Semi-heterogeneous g-C_3N_4/NaI Dual Catalytic C-C Bond Formation under Visible Light

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Table of Content

1. General Information S1

2. General Procedure S3

2.1 Typical Procedure for the Synthesis of 3 ..... S3

2.2 Control Experiments S3

2.3 Procedure for Gram Scale Synthesis of 3aa S4

2.4 Reusability and Stability of Photocatalyst S4

2.5 Effect of Visible Light Irradiation S4

2.6 Calculation of Apparent Quantum Yield S6

3. Characterization Data of Products S6

4. References S14

5. ^{1}H, ^{13}C and ^{19}F NMR Spectra of Products S15

1. General Information

Unless otherwise noted, all reagents and solvents were obtained from commercial suppliers and used without further purification. GC yield was detected by Agilent GC-MS 8890/5977B. ^{1}H NMR spectra were recorded at 500 MHz and ^{13}C NMR spectra were recorded at 125 MHz by using a Bruker Avance 500 spectrometer. ^{19}F NMR data were collected at 471 MHz with complete proton decoupling. 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. Mass spectra were performed on a spectrometer operating on ESI-TOF. UV/vis spectra were recorded using a Shimadzu UV-2600 spectrophotomete. 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.

The Light Source and the Material of the Irradiation Vessel

Manufacturer：Beijing Rogertech Ltd.

Model：RLH-18CU

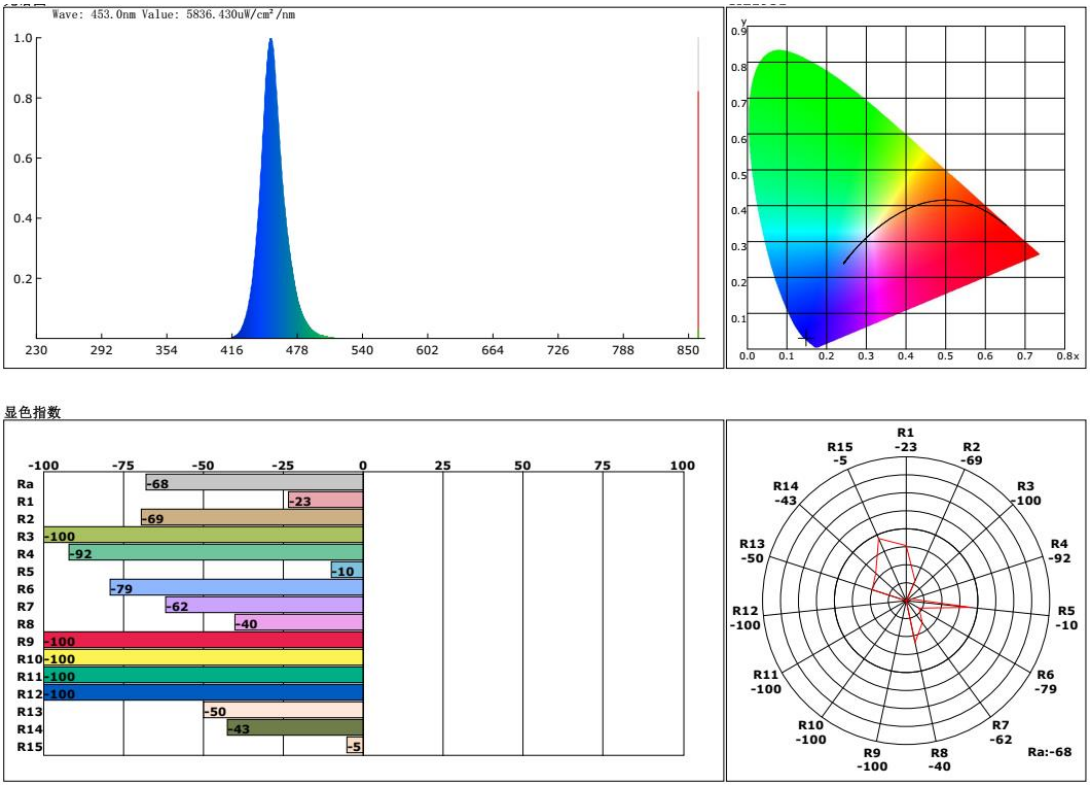
Value: 5836.430 μW/cm²/nm

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

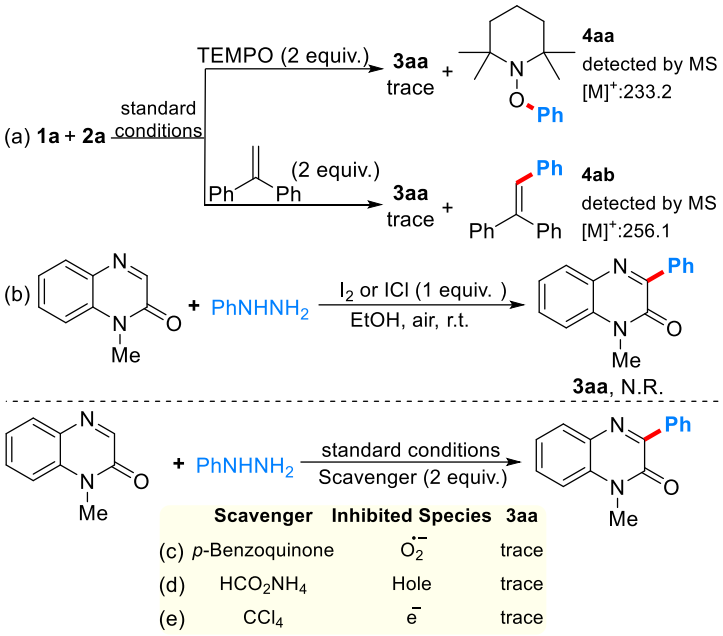
Figure S2. Photo-reactor System

2. General Procedure

2.1 Typical Procedure for the Synthesis of 3

To a 10.0 mL Schlenk flask equipped with a magnetic stirring bar were added quinoxalin-2(1*H*)-ones **1** (0.2 mmol), arylhydrazines **2** (0.4 mmol), g-C_3N_4 (15 mg), NaI (0.001 mmol) and EtOH (3.0 mL). The resulting mixture was charged with air. Then the reaction mixture was stirred and irradiated by 8 W blue LED at ambient temperature for about 30 h. The reaction progress was monitored by thin-layer chromatography analysis. After the completion of the reaction, the insolubles were removed by filtration. The filtrate was evaporated under reduced pressure, which was then purified with chromatography column on silica gel (EtOAc: petroleum ether=5:1) to give the corresponding products **3**.

2.2 Control Experiments



(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), phenylhydrazine **2a** (0.4 mmol), g-C_3N_4 (15 mg), NaI (0.001 mmol), radical scavenger (TEMPO or α,α-diphenylethylene, 0.4 mmol) and EtOH (3.0 mL). Then the reaction mixture was stirred and irradiated by 8 W blue LED at ambient temperature for about 30 h. The reaction mixture was monitored by GC-MS, only trace amount of **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), phenylhydrazine **2a** (0.4 mmol), I_2 (0.2 mmol) or ICl (0.2 mmol) and EtOH (3.0 mL). Then the reaction mixture was stirred at ambient temperature for about 12 h.

(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), phenylhydrazine **2a** (0.4 mmol), g-C_3N_4 (15 mg), NaI (0.001 mmol), *p*-benzoquinone (2.0 mmol) and EtOH (3.0 mL). Then the reaction mixture was stirred and irradiated by 8 W blue LED at ambient temperature for about 30 h. The reaction was monitored by GC-MS, only trace amount of **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), phenylhydrazine **2a** (0.4 mmol), g-C_3N_4 (15 mg), NaI (0.001 mmol), HCO_2NH_4 (2.0 mmol) and EtOH (3.0 mL). Then the reaction mixture was stirred and irradiated by 8 W blue LED at ambient temperature for about 30 h. The reaction was monitored by GC-MS, only trace amount of **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), phenylhydrazine **2a** (0.4 mmol), g-C_3N_4 (15 mg), NaI (0.001 mmol), CCl_4 (2.0 mmol) and EtOH (3.0 mL). Then the reaction mixture was stirred and irradiated by 8 W blue LED at ambient temperature for about 30 h. The reaction was monitored by GC-MS, only trace amount of **3aa** was detected.

2.3 Procedure for Gram Scale Synthesis of 3aa

To a 100 mL round bottom flask equipped with a magnetic stirring bar were added quinoxalin-2(1*H*)-ones **1a** (6 mmol), phenylhydrazine **2a** (12 mmol), g-C_3N_4 (500 mg) NaI (0.034 mmol) and EtOH (50 mL). The resulting mixture was charged with air. Then the reaction mixture was stirred and irradiated by 8 W blue LED at ambient temperature for about 36 h. After the completion of the reaction, the solvent was evaporated under reduced pressure and the residue was purified by HPLC to afford product **3aa** (1.01 g, 72% yield).

2.4 Reusability and Stability of Photocatalyst

The reusability and stability of g-C_3N_4 was tested: In a typical procedure, the mixture of quinoxalin-2(1*H*)-one **1a** (0.2 mmol), phenylhydrazine **2a** (0.4 mmol), NaI (0.001mmol) and g-C_3N_4 (15 mg) were stirred in EtOH (3 mL) irradiated with a 8 W blue LED for 30 h under an air atmosphere at room temperature. After completion of the reaction, the photocatalyst was separated by centrifugation and washed twice with EtOH, then under vacuum removes the residual solvents, and used for next run.

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 (8 W blue LED) followed by stirring in the absence of light. At each time point, one reaction system was suspended and the yield was detected by GC-MS.

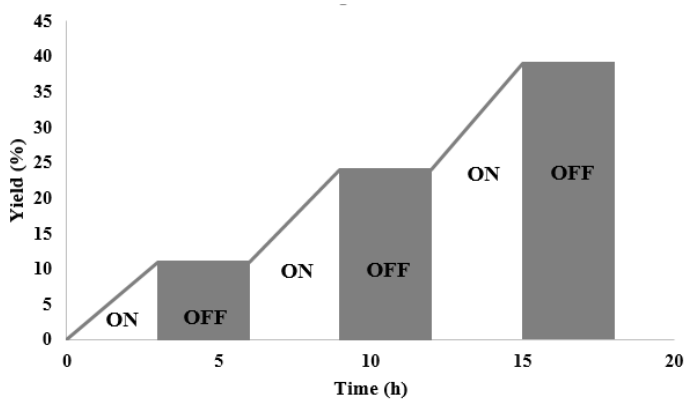


Figure S3: Visible Light Irradiation on/off experiment

2.6 Calculation of Apparent Quantum Yield

$$E_{photon} = \frac{hc}{\lambda_{inc}(455\ nm)} = \frac{6.63x10^{-34}\ J.Sx3x\ 10^{8}\ m.s^{-1}}{455x\ 10^{-9}\ m} = 4.37x10^{-19}\ J$$

$$E_{total}=PSt = 17.47x\ 10^{-3}\ W.cm^{-2}x4.78\ cm^{2}\ x30x3600s = 9.0x10^{3}\ J$$

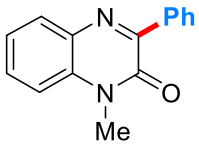
$$\text{Number of incident photons} = \frac{E_{photon}}{E_{tota}} = \frac{9.0x10^{3}\ J}{4.37x10^{-19}\ J} = 2.06x10^{22} = 34.31\ mmol$$

$$A.Q.Y(\%) = \frac{\text{Number of Product}}{\text{Number of incident photons}} = \frac{0.174\ mmol}{34.31\ mmol} = 0.5\% < 1$$

Where h (J·s) is Planck's constant, c ($m \cdot s^{-1}$) is the speed of light and λinc (m) is the wavelength of the incident light. P (W·cm-2) is the power density of the incident light, S (cm^2) is the irradiation area and t (s) is the photoreaction time.

3. Characterization Data of Products

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

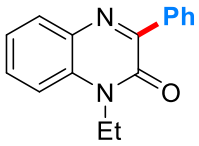


^{1}H NMR (500 MHz, $CDCl_3$) δ 8.38 – 8.23 (m, 2H), 7.95 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.65 – 7.54 (m, 1H), 7.53 – 7.44 (m, 3H), 7.44 – 7.31 (m, 2H), 3.78 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 154.86, 154.33, 136.22, 133.53, 133.26, 130.61, 130.45, 129.68, 128.21, 123.86, 113.71, 29.43.

Melting Point (Experimental): Value: 138-139 °C

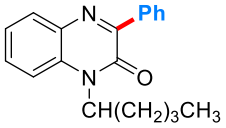
1-ethyl-3-phenylquinoxalin-2(1*H*)-one (3ba)[3]



^{1}H NMR (500 MHz, $CDCl_3$) δ 8.40 – 8.25 (m, 2H), 7.96 (dd, *J* = 8.3, 1.5 Hz, 1H), 7.61 – 7.52 (m, 1H), 7.48 (p, *J* = 3.7 Hz, 3H), 7.36 (dd, *J* = 8.3, 5.8 Hz, 2H), 4.39 (q, *J* = 7.2 Hz, 2H), 1.43 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 154.32, 154.27, 136.19, 133.56, 132.45, 130.87, 130.40, 129.71, 128.18, 123.64, 113.53, 37.71, 12.54.

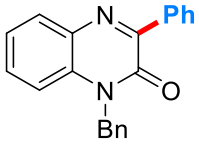
1-pentyl-3-phenylquinoxalin-2(1H)-one (3ca)[3]



^{1}H NMR (500 MHz, $CDCl_3$) δ 8.31 (dd, *J* = 6.7, 3.0 Hz, 2H), 7.96 (d, *J* = 7.9 Hz, 1H), 7.56 (t, *J* = 7.8 Hz, 1H), 7.50 – 7.46 (m, 3H), 7.38 – 7.31 (m, 2H), 4.36 – 4.24 (m, 2H), 1.80 (q, *J* = 7.8 Hz, 2H), 1.45 (dq, *J* = 26.0, 7.7 Hz, 4H), 0.94 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 154.51, 154.27, 136.21, 133.52, 132.69, 130.82, 130.39, 130.35, 129.70, 128.18, 123.63, 113.70, 42.75, 29.30, 27.10, 22.55, 14.11.

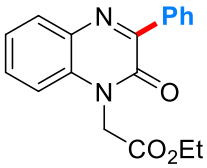
1-benzyl-3-phenylquinoxalin-2(1*H*)-one (3da)[2]



^{1}H NMR (500 MHz, $CDCl_3$) δ 8.33 – 8.25 (m, 2H), 7.87 (d, *J* = 8.0 Hz, 1H), 7.41 (d, *J* = 4.6 Hz, 3H), 7.35 (t, *J* = 7.7 Hz, 1H), 7.28 – 7.13 (m, 7H), 5.48 (s, 2H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 154.89, 154.32, 136.11, 135.46, 133.47, 132.83, 130.68, 130.55, 130.43, 129.75, 129.04, 128.23, 127.80, 127.08, 123.91, 114.46, 46.23.

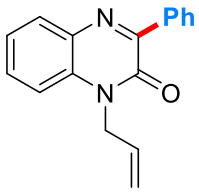
ethyl 2-(2-oxo-3-phenylquinoxalin-1(2*H*)-yl)acetate (3ea)[3]



^{1}H NMR (500 MHz, $CDCl_3$) δ 8.33 (dd, *J* = 6.8, 3.3 Hz, 2H), 7.97 (d, *J* = 7.9 Hz, 1H), 7.57 – 7.45 (m, 4H), 7.37 (t, *J* = 7.7 Hz, 1H), 7.10 (d, *J* = 8.4 Hz, 1H), 5.09 (s, 2H), 4.27 (q, *J* = 7.0 Hz, 2H), 1.29 (t, *J* = 6.9 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 167.29, 154.40, 153.98, 135.84, 133.29, 132.64, 130.89, 130.59, 130.58, 129.69, 128.20, 124.14, 113.14, 62.19, 43.88, 14.24.

1-allyl-3-phenylquinoxalin-2(1*H*)-one (3fa)[3]

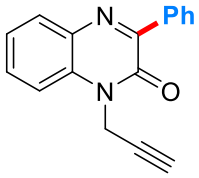


^{1}H NMR (500 MHz, $CDCl_3$) δ 8.34 (dd, *J* = 6.7, 3.1 Hz, 2H), 7.96 (d, *J* = 7.9 Hz, 1H), 7.53 (t, *J* = 7.8 Hz, 1H), 7.53 – 7.44 (m, 3H), 7.36 (t, *J* = 7.6 Hz, 1H), 7.31 (d, *J* = 8.5 Hz, 1H), 6.07 – 5.92 (m, 1H), 5.29 (d, *J* = 10.2 Hz, 1H), 5.22 (d, *J* = 17.2 Hz, 1H), 4.97 (d, *J* = 5.2 Hz, 2H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 154.35, 154.20, 136.06, 133.36, 132.68, 130.76, 130.64, 130.47, 130.34, 129.70, 128.17, 123.82, 118.26, 114.21, 44.84.

Melting Point (Experimental): Value: 98 °C

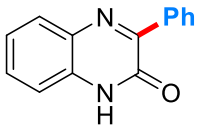
3-phenyl-1-(prop-2-yn-1-yl)quinoxalin-2(1*H*)-one (3ga)[3]



^{1}H NMR (500 MHz, $CDCl_3$) δ 8.32 (dd, *J* = 6.6, 3.0 Hz, 2H), 7.96 (d, *J* = 8.0 Hz, 1H), 7.60 (t, *J* = 7.7 Hz, 1H), 7.54 – 7.46 (m, 4H), 7.40 (t, *J* = 7.6 Hz, 1H), 5.12 (d, *J* = 2.6 Hz, 2H), 2.32 (d, *J* = 2.7 Hz, 1H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 154.09, 153.81, 135.86, 133.40, 131.95, 130.71, 130.62, 130.54, 129.69, 128.22, 124.24, 114.16, 77.03, 73.27, 31.78.

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

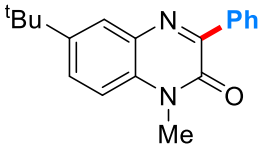


^{1}H NMR (500 MHz, DMSO-d_6) δ 12.59 (s, 1H), 8.44 – 8.21 (m, 2H), 7.95 – 7.84 (m, 1H), 7.60 – 7.47 (m, 4H), 7.34 (t, J = 8.0 Hz, 2H).

^{13}C NMR (125 MHz, DMSO-d_6) δ 154.68, 154.26, 135.68, 132.12, 130.44, 130.31, 129.28, 128.86, 127.96, 123.52, 115.18.

Melting Point (Experimental): Value: 243 °C

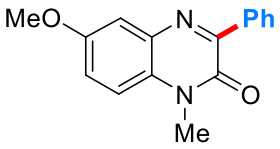
6-(tert-butyl)-1-methyl-3-phenylquinoxalin-2(1*H*)-one (3ia)



^{1}H NMR (500 MHz, $CDCl_3$) δ 8.36 – 8.24 (m, 2H), 7.96 (q, J = 1.8 Hz, 1H), 7.63 (dq, J = 8.9, 1.8 Hz, 1H), 7.52 – 7.42 (m, 3H), 7.36 – 7.22 (m, 3H), 3.76 (s, 3H), 1.41 (s, 9H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 154.84, 154.26, 147.19, 136.35, 132.93, 131.18, 130.29, 129.59, 128.25, 128.19, 126.95, 113.36, 34.60, 31.44, 29.38.

6-methoxy-1-methyl-3-phenylquinoxalin-2(1*H*)-one (3ja)[3]

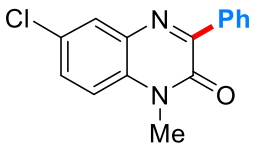


^{1}H NMR (500 MHz, $CDCl_3$) δ 8.25 – 8.16 (m, 1H), 7.42 – 7.35 (m, 2H), 7.31 (d, J = 2.8 Hz, 1H), 7.14 (d, J = 9.1 Hz, 1H), 7.09 (dd, J = 9.1, 2.8 Hz, 1H), 3.80 (s, 2H), 3.65 (s, 1H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 156.12, 154.63, 154.45, 136.27, 133.89, 130.38, 129.63, 128.15, 127.77, 119.79, 114.58, 111.65, 55.86, 29.51.

Melting Point (Experimental): Value: 153-154 °C

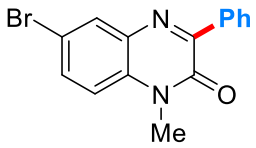
6-chloro-1-methyl-3-phenylquinoxalin-2(1*H*)-one (3ka)[3]



^{1}H NMR (500 MHz, $CDCl_3$) δ 8.36 – 8.25 (m, 2H), 7.90 (d, J = 2.3 Hz, 1H), 7.54 – 7.42 (m, 4H), 7.22 (d, J = 8.9 Hz, 1H), 3.71 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 155.17, 154.42, 135.72, 133.64, 132.11, 130.81, 130.28, 129.74, 129.68, 129.06, 128.20, 114.81, 29.56.

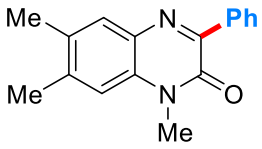
6-bromo-1-methyl-3-phenylquinoxalin-2(1*H*)-one (3la)[3]



^{1}H NMR (500 MHz, $CDCl_3$) δ 8.35 – 8.24 (m, 2H), 8.07 (t, *J* = 1.7 Hz, 1H), 7.65 – 7.60 (m, 1H), 7.48 (d, *J* = 6.6 Hz, 3H), 7.18 (d, *J* = 8.8 Hz, 1H), 3.72 (s, 2H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 155.17, 154.45, 135.72, 133.99, 133.04, 132.80, 132.57, 130.85, 129.76, 128.23, 116.35, 115.12, 29.57.

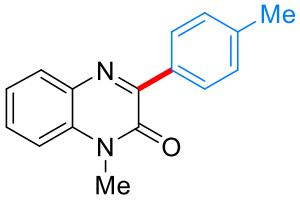
1,6,7-trimethyl-3-phenylquinoxalin-2(1H)-one (3ma)[2]



^{1}H NMR (500 MHz, $CDCl_3$) δ 8.21 (dd, *J* = 6.4, 2.6 Hz, 2H), 7.60 (s, 1H), 7.38 (dd, *J* = 5.5, 1.9 Hz, 3H), 6.99 (s, 1H), 3.64 (s, 3H), 2.34 (s, 3H), 2.27 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 154.89, 153.00, 140.42, 136.48, 132.78, 131.67, 131.52, 130.57, 130.08, 129.55, 128.11, 114.24, 29.30, 20.74, 19.31.

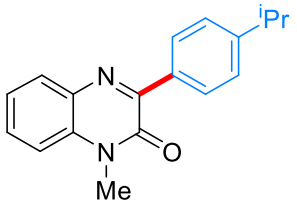
1-methyl-3-(p-tolyl)quinoxalin-2(1*H*)-one (3ab)[2]



^{1}H NMR (500 MHz, $CDCl_3$) δ 8.24 (d, *J* = 7.9 Hz, 2H), 7.93 (d, *J* = 8.0 Hz, 1H), 7.55 (t, *J* = 7.8 Hz, 1H), 7.38 – 7.31 (m, 2H), 7.29 (d, *J* = 7.9 Hz, 2H), 3.77 (s, 3H), 2.42 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 154.92, 154.20, 140.77, 133.46, 133.30, 130.49, 130.46, 130.19, 129.67, 129.64, 128.98, 128.94, 123.81, 113.68, 29.42, 21.67.

