Electronic Supplementary Material (ESI) for RSC Advances.

NBS-Mediated Bromination and Dehydrogenation of Tetrahydroquinoline in One Pot: Scope and Mechanistic Study

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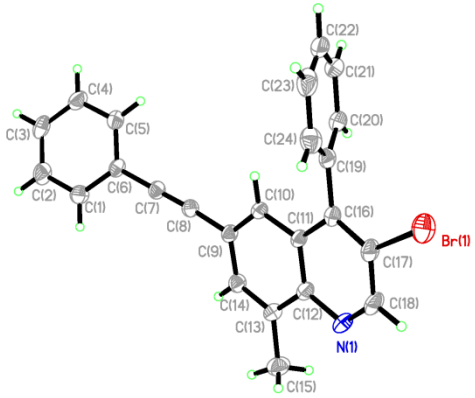
1. Crystal structure of compound 3n



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                alpha=90         beta=106.655(2)    gamma=90
Temperature:    296 K

                Calculated                Reported
Volume          1821.5(4)                 1821.5(4)
Space group     P 21/n                    P 21/n
Hall group      -P 2yn                    -P 2yn
Moiety formula  C24 H16 Br N              ?
Sum formula     C24 H16 Br N              C24 H16 Br N
Mr              398.28                    398.29
Dx,g cm-3       1.452                     1.452
Z               4                         4
Mu (mm-1)       2.263                     2.263
F000            808.0                     808.0
F000'           807.11
h,k,lmax        13,14,16                  13,14,16
Nref            3197                      3192
Tmin,Tmax       0.561,0.581
Tmin'           0.550

Correction method= Not given

Data completeness= 0.998          Theta(max)= 25.000

R(reflections)= 0.0344( 2334)     wR2(reflections)= 0.0932( 3192)

S = 0.990                 Npar= 236
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FigS1 Crystal structure of compound **3n**

2. General remarks

All reagents were purchased from commercial sources and used without further treatment, unless otherwise indicated. Chloroform ($CHCl_3$) was purchased from Adamas Company, safe dry, water<50ppm. ^1H and ^{13}C NMR spectra were recorded on Bruker 400 MHz spectrometers spectrometers, chemical shifts are given in parts per million (ppm) relative to standard tetramethylsilane (0.00 ppm for ^{1} H NMR) or residual solvent peaks for ^{13} C NMR. HRMS was obtained using a Q-TOF instrument equipped with ESI source. Standard column chromatography was performed on 200-300 mesh silica gel. using flash column chromatography techniques.

3. Genernal procedures

3.1 General procedure for the synthesis of raw material

1q and **1r** were purchased from Adamas company and used without further treatment, **1a-1p** were synthesized according to the literature [1].

3.2 General procedure for the construction of 2a-2r via bromination and dehydrogenation reaction

NBS (177.0 mg, 1.0 mmol) was added in batches to the solution of **1a-1r** (0.2 mmol) in $CHCl_3$ (2.0 mL). The reaction mixture was then stirred for 10 min at room temperature. After the reaction completion was monitored by TLC , the reaction mixture was quenched and then extracted with CH_2Cl_2 (3×5 mL). Subsequently, the obtained organic layer was dried with Na_2SO_4 and concentrated. The residue was purified by flash chromatography on silica gel to produce **2a–2r**.

3.3 General procedure for the synthesis of 3-bromo-8-methyl-4-phenyl-6-(phenylethynyl) quinoline (3n)

The reaction was performed under argon atmosphere and then added 3,6-dibromo-4-phenyl-8-methyl-quinoline **2n** (0.90 g, 2.40 mmol), phenylacetylene (0.245 g, 2.40 mmol), CuI (0.046 g, 0.24 mmol), $Pd(PPh_3)_2Cl_2$ (0.014 g, 0.12 mmol) in a reaction flask. And reaction solvents THF (20 mL) and Et_3N (7 mL) were added to the reaction system, and placed the reaction mixture at 50 °C to stirr for 12 h. Subsequently, the phenylacetylene (0.135 g) was added into the above reaction solution per time at 12 h interval until the **2n** was consumed. After the reaction completion was monitored by TLC, the reaction solution was diluted and then extracted with CH_2Cl_2 three times. Subsequently, the obtained organic layer was dried with Na_2SO_4 and concentrated. The residue was purified by flash chromatography on silica gel to produce **3n** in 65% yield.

The colorless solid was recrystallized from the solvent (2% EtOAc in petroleum ether) in a freezer (263 K) to give pure **3n** in the form of colourless needle shaped crystals.

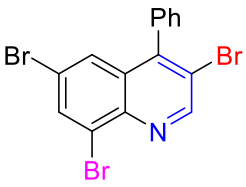
3.4 General procedure for the synthesis of 8-methyl-4-phenyl-6-(phenylethynyl)

-3-(*p*-tolyl)quinoline (4n)

The reaction was performed under argon atmosphere and then added 8-methyl-4-phenyl-6-(phenylethynyl)-3-(*p*-tolyl)quinoline **3n** (80.0 mg, 0.20 mmol), 4-tolylboronic acid (40.8 mg, 0.30 mmol), $Pd(OAc)_2$ (2.25 mg, 0.01 mmol), ligand **L1** (7.8 mg, 0.02 mmol) and K_3PO_4 (84.9 mg, 0.40 mmol) in a pressure reaction tube. And reaction solvent toluene (2 mL) was added to the reaction system, and placed the reaction mixture at 110 °C to stir for 20 h. After the reaction completion was monitored by TLC, After the mixture was cooled to room temperature, the reaction mixture was then cooled to room temperature. The reaction solution was diluted with water and then extracted with EtOAc three times. Subsequently, the obtained organic layer was dried with Na_2SO_4 and concentrated. The residue was purified by flash chromatography on silica gel to produce **4n** in 45% yield.

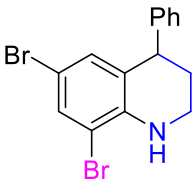
4. Characterization Data of Products

3,6,8-tribromo-4-phenylquinoline, **2a** [2]



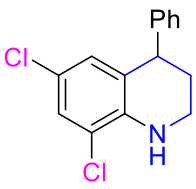
White solid, 70.2 mg, 80%, m.p.196–197 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 9.13 (s, 1H), 8.13 (s, 1H), 7.59–7.56 (m, 4H), 7.29-7.27 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 152.9, 147.3, 142.9, 136.0, 135.7, 130.7, 129.2, 129.1, 128.9, 128.3, 126.2, 121.3, 120.7. HRMS (ESI): *m/z* $[M+H]^+$ calcd for $C_{15}H_9Br_3N$: 439.8280; found: 439.8286. IR (neat, cm^{-1}): 3421, 3021, 2995, 1594, 1590, 1502, 1354, 1276, 1158, 1076, 863, 754, 697, 617, 569, 531.

6,8-dibromo-4-phenyl-1,2,3,4-tetrahydroquinoline**, 2a′**



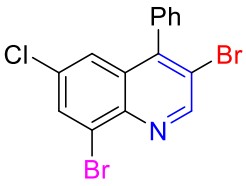
Yellow oil, 59.1 mg, 81%. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.46 (s, 1H), 7.35 (t, J = 7.2 Hz, 2H), 7.28 (d, J = 7.8 Hz, 1H), 7.12 (d, J = 8.0 Hz, 2H), 6.88 (s, 1H), 4.15 (t, J = 8.0 Hz, 1H), 3.43 – 3.29 (m, 2H), 2.22 – 2.15 (m, 1H), 2.10 – 2.04 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 145.1, 141.0, 132.5, 131.9, 128.5, 128.4, 126.6, 126.1, 108.8, 107.2, 43.0, 38.9, 30.0. HRMS (ESI): *m/z* $[M+H]^+$ calcd for $C_{15}H_{14}Br_2N$: 365.9488; found: 365.9490. IR (neat, cm^{-1}): 3421, 3021, 2995, 1594, 1590, 1502, 1354, 1276, 1158, 1076, 863, 754, 697, 617, 569, 531.

6,8-dichloro-4-phenyl-1,2,3,4-tetrahydroquinoline, **3a′** [3]



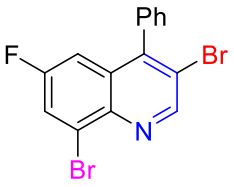
Yellow oil, 12.2 mg, 22 %. ^{1}H NMR (400 MHz, DMSO) δ = 7.32 (t, J = 7.3 Hz, 2H), 7.22 (m, 2H), 7.08 (d, J = 7.2 Hz, 2H), 6.57 (s, 1H), 5.93 (s, 1H), 4.18-4.15 (m, 1H), 3.33-3.31 (m, 1H), 3.13-3.11 (m, 1H), 2.06 – 1.87 (m, 2H). ^{13}C NMR (100 MHz, DMSO) δ = 145.6, 140.8, 128.9, 128.7, 128.2, 126.9, 126.8, 126.0, 118.0, 117.5, 42.4, 38.4, 29.2. HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{15}H_{14}Cl_2N$: 278.0498; found: 278.0499. IR (neat, cm^{-1}): 3425, 3059, 3024, 2950, 2926, 1599, 1502, 1450, 1367, 1278, 1169, 1105, 1058, 1029, 860, 832, 732, 757, 700, 640, 582, 532.

3,8-dibromo-6-chloro-4-phenylquinoline, **2b** [2]



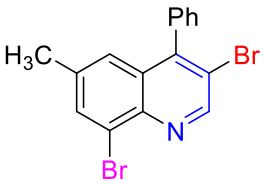
Yellow solid, 64.0 mg, 81%, m.p.170–171 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 9.13 (s, 1H), 8.03 (s, 1H), 7.57 (s, 3H), 7.43 (s, 1H), 7.29 – 7.26 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 152.8, 147.4, 142.7, 135.8, 133.6, 133.3, 130.2, 129.2, 129.1, 128.9, 126.1, 125.1, 120.8. HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{15}H_9Br_2ClN$: 395.8785; found: 395.8787. IR (neat, cm^{-1}): 3638, 3044, 2920, 1889, 1595, 1461, 1443, 1352, 1115, 1093, 1073, 1034, 987, 855, 768, 624, 571, 532.

3,8-dibromo-6-fluoro-4-phenylquinoline, **2c**



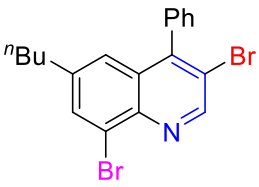
White solid, 65.9 mg, 87%, m.p. 109-111 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 9.11 (s, 1H), 7.86 – 7.84 (m, 1H), 7.57 – 7.56 (m, 3H), 7.29 – 7.26 (m, 2H), 7.11 – 7.08 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 160.0 (d, ^{1}J = 251.0 Hz), 152.5 (d, ^{4}J = 2.0 Hz), 147.7 (d, ^{4}J = 6.0 Hz), 141.5, 136.0, 130.2 (d, ^{3}J = 10.0 Hz), 129.1, 129.0, 128.9, 126.6 (d, ^{3}J = 10.0 Hz), 123.6 (d, ^{2}J = 28.0 Hz), 120.7, 110.0 (d, ^{2}J = 23.0 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -109.7. HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{15}H_9Br_2FN$: 379.9080; found: 379.9078. IR (neat, cm^{-1}): 3675, 3059, 2924, 2853, 1739, 1611, 1549, 1477, 1361, 1195, 1156, 1033, 947, 916, 862, 784, 762, 703, 630, 560.

3,8-dibromo-6-methyl-4-phenylquinoline, **2d** [2]



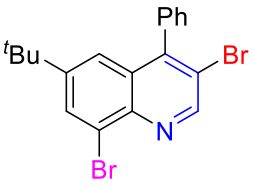
Yellow solid, 45.0 mg, 60%, m.p. 113-115 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 9.07 (s, 1H), 7.88 (s, 1H), 7.56 – 7.54 (m, 3H), 7.27 (d, J = 6.4 Hz 2H), 7.19 (s, 1H), 2.38 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 151.6, 147.3, 142.4, 138.2, 136.5, 135.2, 129.9, 129.1, 128.7, 128.6, 125.1, 124.5, 119.7, 21.4. HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{16}H_{12}Br_2N$: 375.9331; found: 375.9330. IR (neat, cm^{-1}): 3430, 3048, 2910, 1610, 1559, 1473, 1358, 1266, 1157, 1113 1036, 931, 855, 764, 734, 700, 627, 572.

3,8-dibromo-6-butyl-4-phenylquinoline, **2e**



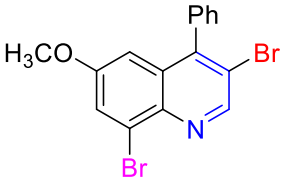
White solid, 55.7 mg, 68%, m.p. 124-125 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 9.09 (s, 1H), 7.92 (s, 1H), 7.57 – 7.55 (m, 3H), 7.30 – 7.28 (m, 2H), 7.18 (s, 1H), 2.62 (t, J = 8.0 Hz, 2H), 1.55 – 1.52 (m, 2H), 1.33 – 1.27 (m, 2H), 0.88 (t, J = 8.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 151.8, 147.6, 143.3, 142.8, 136.8, 134.6, 130.1, 129.3, 128.8, 128.7, 124.8, 124.7, 119.8, 35.5, 33.2, 22.2, 13.8. HRMS (ESI): *m/z* $[M+H]^+$ calcd for $C_{19}H_{18}Br_2N$: 417.9801; found: 417.9805. IR (neat, cm^{-1}): 3356, 3053, 2930, 2868, 1606, 1473, 1367, 1111, 1031, 945, 929, 868, 818, 745, 703, 576.

3,8-dibromo-6-(tert-butyl)-4-phenylquinoline, **2f**



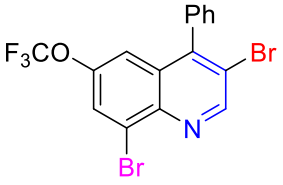
White solid, 56.7 mg, 69%, m.p. 138-139 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 9.10 (s, 1H), 8.12 (s, 1H), 7.56 – 7.54 (m, 3H), 7.37 (s, 1H), 7.32 – 7.29 (m, 2H), 1.25 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 152.0, 151.3, 148.0, 142.5, 136.6, 132.2, 129.7, 129.2, 128.8, 128.6, 124.6, 121.5, 119.6, 35.1, 30.9. HRMS (ESI): *m/z* $[M+H]^+$ calcd for $C_{19}H_{18}Br_2N$: 417.9801; found: 417.9799. IR (neat, cm^{-1}): 3660, 3035, 2962, 1883, 1603, 1543, 1468, 1370, 1256, 1199, 1029, 986, 815, 757, 697, 622, 575.

3,8-dibromo-6-methoxy-4-phenylquinoline, **2g**



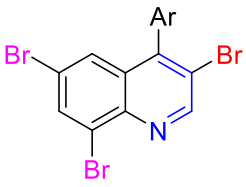
White solid, 46.9 mg, 60%, m.p. 136-137 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.99 (s, 1H), 7.72 (d, J = 1.9 Hz, 1H), 7.57-7.50 (m, 3H), 7.29 (d, J = 6.8 Hz, 2H), 6.69 (s, 1H), 3.68 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 158.0, 150.1, 146.7, 140.2, 136.8, 130.6, 129.1, 128.8, 128.8, 125.9, 125.3, 120.2, 104.8, 55.6. HRMS (ESI): *m/z* $[M+H]^+$ calcd for $C_{16}H_{12}Br_2NO$: 391.9280; found: 391.9281. IR (neat, cm^{-1}): 3670, 3050, 2971, 1608, 1474, 1403, 1232, 1167, 1104, 1041, 871, 842, 764, 703, 636, 571, 521.

3,8-dibromo-4-phenyl-6-(trifluoromethoxy)quinoline, **2h**



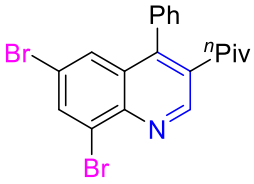
White solid, 71.2 mg, 80%, m.p. 98-99 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 9.17 (s, 1H), 7.95 (s, 1H), 7.59 – 7.56 (m, 3H), 7.30 – 7.26 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 153.2, 148.2, 147.0, 142.7, 135.7, 129.9, 129.3, 129.1, 128.9, 127.1, 126.7, 121.6, 120.9, 119.1, 116.8. ^{19}F NMR (376 MHz, $CDCl_3$) δ -57.9. HRMS (ESI): *m/z* $[M+H]^+$ calcd for $C_{16}H_9Br_2F_3NO$: 445.8998; found: 445.9000. IR (neat, cm^{-1}): 3398, 3053, 2974, 2882, 1613, 1551, 1478, 1441, 1399, 1260, 1198, 1171, 1049, 966, 879, 751, 703, 576, 558.

3,6,8-tribromo-4-(4-fluorophenyl)quinoline, **2i**



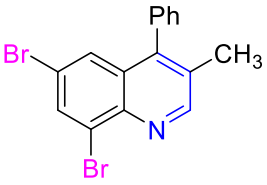
White solid, 81.3 mg, 89%, m.p. 159-161 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ = 9.25 (s, 1H), 8.42 (s, 1H), 7.48 – 7.46 (m, 5H). ^{13}C NMR (100 MHz, DMSO-d_6) δ = 162.6 (d, ^{1}J = 245.0 Hz), 153.2, 146.2, 142.3, 135.7, 131.8 (d, ^{4}J = 4.0 Hz), 131.7 (d, ^{3}J = 9.0 Hz), 130.4, 128.0, 126.3, 121.0, 121.0, 116.2 (d, ^{2}J = 22.0 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -111.9. HRMS (ESI): *m/z* $[M+H]^+$ calcd for $C_{15}H_8Br_3FN$: 457.8185; found: 457.8181. IR (neat, cm^{-1}): 3429, 3069, 2925, 1696, 1604, 1583, 1508, 1349, 1241, 1227, 1018, 988, 866, 836, 793, 740, 653, 578, 551.

6,8-dibromo-3-pentyl-4-phenylquinoline, **2j**



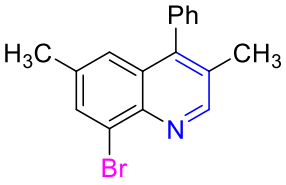
Yellow solid, 71.5 mg, 83%, m.p. 80-81 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.96 (s, 1H), 8.07 (d, J = 4.0 Hz, 1H), 7.53 – 7.49 (m, 4H), 7.23 – 7.20 (m, 2H), 2.58 – 2.54 (m, 2H), 1.51 – 1.47 (m, 2H), 1.19 – 1.15 (m, 5H), 0.80 – 0.77 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 153.3, 145.7, 142.7, 135.5, 134.9, 134.7, 130.0, 129.3, 128.7, 128.5, 128.3, 126.0, 119.9, 31.4, 31.0, 30.7, 22.2, 13.8. HRMS (ESI): *m/z* $[M+H]^+$ calcd for $C_{20}H_{20}Br_2N$: 431.9957; found: 431.9959. IR (neat, cm^{-1}): 3431, 3058, 2954, 2925, 2841, 1585, 1470, 1395, 1349, 1156, 1071, 996, 962, 863, 765, 702, 665, 578, 522.

6,8-dibromo-3-methyl-4-phenylquinoline, **2k**



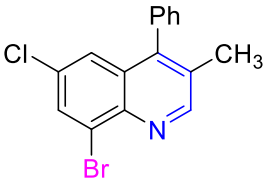
Yellow solid, 46.5 mg, 62%, m.p. 147-149 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.95 (s, 1H), 8.07 (s, 1H), 7.55 – 7.51 (m, 4H), 7.23 – 7.21 (m, 2H), 2.27 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 153.6, 146.1, 142.8, 135.8, 134.7, 130.3, 129.7, 129.1, 128.9, 128.5, 128.1, 126.0, 119.9, 17.7. HRMS (ESI): *m/z* $[M+H]^+$ calcd for $C_{16}H_{12}Br_2N$: 375.9331; found: 375.9330. IR (neat, cm^{-1}): 3664, 3073, 2972, 1582, 1470, 1440, 1349, 1291, 1152, 1089, 953, 866, 832, 704, 665, 523.

8-bromo-3,6-dimethyl-4-phenylquinoline, **2l**



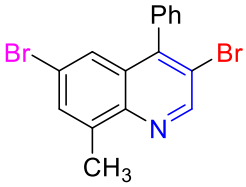
White solid, 33.6 mg, 54%, m.p. 132-133 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.90 (s, 1H), 7.84 (d, J = 4.0 Hz, 1H), 7.56 – 7.49 (m, 3H), 7.24 – 7.22 (m, 2H), 7.14 (s, 1H), 2.37 (s, 3H), 2.25 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 152.4, 146.2, 142.5, 136.9, 136.7, 134.0, 129.1, 128.8, 128.7, 128.0, 124.8, 124.4, 21.4, 17.6. HRMS (ESI): *m/z* $[M+H]^+$ calcd for $C_{17}H_{15}BrN$: 312.0382; found: 312.0385. IR (neat, cm^{-1}): 3367, 3055, 2917, 2849, 1673, 1610, 1479, 1441, 1359, 1293, 1179, 1135, 1075, 1026, 934, 864, 787, 766, 631, 527.

8-bromo-6-chloro-3-methyl-4-phenylquinoline, **2m**



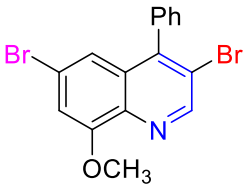
Yellow solid, 41.7 mg, 63%, m.p. 112-114 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ = 9.00 (s, 1H), 8.17 (s, 1H), 7.62 – 7.53 (m, 3H), 7.34 – 7.31 (m, 2H), 7.25 (s, 1H), 2.23 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6) δ = 154.0, 145.6, 141.9, 135.2, 131.9, 131.1, 130.6, 129.2, 129.1, 128.7, 128.6, 126.1, 124.2, 17.4. HRMS (ESI): *m/z* $[M+H]^+$ calcd for $C_{16}H_{12}BrClN$: 331.9836; found: 331.9834. IR (neat, cm^{-1}): 3434, 3014, 2824, 1627, 1530, 1474, 1354, 1025, 769, 703, 624, 584, 526.

3,6-dibromo-8-methyl-4-phenylquinoline, **2n**



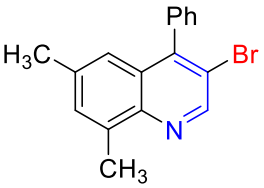
White solid, 60.0 mg, 80%, m.p. 110-112 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 9.05 (s, 1H), 7.66 (s, 1H), 7.56 – 7.53 (m, 3H), 7.46 (d, *J* = 4.0 Hz, 1H), 7.29 – 7.27 (m, 2H), 2.81 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 151.1, 146.9, 144.8, 140.0, 136.6, 132.9, 130.0, 129.3, 128.9, 128.7, 126.4, 121.6, 119.6, 18.0. HRMS (ESI): *m/z* $[M+H]^+$ calcd for $C_{16}H_{12}Br_2N$: 375.9331; found: 375.9333. IR (neat, cm^{-1}): 3674, 3053, 2960, 2920, 1589, 1478, 1440, 1374, 1360, 1240, 1194, 1144, 1093, 1073, 913, 860, 797, 763, 709, 619, 571, 531.

