Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.
This journal is © The Royal Society of Chemistry 2025

Supporting Information

Photodriven, TFA-promoted Oxidative Dehydrogenative Coupling of Quinoxalin-2(*1H*)-ones with 5-Pyrazolones

Peipei Ma,[a] Junyu Wang,[a] Hongli Wu,[a] Haifeng Gan,*[a], Fei Cao[a] and Jianliang Zhu

[a] College of Biotechnology and Pharmaceutical Engineering, Nanjing Tech University, Nanjing, 211816, P. R. Of China

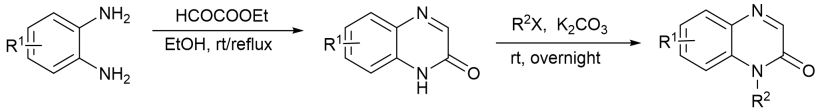
E-mail: ganhaifeng@njtech.edu.cn

Table of Contents

1. General Information

All reactions were conducted on a sealed tub. NMR spectra were recorded on a Bruker spectrometer. ^{1}H NMR spectra were obtained at 400 MHz, 500 MHz or 600 MHz in $CDCl_3$ (δ = 7.26 ppm) or DMSO-d_6 (δ = 2.50 ppm). Coupling constants are given in Hz. ^{13}C NMR spectra were recorded at 101 MHz, 126 MHz or at 151 MHz in $CDCl_3$ (δ = 77.0 ppm) or DMSO-d_6 (δ = 39.50 ppm). ^{19}F NMR spectra were obtained at 376 MHz in $CDCl_3$. Chemical shifts are given in δ ppm and are measured relative to tetramethylsilane (TMS) as internal standard. The peak patterns are indicated as follows: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; qui, quintet; sxt, sextet. High-resolution mass measurement was performed with an electrospray ionization (ESI) or electron ionization (EI) method on a Q-TOF mass spectrometer operating in positive ion mode. Melting point (mp) was measured on a microscopic melting point apparatus. Flash column chromatography was carried out using commercially available 200-300 mesh under pressure unless otherwise indicated. All other starting materials and solvents were commercially available and were used without further purification unless otherwise stated.

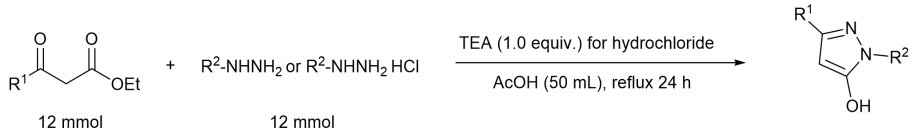
2. General procedure for the synthesis of Quinoxalinones[1] and Pyrazolone[2]



2.1 To a stirred solution of 1,2-phenylenediamines (10 mmol, 1.0 equiv.) in EtOH (40 mL) was added ethyl glyoxalate (12 mmol, 1.2 equiv.). After addition, the resultant reaction mixture was stirred at 85 °C/rt until the raw material disappears. The solid formed was filtered, washed with water/EtOH and dried in vacuo to obtain the product quinoxalin-2(*1H*)-one. For alkylation, the corresponding alkyl halide (1.6 equiv.) was added to a suspension of quinoxalinone (4.0 mmol, 1.0 equiv.) and K_2CO_3 (1.2 equiv.) in DMF (8 mL). The mixture was stirred at room temperature (monitored by TLC). After completion of reaction, saturated solution of NH_4Cl (10 mL) and water (50 mL) were added to the reaction system, extracted with EtOAc (40 mL*3), the combined organic phases were washed with brine (20 mL*2), dried with anhydrous Na_2SO_4, filtered, evaporated in vacuum and purified by silica gel column chromatography (Petroleum/EtOAc = 10:1-2:1 or CH_2Cl_2/EtOAc = 9:1-4:1) to afford the desired products **1a**-**1z**/**4a**.

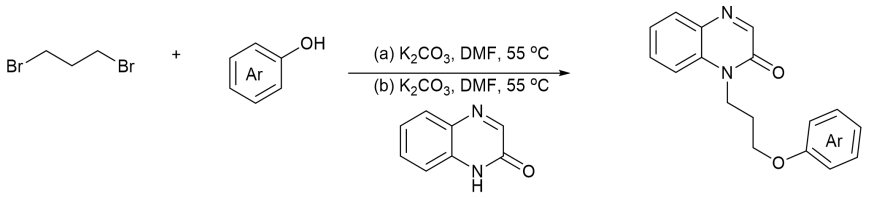
Note: When the raw material is 4-methylbenzene-1,2-diamine, the targeted products obtained are 6-methyl-substituted and 7-methyl-substituted compounds. Due to their similar polarities, they participate in subsequent reactions as a mixture.

2.2 General Procedure for the synthesis of substituted pyrazolones



To 12 mmol (1.0 equiv.) of *β*-ketoester in 50 mL of acetic acid, 12 mmol (1.0 equiv.) of substituted lhydrazine was added (1.0 equv. of TEA was added when hydrazine hydrochloride was used). The contents were refluxed for 24 h, then the mixture was cooled, and the solvent was removed in vacuo. To the precipitate in the flask (some crude were purified by flash chromatography on silica gel), ethyl acetate was added to suspend the product, and it was then filtered to obtain the pure compound. The obtained product was dried to yield substituted pyrazolone.

2.3 General Procedure for Obtaining Quinoxalin-2(1*H*) ones **4b-4e**[3]



A mixture of phenol (4.0 mmol) and K_2CO_3 (1.1 g, 8.0 mmol) in DMF (6.4 mL) was stirred at 55 °C, and then 1,3-dibromopropane (8.0 mmol) was added. After stirring overnight, water was added to the mixture and extracted with dichloromethane (DCM). The organic phase was washed with water (40 mL x 2), then washed with brine (40 mL x 2), dried over Na_2SO_4, followed by concentration and purification on silica gel column chromatography. The resulting compound (1.6 equiv.) was then dissolved in anhydrous DMF (10 mL) and quinoxalin-2(1*H*)-one (1.0 equiv.) was added and the mixture stirred for 12 h at 55 °C. After the reaction was complete, the mixture was quenched with water and extracted with CH_2Cl_2. The combined organic layers were concentrated in vacuo and the residue obtained was purified by flash chromatography on silica gel to obtain the desired product (**4b-4e**).

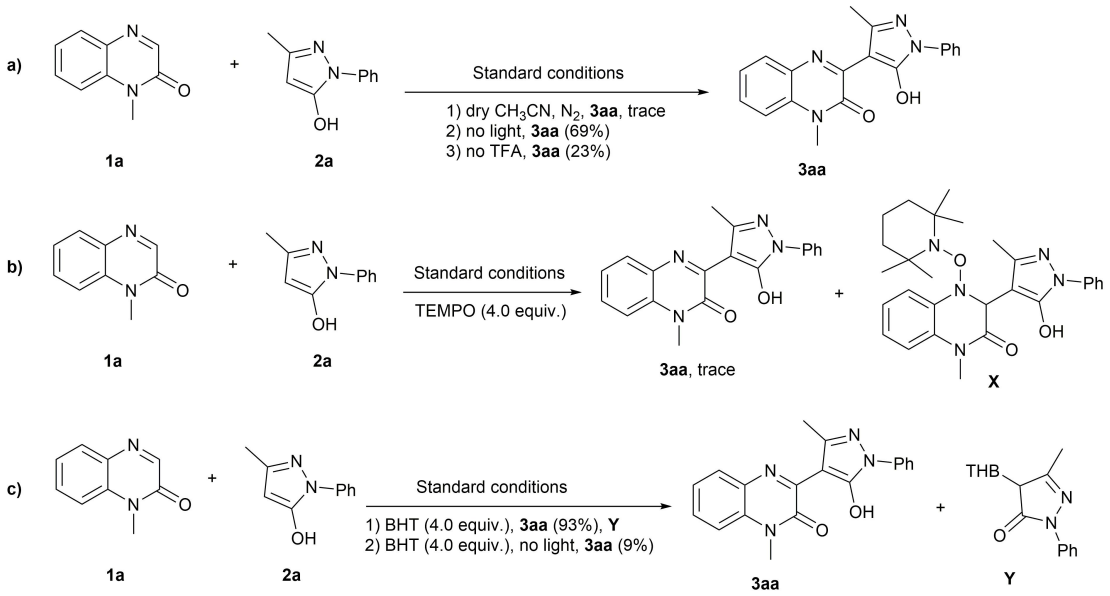
3. General procedure for the synthesis of 4-quinoxalinone-substituted pyrazoles (3/5a-5e)

A mixture of **1a-1z**/**4a-4e** (0.2 mmol), edaravone and its analogs **2a-2n** (0.24 mmol or 0.3 mmol), CH_3CN (2.0 mL) and TFA (15 μL, 0.2 mmol, 1.0 equiv.) were placed in a sealed tub (25 mL) containing a magnetic stirring bar and stirred irradiated with LED (450-455 nm) at rt for 16 h under air atmosphere. After the reaction was completed (TLC), the mixture were diluted with MeOH (5 mL) and dichloromethane (10 mL), evaporated in vacuum and purified by silica gel column chromatography using petroleum ether and EtOAc as eluent (9:1-3:1) to afford the related products **3**/**5a-5e** (51-98%).

4. The mechanistic studies

4.1 Controlled experiments

To further elucidate the reaction mechanism, several control experiments were carried out (scheme S1). Conducting the reaction in dry CH_3CN under N_2 conditions, we found that trace **3aa** could be detected which suggested that oxygen in air played a key role in the reaction (scheme 2a 1). Besides, carried out the reaction without light or TFA, **3aa** could be acquired in 69% and 23% yields, respectively (scheme 2a 2 and 3). The results indicate that both light and TFA are important in the transformations. TEMPO (4.0 equiv.) and BHT (4.0 equiv.) are added to the reaction system with **1a** (0.1 mmol) and **2a** (1.5 equiv.) under standard conditions, 3aa are provided in trace and 93% yields, respectively and adducts **X** and **Y** can be detected by MS (scheme 2b and 2c 1) (Figure S1 and S2). Besides, BHT (4.0 equiv.) are added to the reaction system under standard conditions without light, **3aa** are provided in 9% yield (scheme 2c 2). It showed that radical pathway may be involved in the reactions.



Scheme S1 Controlled experiments

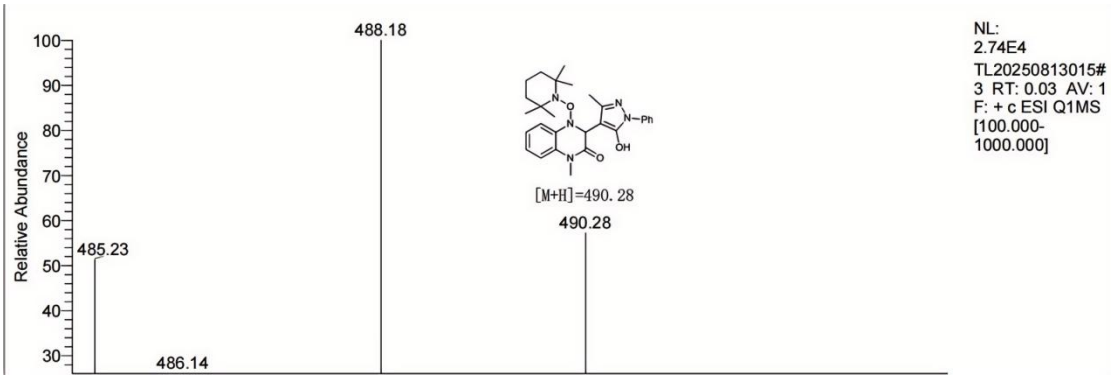


Figure S1 MS spectra of **3aa**-TEMPO adduct (Compound **X**: MS (ESI) $[M+H]^+$ = 490.28 ($C_{28}H_{36}N_5O_3$))

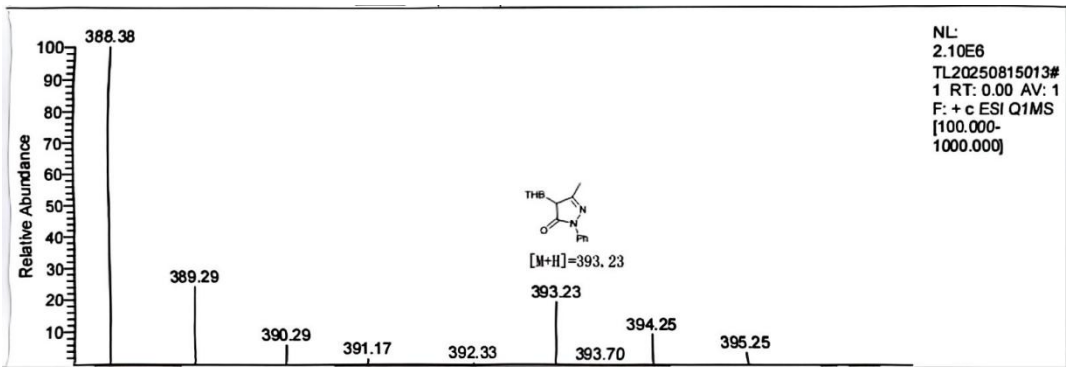
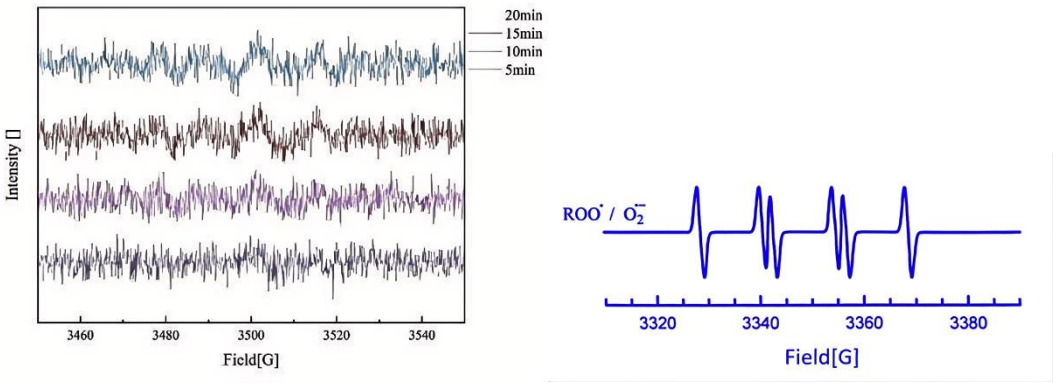


Figure S2 MS spectra of **2a**-BHT adduct (Compound **Y**: MS (ESI) $[M+H]^+$ = 393.23 ($C_{25}H_{33}N_2O_2$))

4.2 EPR Spectra



(a) (b)

Figure S3 EPR OF DMPO captured $O_2^{\cdot-}$ in 5-20 min under standard reaction conditions Simulated EPR of DMPO captured $ROO^{\cdot}/O_2^{\cdot-}$

EPR was measured under standard conditions (5 min-20 min). Superoxide anion radicals ($O_2^{\cdot-}$) can be detected in 10 min and it fades in 20 min.

4.3 *In-situ* ^{1}H NMR analyses

4.3.1 To three sample bottles charged **2a** (17.5 mg, 0.1 mmol) and chloroform-*d* (600 μL) was added CF_3COOH (none), CF_3COOH (3.8 μL, 0.05 mmol), CF_3COOH (7.5 μL, 0.1 mmol), respectively. Then, all the samples were subjected to the NMR test. The chemical shift of **2a** appeared at 7.855 ppm (d, 2H), when 0.5 equiv. and 1.0 equiv. TFA were added into **2a** solution, new peaks appeared at 5.527 ppm (s, 0.79 H) and 5.595 ppm (s, 3.28 H) respectively, indicating existence of tautomerization (Figure S4) (28% and 62% of **2a'** appeared at NMR spectra, see copies of NMR spectra at page 24-25).

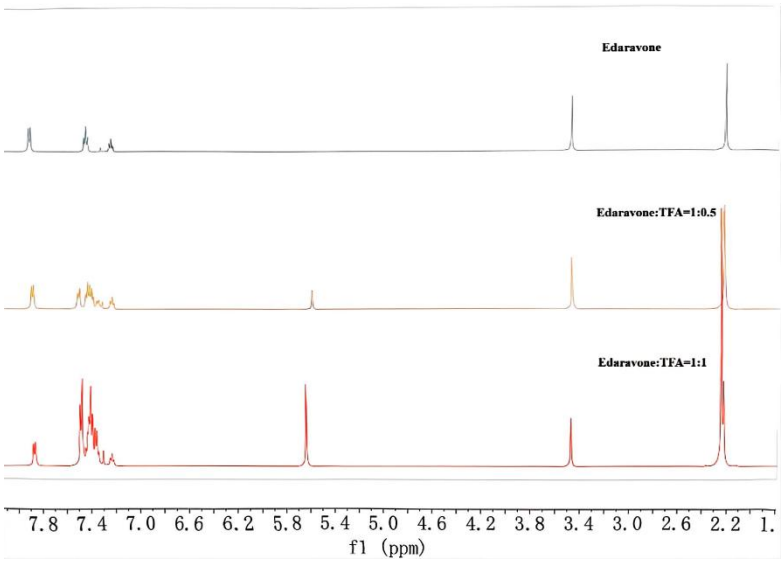


Figure S4 ^{1}H NMR spectra of **2a** and **2a** + CF_3COOH in $CDCl_3$.

4.3.2 ^{1}H NMR used tetramethylsilane as the internal standard. The units of chemical shift (δ) and coupling constant (*J*) were ppm and Hz, respectively. To three sample bottles charged **1a** (16.0 mg, 0.1 mmol) and chloroform-*d* (600 μL) was added CF_3COOH (none), CF_3COOH (3.8 μL, 0.05 mmol), CF_3COOH (7.5 μL, 0.1 mmol), respectively. Then, all the samples were subjected to the NMR test.

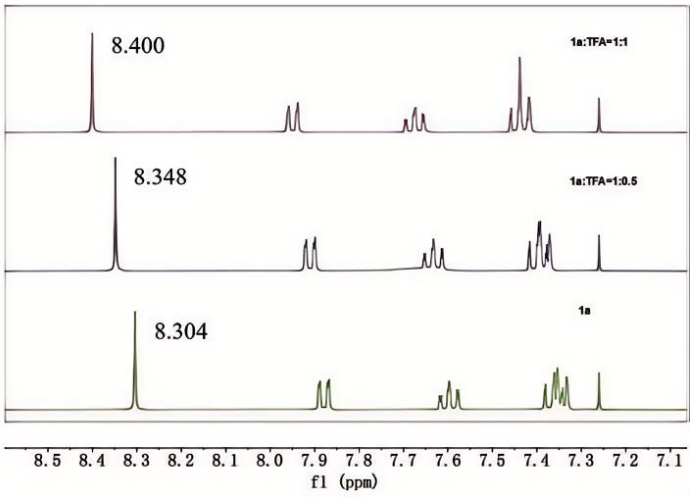


Figure S5 ^{1}H NMR spectra of **1a** and **1a** + CF_3COOH in $CDCl_3$

The chemical shift of **1a** appeared at 8.304 ppm, when 0.5 equiv. and 1 equiv. TFA were added into **1a** solution, the chemical shift changed to 8.348 ppm and 8.400 ppm respectively, indicating existence of protonation (Figure S5).

4.4 Photophysical properties: UV/Vis absorption spectra

4.4.1 The UV/Vis absorption spectra of **1a** and **1a** + CF_3COOH in acetonitrile (0.1 M) were determined in a 1 cm optical program quartz colorimetric dish. The tail absorption of **1a** with system concentration showed at 425 nm, which redshifts to 470 nm when CF_3COOH was added (Figure S6).

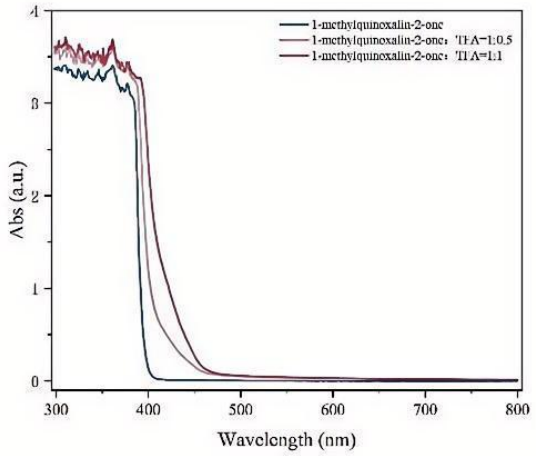


Figure S6 Absorption spectra of **1a** and **1a** + CF_3COOH in acetonitrile at the concentration of the system reaction

4.4.2 The UV/Vis absorption spectra of **2a** and **2a** + CF_3COOH in acetonitrile (0.1 M) were determined in a 1 cm optical program quartz colorimetric dish. The tail absorption of **2a** with system concentration showed at 308 nm, which enhances to 324 nm and then drops when CF_3COOH was added (Figure S7).

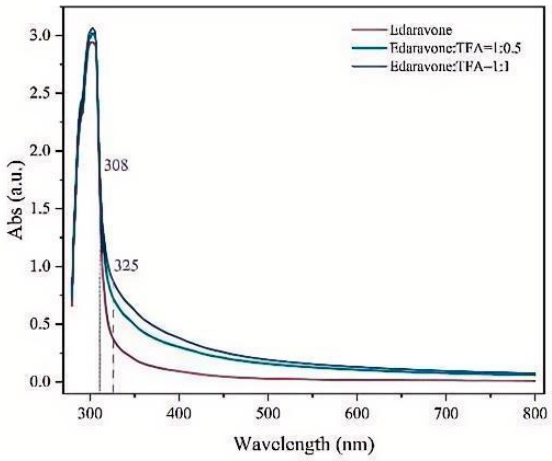
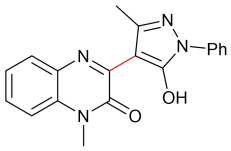


Figure S7 Absorption spectra of **2a** and **2a** + CF_3COOH in acetonitrile at the concentration of the system reaction

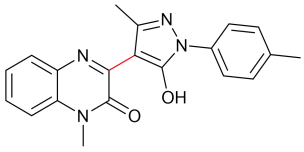
5. Characterization data of the products

3-(5-Hydroxy-3-methyl-1-phenyl-1H-pyrazol-4-yl)-1-methylquinoxalin-2(1*H*)-one (3aa)



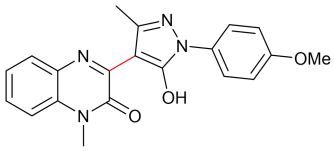
Orange solid (98%, 65 mg); Silica gel column chromatography (PE/EA = 9:2); ^{1}H NMR (500 MHz, $CDCl_3$) δ 15.08 (s, 1H), 7.89 (d, *J* = 8.0 Hz, 2H), 7.49 (d, *J* = 7.4 Hz, 1H), 7.39 (t, *J* = 7.8 Hz, 2H), 7.31 – 7.28 (m, 1H), 7.26 – 7.22 (m, 1H), 7.21 – 7.16 (m, 2H), 3.62 (s, 3H), 2.61 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 155.03, 149.33, 145.74, 138.41, 129.47, 128.66, 127.20, 125.19, 124.68, 120.25, 113.99, 98.81, 29.79, 18.97. HRMS (ESI) m/z calcd for $C_{19}H_{17}N_4O_2$ $[M+H]^+$ 333.1346, found 333.1345.

3-(5-Hydroxy-3-methyl-1-(*p*-tolyl)-1H-pyrazol-4-yl)-1-methylquinoxalin-2(1*H*)-one (3ab)



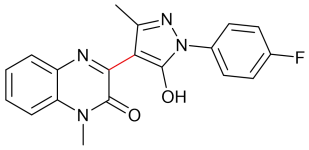
Orange solid (92%, 64 mg); Silica gel column chromatography (PE/EA = 6:1-2:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 14.98 (s, 1H), 7.76 (d, *J* = 8.2 Hz, 2H), 7.55 (d, *J* = 7.4 Hz, 1H), 7.34 (t, *J* = 7.5 Hz, 1H), 7.27 (d, *J* = 9.8 Hz, 1H), 7.21 (t, *J* = 8.2 Hz, 3H), 3.67 (s, 3H), 2.63 (s, 3H), 2.36 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 155.24, 149.28, 146.10, 141.36, 140.34, 135.97, 135.06, 129.57, 129.25, 127.28, 124.73, 120.55, 114.00, 98.88, 29.85, 20.95, 18.85. HRMS (ESI) m/z calcd for $C_{20}H_{19}N_4O_2$ $[M+H]^+$ 347.1503, found 347.1505.

3-(5-Hydroxy-1-(4-methoxyphenyl)-3-methyl-1H-pyrazol-4-yl)-1-methylquinoxalin-2(1*H*)-one (3ac)



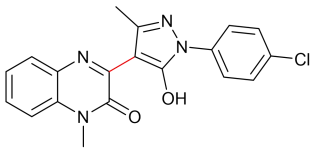
Orange solid (81%, 59 mg); Silica gel column chromatography (PE/EA = 4:1-2:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 14.88 (s, 1H), 7.76 (d, *J* = 8.9 Hz, 2H), 7.54 (d, *J* = 7.7 Hz, 1H), 7.34 (t, *J* = 7.6 Hz, 1H), 7.27 (t, *J* = 7.5 Hz, 1H), 7.21 (d, *J* = 8.2 Hz, 1H), 6.93 (d, *J* = 9.0 Hz, 2H), 3.82 (s, 3H), 3.66 (s, 3H), 2.62 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 157.32, 155.22, 149.19, 146.25, 131.72, 129.53, 127.31, 124.70, 122.29, 113.97, 113.87, 98.71, 55.41, 29.82, 18.74. HRMS (ESI) m/z calcd for $C_{20}H_{19}N_4O_3$ $[M+H]^+$ 363.1413, found 363.1415.

3-(1-(4-Fluorophenyl)-5-hydroxy-3-methyl-1H-pyrazol-4-yl)-1-methylquinoxalin-2(1*H*)-one (3ad)



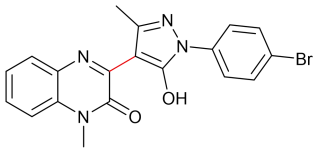
Orange solid (89%, 62 mg); Silica gel column chromatography (PE/EA = 5:1-3:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 15.06 (s, 1H), 7.86 (dd, *J* = 7.8, 5.9 Hz, 2H), 7.51 (d, *J* = 7.4 Hz, 1H), 7.34 (t, *J* = 7.5 Hz, 1H), 7.27 (t, *J* = 7.4 Hz, 1H), 7.21 (d, *J* = 8.2 Hz, 1H), 7.07 (t, *J* = 8.6 Hz, 2H), 3.66 (s, 3H), 2.61 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 161.08, 159.14, 155.02, 149.40, 145.71, 134.58, 129.50, 127.28, 124.75, 122.65 (d, *J* = 8.1 Hz), 121.90 (d, *J* = 4.7 Hz), 115.34 (d, *J* = 22.6 Hz), 114.03, 98.70, 29.85, 18.96; ^{19}F NMR (376 MHz, $CDCl_3$) δ -115.07, -117.01. HRMS (ESI) m/z calcd for $C_{19}H_{16}FN_4O_2$ $[M+H]^+$ 350.1250, found 350.1252.

3-(1-(4-Chlorophenyl)-5-hydroxy-3-methyl-1H-pyrazol-4-yl)-1-methylquinoxalin-2(1*H*)-one (3ae)



Orange solid (85%, 62 mg); Silica gel column chromatography (PE/EA = 6:1-2:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 15.08 (s, 1H), 7.84 (d, *J* = 8.8 Hz, 2H), 7.46 (d, *J* = 7.0 Hz, 1H), 7.35 – 7.22 (m, 4H), 7.17 (d, *J* = 8.2 Hz, 1H), 3.61 (s, 3H), 2.59 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 154.81, 149.47, 145.15, 137.05, 130.00, 129.45, 128.59, 127.13, 124.71, 120.77, 114.05, 98.70, 29.83, 19.17. HRMS (ESI) m/z calcd for $C_{19}H_{16}ClN_4O_2$ $[M+H]^+$ 367.0943, found 367.0945.

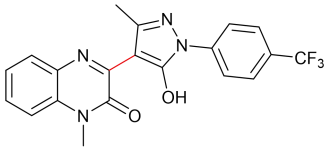
3-(1-(4-Bromophenyl)-5-hydroxy-3-methyl-1H-pyrazol-4-yl)-1-methylquinoxalin-2(1*H*)-one (3af)



Orange solid (83%, 68 mg); Silica gel column chromatography (PE/EA = 6:1-2:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 15.15 (s, 1H), 7.85 (d, *J* = 8.7 Hz, 2H), 7.53 (t, *J* = 8.3 Hz, 1H), 7.47 (d, *J* = 8.7 Hz, 2H), 7.38 (t, *J* = 7.6 Hz, 1H), 7.31 (t, *J* = 7.5 Hz, 1H), 7.28 – 7.25 (m, 1H), 3.70 (s, 3H), 2.65 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 155.05, 149.68, 148.81, 137.59, 131.87, 131.68, 129.58, 127.29, 124.84, 122.18,

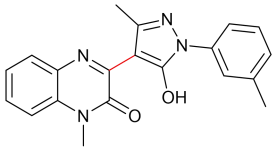
121.38, 118.06, 114.16, 98.91, 29.95, 19.17. HRMS (ESI) m/z calcd for $C_{19}H_{16}BrN_4O_2$ $[M+H]^+$ 411.0457, found 411.0445.

3-(5-Hydroxy-3-methyl-1-(4-(trifluoromethyl)phenyl)-1H-pyrazol-4-yl)-1-methylquinoxalin-2(1*H*)-one (3ag)



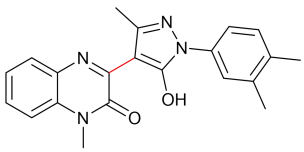
Orange solid (73%, 59 mg); Silica gel column chromatography (PE/EA = 6:1-2:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 15.25 (s, 1H), 8.12 (d, *J* = 8.0 Hz, 2H), 7.62 (d, *J* = 8.2 Hz, 2H), 7.53 (d, *J* = 3.0 Hz, 1H), 7.37 (t, *J* = 7.2 Hz, 1H), 7.32-7.24 (m, 2H), 3.69 (s, 3H), 2.67 (s, 3H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.07. HRMS (ESI) m/z calcd for $C_{20}H_{16}F_3N_4O_2$ $[M+H]^+$ 401.1220, found 401.1227.

3-(5-Hydroxy-3-methyl-1-(*m*-tolyl)-1H-pyrazol-4-yl)-1-methylquinoxalin-2(1*H*)-one (3ah)



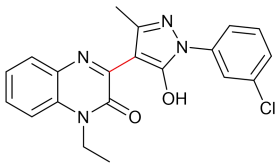
Orange solid (93%, 64 mg); Silica gel column chromatography (PE/EA = 6:1-2:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 15.06 (s, 1H), 7.72 (d, *J* = 6.6 Hz, 2H), 7.53 (d, *J* = 7.6 Hz, 1H), 7.36 – 7.26 (m, 3H), 7.21 (d, *J* = 8.2 Hz, 1H), 7.03 (d, *J* = 7.4 Hz, 1H), 3.66 (s, 3H), 2.64 (s, 3H), 2.41 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 155.09, 149.29, 145.88, 138.59, 138.27, 129.49, 128.49, 127.21, 126.13, 124.69, 120.97, 117.55, 114.00, 98.83, 29.81, 21.53, 18.93. HRMS (ESI) m/z calcd for $C_{20}H_{19}N_4O_2$ $[M+H]^+$ 347.1503, found 347.1507.

3-(1-(3,4-Dimethylphenyl)-5-hydroxy-3-methyl-1H-pyrazol-4-yl)-1-methylquinoxalin-2(1*H*)-one (3ai)



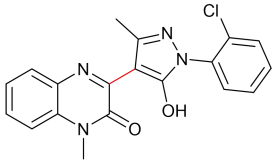
Orange solid (92%, 66 mg); Silica gel column chromatography (PE/EA = 7:1-2:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 14.98 (s, 1H), 7.63 (s, 1H), 7.60 (d, *J* = 8.1 Hz, 1H), 7.52 (d, *J* = 7.6 Hz, 1H), 7.32 (t, *J* = 7.6 Hz, 1H), 7.26 (t, *J* = 7.5 Hz, 1H), 7.19 (d, *J* = 8.2 Hz, 1H), 7.14 (d, *J* = 8.1 Hz, 1H), 3.64 (s, 3H), 2.62 (s, 3H), 2.30 (s, 3H), 2.26 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 155.17, 149.17, 146.08, 136.94, 136.15, 133.77, 129.69, 129.51, 127.22, 124.65, 121.73, 118.07, 113.94, 98.82, 29.78, 19.89, 19.23, 18.81. HRMS (ESI) m/z calcd for $C_{21}H_{21}N_4O_2$ $[M+H]^+$ 361.1659, found 361.1655.

3-(1-(3-Chlorophenyl)-5-hydroxy-3-methyl-1H-pyrazol-4-yl)-1-ethylquinoxalin-2(1*H*)-one (CAS: 3061317-16-3) (3bj)[4]



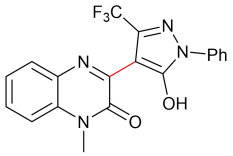
Orange solid (88%, 67 mg); Silica gel column chromatography (PE/EA = 5:1-2:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 15.23 (s, 1H), 7.96 (s, 1H), 7.87 (d, *J* = 8.2 Hz, 1H), 7.49 (d, *J* = 5.4 Hz, 1H), 7.32 (t, *J* = 7.6 Hz, 1H), 7.28-7.21 (m, 3H), 7.11 (d, *J* = 7.9 Hz, 1H), 4.26 (q, *J* = 7.1 Hz, 2H), 2.63 (s, 3H), 1.39 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 154.34, 149.59, 145.39, 143.04, 139.51, 134.30, 129.60, 128.31, 127.21, 124.69, 124.54, 119.54, 117.44, 113.87, 109.97, 102.58, 98.67, 38.26, 19.17, 12.19. HRMS (ESI) m/z calcd for $C_{20}H_{18}ClN_4O_2$ $[M+H]^+$ 381.1113, found 381.1115.

3-(1-(2-Chlorophenyl)-5-hydroxy-3-methyl-1H-pyrazol-4-yl)-1-methylquinoxalin-2(1*H*)-one (3ak)



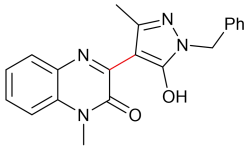
Orange solid (96%, 70 mg); Silica gel column chromatography (PE/EA = 4:1-3:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 14.74 (s, 1H), 7.59 – 7.48 (m, 3H), 7.41 – 7.34 (m, 3H), 7.31-7.26 (m, 2H), 3.70 (s, 3H), 2.67 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 160.45, 155.31, 150.08, 146.71, 135.24, 132.14, 130.20, 129.77, 129.55, 129.46, 127.57, 127.33, 124.78, 113.99, 97.78, 29.85, 18.64. HRMS (ESI) m/z calcd for $C_{19}H_{16}ClN_4O_2$ $[M+H]^+$ 367.0943, found 367.0940.

3-(5-Hydroxy-1-phenyl-3-(trifluoromethyl)-1H-pyrazol-4-yl)-1-methylquinoxalin-2(1*H*)-one (3al)



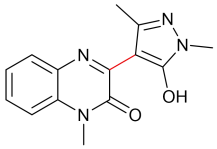
Yellow solid (97%, 75 mg); Silica gel column chromatography (PE/EA = 7:1-3:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 14.43 (s, 1H), 7.90 – 7.80 (m, 3H), 7.53 (t, *J* = 7.7 Hz, 1H), 7.49-7.42 (m, 3H), 7.38-7.34 (m, 2H), 3.81 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 161.55, 160.76, 155.57 (d, *J* = 41.8 Hz), 145.95, 140.56 (q, *J* = 3.7 Hz), 137.67, 133.35, 130.38, 129.84, 129.24, 128.97, 127.37, 125.44, 122.45, 120.12, 113.99, 99.21, 30.15; ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.35. HRMS (ESI) m/z calcd for $C_{19}H_{14}F_3N_4O_2$ $[M+H]^+$ 386.1020, found 386.1025.

3-(1-Benzyl-5-hydroxy-3-methyl-1H-pyrazol-4-yl)-1-methylquinoxalin-2(1*H*)-one (3am)



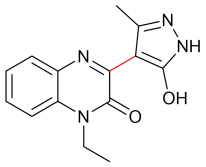
Yellow solid (68%, 47 mg); Silica gel column chromatography (PE/EA = 4:1-3:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 14.30 (s, 1H), 7.61 (d, *J* = 7.9 Hz, 1H), 7.38 – 7.21 (m, 8H), 5.09 (s, 2H), 3.67 (s, 3H), 2.57 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 157.67, 155.63, 149.04, 147.68, 141.84, 136.96, 131.58, 129.62, 128.49, 127.65, 127.42, 126.06, 124.73, 113.83, 97.98, 49.61, 29.76, 18.16. HRMS (ESI) m/z calcd for $C_{20}H_{19}N_4O_2$ $[M+H]^+$ 347.1503, found 347.1508.

3-(5-Hydroxy-1,3-dimethyl-1H-pyrazol-4-yl)-1-methylquinoxalin-2(1*H*)-one (CAS: 3061317-32-3) (3an)[4]



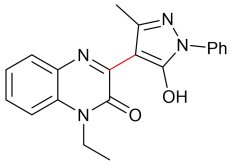
Yellow solid (88%, 48 mg); Silica gel column chromatography (PE/EA = 4:1-2:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 14.07 (s, 1H), 7.58 (d, *J* = 7.8 Hz, 1H), 7.35 (t, *J* = 7.3 Hz, 1H), 7.28 (t, *J* = 7.3 Hz, 1H), 7.22 (d, *J* = 8.3 Hz, 1H), 3.66 (s, 3H), 3.51 (s, 3H), 2.50 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 157.09, 155.57, 148.63, 147.78, 131.89, 129.58, 127.59, 126.38, 124.63, 113.72, 97.69, 32.61, 29.71, 17.92. HRMS (ESI) m/z calcd for $C_{14}H_{15}N_4O_2$ $[M+H]^+$ 271.1190, found 271.1191.

1-Ethyl-3-(5-hydroxy-3-methyl-1H-pyrazol-4-yl)quinoxalin-2(1*H*)-one (CAS: 3061317-19-6) (3bo)[4]



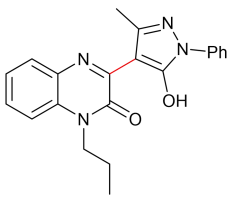
Yellow solid (72%, 39 mg); Silica gel column chromatography (PE/EA = 3:2); ^{1}H NMR (500 MHz, DMSO) δ 7.72 (d, *J* = 8.0 Hz, 1H), 7.64 (d, *J* = 8.4 Hz, 1H), 7.54 (t, *J* = 7.8 Hz, 1H), 7.39 (t, *J* = 7.6 Hz, 1H), 4.34 (q, *J* = 7.0 Hz, 2H), 2.51 (d, *J* = 8.3 Hz, 3H), 1.28 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 159.35, 154.85, 149.90, 144.47, 133.41, 129.12, 128.90, 128.32, 124.44, 114.66, 99.61, 37.92, 14.98, 12.17. HRMS (ESI) m/z calcd for $C_{14}H_{15}N_4O_2$ $[M+H]^+$ 271.1190, found 271.1189.

1-Ethyl-3-(5-hydroxy-3-methyl-1-phenyl-1H-pyrazol-4-yl)quinoxalin-2(1*H*)-one (CAS: 3061317-11-8) (3ba)[4]



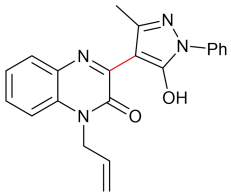
Orange solid (93%, 64 mg); Silica gel column chromatography (PE/EA = 7:1-4:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 15.12 (s, 1H), 7.91 (d, *J* = 7.9 Hz, 2H), 7.56 (d, *J* = 7.4 Hz, 1H), 7.40 (t, *J* = 7.9 Hz, 2H), 7.34 (t, *J* = 7.7 Hz, 1H), 7.28-7.24 (m, 2H), 7.20 (t, *J* = 7.4 Hz, 1H), 4.29 (q, *J* = 7.1 Hz, 2H), 2.66 (s, 3H), 1.38 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 161.11, 154.68, 149.45, 146.19, 138.43, 128.66, 128.40, 127.33, 125.25, 124.57, 120.42, 113.84, 98.86, 38.22, 18.86, 12.20. HRMS (ESI) m/z calcd for $C_{20}H_{19}N_4O_2$ $[M+H]^+$ 347.1503, found 347.1505.

3-(5-Hydroxy-3-methyl-1-phenyl-1H-pyrazol-4-yl)-1-propylquinoxalin-2(1*H*)-one (3ca)



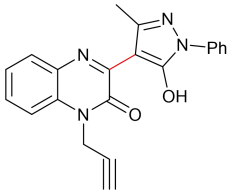
Orange solid (96%, 69 mg); Silica gel column chromatography (PE/EA = 6:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 15.12 (s, 1H), 7.92 (d, *J* = 7.8 Hz, 2H), 7.59 (d, *J* = 7.0 Hz, 1H), 7.42 (t, *J* = 8.0 Hz, 2H), 7.37 (t, *J* = 7.8 Hz, 1H), 7.33 – 7.25 (m, 2H), 7.22 (t, *J* = 7.4 Hz, 1H), 4.28 – 4.15 (m, 2H), 2.68 (s, 3H), 1.89 – 1.75 (m, 2H), 1.07 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 155.04, 149.55, 146.50, 138.46, 128.78, 128.72, 127.35, 125.38, 124.62, 120.61, 114.09, 98.99, 44.65, 20.46, 18.87, 11.27. HRMS (ESI) m/z calcd for $C_{21}H_{21}N_4O_2$ $[M+H]^+$ 361.1659, found 361.1654.

1-Allyl-3-(5-hydroxy-3-methyl-1-phenyl-1H-pyrazol-4-yl)quinoxalin-2(1*H*)-one (3da)



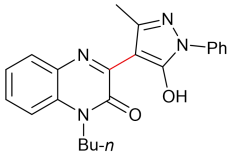
Orange solid (97%, 70 mg); Silica gel column chromatography (PE/EA = 6:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 15.08 (s, 1H), 7.93 (d, *J* = 7.9 Hz, 2H), 7.61 (d, *J* = 6.3 Hz, 1H), 7.44-7.41 (m, 2H), 7.36 (t, *J* = 7.3 Hz, 1H), 7.31 (t, *J* = 7.2 Hz, 1H), 7.27 (d, *J* = 7.6 Hz, 1H), 7.22 (t, *J* = 7.4 Hz, 1H), 6.00-5.92 (m, 1H), 5.32 (d, *J* = 10.4 Hz, 1H), 5.23 (d, *J* = 17.3 Hz, 1H), 4.93 (d, *J* = 5.0 Hz, 2H), 2.69 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 154.99, 149.52, 146.20, 138.43, 130.08, 128.85, 128.77, 127.27, 125.45, 124.82, 120.63, 118.50, 114.67, 99.11, 45.32, 18.94. HRMS (ESI) m/z calcd for $C_{21}H_{19}N_4O_2$ $[M+H]^+$ 359.1508, found 359.1511.

3-(5-Hydroxy-3-methyl-1-phenyl-1H-pyrazol-4-yl)-1-(prop-2-yn-1-yl)quinoxalin-2(1*H*)-one (3ea)



Orange solid (88%, 63 mg); Silica gel column chromatography (PE/EA = 6:1-3:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 15.01 (s, 1H), 7.93 (d, *J* = 7.8 Hz, 2H), 7.57 (d, *J* = 7.4 Hz, 1H), 7.42 (t, *J* = 8.0 Hz, 4H), 7.33 (t, *J* = 7.3 Hz, 1H), 7.22 (t, *J* = 7.4 Hz, 1H), 5.05 (d, *J* = 2.3 Hz, 2H), 2.69 (s, 3H), 2.34 (t, *J* = 2.5 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 154.46, 149.25, 145.24, 138.36, 128.79, 128.09, 127.13, 125.41, 125.13, 120.40, 114.63, 99.18, 73.67, 32.35, 29.67, 19.14. HRMS (ESI) m/z calcd for $C_{21}H_{17}N_4O_2$ $[M+H]^+$ 357.1346, found 357.1344.

