Electronic Supplementary Material (ESI) for Green Chemistry.

Ambient and aerobic carbon-carbon bond cleavage toward α-ketoester synthesis by transition-metal-free photocatalysis

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Contents

General experimental information

All experiments were carried out under air atmosphere. The enaminones **1** were synthesized following literature process,[1-2] all other chemicals used in the experiments were obtained from commercial sources and used directly without further treatment. ^{1}H and ^{13}C NMR spectra were recorded in 400 MHz apparatus in $CDCl_3$. The frequencies for ^{1}H NMR and ^{13}C NMR test are 400 MHz and 100 MHz, respectively. The chemical shifts were reported in ppm with TMS as internal standard. Melting points were tested in X-4A instrument without correcting temperature and the HRMS data for all new products were obtained under ESI model with TOF analyzer.

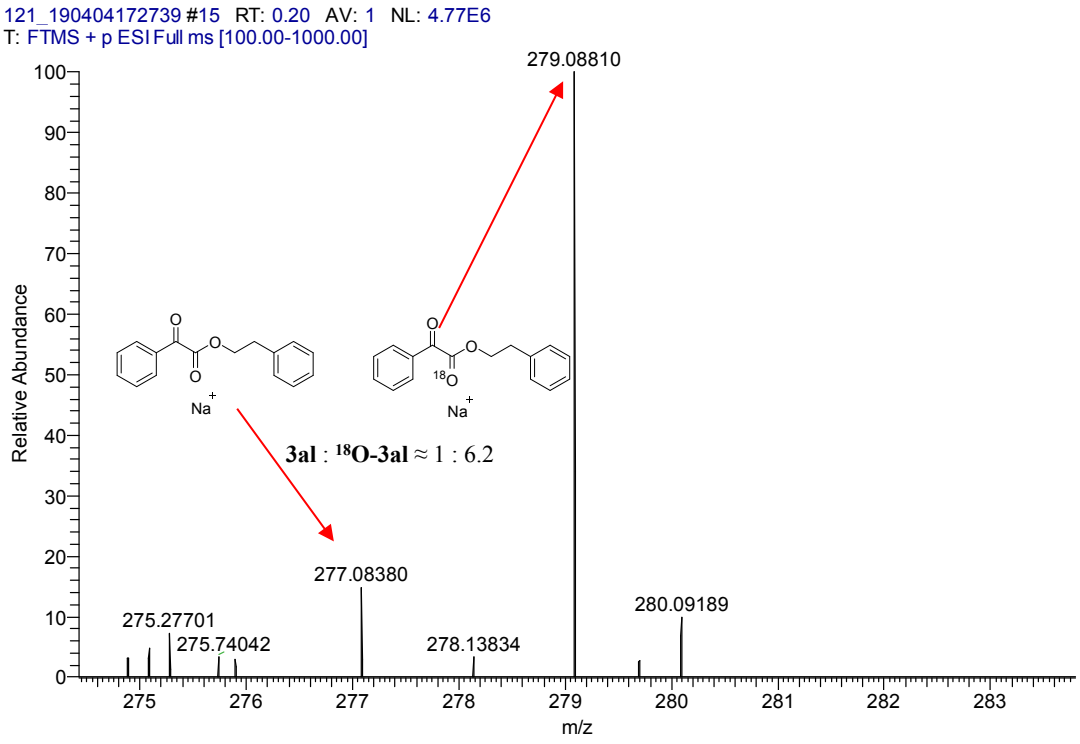


Figure S1 The ESI-HRMS spectra of the ^{18}O-labeled product **3al**

The fluorescence quenching experiments of RB with enaminone 1a. The fluorescence quenching experiments were recorded in a Hitachi F-7000 fluorescence spectrophotometer. The excitation wavelength and emission wavelength were fixed at 527 nm and 537 nm, respectively. In the blank experiment, RB solution of EtOH was recorded in the concentration of 1×10^{-3} mol/L. Subsequently, different amounts of enaminone **1a** was solved in the solution, and the resulting changes in fluorescence intensity in the **1a** concentration of 2×10^{-2} mol/L, 4×10^{-2} mol/L, 6×10^{-2} mol/L, 8×10^{-2} mol/L, 10×10^{-2} mol/L, 12×10^{-2} mol/L were collected in Figure S2. According to the results as well as the corresponding Stern-Volmer plots (Figure S3), the enaminone **1a** did not show quenching effect to the fluorescence intensity of RB, which indicated that enaminone **1** was not the energy acceptor of the excited RB in the titled reaction.

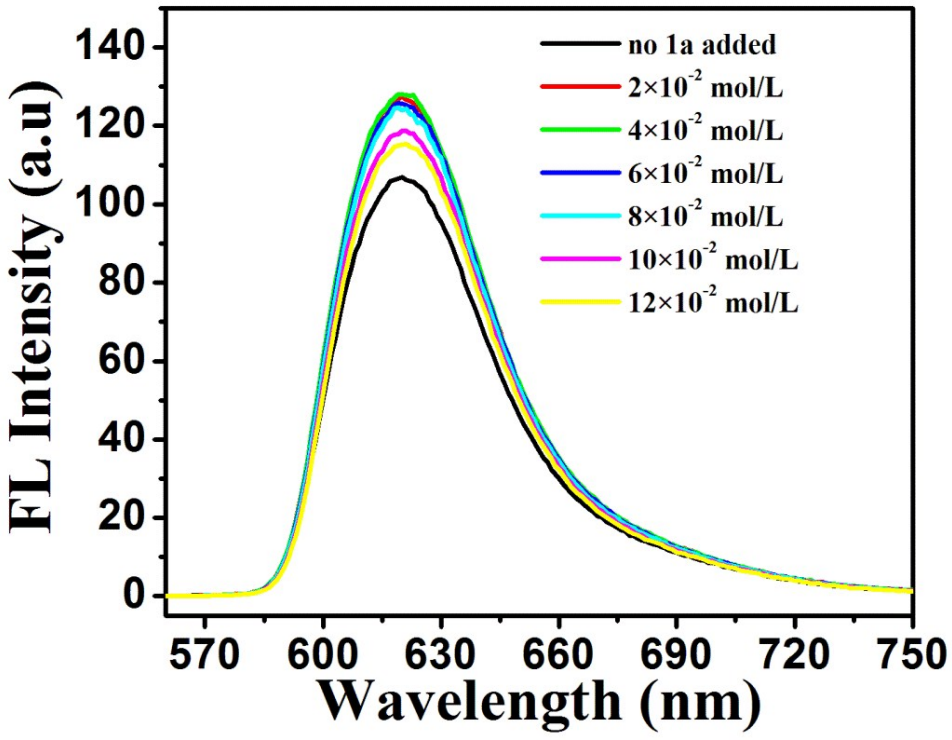


Figure S2 The quenching of RB fluorescence emission with enaminone **1a**

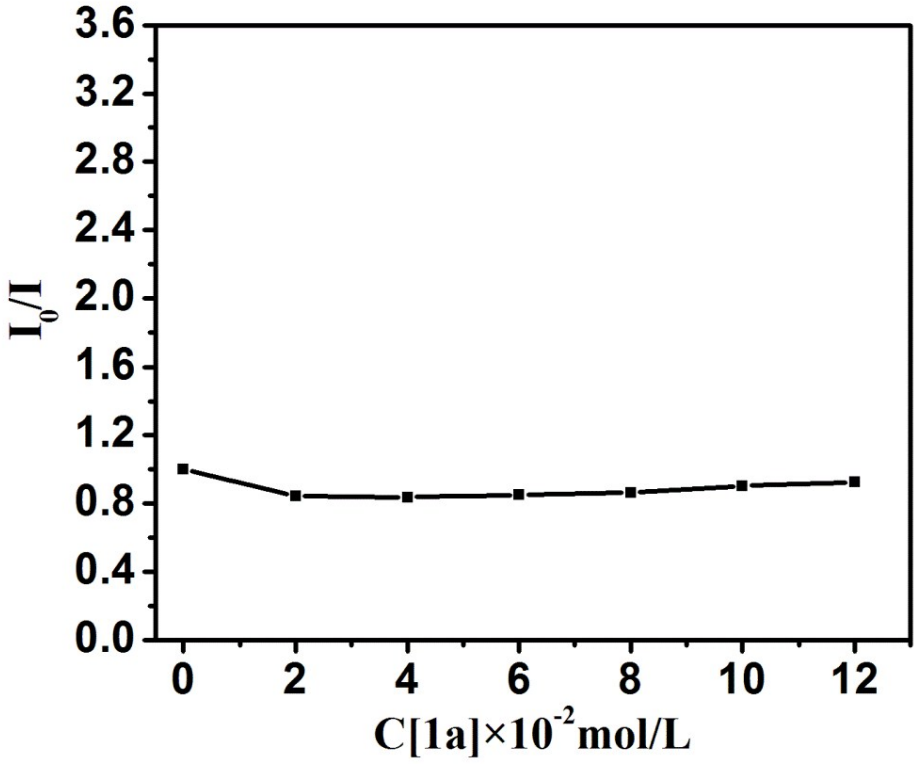


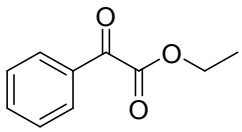
Figure S3 the Stern-Volmer plot. I_0 is the inherent fluorescence intensity of RB. I is the fluorescence intensity of RB in the presence of **1a**

General procedure for the synthesis of of α-ketoesters 3. In a 15 mL test tube were charged with enaminone **1** (0.2 mmol), RB (0.002 mmol), AcOH (0.4 mmol), alcohol **2** (1 mL, or 1 mmol solid alcohol substrate and 1 mL DMF) and 4Å molecular sieve (80 mg). The mixture was irradiation with 20 W green LEDs for 24h at room temperature. Upon completion (TLC), the mixture was moved to the round bottom flask, and the reaction tube was washed additionally with ethyl acetate (5mL) to fully transfer the residue. The solvent in the flask was then removed at reduced pressure, and the residue was purified by silica gel column chromatography with the elution of mixed ethyl acetate and petroleum ether (v/v = 1:20-1:3). For the reaction of solid alcohols, after the reaction completion, water (5 mL) was added to the vessel, and the suspension was extracted with ethyl acetate (3 ×10 mL). The combined organic phase

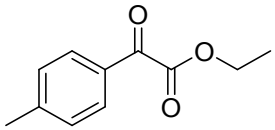
was dried over Na_2SO_4. After filtering, the acquired solution was employed to reduced pressure to remove the organic solvent. And analogous chromatographic purification using mixed ethyl acetate and petroleum (v/v = 1:8) as eluent was executed to obtain corresponding products.

General procedure for the synthesis of quinoxalin-2(1*H*)-ones 5. In a 15 mL test tube were charged with enaminone 1 (0.2 mmol), RB (0.002 mmol), AcOH (0.4 mmol), alcohol 2 (1 mL, or 1 mmol solid alcohol substrate and 1 mL DMF) and 4Å molecular sieve (80 mg). The mixture was irradiation with 20 W green LEDs for 24h at room temperature. Subsequently, diamine 4 (0.2 mmol) solved in EtOH (1 mL) was added, and the resulting mixture was further stirred at room temperature for 12 h. Upon completion (TLC), the mixture was moved to the round bottom flask, and the reaction tube was washed additionally with ethyl acetate (5mL) to fully transfer the residue. The solvent in the flask was then removed at reduced pressure, and the residue was purified by silica gel column chromatography with the elution of mixed ethyl acetate and petroleum ether (v/v = 1:5).

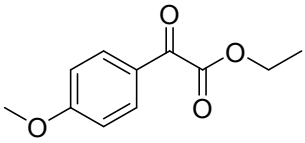
Characterization data of all products



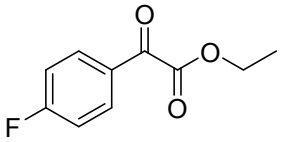
Ethyl 2-oxo-2-phenylacetate (**3a**)[3] Colorless liquid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.04-8.00 (m, 2 H), 7.66 (t, *J* = 7.4 Hz, 1 H), 7.52 (t, *J* = 7.8 Hz, 2 H), 4.46 (q, *J* = 7.0 Hz, 2 H), 1.43 (t, *J* = 7.0 Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 186.4, 163.8, 134.9, 132.5, 130.0, 128.9, 62.3, 14.1.



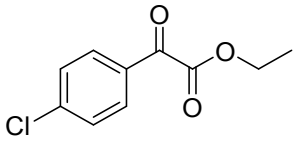
Ethyl 2-oxo-2-(p-tolyl)acetate (**3b**)[4] Colorless liquid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.90 (d, *J* = 8.2 Hz, 2 H), 7.30 (d, *J* = 8.0 Hz, 2 H), 4.44 (q, *J* = 7.0 Hz, 2 H), 2.43 (s, 3 H), 1.42 (t, *J* = 7.2 Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 186.1, 164.0, 146.2, 130.1, 129.6, 129.0, 62.2, 21.9, 14.1.



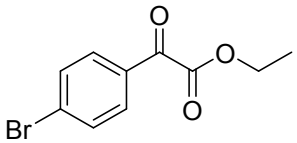
Ethyl 2-(4-methoxyphenyl)-2-oxoacetate (**3c**)[4] Colorless liquid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.00 (d, *J* = 8.0 Hz, 2 H), 6.97 (d, *J* = 8.0 Hz, 2 H), 4.43 (q, *J* = 7.0 Hz, 2 H), 3.89 (s, 3 H), 1.42 (t, *J* = 7.0 Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 184.9, 165.0, 164.2, 132.5, 125.5, 114.2, 62.1, 55.6, 14.1.



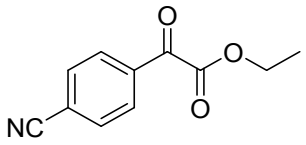
Ethyl 2-(4-fluorophenyl)-2-oxoacetate (**3d**)[3] Colorless liquid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.16-7.99 (m, 2 H), 7.24-7.12 (m, 2 H), 4.45 (q, *J* = 7.2 Hz, 2 H), 1.43 (t, *J* = 7.2 Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 184.5, 166.9 (d, $^1J_{C\text{-}F}$ = 257 Hz), 163.4, 133.0, 132.9, 129.7(d, $^4J_{C\text{-}F}$ = 3 Hz), 116.2 (d, $^2J_{C\text{-}F}$ = 22 Hz), 62.4, 14.1.



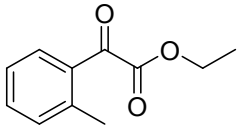
Ethyl 2-(4-chlorophenyl)-2-oxoacetate (**3e**)[4] Colorless liquid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.98 (d, *J* = 8.6 Hz, 2 H), 7.49 (d, *J* = 8.6 Hz, 2 H), 4.45 (q, *J* = 7.0 Hz, 2 H), 1.42 (t, *J* = 7.0 Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 184.9, 163.2, 141.6, 131.4, 134.0, 129.3, 62.5, 14.1.



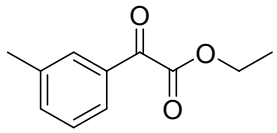
Ethyl 2-(4-bromophenyl)-2-oxoacetate (**3f**)[5] Colorless liquid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.90 (d, *J* = 8.6 Hz, 2 H), 7.66 (d, *J* = 8.6 Hz, 2 H), 4.45 (q, *J* = 7.0 Hz, 2 H), 1.42 (t, *J* = 7.0 Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 185.1, 163.2, 132.3, 131.4, 131.4, 130.5, 62.5, 14.1.



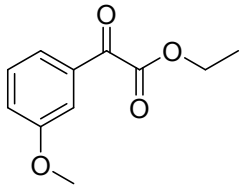
Ethyl 2-(4-cyanophenyl)-2-oxoacetate (**3g**)[6] Colorless liquid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.16 (d, *J* = 8.0 Hz, 2 H), 7.82 (d, *J* = 8.0 Hz, 2 H), 4.47 (q, *J* = 7.0 Hz, 2 H), 1.44 (t, *J* = 7.0 Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 184.4, 162.4, 135.6, 132.6, 130.4, 117.9, 117.5, 62.9, 14.1.



Ethyl 2-oxo-2-(o-tolyl)acetate (**3h**)[3] Colorless liquid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.69 (d, *J* = 7.8 Hz, 1 H), 7.51-7.46 (m, 1 H), 7.31 (t, *J* = 8.0 Hz, 2 H), 4.43 (q, *J* = 7.0 Hz, 2 H), 2.61 (s, 3 H), 1.41 (t, *J* = 7.0 Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 188.8, 164.6, 141.3, 133.6, 132.3, 132.2, 131.3, 125.9, 62.2, 21.4, 14.1.

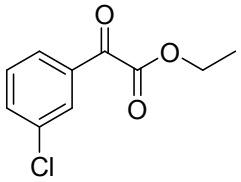


Ethyl 2-oxo-2-(m-tolyl)acetate (**3i**)[7] Colorless liquid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.80 (d, *J* = 7.2 Hz, 2 H), 7.46 (d, *J* = 7.4 Hz, 1 H), 7.39 (t, *J* = 7.8 Hz, 1 H), 4.45 (q, *J* = 7.0 Hz, 2 H), 2.42 (s, 3 H), 1.42 (t, *J* = 7.0 Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 186.6, 164.0, 138.8, 135.7, 132.5, 130.3, 128.8, 127.3, 62.2, 21.2, 14.1.

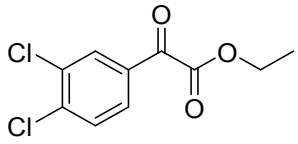


Ethyl 2-(3-methoxyphenyl)-2-oxoacetate (**3j**)[8] Colorless liquid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.59-7.52 (m, 2 H), 7.42 (t, *J* = 7.8 Hz, 1 H), 7.20 (dd, *J* = 8.2, 2.2 Hz, 1 H),

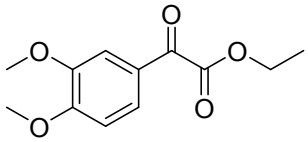
4.45 (q, *J* = 7.0 Hz, 2 H), 3.86 (s, 3 H), 1.43 (t, *J* = 7.0 Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 186.3, 163.9, 156.0, 133.7, 129.9, 123.1, 121.8, 113.3, 62.3, 55.5, 14.1.



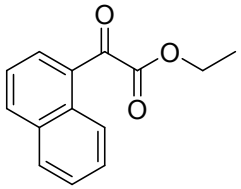
Ethyl 2-(3-chlorophenyl)-2-oxoacetate (**3k**)[8] Colorless liquid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.94 (s, 1 H), 7.84 (d, *J* = 7.8 Hz, 1 H), 7.58-7.52 (m, 1 H), 7.39 (t, *J* = 7.8 Hz, 1 H), 4.38 (q, *J* = 7.0 Hz, 2 H), 1.36 (t, *J* = 7.0 Hz, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 184.8, 163.0, 135.2, 134.8, 134.1, 130.2, 129.9, 128.2, 62.6, 14.1.



Ethyl 2-(3,4-dichlorophenyl)-2-oxoacetate (**3l**)[9] Colorless liquid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.15 (s, 1 H), 7.89 (dd, *J* = 8.2, 1.6 Hz, 1 H), 7.60 (d, *J* = 8.4 Hz, 1 H), 4.46 (q, *J* = 7.0 Hz, 2 H), 1.43 (t, *J* = 7.0 Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 183.6, 162.5, 139.7, 133.7, 132.2, 131.8, 131.0, 129.0, 62.8, 14.1.

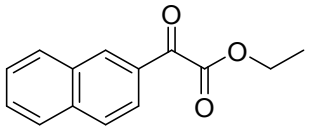


Ethyl 2-(3,4-dimethoxyphenyl)-2-oxoacetate (**3m**)[4] Colorless liquid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.64 (dd, 1 H), 7.56 (d, *J* = 1.8 Hz, 1 H), 6.93 (d, *J* = 8.4 Hz, 1 H), 4.44 (q, *J* = 7.0 Hz, 2 H), 3.96 (s, 6 H), 1.42 (t, *J* = 7.0 Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 185.0, 164.1, 155.0, 149.4, 126.2, 125.6, 110.8, 110.3, 62.1, 56.2, 56.1, 14.1.

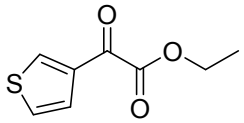


Ethyl 2-(naphthalen-1-yl)-2-oxoacetate (**3n**) Colorless liquid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.04 (d, *J* = 8.6 Hz, 1 H), 8.10 (d, *J* = 8.2 Hz, 1 H), 7.98 (dd, 1 H), 7.90 (d, *J* = 8.0 Hz, 1 H), 7.70-7.66 (m, 1 H), 7.60-7.52 (m, 2 H), 4.48 (q, *J* = 7.0 Hz, 2 H),

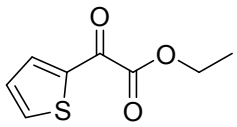
1.43 (t, J = 7.0 Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 188.9, 164.6, 135.8, 134.0, 133.9, 131.0, 129.3, 128.8, 128.3, 127.0, 125.6, 124.3, 62.4, 14.1; ESI-HRMS Calcd for $C_{14}H_{12}O_3Na$ $[M+Na]^+$ 251.06787, found 251.06723.



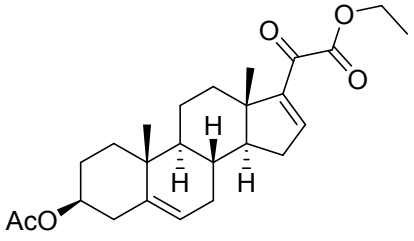
Ethyl 2-(naphthalen-2-yl)-2-oxoacetate (**3o**)[3] Colorless liquid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.55 (s, 1 H), 8.04 (dd, J = 8.6, 1.6 Hz, 1 H), 7.96 (d, J = 8.2 Hz, 1 H), 7.89 (dd, J = 15.6, 8.4 Hz, 2 H), 7.66-7.61 (m, 1 H), 7.59-7.54 (m, 1 H), 4.51 (q, J = 7.0 Hz, 2 H), 1.45 (t, J = 7.2 Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 186.3, 163.9, 136.4, 133.4, 132.3, 123.0, 129.9, 129.5, 128.9, 127.9, 127.2, 124.0, 62.4, 14.2.



Ethyl 2-oxo-2-(thiophen-3-yl)acetate (**3p**)[10] Colorless liquid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.54 (s, 1 H), 7.69 (d, J = 5.0 Hz, 1 H), 7.38-7.34 (m, 1 H), 4.42 (q, J = 7.0 Hz, 2 H), 1.42 (t, J = 7.0 Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 178.2, 162.4, 137.6, 127.9, 126.6, 62.5, 14.1.

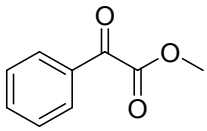


Ethyl 2-oxo-2-(thiophen-2-yl)acetate (**3q**)[4] Colorless liquid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.13 (dd, J = 3.8, 1.0 Hz, 1 H), 7.83 (dd, J = 4.8, 1.0 Hz, 1 H), 7.22-7.17 (m, 1 H), 4.44 (q, J = 7.0 Hz, 2 H), 1.43 (t, J = 7.2 Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 176.4, 161.7, 139.1, 137.4, 137.2, 128.6, 62.7, 14.0.

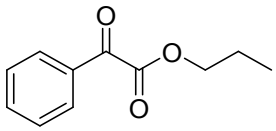


Ethyl 2-((3S,8R,9S,10R,13S,14S)-3-Acetoxy-10,13-dimethyl-2,3,4,7,8,9,10,11,12,13,14,15-dodecahydro-1H-cyclopenta[a]phenanthren-17-yl)-

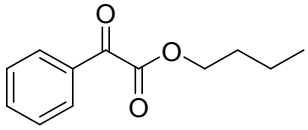
2-oxoacetate (**3r**) White solid; mp 143-144 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.13-7.10 (m, 1 H), 5.39 (d, *J* = 5.0 Hz, 1 H), 4.61 (tt, *J* = 10.4, 5.2 Hz, 1 H), 4.33 (q, *J* = 7.0 Hz, 2 H), 2.47-2.39 (m, 2 H), 2.36-2.31 (m, 2 H), 2.17-2.10 (m, 1 H), 2.04 (s, 3 H), 1.89-1.84 (m, 2 H), 1.72-1.48 (m, 8 H), 1.36 (q, *J* = 6.6, 6.0 Hz, 4 H), 1.19-1.14 (m, 1 H), 1.07 (s, 3 H), 0.97 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 183.7, 170.5, 163.1, 152.7, 151.0, 140.3, 121.9, 73.8, 62.0, 56.0, 50.4, 46.5, 38.1, 36.9, 36.8, 34.1, 33.3, 31.5, 30.1, 27.7, 21.4, 20.6, 19.2, 15.6, 14.1; ESI-HRMS Calcd for $C_{25}H_{34}O_5Na$ $[M+Na]^+$ 437.22985, found 437.22942.



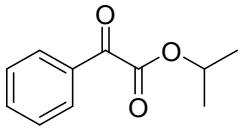
Methyl 2-oxo-2-phenylacetate (**3ab**)[11] Colorless liquid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.04-8.00 (m, 2 H), 7.67 (t, *J* = 7.4 Hz, 1 H), 7.52 (t, *J* = 7.8 Hz, 2 H), 3.98 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 186.0, 164.0, 135.0, 132.5, 130.1, 128.9, 52.7.



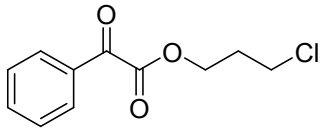
Propyl 2-oxo-2-phenylacetate (**3ac**)[11] Colorless liquid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.04-7.98 (m, 2 H), 7.66 (t, *J* = 7.4 Hz, 1 H), 7.52 (t, *J* = 7.8 Hz, 2 H), 4.36 (t, *J* = 6.6 Hz, 2 H), 1.81 (q, *J* = 7.0 Hz, 2 H), 1.02 (t, *J* = 7.4 Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 186.5, 164.0, 134.8, 132.5, 123.0, 128.9, 67.7, 21.9, 10.3.



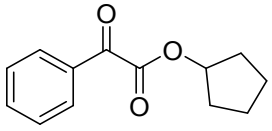
Butyl 2-oxo-2-phenylacetate (**3ad**)[11] Colorless liquid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.06-7.95 (m, 2 H), 7.66 (t, *J* = 7.4 Hz, 1 H), 7.51 (t, *J* = 7.8 Hz, 2 H), 4.40 (t, *J* = 6.6 Hz, 2 H), 1.80-1.73 (m, 2 H), 1.50-1.41 (m, 2 H), 0.97 (t, *J* = 7.4 Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 186.5, 164.0, 134.9, 134.8, 132.5, 123.0, 128.9, 66.1, 30.5, 19.0, 13.6.



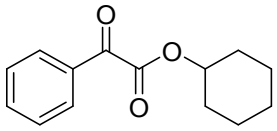
Isopropyl 2-oxo-2-phenylacetate (**3ae**)[11] Colorless liquid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.00 (d, *J* = 7.6 Hz, 2 H), 7.66 (t, *J* = 7.4 Hz, 1 H), 7.51 (t, *J* = 7.8 Hz, 2 H), 5.37-5.29 (m, 1 H), 1.42 (s, 6 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 186.7, 163.6, 134.8, 132.6, 129.9, 128.9, 70.7, 21.7.



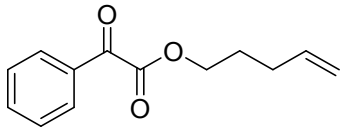
3-Chloropropyl 2-oxo-2-phenylacetate (**3af**)[7] Colorless liquid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.05-7.97 (m, 2 H), 7.70-7.65 (m, 1 H), 7.53 (t, *J* = 7.8 Hz, 2 H), 4.56 (t, *J* = 6.0 Hz, 2 H), 3.67 (t, *J* = 6.2 Hz, 2 H), 2.25 (p, *J* = 6.2 Hz, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 186.0, 163.6, 135.0, 132.4, 130.0, 129.0, 62.7, 40.8, 31.2.



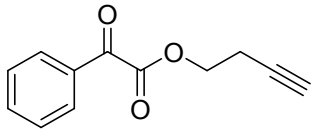
Cyclopentyl 2-oxo-2-phenylacetate (**3ag**)[12] Colorless liquid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.02-7.95 (m, 2 H), 7.68-7.63 (m, 1 H), 7.51 (t, *J* = 7.0 Hz, 2 H), 5.52-5.46 (m, 1 H), 2.03-1.97 (m, 2 H), 1.92-1.86 (m, 2 H), 1.82-1.75 (m, 2 H), 1.68-1.62 (m, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 186.7, 163.9, 134.8, 132.6, 129.9, 128.9, 79.7, 32.7, 23.7.



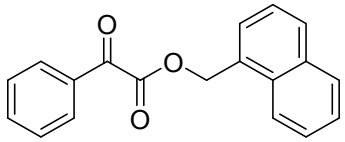
Cyclohexyl 2-oxo-2-phenylacetate (**3ah**)[13] Colorless liquid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.99 (d, *J* = 7.2 Hz, 2 H), 7.66 (t, *J* = 7.4 Hz, 1 H), 7.51 (t, *J* = 7.6 Hz, 2 H), 5.14-5.06 (m, 1 H), 2.04-1.98 (m, 2 H), 1.84-1.76 (m, 2 H), 1.61-1.57 (m, 3 H), 1.48-1.40 (m, 2 H), 1.33-1.28 (m, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 186.8, 163.7, 134.7, 132.6, 129.9, 128.9, 75.4, 31.5, 25.2, 23.6.



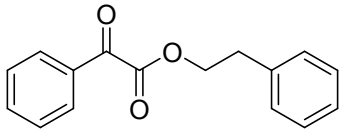
Pent-4-en-1-yl 2-oxo-2-phenylacetate (**3ai**) Colorless liquid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.00 (d, *J* = 7.0 Hz, 2 H), 7.66 (t, *J* = 7.2 Hz, 1 H), 7.52 (t, *J* = 7.0 Hz, 2 H), 5.90-5.72 (m, 1 H), 5.13-4.95 (m, 2 H), 4.40 (t, *J* = 5.6 Hz, 2 H), 2.19 (d, *J* = 7.2 Hz, 2 H), 1.95-1.81 (m, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 186.4, 163.9, 136.9, 134.9, 132.5, 130.0, 128.9, 115.8, 65.6, 29.8, 27.6; ESI-HRMS Calcd for $C_{13}H_{14}O_3Na$ $[M+Na]^+$ 241.08352, found 241.08300.



But-3-yn-1-yl 2-oxo-2-phenylacetate (**3aj**) Colorless liquid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.07-8.00 (m, 2 H), 7.70-7.65 (m, 1 H), 7.52 (t, *J* = 7.6 Hz, 2 H), 4.51 (t, *J* = 6.8 Hz, 2 H), 2.70 (td, *J* = 6.8, 2.6 Hz, 2 H), 2.06 (t, *J* = 2.6 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 185.9, 163.4, 135.0, 132.4, 130.1, 128.9, 79.2, 70.6, 63.6, 18.9; ESI-HRMS Calcd for $C_{12}H_{10}O_3Na$ $[M+Na]^+$ 225.05222, found 225.05182.

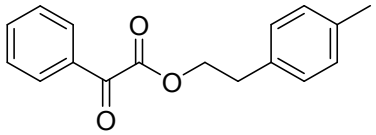


Naphthalen-1-ylmethyl 2-oxo-2-phenylacetate (**3ak**) Colorless liquid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.08 (d, *J* = 8.2 Hz, 1H), 7.94-7.88 (m, 4 H), 7.65-7.43 (m, 7 H), 5.89 (s, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 186.0, 163.8, 134.9, 133.8, 132.4, 131.5, 130.1, 130.0, 129.9, 128.9, 128.2, 126.8, 126.1, 125.3, 123.3, 66.0; ESI-HRMS Calcd for $C_{19}H_{14}O_3Na$ $[M+Na]^+$ 313.08352, found 313.08267.

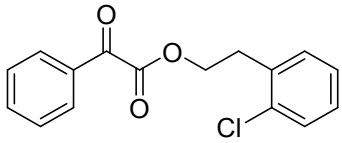


Phenethyl 2-oxo-2-phenylacetate (**3al**)[13] Colorless liquid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.85 (d, *J* = 7.8 Hz, 2 H), 7.63 (t, *J* = 7.4 Hz, 1 H), 7.45 (t, *J* = 7.6 Hz, 2H), 7.33-7.24 (m, 5 H), 4.62 (t, *J* = 7.0 Hz, 2 H), 3.09 (t, *J* = 7.0 Hz, 2 H); ^{13}C NMR (100

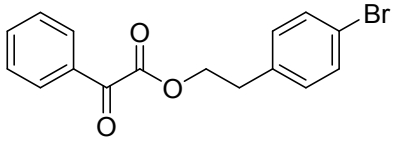
MHz, $CDCl_3$): δ 186.3, 163.7, 137.0, 134.9, 132.4, 130.0, 129.0, 128.9, 128.7, 126.9, 66.4, 35.0.



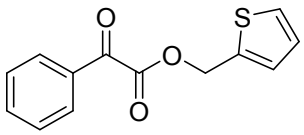
4-Methylphenethyl 2-oxo-2-phenylacetate (**3am**) Colorless liquid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.89-7.84 (m, 2 H), 7.63 (t, *J* = 7.4 Hz, 1 H), 7.45 (t, *J* = 7.8 Hz, 2 H), 7.15-7.10 (m, 4 H), 4.59 (t, *J* = 7.0 Hz, 2 H), 3.05 (t, *J* = 7.0 Hz, 2 H), 2.34 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 186.3, 163.7, 136.4, 134.8, 133.8, 132.4, 130.0, 129.4, 128.9, 128.8, 66.6, 34.6, 21.1; ESI-HRMS Calcd for $C_{17}H_{16}O_3Na$ $[M+Na]^+$ 291.09917, found 291.09852.



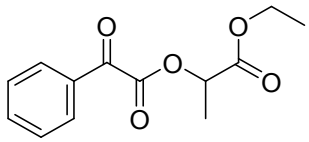
2-Chlorophenethyl 2-oxo-2-phenylacetate (**3an**)[14] Colorless liquid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.88-7.80 (m, 2 H), 7.65 (t, *J* = 7.4 Hz, 1H), 7.47 (t, *J* = 7.8 Hz, 2 H), 7.28 (d, *J* = 8.4 Hz, 2 H), 7.19 (d, *J* = 8.4 Hz, 2 H), 4.60 (t, *J* = 6.8 Hz, 2 H), 3.06 (t, *J* = 6.8 Hz, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 186.1, 163.6, 135.5, 134.9, 132.8, 132.3, 130.4, 123.0, 128.9, 128.8, 66.0, 34.3.



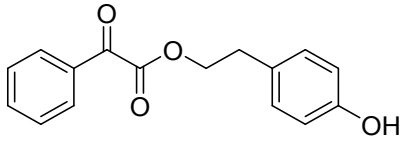
4-Bromophenethyl 2-oxo-2-phenylacetate (**3ao**)[14] Colorless liquid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.83 (d, *J* = 7.8 Hz, 2 H), 7.65 (t, *J* = 7.4 Hz, 1 H), 7.49-7.42 (m, 4 H), 7.13 (d, *J* = 8.2 Hz, 2 H), 4.59 (t, *J* = 6.8 Hz, 2 H), 3.04 (t, *J* = 6.8 Hz, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 186.1, 163.6, 136.0, 135.0, 132.3, 131.8, 130.8, 130.0, 128.9, 120.8, 65.9, 34.4.



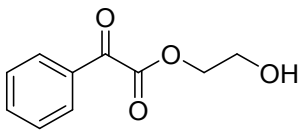
Thiophen-2-ylmethyl 2-oxo-2-phenylacetate (**3ap**) Colorless liquid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.99-7.93 (m, 2 H), 7.66-7.62 (m, 1 H), 7.48 (t, *J* = 7.8 Hz, 3 H), 7.38 (dd, *J* = 5.1, 1.0 Hz, 1 H), 7.22 (d, *J* = 3.4 Hz, 1 H), 7.04-6.99 (m, 1 H), 5.57 (s, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 185.8, 163.4, 136.2, 135.0, 132.4, 130.1, 129.5, 128.9, 127.7, 127.1, 61.8; ESI-HRMS Calcd for $C_{11}H_{12}O_5SNa$ $[M+Na]^+$ 269.02429, found 269.02385.



Ethyl 2-(2-oxo-2-phenylacetoxy)propanoate (**3aq**) Colorless liquid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.13 (d, *J* = 7.4 Hz, 2 H), 7.68 (t, *J* = 7.4 Hz, 1 H), 7.54 (t, *J* = 7.6 Hz, 2 H), 5.33 (q, *J* = 7.0 Hz, 1 H), 4.30 (q, *J* = 7.0 Hz, 2 H), 1.64 (d, *J* = 7.0 Hz, 3 H), 1.34 (t, *J* = 7.0 Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 186.1, 169.8, 163.4, 135.1, 132.4, 130.3, 128.9, 70.3, 61.9, 16.8, 14.1; ESI-HRMS Calcd for $C_{13}H_{14}O_5Na$ $[M+Na]^+$ 273.07334, found 273.07251.