3,6-dibromo-8-methoxy-4-phenylquinoline, **2o**



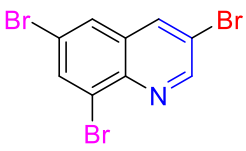
White solid, 54.7 mg, 70%, m.p. 133-134 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 9.03 (s, 1H), 7.56 – 7.55 (m, 3H), 7.29 – 7.27 (m, 2H), 7.18 (d, *J* = 4.0 Hz, 1H), 7.15 (d, *J* = 4.0 Hz, 1H), 4.10 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 156.2, 150.9, 146.8, 137.8, 136.4, 130.7, 129.2, 128.9, 128.8, 121.9, 120.6, 120.2, 112.0, 56.6. HRMS (ESI): *m/z* $[M+H]^+$ calcd for $C_{16}H_{12}Br_2NO$: 391.9280; found: 391.9278. IR (neat, cm^{-1}): 3145, 3045, 1589, 1547, 1452, 1420, 1388, 1269, 1152, 1081, 1001, 906, 841, 765, 699, 612, 589, 529.

3-bromo-6,8-dimethyl-4-phenylquinoline, **2p**



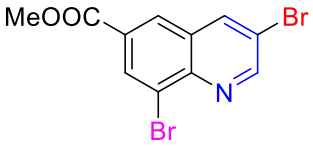
White solid, 32.3 mg, 52%, m.p. 76-78 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.99 (s, 1H), 7.55 – 7.51 (m, 3H), 7.41 (s, 1H), 7.30 – 7.28 (m, 2H), 7.06 (s, 1H), 2.80 (s, 3H), 2.36 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 149.8, 147.0, 144.6, 137.5, 137.3, 137.1, 132.0, 129.3, 129.0, 128.5, 128.4, 123.2, 118.7, 21.8, 18.2. HRMS (ESI): *m/z* $[M+H]^+$ calcd for $C_{17}H_{15}BrN$: 312.0382; found: 312.0384. IR (neat, cm^{-1}): 3537, 3047, 2924, 2851, 1677, 1618, 1575, 1552, 1484, 1386, 1217, 1071, 908, 852, 798, 764, 702, 647, 577, 530.

3,6,8-tribromoquinoline, **2q**[4]



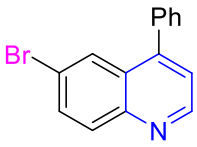
Yellow solid, 56.6 mg, 78%, m.p. 141-143 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ = 9.09 (d, J = 4.0 Hz, 1H), 8.78 (d, J = 4.0 Hz, 1H), 8.37 (d, J = 4.0 Hz, 1H), 8.31 (d, J = 4.0 Hz, 1H). ^{13}C NMR (100 MHz, DMSO-d_6) δ = 153.0, 142.1, 137.8, 136.2, 131.2, 130.0, 125.8, 120.8, 119.4. HRMS (ESI): m/z $[M+H]^+$ calcd for C_9H_5BrN: 363.7967; found: 363.7968. IR (neat, cm^{-1}): 3427, 3051, 2987, 1837, 1589, 1579, 1541, 1458, 1357, 1327, 1232, 1197, 1083, 1072, 968, 895, 816, 681, 595, 527.

Methyl 3,8-dibromoquinoline-6-carboxylate, **2r**



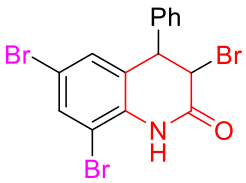
Yellow solid, 34.3 mg, 50%, m.p. 83-84 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 9.06 (d, J = 2.0 Hz, 1H), 8.60 (d, J = 1.6 Hz, 1H), 8.42 (d, J = 1.2 Hz, 1H), 8.40 (d, J = 2.0 Hz, 1H), 4.01 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 165.0, 154.2, 145.2, 138.8, 132.9, 129.7, 129.5, 129.2, 125.3, 119.1, 52.8. HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{11}H_8Br_2NO_2$: 343.8916; found: 343.8914. IR (neat, cm^{-1}): 3419, 3072, 2829, 1726, 1609, 1547, 1464, 1434, 1338, 1256, 1077, 962, 887, 786, 763, 682, 600, 536.

6-bromo-4-phenylquinoline, **2a1**[5]



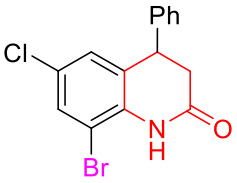
Yellow solid, 15.3 mg (0.6 mmol), 9 %, m.p. 61-63 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.93 (d, J = 4.0 Hz, 1H), 8.05-8.03 (m, 2H), 7.78 (dd, J = 8.9, 2.0 Hz, 1H), 7.56-7.46 (m, 2H), 7.33 (d, J = 4.3 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 152.0, 147.7, 147.2, 137.3, 132.8, 131.6, 129.4, 128.8, 128.7, 128.0, 122.0, 120.9. HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{15}H_{11}BrN$: 284.0069; found: 284.0067. IR (neat, cm^{-1}): 3433, 3055, 2994, 1601, 1555, 1488, 1349, 1263, 1156, 1058, 968, 876, 824, 778, 698, 322, 598, 553.

3,6,8-tribromo-4-phenyl-3,4-dihydroquinolin-2(1H)-one, **2a2**



White oil, 32.3 mg (0.6 mmol), 12 %. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.99 (s, 1H), 7.69 (s, 1H), 7.33 – 7.32 (m, 1H), 7.30 – 7.25 (m, 3H), 7.02 – 7.00 (m, 2H), 4.65 – 4.64 (m, 1H), 4.52-4.51 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 164.4, 134.2, 133.3, 132.0, 129.5, 128.6, 126.2, 116.4, 110.4, 52.1, 44.6. HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{15}H_{11}Br_3NO$: 457.8385; found: 457.8388. IR (neat, cm^{-1}): 3432, 3077, 2883, 2820, 1692, 1474, 1349, 1049, 904, 729, 695, 510, 597, 547.

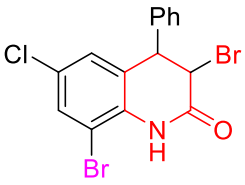
8-bromo-6-chloro-4-phenyl-3,4-dihydroquinolin-2(1*H*)-one, **2b1**



Pale yellow solid, 3.3 mg, 5%, m.p. 138-140 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.91 (s, 1H), 7.45 (s, 1H), 7.39 – 7.30 (m, 3H), 7.17 (d, J = 8.0 Hz, 2H), 6.85 (s, 1H), 4.28 (t, J = 8.0 Hz, 1H), 2.92 (d, J = 8.0 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 169.0, 139.7, 133.8, 130.8, 129.9, 129.2, 128.4, 127.8, 127.7, 127.6, 109.9, 42.5, 37.8. HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{15}H_{12}BrClNO$: 335.9785; found:

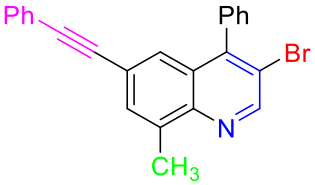
335.9786. IR (neat, cm^{-1}): 3382, 3072, 2982, 1689, 1595, 1467, 1338, 1163, 1089, 863, 759, 703, 671, 553, 502.

3,8-dibromo-6-chloro-4-phenyl-3,4-dihydroquinolin-2(1*H*)-one, **2b2**



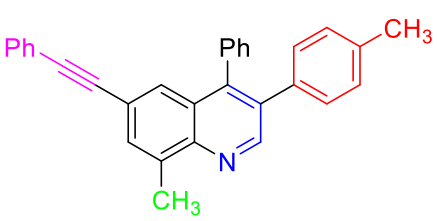
Yellow solid, 6.6 mg, 8%, m.p. 125-127 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.92 (s, 1H), 7.57 (s, 1H), 7.33 – 7.28 (m, 3H), 7.20 (s, 1H), 7.03 – 7.01 (m, 2H), 4.65 – 4.64 (m, 1H), 4.52 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 164.5, 137.3, 132.8, 131.6, 129.5, 129.4, 129.2, 128.6, 127.2, 125.8, 110.2, 52.2, 44.6. HRMS (ESI): *m/z* $[M+H]^+$ calcd for $C_{15}H_{11}Br_2ClNO$: 413.8890; found: 413.8893. IR (neat, cm^{-1}): 3228, 3064, 2925, 1687, 1600, 1570, 1493, 1426, 1354, 1262, 1100, 1081, 946, 866, 761, 697, 581, 565, 525.

3-bromo-8-methyl-4-phenyl-6-(phenylethynyl) quinoline, **3n**



Yellow solid, 619.4 mg, 65%, m.p. 146-148 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 9.05 (s, 1H), 7.69 (s, 1H), 7.58 – 7.56 (m, 3H), 7.51 (s, 3H), 7.33 (s, 5H), 2.83 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 151.2, 147.4, 145.6, 137.8, 136.9, 132.2, 131.7, 129.4, 128.8, 128.7, 128.6, 128.4, 127.6, 122.8, 122.2, 119.4, 90.8, 89.2, 18.1. HRMS (EI): *m/z* $[M+H]^+$ calcd for $C_{24}H_{17}BrN$: 398.0539; found: 398.0542. IR (neat, cm^{-1}): 3074, 3046, 2922, 1609, 1550, 1480, 1441, 1418, 1379, 1234, 1145, 910, 870, 799, 756, 705, 691, 598, 522.

8-methyl-4-phenyl-6-(phenylethynyl)-3-(*p*-tolyl)quinoline, **4n**



White solid, 36.8 mg, 45%, m.p. 143-144 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 9.01 (s, 1H), 7.70 (d, *J* = 4.0 Hz, 2H), 7.53 – 7.51 (m, 2H), 7.39 – 7.37 (m, 3H), 7.34 – 7.33 (m, 3H), 7.22 – 7.20 (m, 2H), 7.05 (s, 4H), 2.88 (s, 3H), 2.31 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 151.3, 146.2, 145.3, 137.4, 136.8, 136.5, 135.1, 133.5, 131.8, 131.7, 130.6, 130.0, 128.9, 128.4, 128.4, 128.3, 128.0, 127.7, 127.3, 127.1, 123.1, 121.3, 90.2, 89.7, 21.1, 18.3. HRMS (EI): *m/z* $[M+H]^+$ calcd for $C_{31}H_{24}N$: 410.1903; found: 410.1905. IR (neat, cm^{-1}): 3357, 3186, 3054, 2921, 2851, 1758, 1659, 1632, 1442, 1384, 1262, 1184, 1113., 1022, 925, 877, 826, 754, 701, 606, 557, 532.

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[2] S. Deng, W. Ouyang, J. Bai, X.-R. Song, R. Yang and Q. Xiao, Synthesis of Multibromo-Substituted Quinolines by NBS-Mediated Cascade Electrophilic Bromination/Cyclization of N-(3-Phenylprop-2-

ynyl)anilines. *Synthesis,* 2021, **53**, 2469-2476.

[3] B. Kaboudin, M. Sohrabi and F. Kazemi, Synthesis of julolidines *via* one-pot cascade three component Povarov reaction in the presence of silica sulfuric acid. J. Heterocyclic Chem. 2021, 58, 1594-1600

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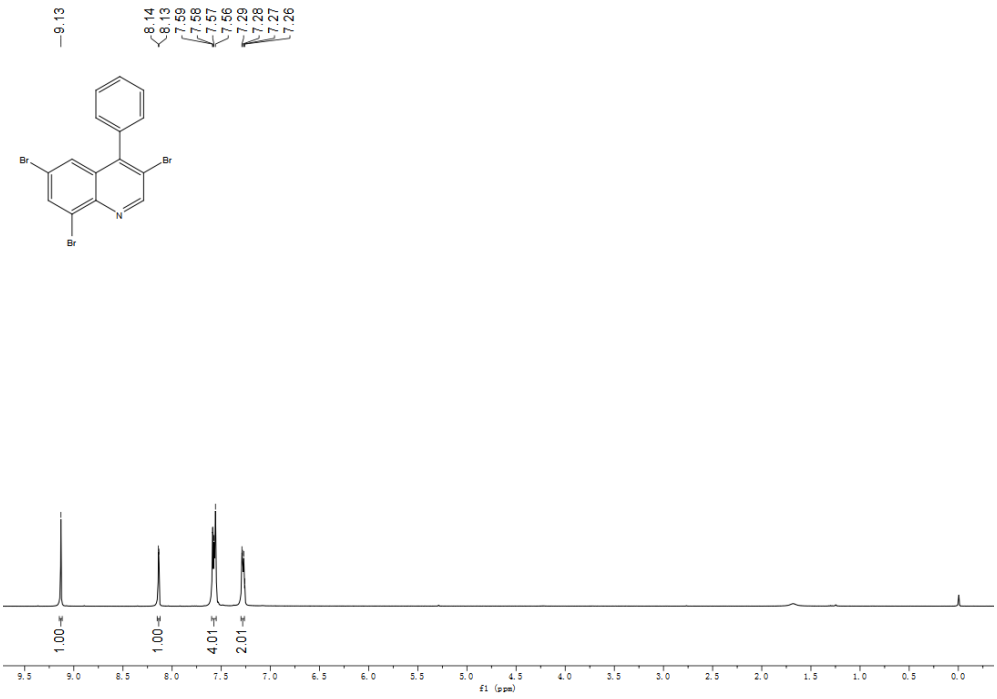
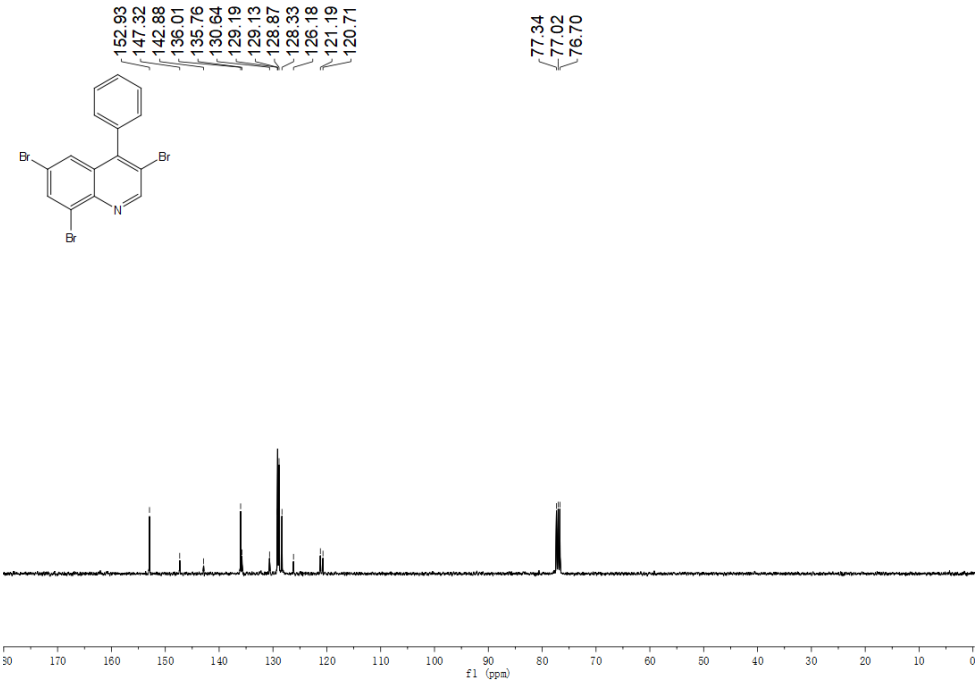
[5] X. Xu, Y. Yang, X. Zhang and W. Yi, Direct Synthesis of Quinolines via Co(III)-Catalyzed and DMSO-Involved C−H Activation/Cyclization of Anilines with Alkynes. *Org. Lett.* 2018, **20**, 566−569.

5. NMR Spectra for Compounds

3,6,8-tribromo-4-phenylquinoline, **2a**

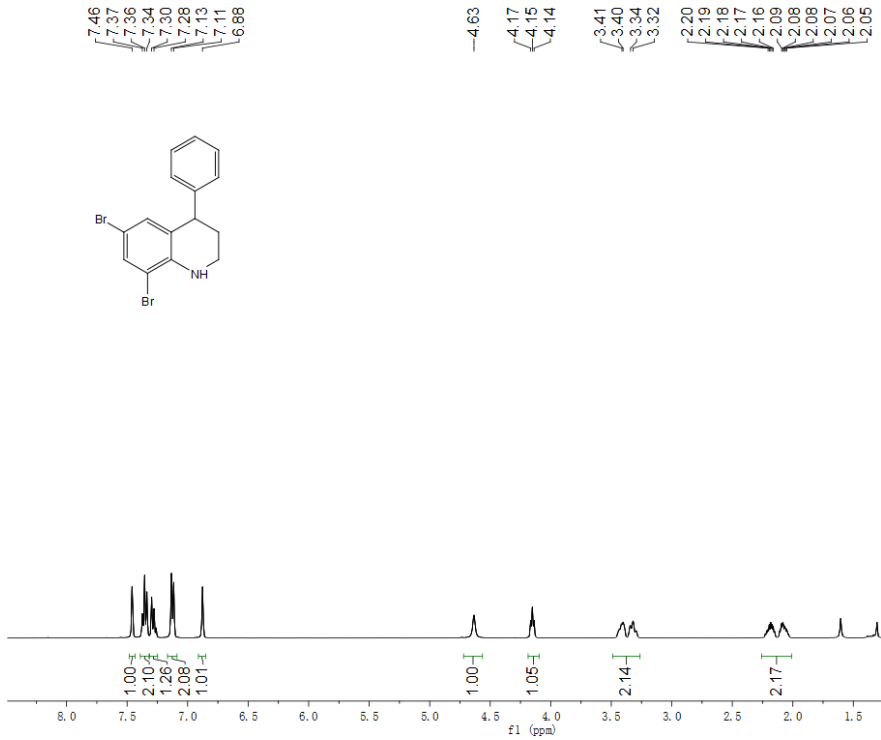


^{1}H NMR (25C°, 400 MHz, $CDCl_3$)

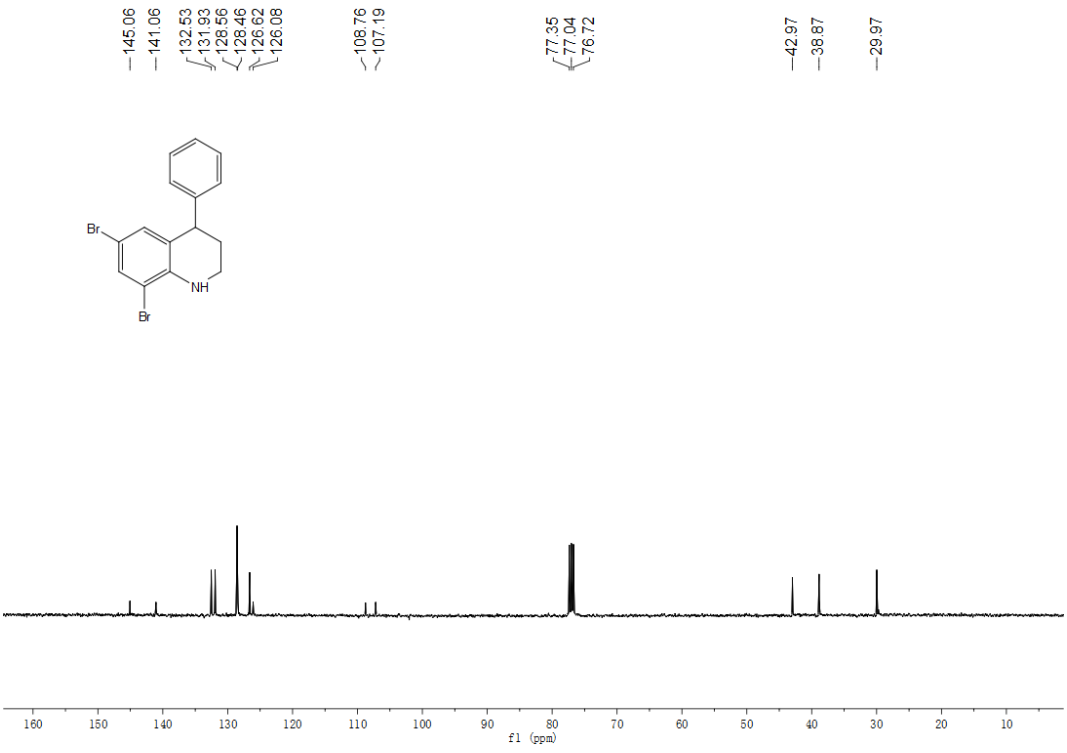


^{13}C NMR (25C°, 100 MHz, $CDCl_3$)

6,8-dibromo-4-phenyl-1,2,3,4-tetrahydroquinoline**, 2a′**

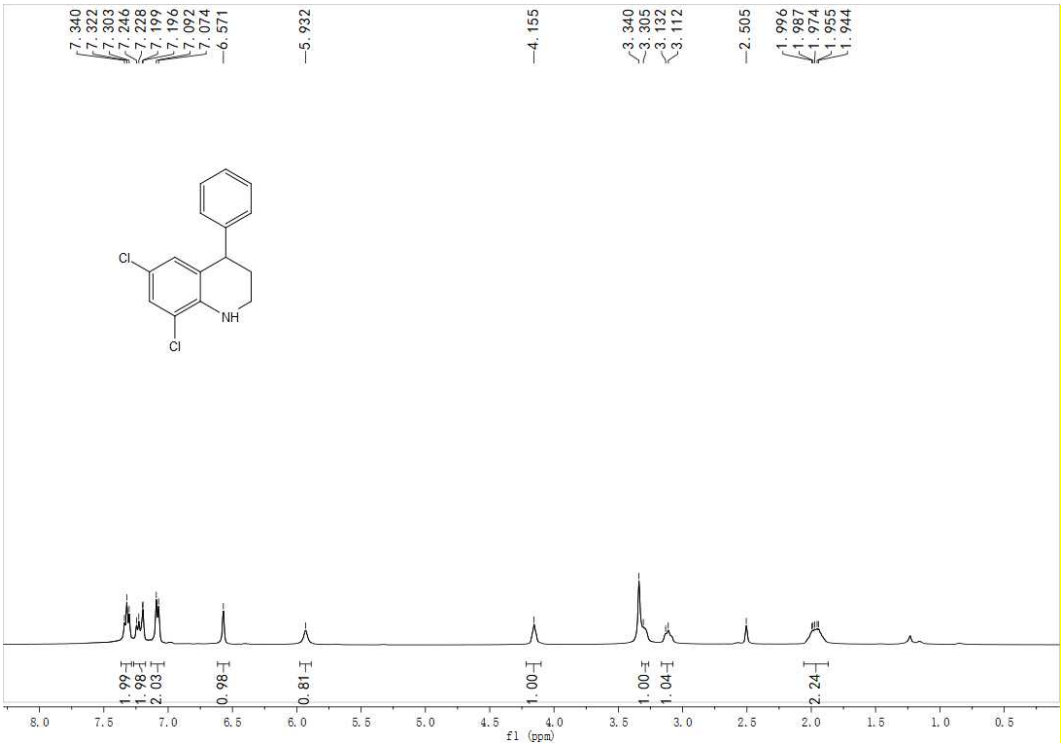


^{1}H NMR (25C°, 400 MHz, $CDCl_3$)

