A combination of heterogeneous catalysis and photocatalysis for the olefination of quinoxalin-2(1*H*)-ones with ketones in water: A green and efficient access to (*Z*)-enaminones

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Supporting Information

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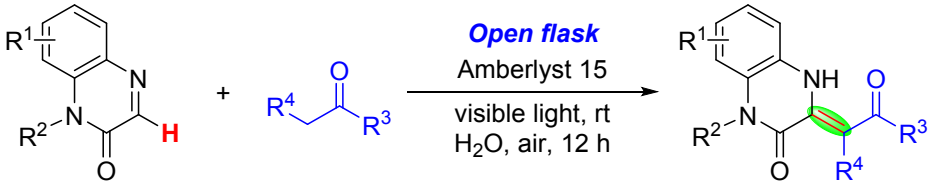
General Information

All reagents and deuterated solvents were commercially available and used without further purification. All products were separated by silica gel (200-300 mesh) column chromatography with petroleum ether (PE) (60-90°C) and ethyl acetate (EA). ^{1}H, ^{13}C and ^{19}F NMR spectra were recorded on a Bruker Advance 500 spectrometer at ambient temperature with $CDCl_3$ or CD_3SOCD_3 as solvent and tetramethylsilane (TMS) as the internal standard. Melting points were determined on an X-5 Data microscopic melting point apparatus. Analytical thin layer chromatography (TLC) was performed on Merk precoated TLC (silica gel 60 F254) plates. Compounds for HRMS were analyzed by positive mode electrospray ionization (ESI) using Agilent 6530 QTOF mass spectrometer. The ESR (Electron Spin Resonance) spectrum was recorded by a JES X320 (JEOL Co.).

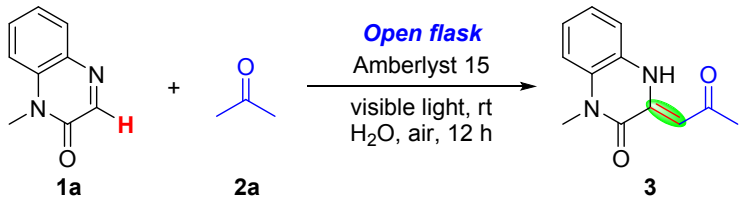
1. Experimental Section

1.1 General procedure for the synthesis of (*Z*)-enaminones



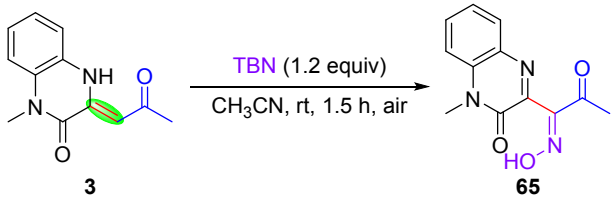
To a 15 mL tube was added quinoxalin-2(1*H*)-ones (**1**) (0.2 mmol), ketones (**2**) (0.6 mmol), Amberlyst 15 (50 mg) and H_2O (3 mL). The above mixture was vigorous stirred under the irradiation of visible light (LEDs, 420 nm, 5 W) for 12 hours. After then, the resulting aqueous phase was extracted with ethyl acetate and the collected organic layer was washed with brine, dried with $MgSO_4$. The solvent was removed under reduced pressure, and the crude product was further purified by silica gel column chromatography (200-300 mesh silica gel, PE/EA = 3:1) to afford the target product.

1.2 General procedure for the gram-scale synthesis of (*Z*)-enaminone 3



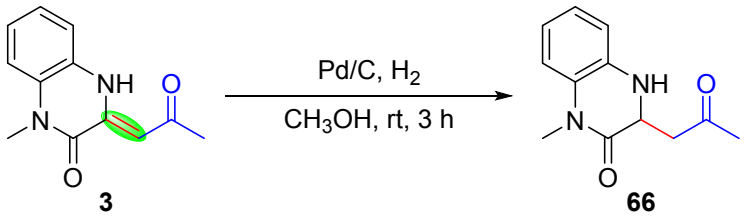
To a 150 mL flask was added quinoxalin-2(1*H*)-one (**1a**) (8 mmol), acetone (**2a**) (24 mmol), Amberlyst 15 (2 g) and H_2O (90 mL). The above mixture was vigorous stirred under the irradiation of visible light (LEDs, 420 nm, 5 W) for 12 hours. After then, the catalyst was removed by filtration. The resulting aqueous phase was extracted with ethyl acetate and the collected organic layer was washed with brine, dried with $MgSO_4$. The solvent was removed under reduced pressure, and the crude product was further purified by silica gel column chromatography (200-300 mesh silica gel, PE/EA = 3:1) to afford target product **3**.

1.3 General procedure for the synthesis of compound 65 using (*Z*)-enaminone 3 as substrate



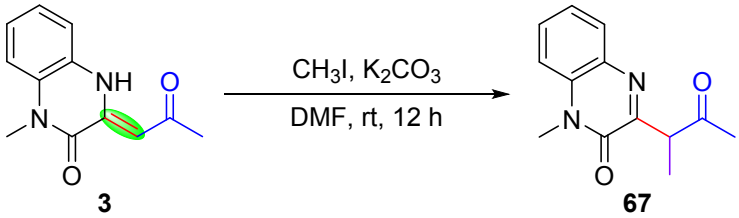
To a dried 15 mL tube was added (*Z*)-enaminone (**3**) (0.2 mmol), CH_3CN (1 mL) and TBN (1.2 equiv.). The mixture was stirred at ambient temperature for 1.5 h. After then, the reaction was quenched with saturated $NaHCO_3$. The mixture was extracted with ethyl acetate and the collected organic layer was washed with brine, dried with $MgSO_4$. The solvent was removed under reduced pressure, and the crude product was further purified by silica gel column chromatography (200-300 mesh silica gel, PE/EA = 2:1) to afford product **65**.

1.4 General procedure for the synthesis of compound 66 using (*Z*)-enaminone 3 as substrate



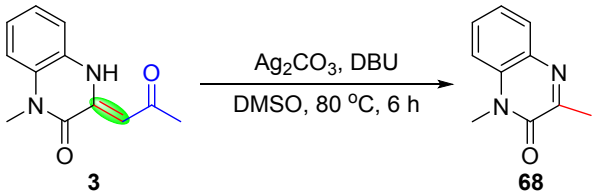
To a dried 15 mL tube with a hydrogen balloon was added (*Z*)-enaminone (**3**) (0.2 mmol), Pd/C (10 mg) and CH_3OH (2 mL). The mixture was stirred at ambient temperature for 3 h. After then, the catalyst was removed by centrifugation. The solvent was removed directly under reduced pressure, and the crude product was further purified by silica gel column chromatography (200-300 mesh silica gel, PE/EA = 3:1) to afford product **66**.

1.5 General procedure for the synthesis of compound 67 using (*Z*)-enaminone 3 as substrate



To a dried 15 mL tube was added (*Z*)-enaminone (**3**) (0.2 mmol), K_2CO_3 (0.4 mmol), CH_3I (0.4 mmol) and DMF (2 mL). The mixture was stirred at ambient temperature for 12 h. After then, the reaction was quenched with saturated $NaHCO_3$. The mixture was extracted with ethyl acetate and the collected organic layer was washed with brine, dried with $MgSO_4$. The solvent was removed under reduced pressure, and the crude product was further purified by silica gel column chromatography (200-300 mesh silica gel, PE/EA = 3:1) to afford product **67**.

1.6 General procedure for the synthesis of compound 68 using (*Z*)-enaminone 3 as substrate



To a dried 15 mL tube was added (*Z*)-enaminone (**3**) (0.2 mmol), Ag_2CO_3 (0.2 mmol), DBU (0.2 mmol) and DMSO (2 mL). The mixture was stirred at 80 °C for 6 h. After then, the reaction was quenched with saturated $NaHCO_3$. The mixture was extracted with ethyl acetate and the collected organic layer was washed with brine, dried with $MgSO_4$. The solvent was removed under reduced pressure, and the crude product was further purified by silica gel column chromatography (200-300 mesh silica gel, PE/EA = 3:1) to afford product **68**.

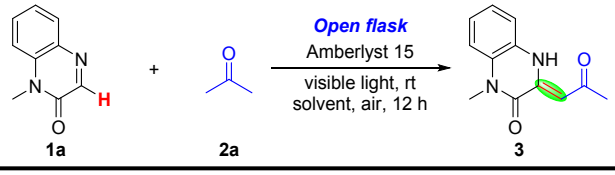
1.7 Testing of the recyclability of catalytic system.

To a 15 mL tube was added quinoxalin-2(1*H*)-one (**1a**) (0.2 mmol), acetone (**2a**) (0.6 mmol), Amberlyst 15 (50 mg) and H_2O (3 mL). The above mixture was vigorous stirred under the irradiation of visible light for 12 hours. After then, the reaction mixture was directly extracted with ethyl acetate and the collected organic layer was washed with brine, dried with $MgSO_4$. The solvent was removed under reduced pressure, and the crude product was further purified by silica gel column chromatography (200-300 mesh silica gel, PE/EA = 3:1) to afford target product. The resulting aqueous solution containing Amberlyst 15 catalyst was reutilized to catalyse the transformation by directly adding starting materials.

1.8 The regeneration of Amberlyst 15 catalyst

After it was recycled for four times, Amberlyst 15 catalyst was first washed with ethanol, ethyl acetate and 1,2-dichloromethane continuously to remove the organic impurities. Then, the catalyst was washed with HCl (2 M), distilled water and NaOH (2 M) for three times to remove the water-soluble impurities. After that, the catalyst was immersed into HCl (2 M) for 12 h, and the resulting catalyst was washed with distilled water repeatedly until the pH value is about 7. Finally, it was dried under vacuum condition to give the regenerated Amberlyst 15 catalyst.

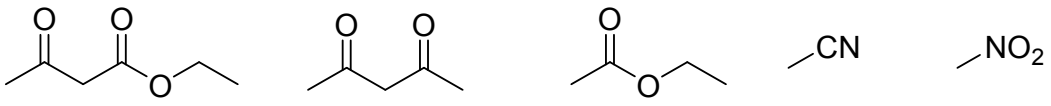
1.9 Optimization of solvents[a,b]



entry	solvent	yield (%)[b]
1	H_2O	83
2	PEG 200	23
3	EtOH	36
4	MeOH	25
5	acetone	88
6	MeCN	85

[a] Reaction conditions: **1a** (0.2 mmol), **2a** (0.6 mmol), Amberlyst 15 (50 mg), solvent (3 mL), visible light (LEDs, 420 nm, 5 W), open flask, rt, air, 12 h. [b] Isolated yields.

1.10 Unreactive substrates



2. Mechanism Studies

2.1 DFT calculations

Table S1 E_T (kJ/mol) and ΔE_{ST} (eV) of 1a, 3, and 66.

	E_T	ΔE_{ST}
1a	246	1.02
3	189	1.23
66	324	0.63

2.1.1 Computational details

The geometries of T_1 state were optimized using unrestricted M06-2X[1] (UM06-2X) with the 6-311G(d,p) basis set by setting the spin multiplicity as 3. The energies of the T_1 state were further calculated using time-dependent (TD) M06-2X. The geometries and energies of S_1 state were obtained using TD M06-2X with the 6-311G(d,p) basis set. The IEFPCM implicit solvation model[2] were employed in all calculations to account for the solvent effect of water.

Geometry optimizations of all intermediates were carried out at the M06-2X/6-311G(d,p) level. Vibrational frequency calculations were performed to confirm that each of the species was a local minimum (no imaginary frequencies). The solvent effect of water was considered with IEFPCM solvation model. All calculations were performed using the Gaussian 16 C.01 package.[3]

2.1.2 Cartesian coordinates of the optimized intermediates

Int1

broken-symmetry singlet

C	4.08361600	-1.15178300	0.54997000
C	3.47629700	0.10029500	0.48220600
C	2.17444500	0.22417500	0.00560700
C	1.46507600	-0.92058600	-0.39680600
C	2.08091400	-2.16720000	-0.31959300
N	1.54738400	1.48390000	-0.13547400
C	0.19061100	1.60743200	-0.23983100
C	-0.59625700	0.29841200	-0.23663100
N	0.17813600	-0.74131600	-0.90493500
C	-1.93496800	0.49381200	-0.92742500
C	-2.86414300	-0.69150700	-0.77299900
O	-2.48364600	-1.74156600	-0.30173700
C	-4.28553400	-0.48415000	-1.22045500
O	-0.37194800	2.68602900	-0.29567900
C	3.38768200	-2.28313500	0.14402800
C	2.35707700	2.69504800	-0.05811600
H	5.09784100	-1.23308000	0.91964000
H	4.02354500	0.97804100	0.79927800
H	1.52785800	-3.04494100	-0.63543000
H	-0.77032800	0.04371200	0.82238400
H	-0.35153800	-1.60546700	-0.93705500

H	-2.42842500	1.38831800	-0.54194000
H	-1.77769700	0.66336000	-1.99875200
H	-4.77815300	0.18589300	-0.50991000
H	-4.31348700	0.00070000	-2.19799200
H	-4.81268600	-1.43532100	-1.24901000
H	3.85348400	-3.25963800	0.19315900
H	3.23330300	2.58652700	-0.69710000
H	1.75141500	3.52770800	-0.40085900
H	2.67916400	2.88505800	0.96842400
O	-3.30061800	0.39824200	1.88815100
O	-2.87151900	-0.49318500	2.54530200

Int2

broken-symmetry singlet

C	4.34130900	-0.37038100	0.43432200
C	3.43356600	0.66636300	0.24618400
C	2.09483400	0.39116600	-0.03990900
C	1.68930300	-0.95311600	-0.14023200
C	2.60449000	-1.98699200	0.05288000
N	1.14561700	1.40584000	-0.21248300
C	-0.18036100	1.12883500	-0.50939700
C	-0.55606900	-0.22687000	-0.64518600
N	0.36730900	-1.21314700	-0.44358900
C	-1.93199300	-0.61885000	-1.05600600
C	-2.65934500	-1.51810800	-0.05791500
O	-2.04928300	-2.23142600	0.70364400
C	-4.16036300	-1.50353100	-0.13759600
O	-0.98914600	2.08401300	-0.66261300
C	3.92929300	-1.69626200	0.34159800
C	1.56347200	2.79450900	-0.06426600
H	5.37420500	-0.13445800	0.65615100
H	3.77234500	1.68934800	0.32650200
H	2.26312800	-3.01220700	-0.03065900
H	-2.28056700	2.05784800	0.06090000
H	0.02960500	-2.16539300	-0.37866800
H	-2.52639300	0.26822500	-1.26751600
H	-1.89463600	-1.19796700	-1.99031700
H	-4.51863200	-0.52965900	0.20430300
H	-4.47933700	-1.62701100	-1.17525100
H	-4.57690200	-2.29291600	0.48445900
H	4.63623600	-2.50223900	0.49044500
H	2.32314400	3.04038400	-0.80888500
H	0.69364400	3.42393600	-0.21078600
H	1.97184600	2.95750900	0.93501300
O	-2.88760000	0.93254500	1.40620000

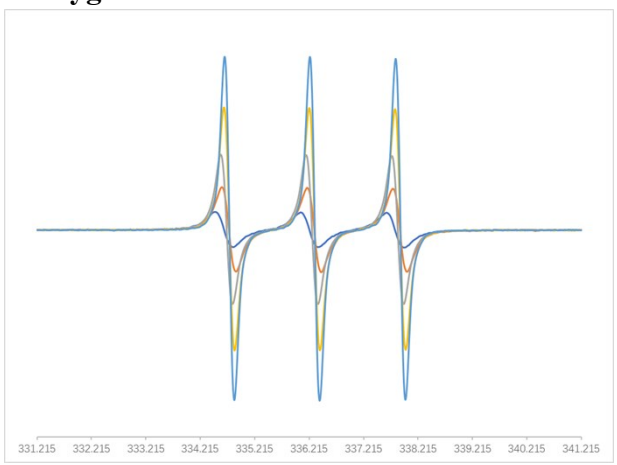
O	-3.12234400	1.96926500	0.64651300

Int3

closed-shell singlet

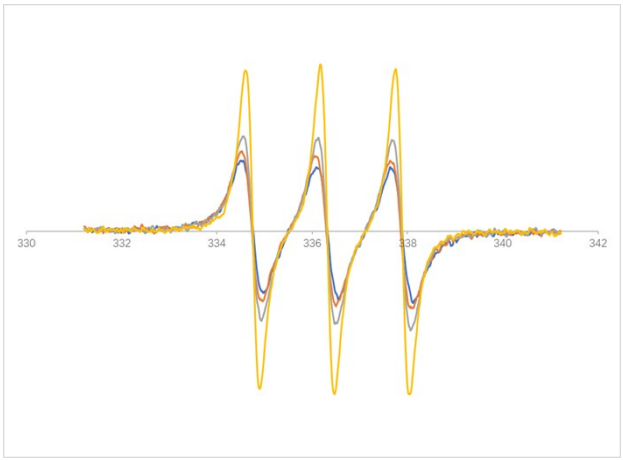
C	4.26666200	-0.51408700	0.32112300
C	3.42144700	0.53550700	-0.01248800
C	2.04766600	0.31876500	-0.13250400
C	1.53815600	-0.96733500	0.08715600
C	2.39239200	-2.01717800	0.42244300
N	1.15560100	1.35565000	-0.46532700
C	-0.18570900	1.17362100	-0.59103600
C	-0.71302800	-0.21538500	-0.36609200
N	0.17598600	-1.17517900	-0.03728400
C	-2.05685900	-0.43686800	-0.50269100
C	-2.65037500	-1.74589900	-0.31505800
O	-1.98933300	-2.73999200	-0.00917700
C	-4.14296600	-1.84648400	-0.51269700
O	-0.95072000	2.08550600	-0.88290800
C	3.75395300	-1.79074100	0.53899200
C	1.69374300	2.69988000	-0.68112200
H	5.32941000	-0.32991000	0.41020900
H	3.83599700	1.51952500	-0.17768100
H	1.97324700	-3.00267900	0.58730700
H	-2.38502800	2.45337900	0.17501300
H	-0.22527100	-2.10355000	0.10351900
H	-2.39632000	0.74212000	1.65545400
H	-2.68354700	0.39510700	-0.78792400
H	-4.65500900	-1.14205100	0.14692800
H	-4.39871700	-1.57575300	-1.53988800
H	-4.47599200	-2.86102400	-0.30465800
H	4.41364500	-2.60849000	0.79902600
H	2.40204300	2.68358300	-1.50973600
H	0.86765400	3.35986400	-0.91765900
H	2.19411700	3.04394300	0.22427400
O	-2.21118800	1.66830600	1.86621400
O	-3.01223900	2.36116300	0.91561300

2.2 Determination of singlet oxygen in the reaction



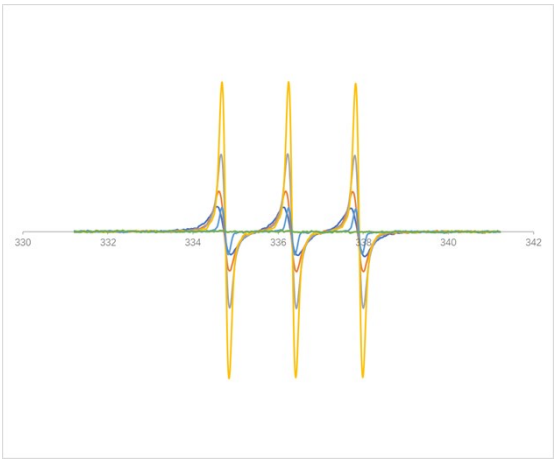
Magnetic Field [mT]

Scheme S1 ESR spectra of $^1O_2$ triggerred by starting material 1



Magnetic Field [mT]

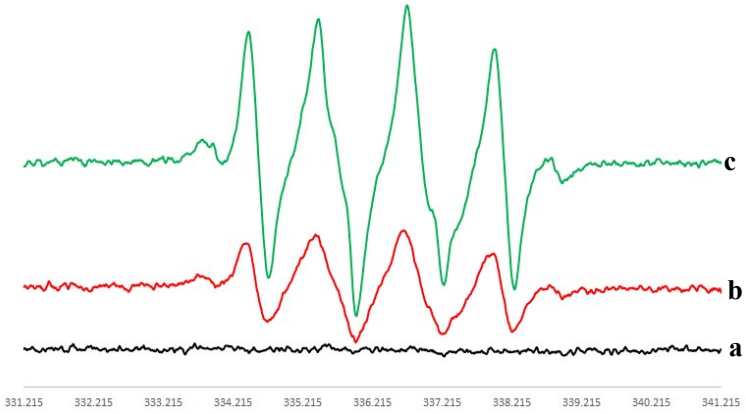
Scheme S2 ESR spectra of $^1O_2$ triggerred by product 3



Magnetic Field [mT]

Scheme S3 ESR spectra of $^1O_2$ triggerred by intermediate 66

2.3 Determination of superoxide radical anion in the reaction

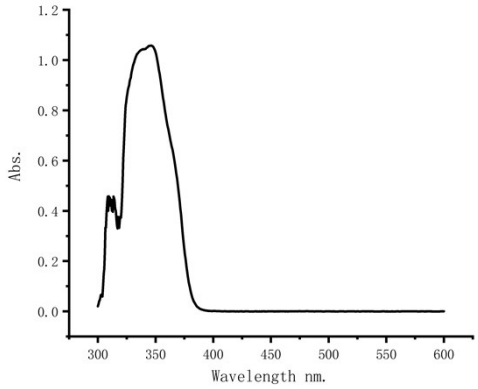


Scheme S4 ESR spectra of superoxide radical anion

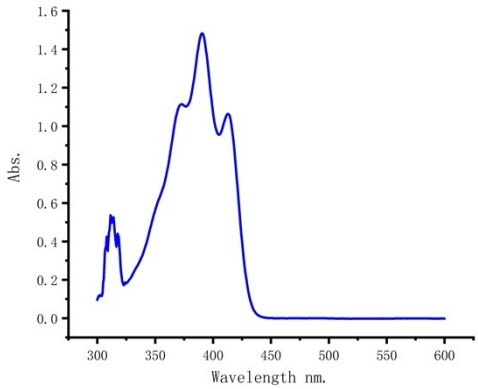
A mixture of intermediate **66** (100 mM) and DMPO (50 mM) in acetone (40 uL) was transferred in a capillary tube, then the capillary tube was transferred to a ESR sample tube, the ESR signal was recorded in dark (**a**); then the tube was irradiated with a 420 nm LED (5 W), then the spectrum was recorded in 2 min (**b**) and 4 min (**c**) separately. A four signal was recorded, with g = 2.0034, A_N = 1.36 mT, A_H = 1.28 mT, which was coincident with superoxide radical.

2.4 UV-vis absorption spectroscopic measurements

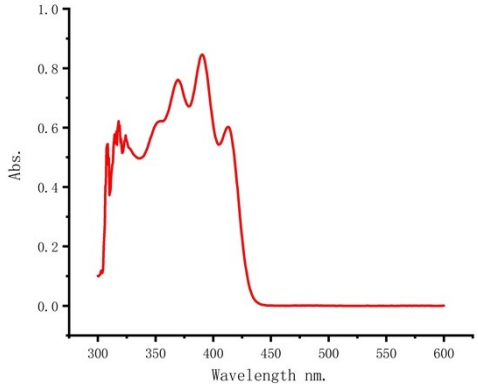
The UV-vis absorption spectrum of **1a**, **3** and **66** was recorded respectively. The sample was prepared by mixing compounds **1a**, **3** or **66** with acetone. The reaction mixture was stirred for 10 min, and the reaction mixture was filtered with a filter. The resulted solution was stored in a light path quartz fluorescence cuvette, and UV-vis absorption spectrum was recorded.



Scheme S5 UV-vis absorption spectroscopy of 1a



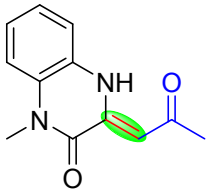
Scheme S6 UV-vis absorption spectroscopy of 3



Scheme S7 UV-vis absorption spectroscopy of 66

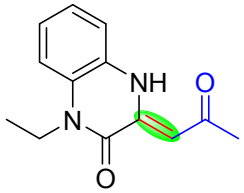
3. Characterization of Products

(*Z*)-1-methyl-3-(2-oxopropylidene)-3,4-dihydroquinoxalin-2(1*H*)-one (3)



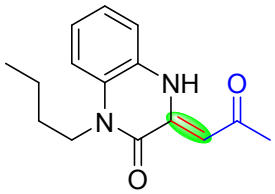
Obtained as a yellow solid (36 mg, 83% yield); M.p. 152-153 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 13.32 (s, 1H), 7.19 – 7.15 (m, 3H), 7.13 (dd, J = 5.3, 2.5 Hz, 1H), 6.27 (s, 1H), 3.63 (s, 3H), 2.27 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 198.9, 156.2, 142.7, 128.0, 125.3, 124.3, 123.6, 116.2, 114.4, 94.5, 30.0, 29.8; HRMS (ESI+): Calculated for $C_{12}H_{12}N_2O_2Na$: $[M + Na]^+$ 217.0972, Found 217.0973.

(*Z*)-1-ethyl-3-(2-oxopropylidene)-3,4-dihydroquinoxalin-2(1*H*)-one (4)



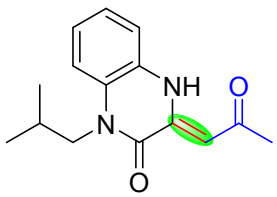
Obtained as a yellow solid (39 mg, 85% yield); M.p. 158-159 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 13.26 (s, 1H), 7.08 (d, J = 10.5 Hz, 4H), 6.18 (s, 1H), 4.17 (dd, J = 13.7, 6.7 Hz, 2H), 2.19 (s, 3H), 1.29 (t, J = 7.1 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 198.7, 155.7, 142.9, 126.8, 125.5, 124.1, 123.7, 116.6, 114.2, 94.2, 37.9, 30.0, 12.2; HRMS (ESI+): Calculated for $C_{13}H_{14}N_2O_2Na$: $[M + Na]^+$ 253.0947, Found 253.0951.

(*Z*)-1-butyl-3-(2-oxopropylidene)-3,4-dihydroquinoxalin-2(1*H*)-one (5)



Obtained as a yellow solid (40 mg, 77% yield); M.p. 165-166 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 13.26 (s, 1H), 7.07 (s, 4H), 6.18 (s, 1H), 4.13 – 4.07 (m, 2H), 2.20 (s, 3H), 1.68 – 1.62 (m, 2H), 1.40 (dd, J = 15.0, 7.5 Hz, 2H), 0.92 (t, J = 7.4 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 198.6, 155.9, 142.9, 127.2, 125.5, 124.1, 123.7, 116.6, 114.4, 94.3, 42.6, 29.9, 29.1, 20.2, 13.8; HRMS (ESI+): Calculated for $C_{15}H_{18}N_2O_2Na$: $[M + Na]^+$ 281.1260, Found 281.1257.

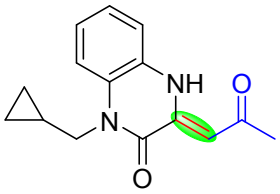
(*Z*)-1-isobutyl-3-(2-oxopropylidene)-3,4-dihydroquinoxalin-2(1*H*)-one (6)



Obtained as a yellow solid (41 mg, 79% yield); M.p. 149-150 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 13.27 (s, 1H), 7.05 (s, 4H), 6.18 (s, 1H), 3.99 (d, J = 7.0 Hz, 2H), 2.19 (s, 3H), 2.14 (dd, J = 13.7, 6.9 Hz, 1H), 0.92 (d, J = 6.7 Hz, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 198.8, 156.4, 142.8, 127.4, 125.4, 124.1,

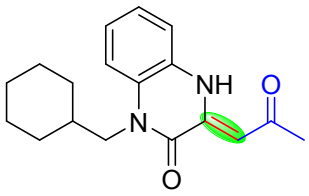
123.5, 116.6, 114.8, 94.5, 49.3, 29.9, 27.0, 20.2; HRMS (ESI+): Calculated for $C_{15}H_{18}N_2O_2Na$: $[M + Na]^+$ 281.1260, Found 281.1264.

(*Z*)-1-(cyclopropylmethyl)-3-(2-oxopropylidene)-3,4-dihydroquinoxalin-2(1*H*)-one (7)



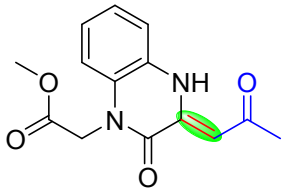
Obtained as a yellow solid (40 mg, 78% yield); M.p. 189-190 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 13.37 (s, 1H), 7.31 – 7.28 (m, 1H), 7.16 (dd, J = 6.4, 3.3 Hz, 3H), 6.26 (s, 1H), 4.13 (d, J = 6.9 Hz, 2H), 2.27 (s, 3H), 1.28 (dd, J = 9.9, 4.2 Hz, 1H), 0.56 (dd, J = 4.4, 3.1 Hz, 2H), 0.54 (d, J = 2.3 Hz, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 198.7, 156.3, 143.0, 127.4, 125.5, 124.1, 123.6, 116.6, 114.7, 94.4, 46.6, 30.0, 9.5, 4.1; HRMS (ESI+): Calculated for $C_{15}H_{16}N_2O_2Na$: $[M + Na]^+$ 257.1285, Found 257.1288.

(*Z*)-1-(cyclohexylmethyl)-3-(2-oxopropylidene)-3,4-dihydroquinoxalin-2(1*H*)-one (8)



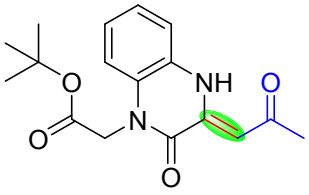
Obtained as a yellow solid (47 mg, 79% yield); M.p. 182-183 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 13.36 (s, 1H), 7.14 (s, 4H), 6.26 (s, 1H), 4.08 (d, J = 6.7 Hz, 2H), 2.26 (s, 3H), 1.89 – 1.84 (m, 1H), 1.74 (d, J = 2.7 Hz, 2H), 1.67 (d, J = 15.0 Hz, 3H), 1.20 – 1.15 (m, 5H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 198.7, 156.4, 142.8, 127.5, 125.5, 124.0, 123.5, 116.6, 114.9, 94.4, 48.4, 36.3, 30.9, 30.0, 26.2, 25.8; HRMS (ESI+): Calculated for $C_{18}H_{22}N_2O_2Na$: $[M + Na]^+$ 321.1573, Found 321.1571.

Methyl (*Z*)-2-(2-oxo-3-(2-oxopropylidene)-3,4-dihydroquinoxalin-1(2*H*)-yl)acetate (9)



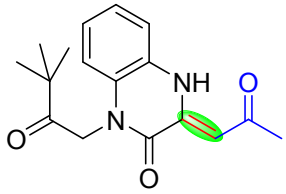
Obtained as a yellow solid (41 mg, 75% yield); M.p. 197-198 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 13.24 (s, 1H), 7.16 (dd, J = 12.6, 5.2 Hz, 2H), 7.11 (dd, J = 8.3, 6.5 Hz, 1H), 6.91 (d, J = 8.1 Hz, 1H), 6.28 (s, 1H), 4.96 (s, 2H), 3.78 (s, 3H), 2.28 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 199.0, 167.7, 156.4, 142.1, 127.0, 125.5, 124.7, 123.7, 116.6, 113.8, 95.0, 52.9, 44.0, 30.0; HRMS (ESI+): Calculated for $C_{14}H_{14}N_2O_4Na$: $[M + Na]^+$ 297.0846, Found 297.0850.

***Tert*-butyl (*Z*)-2-(2-oxo-3-(2-oxopropylidene)-3,4-dihydroquinoxalin-1(2*H*)-yl)acetate (10)**



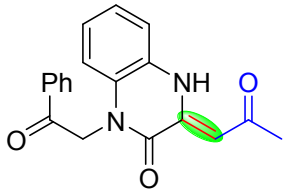
Obtained as a yellow solid (46 mg, 73% yield); M.p. 172-173 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 13.25 (s, 1H), 7.15 (t, J = 4.8 Hz, 2H), 7.13 – 7.09 (m, 1H), 6.91 (d, J = 7.9 Hz, 1H), 6.28 (s, 1H), 4.85 (s, 2H), 2.27 (s, 3H), 1.46 (s, 9H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 199.0, 166.2, 156.4, 142.3, 127.2, 125.4, 124.5, 123.6, 116.5, 113.9, 94.9, 83.1, 44.7, 30.1, 28.0; HRMS (ESI+): Calculated for $C_{17}H_{20}N_2O_4Na$: $[M + Na]^+$ 339.1315, Found 339.1309.

(*Z*)-1-(3,3-dimethyl-2-oxobutyl)-3-(2-oxopropylidene)-3,4-dihydroquinoxalin-2(1*H*)-one (11)



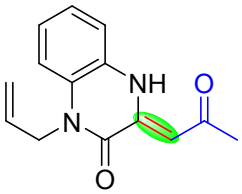
Obtained as a yellow solid (44 mg, 73% yield); M.p. 162-163 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 13.28 (s, 1H), 7.13 (d, J = 4.2 Hz, 2H), 7.09 – 7.04 (m, 1H), 6.71 (d, J = 8.2 Hz, 1H), 6.22 (s, 1H), 5.17 (s, 2H), 2.26 (s, 3H), 1.35 (s, 9H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 206.6, 198.9, 156.4, 142.3, 127.4, 125.4, 124.4, 123.5, 116.6, 113.7, 94.6, 47.5, 43.8, 30.0, 26.5; HRMS (ESI+): Calculated for $C_{17}H_{20}N_2O_3Na$: $[M + Na]^+$ 301.1547, Found 301.1543.

(*Z*)-1-(2-oxo-2-phenylethyl)-3-(2-oxopropylidene)-3,4-dihydroquinoxalin-2(1*H*)-one (12)



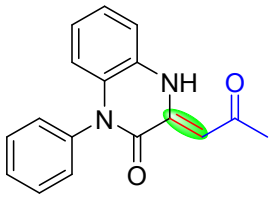
Obtained as a yellow solid (48 mg, 75% yield); M.p. 177-178 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 13.31 (s, 1H), 8.07 (d, J = 7.6 Hz, 2H), 7.68 (t, J = 7.4 Hz, 1H), 7.56 (t, J = 7.7 Hz, 2H), 7.14 (q, J = 7.8 Hz, 2H), 7.03 (t, J = 8.4 Hz, 1H), 6.78 (d, J = 8.1 Hz, 1H), 6.28 (s, 1H), 5.66 (s, 2H), 2.28 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 199.0, 191.1, 156.6, 142.3, 134.6, 134.3, 129.1, 128.2, 127.3, 125.5, 124.5, 123.6, 116.6, 114.2, 94.8, 49.0, 30.1; HRMS (ESI+): Calculated for $C_{19}H_{16}N_2O_3Na$: $[M + Na]^+$ 343.1053, Found 343.1051.

(*Z*)-1-allyl-3-(2-oxopropylidene)-3,4-dihydroquinoxalin-2(1*H*)-one (13)



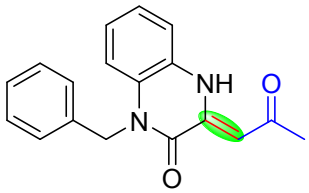
Obtained as a yellow solid (34 mg, 70% yield); M.p. 163-164 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 13.32 (s, 1H), 7.19 – 7.19 (m, 4H), 6.28 (s, 1H), 6.00 – 5.84 (m, 1H), 5.25 (dd, J = 25.1, 13.8 Hz, 2H), 4.83 (d, J = 4.1 Hz, 2H), 2.27 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 198.8, 156.0, 142.6, 130.6, 127.1, 125.4, 124.3, 123.5, 118.0, 116.4, 115.0, 94.5, 45.1, 30.0; HRMS (ESI+): Calculated for $C_{14}H_{14}N_2O_2Na$: $[M + Na]^+$ 265.0947, Found 265.0934.

(*Z*)-3-(2-oxopropylidene)-1-phenyl-3,4-dihydroquinoxalin-2(1*H*)-one (14)



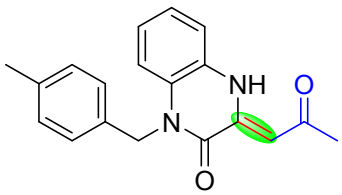
Obtained as a yellow solid (33 mg, 59% yield); M.p. 135-136 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 13.36 (s, 1H), 7.61 (t, *J* = 7.7 Hz, 2H), 7.54 (t, *J* = 7.3 Hz, 1H), 7.29 (d, *J* = 7.5 Hz, 2H), 7.18 – 7.11 (m, 2H), 6.93 (t, *J* = 7.7 Hz, 1H), 6.46 (d, *J* = 8.3 Hz, 1H), 6.30 (s, 1H), 2.29 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 199.1, 156.2, 143.1, 136.3, 130.3, 129.4, 129.2, 128.4, 125.2, 124.4, 123.2, 116.3, 116.0, 94.8, 30.1; HRMS (ESI+): Calculated for $C_{17}H_{14}N_2O_2Na$: $[M + Na]^+$ 301.0947, Found 301.0925.

(*Z*)-1-benzyl-3-(2-oxopropylidene)-3,4-dihydroquinoxalin-2(1*H*)-one (15)



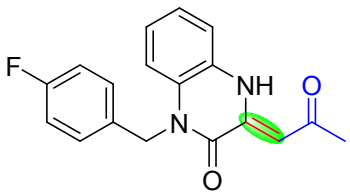
Obtained as a yellow solid (44 mg, 75% yield); M.p. 132-133 °C. ^{1}H NMR (500 MHz, $CDCl_3$) *δ* 13.27 (s, 1H), 7.23 (d, *J* = 7.1 Hz, 2H), 7.18 (t, *J* = 6.2 Hz, 3H), 7.02 (dd, *J* = 13.3, 7.2 Hz, 3H), 6.93 (dd, *J* = 10.6, 4.3 Hz, 1H), 6.26 (s, 1H), 5.34 (s, 2H), 2.21 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) *δ* 198.8, 156.6, 142.6, 135.2, 129.0, 127.7, 127.2, 126.7, 125.5, 124.4, 123.6, 116.4, 115.3, 94.8, 46.5, 30.0; HRMS (ESI+): Calculated for $C_{18}H_{16}N_2O_2Na$: $[M + Na]^+$ 315.1104, Found 315.1108.

(*Z*)-1-(4-methylbenzyl)-3-(2-oxopropylidene)-3,4-dihydroquinoxalin-2(1*H*)-one (16)



Obtained as a yellow solid (47 mg, 77% yield); M.p. 139-140 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 13.35 (s, 1H), 7.13 (dt, *J* = 15.3, 7.7 Hz, 7H), 7.04 – 6.98 (m, 1H), 6.34 (s, 1H), 5.38 (s, 2H), 2.31 (s, 3H), 2.28 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) *δ* 198.9, 156.6, 142.7, 137.4, 132.2, 129.6, 127.3, 126.7, 125.5, 124.3, 123.6, 116.3, 115.3, 94.8, 46.3, 30.0, 21.1; HRMS (ESI+): Calculated for $C_{19}H_{18}N_2O_2Na$: $[M + Na]^+$ 329.1260, Found 329.1263.

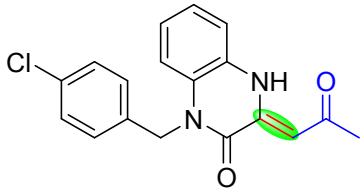
(Z)-1-(4-fluorobenzyl)-3-(2-oxopropylidene)-3,4-dihydroquinoxalin-2(1*H*)-one (17)



Obtained as a yellow solid (45 mg, 73% yield); M.p. 124-125 °C. ^{1}H NMR (500 MHz, $CDCl_3$) *δ* 13.29 (s, 1H), 7.19 – 7.14 (m, 2H), 7.07 (s, 2H), 6.96 (dd, *J* = 22.6, 14.0 Hz, 4H), 6.26 (s, 1H), 5.32 (s, 2H), 2.23 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) *δ* 198.9, 162.2 (d, *J* = 250.0 Hz), 156.6, 142.5, 131.0

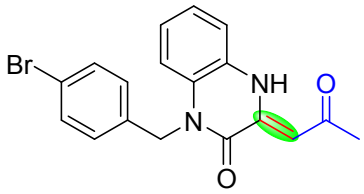
(d, J = 2.5 Hz), 128.5 (d, J = 7.6 Hz), 127.1, 125.6, 124.5, 123.6, 116.5, 115.9 (d, J = 21.4 Hz), 115.1, 94.9, 45.8, 30.0; ^{19}F NMR (471 MHz, $CDCl_3$) δ -114.72; HRMS (ESI+): Calculated for $C_{18}H_{15}FN_2O_2Na$: $[M + Na]^+$ 333.1010, Found 333.1016.

(*Z*)-1-(4-chlorobenzyl)-3-(2-oxopropylidene)-3,4-dihydroquinoxalin-2(1*H*)-one (18)



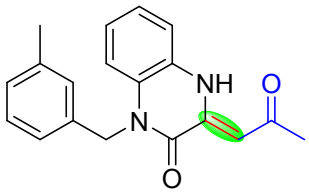
Obtained as a yellow solid (44 mg, 67% yield); M.p. 171-172 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 13.33 (s, 1H), 7.30 (d, J = 8.1 Hz, 2H), 7.20 (d, J = 8.1 Hz, 2H), 7.13 (d, J = 7.4 Hz, 2H), 7.03 (d, J = 3.4 Hz, 2H), 6.34 (s, 1H), 5.39 (s, 2H), 2.29 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 198.9, 156.6, 142.5, 133.7, 133.6, 129.2, 128.2, 127.0, 125.5, 124.6, 123.7, 116.5, 115.1, 94.9, 45.9, 30.0; HRMS (ESI+): Calculated for $C_{18}H_{15}ClN_2O_2Na$: $[M + Na]^+$ 349.0714, Found 349.0718.

(*Z*)-1-(4-bromobenzyl)-3-(2-oxopropylidene)-3,4-dihydroquinoxalin-2(1*H*)-one (19)



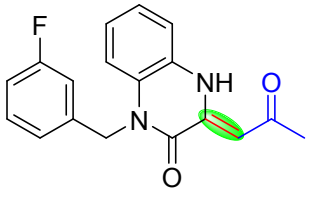
Obtained as a yellow solid (49 mg, 66% yield); M.p. 147-148 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 13.32 (s, 1H), 7.45 (d, J = 8.4 Hz, 2H), 7.14 (d, J = 8.6 Hz, 4H), 7.04 – 7.01 (m, 2H), 6.33 (s, 1H), 5.37 (s, 2H), 2.29 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 199.0, 156.7, 142.4, 134.3, 132.1, 128.5, 127.0, 125.6, 124.6, 123.6, 121.6, 116.5, 115.1, 95.0, 45.9, 30.1; HRMS (ESI+): Calculated for $C_{18}H_{15}BrN_2O_2Na$: $[M + Na]^+$ 393.0209, Found 393.0200.

(*Z*)-1-(3-methylbenzyl)-3-(2-oxopropylidene)-3,4-dihydroquinoxalin-2(1*H*)-one (20)



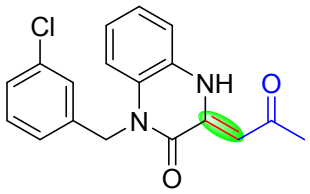
Obtained as a yellow solid (44 mg, 72% yield); M.p. 143-144 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 13.35 (s, 1H), 7.20 (t, J = 7.9 Hz, 1H), 7.10 (dd, J = 15.3, 8.6 Hz, 3H), 7.06 – 6.99 (m, 4H), 6.34 (s, 1H), 5.38 (s, 2H), 2.30 (s, 3H), 2.28 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 198.8, 156.6, 150.3, 142.7, 138.8, 135.2, 128.8, 128.5, 127.3, 125.5, 124.3, 123.7, 123.6, 116.3, 115.4, 94.8, 46.5, 30.0, 21.5; HRMS (ESI+): Calculated for $C_{19}H_{18}N_2O_2Na$: $[M + Na]^+$ 329.1260, Found 329.1260.

(*Z*)-1-(3-fluorobenzyl)-3-(2-oxopropylidene)-3,4-dihydroquinoxalin-2(1*H*)-one (21)



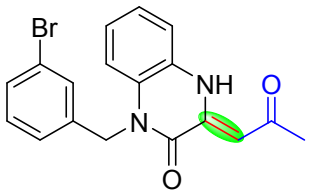
Obtained as a yellow solid (40 mg, 64% yield); M.p. 152-153 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 13.25 (s, 1H), 7.22 – 7.18 (m, 1H), 7.04 (s, 2H), 6.96 (d, J = 11.2 Hz, 3H), 6.86 (d, J = 8.9 Hz, 2H), 6.24 (s, 1H), 5.32 (s, 2H), 2.20 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 198.9, 163.2 (d, J = 248.2 Hz), 156.60, 142.4, 137.8 (d, J = 6.3 Hz), 130.6 (d, J = 8.8 Hz), 127.0, 125.5, 124.5, 123.6, 122.3, 116.5, 115.1, 114.7 (d, J = 21.4 Hz), 113.8 (d, J = 21.4 Hz), 95.0, 46.0, 30.0; ^{19}F NMR (471 MHz, $CDCl_3$) δ -116.51; HRMS (ESI+): Calculated for $C_{18}H_{15}FN_2O_2Na$: $[M + Na]^+$ 333.1010, Found 333.1006.

(*Z*)-1-(3-chlorobenzyl)-3-(2-oxopropylidene)-3,4-dihydroquinoxalin-2(1*H*)-one (22)



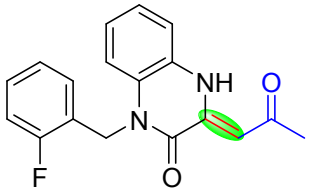
Obtained as a yellow solid (40 mg, 61% yield); M.p. 175-176 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 13.33 (s, 1H), 7.25 (t, J = 3.6 Hz, 3H), 7.16 – 7.12 (m, 3H), 7.05 – 7.00 (m, 2H), 6.34 (s, 1H), 5.39 (s, 2H), 2.29 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 199.0, 156.7, 142.4, 137.3, 135.0, 130.3, 128.0, 127.0, 126.8, 125.6, 124.9, 124.6, 123.6, 116.5, 115.0, 95.0, 46.0, 30.1; HRMS (ESI+): Calculated for $C_{18}H_{15}ClN_2O_2Na$: $[M + Na]^+$ 349.0714, Found 349.0716.

(*Z*)-1-(3-bromobenzyl)-3-(2-oxopropylidene)-3,4-dihydroquinoxalin-2(1*H*)-one (23)



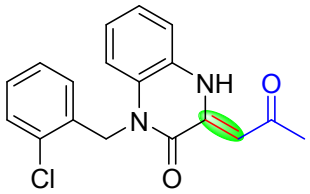
Obtained as a yellow solid (45 mg, 61% yield); M.p. 178-179 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 13.25 (s, 1H), 7.34 – 7.32 (m, 2H), 7.11 (d, J = 7.7 Hz, 2H), 7.06 (d, J = 2.3 Hz, 2H), 6.99 – 6.94 (m, 2H), 6.26 (s, 1H), 5.31 (s, 2H), 2.22 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 197.9, 155.6, 141.3, 136.6, 130
0, 129.5, 128.7, 125.9, 124.5, 124.3, 123.5, 122.6, 122.1, 115.5, 114.0, 94.0, 44.9, 29.0; HRMS (ESI+): Calculated for $C_{18}H_{15}BrN_2O_2Na$: $[M + Na]^+$ 393.0209, Found 393.0211.

(*Z*)-1-(2-fluorobenzyl)-3-(2-oxopropylidene)-3,4-dihydroquinoxalin-2(1*H*)-one (24)



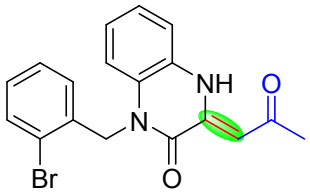
Obtained as a yellow solid (37 mg, 60% yield); M.p. 150-151 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 13.25 (s, 1H), 7.18 – 7.15 (m, 1H), 7.04 (dd, J = 6.5, 3.1 Hz, 3H), 6.97 (dd, J = 13.0, 7.3 Hz, 4H), 6.26 (s, 1H), 5.40 (s, 2H), 2.21 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 199.0, 160.3 (d, J = 247.0 Hz), 156.8, 142.5, 129.4 (d, J = 7.6 Hz), 128.2 (d, J = 3.8 Hz), 126.9, 125.5, 124.7 (d, J = 3.8 Hz), 124.5, 123.7, 122.3 (d, J = 15.1 Hz), 116.4, 115.6 (d, J = 21.4 Hz), 114.9 (d, J = 2.5 Hz), 94.9, 40.0 (d, J = 5.0 Hz), 30.0; ^{19}F NMR (471 MHz, $CDCl_3$) δ -118.38; HRMS (ESI+): Calculated for $C_{18}H_{15}FN_2O_2Na$: $[M + Na]^+$ 333.1010, Found 333.1009.

(*Z*)-1-(2-chlorobenzyl)-3-(2-oxopropylidene)-3,4-dihydroquinoxalin-2(1*H*)-one (25)



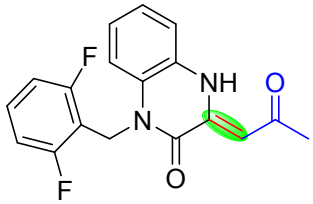
Obtained as a yellow solid (36 mg, 55% yield); M.p. 158-159 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 13.35 (s, 1H), 7.45 (dd, J = 8.0, 1.1 Hz, 1H), 7.22 (td, J = 7.9, 1.5 Hz, 1H), 7.14 (dd, J = 7.2, 1.7 Hz, 3H), 7.03 – 7.00 (m, 1H), 6.90 – 6.86 (m, 2H), 6.34 (s, 1H), 5.50 (s, 2H), 2.30 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 199.0, 156.7, 142.4, 132.6, 132.2, 129.8, 128.9, 127.4, 126.9, 126.7, 125.5, 124.6, 123.8, 116.4, 115.2, 95.0, 44.2, 30.1; HRMS (ESI+): Calculated for $C_{18}H_{15}ClN_2O_2Na$: $[M + Na]^+$ 349.0714, Found 349.0711.

(*Z*)-1-(2-bromobenzyl)-3-(2-oxopropylidene)-3,4-dihydroquinoxalin-2(1*H*)-one (26)



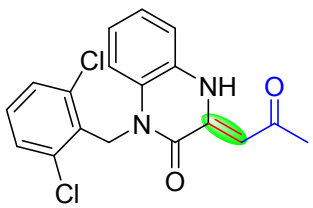
Obtained as a yellow solid (42 mg, 57% yield); M.p. 183-184 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 13.35 (s, 1H), 7.64 (d, J = 7.7 Hz, 1H), 7.15 (dd, J = 16.3, 7.8 Hz, 4H), 7.02 (t, J = 6.7 Hz, 1H), 6.85 (d, J = 8.0 Hz, 2H), 6.35 (s, 1H), 5.47 (s, 2H), 2.30 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 198.9, 156.6, 142.4, 133.6, 133.1, 129.1, 128.0, 126.9, 126.8, 125.5, 124.6, 123.8, 122.5, 116.4, 115.3, 95.0, 46.9, 30.0; HRMS (ESI+): Calculated for $C_{18}H_{15}BrN_2O_2Na$: $[M + Na]^+$ 393.0209, Found 393.0200.

(*Z*)-1-(2,6-difluorobenzyl)-3-(2-oxopropylidene)-3,4-dihydroquinoxalin-2(1*H*)-one (27)



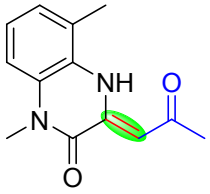
Obtained as a yellow solid (34 mg, 52% yield); M.p. 143-144 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 13.27 (s, 1H), 7.24 (t, J = 7.4 Hz, 1H), 7.14 (d, J = 8.2 Hz, 1H), 7.10 (d, J = 4.2 Hz, 2H), 7.05 (dd, J = 8.2, 4.1 Hz, 1H), 6.88 (t, J = 8.2 Hz, 2H), 6.34 (s, 1H), 5.56 (s, 2H), 2.28 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 199.0, 161.3 (dd, J = 249.5, 7.6 Hz, 2C), 156.5, 142.4, 129.8 (t, J = 10.7 Hz), 126.8, 125.6, 124.3, 123.5, 116.5, 114.4, 111.9 (dd, J = 20.2, 5.0 Hz), 94.9, 35.5, 30.0; ^{19}F NMR (471 MHz, $CDCl_3$) δ -114.01; HRMS (ESI+): Calculated for $C_{18}H_{14}F_2N_2O_2Na$: $[M + Na]^+$ 351.0916, Found 351.0924.

(*Z*)-1-(2,6-dichlorobenzyl)-3-(2-oxopropylidene)-3,4-dihydroquinoxalin-2(1*H*)-one (28)



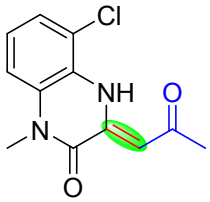
Obtained as a yellow solid (35 mg, 48% yield); M.p. 157-158 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 13.23 (s, 1H), 7.30 (d, J = 8.1 Hz, 2H), 7.16 (t, J = 8.0 Hz, 1H), 7.09 (t, J = 7.2 Hz, 2H), 7.02 – 6.97 (m, 2H), 6.31 (s, 1H), 5.74 (s, 2H), 2.28 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 198.9, 157.2, 142.5, 135.4, 130.6, 129.5, 129.4, 126.8, 125.7, 124.2, 123.3, 116.5, 115.1, 94.9, 42.6, 30.0; HRMS (ESI+): Calculated for $C_{18}H_{14}Cl_2N_2O_2Na$: $[M + Na]^+$ 383.0325, Found 383.0341.

(*Z*)-1,5-dimethyl-3-(2-oxopropylidene)-3,4-dihydroquinoxalin-2(1*H*)-one (29)



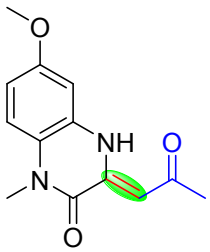
Obtained as a yellow solid (36 mg, 78% yield); M.p. 161-162 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 13.66 (s, 1H), 7.07 (q, J = 5.6 Hz, 3H), 6.31 (s, 1H), 3.64 (s, 3H), 2.48 (s, 3H), 2.30 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 198.7, 156.1, 142.8, 128.1, 125.7, 124.4, 123.9, 123.3, 112.3, 94.5, 29.9, 29.9, 16.8; HRMS (ESI+): Calculated for $C_{13}H_{14}N_2O_2Na$: $[M + Na]^+$ 253.0947, Found 253.0963.

(*Z*)-5-chloro-1-methyl-3-(2-oxopropylidene)-3,4-dihydroquinoxalin-2(1*H*)-one (30)



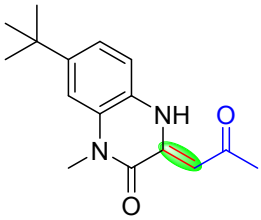
Obtained as a yellow solid (36 mg, 72% yield); M.p. 167-168 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 13.56 (s, 1H), 7.23 (dd, J = 5.8, 3.4 Hz, 1H), 7.08 – 7.06 (m, 2H), 6.35 (s, 1H), 3.62 (s, 3H), 2.31 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 199.2, 156.1, 141.5, 129.0, 124.4, 123.1, 120.6, 112.8, 96.0, 30.1, 30.0; HRMS (ESI+): Calculated for $C_{12}H_{11}ClN_2O_2Na$: $[M + Na]^+$ 273.0401, Found 273.0405.

(*Z*)-6-methoxy-1-methyl-3-(2-oxopropylidene)-3,4-dihydroquinoxalin-2(1*H*)-one (31)



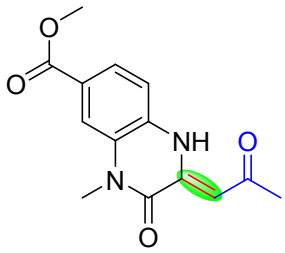
Obtained as a yellow solid (34 mg, 69% yield); M.p. 169-170 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 13.32 (s, 1H), 7.06 (d, J = 9.0 Hz, 1H), 6.72 (dd, J = 9.0, 2.6 Hz, 1H), 6.65 (d, J = 2.5 Hz, 1H), 6.27 (s, 1H), 3.82 (s, 3H), 3.60 (s, 3H), 2.27 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 198.9, 156.6, 155.7, 142.9, 126.1, 122.0, 115.4, 110.3, 100.7, 94.7, 55.7, 30.0, 29.8; HRMS (ESI+): Calculated for $C_{13}H_{14}N_2O_3Na$: $[M + Na]^+$ 269.0897, Found 269.0898.

