Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

Metal- and Photocatalyst-Free Approach to Visible-Light-Induced Acylation of Quinoxalinones

Worawat Niwetmarin,*[a,b] Naiyana Saesian,[a] Rungroj Saruengkhanphasit,[a]
Chatchakorn Eurtivong,[c] Nopporn Thasana,[a,b,d] and Somsak Ruchirawat[a,b,d]

[a] Program in Chemical Sciences, Chulabhorn Graduate Institute, Bangkok 10210, Thailand

[b] Center of Excellence on Environmental Health and Toxicology (EHT), OPS, MHESI, Thailand

[c] Department of Pharmaceutical Chemistry, Faculty of Pharmacy, Mahidol University, Bangkok 10400, Thailand

[d] Laboratory of Medicinal Chemistry, Chulabhorn Research Institute, Bangkok 10210, Thailand

Supporting Information

Table of Contents

1. General Information

All reactions were performed in a Schlenk tube under an argon atmosphere at room temperature. Heat generated from the LED lamps resulted in warming of the reactions to 35 – 40 ºC, and fan cooling was used to maintain this temperature. Chemicals and photocatalysts were commercially available from chemical suppliers and were used without purification. DMSO, DCE, and DMA were anhydrous purchased from Sigma-Aldrich. Anhydrous solvents such as DCM and CH_3CN were obtained from the solvent purification system, by passage through a column of activated alumina. ^{1}H NMR (300 and 600 MHz) and ^{13}C NMR (75 and 151 MHz) were recorded on Bruker AVANCE 300 and Bruker AVANCE NEO 600 spectrometers, respectively. Chemical shifts were reported in part per million (ppm) on the scale using TMS (0 ppm) as an internal standard in $CDCl_3$ and solvent signals (2.50 ppm) in DMSO-d_6. The ^{13}C NMR chemical shifts were determined by using solvent signals (77.0 ppm in $CDCl_3$, and 39.5 ppm in DMSO-d_6). Infrared spectra were measured using PerkinElmer FT-IR spectrometer. High resolution mass spectra (HRMS) were obtained using a Thermo Scientific orbitrap Q Exactive Focus mass spectrometer *via* the electrospray ionization (ESI) or atmospheric pressure chemical ionization (APCI). Melting points were measured on a Thermo Scientific digital melting point apparatus in open capillaries. Flash column chromatography was carried out using silica gel (silica gel 60, size 0.06 – 0.20 mm, 70 – 230 mesh ASTM). TLC-Aluminum sheets on silica gel 60 GF_{254} were used for monitoring the reactions. UV/vis spectra were recorded using a Jasco FP-8550 spectrophotometer with an absorbance measurement cell block.

Photo of reaction setup

8 W PAR38 EVE blue LED bulbs and 40 W Kessil PR160L-440nm lamp were purchased and used for the light sources. The lamps were positioned on opposite sides of the Schlenk tubes at a distance 2 – 3 cm from the tubes. Fan cooling was used to maintain the temperature. With this setup, the temperature near the tubes was at approximately 35 – 40 °C throughout the reaction time of 4 – 24 h.

Figure S1 Photo of reaction setup with two 8 W blue LED bulbs.

2. Additional reaction optimisation

Table S1 Photoinduced acetylation of **1a**

1a + **2l**, R = 4-$CF_3C_6H_4CO$ → **3al**

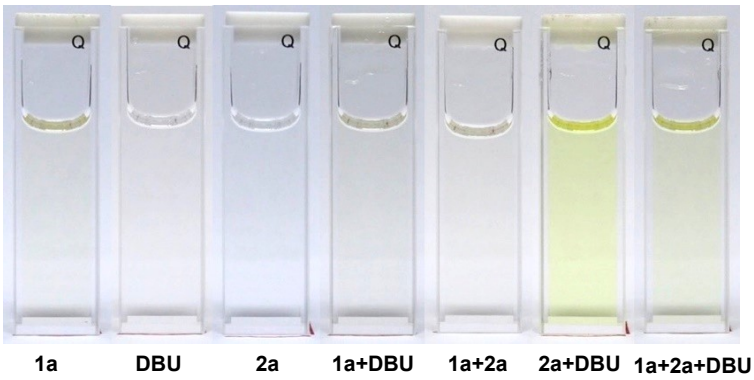
Entry	Deviation from above	NMR yield[a]
1	*None*	43%
2	R = 4-$NO_2C_6H_4CO$	n.r.
3	R = 4-$CH_3OC_6H_4CO$	25%
4	R = C_6F_5CO	10%
5	DCM instead of DMSO	39%
6	THF instead of DMSO	12%
7	CH_3CN instead of DMSO	n.r.
8	DCE instead of DMSO	n.r.
9	q-OAc (2.0 eq.)	27%
10	q-OAc (0.25 eq.)	30%
11	DABCO (2.0 eq.)	18%
12	NEt_3 (2.0 eq.)	19%
13	2,6-lutidine (2.0 eq.)	12%
14	Imidazole (2.0 eq.)	35%
15	Na_2CO_3 (2.0 eq.)	9%
16	DBU (2.0 eq.)	9%
17	**2l** (0.60 mmol)	27%
18	**2l** (0.60 mmol) and DBU (0.5 eq.)	20%
19	**2l** (0.60 mmol) and DBU (0.25 eq.)	38%

Reaction Conditions: **1a** (0.20 mmol), **2l** (0.40 mmol), and DMSO (1.0 mL) were mixed in a Schlenk tube under an argon atmosphere with the blue LEDs irradiation overnight. [a] Determined by ^1H NMR spectroscopy with 1,1,2,2-tetrachloroethane as an internal standard.

3. Mechanistic studies

3.1 UV/vis absorption spectra

Initially, individual absorption spectra of three components *N*-methylquinoxalin-(2*H*)-one (**1a**), *para*-trifluoromethylphenyl oxime ester (**2a**), and DBU were recorded by preparing each 0.05 M in DMSO. Then, the absorption spectra of the all binary mixtures and ternary mixture were also measured in 1:1 or 1:1:1 ratio in a 3-mL quartz cuvette (Figure S2).



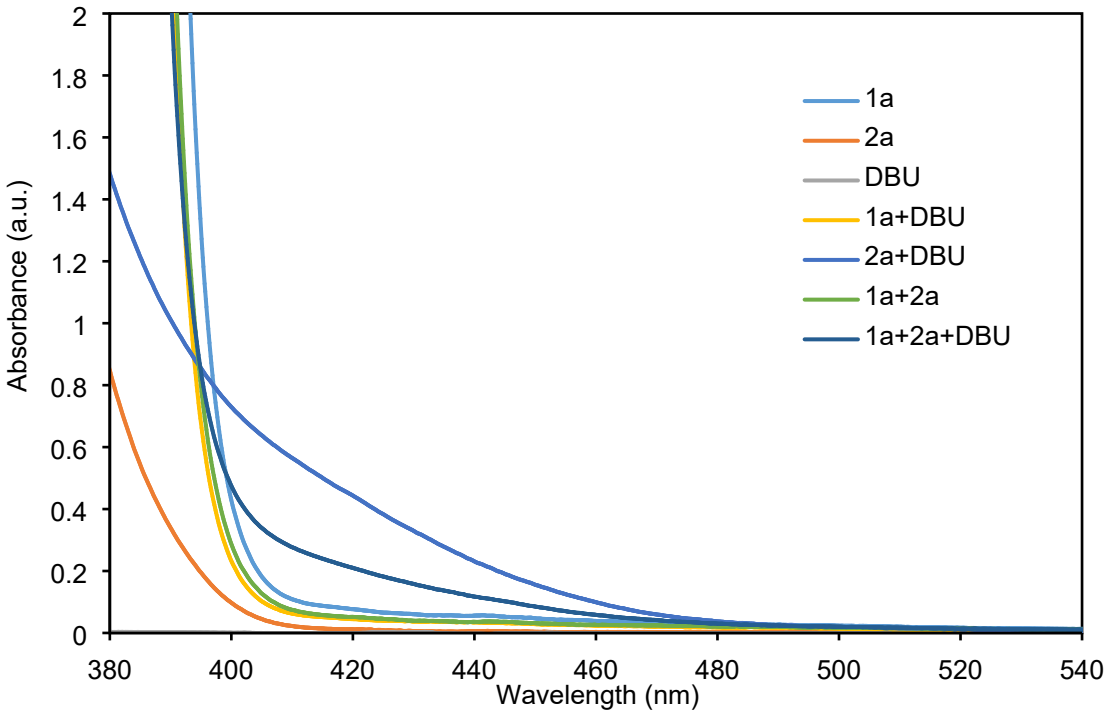


Figure S2 Absorption spectra of individual components, binary and ternary mixture.

3.2 Job's plot

The method of continuous variation (MCV) analysis or Job's plot was carried out following the procedure of Bosque.[1]

Two stock solutions of **2a** and DBU were prepared with a concentration of 0.05 M in DMSO. Seven measurements with various ratio of mixtures were recorded in the amounts shown in Table S2. From absorption spectra of seven measurements (Figure S3), the absorbance at λ = 410 nm was chosen and recorded as a function of the molar fraction of **2a** (χ) as shown in Figure S4. The resulting Job's plot showed the maximum value at χ = 0.5 which indicates the optimal EDA binding stoichiometry is a 1:1 complex between **2a** and DBU.

Table S2 The absorbance of difference solution mixtures.

2a (%)	DBU (%)	Solution of **2a** (mL)	Solution of DBU (mL)	Molar fraction (χ) of **2a**	Abs.
0	100	0.0	3.0	0	0
20	80	0.6	2.4	0.2	0.223339
40	60	1.2	1.8	0.4	0.462124
50	50	1.5	1.5	0.5	0.564858
60	40	1.8	1.2	0.6	0.549804
80	20	2.4	0.6	0.8	0.488458
100	0	3.0	0.0	1.0	0.022410

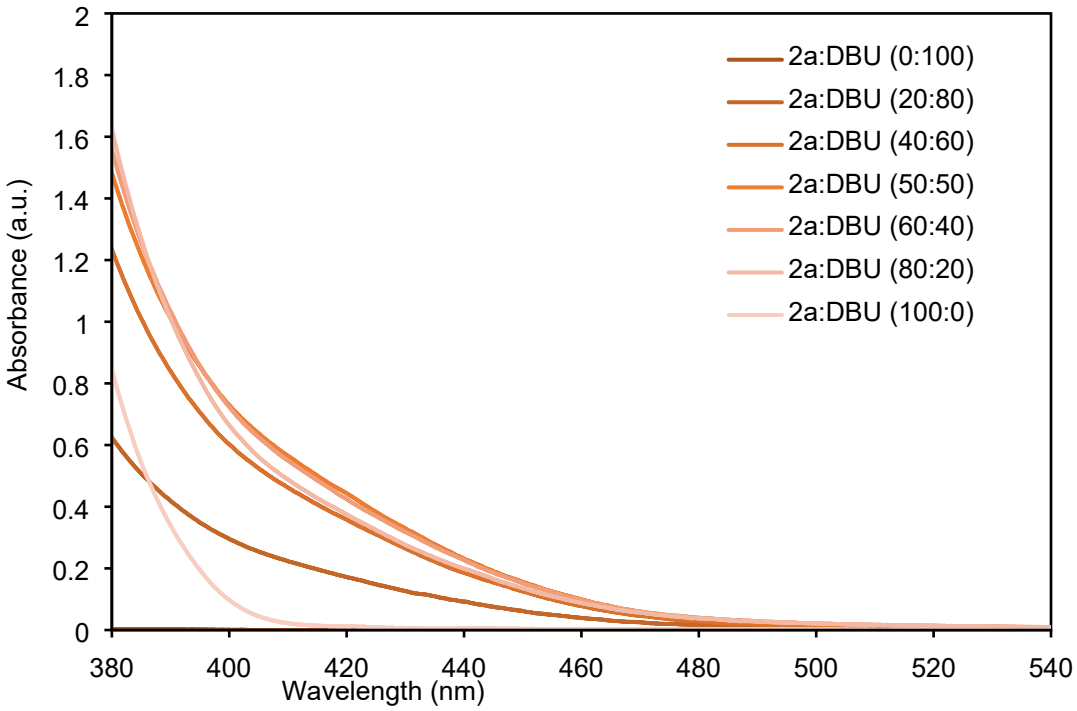


Figure S3 Absorption spectra of mixtures with continuous variation of **2a** and DBU.

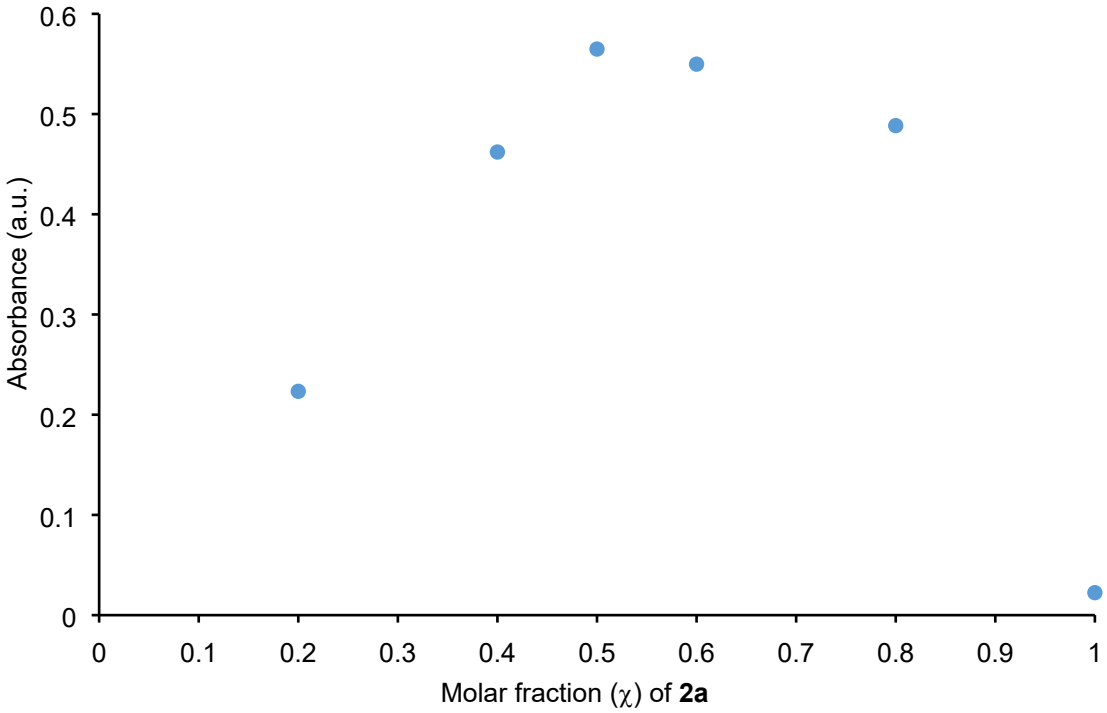


Figure S4 Job's plot of **2a** and DBU at 410 nm.

3.3 Determination of molar absorptivity of EDA complex

The Benesi-Hildebrand-type analysis was carried out following the procedure of Glorious and co-workers.[2]

To a solution of DBU (0.05 M) in DMSO, the varying equivalents of **2a** were added (0.5 – 4.0 eq.). The absorption spectra of the resulting mixtures were measured (Figure S5) and the absorbance at λ = 455 nm was recorded as a function of the concentration of **2a**, which providing a linear relation (Figure S6).

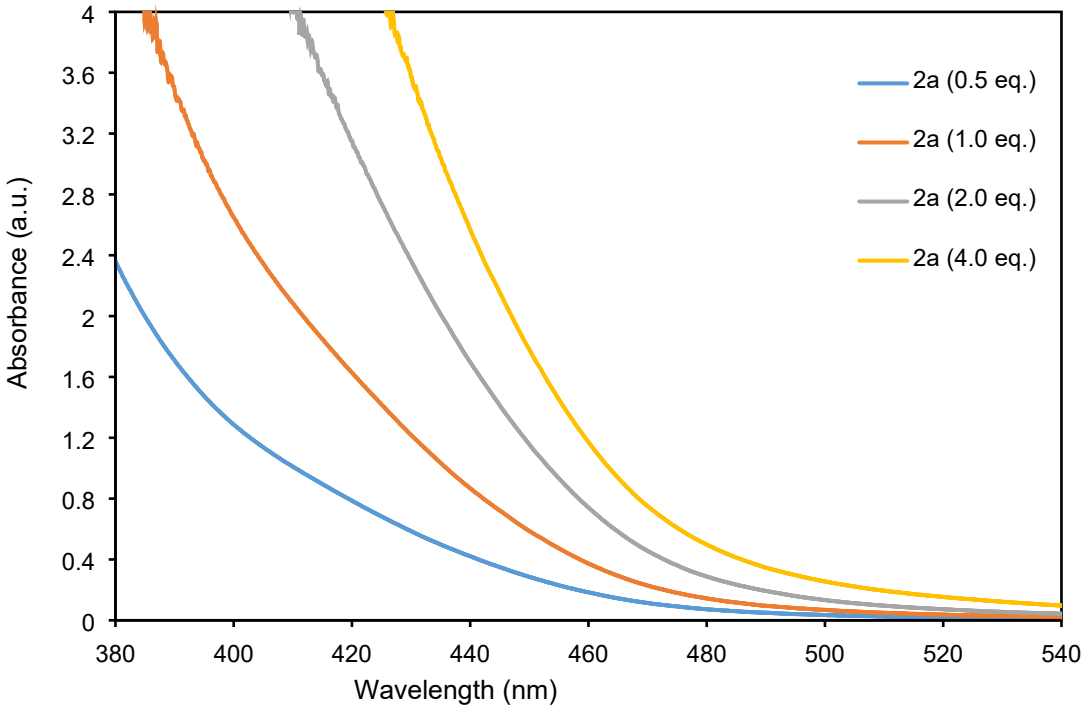


Figure S5 Absorption spectra of mixtures with continuous variation of **2a** and DBU.

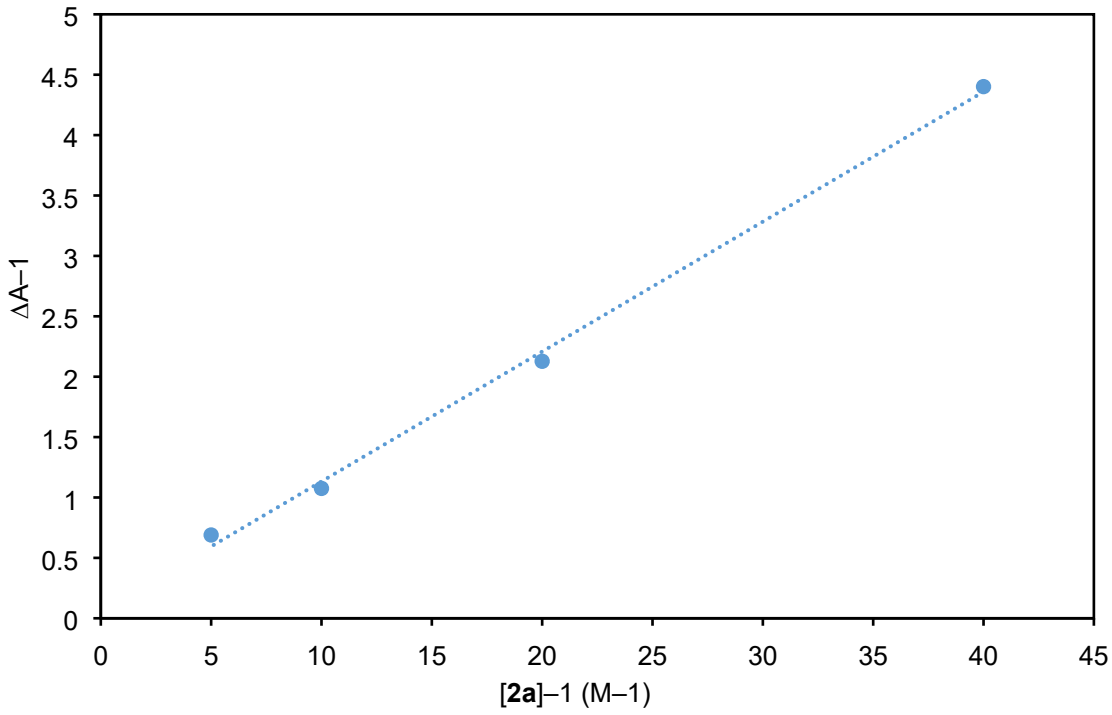
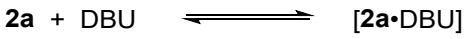


Figure S6 Benesi-Hildebrand-type analysis of the interaction between **2a** and DBU at 455 nm.

On the equilibrium relation



Assuming that the absorption of DBU, compared to that of **2a**, can be neglected at λ = 455 nm; thus $\varepsilon_{\mathbf{2a}} >> \varepsilon_{DBU}$.

