Supplementary Information

Merging 2,3-butanedione and N-hydroxysuccinimide as visible-light-enabled hydrogen atom transfer catalysts for C=C double bond cleavage of 2-cyanoaryl acrylamides toward 4-amino-2-quinolones

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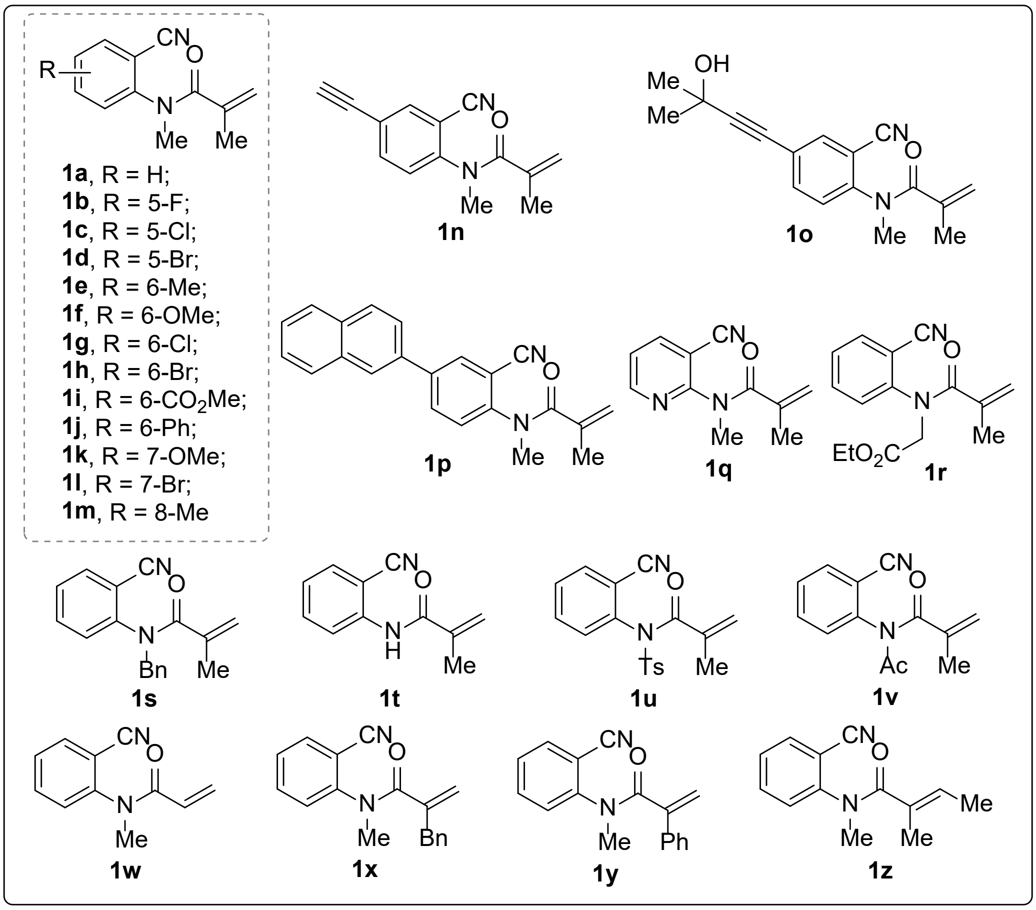
Contents

1. General information

The reactions involved in this article were performed in 10 mL tube or 100 mL round-bottom flask. Unless otherwise noted, all solvents and reagents were obtained from commercial sources. For chromatography, 200-300 mesh silica gel (Qingdao, China) was used. Melting points (mp) were taken on a MEL-TEMP® apparatus and were uncorrected. ^{1}H NMR, ^{13}C NMR and ^{19}F NMR spectras were measured recorded on 400 M spectrometer in $CDCl_3$ or DMSO-d_6 solution. HRMS was measured in ESI mode and the mass analyzer of the HRMS was TOF. MS was performed on Thermo MAT95XP. Chemical shifts (δ) were given in ppm, referenced to the residual proton resonance of $CDCl_3$ (7.26) or DMSO-d_6 (2.50), to the carbon resonance of $CDCl_3$ (77.16) or DMSO-d_6 (39.52). Coupling constants (J) were given in Hertz (Hz). The term m, q, t, d, s referred to multiplet, quartet, triplet, doublet, singlet.

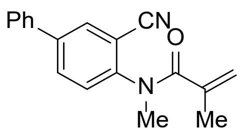
2. Preparation of 2-cyanoaryl acrylamides



Scheme S1 The structure of synthesized substrates.

All 2-cyanoaryl acrylamides were prepared according to the literature procedures.[1] And the characterization data of new compounds are given below:

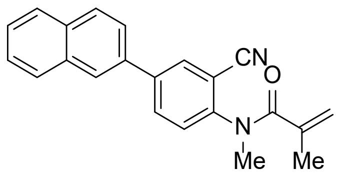
N-(3-cyano-[1,1'-biphenyl]-4-yl)-N-methylmethacrylamide (1j)



White solid (86%, 715.9 mg, eluent: petroleum ether/ethyl acetate = 2/1); mp 79 -80 ºC; ^{1}H NMR (400

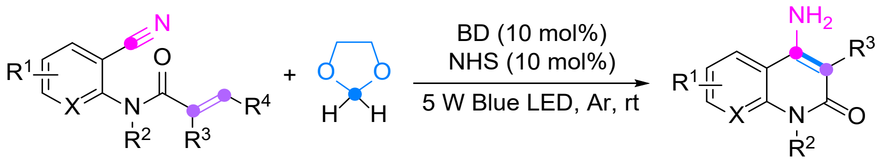
MHz, $CDCl_3$) δ 7.87 (d, *J* = 2.0 Hz, 1H), 7.80 (dd, *J* = 8.3, 2.1 Hz, 1H), 7.55 (d, *J* = 7.2 Hz, 2H), 7.48 (t, *J* = 7.3 Hz, 2H), 7.42 (t, *J* = 7.2 Hz, 1H), 7.32 (d, *J* = 8.3 Hz, 1H), 5.15 (s, 1H), 5.07 (s, 1H), 3.42 (s, 3H), 1.92 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.8, 146.3, 141.3, 140.0, 137.9, 132.5, 132.1, 129.3, 129.1, 128.8, 127.1, 120.1, 116.4, 112.3, 37.9, 20.2; HRMS (ESI) calcd. for $C_{18}H_{16}N_2ONa$ [$(M+Na)^+$] 299.1148, found: 299.1158.

N-(2-cyano-4-(naphthalen-2-yl)phenyl)-N-methylmethacrylamide (1p)



White solid (87%, 565.2 mg, eluent: petroleum ether/ethyl acetate = 2/1); mp 102-103 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 8.05 – 8.00 (m, 2H), 7.98 – 7.87 (m, 4H), 7.68 (dd, *J* = 8.5, 1.8 Hz, 1H), 7.59 – 7.52 (m, 2H), 7.36 (d, *J* = 8.3 Hz, 1H), 5.18 (s, 1H), 5.11 (s, 1H), 3.45 (s, 3H), 1.95 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.9, 146.4, 141.2, 140.1, 135.2, 133.6, 133.2, 132.7, 132.4, 129.3, 129.2, 128.4, 127.9, 127.0, 126.9, 126.4, 124.7, 120.2, 116.4, 112.5, 37.9, 20.3; HRMS (ESI) calcd. for $C_{22}H_{18}N_2ONa$ [$(M+Na)^+$] 349.1312, found: 349.1322.

3. General procedure for the visible-light enabled HAT catalyzed C=C double bond cleavage reaction of 2-cyanoaryl acrylamides

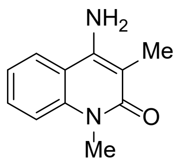


1 **2a** **3**

A 10 mL tube was charged with 2-cyanoaryl acrylamides **1** (0.2 mmol), BD (10 mol%) and NHS (10 mol%), 1,3-dioxolane (**2a**, 2 mL) was added via a syringe under argon. The resulting solution was stirred at room temperature with the irradiation of a 5 W blue LED for 48 h. After the reaction was completed, the volatile compounds were removed in vacuo and the residue was purified by column chromatography to give the desired 4-amino-2-quinolones **3**.

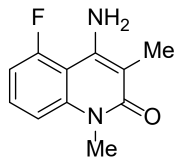
4. Characterization of 4-amino-2-quinolones 3

4-amino-1,3-dimethylquinolin-2(1*H*)-one (3a)[1]



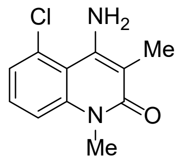
White solid (92%, 34.6 mg, eluent: petroleum ether/ethyl acetate = 1/2); mp 186-187 °C; ^1H NMR (400 MHz, DMSO-d_6) δ 8.01 (dd, *J* = 8.1, 1.1 Hz, 1H), 7.54 – 7.47 (m, 1H), 7.38 (d, *J* = 8.1 Hz, 1H), 7.21 – 7.13 (m, 1H), 6.16 (s, 2H), 3.54 (s, 3H), 1.98 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 162.0, 147.3, 138.4, 129.6, 122.7, 120.5, 114.6, 114.3, 99.4, 28.9, 10.9; EI-MS (*m/z*, relative intensity): 188 (M^+, 100), 173 (25), 159 (70), 145 (30), 117 (15), 91 (10), 77 (23).

4-amino-5-fluoro-1,3-dimethylquinolin-2(1*H*)-one (3b)[1]



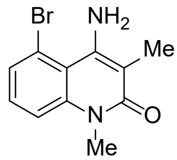
White solid (82%, 33.8 mg, eluent: petroleum ether/ethyl acetate = 1/2); mp 175-176 ºC; ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.54 – 7.44 (m, 1H), 7.27 – 7.19 (m, 1H), 7.05 – 6.94 (m, 1H), 5.93 (s, 2H), 3.53 (s, 3H), 1.96 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 161.4, 159.3 (d, J = 246.4 Hz), 145.7 (d, J = 2.7 Hz), 140.3 (d, J = 6.3 Hz), 130.0 (d, J = 12.1 Hz), 111.1 (d, J = 2.9 Hz), 107.7 (d, J = 24.7 Hz), 103.8 (d, J = 10.4 Hz), 100.4 (d, J = 1.9 Hz), 29.8, 10.5; ^{19}F NMR (376 MHz, DMSO-d_6) δ -114.97; EI-MS (m/z, relative intensity): 206 (M$^+$, 100), 191 (33), 177 (50), 163 (22), 135 (7), 89 (10).

4-amino-5-chloro-1,3-dimethylquinolin-2(1*H*)-one (3c)[1]



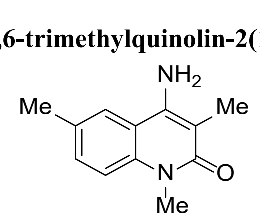
White solid (48%, 21.3 mg, eluent: petroleum ether/ethyl acetate = 1/2); mp 175-177 ºC; ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.50 – 7.40 (m, 2H), 7.25 (dd, J = 7.3, 1.6 Hz, 1H), 6.26 (s, 2H), 3.56 (s, 3H), 1.97 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 160.9, 146.8, 140.9, 129.5, 128.9, 124.5, 114.7, 111.5, 101.8, 30.1, 11.1; EI-MS (m/z, relative intensity): 222 (M$^+$, 100), 207 (30), 193 (45), 179 (28), 130 (10), 97 (12).

4-amino-5-bromo-1,3-dimethylquinolin-2(1*H*)-one (3d)[1]



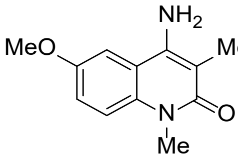
White solid (52%, 27.8 mg, eluent: petroleum ether/ethyl acetate = 1/2); mp 177-179 ºC; The catalysts of BD (50 mol%) and NHS (50 mol%) were used. ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.50 – 7.45 (m, 2H), 7.40 – 7.34 (m, 1H), 6.27 (s, 2H), 3.55 (s, 3H), 1.97 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 160.9, 146.6, 141.0, 129.9, 128.5, 117.0, 115.3, 112.4, 101.9, 30.1, 11.3; EI-MS (m/z, relative intensity): 266 (M$^+$, 3), 218 (100), 207 (30), 175 (15), 131 (8), 95 (5), 73 (5).

4-amino-1,3,6-trimethylquinolin-2(1*H*)-one (3e)[1]



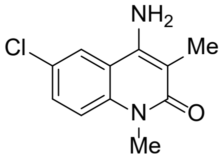
White solid (92%, 37.2 mg, eluent: petroleum ether/ethyl acetate = 1/2); mp 182-184 ºC; ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.83 (s, 1H), 7.35 – 7.23 (m, 2H), 6.07 (s, 2H), 3.51 (s, 3H), 2.37 (s, 3H), 1.97 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 161.9, 147.1, 136.5, 130.6, 129.4, 122.5, 114.4, 114.2, 99.5, 28.9, 20.4, 10.9; EI-MS (m/z, relative intensity): 202 (M$^+$, 100), 188 (50), 173 (77), 159 (55), 86 (20), 77 (17).

4-amino-6-methoxy-1,3-dimethylquinolin-2(1*H*)-one (3f)[1]



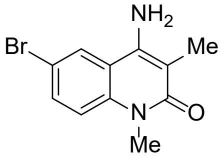
White solid (81%, 35.3 mg, eluent: petroleum ether/ethyl acetate = 1/2); mp 200-202 ºC; ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.53 (d, J = 2.7 Hz, 1H), 7.32 (d, J = 9.2 Hz, 1H), 7.14 (dd, J = 9.1, 2.7 Hz, 1H), 6.11 (s, 2H), 3.82 (s, 3H), 3.52 (s, 3H), 1.98 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 161.6, 153.7, 146.9, 133.0, 117.6, 115.6, 115.2, 105.8, 99.9, 55.7, 29.0, 11.0; EI-MS (*m/z*, relative intensity): 218 (M$^+$, 100), 203 (77), 189 (20), 147 (15), 109 (12), 77 (10).

4-amino-6-chloro-1,3-dimethylquinolin-2(1*H*)-one (3g)[1]



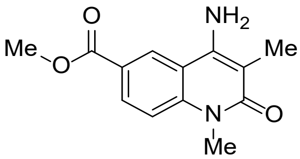
White solid (81%, 35.3 mg, eluent: petroleum ether/ethyl acetate = 1/2); mp 186-187 ºC; ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.12 (d, J = 2.3 Hz, 1H), 7.52 (dd, J = 9.0, 2.3 Hz, 1H), 7.39 (d, J = 9.0 Hz, 1H), 6.22 (s, 2H), 3.52 (s, 3H), 1.97 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 161.8, 146.4, 137.2, 129.2, 125.2, 122.1, 116.4, 115.9, 100.6, 29.1, 10.9; EI-MS (*m/z*, relative intensity): 222 (M$^+$, 100), 207 (40), 193 (65), 179 (30), 130 (17), 97 (20).

4-amino-6-bromo-1,3-dimethylquinolin-2(1*H*)-one (3h)[1]



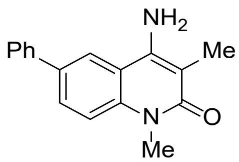
White solid (79%, 42.2 mg, eluent: petroleum ether/ethyl acetate = 1/2); mp 164-166 ºC; ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.24 (d, J = 2.1 Hz, 1H), 7.62 (dd, J = 9.0, 2.1 Hz, 1H), 7.32 (d, J = 9.0 Hz, 1H), 6.22 (s, 2H), 3.51 (s, 3H), 1.97 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 161.8, 146.3, 137.5, 131.9, 125.0, 116.7, 116.4, 113.0, 100.5, 29.1, 10.9; EI-MS (*m/z*, relative intensity): 266 (M$^+$, 50), 239 (20), 207 (100), 159 (15), 85 (38), 57 (55).

methyl 4-amino-1,3-dimethyl-2-oxo-1,2-dihydroquinoline-6-carboxylate (3i)[1]



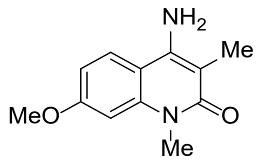
White solid (74%, 36.4 mg, eluent: petroleum ether/ethyl acetate = 1/2); mp 225-226 ºC; ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.61 (d, J = 1.3 Hz, 1H), 8.01 (dd, J = 8.8, 1.4 Hz, 1H), 7.44 (d, J = 8.9 Hz, 1H), 6.36 (s, 2H), 3.87 (s, 3H), 3.55 (s, 3H), 1.97 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 166.1, 162.1, 147.5, 141.6, 129.9, 124.8, 121.8, 114.7, 114.3, 100.1, 52.0, 29.3, 10.9; EI-MS (*m/z*, relative intensity): 246 (M$^+$, 100), 231 (15), 217 (45), 159 (6), 130 (8), 93 (10).

4-amino-1,3-dimethyl-6-phenylquinolin-2(1*H*)-one (3j)



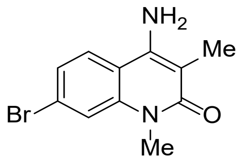
White solid (88%, 46.5 mg, eluent: petroleum ether/ethyl acetate = 1/3); mp 189-190 ºC; ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.34 (d, *J* = 1.8 Hz, 1H), 7.84-7.80 (m, 3H), 7.46 (dd, *J* = 15.6, 8.1 Hz, 3H), 7.35 (t, *J* = 7.3 Hz, 1H), 6.32 (s, 2H), 3.57 (s, 3H), 2.02 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 162.0, 147.5, 139.4, 137.9, 132.5, 128.8, 127.8, 127.1, 126.6, 120.5, 115.0, 114.9, 99.7, 29.0, 10.9; HRMS (ESI) calcd. for $C_{17}H_{16}N_2O$ [$(M+H)^+$] 265.1336, found: 265.1346.

4-amino-7-methoxy-1,3-dimethylquinolin-2(1*H*)-one (3k)[1]



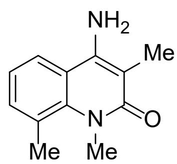
White solid (80%, 34.9 mg, eluent: petroleum ether/ethyl acetate = 1/2); mp 172-173 ºC; ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.93 (d, *J* = 9.6 Hz, 1H), 6.79 (dd, *J* = 6.1, 2.4 Hz, 2H), 6.08 (s, 2H), 3.86 (s, 3H), 3.52 (s, 3H), 1.95 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 162.4, 160.5, 147.5, 140.1, 124.3, 108.5, 108.1, 98.4, 97.1, 55.4, 29.0, 10.7; EI-MS (*m/z*, relative intensity): 218 (M^+, 100), 203 (75), 189 (20), 147 (15), 109 (10), 77 (8).

4-amino-7-bromo-1,3-dimethylquinolin-2(1*H*)-one (3l)[1]



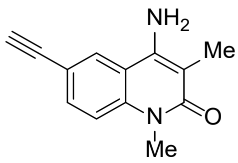
White solid (76%, 40.6 mg, eluent: petroleum ether/ethyl acetate = 1/2); mp 224-225 ºC; ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.93 (d, *J* = 8.5 Hz, 1H), 7.55 (s, 1H), 7.33 (d, *J* = 8.3 Hz, 1H), 6.21 (s, 2H), 3.52 (s, 3H), 1.95 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 161.9, 147.0, 139.6, 124.7, 123.4, 123.0, 116.9, 113.8, 99.9, 29.2, 10.9; EI-MS (*m/z*, relative intensity): 266 (M^+, 10), 253 (12), 191 (10), 133 (8), 96 (10), 73 (7).

4-amino-1,3,8-trimethylquinolin-2(1*H*)-one (3m)[1]



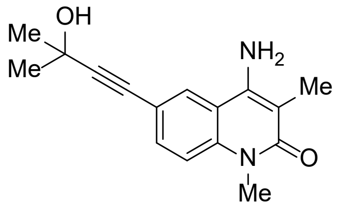
White solid (77%, 31.1 mg, eluent: petroleum ether/ethyl acetate = 1/2); mp 207-209 ºC; The catalysts of BD (50 mol%) and NHS (50 mol%) were used. ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.81 (d, *J* = 7.7 Hz, 1H), 7.30 (d, *J* = 7.2 Hz, 1H), 7.07 (t, *J* = 7.7 Hz, 1H), 6.07 (s, 2H), 3.57 (s, 3H), 2.59 (s, 3H), 1.95 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 164.4, 147.7, 140.1, 133.8, 124.8, 121.0, 120.6, 116.6, 99.2, 36.6, 23.4, 10.8; EI-MS (*m/z*, relative intensity): 202 (M^+, 100), 187 (80), 173 (22), 159 (45), 115 (8), 77 (10).

4-amino-6-ethynyl-1,3-dimethylquinolin-2(1*H*)-one (3n)[1]



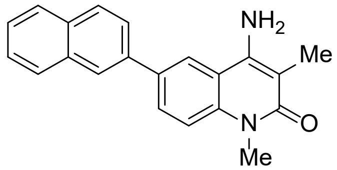
White solid (59%, 25.0 mg, eluent: petroleum ether/ethyl acetate = 1/2); mp 181-182 ºC; The catalysts of BD (50 mol%) and NHS (50 mol%) were used. ^{1}H NMR (400 MHz, DMSO-*d*$_6$) δ 8.20 (d, *J* = 1.7 Hz, 1H), 7.58 (dd, *J* = 8.7, 1.7 Hz, 1H), 7.39 (d, *J* = 8.8 Hz, 1H), 6.25 (s, 2H), 4.14 (s, 1H), 3.53 (s, 3H), 1.96 (s, 3H); ^{13}C NMR (100 MHz, DMSO-*d*$_6$) δ 161.9, 146.7, 138.5, 132.5, 126.4, 114.9, 114.6, 113.8, 100.1, 83.6, 79.9, 29.1, 10.9; EI-MS (*m/z*, relative intensity): 212 (M$^+$, 100), 197 (14), 183 (40), 169 (16), 115 (5), 57 (10).