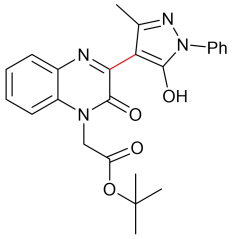
1-Butyl-3-(5-hydroxy-3-methyl-1-phenyl-1H-pyrazol-4-yl)quinoxalin-2(1*H*)-one (3fa)



Orange solid (91%, 68 mg); Silica gel column chromatography (PE/EA = 6:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 14.94 (s, 1H), 7.92 (d, *J* = 8.0 Hz, 2H), 7.61 (d, *J* = 6.5 Hz, 1H), 7.46 – 7.35 (m, 3H), 7.33 – 7.26 (m, 2H), 7.22 (t, *J* = 7.4 Hz, 1H), 4.26 (t, *J* = 7.0 Hz, 2H), 2.68 (s, 3H), 1.83 – 1.70 (m, 2H), 1.57 – 1.44 (m, 2H), 1.02 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 155.02, 149.64, 146.49, 138.39,

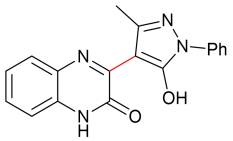
133.77, 128.80, 128.73, 127.43, 125.46, 124.63, 120.71, 116.67, 114.07, 99.00, 43.02, 29.11, 20.19, 18.78, 13.70. HRMS (ESI) m/z calcd for $C_{22}H_{23}N_4O_2$ $[M+H]^+$ 375.1743, found 375.1751.

tert-Butyl 2-(3-(5-hydroxy-3-methyl-1-phenyl-1H-pyrazol-4-yl)-2-oxoquinoxalin-1(2*H*)-yl)acetate (3ga)



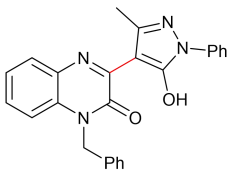
Orange solid (85%, 58 mg); Silica gel column chromatography (PE/EA = 7:1-4:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 14.98 (s, 1H), 7.93 (d, *J* = 7.8 Hz, 2H), 7.57 (d, *J* = 7.4 Hz, 1H), 7.42 (t, *J* = 8.0 Hz, 2H), 7.35-7.28 (m, 2H), 7.22 (t, *J* = 7.4 Hz, 1H), 7.04 (d, *J* = 8.0 Hz, 1H), 4.92 (s, 2H), 2.67 (s, 3H), 1.48 (s, 9H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 165.61, 155.04, 149.26, 145.33, 138.35, 128.86, 128.76, 127.14, 125.38, 124.93, 120.45, 118.81, 113.59, 99.11, 83.49, 44.87, 27.96, 19.04. HRMS (ESI) m/z calcd for $C_{24}H_{25}N_4O_4$ $[M+H]^+$ 433.1850, found 433.1855.

3-(5-Hydroxy-3-methyl-1-phenyl-1H-pyrazol-4-yl)quinoxalin-2(1*H*)-one (3ha)



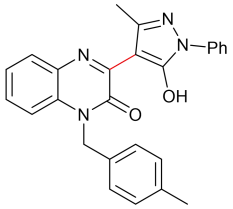
Orange solid (95%, 61 mg); The reaction mixture was filtered, washed with EtOAc and dried under vacuum; ^{1}H NMR (500 MHz, DMSO) δ 15.40 (s, 1H), 12.97 (s, 1H), 7.88 (d, *J* = 7.7 Hz, 2H), 7.65 (d, *J* = 7.8 Hz, 1H), 7.45 (t, *J* = 7.9 Hz, 2H), 7.41 (t, *J* = 7.6 Hz, 1H), 7.36 – 7.29 (m, 2H), 7.24 (t, *J* = 7.4 Hz, 1H), 2.56 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 159.59, 155.76, 148.64, 147.64, 138.24, 128.82, 128.21, 127.63, 125.22, 124.53, 123.19, 119.87, 115.61, 98.27, 18.51. HRMS (ESI) m/z calcd for $C_{18}H_{15}N_4O_2$ $[M+H]^+$ 319.1190, found 319.1197.

1-Benzyl-3-(5-hydroxy-3-methyl-1-phenyl-1H-pyrazol-4-yl)quinoxalin-2(1*H*)-one (3ia)



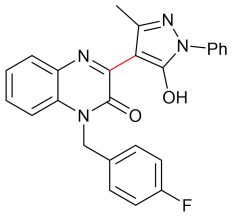
Orange solid (94%, 77 mg); Silica gel column chromatography (PE/EA = 7:1-4:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 15.05 (s, 1H), 7.95 (d, *J* = 7.9 Hz, 2H), 7.58 (s, 1H), 7.43 (t, *J* = 8.0 Hz, 2H), 7.34 (t, *J* = 7.3 Hz, 2H), 7.30-7.20 (m, 7H), 5.51 (s, 2H), 2.70 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 155.46, 149.52, 146.04, 138.42, 134.55, 129.01, 128.94, 128.75, 127.86, 127.28, 126.67, 125.40, 124.82, 120.54, 114.91, 99.18, 46.64, 18.99. HRMS (ESI) m/z calcd for $C_{18}H_{15}N_4O_2$ $[M+H]^+$ 319.1190, found 319.1197.

3-(5-Hydroxy-3-methyl-1-phenyl-1H-pyrazol-4-yl)-1-(4-methylbenzyl)quinoxalin-2(1*H*)-one (3ja)



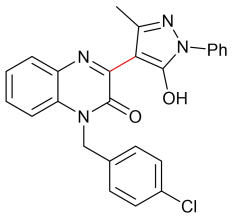
Orange solid (97%, 82 mg); Silica gel column chromatography (PE/EA = 7:1-3:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 15.01 (s, 1H), 7.94 (d, *J* = 7.9 Hz, 2H), 7.59 (s, 1H), 7.43 (t, *J* = 8.0 Hz, 2H), 7.30 – 7.22 (m, 4H), 7.18 – 7.12 (m, 4H), 5.47 (s, 2H), 2.71 (s, 3H), 2.31 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 155.46, 149.57, 146.25, 138.41, 137.65, 136.44, 131.52, 130.38, 129.66, 128.99, 128.75, 127.30, 126.70, 125.43, 124.78, 120.62, 114.95, 99.18, 46.44, 21.03, 18.95. HRMS (ESI) m/z calcd for $C_{26}H_{23}N_4O_2$ $[M+H]^+$ 422.1743, found 422.1751.

1-(4-Fluorobenzyl)-3-(5-hydroxy-3-methyl-1-phenyl-1H-pyrazol-4-yl)quinoxalin-2(1*H*)-one (3ka)



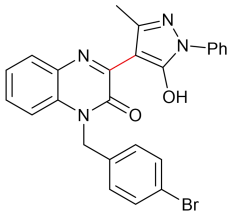
Orange solid (87%, 74 mg); Silica gel column chromatography (PE/EA = 6:1-3:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 15.01 (s, 1H), 7.93 (d, *J* = 7.9 Hz, 2H), 7.59 (s, 1H), 7.43 (t, *J* = 7.9 Hz, 2H), 7.31 – 7.20 (m, 6H), 7.03 (t, *J* = 8.6 Hz, 2H), 5.46 (s, 2H), 2.69 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 163.28, 161.31, 155.45, 149.50, 138.38, 130.34 (d, *J* = 3.2 Hz), 128.78, 128.62 (d, *J* = 8.2 Hz), 127.31, 125.47, 124.96, 120.56, 116.00 (d, *J* = 9.2 Hz), 114.70, 99.21, 46.00, 19.00; ^{19}F NMR (376 MHz, $CDCl_3$) δ -113.84. HRMS (ESI) m/z calcd for $C_{25}H_{20}FN_4O_2$ $[M+H]^+$ 426.1550, found 426.1554.

1-(4-Chlorobenzyl)-3-(5-hydroxy-3-methyl-1-phenyl-1H-pyrazol-4-yl)quinoxalin-2(1*H*)-one (3la)



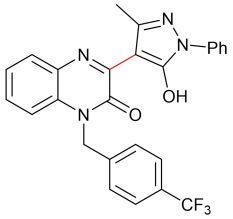
Orange solid (81%, 72 mg); Silica gel column chromatography (PE/EA = 6:1-3:1);^{1}H NMR (500 MHz, $CDCl_3$) δ 14.94 (s, 1H), 7.93 (d, *J* = 8.0 Hz, 2H), 7.58 (s, 1H), 7.42 (t, *J* = 7.9 Hz, 2H), 7.33 – 7.26 (m, 4H), 7.24 – 7.14 (m, 4H), 5.45 (s, 2H), 2.68 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 155.42, 149.46, 138.37, 133.83, 133.09, 129.21, 128.77, 128.72, 128.17, 127.31, 125.45, 124.99, 120.53, 114.66, 99.21, 46.04, 19.00. HRMS (ESI) m/z calcd for $C_{25}H_{20}ClN_4O_2$ $[M+H]^+$ 443.1241, found 443.1244.

1-(4-Bromobenzyl)-3-(5-hydroxy-3-methyl-1-phenyl-1H-pyrazol-4-yl)quinoxalin-2(1*H*)-one (3ma)



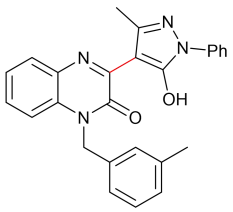
Orange solid (86%, 84 mg); Silica gel column chromatography (PE/EA = 7:1-4:1);^{1}H NMR (500 MHz, $CDCl_3$) δ 14.98 (s, 1H), 7.93 (d, *J* = 7.9 Hz, 2H), 7.56 (d, *J* = 3.0 Hz, 1H), 7.48 – 7.39 (m, 4H), 7.28-7.21 (m, 3H), 7.13 (t, *J* = 7.2 Hz, 3H), 5.41 (s, 2H), 2.68 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 155.38, 149.43, 138.36, 133.62, 132.14, 128.75, 128.68, 128.46, 127.28, 125.41, 124.97, 121.84, 120.46, 114.64, 99.18, 46.07, 19.01. HRMS (ESI) m/z calcd for $C_{25}H_{20}BrN_4O_2$ $[M+H]^+$ 487.0764, found 487.0769.

3-(5-Hydroxy-3-methyl-1-phenyl-1H-pyrazol-4-yl)-1-(4-(trifluoromethyl)benzyl)quinoxalin-2(1*H*)-one (3na)



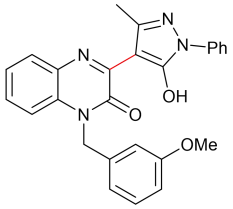
Yellow solid (82%, 78 mg); Silica gel column chromatography (PE/EA = 7:1-3:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 15.01 (s, 1H), 7.93 (d, *J* = 8.0 Hz, 2H), 7.60 (d, *J* = 8.2 Hz, 3H), 7.42 (t, *J* = 7.9 Hz, 2H), 7.36 (d, *J* = 8.1 Hz, 2H), 7.31 – 7.21 (m, 3H), 7.12 (d, *J* = 7.7 Hz, 1H), 5.54 (s, 2H), 2.68 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 155.45, 150.05, 149.44, 138.49 (d, *J* = 35.8 Hz), 130.31 (q, *J* = 32.8 Hz), 128.79, 128.67, 127.36, 127.01, 126.05 (d, *J* = 3.4 Hz), 125.49, 125.11, 124.91, 122.74, 120.52, 114.56, 99.25, 46.25, 19.01; ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.69. HRMS (ESI) m/z calcd for $C_{26}H_{19}F_3N_4O_2Na$ $[M+Na]^+$ 499.1352, found 499.1370.

3-(5-Hydroxy-3-methyl-1-phenyl-1H-pyrazol-4-yl)-1-(3-methylbenzyl)quinoxalin-2(1*H*)-one (3oa)



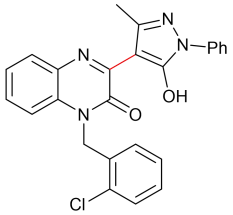
Orange solid (97%, 82 mg); Silica gel column chromatography (PE/EA = 7:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 15.11 (s, 1H), 7.95 (d, *J* = 8.0 Hz, 2H), 7.57 (s, 1H), 7.43 (t, *J* = 7.9 Hz, 2H), 7.26 – 7.18 (m, 5H), 7.09 (d, *J* = 7.6 Hz, 1H), 7.03 (d, *J* = 11.8 Hz, 2H), 5.45 (s, 2H), 2.70 (s, 3H), 2.31 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 155.42, 149.50, 146.06, 138.80, 138.43, 134.79, 134.48, 128.97, 128.84, 128.71, 128.61, 127.19, 125.34, 124.75, 123.65, 120.48, 114.95, 99.15, 46.63, 21.36, 18.98. HRMS (ESI) m/z calcd for $C_{26}H_{23}N_4O_2$ $[M+H]^+$ 422.1743, found 422.1746.

3-(5-Hydroxy-3-methyl-1-phenyl-1H-pyrazol-4-yl)-1-(3-methoxybenzyl)quinoxalin-2(1*H*)-one (3pa)



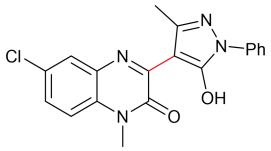
Orange solid (83%, 73 mg), Silica gel column chromatography (PE/EA = 6:1-2:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 15.09 (s, 1H), 7.95 (d, *J* = 8.0 Hz, 2H), 7.59 (s, 1H), 7.43 (t, *J* = 7.9 Hz, 2H), 7.29 – 7.21 (m, 5H), 6.85 – 6.77 (m, 3H), 5.48 (s, 2H), 3.76 (s, 3H), 2.70 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 160.10, 155.45, 149.53, 138.41, 136.14, 130.10, 128.96, 128.76, 127.31, 125.42, 124.84, 120.58, 118.82, 114.94, 112.88, 112.71, 99.18, 55.20, 46.58, 18.98. HRMS (ESI) m/z calcd for $C_{26}H_{23}N_4O_3$ $[M+H]^+$ 439.1765, found 439.1771.

1-(2-Chlorobenzyl)-3-(5-hydroxy-3-methyl-1-phenyl-1H-pyrazol-4-yl)quinoxalin-2(1*H*)-one (3qa)



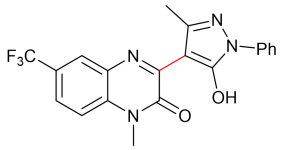
Yellow solid (85%, 75 mg), Silica gel column chromatography (PE/EA = 7:1-4:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 14.94 (s, 1H), 7.93 (d, *J* = 7.9 Hz, 2H), 7.58 (d, *J* = 6.5 Hz, 1H), 7.47 (d, *J* = 8.0 Hz, 1H), 7.41 (t, *J* = 8.0 Hz, 2H), 7.29-7.20 (m, 4H), 7.14 (t, *J* = 7.5 Hz, 1H), 6.99 (d, *J* = 7.9 Hz, 1H), 6.82 (d, *J* = 7.7 Hz, 1H), 5.57 (s, 2H), 2.68 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 155.47, 149.40, 145.62, 138.37, 132.61, 131.61, 129.88, 129.00, 128.75, 128.60, 127.38, 126.56, 125.39, 125.03, 120.42, 114.79, 99.21, 44.44, 19.05. HRMS (ESI) m/z calcd for $C_{25}H_{20}ClN_4O_2$ $[M+H]^+$ 443.1241, found 443.1237.

6-Chloro-3-(5-hydroxy-3-methyl-1-phenyl-1H-pyrazol-4-yl)-1-methylquinoxalin-2(1*H*)-one (3ra)



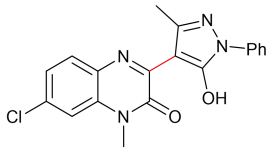
Yellow solid (69% yield, 51 mg), Silica gel column chromatography (PE/EA = 7:1-3:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 14.74 (s, 1H), 7.84 (d, *J* = 7.9 Hz, 2H), 7.55 (s, 1H), 7.39 (t, *J* = 7.9 Hz, 2H), 7.26 – 7.18 (m, 2H), 7.09 (d, *J* = 8.9 Hz, 1H), 3.62 (s, 3H), 2.58 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 155.22, 149.94, 146.56, 138.25, 133.53, 130.33, 128.71, 128.24, 127.47, 125.59, 120.62, 115.04, 99.34, 30.03, 18.61. HRMS (ESI) m/z calcd for $C_{19}H_{16}ClN_4O_2$ $[M+H]^+$ 367.0962, found 367.0948.

3-(5-Hydroxy-3-methyl-1-phenyl-1H-pyrazol-4-yl)-1-methyl-6-(trifluoromethyl)quinoxalin-2(1*H*)-one (3sa)



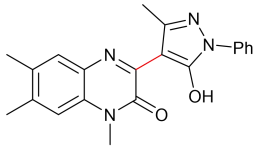
Yellow solid (51%, 41 mg); Silica gel column chromatography (PE/EA = 7:1-3:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 14.60 (s, 1H), 7.91-7.86 (m, 3H), 7.61 (d, *J* = 6.0 Hz, 1H), 7.48 – 7.33 (m, 3H), 7.26-7.22 (m, 1H), 3.75 (d, *J* = 4.4 Hz, 3H), 2.66 (s, 3H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.16. HRMS (ESI) m/z calcd for $C_{20}H_{16}F_3N_4O_2$ $[M+H]^+$ 401.1219, found 401.1224.

7-Chloro-3-(5-hydroxy-3-methyl-1-phenyl-1H-pyrazol-4-yl)-1-methylquinoxalin-2(1*H*)-one (3ta)



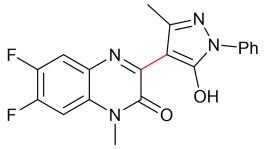
Yellow solid (56%, 41 mg); Silica gel column chromatography (PE/EA = 8:1-4:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 14.71 (s, 1H), 7.81 (t, *J* = 7.3 Hz, 2H), 7.44 (s, 1H), 7.41 – 7.34 (m, 2H), 7.28 (s, 1H), 7.20 (t, *J* = 7.3 Hz, 2H), 7.14 (s, 1H), 6.97 (s, 1H), 3.56 (s, 3H), 2.57 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 177.08, 155.19, 149.69, 147.19, 138.23, 138.09, 133.21, 131.18, 130.35, 128.71, 125.47, 125.05, 120.40, 114.08, 112.77, 99.74, 99.04, 29.96, 18.66. HRMS (ESI) m/z calcd for $C_{19}H_{16}ClN_4O_2$ $[M+H]^+$ 367.0962, found 367.0956.

3-(5-Hydroxy-3-methyl-1-phenyl-1H-pyrazol-4-yl)-1,6,7-trimethylquinoxalin-2(1*H*)-one (3ua)



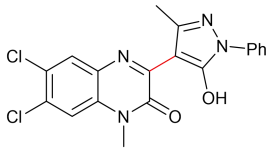
Orange solid (76%, 55 mg); Silica gel column chromatography (PE/EA = 6:1-3:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 14.99 (s, 1H), 7.93 (d, *J* = 7.8 Hz, 2H), 7.43 (t, *J* = 7.1 Hz, 2H), 7.37 (s, 1H), 7.22 (t, *J* = 7.4 Hz, 1H), 7.05 (s, 1H), 3.72 (s, 3H), 2.68 (s, 3H), 2.36 (s, 3H), 2.32 (s, 3H). HRMS (ESI) m/z calcd for $C_{21}H_{21}N_4O_2$ $[M+H]^+$ 361.1659, found 361.1657.

6,7-Difluoro-3-(5-hydroxy-3-methyl-1-phenyl-1H-pyrazol-4-yl)-1-methylquinoxalin-2(1*H*)-one (3va)



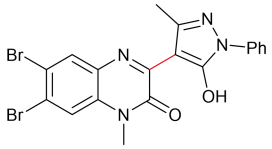
Orange solid (76%, 55 mg); Silica gel column chromatography (PE/EA = 8:1-3:1); ^{1}H NMR (600 MHz, $CDCl_3$) δ 14.35 (s, 1H), 7.83 (d, *J* = 7.7 Hz, 2H), 7.56 (t, *J* = 9.0 Hz, 1H), 7.44 (t, *J* = 8.0 Hz, 2H), 7.28 – 7.26 (m, 1H), 7.14 (dd, *J* = 11.0, 7.0 Hz, 1H), 3.74 (s, 3H), 2.63 (s, 3H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -132.73, -132.90, -133.12, -139.92 (d, *J* = 23.7 Hz). HRMS (ESI) m/z calcd for $C_{19}H_{14}F_2N_4O_2$ $[M]^+$ 368.1085, found 368.1087.

6,7-Dichloro-3-(5-hydroxy-3-methyl-1-phenyl-1H-pyrazol-4-yl)-1-methylquinoxalin-2(1*H*)-one (3wa)



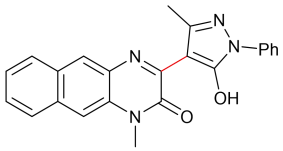
Orange solid (81%, 65 mg); Silica gel column chromatography (PE/EA = 8:1-3:1); ^{1}H NMR (600 MHz, $CDCl_3$) δ 14.50 (s, 1H), 7.82 (d, *J* = 7.9 Hz, 2H), 7.74 (s, 1H), 7.42 (t, *J* = 7.8 Hz, 2H), 7.33 (s, 1H), 7.24 (d, *J* = 7.4 Hz, 1H), 3.68 (s, 3H), 2.62 (s, 3H). HRMS (ESI) m/z calcd for $C_{19}H_{15}Cl_2N_4O_2$ $[M+H]^+$ 401.0571, found 401.0566.

6,7-Dibromo-3-(5-hydroxy-3-methyl-1-phenyl-1H-pyrazol-4-yl)-1-methylquinoxalin-2(1*H*)-one (3xa)



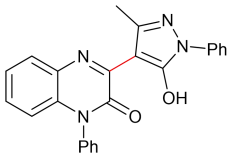
Orange solid (65%, 63 mg); Silica gel column chromatography (PE/EA = 9:1-3:1); ^{1}H NMR (600 MHz, $CDCl_3$) δ 14.56 (s, 1H), 7.88 (s, 1H), 7.82 (d, *J* = 7.8 Hz, 2H), 7.49 (s, 1H), 7.44 – 7.38 (m, 2H), 7.24 (t, *J* = 7.4 Hz, 1H), 3.66 (s, 3H), 2.61 (s, 3H). HRMS (ESI) m/z calcd for $C_{19}H_{16}Br_2N_4O_2$ $[M+2]^+$ 490.9562, found 490.9535.

3-(5-Hydroxy-3-methyl-1-phenyl-1H-pyrazol-4-yl)-1-methylbenzo[g]quinoxalin-2(1*H*)-one (3ya)



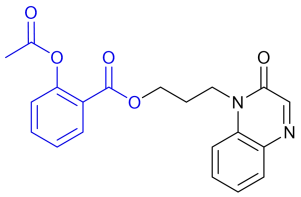
Orange solid (65%, 63 mg); Silica gel column chromatography (PE/EA = 6:1-3:1); ^{1}H NMR (600 MHz, $CDCl_3$) δ 15.42 (s, 1H), 7.97 (s, 2H), 7.91 (s, 1H), 7.85 (d, *J* = 7.3 Hz, 2H), 7.58 (s, 1H), 7.53 – 7.46 (m, 2H), 7.44 (t, *J* = 7.9 Hz, 2H), 7.22 (t, *J* = 7.3 Hz, 1H), 3.80 (s, 3H), 2.71 (s, 3H). HRMS (ESI) m/z calcd for $C_{23}H_{19}N_4O_2$ $[M+H]^+$ 383.1508, found 383.1512.

3-(5-Hydroxy-3-methyl-1-phenyl-1*H*-pyrazol-4-yl)-1-phenylquinoxalin-2(1*H*)-one (3za)



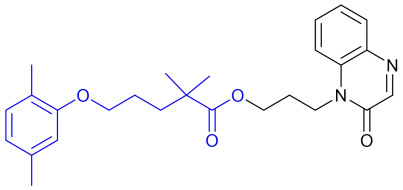
Orange solid (84%, 66 mg); Silica gel column chromatography (PE/EA = 6:1-4:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 13.64 (s, 1H), 7.94 (d, *J* = 7.6 Hz, 2H), 7.67-7.59 (m, 4H), 7.44 – 7.13 (m, 8H), 6.58 (d, *J* = 8.2 Hz, 1H), 2.66 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 155.17, 149.36, 138.37, 135.65, 130.66, 130.47, 129.77, 128.73, 128.07, 126.72, 125.32, 124.89, 120.41, 115.93, 99.24, 77.25, 77.00, 76.75, 19.16. HRMS (ESI) m/z calcd for $C_{24}H_{19}N_4NaO_2$ $[M+Na]^+$ 417.1322, found 417.1322.

3-(2-Oxoquinoxalin-1(2*H*)-yl)propyl 2-acetoxybenzoate (4a, CAS: 3056011-80-1)[3c]



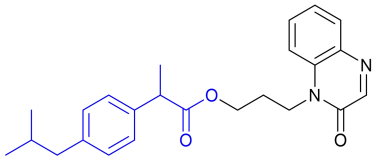
Light yellow oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.30 (s, 1H), 8.00 (dd, *J* = 7.8, 1.4 Hz, 1H), 7.89 (d, *J* = 8.0 Hz, 1H), 7.61-7.55 (m, 2H), 7.38-7.33 (m, 3H), 7.13 (d, *J* = 8.1 Hz, 1H), 4.47 – 4.38 (m, 4H), 2.34 (s, 3H), 2.27 – 2.21 (m, 2H). HRMS (ESI) m/z calcd for $C_{20}H_{19}N_2O_5$ $[M+H]^+$ 367.1288, found 367.1292.

3-(2-Oxoquinoxalin-1(2*H*)-yl)propyl 5-(2,5-dimethylphenoxy)-2,2-dimethylpentanoate (4b, CAS: 3067017-81-3)[3d,e]



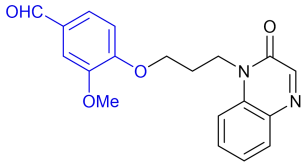
Light yellow oil; Silica gel column chromatography (PE/EA = 5:1-4:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.30 (s, 1H), 7.90 (d, *J* = 8.2 Hz, 1H), 7.56 (t, *J* = 7.2 Hz, 1H), 7.35 (d, *J* = 7.9 Hz, 2H), 6.96 (d, *J* = 7.4 Hz, 1H), 6.66 – 6.58 (m, 2H), 4.36 – 4.30 (m, 2H), 4.22 (t, *J* = 6.1 Hz, 2H), 3.94 (t, *J* = 6.6 Hz, 2H), 2.29 (s, 3H), 2.16 – 2.09 (m, 5H), 1.76 (d, *J* = 2.9 Hz, 4H), 1.26 (s, 6H). HRMS (ESI) m/z calcd for $C_{26}H_{32}N_2O_4$ $[M]^+$ 436.2362, found 436.2356.

3-(2-Oxoquinoxalin-1(2*H*)-yl)propyl 2-(4-isobutylphenyl)propanoate (4c, CAS: 2647904-18-3)[3a]



Light yellow oil; Silica gel column chromatography (PE/EA = 4:1-3:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.27 (s, 1H), 7.87 (d, *J* = 8.0 Hz, 1H), 7.45 (t, *J* = 7.2 Hz, 1H), 7.33 (t, *J* = 7.6 Hz, 1H), 7.24 (d, *J* = 8.0 Hz, 2H), 7.11 (d, *J* = 8.0 Hz, 2H), 7.07 (d, *J* = 8.4 Hz, 1H), 4.27-4.22 (m, 1H), 4.20 – 4.14 (m, 3H), 3.73 (q, *J* = 7.1 Hz, 1H), 2.41 (d, *J* = 7.2 Hz, 2H), 2.07 – 2.00 (m, 2H), 1.83-1.74 (m, 1H), 1.52 (d, *J* = 7.2 Hz, 3H), 0.83 (dd, *J* = 6.6, 1.6 Hz, 6H). HRMS (ESI) m/z calcd for $C_{24}H_{29}N_2O_3$ $[M+H]^+$ 393.2156, found 393.2159.

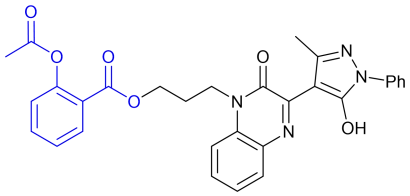
3-Methoxy-4-(3-(2-oxoquinoxalin-1(2*H*)-yl)propoxy)benzaldehyde (4d, CAS: 2414081-19-7)[3b]



Light yellow solid. ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.86 (s, 1H), 8.30 (s, 1H), 7.90 (d, *J* = 8.0 Hz, 1H), 7.62 (d, *J* = 8.4 Hz, 1H), 7.53 (t, *J* = 7.8 Hz, 1H), 7.43 (dd, *J* = 5.5, 1.7 Hz, 2H), 7.35 (t, *J* = 7.6 Hz,

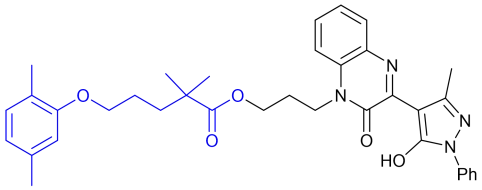
1H), 6.94 (d, *J* = 8.6 Hz, 1H), 4.52 (t, *J* = 7.2 Hz, 2H), 4.21 (t, *J* = 5.8 Hz, 2H), 3.95 (s, 3H), 2.41 – 2.34 (m, 2H). HRMS (ESI) m/z calcd for $C_{19}H_{17}N_2O_4$ $[M-H]^-$ 337.1315, found 337.1319.

3-(3-(5-Hydroxy-3-methyl-1-phenyl-1*H*-pyrazol-4-yl)-2-oxoquinoxalin-1(2*H*)-yl)propyl 2-acetoxybenzoate (5a, CAS: 3061317-60-3, from Aspirin and Edaravone)[4]



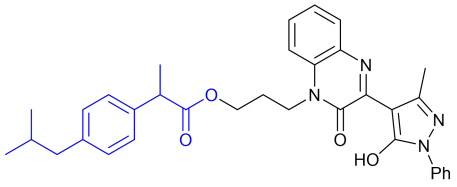
Orange oil (91%, 98 mg); Silica gel column chromatography (PE/EA = 4:1-3:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 14.98 (s, 1H), 7.96 (d, *J* = 7.8 Hz, 1H), 7.91 (d, *J* = 8.0 Hz, 2H), 7.54 (dd, *J* = 12.3, 4.6 Hz, 2H), 7.42 (t, *J* = 7.9 Hz, 2H), 7.37 – 7.32 (m, 1H), 7.32 – 7.27 (m, 3H), 7.21 (t, *J* = 7.4 Hz, 1H), 7.09 (d, *J* = 8.0 Hz, 1H), 4.44 (dd, *J* = 11.9, 6.2 Hz, 4H), 2.65 (s, 3H), 2.32 – 2.21 (m, 5H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 169.53, 164.14, 155.14, 150.65, 149.44, 138.40, 134.04, 131.37, 128.74, 128.54, 127.41, 125.96, 125.39, 124.79, 123.75, 122.94, 120.53, 113.83, 98.92, 62.62, 40.45, 26.42, 20.90, 18.94. HRMS (ESI) m/z calcd for $C_{30}H_{27}N_4O_6$ $[M+H]^+$ 539.1925, found 539.1918.

3-(3-(5-Hydroxy-3-methyl-1-phenyl-1*H*-pyrazol-4-yl)-2-oxoquinoxalin-1(2*H*)-yl)propyl 5-(2,5-dimethylphenoxy)-2,2-dimethylpentanoate (5b, from Gemfibrozil and Edaravone)



Orange oil (97%, 118 mg); Silica gel column chromatography (PE/EA = 7:1-6:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 14.11 (s, 1H), 7.92 (d, *J* = 7.8 Hz, 2H), 7.57 (d, *J* = 6.9 Hz, 1H), 7.41 (t, *J* = 7.9 Hz, 2H), 7.36 – 7.18 (m, 4H), 6.96 (d, *J* = 7.4 Hz, 1H), 6.65 – 6.57 (m, 2H), 4.29 (t, *J* = 7.4 Hz, 2H), 4.22 (t, *J* = 6.0 Hz, 2H), 3.94 (s, 2H), 2.66 (s, 3H), 2.29 (s, 3H), 2.15 (s, 3H), 2.14-2.08 (m, 2H), 1.78 (s, 4H), 1.29 (s, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 177.38, 156.72, 154.85, 149.37, 145.81, 138.29, 136.30, 130.14, 128.60, 128.46, 127.28, 125.23, 124.66, 123.33, 120.62, 120.31, 113.57, 111.84, 98.84, 67.85, 61.59, 42.04, 40.36, 37.01, 26.42, 25.06, 21.25, 18.79, 15.63. HRMS (ESI) m/z calcd for $C_{36}H_{41}N_4O_5$ $[M+H]^+$ 609.3136, found 609.3118.

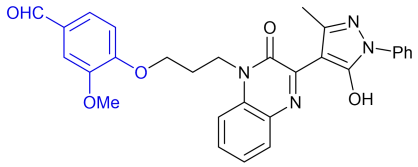
3-(3-(5-Hydroxy-3-methyl-1-phenyl-1*H*-pyrazol-4-yl)-2-oxoquinoxalin-1(2*H*)-yl)propyl 2-(4-isobutylphenyl)propanoate (5c, from Ibuprofen and Edaravone)



Orange solid (95%, 107 mg); Silica gel column chromatography (PE/EA = 6:1-5:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 15.01 (s, 1H), 7.92 (d, *J* = 7.9 Hz, 2H), 7.57 (d, *J* = 5.4 Hz, 1H), 7.41 (t, *J* = 7.9 Hz, 2H), 7.30 – 7.19 (m, 5H), 7.12 (d, *J* = 8.0 Hz, 2H), 7.01 (d, *J* = 7.9 Hz, 1H), 4.26 (dt, *J* = 11.6, 5.8 Hz,

1H), 4.22 – 4.13 (m, 3H), 3.74 (q, *J* = 7.1 Hz, 1H), 2.66 (s, 3H), 2.42 (d, *J* = 7.2 Hz, 2H), 2.10 – 2.01 (m, 2H), 1.84-1.76 (m, 1H), 1.53 (d, *J* = 7.2 Hz, 3H), 0.85 (dd, *J* = 6.6, 1.5 Hz, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 174.39, 154.99, 149.45, 144.88, 140.68, 138.38, 137.60, 129.42, 128.70, 128.54, 127.37, 127.08, 125.36, 124.67, 120.50, 113.74, 98.92, 61.85, 45.13, 44.94, 40.22, 30.06, 26.29, 22.26, 18.86, 18.28. HRMS (ESI) m/z calcd for $C_{34}H_{37}N_4O_4$ $[M+H]^+$ 565.2815, found 565.2824.

4-(3-(3-(5-Hydroxy-3-methyl-1-phenyl-1*H*-pyrazol-4-yl)-2-oxoquinoxalin-1(2*H*)-yl)propoxy)-3-methoxybenzaldehyde (5d, from Vanillin and Edaravone)



Light yellow solid (72%, 73 mg); Silica gel column chromatography (DCM/MeOH = 500:1-300:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 15.05 (s, 1H), 9.84 (s, 1H), 7.91 (d, *J* = 7.9 Hz, 2H), 7.60 (dd, *J* = 20.5, 5.5 Hz, 2H), 7.44-7.39 (m, 4H), 7.37 – 7.29 (m, 2H), 7.22 (t, *J* = 7.4 Hz, 1H), 6.93 (d, *J* = 8.1 Hz, 1H), 4.57 (t, *J* = 7.0 Hz, 2H), 4.24 (t, *J* = 5.5 Hz, 2H), 3.90 (s, 3H), 2.64 (s, 3H), 2.44 – 2.36 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 190.77, 155.39, 153.39, 149.84, 138.40, 130.46, 128.85, 128.79, 127.46, 126.60, 125.51, 124.85, 120.68, 114.31, 111.57, 109.21, 98.92, 66.34, 55.86, 40.54, 26.96, 18.88. HRMS (ESI) m/z calcd for $C_{29}H_{25}N_4O_5$ $[M-H]^-$ 509.1910, found 509.1915.

5. References

[1] a) K. Zheng, K. Liang, J. Zhu, H. Chen, P. Zhang, C. Shen and J. Cao, Self-catalytic photochemical three-component reaction for the synthesis of multifunctional 3,3-disubstituted oxindoles, *Mol. Catal.*, 2024, **565**, 114379; b) W. Zhao, Y. Zhang, S. Yuan, X. Yu, L. Liu and J. Li, Direct Alkylation of Quinoxalinones with Boracene-Based Alkylborate under Visible Light Irradiation, *J. Org. Chem.*, 2023, **88**, 6218-6226; c) S. Cao, J.-X. Chen, X.-L. Zhang, X. Song, W.-Y. Song, Y.-S. Wu, Y.-H. Zhang and Z. Liu, Merging Quinoxalin-2(1H)-ones Excitation with Cobaloxime Catalysis: C3 Alkylation of Quinoxalin-2(1H)-ones with Unactivated Alkyl Iodides and Carboxylic Acids under Light, *Org. Lett.*, 2024, **26**, 5833-5838; d) Singh, S. R. Nasireddy, G. C. Upreti, S. Arora and A. Singh, Photocatalytic, Intermolecular Olefin Alkylcarbofunctionalization Triggered by Haloalkyl Radicals Generated via Halogen Atom Transfer, *Org. Lett.*, 2023, **25**, 5558-5562; e) N. Yadav, A. K. Sahoo, D. Sarkar and J. N. Moorthy, Metal-free Generation of Halogen Radicals Using NXS/TBHP: Application in Site-Selective Halogenation of Quinoxalin-2(1*H*)-Ones and Synthesis of Gem-Dihaloketones, *ChemRxiv*, 2024, 1-12; f) Liu, Y. Huang, F.-L. Qing and X.-H. Xu, Transition-Metal-Free Decarboxylation of 3,3,3-Trifluoro-2,2-dimethylpropanoic Acid for the Preparation of C(CF3)Me2-Containing Heteroarenes, *Org. Lett.*, 2018, **20**, 5497-5501. g) S. Song, X. Peng, B. Zhou, L. Zheng, J. Sun, Z. Chen, and J. Li, Acid-Promoted Self-Photocatalyzed Regioselective Oxidation: A Novel Strategy for Accessing Quinoxaline-2,3-diones, *Chem. Eur. J.*, 2024, **30**, e202402848.

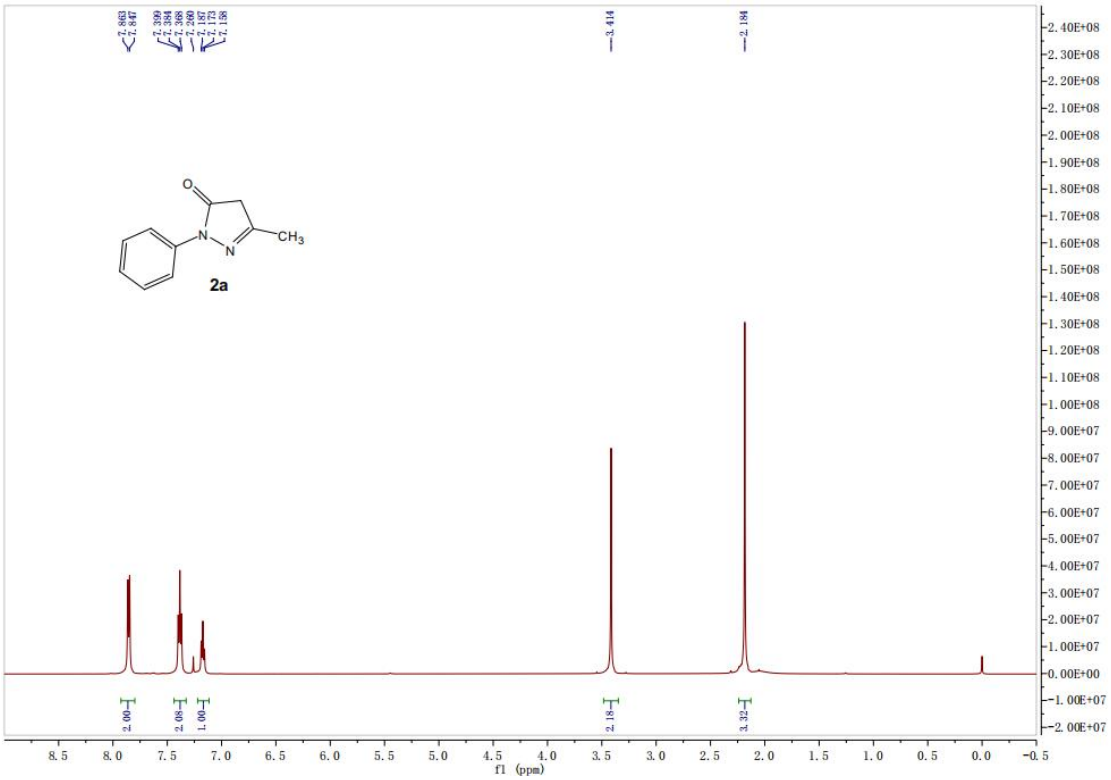
[2] a) Y. Yuan, L.-S. Li, L. Zhang, F. Wang, L. Jiang, L. Zuo, Q. Wang, J.-G. Hu and A. Lei, Electrochemical synthesis of versatile ammonium oxides under metal catalyst-, exogenous-oxidant-, and exogenous-electrolyte-free conditions, *Chem. Commun.,* 2021, **57**, 2768-2771; b) M. Li, S. Yang, J. Zhang, Z. Gao, L. Zheng, F. Lu and Y. Feng, Electrochemical oxidative selective halogenation of pyrazolones for the synthesis of 4-halopyrazolones, *Org. Biomol. Chem.*, 2024, **22**, 6080-6684; c) F.

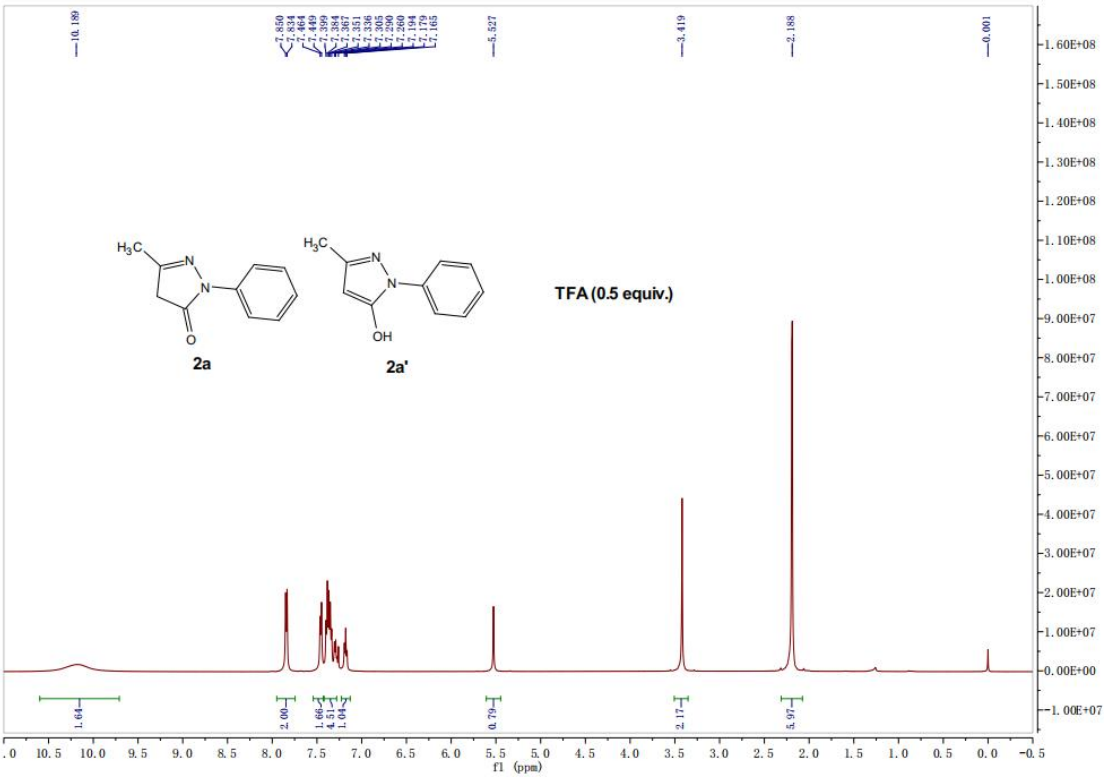
Fang, S. Hu, C. Li, Q. Wang, R. Wang, X. Han, Y. Zhou and H. Liu, Catalytic System-Controlled Divergent Reaction Strategies for the Construction of Diversified Spiropyrazolone Skeletons from Pyrazolidinones and Diazopyrazolones, *Angew. Chem., Int. Ed.*, 2021, **60**, 21327-21333; d) R.-H. Wang, Y.-L. Li, H.-J. He, Y.-C. Xiao and F.-E. Chen, Catalytic Asymmetric Addition of Diorganozinc Reagents to Pyrazole-4,5-Diones and Indoline-2,3-Diones, *Chem. Eur. J.*, 2021, **27**, 4302-4306.

