Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

Alkylation of Quinoxalin-2(1*H*)-Ones Using Phosphonium Ylides as Alkylating Reagents

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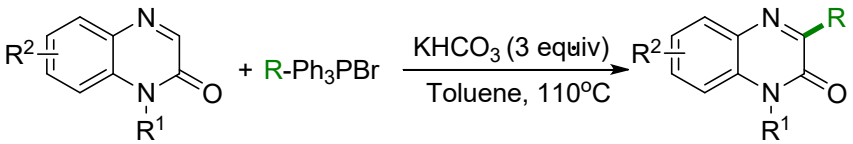
1. General information

Unless otherwise specified, all reagents and solvents were obtained from commercial suppliers and used without further purification. Dry solvents (toluene, xylene, 1,2-dichloroethane, acetonitrile, *N*,*N*-dimethylformamide, dimethyl sulfoxide, tetrahydrofuran) were used as commercially available. ^{1}H NMR spectra were recorded at 400 MHz and ^{13}C NMR spectra were recorded at 101 MHz by using a Bruker Avance 400 spectrometer. Chemical shifts were calibrated using residual undeuterated solvent as an internal reference (^{1}H NMR: $CDCl_3$ 7.26 ppm, ^{13}C NMR: $CDCl_3$ 77.0 ppm). The following abbreviations were used to describe peak splitting patterns when appropriate: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, brs = broad singlet. Mass spectra were performed on a spectrometer operating on ESI-TOF.

2. Experimental Section

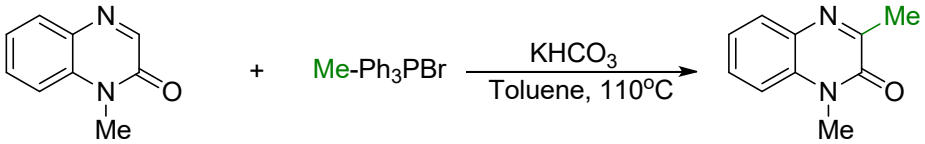
General procedure for the preparation of 3-alkylquinoxalin-2(1*H*)-ones



1 **2** **3**

An oven-dried tube was charged with 1-methylquinoxalin-2(1*H*)-one **1a** (0.048 g, 0.3 mmol), $KHCO_3$ (0.090 g, 0.9 mmol), methyltriphenylphosphonium bromide **2a** (0.321 g**,** 0.9 mmol) and toluene (3 mL) at room temperature. The reaction mixture was open to the air and stirred at 110 °C with a condenser for about 24 h. After completion, the reaction mixture was cooled to room temperature and quenched with water (5mL), extracted with EtOAc (5 mL× 3), the solvent was then removed under vacuum. The residue was purified by flash column chromatography using a mixture of petroleum ether and ethyl acetate as eluent to give the desired products **3aa.**

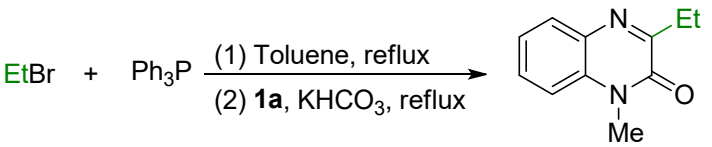
Gram-scale synthesis of 3aa



1a, 8mmol, 1.281 g **3aa**, 1.295 g, 93% yield

An oven-dried round-bottom flask was charged with 1-methylquinoxalin-2(1*H*)-one **1a** (1.281 g, 8 mmol), $KHCO_3$ (2.402 g, 24 mmol), methyltriphenylphosphonium bromide **2a** (8.573 g, 24 mmol) and toluene (80 mL) at room temperature. The reaction mixture was open to the air and stirred at 110 °C with a condenser for about 24 h. After completion, the reaction mixture was cooled to room temperature and quenched with water (30 mL), extracted with EtOAc (20 mL× 3), the organic phase was then removed under vacuum. The residue was purified by flash column chromatography using a mixture of petroleum ether and ethyl acetate as eluent to give 1.295 g of **3aa**, yield 93%.

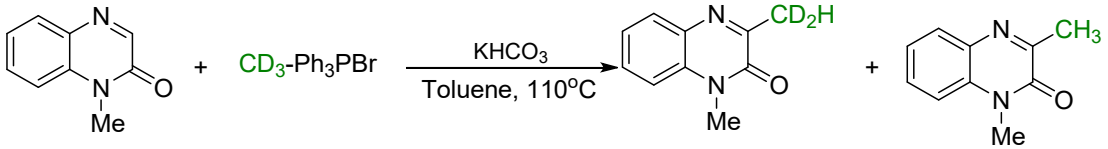
One pot synthesis of 3-ethylquinoxalin-2(1*H*)-one (3ab)



3ab, 73%

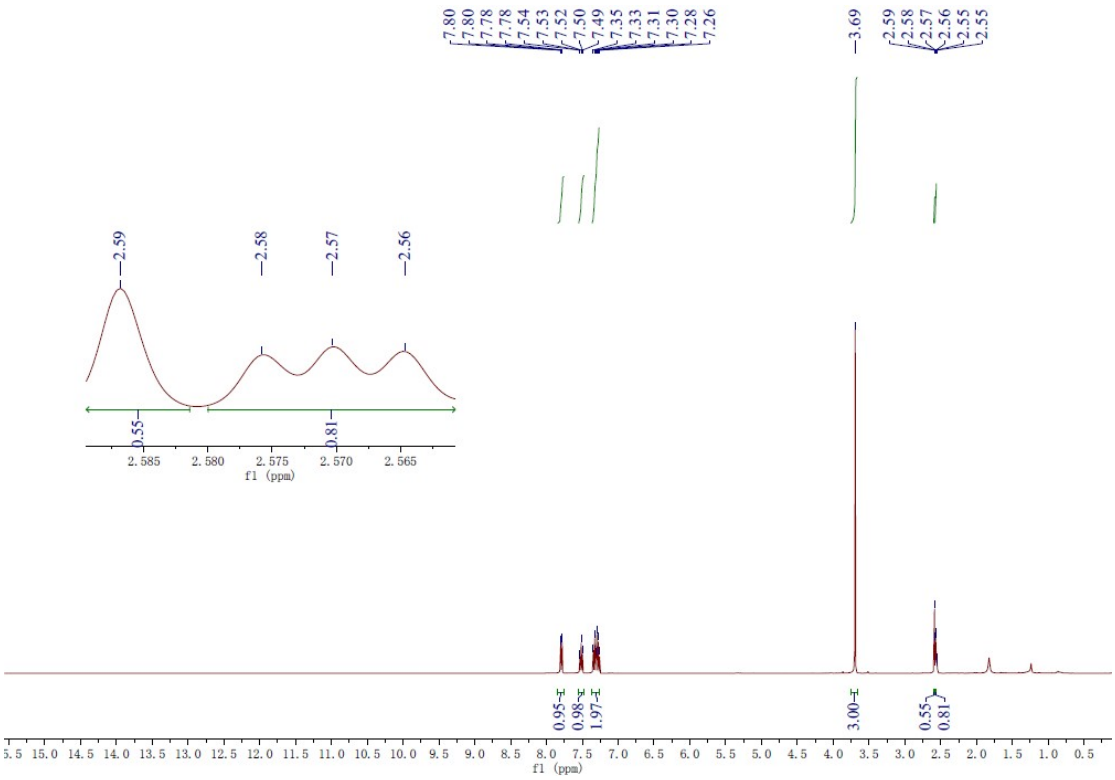
To an oven-dried round-bottom flask was added ethyl bromide (0.981 g, 9 mmol) and Ph_3P (2.361 g, 9 mmol) in toluene (30 mL), the reaction mixture was stirred at 110 °C with a condenser for 24h under N_2 conditions, the reaction was allowed to room temperature, then, 1-methylquinoxalin-2(1*H*)-one **1a** (0.480 g, 3 mmol) and $KHCO_3$ (0.901 g, 9 mmol) were added to the reaction mixture, The reaction mixture was open to the air and stirred at 110 °C with a condenser for about 24 h. After completion, the reaction mixture was cooled to room termperature and quenched with water (20mL), extracted with EtOAc (10 mL× 3), the solvent was then removed under vacuum. The residue was purified by flash column chromatography using a mixture of petroleum ether and ethyl acetate as eluent to give 0. 412 g of **3ab**, total yield 73%, based on 1-methylquinoxalin-2(1*H*)-one.

KIE experiment



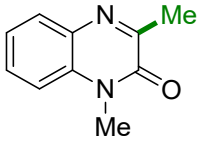
1a **2f** **3af-d2,** 81% **3af,** 18%

An oven-dried tube was charged with 1-methylquinoxalin-2(1*H*)-one **1a** (0.048 g, 0.3 mmol), $KHCO_3$ (0.090 g. 0.9 mmol), trideuteromethylphenylphosphonium bromide **2f** (0.324 g, 0.9 mmol) and toluene (3 mL) at room temperature. The reaction mixture was open to the air and stirred at 110 °C with a condenser for about 24 h. After completion, the reaction mixture was cooled to room temperature and quenched with water (5 mL), extracted with EtOAc (5 mL× 3), the solvent was then removed under vacuum. The residue was purified by flash column chromatography using a mixture of petroleum ether and ethyl acetate as eluent to give the methylated products, the yields of **3af-d2** and **3af** were calculated by ^{1}H NMR of the isolated mixture. Peak areas at 2.59 ppm (single peak) belong to CH_3 peak of **3af**, the integral value is 0.55 relative to CH_3 peak at 3.69 whose integral value is defined as 3.00, Peak areas at 2.57 ppm (triple peak) belong to CD_2H peak of **3af-d2**, the integral value is 0.81 relative to CH_3 peak at 3.69, the NMR yield of **3af** is (0.55/3)*100% = 18%, and the NMR yield of **3af-d2** is 0.81*100% = 81%. (note: compound **2f** was prepared from CD_3OD and triphenylphosphine hydrobromide according to Hamanaka's work[1])



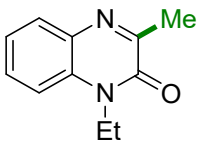
3. Characterization data of products

1,3-dimethylquinoxalin-2(1*H*)-one (3aa)[2]



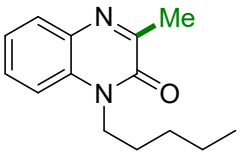
Purified by using a flash column chromatography; isolated yield = 96%, 50.1 mg; white solid; mp: 86-87 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (d, *J* = 7.9 Hz, 1H), 7.53 (t, *J* = 7.8 Hz, 1H), 7.37 – 7.28 (m, 2H), 3.71 (s, 3H), 2.60 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.4, 155.2, 133.2, 132.6, 129.6, 129.4, 123.6, 113.6, 29.1, 21.6.

1-ethyl-3-methylquinoxalin-2(1*H*)-one (3ba)[3]



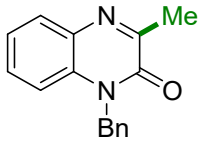
Purified by using a flash column chromatography; isolated yield = 86%, 48.5 mg; white solid; mp: 79-80 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (dd, *J* = 8.2, 1.4 Hz, 1H), 7.55 – 7.48 (m, 1H), 7.36 – 7.29 (m, 2H), 4.31 (q, *J* = 7.2 Hz, 2H), 2.59 (s, 3H), 1.37 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.4, 154.6, 132.9, 132.1, 129.6, 129.5, 123.4, 113.4, 37.2, 21.5, 12.4.

3-methyl-1-pentylquinoxalin-2(1*H*)-one (3ca)[2]



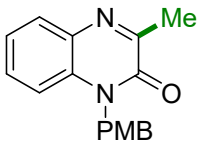
Purified by using a flash column chromatography; isolated yield = 76%, 52.4 mg; colorless liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (dd, *J* = 7.9, 1.2 Hz, 1H), 7.53 – 7.47 (m, 1H), 7.35 – 7.27 (m, 2H), 4.28 – 4.19 (m, 2H), 2.59 (s, 3H), 1.78 – 1.71 (m, 2H), 1.42 (tt, *J* = 9.8, 5.0 Hz, 4H), 0.92 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.4, 132.9, 132.4, 129.6, 129.5, 123.3, 113.6, 42.3, 29.1, 26.9, 22.4, 21.5, 13.9.

1-benzyl-3-methylquinoxalin-2(1*H*)-one (3da)[4]



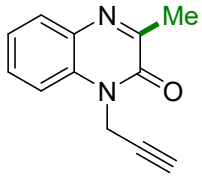
Purified by using a flash column chromatography; isolated yield = 96%, 72.0 mg; white solid; mp: 88-89 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 – 7.78 (m, 1H), 7.43 – 7.36 (m, 1H), 7.34 – 7.21 (m, 7H), 5.50 (s, 2H), 2.66 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.5, 155.3, 135.2, 132.9, 132.5, 129.6, 129.5, 128.9, 127.7, 126.8, 123.6, 114.4, 45.9, 21.7.

1-(4-methoxybenzyl)-3-methylquinoxalin-2(1*H*)-one (3ea)[5]



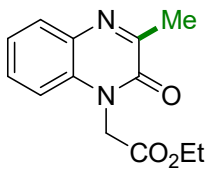
Purified by using a flash column chromatography; isolated yield = 94%, 78.9 mg; white solid; mp: 96-98 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 – 7.75 (m, 1H), 7.40 (t, *J* = 8.4 Hz, 1H), 7.31 – 7.25 (m, 2H), 7.19 (d, *J* = 8.6 Hz, 2H), 6.83 (d, *J* = 8.7 Hz, 2H), 5.41 (s, 2H), 3.74 (s, 3H), 2.64 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.0, 158.4, 155.2, 132.8, 132.5, 129.5, 129.5, 128.3, 127.2, 123.6, 114.3, 114.2, 55.2, 45.3, 21.6.

3-methyl-1-(prop-2-yn-1-yl)quinoxalin-2(1*H*)-one (3fa)[6]



Purified by using a flash column chromatography; isolated yield = 93%, 55.3 mg; white solid; mp: 131-133 °C..^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.59 – 7.53 (m, 1H), 7.45 (d, *J* = 8.3 Hz, 1H), 7.40 – 7.34 (m, 1H), 5.06 (s, 2H), 2.60 (s, 3H), 2.29 (t, *J* = 2.5 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.2, 154.1, 132.8, 131.6, 129.7, 129.5, 124.0, 114.1, 73.2, 31.5, 21.5.

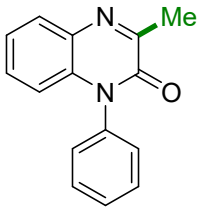
ethyl 2-(3-methyl-2-oxoquinoxalin-1(2*H*)-yl)acetate (3ga)[5]



Purified by using a flash column chromatography; isolated yield = 94%, 69.4 mg; white solid; mp: 128-130 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (d, *J* = 8.0 Hz, 1H), 7.49 (t, *J* = 8.5 Hz, 1H), 7.34 (t, *J* = 7.6 Hz, 1H), 7.06 (d, *J* = 8.2 Hz, 1H), 5.03 (s, 2H), 4.25 (q, *J* = 7.1 Hz, 2H), 2.61 (s, 3H), 1.27 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (101 MHz,

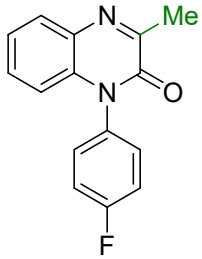
$CDCl_3$) δ 167.1, 158.2, 154.7, 132.6, 132.3, 129.8, 129.7, 123.9, 113.0, 62.1, 43.5, 21.5.

3-methyl-1-phenylquinoxalin-2(1*H*)-one (3ha)[7]



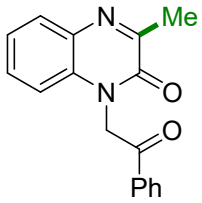
Purified by using a flash column chromatography; isolated yield = 91%, 64.4 mg; white solid; mp: 166-168 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (dd, *J* = 6.0, 3.5 Hz, 1H), 7.62 (t, *J* = 7.4 Hz, 2H), 7.55 (t, *J* = 7.4 Hz, 1H), 7.34 – 7.27 (m, 4H), 6.66 (dq, *J* = 7.2, 3.7 Hz, 1H), 2.64 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.2, 154.9, 135.8, 134.1, 132.4, 130.3, 129.4, 129.2, 129.0, 128.2, 123.8, 115.4, 21.4.

1-(4-fluorophenyl)-3-methylquinoxalin-2(1*H*)-one (3ia)[2]



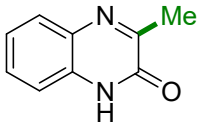
Purified by using a flash column chromatography; isolated yield = 86%, 65.5 mg; white solid; mp: 153-155 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18 – 7.74 (m, 1 H), 7.35 – 7.26 (m, 6 H), 6.81 – 6.49 (m, 1H), 2.63 (s, 3 H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.8 (d, $J_{C\text{-}F}$ = 251.5 Hz), 159.1, 154.9, 134.0, 132.4, 131.6 (d, *J* = 3.0 Hz), 130.1 (d, *J* = 8.9 Hz), 129.4, 129.1, 123.9, 117.4 (d, *J* = 23.2 Hz), 115.2, 21.4; ^{19}F NMR (376 MHz, $CDCl_3$) δ -111.3.

3-methyl-1-(2-oxo-2-phenylethyl)quinoxalin-2(1*H*)-one (3ja)[5]



Purified by using a flash column chromatography; isolated yield = 64%, 53.4 mg; white solid; mp: 168-170 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (d, *J* = 8.0 Hz, 1H), 7.57 – 7.49 (m, 2H), 7.49 – 7.30 (m, 5H), 7.19 (d, *J* = 8.3 Hz, 1H), 5.27 (s, 2H), 2.64 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.4, 154.9, 140.5, 138.5, 132.8, 129.6, 129.4, 128.6, 128.4, 126.1, 123.7, 114.6, 112.6, 45.7, 21.6.

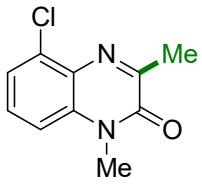
3-methylquinoxalin-2(1*H*)-one (3ka)[6]



Purified by using a flash column chromatography; isolated yield = 53%, 25.4 mg; yellow solid; mp: 195-196 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 12.30 (s, 1H), 7.67 (d, *J* = 8.0 Hz, 1H), 7.45 (t, *J* = 7.7 Hz, 1H), 7.26 (d, *J* = 7.7

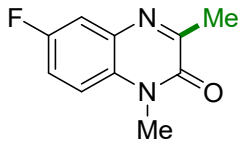
Hz, 2H), 2.38 (s, 3H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 160.0, 155.8, 132.6, 132.4, 130.2, 128.6, 124.0, 116.1, 21.3.

5-chloro-1,3-dimethylquinoxalin-2(1*H*)-one (3la)



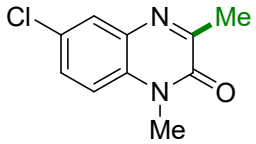
Purified by using a flash column chromatography; isolated yield = 97%, 60.5 mg; white solid; mp: 132-134 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 – 7.38 (m, 2H), 7.23 – 7.16 (m, 1H), 3.68 (s, 3H), 2.63 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.1, 154.7, 134.6, 134.0, 129.5, 129.2, 124.4, 112.5, 29.5, 21.9; HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{10}H_{10}ClN_2O$: 209.0476; found: 209.0481.

6-fluoro-1,3-dimethylquinoxalin-2(1*H*)-one (3ma)[5]



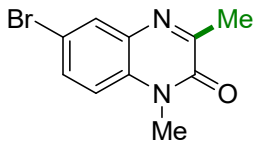
Purified by using a flash column chromatography; isolated yield = 91%, 52.4 mg; white solid; mp: 147-149 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 (dd, J = 8.6, 2.3 Hz, 1H), 7.27 (dd, J = 6.4, 3.6 Hz, 2H), 3.70 (s, 3H), 2.60 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.0, 158.5 (d, $J_{C\text{-}F}$ = 244.4 Hz), 154.8, 133.1 (d, $J_{C\text{-}F}$ = 11.1 Hz), 129.9 (d, $J_{C\text{-}F}$ = 2.0 Hz), 117.3 (d, $J_{C\text{-}F}$ = 24.2 Hz), 114.9 (d, $J_{C\text{-}F}$ = 23.2 Hz), 114.7(d, $J_{C\text{-}F}$ = 9.1 Hz), 29.3, 21.7.

6-chloro-1,3-dimethylquinoxalin-2(1*H*)-one (3na)[4]



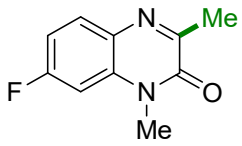
Purified by using a flash column chromatography; isolated yield = 87%, 54.3 mg; white solid; mp: 137-138 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (d, J = 2.4 Hz, 1H), 7.47 (dd, J = 8.9, 2.4 Hz, 1H), 7.22 (d, J = 8.9 Hz, 1H), 3.68 (s, 3H), 2.59 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.9, 154.8, 133.1, 131.9, 129.6, 128.9, 128.8, 114.7, 29.2, 21.7.

6-bromo-1,3-dimethylquinoxalin-2(1*H*)-one (3oa)[6]



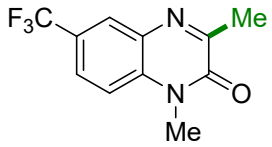
Purified by using a flash column chromatography; isolated yield = 92%, 69.5 mg; white solid; mp: 185-187 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (d, J = 2.1 Hz, 1H), 7.60 (dd, J = 8.9, 2.1 Hz, 1H), 7.16 (d, J = 8.9 Hz, 1H), 3.67 (s, 3H), 2.59 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.8, 154.8, 133.4, 132.3, 132.3, 131.9, 116.1, 115.0, 29.2, 21.7.

7-fluoro-1,3-dimethylquinoxalin-2(1*H*)-one (3pa)[4]



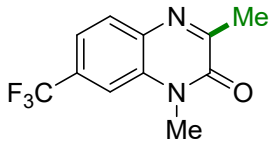
Purified by using a flash column chromatography; isolated yield = 88%, 50.7 mg; white solid; mp: 131-132 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (dd, J = 8.8, 5.9 Hz, 1H), 7.05 (td, J = 8.5, 2.6 Hz, 1H), 6.98 (dd, J = 10.0, 2.6 Hz, 1H), 3.66 (s, 3H), 2.57 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.9 (d, $J_{C\text{-}F}$ = 250.5 Hz), 157.2 (d, $J_{C\text{-}F}$ = 4.0 Hz), 155.1, 134.6 (d, $J_{C\text{-}F}$ = 12.1 Hz), 131.3 (d, $J_{C\text{-}F}$ = 10.1 Hz), 129.3 (d, $J_{C\text{-}F}$ = 3.0 Hz), 111.4 (d, $J_{C\text{-}F}$ = 23.2 Hz), 100.6 (d, $J_{C\text{-}F}$ = 28.3 Hz), 29.3, 21.5.

1,3-dimethyl-7-(trifluoromethyl)quinoxalin-2(1*H*)-one (3qa)[4]



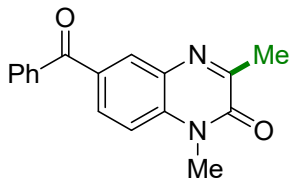
Purified by using a flash column chromatography; isolated yield = 93%, 67.5 mg; white solid; mp: 148-150 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (d, J = 8.3 Hz, 1H), 7.56 (d, J = 8.3 Hz, 1H), 7.52 (s, 1H), 3.72 (s, 3H), 2.61 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.1, 154.8, 134.2, 133.2, 131.1 (q, $J_{C\text{-}F}$ = 33.3 Hz), 130.1, 123.6 (q, $J_{C\text{-}F}$ = 273.7 Hz), 120.1 (q, $J_{C\text{-}F}$ = 4.0 Hz), 111.0 (q, $J_{C\text{-}F}$ = 4.0 Hz), 29.2, 21.8; ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.3.

1,3-dimethyl-6-(trifluoromethyl)quinoxalin-2(1*H*)-one (3ra)[2]



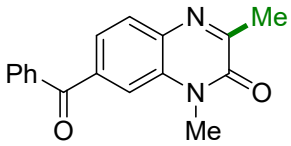
Purified by using a flash column chromatography; isolated yield = 95%, 69.0 mg; white solid; mp: 135-137 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (s, 1H), 7.73 (dd, J = 8.7, 1.8 Hz, 1H), 7.38 (d, J = 8.7 Hz, 1H), 3.71 (s, 3H), 2.60 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.1, 155.0, 135.5, 132.0, 126.9 (q, $J_{C\text{-}F}$ = 4.0 Hz), 125.9 (q, $J_{C\text{-}F}$ = 4.0 Hz), 125.7, 123.7 (q, $J_{C\text{-}F}$ = 272.7 Hz), 114.2, 29.3, 21.6; ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.0.

6-benzoyl-1,3-dimethylquinoxalin-2(1*H*)-one (3sa)[2]



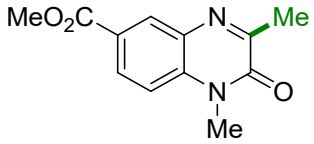
Purified by using a flash column chromatography; isolated yield = 90%, 75.1 mg; white solid; mp: 176-178 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20 (d, J = 1.9 Hz, 1H), 8.09 (dd, J = 8.7, 1.9 Hz, 1H), 7.80 (d, J = 7.0 Hz, 2H), 7.61 (t, J = 7.4 Hz, 1H), 7.50 (t, J = 7.6 Hz, 2H), 7.42 (d, J = 8.7 Hz, 1H), 3.75 (s, 3H), 2.60 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 195.0, 159.5, 155.1, 137.3, 136.3, 132.6, 132.5, 132.2, 131.5, 130.8, 129.8, 128.4, 114.0, 29.4, 21.6.