From Benesi-Hildebrand equation,

$$\frac{1}{\Delta A} = \frac{1}{d\Delta\varepsilon[2a][DBU]K} + \frac{1}{d\Delta\varepsilon[DBU]}$$

The following equation can be derived,

$$\frac{1}{A - \varepsilon_{2a}[2a]d} = \frac{1}{(\varepsilon_{EDA} - \varepsilon_{2a})d[DBU]K} \cdot \frac{1}{[2a]} + \frac{1}{(\varepsilon_{EDA} - \varepsilon_{2a})d[DBU]}$$

From the linear fitting of the plotted data (Figure S6), the binding constant was calculated to be

$$The\ binding\ energy\ (K) = \frac{Intercept}{Slope} = \frac{0.0569}{0.1076} = 0.529\ M^{-1}$$

According to the absorption spectra of **2a** at C_0 = 0.05 M, the molar extinction coefficient (ε) of the EDA complex at λ = 455 nm can be calculated as:

$$\varepsilon_{EDA}(455\ nm) = \frac{A(455\ nm) - \varepsilon_{2a} \times d \times (C_0 - [EDA])}{[EDA] \times d}$$

$$[EDA] = \frac{[DBU][2a]K}{1 + K[2a]} = \frac{(0.05)(0.05)(0.529)}{1 + (0.529 \times 0.05)} = 0.0013\ M$$

Where;

ε = Molar extinction coefficient (L·mol^{-1}·cm^{-1})

A = Absorbance at λ = 455 nm of EDA complex

d = cuvette path length (cm)

K = binding constant

The required $\varepsilon_{\mathbf{2a}}$·d was determined by the absorption spectra of **2a** to be 0.00571 M^{-1}; therefore,

$\varepsilon_{EDA(455\ nm)}$ = 365.0 L·mol^{-1}·cm^{-1}

3.4 Quantum yield

The quantum yield of the reaction was measured following the previous protocol by using chemical actinometry (potassium ferrioxalate) with blue LEDs at λ_{max} = 438 nm.[3]

To prepare the 0.15 M solution of potassium ferrioxalate, 1.85 g of potassium ferrioxalate trihydrate was dissolved in H_2SO_4 (25 mL, 0.05 M) and placed in the dark. A buffer solution was prepared by dissolving 2.50 g of sodium acetate 2.50 g and 0.5 mL of conc. H_2SO_4 0.50 mL in 50 mL of distilled water.

General procedure to determine the photon flux of blue LEDs (438 nm)

To a 10 mL Schlenk tube with magnetic bar, the ferrioxalate solution (1 mL, 0.15 M) was added and irradiated for 60 s under 2 × 8 W blue LEDs. After that, a 100 µL of irradiated ferrioxalate solution was taken to a 10 mL volumetric flask containing 15 mg of 1,10-phenanthroline in 3 mL of the buffer solution, and diluting with water to a final volume of 10 mL. The absorption at 510 nm of the obtained solution was determined by UV-vis spectrophotometry. In a similar manner, the experiment with ferrioxalate solution without the irradiation was carried out. The number of moles of Fe^{2+} generated from photoredox reaction could be determined by Beer's law as shown below.

$$mol\left(Fe^{2+}\right) = \frac{v_1 v_3 \Delta A\ (510\ nm)}{10^3 v_2 l \varepsilon\ (510\ nm)} = \frac{1\ mL \times 10\ mL \times 3.09}{10^3 \times 100\ \mu L \times 1\ cm \times 11{,}100\ L\ mol^{-1} cm^{-1}}$$

$$= 2.79 \times 10^{-5}\ mol$$

Where;

v_1 = Irradiated volume (1 mL)

v_2 = The aliquot taken for the estimation of Fe^{2+} ions (100 µL)

v_3 = Final volume after complexation with 1,10-phenanthroline (10 mL)

ΔA(510 nm) = absorbance difference between the irradiated solution and the solution stored in the dark (3.09)

l = cuvette path length (1 cm)

ε(510 nm) = Molar extinction coefficient of $[Fe(Phen)_3]^{2+}$ (11,100 L $mol^{-1}cm^{-1}$)

The photo flux (F) at 438 nm is obtained by using the following equation:

$$\Phi\ (438\ nm) = \frac{mol\ (Fe^{2+})}{F\left(1 - 10^{-A(438\ nm)}\right)t}$$

Where;

Φ(438 nm) = The quantum yield for Fe^{2+} formation at 438 nm (1.01)

F = Photon flux

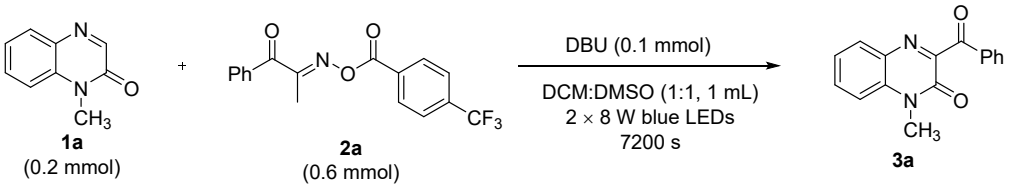
A(438 nm) = ferrioxalate actinometer absorbance at 438 nm (2.31)

t = the reaction time (60 s)

Therefore;

$$F = \frac{mol\left(Fe^{2+}\right)}{\Phi\,(438\,nm)\left(1 - 10^{-A(438\,nm)}\right)t}$$

$$F = \frac{2.79 \times 10^{-5}\,mol}{1.01 \times \left(1 - 10^{-2.31}\right) \times 60\,s} = 4.62 \times 10^{-7}\,einsteins/s$$



1a (0.2 mmol) + **2a** (0.6 mmol) → **3a**

To obtain the quantum yield (Φ) of the photoinduced acylation. The moles of the product **3a** formed for the model reaction were determined by ^{1}H NMR spectroscopy using 1,1,2,2,-tetrachloroethane as internal standard. After the reaction was carried out for 7200 s, 1.038 × 10^{-4} moles of **3a** were obtained. The quantum yield of this reaction was calculated using the following equation:

$$\Phi\,(438\,nm) = \frac{mol\ of\ product}{F\left(1 - 10^{-A(438\,nm)}\right)t}$$

$$\Phi\,(438\,nm) = \frac{1.04 \times 10^{-4}\,mol}{4.62 \times 10^{-7}\,einsteins\,s^{-1} \times \left(1 - 10^{-1.538}\right) \times 7200\,s} = 0.032$$

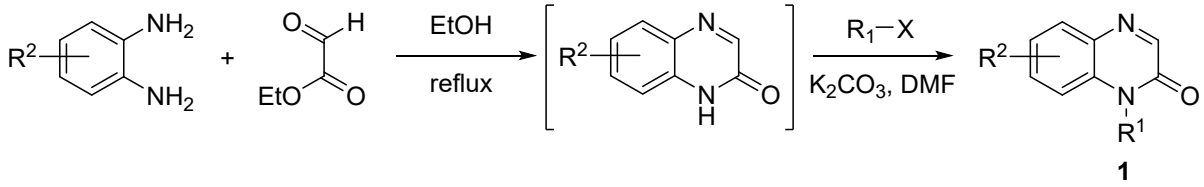
Where;

A(438 nm) = The absorbance at 438 nm of the reaction mixture which measured in a 1 cm cuvette (1.538)

t = the reaction time (7200 s)

4. Synthesis of the compounds

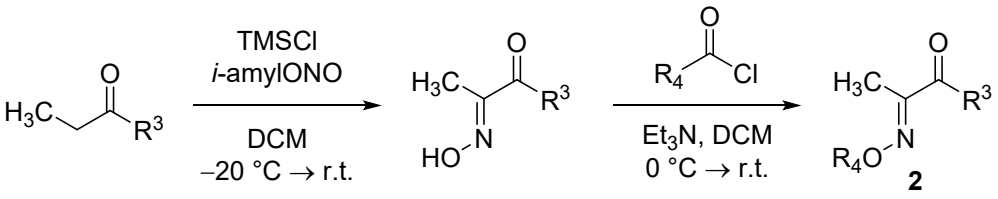
General procedure for the preparation of quinoxalinones (1).



Quinoxalin-2(1*H*)-ones **1** were prepared from 1,2-phenylenediamines following the procedure of Wang and co-workers.[4] To a solution of 1,2-phenylenediamine (5.0 mmol, 1.0 eq.) in ethanol (40 mL), was added ethyl glyoxylate (6.0 mmol, 47% in toluene, 1.2 eq.). The resulting reaction mixture was stirred at reflux. After the reaction was complete by monitoring with TLC, the reaction mixture was filtered and washed with ethanol. The obtained solid was dried *in vacuo* and used in the next step without further purification.

To a solution of quinoxalinone crude, K_2CO_3 (6.0 mmol, 1.2 eq.) in DMF (16 mL), was added the corresponding haloalkane (8.0 mmol, 1.6 eq.). The reaction mixture was stirred at room temperature for an overnight. Brine (50 mL) was added and the aqueous phase was extracted with EtOAc (3 × 50 mL). Combined organic phase was washed with a saturated aqueous NH_4Cl solution (50 mL), brine (50 mL), dried over Na_2SO_4, and concentrated *in vacuo*. Purification of the crude by column chromatography gave the desired product.

General procedure for the preparation of oxime esters (2).

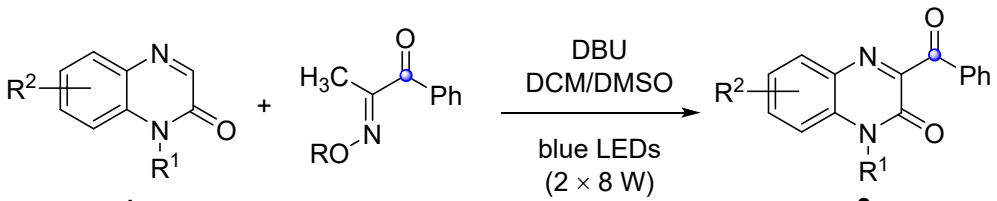


Oxime esters **2** were prepared from corresponding ketones following the procedure of Huang and co-workers.[5] To a solution of ketone (5.0 mmol, 1.0 eq.) in DCM (5 mL) at –20 °C, were added TMSCl (5.0 mmol, 1.0 eq.) and isoamyl nitrite (5.0 mmol, 1.0 eq.) dropwise. The reaction mixture was warmed to room temperature, stirred for 1 h, and concentrated *in vacuo*. Purification of the crude by column chromatography gave the corresponding oxime.

To a solution of oxime and Et_3N (7.5 mmol, 1.5 eq.) in DCM (20 mL) at 0 °C, was added the corresponding acid chloride (6.0 mmol, 1.2 eq.) dropwise. The reaction mixture was warmed to room temperature and stirred for an overnight. Saturated aqueous $NaHCO_3$ solution (20 mL) was added and the aqueous phase was extracted with EtOAc (3 × 50 mL). Combined organic phase was washed with H_2O (20 mL), brine (20 mL), dried over Na_2SO_4, and

concentrated *in vacuo*. Purification of the crude by column chromatography gave the corresponding oxime ester.

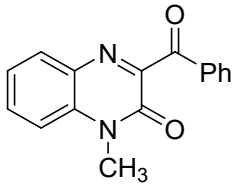
General procedure for the synthesis of compounds 3.



1 **2a**, R = 4-$CF_3C_6H_4CO$ **3**

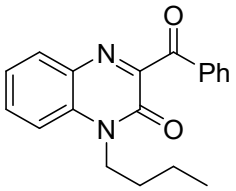
Under Ar atmosphere, a Schlenk tube was charged with quinoxalinone **1** (0.20 mmol, 1.0 eq.), oxime ester **2** (0.60 mmol, 3.0 eq.), DBU (0.10 mmol, 0.5 eq.), DCM (0.5 mL) and DMSO (0.5 mL). The reaction mixture was degassed by ultra-sonication for 30 s and stirred overnight under the irradiation of blue LEDs (8 W × 2, at approximately 2 – 3 cm away from the light source, ca. 35 °C). Saturated aqueous $NaHCO_3$ solution (5 mL) was added and the aqueous phase was extracted with EtOAc (3 × 5 mL). Combined organic phase was washed with water (10 mL) and brine (10 mL), dried over Na_2SO_4, and concentrated *in vacuo*. Purification of the crude by column chromatography gave the desired product.

Scope of quinoxalinones

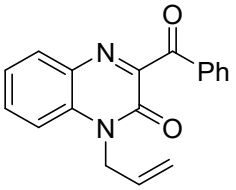


*3-Benzoyl-1-methylquinoxalin-2(1H)-one (**3aa**).* Flash column chromatography [EtOAc:DCM (0:100 – 5:95)]; Yellow solid (86%, 46 mg). R_f = 0.7 (EtOAc:DCM, 5:95). ^{1}H NMR (300 MHz, Chloroform-*d*) δ 8.07 – 7.91 (m, 3H), 7.78 – 7.59 (m, 2H), 7.57 – 7.39 (m, 4H), 3.78 (s, 3H). ^{13}C NMR (75 MHz, Chloroform-*d*) δ 191.8, 154.7, 153.3, 134.9, 134.3, 133.9, 132.2, 132.1, 131.0, 130.0, 128.7, 124.2, 114.0, 29.1. HRMS (ESI+) calcd for $C_{16}H_{13}O_2N_2$ $[M+H]^+$: 265.0972, found 265.0968. Spectroscopic data were consistent with those reported in the literature.[6]

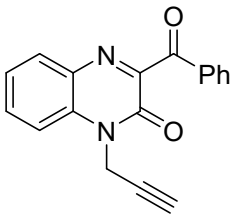
For large-scale synthesis. According to the general procedure, *N*-methyl-quinoxalin-2(1*H*)-one **1a** (320 mg, 2.00 mmol), phenyl oxime ester **2a** (2.01 g, 6.00 mmol), DBU (0.15 mL, 1.00 mmol), anhydrous DCM (5 mL) and DMSO (5 mL) were used. The product **3aa** was obtained in 85% yield (451 mg).



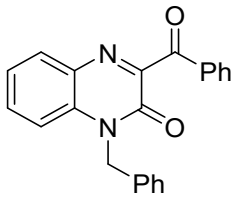
*3-Benzoyl-1-butylquinoxalin-2(1H)-one (**3ba**).* Flash column chromatography [EtOAc:hexanes (1:4)]; Dark yellow solid (99%,62 mg). R_f = 0.25 (EtOAc:hexanes, 1:4). ^{1}H NMR (300 MHz, Chloroform-*d*) δ 8.03 – 7.98 (m, 2H), 7.97 – 7.93 (m, 1H), 7.74 – 7.59 (m, 2H), 7.53 – 7.47 (m, 2H), 7.46 – 7.39 (m, 2H), 4.40 – 4.24 (m, 2H), 1.85 – 1.77 (m, 2H), 1.57 – 1.47 (m, 2H), 1.02 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (75 MHz, Chloroform-*d*) δ 192.0, 154.8, 153.1, 134.9, 134.2, 133.2, 132.5, 131.9, 131.3, 130.0, 128.7, 124.0, 114.0, 42.2, 29.3, 20.3, 13.8. IR (ν/cm^{-1}) 2962, 2932, 2875, 1682, 1646, 1602, 1467, 1169, 914, 757. HRMS (ESI+) calcd for $C_{19}H_{19}O_2N_2$ [M+H]$^+$: 307.1441, found 307.1437. Spectroscopic data were consistent with those reported in the literature.[6]



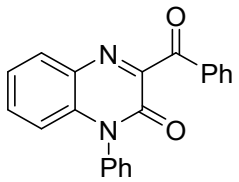
*1-Allyl-3-benzoylquinoxalin-2(1H)-one (**3ca**).* Flash column chromatography [EtOAc:hexanes (1:4)]; Yellow solid (93%, 54 mg). R_f = 0.16 (EtOAc:hexanes, 1:4). ^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.03 – 7.99 (m, 2H), 7.96 (dd, *J* = 8.2, 1.6 Hz, 1H), 7.69 – 7.62 (m, 2H), 7.54 – 7.48 (m, 2H), 7.45 – 7.39 (m, 2H), 5.98 (ddt, *J* = 17.2, 10.5, 5.3 Hz, 1H), 5.40 – 5.24 (m, 1H), 4.97 (dt, *J* = 5.5, 1.7 Hz, 2H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 191.7, 154.7, 152.9, 134.9, 134.3, 133.2, 132.4, 132.0, 131.1, 130.3, 130.0, 128.7, 124.2, 118.8, 114.6, 44.5. HRMS (ESI+) calcd for $C_{18}H_{15}O_2N_2$ [M+H]$^+$: 291.1128, found 291.1124. Spectroscopic data were consistent with those reported in the literature.[6]



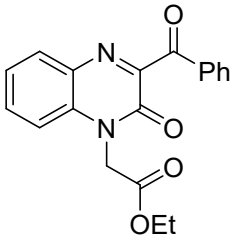
*3-Benzoyl-1-(prop-2-yn-1-yl)quinoxalin-2(1H)-one (**3da**).* Flash column chromatography [EtOAc:hexanes (1:4)]; Yellow solid (84%, 46 mg). R_f = 0.21 (EtOAc:hexanes, 1:4). ^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.05 – 8.00 (m, 2H), 8.00 – 7.95 (m, 1H), 7.77 – 7.71 (m, 1H), 7.69 – 7.62 (m, 1H), 7.62 – 7.58 (m, 1H), 7.56 – 7.45 (m, 3H), 5.12 (d, *J* = 2.5 Hz, 2H), 2.36 (t, *J* = 2.5 Hz, 1H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 191.3, 154.4, 152.3, 134.7, 134.3, 132.4, 132.4, 132.2, 131.2, 130.1, 128.7, 124.6, 114.6, 76.3, 73.8, 31.4. IR (ν/cm^{-1}) 3264, 1651, 1600, 1581, 1466, 1258, 1160, 758, 682. HRMS (ESI+) calcd for $C_{18}H_{13}O_2N_2$ $[M+H]^+$: 289.0972, found 289.0962. Spectroscopic data were consistent with those reported in the literature.[6]



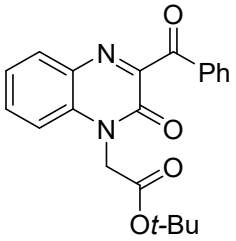
*3-Benzoyl-1-benzylquinoxalin-2(1H)-one (**3ea**).* Flash column chromatography [EtOAc:hexanes (1:4)]; Yellow solid (91%, 62 mg). R_f = 0.17 (EtOAc:hexanes, 1:4). ^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.07 – 8.03 (m, 2H), 7.98 – 7.93 (m, 1H), 7.69 – 7.63 (m, 1H), 7.62 – 7.50 (m, 3H), 7.42 – 7.27 (m, 7H), 5.56 (s, 2H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 191.7, 154.8, 153.5, 134.9, 134.9, 134.3, 133.3, 132.5, 132.0, 131.2, 130.0, 129.1, 128.8, 128.0, 127.2, 124.3, 114.8, 45.9. HRMS (ESI+) calcd for $C_{22}H_{17}O_2N_2$ $[M+H]^+$: 341.1284, found 341.1282. Spectroscopic data were consistent with those reported in the literature.[6]



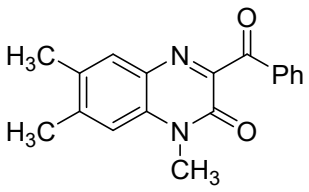
*3-Benzoyl-1-phenylquinoxalin-2(1H)-one (**3fa**).* Flash column chromatography [EtOAc:hexanes (1:4)]; Yellow solid (94%, 61 mg). R_f = 0.20 (EtOAc:hexanes, 1:4). ^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.09 – 8.04 (m, 2H), 8.01 – 7.96 (m, 1H), 7.68 – 7.61 (m, 3H), 7.61 – 7.55 (m, 1H), 7.55 – 7.45 (m, 3H), 7.44 – 7.35 (m, 3H), 6.84 – 6.79 (m, 1H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 191.6, 155.4, 153.0, 134.9, 134.9, 134.8, 134.3, 132.1, 131.7, 130.6, 130.4, 130.1, 129.8, 128.7, 128.3, 124.4, 115.8. HRMS (ESI+) calcd for $C_{21}H_{15}O_2N_2$ $[M+H]^+$: 327.1128, found 327.1123. Spectroscopic data were consistent with those reported in the literature.[6]



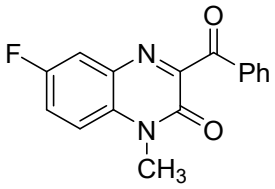
*Ethyl 2-(3-benzoyl-2-oxoquinoxalin-1(2H)-yl)acetate (**3ga**).* Flash column chromatography [EtOAc:hexanes (1:1)]; Yellow solid (79%, 54 mg). R_f = 0.09 (EtOAc:hexanes, 1:4). ^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.06 – 7.92 (m, 3H), 7.72 – 7.60 (m, 2H), 7.55 – 7.48 (m, 2H), 7.47 – 7.41 (m, 1H), 7.19 (dd, *J* = 8.5, 1.1 Hz, 1H), 5.09 (s, 2H), 4.28 (q, *J* = 7.2 Hz, 2H), 1.30 (d, *J* = 7.2 Hz, 3H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 191.3, 166.7, 154.5, 152.9, 134.8, 134.3, 133.1, 132.3, 132.3, 131.4, 130.1, 128.7, 124.5, 113.5, 62.3, 43.3, 14.1. HRMS (ESI+) calcd for $C_{19}H_{17}O_4N_2$ $[M+H]^+$: 337.1183, found 337.1177. Spectroscopic data were consistent with those reported in the literature.[6]



