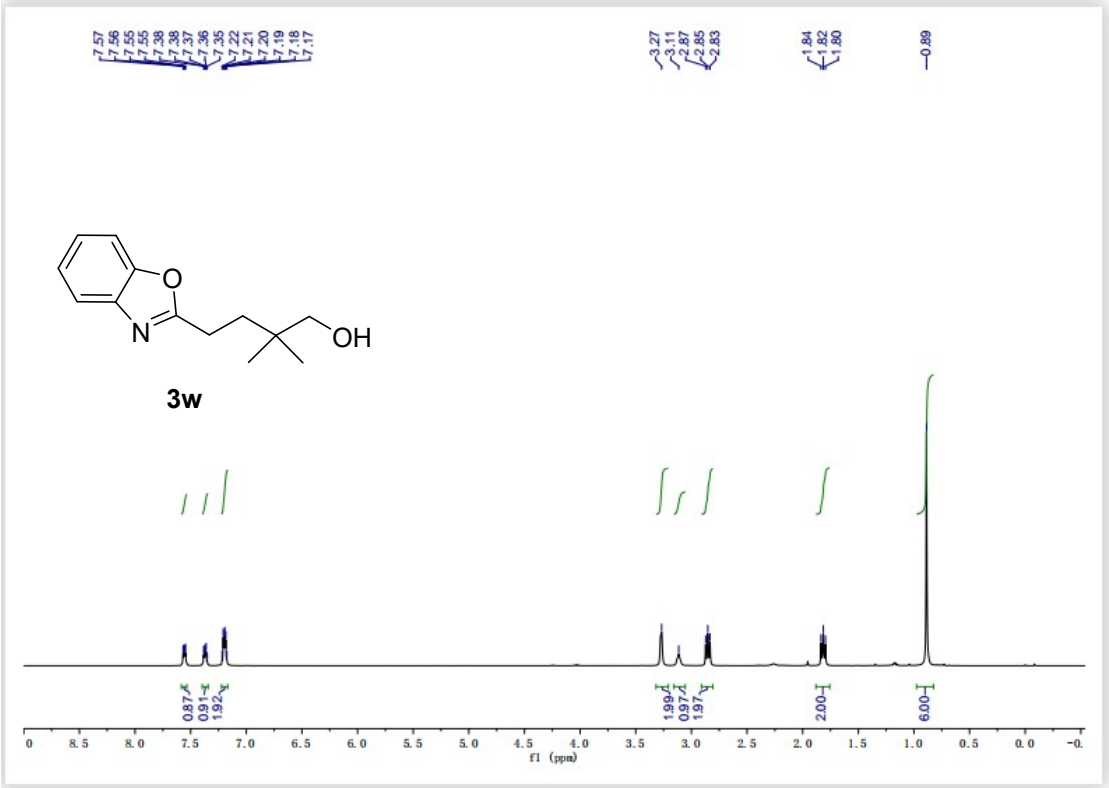
^{1}H NMR (400 MHz, $CDCl_3$) of **3v**



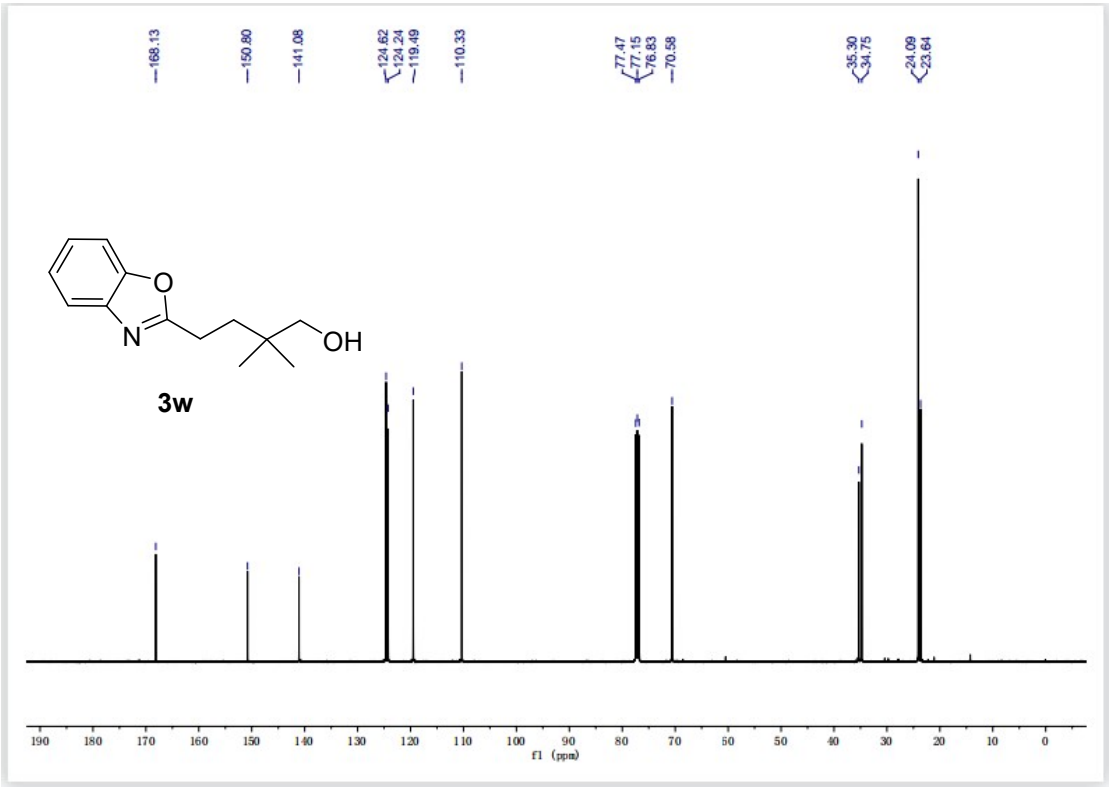
^{13}C NMR (100 MHz, $CDCl_3$) of **3v**



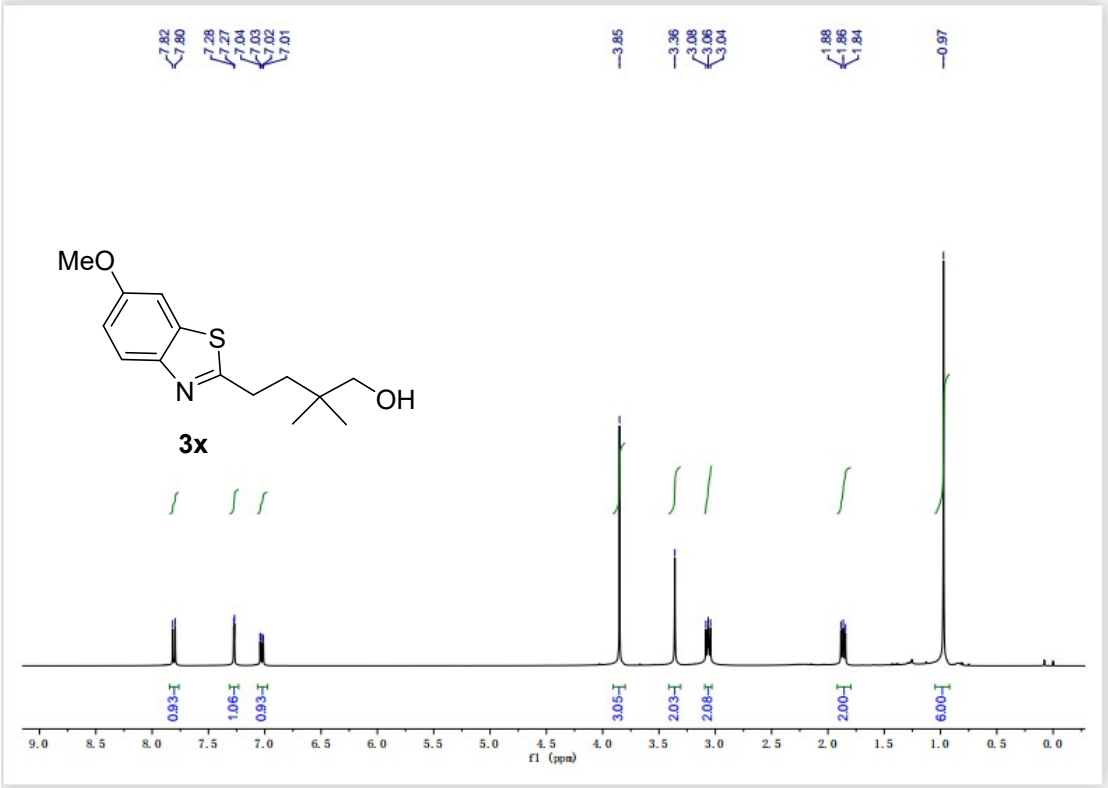
^{1}H NMR (400 MHz, $CDCl_3$) of **3w**



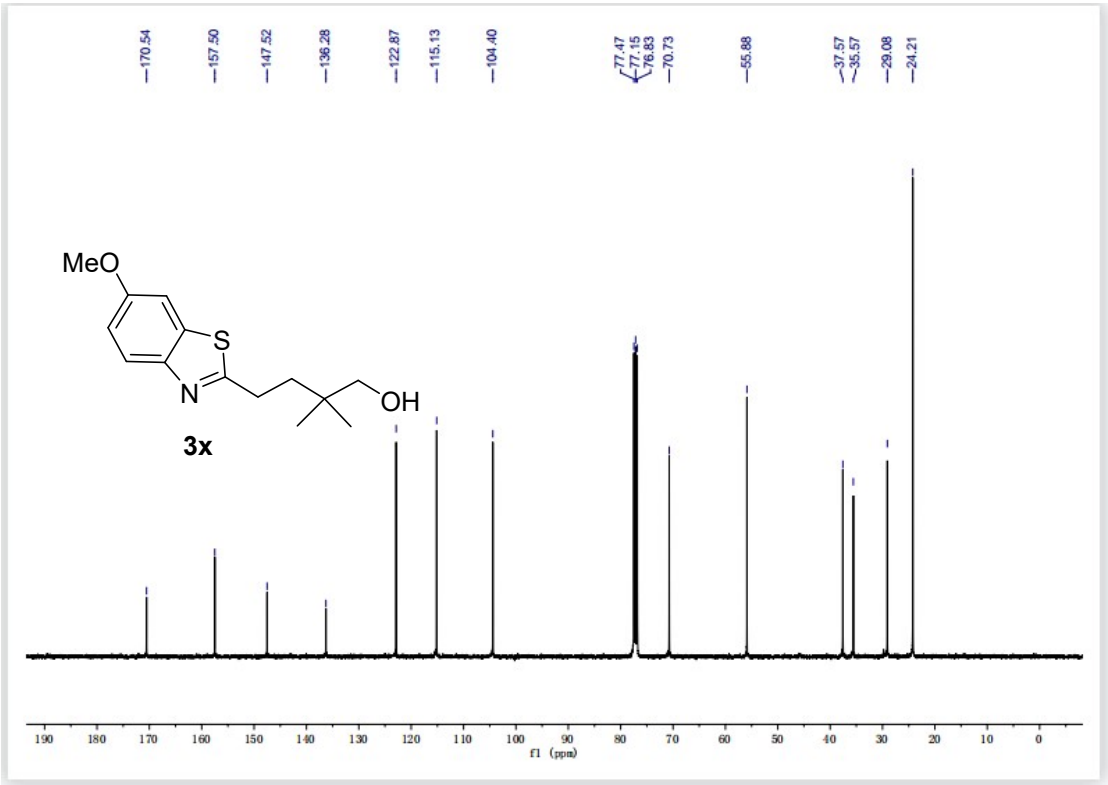
^{13}C NMR (100 MHz, $CDCl_3$) of **3w**



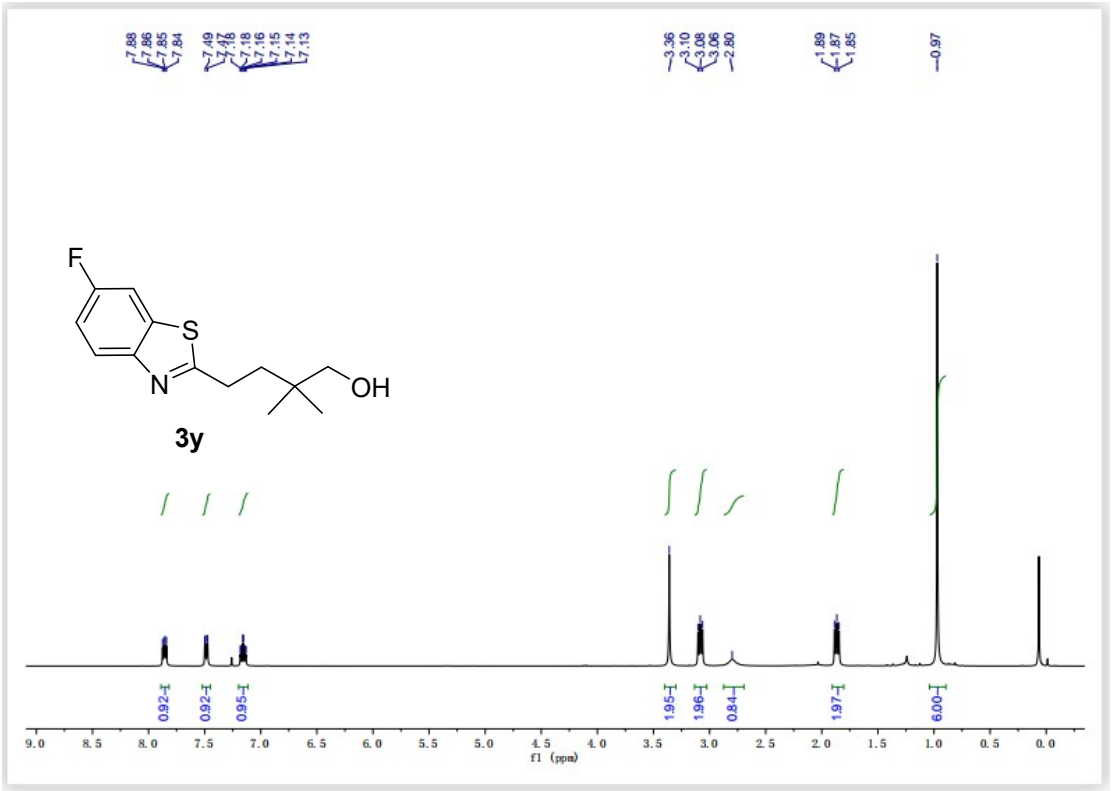
^{1}H NMR (400 MHz, $CDCl_3$) of **3x**



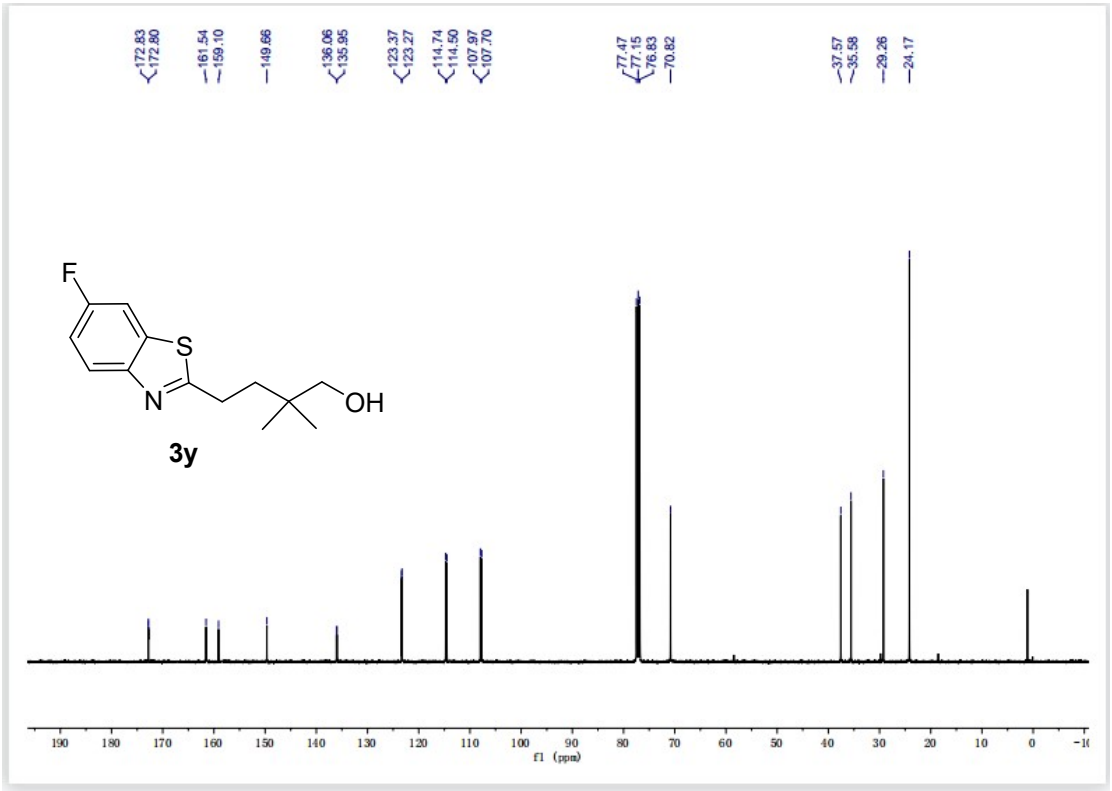
^{13}C NMR (100 MHz, $CDCl_3$) of **3x**