7-benzoyl-1,3-dimethylquinoxalin-2(1*H*)-one (3ta)[8]



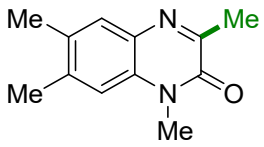
Purified by using a flash column chromatography; isolated yield = 87%, 72.5 mg; white solid; mp: 167-169 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 – 7.79 (m, 4H), 7.70 – 7.61 (m, 2H), 7.52 (t, J = 7.6 Hz, 2H), 3.74 (s, 3H), 2.64 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 195.6, 161.0, 155.0, 138.0, 137.0, 134.9, 133.3, 132.9, 130.1, 129.1, 128.5, 125.2, 115.4, 29.3.

methyl 1,3-dimethyl-2-oxo-1,2-dihydroquinoxaline-6-carboxylate (3ua)[2]



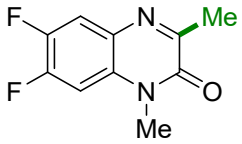
Purified by using a flash column chromatography; isolated yield = 84%, 58.5 mg; white solid; mp: 154-156 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.48 (d, J = 1.9 Hz, 1H), 8.17 (dd, J = 8.7, 1.9 Hz, 1H), 7.33 (d, J = 8.8 Hz, 1H), 3.95 (s, 3H), 3.72 (s, 3H), 2.60 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.1, 159.4, 155.1, 136.5, 131.9, 131.2, 130.4, 125.5, 113.7, 52.4, 29.3, 21.7.

1,3,6,7-tetramethylquinoxalin-2(1*H*)-one (3va)[6]



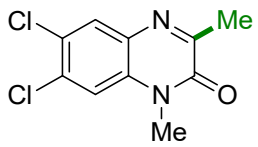
Purified by using a flash column chromatography; isolated yield = 83%, 50.3 mg; white solid; mp: 140-142 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (s, 1H), 7.05 (s, 1H), 3.67 (s, 3H), 2.56 (s, 3H), 2.39 (s, 3H), 2.33 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.9, 155.2, 139.3, 132.5, 131.2, 130.9, 129.4, 114.2, 29.0, 21.5, 20.5, 19.2.

6,7-difluoro-1,3-dimethylquinoxalin-2(1*H*)-one (3wa)[6]



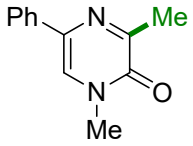
Purified by using a flash column chromatography; isolated yield = 74%, 46.6 mg; white solid; mp: 205-207 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (dd, J = 10.2, 8.2 Hz, 1H), 7.09 (dd, J = 11.3, 7.1 Hz, 1H), 3.65 (s, 3H), 2.56 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.0 (d, $J_{C\text{-}F}$ = 4.0 Hz), 154.7, 150.9 (dd, $J_{C\text{-}F}$ = 14.1 Hz, $J_{C\text{-}F}$ = 253.5 Hz), 146.6 (dd, $J_{C\text{-}F}$ = 14.1 Hz, $J_{C\text{-}F}$ = 247.5 Hz), 130.3 (dd, $J_{C\text{-}F}$ = 2.0 Hz, $J_{C\text{-}F}$ = 9.1 Hz), 128.8 (dd, $J_{C\text{-}F}$ = 3.0 Hz, $J_{C\text{-}F}$ = 9.1 Hz), 117.1 (dd, $J_{C\text{-}F}$ = 2.0 Hz, $J_{C\text{-}F}$ = 18.2 Hz), 102.2 (d, $J_{C\text{-}F}$ = 23.2 Hz), 29.6, 21.6; ^{19}F NMR (376 MHz, $CDCl_3$) δ -131.8 (d, $J_{F\text{-}F}$ = 22.6 Hz), -142.2 (d, $J_{F\text{-}F}$ = 22.6 Hz).

6,7-dichloro-1,3-dimethylquinoxalin-2(1*H*)-one (3xa)[3]



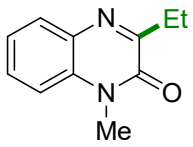
Purified by using a flash column chromatography; isolated yield = 86%, 62.4 mg; white solid; mp: 217-219 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (s, 1H), 7.37 (s, 1H), 3.65 (s, 3H), 2.57 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.0, 154.6, 133.6, 132.6, 131.7, 130.3, 115.2, 29.4, 21.7.

1,3-dimethyl-5-phenylpyrazin-2(1*H*)-one (3ya)[9]



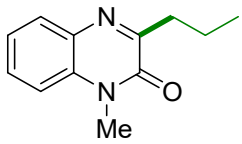
Purified by using a flash column chromatography; isolated yield = 34%, 20.4 mg; yellow solid; mp: 103-105 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.74 (d, *J* = 7.5 Hz, 2H), 7.47 – 7.38 (m, 3H), 7.32 (t, *J* = 7.3 Hz, 1H), 3.60 (s, 3H), 2.56 (s, 3H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 157.1, 156.0, 135.9, 132.4, 128.8, 127.8, 125.0, 124.0, 37.6, 21.1.

3-ethyl-1-methylquinoxalin-2(1*H*)-one (3ab)[10]



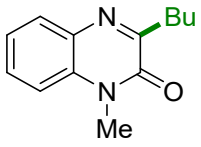
Purified by using a flash column chromatography; isolated yield = 82%, 46.2 mg; white solid; mp: 95-97 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (dd, *J* = 8.0, 1.4 Hz, 1H), 7.54 – 7.48 (m, 1H), 7.35 – 7.27 (m, 2H), 3.69 (s, 3H), 2.97 (q, *J* = 7.4 Hz, 2H), 1.33 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.9, 154.8, 133.0, 132.7, 129.6, 129.5, 123.5, 113.5, 29.0, 27.5, 10.8.

methyl-3-propylquinoxalin-2(1*H*)-one (3ac)[11]



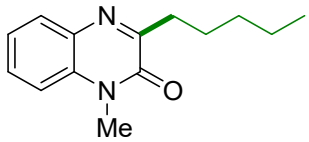
Purified by using a flash column chromatography; isolated yield = 76%, 46.1 mg; white solid; mp: 79-81 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (d, *J* = 9.2 Hz, 1H), 7.50 (t, *J* = 8.5 Hz, 1H), 7.36 – 7.25 (m, 2H), 3.68 (s, 3H), 3.01 – 2.84 (m, 2H), 1.87 – 1.77 (m, 2H), 1.04 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.1, 154.9, 133.0, 132.6, 129.5, 129.5, 123.5, 113.5, 36.2, 29.0, 20.2, 14.0.

3-butyl-1-methylquinoxalin-2(1*H*)-one (3ad)[12]



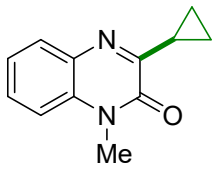
Purified by using a flash column chromatography; isolated yield = 65%, 42.1 mg; white solid; mp: 56-58 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (d, *J* = 7.9 Hz, 1H), 7.52 (t, *J* = 7.8 Hz, 1H), 7.38 – 7.27 (m, 2H), 3.70 (s, 3H), 2.99 – 2.89 (m, 2H), 1.77 (p, *J* = 7.7 Hz, 2H), 1.51 – 1.43 (m, 2H), 0.97 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.4, 154.9, 133.1, 132.7, 129.6, 129.5, 123.5, 113.5, 34.1, 29.0, 29.0, 22.7, 14.0.

methyl-3-pentylquinoxalin-2(1*H*)-one (3ae)[10]



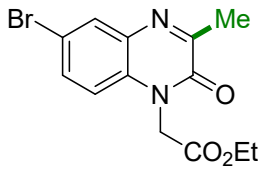
Purified by using a flash column chromatography; isolated yield = 26%, 17.9 mg; white solid; mp: 58-60 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (dd, *J* = 8.0, 1.3 Hz, 1H), 7.55 – 7.48 (m, 1H), 7.37 – 7.27 (m, 2H), 3.70 (s, 3H), 3.00 – 2.89 (m, 2H), 1.85 – 1.74 (m, 2H), 1.40 (dq, *J* = 12.9, 6.9 Hz, 4H), 0.91 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.4, 154.9, 133.1, 132.7, 129.6, 129.5, 123.5, 113.5, 34.3, 31.8, 29.0, 26.6, 22.5, 14.0.

3-cyclopropyl-1-methylquinoxalin-2(1*H*)-one (3af)[2]



Purified by using a flash column chromatography; isolated yield = 46%, 27.6 mg; white solid; mp: 66-68 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.71 (d, *J* = 7.9 Hz, 1H), 7.51 – 7.42 (m, 1H), 7.32 – 7.25 (m, 2H), 3.71 (s, 3H), 2.83 (ddd, *J* = 13.1, 8.2, 4.9 Hz, 1H), 1.21 (dt, *J* = 7.9, 3.7 Hz, 2H), 1.09 (dq, *J* = 7.1, 3.6 Hz, 2H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 161.5, 155.2, 132.9, 132.4, 129.2, 128.8, 123.4, 113.4, 29.1, 12.4, 11.1.

ethyl 2-(6-bromo-3-methyl-2-oxoquinoxalin-1(2*H*)-yl)acetate (4ca)[13]



Purified by using a flash column chromatography; isolated yield = 96%, 93.3 mg; white solid; mp: 125-127 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (d, *J* = 2.2 Hz, 1H), 7.57 (dd, *J* = 8.9, 2.2 Hz, 1H), 6.92 (d, *J* = 8.9 Hz, 1H), 4.98 (s, 2H), 4.24 (q, *J* = 7.1 Hz, 2H), 2.60 (s, 3H), 1.28 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.8, 159.6, 154.3, 133.5, 132.4, 132.2, 131.5, 116.4, 114.5, 62.2, 43.5, 21.6, 14.1.

4. Reference

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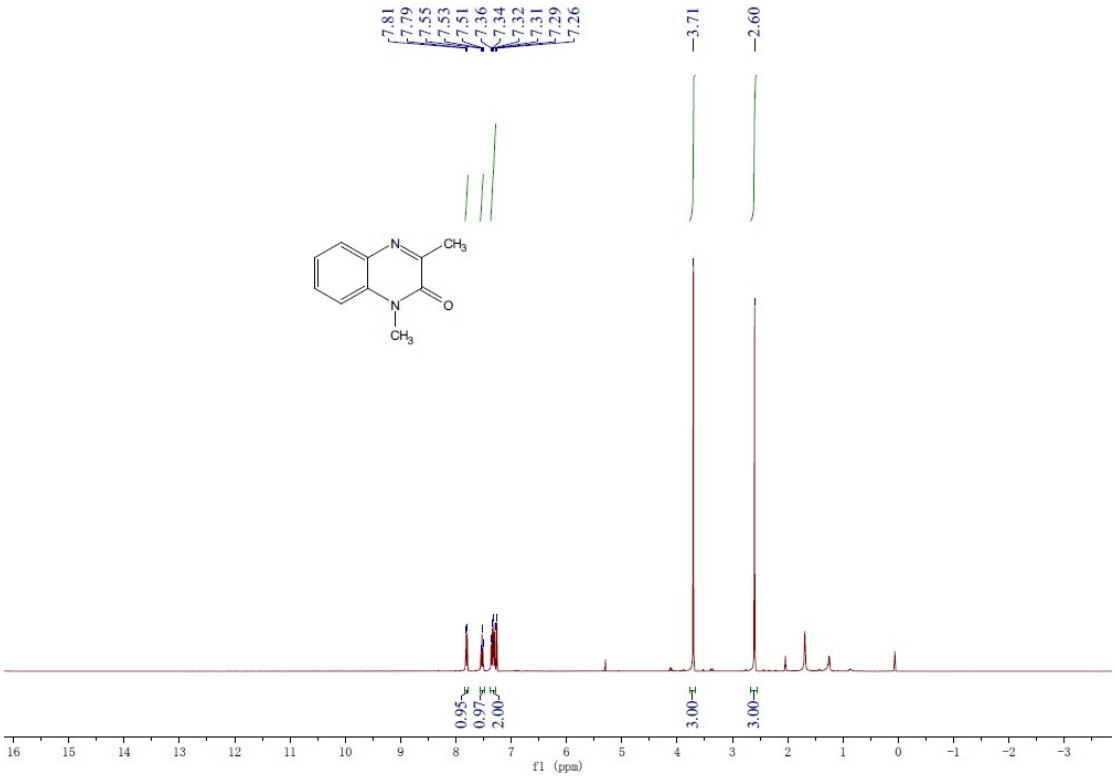
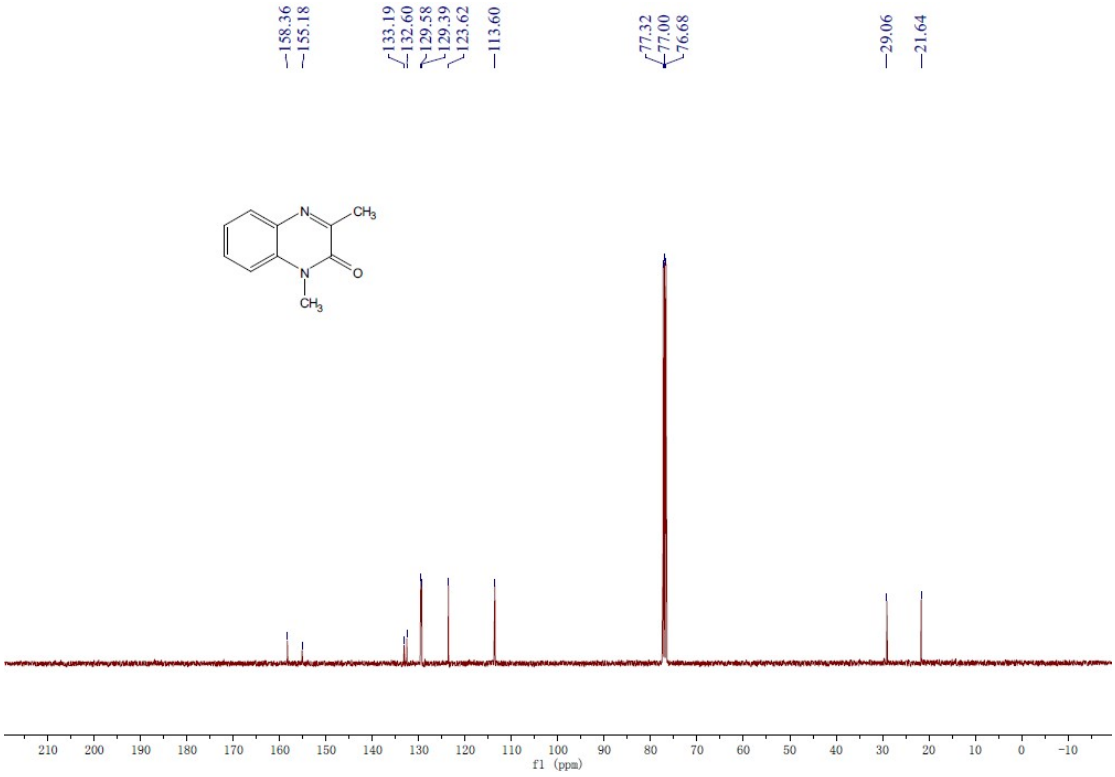
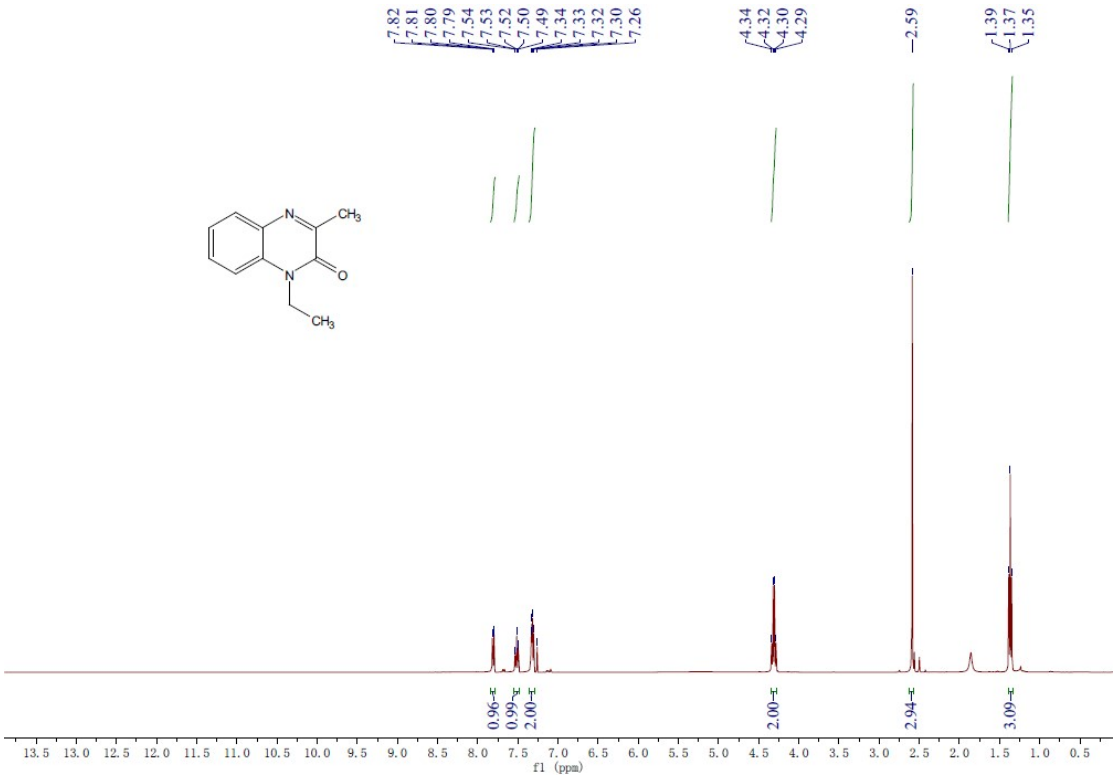
5. ^{1}H and ^{13}C NMR spectra of products