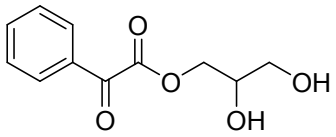


4-Hydroxyphenethyl 2-oxo-2-phenylacetate (3ar) Yellow liquid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.86 (d, *J* = 8.0 Hz, 2 H), 7.64 (t, *J* = 7.0 Hz, 1 H), 7.47 (t, *J* = 7.6 Hz, 2 H), 7.12 (d, *J* = 8.0 Hz, 2 H), 6.78 (d, *J* = 8.0 Hz, 2 H), 4.99 (s, 1 H), 4.57 (t, *J* = 6.8 Hz, 2 H), 3.01 (t, *J* = 7.0 Hz, 2 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 186.4, 163.8, 154.5, 134.9, 132.4, 130.2, 130.0, 129.1, 128.8, 115.5, 66.6, 34.1; ESI-HRMS Calcd for $C_{16}H_{14}O_4Na$ $[M+Na]^+$ 293.07843, found 293.07780.

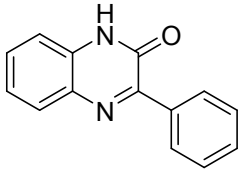


2-Hydroxyethyl 2-oxo-2-phenylacetate (**3as**) Reddish brown liquid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.03 (d, *J* = 7.2 Hz, 2 H), 7.67 (t, *J* = 7.4 Hz, 1 H), 7.51 (t, *J* = 7.6 Hz, 2 H), 4.54-4.47 (m, 2 H), 3.99-3.93 (m, 2 H), 2.24 (s, 1 H); ^{13}C NMR (100 MHz,

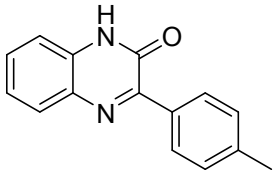
$CDCl_3$): δ 186.1, 163.6, 135.1, 132.4, 130.2, 128.9, 67.5, 60.6; ESI-HRMS Calcd for $C_{10}H_{10}O_4Na$ $[M+Na]^+$ 217.04713, found 217.04684.



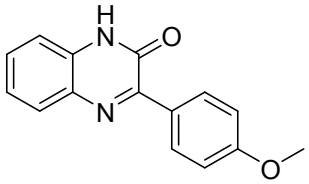
2,3-Dihydroxypropyl 2-oxo-2-phenylacetate (**3at**) Light brown liquid; ^1H NMR (400 MHz, $CDCl_3$): δ 8.02 (d, *J* = 8.2 Hz, 2 H), 7.66 (t, *J* = 7.4 Hz, 1 H), 7.50 (t, *J* = 7.0 Hz, 2 H), 4.51-4.38 (m, 2 H), 4.12-4.05 (m, 1 H), 3.81-3.74 (m, 1 H), 3.72-3.65 (m, 1 H), 3.13-3.02 (m, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 186.0, 163.4, 135.2, 132.2, 130.2, 129.0, 69.8, 66.8, 63.2; ESI-HRMS Calcd for $C_{11}H_{12}O_5Na$ $[M+Na]^+$ 247.05769, found 247.05710.



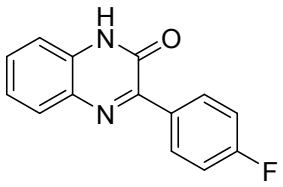
3-Phenylquinoxalin-2(1H)-one (**5a**)[15] Yellow solid; mp 244-245 °C; ^1H NMR (400 MHz, DMSO-d_6): δ 12.57 (s, 1 H), 8.33-8.30 (m, 2 H), 7.86-7.83 (m, 1 H), 7.56-7.49 (m, 4 H), 7.37-7.33 (m, 2 H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 155.1, 154.6, 136.1, 132.5, 132.5, 130.8, 130.6, 129.7, 129.2, 128.3, 123.8, 115.6.



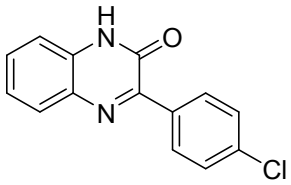
3-(*p*-Tolyl)quinoxalin-2(1H)-one (**5b**)[15] Yellow solid; mp 264-265 °C; ^1H NMR (400 MHz, DMSO-d_6): δ 12.50 (s, 1 H), 8.27 (d, *J* = 8.0 Hz, 2 H), 7.82 (d, *J* = 8.0 Hz, 1 H), 7.52 (t, *J* = 7.6 Hz, 1 H), 7.35-7.27 (m, 4 H), 2.38 (s, 3 H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 155.1, 154.2, 140.5, 133.4, 132.5, 132.4, 130.5, 129.6, 129.1, 128.9, 123.8, 115.5, 21.5.



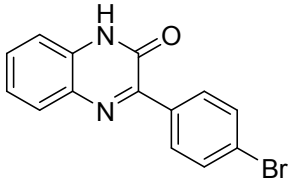
3-(4-Methoxyphenyl)quinoxalin-2(1H)-one (**5c**)[15] Light yellow solid; mp 275-276 ^{o}C; ^{1}H NMR (400 MHz, DMSO-d_6): δ 12.49 (s, 1 H), 8.40 (d, J = 8.8 Hz, 2 H), 7.81 (d, J = 7.8 Hz, 1 H), 7.51 (t, J = 7.4 Hz, 1H), 7.35-7.29 (m, 2 H), 7.05 (d, J = 8.0 Hz, 2 H), 3.85 (s, 3 H); ^{13}C NMR (100 MHz, DMSO-d_6): δ 161.5, 155.2, 153.6, 132.5, 132.2, 131.4, 130.2, 128.9, 128.6, 123.8, 115.5, 113.8, 55.8.



3-(4-Fluorophenyl)quinoxalin-2(1H)-one (**5d**) Yellow solid; mp 273-274 ^{o}C; ^{1}H NMR (400 MHz, DMSO-d_6): δ 12.60 (s, 1 H), 8.46-8.39 (m, 2 H), 7.84 (d, J = 8.0 Hz, 1 H), 7.58-7.53 (m, 1 H), 7.37-7.30 (m, 4 H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 163.8 (d, $^{1}J_{C\text{-}F}$ = 247 Hz), 155.0, 153.3, 132.6, 132.6, 132.5, 132.4, 132.2, 132.1 (d, $^{3}J_{C\text{-}F}$ = 8 Hz), 129.2, 123.9, 115.6, 115.3 (d, $^{2}J_{C\text{-}F}$ = 21 Hz); ESI-HRMS Calcd for $C_{14}H_{10}FN_2O$ $[M+Na]^+$ 241.07717, found 241.07677.

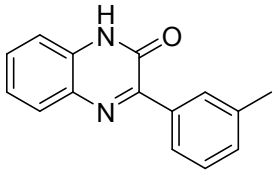


3-(4-Chlorophenyl)quinoxalin-2(1H)-one (**5e**)[15] Yellow solid; mp 286-287 ^{o}C; ^{1}H NMR (400 MHz, DMSO-d_6): δ 12.62 (s, 1 H), 8.39 (d, J = 8.0 Hz, 2 H), 7.84 (d, J = 8.0 Hz, 2 H), 7.59-7.55 (m, 3 H), 7.35 (d, J = 7.6 Hz, 2 H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 155.0, 153.2, 135.6, 134.8, 132.6, 132.4, 131.4, 131.0, 129.3, 128.4, 123.9, 115.6.

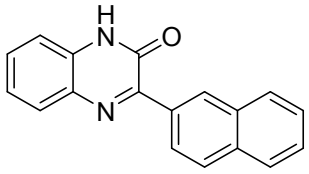


3-(4-Bromophenyl)quinoxalin-2(1H)-one (**5f**)[15] Yellow solid; mp 282-283 ^{o}C; ^{1}H NMR (400 MHz, DMSO-d_6): δ 12.63 (s, 1 H), 8.31 (d, J = 8.0 Hz, 2 H), 7.86-7.83 (m, 1 H), 7.71 (d, J = 8.0 Hz, 2 H), 7.58-7.54 (m, 1 H), 7.35 (d, J = 8.0 Hz, 2 H). ^{13}C

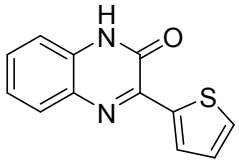
NMR (100 MHz, DMSO-d_6): δ 155.0, 153.3, 135.2, 132.6, 132.4, 131.7, 131.4, 131.0, 129.3, 124.5, 124.0, 115.6.



3-(*m*-Tolyl)quinoxalin-2(1H)-one (**5g**) Yellow solid; mp 225-226 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ 12.56 (s, 1 H), 8.13 (d, J = 6.4 Hz, 2 H), 7.86-7.83 (m, 1 H), 7.57-7.52 (m, 1 H), 7.41-7.32 (m, 4 H), 2.41 (s, 3 H); ^{13}C NMR (100 MHz, DMSO-d_6): δ 155.0, 154.7, 137.4, 136.1, 132.5, 131.3, 130.7, 130.0, 129.2, 128.2, 127.0, 123.8, 115.5, 21.6; ESI-HRMS Calcd for $C_{15}H_{12}N_2ONa$ $[M+Na]^+$ 259.08418, found 259.08373.



3-(Naphthalen-2-yl)quinoxalin-2(1H)-one (**5h**) Yellow solid; mp 135-136 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ 12.64 (s, 1 H), 9.12 (s, 1 H), 8.40 (dd, J = 8.0, 4.0 Hz, 1 H), 8.06 (d, J = 7.2 Hz, 1 H), 7.99 (m, 2 H), 7.90 (d, J = 7.8 Hz, 1 H), 7.61-7.54 (m, 3 H), 7.40-7.33 (m, 2 H); ^{13}C NMR (100 MHz, DMSO-d_6): δ 155.2, 154.0, 134.1, 133.5, 132.8, 132.6, 132.5, 130.8, 130.3, 129.5, 129.3, 128.0, 127.9, 127.7, 126.9, 126.4, 123.9, 115.6; ESI-HRMS Calcd for $C_{18}H_{12}N_2ONa$ $[M+Na]^+$ 295.08418, found 295.08369.



3-(Thiophen-2-yl)quinoxalin-2(1H)-one (**5i**)[16] Yellow solid; mp 167-168 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ 12.70 (s, 1 H), 8.44-8.41 (m, 1 H), 7.86-7.83 (m, 1 H), 7.79 (d, J = 8.0 Hz, 1 H), 7.55-7.51 (m, 1 H), 7.38-7.32 (m, 2 H), 7.27-7.24 (m, 1 H); ^{13}C NMR (100 MHz, DMSO-d_6): δ 153.9, 149.4, 139.4, 132.5, 132.4, 131.9, 131.8, 130.2, 128.6, 128.4, 124.1, 115.8.

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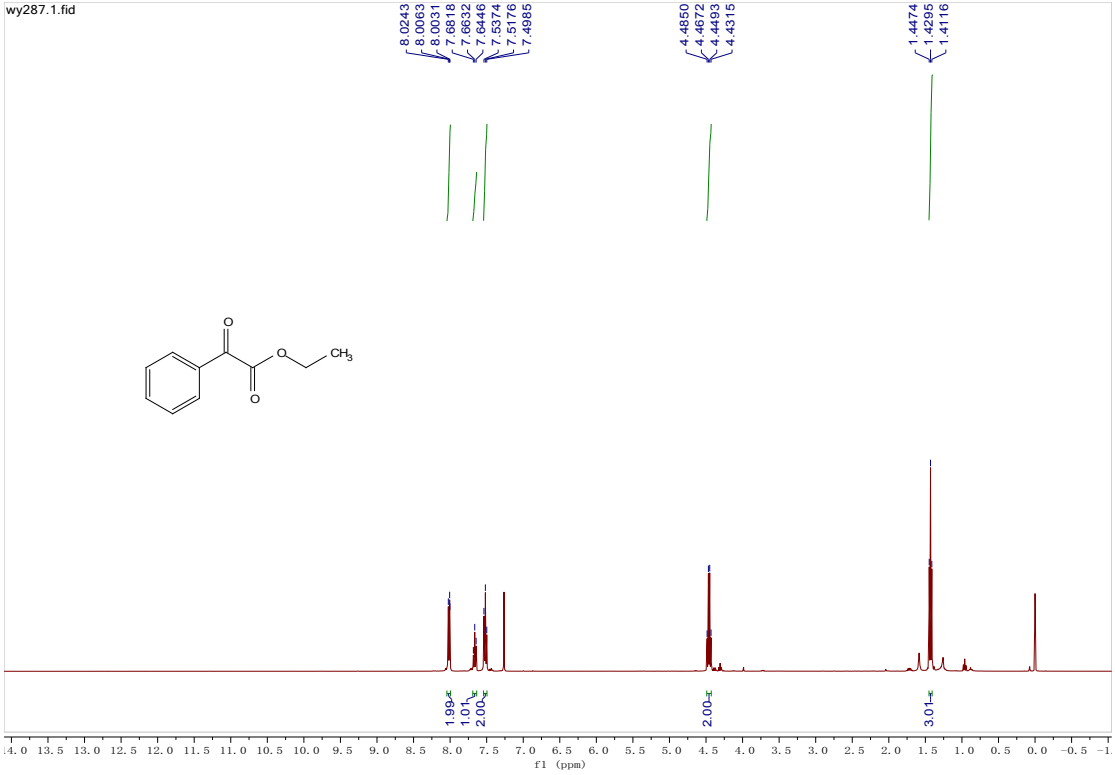
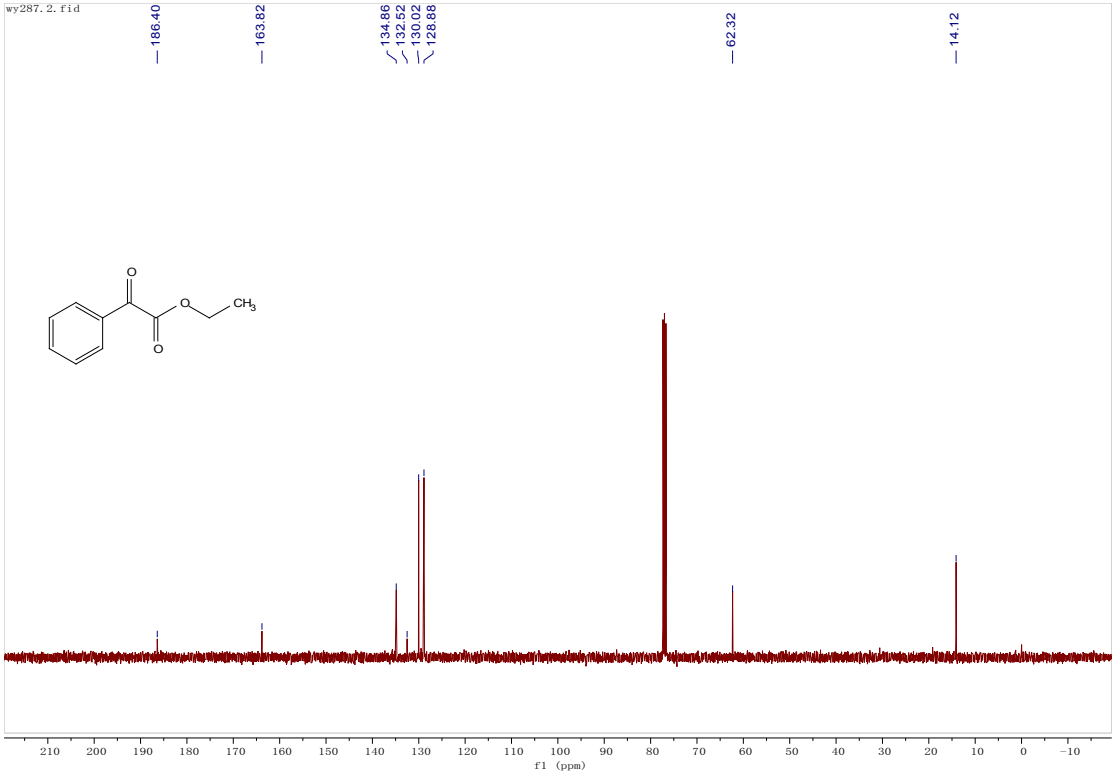
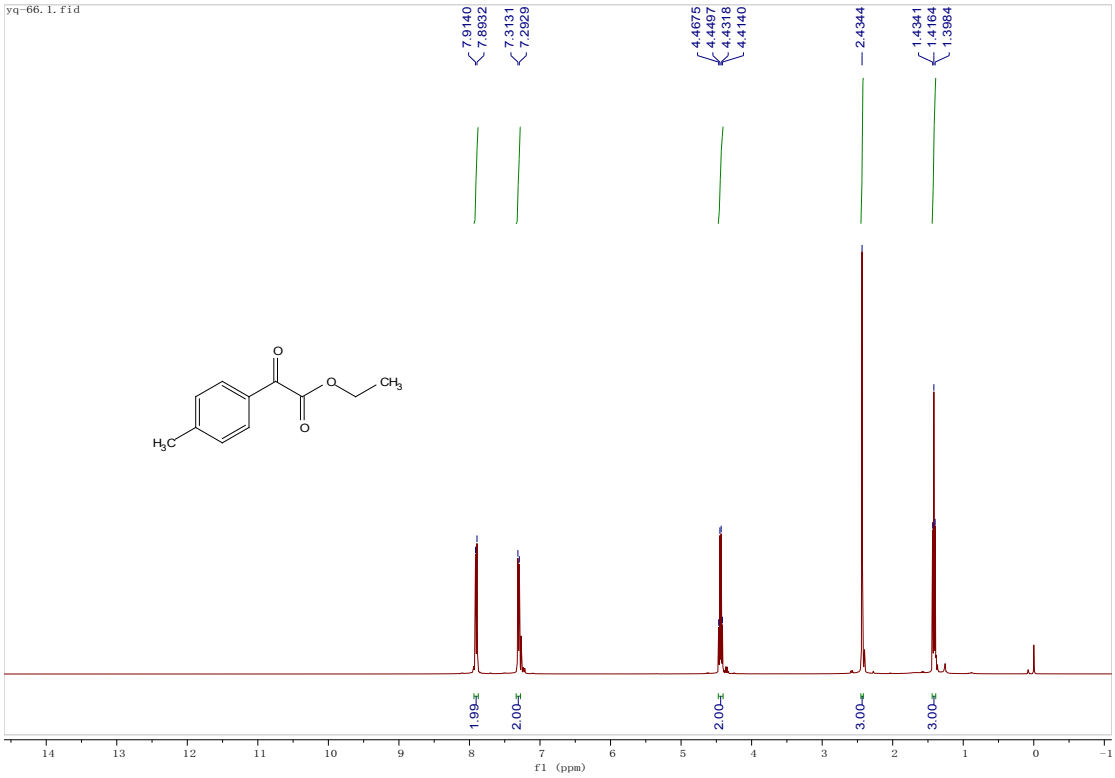
^{1}H and ^{13}C NMR spectra of all products

