

Supporting Information

Synthesis of 4-quinolones via a palladium-catalyzed carbonylative cyclization of o-iodoanilines and alkynes

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Table of Contents

S-1. General Experimental.....	S3
S-2. General procedure for the synthesis of 4-quinolones.....	S4
S-3. The scale-up reaction.....	S5
S-4. Proposed mechanism.....	S6
S-5. NMR-Data of 4-quinolones.....	S7
S-6. NMR Spectrum of 4-quinolones.....	S13
S-7. References.....	S32

S-1 General Experimental

Reagents were purchased from commercial sources and were used as received unless mentioned otherwise. Reactions were monitored by thin layer chromatography using silica gel. The thin layer chromatography (TLC) employed glass 0.25 mm silica gel plates. Flash chromatography columns were packed with 200-300 mesh silica gel in petroleum (boiling point was between 60-90 °C). Gradient flash chromatography was conducted eluting with a continuous gradient from petroleum to the indicated solvent, and they were listed as volume/volume ratios. ¹H NMR and ¹³C NMR were recorded on a Bruker-600 MHz Spectrometer (¹H: 600 MHz, ¹³C: 151 MHz), using DMSO as the solvent at room temperature. The chemical shifts (δ) were expressed in ppm and the coupling constants (J) were expressed in Hz. High-resolution mass spectra (HRMS) were recorded on a Bruker MAXIS spectrometer.

S-2. General procedure for the synthesis of 4-quinolones

A representative example for preparation of 3aa is as following: In 10 mL reaction tube, 2-iodoaniline **1a** (1.0 mmol), phenylacetylene **2a** (1.2 mmol), Et₃N (2.0 mmol) and piperazine (1.0 mmol) were added. Then, 1 mL stock solution containing 100 ppm T-NHC-Pd was added. The reaction tube was loaded in autoclave. After being charged, released and refilled CO (10 atm) for three times, the reaction was stirred at 100 °C for 8 h. The reaction was cool down to room temperature. The solvent was evaporated in vacuo and the residue was purified by flash column chromatography on silica gel with methanol/dichloromethane as an eluent to give the desired product **3aa** 210 mg as yellow solid. Yield: 95%.

The Pd catalysed carbonylation was carried out using a high-pressure steel autoclave with heating jacket (from WATTCAS). For each carbonylation procedure, seven reactions were carried out in a parallel reaction modulator, a spare vial was used to monitor the reaction temperature. The pressure of CO can be adjusted (1-20 atm).

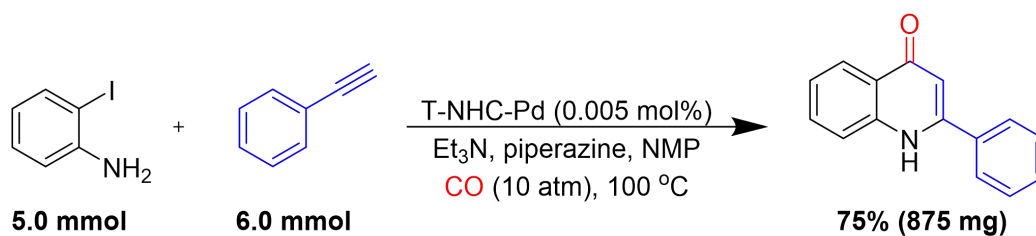


Figure S1. High-pressure steel autoclave and parallel reaction modulator.

The stock solutions prepared by the step-wise diluting Pd precatalyst with toluene. For instance, T-NHC-Pd (6.0 mg, 0.01 mmol) was dissolved in 100 mL of toluene solution, and 100 ppm of T-NHC-Pd in toluene was prepared. Then, 1 mL of 100 ppm T-NHC-Pd solution was diluted with 9 mL NMP, and 10 ppm T-NHC-Pd solution was prepared. In the reaction, 1 mL of 10 ppm stock solution was added to the mixture of 1 mmol of 2-iodoanilines, 1.2 mmol of alkynes, 2.0 mmol of triethylamine and 1.0 mmol of piperazine in reaction vials. No special precautions for the preparation of the catalyst stock solutions were not taken, and the catalysts were handled in air. In order to avoid the contamination of residue Pd in each experiment, the following general procedure was used: A test glass tube and a stirrer bar coated with PTFE were treated with aqua regia (1:3 concd aq HCl–concd aq HNO₃) for 30 min and then washed sequentially with pure water and acetone, and dried with heating.

S-3 The scale-up reaction

The large-scale reaction was performed using 5.0 mmol of starting materials, affording 875 mg of **3aa** with 75% yield. The gram-scale experimental procedure was as follows: In 25 mL reaction tube, 2-iodoaniline **1a** (5.0 mmol), phenylacetylene **2a** (6.0 mmol) and Et₃N (10.0 mmol) and piperazine (5.0 mmol) were added. Then, 5 mL stock solution containing 10 ppm T-NHC-Pd was added. The reaction tube was loaded in autoclave. After being charged, released and refilled CO (10 atm) for three times, the reaction was stirred at 100 °C for 12 h and then end the reaction. The reaction was cool down to room temperature. The solvent was evaporated in vacuo and the residue was purified by flash column chromatography on silica gel with methanol/dichloromethane as an eluent to give the desired product **3aa** 829mg as yellow solid. Yield: 75%.



Scheme S1. The scale-up reaction.

S-4 Proposed mechanism.

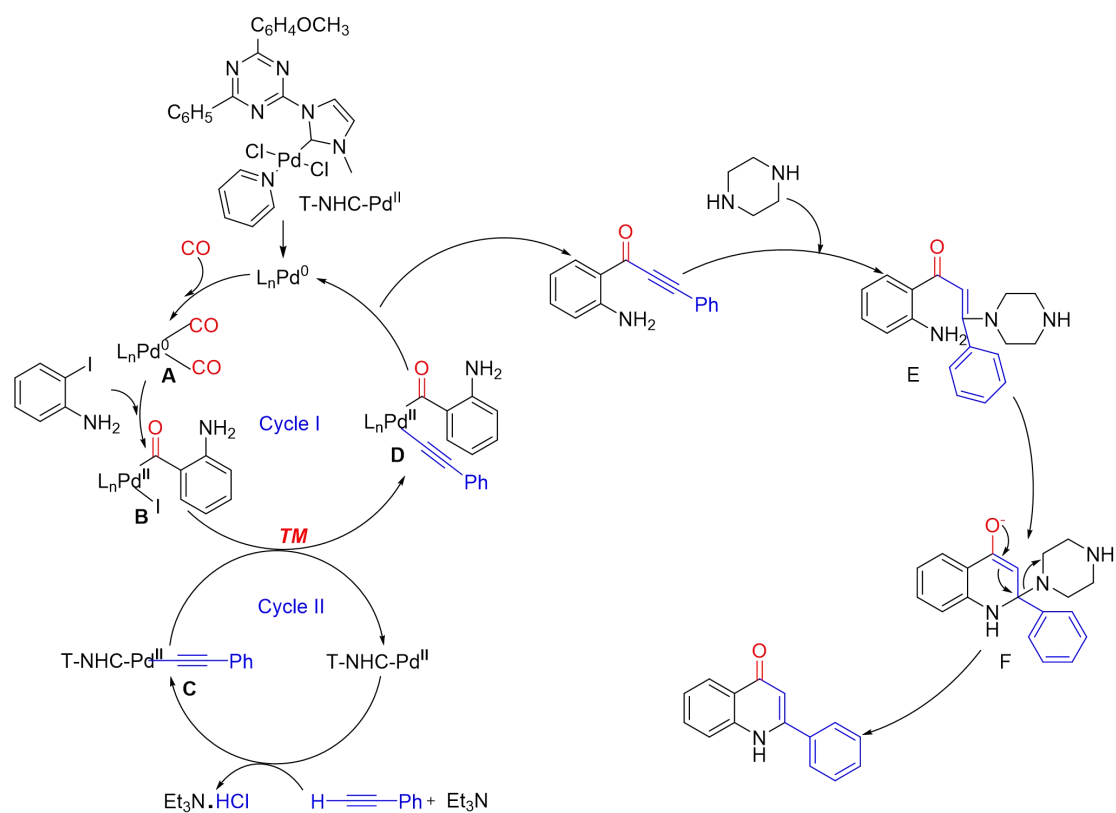
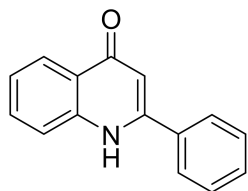
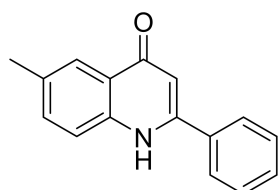


Figure S2. Proposed mechanism of T-NHC-Pd catalyzed carbonylative Sonogashira cyclization reaction.

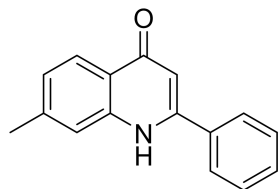
S-5 NMR-Data of 4-quinolones



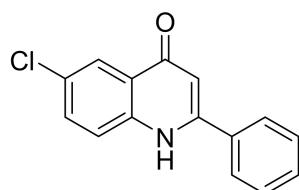
2-phenylquinolin-4(1H)-one(3aa).¹ (Yellow solid was obtained in 95% isolated yield, 210 mg). ¹H NMR (600 MHz, DMSO-*d*₆) δ 11.71 (s, 1H), 8.12 - 8.08 (m, 1H), 7.83 (dd, *J* = 6.4, 3.1 Hz, 2H), 7.76 (d, *J* = 8.2 Hz, 1H), 7.70 - 7.64 (m, 1H), 7.59 (dd, *J* = 5.0, 1.8 Hz, 3H), 7.36 - 7.30 (m, 1H), 6.33 (s, 1H). ¹³C NMR (151 MHz, DMSO-*d*₆) δ 176.9, 150.0, 140.5, 134.2, 131.8, 130.4, 129.0, 127.4, 124.9, 124.7, 123.3, 118.7, 107.3. IR (KBr): 3070, 2963, 1634, 1570, 1544, 1501, 1358, 1247, 1136, 845, 803, 760, 681, 517 cm⁻¹. HRMS(ESI) *m/z*: [M+H]⁺ calcd for C₁₅H₁₂NO: 222.0913. found: 222.0912.



6-methyl-2-phenylquinolin-4(1H)-one(3ba).¹ (White solid was obtained in 94% isolated yield, 220 mg). ¹H NMR (600 MHz, DMSO-*d*₆) δ 11.65 (s, 1H), 7.91 (s, 1H), 7.85 - 7.77 (m, 2H), 7.68 (d, *J* = 8.4 Hz, 1H), 7.57 (s, 3H), 7.49 (d, *J* = 8.1 Hz, 1H), 6.30 (s, 1H), 2.41 (s, 3H). ¹³C NMR (151 MHz, DMSO-*d*₆) δ 176.8, 149.6, 138.6, 134.3, 133.1, 132.5, 130.3, 128.9, 127.3, 124.8, 123.9, 118.6, 107.1, 20.7. IR (KBr): 3070, 2959, 1533, 1501, 1247, 1195, 898, 824, 776, 692, 560 cm⁻¹. HRMS(ESI) *m/z*: [M+H]⁺ calcd for C₁₆H₁₄NO: 236.1070. found: 236.1072.

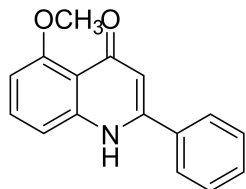


7-methyl-2-phenylquinolin-4(1H)-one(3ca).² (Yellow solid was obtained in 85% isolated yield, 200 mg). ¹H NMR (600 MHz, DMSO-*d*₆) δ 11.64 (s, 1H), 7.99 (d, *J* = 8.2 Hz, 1H), 7.82 (dd, *J* = 6.7, 2.9 Hz, 2H), 7.57 (h, *J* = 3.9 Hz, 4H), 7.16 (dd, *J* = 8.2, 1.5 Hz, 1H), 6.29 (s, 1H), 2.43 (s, 3H). ¹³C NMR (151 MHz, DMSO-*d*₆) δ 176.8, 149.7, 141.8, 140.7, 134.3, 130.3, 128.9, 127.3, 124.9, 124.7, 122.9, 118.0, 107.1, 21.4. IR (KBr): 3112, 3064, 2963, 1613, 1549, 1501, 1242, 824, 760, 686, 527 cm⁻¹. HRMS(ESI) *m/z*: [M+H]⁺ calcd for C₁₆H₁₄NO: 236.1070. found: 236.1073.

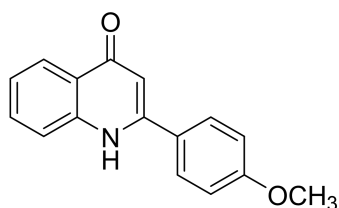


6-chloro-2-phenylquinolin-4(1H)-one(3da).³ (White solid was obtained in 77% isolated yield, 196 mg). ¹H NMR (600 MHz, DMSO-*d*₆) δ 11.87 (s, 1H), 8.04 (s, 1H), 7.82 (dd, *J* = 17.1,

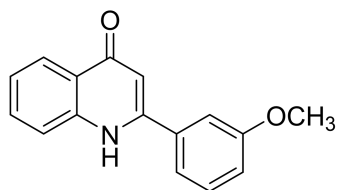
7.3 Hz, 3H), 7.72 (d, $J = 8.9$ Hz, 1H), 7.59 (s, 3H), 6.39 (s, 1H). ^{13}C NMR (151 MHz, $\text{DMSO-}d_6$) δ 175.8, 150.4, 139.1, 133.9, 131.9, 130.6, 129.0, 127.9, 127.4, 123.6, 121.2, 107.5. IR (KBr): 3069, 2932, 1724, 1581, 1544, 1497, 871, 835, 760, 681, 543 cm^{-1} . HRMS(ESI) m/z : $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{15}\text{H}_{11}\text{ClNO}$: 256.0524. found: 256.0521.



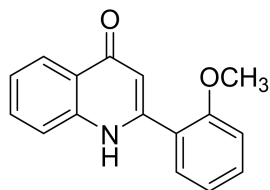
5-methoxy-2-phenylquinolin-4(1H)-one(3ea).³ (White solid was obtained in 29% isolated yield, 196 mg). ^1H NMR (600 MHz, $\text{DMSO-}d_6$) δ 11.67 (s, 1H), 8.04 (d, $J = 8.1$ Hz, 1H), 7.63 - 7.54 (m, 2H), 7.47 - 7.38 (m, 2H), 7.24 (ddd, $J = 8.1, 5.1, 3.0$ Hz, 1H), 7.12 (d, $J = 8.3$ Hz, 1H), 7.02 (t, $J = 7.4$ Hz, 1H), 6.01 (s, 1H), 3.74 (s, 3H). ^{13}C NMR (151 MHz, $\text{DMSO-}d_6$) δ 176.8, 159.4, 149.6, 140.3, 135.4, 131.6, 130.0, 124.8, 124.5, 123.1, 119.4, 118.6, 115.9, 112.7, 107.2, 55.2. IR (KBr): 3097, 2967, 1635, 1602, 1501, 1248, 1024, 815, 752, 513 cm^{-1} . HRMS(ESI) m/z : $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{16}\text{H}_{14}\text{NO}_2$: 252.1019. found: 252.1021.



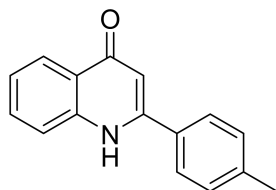
2-(4-methoxyphenyl)quinolin-4(1H)-one(3ea).⁴ (White solid was obtained in 96% isolated yield, 240 mg). ^1H NMR (600 MHz, $\text{DMSO-}d_6$) δ 11.67 (s, 1H), 8.08 (d, $J = 7.9$ Hz, 1H), 7.81 (t, $J = 7.8$ Hz, 3H), 7.65 (t, $J = 7.5$ Hz, 1H), 7.32 (t, $J = 7.4$ Hz, 1H), 7.13 (d, $J = 8.7$ Hz, 2H), 6.31 (s, 1H), 3.85 (s, 3H). ^{13}C NMR (151 MHz, $\text{DMSO-}d_6$) δ 176.8, 161.0, 149.7, 140.5, 131.6, 128.8, 126.2, 124.8, 124.6, 123.1, 118.6, 114.4, 106.5, 55.4. IR (KBr): 3075, 2979, 1597, 1497, 1295, 1237, 1184, 1026, 813, 744, 569, 549 cm^{-1} . HRMS(ESI) m/z : $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{16}\text{H}_{14}\text{NO}_2$: 252.1019. found: 252.1023.



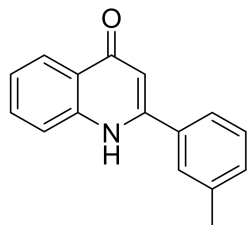
2-(3-methoxyphenyl)quinolin-4(1H)-one(3ac).² (Yellow solid was obtained in 95% isolated yield, 238 mg). ^1H NMR (600 MHz, $\text{DMSO-}d_6$) δ 11.73 (s, 1H), 8.11 (dd, $J = 8.1, 1.5$ Hz, 1H), 7.80 (d, $J = 8.3$ Hz, 1H), 7.71 - 7.64 (m, 1H), 7.49 (t, $J = 7.9$ Hz, 1H), 7.43 - 7.36 (m, 2H), 7.34 (t, $J = 7.5$ Hz, 1H), 7.14 (dd, $J = 8.3, 2.2$ Hz, 1H), 6.37 (s, 1H), 3.87 (s, 3H). ^{13}C NMR (151 MHz, $\text{DMSO-}d_6$) δ 176.9, 159.5, 149.8, 140.5, 135.6, 131.7, 130.1, 124.9, 124.7, 123.2, 119.6, 118.7, 116.1, 112.8, 107.4, 55.4. IR (KBr): 2974, 2942, 2762, 2683, 2476, 1581, 1497, 1460, 1258, 1036, 851, 792, 760, 506 cm^{-1} . HRMS(ESI) m/z : $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{16}\text{H}_{14}\text{NO}_2$: 252.1019. found: 252.1020.



