Electronic Supplementary Information

Visible-light-mediated direct C3 alkylation of quinoxalin-2(1*H*)-ones with alkanes

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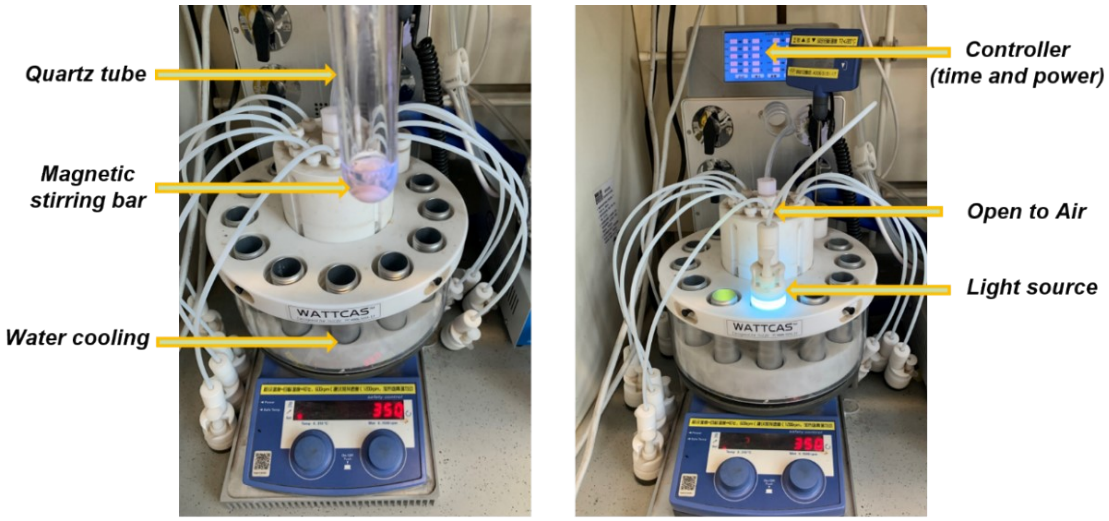
Contents

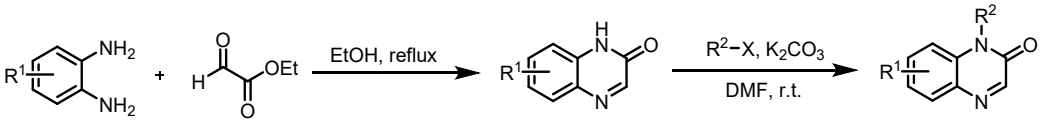
1. General Information

Unless specifically mentioned, all chemicals are commercially available and were used as received. ^{1}H NMR and ^{13}C NMR spectra was recorded on a Bruker Advance 400 spectrometer (400 MHz) at 298 K, and the chemical shifts (δ) were expressed in ppm and J values were given in Hz. For ^{1}H NMR: $CDCl_3$, δ 7.26; CD_3CN, δ 1.94; CD_2Cl_2, δ 5.32, acetone-d_6, δ 2.05; $(CD_3)_2SO$, δ 2.50. For ^{13}C NMR: $CDCl_3$, δ 77.06; CD_3CN, δ 1.32; CD_2Cl_2, δ 53.84, $(CD_3)_2SO$, δ 39.52. NMR data is reported as follows: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, brs = broad singlet; coupling constants in Hz. High-resolution mass spectrometry (HRMS) data were obtained on an FTICR-MS instrument (Ionspec 7.0 T). Conversion was monitored by thin layer chromatography (TLC). Flash column chromatography was performed over silica gel (100-200 mesh). The photocatalytic reaction was performed on WATTCAS Parallel Photocatalytic Reactor (WP-TEC-HSL) with 10W COB LED.



A: Experiment set up without light. **B:** Experiment set up with light.

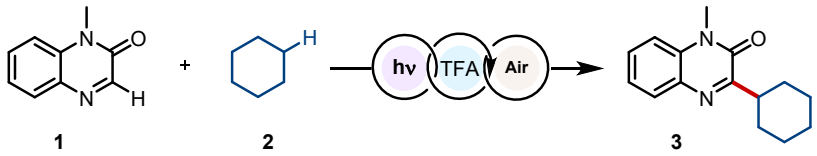
2. Preparation of quinoxalin-2(1H)-one



Quinoxalin-2(1*H*)-one was prepared from 1,2-phenylenediamines following the procedure of Cui and co-workers[1] on 5 mmol scale. To a solution of 1,2-phenylenediamines (5 mmol, 1.0 equiv.) in ethanol (40 mL) was added ethyl glyoxalate (6 mmol, 1.2 equiv.). The resultant reaction mixture was stirred at reflux until the raw material disappears. Then, the mixture was filtered and washed by ethanol. The solid was dried *in vacuo*. For alkylation, the corresponding halogenoalkane (1.6 equiv.) was added to a suspension of quinoxalinone (1.0 equiv.) and potassium carbonate (1.2 equiv.) in DMF (16 mL). The mixture was stirred at room temperature overnight. After complete reaction, brine was added, and then extracted three times with EtOAc. The combined organic layers were washed with a saturated solution of NH_4Cl then brine, dried

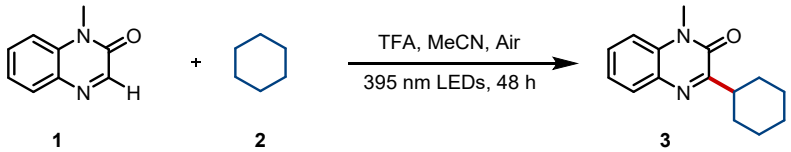
over anhydrous Na_2SO_4, filtered and evaporated *in vacuo*. The residue was purified by column chromatography on silica gel to afford the desired product. All the compounds were previously reported.

3. General photochemical procedures



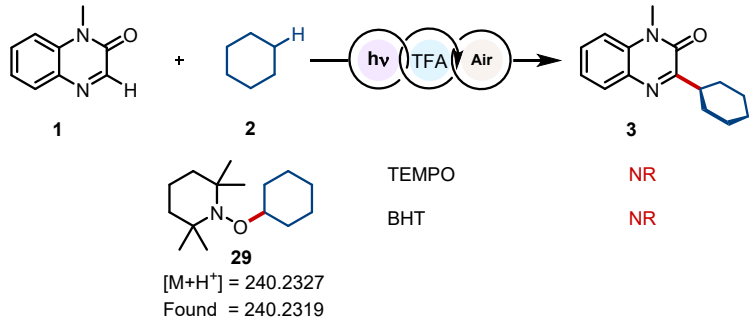
Quinoxalin-2(1*H*)-one (32.0 mg, 0.2 mmol, 1.0 equiv.), cyclohexane (0.5 mL), TFA (30.6 μL) and MeCN (2.0 mL) was added to an oven-dried quartz tube equipped with magnetic stirring bar. The reaction mixture was irradiated by purple LEDs (395 nm) for 24 h under air atmosphere at 25 °C. After irradiation, the reaction mixture was transferred to a 25 mL round-bottom flask and the solvent dried over anhydrous Na_2SO_4 and concentrated in vacuo. The pure product was obtained by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1).

4. Gram scale preparation



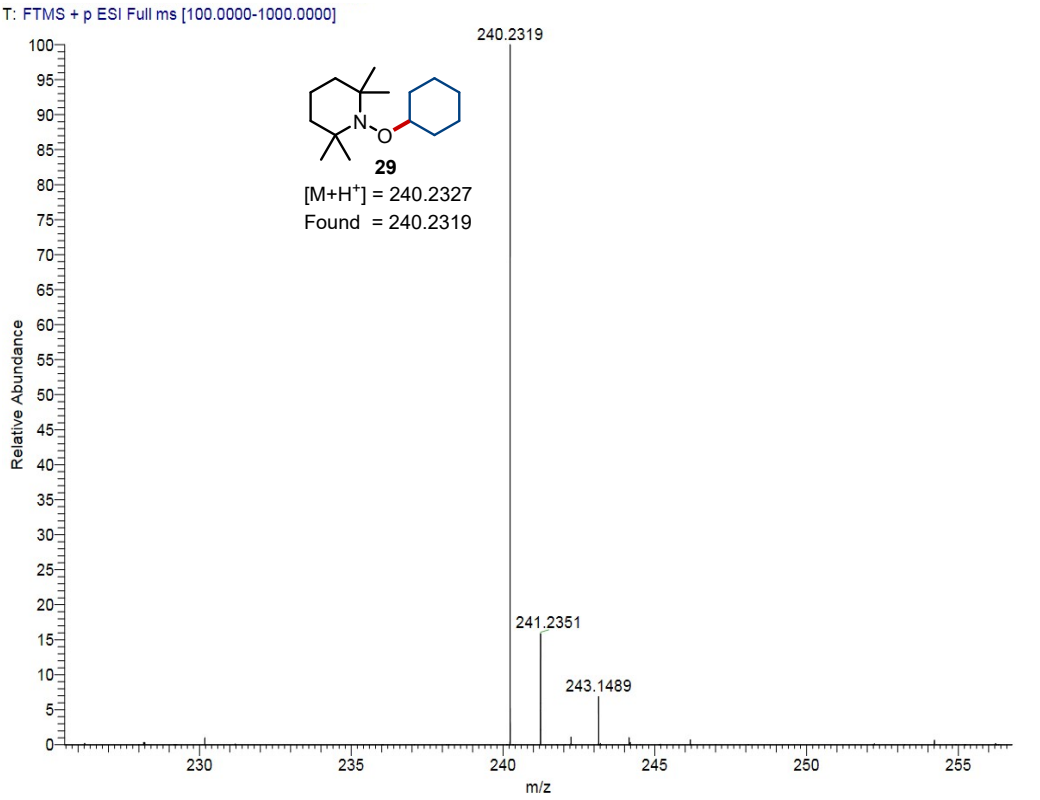
Quinoxalin-2(1*H*)-one (0.80 g, 5.0 mmol, 1.0 equiv.), cyclohexane (12.5 mL), TFA (0.7 mL) and MeCN (50 mL) was added to an oven-dried quartz tube equipped with magnetic stirring bar. The reaction mixture was irradiated by four purple LEDs (395 nm) for 48 h under air atmosphere at 25 °C. After irradiation, the reaction mixture was transferred to a 250 mL round-bottom flask and concentrated in vacuo, the remaining mixture was dissolved in dichloromethane, washed with saturated $NaHCO_3$ solution (50 mL×3), and the organic phase was dried over anhydrous Na_2SO_4. The pure product was obtained by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1) as white solid 0.95 g in 78% yield.

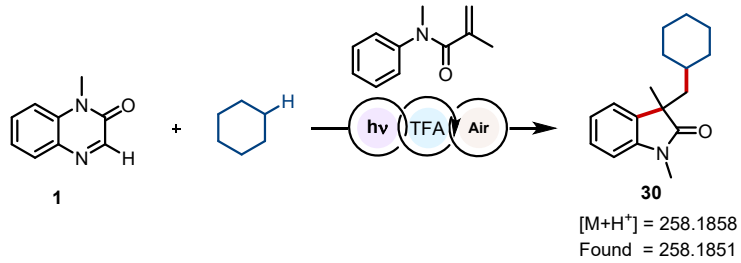
5. Mechanistic Studies



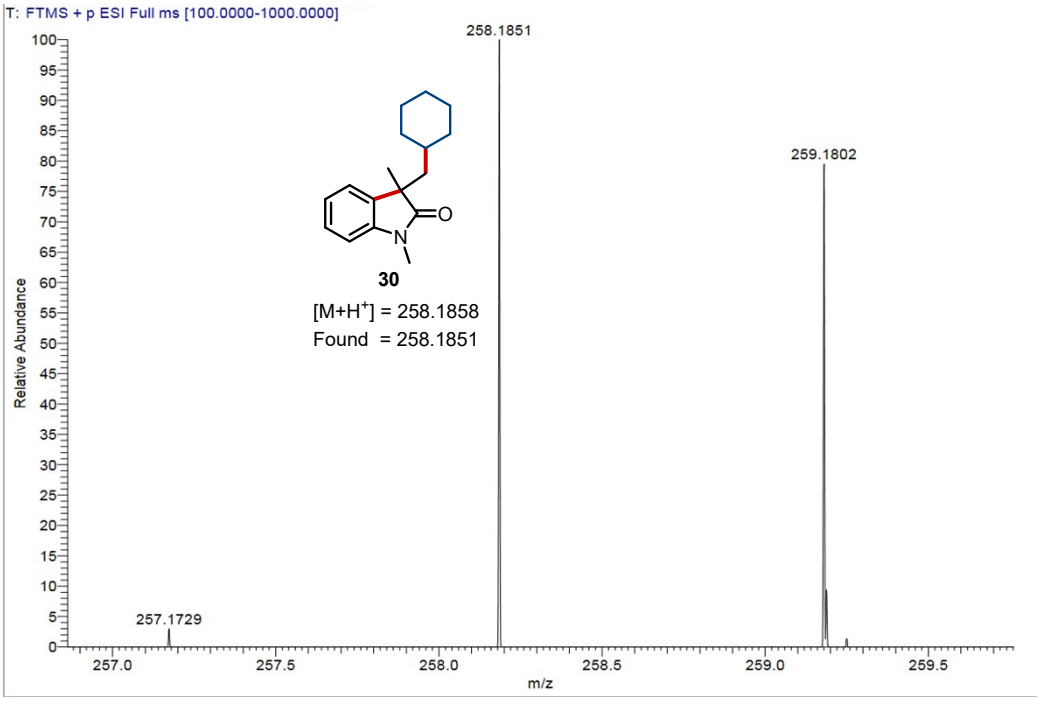
To a 10 mL oven-dried undivided bottle was added quinoxalin-2(1*H*)-one (32.0 mg, 0.2 mmol, 1.0 equiv.), cyclohexane (0.5 mL), TFA (30.6 μL), TEMPO (62.5 mg, 0.4 mmol, 2.0 equiv.) and MeCN (2.0 mL). The reaction mixture was irradiated by purple LEDs (395 nm) for 24 h under air

atmosphere at 25 °C. The reaction was completely suppressed and the radical trapping product 1-(cyclohexyloxy)-2,2,6,6-tetramethylpiperidine **29** can be observed by HR-MS (positive mode ESI). A similar procedure was conducted with BHT (220.4 mg, 1.0 mmol, 2.0 equiv.). The reaction was also completely suppressed.



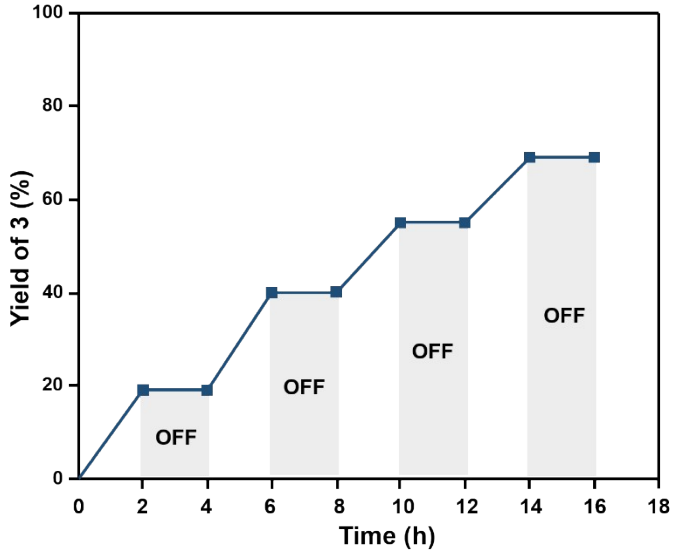


To a 10 mL oven-dried undivided bottle was added quinoxalin-2(1*H*)-one (32.0 mg, 0.2 mmol, 1.0 equiv.), cyclohexane (0.5 mL), N-methyl-N-phenyl methacrylamide (43.8 mg, 0.2 mmol, 1.0 equiv.), TFA (30.6 μL) and MeCN (2.0 mL). The reaction mixture was irradiated by purple LEDs (395 nm) for 24 h under air atmosphere at 25 °C. The product **30** can be observed by HR-MS (positive mode ESI).

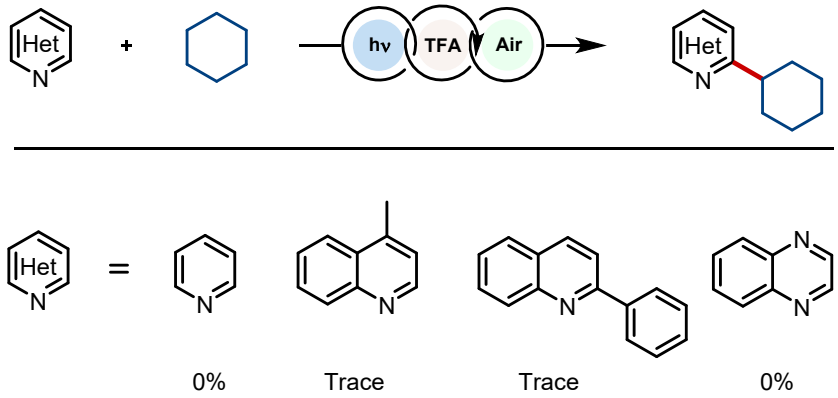


6. Light ON/OFF experiment

Eight standard reaction mixtures of an oven-dried 10 mL quartz tube were charged with Quinoxalin-2(1*H*)-one (32.0 mg, 0.2 mmol, 1.0 equiv.), cyclohexane (0.5 mL), TFA (30.6 μL) and MeCN (2.0 mL). The mixtures were then stirred and irradiated with purple LEDs (395 nm) at room temperature. After 2 h, the LED was turned off, and one vial was removed from the irradiation setup for analysis. The remaining seven vials were stirred in the absence of light for an additional 2 h. Then, one vial was removed for analysis, and the LED was turned back on to irradiate the remaining four reaction mixtures. After an additional 2 h of irradiation, the LED was turned off, and one vial was removed for analysis. The remaining six vials were stirred in the absence of light for an additional 2 h. Then, a vial was removed for analysis, and the LED was turned back on to irradiate the remaining two reaction mixtures. After 2 h, the LED was turned off, and one vial was removed for analysis. The remaining five vials were stirred in the absence of light for an additional 2 h and then it was analyzed. Then, a vial was removed for analysis, and the LED was turned back on to irradiate the remaining two reaction mixtures. After 2h, the LED was turned off, and one vial was removed for analysis. The remaining four vials were stirred in the absence of light for an additional 2 h and then it was analyzed. Then, a vial was removed for analysis, and the LED was turned back on to irradiate the remaining two reaction mixtures. After 2 h, the LED was turned off, and one vial was removed for analysis. The yield was determined by ^{1}H NMR spectroscopy using dibromomethane as the internal standard.

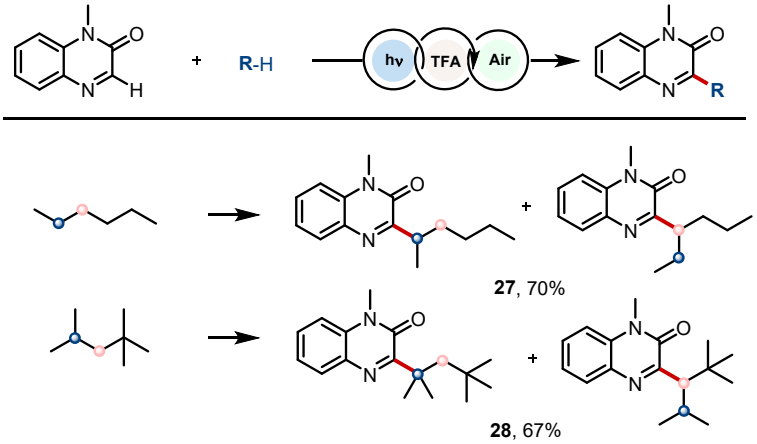


7. Details of Unsuccessful Substrates



Reaction conditions: Heterocycles (0.2 mmol), Cyclohexane (0.5 mL), TFA (2.0 equiv.), MeCN (1.5 mL), Purple LEDs (λ = 395 nm), room temperature (r.t.), under Air, 24 h.

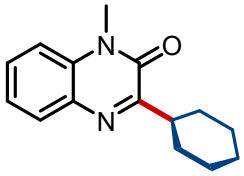
8. Details of other alkane Substrates



Reaction conditions: 1-methylquinoxalin-2(1*H*)-one (0.2 mmol), alkanes (0.5 mL), TFA (2.0 equiv.), MeCN (1.5 mL), Purple LEDs (λ = 395 nm), room temperature (r.t.), under Air, 24 h.

9. Characterization Data for Products

3-cyclohexyl-1-methylquinoxalin-2(1*H*)-one 3



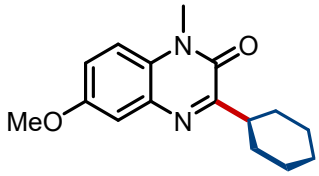
Photochemical reaction synthesis was conducted following the general procedure. The crude material was purified by flash column chromatography (silica gel, 20% EtOAc in petroleum ether) to give **3** as a white solid (42.1 mg, 87% yield).

Rf = 0.50 (Petroleum ether /EtOAc = 10:1);

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.84 (dd, J = 7.9, 1.1 Hz, 1H), 7.56 – 7.46 (m, 1H), 7.36 – 7.25 (m, 2H), 3.70 (s, 3H), 3.34 (tt, J = 11.5, 3.1 Hz, 1H), 1.96 (d, J = 11.6 Hz, 2H), 1.87 (d, J = 12.7 Hz, 2H), 1.77 (d, J = 12.6 Hz, 1H), 1.61 – 1.42 (m, 4H), 1.38 – 1.28 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 164.2, 154.5, 132.8, 132.8, 129.7, 129.3, 123.4, 113.4, 40.7, 30.5, 29.0, 26.3, 26.1.

3-cyclohexyl-6-methoxy-1-methylquinoxalin-2(1*H*)-one 4



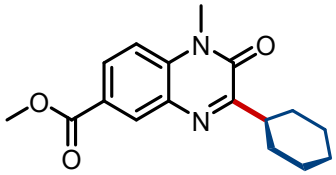
Photochemical reaction synthesis was conducted following the general procedure. The crude material was purified by flash column chromatography (silica gel, 10% EtOAc in petroleum ether) to give **4** as a white solid (39.7 mg, 73% yield).

Rf = 0.50 (Petroleum ether /EtOAc = 5:1);

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.74 (d, J = 8.8 Hz, 1H), 6.90 (dd, J = 8.9, 2.5 Hz, 1H), 6.69 (d, J = 2.4 Hz, 1H), 3.91 (s, 3H), 3.65 (s, 3H), 3.33 – 3.23 (m, 1H), 1.94 (d, J = 12.2 Hz, 2H), 1.86 (d, J = 12.5 Hz, 2H), 1.76 (d, J = 12.6 Hz, 1H), 1.60 – 1.43 (m, 4H), 1.36 – 1.29 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 160.9, 160.6, 154.9, 134.3, 131.0, 127.8, 110.2, 98.0, 55.8, 40.6, 30.6, 29.1, 26.4, 26.2.

3-cyclohexyl-1-methyl-2-oxo-1,2-dihydroquinoxaline-6-carboxylate 5

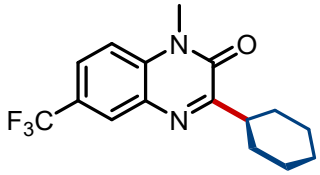


Photochemical reaction synthesis was conducted following the general procedure. The crude material was purified by flash column chromatography (silica gel, 10% EtOAc in petroleum ether) to give **5** as a yellow oil (49.2 mg, 82% yield).

Rf = 0.30 (Petroleum ether /EtOAc = 5:1);

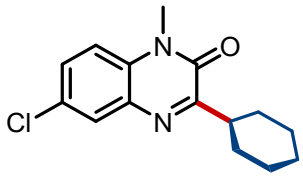
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.02 – 7.94 (m, 2H), 7.87 (d, J = 8.2 Hz, 1H), 3.98 (s, 3H), 3.74 (s, 3H), 3.36 (dd, J = 12.7, 9.8 Hz, 1H), 1.96 (d, J = 12.8 Hz, 2H), 1.87 (d, J = 12.5 Hz, 2H), 1.77 (d, J = 12.8 Hz, 1H), 1.59 – 1.46 (m, 4H), 1.35 – 1.28 (m, 1H).
^{13}C NMR (101 MHz, $CDCl_3$): δ 167.0, 166.3, 154.4, 135.6, 132.8, 130.4, 129.9, 124.2, 115.3, 52.6, 41.1, 30.5, 29.3, 26.3, 26.2.

3-cyclohexyl-1-methyl-6-(trifluoromethyl)quinoxalin-2(1*H*)-one 6



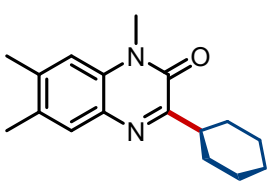
Photochemical reaction synthesis was conducted following the general procedure. The crude material was purified by flash column chromatography (silica gel, 20% EtOAc in petroleum ether) to give **6** as a white solid (56.4 mg, 91% yield).
Rf = 0.50 (Petroleum ether /EtOAc = 5:1);
^{1}H NMR (400 MHz, $CDCl_3$: δ 8.13 (s, 1H), 7.73 (d, J = 8.7 Hz, 1H), 7.37 (d, J = 8.7 Hz, 1H), 3.72 (s, 3H), 3.39 – 3.30 (m, 1H), 1.96 (d, J = 12.6 Hz, 2H), 1.88 (d, J = 12.5 Hz, 2H), 1.78 (d, J = 12.8 Hz, 1H), 1.57 – 1.46 (m, 4H), 1.35 – 1.30 (m, 1H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 166.1, 154.4, 135.3, 132.3, 127.3 (d, J = 3.7 Hz), 126.6 – 124.9 (m), 114.1, 40.9, 30.5, 29.8, 29.4, 26.3, 26.2.
^{19}F NMR (376 MHz, $CDCl_3$): δ -61.88.