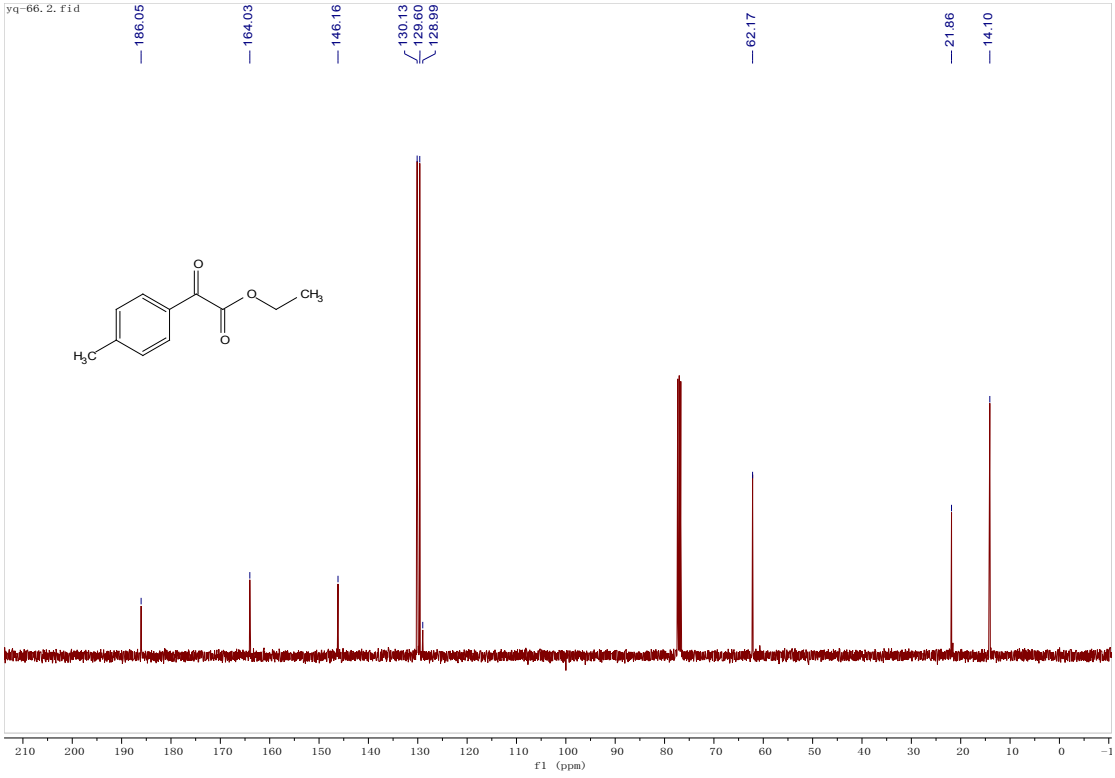
^{1}H and ^{13}C NMR spectra of **3a**



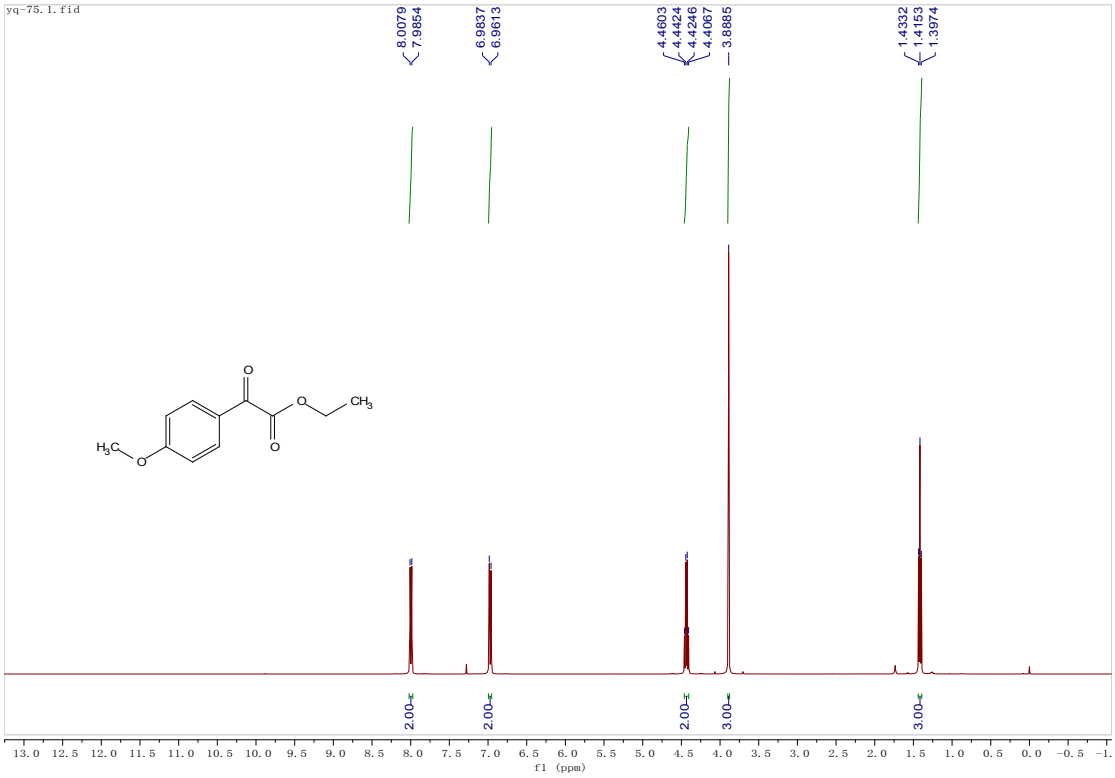


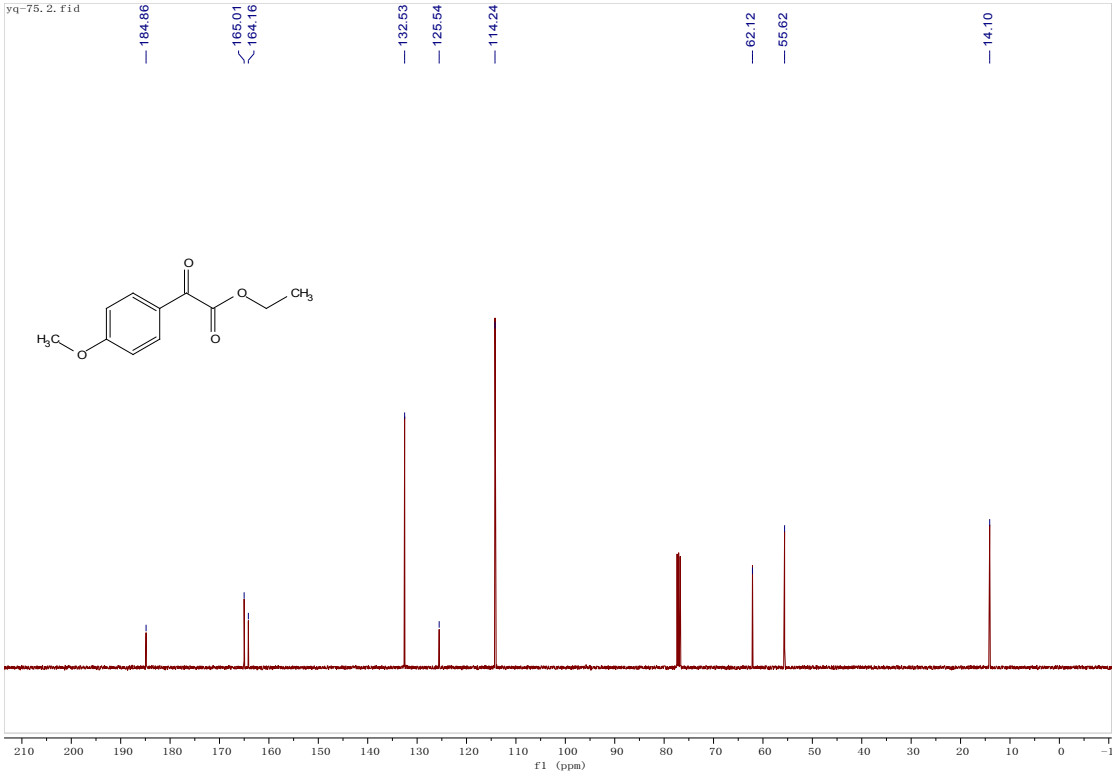
^{1}H and ^{13}C NMR spectra of **3b**



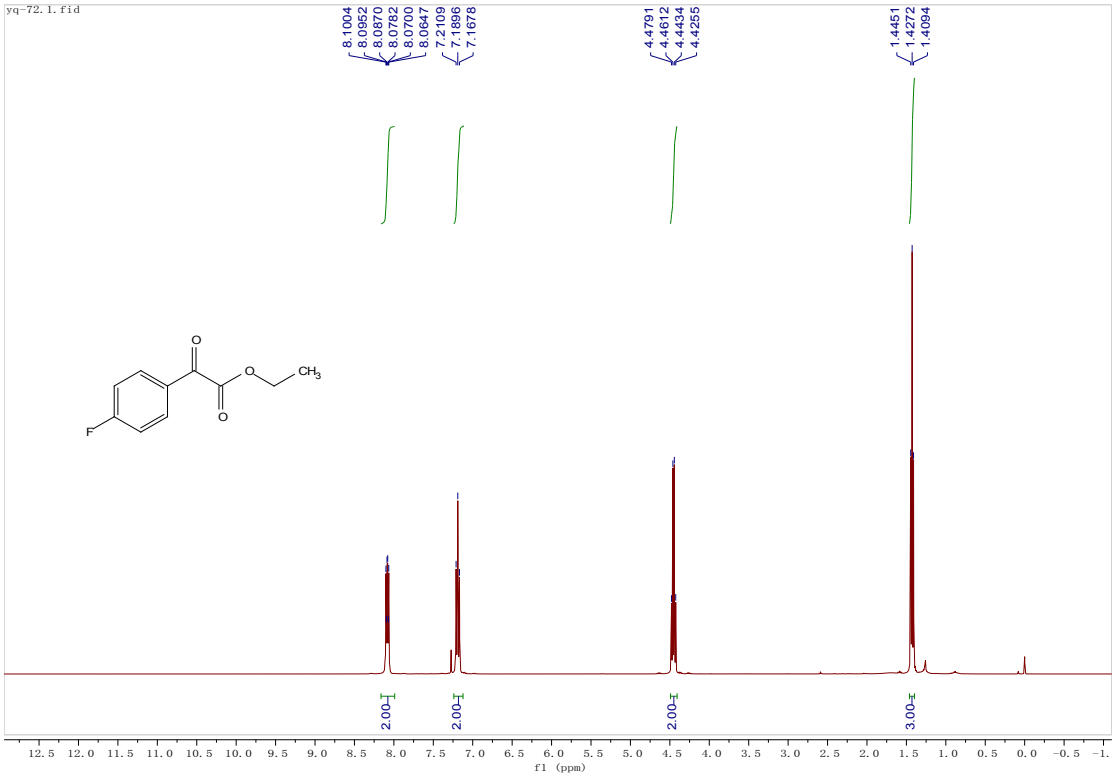


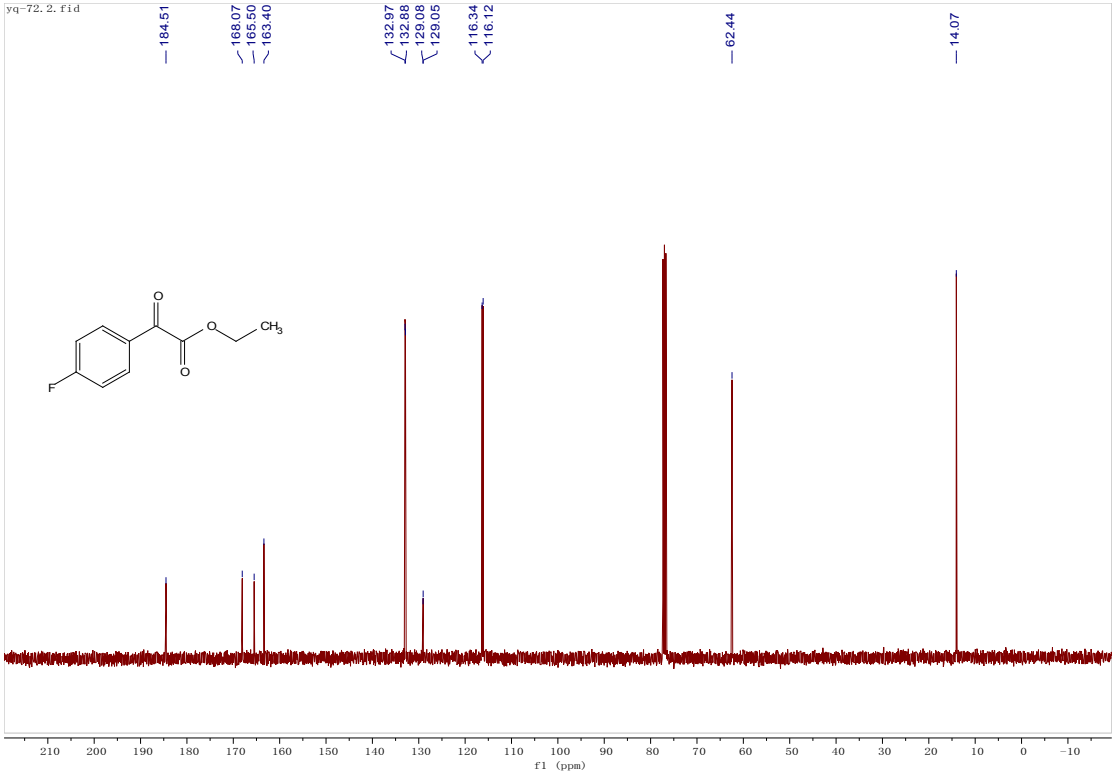
^{1}H and ^{13}C NMR spectra of **3c**



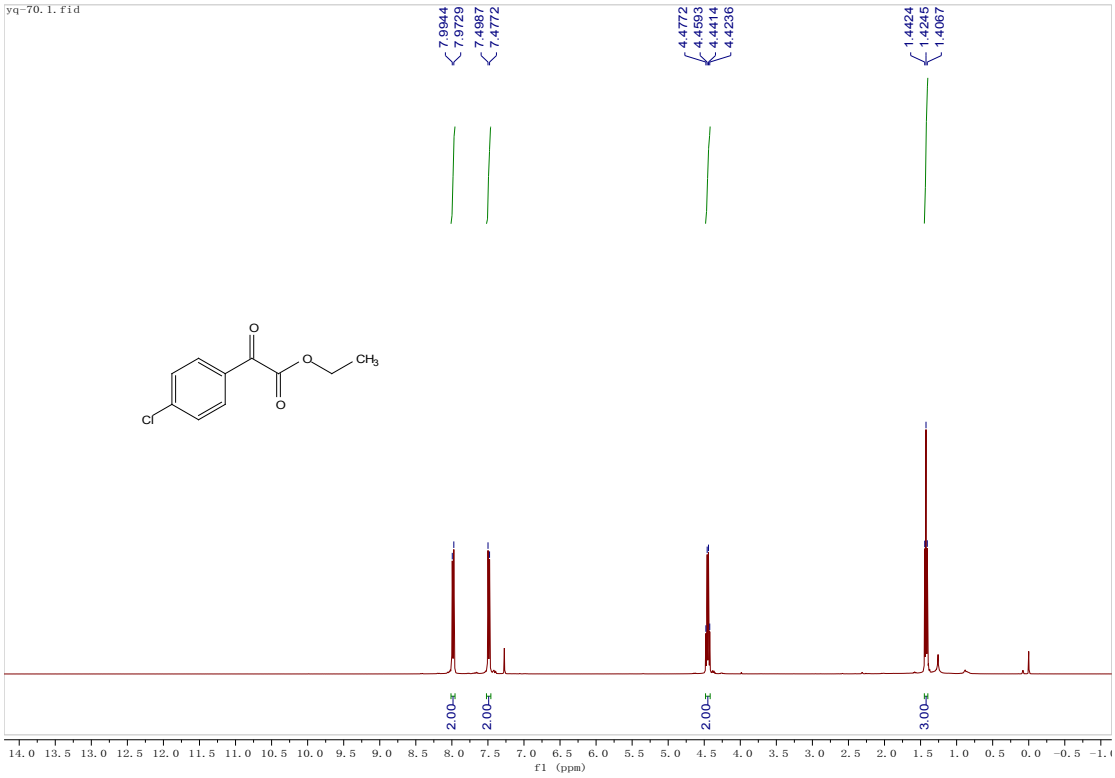


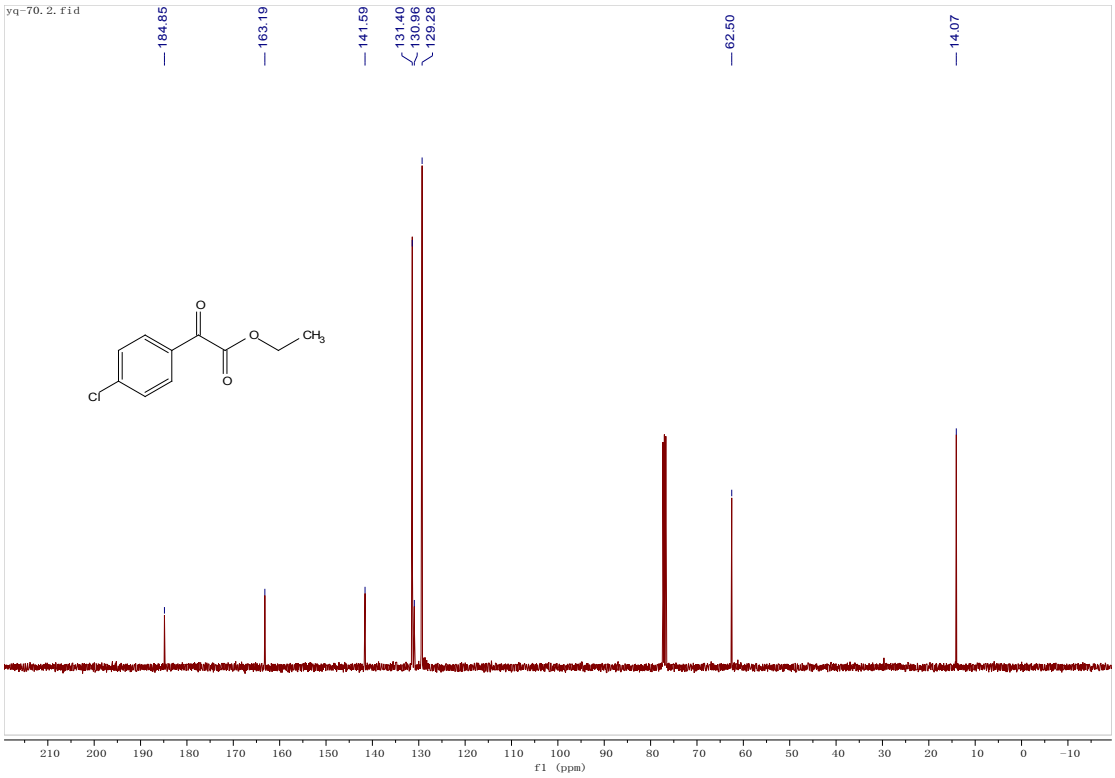
^{1}H and ^{13}C NMR spectra of **3d**



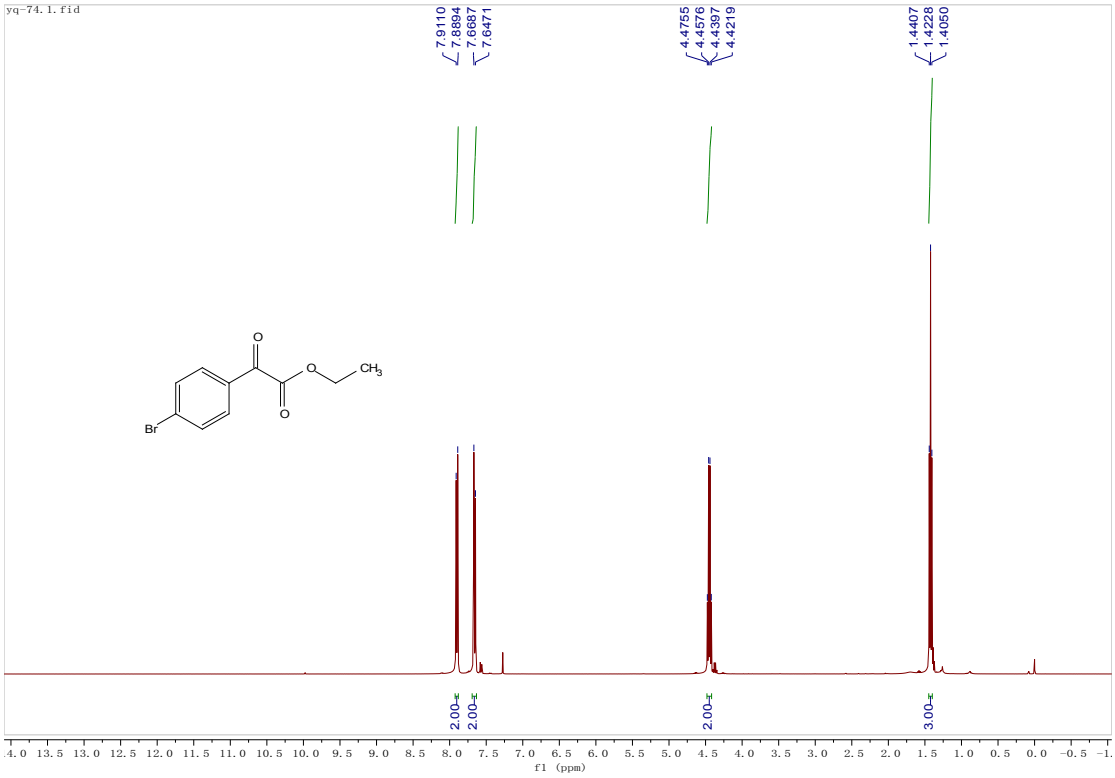


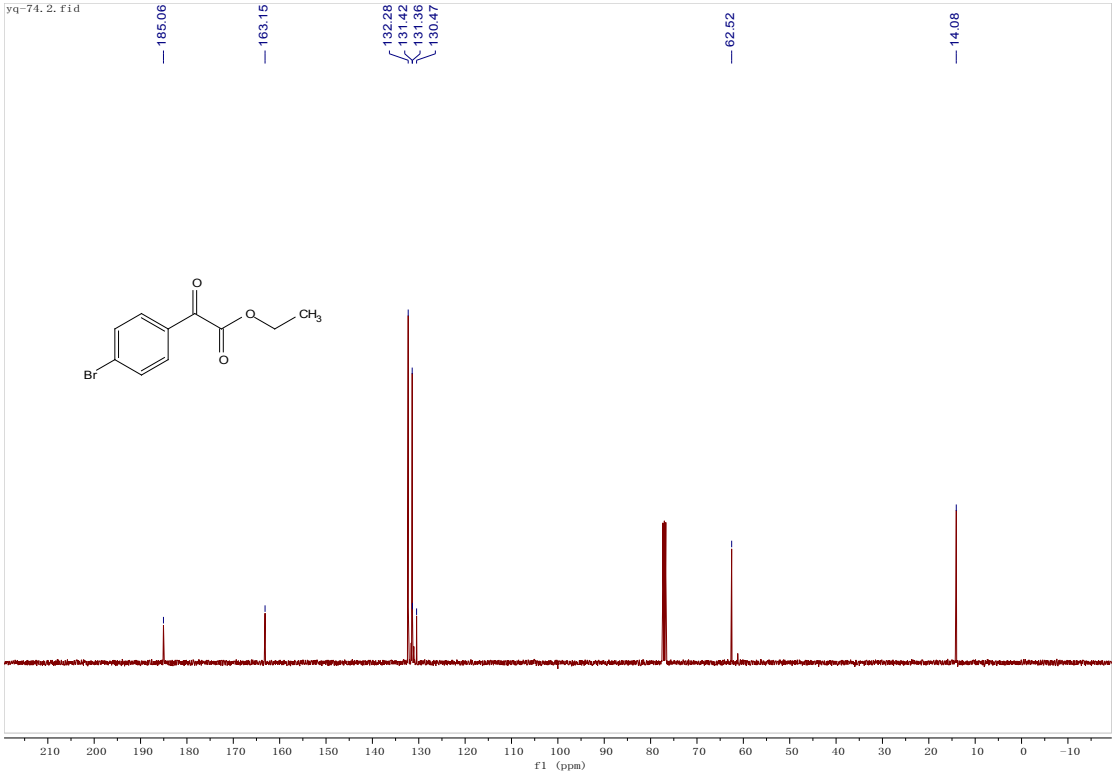
^{1}H and ^{13}C NMR spectra of **3e**



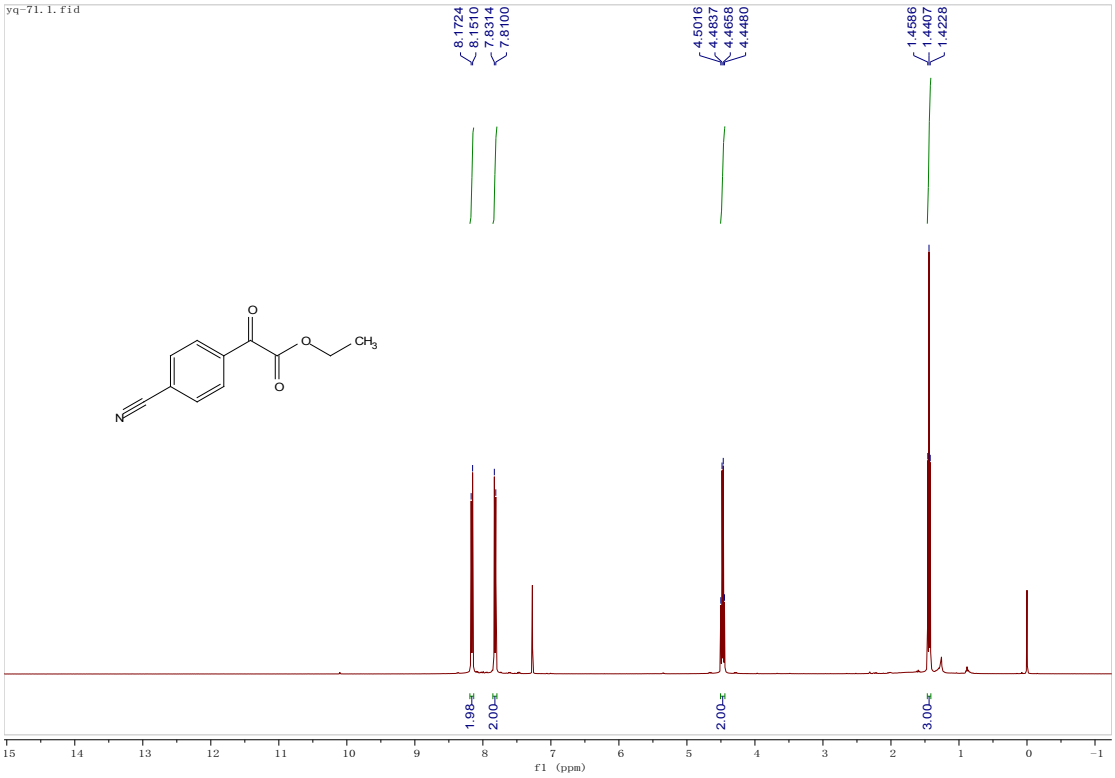


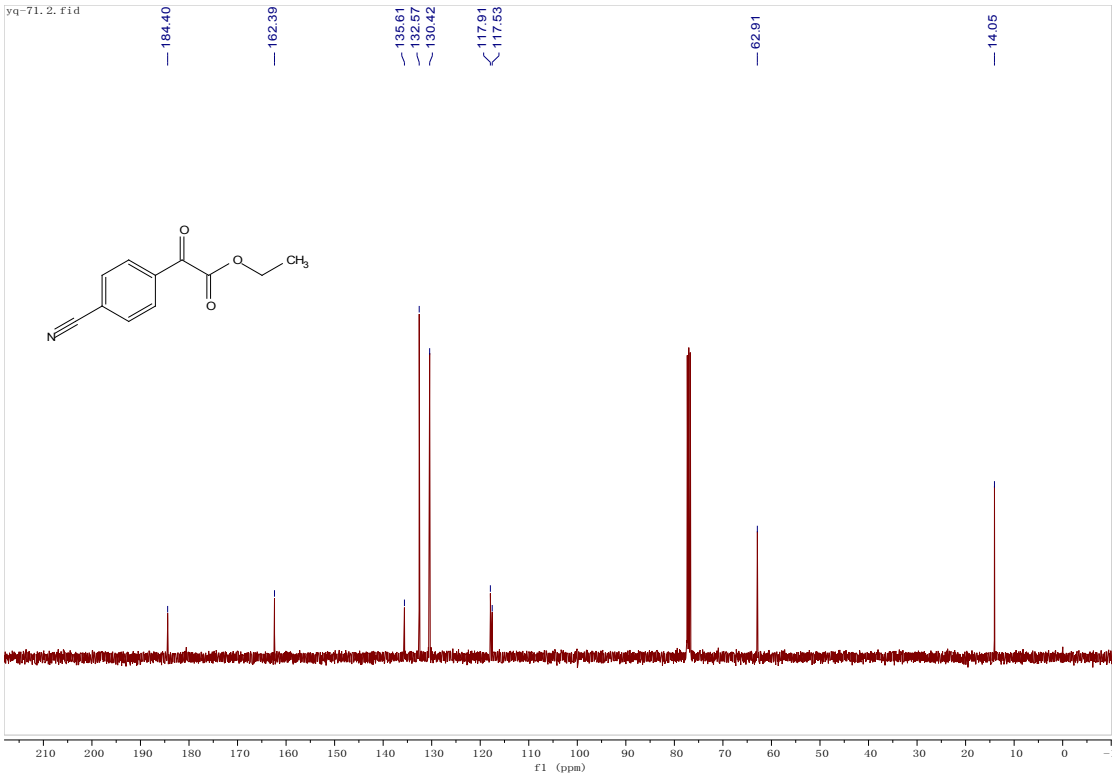
^{1}H and ^{13}C NMR spectra of **3f**



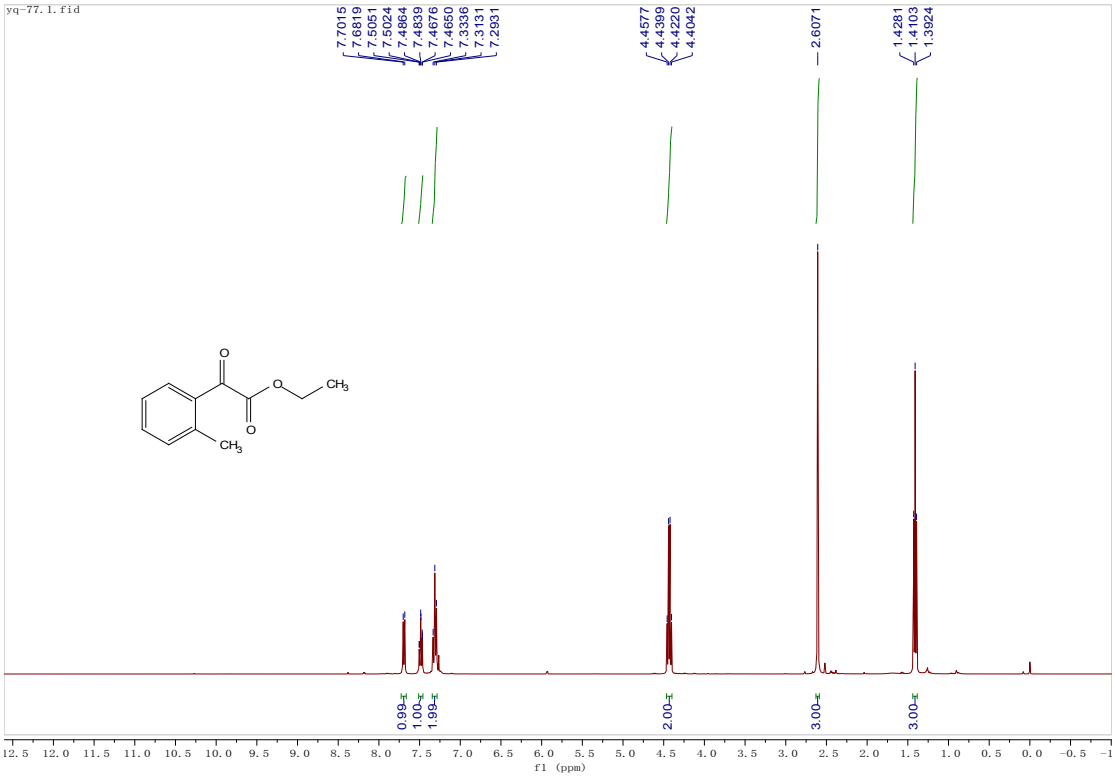


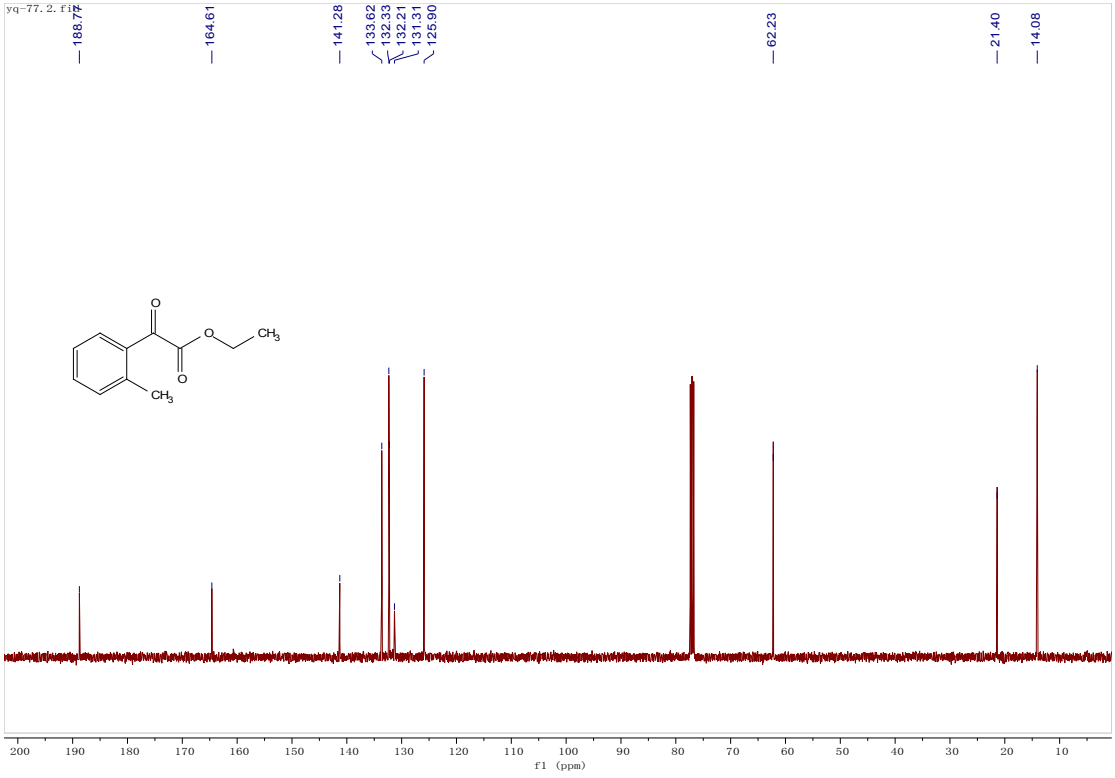
^{1}H and ^{13}C NMR spectra of **3g**



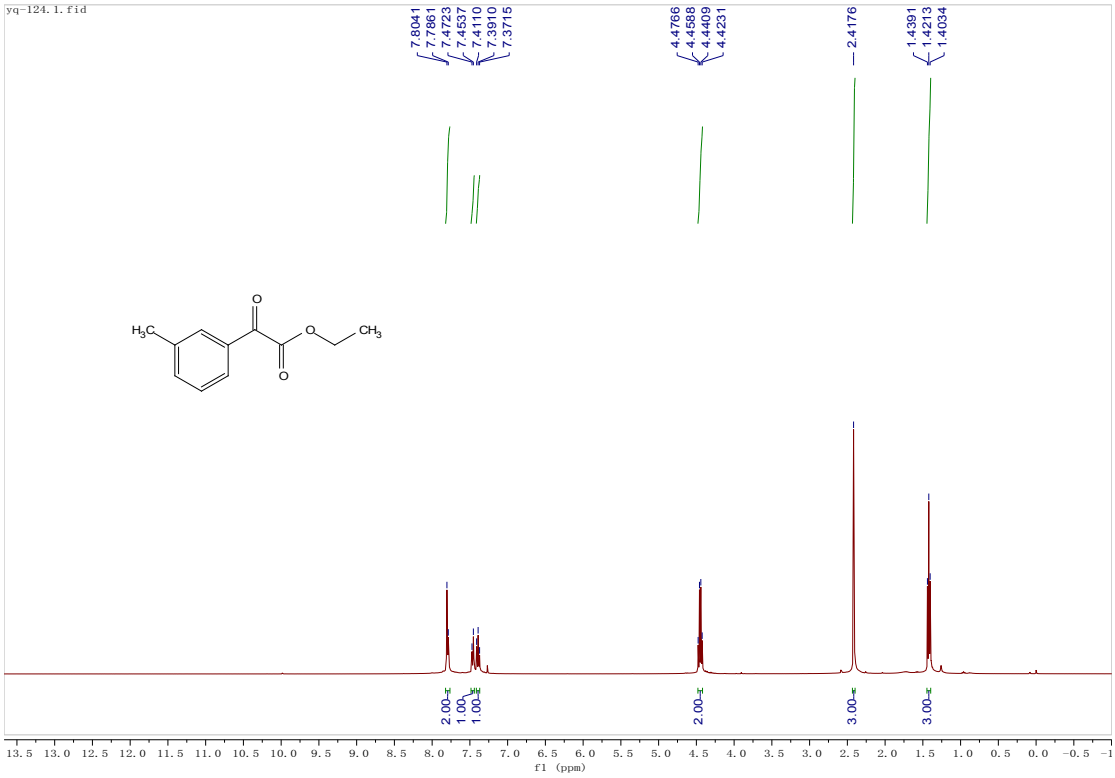


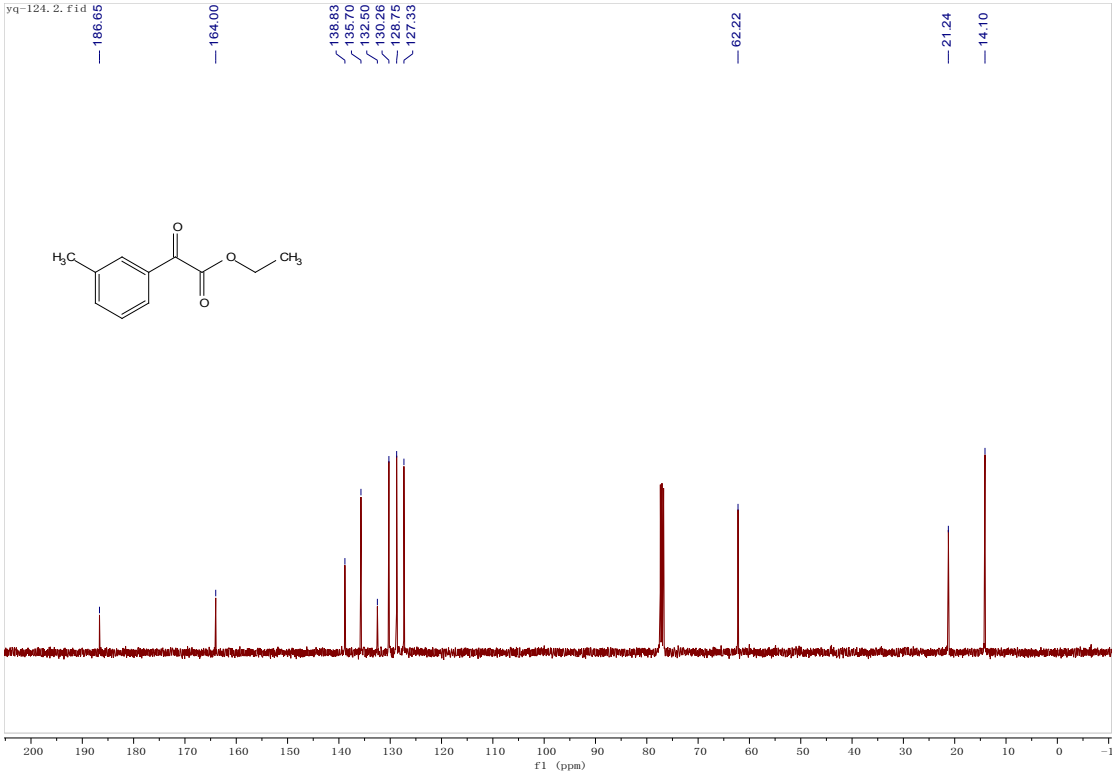