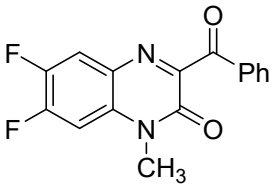
*tert-Butyl 2-(3-benzoyl-2-oxoquinoxalin-1(2H)-yl)acetate (**3ha**).* Flash column chromatography [MeOH:DCM (0:100 – 1:99)]; Yellow solid (28%, 21 mg). R_f = 0.62 (DCM). ^{1}H NMR (300 MHz, Chloroform-*d*) δ 8.04 – 7.95 (m, 3H), 7.70 – 7.62 (m, 2H), 7.54 – 7.48 (m, 2H), 7.47 – 7.41 (m, 1H), 7.19 (dd, *J* = 8.5, 1.1 Hz, 1H), 5.00 (s, 2H), 1.49 (s, 9H). ^{13}C NMR (75 MHz, Chloroform-*d*) δ 191.4, 165.7, 154.5, 152.9, 134.8, 134.3, 133.2, 132.3, 132.1, 131.3, 130.1, 128.7, 124.4, 113.5, 83.5, 44.0, 28.0. IR (ν/cm^{-1}) 2977, 1739, 1682, 1652, 1368, 1233, 1150, 909, 755. HRMS (ESI+) calcd for $C_{21}H_{22}O_4N_2$ $[M+H]^+$: 365.1496, found 365.1484. Spectroscopic data were consistent with those reported in the literature.[6]



*3-Benzoyl-1,6,7-trimethylquinoxalin-2(1H)-one (**3ja**).* Flash column chromatography [EtOAc:DCM (5:95 – 10:90)]; Yellow solid (74%, 43 mg). R_f = 0.42 (EtOAc:DCM, 5:95). ^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.02 – 7.98 (m, 2H), 7.69 (s, 1H), 7.66 – 7.60 (m, 1H), 7.52 – 7.46 (m, 2H), 7.19 (s, 1H), 3.75 (s, 3H), 2.49 (s, 3H), 2.38 (s, 3H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 192.0, 153.5, 153.3, 142.5, 135.1, 134.1, 133.4, 132.0, 131.0, 130.7, 130.1, 128.6, 114.5, 29.0, 20.8, 19.2. HRMS (ESI+) calcd for $C_{18}H_{17}O_2N_2$ $[M+H]^+$: 293.1284, found 293.1279. Spectroscopic data were consistent with those reported in the literature.[6]

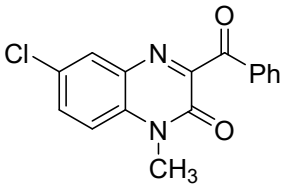


*3-Benzoyl-6-fluoro-1-methylquinoxalin-2(1H)-one (**3ka**)*. Flash column chromatography [EtOAc:DCM (5:95 – 10:90)]; Yellow solid (73%, 41 mg). R_f = 0.31 (EtOAc:DCM, 5:95). ^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.01 – 7.97 (m, 2H), 7.68 – 7.62 (m, 2H), 7.54 – 7.48 (m, 2H), 7.48 – 7.43 (m, 1H), 7.43 – 7.38 (m, 1H), 3.77 (s, 3H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 191.4, 158.9 (d, $J_{C–F}$ = 246 Hz), 156.1, 153.0, 134.6, 134.4, 132.8 (d, $J_{C–F}$ = 11 Hz), 130.6, (d, $J_{C–F}$ = 2 Hz), 130.0, 128.8, 119.9 (d, $J_{C–F}$ = 24 Hz), 116.3 (d, $J_{C–F}$ = 23 Hz), 115.2 (d, $J_{C–F}$ = 8 Hz), 29.3. ^{19}F NMR (564 MHz, Chlorofrom-*d*) δ –117.7. HRMS (ESI+) calcd for $C_{16}H_{12}O_2N_2F$ $[M+H]^+$: 283.0877, found 283.0873. Spectroscopic data were consistent with those reported in the literature.[6]

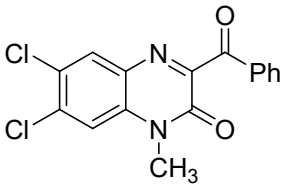


*3-Benzoyl-6,7-difluoro-1-methylquinoxalin-2(1H)-one (**3la**).* Flash column chromatography [EtOAc:DCM (5:95 – 10:90)]; Yellow solid (45%, 27 mg). R_f = 0.64 (EtOAc:DCM, 5:95). ^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.00 – 7.95 (m, 2H), 7.76 (dd, *J* = 9.8, 8.1 Hz, 1H), 7.66 (tt, *J* = 7.3, 1.4 Hz, 1H), 7.54 – 7.49 (m, 2H), 7.23 (dd, *J* = 11.1, 6.9 Hz, 1H), 3.73 (s, 3H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 191.1, 155.0 (d, $J_{C–F}$ = 4 Hz), 152.9, 152.7 (dd, $J_{C–F}$ = 257, 14 Hz), 147.0 (dd, $J_{C–F}$ = 249, 14 Hz), 134.6, 134.5, 131.4 (d, $J_{C–F}$ = 9 Hz), 130.0, 128.4 (dd, $J_{C–F}$ = 9, 3 Hz), 118.6 (dd, $J_{C–F}$ = 18, 3 Hz), 102.8 (d, $J_{C–F}$ = 23 Hz), 29.6. ^{19}F NMR (564 MHz,

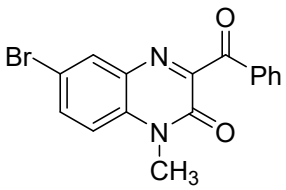
Chlorofrom-*d*) δ –127.1, –140.5. HRMS (ESI+) calcd for $C_{16}H_{11}O_2N_2F_2$ $[M+H]^+$: 301.0783, found 301.0779. Spectroscopic data were consistent with those reported in the literature.[6]



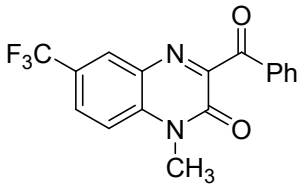
*3-Benzoyl-6-chloro-1-methylquinoxalin-2(1H)-one (**3ma**).* Flash column chromatography [EtOAc:DCM (5:95 – 10:90)]; Yellow solid (47%, 28 mg). R_f = 0.51 (EtOAc:DCM, 5:95). ^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.01 – 7.96 (m, 2H), 7.94 (d, *J* = 2.4 Hz, 1H), 7.69 – 7.62 (m, 2H), 7.54 – 7.48 (m, 2H), 7.37 (d, *J* = 9.0 Hz, 1H), 3.75 (s, 3H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 191.3, 155.9, 153.0, 134.6, 134.4, 132.7, 132.6, 132.0, 130.2, 130.0, 129.7, 128.8, 115.2, 29.3. HRMS (ESI+) calcd for $C_{16}H_{12}O_2N_2{}^{35}Cl$ $[M+H]^+$: 299.0582, found 299.0578. Spectroscopic data were consistent with those reported in the literature.[6]



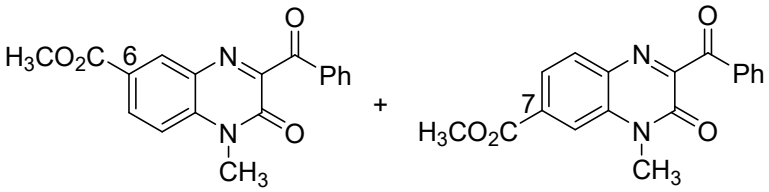
*3-Benzoyl-6,7-dichloro-1-methylquinoxalin-2(1H)-one (**3na**).* Flash column chromatography [EtOAc:DCM (2:98 – 5:95)]; Yellow solid (79%, mg). R_f = 0.60 (EtOAc:DCM, 5:95). ^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.02 (s, 1H), 8.00 – 7.95 (m, 2H), 7.69 – 7.63 (m, 1H), 7.56 – 7.47 (m, 3H), 3.72 (s, 3H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 191.0, 155.8, 152.7, 136.4, 134.5, 134.5, 133.2, 131.7, 131.1, 130.0, 128.8, 128.2, 115.6, 29.4. HRMS (ESI+) calcd for $C_{16}H_{11}O_2N_2{}^{35}Cl_2$ $[M+H]^+$: 333.0192, found 333.0186. Spectroscopic data were consistent with those reported in the literature.[6]



*3-Benzoyl-6-bromo-1-methylquinoxalin-2(1H)-one (**3oa**).* Flash column chromatography [EtOAc:DCM (5:95)]; Yellow solid (59%, 40 mg). R_f = 0.65 (EtOAc:DCM, 5:95). ^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.09 (d, *J* = 2.3 Hz, 1H), 8.01 – 7.96 (m, 2H), 7.77 (dd, *J* = 8.9, 2.3 Hz, 1H), 7.68 – 7.63 (m, 1H), 7.54 – 7.48 (m, 2H), 7.31 (d, *J* = 9.0 Hz, 1H), 3.75 (s, 3H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 191.2, 155.8, 153.0, 134.8, 134.6, 134.5, 133.3, 133.0, 132.9, 130.0, 128.8, 116.8, 115.5, 29.3. HRMS (ESI+) calcd for $C_{16}H_{12}O_2N_2{}^{78}Br$ $[M+H]^+$: 343.0077, found 343.0072. Spectroscopic data were consistent with those reported in the literature.[6]

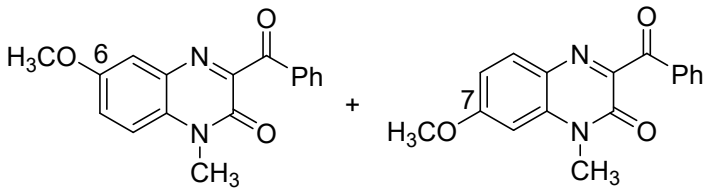


*3-Benzoyl-1-methyl-6-(trifluoromethyl)quinoxalin-2(1H)-one (**3pa**).* Flash column chromatography [EtOAc:DCM (5:95 – 10:90)]; Dark yellow solid (87%, 58 mg). R_f = 0.50 (EtOAc:DCM, 5:95). ^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.23 – 8.20 (m, 1H), 8.01 – 7.97 (m, 2H), 7.92 – 7.88 (m, 1H), 7.69 – 7.63 (m, 1H), 7.56 – 7.49 (m, 3H), 3.79 (s, 3H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 191.0, 156.1, 153.1, 136.2, 134.6, 134.5, 131.5, 130.0, 128.8, 128.4 (q, $J_{C–F}$ = 4 Hz), 128.3 (q, $J_{C–F}$ = 3.5 Hz), 126.6 (q, $J_{C–F}$ = 34 Hz), 123.5 (q, $J_{C–F}$ = 272 Hz), 29.4. ^{19}F NMR (564 MHz, Chlorofrom-*d*) δ –62.2. HRMS (ESI+) calcd for $C_{17}H_{12}O_2N_2F_3$ $[M+H]^+$: 333.0845, found 333.0840. Spectroscopic data were consistent with those reported in the literature.[6]

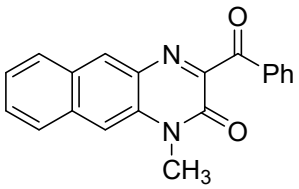


Methyl 2-benzoyl-4-methyl-3-oxo-3,4-dihydroquinoxaline-6-carboxylate (**3qa**) and *methyl 2-benzoyl-4-methyl-3-oxo-3,4-dihydroquinoxaline-7-carboxylate* (**3qa'**). Flash column chromatography [EtOAc:DCM (5:95 – 10:90)]; Yellow solid (94%, 61 mg, 66:34 ratio). m.p. 134 – 139 °C (DCM). R_f = 0.59 (EtOAc:DCM, 5:95). ^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.59 (d, *J* = 2.0 Hz, 0.34H), 8.31 (dd, *J* = 8.8, 2.0 Hz, 0.34H), 8.11 (d, *J* = 1.7 Hz, 0.66H), 8.08 – 7.93 (m, 3.31H), 7.71 – 7.60 (m, 1H), 7.54 – 7.42 (m, 2.31H), 4.02 (s, 2H), 3.97 (s, 1H), 3.80 (s, 2H), 3.78 (s, 1H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 191.4, 191.1, 165.8, 165.8, 165.7,

156.9, 155.4, 153.2, 153.1, 137.1, 134.7, 134.6, 134.5, 134.5, 134.4, 133.7, 132.8, 132.7, 132.6, 131.5, 131.1, 130.0, 130.0, 128.8, 128.8, 126.1, 124.7, 115.7, 114.2, 52.9, 52.5, 29.4, 29.3. IR (ν/cm^{-1}) 2952, 2850, 1703, 1681, 1654, 1441, 1271, 1226, 787, 738. HRMS (ESI+) calcd for $C_{18}H_{15}O_4N_2$ $[M+H]^+$: 323.1026, found 323.1021.

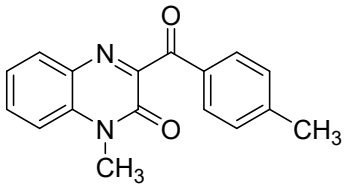


*3-Benzoyl-6-methoxy-1-methylquinoxalin-2(1H)-one (**3ra**) and 3-benzoyl-7-methoxy-1-methylquinoxalin-2(1H)-one (**3ra'**).* Flash column chromatography [EtOAc:DCM (10:90)]; Yellow solid (68%, 40 mg, 79:21 ratio). R_f = 0.44 (EtOAc:DCM, 10:90). m.p. 154 – 158 °C (DCM). ^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.05 – 7.95 (m, 2H), 7.84 (d, *J* = 8.9 Hz, 0.21H), 7.67 – 7.59 (m, 1H), 7.54 – 7.46 (m, 2H), 7.41 – 7.38 (m, 0.79H), 7.37 – 7.29 (m, 1.56H), 6.99 (dd, *J* = 8.9, 2.5 Hz, 0.21H), 6.79 (d, *J* = 2.6 Hz, 0.21H), 3.98 (s, 0.63H), 3.89 (s, 2.36H), 3.75 (s, 2.36H), 3.72 (s, 0.63H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 191.9, 162.8, 156.3, 155.1, 153.7, 153.0, 150.7, 135.8, 135.3, 134.9, 134.2, 134.0, 133.0, 132.5, 130.1, 130.0, 128.7, 128.6, 128.2, 127.1, 121.6, 114.9, 111.9, 111.7, 56.0, 55.8, 29.2, 29.1. IR (ν/cm^{-1}) 2920, 2848, 1677, 1636, 1499, 1366, 1266, 1163, 1027, 724, 646. HRMS (ESI+) calcd for $C_{17}H_{15}O_3N_2$ $[M+H]^+$: 295.1077, found 295.1072.

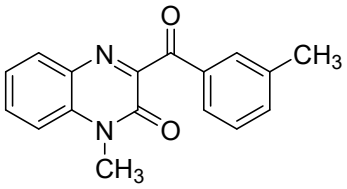


*3-Benzoyl-1-methylbenzo[g]quinoxalin-2(1H)-one (**3sa**)*. Flash column chromatography [EtOAc:DCM (5:95 – 10:90)]; Yellow solid (69%, 44 mg). R_f = 0.48 (EtOAc:DCM, 5:95). ^{1}H NMR (300 MHz, Chloroform-*d*) δ 8.47 (s, 1H), 8.08 – 8.03 (m, 2H), 8.03 – 7.95 (m, 2H), 7.72 (s, 1H), 7.69 – 7.63 (m, 2H), 7.58 – 7.50 (m, 3H), 3.83 (s, 3H). ^{13}C NMR (75 MHz, Chloroform-*d*) δ 191.7, 155.2, 153.2, 134.8, 134.6, 134.3, 131.7, 131.4, 130.9, 130.1, 129.8, 128.8, 128.8, 128.8, 127.3, 125.8, 110.5, 29.0. HRMS (ESI+) calcd for $C_{20}H_{15}O_2N_2$ $[M+H]^+$: 315.1128, found 315.1122. Spectroscopic data were consistent with those reported in the literature.[6]

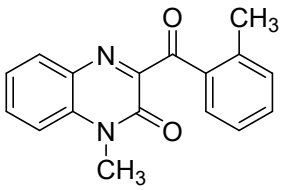
Scope of acyl oxime ester



*1-Methyl-3-(4-methylbenzoyl)quinoxalin-2(1H)-one (**3ab**)*. Flash column chromatography [EtOAc:DCM (5:95)]; Yellow solid (75%, 42 mg). R_f = 0.49 (EtOAc:DCM, 5:95). ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.97 – 7.93 (m, 1H), 7.92 – 7.88 (m, 2H), 7.72 – 7.66 (m, 1H), 7.47 – 7.40 (m, 2H), 7.32 – 7.28 (m, 2H), 3.77 (s, 3H), 2.45 (s, 3H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 191.4, 155.0, 153.4, 145.4, 133.9, 132.4, 132.2, 132.0, 131.0, 130.2, 129.4, 124.2, 114.0, 29.1, 21.9. HRMS (ESI+) calcd for $C_{17}H_{15}O_2N_2$ $[M+H]^+$: 279.1128, found 279.1125. Spectroscopic data were consistent with those reported in the literature.[6]

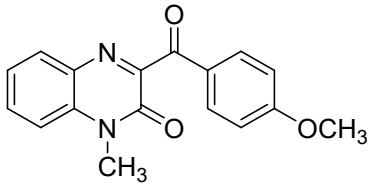


*1-Methyl-3-(3-methylbenzoyl)quinoxalin-2(1H)-one (**3ac**)*. Flash column chromatography [EtOAc:DCM (5:95)]; Yellow solid (99%, 56 mg). R_f = 0.47 (EtOAc:DCM, 5:95). ^{1}H NMR (300 MHz, Chloroform-*d*) δ 8.00 – 7.91 (m, 1H), 7.85 – 7.64 (m, 3H), 7.51 – 7.33 (m, 4H), 3.78 (s, 3H), 2.42 (s, 3H). ^{13}C NMR (75 MHz, Chloroform-*d*) δ 192.1, 155.0, 153.4, 138.6, 135.1, 134.9, 133.9, 132.3, 132.0, 131.0, 130.3, 128.6, 127.4, 124.2, 114.0, 29.1, 21.3. HRMS (ESI+) calcd for $C_{17}H_{15}O_2N_2$ $[M+H]^+$: 279.1128, found 279.1127. Spectroscopic data were consistent with those reported in the literature.[6]

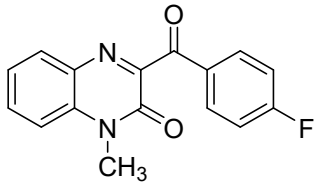


*1-Methyl-3-(2-methylbenzoyl)quinoxalin-2(1H)-one (**3ad**).* Flash column chromatography [EtOAc:DCM (5:95 – 10:90)]; Yellow solid (60%, 33 mg). R_f = 0.31 (EtOAc:DCM, 5:95). ^{1}H

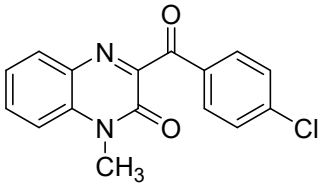
NMR (300 MHz, Chloroform-*d*) δ 7.98 – 7.89 (m, 1H), 7.74 – 7.58 (m, 2H), 7.54 – 7.31 (m, 4H), 7.28 – 7.19 (m, 1H), 3.76 (s, 3H), 2.71 (s, 3H). ^{13}C NMR (75 MHz, Chloroform-*d*) δ 194.0, 155.7, 153.4, 140.8, 134.3, 133.9, 132.9, 132.3, 132.3, 132.0, 131.9, 131.0, 125.7, 124.2, 114.0, 29.0, 21.8. HRMS (ESI+) calcd for $C_{17}H_{15}O_2N_2$ $[M+H]^+$: 279.1128, found 279.1124. Spectroscopic data were consistent with those reported in the literature.[6]



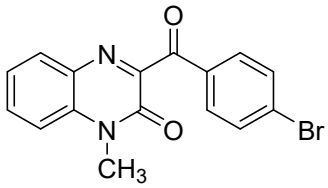
*3-(4-Methoxybenzoyl)-1-methylquinoxalin-2(1H)-one (**3ae**).* Flash column chromatography [EtOAc:DCM (5:95 – 10:90)]; Colourless solid (45%, 26 mg). R_f = 0.66 (EtOAc:DCM,5:95). ^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.01 – 7.92 (m, 3H), 7.72 – 7.66 (m, 1H), 7.46 – 7.40 (m, 2H), 7.00 – 6.93 (m, 2H), 3.89 (s, 3H), 3.77 (s, 3H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 190.3, 164.6, 155.0, 153.4, 133.9, 132.5, 132.2, 131.9, 131.0, 127.9, 124.2, 114.0, 114.0, 55.6, 29.1. HRMS (ESI+) calcd for $C_{17}H_{15}O_3N_2$ $[M+H]^+$: 295.1077, found 295.1074. Spectroscopic data were consistent with those reported in the literature.[6]