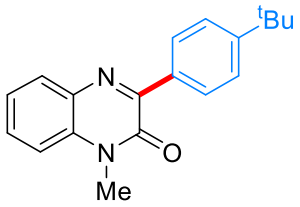
3-(4-isopropylphenyl)-1-methylquinoxalin-2(1*H*)-one (3ac)[3]



^{1}H NMR (500 MHz, $CDCl_3$) δ 8.23 (d, *J* = 8.0 Hz, 2H), 7.94 (d, *J* = 8.1 Hz, 1H), 7.56 (t, *J* = 7.9 Hz, 1H), 7.35 (q, *J* = 6.8, 5.8 Hz, 4H), 3.78 (s, 3H), 2.97 (h, *J* = 7.0 Hz, 1H), 1.29 (d, *J* = 7.1 Hz, 6H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 154.93, 154.38, 151.59, 133.85, 133.43, 133.33, 130.49, 130.19, 129.71, 125.40, 123.81, 113.68, 34.31, 29.43, 23.98.

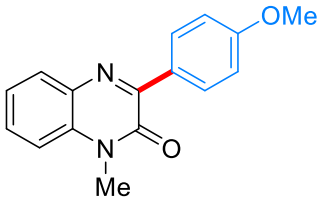
3-(4-(tert-butyl)phenyl)-1-methylquinoxalin-2(1*H*)-one (3ad)[1]



^{1}H NMR (500 MHz, $CDCl_3$) δ 8.24 (d, *J* = 8.2 Hz, 2H), 8.06 – 7.89 (m, 1H), 7.68 – 7.47 (m, 3H), 7.46 – 7.29 (m, 2H), 3.77 (s, 3H), 1.37 (s, 9H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 154.90, 154.33, 153.73, 133.45, 133.41, 133.32, 130.48, 130.17, 129.39, 125.25, 123.77, 113.66, 34.98, 31.34, 29.40.

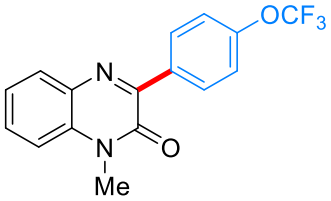
3-(4-methoxyphenyl)-1-methylquinoxalin-2(1*H*)-one (3ae)[2]



^{1}H NMR (500 MHz, $CDCl_3$) δ 8.32 (d, *J* = 8.5 Hz, 2H), 7.84 (dd, *J* = 7.9, 1.5 Hz, 1H), 7.51 – 7.43 (m, 1H), 7.33 – 7.23 (m, 2H), 6.92 (d, *J* = 8.6 Hz, 2H), 3.81 (s, 3H), 3.69 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 161.63, 155.00, 153.37, 133.33, 133.28, 131.51, 130.29, 129.90, 128.91, 123.80, 113.64, 113.62, 55.52, 29.41.

1-methyl-3-(4-(trifluoromethoxy)phenyl)quinoxalin-2(1*H*)-one (3af)[3]

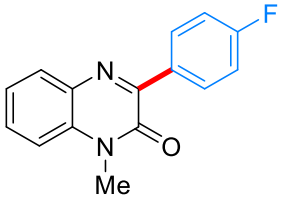


^{1}H NMR (500 MHz, $CDCl_3$) δ 8.46 (d, *J* = 8.1 Hz, 2H), 7.96 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.73 (d, *J* = 8.1 Hz, 2H), 7.65 – 7.57 (m, 1H), 7.44 – 7.36 (m, 2H), 3.79 (s, 3H).

^{13}C NMR (125 MHz, CDCl3) δ 154.70, 152.74, 139.43, 133.65, 133.12, 131.92 (*J* = 125.0 Hz) 131.20, 130.89, 130.03, 125.09 (*J* = 32.5 Hz) 124.15, 113.86, 29.52.

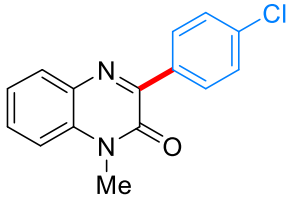
^{19}F NMR (471 MHz, $CDCl_3$) δ -62.79.

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



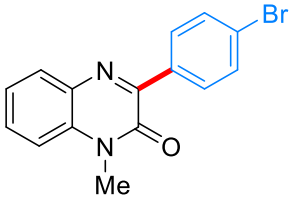
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.39 (dd, *J* = 8.5, 5.6 Hz, 2H), 7.93 (d, *J* = 8.0 Hz, 1H), 7.58 (t, *J* = 7.8 Hz, 1H), 7.41 – 7.32 (m, 2H), 7.16 (t, *J* = 8.5 Hz, 2H), 3.77 (s, 3H).
^{13}C NMR (125 MHz, CDCl3) δ 164.22 (*J* = 17.5 Hz), 154.69, 152.79, 133.33, 133.03, 132.20 (*J* = 7.5 Hz), 131.85 (*J* = 17.5 Hz), 130.41 (*J* = 7.5 Hz), 123.84, 115.16 114.99, 113.62, 29.34.
^{19}F NMR (471 MHz, $CDCl_3$) δ -110.01 (d, *J* = 7.9 Hz).

3-(4-chlorophenyl)-1-methylquinoxalin-2(1*H*)-one (3ah)[1]



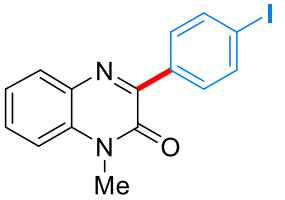
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.43 – 8.26 (m, 2H), 7.94 (d, *J* = 8.0 Hz, 1H), 7.59 (t, *J* = 7.8 Hz, 1H), 7.51 – 7.43 (m, 2H), 7.43 – 7.31 (m, 2H), 3.84 – 3.72 (m, 3H).
^{13}C NMR (125 MHz, $CDCl_3$) δ 154.77, 152.85, 136.69, 134.56, 133.49, 133.15, 131.12, 130.75, 130.64, 128.45, 124.06, 113.80, 29.51.

3-(4-bromophenyl)-1-methylquinoxalin-2(1*H*)-one (3ai)[3]



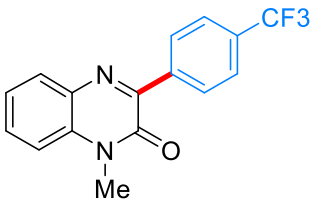
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.33 – 8.22 (m, 2H), 7.94 (dd, *J* = 7.9, 1.5 Hz, 1H), 7.65 – 7.56 (m, 3H), 7.44 – 7.32 (m, 2H), 3.77 (s, 3H).
^{13}C NMR (125 MHz, $CDCl_3$) δ 154.73, 152.91, 135.03, 133.53, 133.16, 131.41, 131.35, 130.77, 130.67, 125.25, 124.04, 113.79, 29.49.

3-(4-iodophenyl)-1-methylquinoxalin-2(1*H*)-one (3aj)[3]



^{1}H NMR (500 MHz, $CDCl_3$) δ 8.17 – 8.06 (m, 2H), 7.93 (dd, *J* = 8.1, 1.7 Hz, 1H), 7.85 – 7.78 (m, 2H), 7.64 – 7.55 (m, 1H), 7.42 – 7.30 (m, 2H), 3.77 (s, 2H).
^{13}C NMR (125 MHz, $CDCl_3$) δ 154.67, 137.38, 135.61, 133.50, 133.13, 131.37, 130.78, 130.66, 129.67, 124.02, 113.78, 97.57, 29.47.

1-methyl-3-(4-(trifluoromethyl)phenyl)quinoxalin-2(1*H*)-one (3ak)[2]

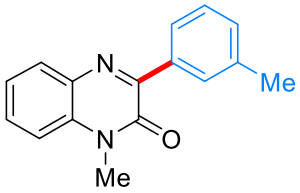


^{1}H NMR (471 MHz, $CDCl_3$) δ 8.41 (d, *J* = 8.5 Hz, 2H), 7.94 (dd, *J* = 7.9, 1.4 Hz, 1H), 7.74 – 7.56 (m, 1H), 7.42 – 7.34 (m, 2H), 7.32 (d, *J* = 8.4 Hz, 2H), 3.78 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 154.76, 152.69, 150.84, 134.68, 133.55, 133.14, 131.48, 130.83, 130.69, 124.06, 120.61 (d, *J* = 255 Hz), 120.37, 113.81, 29.50.

^{19}F NMR (500 MHz, $CDCl_3$) δ -57.57.

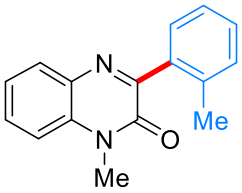
1-methyl-3-(m-tolyl)quinoxalin-2(1*H*)-one (3al)[2]



^{1}H NMR (500 MHz, $CDCl_3$) δ 8.09 (t, *J* = 3.3 Hz, 2H), 7.95 (d, *J* = 8.0 Hz, 1H), 7.57 (t, *J* = 7.8 Hz, 1H), 7.40 – 7.28 (m, 3H), 3.77 (s, 3H), 2.45 (s, 3H).

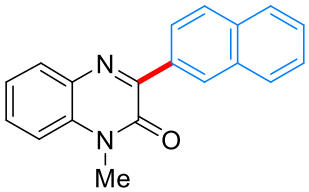
^{13}C NMR (125 MHz, $CDCl_3$) δ 154.88, 154.59, 137.79, 136.15, 133.48, 133.26, 131.28, 130.56, 130.36, 130.12, 128.12, 126.88, 123.83, 113.69, 29.42, 21.69.

1-methyl-3-(o-tolyl)quinoxalin-2(1*H*)-one (3am)[2]



^{1}H NMR (500 MHz, $CDCl_3$) δ 7.94 (d, *J* = 7.9 Hz, 1H), 7.61 (t, *J* = 7.7 Hz, 1H), 7.46 (d, *J* = 7.4 Hz, 1H), 7.41 – 7.33 (m, 3H), 7.30 (d, *J* = 7.2 Hz, 2H), 3.78 (s, 3H), 2.35 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 158.54, 154.69, 136.96, 136.25, 133.71, 133.01, 130.68, 130.66, 130.57, 129.46, 129.30, 125.73, 123.87, 113.82, 29.50, 20.06.

1-methyl-3-(naphthalen-2-yl)quinoxalin-2(1*H*)-one (3an)[3]



^{1}H NMR (500 MHz, $CDCl_3$) δ 9.08 (s, 1H), 8.48 – 8.36 (m, 1H), 7.99 (d, *J* = 7.9 Hz, 2H), 7.93 (d, *J* = 8.7 Hz, 1H), 7.87 (d, *J* = 7.7 Hz, 1H), 7.63 – 7.47 (m, 3H), 7.40 (t, *J* = 7.6 Hz, 1H), 7.35 (d, *J* = 8.4 Hz, 1H), 3.80 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 155.02, 153.61, 134.39, 133.48, 133.41, 133.31, 133.07, 130.69, 130.60, 130.47, 129.53, 127.72, 127.67, 127.36, 126.26, 126.23, 123.92, 113.73, 29.46.

4. References

[1] S. J. Song, X. J. Shi, Y. S. Zhu, Q. L. Ren, P. Zhou, J. D. Zhou and J. J. Li, *J. Org. Chem.*, 2022, **7**, 4764 - 4776.

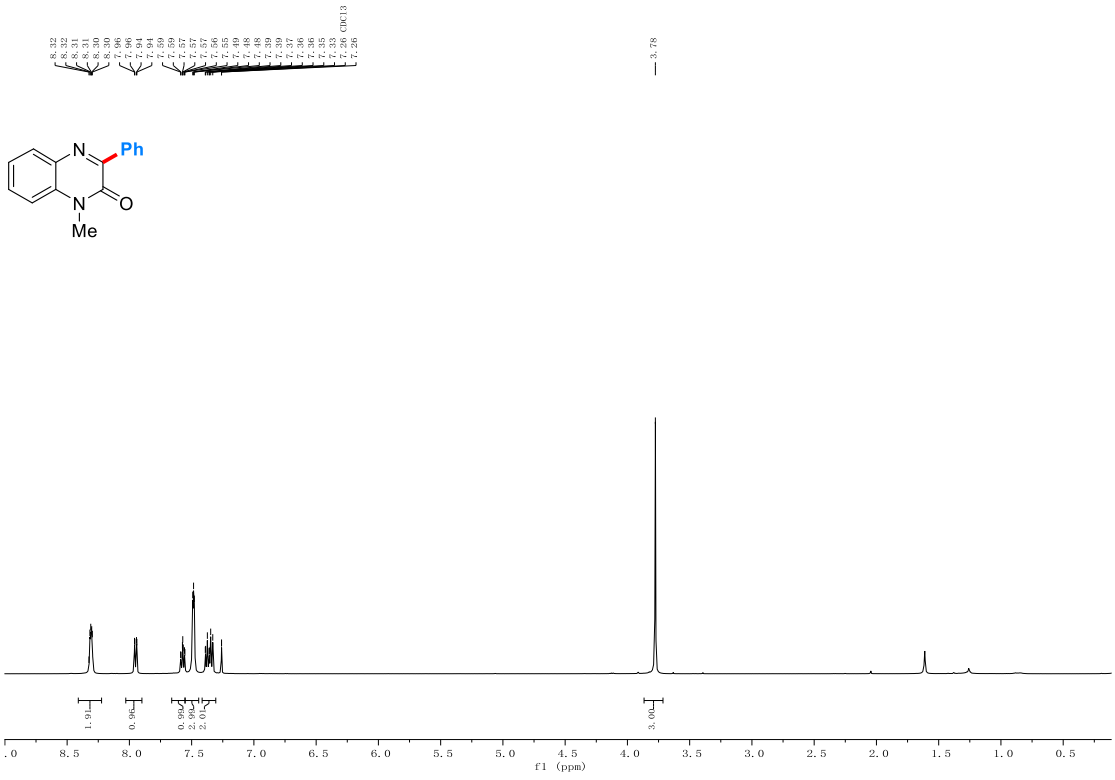
[2] M. Tian, S. Y. Liu, X. B. Bu, J. P. Yu, and X. B. Yang, *Chem. Eur. J.* 2020, **26**, 369.

[3] L. Y. Xie, S. Peng, L. H. Yang, C. Peng, Y. W. Lin, X. Y. Yu, Z. Cao, Y. Y. Peng and W. M. He *Green Chem.*, 2021, **23**, 374 - 378.

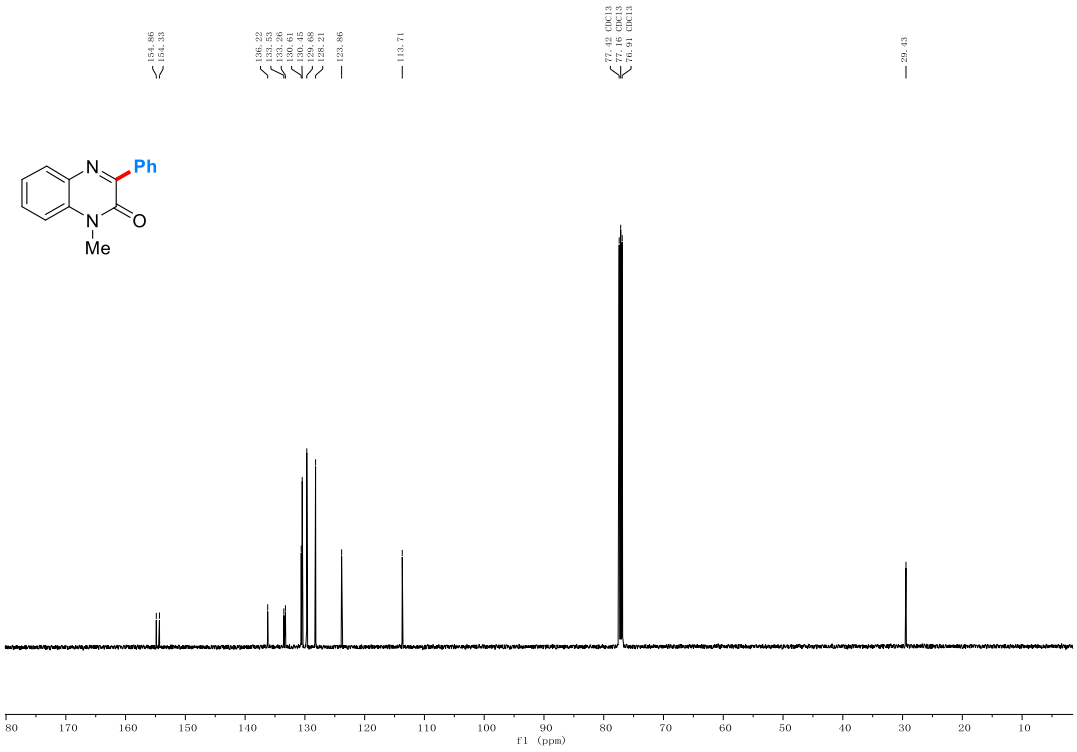
5. ^{1}H, ^{13}C and ^{19}F NMR Spectra of Products

1-methyl-3-phenylquinoxalin-2(1*H*)-one (3aa)

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

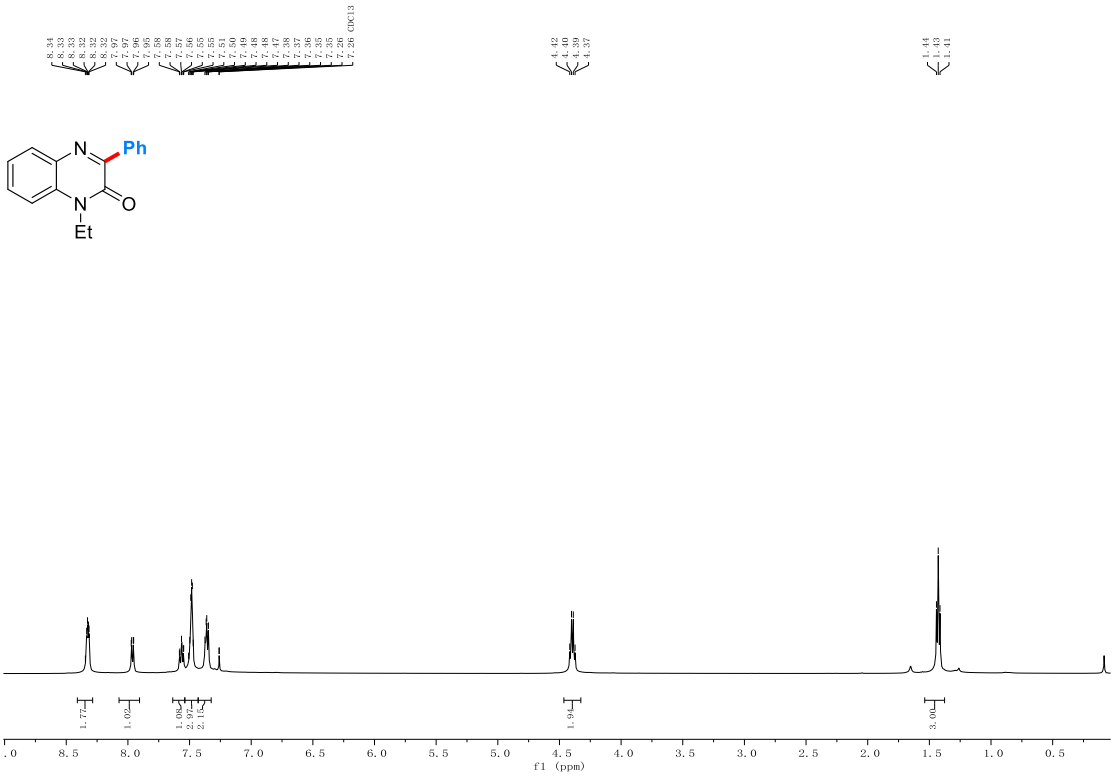


^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) spectrum of **3aa**

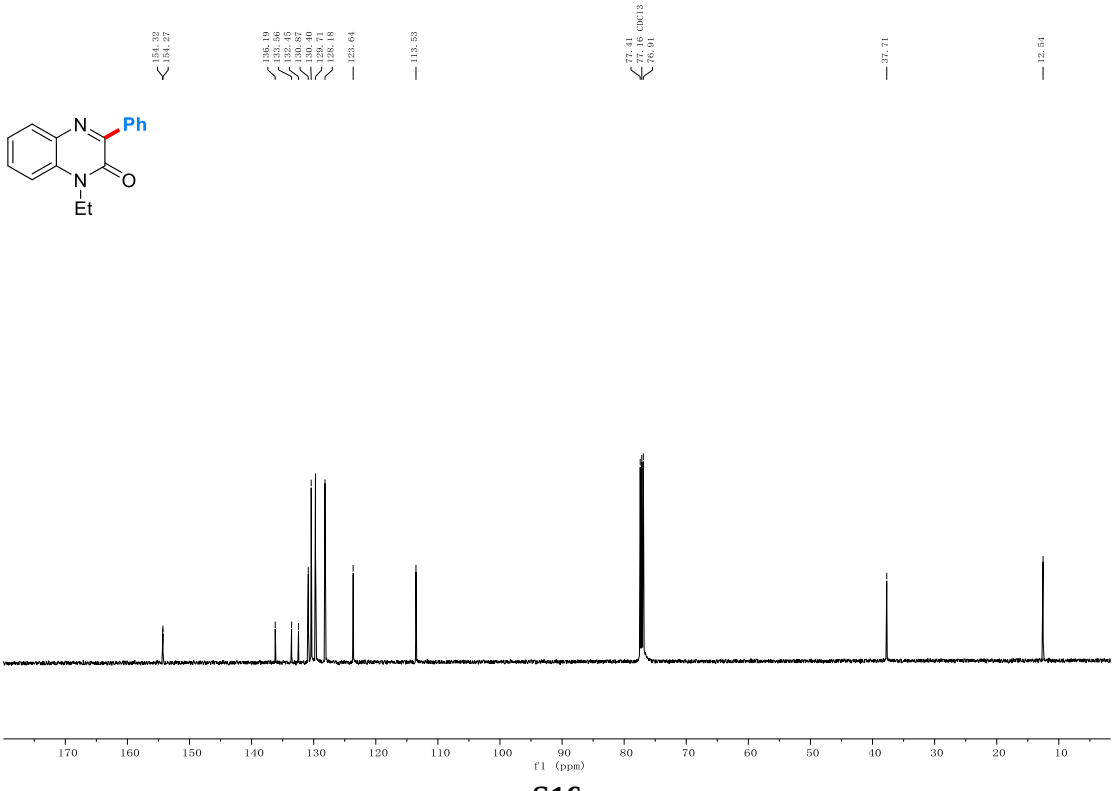


1-ethyl-3-phenylquinoxalin-2(1*H*)-one (3ba)