(*Z*)-7-(*tert*-butyl)-1-methyl-3-(2-oxopropylidene)-3,4-dihydroquinoxalin-2(1*H*)-one (32)



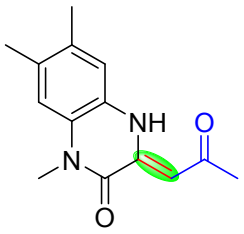
Obtained as a yellow solid (40 mg, 73% yield); M.p. 156-157 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 13.29 (s, 1H), 7.12 (d, J = 8.7 Hz, 1H), 7.06 – 7.01 (m, 2H), 6.19 (s, 1H), 3.55 (s, 3H), 2.20 (s, 3H), 1.26 (s, 9H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 198.7, 156.2, 148.00 142.9, 125.8, 124.9, 120.9, 114.1, 113.3, 94.3, 34.5, 31.3, 30.0, 29.7; HRMS (ESI+): Calculated for $C_{16}H_{20}N_2O_2Na$: $[M + Na]^+$ 295.1417, Found 295.1416.

(*Z*)-1-methyl-2-oxo-3-(2-oxopropylidene)-1,2,3,4-tetrahydroquinoxaline-7-carboxylate (33)



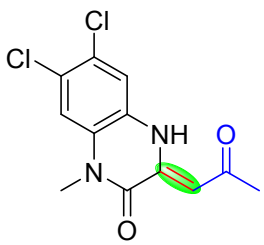
Obtained as a yellow solid (41 mg, 75% yield); M.p. 178-179 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 13.12 (s, 1H), 7.79 – 7.76 (m, 2H), 7.05 (d, J = 8.7 Hz, 1H), 6.28 (s, 1H), 3.87 (s, 3H), 3.60 (s, 3H), 2.23 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 200.0, 166.2, 156.1, 141.7, 129.1, 127.7, 125.9, 124.9, 116.0, 115.6, 96.4, 52.4, 30.4, 30.0; HRMS (ESI+): Calculated for $C_{14}H_{14}N_2O_4Na$: $[M + Na]^+$ 297.0846, Found 297.0848.

(*Z*)-1,6,7-trimethyl-3-(2-oxopropylidene)-3,4-dihydroquinoxalin-2(1*H*)-one (34)



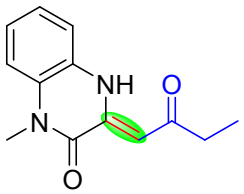
Obtained as a yellow solid (36 mg, 74% yield); M.p. 166-167 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 13.36 (s, 1H), 6.93 (s, 2H), 6.23 (s, 1H), 3.61 (s, 3H), 2.31 (s, 3H), 2.26 (d, J = 2.9 Hz, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 198.0, 156.1, 143.1, 133.0, 132.5, 126.0, 123.1, 117.2, 115.3, 93.8, 29.8, 29.7, 19.8, 19.2; HRMS (ESI+): Calculated for $C_{14}H_{16}N_2O_2Na$: $[M + Na]^+$ 267.1104, Found 267.1109.

(*Z*)-6,7-dichloro-1-methyl-3-(2-oxopropylidene)-3,4-dihydroquinoxalin-2(1*H*)-one (35)



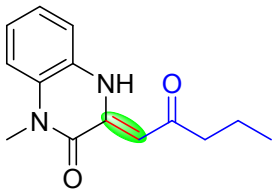
Obtained as a yellow solid (40 mg, 70% yield); M.p. 172-173 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 13.18 (s, 1H), 7.21 (s, 2H), 6.30 (s, 1H), 3.58 (s, 3H), 2.28 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 199.2, 155.8, 141.8, 127.8, 127.6, 126.8, 125.0, 117.1, 115.9, 96.0, 30.1, 30.0; HRMS (ESI+): Calculated for $C_{12}H_{10}Cl_2N_2O_2Na$: $[M + Na]^+$ 307.0012, Found 307.0035.

(*Z*)-1-methyl-3-(2-oxobutylidene)-3,4-dihydroquinoxalin-2(1*H*)-one (36)



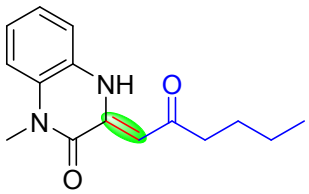
Obtained as a yellow solid (38 mg, 83% yield); M.p. 164-165 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 13.25 (s, 1H), 7.08 (s, 3H), 7.04 (d, J = 2.5 Hz, 1H), 6.21 (s, 1H), 3.56 (s, 3H), 2.49 (q, J = 7.5 Hz, 2H), 1.11 (t, J = 7.5 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 202.5, 156.3, 142.8, 128.0, 125.4, 124.3, 123.5, 116.1, 114.4, 93.6, 36.0, 29.7, 9.4; HRMS (ESI+): Calculated for $C_{13}H_{14}N_2O_2Na$: $[M + Na]^+$ 253.0947, Found 253.0940.

(*Z*)-1-methyl-3-(2-oxopentylidene)-3,4-dihydroquinoxalin-2(1*H*)-one (37)



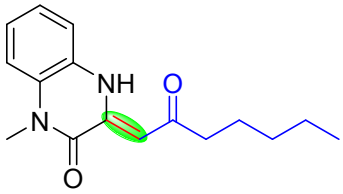
Obtained as a yellow solid (39 mg, 80% yield); M.p. 172-173 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 13.37 (s, 1H), 7.15 (d, J = 2.7 Hz, 3H), 7.11 – 7.08 (m, 1H), 6.26 (s, 1H), 3.62 (s, 3H), 2.49 (t, J = 7.5 Hz, 2H), 1.71 (dd, J = 14.8, 7.4 Hz, 2H), 0.98 (t, J = 7.4 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 201.9, 156.3, 142.7, 128.0, 125.4, 124.3, 123.5, 116.1, 114.4, 94.1, 44.9, 29.7, 19.0, 13.9; HRMS (ESI+): Calculated for $C_{14}H_{16}N_2O_2Na$: $[M + Na]^+$ 267.1104, Found 267.1104.

(*Z*)-1-methyl-3-(2-oxohexylidene)-3,4-dihydroquinoxalin-2(1*H*)-one (38)



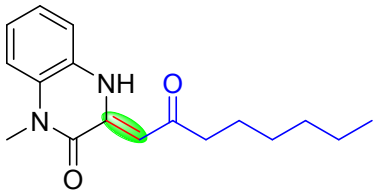
Obtained as a yellow solid (39 mg, 75% yield); M.p. 177-179 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 13.37 (s, 1H), 7.15 (s, 3H), 7.13 – 7.09 (m, 1H), 6.27 (s, 1H), 3.63 (s, 3H), 2.52 (t, J = 7.6 Hz, 2H), 1.69 – 1.64 (m, 2H), 1.38 (dd, J = 15.0, 7.5 Hz, 2H), 0.94 (t, J = 7.4 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 202.2, 156.3, 142.7, 128.0, 125.4, 124.3, 123.5, 116.1, 114.4, 94.1, 42.8, 29.7, 27.8, 22.5, 13.9; HRMS (ESI+): Calculated for $C_{15}H_{18}N_2O_2Na$: $[M + Na]^+$ 281.1260, Found 281.1253.

(*Z*)-1-methyl-3-(2-oxoheptylidene)-3,4-dihydroquinoxalin-2(1*H*)-one (39)



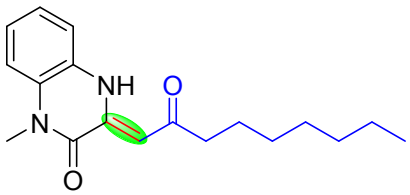
Obtained as a yellow solid (40 mg, 73% yield); M.p. 185-186 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 13.38 (s, 1H), 7.18 – 7.15 (m, 3H), 7.12 (d, J = 2.8 Hz, 1H), 6.28 (s, 1H), 3.63 (s, 3H), 2.51 (t, J = 7.5 Hz, 2H), 1.71 – 1.66 (m, 2H), 1.34 (dd, J = 6.8, 3.4 Hz, 4H), 0.90 (t, J = 6.6 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 202.2, 156.3, 142.8, 128.0, 125.4, 124.3, 123.5, 116.2, 114.4, 94.1, 43.0, 31.6, 29.8, 25.4, 22.5, 14.0; HRMS (ESI+): Calculated for $C_{16}H_{20}N_2O_2Na$: $[M + Na]^+$ 295.1417, Found 295.1411.

(*Z*)-1-methyl-3-(2-oxooctylidene)-3,4-dihydroquinoxalin-2(1*H*)-one (40)



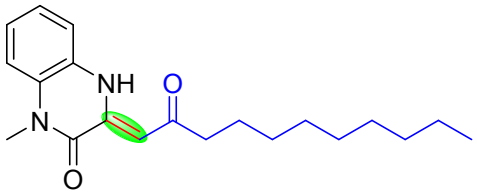
Obtained as a yellow solid (44 mg, 77% yield); M.p. 189-190 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 13.38 (s, 1H), 7.16 – 7.12 (m, 4H), 6.28 (s, 1H), 3.63 (s, 3H), 2.51 (t, J = 7.5 Hz, 2H), 1.69 – 1.65 (m, 2H), 1.36 – 1.30 (m, 6H), 0.89 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 202.2, 156.3, 142.8, 128.0, 125.4, 124.3, 123.6, 116.2, 114.4, 94.1, 43.0, 31.7, 29.8, 29.1, 25.7, 22.6, 14.1; HRMS (ESI+): Calculated for $C_{17}H_{22}N_2O_2Na$: $[M + Na]^+$ 309.1573, Found 309.1567.

(*Z*)-1-methyl-3-(2-oxononylidene)-3,4-dihydroquinoxalin-2(1*H*)-one (41)



Obtained as a yellow solid (41 mg, 68% yield); M.p. 184-185 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 13.31 (s, 1H), 7.10 – 7.07 (m, 3H), 7.06 – 7.02 (m, 1H), 6.20 (s, 1H), 3.56 (s, 3H), 2.46 – 2.42 (m, 2H), 1.63 – 1.59 (m, 2H), 1.27 – 1.21 (m, 8H), 0.81 (t, J = 6.9 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 202.2, 156.4, 142.8, 128.0, 125.4, 124.3, 123.5, 116.2, 114.4, 94.1, 43.1, 31.7, 29.8, 29.4, 29.2, 25.7, 22.6, 14.1; HRMS (ESI+): Calculated for $C_{18}H_{24}N_2O_2Na$: $[M + Na]^+$ 323.1730, Found 323.1718.

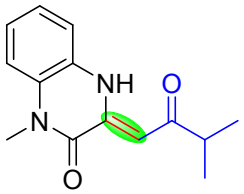
(*Z*)-1-methyl-3-(2-oxoundecylidene)-3,4-dihydroquinoxalin-2(1*H*)-one (42)



Obtained as a yellow solid (47 mg, 72% yield); M.p. 198-199 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 13.37 (s, 1H), 7.17 – 7.14 (m, 3H), 7.11 (dd, J = 5.5, 2.4 Hz, 1H), 6.27 (s, 1H), 3.63 (s, 3H), 2.52 – 2.49 (m, 2H), 1.69 – 1.65 (m, 2H), 1.30 (dd, J = 18.1, 10.8 Hz, 12H), 0.87 (t, J = 6.9 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 202.2, 156.3, 142.8, 128.0, 125.4, 124.3, 123.5, 116.2, 114.4, 94.1, 43.1,

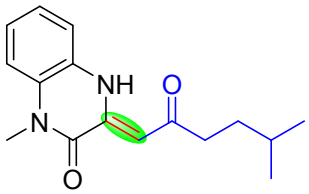
31.9, 29.7, 29.5, 29.5, 29.4, 29.3, 25.7, 22.7, 14.1; HRMS (ESI+): Calculated for $C_{20}H_{28}N_2O_2Na$: $[M + Na]^+$ 351.2043, Found 351.2047.

(*Z*)-1-methyl-3-(3-methyl-2-oxobutylidene)-3,4-dihydroquinoxalin-2(1*H*)-one (43)



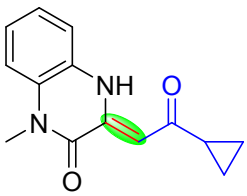
Obtained as a yellow solid (39 mg, 80% yield); M.p. 163-164 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 13.38 (s, 1H), 7.16 – 7.13 (m, 3H), 7.11 – 7.07 (m, 1H), 6.31 (s, 1H), 3.62 (s, 3H), 2.72 (dt, J = 13.8, 6.9 Hz, 1H), 1.19 (d, J = 6.9 Hz, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 205.9, 156.4, 143.3, 128.0, 125.4, 124.3, 123.5, 116.1, 114.4, 92.6, 40.6, 29.7, 19.4; HRMS (ESI+): Calculated for $C_{14}H_{16}N_2O_2Na$: $[M + Na]^+$ 267.1104, Found 267.1103.

(*Z*)-1-methyl-3-(5-methyl-2-oxohexylidene)-3,4-dihydroquinoxalin-2(1*H*)-one (44)



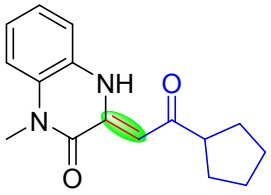
Obtained as a yellow solid (39 mg, 72% yield); M.p. 174-175 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 13.37 (s, 1H), 7.24 – 7.07 (m, 4H), 6.28 (s, 1H), 3.63 (s, 3H), 2.59 – 2.43 (m, 2H), 1.64 – 1.55 (m, 3H), 0.93 (d, J = 5.5 Hz, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 202.3, 156.3, 142.7, 128.0, 125.4, 124.3, 123.5, 116.1, 114.4, 94.1, 41.1, 34.6, 29.7, 27.9, 22.4; HRMS (ESI+): Calculated for $C_{16}H_{20}N_2O_2Na$: $[M + Na]^+$ 295.1417, Found 295.1410.

(*Z*)-3-(2-cyclopropyl-2-oxoethylidene)-1-methyl-3,4-dihydroquinoxalin-2(1*H*)-one (45)



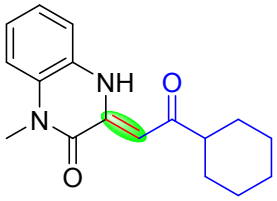
Obtained as a yellow solid (31 mg, 65% yield); M.p. 155-156 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 13.28 (s, 1H), 7.16 – 7.12 (m, 3H), 7.08 – 7.05 (m, 1H), 6.41 (s, 1H), 3.63 (s, 3H), 1.98 (td, J = 7.9, 4.0 Hz, 1H), 1.12 – 1.09 (m, 2H), 0.92 (dd, J = 7.7, 3.3 Hz, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 201.2, 156.4, 141.8, 127.9, 125.4, 124.3, 123.3, 115.9, 114.4, 94.3, 29.8, 21.5, 10.6; HRMS (ESI+): Calculated for $C_{14}H_{14}N_2O_2Na$: $[M + Na]^+$ 265.0947, Found 265.0938.

(*Z*)-3-(2-cyclopentyl-2-oxoethylidene)-1-methyl-3,4-dihydroquinoxalin-2(1*H*)-one (46)



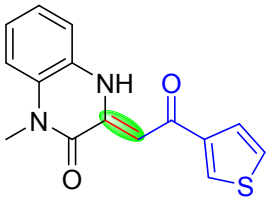
Obtained as a yellow solid (39 mg, 72% yield); M.p. 173-174 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 13.34 (s, 1H), 7.14 (dd, J = 5.2, 3.0 Hz, 3H), 7.10 – 7.06 (m, 1H), 6.30 (s, 1H), 3.62 (s, 3H), 2.97 (p, J = 8.1 Hz, 1H), 1.94 – 1.88 (m, 2H), 1.85 – 1.79 (m, 2H), 1.73 (dd, J = 9.3, 5.5 Hz, 2H), 1.63 (dd, J = 7.1, 4.5 Hz, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 204.9, 156.4, 142.8, 127.9, 125.4, 124.3, 123.4, 116.0, 114.4, 93.7, 51.6, 30.2, 29.7, 26.2; HRMS (ESI+): Calculated for $C_{16}H_{18}N_2O_2Na$: $[M + Na]^+$ 293.1260, Found 293.1264.

(*Z*)-3-(2-cyclohexyl-2-oxoethylidene)-1-methyl-3,4-dihydroquinoxalin-2(1*H*)-one (47)



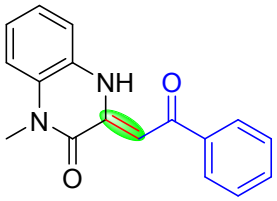
Obtained as a yellow solid (39 mg, 69% yield); M.p. 190-191 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 13.33 (s, 1H), 7.05 (d, J = 26.4 Hz, 4H), 6.22 (s, 1H), 3.55 (s, 3H), 2.37 (t, J = 10.8 Hz, 1H), 1.84 (d, J = 12.1 Hz, 2H), 1.76 – 1.72 (m, 2H), 1.63 (d, J = 12.5 Hz, 1H), 1.41 – 1.33 (m, 2H), 1.29 – 1.23 (m, 2H), 1.17 (d, J = 4.9 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 205.1, 156.4, 143.3, 128.0, 125.43 124.3, 123.5, 116.1, 114.3, 93.0, 50.8, 29.7, 29.5, 26.0, 25.9; HRMS (ESI+): Calculated for $C_{17}H_{20}N_2O_2Na$: $[M + Na]^+$ 307.1417, Found 307.1410.

(*Z*)-1-methyl-3-(2-oxo-2-(thiophen-3-yl)ethylidene)-3,4-dihydroquinoxalin-2(1*H*)-one (48)



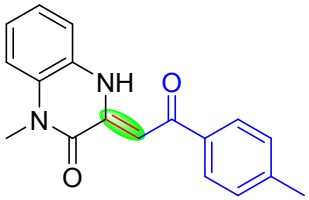
Obtained as a yellow solid (32 mg, 56% yield); M.p. 183-184 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 13.74 (s, 1H), 8.03 (d, J = 2.8 Hz, 1H), 7.56 (d, J = 5.0 Hz, 1H), 7.28 (dd, J = 5.0, 3.0 Hz, 1H), 7.12 (s, 4H), 6.76 (s, 1H), 3.60 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 185.1, 156.3, 144.4, 143.6, 129.7, 128.3, 126.7, 126.2, 125.4, 124.5, 123.9, 116.5, 114.5, 92.1, 29.8; HRMS (ESI+): Calculated for $C_{15}H_{12}N_2O_2SNa$: $[M + Na]^+$ 307.0512, Found 307.0505.

(*Z*)-1-methyl-3-(2-oxo-2-phenylethylidene)-3,4-dihydroquinoxalin-2(1*H*)-one (49)



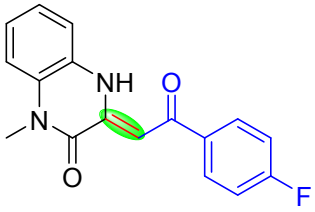
Obtained as a yellow solid (39 mg, 70% yield); M.p. 182-183 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 14.03 (s, 1H), 8.06 – 8.01 (m, 2H), 7.52 (dd, J = 8.2, 6.1 Hz, 1H), 7.47 (t, J = 7.3 Hz, 2H), 7.20 (dd, J = 8.8, 2.4 Hz, 4H), 7.03 (s, 1H), 3.67 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 190.2, 156.3, 144.7, 139.0, 131.9, 128.5, 128.4, 127.5, 125.3, 124.4, 124.0, 116.7, 114.4, 91.1, 29.8; HRMS (ESI+): Calculated for $C_{17}H_{14}N_2O_2Na$: $[M+Na]^+$ 301.0947, Found 301.0930.

(*Z*)-1-methyl-3-(2-oxo-2-(*p*-tolyl)ethylidene)-3,4-dihydroquinoxalin-2(1*H*)-one (50)



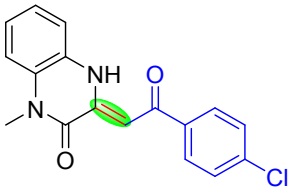
Obtained as a yellow solid (42 mg, 72% yield); M.p. 172-173 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 13.99 (s, 1H), 7.95 (d, J = 8.1 Hz, 2H), 7.28 (d, J = 8.0 Hz, 2H), 7.20 (dd, J = 9.8, 3.7 Hz, 4H), 7.01 (s, 1H), 3.67 (s, 3H), 2.42 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 190.2, 156.5, 144.4, 142.6, 136.4, 129.3, 128.3, 127.6, 125.4, 124.4, 123.8, 116.6, 114.4, 91.0, 29.8, 21.6; HRMS (ESI+): Calculated for $C_{18}H_{16}N_2O_2Na$: $[M + Na]^+$ 315.1104, Found 315.1100.

(*Z*)-3-(2-(4-fluorophenyl)-2-oxoethylidene)-1-methyl-3,4-dihydroquinoxalin-2(1*H*)-one (51)



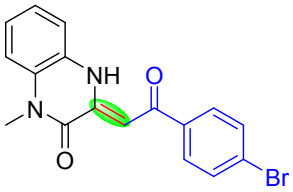
Obtained as a yellow solid (40 mg, 67% yield); M.p. 162-163 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 13.97 (s, 1H), 8.05 (dd, J = 8.8, 5.5 Hz, 2H), 7.21 (t, J = 3.4 Hz, 4H), 7.15 (t, J = 8.6 Hz, 2H), 6.97 (s, 1H), 3.68 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 188.9, 165.1 (d, J = 253.3 Hz), 156.3, 144.7, 135.3 (d, J = 3.8 Hz), 129.9 (d, J = 8.8 Hz), 128.4, 125.2, 124.5, 124.1, 116.7, 115.6 (d, J = 21.4 Hz), 114.5, 90.7, 29.9; ^{19}F NMR (471 MHz, $CDCl_3$) δ -114.57; HRMS (ESI+): Calculated for $C_{17}H_{13}FN_2O_2Na$: $[M + Na]^+$ 319.0853, Found 319.0851.

(*Z*)-3-(2-(4-chlorophenyl)-2-oxoethylidene)-1-methyl-3,4-dihydroquinoxalin-2(1*H*)-one (52)



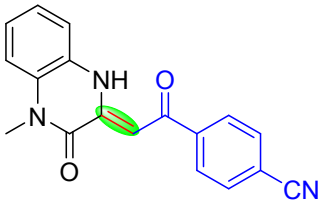
Obtained as a yellow solid (37 mg, 59% yield); M.p. 188-189 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 14.02 (s, 1H), 7.97 (d, J = 8.6 Hz, 2H), 7.44 (d, J = 8.6 Hz, 2H), 7.22 (dd, J = 5.2, 2.6 Hz, 4H), 6.97 (s, 1H), 3.68 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 188.7, 156.2, 144.9, 138.1, 137.3, 128.8, 128.8, 128.5, 125.2, 124.5, 124.3, 116.8, 114.5, 90.7, 29.9; HRMS (ESI+): Calculated for $C_{17}H_{13}ClN_2O_2Na$: $[M + Na]^+$ 335.0558, Found 335.0552.

(*Z*)-3-(2-(4-bromophenyl)-2-oxoethylidene)-1-methyl-3,4-dihydroquinoxalin-2(1*H*)-one (53)



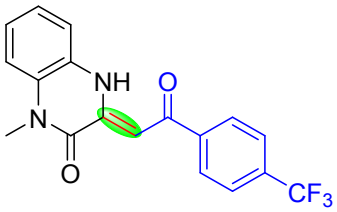
Obtained as a yellow solid (36 mg, 50% yield); M.p. 194-195 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 14.04 (s, 1H), 7.90 (d, J = 8.6 Hz, 2H), 7.61 (d, J = 8.6 Hz, 2H), 7.23 (dd, J = 8.5, 2.9 Hz, 4H), 6.97 (s, 1H), 3.69 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 188.8, 156.1, 145.0, 137.8, 136.8, 131.8, 129.0, 128.5, 125.2, 124.5, 124.3, 116.9, 114.5, 90.7, 29.9; HRMS (ESI+): Calculated for $C_{17}H_{13}BrN_2O_2Na$: $[M + Na]^+$ 379.0053, Found 379.0046.

(*Z*)-4-(2-(4-methyl-3-oxo-3,4-dihydroquinoxalin-2(1*H*)-ylidene)acetyl)benzonitrile (54)



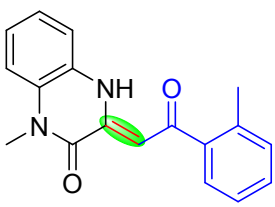
Obtained as a yellow solid (33 mg, 54% yield); M.p. 206-207 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 14.19 (s, 1H), 8.11 (d, J = 8.2 Hz, 2H), 7.77 (d, J = 8.3 Hz, 2H), 7.28 – 7.21 (m, 4H), 7.00 (s, 1H), 3.71 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 187.2, 155.9, 153.4, 145.8, 142.5, 132.4, 128.8, 127.8, 125.0, 124.6, 118.4, 117.4, 114.9, 114.6, 91.0, 30.0; HRMS (ESI+): Calculated for $C_{18}H_{13}N_3O_2Na$: $[M + Na]^+$ 326.0900, Found 326.0906.

(*Z*)-1-methyl-3-(2-oxo-2-(4-(trifluoromethyl)phenyl)ethylidene)-3,4-dihydroquinoxalin-2(1*H*)-one (55)



Obtained as a yellow solid (34 mg, 49% yield); M.p. 177-178 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 14.14 (s, 1H), 8.13 (d, J = 8.2 Hz, 2H), 7.74 (d, J = 8.3 Hz, 2H), 7.25 (dd, J = 7.2, 3.6 Hz, 4H), 7.02 (s, 1H), 3.70 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 188.3, 156.0, 153.7, 145.5, 128.7, 128.7, 127.7, 125.6 (q, J = 3.8 Hz), 125.1, 124.6, 124.6, 122.8 (q, J = 253.3 Hz), 117.1, 114.5, 91.0, 29.9; ^{19}F NMR (471 MHz, $CDCl_3$) δ -70.0; HRMS (ESI+): Calculated for $C_{18}H_{13}F_3N_2O_2Na$: $[M + Na]^+$ 369.0821, Found 369.0803.

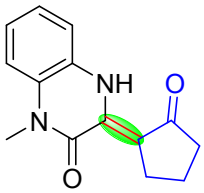
(*Z*)-1-methyl-3-(2-oxo-2-(*o*-tolyl)ethylidene)-3,4-dihydroquinoxalin-2(1*H*)-one (56)



Obtained as a yellow solid (40 mg, 68% yield); M.p. 179-180 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 13.70 (s, 1H), 7.50 (d, J = 7.5 Hz, 1H), 7.22 (d, J = 7.4 Hz, 1H), 7.13 (d, J = 8.0 Hz, 2H), 7.08 (dd, J =

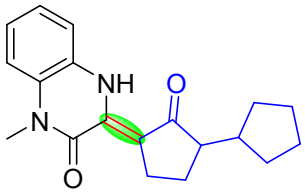
10.6, 4.0 Hz, 4H), 6.57 (s, 1H), 3.53 (s, 3H), 2.44 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 195.2, 156.2, 144.0, 140.4, 136.6, 131.3, 130.1, 128.4, 128.2, 125.7, 125.2, 124.3, 123.9, 116.6, 114.4, 94.9, 29.8, 20.7; HRMS (ESI+): Calculated for $C_{18}H_{16}N_2O_2Na$: $[M + Na]^+$ 315.1104, Found 315.1105.

(*Z*)-1-methyl-3-(2-oxocyclopentylidene)-3,4-dihydroquinoxalin-2(1*H*)-one (57)



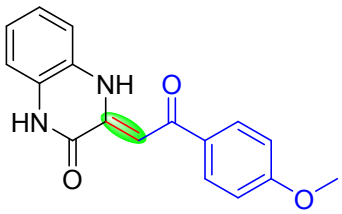
Obtained as a yellow solid (29 mg, 60% yield); M.p. 150-151 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 13.23 (s, 1H), 7.11 – 7.02 (m, 4H), 3.55 (s, 3H), 3.27 (t, J = 7.3 Hz, 2H), 2.44 (t, J = 7.9 Hz, 2H), 1.97 – 1.91 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 208.9, 157.5, 130.0, 128.3, 126.2, 124.1, 122.7, 115.4, 114.0, 108.0, 38.9, 29.3, 29.2, 20.5; HRMS (ESI+): Calculated for $C_{14}H_{14}N_2O_2Na$: $[M + Na]^+$ 265.0947, Found 265.0938.

(*Z*)-1-methyl-3-(2-oxo-[1,1'-bi(cyclopentan)]-3-ylidene)-3,4-dihydroquinoxalin-2(1*H*)-one (58)



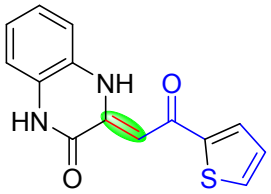
Obtained as a yellow solid (34 mg, 55% yield); M.p. 165-166 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 13.29 (s, 1H), 7.11 – 7.03 (m, 3H), 7.00 (d, J = 7.2 Hz, 1H), 3.54 (s, 3H), 3.33 (ddd, J = 17.2, 8.5, 3.8 Hz, 1H), 3.06 – 2.98 (m, 1H), 2.48 – 2.40 (m, 1H), 2.15 – 2.06 (m, 2H), 1.98 – 1.91 (m, 1H), 1.73 (d, J = 4.3 Hz, 2H), 1.61 (d, J = 8.3 Hz, 2H), 1.53 (d, J = 6.3 Hz, 2H), 1.42 – 1.35 (m, 1H), 1.24 (d, J = 20.7 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 210.3, 157.6, 136.7, 128.3, 126.3, 124.1, 122.5, 115.3, 114.0, 108.6, 53.2, 41.1, 30.9, 29.7, 27.4, 25.3, 25.0; HRMS (ESI+): Calculated for $C_{19}H_{22}N_2O_2Na$: $[M + Na]^+$ 333.1573, Found 333.1578.

(*Z*)-3-(2-(4-methoxyphenyl)-2-oxoethylidene)-3,4-dihydroquinoxalin-2(1*H*)-one (59)[4]



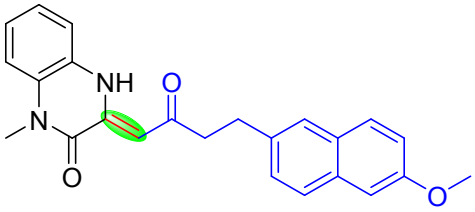
Obtained as a yellow solid (33 mg, 56% yield); ^{1}H NMR (500 MHz, DMSO) δ 13.60 (s, 1H), 11.99 (s, 1H), 7.99 (d, J = 8.8 Hz, 2H), 7.52 – 7.45 (m, 1H), 7.14 (d, J = 4.4 Hz, 3H), 7.07 (d, J = 8.8 Hz, 2H), 6.79 (s, 1H), 3.86 (s, 3H).

(*Z*)-3-(2-oxo-2-(thiophen-2-yl)ethylidene)-3,4-dihydroquinoxalin-2(1*H*)-one (60)[4]



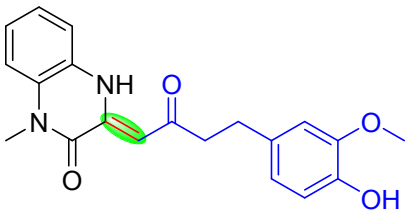
Obtained as a yellow solid (28 mg, 52% yield); ^{1}H NMR (500 MHz, DMSO) δ 13.27 (s, 1H), 12.04 (s, 1H), 7.90 (dd, J = 8.9, 4.1 Hz, 2H), 7.50 – 7.45 (m, 1H), 7.25 – 7.21 (m, 1H), 7.13 (dd, J = 7.6, 4.3 Hz, 3H), 6.68 (s, 1H).

(*Z*)-3-(4-(6-methoxynaphthalen-2-yl)-2-oxobutylidene)-1-methyl-3,4-dihydroquinoxalin-2(1*H*)-one (61)



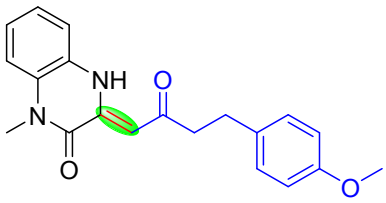
Obtained as a yellow solid (50 mg, 65% yield); M.p. 170-171 ^{o}C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 13.29 (s, 1H), 7.60 (d, J = 8.4 Hz, 2H), 7.52 (s, 1H), 7.27 (d, J = 8.2 Hz, 1H), 7.10 – 7.02 (m, 6H), 6.25 (s, 1H), 3.83 (s, 3H), 3.55 (s, 3H), 3.09 – 3.04 (m, 2H), 2.86 (t, J = 7.8 Hz, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 200.5, 157.2, 156.3, 143.0, 136.4, 133.1, 129.1, 129.0, 128.1, 127.6, 126.9, 126.2, 125.3, 124.4, 123.6, 118.7, 116.2, 114.4, 105.7, 94.0, 55.3, 44.3, 31.3, 29.8; HRMS (ESI+): Calculated for $C_{24}H_{22}N_2O_3Na$: $[M + Na]^+$ 409.1523, Found 409.1520.

(*Z*)-3-(4-(4-hydroxy-3-methoxyphenyl)-2-oxobutylidene)-1-methyl-3,4-dihydroquinoxalin-2(1*H*)-one (62)



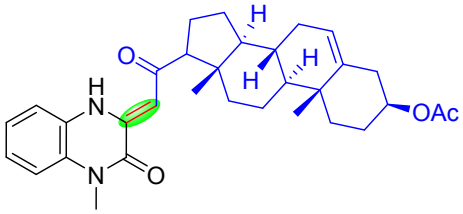
Obtained as a yellow solid (42 mg, 60% yield); M.p. 171-172 ^{o}C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 13.35 (s, 1H), 7.18 – 7.15 (m, 3H), 7.13 – 7.10 (m, 1H), 6.83 (d, J = 7.9 Hz, 1H), 6.74 – 6.71 (m, 2H), 6.29 (s, 1H), 3.87 (s, 3H), 3.62 (s, 3H), 2.95 – 2.92 (m, 2H), 2.83 – 2.80 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 200.6, 156.2, 146.5, 143.9, 143.0, 133.1, 128.0, 125.3, 124.4, 123.7, 120.8, 116.2, 114.4, 114.3, 111.0, 94.0, 55.9, 44.7, 31.2, 29.8; HRMS (ESI+): Calculated for $C_{20}H_{20}N_2O_4Na$: $[M + Na]^+$ 375.1315, Found 375.1316.

(*Z*)-3-(4-(4-methoxyphenyl)-2-oxobutylidene)-1-methyl-3,4-dihydroquinoxalin-2(1*H*)-one (63)



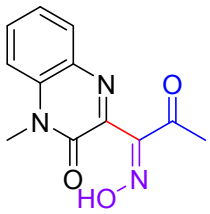
Obtained as a yellow solid (48 mg, 71% yield); M.p. 158-159 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 13.31 (s, 1H), 7.13 (dd, J = 10.1, 5.6 Hz, 5H), 7.07 (dt, J = 5.0, 2.3 Hz, 1H), 6.81 (d, J = 8.6 Hz, 2H), 6.26 (s, 1H), 3.76 (s, 3H), 3.58 (s, 3H), 2.96 – 2.92 (m, 2H), 2.82 – 2.78 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 200.5, 157.9, 156.2, 142.9, 133.3, 129.2, 128.0, 125.3, 124.3, 123.6, 116.2, 114.4, 113.9, 94.0, 55.2, 44.6, 30.5, 29.7; HRMS (ESI+): Calculated for $C_{20}H_{20}N_2O_3Na$: $[M + Na]^+$ 359.1366, Found 359.1374.

(3*S*,8*S*,9*S*,10*R*,13*S*,14*S*)-10,13-dimethyl-17-(2-((*Z*)-4-methyl-3-oxo-3,4-dihydroquinoxalin-2(1*H*)-ylidene)acetyl)-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1*H*-cyclopenta[*a*]phenanthren-3-yl acetate (64)



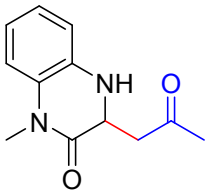
Obtained as a yellow solid (44 mg, 50% yield); M.p. 216-217 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 13.49 (s, 1H), 7.18 – 7.13 (m, 3H), 7.11 (d, J = 2.4 Hz, 1H), 6.24 (s, 1H), 5.38 (d, J = 4.8 Hz, 1H), 4.62 (dt, J = 16.5, 5.4 Hz, 1H), 3.63 (s, 3H), 2.65 (t, J = 8.9 Hz, 1H), 2.32 (t, J = 7.7 Hz, 4H), 2.05 (d, J = 11.5 Hz, 4H), 1.87 (d, J = 10.2 Hz, 2H), 1.74 (d, J = 8.2 Hz, 2H), 1.59 (d, J = 15.0 Hz, 3H), 1.48 (d, J = 18.5 Hz, 4H), 1.25 (d, J = 7.0 Hz, 2H), 1.04 – 1.00 (m, 4H), 0.65 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 201.7, 170.6, 156.5, 142.0, 139.7, 128.0, 125.5, 124.3, 123.4, 122.4, 116.1, 114.3, 95.4, 73.9, 62.9, 56.8, 50.0, 45.2, 38.7, 38.1, 37.0, 36.7, 32.0, 31.9, 29.7, 27.7, 24.7, 22.6, 21.4, 20.9, 19.3, 13.3; HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{32}H_{40}N_2O_4H$ 517.3061; Found 517.3018.

(*E*)-3-(1-(hydroxyimino)-2-oxopropyl)-1-methylquinoxalin-2(1*H*)-one (65)



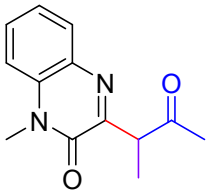
Obtained as a yellow solid (44 mg, 90% yield); M.p. 223-224 °C. ^{1}H NMR (500 MHz, DMSO) δ 12.92 (s, 1H), 7.86 (dd, J = 8.0, 1.0 Hz, 1H), 7.76 – 7.70 (m, 1H), 7.63 (d, J = 8.2 Hz, 1H), 7.44 (t, J = 7.2 Hz, 1H), 3.65 (s, 3H), 2.48 (s, 3H); ^{13}C NMR (126 MHz, DMSO) δ 195.9, 153.4, 152.7, 152.4, 133.6, 132.3, 132.1, 130.1, 124.4, 115.6, 29.4, 25.9; HRMS (ESI+): Calculated for $C_{12}H_{11}N_3O_3Na$: $[M + Na]^+$ 268.0693, Found 268.0703.

1-Methyl-3-(2-oxopropyl)-3,4-dihydroquinoxalin-2(1*H*)-one (66)[5]



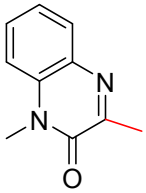
Obtained as a yellow liquid (39 mg, 89% yield); ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.94 – 6.89 (m, 2H), 6.87 – 6.83 (m, 1H), 6.72 (dd, J = 7.7, 1.3 Hz, 1H), 4.28 (dd, J = 10.2, 2.3 Hz, 1H), 3.34 (s, 3H), 3.34 – 3.29 (m, 1H), 2.81 (dd, J = 18.5, 10.2 Hz, 1H), 2.21 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 207.8, 166.9, 134.4, 128.7, 123.8, 119.9, 114.8, 114.7, 52.6, 44.7, 30.4, 29.2.

1-Methyl-3-(3-oxobutan-2-yl)quinoxalin-2(1*H*)-one (67)



Obtained as a white solid (44 mg, 96% yield); M.p. 134-135 ^{o}C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.88 (dd, J = 8.0, 1.3 Hz, 1H), 7.59 – 7.54 (m, 1H), 7.36 (t, J = 7.6 Hz, 1H), 7.32 (d, J = 8.1 Hz, 1H), 4.39 (q, J = 7.1 Hz, 1H), 3.70 (s, 3H), 2.34 (s, 3H), 1.53 (d, J = 7.1 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 207.5, 158.9, 154.5, 133.1, 132.7, 130.3, 123.8, 123.6, 113.7, 50.8, 29.2, 29.2, 13.7; HRMS (ESI+): Calculated for $C_{13}H_{14}N_2O_2Na$: $[M + Na]^+$ 253.0947, Found 253.0955.

1,3-Dimethylquinoxalin-2(1*H*)-one (68)[6]



Obtained as a white solid (29 mg, 83% yield); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.74 (dd, J = 8.0, 1.2 Hz, 1H), 7.48 – 7.43 (m, 1H), 7.26 (dd, J = 11.1, 4.1 Hz, 1H), 7.23 (d, J = 8.3 Hz, 1H), 3.64 (s, 3H), 2.53 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 158.5, 155.2, 133.3, 132.5, 129.7, 129.4, 123.7, 113.6, 29.1, 21.6; HRMS (ESI+): Calculated for $C_{10}H_{10}N_2ONa$: $[M + Na]^+$ 197.0685, Found 197.0678.

4. X-ray Crystal Data for 20

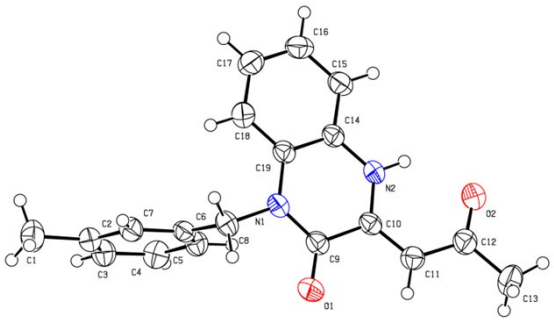


Figure S2 Single-crystal X-Ray structure of **19**. Ellipsoids are represented at 30% Probability.

Table S1. Crystallographic Data and Structure Refinement for **20**

CCDC	2042085
Empirical formula	$C_{19}H_{18}N_2O_2$
Formula weight	306.35
Temperature, K	296.15
Wavelength, Å	0.71073
Crystal system	monoclinic
Space group	$P2_1/n$
a, *b*, *c*, Å	10.6894 (13), 10.6948 (14), 13.7194 (17)
α, β, γ, °	90, 91.046 (2), 90
Volume, Å^3	1568.2 (3)
Z	4
Calculated density, Mg/m^3	1.298
Absorption coefficient, mm^{-1}	0.085
F (000)	648
Theta range for data collection, °	5.388 to 50.014
Limiting indices	-12≤h≤6, -11≤k≤12, -15≤l≤16
Reflections collected / unique	7788 / 2767 [R(int) = 0.0175]
Absorption correction	Semi-empirical from equivalents
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	2767/0/210
Goodness of fit on F^2	1.038
Final R indices [I>2sigma(I)]	R1 = 0.0397, wR2 = 0.1010
R indices (all data)	R1 = 0.0533, wR2 = 0.1121

5. References

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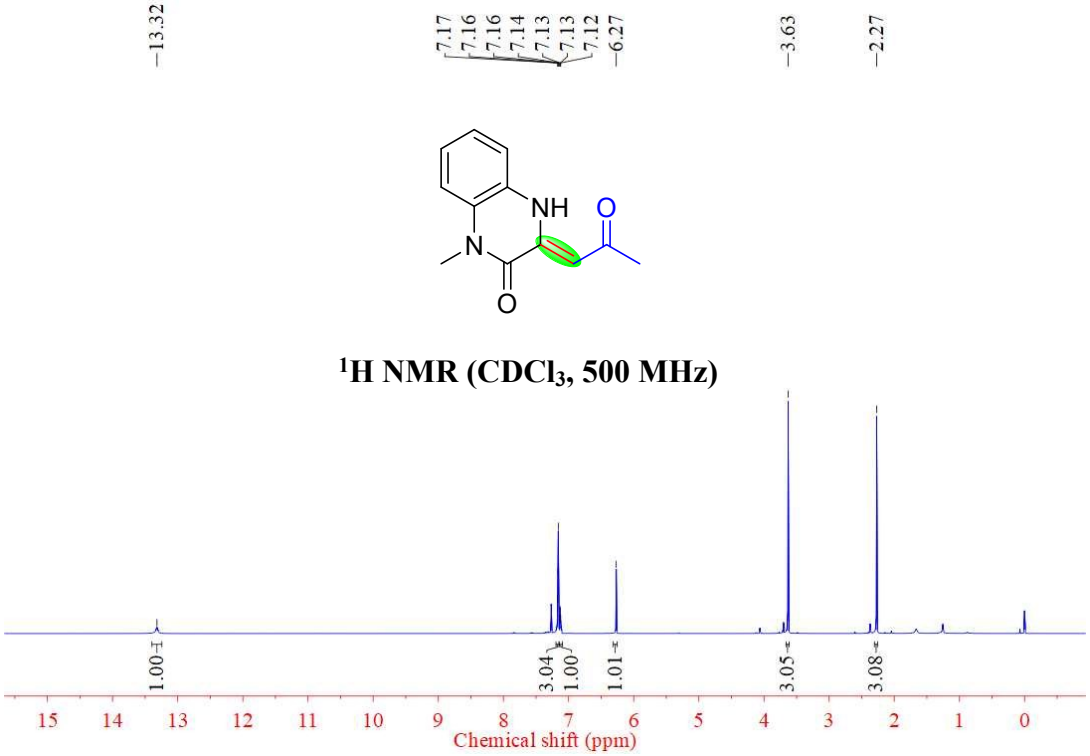
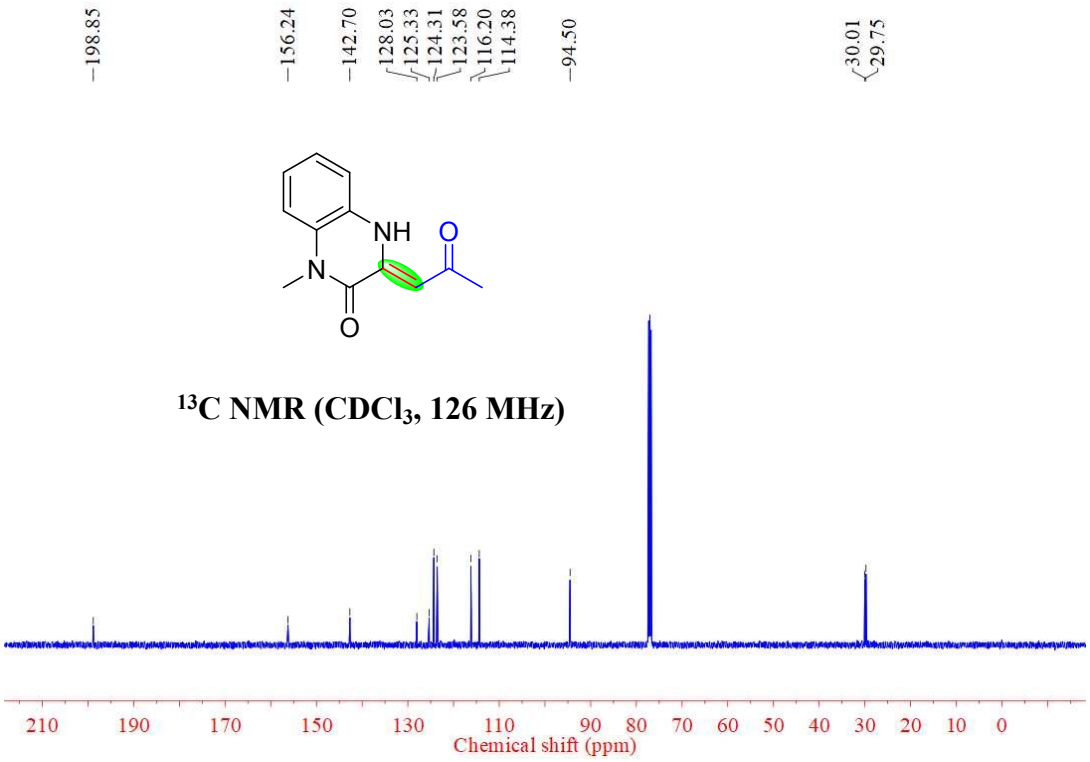
(6) L.-Y. Xie, L.-L. Jiang, J.-X. Tan, Y. Wang, X.-Q. Xu, B. Zhang, Z. Cao and W.-M. He, *ACS Sustain. Chem. Eng*., 2019, **7**, 14153.

6. Copies of ^{1}H, ^{13}C and ^{19}F NMR Spectra



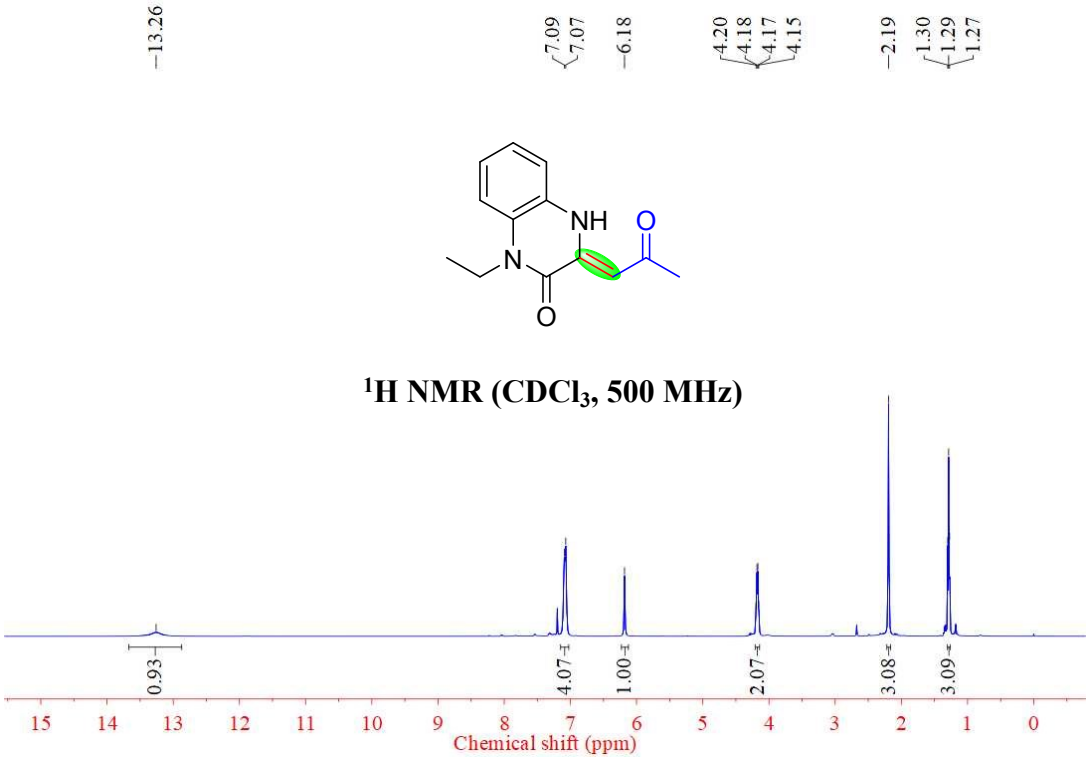
^{1}H NMR ($CDCl_3$, 500 MHz)

^{1}H NMR Spectrum of Compound 3



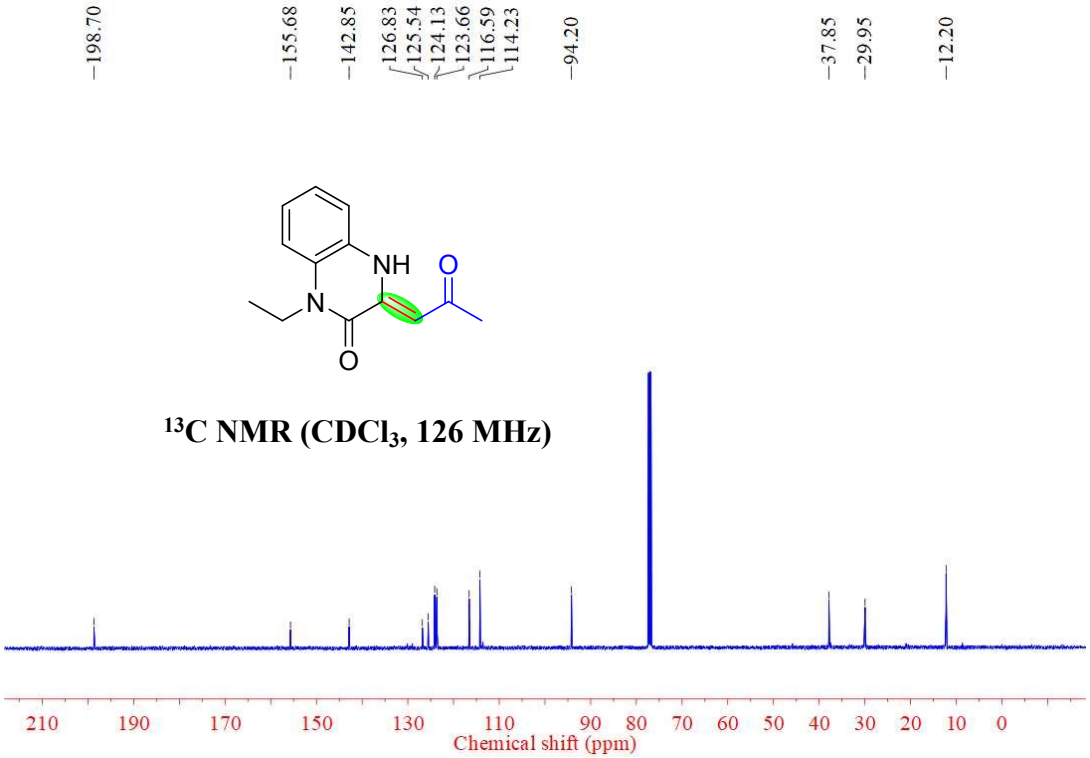
^{13}C NMR ($CDCl_3$, 126 MHz)

$^{13}C\{^{1}H\}$ NMR Spectrum of Compound 3



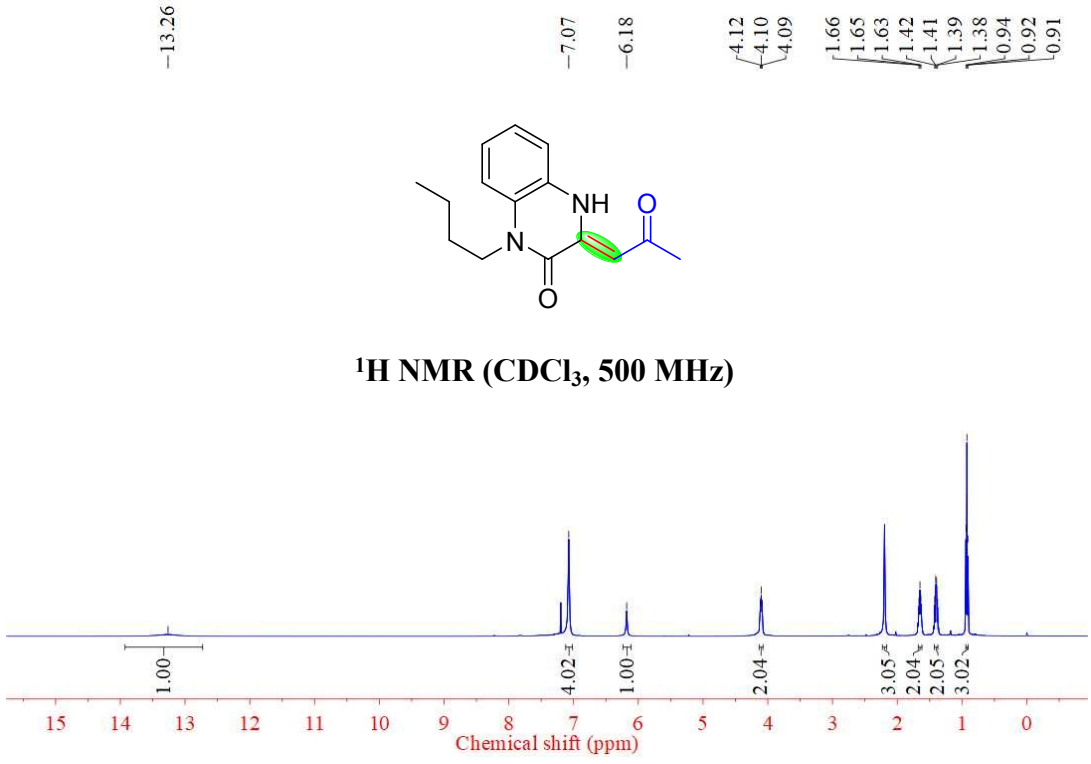
^{1}H NMR ($CDCl_3$, 500 MHz)