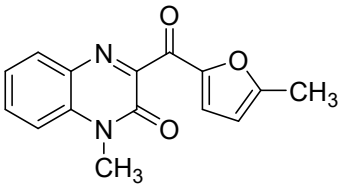
*3-(4-Fluorobenzoyl)-1-methylquinoxalin-2(1H)-one (**3af**)*. Flash column chromatography [EtOAc:DCM (5:95 – 10:90)]; Yellow solid (82%, 46 mg). R_f = 0.55 (EtOAc:DCM, 5:95). ^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.11 – 8.00 (m, 2H), 7.99 – 7.90 (m, 1H), 7.75 – 7.66 (m, 1H), 7.50 – 7.39 (m, 2H), 7.23 – 7.12 (m, 2H), 3.78 (s, 3H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 190.1, 167.3, 165.6, 154.2, 153.3, 133.9, 132.8 (d, $J_{C–F}$ = 10 Hz), 132.3, 132.2, 131.4 (d, $J_{C–F}$ = 3 Hz), 131.1, 124.3, 116.0 (d, $J_{C–F}$ = 22 Hz), 114.0, 29.1. ^{19}F NMR (564 MHz, Chlorofrom-*d*) δ –102.8. HRMS (ESI+) calcd for $C_{16}H_{12}O_2N_2F$ $[M+H]^+$: 283.0877, found 283.0873. Spectroscopic data were consistent with those reported in the literature.[6]



*3-(4-Chlorobenzoyl)-1-methylquinoxalin-2(1H)-one (**3ag**).* Flash column chromatography [EtOAc:DCM (5:95)]; Yellow solid (37%, 22 mg). R_f = 0.55 (EtOAc:DCM, 5:95). ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.99 – 7.93 (m, 3H), 7.75 – 7.69 (m, 1H), 7.51 – 7.41 (m, 4H), 3.78 (s, 3H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 190.5, 154.0, 153.3, 140.8, 134.0, 133.3, 132.3, 132.2, 131.4, 131.1, 129.1, 124.3, 114.0, 29.1. HRMS (ESI+) calcd for $C_{16}H_{12}O_2N_2{}^{35}Cl$ $[M+H]^+$: 299.0582, found 299.0578. Spectroscopic data were consistent with those reported in the literature.[6]

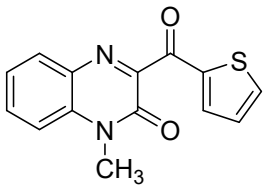


*3-(4-Bromobenzoyl)-1-methylquinoxalin-2(1H)-one (**3ah**)*. Flash column chromatography [EtOAc:DCM (5:95)]; Yellow solid (45%, 31 mg). R_f = 0.70 (EtOAc:DCM, 10:90). ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.97 – 7.92 (m, 1H), 7.91 – 7.85 (m, 2H), 7.74 – 7.69 (m, 1H), 7.68 – 7.63 (m, 2H), 7.48 – 7.41 (m, 2H), 3.78 (s, 3H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 190.7, 153.9, 153.3, 134.0, 133.7, 132.3, 132.2, 132.1, 131.4, 131.1, 129.7, 124.3, 114.0, 29.1. HRMS (ESI+) calcd for $C_{16}H_{12}O_2N_2{}^{79}Br$ $[M+H]^+$: 343.0077, found 343.0072. Spectroscopic data were consistent with those reported in the literature.[6]

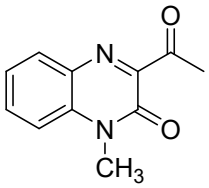


*1-Methyl-3-(5-methylfuran-2-carbonyl)quinoxalin-2(1H)-one (**3ai**)*. Flash column chromatography [EtOAc:DCM (5:95 – 10:90)]; Yellow solid (73%, 39 mg). R_f = 0.34 (EtOAc:DCM,5:95). ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.96 – 7.92 (m, 1H), 7.72 – 7.66 (m, 1H), 7.46 – 7.38 (m, 2H), 7.24 (d, *J* = 3.6 Hz, 1H), 6.25 (dd, *J* = 3.5, 1.1 Hz, 1H), 3.76 (s, 3H), 2.44 (s, 3H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 177.8, 160.4, 153.1, 150.0, 134.1, 132.2,

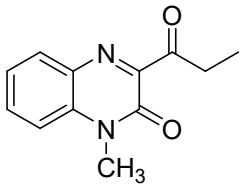
132.1, 131.1, 124.4, 124.2, 114.0, 109.8, 29.1, 14.3. HRMS (ESI+) calcd for $C_{15}H_{13}O_2N_2$ $[M+H]^+$: 269.0921, found 269.0916. Spectroscopic data were consistent with those reported in the literature.[6]



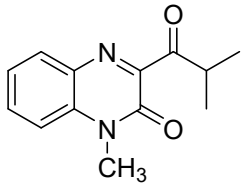
*1-Methyl-3-(thiophene-2-carbonyl)quinoxalin-2(1H)-one (**3aj**)*. Flash column chromatography [EtOAc:DCM (5:95 – 10:90)]; Yellow solid (55%, 30 mg). R_f = 0.27 (EtOAc:DCM, 5:95). ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.99 – 7.94 (m, 1H), 7.85 – 7.78 (m, 2H), 7.74 – 7.68 (m, 1H), 7.48 – 7.40 (m, 2H), 7.21 – 7.16 (m, 1H), 3.78 (s, 3H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 183.1, 153.0, 152.9, 141.6, 136.1, 136.1, 134.2, 132.5, 131.9, 131.1, 128.3, 124.2, 114.0, 29.2. HRMS (ESI+) calcd for $C_{14}H_{11}O_2N_2{}^{32}S$ $[M+H]^+$: 271.0536, found 271.0533. Spectroscopic data were consistent with those reported in the literature.[6]



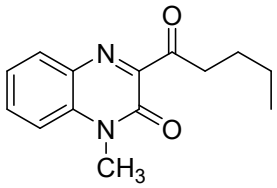
*3-Acetyl-1-methylquinoxalin-2(1H)-one (**3al**).* Flash column chromatography [EtOAc:DCM (5:95 – 10:90)]; Yellow solid (38%, 16 mg). R_f = 0.42 (EtOAc:DCM, 5:95). ^{1}H NMR (300 MHz, Chloroform-*d*) δ 8.04 – 7.90 (m, 1H), 7.76 – 7.63 (m, 1H), 7.47 – 7.33 (m, 2H), 3.75 (s, 3H), 3.01 (s, 3H), 2.73 (s, 3H). ^{13}C NMR (75 MHz, Chloroform-*d*) δ 198.2, 152.9, 151.8, 134.5, 132.8, 131.9, 131.6, 124.2, 113.9, 29.1, 28.6. HRMS (ESI+) calcd for $C_{11}H_{11}O_2N_2$ $[M+H]^+$: 203.0815, found 203.0814. Spectroscopic data were consistent with those reported in the literature.[6]



*1-Methyl-3-propionylquinoxalin-2(1H)-one (**3am**)*. Flash column chromatography [EtOAc:DCM (5:95 – 10:90)]; Yellow solid (25%, 11 mg). R_f = 0.60 (EtOAc:DCM, 5:95). ^{1}H NMR (300 MHz, Chloroform-*d*) δ 8.00 – 7.91 (m, 1H), 7.75 – 7.63 (m, 1H), 7.47 – 7.34 (m, 2H), 3.75 (s, 3H), 3.13 (q, *J* = 7.2 Hz, 2H), 1.28 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (75 MHz, Chloroform-*d*) δ 201.4, 153.0, 152.9, 134.3, 132.5, 132.0, 131.3, 124.2, 113.9, 34.2, 29.0, 7.5. HRMS (ESI+) calcd for $C_{12}H_{13}O_2N_2$ $[M+H]^+$: 217.0972, found 217.0970. Spectroscopic data were consistent with those reported in the literature.[6]

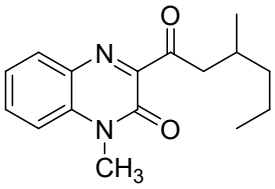


*3-Isobutyryl-1-methylquinoxalin-2(1H)-one (**3an**)*. Flash column chromatography [EtOAc:DCM (0:100 – 5:950.5)]; Yellow solid (45%, 21 mg). R_f = 0.58 (EtOAc:DCM, 10:90). ^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.96 – 7.92 (m, 1H), 7.71 – 7.65 (m, 1H), 7.46 – 7.36 (m, 2H), 3.74 (s, 3H), 3.61 (hept, *J* = 7.0 Hz, 1H), 1.27 (d, *J* = 7.0 Hz, 6H). ^{13}C NMR (75 MHz, Chloroform-*d*) δ 204.5, 153.9, 153.0, 134.1, 132.2, 132.1, 131.2, 124.1, 113.9, 38.3, 29.0, 17.6. HRMS (ESI+) calcd for $C_{13}H_{15}O_2N_2$ $[M+H]^+$: 231.1128, found 231.1126. Spectroscopic data were consistent with those reported in the literature.[6]



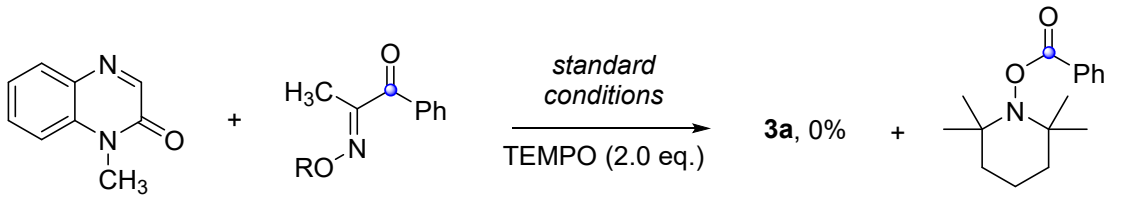
*1-Methyl-3-pentanoylquinoxalin-2(1H)-one (**3ao**)*. Flash column chromatography [EtOAc:DCM (5:95 – 10:90)]; Yellow solid (59%, 29 mg). R_f = 0.52 (EtOAc:DCM, 10:90). ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.97 – 7.93 (m, 1H), 7.71 – 7.65 (m, 1H), 7.44 – 7.35 (m, 2H), 3.74 (s, 3H), 3.09 (t, *J* = 7.4 Hz, 2H), 1.76 (p, *J* = 7.5 Hz, 2H), 1.45 (h, *J* = 7.4 Hz, 2H), 0.96 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 201.1, 153.1, 152.9, 134.3, 132.4,

132.0, 131.3, 124.1, 113.9, 40.6, 29.0, 25.5, 22.3, 13.9. HRMS (ESI+) calcd for $C_{14}H_{17}O_2N_2$ $[M+H]^+$: 245.1284, found 245.1281. Spectroscopic data were consistent with those reported in the literature.[6]



*1-Methyl-3-(3-methylhexanoyl)quinoxalin-2(1H)-one (**3ap**)*. Flash column chromatography [EtOAc:DCM (0:100 – 5:95)]; Yellow solid (37%, 19 mg). m.p. 63 – 65 °C (DCM). R_f = 0.22 (DCM). ^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.98 – 7.94 (m, 1H), 7.71 – 7.65 (m, 1H), 7.46 – 7.34 (m, 2H), 3.74 (s, 3H), 3.11 (dd, *J* = 16.5, 5.6 Hz, 1H), 2.89 (dd, *J* = 16.5, 8.1 Hz, 1H), 2.17 – 2.08 (m, 1H), 1.54 – 1.42 (m, 1H), 1.37 – 1.26 (m, 1H), 1.02 (d, *J* = 6.7 Hz, 3H), 0.94 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (75 MHz, Chloroform-*d*) δ 201.0, 153.2, 152.9, 134.3, 132.4, 132.0, 131.4, 124.1, 113.9, 47.7, 30.7, 29.6, 29.0, 19.5, 11.4. IR (ν/cm^{-1}) 2957, 2922, 1702, 1645, 1463, 1322, 1030, 757. HRMS (ESI+) calcd for $C_{15}H_{19}O_2N_2$ $[M+H]^+$: 259.1441, found 259.1446.

5. Radical trapping experiment



1a **2a**, R = 4-$CF_3C_6H_4CO$

Under Ar atmosphere, a Schlenk tube was charged with quinoxalinone **1a** (0.20 mmol, 1.0 eq.), oxime ester **2a** (0.60 mmol, 3.0 eq.), and TEMPO (0.20 mmol, 2.0 eq.). DBU (0.10 mmol, 0.5 eq.), anhydrous DMSO (0.5 mL), and DCM (0.5 mL) were consecutively added. The reaction mixture was degassed by ultra-sonication for 30 s and stirred for an overnight under the irradiation of blue LEDs (8 W × 2, at approximately 2 – 3 cm away from the light sources, ca. 35 °C). Saturated solution of $NaHCO_3$ (10 mL) was added and the aqueous phase was extracted with EtOAc (3 × 10 mL). Combined organic phase was washed with water (10 mL) and brine (10 mL), dried over Na_2SO_4, and concentrated *in vacuo*. The acyl-TEMPO adduct was detected by LC-MS (calcd for $C_{16}H_{24}O_2N$ $[M+H]^+$: 262.1802, found 262.1796).

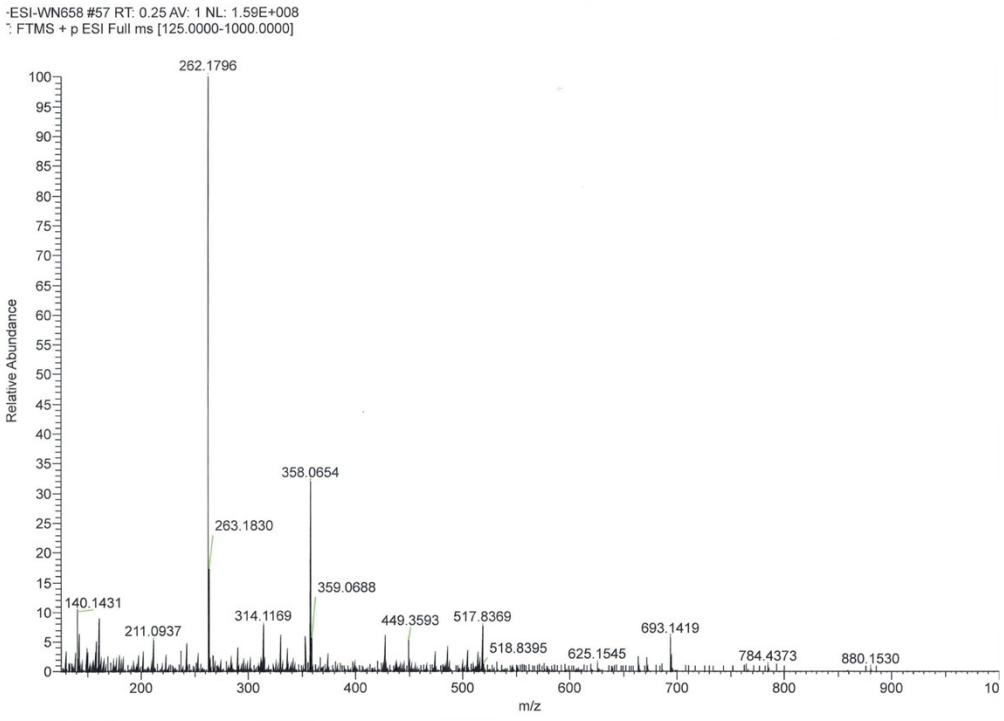


Figure S7 Mass spectrum of TEMPO-trapping experiment.

6. References

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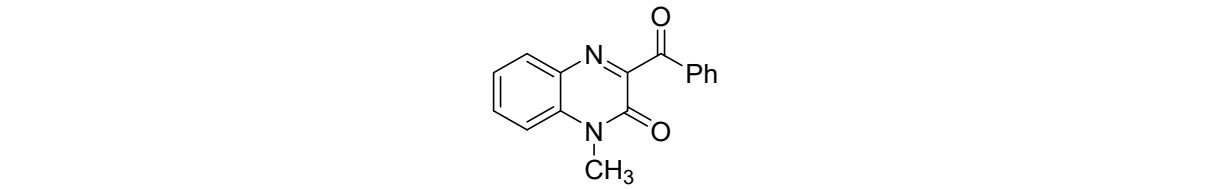
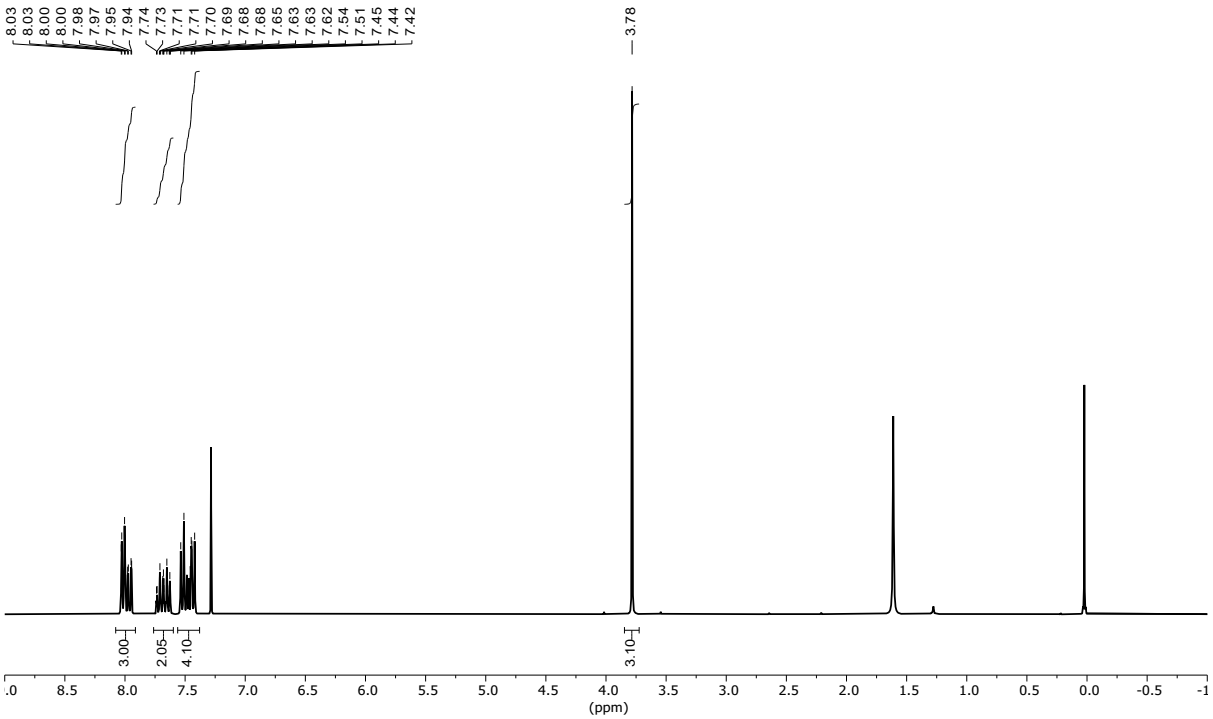
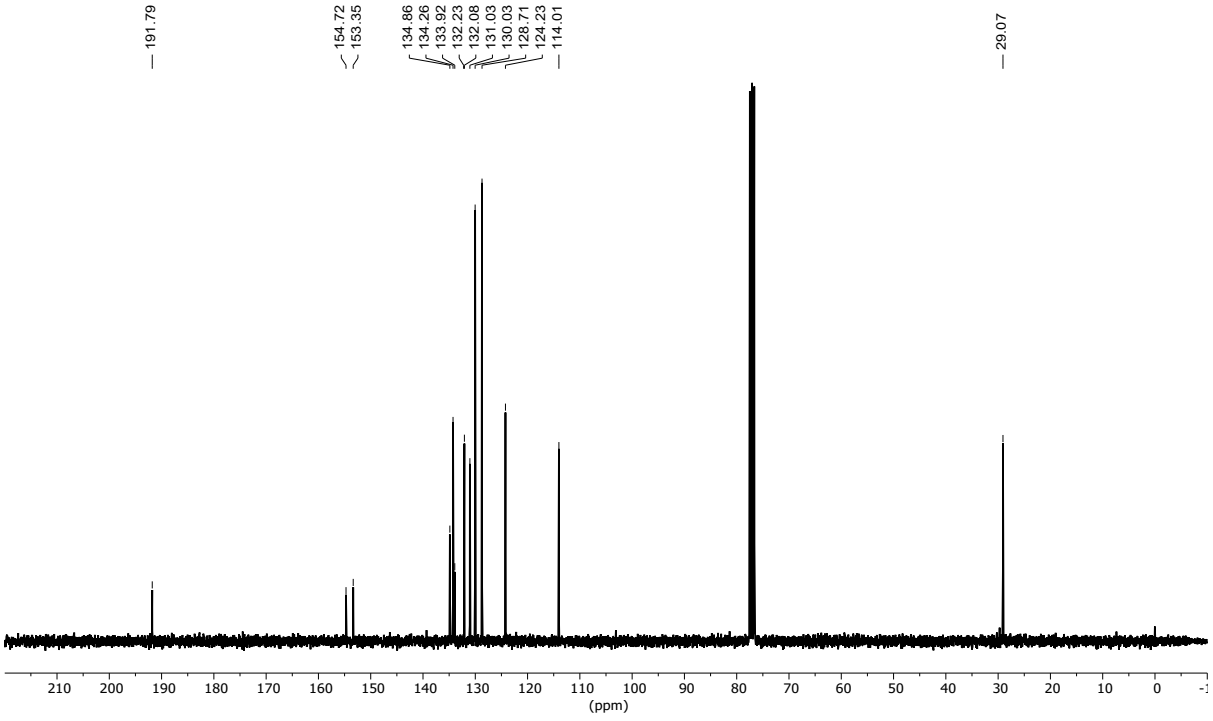
7. ^{1}H and ^{13}C NMR spectra of all compounds