^{1}H and ^{13}C NMR spectra of **3h**



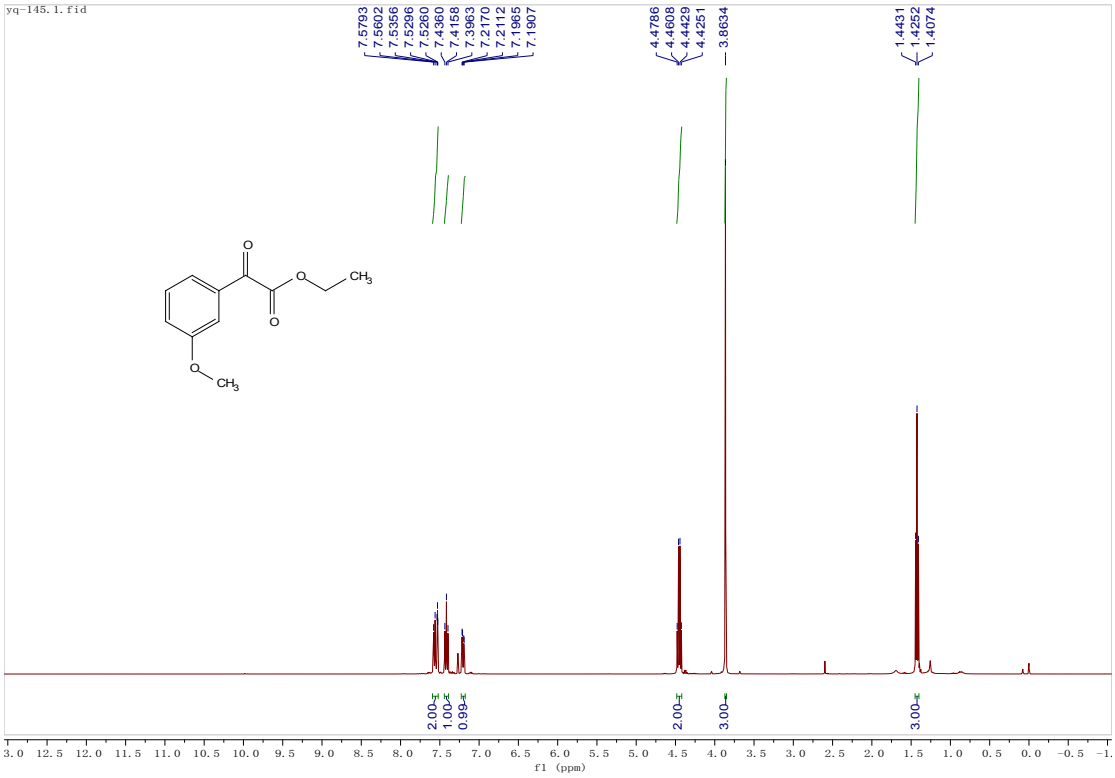


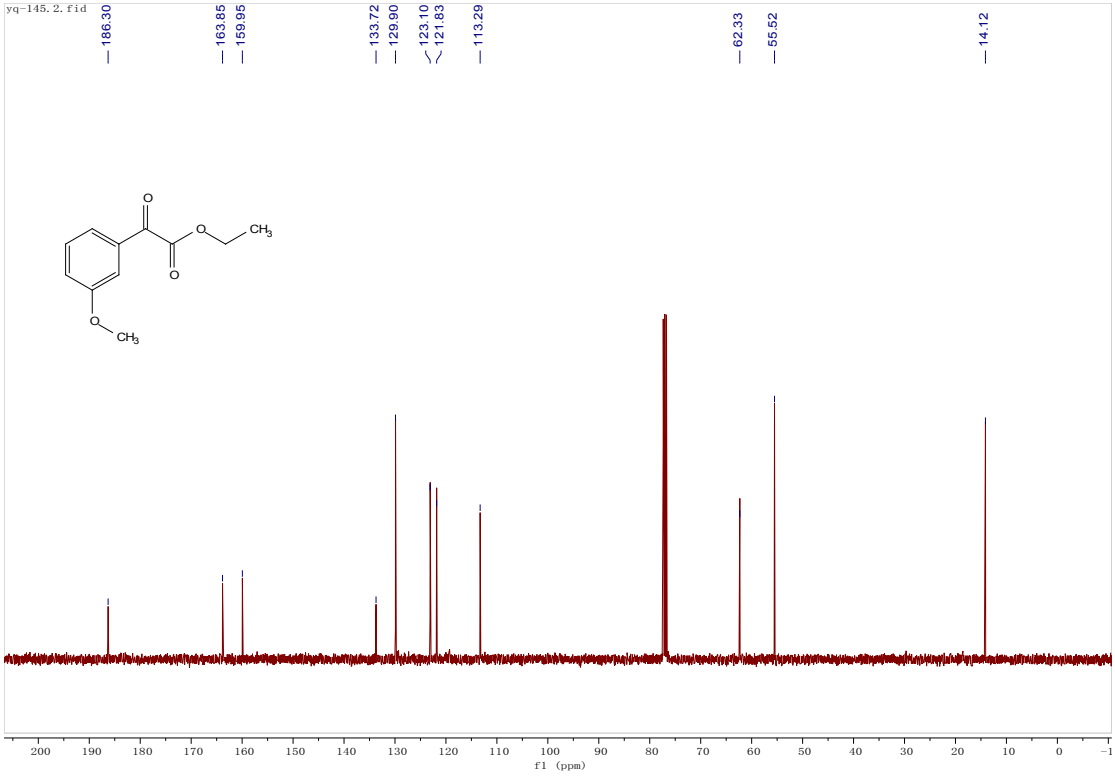
^{1}H and ^{13}C NMR spectra of **3i**



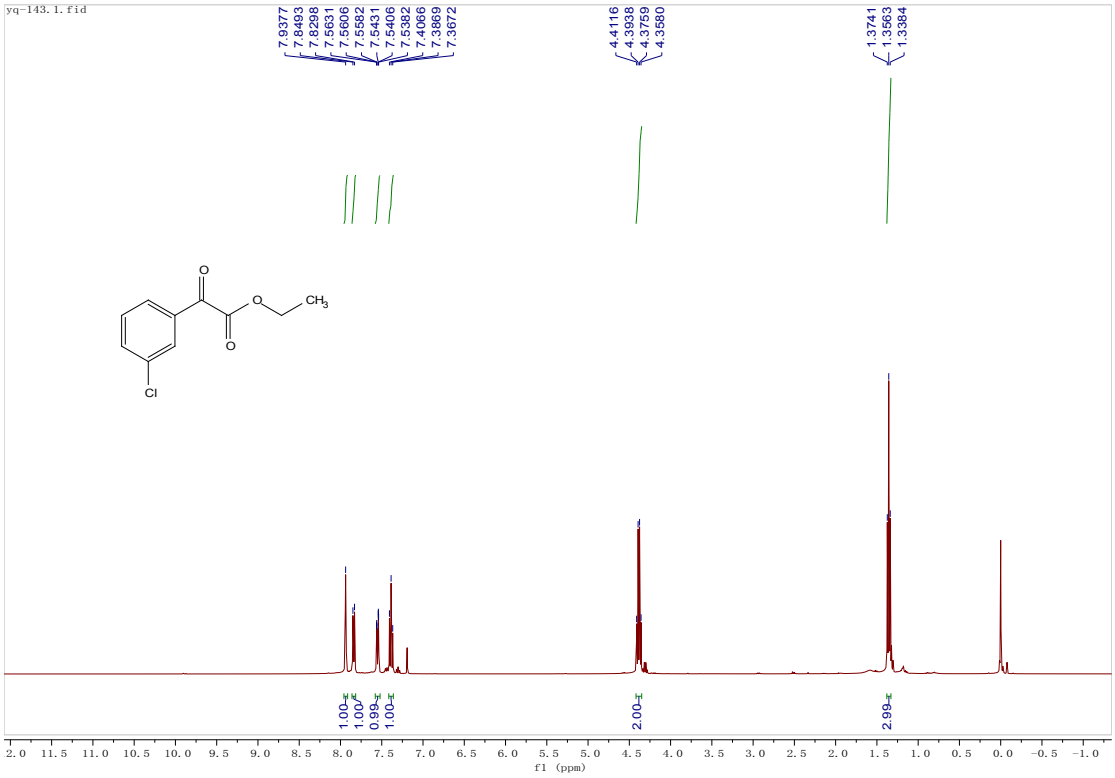


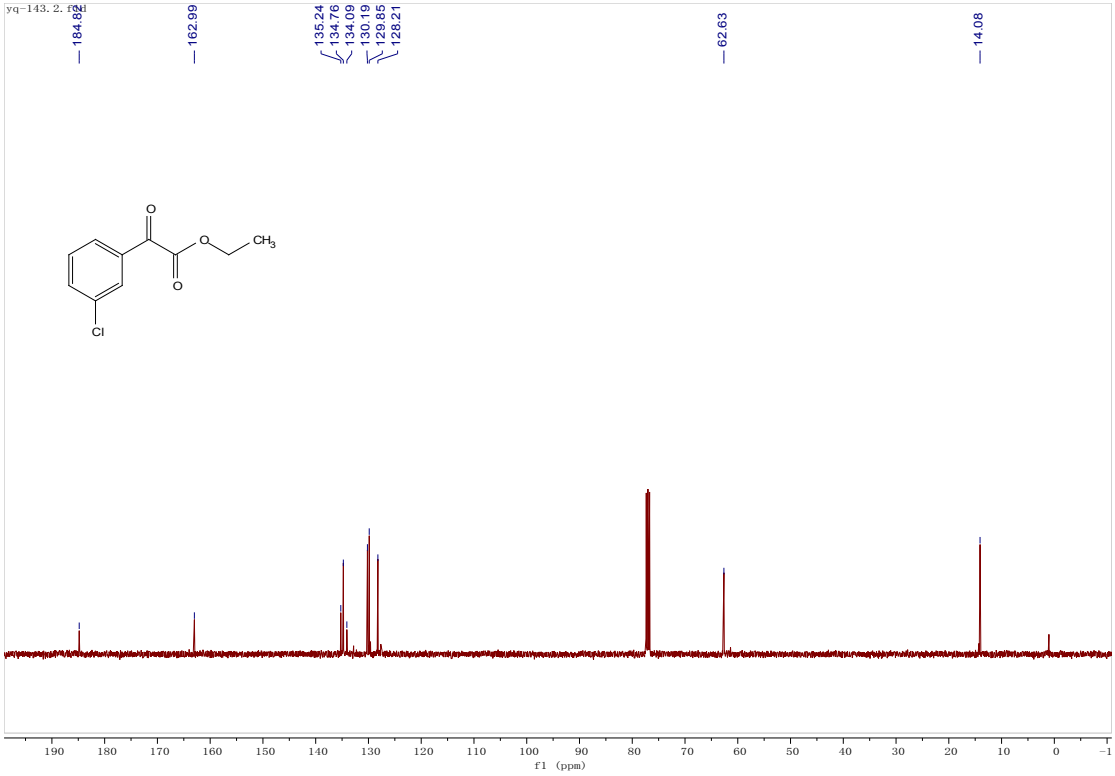
^{1}H and ^{13}C NMR spectra of **3j**



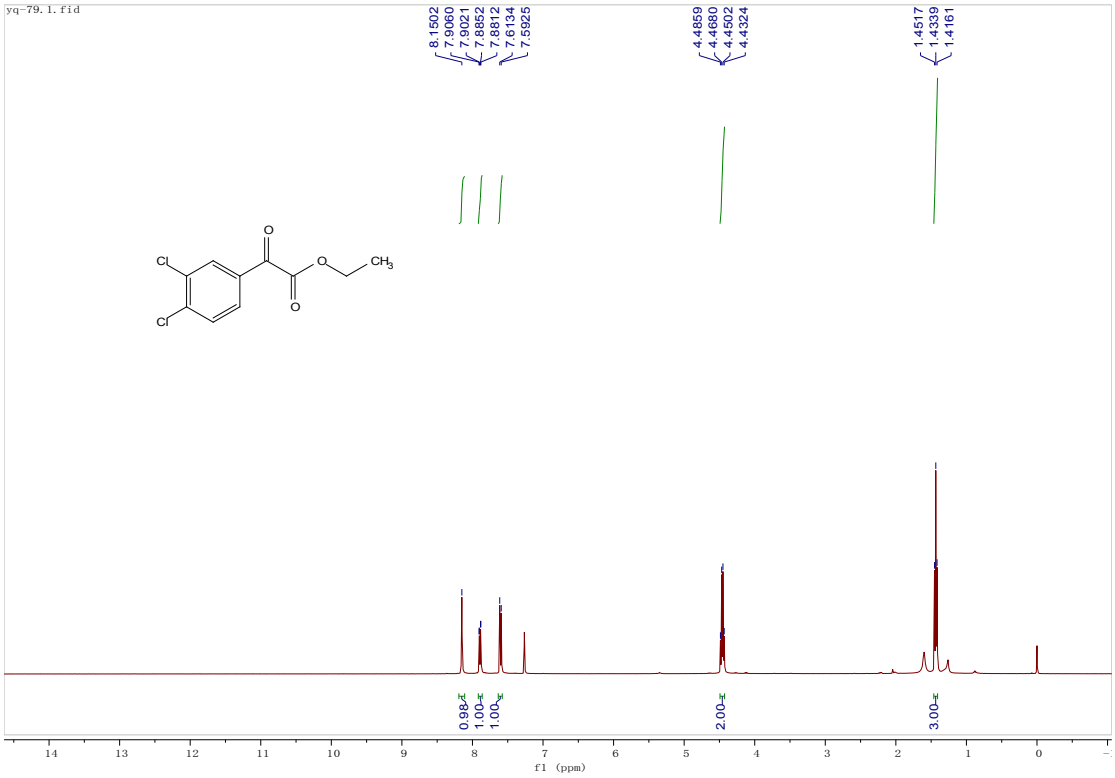


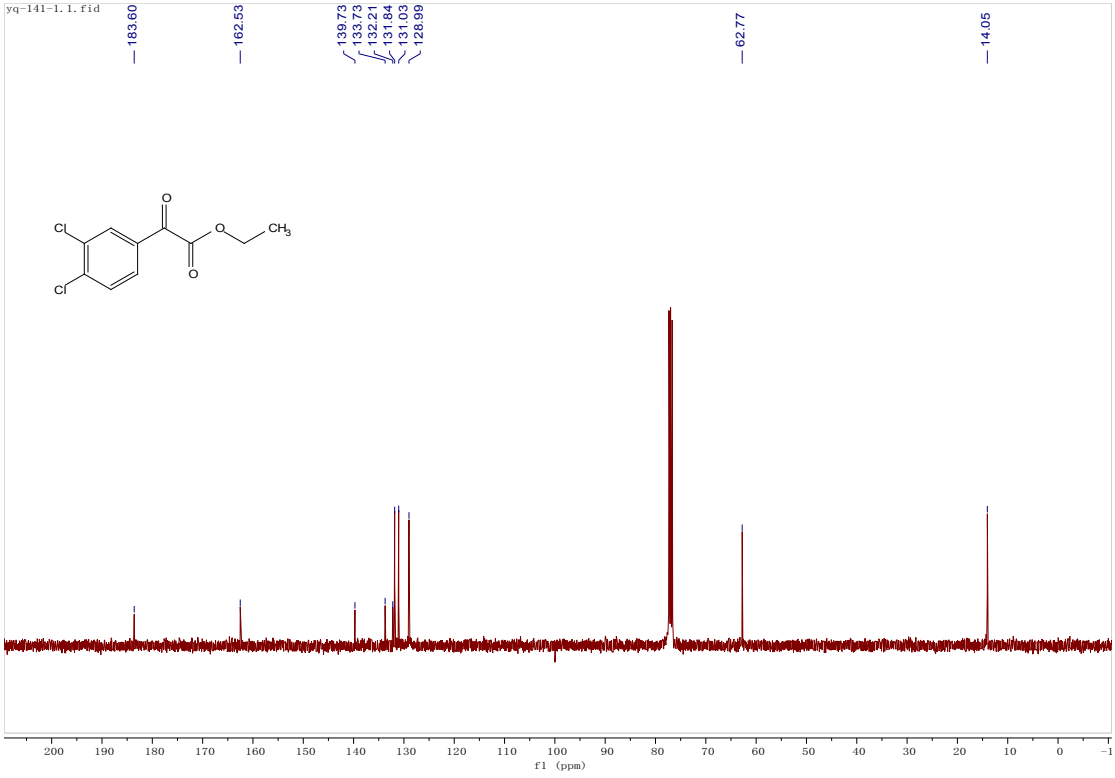
^{1}H and ^{13}C NMR spectra of **3k**



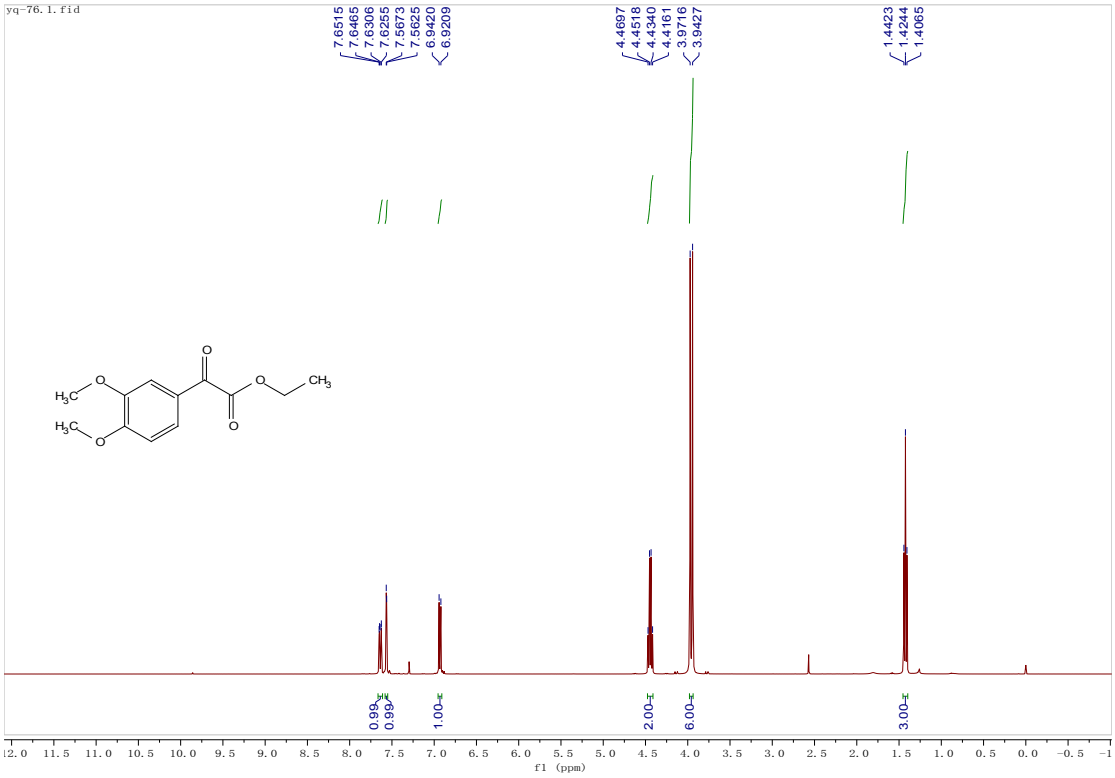


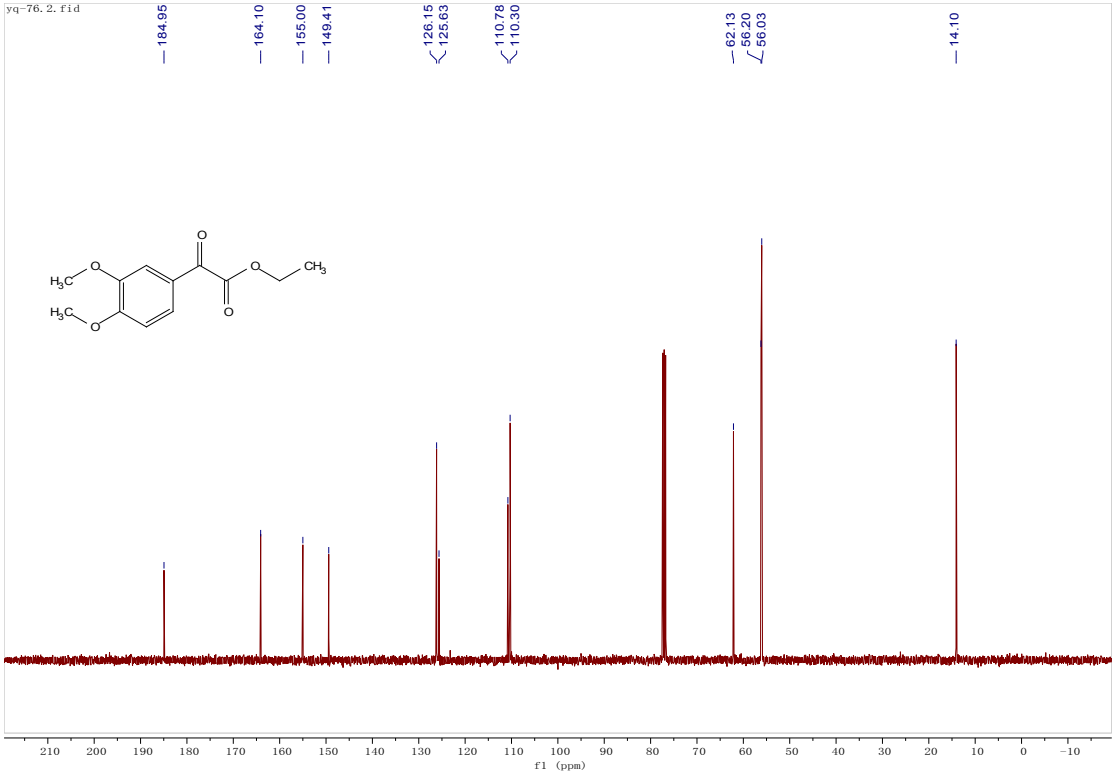
^{1}H and ^{13}C NMR spectra of **3l**



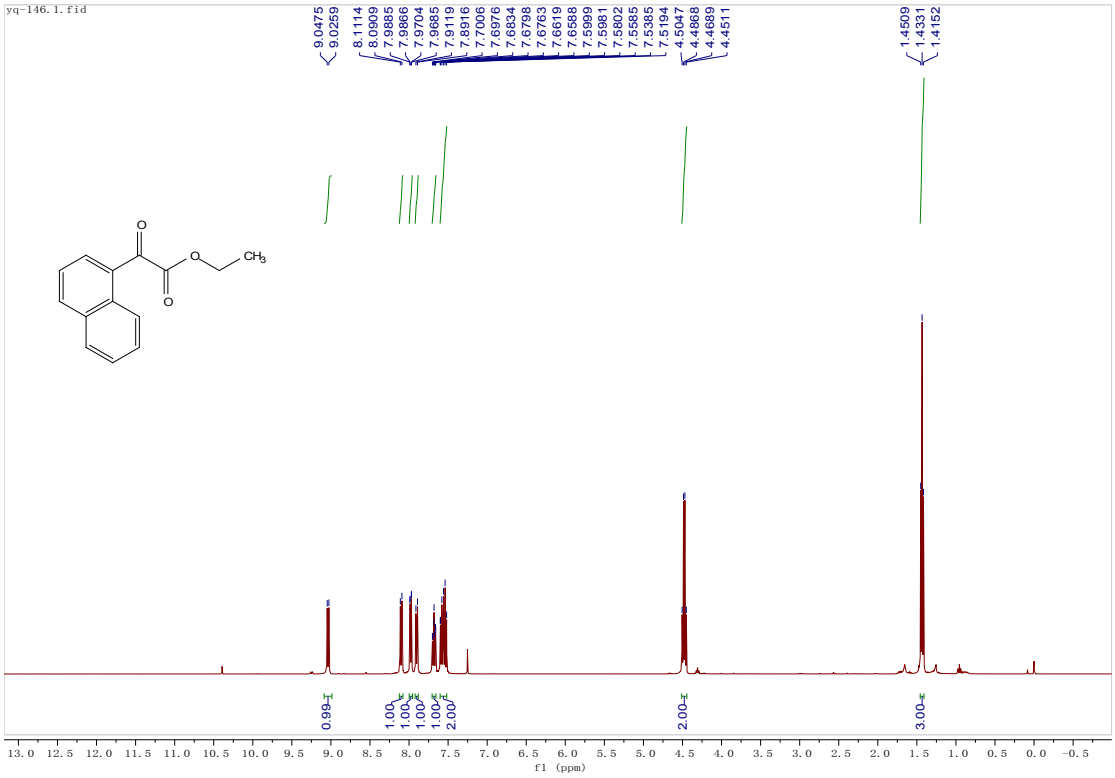


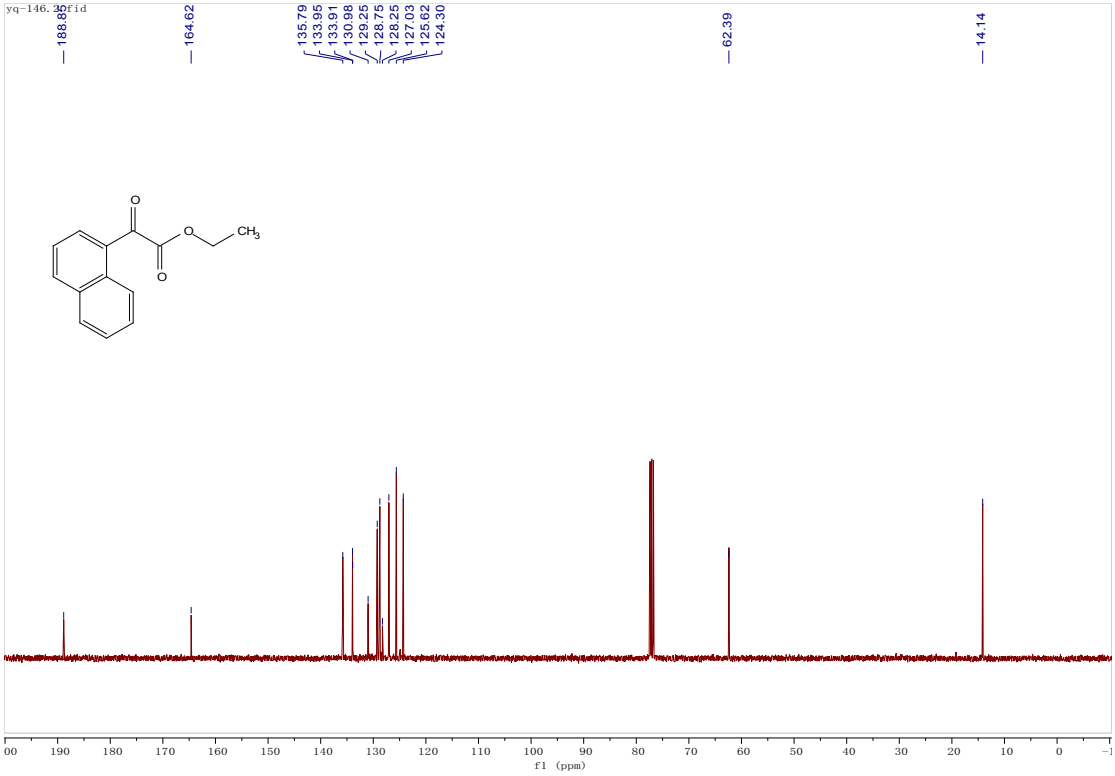
^{1}H and ^{13}C NMR spectra of **3m**



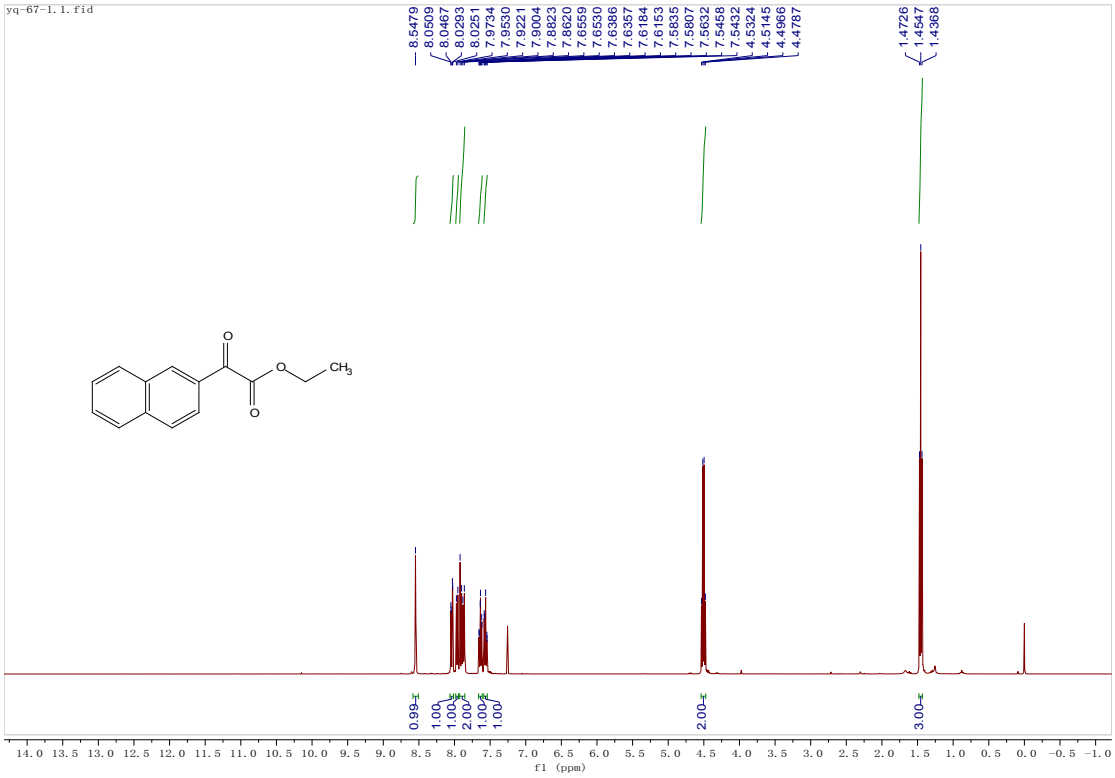


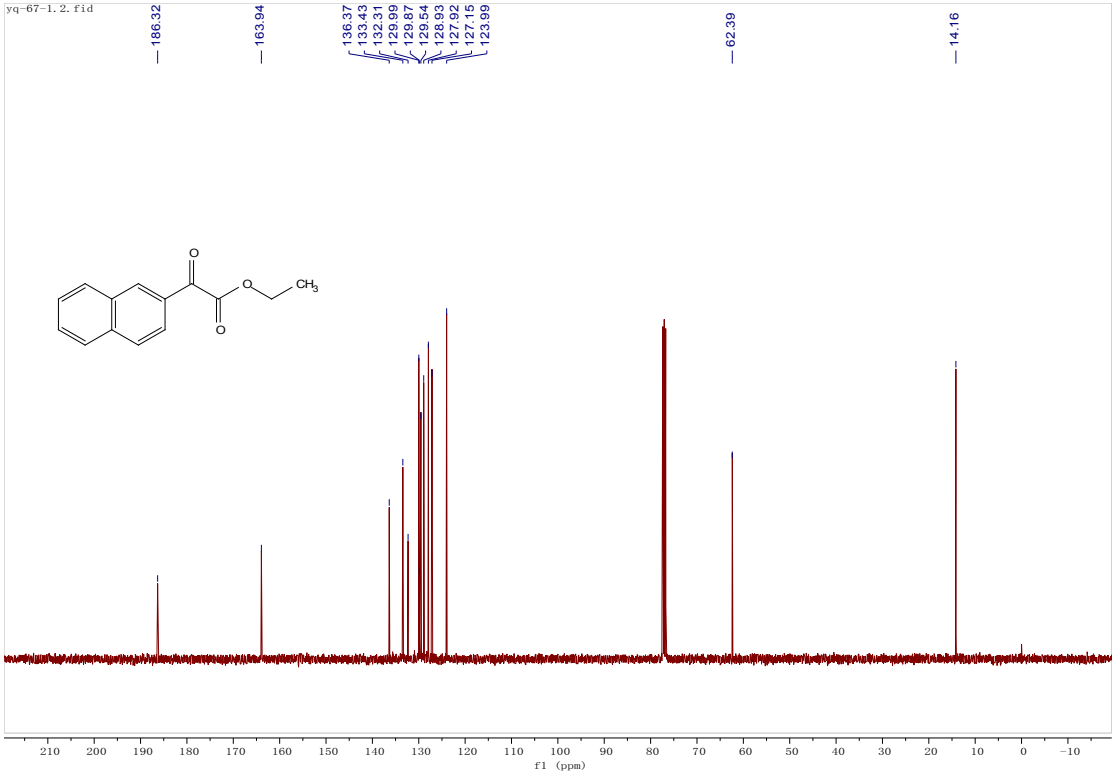
^{1}H and ^{13}C NMR spectra of **3n**



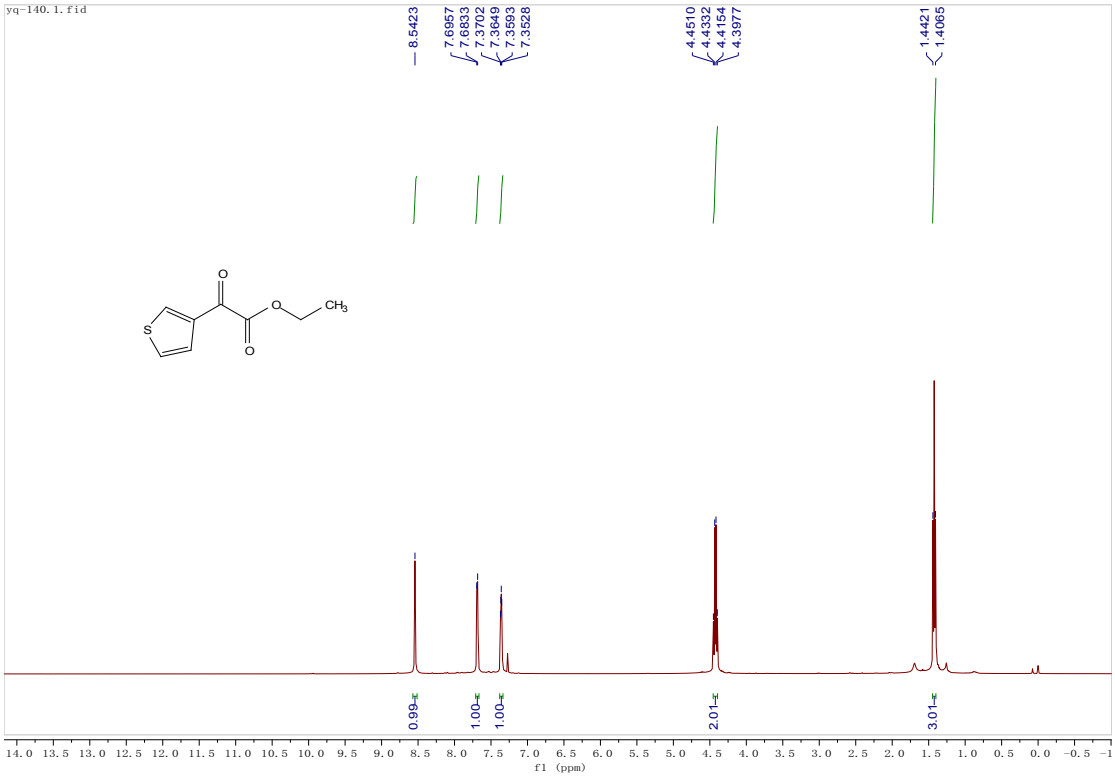


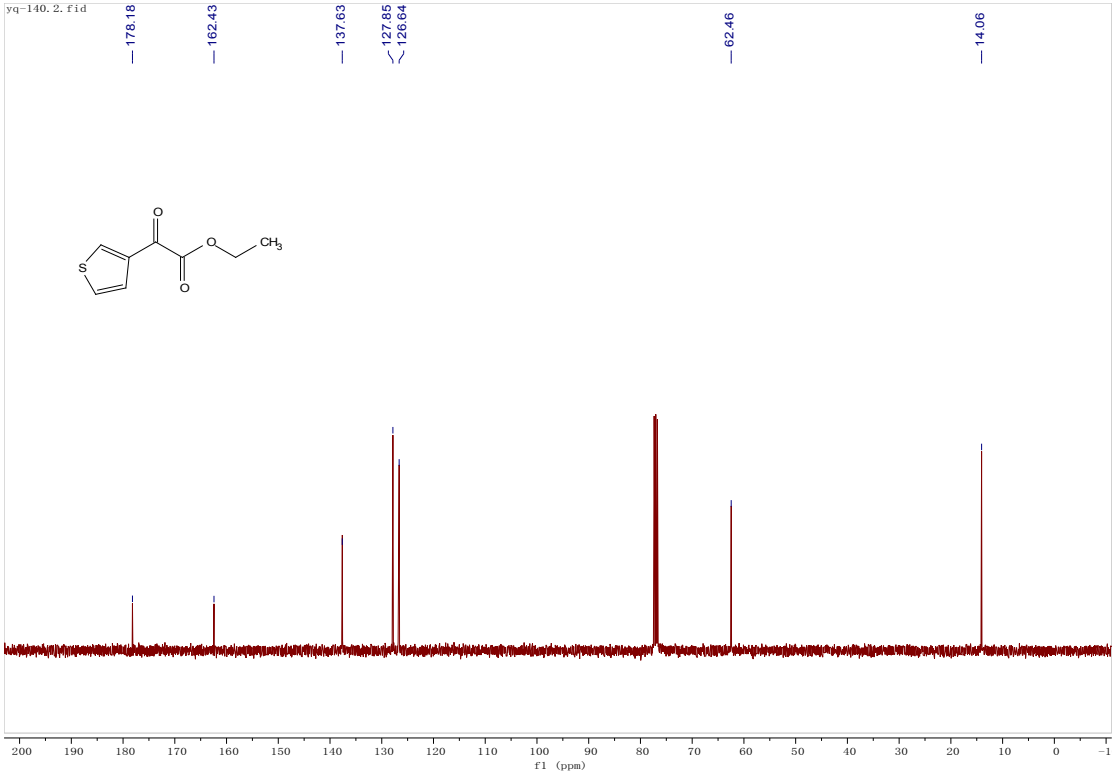
^{1}H and ^{13}C NMR spectra of **3o**



