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Electrochemical Oxidative Synthesis of 2-Benzoylquinazolin-4(3H)-one via C(sp^3)−H Amination under Metal-Free Condition

Yongzhi Hu,[†a] Xinhua Ma,[†a] Huiqing Hou,[a] Weiming Sun,[a] Shuqing Tu,[b] Mei Wu,[a] Rongkun, Lin,[a] Xiuzhi Xu[*a] and Fang Ke[*a]

a. *Institute of Materia Medica, School of Pharmacy, Fujian Provincial Key Laboratory of Natural Medicine Pharmacology, Fujian Medical University, Fuzhou 350122, China Tel.: +86-0591-22862016; fax: +86-0591-22862016; E-mail: kefang@mail.fjmu.edu.cn*

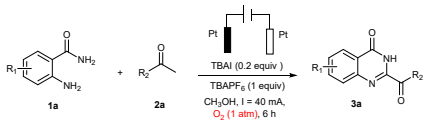
b. *Fujian Maternity and Child Health Hospital, Affiliated Hospital of Fujian Medical University, Fuzhou 350000, China.*

Supporting information

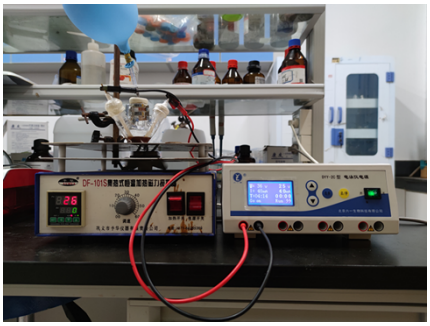
1. General information

All reagents were purchased from commercial sources and used without further purification. All solvents were dried in a standard manner. Reactions were monitored by TLC on silica gel plates. Column chromatography was performed over silica gel (200-300 mesh) and petroleum ether/ethyl acetate. Shanghai chenhua CHI600E electrochemical workstation was used in the standard configuration as delivered, including proprietary software. Beijing Perfectligt PCX50C Discover was used in the reaction system. All products were characterized by NMR. ^{1}H NMR spectra were recorded at 400 MHz and ^{13}C NMR spectra were recorded at 101 MHz (Bruker DPX) with $CDCl_3$ and DMSO-d_6 as solvent. Chemical shifts are reported in ppm using TMS as internal standard. NMR by the services provided at the Shandong Liaocheng University. HPLC were recorded on an SHIMDZU LC-20A instrument with a HP5-MS 30 m x 0.25 mm capillary apolar columns.

2. General procedure for the catalytic reactions



2-aminobenzamide **1a** (68.0 mg, 0.5 mmol), acetophenone **2a** (72.0 mg, 0.6 mmol), TBAI (0.1 mmol), $TBAPF_6$ (0.5 mmol), CH_3OH (5 ml) were added into a 25-mL three-necked flask equipped with a platinum anode and cathode (plate, 1.0 cm × 1.0 cm). A balloon charged with O_2 was added and the three-necked bottle was evacuated and backfilled with O_2 thrice (1 atm O_2). The reaction mixture was stirred for 6 h at a constant current of 40 mA under oxygen ball at ambient temperature. After completion of the reaction (monitored by TLC), the reaction mixture was purified by column chromatography on silica gel (PE/DCM) to afford pure product **3aa**.

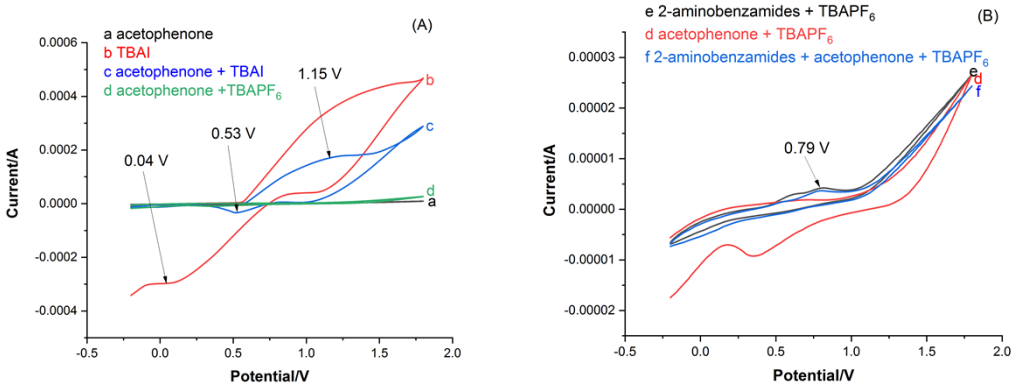


3. General procedure for the gram scale experiment

2-aminobenzamide **1a** (10 mmol), acetophenone **2a** (12 mmol), TBAI (2 mmol), $TBAPF_6$ (10 mmol), CH_3OH (20 ml) were added into a 50-mL three-necked flask equipped with a platinum anode and cathode (plate, 1.0 cm × 1.0 cm). A balloon charged with O_2 was added and the three-necked bottle was evacuated and backfilled with O_2 thrice (1 atm O_2). The reaction mixture were stirred for 24 h at a constant current of 40 mA under oxygen ball at ambient temperature. After completion of the reaction (monitored by TLC), the reaction mixture was purified by column chromatography on silica gel (PE/DCM) to afford pure product 3aa in 74% yield.

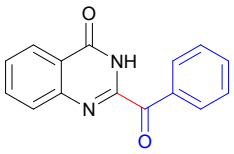
4. Cyclic voltammetry experiment

Cyclic voltammograms were measured using Shanghai chenhua CHI600E electrochemical workstation with electrochemical analysis software, using a conventional three-electrode cell. The working electrode was a Pt disk working electrode, the counter and reference electrodes consisted of a Pt wire and a SCE, respectively. The glassy carbon working electrode was polished with a polishing cloth before each measurement. The concentration of all tested compounds was 1 mmol L^{-1}. The scan rate was 0.1 V/s.



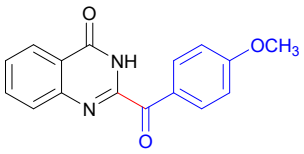
5. Characterization data

2-benzoylquinazolin-4(3H)-one (3aa)[1]



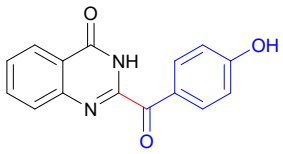
^{1}H NMR (400 MHz, DMSO-d_6) δ 12.66 (s, 1H), 8.21 (dd, J = 22.4, 7.8 Hz, 3H), 7.95 – 7.85 (m, 1H), 7.77 (dd, J = 17.7, 7.9 Hz, 2H), 7.64 (dt, J = 24.7, 7.8 Hz, 3H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 187.61 (s), 161.50 (s), 149.54 (s), 147.61 (s), 135.22 (s), 134.65 (d, J = 17.4 Hz), 131.31 (s), 129.03 (d, J = 4.3 Hz), 128.81 (s), 126.52 (s), 123.34 (s). **MS** [EI, m/z]: 250 [M^+].

2-(4-methoxybenzoyl)quinazolin-4(3H)-one (3ab)[1]



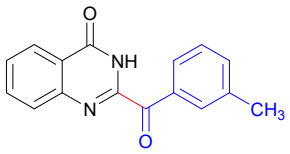
^{1}H NMR (400 MHz, DMSO-d_6) δ 12.59 (s, 1H), 8.29 – 8.12 (m, 3H), 7.96 – 7.84 (m, 1H), 7.79 (d, J = 8.1 Hz, 1H), 7.70 – 7.60 (m, 1H), 7.19 – 7.07 (m, 2H), 3.90 (s, 3H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 185.76 (s), 164.76 (s), 161.50 (s), 150.02 (s), 147.71 (s), 135.20 (s), 133.90 (s), 128.74 (d, J = 9.8 Hz), 127.13 (s), 126.49 (s), 123.23 (s), 114.56 (s), 56.23 (s). **MS** [EI, m/z]: 280 [M^+].

2-(4-hydroxybenzoyl)quinazolin-4(3H)-one (3ac)[2]



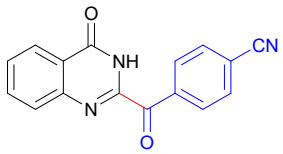
^{1}H NMR (400 MHz, DMSO-d_6) δ 12.57 (s, 1H), 10.74 (s, 1H), 8.22 (d, J = 7.9 Hz, 1H), 8.11 (t, J = 6.2 Hz, 2H), 7.89 (t, J = 7.4 Hz, 1H), 7.79 (d, J = 8.2 Hz, 1H), 7.65 (q, J = 7.5, 6.5 Hz, 1H), 7.10 – 6.89 (m, 2H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 185.54 , 164.02 , 161.50 , 150.34 , 147.77 , 135.17 , 134.18 , 128.64 , 127.51 , 126.47 , 125.70 , 123.12 , 116.00. **MS** [EI, m/z]: 266 [M$^+$].

2-(3-methylbenzoyl)quinazolin-4(3H)-one (3ad)[1]



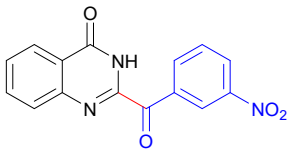
^{1}H NMR (400 MHz, DMSO-d_6) δ 12.63 (s, 1H), 8.23 (dd, J = 7.9, 1.5 Hz, 1H), 8.12 – 8.04 (m, 2H), 7.90 (ddd, J = 8.5, 7.1, 1.6 Hz, 1H), 7.82 – 7.75 (m, 1H), 7.71 – 7.62 (m, 1H), 7.41 (d, J = 7.9 Hz, 2H), 2.44 (s, 3H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 187.12 , 161.51 , 149.77 , 147.66 , 145.76 , 145.63 , 135.22 , 131.96 , 131.44 , 129.69 , 128.91 , 128.76 , 126.51 , 123.28 , 21.83. **MS** [EI, m/z]: 264 [M$^+$].

4-(4-oxo-3,4-dihydroquinazoline-2-carbonyl)benzonitrile (3ae)[2]



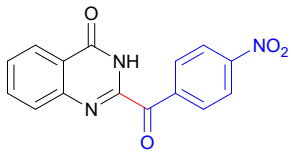
^{1}H NMR (400 MHz, DMSO-d_6) δ 12.70 (s, 1H), 8.32 (d, J = 8.2 Hz, 2H), 8.23 (dd, J = 8.0, 1.4 Hz, 1H), 8.11 – 8.01 (m, 2H), 7.95 – 7.84 (m, 1H), 7.79 (d, J = 8.1 Hz, 1H), 7.68 (t, J = 7.5 Hz, 1H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 186.68 , 161.49 , 148.53 , 147.39 , 138.42 , 135.26 , 132.71 , 131.90 , 129.43 , 126.56 , 123.54 , 118.60 , 116.06. **MS** [EI, m/z]: 275 [M$^+$].

2-(3-nitrobenzoyl)quinazolin-4(3H)-one (3af)[1]



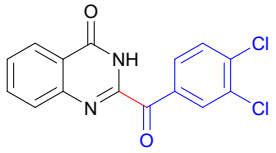
^{1}H NMR (400 MHz, DMSO-d_6) δ 12.72 (s, 1H), 9.03 (t, J = 2.1 Hz, 1H), 8.69 – 8.48 (m, 2H), 8.31 – 8.20 (m, 1H), 7.90 (dt, J = 11.1, 7.4 Hz, 2H), 7.80 (d, J = 8.0 Hz, 1H), 7.69 (t, J = 7.5 Hz, 1H).
^{13}C NMR (101 MHz, DMSO-d_6) δ 185.41 , 161.47 , 148.39 , 147.95 , 147.35 , 137.45 , 136.04 , 135.30 , 130.56 , 129.51 , 129.04 , 128.35 , 126.58 , 126.14 , 123.59. **MS** [EI, m/z]: 295 [M$^+$].

2-(4-nitrobenzoyl)quinazolin-4(3H)-one (3ag)[1]



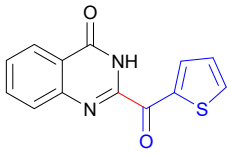
^{1}H NMR (400 MHz, DMSO-d_6) δ 12.69 (s, 1H), 8.40 (s, 5H), 8.24 (dd, J = 8.0, 1.5 Hz, 1H), 7.92 (ddd, J = 8.6, 7.1, 1.6 Hz, 1H), 7.80 (dd, J = 8.1, 1.1 Hz, 1H), 7.70 (ddd, J = 8.1, 7.1, 1.2 Hz, 1H).
^{13}C NMR (101 MHz, DMSO-d_6) δ 186.61 , 148.66 , 147.43 , 135.26 , 132.74 , 129.47 , 129.01 , 126.58 , 123.75 , 123.55. **MS** [EI, m/z]: 295 [M$^+$].

2-(3,4-dichlorobenzoyl)quinazolin-4(3H)-one (3ah)[2]



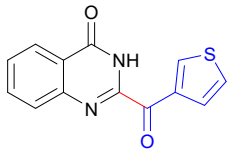
^{1}H NMR (400 MHz, DMSO-d_6 and $CDCl_3$) δ 12.27 (s, 1H), 8.45 (t, J = 2.5 Hz, 1H), 8.23 (ddt, J = 8.1, 5.4, 2.3 Hz, 2H), 7.85 – 7.75 (m, 3H), 7.66 – 7.62 (m, 1H). ^{13}C NMR (101 MHz, DMSO-d_6 and $CDCl_3$) δ 184.23 , 161.44 , 147.51 , 147.23 , 138.13 , 134.75 , 134.20 , 133.18 , 132.42 , 130.91 , 130.66 , 129.18 , 129.00 , 126.47 , 123.53. **MS** [EI, m/z]: 318 [M^+].

2-(thiophene-2-carbonyl)quinazolin-4(3H)-one (3ai)[1]



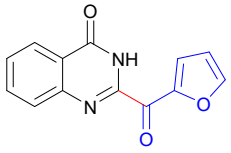
^{1}H NMR (400 MHz, DMSO-d_6) δ 12.64 (s, 1H), 8.24 (dt, J = 3.1, 1.5 Hz, 1H), 8.13 (dd, J = 7.9, 1.6 Hz, 1H), 7.91 – 7.76 (m, 2H), 7.66 (dd, J = 8.2, 1.1 Hz, 1H), 7.49 (ddd, J = 8.1, 7.1, 1.2 Hz, 1H), 7.24 (dd, J = 5.0, 3.8 Hz, 1H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 162.24 , 149.13 , 148.31 , 137.85 , 135.14 , 132.60 , 129.87 , 128.96 , 127.42 , 126.79 , 126.45 , 121.37. **MS** [EI, m/z]: 256 [M^+].

2-(thiophene-3-carbonyl)quinazolin-4(3H)-one (3aj)[1]



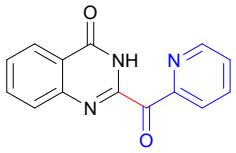
^{1}H NMR (400 MHz, DMSO-d_6) δ 12.47 (s, 1H), 9.13 (dd, J = 2.8, 1.1 Hz, 1H), 8.23 (d, J = 7.7 Hz, 1H), 7.96 – 7.88 (m, 2H), 7.82 (dd, J = 5.1, 1.1 Hz, 1H), 7.73 (dd, J = 5.1, 2.9 Hz, 1H), 7.67 (ddd, J = 8.1, 5.9, 2.4 Hz, 1H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 179.94 (s), 161.41 (s), 149.04 (s), 147.66 (s), 139.88 (s), 138.05 (s), 135.21 (s), 129.15 (d, J = 8.0 Hz), 128.82 (s), 127.73 (s), 126.52 (s), 123.46 (s). **MS** [EI, m/z]: 256 [M^+].

2-(furan-2-carbonyl)quinazolin-4(3H)-one (3ak)[1]



^{1}H NMR (400 MHz, DMSO-d_6) δ 12.48 (s, 1H), 8.28 – 8.17 (m, 3H), 7.98 – 7.87 (m, 2H), 7.67 (dt, J = 8.2, 4.3 Hz, 1H), 6.87 (dd, J = 3.6, 1.7 Hz, 1H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 172.98 , 161.28 , 150.77 , 149.72 , 148.03 , 147.60 , 135.25 , 129.65 , 128.83 , 126.55 , 126.51 , 123.58 , 113.79. **MS** [EI, m/z]: 240 [M^+].

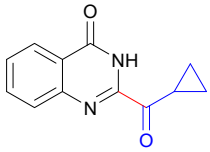
2-picolinoylquinazolin-4(3H)-one (3al)[1]



^{1}H NMR (400 MHz, DMSO-d_6) δ 11.76 (s, 1H), 8.76 (d, J = 4.2 Hz, 1H), 8.45 (d, J = 7.9 Hz, 1H), 8.19 (dd, J = 7.9, 1.1 Hz, 1H), 8.07 (td, J = 7.8, 1.7 Hz, 1H), 7.92 – 7.83 (m, 1H), 7.80 (d, J = 7.6 Hz, 1H),

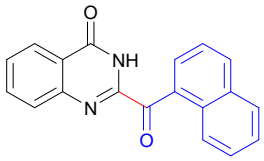
7.66 (ddd, J = 7.5, 4.8, 1.0 Hz, 1H), 7.61 – 7.54 (m, 1H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 161.20 (s), 150.36 (s), 149.43 (s), 149.12 (s), 148.91 (s), 138.44 (s), 135.15 (s), 128.19 (s), 127.73 (s), 127.03 (s), 126.56 (s), 122.55 (d, J = 10.7 Hz). **MS** [EI, m/z]: 251 [M$^+$].

2-(cyclopropanecarbonyl)quinazolin-4(3H)-one (3am)[2]



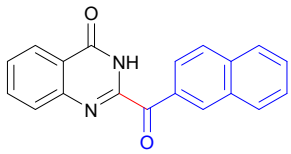
^{1}H NMR (400 MHz, DMSO-d_6) δ 12.26 (s, 1H), 8.20 (dd, J = 7.9, 1.4 Hz, 1H), 7.96 – 7.85 (m, 2H), 7.71 – 7.64 (m, 1H), 2.51 (p, J = 1.8 Hz, 1H), 1.23 (dq, J = 7.6, 3.3 Hz, 2H), 1.12 (p, J = 3.5 Hz, 2H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 195.66 , 161.31 , 147.73 , 135.26 , 129.38 , 129.03 , 126.64 , 123.67 , 16.21 , 13.74. **MS** [EI, m/z]: 214 [M$^+$].

2-(1-naphthoyl)quinazolin-4(3H)-one (3an)[1]



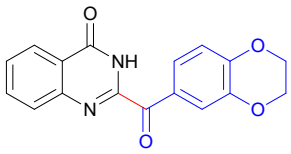
^{1}H NMR (400 MHz, DMSO-d_6) δ 12.84 (s, 1H), 8.48 (d, J = 8.3 Hz, 1H), 8.26 (dd, J = 13.1, 4.9 Hz, 2H), 8.19 – 8.06 (m, 2H), 7.86 (ddd, J = 8.4, 7.3, 1.5 Hz, 1H), 7.74 – 7.61 (m, 5H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 190.13 (s), 161.59 (s), 150.53 (s), 147.71 (s), 135.19 (s), 134.29 (s), 133.80 (s), 133.19 (s), 131.70 (s), 130.95 (s), 129.19 (d, J = 16.9 Hz), 128.85 (d, J = 6.9 Hz), 127.19 (s), 126.55 (s), 125.35 (s), 125.07 (s), 123.42 (s). **MS** [EI, m/z]: 300 [M$^+$].

2-(2-naphthoyl)quinazolin-4(3H)-one (3ao)[1]



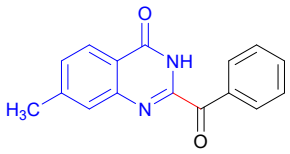
^{1}H NMR (400 MHz, DMSO-d_6) δ 12.75 (s, 1H), 8.91 (s, 1H), 8.26 (dd, J = 7.9, 1.2 Hz, 1H), 8.19 – 8.13 (m, 2H), 8.10 (d, J = 8.7 Hz, 1H), 8.05 (d, J = 8.1 Hz, 1H), 7.95 – 7.88 (m, 1H), 7.83 (d, J = 7.5 Hz, 1H), 7.77 – 7.71 (m, 1H), 7.70 – 7.62 (m, 2H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 187.58 (s), 161.55 (s), 149.92 (s), 147.75 (s), 135.95 (s), 135.22 (s), 134.48 (s), 132.32 (s), 131.88 (s), 130.47 (s), 129.91 (s), 129.13 – 128.61 (m), 128.24 (s), 127.63 (s), 126.53 (s), 125.53 (s), 123.37 (s). **MS** [EI, m/z]: 300[M$^+$].

2-(2,3-dihydrobenzo[b][1,4]dioxine-6-carbonyl)quinazolin-4(3H)-one (3ap)[1]



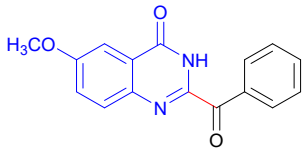
^{1}H NMR (400 MHz, DMSO-d_6 and $CDCl_3$) δ 8.21 (dt, J = 7.2, 2.6 Hz, 1H), 7.89 – 7.82 (m, 2H), 7.82 – 7.74 (m, 2H), 7.55 (dtd, J = 8.2, 6.0, 2.5 Hz, 1H), 6.92 (ddd, J = 9.1, 5.1, 1.4 Hz, 1H), 4.35 – 4.30 (m, 2H), 4.27 (td, J = 4.4, 3.3, 1.8 Hz, 2H). ^{13}C NMR (101 MHz, DMSO-d_6 and $CDCl_3$) δ 184.57 , 161.52 , 149.48 , 148.63 , 147.50 , 143.31 , 134.63 , 128.72 , 128.59 , 127.59 , 126.38 , 125.85 , 123.26 , 120.71 , 117.27 , 64.99 , 64.16. **MS** [EI, m/z]: 308 [M$^+$].