6-chloro-3-cyclohexyl-1-methylquinoxalin-2(1*H*)-one 7



Photochemical reaction synthesis was conducted following the general procedure. The crude material was purified by flash column chromatography (silica gel, 20% EtOAc in petroleum ether) to give **7** as a white solid (44.2 mg, 80% yield).
Rf = 0.60 (Petroleum ether /EtOAc = 1:1);
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.84 (d, J = 2.1 Hz, 1H), 7.46 (dd, J = 8.9, 2.2 Hz, 1H), 7.21 (d, J = 8.9 Hz, 1H), 3.68 (s, 3H), 3.37 – 3.28 (m, 1H), 1.94 (d, J = 11.8 Hz, 2H), 1.86 (d, J = 12.3 Hz, 2H), 1.77 (d, J = 12.8 Hz, 1H), 1.57 – 1.44 (m, 4H), 1.35 – 1.27 (m, 1H).
^{13}C NMR (101 MHz, $CDCl_3$): δ 165.8, 154.2, 133.5, 131.6, 129.3, 129.2, 128.7, 114.6, 40.9, 30.5, 29.3, 26.3, 26.2.

3-cyclohexyl-1,6,7-trimethylquinoxalin-2(1*H*)-one 8



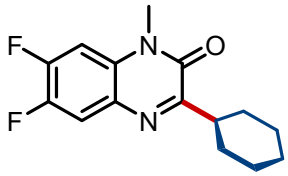
Photochemical reaction synthesis was conducted following the general procedure. The crude material was purified by flash column chromatography (silica gel, 10% EtOAc in petroleum ether) to give **8** as a white solid (37.3 mg, 69% yield).

Rf = 0.60 (Petroleum ether /EtOAc = 5:1);

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.60 (s, 1H), 7.04 (s, 1H), 3.67 (s, 3H), 3.31 (t, J = 11.3 Hz, 1H), 2.40 (s, 3H), 2.34 (s, 3H), 1.94 (d, J = 12.6 Hz, 2H), 1.86 (d, J = 12.5 Hz, 2H), 1.76 (d, J = 13.2 Hz, 1H), 1.59 – 1.44 (m, 4H), 1.36 – 1.27 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 163.0, 154.7, 139.0, 132.3, 131.3, 130.9, 129.9, 114.1, 40.7, 30.6, 29.0, 26.4, 26.2, 20.5, 19.1.

3-cyclohexyl-6,7-difluoro-1-methylquinoxalin-2(1*H*)-one 9



Photochemical reaction synthesis was conducted following the general procedure. The crude material was purified by flash column chromatography (silica gel, 20% EtOAc in petroleum ether) to give **9** as a white solid (49.5 mg, 89% yield).

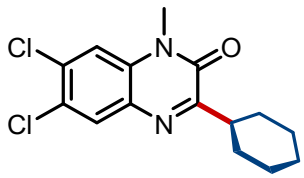
Rf = 0.50 (Petroleum ether /EtOAc = 5:1);

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.64 (t, J = 8.5 Hz, 1H), 7.07 (dd, J = 11.4, 7.1 Hz, 1H), 3.64 (s, 3H), 3.30 (t, J = 10.3 Hz, 1H), 1.92 (d, J = 11.5 Hz, 2H), 1.86 (d, J = 11.7 Hz, 2H), 1.76 (d, J = 13.2 Hz, 1H), 1.57 – 1.42 (m, 4H), 1.35 – 1.28 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 164.8, 154.1(d, J = 1.5 Hz), 150.8 (dd, J = 252.3, 16.3 Hz), 146.5 (dd, J = 245.3, 13.0 Hz), 130.0 (d, J = 9.1 Hz), 129.1 (d, J = 9.3 Hz), 117.3 (d, J = 18.0 Hz), 102.0 (d, J = 23.4 Hz), 40.8, 30.5, 29.5, 26.2, 26.1.

^{19}F NMR (376 MHz, $CDCl_3$): δ -132.22 – -132.38 (m), -142.63 – -142.78 (m).

6,7-dichloro-3-cyclohexyl-1-methylquinoxalin-2(1*H*)-one 10



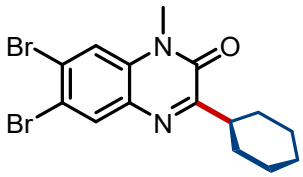
Photochemical reaction synthesis was conducted following the general procedure. The crude material was purified by flash column chromatography (silica gel, 20% EtOAc in petroleum ether) to give **10** as a white solid (52.1 mg, 84% yield).

Rf = 0.50 (Petroleum ether /EtOAc = 5:1);

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.92 (s, 1H), 7.36 (s, 1H), 3.65 (s, 3H), 3.30 (td, J = 11.1, 3.1 Hz, 1H), 1.93 (d, J = 11.0 Hz, 2H), 1.86 (d, J = 12.4 Hz, 2H), 1.77 (d, J = 12.8 Hz, 1H), 1.54 – 1.42 (m, 4H), 1.34 – 1.27 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 165.9, 154.0, 133.4, 132.4, 132.0, 130.7, 127.2, 115.0, 40.9, 30.5, 29.4, 26.2, 26.1.

6,7-dibromo-3-cyclohexyl-1-methylquinoxalin-2(1*H*)-one 11



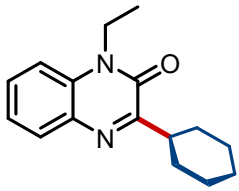
Photochemical reaction synthesis was conducted following the general procedure. The crude material was purified by flash column chromatography (silica gel, 20% EtOAc in petroleum ether) to give **11** as a yellow oil (63.7 mg, 80% yield).

Rf = 0.50 (Petroleum ether /EtOAc = 5:1);

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.08 (s, 1H), 7.54 (s, 1H), 3.64 (s, 3H), 3.30 (t, *J* = 11.0 Hz, 1H), 1.93 (d, *J* = 10.7 Hz, 2H), 1.86 (d, *J* = 12.3 Hz, 2H), 1.76 (d, *J* = 13.0 Hz, 1H), 1.54 – 1.42 (m, 4H), 1.32 (d, *J* = 12.6 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 166.1, 154.0, 133.8, 132.9, 130.4, 125.5, 118.2, 100.0, 40.9, 30.5, 29.3, 26.2, 26.1.

3-cyclohexyl-1-ethylquinoxalin-2(1*H*)-one 12



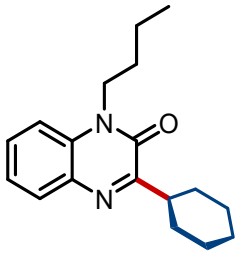
Photochemical reaction synthesis was conducted following the general procedure. The crude material was purified by flash column chromatography (silica gel, 10% EtOAc in petroleum ether) to give **12** as a white solid (41.5 mg, 81% yield).

Rf = 0.80 (Petroleum ether /EtOAc = 2:1);

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.85 (dd, *J* = 8.3, 1.2 Hz, 1H), 7.54 – 7.48 (m, 1H), 7.32 (dd, *J* = 7.6, 6.5 Hz, 2H), 4.32 (q, *J* = 7.1 Hz, 2H), 3.41 – 3.30 (m, 1H), 1.96 (d, *J* = 11.9 Hz, 2H), 1.87 (d, *J* = 12.6 Hz, 2H), 1.77 (d, *J* = 12.6 Hz, 1H), 1.54 (dt, *J* = 28.4, 11.9 Hz, 4H), 1.38 (t, *J* = 7.2 Hz, 3H), 1.31 (d, *J* = 12.5 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$): δ164.3, 154.0, 133.2, 131.8, 130.1, 129.4, 123.2, 113.3, 40.6, 37.3, 30.6, 26.4, 26.2, 12.5.

1-butyl-3-cyclohexylquinoxalin-2(1*H*)-one 13



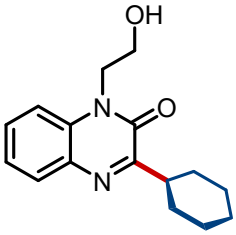
Photochemical reaction synthesis was conducted following the general procedure. The crude material was purified by flash column chromatography (silica gel, 20% EtOAc in petroleum ether) to give **13** as a yellow oil (43.7 mg, 77% yield).

Rf = 0.70 (Petroleum ether /EtOAc = 5:1);

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (dd, J = 7.9, 1.3 Hz, 1H), 7.52 – 7.46 (m, 1H), 7.33 – 7.27 (m, 2H), 4.28 – 4.22 (m, 2H), 3.34 (tt, J = 11.5, 3.2 Hz, 1H), 1.96 (d, J = 11.7 Hz, 2H), 1.90 – 1.84 (m, 2H), 1.82 – 1.68 (m, 4H), 1.62 – 1.54 (m, 2H), 1.52 – 1.46 (m, 3H), 1.37 – 1.28 (m, 1H), 1.00 (t, J = 7.3 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 164.3, 154.3, 133.2, 132.1, 130.0, 129.3, 123.2, 113.5, 42.2, 40.8, 30.6, 29.4, 26.4, 26.2, 20.4, 13.8.

3-cyclohexyl-1-(2-hydroxyethyl)quinoxalin-2(1*H*)-one 14



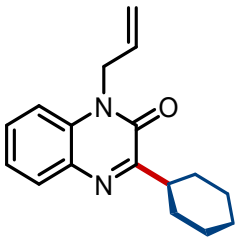
Photochemical reaction synthesis was conducted following the general procedure. The crude material was purified by flash column chromatography (silica gel, 20% EtOAc in petroleum ether) to give **14** as a white solid (42.5 mg, 78% yield).

Rf = 0.10 (Petroleum ether /EtOAc = 5:1);

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.97 (d, J = 8.1 Hz, 1H), 7.75 (d, J = 8.1 Hz, 1H), 7.56 (dt, J = 15.0, 7.1 Hz, 2H), 4.72 – 4.66 (m, 2H), 4.09 – 4.03 (m, 2H), 3.43 (s, 1H), 3.19 (tt, J = 11.7, 3.1 Hz, 1H), 1.97 (d, J = 12.3 Hz, 2H), 1.90 (d, J = 12.8 Hz, 2H), 1.83 – 1.75 (m, 1H), 1.74 – 1.65 (m, 2H), 1.52 – 1.40 (m, 2H), 1.39 – 1.32 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 155.6, 154.8, 139.0, 138.7, 129.0, 128.5, 126.6, 126.3, 69.2, 62.3, 40.7, 30.8, 26.5, 26.1.

1-allyl-3-cyclohexylquinoxalin-2(1*H*)-one 15



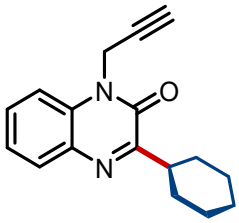
Photochemical reaction synthesis was conducted following the general procedure. The crude material was purified by flash column chromatography (silica gel, 20% EtOAc in petroleum ether) to give **15** as a white solid (43.9 mg, 82% yield).

Rf = 0.40 (Petroleum ether /EtOAc = 5:1);

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.84 (d, J = 8.0 Hz, 1H), 7.47 (t, J = 7.8 Hz, 1H), 7.30 (dd, J = 15.4, 7.9 Hz, 2H), 6.00 – 5.88 (m, 1H), 5.26 (d, J = 10.4 Hz, 1H), 5.17 (d, J = 17.2 Hz, 1H), 4.90 (dd, J = 3.5, 1.6 Hz, 2H), 3.41 – 3.31 (m, 1H), 1.97 (d, J = 11.7 Hz, 2H), 1.87 (d, J = 12.5 Hz, 2H), 1.77 (d, J = 12.5 Hz, 1H), 1.61 – 1.45 (m, 4H), 1.38 – 1.29 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 164.4, 154.1, 133.1, 132.1, 130.8, 129.9, 129.3, 123.4, 118.0, 114.0, 44.6, 40.8, 30.6, 26.4, 26.2.

3-cyclohexyl-1-(prop-2-yn-1-yl)quinoxalin-2(1*H*)-one 16



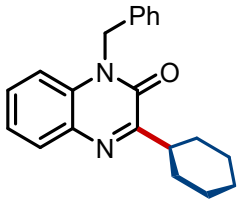
Photochemical reaction synthesis was conducted following the general procedure. The crude material was purified by flash column chromatography (silica gel, 10% EtOAc in petroleum ether) to give **16** as a white solid (41.0 mg, 77% yield).

Rf = 0.3 (Petroleum ether /EtOAc = 5:1);

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.85 (d, J = 7.9 Hz, 1H), 7.54 (t, J = 7.8 Hz, 1H), 7.44 (s, 1H), 7.35 (t, J = 7.6 Hz, 1H), 5.05 (d, J = 2.3 Hz, 2H), 3.33 (tt, J = 11.6, 3.2 Hz, 1H), 2.28 (t, J = 2.3 Hz, 1H), 1.96 (d, J = 11.5 Hz, 2H), 1.87 (d, J = 12.6 Hz, 2H), 1.77 (d, J = 12.8 Hz, 1H), 1.59 – 1.42 (m, 4H), 1.37 – 1.27 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 164.2, 153.5, 133.1, 131.4, 130.0, 129.5, 123.8, 114.0, 73.1, 40.9, 31.5, 30.6, 29.7, 26.3, 26.2.

1-benzyl-3-cyclohexylquinoxalin-2(1*H*)-one 17



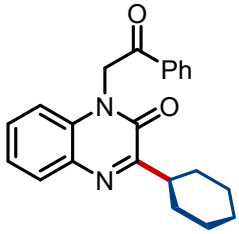
Photochemical reaction synthesis was conducted following the general procedure. The crude material was purified by flash column chromatography (silica gel, 20% EtOAc in petroleum ether) to give **17** as a white solid (52.8 mg, 83% yield).

Rf = 0.50 (Petroleum ether /EtOAc = 5:1);

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.12 – 8.06 (m, 2H), 7.87 (dd, J = 7.9, 1.3 Hz, 1H), 7.67 (t, J = 7.4 Hz, 1H), 7.55 (t, J = 7.7 Hz, 2H), 7.42 – 7.36 (m, 1H), 7.31 (dd, J = 11.1, 4.1 Hz, 1H), 6.93 (d, J = 8.3 Hz, 1H), 5.72 (s, 2H), 3.33 (tt, J = 11.6, 3.2 Hz, 1H), 1.99 (d, J = 11.8 Hz, 2H), 1.87 (d, J = 12.8 Hz, 2H), 1.76 (d, J = 12.4 Hz, 1H), 1.61 – 1.39 (m, 4H), 1.38 – 1.28 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 164.0, 154.3, 134.6, 134.3, 133.1, 132.3, 130.1, 129.5, 129.1, 128.3, 123.6, 113.4, 48.5, 40.9, 30.5, 26.3, 26.2.

3-cyclohexyl-1-(2-oxo-2-phenylethyl)quinoxalin-2(1*H*)-one 18



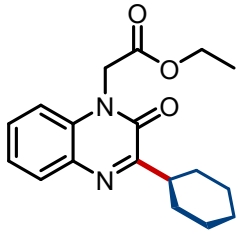
Photochemical reaction synthesis was conducted following the general procedure. The crude material was purified by flash column chromatography (silica gel, 20% EtOAc in petroleum ether) to give **18** as a white solid (60.9 mg, 88% yield).

Rf = 0.20 (Petroleum ether /EtOAc = 5:1);

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.08 (d, J = 7.3 Hz, 2H), 7.87 (dd, J = 7.9, 1.4 Hz, 1H), 7.67 (t, J = 7.4 Hz, 1H), 7.55 (t, J = 7.7 Hz, 2H), 7.42 – 7.36 (m, 1H), 7.30 (dd, J = 11.1, 4.1 Hz, 1H), 6.93 (d, J = 8.2 Hz, 1H), 5.72 (s, 2H), 3.38 – 3.28 (m, 1H), 1.99 (d, J = 11.8 Hz, 2H), 1.92 – 1.84 (m, 2H), 1.76 (d, J = 12.5 Hz, 1H), 1.65 – 1.55 (m, 2H), 1.52 – 1.40 (m, 2H), 1.37 – 1.29 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 191.5, 163.9, 154.3, 134.3, 133.1, 132.3, 130.1, 129.5, 129.1, 128.2, 123.6, 113.3, 48.5, 40.9, 30.5, 26.3, 26.2.

2-(3-cyclohexyl-2-oxoquinoxalin-1(2*H*)-yl)acetate 19



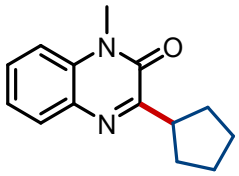
Photochemical reaction synthesis was conducted following the general procedure. The crude material was purified by flash column chromatography (silica gel, 20% EtOAc in petroleum ether) to give **19** as a white solid (53.4 mg, 85% yield).

Rf = 0.20 (Petroleum ether /EtOAc = 10:1);

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.86 (d, J = 7.9 Hz, 1H), 7.47 (t, J = 7.8 Hz, 1H), 7.32 (t, J = 7.4 Hz, 1H), 7.05 (d, J = 8.3 Hz, 1H), 5.01 (s, 2H), 4.25 (q, J = 7.1 Hz, 2H), 3.32 (ddd, J = 11.5, 8.4, 3.1 Hz, 1H), 1.97 (d, J = 12.0 Hz, 2H), 1.87 (d, J = 12.6 Hz, 2H), 1.76 (d, J = 12.5 Hz, 1H), 1.66 – 1.52 (m, 3H), 1.52 – 1.41 (m, 2H), 1.27 (t, J = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 167.3, 164.1, 154.1, 133.0, 132.0, 130.2, 129.6, 123.7, 112.9, 62.0, 43.6, 40.8, 30.5, 26.3, 26.2, 14.1.

3-cyclopentyl-1-methylquinoxalin-2(1*H*)-one 20



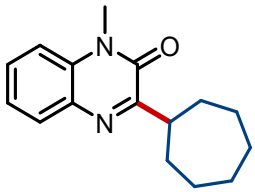
Photochemical reaction synthesis was conducted following the general procedure. The crude material was purified by flash column chromatography (silica gel, 20% EtOAc in petroleum ether) to give **20** as a white solid (40.6 mg, 89% yield).

Rf = 0.50 (Petroleum ether /EtOAc = 1:1);

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.82 (dd, J = 8.0, 1.3 Hz, 1H), 7.53 – 7.47 (m, 1H), 7.36 – 7.27 (m, 2H), 3.74 – 3.71 (m, 1H), 3.70 (s, 3H), 2.13 – 2.03 (m, 2H), 1.97 – 1.88 (m, 2H), 1.87 – 1.78 (m, 2H), 1.76 – 1.66 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 163.8, 155.0, 133.0, 132.7, 129.8, 129.3, 123.4, 113.5, 42.8, 31.9, 29.1, 26.0.

3-cycloheptyl-1-methylquinoxalin-2(1*H*)-one 21



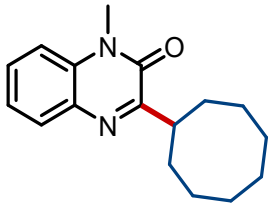
Photochemical reaction synthesis was conducted following the general procedure. The crude material was purified by flash column chromatography (silica gel, 20% EtOAc in petroleum ether) to give **21** as a white solid (34.8 mg, 68% yield).

Rf = 0.60 (Petroleum ether /EtOAc = 1:1);

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.83 (dd, *J* = 8.0, 1.4 Hz, 1H), 7.54 – 7.48 (m, 1H), 7.35 – 7.27 (m, 2H), 3.70 (s, 3H), 3.53 – 3.45 (m, 1H), 2.03 – 1.97 (m, 1H), 1.97 – 1.94 (m, 1H), 1.86 (dd, *J* = 11.1, 4.5 Hz, 2H), 1.81 (d, *J* = 3.3 Hz, 1H), 1.80 – 1.77 (m, 1H), 1.75 – 1.67 (m, 2H), 1.67 – 1.62 (m, 3H), 1.25 (s, 1H).

^{13}C NMR (101 MHz, $CDCl_3$): *δ* 165.4, 154.5, 132.9, 132.8, 129.8, 129.4, 123.5, 113.5, 42.5, 32.3, 29.1, 28.2, 27.2.

3-cyclooctyl-1-methylquinoxalin-2(1*H*)-one 22



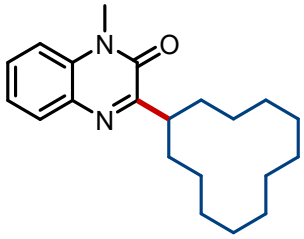
Photochemical reaction synthesis was conducted following the general procedure. The crude material was purified by flash column chromatography (silica gel, 30% EtOAc in petroleum ether) to give **22** as a white solid (38.4 mg, 71% yield).

Rf = 0.60 (Petroleum ether /EtOAc = 1:1);

^{1}H NMR (400 MHz, $CDCl_3$): *δ* 7.83 (d, *J* = 7.9 Hz, 1H), 7.51 (t, *J* = 7.7 Hz, 1H), 7.36 – 7.27 (m, 2H), 3.70 (s, 3H), 3.61 – 3.51 (m, 1H), 1.92 – 1.86 (m, 4H), 1.82 – 1.78 (m, 1H), 1.73 – 1.61 (m, 9H).

^{13}C NMR (101 MHz, $CDCl_3$): *δ* 165.9, 154.6, 132.9, 132.8, 129.8, 129.3, 123.5, 113.5, 40.5, 30.6, 29.1, 26.7, 26.6, 26.0.

3-cyclododecyl-1-methylquinoxalin-2(1*H*)-one 23



Photochemical reaction synthesis was conducted following the general procedure. The crude material was purified by flash column chromatography (silica gel, 20% EtOAc in petroleum ether) to give **23** as a white solid (43.7 mg, 67% yield).

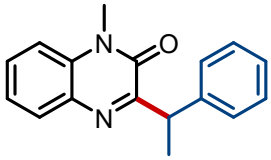
Rf = 0.60 (Petroleum ether /EtOAc = 5:1);

^{1}H NMR (400 MHz, $CDCl_3$): *δ* 7.87 – 7.83 (m, 1H), 7.54 – 7.48 (m, 1H), 7.35 – 7.27 (m, 2H), 3.71 (s, 3H), 3.70 – 3.67 (m, 1H), 1.79 – 1.76 (m, 3H), 1.63 – 1.59 (m, 2H), 1.49 – 1.41 (m, 8H), 1.40 – 1.33

(m, 9H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 164.5, 155.0, 132.9, 132.9, 129.8, 129.4, 123.4, 113.5, 36.2, 29.1, 28.1, 24.0, 23.9, 23.6, 23.3, 23.1.

(*R*)-1-methyl-3-(1-phenylethyl)quinoxalin-2(1*H*)-one 24



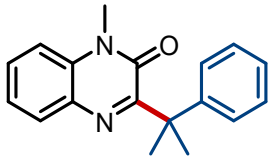
Photochemical reaction synthesis was conducted following the general procedure. The crude material was purified by flash column chromatography (silica gel, 20% EtOAc in petroleum ether) to give **24** as a white solid (38.0 mg, 72% yield; For 10 equiv. ethylbenzene 25.9 mg, 49% yield).

Rf = 0.30 (Petroleum ether /EtOAc = 5:1);

^{1}H NMR (400 MHz, $CDCl_3$): *δ* 7.92 (dd, *J* = 8.0, 1.3 Hz, 1H), 7.54 – 7.48 (m, 1H), 7.44 (d, *J* = 7.2 Hz, 2H), 7.37 – 7.32 (m, 1H), 7.30 – 7.23 (m, 3H), 7.17 (t, *J* = 7.3 Hz, 1H), 4.82 (q, *J* = 7.1 Hz, 1H), 3.62 (s, 3H), 1.68 (d, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): *δ* 161.9, 154.5, 143.2, 133.1, 132.8, 130.2, 129.7, 128.4, 128.2, 126.5, 123.5, 113.5, 41.9, 29.1, 19.7.

1-methyl-3-(2-phenylpropan-2-yl)quinoxalin-2(1*H*)-one 25



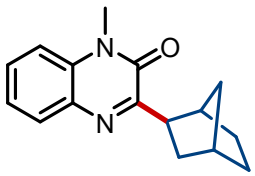
Photochemical reaction synthesis was conducted following the general procedure. The crude material was purified by flash column chromatography (silica gel, 20% EtOAc in petroleum ether) to give **25** as a white solid (44.5 mg, 80% yield; For 10 equiv. cumene 31.7 mg, 57% yield).