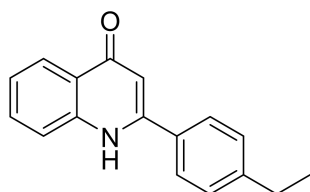
2-(2-methoxyphenyl)quinolin-4(1H)-one(3ad).⁵ (Yellow solid was obtained in 93% isolated yield, 233 mg). ¹H NMR (600 MHz, DMSO-*d*₆) δ 11.75 (s, 1H), 8.12 (d, *J* = 8.1 Hz, 1H), 7.71 - 7.62 (m, 2H), 7.55 - 7.46 (m, 2H), 7.33 (ddd, *J* = 8.1, 5.1, 3.0 Hz, 1H), 7.20 (d, *J* = 8.3 Hz, 1H), 7.10 (t, *J* = 7.4 Hz, 1H), 6.09 (s, 1H), 3.83 (s, 3H). ¹³C NMR (151 MHz, DMSO-*d*₆) δ 176.6, 156.4, 148.2, 140.1, 131.5, 131.3, 130.1, 124.6, 123.5, 122.9, 120.5, 118.3, 111.7, 109.4, 55.6. IR (KBr): 3091, 2968, 1634, 1497, 1242, 1030, 755, 665, 522 cm⁻¹. HRMS(ESI) *m/z*: [M+H]⁺ calcd for C₁₆H₁₄NO₂: 252.1019. found: 252.1021.



2-(*p*-tolyl)quinolin-4(1H)-one(3ae).² (White solid was obtained in 92% isolated yield, 216 mg). ¹H NMR (600 MHz, DMSO-*d*₆) δ 11.79 (s, 1H), 8.09 (dd, *J* = 8.1, 1.5 Hz, 1H), 7.86 (d, *J* = 8.3 Hz, 1H), 7.76 (d, *J* = 7.8 Hz, 2H), 7.69 - 7.61 (m, 1H), 7.38 (d, *J* = 7.9 Hz, 2H), 7.32 (t, *J* = 7.5 Hz, 1H), 6.32 (s, 1H), 2.39 (s, 3H). ¹³C NMR (151 MHz, DMSO-*d*₆) δ 176.9, 149.9, 140.5, 140.3, 131.6, 131.2, 129.5, 127.2, 124.8, 124.6, 123.1, 118.7, 106.8, 20.9. IR (KBr): 3053, 2889, 2794, 1628, 1592, 1539, 1497, 1242, 1136, 808, 744, 565, 506 cm⁻¹. HRMS(ESI) *m/z*: [M+H]⁺ calcd for C₁₆H₁₄NO: 236.1070. found: 236.1074.

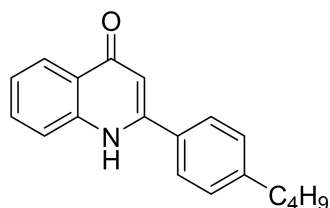


2-(*m*-tolyl)quinolin-4(1H)-one(3af).⁶ (White solid was obtained in 90% isolated yield, 211 mg). ¹H NMR (600 MHz, DMSO-*d*₆) δ 11.70 (s, 1H), 8.11 (d, *J* = 7.8 Hz, 1H), 7.78 (d, *J* = 8.3 Hz, 1H), 7.71 - 7.64 (m, 2H), 7.62 (d, *J* = 7.5 Hz, 1H), 7.46 (t, *J* = 7.6 Hz, 1H), 7.38 (d, *J* = 7.5 Hz, 1H), 7.33 (t, *J* = 7.4 Hz, 1H), 6.33 (s, 1H). ¹³C NMR (151 MHz, DMSO-*d*₆) δ 176.9, 150.1, 140.5, 138.3, 134.2, 131.7, 131.0, 128.8, 127.8, 124.8, 124.7, 124.5, 123.2, 118.7, 107.2, 21.0. IR (KBr): 3095, 2968, 1634, 1581, 1497, 1534, 1253, 1141, 1020, 851, 760, 692, 522 cm⁻¹. HRMS(ESI) *m/z*: [M+H]⁺ calcd for C₁₆H₁₄NO: 236.1070. found: 236.1073.

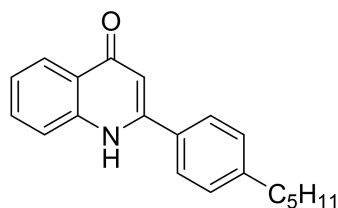


2-(4-ethynylphenyl)quinolin-4(1H)-one (3ag).⁴ (White solid was obtained in 96% isolated yield, 241 mg). ¹H NMR (600 MHz, DMSO-*d*₆) δ 11.72 (s, 1H), 8.10 (dd, *J* = 8.1, 1.5 Hz, 1H),

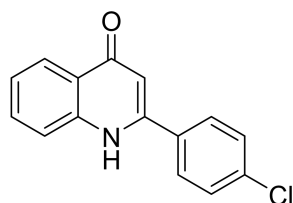
7.81 (d, $J = 8.3$ Hz, 1H), 7.77 (d, $J = 7.9$ Hz, 2H), 7.66 (ddd, $J = 8.4, 6.9, 1.6$ Hz, 1H), 7.42 (d, $J = 8.1$ Hz, 2H), 7.33 (t, $J = 7.4$ Hz, 1H), 6.33 (s, 1H), 2.70 (q, $J = 7.6$ Hz, 2H), 1.22 (t, $J = 7.6$ Hz, 3H). ^{13}C NMR (151 MHz, DMSO- d_6) δ 176.9, 149.9, 146.5, 140.5, 131.6, 131.5, 128.3, 127.3, 124.8, 124.6, 123.1, 118.7, 106.9, 27.9, 15.4. IR (KBr): 3244, 3063, 2968, 1682, 1628, 1597, 1533, 1501, 1438, 1253, 1189, 1136, 824, 755, 501 cm^{-1} . HRMS(ESI) m/z : $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{17}\text{H}_{16}\text{NO}$: 250.1226. found: 250.1224.



2-(4-butylphenyl)quinolin-4(1H)-one(3ah).⁷ (White solid was obtained in 90% isolated yield, 249 mg). ^1H NMR (600 MHz, DMSO- d_6) δ 11.64 (s, 1H), 8.10 (dd, $J = 8.1, 1.5$ Hz, 1H), 7.76 (dd, $J = 13.5, 8.0$ Hz, 3H), 7.70 - 7.62 (m, 1H), 7.39 (d, $J = 7.9$ Hz, 2H), 7.36 - 7.29 (m, 1H), 6.33 (s, 1H), 2.66 (t, $J = 7.7$ Hz, 2H), 1.59 (p, $J = 7.5$ Hz, 2H), 1.32 (h, $J = 7.4$ Hz, 2H), 0.91 (t, $J = 7.4$ Hz, 3H). ^{13}C NMR (151 MHz, DMSO- d_6) δ 176.9, 150.0, 145.1, 140.5, 131.6, 128.8, 127.2, 124.8, 124.7, 123.1, 118.6, 106.9, 99.5, 34.5, 32.9, 21.7, 13.7. IR (KBr): 3208, 2959, 2248, 2131, 1560, 1036, 998, 824, 766, 692, 628, 526 cm^{-1} . HRMS(ESI) m/z : $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{19}\text{H}_{20}\text{NO}$: 278.1539. found: 278.1542

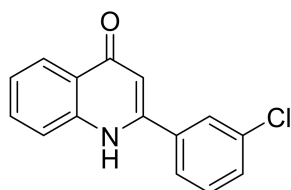


2-(4-pentylphenyl)quinolin-4(1H)-one(3ai).¹ (White solid was obtained in 87% isolated yield, 253 mg). ^1H NMR (600 MHz, DMSO- d_6) δ 11.75 (s, 1H), 8.09 (d, $J = 8.0$ Hz, 1H), 7.83 (d, $J = 8.3$ Hz, 1H), 7.76 (d, $J = 7.8$ Hz, 2H), 7.66 (t, $J = 8.2$ Hz, 1H), 7.39 (d, $J = 8.0$ Hz, 2H), 7.32 (t, $J = 7.4$ Hz, 1H), 6.32 (s, 1H), 2.66 (t, $J = 7.7$ Hz, 2H), 1.61 (p, $J = 7.5$ Hz, 2H), 1.31 (dt, $J = 13.4, 7.2$ Hz, 4H), 0.87 (t, $J = 6.9$ Hz, 3H). ^{13}C NMR (151 MHz, DMSO- d_6) δ 177.4, 150.4, 145.6, 141.0, 132.1, 129.3, 127.8, 125.1, 123.6, 119.2, 107.4, 100.0, 35.3, 31.3, 30.9, 22.4, 14.4. IR (KBr): 3234, 3079, 2947, 2926, 2868, 1628, 1497, 1443, 1263, 1136, 1014, 845, 803, 755, 522 cm^{-1} . HRMS(ESI) m/z : $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{20}\text{H}_{22}\text{NO}$: 292.1696. found: 292.1699.

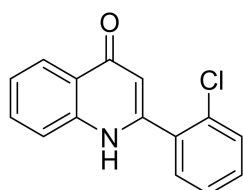


2-(4-chlorophenyl)quinolin-4(1H)-one(3aj).² (Yellow solid was obtained in 95% isolated yield, 242 mg). ^1H NMR (600 MHz, DMSO- d_6) δ 11.73 (s, 1H), 8.10 (d, $J = 8.0$ Hz, 1H), 7.87 (d, $J = 8.1$ Hz, 2H), 7.75 (d, $J = 8.2$ Hz, 1H), 7.67 (dd, $J = 17.3, 7.9$ Hz, 3H), 7.34 (t, $J = 7.3$ Hz, 1H), 6.35 (s, 1H). ^{13}C NMR (151 MHz, DMSO- d_6) δ 176.9, 148.7, 140.4, 135.2, 132.9, 131.9, 129.2, 129.0, 124.8, 124.7, 123.3, 118.7, 107.5. IR (KBr): 3095, 3075, 2958, 1544, 1497, 1433, 1099,

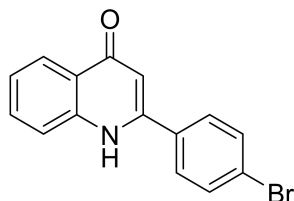
803, 744, 533 cm^{-1} . HRMS(ESI) m/z : $[M+H]^+$ calcd for $\text{C}_{15}\text{H}_{11}\text{ClNO}$: 256.0524. found: 256.0521.



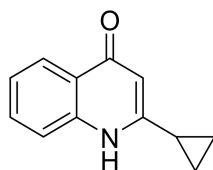
2-(3-chlorophenyl)quinolin-4(1H)-one(3ak).² (Yellow solid was obtained in 90% isolated yield, 230 mg). ^1H NMR (600 MHz, $\text{DMSO-}d_6$) δ 11.95 (s, 1H), 8.10 (d, $J = 7.6$ Hz, 1H), 7.96 (s, 1H), 7.85 (dd, $J = 15.9, 8.0$ Hz, 2H), 7.68 (m, 1H), 7.63 (d, $J = 8.1$ Hz, 1H), 7.59 (t, $J = 7.8$ Hz, 1H), 7.34 (t, $J = 7.6$ Hz, 1H), 6.38 (s, 1H). ^{13}C NMR (151 MHz, $\text{DMSO-}d_6$) δ 176.9, 148.4, 140.5, 136.1, 133.6, 131.8, 130.8, 130.2, 127.2, 126.3, 124.6, 123.3, 118.8, 107.7. IR (KBr): 3095, 3069, 2960, 1634, 1507, 1136, 787, 744, 607, 522 cm^{-1} . HRMS(ESI) m/z : $[M+H]^+$ calcd for $\text{C}_{15}\text{H}_{11}\text{ClNO}$: 256.0524. found: 256.0523.



2-(2-chlorophenyl)quinolin-4(1H)-one (3al).⁸ (Yellow solid was obtained in 92% isolated yield, 234 mg). ^1H NMR (600 MHz, $\text{DMSO-}d_6$) δ 12.00 (s, 1H), 8.14 (d, $J = 7.9$ Hz, 1H), 7.66 (m, 4H), 7.57 (t, $J = 7.7$ Hz, 1H), 7.52 (t, $J = 7.3$ Hz, 1H), 7.36 (t, $J = 7.4$ Hz, 1H), 6.04 (s, 1H). ^{13}C NMR (151 MHz, $\text{DMSO-}d_6$) δ 176.8, 148.2, 140.2, 133.9, 132.0, 131.7, 131.5, 131.1, 129.9, 127.5, 124.9, 124.8, 123.4, 118.5, 109.8. IR (KBr): 3069, 2932, 1676, 1300, 1131, 867, 771, 644, 522, 480 cm^{-1} . HRMS(ESI) m/z : $[M+H]^+$ calcd for $\text{C}_{15}\text{H}_{11}\text{ClNO}$: 256.0524. found: 256.0521.

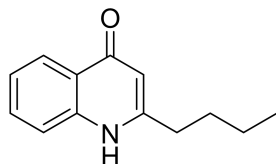


2-(4-bromophenyl)quinolin-4(1H)-one (3am).¹ (Yellow solid was obtained in 80% isolated yield, 239 mg). ^1H NMR (600 MHz, $\text{DMSO-}d_6$) δ 11.73 (s, 1H), 8.10 (d, $J = 7.8$ Hz, 1H), 7.77 (d, $J = 26.7$ Hz, 5H), 7.68 (t, $J = 7.3$ Hz, 1H), 7.34 (t, $J = 7.3$ Hz, 1H), 6.35 (s, 1H). ^{13}C NMR (151 MHz, $\text{DMSO-}d_6$) δ 176.6, 148.5, 140.2, 133.0, 131.6, 131.6, 129.2, 124.6, 124.4, 123.7, 123.0, 118.4, 107.1. IR (KBr): 3106, 3079, 2968, 1592, 1539, 1501, 1438, 1247, 1004, 824, 755, 537 cm^{-1} . HRMS(ESI) m/z : $[M+H]^+$ calcd for $\text{C}_{15}\text{H}_{11}\text{BrNO}$: 300.0019. found: 300.0020.



2-cyclopropylquinolin-4(1H)-one(3an).⁴ (White solid was obtained in 94% isolated yield, 174 mg). ^1H NMR (600 MHz, $\text{DMSO-}d_6$) δ 11.51 (s, 1H), 8.01 (d, $J = 8.0$ Hz, 1H), 7.63 - 7.53 (m, 2H), 7.25 (t, $J = 7.9$ Hz, 1H), 5.71 (s, 1H), 1.93 (tt, $J = 8.4, 5.0$ Hz, 1H), 1.11 - 1.02 (m, 2H),

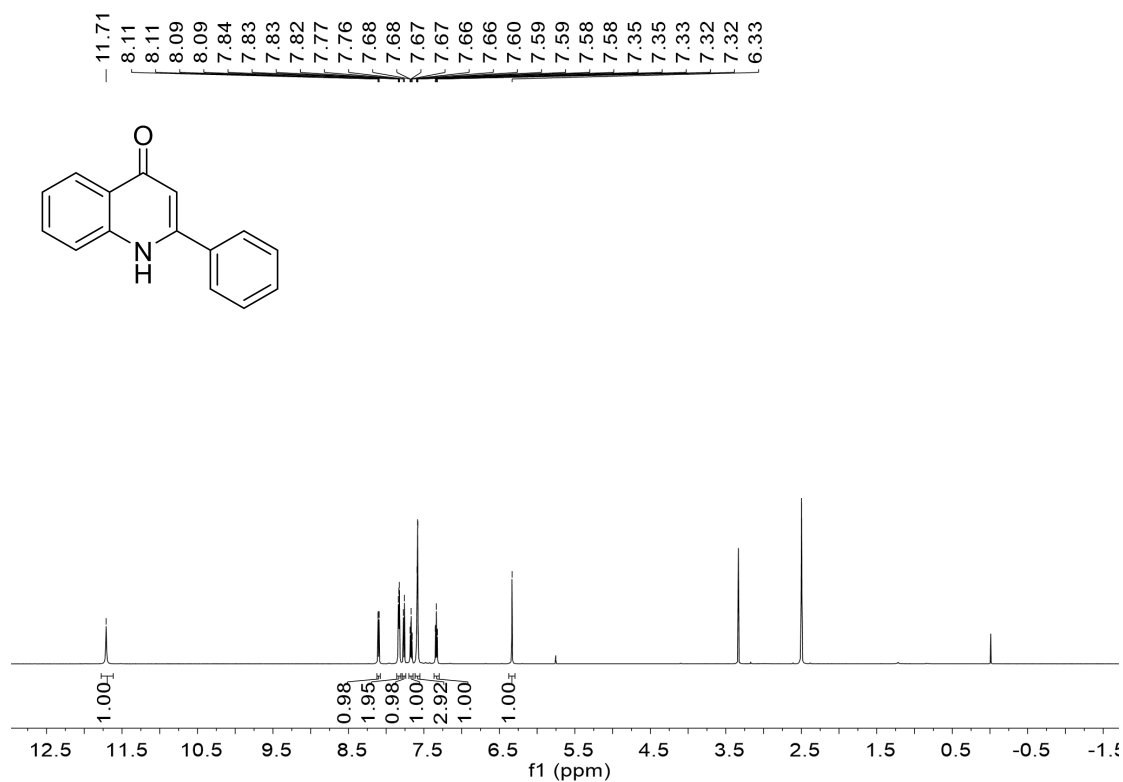
0.96 - 0.87 (m, 2H). ^{13}C NMR (151 MHz, $\text{DMSO-}d_6$) δ 176.5, 155.6, 140.1, 131.3, 124.8, 124.7, 122.7, 117.7, 103.0, 13.4, 8.8. IR (KBr): 3254, 3063, 2889, 2783, 1640, 1592, 1491, 1358, 1300, 1247, 972, 750, 517 cm^{-1} . HRMS(ESI) m/z : $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{12}\text{H}_{12}\text{NO}$: 186.0913. found: 186.0919.



