Supporting Information

Cu@g-C_3N_4 Heterojunction Catalyzed Visible-Light-Driven Direct C-H Alkylation of Heterocycles

Hong-Tao Ji[a]*, Jia-Sheng Wang[d], Jin-Feng Shang[a], Rong-Qiang Li[a]*, Zi Yang[b]*, Hai-Tao Zhu[c], Wei-Min He[d]*

[a]College of Chemistry and Pharmaceutical Engineering, Huanghuai University, Zhumadian 463000, China

[b]Hunan Provincial University Key Laboratory of the Fundamental and Clinical Research on Functional Nucleic Acid, Changsha Medical University, Changsha 410219, China

[c]College of Chemistry and Chemical Engineering, Baoji University of Arts and Sciences, Baoji 721013, China

[d]School of Chemistry and Chemical Engineering, University of South China, Hengyang 421001, China

E-mail: jihongtao@huanghuai.edu.cn; rqli@iccas.ac.cn; yangziycy@163.com; weiminhe@usc.edu.cn

Table of Content

1. General Information

Unless otherwise noted, materials were obtained from commercial suppliers and used without further purification. Thin layer chromatography (TLC) employed glass 0.25 mm silica gel plates. Flash chromatography columns were packed with 200-300 mesh silica gel. ^{1}H NMR spectra were recorded at 500 MHz or 400 MHz, ^{13}C{^{1}H} NMR spectra were recorded at 125 MHz or 100 MHz and ^{19}F NMR spectra were recorded at 500 MHz by using a Bruker Avance 500 or 400 spectrometer. Chemical shifts were calibrated using residual undeuterated solvent as an internal reference (^{1}H NMR: $CDCl_3$ 7.26 ppm, ^{13}C NMR: $CDCl_3$ 77.16 ppm), the chemical shifts (δ) were expressed in ppm, and J values were given in Hz. The following abbreviations were used to describe peak splitting patterns when appropriate: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, dd = doublet of doublets, br = broad. HRMS were performed on a spectrometer operating on ESI-TOF. UV/Vis spectra were recorded using a Hitachi U-3900 spectrophotometer. The crude products were purified by HPLC (LaboACE LC-5060, Japan Analytical Industry Co., Ltd., Japan) equipped with Jaigel 2.5 HR columns with dichloromethane as the eluent. Field emission scanning electron microscopy (SEM) observations were performed on a Hitachi SU8100 scanning electron microscopy operated at an accelerating voltage of 10.0 kV. XRD analysis was conducted by using Bruker D8 advance X ray diffractometer (λ= 1.5406 nm, V= 40 KV, I= 40 mA). Fourier transform infrared (FT-IR) spectra in the range of wavenumbers from 4000 to 400 cm^{-1} were obtained on a Perkin-Elmer Spectrum One spectrometer using KBr pellets. The X-ray photoelectron spectroscopy (XPS) measurements were performed by a Thermo Fisher K-Alpha spectrometer, equipped with an Al Kα X-ray source, and the binding energies were calibrated using the carbonaceous C 1s line (284.8 eV) as the reference. The distance from the light source to the irradiation vessel is 1 cm.

The Light Source and the Material of the Irradiation Vessel

Manufacturer：Beijing Rogertech Ltd.

Model：RLR-22CU

Value: 5836.430 µW/cm²/nm

Energy peak wavelength：453.0 nm

Peak width at half-height：22.1 nm

Material of the irradiation vessel：Schlenk flask

Not use any filters

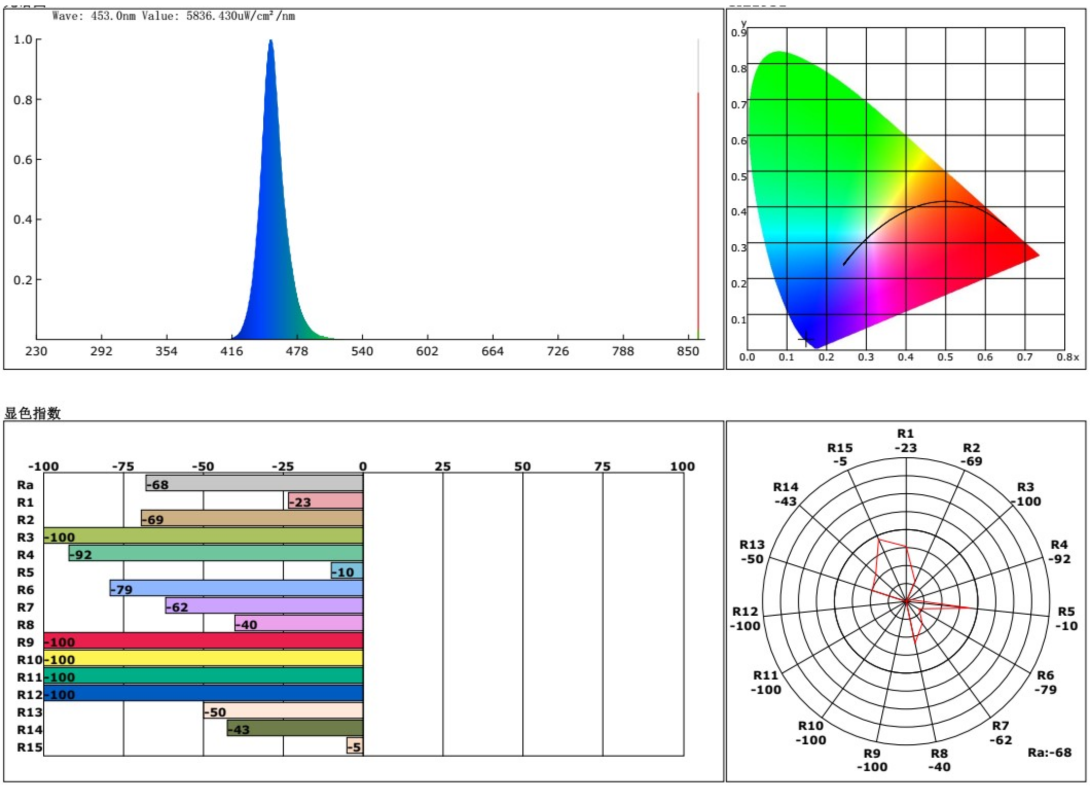


Figure S1: LED spectrum test report

2. General Experimental Procedure

2.1 Preparation and Characterizations of 20 mol% Cu@g-C_3N_4 Photocatalysts

2.1.1 Synthesis of 20 mol% Cu@g-C_3N_4 Photocatalysts

Copper-doped carbon nitride photocatalysts were prepared[1] : Melamine (15.8 mmol) and copper salts (3.13 mmol) were carefully ground using a mortar and pestle, afterwards, the mixture was then placed in a ceramic crucible and heated to 550 °C at a rate of 2 °C/min. After 2 hours, the samples were cooled to room temperature. The resulting solid products were collected and subsequently washed with DMF, deionized water, and ethanol and then dried for characterization and catalysis.

2.1.2 XRD Pattern of 20 mol% Cu@g-C_3N_4 and g-C_3N_4

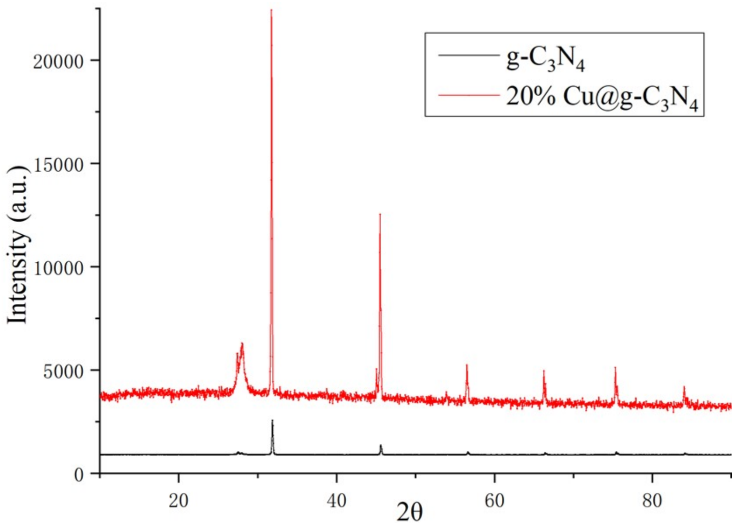


Figure S2: XRD analysis of 20 mol% Cu@g-C_3N_4 and g-C_3N_4

X-ray diffraction analysis (XRD) of 20 mol% Cu@g-C_3N_4 samples and g-C_3N_4 was recorded in Figure S2. The XRD patterns were obtained with a scan range from 10° to 90°. Compared to the weak diffraction peaks of pristine g-C_3N_4, the distinct diffraction peaks observed in the samples could be attributed to 20 mol% Cu@g - C_3N_4, suggesting that Cu was successfully doped and the inclusion of Cu did not impact the basic structure of the support g-C_3N_4. Moreover, the intensity of diffraction peaks of the doped sample is significantly enhanced, indicating the crystallinity of 20 mol% Cu@g-C_3N_4 is remarkably higher than that of pristine g - C_3N_4. Cu doping promotes the crystal growth and ordered arrangement of g-C_3N_4, which is beneficial for improving the structural stability of the material, charge separation and transport in photocatalysis.

2.1.3 FT-IR Spectra of 20 mol% Cu@g-C_3N_4 and g-C_3N_4

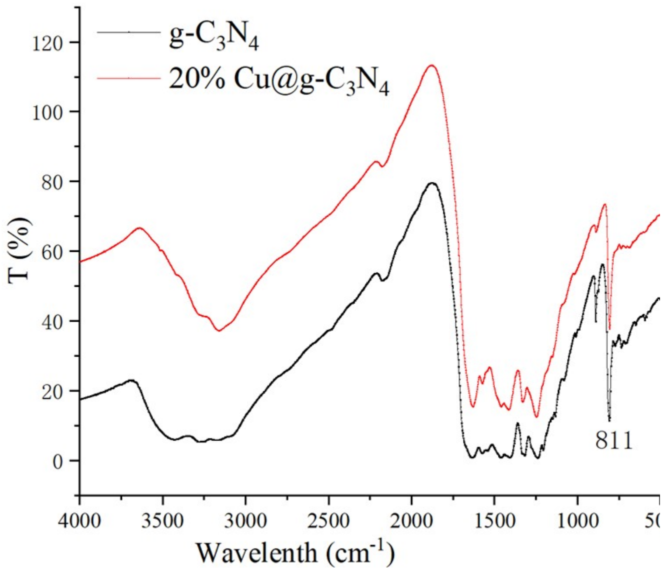


Figure S3: FT-IR spectra of 20 mol% Cu@g-C_3N_4 samples and g-C_3N_4

A broad peak of the N-H from residual amino groups and O-H from H_2O molecules were observed in the range of 2900 to 3200 cm^{-1}, which were attributed to the presence of residual amino groups and absorbed H_2O molecules, respectively. Additionally, the absorption band between 1300 and 1600 cm^{-1} corresponds to the characteristic vibration signal of the aromatic CN heterocycles. At 811 cm^{-1}, this sharp and intense peak corresponds to the absorption peak of g-C_3N_4.

2.1.4 UV/Vis Absorption Experiment of 20 mol% Cu@g-C_3N_4 and g-C_3N_4

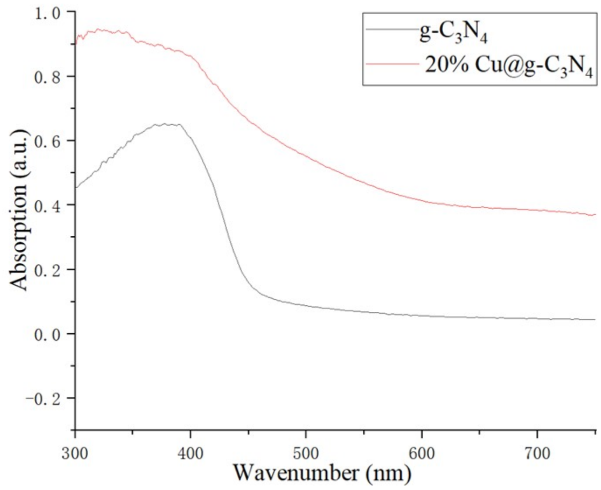
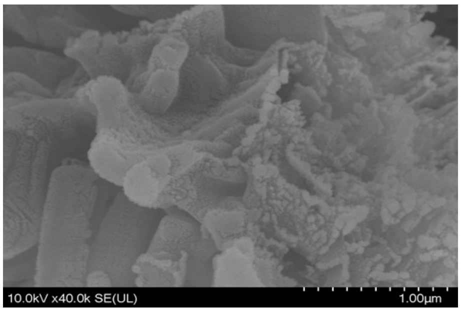


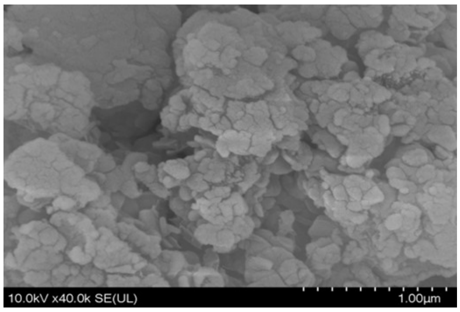
Figure S4: UV/Vis spectroscopic measurements

The optical properties and light harvesting ability of g-C_3N_4 and 20 mol% Cu@g-C_3N_4 were analyzed by the UV/Vis absorption spectra of 20 mol% Cu@g-C_3N_4 samples and g-C_3N_4 as recorded in Figure S4, respectively. g-C_3N_4 has a strong absorption in the ultraviolet region (approximately 300 - 400 nm), while the absorption in the visible light region is weak; In comparison to g-C_3N_4, 20 mol% Cu@g-C_3N_4 has enhanced optical absorption ability throughout the tested wavelength range (300 - 700 nm), and in particular，the absorption in the visible light region (400 - 700 nm) is significantly enhanced. This indicates that after doping, the light response range is broadened and the ability to utilize visible light is improved. Moreover, the absorption intensity of the doped sample is much higher than that of the pristine g-C_3N_4, which means that the 20 mol% Cu@g-C_3N_4 can capture more visible light photons, and the light response ability (especially the visible light response) is significantly enhanced, reflecting that the doping of Cu has a positive effect on improving the light response characteristics of g - C_3N_4.

2.1.5 SEM Image of g-C_3N_4 and 20 mol% Cu@g-C_3N_4



(a) g-C_3N_4



(b) 20 mol% Cu@g-C_3N_4

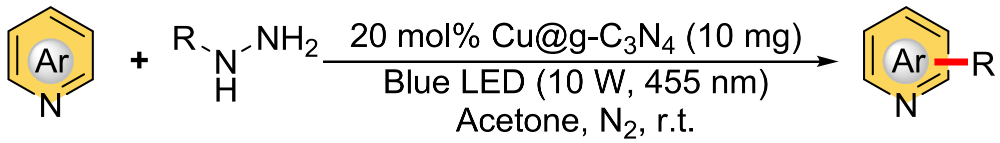
Figure S5: SEM images of g-C_3N_4 and 20 mol% Cu@g-C_3N_4

The morphology of g-C_3N_4 and 20 mol% Cu@g-C_3N_4 samples were analyzed using scanning electron microscope. The powder samples were dispersed in ethanol and deposited onto a silicon chip for examination. The classical morphology of g-C_3N_4 was recorded in (a), showing a typical layered stacking structure due to its two-dimensional layered nature. In contrast to g-C_3N_4, 20 mol% Cu@g-C_3N_4 still retains the layered structure, but the significant difference from g-C_3N_4 is that a large number of bright, particulate matter is uniformly distributed on the surface of the support g-

C_3N_4. These particles are small in size and well-dispersed, without large-scale agglomeration.

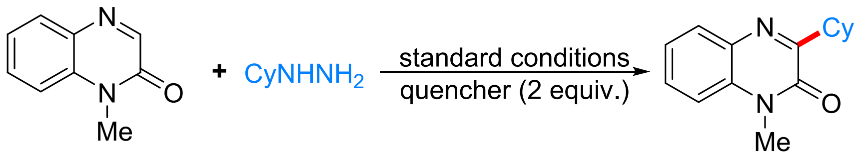
2.2. 20 mol % Cu@g-C_3N_4 Catalyzed Photocatalytic Transformation

2.2.1 Typical Procedure for the Synthesis of 3



To a 10.0 mL Schlenk flask equipped with a magnetic stirring bar were added heterocycles **1** (0.2 mmol), alkylhydrazines **2** (0.4 mmol), 20 mol% Cu@g-C_3N_4 (10 mg) and acetone (3.0 mL). The resulting mixture was degassed with nitrogen three times. Then the reaction mixture was stirred and irradiated by 10 W blue LED at ambient temperature for about 16 hrs. The reaction progress was monitored by thin-layer chromatography analysis. After the completion of the reaction, solids were removed by filtration. The filtrate was evaporated under reduced pressure, and the pure product **3** was obtained by chromatography column on silica gel (EtOAc: petroleum ether=5:1).

2.2.2 Radical Trapped Experiments



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

	Scavenger	Inhibited Species	3aa
(a)	Tempo	Radical	N.R.
(b)	BHT	Radical	N.R.
(c)	1,1-diphenylethylene	Radical	N.R.
(d)	$K_2S_2O_8$	e^-	N.R.
(e)	$[NH_4]_2C_2O_4$	h^+	N.R.
(f)	$CuCl_2$	SET	N.R.

(a) To a 10.0 mL Schlenk flask equipped with a magnetic stirring bar were added quinoxalin-2(1*H*)-ones **1a** (0.2 mmol), cyclohexylhydrazine **2a** (0.4 mmol), 20 mol % Cu@g-C_3N_4 (10 mg), radical scavengers (TEMPO, 0.4 mmol) and acetone (3.0 mL). Then the reaction mixture was stirred and irradiated by 10 W blue LED at ambient temperature under nitrogen for about 16 hrs. The reaction mixture was analyzed by GC and no **3aa** was detected.

(b) To a 10.0 mL Schlenk flask equipped with a magnetic stirring bar were added quinoxalin-2(1*H*)-ones **1a** (0.2 mmol), cyclohexylhydrazine **2a** (0.4 mmol), 20 mol% Cu@g-C_3N_4 (10 mg), radical scavengers (BHT, 0.4 mmol) and acetone (3.0 mL). Then the reaction mixture was stirred and irradiated by 10 W blue LED at ambient temperature under nitrogen for about 16 hrs. The reaction mixture was analyzed by GC and no **3aa** was detected.

(c) To a 10.0 mL Schlenk flask equipped with a magnetic stirring bar were added quinoxalin-2(1*H*)-ones **1a** (0.2 mmol), cyclohexylhydrazine **2a** (0.4 mmol), 20 mol% Cu@g-C_3N_4 (10 mg), radical scavengers (1,1-diphenylethylene, 0.4 mmol) and acetone (3.0 mL). Then the reaction mixture was stirred and irradiated by 10 W blue LED at ambient temperature under nitrogen for about 16 hrs. The reaction mixture was analyzed by GC and no **3aa** was detected.

(d) To a 10.0 mL Schlenk flask equipped with a magnetic stirring bar were added quinoxalin-2(1*H*)-ones **1a** (0.2 mmol), cyclohexylhydrazine **2a** (0.4 mmol), 20 mol% Cu@g-C_3N_4 (10 mg), $K_2S_2O_8$ (0.4 mmol) and acetone (3.0 mL). Then the reaction mixture was stirred and irradiated by 10 W blue LED at ambient temperature under nitrogen for about 16 hrs. The reaction mixture was analyzed by GC and no **3aa** was detected.

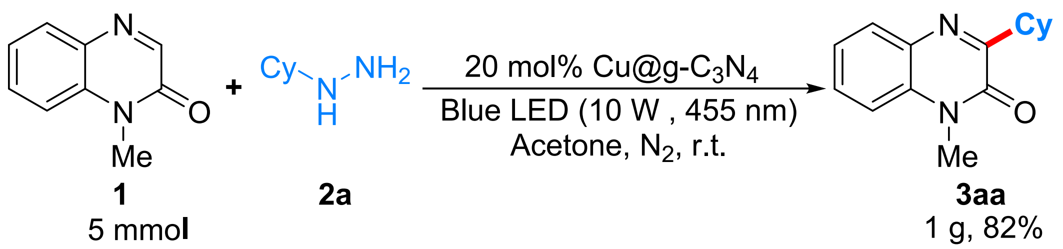
(e) To a 10.0 mL Schlenk flask equipped with a magnetic stirring bar were added quinoxalin-2(1*H*)-ones **1a** (0.2 mmol), cyclohexylhydrazine **2a** (0.4 mmol), 20 mol% Cu@g-C_3N_4 (10 mg), $K_2S_2O_8$ (0.4 mmol) and acetone (3.0 mL). Then the reaction mixture was stirred and irradiated by 10 W blue LED at ambient temperature under nitrogen for about 16 hrs. The reaction mixture was analyzed by GC and no **3aa** was detected.

(f) To a 10.0 mL Schlenk flask equipped with a magnetic stirring bar were added quinoxalin-2(1*H*)-ones **1a** (0.2 mmol), cyclohexylhydrazine **2a** (0.4 mmol), 20 mol% Cu@g-C_3N_4 (10 mg), ammonium oxalate (0.4 mmol) and acetone (3.0 mL).

Then the reaction mixture was stirred and irradiated by 10 W blue LED at ambient temperature under nitrogen for about 16 hrs. The reaction mixture was analyzed by GC and no **3aa** was detected.

(g) To a 10.0 mL Schlenk flask equipped with a magnetic stirring bar were added quinoxalin-2(1*H*)-ones **1a** (0.2 mmol), cyclohexylhydrazine **2a** (0.4 mmol), 20 mol% Cu@g-C_3N_4 (10 mg), $CuCl_2$ (0.4 mmol) and acetone (3.0 mL). Then the reaction mixture was stirred and irradiated by 10 W blue LED at ambient temperature under nitrogen for about 16 hrs. The reaction mixture was analyzed by GC and no **3aa** was detected.

2.2.3 Procedure for Gram Scale Synthesis of 3aa



To a 150 mL round bottom flask equipped with a magnetic stirring bar were added quinoxalin-2(1*H*)-ones **1a** (5 mmol), cyclohexylhydrazine **2a** (10 mmol), 20 mol% Cu@g-C_3N_4 (200 mg), and acetone (70 mL). The resulting mixture was degassed with argon three times. Then the reaction mixture was stirred and irradiated by 10 W blue LED at ambient temperature under nitrogen. After the completion of the reaction, the mixture was evaporated under reduced pressure and the residue was purified by HPLC to afford product **3aa** (1 g, 82% yield).

2.2.4 Reusability and Stability of Photocatalysts

The reusability and stability of 20 mol% Cu@g-C_3N_4 was tested: In a typical procedure, the mixture of quinoxalin-2(1*H*)-one **1a** (0.2 mmol), cyclohexylhydrazine **2a** (0.4 mmol), 20 mol% Cu@g-C_3N_4 (10 mg) were stirred in acetone (3 mL) irradiated with a 10 W blue LED for about 16 hrs under nitrogen at room temperature. After completion of the reaction, photocatalysts were separated by centrifugation and washed twice with acetone, then residual solvents were evaporated under reduced pressure for the next use.

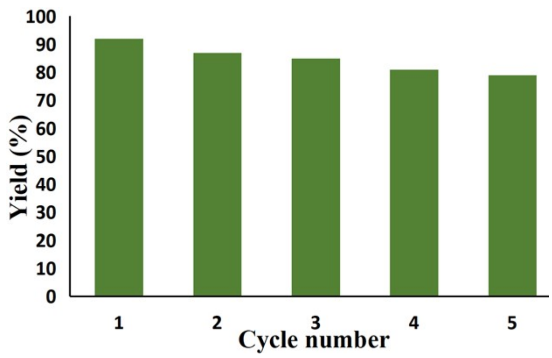


Figure S6: Reusability tests of 20 mol% Cu@g-C_3N_4

2.2.5 Effect of Visible Light Irradiation

The reaction between **1a** and **2a** was conducted under the standard conditions on a 0.2 mmol scale. The mixture was subjected to sequential periods of stirring under visible light irradiation (10 W blue LED) at room temperature with 3 hrs and followed by stirring in the absence of light with 3 hrs. At each time point, one reaction system was suspended, and the yield was detected by GC.

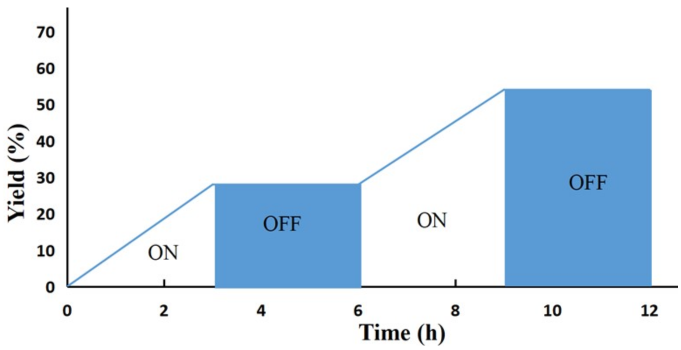
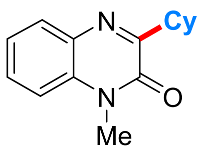
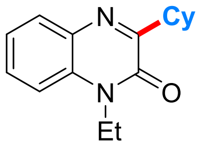


Figure S7: Visible light irradiation on/off experiment

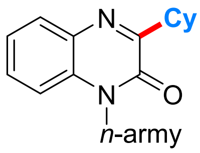
3. Characterization Data of Products



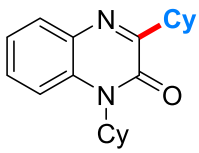
3-cyclohexyl-1-methylquinoxalin-2(1H)-one (**3aa**)[2] : White solid, 44.6 mg, 92% yield; petroleum ether/ethyl acetate (5:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.76 (d, *J* = 8.0 Hz, 1H), 7.43 (t, *J* = 7.8 Hz, 1H), 7.28 – 7.16 (m, 2H), 3.62 (s, 3H), 3.27 (td, *J* = 11.3, 8.2, 3.8 Hz, 1H), 1.88 (d, *J* = 12.7 Hz, 4H), 1.69 (d, *J* = 13.1 Hz, 1H), 1.54 – 1.33 (m, 4H), 1.28 – 1.18 (m, 1H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 164.3, 154.6, 132.9, 132.9, 129.8, 129.4, 123.4, 113.5, 40.8, 30.5, 29.1, 26.3, 26.2.



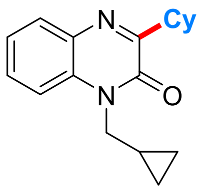
*3-cyclohexyl-1-ethylquinoxalin-2(1H)-one (***3ba**)[2] : Yellow solid, 44.1 mg, 86% yield; petroleum ether/ethyl acetate (5:1); ^1H NMR (500 MHz, $CDCl_3$) *δ* 7.85 (dd, *J* = 8.3, 1.6 Hz, 1H), 7.52 –7.49 (m, 1H), 7.37 – 7.24 (m, 2H), 4.32 (q, *J* = 7.2 Hz, 2H), 3.38 – 3.32 (m, 1H), 2.01 – 1.93 (m, 2H), 1.89-1.84 (m, 2H), 1.81 – 1.72 (m, 1H), 1.61 – 1.53 (m, 2H), 1.51 – 1.42 (m, 2H), 1.38 (t, *J* = 7.2 Hz, 3H), 1.34 – 1.23 (m, 1H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 164.4, 154.1, 133.3, 131.9, 130.2, 129.5, 123.3, 113.4, 77.4, 77.2, 76.9, 40.8, 37.4, 30.7, 26.5, 26.3, 12.5.



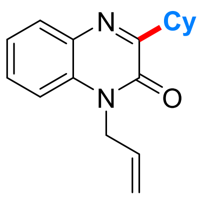
3-cyclohexyl-1-pentylquinoxalin-2(1H)-one (**3ca**)[2] : Yellow oil, 53.7 mg, 90% yield; petroleum ether/ethyl acetate (5:1); ^1H NMR (500 MHz, $CDCl_3$) *δ* 7.84 (d, *J* = 8.0 Hz, 1H), 7.49 (t, *J* = 7.8 Hz, 1H), 7.32 – 7.24 (m, 2H), 4.23 (t, *J* = 7.5 Hz, 2H), 3.37 – 3.31 (m, 1ccH), 1.97 – 1.94 (m, 2H), 1.89 – 1.84 (m, 2H), 1.78 – 1.72 (m, 3H), 1.61 – 1.53 (m, 2H), 1.51 – 1.38 (m, 6H), 1.35 – 1.24 (m, 1H), 0.93 (t, *J* = 6.9 Hz, 3H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) *δ* 164.4, 154.3, 133.3, 132.1, 130.1, 129.4, 123.3, 113.6, 42.5, 40.8, 30.7, 29.3, 27.1, 26.5, 26.3, 22.5, 14.1.



1,3-dicyclohexylquinoxalin-2(1H)-one (**3da**): Colorless oil, 45.3 mg, 73% yield; petroleum ether/ethyl acetate (5:1); ^1H NMR (500 MHz, $CDCl_3$) δ 7.96 (dd, *J* = 8.2, 1.5 Hz, 1H), 7.76 (dd, J = 8.3, 1.4 Hz, 1H), 7.63 – 7.47 (m, 2H), 4.52 (t, J = 6.0 Hz, 2H), 3.54 (t, J = 6.4 Hz, 2H), 3.19 – 3.13 (m, 1H), 2.14 – 2.03 (m, 4H), 1.98 – 1.88 (m, 4H), 1.82 – 1.61 (m, 4H), 1.59 – 1.17 (m, 4H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 155.6, 154.8, 139.5, 138.9, 128.9, 128.6, 126.7, 126.3, 65.4, 40.9, 33.5, 30.8, 29.8, 27.6, 26.7, 26.3; HRMS (ESI) m/z calcd for $C_{20}H_{27}N_2O$ $[M+H]^+$ 311.2118, found 311.2120.

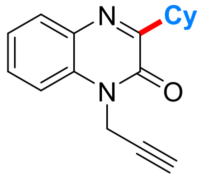


3-cyclohexyl-1-(cyclopropylmethyl)quinoxalin-2(1H)-one (**3ea**)[3] : Yellow oil, 50.8 mg, 90% yield; petroleum ether/ethyl acetate (5:1); ^1H NMR (500 MHz, $CDCl_3$) δ 7.84 (dd, J = 7.9, 1.6 Hz, 1H), 7.50 (m, 1H), 7.40 (dd, J = 8.5, 1.3 Hz, 1H), 7.34 – 7.27 (m, 1H), 4.19 (d, J = 7.0 Hz, 2H), 3.36 – 3.30 (m, 1H), 2.04 – 1.93 (m, 2H), 1.89 – 1.84 (m, 2H), 1.80 – 1.72 (m, 1H), 1.60 – 1.52 (m, 2H), 1.50 – 1.42 (m, 2H), 1.34 – 1.24 (m, 2H), 0.55 (m, 4H). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 164.6, 154.6, 133.2, 132.4, 130.1, 129.4, 123.3, 113.9, 46.2, 40.9, 30.7, 26.47, 26.3, 9.8, 4.3.

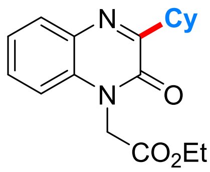


1-allyl-3-cyclohexylquinoxalin-2(1H)-one (**3fa**)[2] : Yellow oil, 47.2 mg, 88% yield; petroleum ether/ethyl acetate (5:1); ^1H NMR (500 MHz, $CDCl_3$) δ 7.84 (dd, J = 8.1, 1.5 Hz, 1H), 7.46 (dd, J = 15.7, 1.5 Hz, 1H), 7.35 – 7.23 (m, 2H), 5.94 (m, 1H), 5.26 (d, J = 10.4 Hz, 1H), 5.17 (d, J = 17.1 Hz, 1H), 4.96 – 4.87 (m, 2H), 3.37 – 3.33 (m, 1H), 2.01 – 1.93 (m, 2H), 1.89 – 1.89 (m, 2H), 1.80 – 1.74 (m, 1H), 1.62 – 1.54 (m, 2H), 1.51 – 1.42 (m, 2H), 1.35 – 1.29 (m, 1H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ

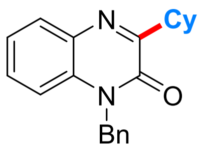
164.4, 154.2, 133.2, 132.2, 130.9, 130.0, 129.4, 123.5, 118.1, 114.1, 44.7, 40.8, 30.7, 26.4, 26.3.



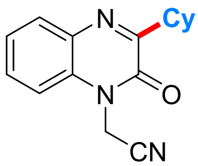
3-cyclohexyl-1-(prop-2-yn-1-yl)quinoxalin-2(1H)-one (**3ga**)[2] : Yellow oil, 42.6 mg, 80% yield; petroleum ether/ethyl acetate (5:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (dd, J = 8.0, 1.5 Hz, 1H), 7.53 – 7.42 (m, 1H), 7.35 (d, J = 8.3 Hz, 1H), 7.27 (t, J = 7.6 Hz, 1H), 4.97 (d, J = 2.5 Hz, 2H), 3.28 – 3.23 (m, 1H), 2.21 (d, J = 5.2 Hz, 1H), 1.94 – 1.84 (m, 2H), 1.81 – 1.75 (m, 2H), 1.72 – 1.65 (m, 1H), 1.55 – 1.32 (m, 4H), 1.28 – 1.18 (m, 1H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 164.2, 153.5, 133.1, 131.4, 129.9, 129.5, 123.8, 114.0, 77.1, 73.1, 40.8, 31.5, 30.5, 26.3, 26.1.



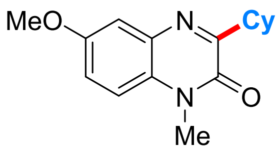
Ethyl 2-(3-cyclohexyl-2-oxoquinoxalin-1(2H)-yl)acetate (**3ha**)[2] : Yellow oil, 47.1 mg, 75% yield; petroleum ether/ethyl acetate (5:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.84 (dd, J = 8.0, 1.6 Hz, 1H), 7.47 – 7.44 (m, 1H), 7.33 – 7.30 (m, 1H), 7.04 (dd, J = 8.4, 1.3 Hz, 1H), 5.01 (s, 2H), 4.26 – 4.22 (m, 2H), 3.34 – 3.28 (m, 1H), 2.02 – 1.91 (m, 2H), 1.88 – 1.83 (m, 2H), 1.78 – 1.73 (m, 1H), 1.61 – 1.53 (m, 2H), 1.49 – 1.41 (m, 2H), 1.35 – 1.24 (m, 4H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 167.4, 164.1, 154.2, 133.1, 132.1, 130.2, 129.7, 123.8, 113.0, 62.1, 43.7, 40.9, 30.6, 26.4, 26.2, 14.2.



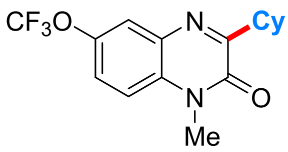
1-benzyl-3-cyclohexylquinoxalin-2(1H)-one (**3ia**)[2] : Yellow solid, 50.9 mg, 80% yield; petroleum ether/ethyl acetate (5:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (d, J = 7.9 Hz, 1H), 7.29 – 7.12 (m, 8H), 5.39 (s, 2H), 3.35 – 3.28 (m, 1H), 1.93 (dd, J = 13.2, 3.5 Hz, 2H), 1.82 – 1.77 (m, 2H), 1.71 – 1.66 (m, 1H), 1.57 – 1.47 (m, 2H), 1.45 – 1.35 (m, 2H), 1.29 – 1.17 (m, 1H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 164.5, 154.7, 135.6, 133.3, 132.3, 130.0, 129.5, 129.0, 127.7, 127.0, 123.5, 114.3, 46.0, 40.9, 30.7, 26.4, 26.3.



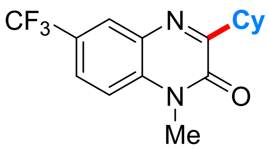
2-(3-cyclohexyl-2-oxoquinoxalin-1(2H)-yl)acetonitrile (**3ja**)[4] : White solid, 39.5 mg, 74% yield; petroleum ether/ethyl acetate (5:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.82 (dd, J = 8.0, 1.5 Hz, 1H), 7.53 – 7.50 (m, 1H), 7.38 – 7.31 (m, 1H), 7.22 (d, J = 8.3 Hz, 1H), 5.12 (s, 2H), 3.25 – 3.20 (m, 1H), 1.90 – 1.87 (m, 2H), 1.82 – 1.78 (m, 2H), 1.74 – 1.66 (m, 1H), 1.55 –1.46 (m, 2H), 1.43 – 1.35 (m, 2H), 1.27 – 1.18 (m, 1H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 164.0, 153.3, 133.1, 130.7, 130.7, 130.3, 124.8, 113.9, 112.9, 41.1, 30.6, 29.5, 26.3, 26.2.