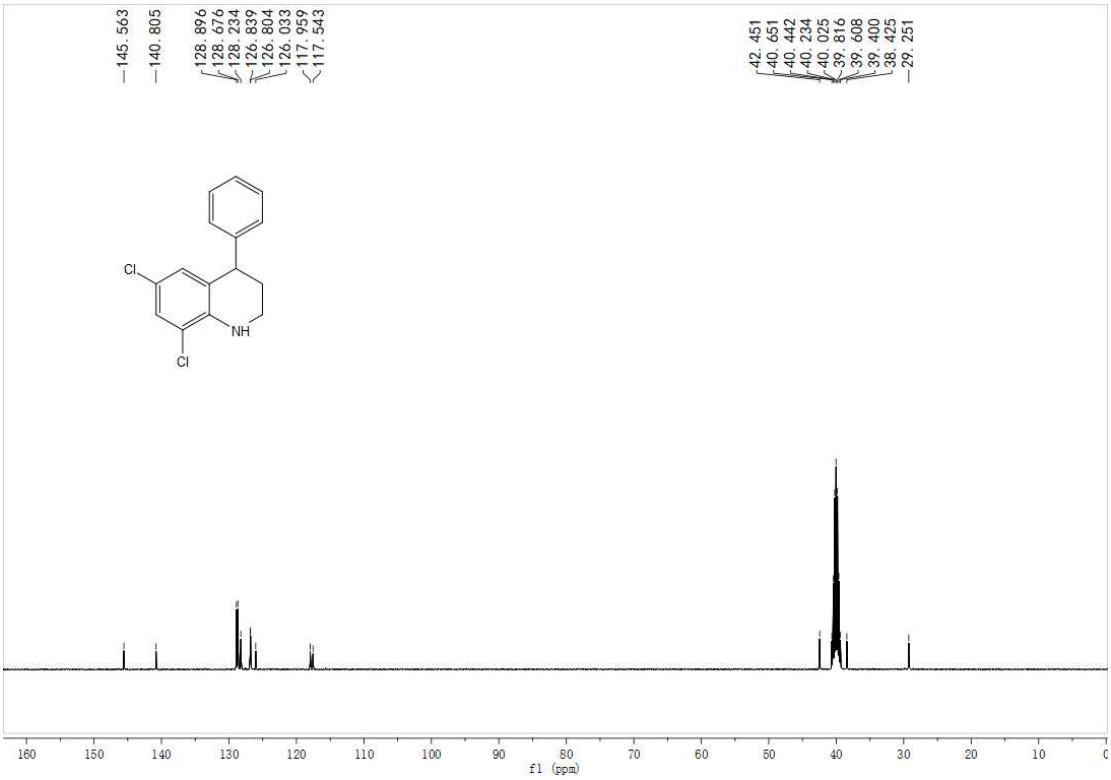


^{13}C NMR (25C°, 100 MHz, $CDCl_3$)

6,8-dichloro-4-phenyl-1,2,3,4-tetrahydroquinoline, **3a′**

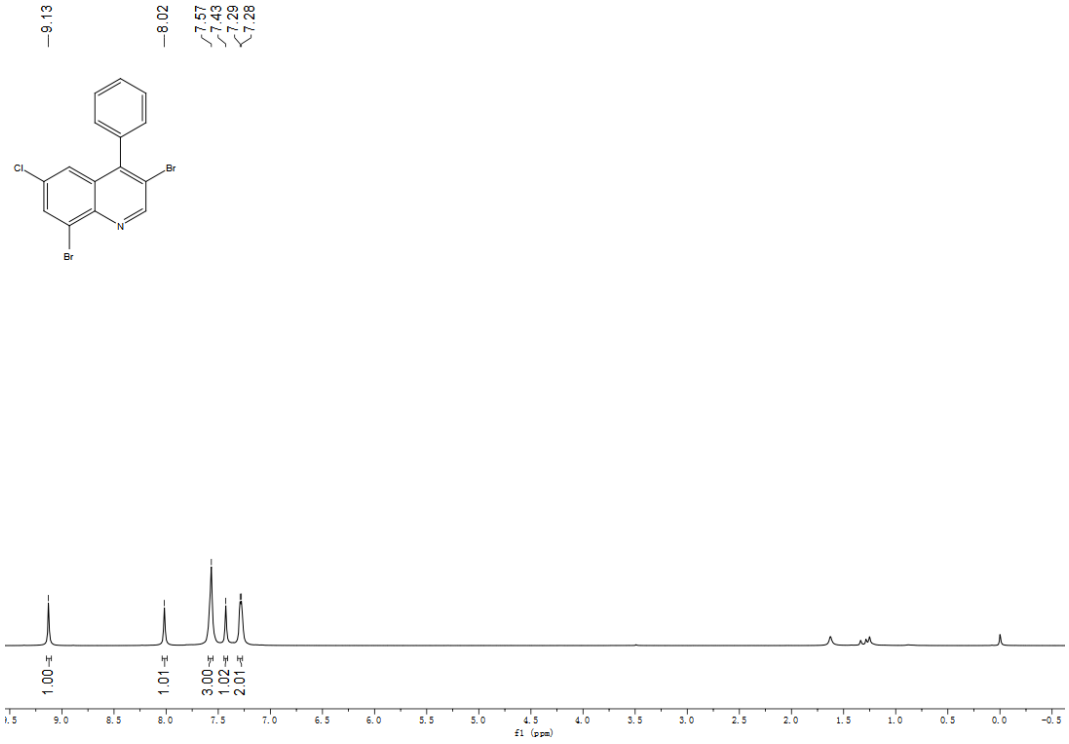


^{1}H NMR (25℃, 400 MHz, DMSO)

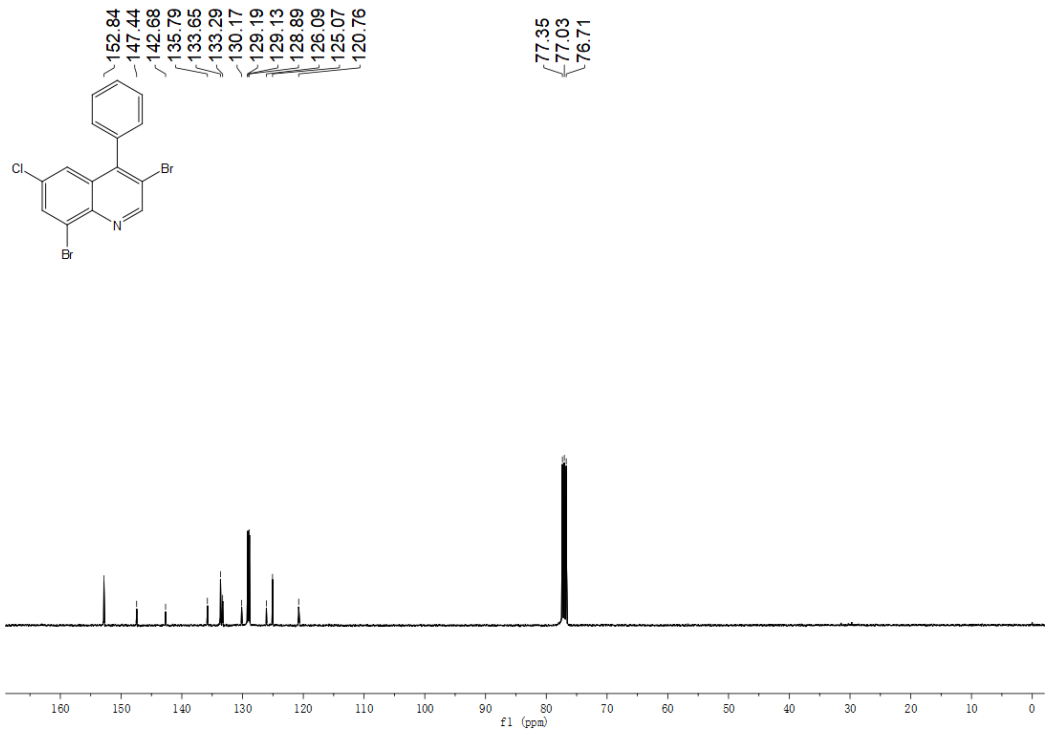


^{13}C NMR (25℃, 100 MHz, DMSO)

3,8-dibromo-6-chloro-4-phenylquinoline, **2b**

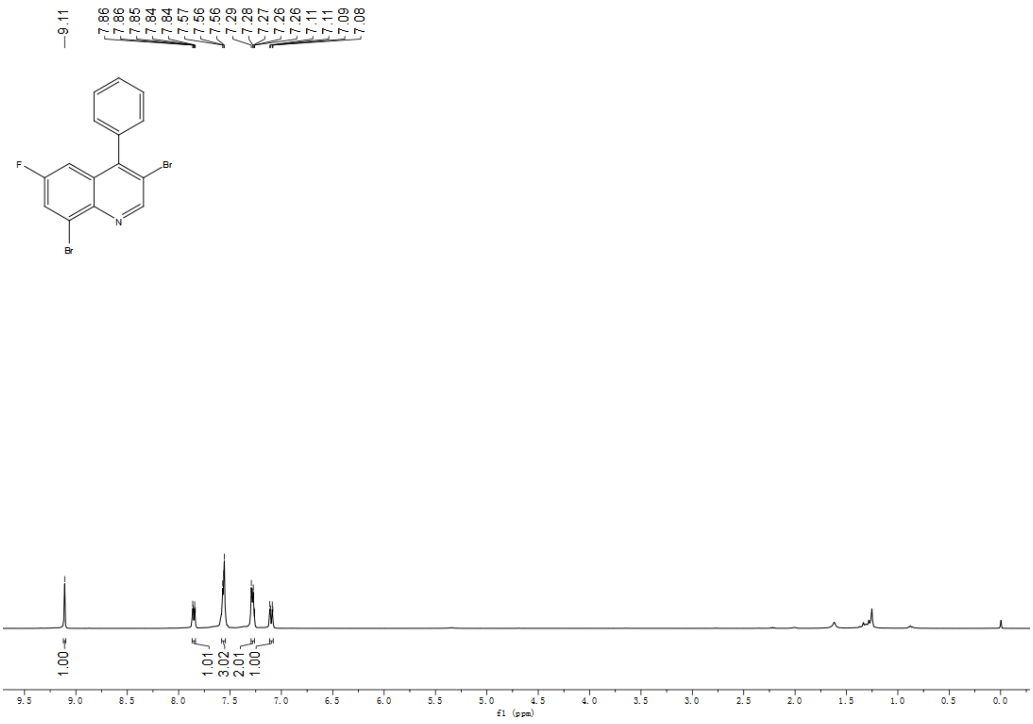


^{1}H NMR (25℃, 400 MHz, $CDCl_3$)

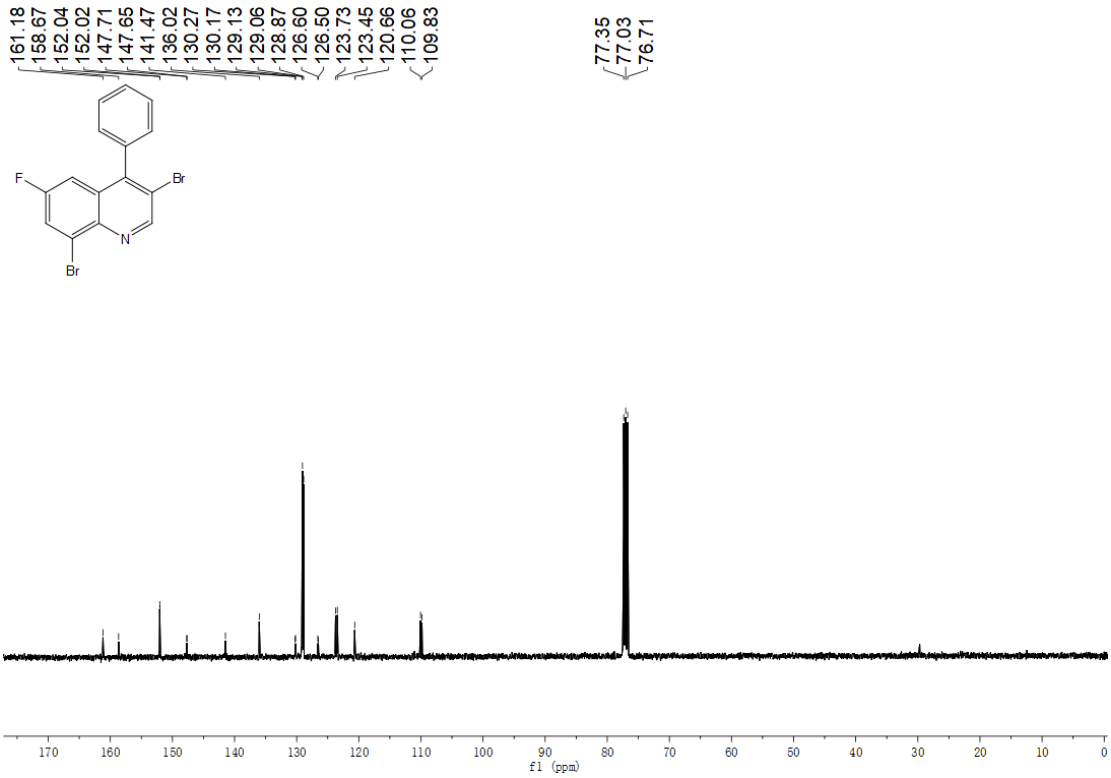


^{13}C NMR (25℃, 100 MHz, $CDCl_3$)

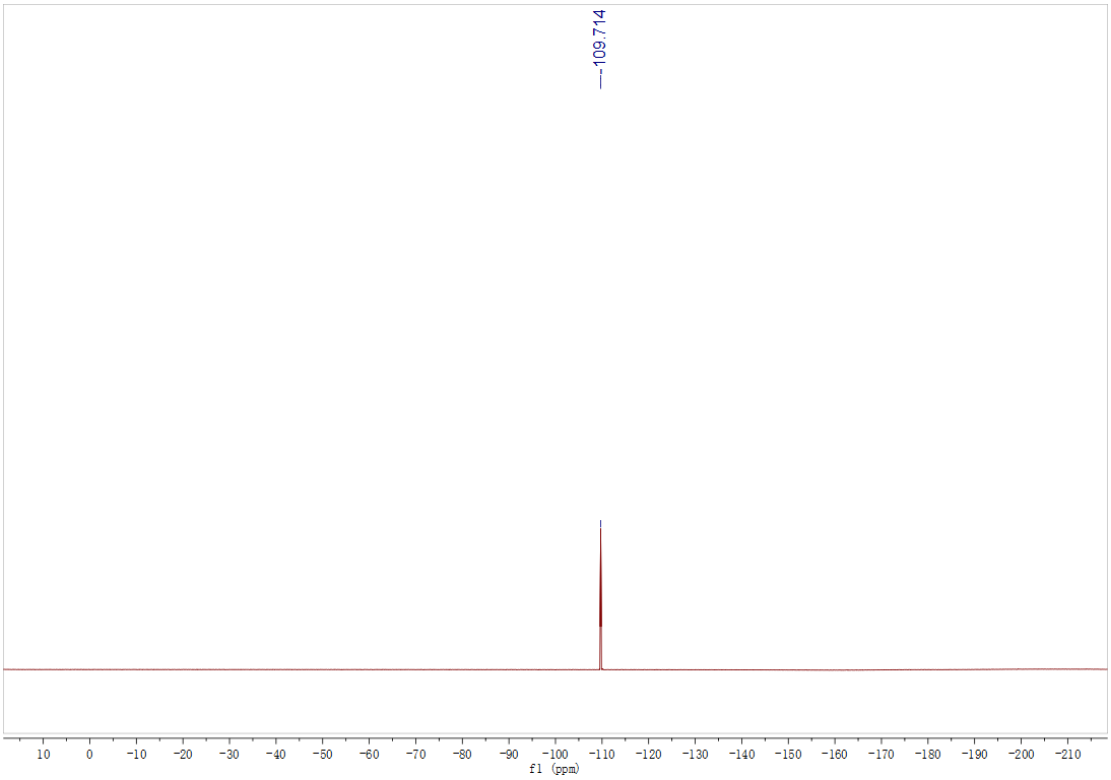
3,8-dibromo-6-fluoro-4-phenylquinoline, **2c**



^{1}H NMR (25℃, 400 MHz, $CDCl_3$)

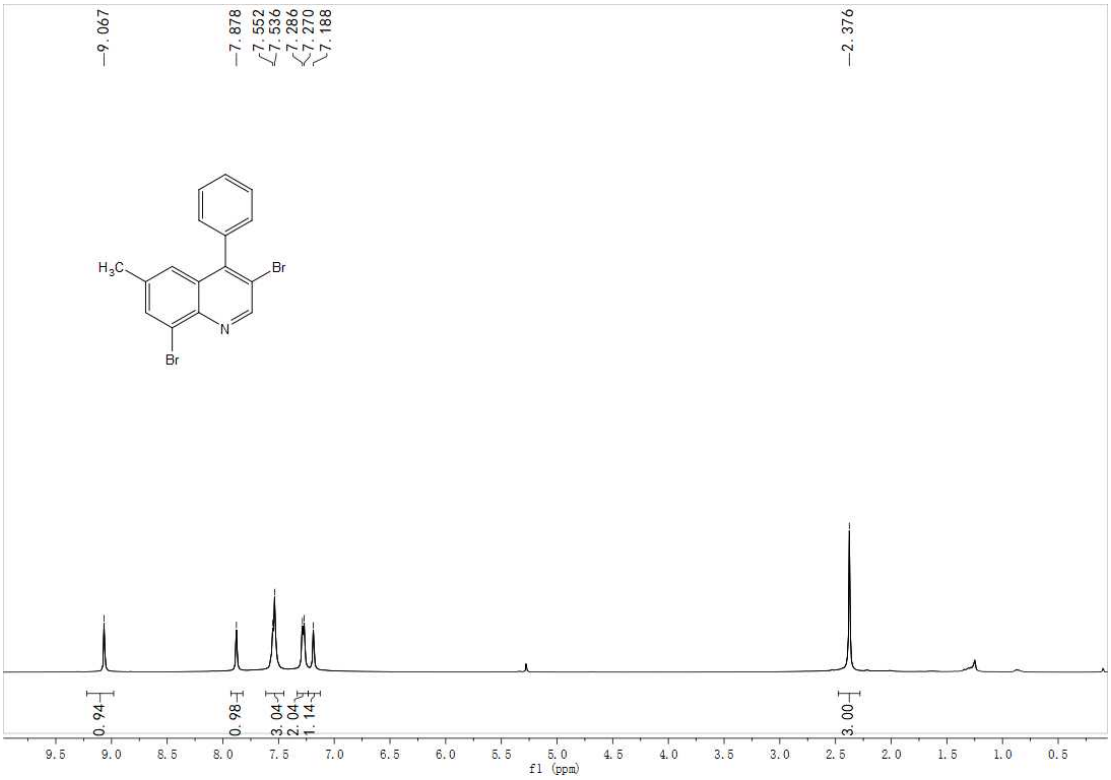


^{13}C NMR (25℃, 100 MHz, $CDCl_3$)

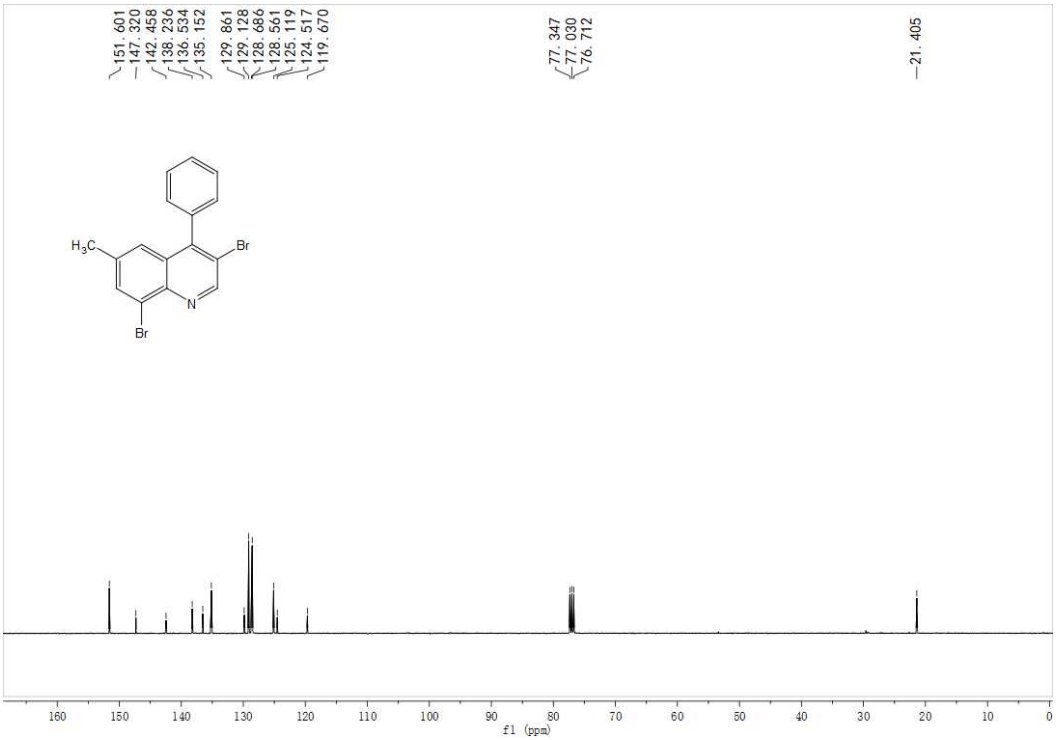


^{19}F NMR (25℃, 376 MHz, $CDCl_3$)