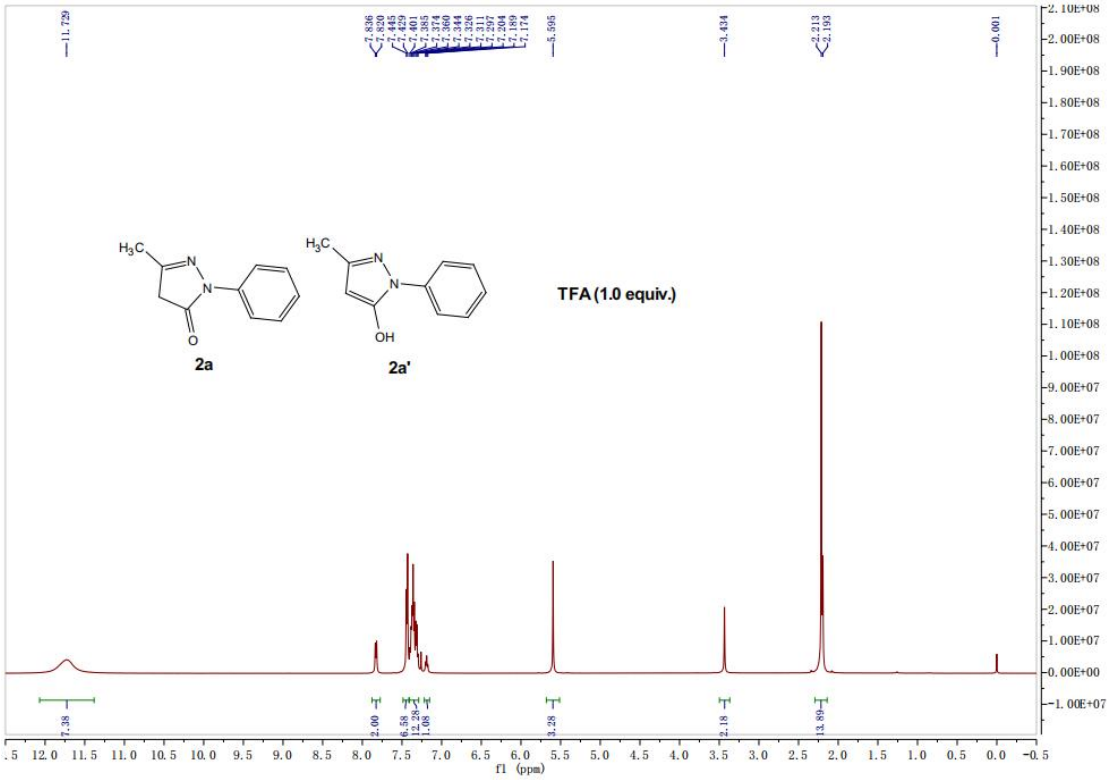
[3] a) L. Laze, P. Romero, I. Bosque and J. C. Gonzalez-Gomez, Oxidative Coupling of 4-Hydroxycoumarins with Quinoxalin-2(1H)-ones Induced by Visible Light under Aerobic Conditions, *Eur. J. Org. Chem.*, 2023, **26**, e202201484; b) Y. Yang, Z. Wei, A. T. Teichmann, F. H. Wieland, A. Wang, X. Lei, Y. Zhu, J. Yin, T. Fan, L. Zhou, C. Wang and L. Chen, Development of a novel nitric oxide (NO) production inhibitor with potential therapeutic effect on chronic inflammation, *Eur. J. Med. Chem*., 2020, **193**, 112216; c) X.-K. He, J. Lu, A.-J. Zhang, Q.-Q. Zhang, G.-Y. Xu and J. Xuan, BI-OAc-Accelerated C3–H Alkylation of Quinoxalin-2(1H)-ones under Visible-Light Irradiation, *Org. Lett.*, 2020, **22**, 5984-5989; d) E. Falk, A. Franchino, T. Horak, L. Gürtler and B. Morandi, Azide-Free Synthesis of N-Alkyliminophosphoranes from Phosphines and Hydroxylamine Derivatives, *Org. Lett.*, 2023, **25**, 1695-1700; (e) A. Kumar Ghosh, A. Mondal, S. Neogi, F. Mahato, S. Bhunya, L. Roy, A. Hajra, Copper-Catalyzed Carbogermylation of Electron-Deficient Alkenes via 3,4-Difunctionalization of Quinoxalin-2(1H)-ones: Mechanistic Insights from Computational Studies, *Chem. Eur. J.*, 2025, **31**, e202404186.

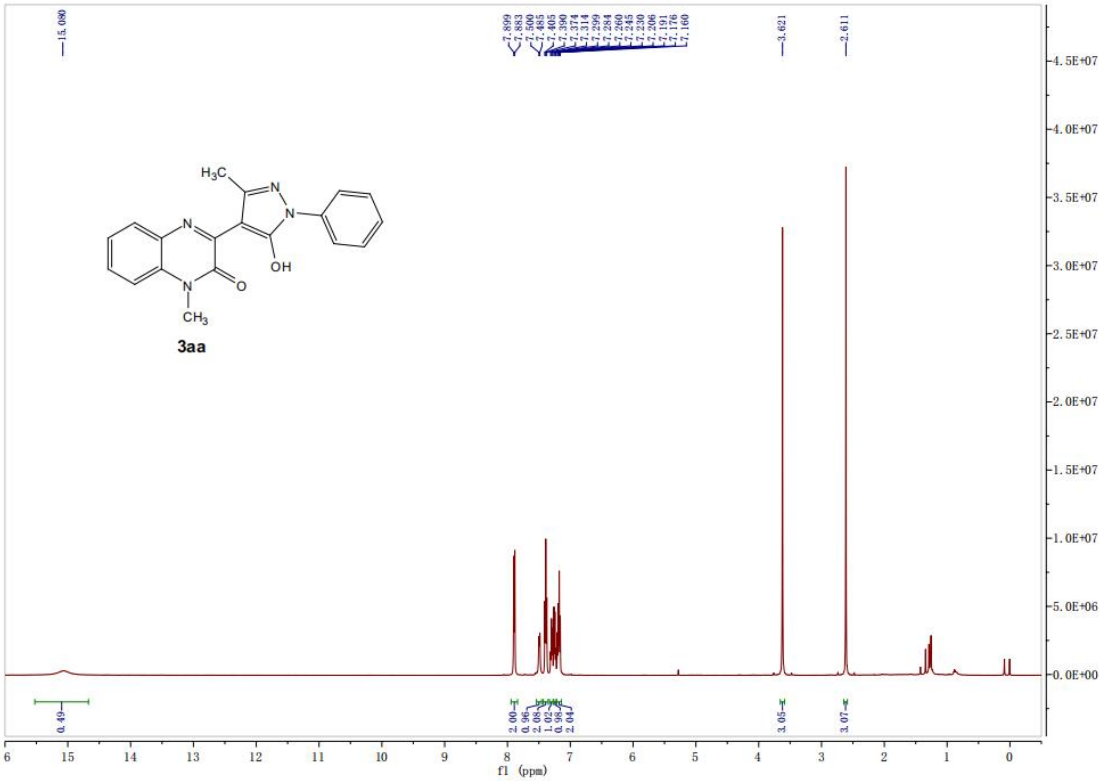
[4] S. Zhang, Z. Zhang, C. Qin, M. Hu, J. Wang, F. Ji and G. Jiang, Electrochemical Oxidative Functionalization of Pyrazolin-5-Ones: Access to 4-Quinoxalinone-Substistuted Pyrazoles, *Adv. Synth. Catal.*, 2025, **367**, e202400825.

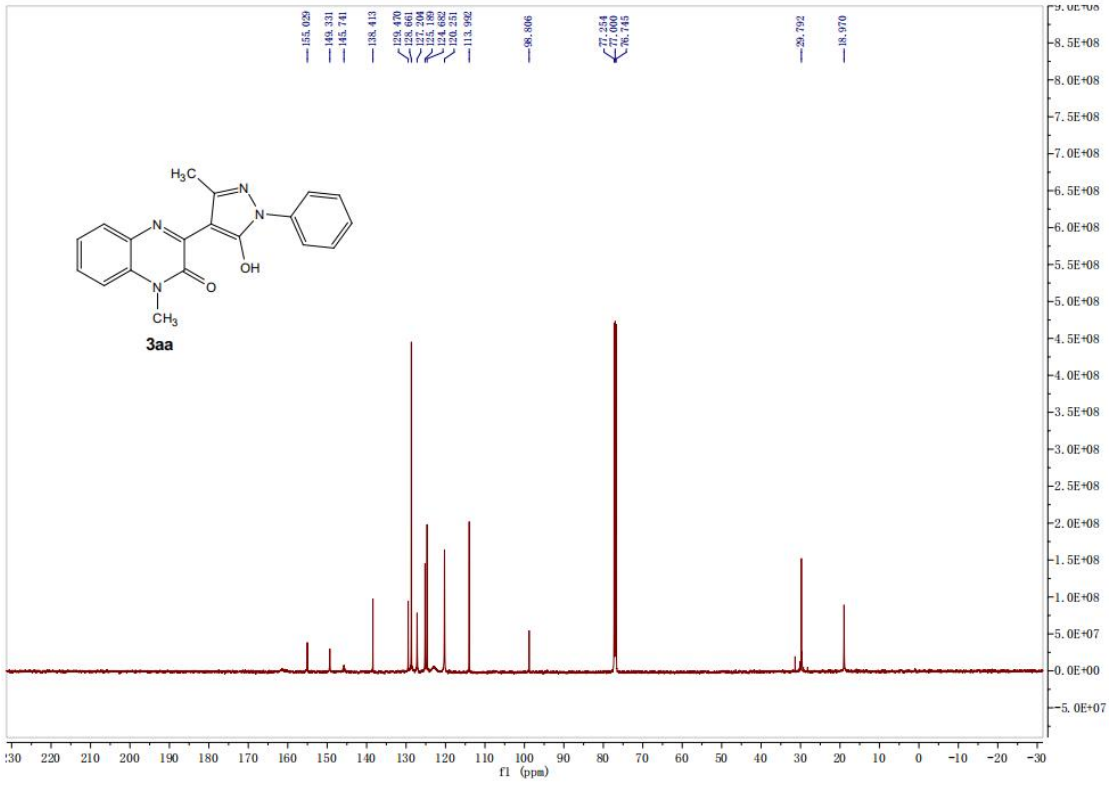
6. NMR spectra of products

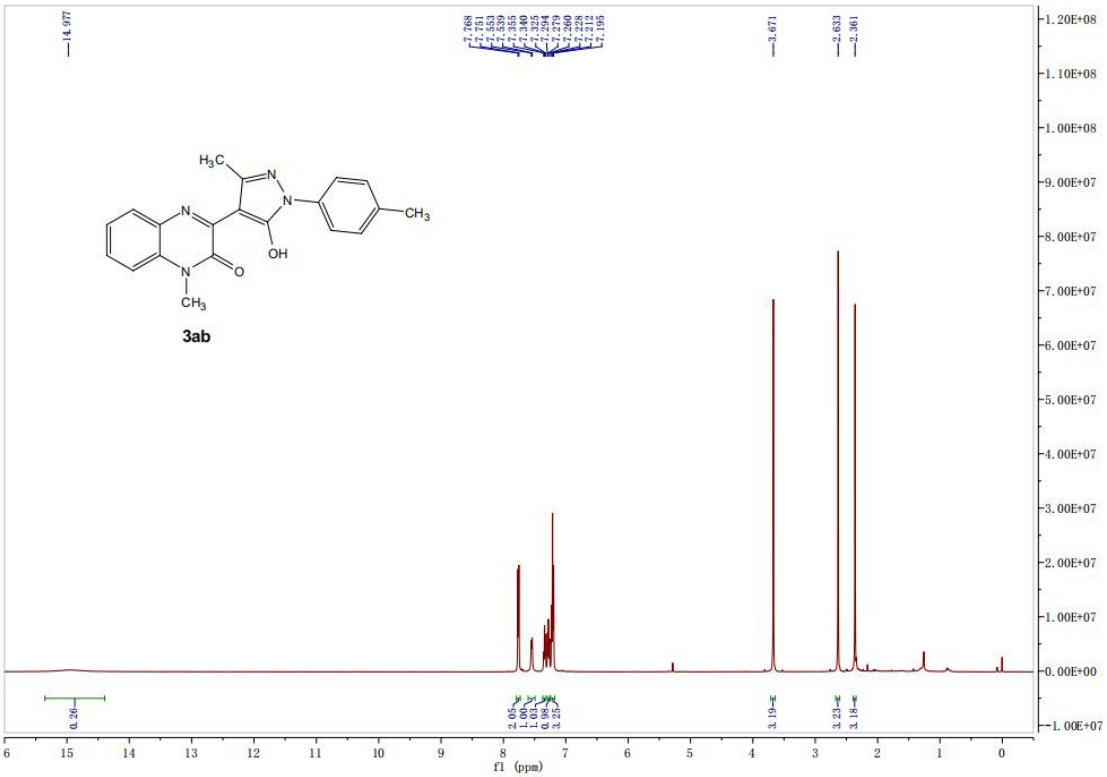


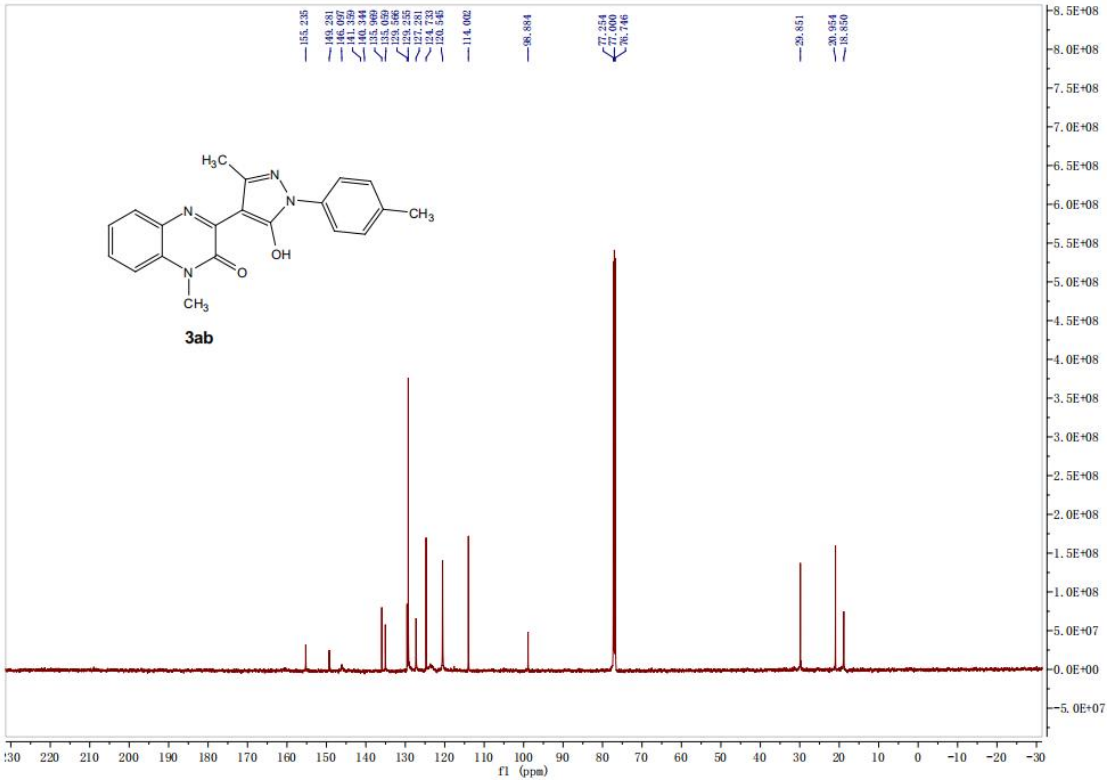


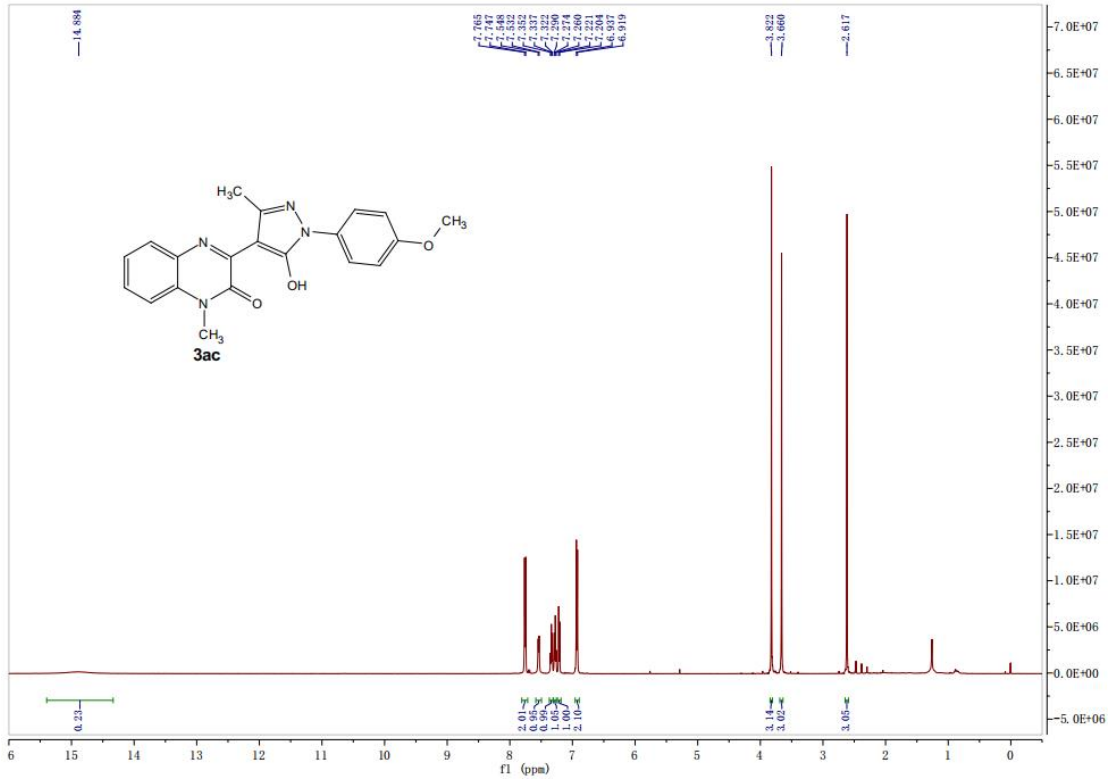

11.729
7.836
7.820
7.445
7.429
7.401
7.385
7.374
7.360
7.344
7.326
7.311
7.297
7.284
7.189
7.174
5.595
3.434
2.213
2.193
0.001
TFA (1.0 equiv.)
2a
2a'
7.38
2.00
6.58
12.28
1.08
3.28
2.18
3.89
f1 (ppm)

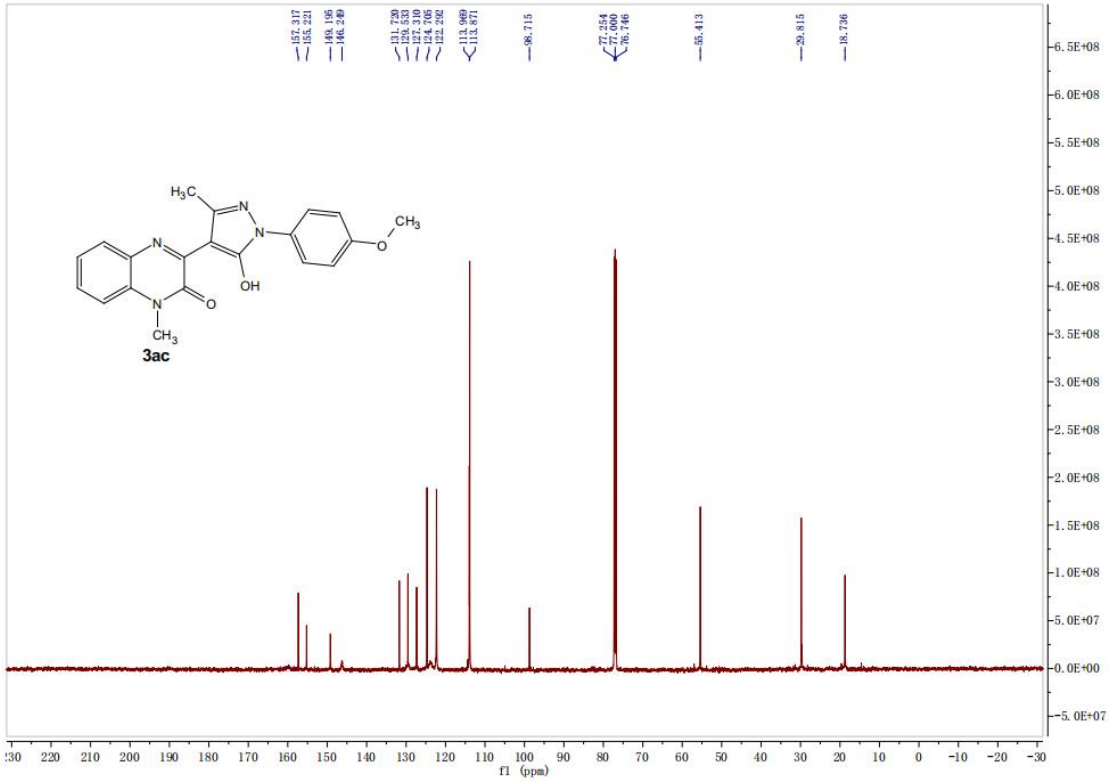

15.080
7.899
7.883
7.560
7.545
7.405
7.390
7.374
7.314
7.299
7.284
7.260
7.245
7.230
7.006
7.191
7.176
7.160
3.621
2.611
3aa
0.49
2.00
2.08
1.02
0.98
2.04
3.05
3.07
f1 (ppm)

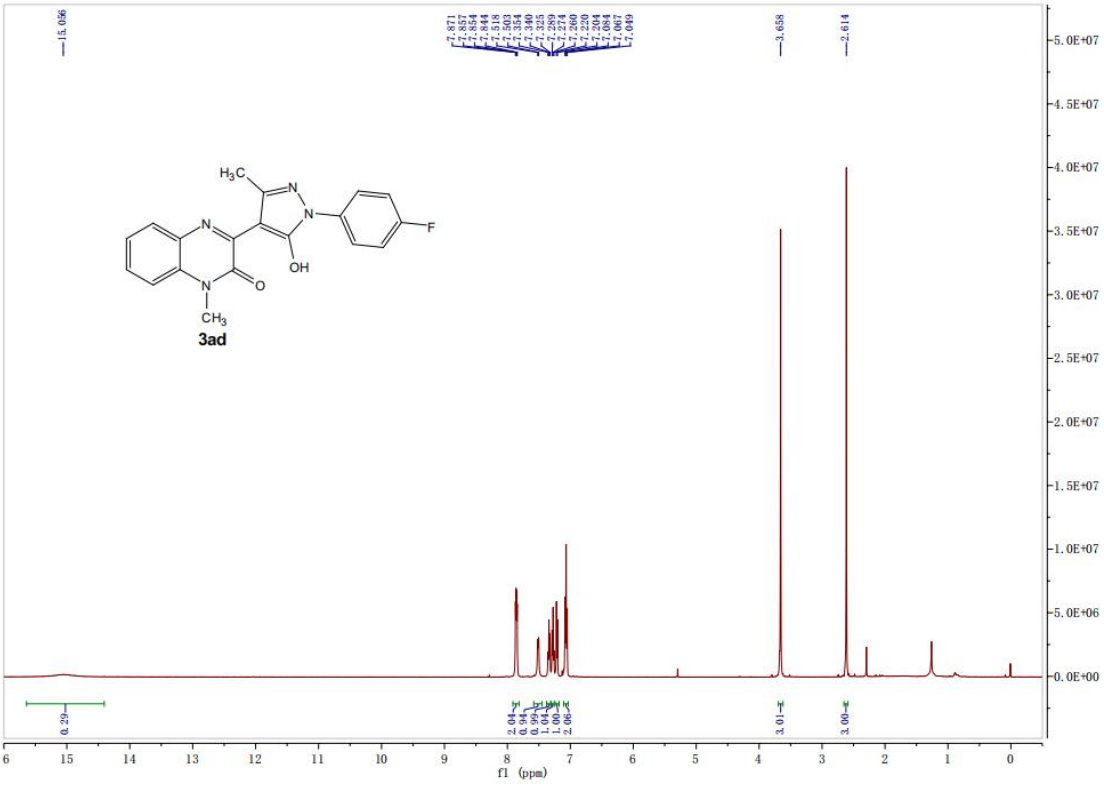

155.029
149.331
145.741
138.413
129.470
128.661
127.194
125.198
124.682
120.251
113.992
98.806
77.254
77.000
76.745
29.792
18.970
H3C
N
N
N
OH
O
CH3
3aa
f1 (ppm)

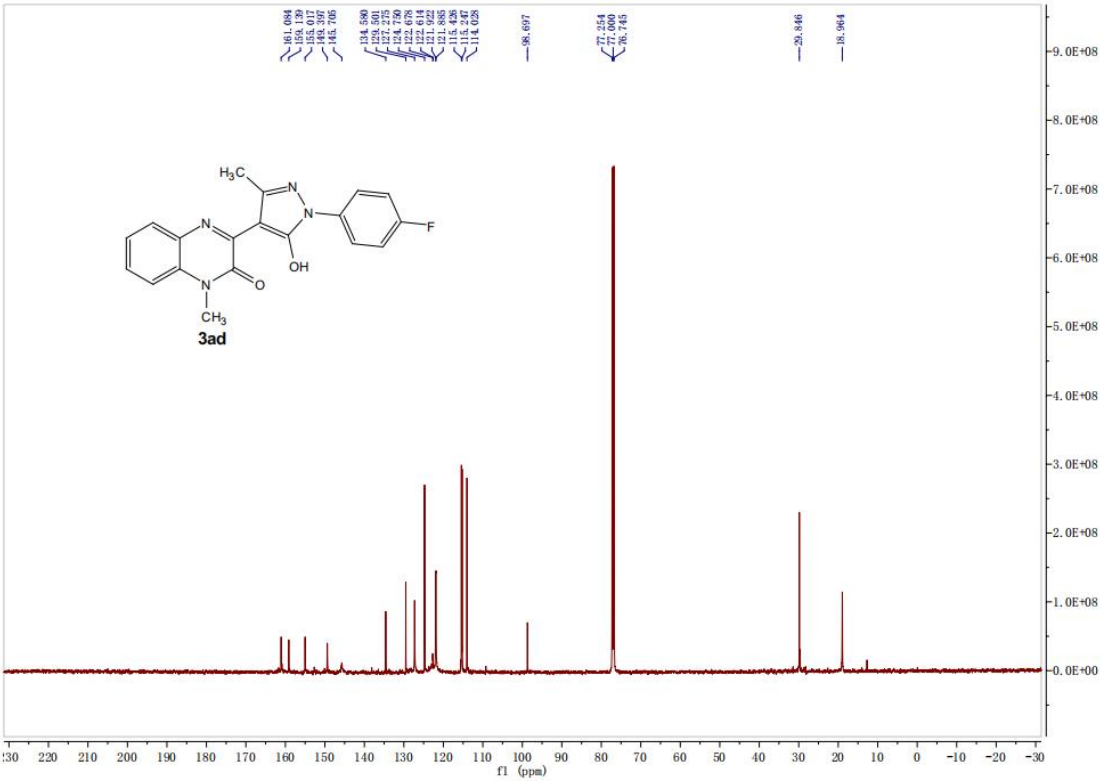

14.977
7.768
7.751
7.553
7.539
7.355
7.340
7.325
7.294
7.279
7.260
7.228
7.212
7.195
3.671
2.633
2.361
H3C
N
N
CH3
N
OH
O
N
CH3
3ab
1.20E+08
1.10E+08
1.00E+08
9.00E+07
8.00E+07
7.00E+07
6.00E+07
5.00E+07
4.00E+07
3.00E+07
2.00E+07
1.00E+07
0.00E+00
-1.00E+07
0.26
2.05
1.00
1.03
0.98
3.23
3.19
3.23
3.18
f1 (ppm)

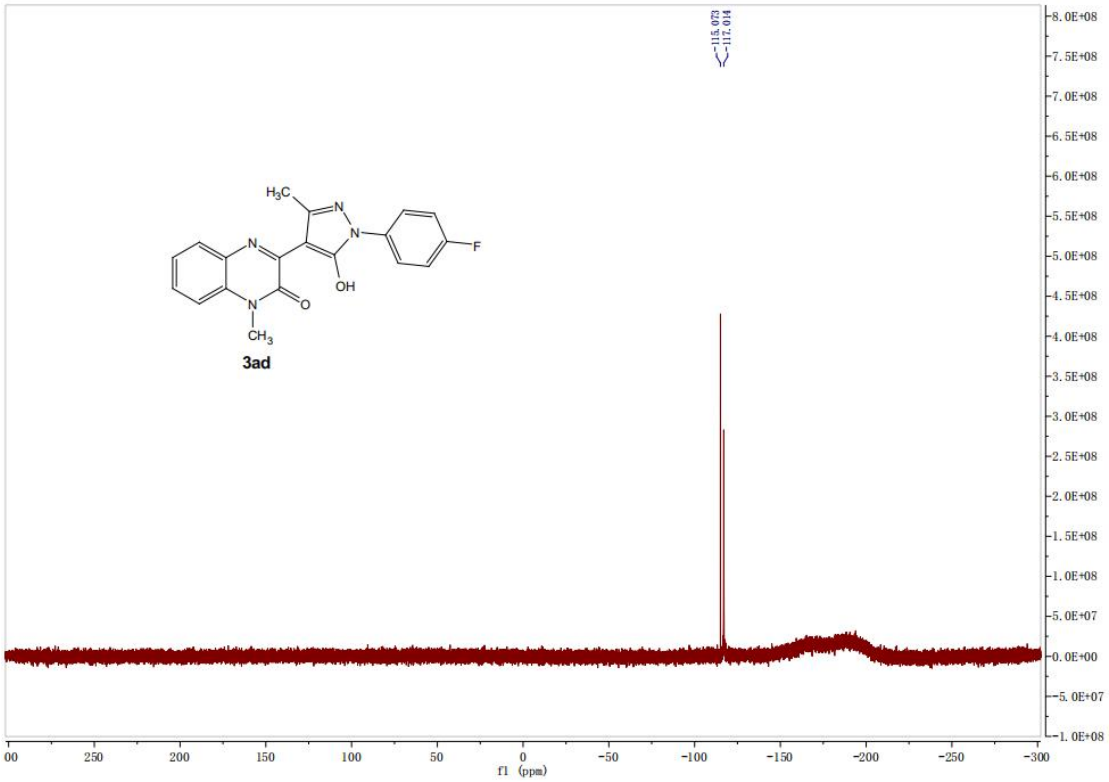

155.235
149.281
146.097
141.359
140.344
135.969
135.059
129.566
129.255
127.281
124.733
120.545
114.002
98.884
77.254
77.000
76.746
29.851
20.954
18.850
H3C
N
N
CH3
N
OH
O
N
CH3
3ab
8.5E+08
8.0E+08
7.5E+08
7.0E+08
6.5E+08
6.0E+08
5.5E+08
5.0E+08
4.5E+08
4.0E+08
3.5E+08
3.0E+08
2.5E+08
2.0E+08
1.5E+08
1.0E+08
5.0E+07
0.0E+00
-5.0E+07
f1 (ppm)

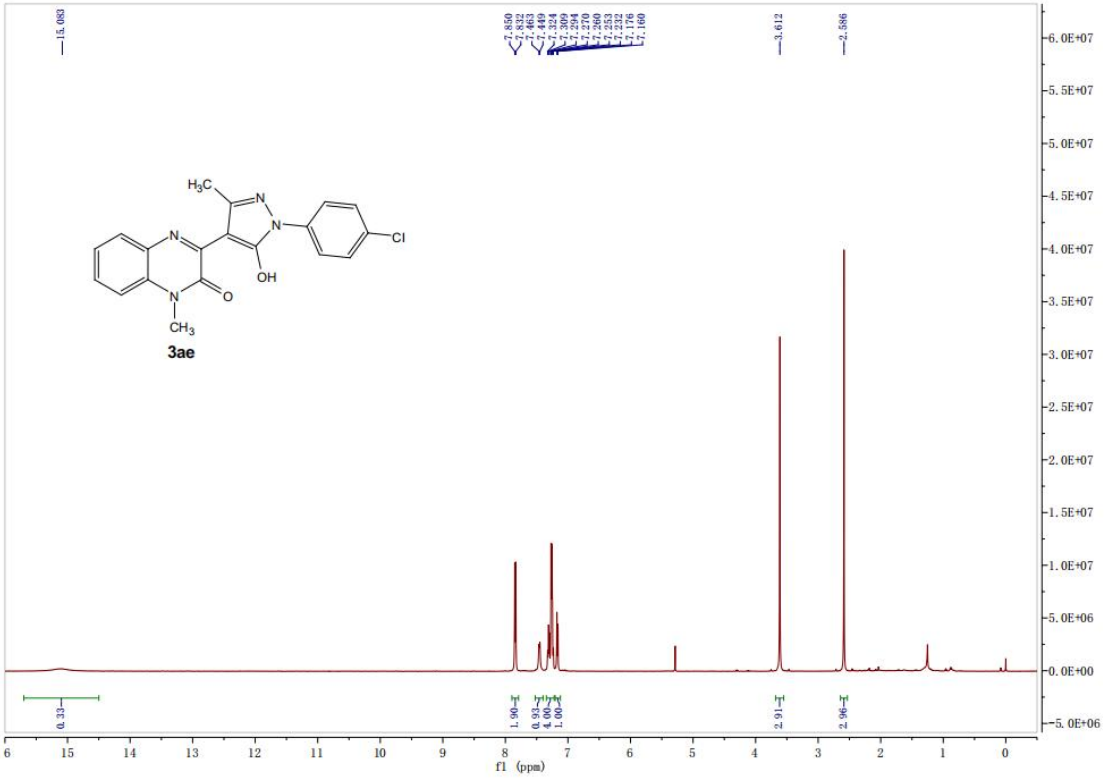

14.884
7.765
7.747
7.548
7.532
7.352
7.337
7.322
7.290
7.274
7.260
7.221
7.208
6.937
6.919
3.822
3.660
2.617
H3C
N
N
CH3
O
OH
N
O
CH3
3ac
0.23
2.01
0.95
0.98
1.05
1.00
2.10
3.14
3.02
3.05
f1 (ppm)

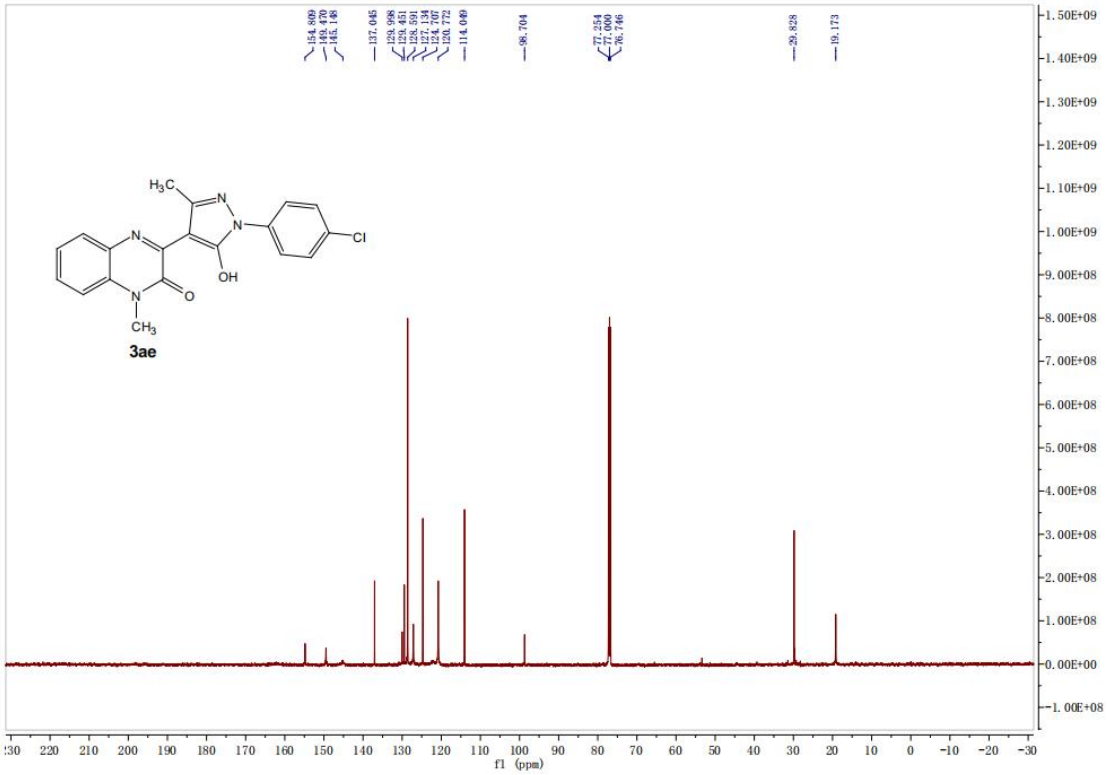

157.317
155.221
149.195
146.249
131.220
129.353
122.310
124.705
122.292
113.989
113.971
98.715
77.254
77.000
76.746
55.413
29.815
18.736
H3C
N
N
CH3
O
OH
N
O
CH3
3ac
f1 (ppm)

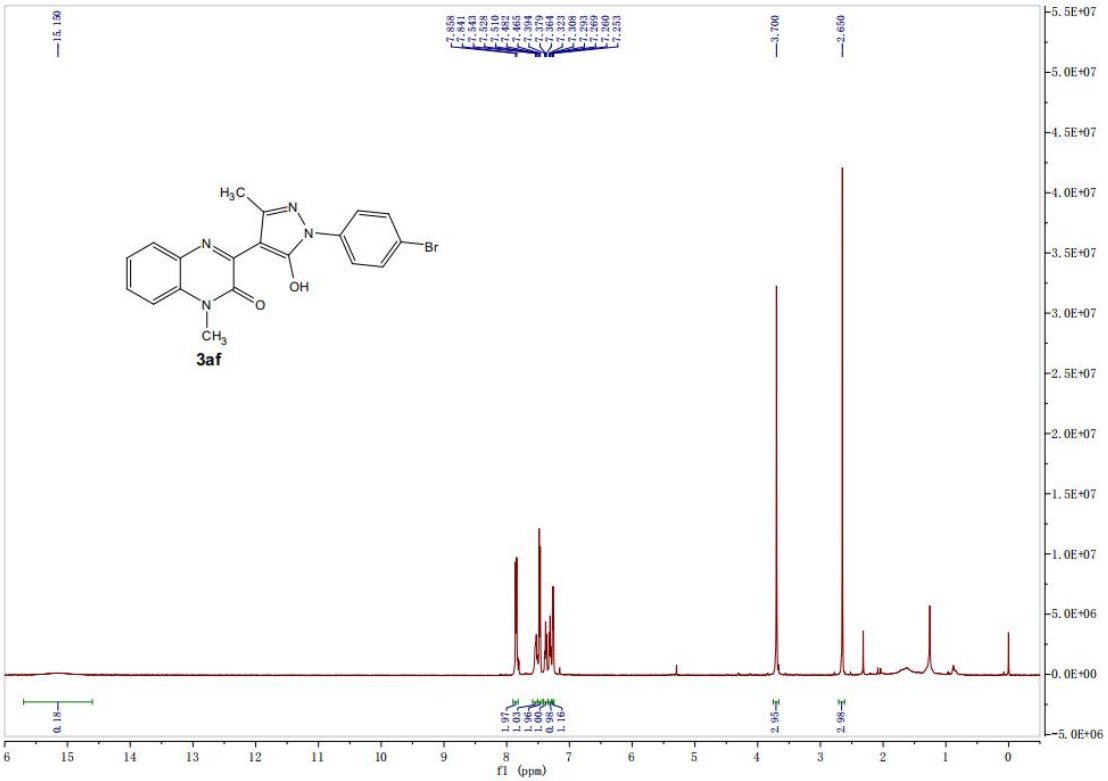

15.066
7.871
7.857
7.854
7.844
7.518
7.503
7.354
7.340
7.335
7.289
7.274
7.260
7.220
7.204
7.084
7.067
7.049
3.658
2.614
3ad
0.29
2.04
0.94
0.99
1.04
1.00
2.06
3.01
3.00
f1 (ppm)

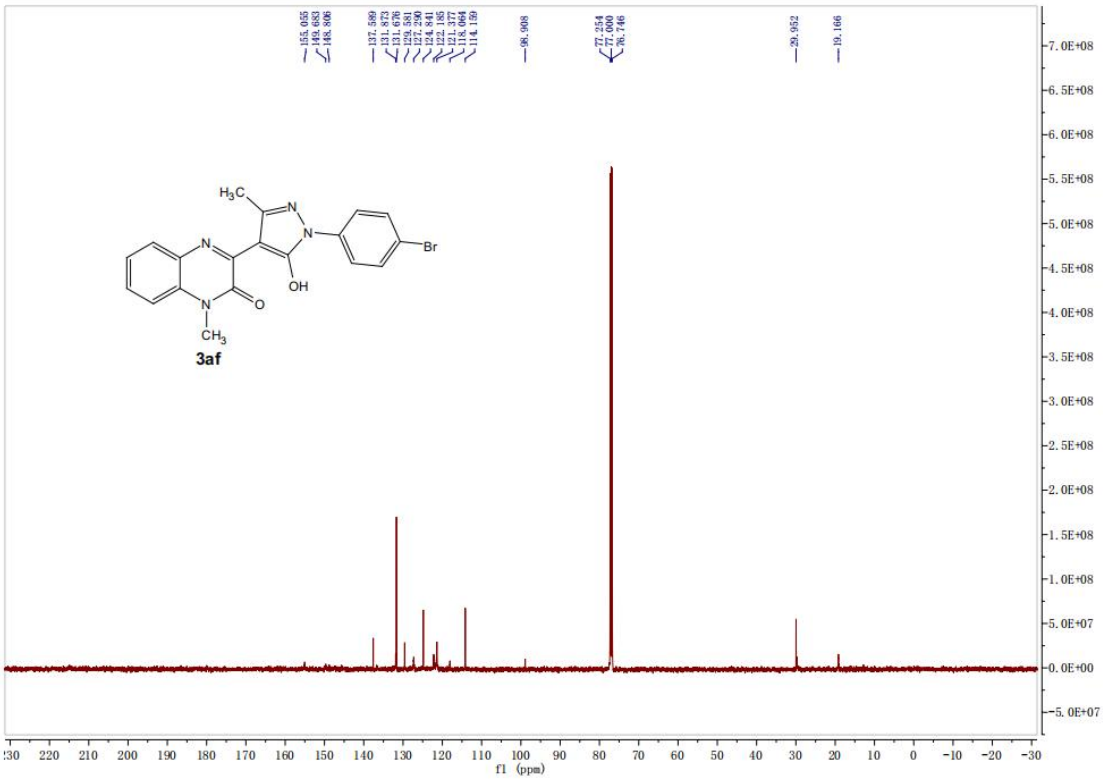

161.084
159.139
155.017
143.397
145.705
134.580
129.501
127.775
124.750
122.678
122.614
121.922
121.865
115.436
115.247
114.028
98.697
77.254
77.000
76.745
29.846
18.964
3ad
f1 (ppm)

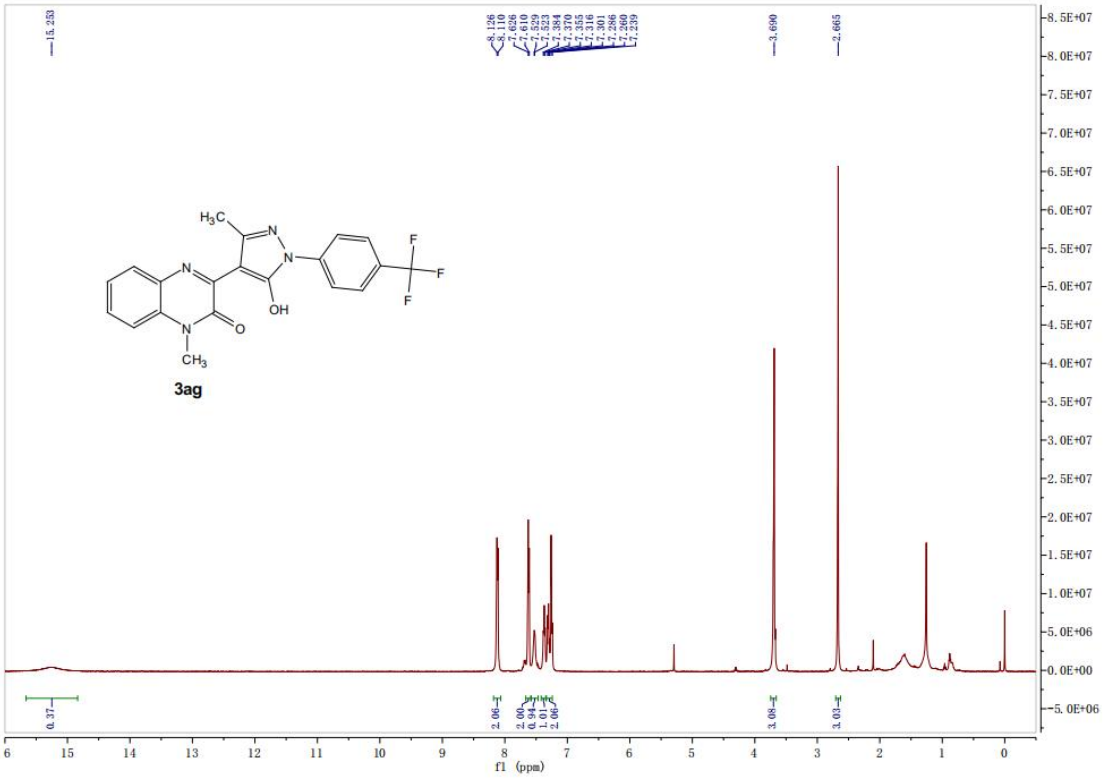

115.073
117.044
3ad
f1 (ppm)