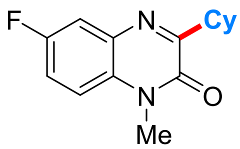
3-*cyclohexyl-6-methoxy-1-methylquinoxalin-2(1H)-one* (**3ka**)[2] : Yellow solid, 48.4 mg, 89% yield; petroleum ether/ethyl acetate (5:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.24 (d, J = 2.9 Hz, 1H), 7.13 (d, J = 9.0 Hz, 1H), 7.05 (dd, J = 9.1, 2.8 Hz, 1H), 3.81 (s, 3H), 3.61 (s, 3H), 3.31 – 3.25 (m, 1H), 1.93 – 1.85 (m, 2H), 1.81 – 1.77 (m, 2H), 1.73 – 1.67 (m, 1H), 1.55 – 1.36 (m, 4H), 1.27 – 1.18 (m, 1H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 165.0, 156.0, 154.3, 133.7, 127.2 118.7, 114.5, 111.3, 55.9, 40.9, 30.7, 29.3, 26.4, 26.3.



3-cyclohexyl-1-methyl-6-(trifluoromethoxy)quinoxalin-2(1H)-one (**3la**)[2] : White solid, 50.9 mg, 78% yield; petroleum ether/ethyl acetate (5:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.73 (d, J = 2.8 Hz, 1H), 7.38 (dd, J = 9.1, 2.7 Hz, 1H), 7.29 (d, J = 9.1 Hz, 1H), 3.70 (s, 3H), 3.38 – 3.34 (m, 1H), 2.00 – 1.92 (m, 2H), 1.89 – 1.86 (m, 2H), 1.80 – 1.74 (m, 1H), 1.60 – 1.43 (m, 4H), 1.35 – 1.25 (m, 1H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 166.22, 154.34, 144.78, 144.76 (d, J = 1.25 Hz), 133.27, 131.74, 122.53, 121.83, 121.67, 119.62 (d, J = 256.25 Hz), 114.6, 41.0, 30.6, 29.4, 26.4, 26.2; ^{19}F NMR (471 MHz, $CDCl_3$) δ -58.19.

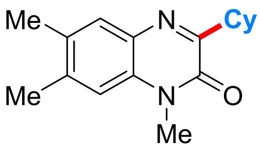


3-cyclohexyl-1-methyl-6-(trifluoromethyl)quinoxalin-2(1H)-one (**3ma**)[2] : White solid, 52.7 mg, 85% yield; petroleum ether/ethyl acetate (5:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.94 (d, J = 8.3 Hz, 1H), 7.59 – 7.49 (m, 2H), 3.73 (s, 3H), 3.36 – 3.32 (m, 1H), 1.99 – 1.93 (m, 2H), 1.89 – 184 (m, 2H), 1.81 – 1.75 (m, 1H), 1.59 – 1.43 (m, 4H), 1.33 – 1.27 (m, 1H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 167.0, 154.2, 134.6, 132.9, 131.1, 130.8, 130.4, 124.8, 122.7, 119.9, 119.9, 110.9, 110.9, 41.0, 30.5, 29.3, 26.2, 26.1; ^{19}F NMR (471 MHz, $CDCl_3$) δ -62.22.

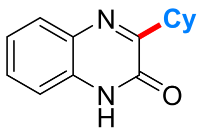


3-cyclohexyl-6-fluoro-1-methylquinoxalin-2(1H)-one (**3na**)[5] : White solid, 37.5 mg, 72% yield; petroleum ether/ethyl acetate (5:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.47 (dd, J = 8.8, 2.6 Hz, 1H), 7.21 – 7.15 (m, 2H), 3.62 (s, 2H), 3.29 – 3.24 (m, 1H), 1.92

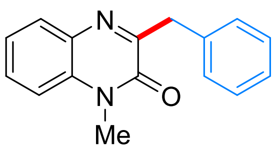
– 1.84 (m, 2H), 1.81 – 1.77 (m, 2H), 1.74 – 1.65 (m, 1H), 1.56 – 1.33 (m, 4H), 1.28 – 1.19 (m, 1H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 166.0, 159.7, 157.8, 154.3, 133.7, 133.6, 129.7, 129.7, 117.2, 117.0, 115.5, 115.3, 114.7, 114.6, 41.0, 30.6, 29.5, 26.4, 26.3; ^{19}F NMR (471 MHz, $CDCl_3$) δ -119.52.



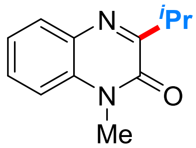
3-cyclohexyl-1,6,7-trimethylquinoxalin-2(1H)-one (**3oa**)[2] : Yellow solid, 47.0 mg, 87% yield; petroleum ether/ethyl acetate (5:1); ^1H NMR (500 MHz, $CDCl_3$) δ 7.60 (s, 1H), 7.04 (s, 1H), 3.67 (s, 3H), 3.37 – 3.25 (m, 1H), 2.40 (s, 3H), 2.34 (s, 3H), 1.98 – 1.91 (m, 2H), 1.87 – 1.84 (m, 2H), 1.79 – 1.74 (m, 1H), 1.59 – 1.42 (m, 4H), 1.34 – 1.26 (m, 1H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 163.2, 154.8, 139.1, 132.4, 131.4, 130.9, 130.0, 114.2, 40.8, 30.7, 29.1, 26.5, 26.3, 20.6, 19.2.



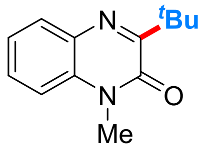
3-cyclohexylquinoxalin-2(1H)-one (**3pa**)[2] : Yellow oil, 47.0 mg, 87% yield; petroleum ether/ethyl acetate (2:1); ^1H NMR (500 MHz, $CDCl_3$) δ 7.85 – 7.83 (m, 1H), 7.49 – 7.45 (m, 1H), 7.34 – 7.31 (m, 1H), 7.27 – 7.25 (m, 2H), 3.38 – 3.32 (m, 1H), 2.01 – 1.98 (m, 2H), 1.91 – 1.87 (m, 2H), 1.81 – 1.77 (m, 1H), 1.64 – 1.57 (m, 2H), 1.54 – 1.46 (m, 2H), 1.37 – 1.25 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 165.13, 155.78, 133.07, 130.70, 129.60, 129.08, 124.09, 115.32, 40.29, 30.63, 26.45, 26.27.



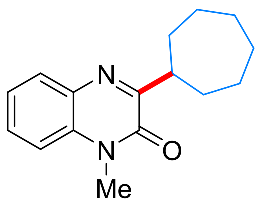
3-benzyl-1-methylquinoxalin-2(1H)-one (**3ab**)[6] : Yellow solid, 36.0 mg, 72% yield; petroleum ether/ethyl acetate (5:1);^1H NMR (500 MHz, $CDCl_3$) δ 7.78 (dd, J = 8.0, 1.5 Hz, 1H), 7.46-7.43 (m, 1H), 7.42 – 7.34 (m, 2H), 7.27 – 7.18 (m, 4H), 7.13 (t, *J* = 7.4 Hz, 1H), 4.19 (s, 2H), 3.58 (s, 3H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) *δ* 159.4, 154.9, 137.2, 133.5, 132.9, 130.1, 130.0, 129.7, 128.5, 126.7, 123.7, 113.7, 40.9, 29.2.



3-isopropyl-1-methylquinoxalin-2(1H)-one (**3ac**)[2] : Yellow solid, 36.0 mg, 89% yield; petroleum ether/ethyl acetate (5:1); ^1H NMR (500 MHz, $CDCl_3$) δ 7.77 (d, *J* = 7.9 Hz, 1H), 7.43 (t, *J* = 7.8 Hz, 1H), 7.25 (t, *J* = 7.6 Hz, 1H), 7.23 – 7.18 (m, 1H), 3.63 (s, 3H), 3.58 – 3.53 (m, 1H), 1.24 (d, *J* = 6.9 Hz, 6H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 165.1, 154.6, 133.1, 132.9, 129.9, 129.6, 123.5, 113.6, 31.3, 29.2, 20.3.

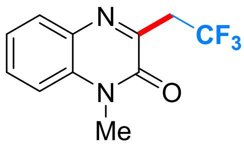


(tert-butyl)-1-methylquinoxalin-2(1H)-one (**3ad**)[2] : White solid, 36.7 mg, 85% yield; petroleum ether/ethyl acetate (5:1); ^1H NMR (500 MHz, $CDCl_3$) *δ* 7.76 (dd, *J* = 7.9, 1.5 Hz, 1H), 7.45 – 7.41 (m, 1H), 7.27 – 7.21 (m, 1H), 7.20 (d, *J* = 9.0 Hz, 1H), 3.60 (s, 3H), 1.41 (s, 9H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) *δ* 165.4, 153.9, 133.5, 132.3, 130.3, 129.7, 123.3, 113.4, 39.6, 28.9, 28.0.

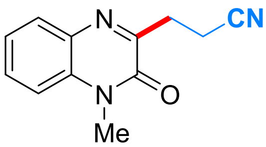


3-cycloheptyl-1-methylquinoxalin-2(1H)-one (**3ae**)[7] : White solid, 31.3 mg, 61% yield; petroleum ether/ethyl acetate (5:1); ^1H NMR (500 MHz, $CDCl_3$) *δ* 7.82 (d, *J* = 8.0 Hz, 1H), 7.50 (t, *J* = 7.8 Hz, 1H), 7.37 – 7.20 (m, 2H), 3.69 (s, 3H), 3.48 (m, 1H), 1.97 (m, 3H), 1.87 – 1.76 (m, 4H), 1.71 – 1.68 (m, 2H), 1.65 – 1.59 (m, 4H); $^{13}C\{^1H\}$

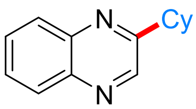
NMR (125 MHz, $CDCl_3$) δ 165.4, 154.5, 132.9, 132.8, 129.8, 129.4, 123.5, 113.5, 42.5, 32.4, 29.1, 28.3, 27.2.



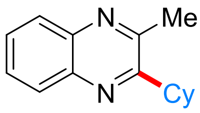
1-methyl-3-(2,2,2-trifluoroethyl)quinoxalin-2(1H)-one (**3af**)[8] : Yellow solid, 36.3 mg, 75% yield; petroleum ether/ethyl acetate (5:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.83 (dd, J = 7.9, 1.5 Hz, 1H), 7.56-7.53 (m, 1H), 7.32 (t, J = 7.6 Hz, 1H), 7.27 (d, J = 8.4 Hz, 1H), 3.78 (q, J = 10.3 Hz, 2H), 3.66 (s, 3H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 154.6, 150.6, 133.4, 132.5, 131.2, 130.6, 124.0, 113.8, 37.9, 37.6, 37.4, 37.2 (q, J = 59.4 Hz), 29.4; ^{19}F NMR (471 MHz, $CDCl_3$) δ -62.95.



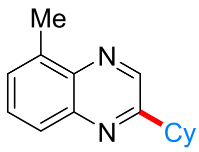
3-(4-methyl-3-oxo-3,4-dihydroquinoxalin-2-yl)propanenitrile (**3ag**)[9] : Colorless oil, 30.7 mg, 72% yield; petroleum ether/ethyl acetate (5:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.81 (dd, J = 8.0, 1.5 Hz, 1H), 7.53 – 7.50 (m, 1H), 7.36 – 7.22 (m, 2H), 3.65 (s, 3H), 3.24 (t, J = 7.2 Hz, 2H), 2.86 (t, J = 7.1 Hz, 2H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 155.9, 154.5, 133.1, 132.4, 130.5, 130.1, 123.9, 119.6, 113.7, 29.4, 29.1, 13.6.



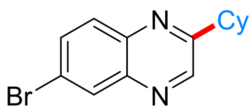
2-cyclohexylquinoxaline (**3qa**)[10] : Yellow oil, 36.5 mg, 86% yield; petroleum ether/ethyl acetate (5:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.77 (s, 1H), 8.08 – 8.04 (m, 2H), 7.79 – 7.64 (m, 2H), 3.00 – 2.94 (m, 1H), 2.08 – 2.02 (m, 2H), 1.96 – 1.90 (m, 2H), 1.83 – 1.78 (m, 1H), 1.76 – 1.67 (m, 2H), 1.52 – 1.48 (m, 2H), 1.40 – 1.34 (m, 1H); $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$) δ 161.2, 145.1, 142.3, 141.5, 129.9, 129.2, 129.1, 128.9, 45.2, 32.4, 26.5, 26.0.



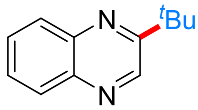
2-cyclohexyl-3-methylquinoxaline (**3ra**)[11] : Yellow oil, 29.4 mg, 65% yield; petroleum ether/ethyl acetate (5:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.07 – 7.92 (m, 2H), 7.70 – 7.60 (m, 2H), 3.07 – 3.04 (m, 1H), 2.79 (s, 3H), 1.98 – 1.89 (m, 4H), 1.82 – 1.74 (m, 4H), 1.48 – 1.37 (m, 2H); $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$) δ 160.5, 152.8, 141.5, 140.7, 128.9, 128.8, 128.7, 128.3, 42.8, 31.7, 26.8, 26.1, 22.8.



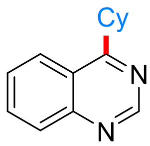
2-cyclohexyl-8-methylquinoxaline (**3sa**): Yellow oil, 31.7 mg, 70% yield; petroleum ether/ethyl acetate (5:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.73 (s, 1H), 7.89 (dd, J = 6.9, 3.0 Hz, 1H), 7.60 – 7.52 (m, 2H), 3.00-2.94 (m, 1H), 2.79 (s, 3H), 2.08 – 2.02 (m, 2H), 1.95 – 1.90 (m, 2H), 1.83 – 1.78 (m, 1H), 1.77 – 1.71 (d, J = 3.5 Hz, 2H), 1.53 – 1.44 (m, 2H), 1.40 – 1.34 (m, 1H); $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$) δ 159.9, 144.6, 141.5, 141.4, 137.6, 129.8, 128.6, 126.9, 44.9, 32.5, 26.5, 26.1, 17.2. HRMS (ESI) m/z calcd for $C_{15}H_{19}N_2$ $[M+H]^+$ 227.1543, found 227.1540.



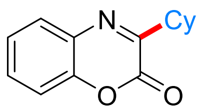
6-bromo-2-cyclohexylquinoxaline (**3ta**): Yellow oil, 42.3 mg, 73% yield; petroleum ether/ethyl acetate (5:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.76 (s, 1H), 8.24 (d, J = 2.1 Hz, 1H), 7.93 (d, J = 8.9 Hz, 1H), 7.77 (dd, J = 8.9, 2.2 Hz, 1H), 2.98 – 2.93 (m, 1H), 2.06 – 1.99 (m, 2H), 1.96 – 1.91 (m, 2H), 1.83 – 1.78 (m, 1H), 1.73 – 1.64 (m, 2H), 1.52 – 1.43 (m, 2H), 1.37 – 1.33 (m, 1H); $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$) δ 162.2, 145.5, 143.0, 140.3, 132.5, 131.6, 130.6, 123.9, 45.1, 32.3, 26.5, 26.0. HRMS (ESI) m/z calcd for $C_{14}H_{16}BrN_2$ $[M+H]^+$ 291.0491, found 291.0494.



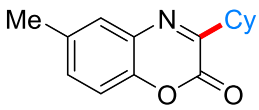
2-(tert-butyl)quinoxaline (**3ua**)[12] : Yellow oil, 30.2 mg, 81% yield; petroleum ether/ethyl acetate (5:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.99 (s, 1H), 8.07 – 8.05 (m, 2H), 7.75 – 7.68 (m, 2H), 1.52 (s, 9H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 163.8, 143.5, 141.8, 140.9, 129.8, 129.4, 129.0, 129.0, 37.4, 29.9.



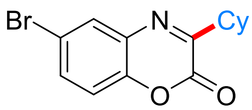
4-cyclohexylquinazoline (**3va**)[13] : Yellow oil, 37.8 mg, 89% yield; petroleum ether/ethyl acetate (5:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.25 (s, 1H), 8.19 (d, J = 8.4 Hz, 1H), 8.04 (d, J = 8.4 Hz, 1H), 7.87 (t, J = 7.7 Hz, 1H), 7.63 (t, J = 7.6 Hz, 1H), 3.59 – 3.53 (m, 1H), 2.20 – 1.92 (m, 5H), 1.86 – 1.78 (m, 3H), 1.57 – 1.48 (m, 2H), 1.43 – 1.35 (m, 1H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 175.2, 154.9, 150.2, 133.4, 129.4, 127.4, 124.3, 123.3, 41.4, 32.1, 26.6, 26.1.



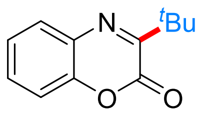
3-cyclohexyl-2H-benzo[b][1,4]oxazin-2-one (**3wa**)[10] : Yellow oil, 36.7 mg, 73% yield; petroleum ether/ethyl acetate (5:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.74 (d, J = 7.7 Hz, 1H), 7.48 – 7.43 (m, 1H), 7.34 (t, J = 7.6 Hz, 1H), 7.27 (d, J = 8.2 Hz, 1H), 3.19 – 3.13 (m, 1H), 2.04 – 1.96 (m, 2H), 1.90 – 1.85 (m, 2H), 1.79 – 1.75 (m, 1H), 1.59 – 1.51 (m, 2H), 1.48 – 1.39 (m, 2H), 1.34 – 1.25 (m, 1H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 161.3, 152.7, 146.2, 131.4, 130.3, 128.9, 125.3, 116.3, 41.4, 30.3, 26.1, 26.0.



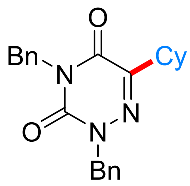
3-cyclohexyl-6-methyl-2H-benzo[b][1,4]oxazin-2-one (**3xa**)[10] : Yellow oil, 36.5 mg, 75% yield; petroleum ether/ethyl acetate (5:1); ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.54 (d, J = 2.1 Hz, 1H), 7.28 – 7.23 (m, 1H), 7.14 (s, 1H), 3.17 – 3.11 (m, 1H), 2.42 (s, 3H), 2.02 – 1.96 (m, 2H), 1.90 – 1.85 (m, 2H), 1.79 – 1.75 (m, 1H), 1.57 – 1.49 (m, 2H), 1.48 – 1.39 (m, 2H), 1.34 – 1.25 (m, 1H); ^{13}C{^{1}H} NMR (125 MHz, CDCl$_3$) δ 161.3, 153.0, 144.2, 135.3, 131.3, 131.2, 128.9, 115.9.



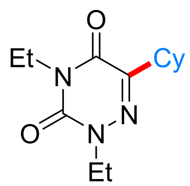
6-bromo-3-cyclohexyl-2H-benzo[b][1,4]oxazin-2-one (**3ya**)[10] : Yellow oil, 43.0 mg, 70% yield; petroleum ether/ethyl acetate (5:1); ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.90 (d, J = 2.3 Hz, 1H), 7.55 (dd, J = 8.8, 2.4 Hz, 1H), 7.15 (d, J = 8.7 Hz, 1H), 3.18 – 3.12 (m, 1H), 2.01 – 1.95 (m, 2H), 1.90 – 1.86 (m, 2H), 1.80 – 1.75 (m, 1H), 1.56 – 1.39 (m, 4H), 1.34 – 1.26 (m, 1H); ^{13}C{^{1}H} NMR (125 MHz, CDCl$_3$) δ 162.7, 152.2, 145.4, 133.2, 132.3, 131.6, 117.8, 117.7, 41.6, 30.4, 26.2, 26.0.



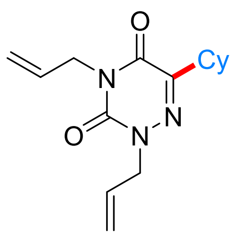
3-(tert-butyl)-2H-benzo[b][1,4]oxazin-2-one (**3za**): Colorless oil, 28.4 mg, 70% yield; petroleum ether/ethyl acetate (5:1); ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.74 (dd, J = 7.9, 1.6 Hz, 1H), 7.49 – 7.42 (m, 1H), 7.35 – 7.32 (m, 1H), 7.27 – 7.26 (m, 1H), 1.46 (s, 9H); ^{13}C{^{1}H} NMR (125 MHz, CDCl$_3$) δ 162.0, 151.1, 146.8, 131.0, 130.6, 129.3, 125.2, 116.1, 39.5, 27.8. HRMS (ESI) m/z calcd for $C_{12}H_{14}NO_2$ $[M+H]^+$ 204.1019, found 204.1020.



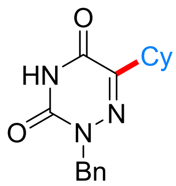
2,4-dibenzyl-6-cyclohexyl-1,2,4-triazine-3,5(2H,4H)-dione (**3Aa**)[14] : Yellow oil, 63.8 mg, 85% yield; petroleum ether/ethyl acetate (5:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.50 – 7.46 (m, 2H), 7.42 – 7.38 (m, 2H), 7.37 – 7.24 (m, 6H), 5.07 (d, J = 4.3 Hz, 4H), 2.88 – 1.84 (m, 1H), 1.88 – 1.77 (m, 4H), 1.74 – 1.69 (m, 1H), 1.41 – 1.31 (m, 4H), 1.28 – 1.20 (m, 1H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 155.8, 149.1, 149.0, 136.0, 135.9, 129.6, 128.9, 128.8, 128.7, 128.2, 128.1, 55.4, 44.3, 38.6, 30.6, 26.3, 26.1.



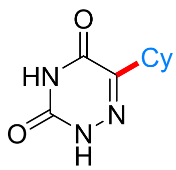
6-cyclohexyl-2,4-diethyl-1,2,4-triazine-3,5(2H,4H)-dione (**3Ba**)[10] : Yellow oil, 38.7 mg, 77% yield; petroleum ether/ethyl acetate (5:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.95 – 3.89 (m, 4H), 2.83 – 2.77 (m, 1H), 1.76 – 1.70 (m, 2H), 1.68 – 1.60 (m, 1H), 1.34 – 1.27 (m, 4H), 1.24 (t, J = 7.2 Hz, 3H), 1.16 (t, J = 7.2 Hz, 4H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 155.70, 148.67, 148.53, 46.63, 38.37, 36.09, 30.54, 26.23, 26.09, 13.41, 12.62.



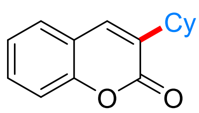
2,4-diallyl-6-cyclohexyl-1,2,4-triazine-3,5(2H,4H)-dione (**3Ca**)[15] : Yellow oil, 44.0 mg, 80% yield; petroleum ether/ethyl acetate (5:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.03 – 5.67 (m, 2H), 5.28 – 5.13 (m, 4H), 4.47 (t, J = 5.8 Hz, 4H), 2.84 – 2.78 (m, 1H), 1.80 – 1.70 (m, 2H), 1.76 – 1.71 (m, 2H), 1.67 – 1.62 (m, 1H), 1.35 – 1.25 (m, 4H), 1.21 – 1.12 (m, 1H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 155.6, 149.1, 148.6, 131.8, 130.7, 119.2, 118.9, 54.0, 43.0, 38.5, 30.5, 26.2, 26.1.



2-benzyl-6-cyclohexyl-1,2,4-triazine-3,5(2H,4H)-dione (**3Da**)[16] : Yellow oil, 35.9 mg, 63% yield; petroleum ether/ethyl acetate (3:1); ^1H NMR (500 MHz, $CDCl_3$) δ 7.47 – 7.37 (m, 2H), 7.30 – 7.16 (m, 3H), 5.01 (s, 2H), 2.82 – 2.77 (m, 1H), 1.80 – 1.79 (m, 2H), 1.75 – 1.70 (m, 2H), 1.67 – 1.58 (m, 1H), 1.33 – 1.22 (m, 4H), 1.18 – 1.11 (m, 1H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 155.9, 150.1, 150.0, 135.6, 129.6, 128.7, 128.2, 43.7, 38.5, 30.5, 26.2, 26.1.



5-cyclohexyl-1,2,4-triazine-3,5(2H,4H)-dione (**3Ea**): Yellow oil, 21.5 mg, 55% yield; petroleum ether/ethyl acetate (3:1); ^1H NMR (500 MHz, DMSO-d_6) δ 2.72-2.66 (m, 1H), 1.81 – 1.72 (m, 4H), 1.69 – 1.63 (m, 1H), 1.36 – 1.02 (m, 6H); $^{13}C\{^1H\}$ NMR (125 MHz, DMSO-d_6) δ 157.2, 149.8, 148.9, 37.6, 30.4, 26.2, 26.1. HRMS (ESI) m/z calcd for $C_9H_{14}N_3O_2$ $[M+H]^+$ 196.1081, found 196.1079.



3-cyclohexyl-2H-chromen-2-one (**3Fa**)[17] : Yellow oil, 31.0 mg, 68% yield; petroleum ether/ethyl acetate (5:1); ^1H NMR (500 MHz, $CDCl_3$) δ 7.44 (d, J = 7.0 Hz, 3H), 7.30 (d, J = 8.3 Hz, 1H), 7.31 –7.23 (m, 1H), 2.78 (m, 1H), 2.05 – 1.94 (m, 2H), 1.87 – 1.83 (m, 2H), 1.79 (s, 1H), 1.50 – 1.40 (m, 2H), 1.35 – 1.22 (m, 3H); $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$) δ 161.7, 152.9, 136.4, 135.0, 130.5, 127.4, 124.3, 119.8, 116.4, 38.3, 32.2, 26.6, 26.3.

4. References

[1] M. H. Muhammad, X.-L. Chen, Y. Liu, T. Shi, Y. Peng, L. Qu, B. Yu, *ACS Sustainable Chemistry & Engineering* **2020**, *8*, 2682.

[2] H.-Y. Song, Z.-T. Zhang, H.-Y. Tan, Y.-H. Lu, T.-B. Yang, J.-Y. Chen, H.-T. Ji, W.-M. He, *Asian J. Org. Chem.* **2023**, *12*, e202200658.

[3] S. Singh, N. Dagar, S. Raha Roy, *Organic & Biomolecular Chemistry* **2021**, *19*, 5383.

[4] Y. Deng, X. Cheng, H. Tan, Y. He, C. Zhang, G. Qiu, D. Zheng, *Adv. Synth. Catal.* **2023**, *365*, 865.

[5] H. Jiao, K. Niu, H. Song, Y. Liu, Q. Wang, *ChemistrySelect* **2023**, *8*, e202301738.

[6] J.-C. Hou, J. Jiang, H. Dai, J.-S. Wang, T. Li, X. Chen, W.-M. He, *Science China Chemistry* **2025**, *68*, 1945.

[7] X.-Y. Yuan, Y.-F. Si, X. Li, S.-J. Wu, F.-L. Zeng, Q.-Y. Lv, B. Yu, *Org. Chem. Front.* **2022**, *9*, 2728.

[8] T. Yang, H. Zhu, W. Yu, *Organic & Biomolecular Chemistry* **2016**, *14*, 3376.

[9] H. Wang, R. Liu, Q. Sun, K. Xu, *Chemical Communications* **2023**, *59*, 12763.

[10] H. T. Ji, Y. Q. Tang, Y. H. Wang, J. S. Wang, Y. D. Xu, Y. Y. Zeng, T. Li, S. F. Gong, W. M. He, *Org. Lett.* **2024**, *26*, 9822.

[11] Q. Yang, Y. Zhang, Q. Sun, K. Shang, H. Y. Zhang, J. Zhao, *Adv. Synth. Catal.* **2018**, *360*, 4509.

[12] X. Shi, Y. Cao, Y. Liu, K. Niu, H. Song, J. Zhang, Q. Wang, *Org. Chem. Front.* **2023**, *10*, 1296.

[13] Y. Liu, B. Shi, Z. Liu, R. Gao, C. Huang, H. Alhumade, S. Wang, X. Qi, A. Lei, *Journal of the American Chemical Society* **2021**, *143*, 20863.

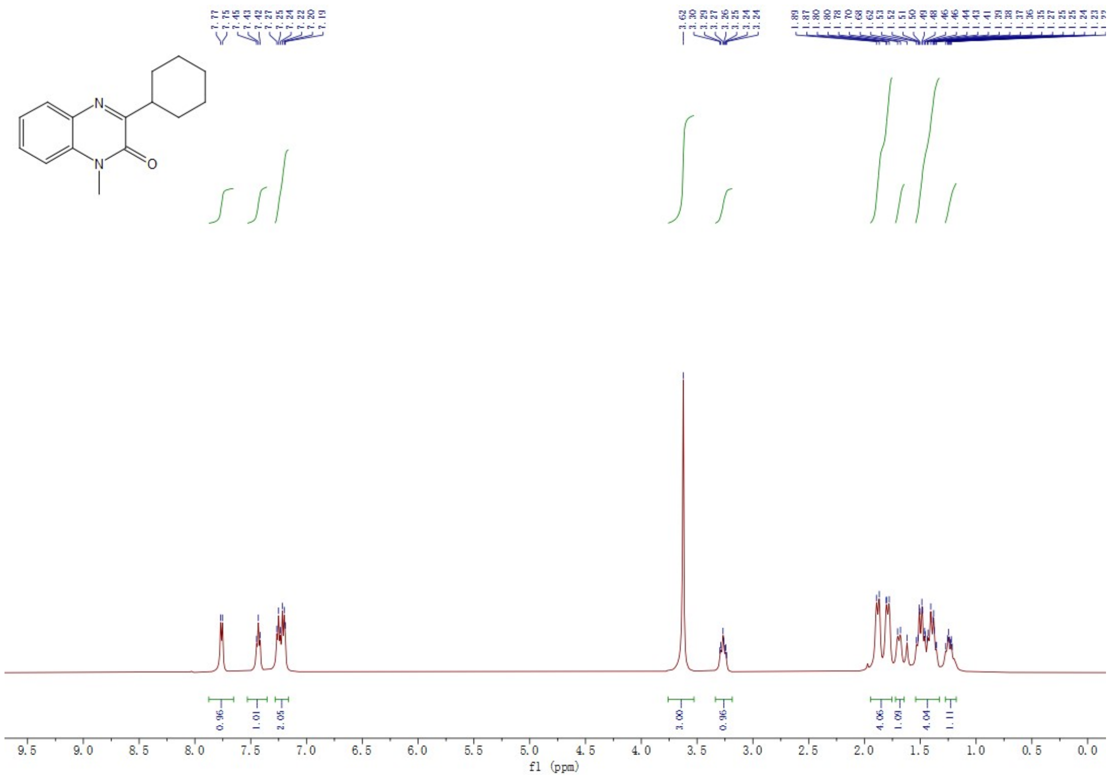
[14] F. Cheng, L. Fan, Q. Lv, X. Chen, B. Yu, *Green Chem.* **2023**, *25*, 7971.

[15] J. Xu, Y. Zhang, R. Xu, Y. Wang, J. Shen, W. Li, *Org. Chem. Front.* **2024**, *11*, 5122.

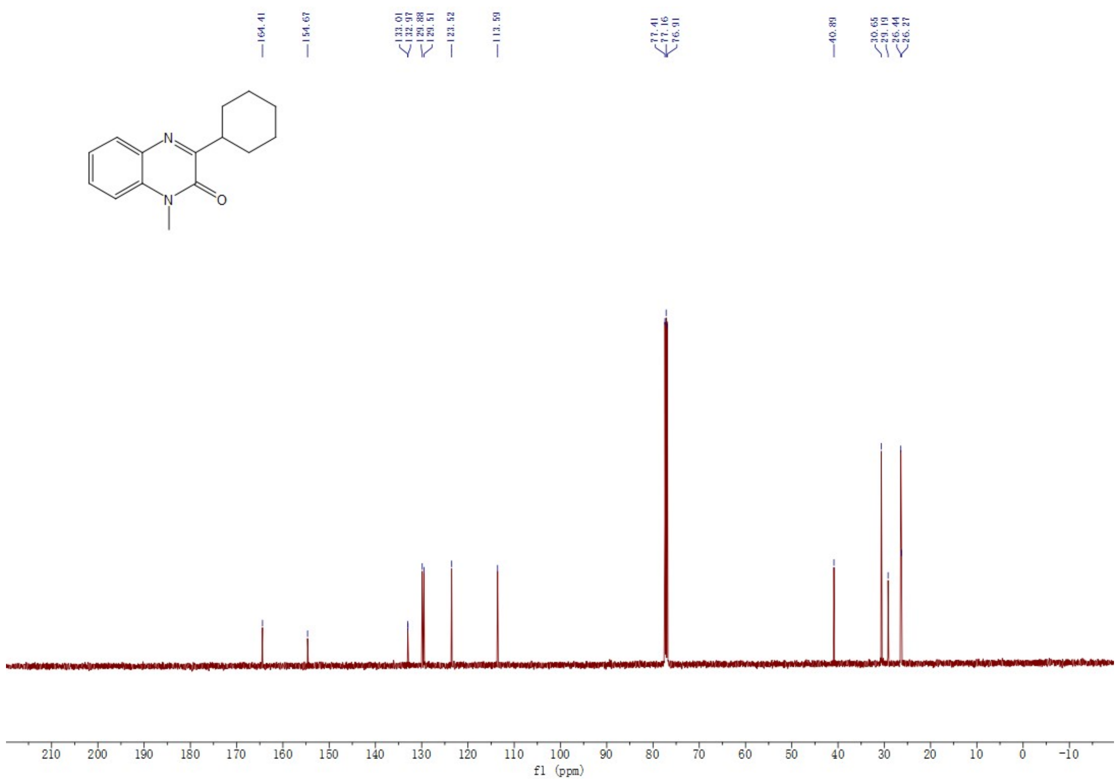
[16] Y. Hussain, G. Sankar, M. Rueping, R. M. Koenigs, *Chemical Communications* **2025**, *61*, 8691.

[17] H.-Y. Song, M.-Y. Liu, J. Huang, D. Wang, J. Jiang, J.-Y. Chen, T.-B. Yang, W.-M. He, *J. Org. Chem.* **2023**, *88*, 2288.