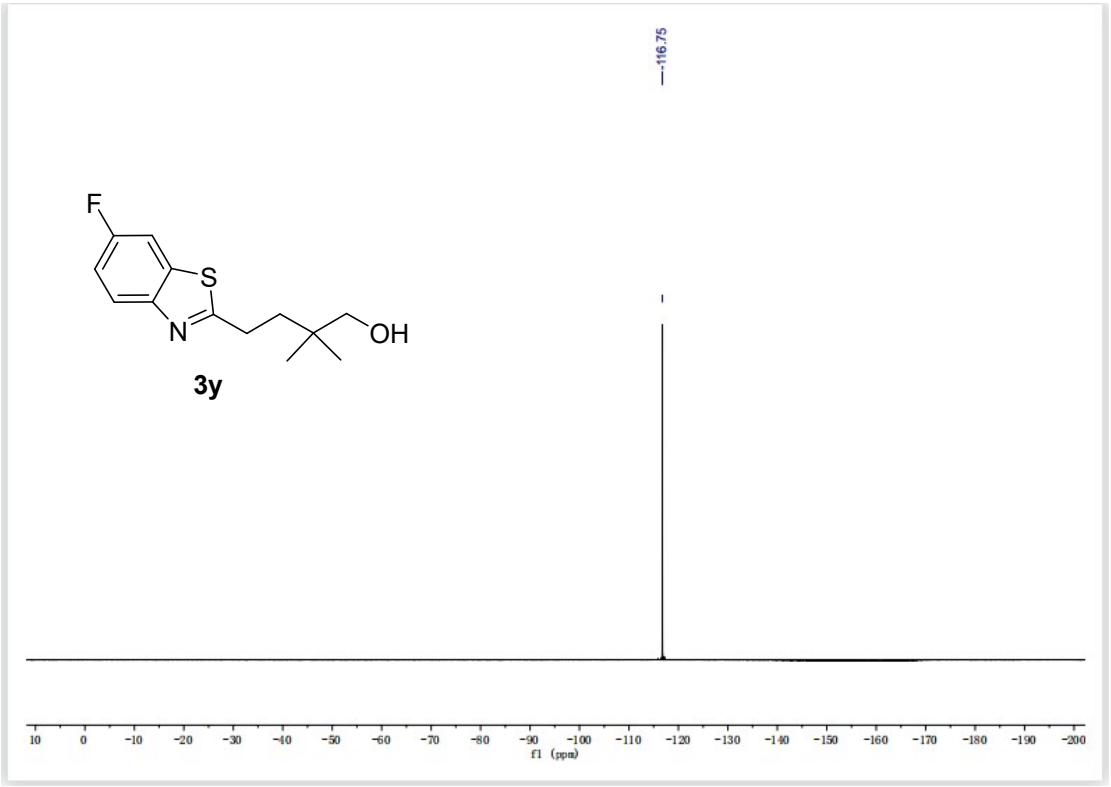
^{1}H NMR (400 MHz, $CDCl_3$) of **3y**



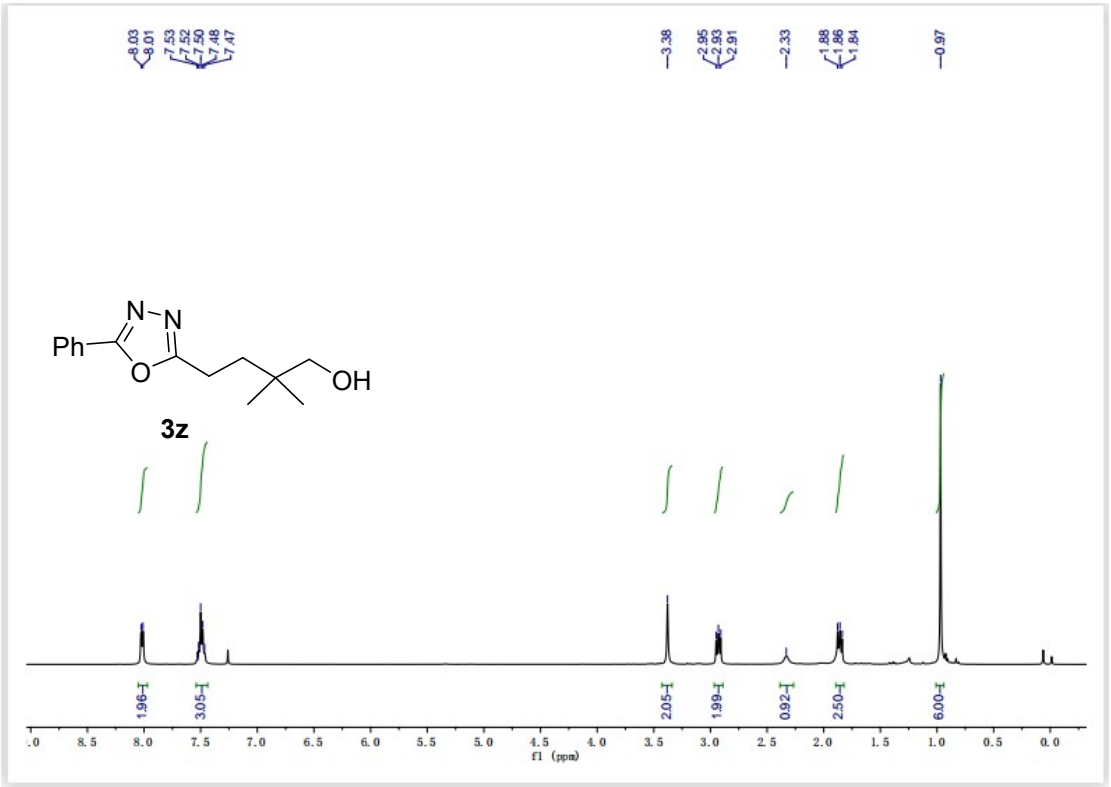
^{13}C NMR (100 MHz, $CDCl_3$) of **3y**



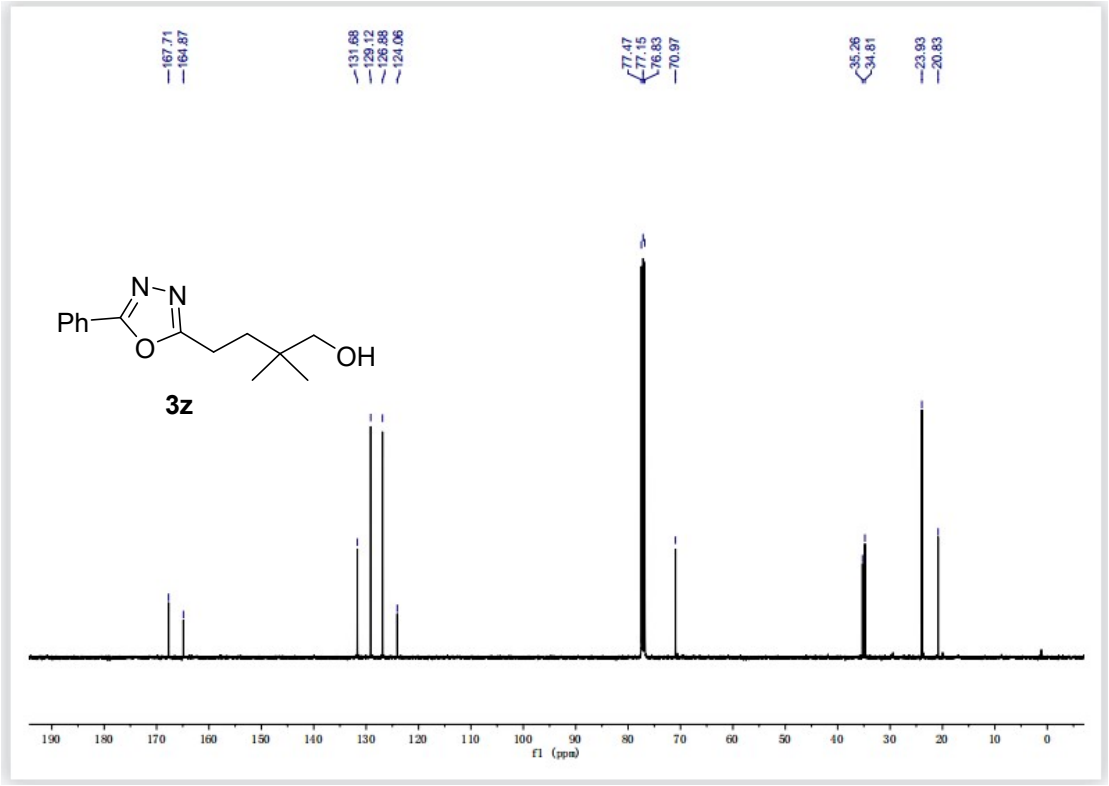
^{19}F NMR (377 MHz, $CDCl_3$, ppm) of **3y**



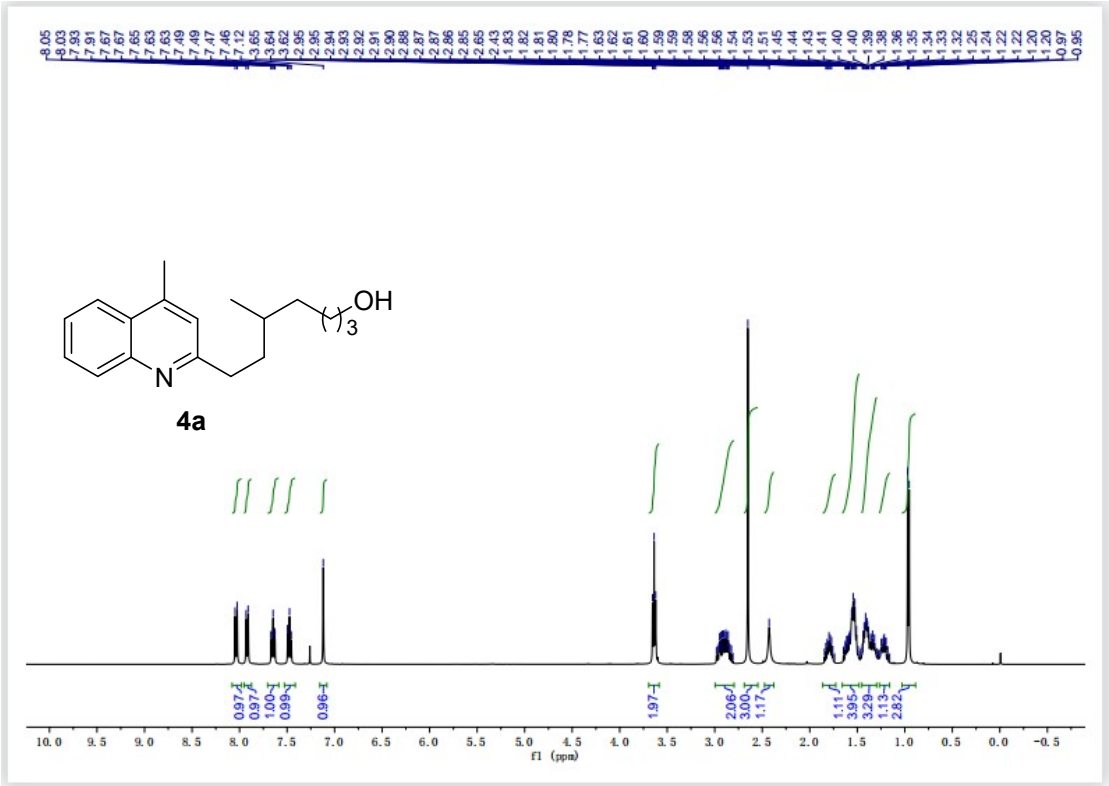
^{1}H NMR (400 MHz, $CDCl_3$) of **3z**



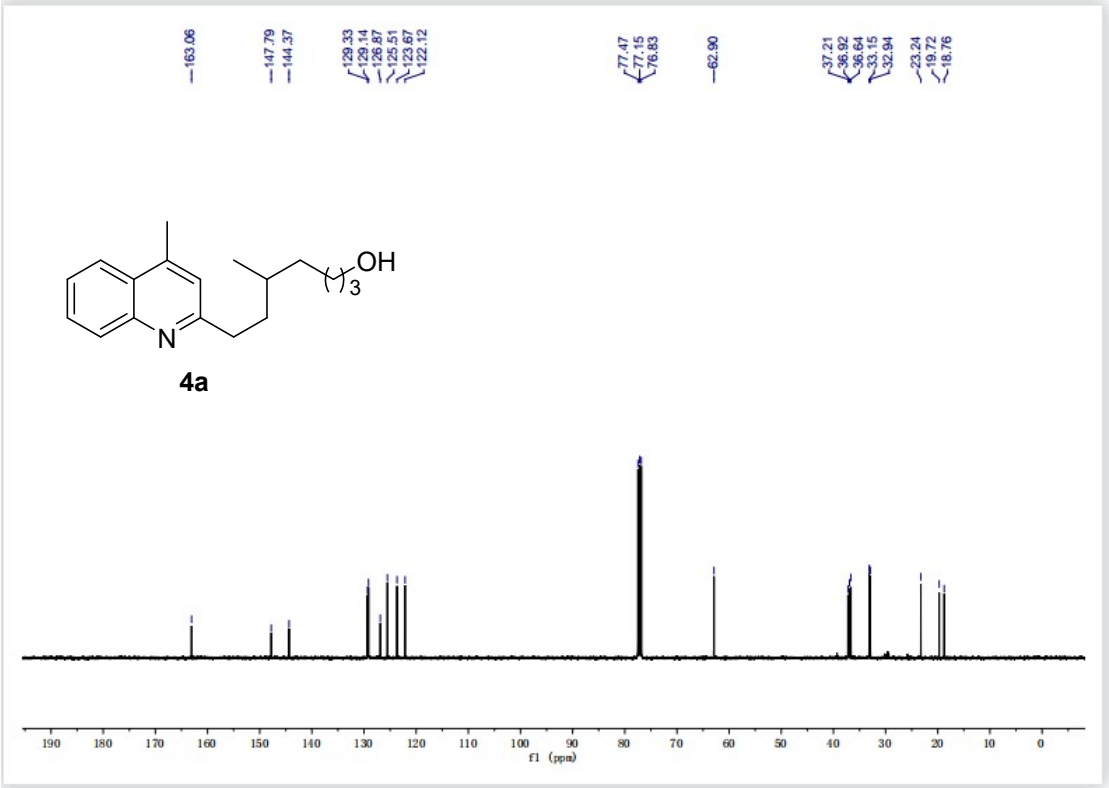
^{13}C NMR (100 MHz, $CDCl_3$) of **3z**