4-amino-6-(3-hydroxy-3-methylbut-1-yn-1-yl)-1,3-dimethylquinolin-2(1*H*)-one (3o)[1]



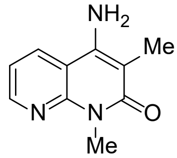
White solid (74%, 40.0 mg, eluent: petroleum ether/ethyl acetate = 1/3); mp 245-247 ºC; ^{1}H NMR (400 MHz, DMSO-*d*$_6$) δ 8.10 (d, *J* = 1.6 Hz, 1H), 7.49 (dd, *J* = 8.7, 1.6 Hz, 1H), 7.36 (d, *J* = 8.8 Hz, 1H), 6.24 (s, 2H), 5.46 (s, 1H), 3.53 (s, 3H), 1.96 (s, 3H), 1.49 (s, 6H); ^{13}C NMR (100 MHz, DMSO-*d*$_6$) δ 161.9, 146.8, 138.0, 132.3, 125.7, 114.8, 114.8, 114.6, 100.0, 95.1, 80.3, 63.7, 31.7, 29.0, 10.9; EI-MS (*m/z*, relative intensity): 270 (M$^+$, 8), 252 (100), 223 (30), 193 (5), 126 (8), 97 (3).

4-amino-1,3-dimethyl-6-(naphthalen-2-yl)quinolin-2(1*H*)-one (3p)



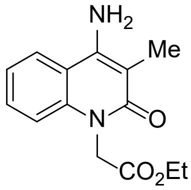
White solid (69%, 43.4 mg, eluent: petroleum ether/ethyl acetate = 1/3); mp 197-198 ºC; ^{1}H NMR (400 MHz, DMSO-*d*$_6$) δ 8.50 (d, *J* = 1.6 Hz, 1H), 8.34 (s, 1H), 8.04 – 7.92 (m, 5H), 7.56-7.46 (m, 3H), 6.40 (s, 2H), 3.58 (s, 3H), 2.05 (s, 3H); ^{13}C NMR (100 MHz, DMSO-*d*$_6$) δ 162.0, 147.6, 138.0, 136.8, 133.4, 132.2, 132.1, 128.4, 128.1, 128.1, 127.6, 126.4, 126.0, 125.2, 124.8, 120.8, 115.1,115.1, 99.8, 29.1, 11.0; HRMS (ESI) calcd. for $C_{21}H_{18}N_2O$ [(M+H)$^+$] 315.1495, found: 315.1505.

4-amino-1,3-dimethyl-1,8-naphthyridin-2(1*H*)-one (3q)[1]



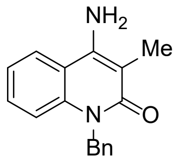
White solid (64%, 24.2 mg, eluent: petroleum ether/ethyl acetate = 1/3); mp 210-211 ºC; ^{1}H NMR (400 MHz, DMSO-*d*$_6$) δ 8.52 (d, *J* = 3.4 Hz, 1H), 8.40 (d, *J* = 7.7 Hz, 1H), 7.22 (dd, *J* = 7.0, 4.7 Hz, 1H), 6.31 (s, 2H), 3.59 (s, 3H), 1.98 (s, 3H); ^{13}C NMR (100 MHz, DMSO-*d*$_6$) δ 163.0, 148.9, 148.4, 146.4, 131.4, 116.8, 110.2, 100.1, 27.9, 10.7. EI-MS (*m/z*, relative intensity): 189 (M^+, 90), 161 (80), 146 (40), 133 (15), 96 (15), 87 (20).

ethyl 2-(4-amino-3-methyl-2-oxoquinolin-1(2*H*)-yl)acetate (3r)[1]



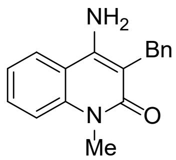
White solid (79%, 41.1 mg, eluent: petroleum ether/ethyl acetate = 1/2); mp 162-164 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.04 (d, *J* = 8.0 Hz, 1H), 7.48 (t, *J* = 7.8 Hz, 1H), 7.26 – 7.15 (m, 2H), 6.30 (s, 2H), 5.04 (s, 2H), 4.13 (q, *J* = 7.1 Hz, 2H), 1.99 (s, 3H), 1.19 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 169.1, 161.9, 148.1, 137.9, 129.7, 122.9, 120.9, 114.6, 114.2, 98.7, 60.8, 43.3, 14.1, 10.7; EI-MS (*m/z*, relative intensity): 260 (M^+, 40), 214 (50), 187 (40), 130 (15), 96 (12), 77 (10).

4-amino-1-benzyl-3-methylquinolin-2(1*H*)-one (3s)[1]



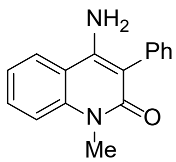
White solid (90%, 47.5 mg, eluent: petroleum ether/ethyl acetate = 1/2); mp 223-224 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.07 (d, *J* = 7.8 Hz, 1H), 7.37 (t, *J* = 7.5 Hz, 1H), 7.29 – 7.10 (m, 7H), 6.32 (s, 2H), 5.47 (s, 2H), 2.06 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 162.3, 147.9, 138.0, 137.7, 129.6, 128.5, 126.7, 126.4, 123.0, 120.7, 114.9, 114.9, 99.1, 44.5, 11.0; EI-MS (*m/z*, relative intensity): 264 (M^+, 100), 249 (15), 187 (15), 159 (25), 131 (10), 77 (8).

4-amino-3-benzyl-1-methylquinolin-2(1*H*)-one (3x)[1]



White solid (56%, 29.6 mg, eluent: petroleum ether/ethyl acetate = 1/3); mp 126-128 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.03 (d, J = 8.0 Hz, 1H), 7.58 – 7.50 (m, 1H), 7.43 – 7.36 (m, 1H), 7.29 (d, J = 7.0 Hz, 2H), 7.20 (t, J = 7.5 Hz, 3H), 7.14 – 7.06 (m, 1H), 6.29 (s, 2H), 3.93 (s, 2H), 3.56 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 162.1, 147.7, 141.0, 138.8, 130.1, 128.3, 128.0, 125.5, 123.1, 120.8, 114.7, 114.5, 103.6, 30.0, 29.1; EI-MS (*m/z*, relative intensity): 264 (M^+, 100), 249 (13), 187 (15), 159 (22), 131 (10), 77 (8).

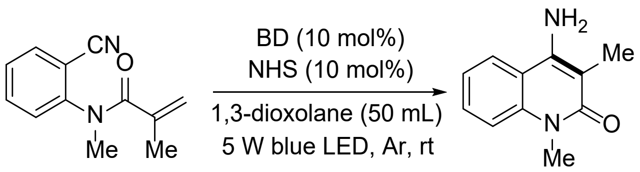
4-amino-1-methyl-3-phenylquinolin-2(1*H*)-one (3y)[1]



White solid (24%, 12.0 mg, eluent: petroleum ether/ethyl acetate = 1/3); mp 208-209 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.08 (d, *J* = 8.0 Hz, 1H), 7.64 – 7.57 (m, 1H), 7.48 – 7.41 (m, 3H), 7.35 – 7.20

(m, 4H), 5.82 (s, 2H), 3.56 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 161.0, 147.5, 139.3, 135.6, 131.0, 130.7, 128.5, 126.8, 123.6, 120.9, 114.6, 114.5, 106.1, 28.9; EI-MS (*m/z*, relative intensity): 250 (M^+, 65), 234 (13), 165 (4), 125 (7), 95 (5), 77 (5).

5. Gram-scale preparation

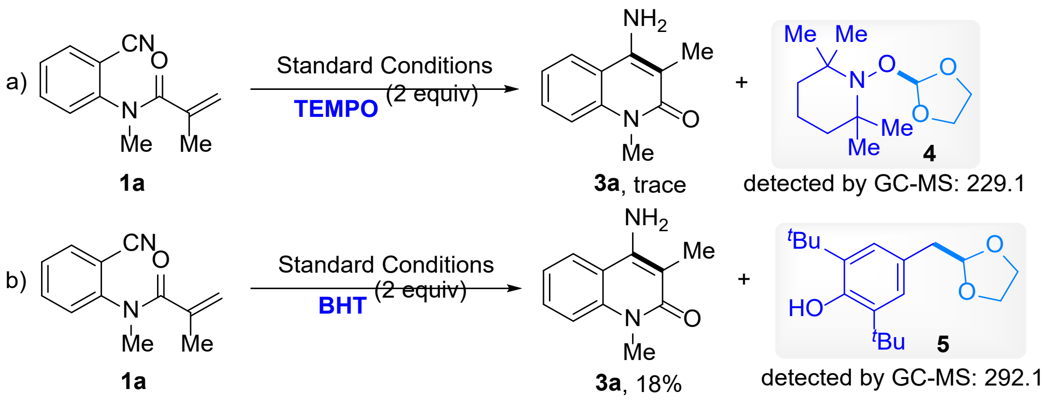


1a, 1.00 g　　**3a**, 86%

A 100 mL oven-dried round bottom flask equipped with a magnetic stirring bar was added **1a** (5.0 mmol, 1.00 g), BD (10 mol%) and NHS (10 mol%), 1,3-dioxolane (**2a**, 50 mL). The reaction flask was purged with argon for three times and connected with an argon balloon. The reaction flask was stirred at room temperature with the irradiation of 5 W blue LEDs for 48 h. After the reaction was completed, the volatile compounds were removed in vacuo and the residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 1/2) to give the desired product **3a** as white solid, 0.8084 g, 86% yield.

6. Mechanistic Studies[2-5]

(1) Control experiments with respect to TEMPO and BHT



A 10 mL tube was charged with **1a** (0.2 mmol, 40.0 mg), BD (10 mol%), NHS (10 mol%) and TEMPO (0.4 mmol, 2 equiv, 62.5 mg) or BHT (0.4 mmol, 2 equiv, 88.1 mg), 1,3-dioxolane (**2a**, 2 mL) was added via a syringe under argon. The resulting solution was stirred at room temperature with the irradiation of a 5 W blue LED for 48 h. The mixtures were detected by GC-MS (EI mode). The spectras were as depicted in Figures S1 and S2.

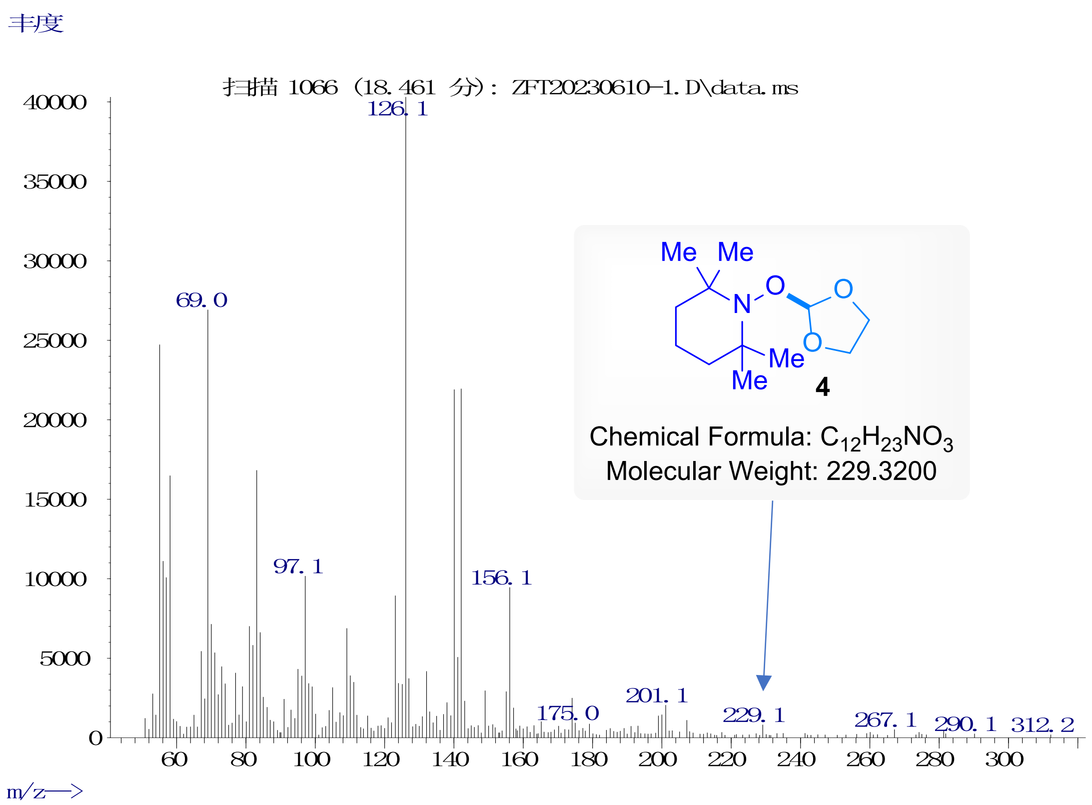


Figure S1 GC-MS spectra for compound **4**

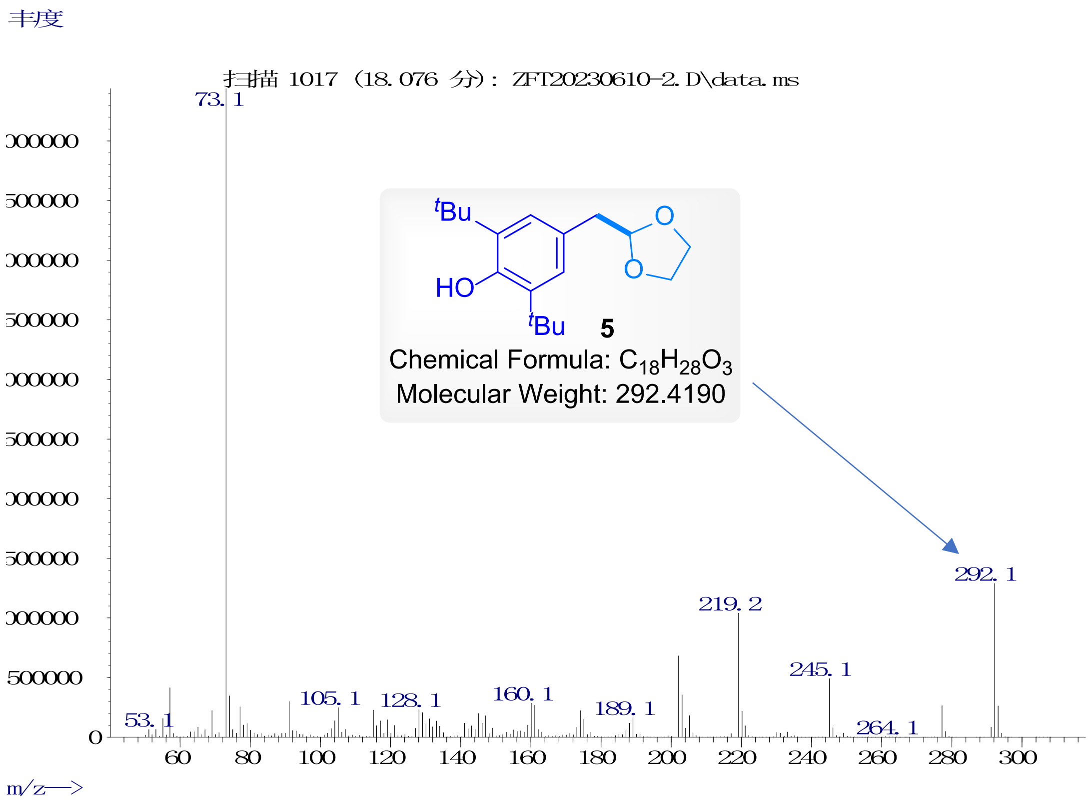
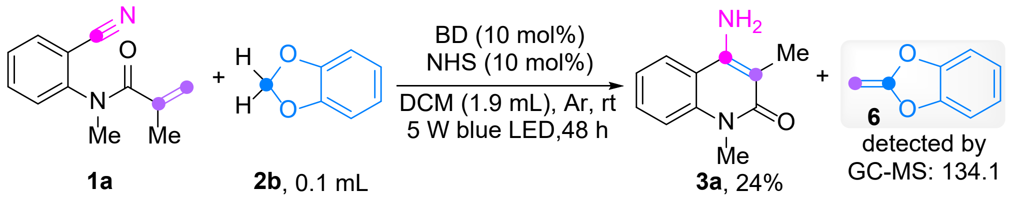


Figure S2 GC-MS spectra for compound **5**

(2) Control experiments with respect to 1,3-benzodioxole



A 10 mL tube was charged with **1a** (0.2 mmol, 40.0 mg), BD (10 mol%) and NHS (10 mol%), 1,3-benzodioxole (**2b**, 0.1 mL) and dichloromethane (DCM, 1.9 mL) was added via a syringe under argon. The resulting solution was stirred at room temperature with the irradiation of a 5 W blue LED for 48 h. The mixtures were detected by GC-MS (EI mode). The spectra was as depicted in Figure S3.

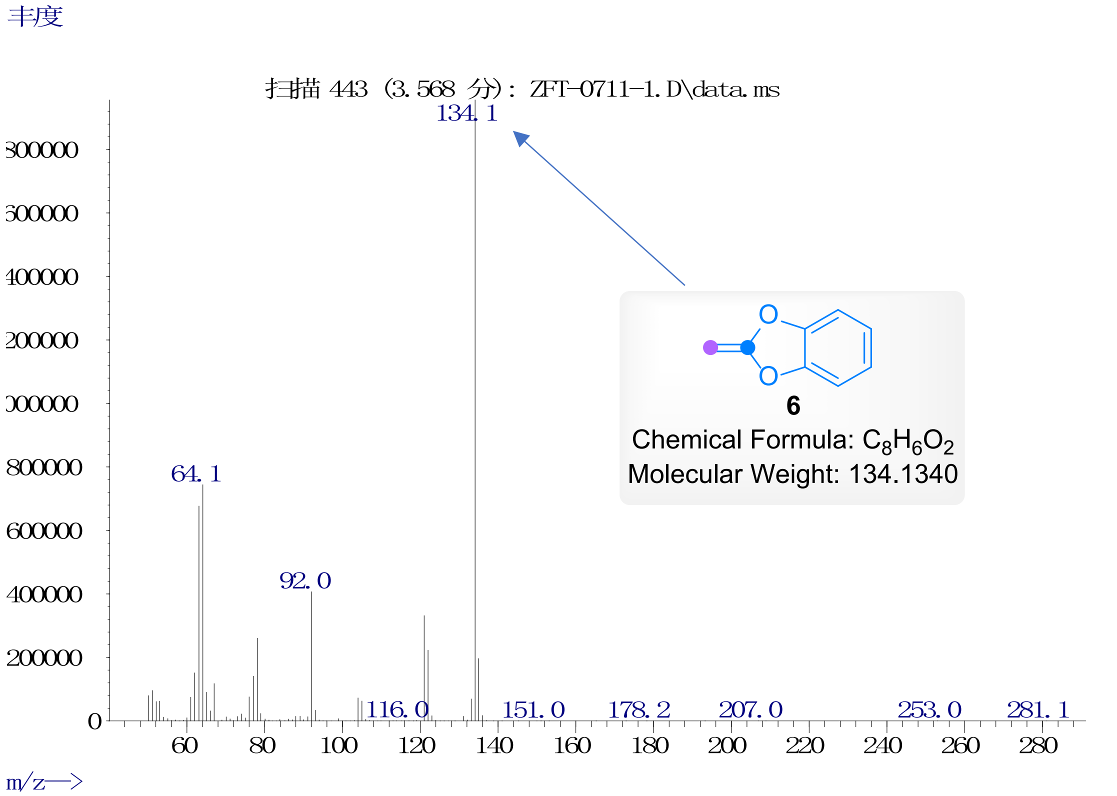
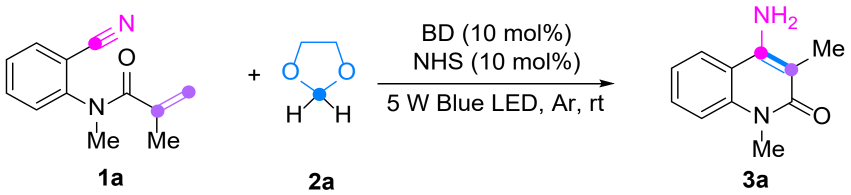


Figure S3 GC-MS spectra for compound **6**

(3) **The light on/off experiment**



A 10 mL tube was charged with 2-cyanoaryl acrylamides **1a** (0.5 mmol), BD (10 mol%), NHS (10 mol%) and 1,3,5-trimethylbenzene (0.5 mmol) 1,3-dioxolane (**2a**, 5 mL) was added via a syringe under argon. The reaction mixture was stirred under alternating periods (1 h) of irradiation and darkness. 100 μL of reaction mixture was taken by a syringe at indicated time (1.0 h, 2.0 h, 3.0 h, 4.0 h, 5.0 h, 6.0 h) and diluted with chloroform-*d* (0.5 mL) and submitted for quantitative ^{1}H NMR analysis. The results were list in Table S1 and Figure S4.