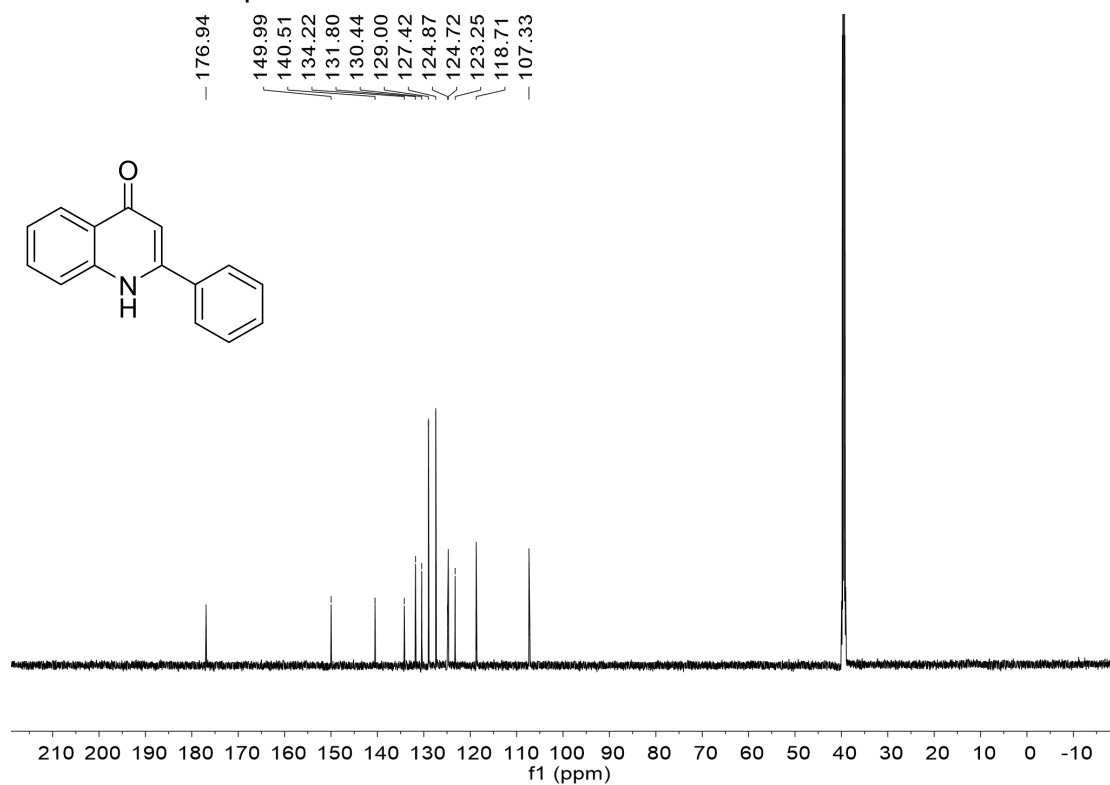
2-butylquinolin-4(1H)-one(3ao).⁴ (White solid was obtained in 67% isolated yield, 134 mg). ^1H NMR (600 MHz, $\text{DMSO-}d_6$) δ 11.57 (s, 1H), 8.05 (d, $J = 7.9$ Hz, 1H), 7.65 - 7.59 (m, 1H), 7.55 (d, $J = 8.2$ Hz, 1H), 7.28 (t, $J = 7.5$ Hz, 1H), 2.51 (s, 1H), 1.66 (p, $J = 7.6$ Hz, 2H), 1.36 (h, $J = 7.4$ Hz, 2H), 0.92 (t, $J = 7.4$ Hz, 3H). ^{13}C NMR (151 MHz, $\text{DMSO-}d_6$) δ 177.3, 154.2, 140.6, 131.9, 125.2, 125.0, 123.2, 118.4, 108.0, 33.4, 30.9, 22.1, 14.1. IR (KBr): 3071, 2959, 1615, 1551, 1449, 1242, 926, 839, 763, 687, 554 cm^{-1} . HRMS(ESI) m/z : $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{13}\text{H}_{16}\text{NO}$: 202.1226. found: 202.1229.