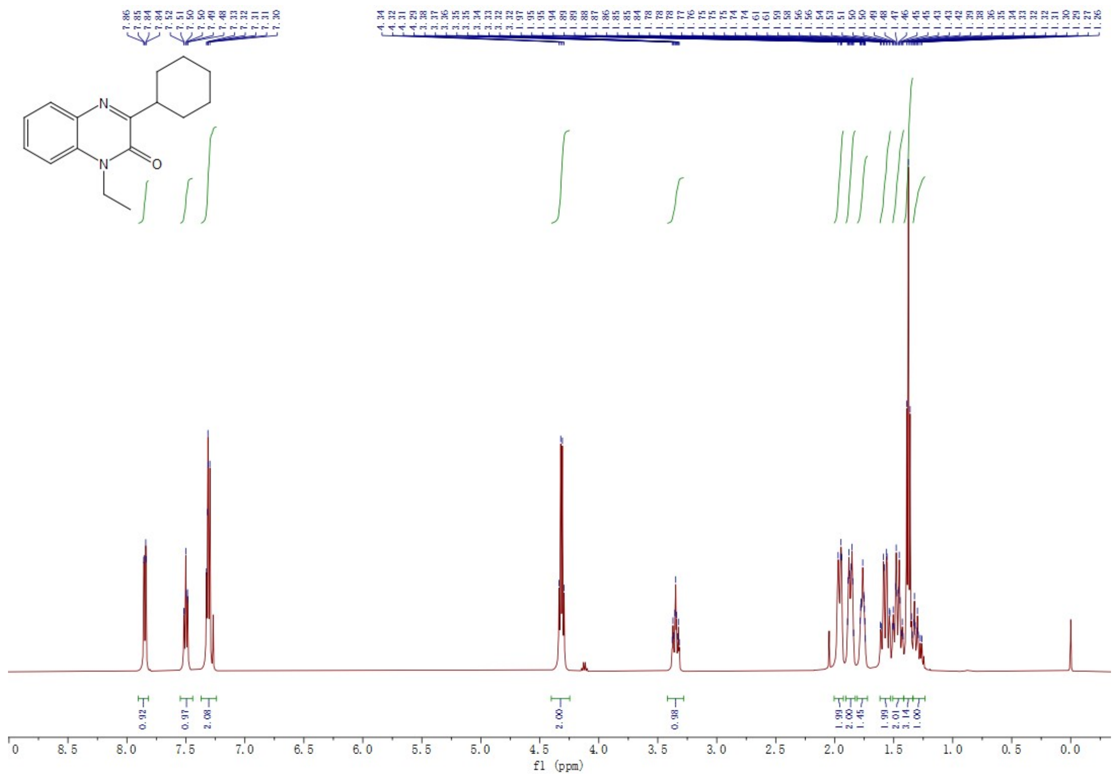
5. ^{1}H, ^{13}C and ^{19}F NMR Spectra of Products



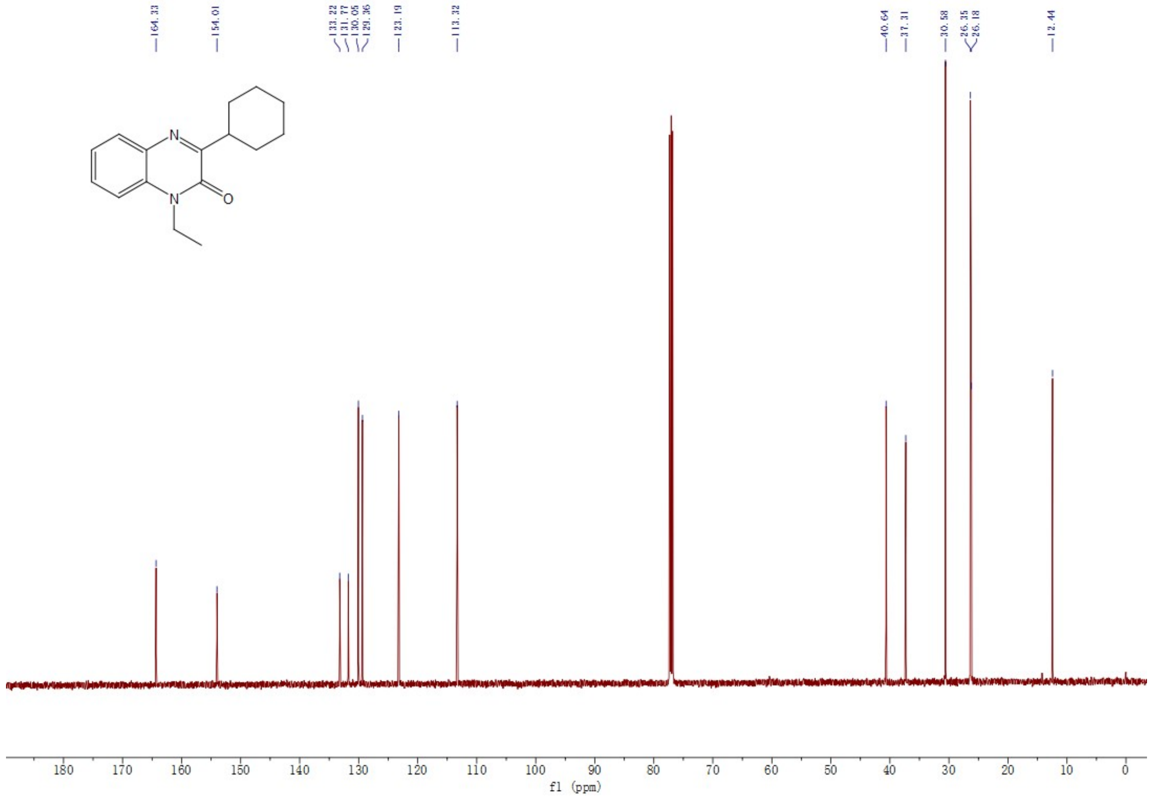
^{1}H NMR (500 MHz, $CDCl_3$) of **3aa**



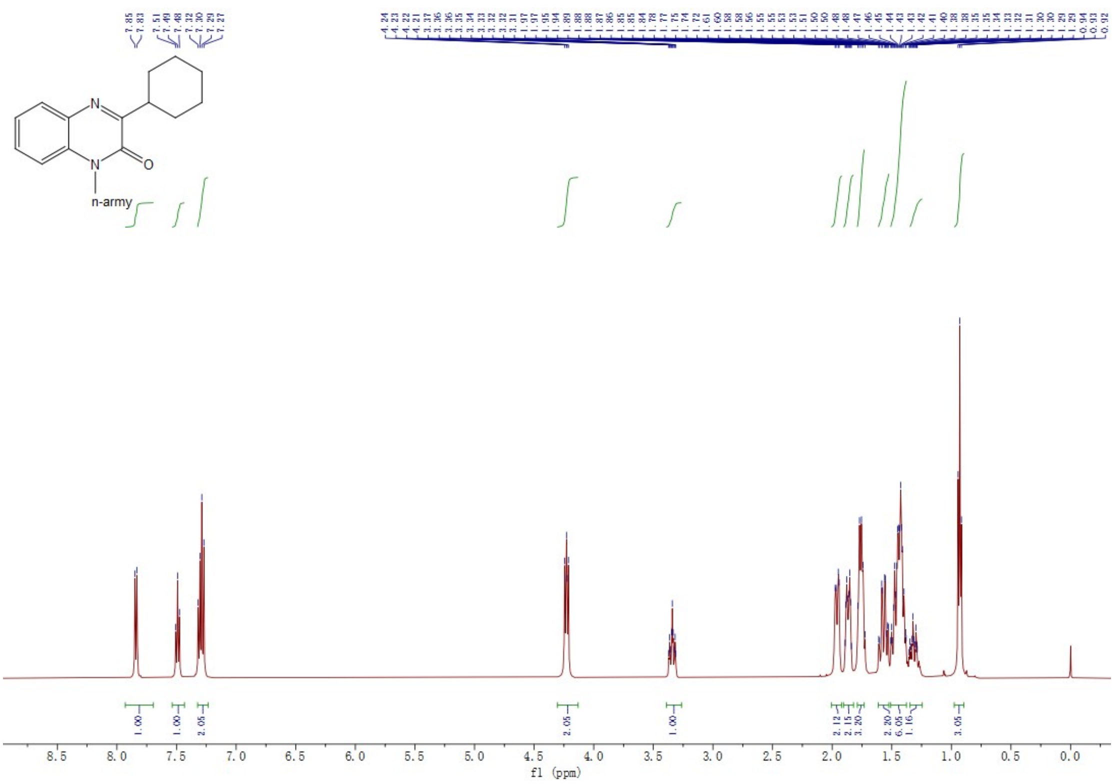
^{13}C NMR (125 MHz, $CDCl_3$) of **3aa**



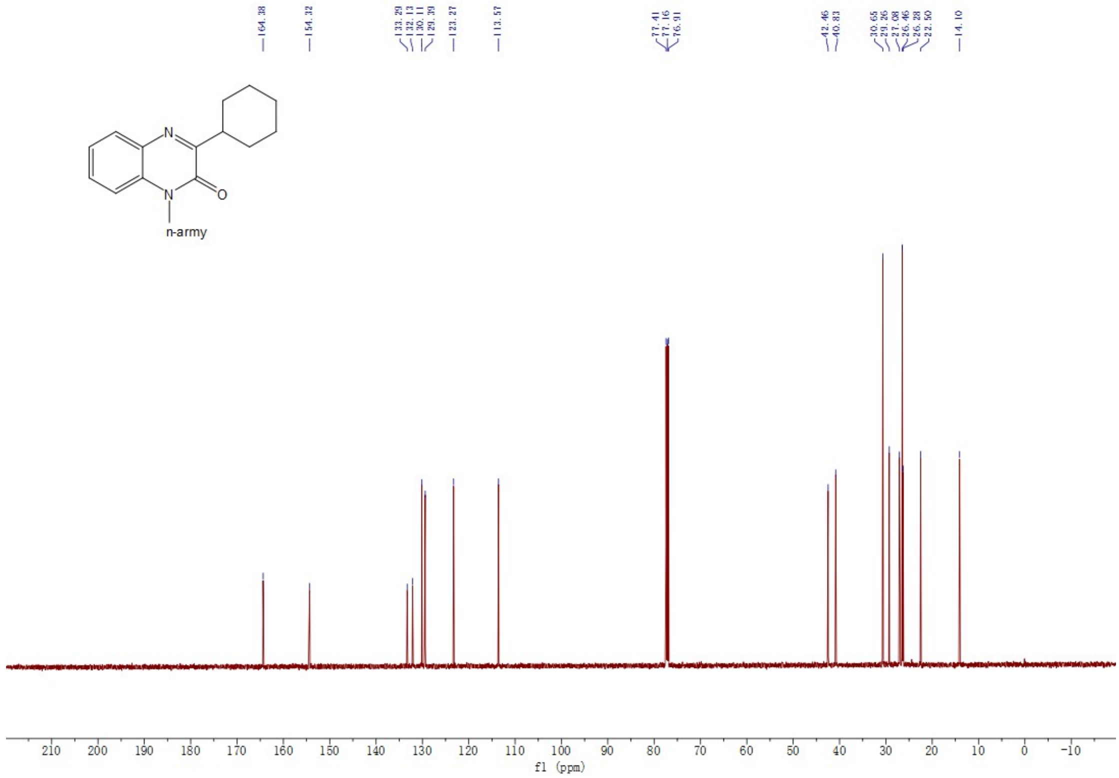
^{1}H NMR (500 MHz, $CDCl_3$) of **3ba**



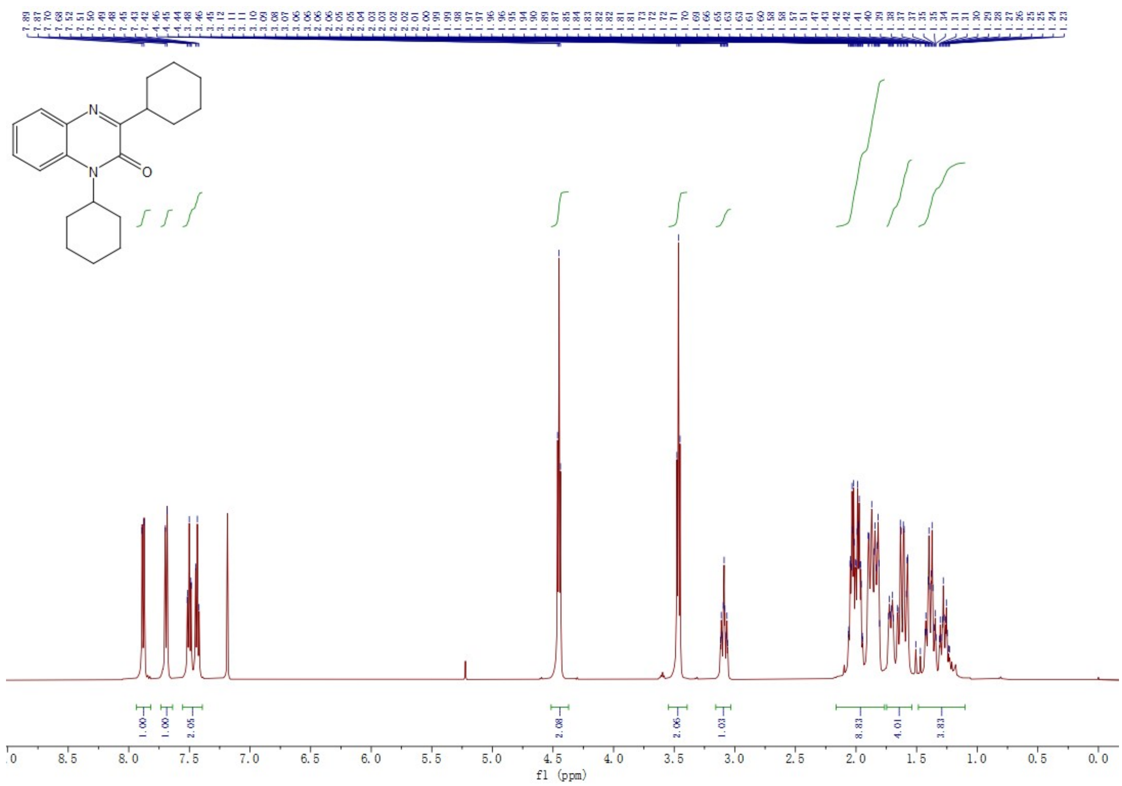
^{13}C NMR (125 MHz, $CDCl_3$) of **3ba**



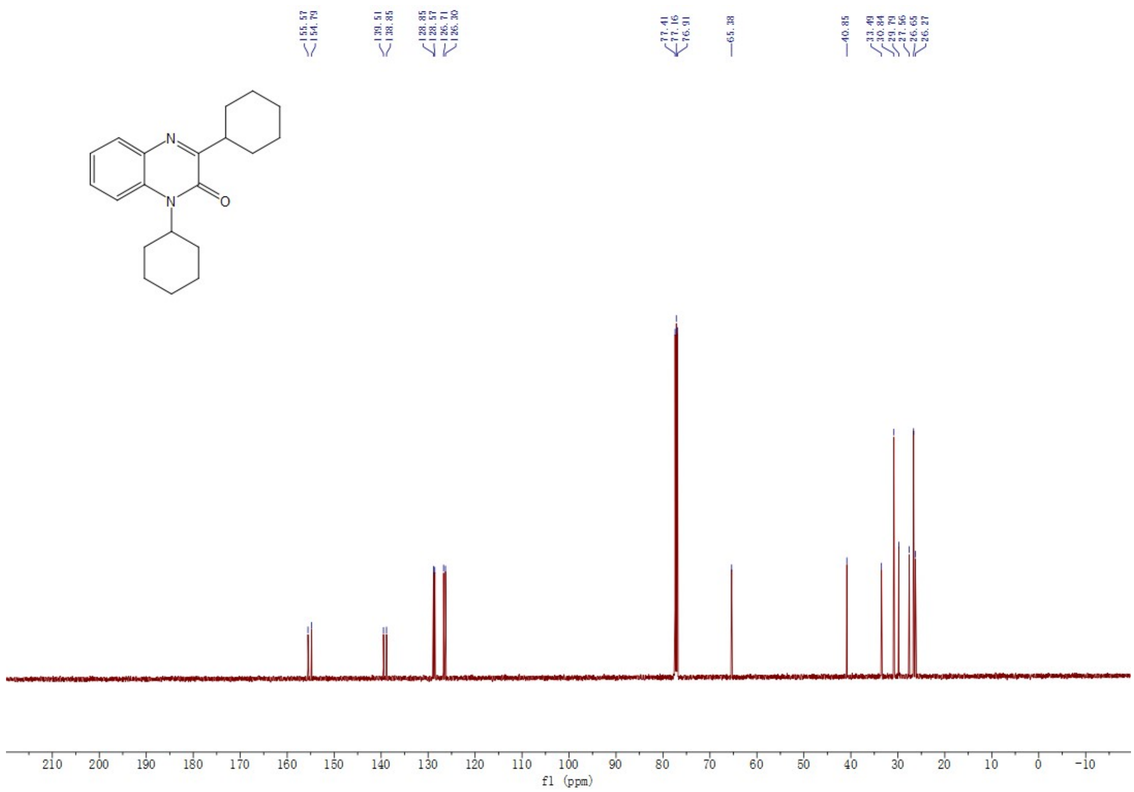
^{1}H NMR (500 MHz, $CDCl_3$) of **3ca**



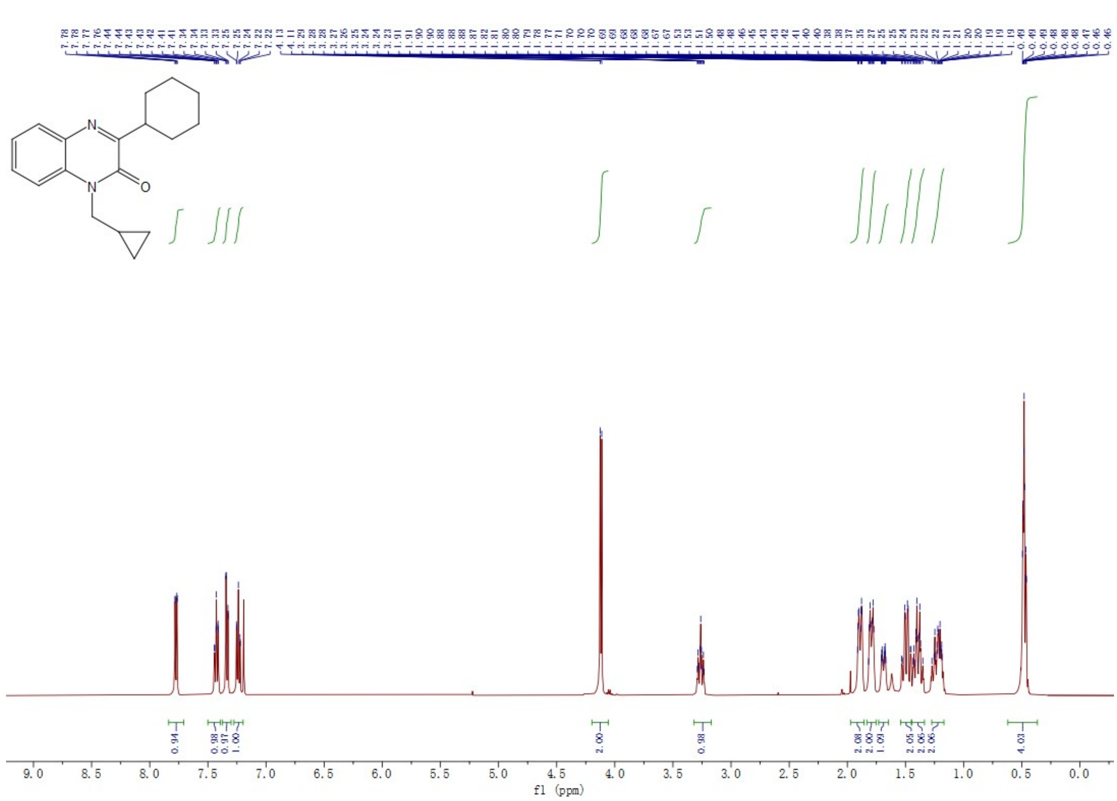
^{13}C NMR (125 MHz, $CDCl_3$) of **3ca**



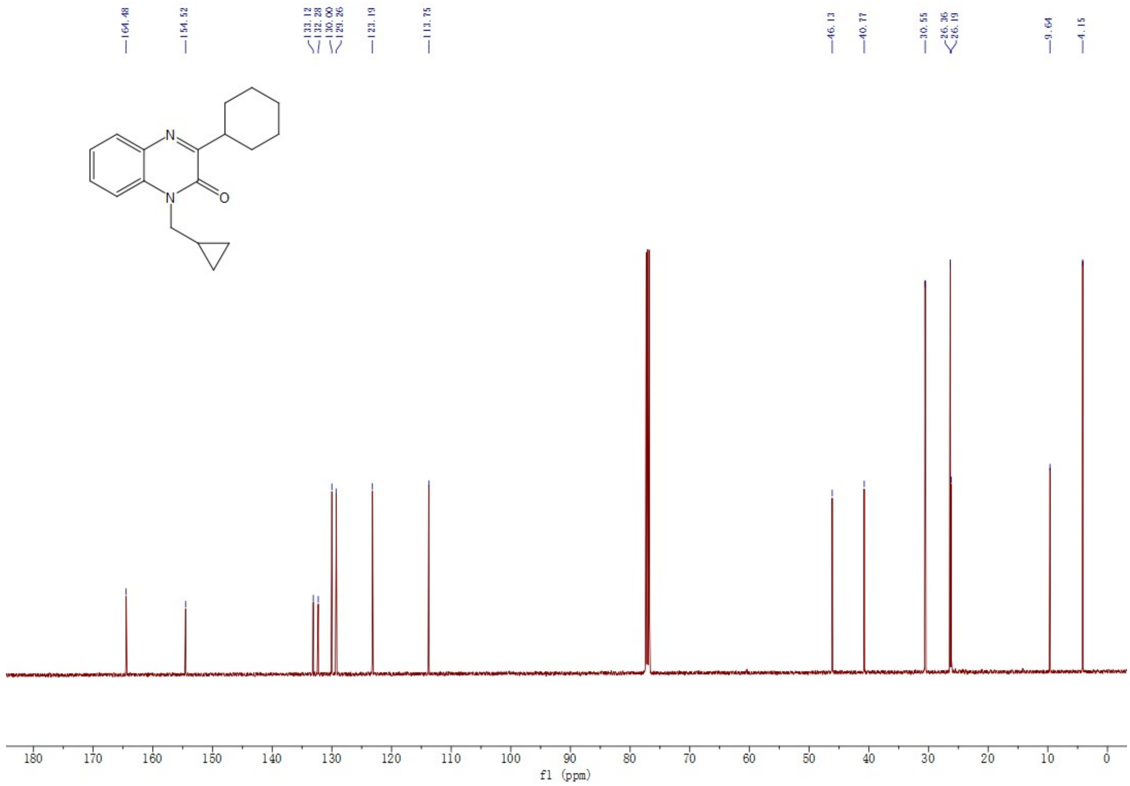
^{1}H NMR (500 MHz, $CDCl_3$) of **3da**



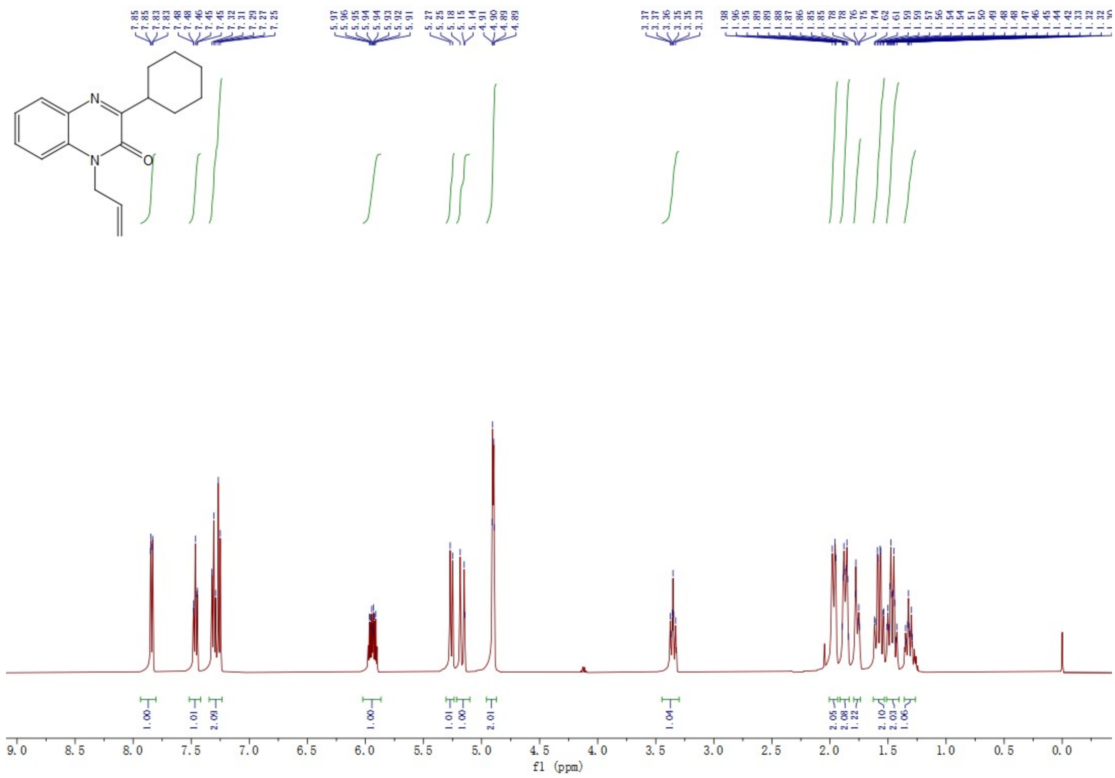
^{13}C NMR (125 MHz, $CDCl_3$) of **3da**



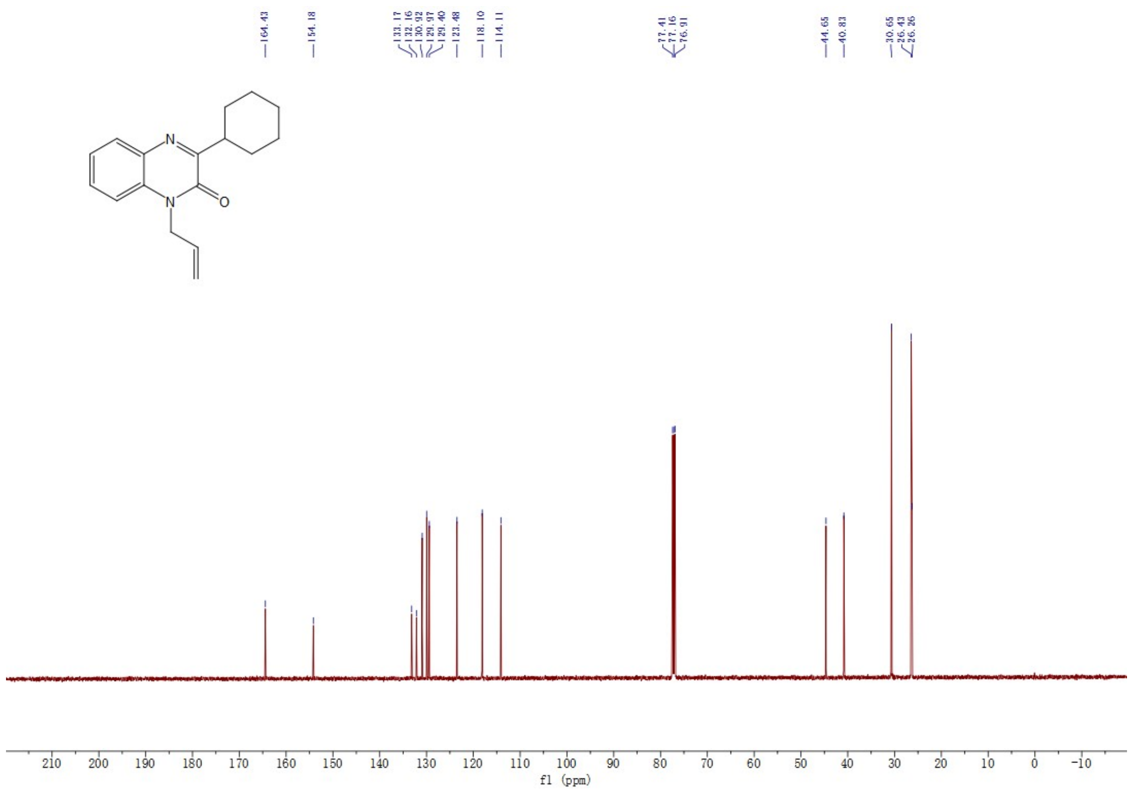
^{1}H NMR (500 MHz, $CDCl_3$) of **3ea**



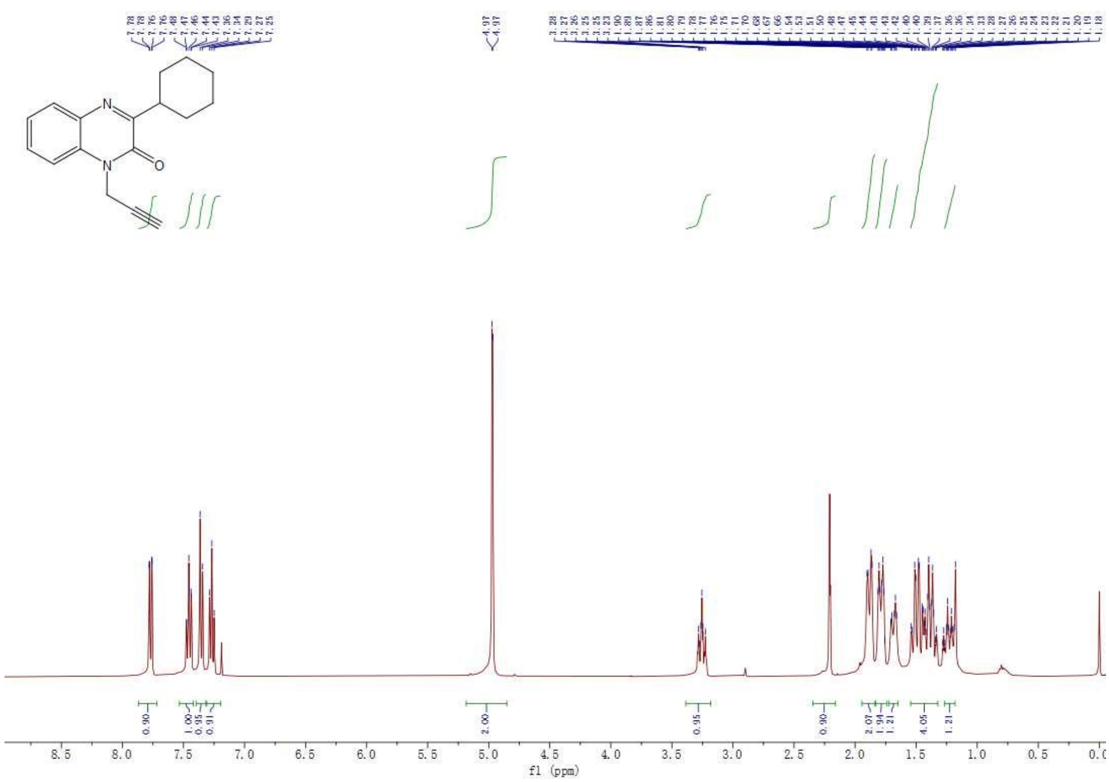
^{13}C NMR (125 MHz, $CDCl_3$) of **3ea**



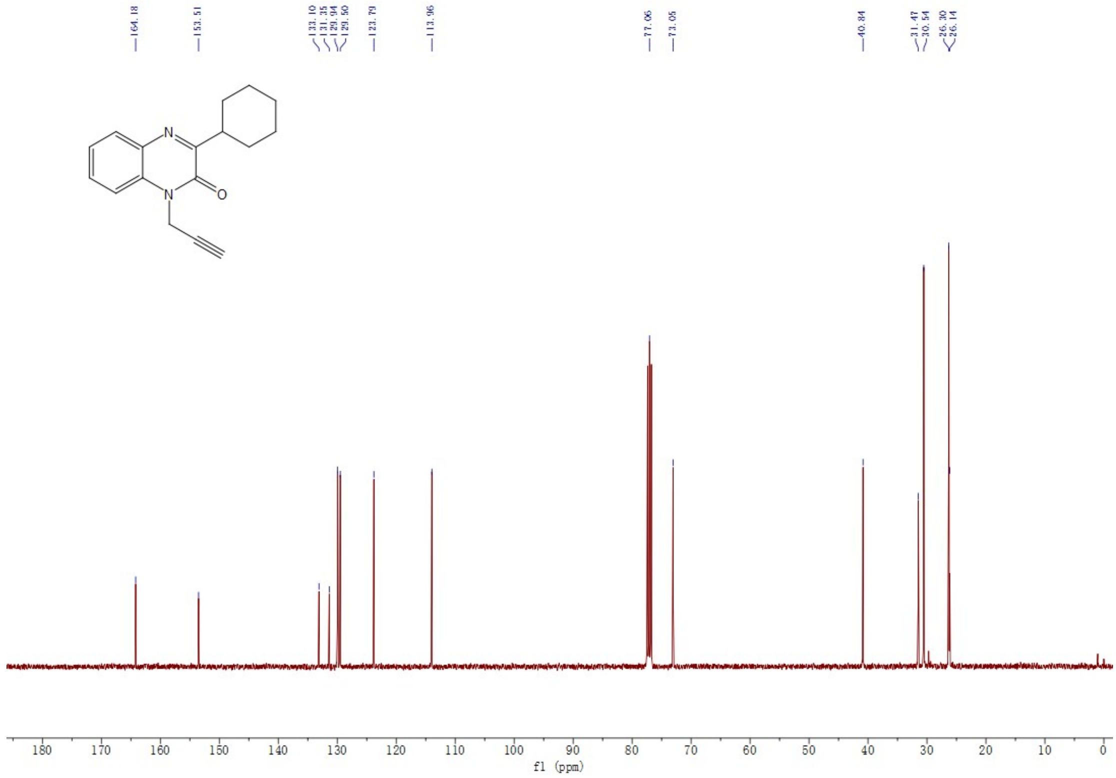
^{1}H NMR (500 MHz, $CDCl_3$) of **3fa**



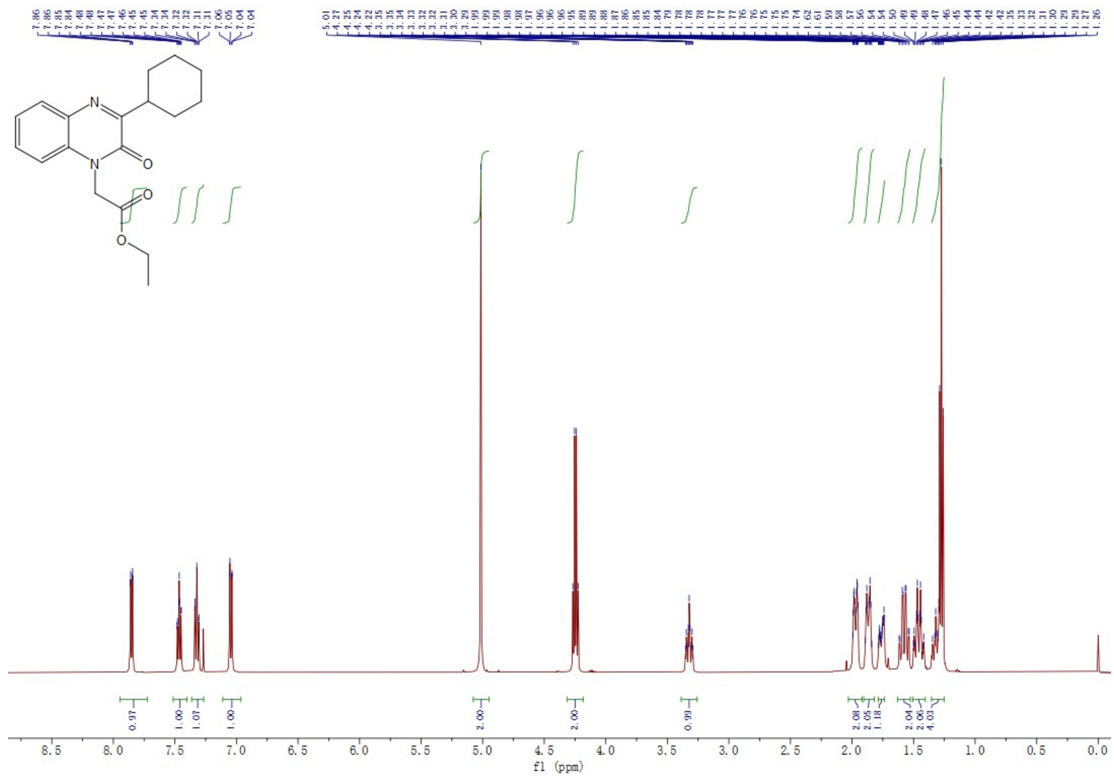
^{13}C NMR (125 MHz, $CDCl_3$) of **3fa**