^{1}H NMR Spectrum of Compound 4



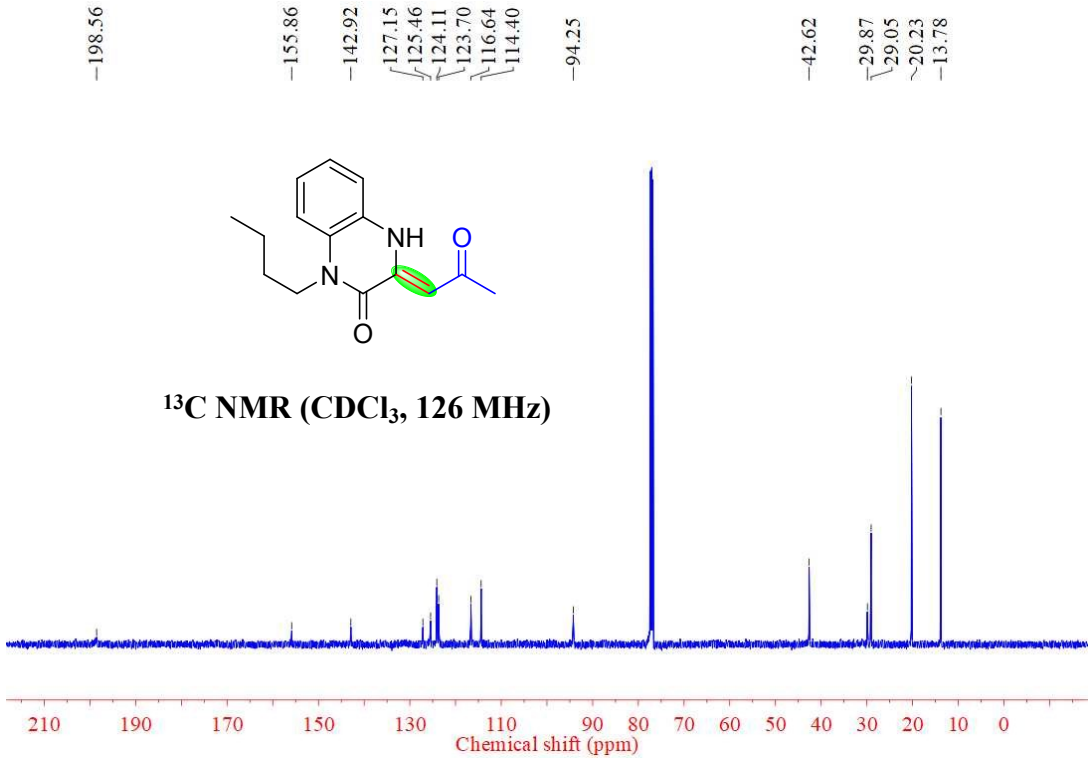
^{13}C NMR ($CDCl_3$, 126 MHz)

^{13}C{^{1}H} NMR Spectrum of Compound 4



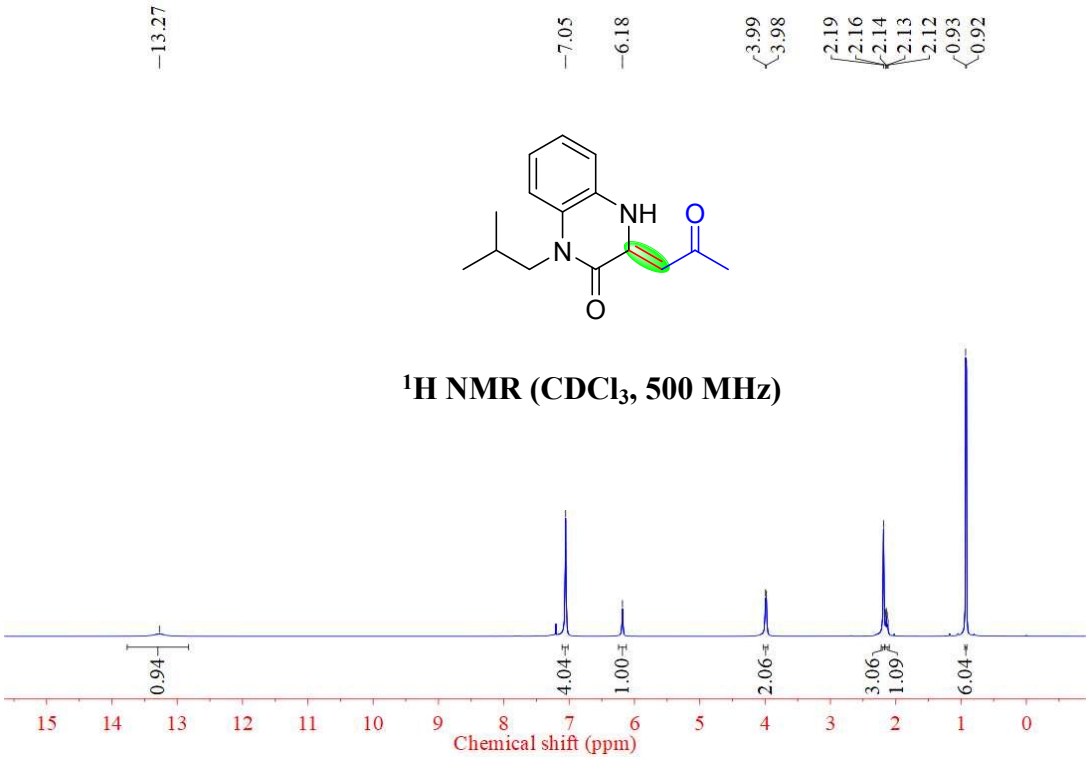
^{1}H NMR ($CDCl_3$, 500 MHz)

^{1}H NMR Spectrum of Compound 5



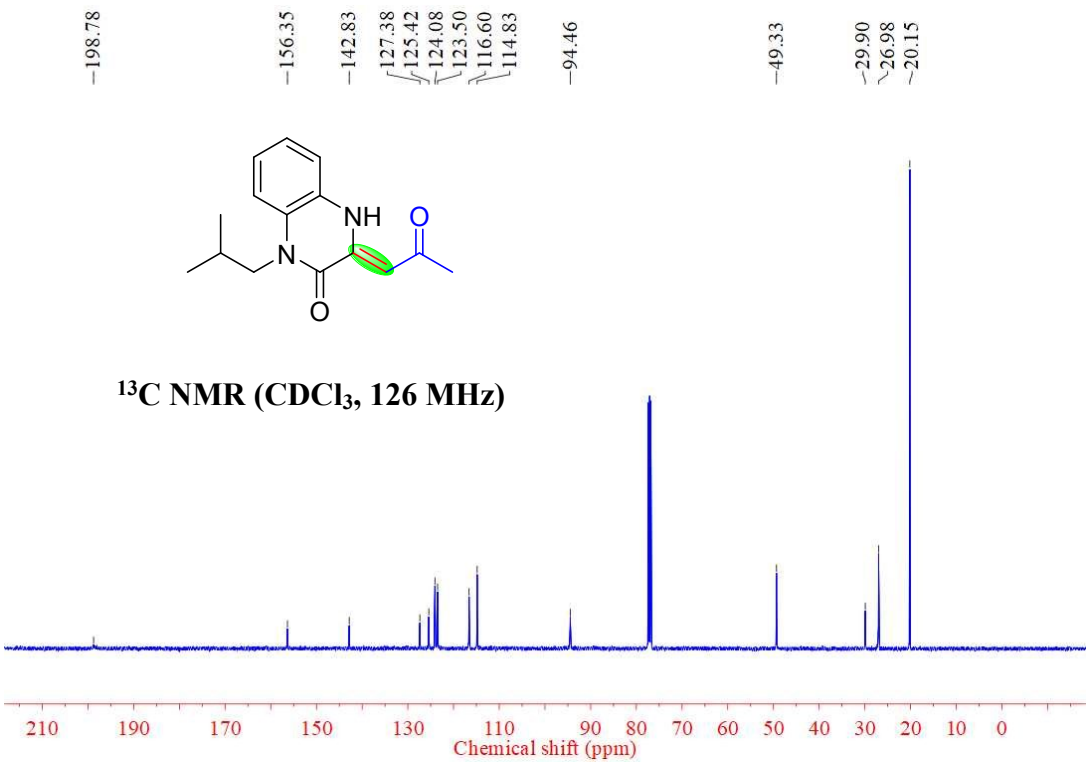
^{13}C NMR ($CDCl_3$, 126 MHz)

^{13}C{^{1}H} NMR Spectrum of Compound 5



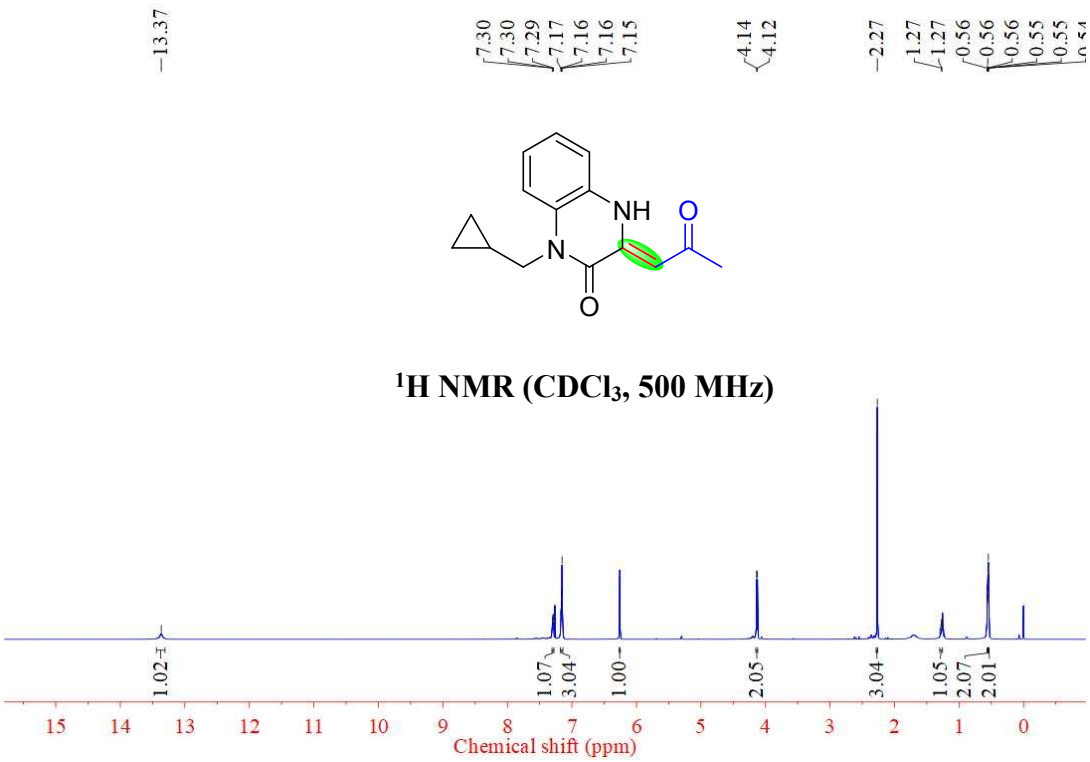
^{1}H NMR ($CDCl_3$, 500 MHz)

^{1}H NMR Spectrum of Compound 6



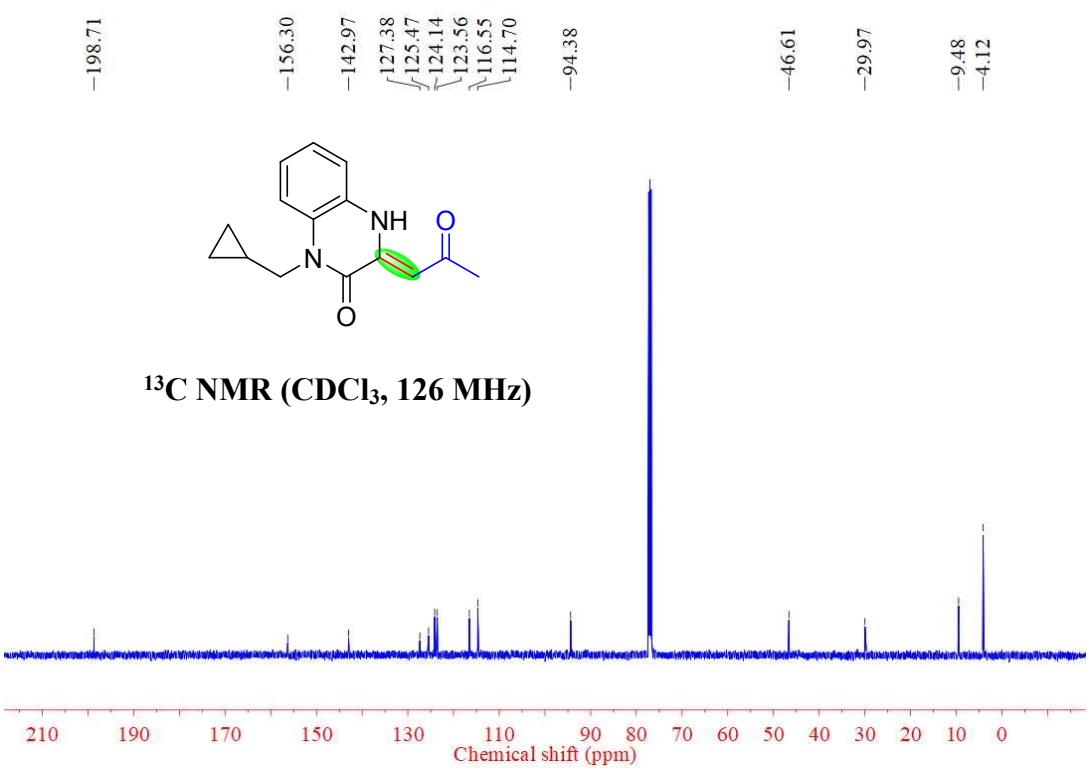
^{13}C NMR ($CDCl_3$, 126 MHz)

^{13}C{^{1}H} NMR Spectrum of Compound 6



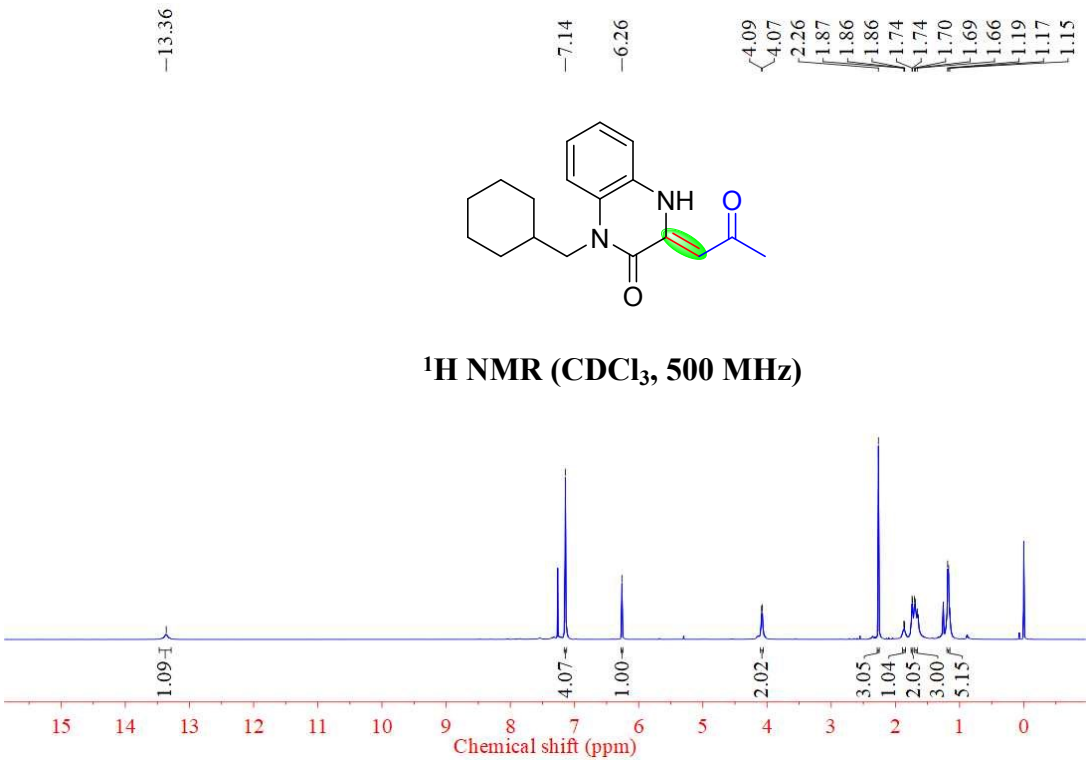
^{1}H NMR ($CDCl_3$, 500 MHz)

^{1}H NMR Spectrum of Compound 7



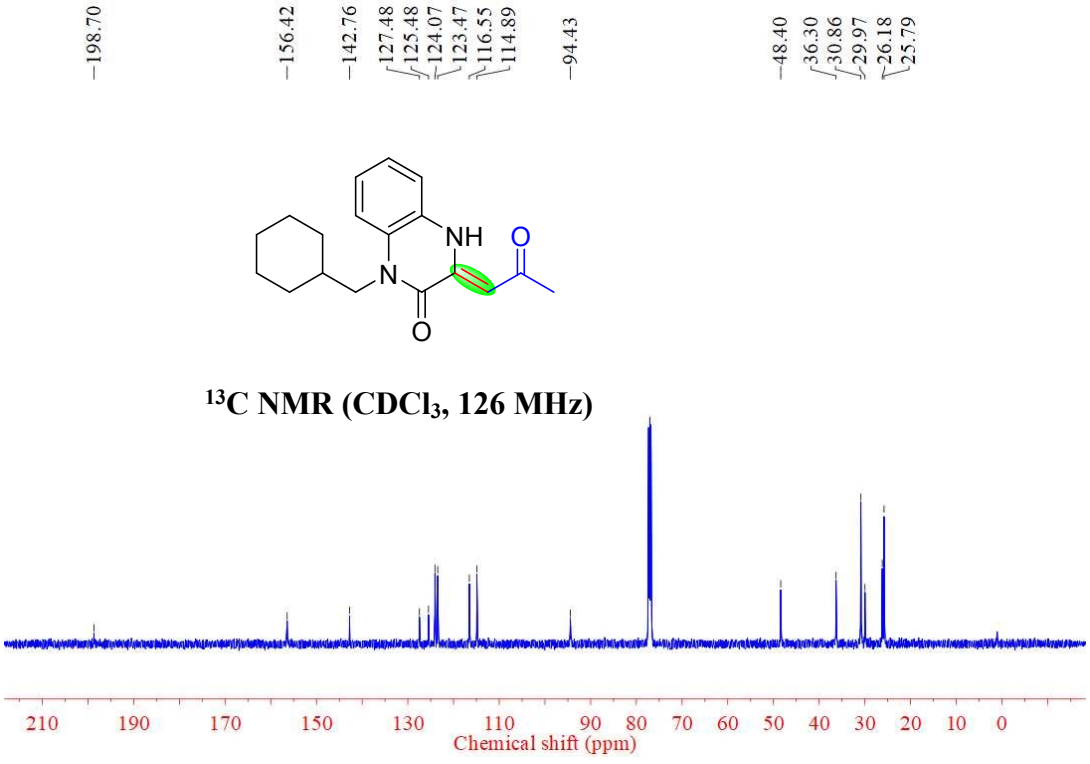
^{13}C NMR ($CDCl_3$, 126 MHz)

^{13}C{^{1}H} NMR Spectrum of Compound 7



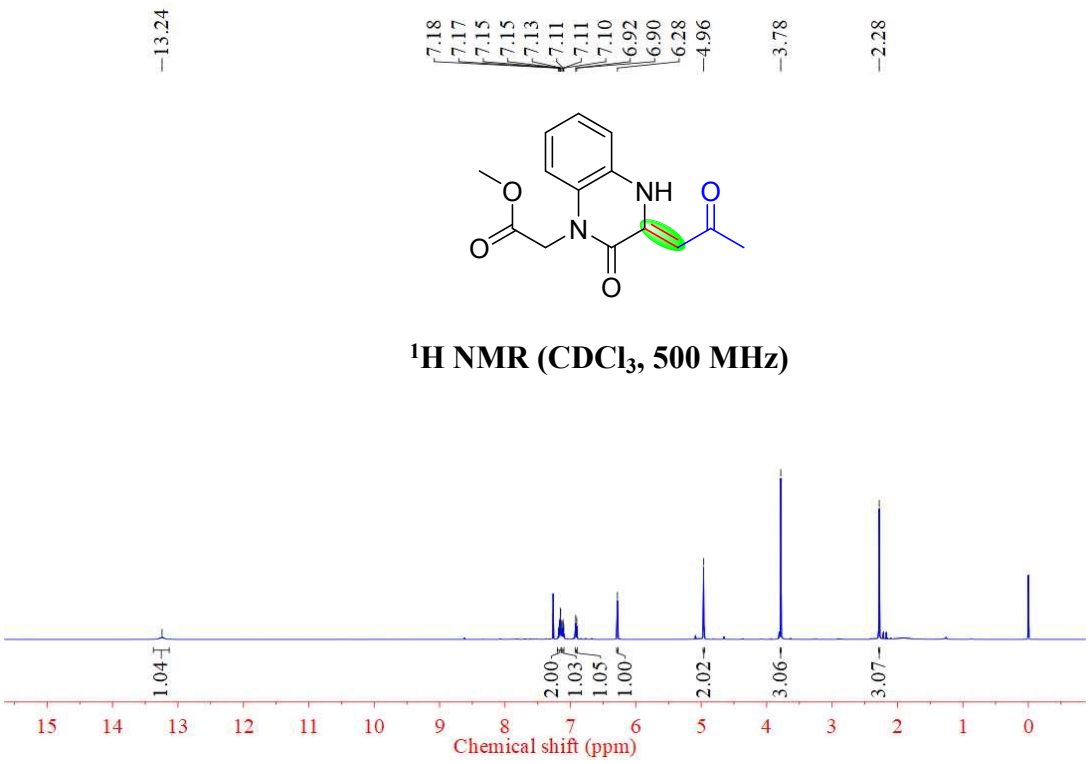
^{1}H NMR ($CDCl_3$, 500 MHz)

^{1}H NMR Spectrum of Compound 8



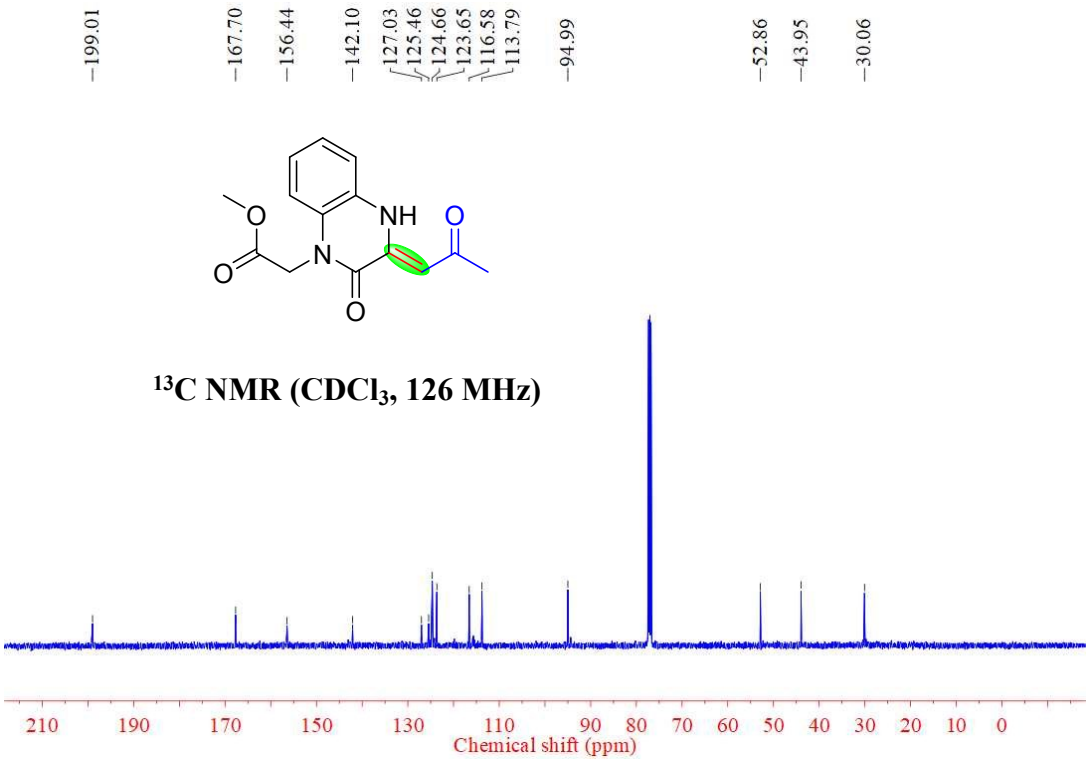
^{13}C NMR ($CDCl_3$, 126 MHz)

^{13}C{^{1}H} NMR Spectrum of Compound 8



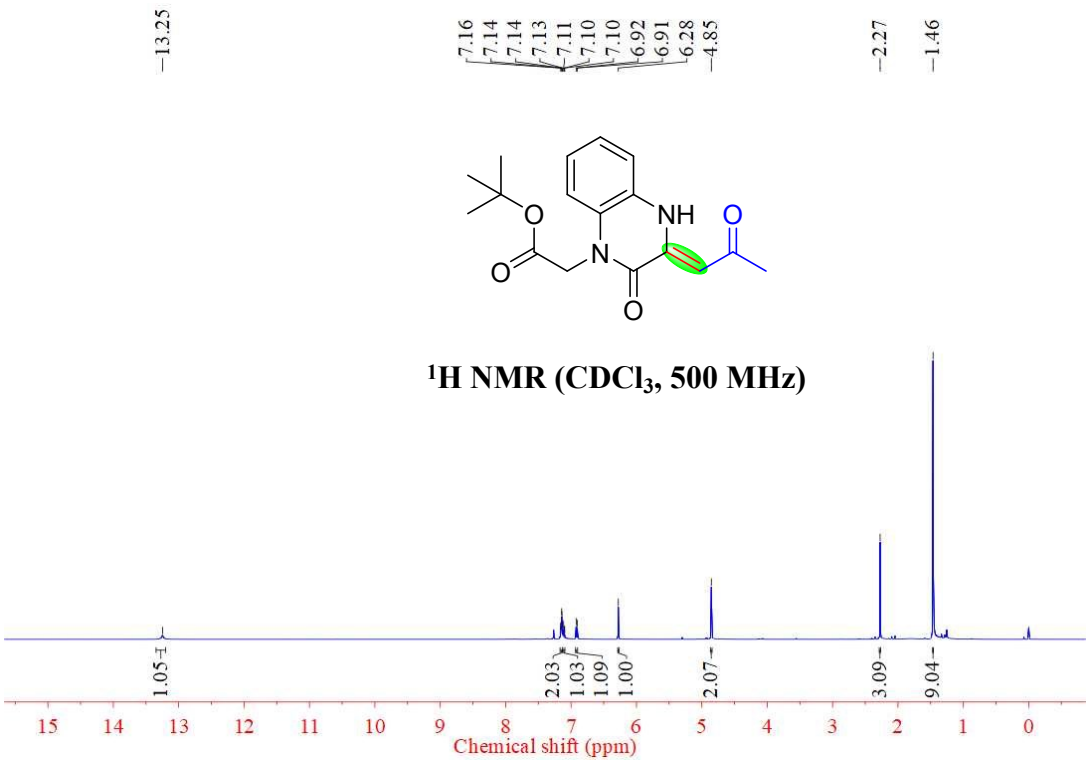
^{1}H NMR ($CDCl_3$, 500 MHz)

^{1}H NMR Spectrum of Compound 9



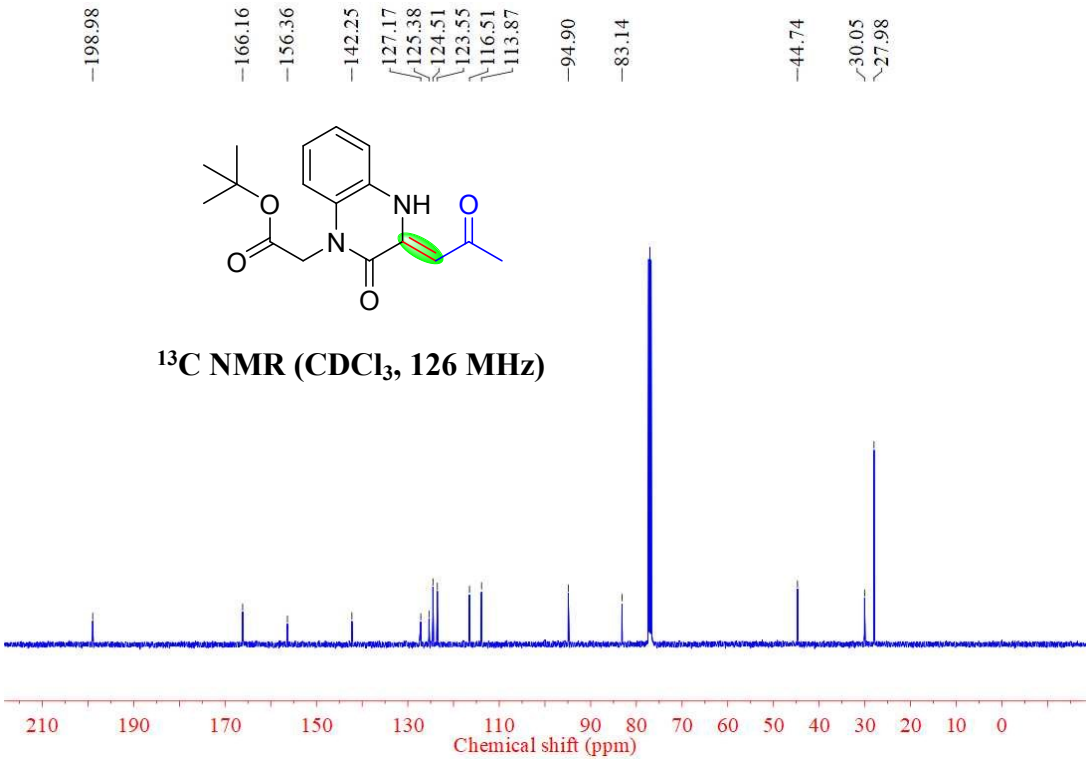
^{13}C NMR ($CDCl_3$, 126 MHz)

^{13}C{^{1}H} NMR Spectrum of Compound 9



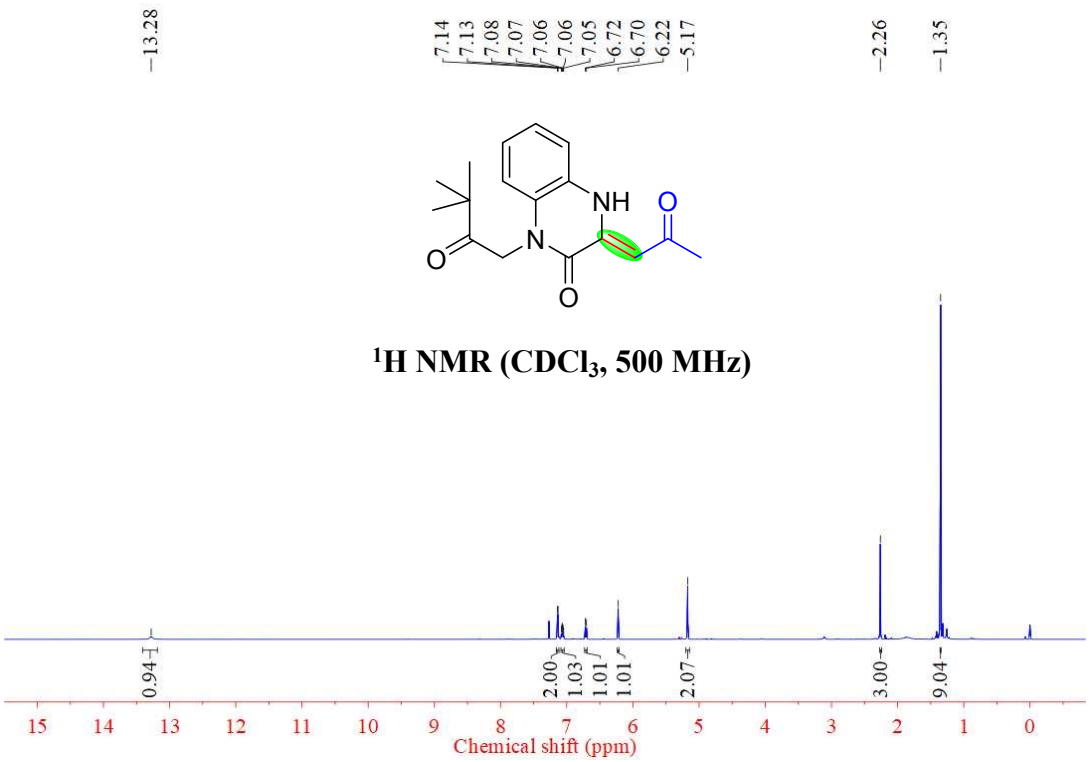
^{1}H NMR ($CDCl_3$, 500 MHz)

^{1}H NMR Spectrum of Compound 10



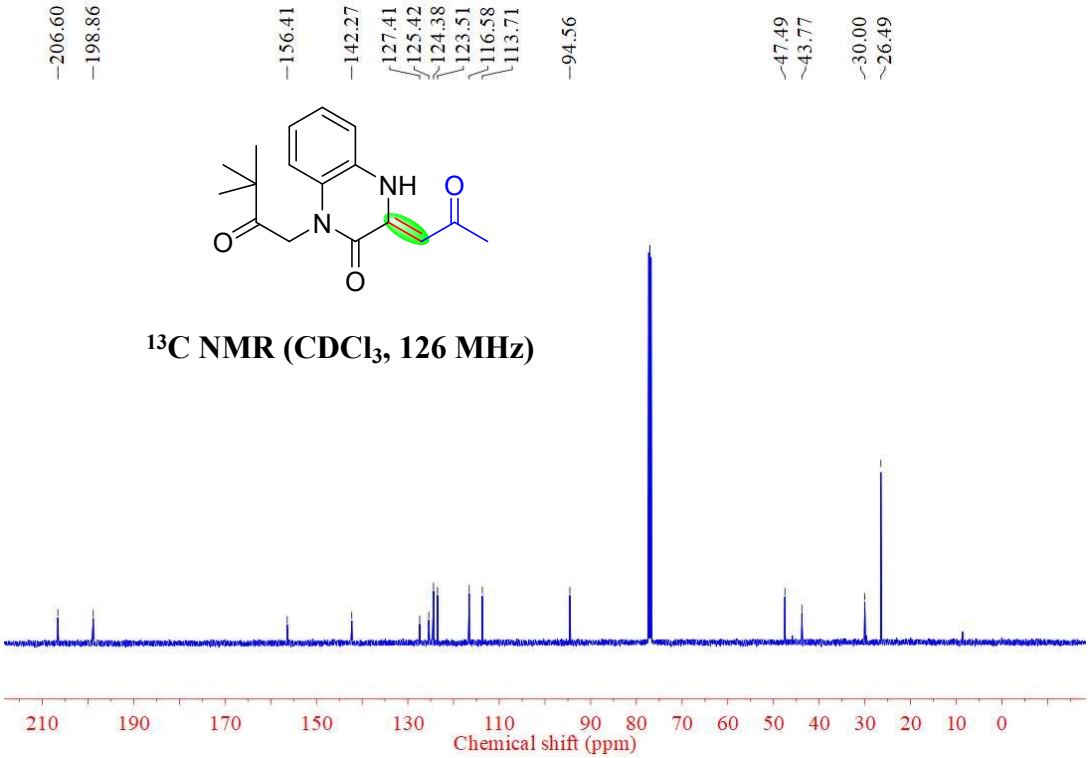
^{13}C NMR ($CDCl_3$, 126 MHz)

^{13}C{^{1}H} NMR Spectrum of Compound 10



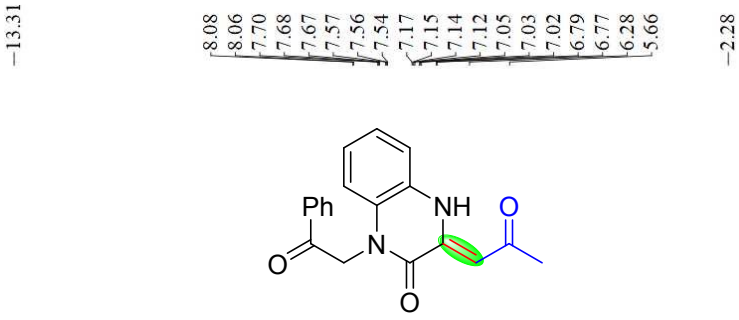
^{1}H NMR ($CDCl_3$, 500 MHz)

^{1}H NMR Spectrum of Compound 11

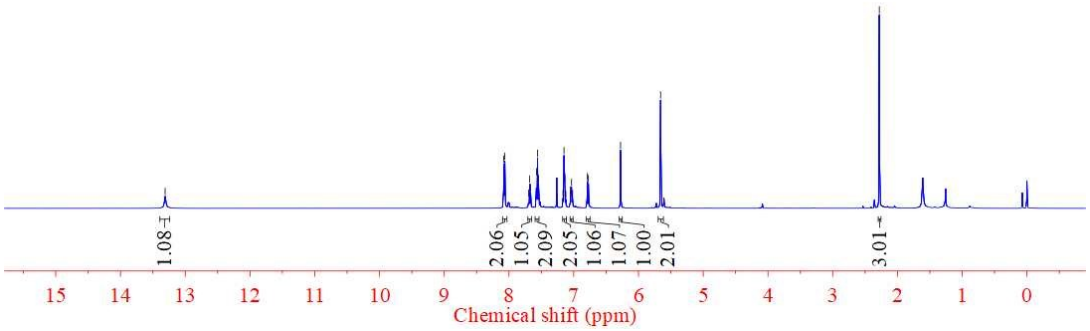


^{13}C NMR ($CDCl_3$, 126 MHz)

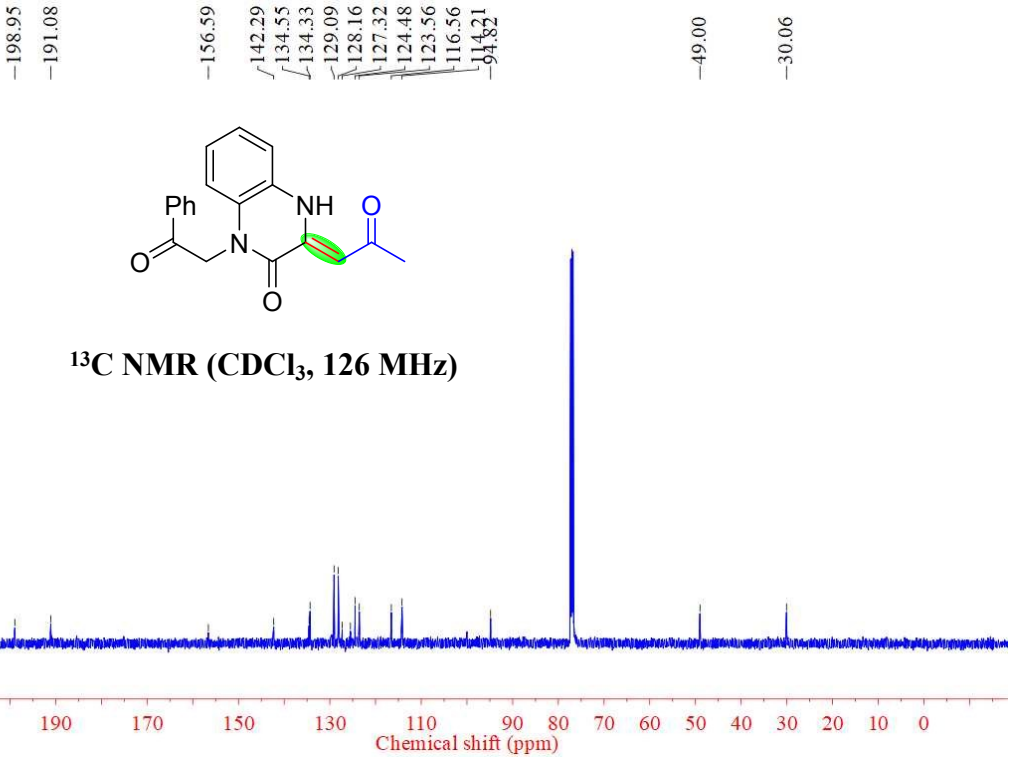
^{13}C{^{1}H} NMR Spectrum of Compound 11



^{1}H NMR ($CDCl_3$, 500 MHz)

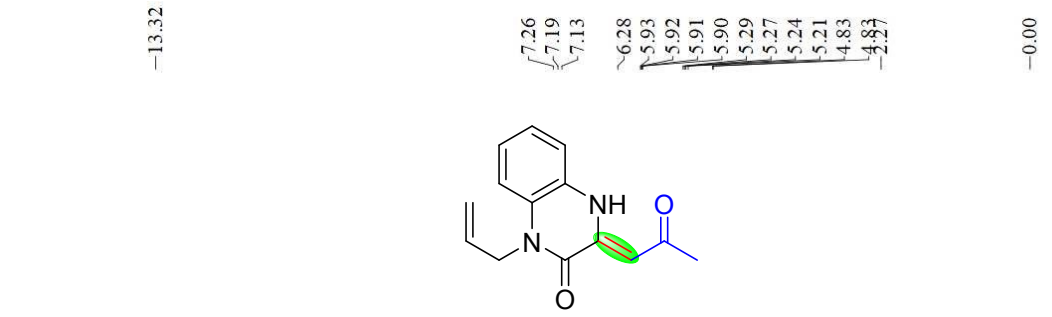


^{1}H NMR Spectrum of Compound 12

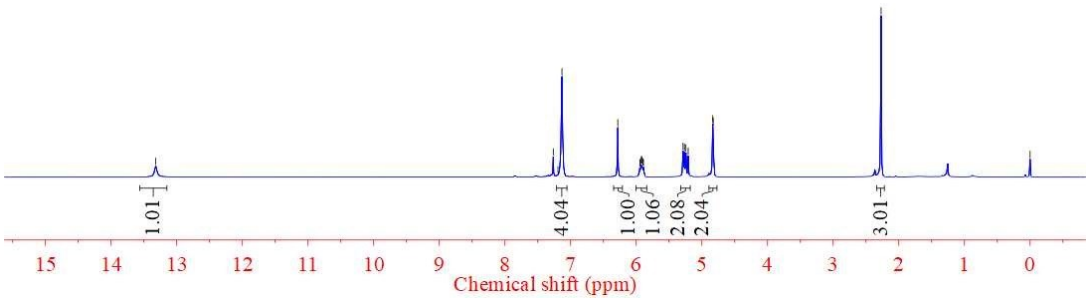


^{13}C NMR ($CDCl_3$, 126 MHz)

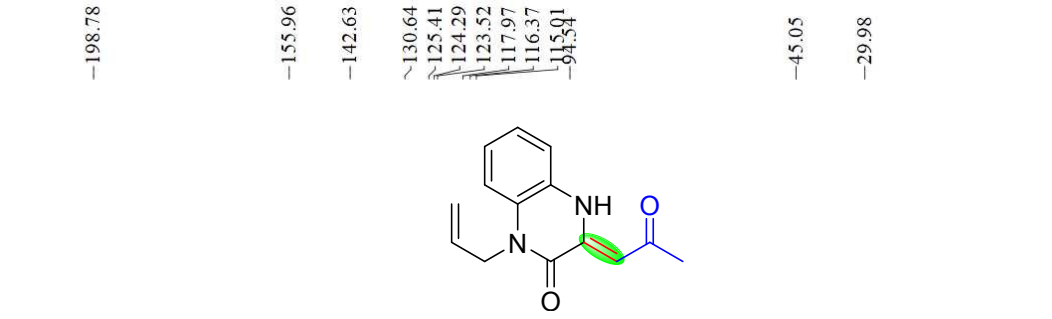
^{13}C{^{1}H} NMR Spectrum of Compound 12



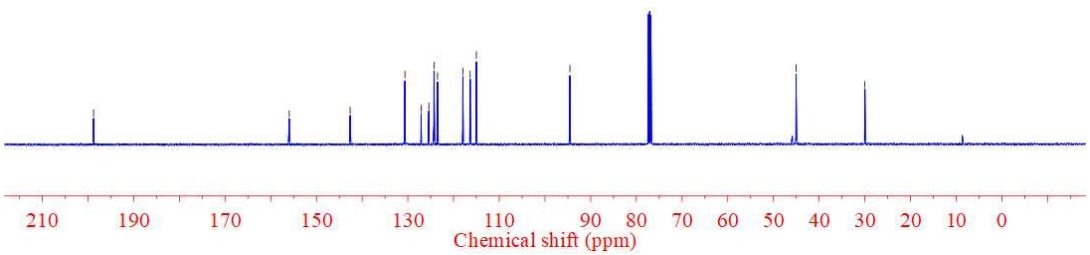
^{1}H NMR ($CDCl_3$, 500 MHz)



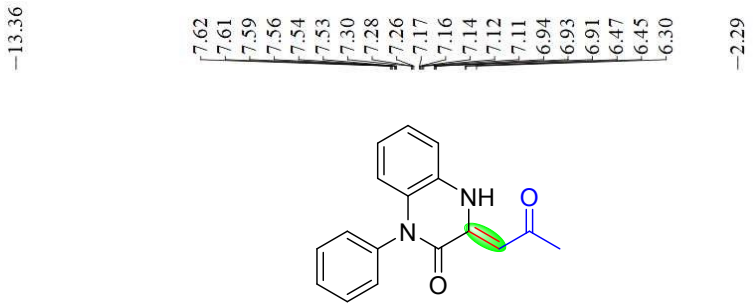
^{1}H NMR Spectrum of Compound 13



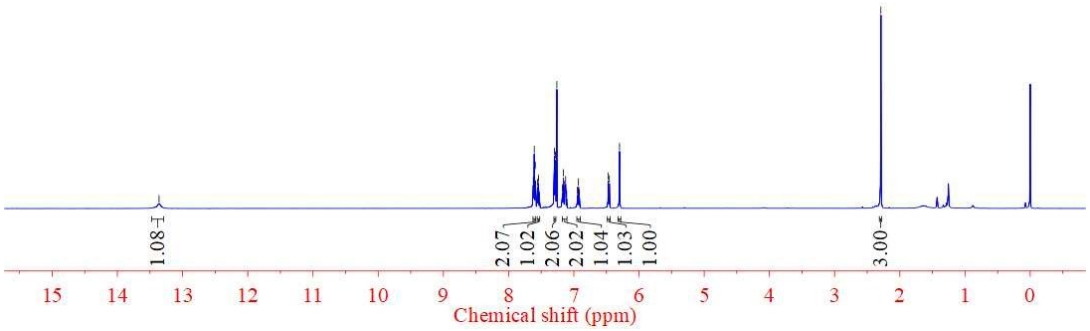
^{13}C NMR ($CDCl_3$, 126 MHz)



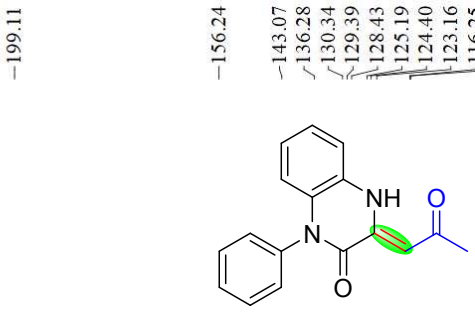
^{13}C{^{1}H} NMR Spectrum of Compound 13



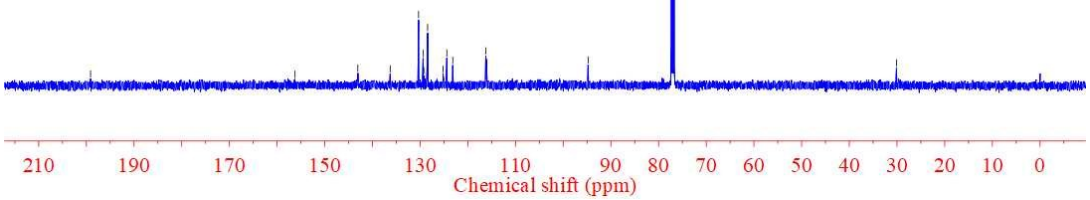
^{1}H NMR ($CDCl_3$, 500 MHz)



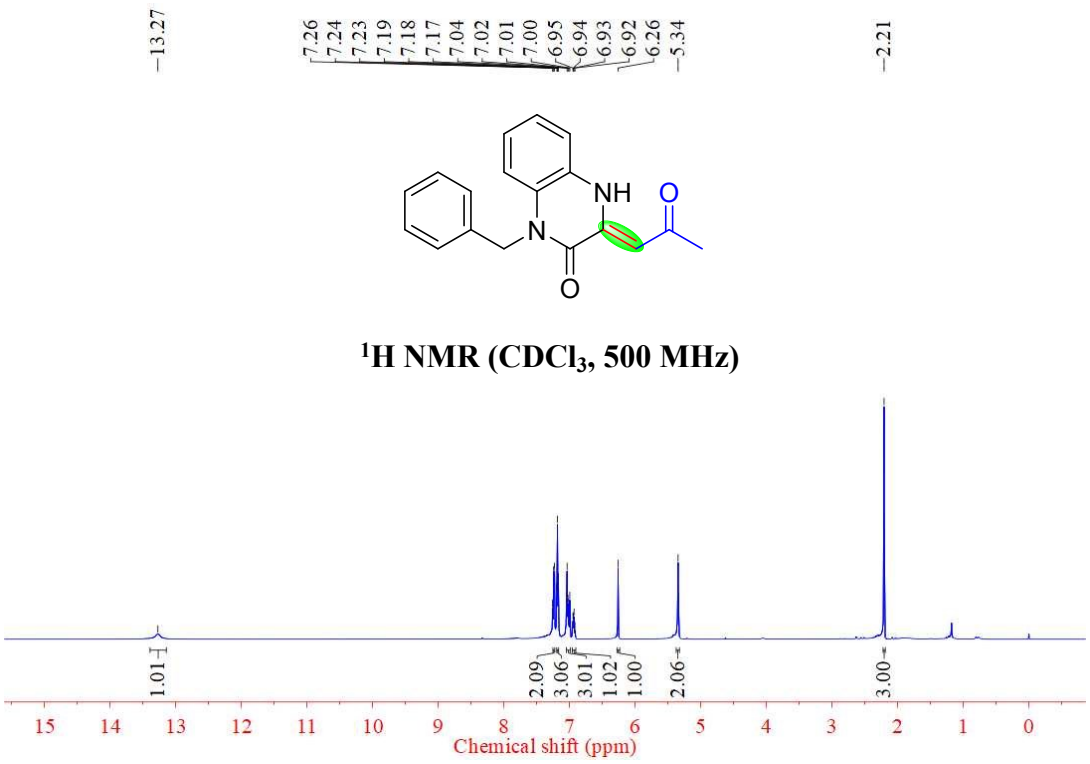
^{1}H NMR Spectrum of Compound 14



^{13}C NMR ($CDCl_3$, 126 MHz)

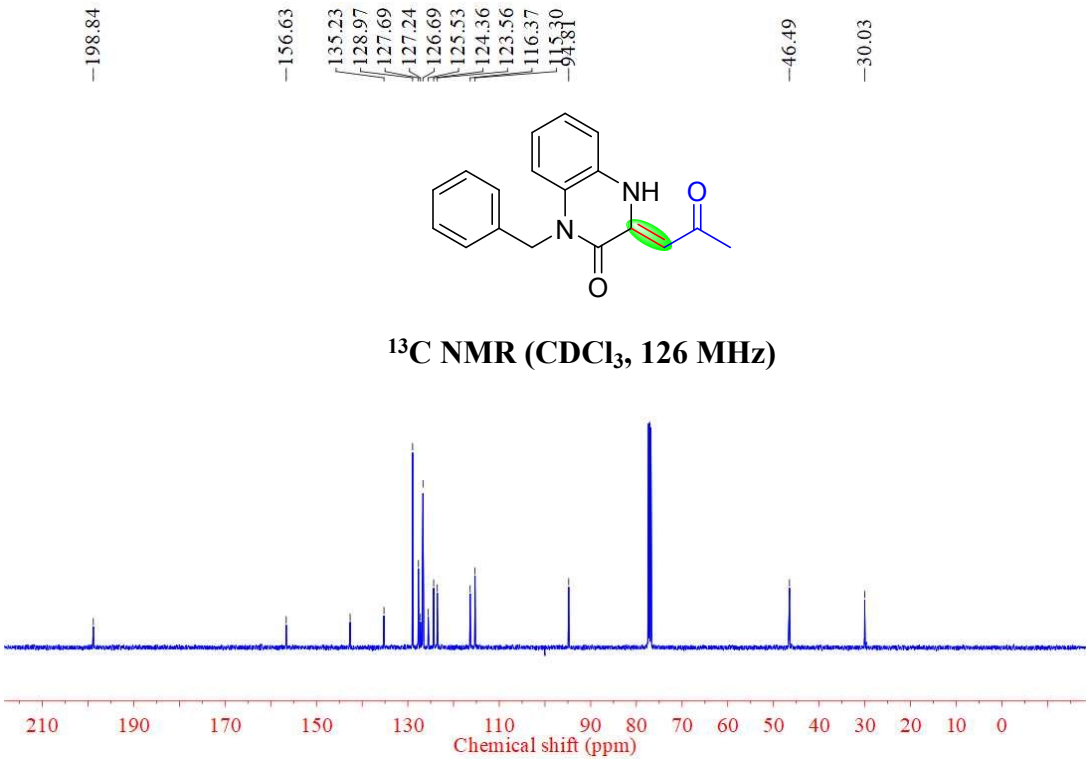


^{13}C{^{1}H} NMR Spectrum of Compound 14



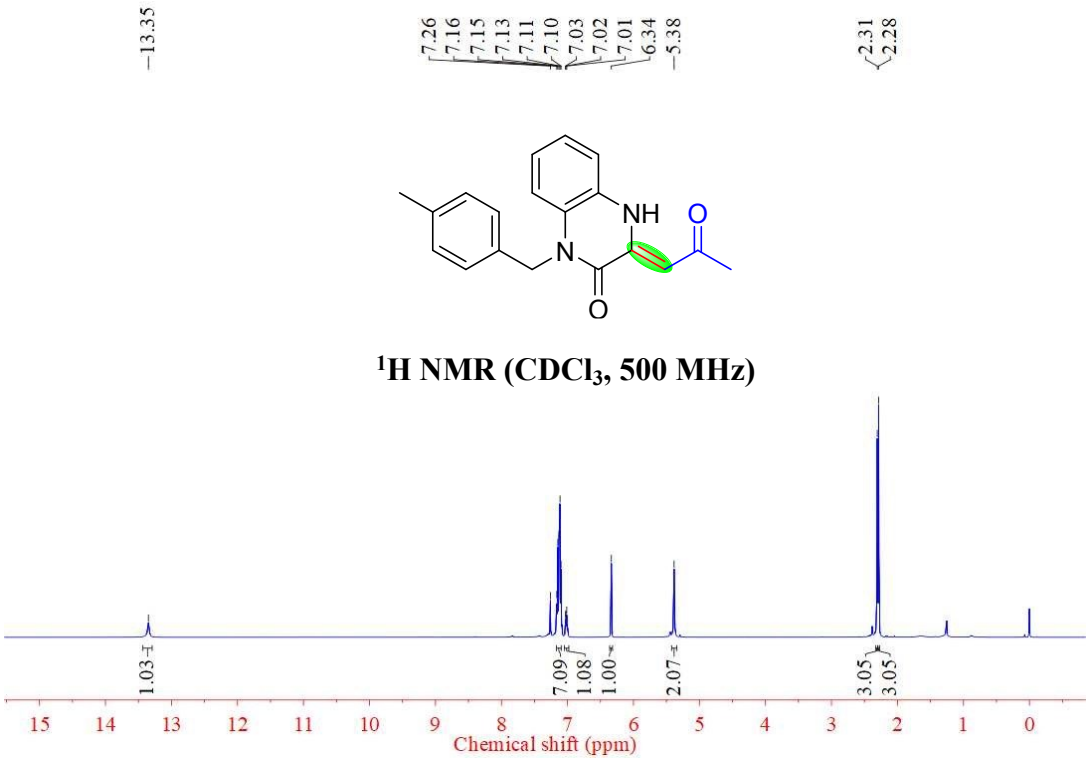
^{1}H NMR ($CDCl_3$, 500 MHz)