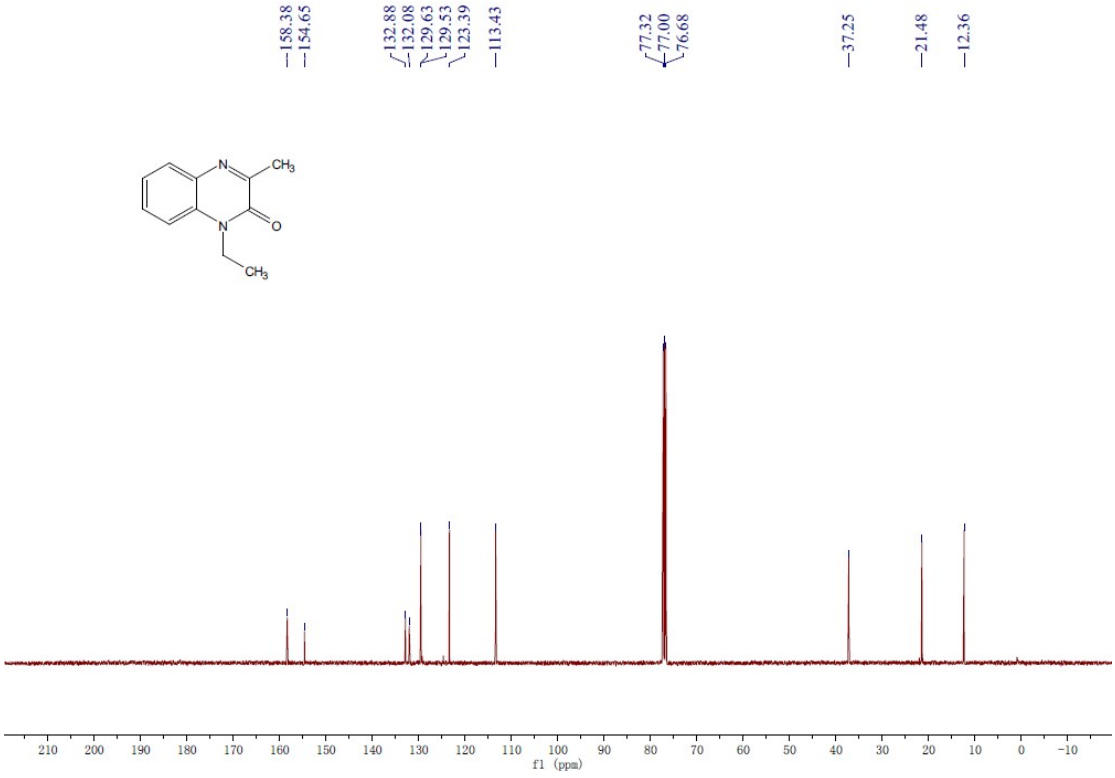
^{1}H spectra of **3aa**



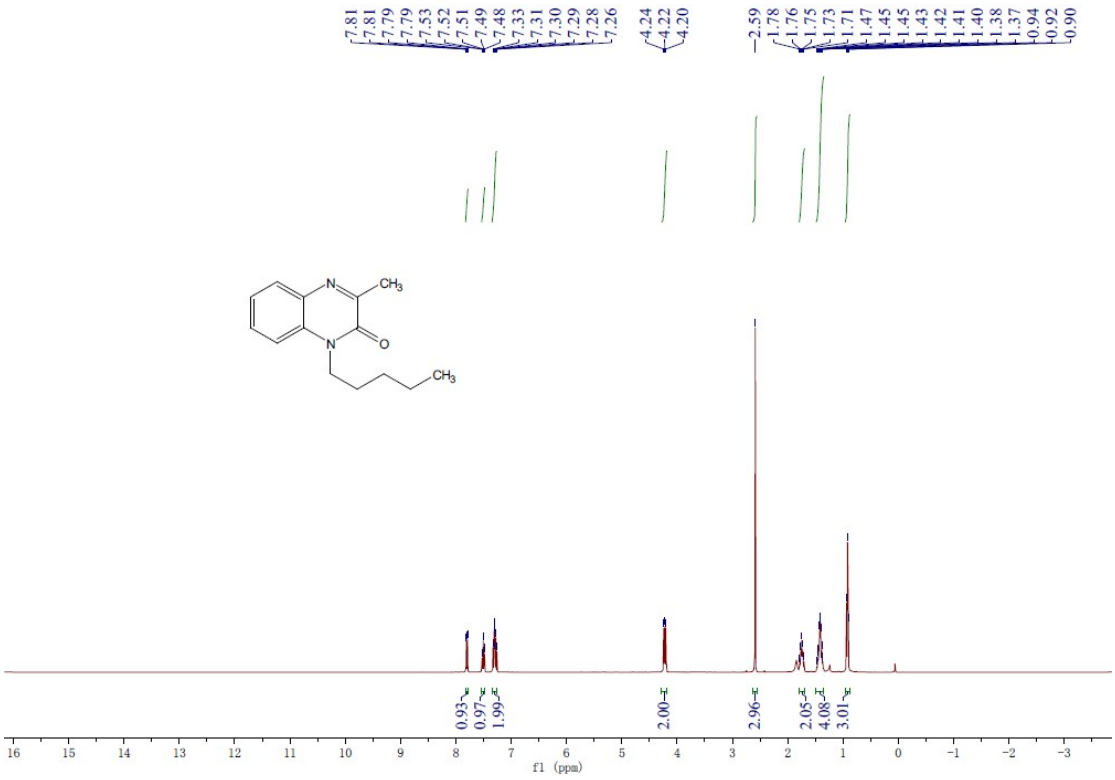
^{13}C spectra of **3aa**



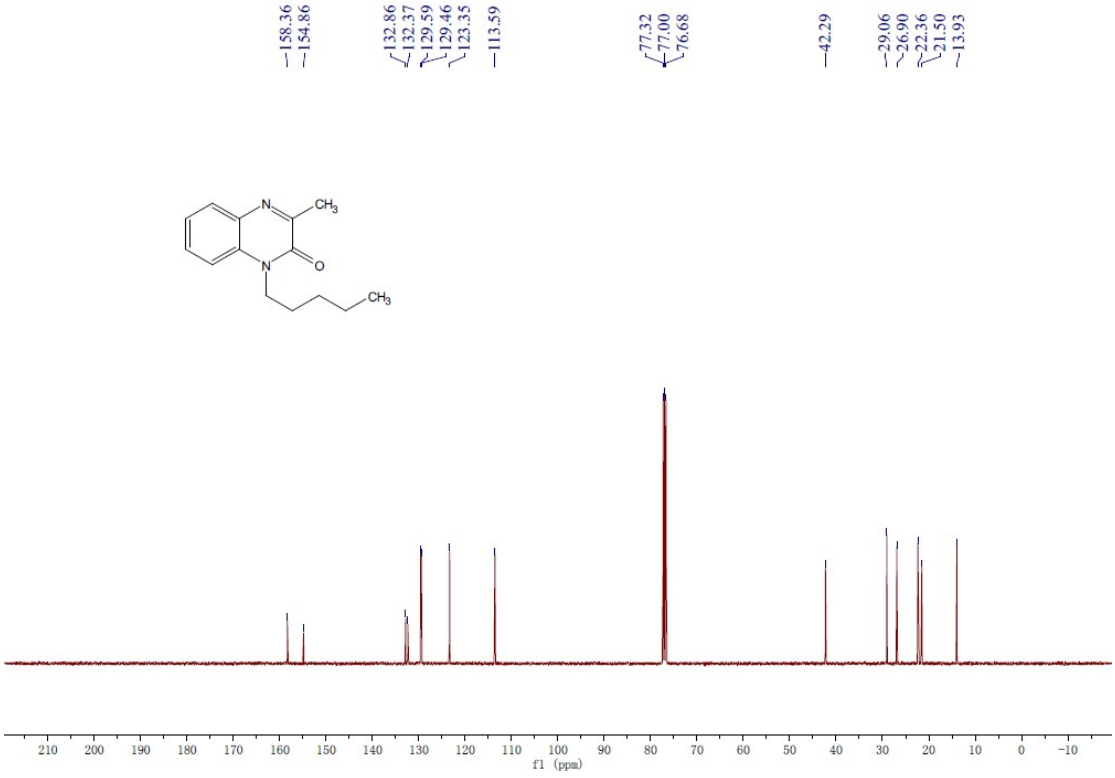
^{1}H spectra of **3ba**



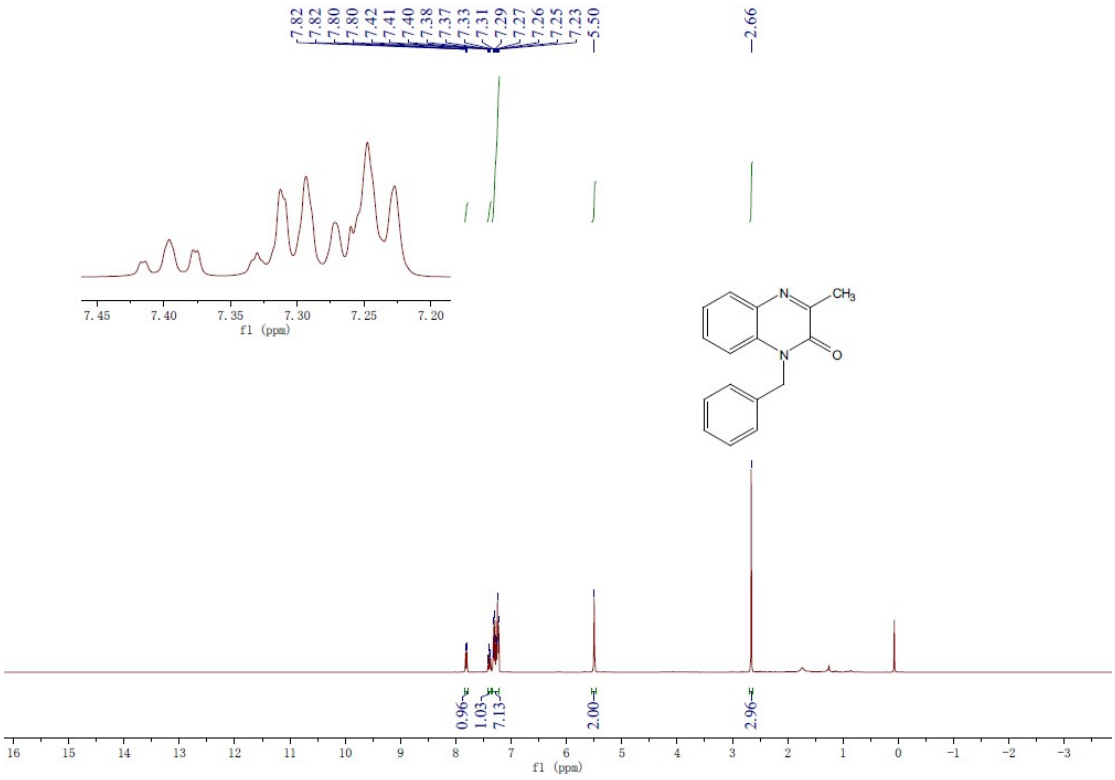
^{13}C spectra of **3ba**



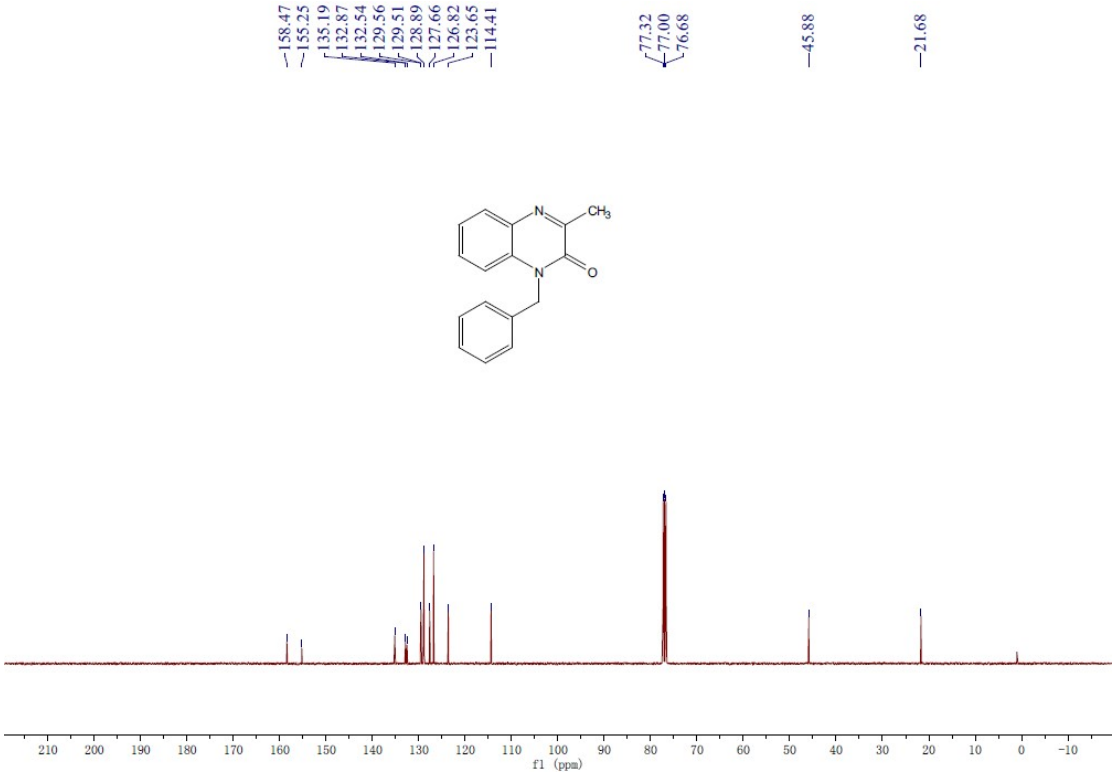
^{1}H spectra of **3ca**



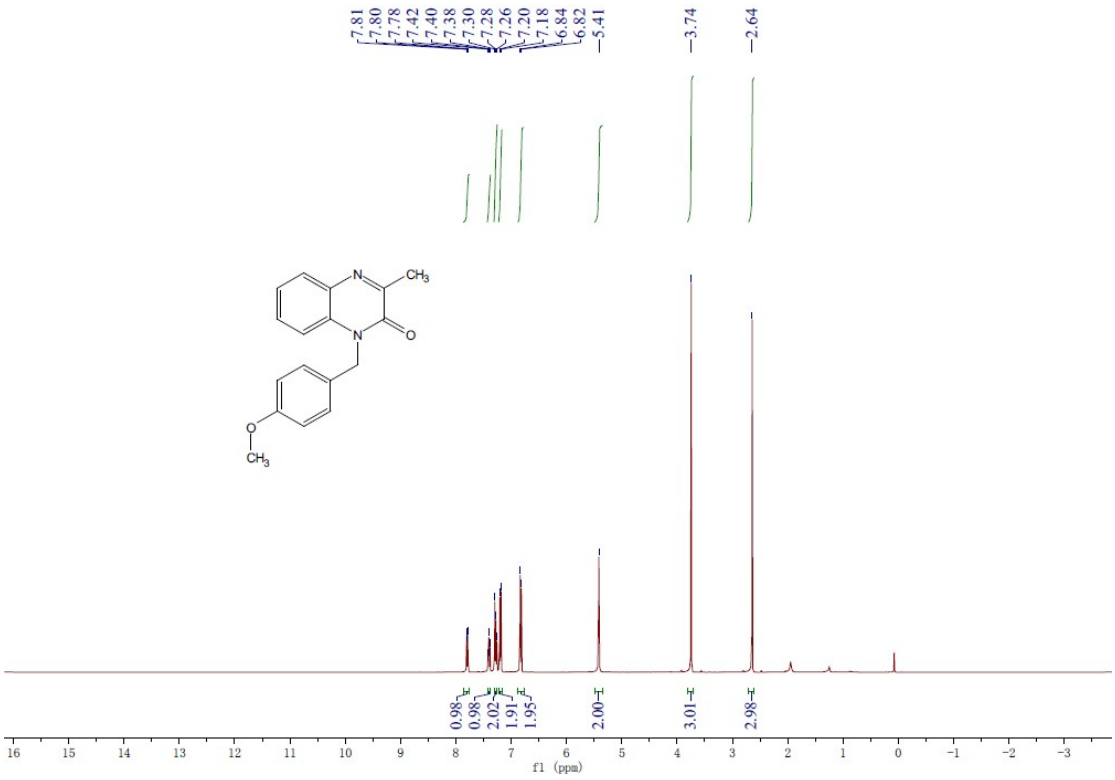
^{13}C spectra of **3ca**



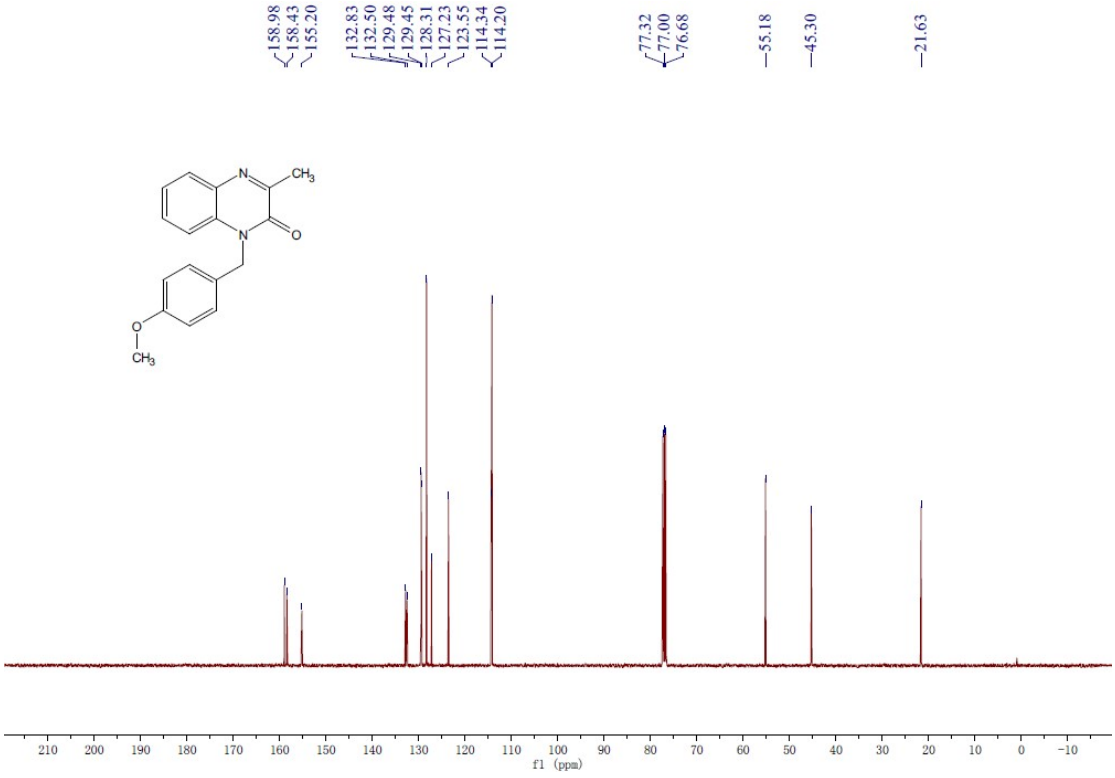
^{1}H spectra of **3da**



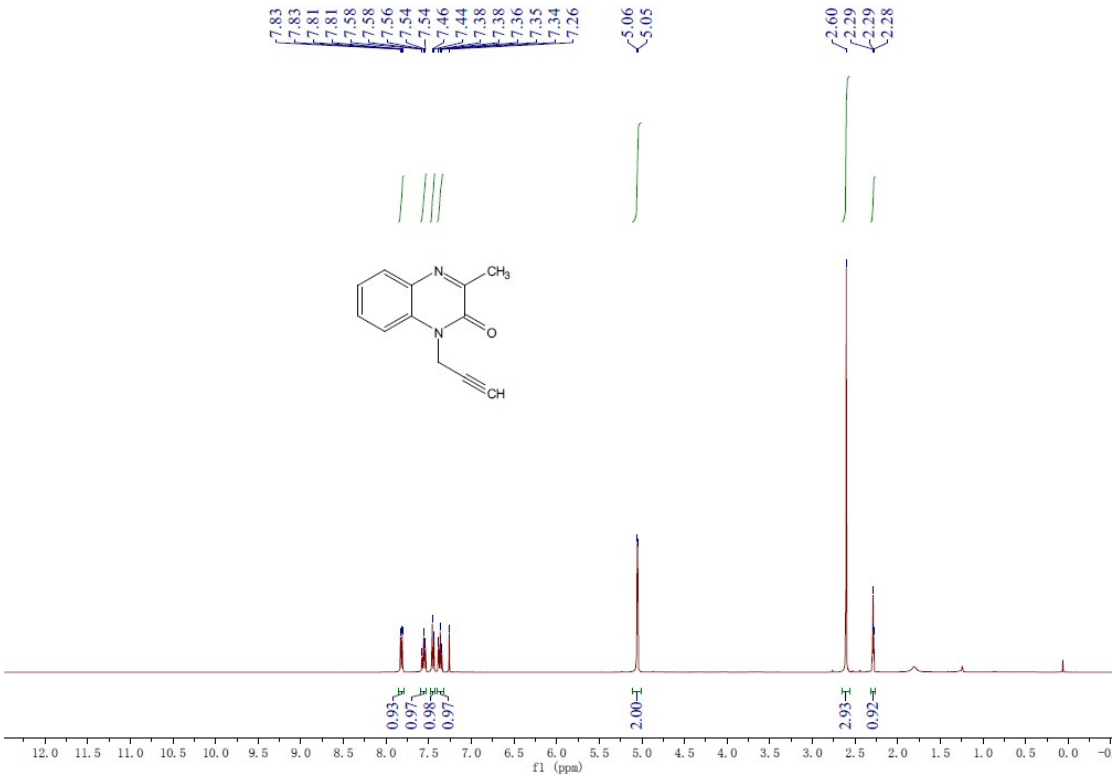
^{13}C spectra of **3da**



^{1}H spectra of **3ea**



^{13}C spectra of **3ea**



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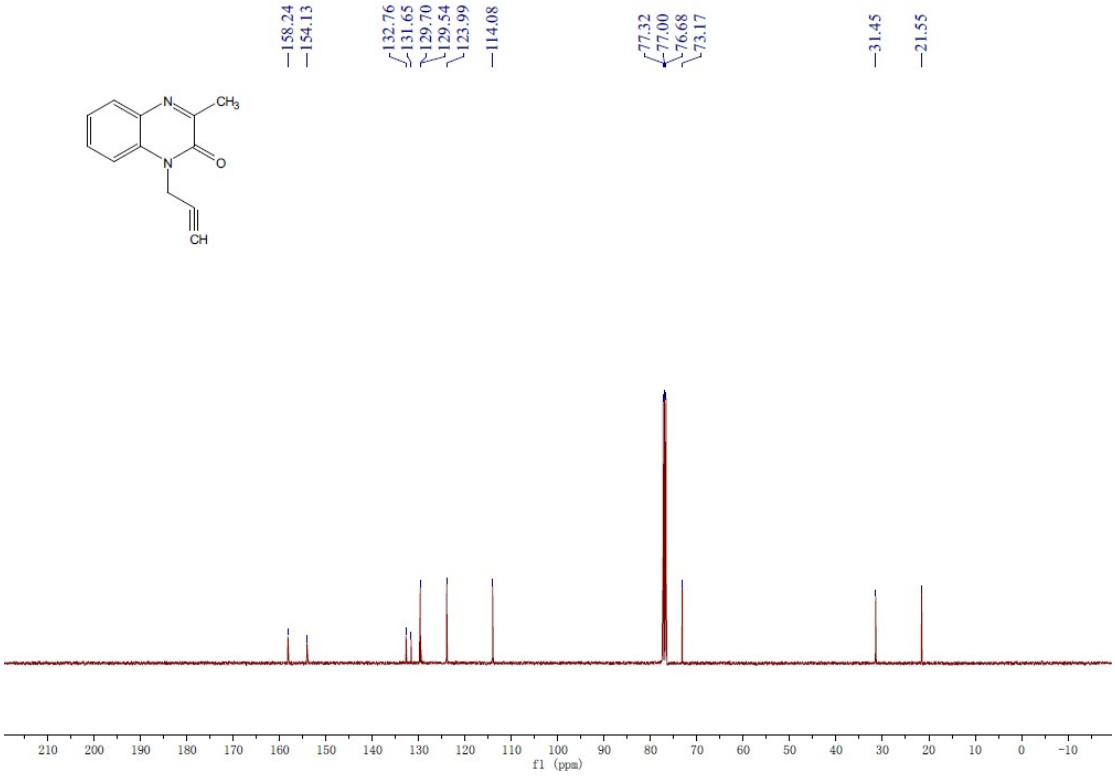

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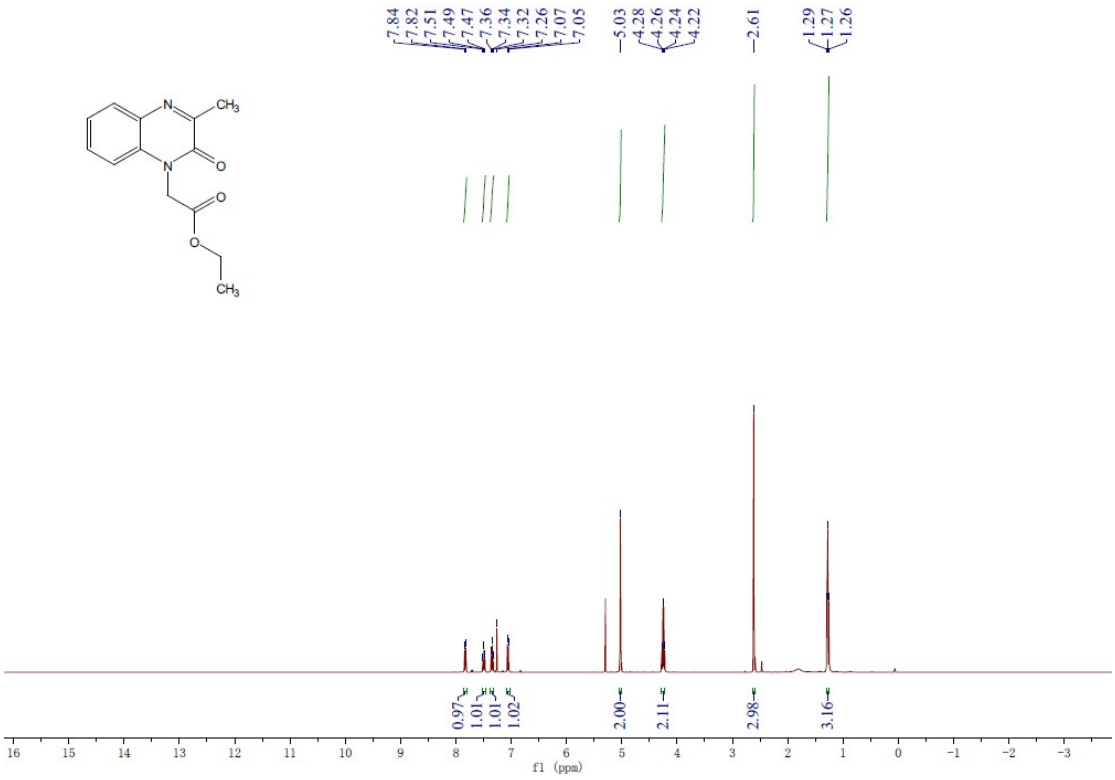
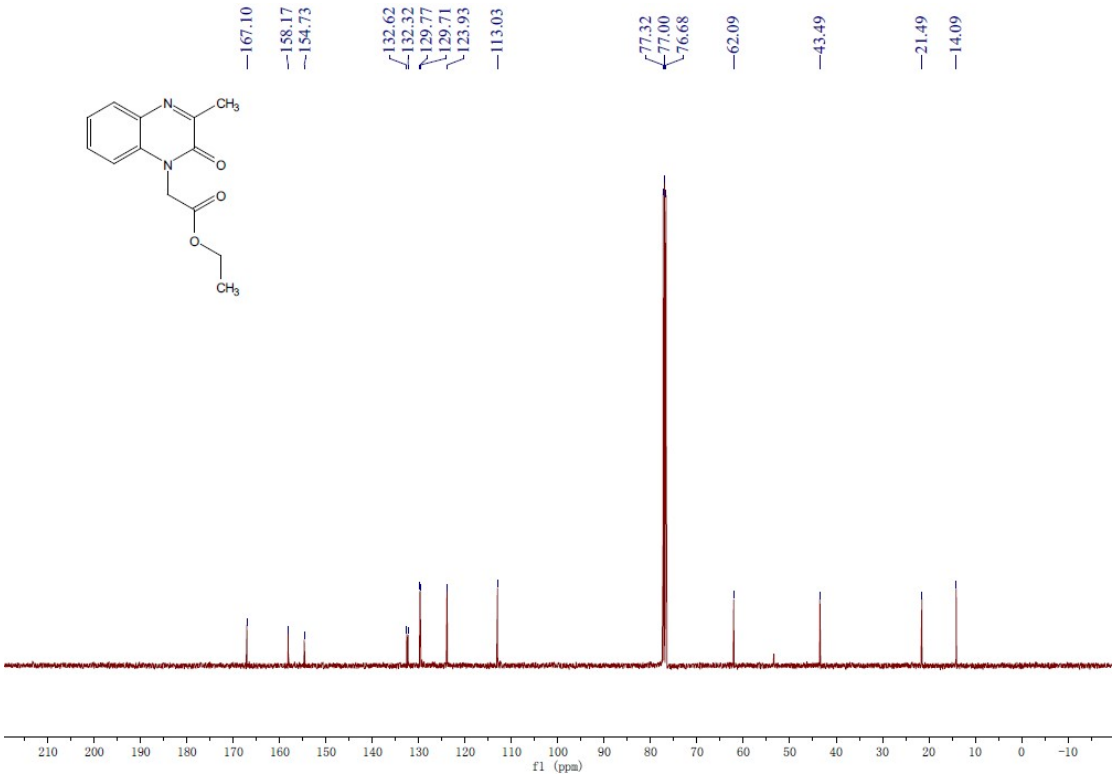