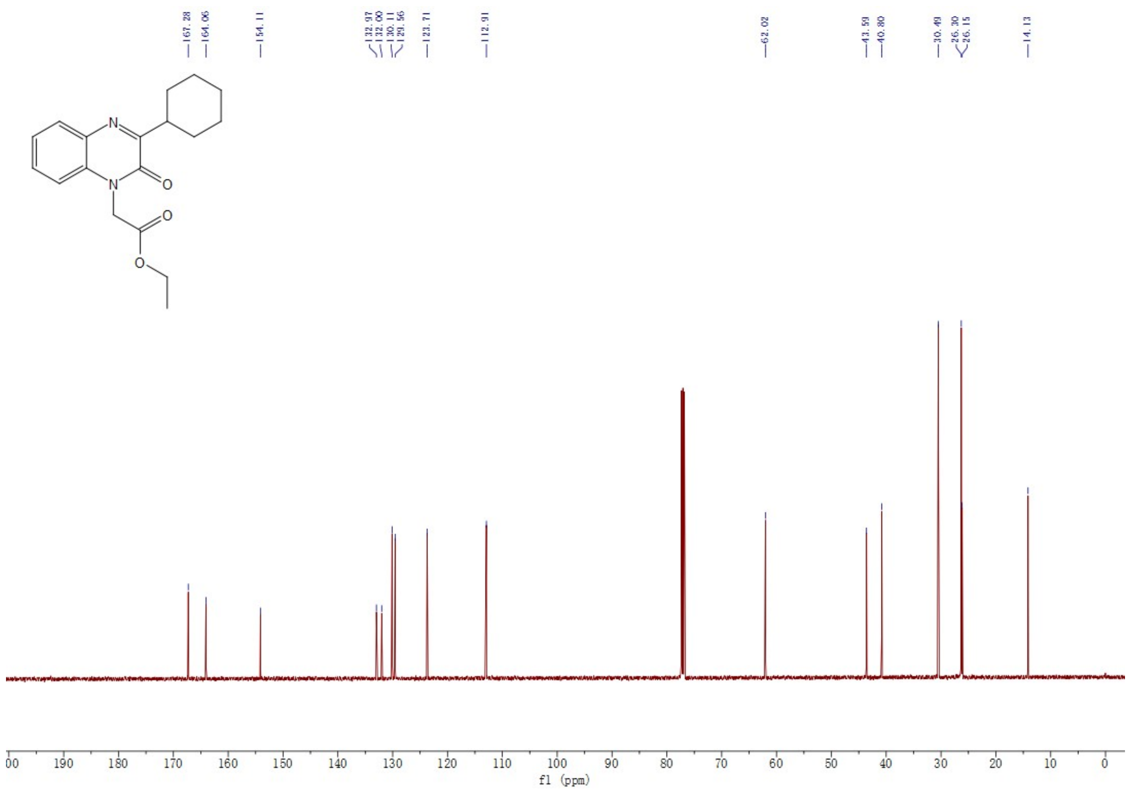
^{1}H NMR (400 MHz, $CDCl_3$) of **3ga**



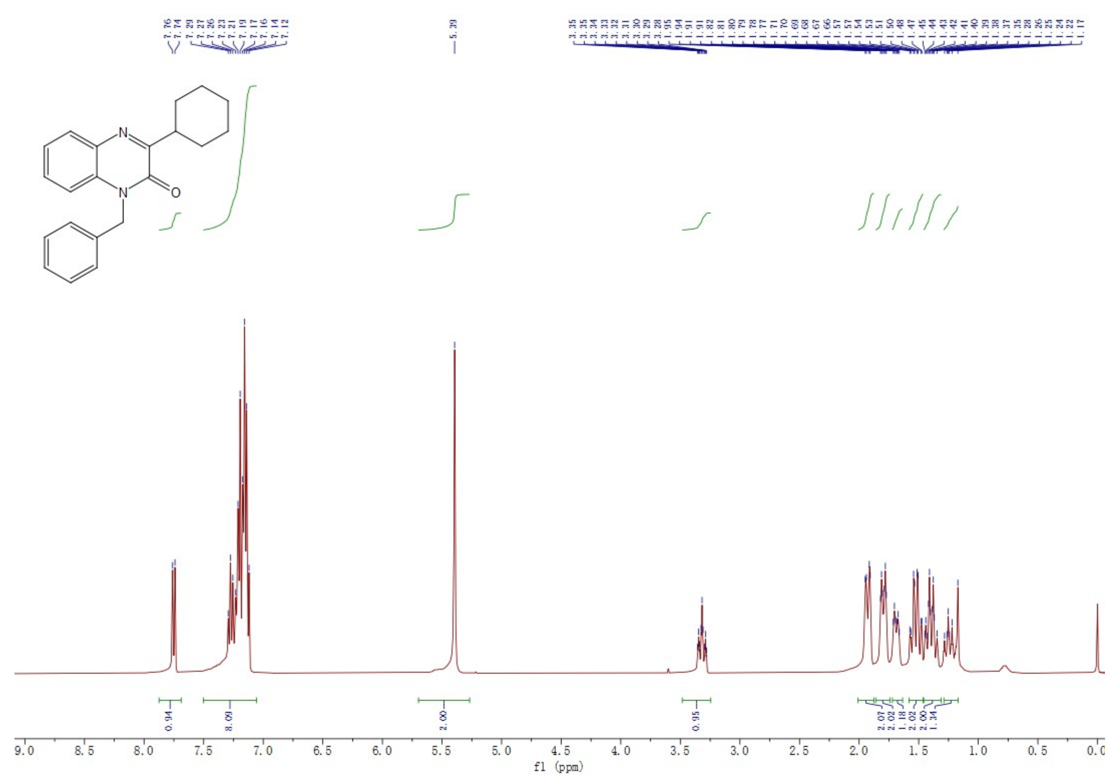
^{13}C NMR (100 MHz, $CDCl_3$) of **3ga**



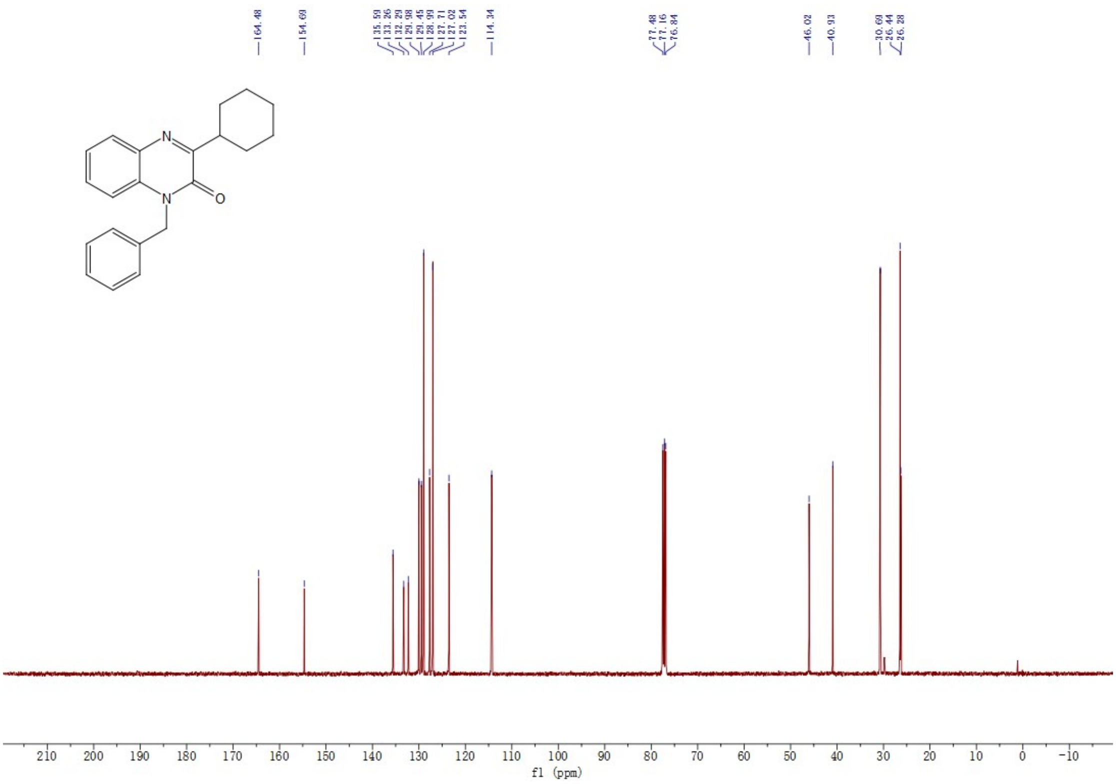
^{1}H NMR (500 MHz, $CDCl_3$) of **3ha**



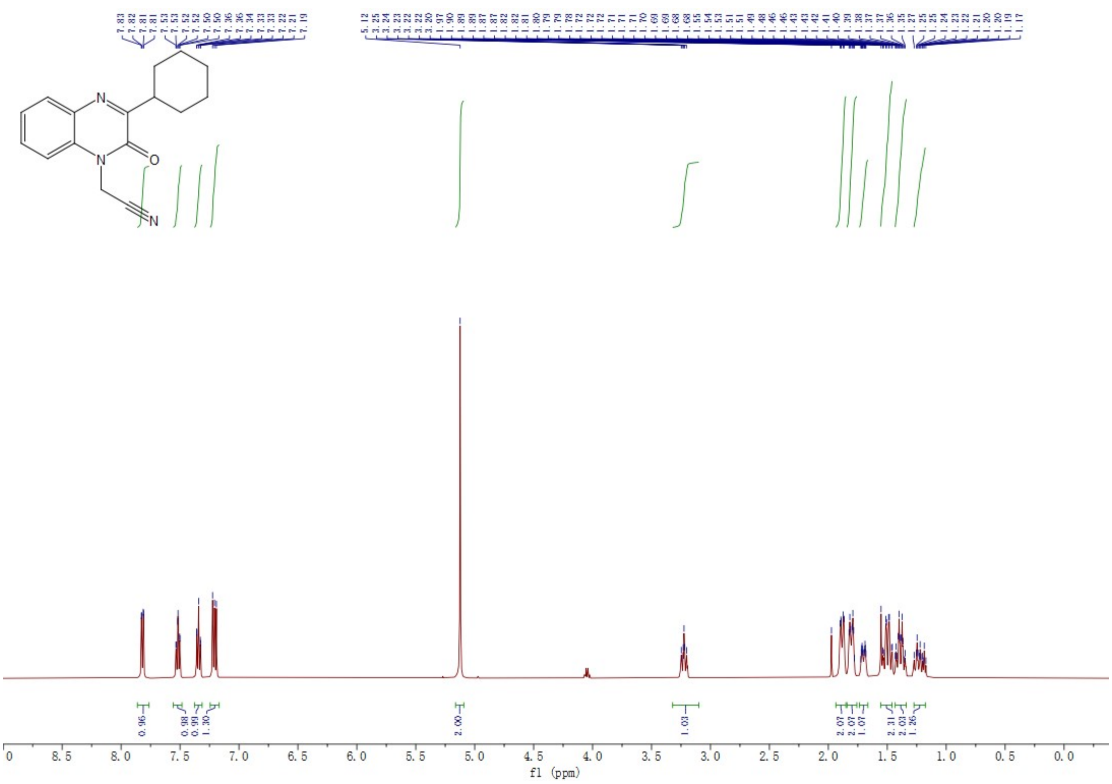
^{13}C NMR (125 MHz, $CDCl_3$) of **3ha**



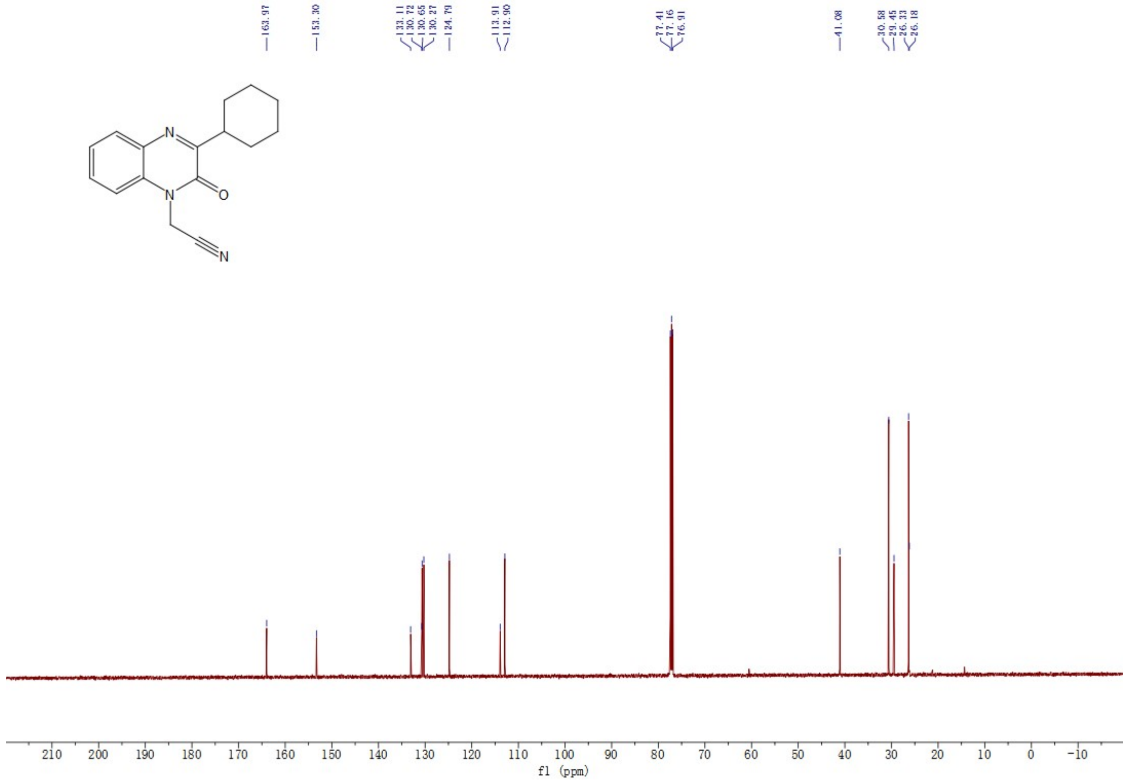
^{1}H NMR (400 MHz, $CDCl_3$) of **3ia**



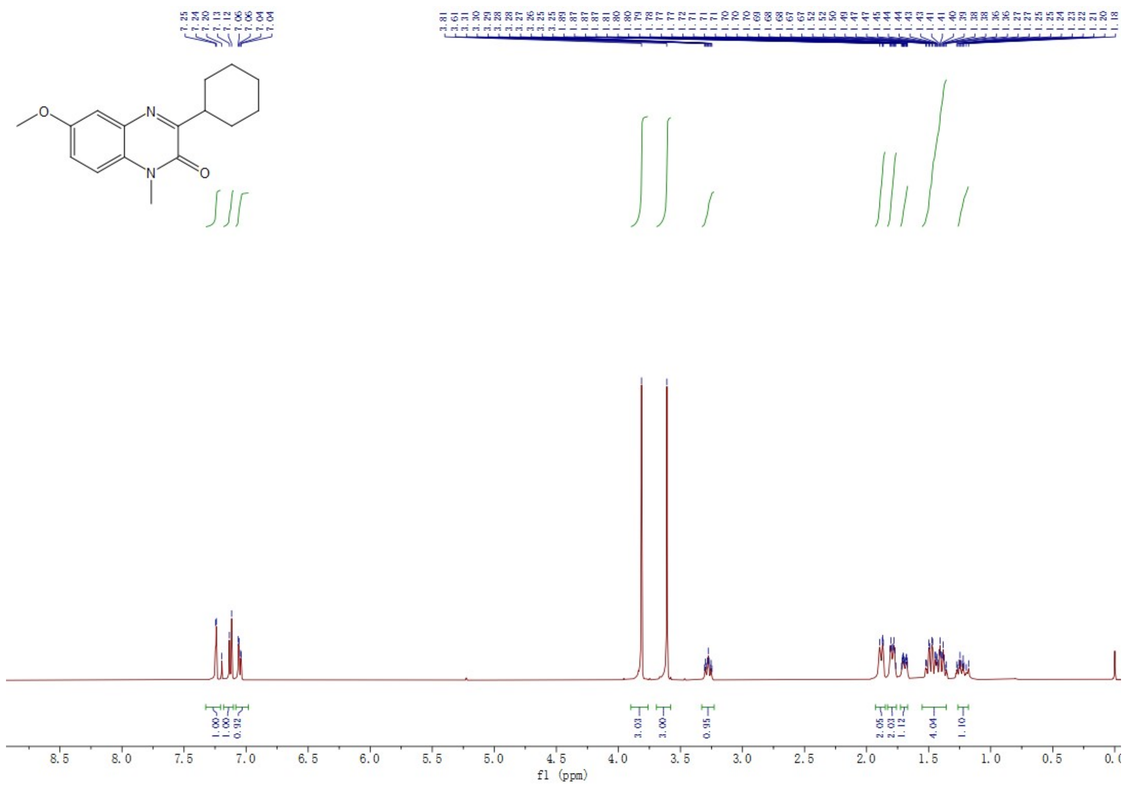
^{13}C NMR (100 MHz, $CDCl_3$) of **3ia**



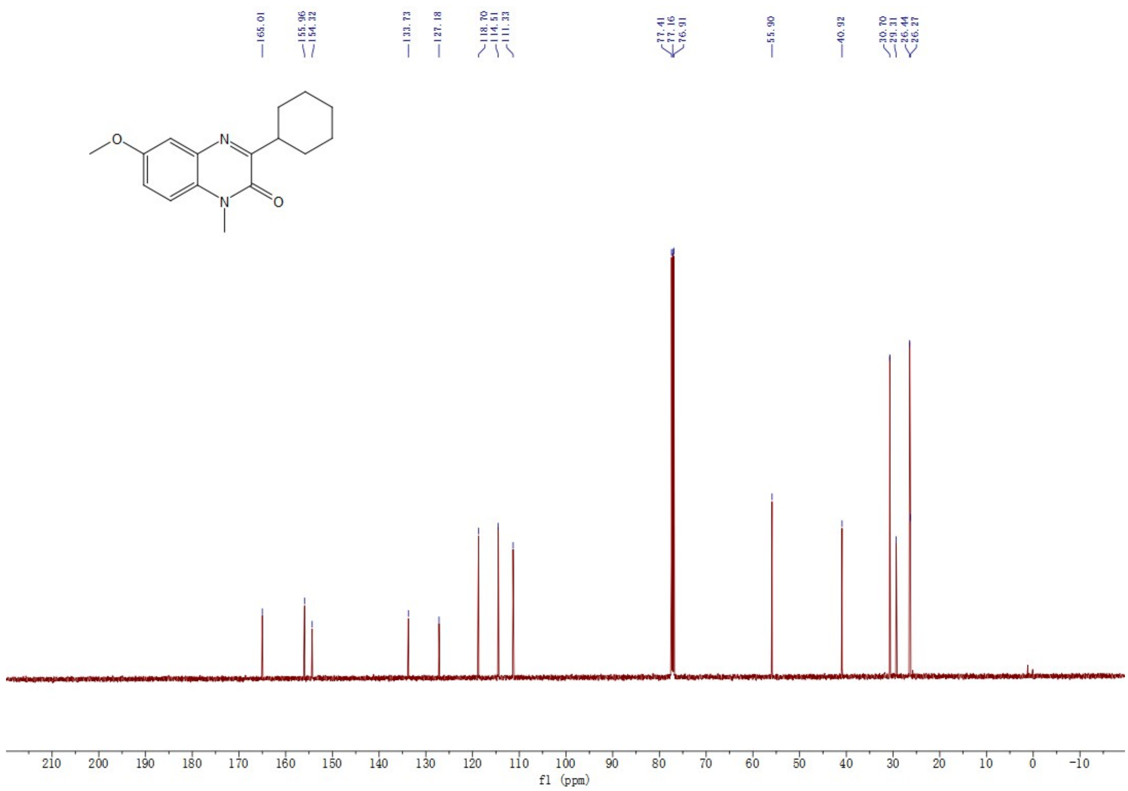
^{1}H NMR (500 MHz, $CDCl_3$) of **3ja**



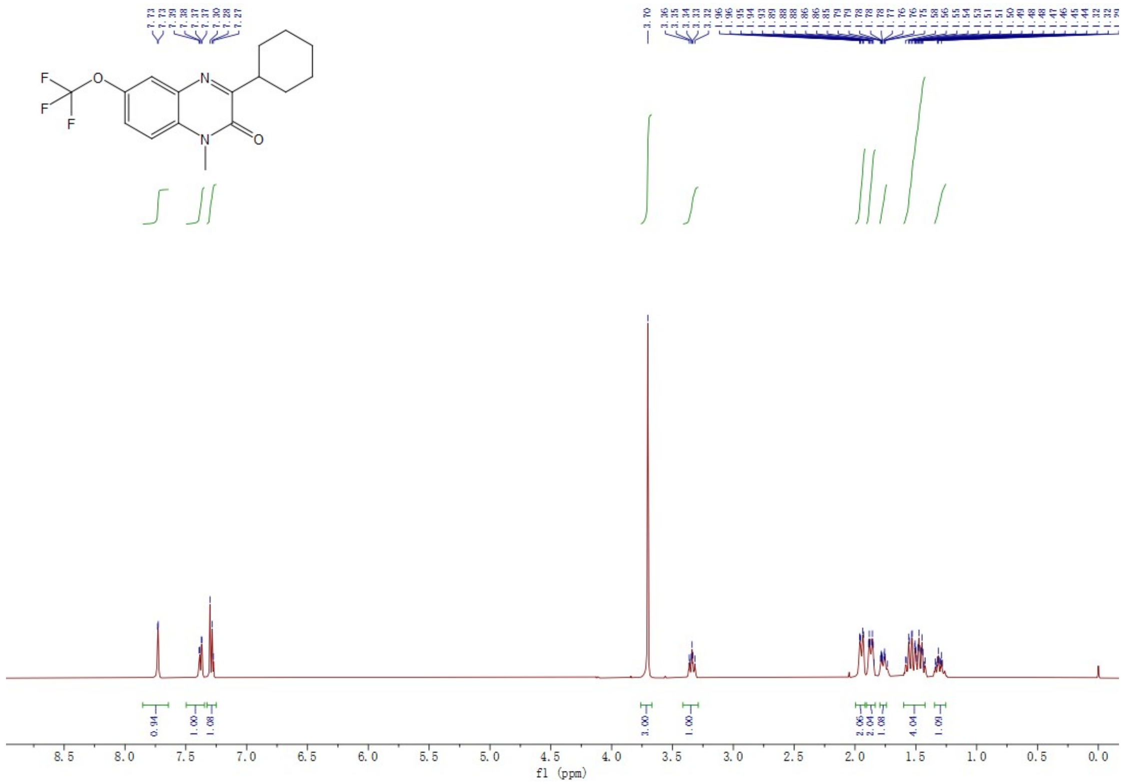
^{13}C NMR (125 MHz, $CDCl_3$) of **3ja**



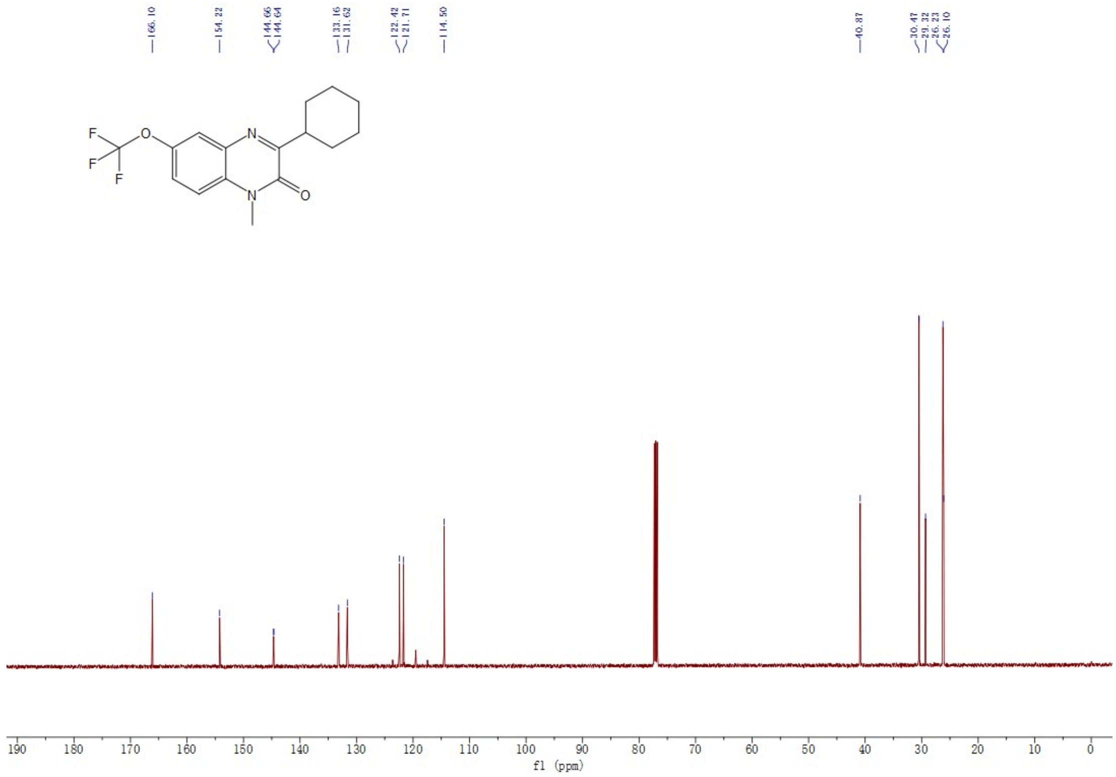
^{1}H NMR (500 MHz, $CDCl_3$) of **3ka**



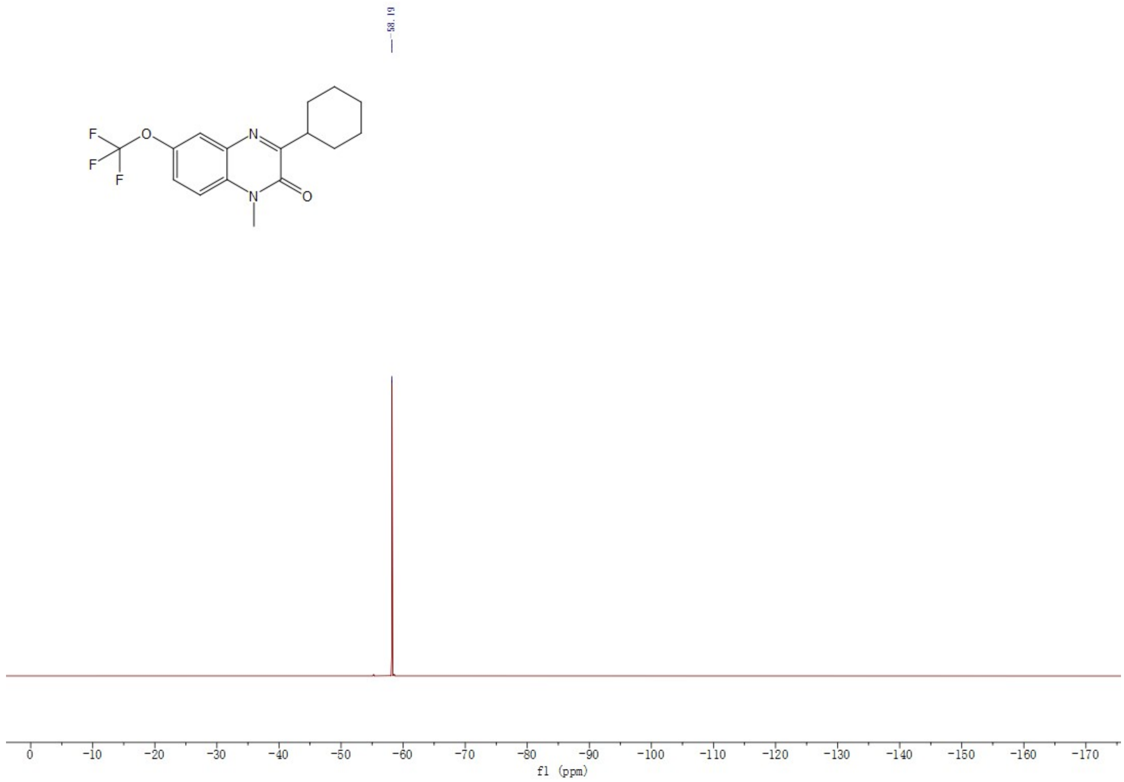
^{13}C NMR (125 MHz, $CDCl_3$) of **3ka**



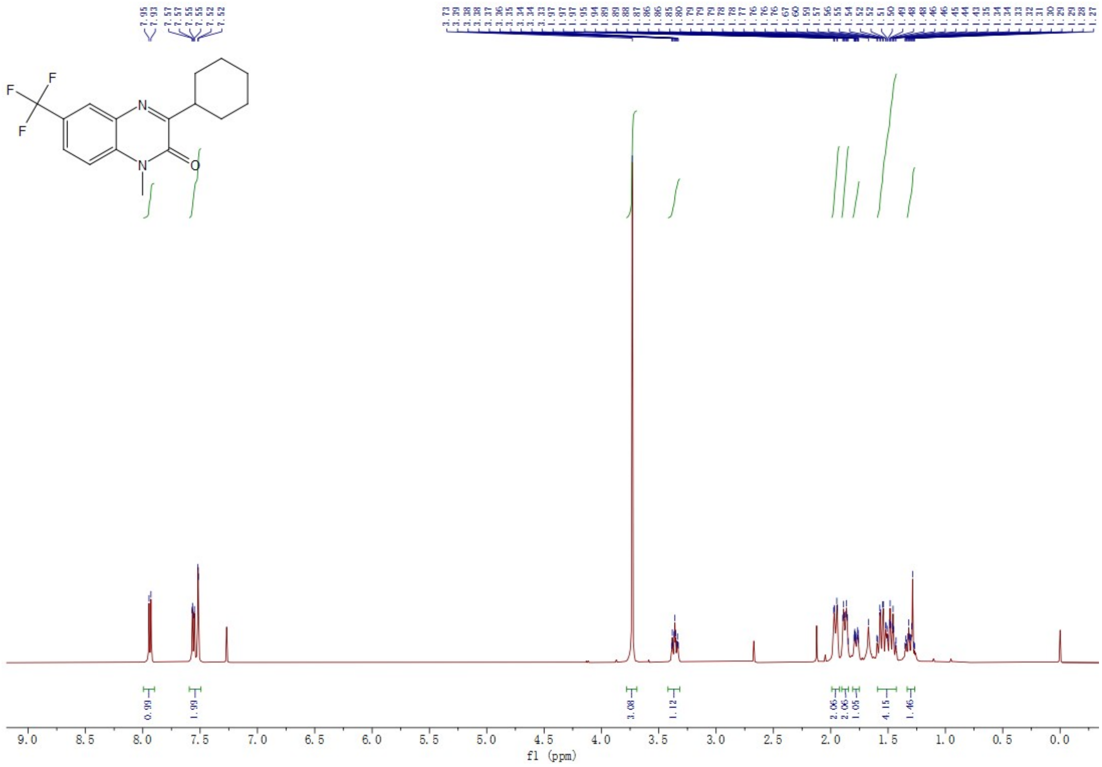
^{1}H NMR (500 MHz, $CDCl_3$) of **3la**



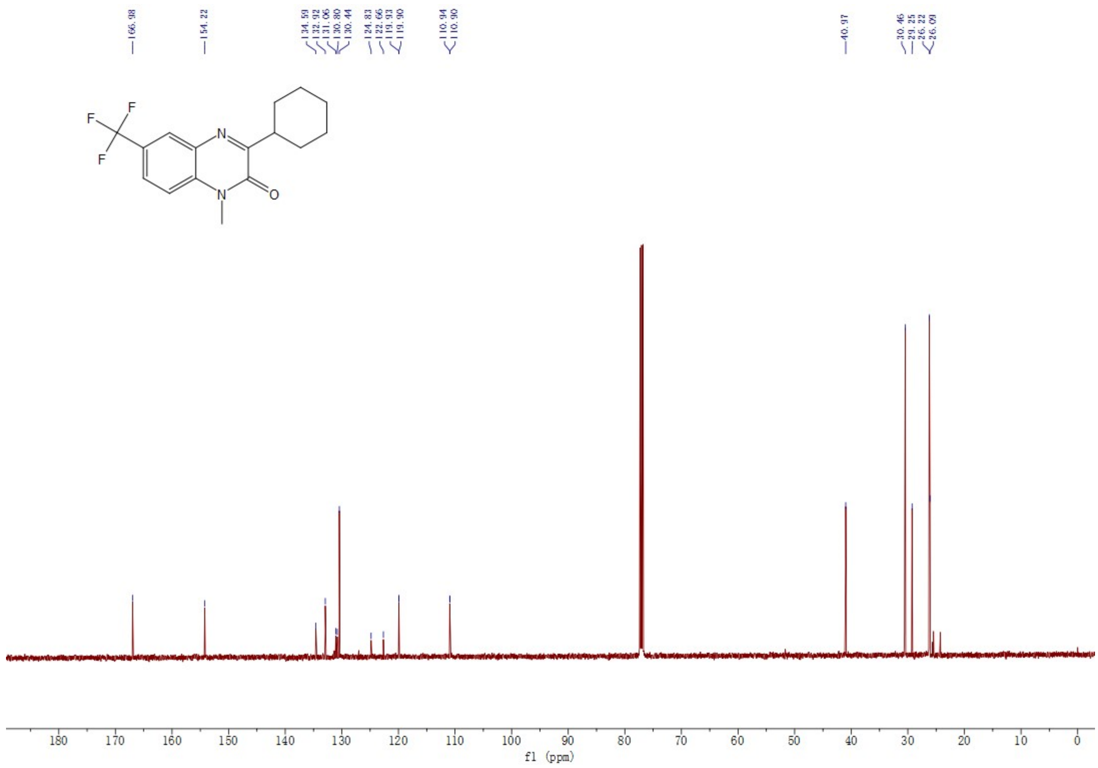
^{13}C NMR (125 MHz, $CDCl_3$) of **3la**



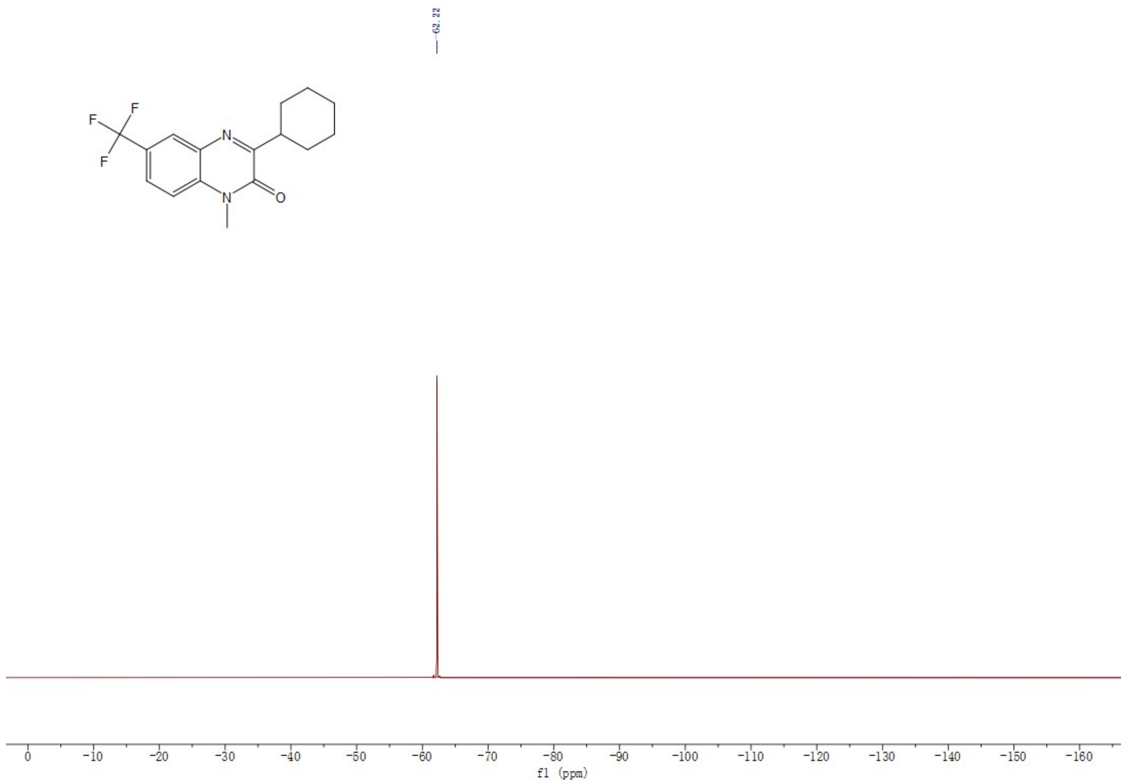
^{19}F NMR (471 MHz, $CDCl_3$) of **3la**