^{1}H NMR Spectrum of Compound 15



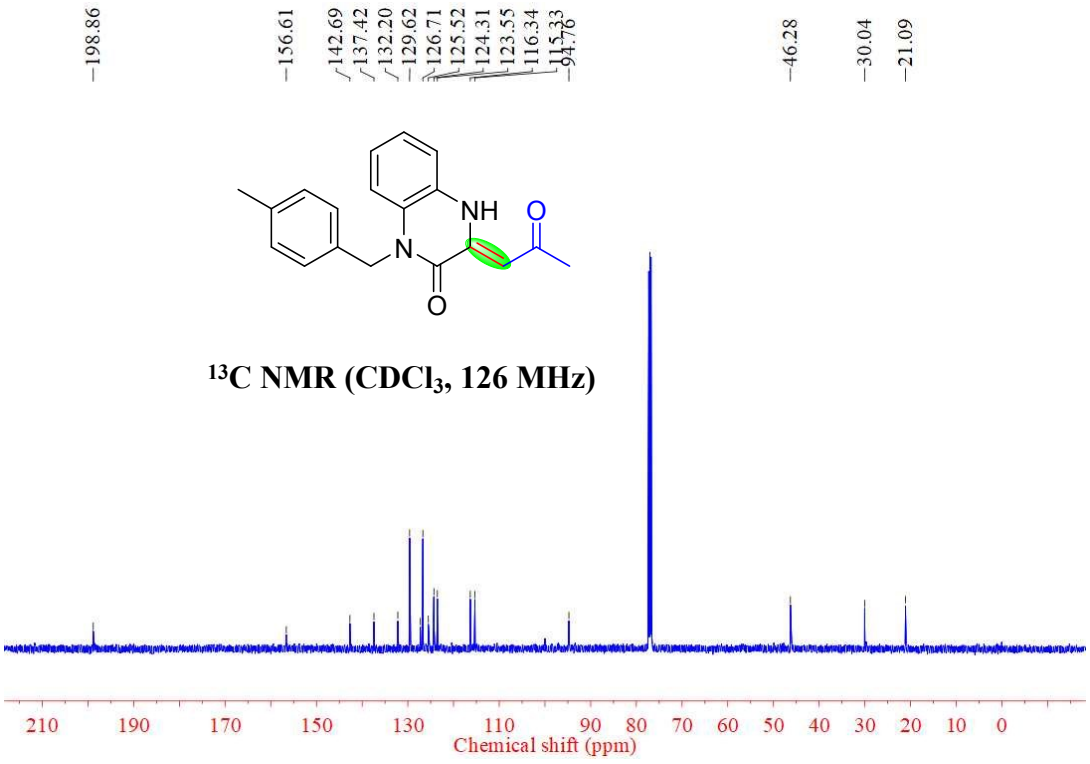
^{13}C NMR ($CDCl_3$, 126 MHz)

^{13}C{^{1}H} NMR Spectrum of Compound 15



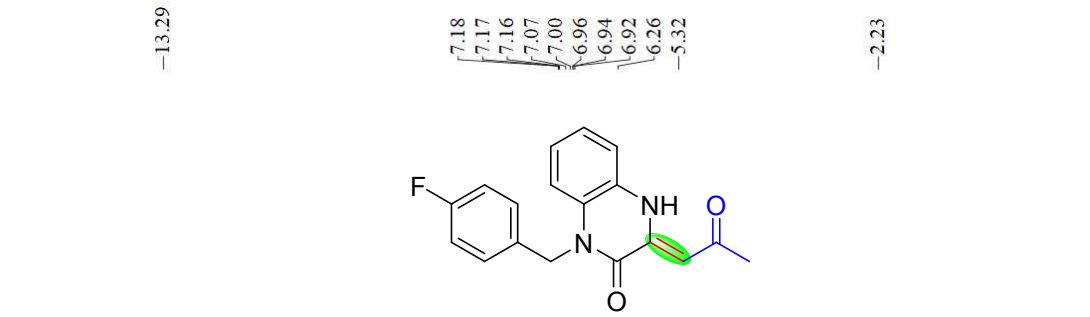
^{1}H NMR ($CDCl_3$, 500 MHz)

^{1}H NMR Spectrum of Compound 16

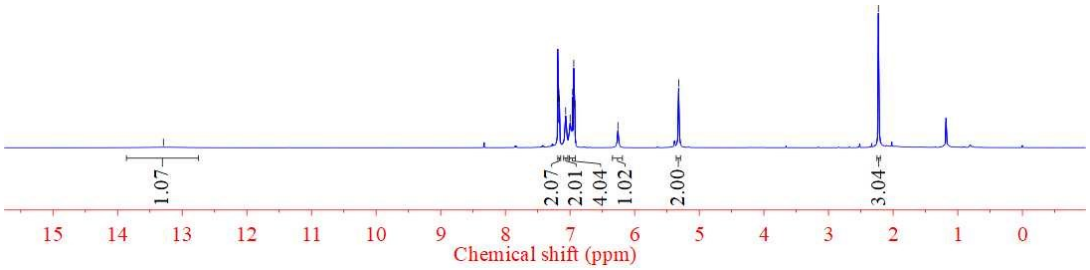


^{13}C NMR ($CDCl_3$, 126 MHz)

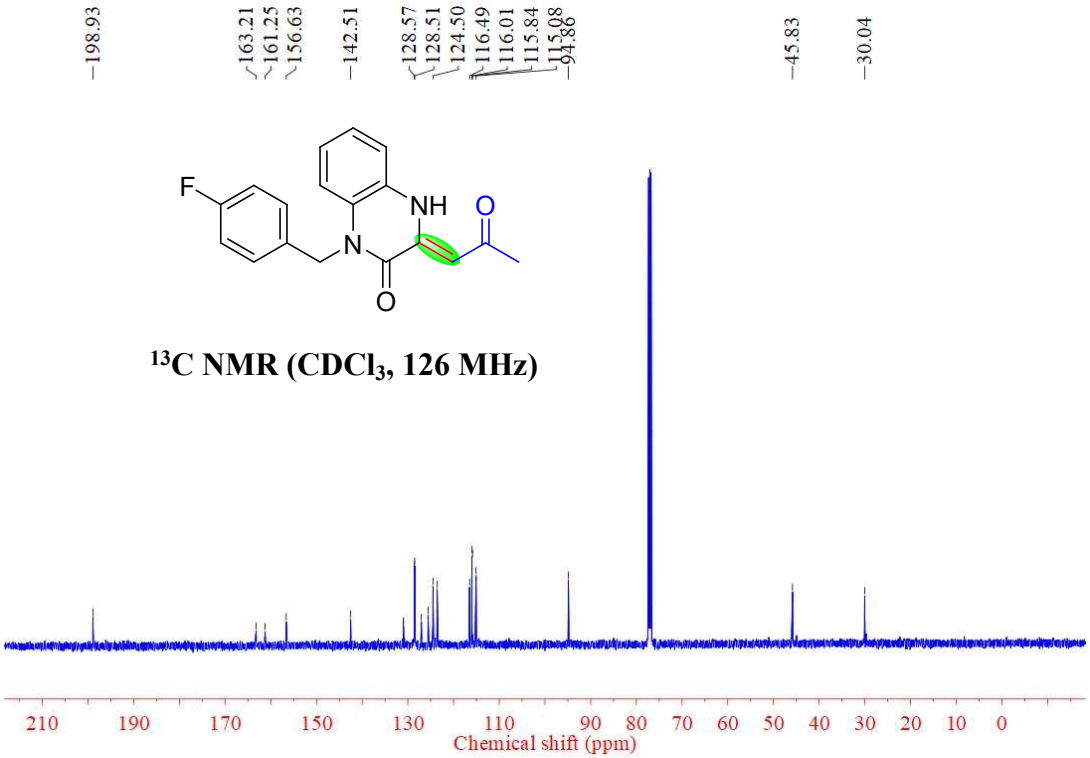
^{13}C{^{1}H} NMR Spectrum of Compound 16



^{1}H NMR ($CDCl_3$, 500 MHz)

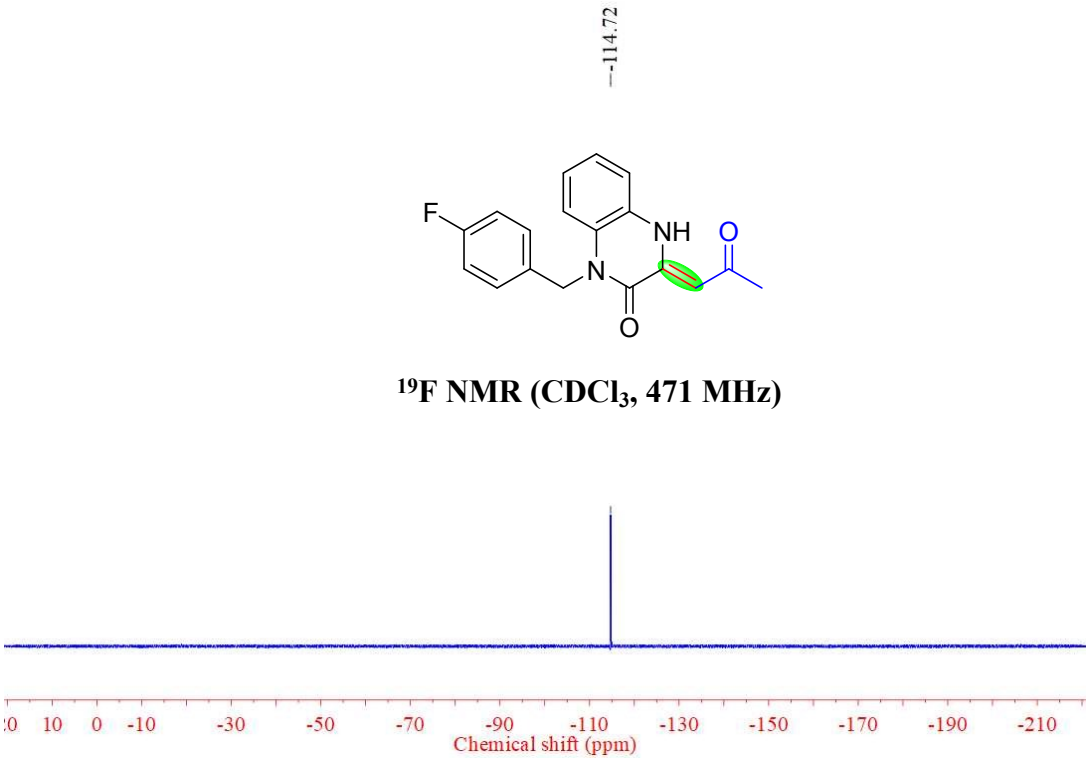


^{1}H NMR Spectrum of Compound 17



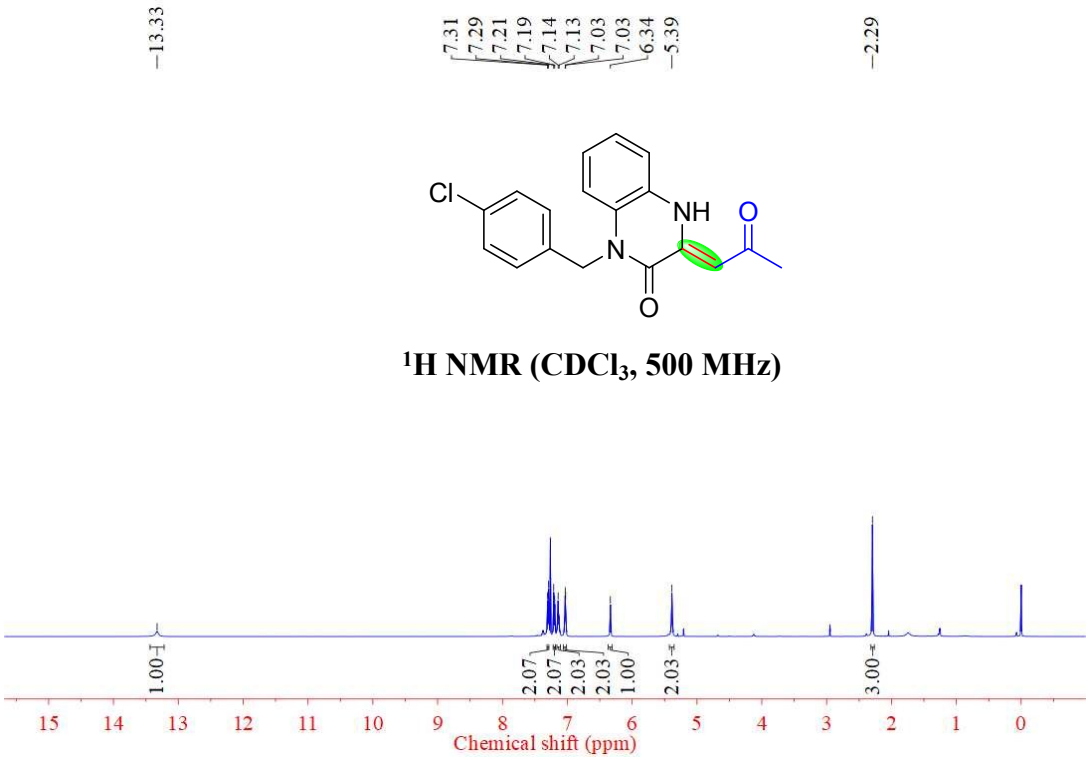
^{13}C NMR ($CDCl_3$, 126 MHz)

^{13}C{^{1}H} NMR Spectrum of Compound 17



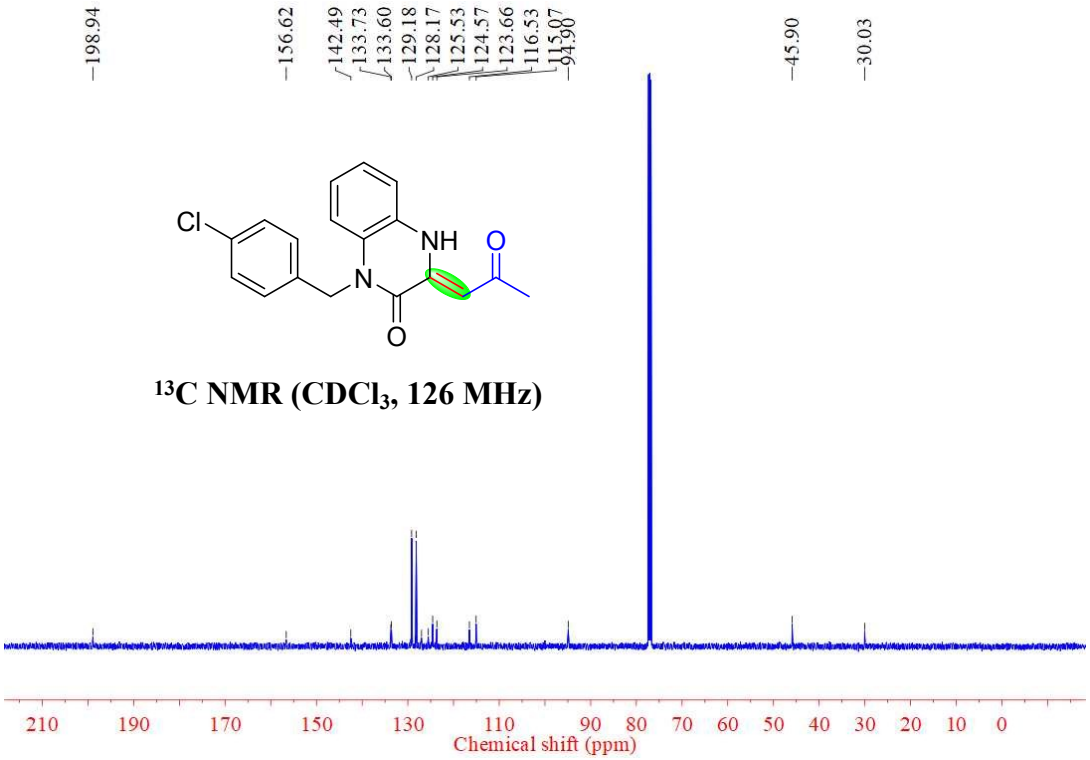
^{19}F NMR ($CDCl_3$, 471 MHz)

^{19}F{^{1}H} NMR Spectrum of Compound 17



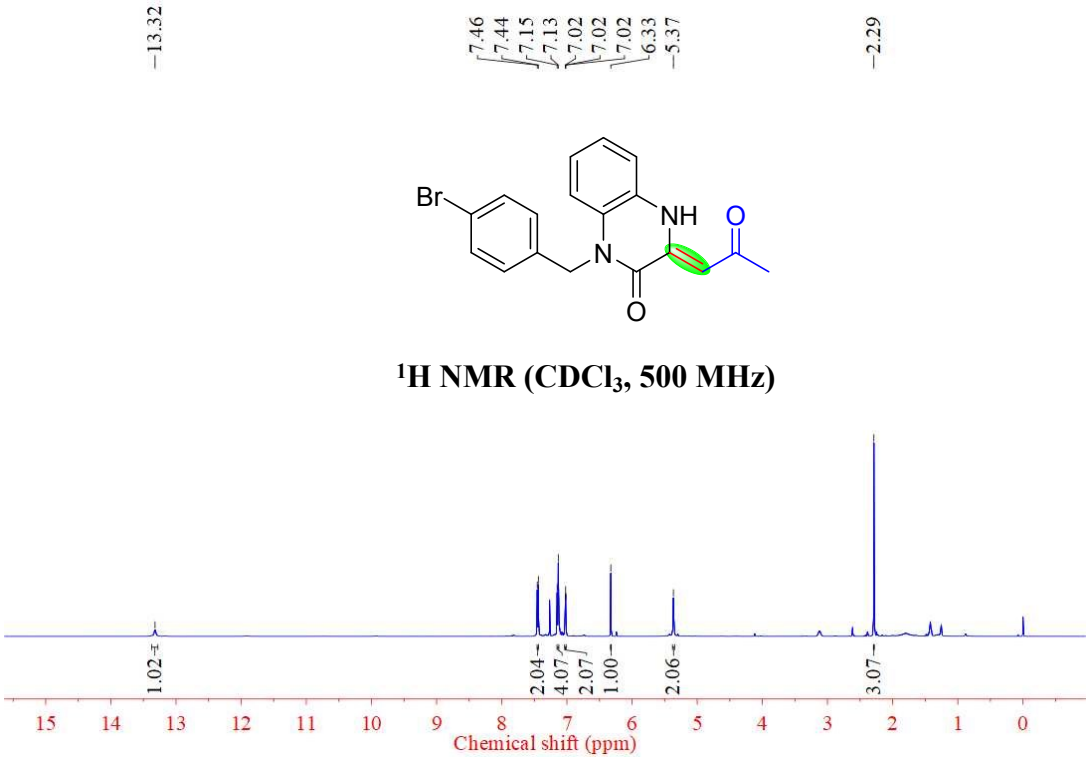
^{1}H NMR ($CDCl_3$, 500 MHz)

^{1}H NMR Spectrum of Compound 18



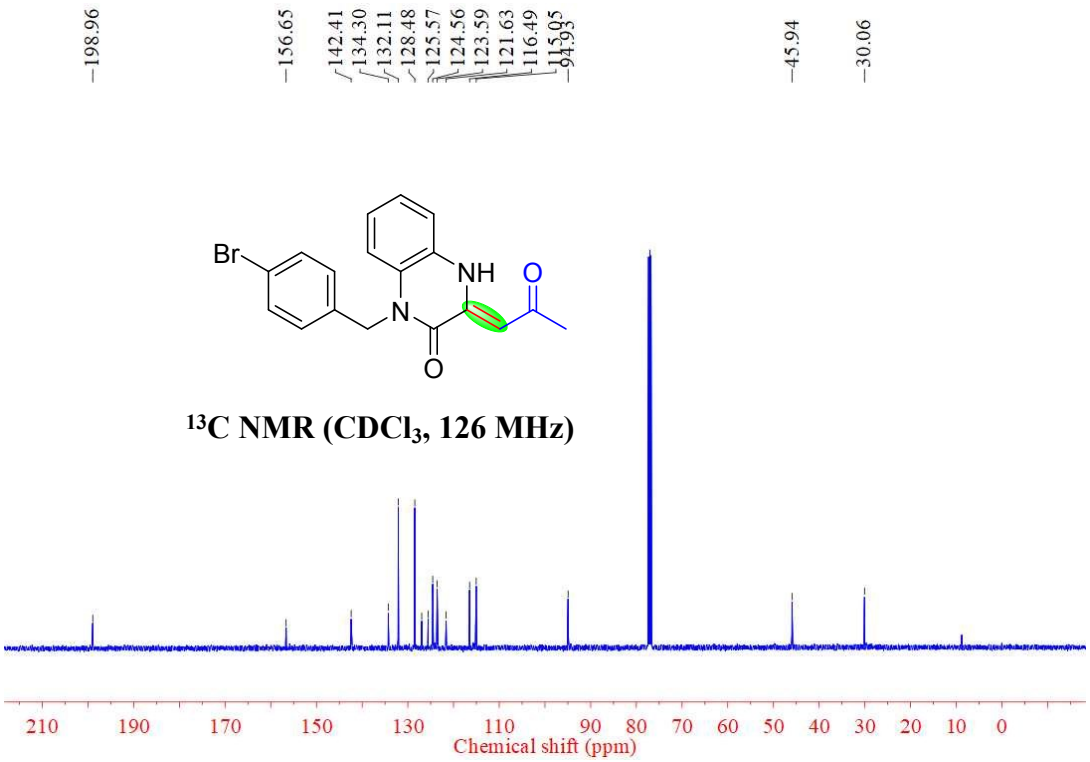
^{13}C NMR ($CDCl_3$, 126 MHz)

^{13}C{^{1}H} NMR Spectrum of Compound 18



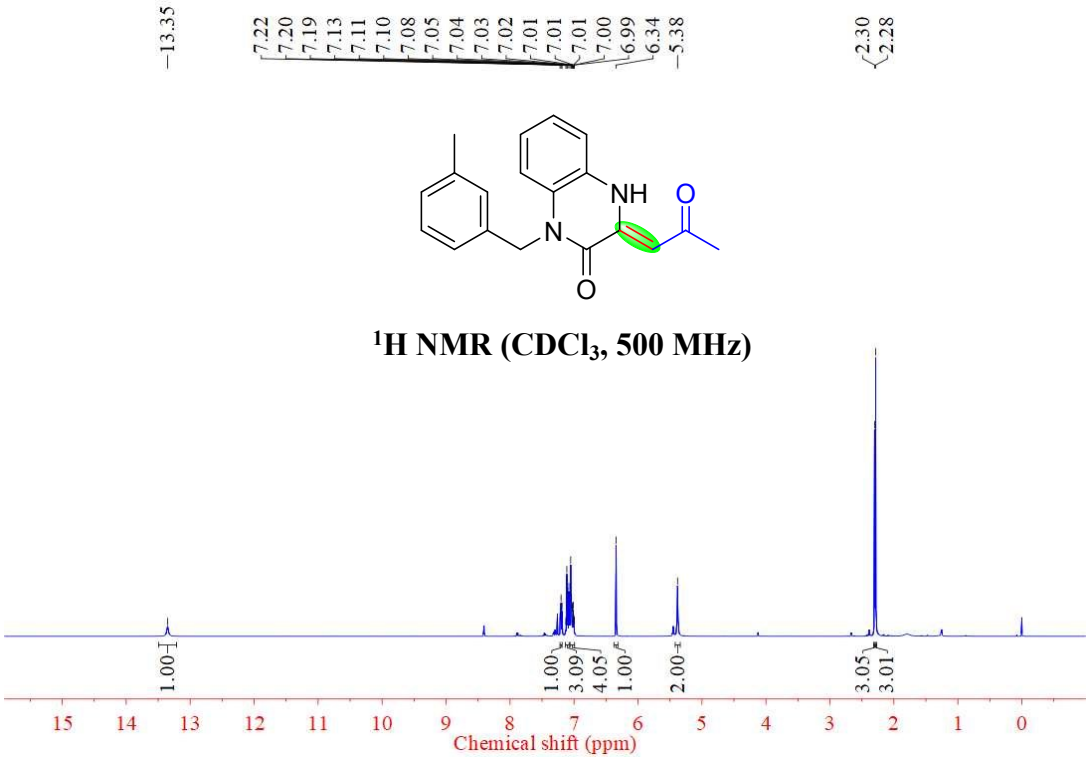
^{1}H NMR ($CDCl_3$, 500 MHz)

^{1}H NMR Spectrum of Compound 19



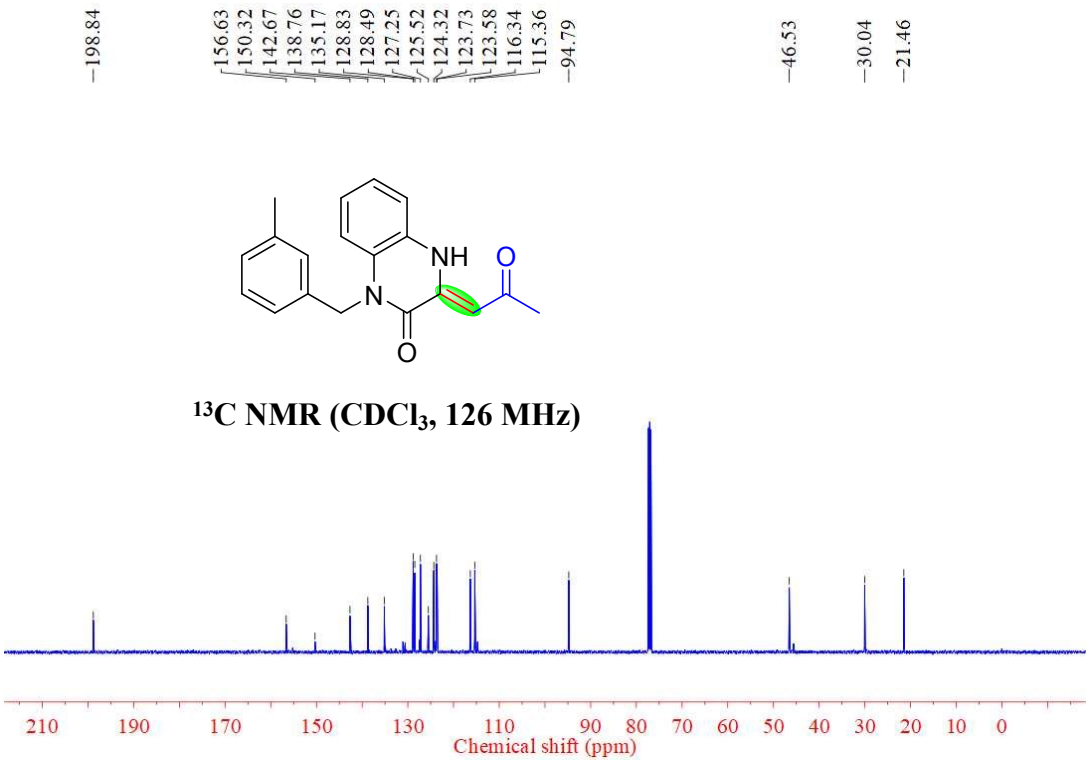
^{13}C NMR ($CDCl_3$, 126 MHz)

^{13}C{^{1}H} NMR Spectrum of Compound 19



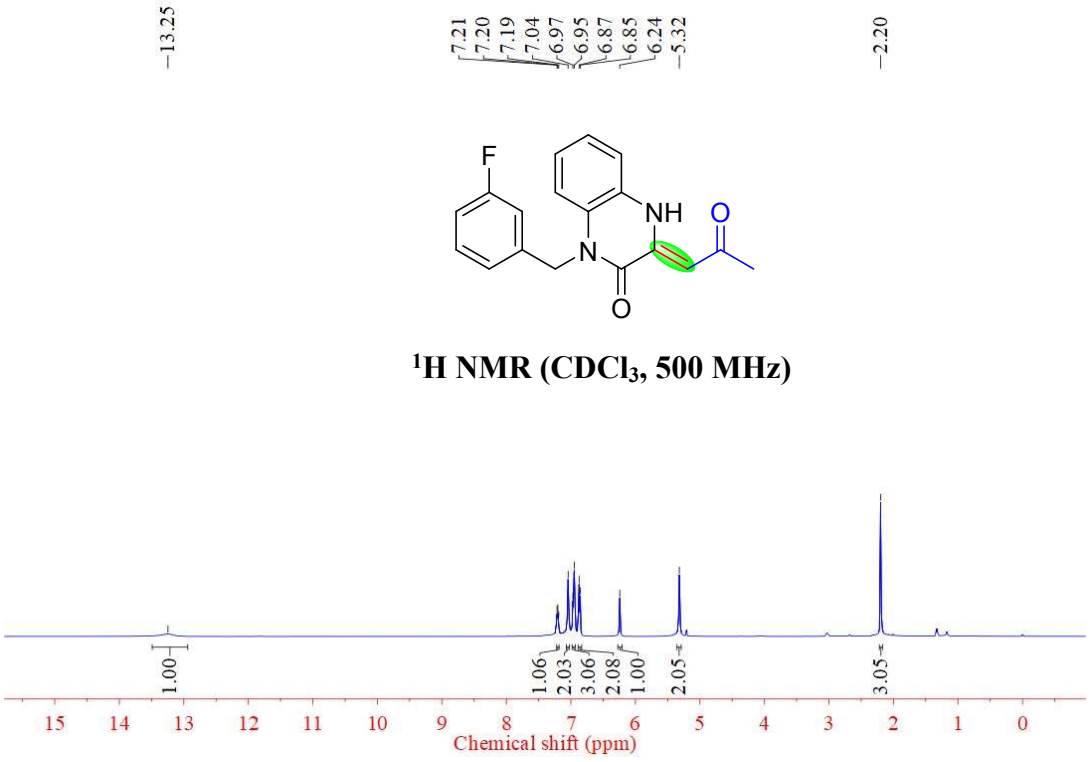
^{1}H NMR ($CDCl_3$, 500 MHz)

^{1}H NMR Spectrum of Compound 20



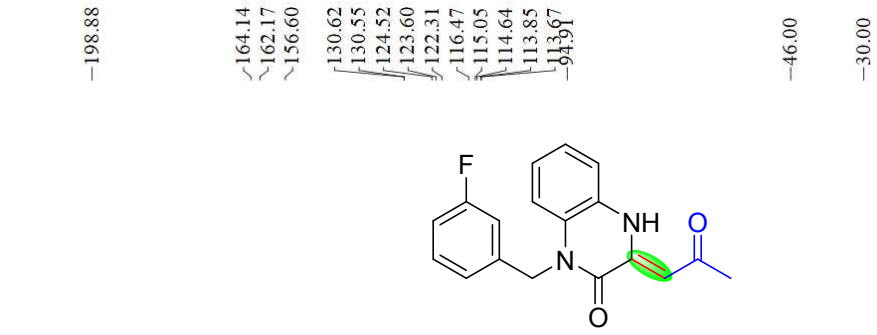
^{13}C NMR ($CDCl_3$, 126 MHz)

$^{13}C\{^1H\}$ NMR Spectrum of Compound 20

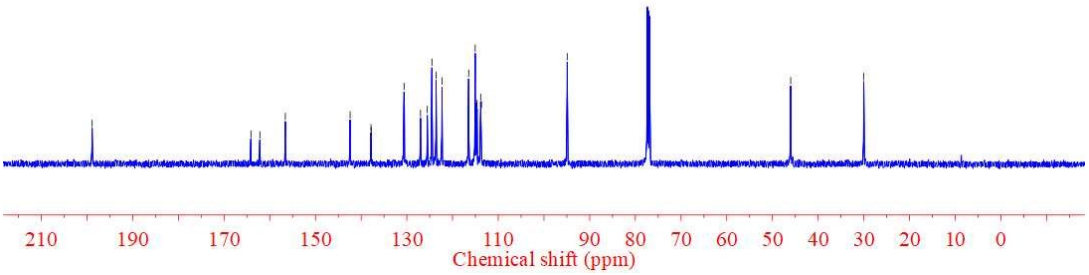


^1H NMR ($CDCl_3$, 500 MHz)

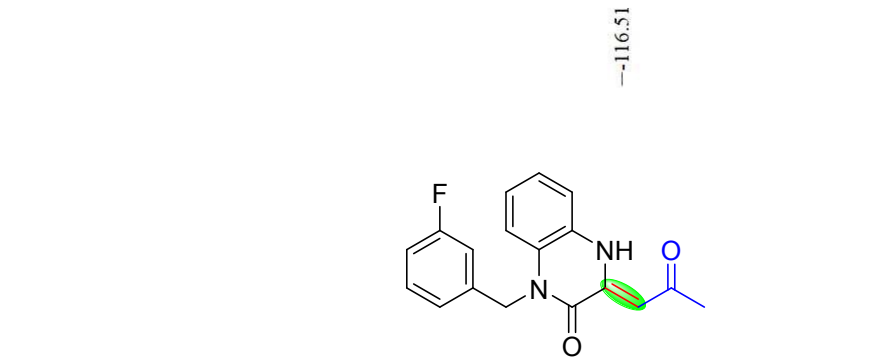
^1H NMR Spectrum of Compound 21



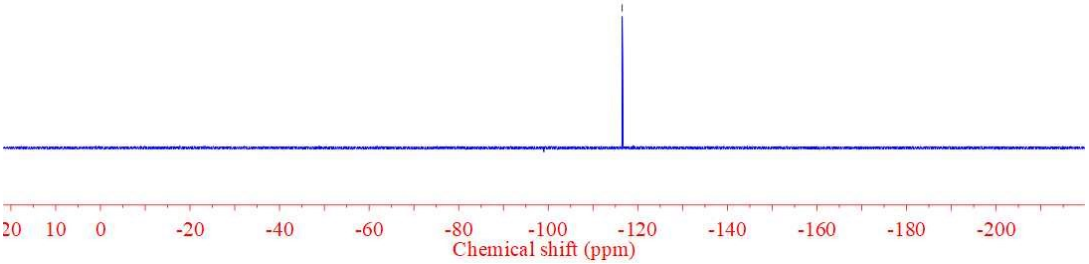
^{13}C NMR ($CDCl_3$, 126 MHz)



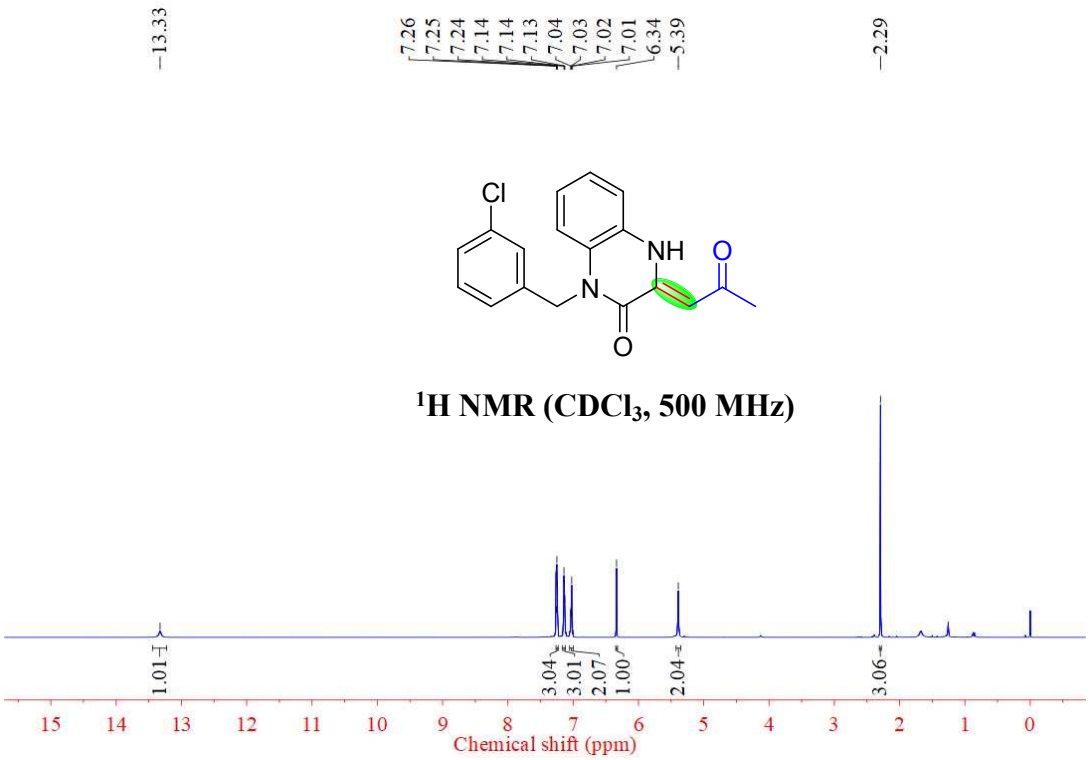
^{13}C{^{1}H} NMR Spectrum of Compound 21



^{19}F NMR ($CDCl_3$, 471 MHz)

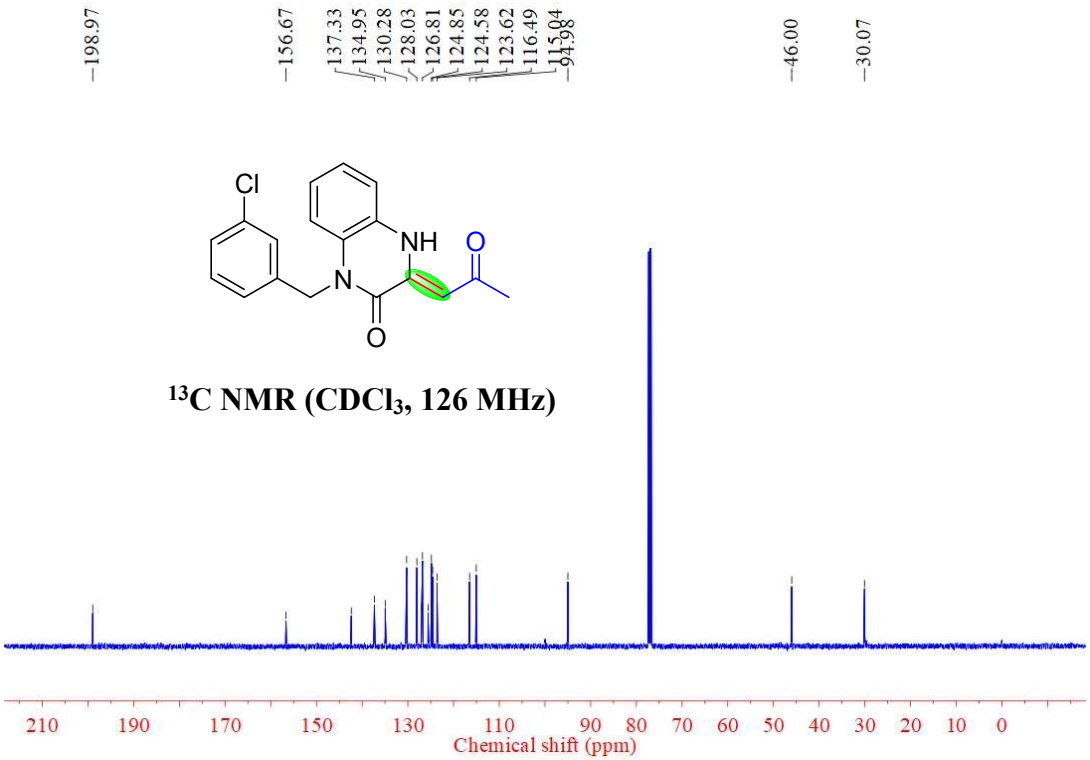


^{19}F{^{1}H} NMR Spectrum of Compound 21



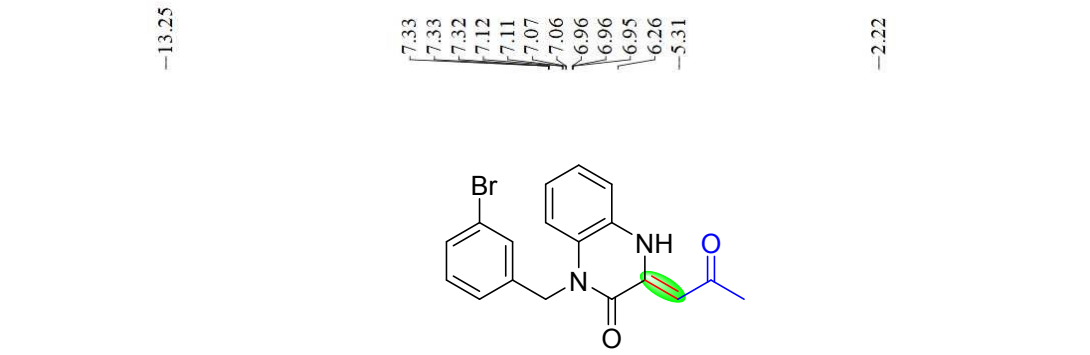
^{1}H NMR ($CDCl_3$, 500 MHz)

^{1}H NMR Spectrum of Compound 22

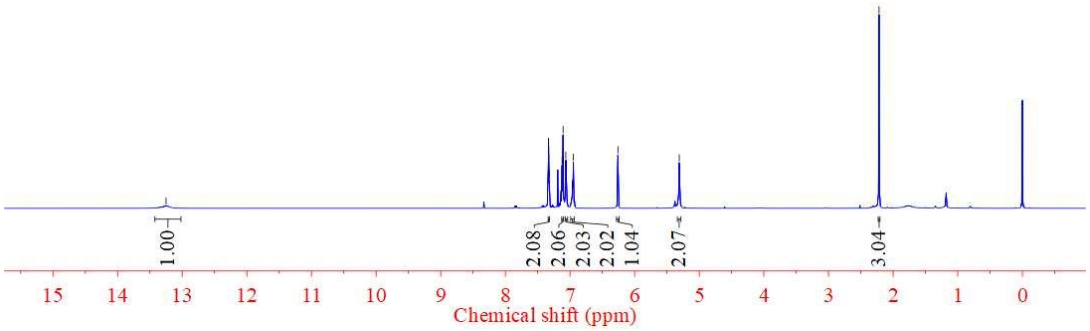


^{13}C NMR ($CDCl_3$, 126 MHz)

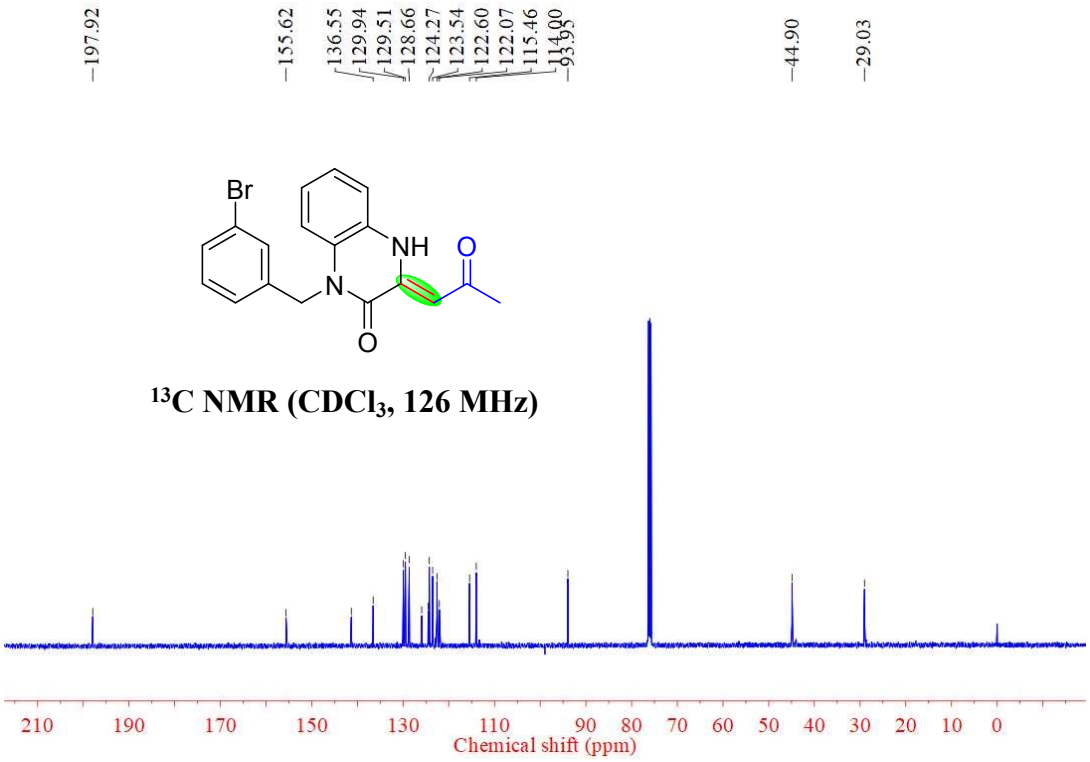
^{13}C{^{1}H} NMR Spectrum of Compound 22



^{1}H NMR ($CDCl_3$, 500 MHz)

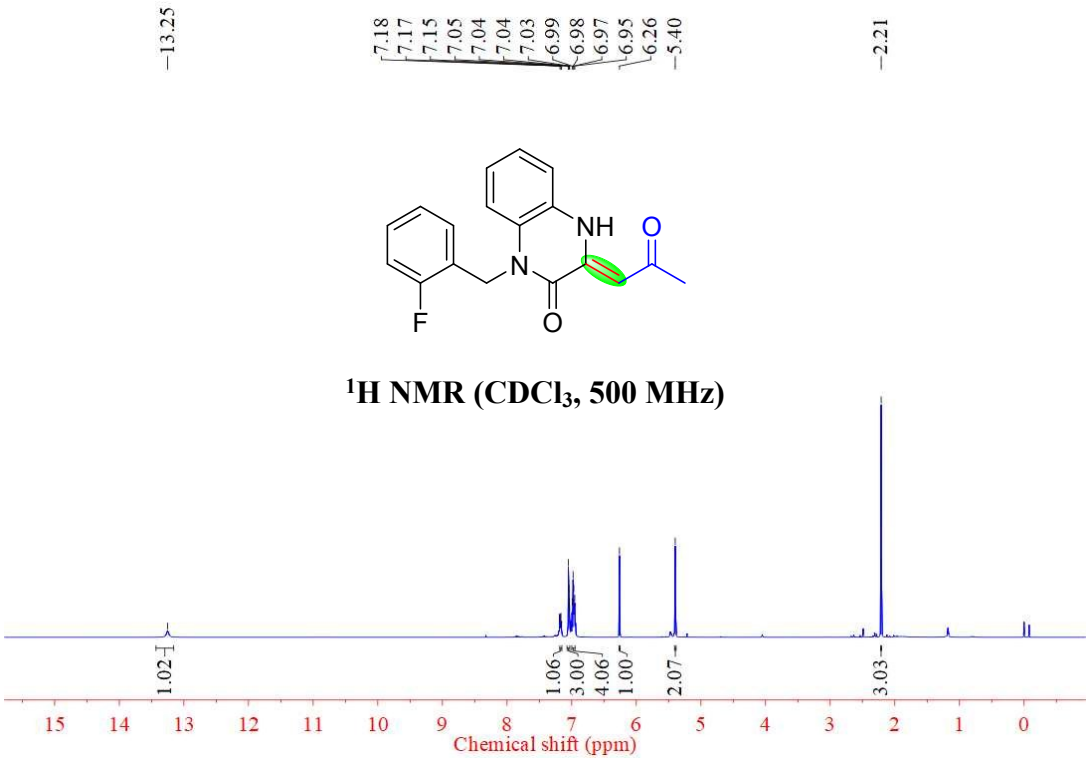


^{1}H NMR Spectrum of Compound 23



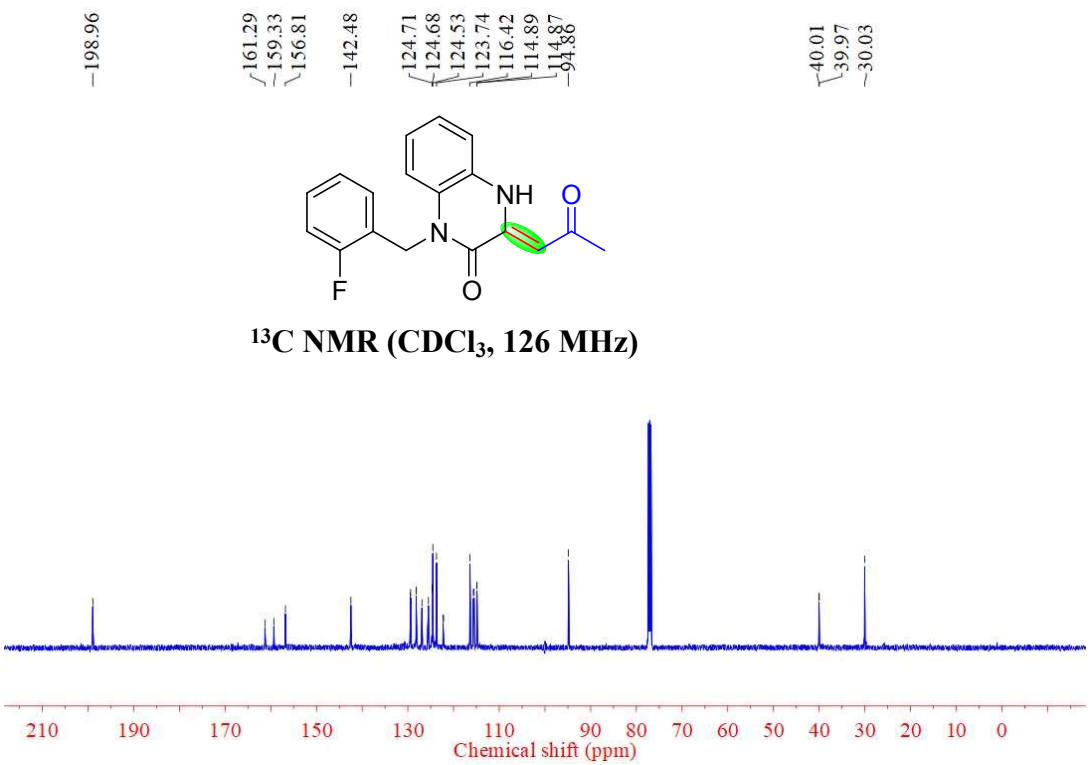
^{13}C NMR ($CDCl_3$, 126 MHz)

^{13}C{^{1}H} NMR Spectrum of Compound 23



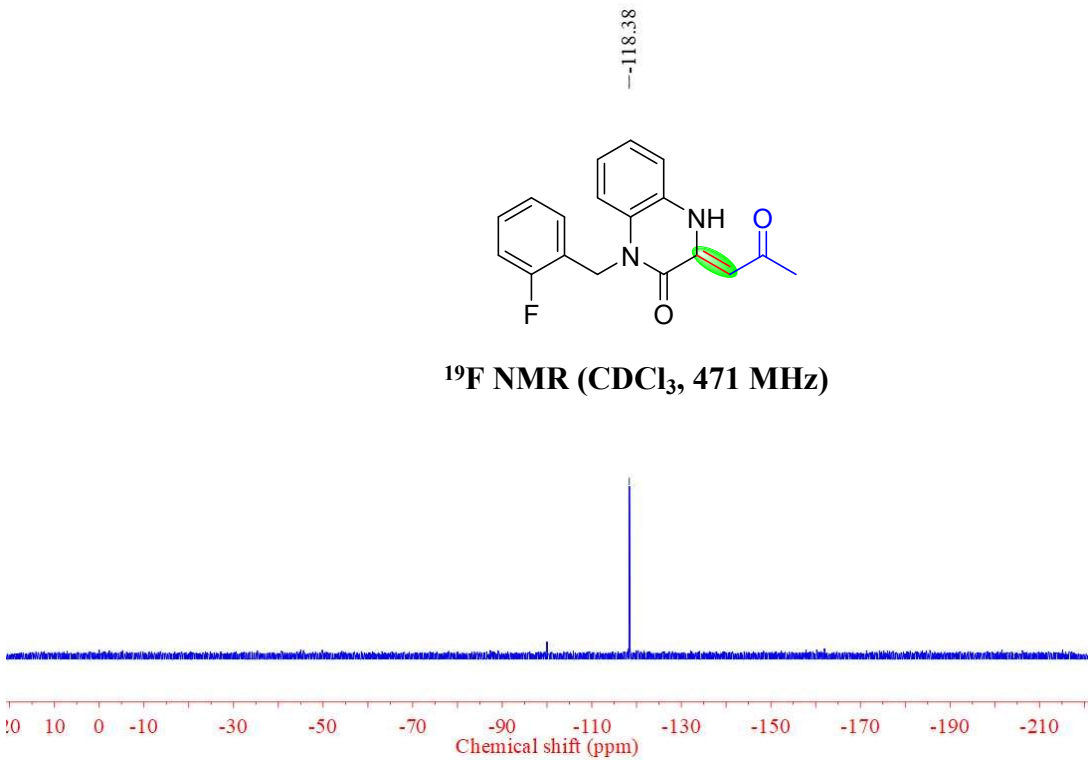
^{1}H NMR ($CDCl_3$, 500 MHz)

^{1}H NMR Spectrum of Compound 24



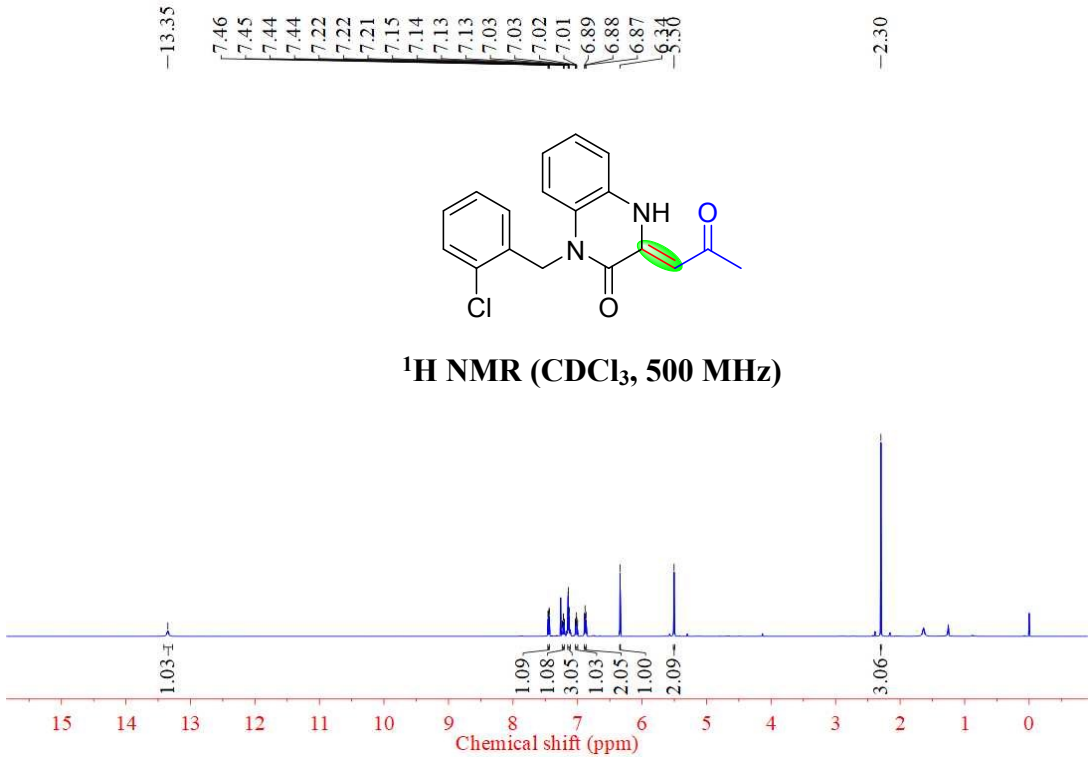
^{13}C NMR ($CDCl_3$, 126 MHz)

^{13}C{^{1}H} NMR Spectrum of Compound 24



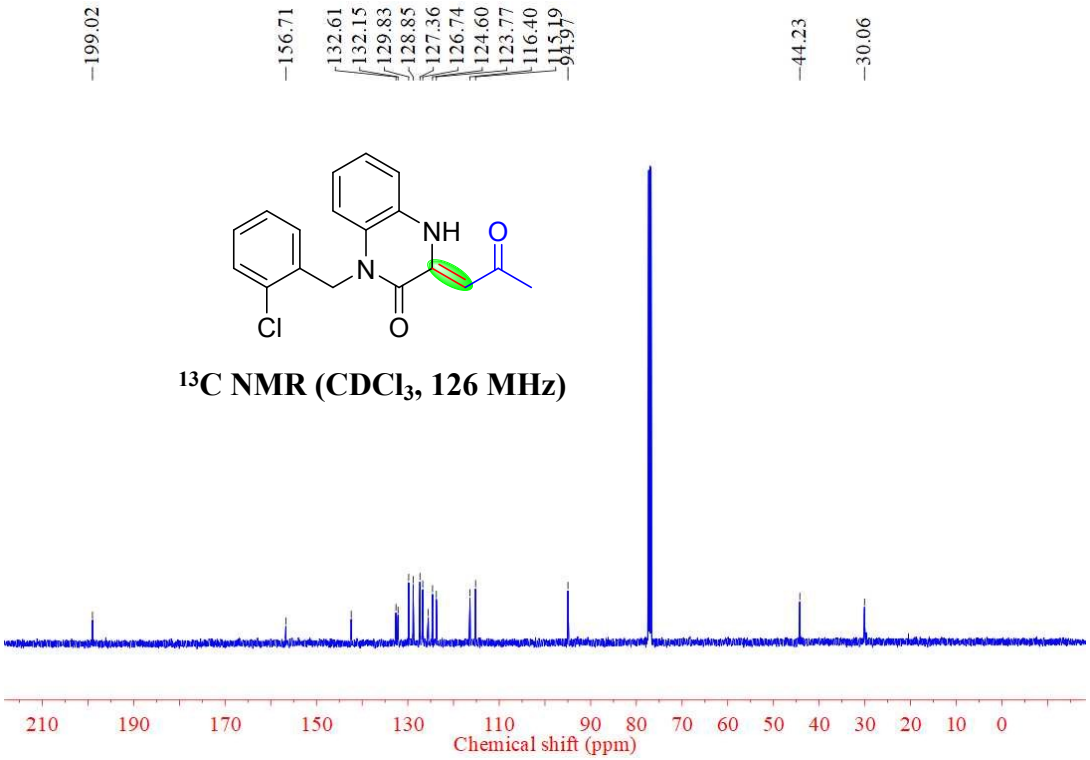
^{19}F NMR ($CDCl_3$, 471 MHz)