^{1}H spectra of **3ga**



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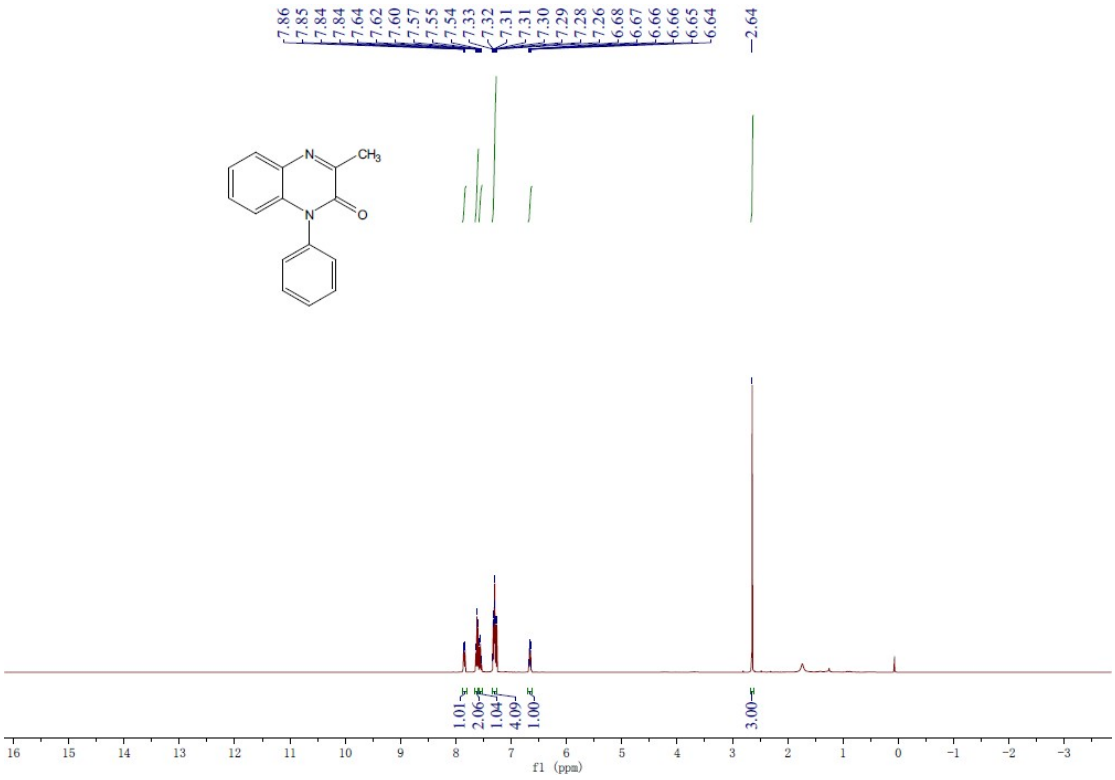
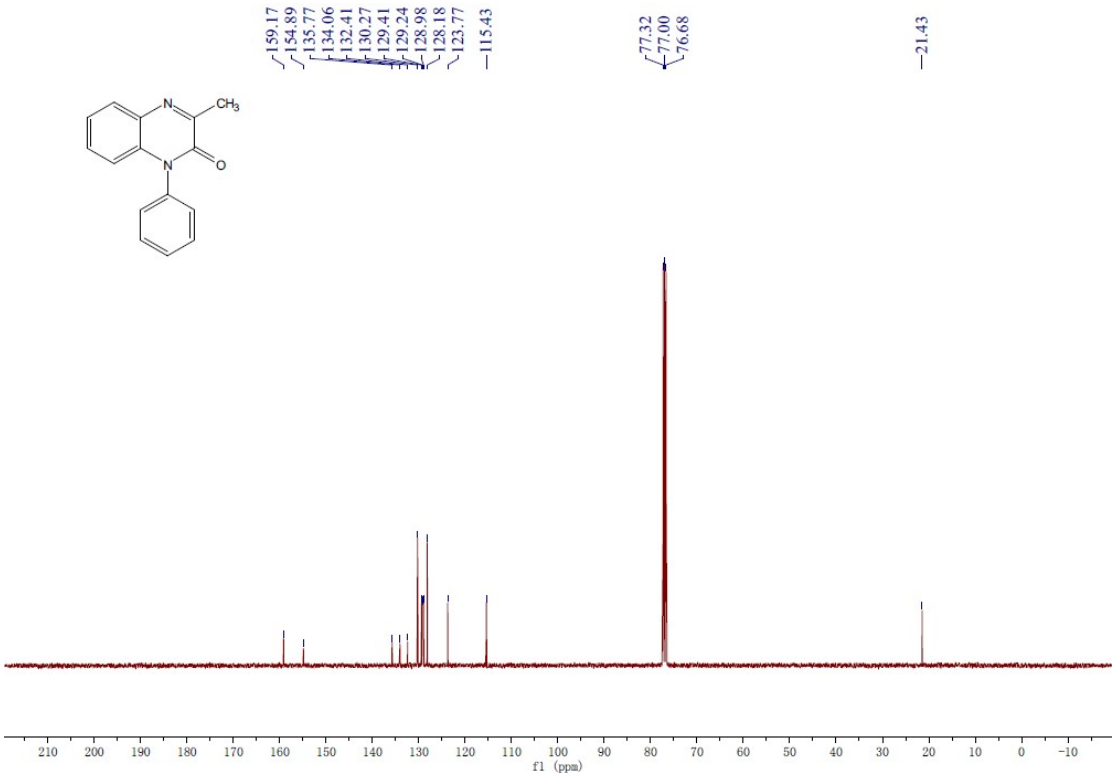
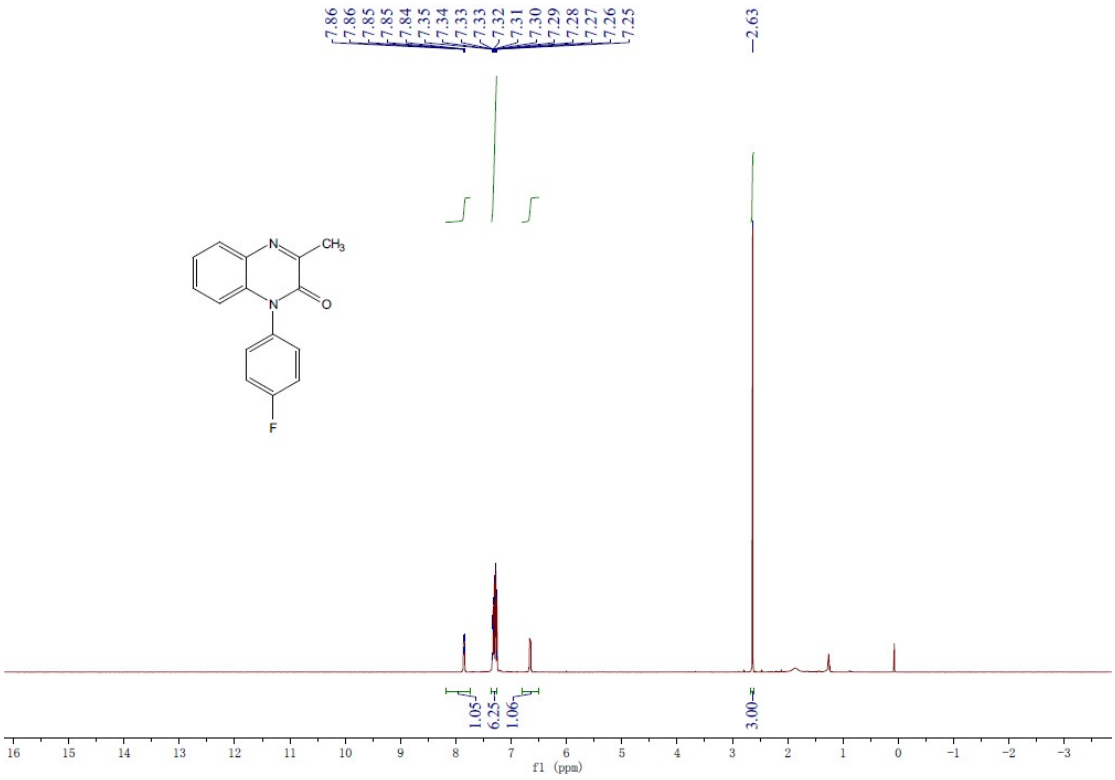