2-benzoyl-7-methylquinazolin-4(3H)-one (3aq)[3]



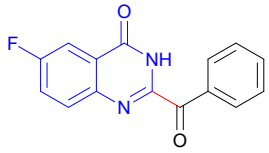
^{1}H NMR (400 MHz, DMSO-d_6) δ 12.57 (s, 1H), 8.25 – 8.14 (m, 2H), 8.10 (d, J = 8.1 Hz, 1H), 7.79 – 7.71 (m, 1H), 7.60 (t, J = 7.8 Hz, 3H), 7.47 (dd, J = 8.1, 1.2 Hz, 1H), 2.47 (s, 3H).^{13}C NMR (101 MHz, DMSO-d_6) δ 187.56 (s), 161.39 (s), 149.47 (s), 147.67 (s), 145.85 (s), 134.63 (d, J = 9.8 Hz), 131.33 (s), 130.38 (s), 129.00 (s), 128.47 (s), 126.35 (s), 120.90 (s), 21.69 (s). **MS** [EI, m/z]: 264 [M$^+$].

2-benzoyl-6-methoxyquinazolin-4(3H)-one (3ar)[1]



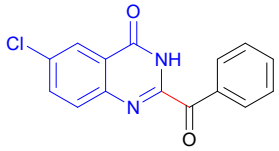
^{1}H NMR (400 MHz, DMSO-d_6) δ 12.54 (s, 1H), 8.21 – 8.14 (m, 2H), 7.79 – 7.70 (m, 2H), 7.64 – 7.55 (m, 3H), 7.49 (dd, J = 8.9, 3.0 Hz, 1H), 3.93 (s, 3H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 187.35 , 161.20 , 159.88 , 147.16 , 141.78 , 134.84 , 134.46 , 131.32 , 130.76 , 128.93 , 124.56 , 124.45 , 106.90 , 56.32. **MS** [EI, m/z]: 280 [M$^+$].

2-benzoyl-6-fluoroquinazolin-4(3H)-one (3as)[1]



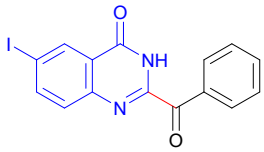
^{1}H NMR (400 MHz, DMSO-d_6) δ 12.80 (s, 1H), 8.18 (d, J = 7.0 Hz, 2H), 7.89 (t, J = 9.5 Hz, 2H), 7.77 (dd, J = 16.3, 8.0 Hz, 2H), 7.61 (t, J = 7.6 Hz, 2H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 187.48 (s), 162.91 (s), 160.95 (s), 160.45 (s), 149.02 (s), 144.47 (s), 134.75 (s), 134.54 (s), 131.79 (d, J = 7.5 Hz), 131.33 (s), 129.04 (s), 124.94 (d, J = 8.1 Hz), 123.74 (s), 123.50 (s), 111.56 (s), 111.32 (s). **MS** [EI, m/z]: 268 [M$^+$].

2-benzoyl-6-chloroquinazolin-4(3H)-one (3at)[1]



^{1}H NMR (400 MHz, DMSO-d_6) δ 12.86 (s, 1H), 8.16 (dd, J = 6.5, 5.0 Hz, 3H), 7.92 (dd, J = 8.7, 2.5 Hz, 1H), 7.81 (d, J = 8.7 Hz, 1H), 7.76 (t, J = 7.4 Hz, 1H), 7.60 (t, J = 7.8 Hz, 2H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 187.42 (s), 160.60 (s), 149.88 (s), 146.39 (s), 135.29 (s), 134.83 (s), 134.44 (s), 133.35 (s), 131.33 (s), 131.00 (s), 129.07 (s), 125.58 (s), 124.71 (s). **MS** [EI, m/z]: 284 [M$^+$].

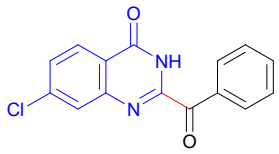
2-benzoyl-6-iodoquinazolin-4(3H)-one (3au)[1]



^{1}H NMR (400 MHz, DMSO-d_6) δ 12.81 (s, 1H), 8.49 (d, J = 2.1 Hz, 1H), 8.17 (ddd, J = 8.3, 6.4, 1.8 Hz, 3H), 7.81 – 7.72 (m, 1H), 7.65 – 7.53 (m, 3H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 187.43 , 160.26 , 150.00 , 146.95 , 143.62 , 134.85 , 134.81 , 134.45 , 131.32 , 130.82 , 129.06 , 125.06 , 94.67. **MS** [EI,

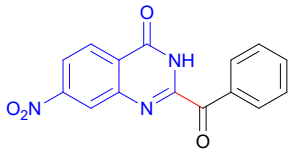
m/z]: 376 [M$^+$].

2-benzoyl-7-chloroquinazolin-4(3H)-one (3av)[1]



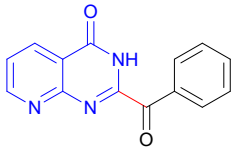
^{1}H NMR (400 MHz, DMSO-d_6) δ 12.86 (s, 1H), 8.25 – 8.12 (m, 3H), 7.87 (d, J = 2.0 Hz, 1H), 7.81 – 7.73 (m, 1H), 7.69 (dd, J = 8.5, 2.1 Hz, 1H), 7.61 (t, J = 7.8 Hz, 2H).^{13}C NMR (101 MHz, DMSO-d_6) δ 187.44 (s), 161.02 (s), 150.89 (s), 148.83 (s), 139.78 (s), 134.94 (s), 134.32 (s), 131.36 (s), 129.10 (d, J = 3.5 Hz), 128.54 (s), 127.90 (s), 122.20 (s). **MS** [EI, m/z]: 284 [M$^+$].

2-benzoyl-7-nitroquinazolin-4(3H)-one (3aw)[1]



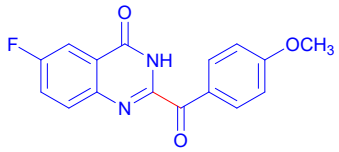
^{1}H NMR (400 MHz, DMSO-d_6) δ 13.09 (s, 1H), 8.47 (d, J = 2.1 Hz, 1H), 8.42 (d, J = 8.7 Hz, 1H), 8.34 (dd, J = 8.7, 2.2 Hz, 1H), 8.21 (dd, J = 8.2, 1.1 Hz, 2H), 7.83 – 7.73 (m, 1H), 7.62 (t, J = 7.8 Hz, 2H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 187.23 (s), 160.82 (s), 151.65 (d, J = 15.1 Hz), 148.17 (s), 135.03 (s), 134.20 (s), 131.40 (s), 129.14 (s), 128.76 (s), 127.73 (s), 123.57 (s), 122.34 (s). **MS** [EI, m/z]: 295 [M$^+$].

2-benzoylpyrido[2,3-d]pyrimidin-4(3H)-one (3ax)[1]



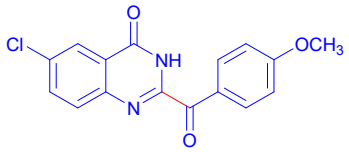
^{1}H NMR (400 MHz, DMSO-d_6 and $CDCl_3$) δ 12.68 (s, 1H), 8.90 (dd, J = 4.6, 2.0 Hz, 1H), 8.51 (dd, J = 7.8, 2.1 Hz, 1H), 8.31 – 8.19 (m, 2H), 7.56 – 7.45 (m, 3H). ^{13}C NMR (101 MHz, DMSO-d_6 and $CDCl_3$) δ 167.92 , 163.51 , 159.08 , 156.02 , 135.86 , 132.65 , 132.07 , 129.62 , 128.72 , 128.41 , 122.10 , 116.62. **MS** [EI, m/z]: 251 [M$^+$].

6-fluoro-2-(4-methoxybenzoyl)quinazolin-4(3H)-one (3ay)[1]



^{1}H NMR (400 MHz, DMSO-d_6 and $CDCl_3$) δ 12.16 (s, 1H), 8.32 (ddd, J = 9.0, 5.5, 2.7 Hz, 2H), 7.87 – 7.78 (m, 2H), 7.53 (td, J = 8.6, 4.1 Hz, 1H), 6.96 (ddd, J = 8.7, 5.2, 2.5 Hz, 2H), 3.91 – 3.83 (m, 3H). ^{13}C NMR (101 MHz, DMSO-d_6 and $CDCl_3$) δ 184.39 , 164.58 , 160.92 , 147.97 , 144.22 , 133.99 , 131.47 , 131.39 , 126.97 , 123.18 , 122.94 , 113.90 , 55.72. **MS** [EI, m/z]: 298 [M$^+$].

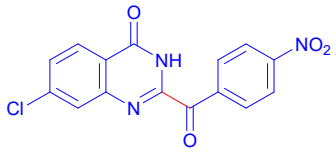
6-chloro-2-(4-methoxybenzoyl)quinazolin-4(3H)-one (3az)[2]



^{1}H NMR (400 MHz, DMSO-d_6 and $CDCl_3$) δ 12.41 (s, 1H), 8.34 – 8.22 (m, 2H), 8.19 – 8.10 (m, 1H),

7.75 (dt, J = 7.8, 2.3 Hz, 2H), 7.04 – 6.92 (m, 2H), 3.24 (s, 3H). ^{13}C NMR (101 MHz, DMSO-d_6 and $CDCl_3$) δ 184.52 , 164.64 , 160.61 , 149.12 , 146.16 , 134.89 , 133.93 , 133.84 , 130.55 , 126.93 , 125.68 , 124.45 , 114.00 , 55.80. **MS** [EI, m/z]: 314 [M^+].

7-chloro-2-(4-nitrobenzoyl)quinazolin-4(3H)-one (3ba)[1]



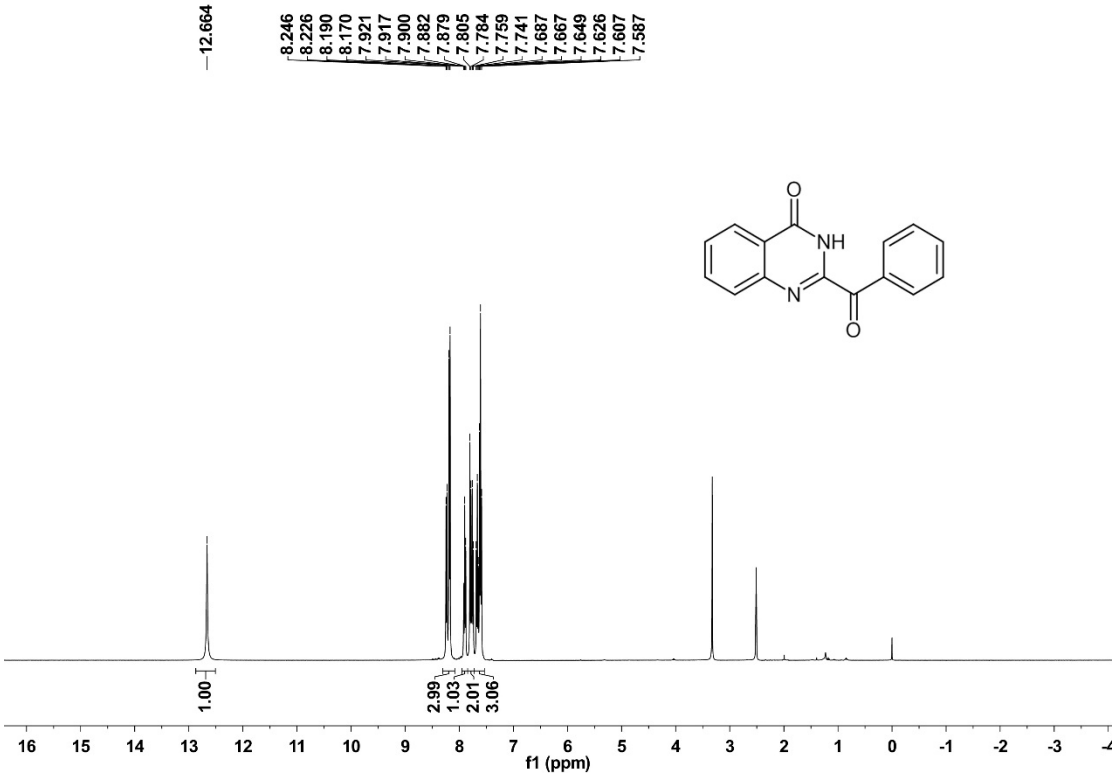
^{1}H NMR (400 MHz, DMSO-d_6 and $CDCl_3$) δ 12.68 (s, 1H), 8.47 – 8.40 (m, 2H), 8.33 (dd, J = 8.9, 2.2 Hz, 2H), 8.00 (d, J = 1.1 Hz, 1H), 7.79 (d, J = 2.1 Hz, 1H), 7.58 (dd, J = 8.5, 2.1 Hz, 1H). ^{13}C NMR (101 MHz, DMSO-d_6 and $CDCl_3$) δ 185.50 , 160.85 , 150.53 , 148.92 , 148.41 , 139.42 , 132.68 , 129.47 , 128.28 , 128.23 , 123.40 , 122.29. **MS** [EI, m/z]: 329 [M^+].

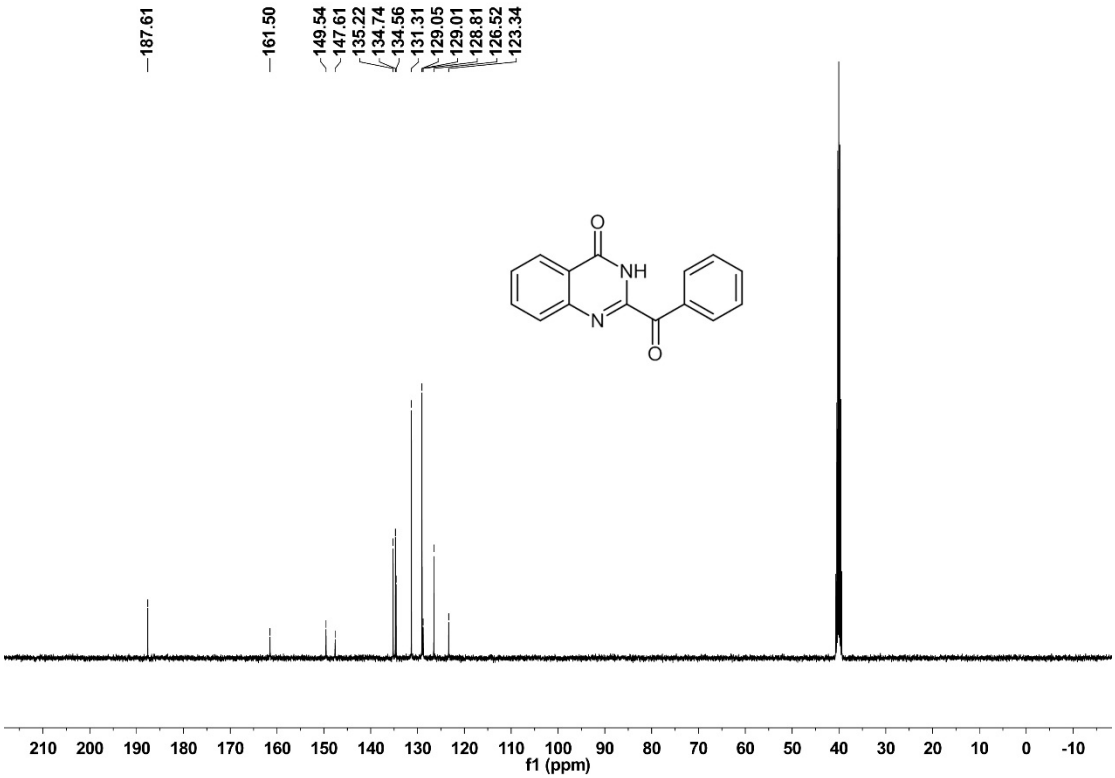
6. References

1. Y.-P. Zhu, Z. Fei, M.-C. Liu, F.-C. Jia and A.-X. Wu, Org. Lett., **2013**, *15*, 378-381.
2. T. B. Nguyen, H. Jing-ya and P. Retailleau, *Adv. Synth. Catal*., **2019**, *361,* 3337-3341.
3. Z. Li, Y. Pu, D. Qiu, X. Zhang and Q. Zeng, *Asian J. Chem*. **2015**, *27*, 1157-1159.

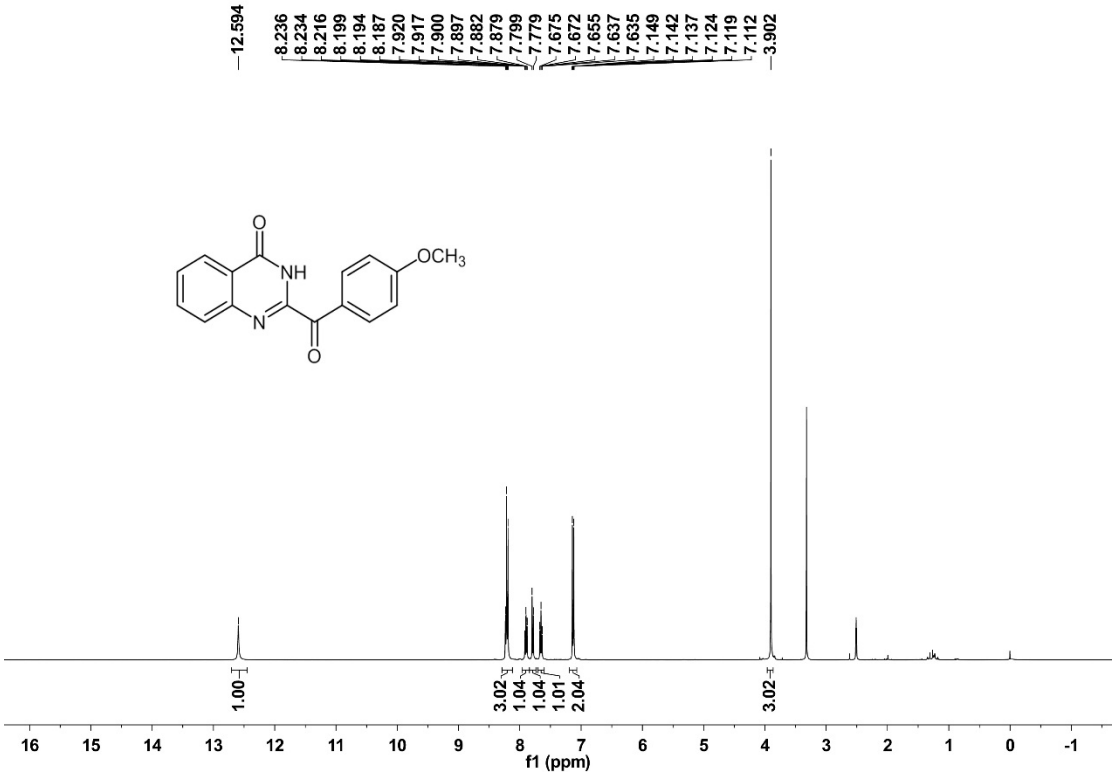
7. ^{1}H NMR and ^{13}C NMR spectra for the products

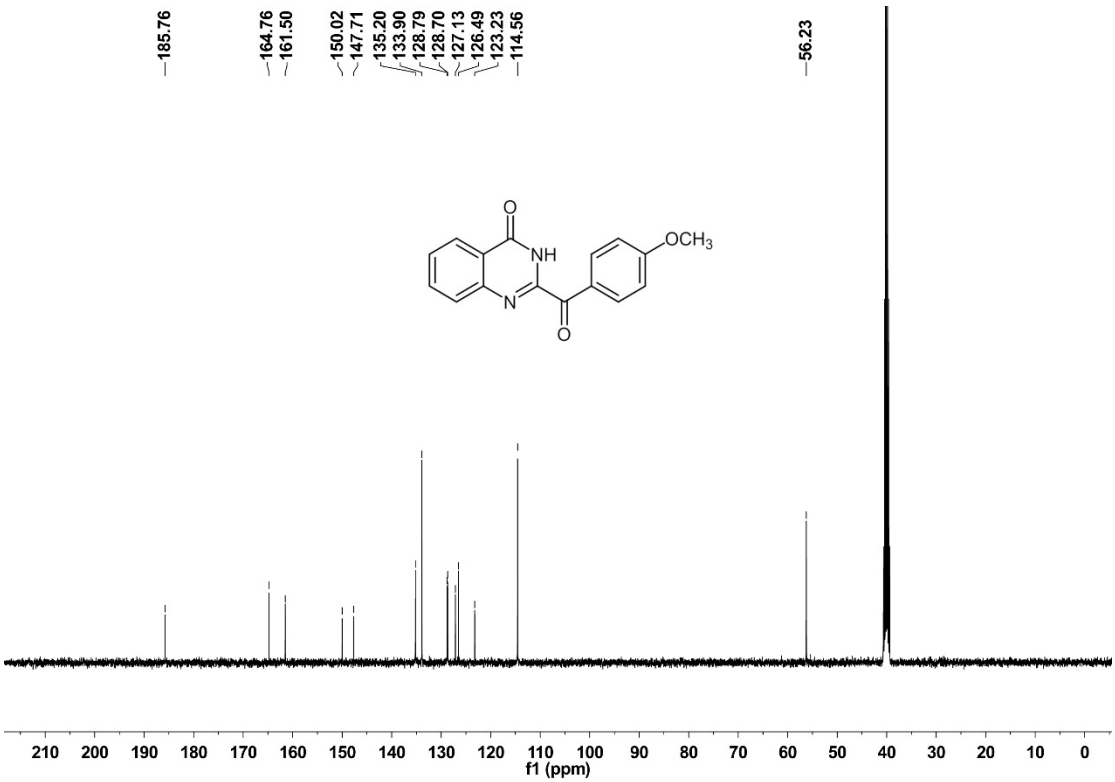
2-benzoylquinazolin-4(3H)-one (3aa)