S-6. NMR Spectrum of products

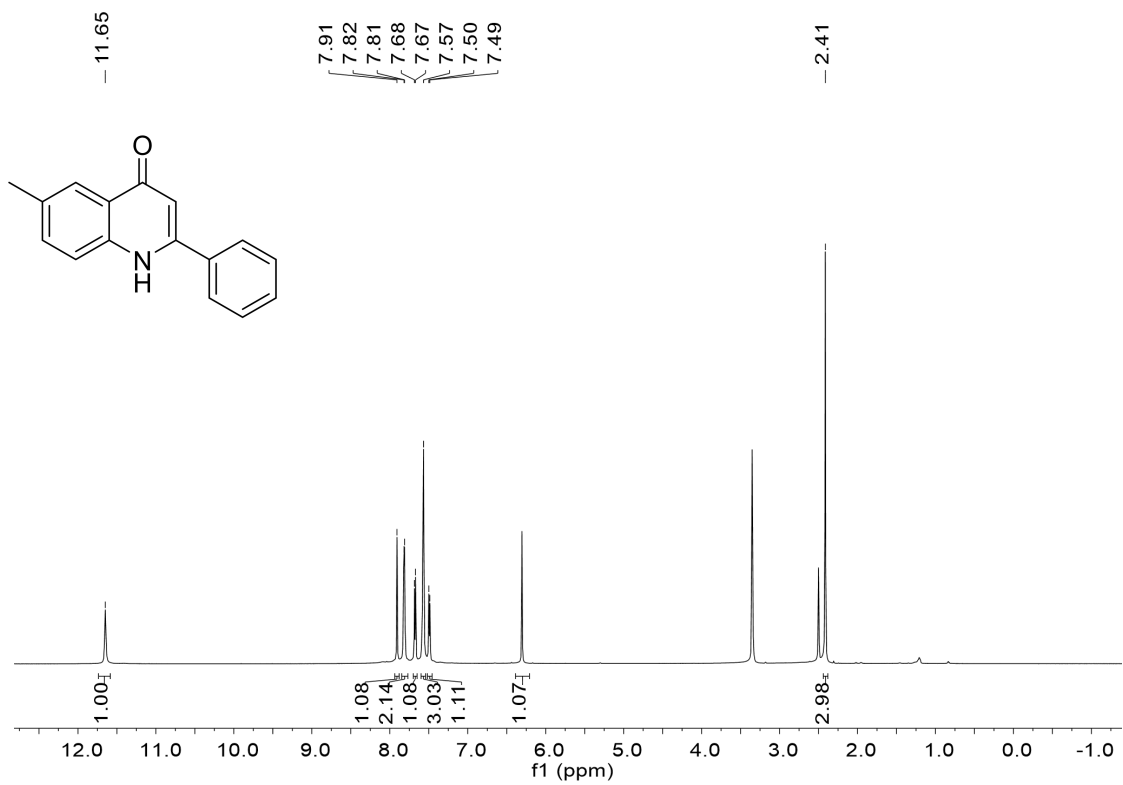
¹H NMR of compound **3aa**



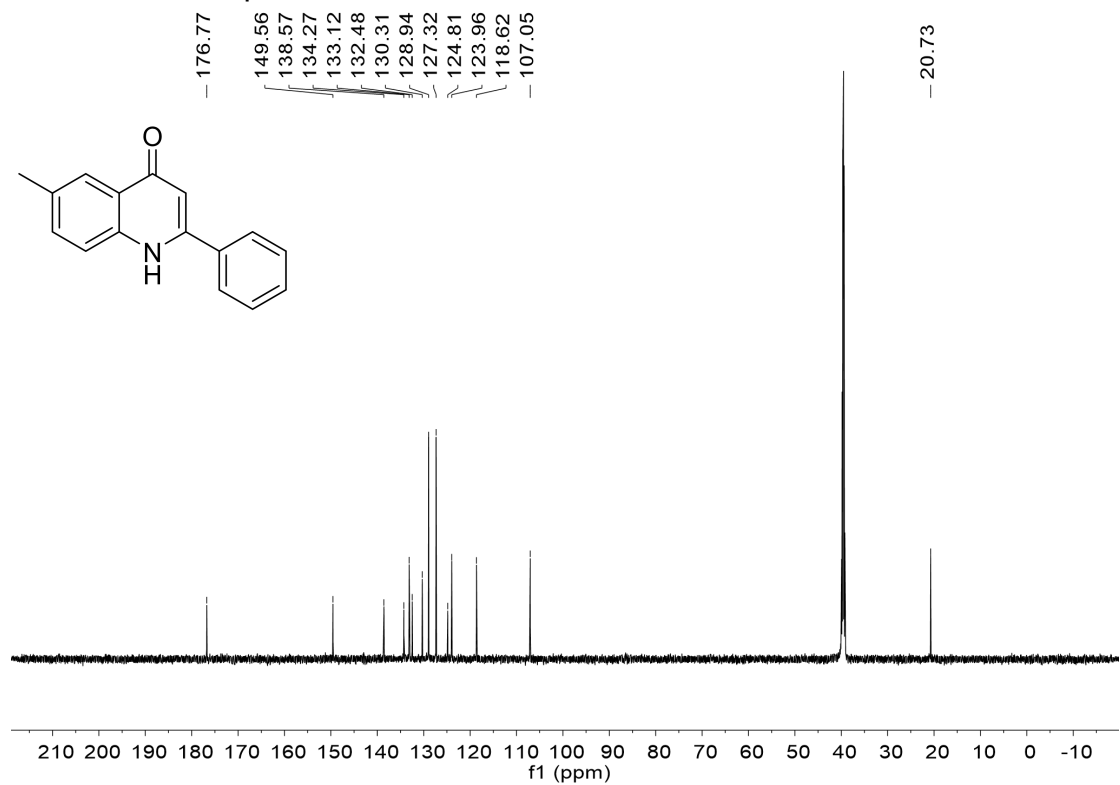
¹³C NMR of compound **3aa**



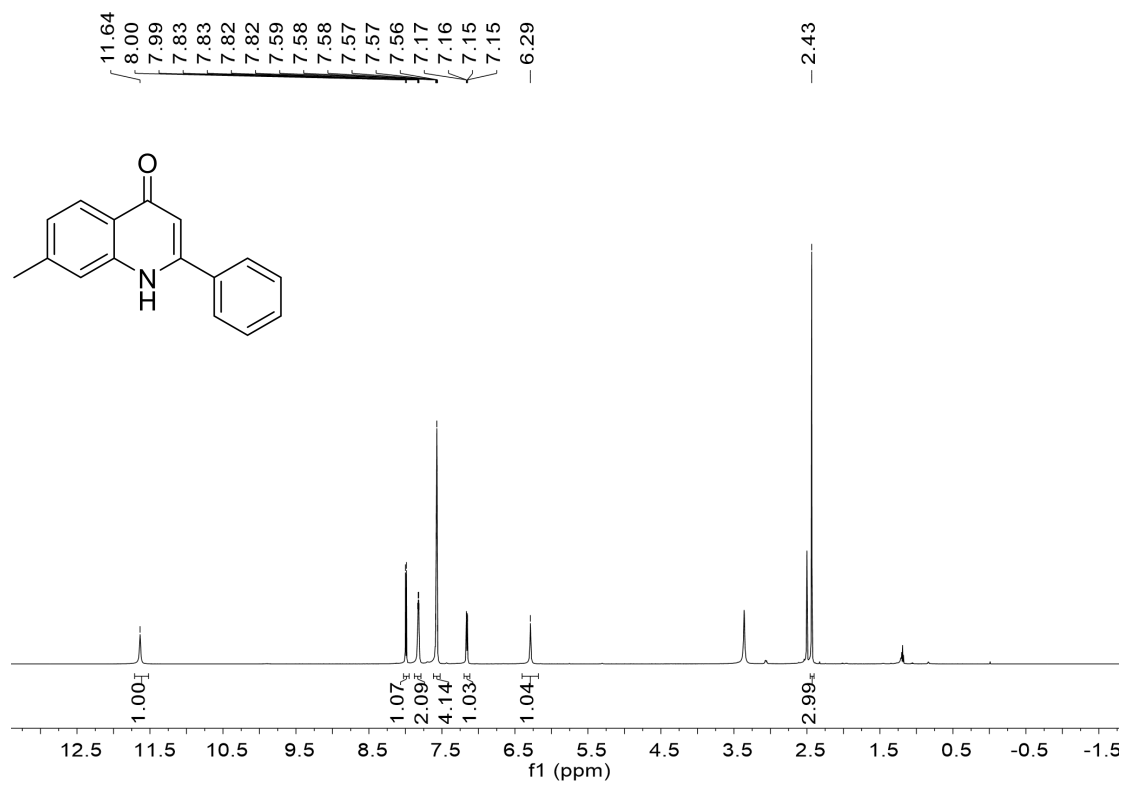
¹H NMR of compound **3ba**



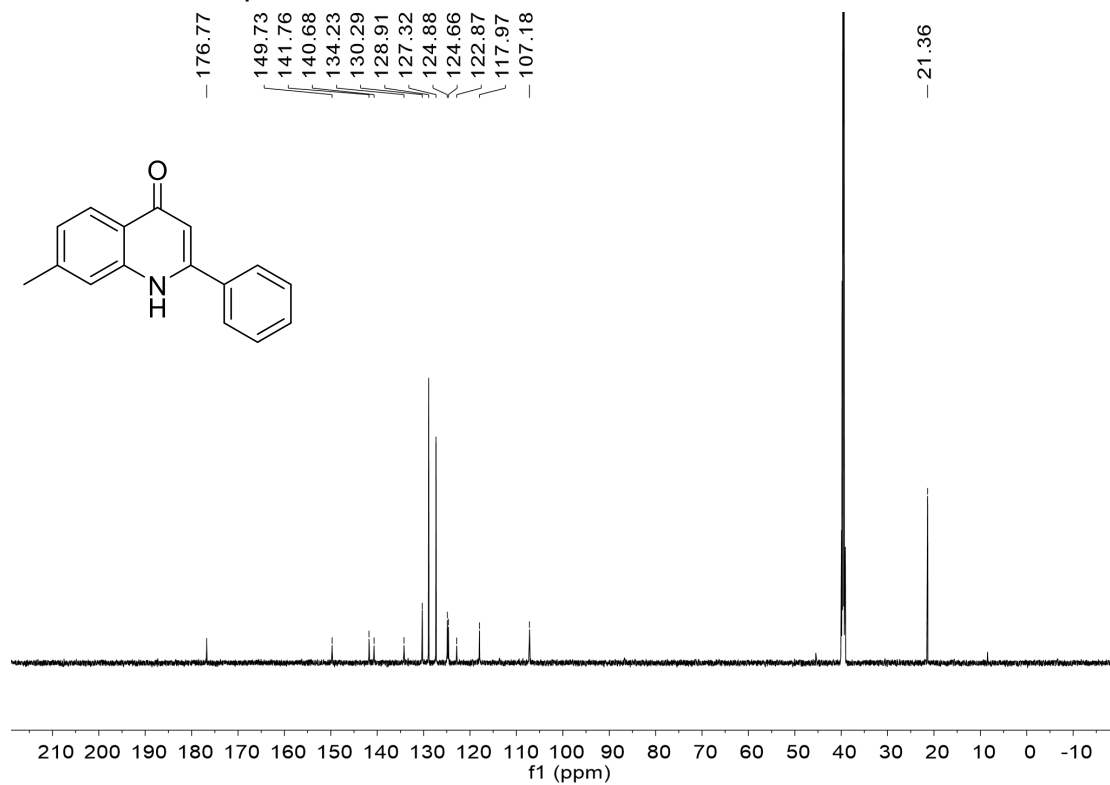
¹³C NMR of compound **3ba**



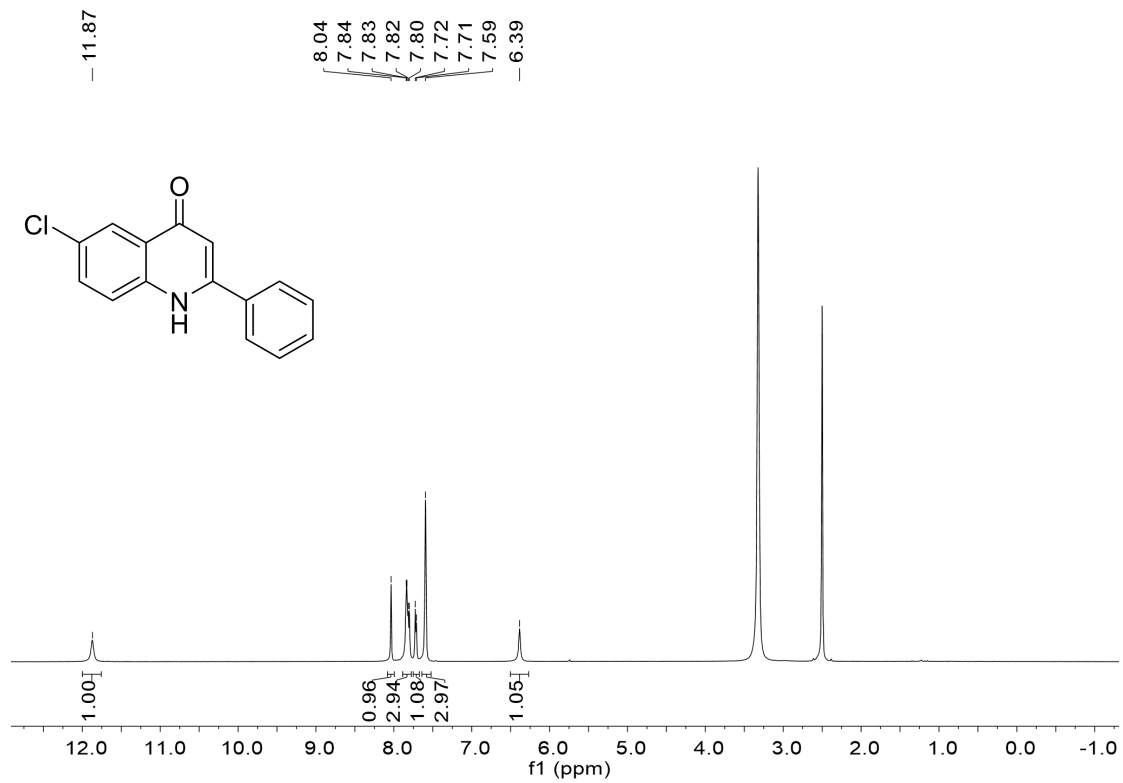
¹H NMR of compound **3ca**



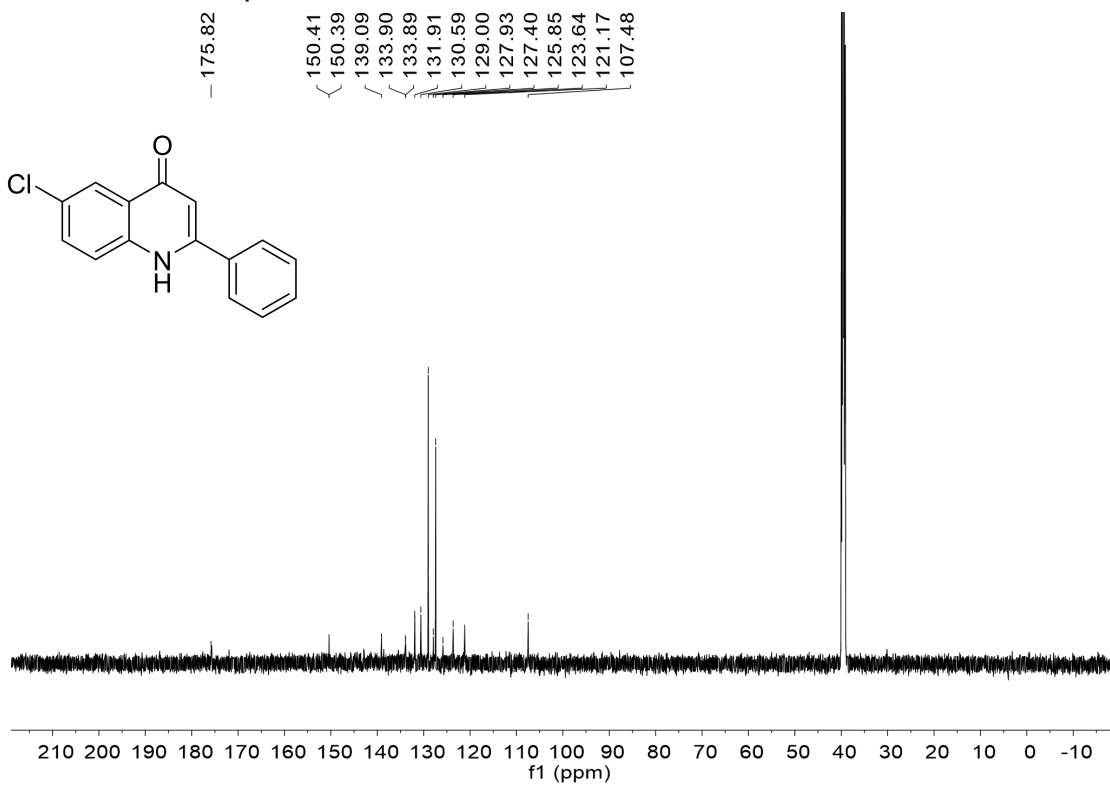
¹³C NMR of compound **3ca**



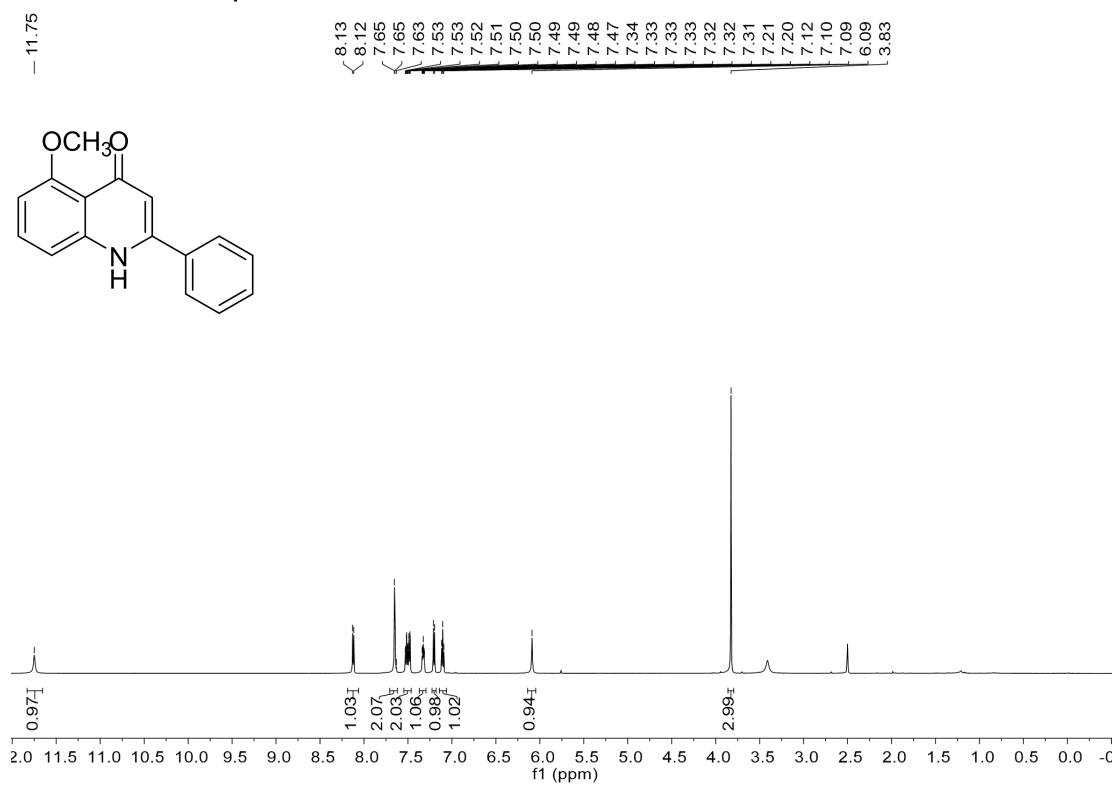
¹H NMR of compound **3da**