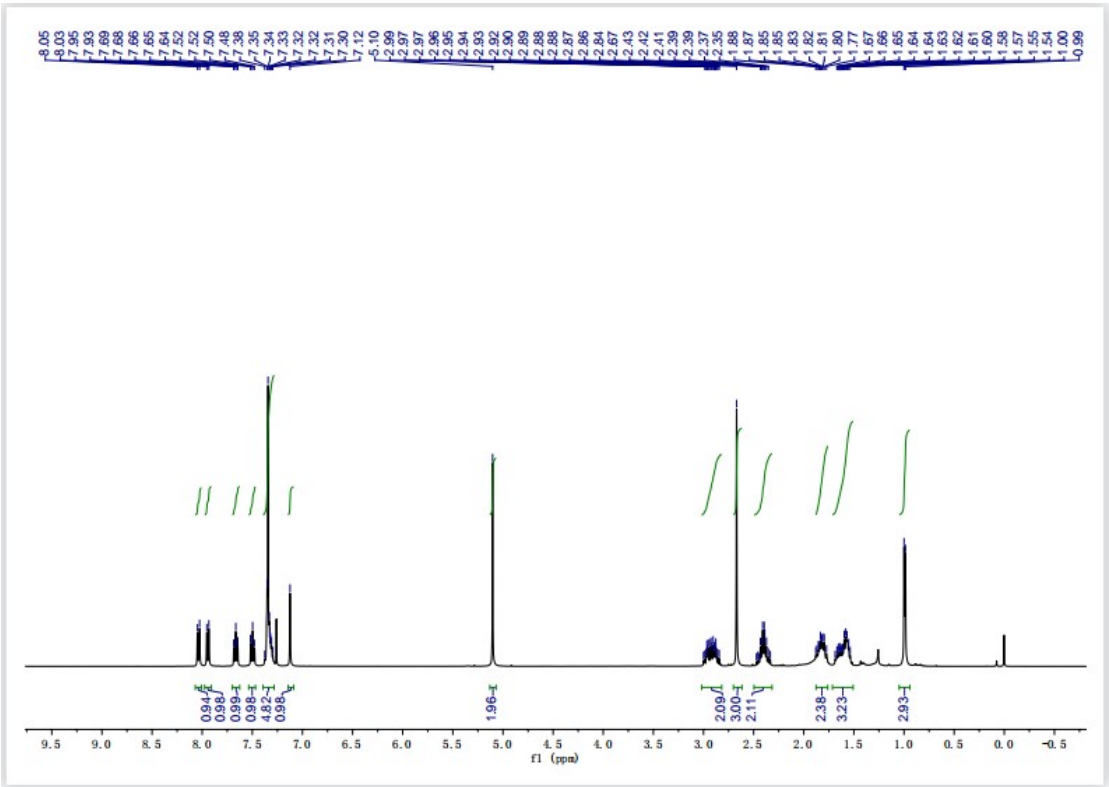
^{1}H NMR (400 MHz, $CDCl_3$) of **4a**



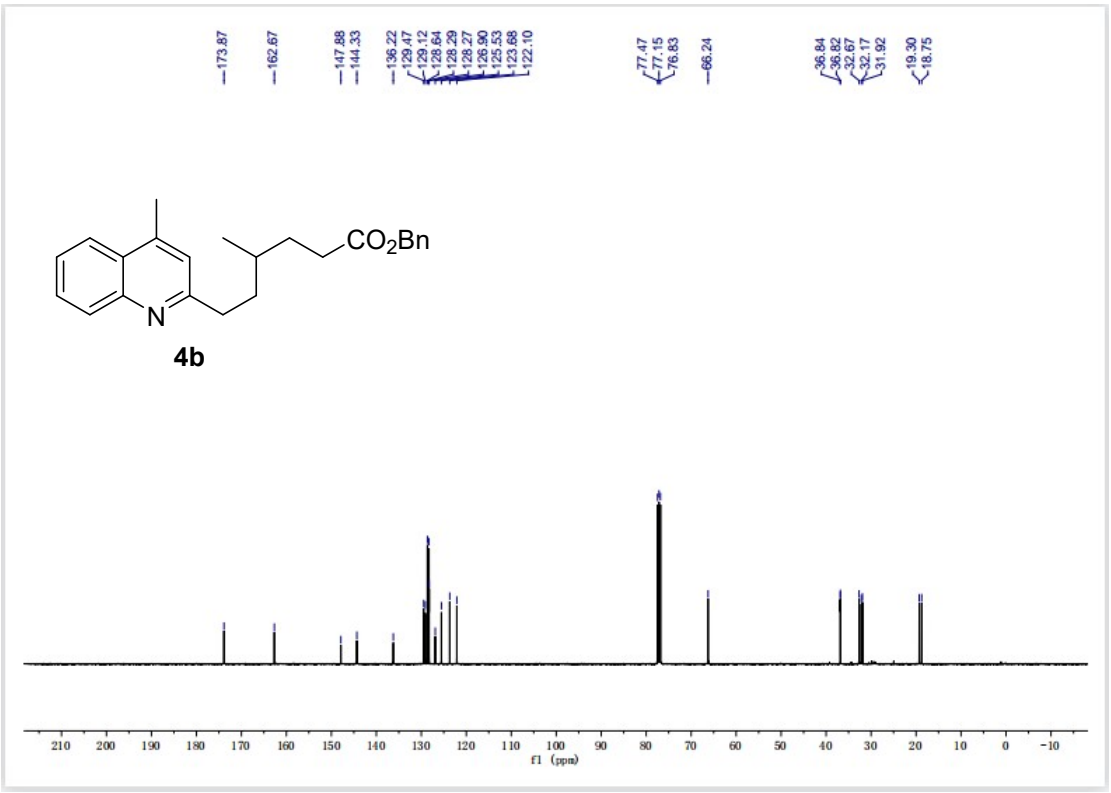
^{13}C NMR (100 MHz, $CDCl_3$) of **4a**



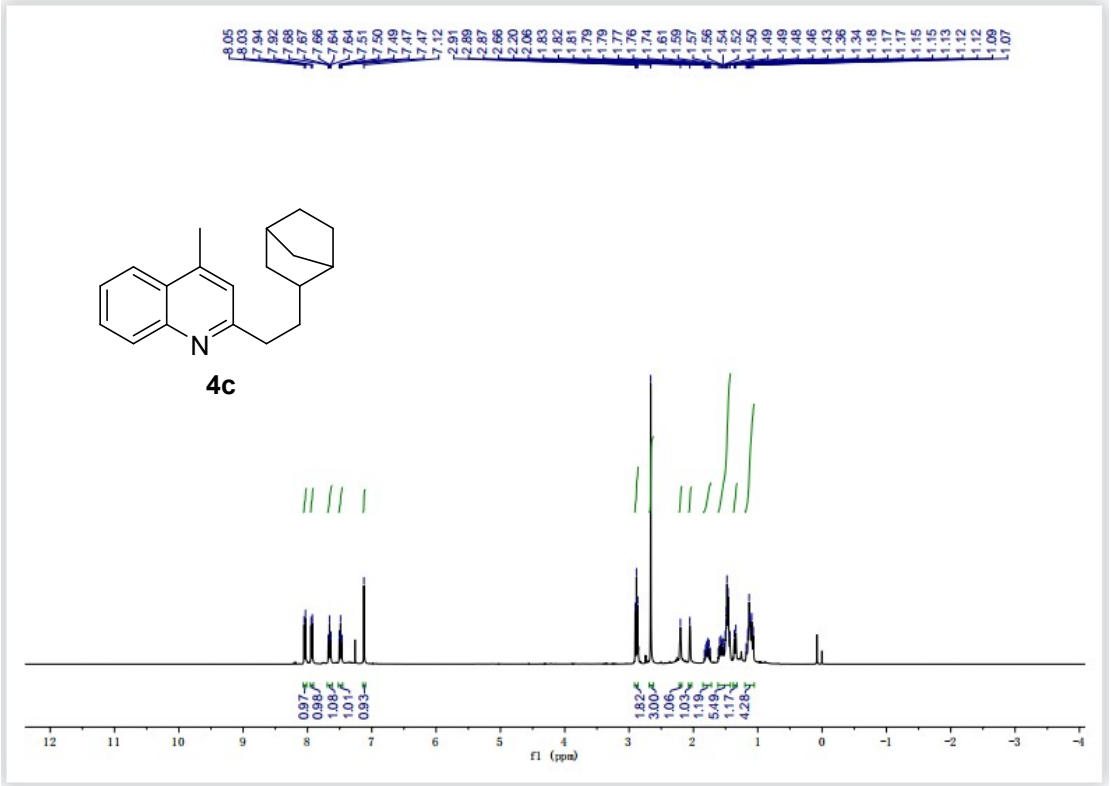
^{1}H NMR (400 MHz, $CDCl_3$) of **4b**



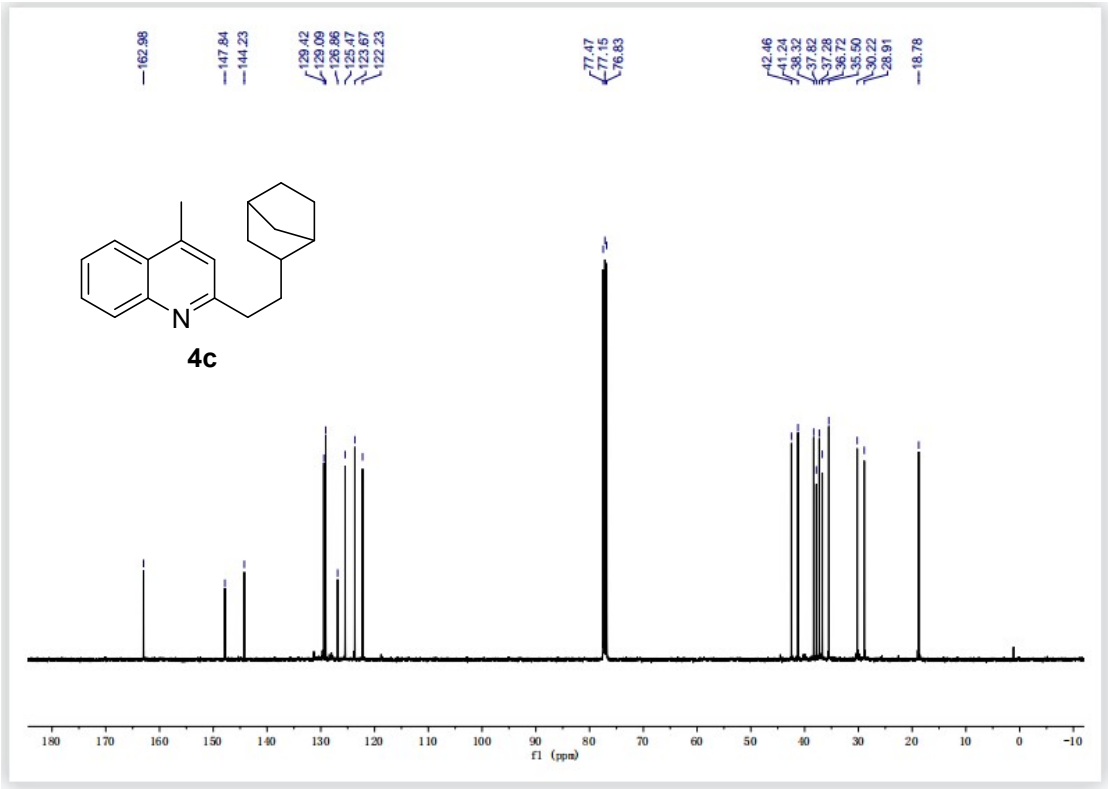
^{13}C NMR (100 MHz, $CDCl_3$) of **4b**



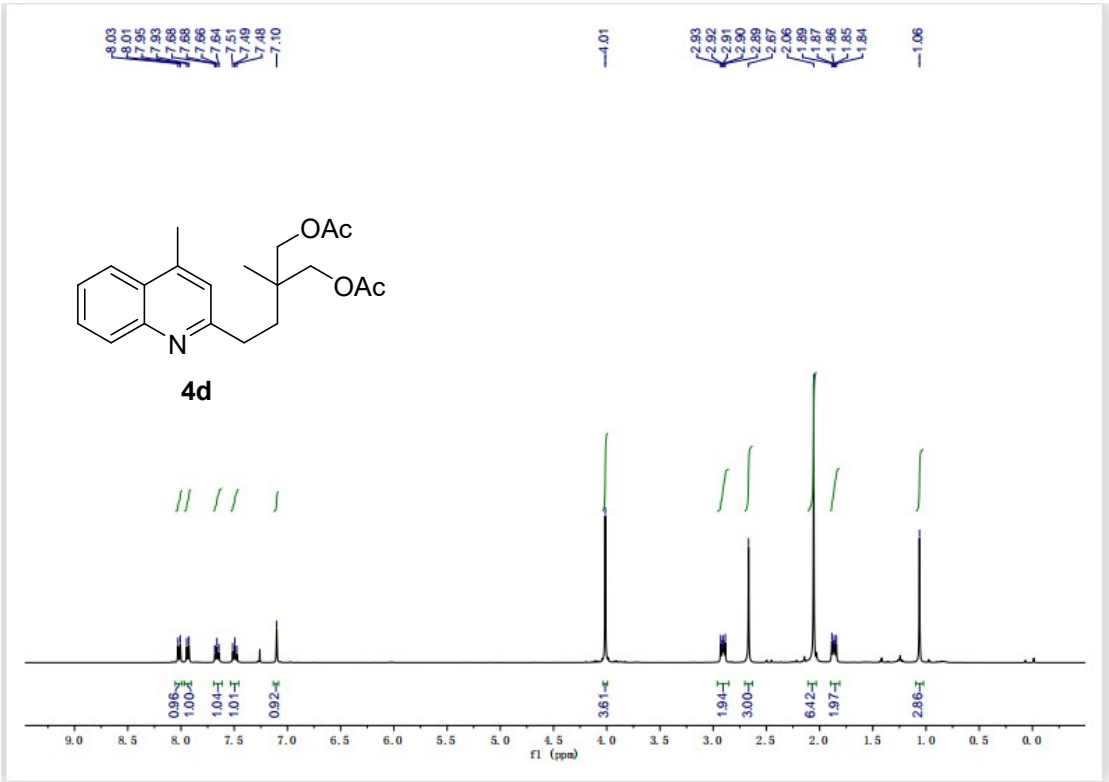
^{1}H NMR (400 MHz, $CDCl_3$) of **4c**



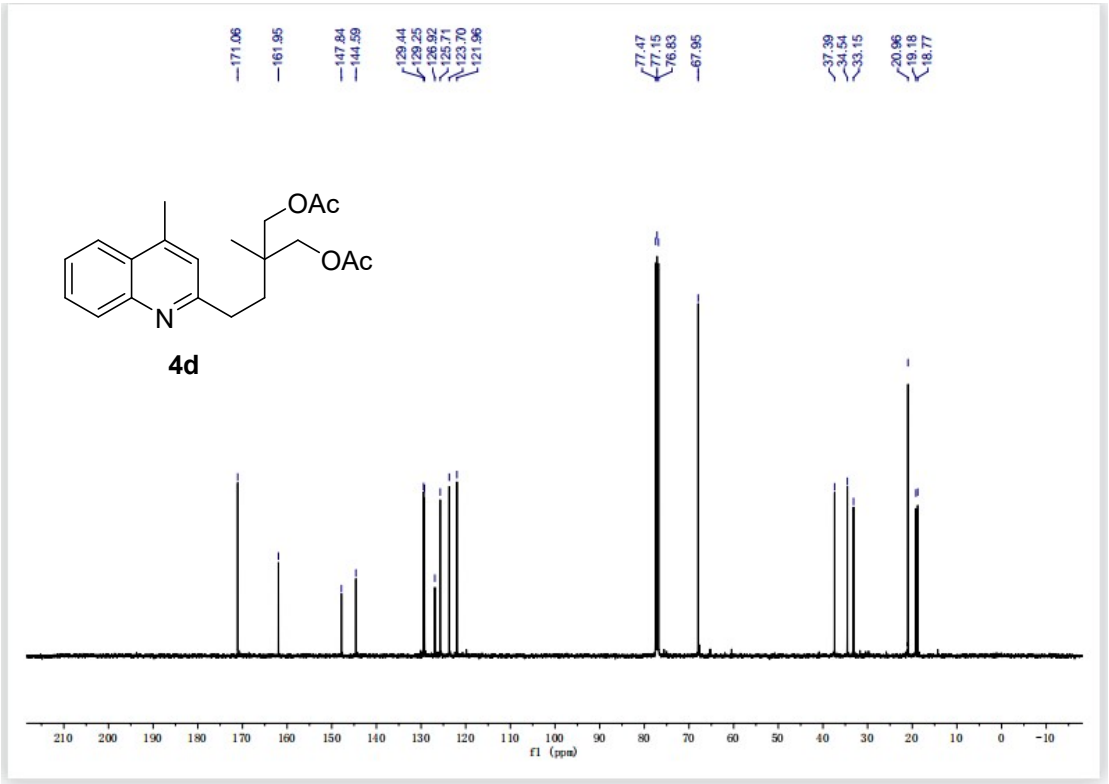
^{13}C NMR (100 MHz, $CDCl_3$) of **4c**