^{19}F{^{1}H} NMR Spectrum of Compound 24



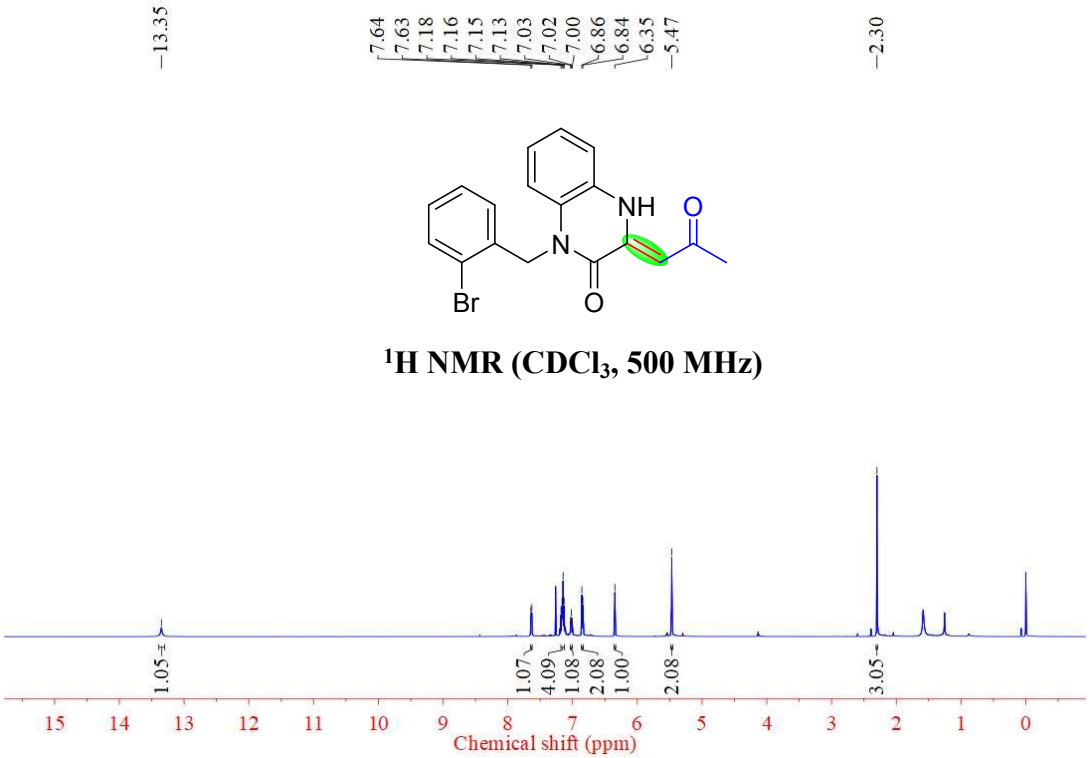
^{1}H NMR ($CDCl_3$, 500 MHz)

^{1}H NMR Spectrum of Compound 25



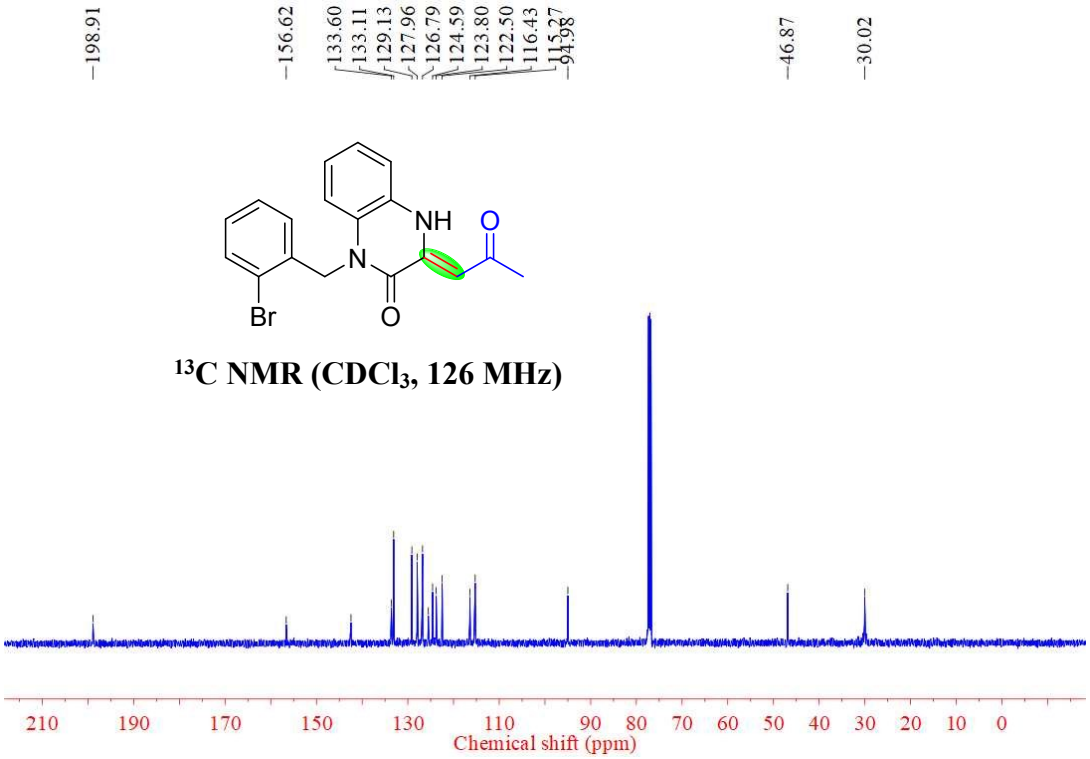
^{13}C NMR ($CDCl_3$, 126 MHz)

^{13}C{^{1}H} NMR Spectrum of Compound 25



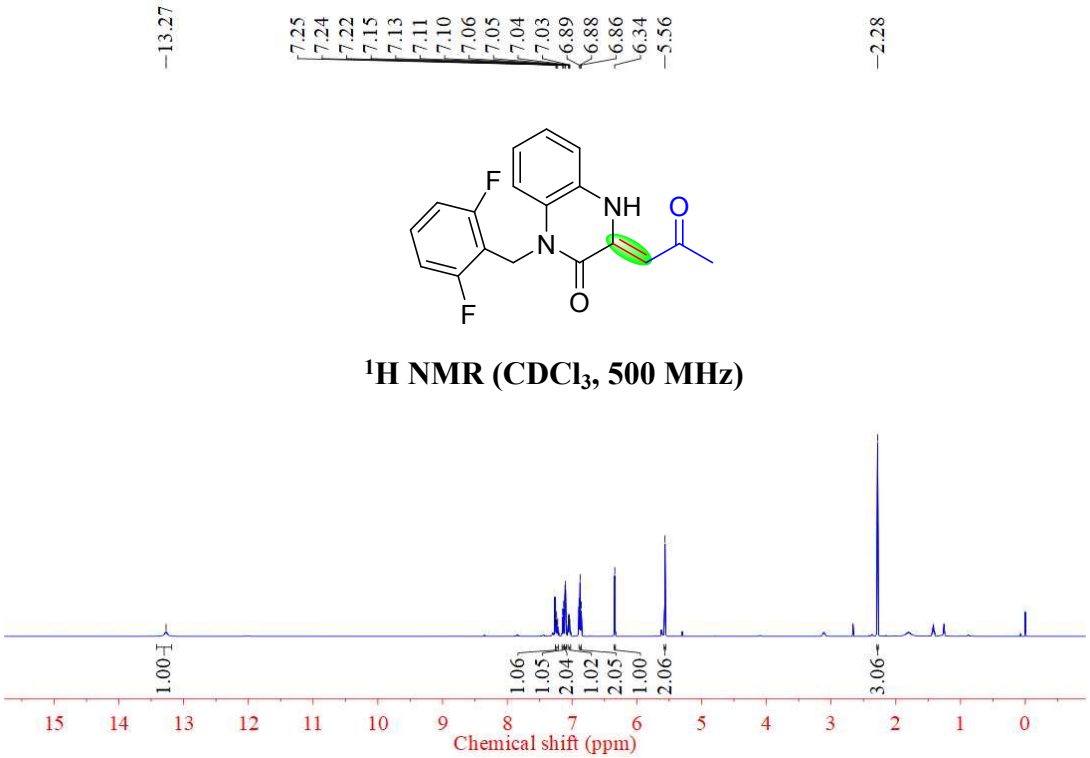
^{1}H NMR ($CDCl_3$, 500 MHz)

^{1}H NMR Spectrum of Compound 26



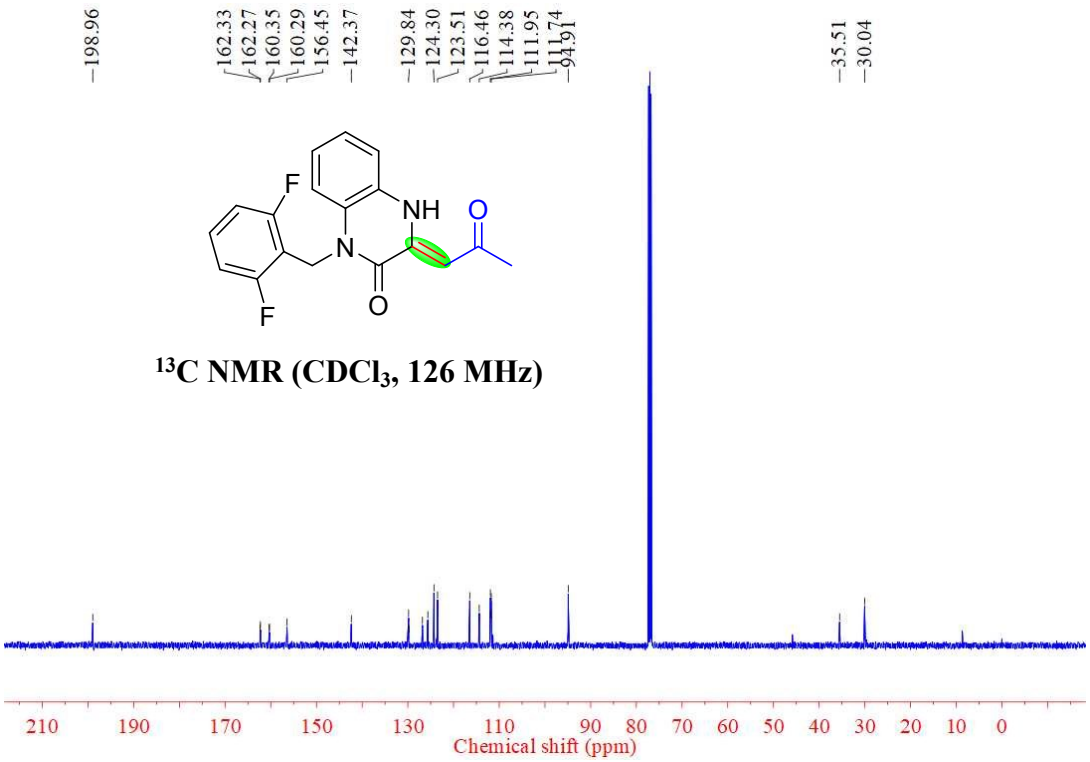
^{13}C NMR ($CDCl_3$, 126 MHz)

^{13}C{^{1}H} NMR Spectrum of Compound 26



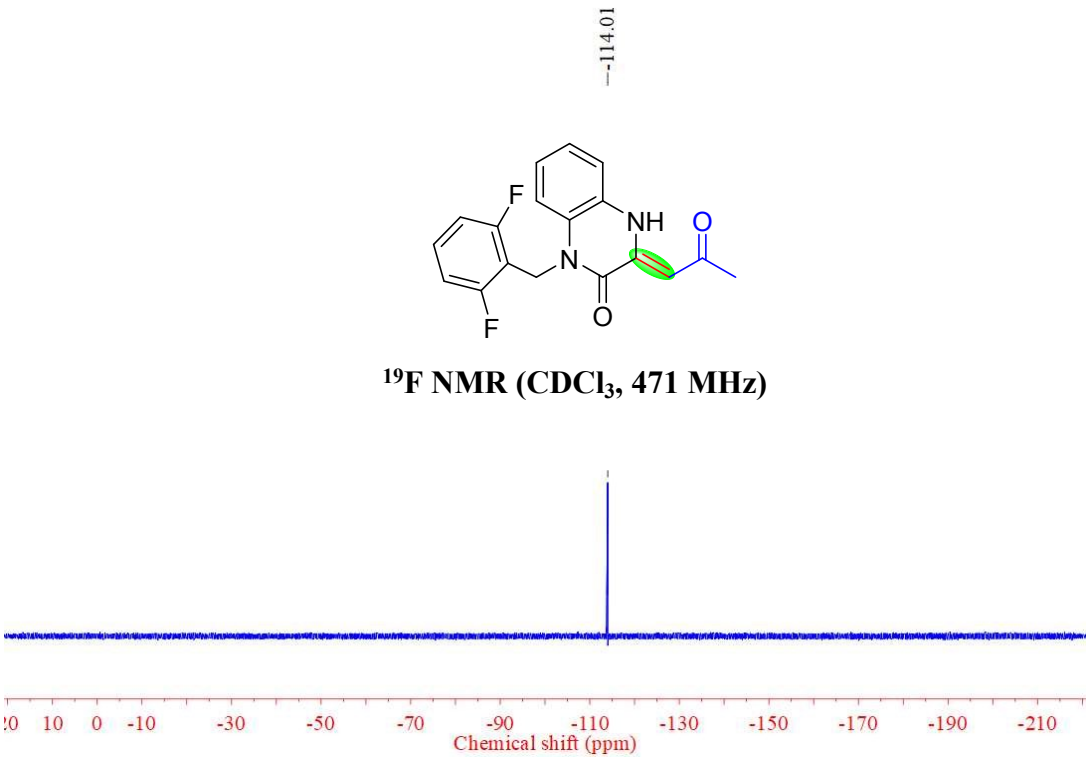
^{1}H NMR ($CDCl_3$, 500 MHz)

^{1}H NMR Spectrum of Compound 27



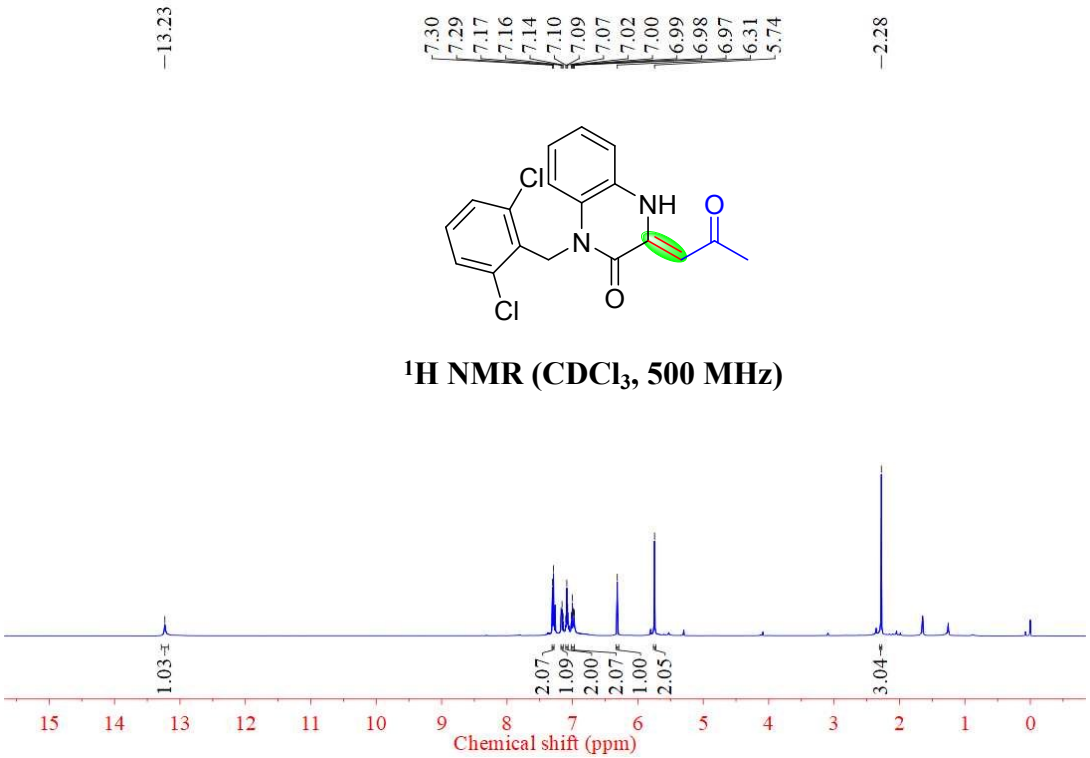
^{13}C NMR ($CDCl_3$, 126 MHz)

$^{13}C\{^1H\}$ NMR Spectrum of Compound 27



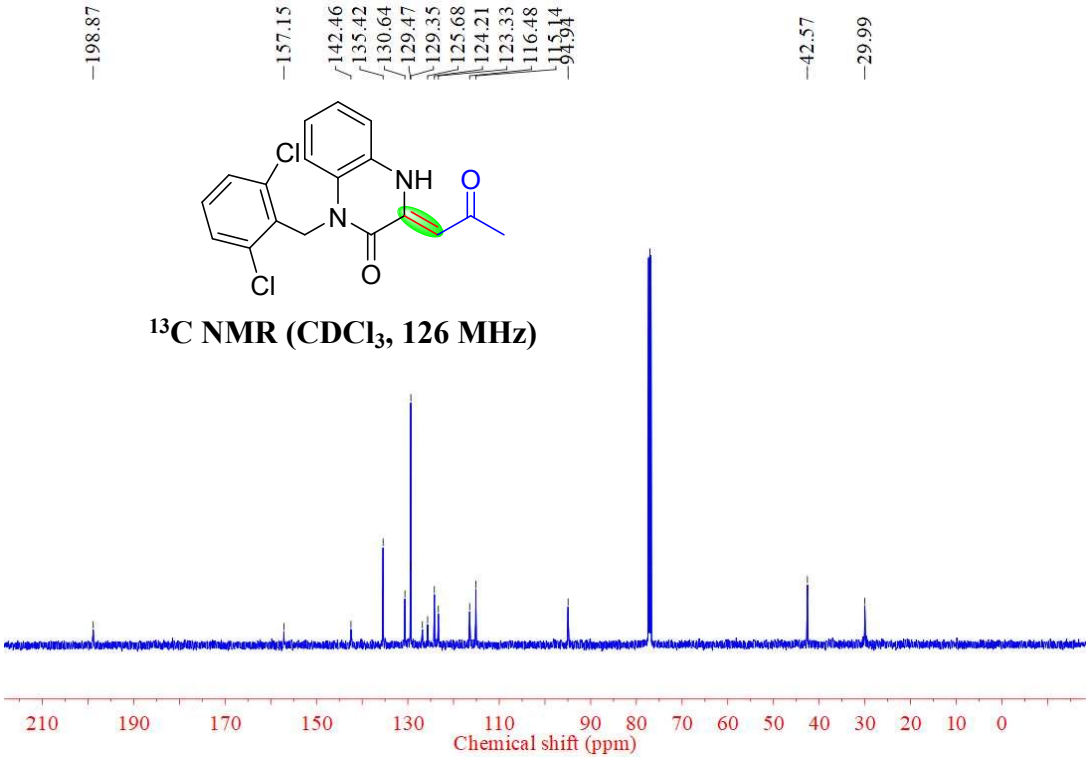
^{19}F NMR ($CDCl_3$, 471 MHz)

$^{19}F\{^1H\}$ NMR Spectrum of Compound 27



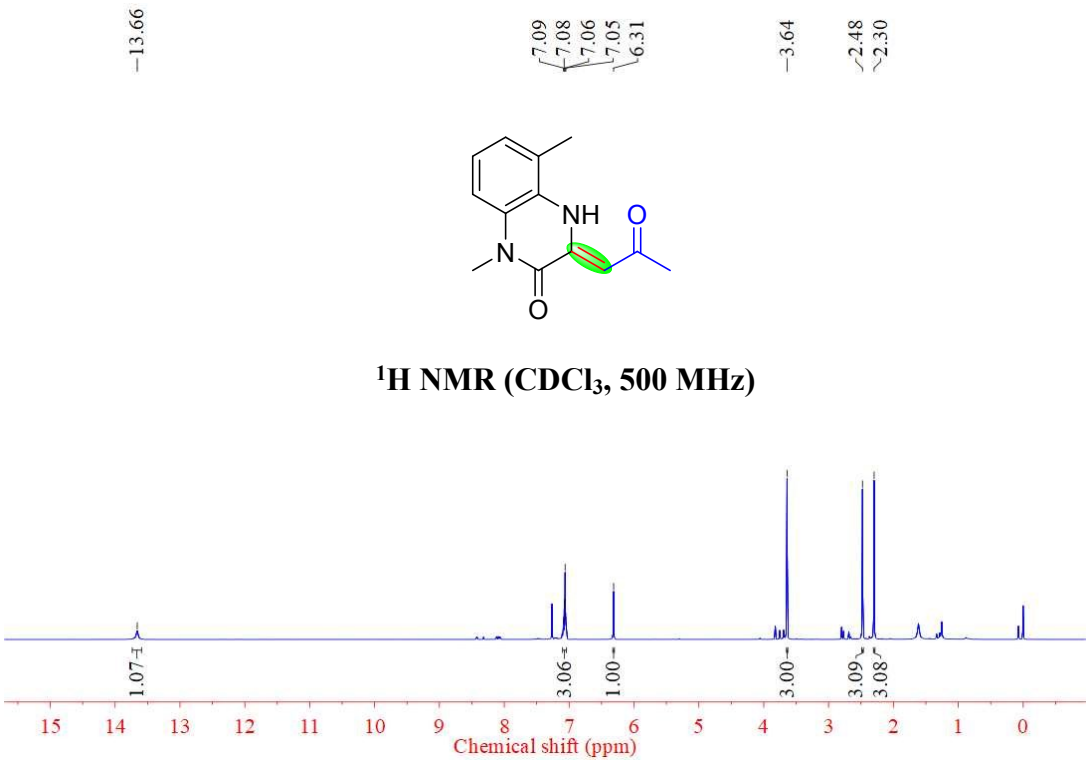
^{1}H NMR ($CDCl_3$, 500 MHz)

^{1}H NMR Spectrum of Compound 28



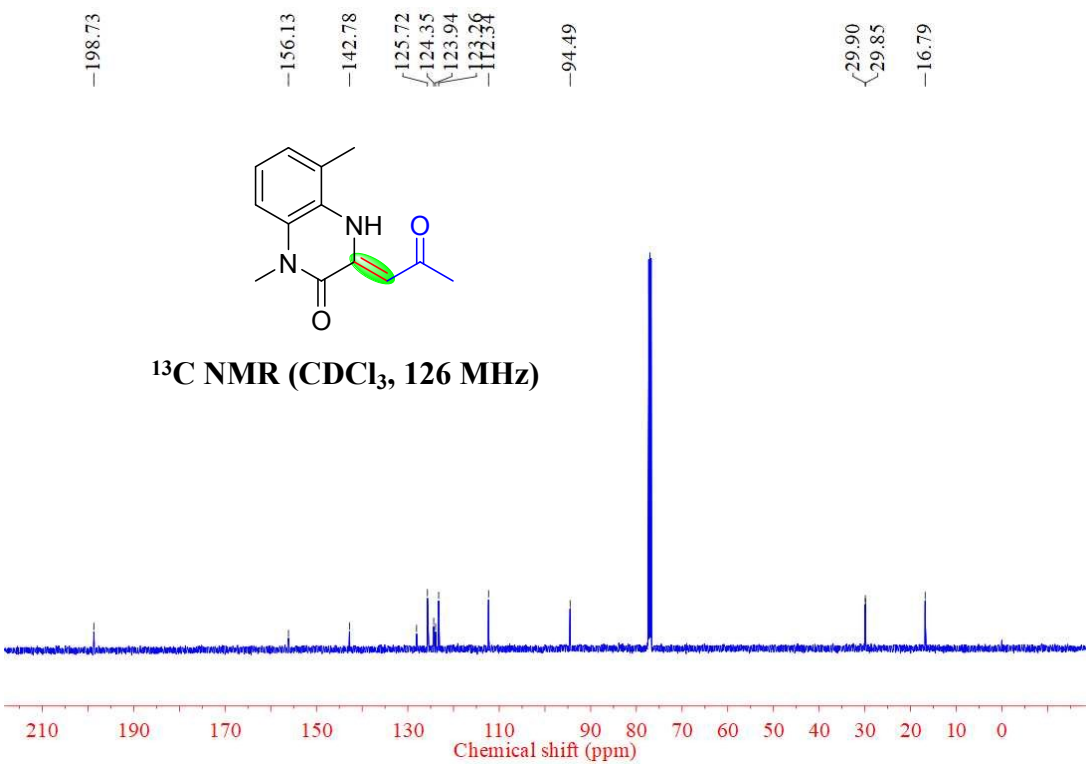
^{13}C NMR ($CDCl_3$, 126 MHz)

^{13}C{^{1}H} NMR Spectrum of Compound 28



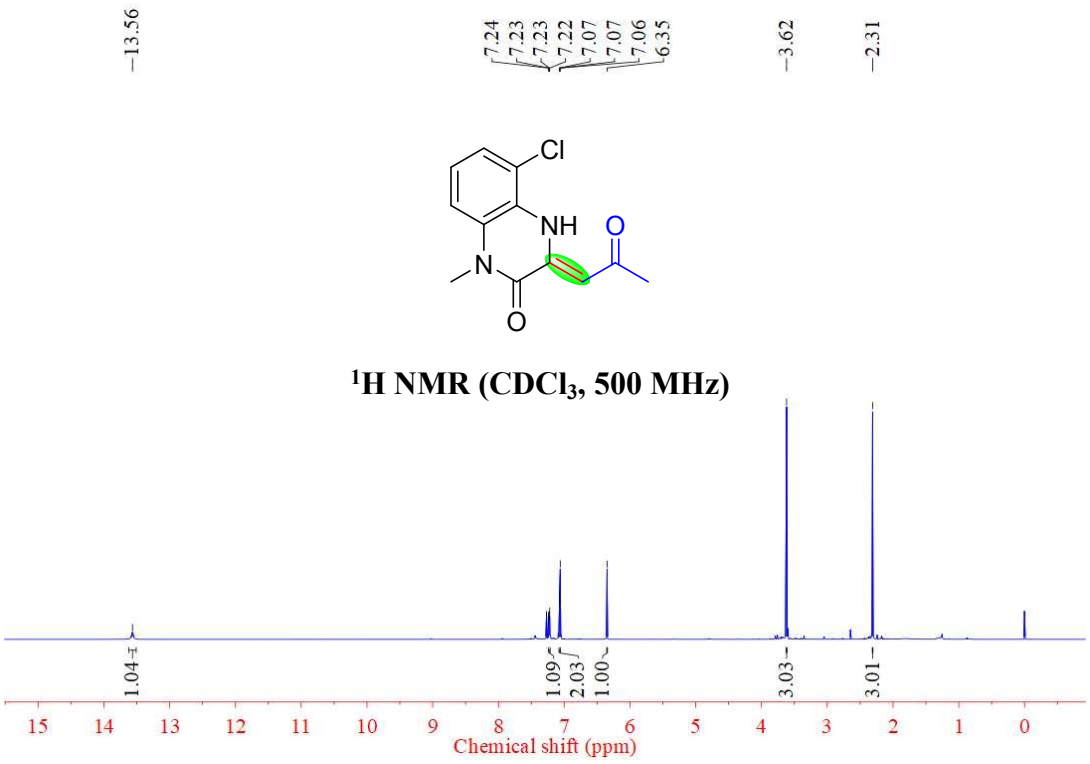
^{1}H NMR (CDCl$_3$, 500 MHz)

^{1}H NMR Spectrum of Compound 29



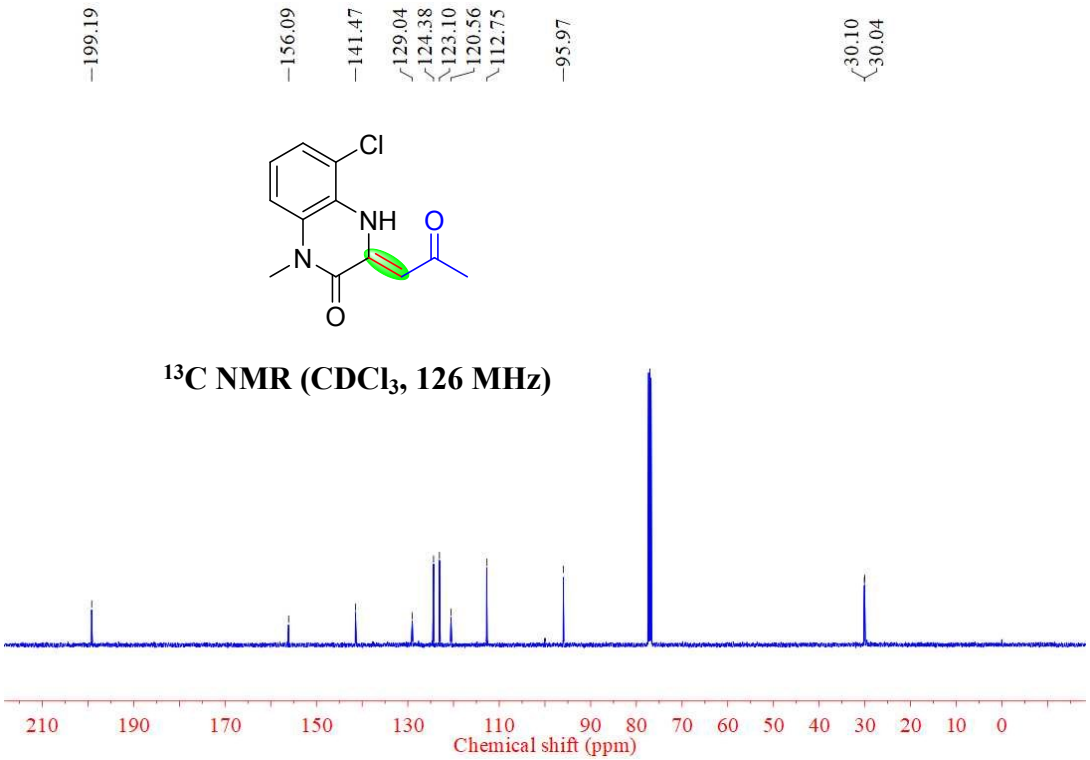
^{13}C NMR (CDCl$_3$, 126 MHz)

^{13}C{^{1}H} NMR Spectrum of Compound 29



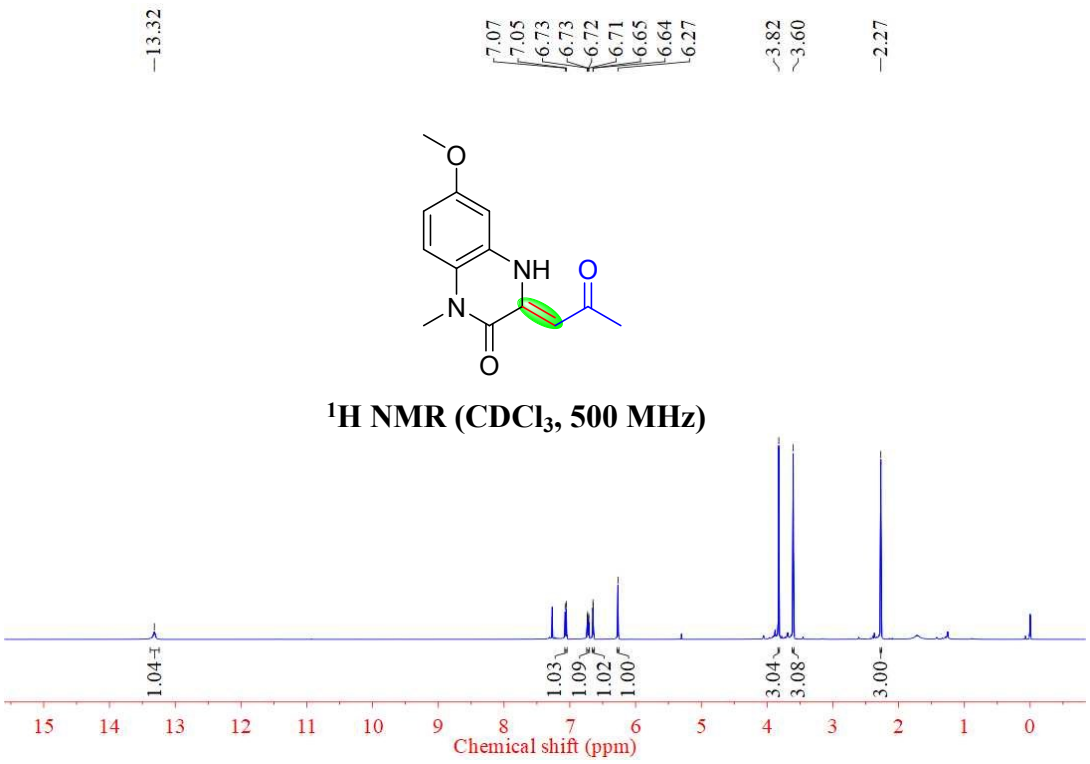
^{1}H NMR ($CDCl_3$, 500 MHz)

^{1}H NMR Spectrum of Compound 30



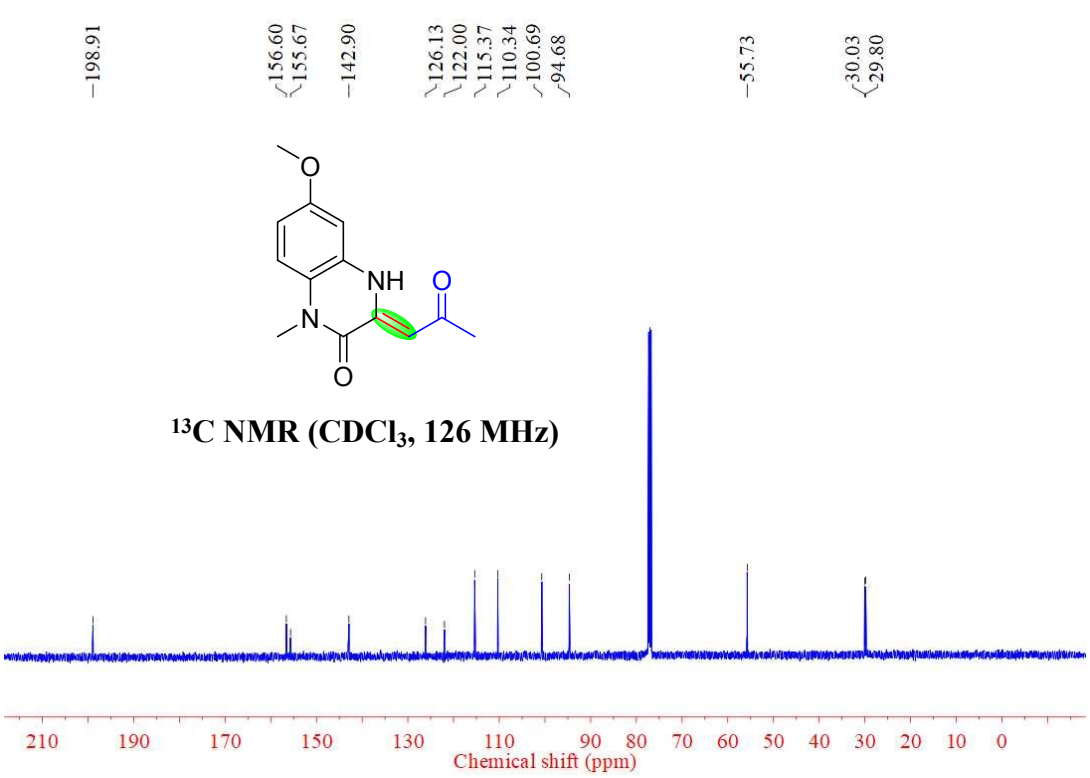
^{13}C NMR ($CDCl_3$, 126 MHz)

^{13}C{^{1}H} NMR Spectrum of Compound 30



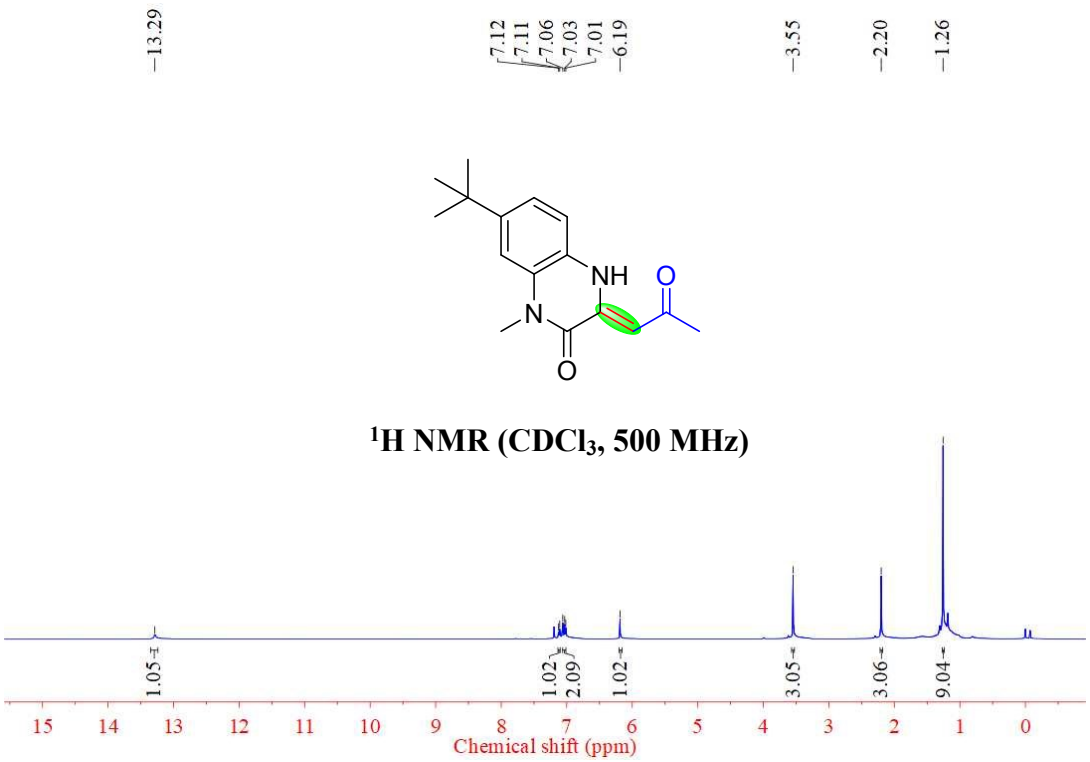
^{1}H NMR ($CDCl_3$, 500 MHz)

^{1}H NMR Spectrum of Compound 31



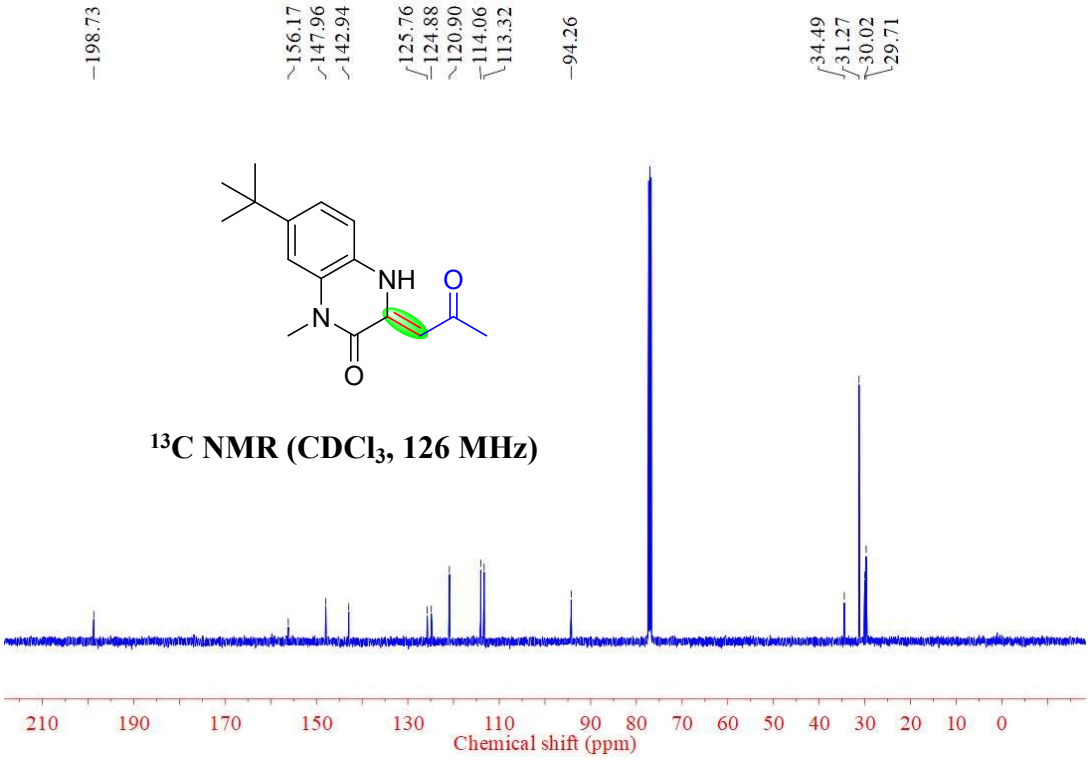
^{13}C NMR ($CDCl_3$, 126 MHz)

^{13}C{^{1}H} NMR Spectrum of Compound 31



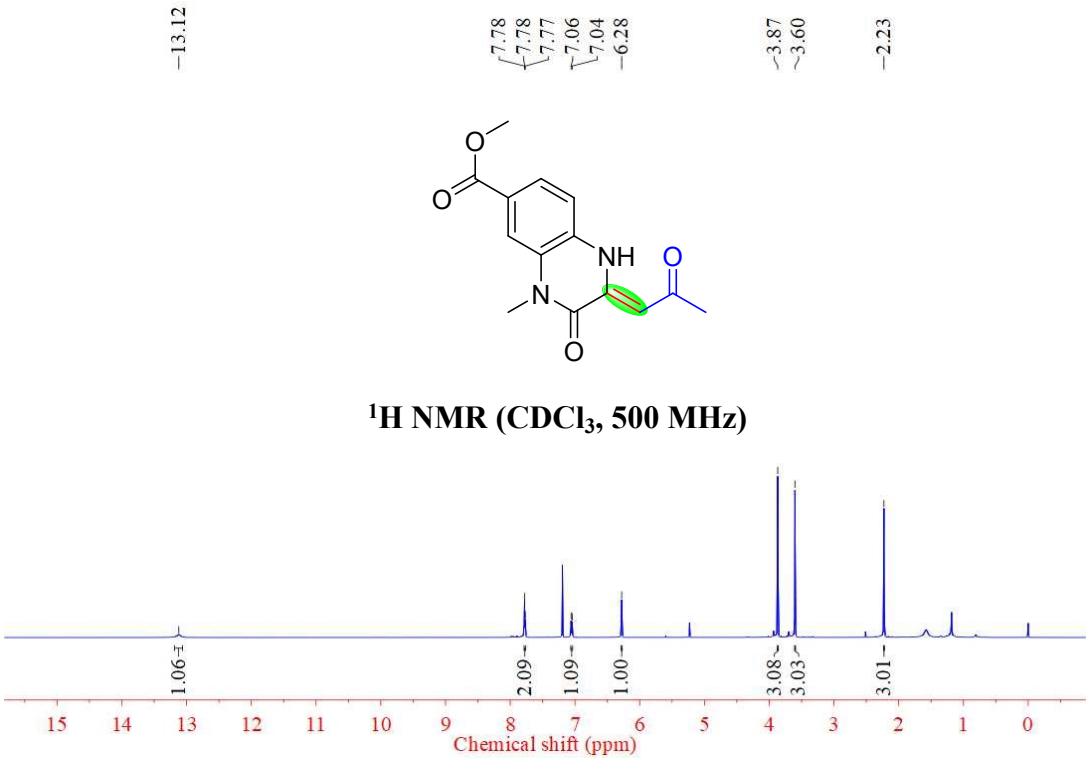
^{1}H NMR ($CDCl_3$, 500 MHz)

^{1}H NMR Spectrum of Compound 32



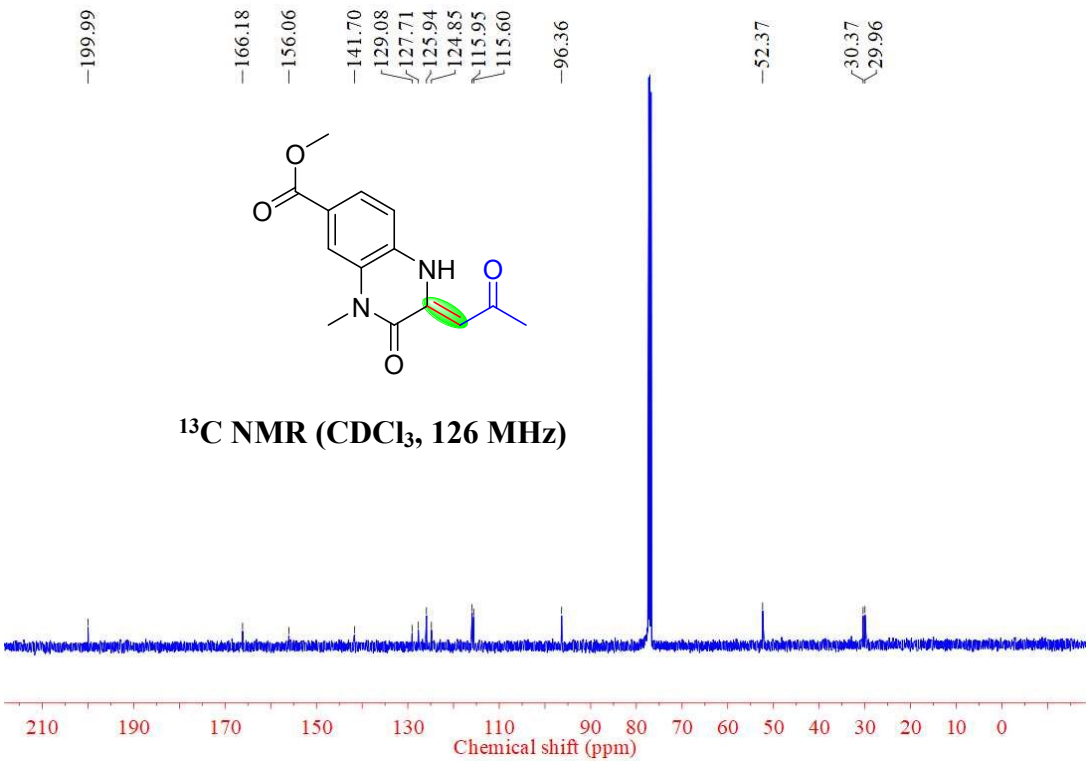
^{13}C NMR ($CDCl_3$, 126 MHz)

^{13}C{^{1}H} NMR Spectrum of Compound 32



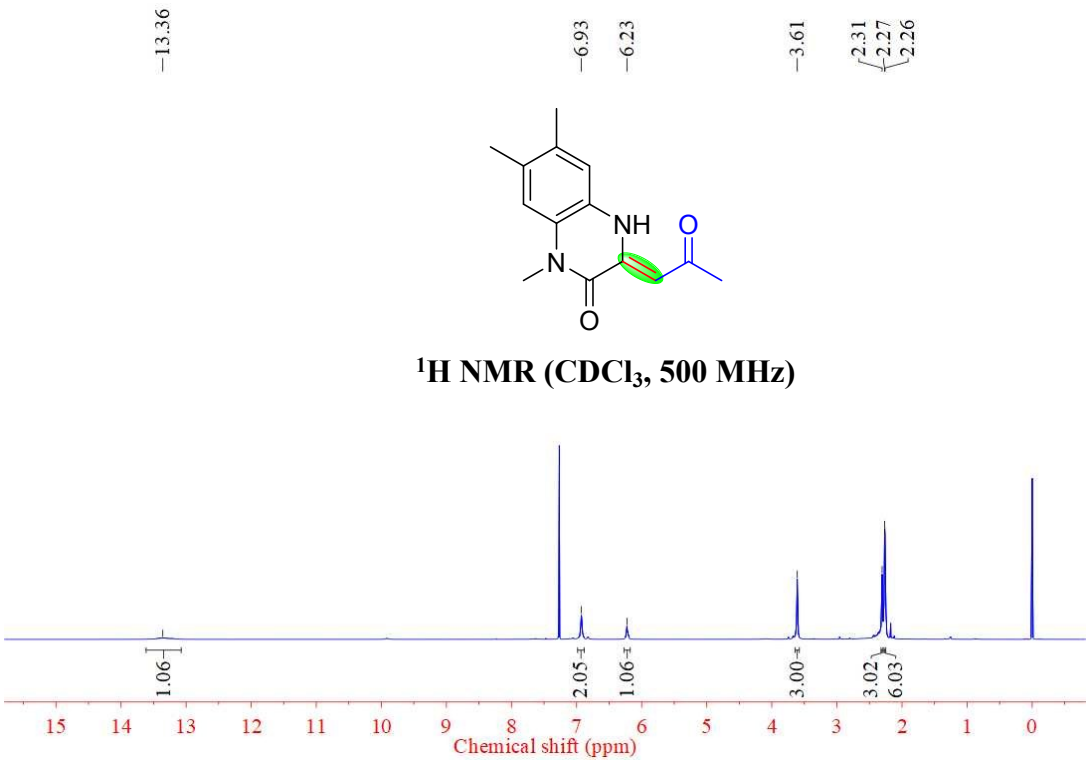
^{1}H NMR ($CDCl_3$, 500 MHz)

^{1}H NMR Spectrum of Compound 33



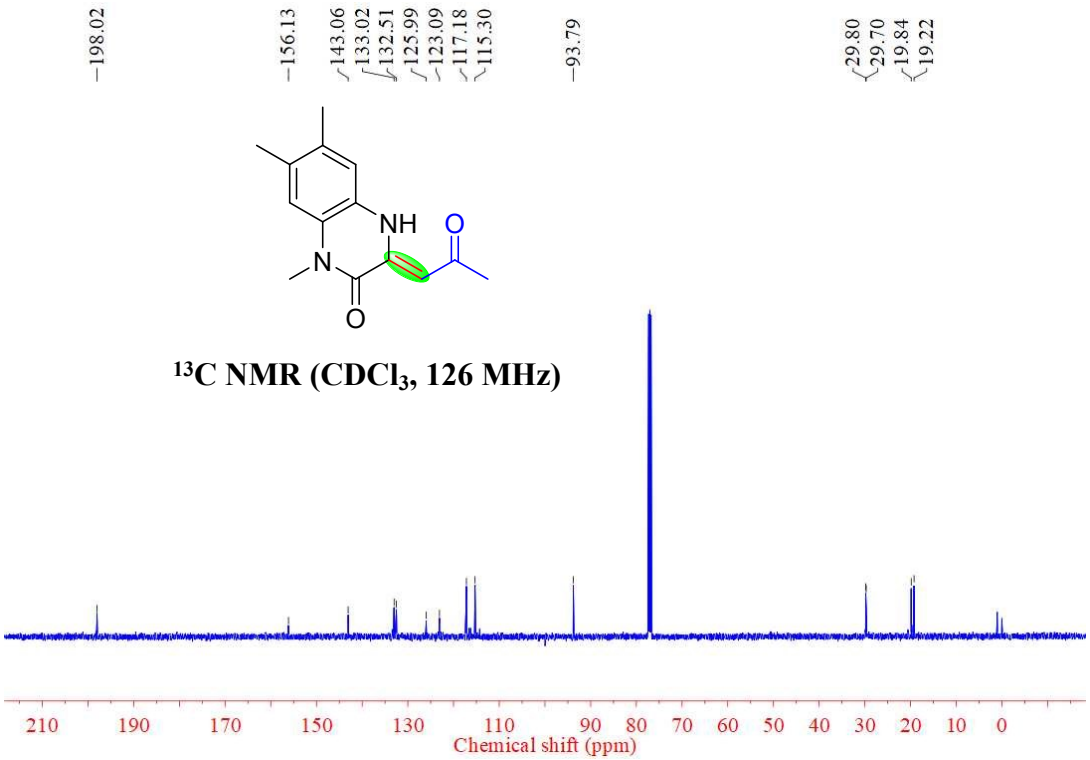
^{13}C NMR ($CDCl_3$, 126 MHz)

^{13}C{^{1}H} NMR Spectrum of Compound 33



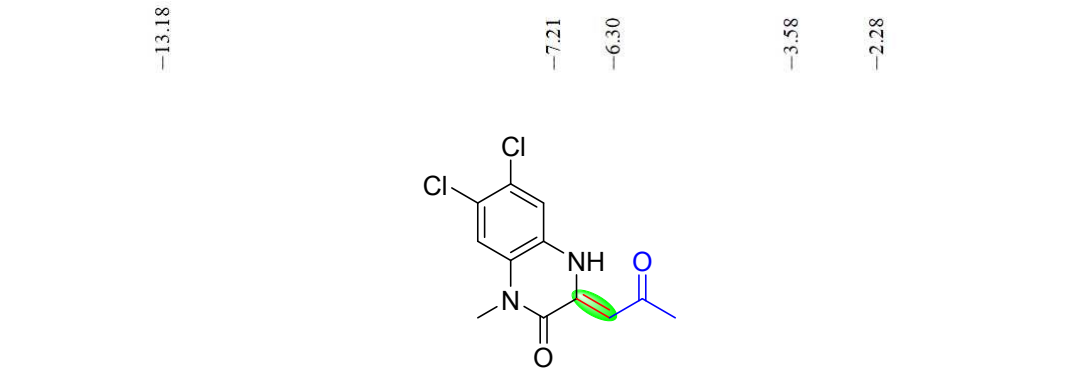
^{1}H NMR ($CDCl_3$, 500 MHz)

^{1}H NMR Spectrum of Compound 34



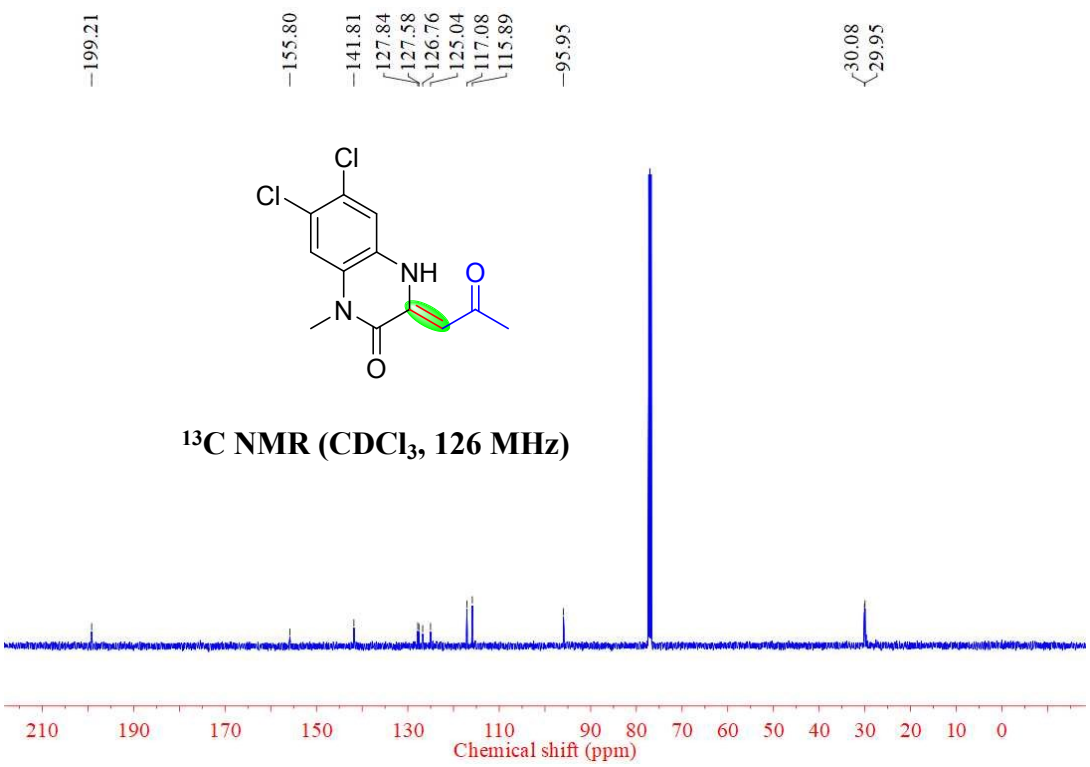
^{13}C NMR ($CDCl_3$, 126 MHz)