Rf = 0.50 (Petroleum ether /EtOAc = 5:1);

^{1}H NMR (400 MHz, $CDCl_3$): *δ* 7.94 (dd, *J* = 8.0, 1.3 Hz, 1H), 7.57 – 7.51 (m, 1H), 7.39 – 7.34 (m, 1H), 7.31 – 7.27 (m, 5H), 7.21 – 7.15 (m, 1H), 3.55 (s, 3H), 1.80 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$): *δ* 164.2, 153.2, 147.4, 133.7, 132.1, 130.3, 129.8, 128.2, 125.9, 125.4, 123.3, 113.4, 46.1, 28.9, 27.7.

3-((1*R*,2*R*,4*S*)-bicyclo[2.2.1]heptan-2-yl)-1-methylquinoxalin-2(1*H*)-one 26



Photochemical reaction synthesis was conducted following the general procedure. The crude material was purified by flash column chromatography (silica gel, 20% EtOAc in petroleum ether) to give **26** as a white solid (32.0 mg, 63% yield).

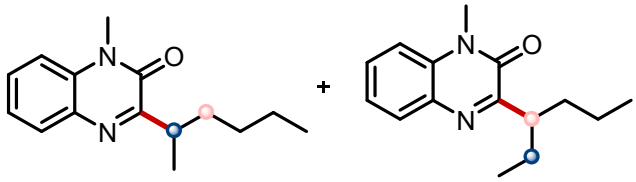
Rf = 0.40 (Petroleum ether /EtOAc = 5:1);

^{1}H NMR (400 MHz, $CDCl_3$): *δ* 7.84 (dd, *J* = 8.0, 1.3 Hz, 1H), 7.54 – 7.47 (m, 1H), 7.36 – 7.28 (m,

2H), 3.70 (s, 3H), 3.32 (dd, *J* = 8.6, 5.6 Hz, 1H), 2.49 (s, 1H), 2.38 (s, 1H), 2.25 – 2.18 (m, 1H), 1.65 (d, *J* = 3.8 Hz, 1H), 1.61 (d, *J* = 2.0 Hz, 1H), 1.60 – 1.56 (m, 1H), 1.56 – 1.51 (m, 2H), 1.37 – 1.32 (m, 1H), 1.11 (d, *J* = 9.4 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$): *δ* 162.9, 155.0, 132.9, 132.6, 129.9, 129.3, 123.4, 113.4, 44.5, 41.6, 36.7, 35.6, 34.0, 30.2, 29.2, 29.0.

(*R*)-3-(hexan-2-yl)-1-methylquinoxalin-2(1*H*)-one and **(*R*)-3-(hexan-3-yl)-1-methylquinoxalin-2(1*H*)-one 27**



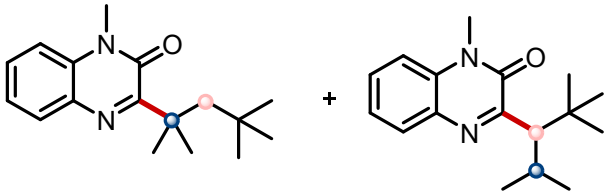
Photochemical reaction synthesis was conducted following the general procedure. The crude material was purified by flash column chromatography (silica gel, 20% EtOAc in petroleum ether) to give **27** as a white solid (34.1 mg, 70% yield).

Rf = 0.50 (Petroleum ether /EtOAc = 5:1);

^{1}H NMR (400 MHz, $CDCl_3$) *δ* 7.85 (d, *J* = 7.9 Hz, 2H), 7.51 (t, *J* = 7.8 Hz, 2H), 7.37 – 7.27 (m, 4H), 3.71 (s, 6H), 3.57 – 3.48 (m, 1H), 3.47 – 3.39 (m, 1H), 1.94 – 1.80 (m, 3H), 1.75 – 1.65 (m, 2H), 1.64 – 1.51 (m, 2H), 1.35 – 1.30 (m, 4H), 1.28 (d, *J* = 6.9 Hz, 4H), 0.92 – 0.85 (m, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) *δ* 164.8, 164.1, 155.1, 154.7, 132.9, 132.8, 132.8, 129.8, 129.8, 129.5, 123.4, 123.4, 113.5, 42.9, 36.1, 35.3, 34.5, 29.8, 29.2, 29.1, 26.2, 22.9, 20.8, 18.3, 14.4, 14.1, 12.1.

1-methyl-3-(2,4,4-trimethylpentan-2-yl)quinoxalin-2(1*H*)-one and **(*R*)-1-methyl-3-(2,2,4-trimethylpentan-3-yl)quinoxalin-2(1*H*)-one 28**



Photochemical reaction synthesis was conducted following the general procedure. The crude material was purified by flash column chromatography (silica gel, 20% EtOAc in petroleum ether) to give **28** as a yellow oil (36.5 mg, 67% yield).

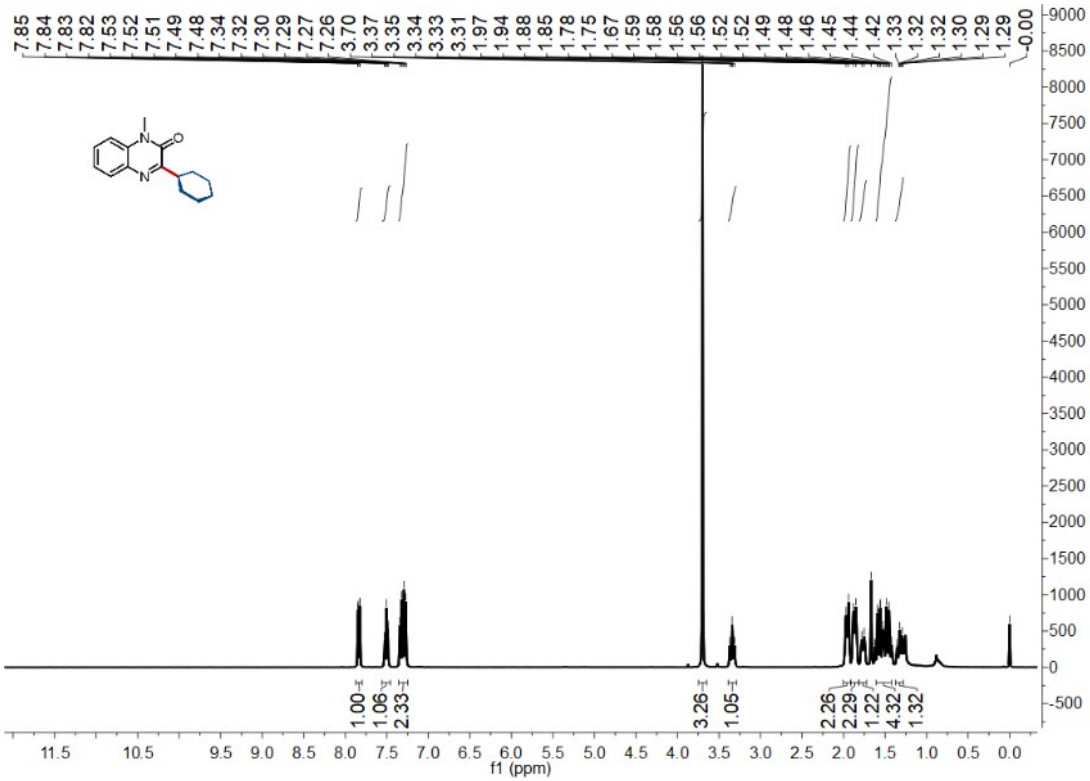
Rf = 0.50 (Petroleum ether /EtOAc = 5:1);

^{1}H NMR (400 MHz, $CDCl_3$) *δ* 7.84 (d, *J* = 7.9 Hz, 2H), 7.53 (t, *J* = 7.8 Hz, 2H), 7.37 – 7.28 (m, 4H), 3.70 (s, 6H), 2.93 (s, 4H), 1.88 – 1.77 (m, 2H), 1.35 (d, *J* = 5.1 Hz, 4H), 1.03 (s, 12H), 0.96 (d, *J* = 6.6 Hz, 12H).

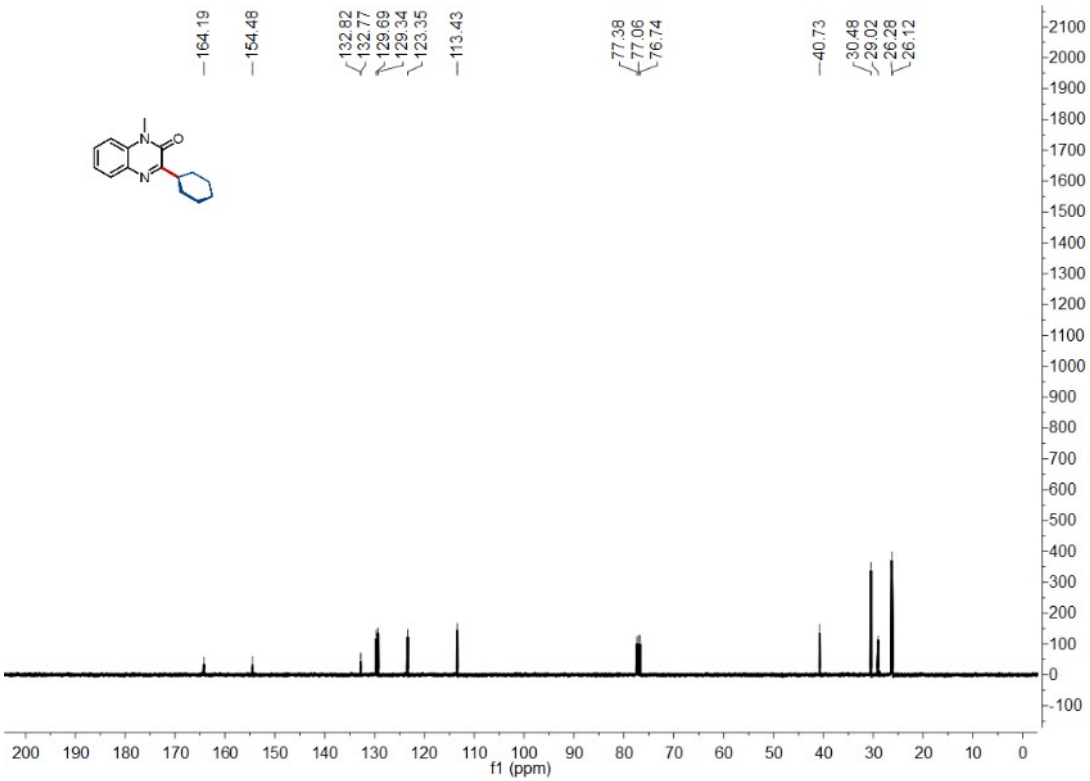
^{13}C NMR (101 MHz, $CDCl_3$) *δ* 160.3, 155.6, 133.1, 132.6, 129.8, 129.6, 123.5, 113.6, 51.9, 44.0, 36.6, 30.0, 29.7, 29.3, 27.5, 25.6, 24.3.

10. Spectra of prepared compounds

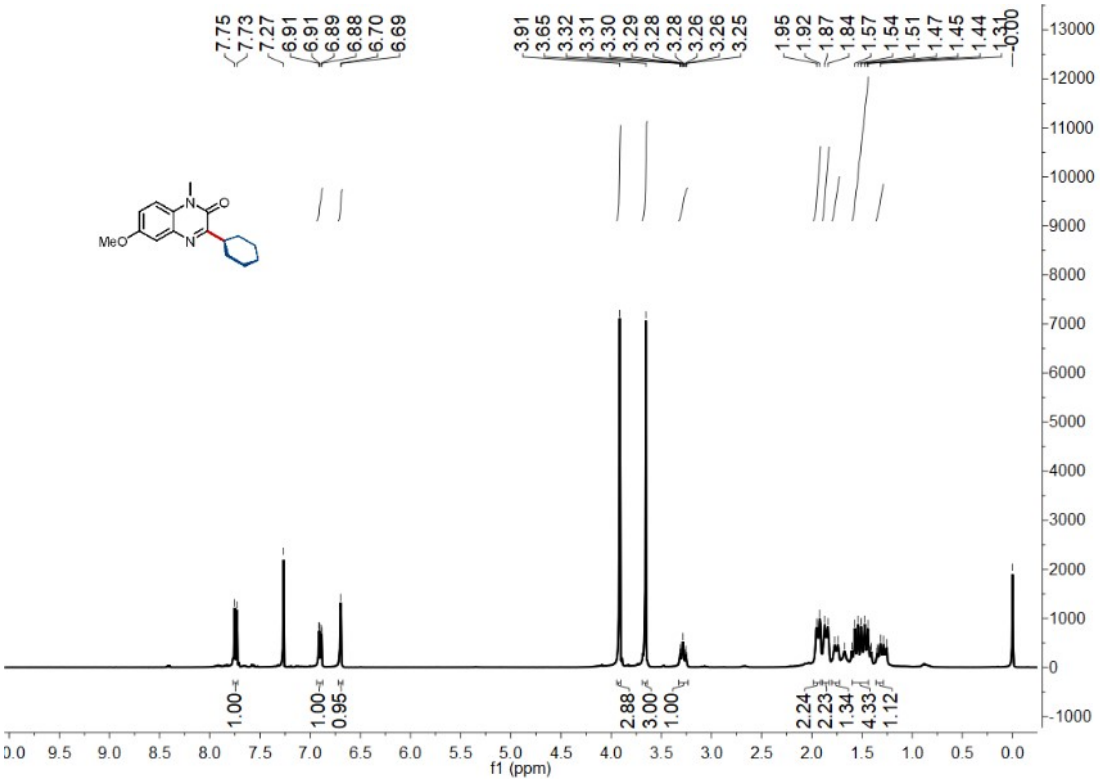
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **3**



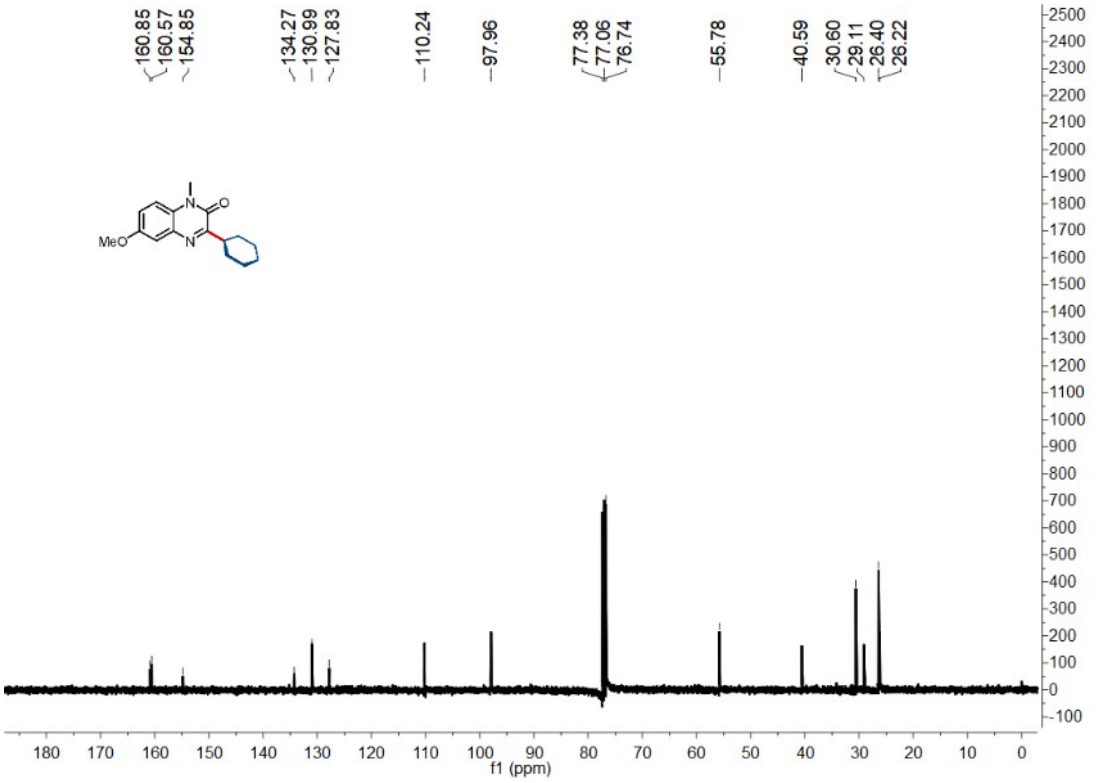
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of compound **3**



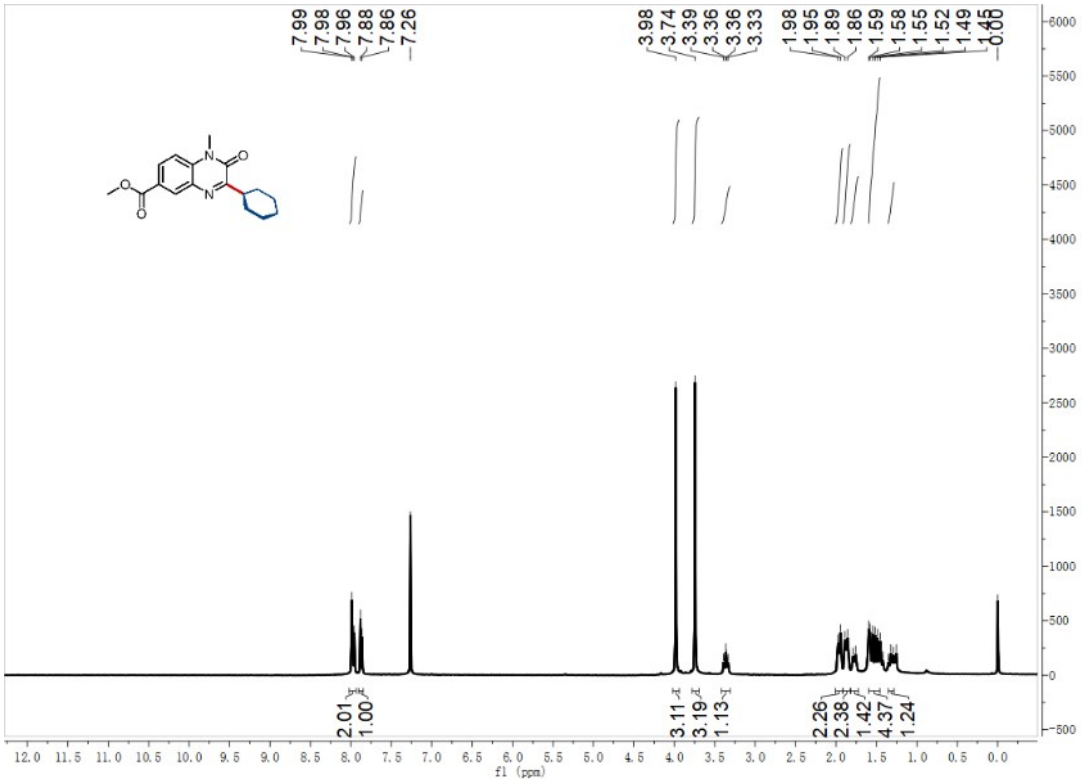
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **4**



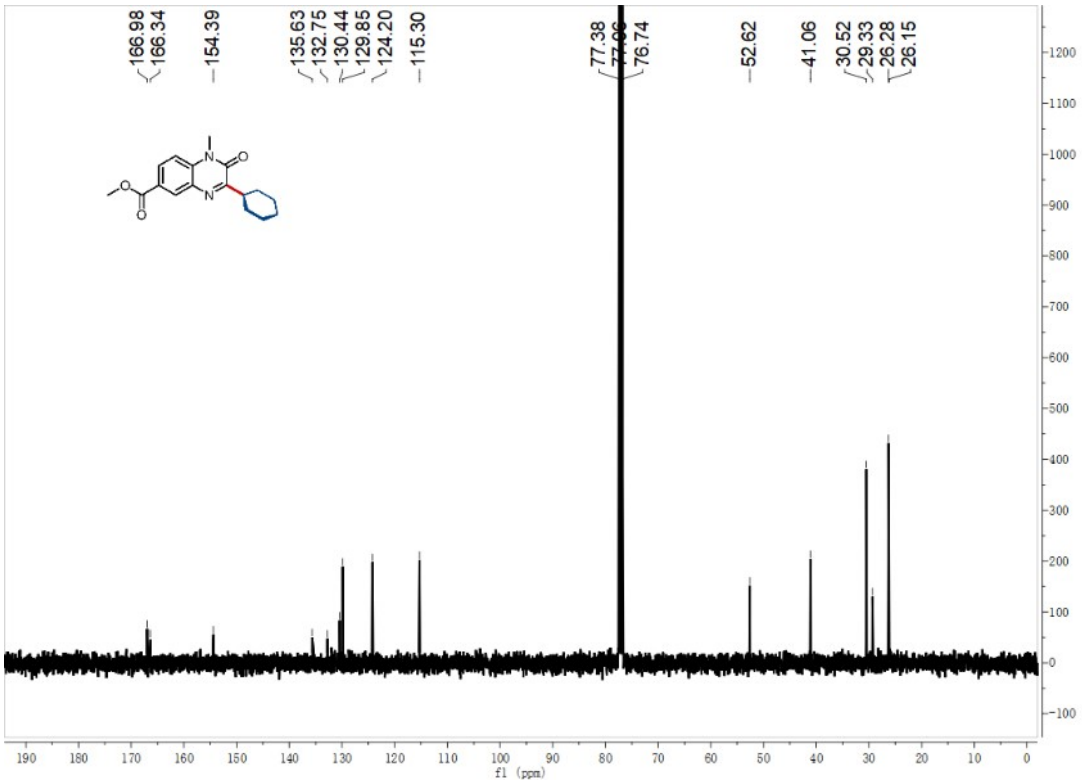
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of compound **4**



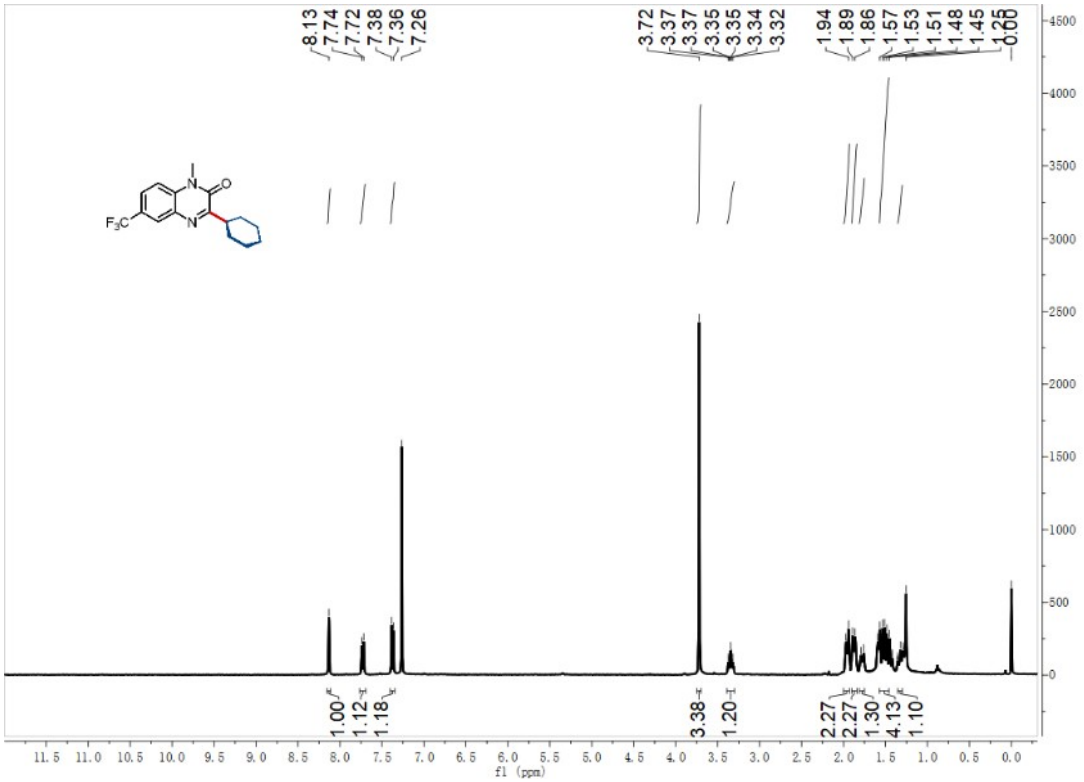
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **5**