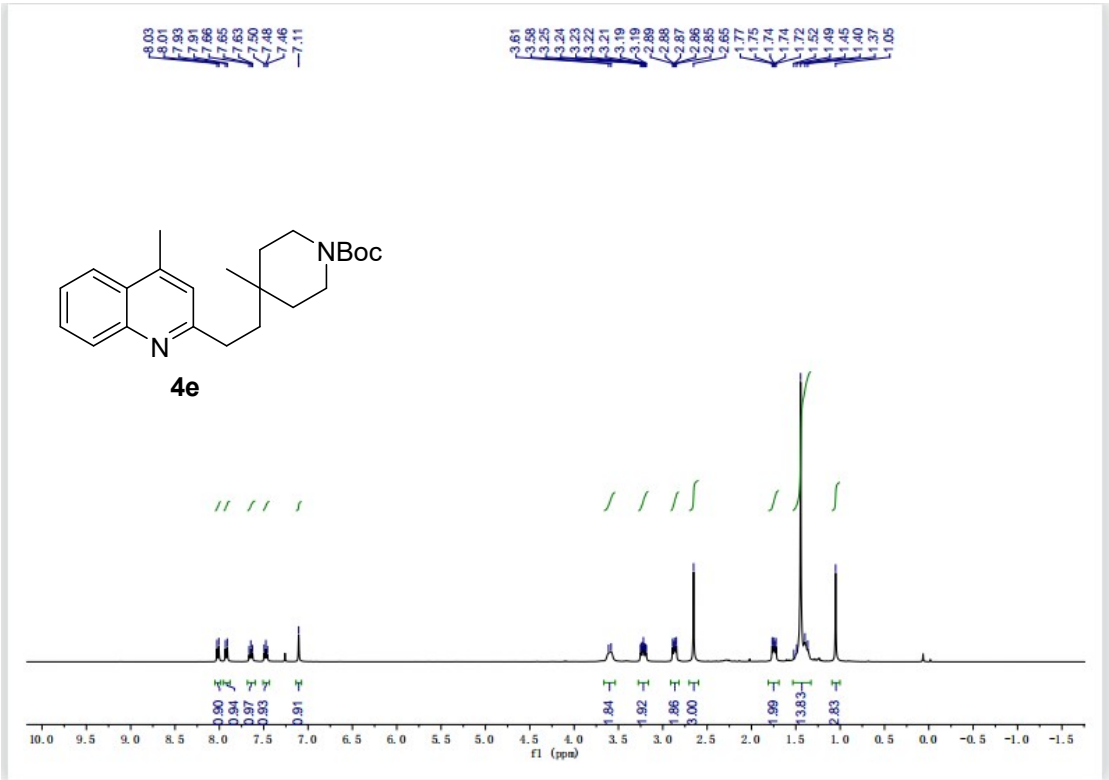
^{1}H NMR (400 MHz, $CDCl_3$) of **4d**



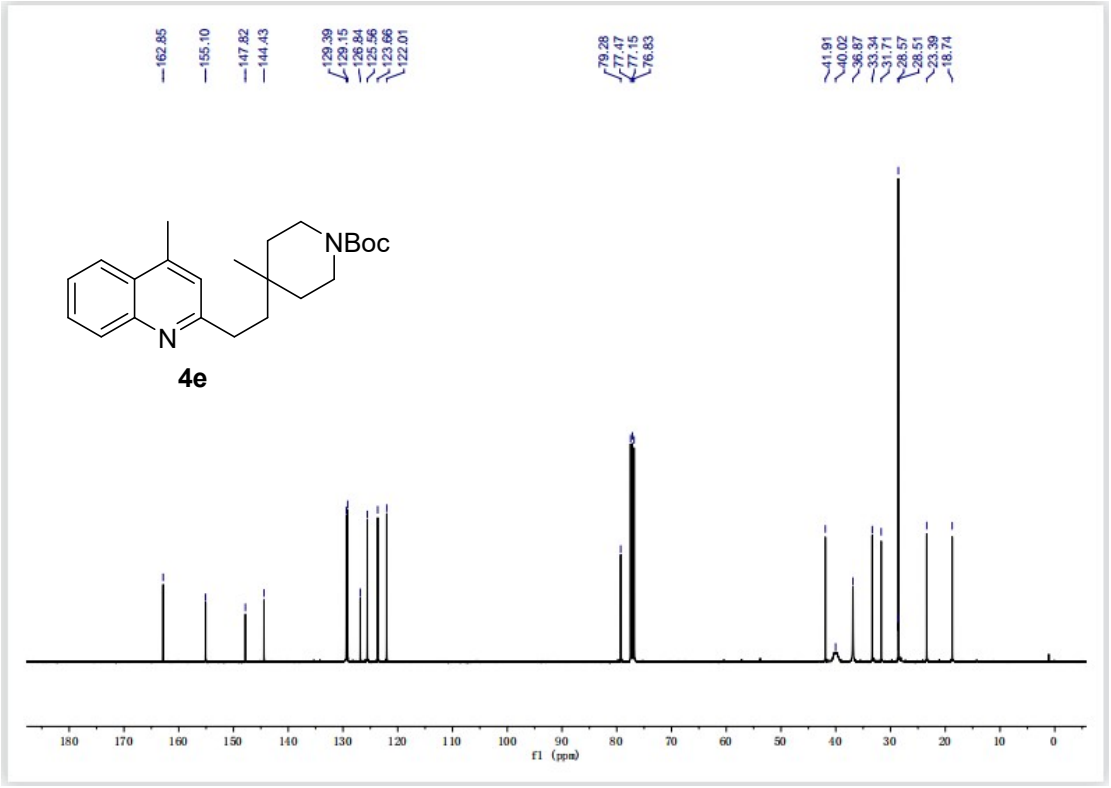
^{13}C NMR (100 MHz, $CDCl_3$) of **4d**



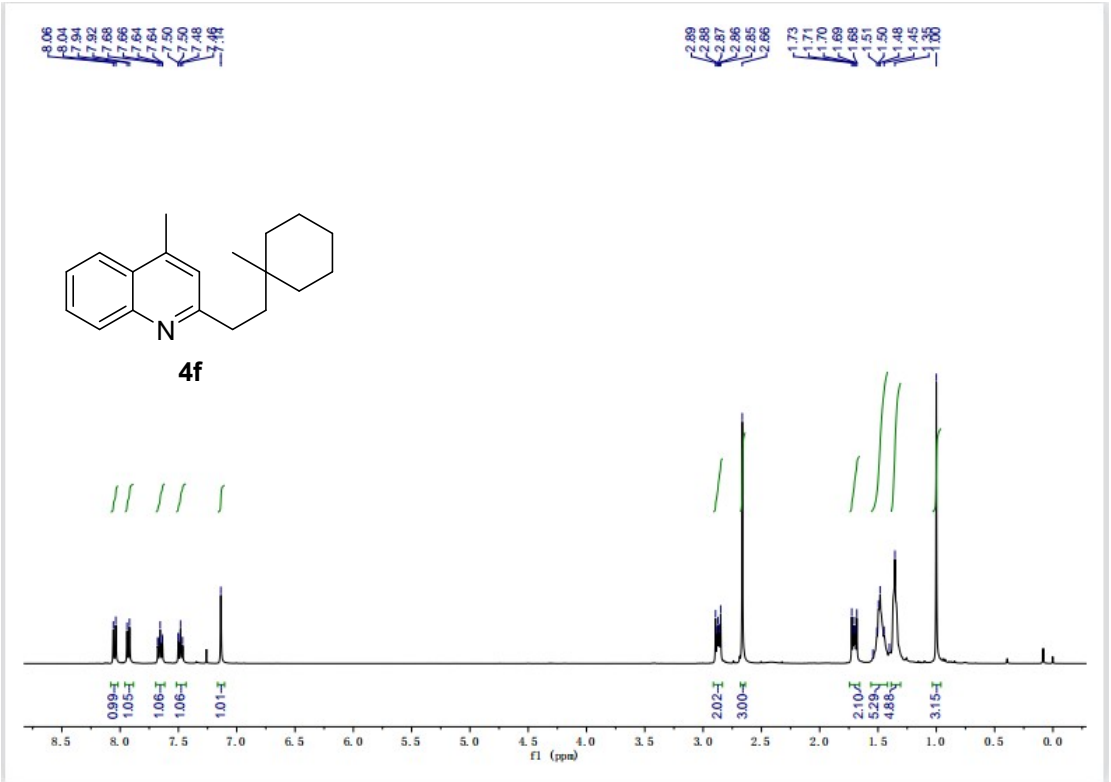
^{1}H NMR (400 MHz, $CDCl_3$) of **4e**



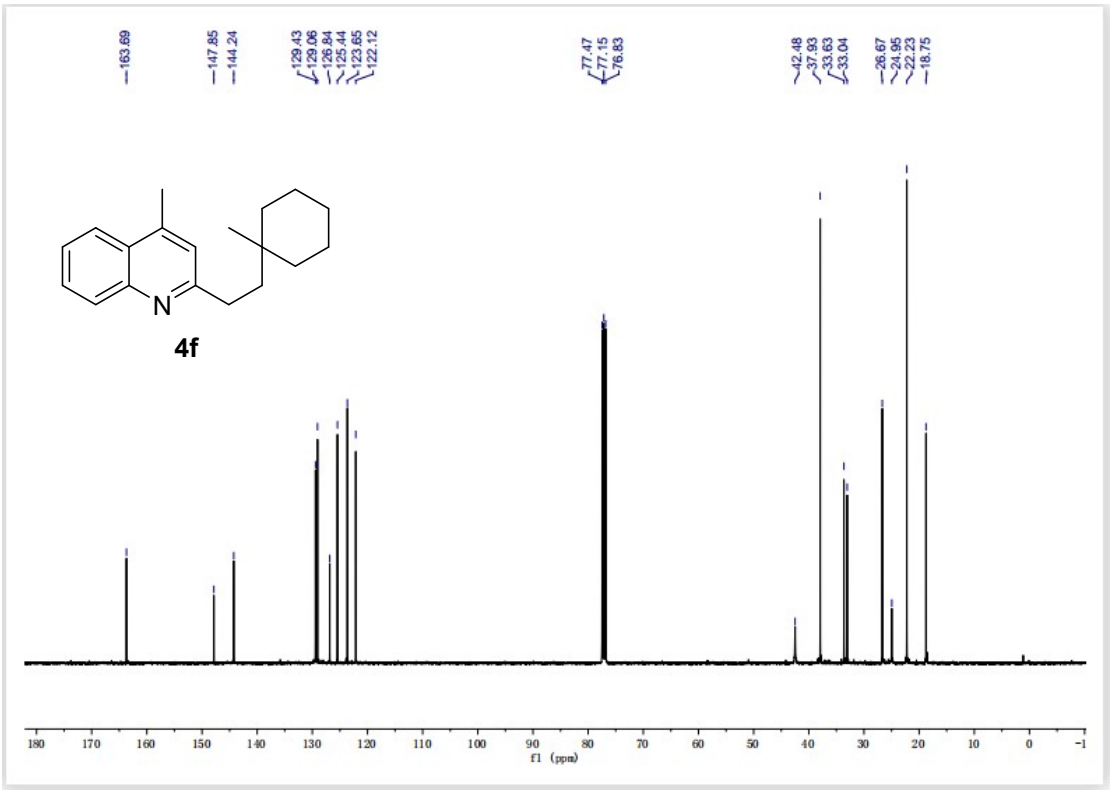
^{13}C NMR (100 MHz, $CDCl_3$) of **4e**



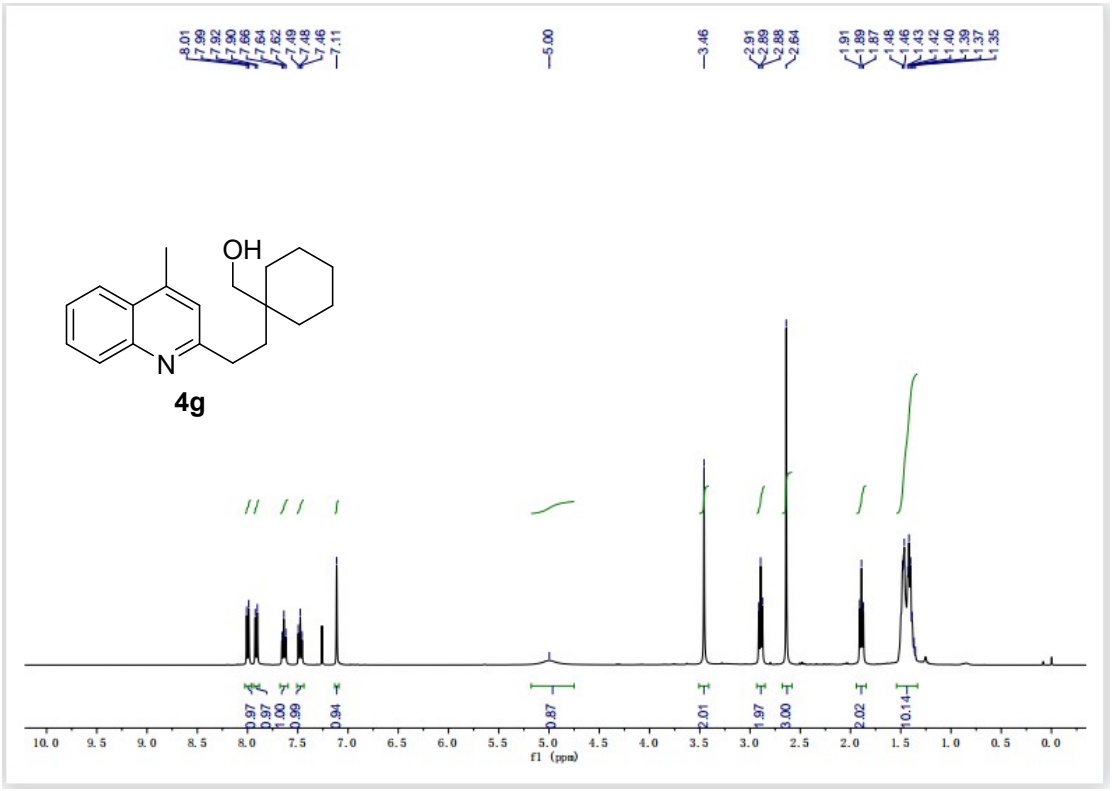
^{1}H NMR (400 MHz, $CDCl_3$) of **4f**



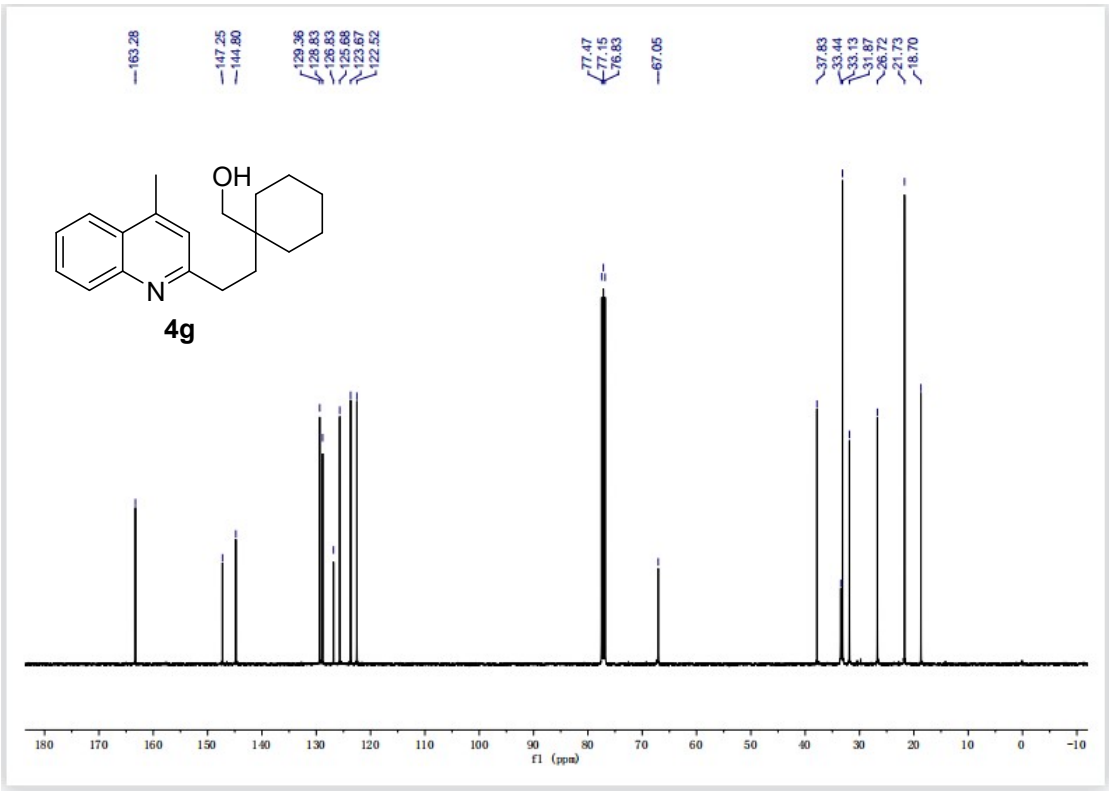
^{13}C NMR (100 MHz, $CDCl_3$) of **4f**