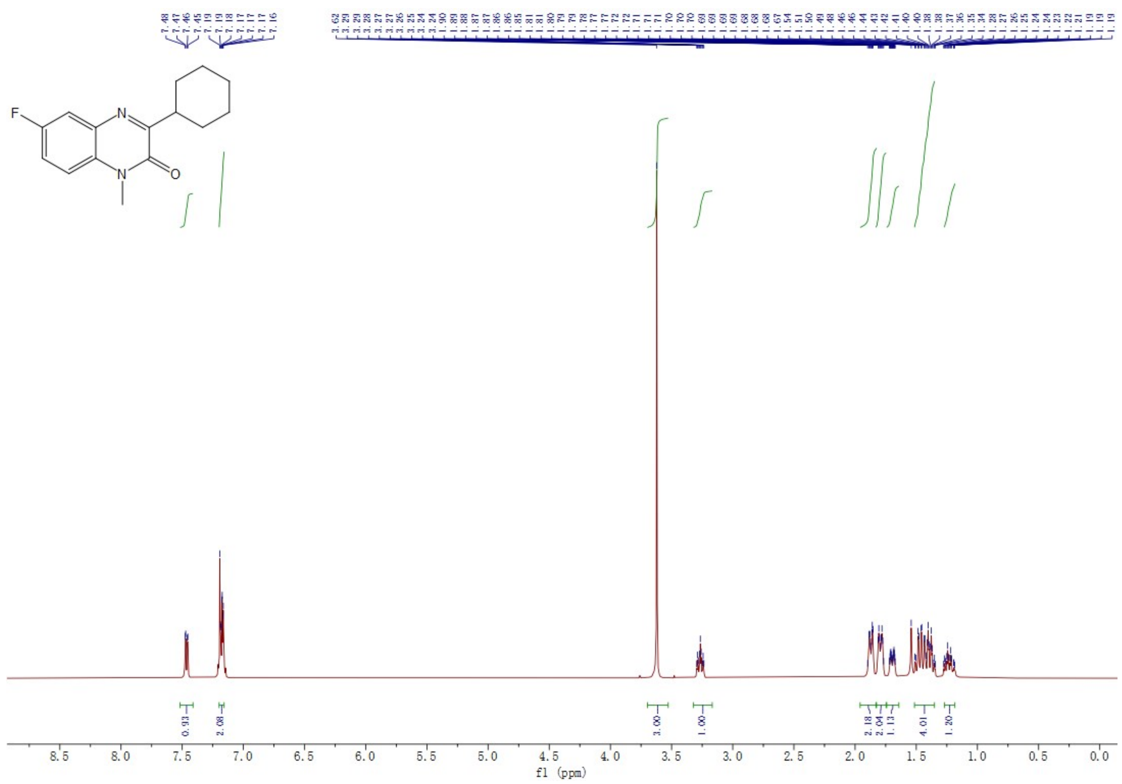
^{1}H NMR (500 MHz, $CDCl_3$) of **3ma**



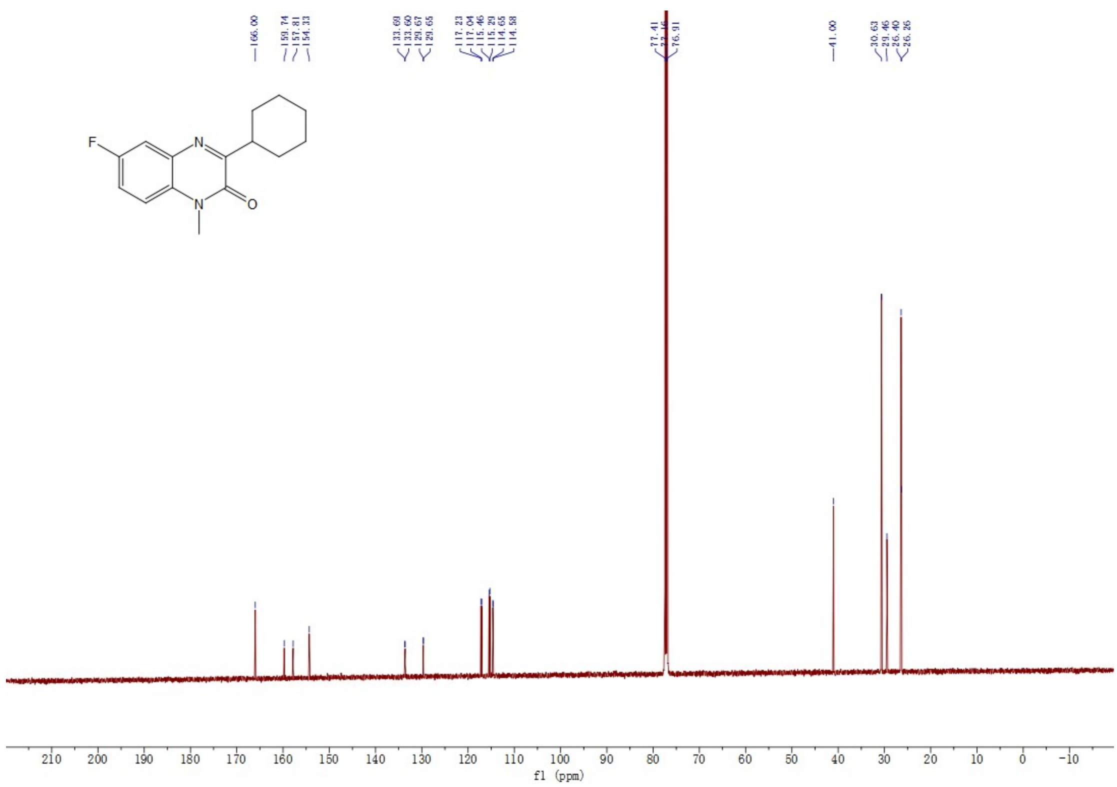
^{13}C NMR (125 MHz, $CDCl_3$) of **3ma**



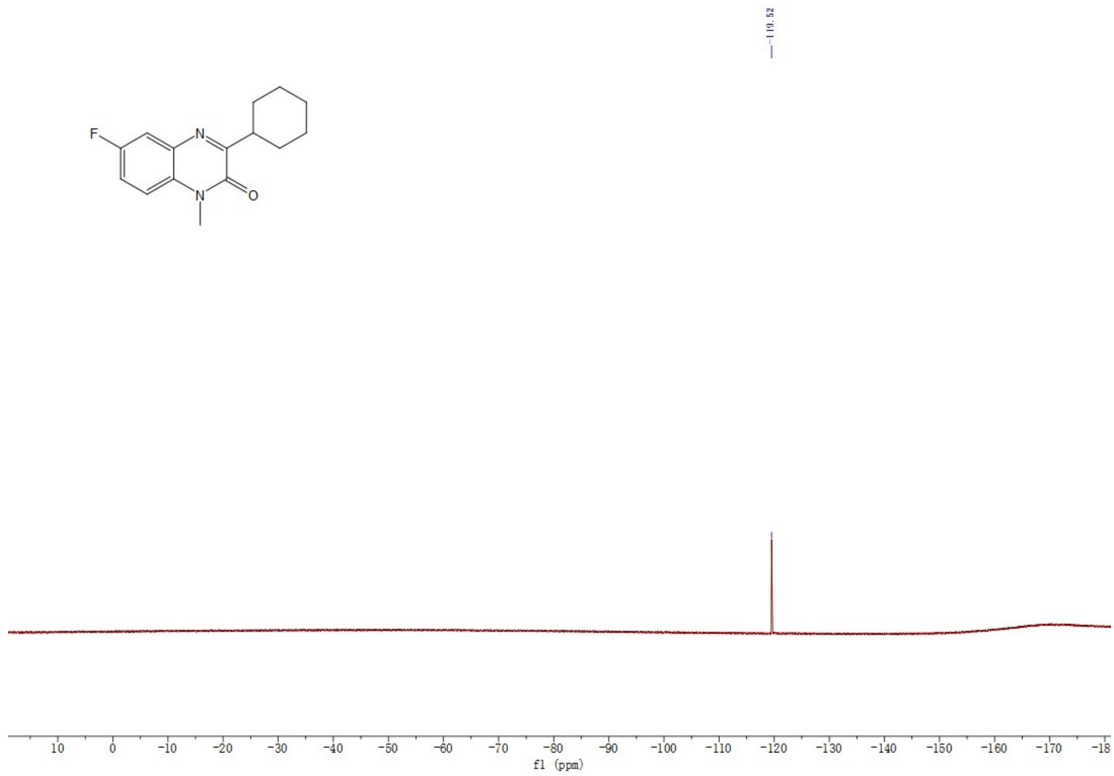
^{19}F NMR (471 MHz, $CDCl_3$) of **3ma**



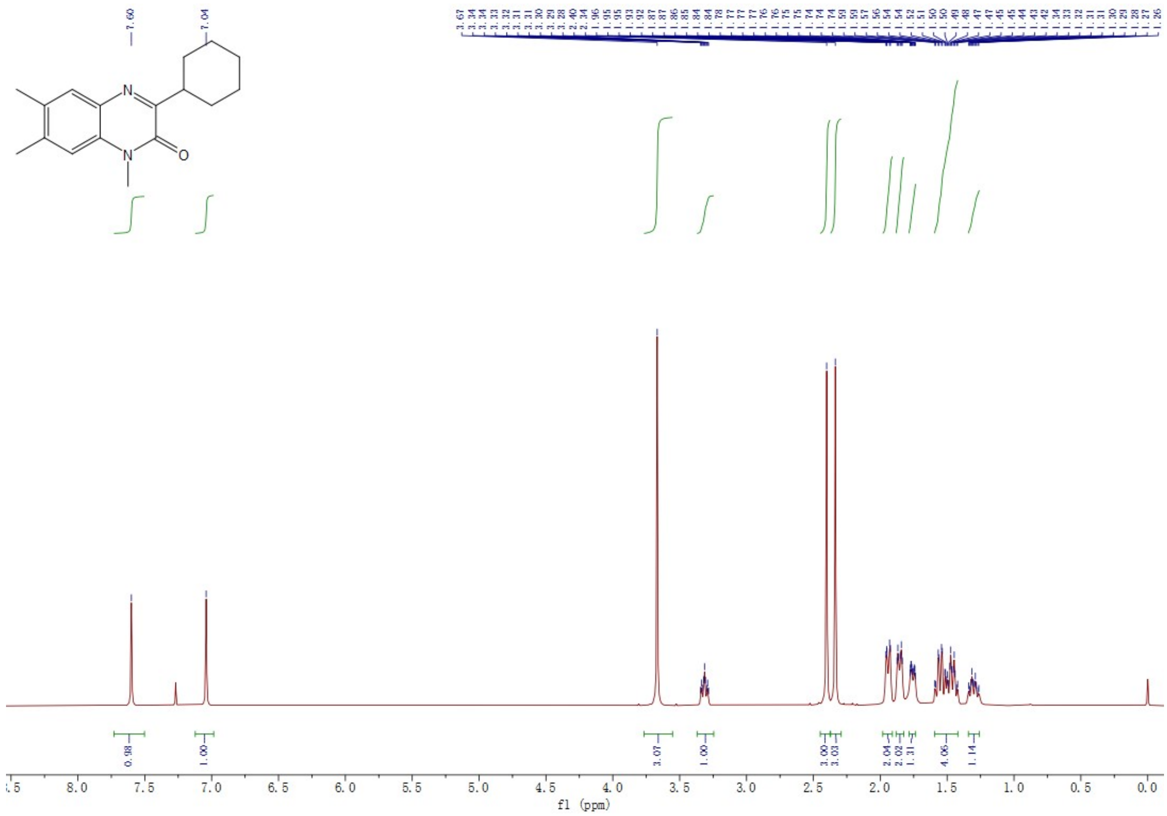
^{1}H NMR (500 MHz, $CDCl_3$) of **3na**



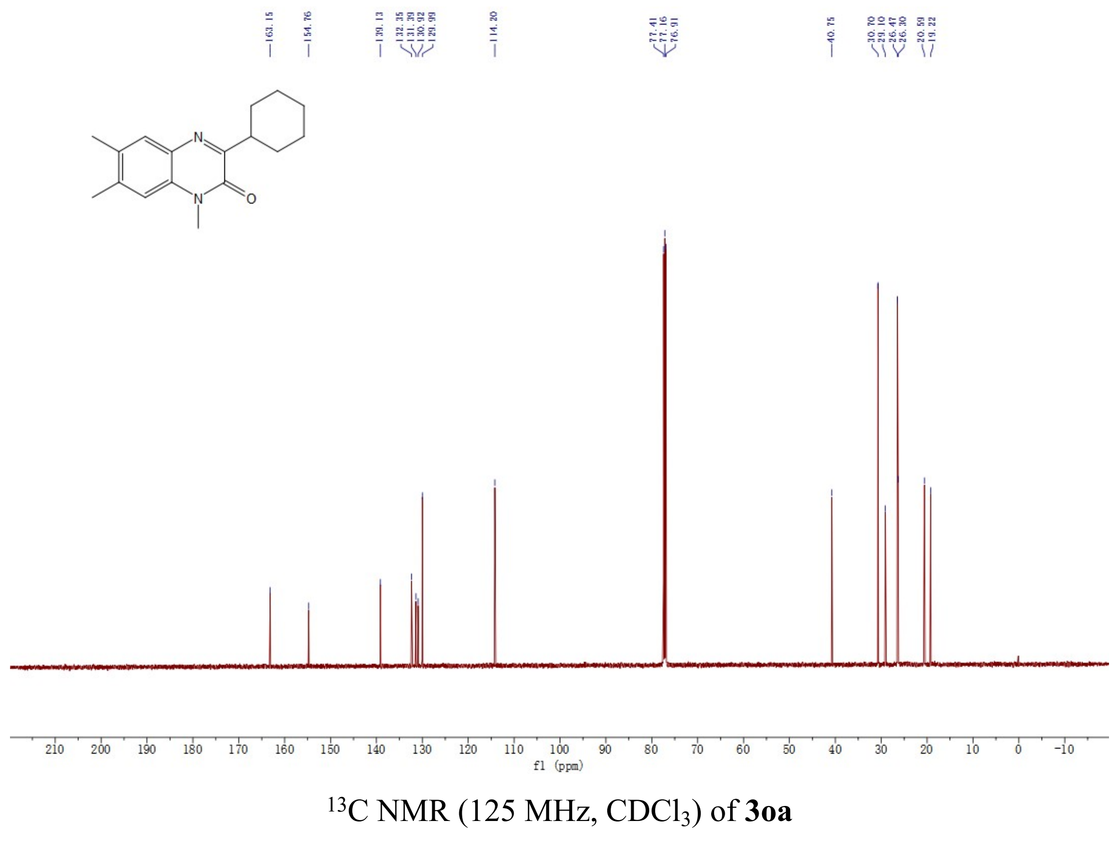
^{13}C NMR (125 MHz, $CDCl_3$) of **3na**



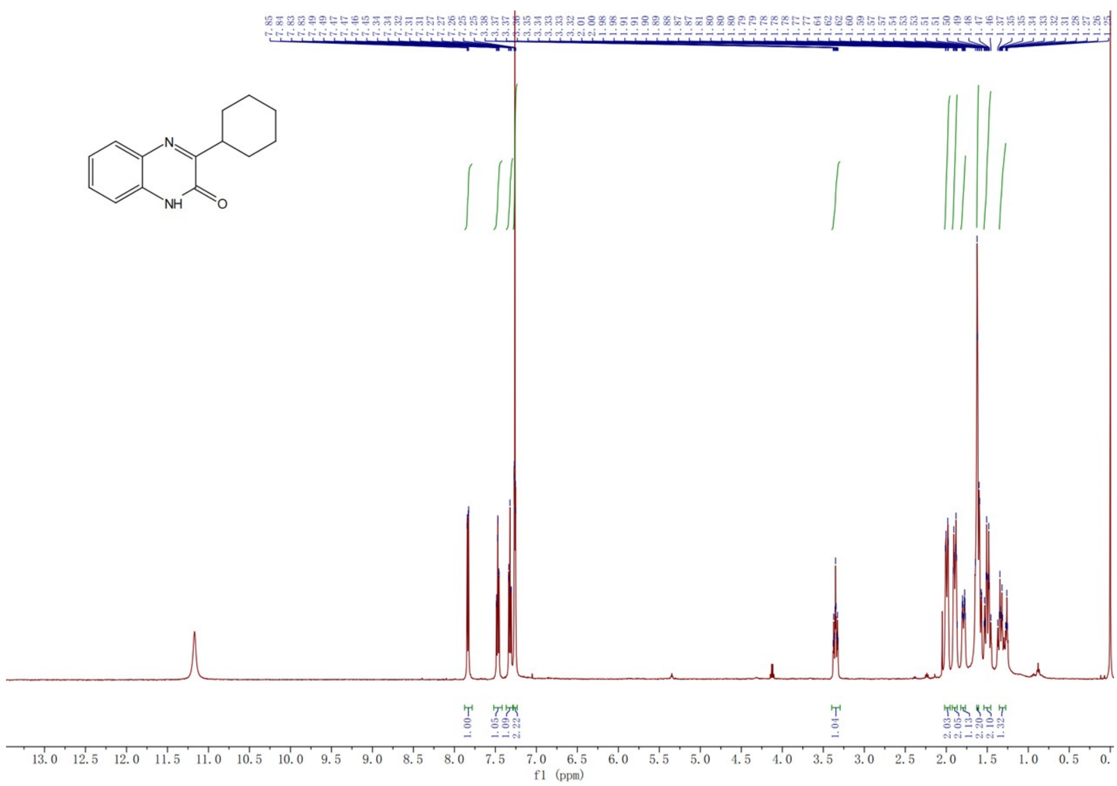
^{19}F NMR (471 MHz, $CDCl_3$) of **3na**



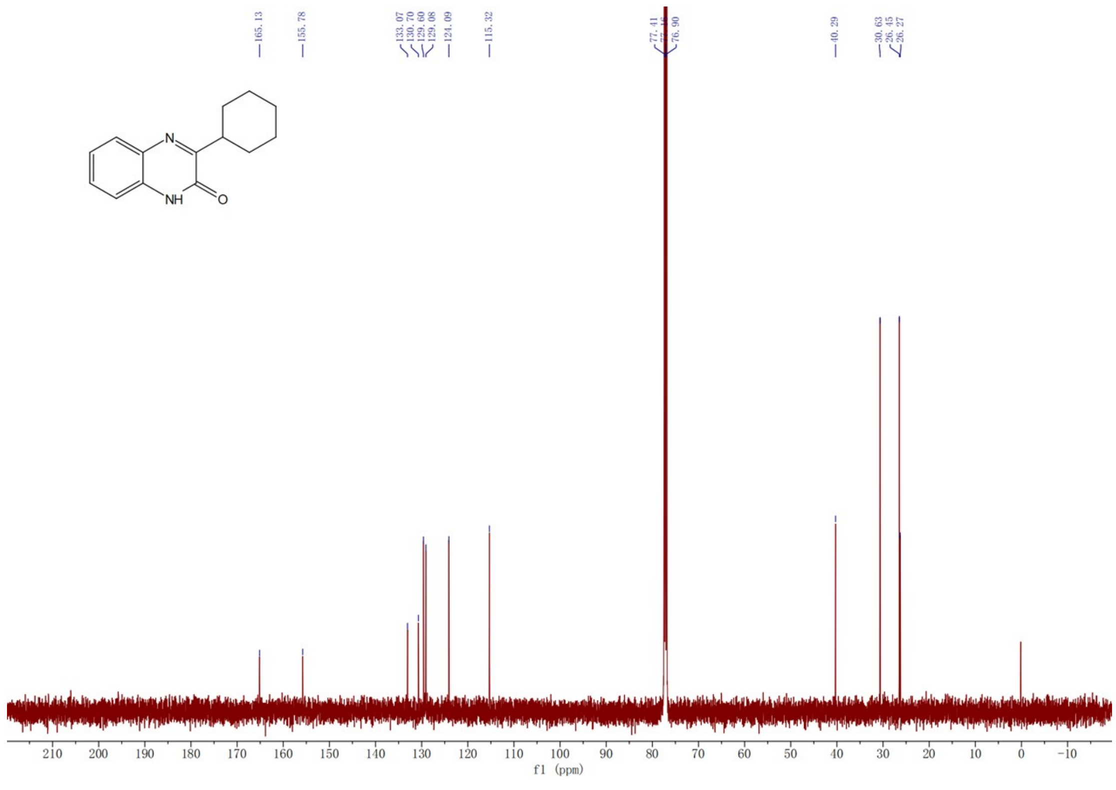
^{1}H NMR (500 MHz, $CDCl_3$) of **3oa**



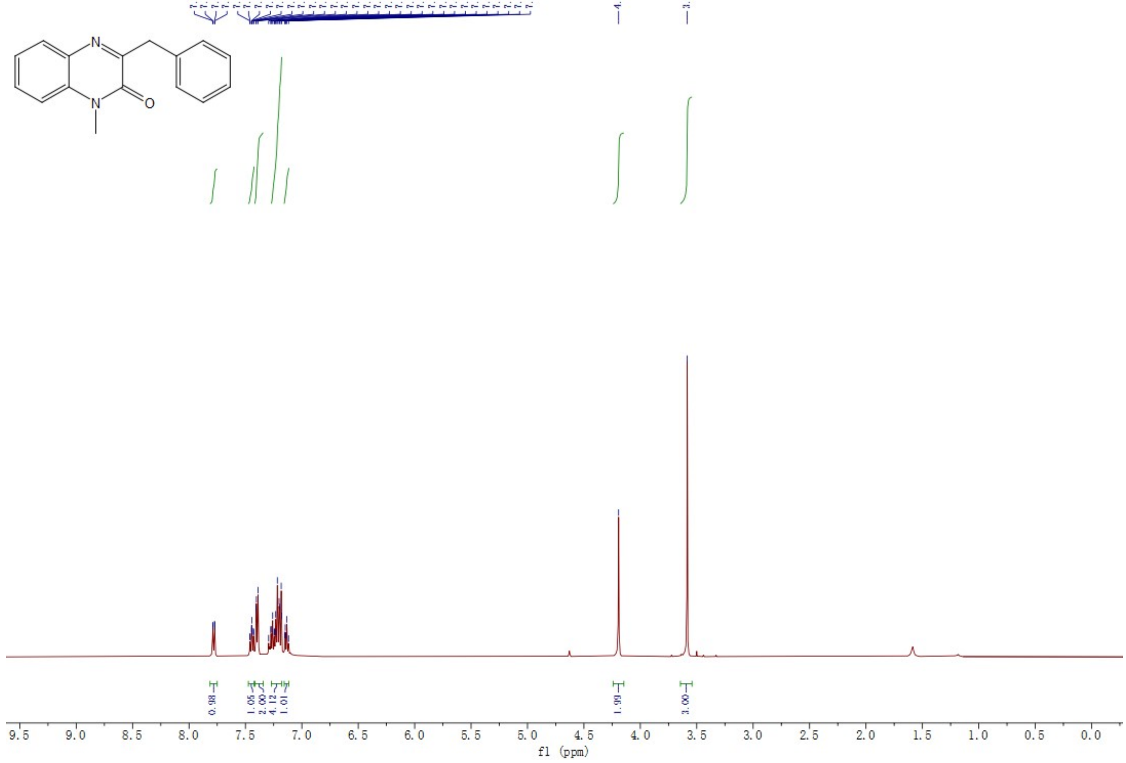
^{13}C NMR (125 MHz, $CDCl_3$) of **3oa**



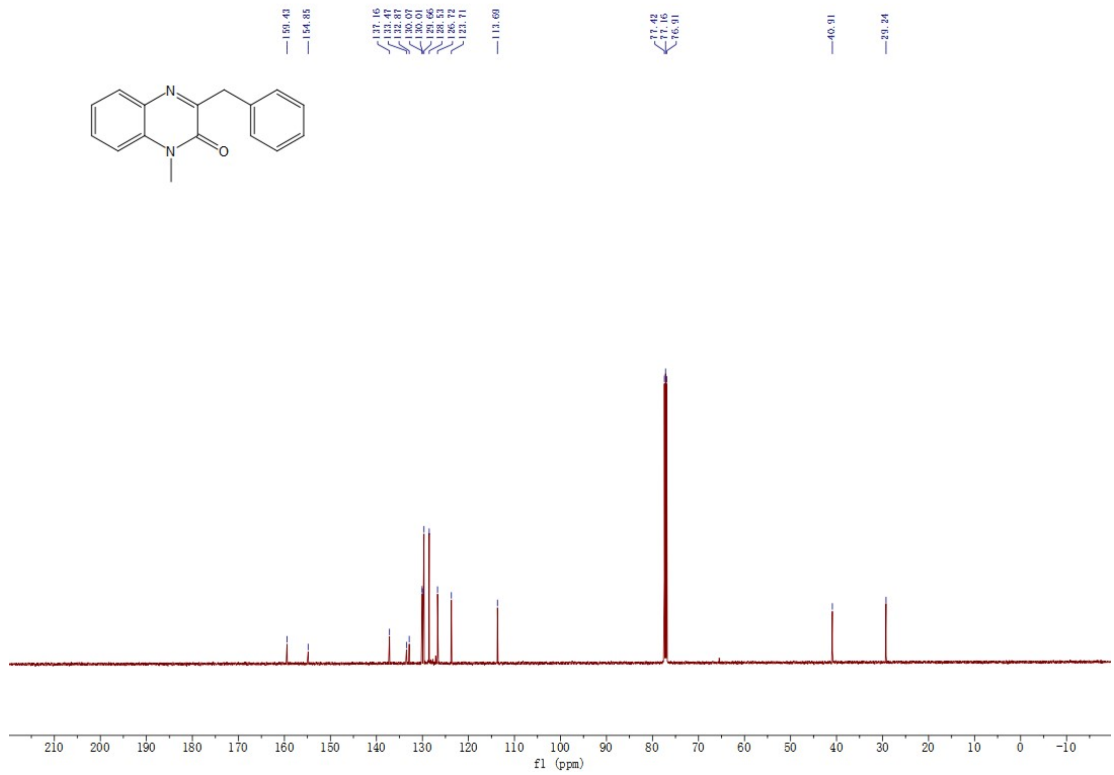
^{1}H NMR (500 MHz, $CDCl_3$) of **3pa**



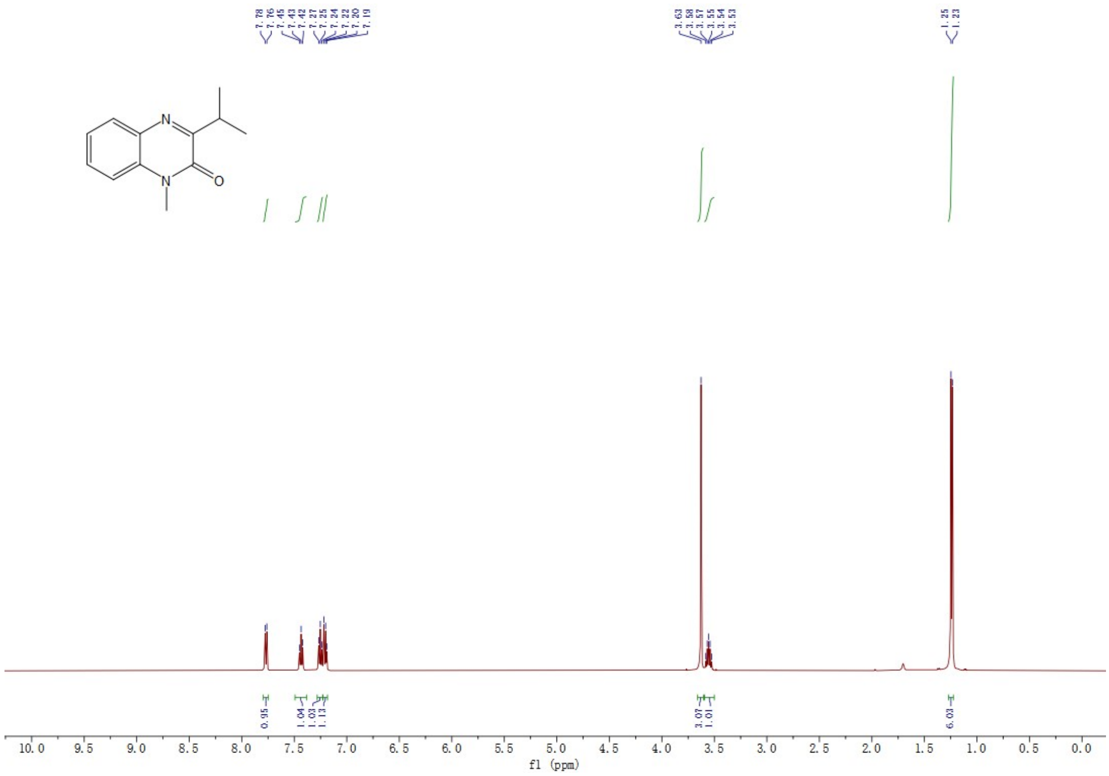
^{13}C NMR (125 MHz, $CDCl_3$) of **3pa**



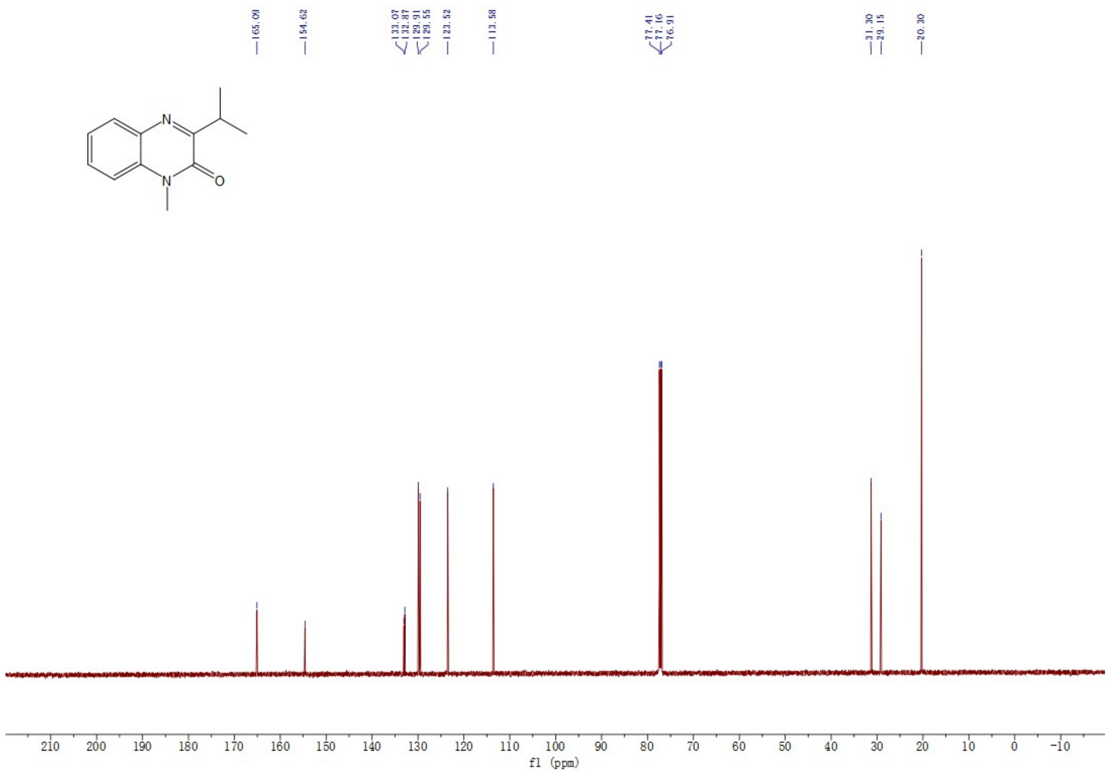
^1H NMR (500 MHz, $CDCl_3$) of **3ab**



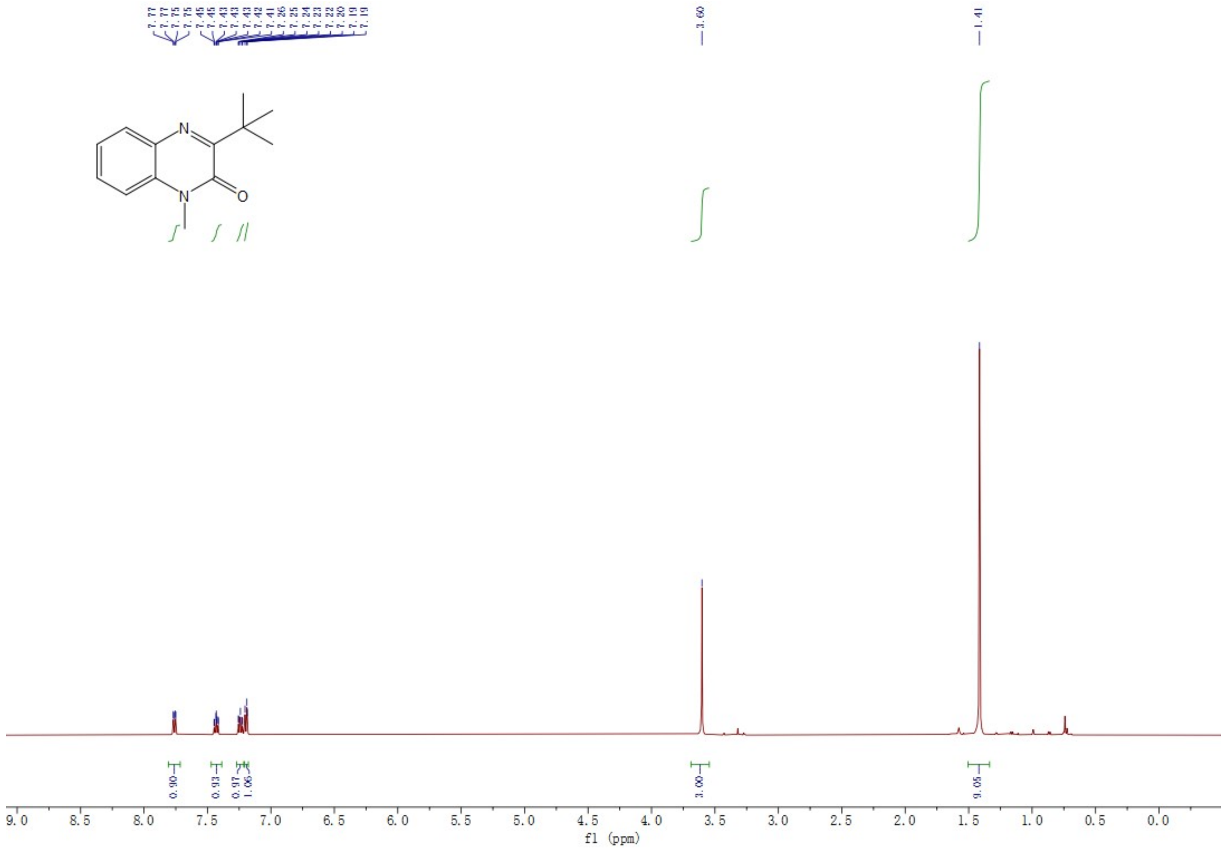
^{13}C NMR (125 MHz, $CDCl_3$) of **3ab**



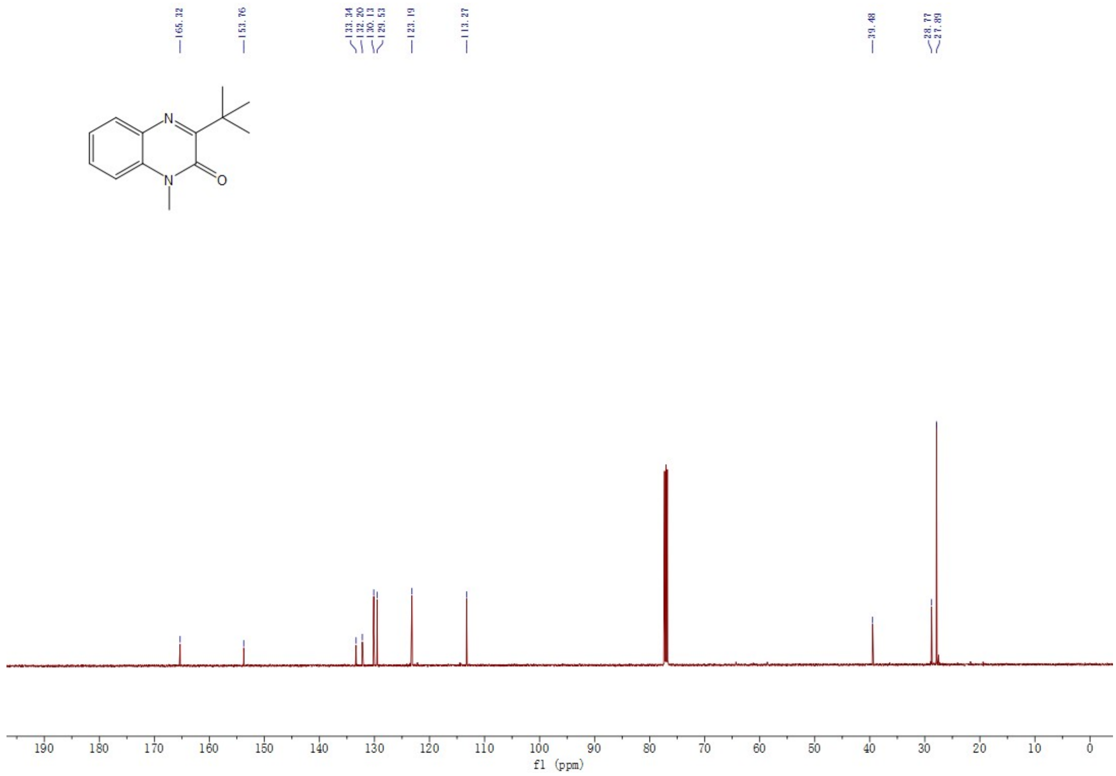
^{1}H NMR (500 MHz, $CDCl_3$) of **3ac**