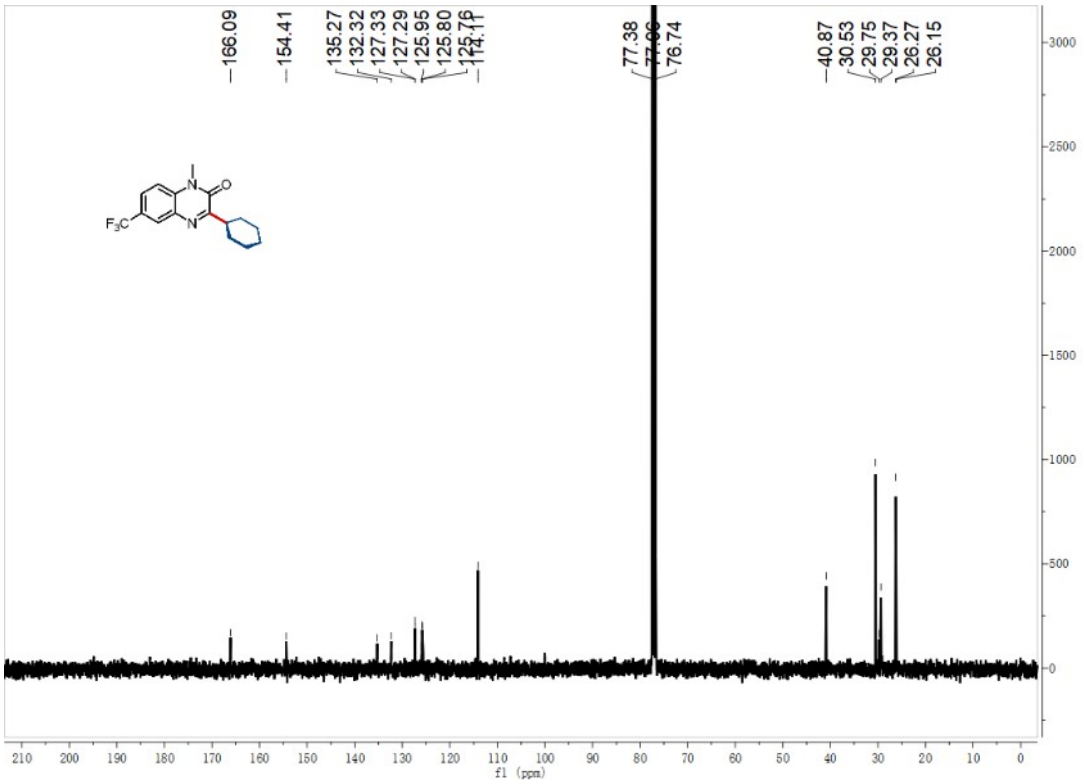
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of compound **5**



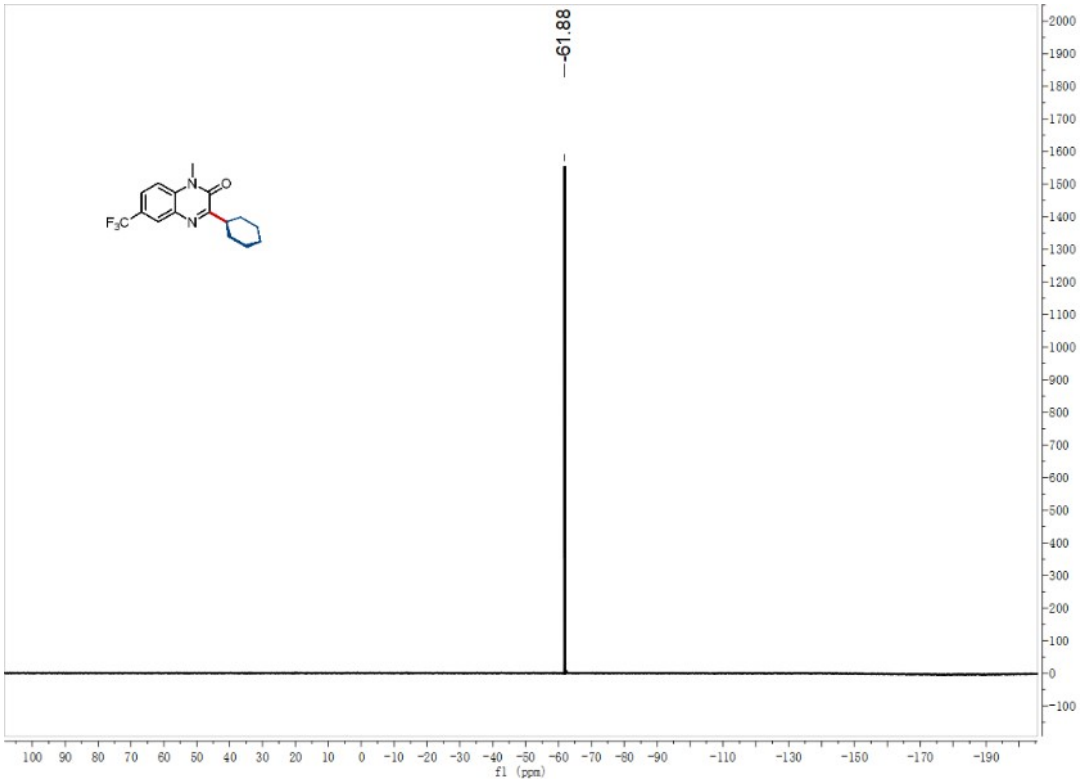
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **6**



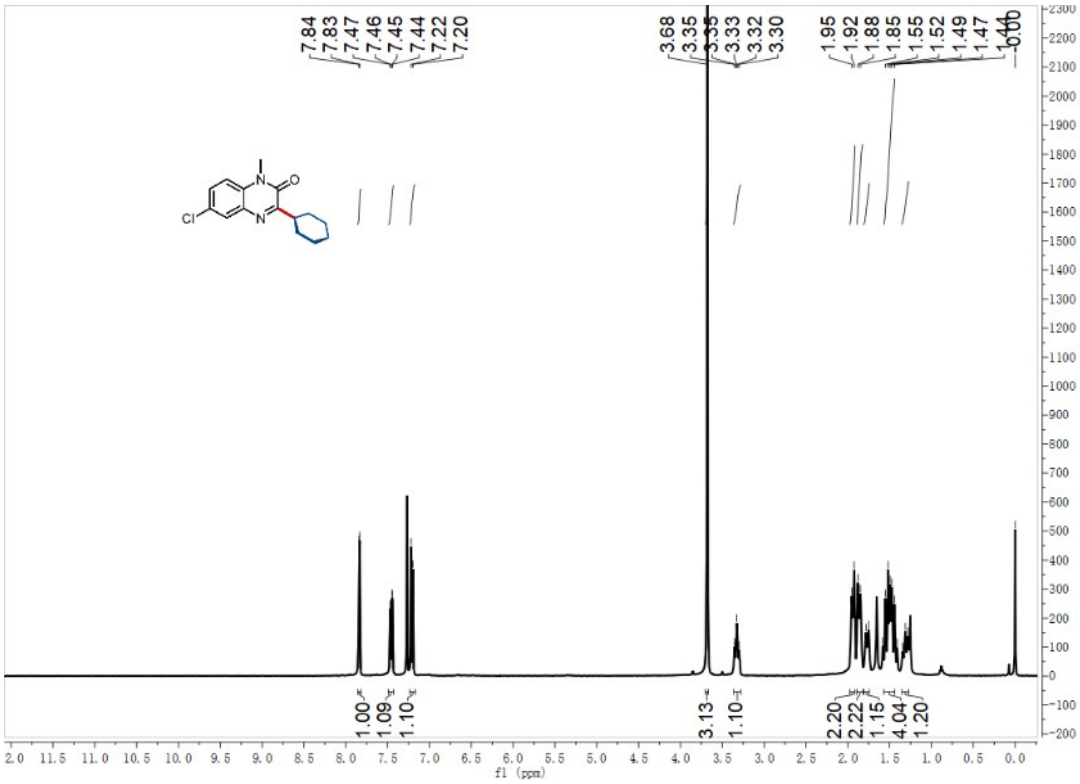
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of compound **6**



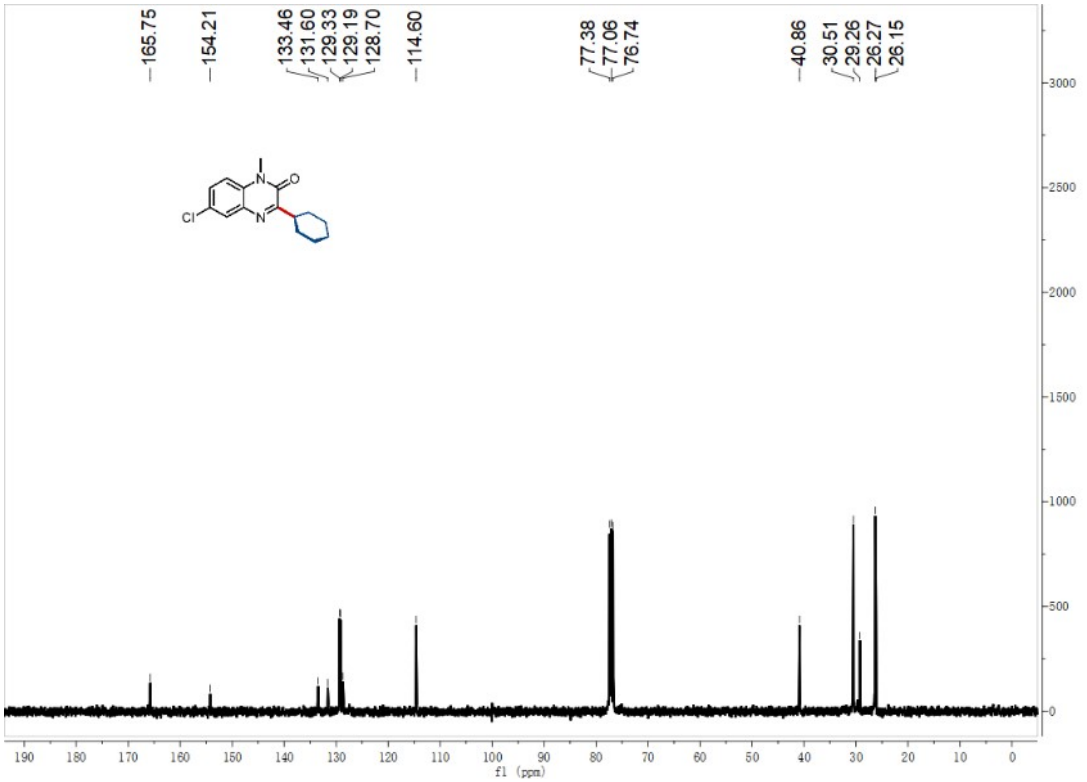
^{19}F NMR spectrum (376 MHz, $CDCl_3$) of compound **6**



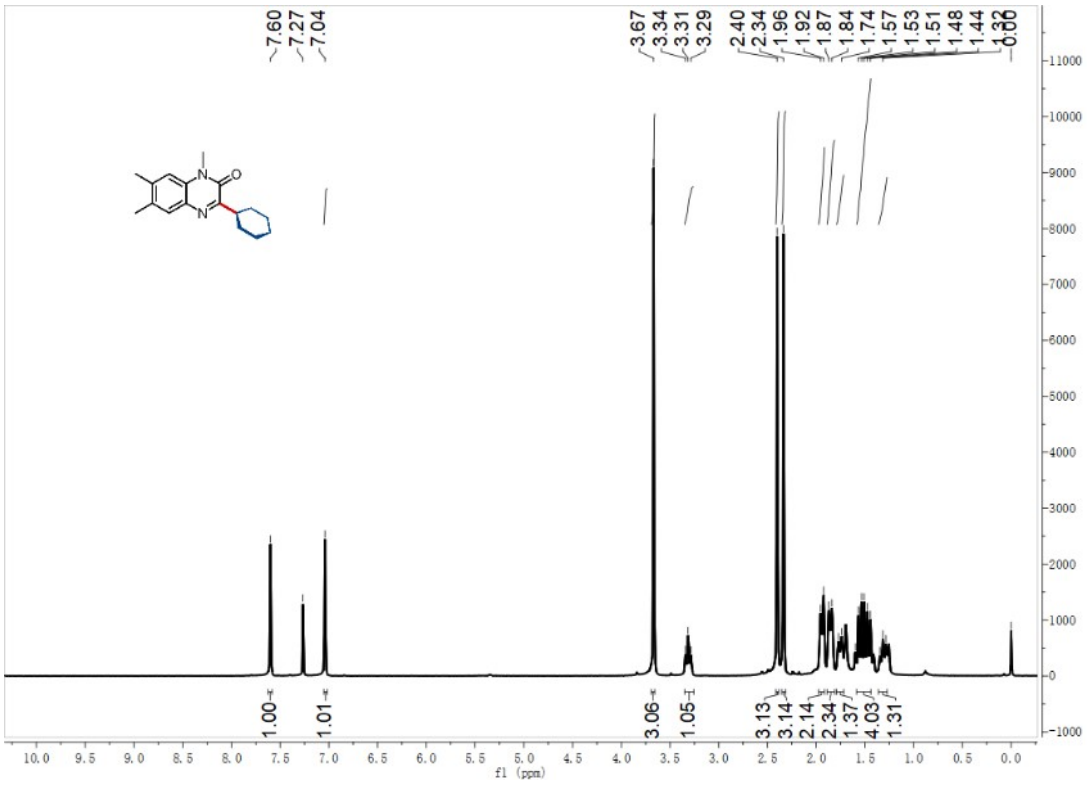
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **7**



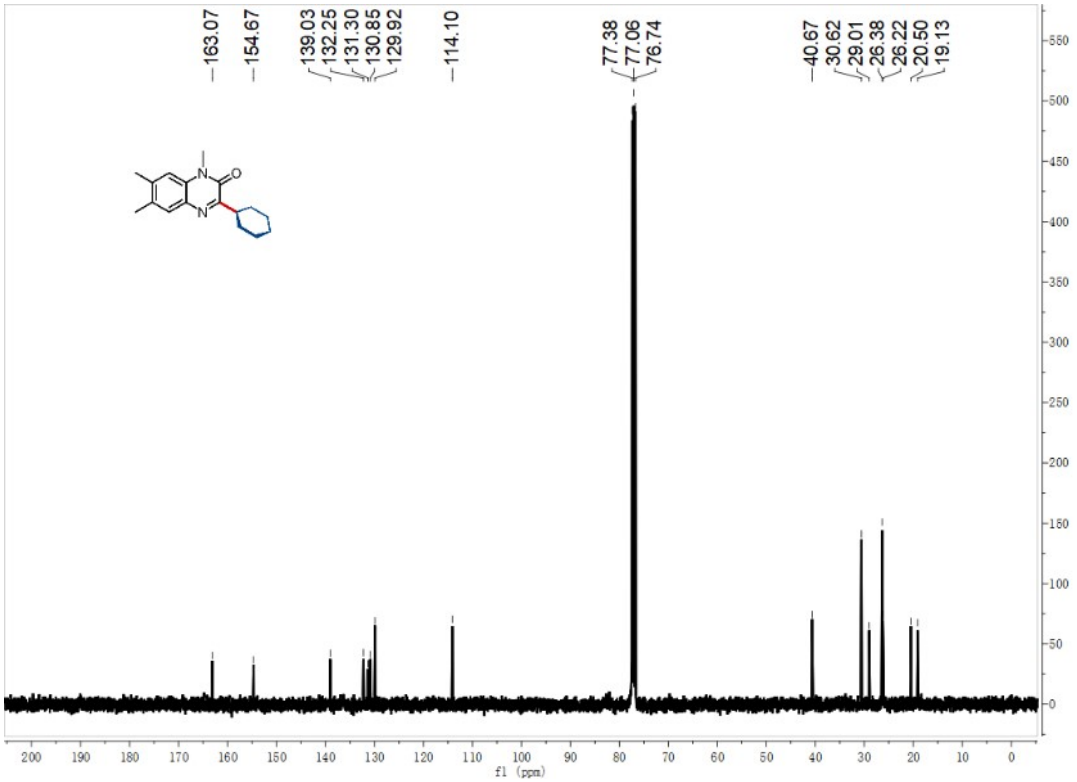
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of compound **7**



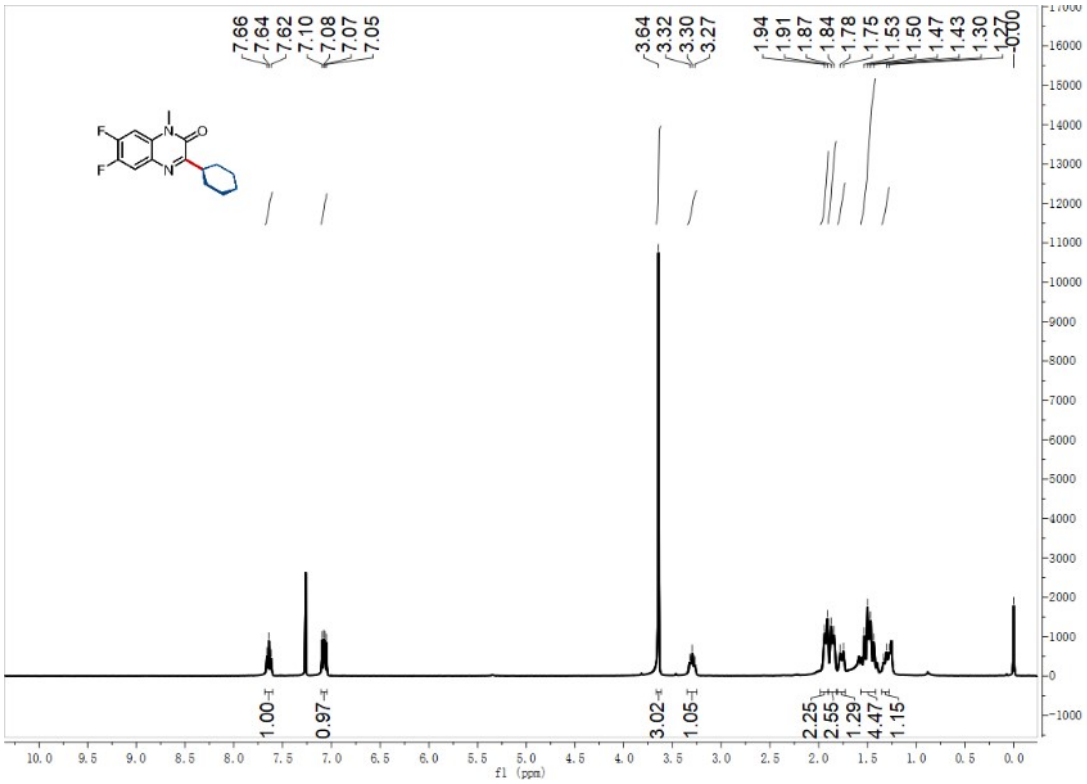
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **8**



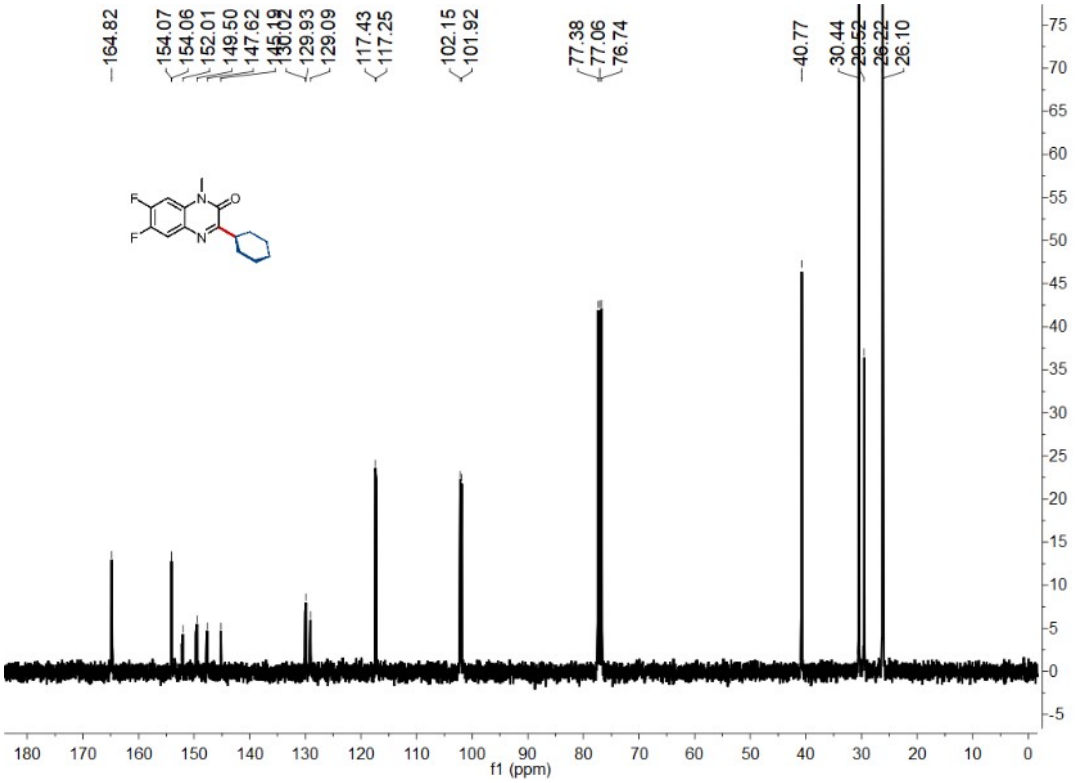
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of compound **8**



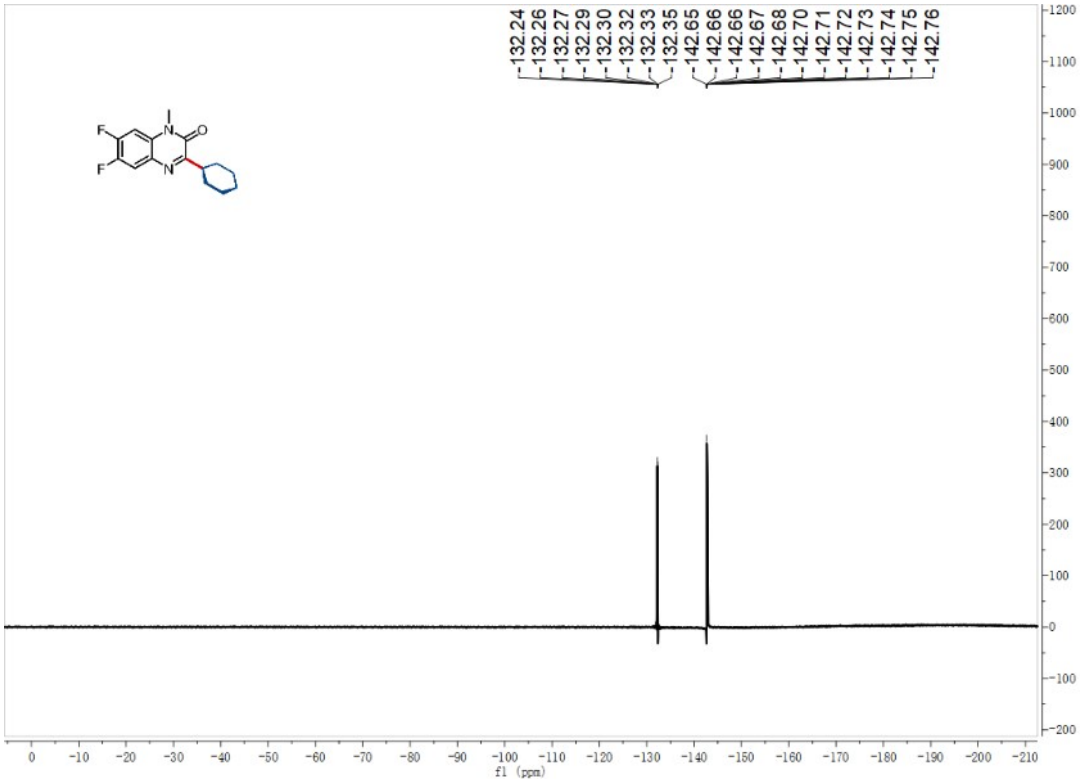
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **9**



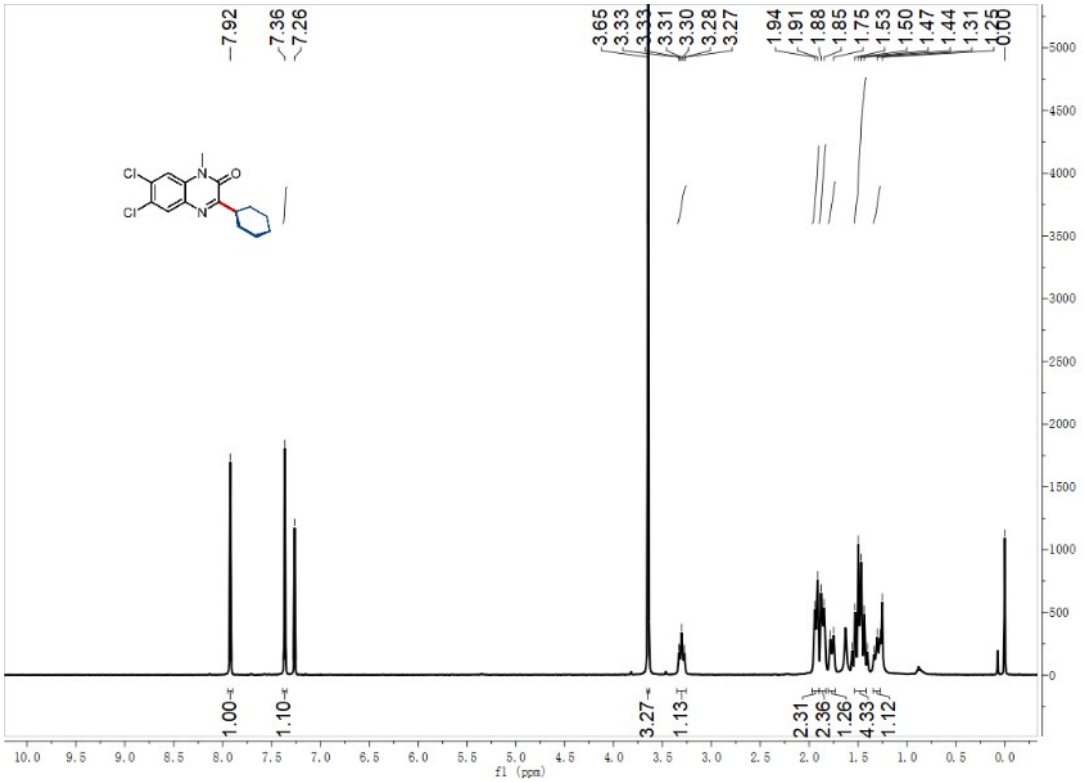
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of compound **9**