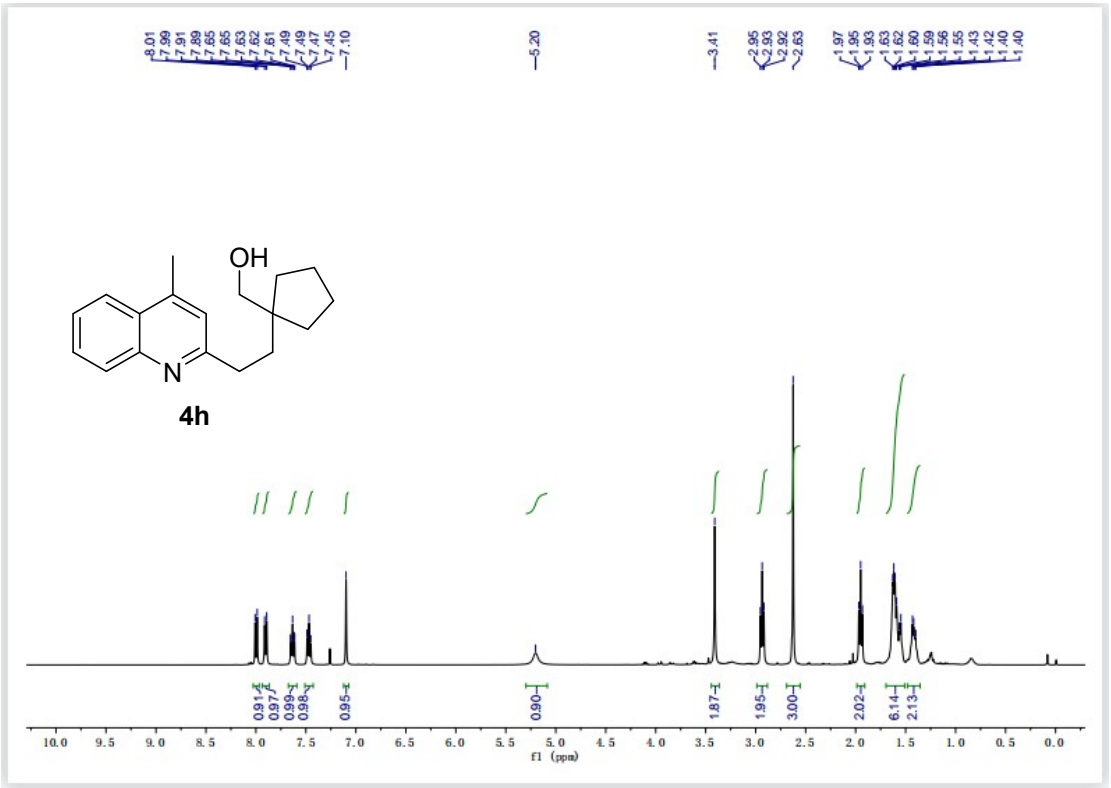
^{1}H NMR (400 MHz, $CDCl_3$) of **4g**



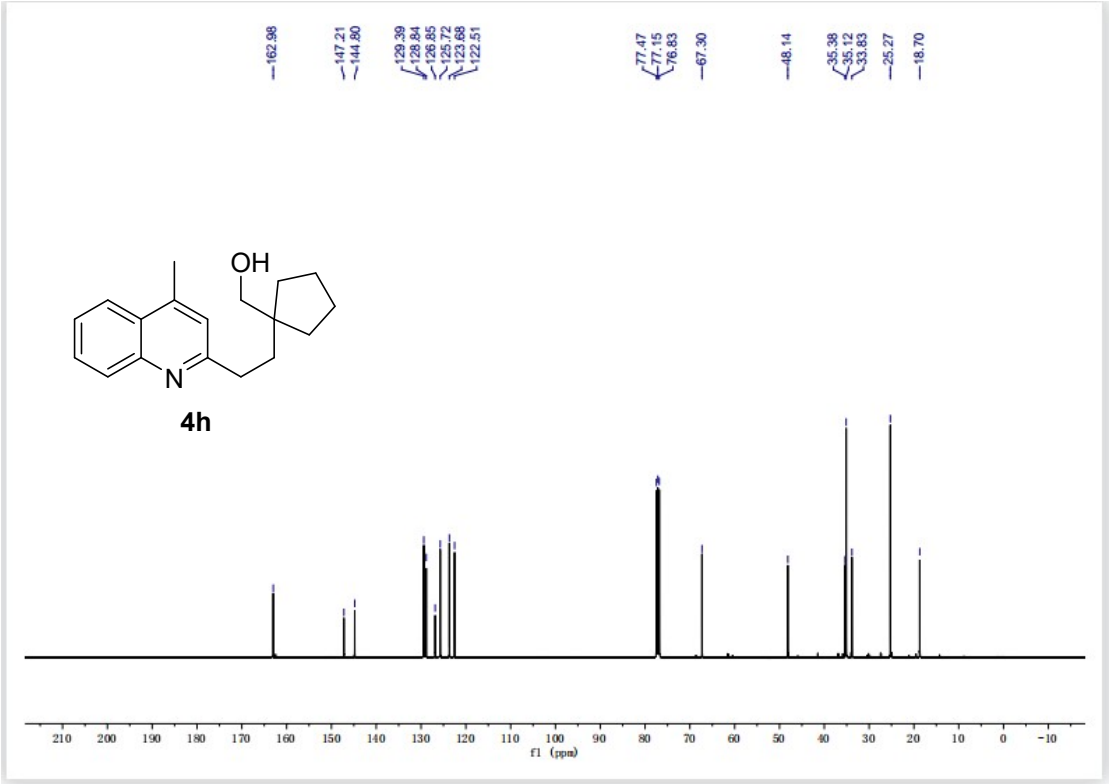
^{13}C NMR (100 MHz, $CDCl_3$) of **4g**



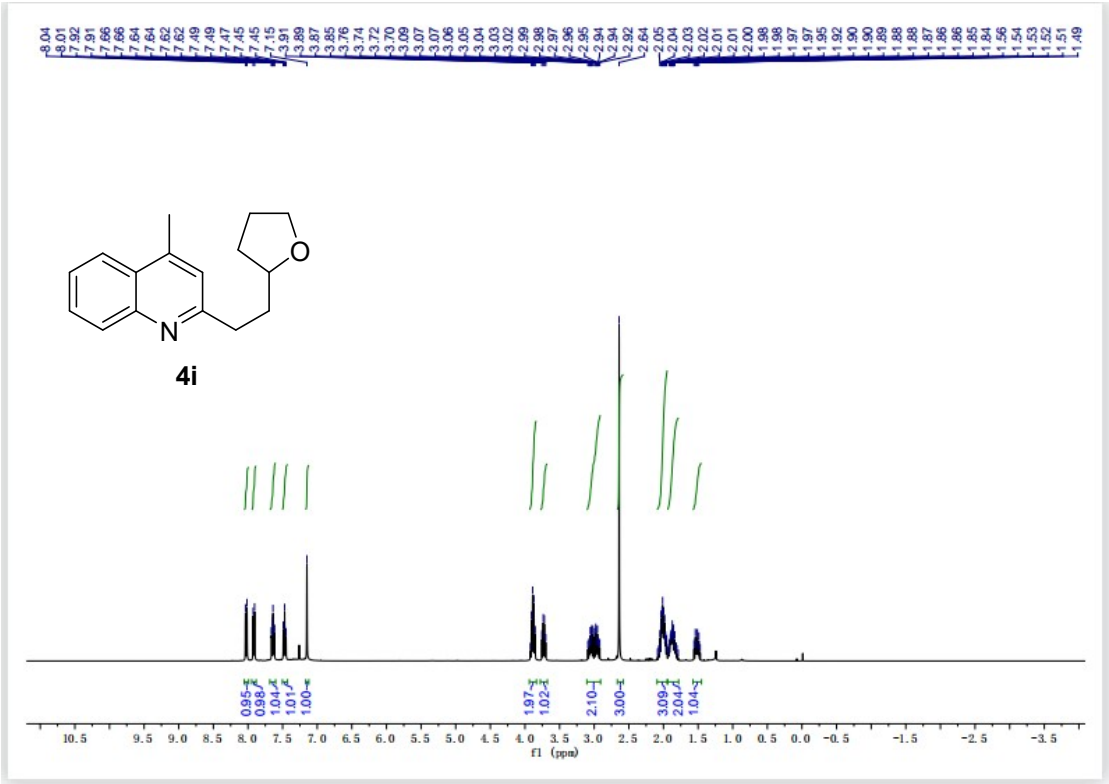
^{1}H NMR (400 MHz, $CDCl_3$) of **4h**



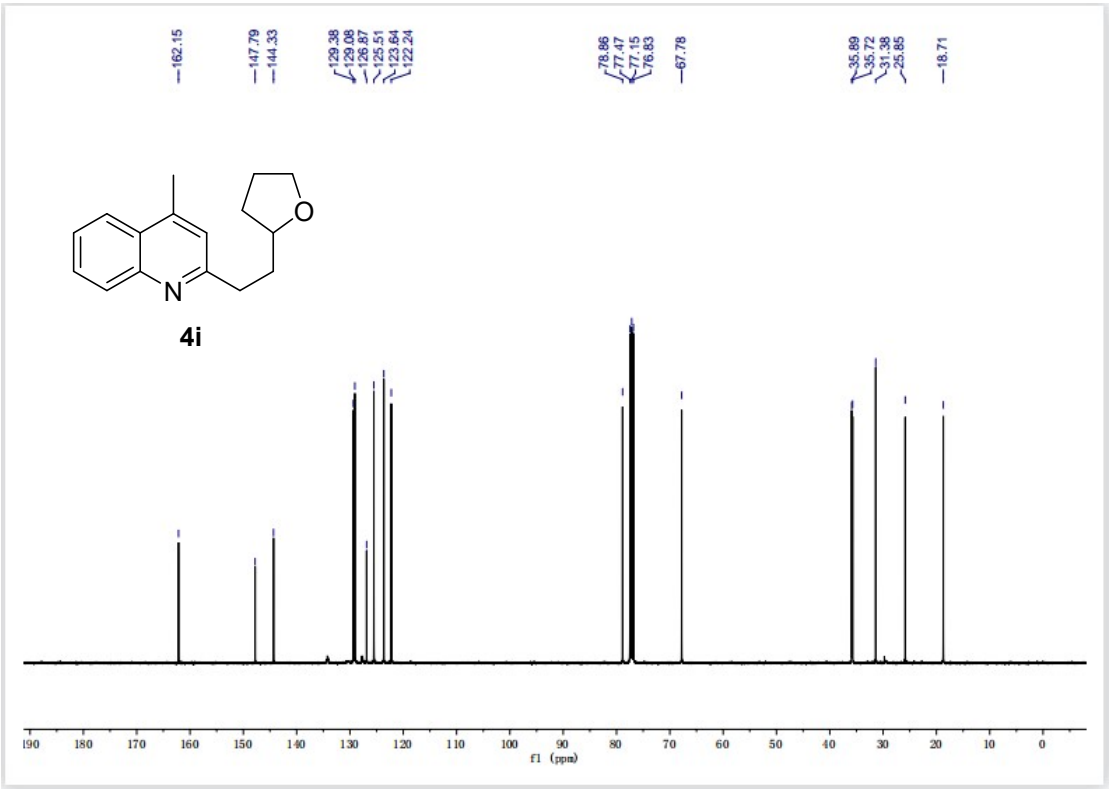
^{13}C NMR (100 MHz, $CDCl_3$) of **4h**



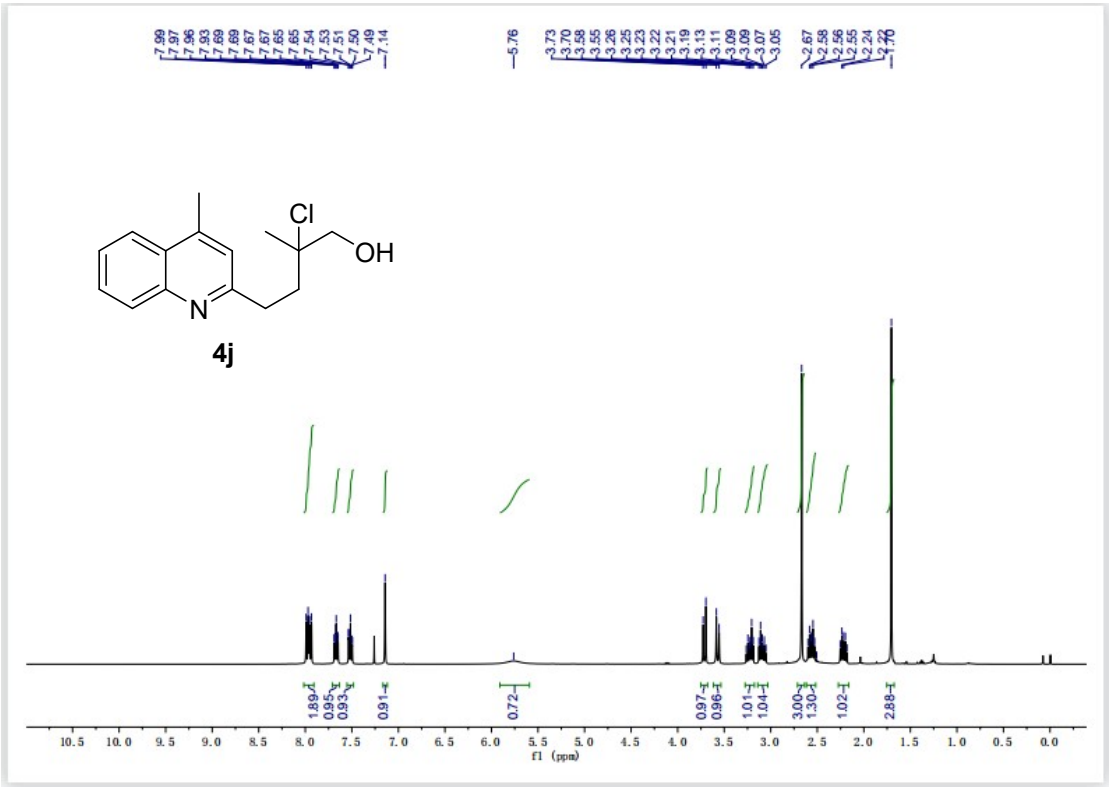
^{1}H NMR (400 MHz, $CDCl_3$) of **4i**



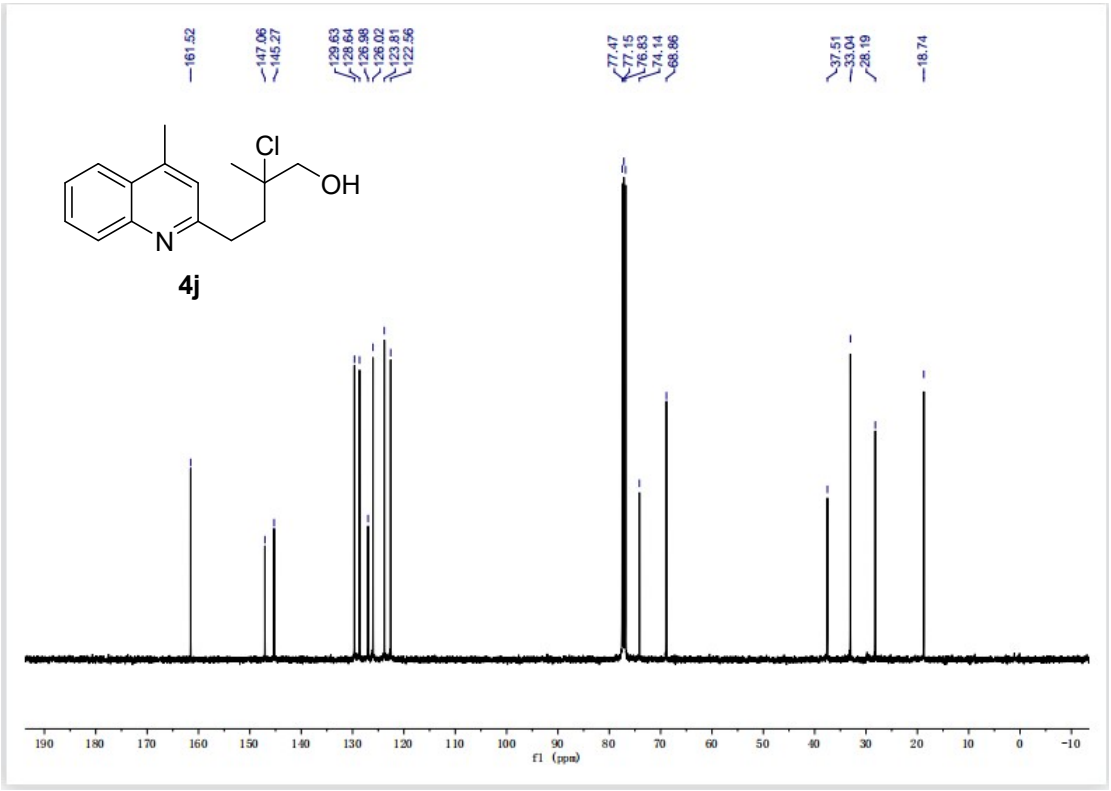
^{13}C NMR (100 MHz, $CDCl_3$) of **4i**