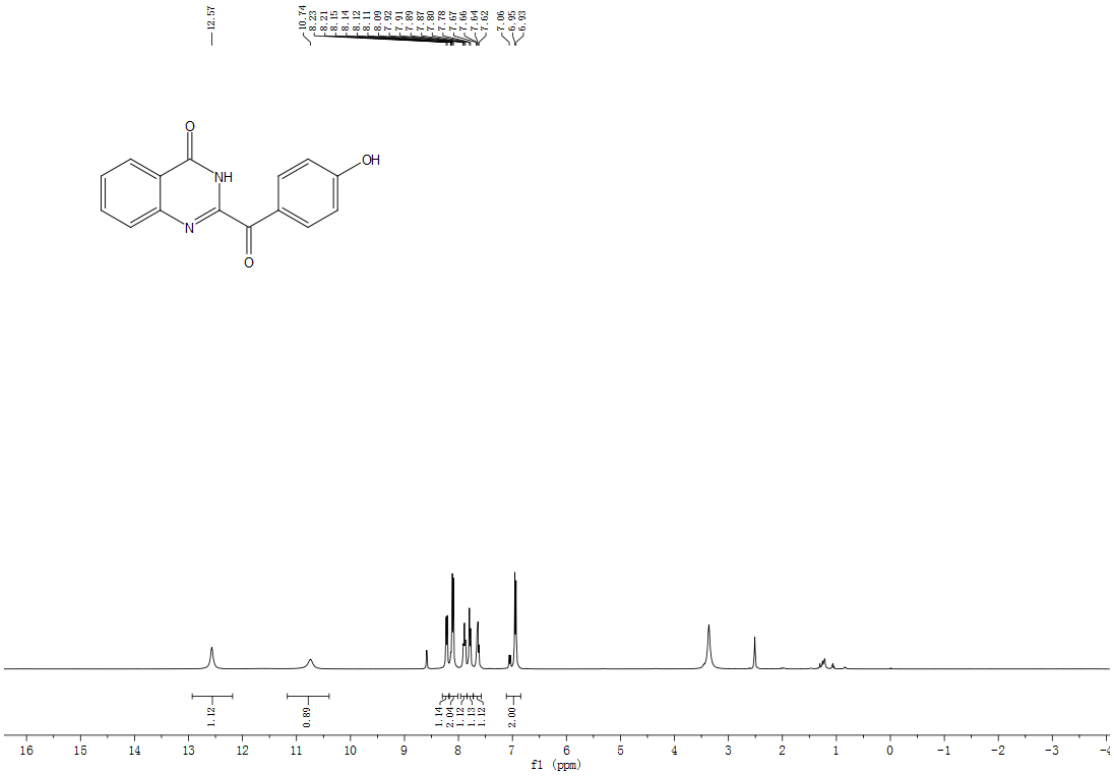


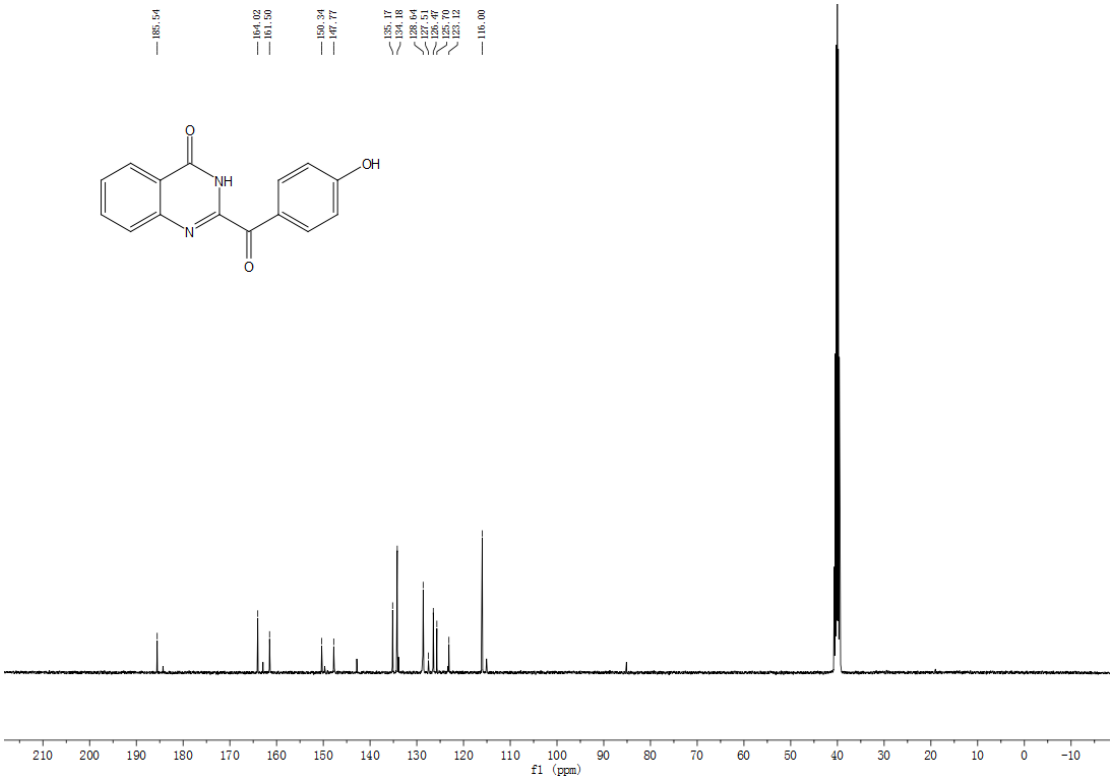
2-(4-methoxybenzoyl)quinazolin-4(3H)-one (3ab)



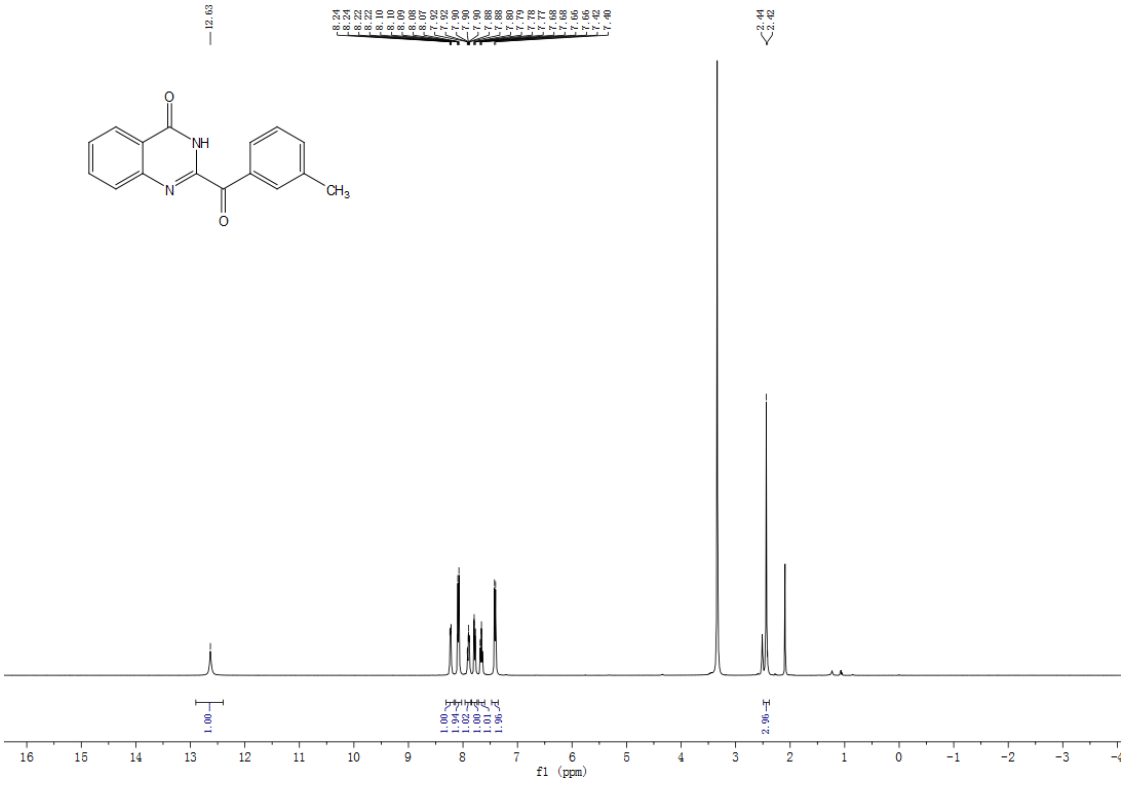


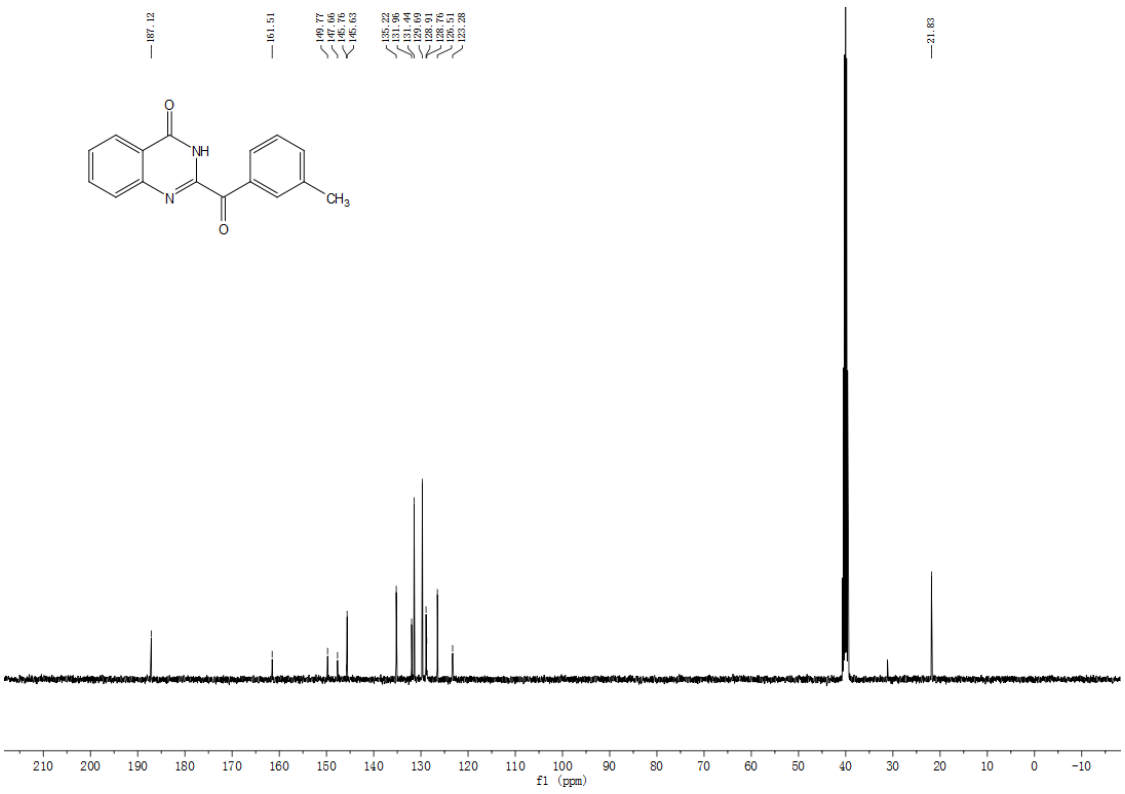
2-(4-hydroxybenzoyl)quinazolin-4(3H)-one (3ac)



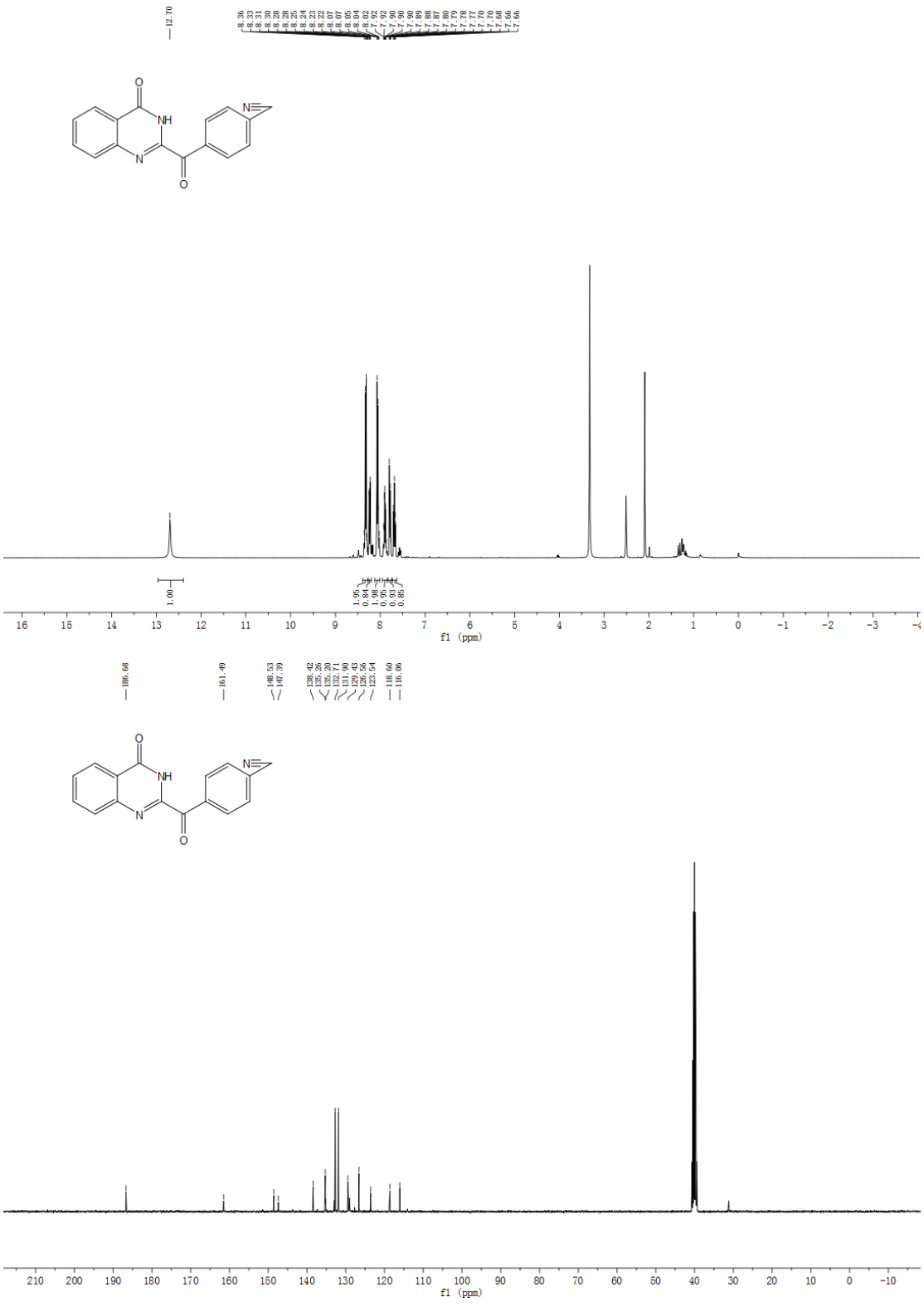


2-(3-methylbenzoyl)quinazolin-4(3H)-one (3ad)

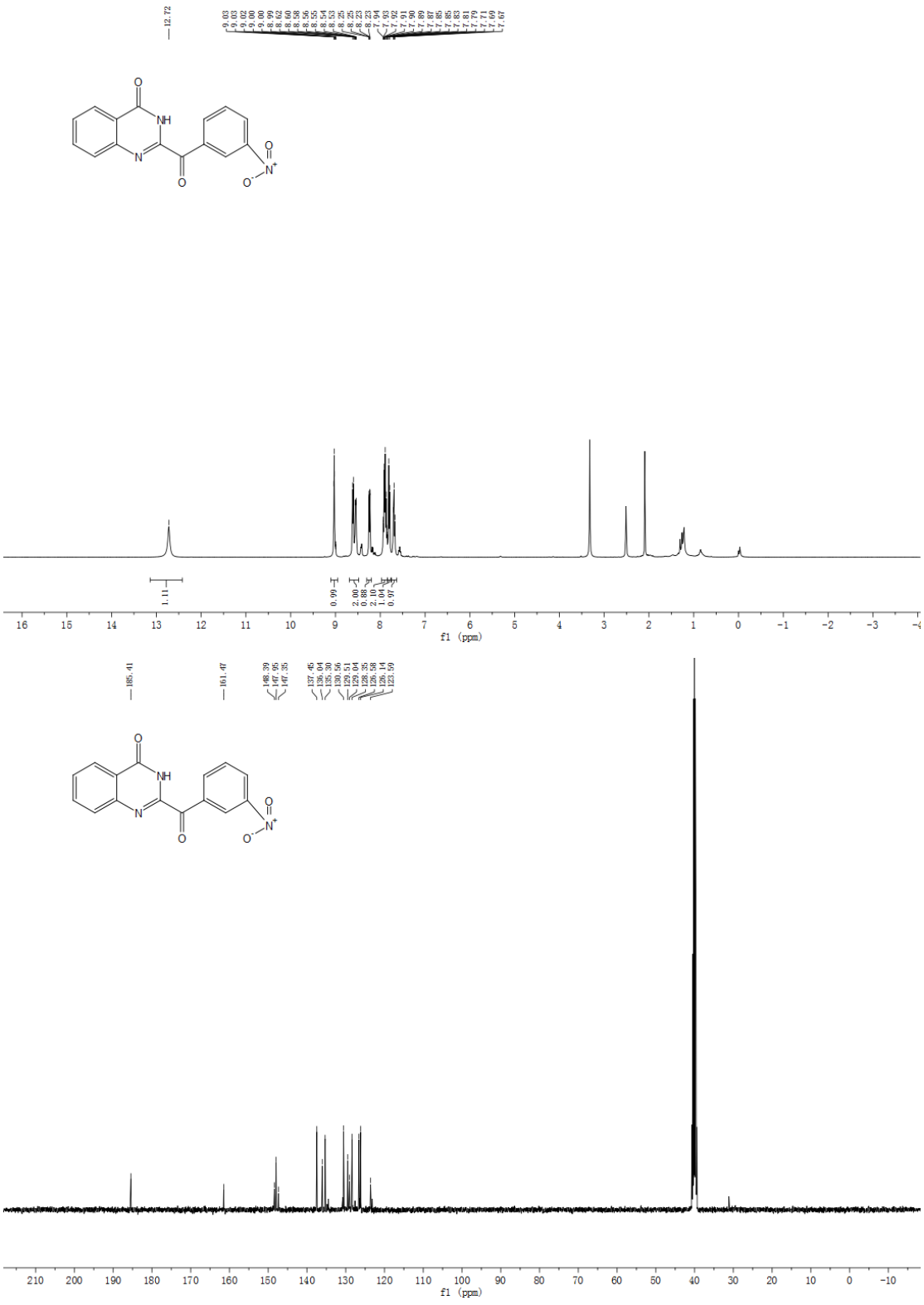




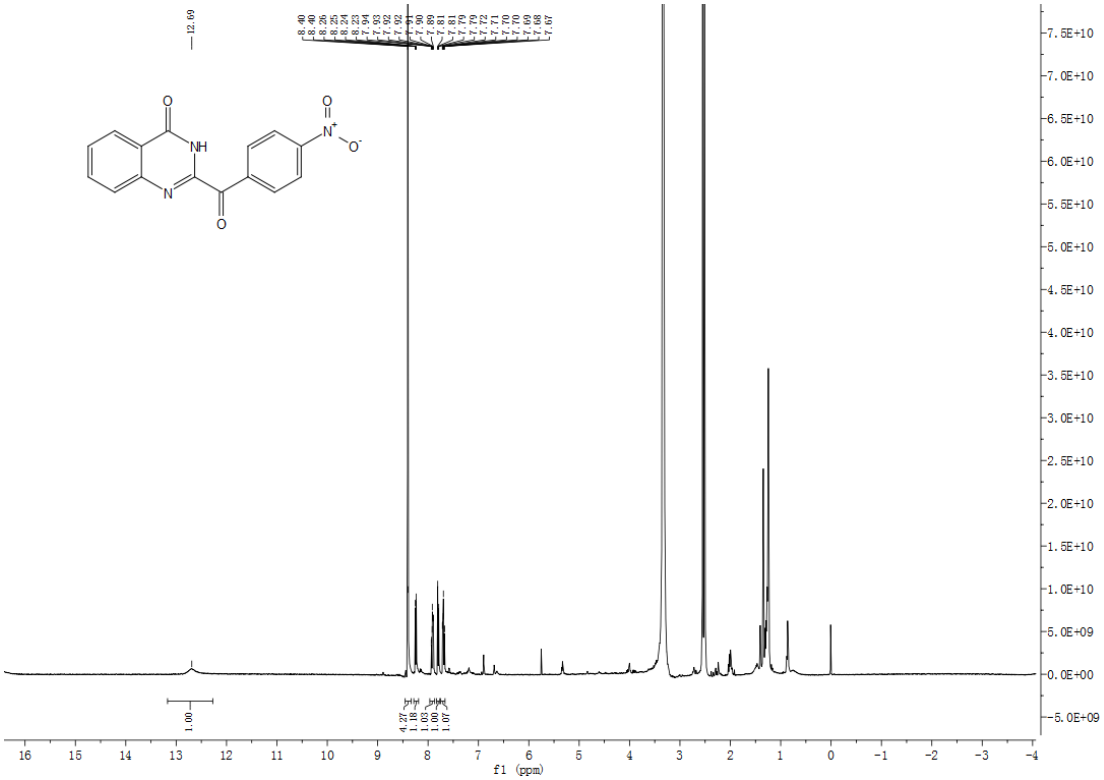
4-(4-oxo-3,4-dihydroquinazoline-2-carbonyl)benzonitrile (3ae)