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

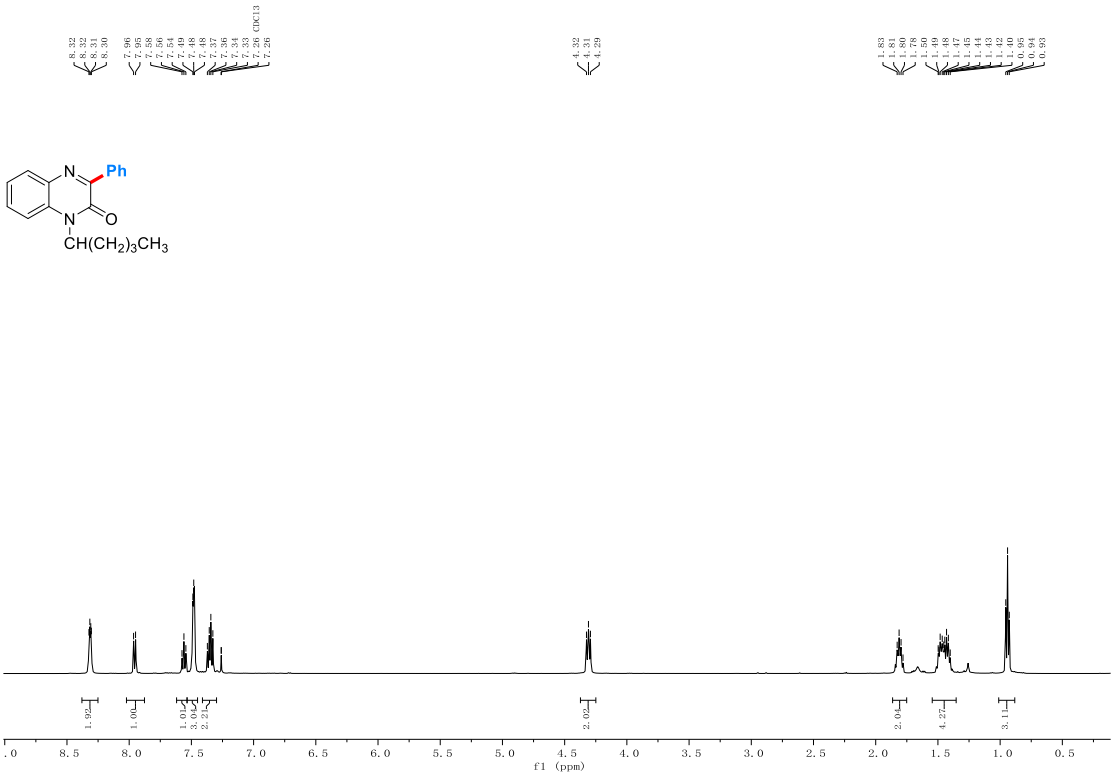


^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) spectrum of **3ba**

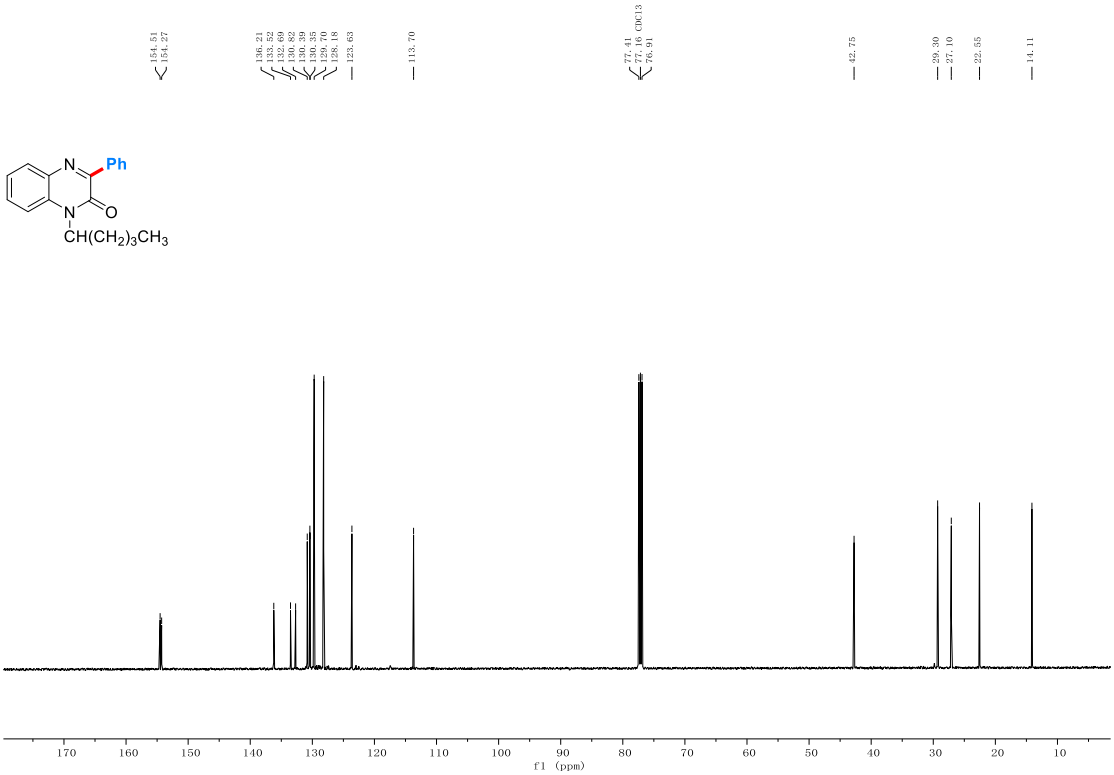


1-pentyl-3-phenylquinoxalin-2(1H)-one (3ca)

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

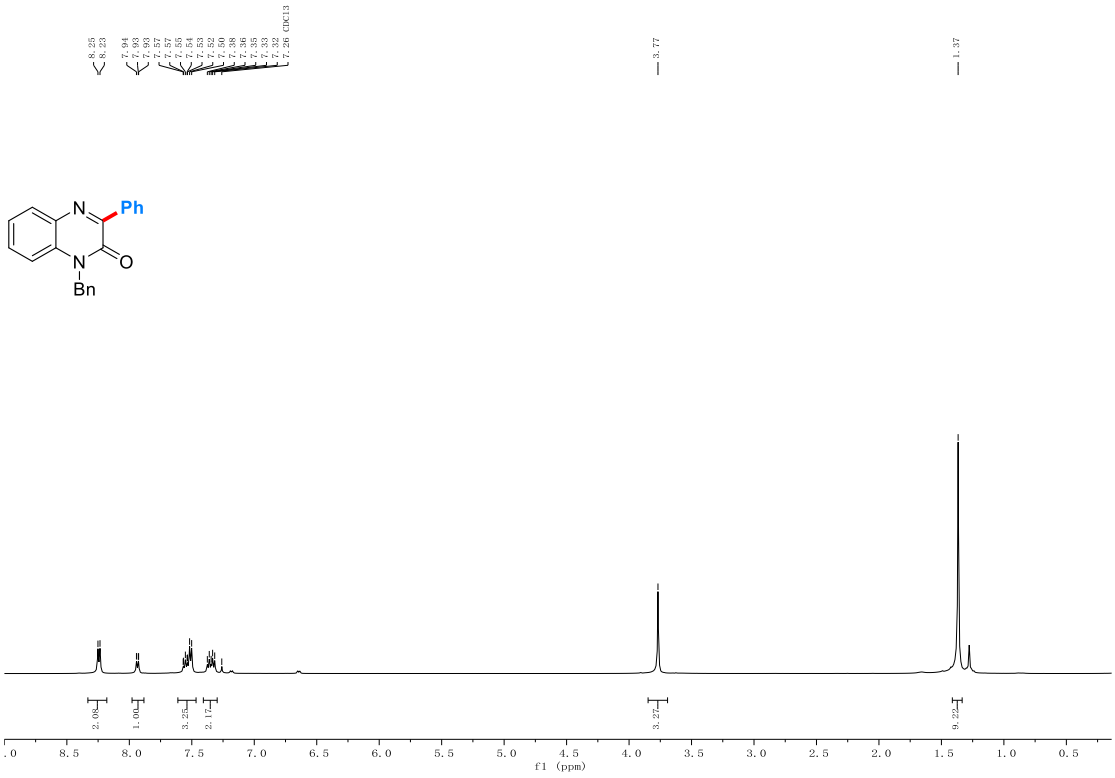


^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) spectrum of **3ca**

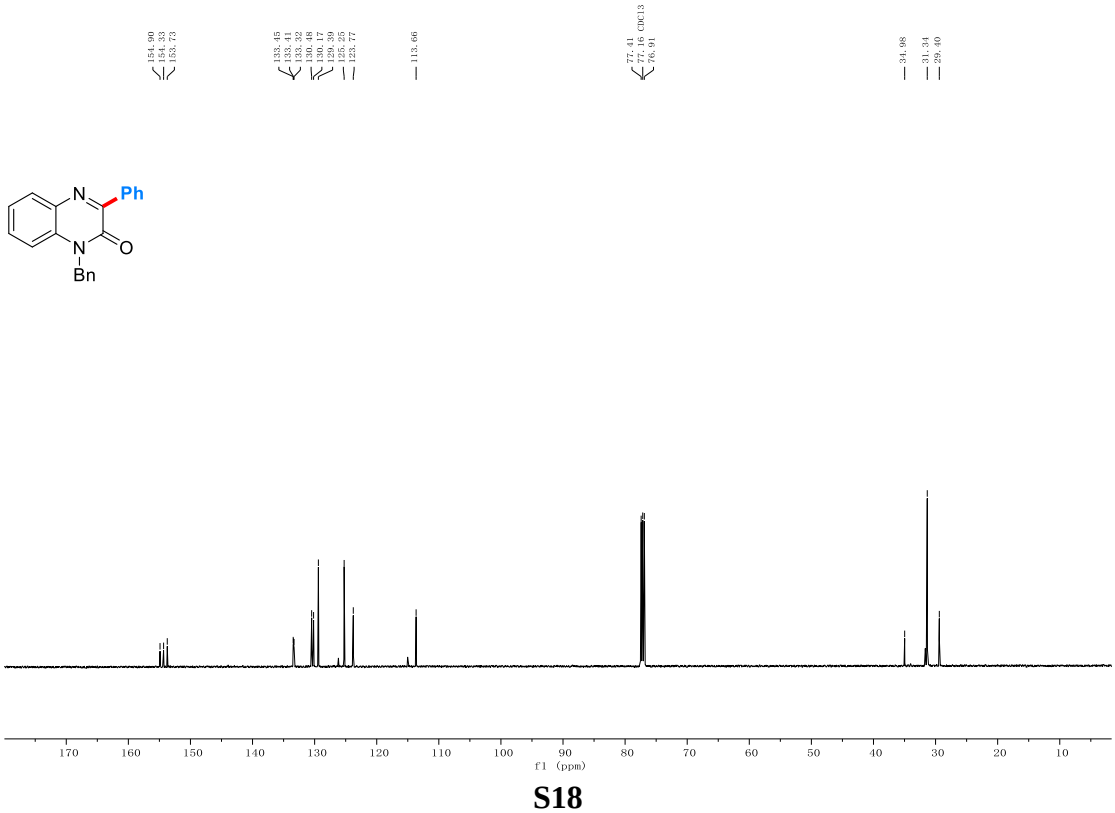


1-benzyl-3-phenylquinoxalin-2(1*H*)-one (3da)

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

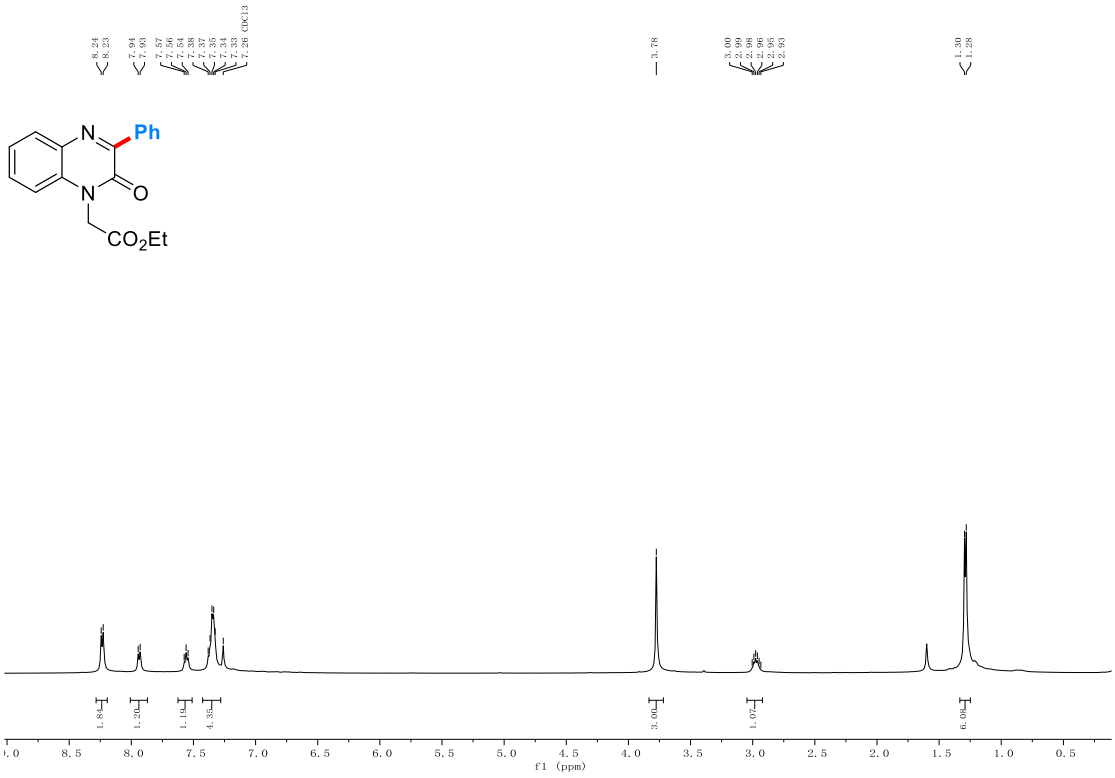


^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) spectrum of **3da**

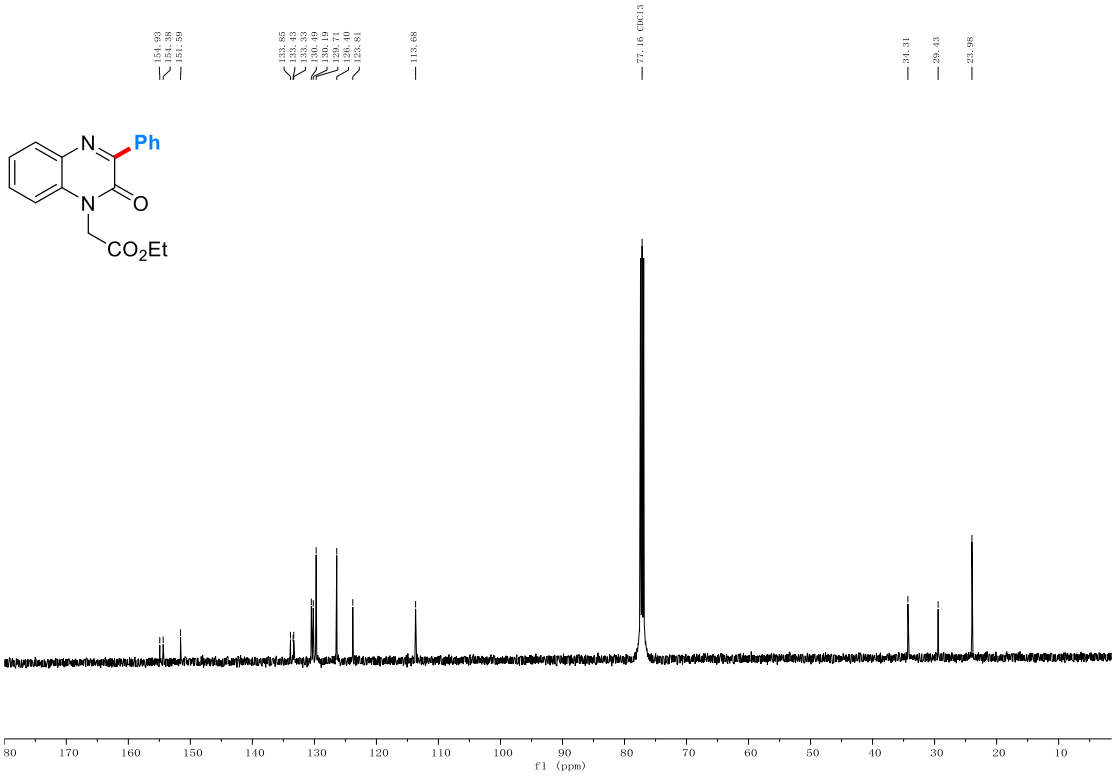


ethyl 2-(2-oxo-3-phenylquinoxalin-1(2*H*)-yl)acetate (3ea)

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

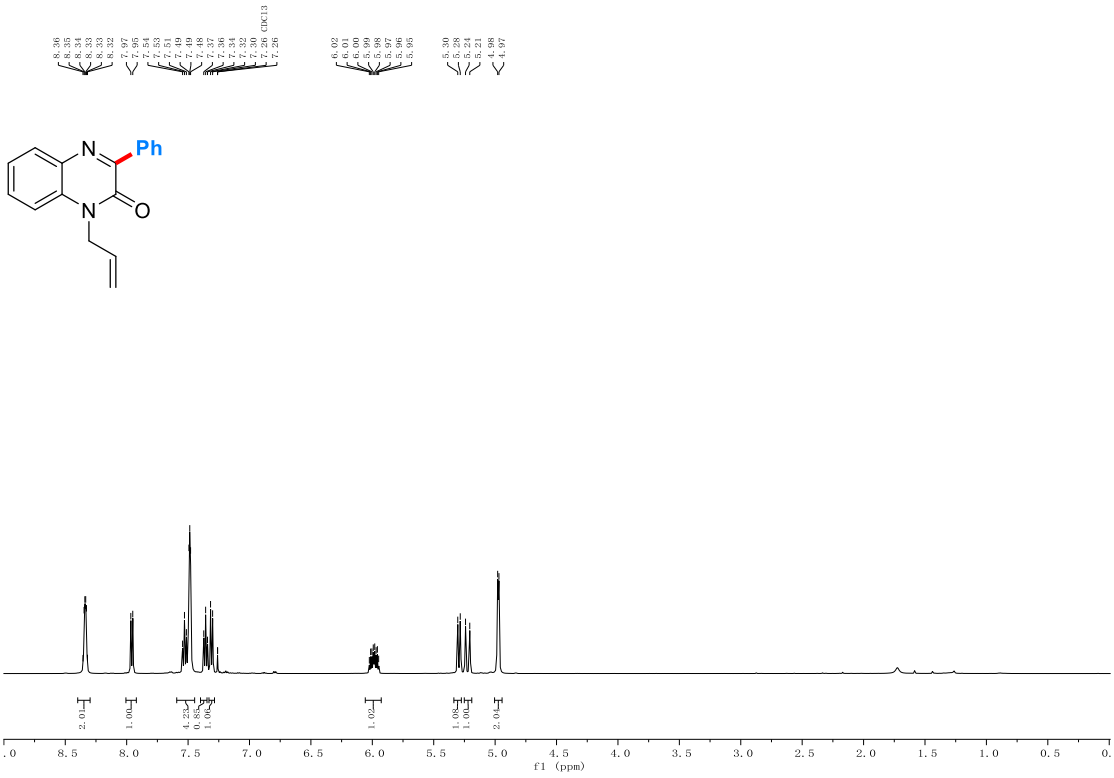


^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) spectrum of **3ea**

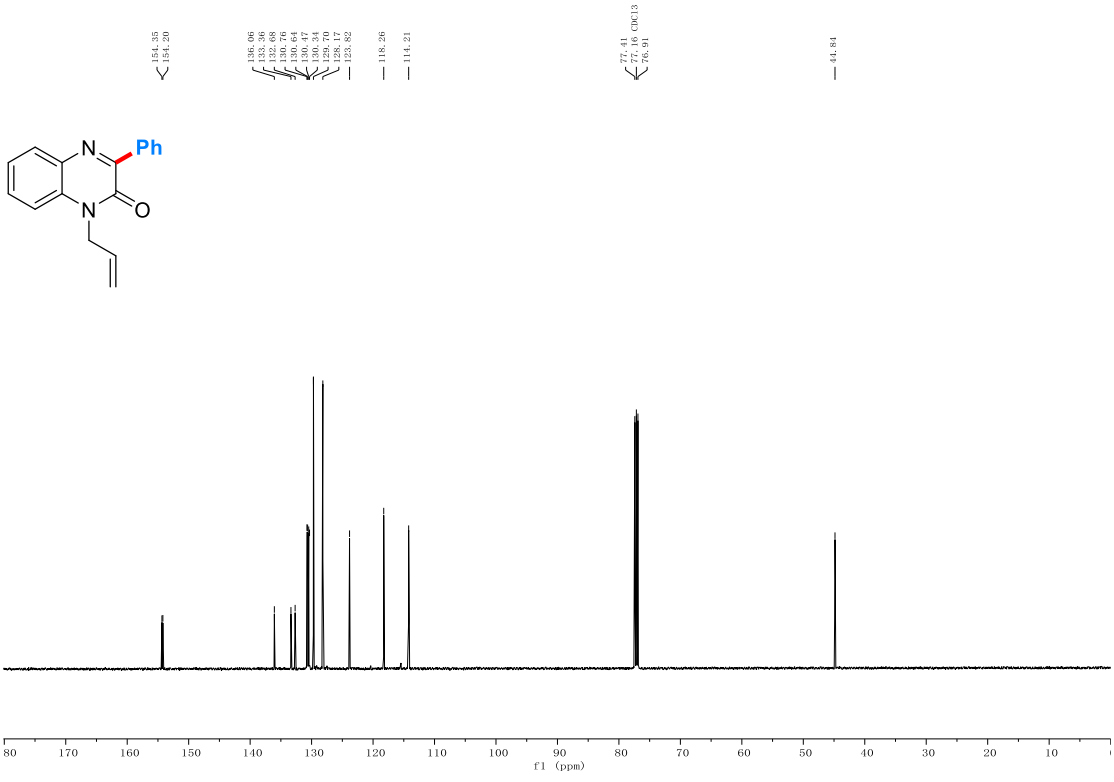


1-allyl-3-phenylquinoxalin-2(1*H*)-one (3fa)