^{13}C{^{1}H} NMR Spectrum of Compound 34



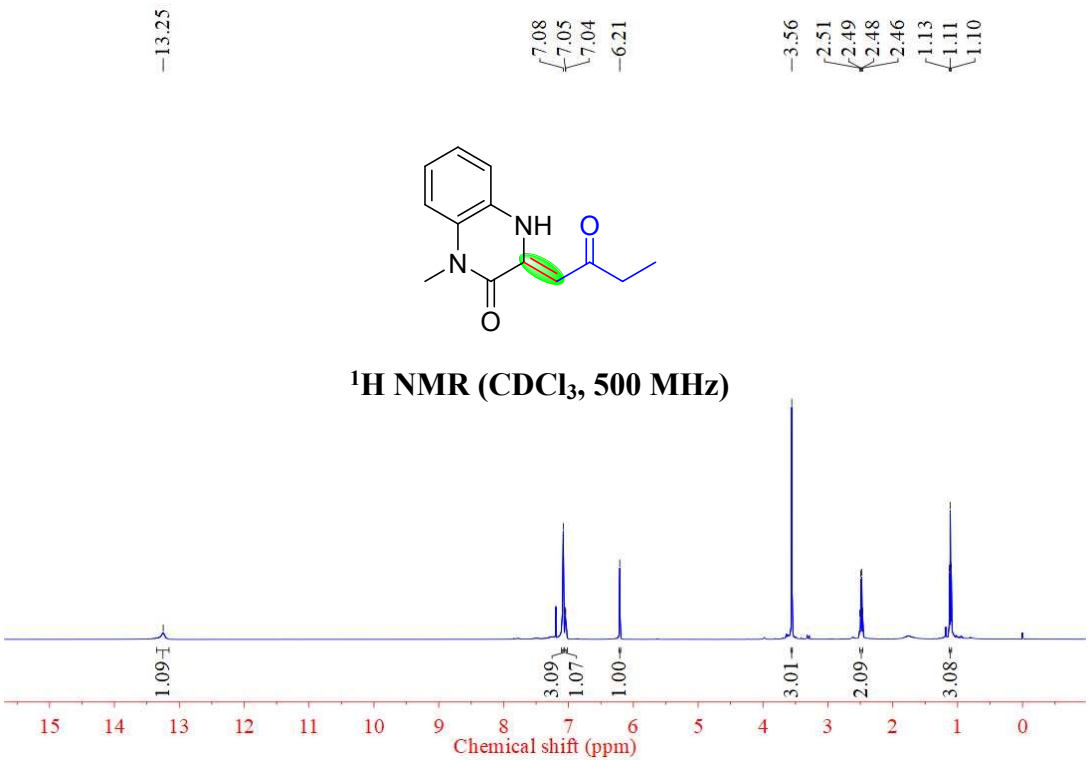
^{1}H NMR ($CDCl_3$, 500 MHz)

^{1}H NMR Spectrum of Compound 35



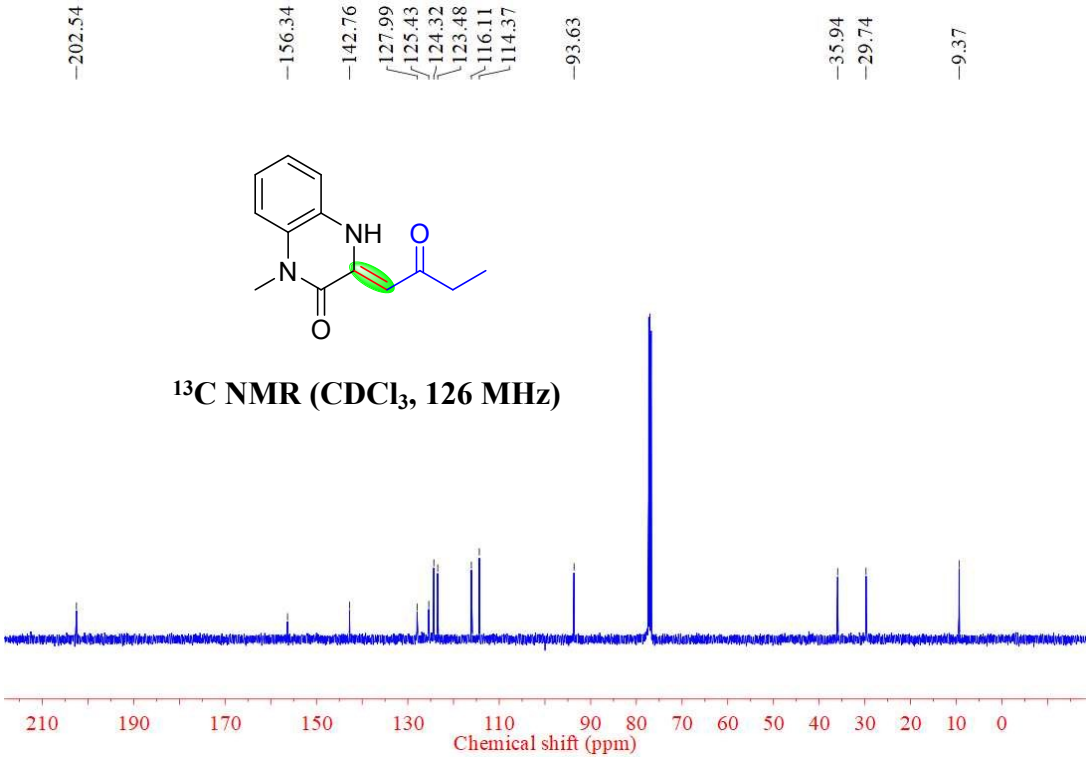
^{13}C NMR ($CDCl_3$, 126 MHz)

^{13}C{^{1}H} NMR Spectrum of Compound 35



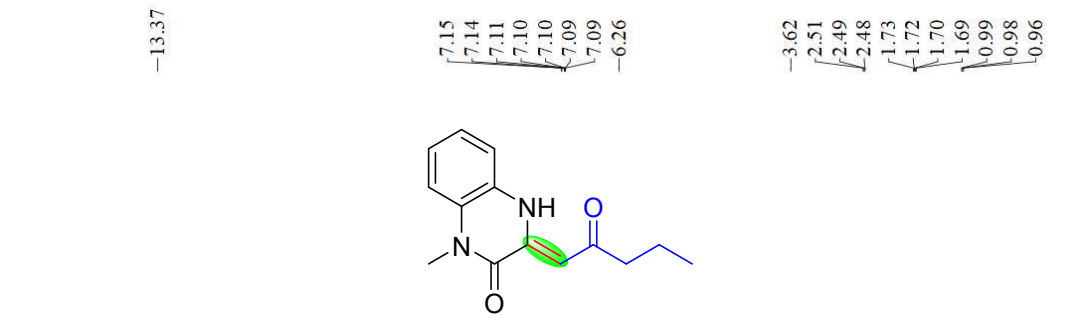
^{1}H NMR ($CDCl_3$, 500 MHz)

^{1}H NMR Spectrum of Compound 36

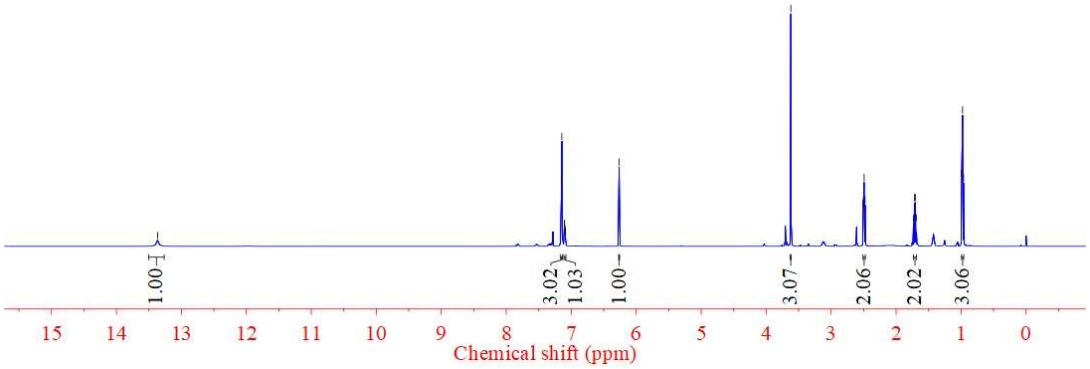


^{13}C NMR ($CDCl_3$, 126 MHz)

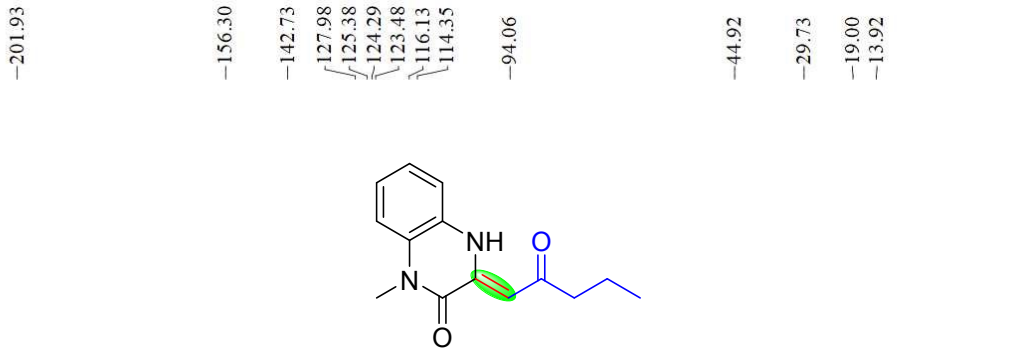
^{13}C{^{1}H} NMR Spectrum of Compound 36



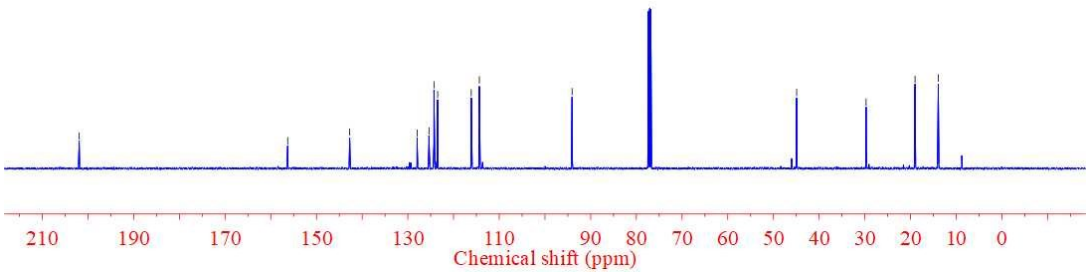
^{1}H NMR ($CDCl_3$, 500 MHz)



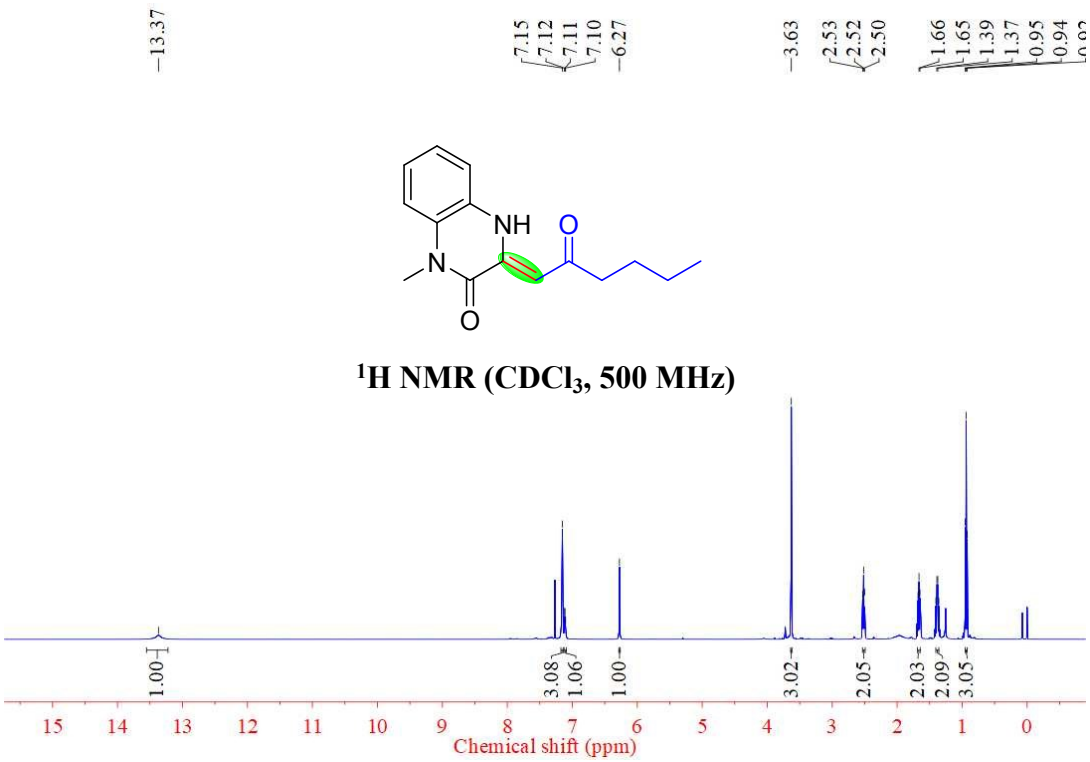
^{1}H NMR Spectrum of Compound 37



^{13}C NMR ($CDCl_3$, 126 MHz)

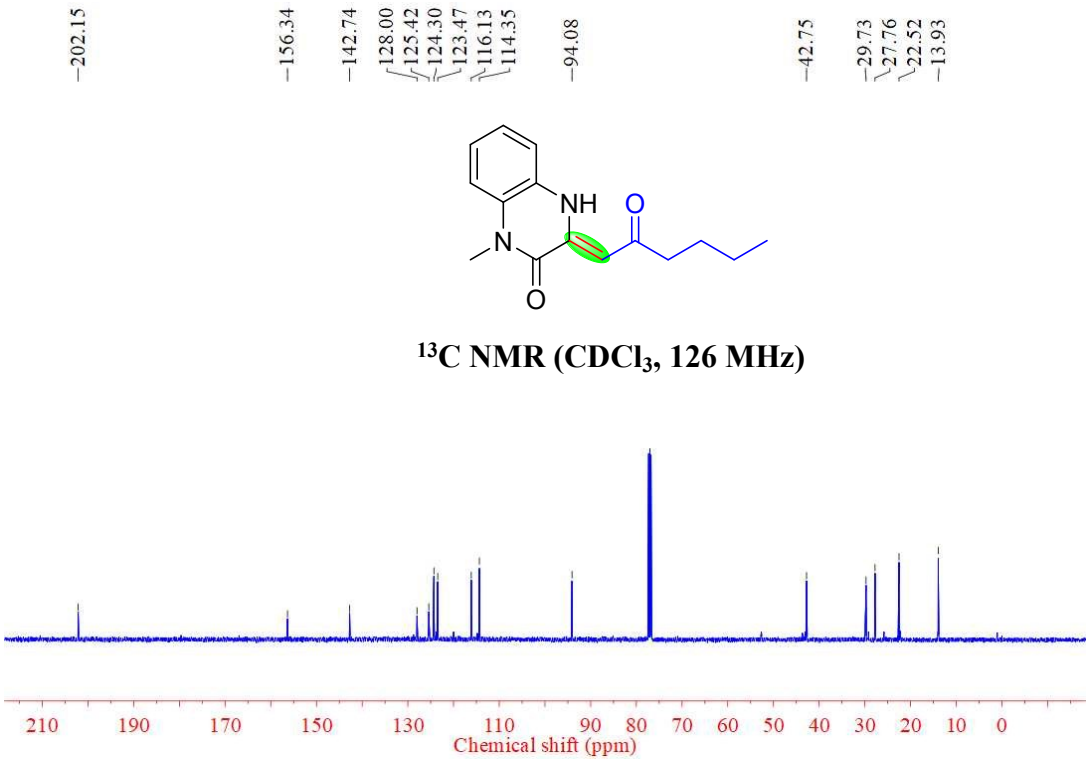


^{13}C{^{1}H} NMR Spectrum of Compound 37



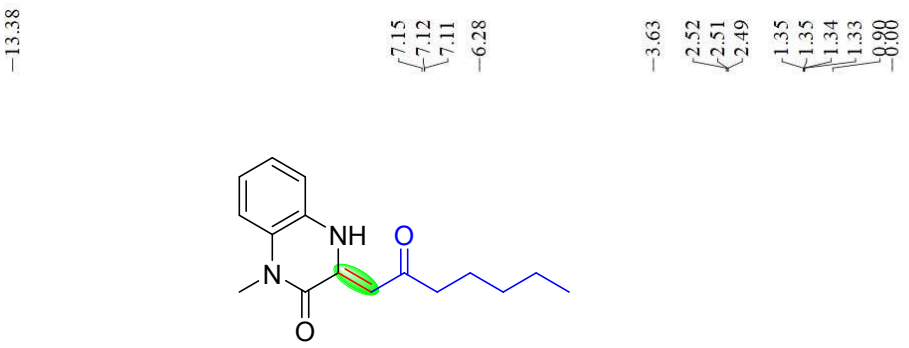
^{1}H NMR ($CDCl_3$, 500 MHz)

^{1}H NMR Spectrum of Compound 38

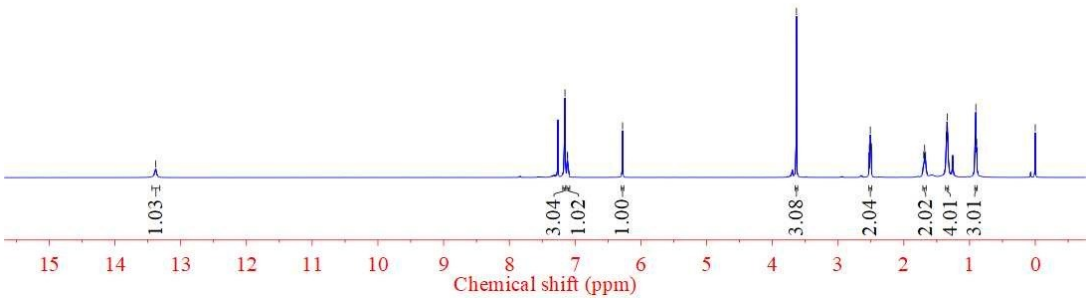


^{13}C NMR ($CDCl_3$, 126 MHz)

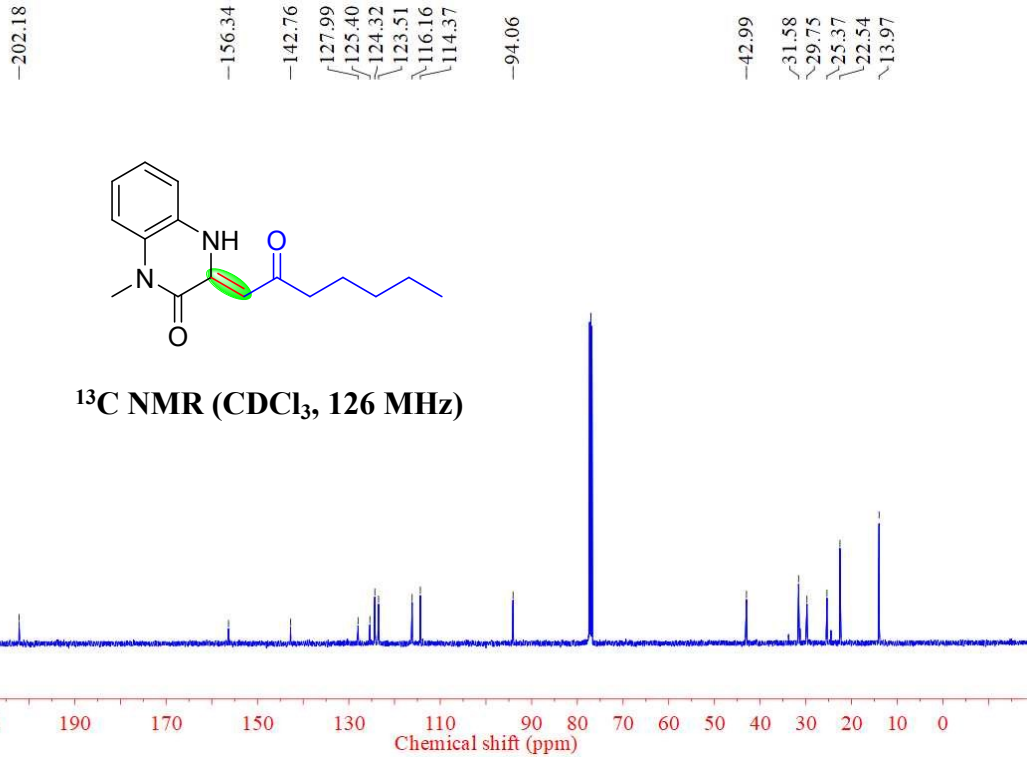
^{13}C{^{1}H} NMR Spectrum of Compound 38



^{1}H NMR ($CDCl_3$, 500 MHz)

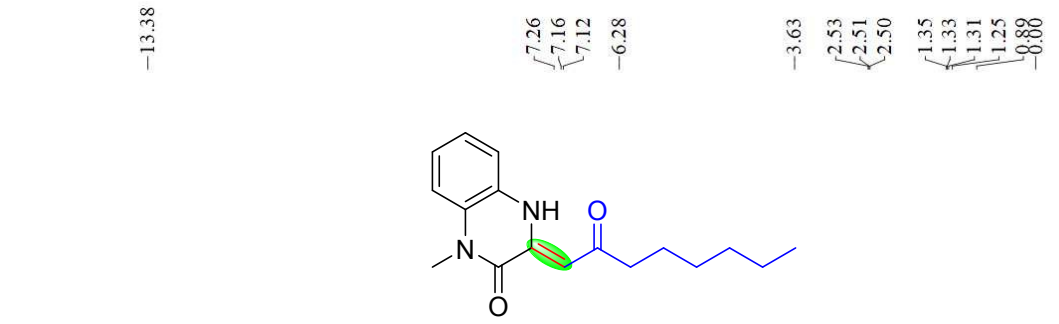


^{1}H NMR Spectrum of Compound 39

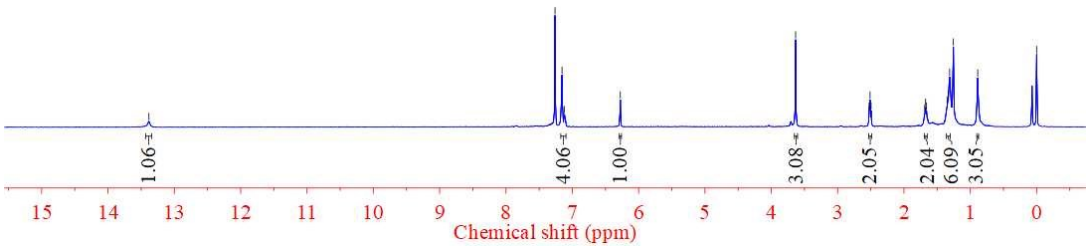


^{13}C NMR ($CDCl_3$, 126 MHz)

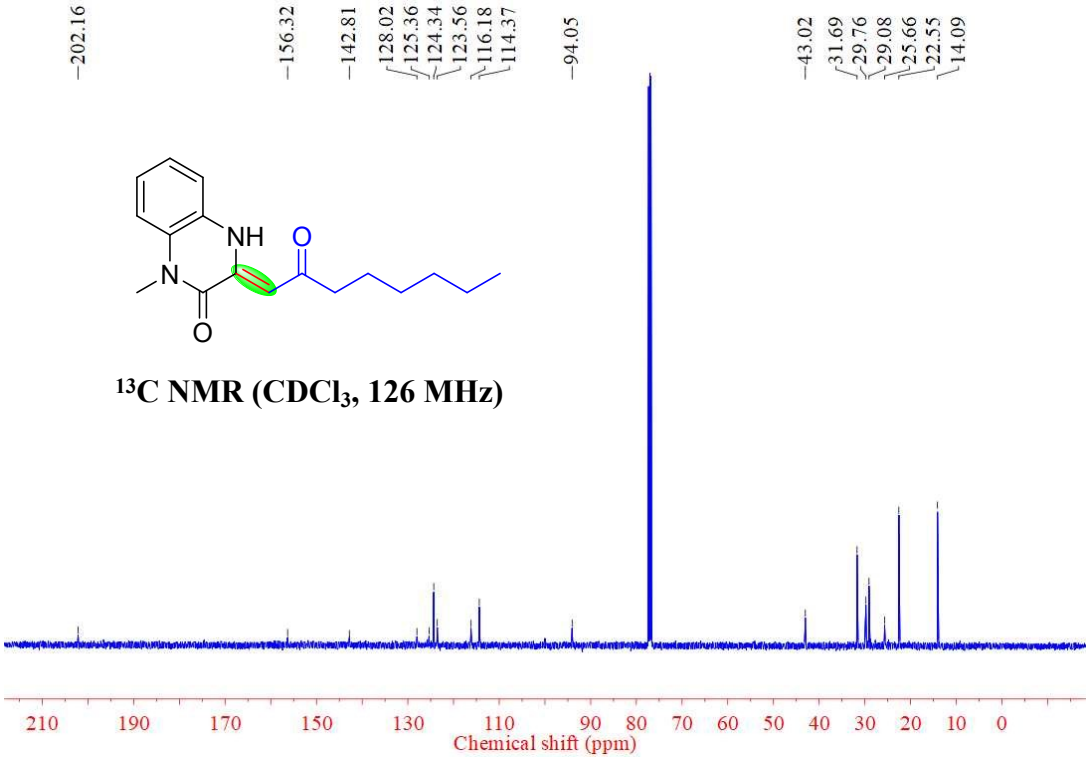
^{13}C{^{1}H} NMR Spectrum of Compound 39



^{1}H NMR ($CDCl_3$, 500 MHz)

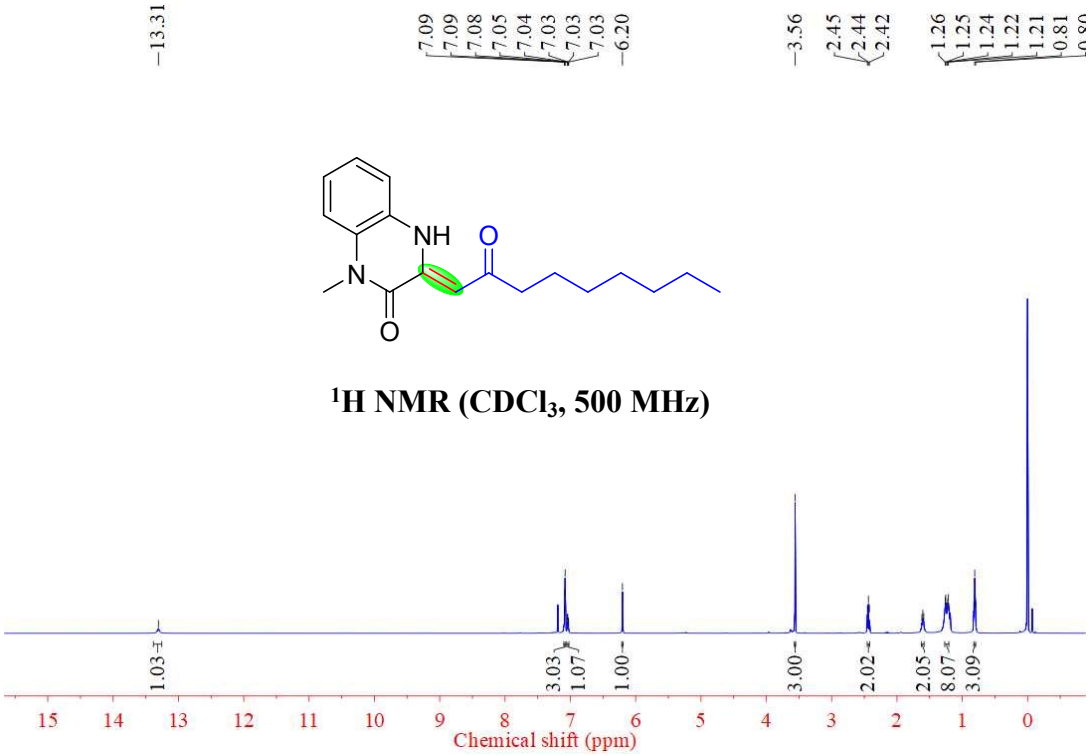


^{1}H NMR Spectrum of Compound 40



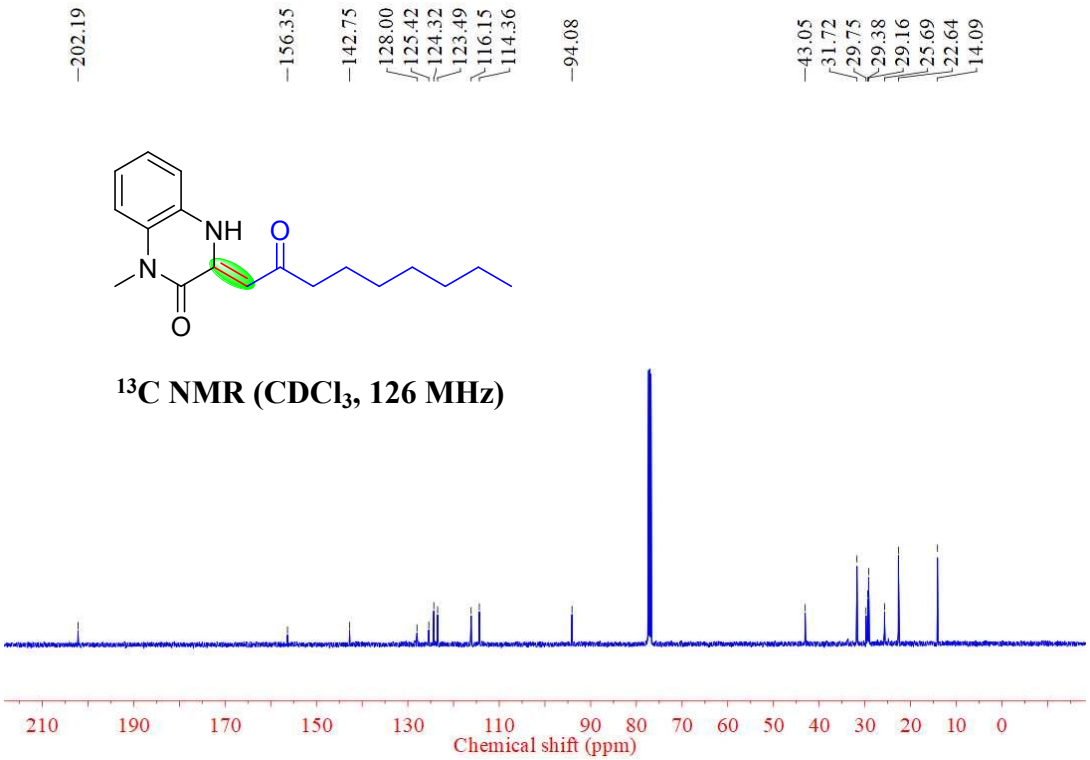
^{13}C NMR ($CDCl_3$, 126 MHz)

^{13}C{^{1}H} NMR Spectrum of Compound 40



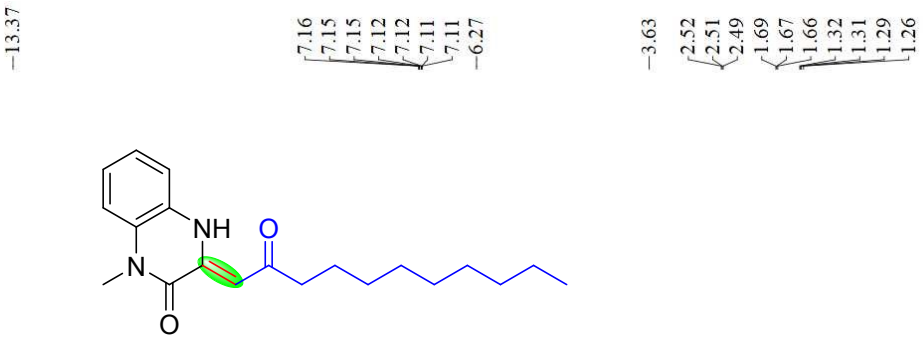
^{1}H NMR ($CDCl_3$, 500 MHz)

^{1}H NMR Spectrum of Compound 41

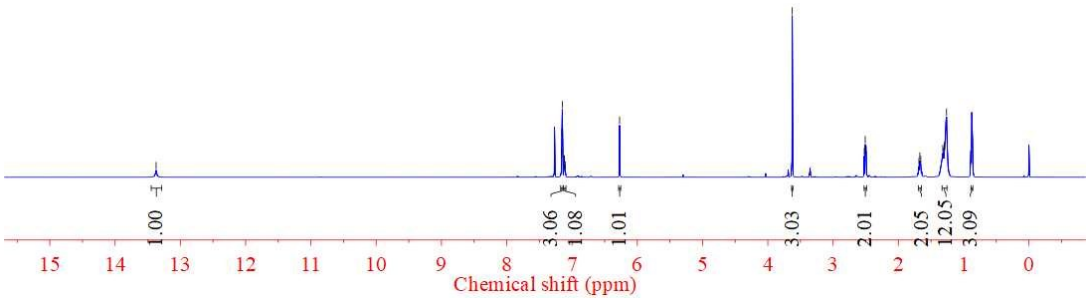


^{13}C NMR ($CDCl_3$, 126 MHz)

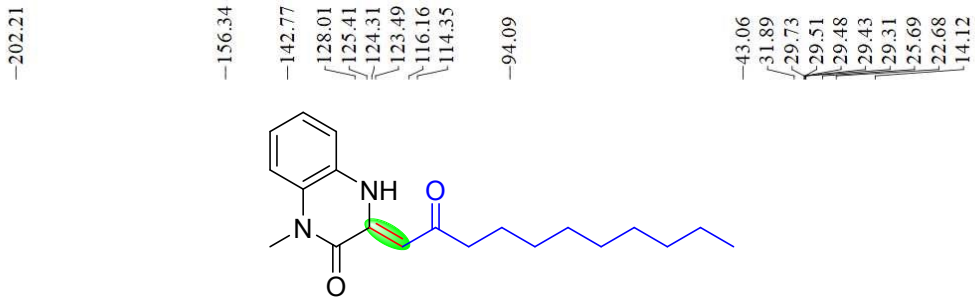
^{13}C{^{1}H} NMR Spectrum of Compound 41



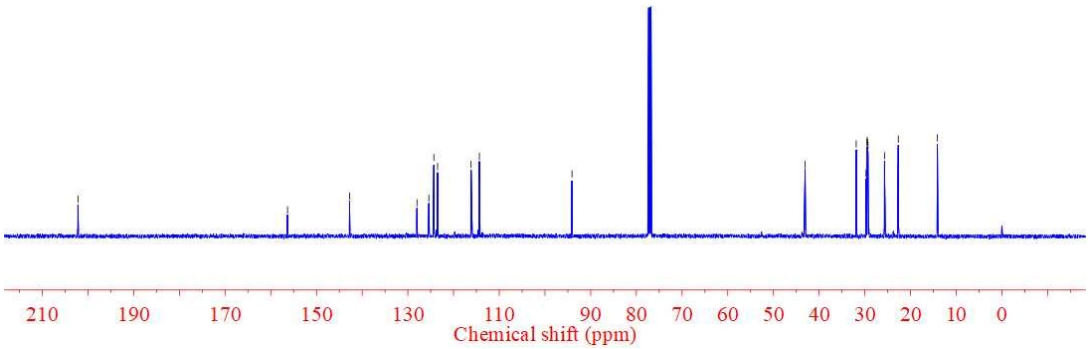
^{1}H NMR ($CDCl_3$, 500 MHz)



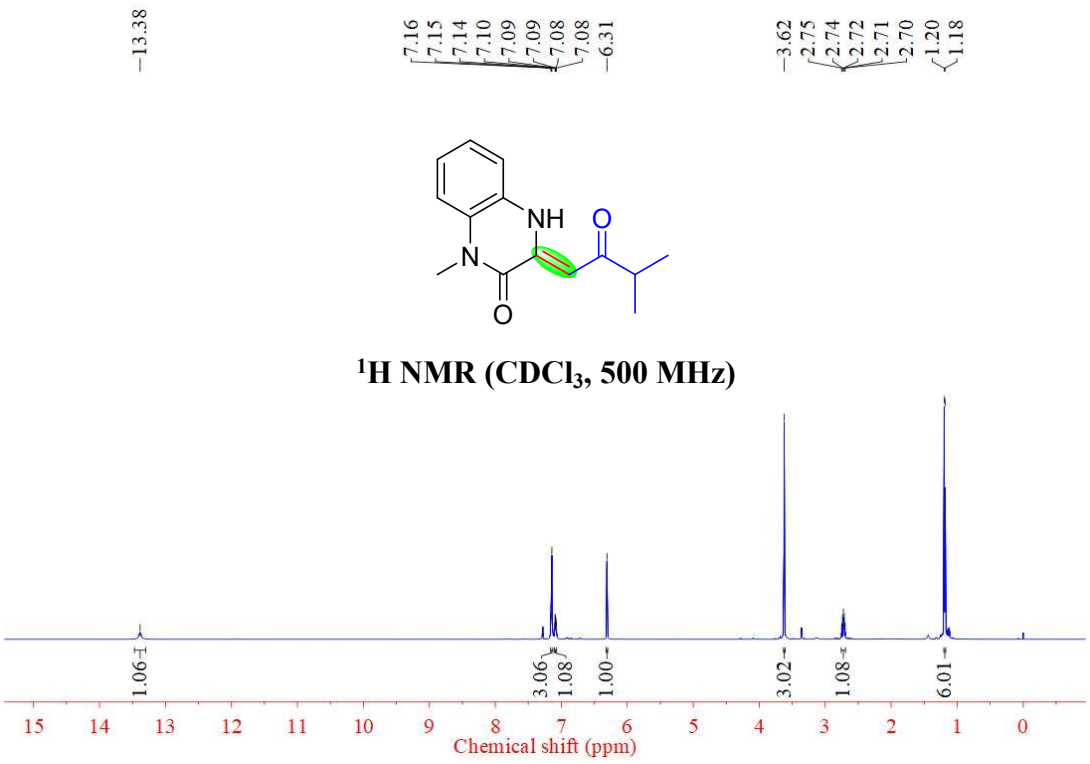
^{1}H NMR Spectrum of Compound 42



^{13}C NMR ($CDCl_3$, 126 MHz)

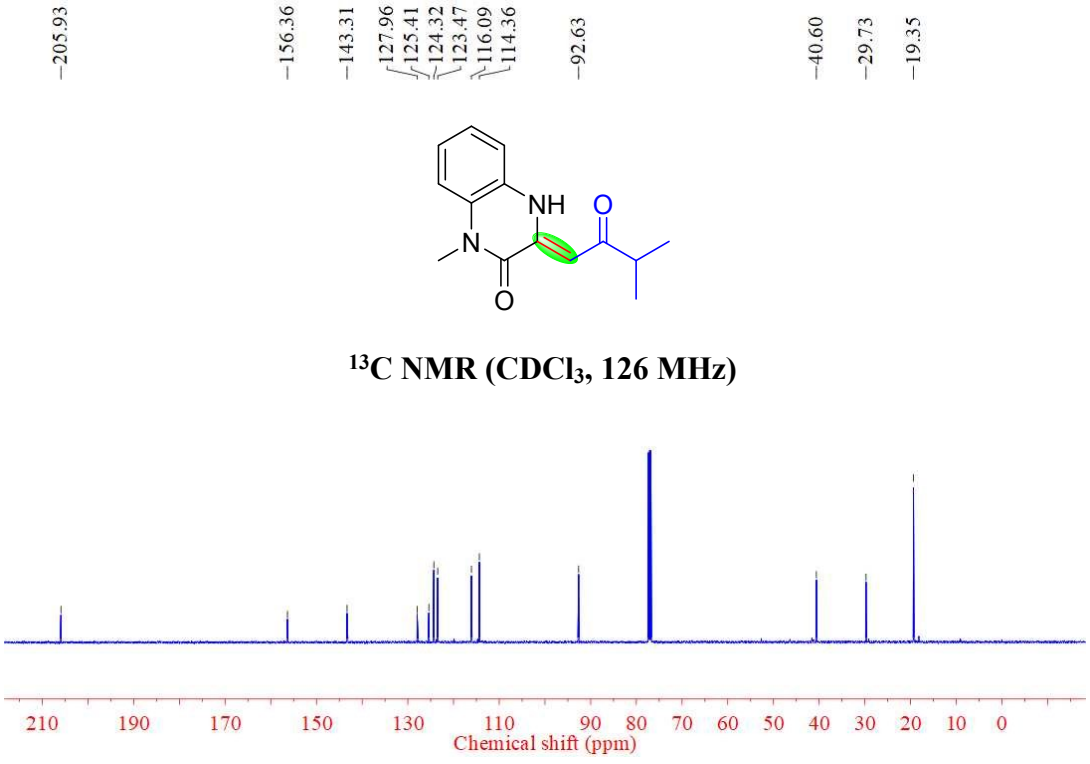


^{13}C{^{1}H} NMR Spectrum of Compound 42



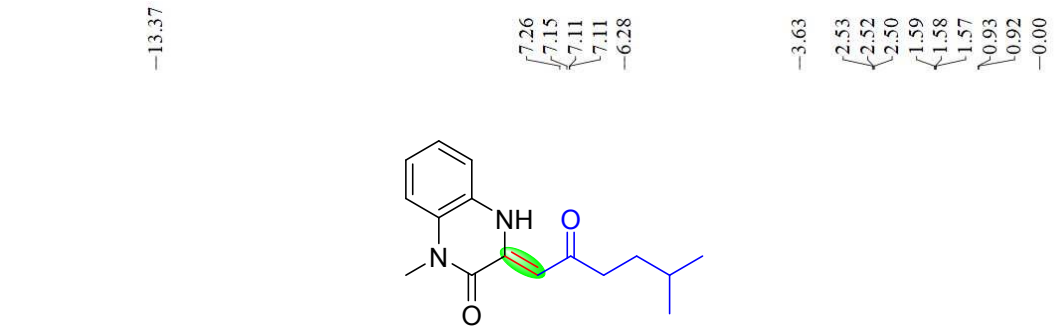
^{1}H NMR ($CDCl_3$, 500 MHz)

^{1}H NMR Spectrum of Compound 43

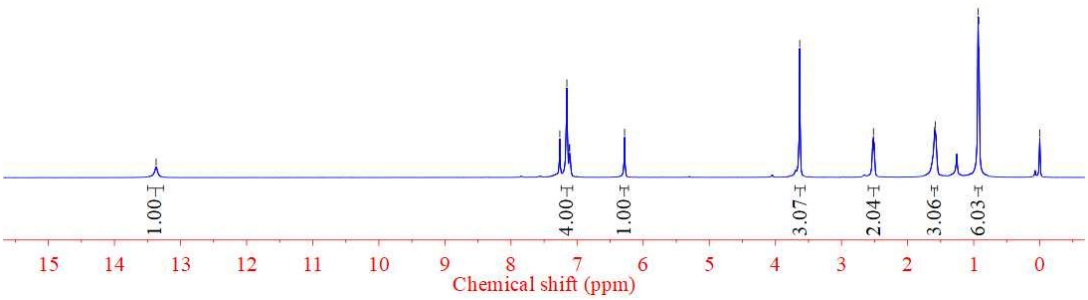


^{13}C NMR ($CDCl_3$, 126 MHz)

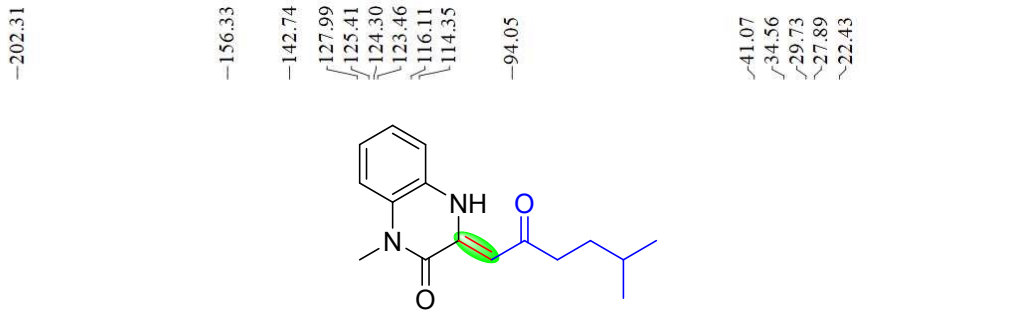
^{13}C{^{1}H} NMR Spectrum of Compound 43



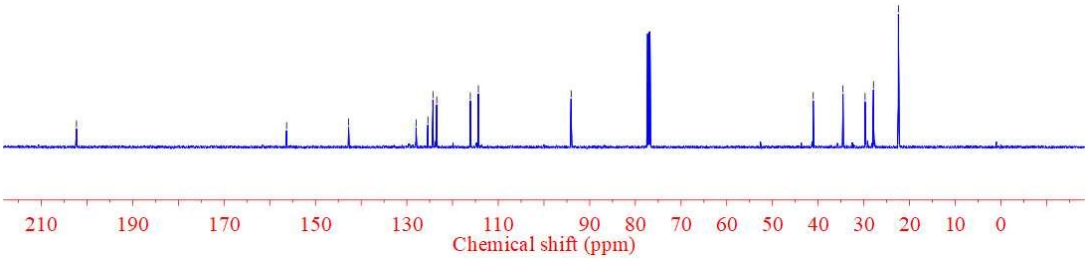
^{1}H NMR ($CDCl_3$, 500 MHz)



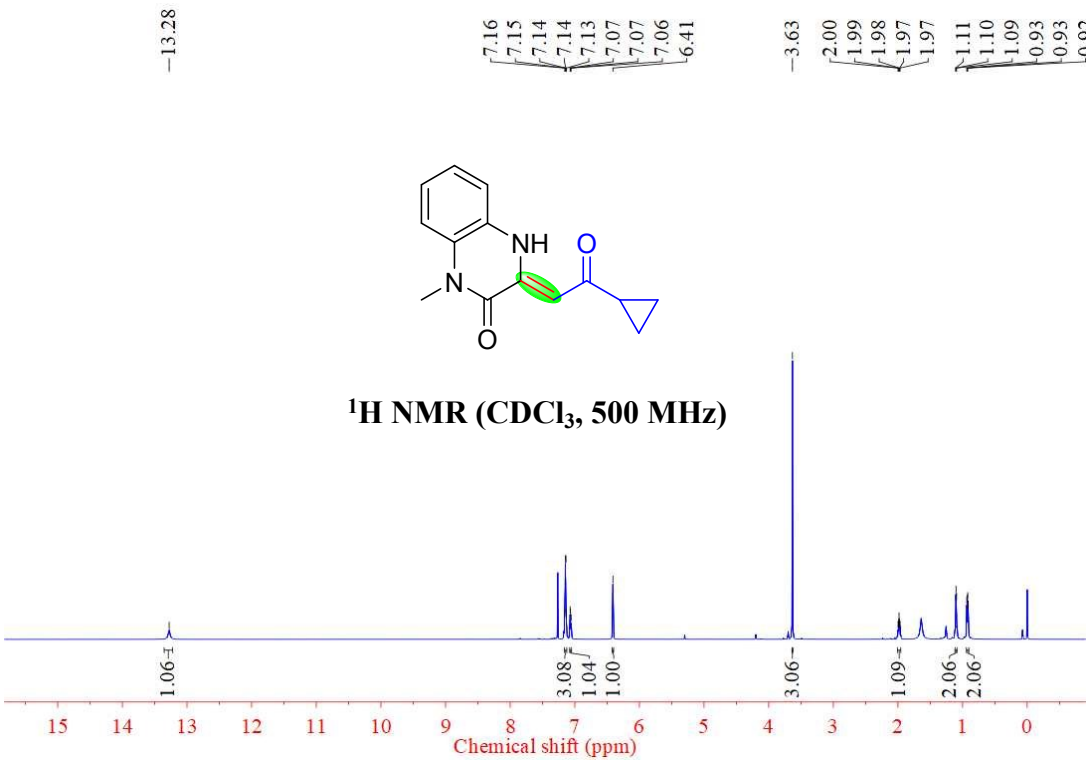
^{1}H NMR Spectrum of Compound 44



^{13}C NMR ($CDCl_3$, 126 MHz)

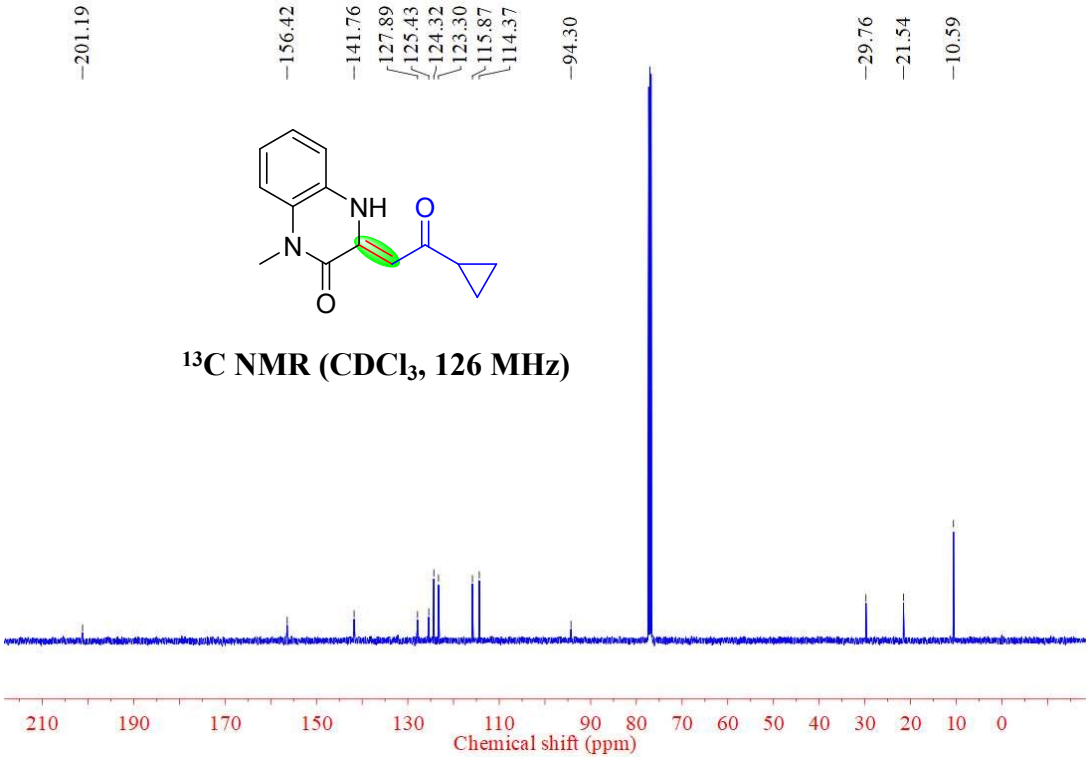


^{13}C{^{1}H} NMR Spectrum of Compound 44



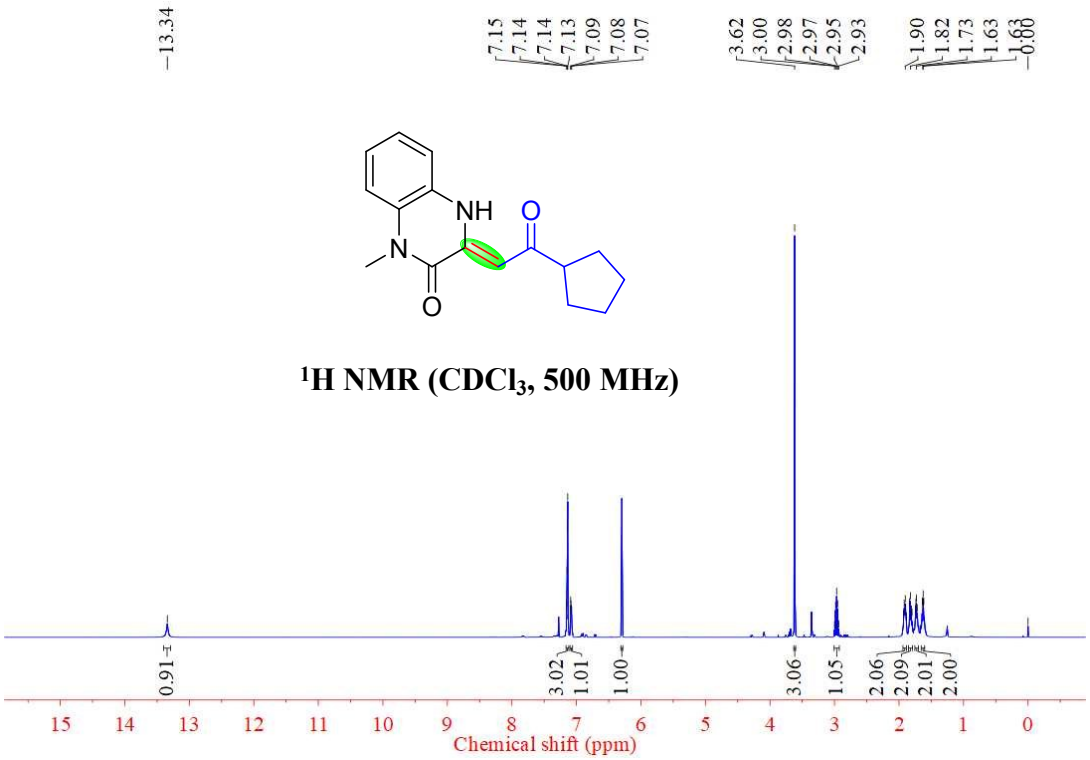
^{1}H NMR ($CDCl_3$, 500 MHz)

^{1}H NMR Spectrum of Compound 45



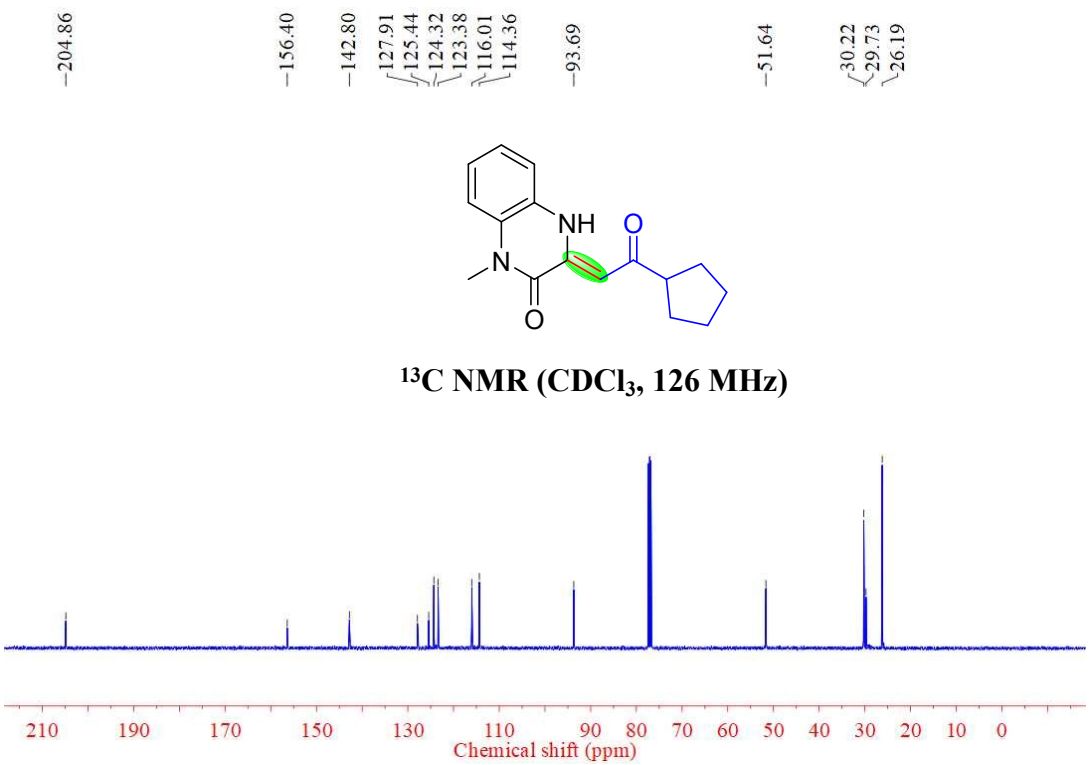
^{13}C NMR ($CDCl_3$, 126 MHz)