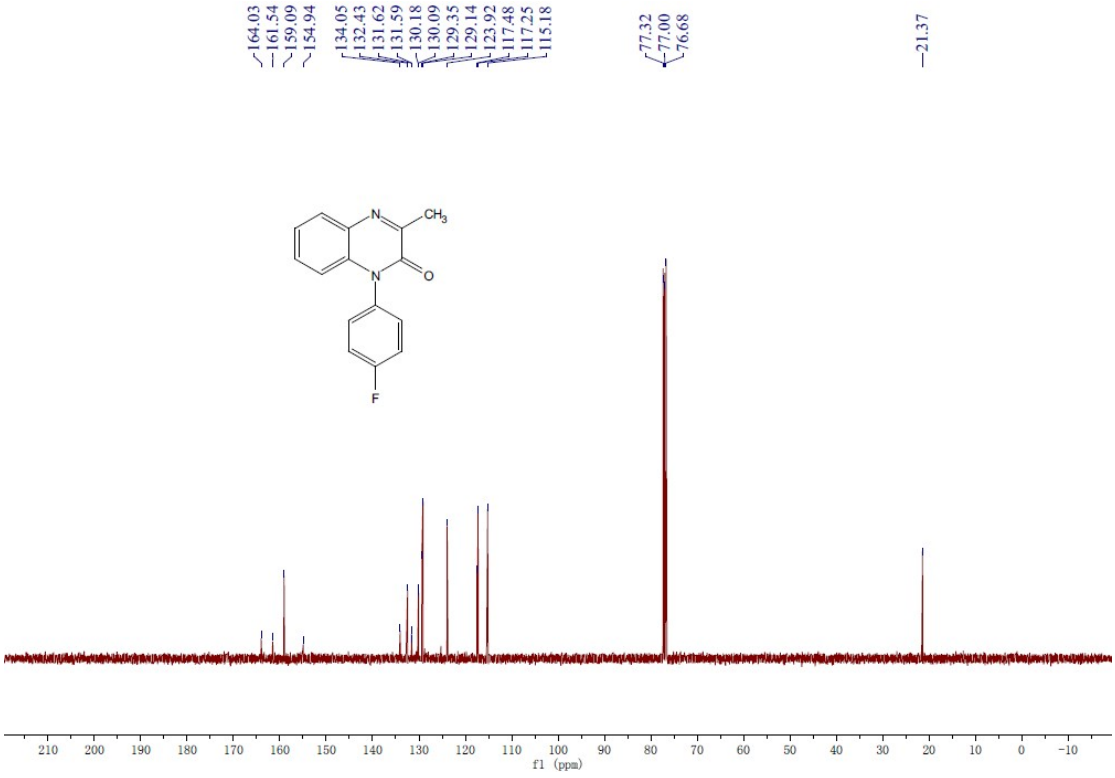
^{1}H spectra of **3ha**



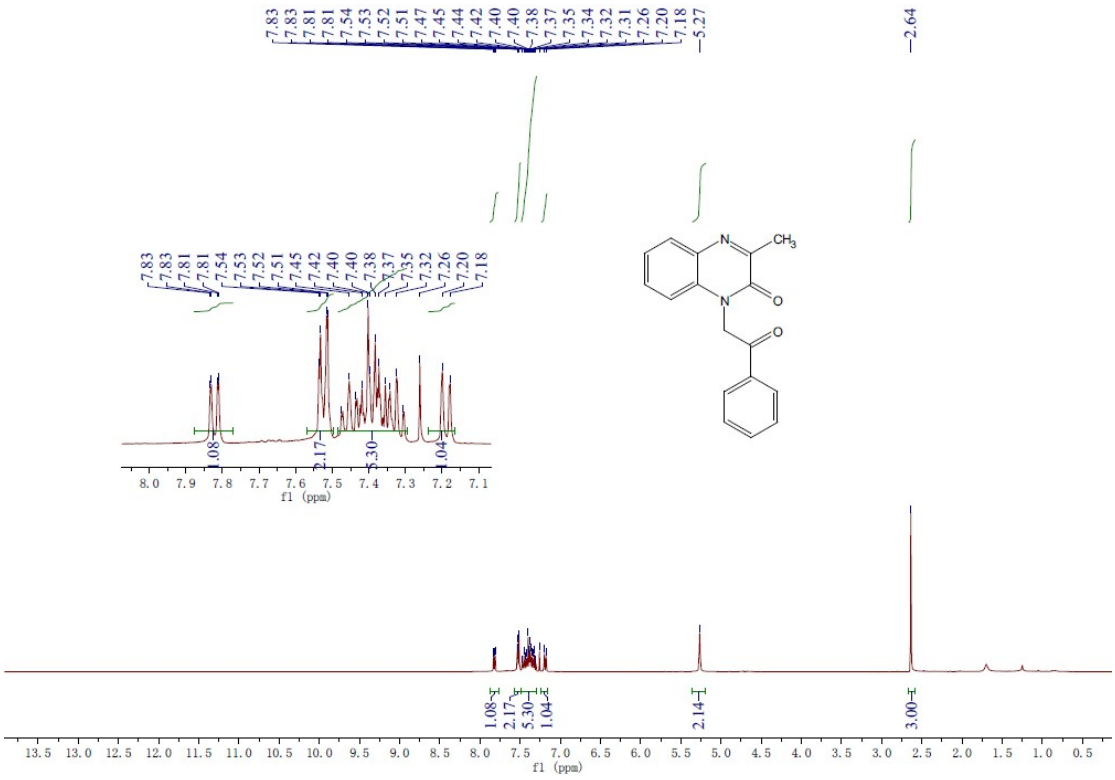
^{13}C spectra of **3ha**



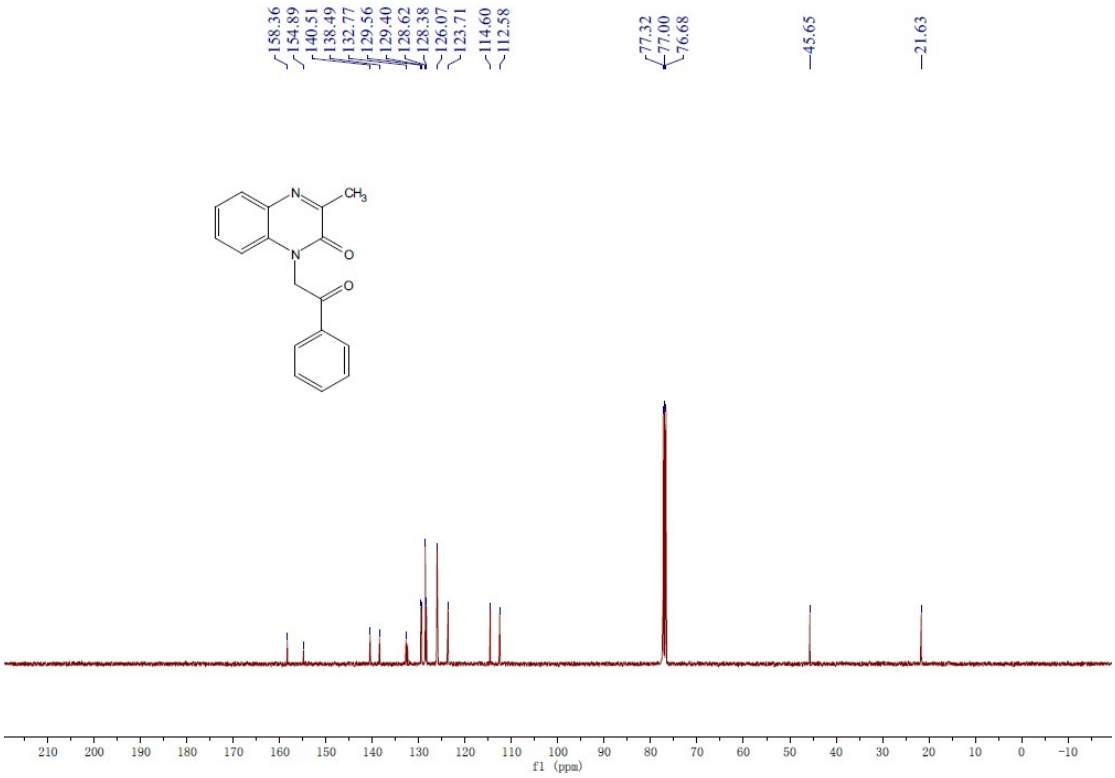
^{1}H spectra of **3ia**



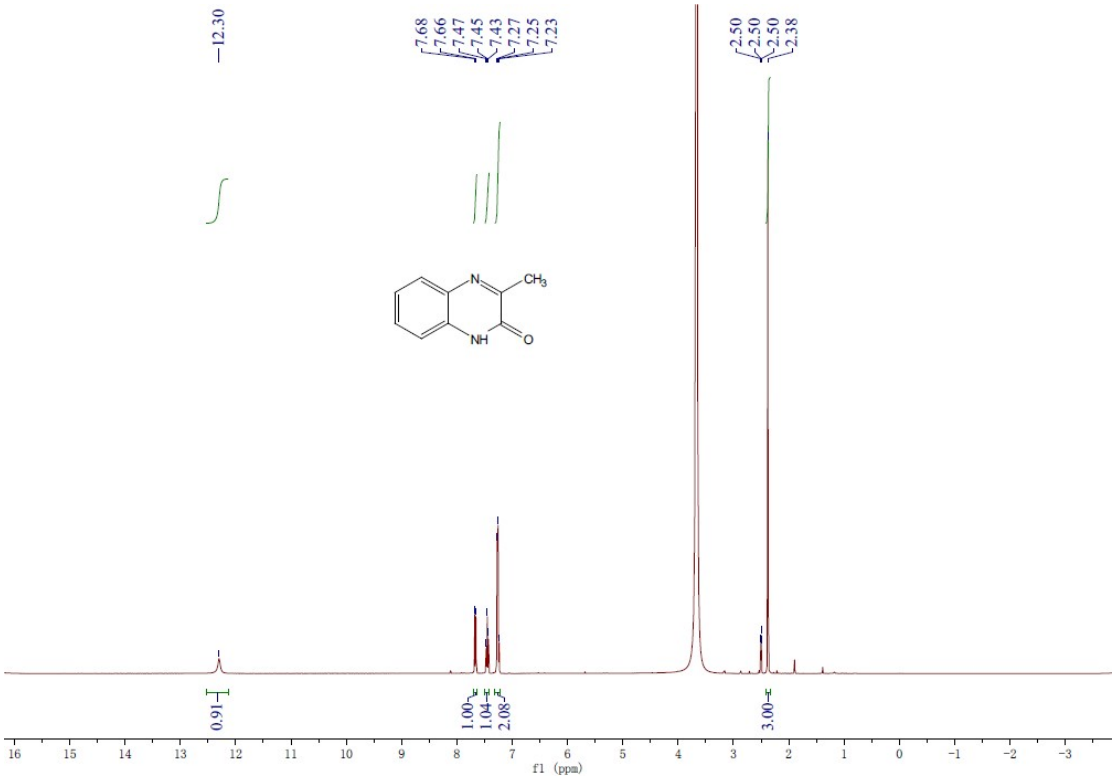
^{13}C spectra of **3ia**



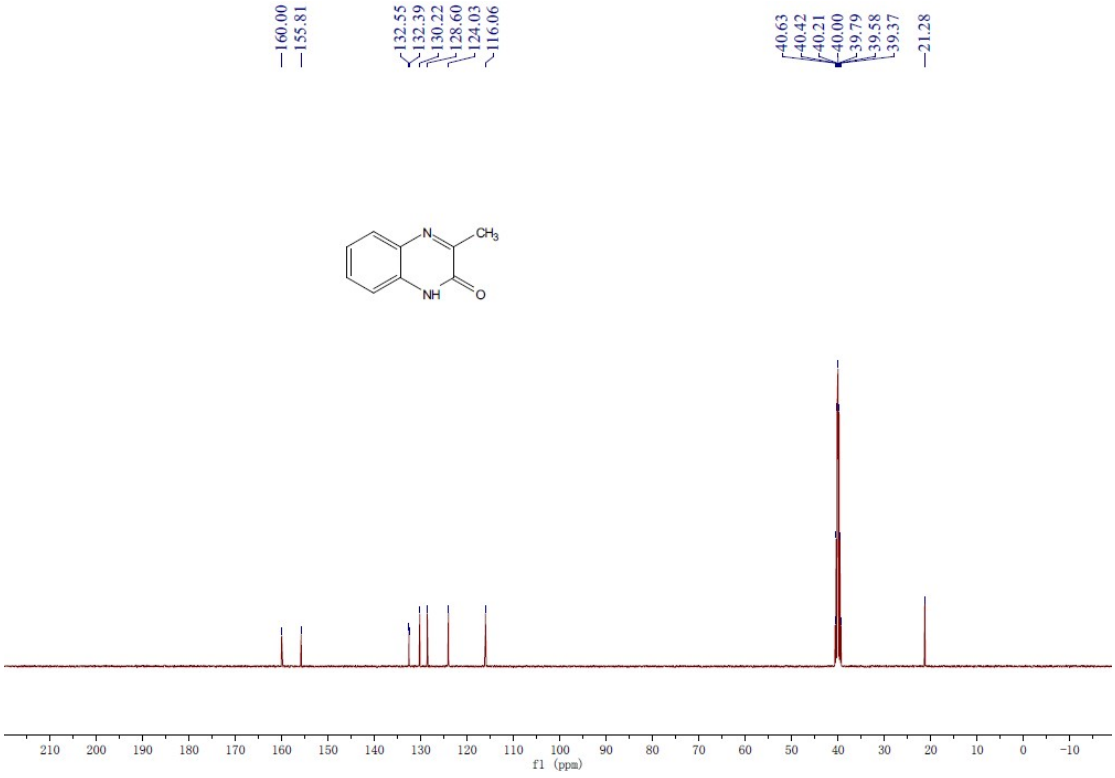
^{1}H spectra of **3ja**



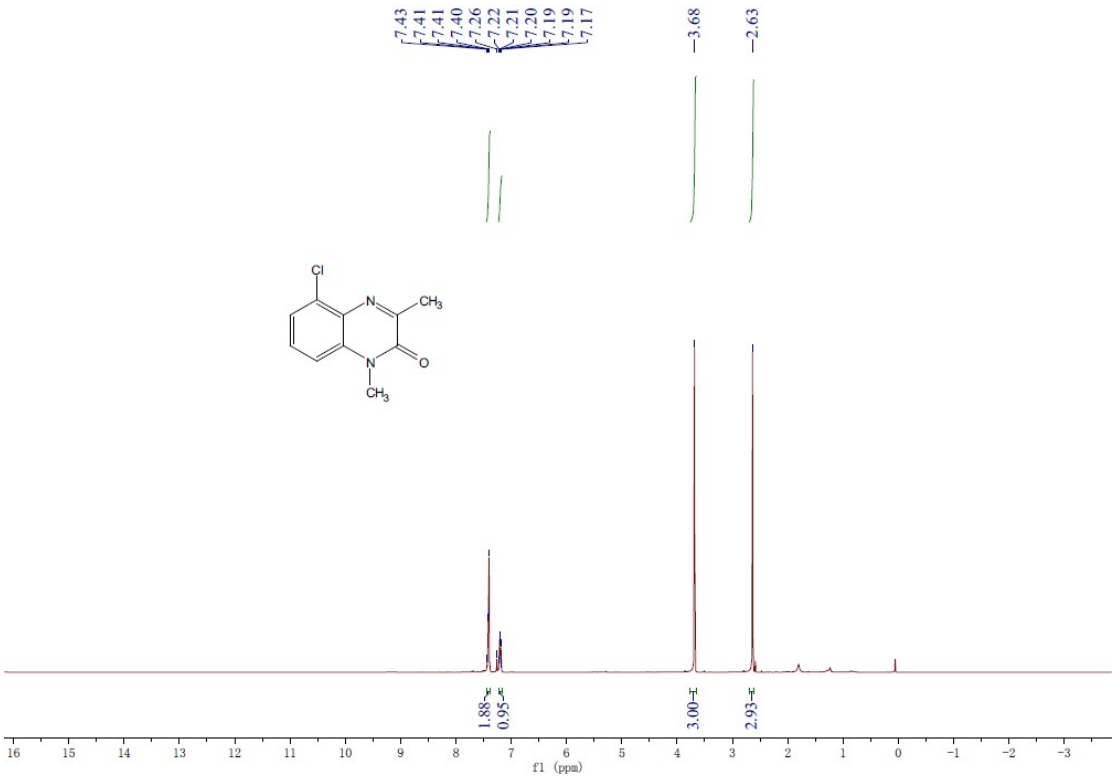
^{13}C spectra of **3ja**



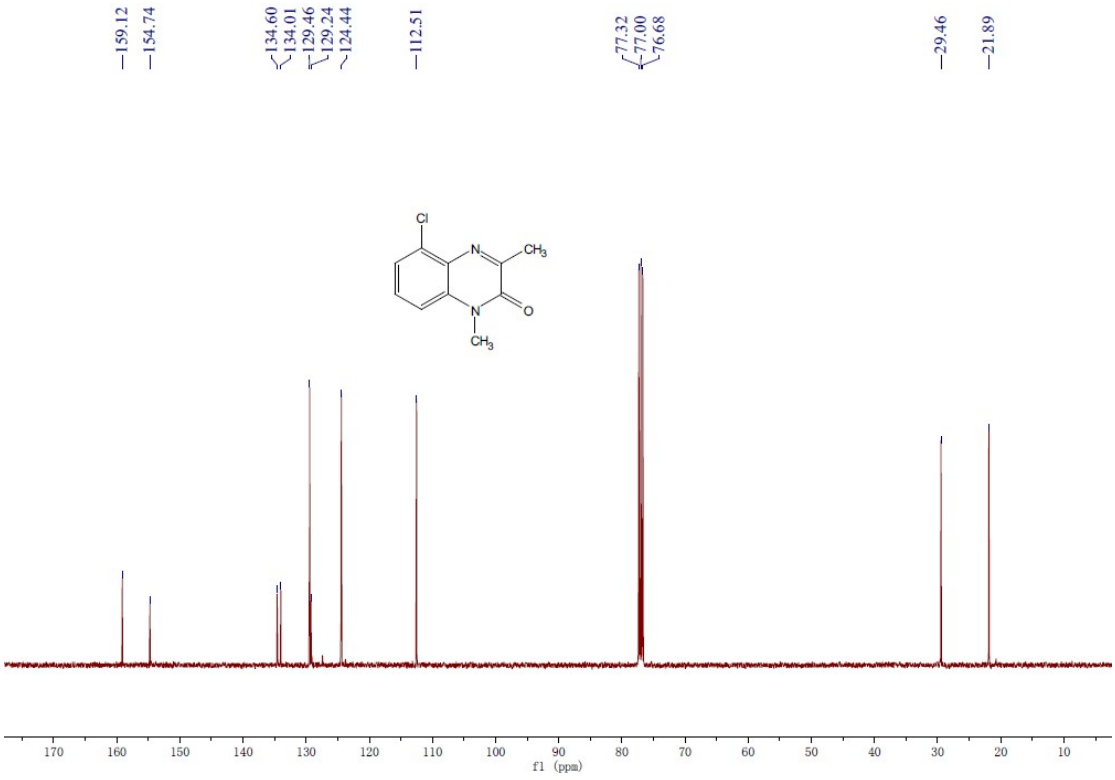
^{1}H spectra of **3ka**



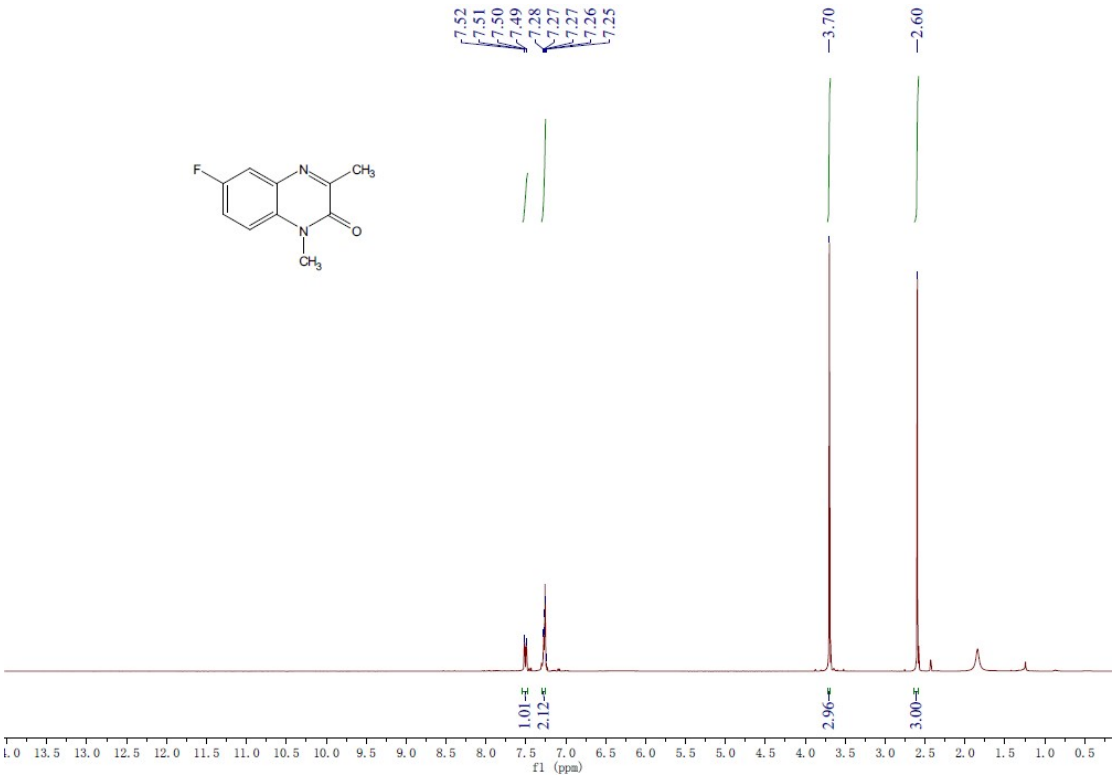
^{13}C spectra of **3ka**



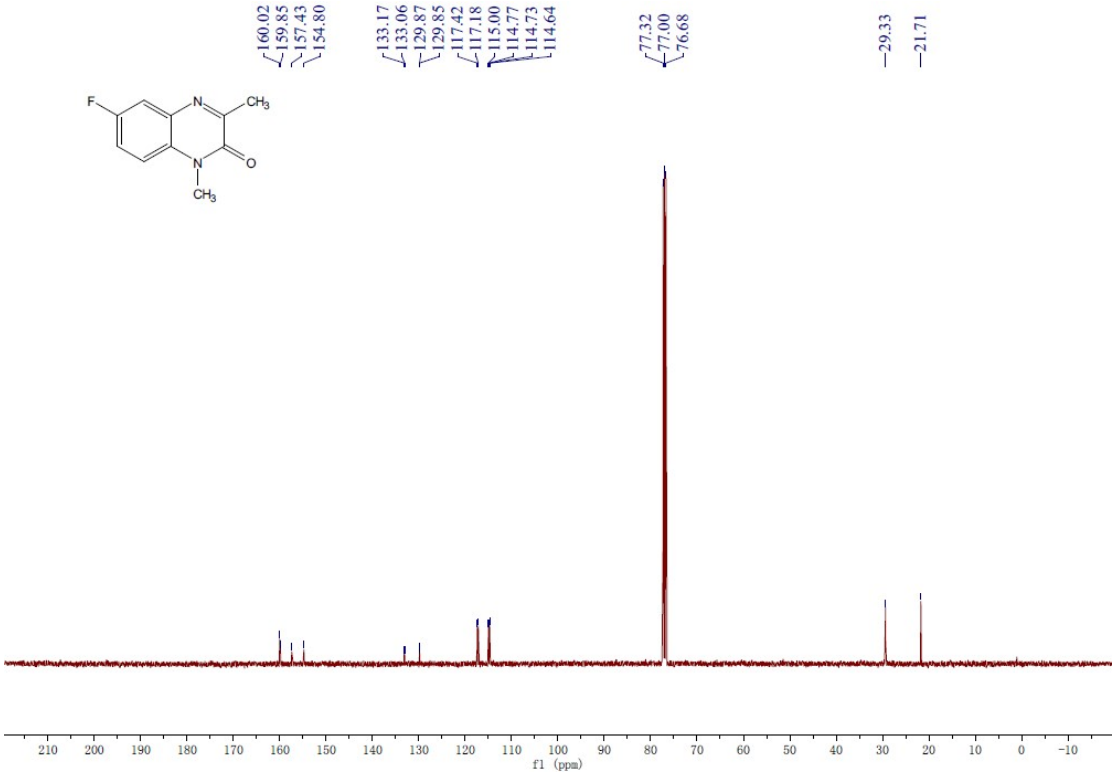
^{1}H spectra of **3la**



^{13}C spectra of **3la**



^{1}H spectra of **3ma**



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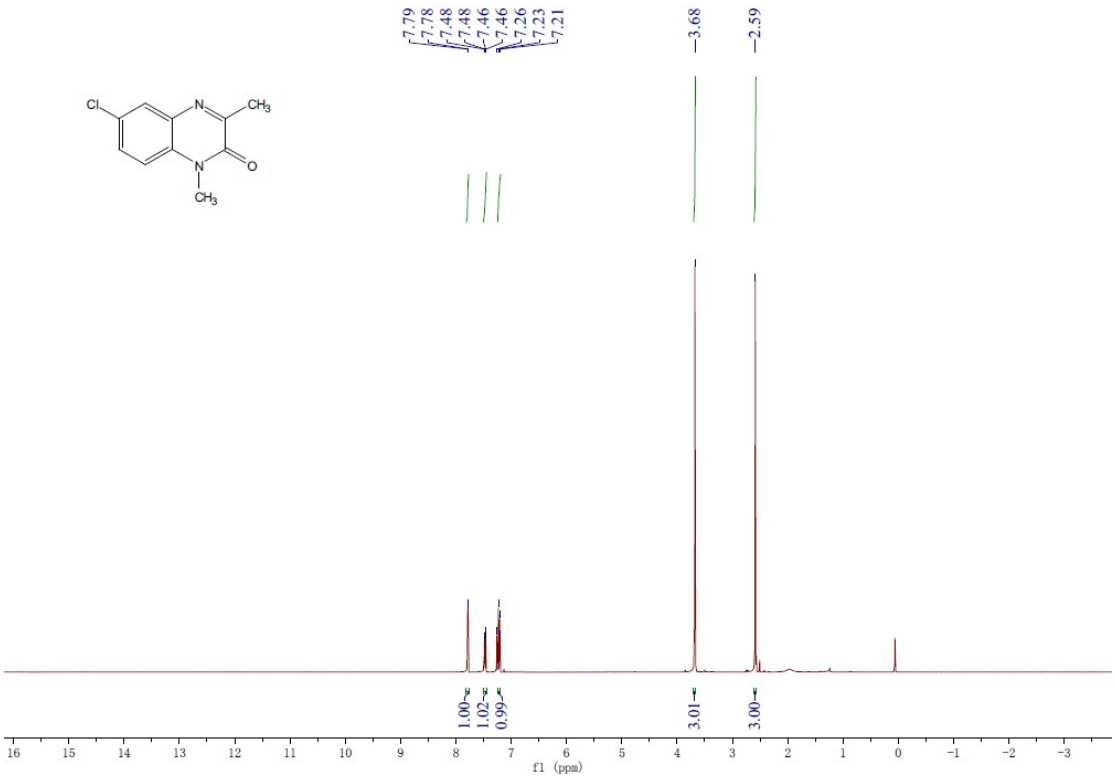

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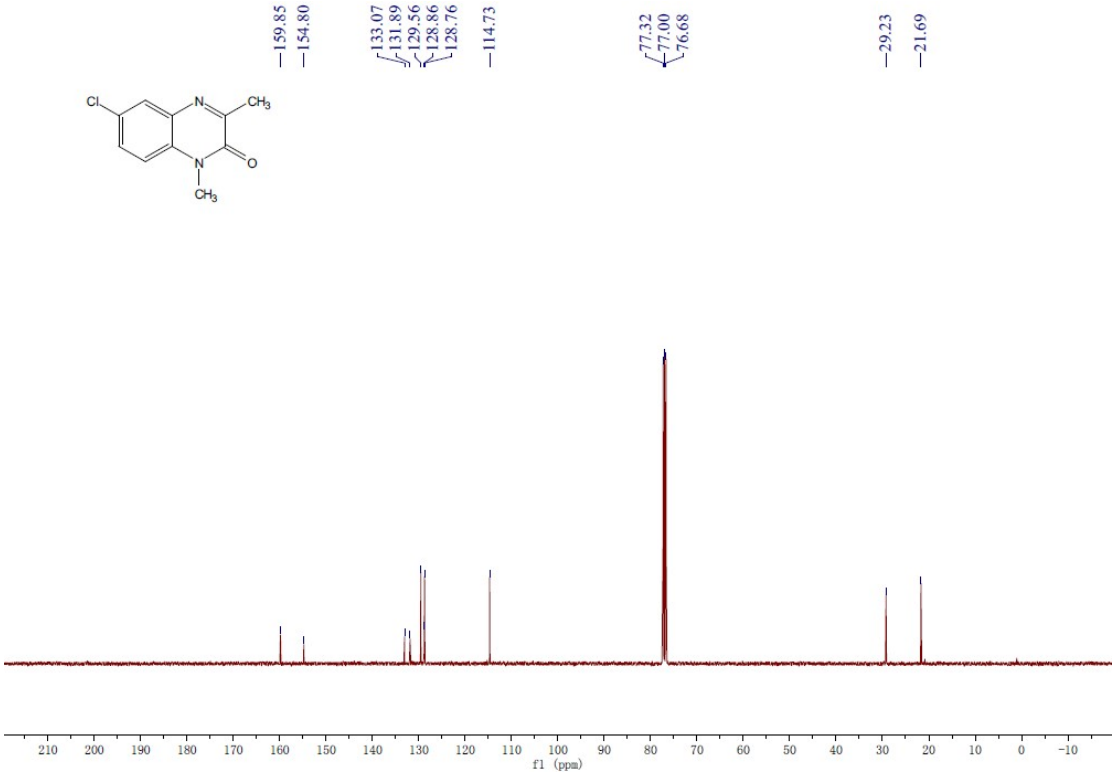

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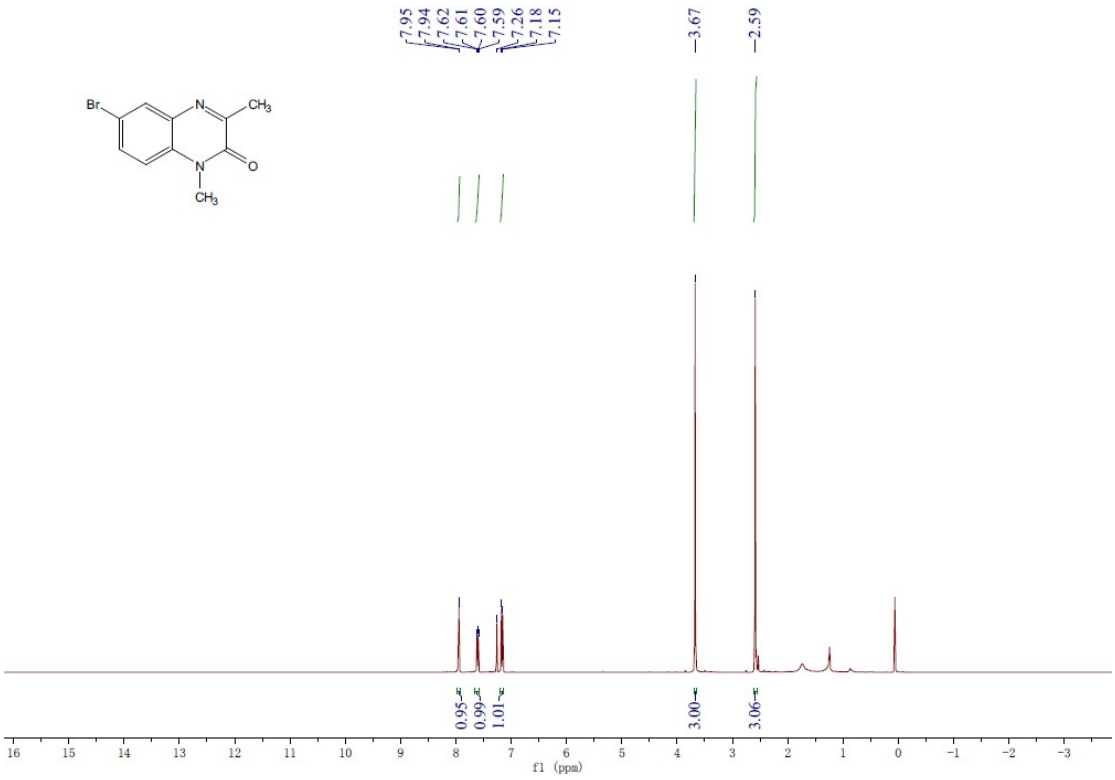
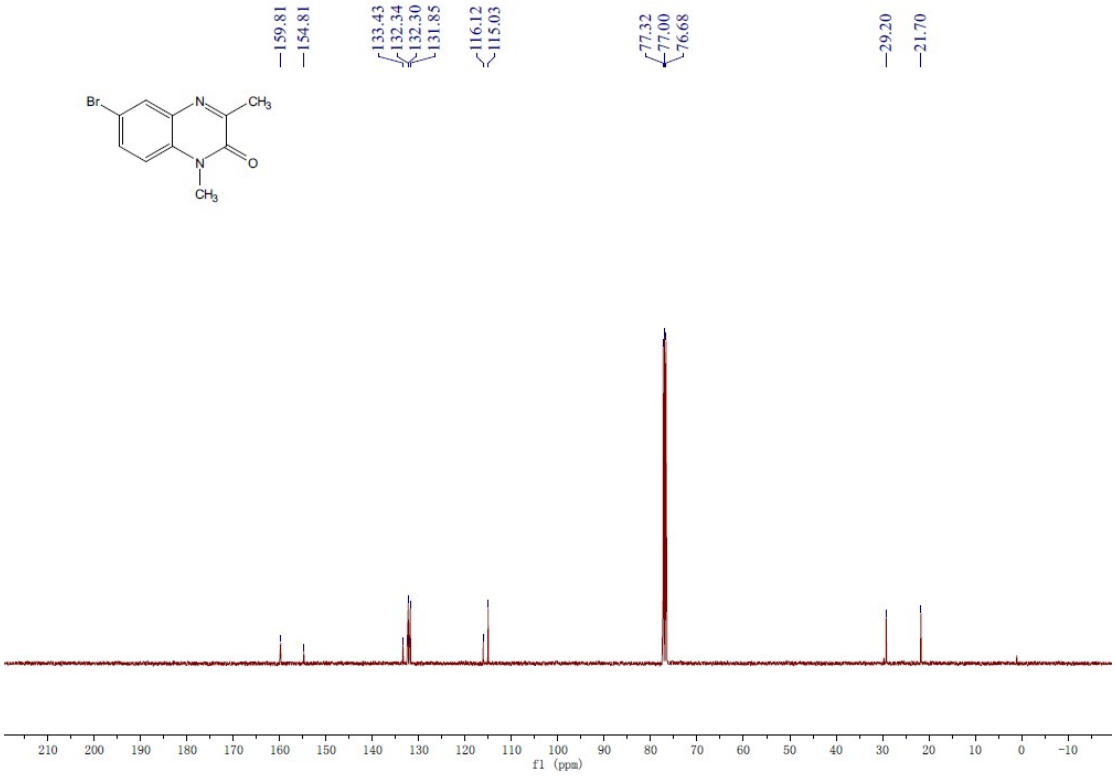


^{1}H spectra of **3oa**



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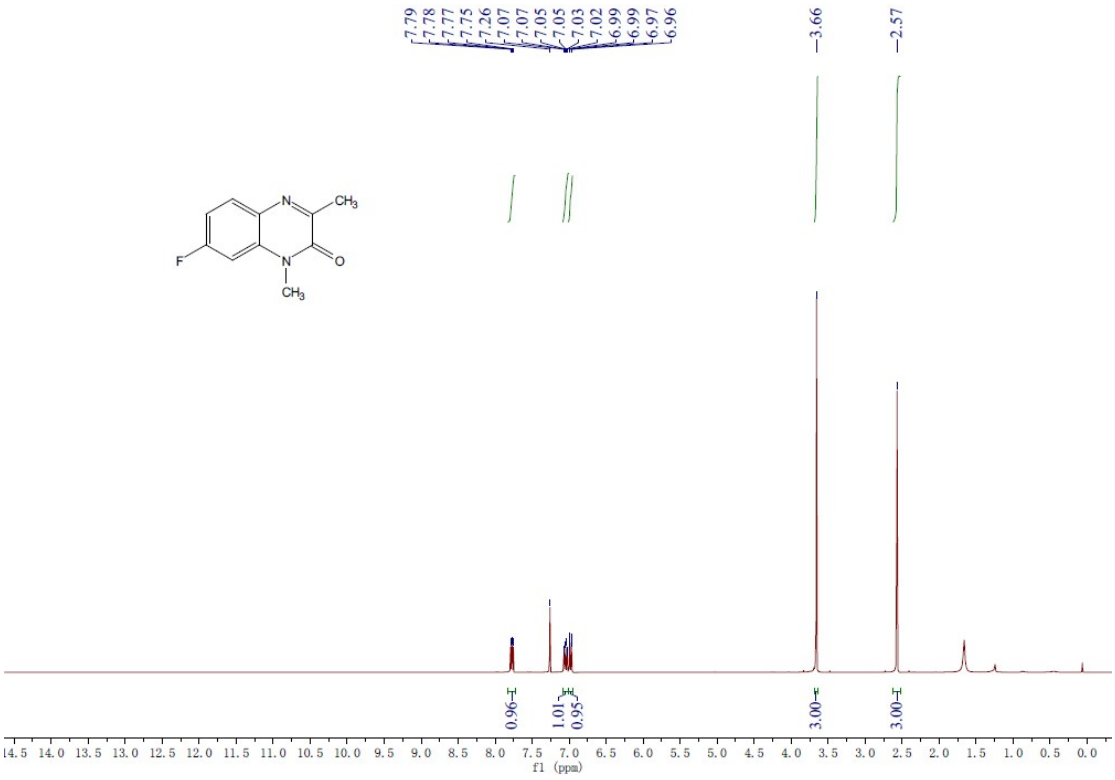
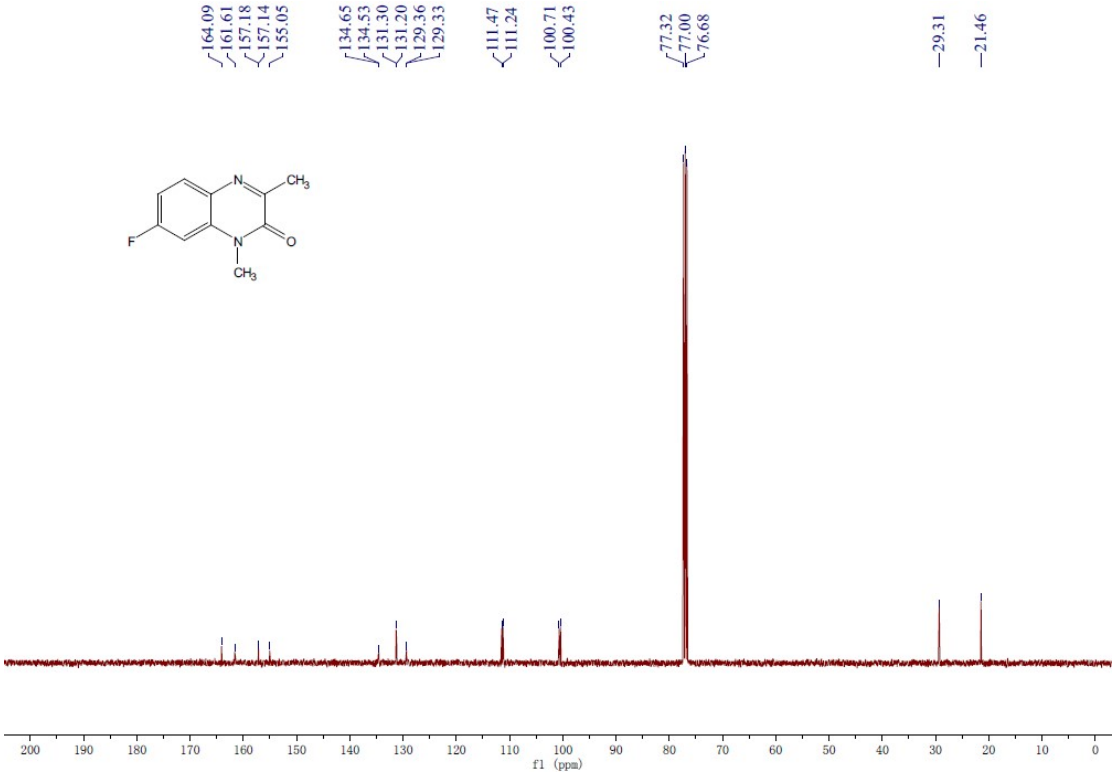


^{1}H spectra of **3pa**



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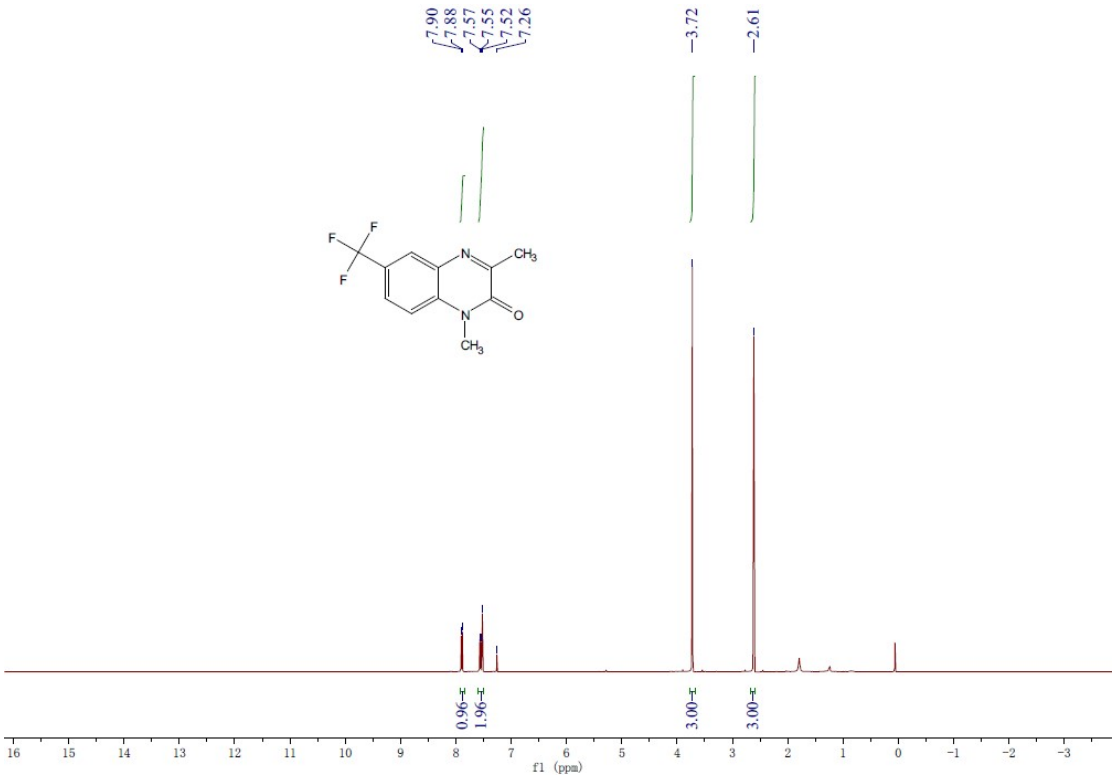

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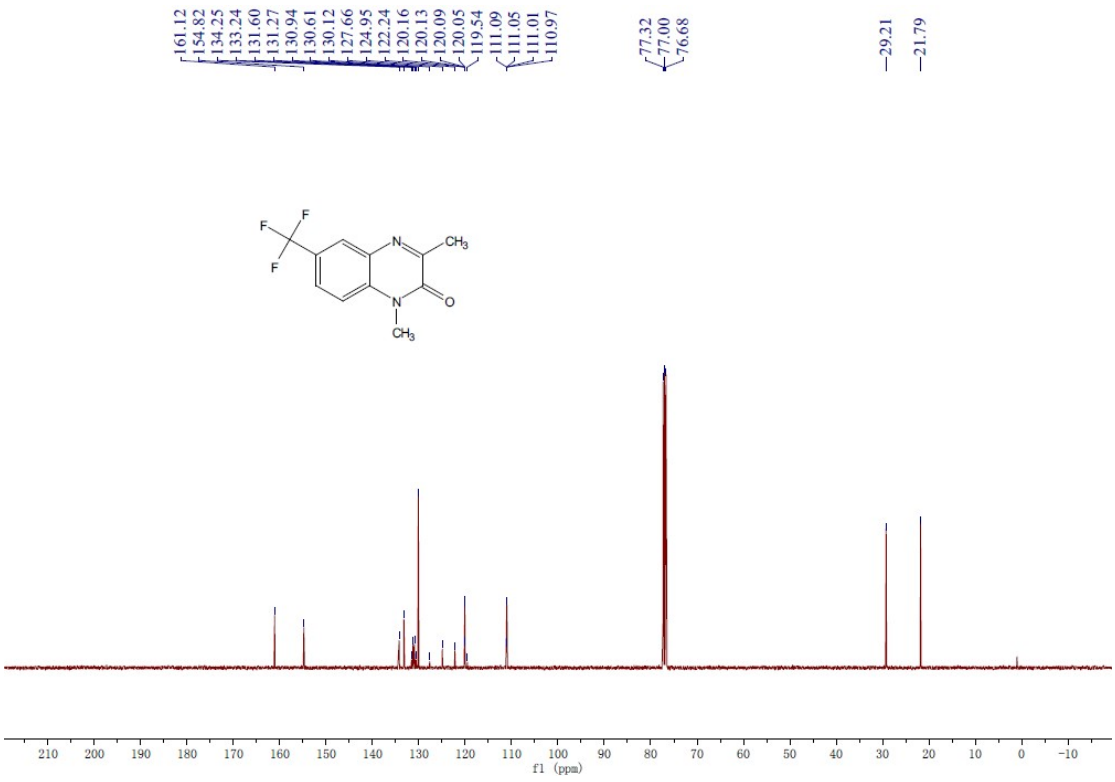