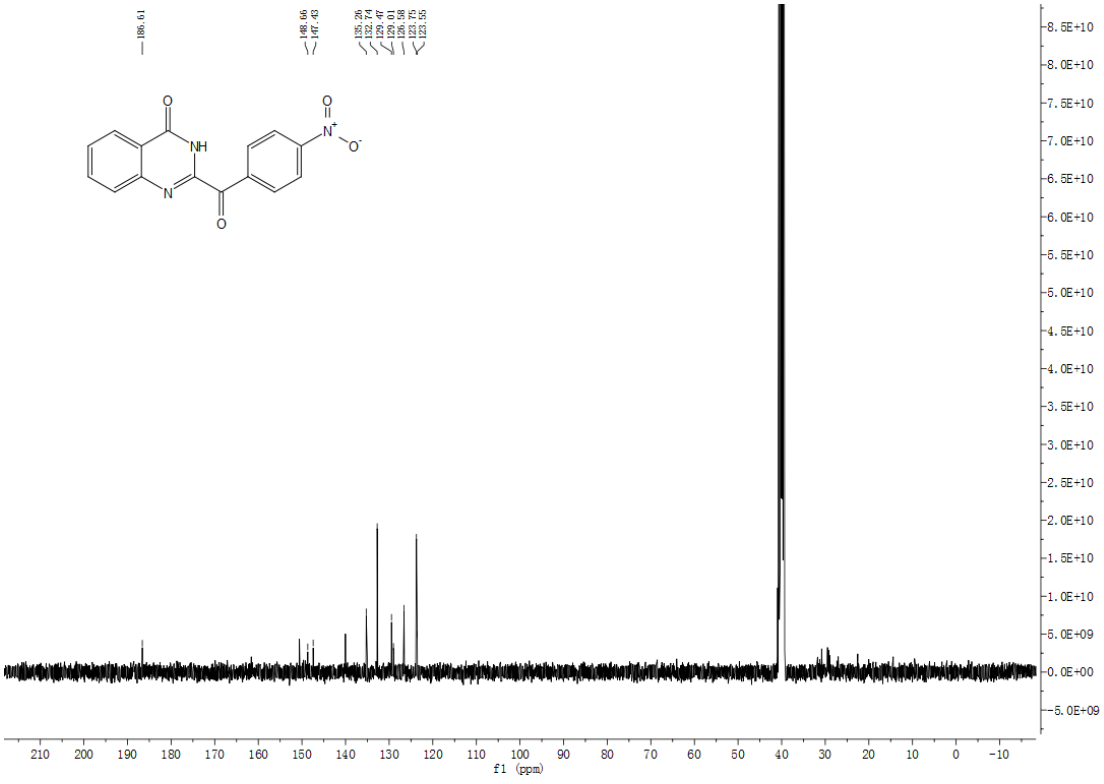


2-(3-nitrobenzoyl)quinazolin-4(3H)-one (3af)

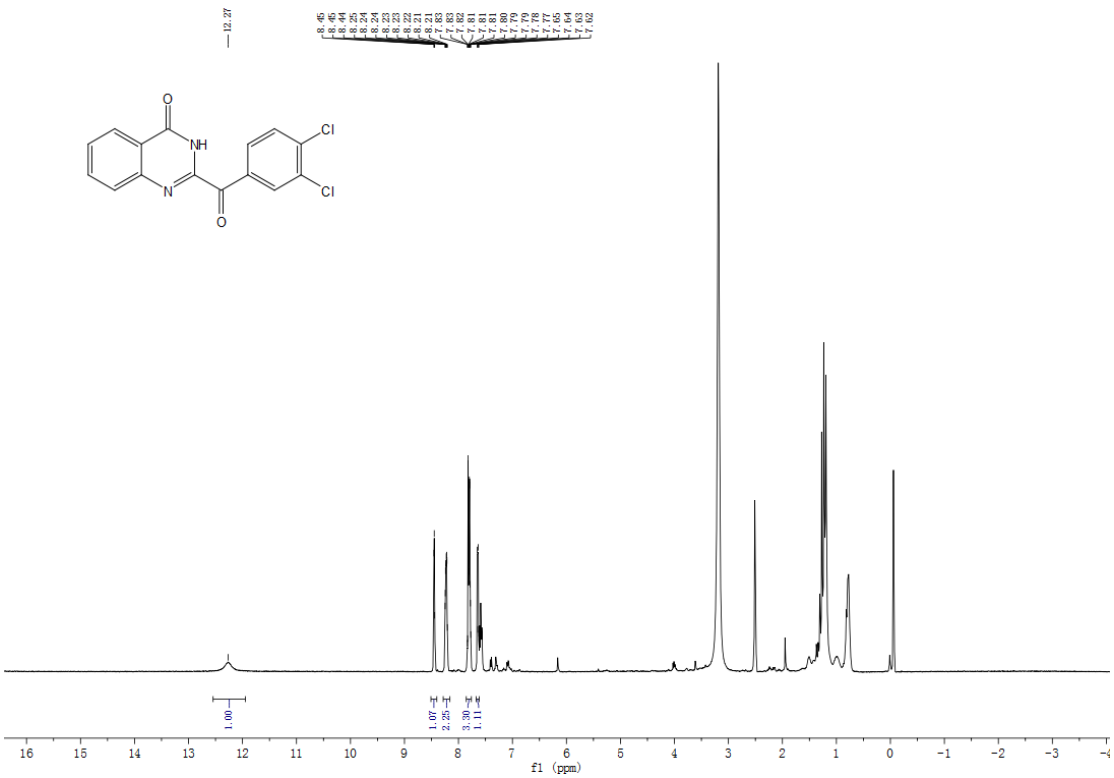


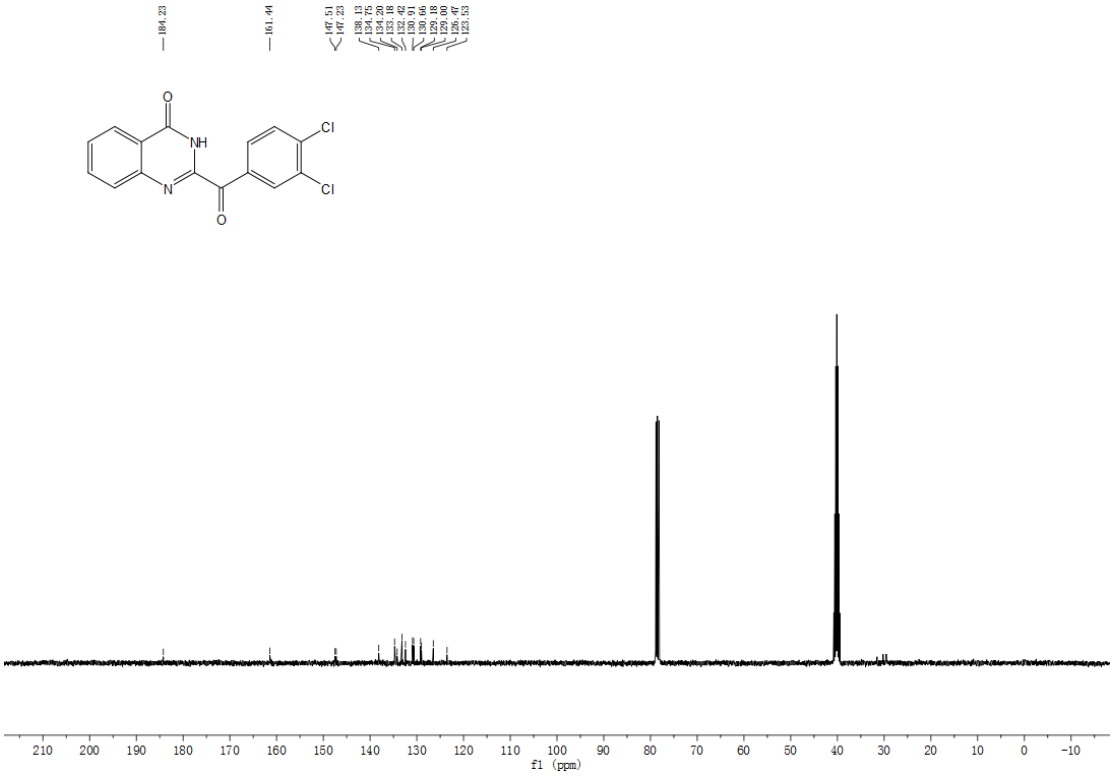
2-(4-nitrobenzoyl)quinazolin-4(3H)-one (3ag)



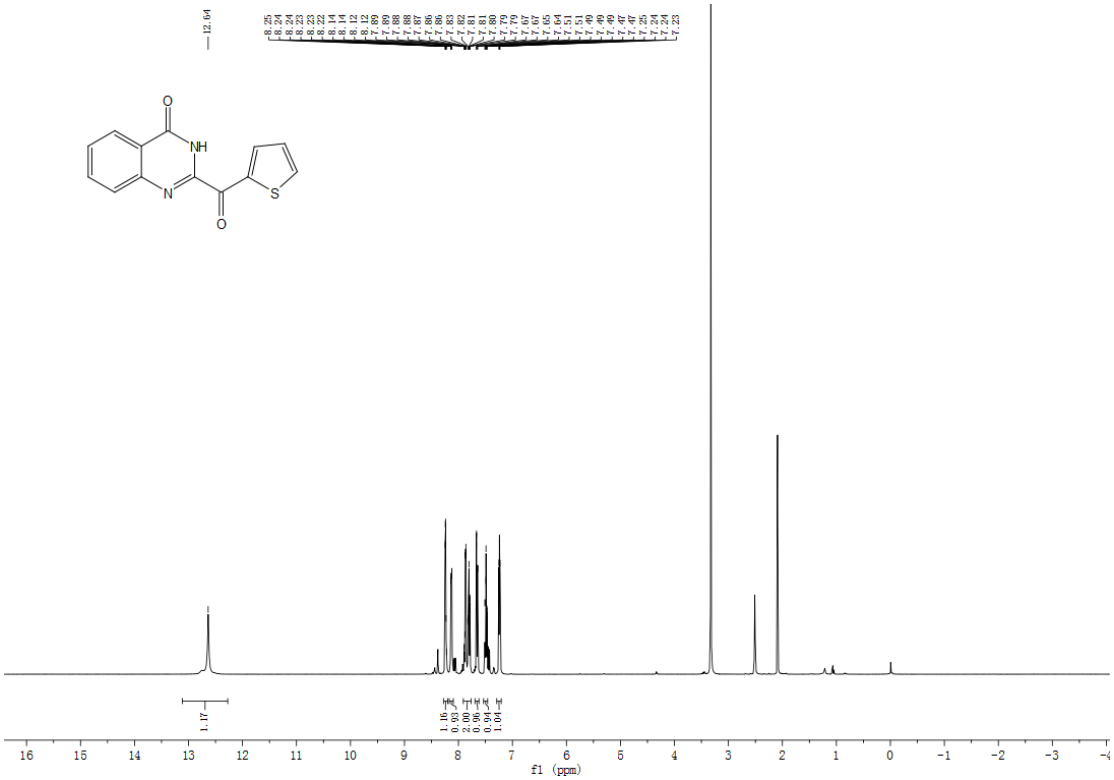


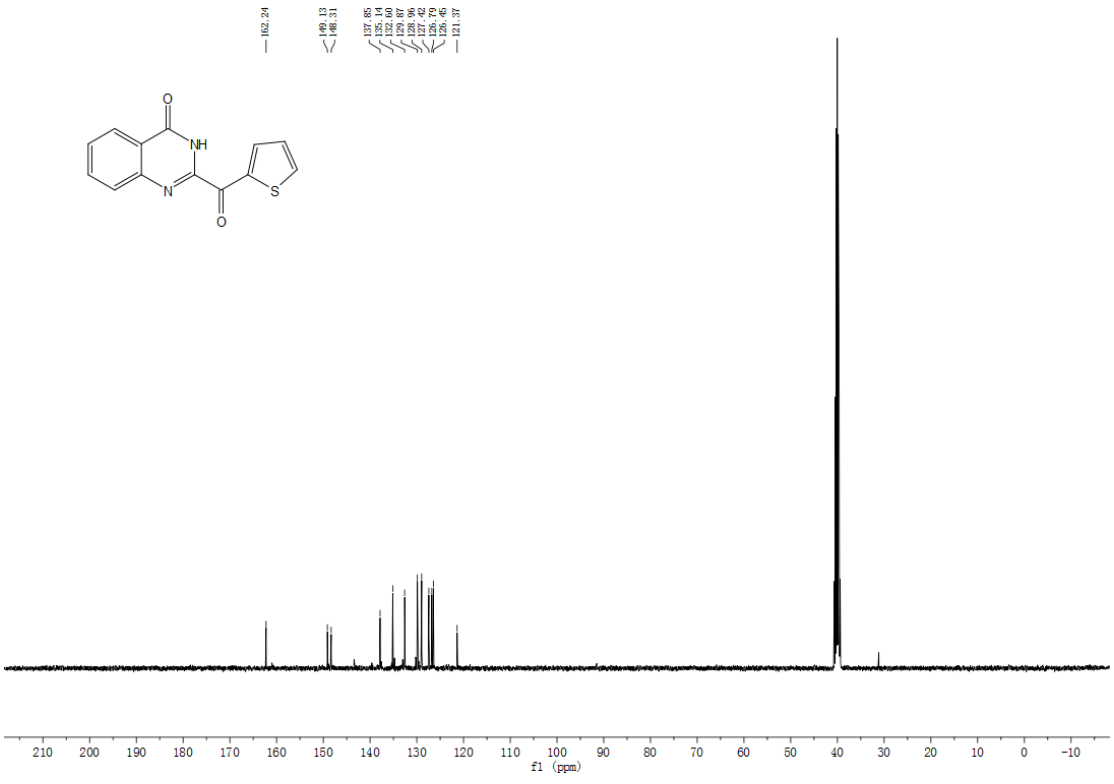
2-(3,4-dichlorobenzoyl)quinazolin-4(3H)-one (3ah)



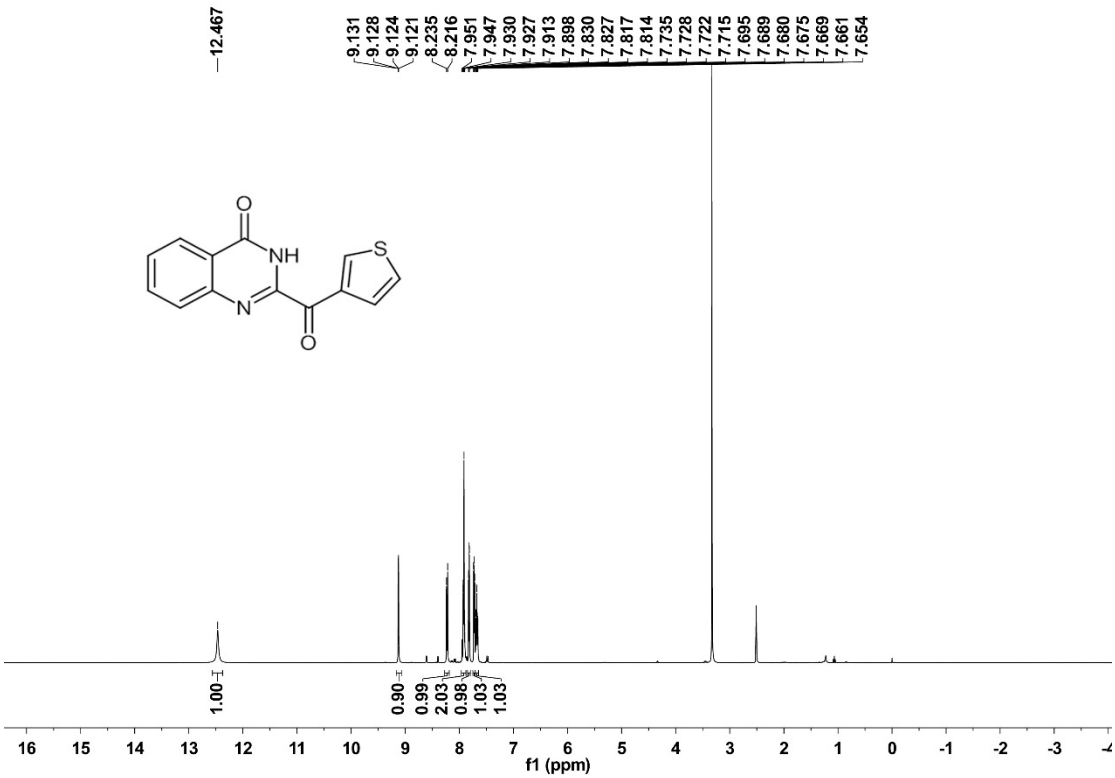


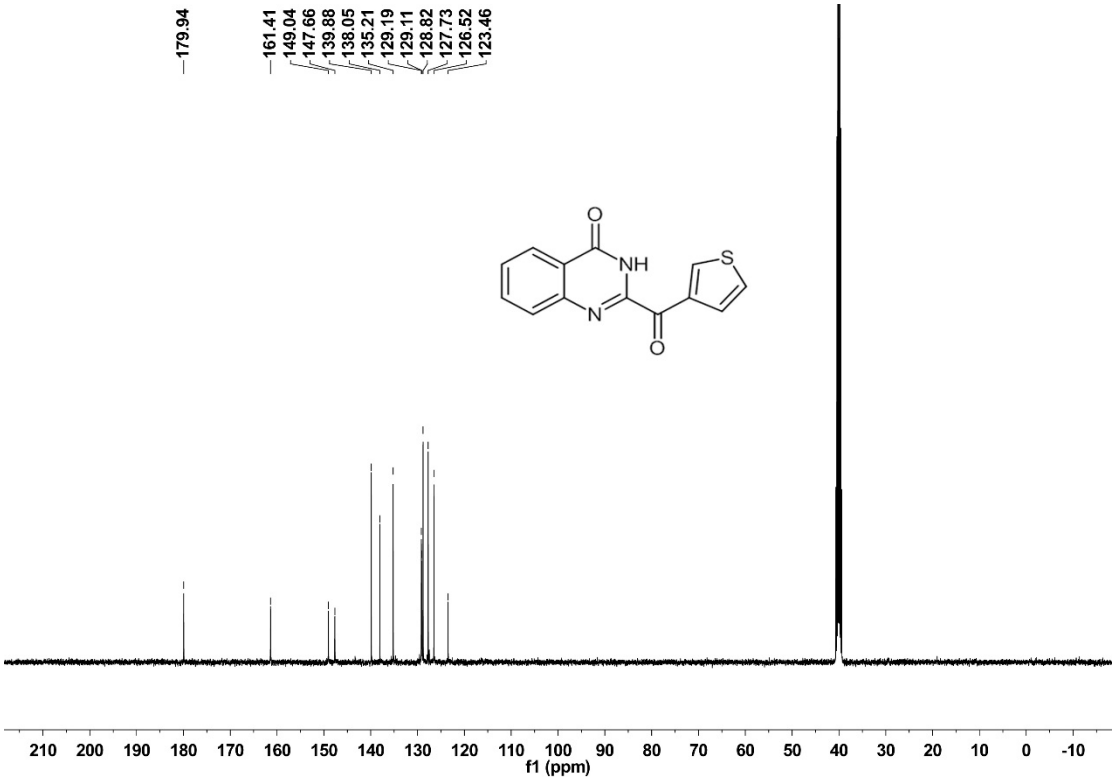
2-(thiophene-2-carbonyl)quinazolin-4(3H)-one (3ai)