3,8-dibromo-6-methyl-4-phenylquinoline, **2d**

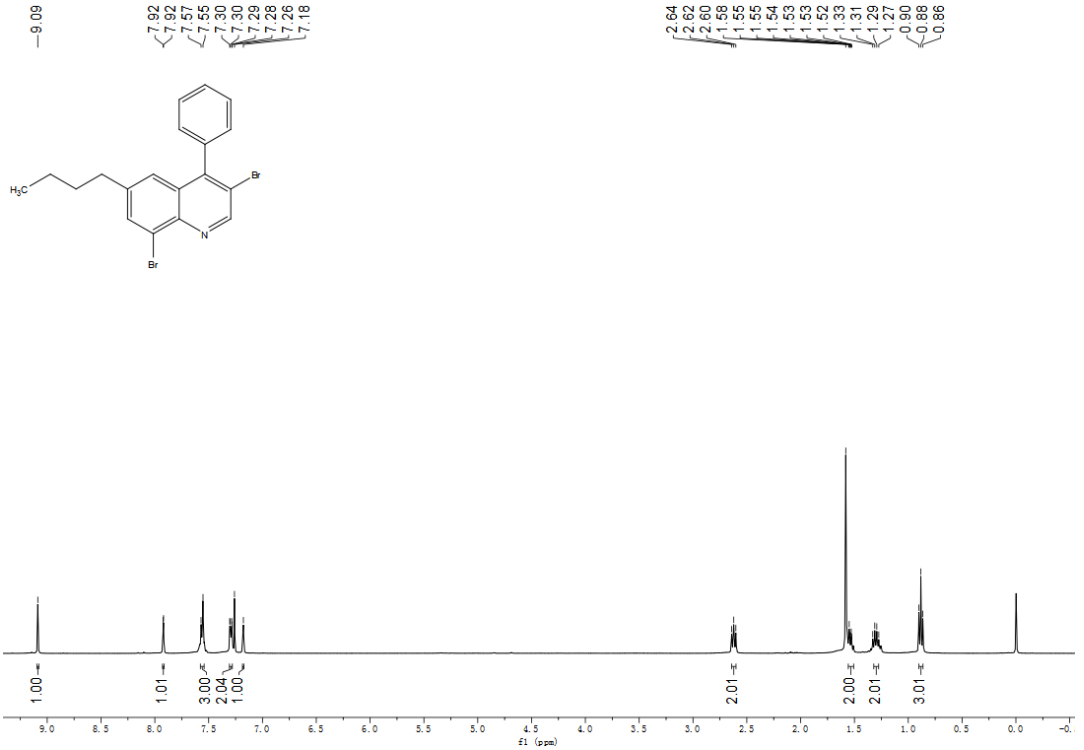


^{1}H NMR (25℃, 400 MHz, $CDCl_3$)

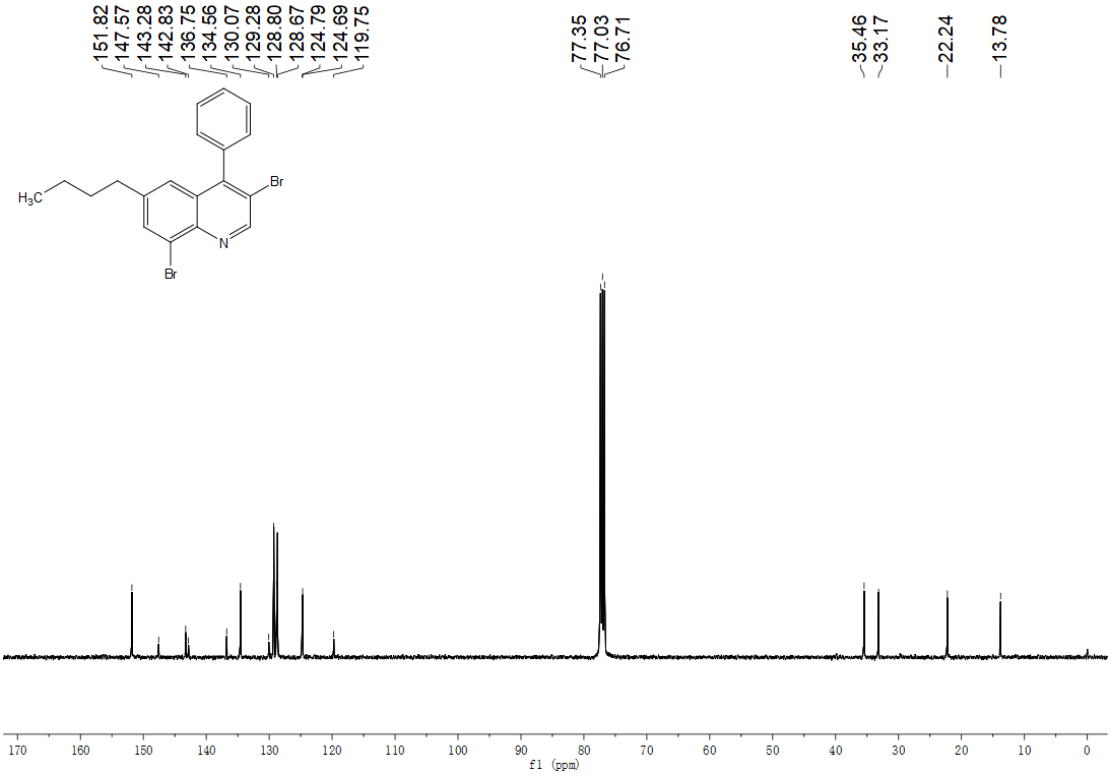


^{13}C NMR (25℃, 100 MHz, $CDCl_3$)

3,8-dibromo-6-butyl-4-phenylquinoline, **2e**

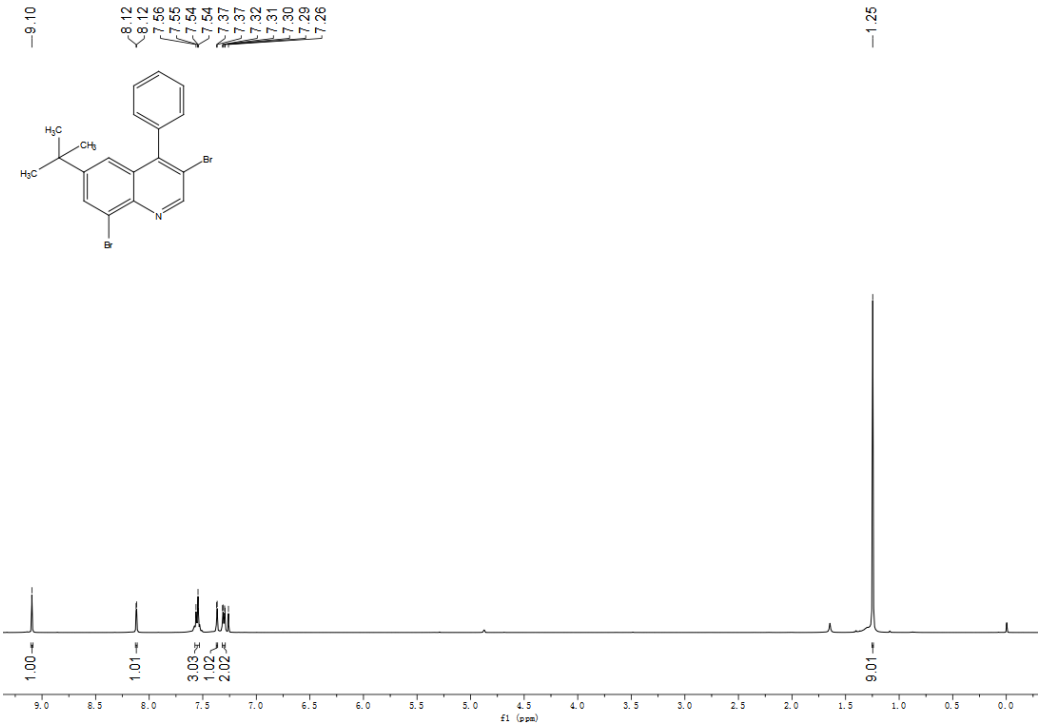


^{1}H NMR (25℃, 400 MHz, $CDCl_3$)

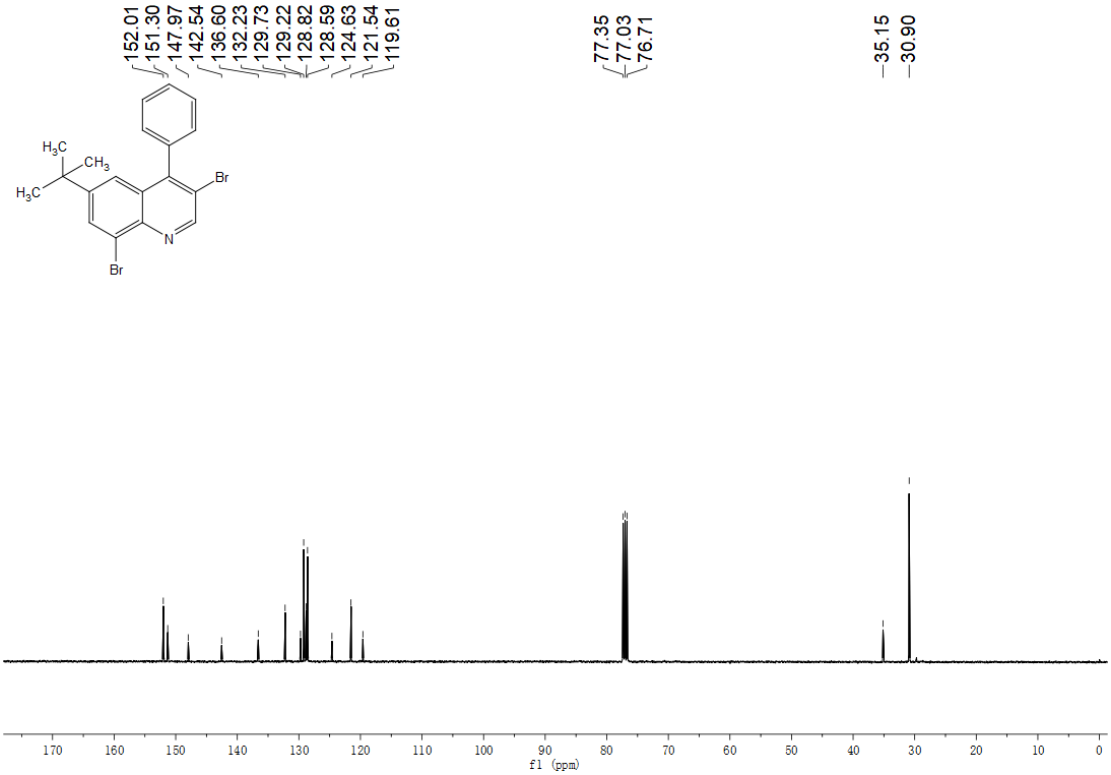


^{13}C NMR (25℃, 100 MHz, $CDCl_3$)

3,8-dibromo-6-(tert-butyl)-4-phenylquinoline, **2f**

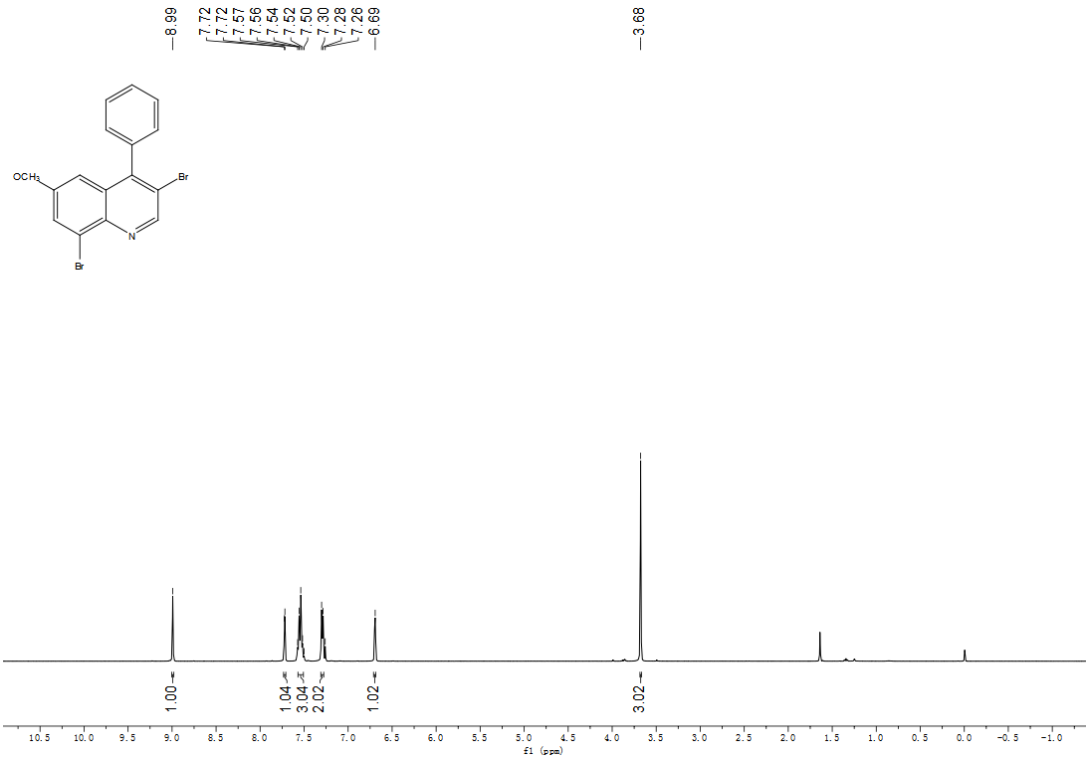


^{1}H NMR (25℃, 400 MHz, $CDCl_3$)

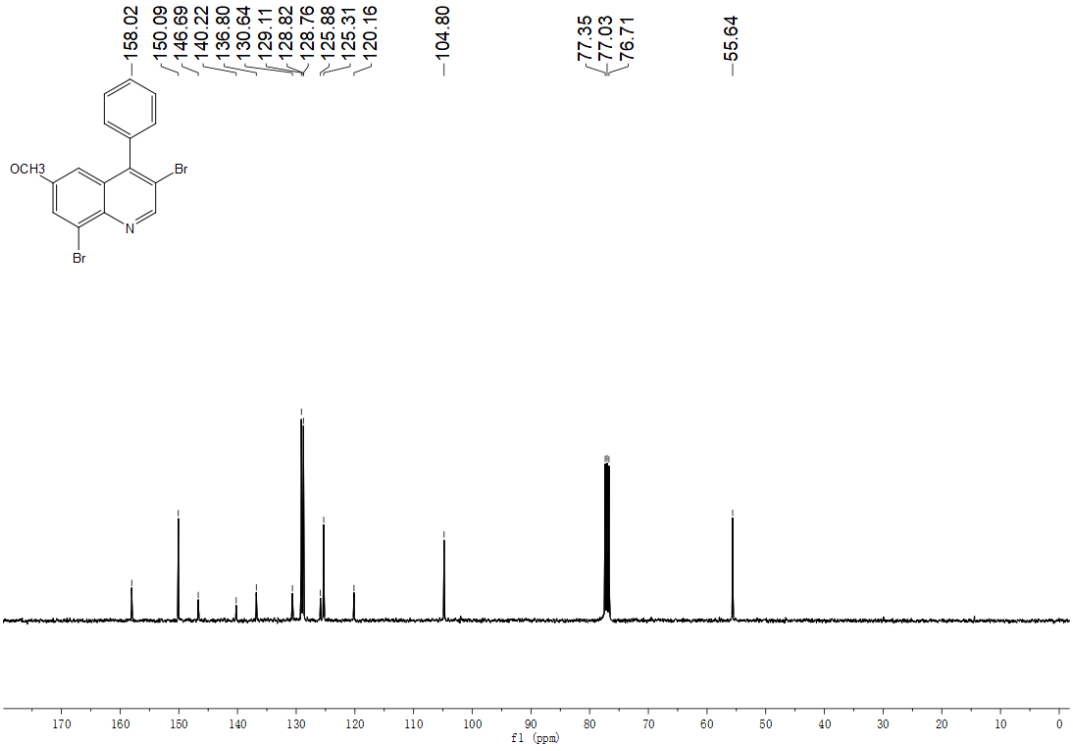


^{13}C NMR (25℃, 100 MHz, $CDCl_3$)

3,8-dibromo-6-methoxy-4-phenylquinoline, **2g**

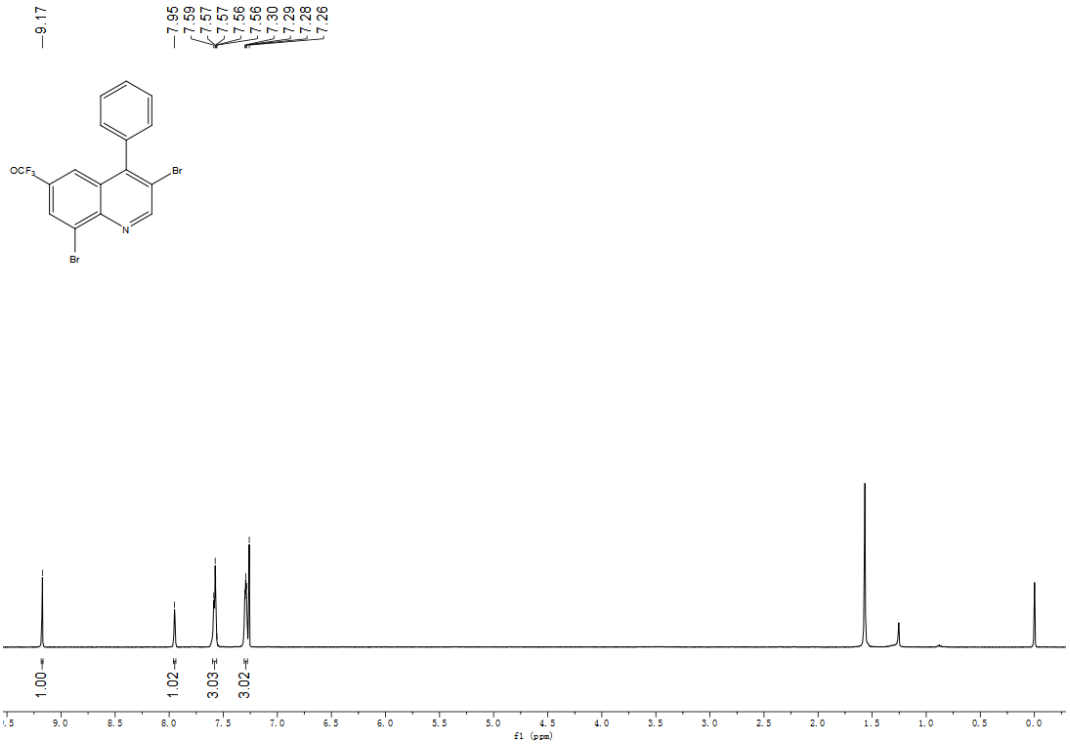


^{1}H NMR (25℃°, 400 MHz, $CDCl_3$)

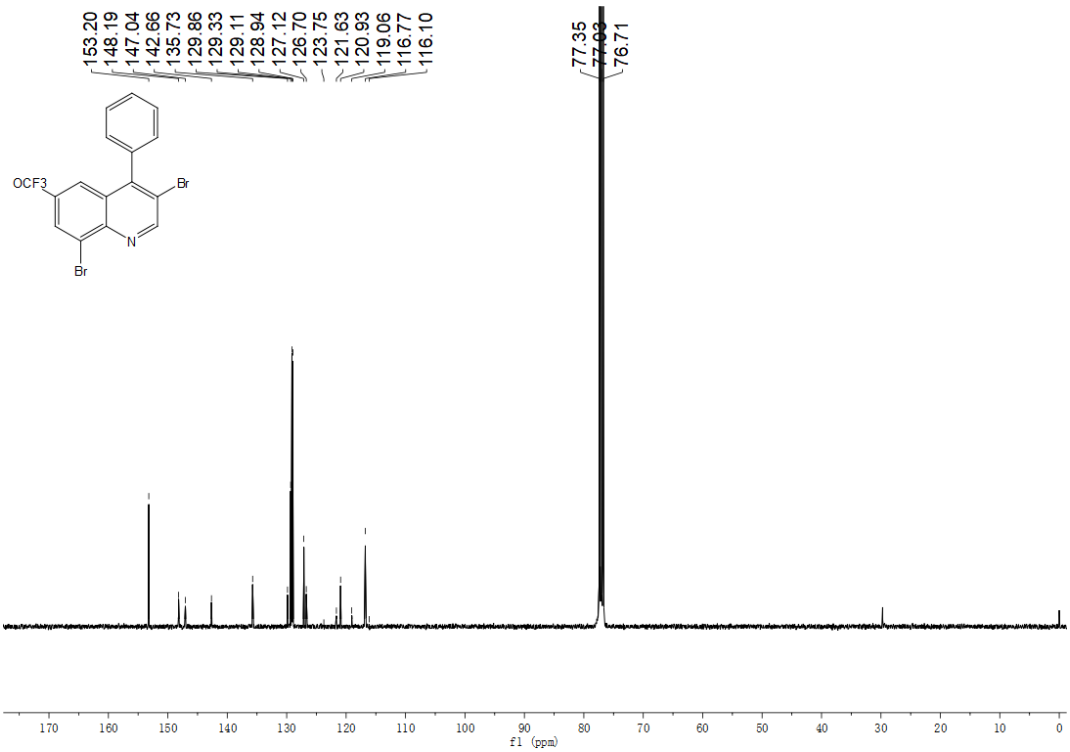


^{13}C NMR (25C°, 100 MHz, $CDCl_3$)