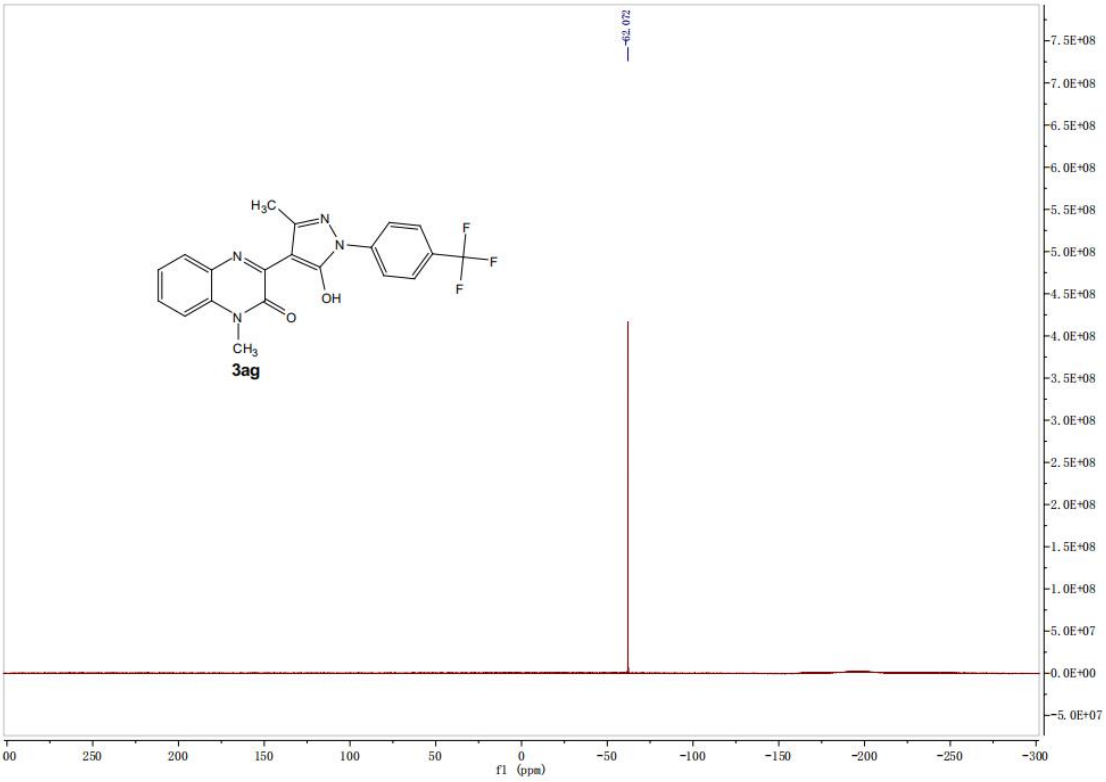

15.083
7.850
7.832
7.463
7.449
7.334
7.309
7.294
7.270
7.253
7.232
7.176
7.160
3.612
2.586
3ae
0.33
1.90
0.93
4.00
1.00
2.91
2.96
f1 (ppm)

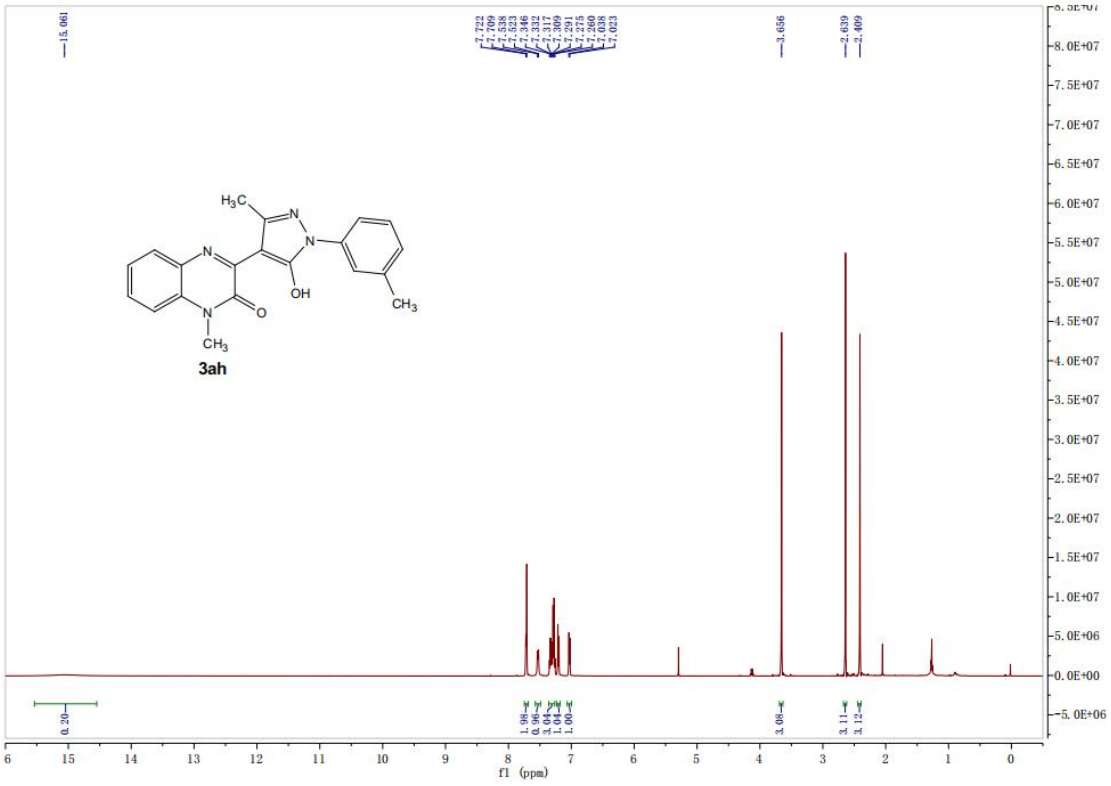

154.869
149.470
145.148
137.045
129.998
128.951
128.501
127.134
124.707
120.772
114.049
98.704
77.254
77.000
76.746
29.828
19.173
H3C
N
N
Cl
OH
N
O
CH3
3ae
f1 (ppm)

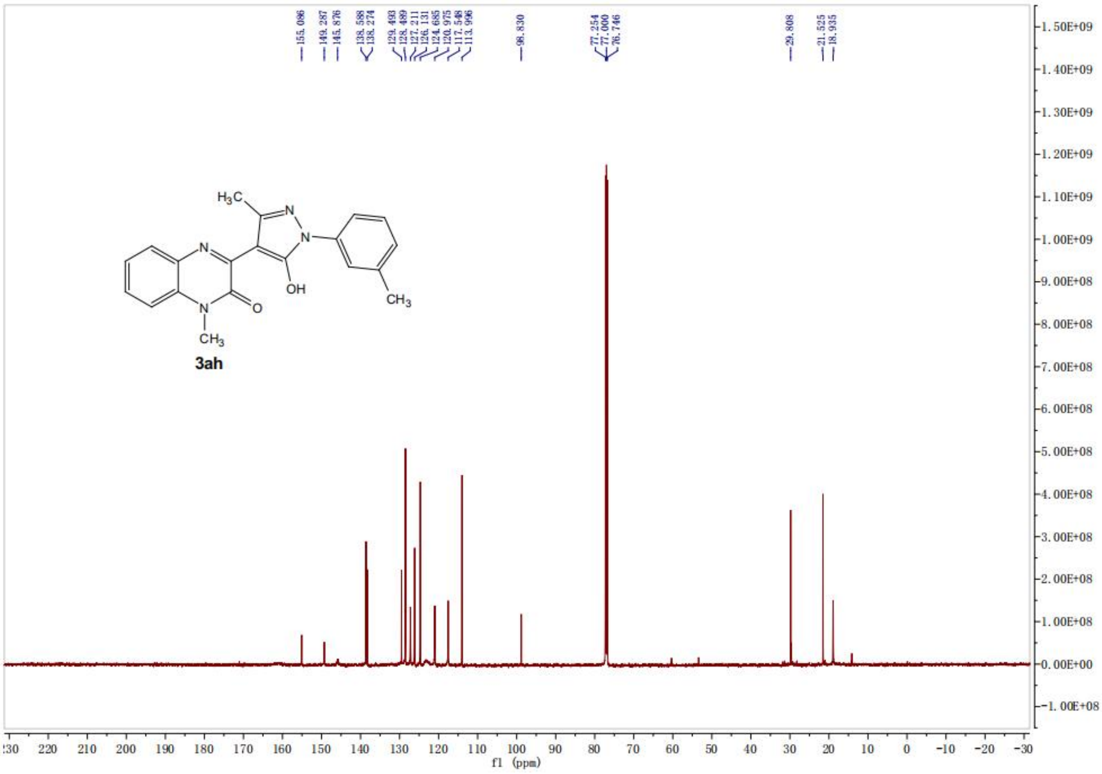

15.150
7.858
7.841
7.543
7.525
7.510
7.482
7.465
7.394
7.379
7.364
7.323
7.308
7.293
7.269
7.260
7.253
3.700
2.650
H3C
N
N
Br
OH
N
O
CH3
3af
0.18
1.97
1.03
1.00
1.00
0.98
1.16
2.95
2.98
f1 (ppm)

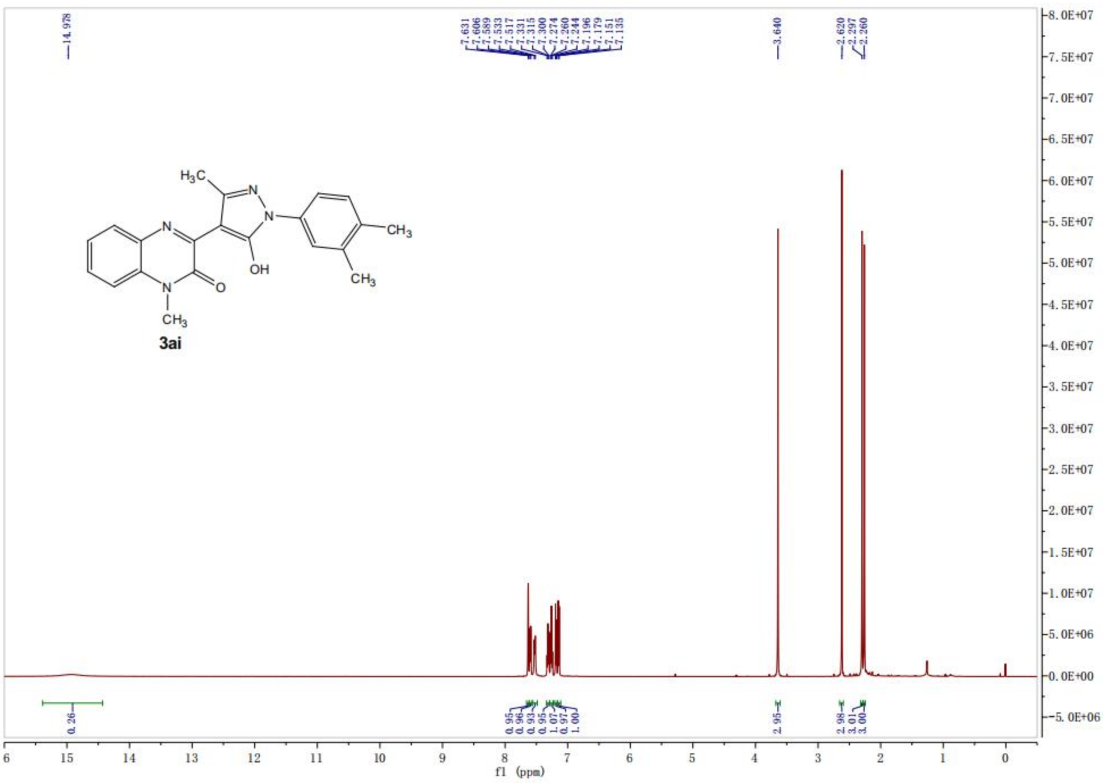

155.055
149.953
148.806
137.589
131.873
131.676
129.581
127.290
124.641
122.955
121.377
118.064
114.159
96.908
77.254
77.000
76.746
29.952
19.166
H_3C
N
N
Br
OH
O
N
CH_3
3af
7.0E+08
6.5E+08
6.0E+08
5.5E+08
5.0E+08
4.5E+08
4.0E+08
3.5E+08
3.0E+08
2.5E+08
2.0E+08
1.5E+08
1.0E+08
5.0E+07
0.0E+00
-5.0E+07
f1 (ppm)

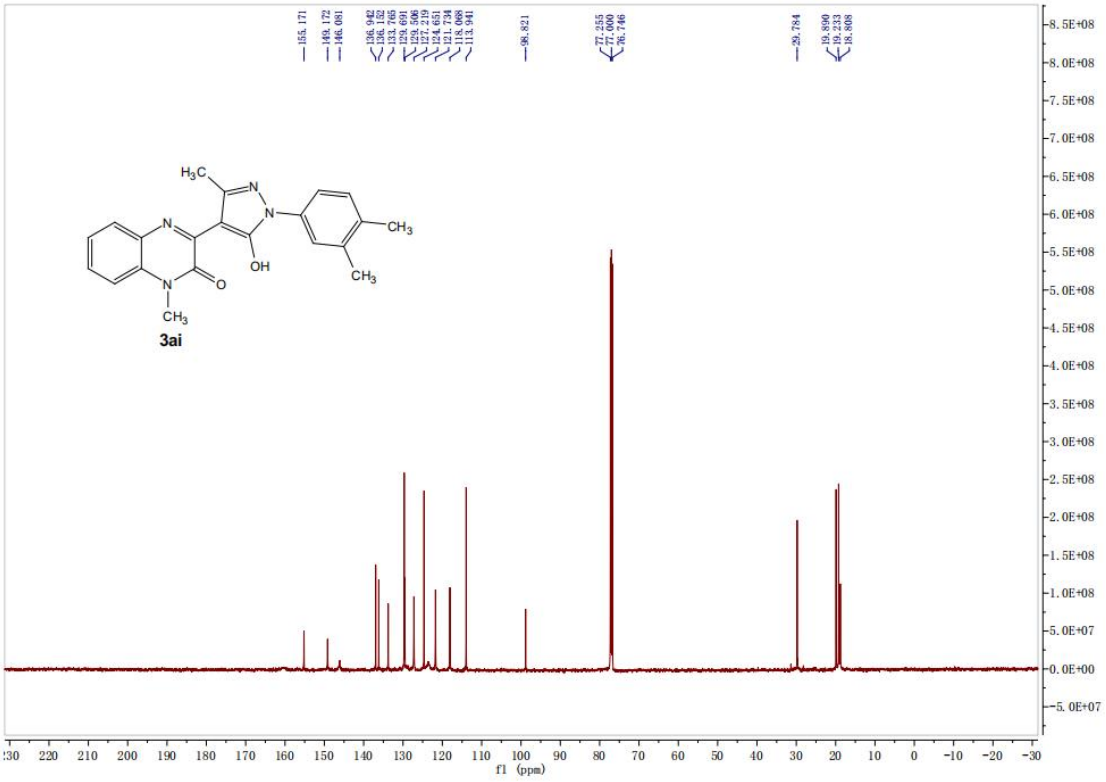

15.253
8.126
8.110
7.616
7.610
7.529
7.523
7.384
7.378
7.355
7.316
7.301
7.286
7.260
7.239
3.690
2.665
H_3C
N
N
F
F
F
OH
O
N
CH_3
3ag
0.37
2.06
2.00
0.94
1.01
2.06
3.08
3.03
8.5E+07
8.0E+07
7.5E+07
7.0E+07
6.5E+07
6.0E+07
5.5E+07
5.0E+07
4.5E+07
4.0E+07
3.5E+07
3.0E+07
2.5E+07
2.0E+07
1.5E+07
1.0E+07
5.0E+06
0.0E+00
-5.0E+06
f1 (ppm)

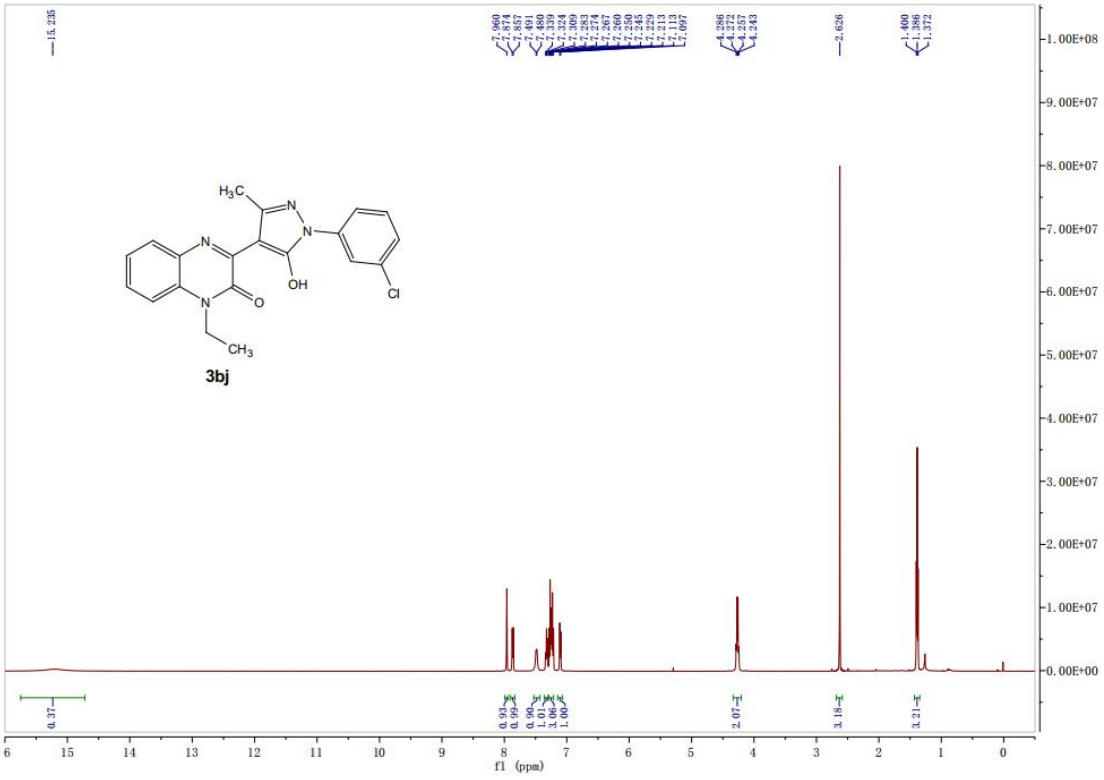

-62.072
3ag
f1 (ppm)

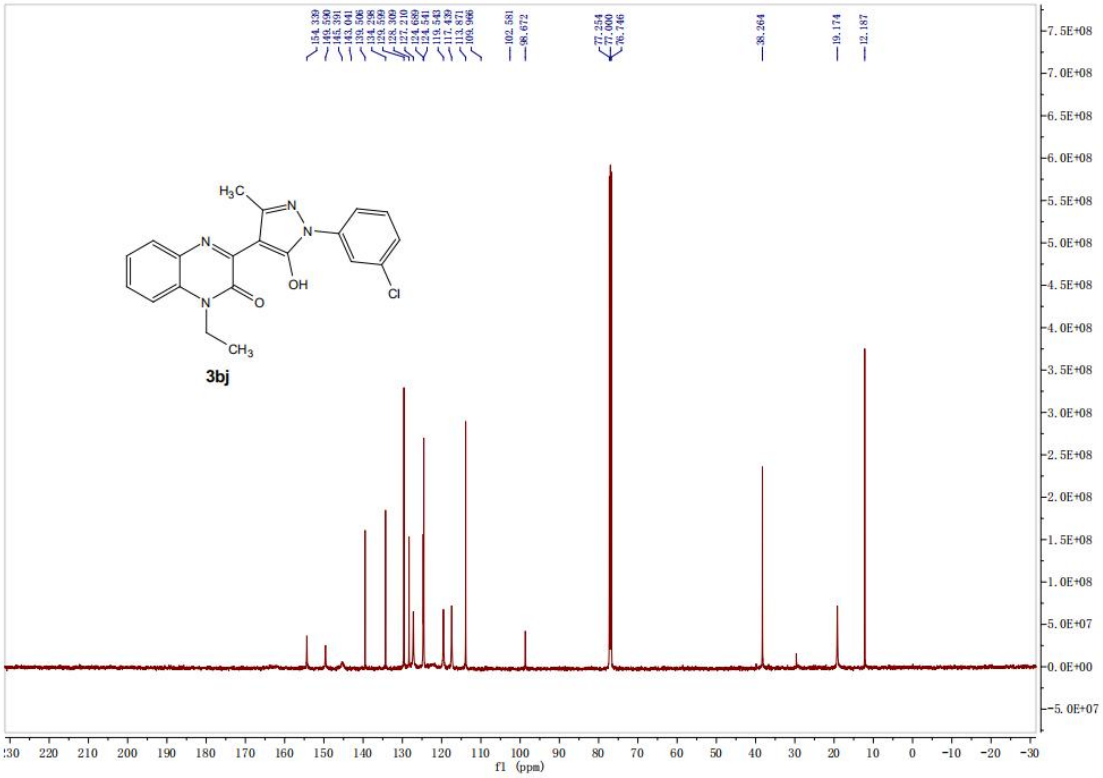

15.061
7.722
7.709
7.538
7.523
7.346
7.332
7.317
7.309
7.291
7.275
7.260
7.038
7.023
3.656
2.639
2.409
3ah
f1 (ppm)

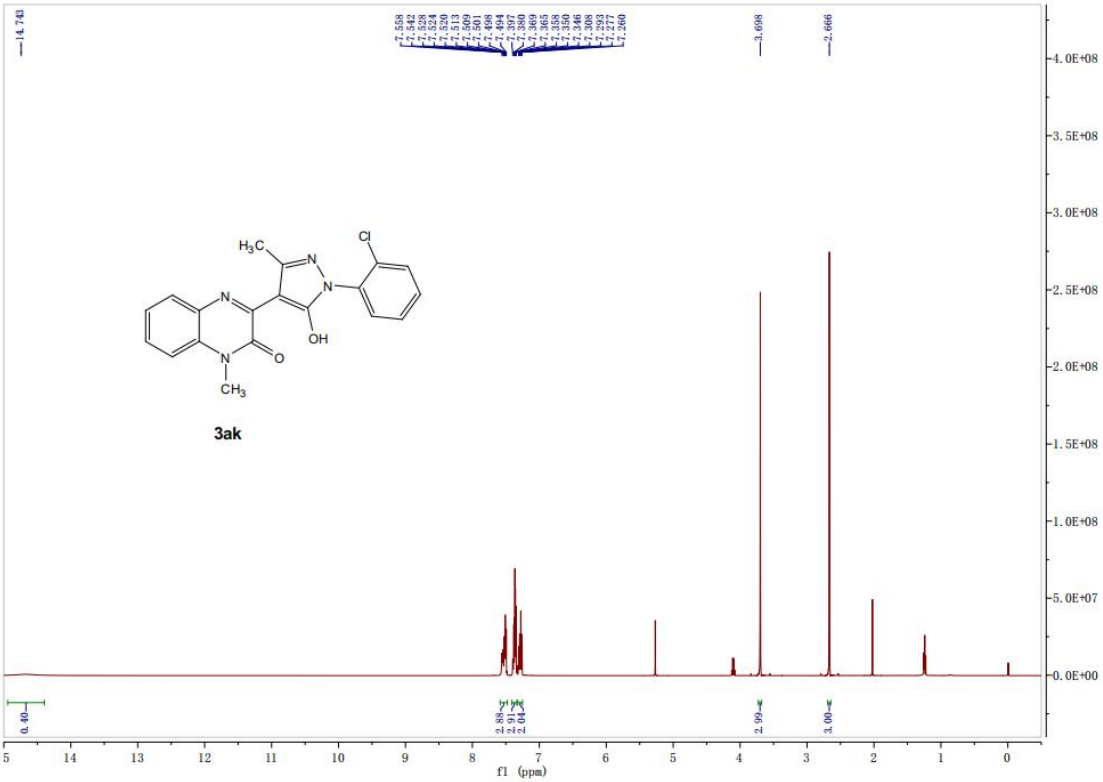

3ah
f1 (ppm)

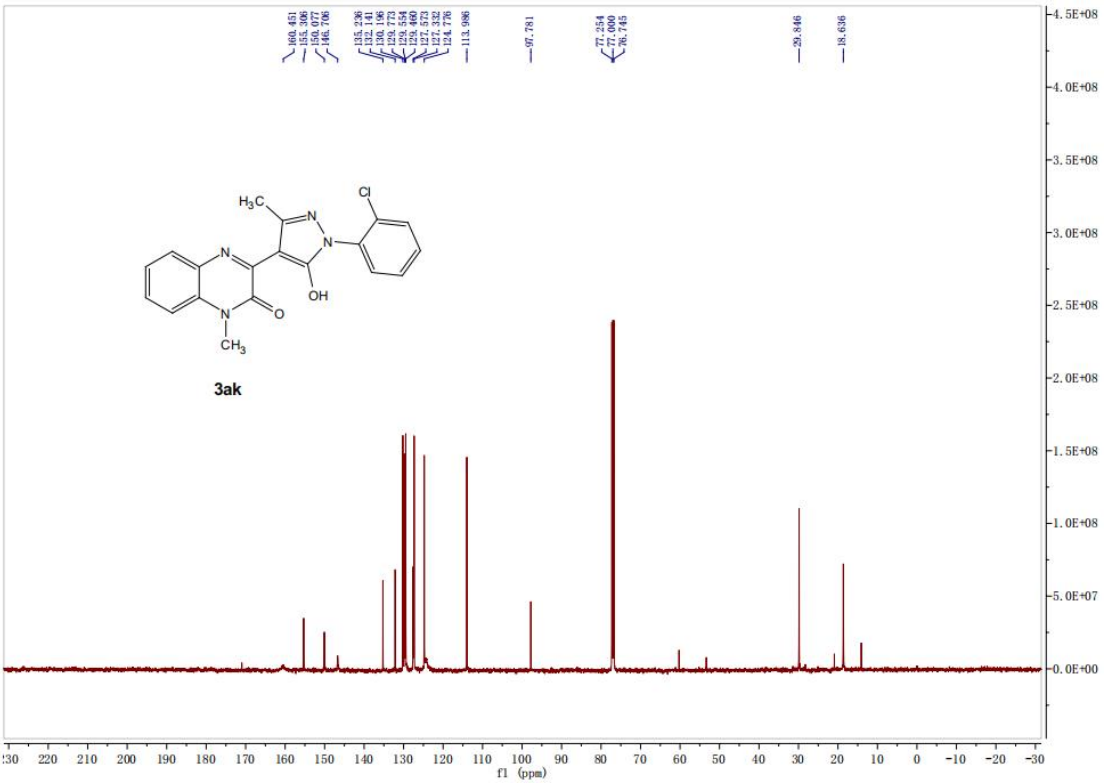

3ai
f1 (ppm)

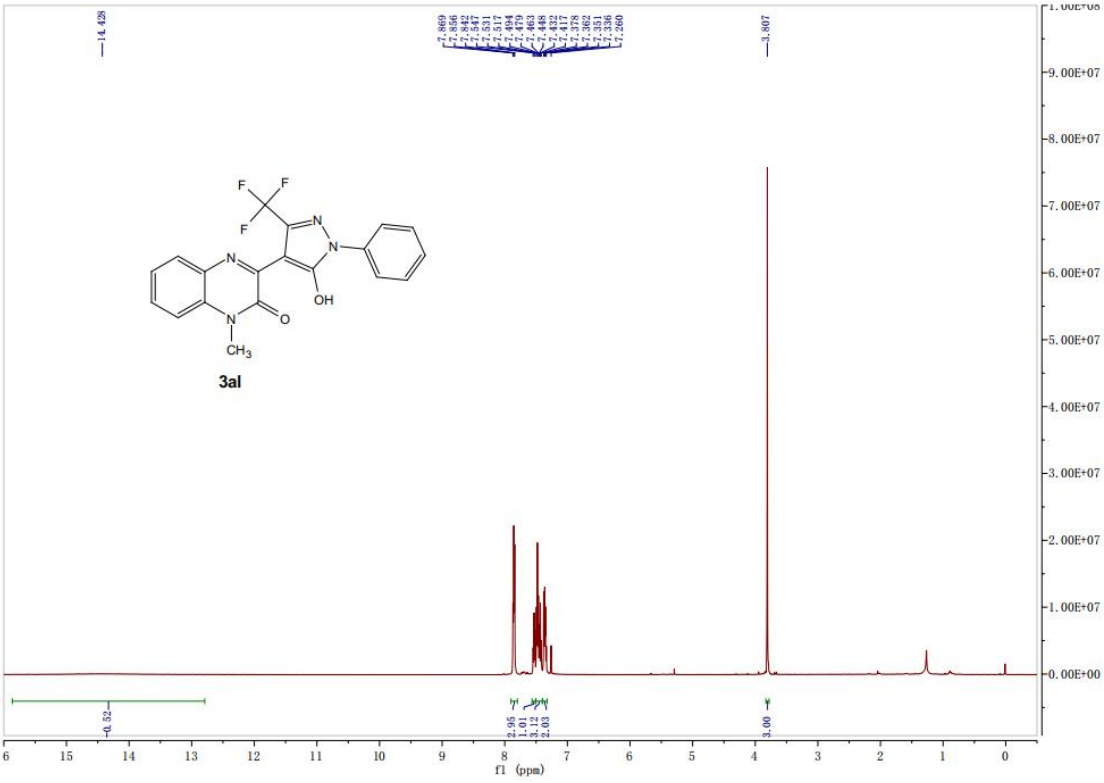

155.171
149.172
146.081
136.942
136.132
133.765
129.691
129.068
127.219
124.651
121.734
118.606
113.941
98.821
77.255
77.000
76.746
29.784
19.899
19.233
18.606
3ai

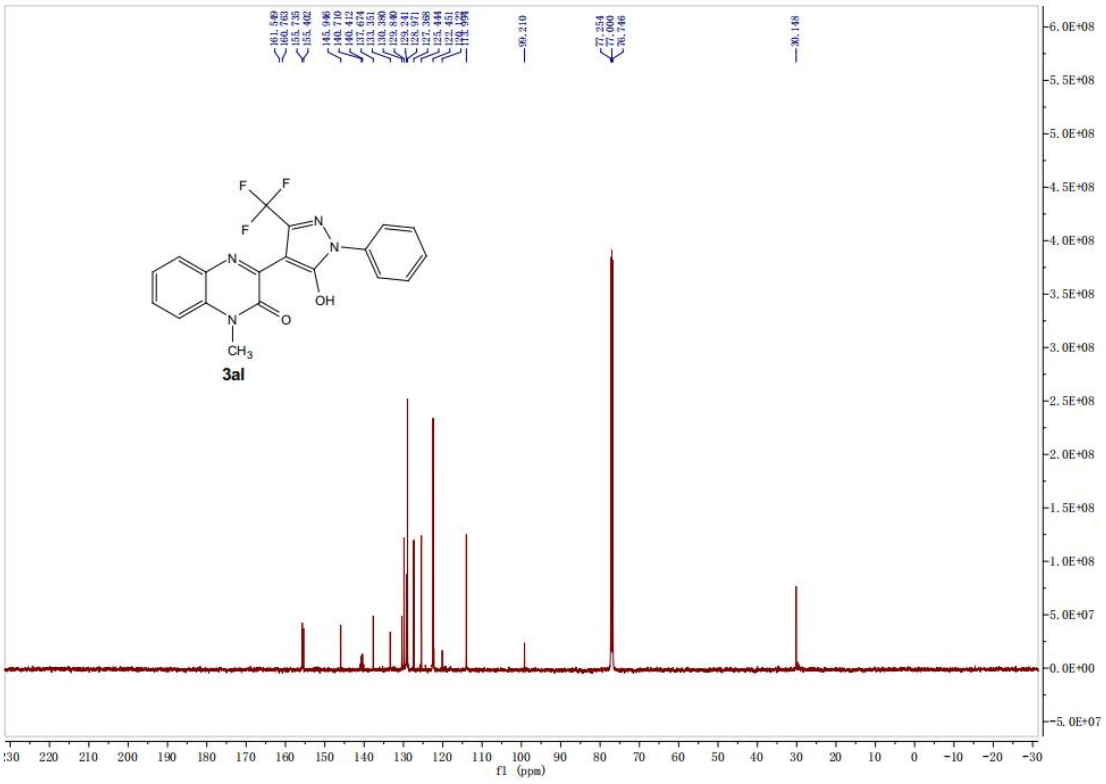

15.235
7.960
7.874
7.857
7.491
7.460
7.339
7.324
7.309
7.283
7.274
7.267
7.260
7.250
7.245
7.229
7.213
7.113
7.097
4.286
4.272
4.257
4.243
2.626
1.400
1.386
1.372
0.37
0.93
0.99
0.90
1.01
1.86
1.00
2.07
3.18
3.21
3bj

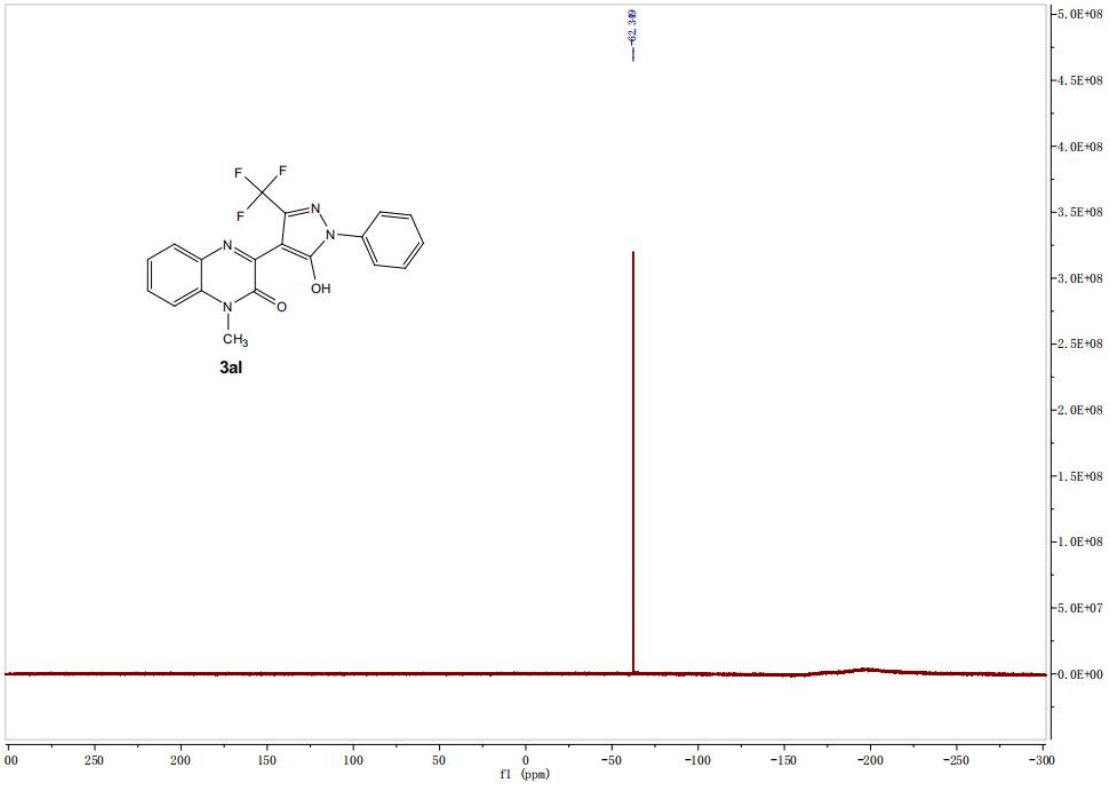

154.339
149.590
145.391
143.041
138.906
134.298
129.599
128.309
127.210
124.649
124.541
119.543
117.439
113.871
108.986
102.581
98.672
77.254
77.000
76.746
38.264
19.174
12.187
3bj
f1 (ppm)

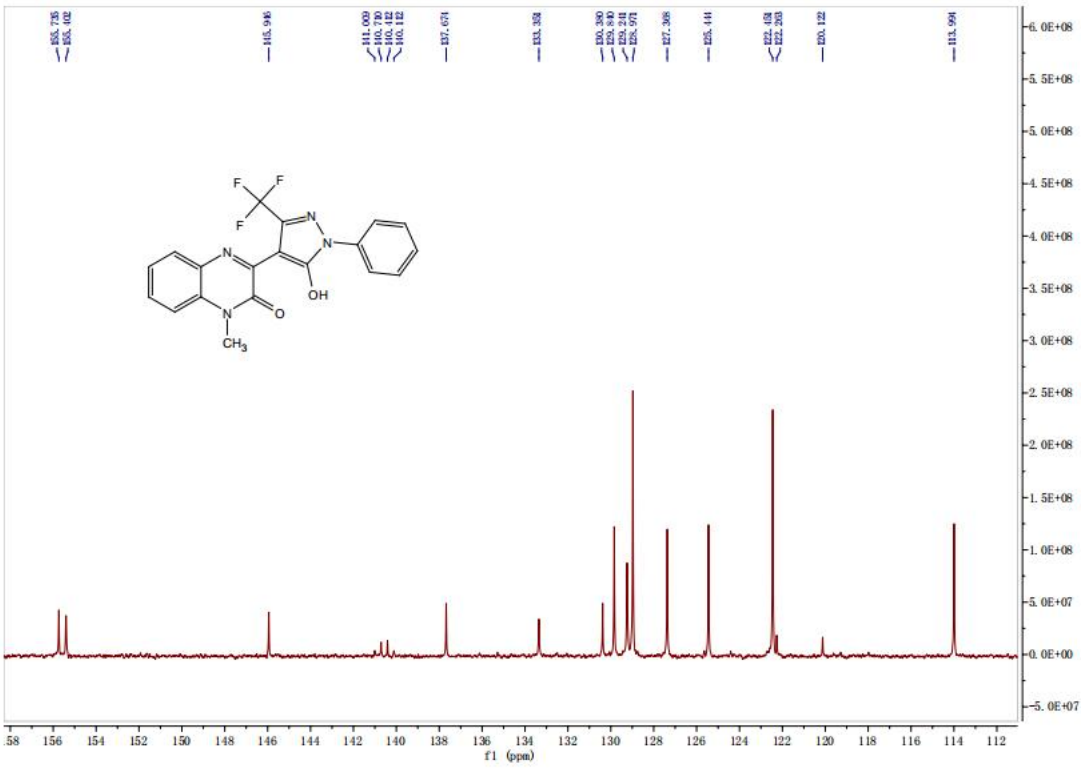

14.743
7.558
7.542
7.528
7.524
7.520
7.513
7.509
7.501
7.498
7.494
7.377
7.369
7.365
7.358
7.350
7.346
7.308
7.293
7.277
7.260
3.698
2.666
3ak
f1 (ppm)

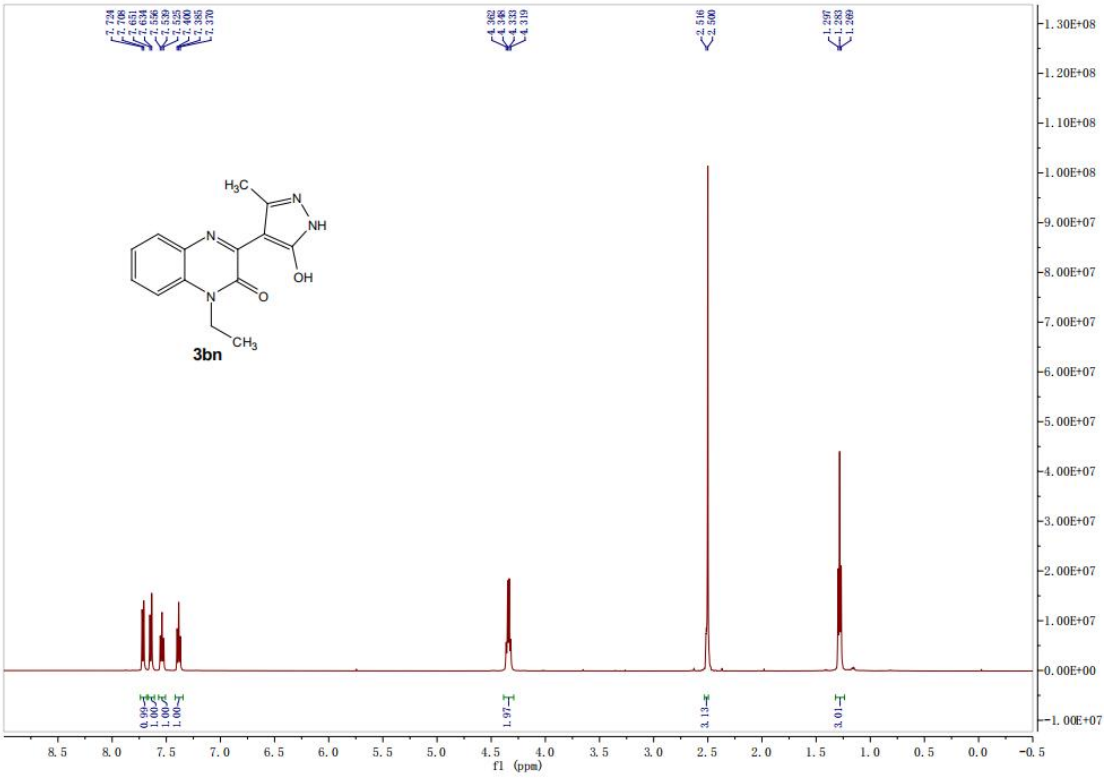

160.451
155.306
150.077
146.706
135.236
132.141
130.196
129.773
129.554
129.460
127.573
127.332
124.776
113.986
97.781
77.254
77.000
76.745
29.846
18.636
H3C
N
Cl
N
OH
N
O
CH3
3ak
f1 (ppm)

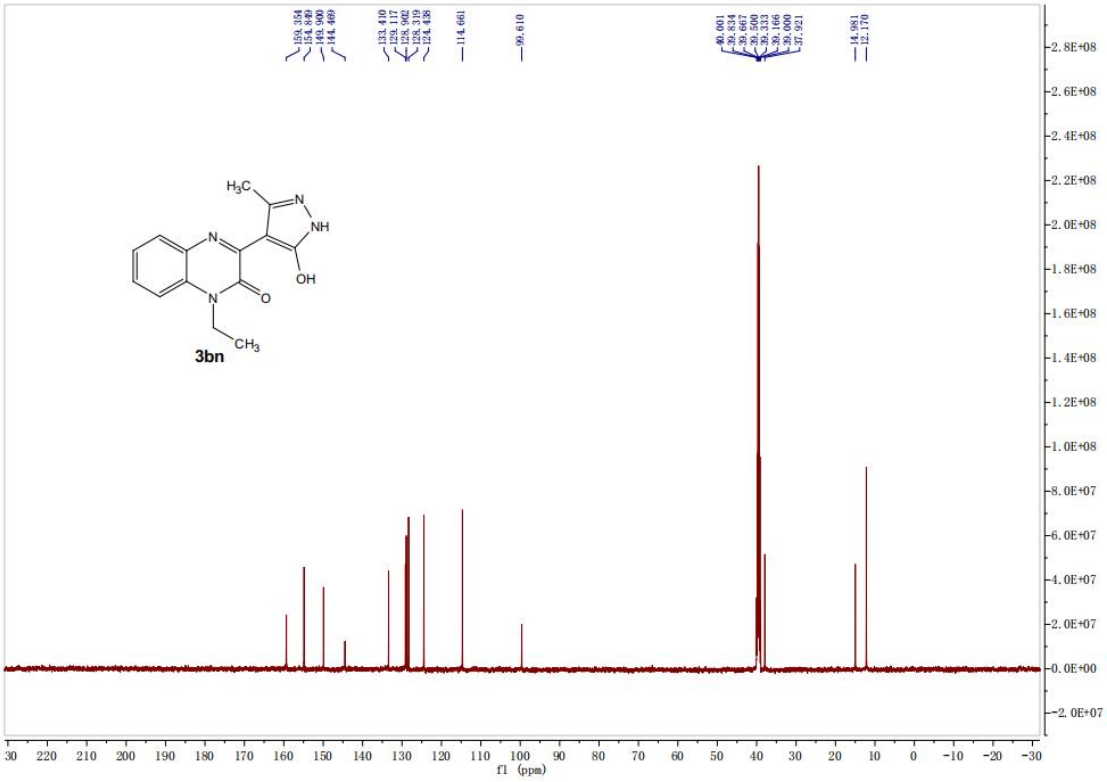

14.428
7.869
7.856
7.842
7.547
7.531
7.517
7.494
7.479
7.463
7.448
7.432
7.417
7.378
7.362
7.351
7.336
7.260
3.807
F
F
F
N
N
OH
N
O
CH3
3al
0.52
2.95
1.01
3.12
2.03
3.00
f1 (ppm)