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

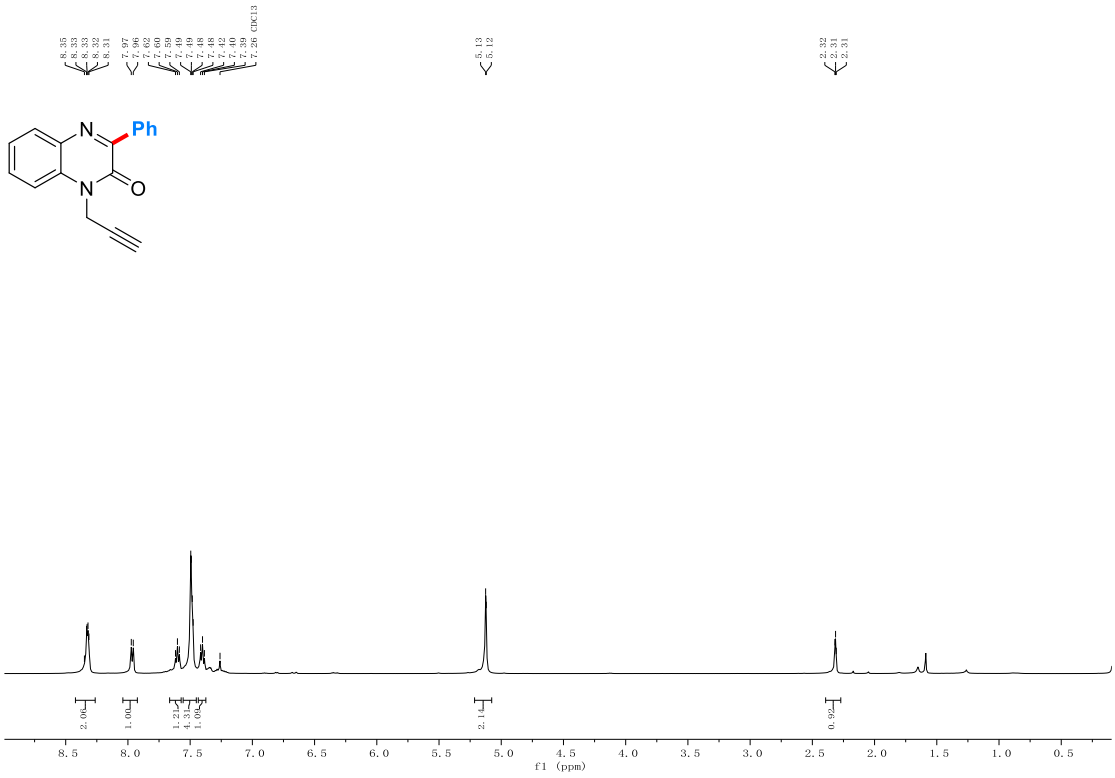


^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) spectrum of **3fa**

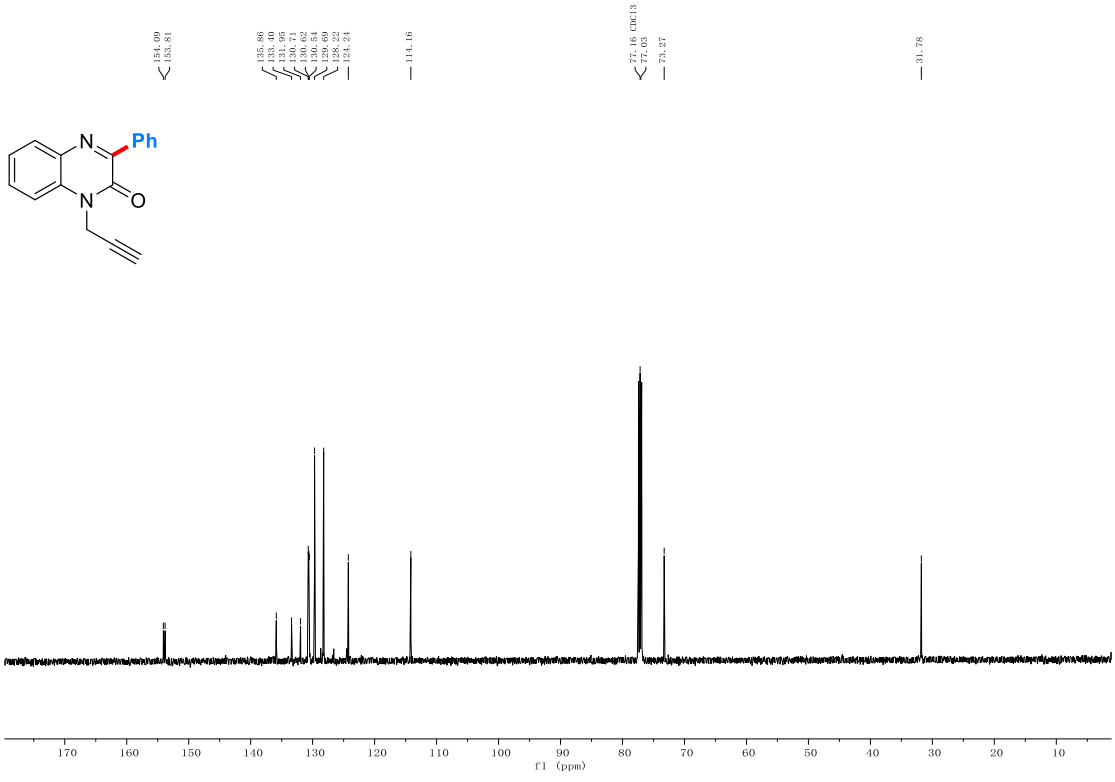


3-phenyl-1-(prop-2-yn-1-yl)quinoxalin-2(1*H*)-one (3ga)

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

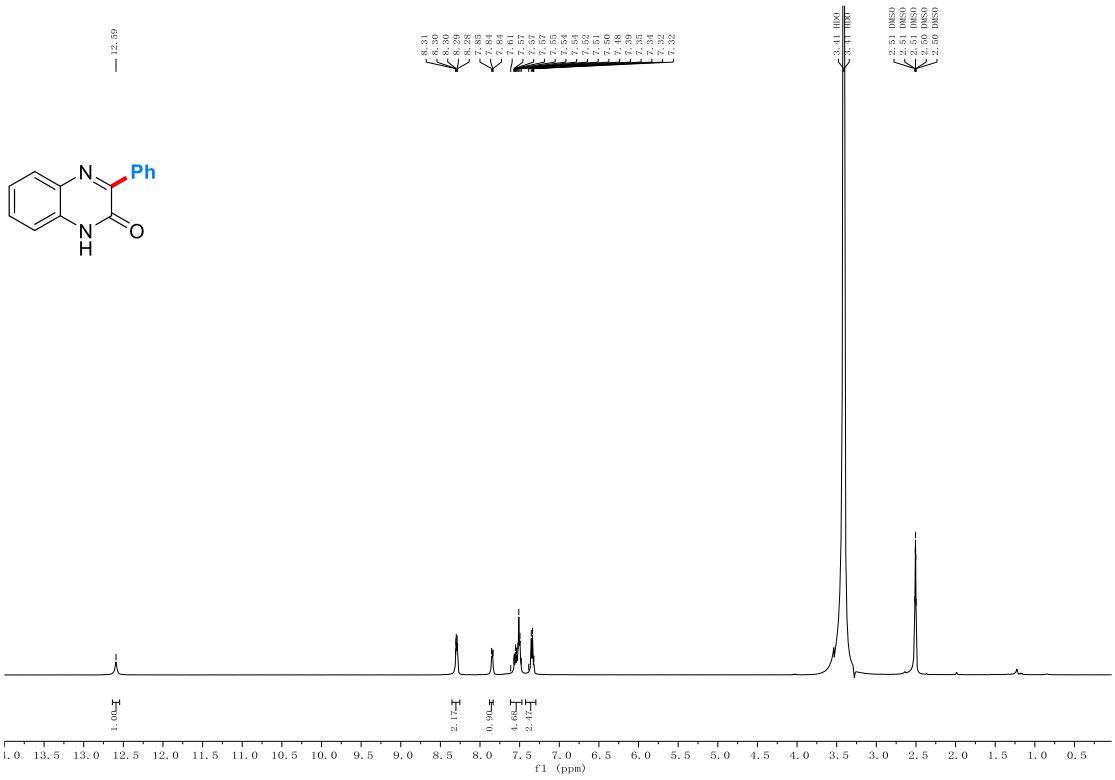


^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) spectrum of **3ga**

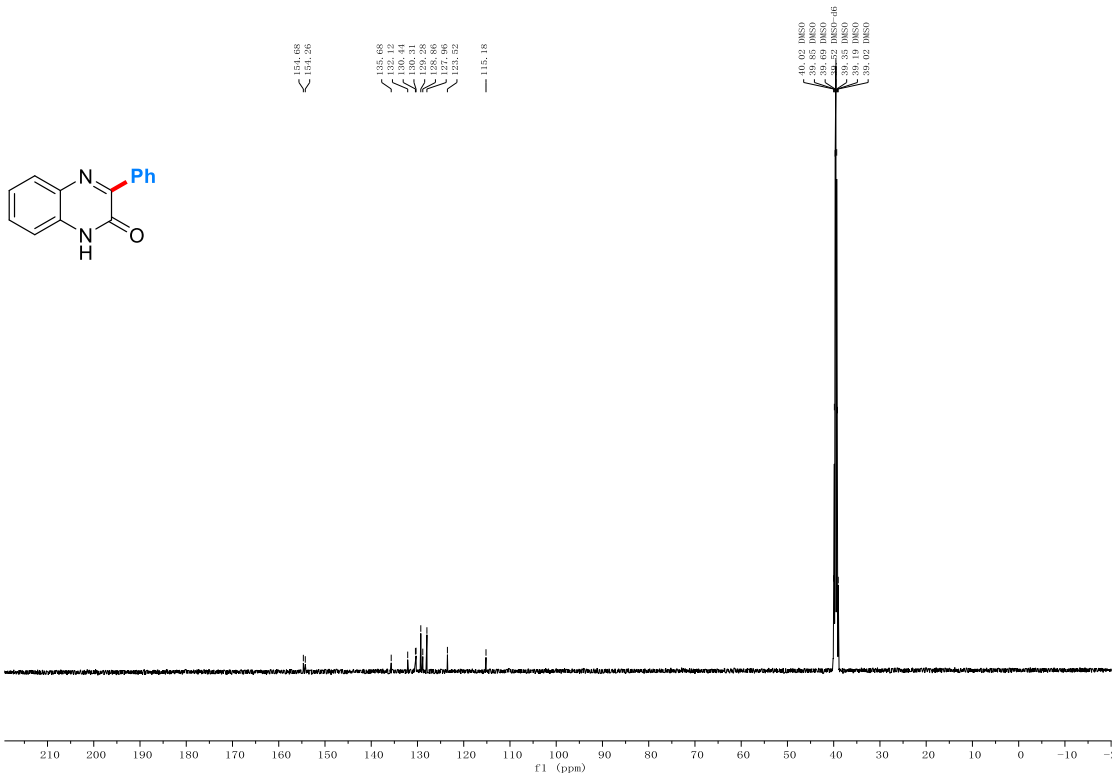


3-phenylquinoxalin-2(1*H*)-one (3ha)

^{1}H NMR (500 MHz, DMSO-d_6) spectrum of **3ha**

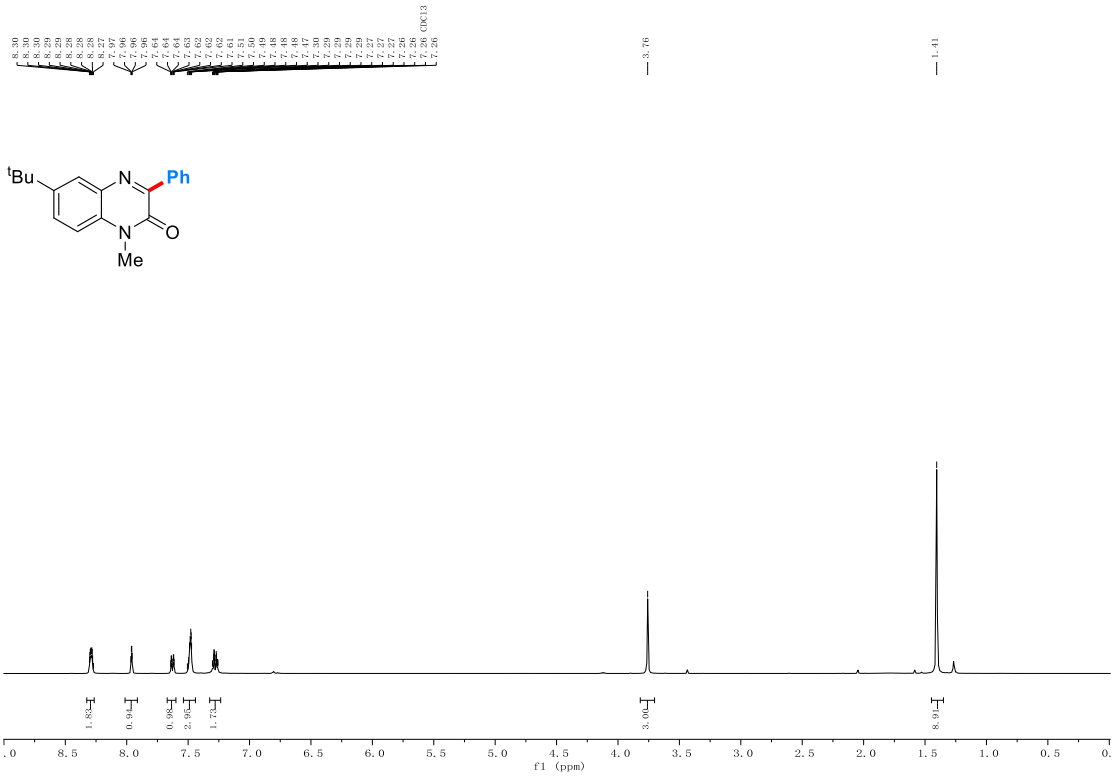


^{13}C{^{1}H} NMR (125 MHz, DMSO-d_6) spectrum of **3ha**

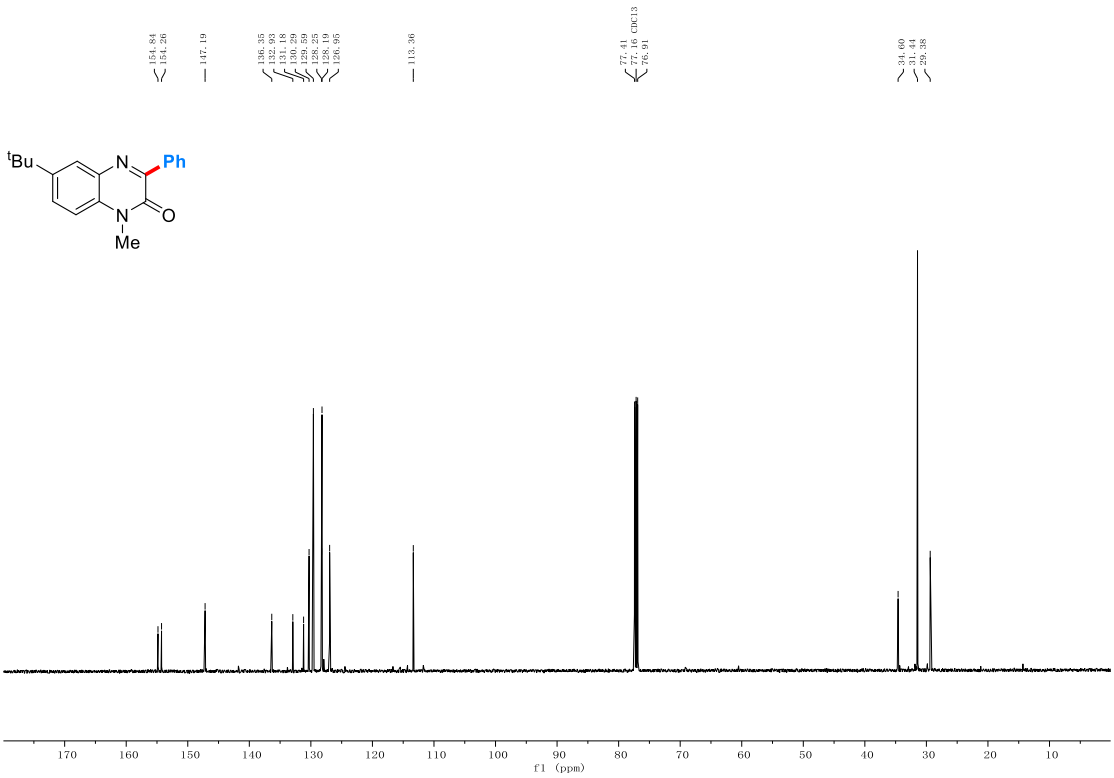


6-(tert-butyl)-1-methyl-3-phenylquinoxalin-2(1*H*)-one (3ia)

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

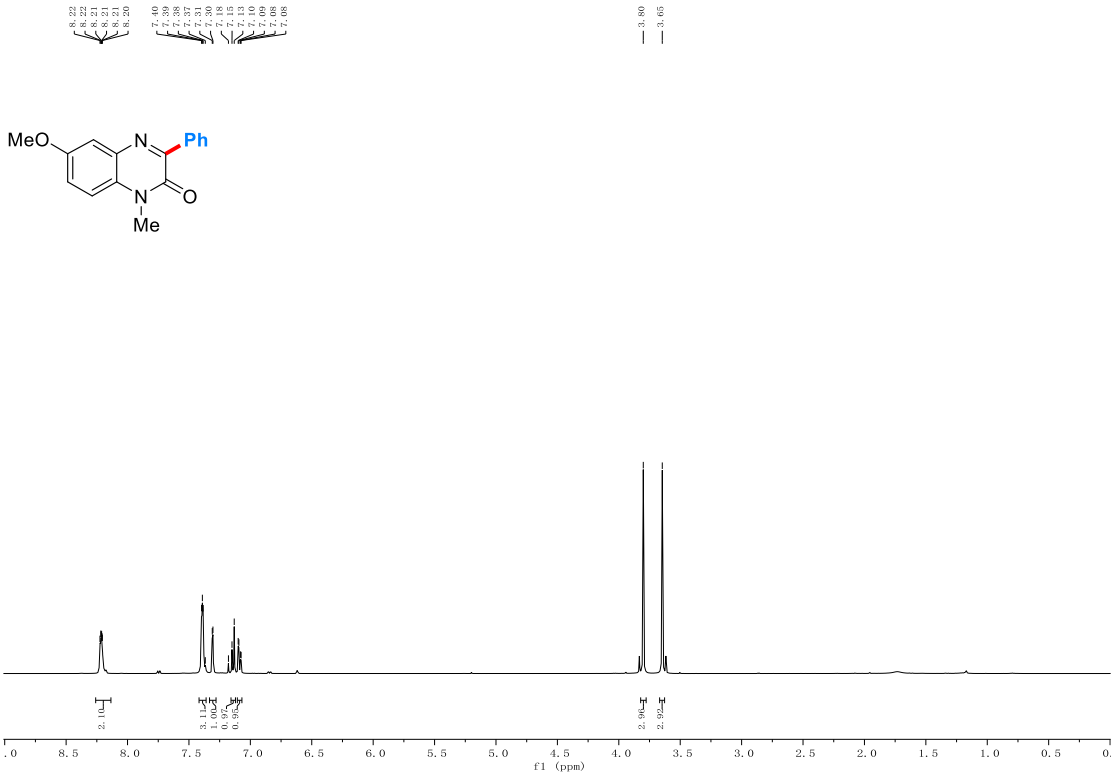


^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) spectrum of **3ia**

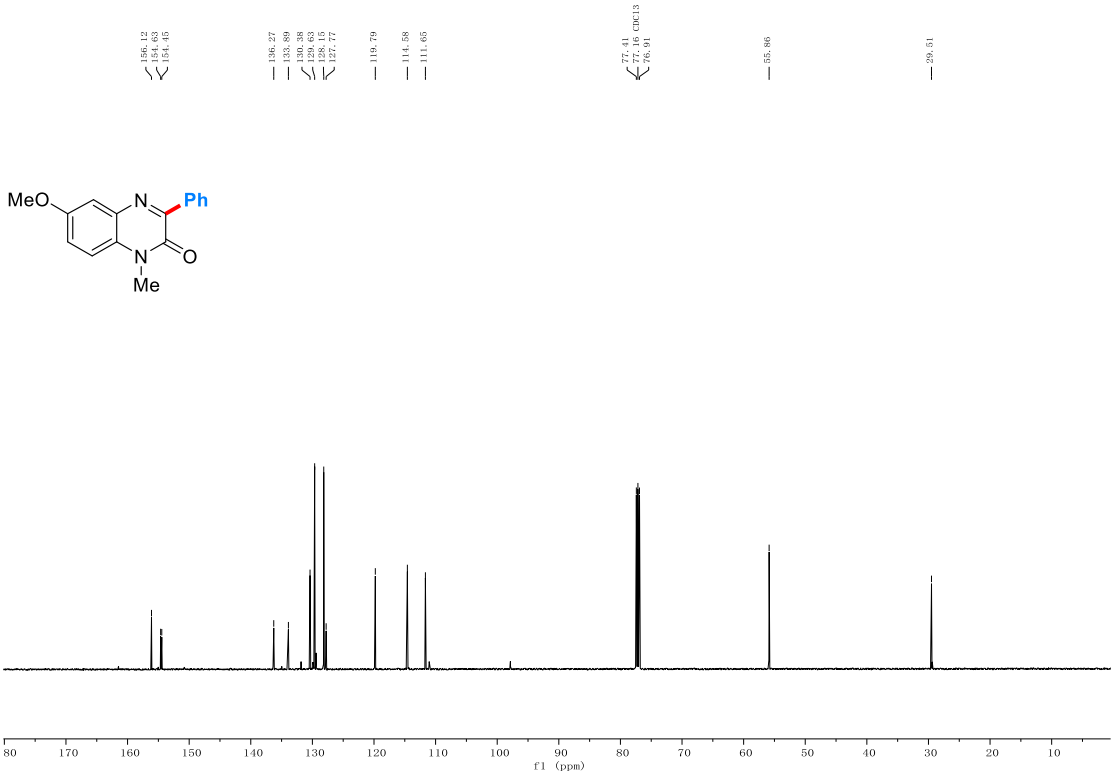


6-methoxy-1-methyl-3-phenylquinoxalin-2(1*H*)-one (3ja)