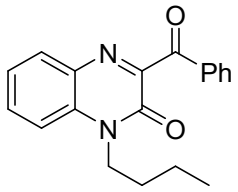
*3-Benzoyl-1-methylquinoxalin-2(1H)-one (**3aa**).*

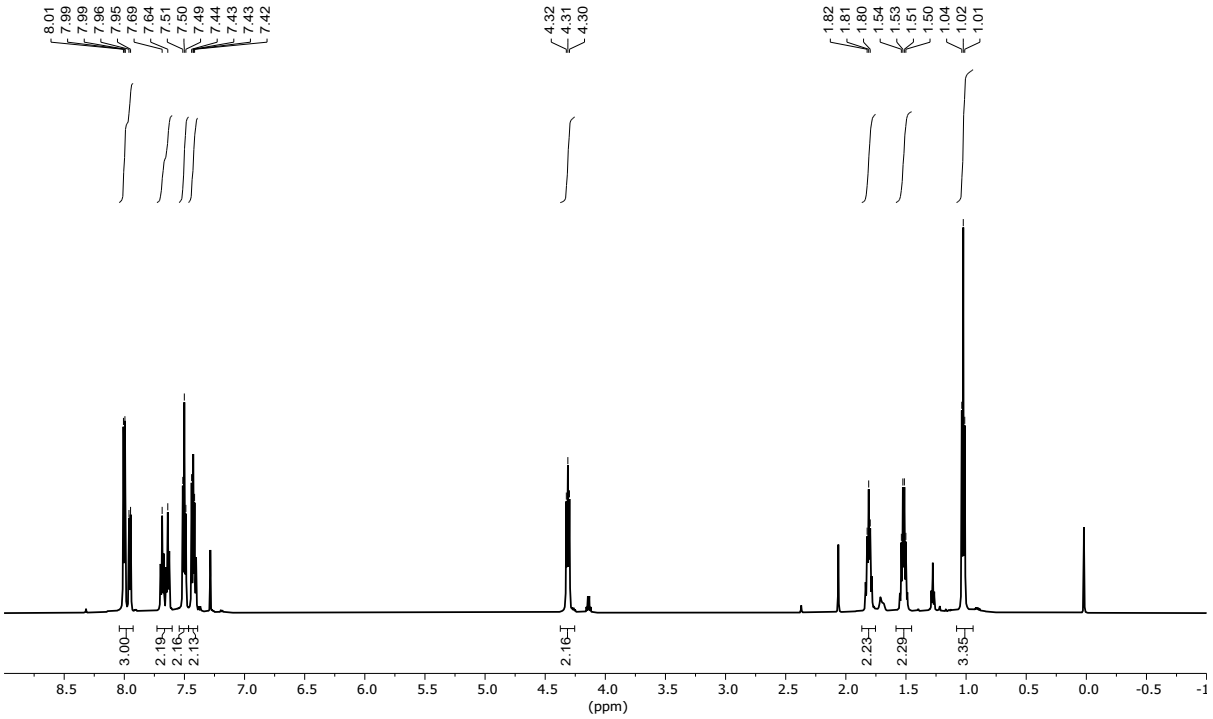


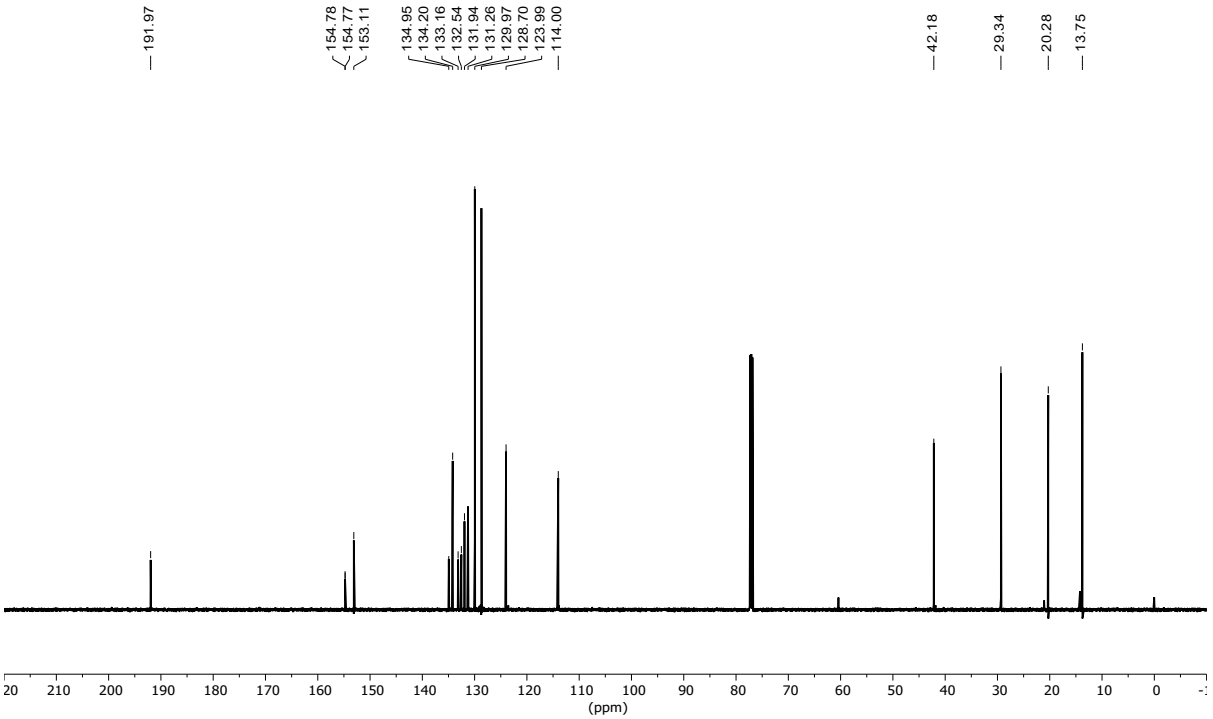




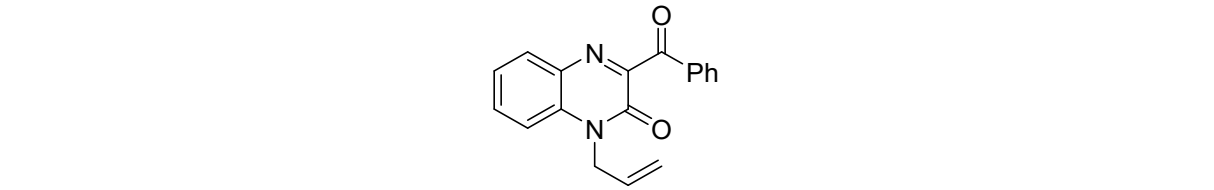
*3-Benzoyl-1-butylquinoxalin-2(1H)-one (**3ba**)*

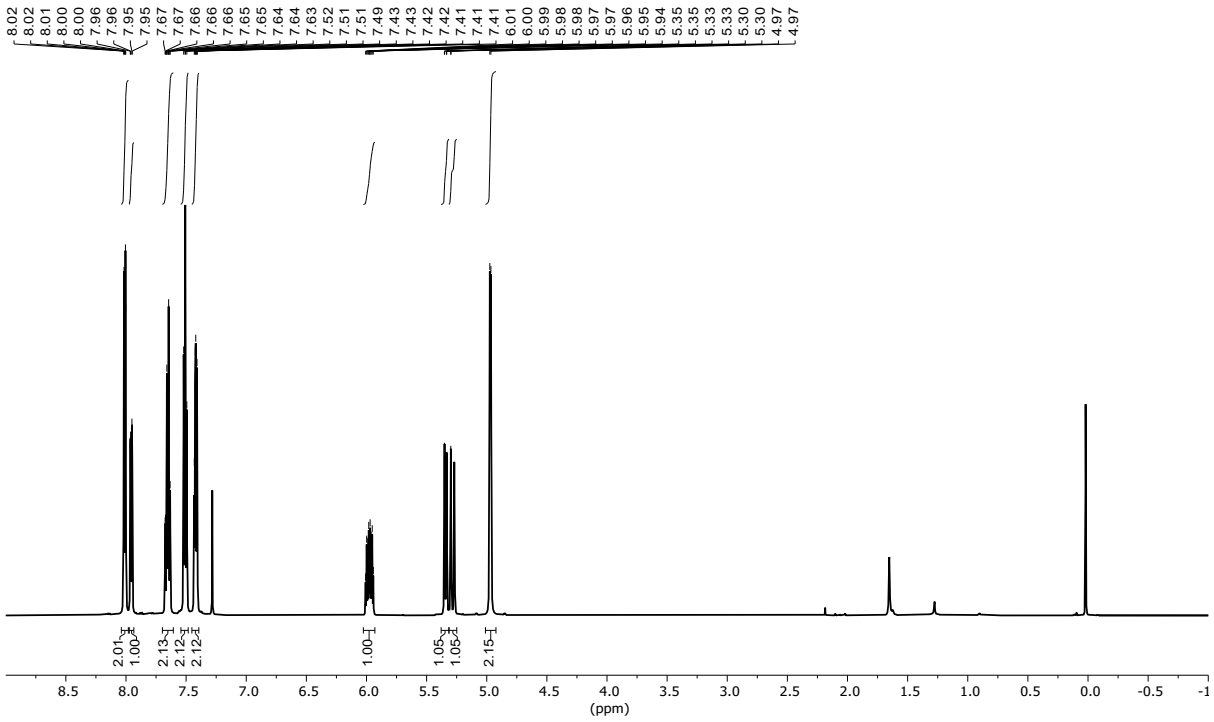


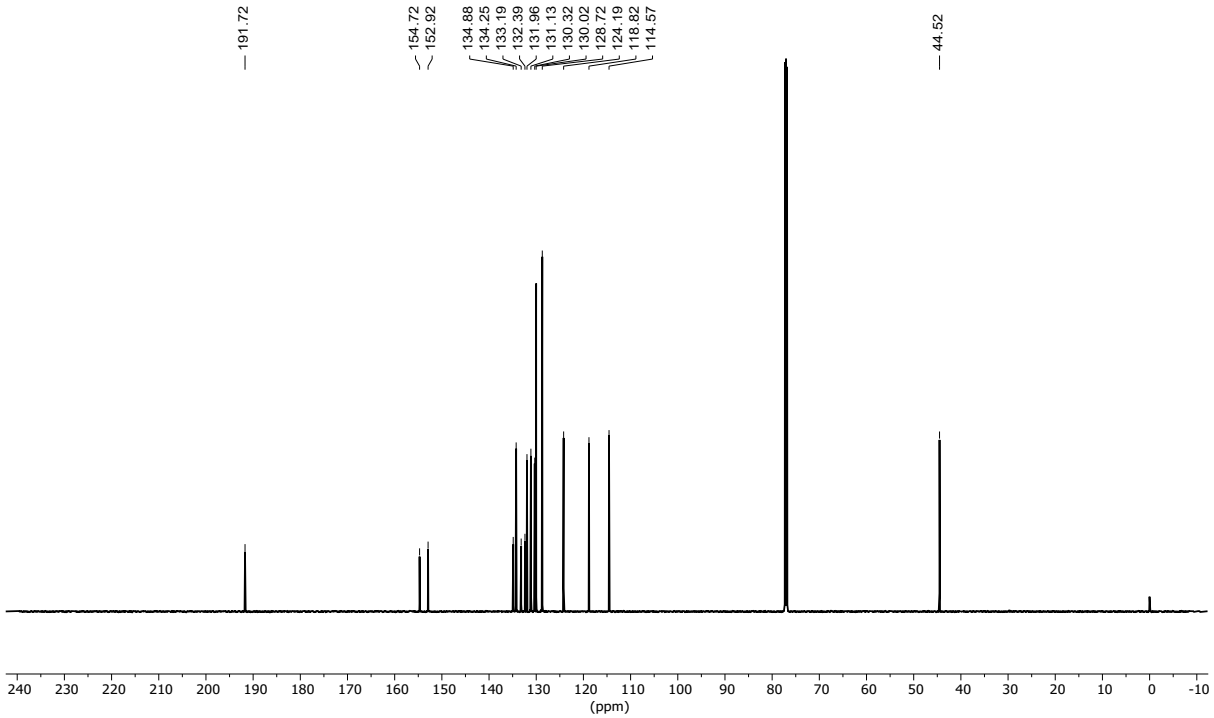




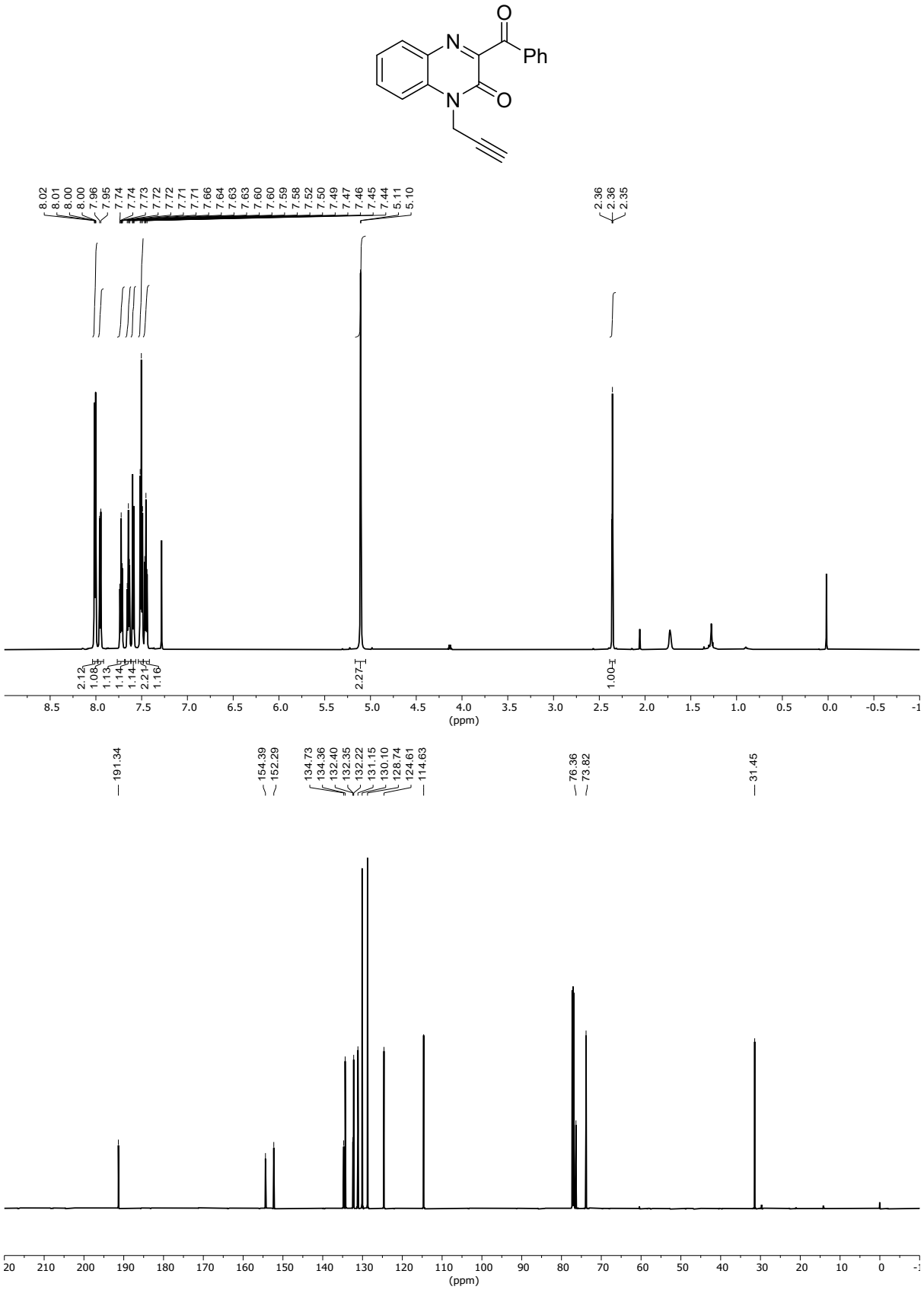
*1-Allyl-3-benzoylquinoxalin-2(1H)-one (**3ca**).*



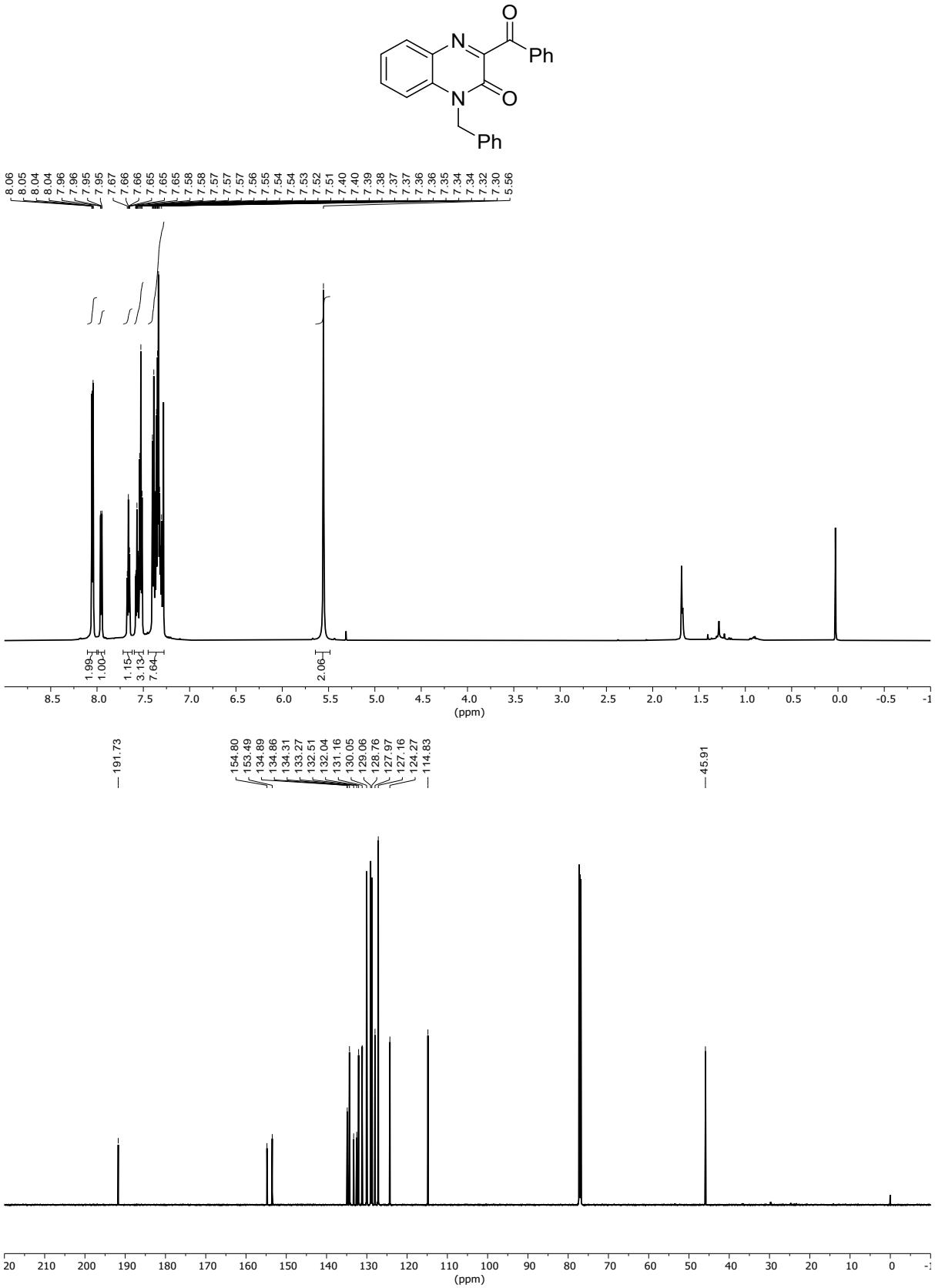




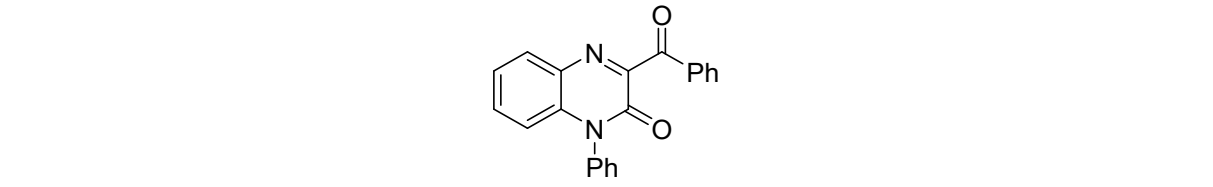
*3-Benzoyl-1-(prop-2-yn-1-yl)quinoxalin-2(1H)-one (**3da**).*