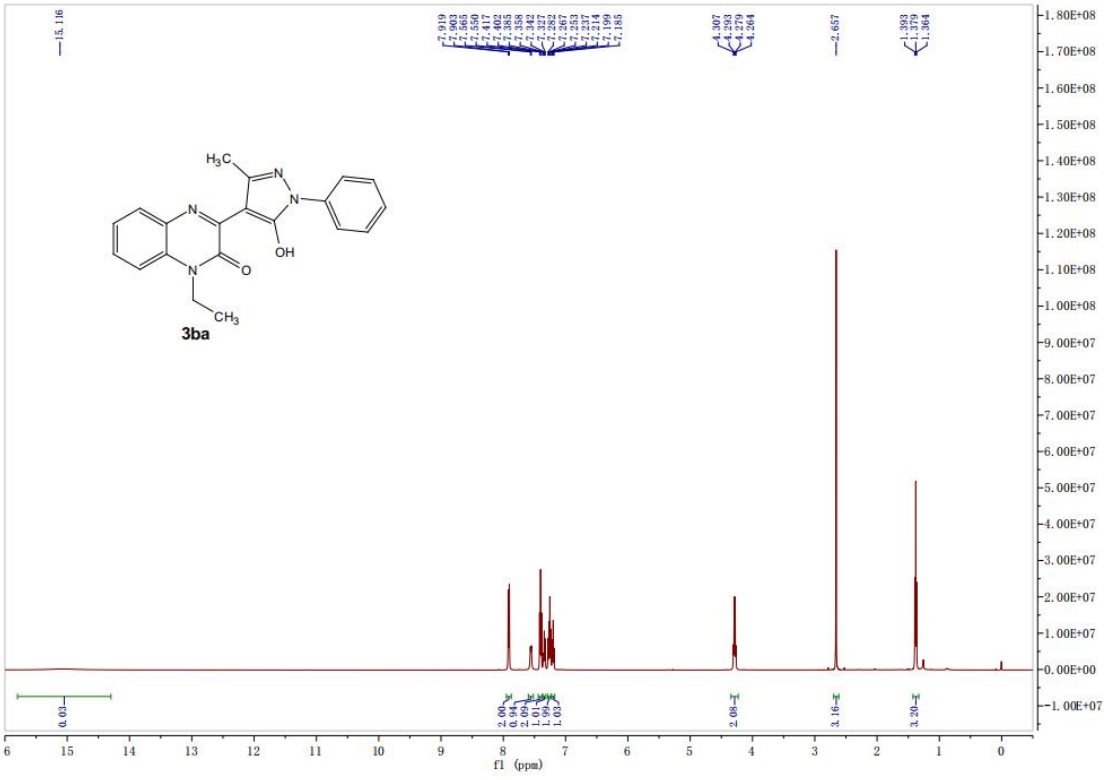

3al
f1 (ppm)

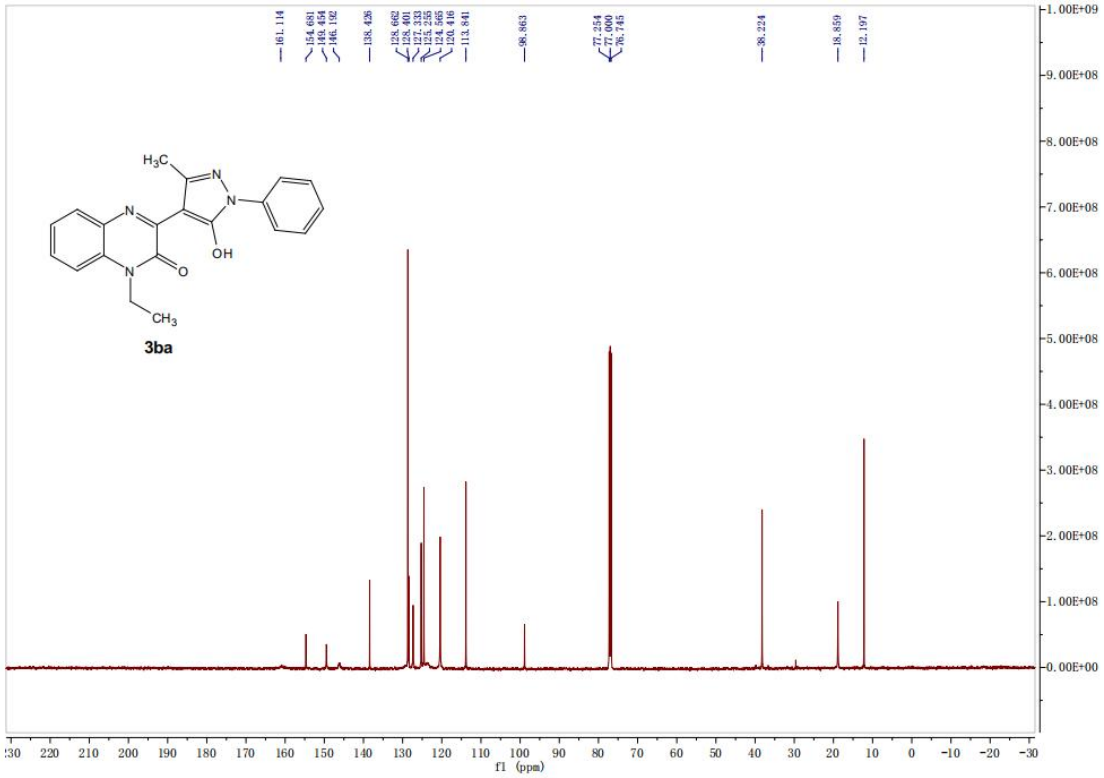

3al
f1 (ppm)

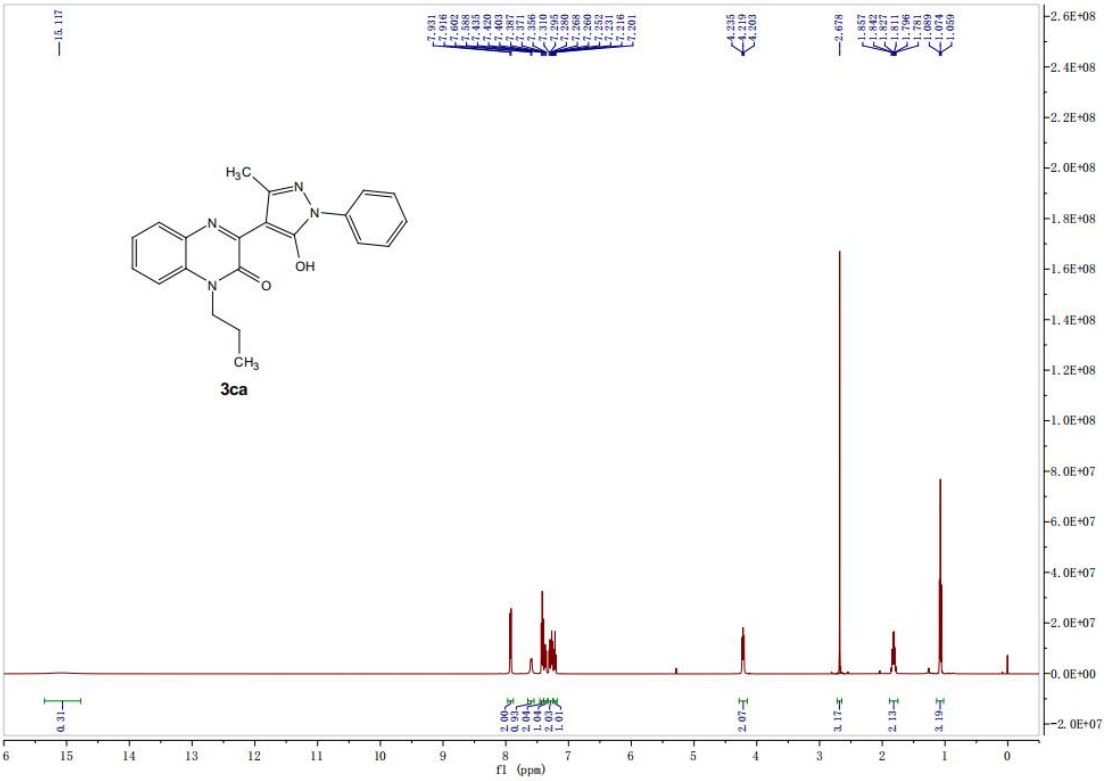

F
F
F
N
N
OH
N
O
CH3
f1 (ppm)

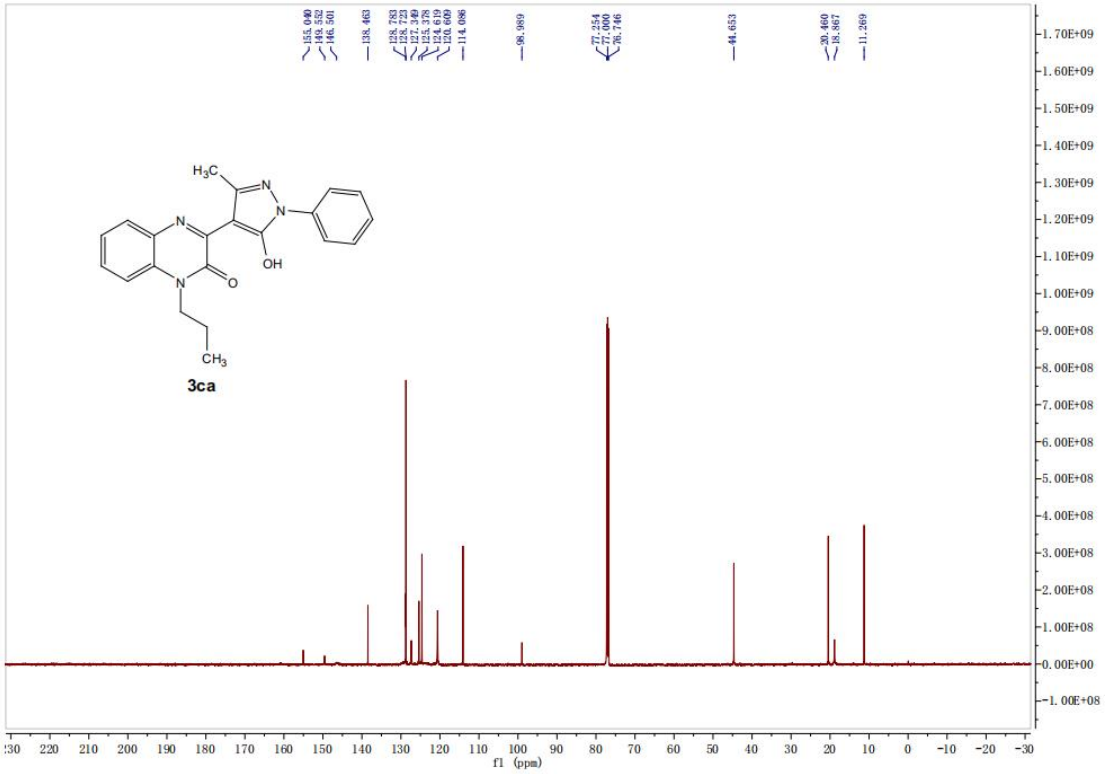

H3C
N
NH
OH
N
O
CH3
3bn
f1 (ppm)

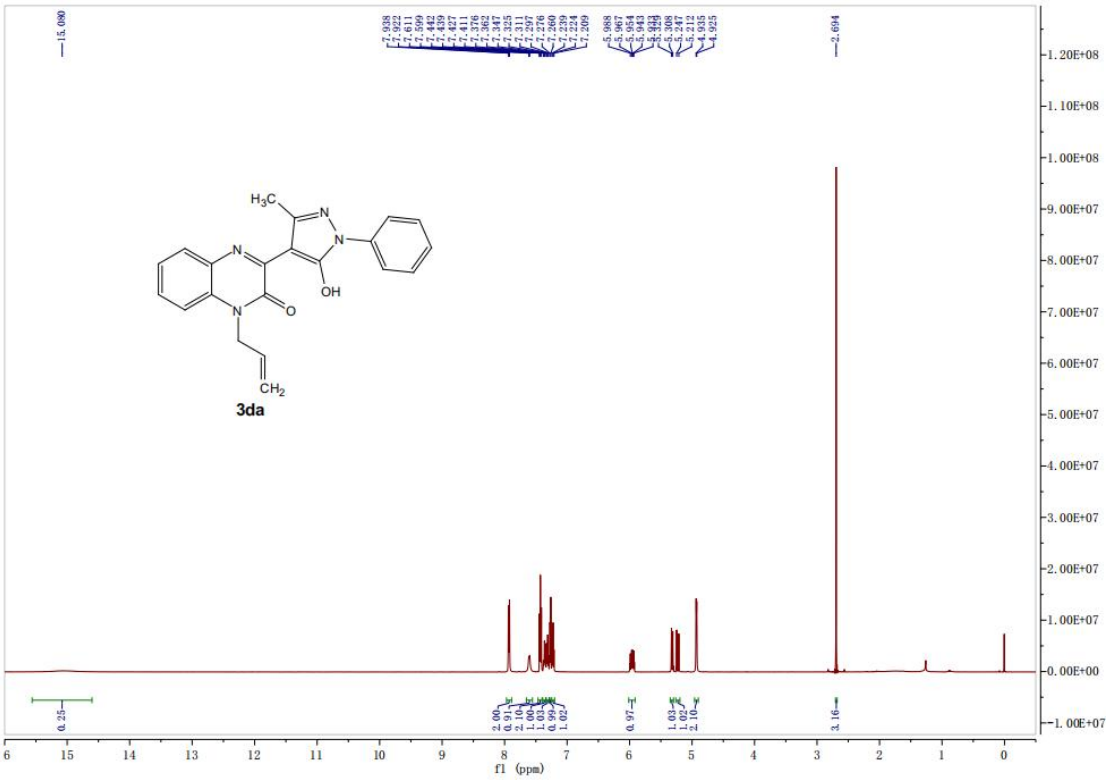

159.354
154.949
149.999
144.469
133.410
129.117
128.962
126.310
124.438
114.661
99.610
40.001
39.834
39.667
39.500
39.333
39.166
39.000
37.921
14.981
12.170
3bn
f1 (ppm)

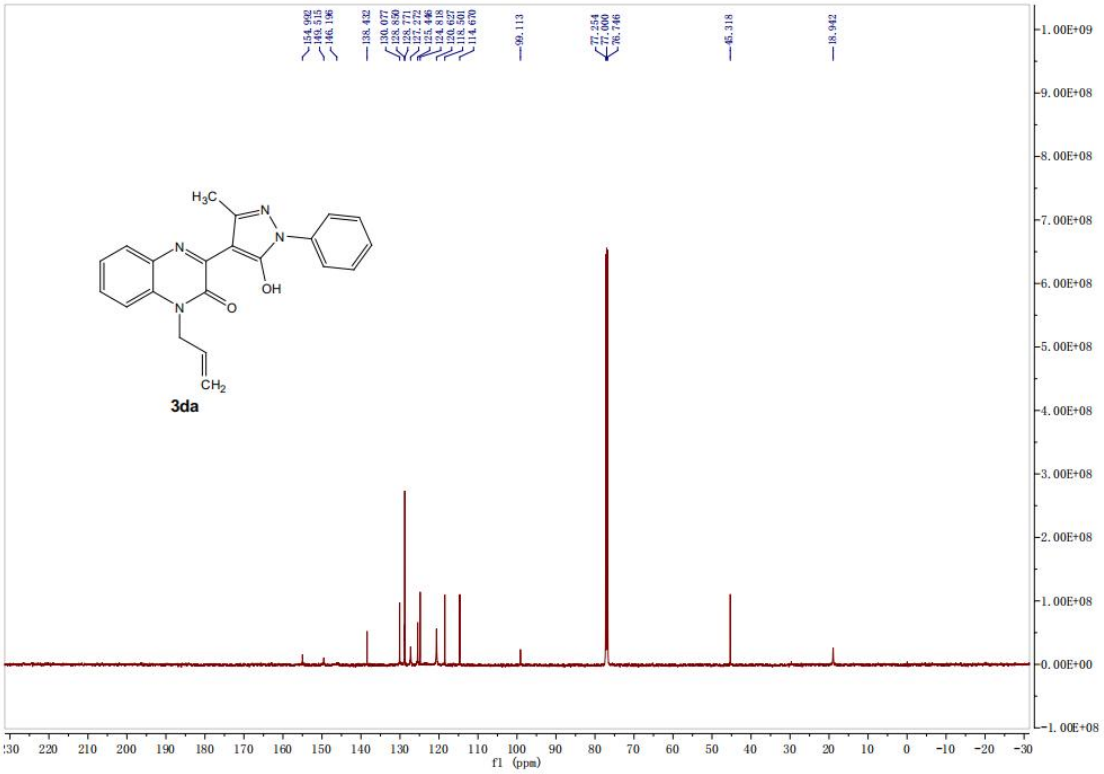

15.116
7.919
7.903
7.565
7.550
7.417
7.402
7.385
7.358
7.342
7.327
7.282
7.267
7.253
7.237
7.214
7.199
7.185
4.307
4.293
4.279
4.264
2.657
1.393
1.379
1.364
0.03
2.00
0.94
2.00
1.01
1.99
1.03
2.08
3.16
3.20
3ba
f1 (ppm)

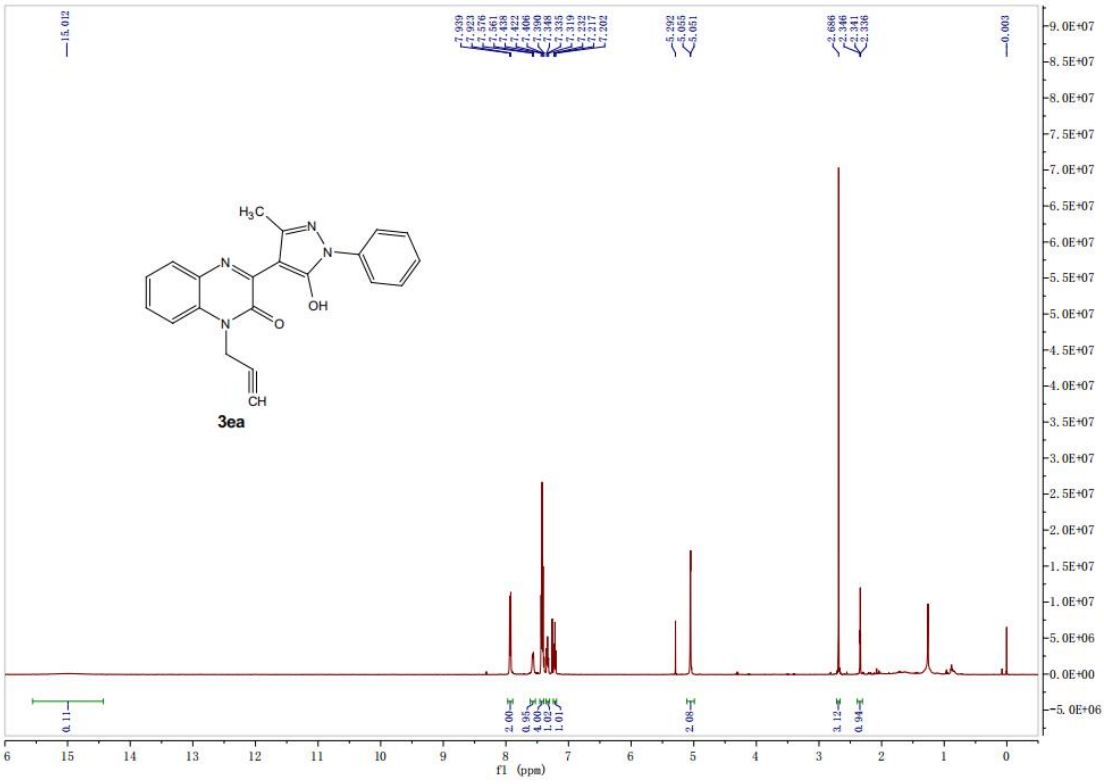

161.114
154.681
149.454
146.192
138.426
128.662
128.401
127.333
125.355
124.566
120.416
113.841
98.863
77.254
77.000
76.745
38.224
18.859
12.197
3ba
f1 (ppm)

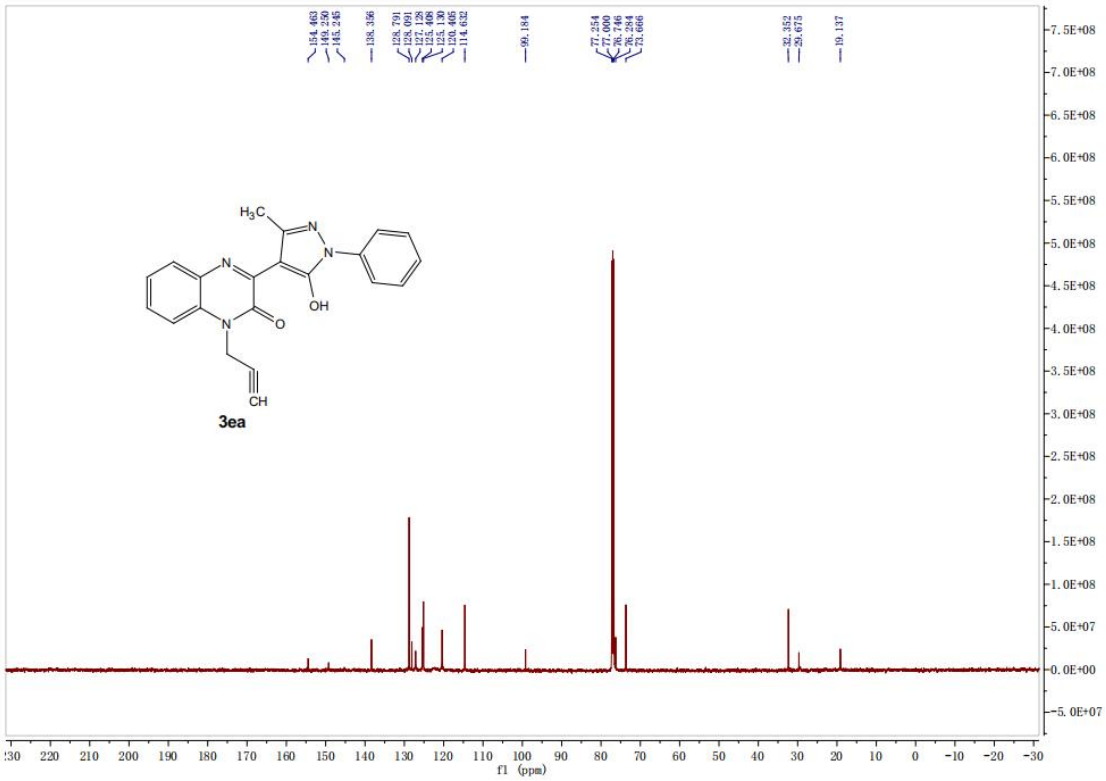

15.117
7.931
7.916
7.602
7.588
7.435
7.420
7.403
7.387
7.371
7.356
7.310
7.295
7.285
7.268
7.260
7.232
7.221
7.216
7.201
4.235
4.219
4.203
2.678
1.857
1.842
1.827
1.811
1.796
1.781
1.089
1.074
1.059
3ca
f1 (ppm)

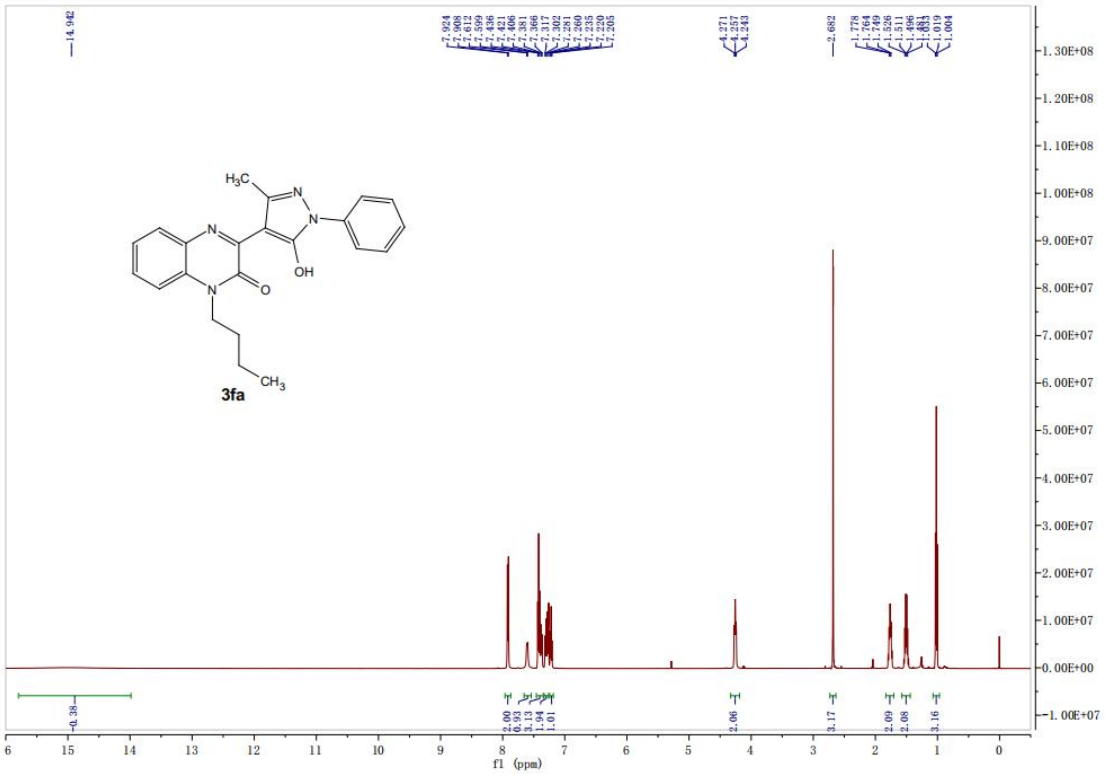

3ca
f1 (ppm)

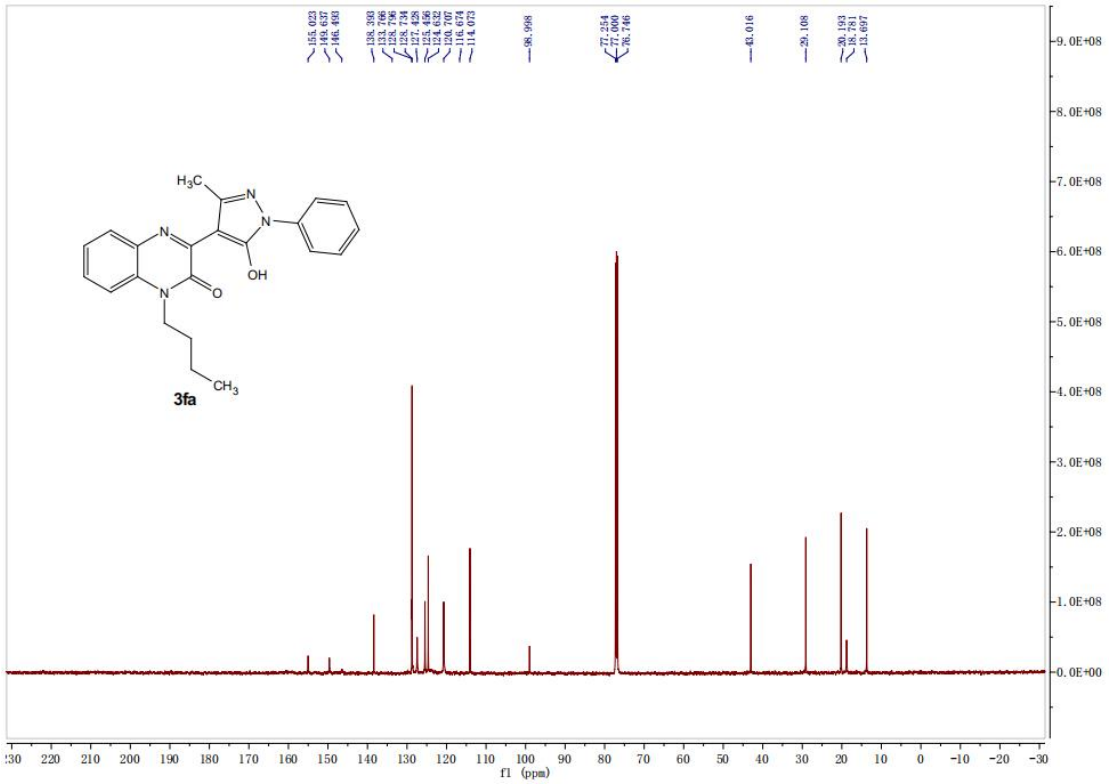

3da
f1 (ppm)

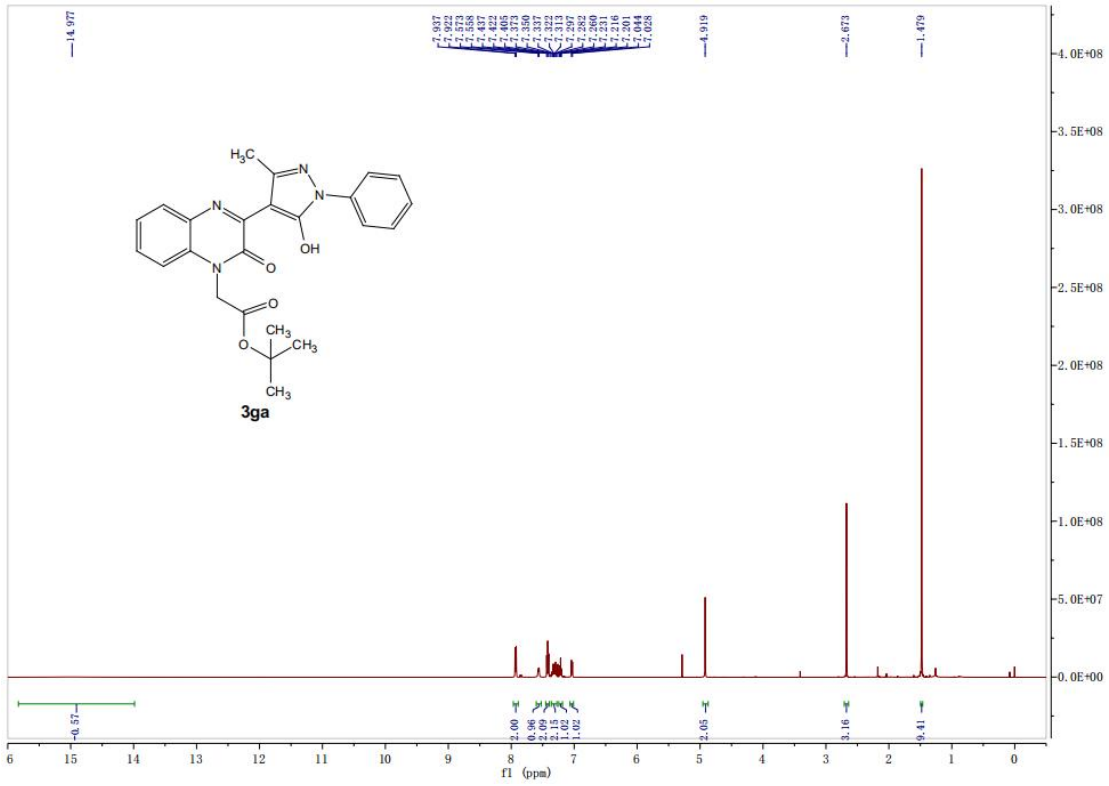

154.992
148.515
146.196
138.432
130.077
128.850
128.771
127.272
125.466
124.838
120.627
118.501
114.670
99.113
77.254
77.000
76.746
45.318
18.942
3da
f1 (ppm)

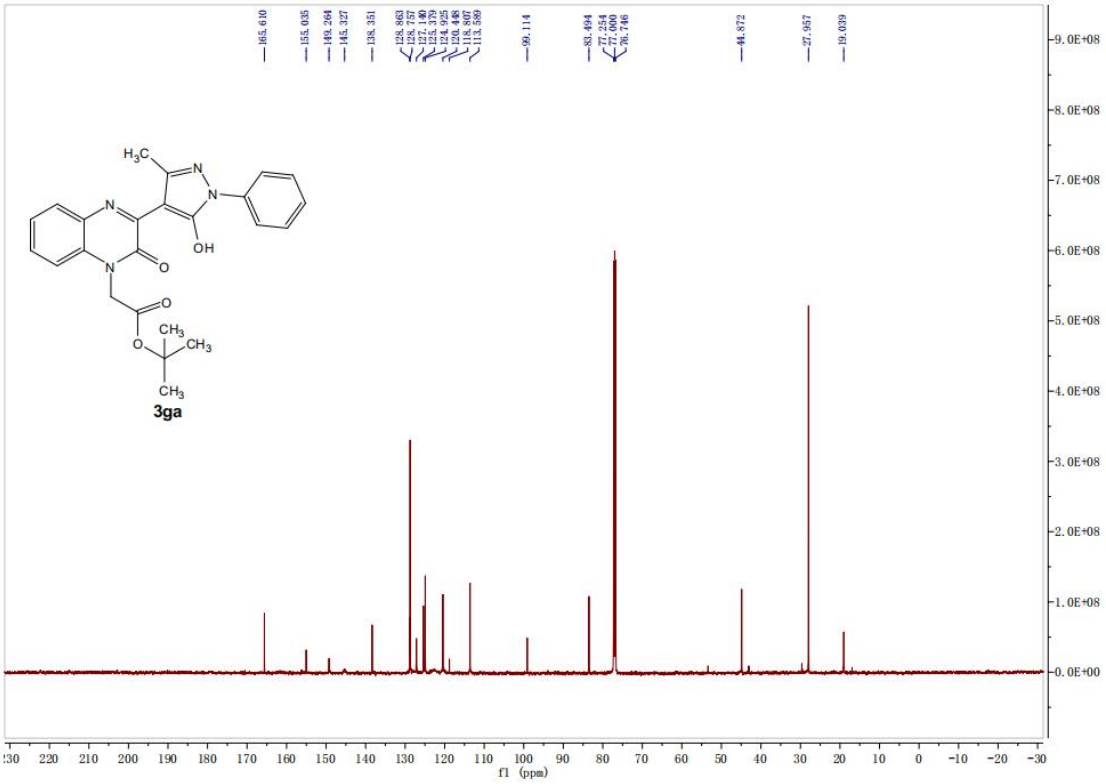

15.012
7.939
7.933
7.576
7.561
7.438
7.422
7.406
7.399
7.348
7.335
7.319
7.232
7.217
7.202
5.292
5.055
5.051
2.686
2.346
2.341
2.336
0.003
0.11
2.00
0.05
4.60
1.02
1.01
2.08
3.12
0.94
3ea
f1 (ppm)

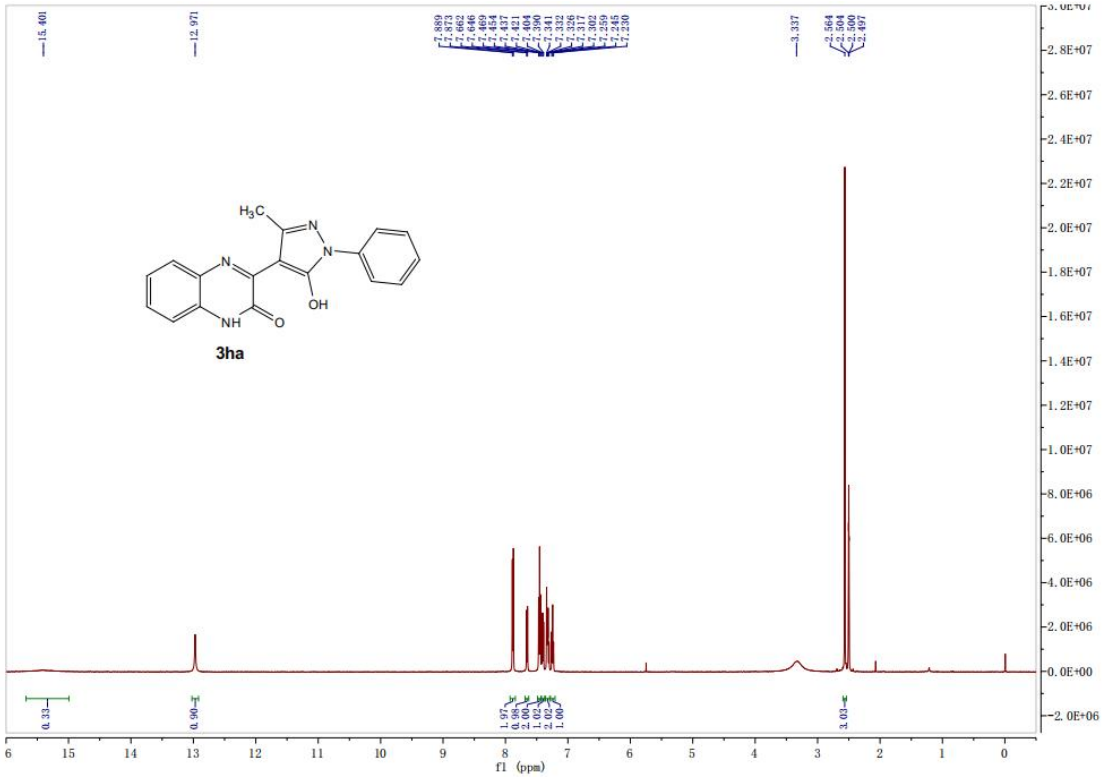

154.463
149.250
145.245
138.356
128.791
128.091
127.128
125.400
125.130
120.405
114.632
90.184
77.254
77.000
76.746
26.284
10.137
3ea
f1 (ppm)

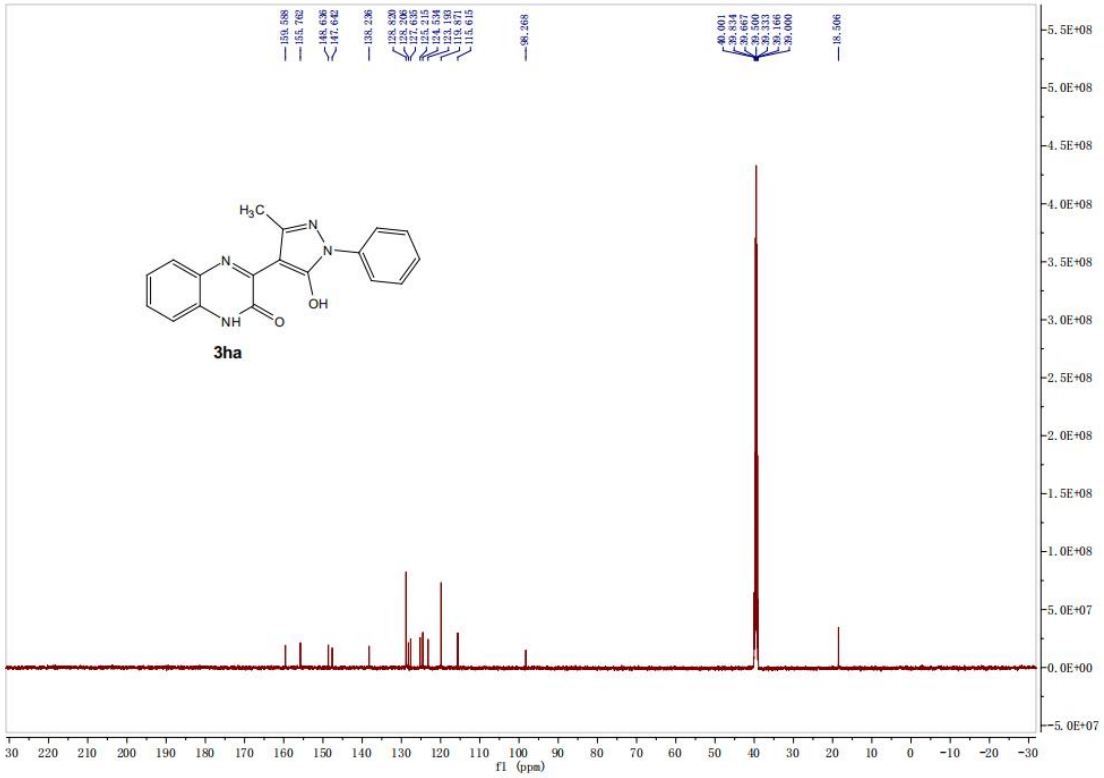

14.942
7.924
7.908
7.612
7.599
7.436
7.421
7.408
7.381
7.366
7.317
7.302
7.281
7.260
7.235
7.220
7.205
4.271
4.257
4.243
2.682
1.778
1.764
1.749
1.526
1.511
1.496
1.019
1.004
0.38
2.00
0.93
3.13
1.94
1.01
2.06
3.17
2.09
2.08
3.16
3fa
f1 (ppm)

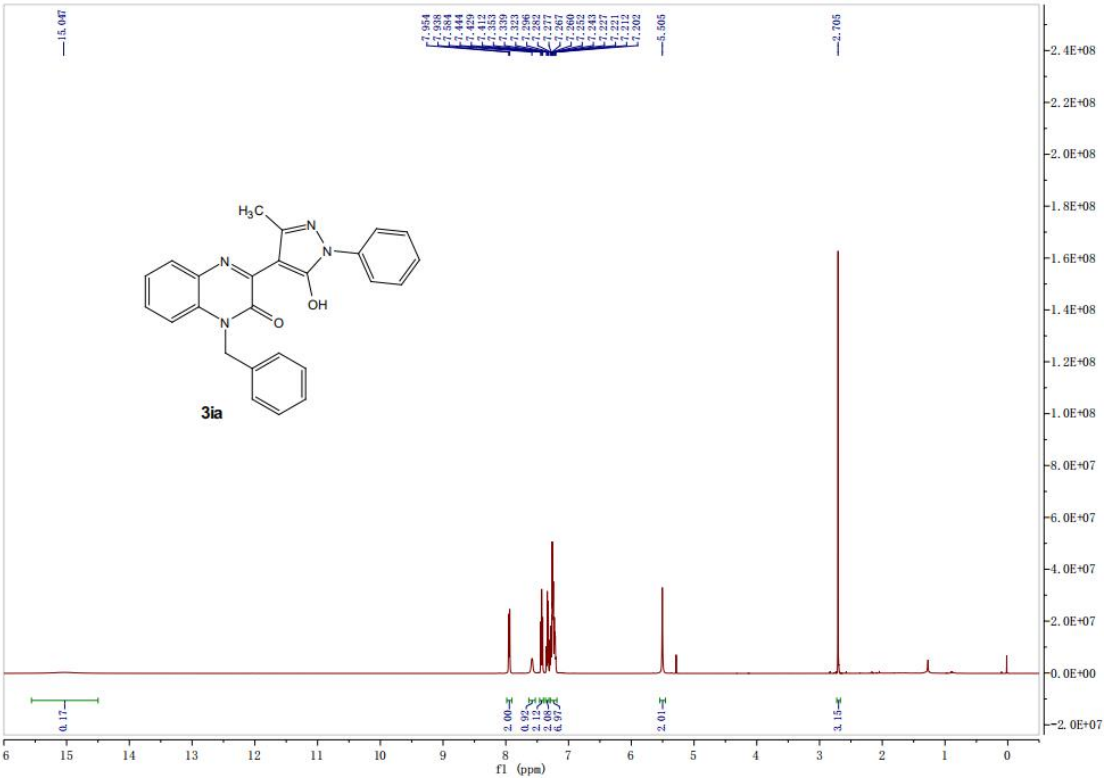

155.023
149.637
146.493
138.393
133.796
128.796
128.734
127.428
125.456
124.632
120.707
116.654
114.073
98.998
77.254
77.000
76.746
43.016
29.108
20.193
18.781
13.697
3fa
f1 (ppm)

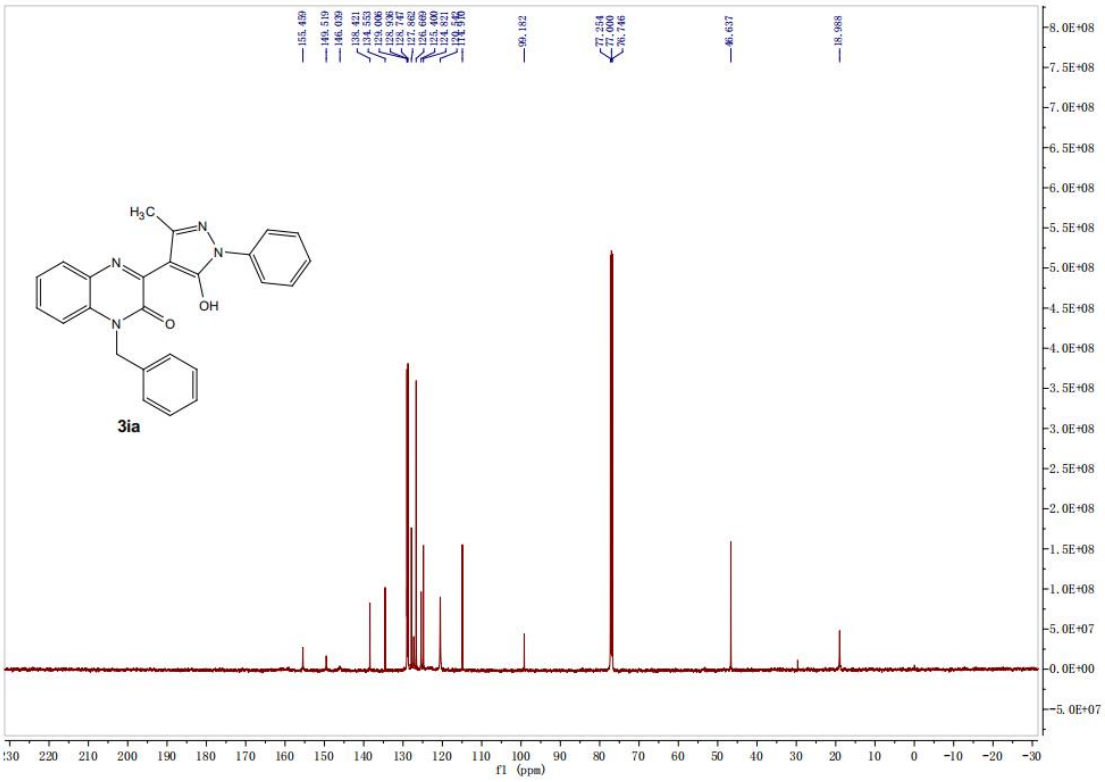

14.977
7.937
7.922
7.523
7.558
7.437
7.422
7.405
7.391
7.350
7.337
7.322
7.313
7.297
7.282
7.260
7.231
7.216
7.201
7.044
7.028
4.919
2.673
1.479
0.57
2.00
0.96
2.09
2.15
1.02
1.02
2.05
3.16
9.41
3ga
f1 (ppm)