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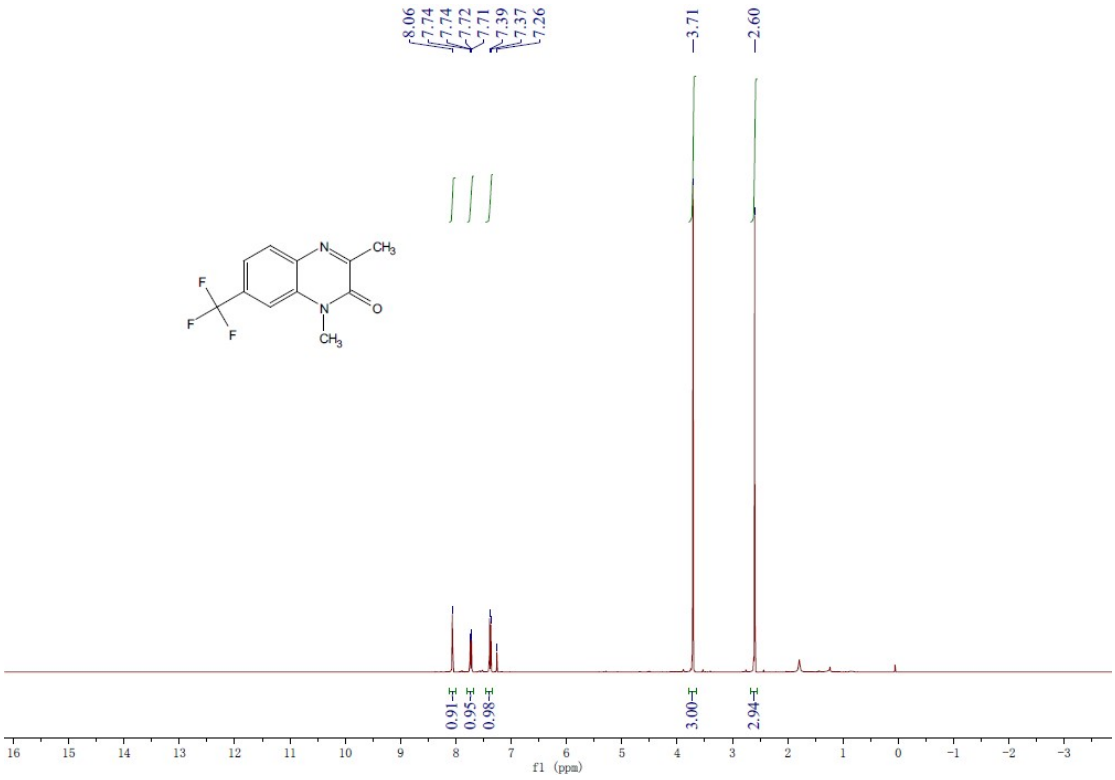

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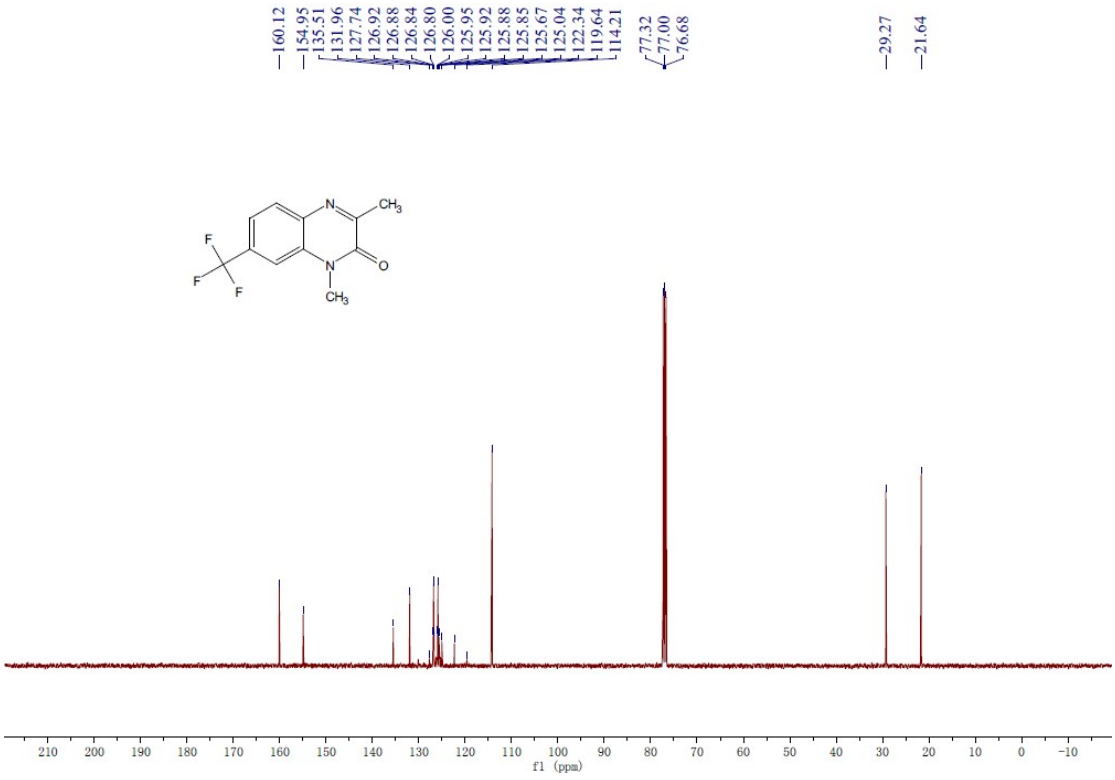

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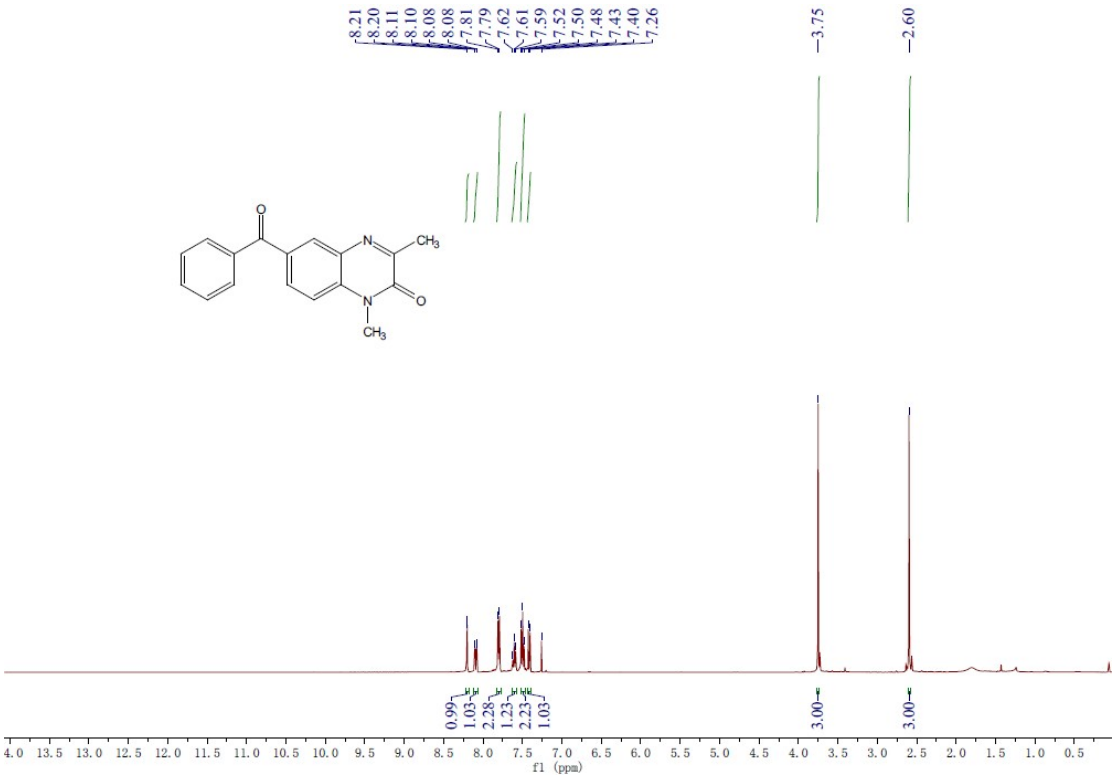

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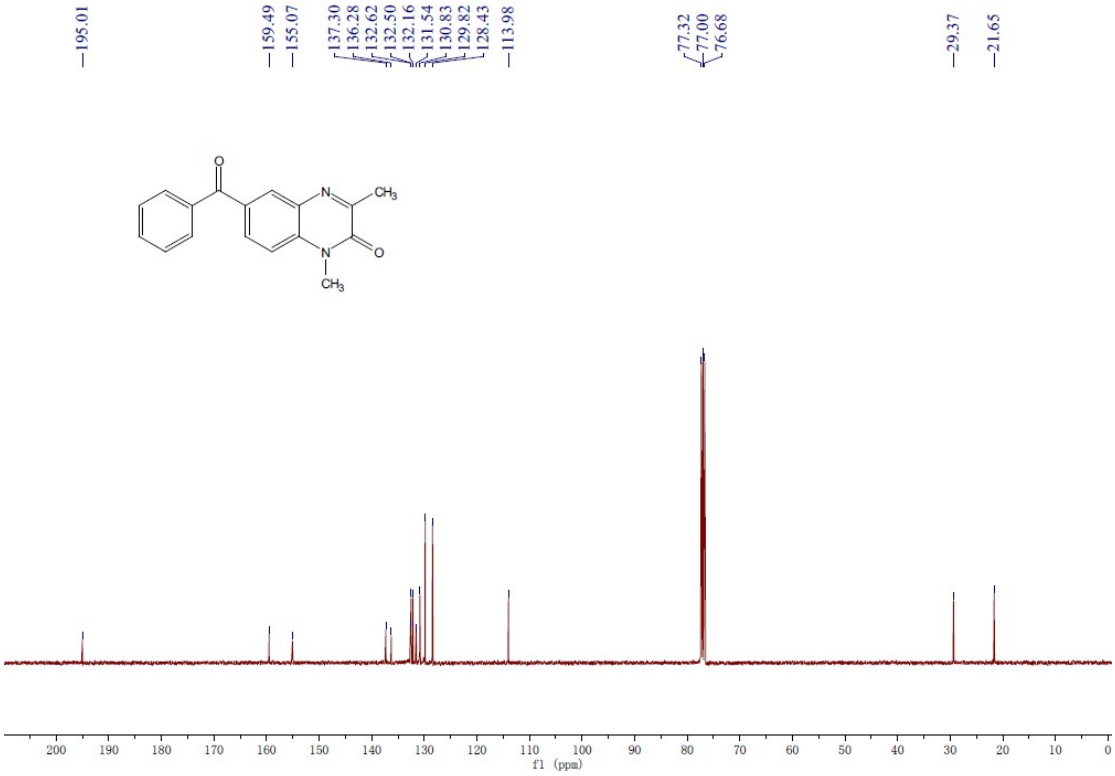

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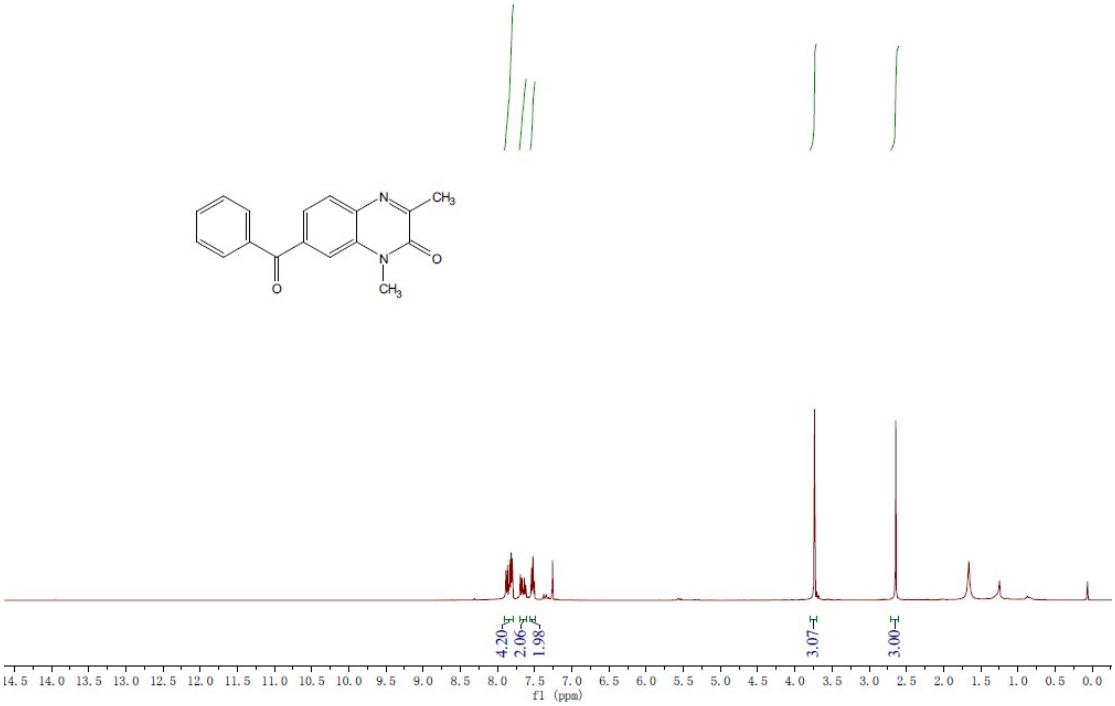
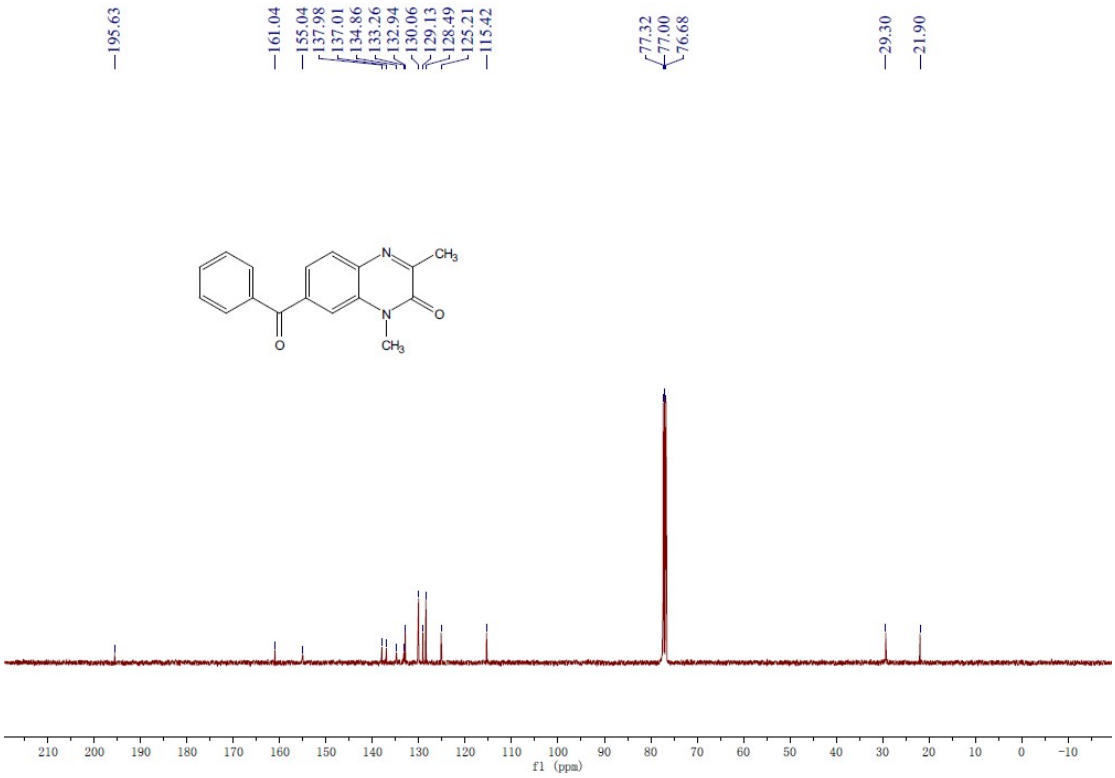


^{1}H spectra of **3ta**



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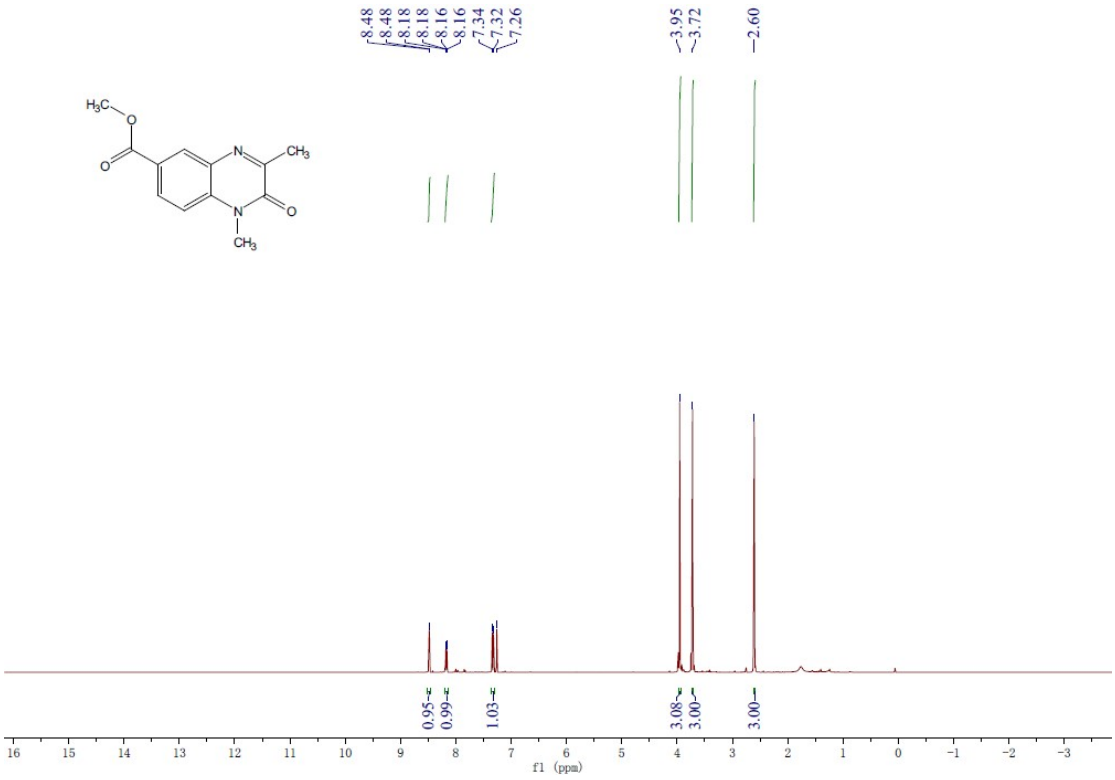

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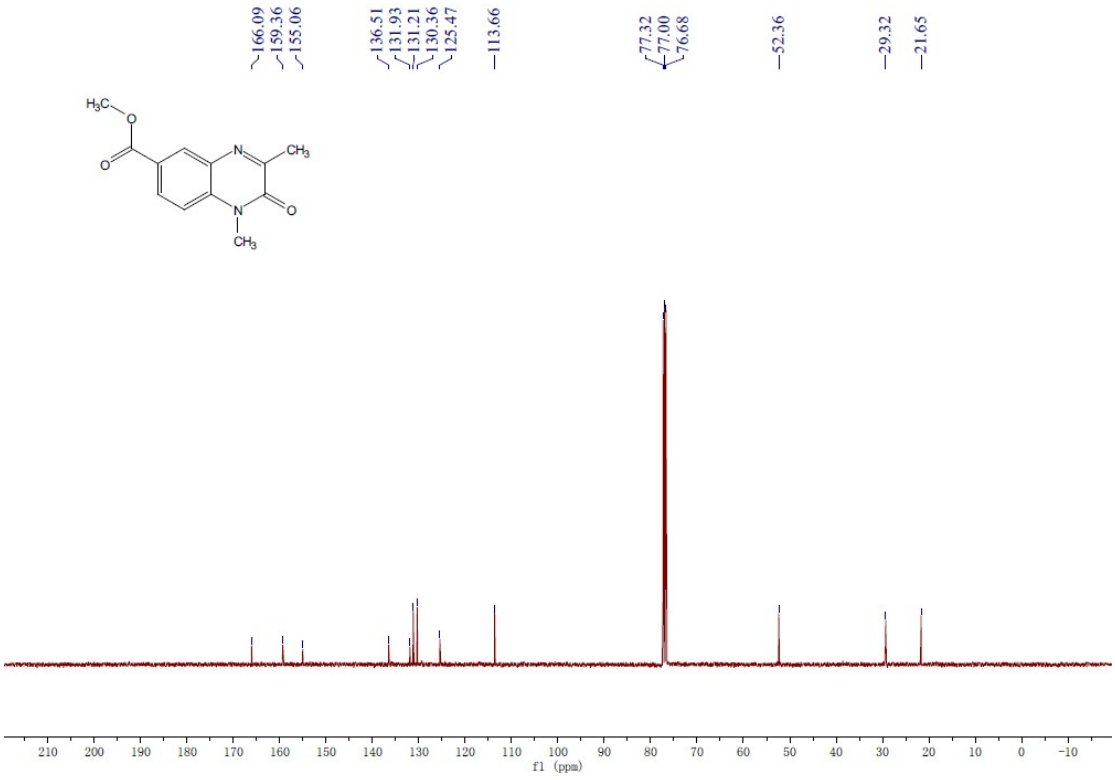

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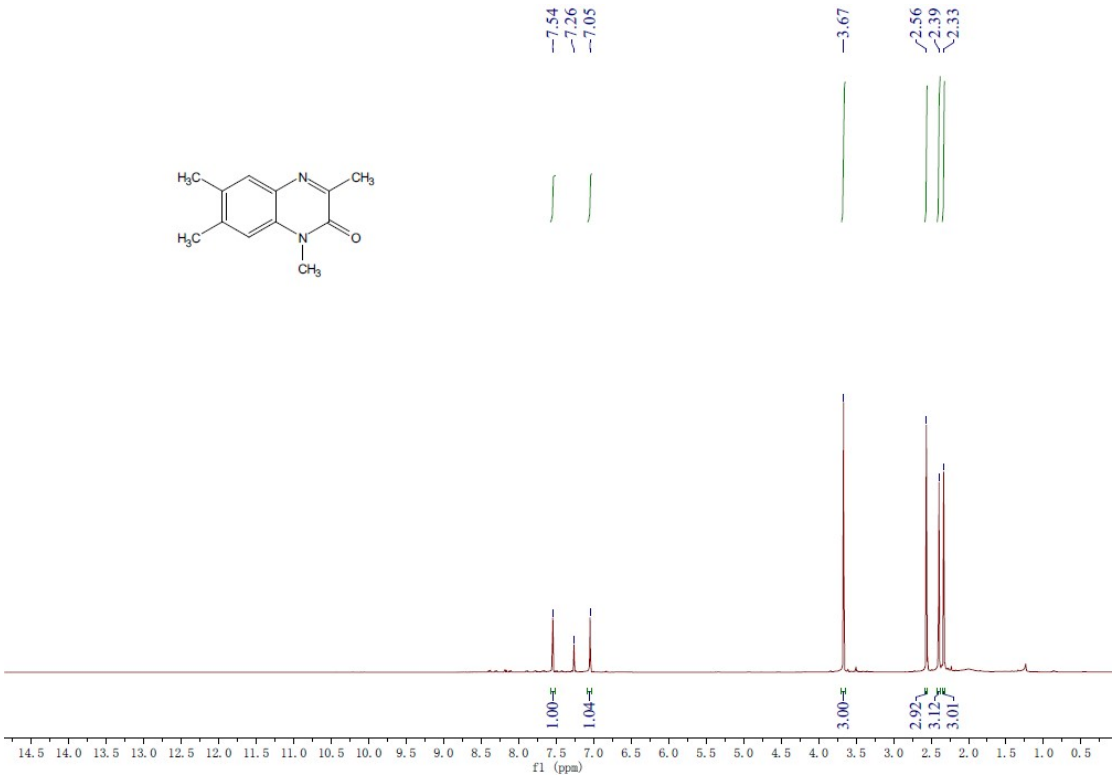