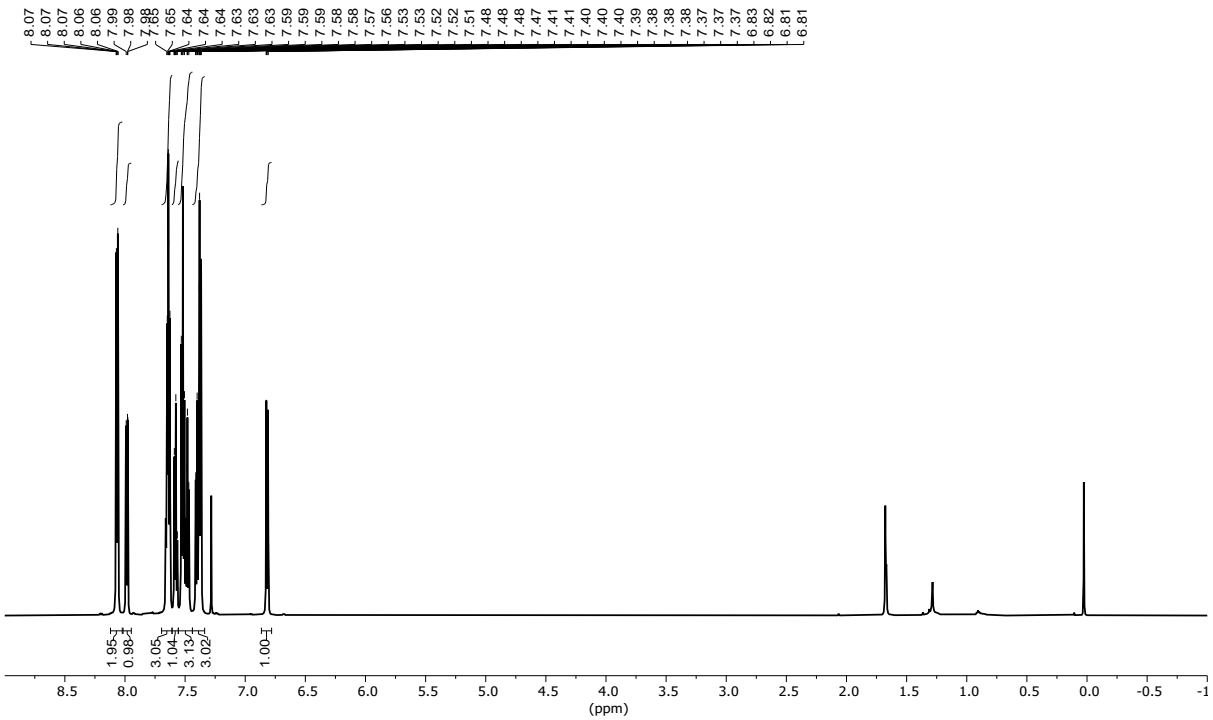


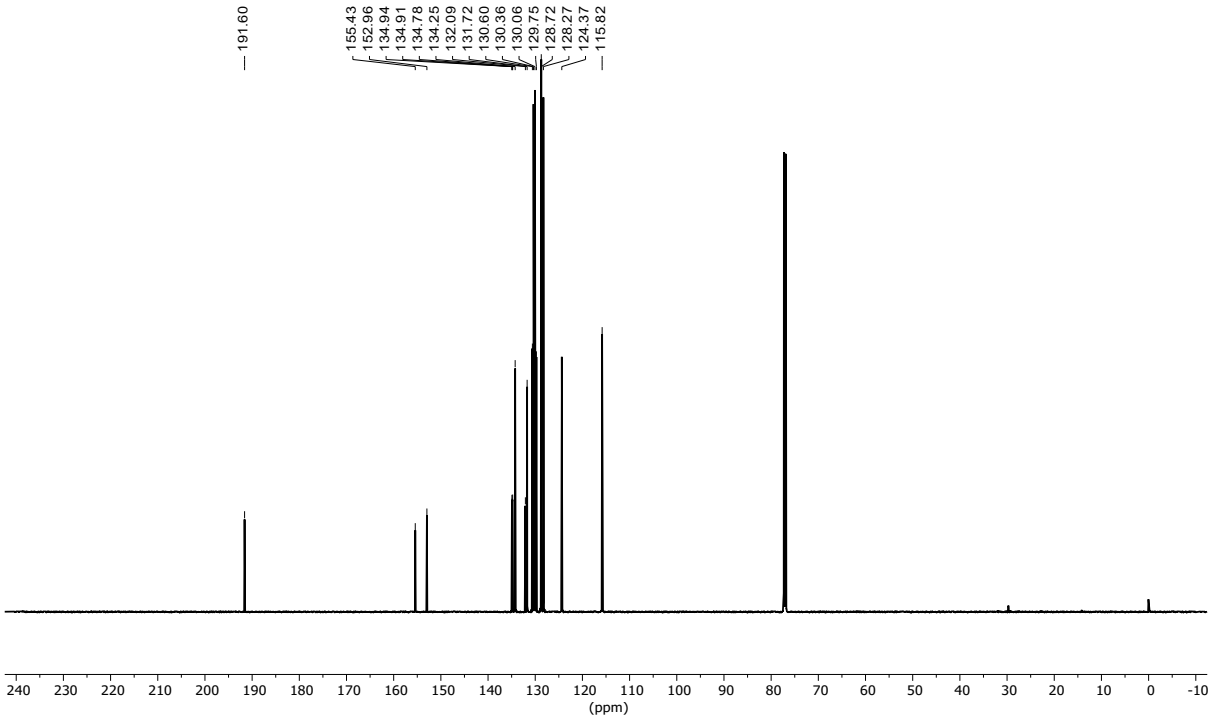
*3-Benzoyl-1-benzylquinoxalin-2(1H)-one (**3ea**).*



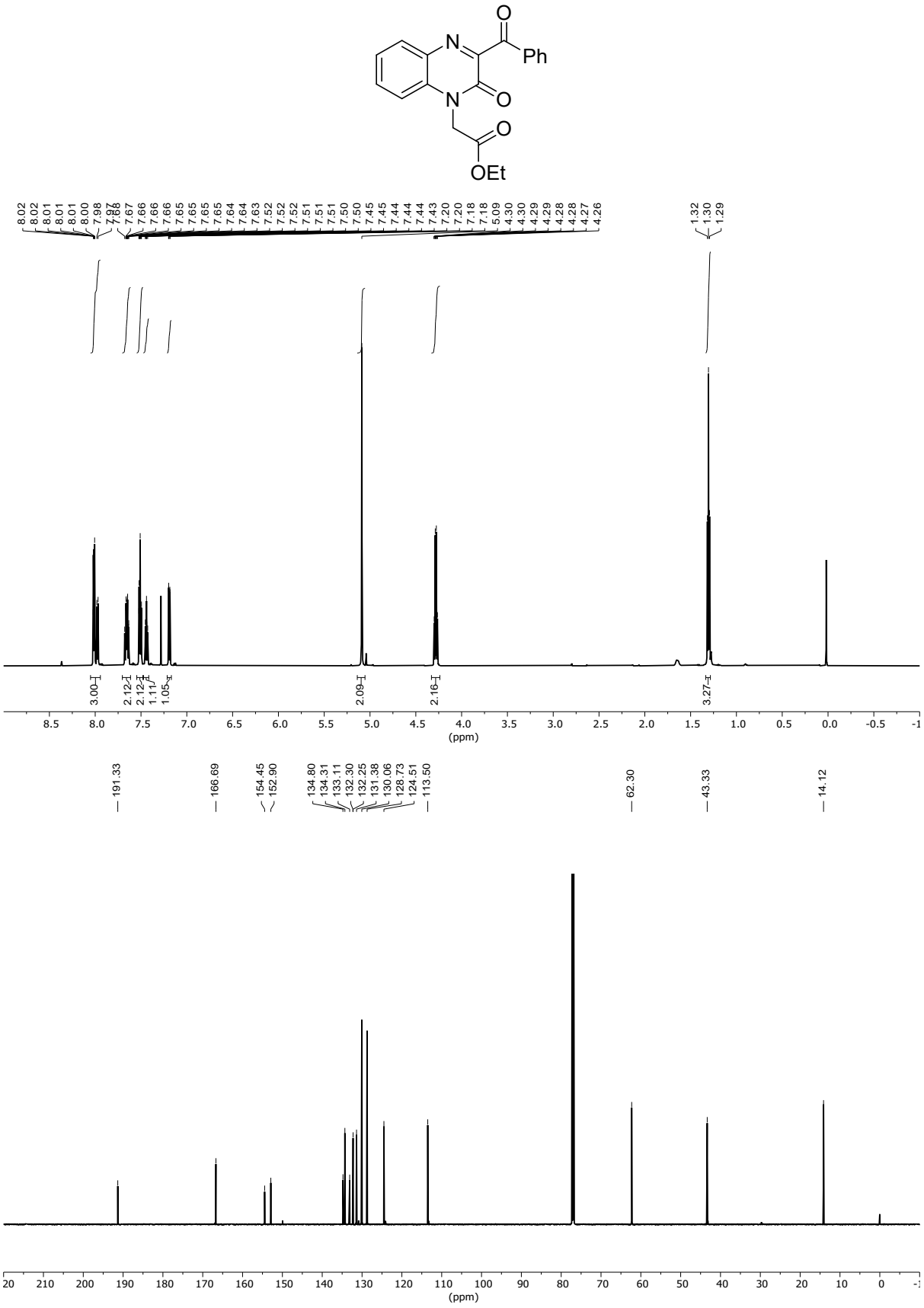
*3-Benzoyl-1-phenylquinoxalin-2(1H)-one (**3fa**).*



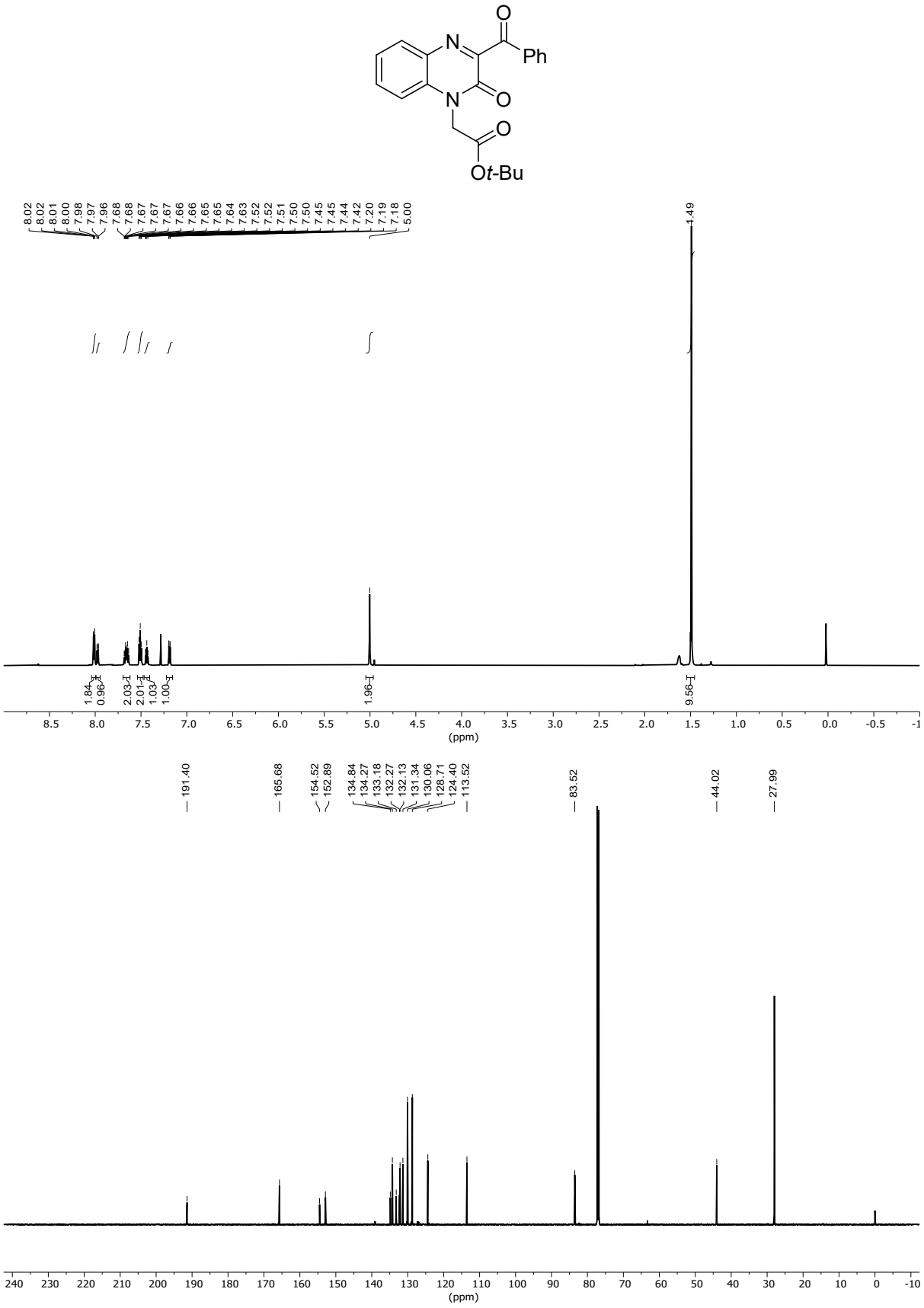




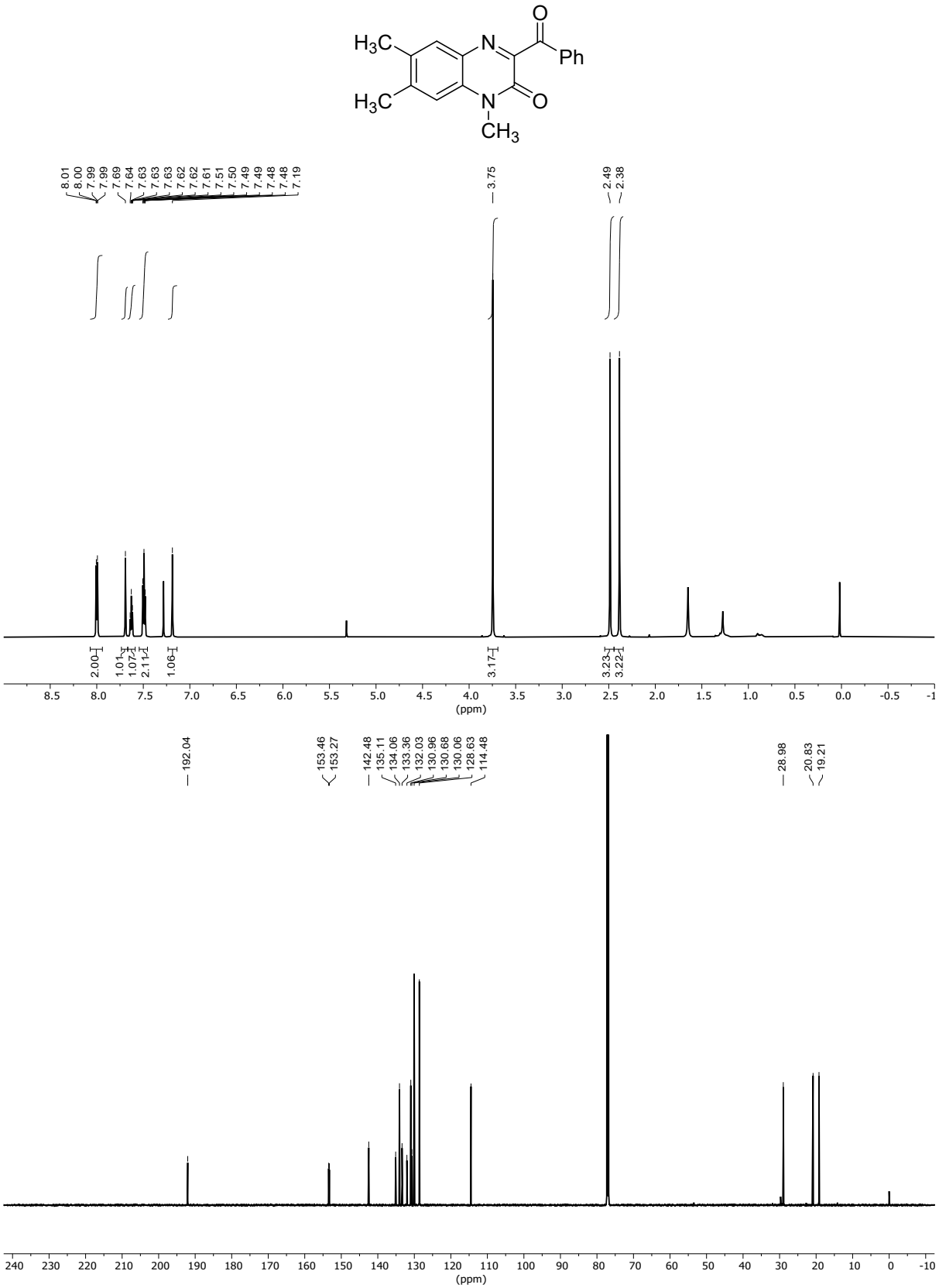
*Ethyl 2-(3-benzoyl-2-oxoquinoxalin-1(2H)-yl)acetate (**3ga**).*



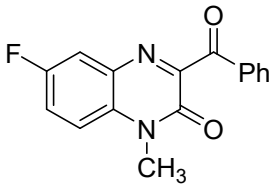
*tert-Butyl 2-(3-benzoyl-2-oxoquinoxalin-1(2H)-yl)acetate (**3ha**).*