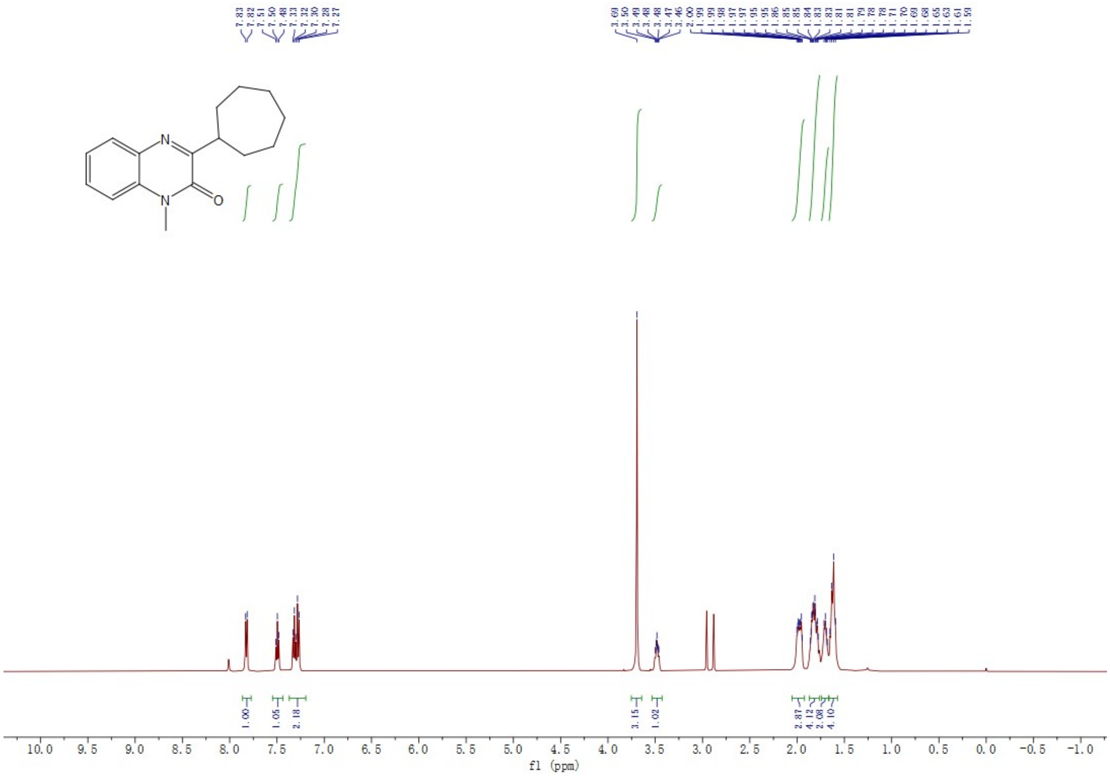
^{13}C NMR (125 MHz, $CDCl_3$) of **3ac**



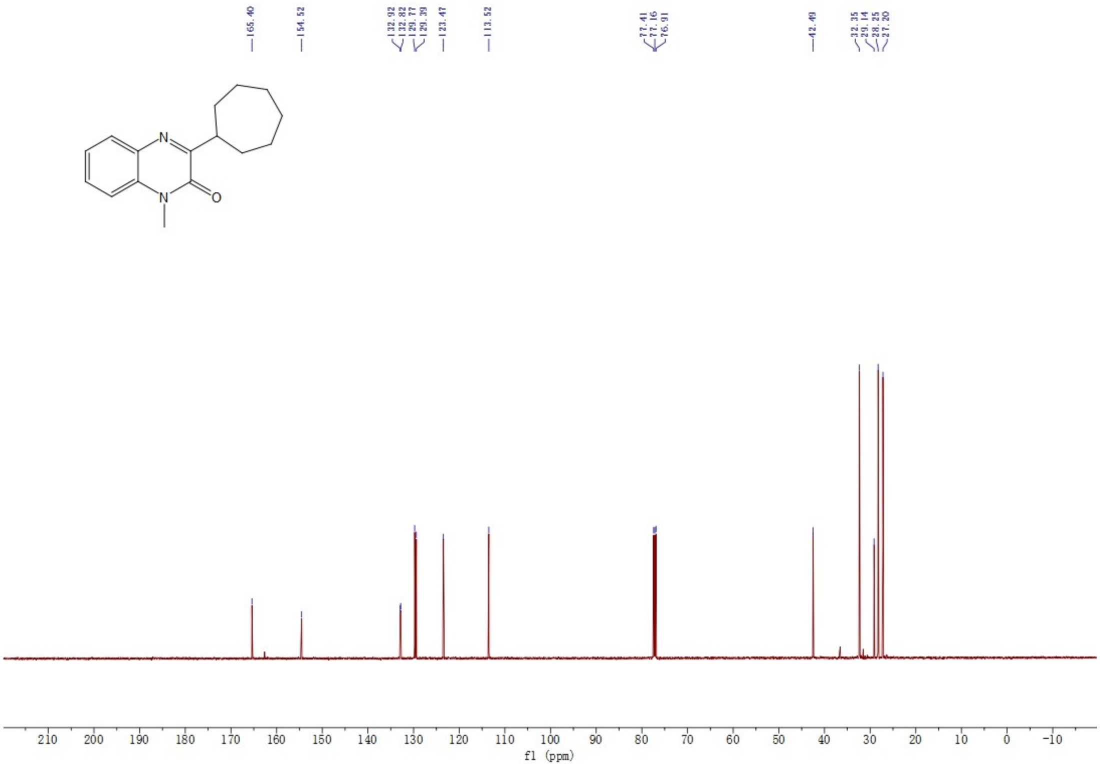
^{1}H NMR (500 MHz, $CDCl_3$) of **3ad**



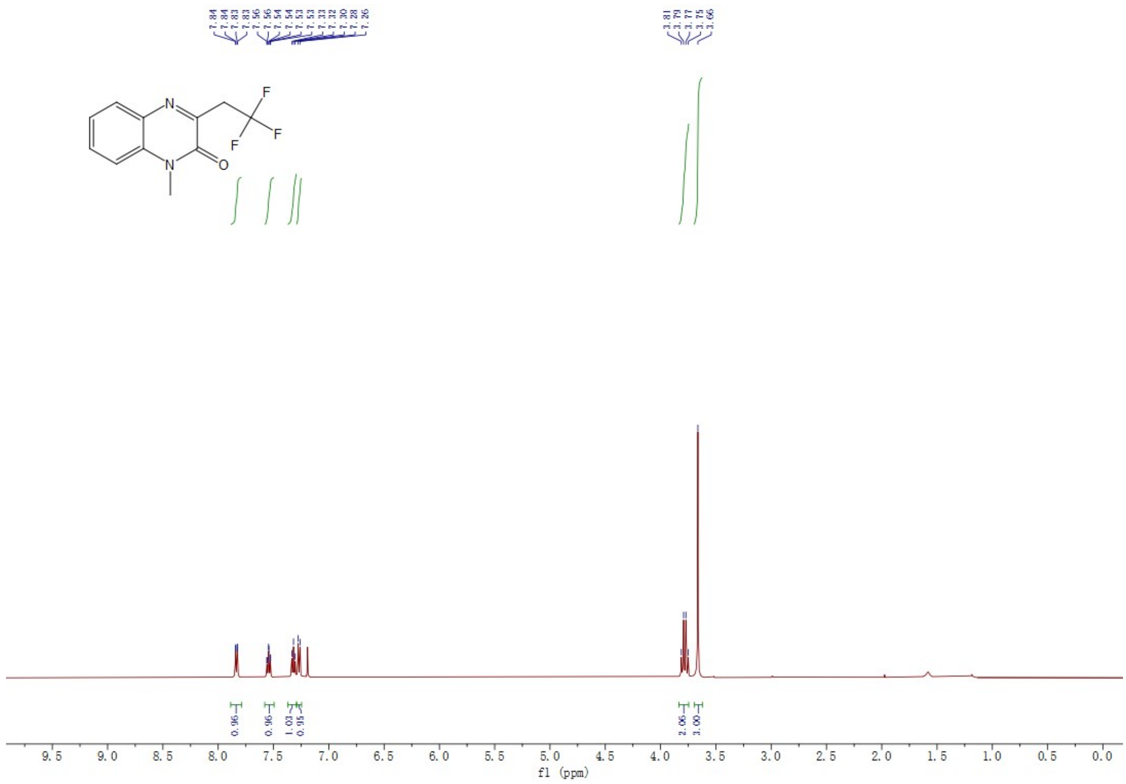
^{13}C NMR (125 MHz, $CDCl_3$) of **3ad**



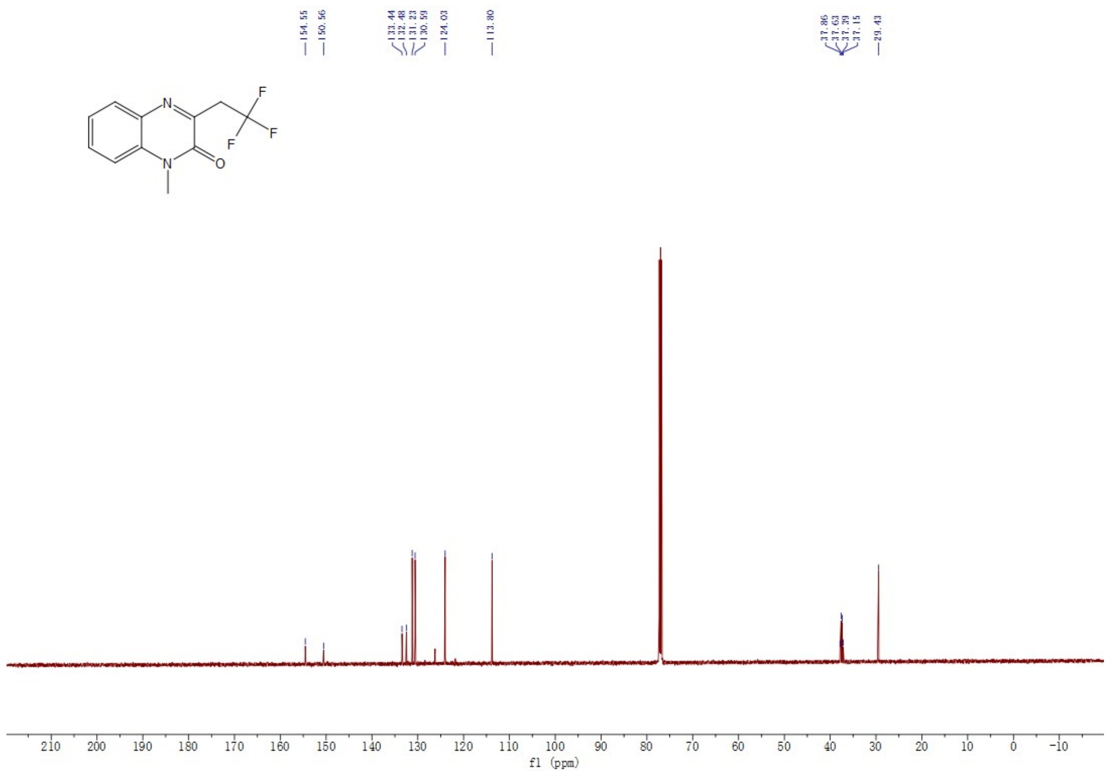
^{1}H NMR (500 MHz, $CDCl_3$) of **3ae**



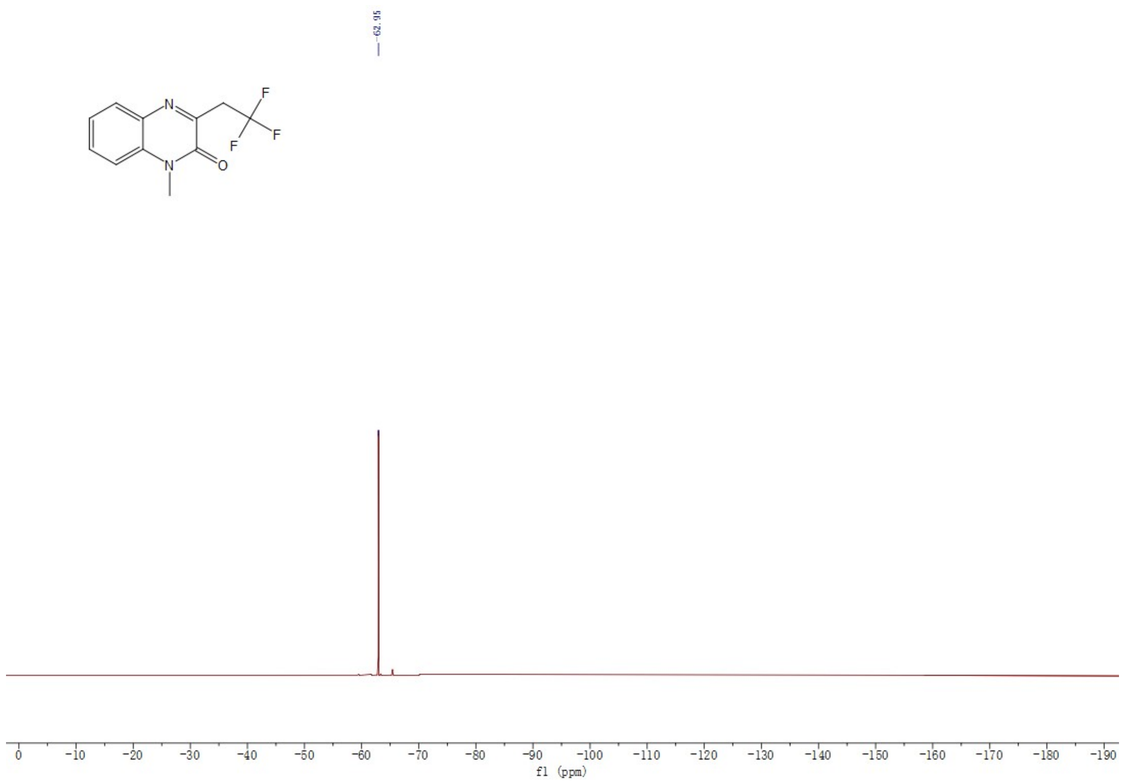
^{13}C NMR (125 MHz, $CDCl_3$) of **3ae**



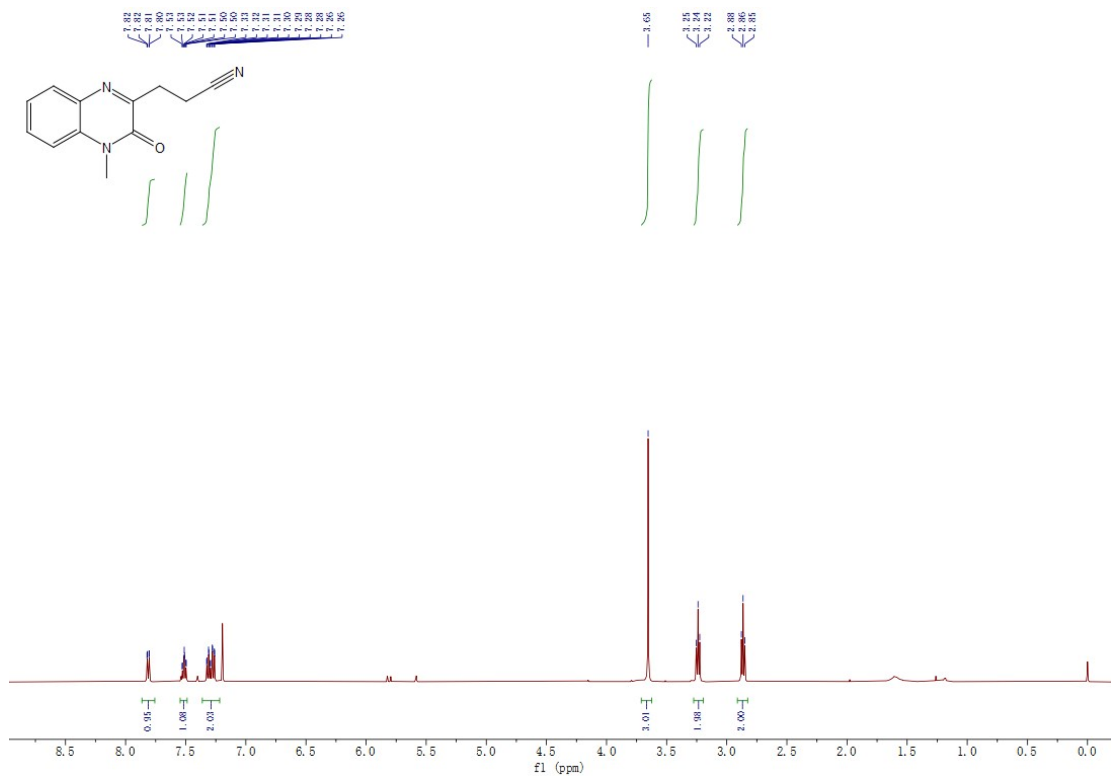
^{1}H NMR (500 MHz, $CDCl_3$) of **3af**



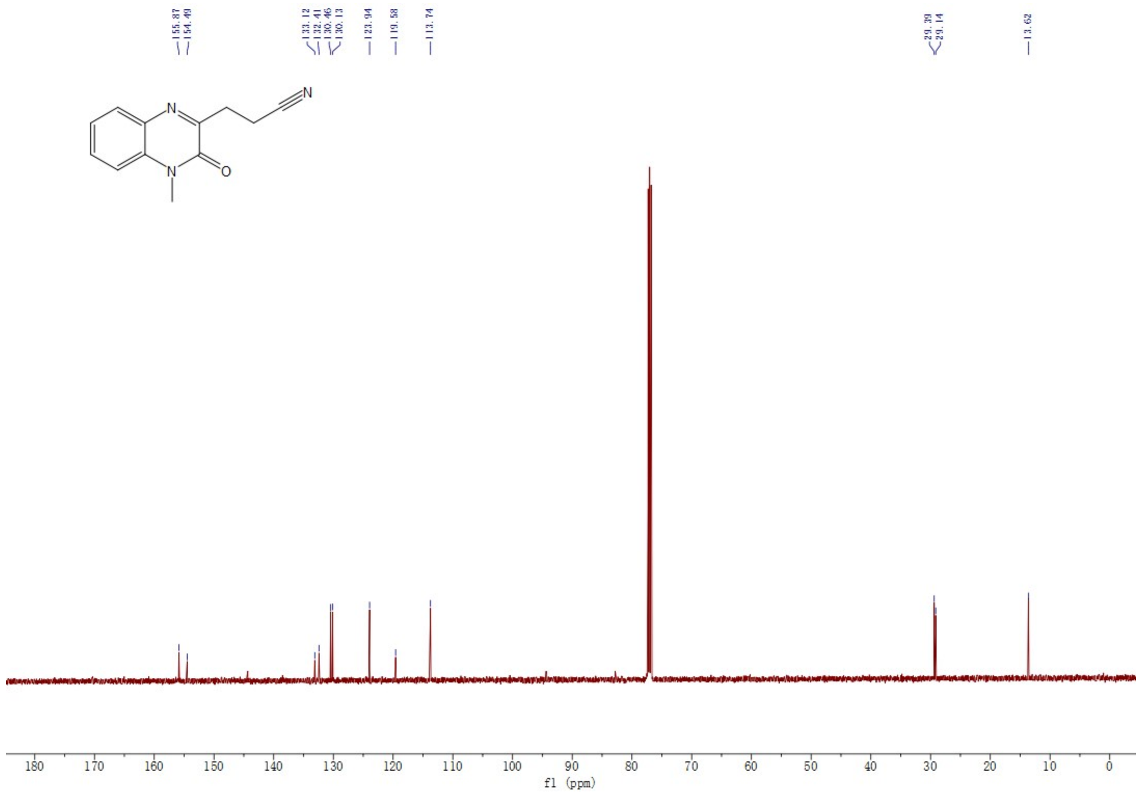
^{13}C NMR (125 MHz, $CDCl_3$) of **3af**



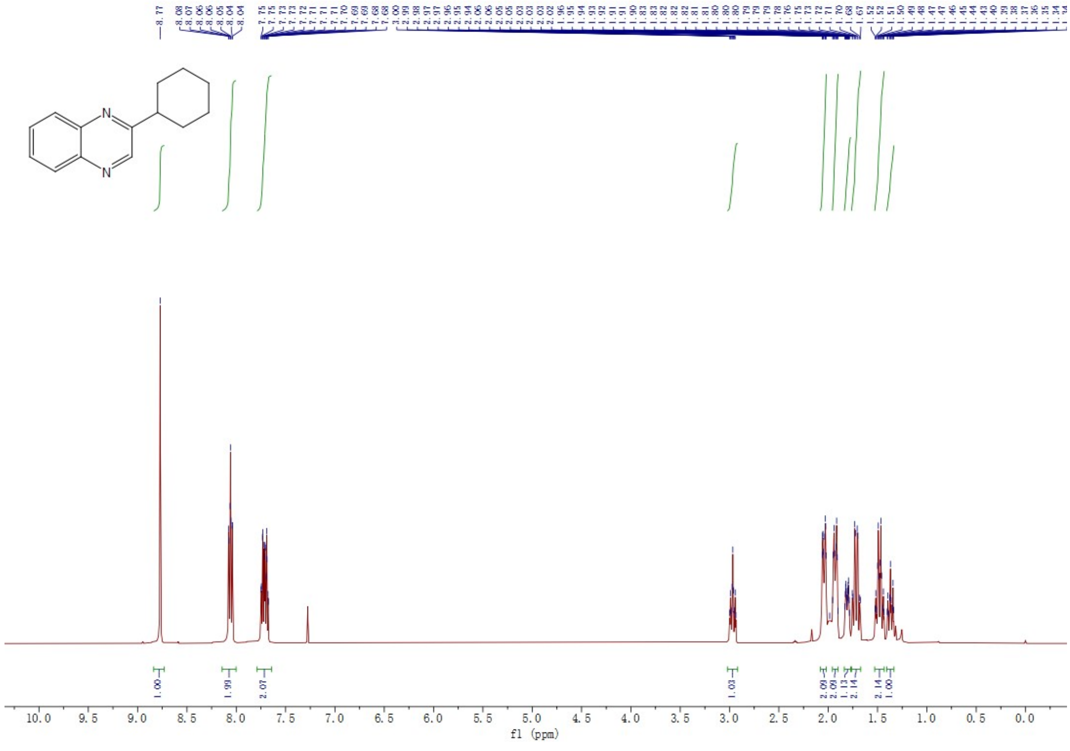
^{19}F NMR (471 MHz, $CDCl_3$) of **3af**



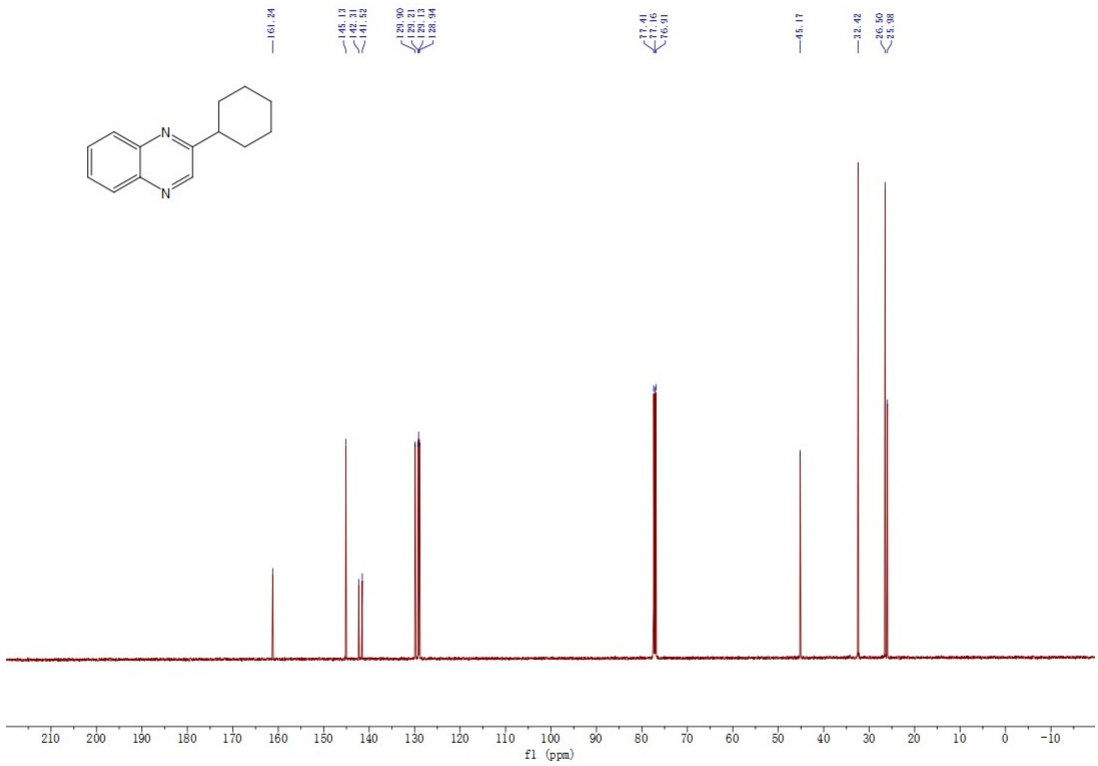
^{1}H NMR (500 MHz, $CDCl_3$) of **3ag**



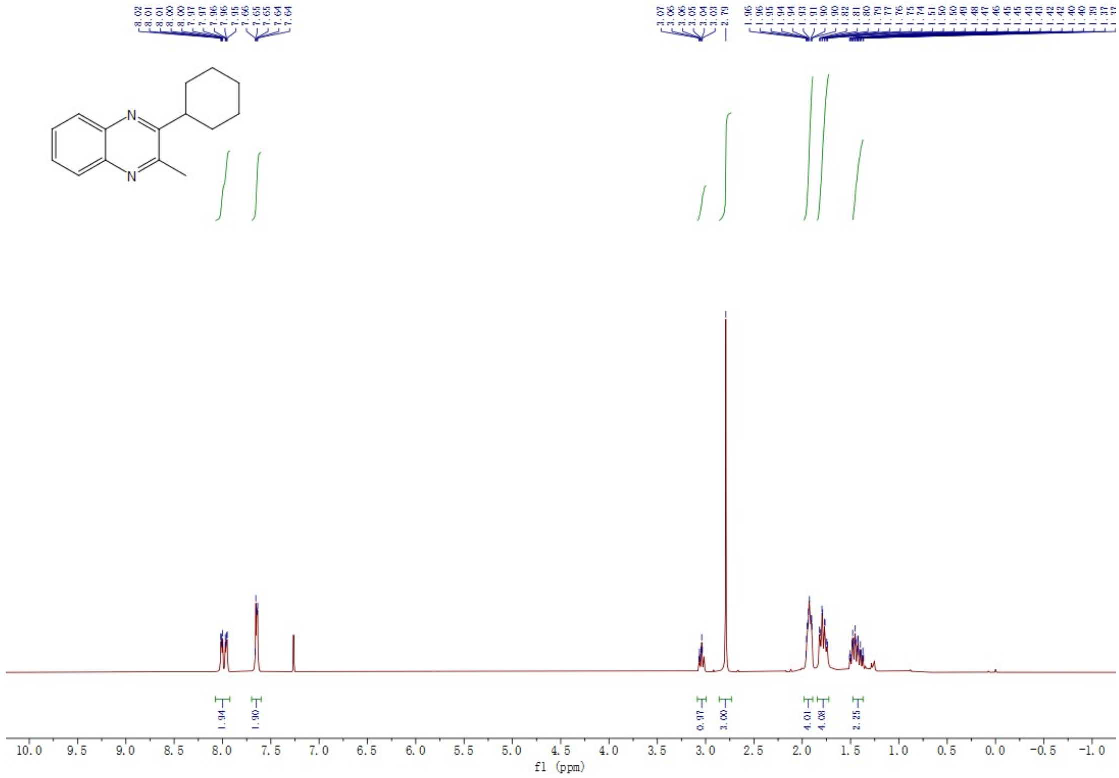
^{13}C NMR (125 MHz, $CDCl_3$) of **3ag**



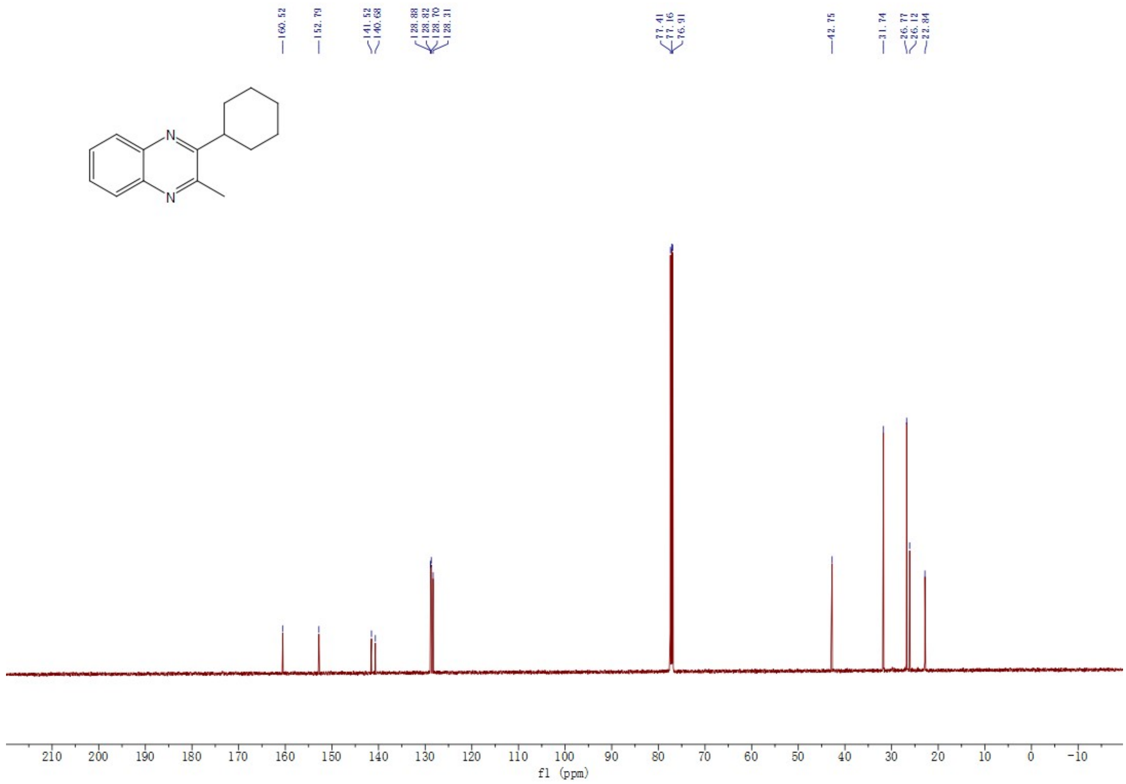
^{1}H NMR (500 MHz, $CDCl_3$) of **3qa**



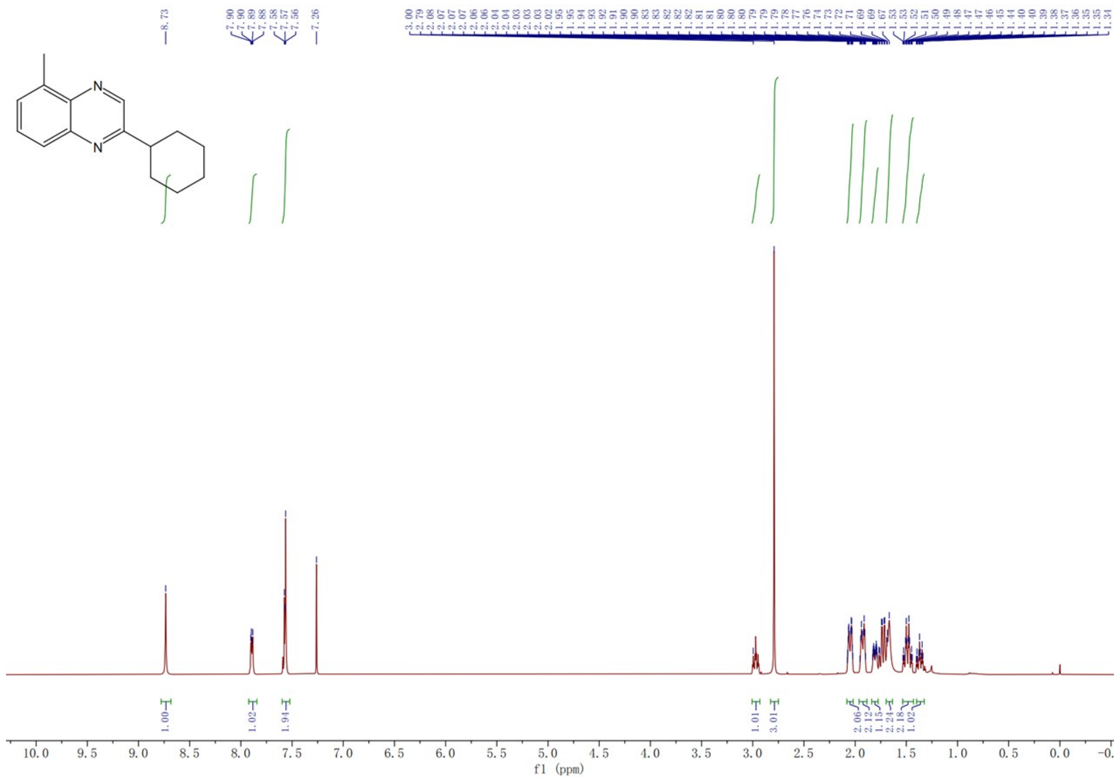
^{13}C NMR (125 MHz, $CDCl_3$) of **3qa**



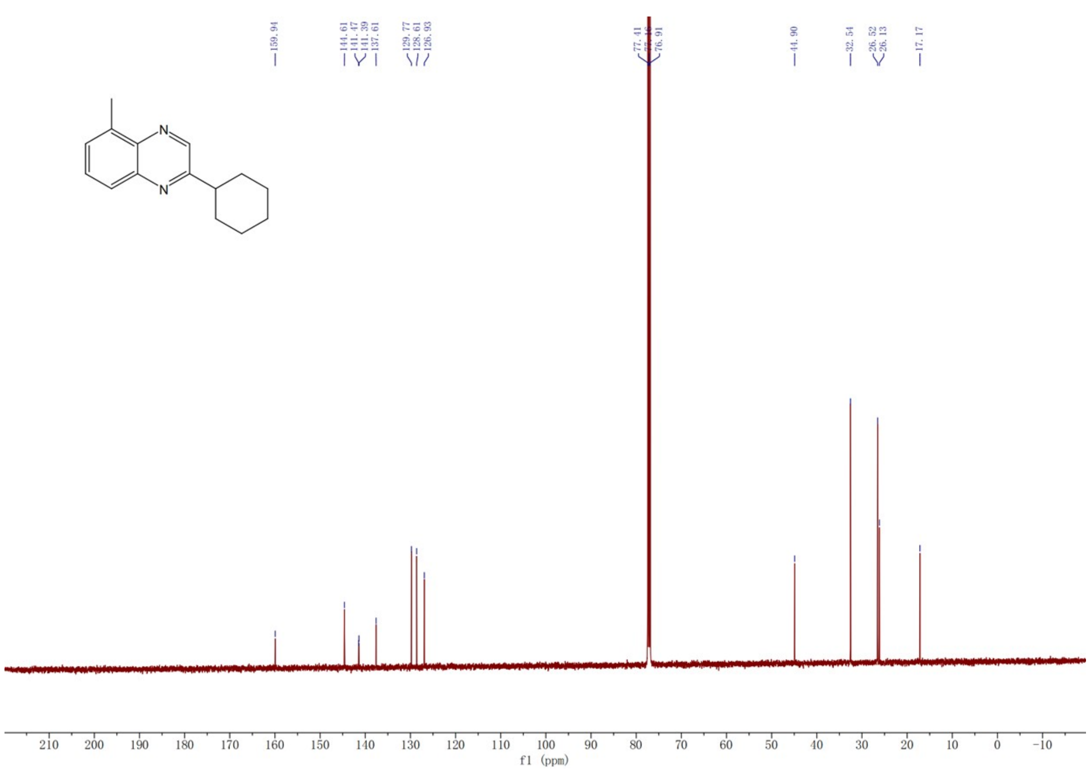
^{1}H NMR (500 MHz, $CDCl_3$) of **3ra**