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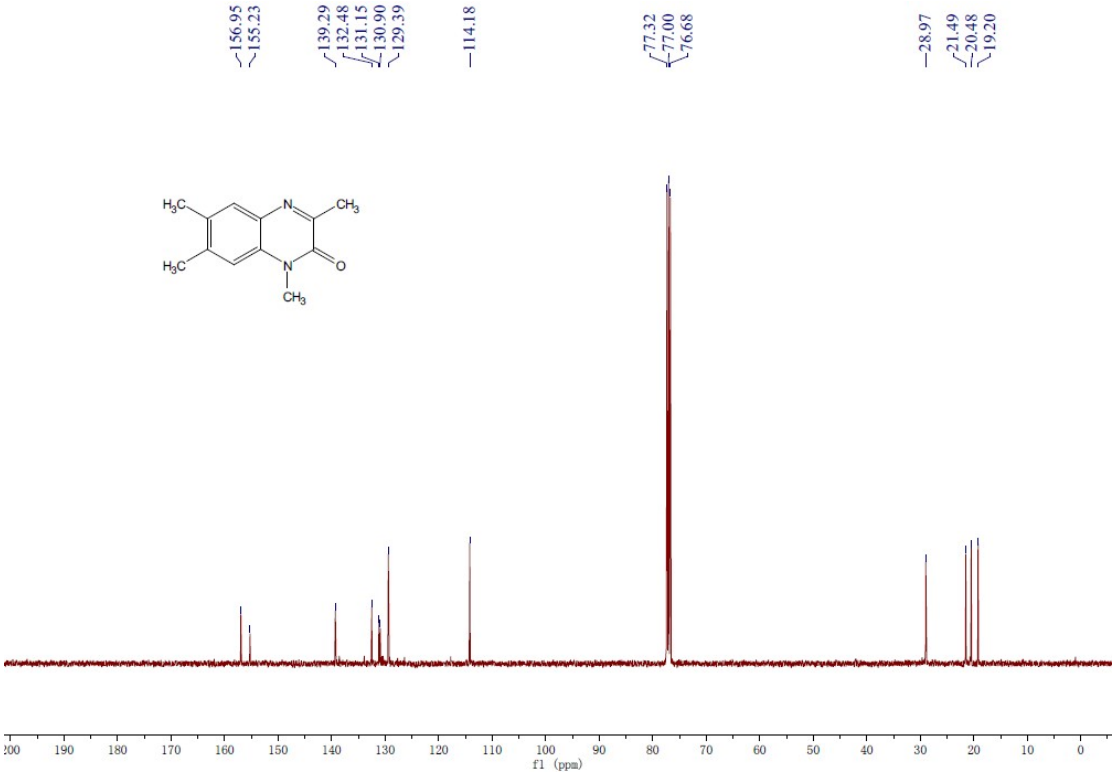
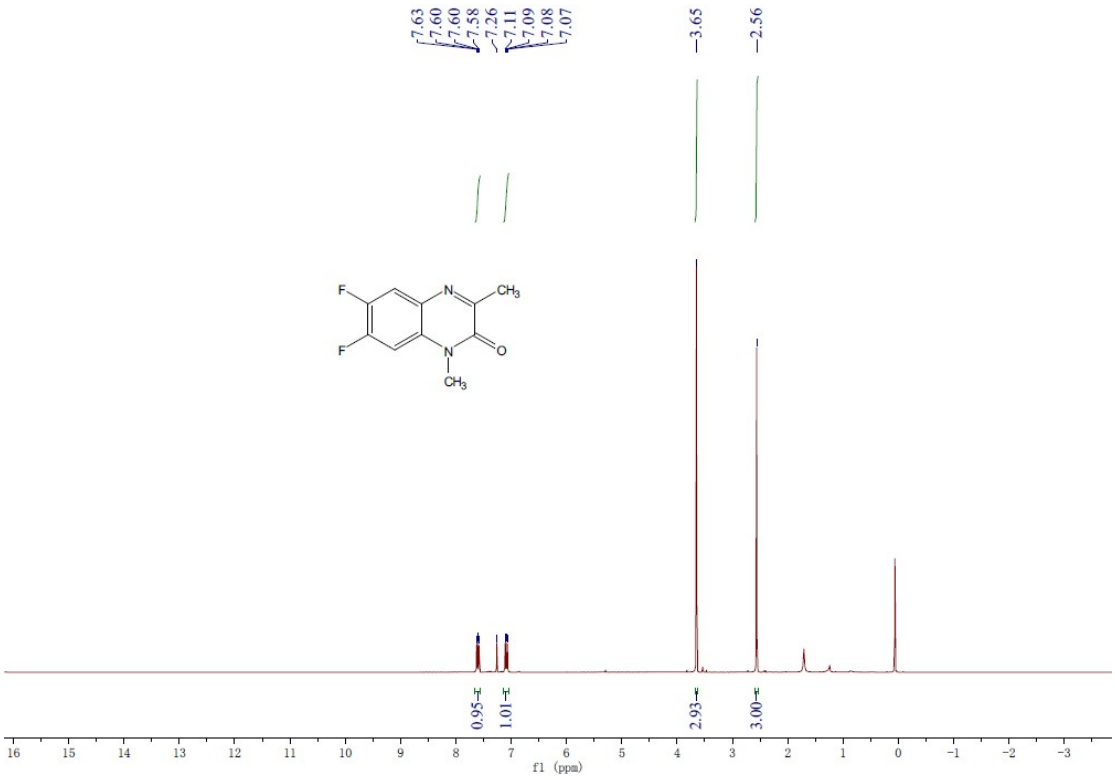
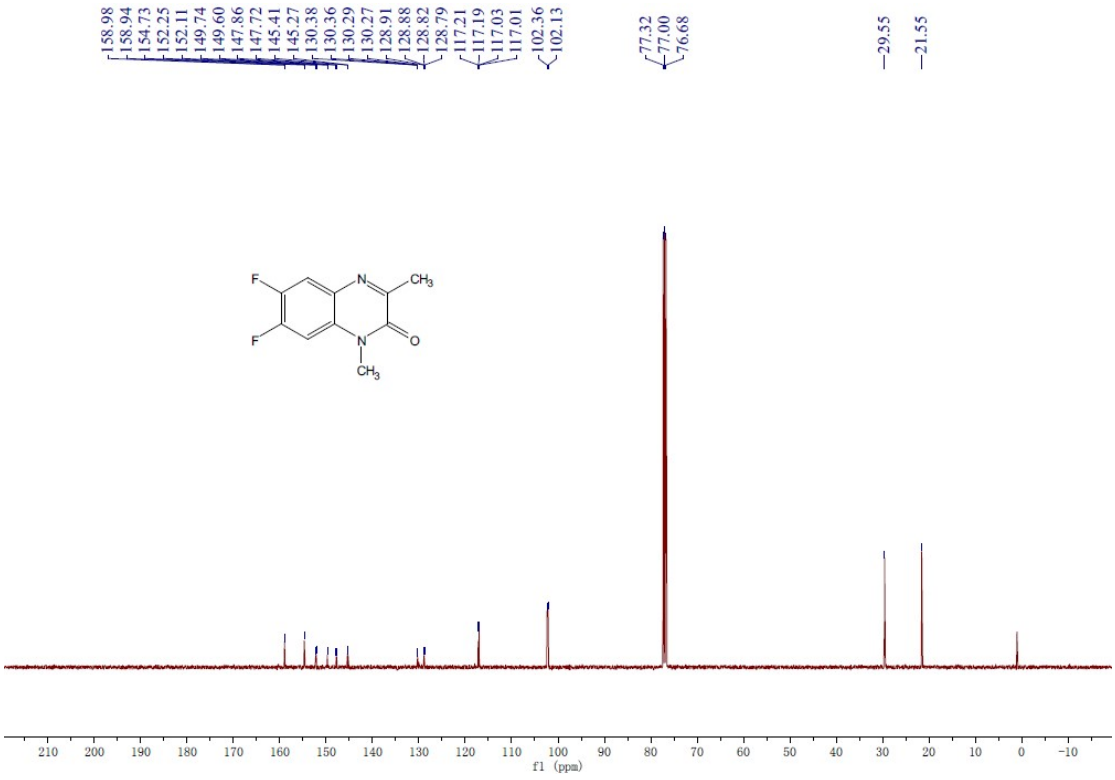


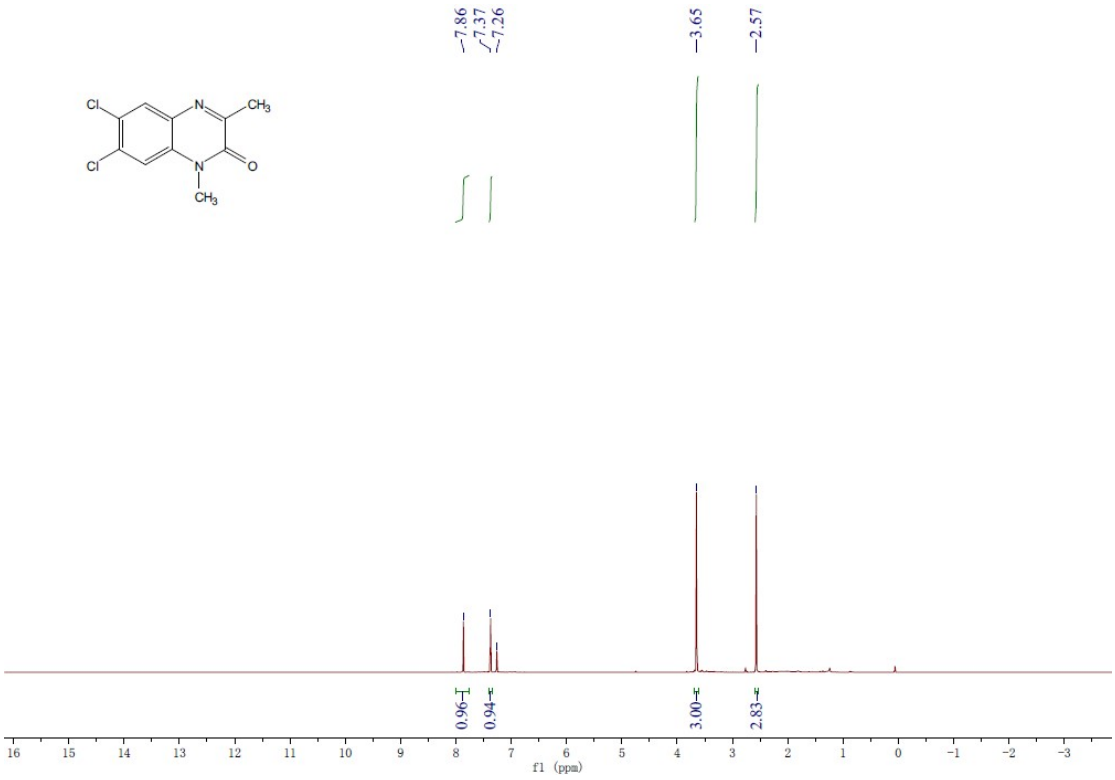
^{13}C spectra of **3va**



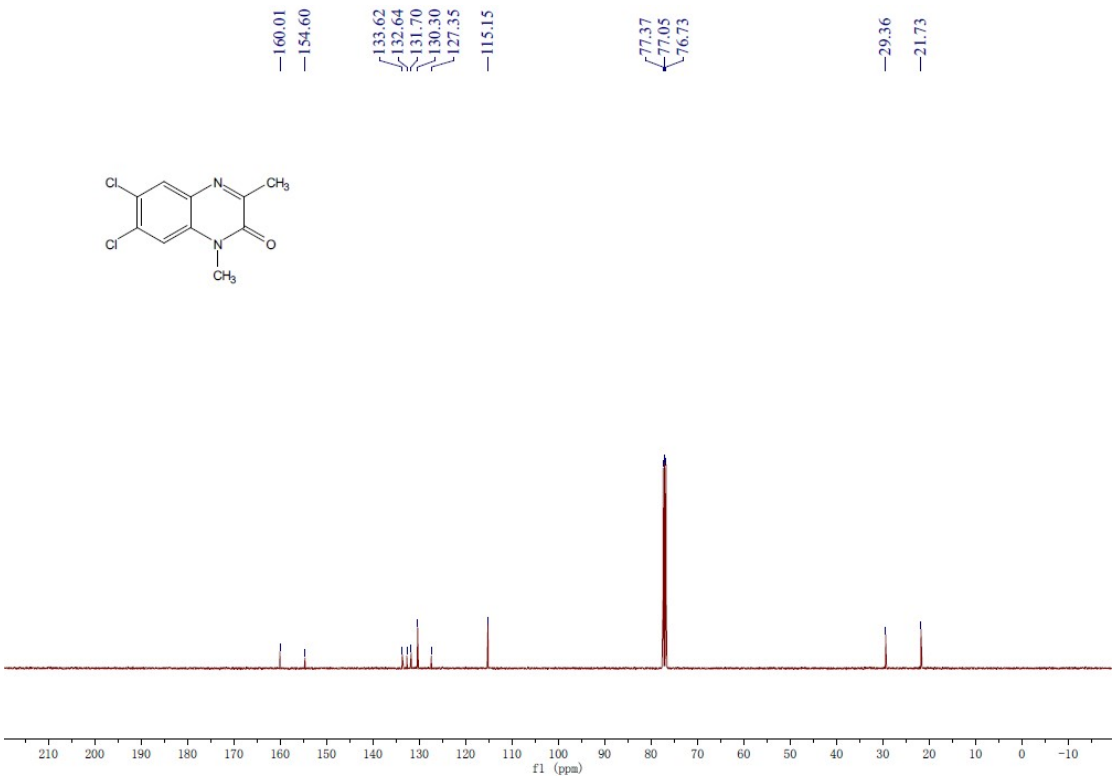
^{1}H spectra of **3wa**



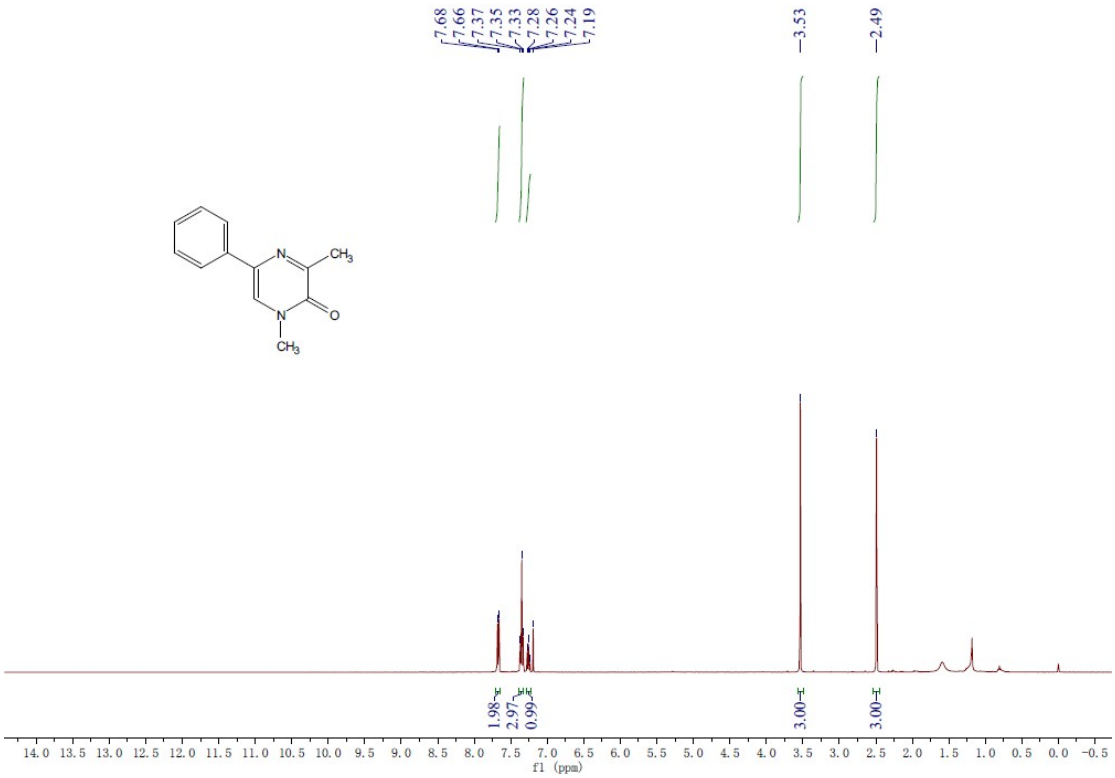
^{1}H spectra of **3wa**



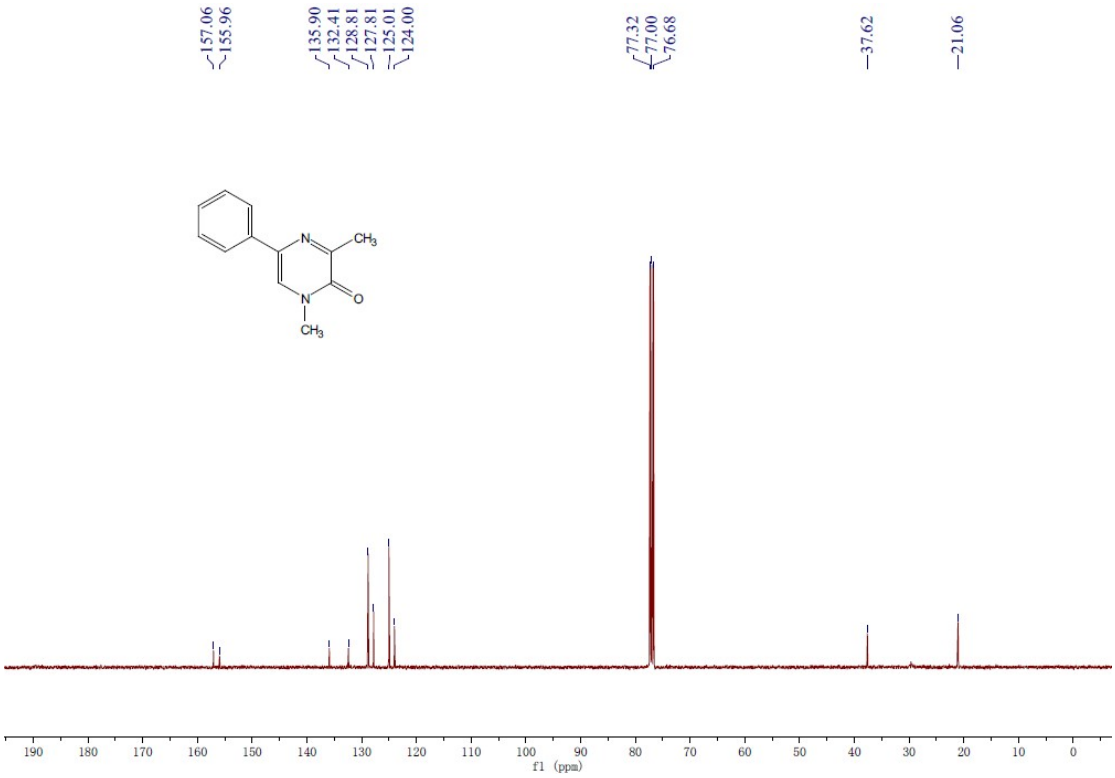
^{1}H spectra of **3xa**



^{13}C spectra of **3xa**



^{1}H spectra of **3ya**



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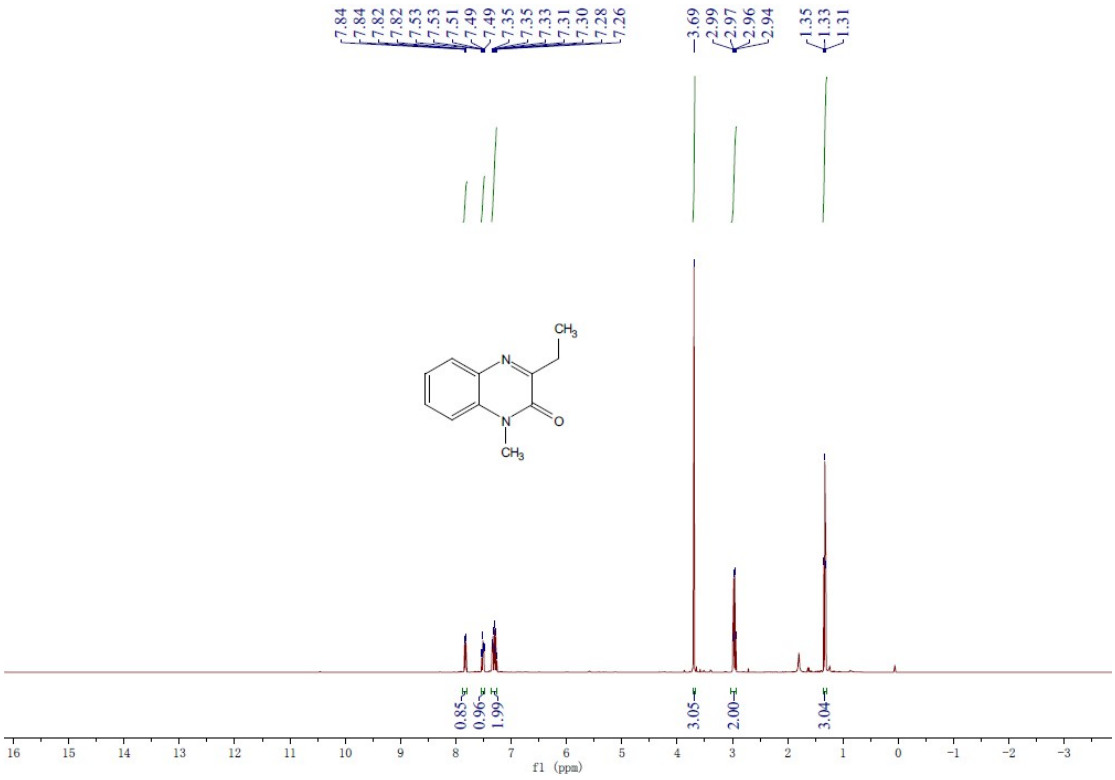
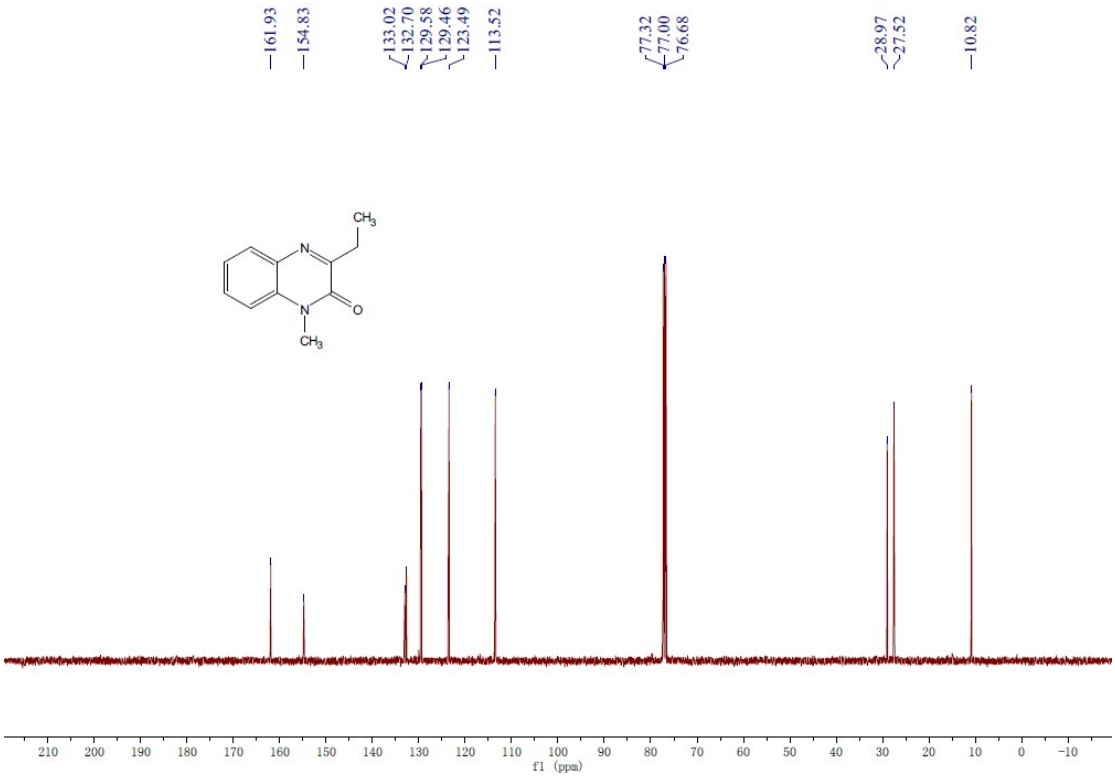
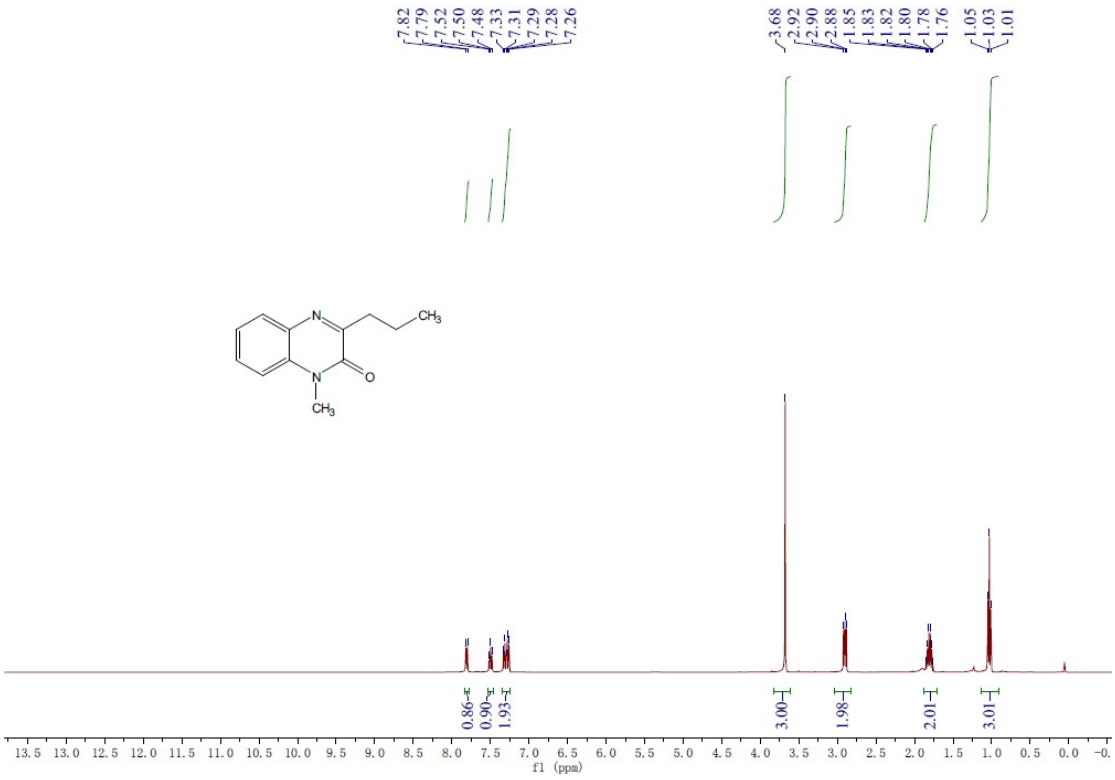