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

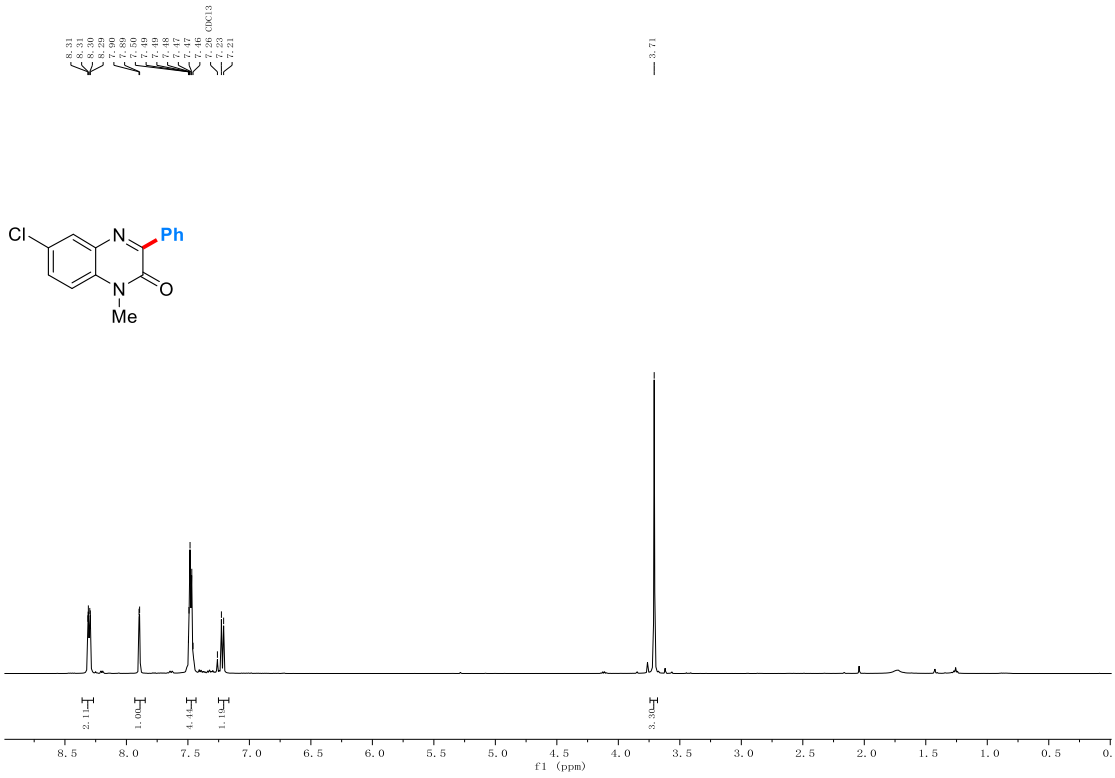


^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) spectrum of **3ja**

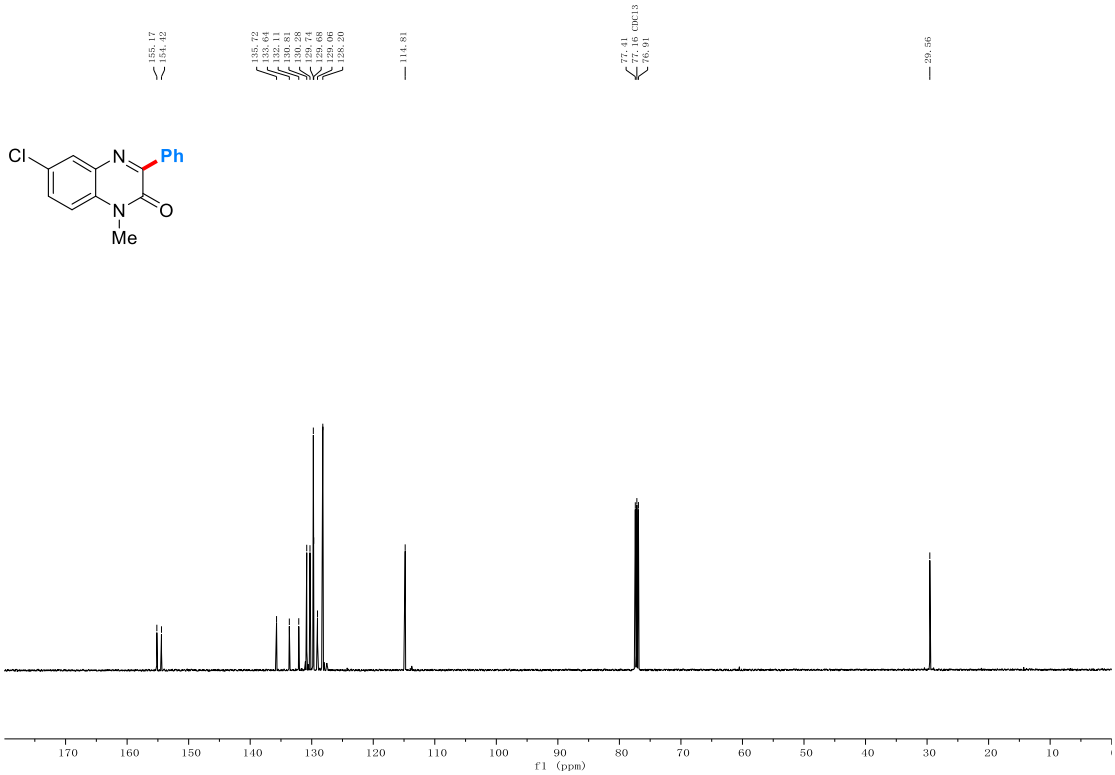


6-chloro-1-methyl-3-phenylquinoxalin-2(1*H*)-one (3ka)

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

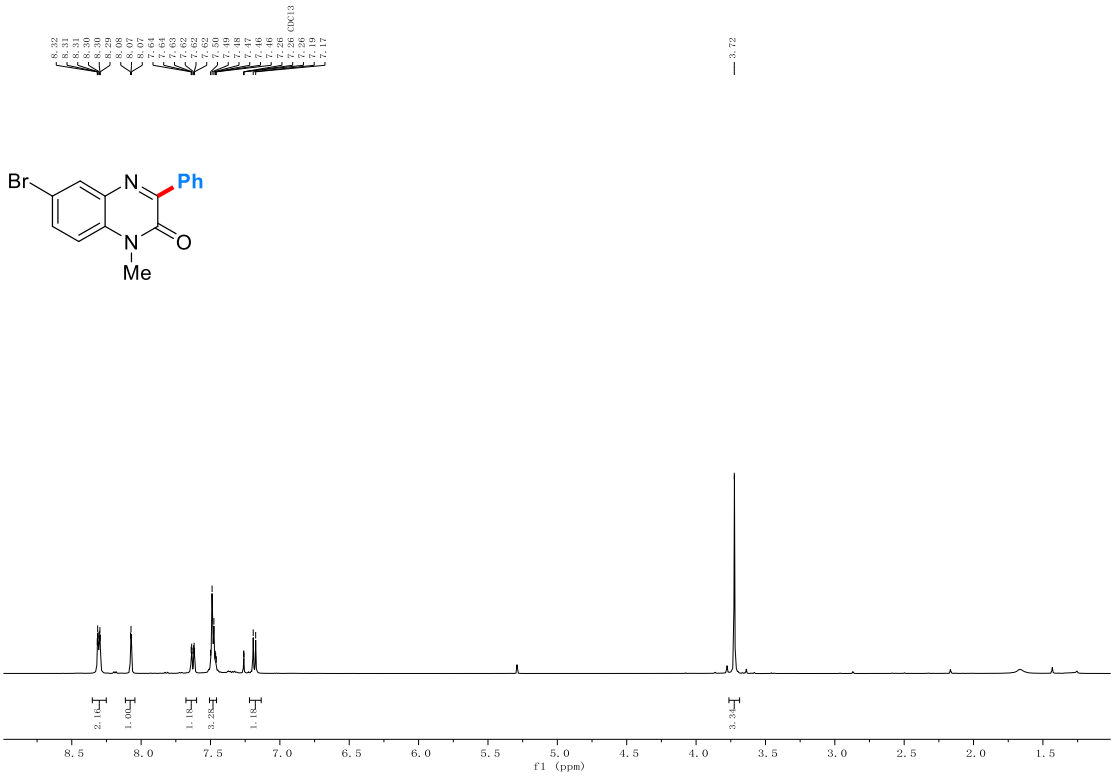


^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) spectrum of **3ka**

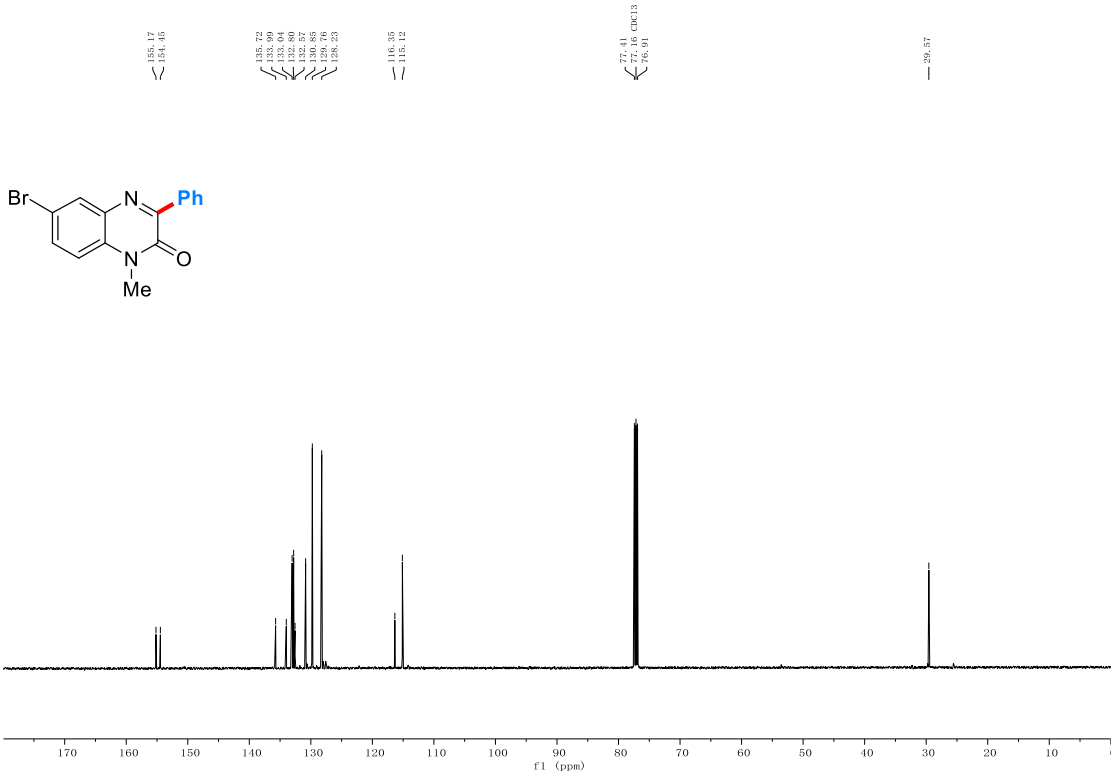


6-bromo-1-methyl-3-phenylquinoxalin-2(1*H*)-one (3la)

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

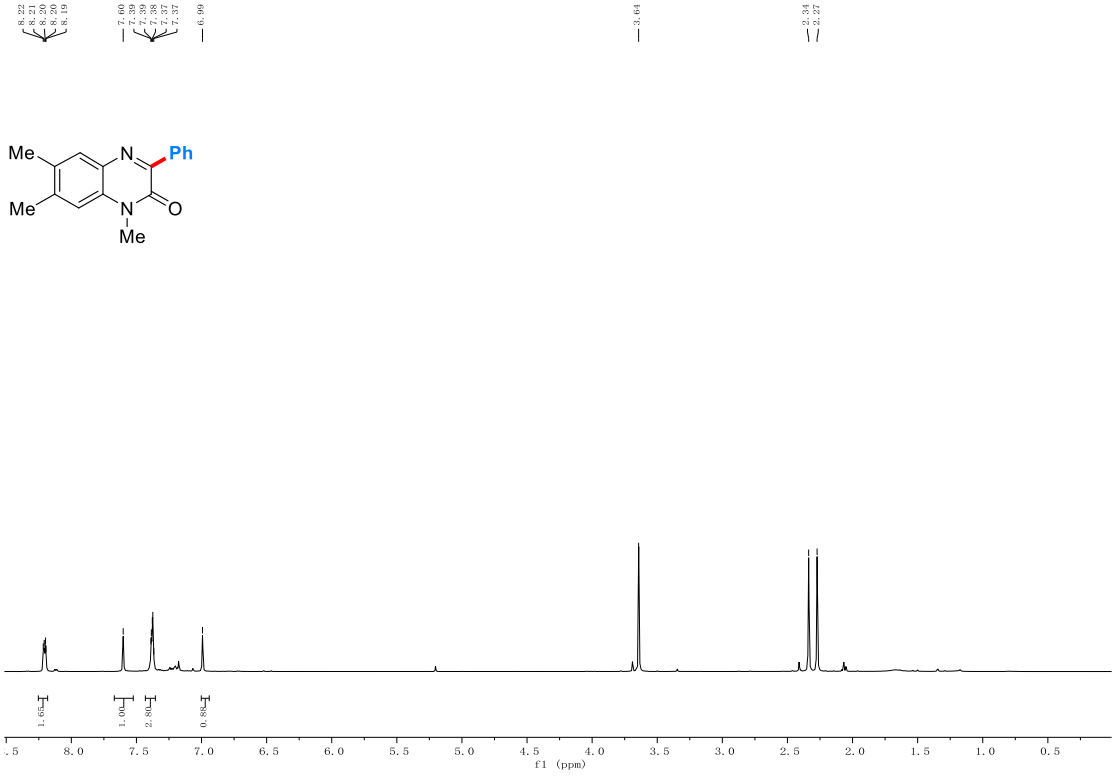


^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) spectrum of **3la**

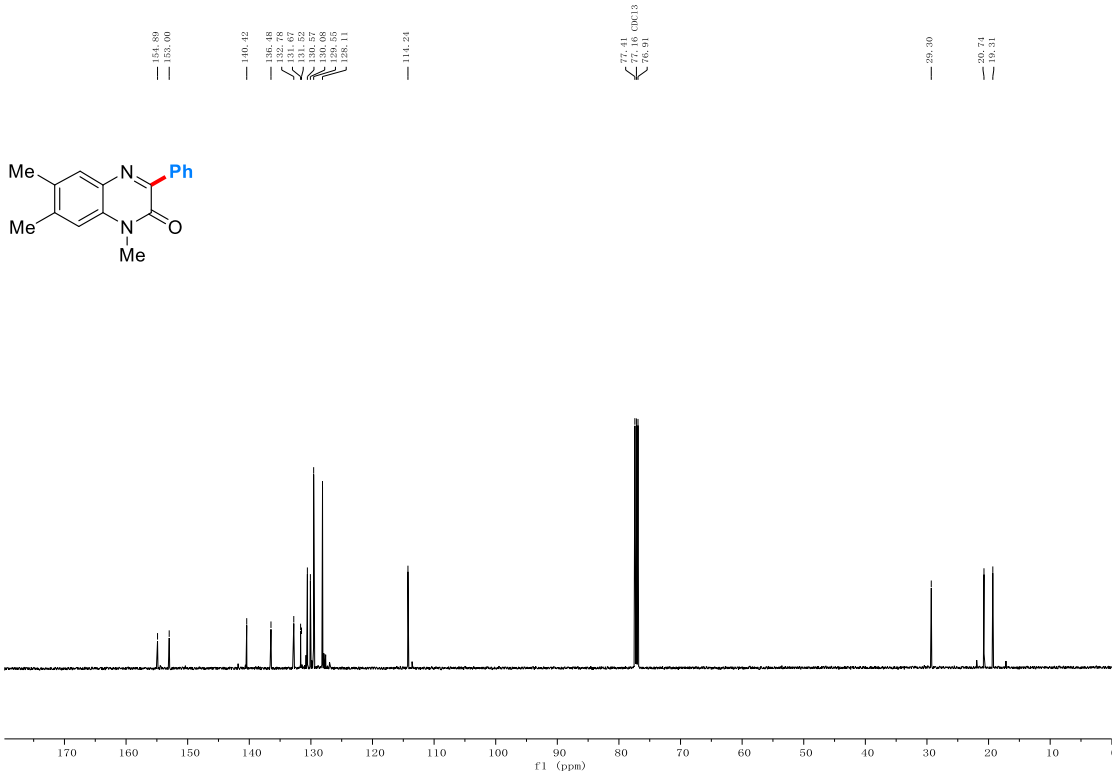


1,6,7-trimethyl-3-phenylquinoxalin-2(1H)-one (3ma)

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

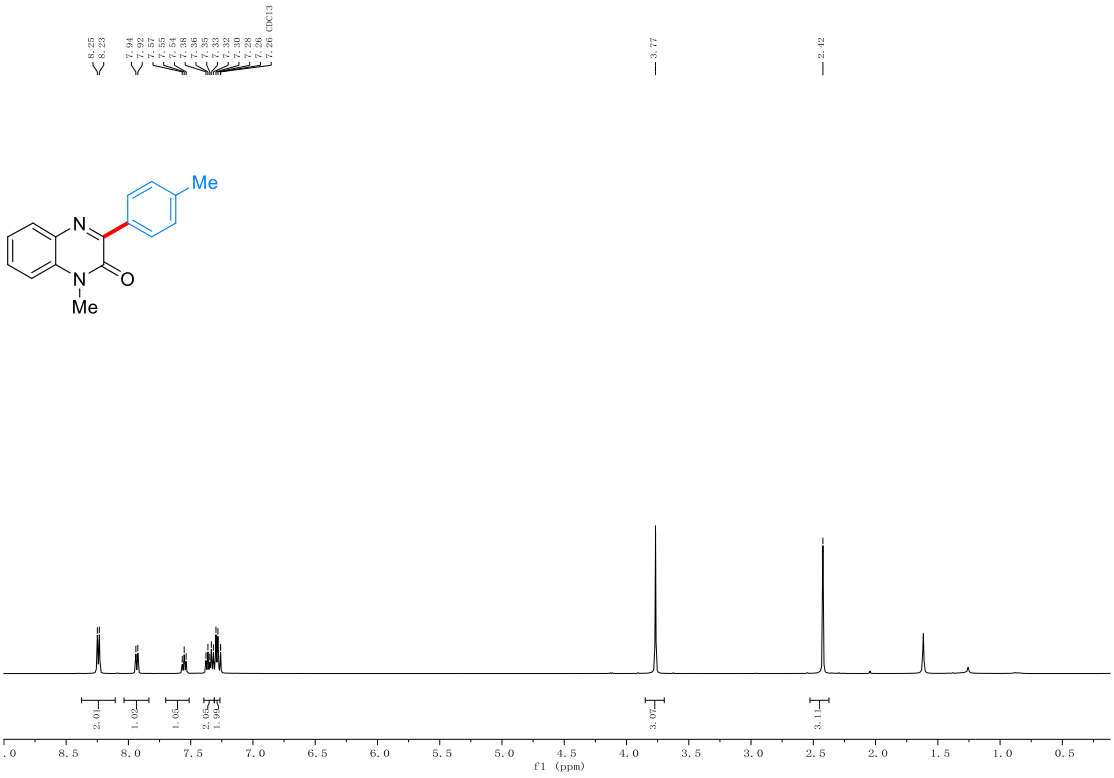


^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) spectrum of **3ma**

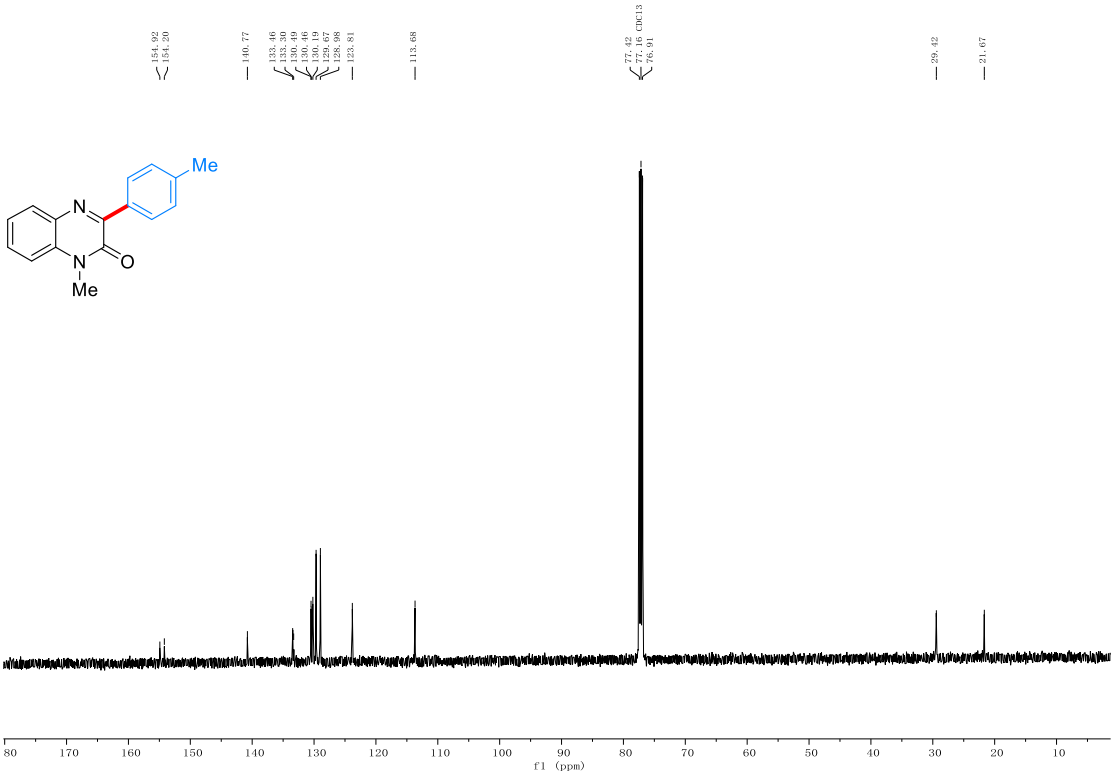


1,6,7-trimethyl-3-phenylquinoxalin-2(1H)-one (3ab)

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

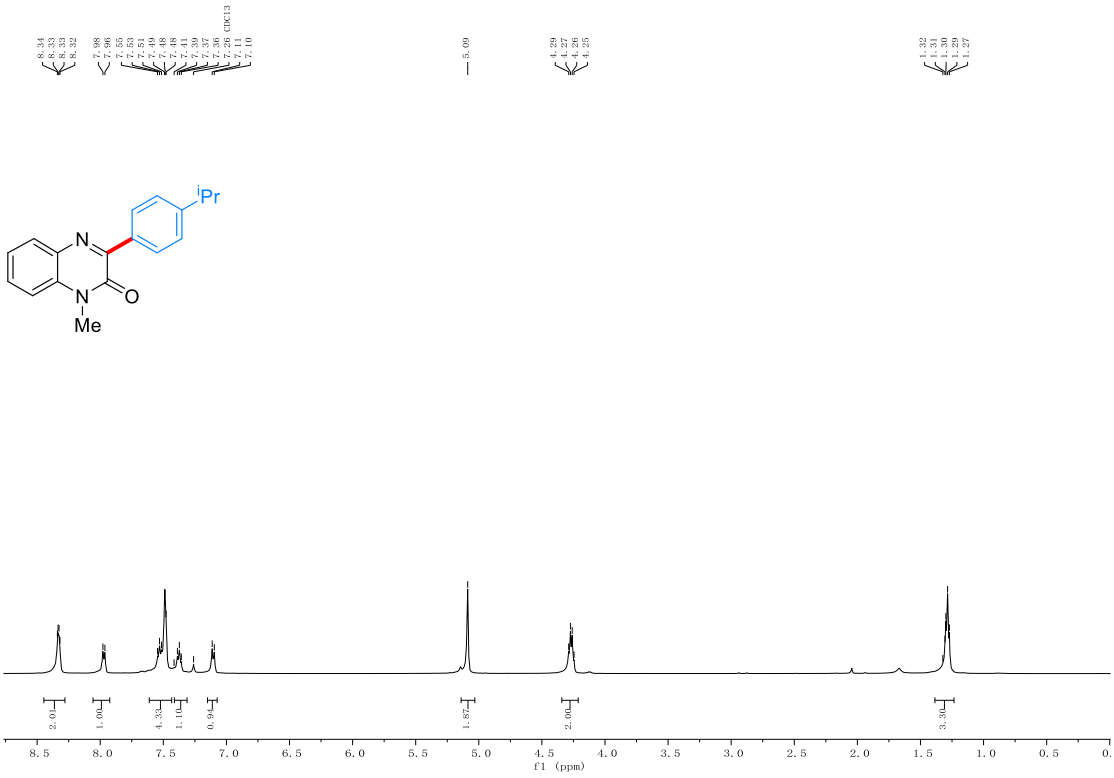


^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) spectrum of **3ab**

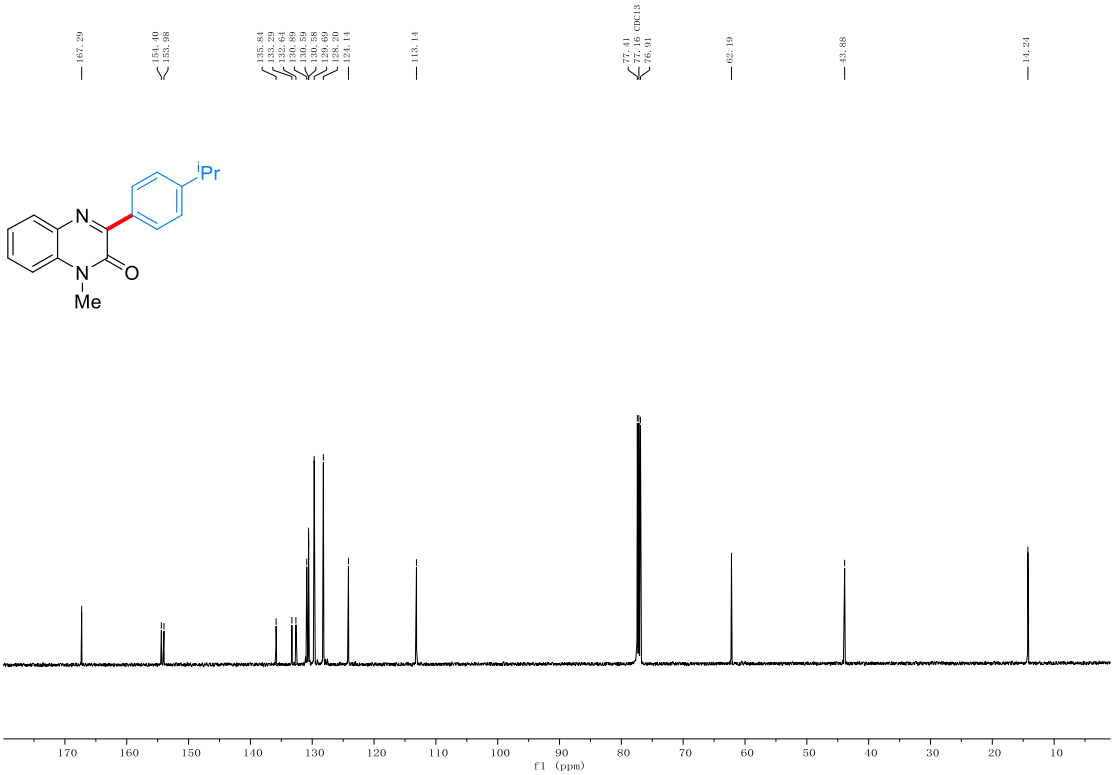


3-(4-isopropylphenyl)-1-methylquinoxalin-2(1*H*)-one (3ac)