Table S1 The data of the light on/off experiment

Time	Yield (%)
0 h	0
1 h	31
2 h	32
3 h	39
4 h	40
5 h	50
6 h	50

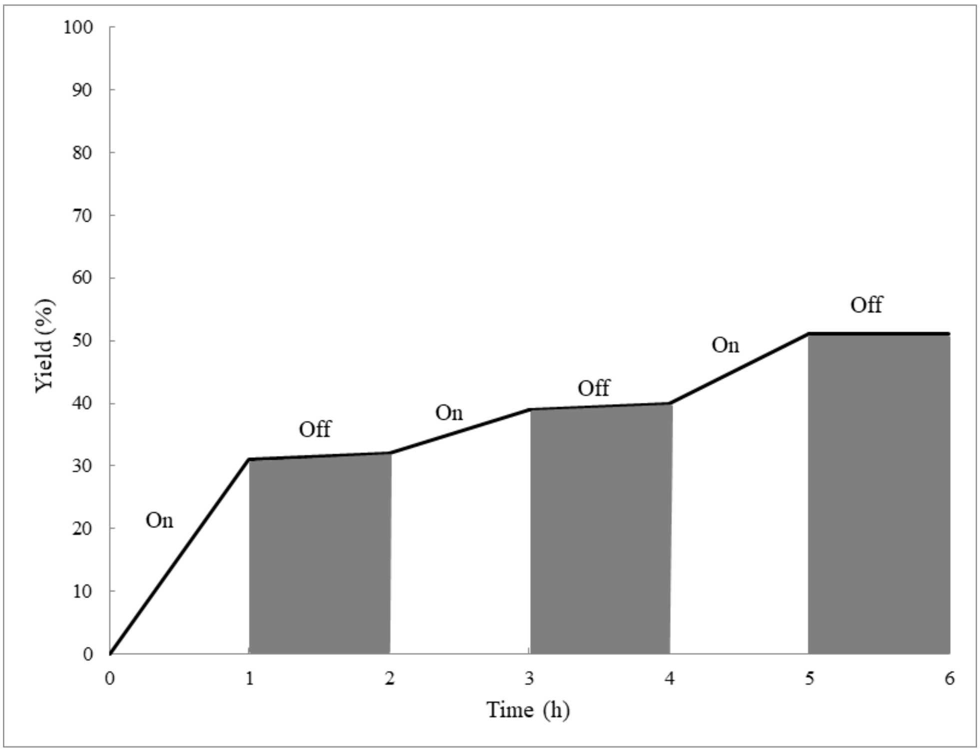
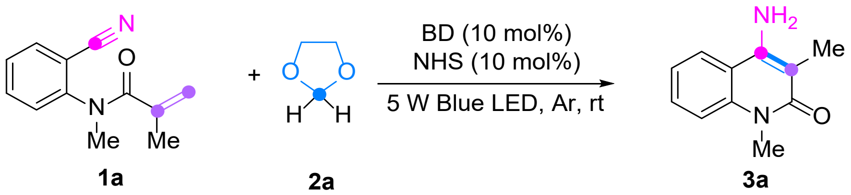


Figure S4 Light on/off experiment

(4) **The experiment on detecting BD after completing the reaction**



A 10 mL tube was charged with 2-cyanoaryl acrylamides **1a** (0.2 mmol), BD (10 mol%) and NHS (10 mol%), 1,3-dioxolane (**2a**, 2 mL) was added via a syringe under argon. The resulting solution was stirred at room temperature with the irradiation of a 5 W blue LED. After the reaction was completed, the mixtures were detected by GC-MS (EI mode). The spectra of **BD** was as depicted in Figure S5.

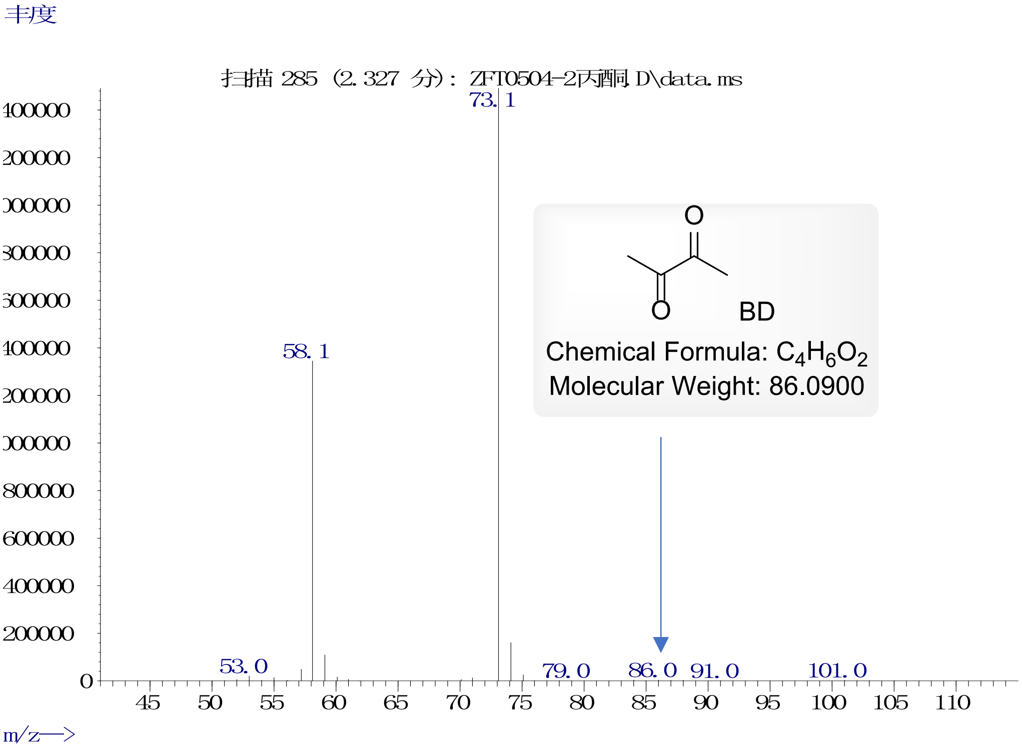


Figure S5 GC-MS spectra for **BD**

7. References

(1) W.-J. Xia, T.-G. Fan, Z.-W. Zhao, X. Chen, X.-X. Wang and Y.-M. Li, *Org. Lett.*, 2021, **23**, 6158.

(2) P. Du, H. Li, Y. Wang, J. Cheng and X. Wan, *Org. Lett.*, 2014, **16**, 6350.

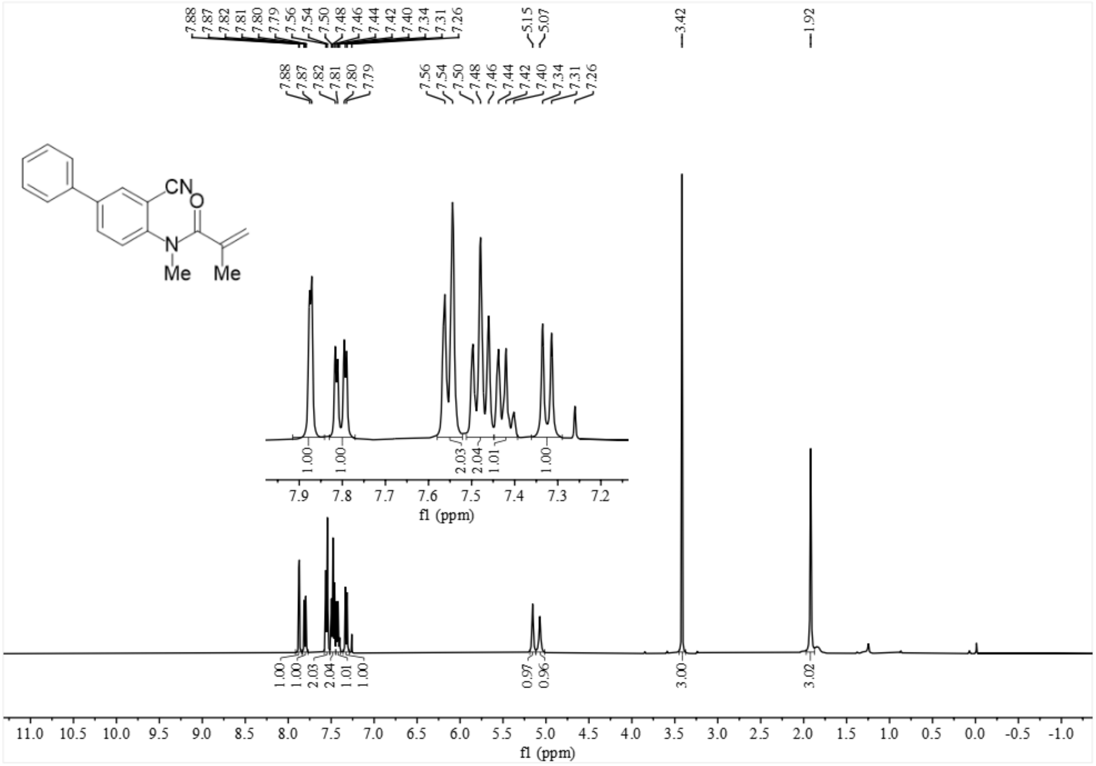
(3) K. Sun, G. Li, Y. Li, J. Yu, Q. Zhao, Z. Zhang and G. Zhang, *Adv. Synth. Catal.*, 2020, **362**, 1947.

(4) S. Jiang, X.-J. Tian, S.-Y. Feng, J.-S. Li, Z.-W. Li, C.-H. Lu, C.-J. Li and W.-D. Liu, *Org. Lett.*, 2020, **22**, 692.

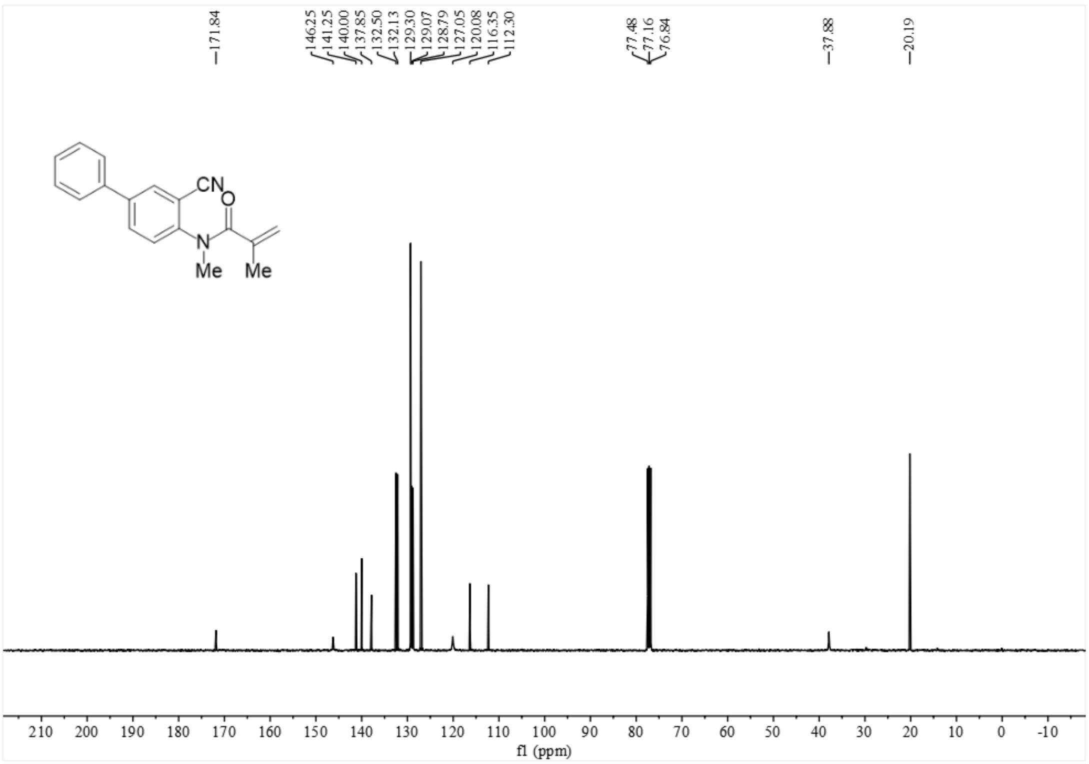
(5) S. G. More, R. B. Kamble and G. Suryavanshi, *J. Org. Chem.*, 2021, **86**, 2107.

8. NMR spectra

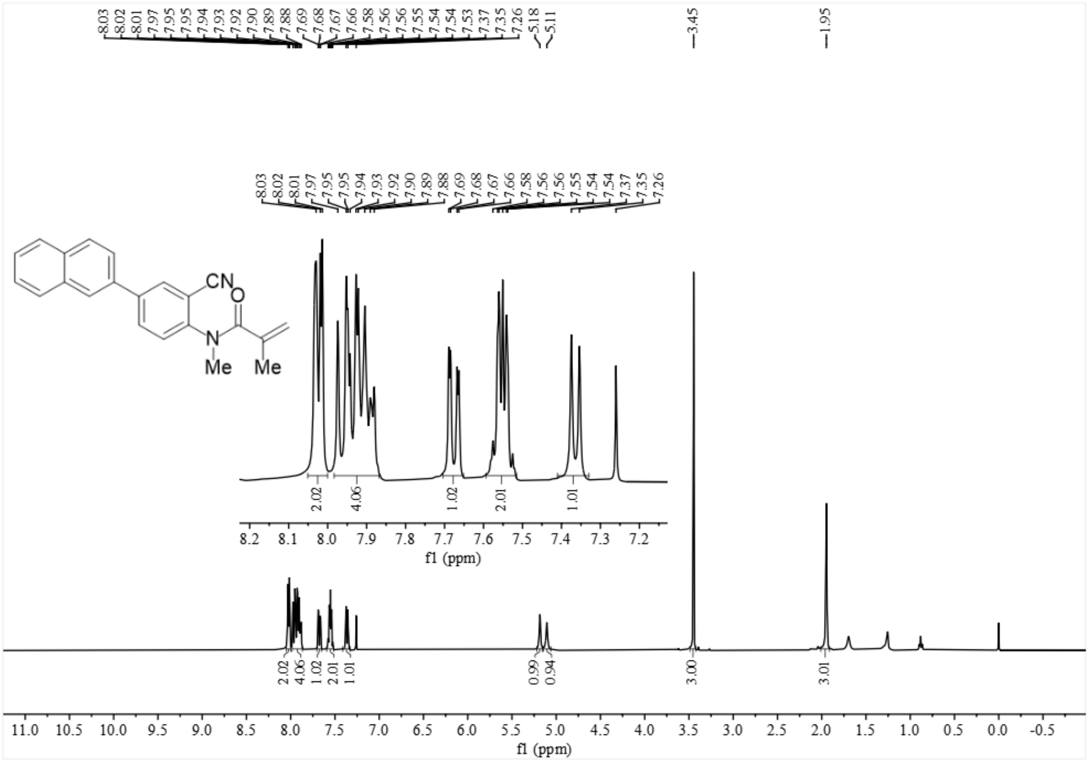
[1]H NMR of **1j** (400 MHz, $CDCl_3$):



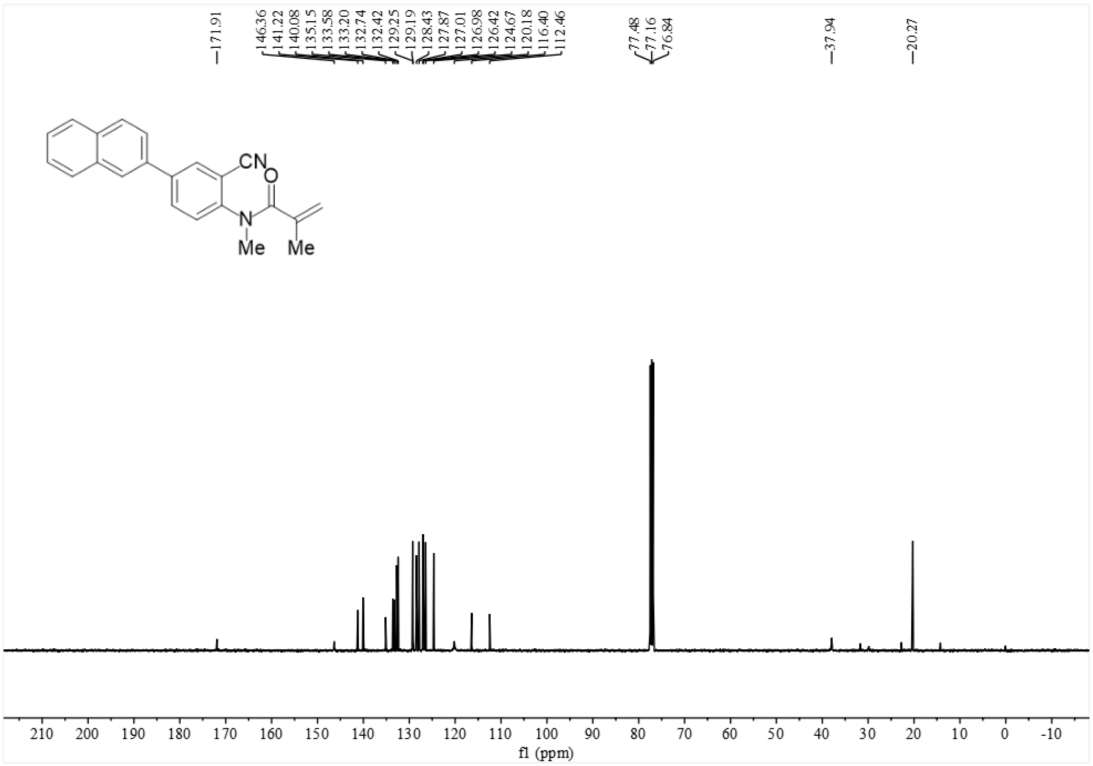
[13]C NMR of **1j** (100 MHz, $CDCl_3$):



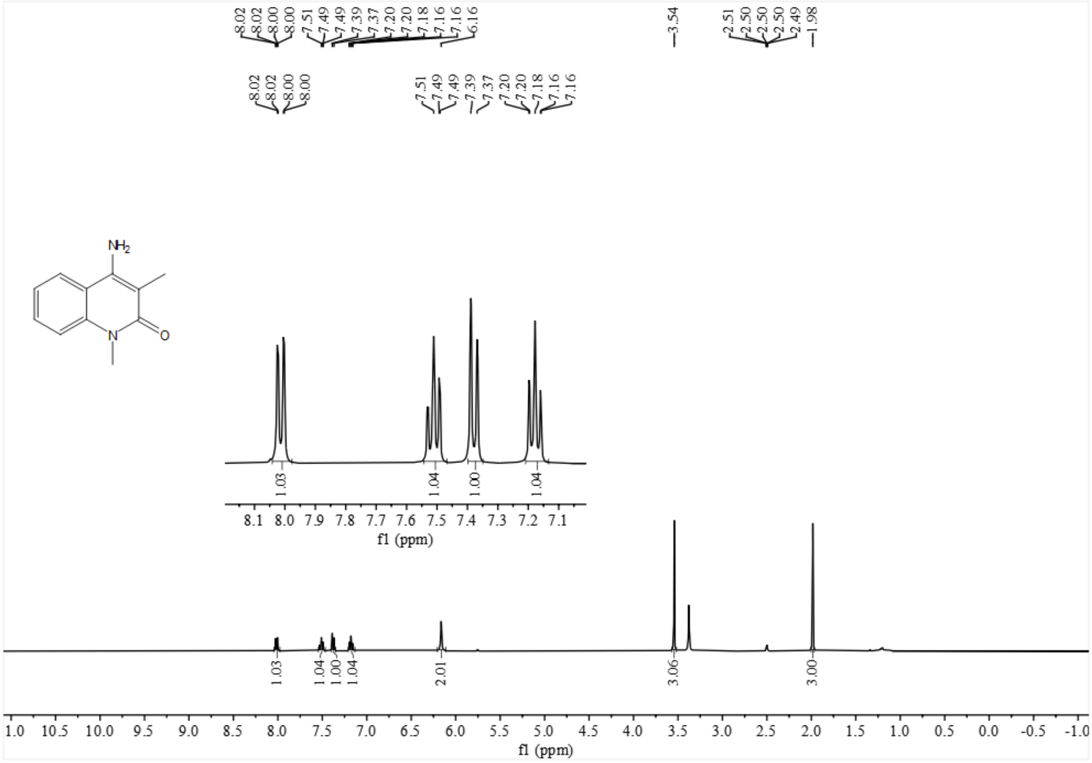
^{1}H NMR of **1p** (400 MHz, $CDCl_3$):



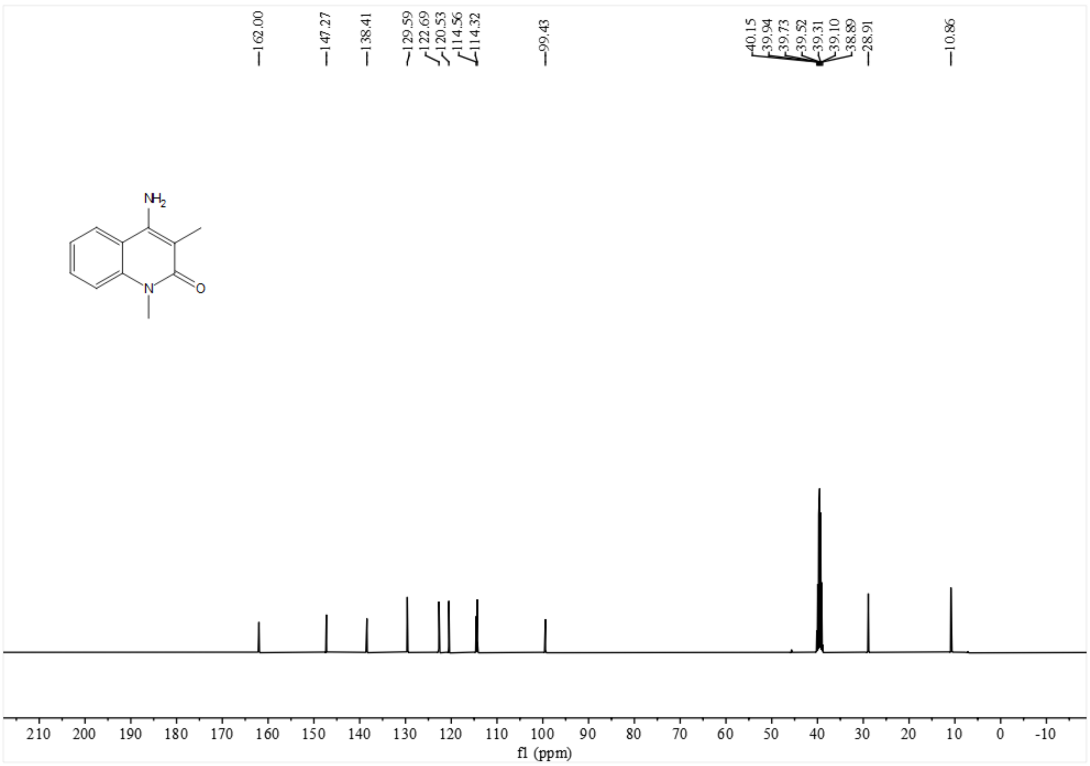
^{13}C NMR of **1p** (100 MHz, $CDCl_3$):