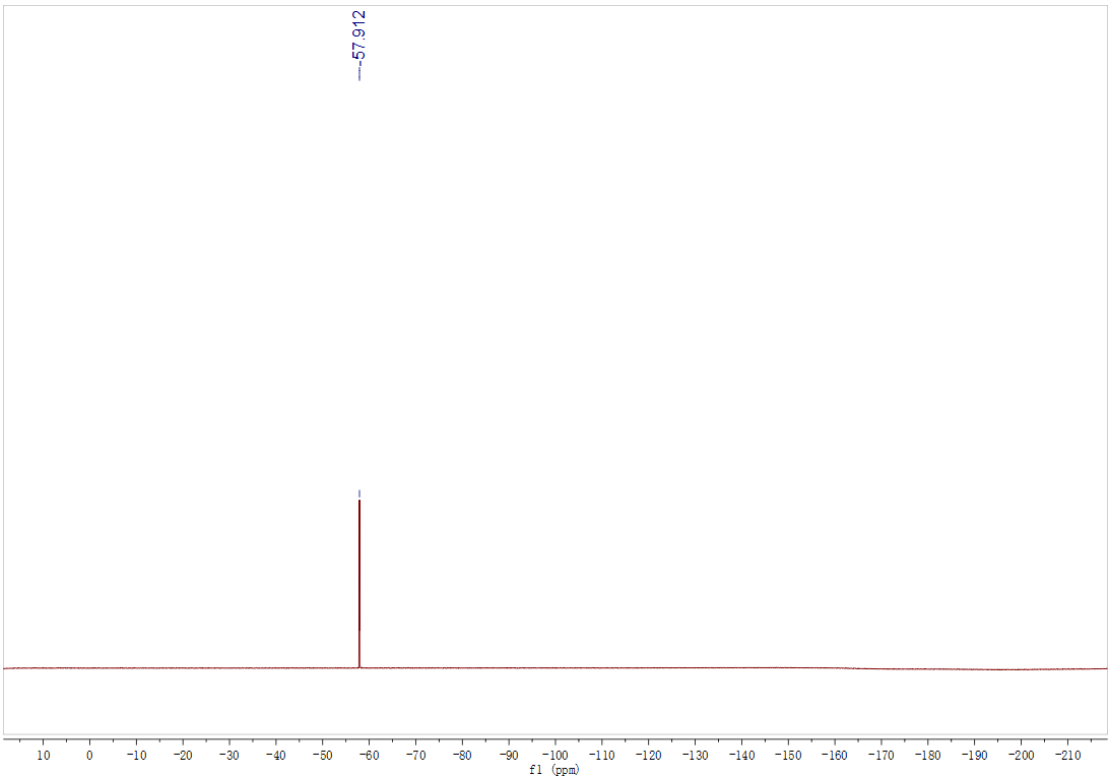
3,8-dibromo-4-phenyl-6-(trifluoromethoxy)quinoline, **2h**



^{1}H NMR (25℃, 400 MHz, $CDCl_3$)

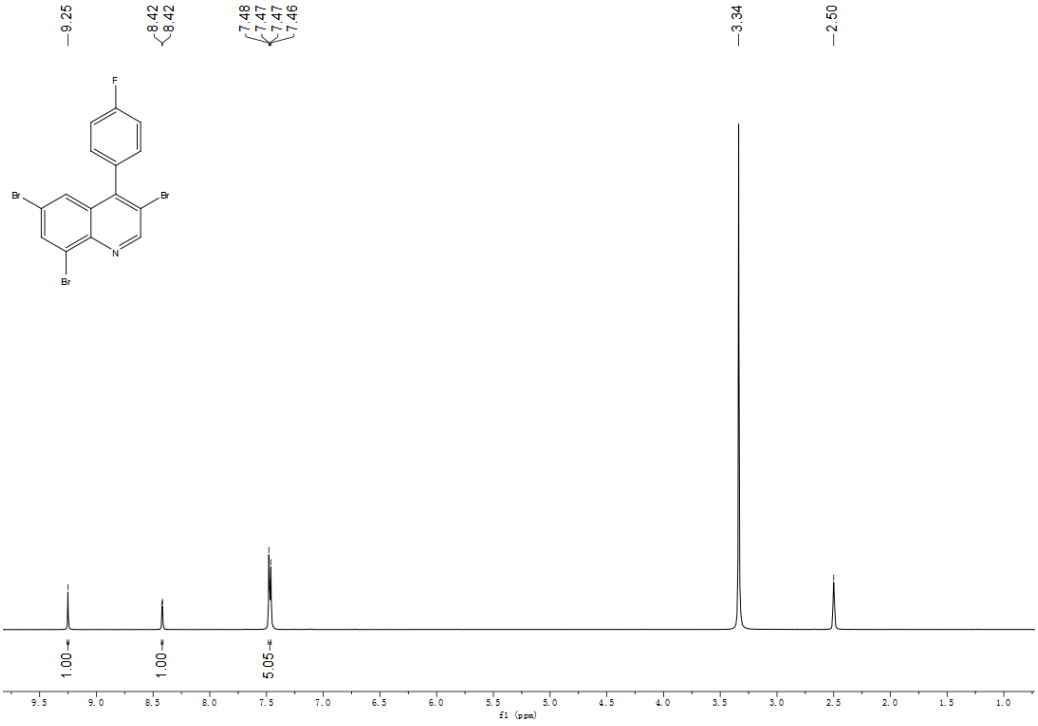


^{13}C NMR (25℃, 100 MHz, $CDCl_3$)

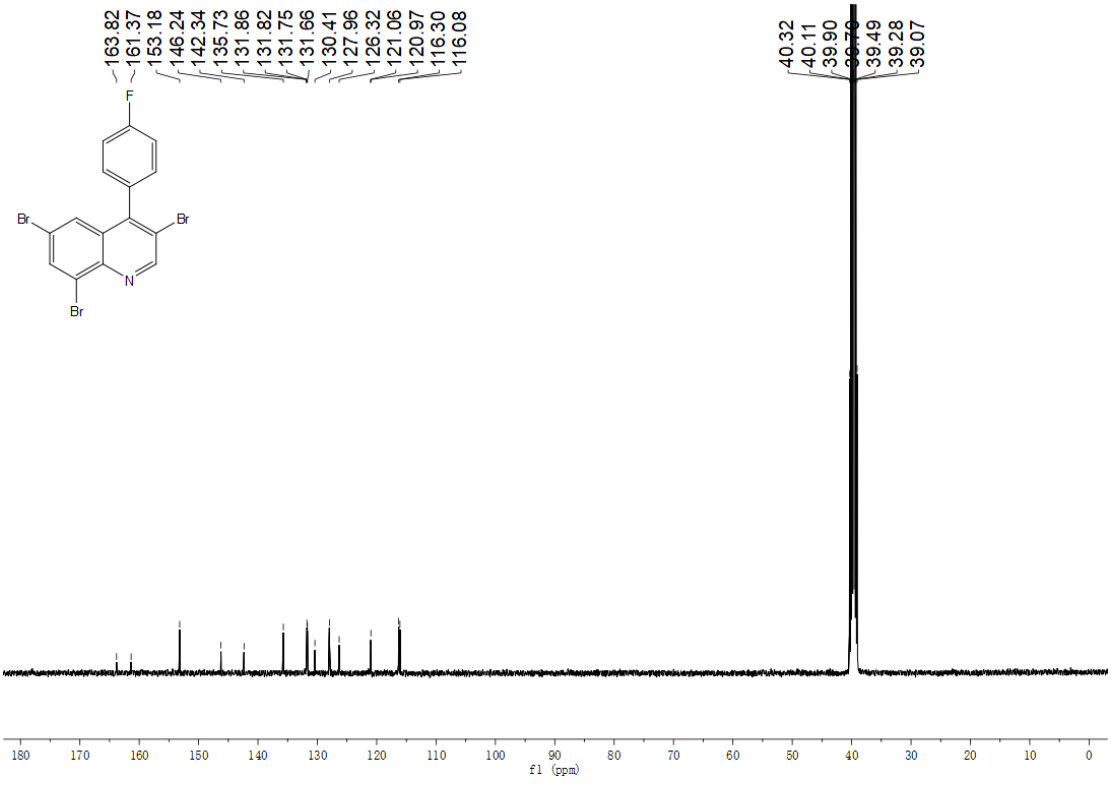


^{19}F NMR (25℃, 376 MHz, $CDCl_3$)

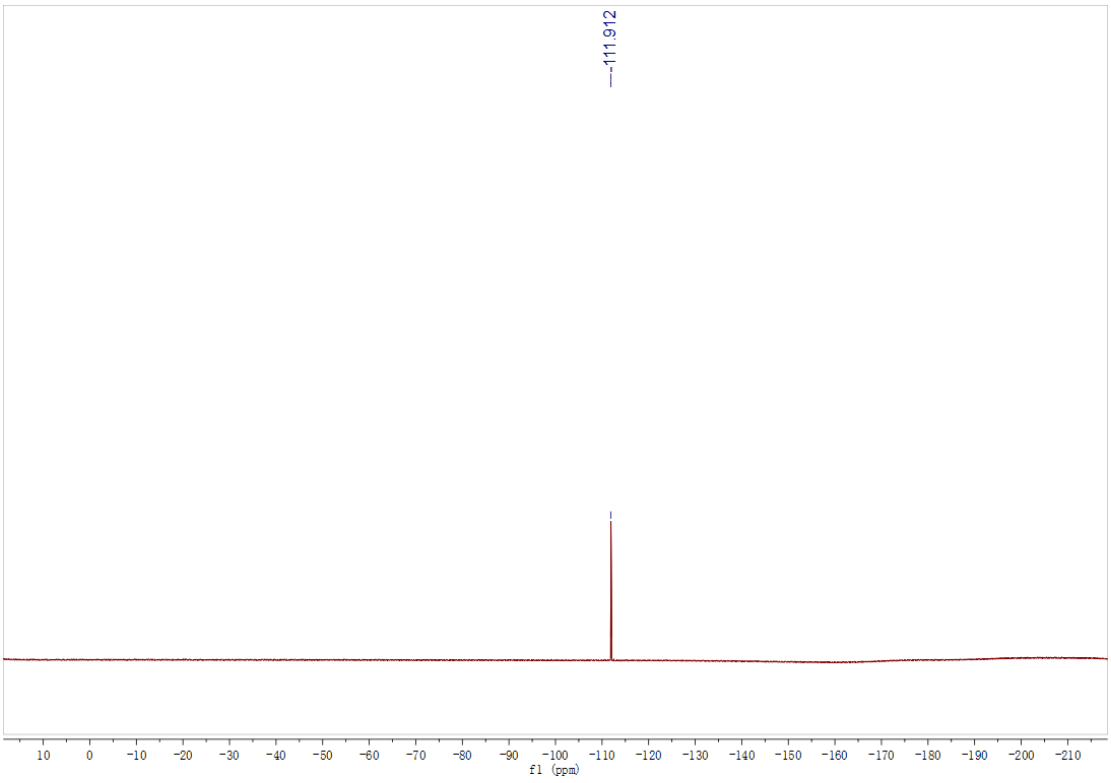
3,6,8-tribromo-4-(4-fluorophenyl)quinoline, **2i**



^{1}H NMR (25℃, 400 MHz, DMSO)

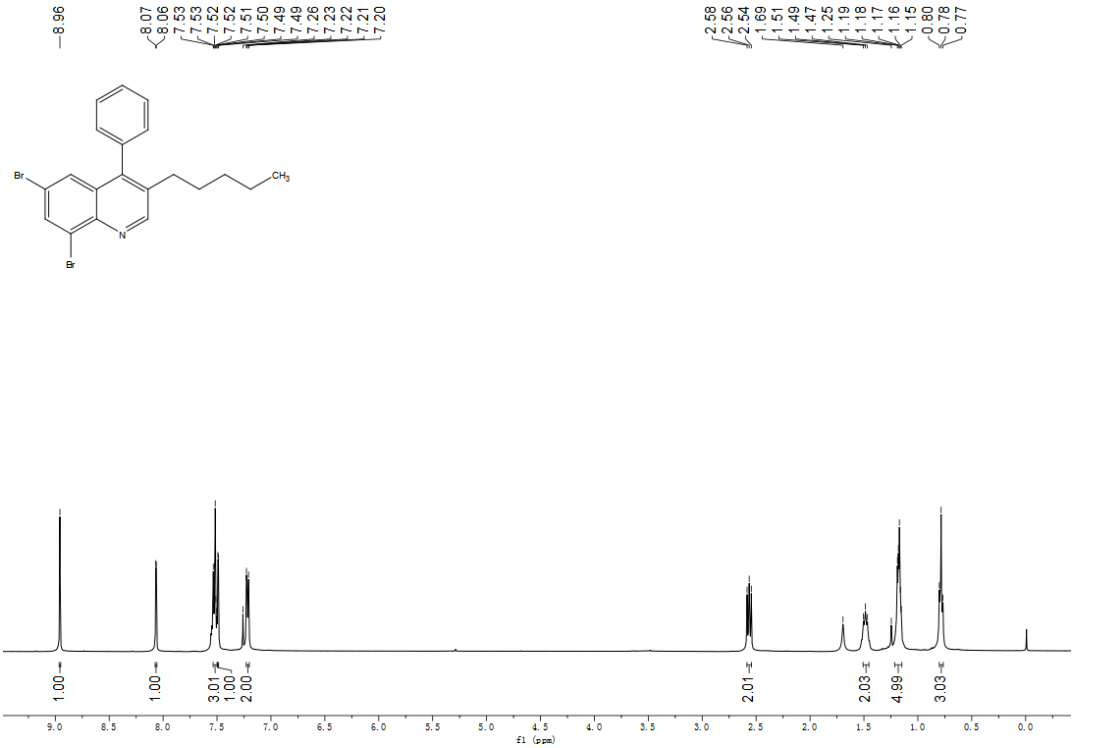


^{13}C NMR (25℃, 100 MHz, DMSO)

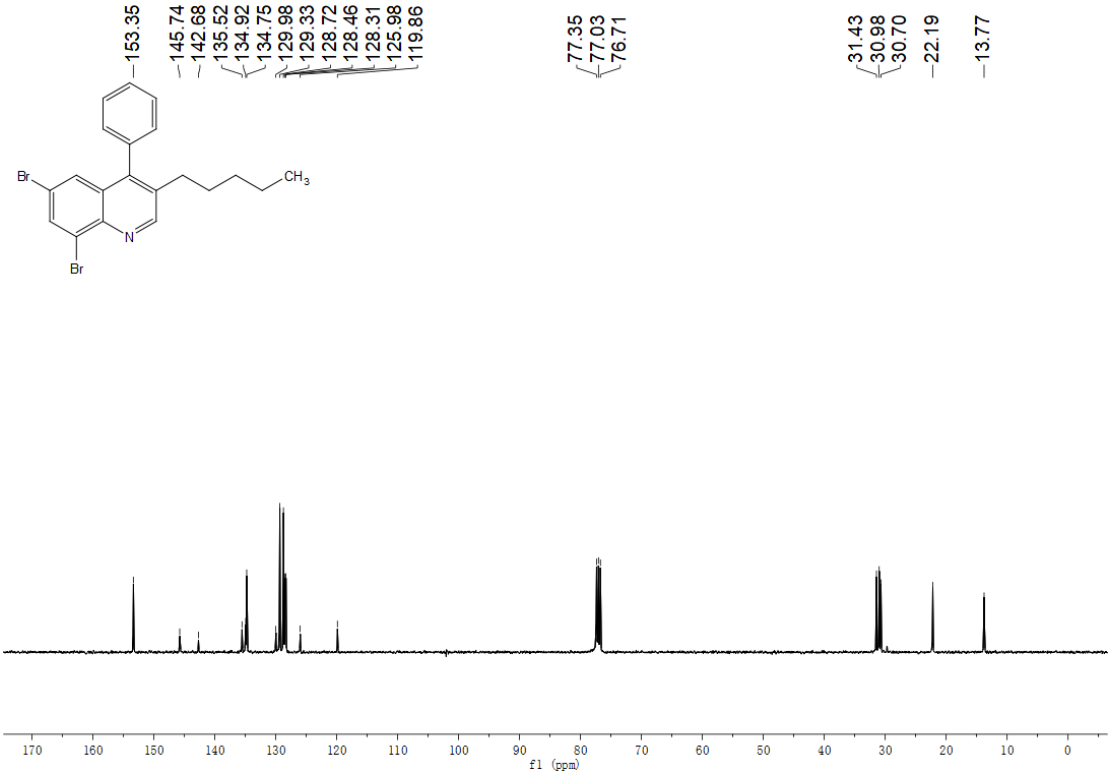


^{19}F NMR (25℃, 376 MHz, DMSO)

6,8-dibromo-3-pentyl-4-phenylquinoline, **2j**

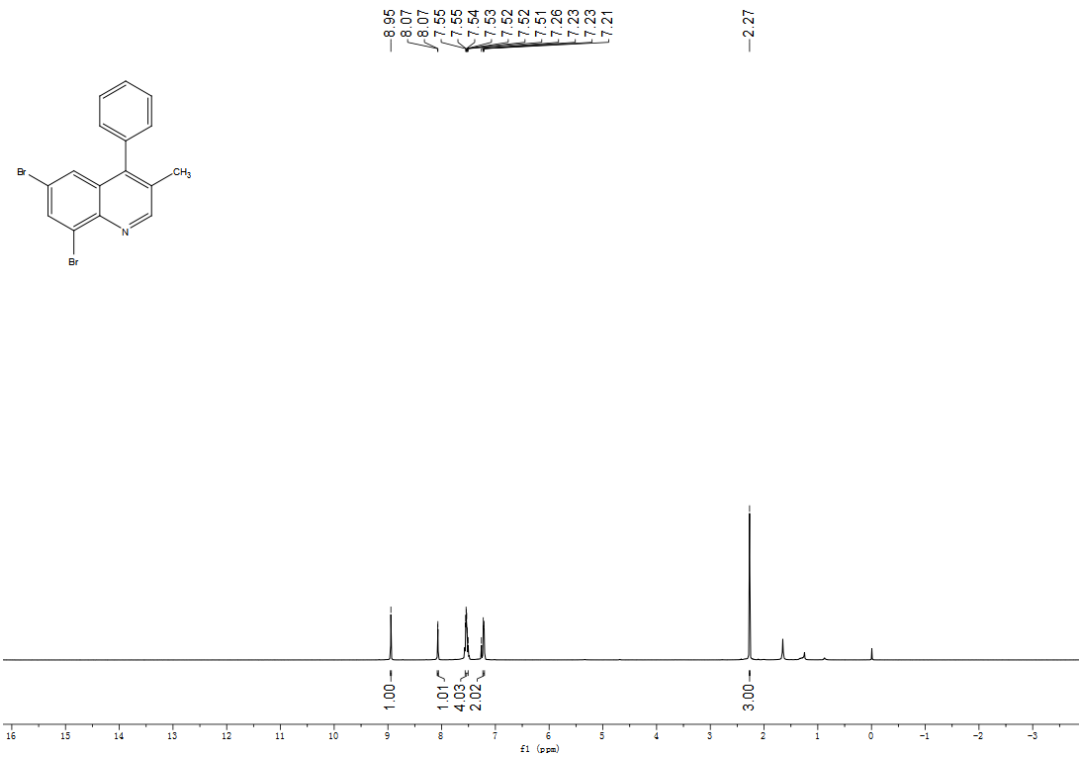


^{1}H NMR (25℃, 400 MHz, $CDCl_3$)

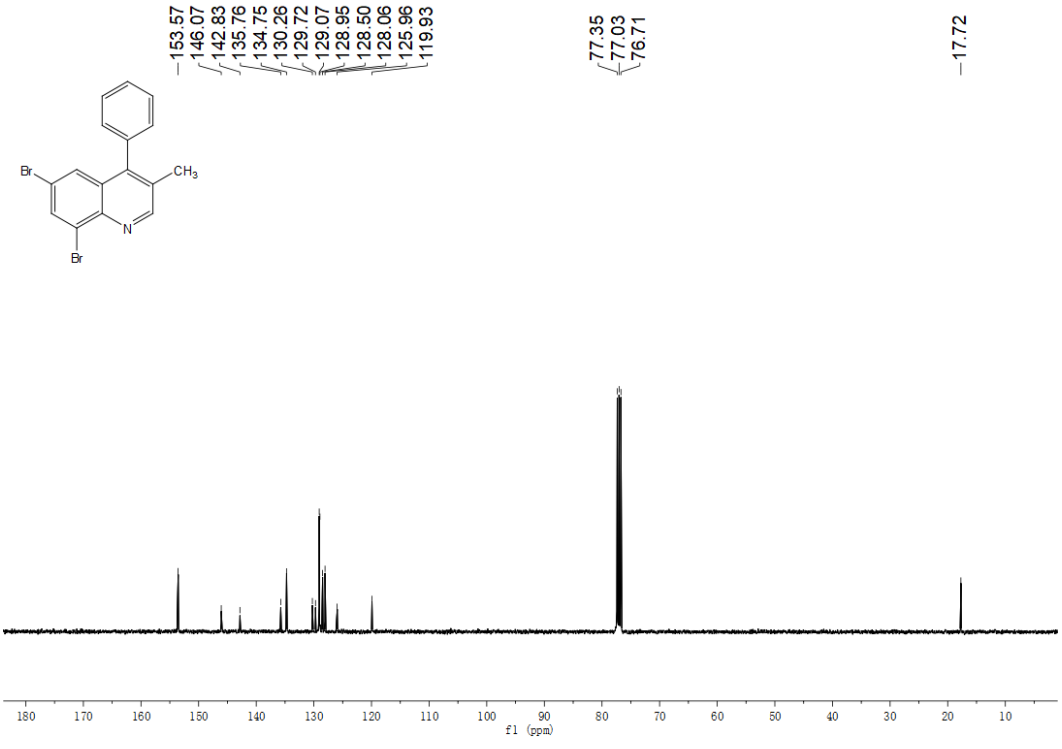


^{13}C NMR (25℃, 100 MHz, $CDCl_3$)

6,8-dibromo-3-methyl-4-phenylquinoline, **2k**

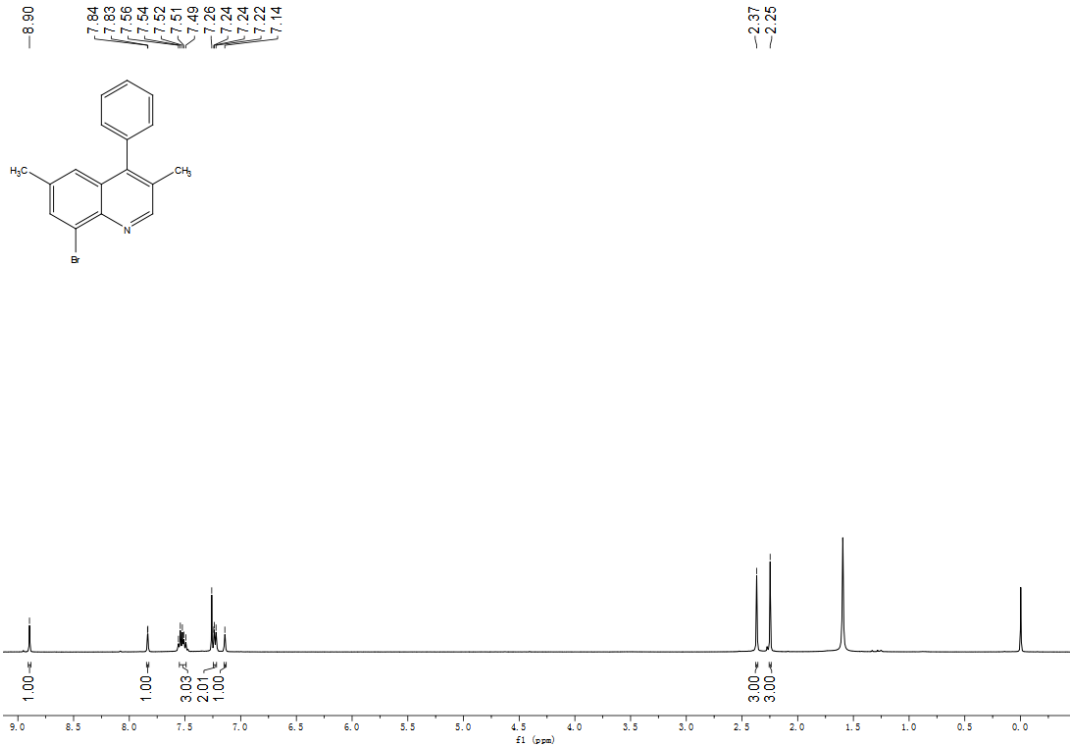


^{1}H NMR (25℃°, 400 MHz, $CDCl_3$)