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

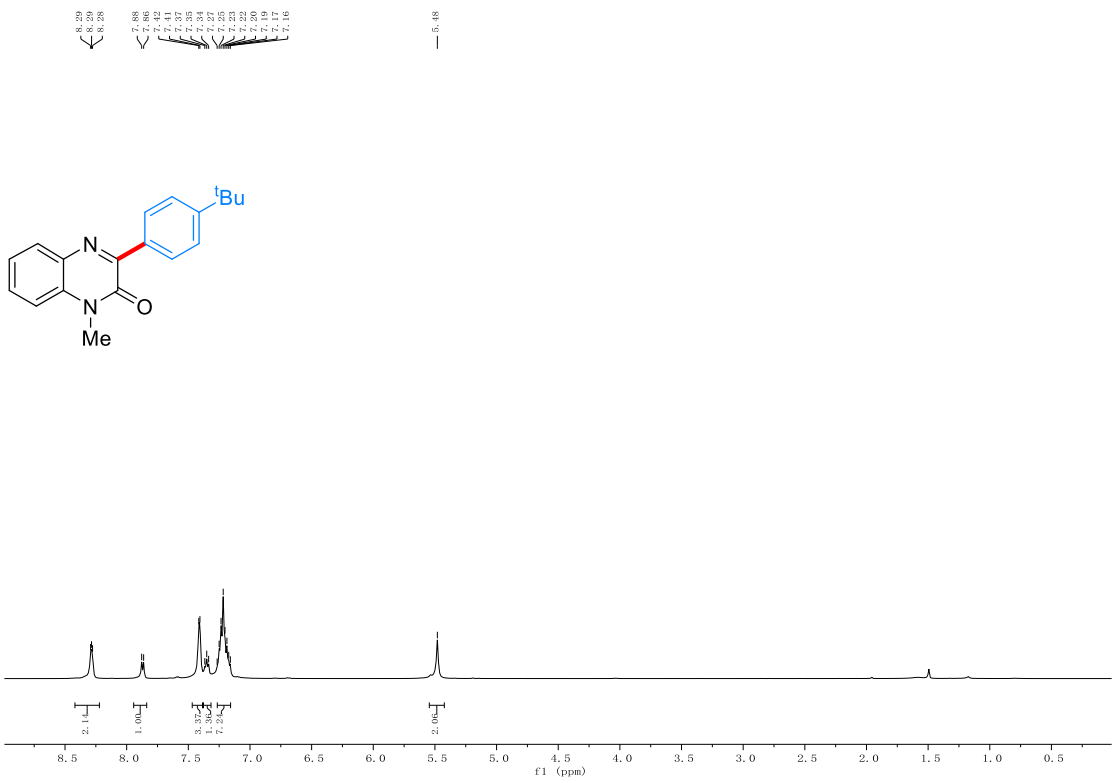


^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) spectrum of **3ac**

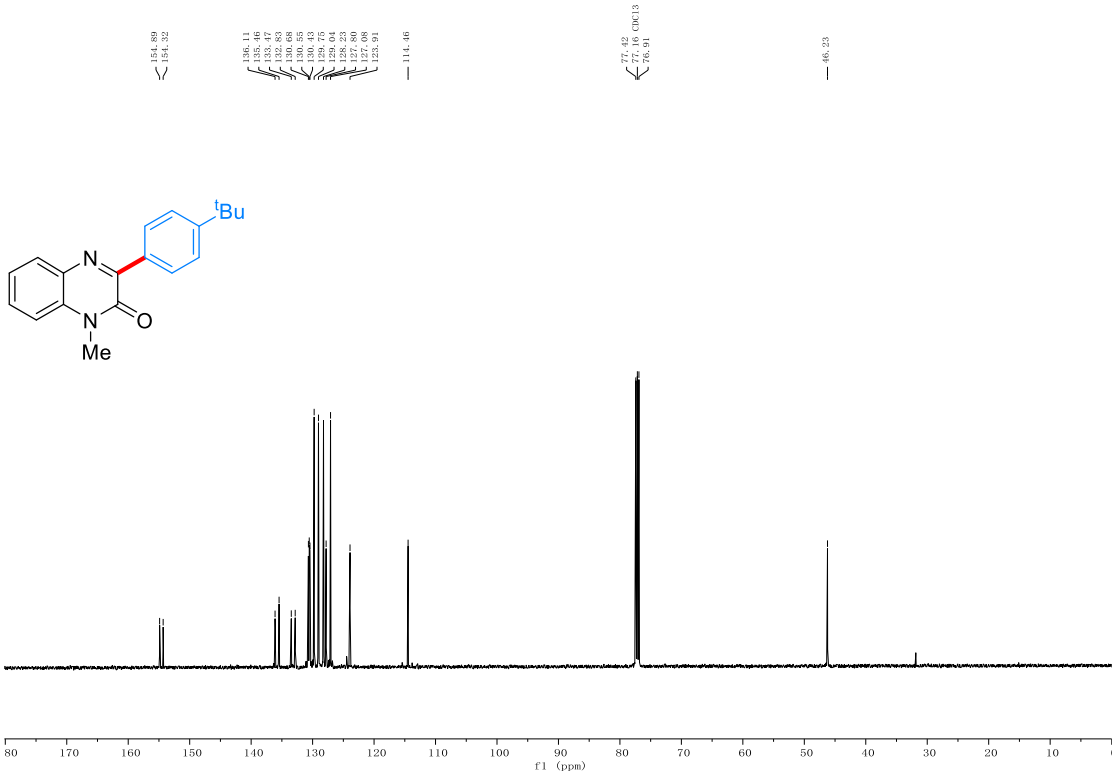


3-(4-(tert-butyl)phenyl)-1-methylquinoxalin-2(1*H*)-one (3ad)

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

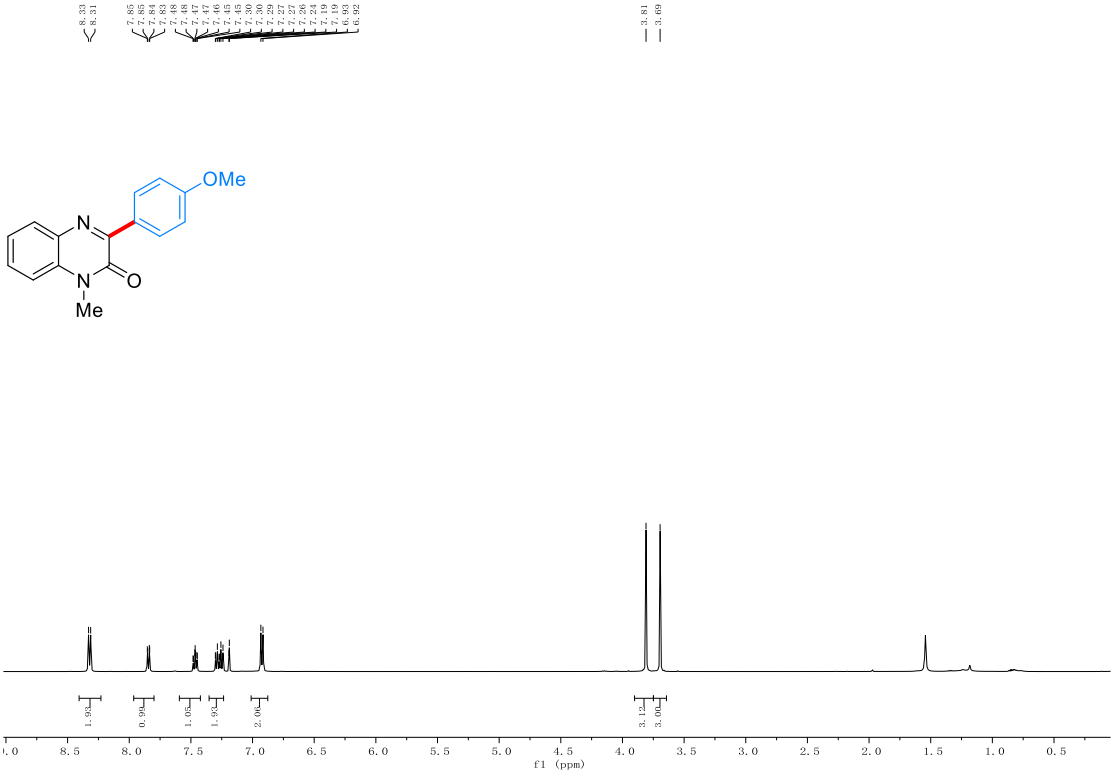


^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) spectrum of **3ad**

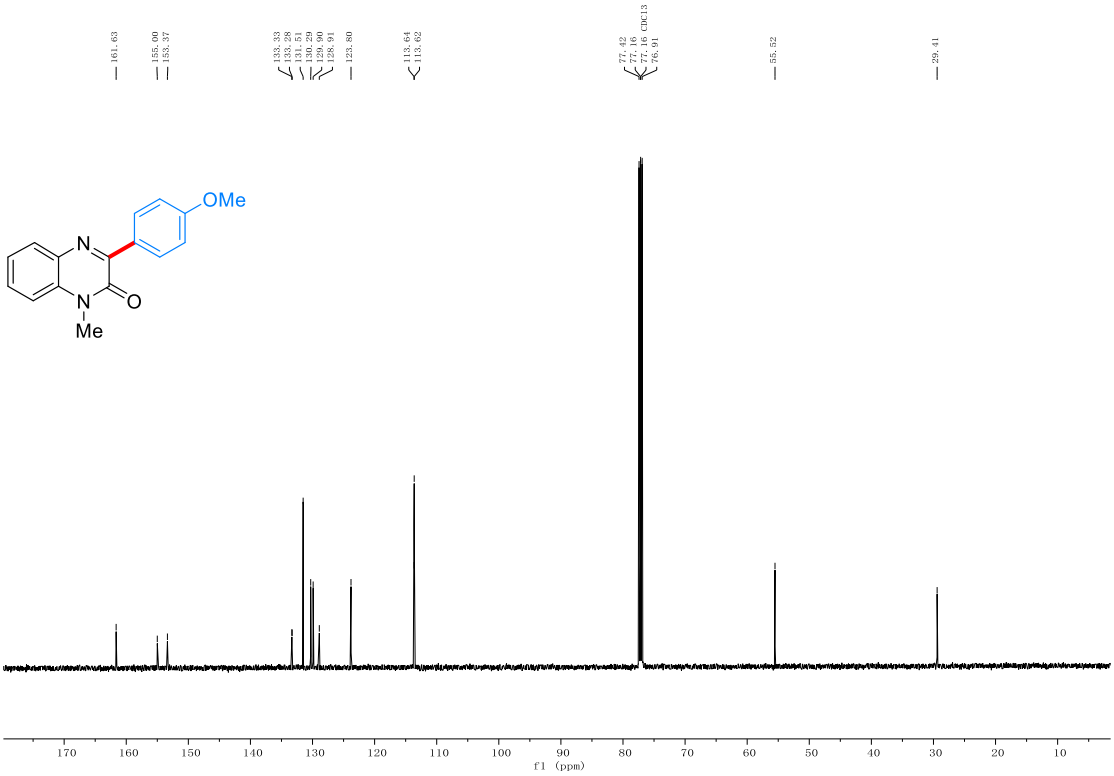


3-(4-methoxyphenyl)-1-methylquinoxalin-2(1*H*)-one (3ae)

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

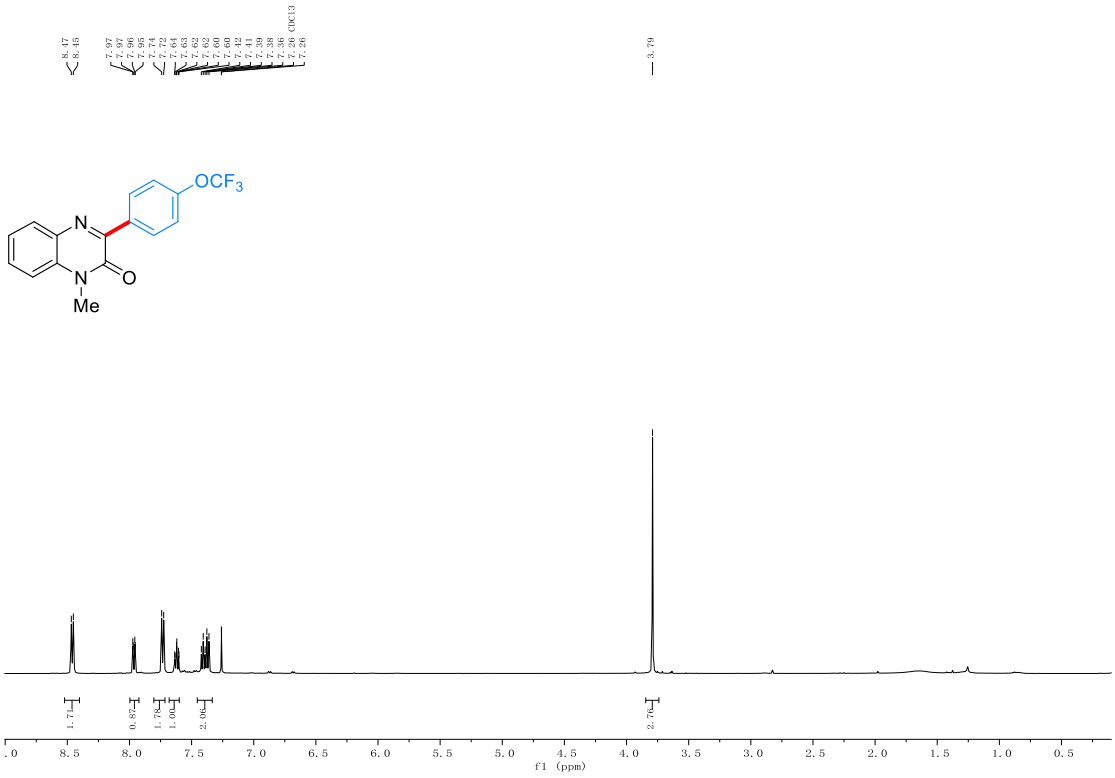


^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) spectrum of **3ae**

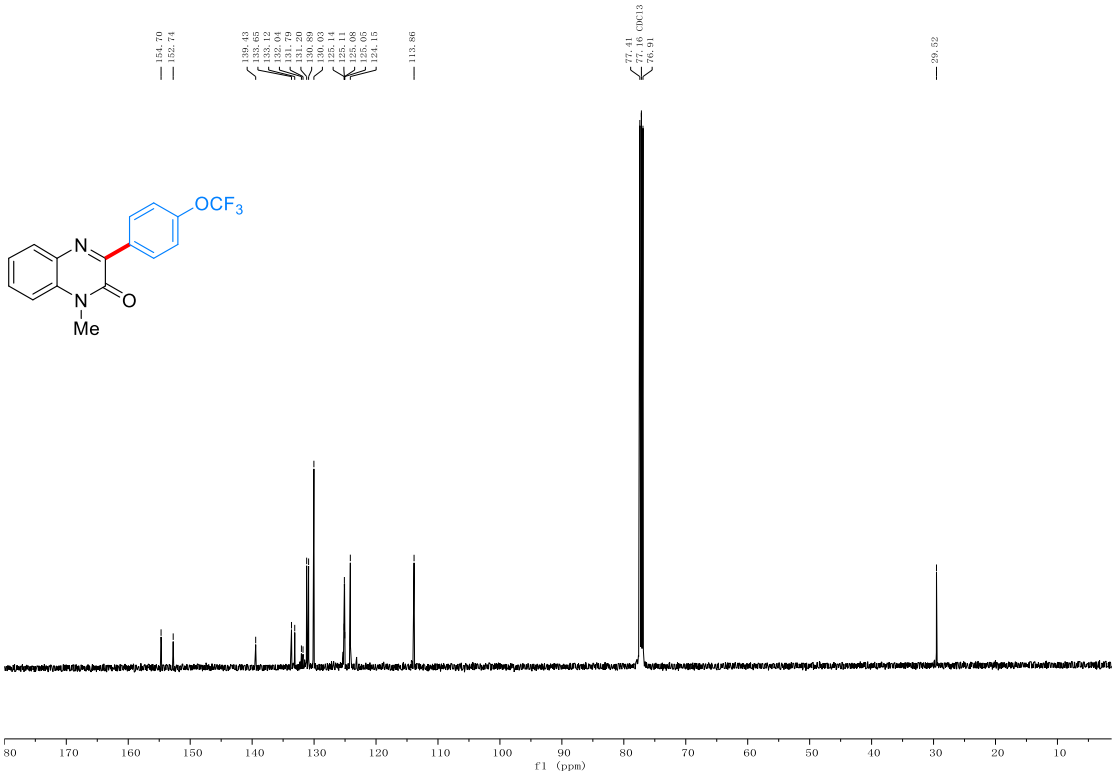


1-methyl-3-(4-(trifluoromethoxy)phenyl)quinoxalin-2(1*H*)-one (3af)

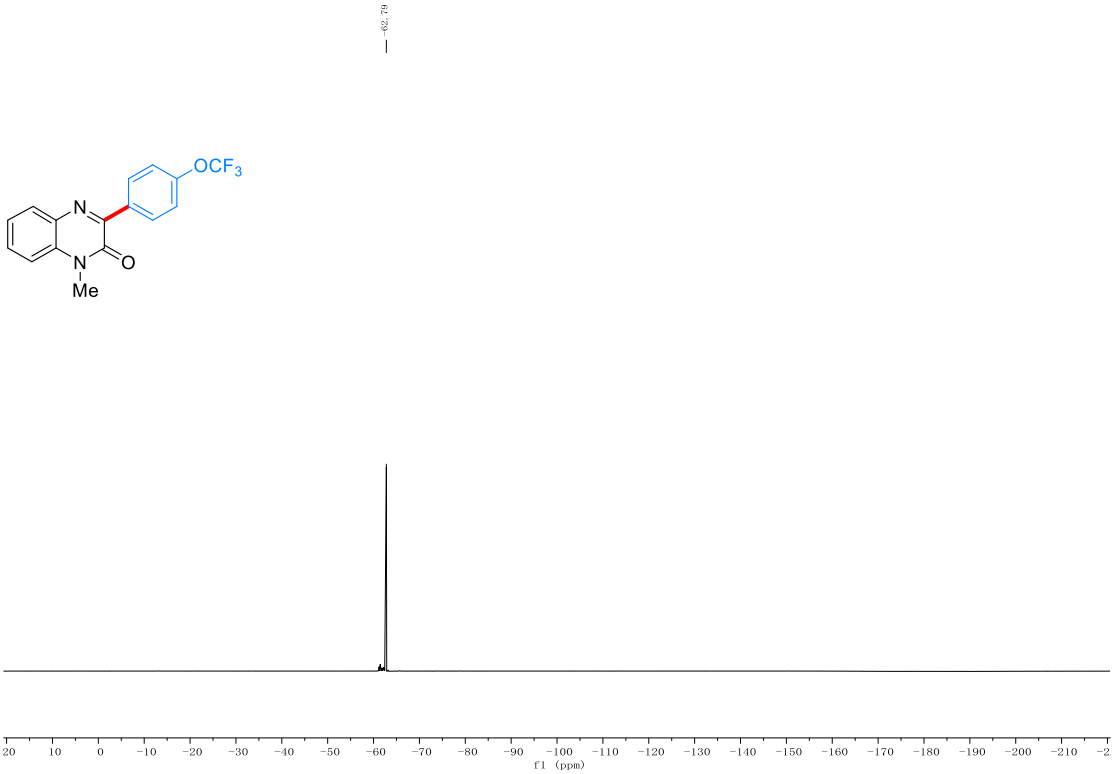
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **3af**