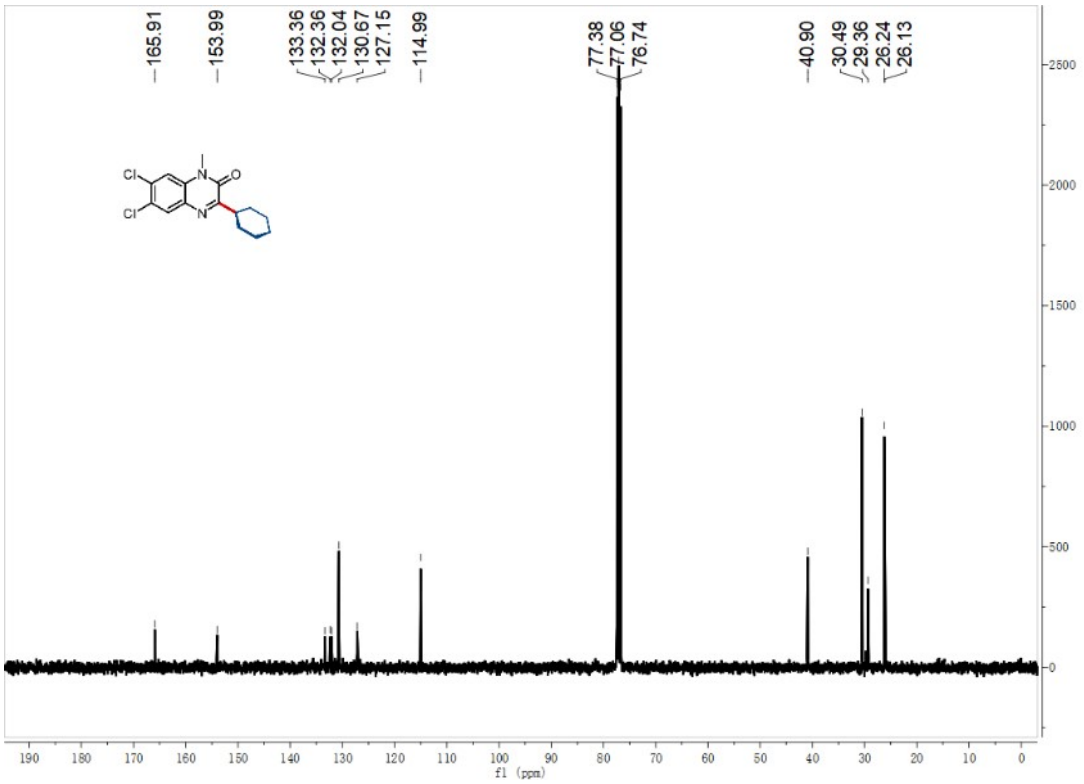
^{19}F NMR spectrum (376 MHz, $CDCl_3$) of compound **9**



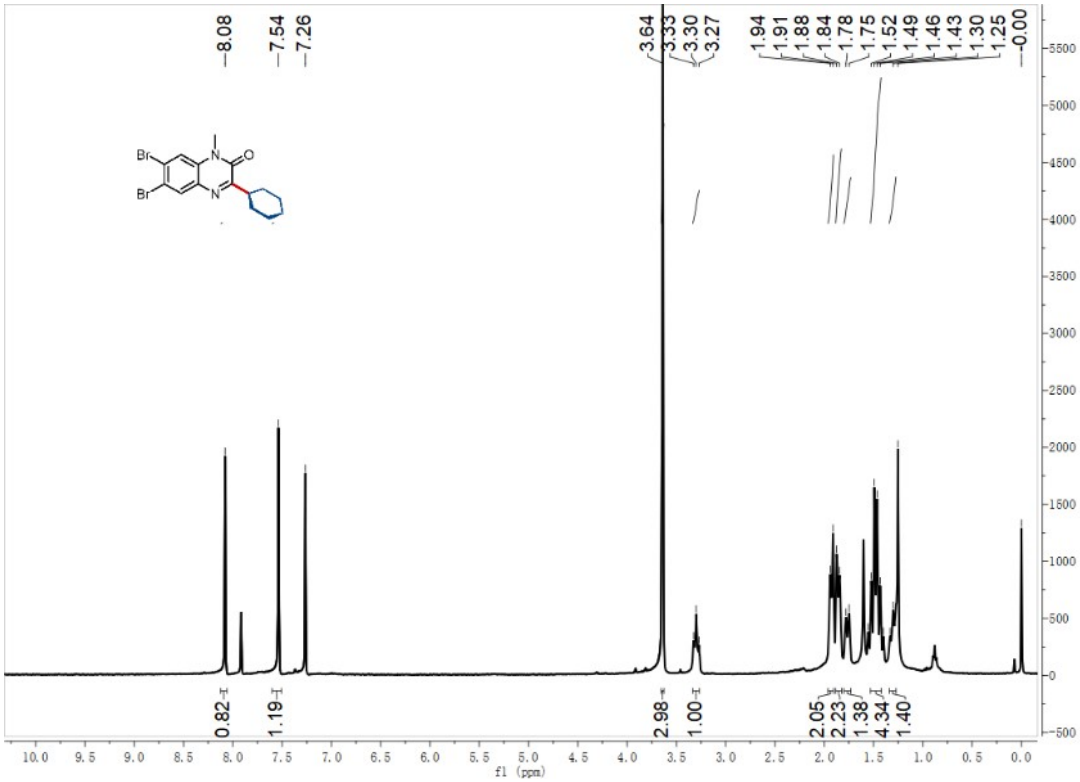
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **10**



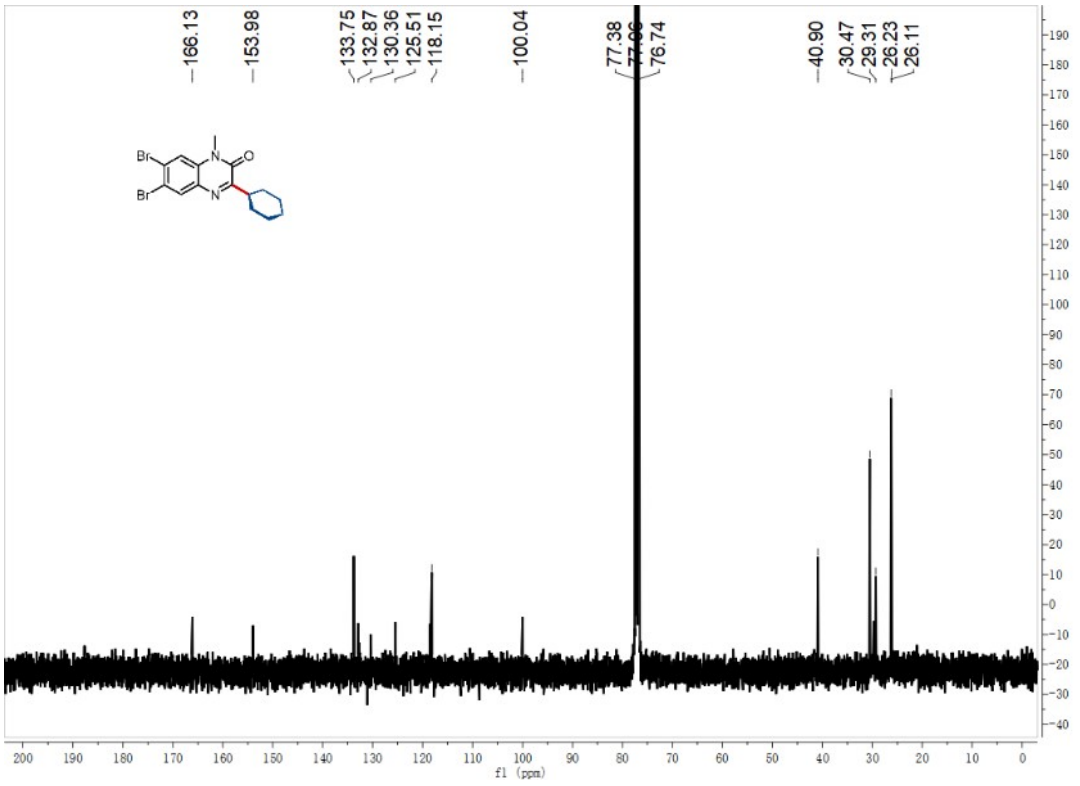
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of compound **10**



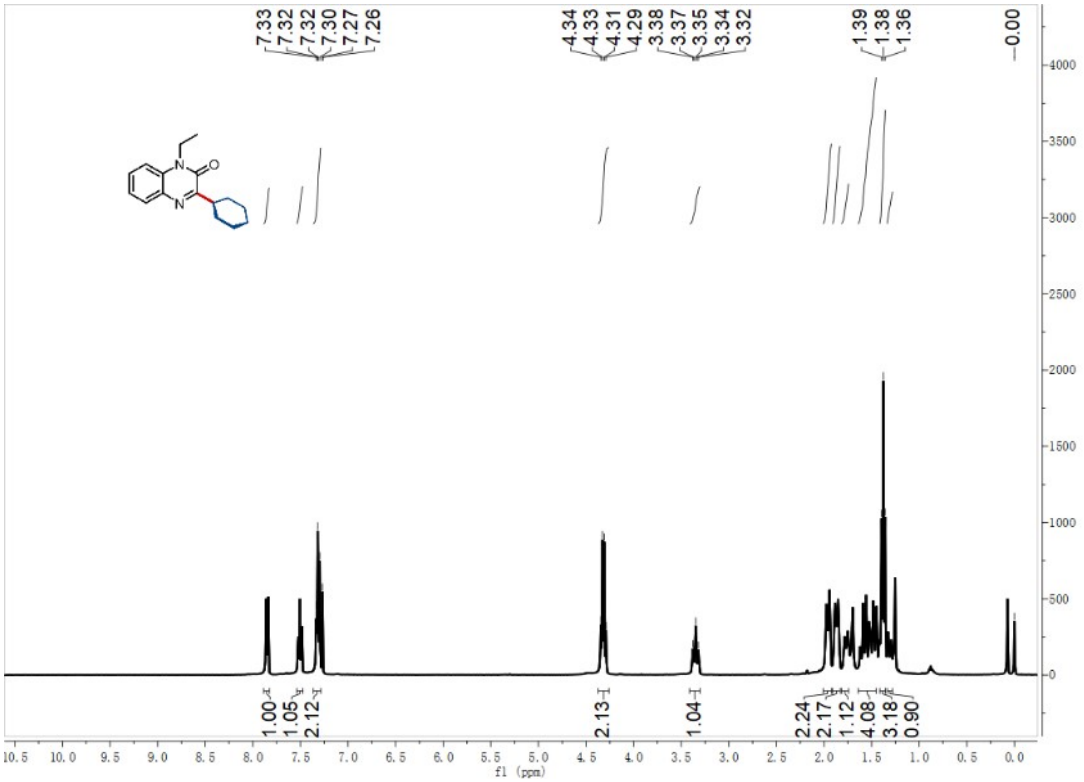
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **11**



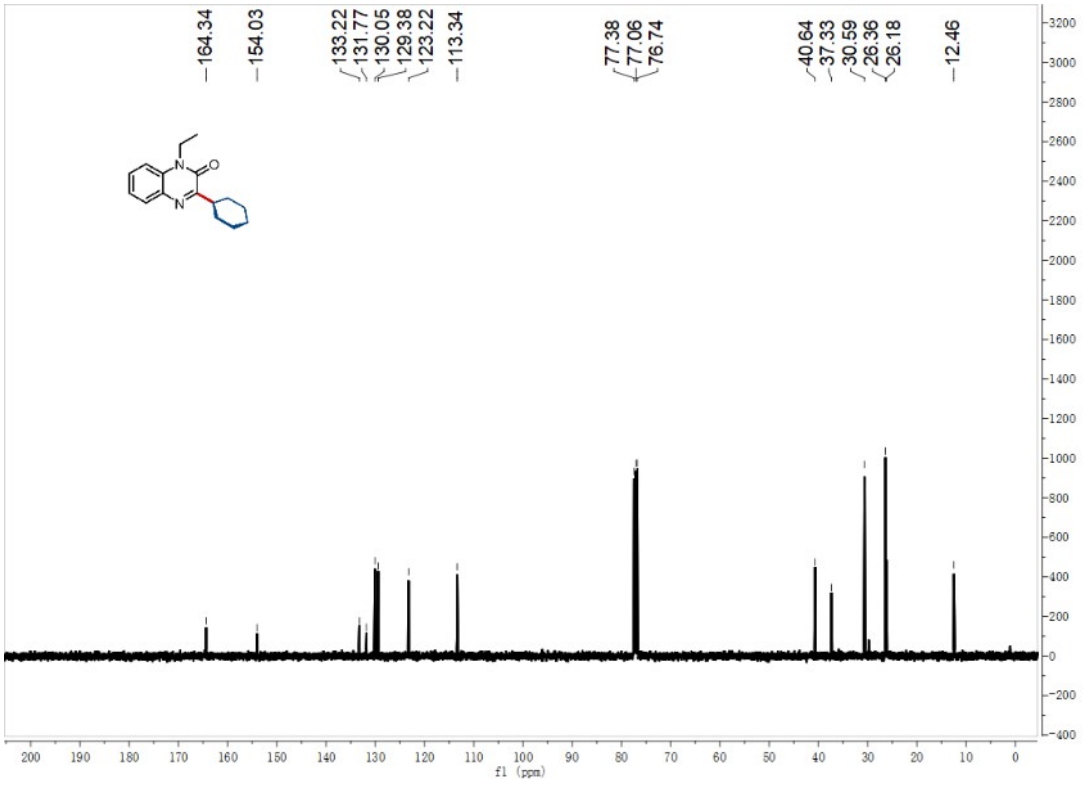
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of compound **11**



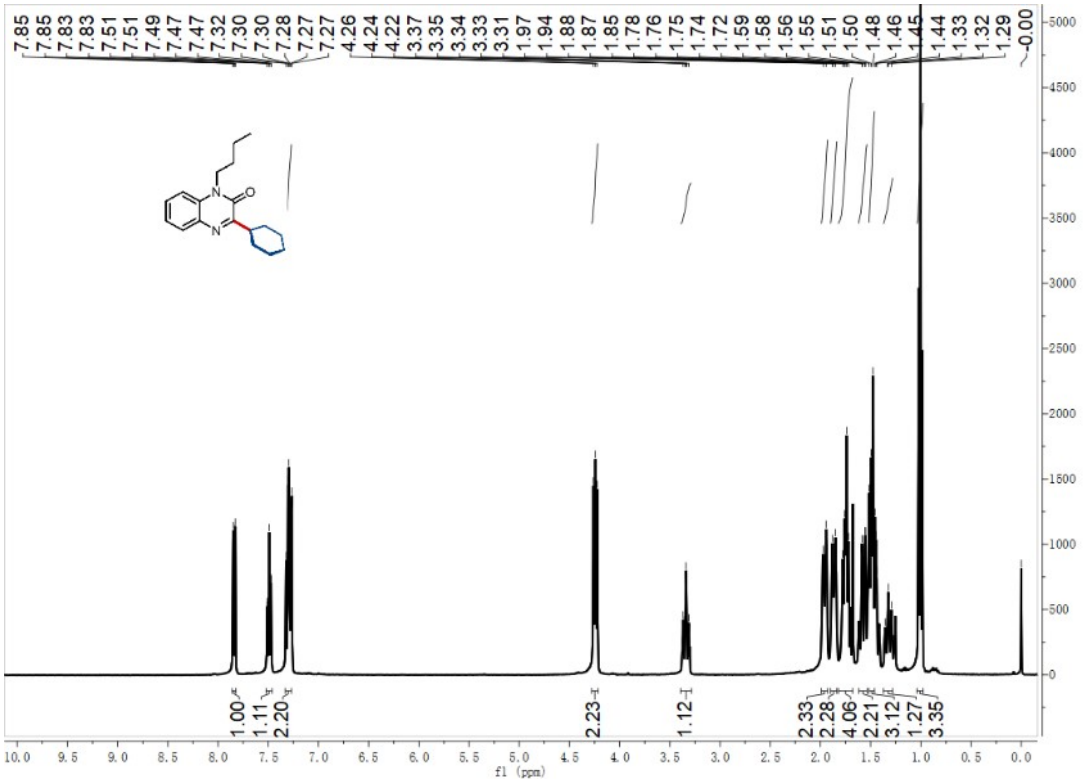
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **12**



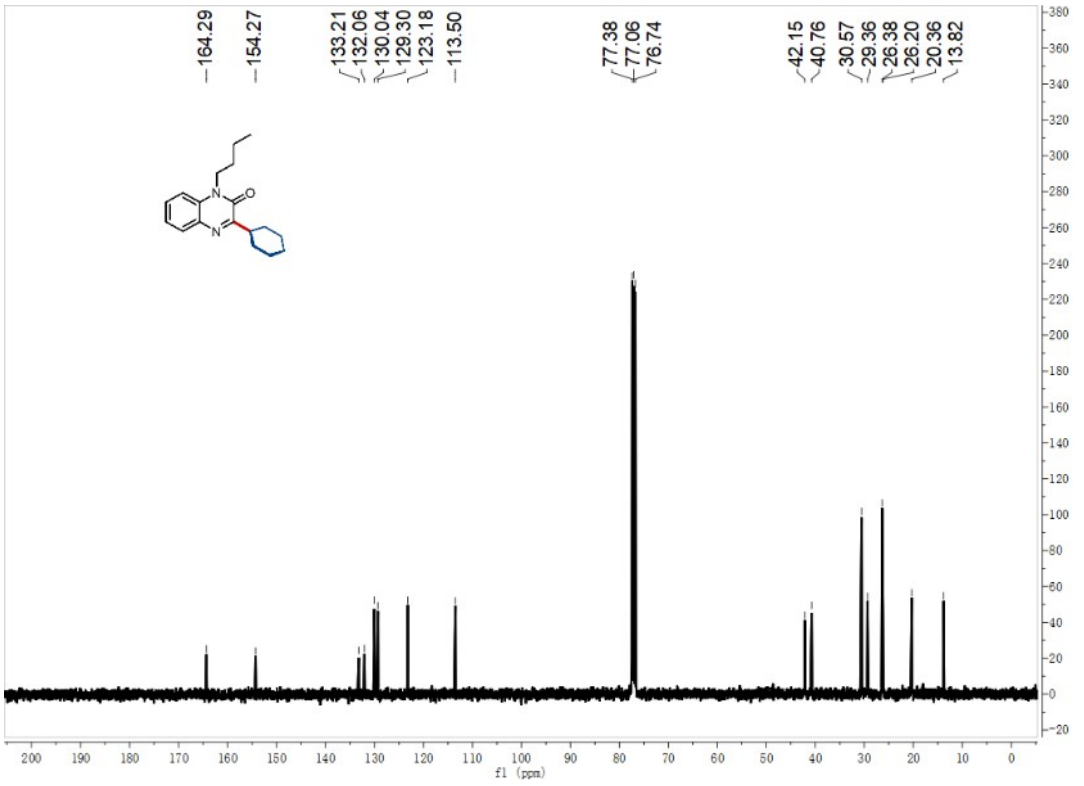
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of compound **12**



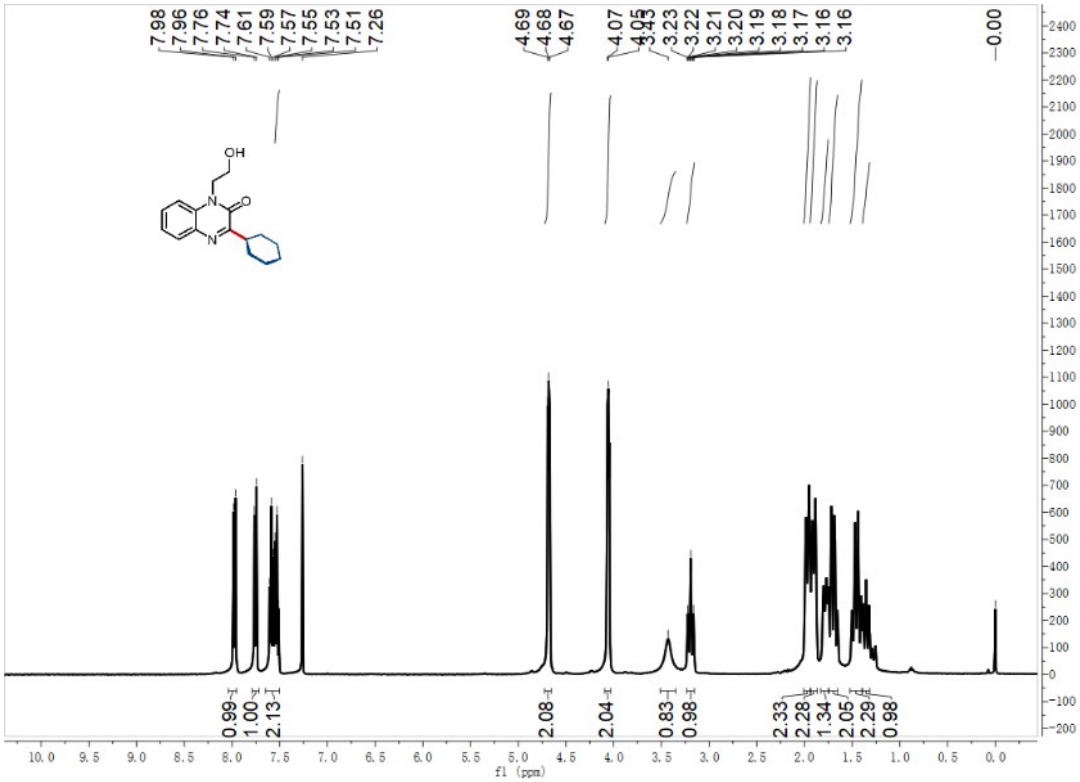
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **13**



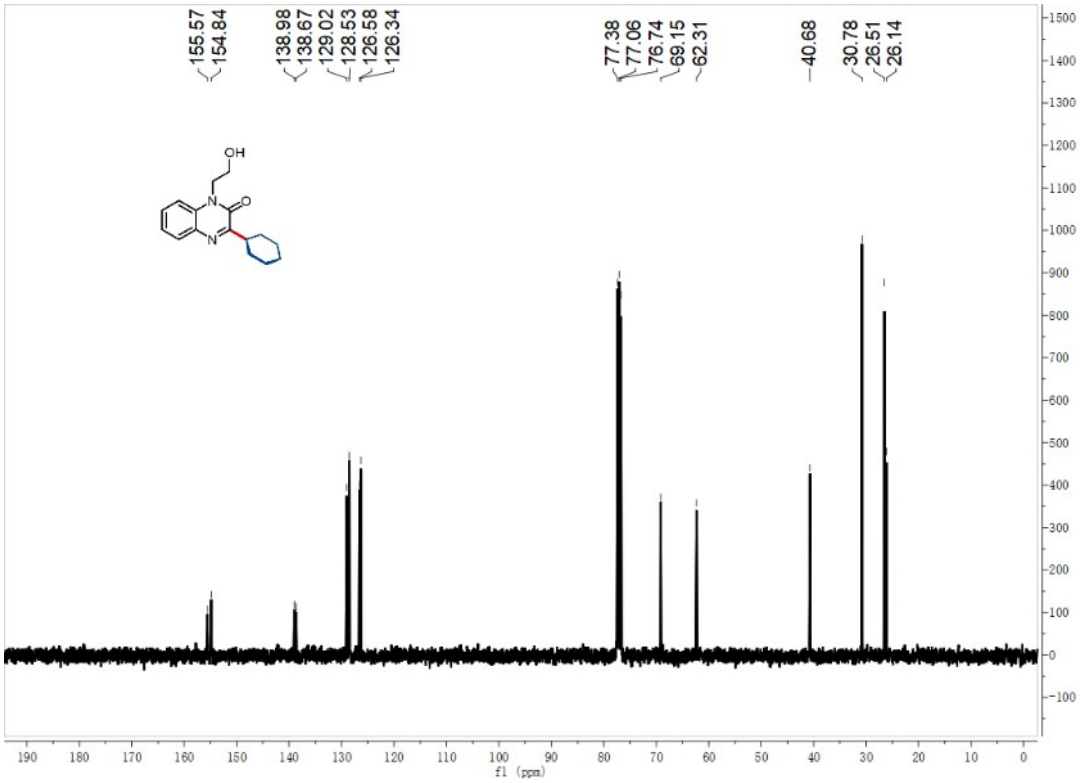
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of compound **13**