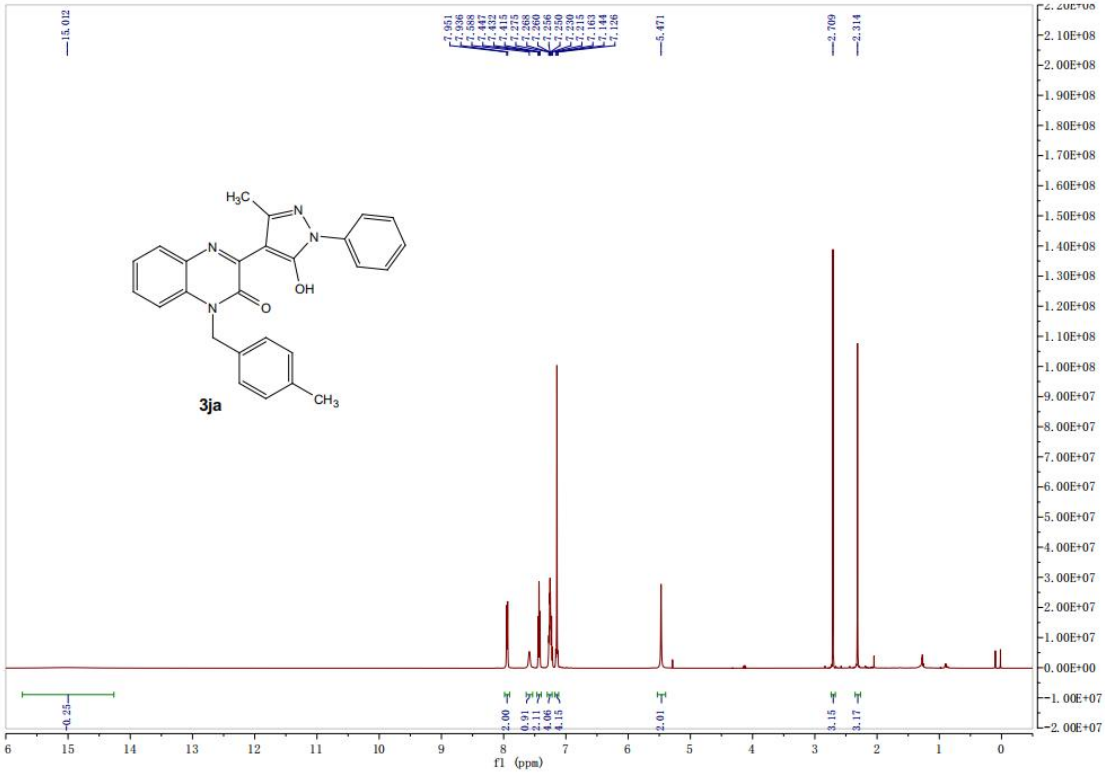

165.610
155.035
149.264
145.327
138.351
128.863
128.757
127.140
125.379
124.695
120.448
118.807
113.589
99.114
83.494
77.254
77.000
76.746
44.872
27.957
19.039
3ga
f1 (ppm)

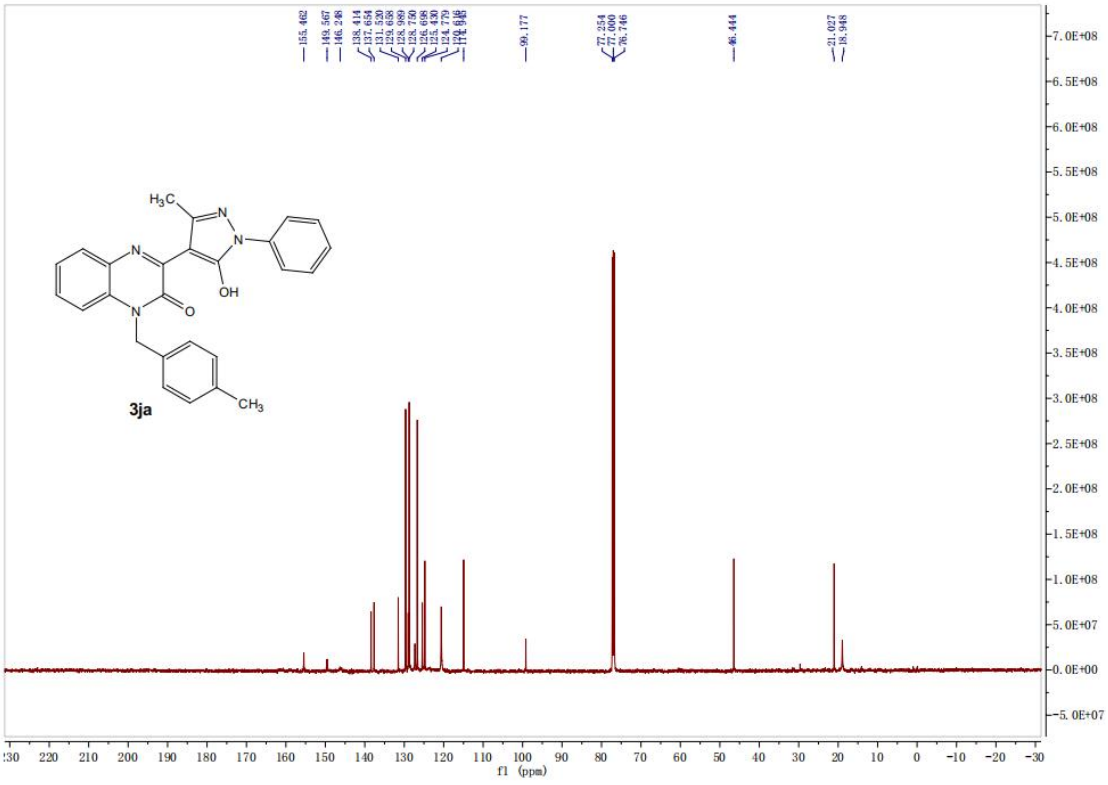

15.401
12.971
7.889
7.873
7.662
7.646
7.469
7.454
7.437
7.421
7.404
7.399
7.341
7.332
7.326
7.317
7.302
7.259
7.245
7.230
3.337
2.564
2.504
2.500
2.497
0.33
0.90
1.97
0.98
2.00
1.02
2.02
1.00
3.03
3ha
f1 (ppm)

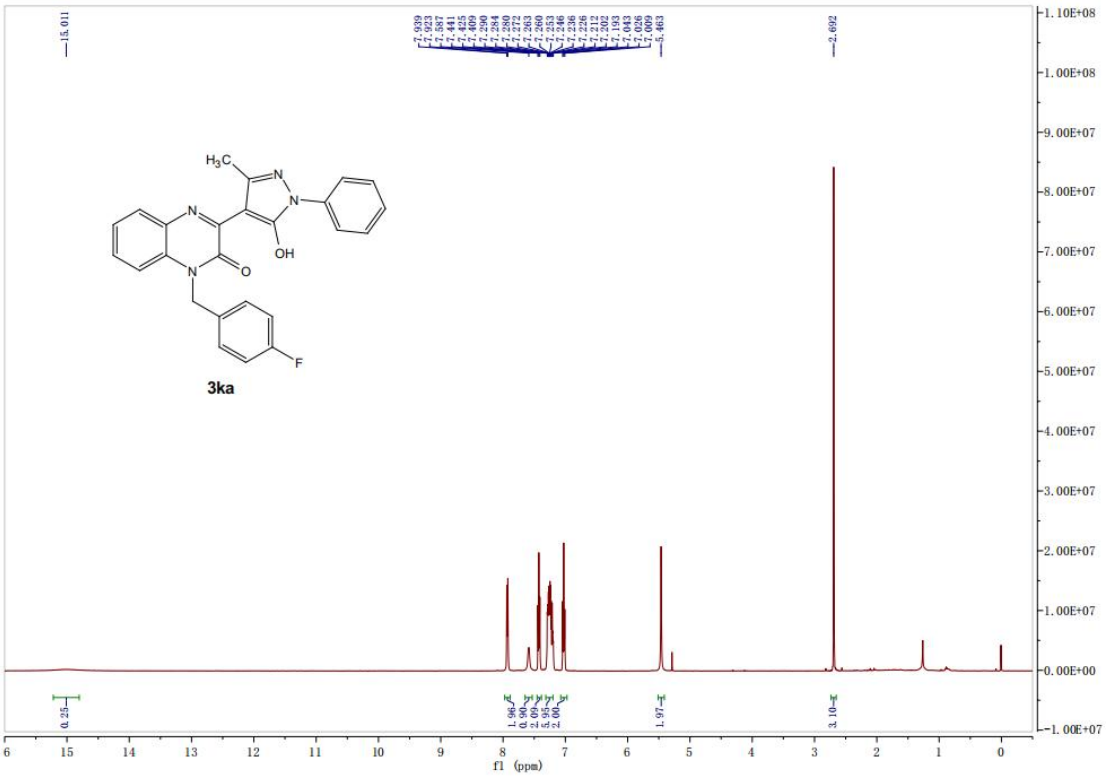

159.588
155.762
148.636
147.642
138.236
128.820
128.206
127.685
125.215
124.534
123.193
119.871
116.615
98.268
40.001
39.834
39.667
39.500
39.333
39.166
39.000
18.506
3ha
f1 (ppm)

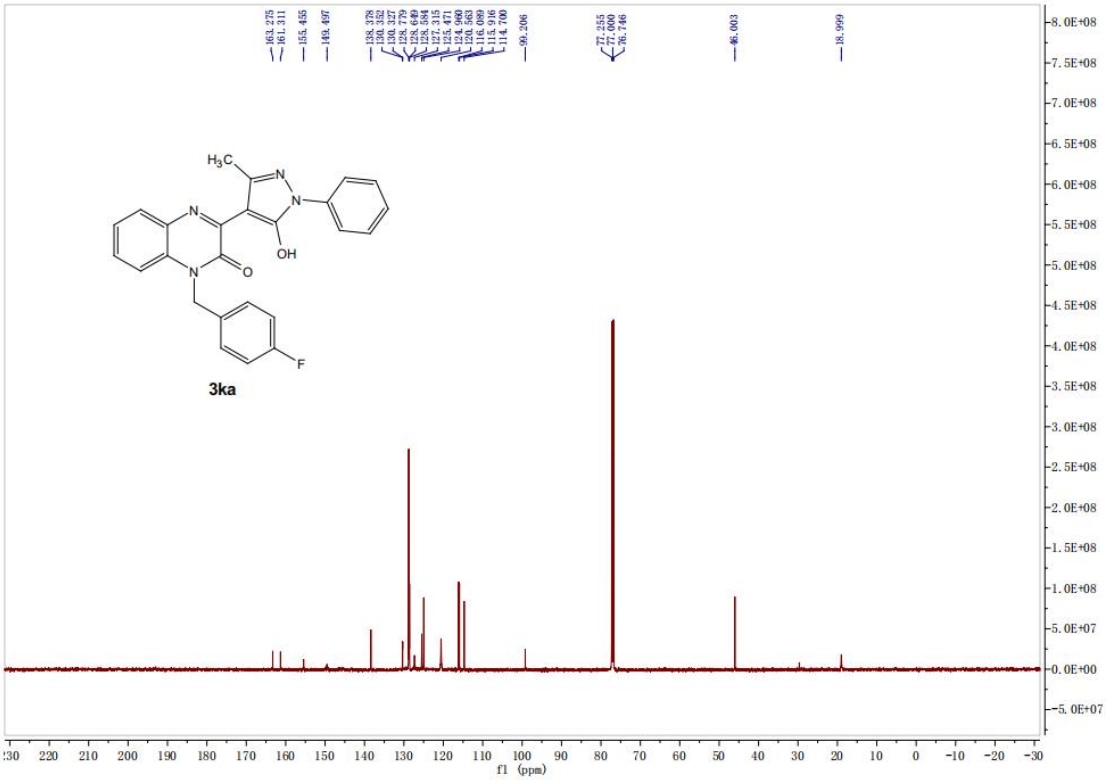

15.047
7.954
7.938
7.584
7.444
7.429
7.412
7.353
7.339
7.323
7.296
7.282
7.277
7.267
7.260
7.252
7.243
7.227
7.221
7.212
7.202
5.505
2.705
3ia
f1 (ppm)

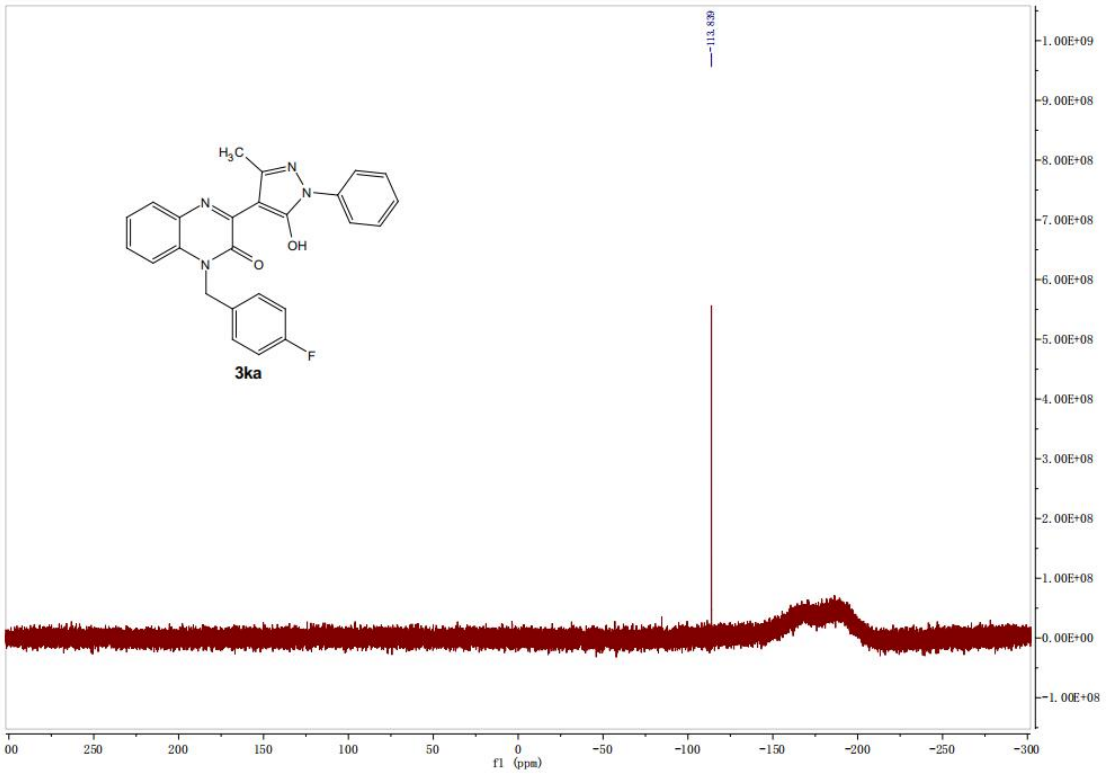

155.439
149.519
146.039
138.421
134.553
129.006
128.928
128.747
127.882
126.669
125.400
124.871
114.916
99.182
77.254
77.000
76.746
46.637
18.988
3ia
f1 (ppm)

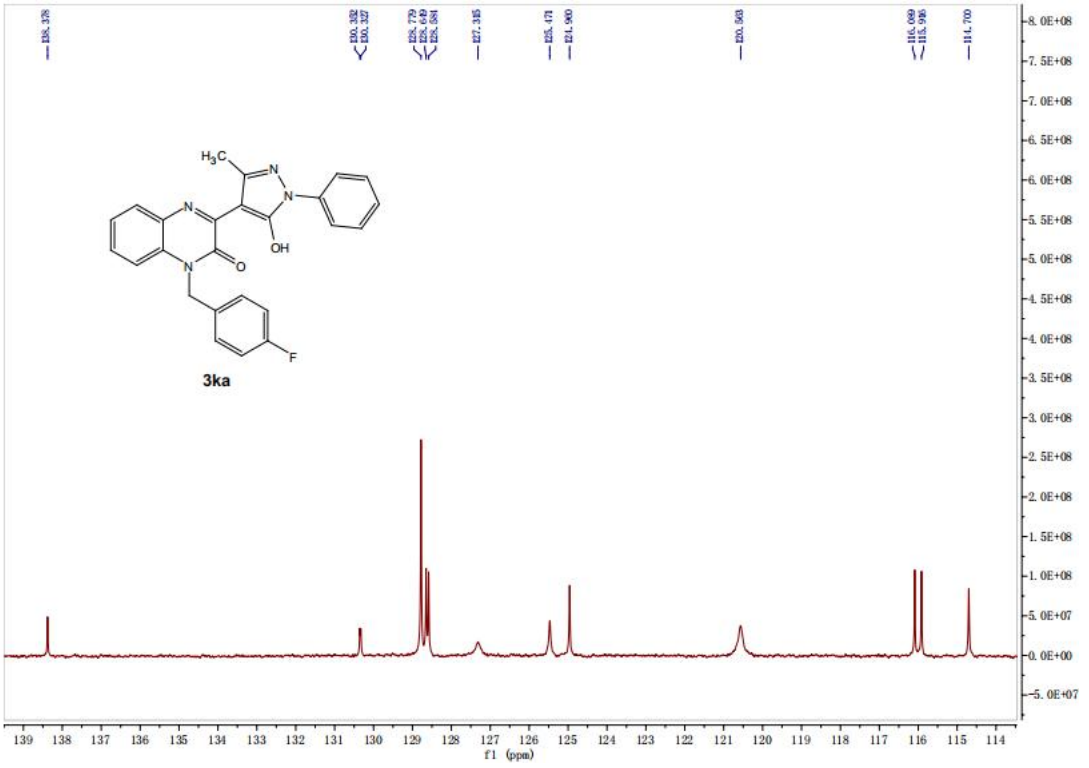

15.012
7.951
7.936
7.588
7.447
7.432
7.415
7.275
7.265
7.260
7.256
7.250
7.230
7.215
7.163
7.144
7.126
5.471
2.709
2.314
0.25
2.00
0.91
2.11
4.06
4.15
2.01
3.15
3.17
3ja
f1 (ppm)

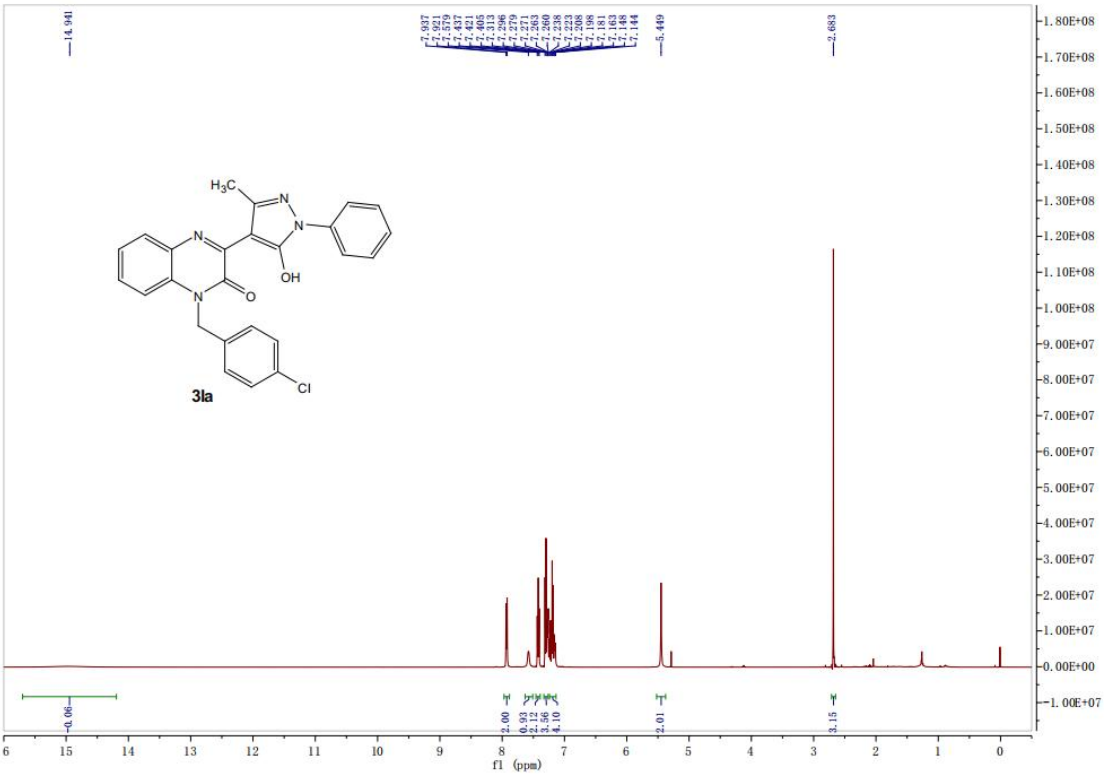

155.462
149.567
146.298
138.414
137.654
131.520
129.698
128.790
126.698
125.430
124.779
99.177
77.254
76.746
46.444
21.027
18.948
3ja
f1 (ppm)

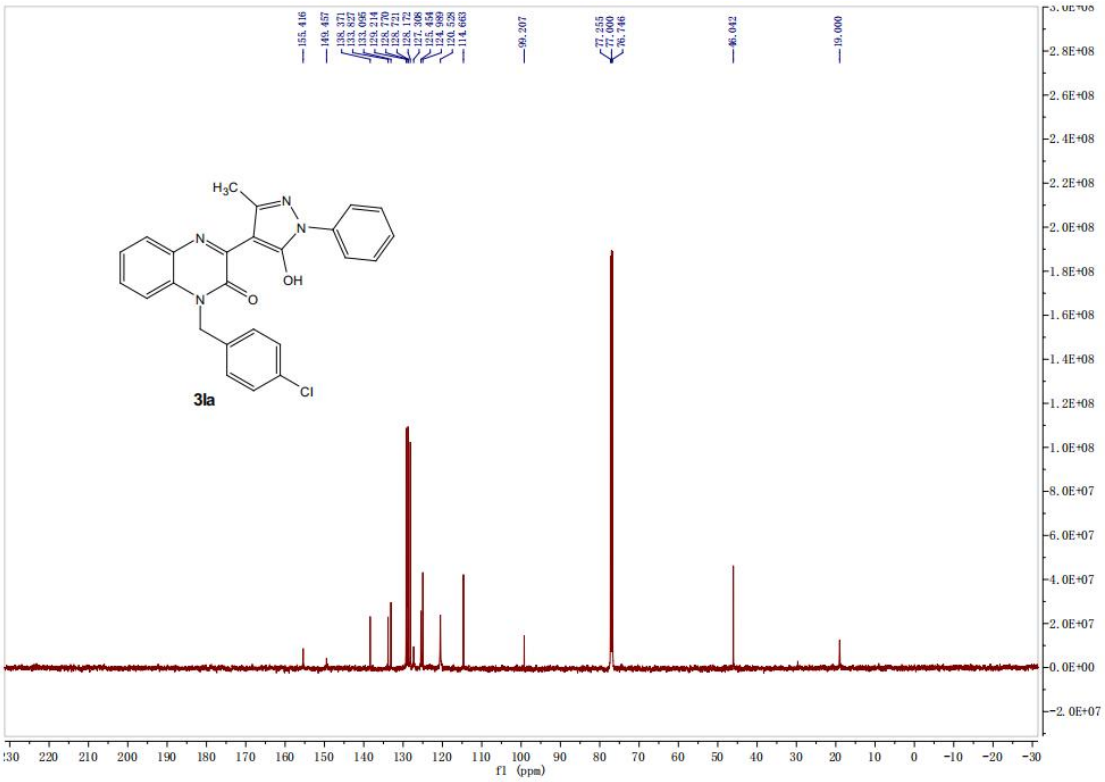

15.011
7.939
7.933
7.587
7.441
7.425
7.299
7.284
7.280
7.272
7.269
7.253
7.246
7.236
7.226
7.212
7.202
7.193
7.043
7.006
7.009
5.463
2.692
0.25
1.96
0.90
2.09
5.95
2.00
1.97
3.10
3ka
f1 (ppm)

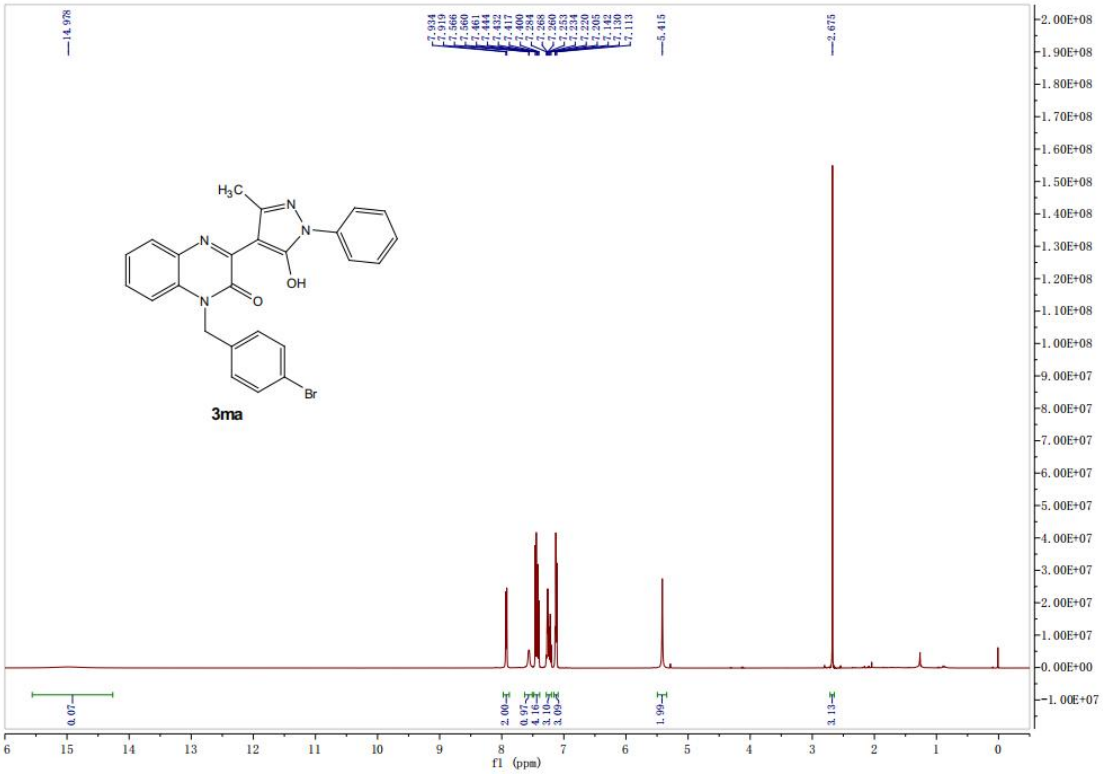

163.275
161.311
155.455
149.497
138.378
130.352
130.327
128.779
128.449
128.384
127.315
125.471
124.960
124.585
116.089
115.916
114.700
99.296
77.255
77.000
76.746
46.003
18.999
3ka
f1 (ppm)

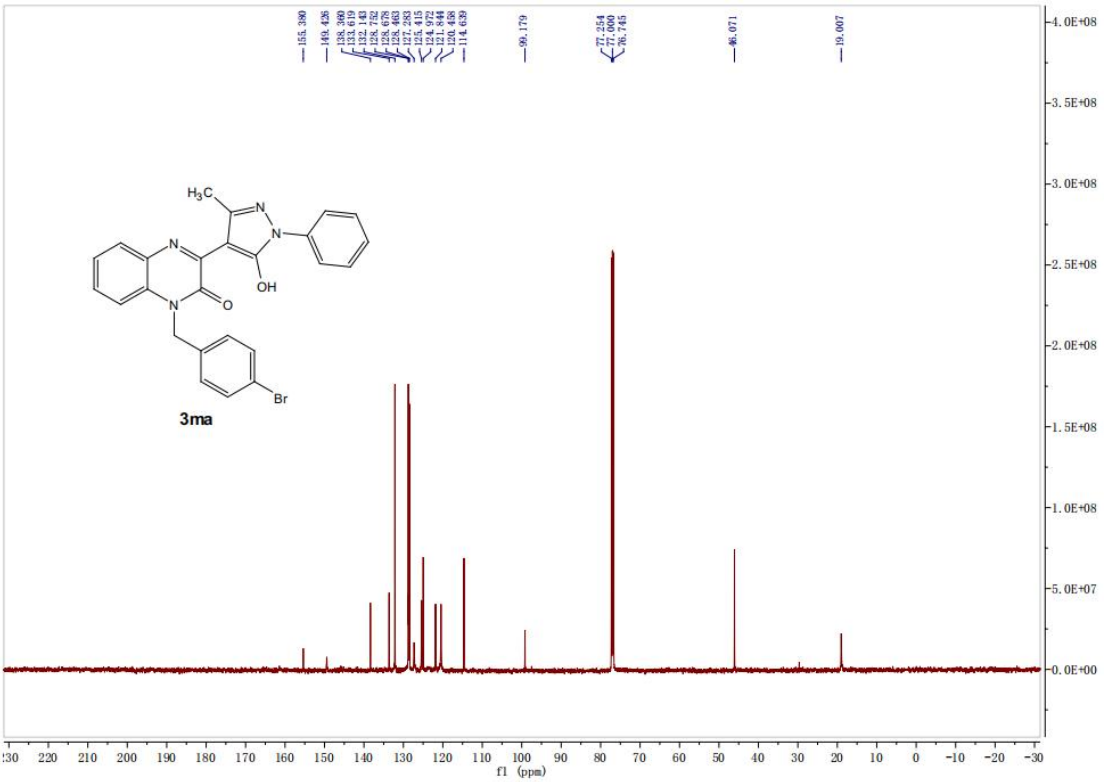

113.839
3ka
f1 (ppm)

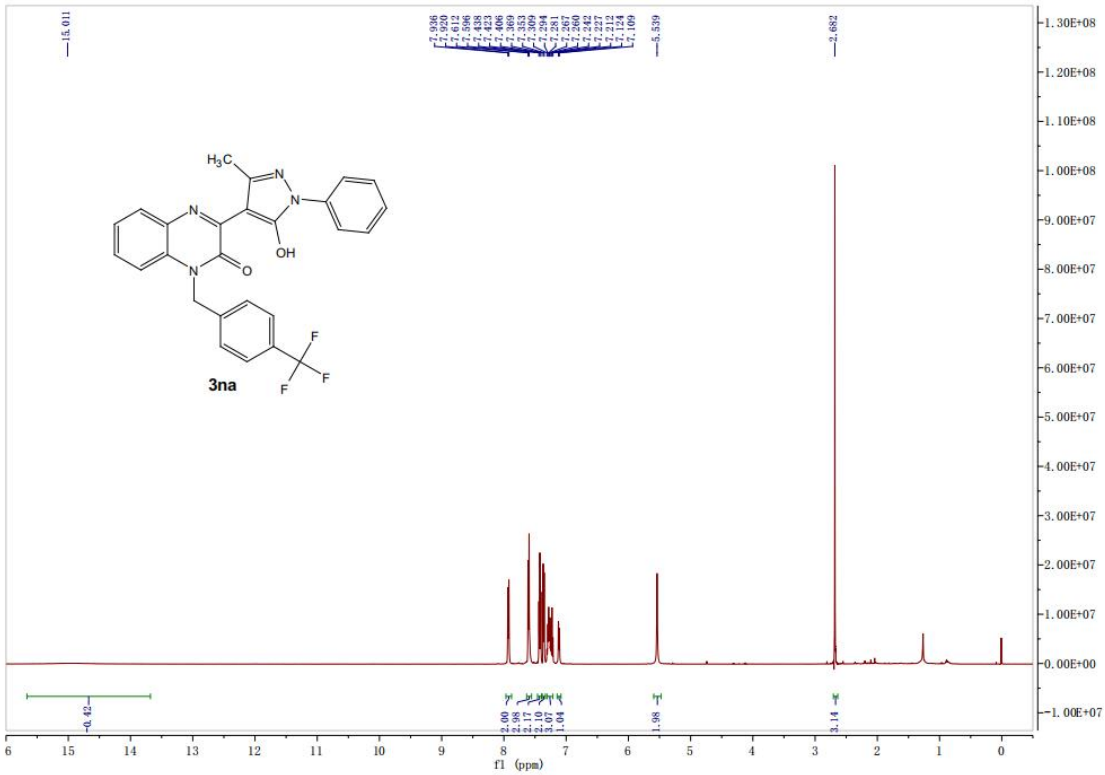

3ka
f1 (ppm)

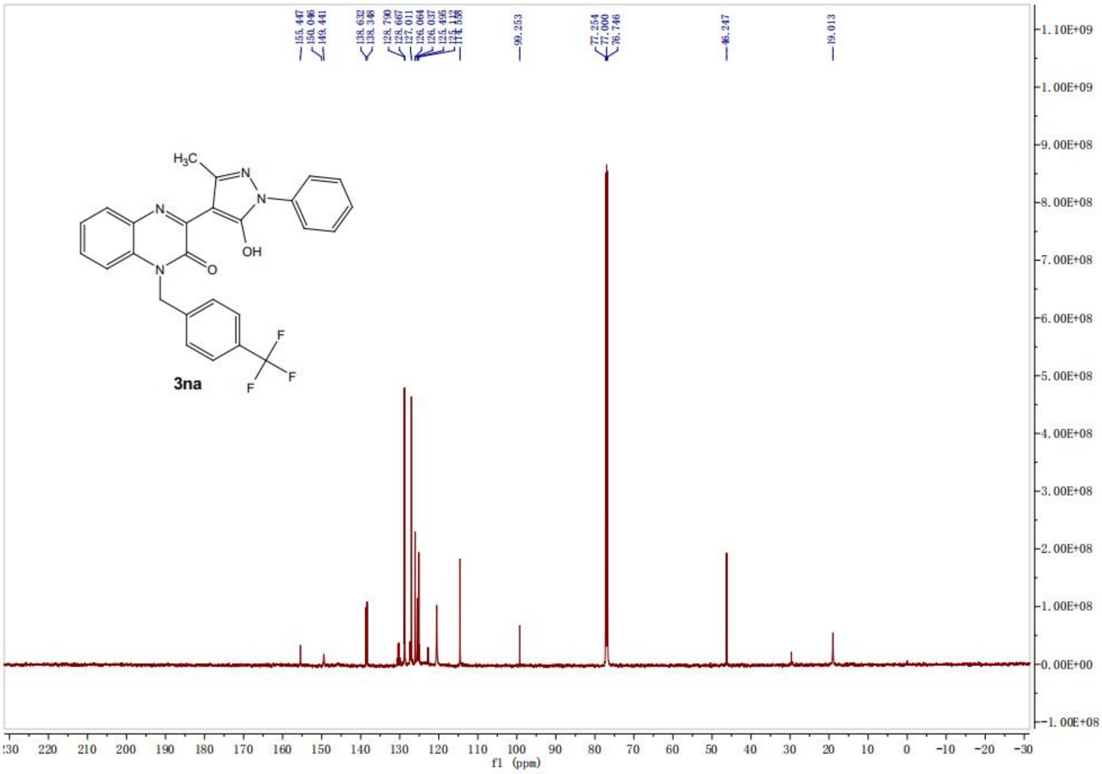

3la
f1 (ppm)

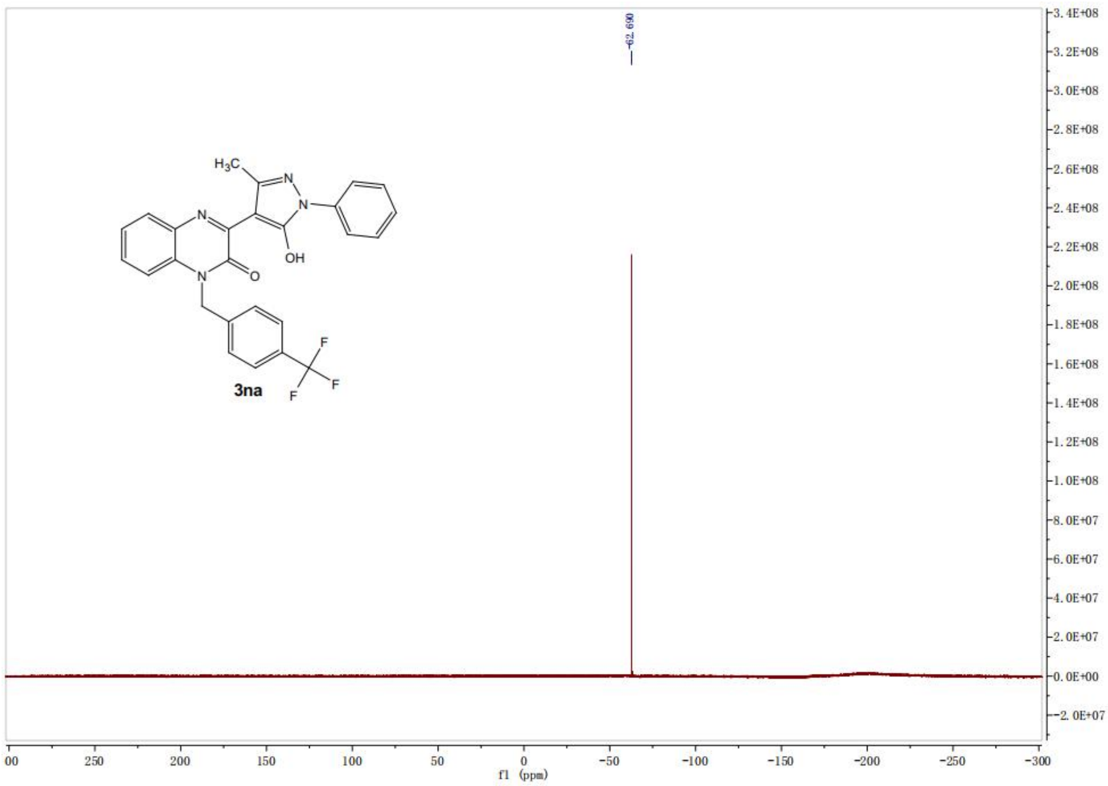

155.416
149.457
138.371
133.827
133.096
131.314
128.770
128.721
128.172
127.306
125.454
124.999
120.528
114.663
99.207
77.255
77.000
76.746
46.042
19.000
3la
f1 (ppm)

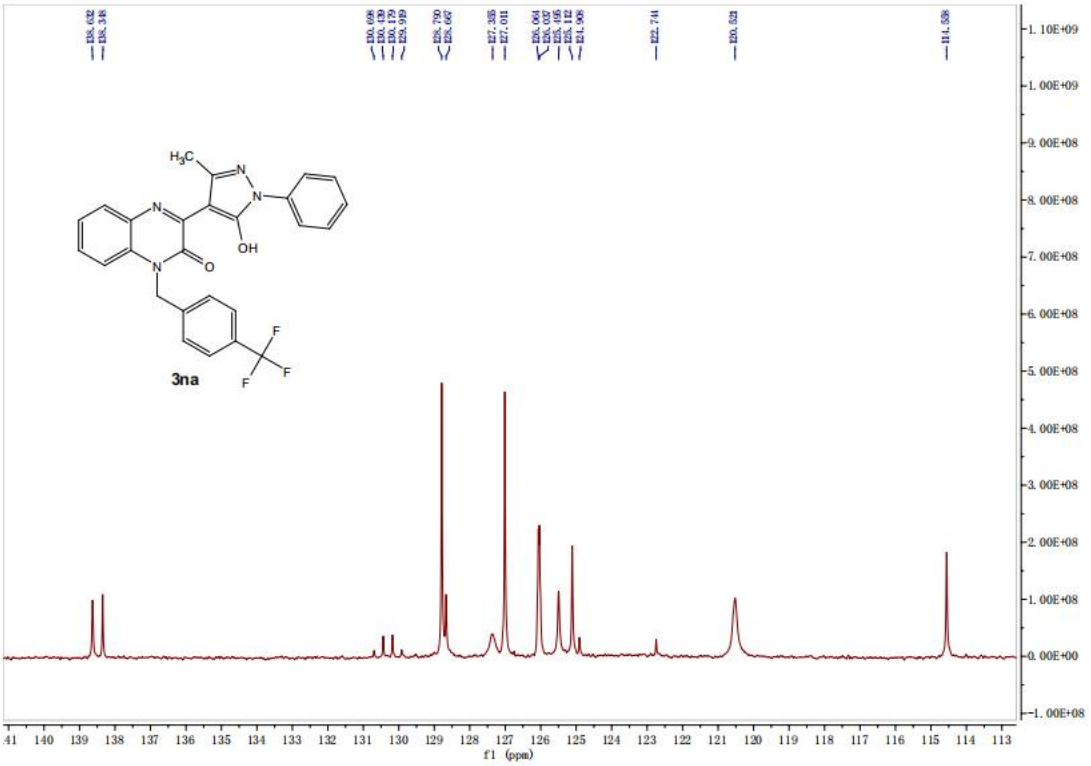

14.978
7.934
7.919
7.566
7.560
7.461
7.444
7.432
7.417
7.400
7.284
7.268
7.260
7.253
7.234
7.220
7.095
7.142
7.130
7.113
5.415
2.675
0.07
2.00
0.97
4.16
3.10
3.09
1.99
3.13
3ma
f1 (ppm)

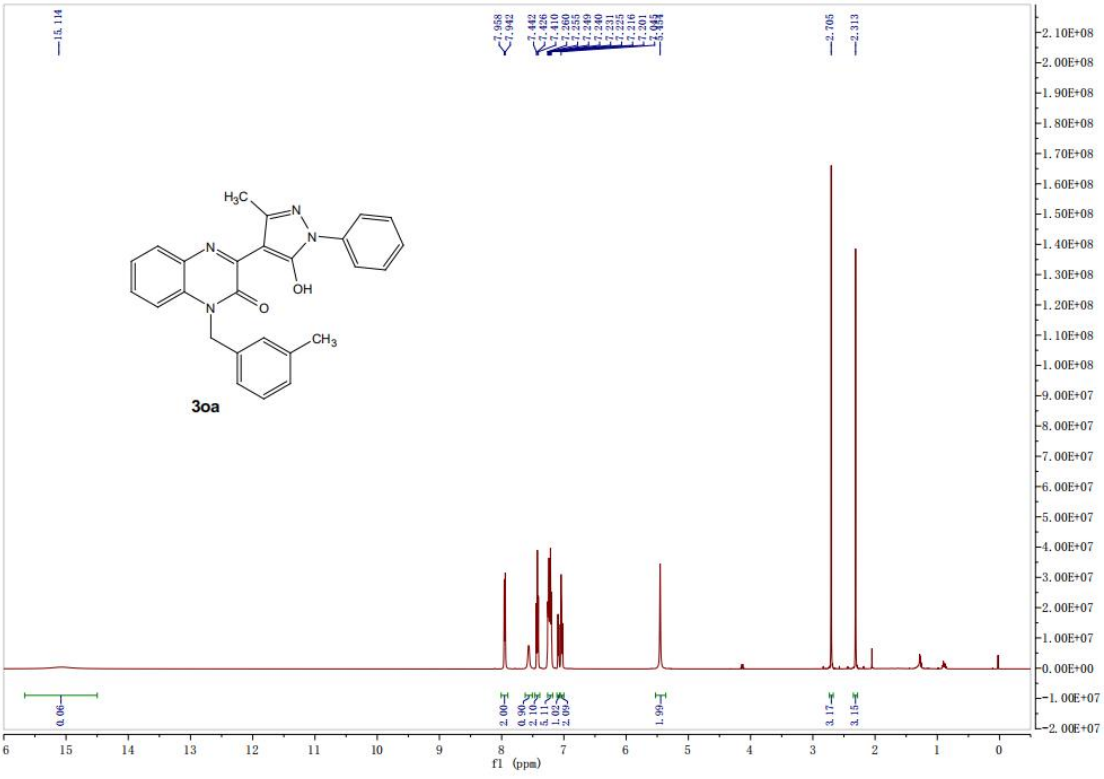

155.380
149.426
138.360
133.619
132.143
128.752
128.670
128.463
127.283
125.415
124.972
121.864
120.438
114.639
99.179
77.254
77.000
76.746
46.071
19.007
H3C
N
N
OH
O
N
Br
3ma
4.0E+08
3.5E+08
3.0E+08
2.5E+08
2.0E+08
1.5E+08
1.0E+08
5.0E+07
0.0E+00
f1 (ppm)