^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) spectrum of **3af**

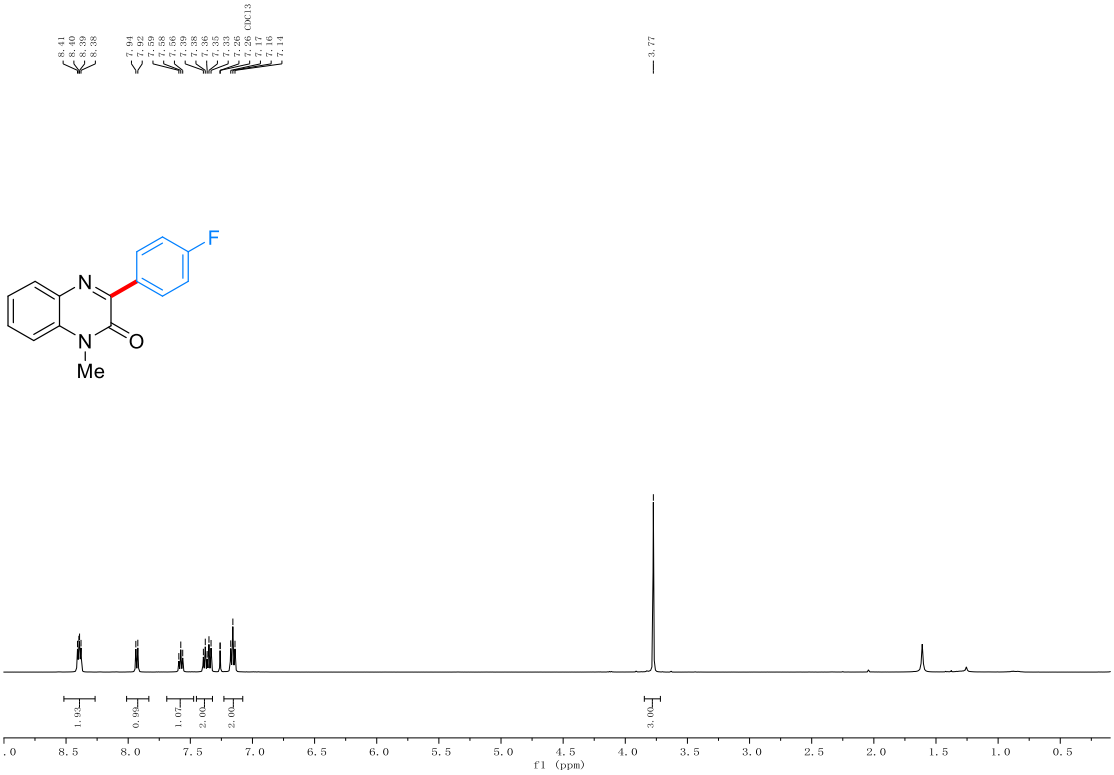


^{19}F NMR (471 MHz, $CDCl_3$) spectrum of **3af**

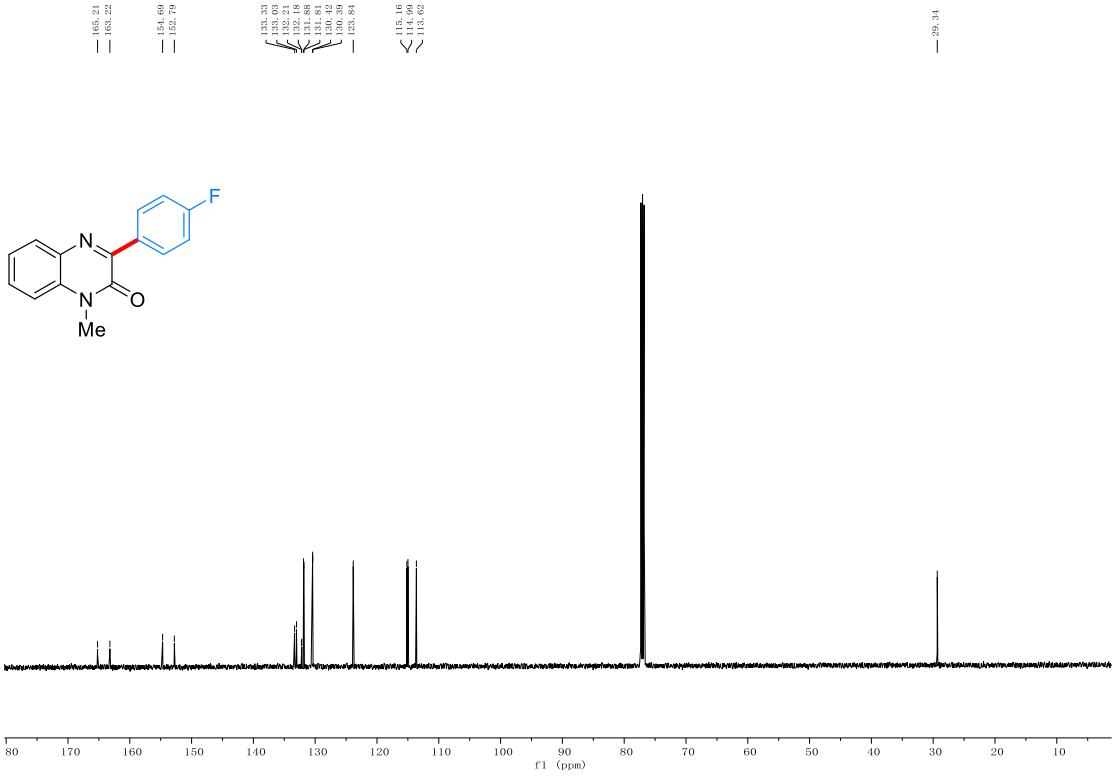


3-(4-fluorophenyl)-1-methylquinoxalin-2(1*H*)-one (3ag)

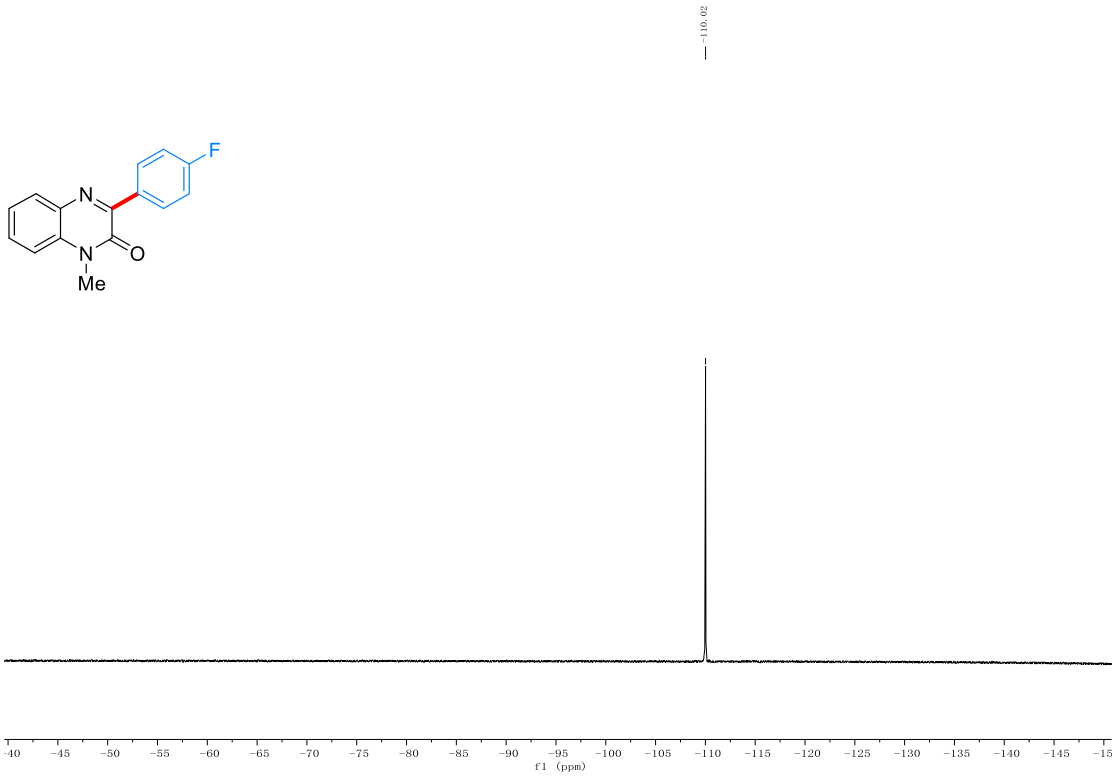
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **3ag**



$^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$) spectrum of **3ag**

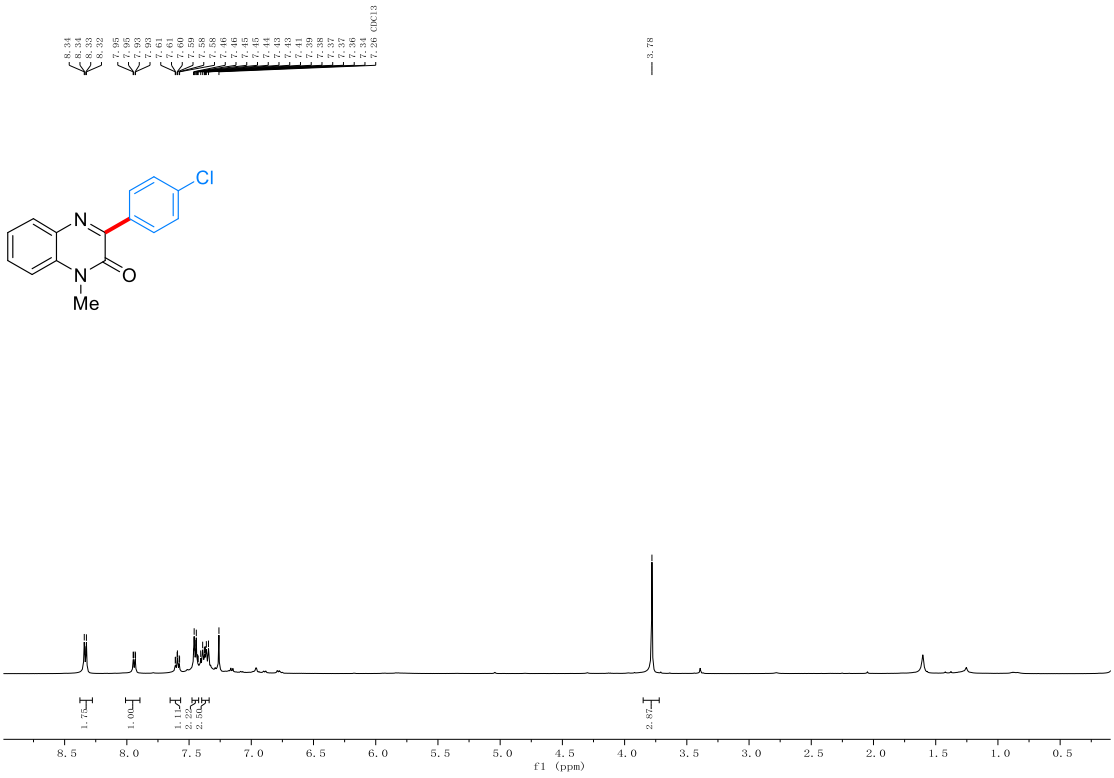


^{19}F NMR (471 MHz, $CDCl_3$) spectrum of **3ag**

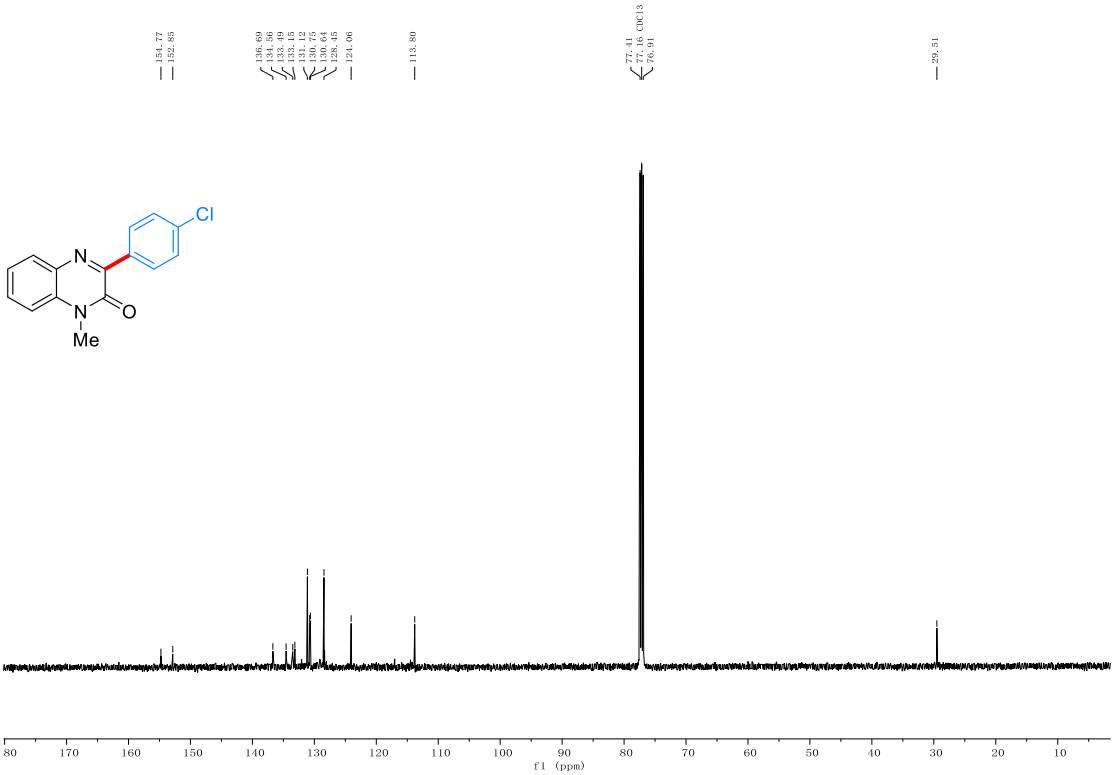


3-(4-chlorophenyl)-1-methylquinoxalin-2(1*H*)-one (3ah)

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

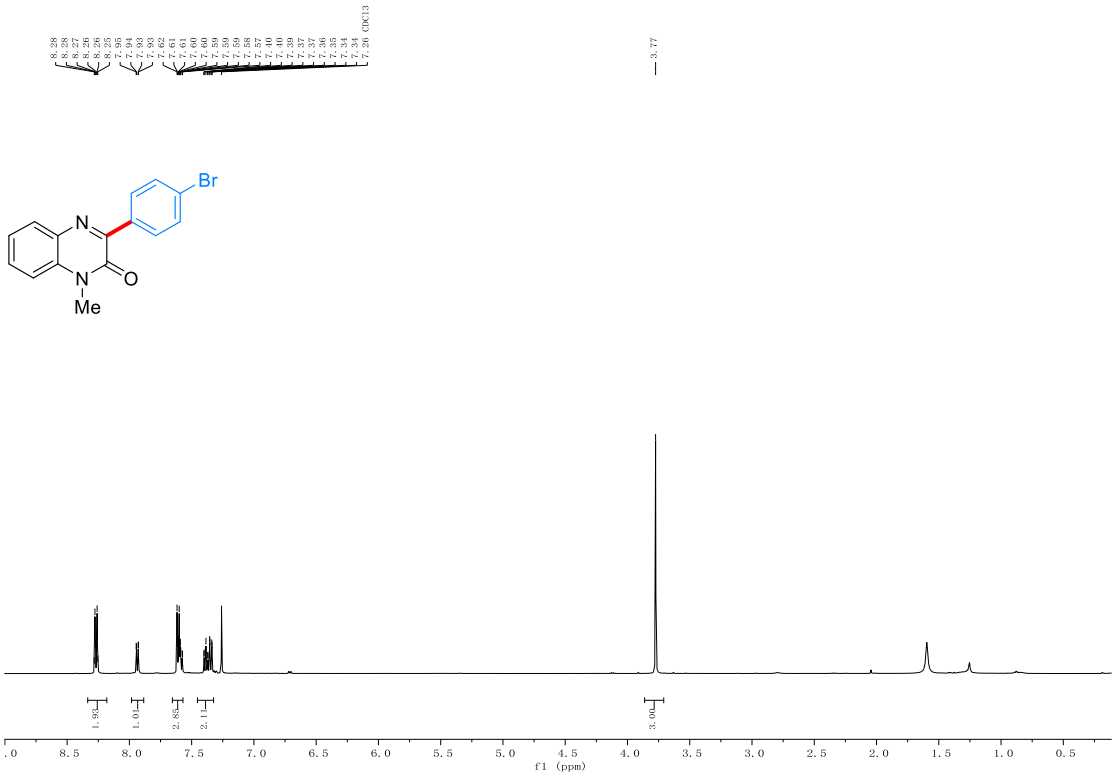


^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) spectrum of **3ah**

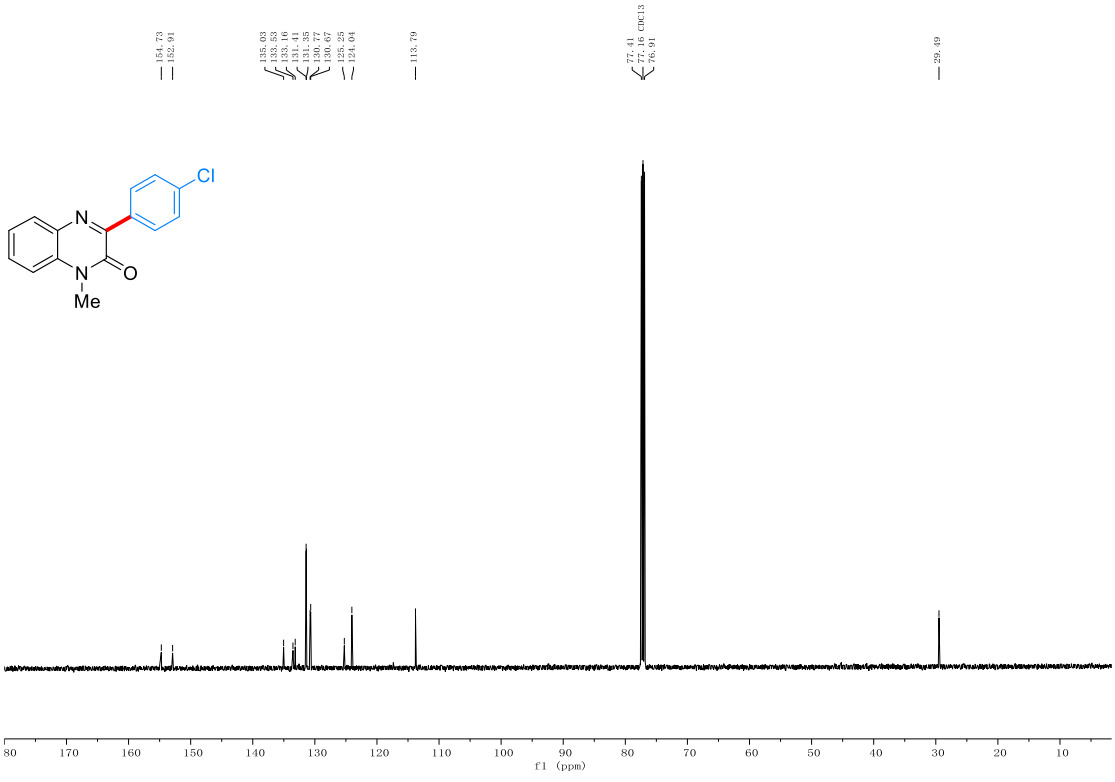


3-(4-bromophenyl)-1-methylquinoxalin-2(1*H*)-one (3ai)

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

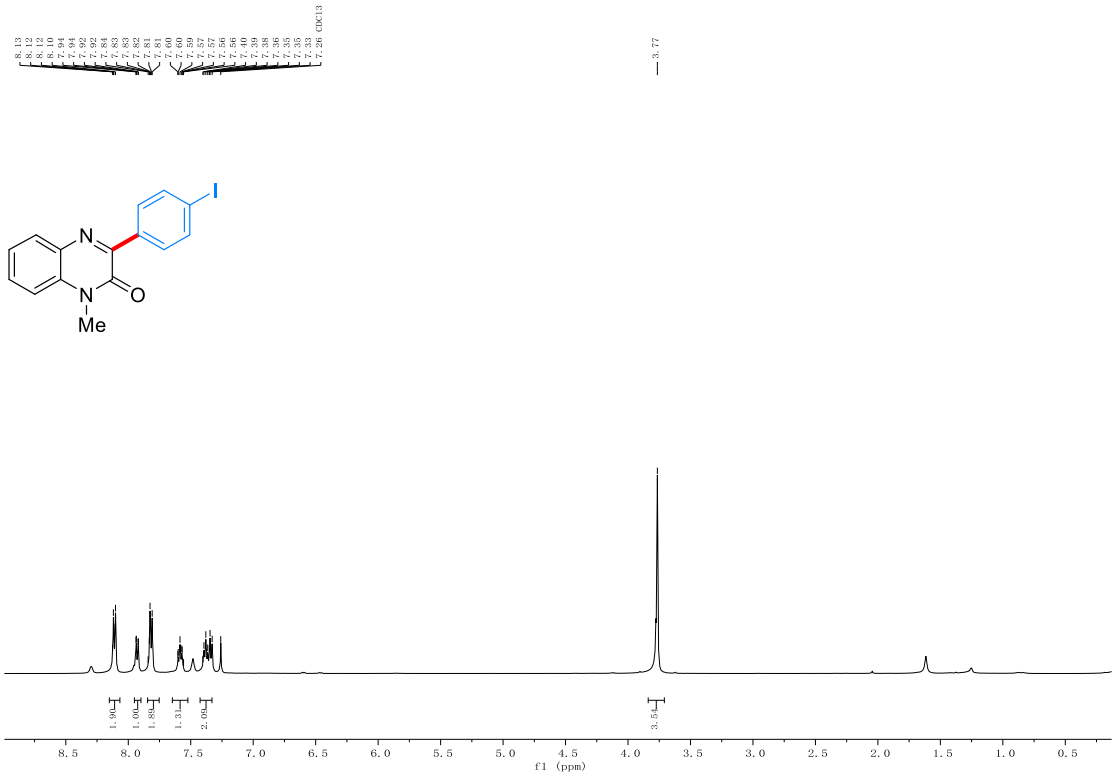


^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) spectrum of **3ai**



3-(4-iodophenyl)-1-methylquinoxalin-2(1*H*)-one (3aj)