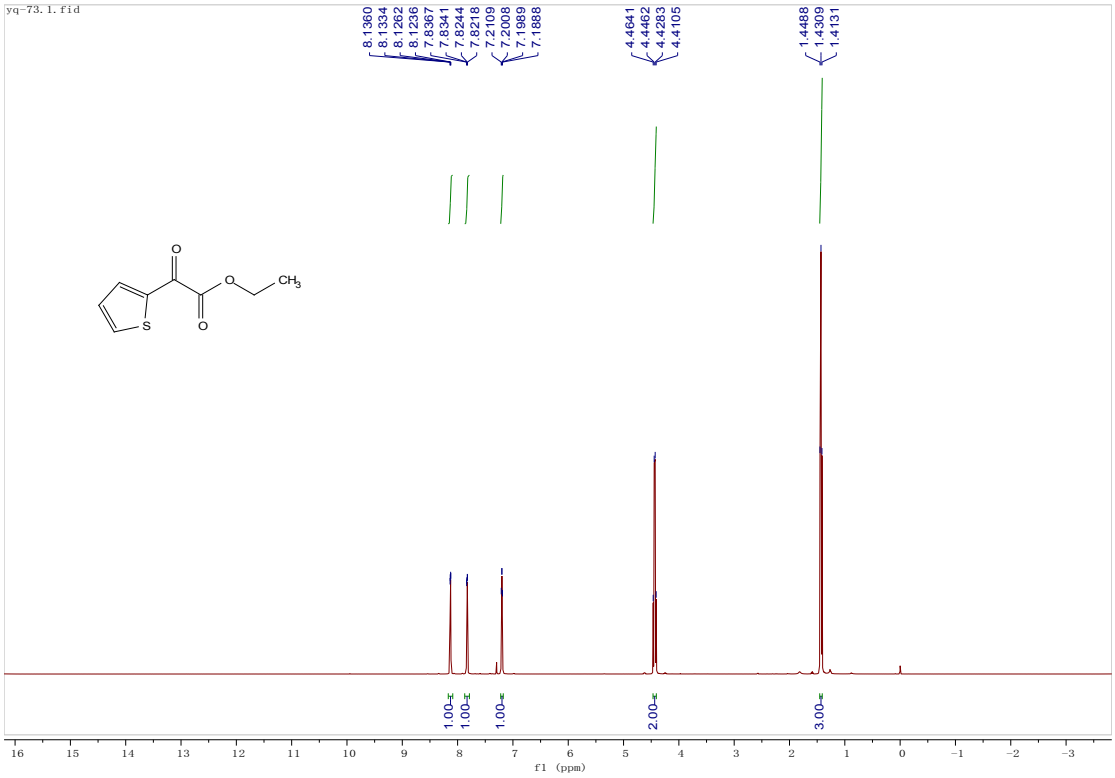


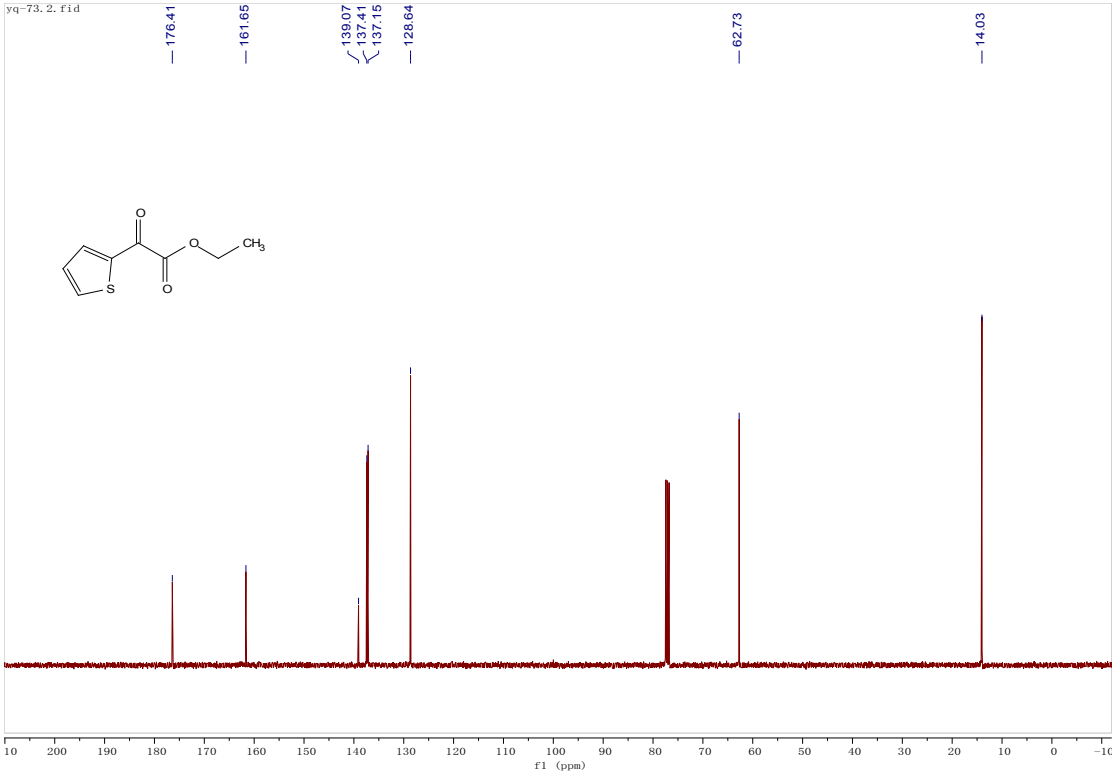
^{1}H and ^{13}C NMR spectra of **3p**



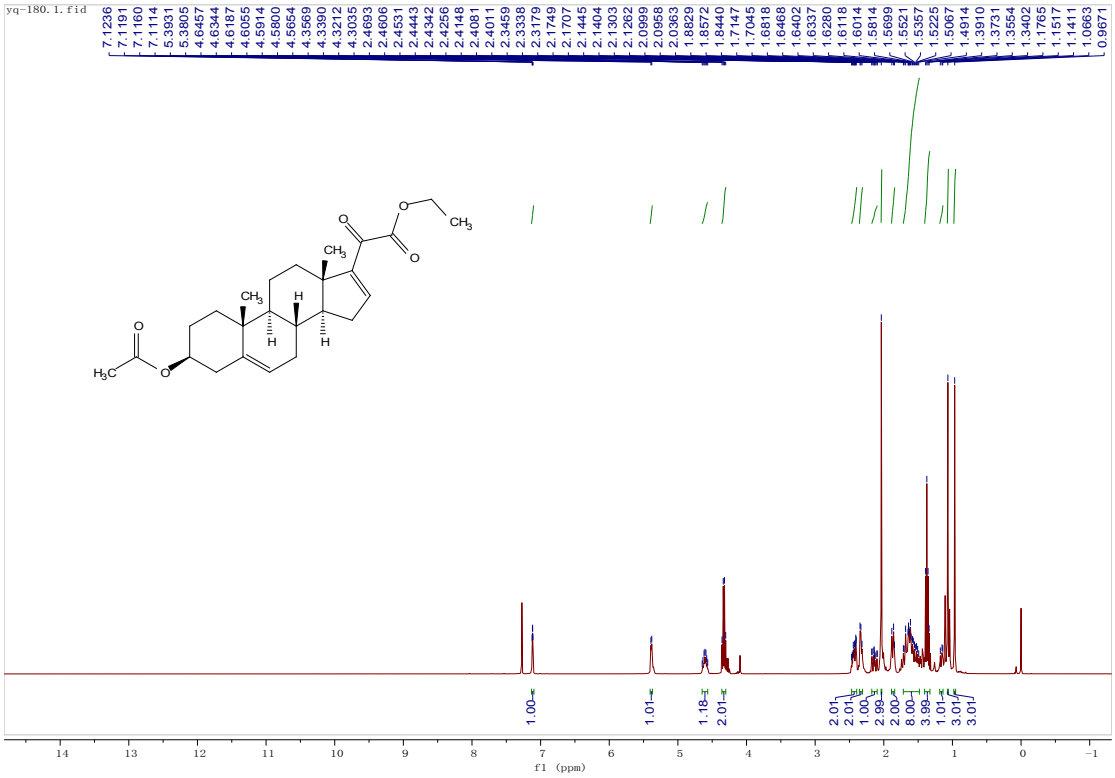


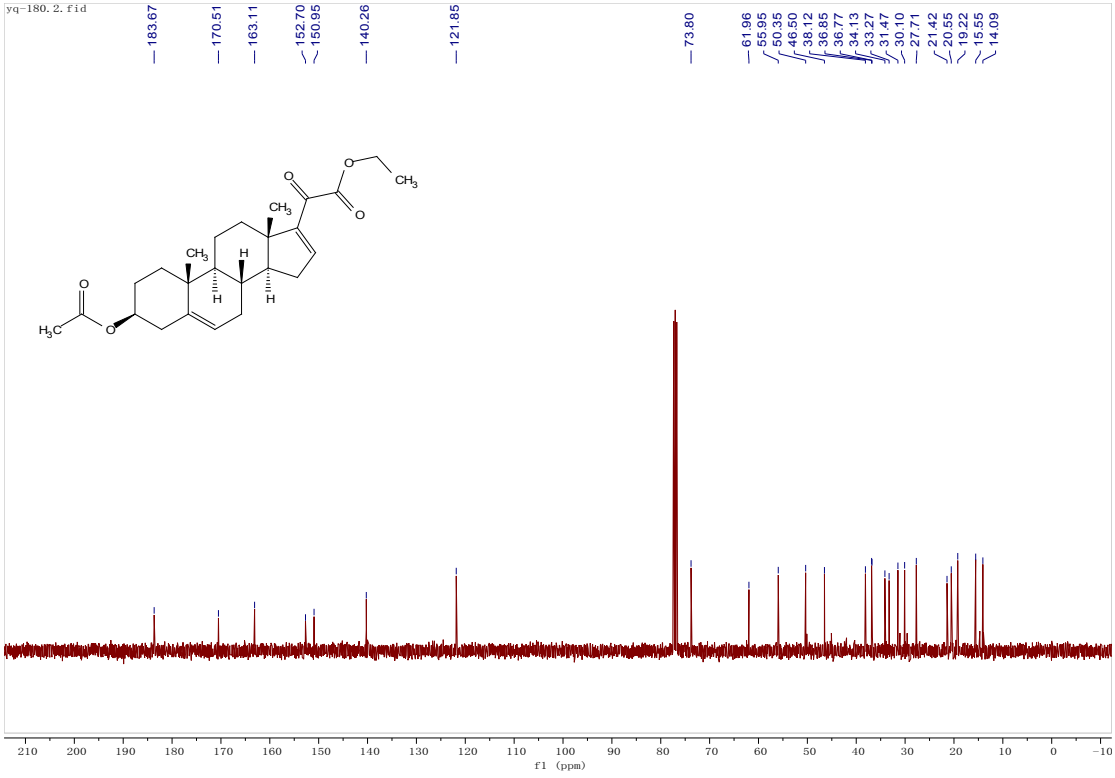
^{1}H and ^{13}C NMR spectra of **3q**



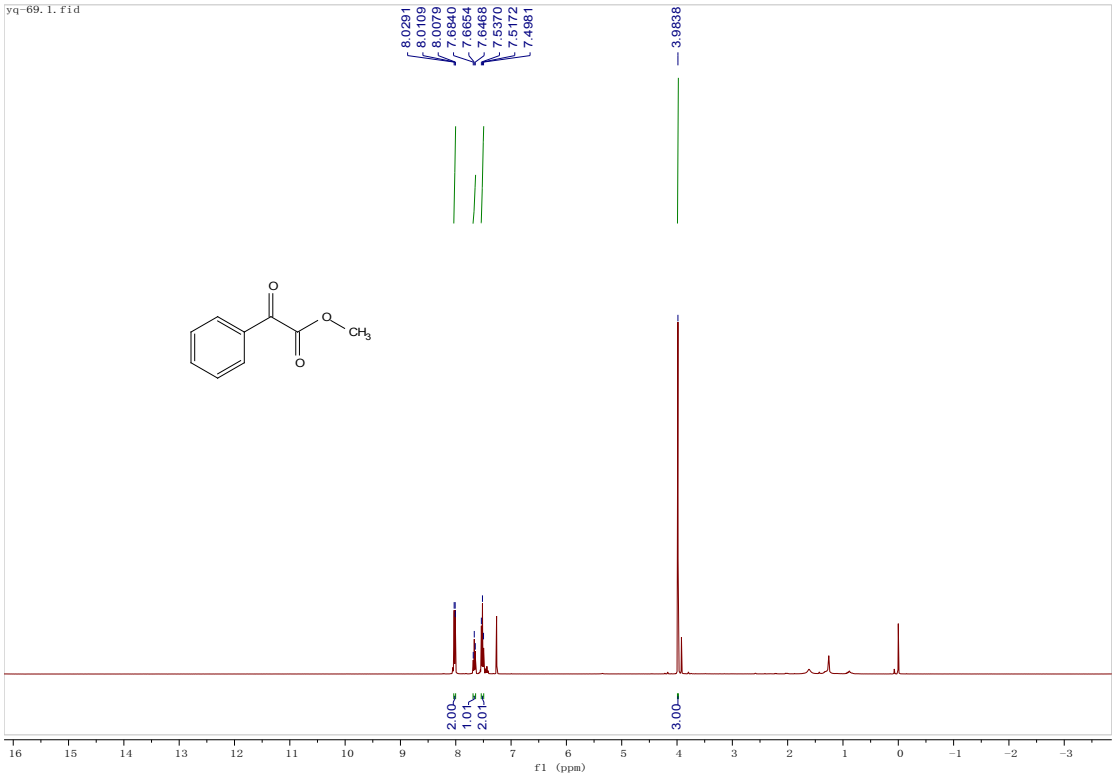


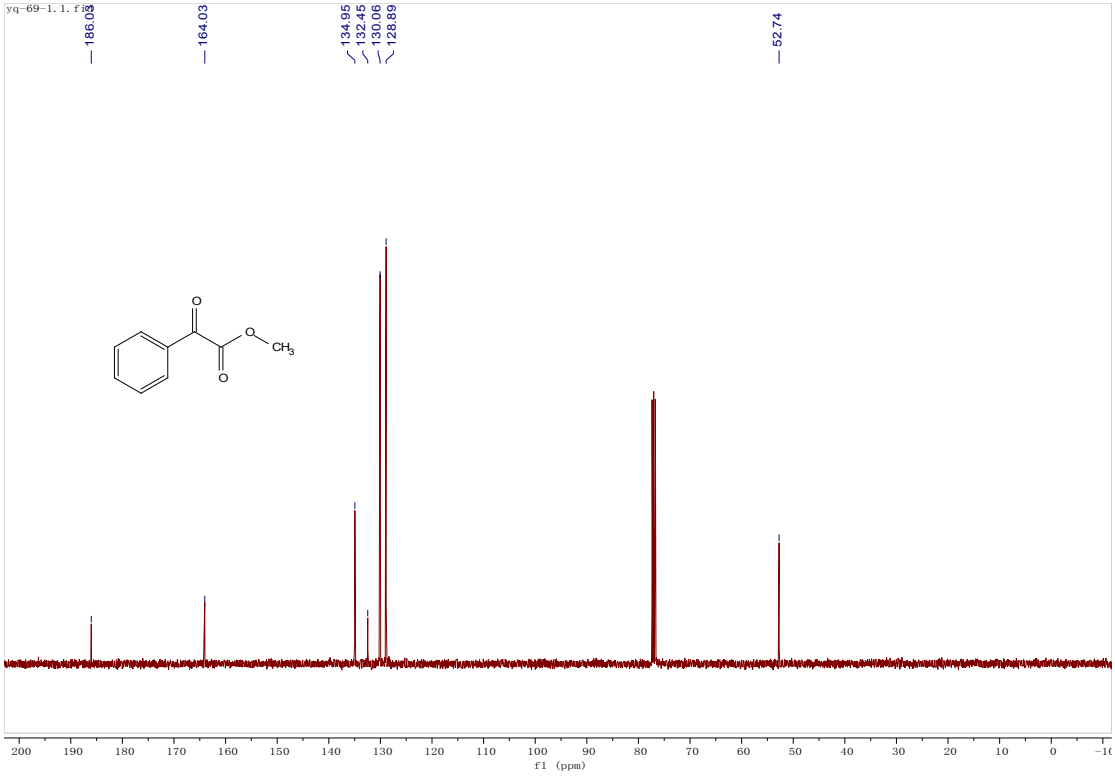
^{1}H and ^{13}C NMR spectra of **3r**



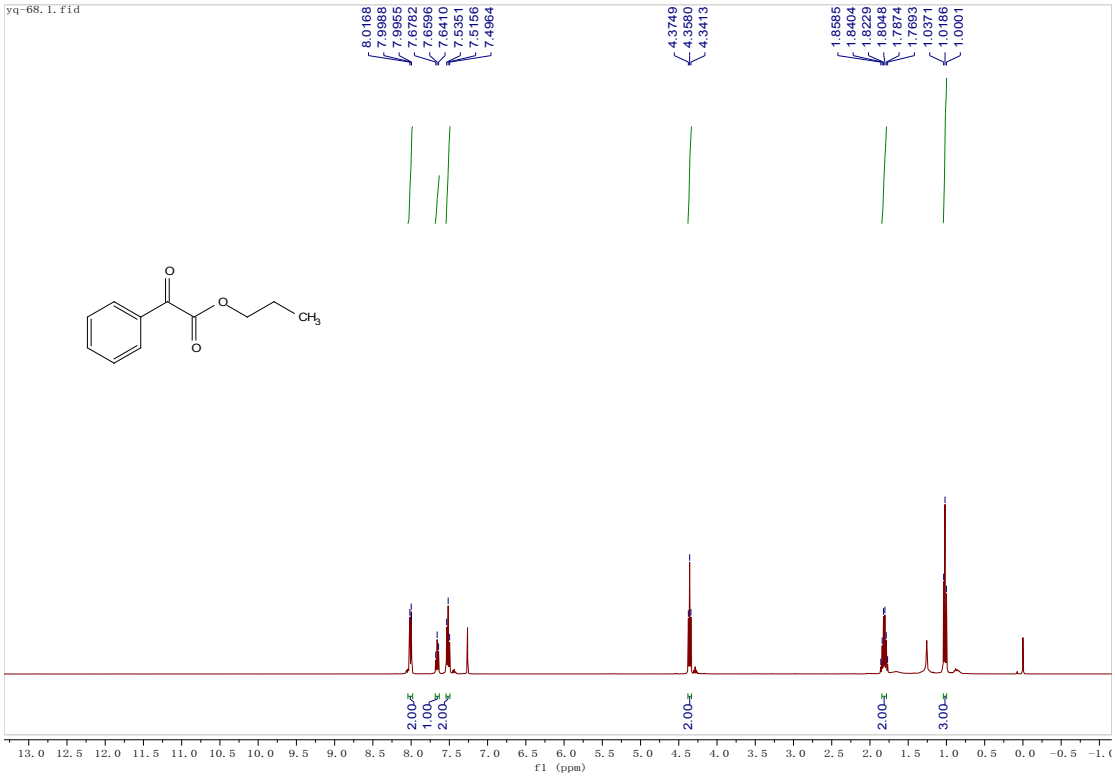


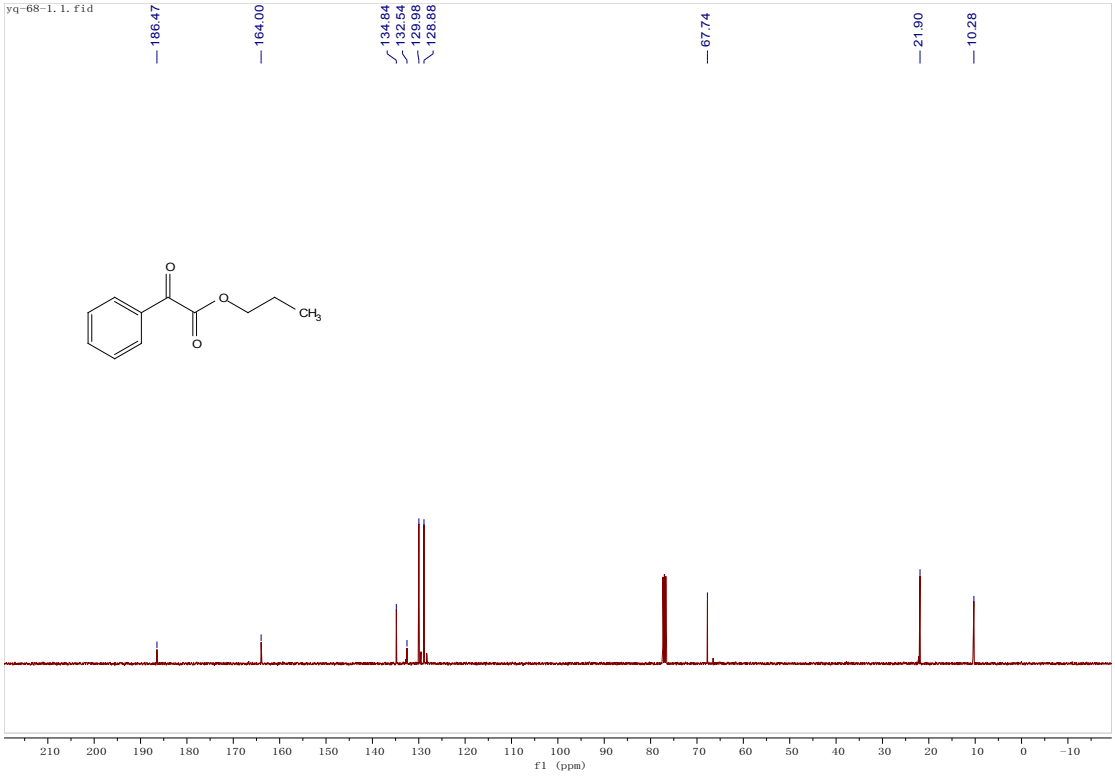
^{1}H and ^{13}C NMR spectra of **3ab**



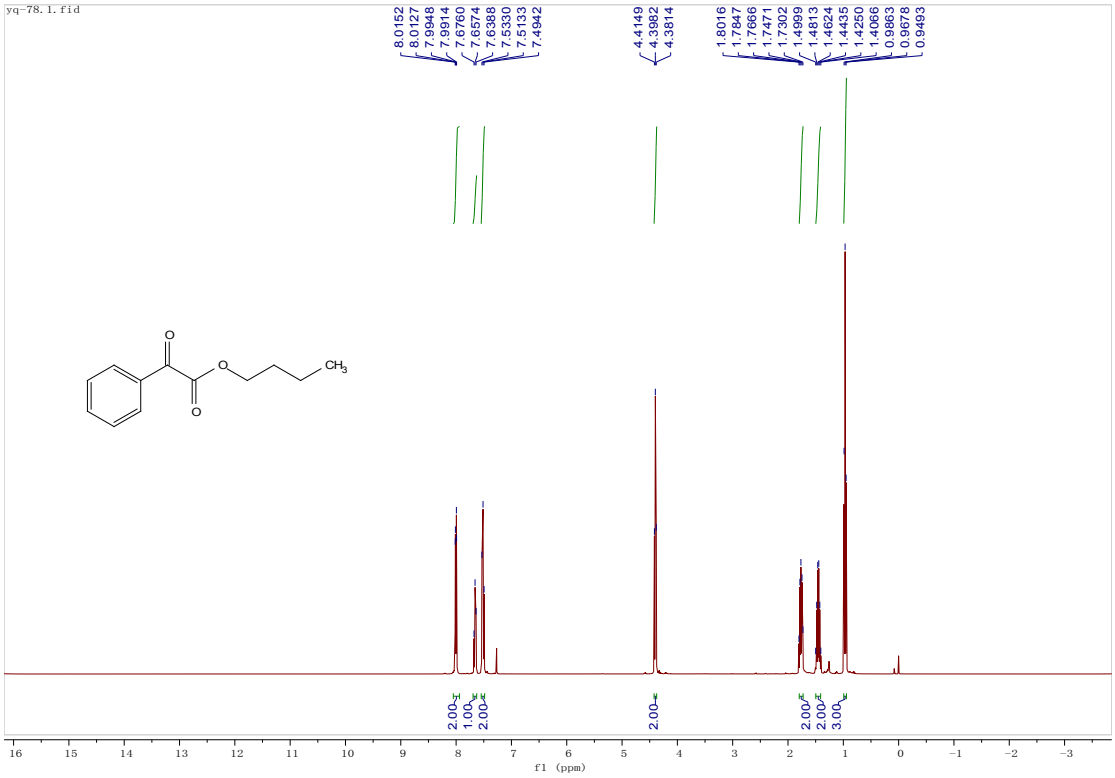


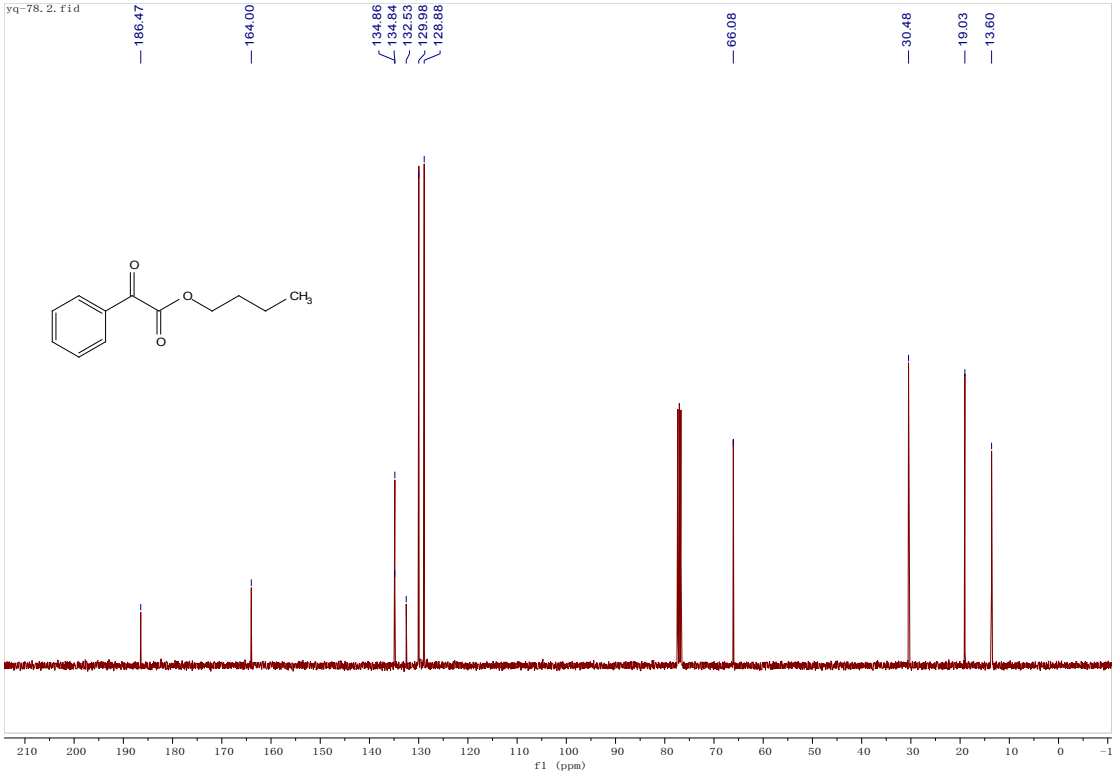
^{1}H and ^{13}C NMR spectra of **3ac**



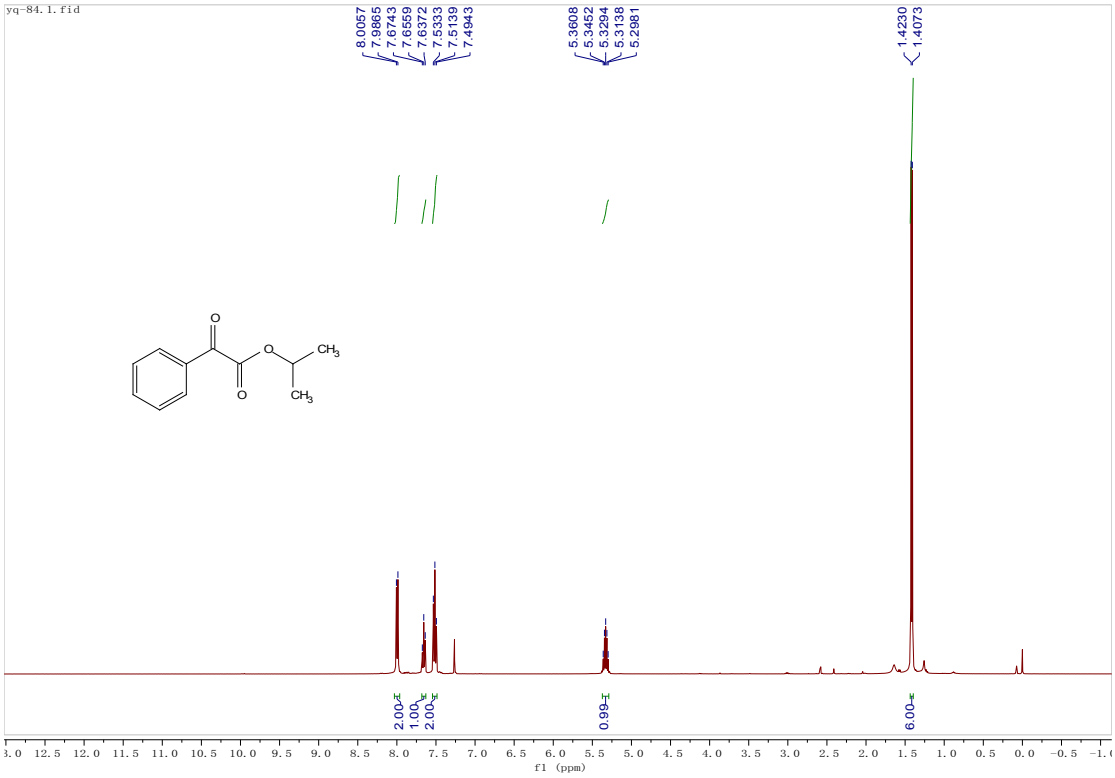


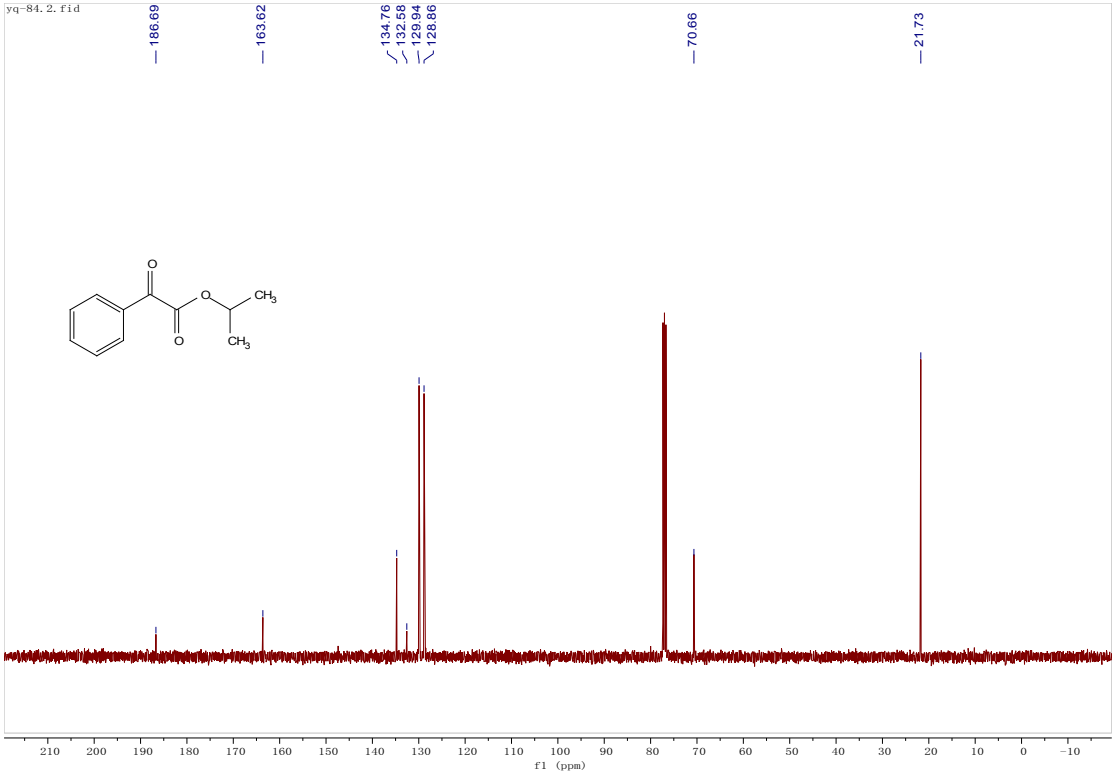
^{1}H and ^{13}C NMR spectra of **3ad**



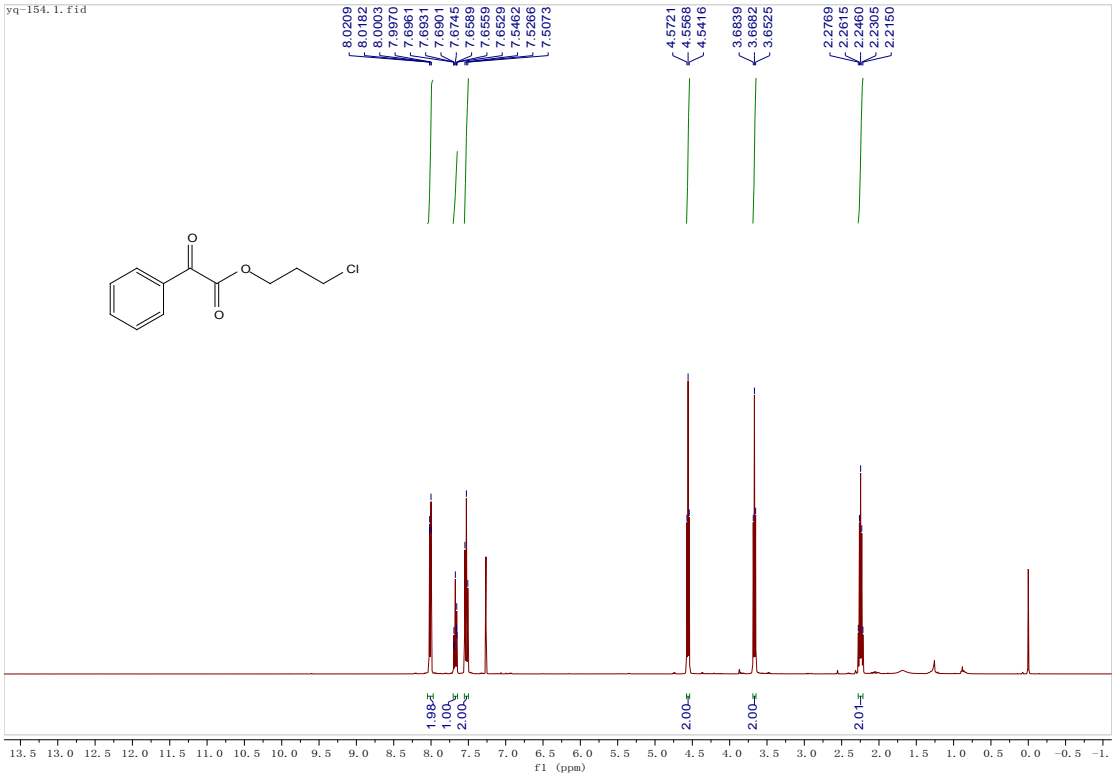


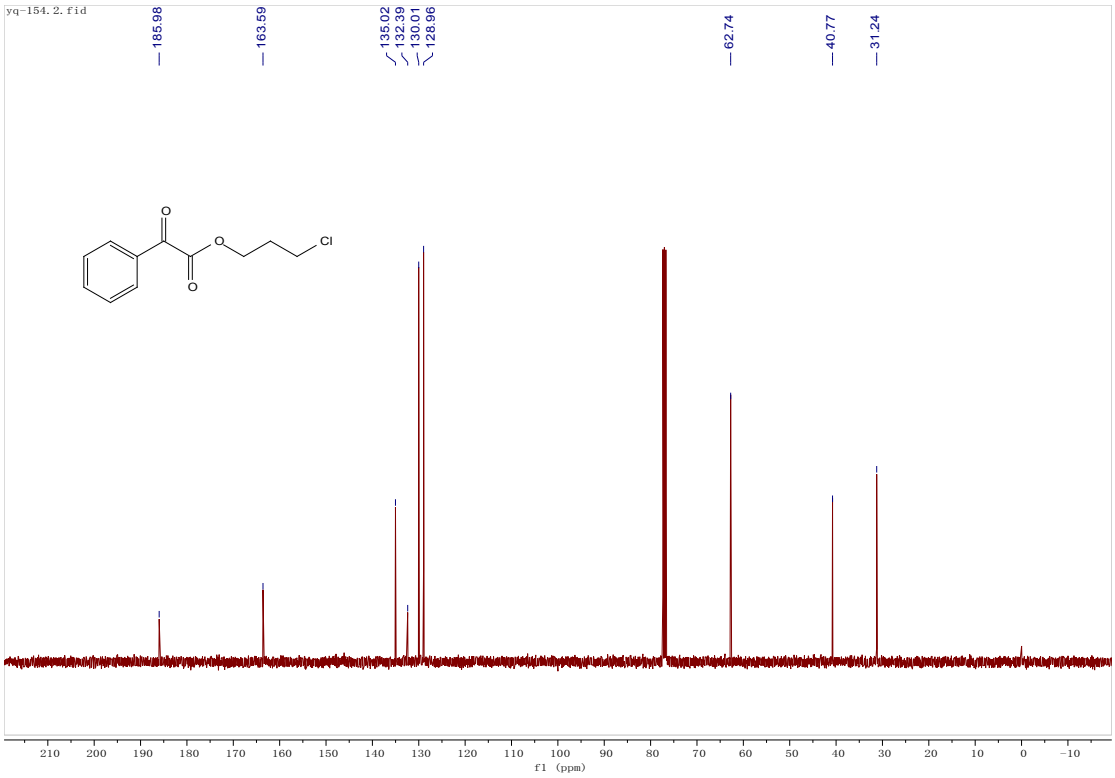
^{1}H and ^{13}C NMR spectra of **3ae**



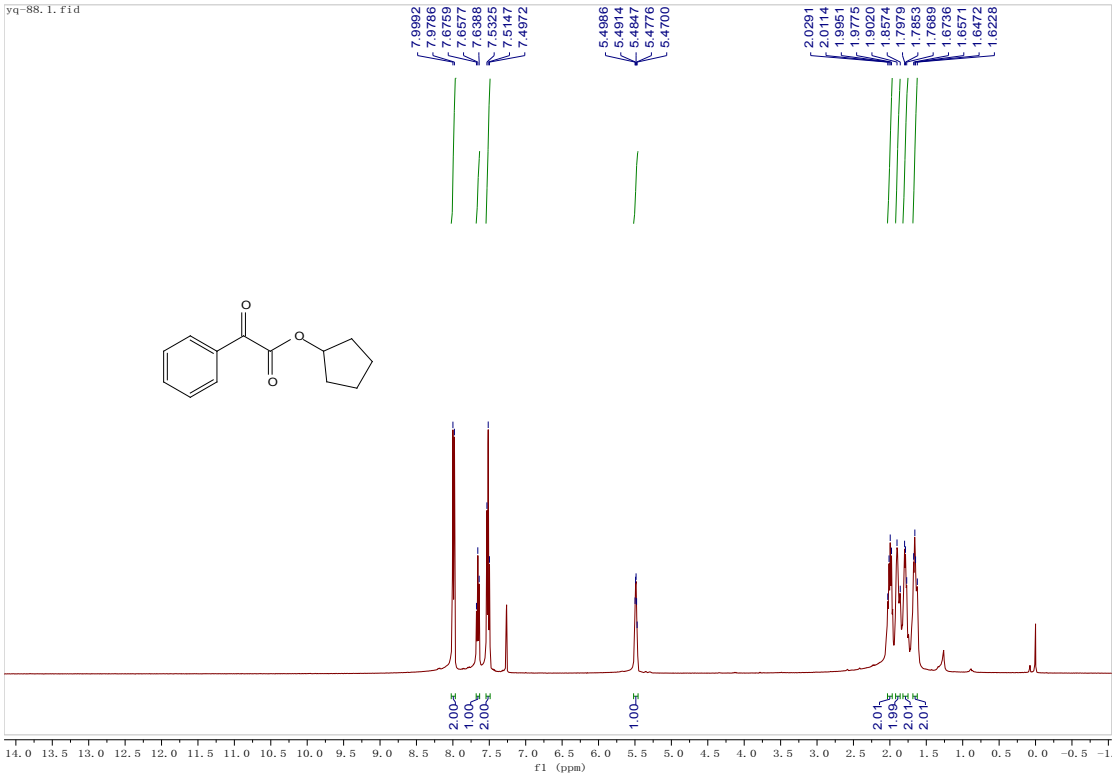


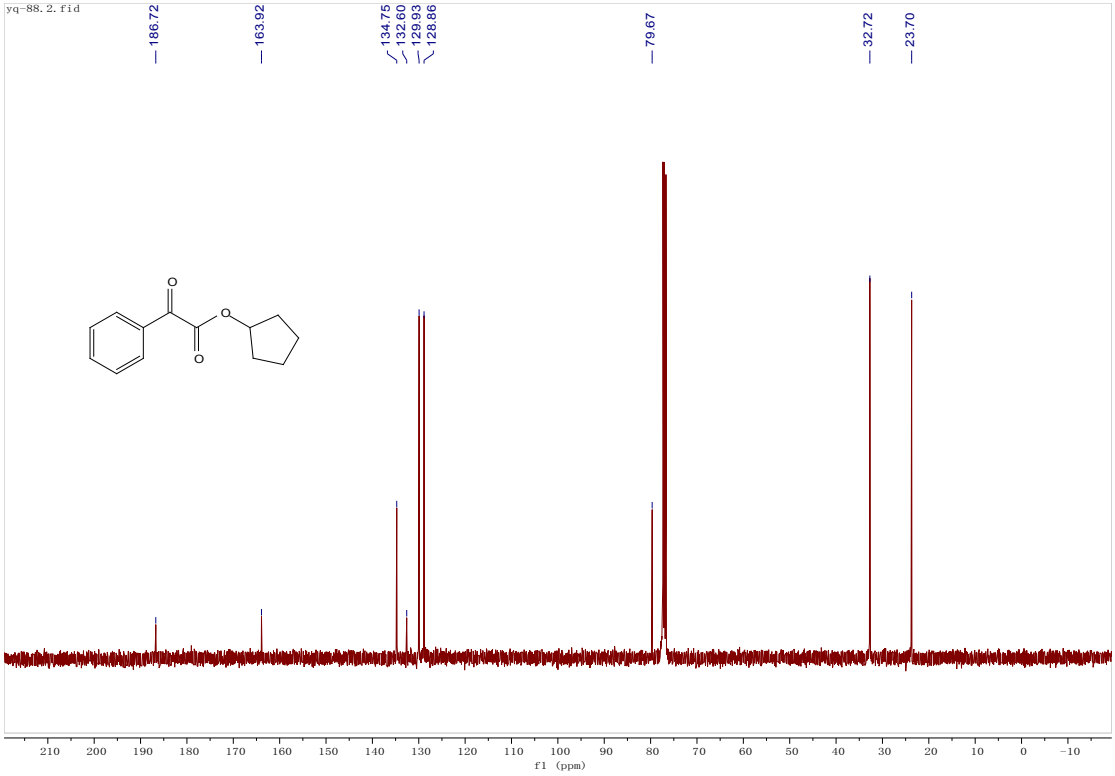