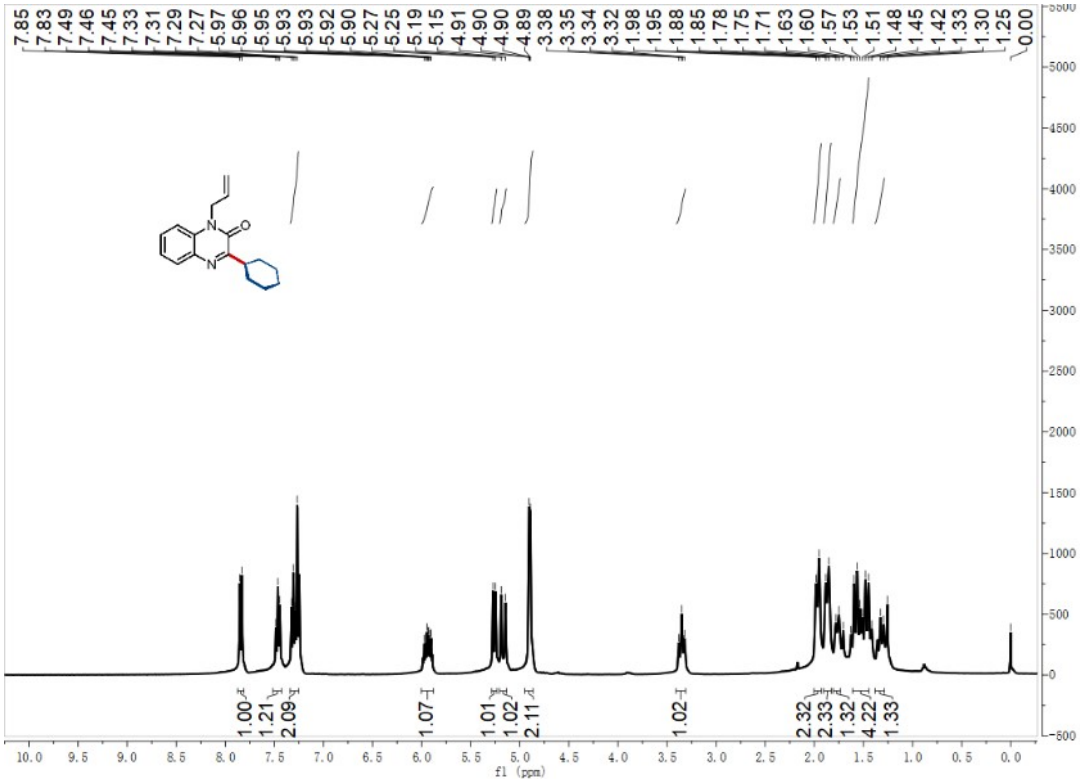
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **14**



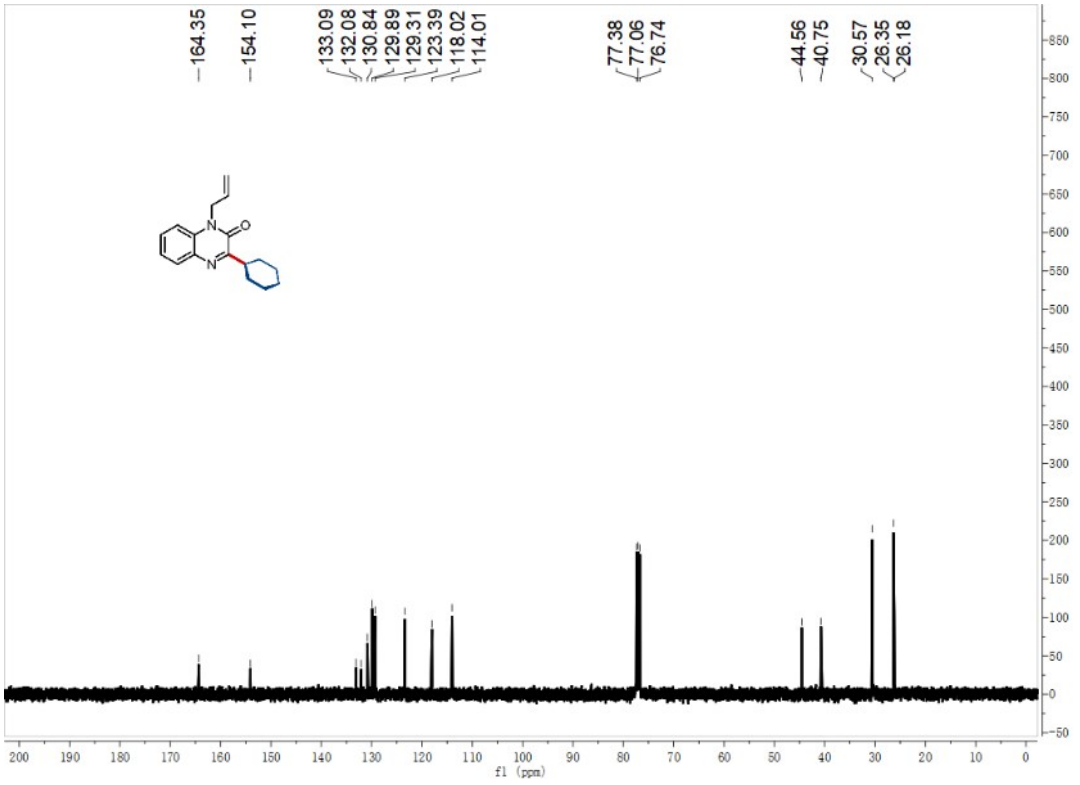
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of compound **14**



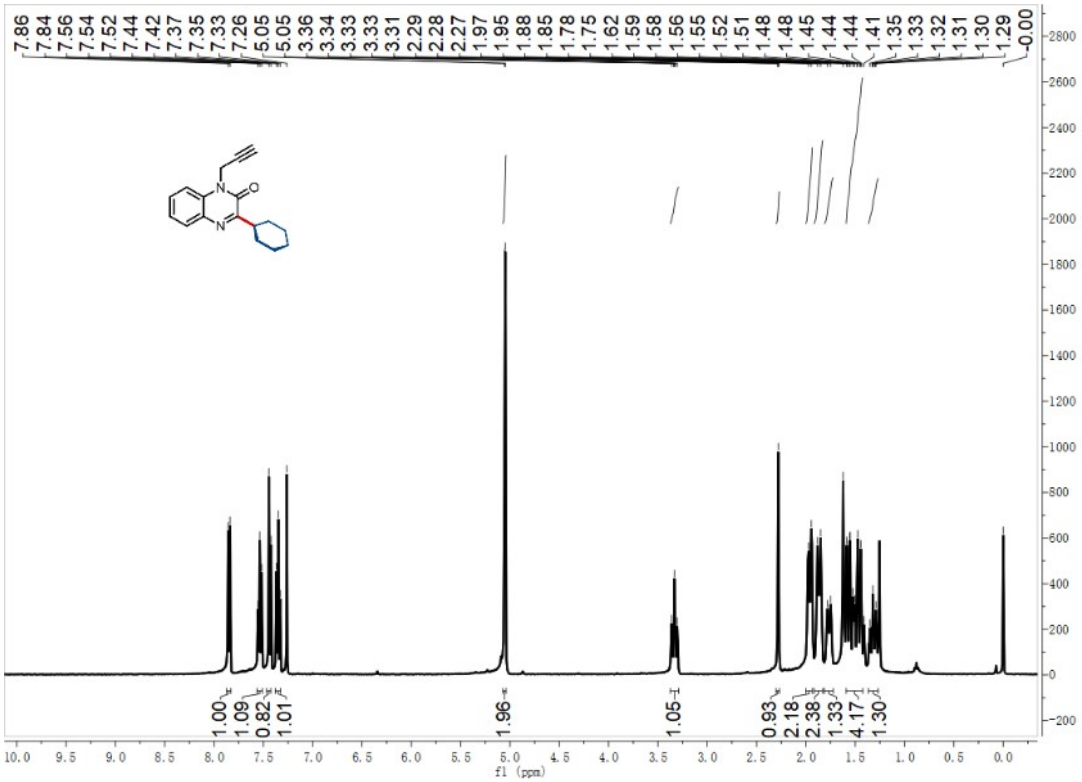
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **15**



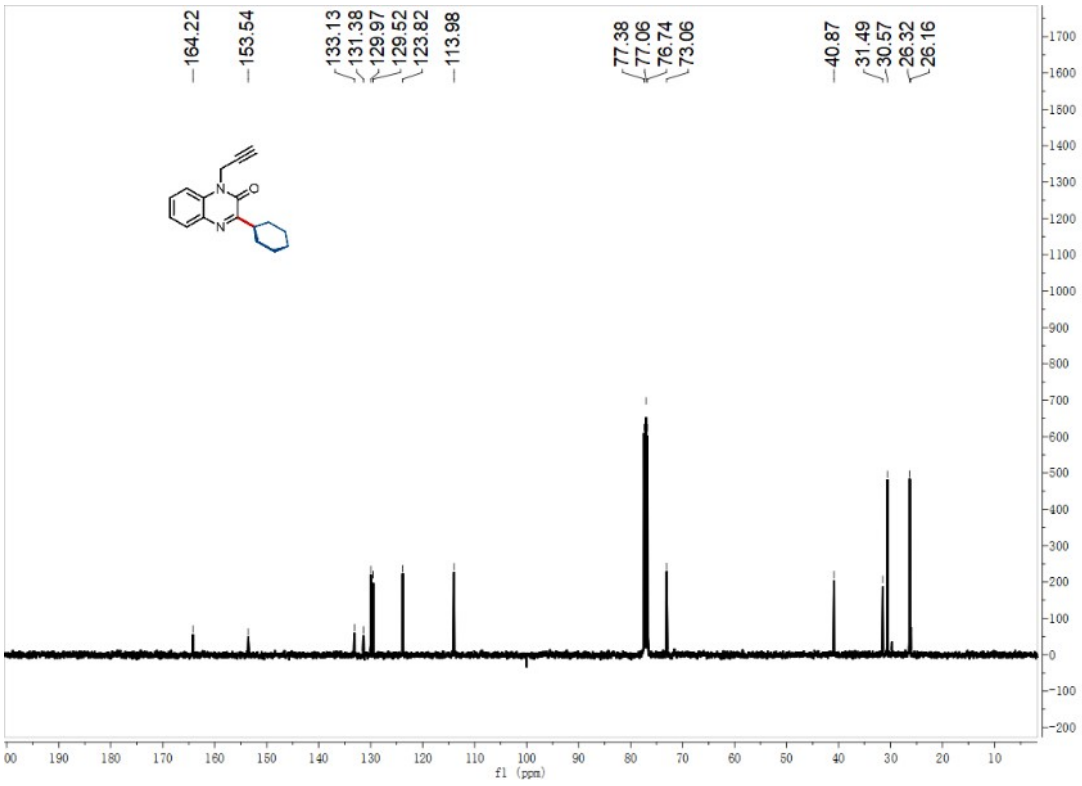
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of compound **15**



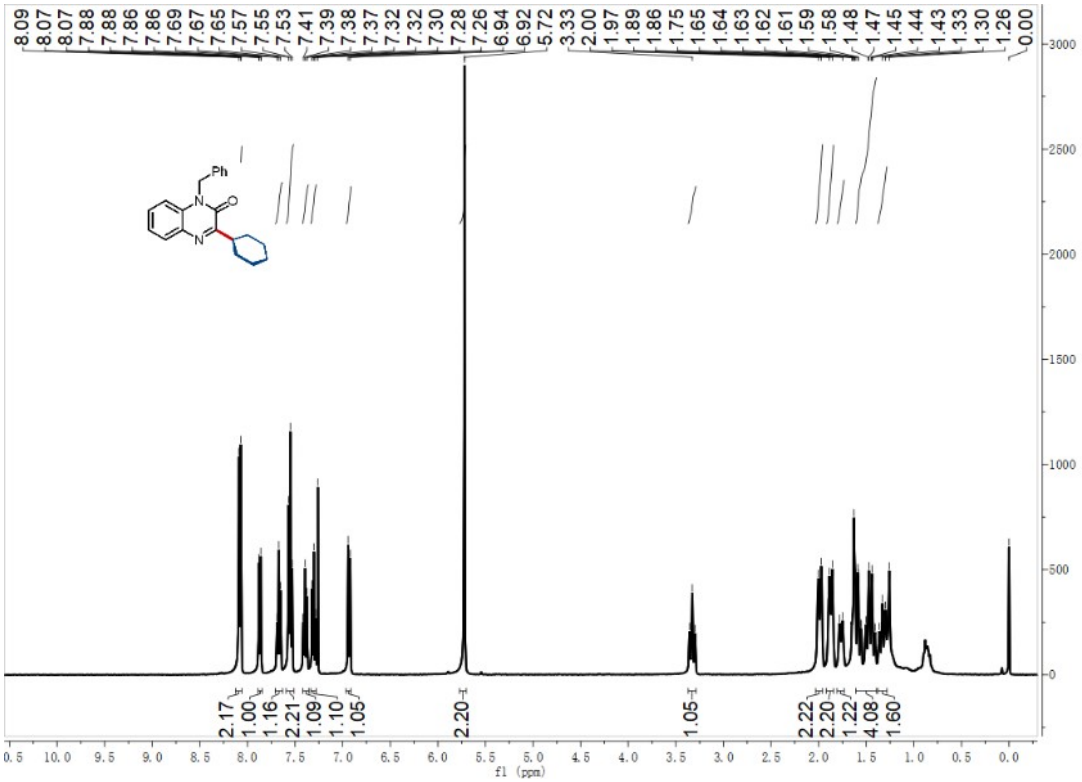
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **16**



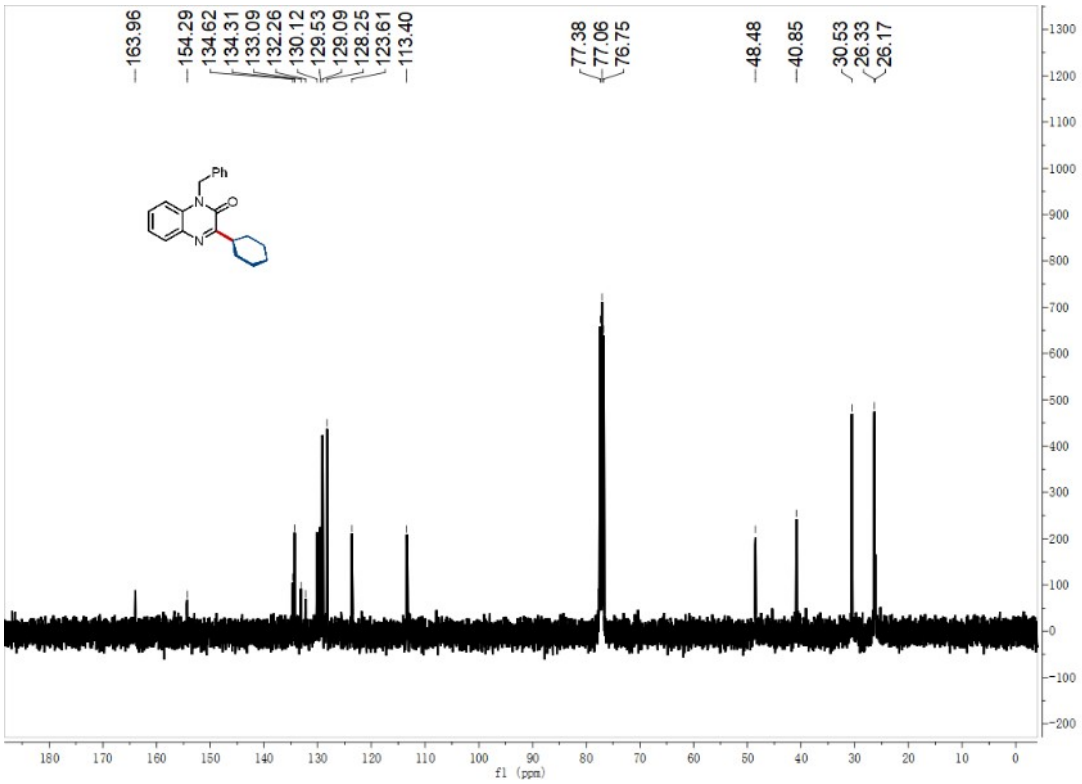
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of compound **16**



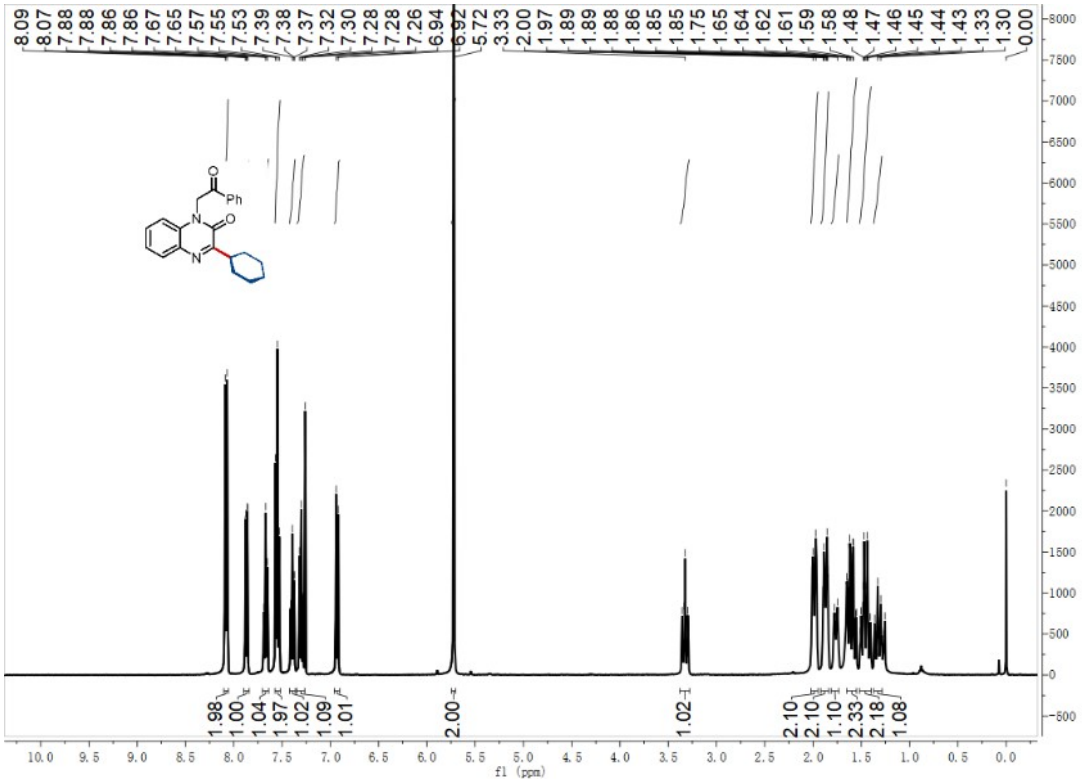
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **17**



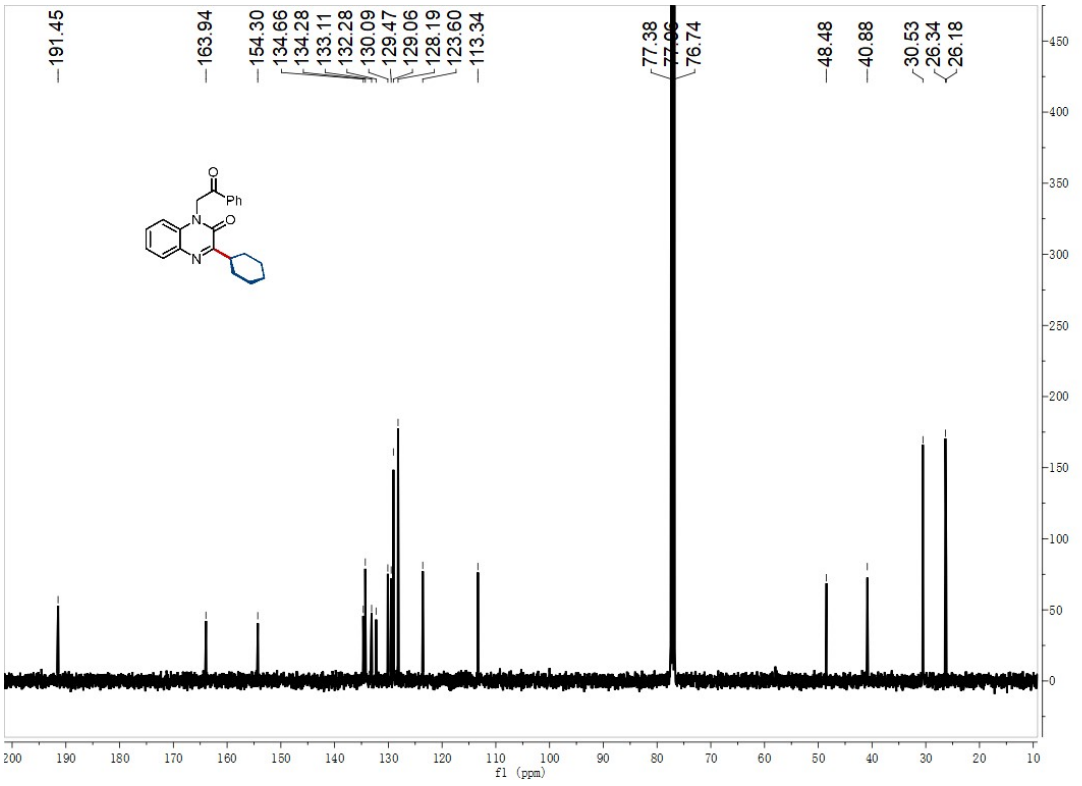
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of compound **17**



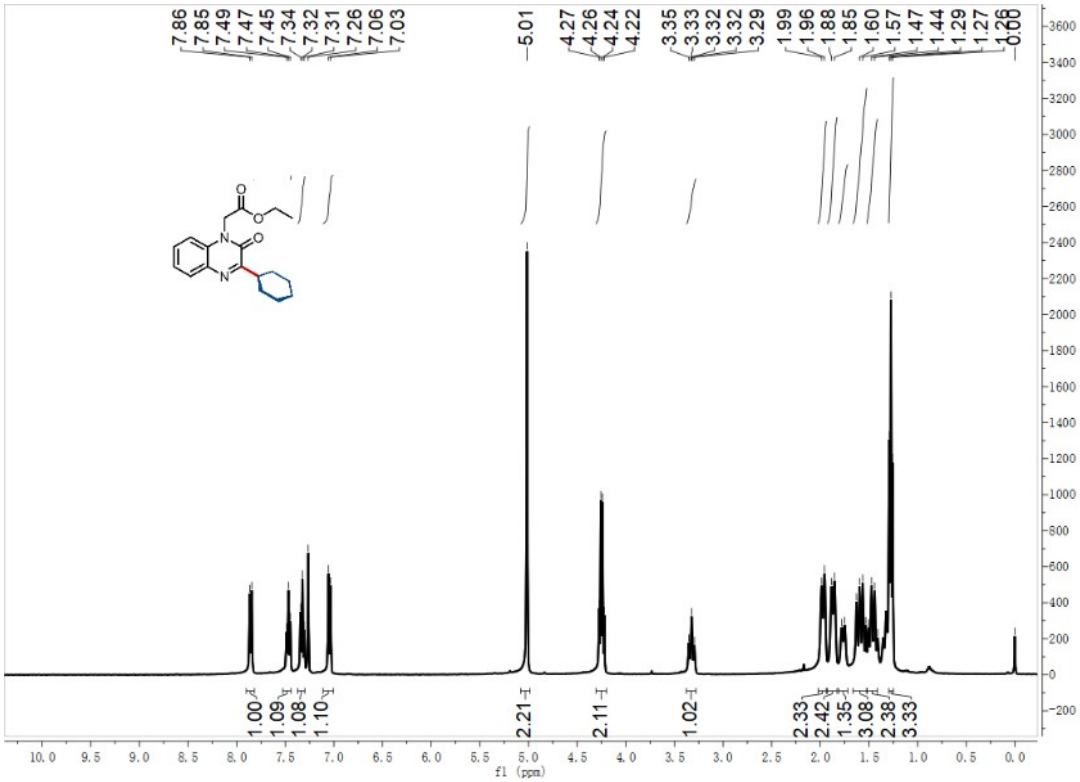
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **18**



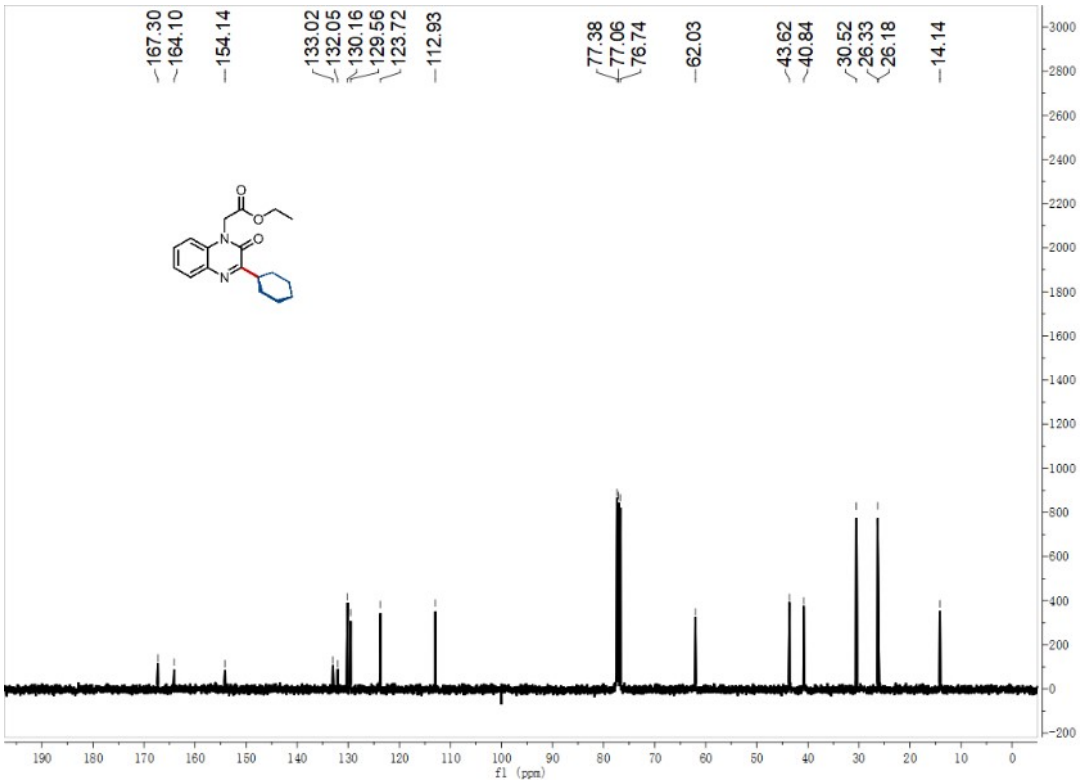
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of compound **18**