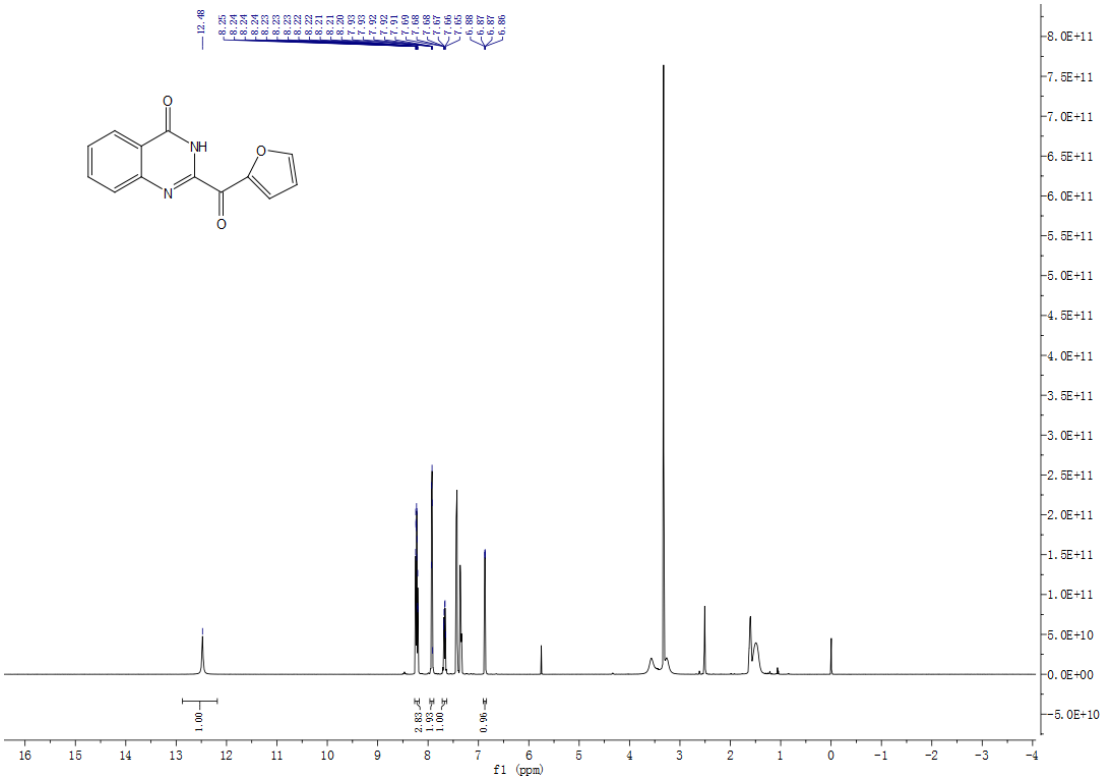


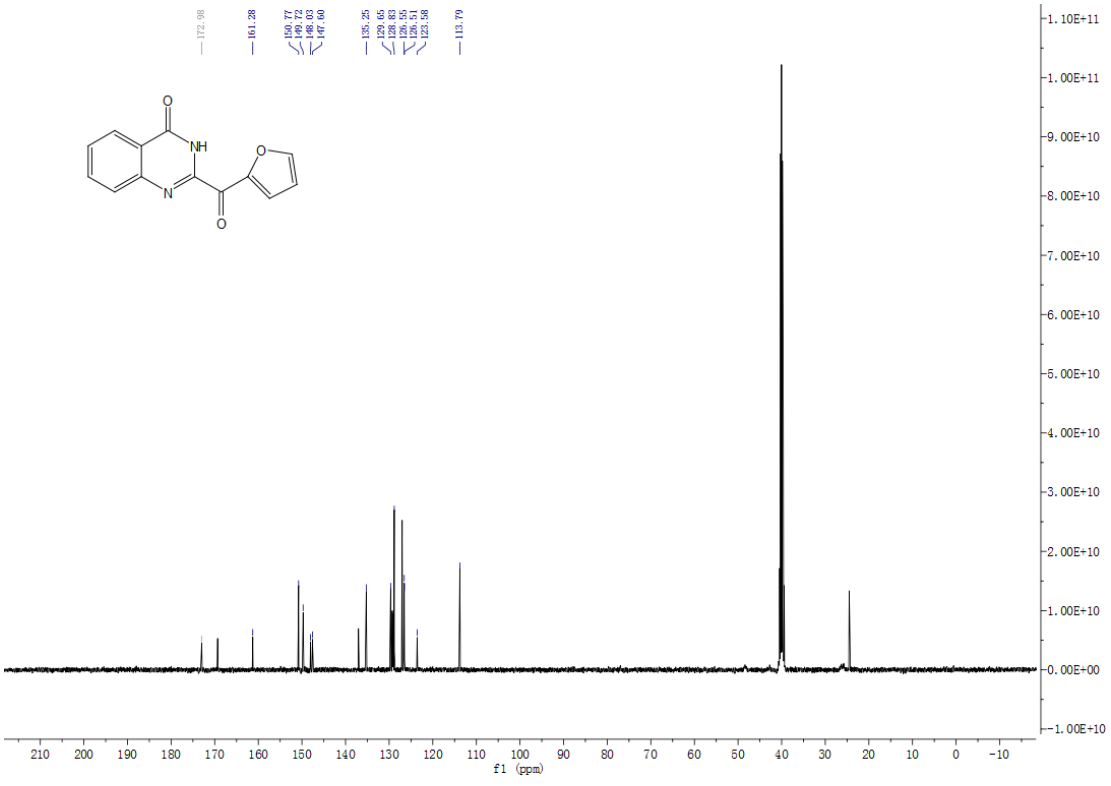
2-(thiophene-3-carbonyl)quinazolin-4(3H)-one (3aj)



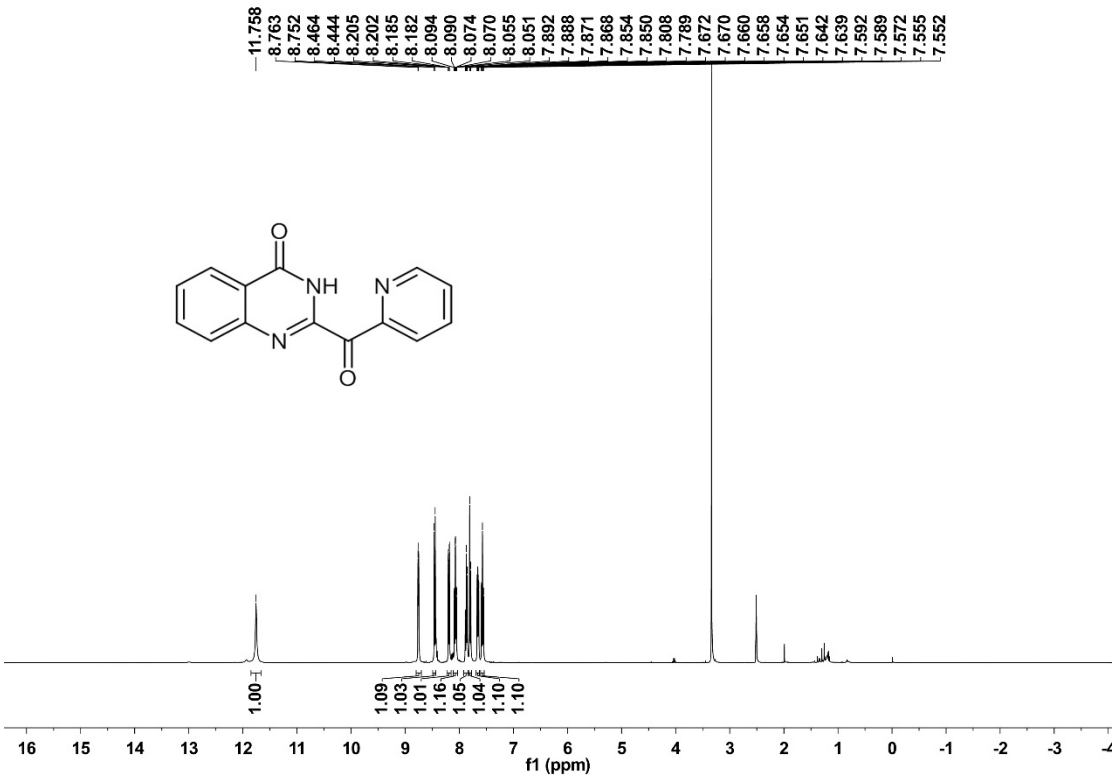


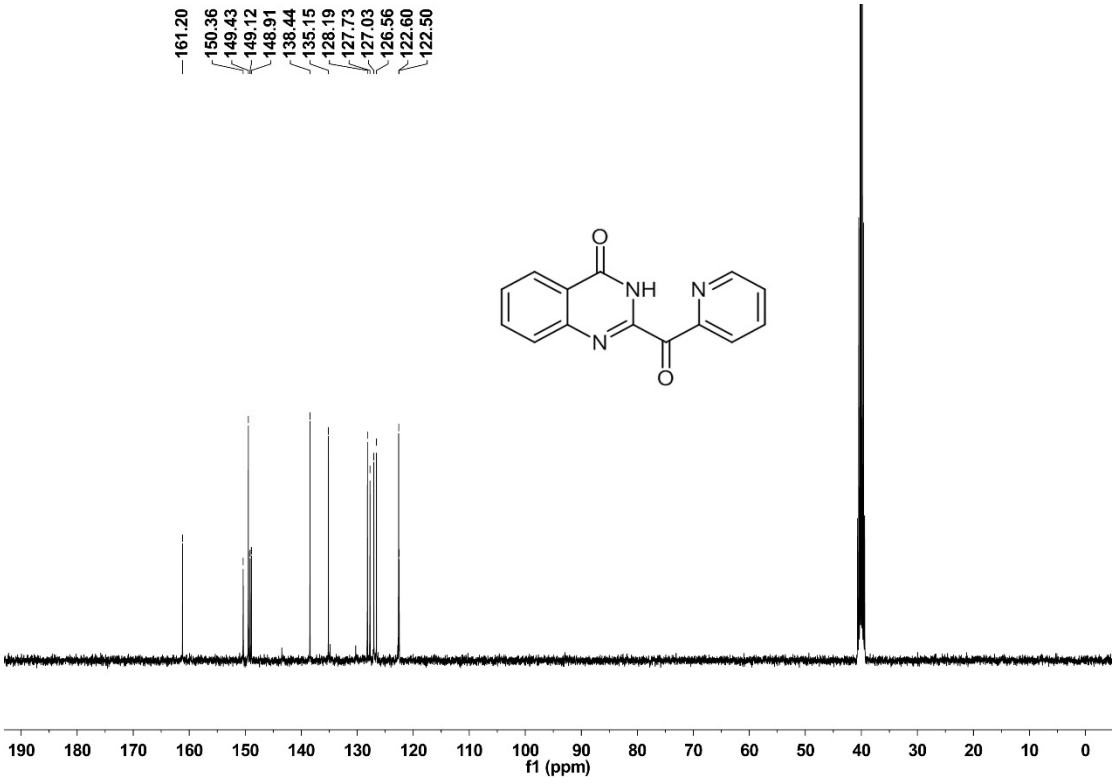
2-(furan-2-carbonyl)quinazolin-4(3H)-one (3ak)



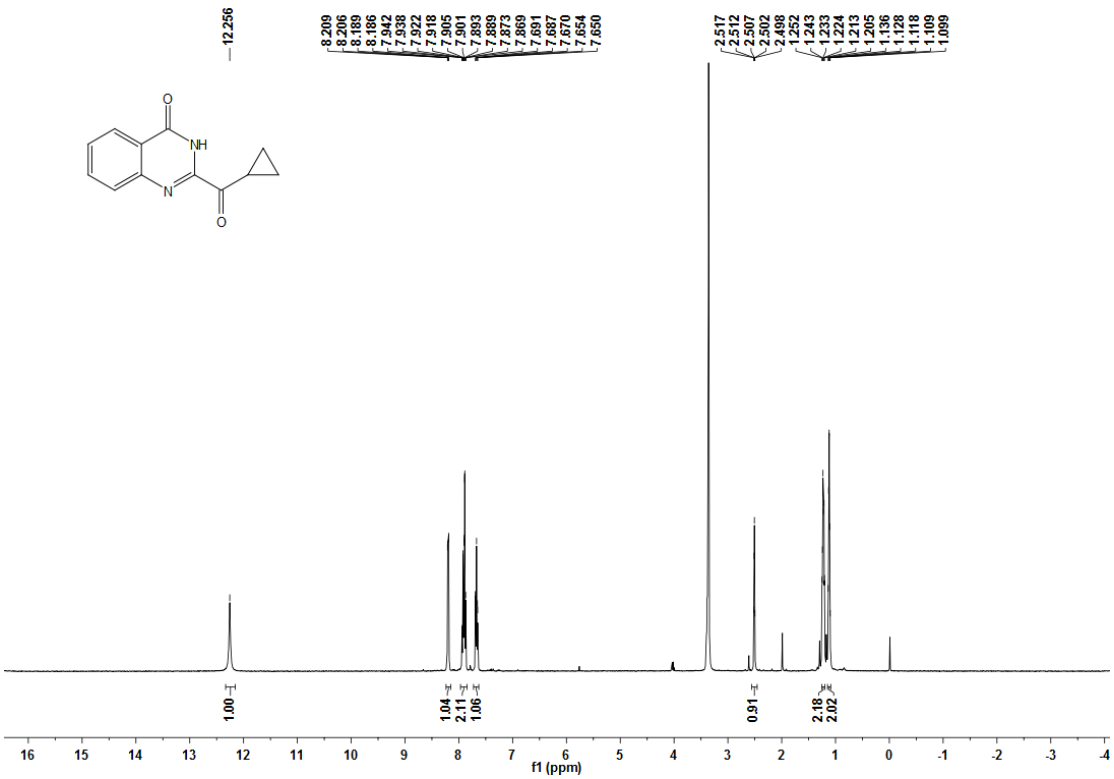


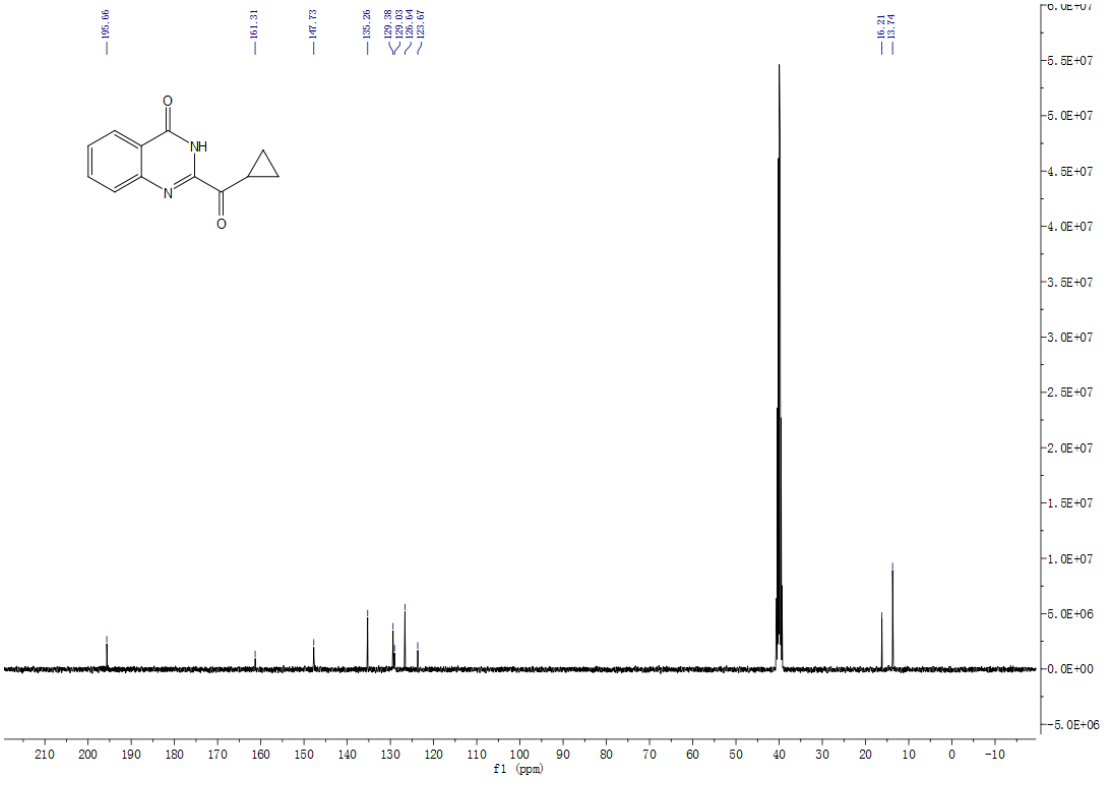
2-picolinoylquinazolin-4(3H)-one (3al)



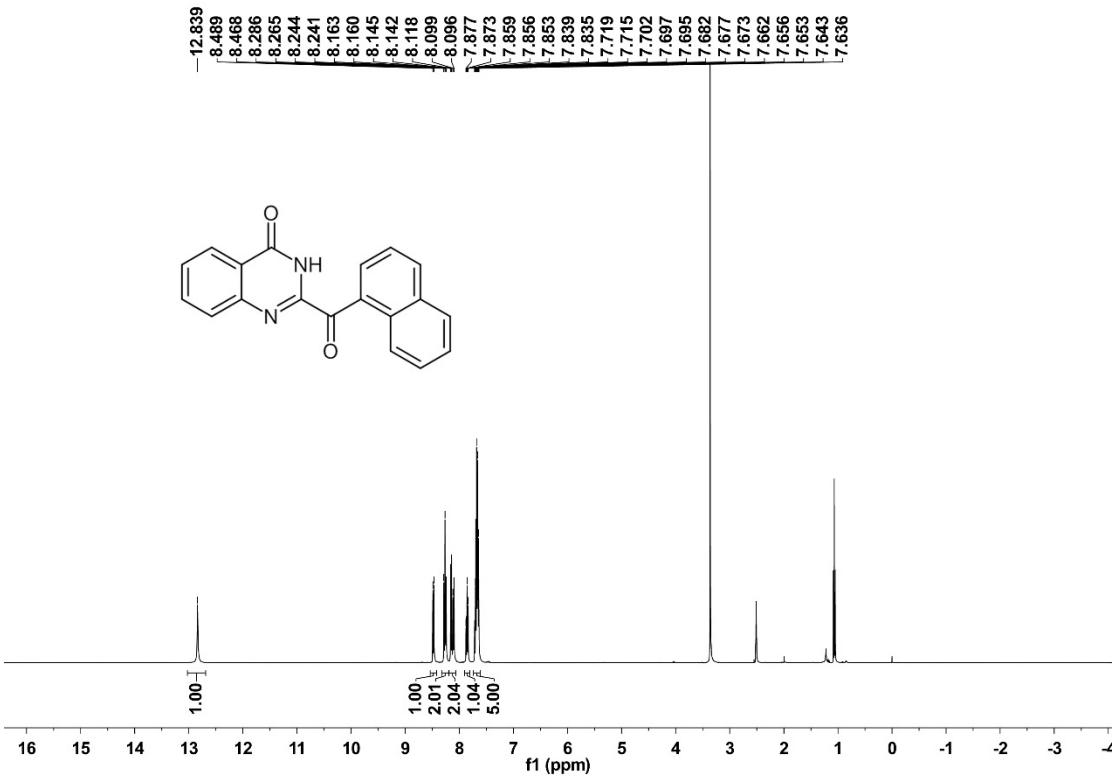


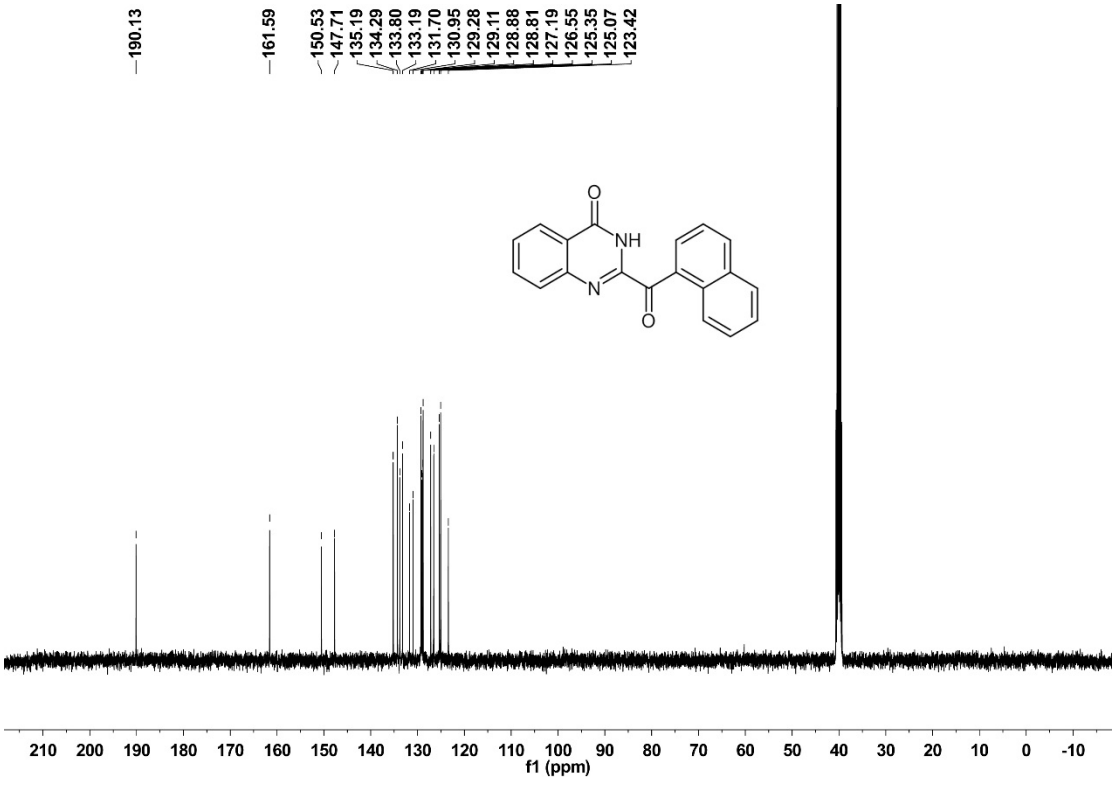
2-(cyclopropanecarbonyl)quinazolin-4(3H)-one (3am)