^{1}H and ^{13}C NMR spectra of **3af**



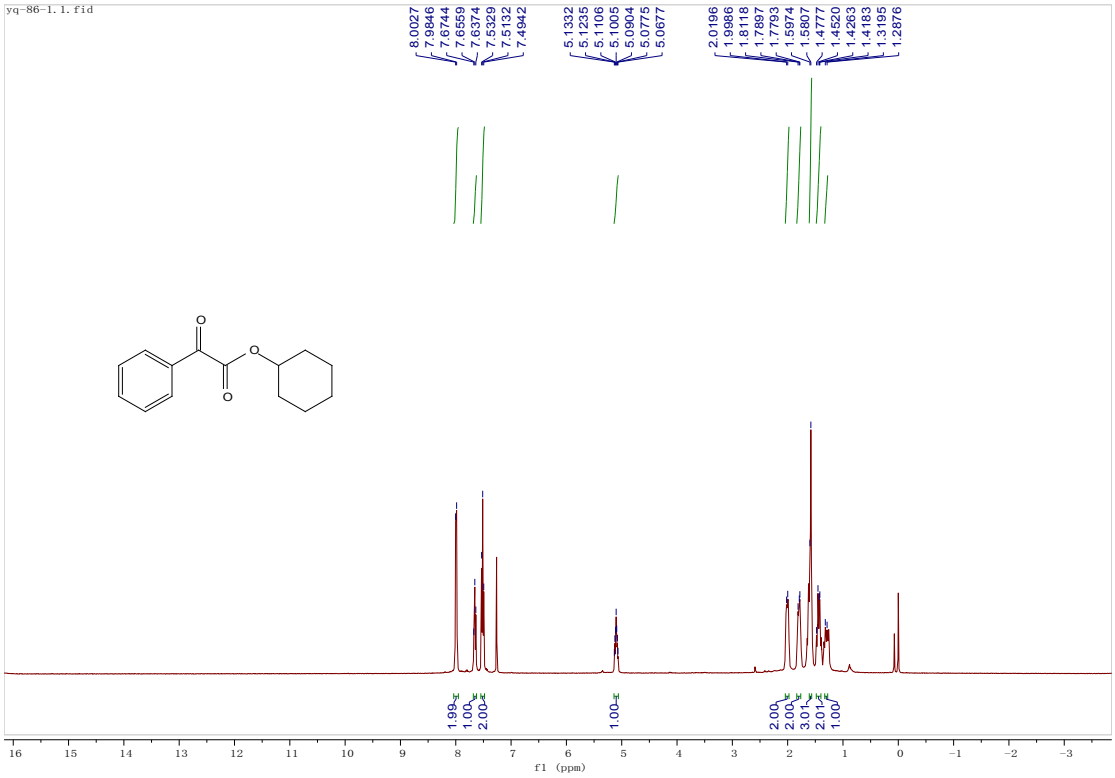


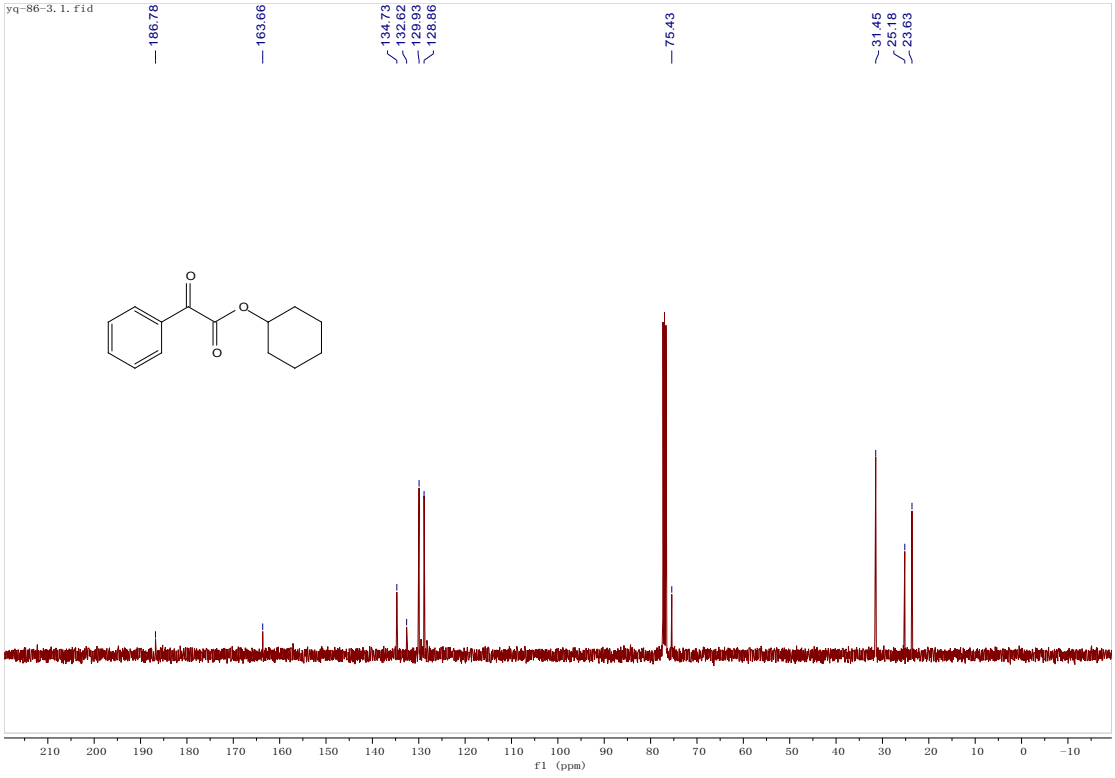
^{1}H and ^{13}C NMR spectra of **3ag**



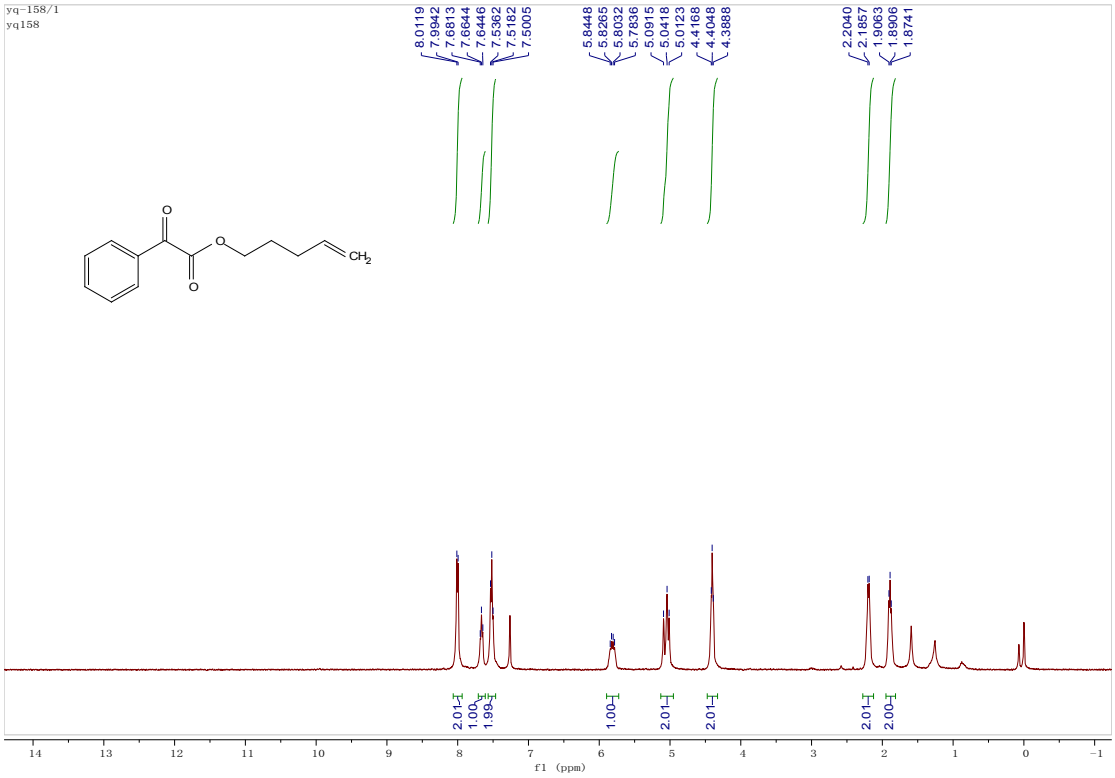


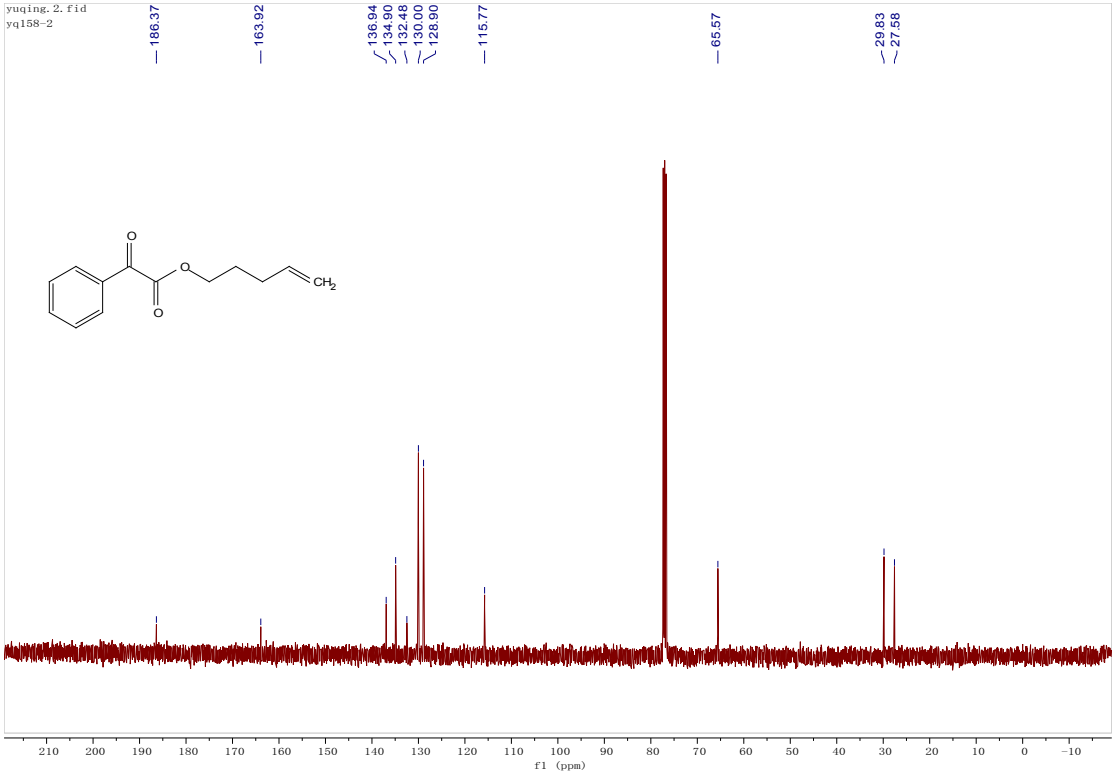
^{1}H and ^{13}C NMR spectra of **3ah**



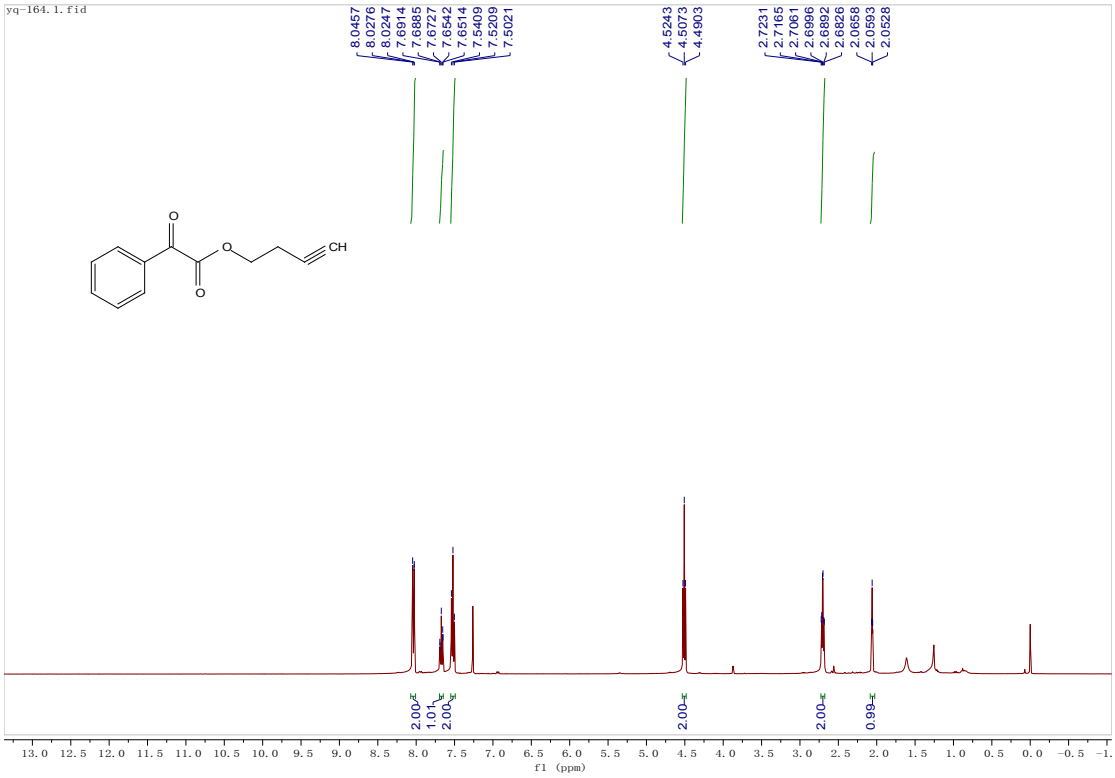


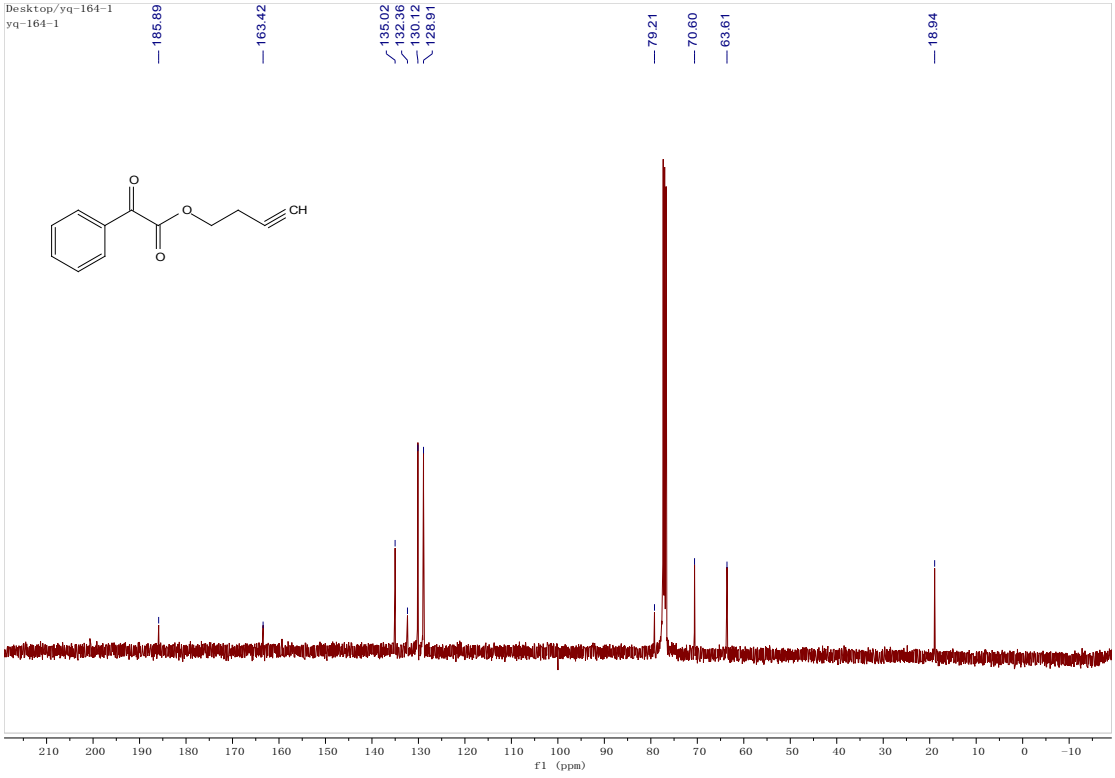
^{1}H and ^{13}C NMR spectra of **3ai**



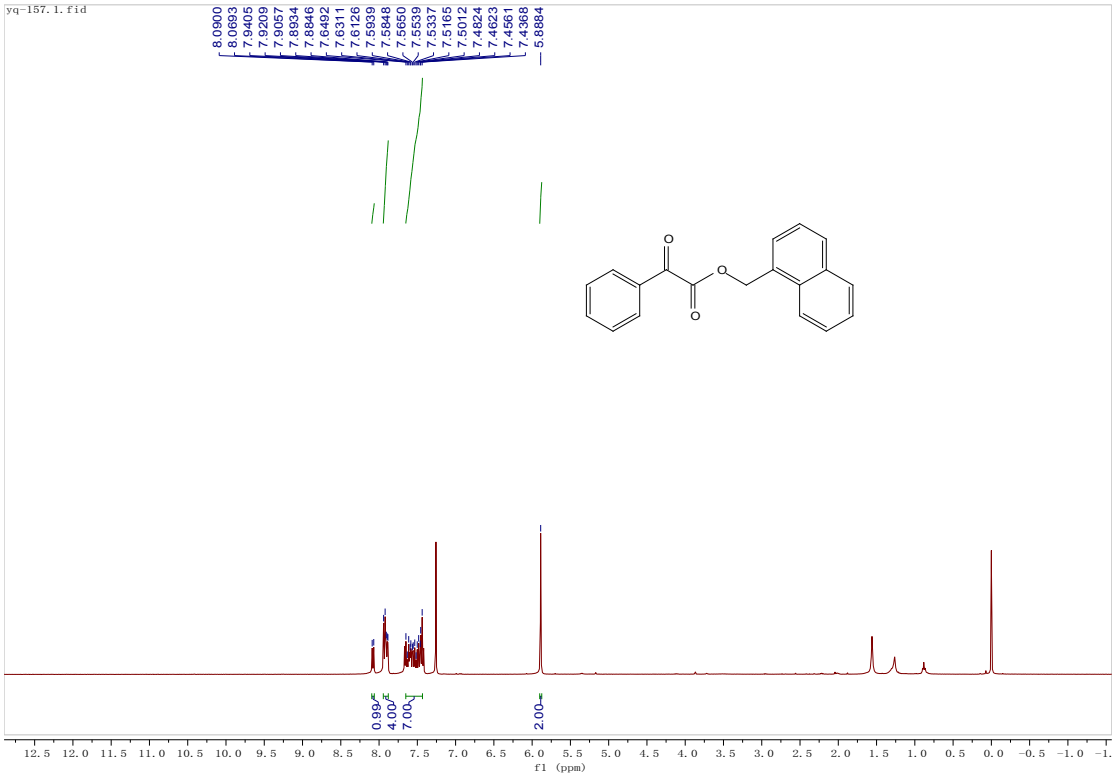


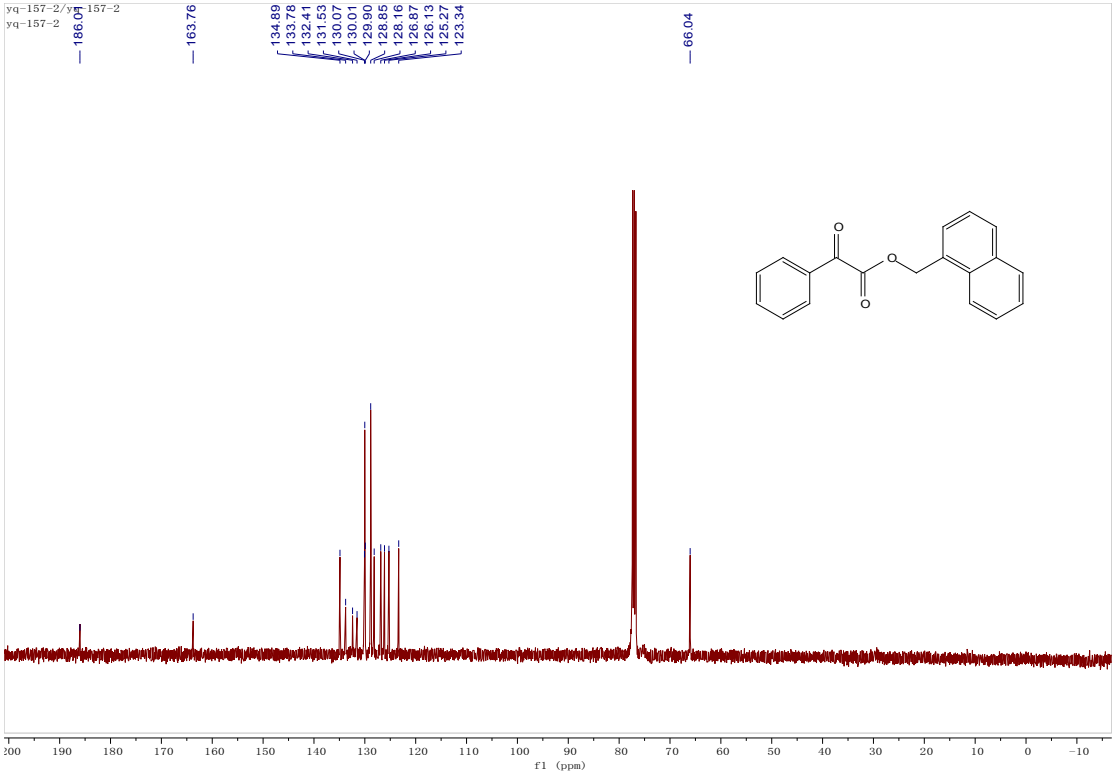
^{1}H and ^{13}C NMR spectra of **3aj**



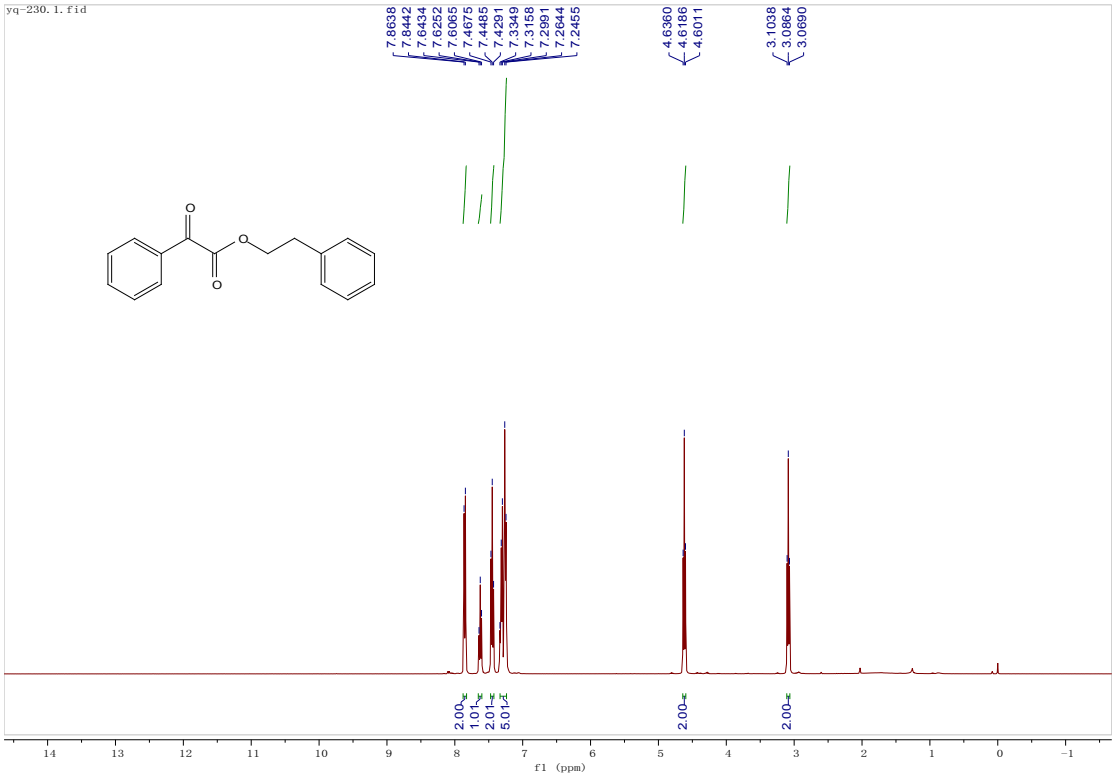


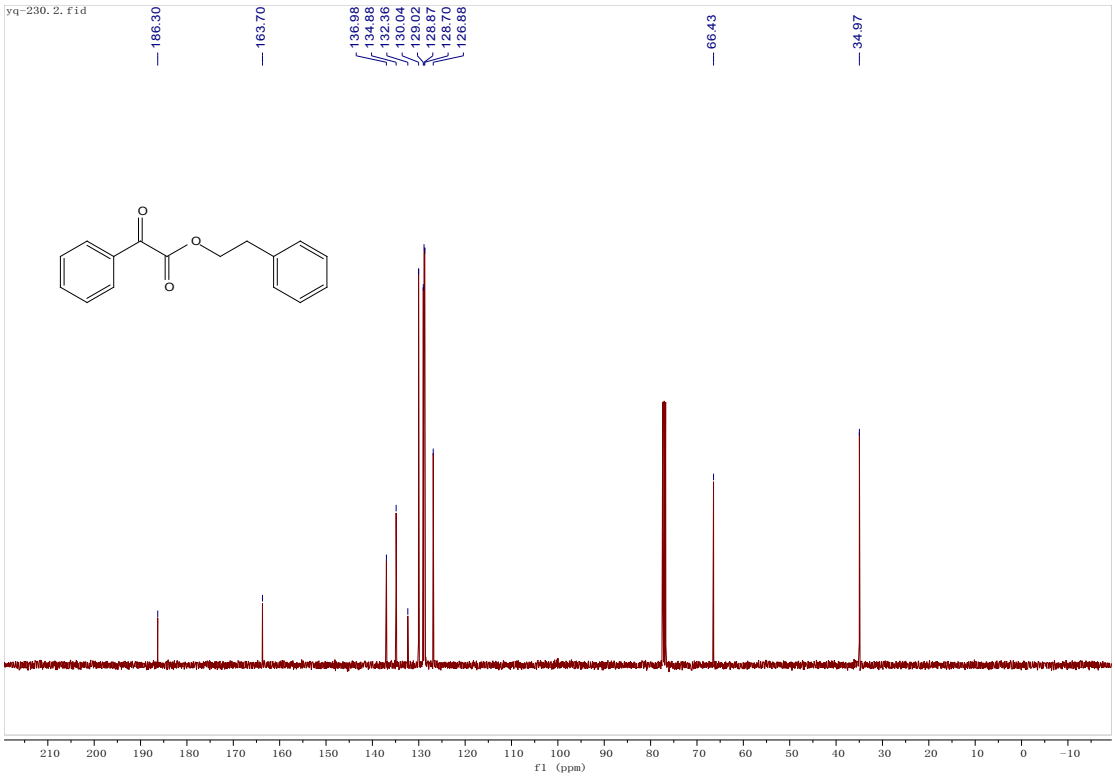
^{1}H and ^{13}C NMR spectra of **3ak**



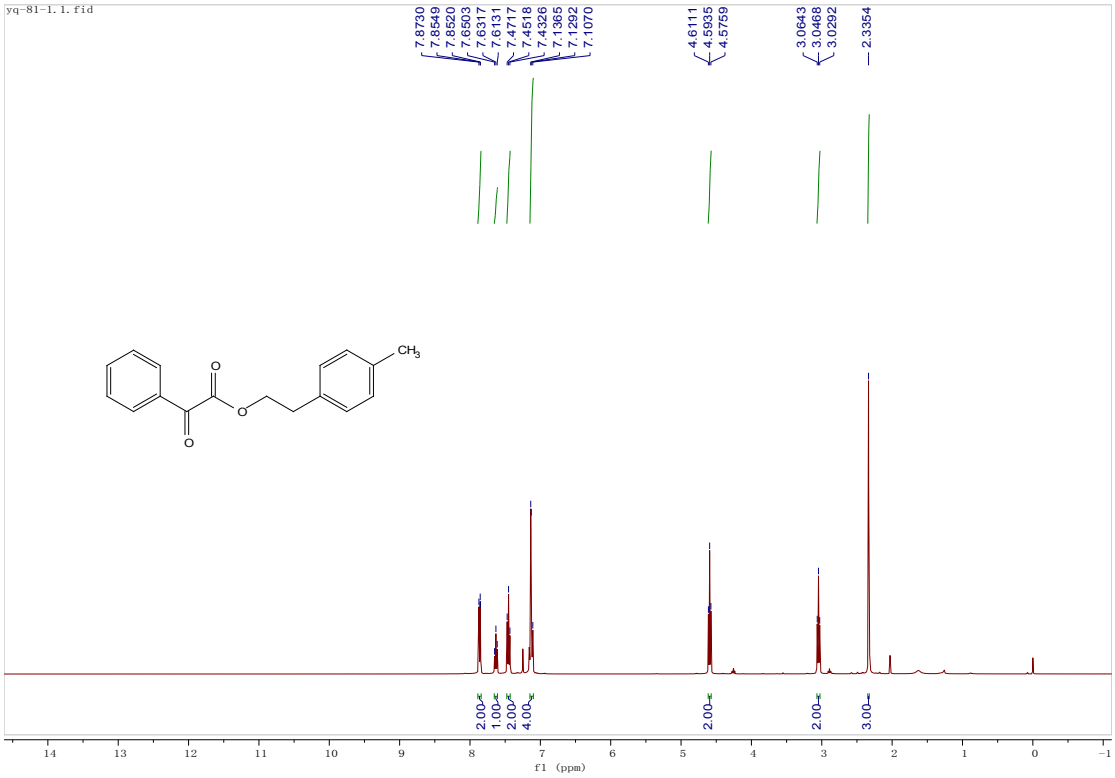


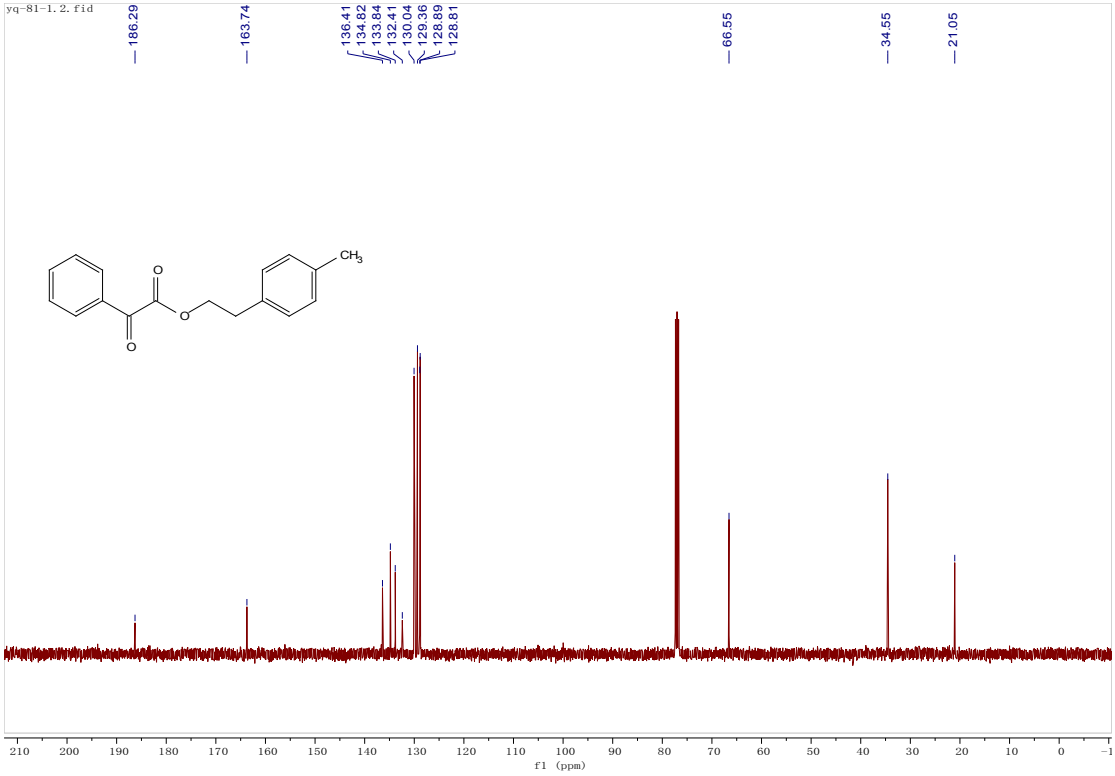
^{1}H and ^{13}C NMR spectra of **3al**



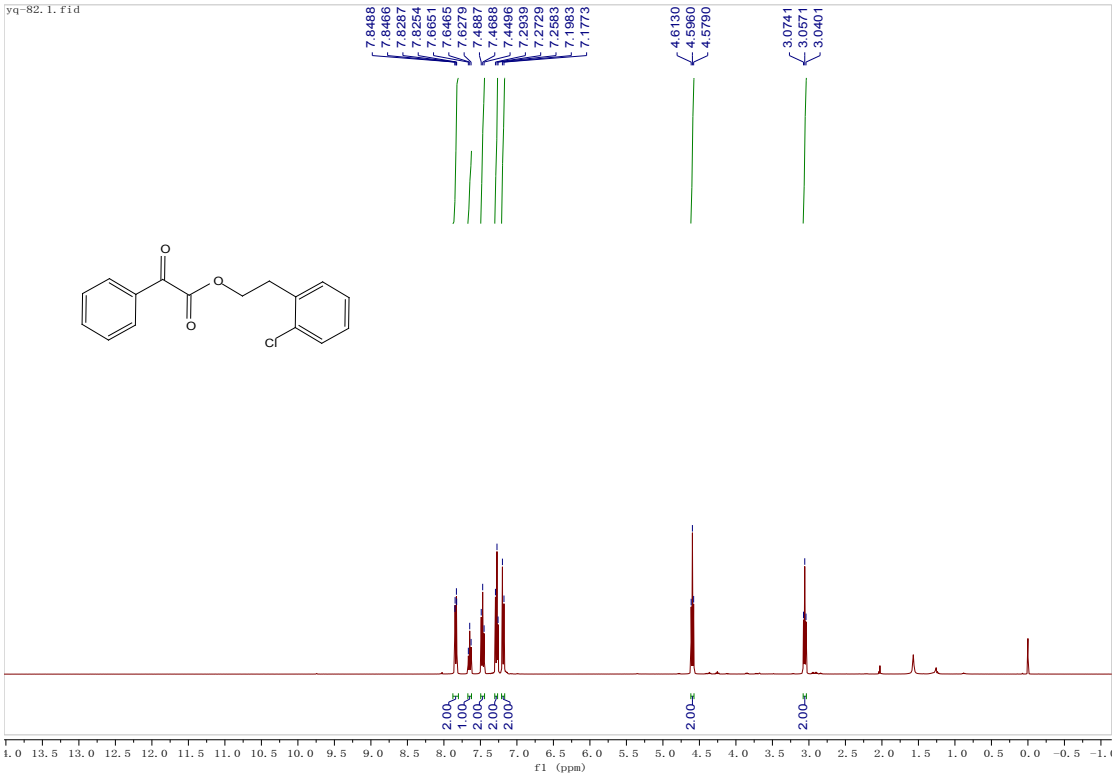


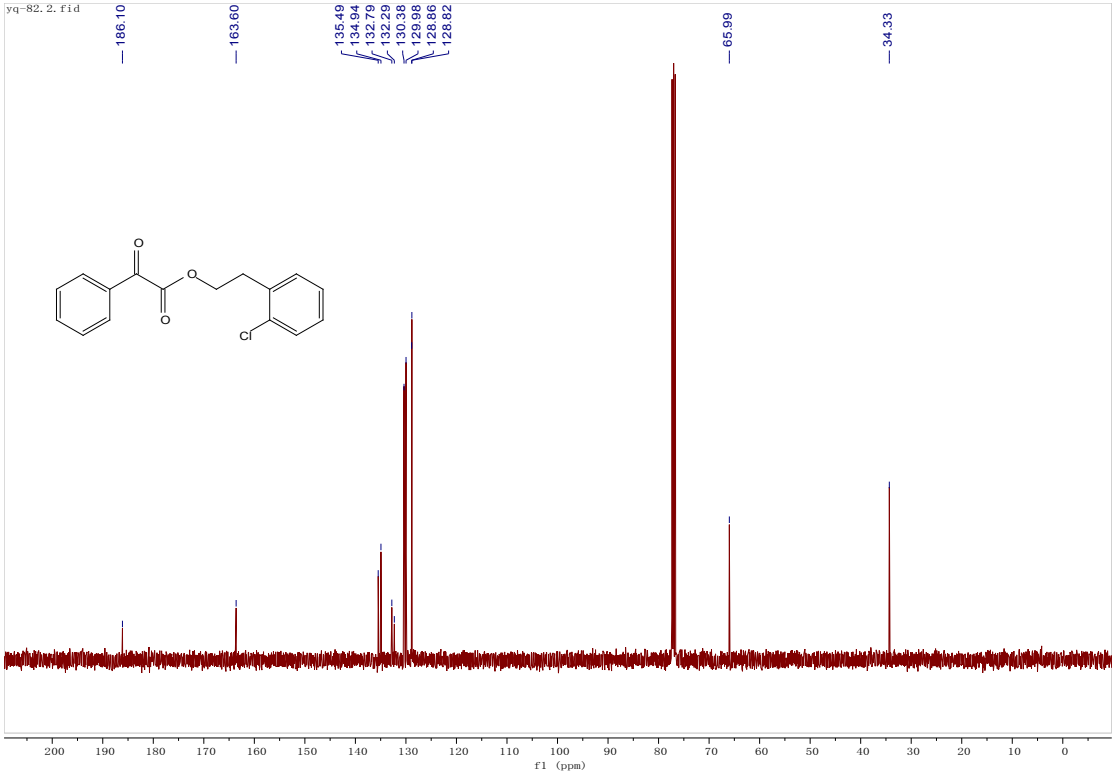
^{1}H and ^{13}C NMR spectra of **3am**