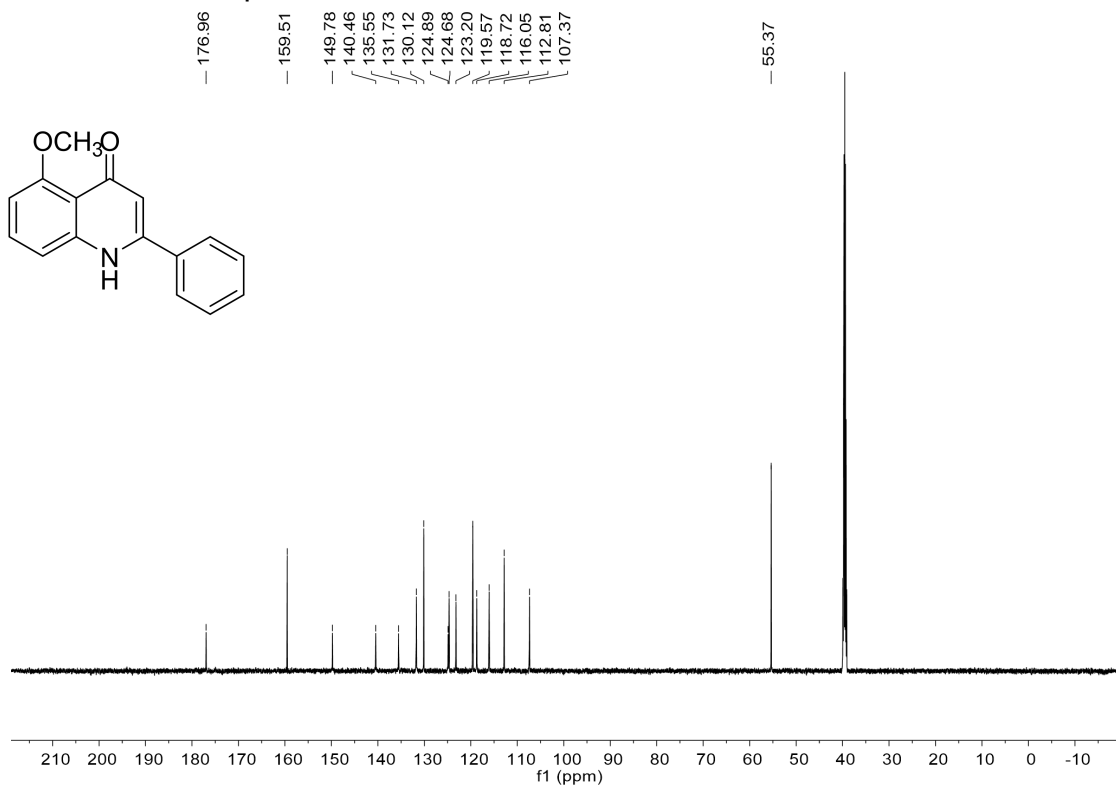
¹³C NMR of compound **3da**



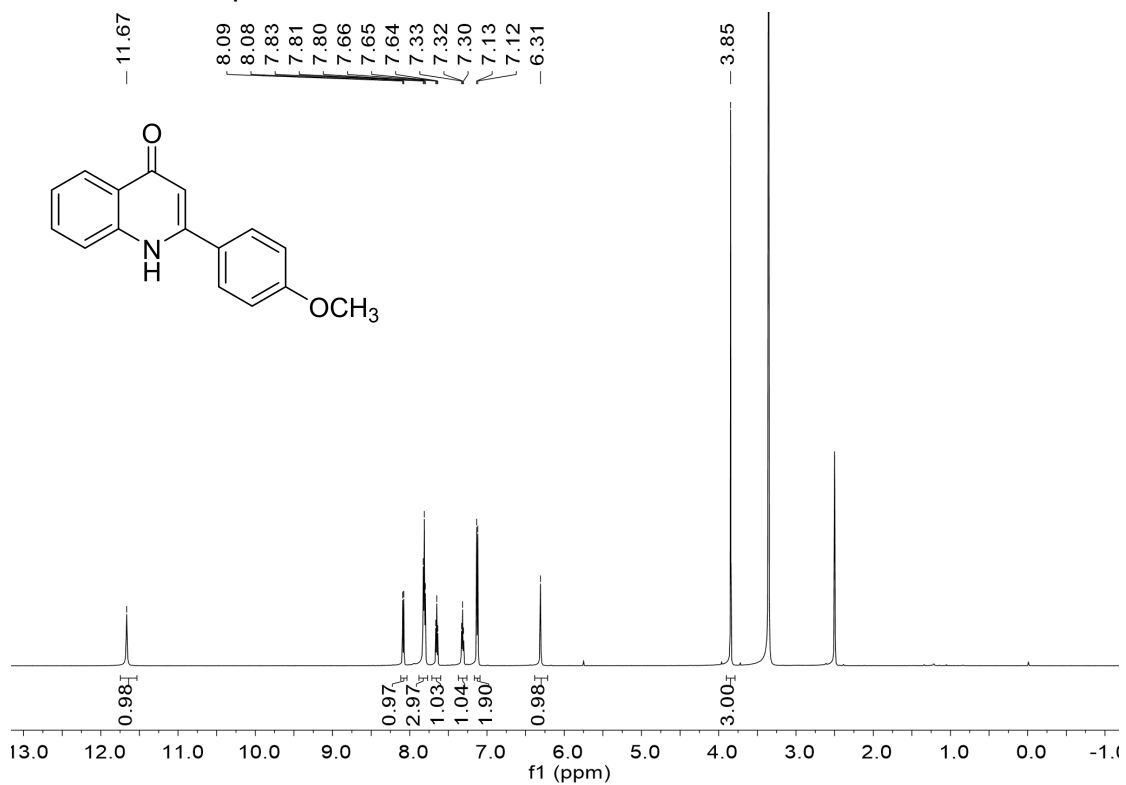
¹H NMR of compound **3ea**



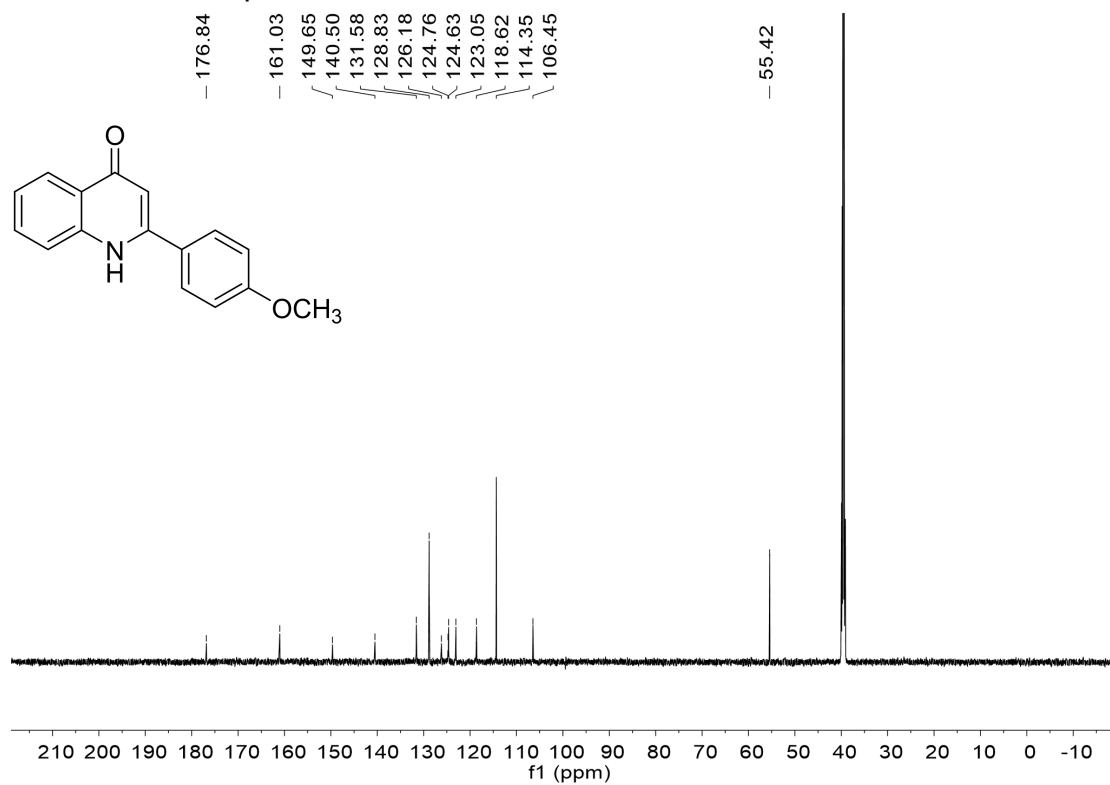
¹³C NMR of compound **3ea**



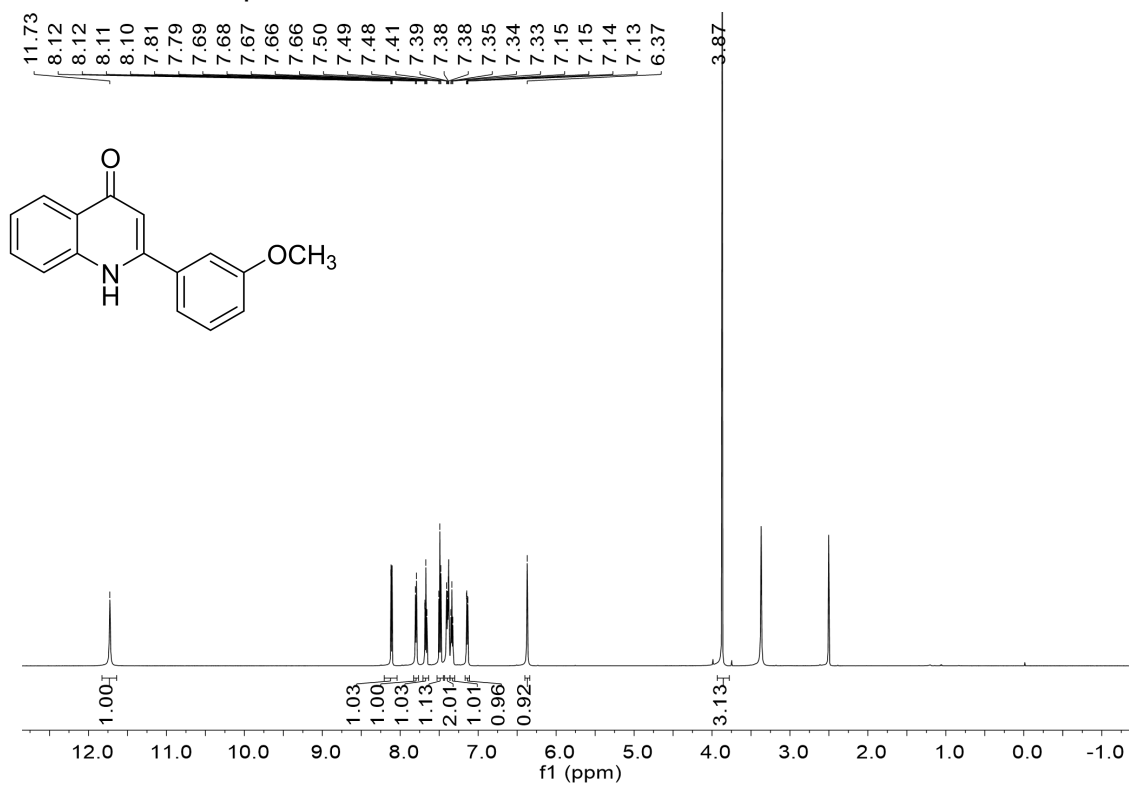
¹H NMR of compound **3ab**



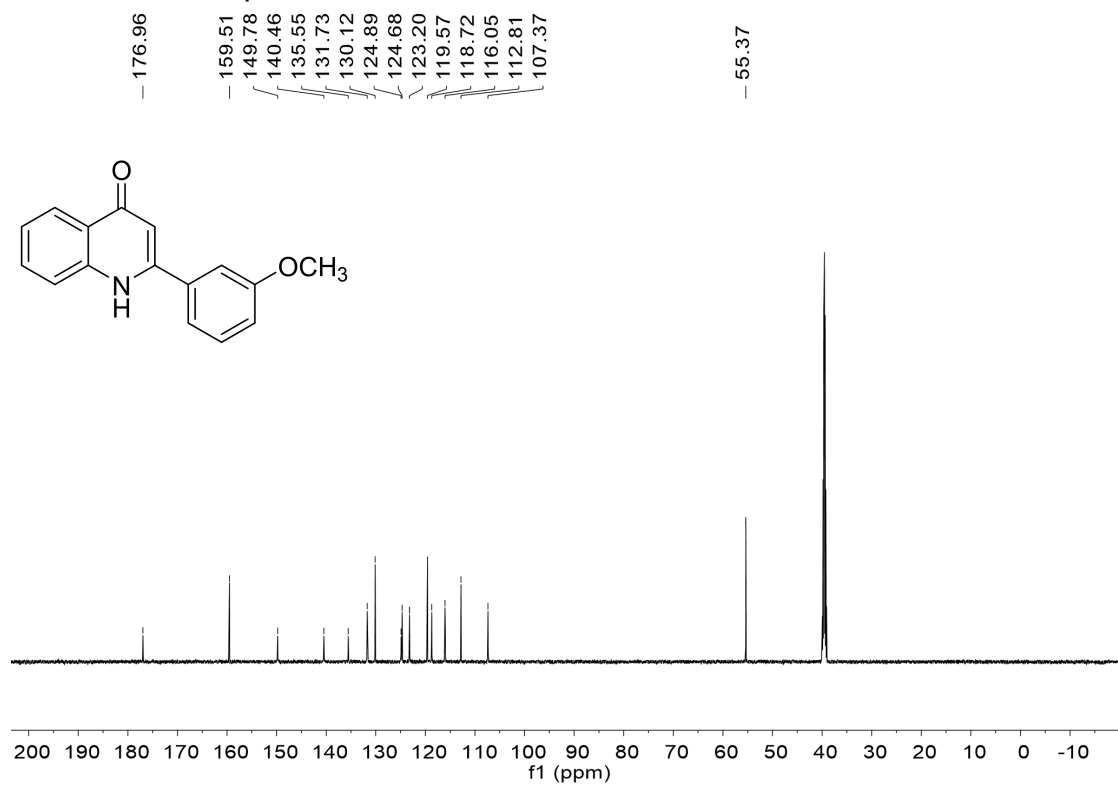
¹³C NMR of compound **3ab**



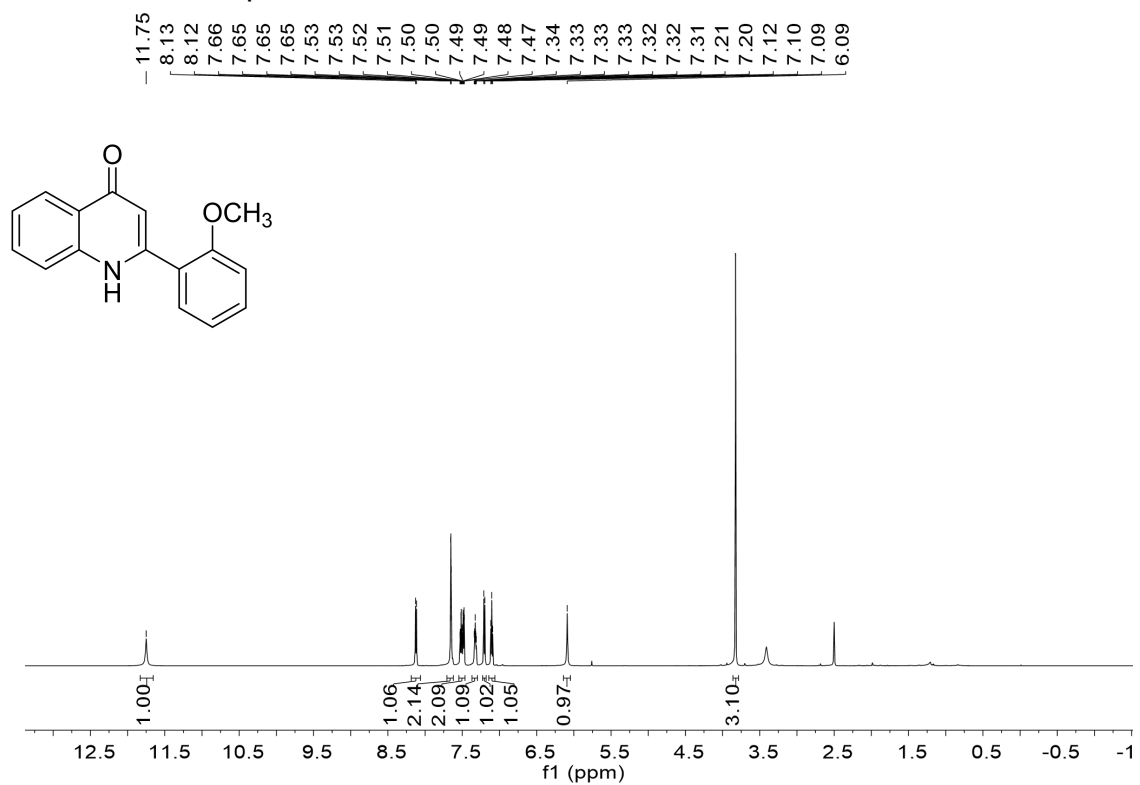
¹H NMR of compound **3ac**



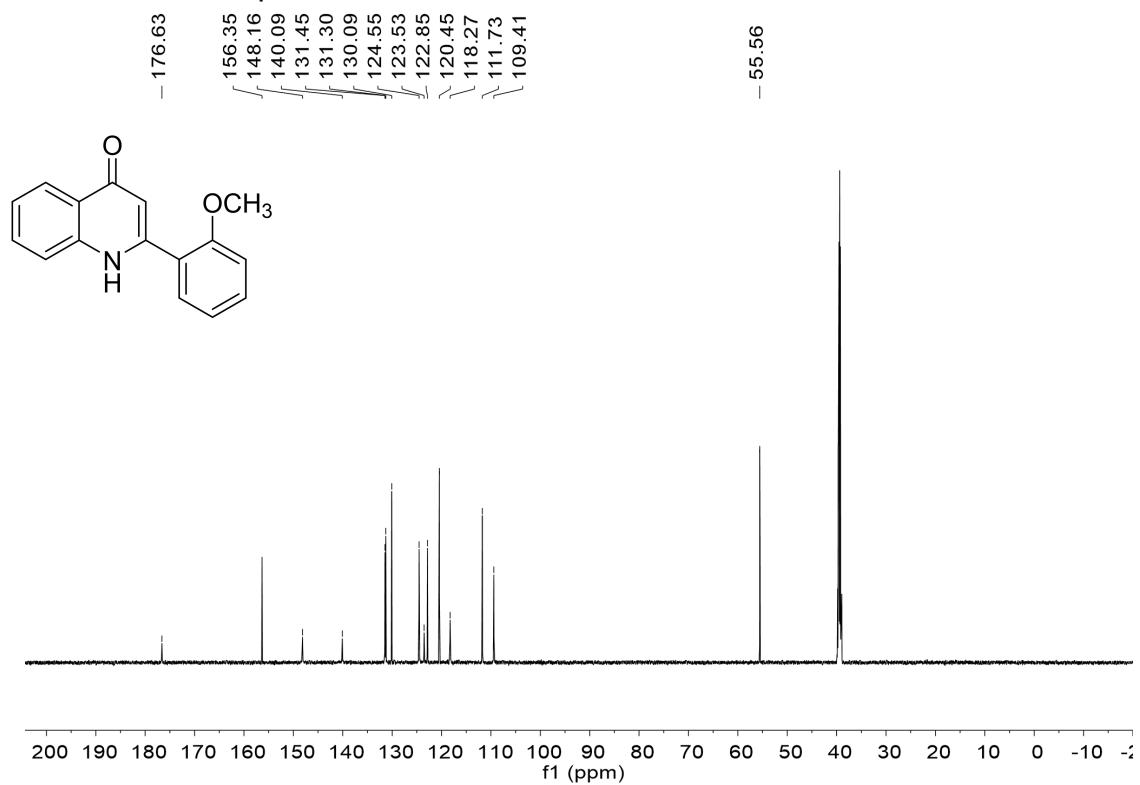
¹³C NMR of compound **3ac**



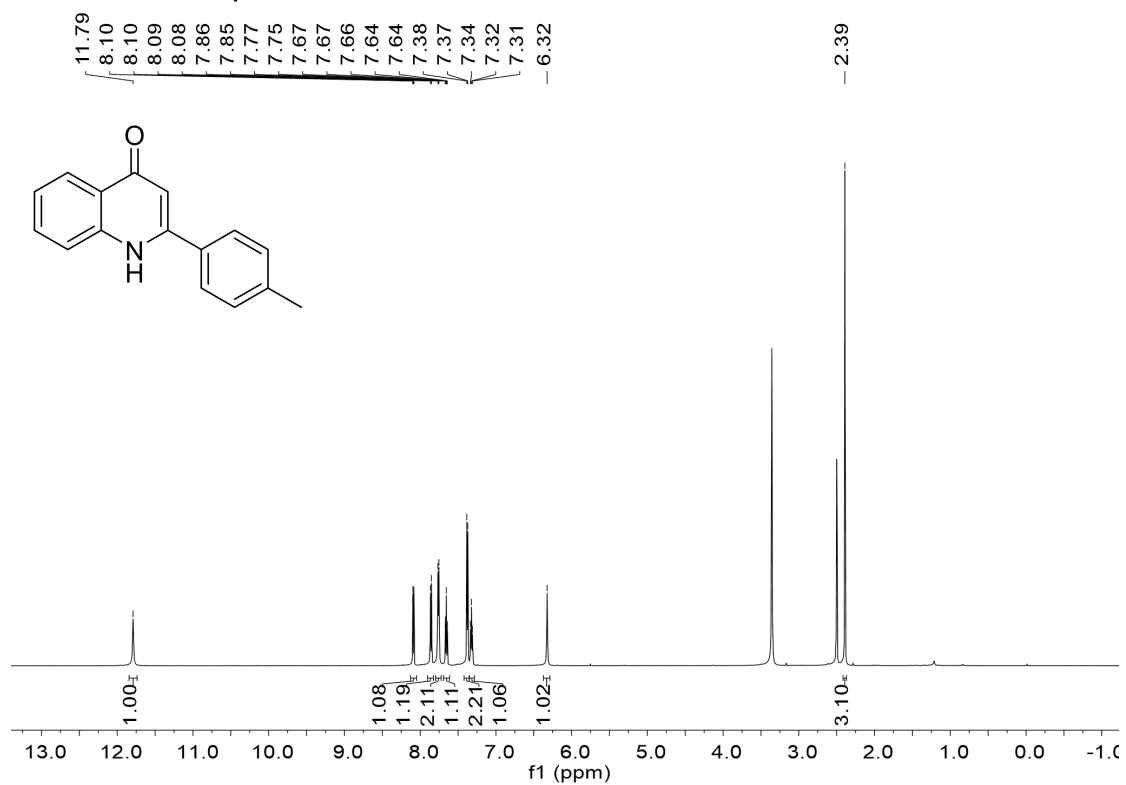
¹H NMR of compound **3ad**