^{13}C{^{1}H} NMR Spectrum of Compound 45



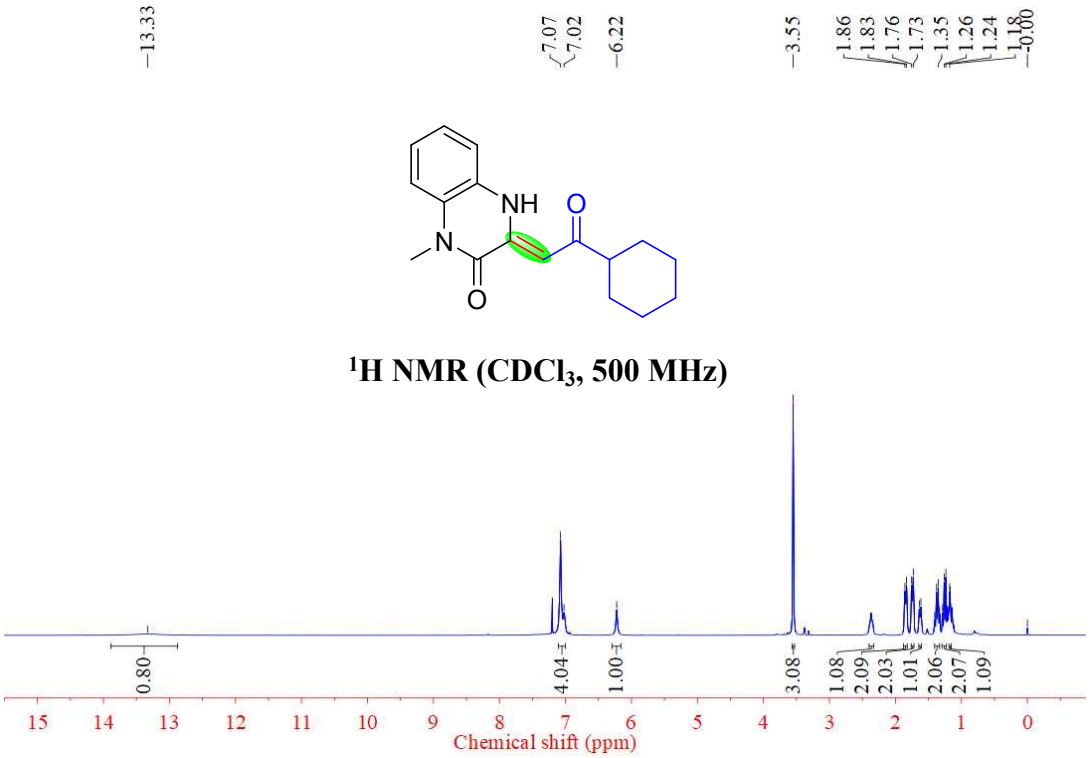
^{1}H NMR ($CDCl_3$, 500 MHz)

^{1}H NMR Spectrum of Compound 46



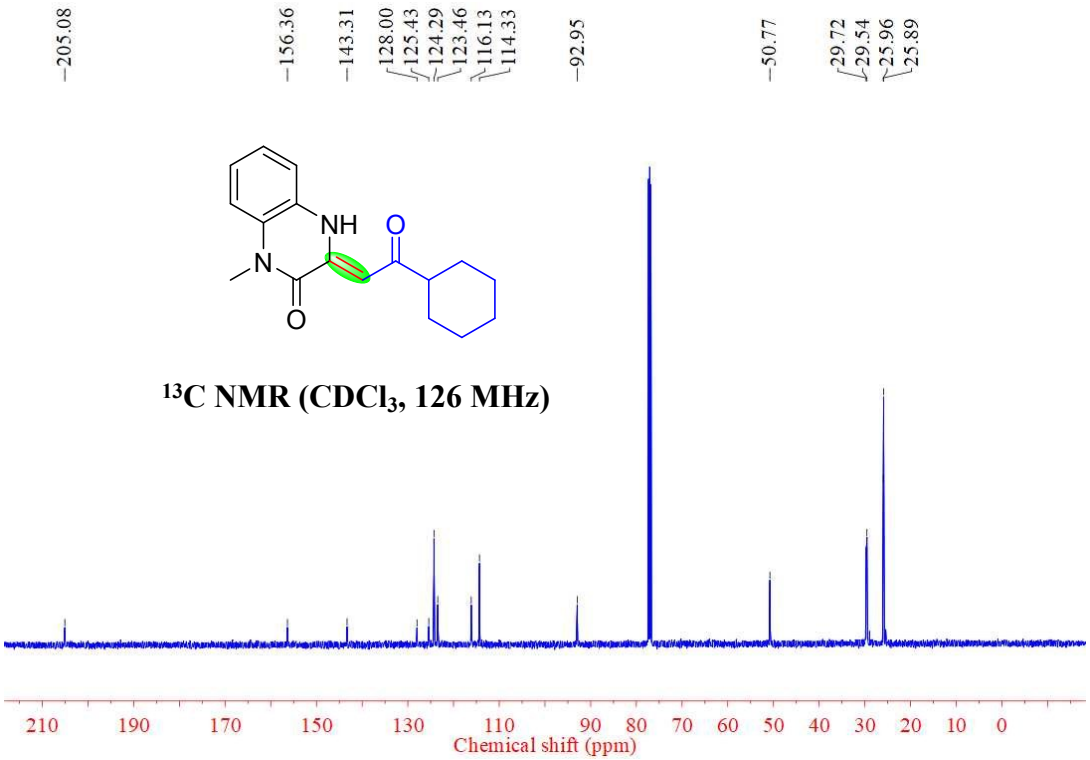
^{13}C NMR ($CDCl_3$, 126 MHz)

^{13}C{^{1}H} NMR Spectrum of Compound 46



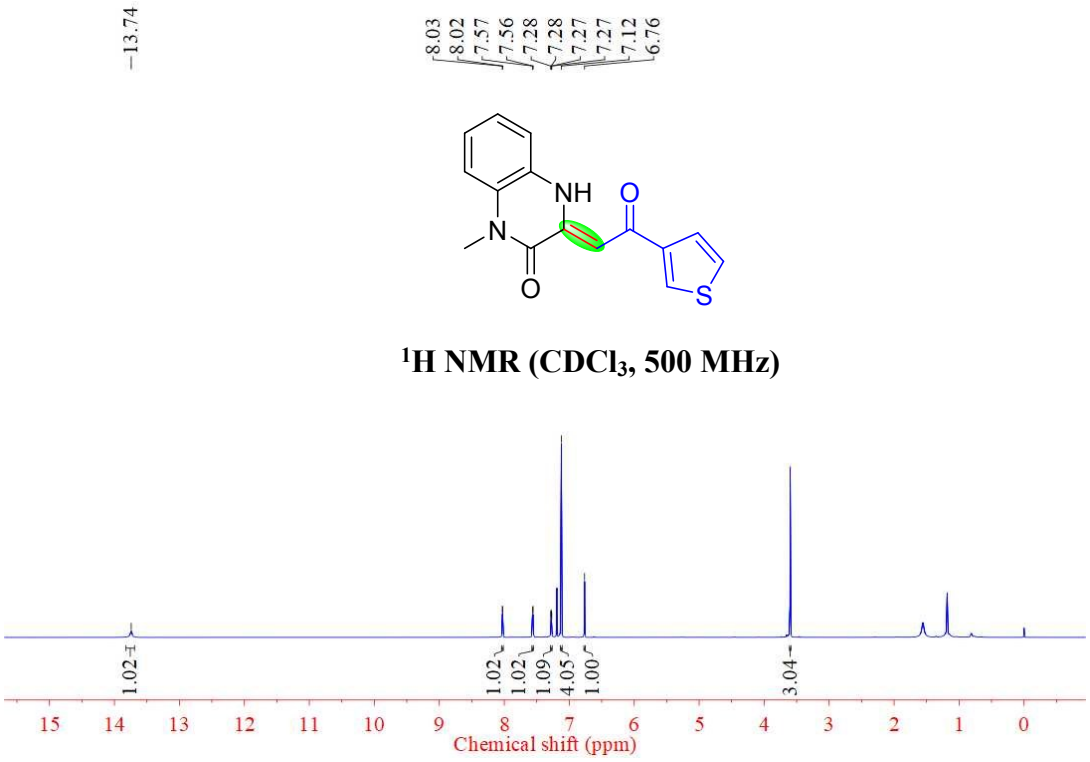
^{1}H NMR ($CDCl_3$, 500 MHz)

^{1}H NMR Spectrum of Compound 47



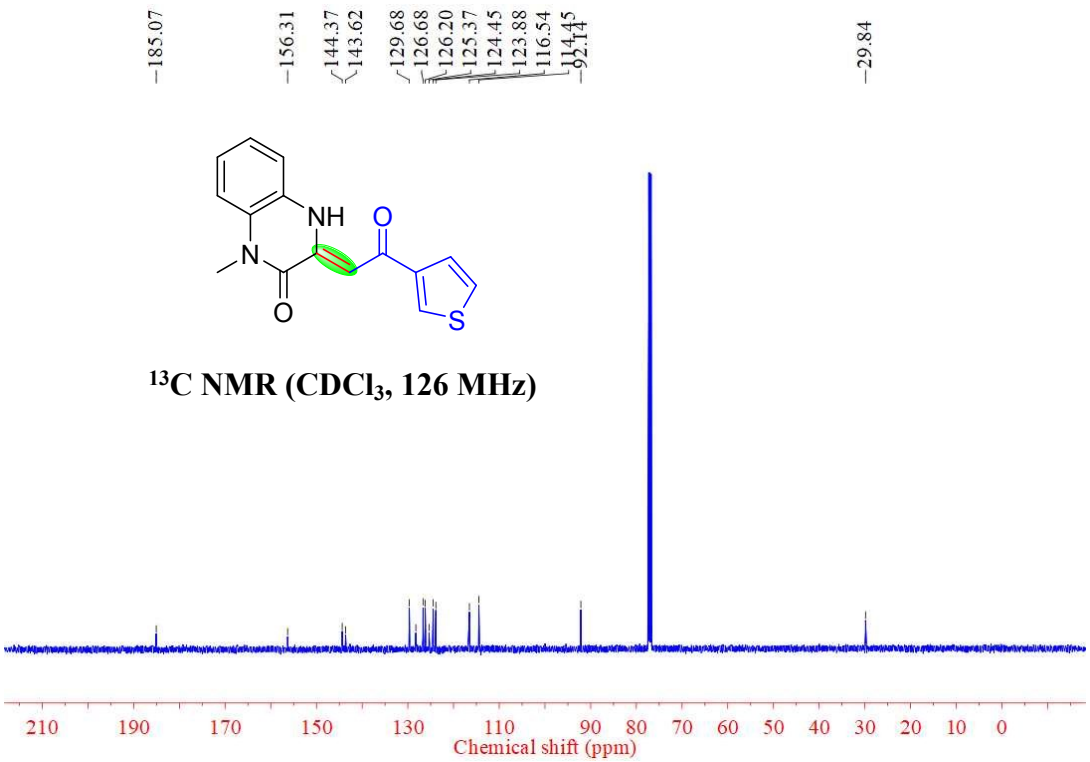
^{13}C NMR ($CDCl_3$, 126 MHz)

^{13}C{^{1}H} NMR Spectrum of Compound 47



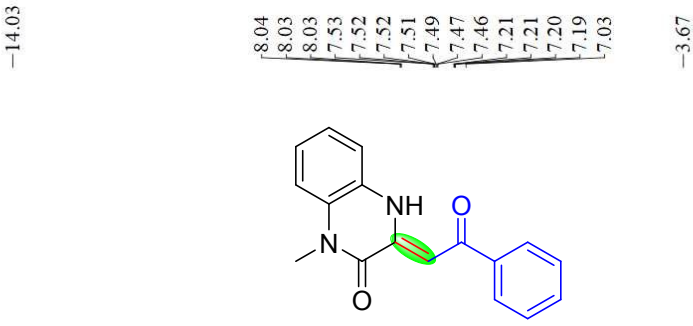
^{1}H NMR ($CDCl_3$, 500 MHz)

^{1}H NMR Spectrum of Compound 48

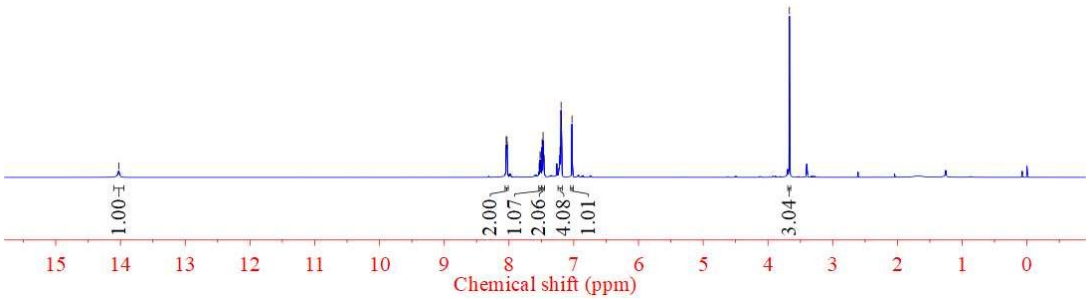


^{13}C NMR ($CDCl_3$, 126 MHz)

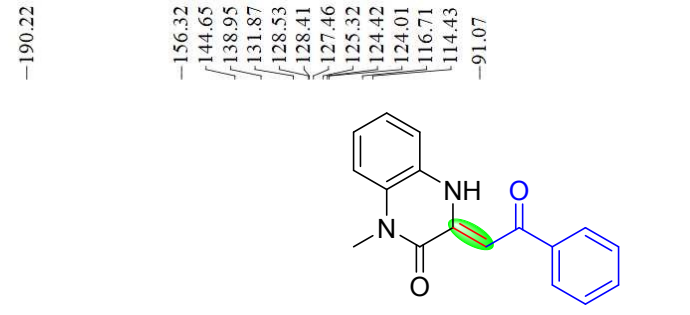
^{13}C{^{1}H} NMR Spectrum of Compound 48



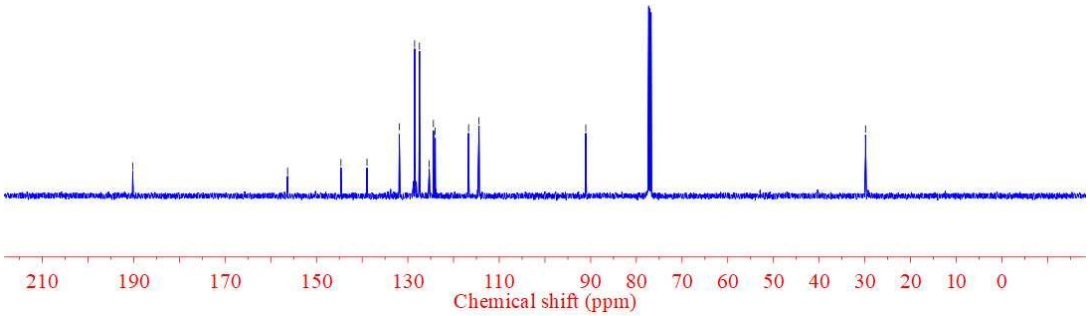
^{1}H NMR ($CDCl_3$, 500 MHz)



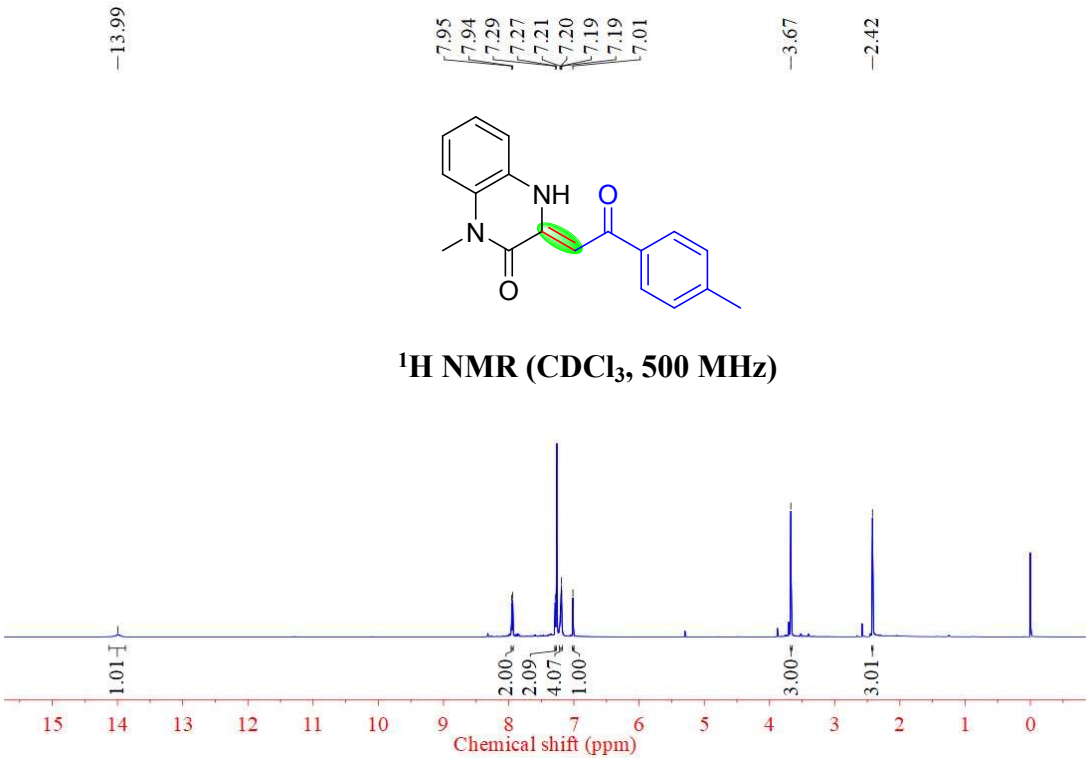
^{1}H NMR Spectrum of Compound 49



^{13}C NMR ($CDCl_3$, 126 MHz)

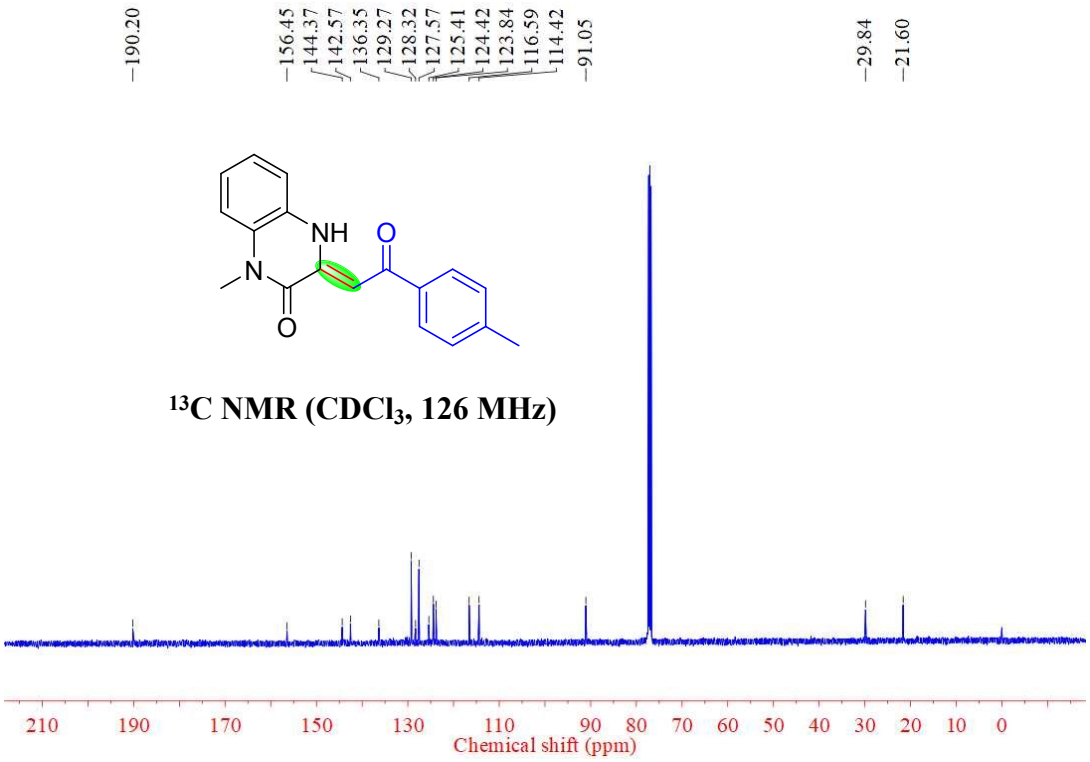


^{13}C{^{1}H} NMR Spectrum of Compound 49



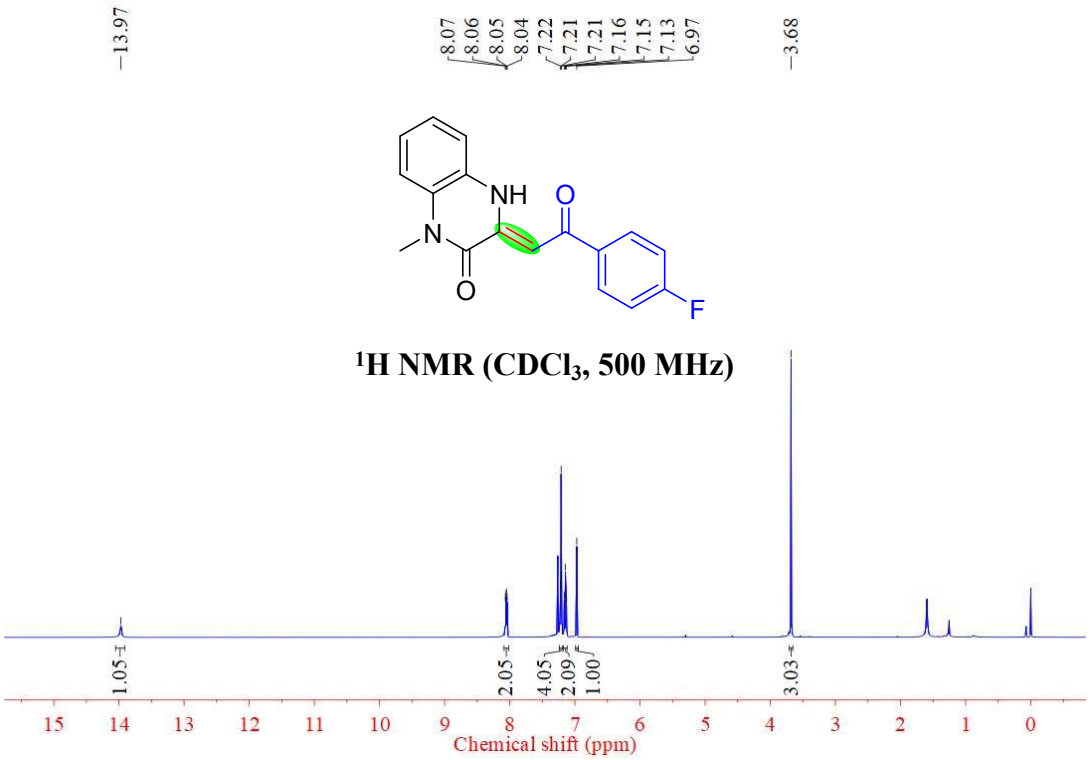
^{1}H NMR ($CDCl_3$, 500 MHz)

^{1}H NMR Spectrum of Compound 50



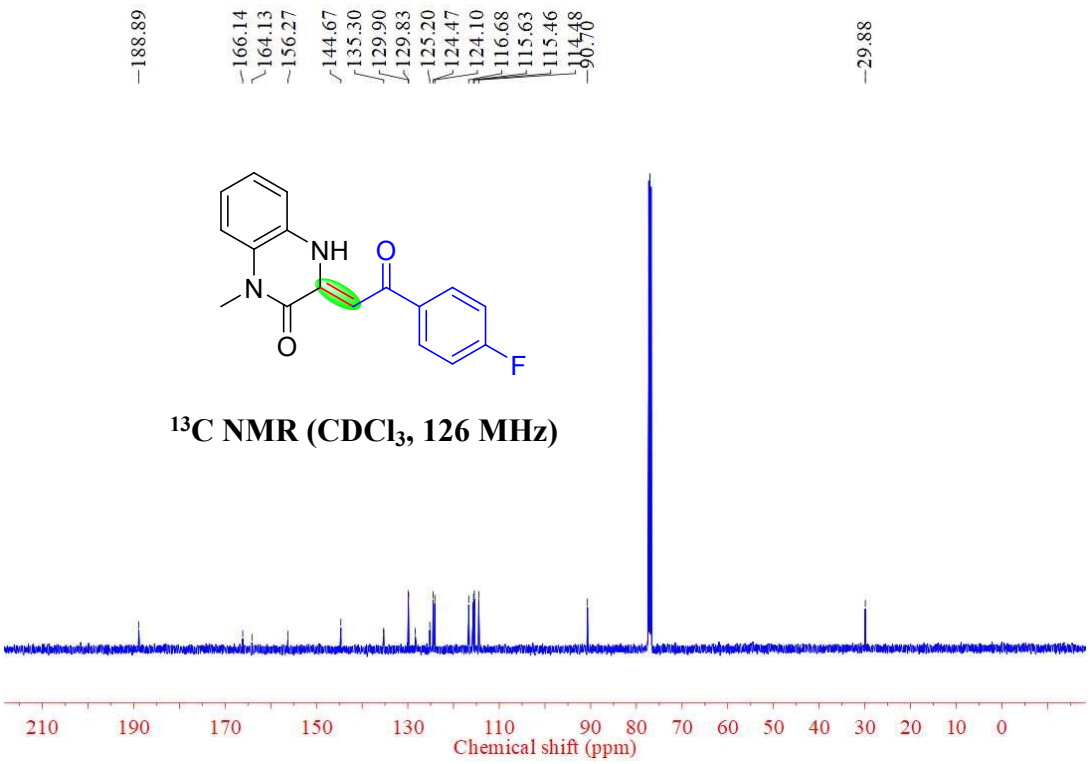
^{13}C NMR ($CDCl_3$, 126 MHz)

^{13}C{^{1}H} NMR Spectrum of Compound 50



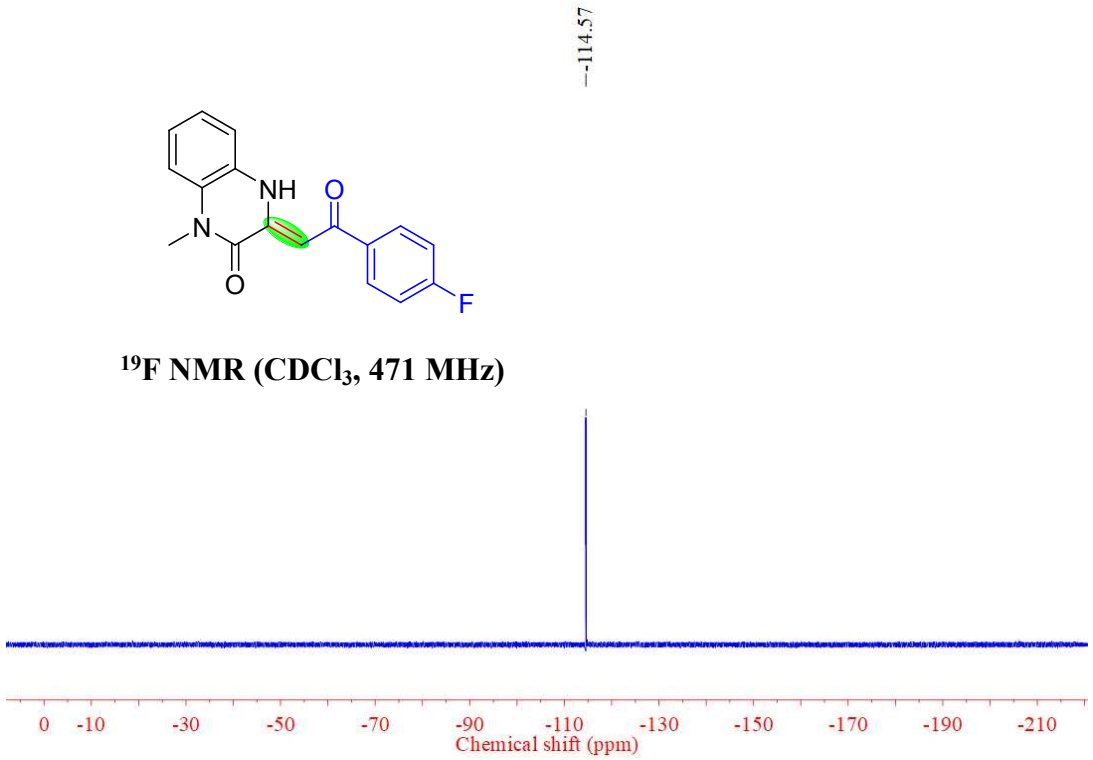
^{1}H NMR ($CDCl_3$, 500 MHz)

^{1}H NMR Spectrum of Compound 51



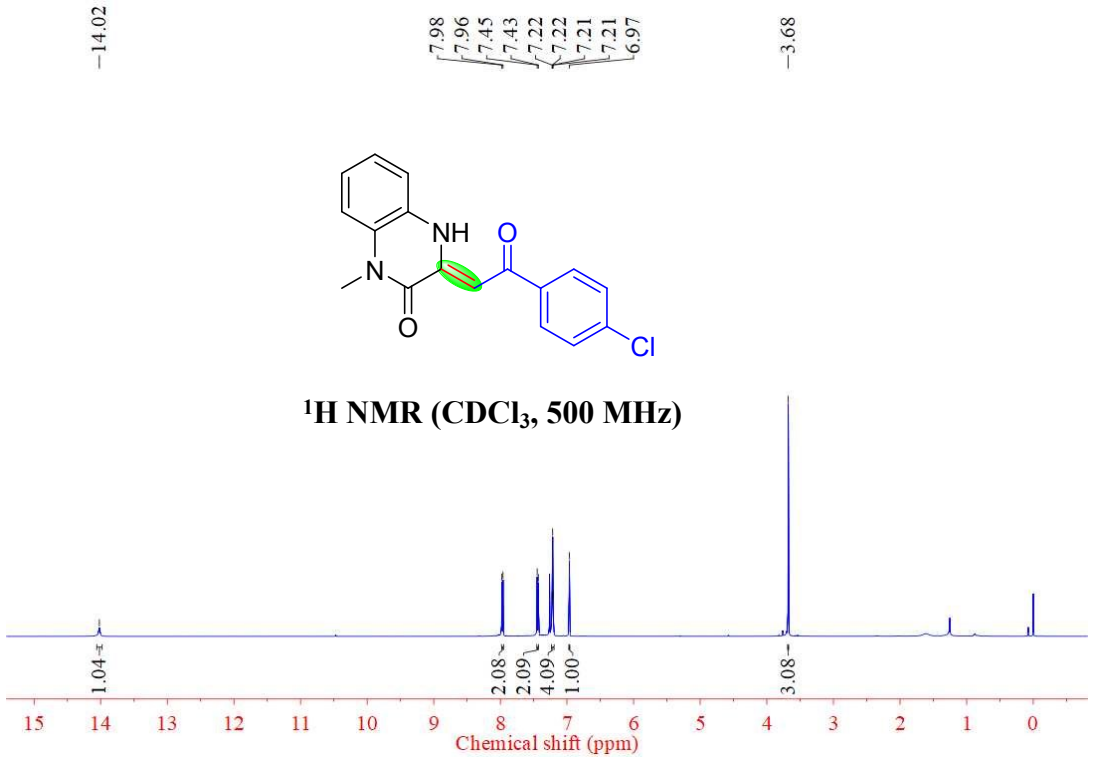
^{13}C NMR ($CDCl_3$, 126 MHz)

^{13}C{^{1}H} NMR Spectrum of Compound 51



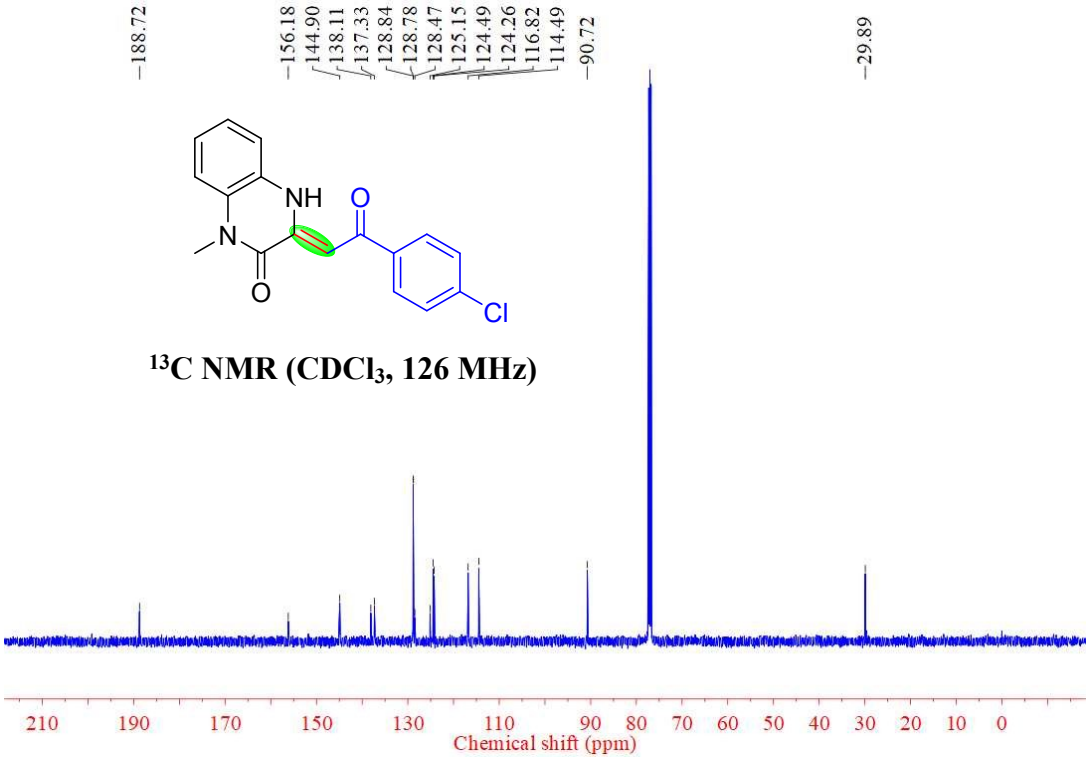
^{19}F NMR ($CDCl_3$, 471 MHz)

^{19}F{^{1}H} NMR Spectrum of Compound 51



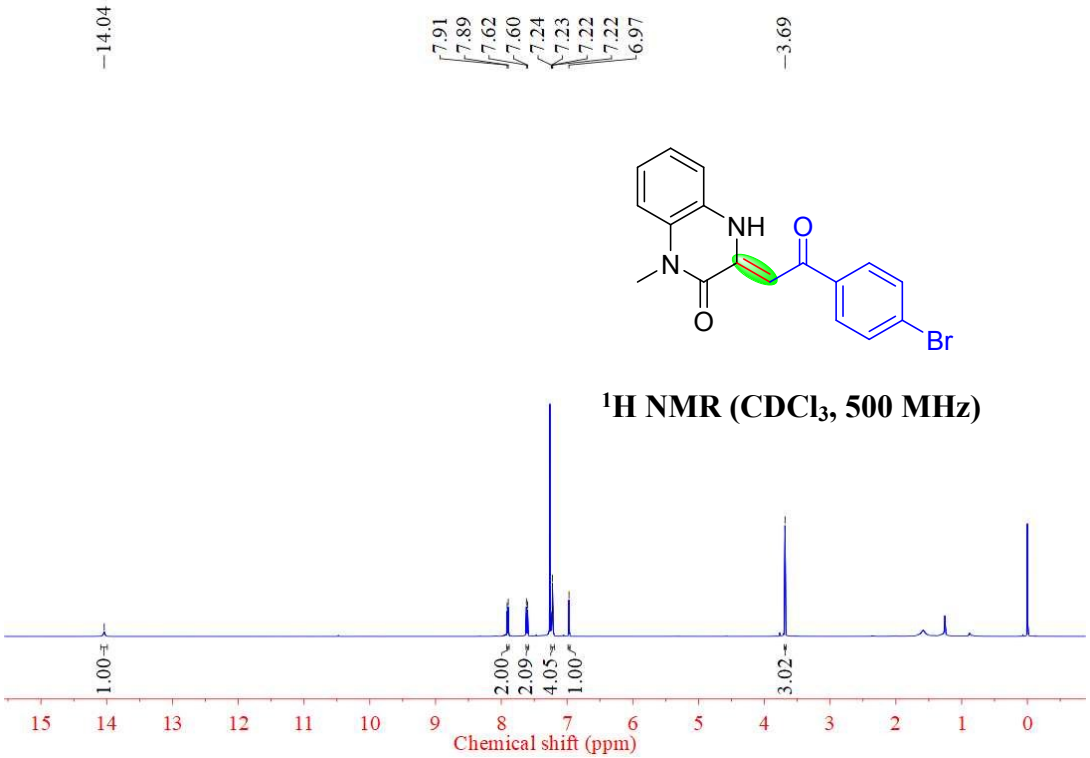
^{1}H NMR ($CDCl_3$, 500 MHz)

^{1}H NMR Spectrum of Compound 52



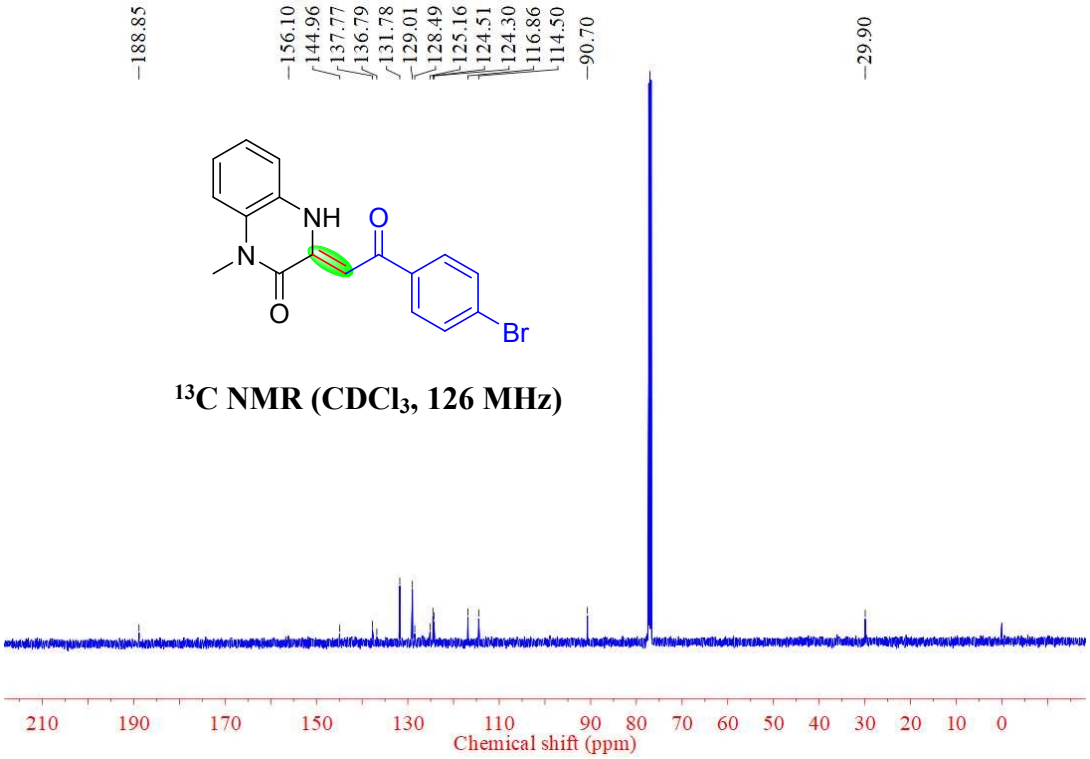
^{13}C NMR ($CDCl_3$, 126 MHz)

^{13}C{^{1}H} NMR Spectrum of Compound 52



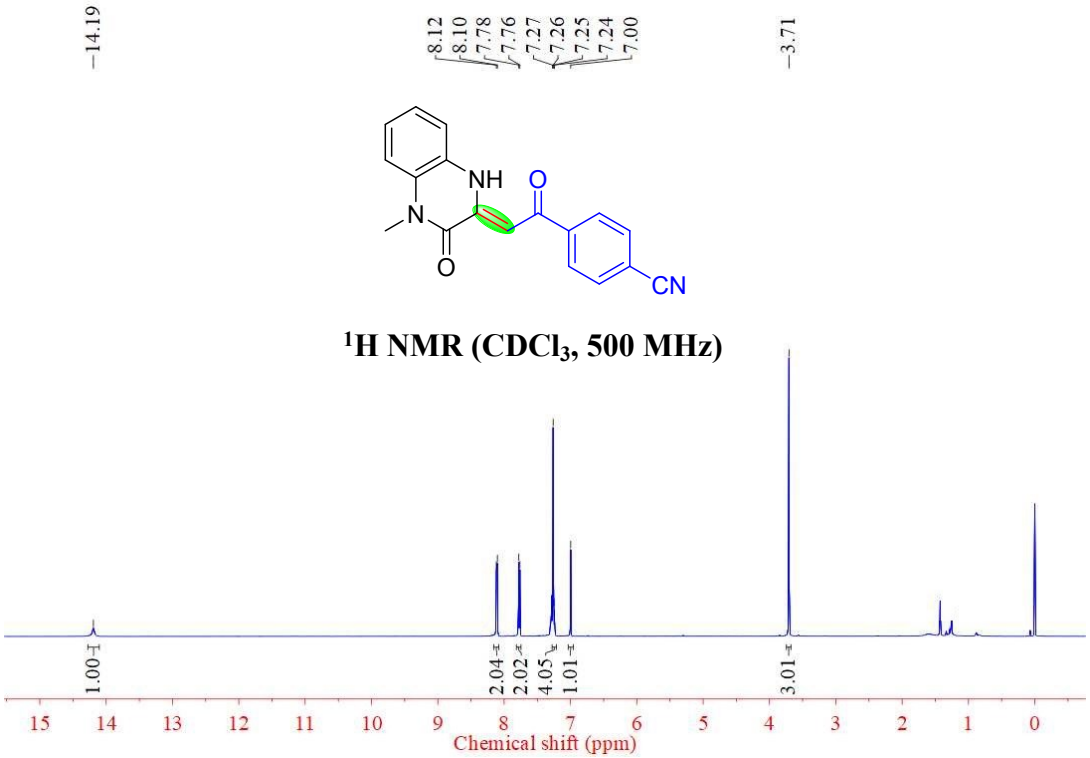
^{1}H NMR ($CDCl_3$, 500 MHz)

^{1}H NMR Spectrum of Compound 53



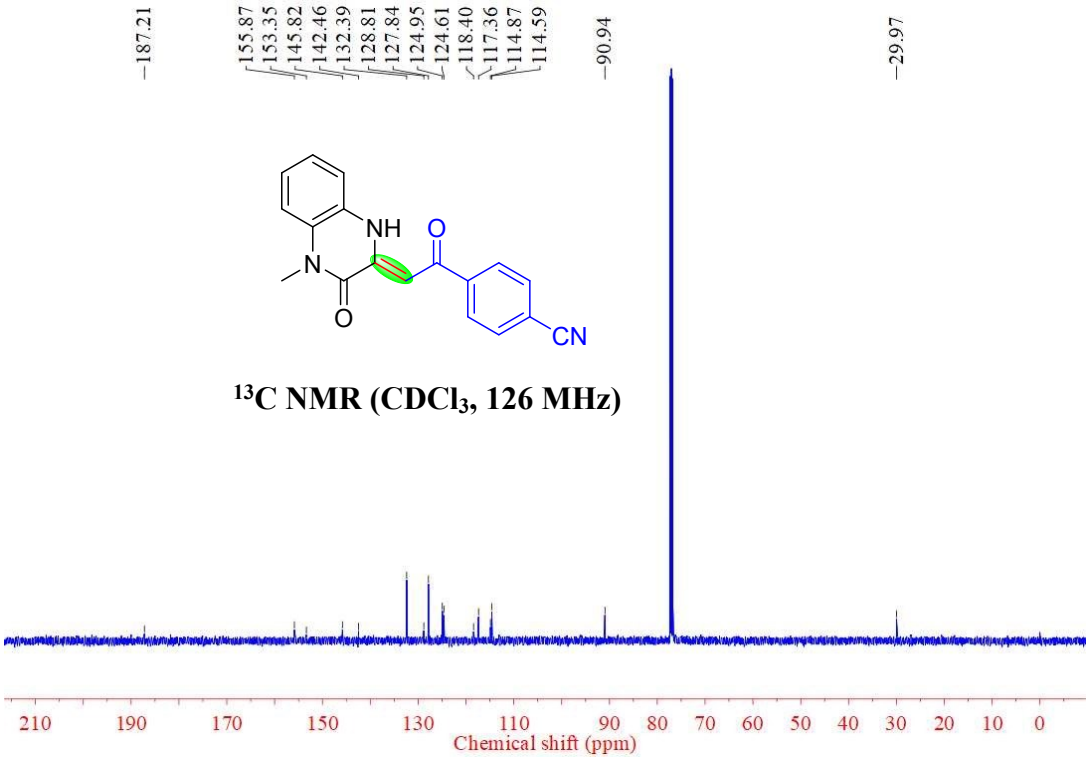
^{13}C NMR ($CDCl_3$, 126 MHz)

^{13}C{^{1}H} NMR Spectrum of Compound 53



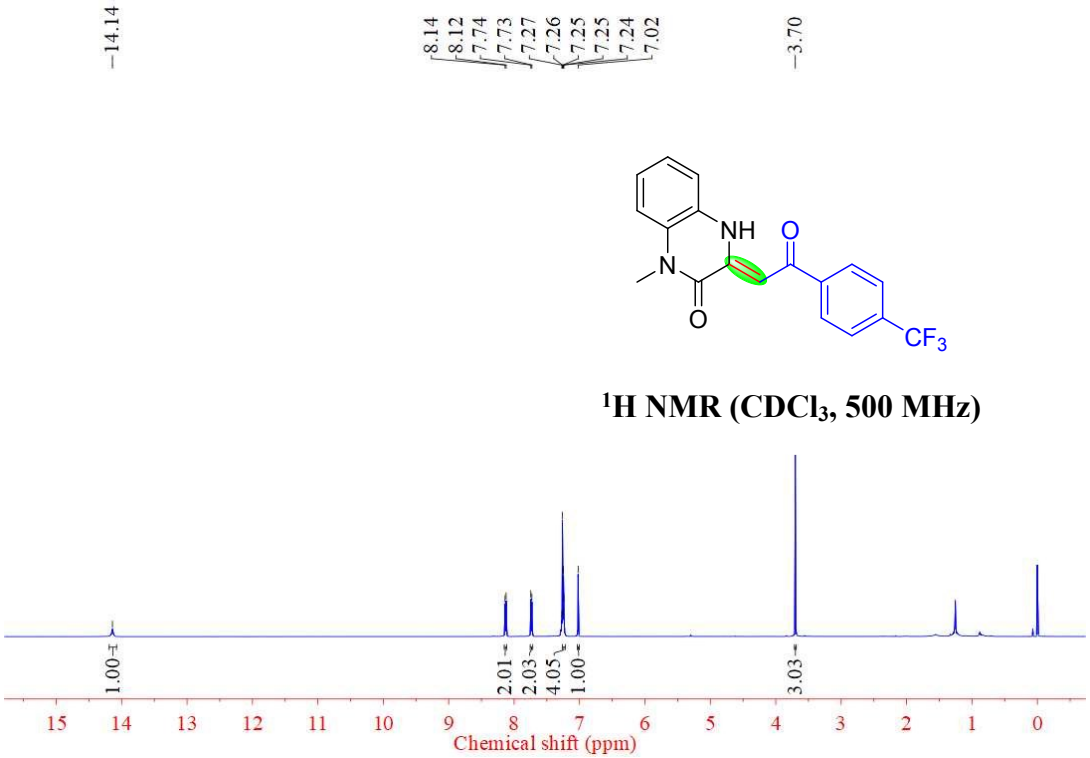
^{1}H NMR ($CDCl_3$, 500 MHz)

^{1}H NMR Spectrum of Compound 54



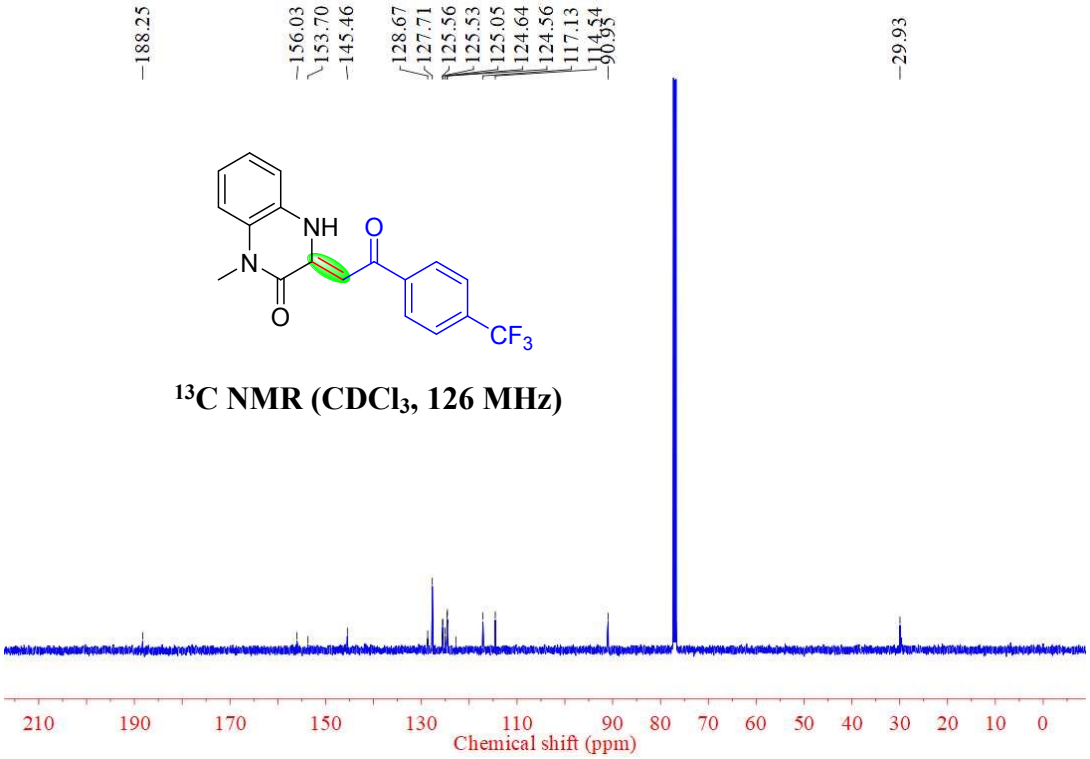
^{13}C NMR ($CDCl_3$, 126 MHz)

^{13}C{^{1}H} NMR Spectrum of Compound 54



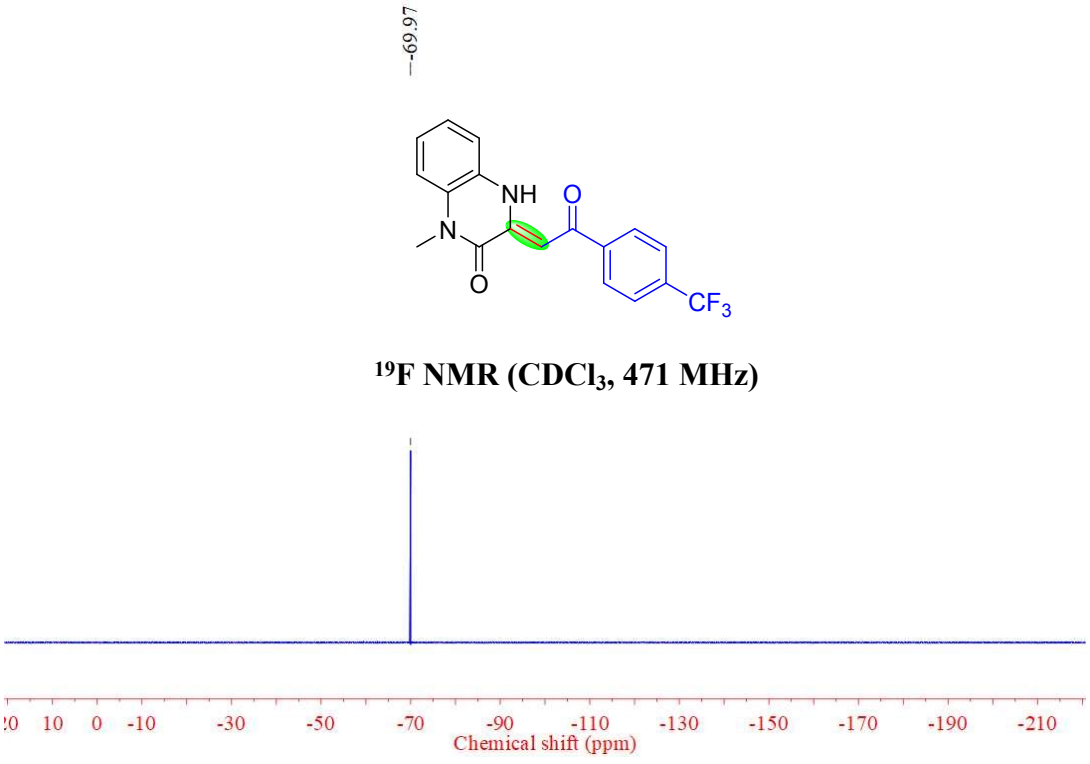
^{1}H NMR ($CDCl_3$, 500 MHz)

^{1}H NMR Spectrum of Compound 55



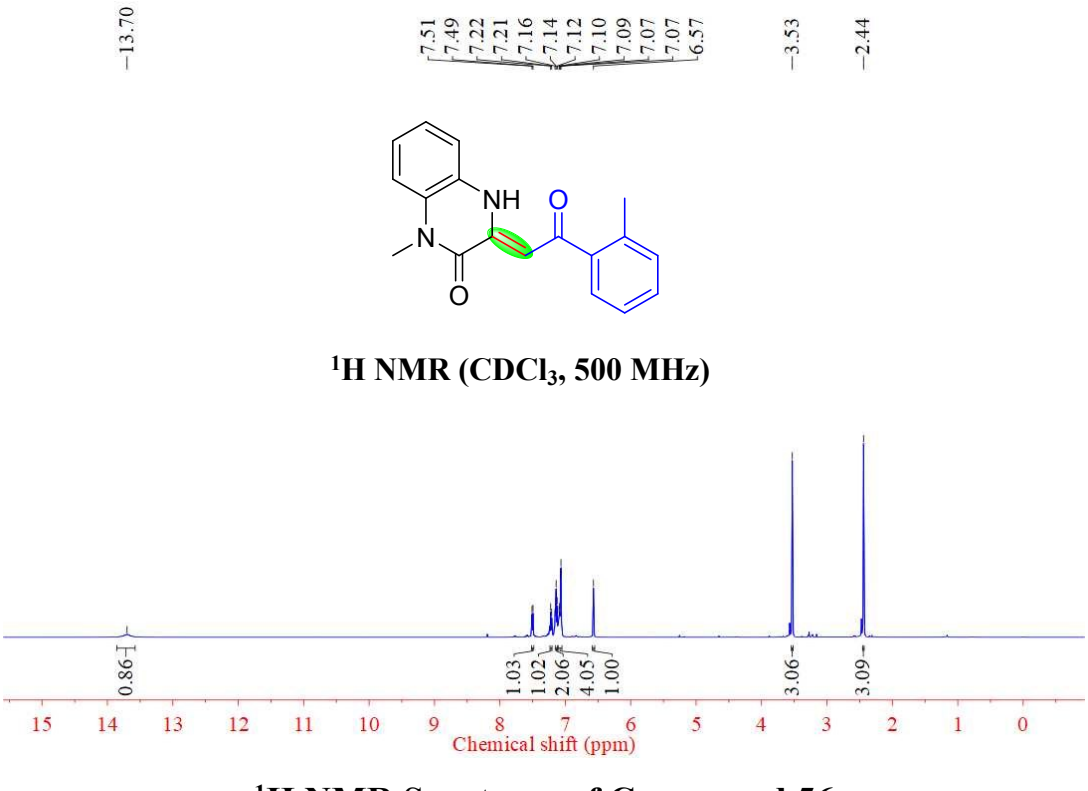
^{13}C NMR ($CDCl_3$, 126 MHz)