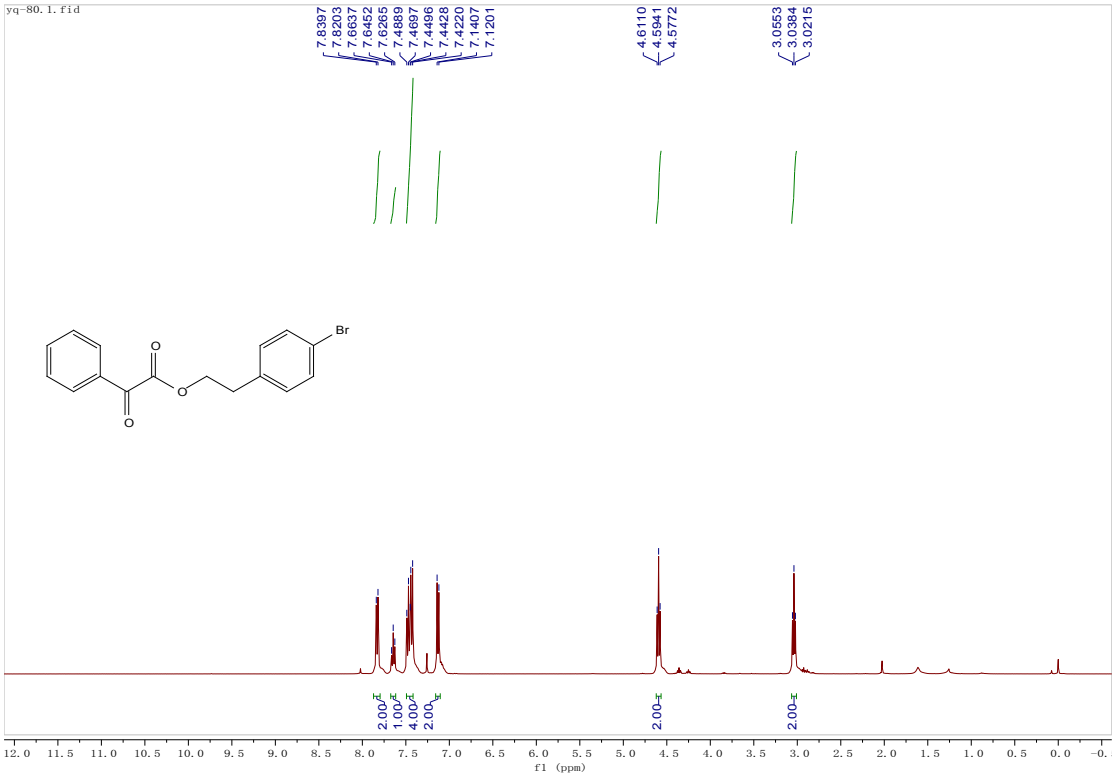


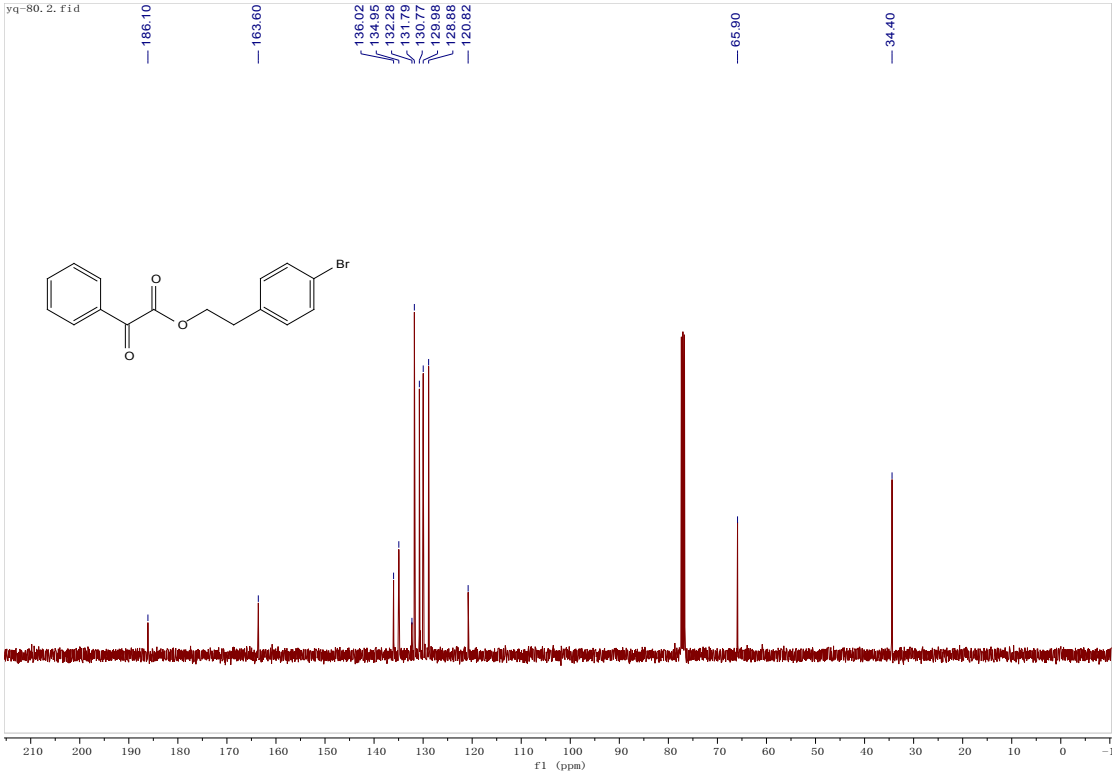
^{1}H and ^{13}C NMR spectra of **3an**



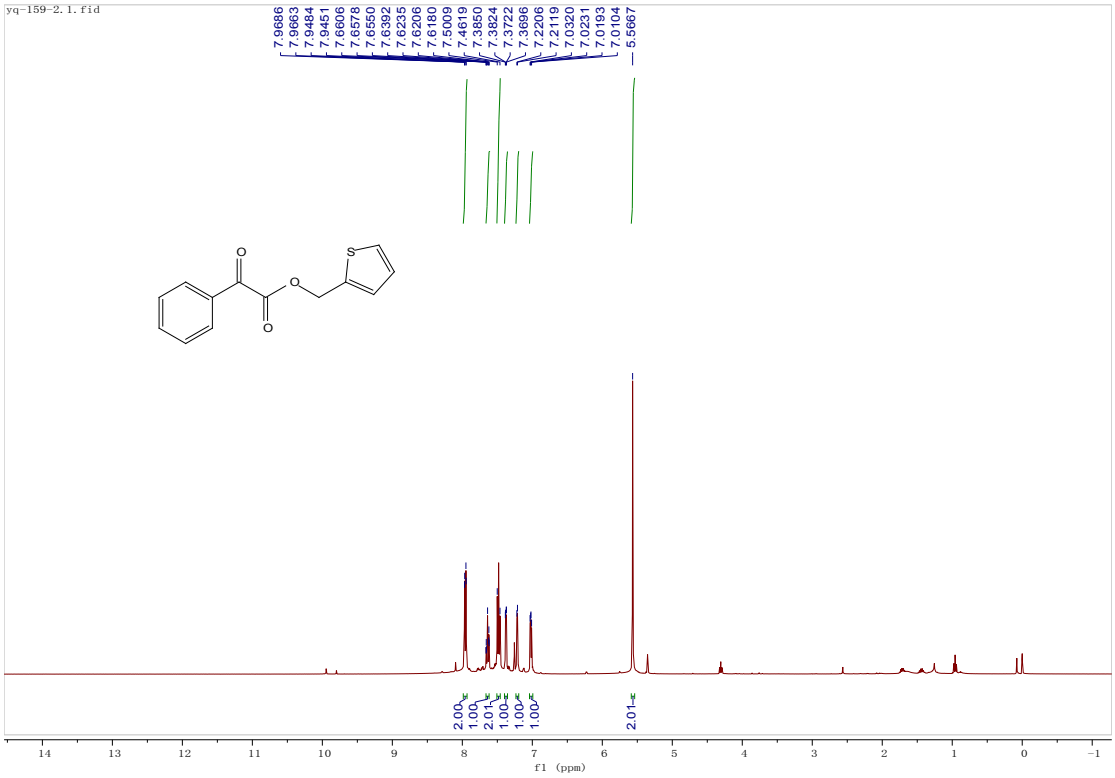


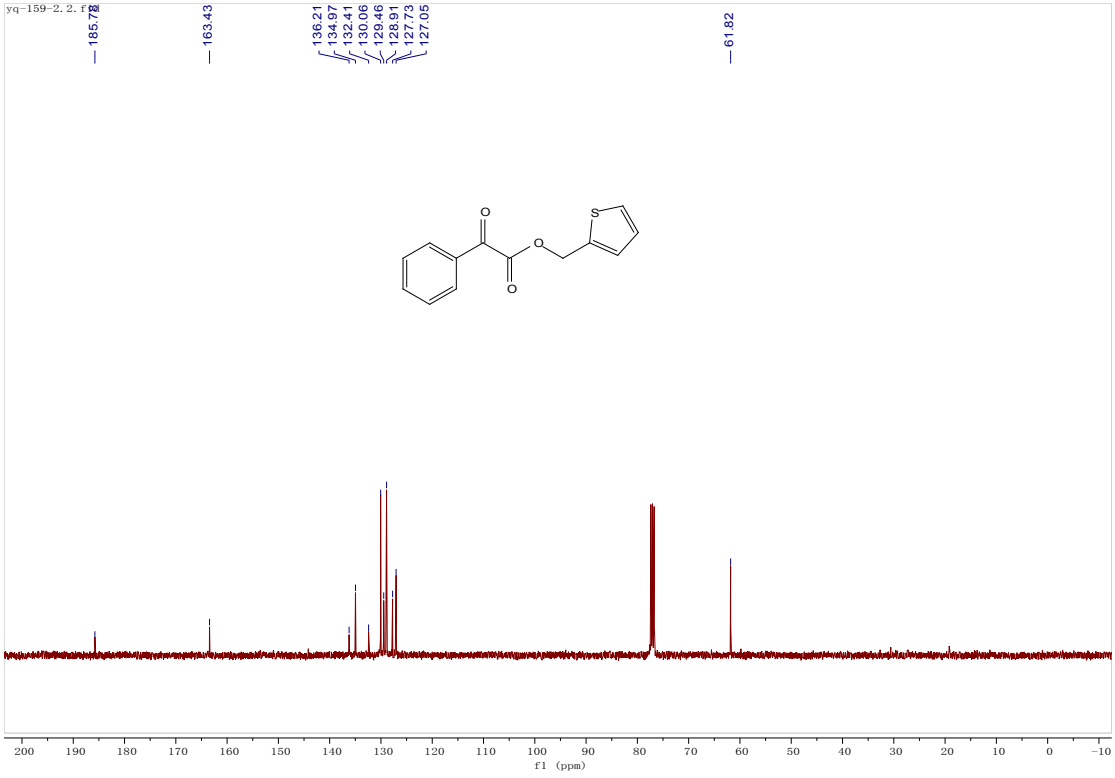
^{1}H and ^{13}C NMR spectra of **3ao**



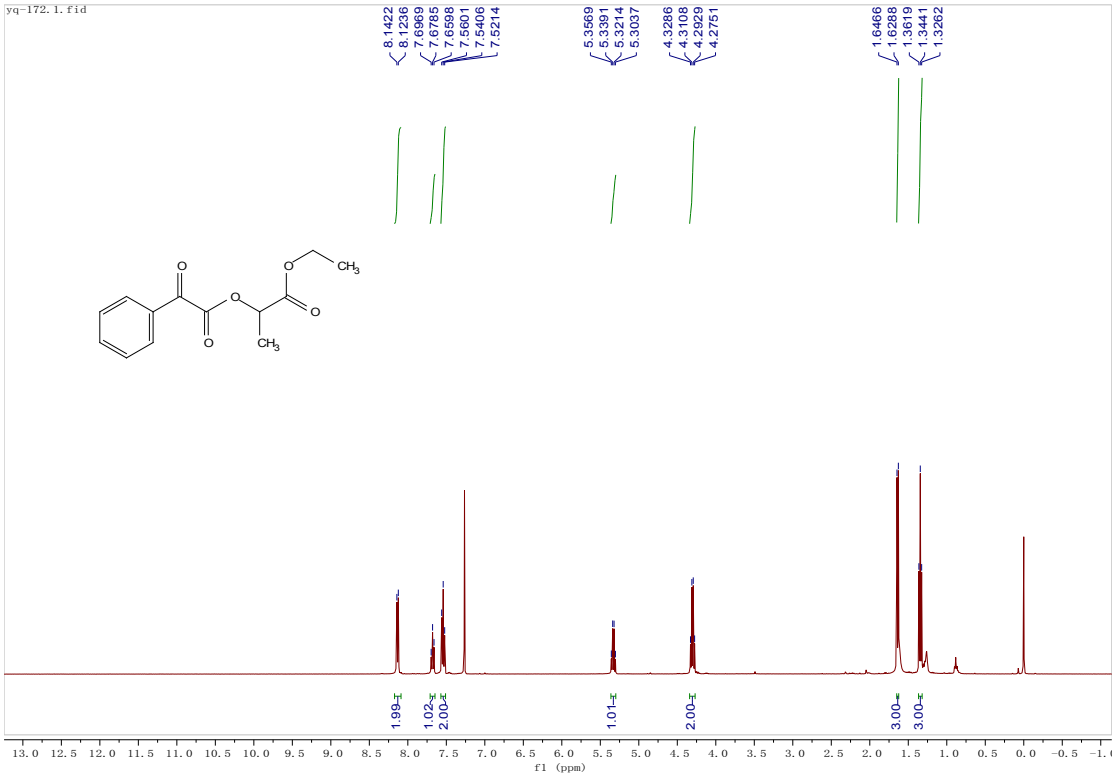


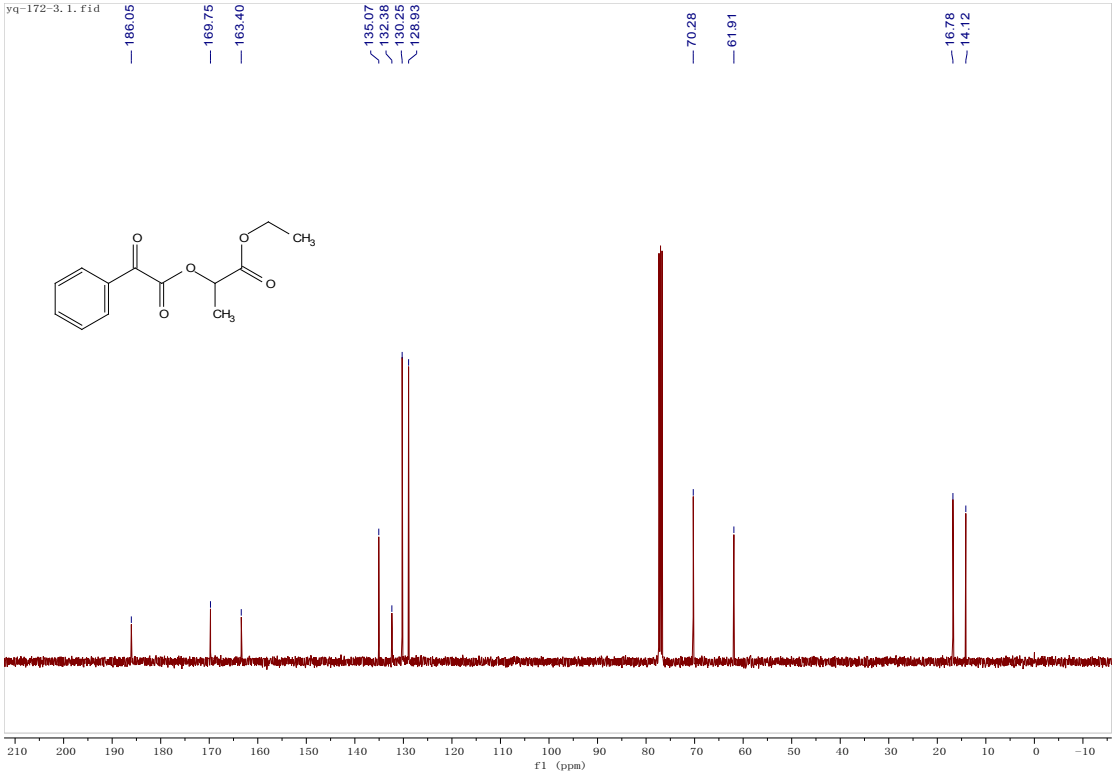
^{1}H and ^{13}C NMR spectra of **3ap**



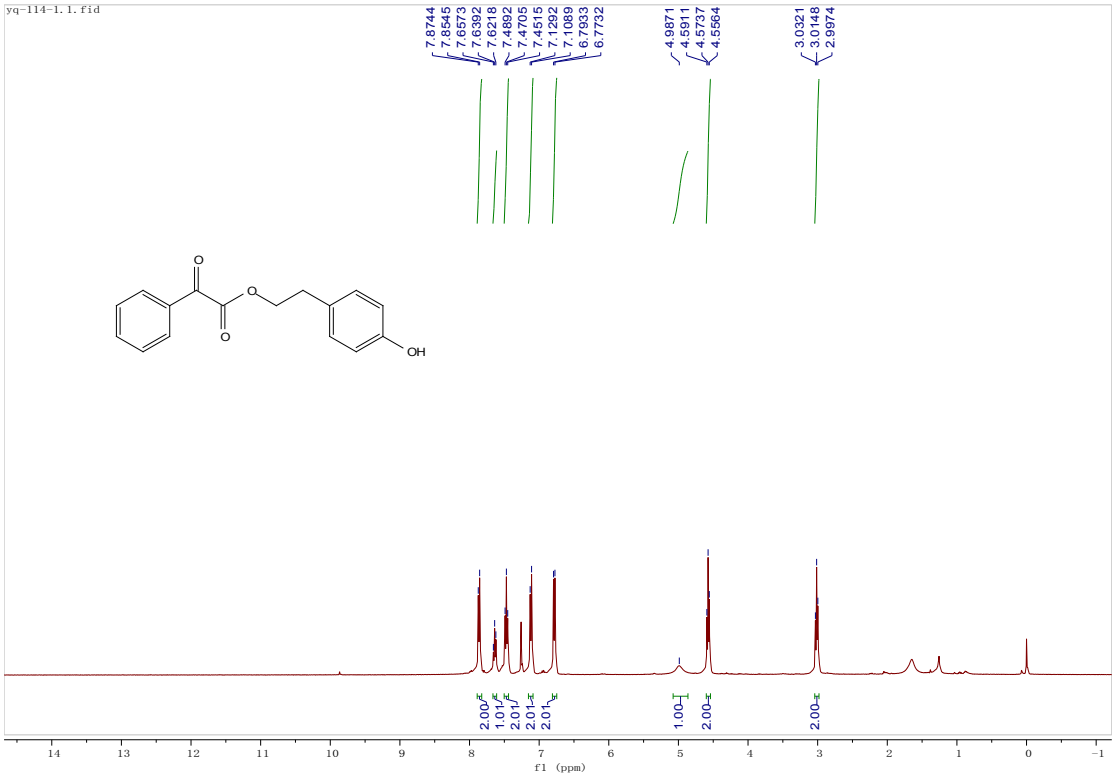


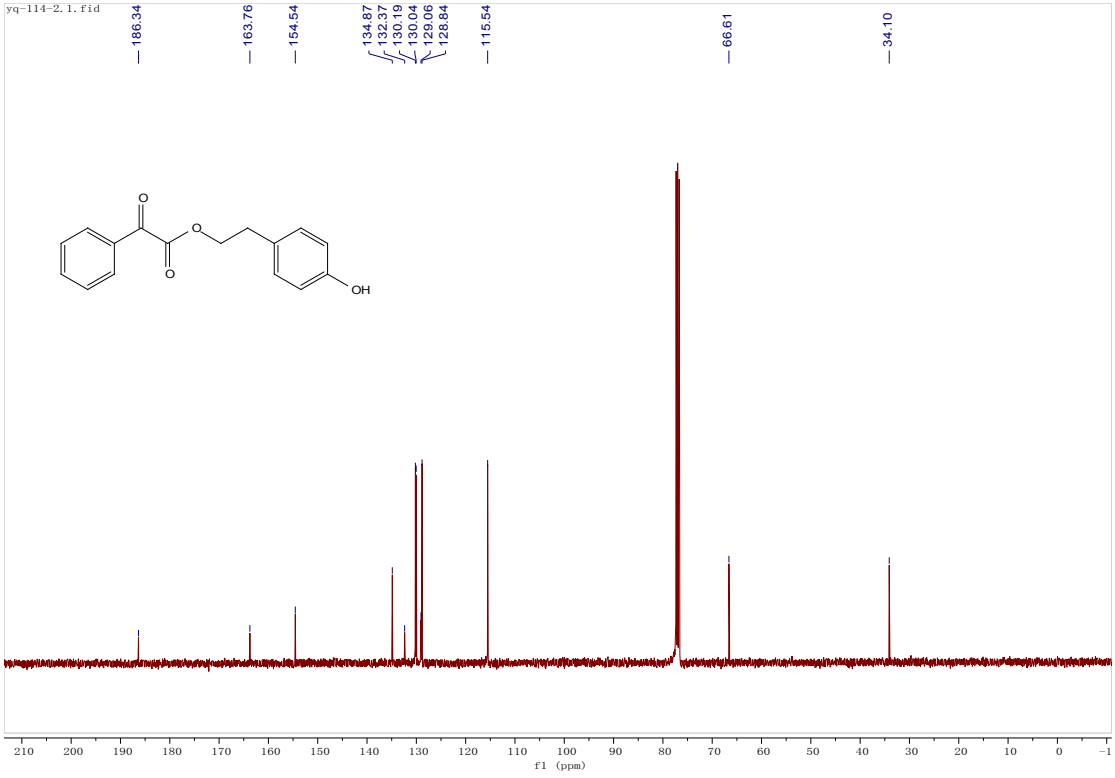
^{1}H and ^{13}C NMR spectra of **3aq**



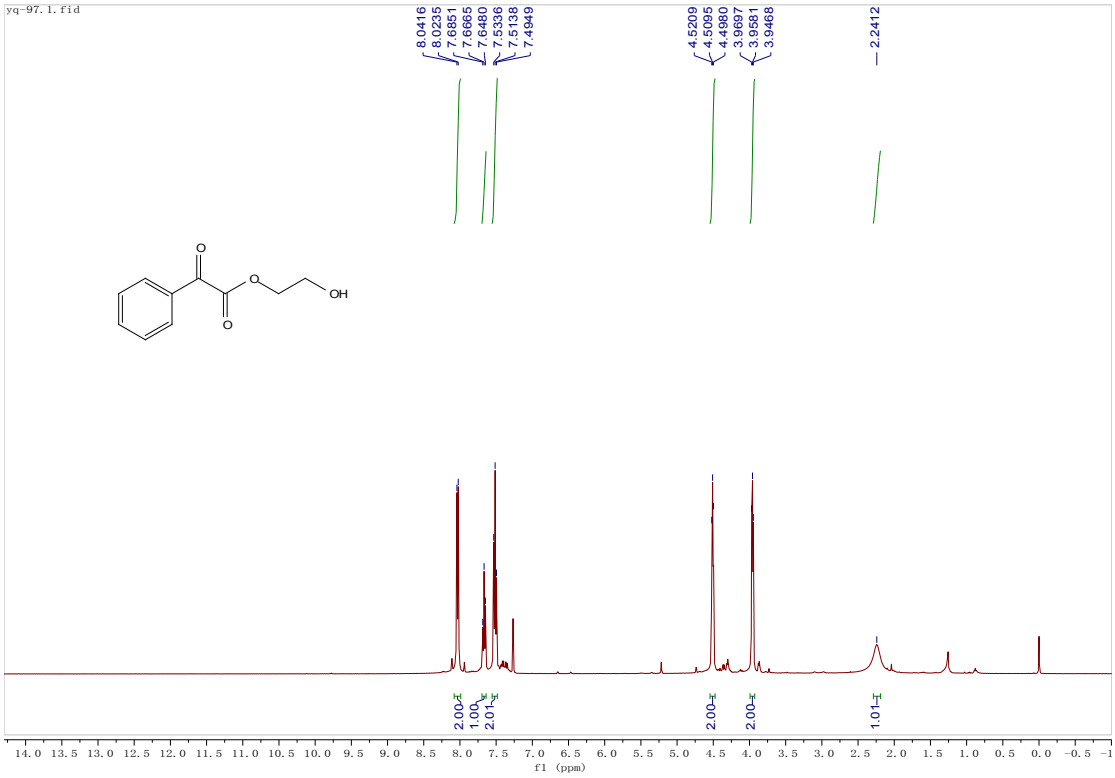


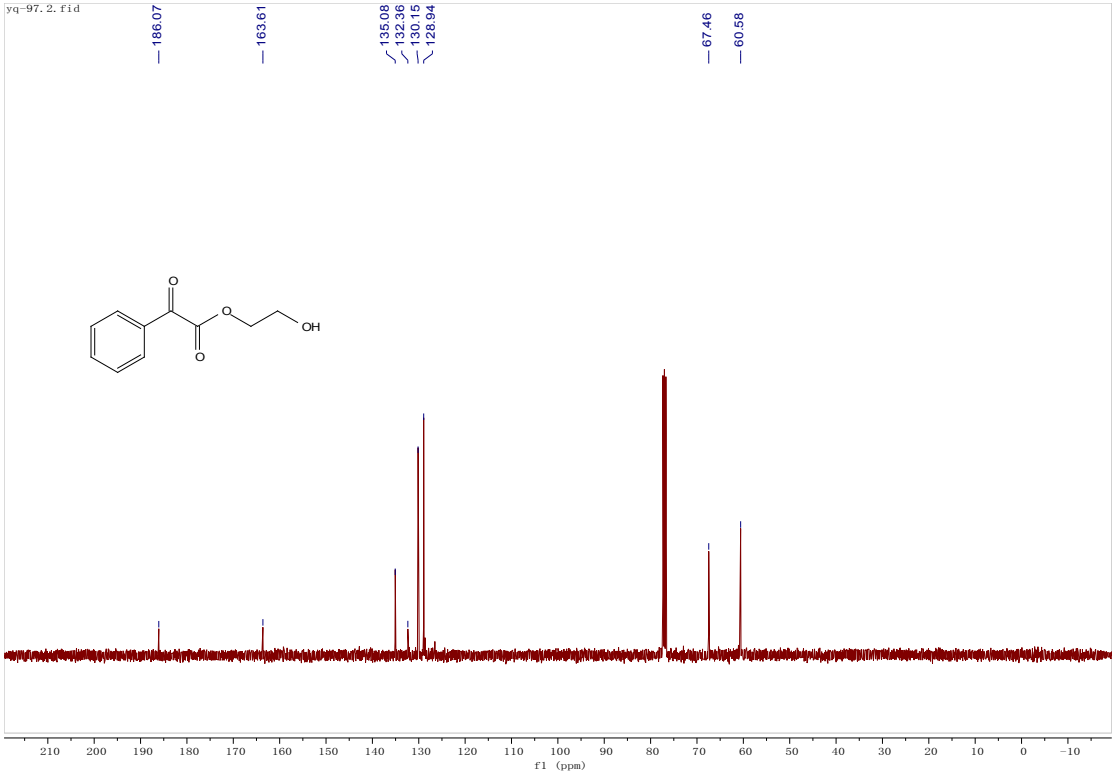
^{1}H and ^{13}C NMR spectra of **3ar**



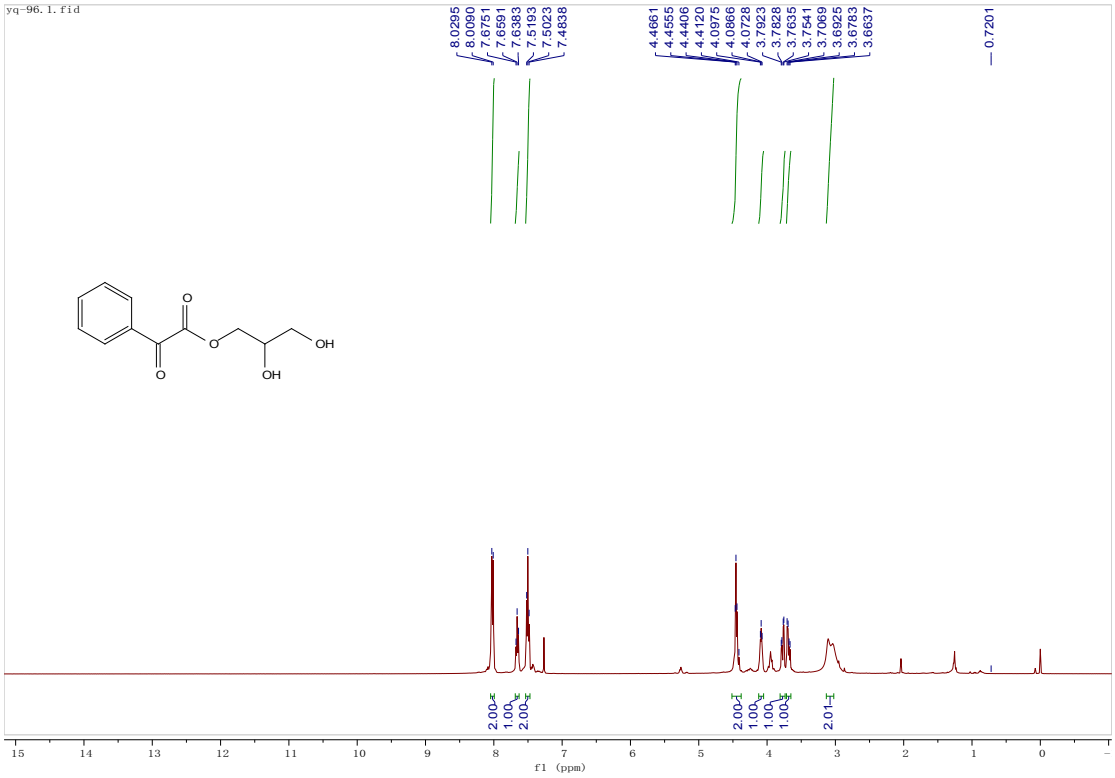


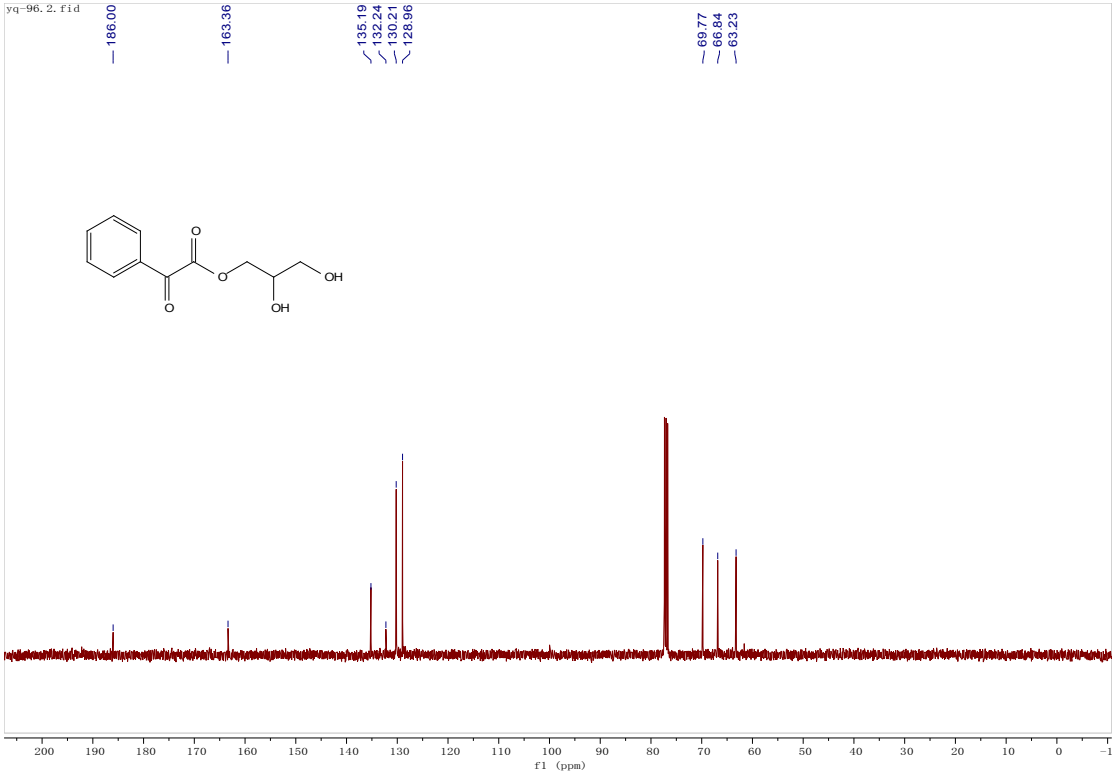
^{1}H and ^{13}C NMR spectra of **3as**



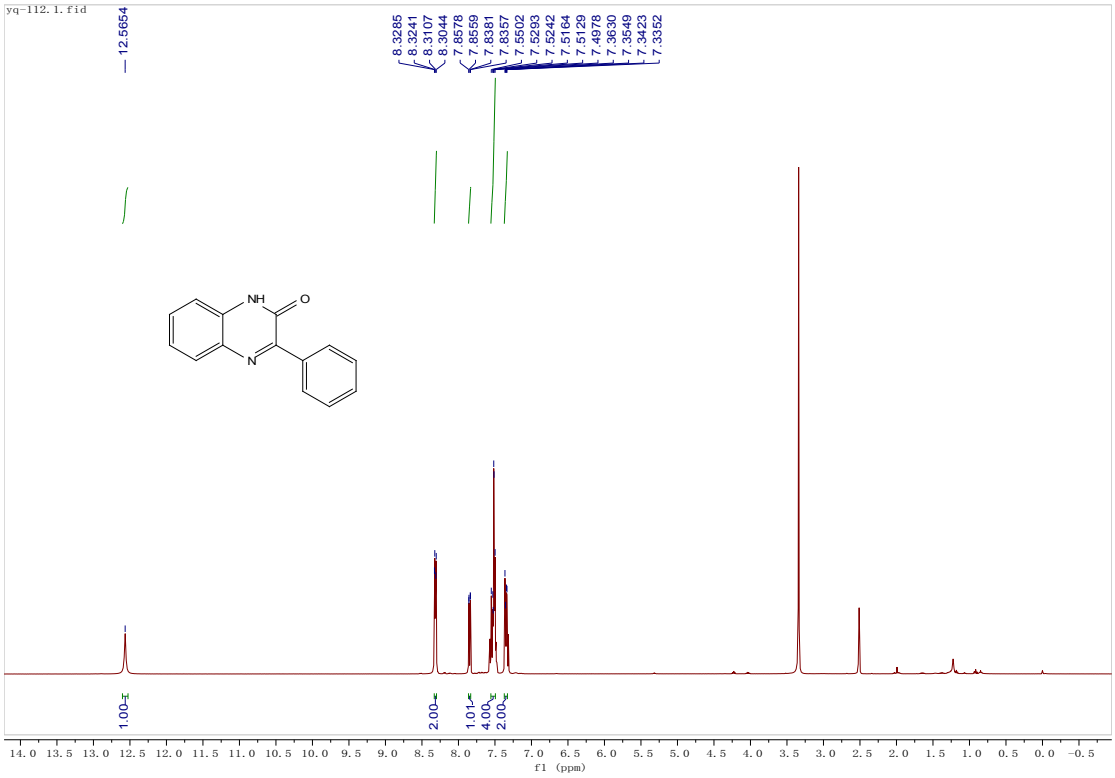


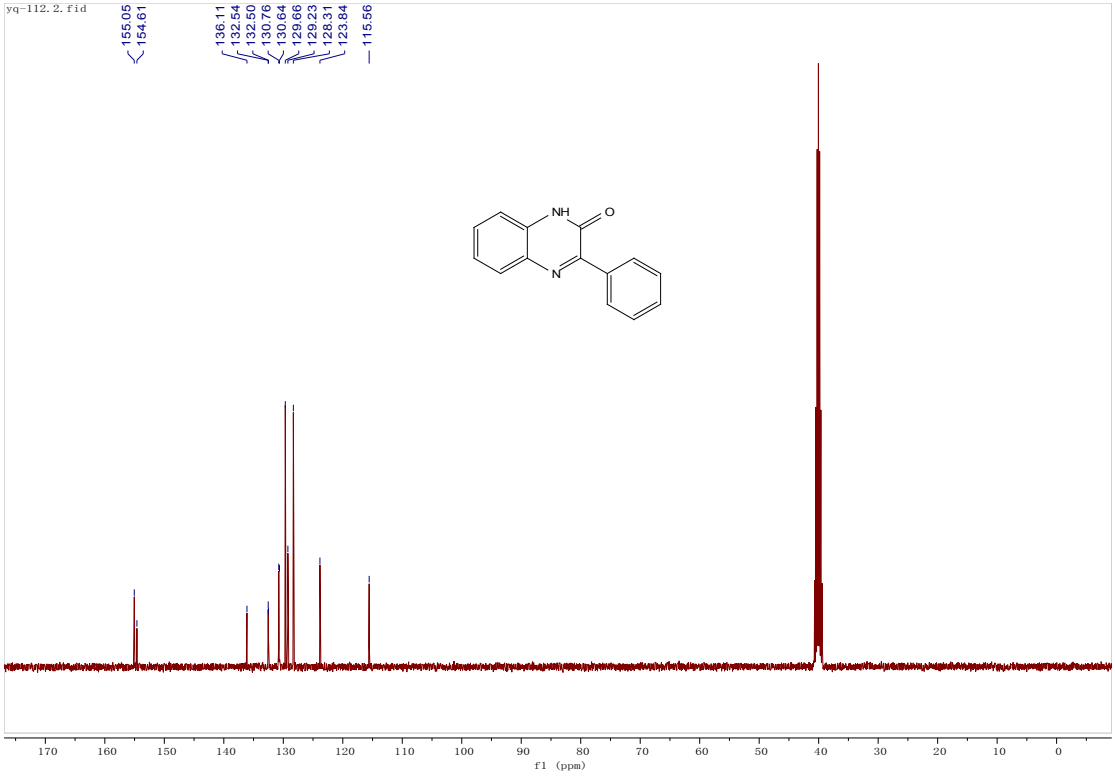
^{1}H and ^{13}C NMR spectra of **3at**



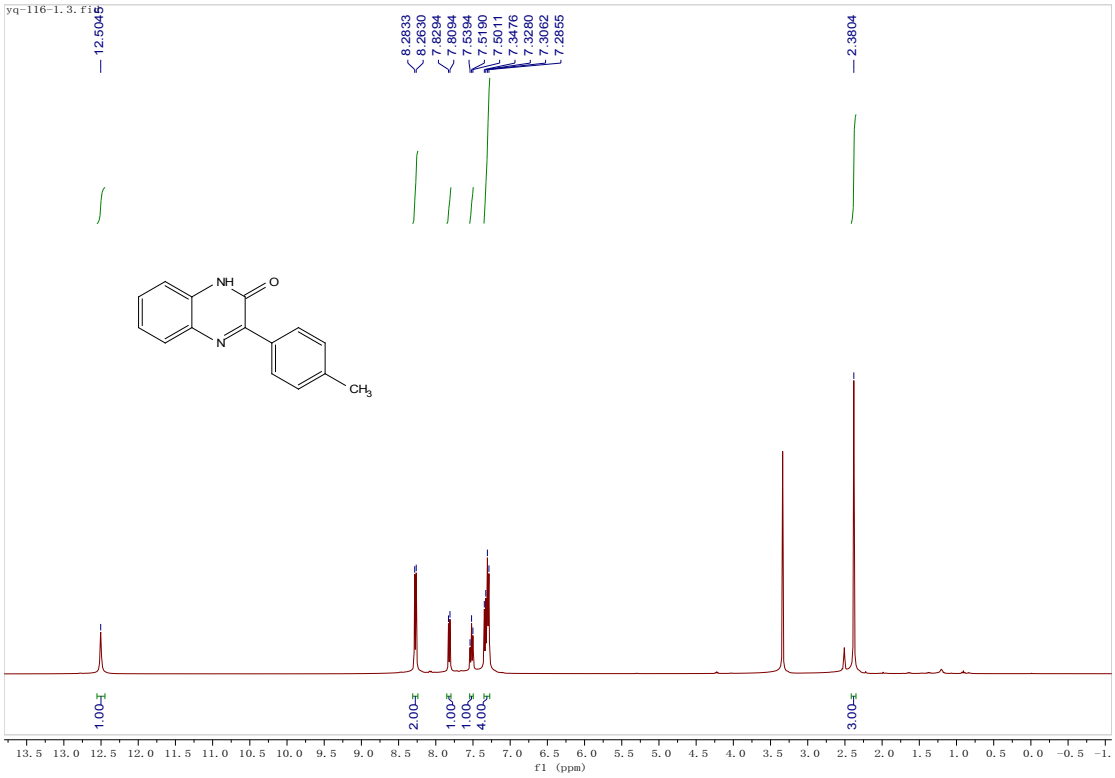