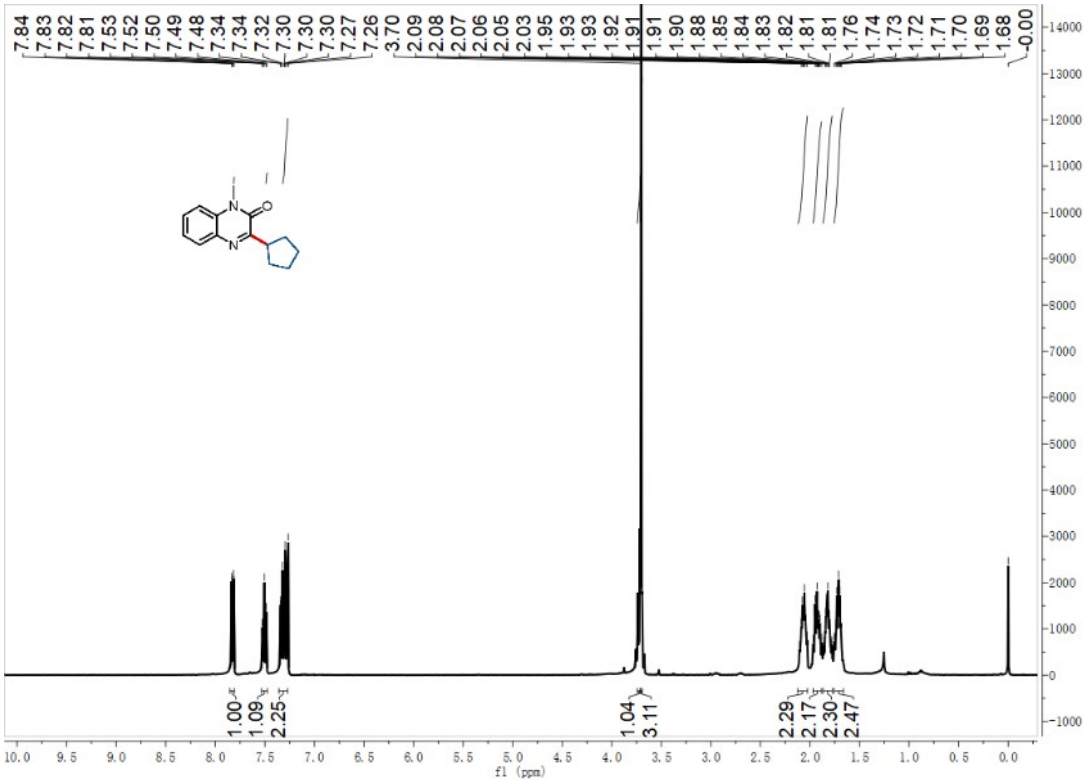
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **19**



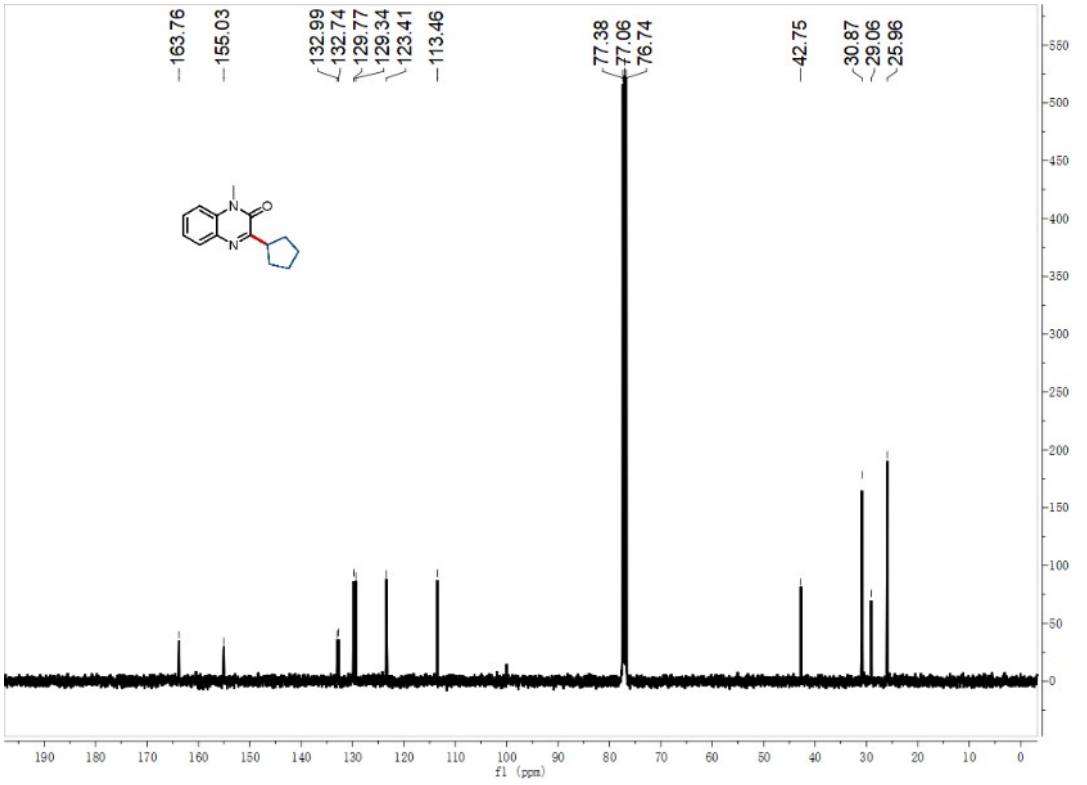
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of compound **19**



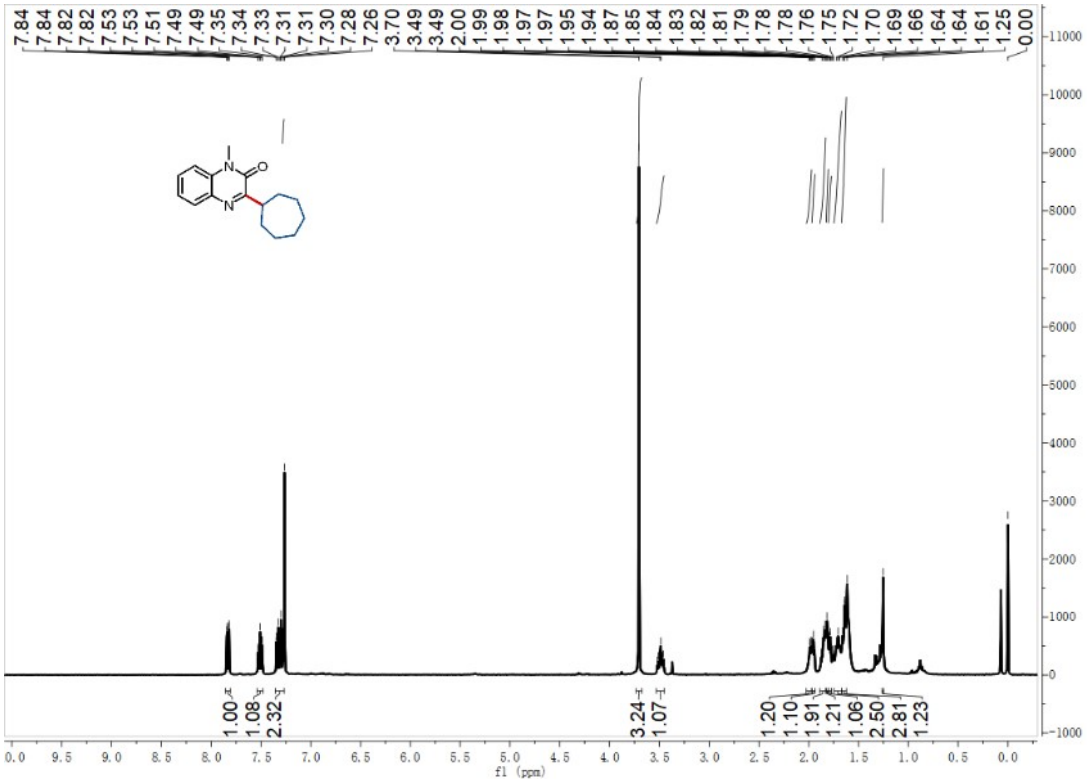
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **20**



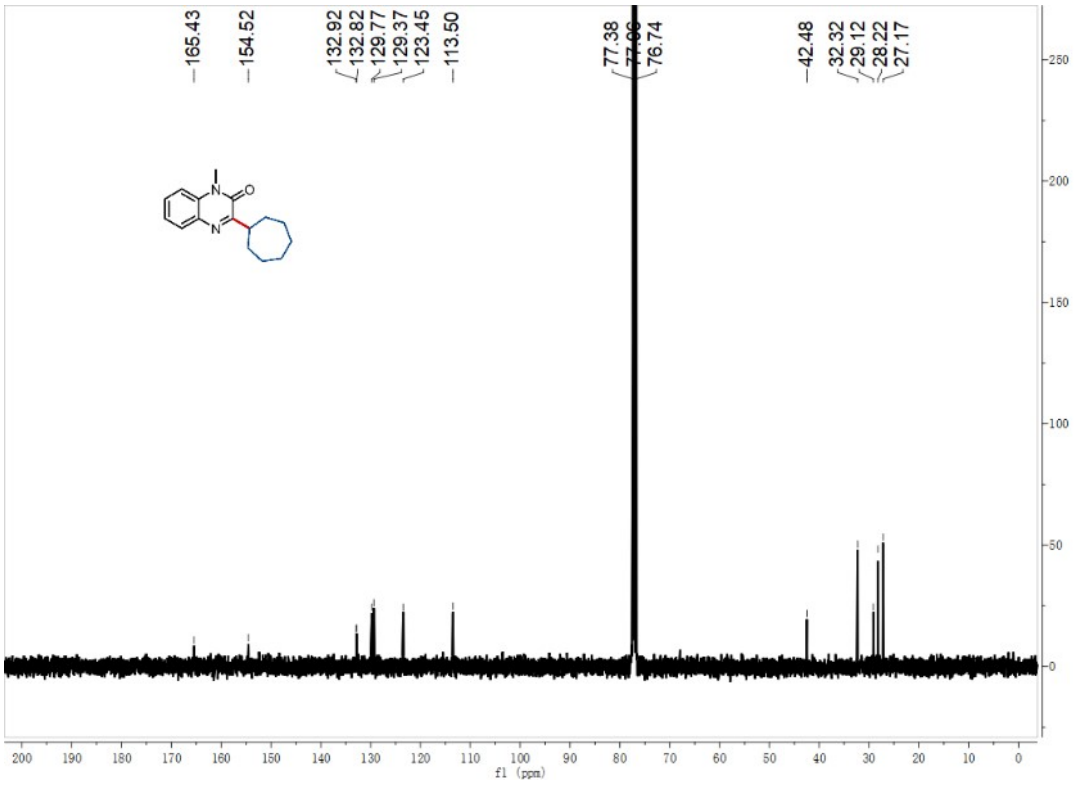
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of compound **20**



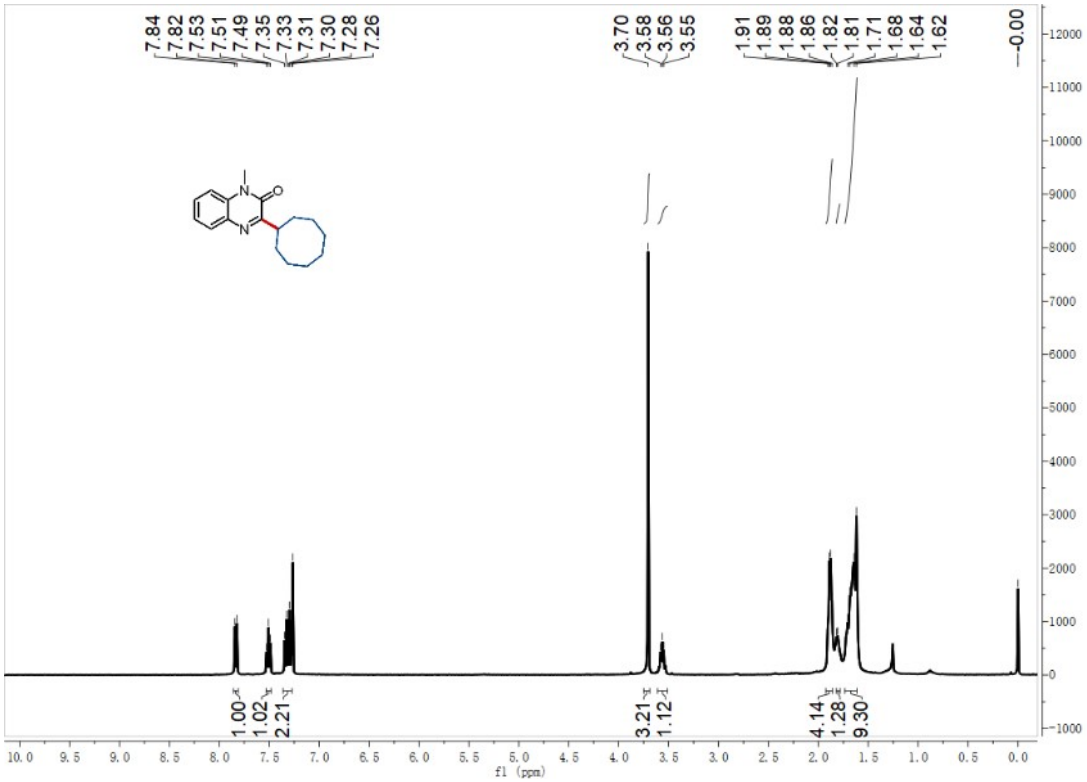
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **21**



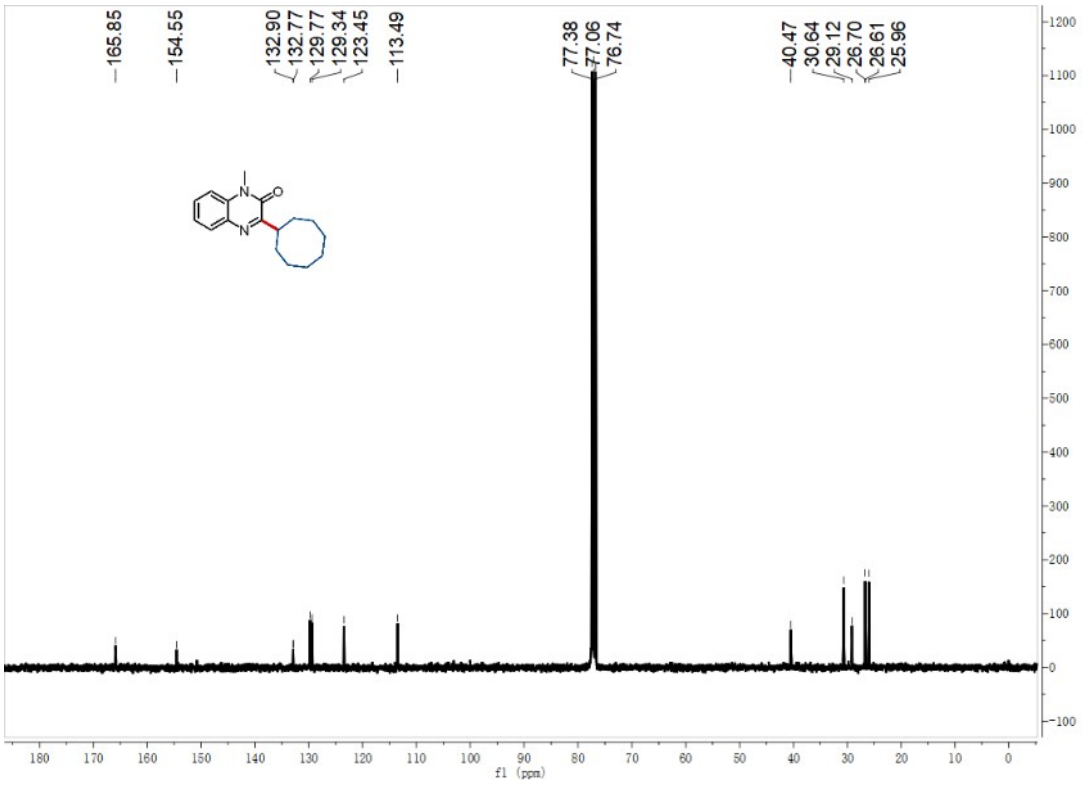
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of compound **21**



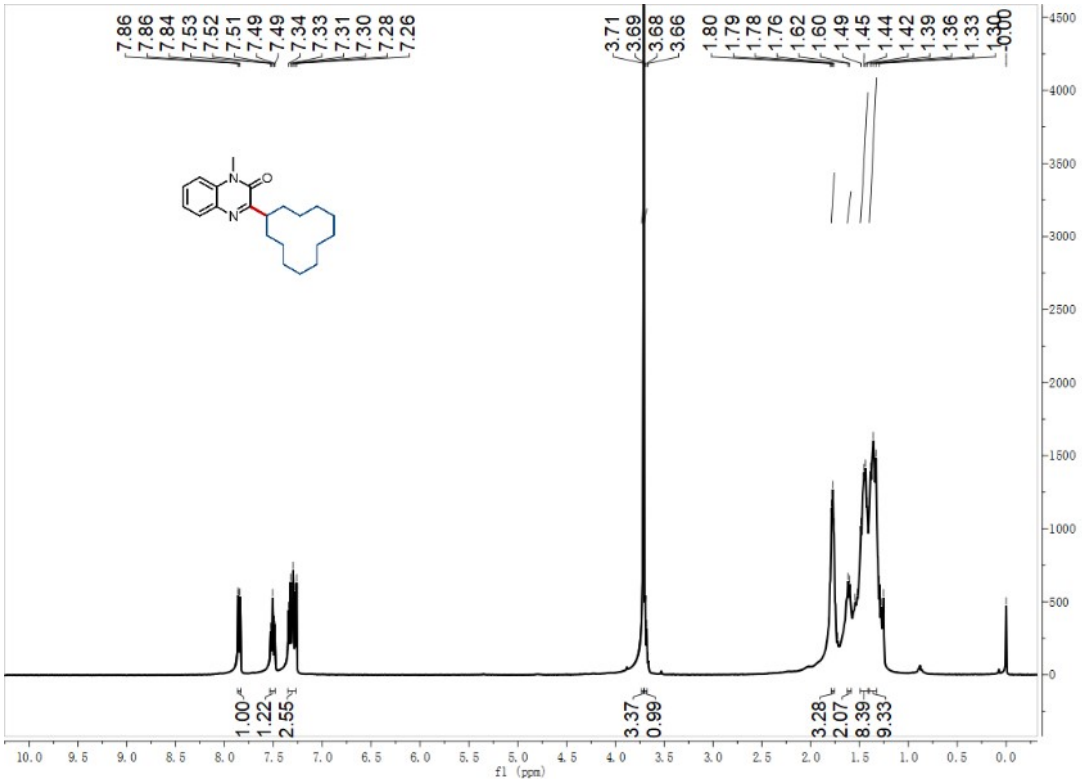
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **22**



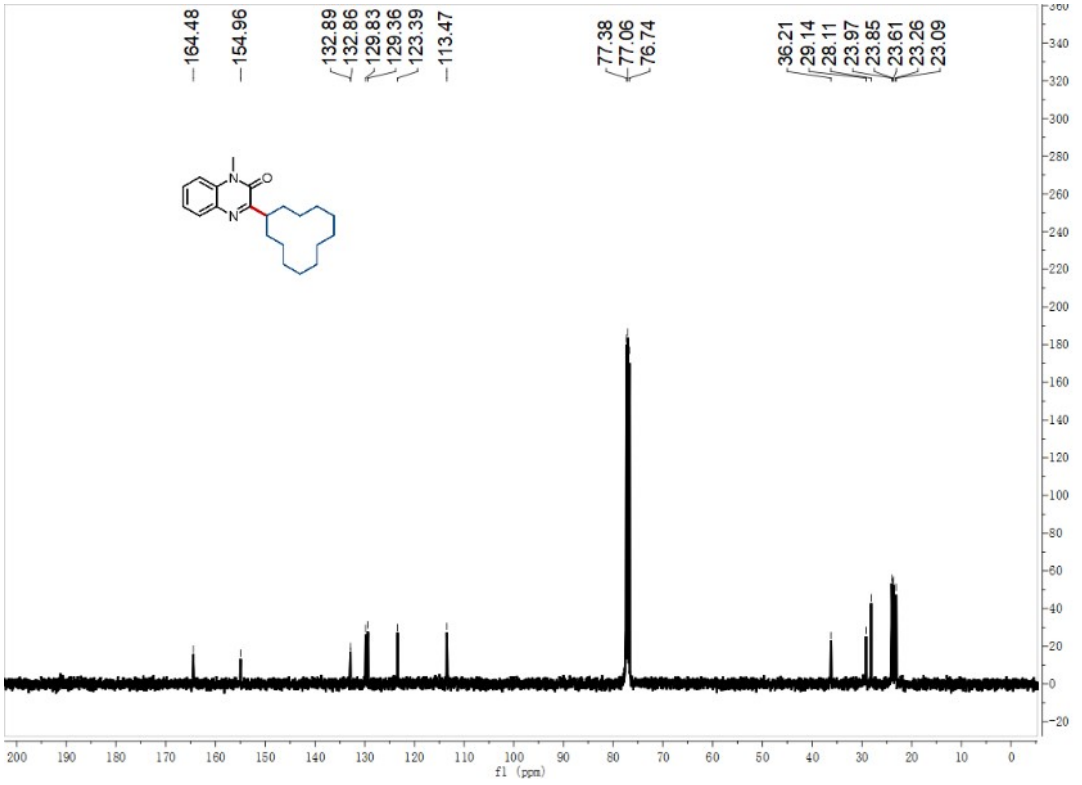
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of compound **22**



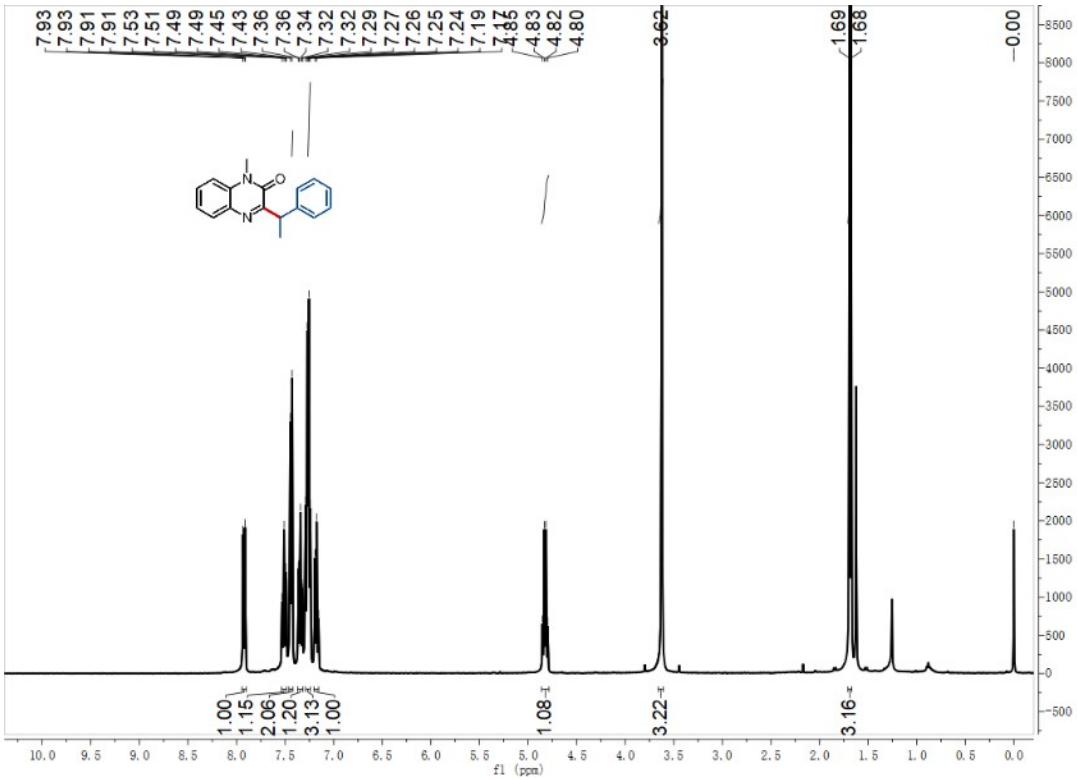
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **23**