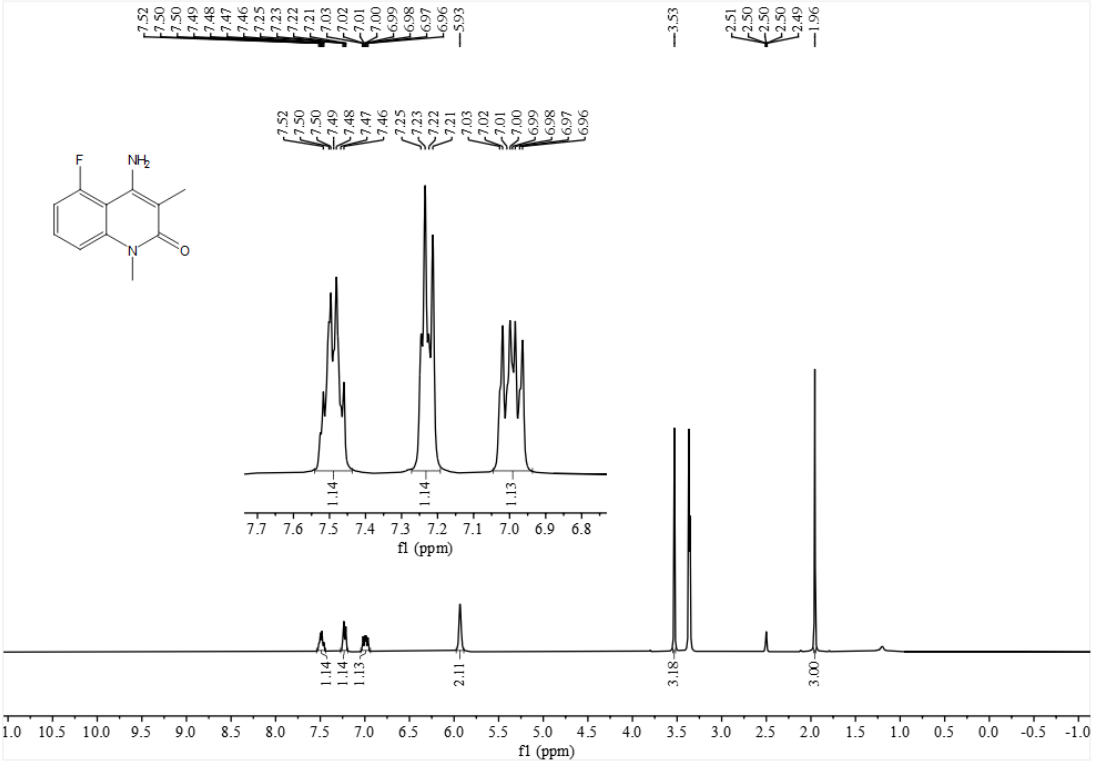
^{1}H NMR of **3a** (400 MHz, DMSO-d_6):



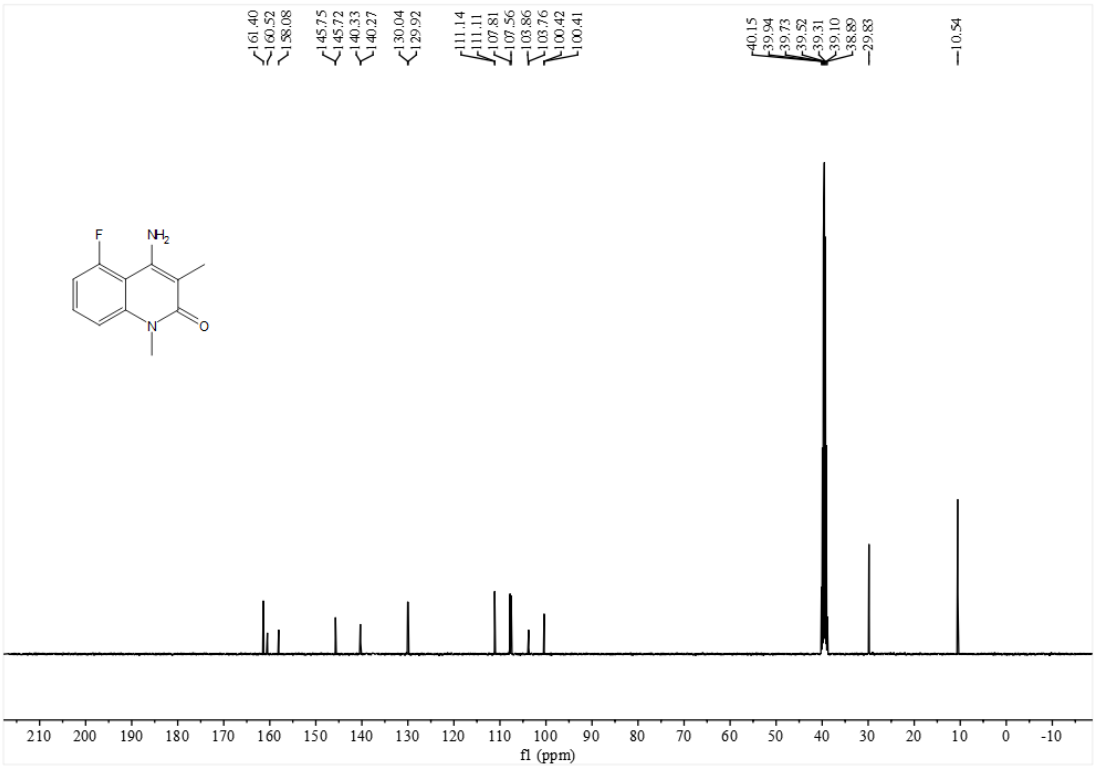
^{13}C NMR of **3a** (100 MHz, DMSO-d_6):



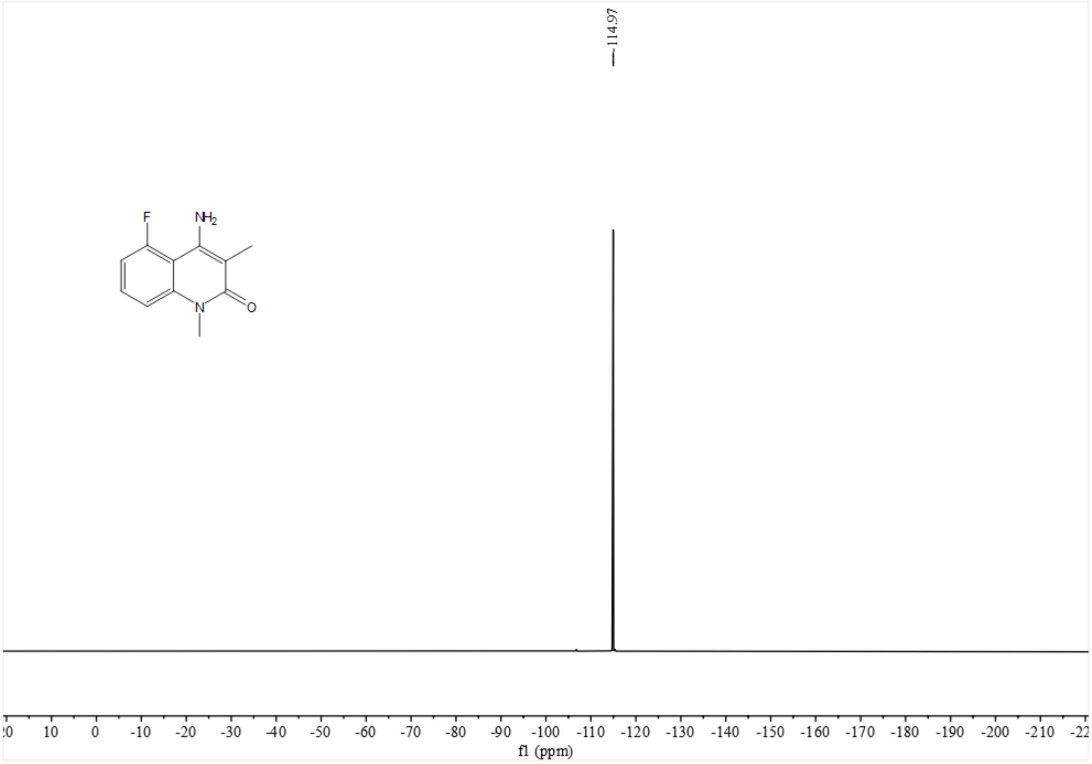
[1]H NMR of **3b** (400 MHz, DMSO-d_6):



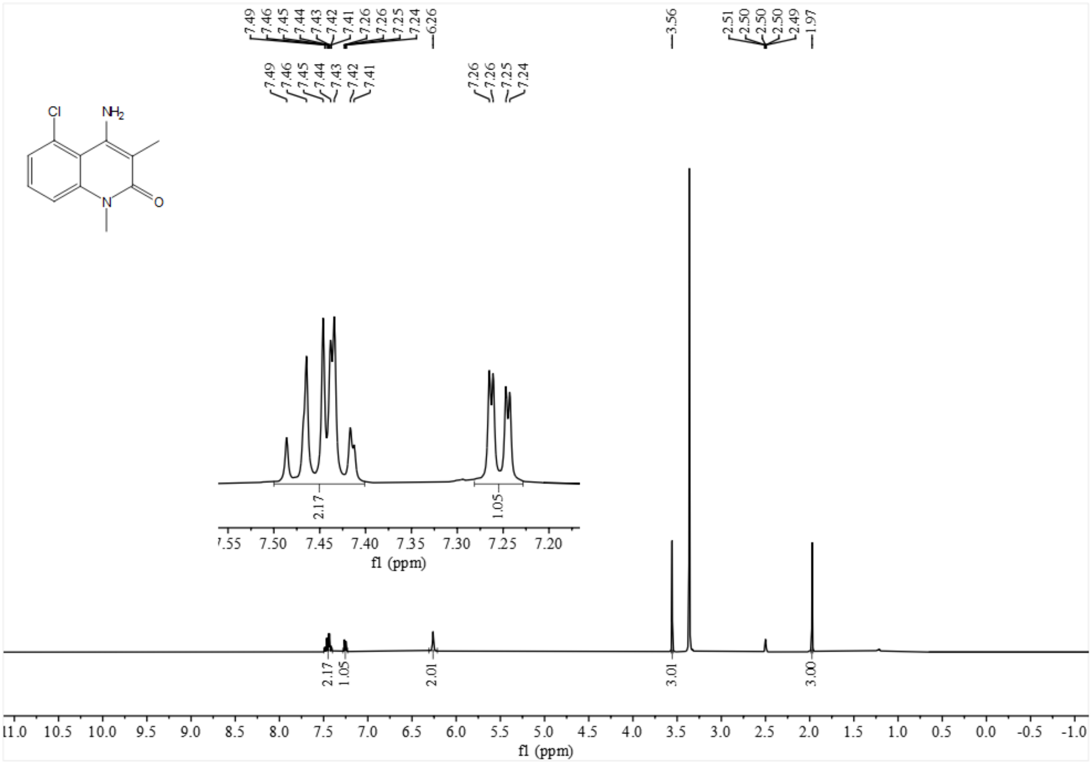
[13]C NMR of **3b** (100 MHz, DMSO-d_6):



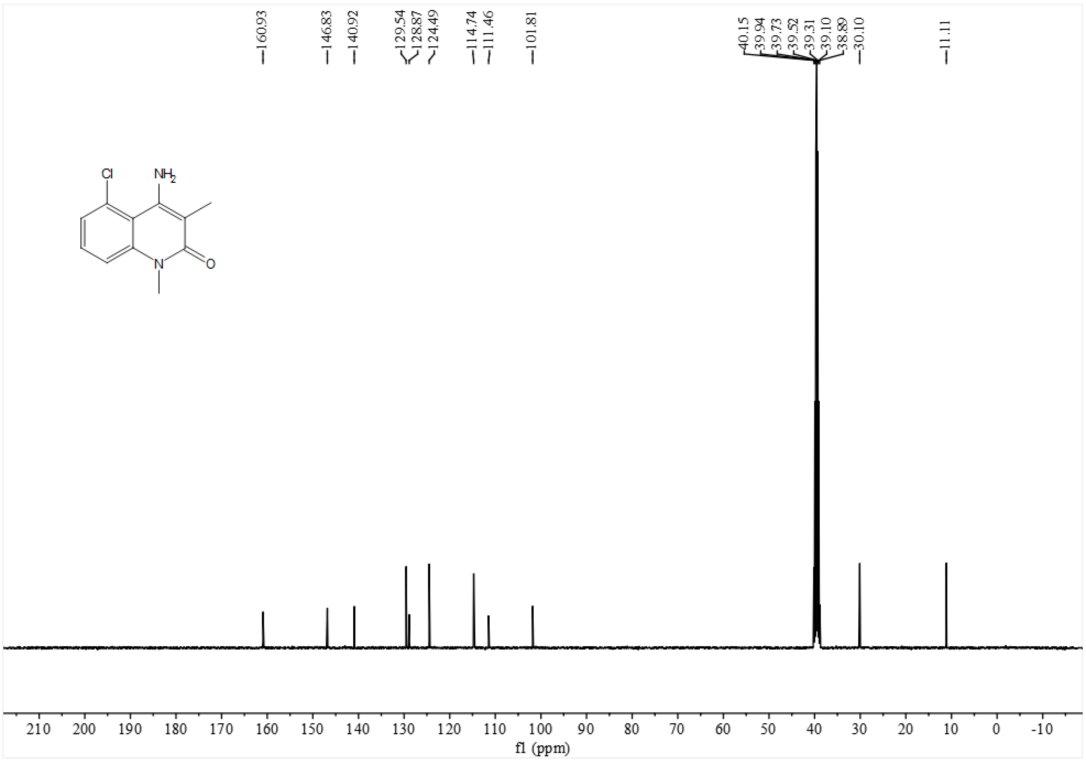
^{19}F NMR of **3b** (376 MHz, DMSO-d_6):



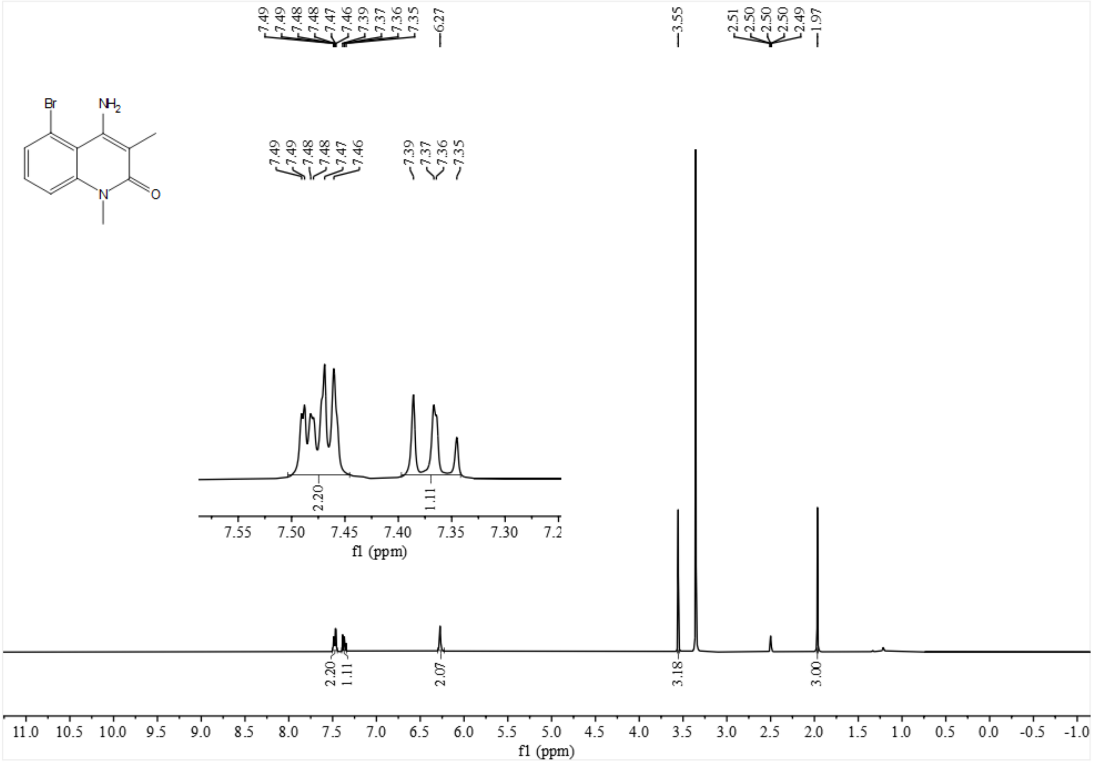
^{1}H NMR of **3c** (400 MHz, DMSO-d_6):



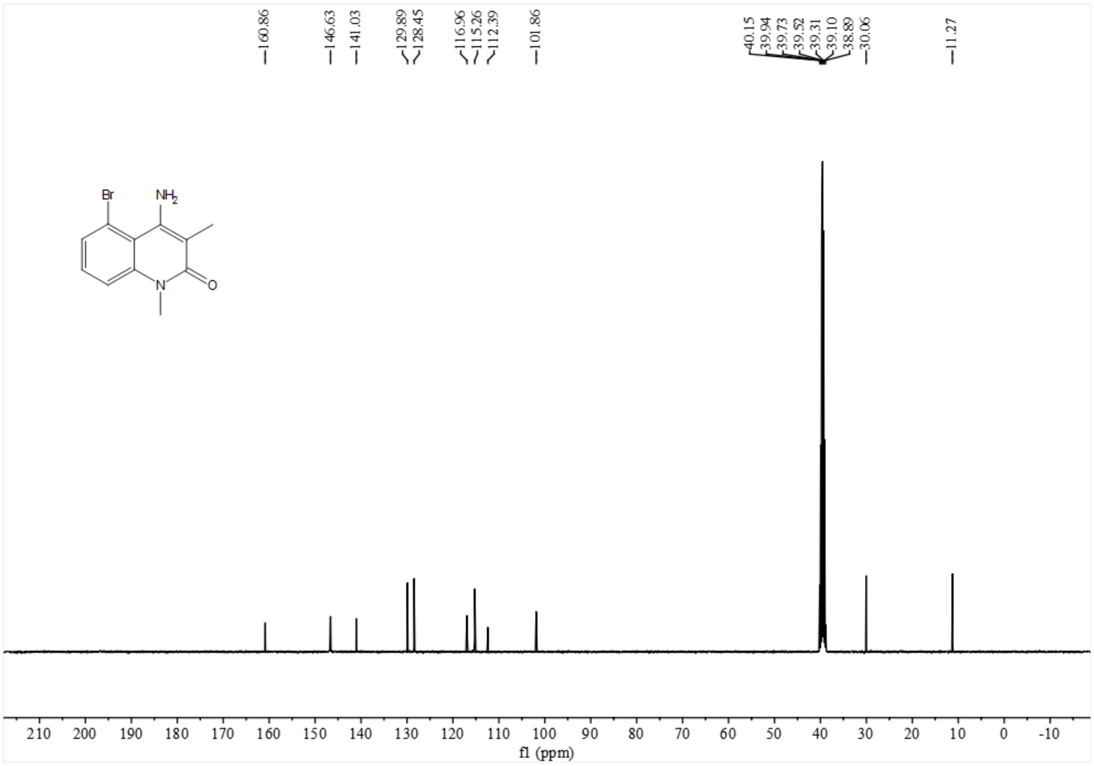
^{13}C NMR of **3c** (100 MHz, DMSO-d_6):



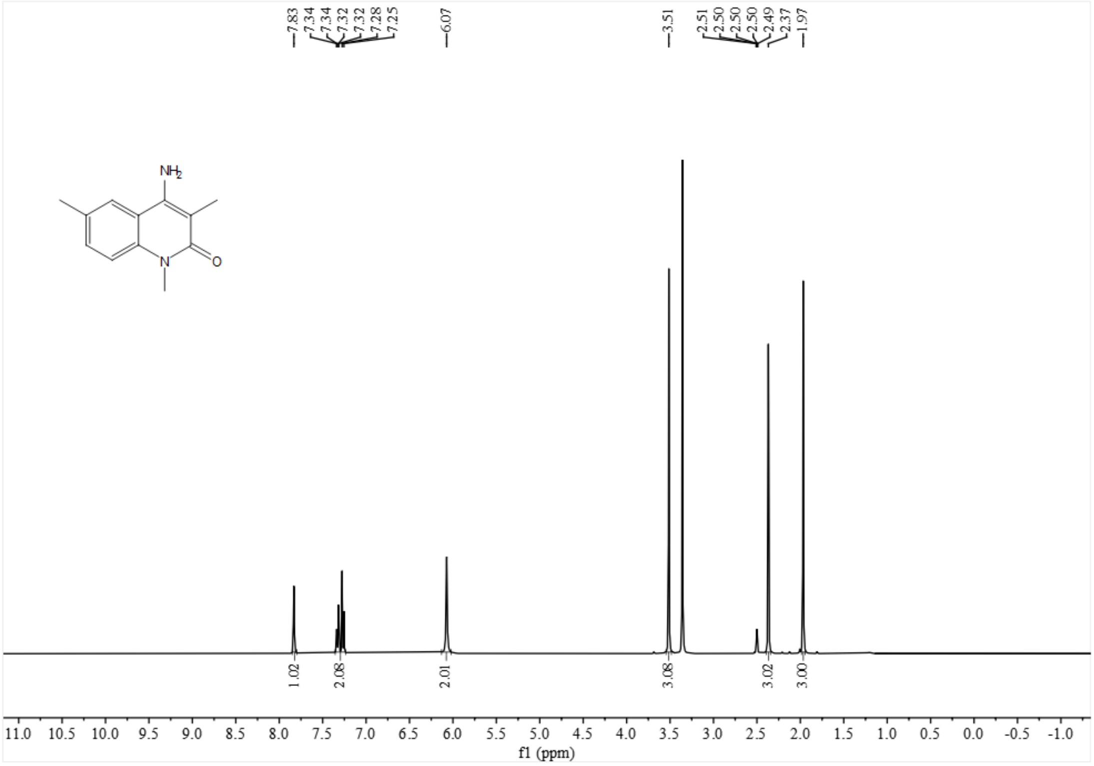
[1]H NMR of **3d** (400 MHz, DMSO-d_6):