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



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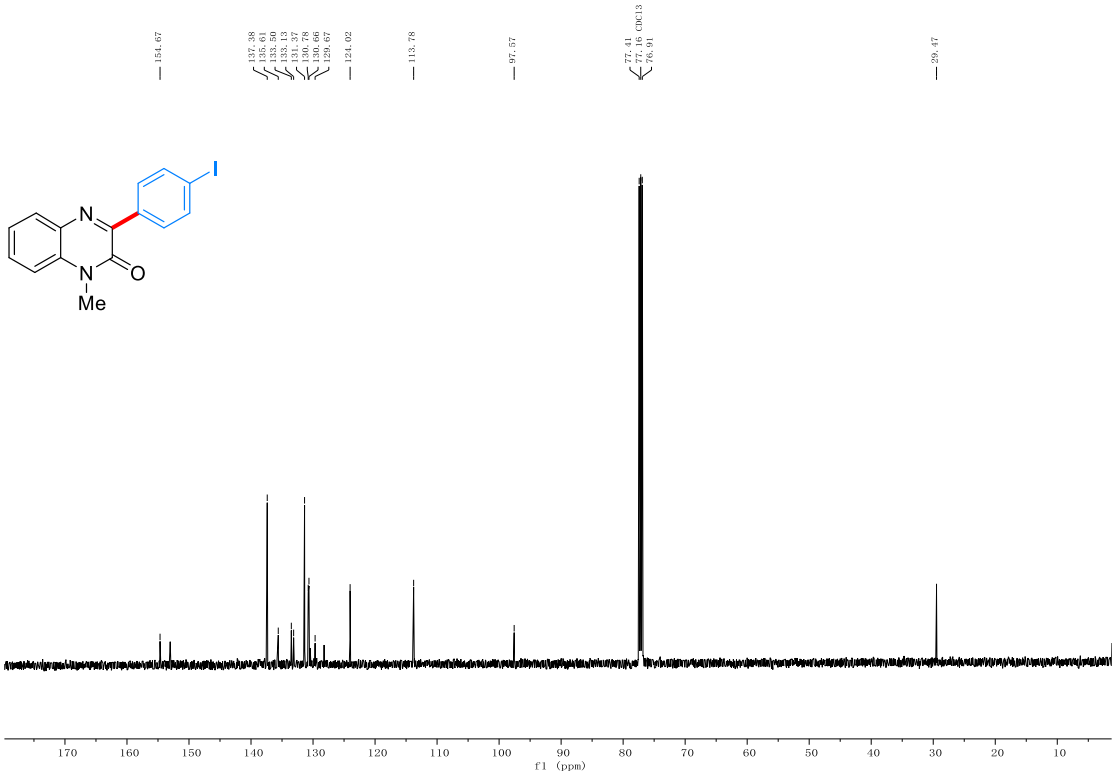
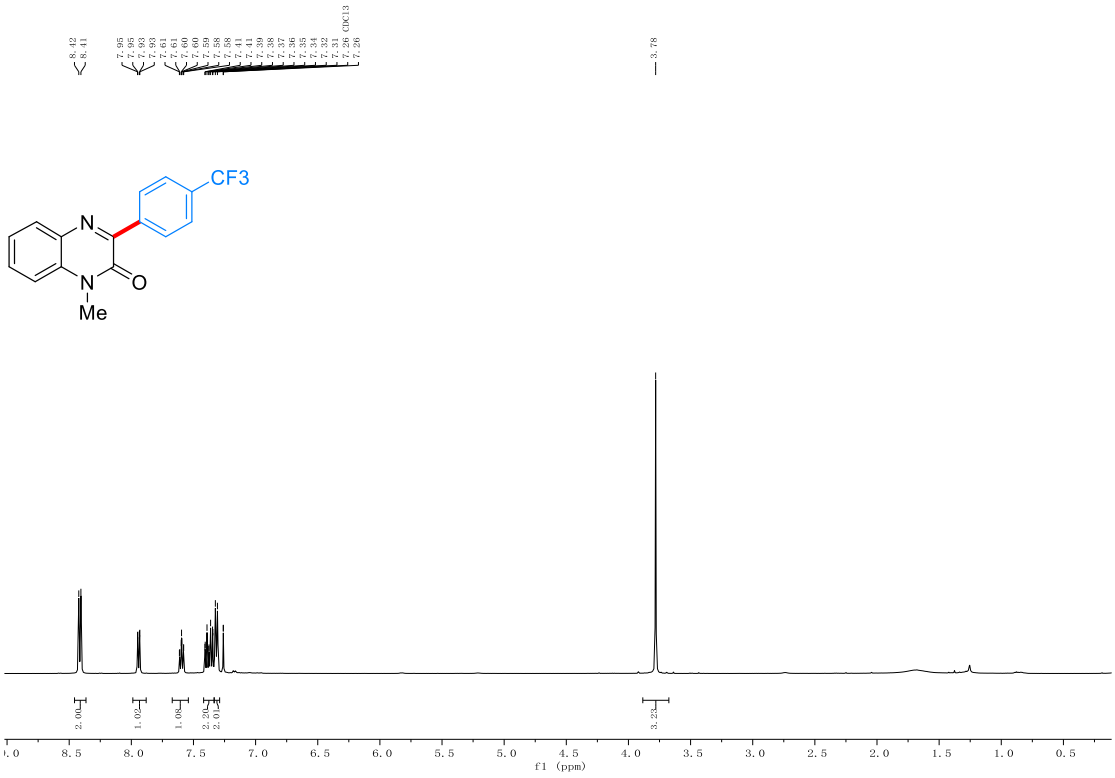
^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) spectrum of **3aj**

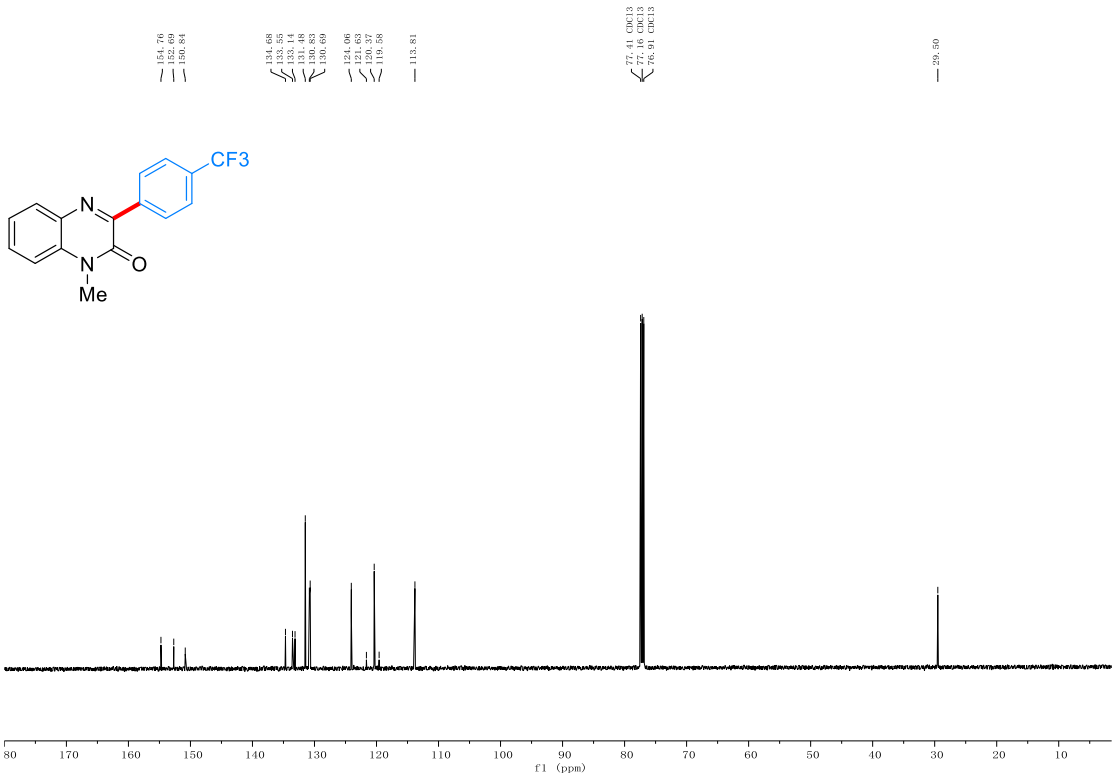


1-methyl-3-(4-(trifluoromethyl)phenyl)quinoxalin-2(1*H*)-one (3ak)

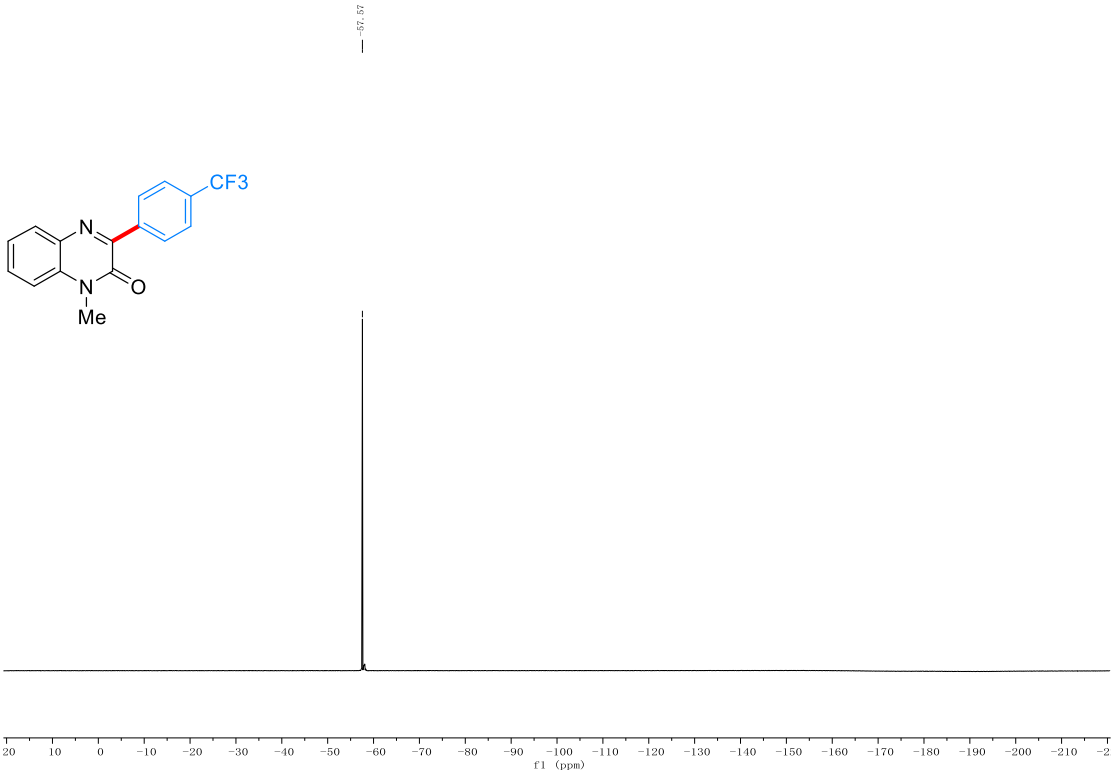
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **3ak**



^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) spectrum of **3ak**

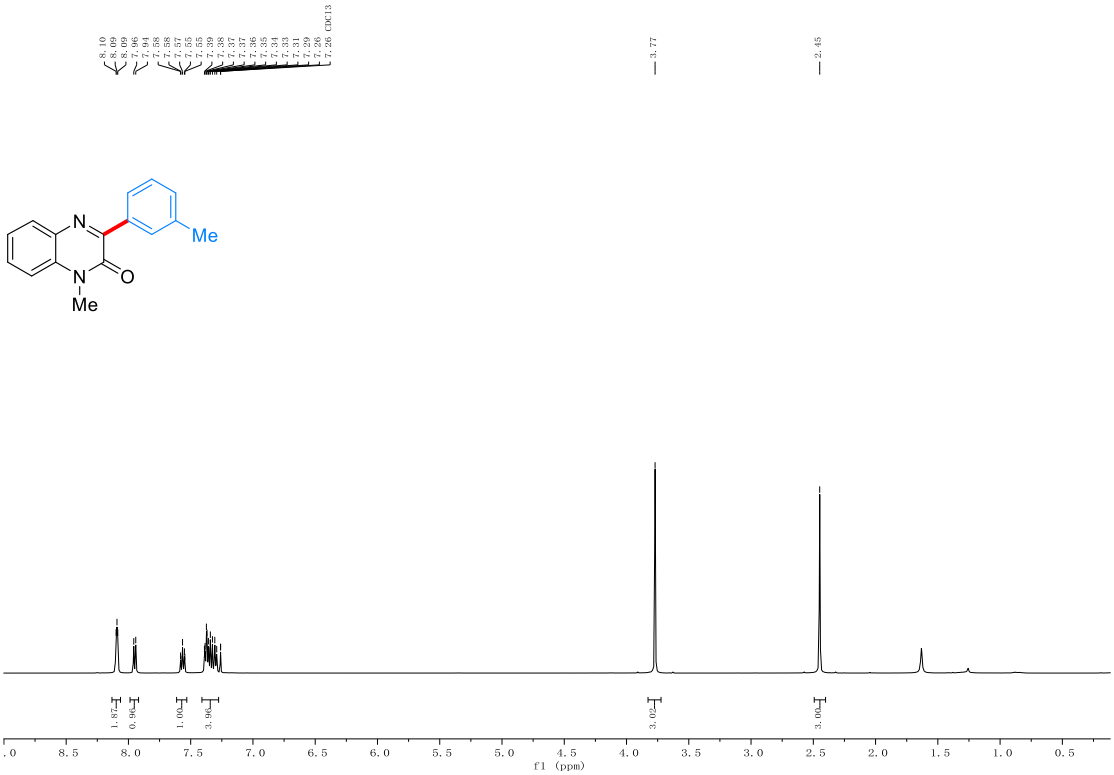


^{19}F NMR (471 MHz, $CDCl_3$) spectrum of **3ak**

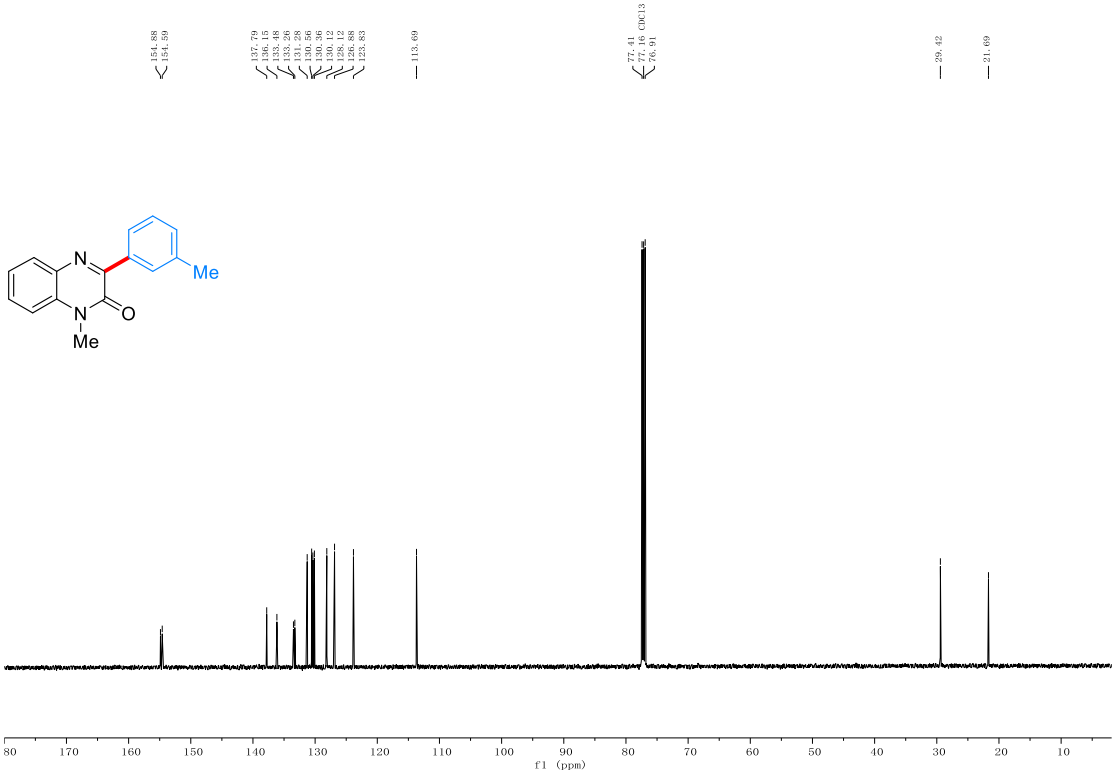


1-methyl-3-(m-tolyl)quinoxalin-2(1*H*)-one (3al)

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

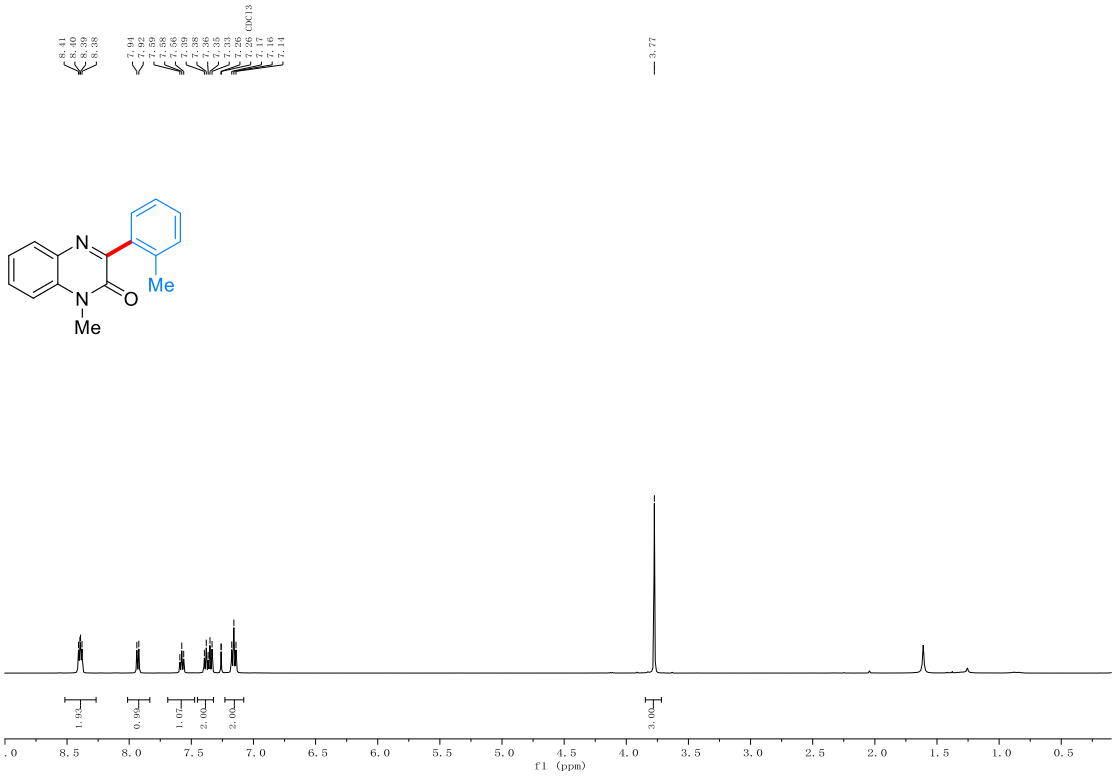


$^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$) spectrum of **3al**

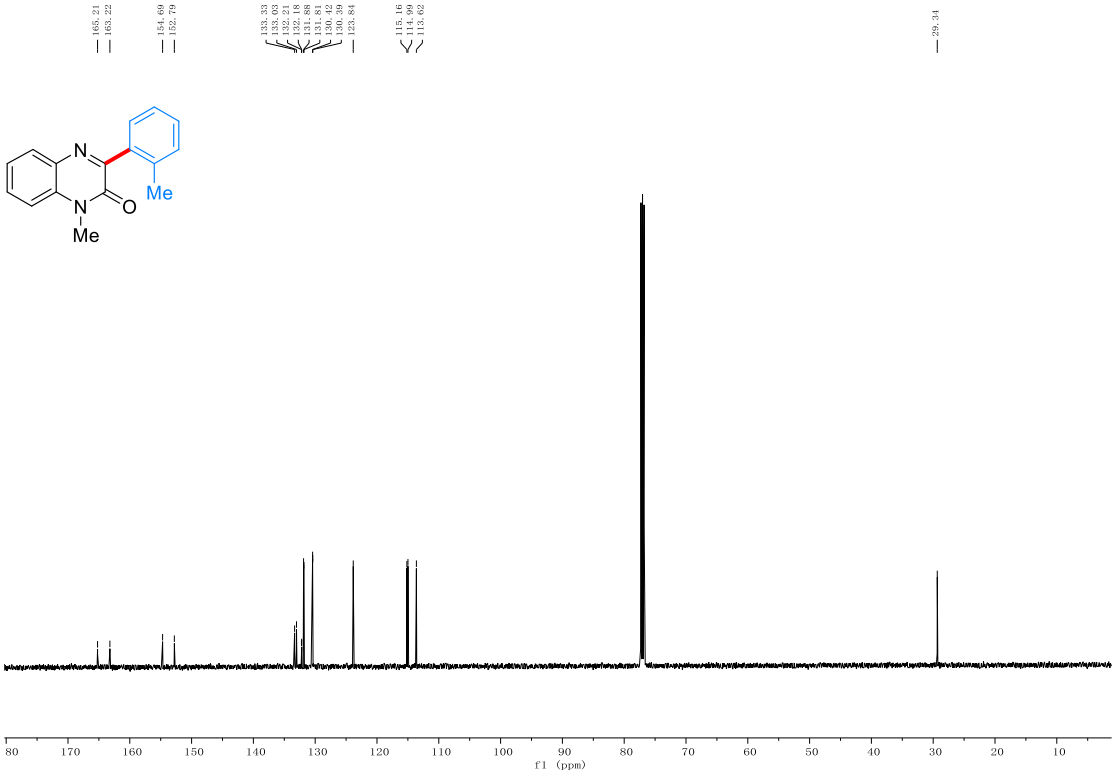


1-methyl-3-(o-tolyl)quinoxalin-2(1*H*)-one (3am)

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

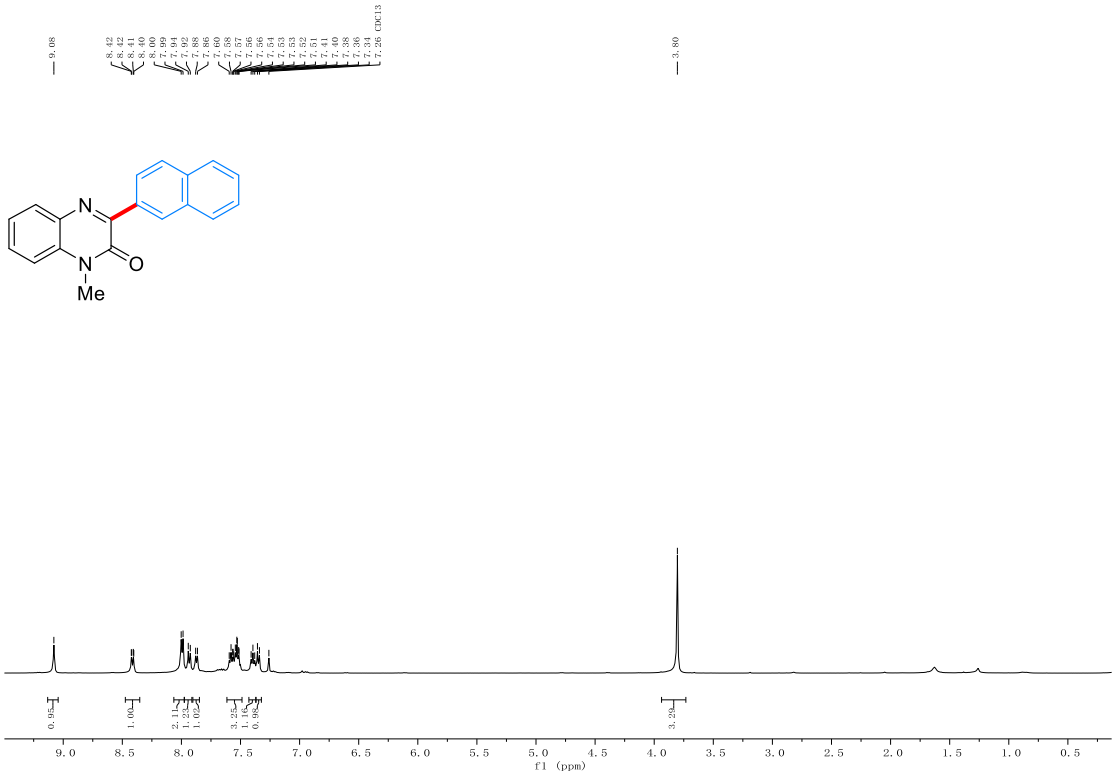


$^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$) spectrum of **3am**



1-methyl-3-(naphthalen-2-yl)quinoxalin-2(1*H*)-one (3an)

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



$^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$) spectrum of **3an**