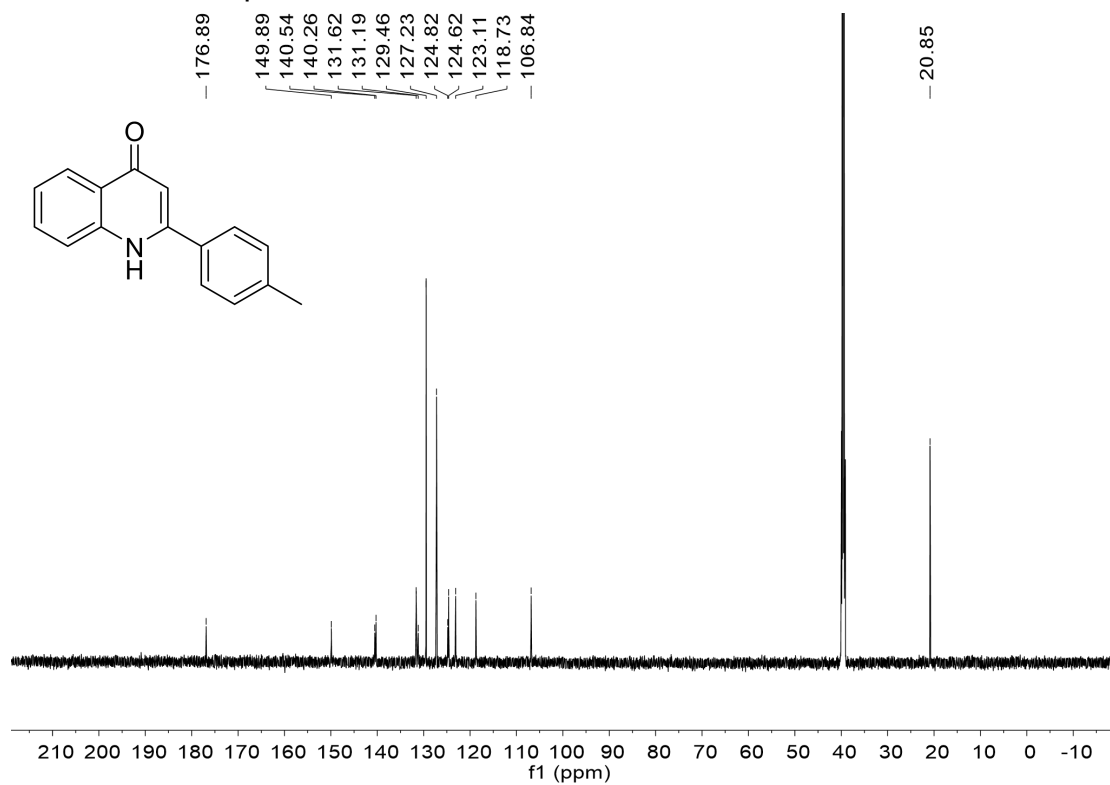
¹³C NMR of compound **3ad**



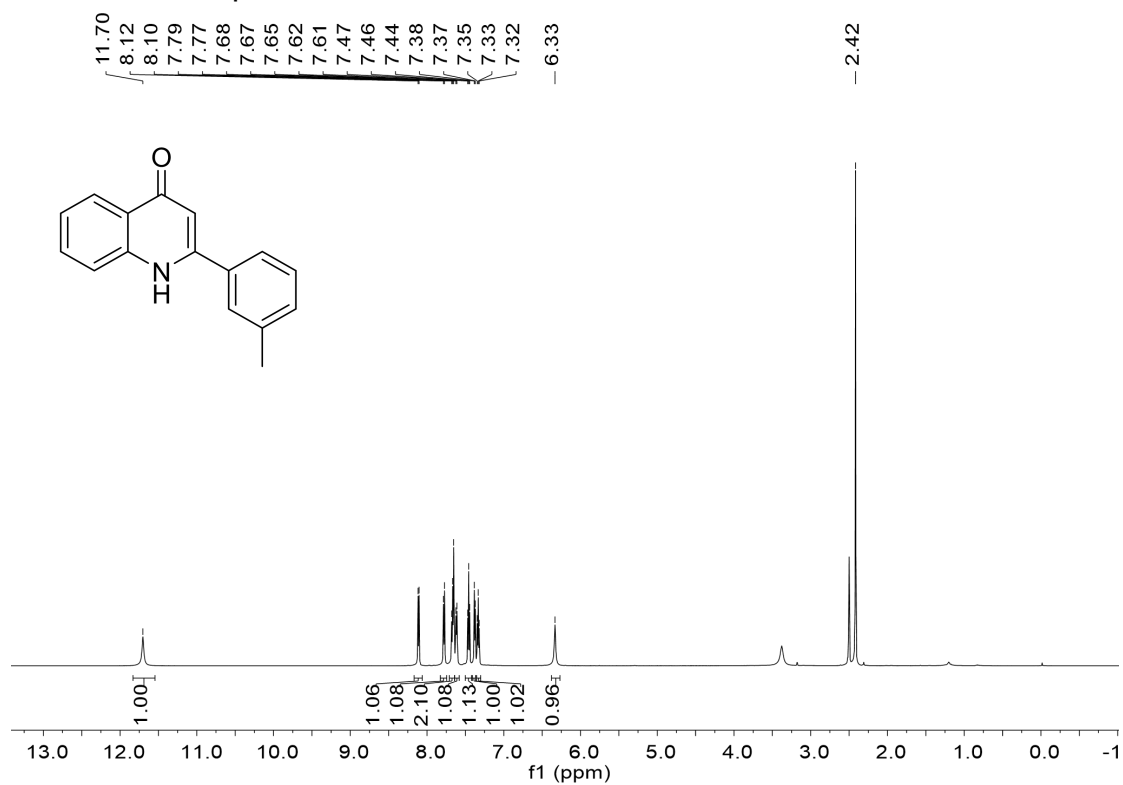
¹H NMR of compound **3ae**



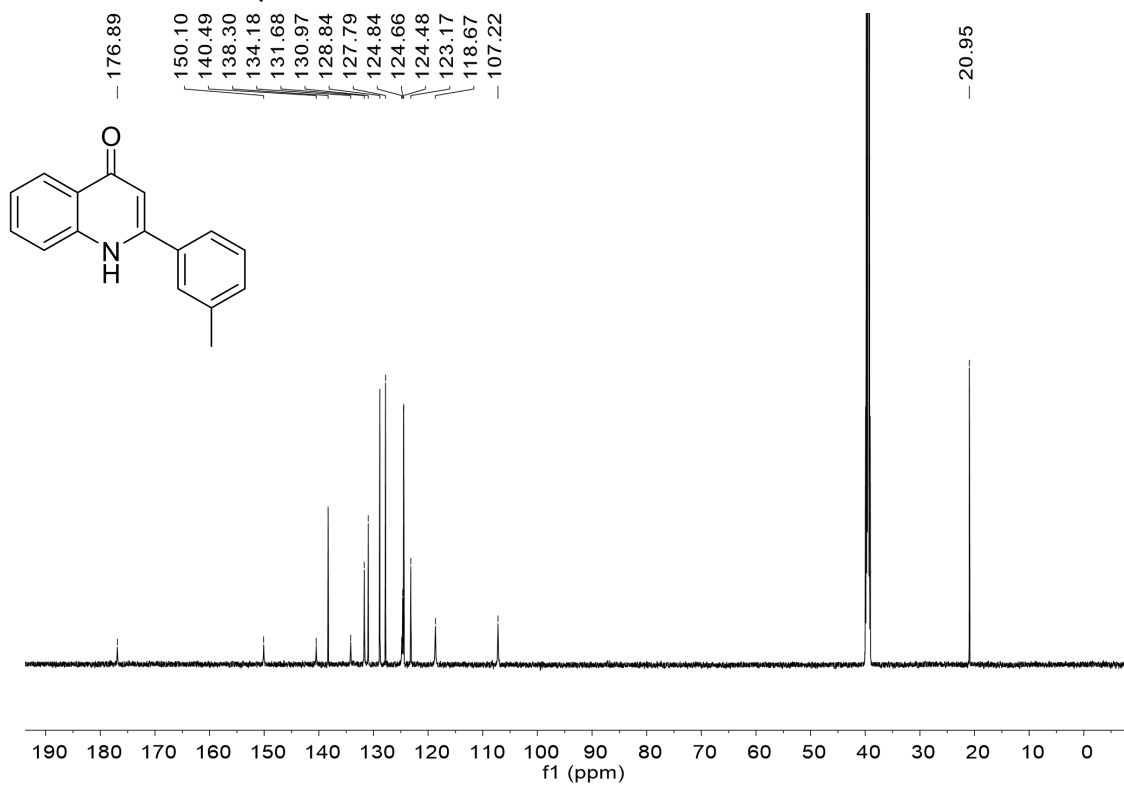
¹³C NMR of compound **3ae**



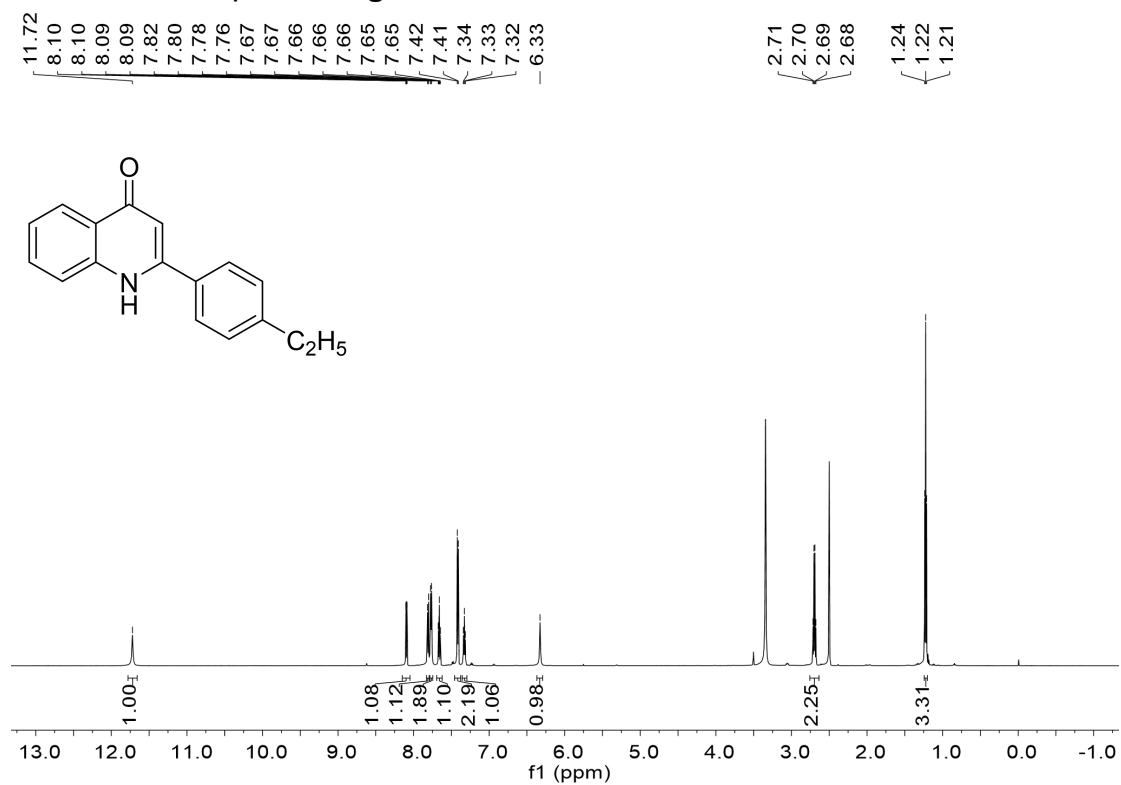
¹H NMR of compound **3af**



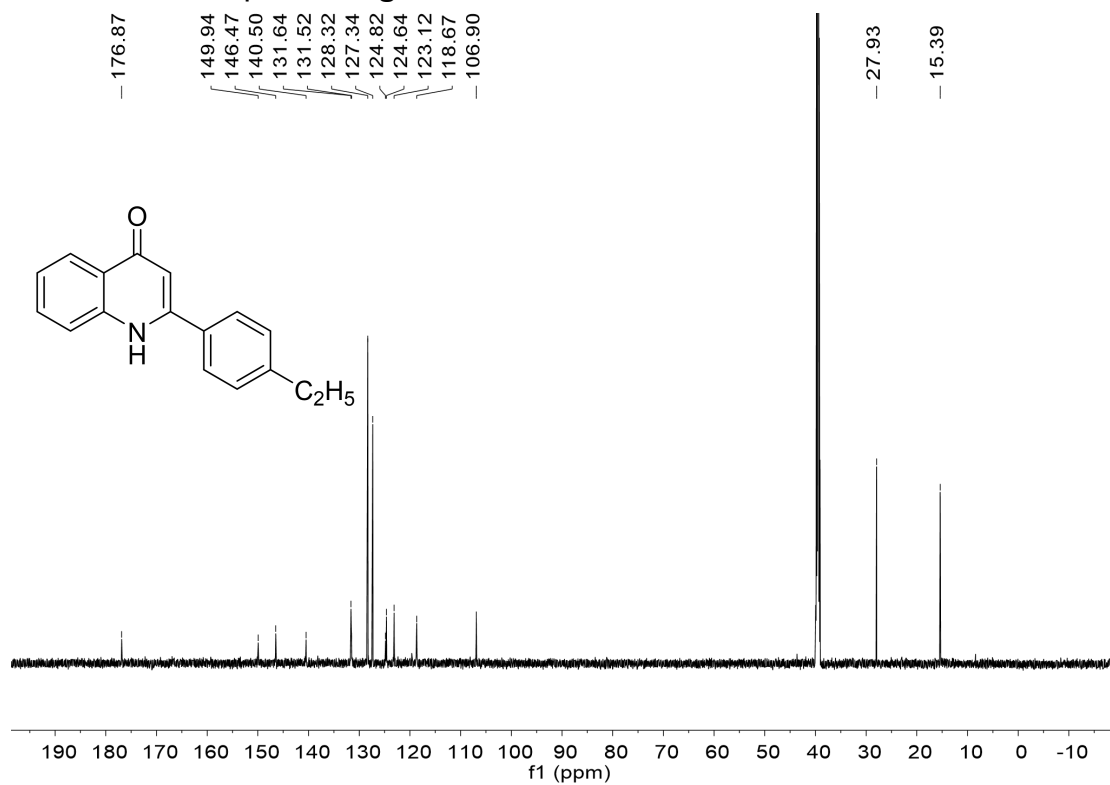
¹³C NMR of compound **3af**



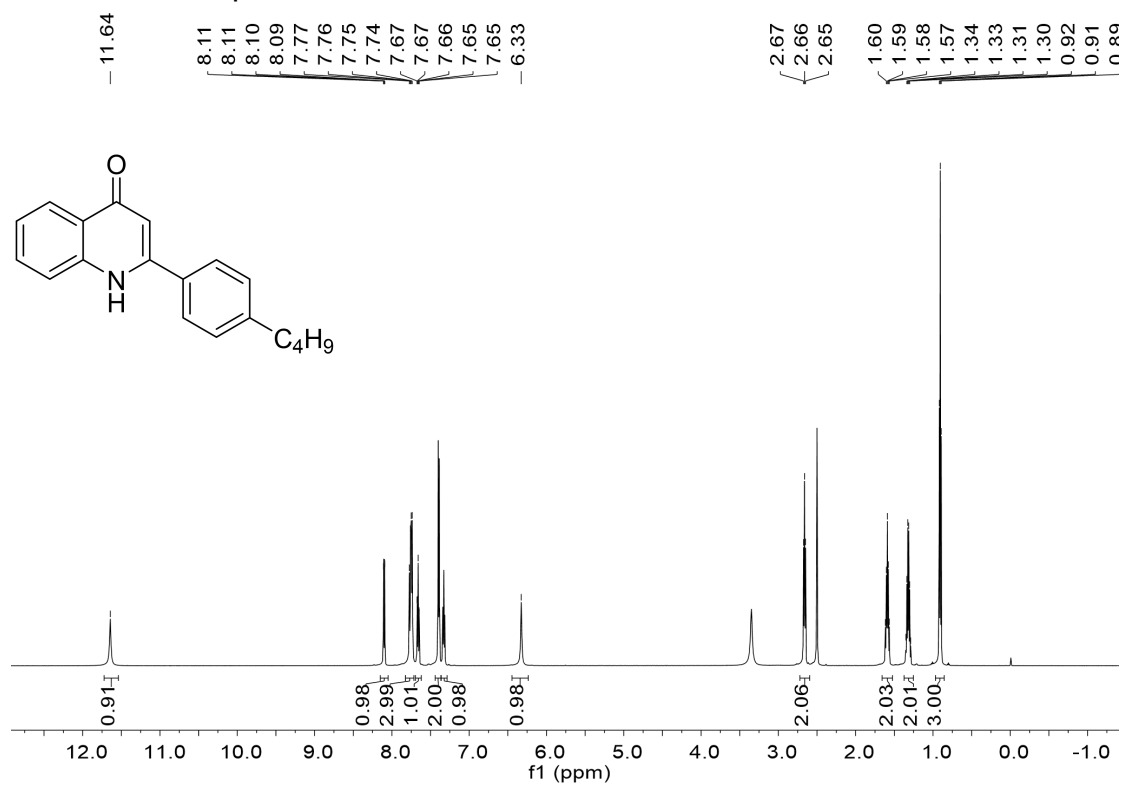
¹H NMR of compound **3ag**



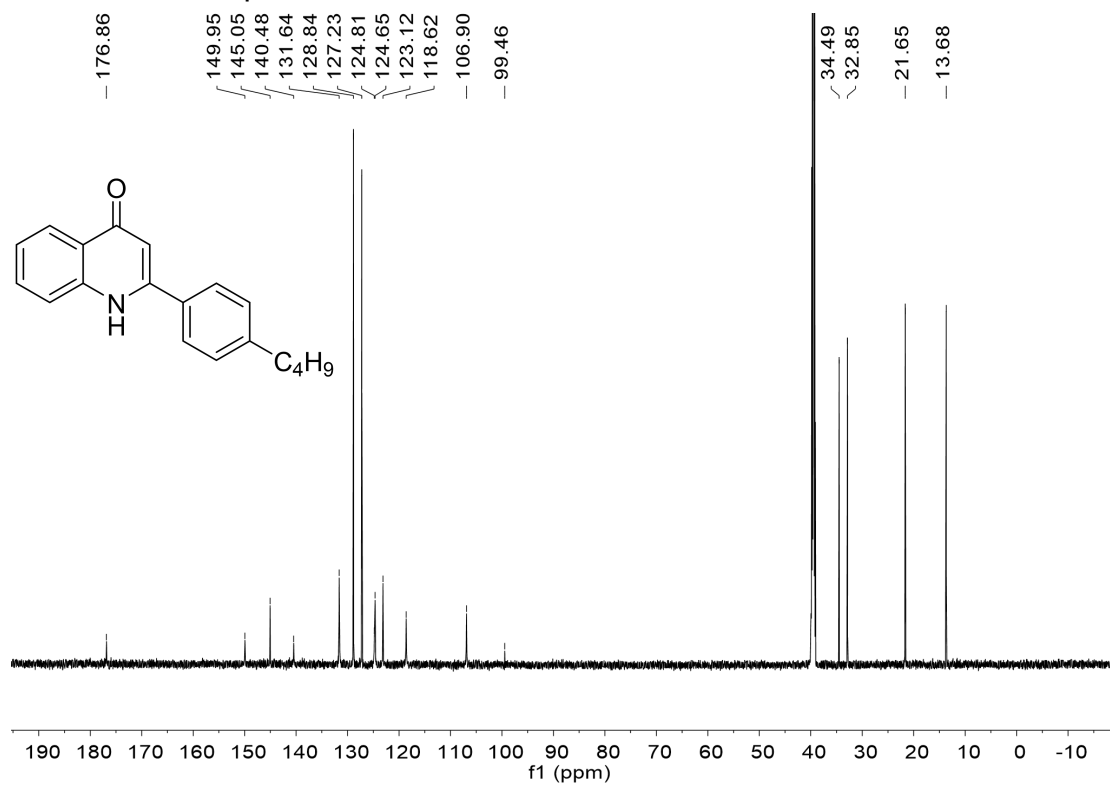
¹³C NMR of compound **3ag**



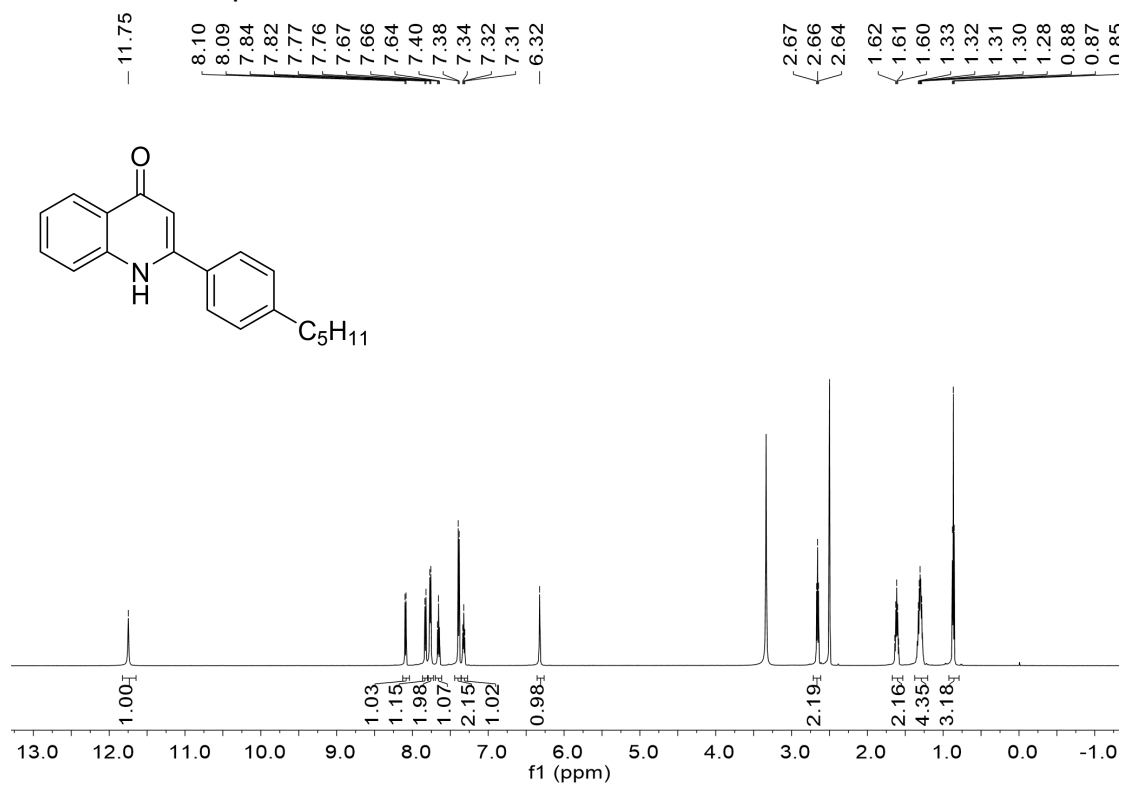