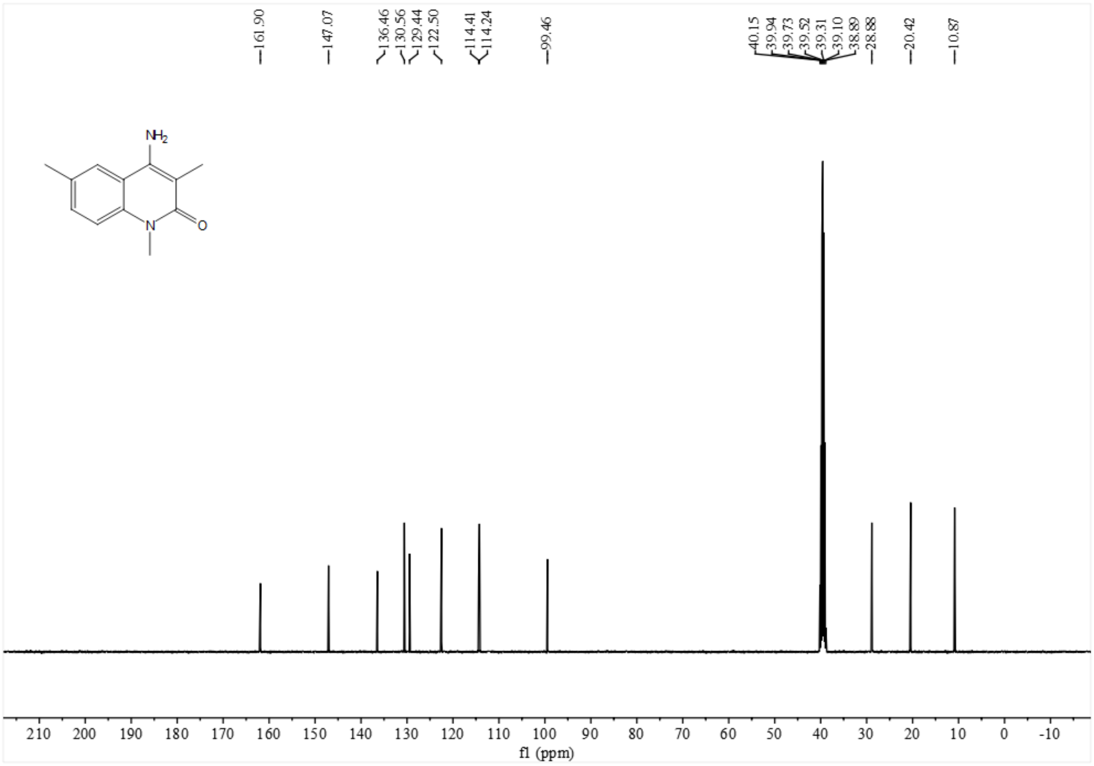
[13]C NMR of **3d** (100 MHz, DMSO-d_6):



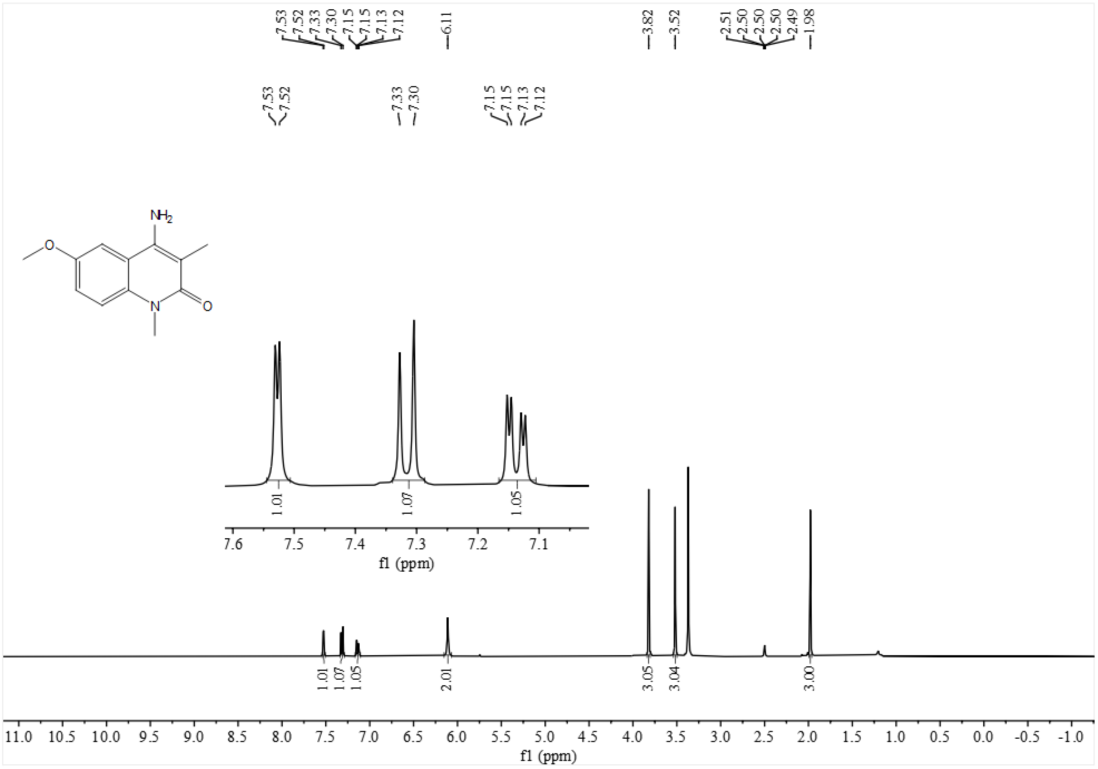
^{1}H NMR of **3e** (400 MHz, DMSO-d_6):



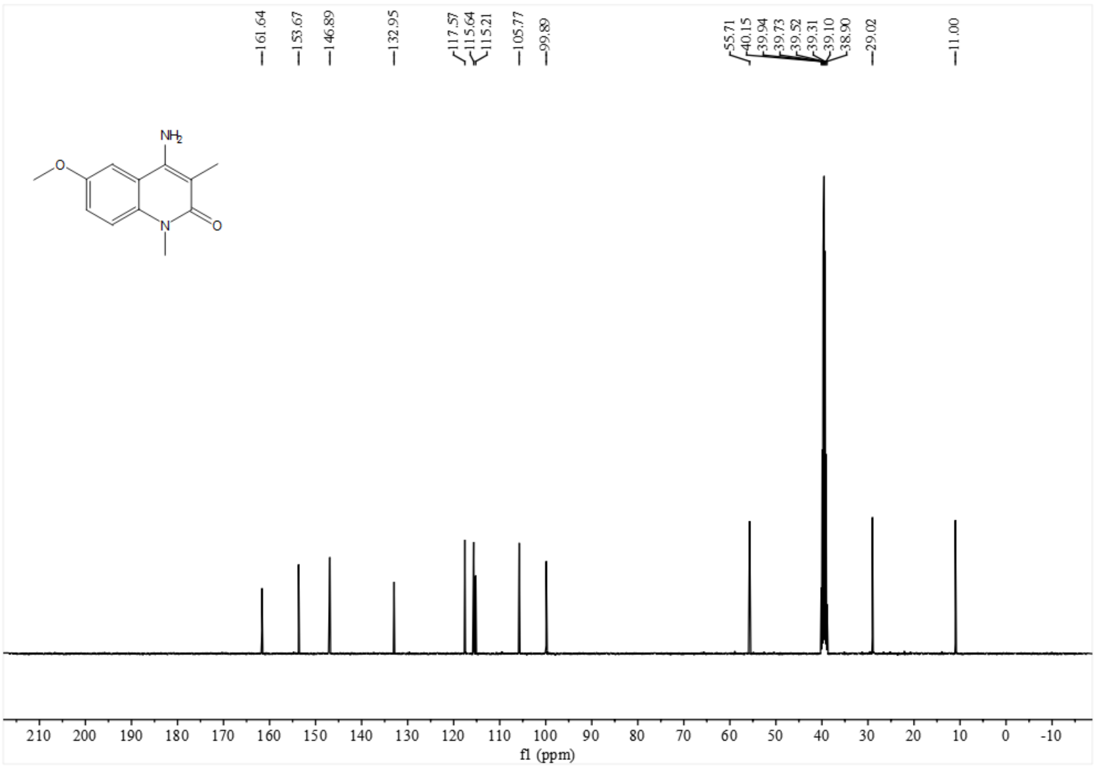
^{13}C NMR of **3e** (100 MHz, DMSO-d_6):



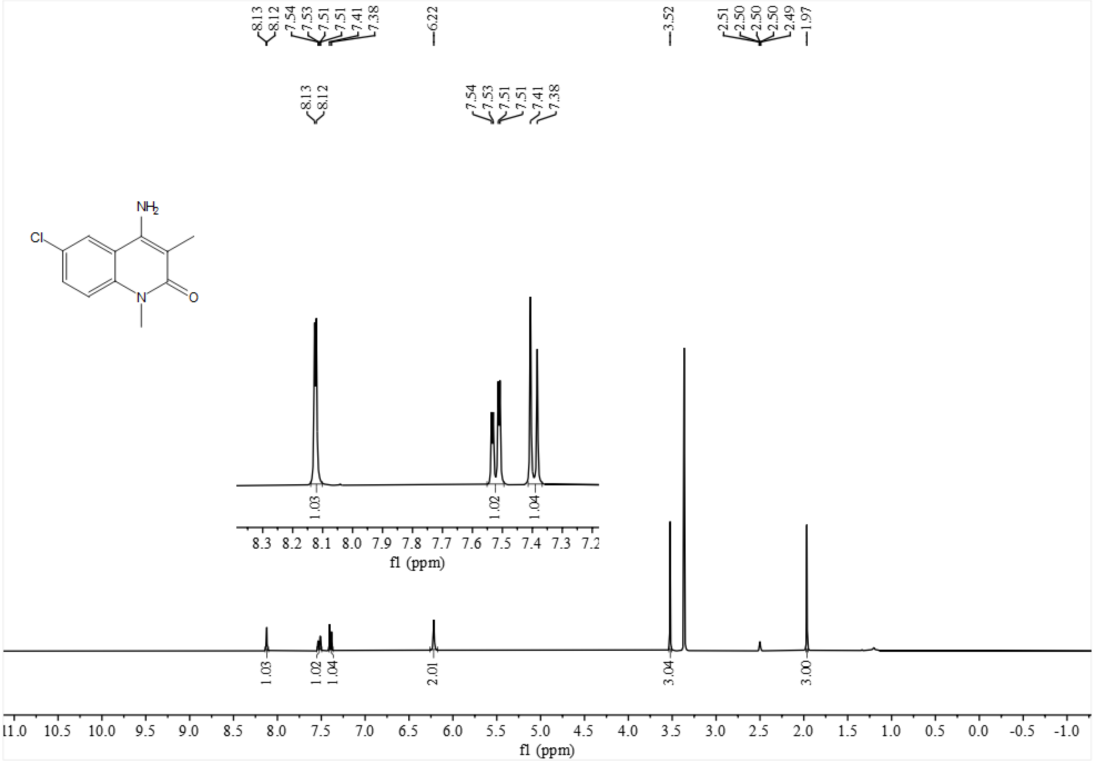
[1]H NMR of **3f** (400 MHz, DMSO-d_6):



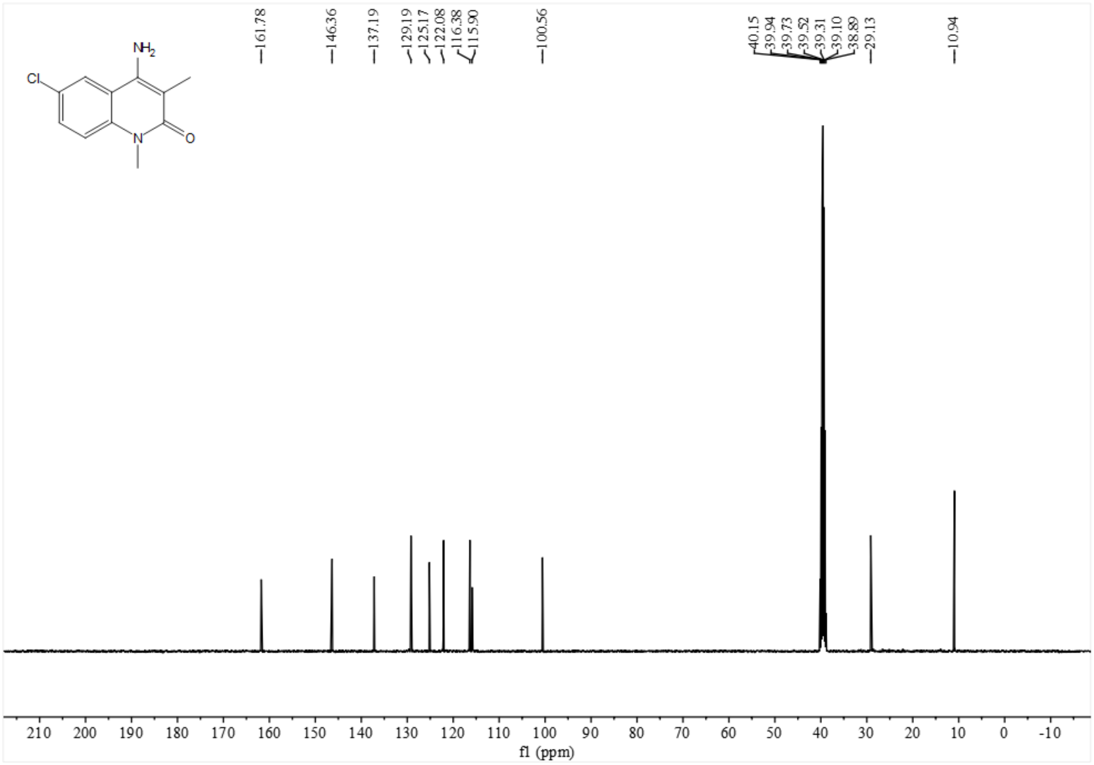
[13]C NMR of **3f** (100 MHz, DMSO-d_6):



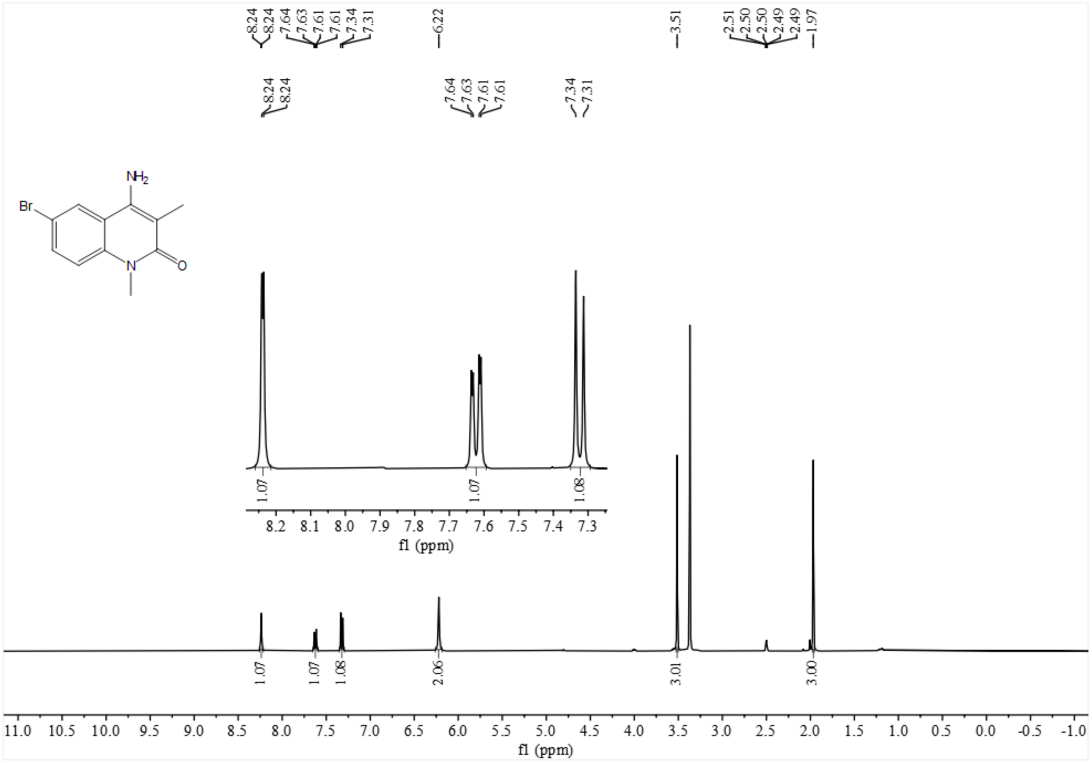
[1]H NMR of **3g** (400 MHz, DMSO-d_6):



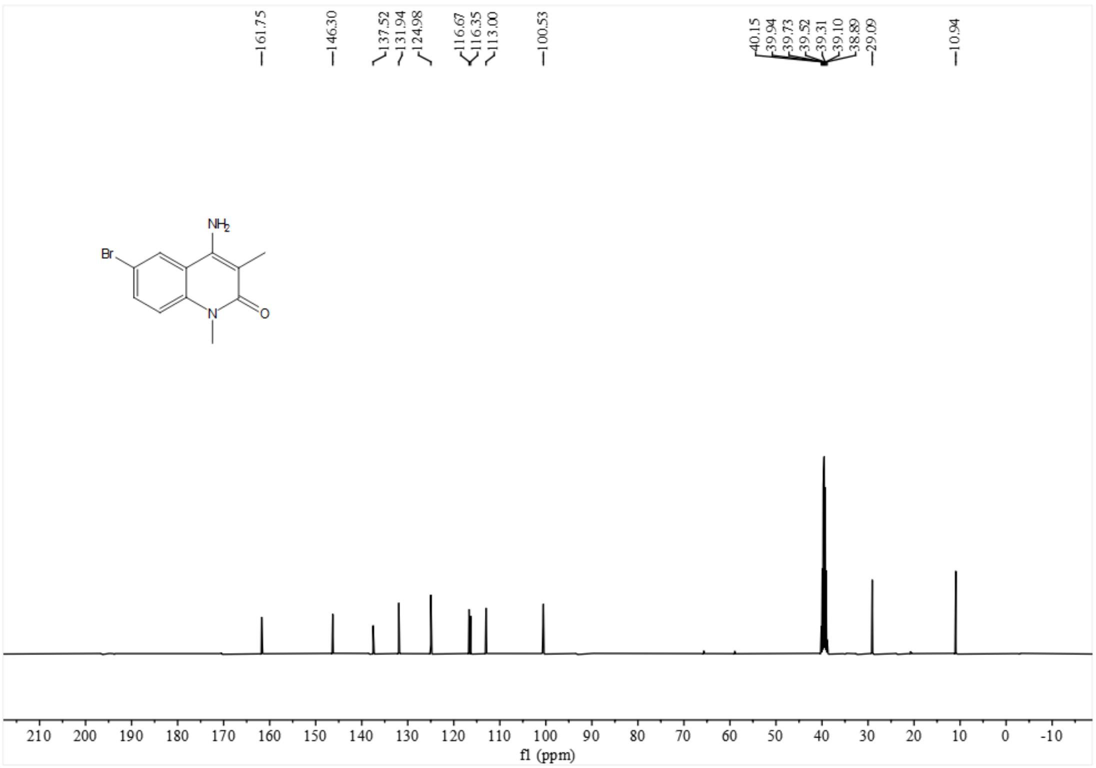
[13]C NMR of **3g** (100 MHz, DMSO-d_6):



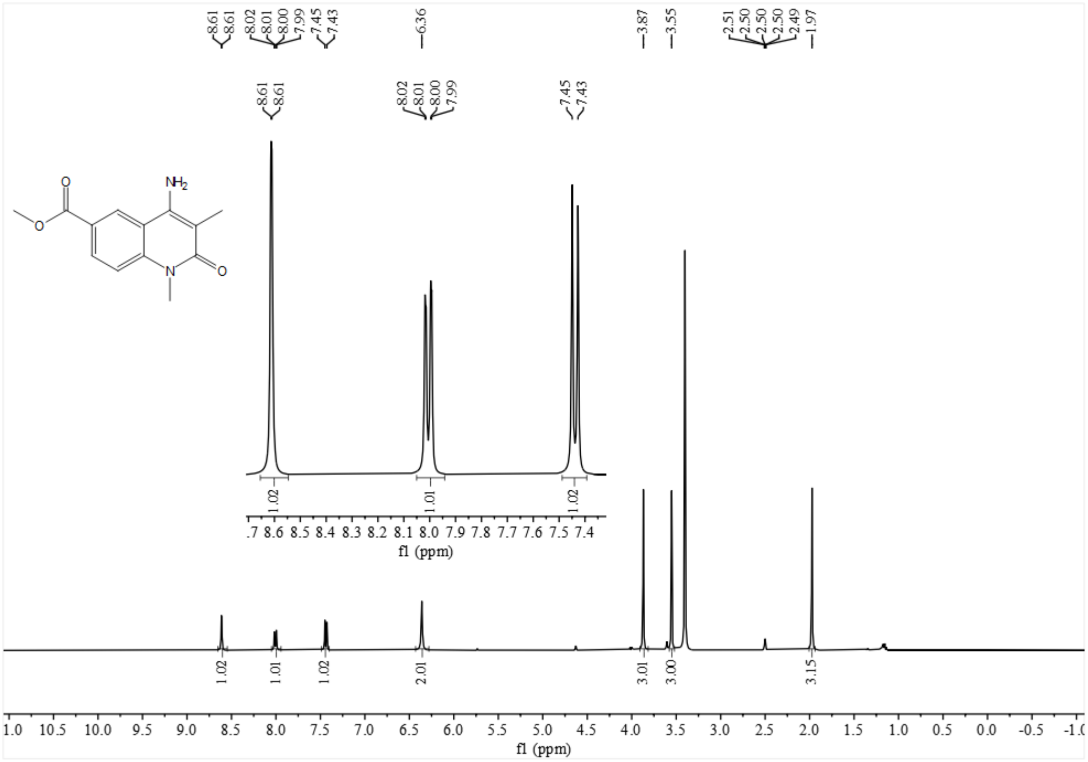
^{1}H NMR of **3h** (400 MHz, DMSO-d_6):