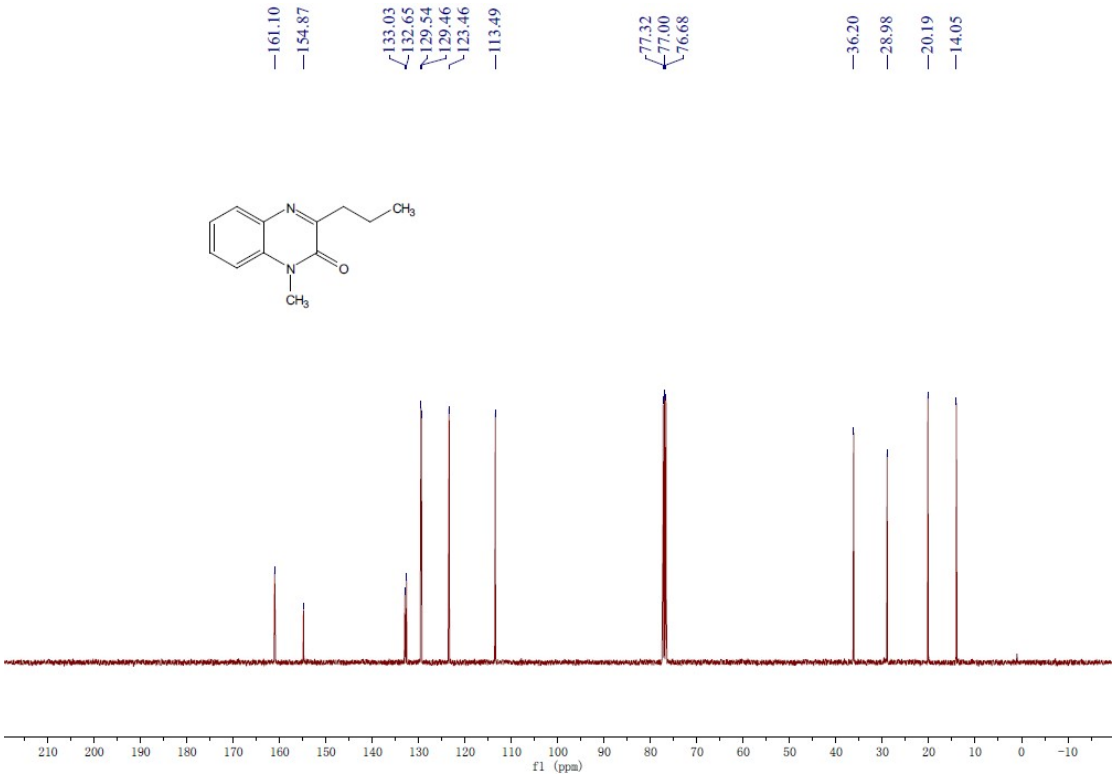
^{1}H spectra of **3ab**



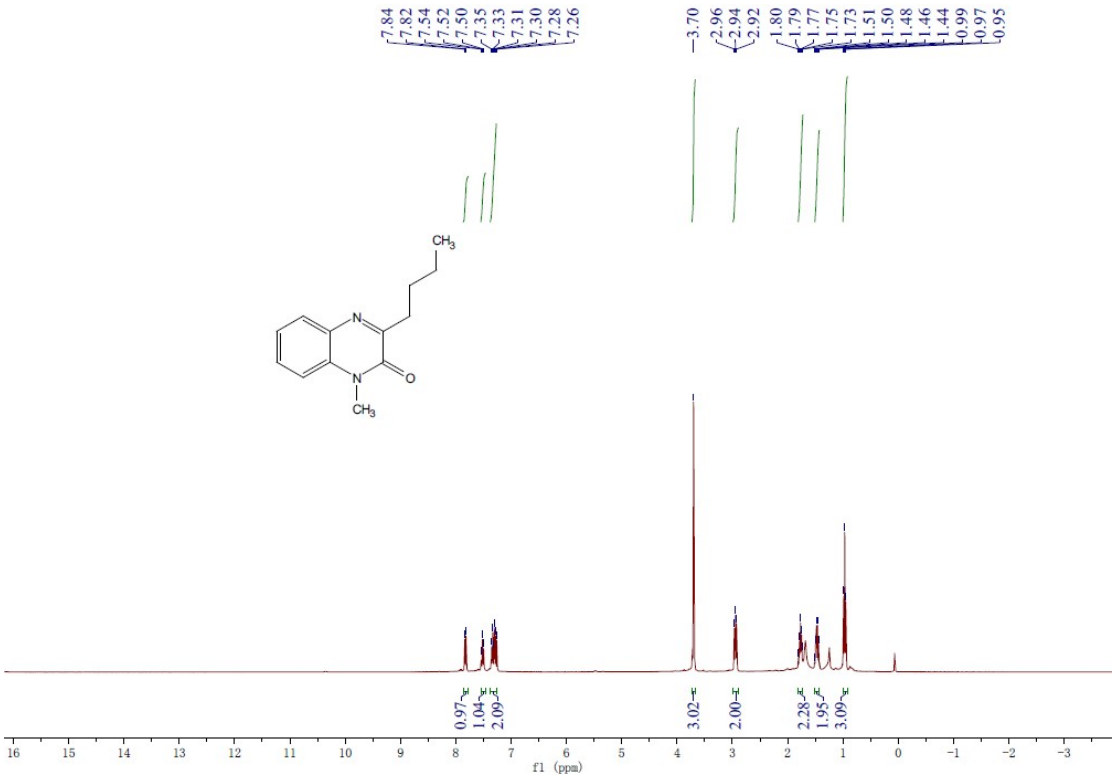
^{13}C spectra of **3ab**



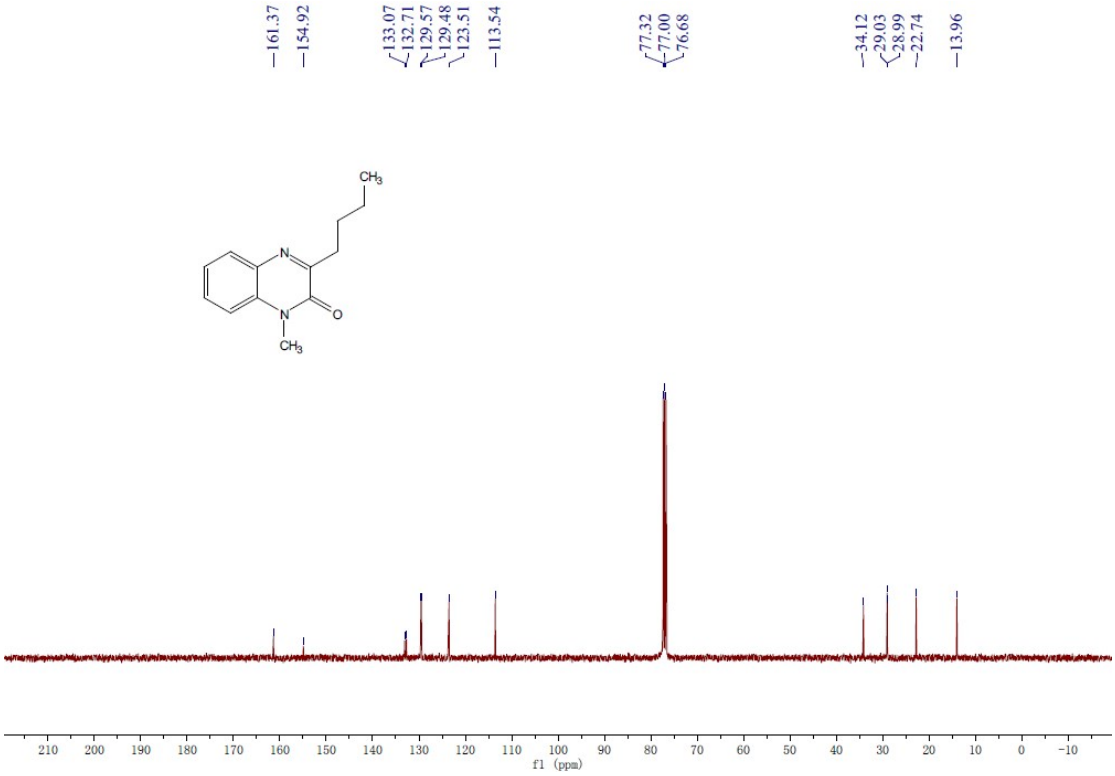
^{1}H spectra of **3ac**



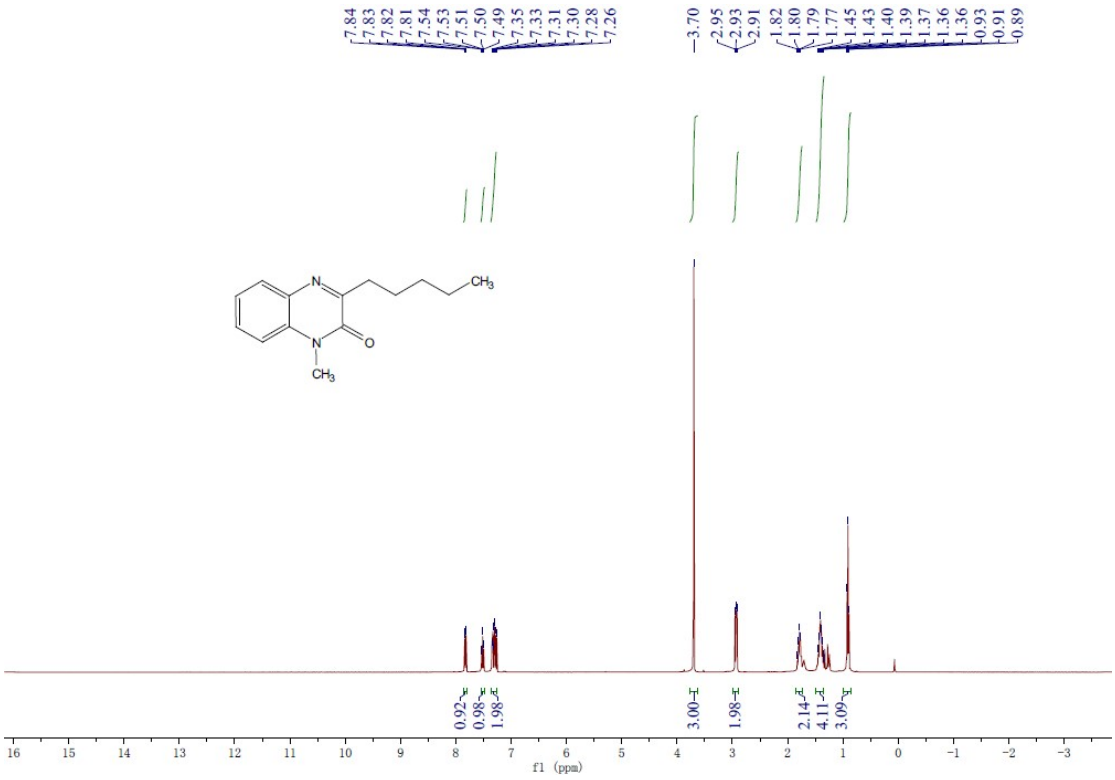
^{13}C spectra of **3ac**



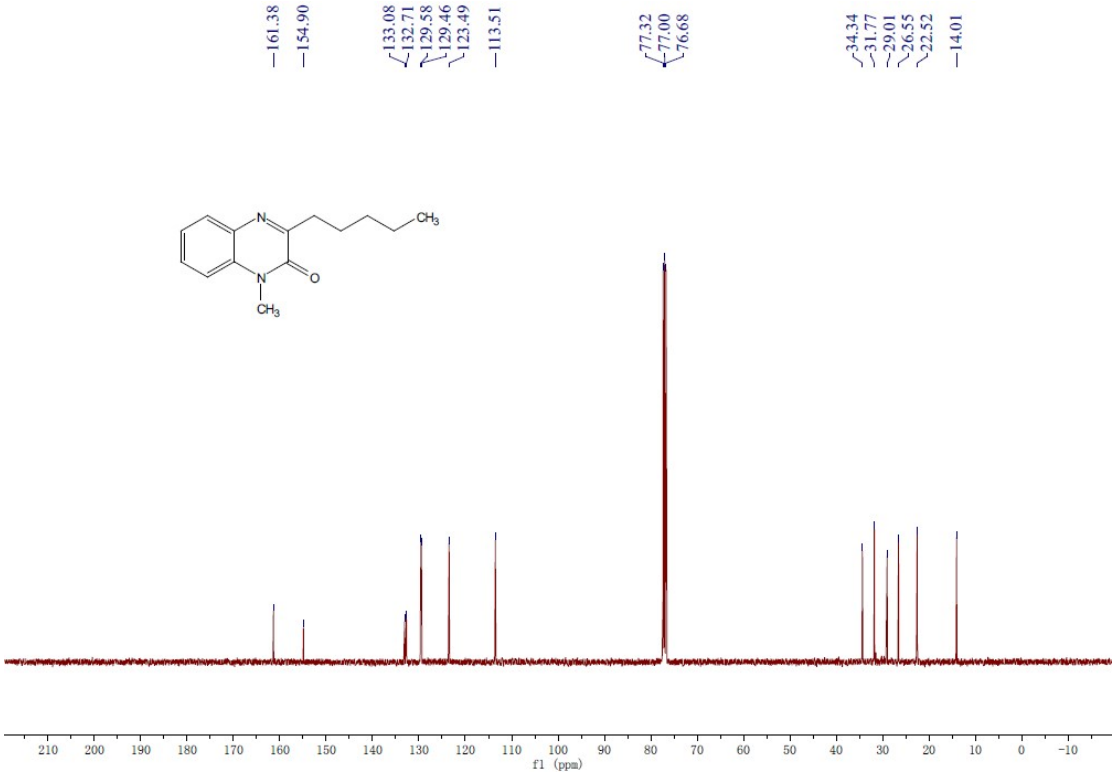
^{1}H spectra of **3ad**



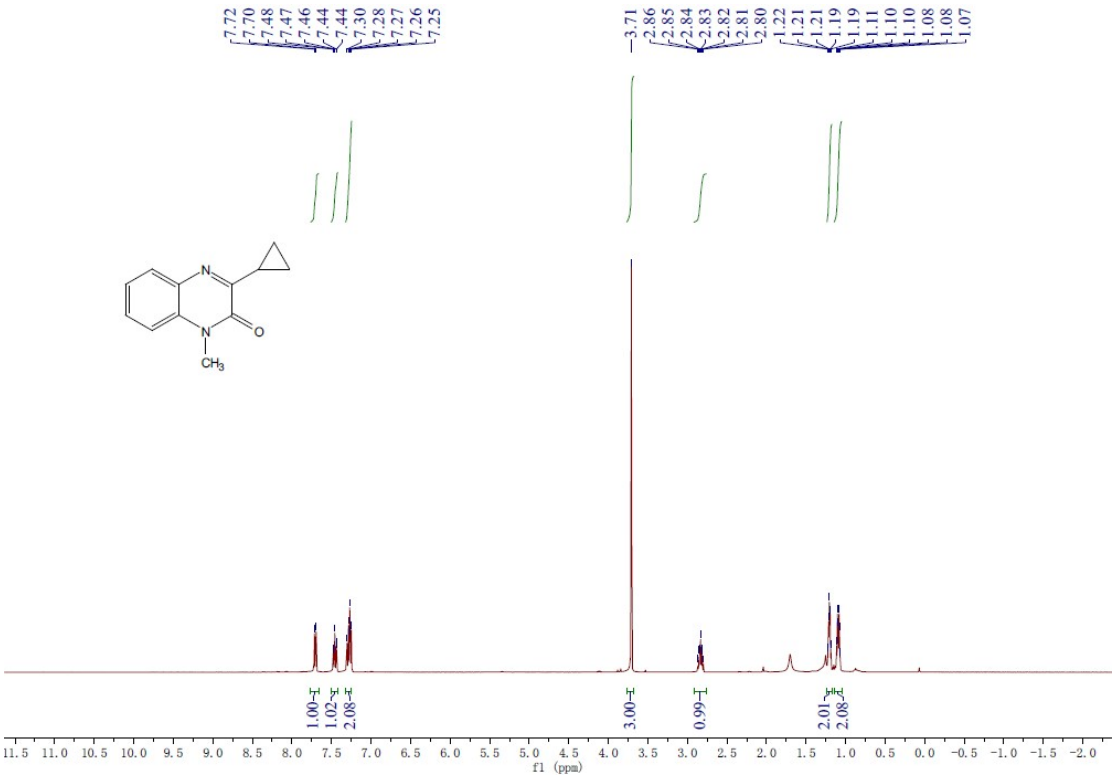
^{13}Cspectra of **3ad**



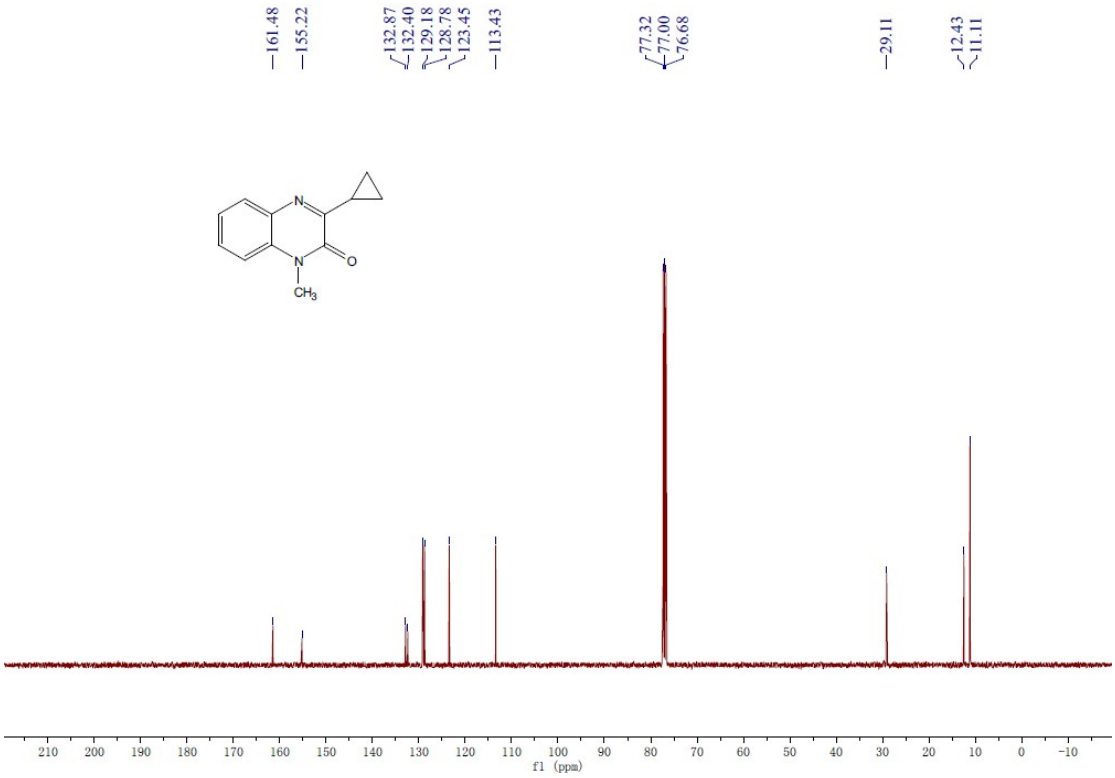
^{1}H spectra of **3ae**



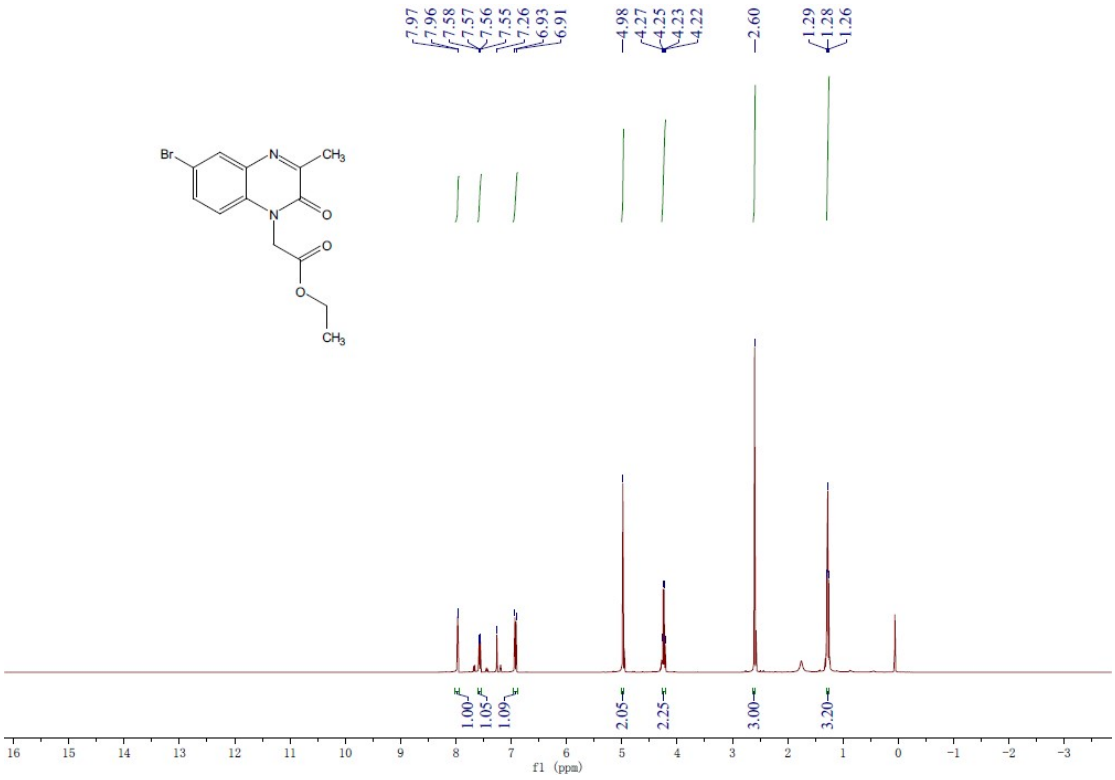
^{13}C spectra of **3ae**



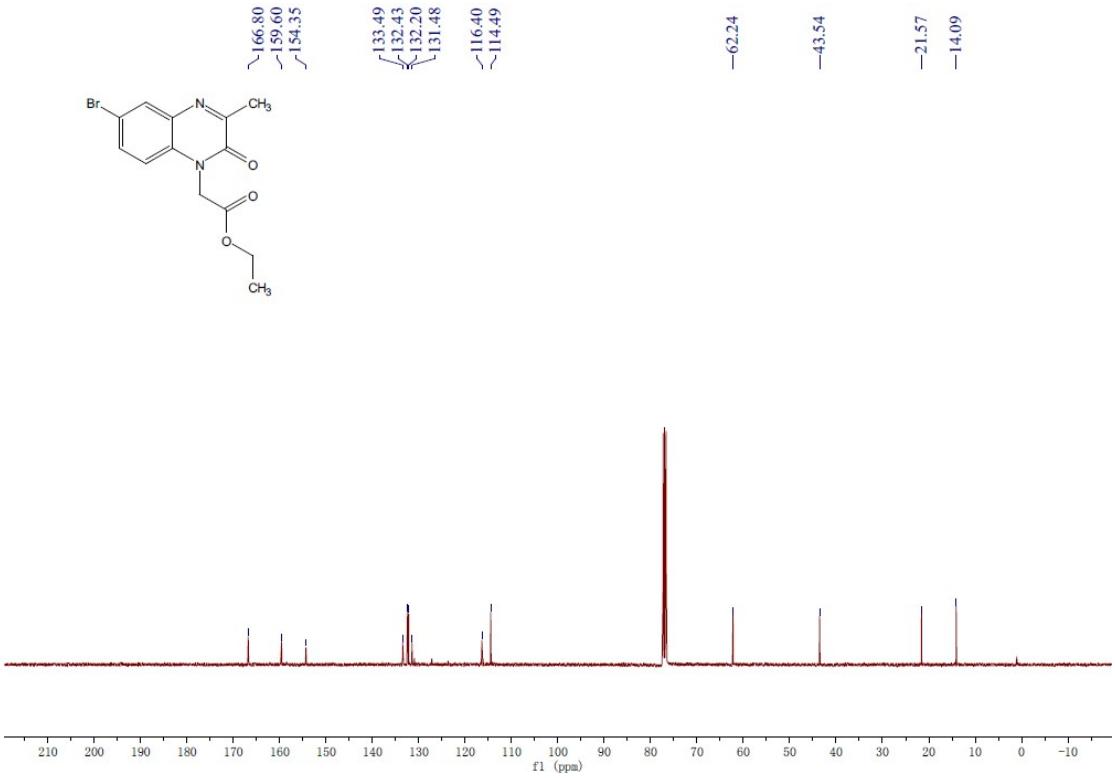
^{1}H spectra of **3af**



^{13}C spectra of **3af**



^{1}H spectra of **4ca**



^{13}C spectra of **4ca**