¹H NMR of compound **3ah**



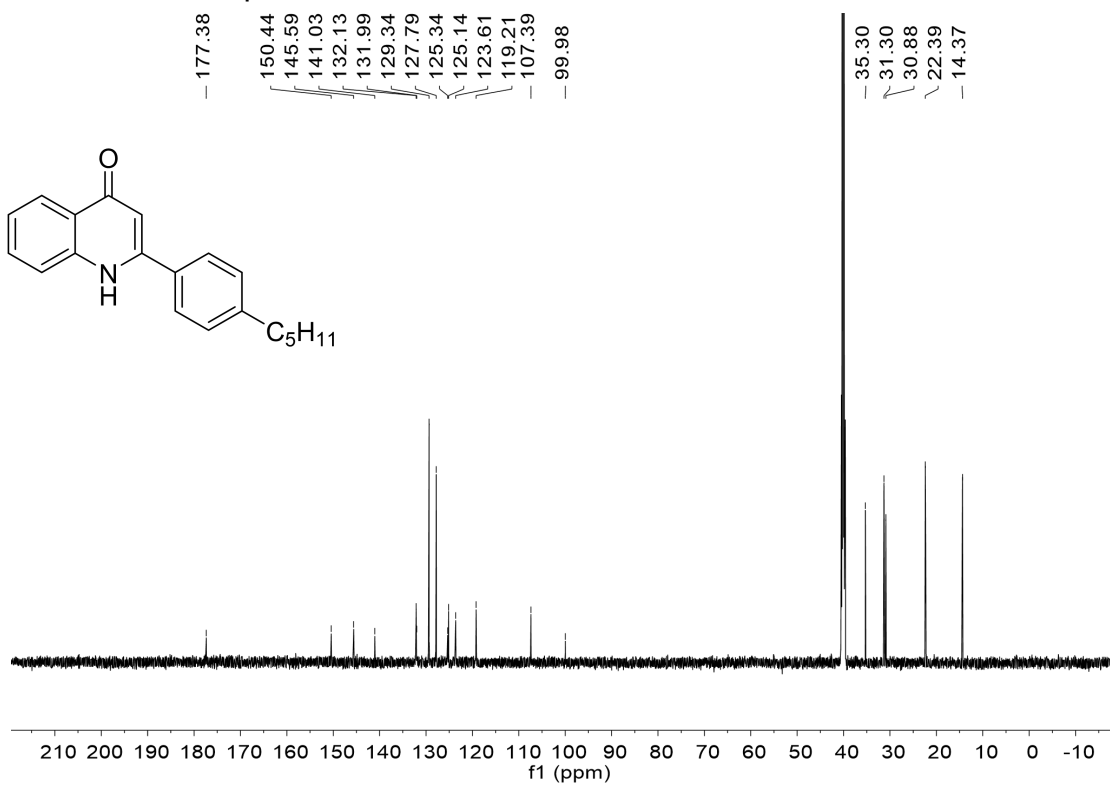
¹³C NMR of compound **3ah**



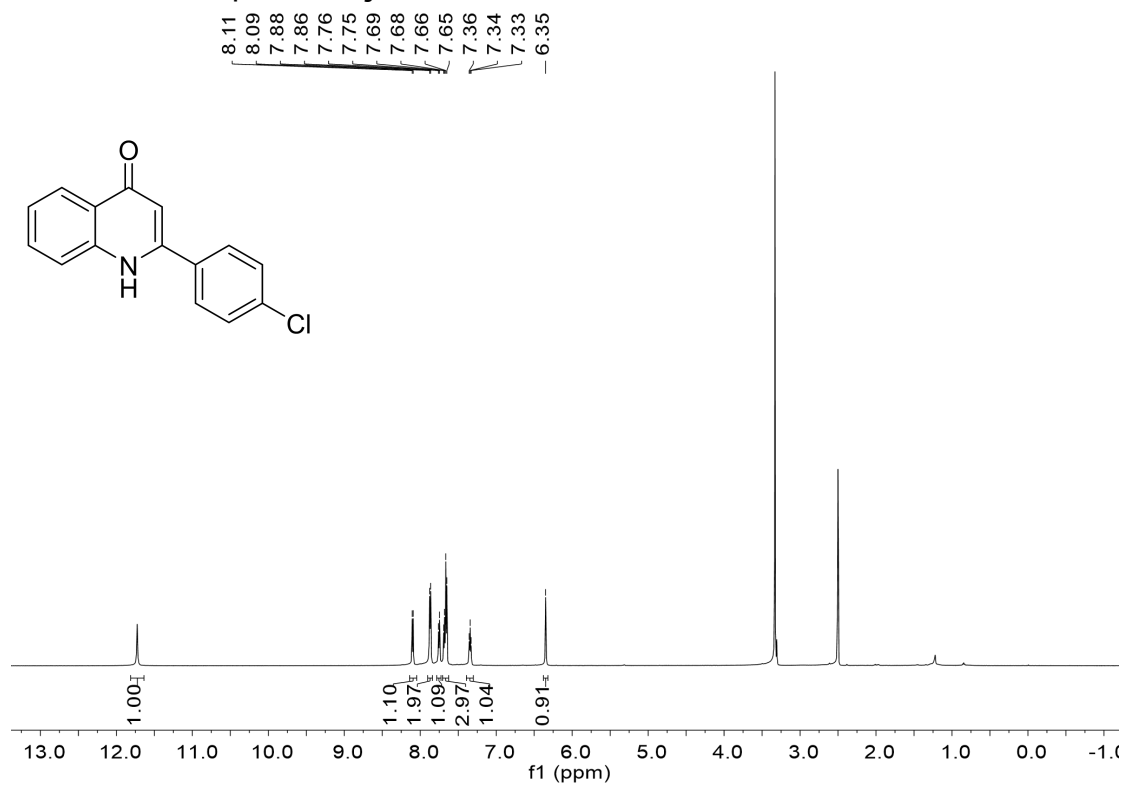
¹H NMR of compound **3ai**



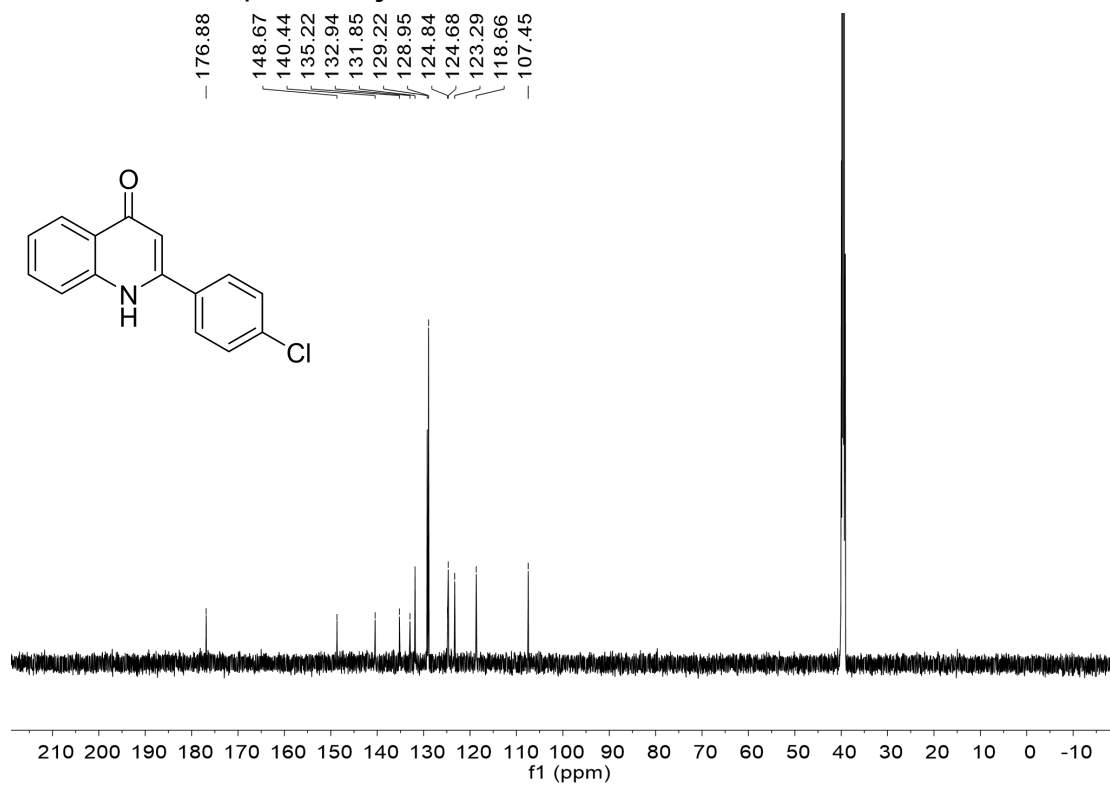
¹³C NMR of compound **3ai**



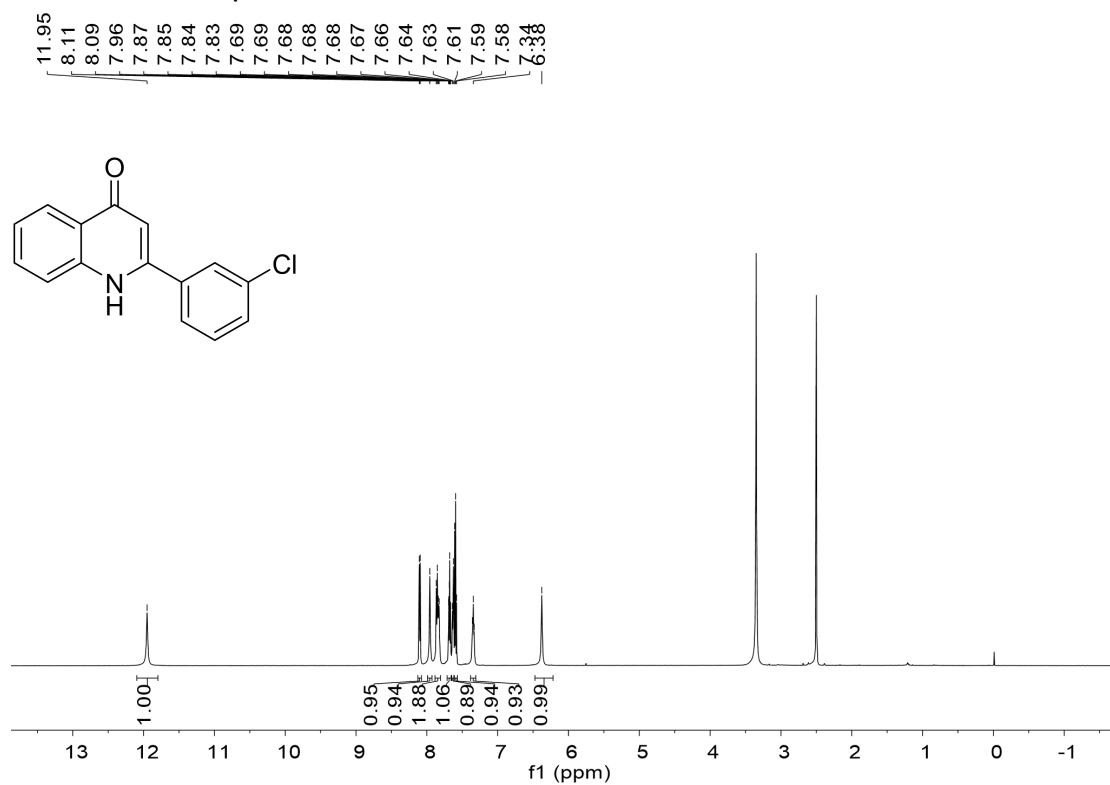
¹H NMR of compound **3aj**



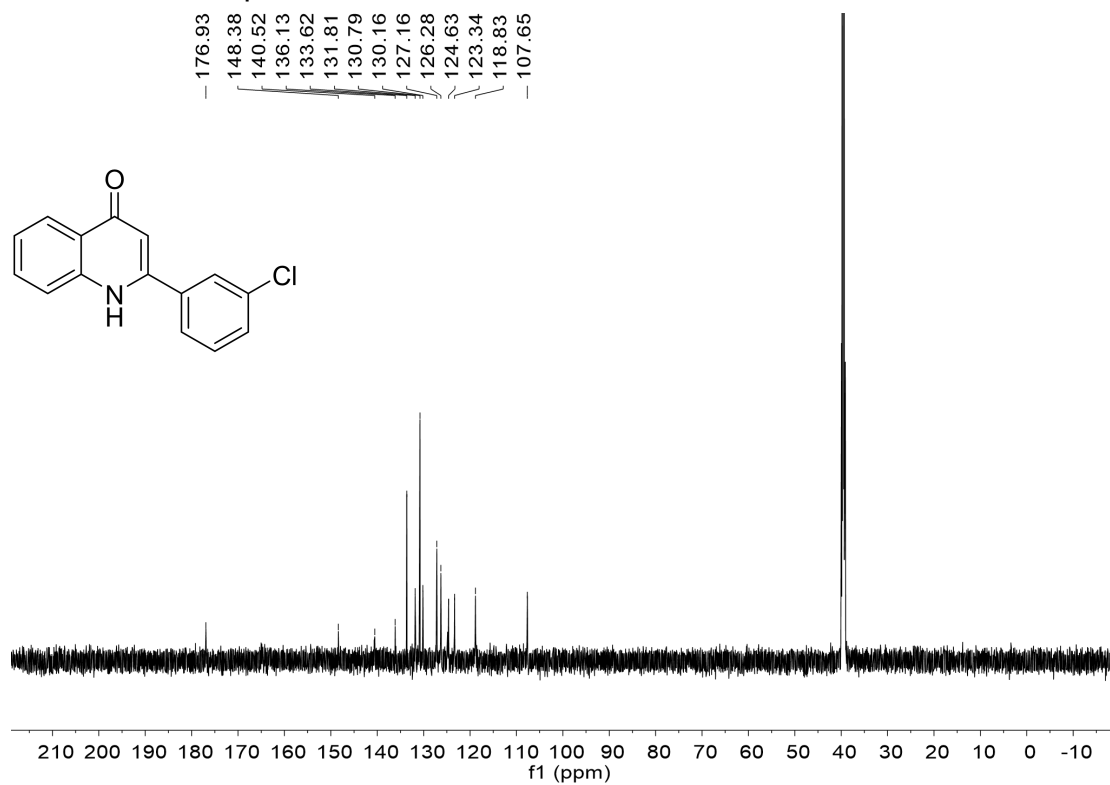
¹³C NMR of compound **3aj**



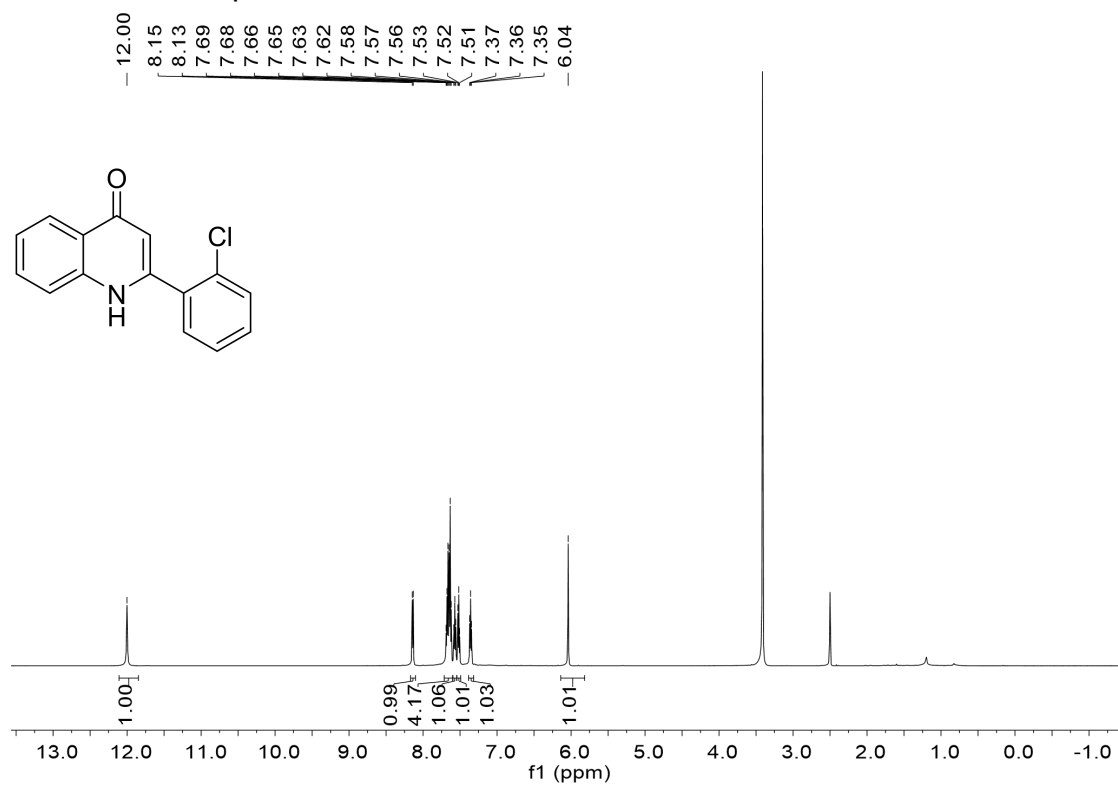
¹H NMR of compound **3ak**



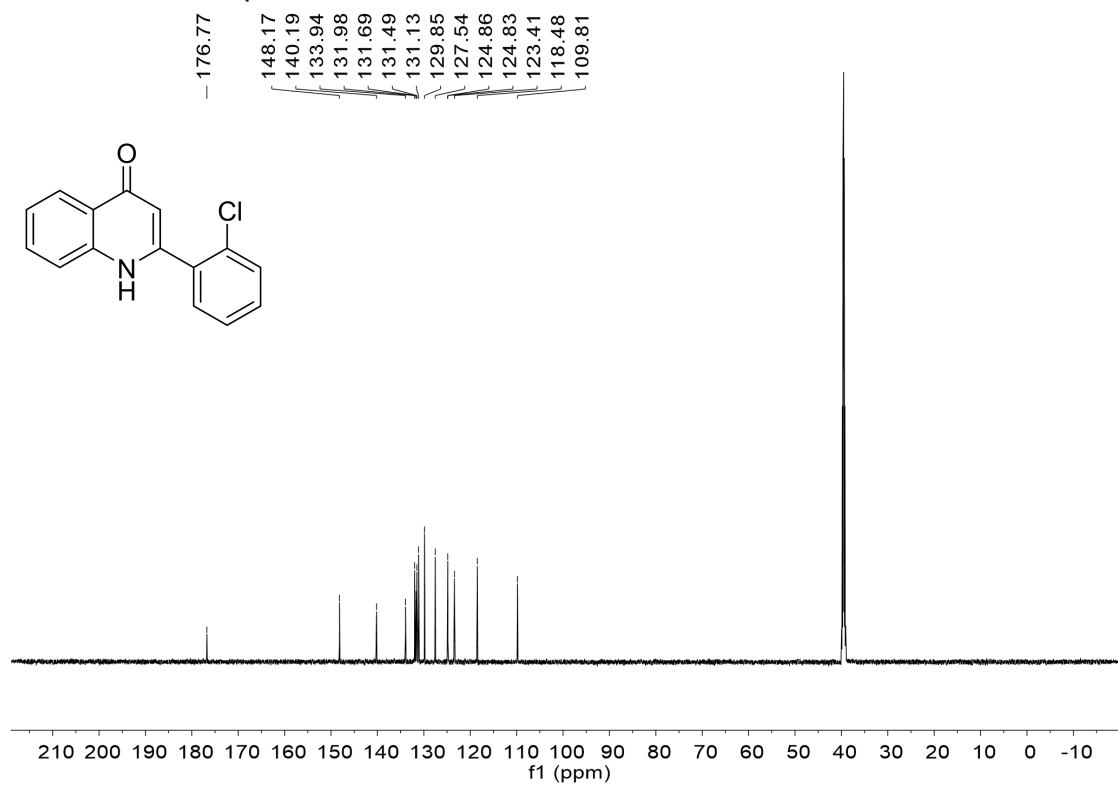
¹³C NMR of compound **3ak**