^{13}C{^{1}H} NMR Spectrum of Compound 55



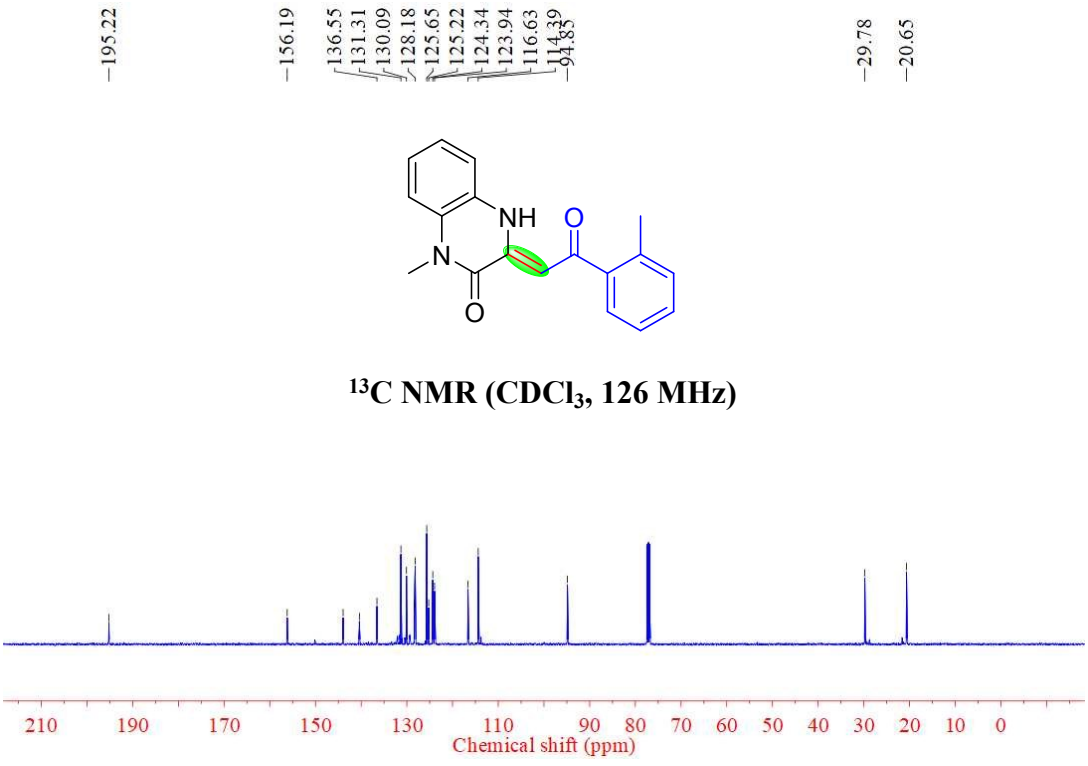
^{19}F NMR ($CDCl_3$, 471 MHz)

^{19}F{^{1}H} NMR Spectrum of Compound 55



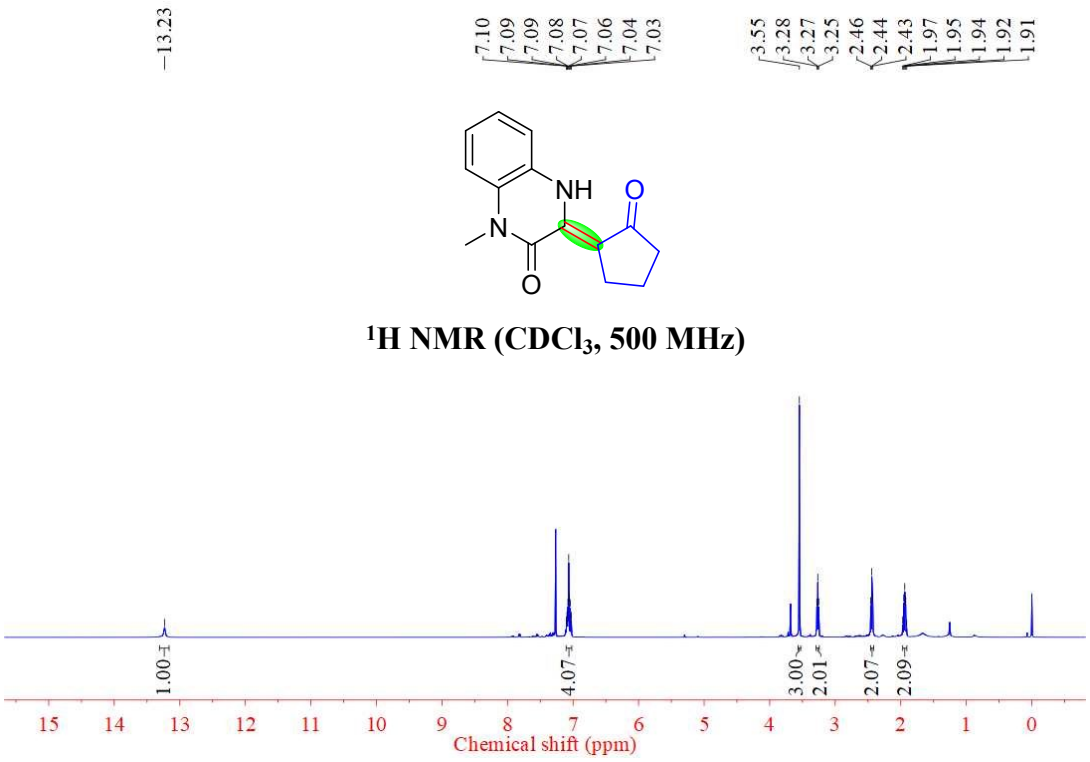
^{1}H NMR ($CDCl_3$, 500 MHz)

^{1}H NMR Spectrum of Compound 56



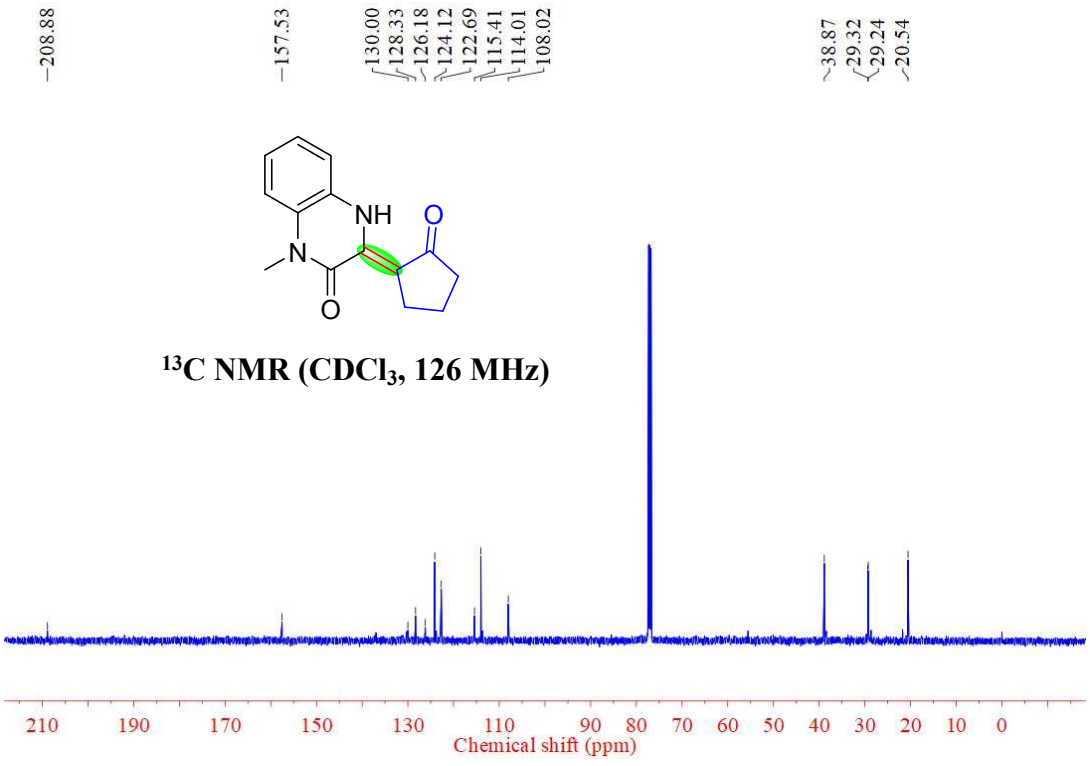
^{13}C NMR ($CDCl_3$, 126 MHz)

^{13}C{^{1}H} NMR Spectrum of Compound 56



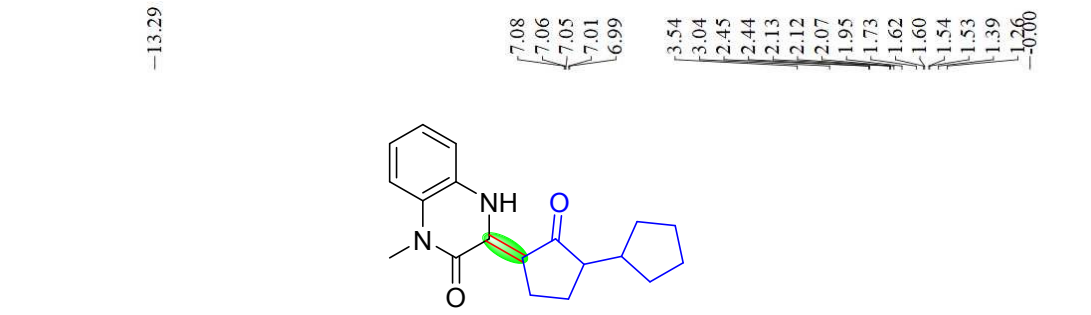
^{1}H NMR ($CDCl_3$, 500 MHz)

^{1}H NMR Spectrum of Compound 57

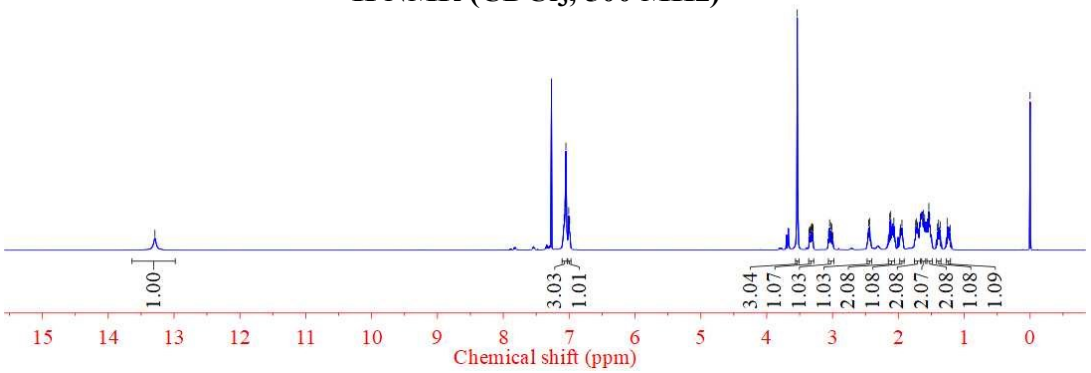


^{13}C NMR ($CDCl_3$, 126 MHz)

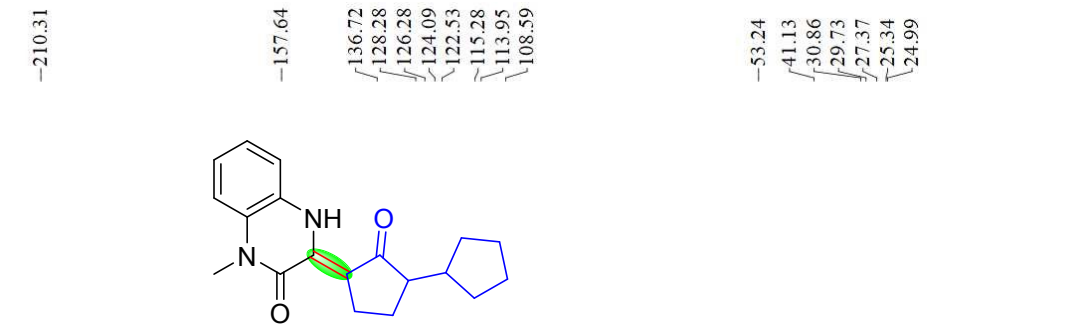
^{13}C{^{1}H} NMR Spectrum of Compound 57



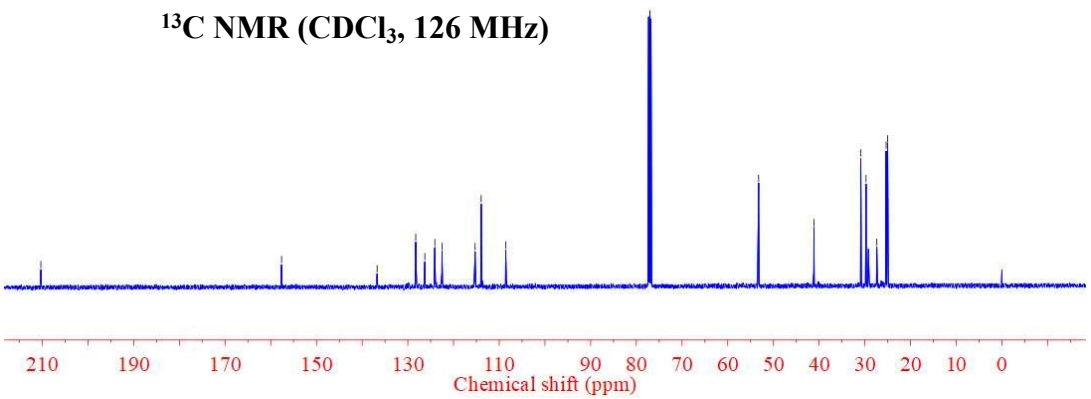
^{1}H NMR ($CDCl_3$, 500 MHz)



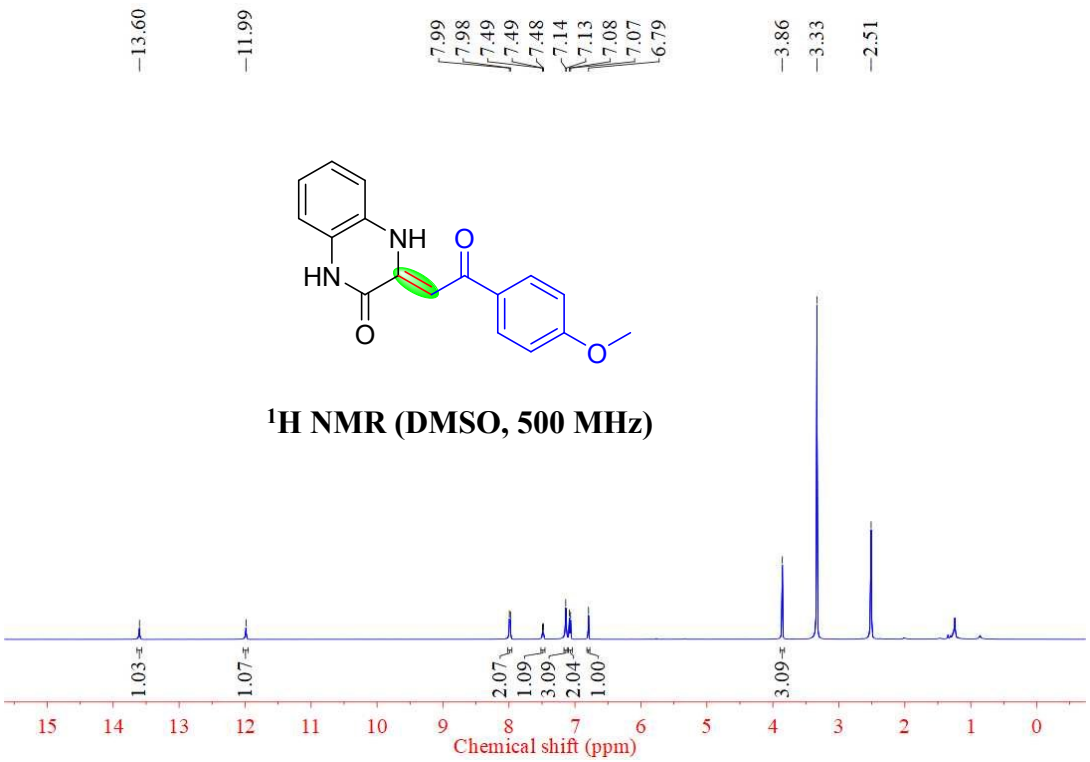
^{1}H NMR Spectrum of Compound 58



^{13}C NMR ($CDCl_3$, 126 MHz)

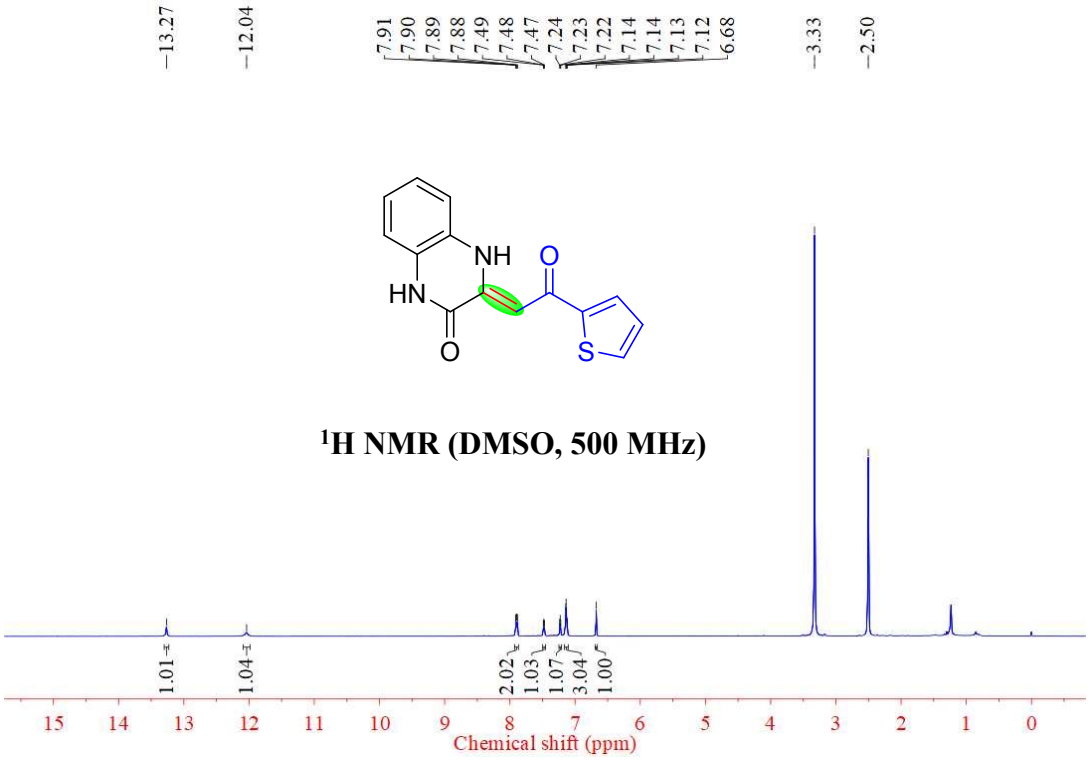


^{13}C{^{1}H} NMR Spectrum of Compound 58



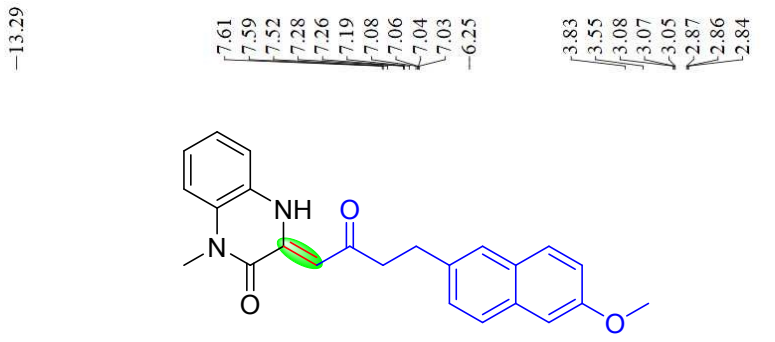
^{1}H NMR (DMSO, 500 MHz)

^{1}H NMR Spectrum of Compound 59

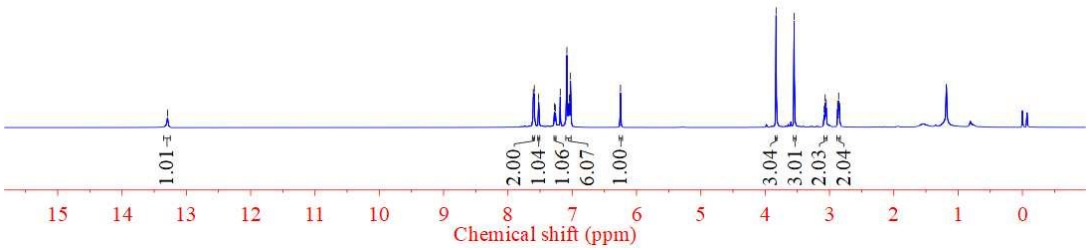


^{1}H NMR (DMSO, 500 MHz)

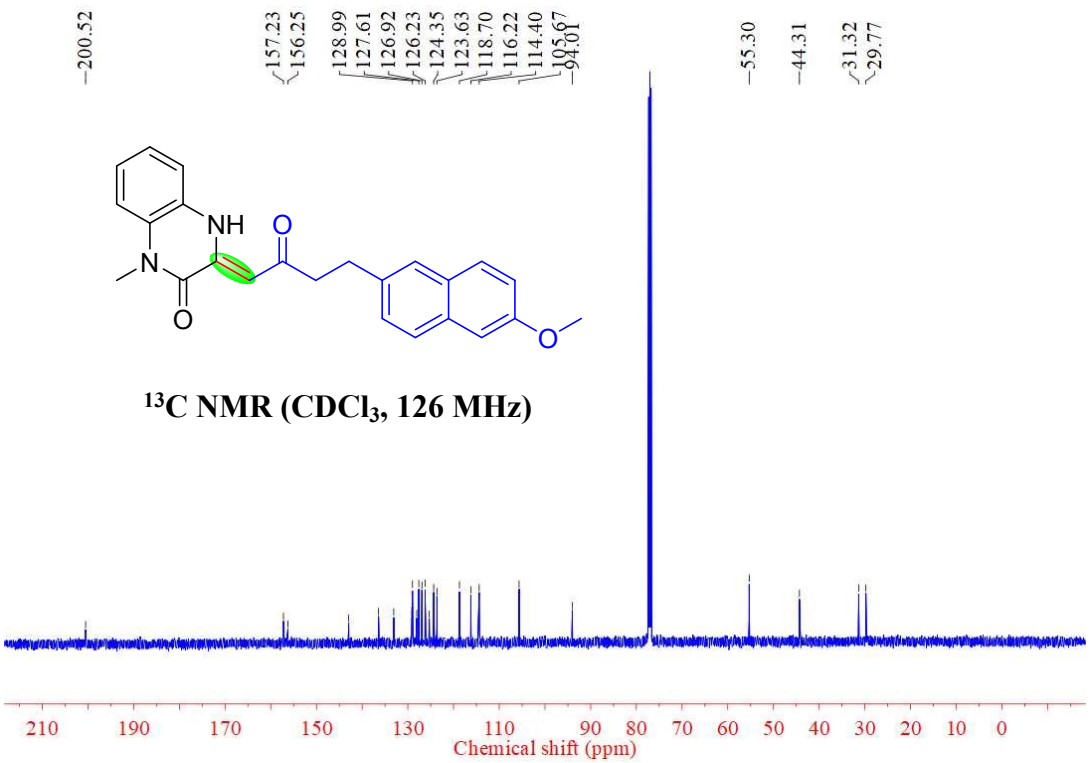
^{1}H NMR Spectrum of Compound 60



^{1}H NMR ($CDCl_3$, 500 MHz)

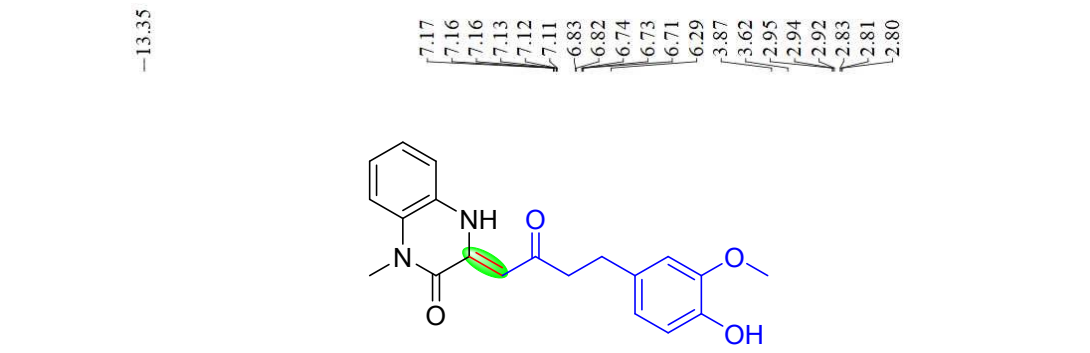


^{1}H NMR Spectrum of Compound 61

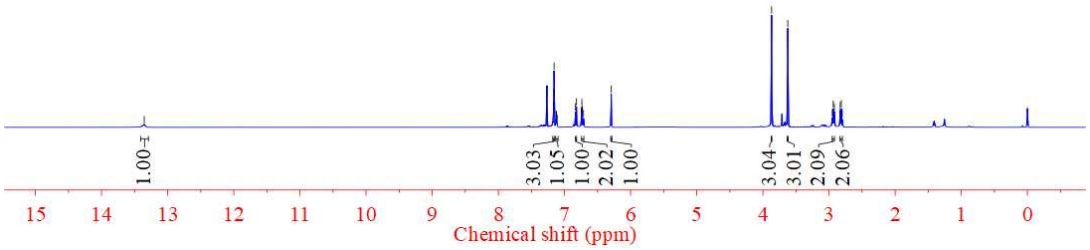


^{13}C NMR ($CDCl_3$, 126 MHz)

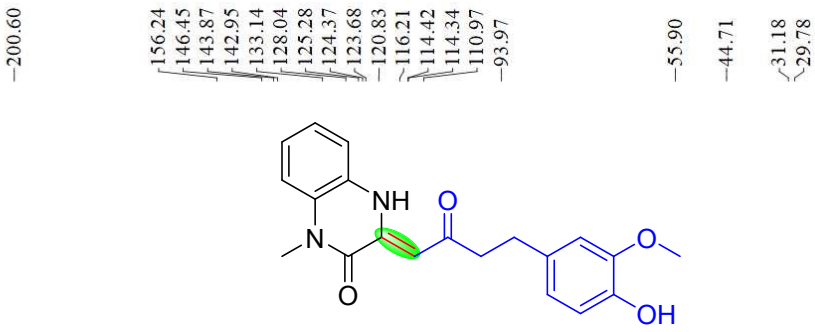
^{13}C{^{1}H} NMR Spectrum of Compound 61



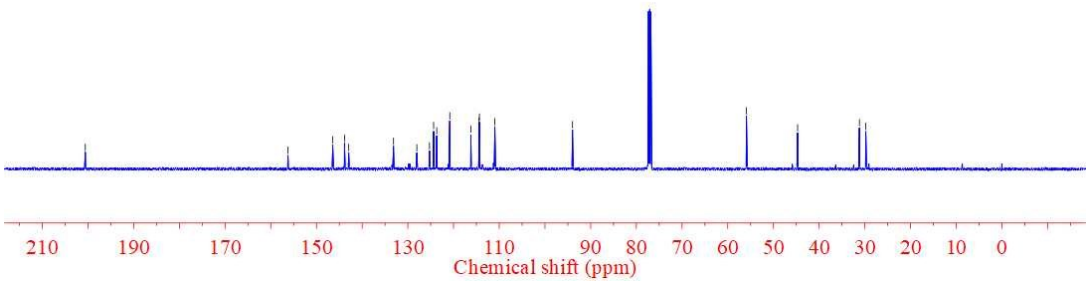
^{1}H NMR ($CDCl_3$, 500 MHz)



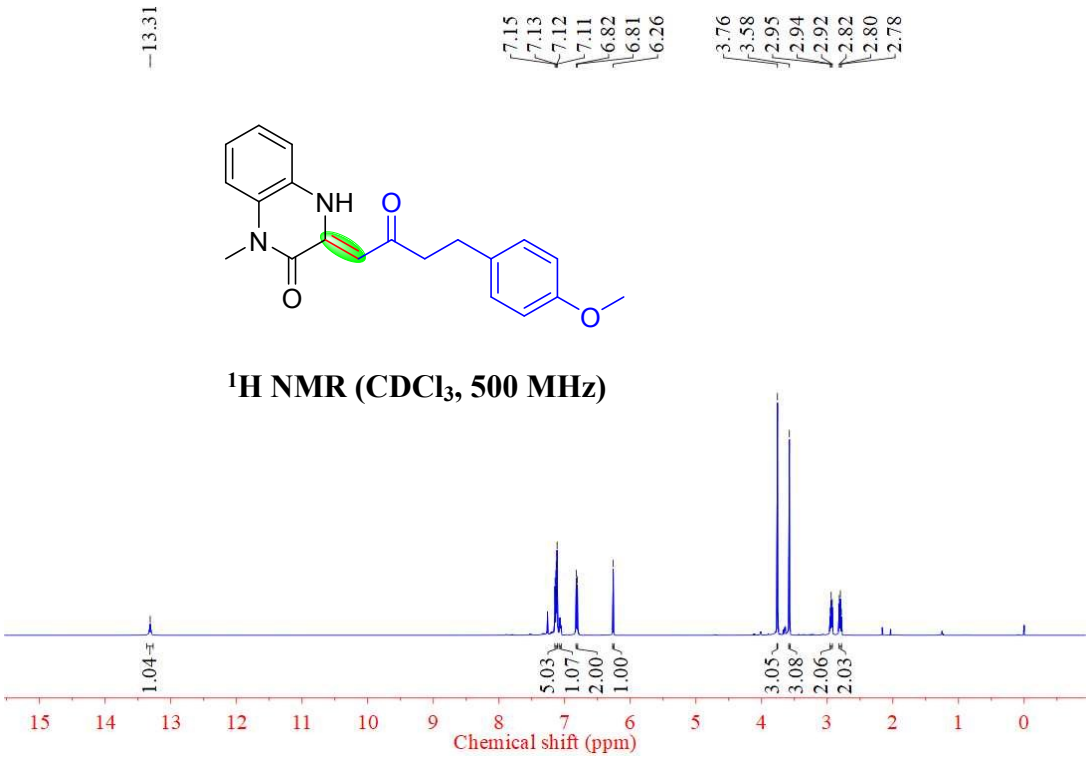
^{1}H NMR Spectrum of Compound 62



^{13}C NMR ($CDCl_3$, 126 MHz)

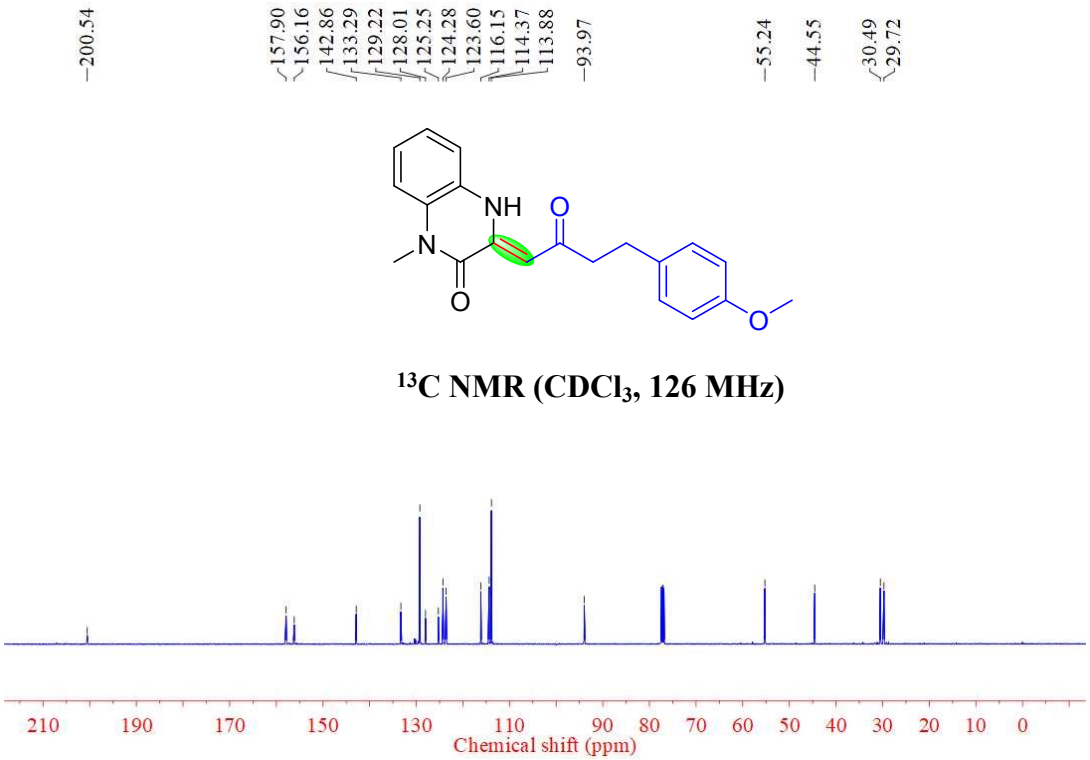


^{13}C{^{1}H} NMR Spectrum of Compound 62



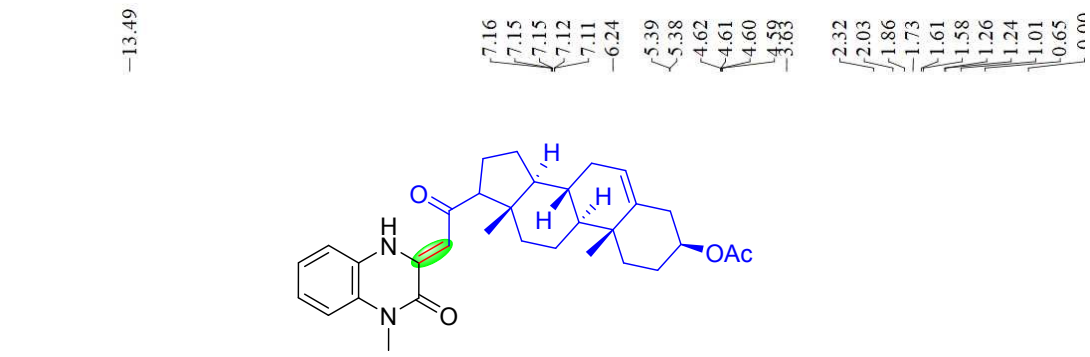
^{1}H NMR ($CDCl_3$, 500 MHz)

^{1}H NMR Spectrum of Compound 63

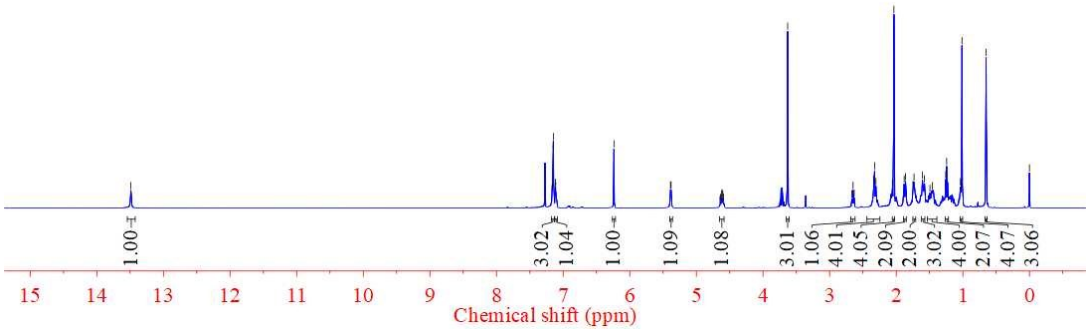


^{13}C NMR ($CDCl_3$, 126 MHz)

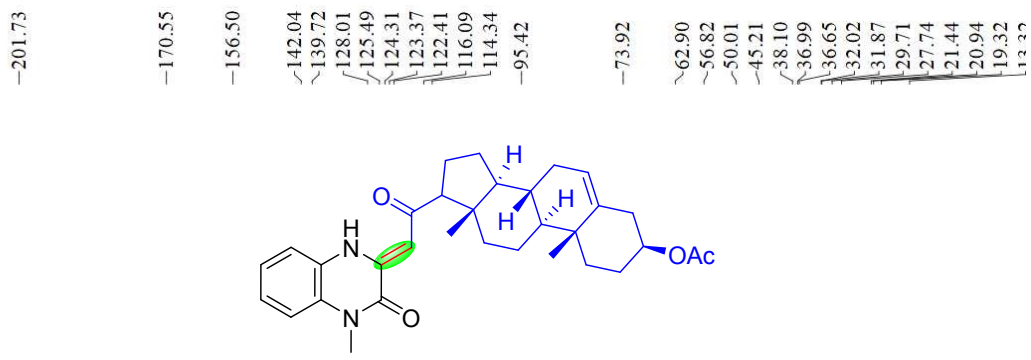
^{13}C{^{1}H} NMR Spectrum of Compound 63



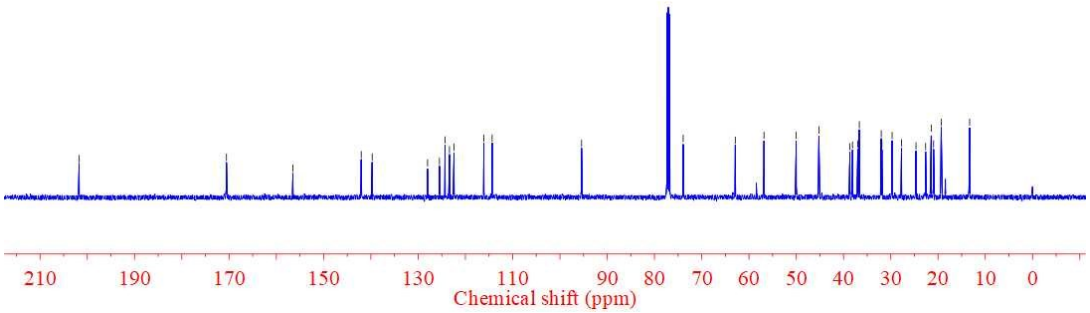
^{1}H NMR ($CDCl_3$, 500 MHz)



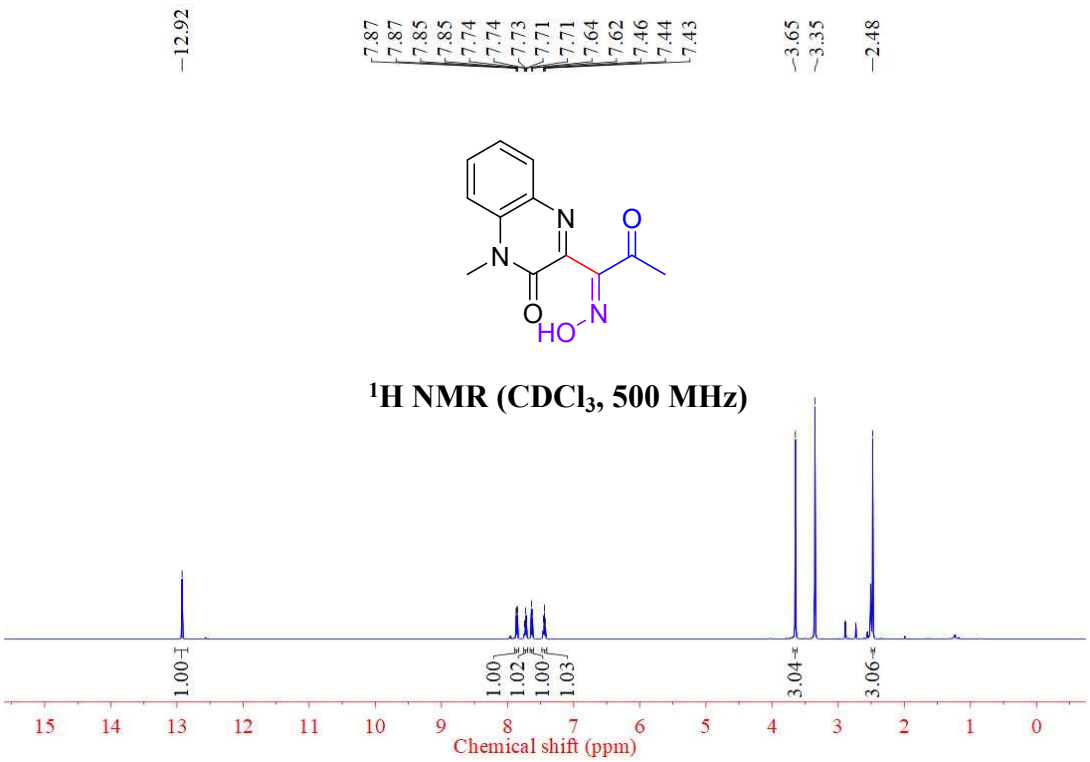
^{1}H NMR Spectrum of Compound 64



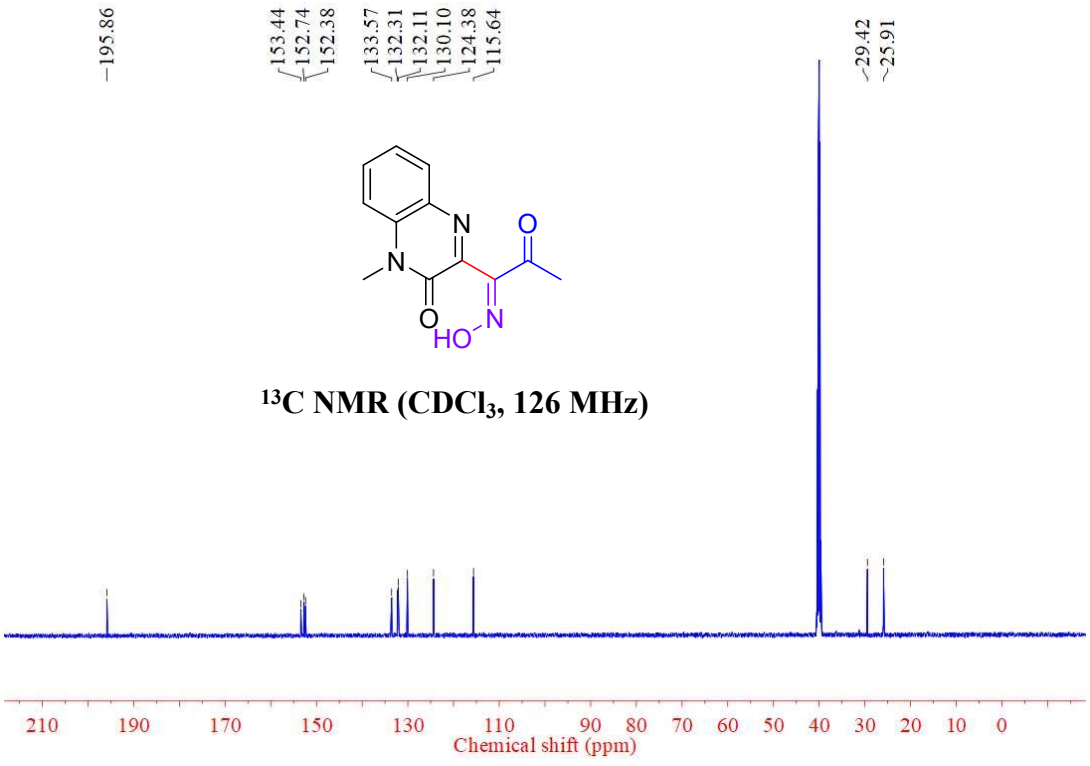
^{13}C NMR ($CDCl_3$, 126 MHz)



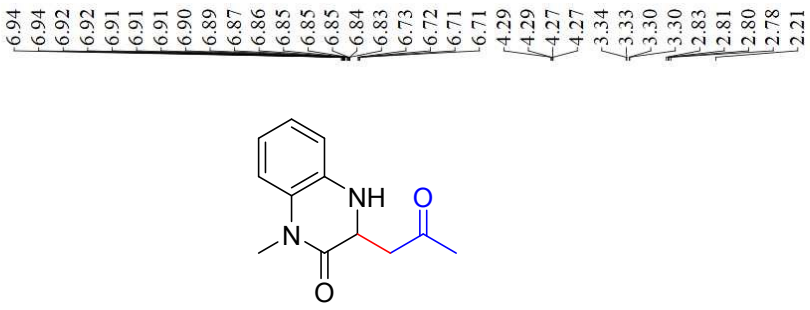
^{13}C{^{1}H} NMR Spectrum of Compound 64



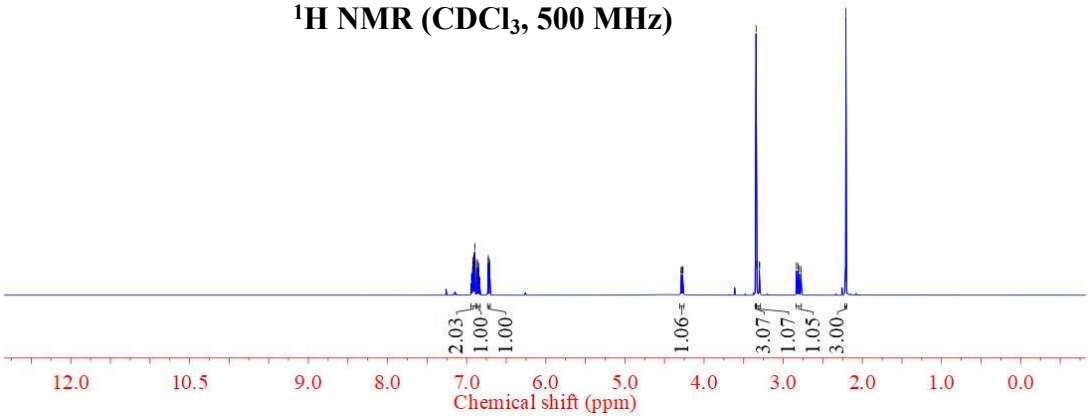
^{1}H NMR Spectrum of Compound 65



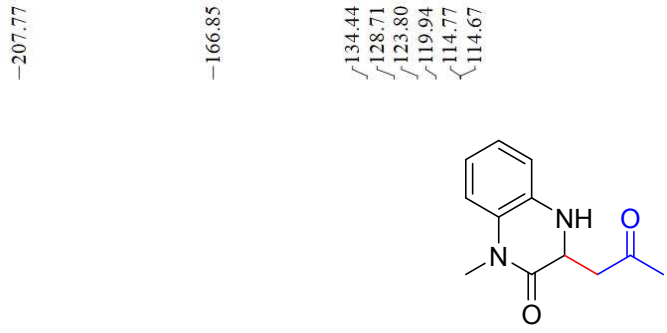
^{13}C{^{1}H} NMR Spectrum of Compound 65



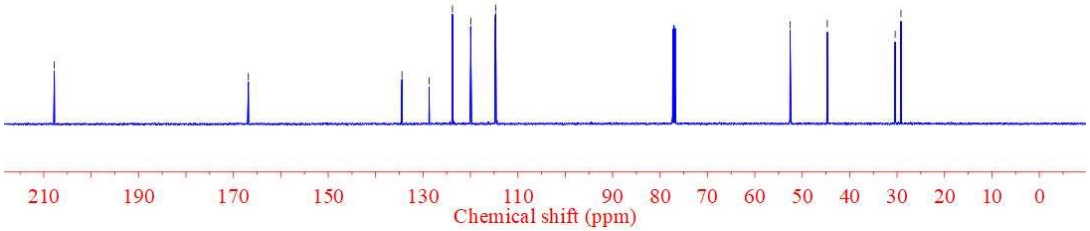
^{1}H NMR ($CDCl_3$, 500 MHz)



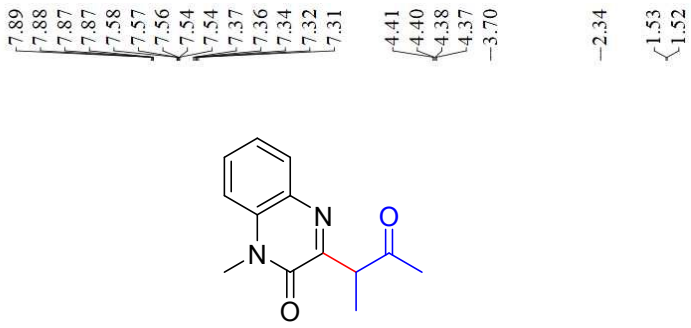
^{1}H NMR Spectrum of Compound 66



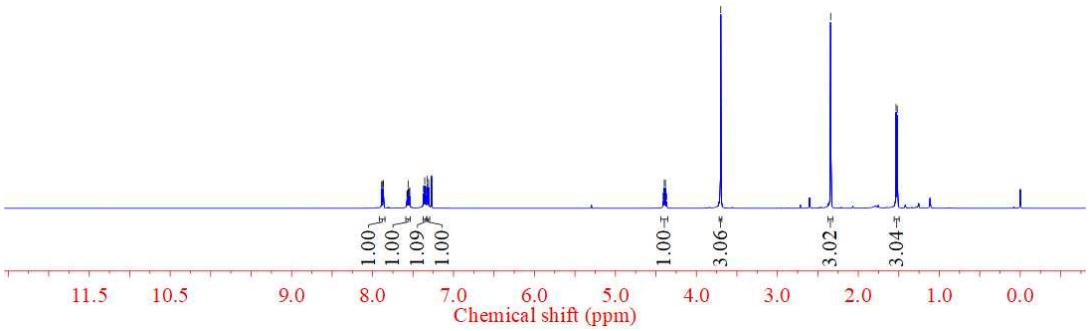
^{13}C NMR ($CDCl_3$, 126 MHz)



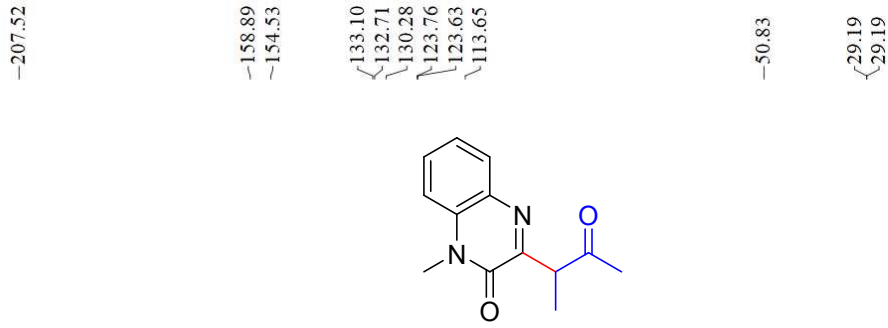
^{13}C{^{1}H} NMR Spectrum of Compound 66



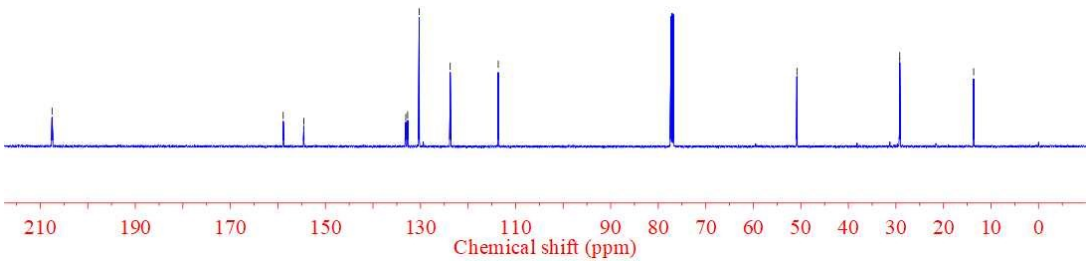
^{1}H NMR ($CDCl_3$, 500 MHz)



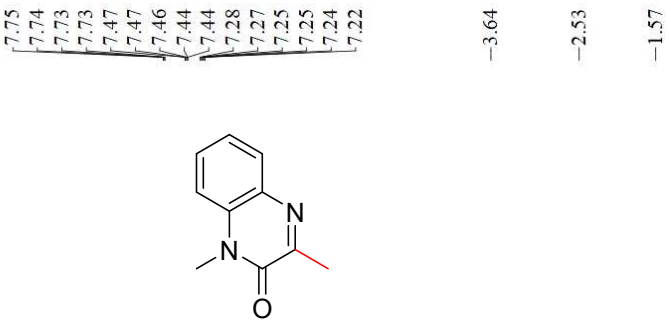
^{1}H NMR Spectrum of Compound 67



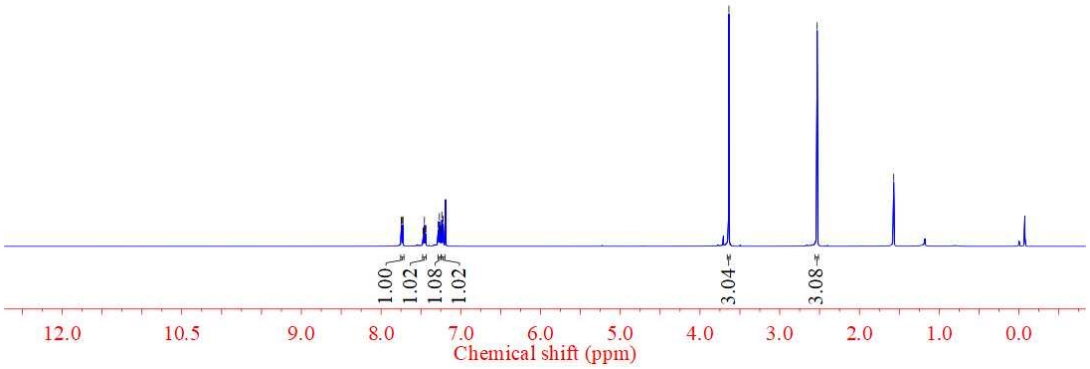
^{13}C NMR ($CDCl_3$, 126 MHz)



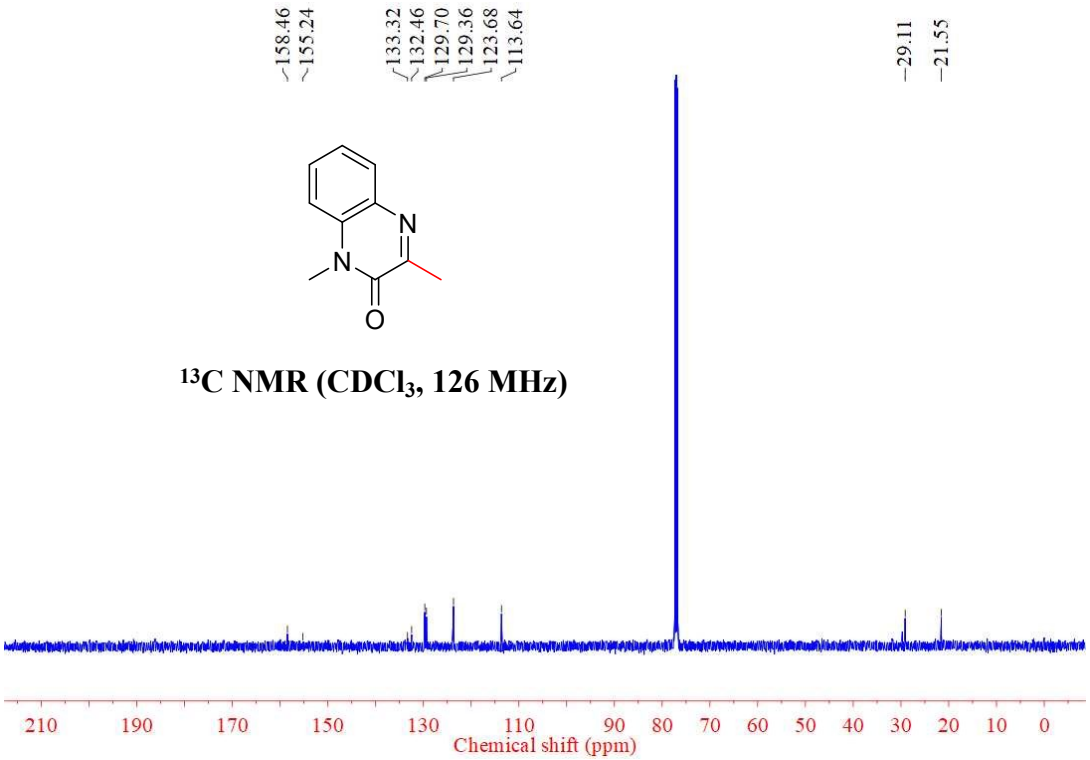
^{13}C{^{1}H} NMR Spectrum of Compound 67



^{1}H NMR ($CDCl_3$, 500 MHz)



^{1}H NMR Spectrum of Compound 68



^{13}C{^{1}H} NMR Spectrum of Compound 68