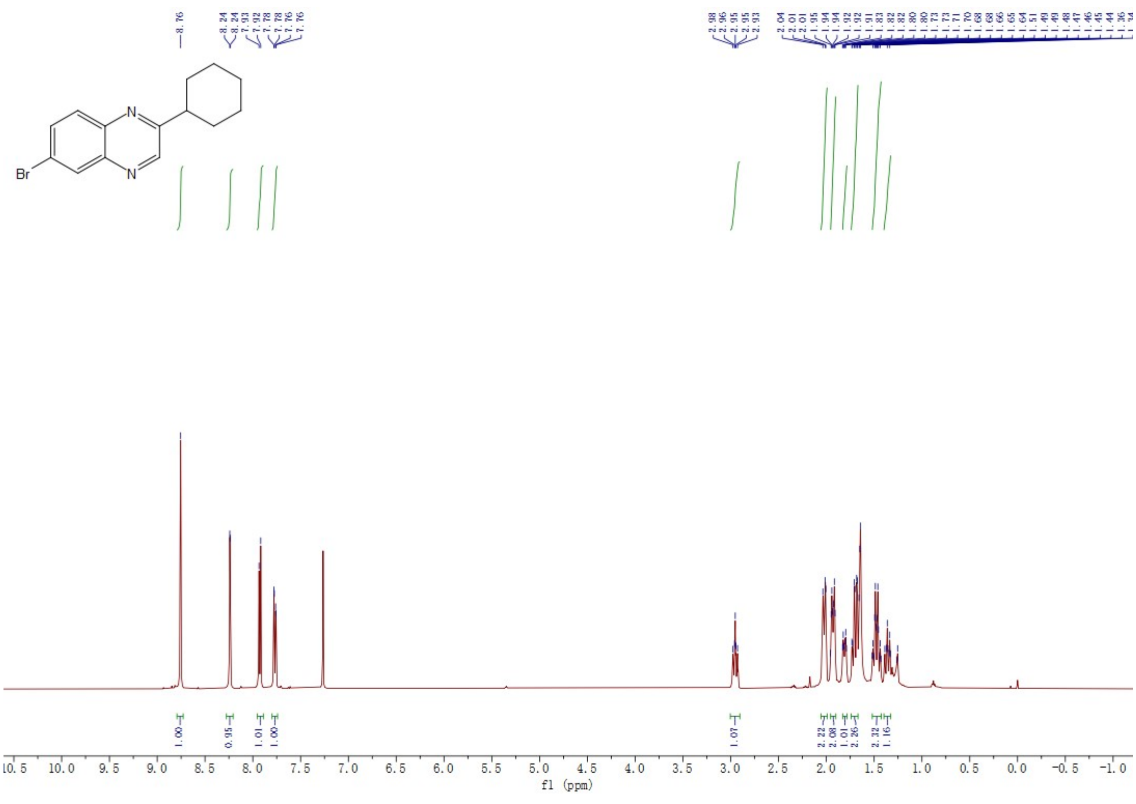
^{13}C NMR (125 MHz, $CDCl_3$) of **3ra**



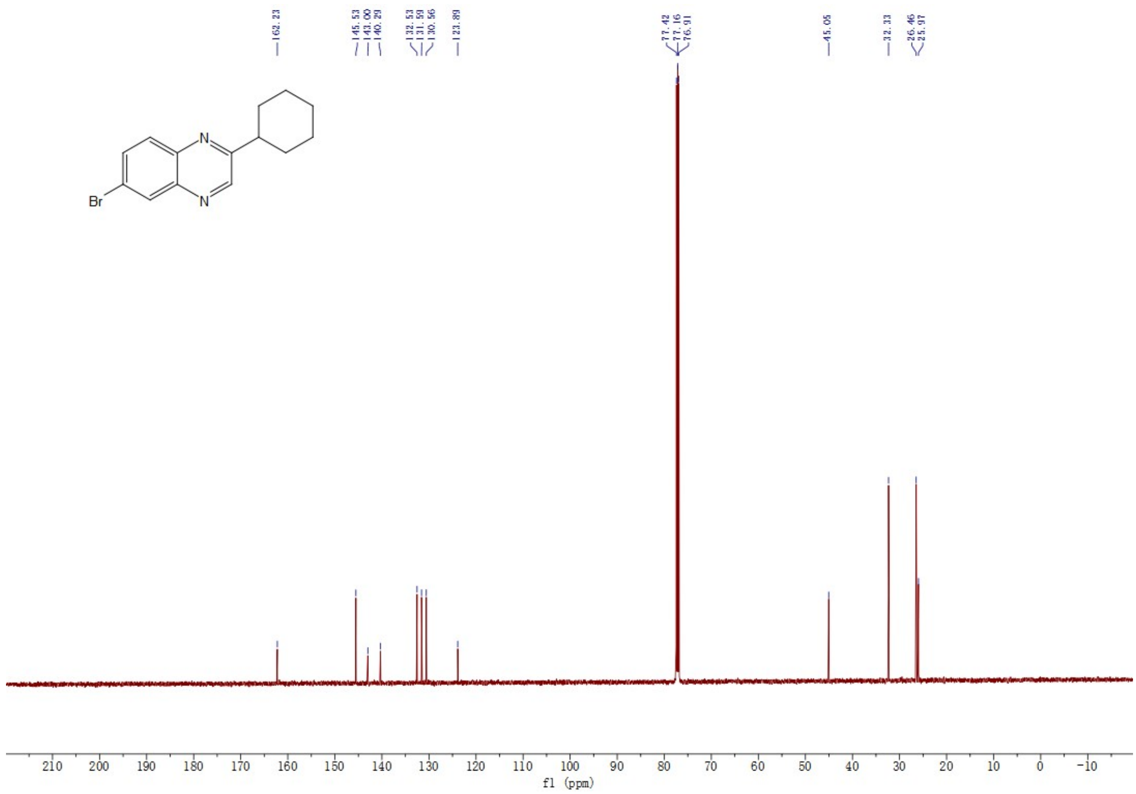
^{1}H NMR (500 MHz, $CDCl_3$) of **3sa**



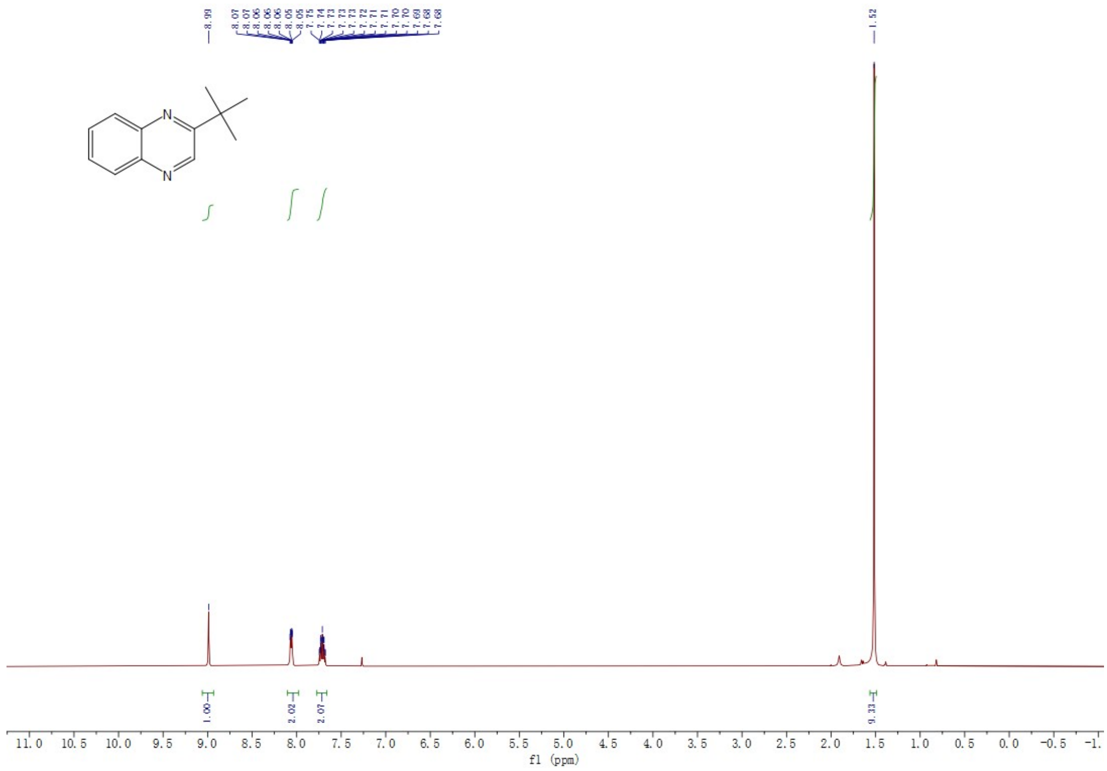
^{13}C NMR (125 MHz, $CDCl_3$) of **3sa**



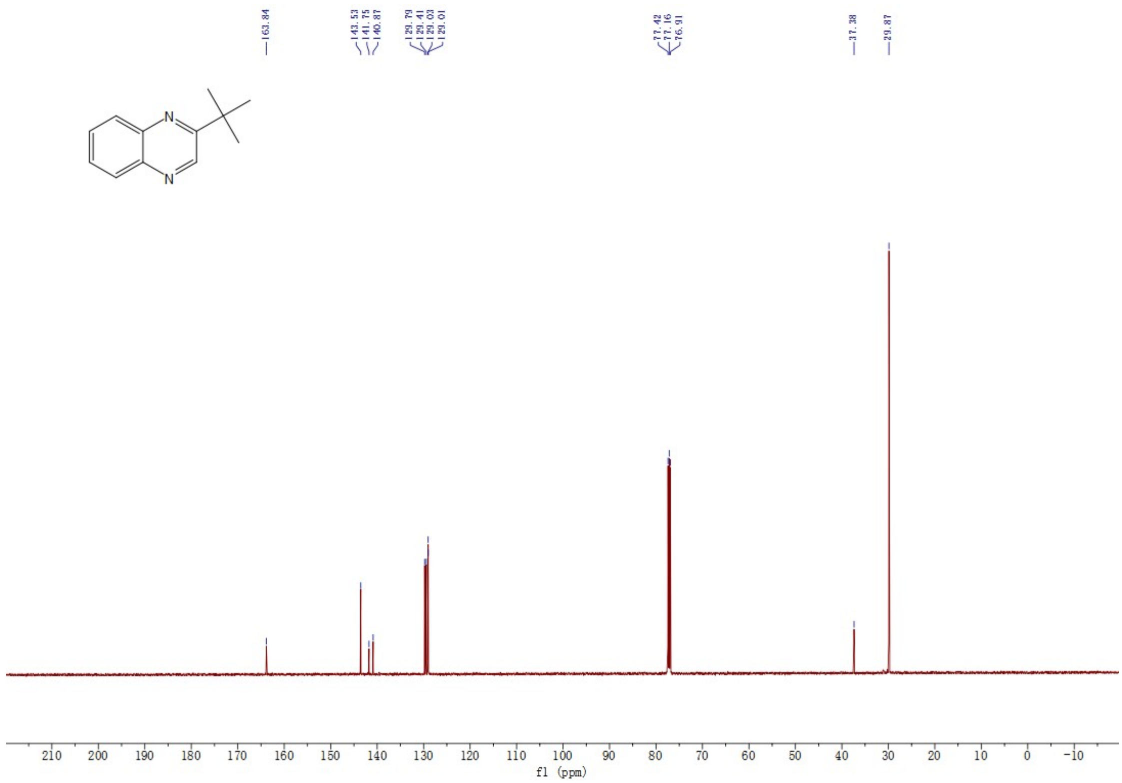
^{1}H NMR (500 MHz, $CDCl_3$) of **3ta**



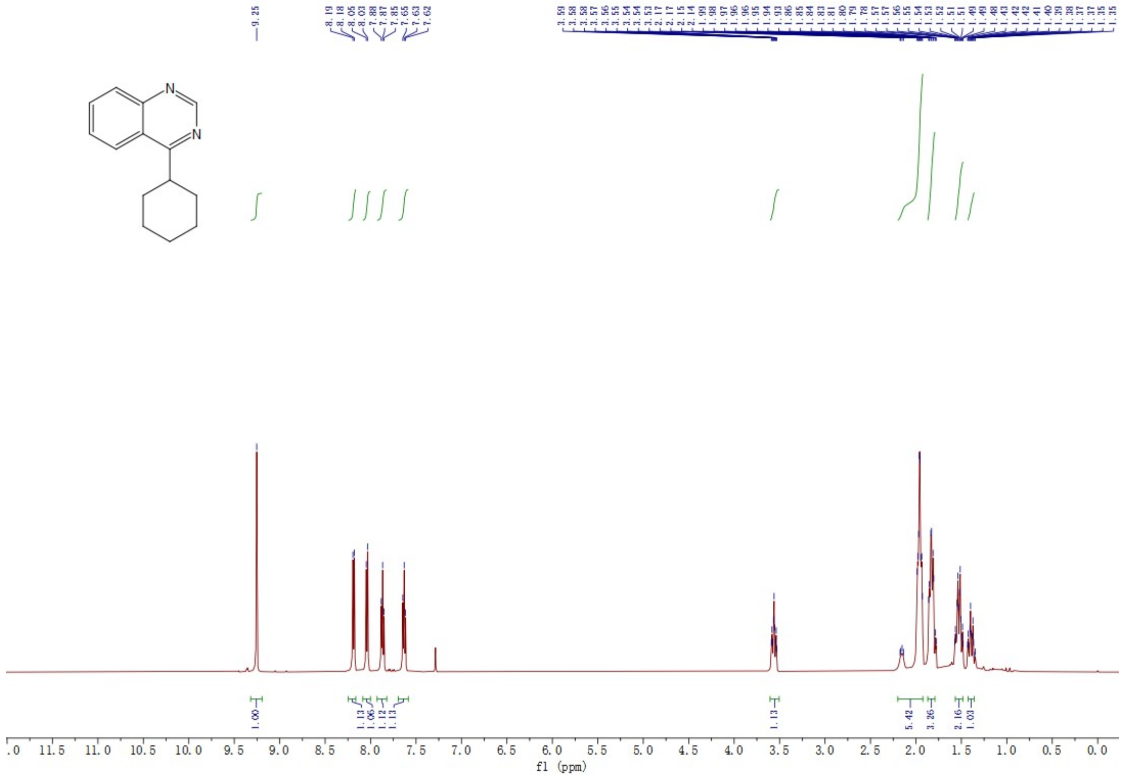
^{13}C NMR (125 MHz, $CDCl_3$) of **3ta**



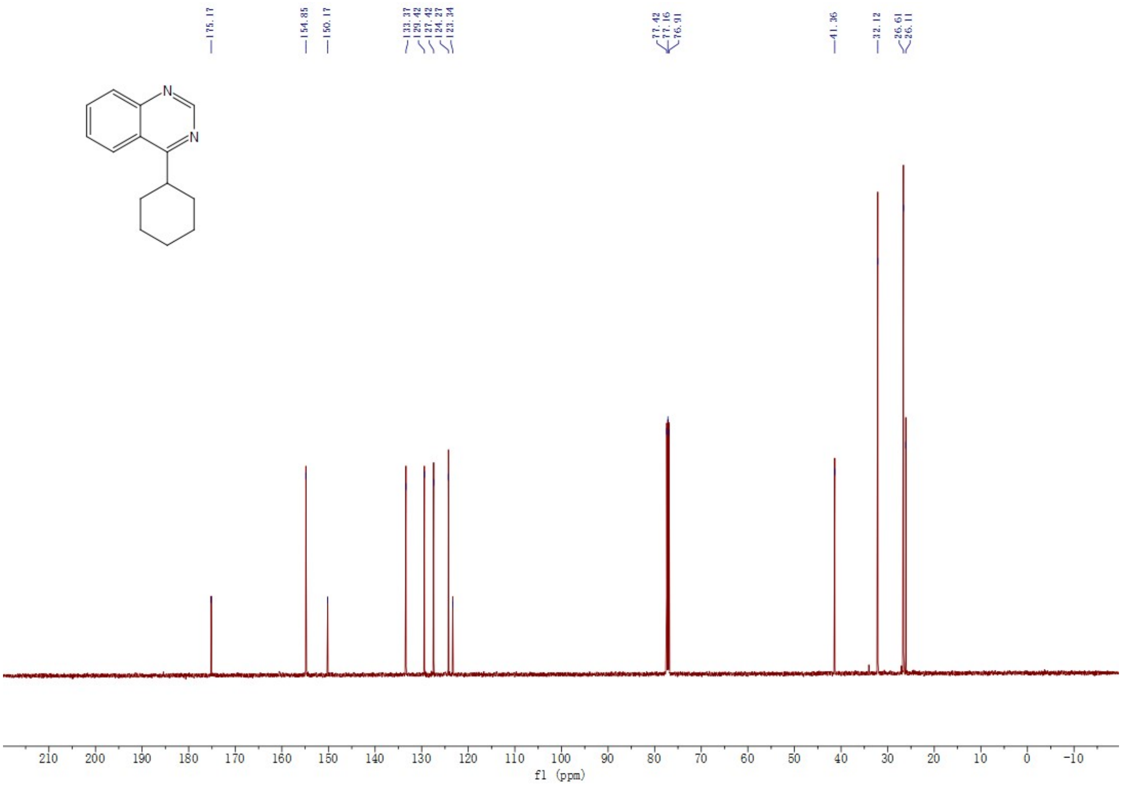
^{1}H NMR (500 MHz, $CDCl_3$) of **3ua**



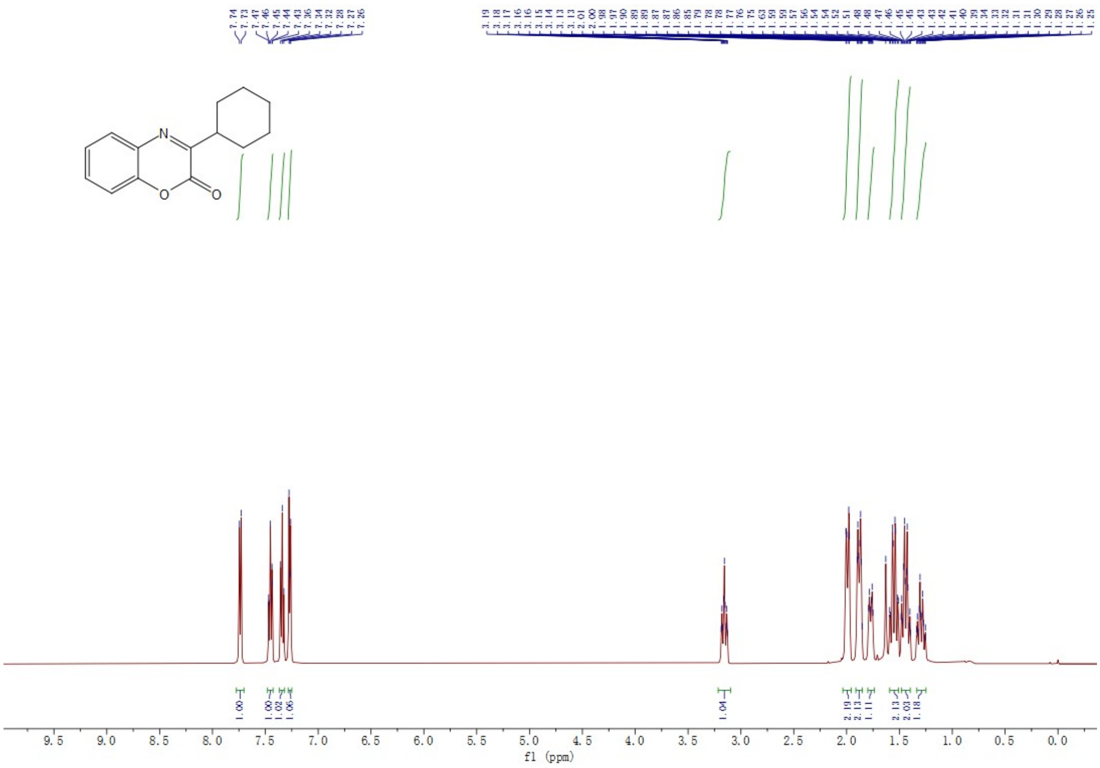
^{13}C NMR (125 MHz, $CDCl_3$) of **3ua**



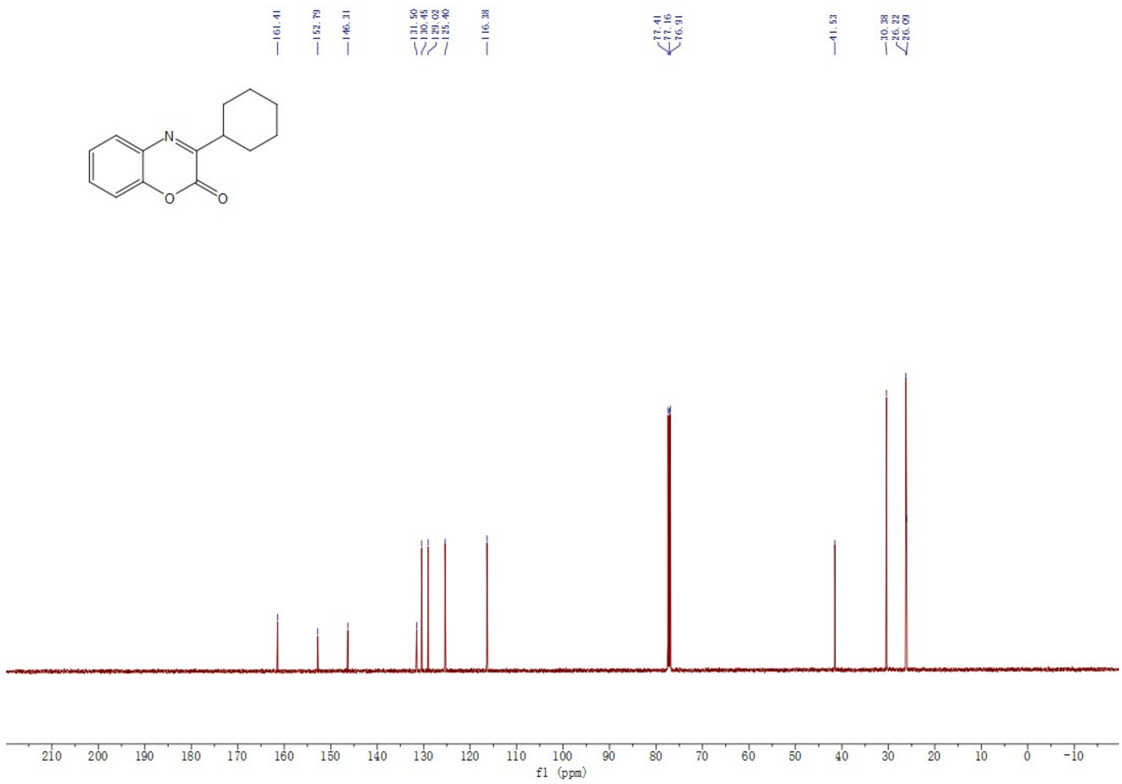
^{1}H NMR (500 MHz, $CDCl_3$) of **3va**



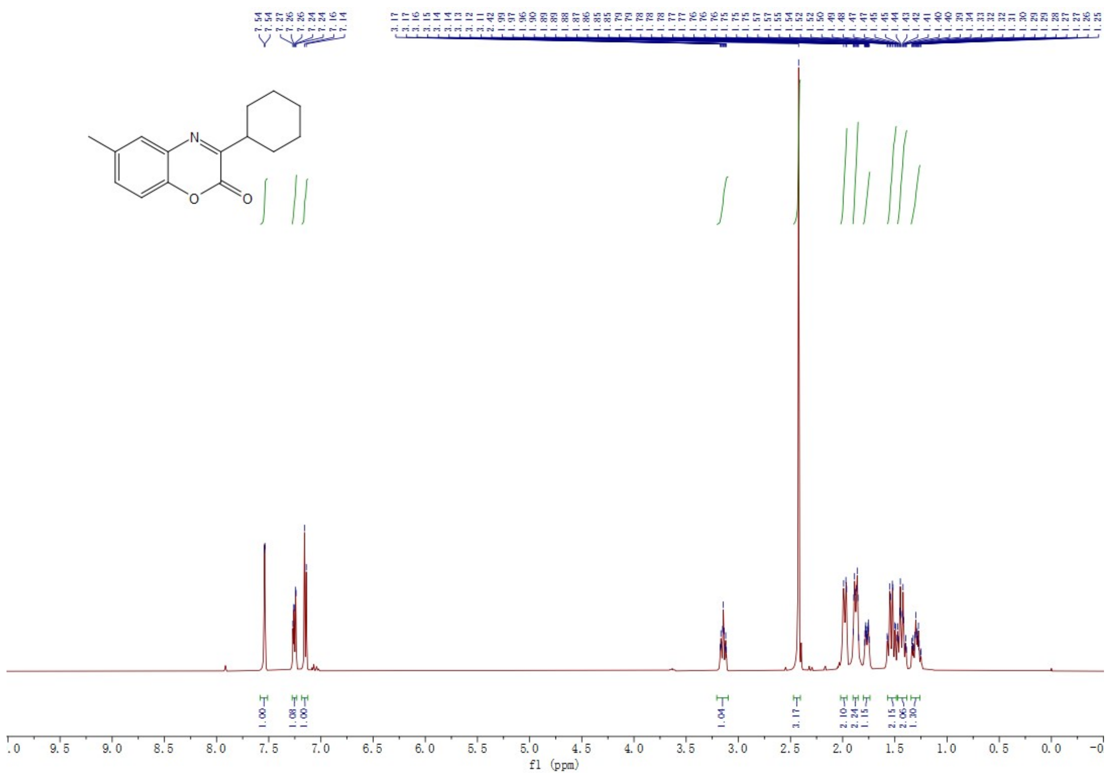
^{13}C NMR (125 MHz, $CDCl_3$) of **3va**



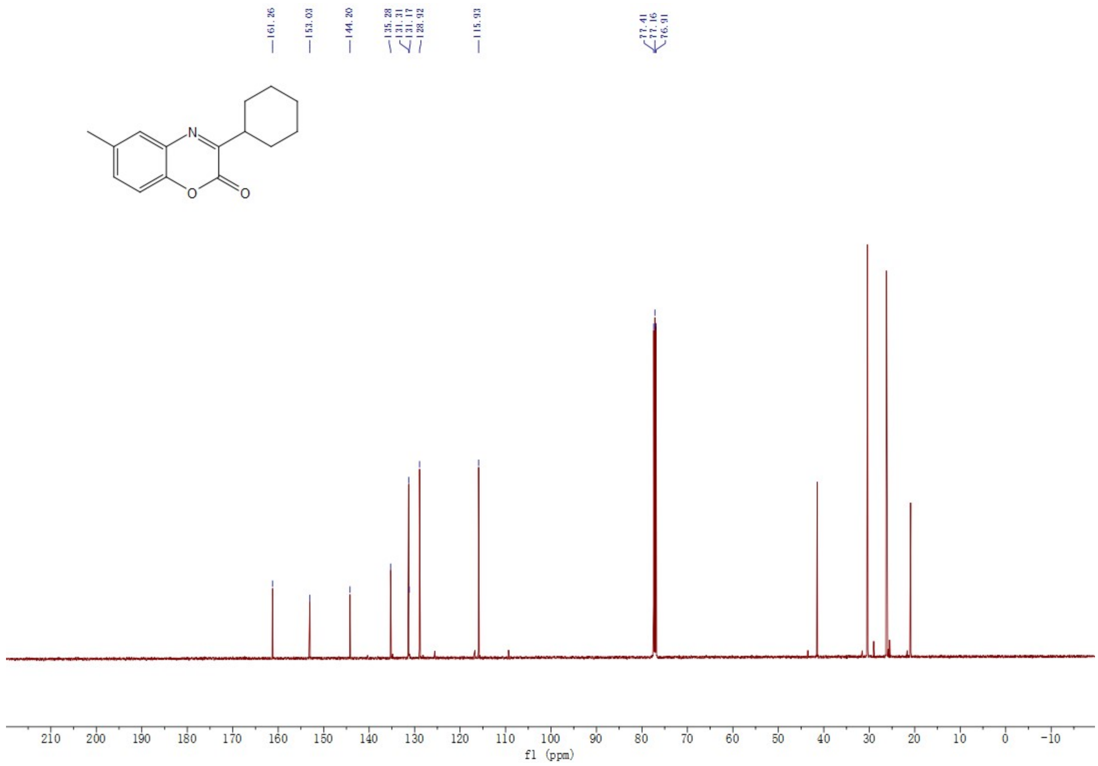
^{1}H NMR (500 MHz, $CDCl_3$) of **3wa**



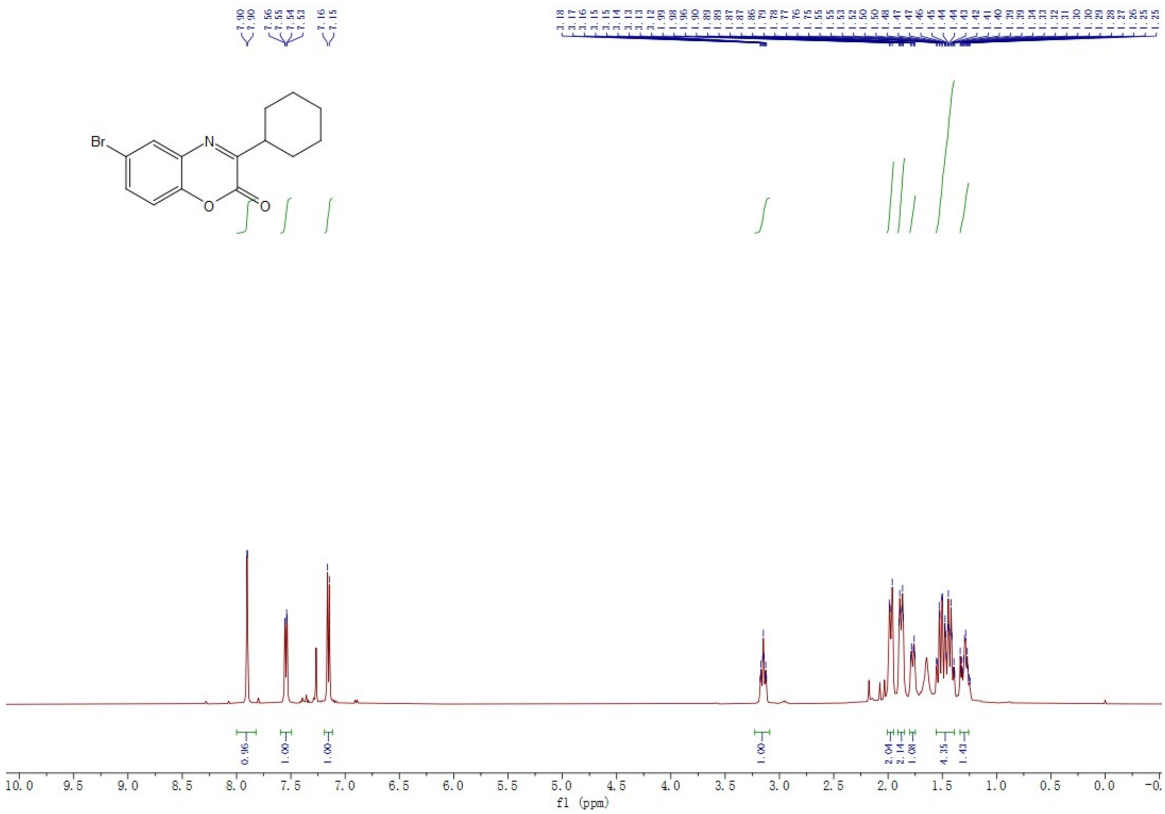
^{13}C NMR (125 MHz, $CDCl_3$) of **3wa**



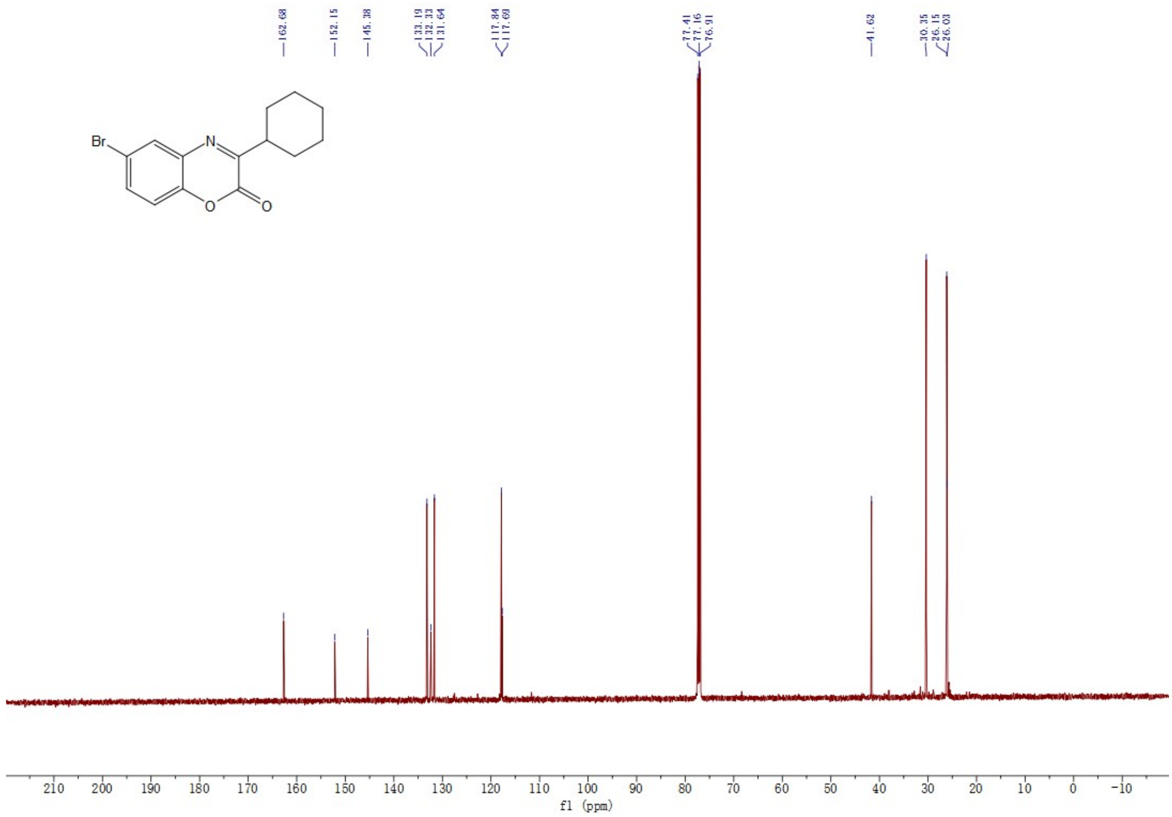
^{1}H NMR (500 MHz, $CDCl_3$) of **3xa**