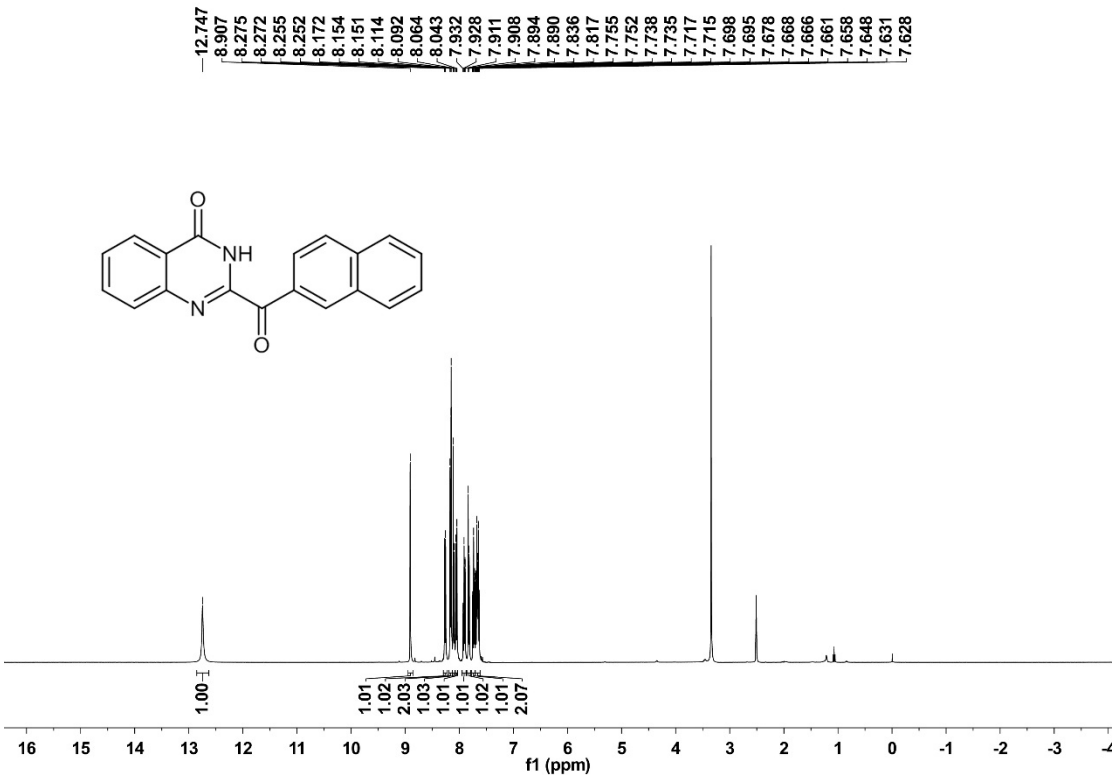


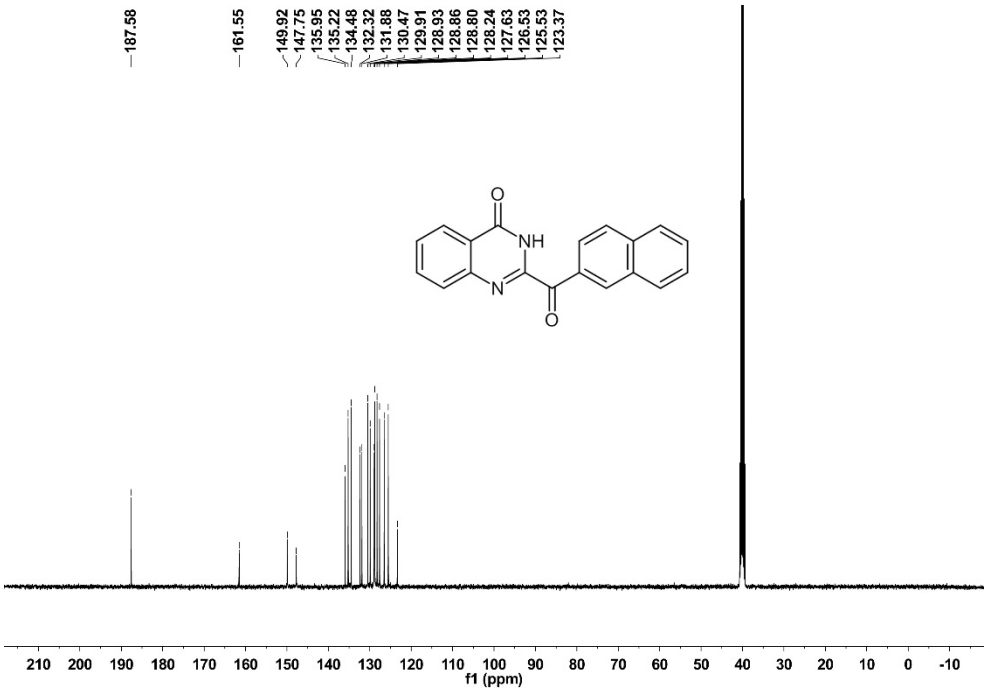
2-(1-naphthoyl)quinazolin-4(3H)-one (3an)



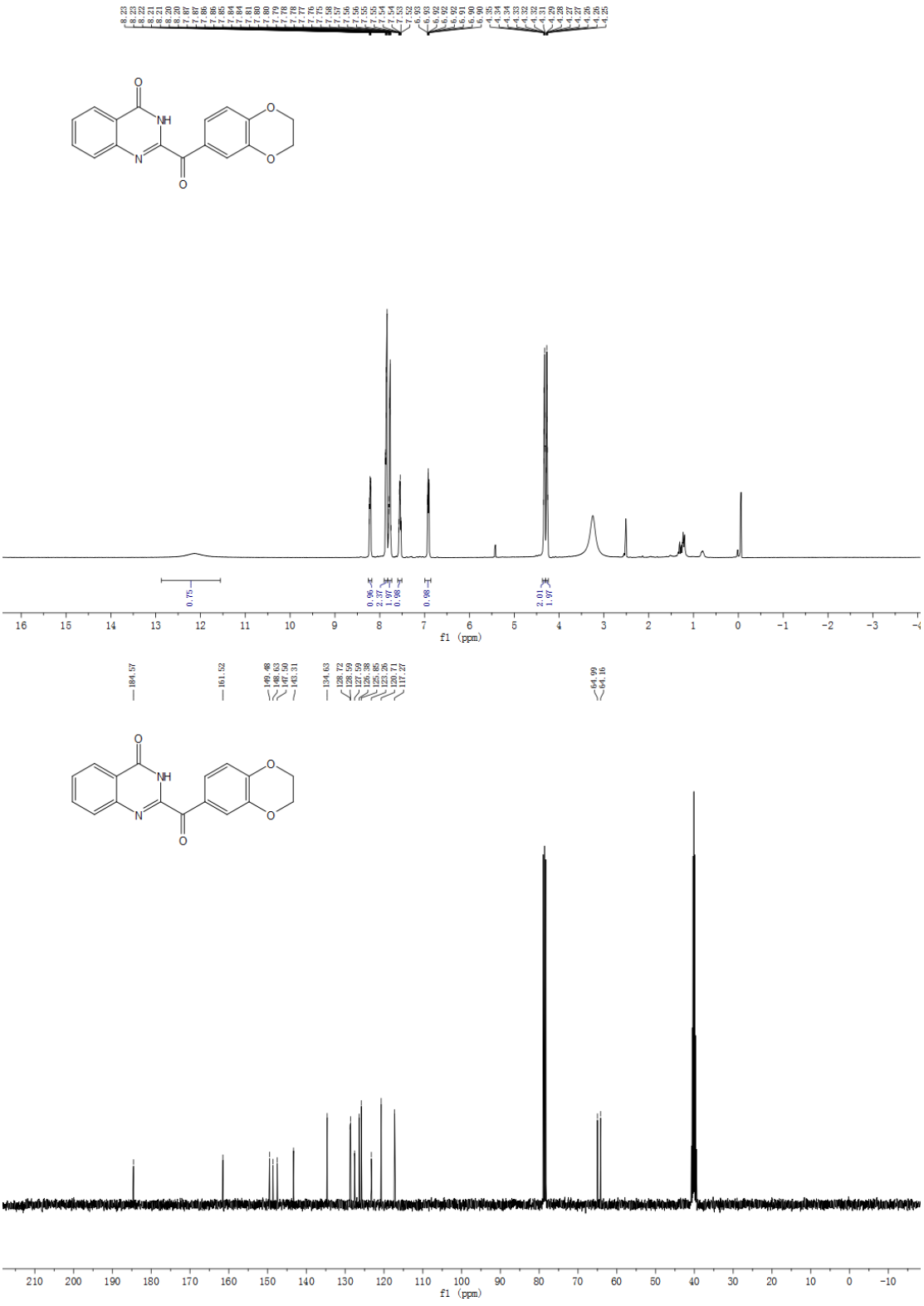


2-(2-naphthoyl)quinazolin-4(3H)-one (3ao)

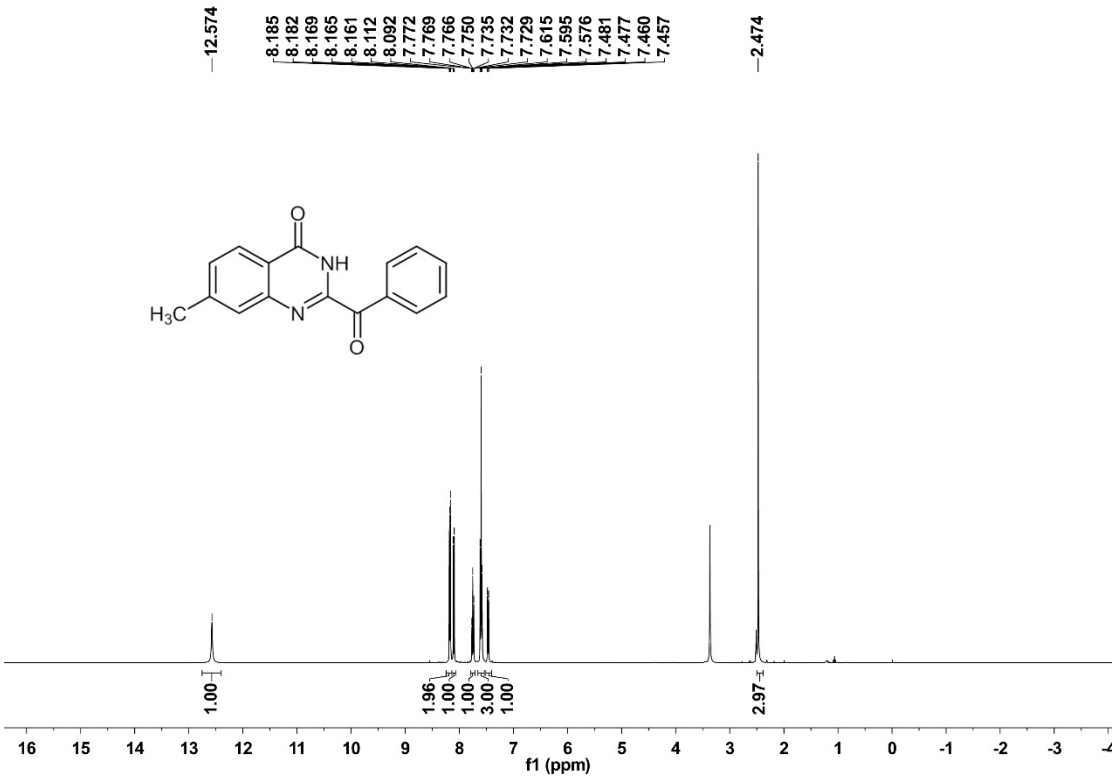


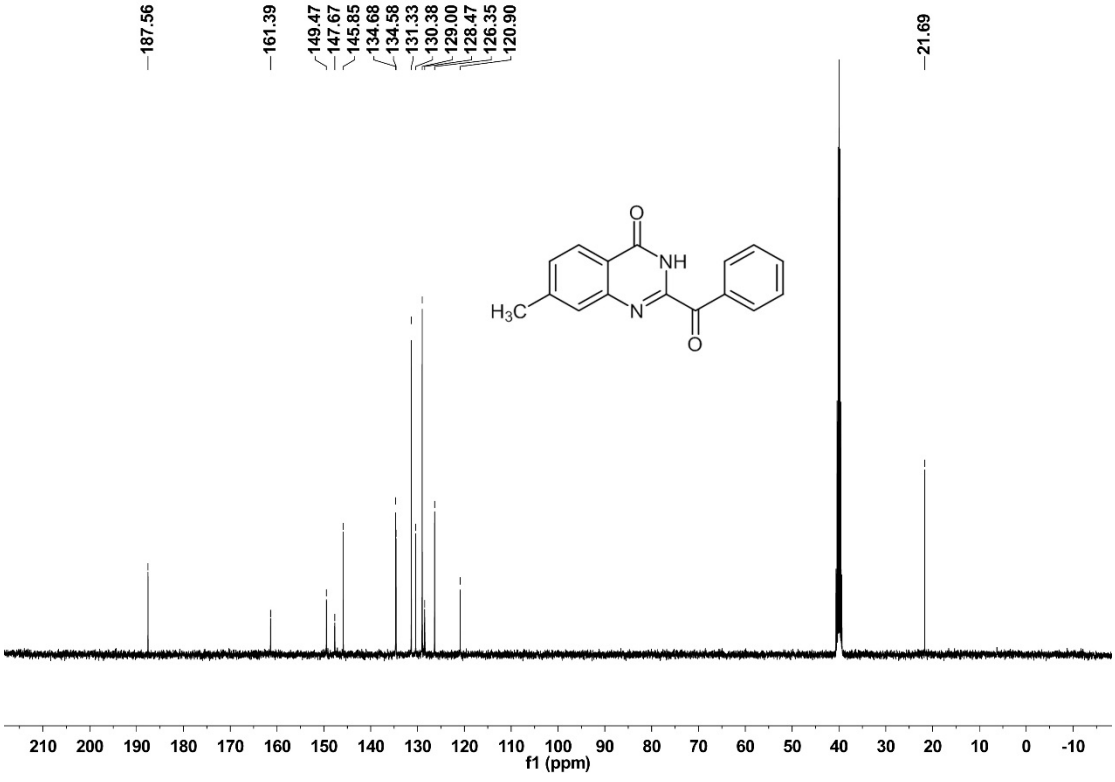


2-(2,3-dihydrobenzo[b][1,4]dioxine-6-carbonyl)quinazolin-4(3H)-one (3ap)

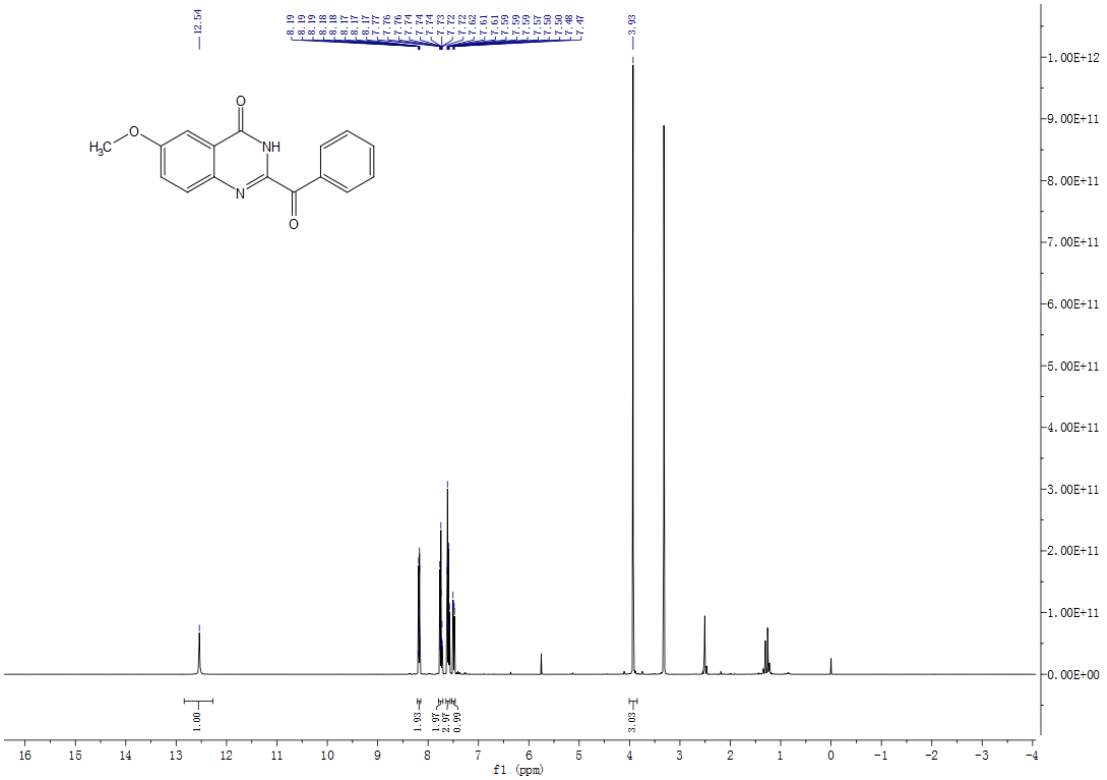


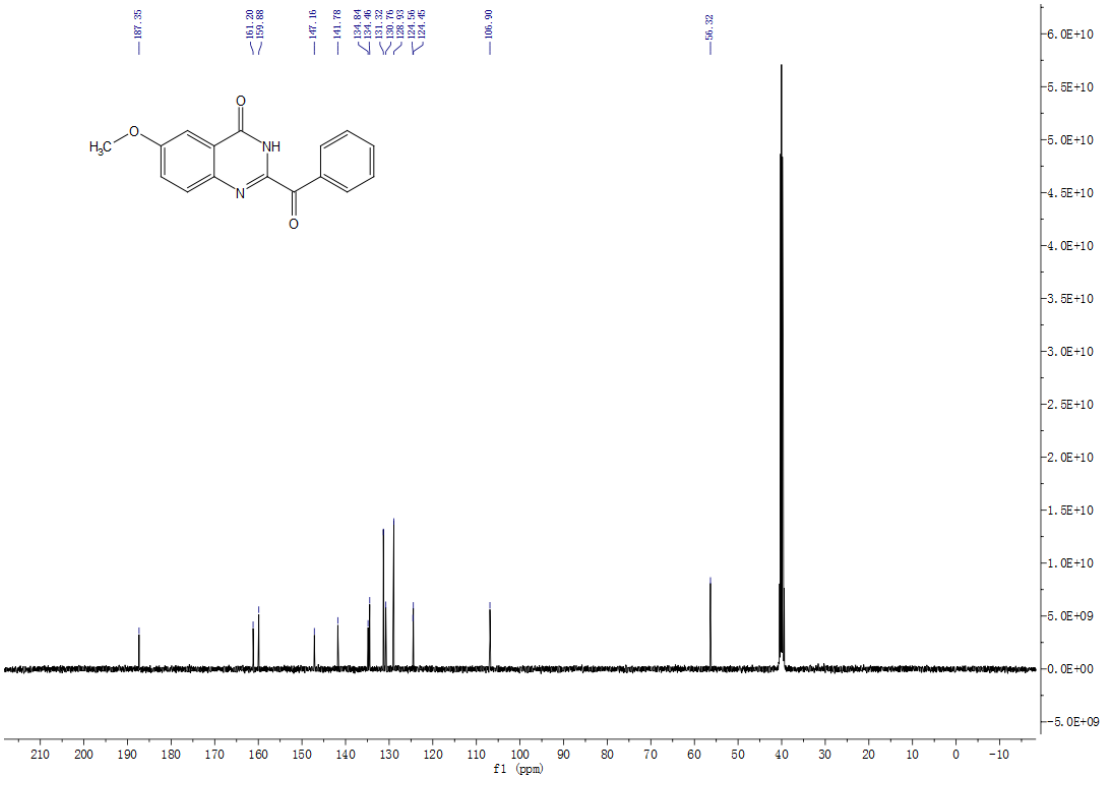
2-benzoyl-7-methylquinazolin-4(3H)-one (3aq)





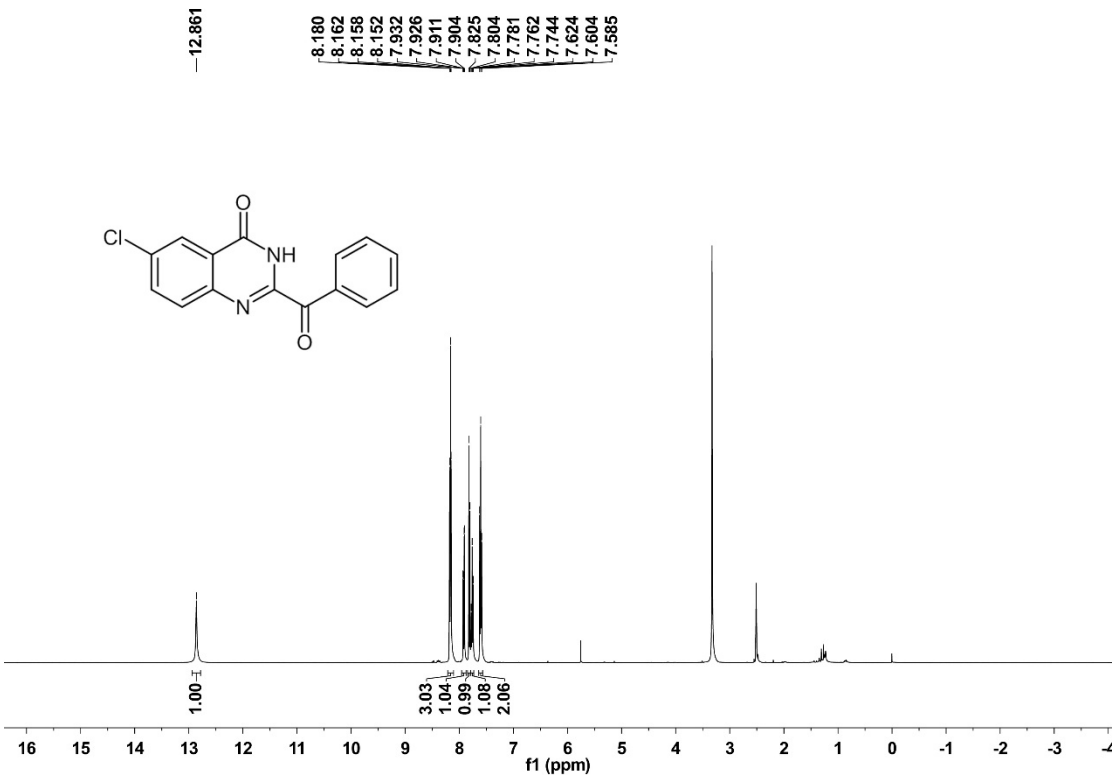
2-benzoyl-6-methoxyquinazolin-4(3H)-one (3ar)