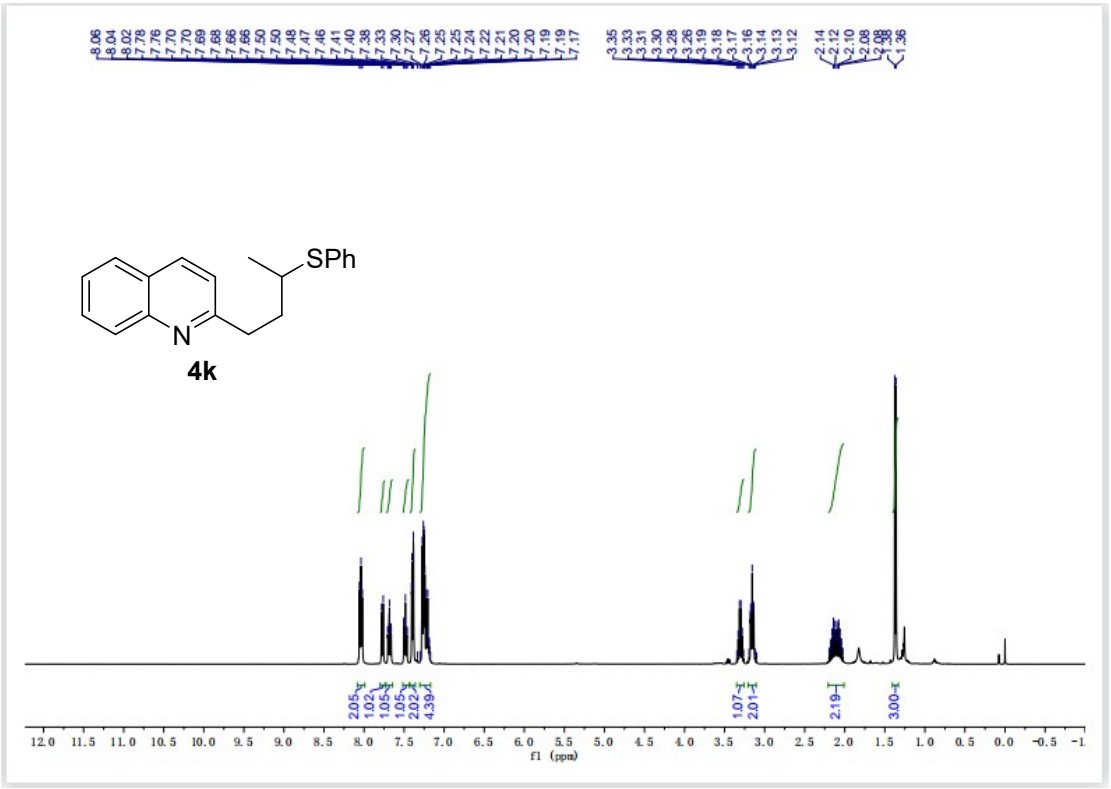
^{1}H NMR (400 MHz, $CDCl_3$) of **4j**



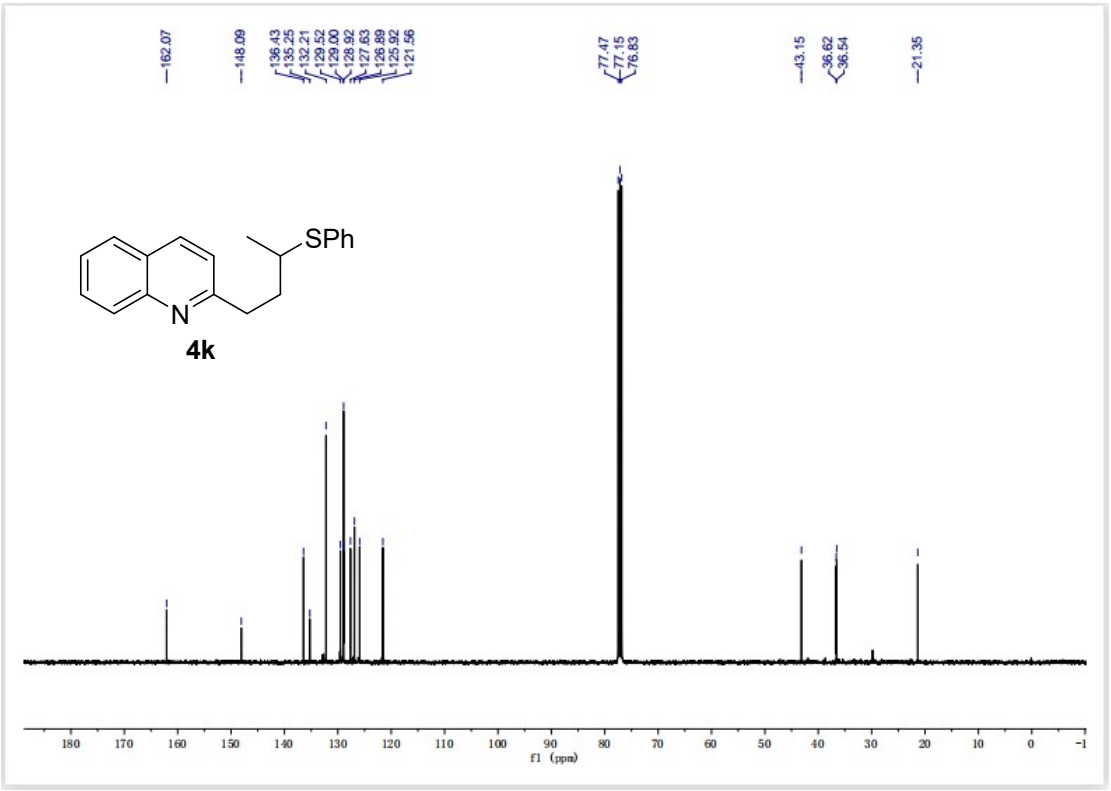
^{13}C NMR (100 MHz, $CDCl_3$) of **4j**



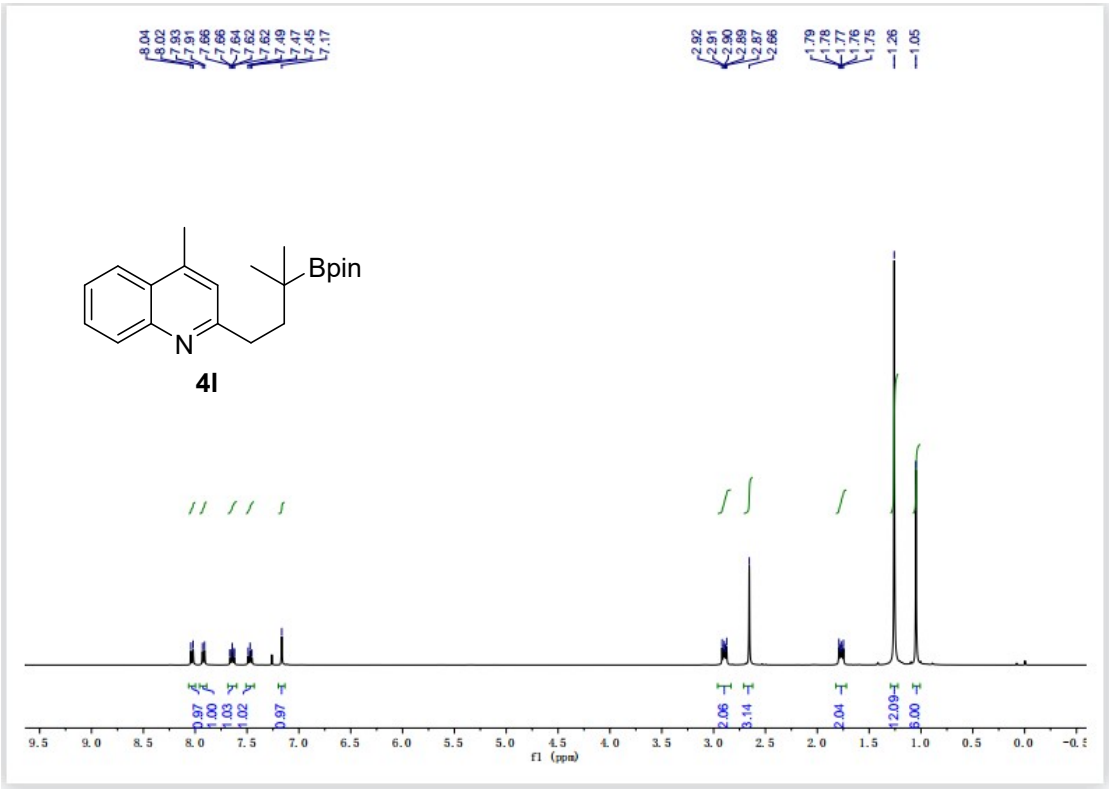
^{1}H NMR (400 MHz, $CDCl_3$) of **4k**



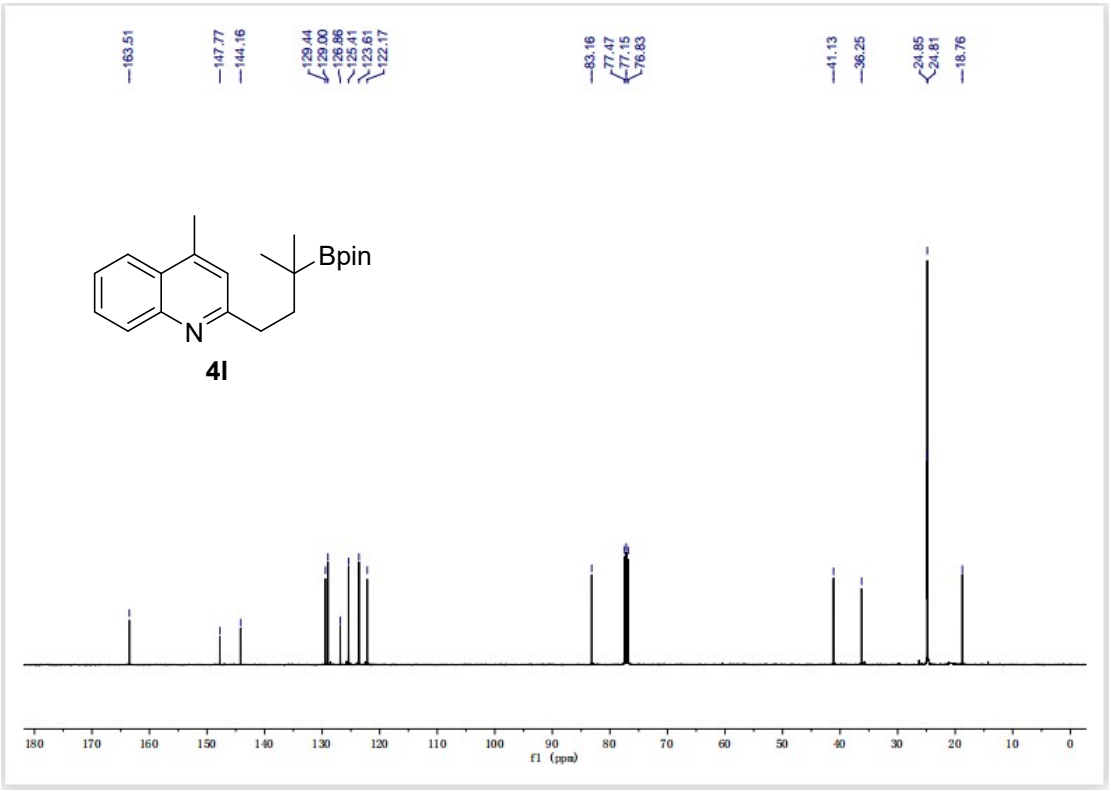
^{13}C NMR (100 MHz, $CDCl_3$) of **4k**



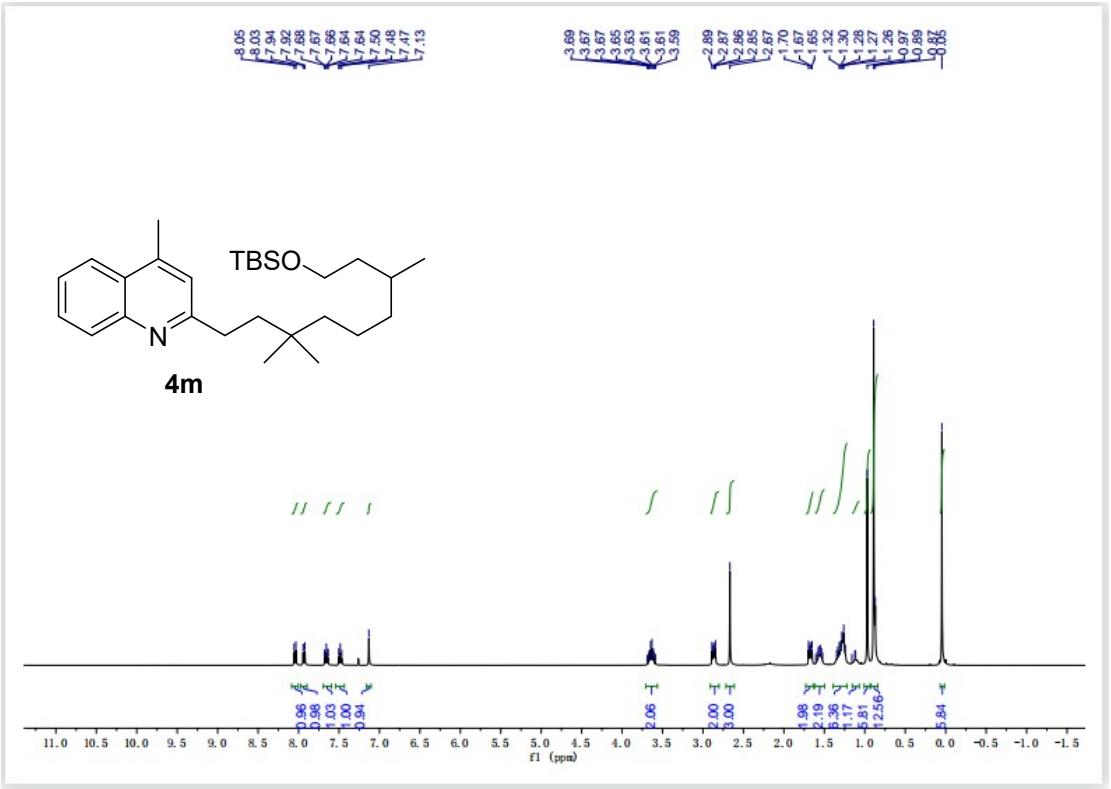
^{1}H NMR (400 MHz, $CDCl_3$) of **4l**



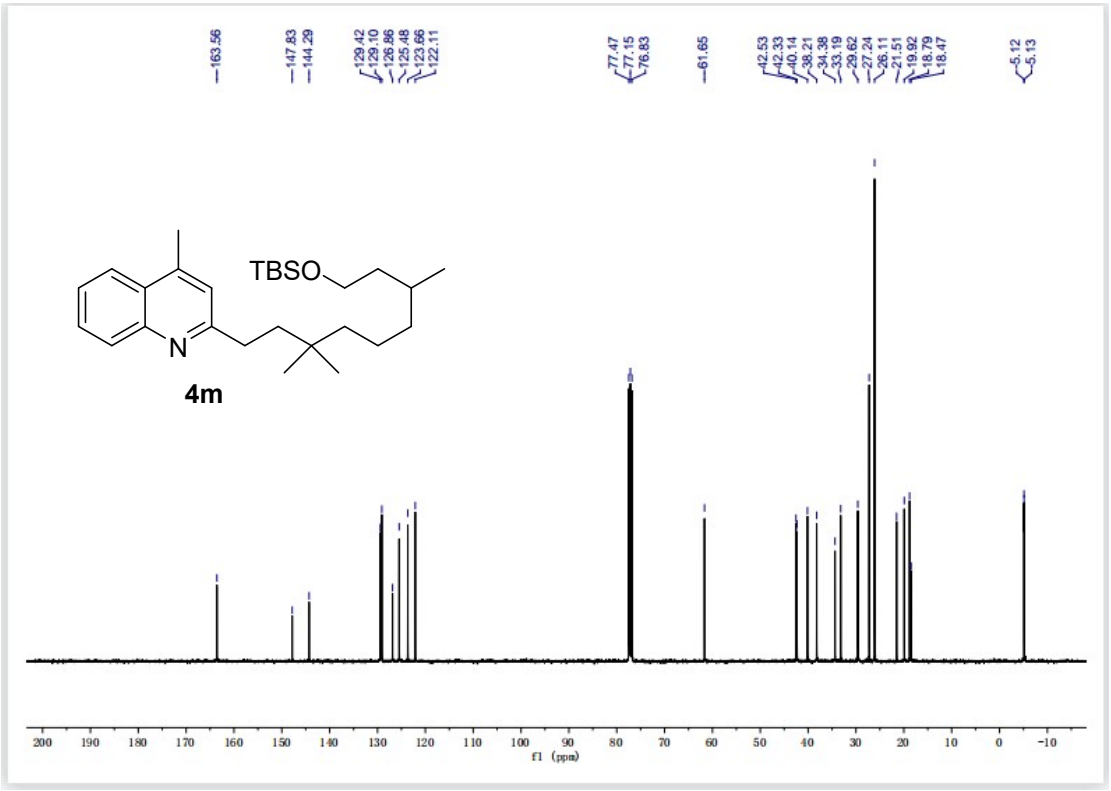
^{13}C NMR (100 MHz, $CDCl_3$) of **4l**