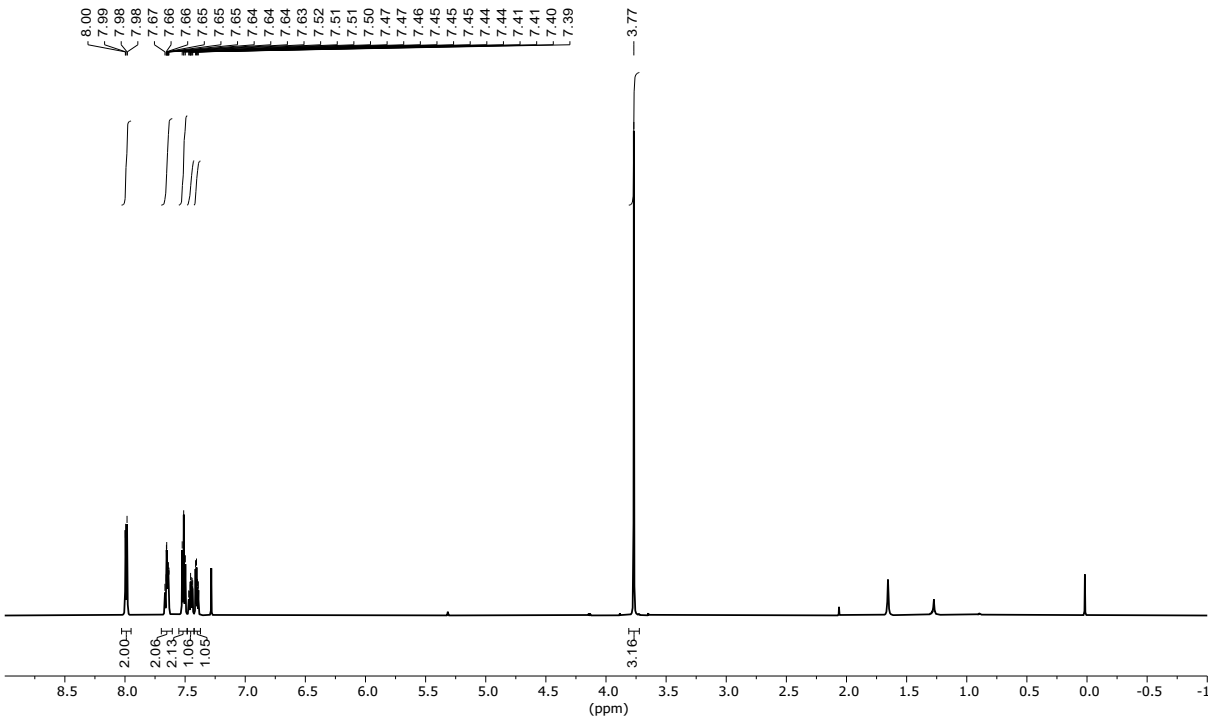


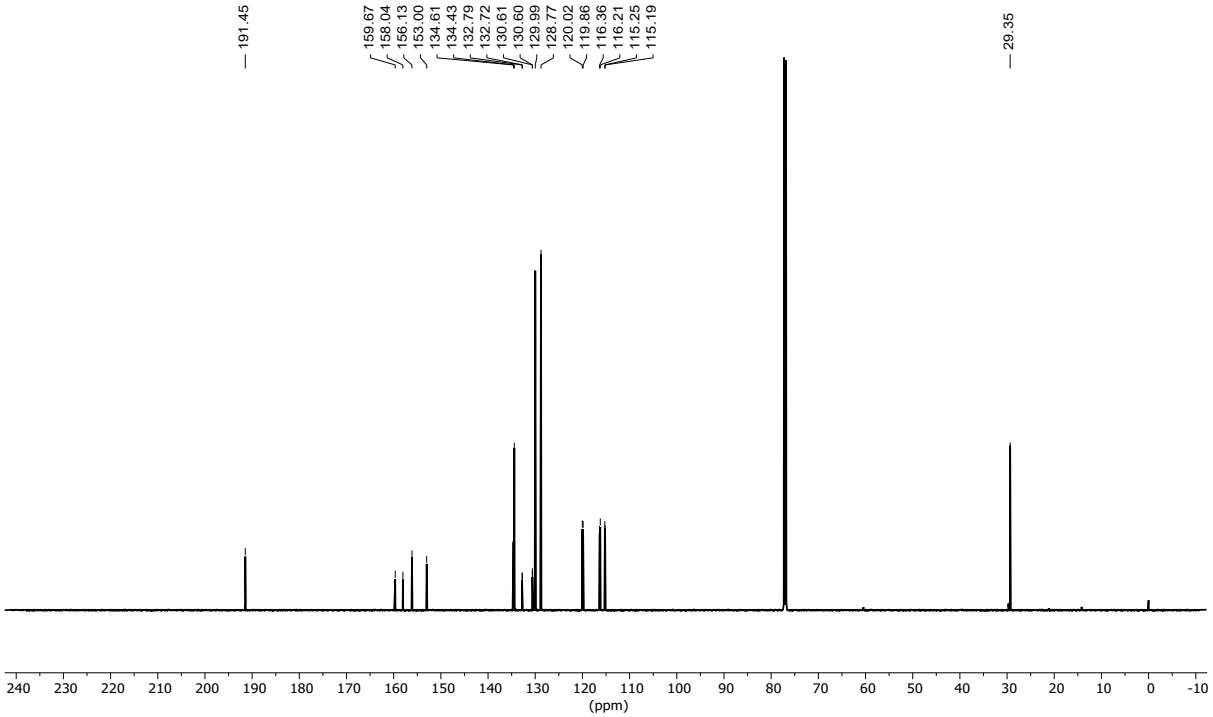
*3-Benzoyl-1,6,7-trimethylquinoxalin-2(1H)-one (**3ja**).*

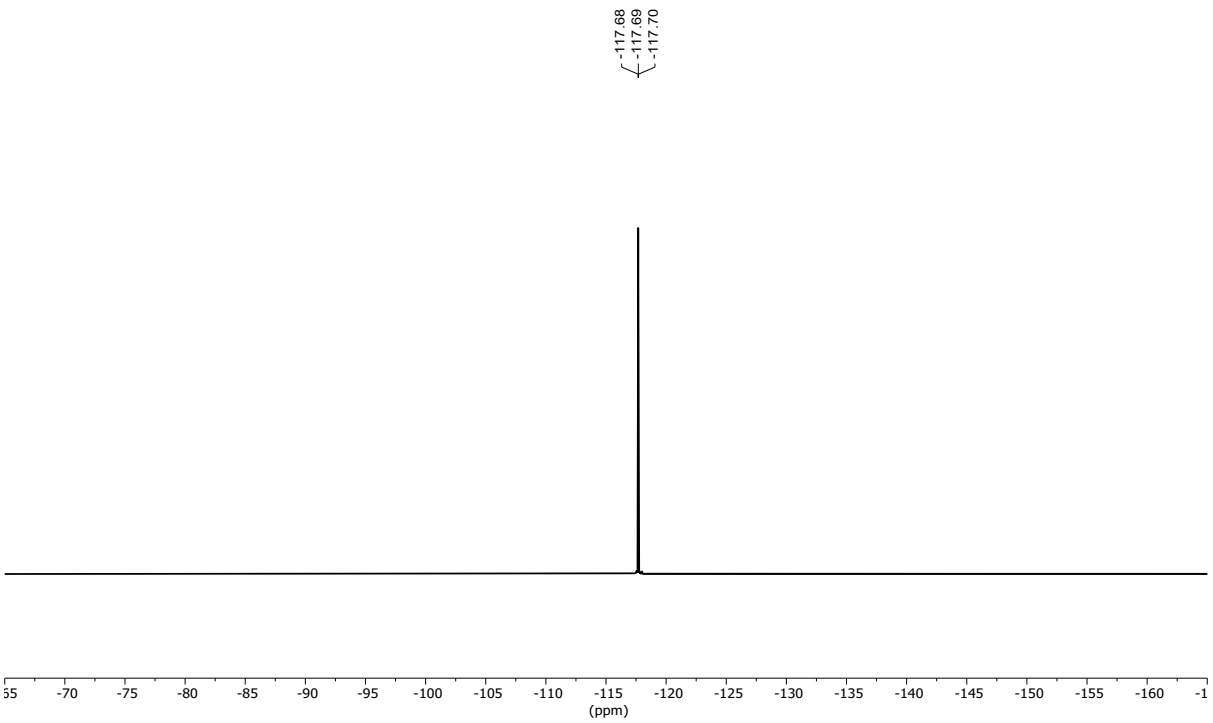


*3-Benzoyl-6-fluoro-1-methylquinoxalin-2(1H)-one (**3ka**).*

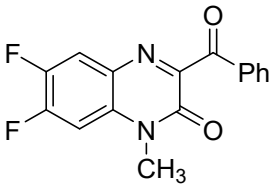


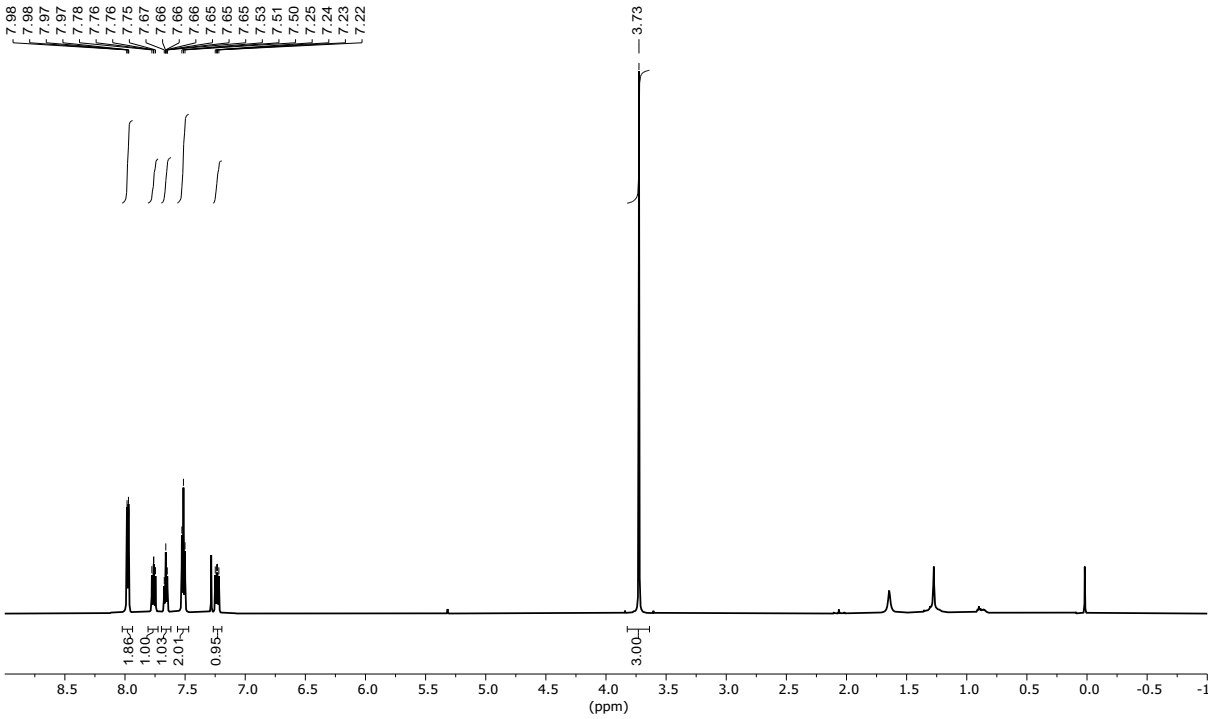


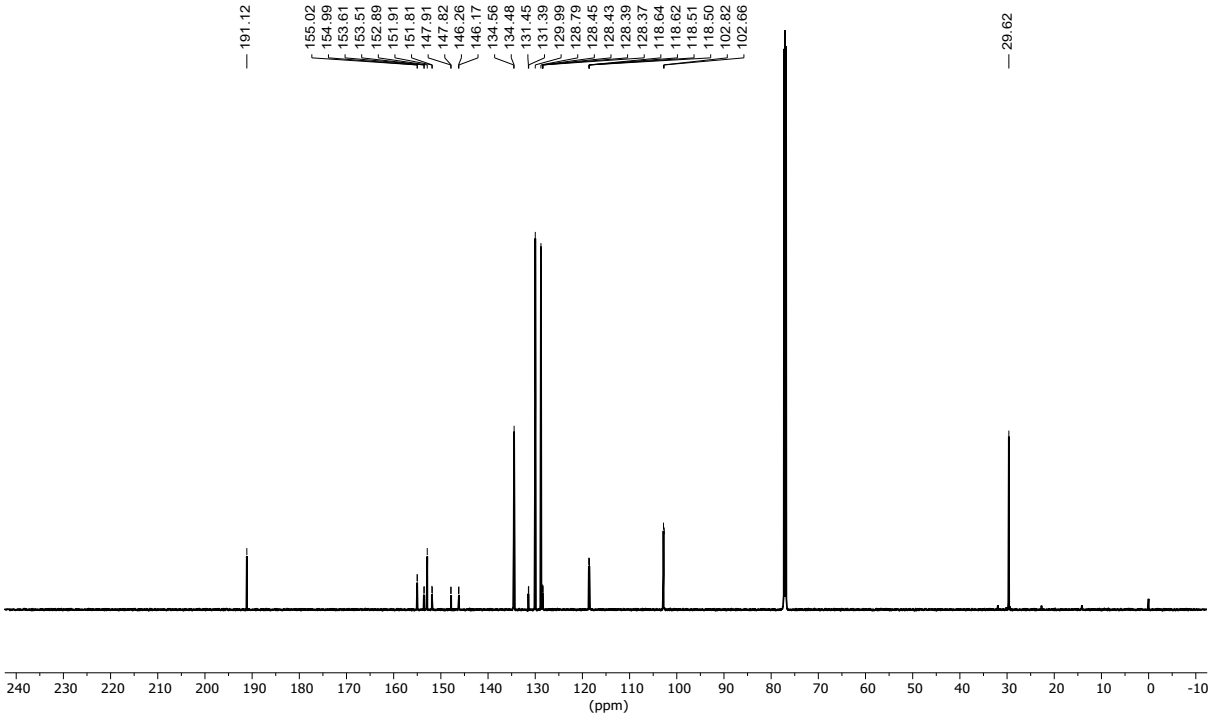


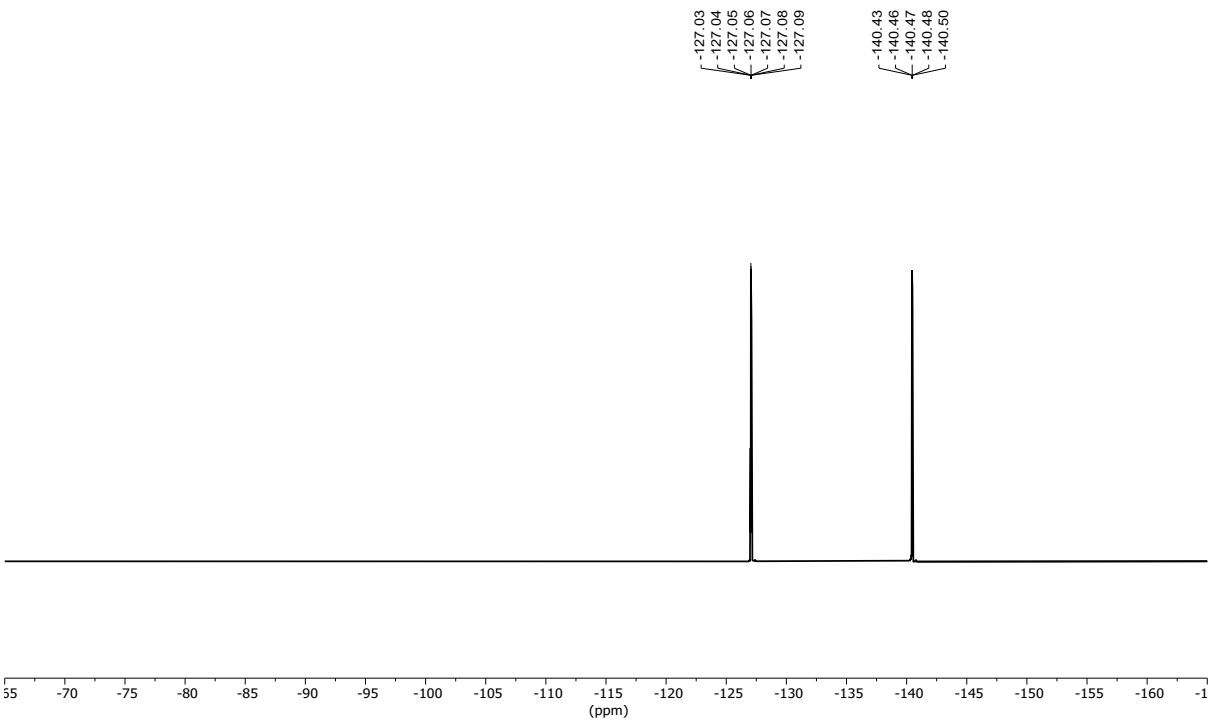

-117.68
-117.69
-117.70
-70
-75
-80
-85
-90
-95
-100
-105
-110
-115
-120
-125
-130
-135
-140
-145
-150
-155
-160
(ppm)

*3-Benzoyl-6,7-difluoro-1-methylquinoxalin-2(1H)-one (**3la**).*





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-127.04
-127.05
-127.06
-127.07
-127.08
-127.09
-140.43
-140.46
-140.47
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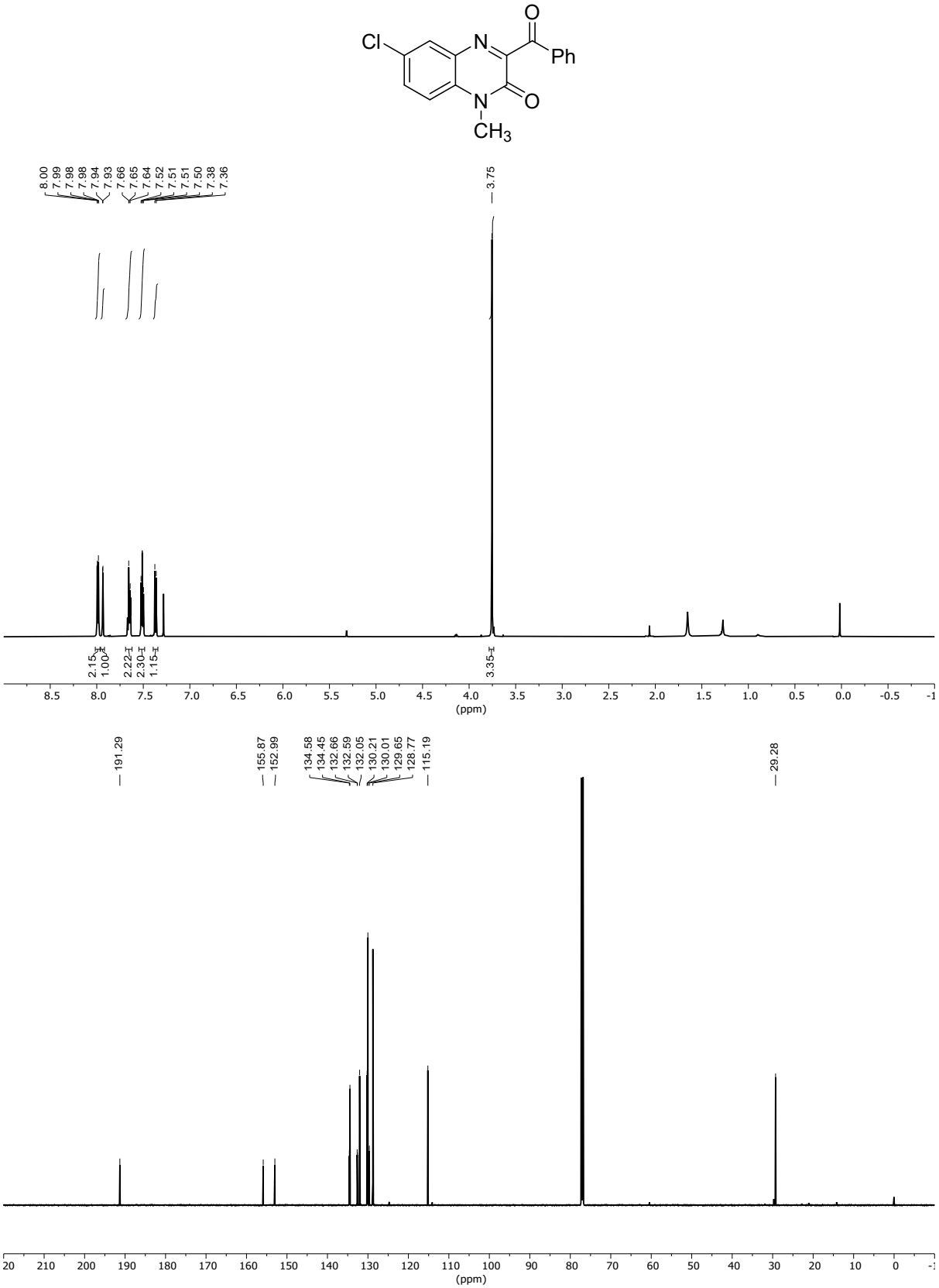
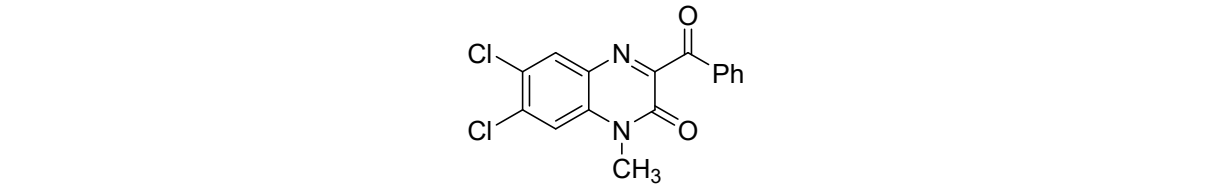
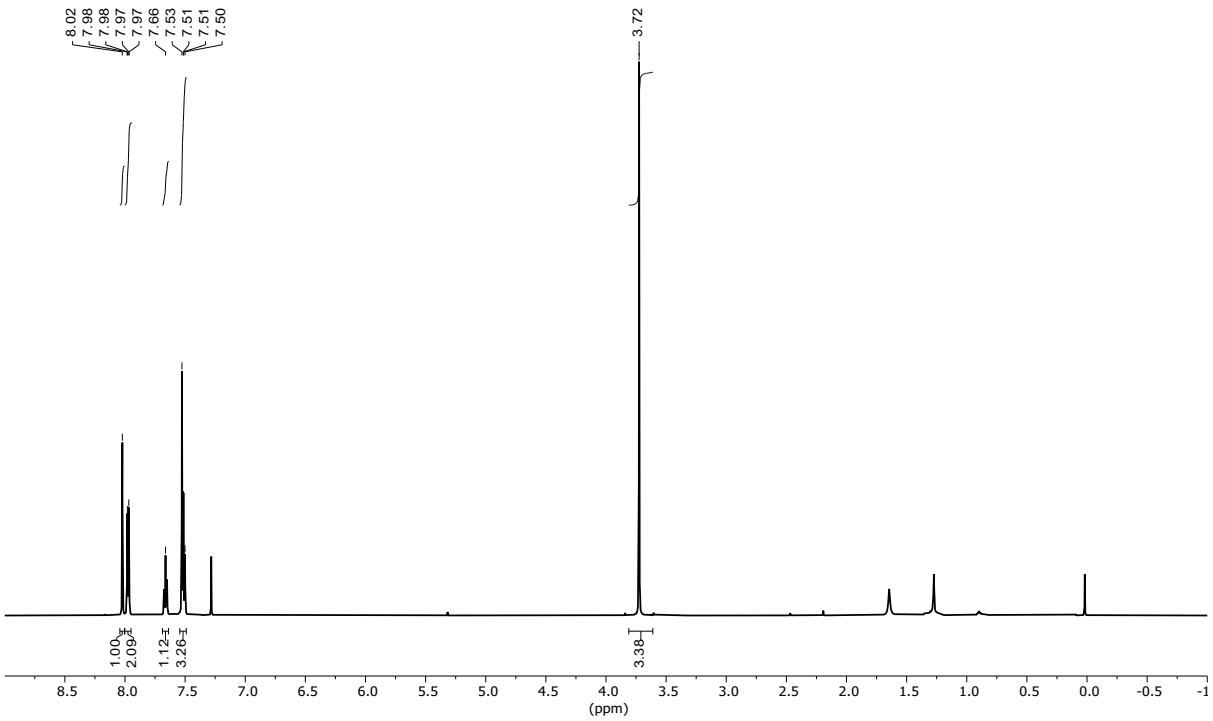
-140.50
-70
-75
-80
-85
-90
-95
-100
-105
-110
-115
-120
-125
-130
-135
-140
-145
-150
-155
-160
(ppm)