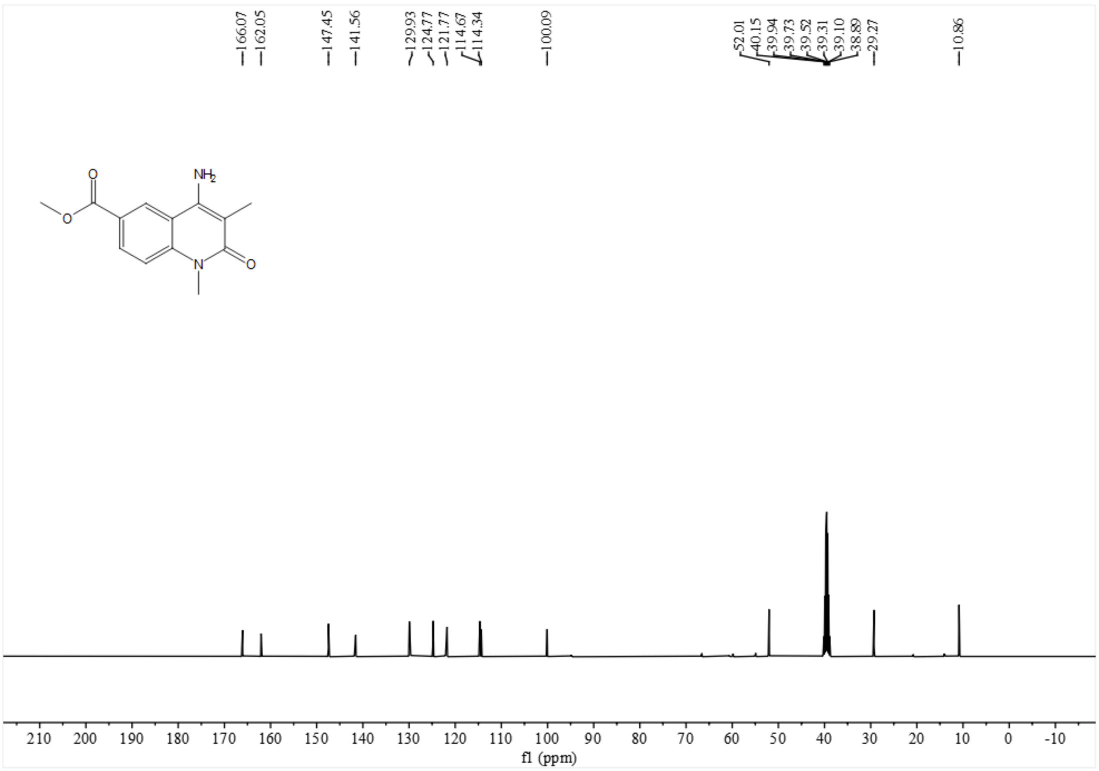
^{13}C NMR of **3h** (100 MHz, DMSO-d_6):



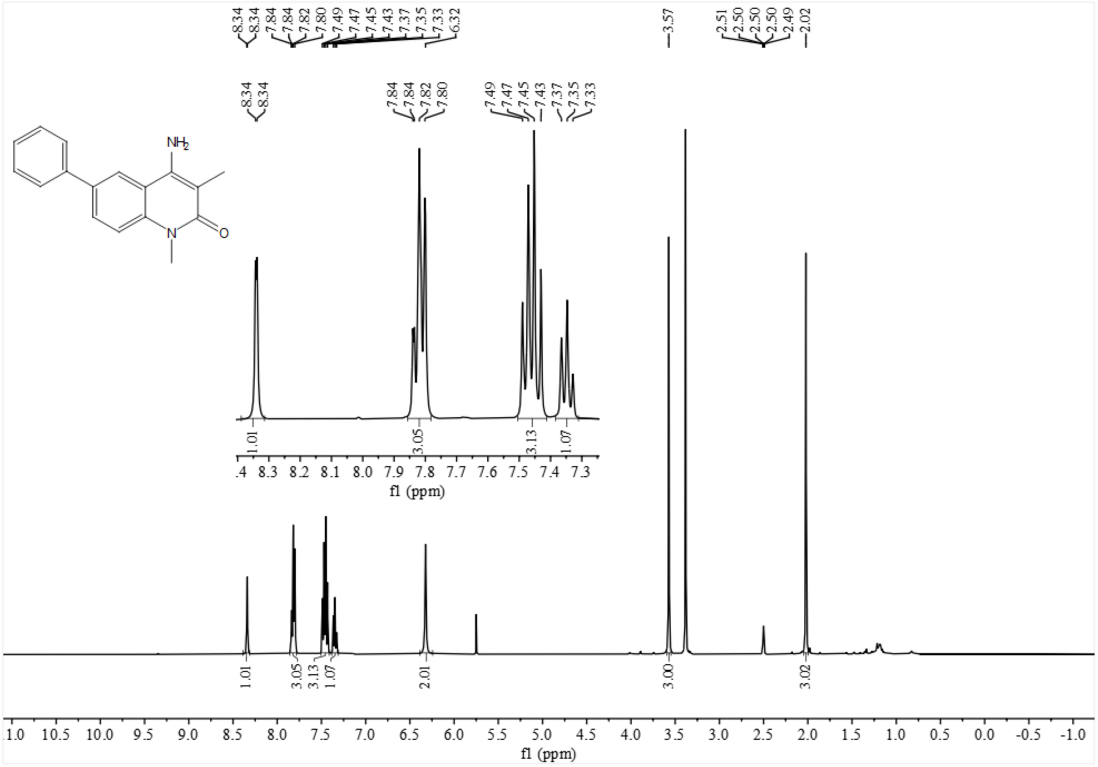
^{1}H NMR of **3i** (400 MHz, DMSO-d_6):



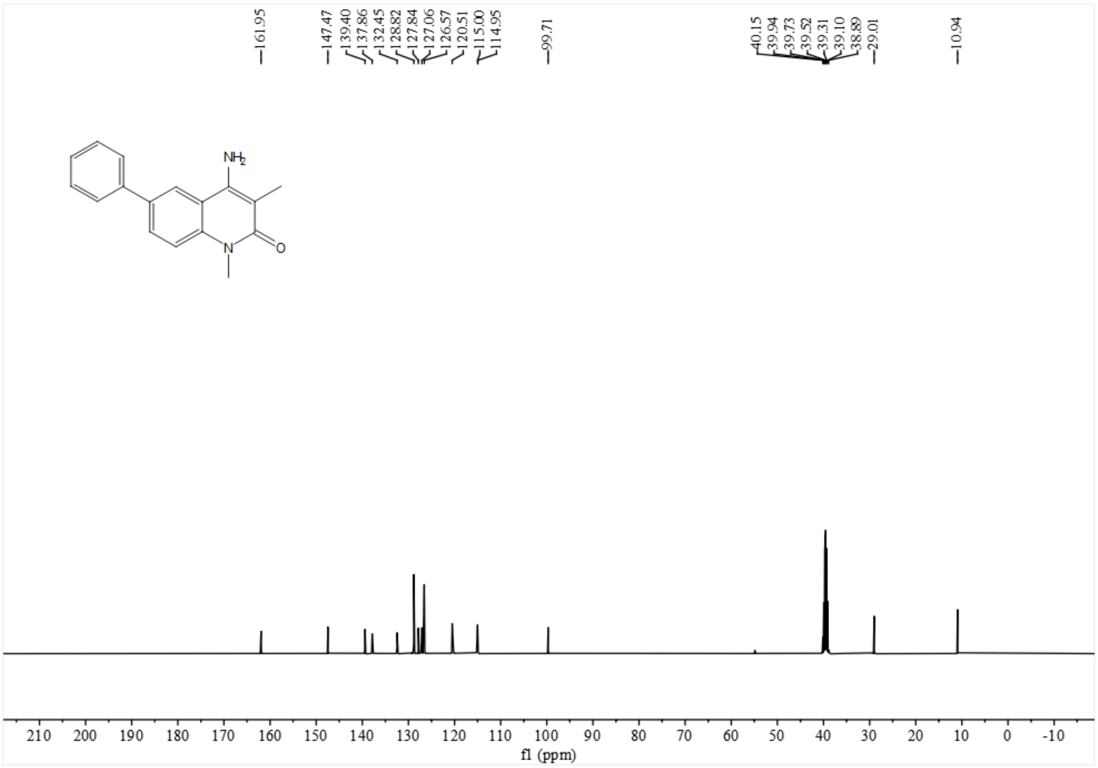
^{13}C NMR of **3i** (100 MHz, DMSO-d_6):



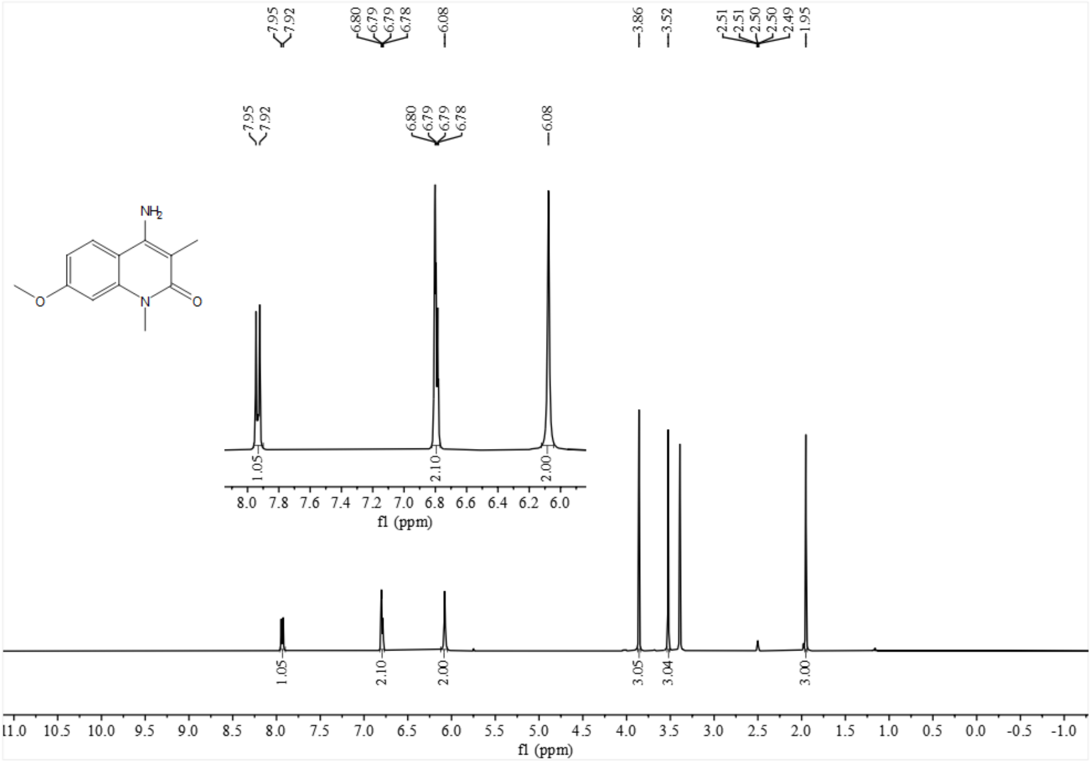
^{1}H NMR of **3j** (400 MHz, DMSO-d_6):



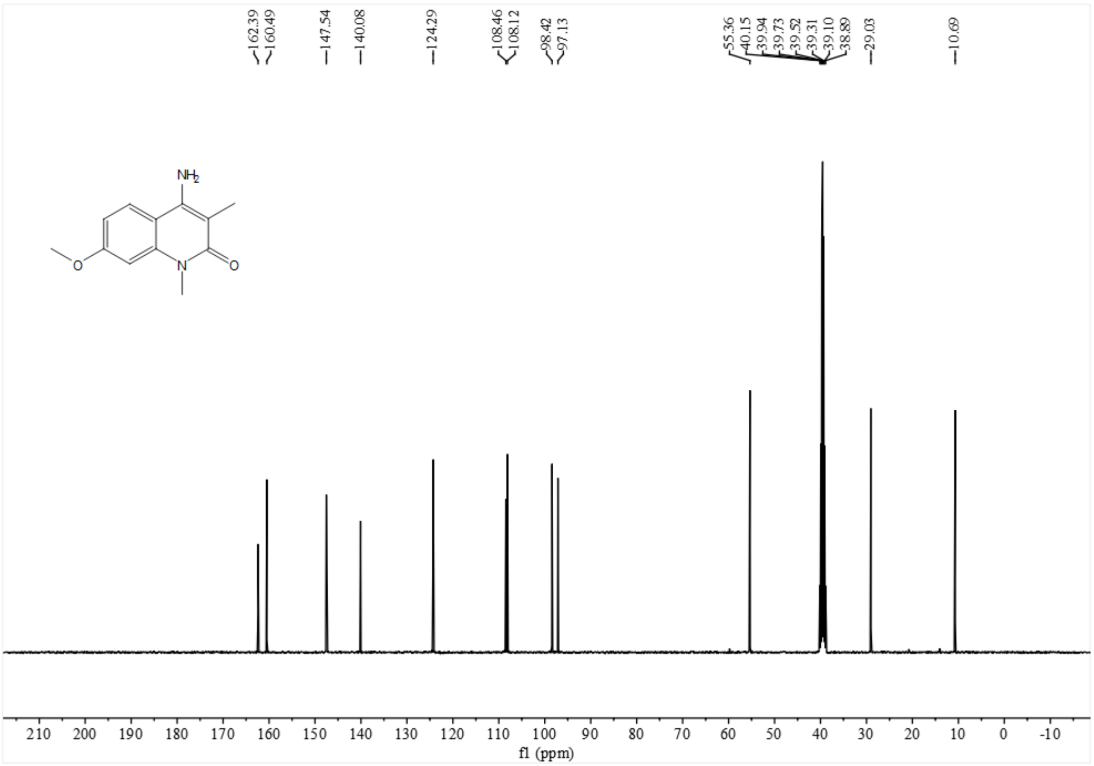
^{13}C NMR of **3j** (100 MHz, DMSO-d_6):



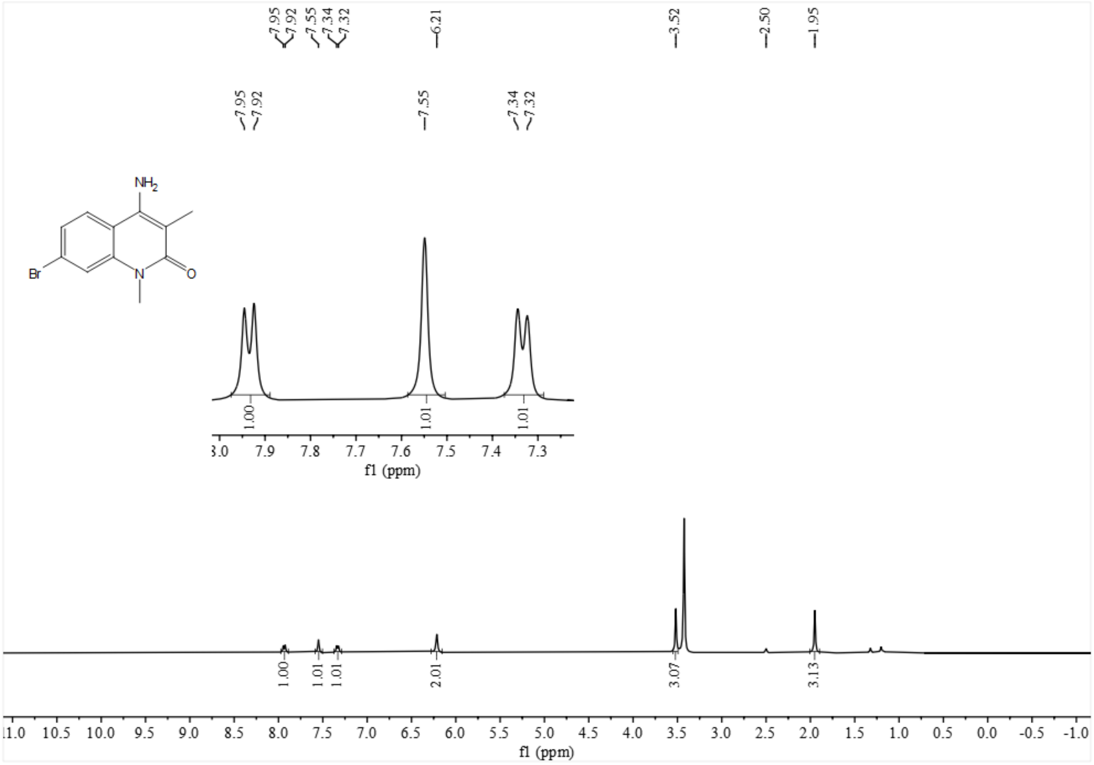
[1]H NMR of **3k** (400 MHz, DMSO-d_6):



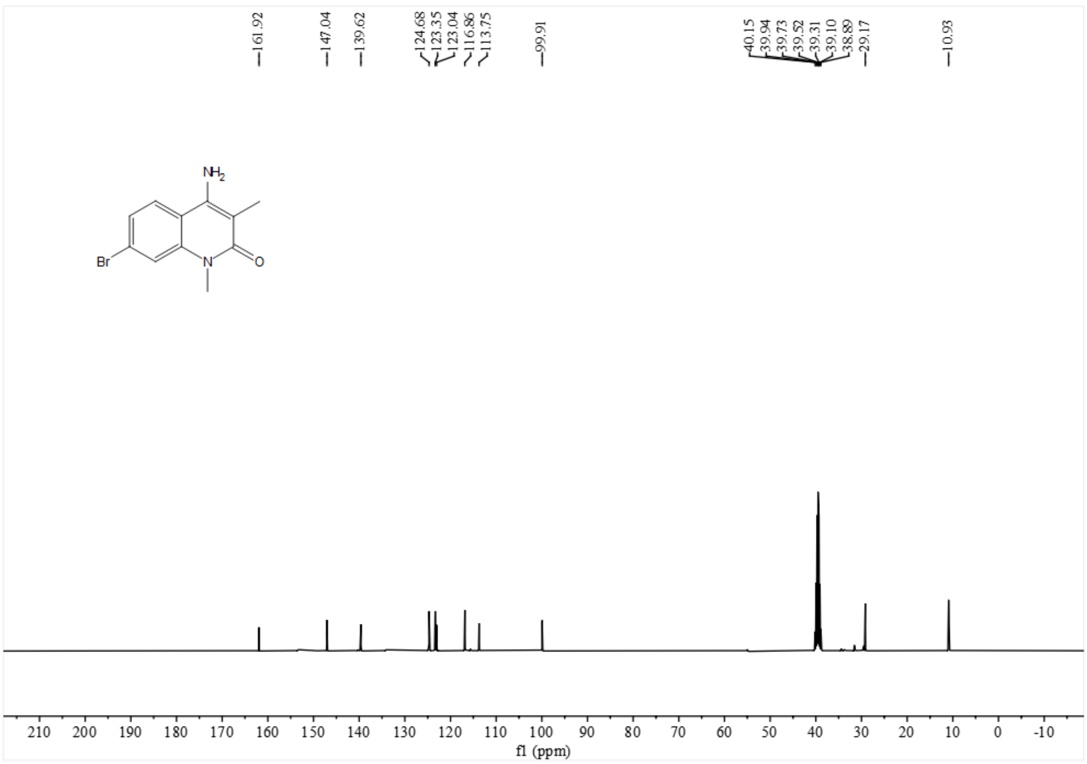
[13]C NMR of **3k** (100 MHz, DMSO-d_6):



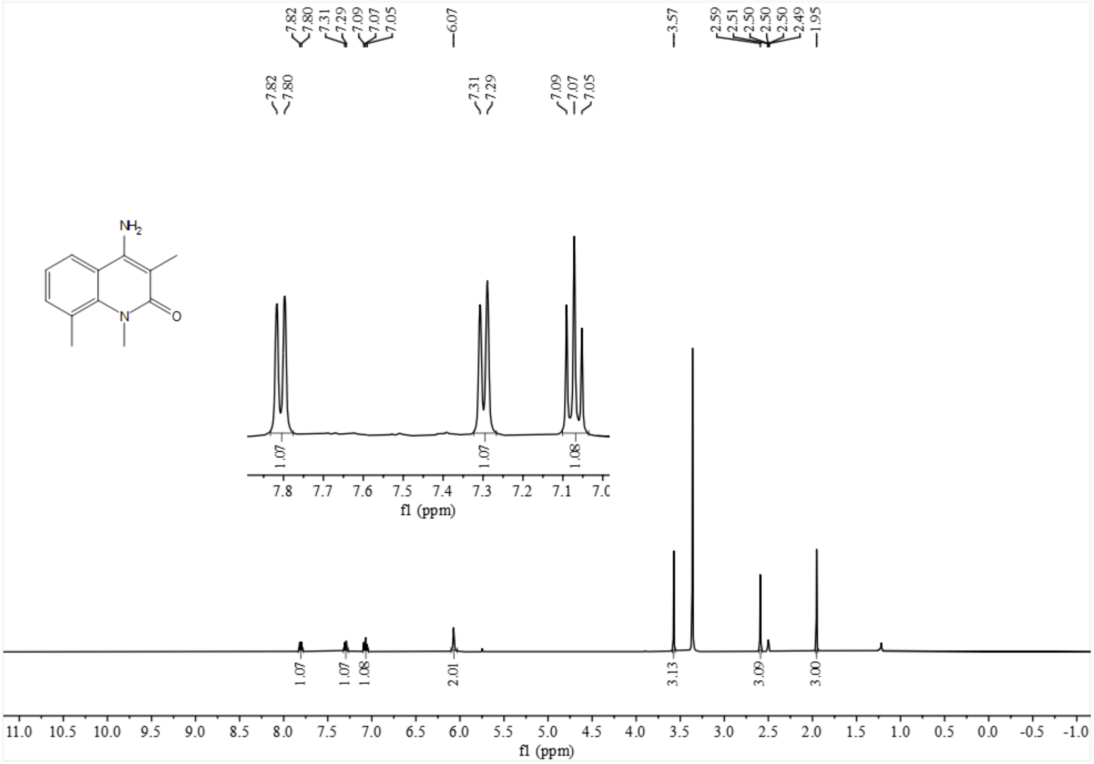
^{1}H NMR of **3l** (400 MHz, DMSO-d_6):