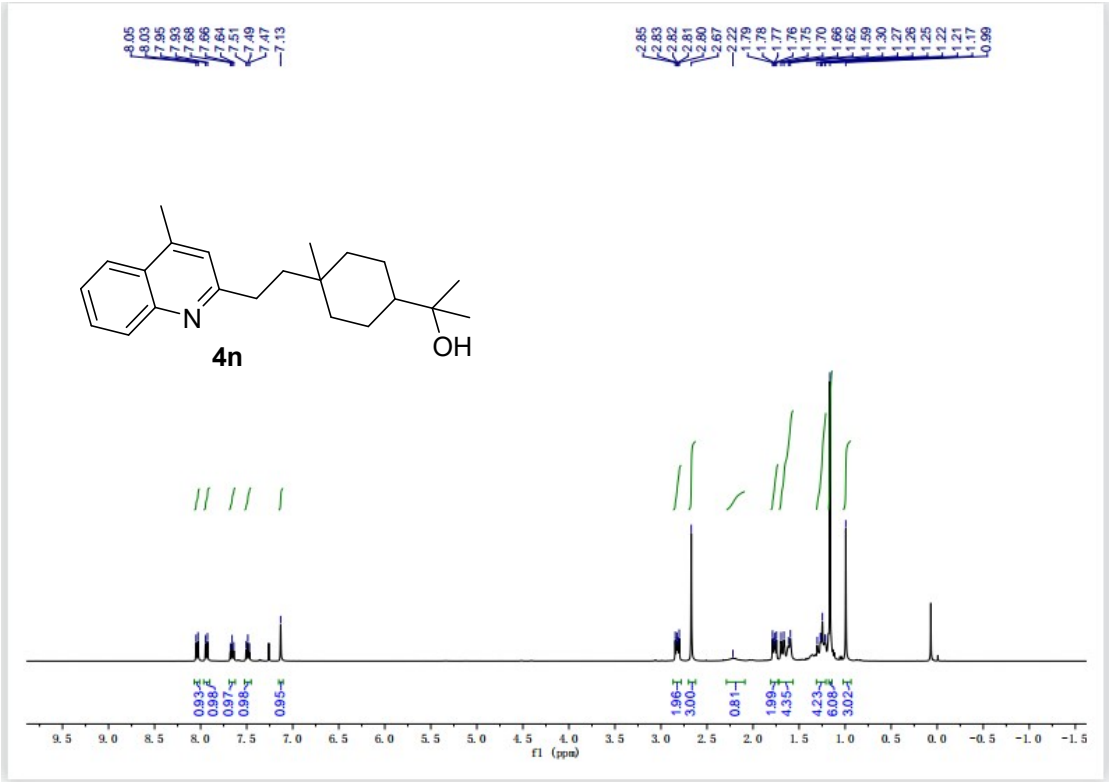
^{1}H NMR (400 MHz, $CDCl_3$) of **4m**



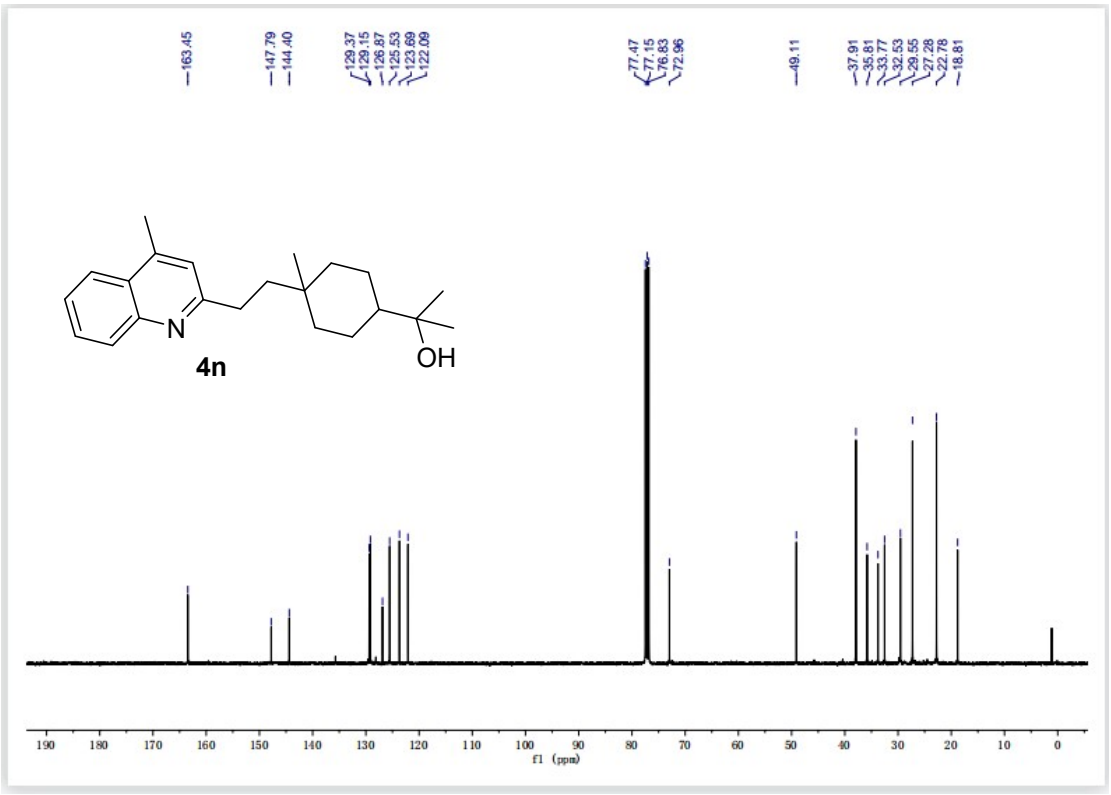
^{13}C NMR (100 MHz, $CDCl_3$) of **4m**



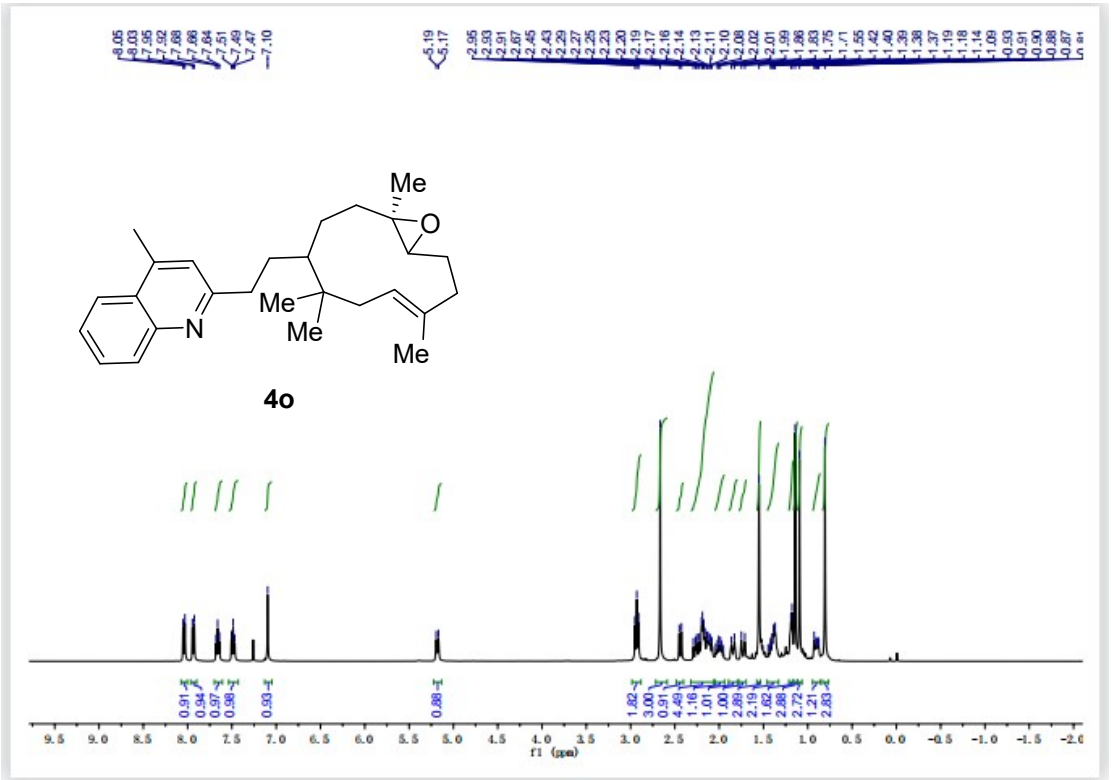
^{1}H NMR (400 MHz, $CDCl_3$) of **4n**



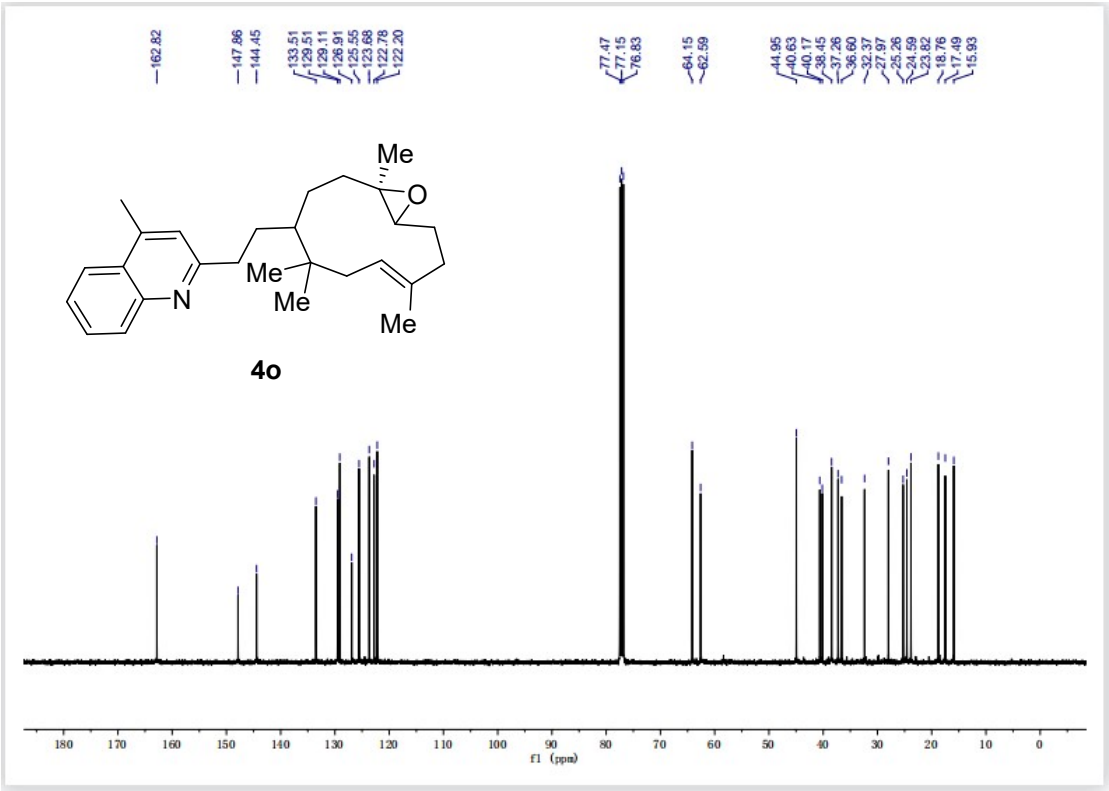
^{13}C NMR (100 MHz, $CDCl_3$) of **4n**



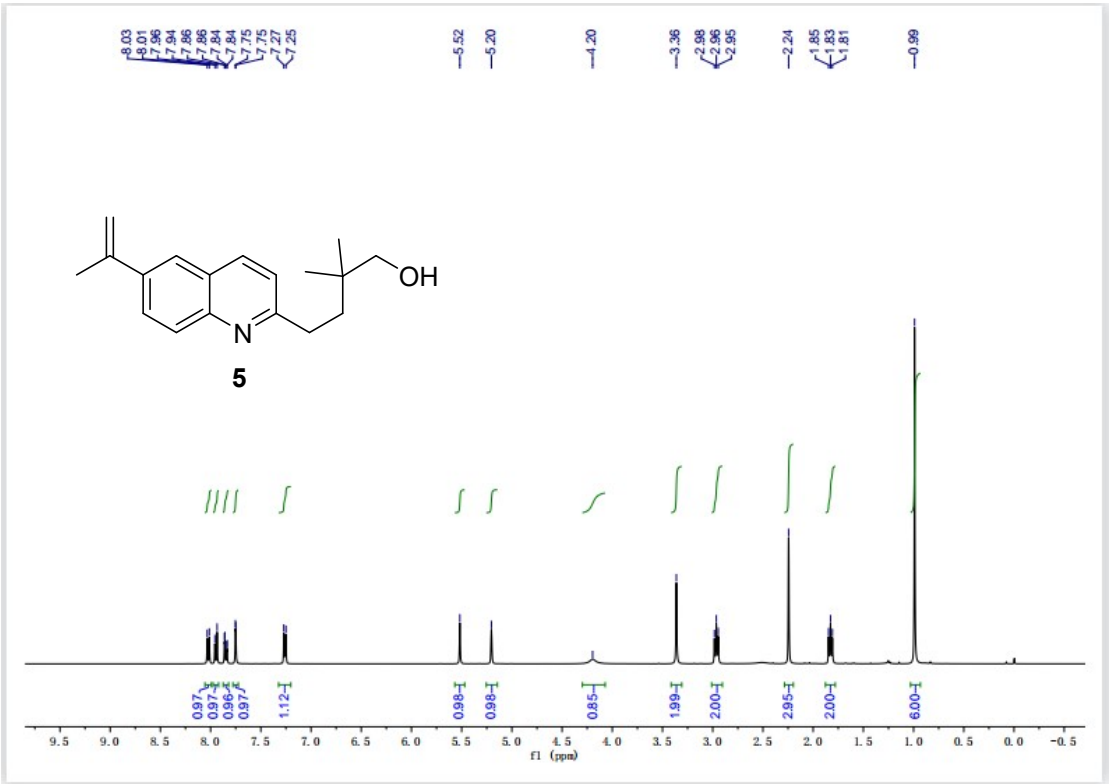
^{1}H NMR (400 MHz, $CDCl_3$) of **4o**



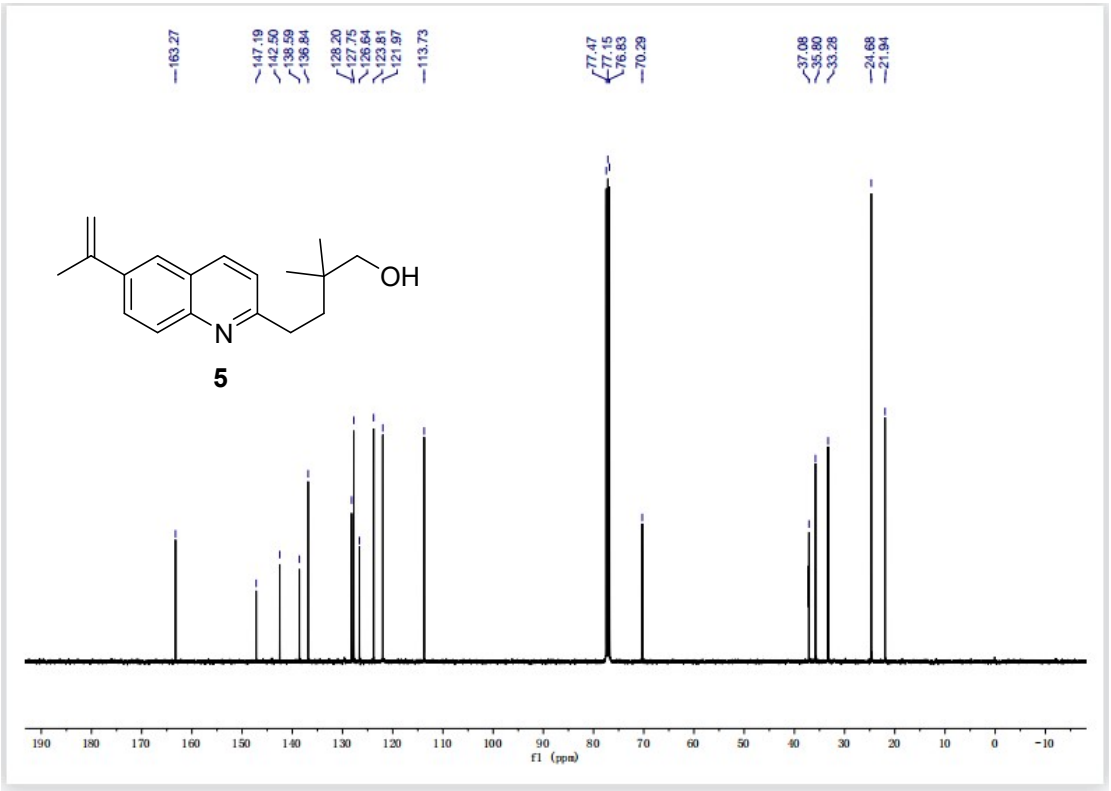
^{13}C NMR (100 MHz, $CDCl_3$) of **4o**