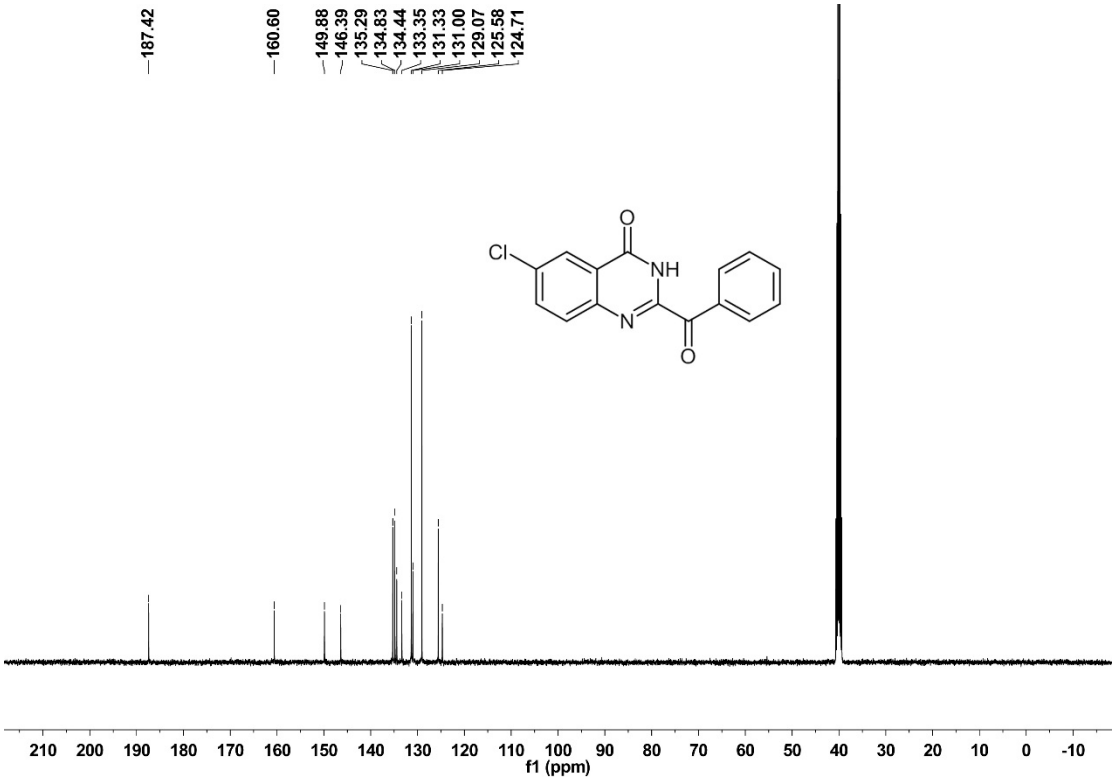




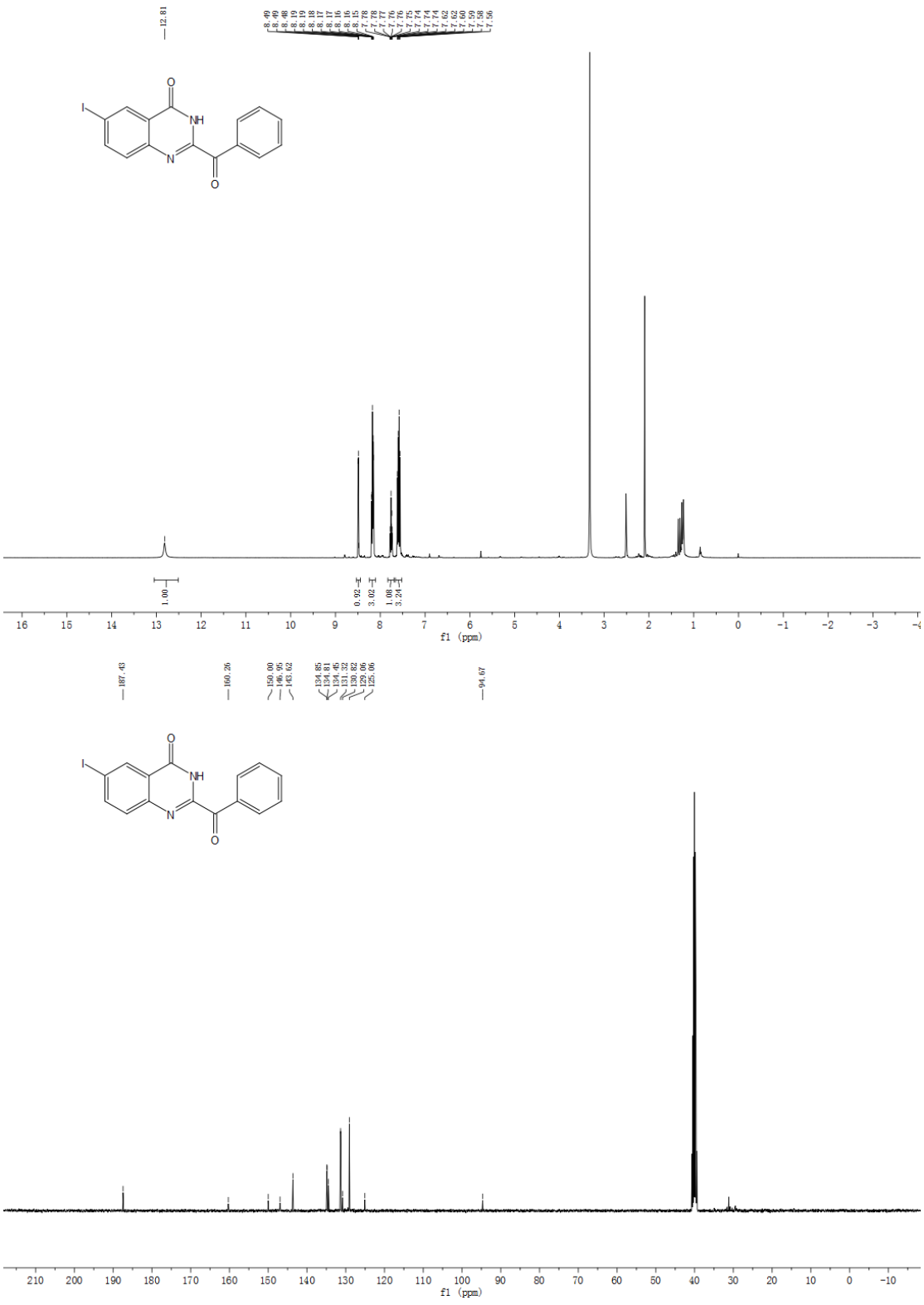
2-benzoyl-6-fluoroquinazolin-4(3H)-one (3as)

2-benzoyl-6-chloroquinazolin-4(3H)-one (3at)





2-benzoyl-6-iodoquinazolin-4(3H)-one (3au)



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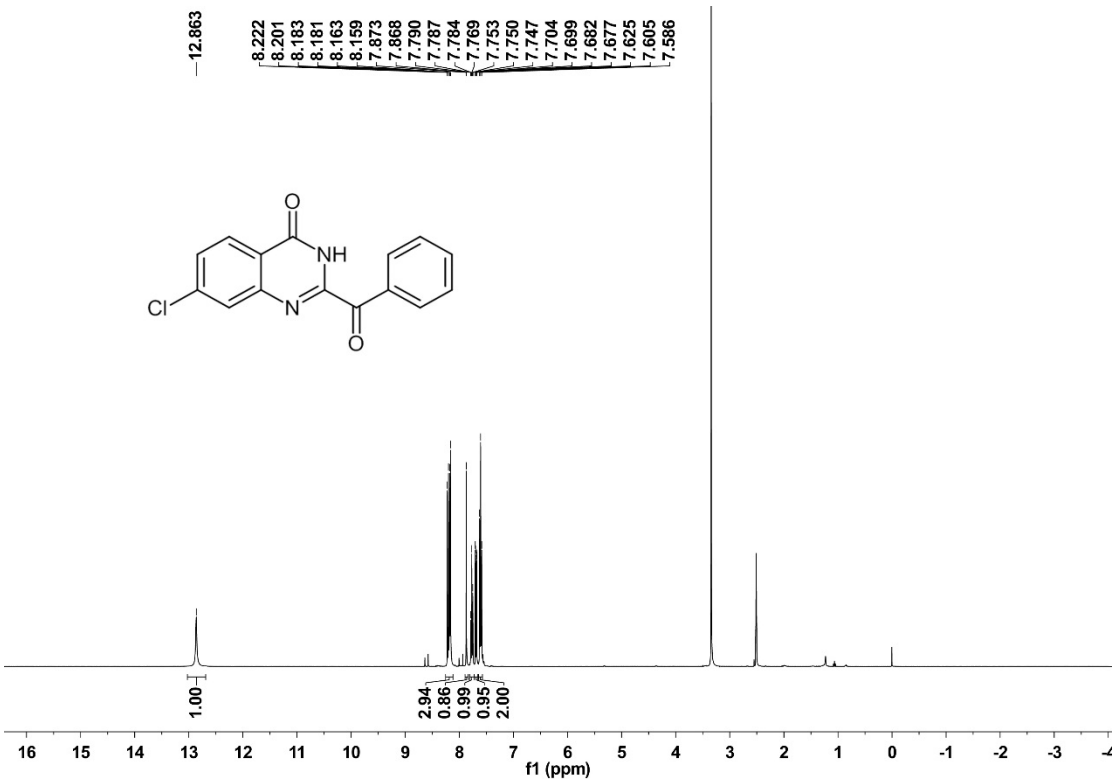
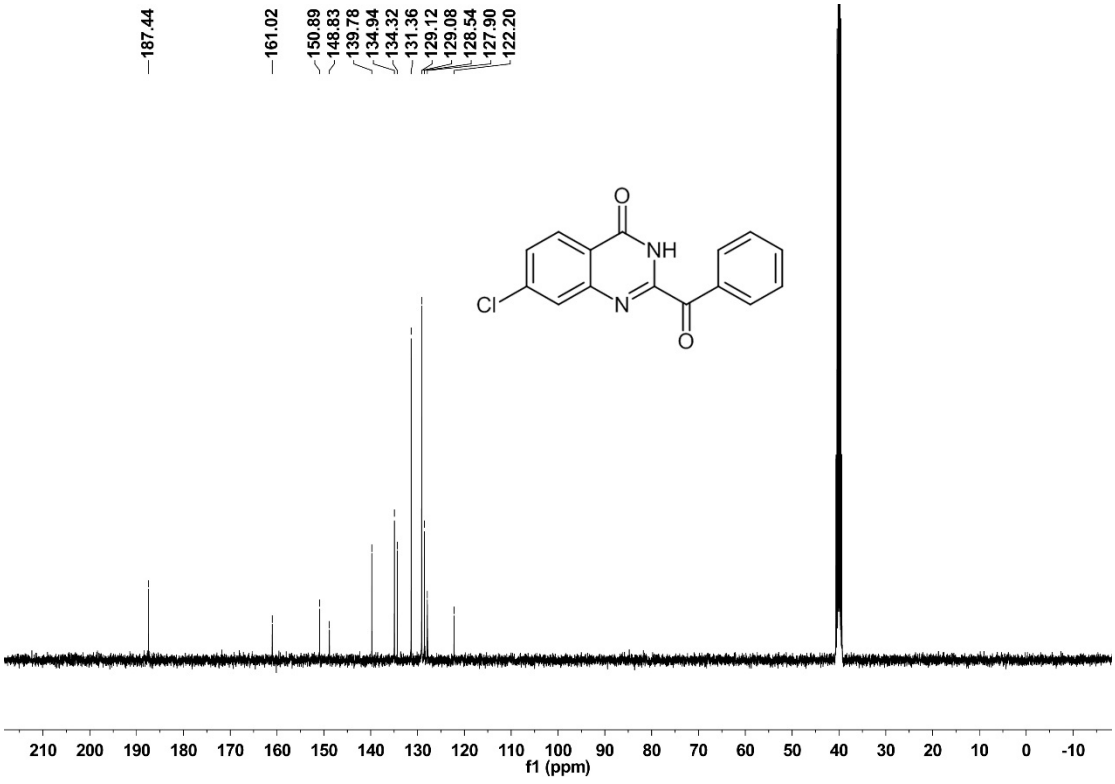
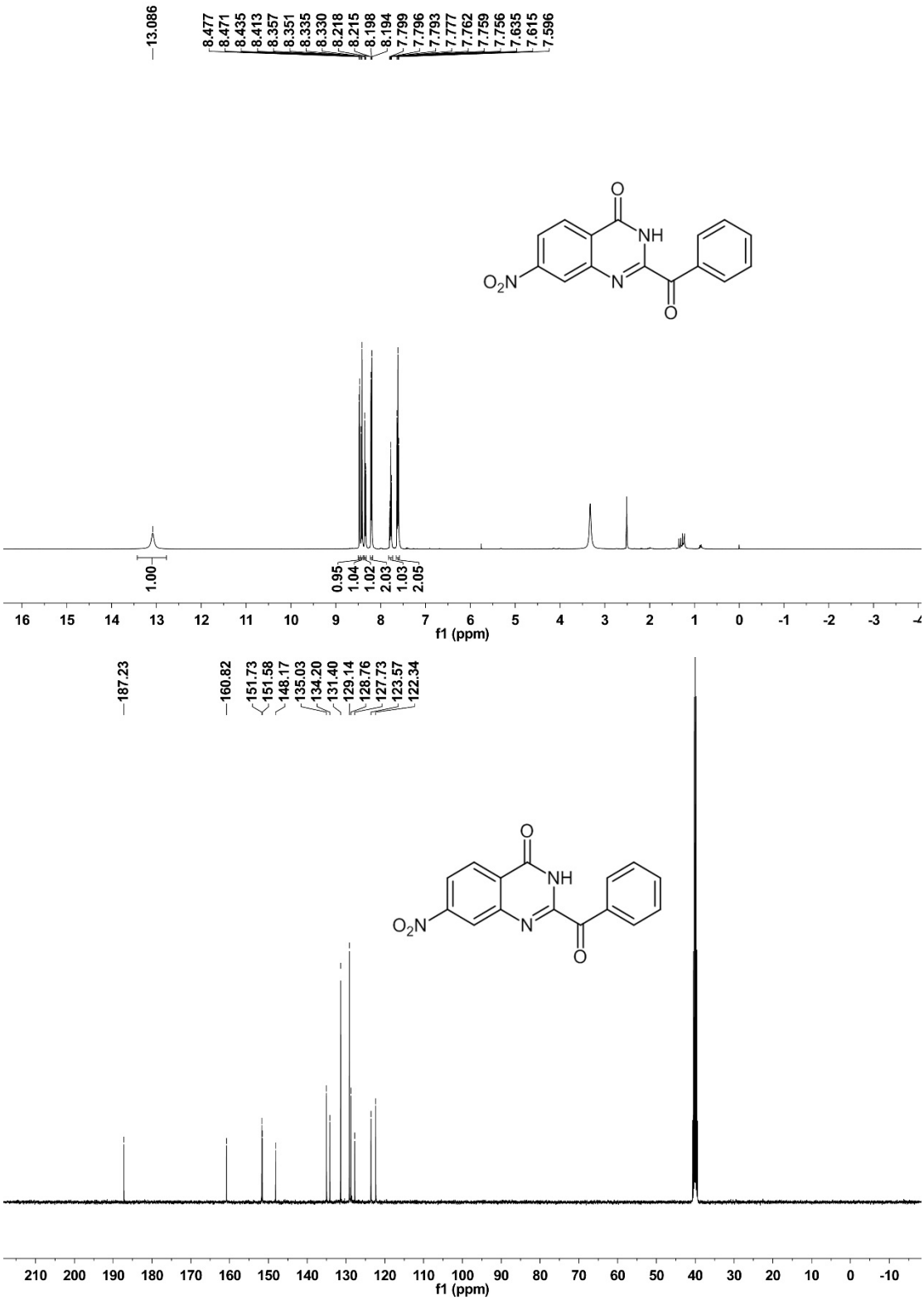
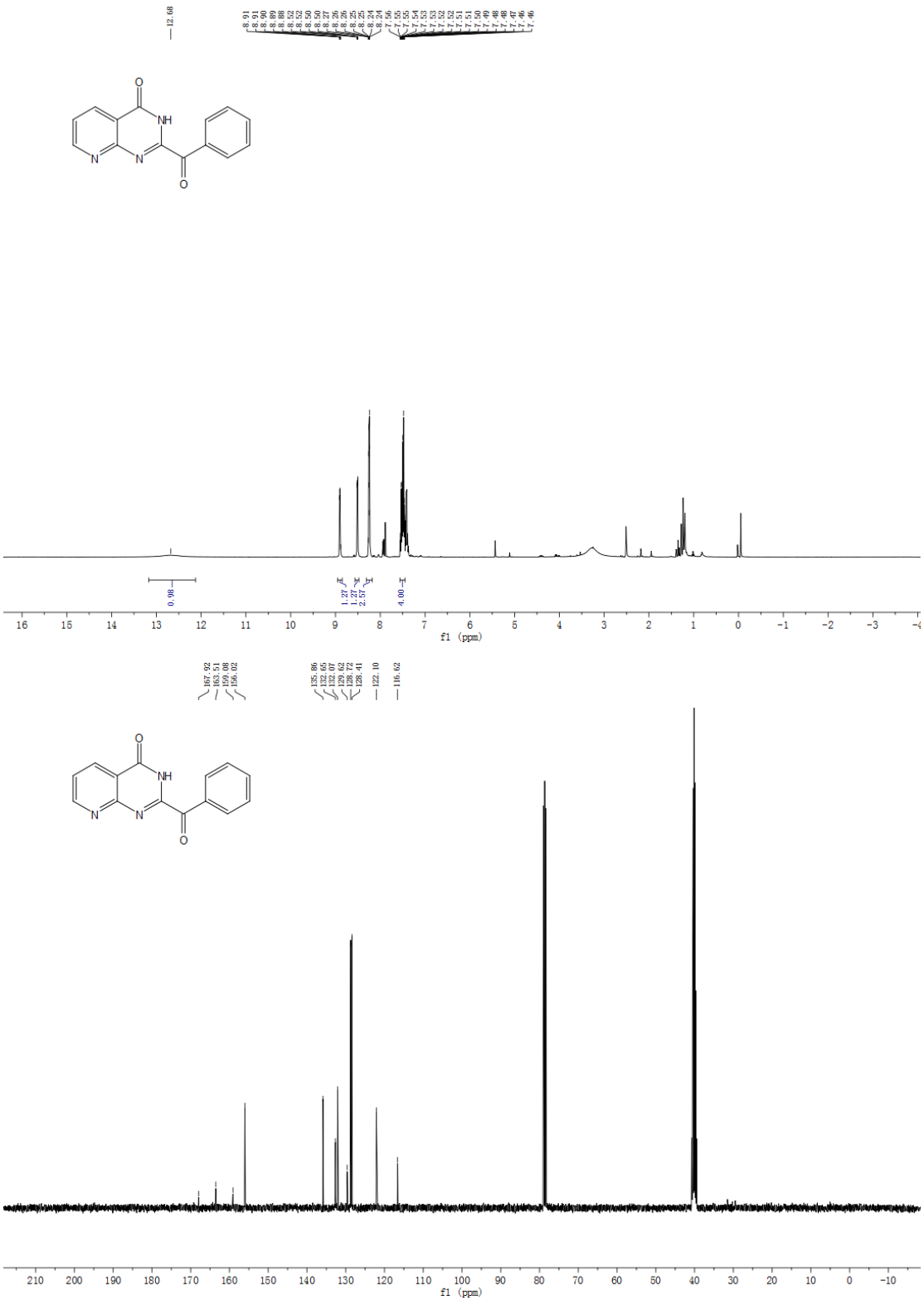




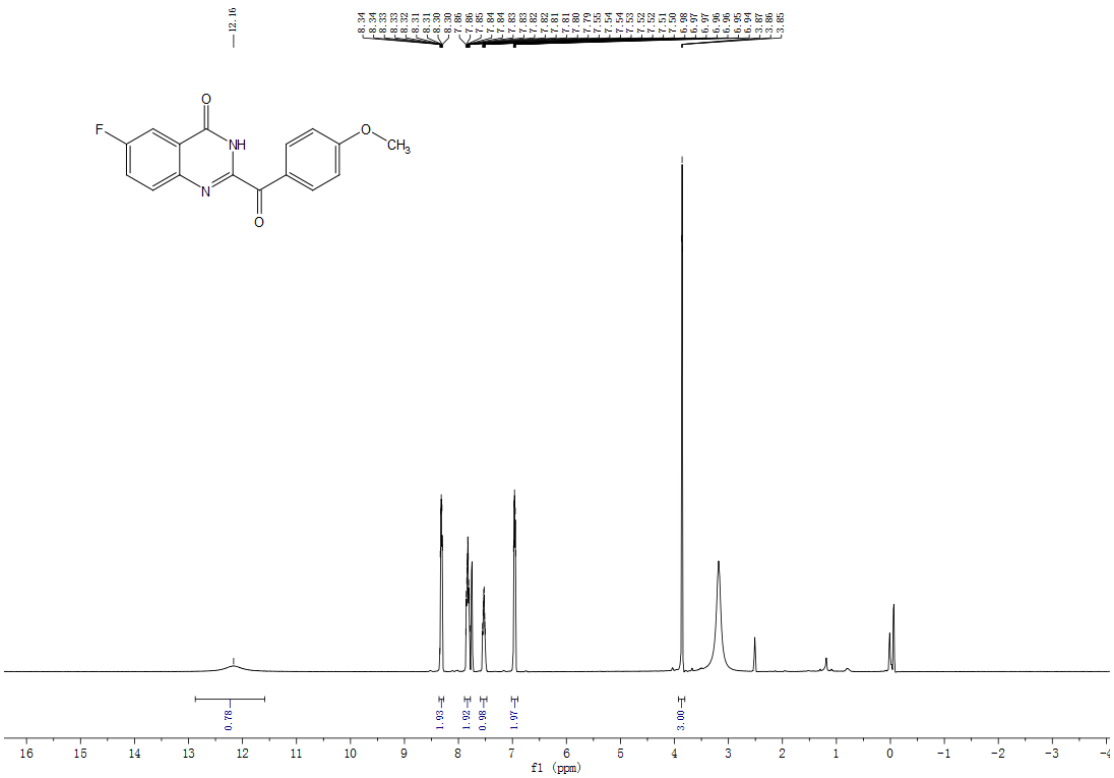
2-benzoyl-7-nitroquinazolin-4(3H)-one (3aw)