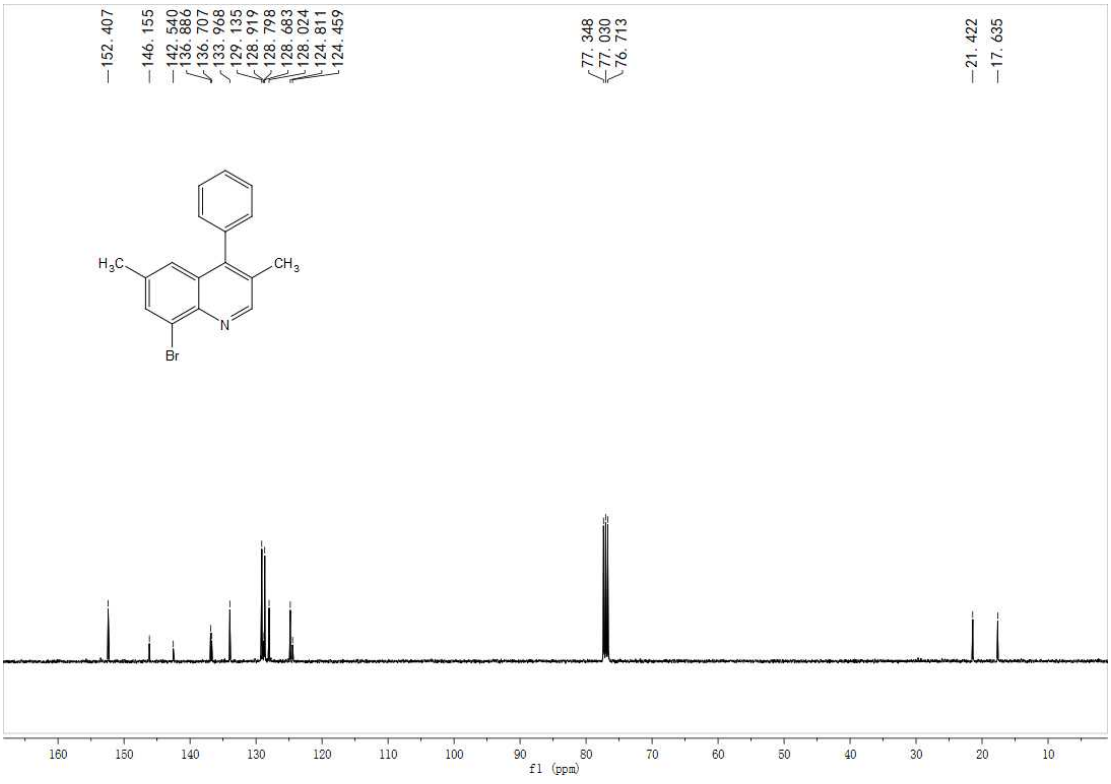


^{13}C NMR (25C°, 100 MHz, $CDCl_3$)

8-bromo-3,6-dimethyl-4-phenylquinoline, **2l**

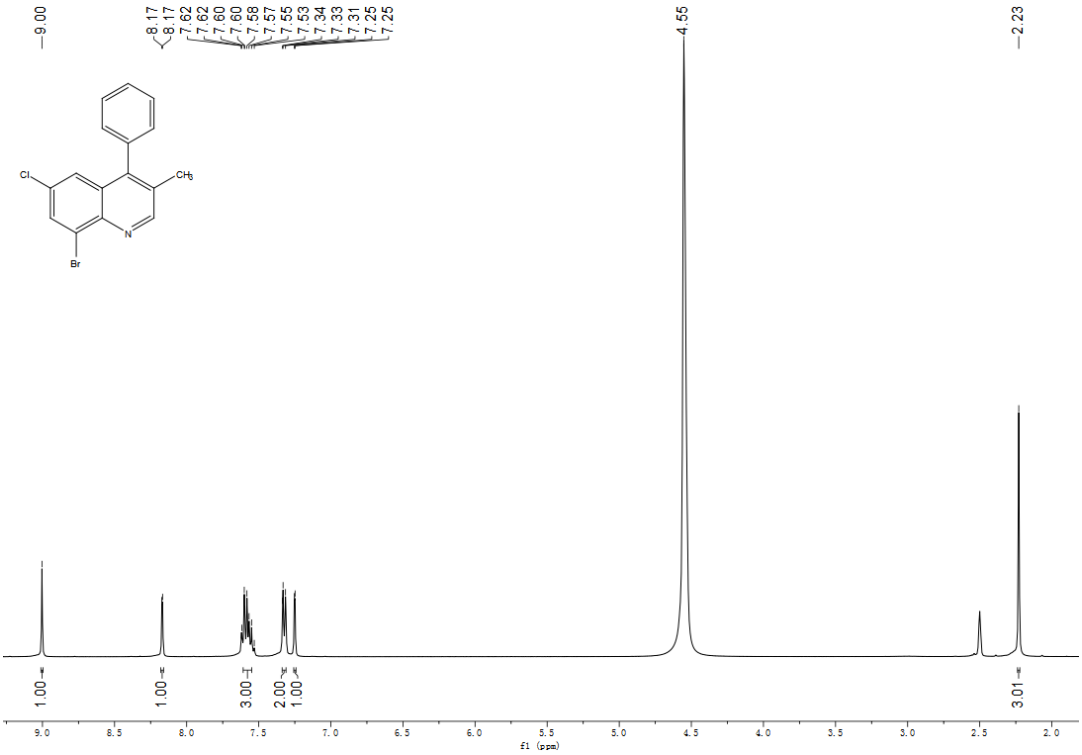


^{1}H NMR (25℃, 400 MHz, $CDCl_3$)

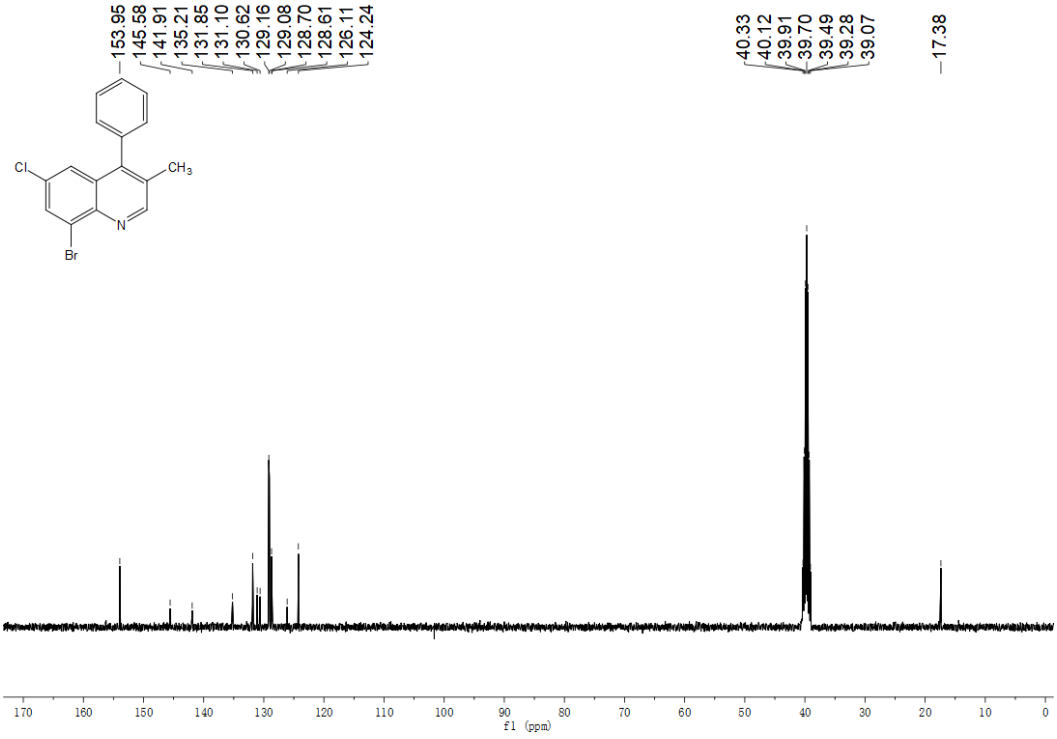


^{13}C NMR (25℃, 100 MHz, $CDCl_3$)

8-bromo-6-chloro-3-methyl-4-phenylquinoline, **2m**

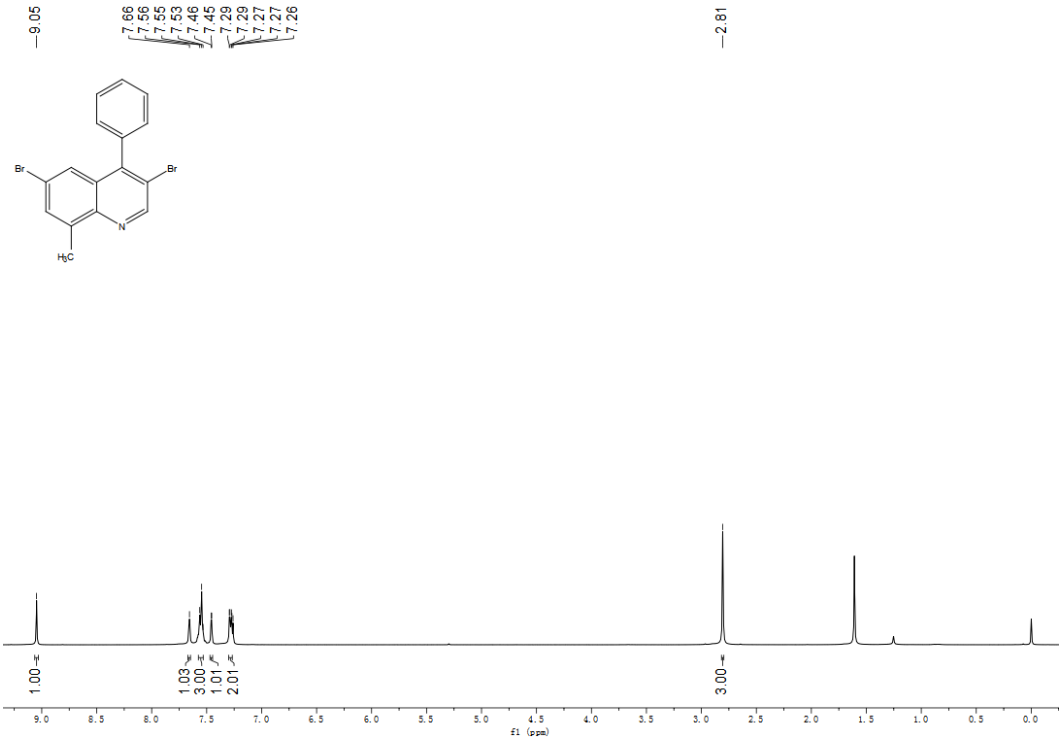


^{1}H NMR (25℃, 400 MHz, DMSO)

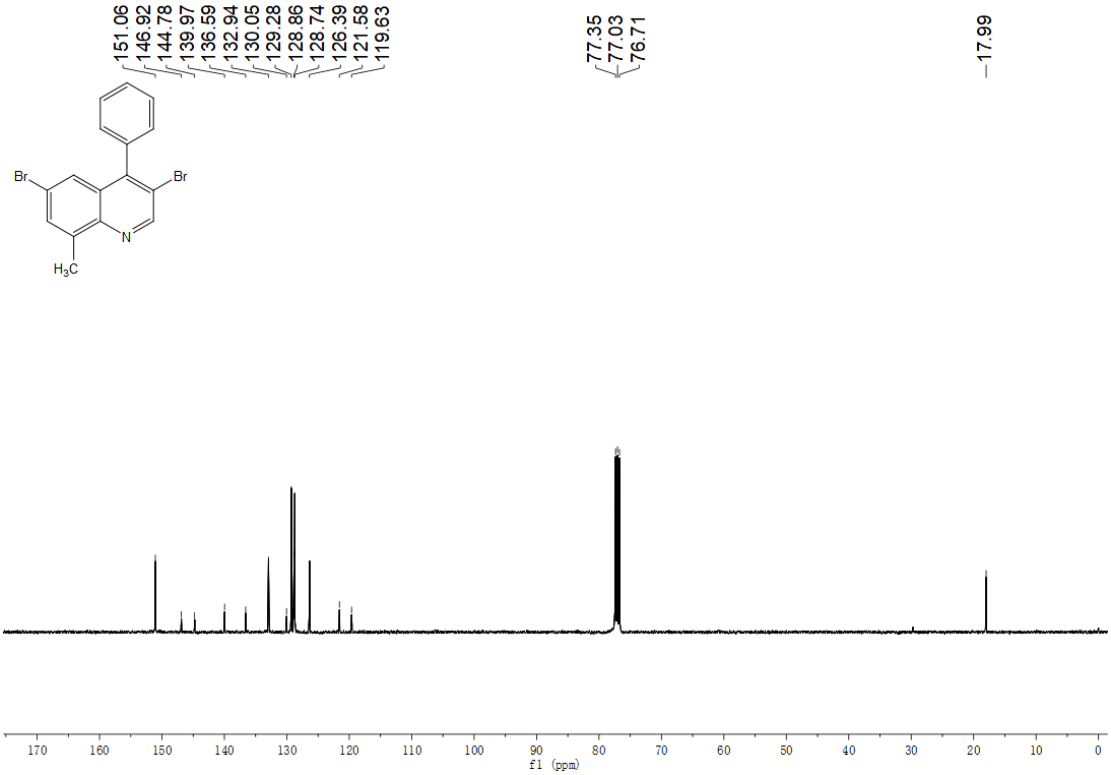


^{13}C NMR (25℃, 100 MHz, DMSO)

3,6-dibromo-8-methyl-4-phenylquinoline, **2n**

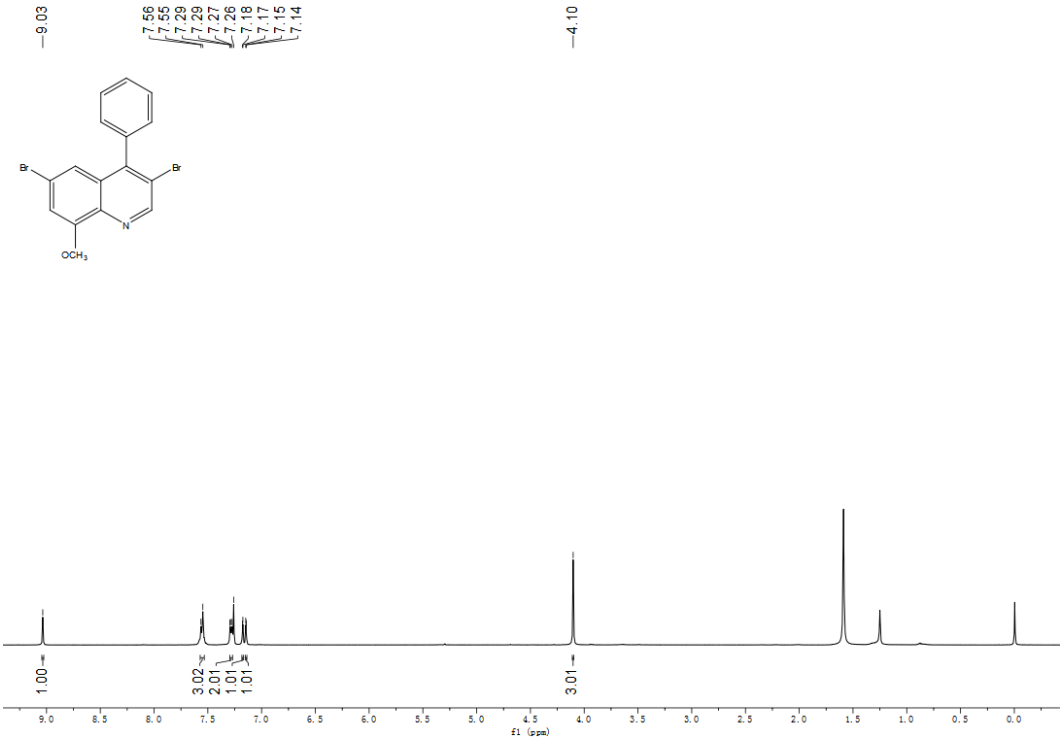


^{1}H NMR (25℃, 400 MHz, $CDCl_3$)

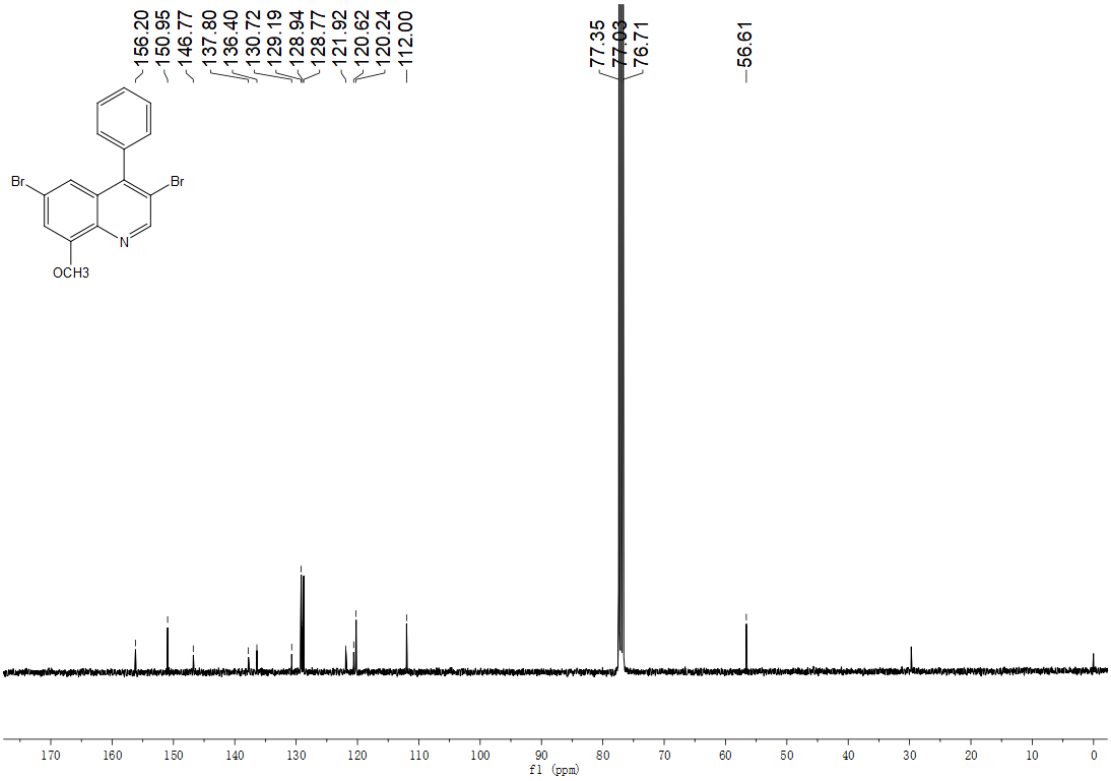


^{13}C NMR (25℃, 100 MHz, $CDCl_3$)

3,6-dibromo-8-methoxy-4-phenylquinoline, **2o**

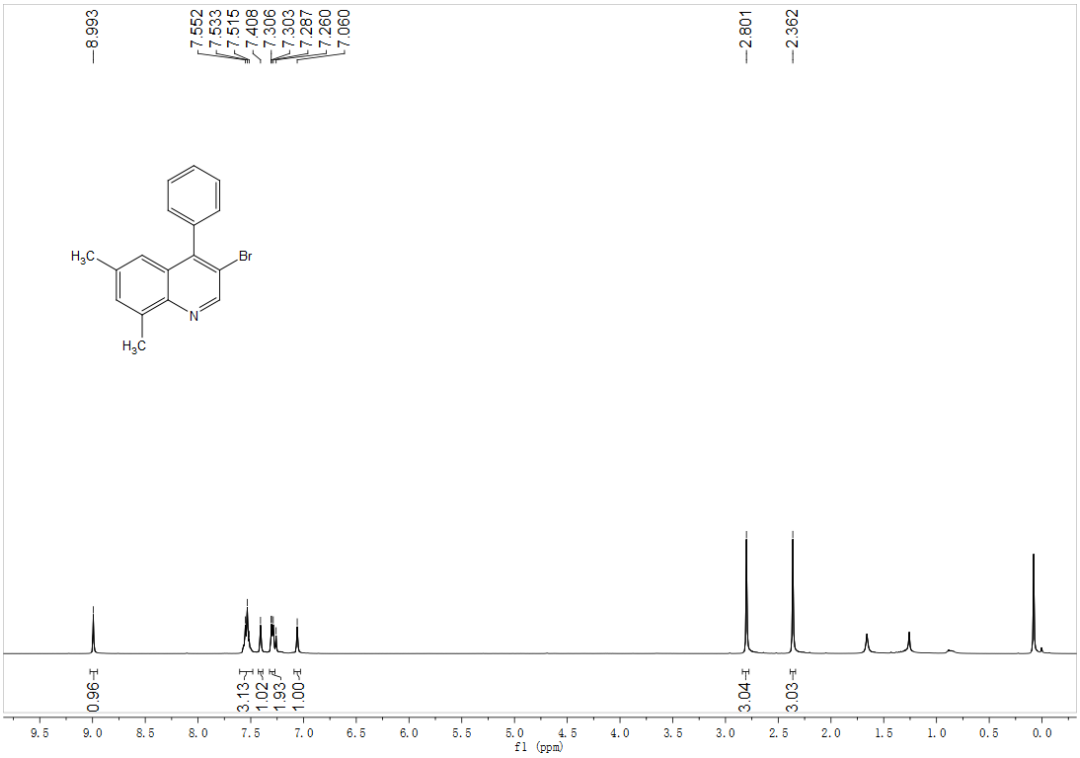


^{1}H NMR (25℃, 400 MHz, $CDCl_3$)