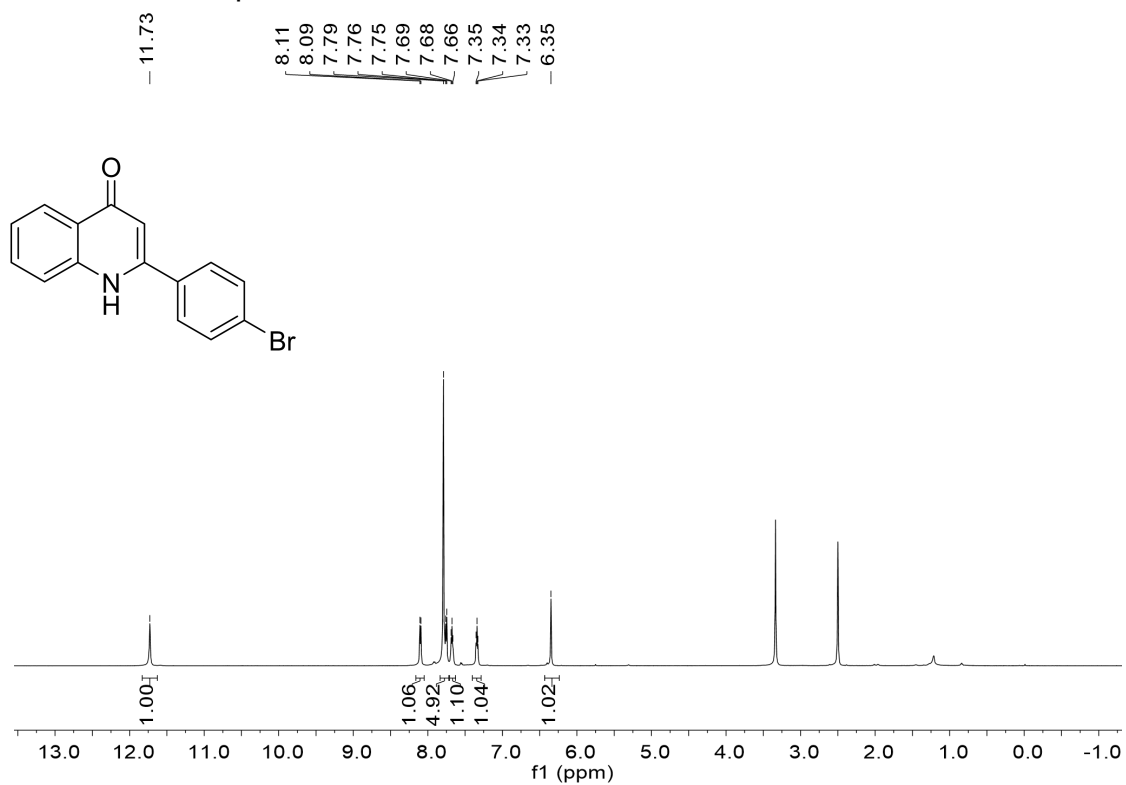
¹H NMR of compound **3al**



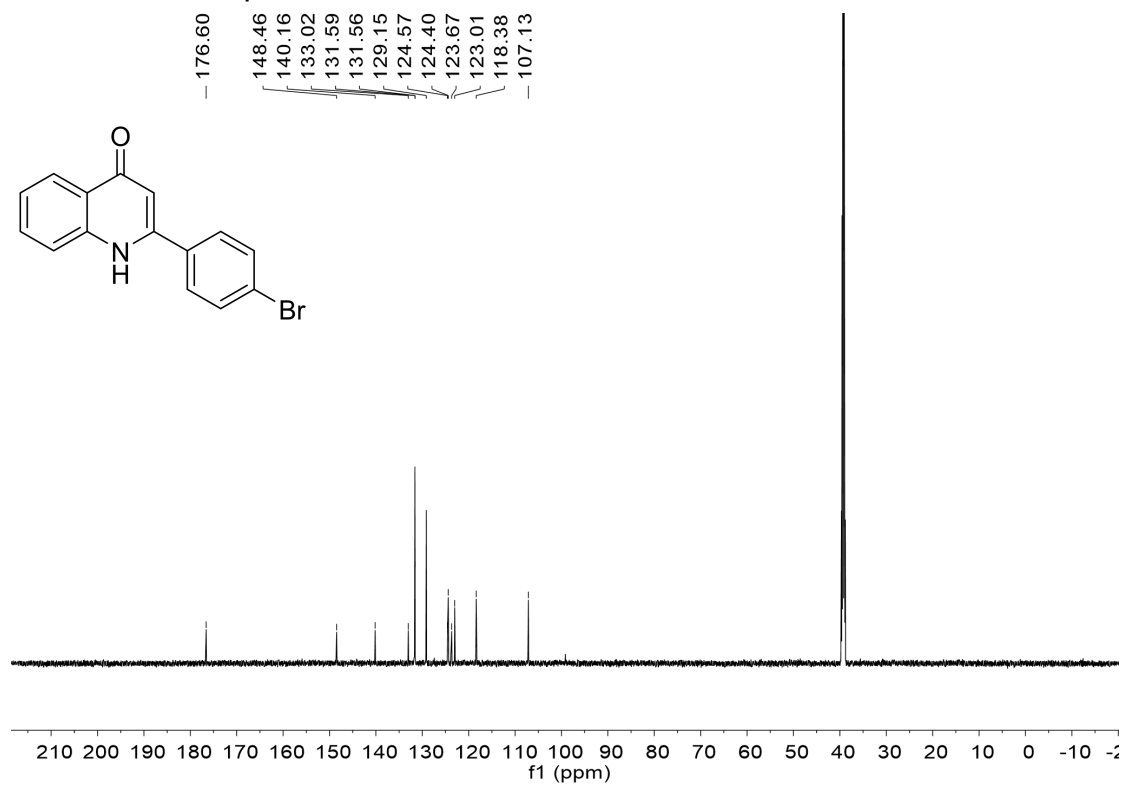
¹³C NMR of compound **3al**



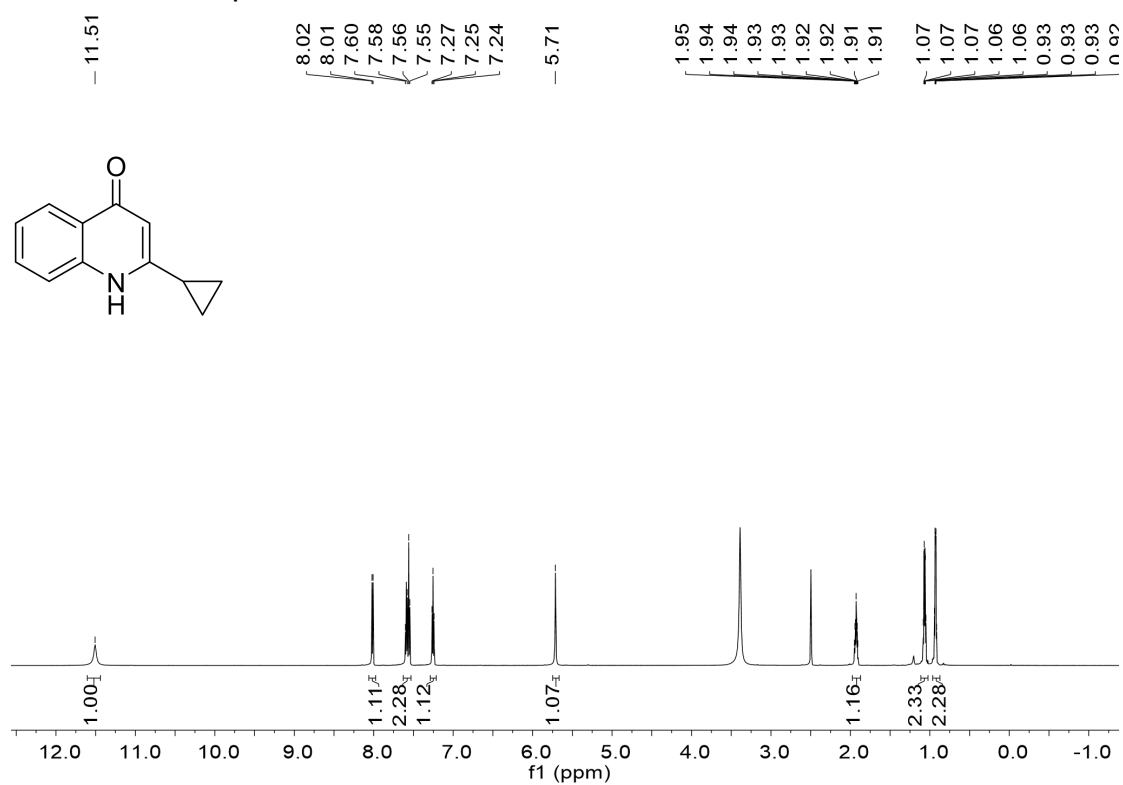
¹H NMR of compound **3am**



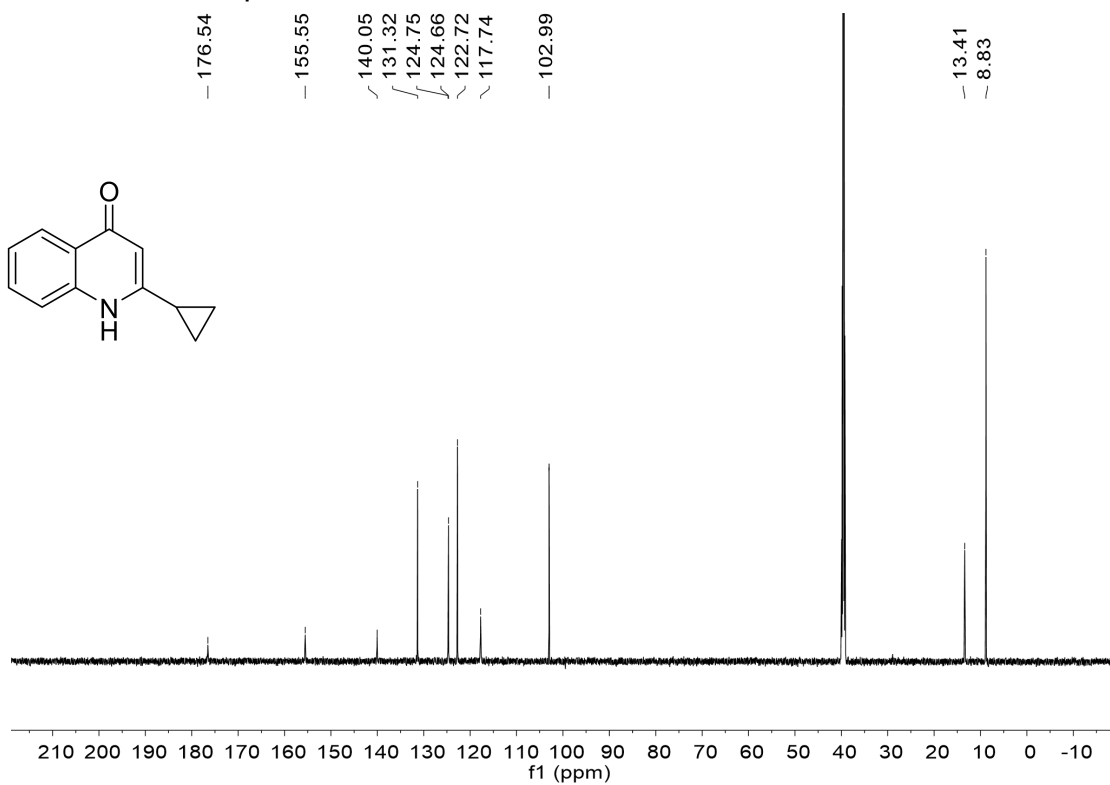
¹³C NMR of compound **3am**



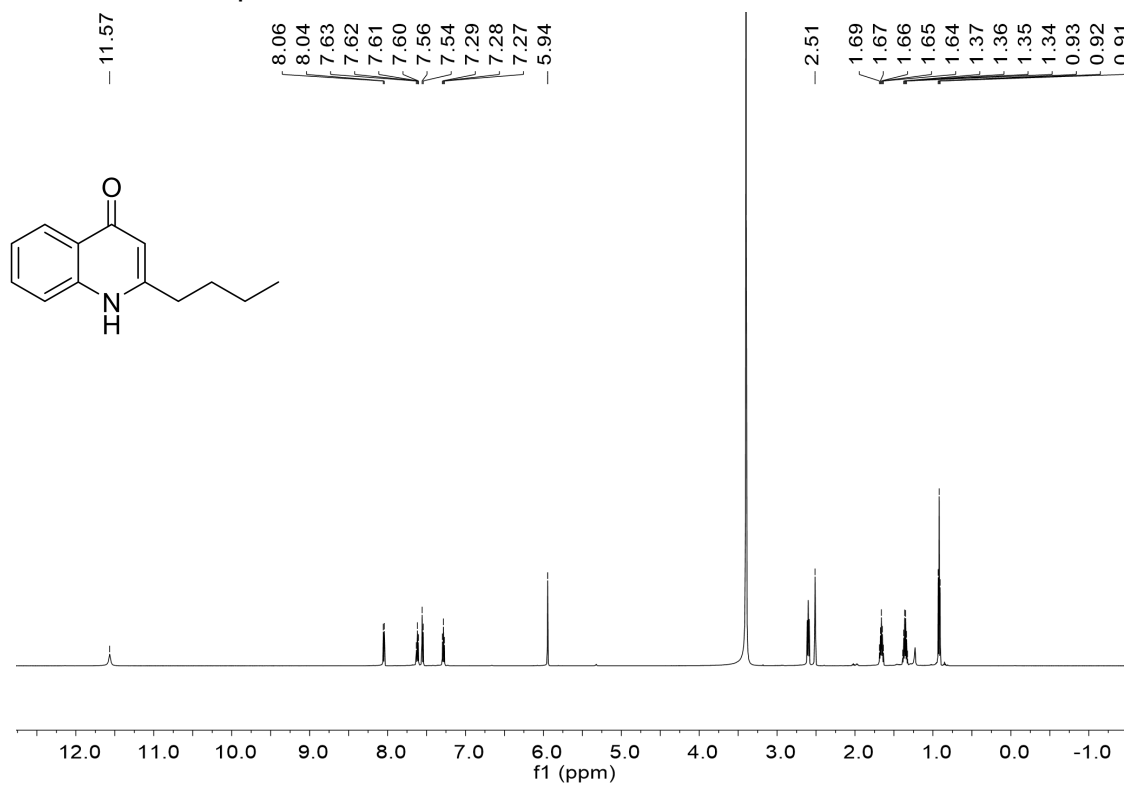
¹H NMR of compound **3an**



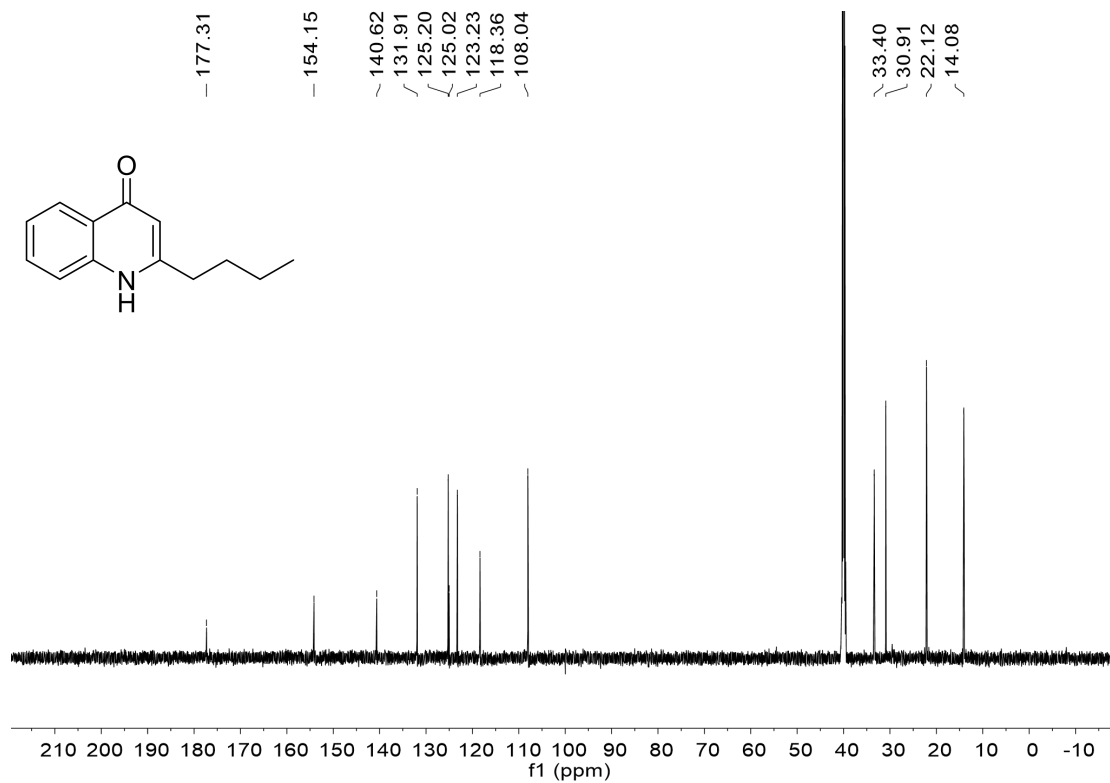
¹³C NMR of compound **3an**



¹H NMR of compound **3ao**



¹³C NMR of compound **3ao**



S-7. References

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