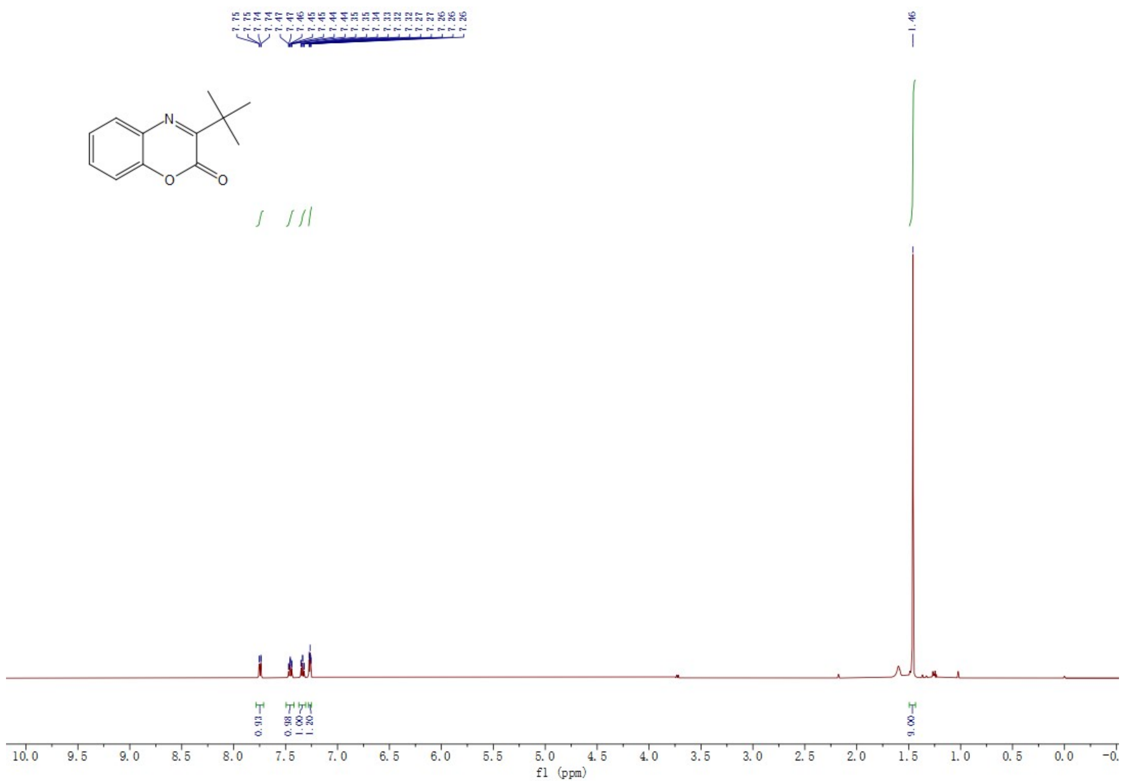
^{13}C NMR (125 MHz, $CDCl_3$) of **3xa**



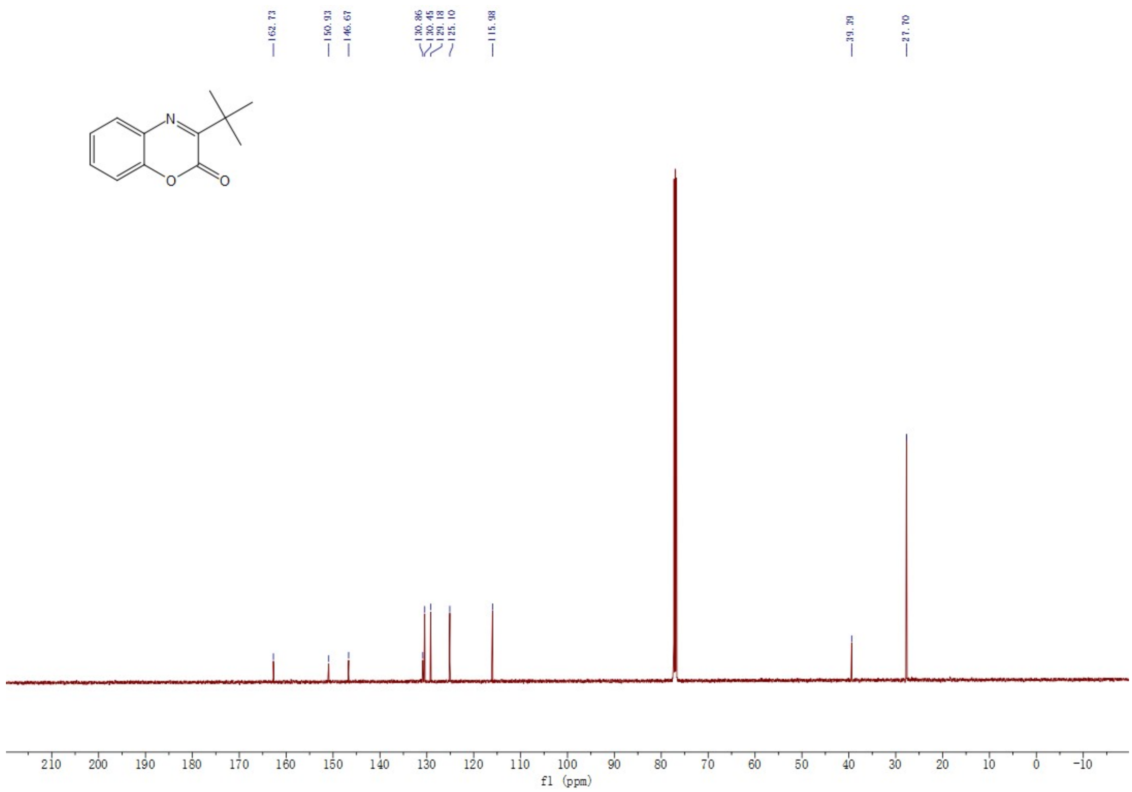
^{1}H NMR (500 MHz, $CDCl_3$) of **3ya**



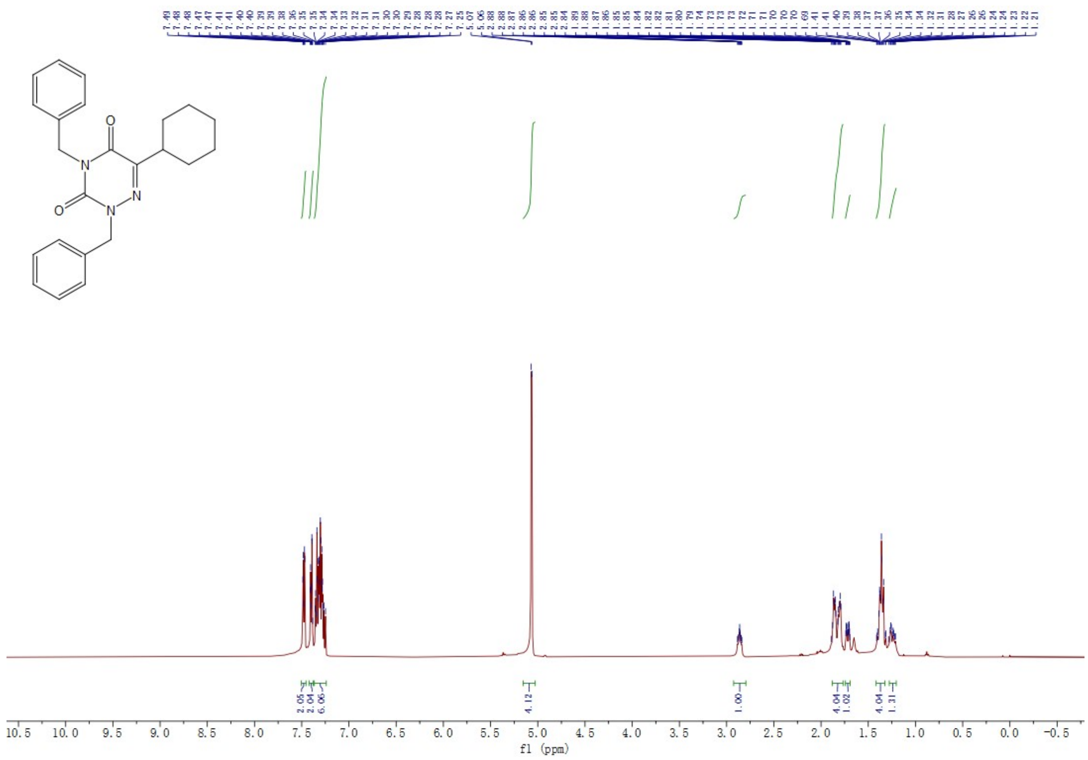
^{13}C NMR (125 MHz, $CDCl_3$) of **3ya**



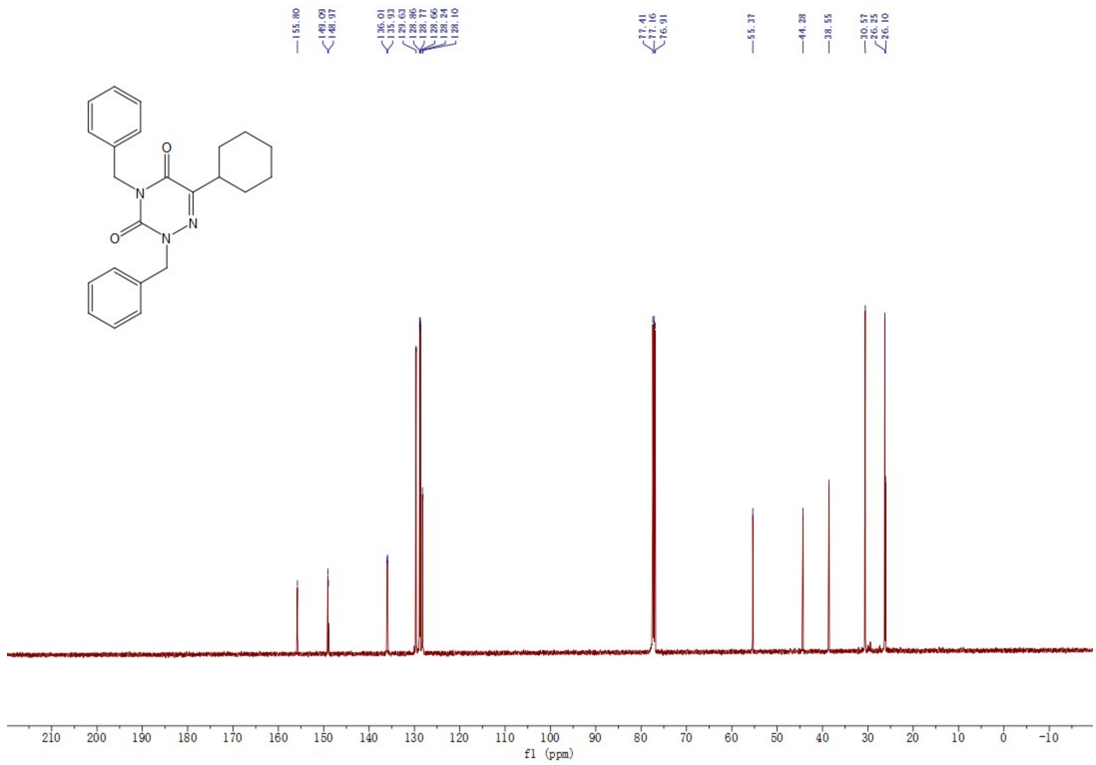
^{1}H NMR (500 MHz, $CDCl_3$) of **3za**



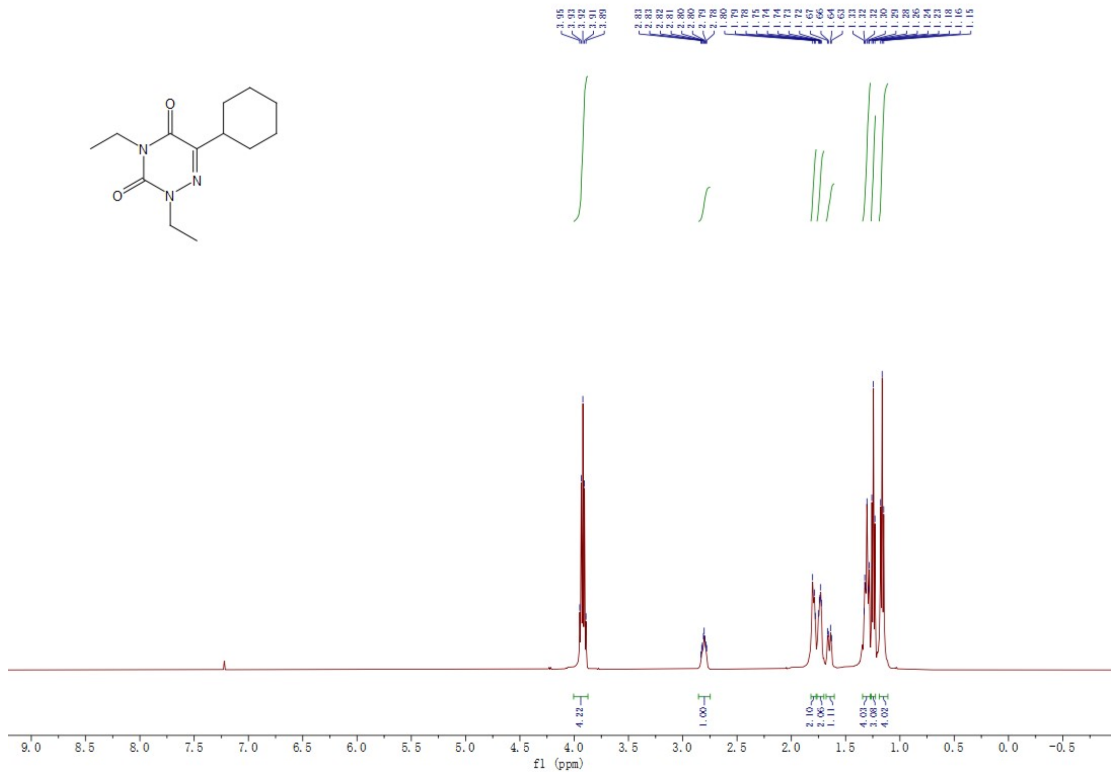
^{13}C NMR (125 MHz, $CDCl_3$) of **3za**



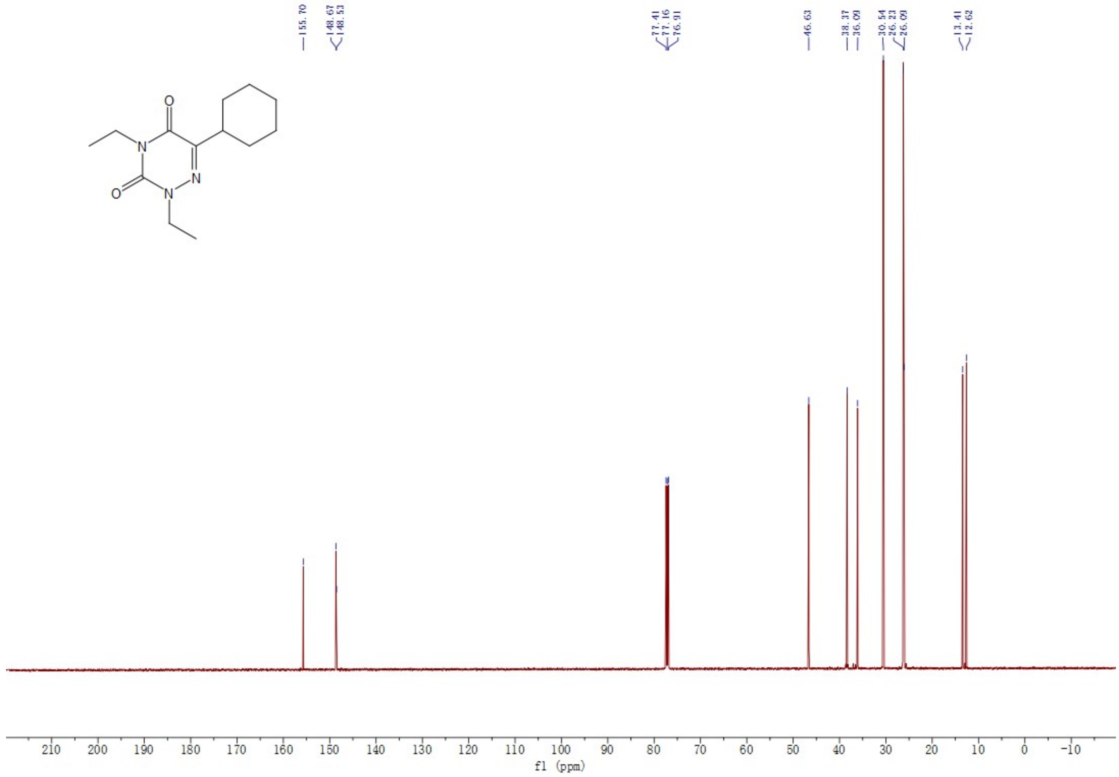
^{1}H NMR (500 MHz, $CDCl_3$) of **3Aa**



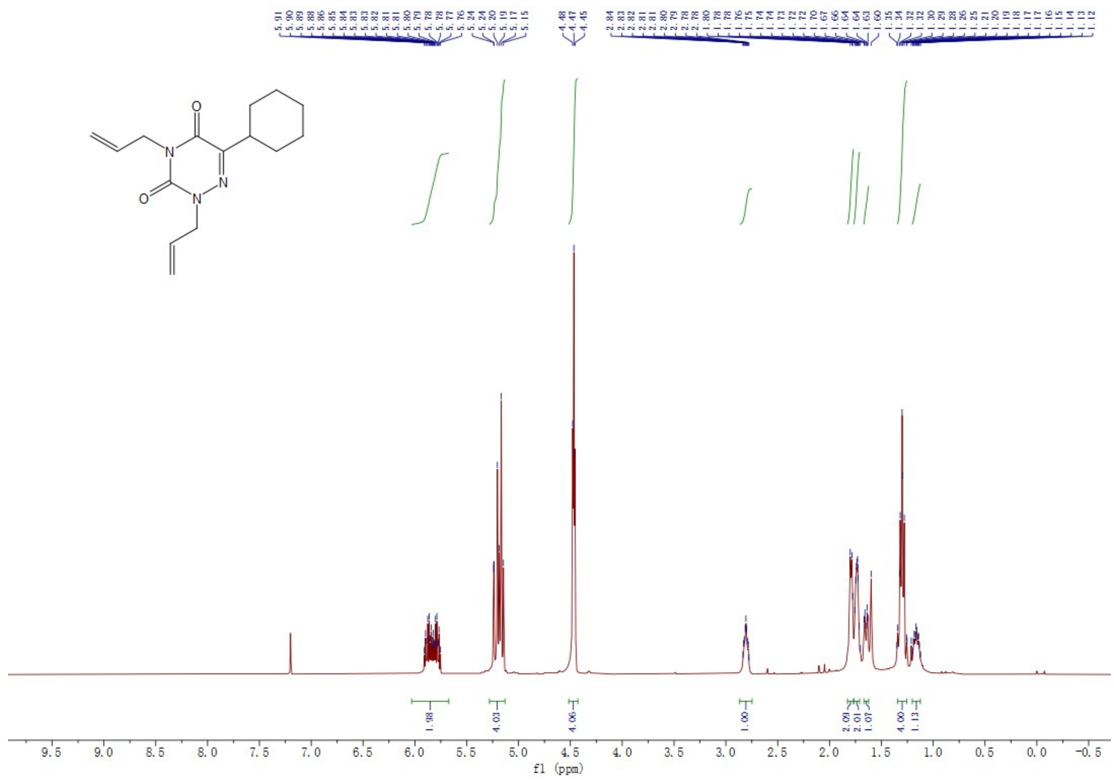
^{13}C NMR (125 MHz, $CDCl_3$) of **3Aa**



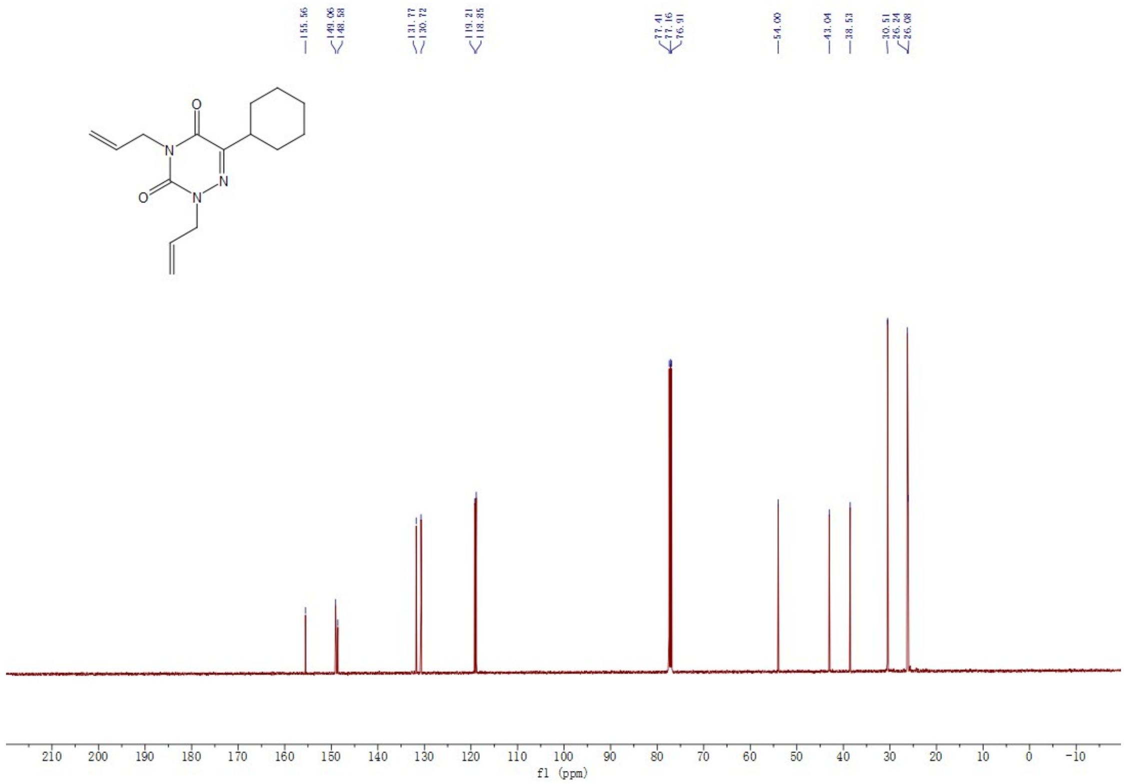
^{1}H NMR (500 MHz, $CDCl_3$) of **3Ba**



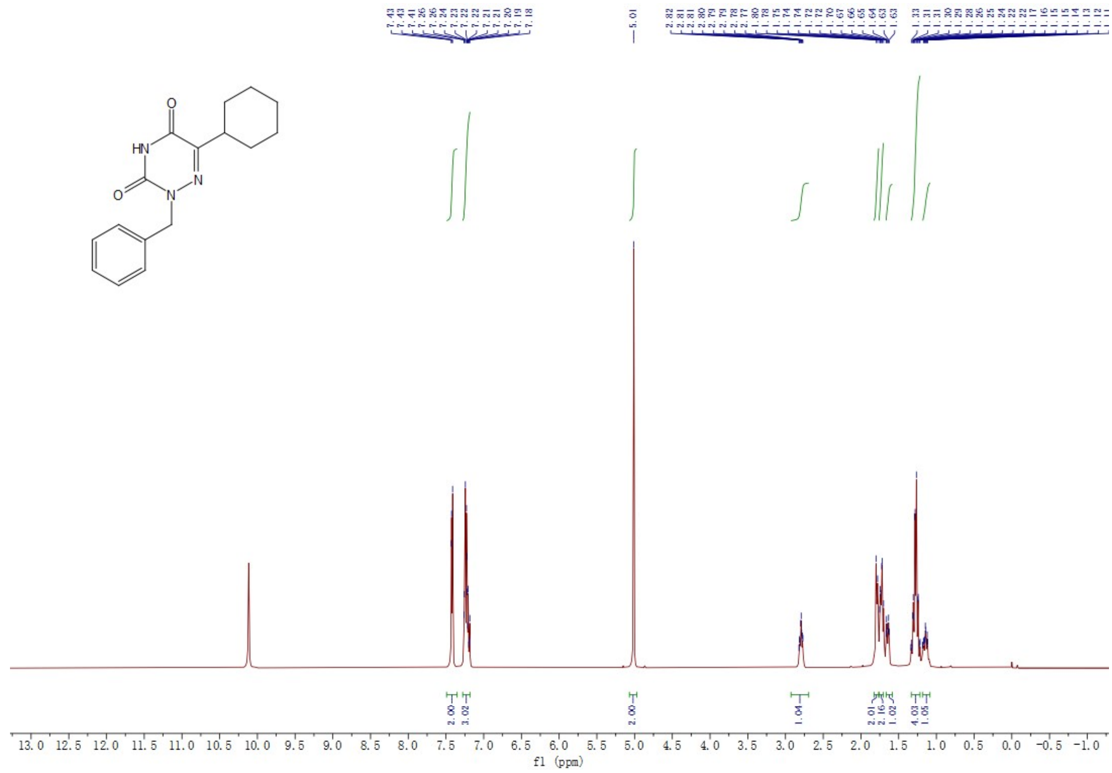
^{13}C NMR (125 MHz, $CDCl_3$) of **3Ba**



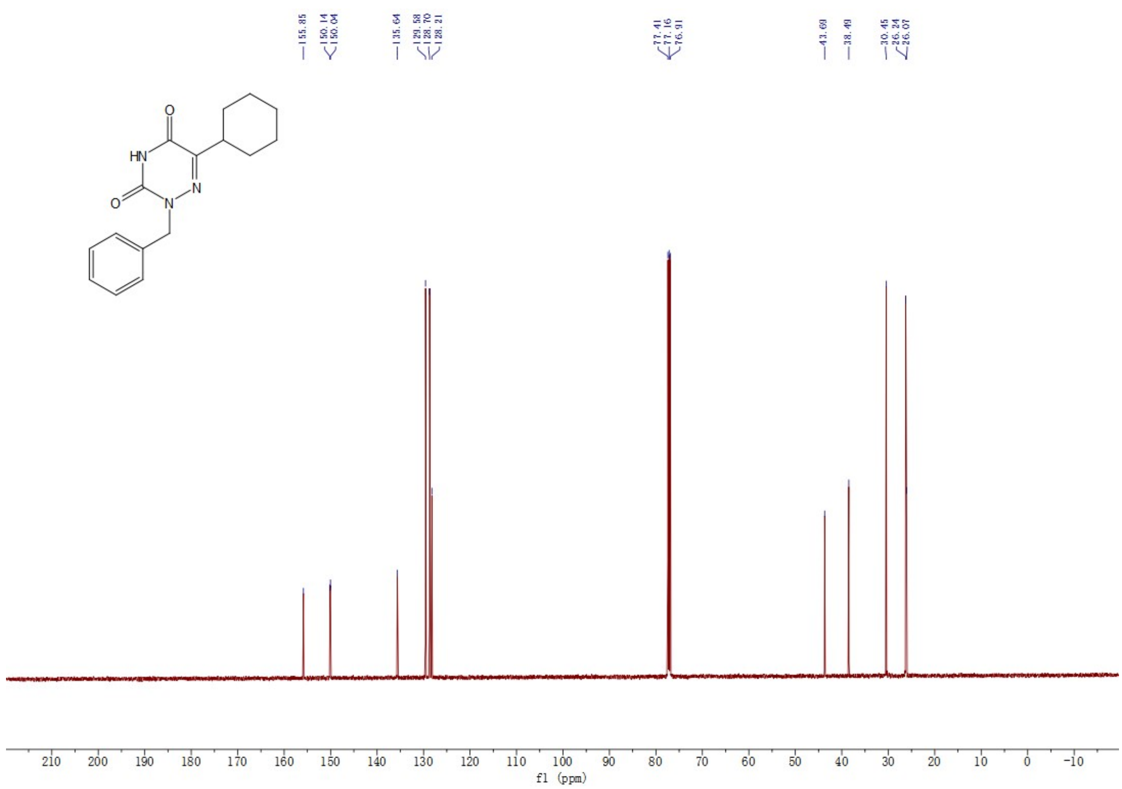
^{1}H NMR (500 MHz, $CDCl_3$) of **3Ca**



^{13}C NMR (125 MHz, $CDCl_3$) of **3Ca**

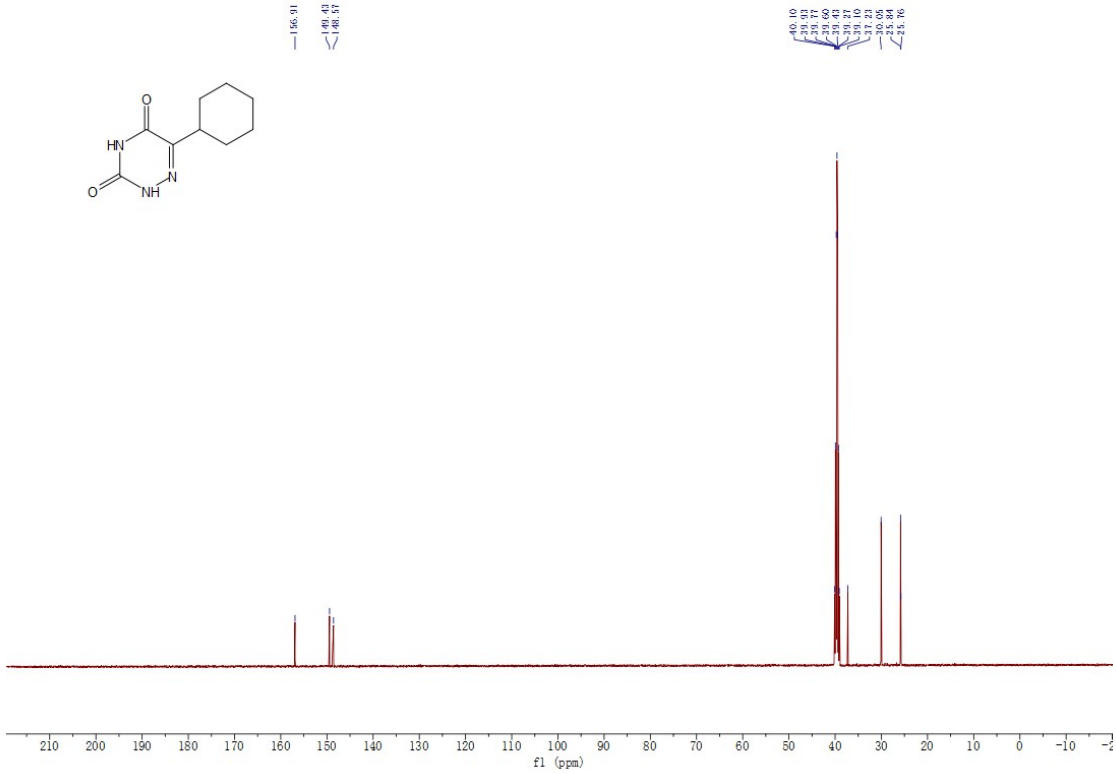


^{1}H NMR (500 MHz, $CDCl_3$) of **3Da**

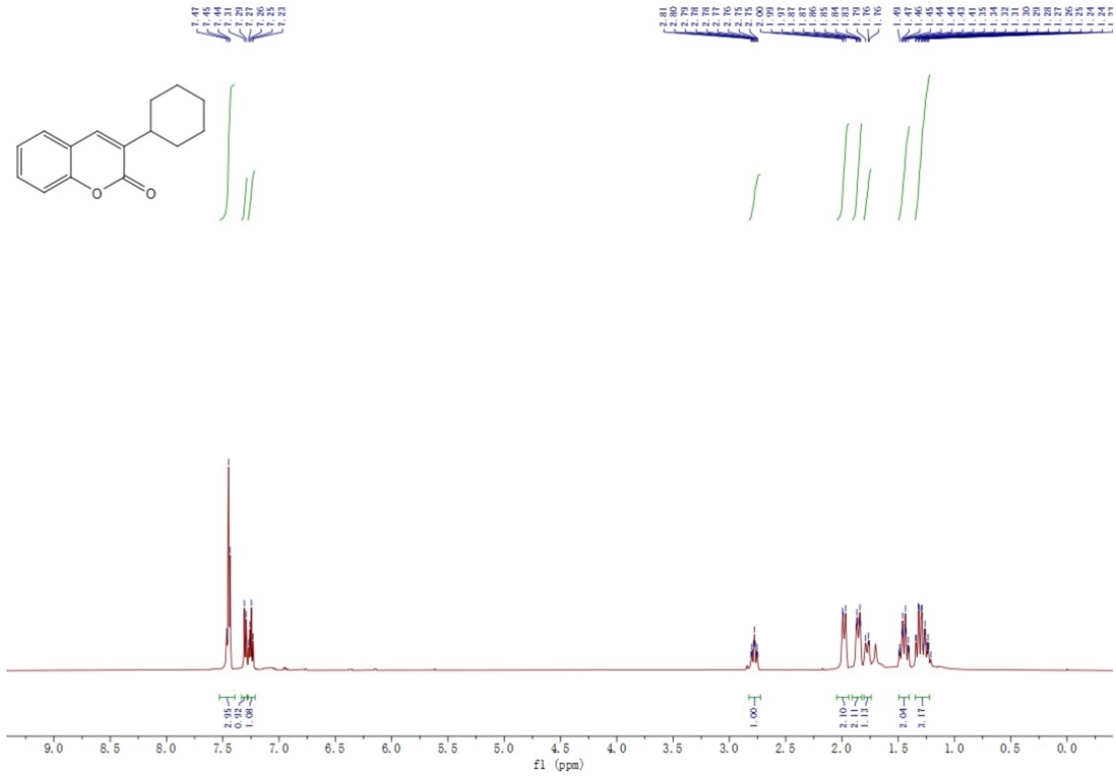


^{13}C NMR (125 MHz, $CDCl_3$) of **3Da**

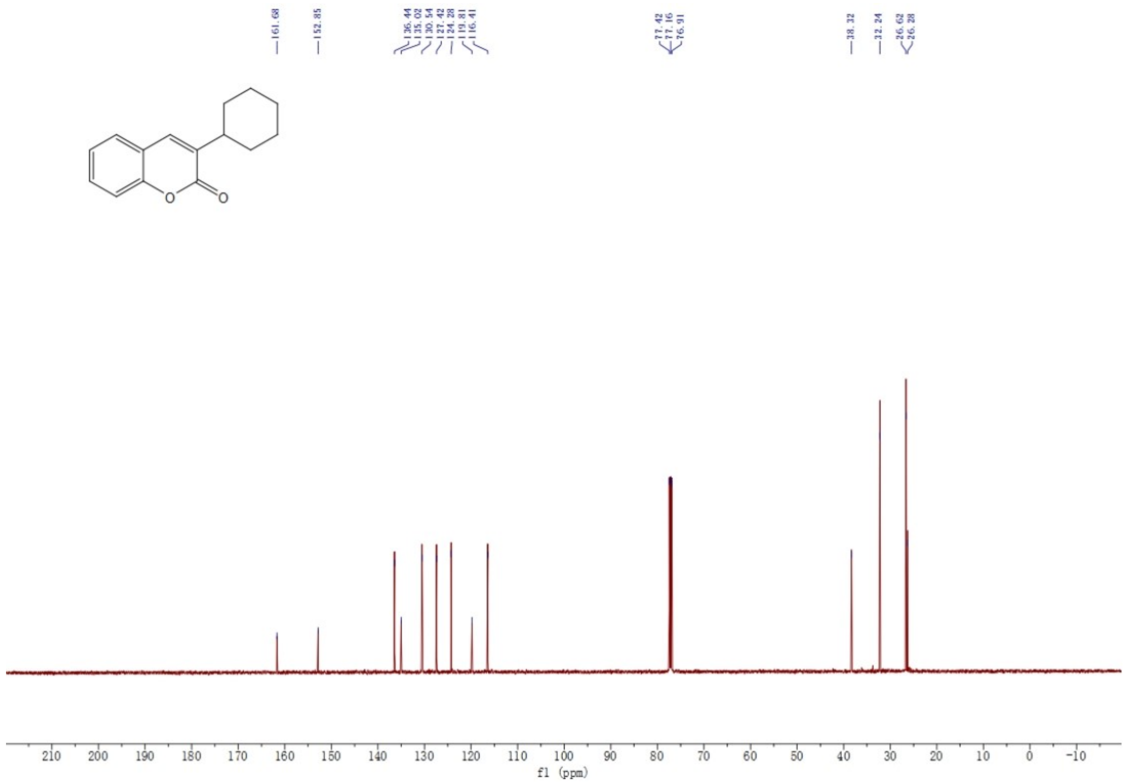
^{1}H NMR (500 MHz, $CDCl_3$) of **3Ea**



^{13}C NMR (125 MHz, $CDCl_3$) of **3Ea**



^{1}H NMR (500 MHz, $CDCl_3$) of **3Fa**



^{13}C NMR (125 MHz, $CDCl_3$) of **3Fa**