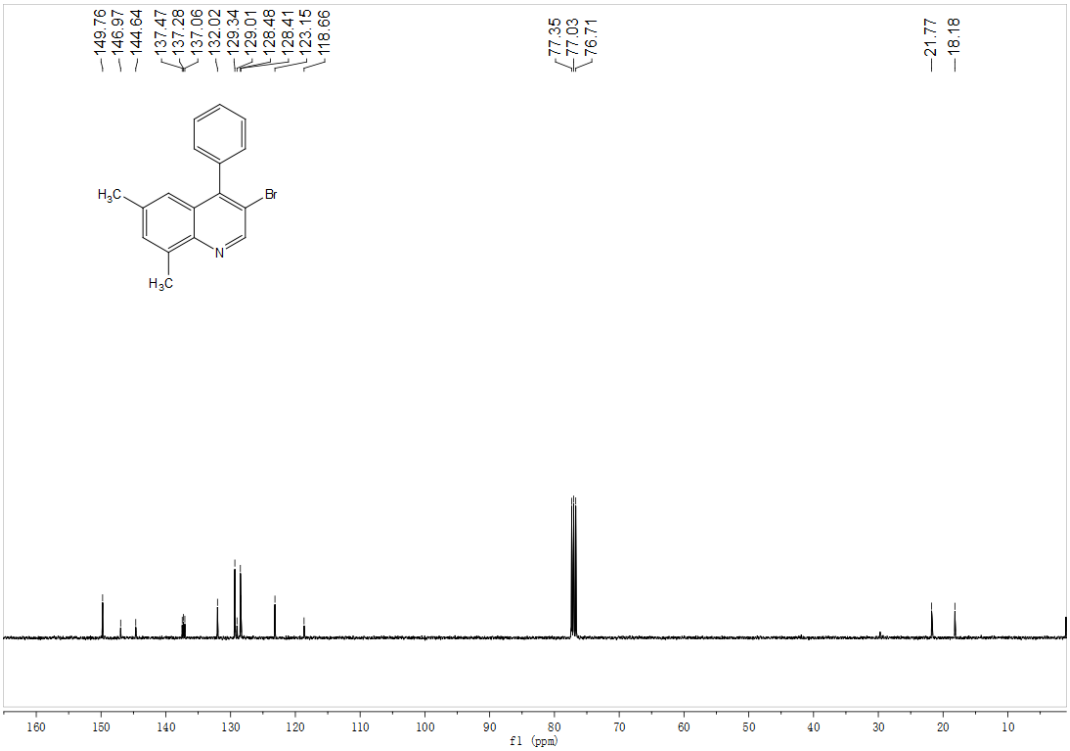


^{13}C NMR (25℃, 100 MHz, $CDCl_3$)

3-bromo-6,8-dimethyl-4-phenylquinoline, **2p**

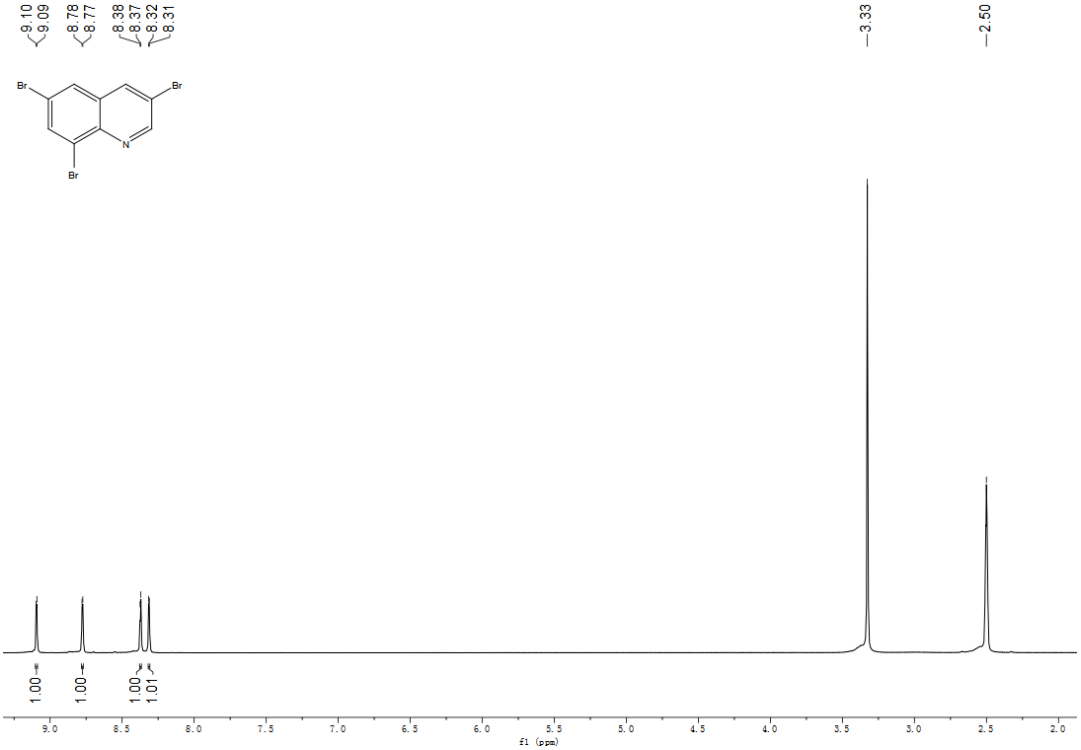


^{1}H NMR (25℃, 400 MHz, $CDCl_3$)

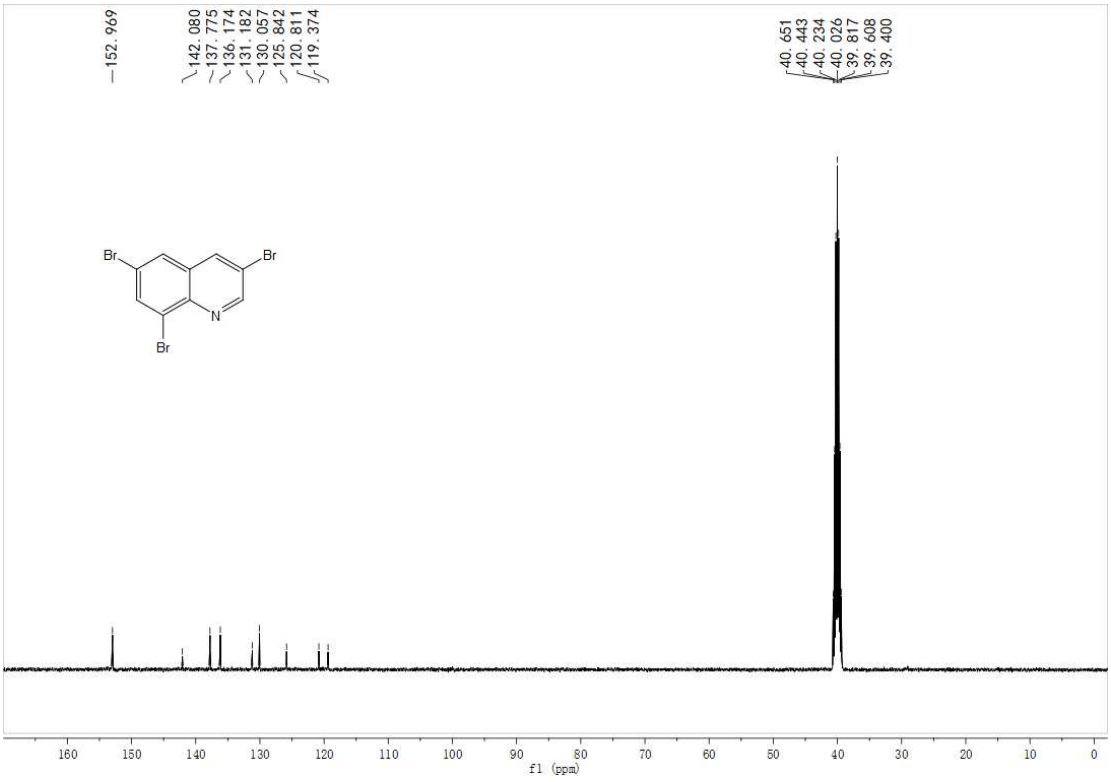


^{13}C NMR (25℃, 100 MHz, $CDCl_3$)

3,6,8-tribromoquinoline, **2q**

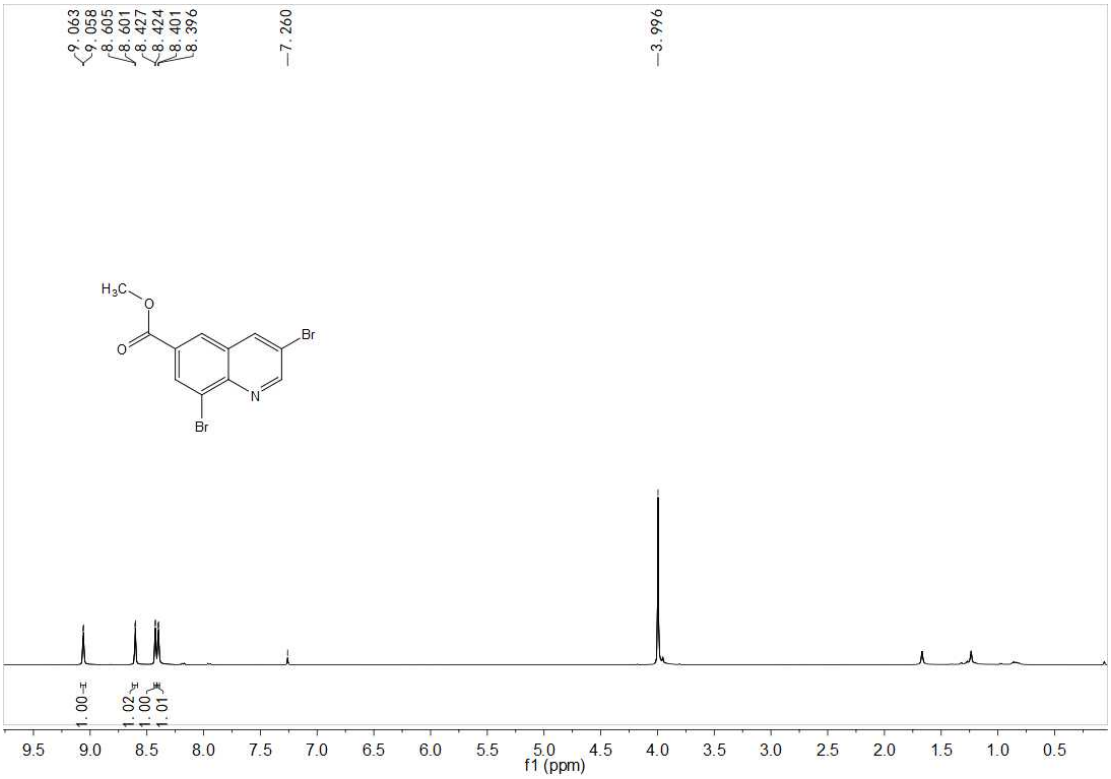


^{1}H NMR (25℃, 400 MHz, DMSO)

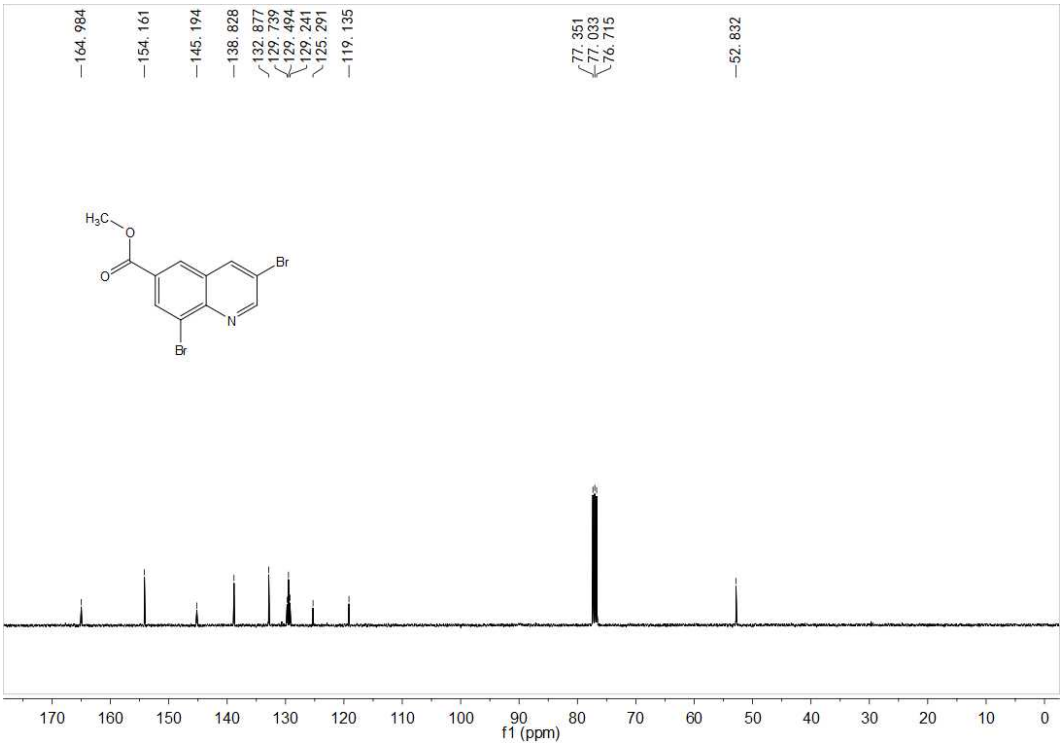


^{13}C NMR (25℃, 100 MHz, DMSO)

methyl 3,8-dibromoquinoline-6-carboxylate, **2r**

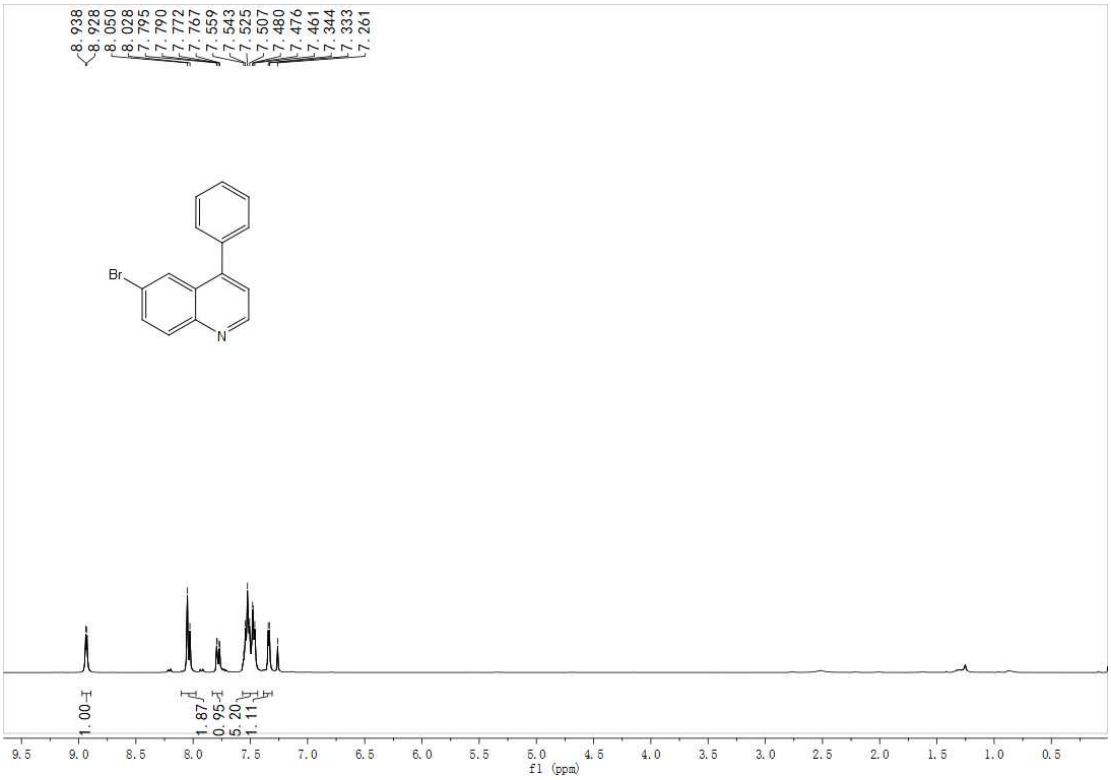


^{1}H NMR(25℃, 400 MHz, $CDCl_3$)

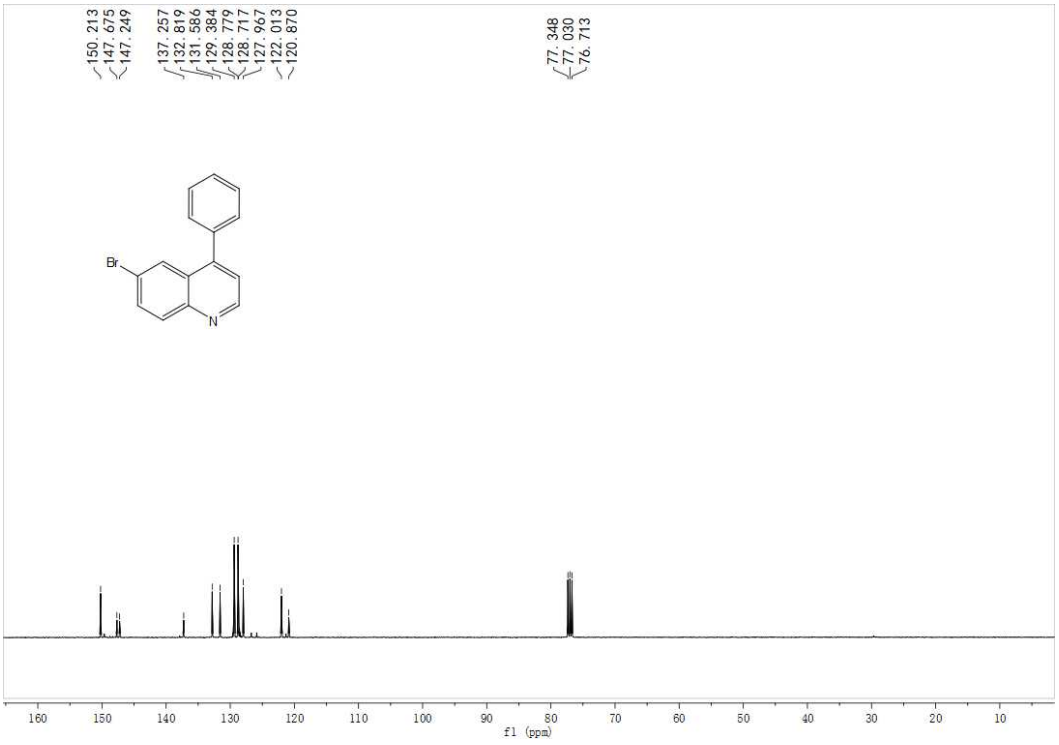


^{13}C NMR (25℃, 100 MHz, $CDCl_3$)

6-bromo-4-phenylquinoline, **2a1**

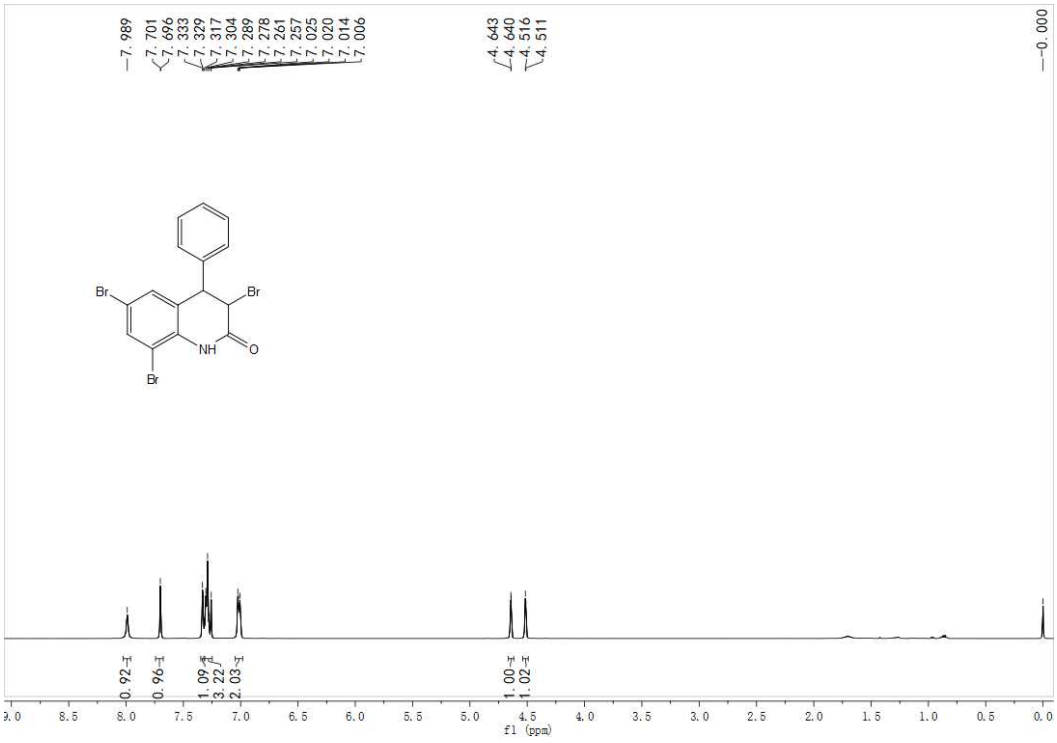


^{1}H NMR(25℃, 400 MHz, $CDCl_3$)

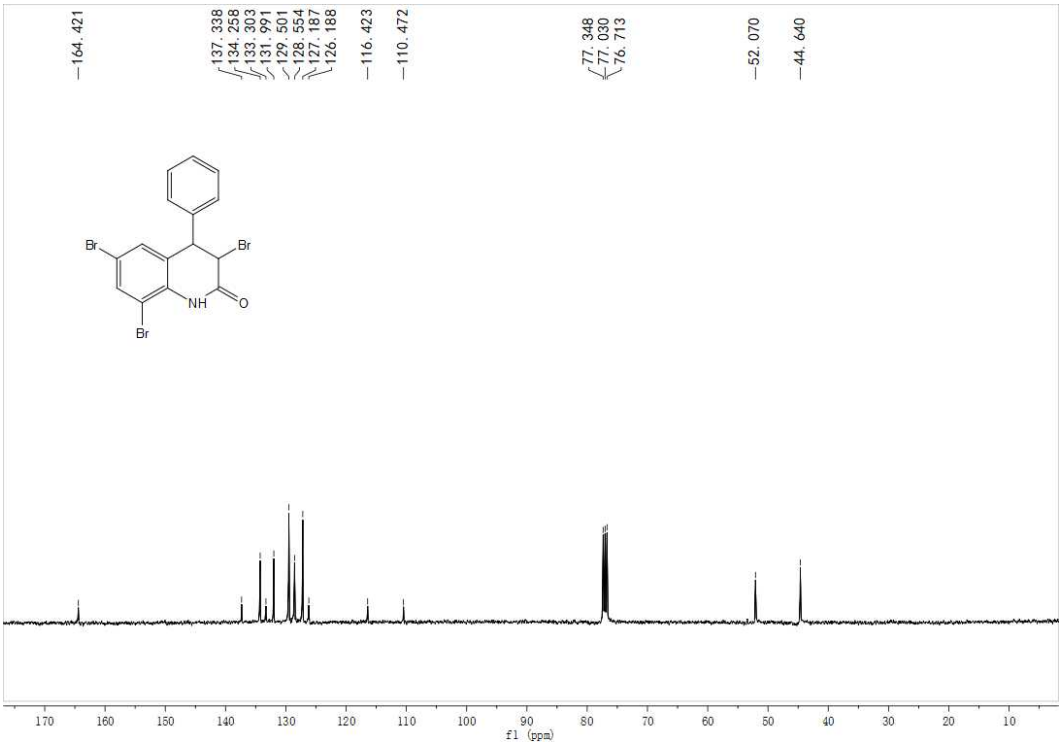


^{13}C NMR (25℃, 100 MHz, $CDCl_3$)