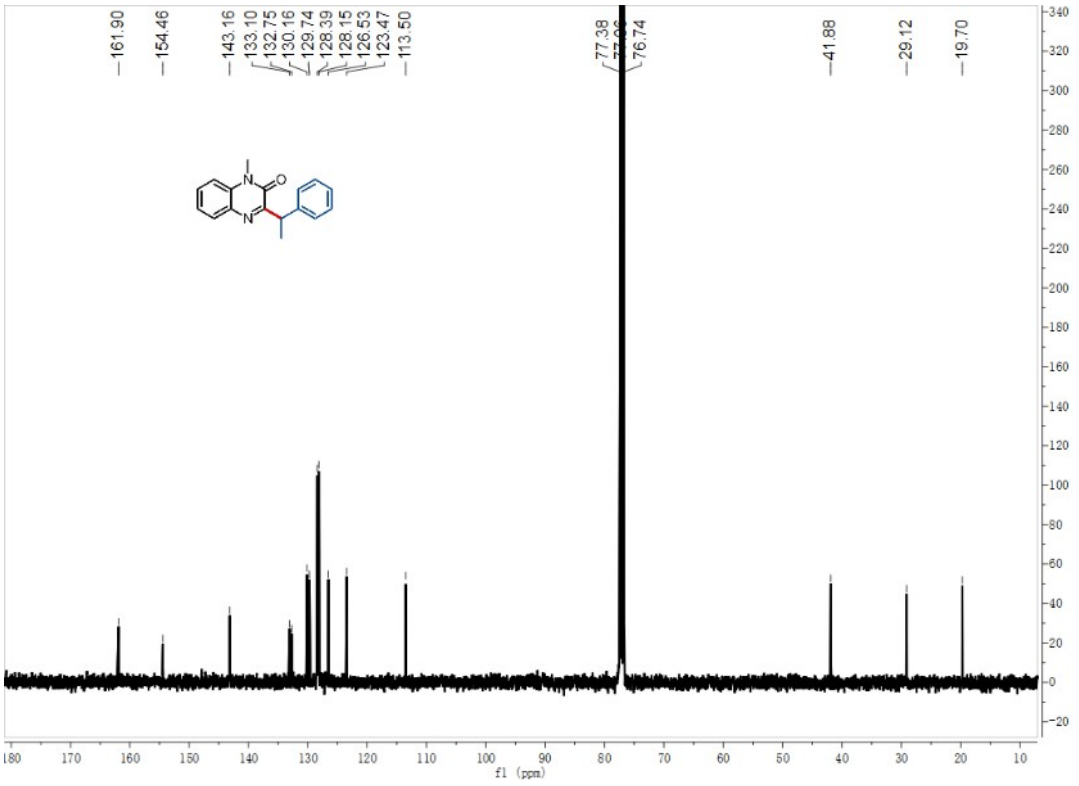
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of compound **23**



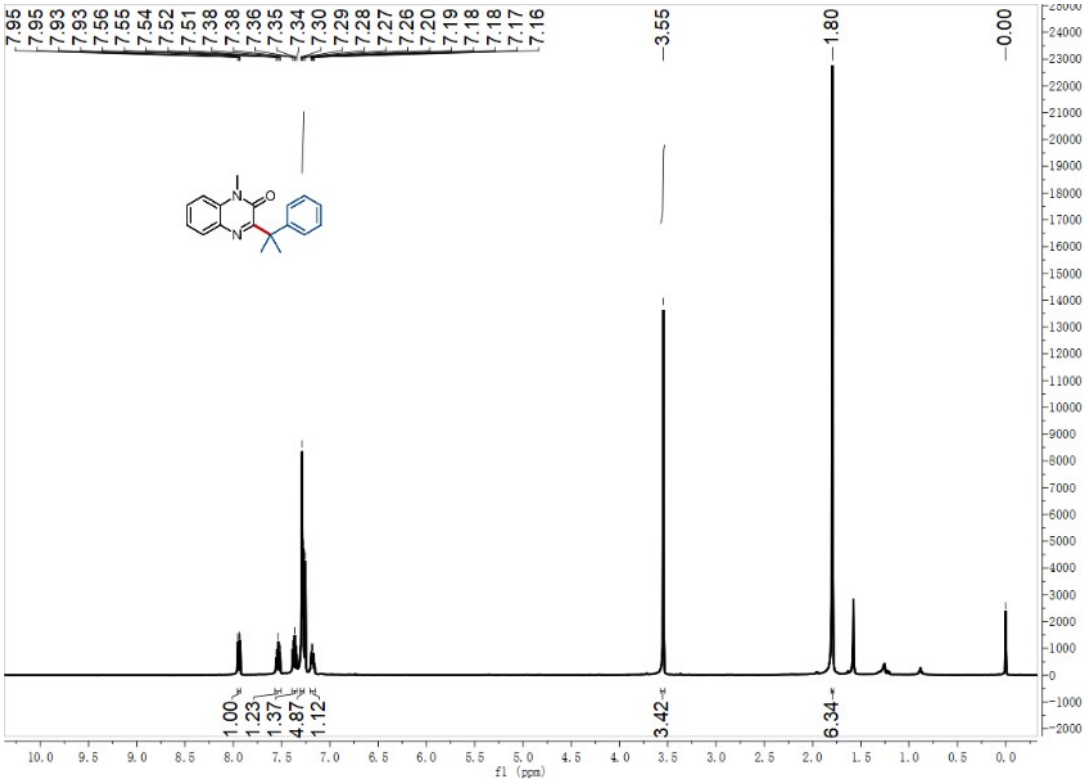
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **24**



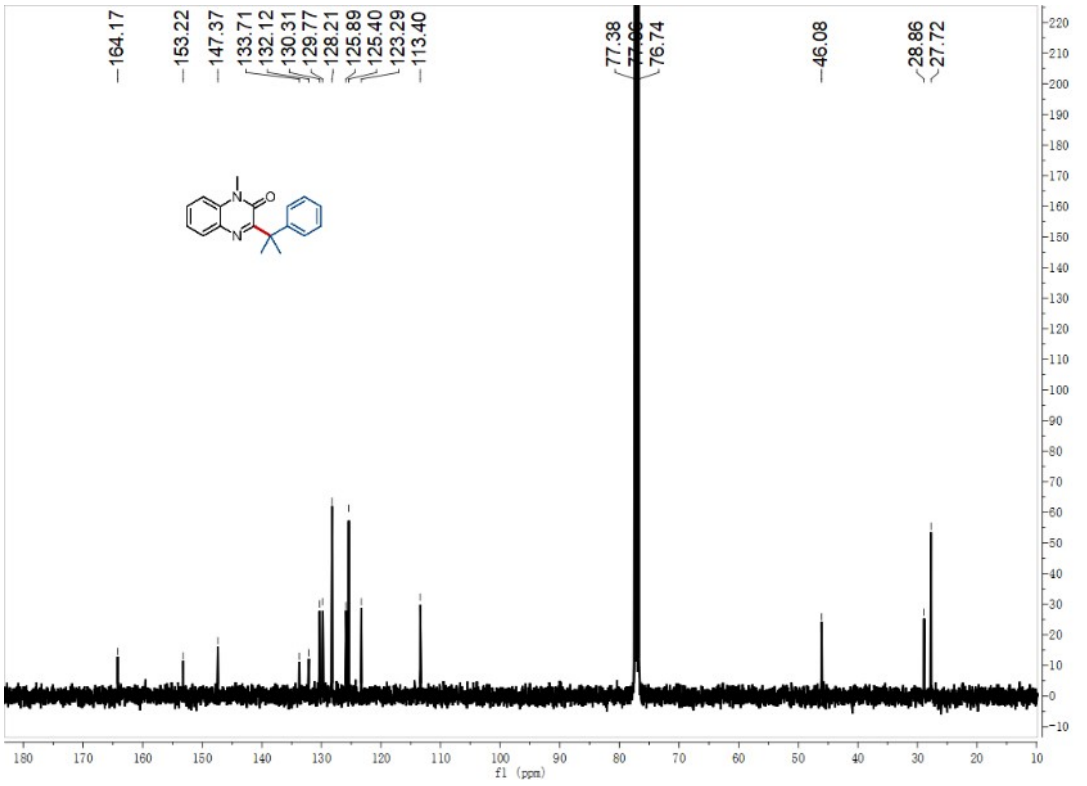
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of compound **24**



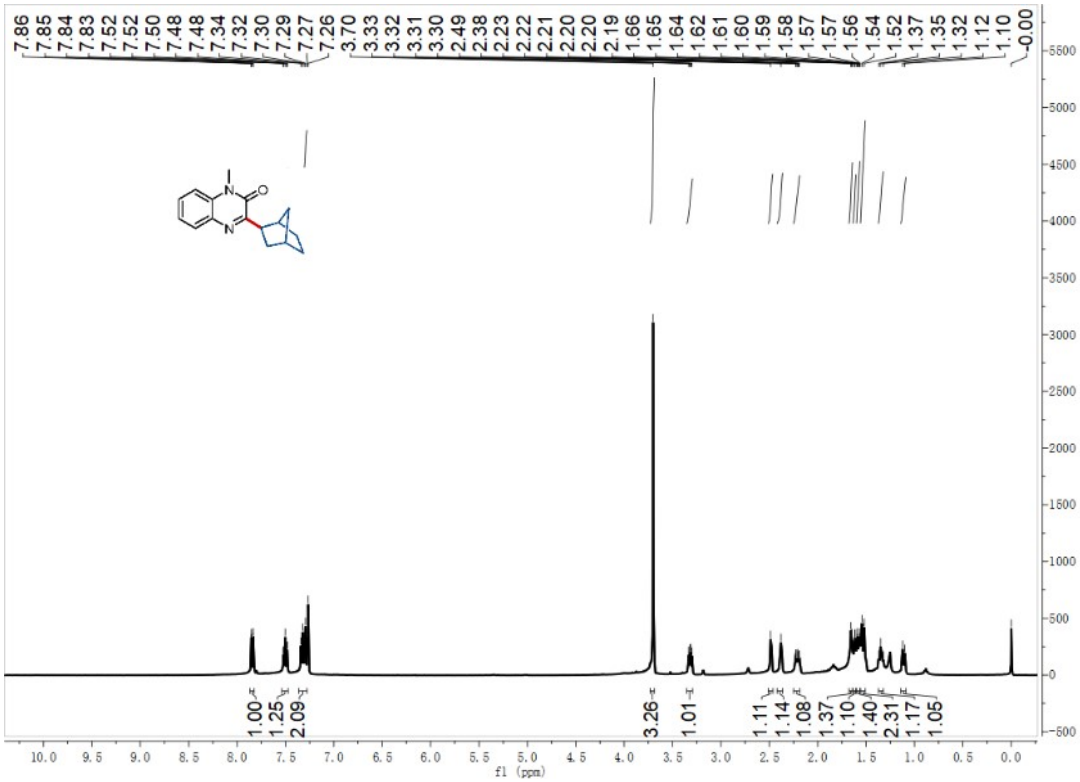
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **25**



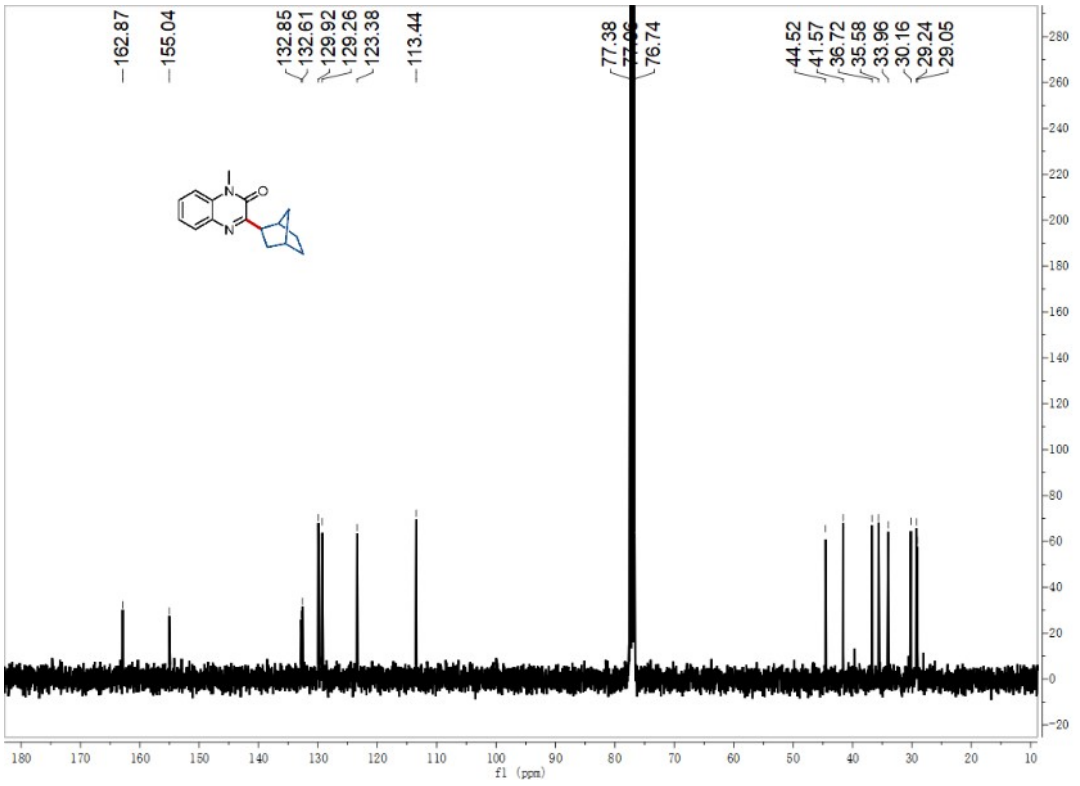
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of compound **25**



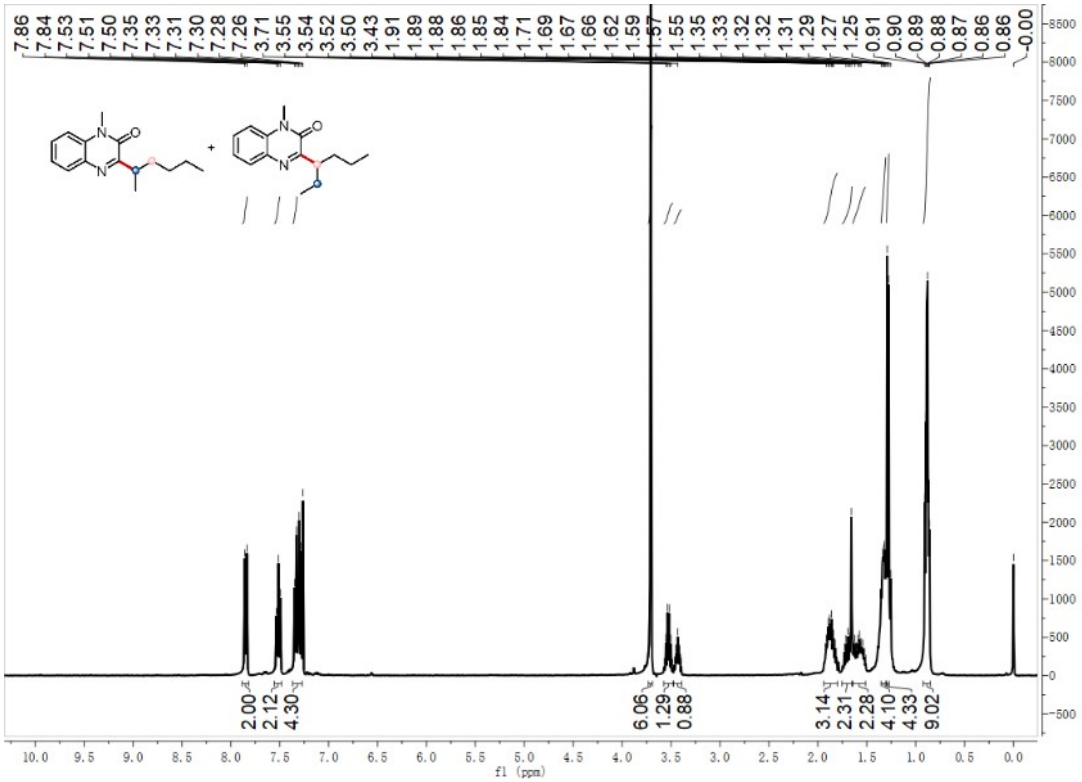
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **26**



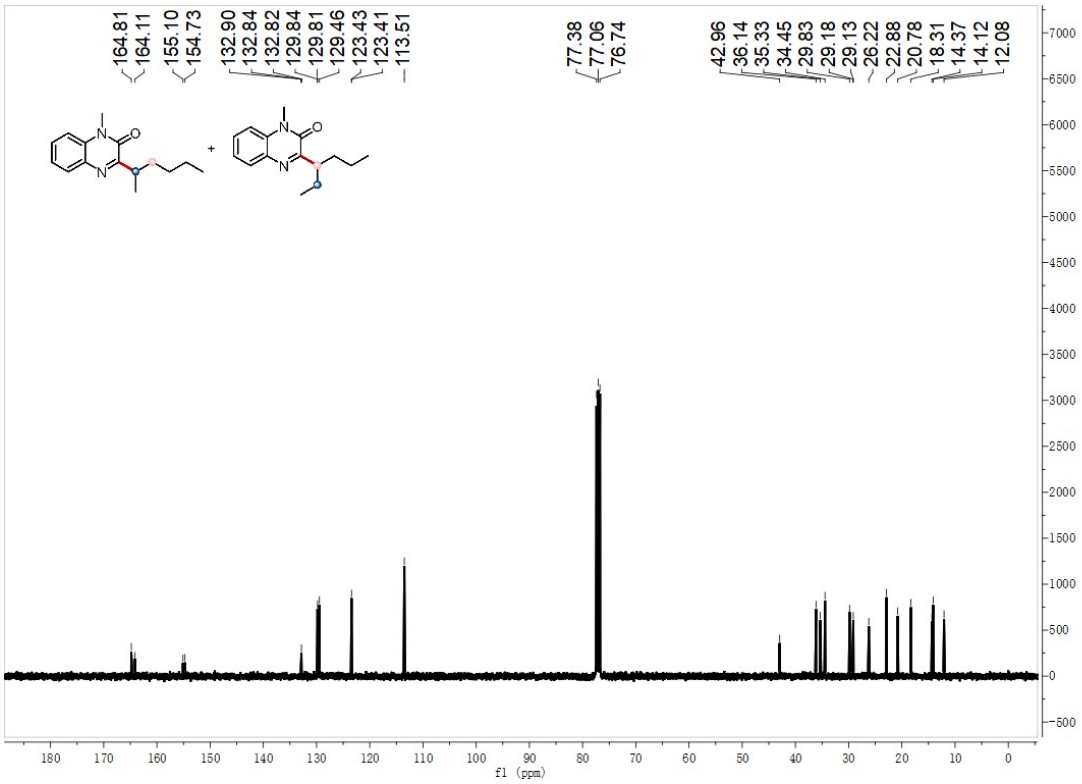
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of compound **26**



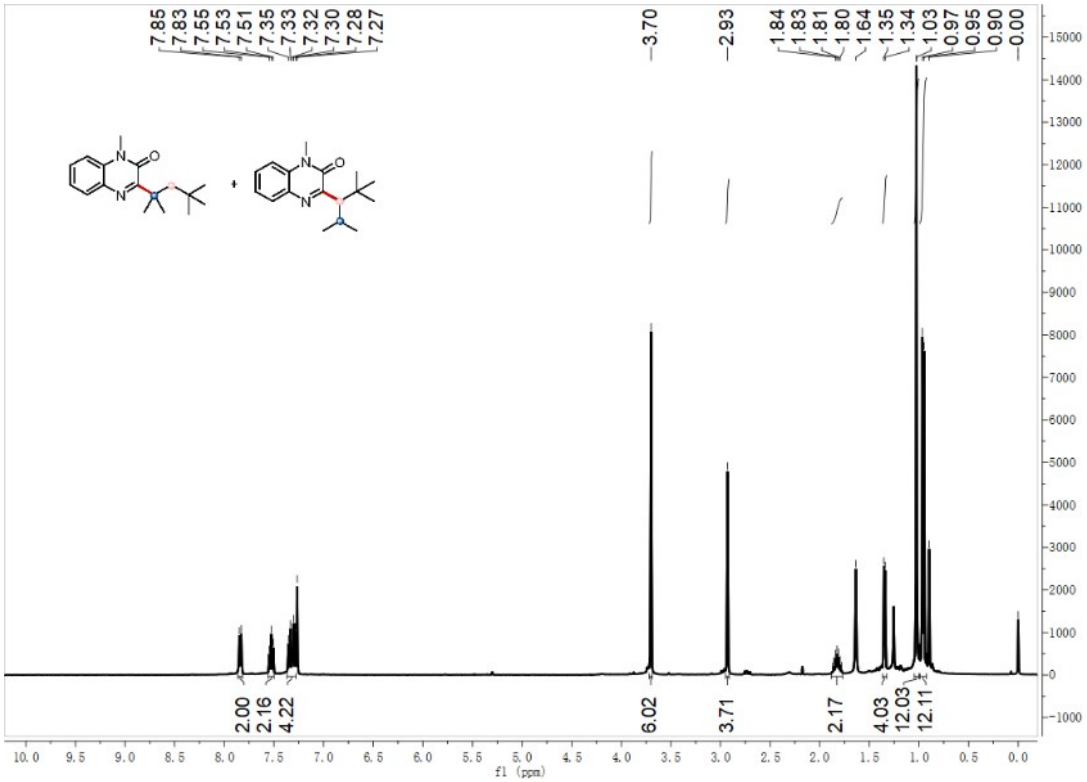
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **27**



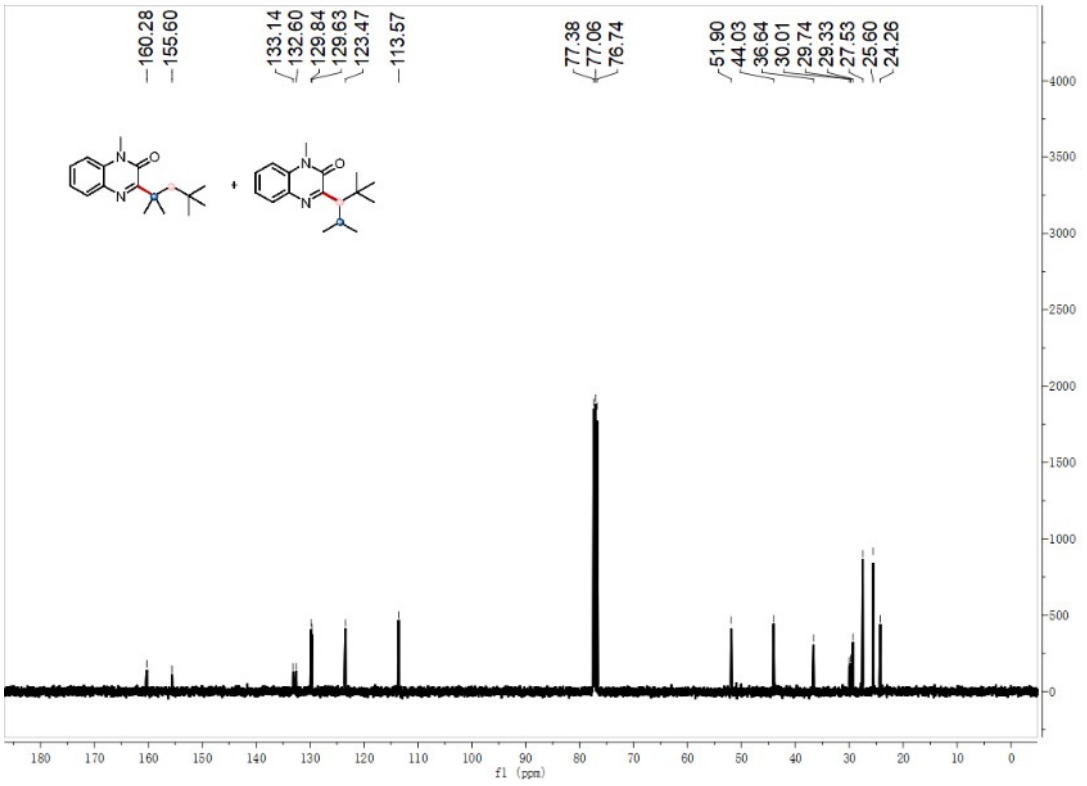
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of compound **27**



^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **28**



^{13}C NMR spectrum (101 MHz, $CDCl_3$) of compound **28**



11. Reference

1. Gao, M.; Li, Y.; Xie, L.; Chauvin, R.; Cui, X., Direct phosphonation of quinoxalin-2(1*H*)-ones under transition-metal-free conditions. *Chem. Commun.* **2016,** *52*, 2846-9.