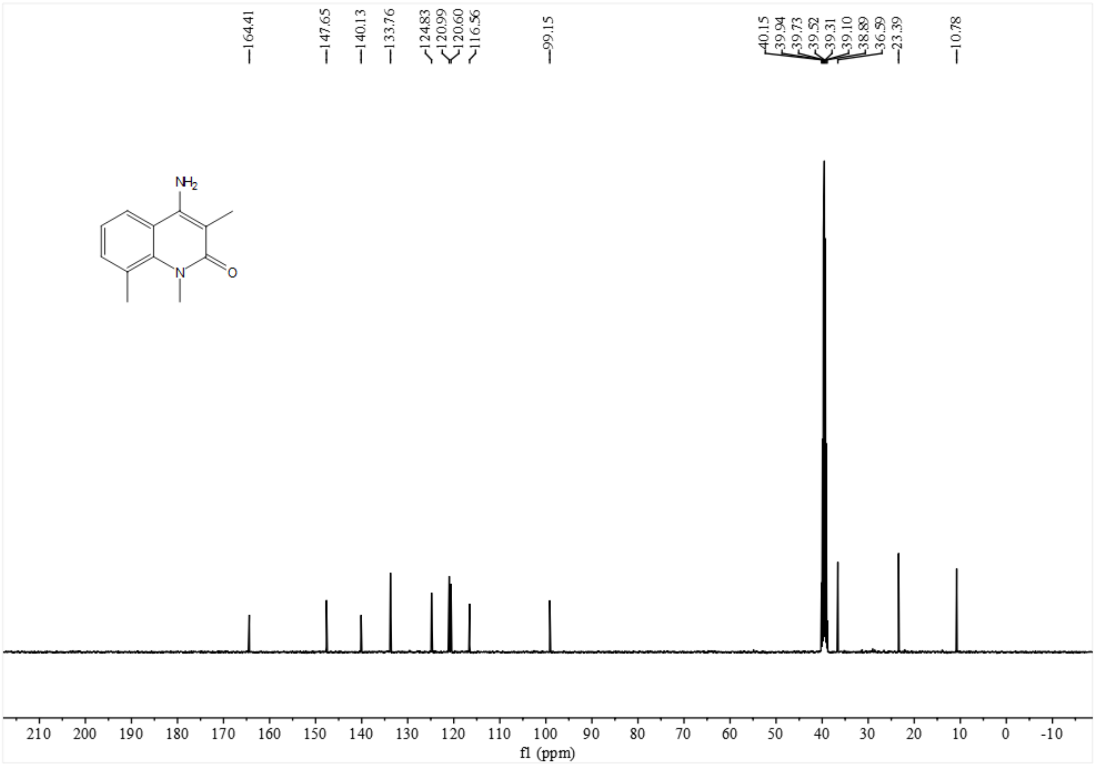
^{13}C NMR of **3l** (100 MHz, DMSO-d_6):



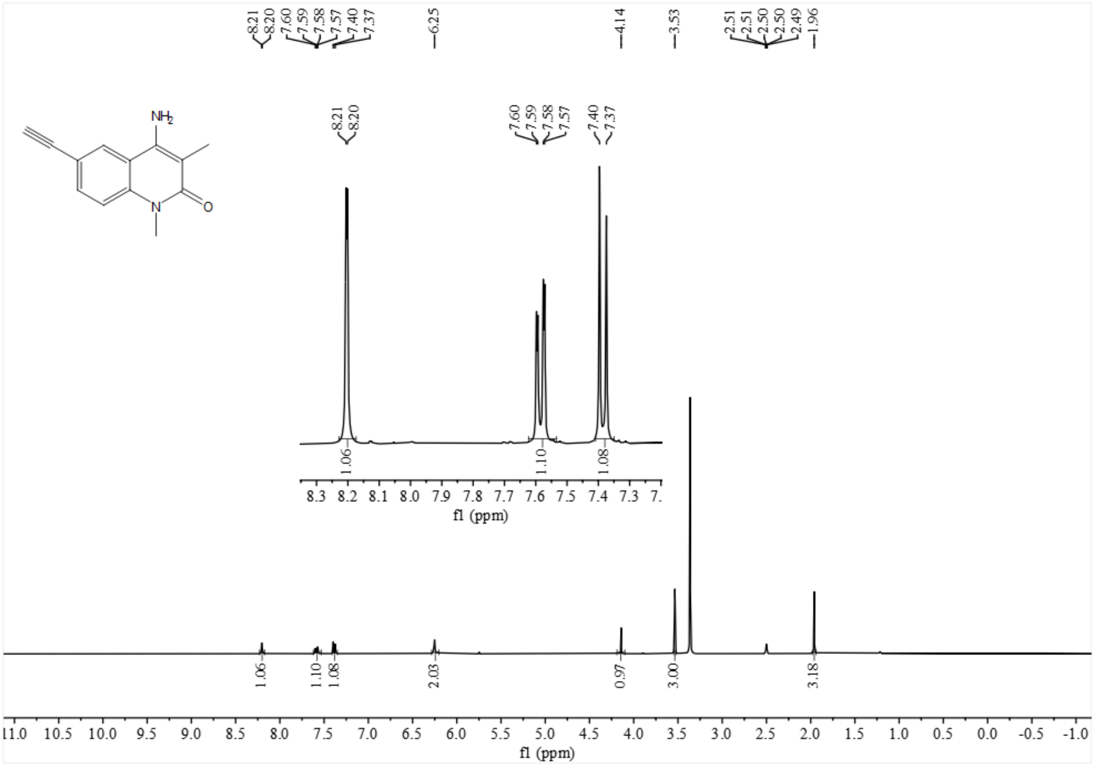
[1]H NMR of **3m** (400 MHz, DMSO-d_6):



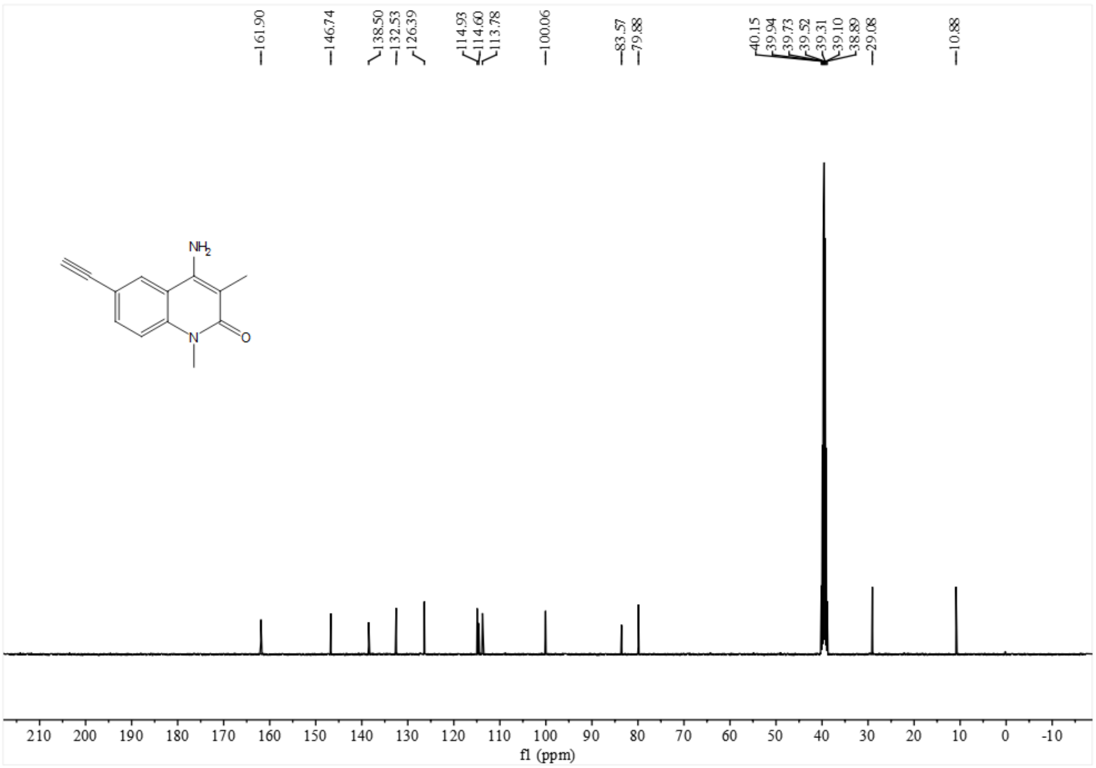
[13]C NMR of **3m** (100 MHz, DMSO-d_6):



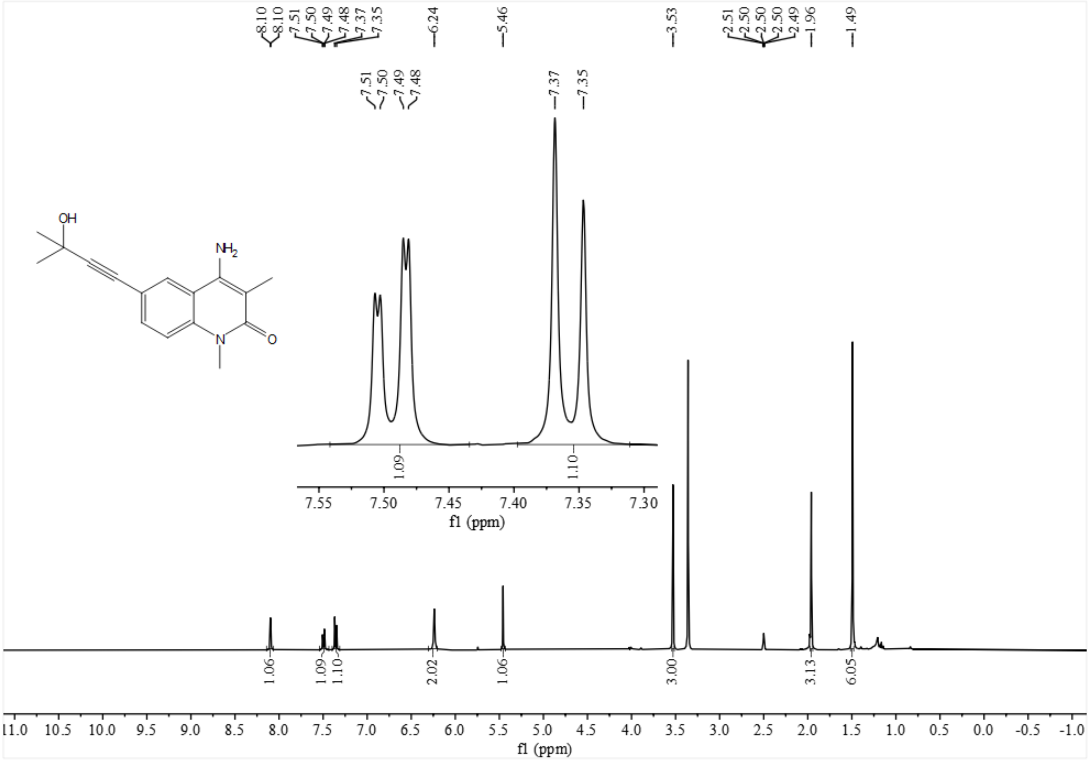
^{1}H NMR of **3n** (400 MHz, DMSO-d_6):



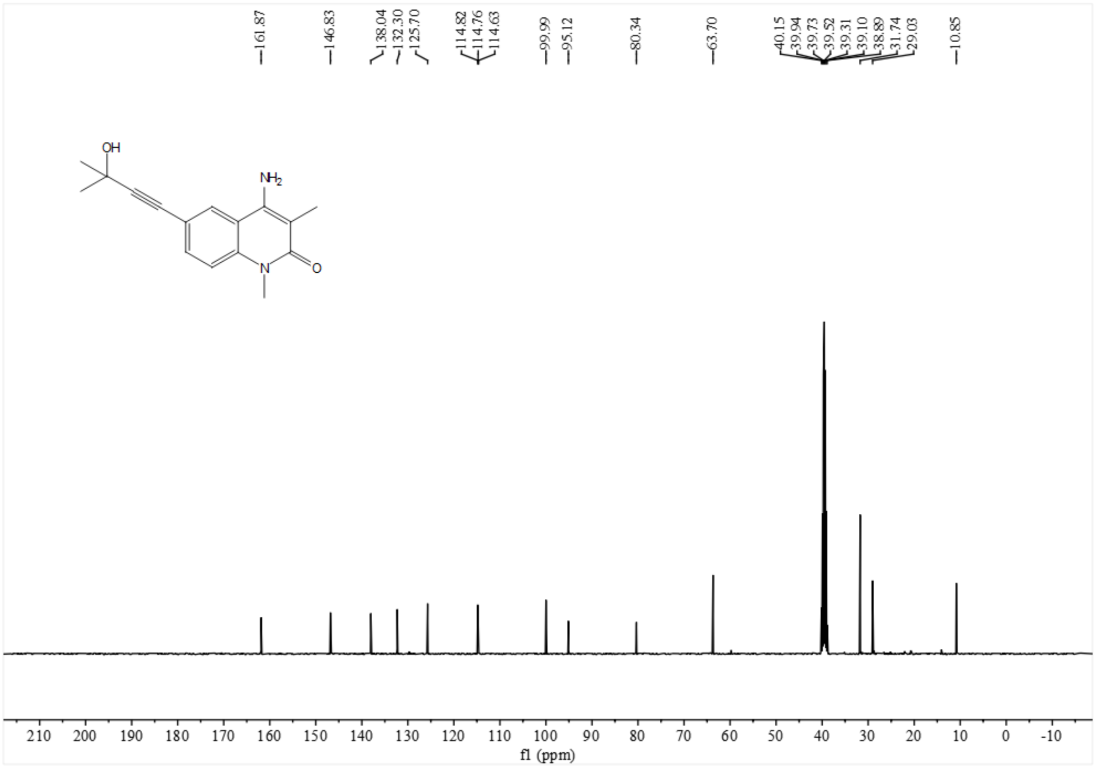
^{13}C NMR of **3n** (100 MHz, DMSO-d_6):



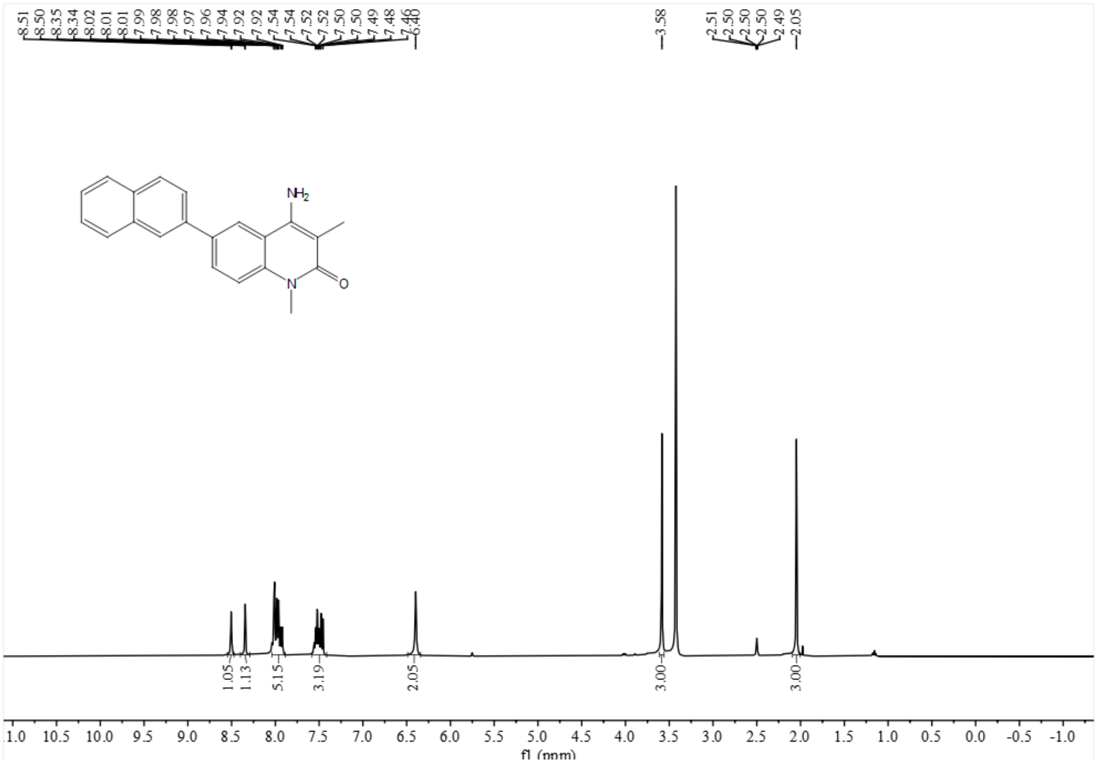
^{1}H NMR of **3o** (400 MHz, DMSO-d_6):



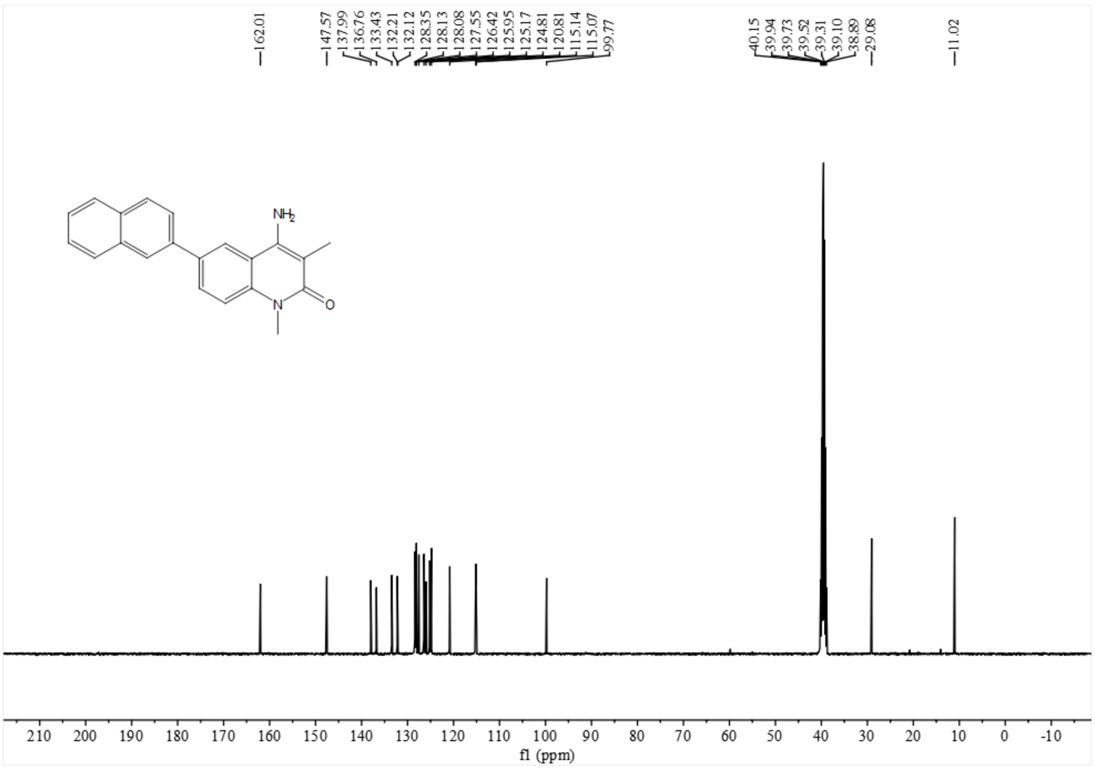
^{13}C NMR of **3o** (100 MHz, DMSO-d_6):



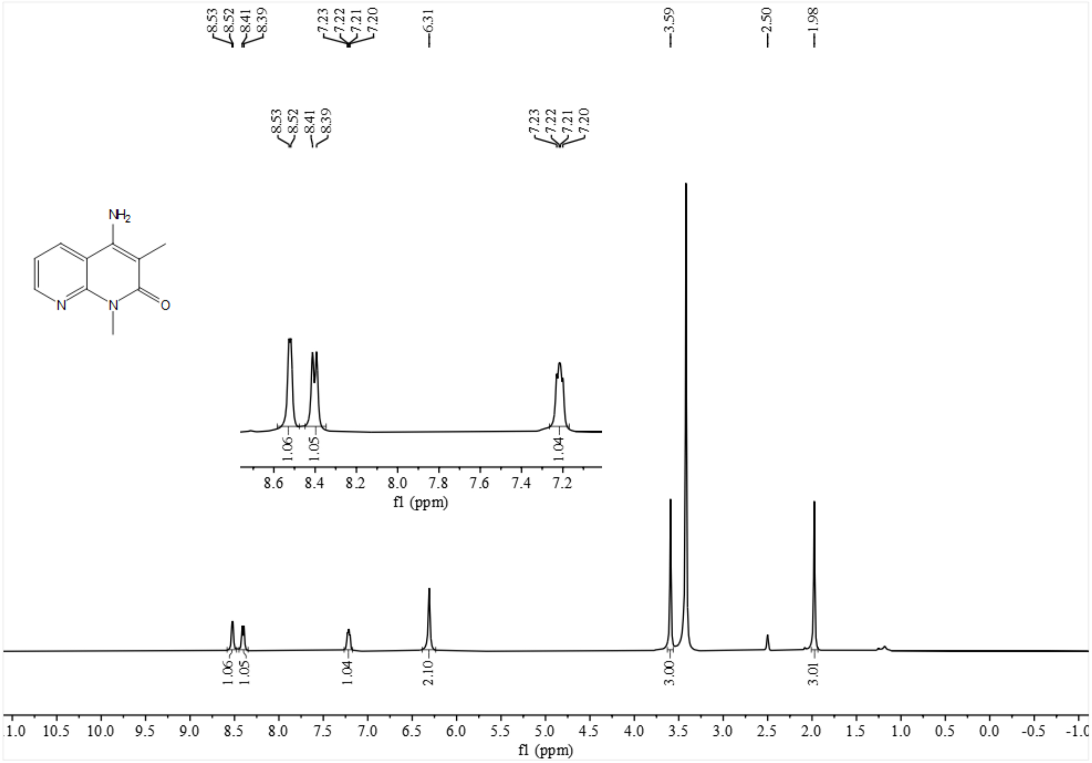
[1]H NMR of **3p** (400 MHz, DMSO-d_6):