3,6,8-tribromo-4-phenyl-3,4-dihydroquinolin-2(1H)-one, **2a2**

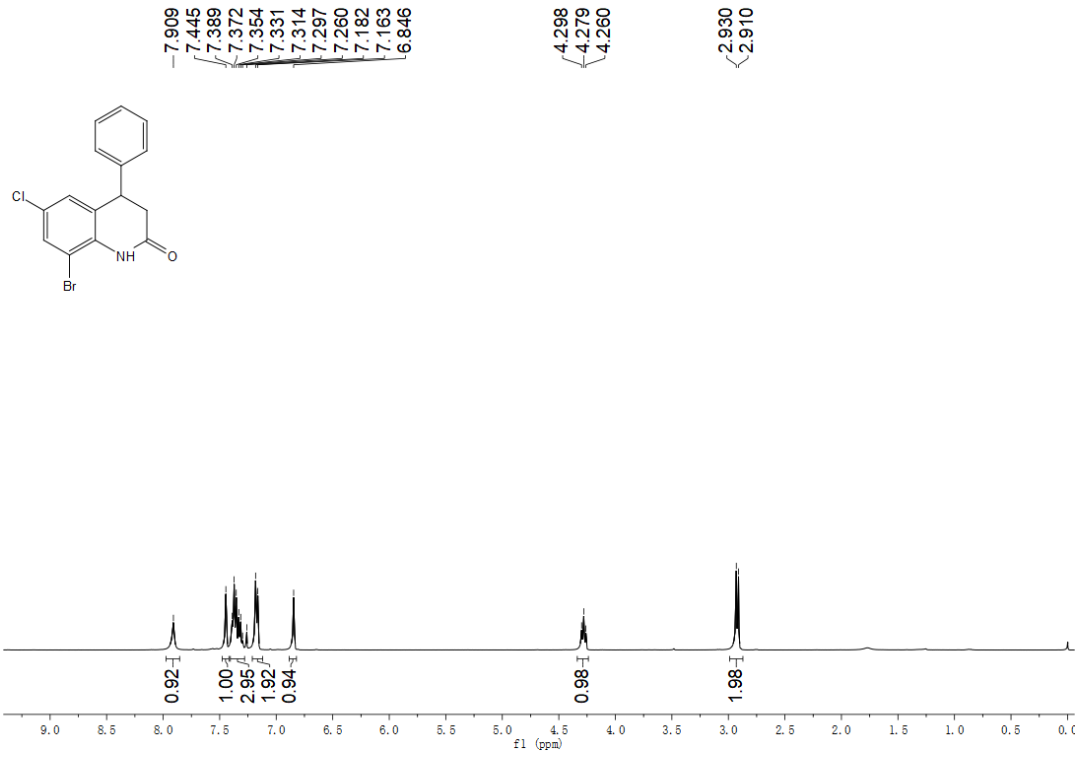


^{1}H NMR (25℃, 400 MHz, $CDCl_3$)

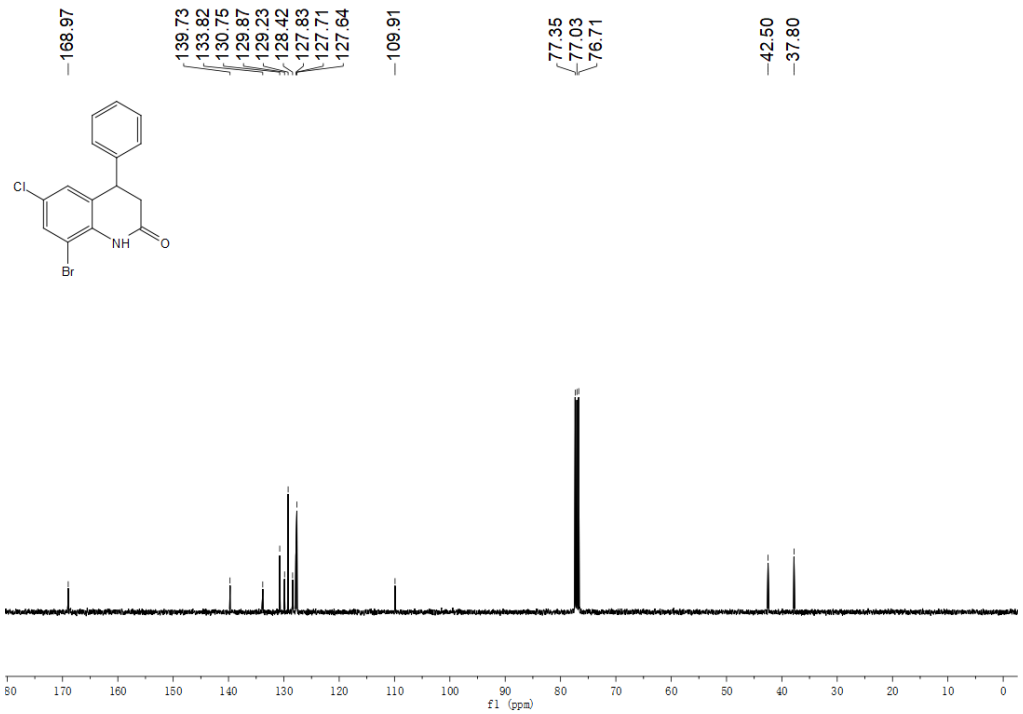


^{13}C NMR (25℃, 100 MHz, $CDCl_3$)

8-bromo-6-chloro-4-phenyl-3,4-dihydroquinolin-2(1*H*)-one, **2b1**

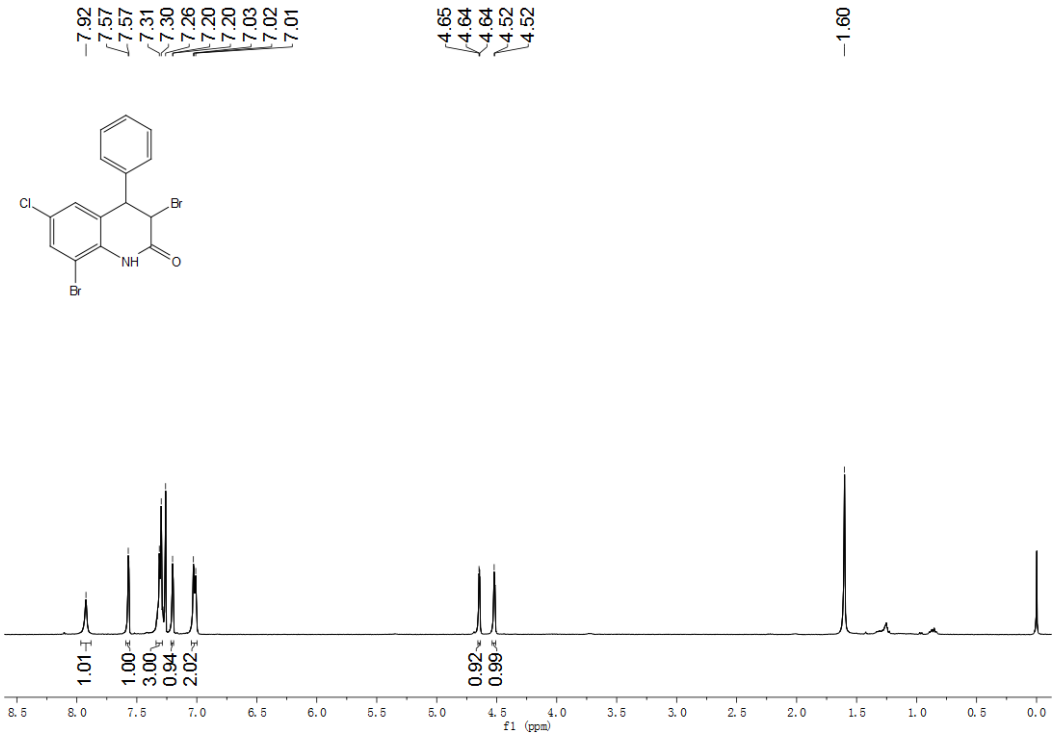


^{1}H NMR (25℃, 400 MHz, $CDCl_3$)

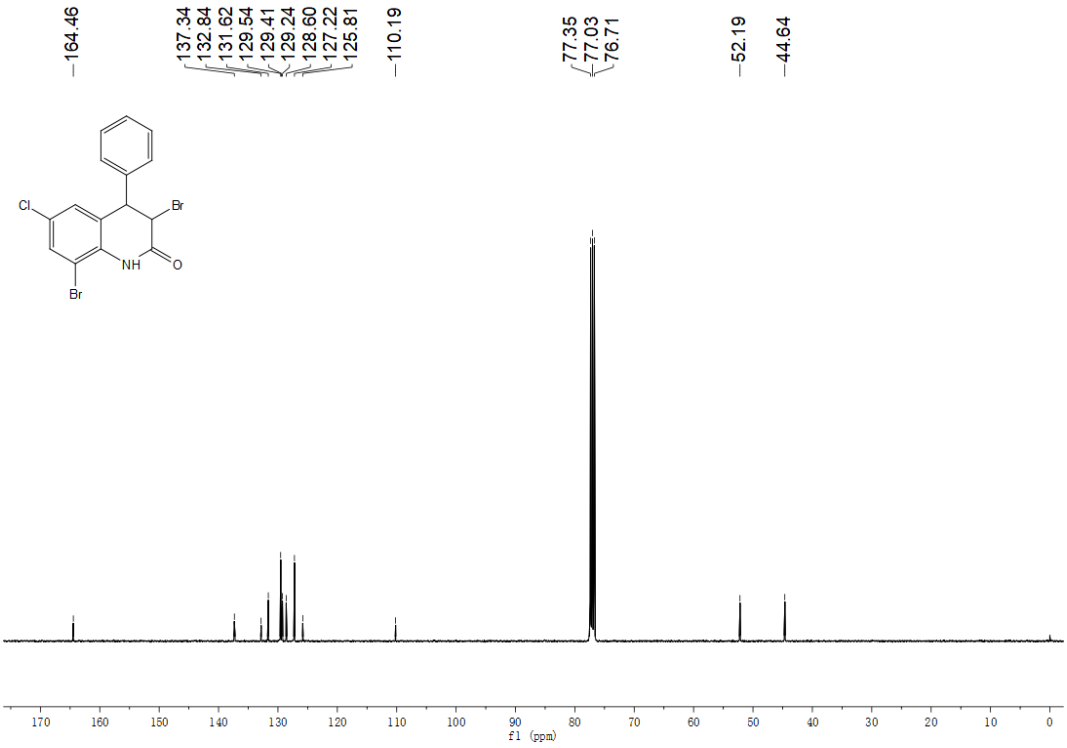


^{13}C NMR (25℃, 100 MHz, $CDCl_3$)

3,8-dibromo-6-chloro-4-phenyl-3,4-dihydroquinolin-2(1*H*)-one, **2b2**

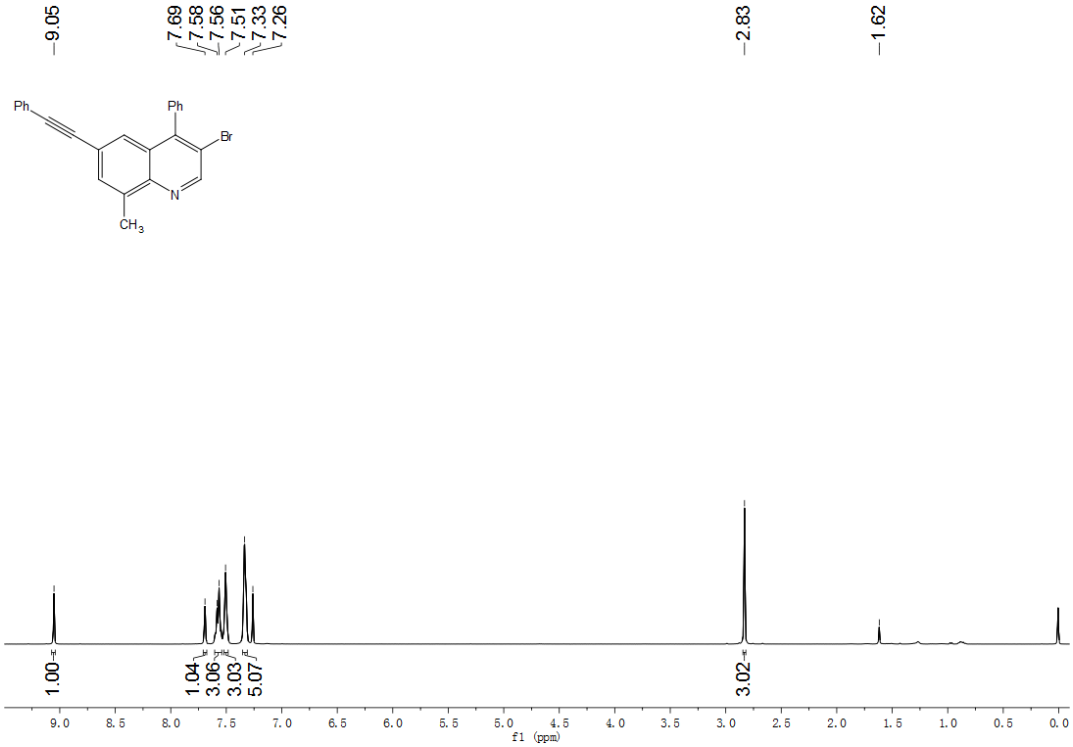


^{1}H NMR (25℃, 400 MHz, $CDCl_3$)

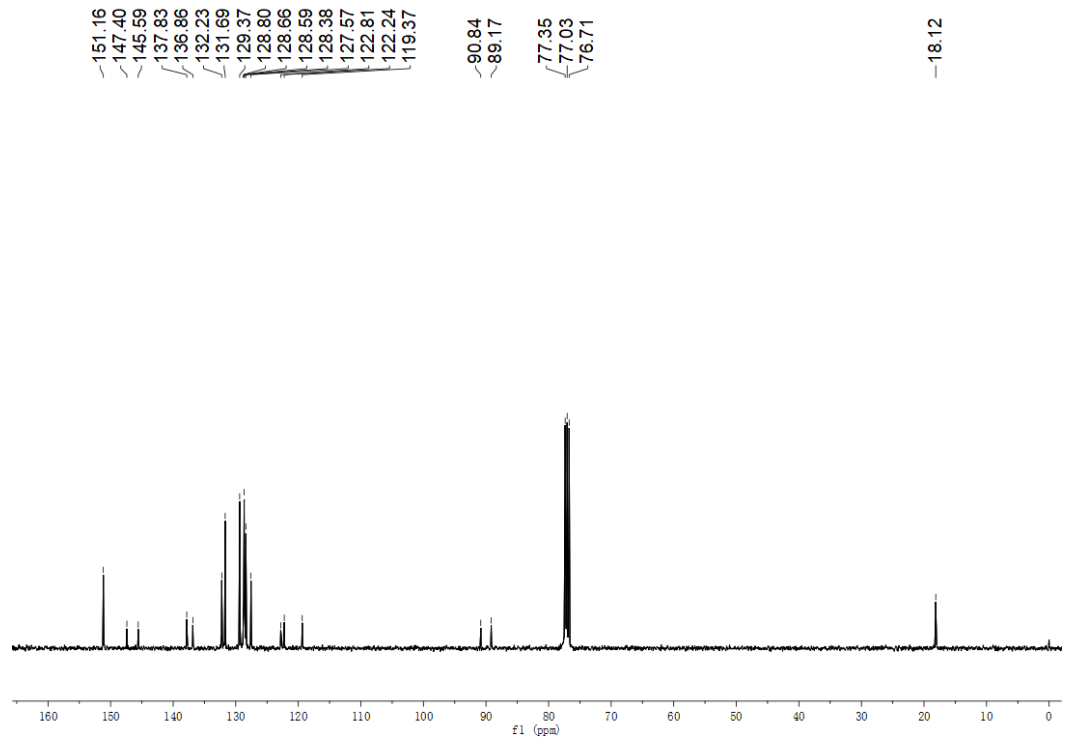


^{13}C NMR (25℃, 100 MHz, $CDCl_3$)

3-bromo-8-methyl-4-phenyl-6-(phenylethynyl) quinoline**, 3n**

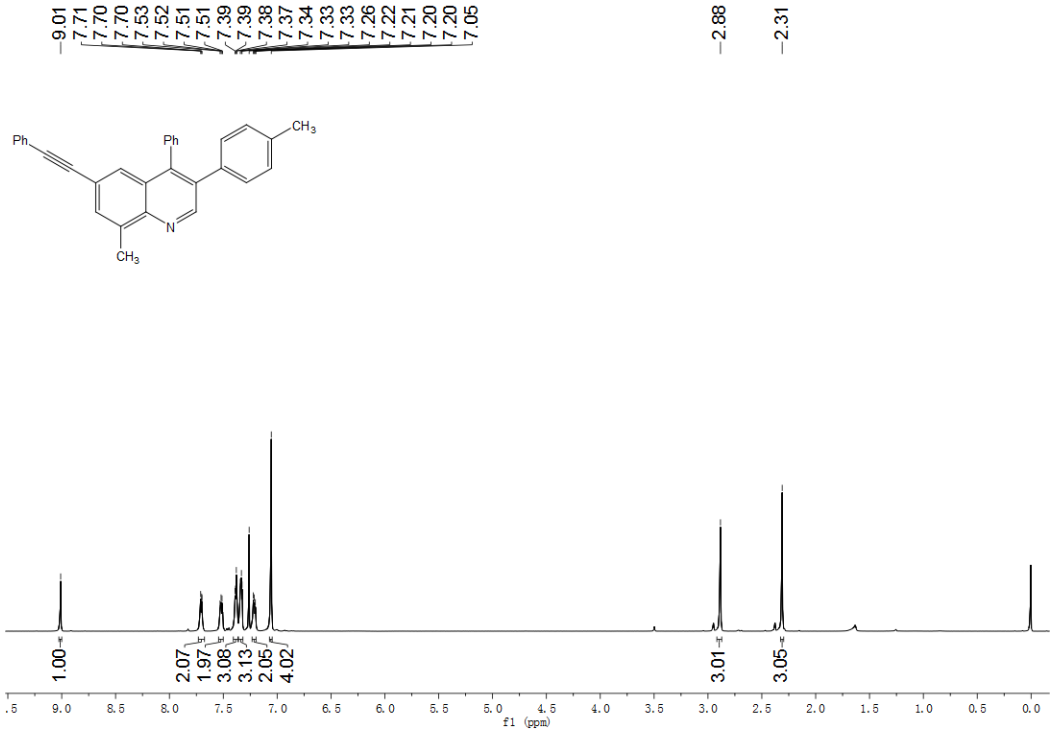


^{1}H NMR (25℃, 400 MHz, $CDCl_3$)

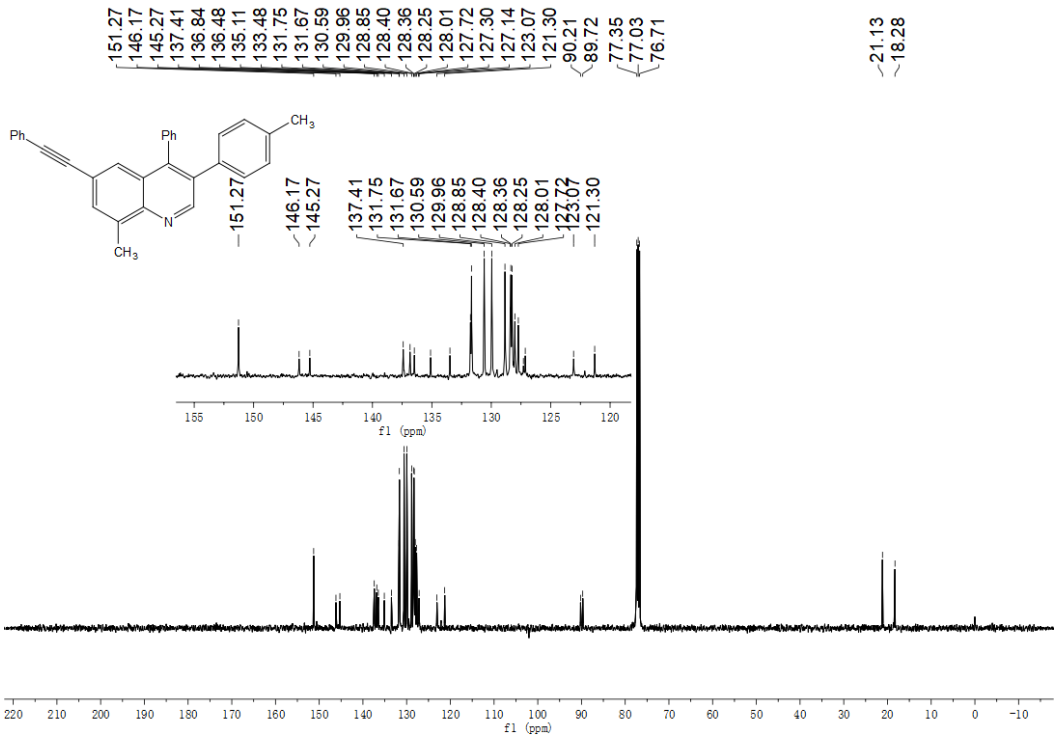


^{13}C NMR (25℃, 100 MHz, $CDCl_3$)

8-methyl-4-phenyl-6-(phenylethynyl)-3-(*p*-tolyl)quinoline, **4n**



^{1}H NMR (25℃, 400 MHz, $CDCl_3$)



^{13}C NMR (25℃, 100 MHz, $CDCl_3$)