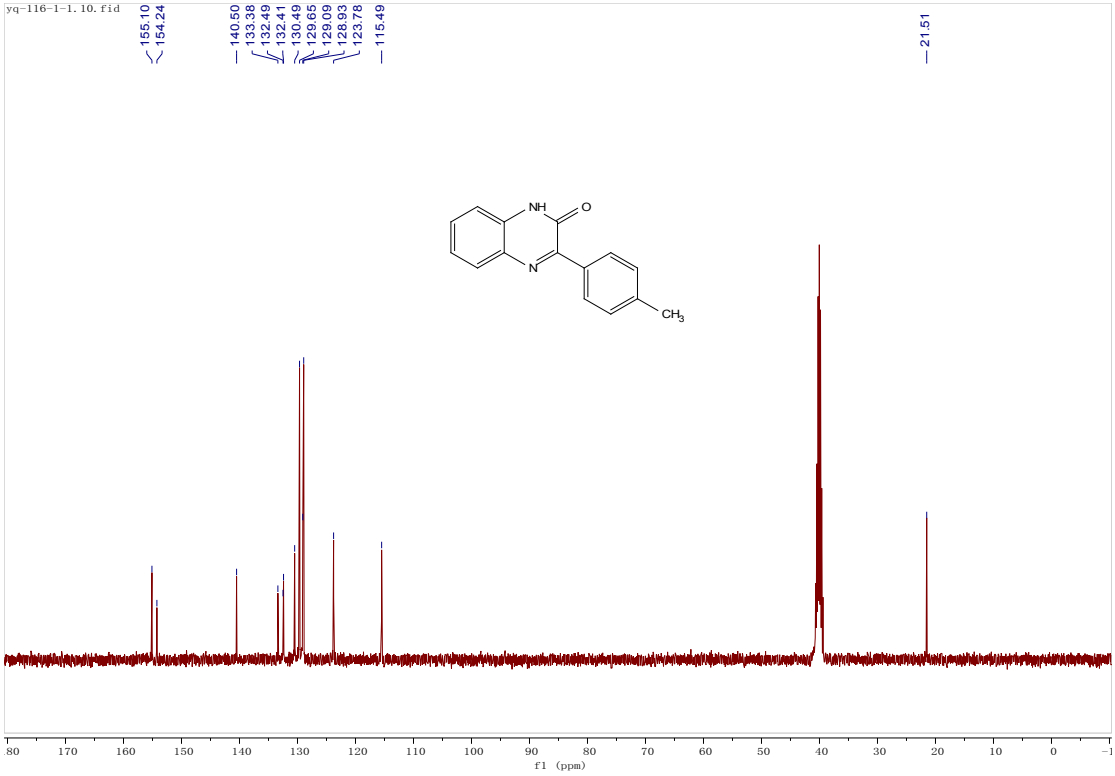
^{1}H and ^{13}C NMR spectra of **5a**



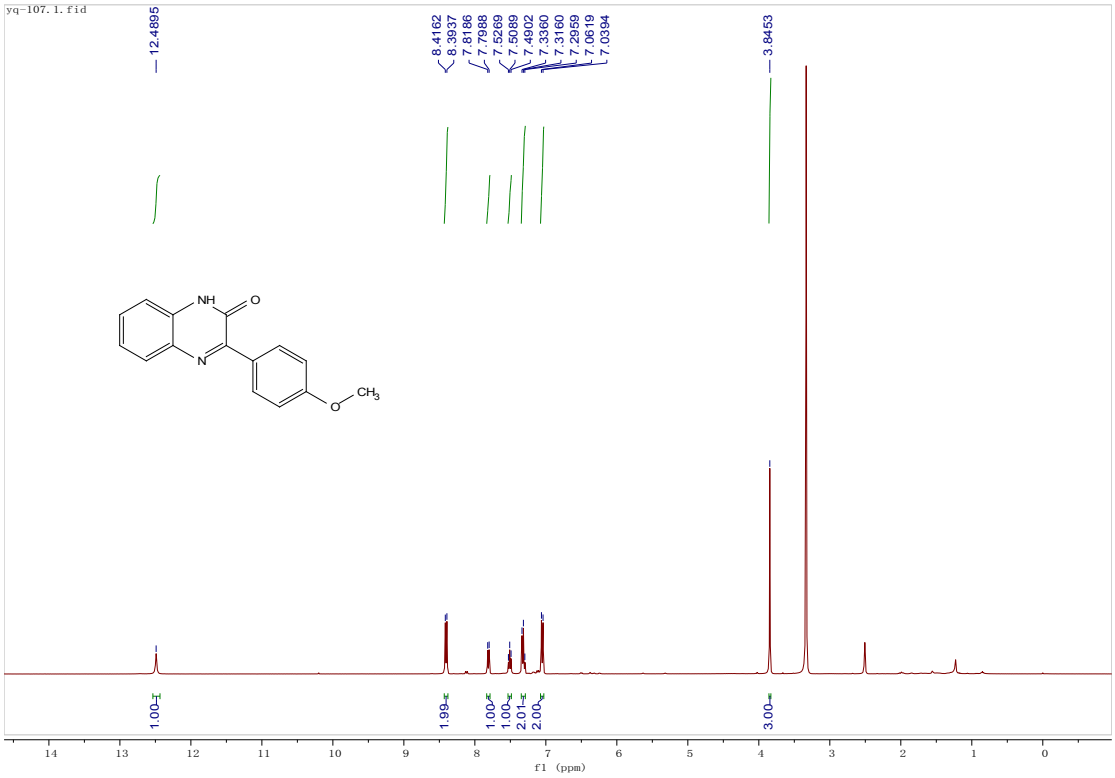


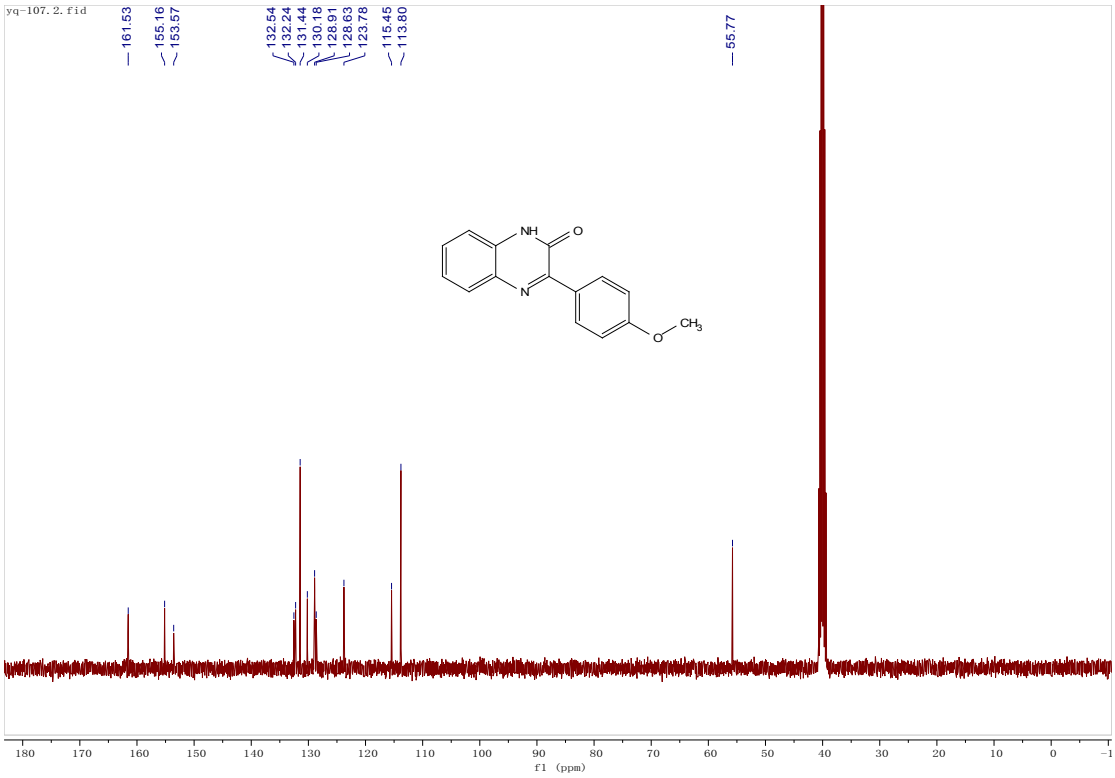
^{1}H and ^{13}C NMR spectra of **5b**



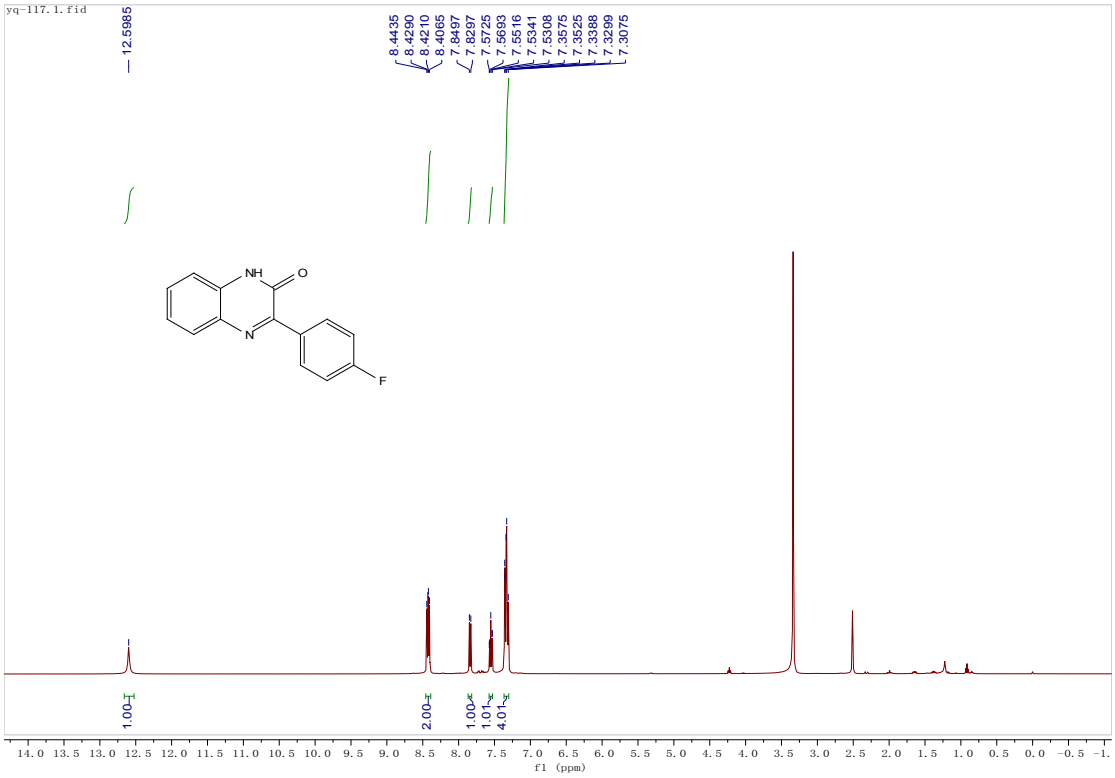


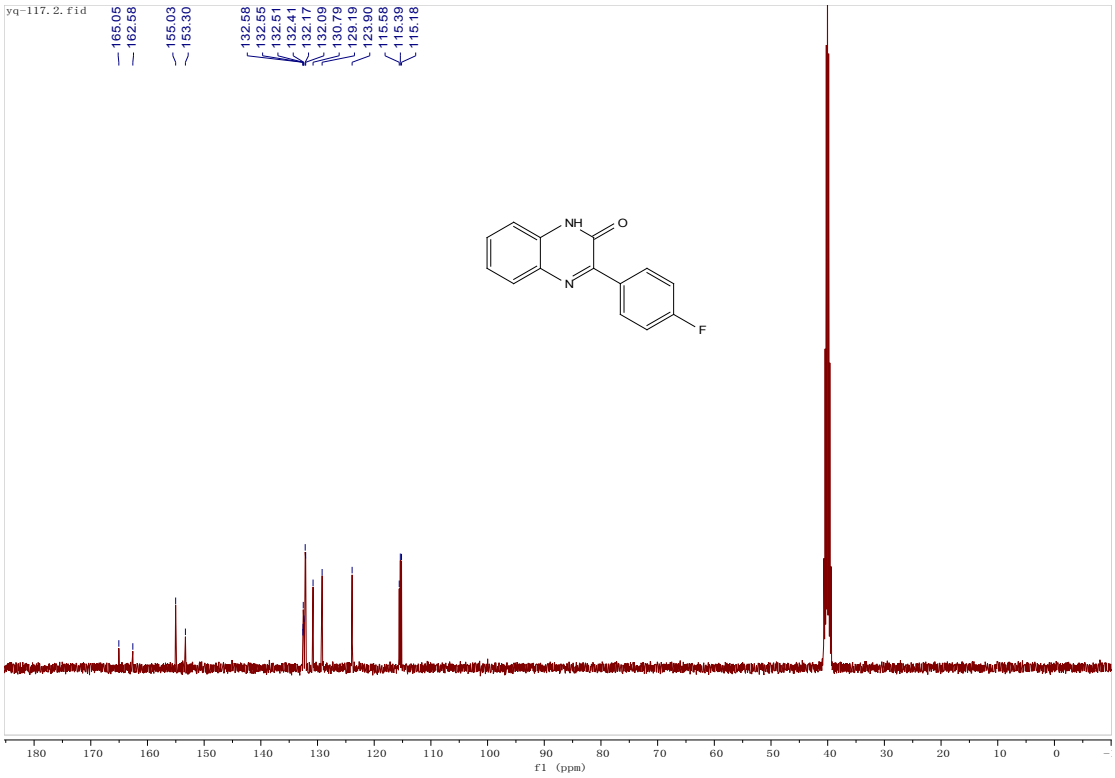
^{1}H and ^{13}C NMR spectra of **5c**



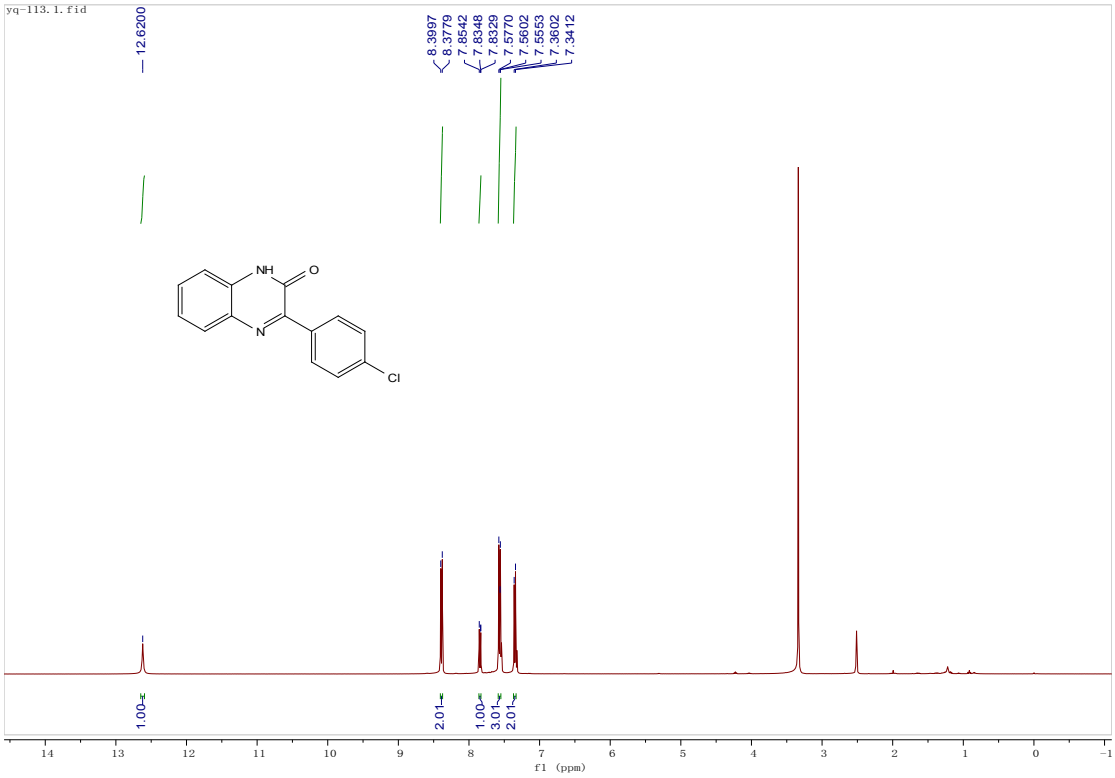


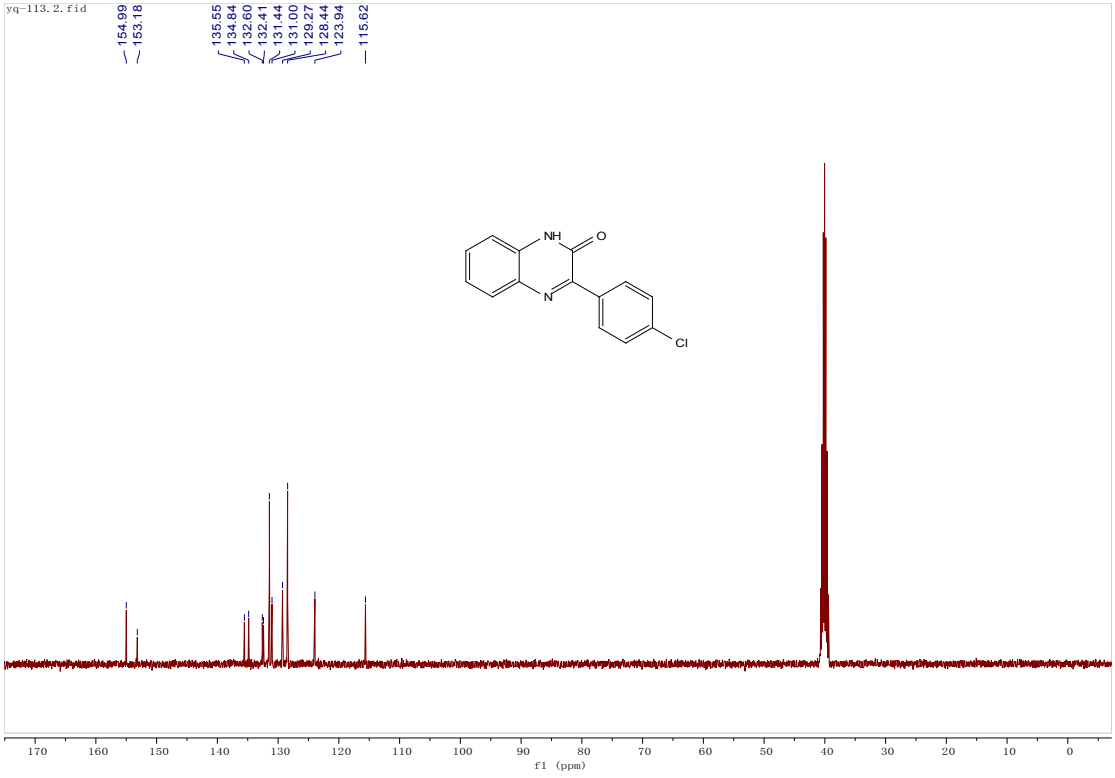
^{1}H and ^{13}C NMR spectra of **5d**



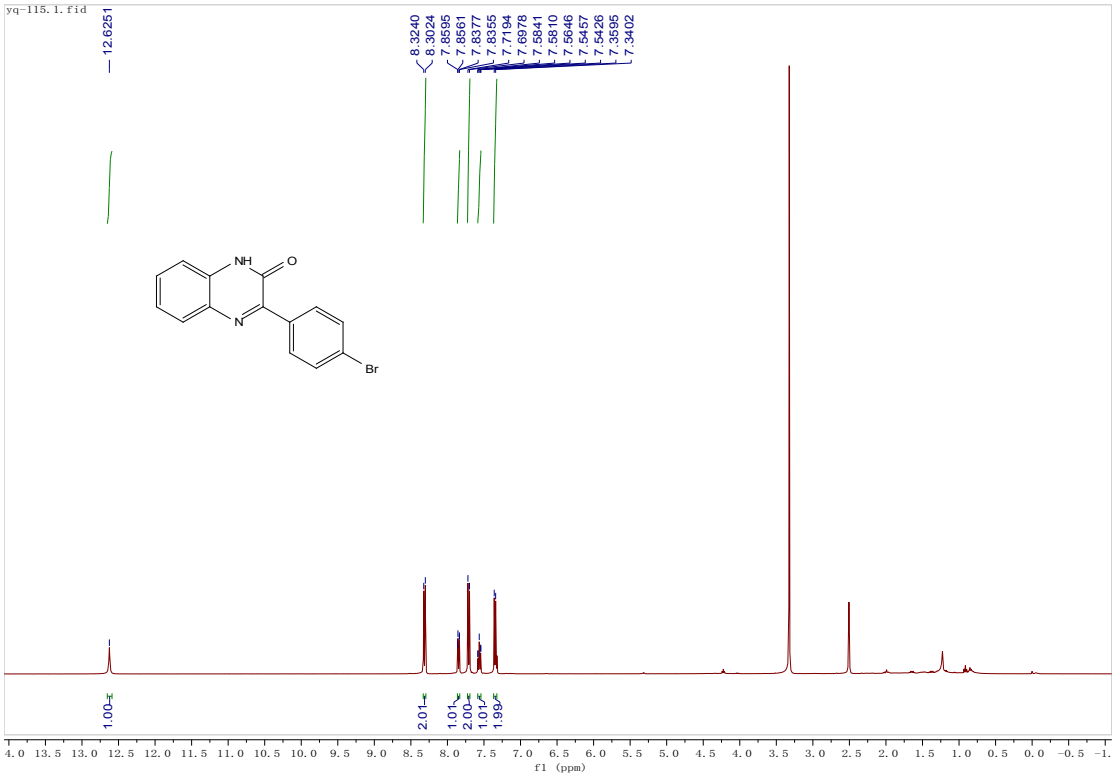


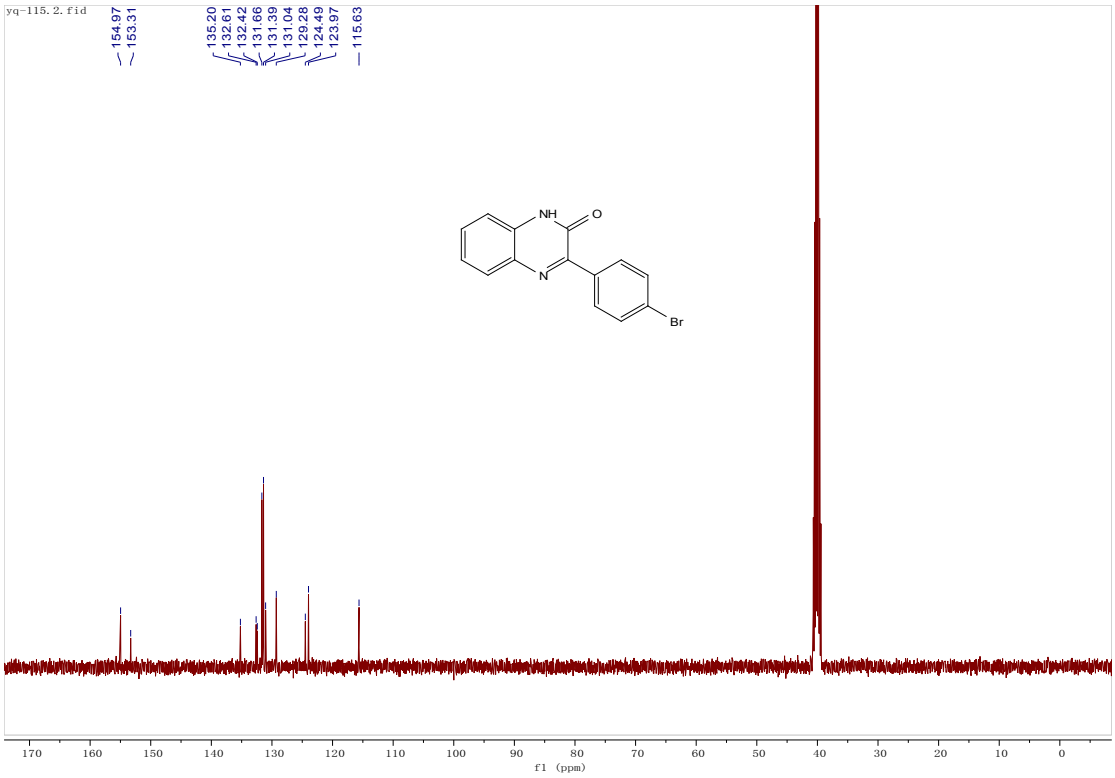
^{1}H and ^{13}C NMR spectra of **5e**



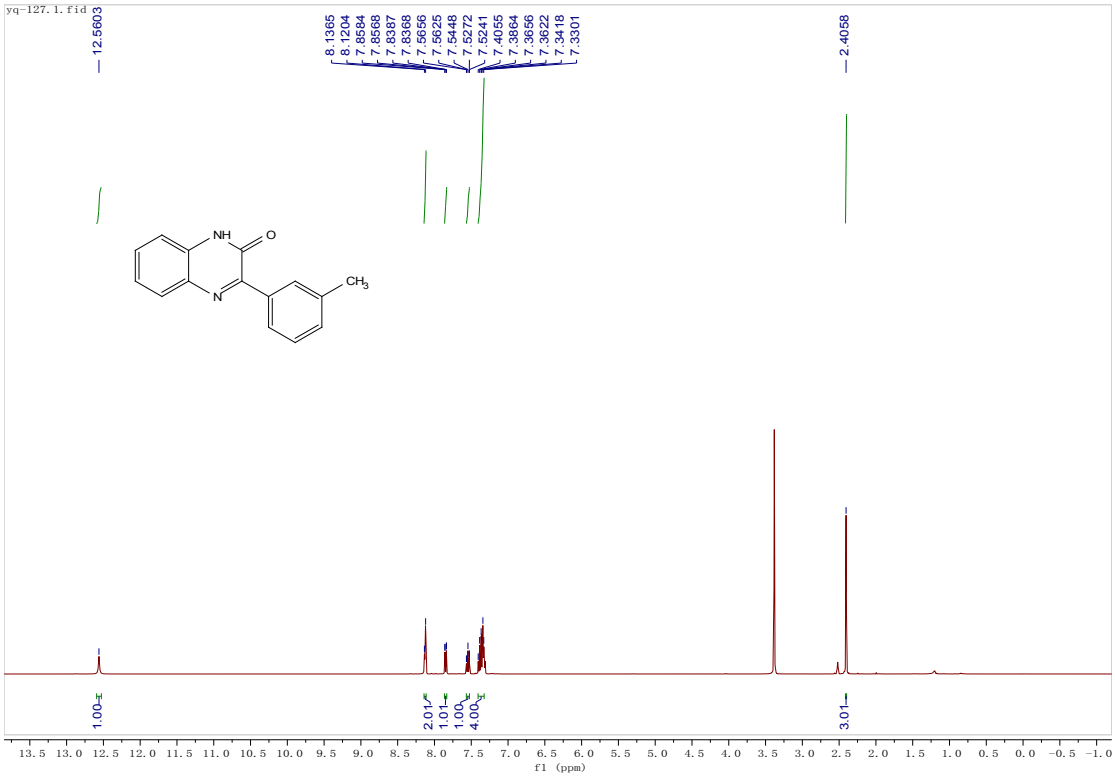


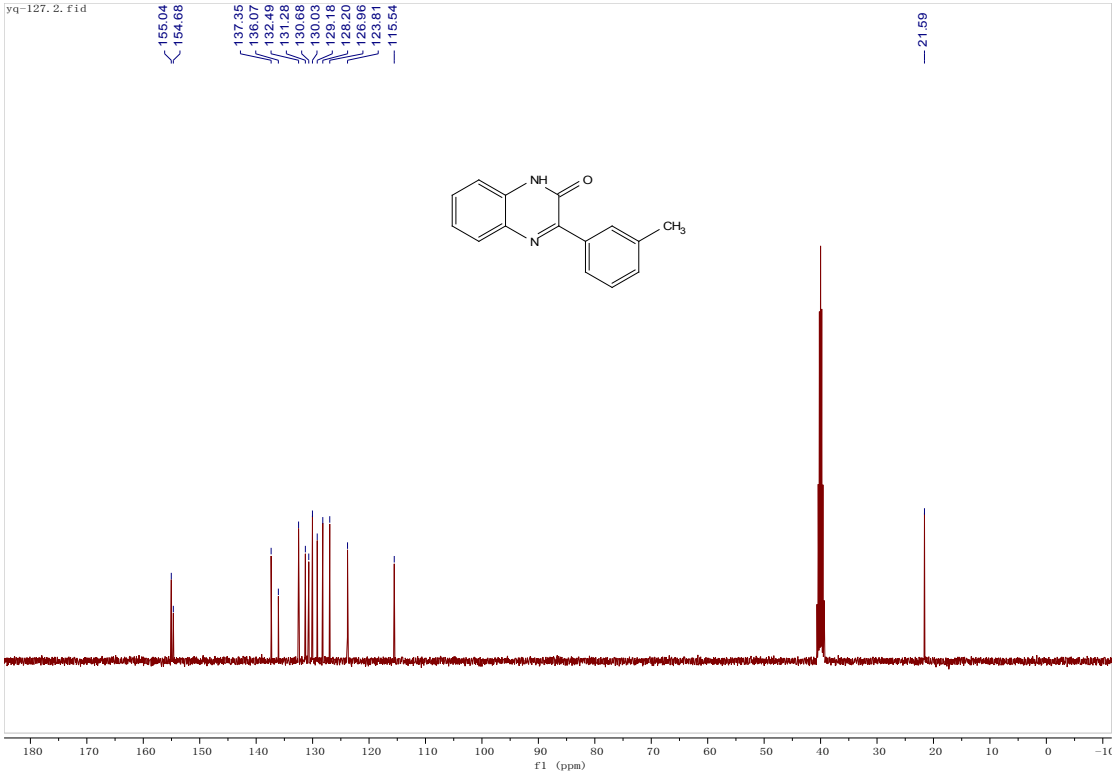
^{1}H and ^{13}C NMR spectra of **5f**



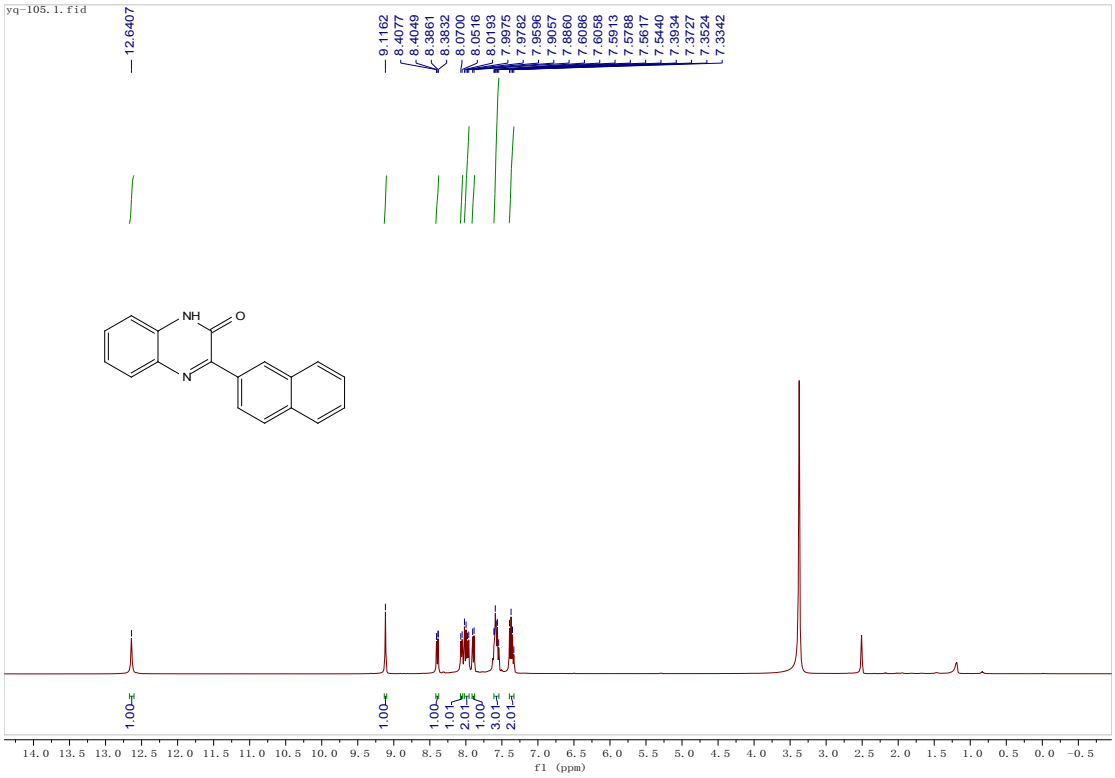


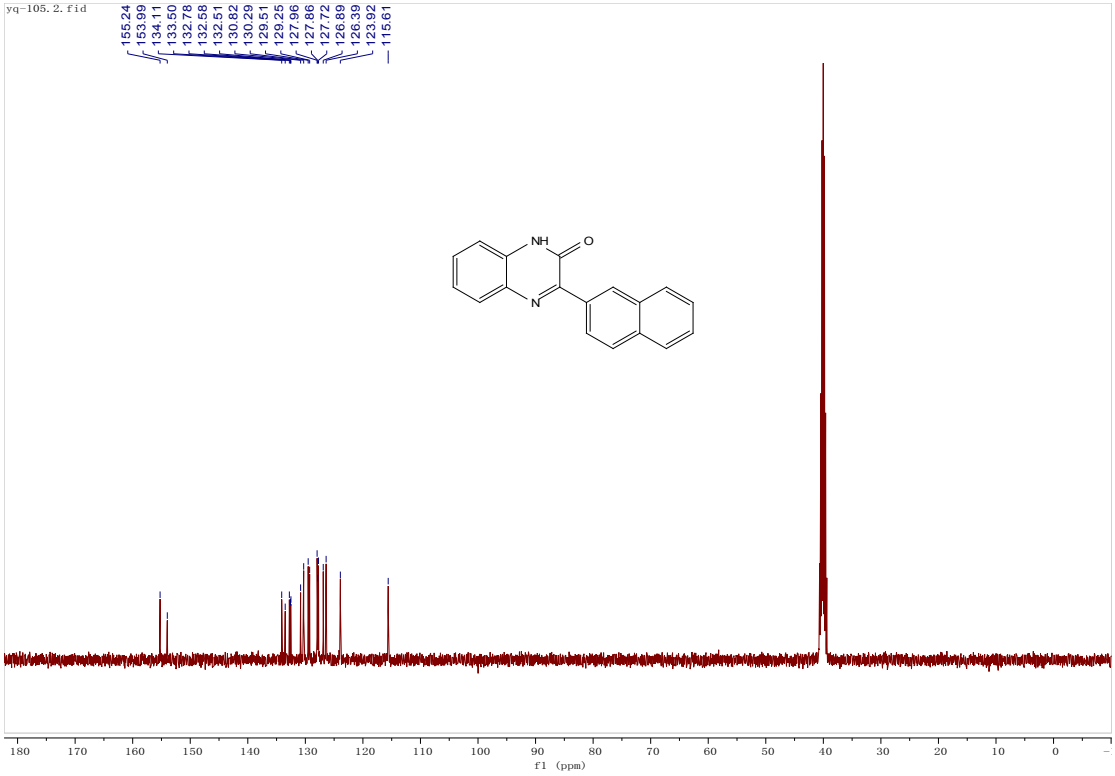
^{1}H and ^{13}C NMR spectra of **5g**





^{1}H and ^{13}C NMR spectra of **5h**





^{1}H and ^{13}C NMR spectra of **5i**