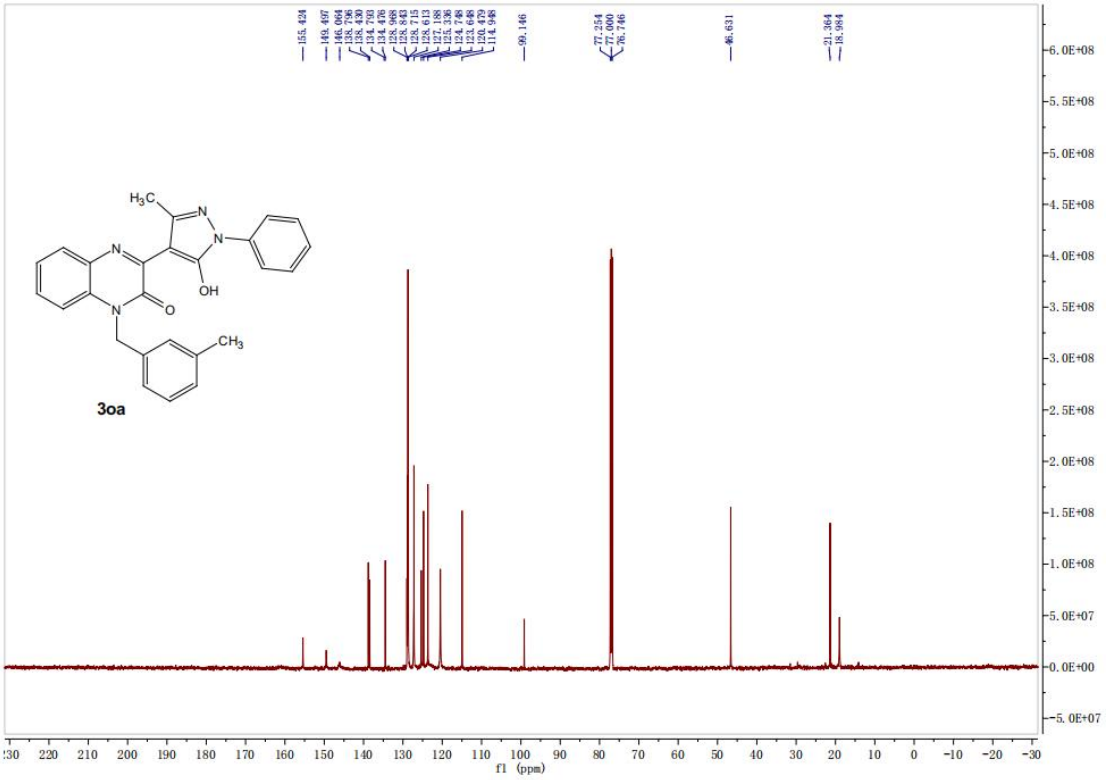

15.011
7.936
7.920
7.653
7.596
7.438
7.423
7.406
7.369
7.353
7.309
7.294
7.281
7.267
7.260
7.242
7.227
7.213
7.124
7.109
5.539
2.682
H3C
N
N
OH
O
N
F
F
F
3na
1.30E+08
1.20E+08
1.10E+08
1.00E+08
9.00E+07
8.00E+07
7.00E+07
6.00E+07
5.00E+07
4.00E+07
3.00E+07
2.00E+07
1.00E+07
0.00E+00
1.00E+07
0.42
2.00
2.08
2.17
2.10
3.07
1.04
1.98
3.14
f1 (ppm)

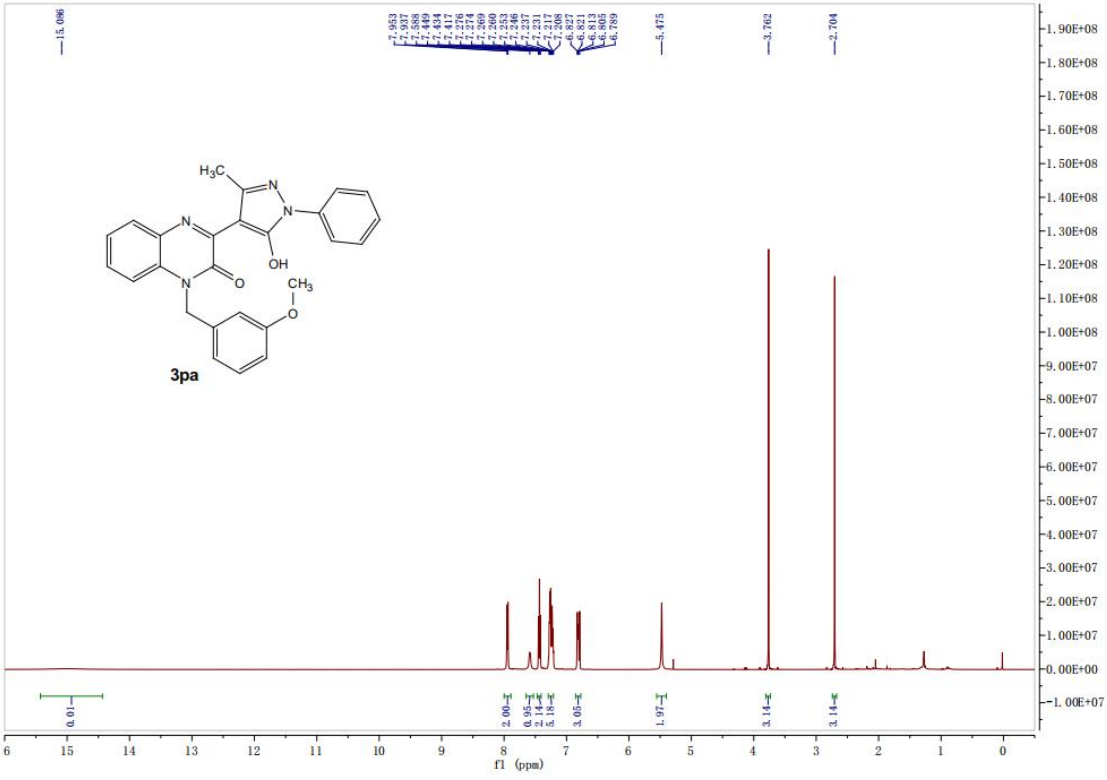

155.447
150.046
149.441
138.632
138.348
128.790
128.667
127.011
126.064
126.037
125.495
99.253
77.254
77.000
76.746
46.247
19.013
H3C
N
OH
O
F
3na
f1 (ppm)

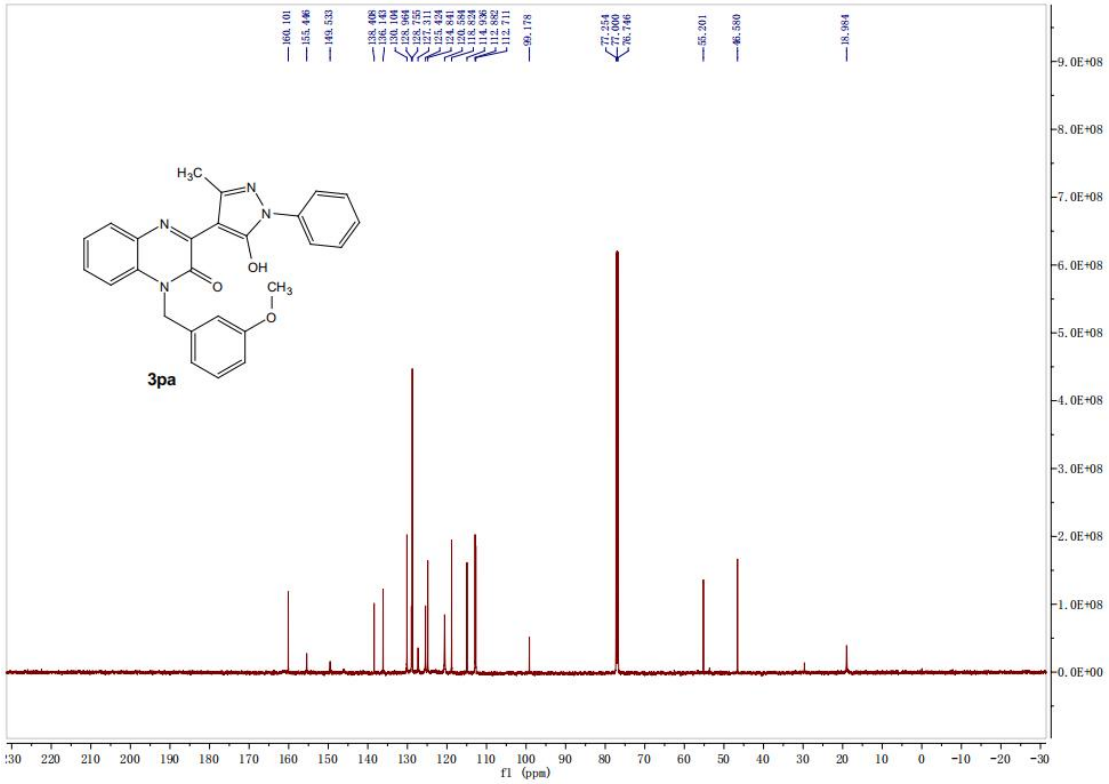

-62.690
H3C
N
OH
O
F
3na
f1 (ppm)

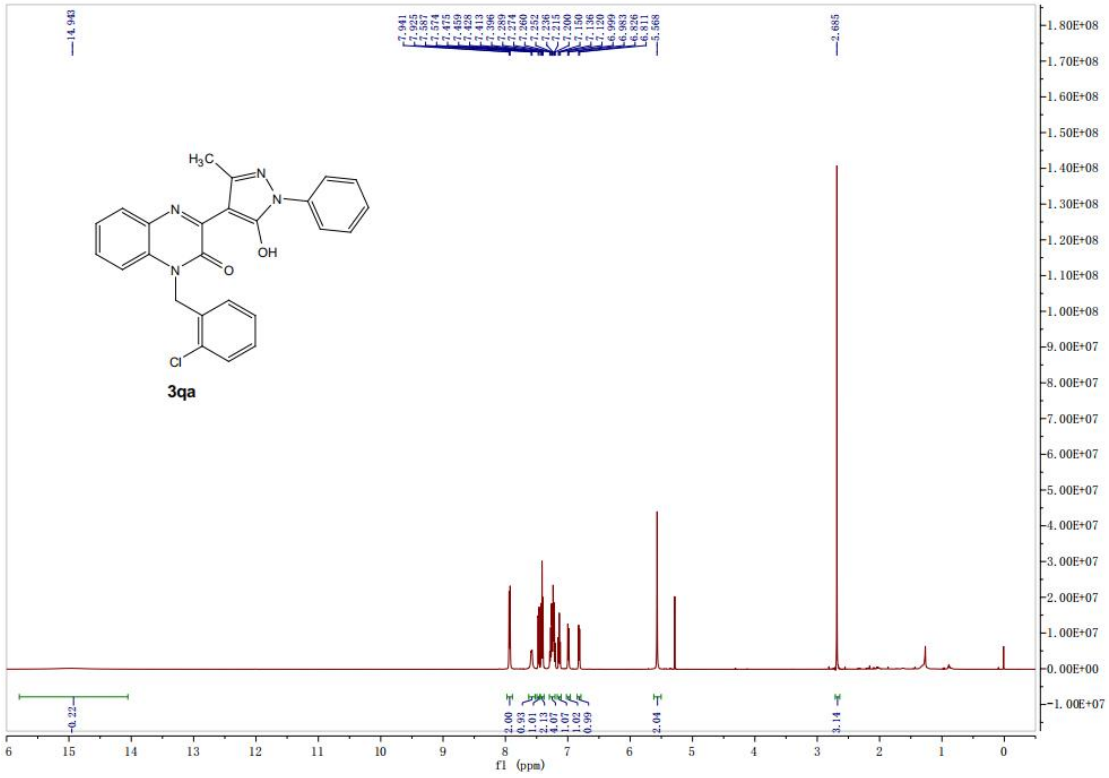

3na

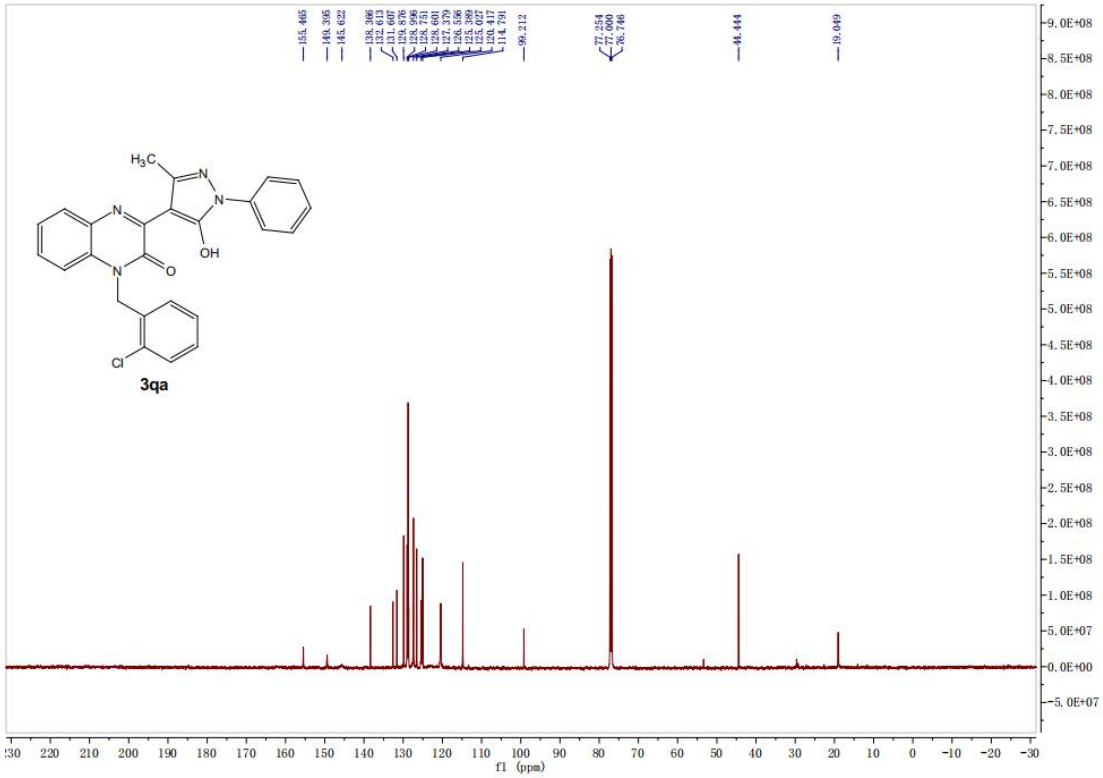

3oa

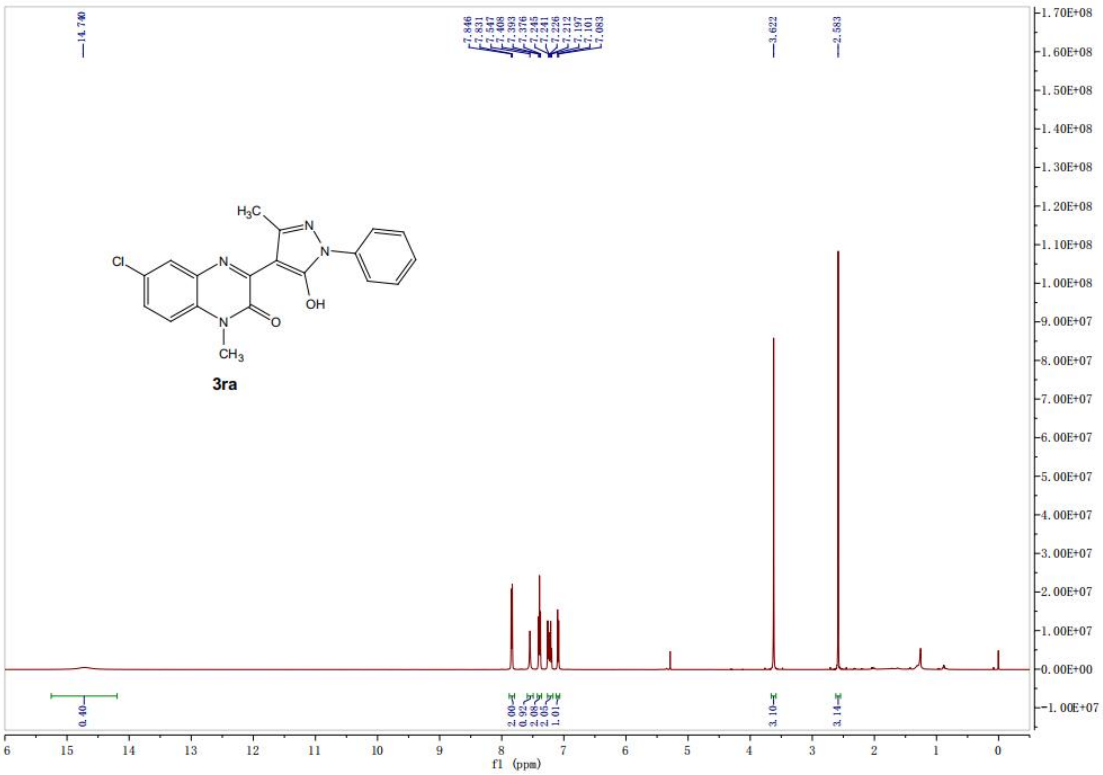

155.424
149.497
146.064
138.796
138.440
134.793
134.476
128.968
128.643
128.715
128.613
127.188
125.336
124.748
123.648
120.479
114.948
99.146
77.354
77.000
76.746
46.631
21.364
18.984
3oa
f1 (ppm)

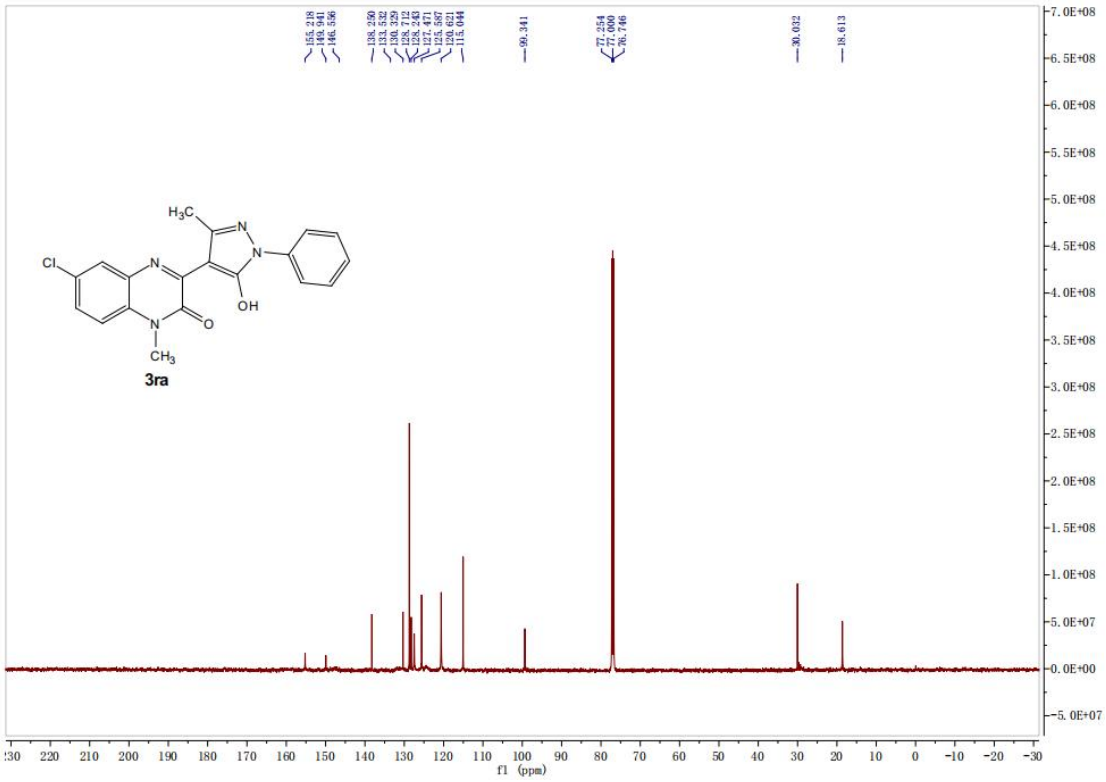

15.086
7.953
7.937
7.588
7.449
7.434
7.417
7.276
7.274
7.269
7.260
7.253
7.246
7.237
7.231
7.217
7.208
6.827
6.821
6.813
6.805
6.789
5.475
3.762
2.704
0.01
2.00
0.95
2.14
5.18
3.05
1.97
3.14
3.14
3pa
f1 (ppm)

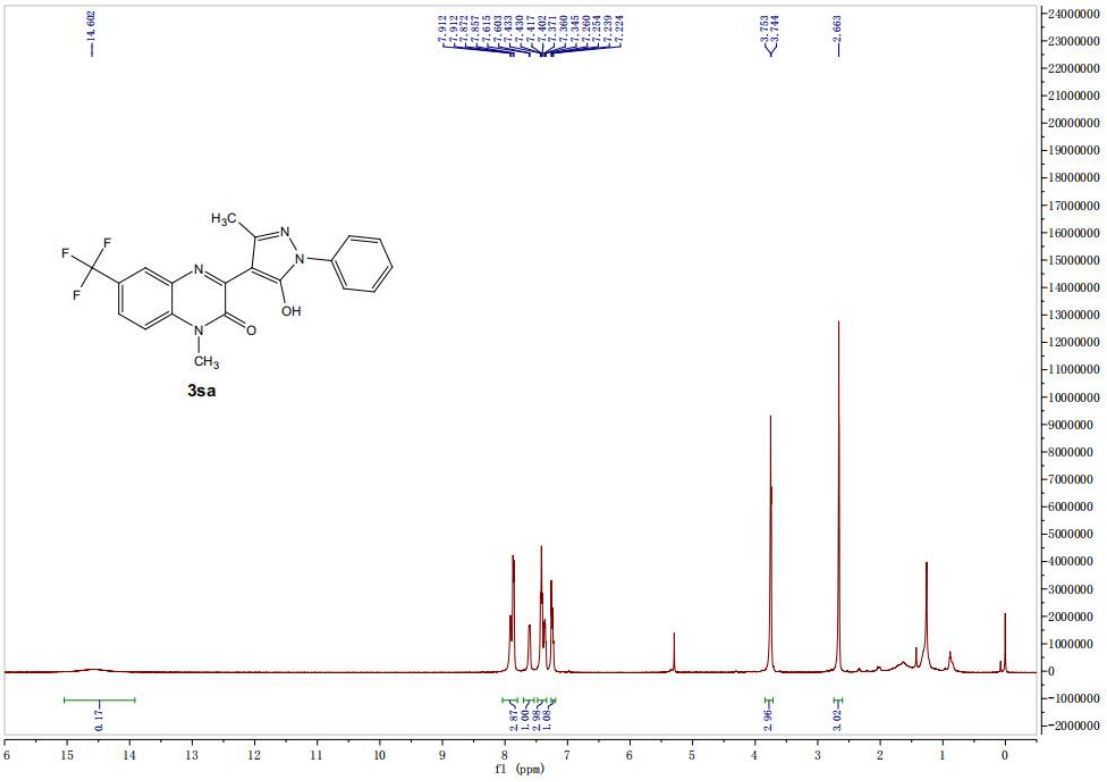

160.101
155.446
149.533
138.408
136.143
130.104
129.964
128.755
127.311
125.424
124.641
120.864
118.824
114.936
112.882
112.711
99.178
77.254
77.000
76.746
65.201
46.580
18.984
3pa

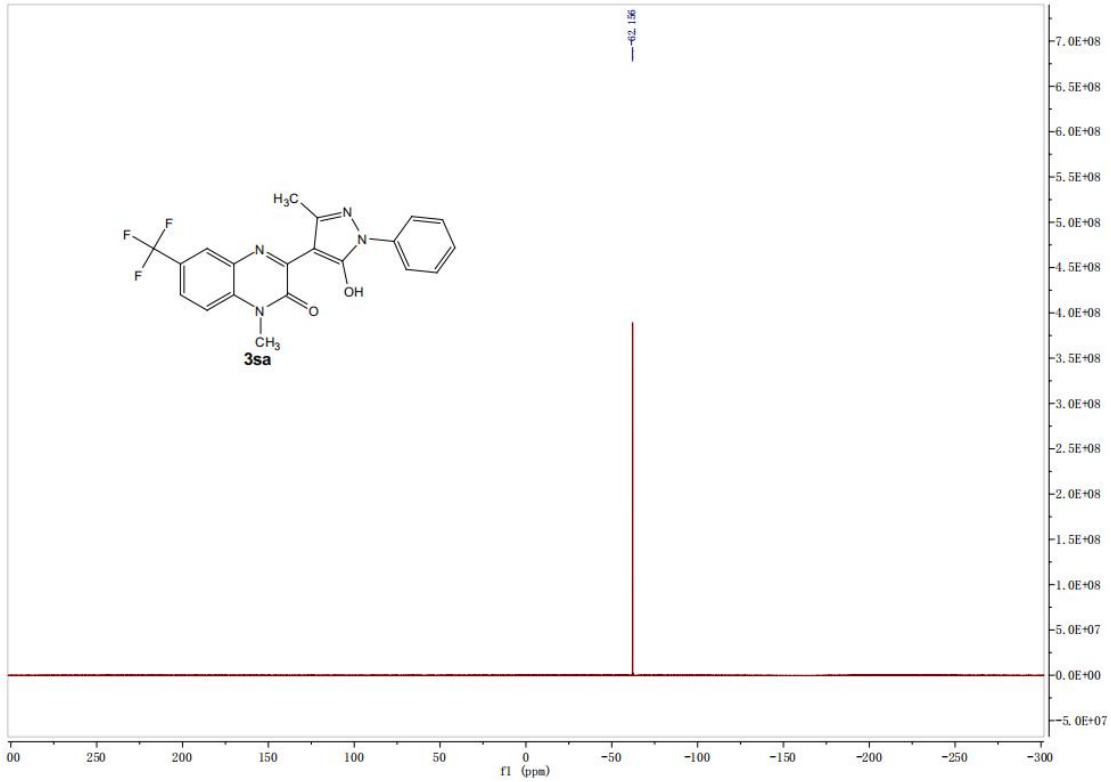

14.943
7.941
7.925
7.587
7.574
7.475
7.459
7.428
7.413
7.396
7.389
7.274
7.260
7.252
7.236
7.215
7.200
7.150
7.136
7.129
6.999
6.983
6.826
6.811
6.566
2.685
0.22
2.00
0.93
1.01
1.13
4.07
1.07
1.02
0.99
2.04
3.14
3qa

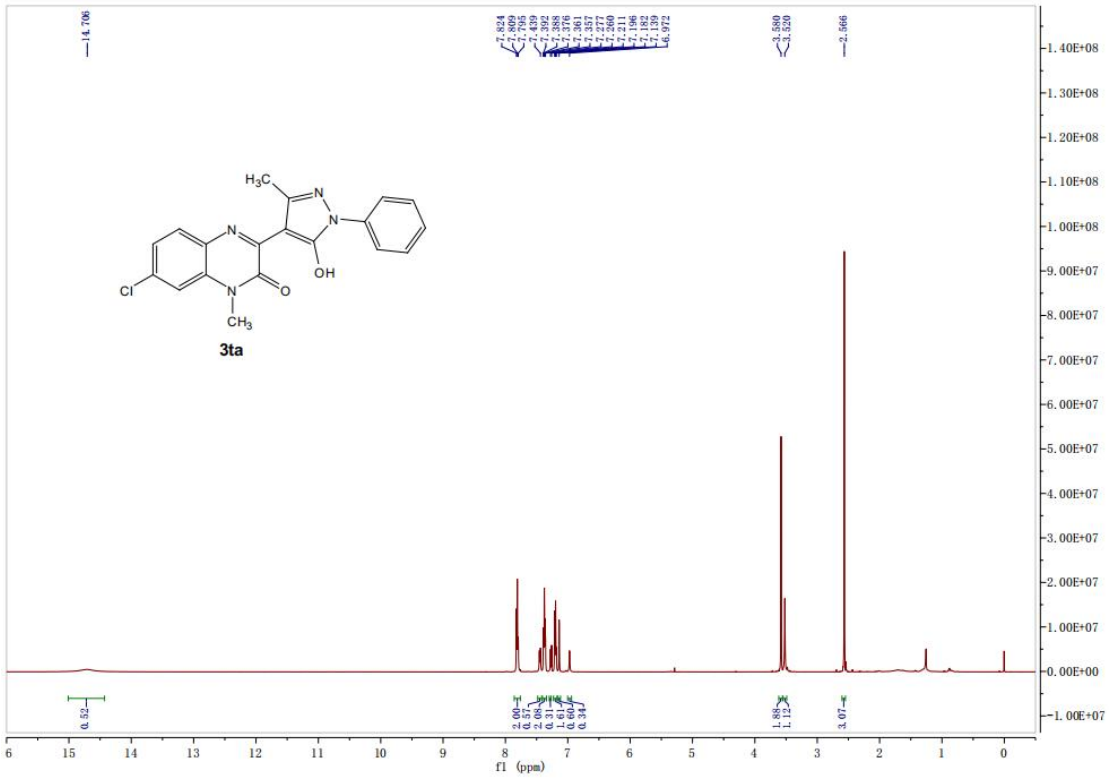

155.465
149.395
145.622
138.366
132.613
131.607
129.876
129.366
128.751
128.601
127.379
126.556
125.369
125.027
120.417
114.791
99.212
77.254
77.000
76.746
44.444
19.049
3qa

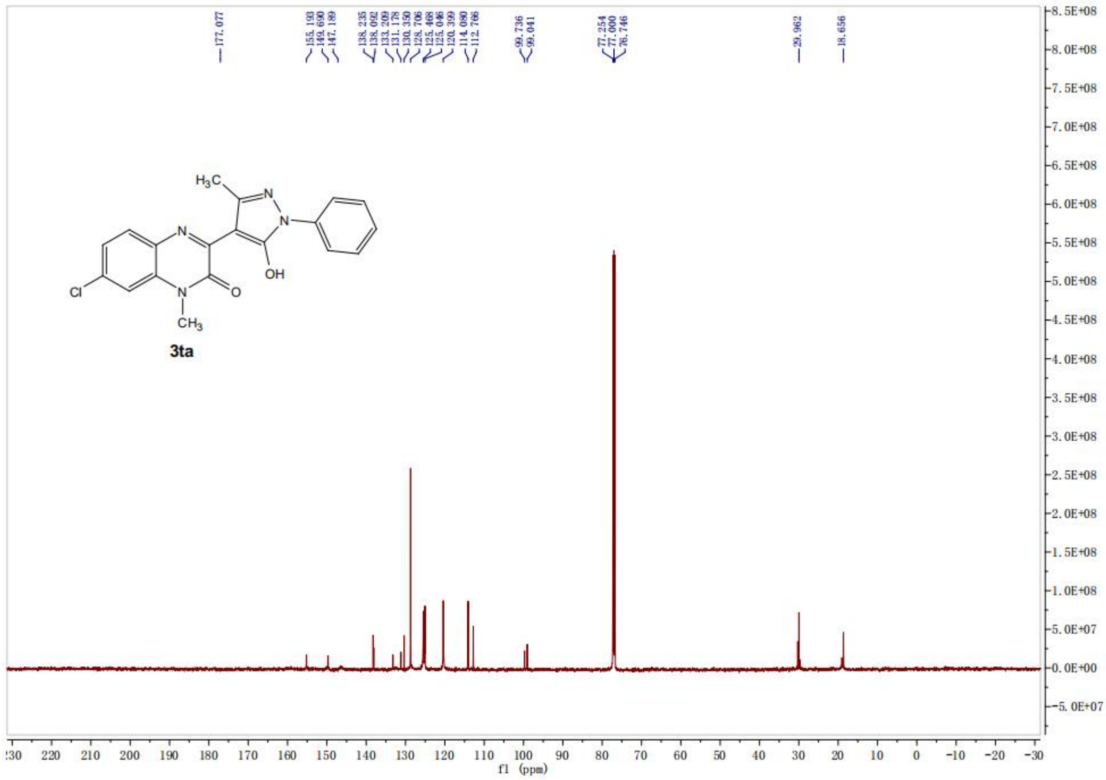

14.740
7.846
7.831
7.547
7.406
7.393
7.376
7.245
7.241
7.226
7.212
7.197
7.101
7.083
3.622
2.583
3ra

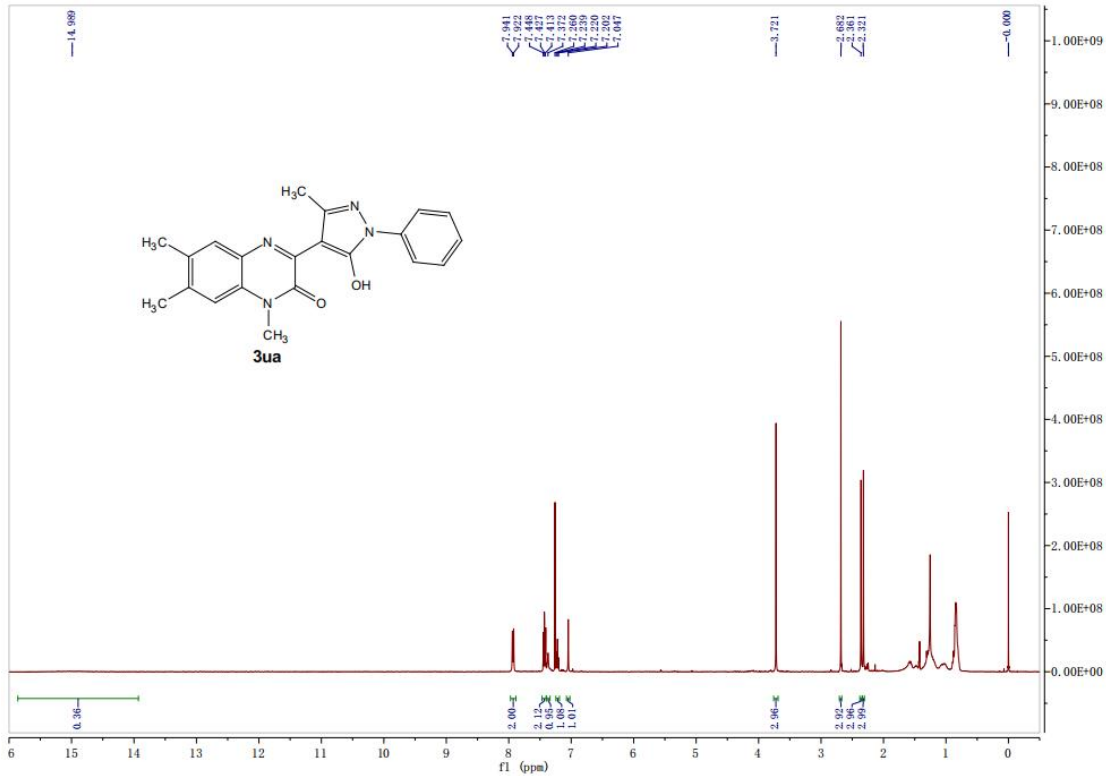

155.218
143.941
140.536
138.250
133.532
130.329
128.712
128.143
127.471
125.567
120.621
115.044
99.341
77.254
77.000
76.746
30.032
18.613
3ra
f1 (ppm)

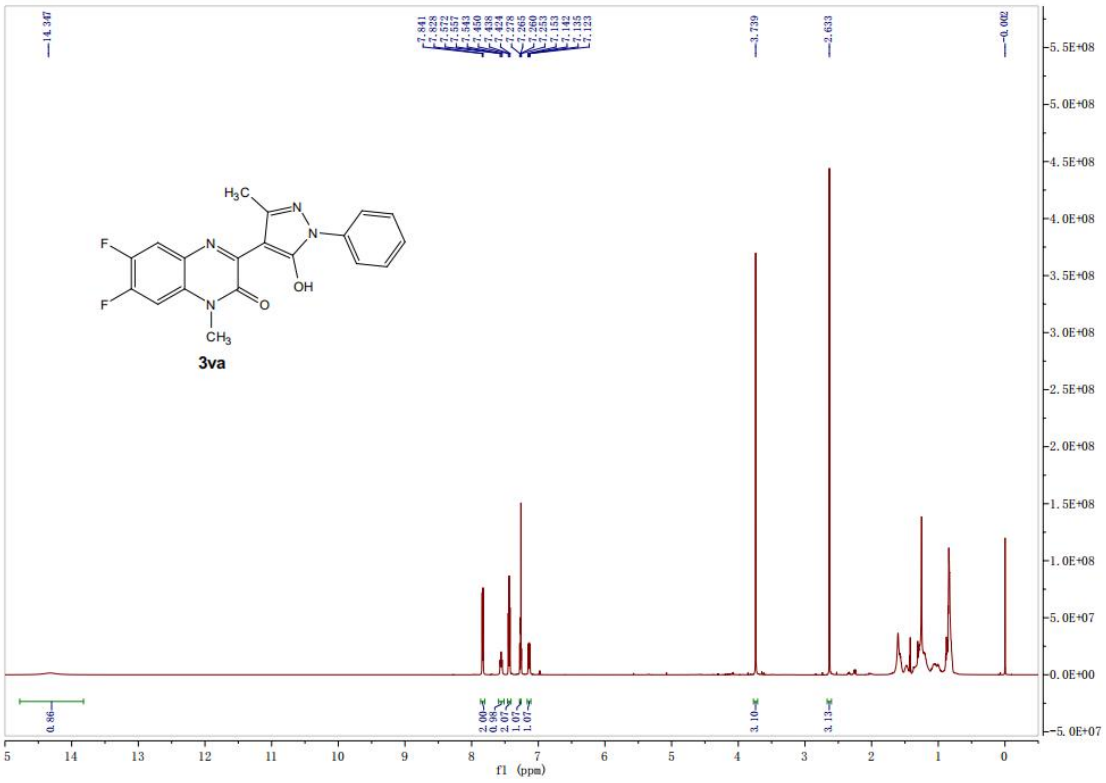

14.602
7.912
7.912
7.872
7.857
7.615
7.603
7.433
7.430
7.417
7.402
7.371
7.360
7.345
7.290
7.254
7.239
7.224
3.753
3.744
2.663
0.17
2.87
1.00
2.98
1.08
2.96
3.02
3sa
f1 (ppm)

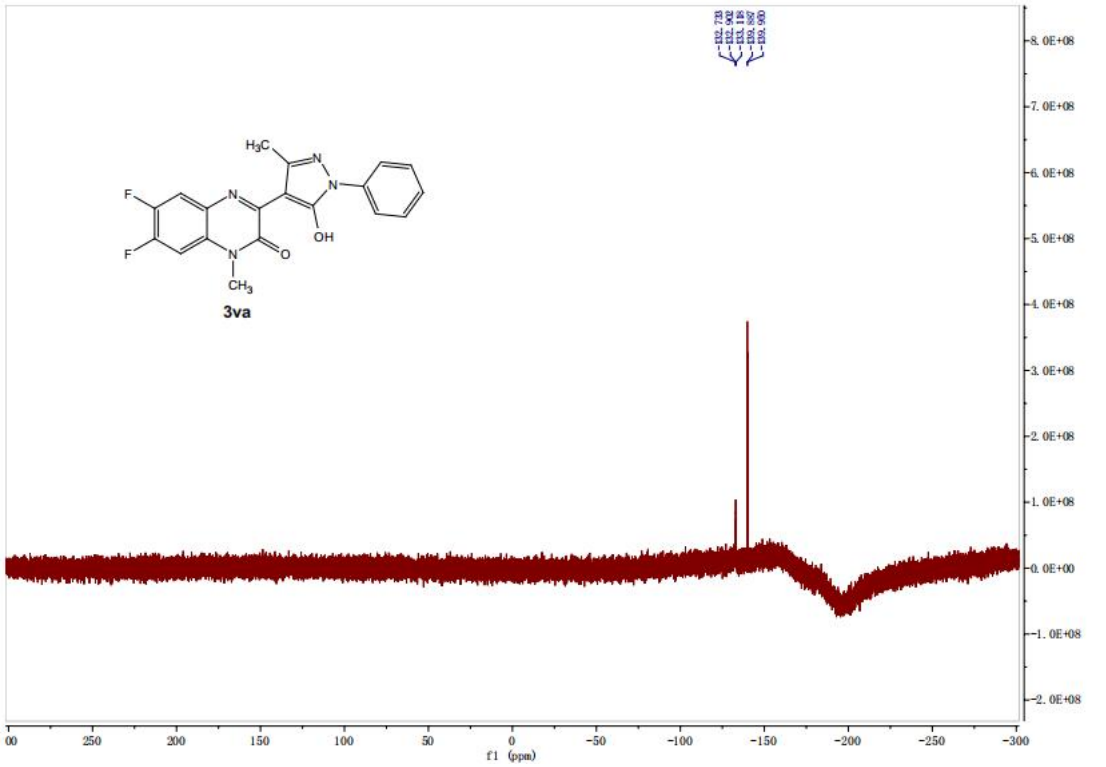

-62.156
F
F
F
N
N
N
H3C
OH
O
CH3
3sa
f1 (ppm)

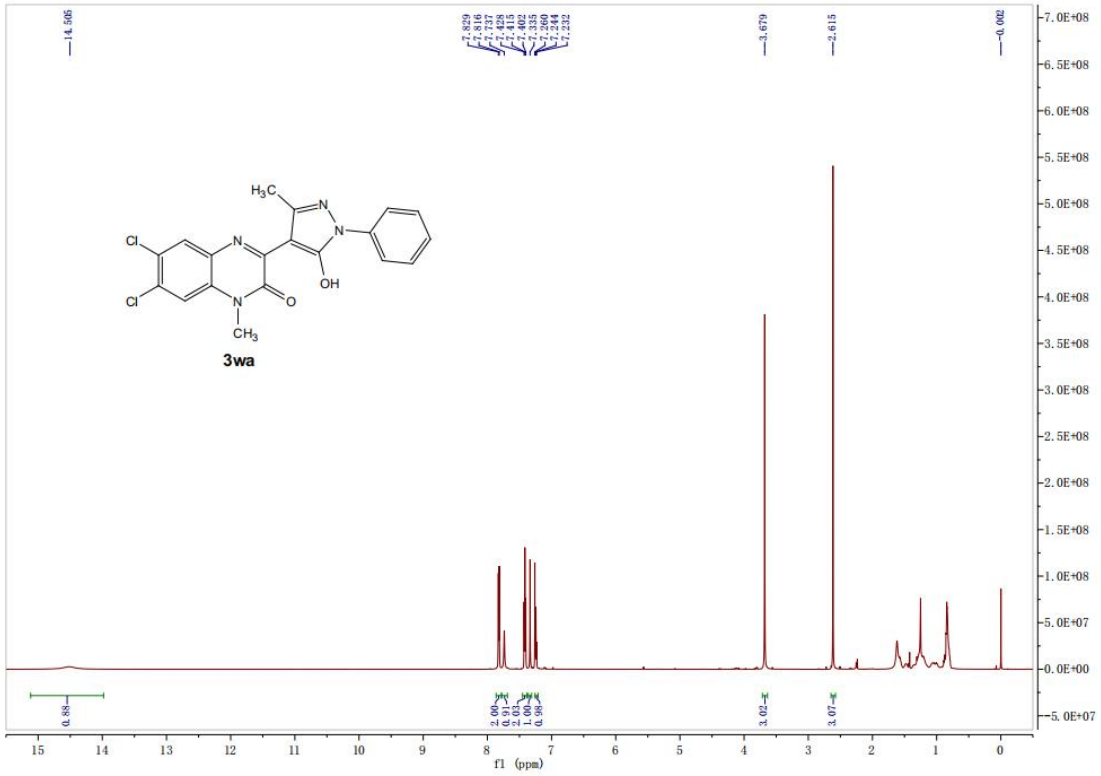

14.706
7.824
7.809
7.795
7.439
7.392
7.388
7.376
7.361
7.357
7.337
7.260
7.211
7.196
7.182
7.159
6.972
3.580
3.520
2.566
Cl
N
N
H3C
OH
O
CH3
3ta
f1 (ppm)

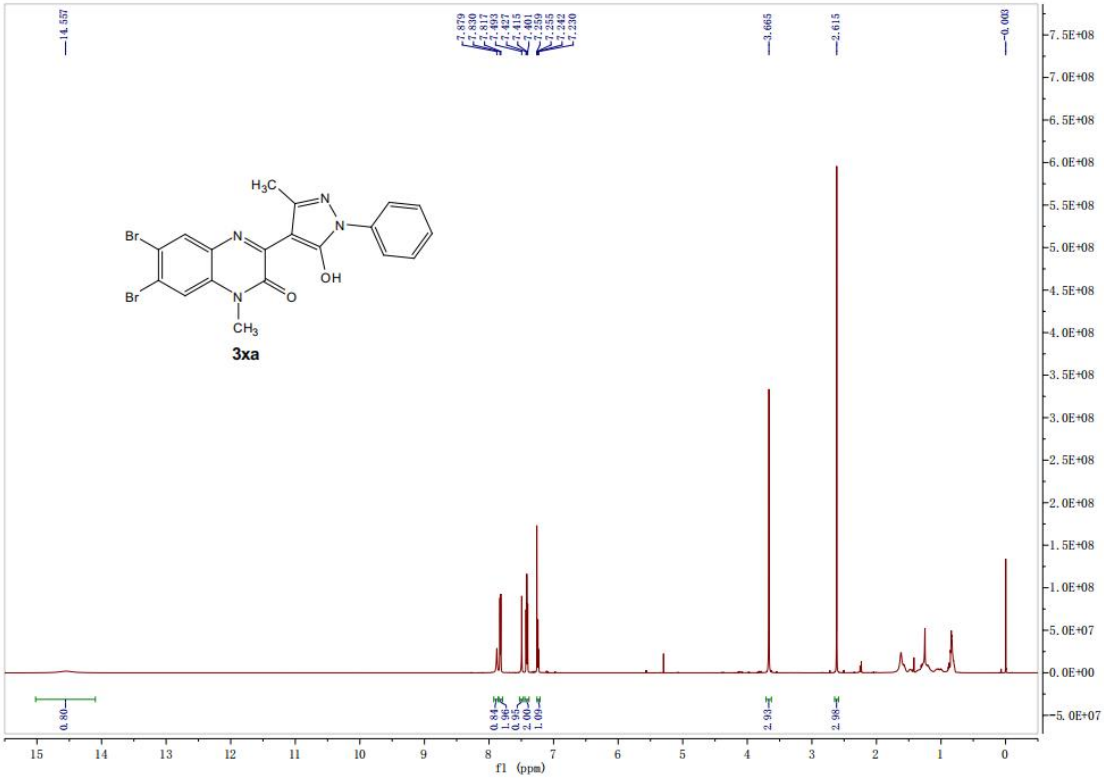

3ta
177.077
155.193
149.690
147.189
138.235
138.092
133.209
131.178
130.350
128.706
125.468
125.046
120.399
114.080
112.766
99.736
99.041
77.254
77.000
76.746
29.962
18.656
f1 (ppm)