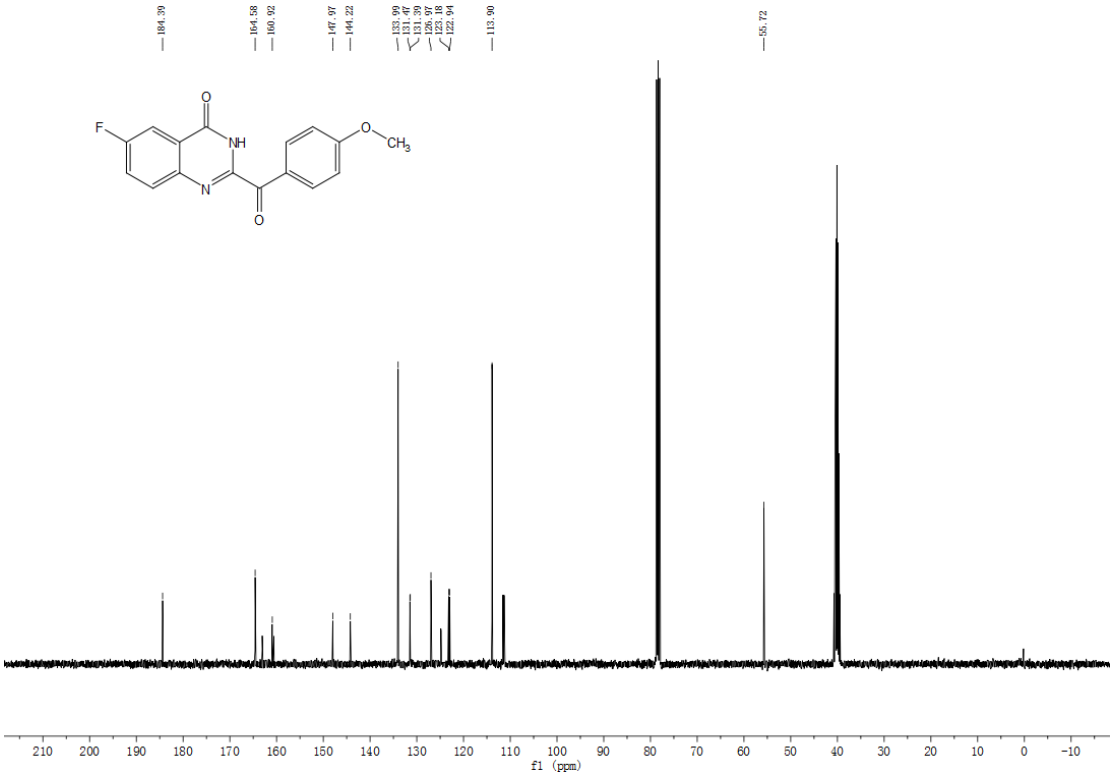


2-benzoylpyrido[2,3-d]pyrimidin-4(3H)-one (3ax)

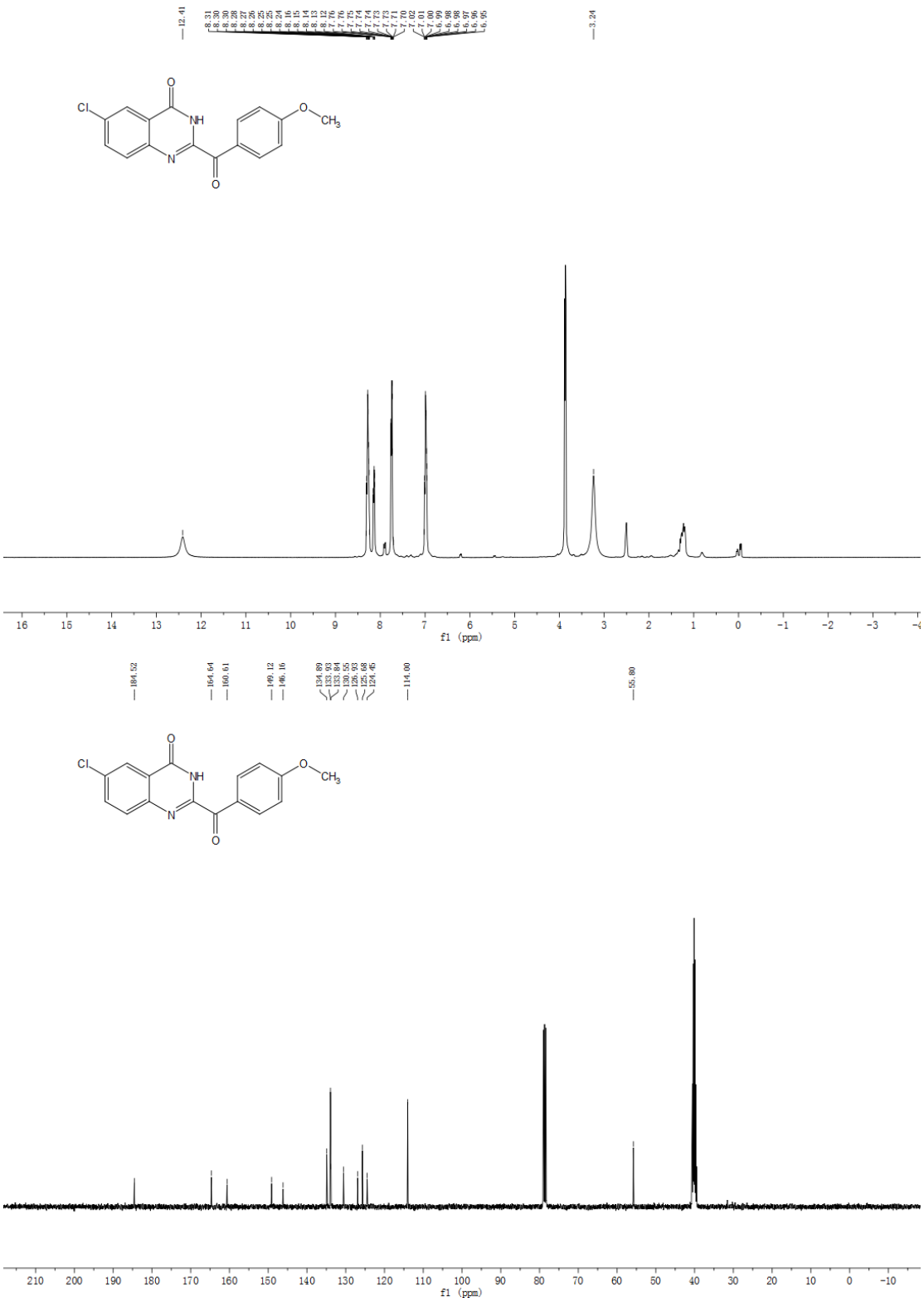


6-fluoro-2-(4-methoxybenzoyl)quinazolin-4(3H)-one (3ay)

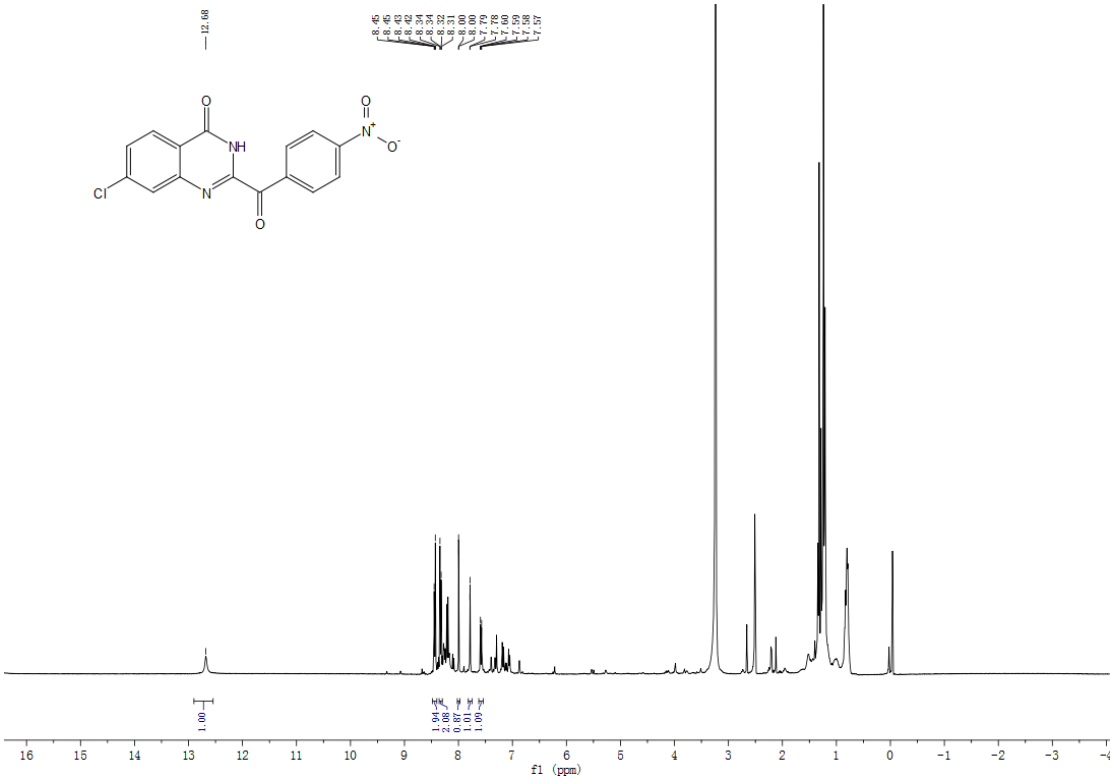


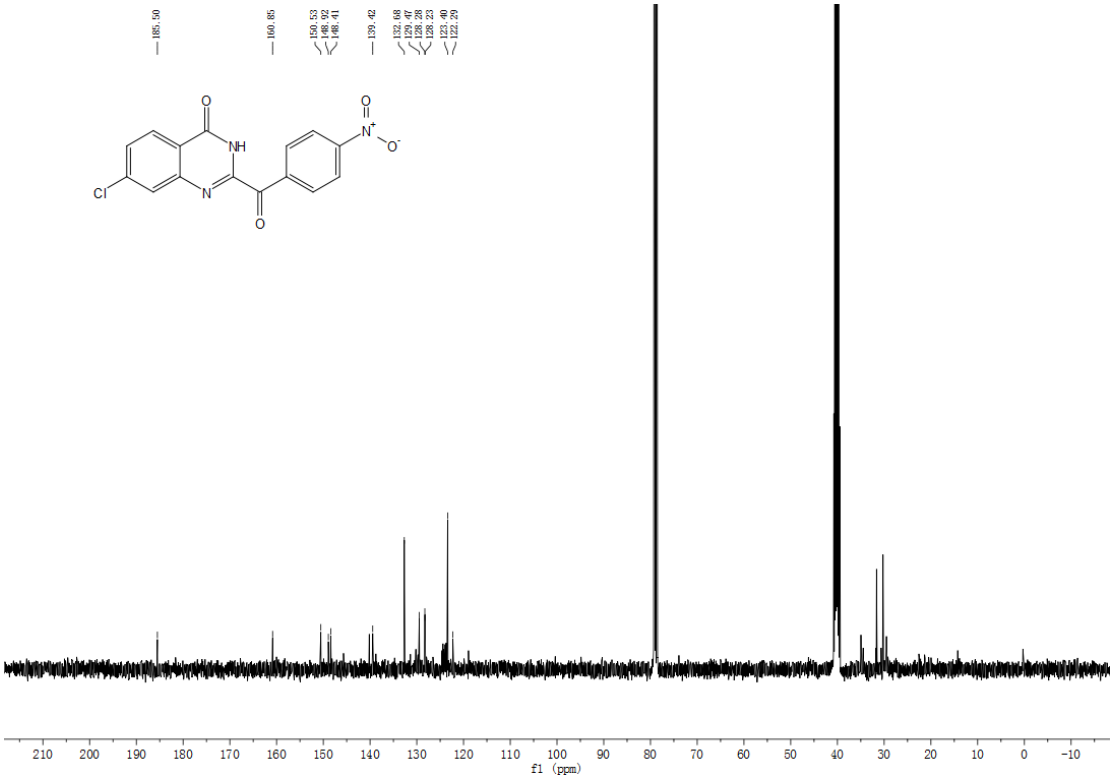


6-chloro-2-(4-methoxybenzoyl)quinazolin-4(3H)-one (3az)

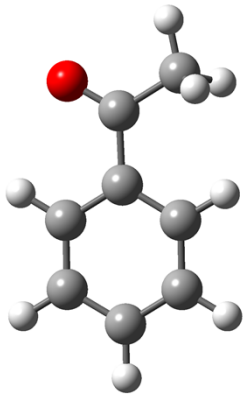


7-chloro-2-(4-nitrobenzoyl)quinazolin-4(3H)-one (3ba)


12.68
8.45
8.43
8.42
8.34
8.32
8.31
8.00
7.79
7.78
7.60
7.59
7.58
7.57
O
NH
N
Cl
O
N+
O-
O
1.00
1.94
2.08
0.87
1.01
1.09
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3
f1 (ppm)


185.50
160.85
150.53
148.92
148.41
139.42
132.68
129.47
128.28
128.23
123.40
122.29
O
NH
N
Cl
O
N+
O-
O
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

8. Optimized Structures and Cartesian Coordinates



2a / $C_6H_5COCH_3$

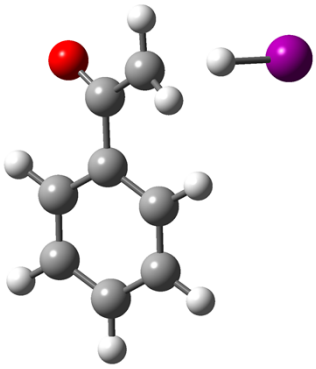
Gibbs Free Energies= -384.939568 a.u

C	**-1.96675000**	**-1.13442300**	**-0.00008200**
C	**-0.58075000**	**-1.22465000**	**-0.00004700**
C	**0.20789800**	**-0.06419800**	**-0.00000600**
C	**-0.42099000**	**1.18912000**	**0.00000400**
C	**-1.81051100**	**1.27747400**	**-0.00003100**
C	**-2.58454000**	**0.11815400**	**-0.00007500**
H	**-2.56768200**	**-2.03661000**	**-0.00011500**
H	**-0.09683600**	**-2.19325100**	**-0.00005000**
H	**0.16517000**	**2.09907900**	**0.00004000**
H	**-2.28832700**	**2.25033000**	**-0.00002400**
H	**-3.66652200**	**0.18890900**	**-0.00010300**
C	**1.69352500**	**-0.19700000**	**0.00002900**
O	**2.21947200**	**-1.30801200**	**0.00005800**
C	**2.53925700**	**1.04703800**	**0.00010800**
H	**2.32118500**	**1.65743600**	**-0.88100400**
H	**2.32108000**	**1.65738600**	**0.88123000**
H	**3.59331600**	**0.77173000**	**0.00016400**

I•

Gibbs Free Energies= -11.383499 a.u

I	**0.00000000**	**0.00000000**	**0.00000000**

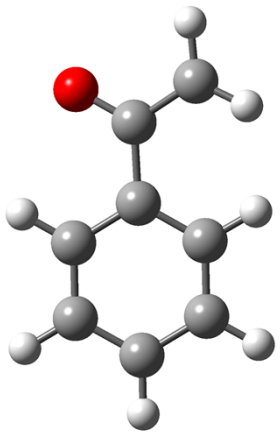


TS

Gibbs Free Energies= -396.289024 a.u

C	**-3.92232500**	**-0.43979800**	**-0.76047500**
C	**-3.04414300**	**0.62880300**	**-0.63119400**
C	**-1.89458900**	**0.51056400**	**0.16348300**
C	**-1.63655500**	**-0.70202200**	**0.81921000**
C	**-2.51057800**	**-1.77562900**	**0.67560100**
C	**-3.65566500**	**-1.64598200**	**-0.10902600**
H	**-4.81387600**	**-0.33585900**	**-1.36811800**
H	**-3.24393600**	**1.56506200**	**-1.13738600**
H	**-0.74746500**	**-0.82491000**	**1.42365900**
H	**-2.29724200**	**-2.71280300**	**1.17653500**
H	**-4.33894400**	**-2.48126900**	**-0.21357700**
C	**-0.96675900**	**1.66986300**	**0.26194000**
O	**-1.03217700**	**2.61196600**	**-0.54952600**
C	**0.01950500**	**1.71749800**	**1.31697300**
H	**0.67884200**	**2.57686100**	**1.34918800**
H	**-0.02030700**	**1.06212000**	**2.17670200**
H	**1.30850200**	**0.64036500**	**0.50222600**

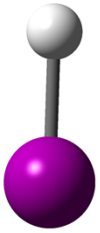
I	**2.40374500**	**-0.38047300**	**-0.18739800**



A / $C_6H_5COCH_2$•

Gibbs Free Energies= -384.290493 a.u

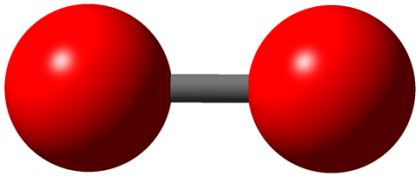
C	**1.88073400**	**-1.16970200**	**0.09593600**
C	**0.49181400**	**-1.20421800**	**0.08494100**
C	**-0.24996200**	**-0.01696500**	**-0.00375200**
C	**0.43150900**	**1.20623400**	**-0.08944300**
C	**1.82333300**	**1.23749800**	**-0.08870500**
C	**2.55069100**	**0.05227600**	**0.00758800**
H	**2.44291900**	**-2.09332100**	**0.17346100**
H	**-0.03004100**	**-2.15053900**	**0.15201300**
H	**-0.11284900**	**2.13774300**	**-0.17376400**
H	**2.33919400**	**2.18778600**	**-0.16433900**
H	**3.63459300**	**0.07911200**	**0.01330200**
C	**-1.73990600**	**-0.10148800**	**-0.02042900**
O	**-2.30764400**	**-1.20266100**	**-0.19505000**
C	**-2.53566800**	**1.07149100**	**0.18343200**
H	**-2.11462600**	**2.04599400**	**0.38733200**
H	**-3.61330100**	**0.96376100**	**0.15499000**



HI

Gibbs Free Energies= -12.006263 a.u

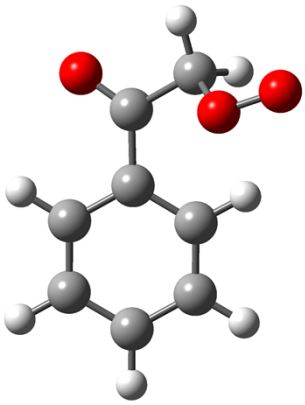
H	**0.00000000**	**0.00000000**	**-1.57712500**
I	**0.00000000**	**0.00000000**	**0.02975700**



O_2

Gibbs Free Energies= -150.387378 a.u

O	**0.00000000**	**0.00000000**	**0.60198700**
O	**0.00000000**	**0.00000000**	**-0.60198700**



B / $C_8H_7O_3$•

Gibbs Free Energies= -534.69658 a.u

C	**2.81545000**	**0.43093200**	**-0.47207800**
C	**1.59662900**	**1.08700500**	**-0.36891700**
C	**0.47033000**	**0.41026000**	**0.12496800**
C	**0.58646300**	**-0.93039600**	**0.52221900**
C	**1.81391700**	**-1.57860600**	**0.43048300**
C	**2.92560000**	**-0.90266200**	**-0.07086900**
H	**3.68003600**	**0.95322800**	**-0.86478900**
H	**1.50048300**	**2.12051400**	**-0.67834900**
H	**-0.26497100**	**-1.46536900**	**0.92179100**
H	**1.90220700**	**-2.61070300**	**0.74871900**
H	**3.87831300**	**-1.41401400**	**-0.15009800**
C	**-0.80657800**	**1.14695700**	**0.23326200**

O	**-0.86007400**	**2.36905700**	**0.23458200**
C	**-2.11101900**	**0.37650300**	**0.38538700**
H	**-2.17701900**	**-0.08932800**	**1.37100800**
H	**-2.95585600**	**1.04193000**	**0.21497200**
O	**-2.16440100**	**-0.68286200**	**-0.62180200**
O	**-3.13901900**	**-1.53322100**	**-0.39652900**

9. Computational methods

All calculation were performed by using the the B3LYP functional[1,2] method in conjunction with the Grimme's dispersion contribution correction[3]. Herein, the 6-311++G** basis set was used for C, H and O atoms while the LANL2DZ was applied for Iodine atom. The solvation model based on electron density (SMD)[4] with Methanol solvent attached was used throughout. Vibrational frequency calculations, from which the thermal corrections to Gibbs free energy (G) were derived, have been performed for each optimized structure at the same computational level to ensure these structures without imaginary frequences.Then, the changes of zero-point-corrected Gibbs free energies of the considered reactions were calculated at 298 K and pressure 1 atm on the basis of the optimized structures. Finally, all the abovementioned calculations in this work were performed using the Gaussian 16 software[5]. Dimensional plots of molecular configurations were generated with the GaussView program[6].

[1] A. D. Becke, *J. Chem. Phys*., 1993, **98**, 5648–5652.
[2] C. Lee, W. Yang and R. G. Parr, *Phys. Rev. B*., 1988, **37**, 785–789.
[3] S. Grimme, S. Ehrlich, L. Goerigk, J. Comput. Chem. 2011, **32**, 1456.
[4] A. V. Marenich, C. J. Cramer, D. G. Truhlar, J. Phys. Chem. B 2009, **113**, 6378.
[5] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, G. Z. J. Bloino, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, D. J. Fox, Gaussian 16, Revision A.03, Gaussian, Inc., Wallingford, CT 2016.
[6] R. D. Dennington II., T. A. Keith, J. M. Millam, GaussView, Version 6, Semichem Inc., Shawnee Mission, KS 2016.