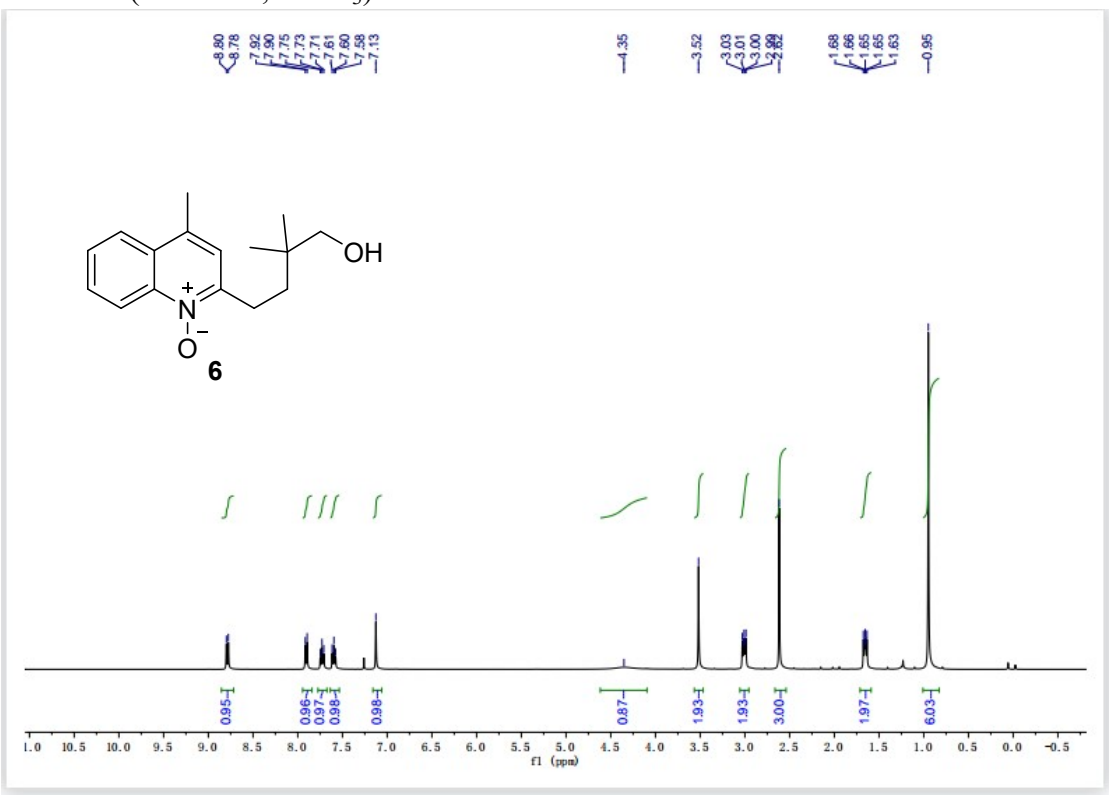
^{1}H NMR (400 MHz, $CDCl_3$) of **5**



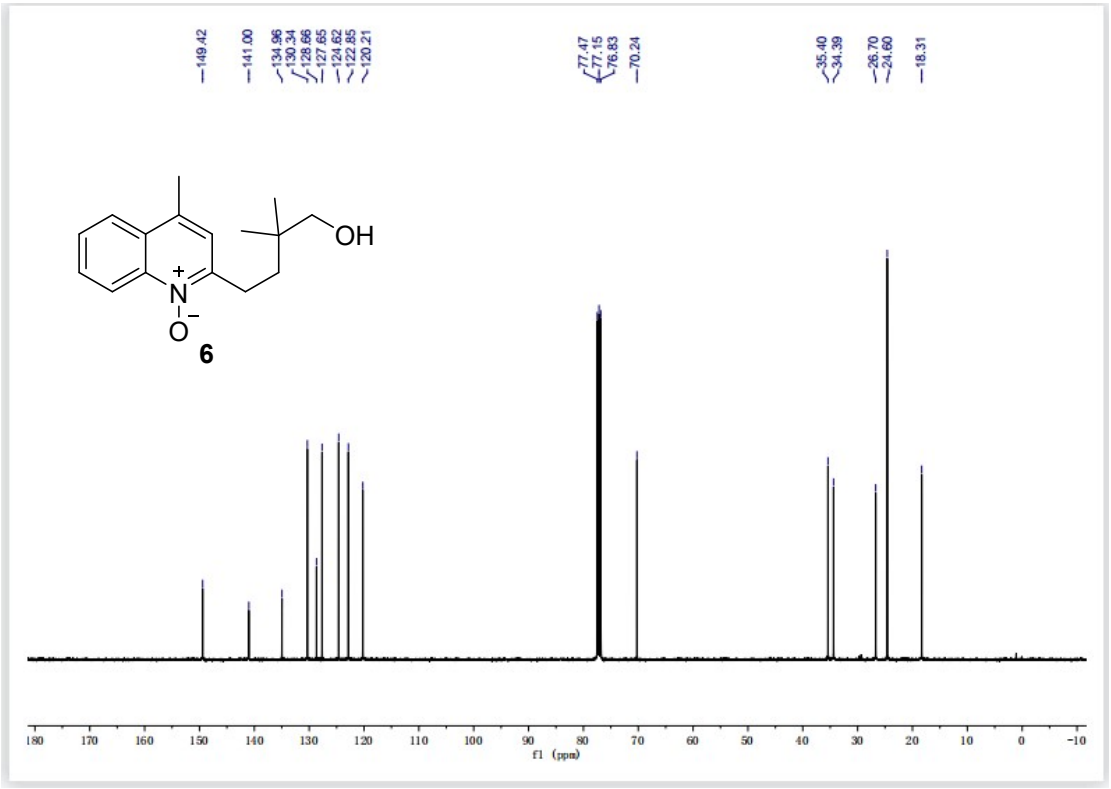
^{13}C NMR (100 MHz, $CDCl_3$) of **5**



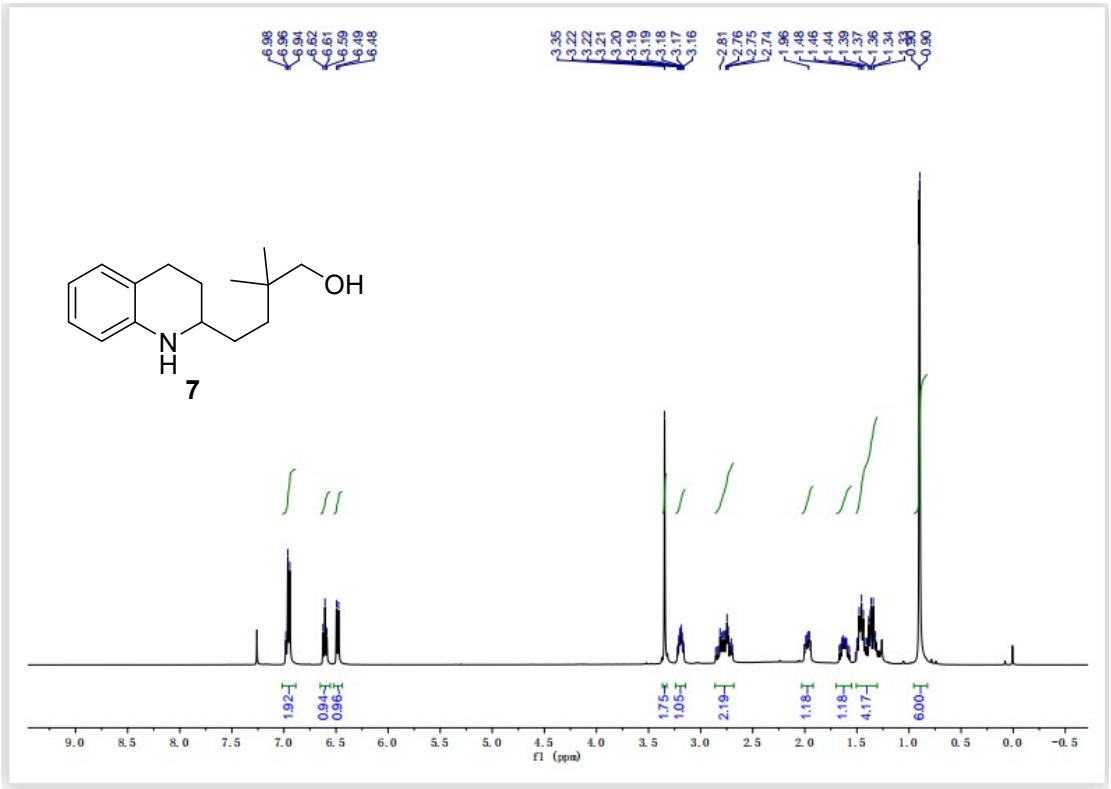
^{1}H NMR (400 MHz, $CDCl_3$) of **6**



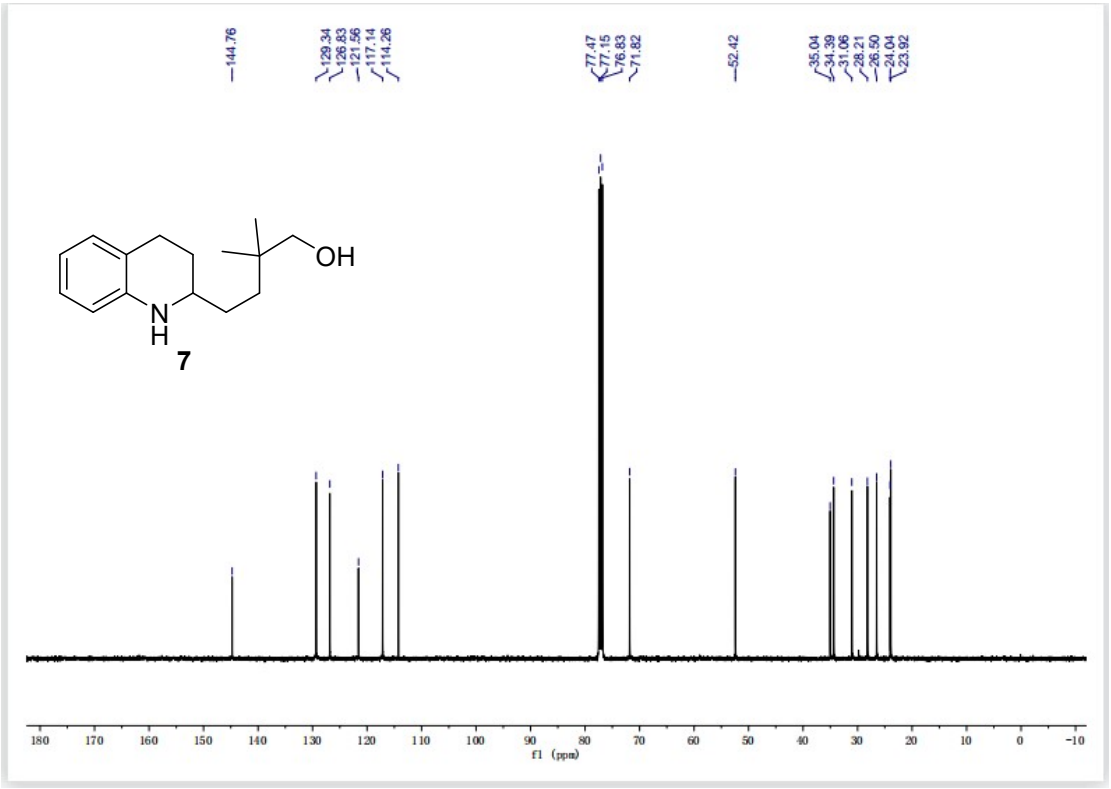
^{13}C NMR (100 MHz, $CDCl_3$) of **6**



^{1}H NMR (400 MHz, $CDCl_3$) of **7**

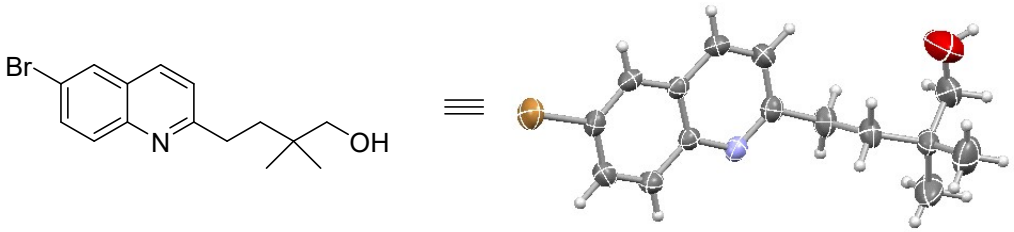


^{13}C NMR (100 MHz, $CDCl_3$) of **7**



8. X-ray crystallographic data of 3h

The single crystal of **3h**, which was used for the determination of its configuration via X-ray crystallography (see below), was recrystallized from a mixed solution of **3h** in EtOAc and hexane.



3h structure of **3h**

ORTEP drawing (50% probability ellipsoids) of **3h** (CCDC 2205053)

Crystal data and structure refinement for **3h**

Identification code	**3h**
CCDC Deposit number	2205053
Empirical formula	$C_{15}H_{18}BrNO$
Formula weight	308.22
Temperature (K)	293.15
Wavelength (Å)	0.71073
Crystal system	orthorhombic
space group	P 1 21/n 1
a/Å	6.034(3)
b/Å	23.507(11)
c/Å	9.961(6)
α/°	90
β/°	93.291(13)
γ/°	90
Volume/ $Å^3$	1410.6(14)
Z	4
$\rho_{calc}g/cm^3$	1.451
μ /mm^{-1}	2.902
F (000)	631.4
Crystal size/mm^3	0.21 × 0.18 × 0.16
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.44 to 53.96

Index ranges	$-7 \leq h \leq 7, -30 \leq k \leq 30, -12 \leq l \leq 12$
Reflections collected	20844
Goodness-of-fit on F^2	1.0325
Independent reflections	3225 [R_{int} =0.0371 , R_{sigma} =0.0250]
Data/restraints/parameters	3225/0/166
Final R indexes [I>=2σ (I)]	R_1 = 0.0493, wR_2 = 0.1356
Final R indexes [all data]	R_1 = 0.0647, wR_2 = 0.1466
Largest diff. peak/hole / e $Å^{-3}$	0.85/-0.82