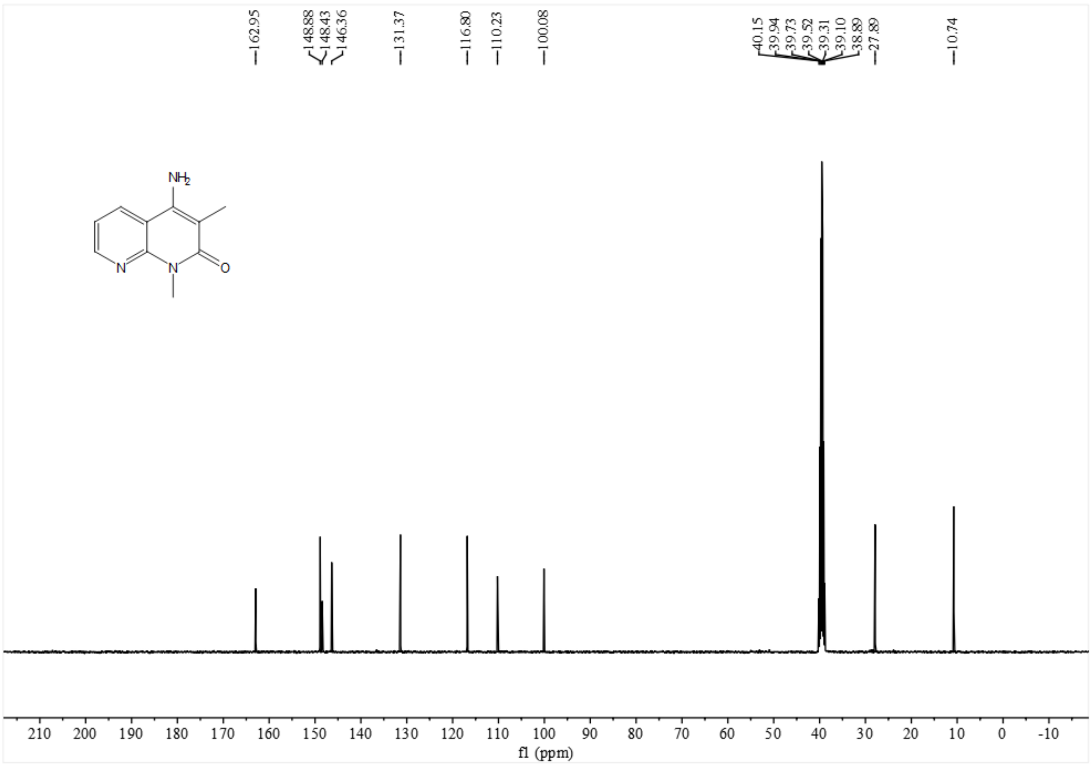
[13]C NMR of **3p** (100 MHz, DMSO-d_6):



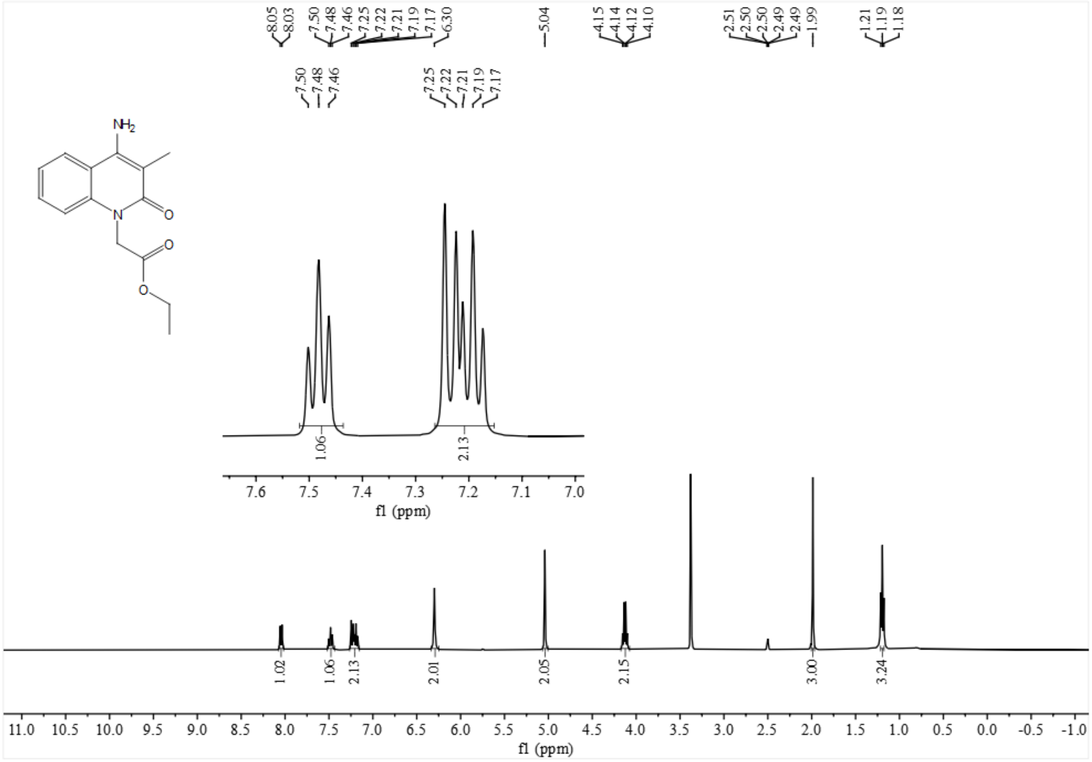
[1]H NMR of **3q** (400 MHz, DMSO-d_6):



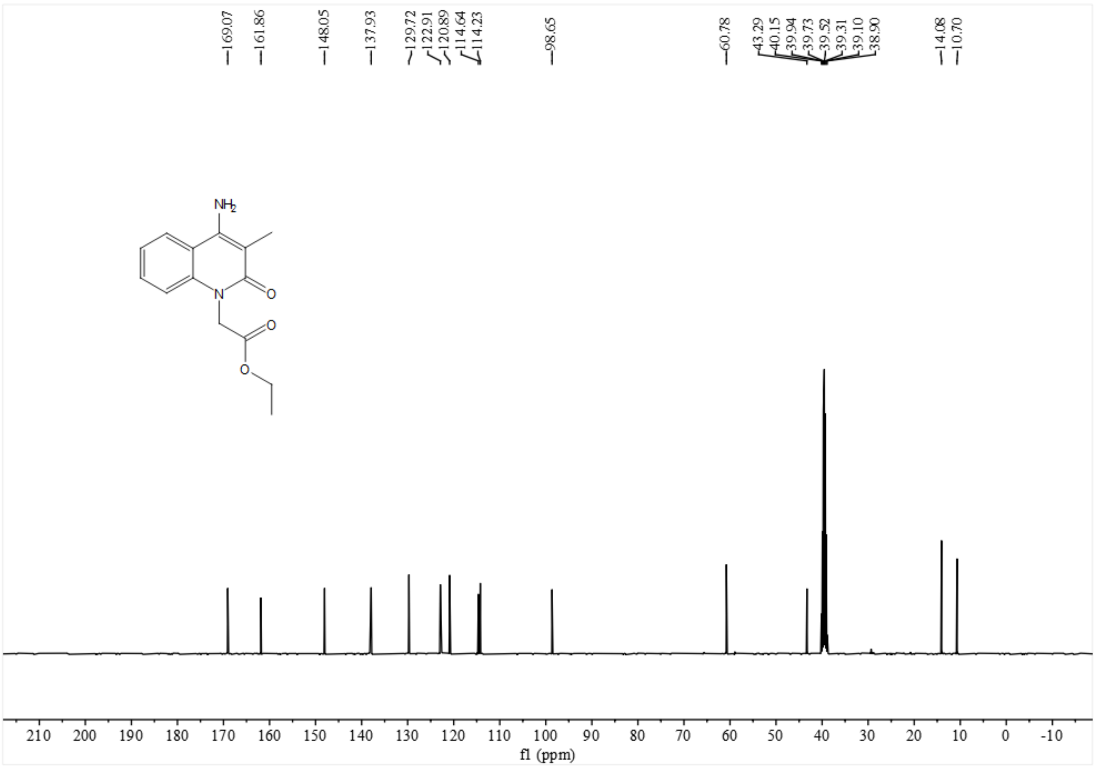
[13]C NMR of **3q** (100 MHz, DMSO-d_6):



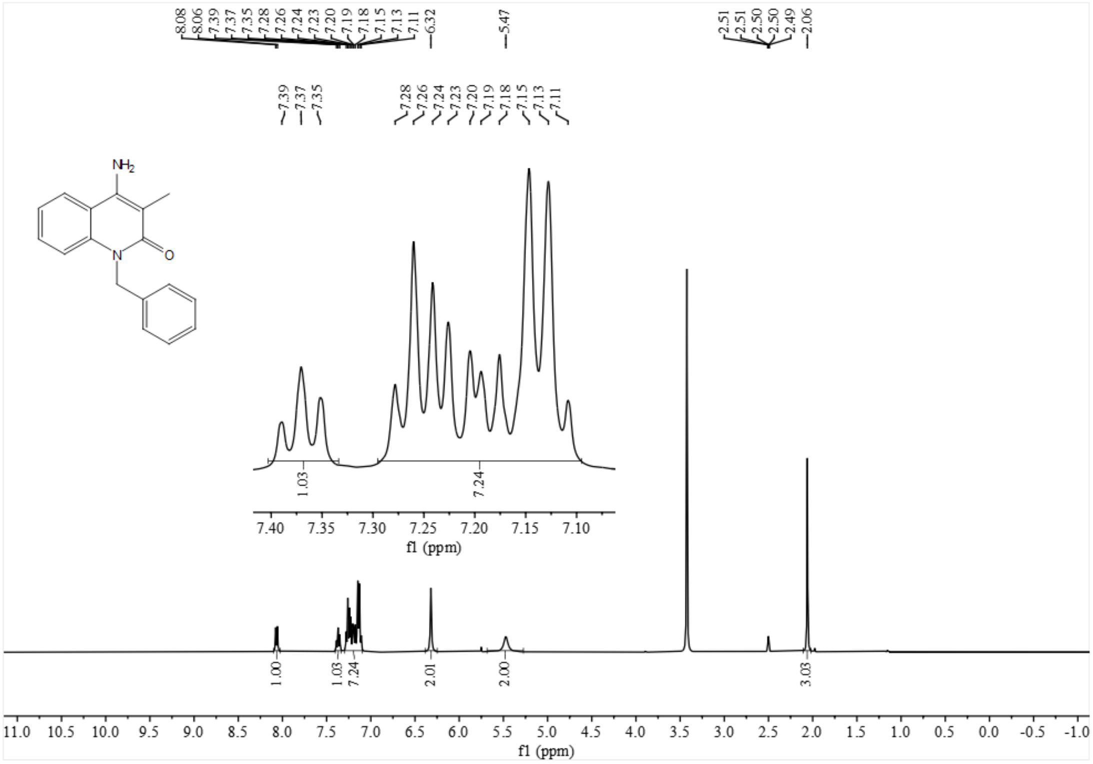
[1]H NMR of **3r** (400 MHz, DMSO-d_6):



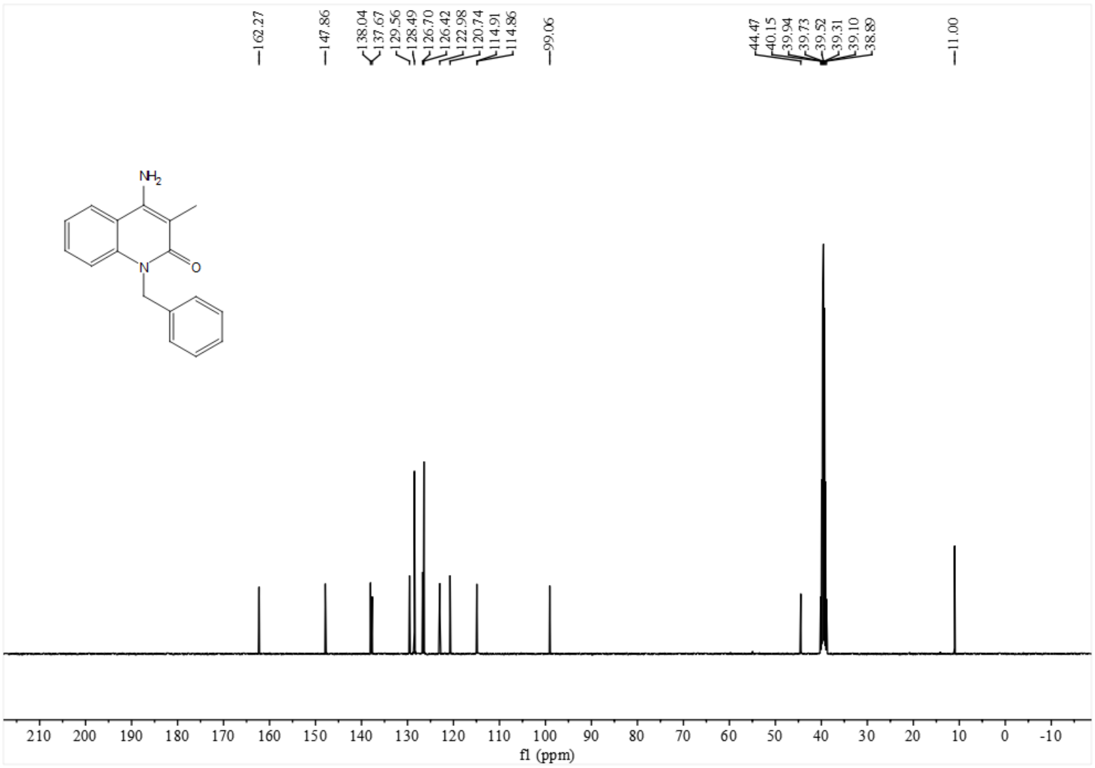
[13]C NMR of **3r** (100 MHz, DMSO-d_6):



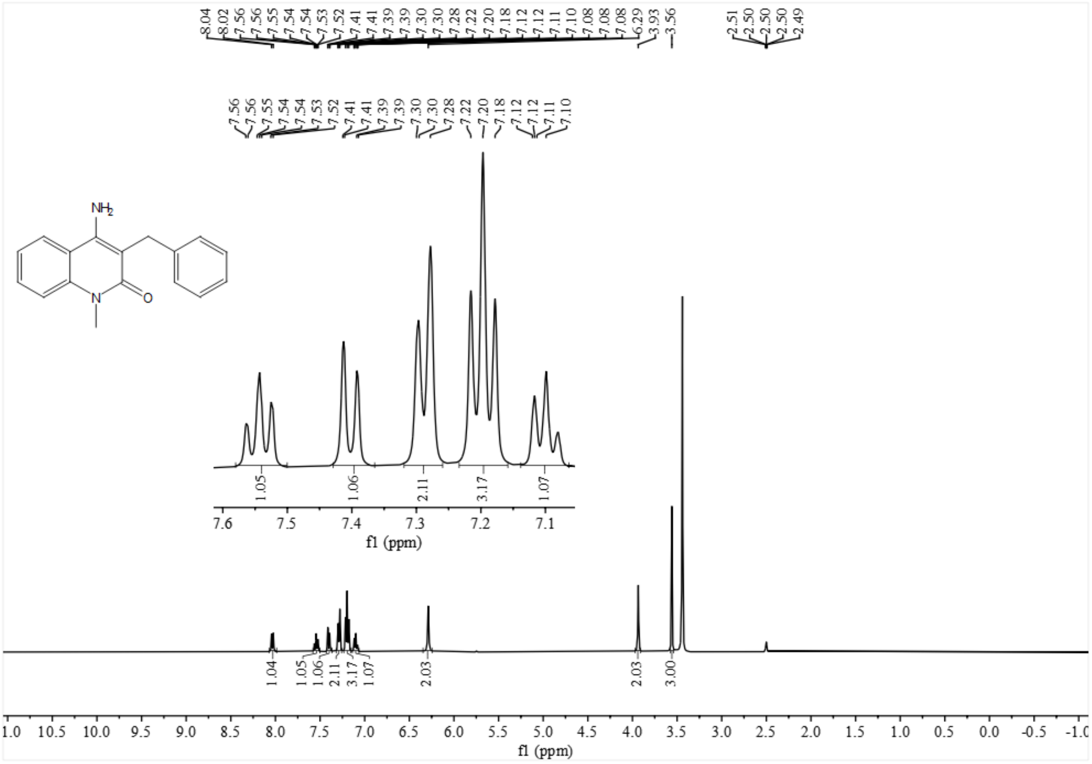
^{1}H NMR of **3s** (400 MHz, DMSO-d_6):



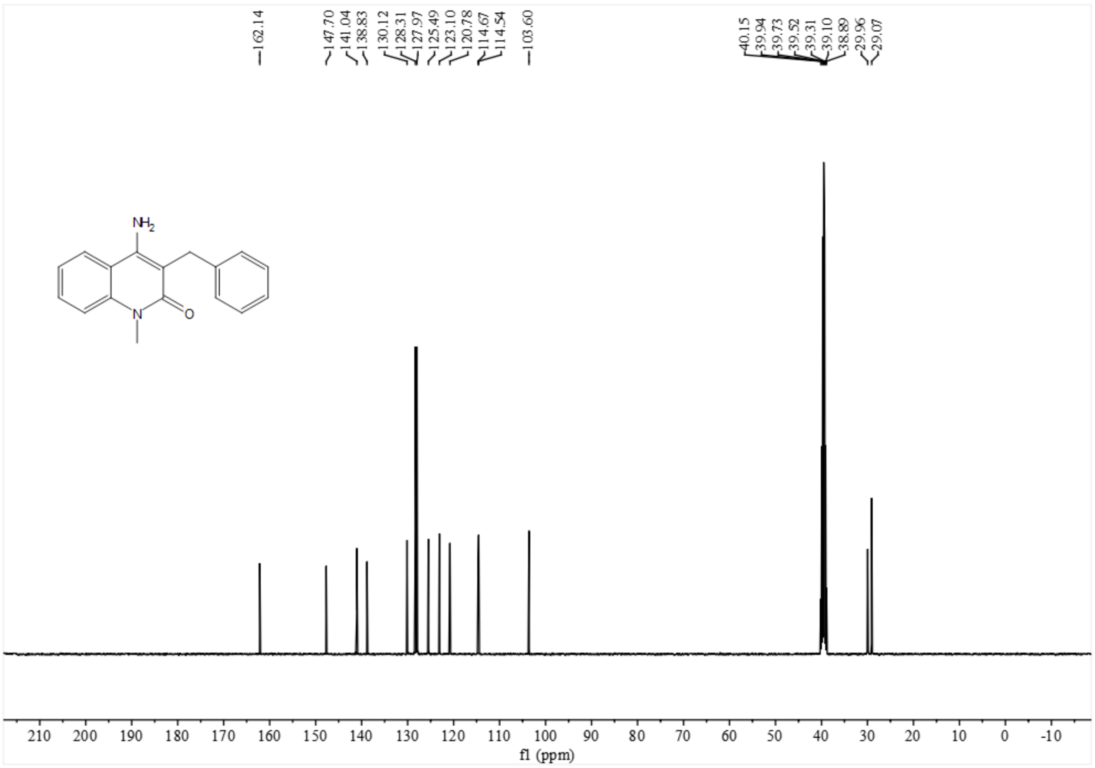
^{13}C NMR of **3s** (100 MHz, DMSO-d_6):



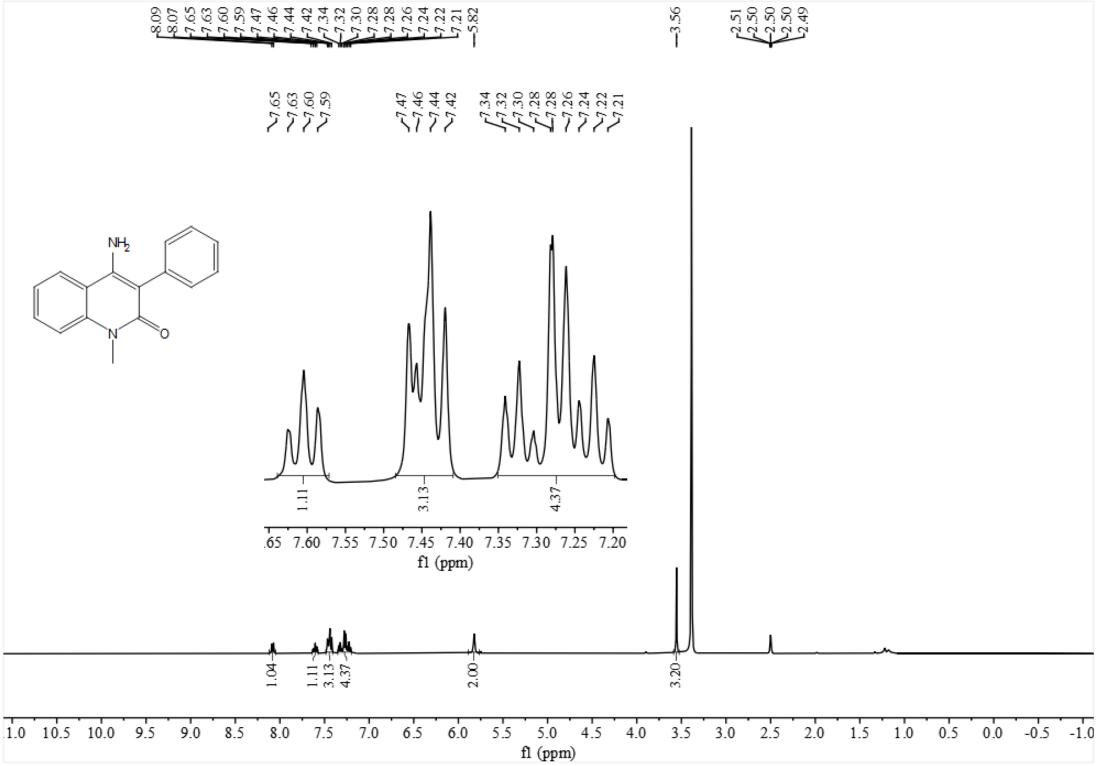
^{1}H NMR of **3x** (400 MHz, DMSO-d_6):



^{13}C NMR of **3x** (100 MHz, DMSO-d_6):



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



^{13}C NMR of **3y** (100 MHz, DMSO-d_6):