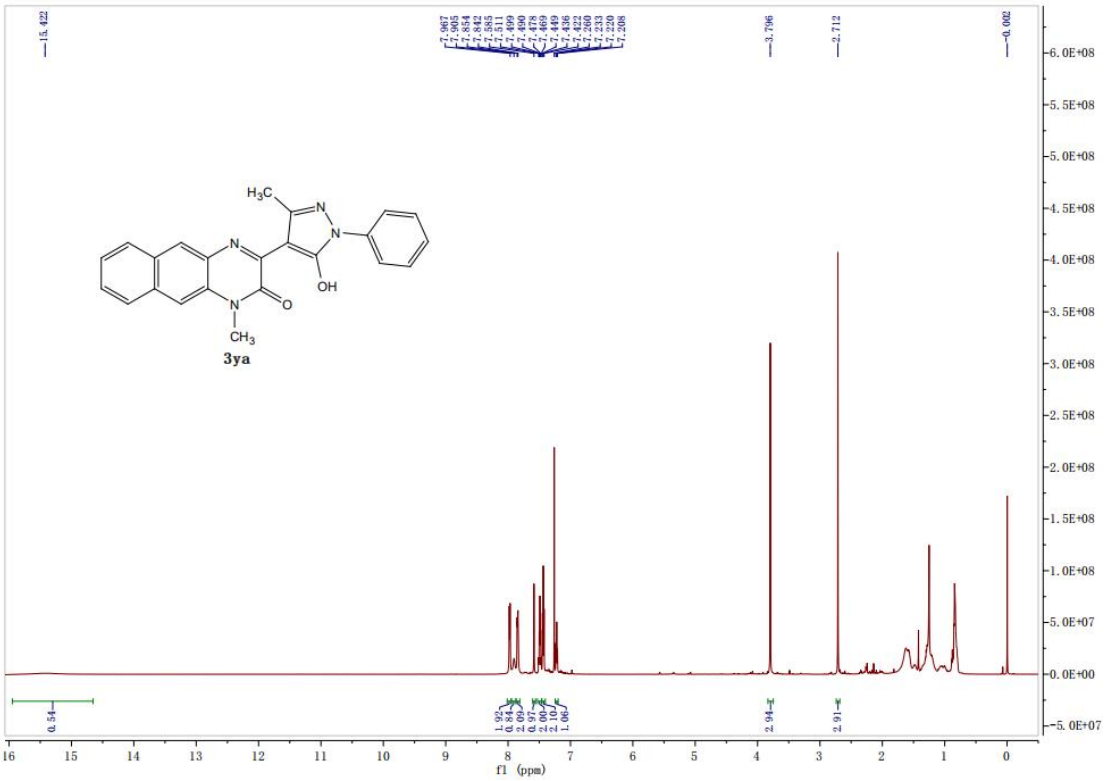

3ua
14.989
7.941
7.922
7.448
7.427
7.413
7.372
7.260
7.239
7.220
7.202
7.047
3.721
2.682
2.361
2.321
0.000
f1 (ppm)

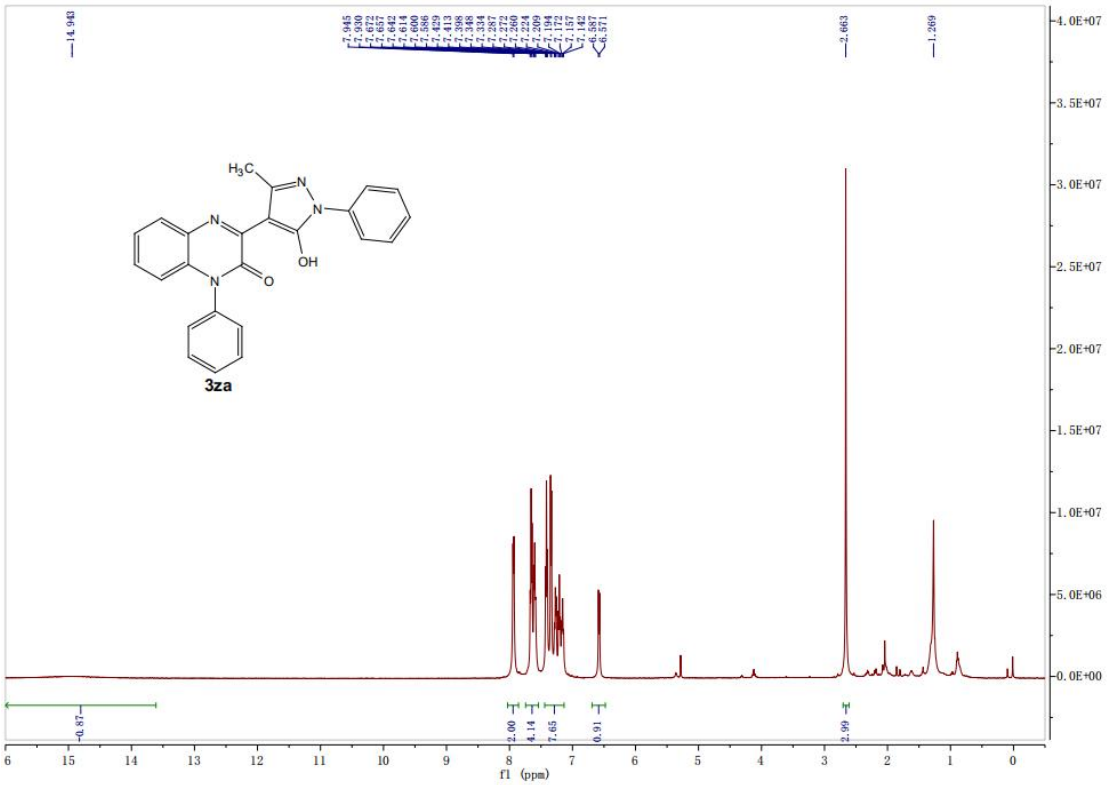

14.347
7.841
7.828
7.572
7.557
7.543
7.450
7.438
7.424
7.276
7.265
7.260
7.253
7.143
7.142
7.135
7.123
3.739
2.633
0.002
0.86
2.00
0.98
2.07
1.07
1.07
3.10
3.13
f1 (ppm)
3va

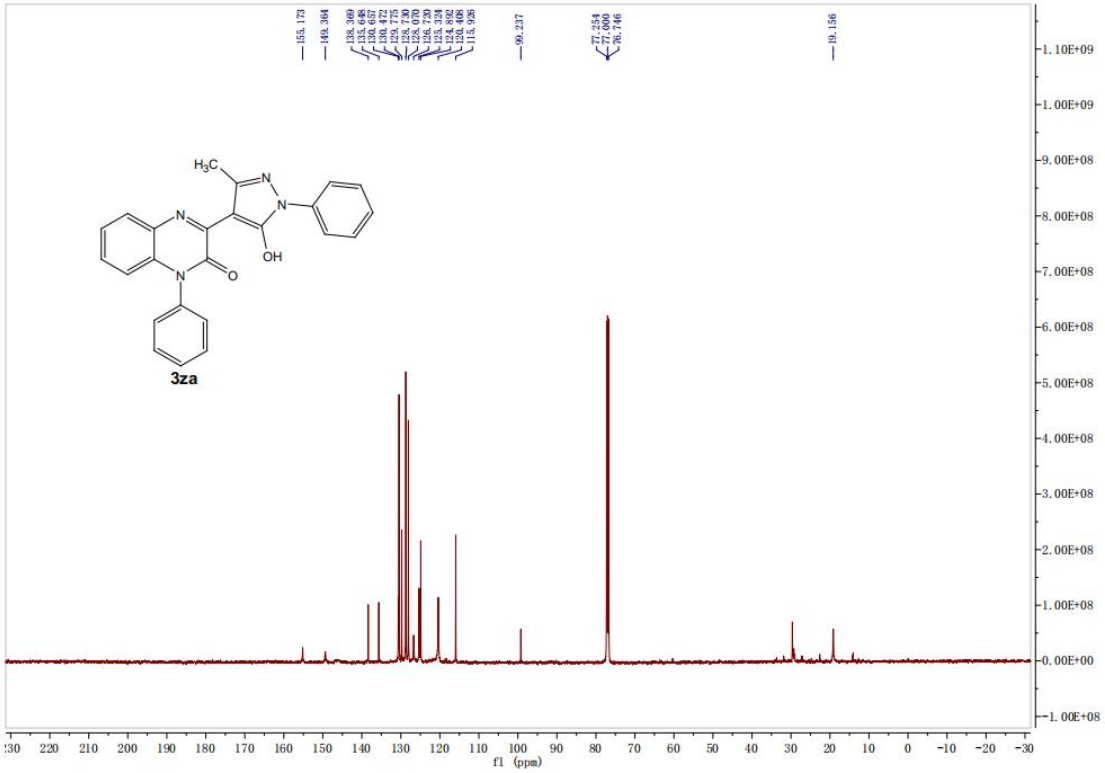

f1 (ppm)
3va

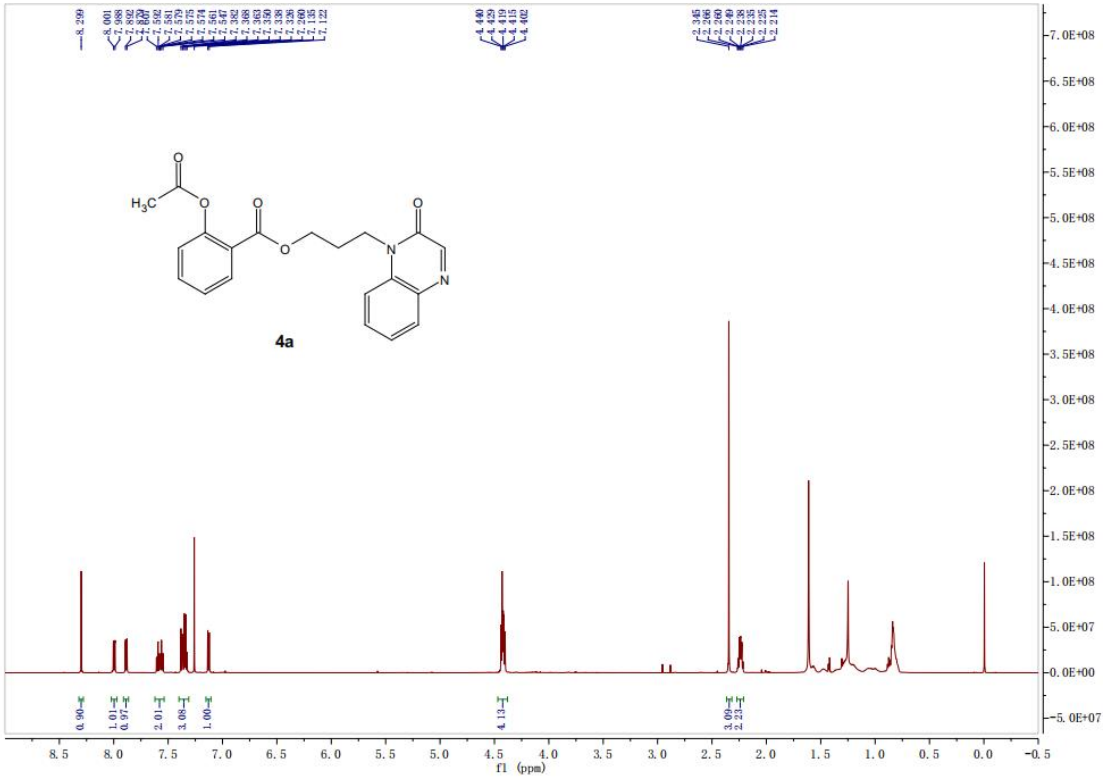

14.506
7.829
7.816
7.737
7.428
7.415
7.402
7.335
7.260
7.244
7.232
3.679
2.615
0.002
Cl
Cl
N
N
N
O
OH
H_3C
CH_3
3wa
f1 (ppm)

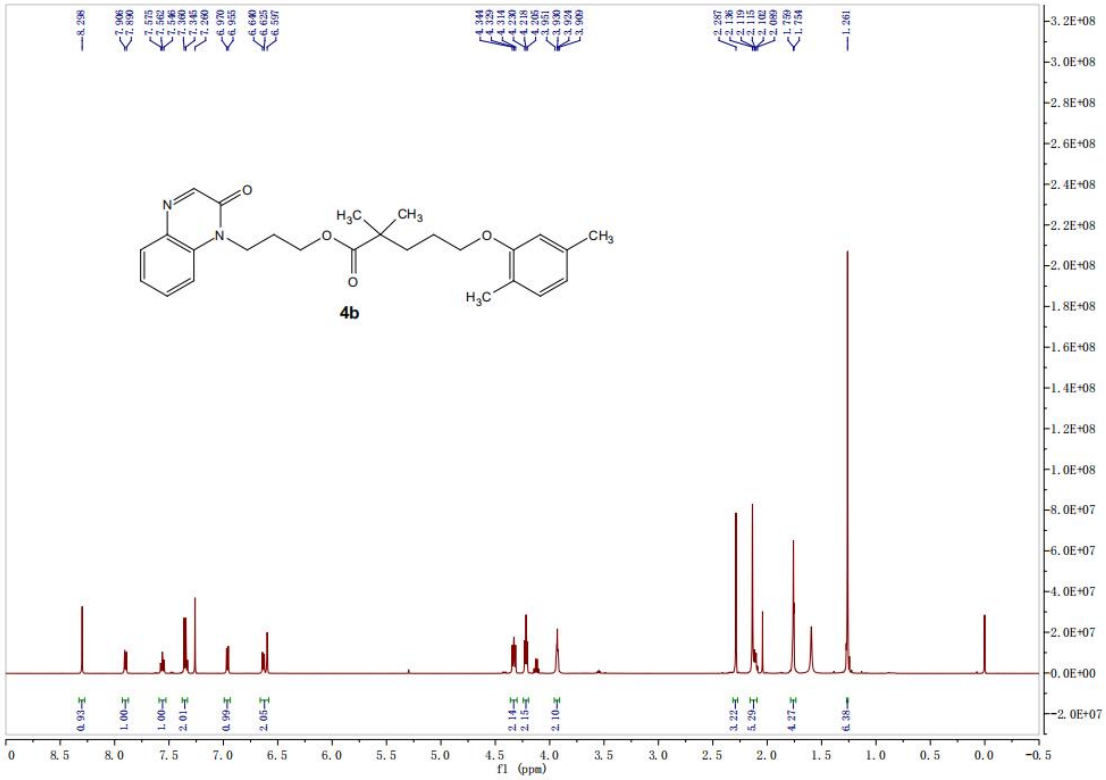

14.557
7.879
7.830
7.817
7.493
7.427
7.415
7.401
7.259
7.255
7.242
7.230
3.665
2.615
0.003
Br
Br
N
N
N
O
OH
H_3C
CH_3
3xa
f1 (ppm)

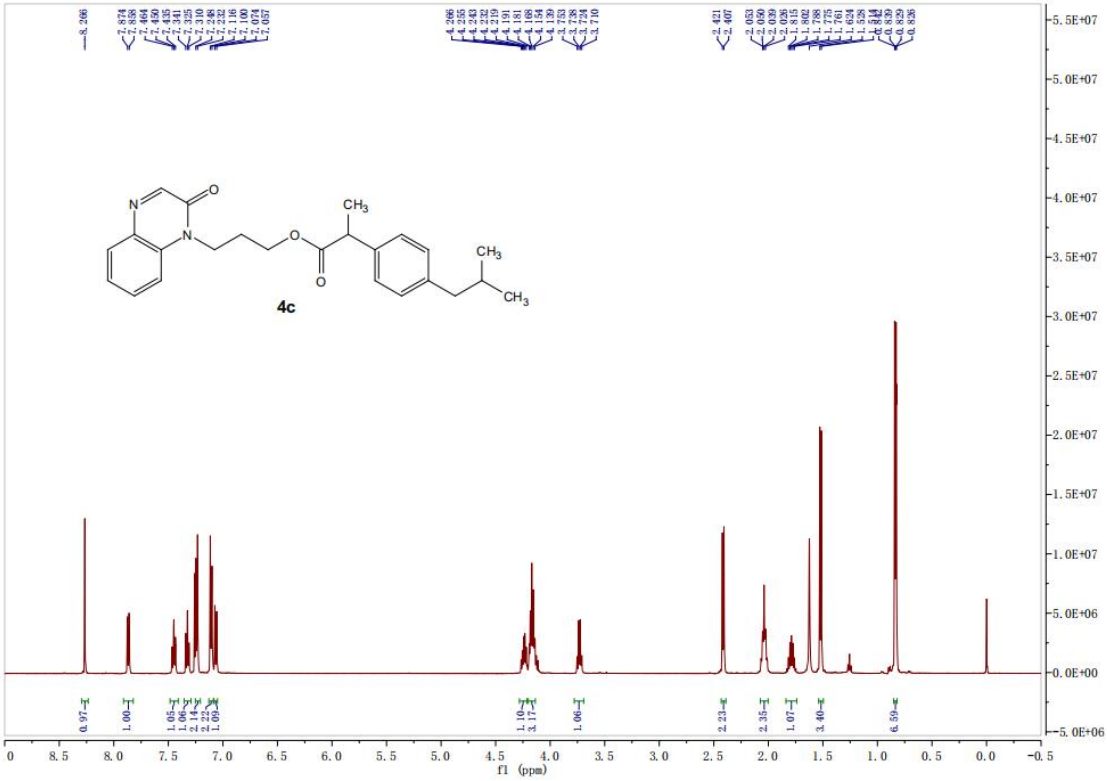

15.422
7.967
7.965
7.854
7.842
7.585
7.511
7.499
7.490
7.478
7.469
7.449
7.436
7.422
7.260
7.233
7.220
7.208
3.796
2.712
0.002
OH
O
CH3
H3C
3ya
0.54
1.92
0.84
2.09
0.97
2.00
2.10
1.06
2.94
2.91
f1 (ppm)

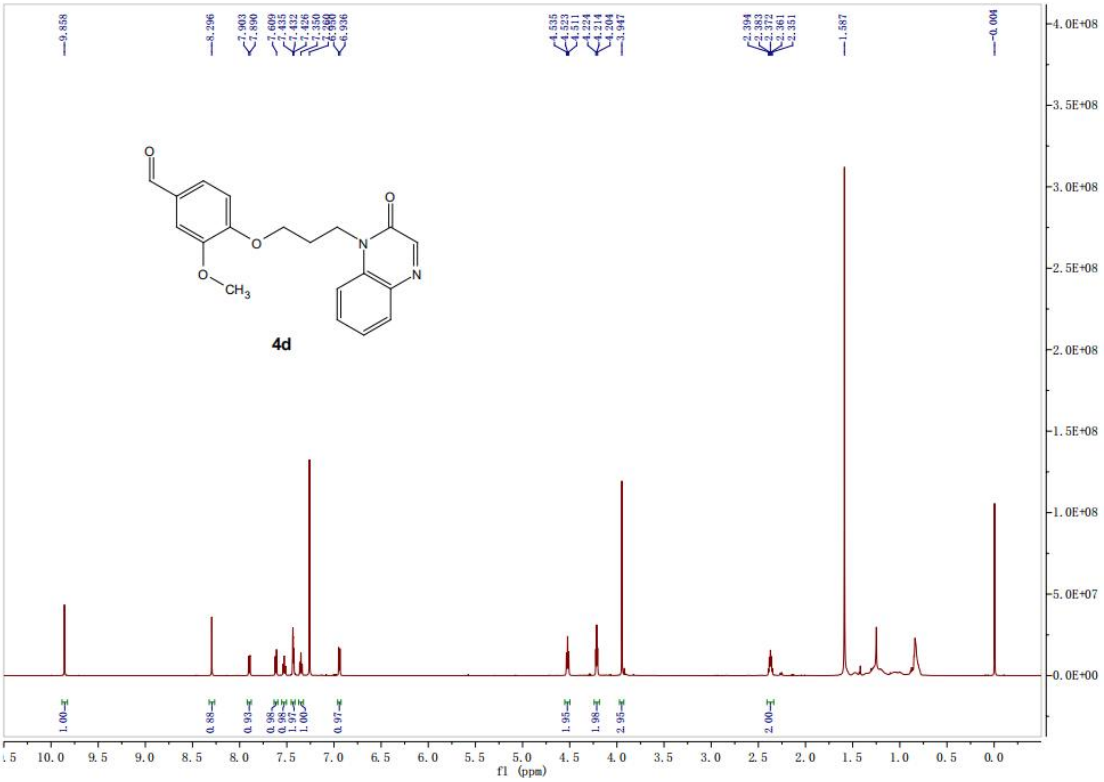

14.943
7.945
7.930
7.672
7.657
7.642
7.614
7.600
7.586
7.429
7.413
7.398
7.348
7.334
7.287
7.272
7.260
7.224
7.209
7.194
7.172
7.157
7.142
6.587
6.571
2.663
1.269
OH
O
H3C
3za
0.87
2.00
4.14
7.65
0.91
2.99
f1 (ppm)

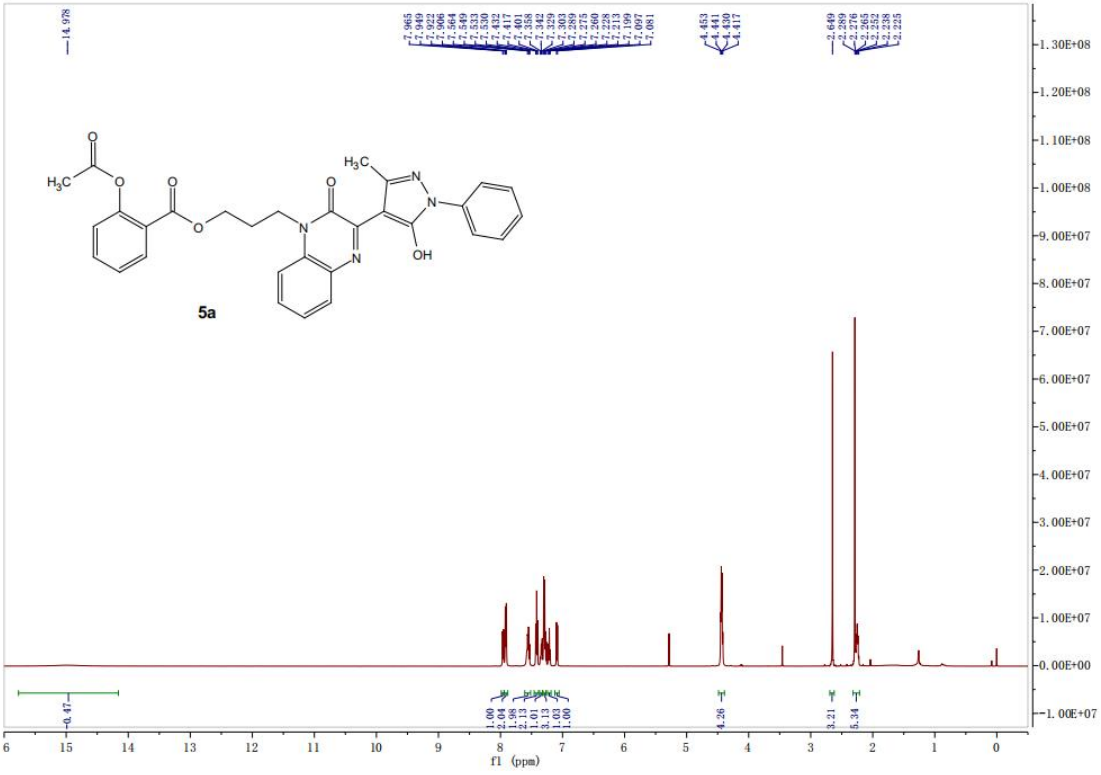

155.173
149.364
138.369
135.648
130.655
130.472
123.775
123.730
123.670
123.730
123.324
124.892
124.408
118.926
99.237
77.254
77.000
76.746
19.156
H3C
N
N
OH
N
O
3za
f1 (ppm)

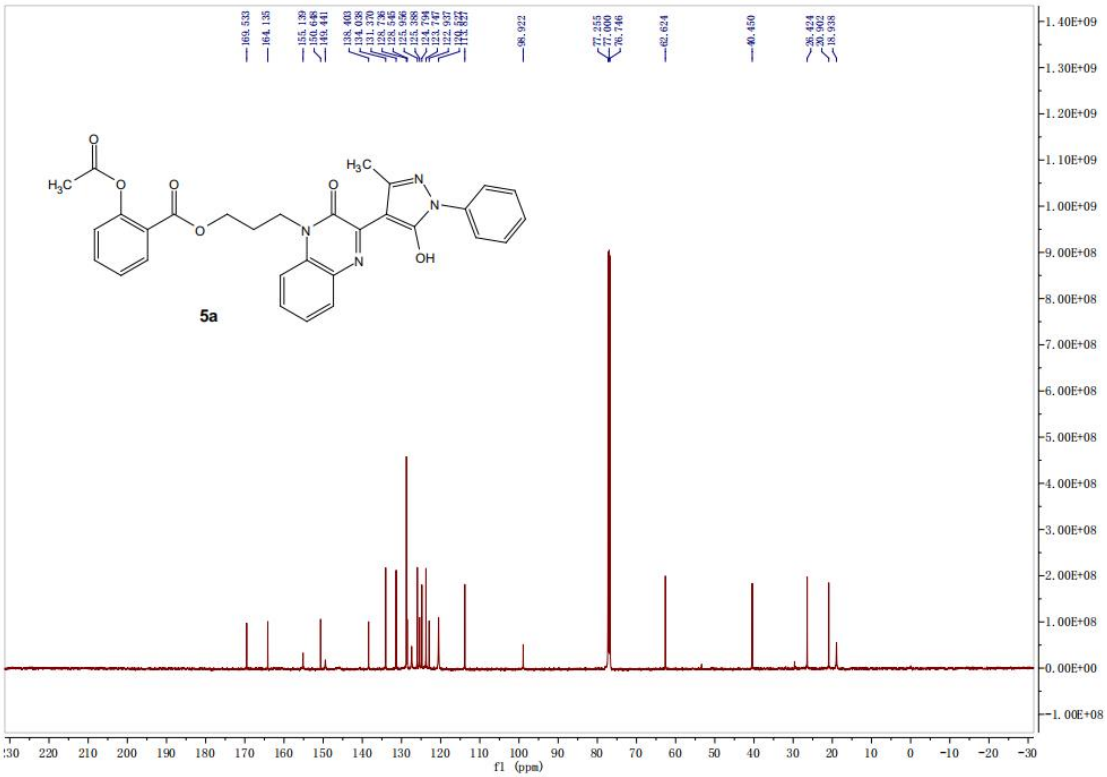

8.299
8.001
7.998
7.802
7.592
7.581
7.579
7.575
7.574
7.561
7.547
7.382
7.368
7.350
7.338
7.335
7.260
7.135
7.122
4.440
4.429
4.419
4.415
4.402
2.345
2.266
2.249
2.238
2.235
2.214
H3C
O
O
O
O
N
N
4a
0.90
1.01
0.97
2.01
3.88
1.00
4.13
3.09
2.23
f1 (ppm)

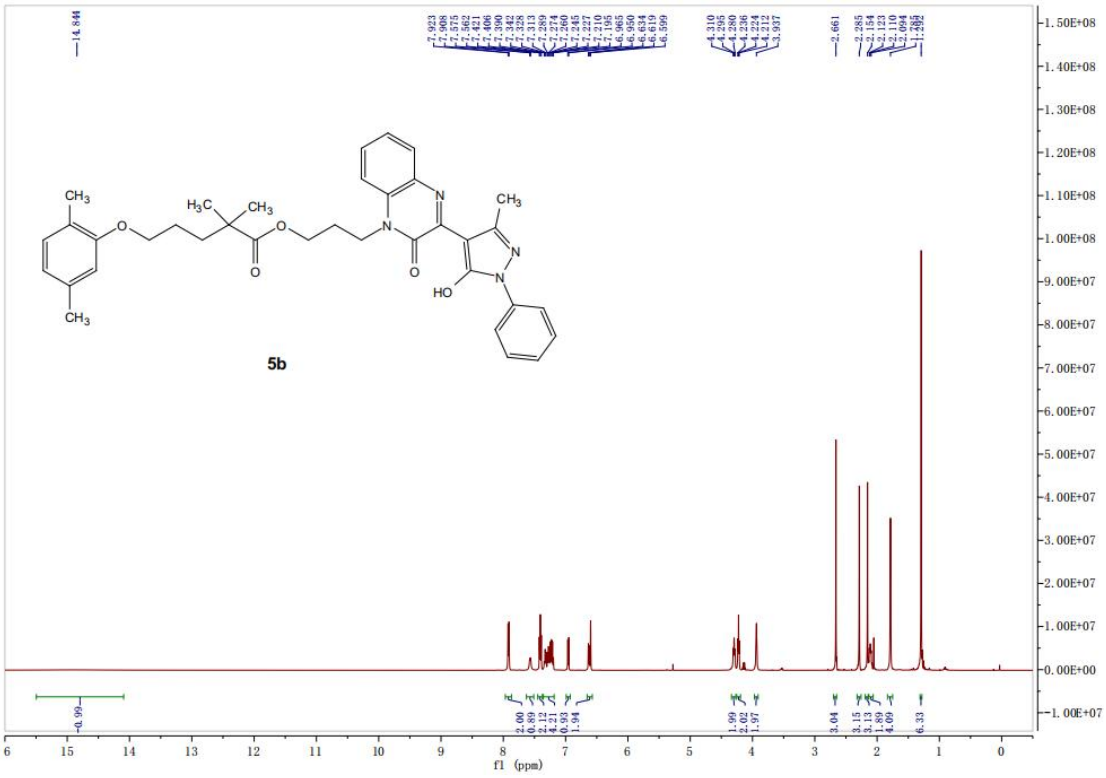

4b
f1 (ppm)

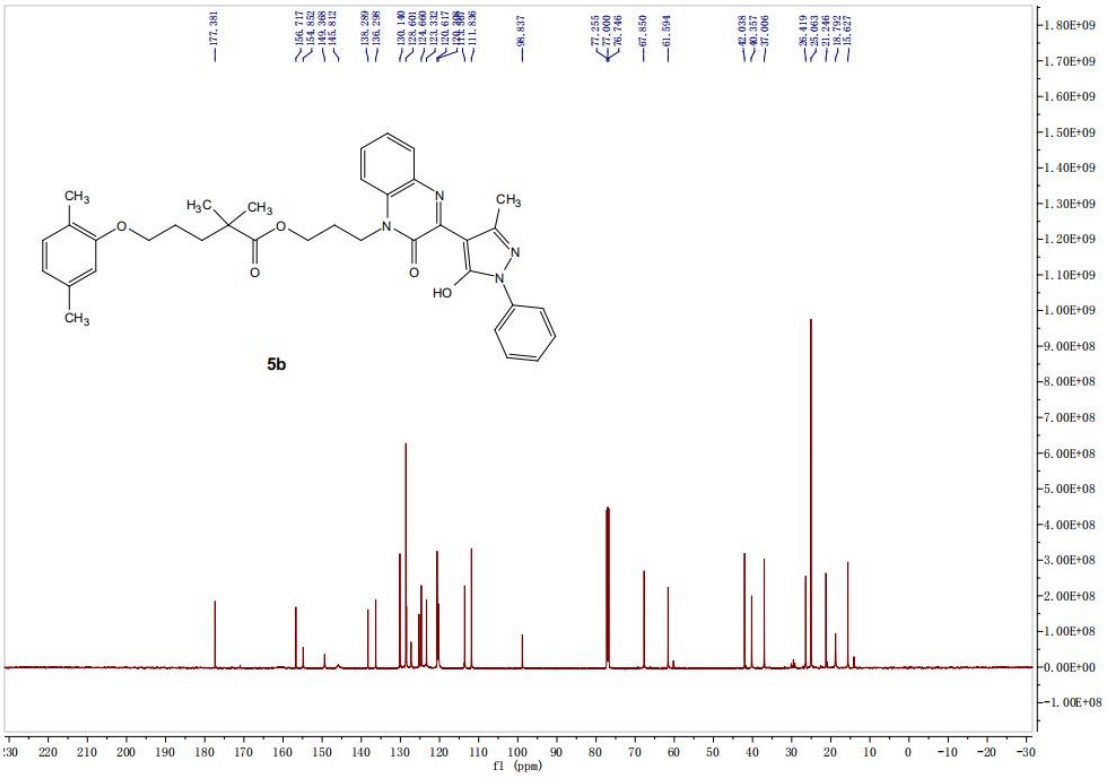

4c
f1 (ppm)

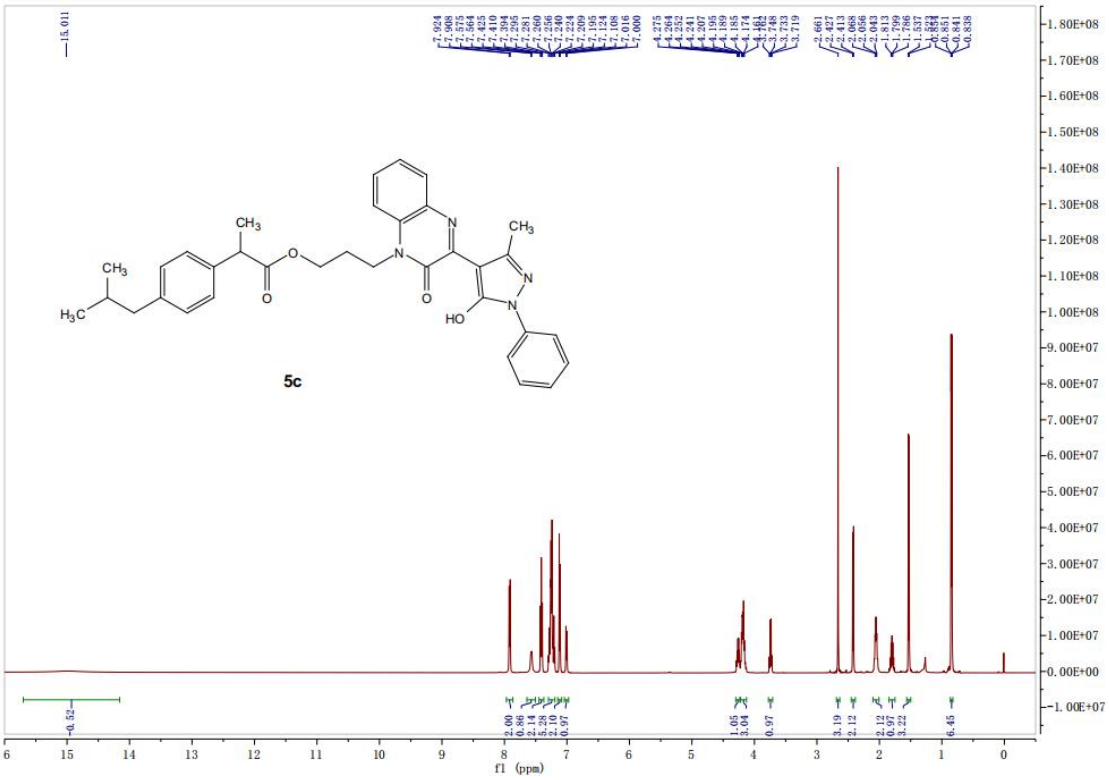

4d
f1 (ppm)

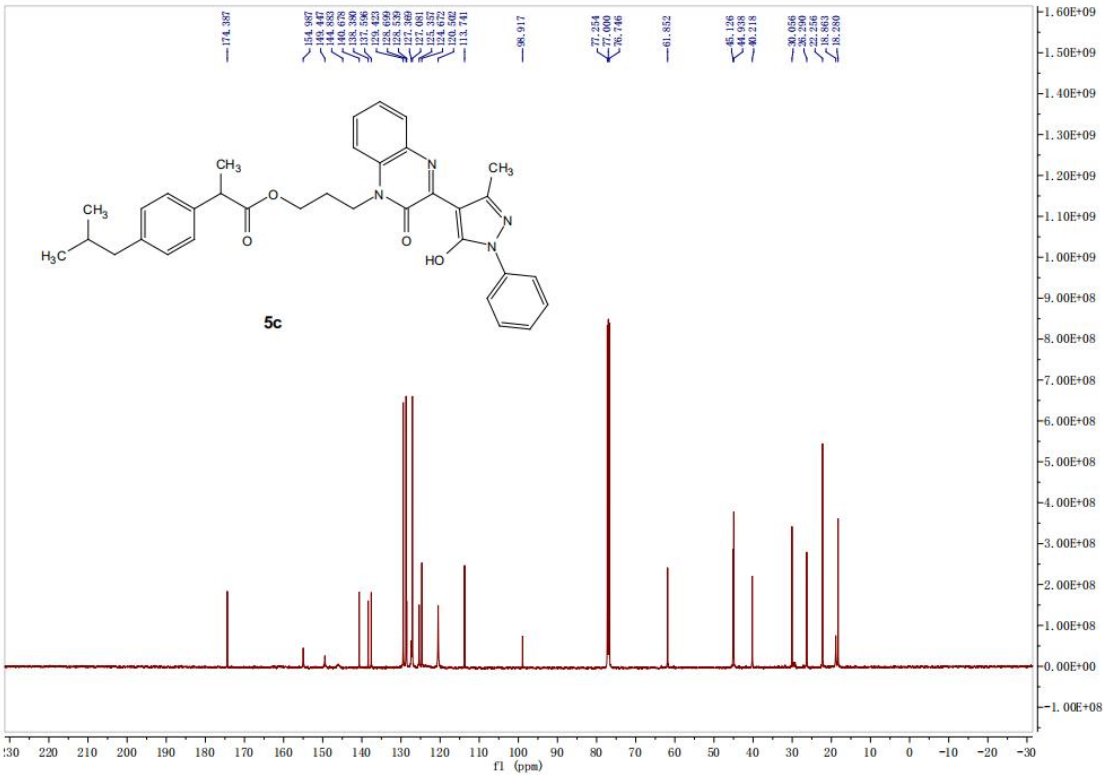

5a
f1 (ppm)

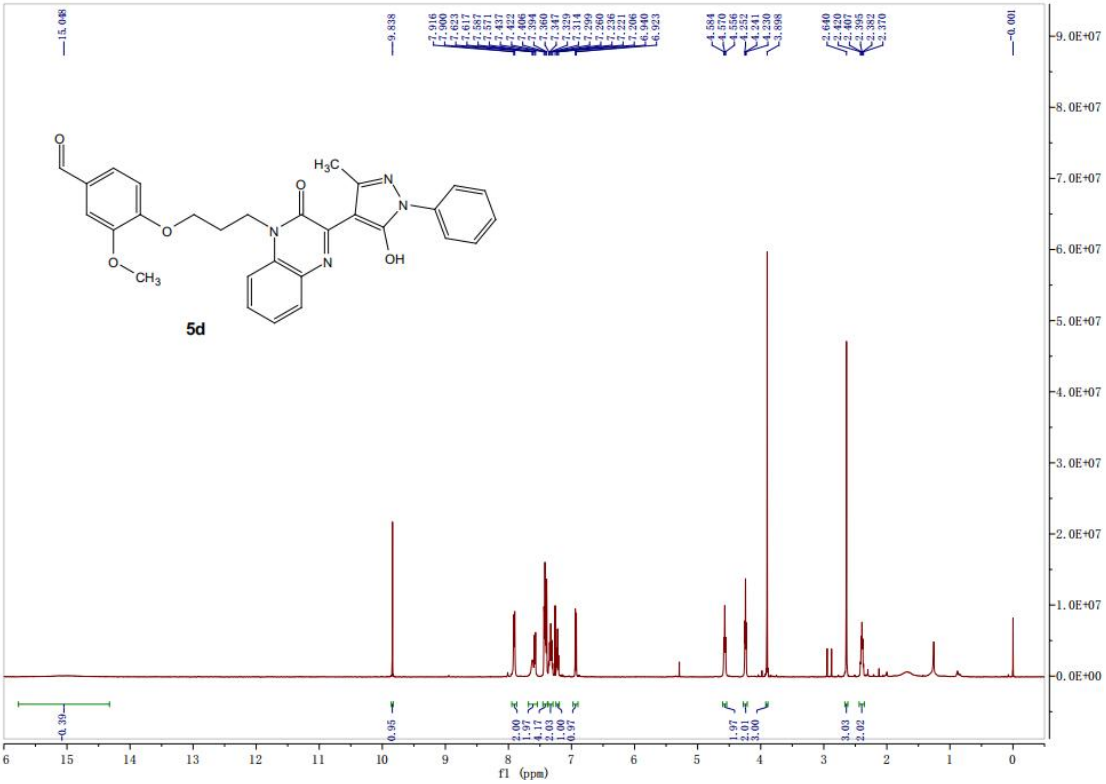

169.533
164.135
155.139
150.648
149.441
98.922
77.255
77.000
76.746
62.624
40.450
26.424
20.982
18.938
5a
f1 (ppm)

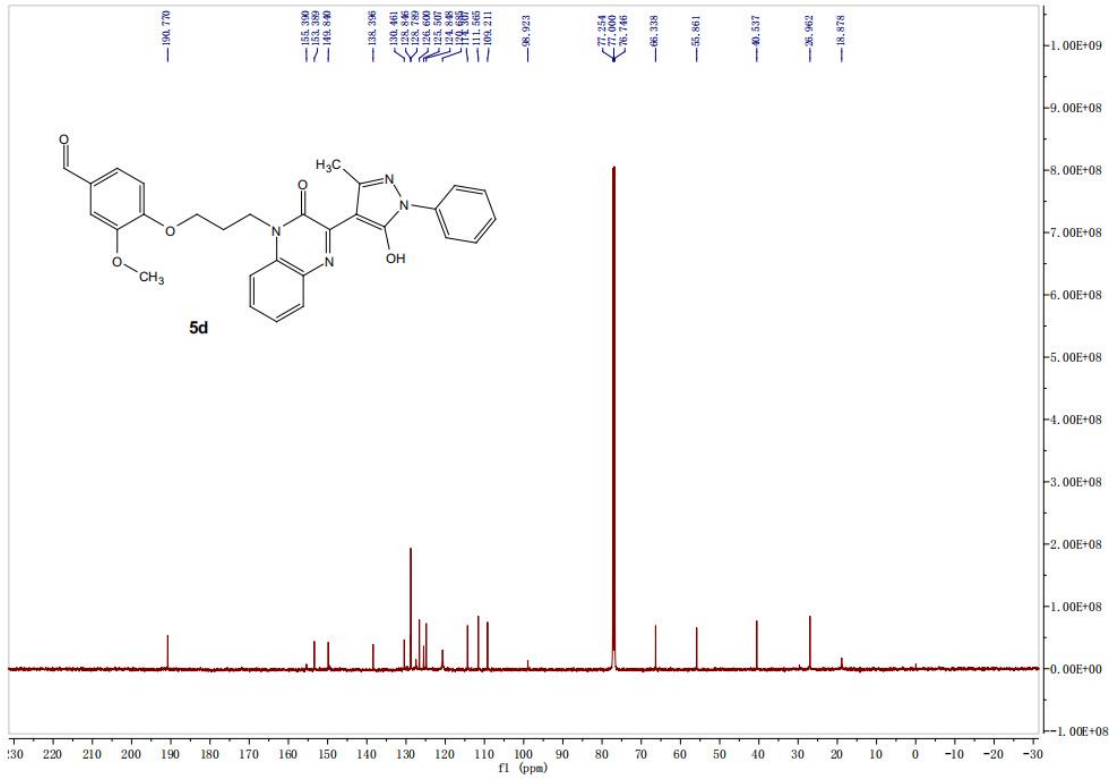

14.844
7.923
7.906
7.575
7.562
7.421
7.406
7.340
7.328
7.313
7.289
7.274
7.260
7.245
7.227
7.210
7.195
6.965
6.950
6.634
6.619
6.599
4.310
4.295
4.280
4.236
4.224
4.212
3.987
2.661
2.285
2.154
2.123
2.110
2.064
1.292
5b
f1 (ppm)


5b
f1 (ppm)


5c
f1 (ppm)


5c
f1 (ppm)


5d
f1 (ppm)


190.770
155.309
153.389
149.840
138.396
130.461
128.798
126.600
125.567
111.565
108.211
68.923
77.254
77.000
76.746
66.338
55.861
40.537
26.962
18.878
5d
f1 (ppm)