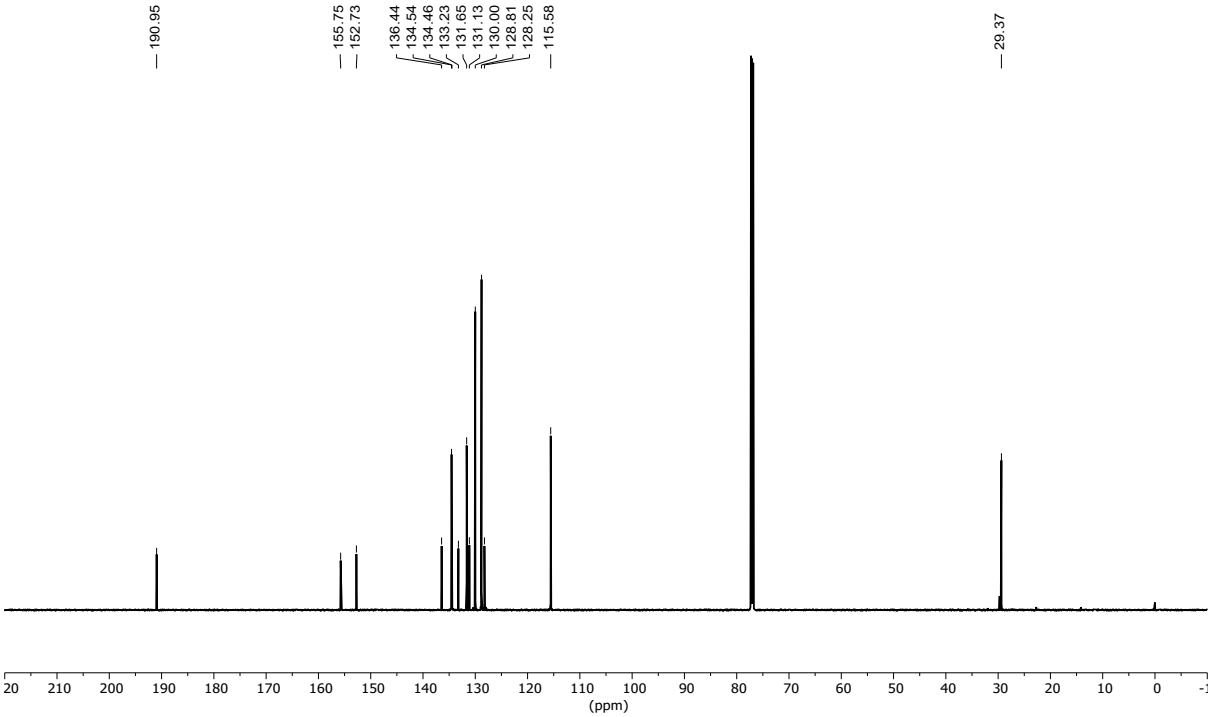
*3-Benzoyl-6-chloro-1-methylquinoxalin-2(1H)-one (**3ma**).*



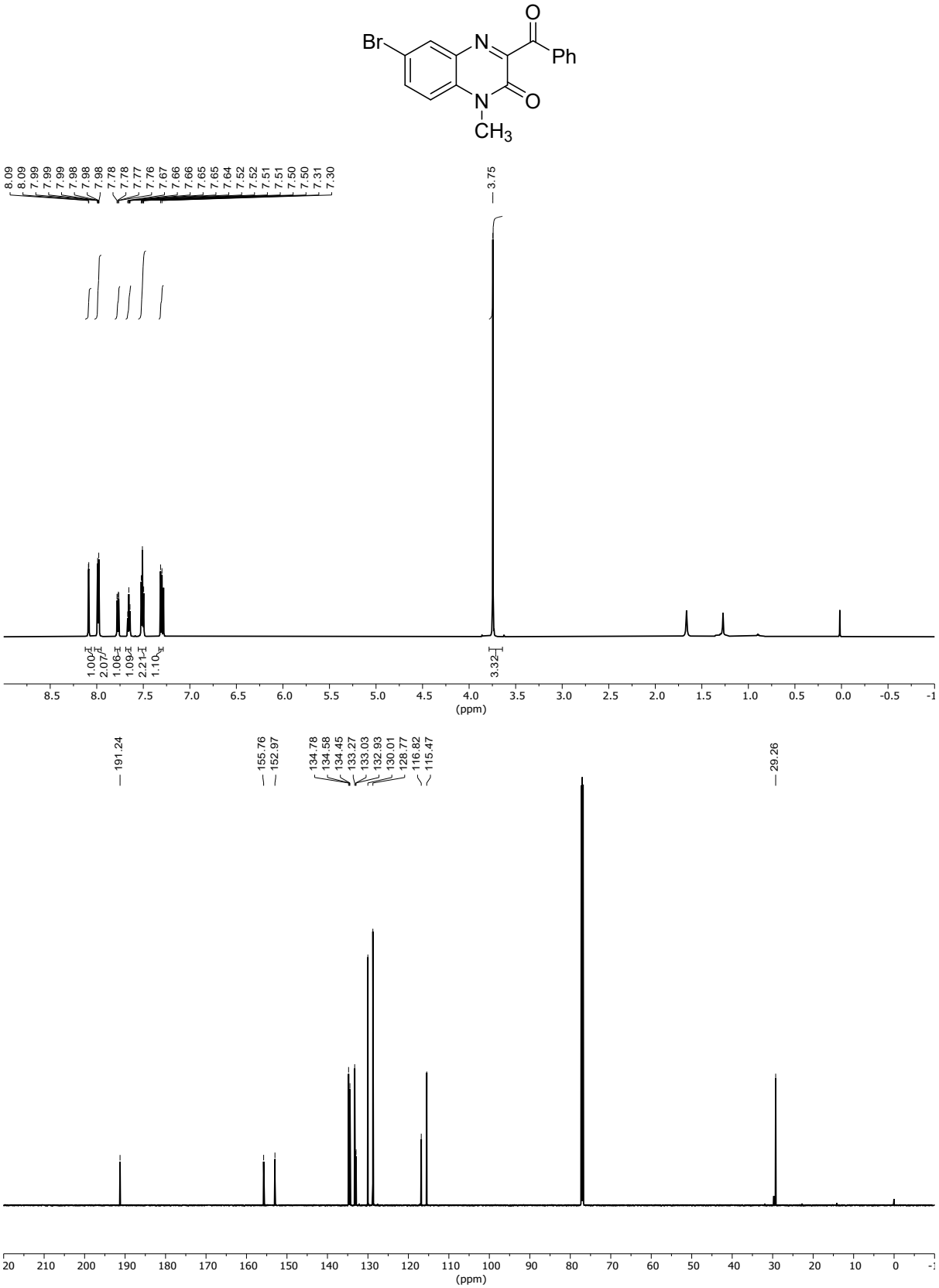
*3-Benzoyl-6,7-dichloro-1-methylquinoxalin-2(1H)-one (**3na**).*



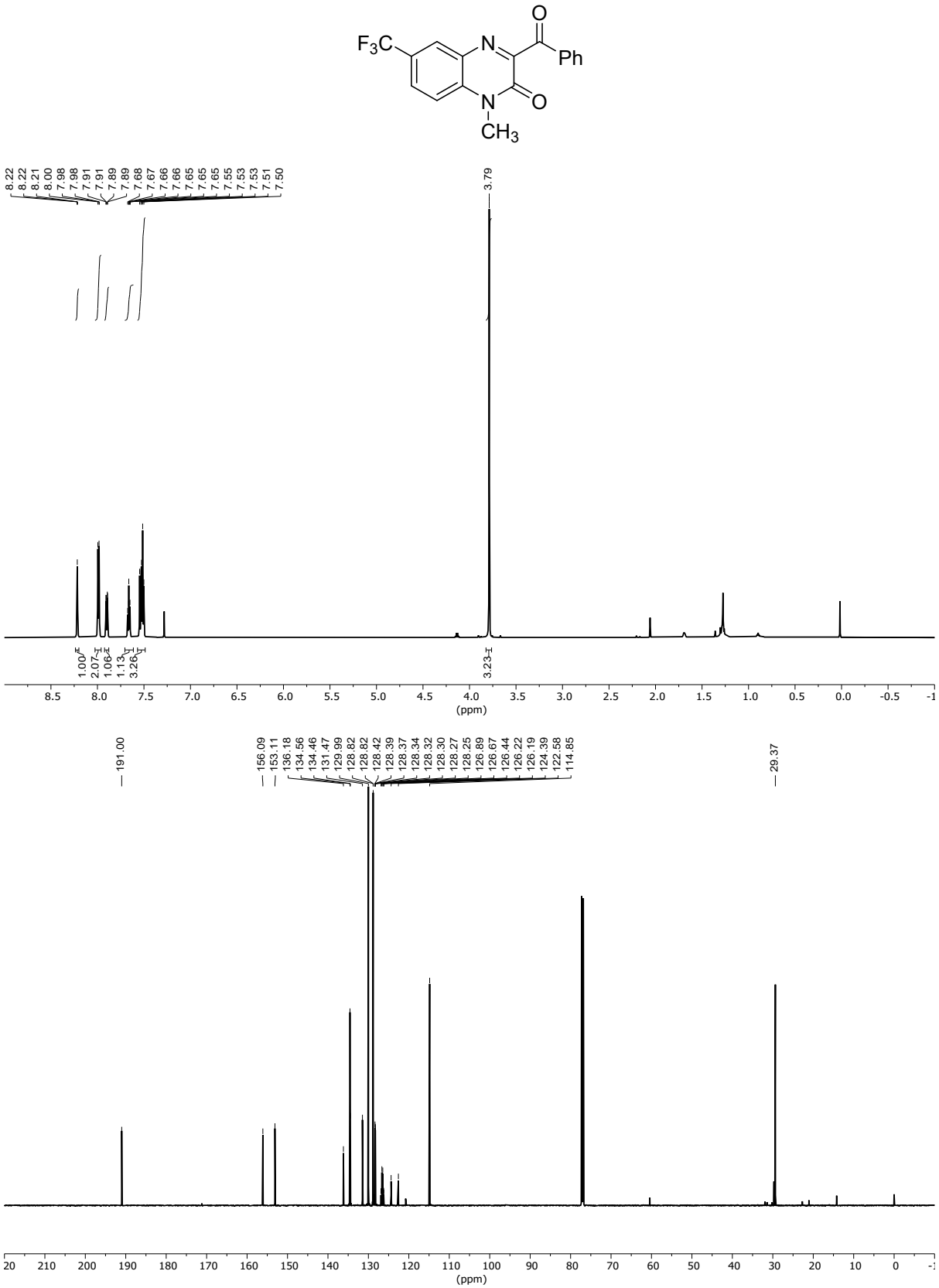


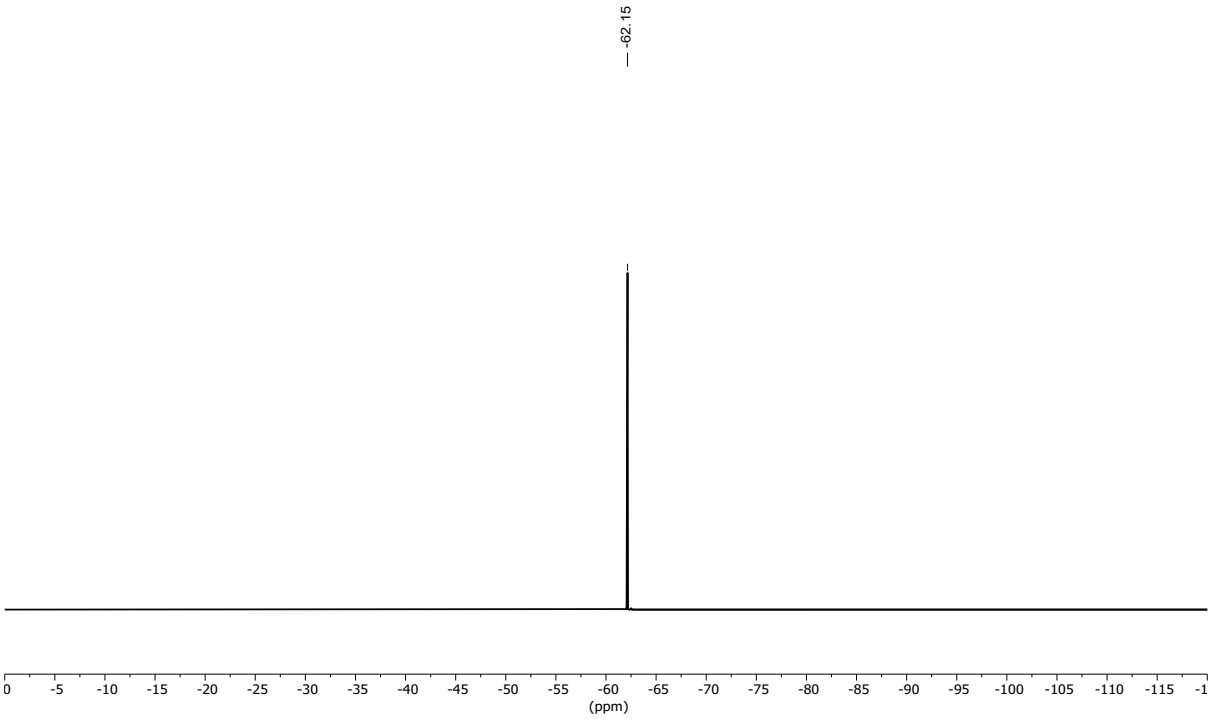


*3-Benzoyl-6-bromo-1-methylquinoxalin-2(1H)-one (**3oa**).*

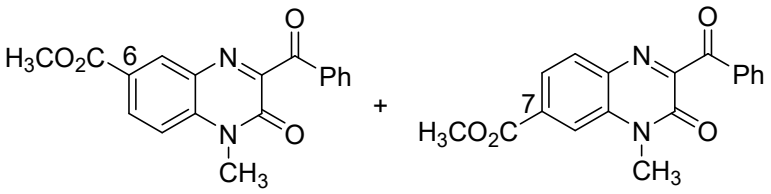


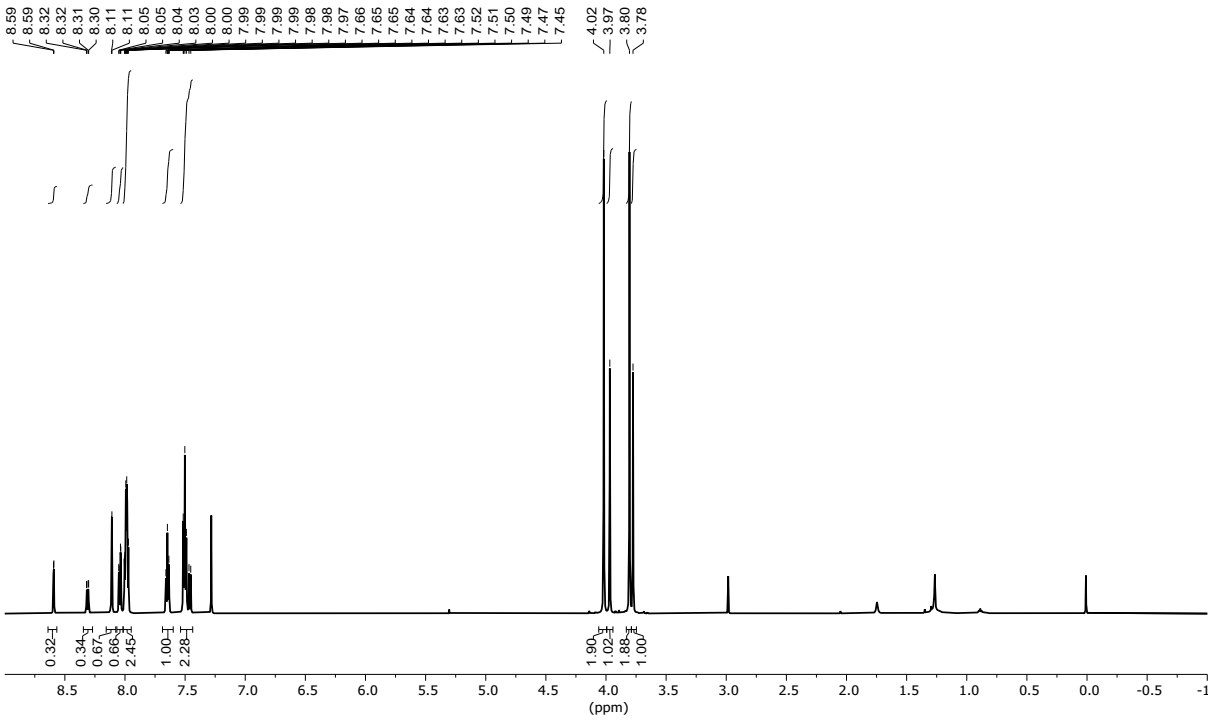
*3-Benzoyl-1-methyl-6-(trifluoromethyl)quinoxalin-2(1H)-one (**3pa**).*

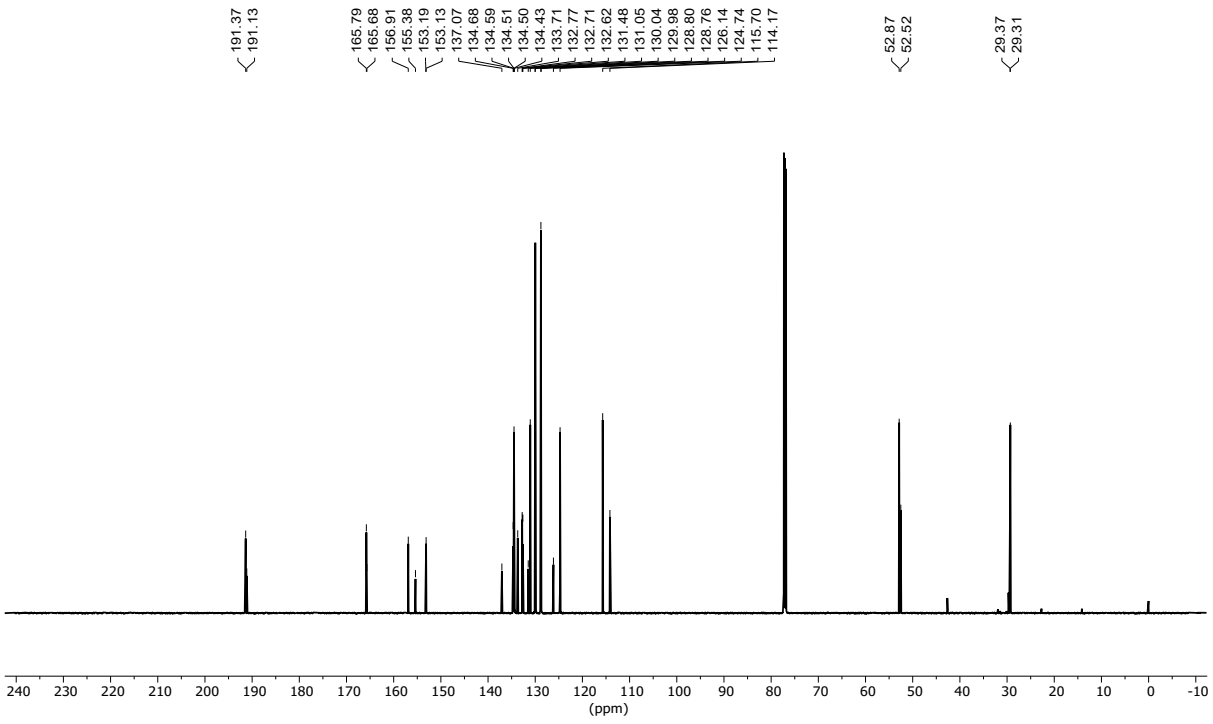



-62.15
0
-5
-10
-15
-20
-25
-30
-35
-40
-45
-50
-55
-60
-65
-70
-75
-80
-85
-90
-95
-100
-105
-110
-115
(ppm)

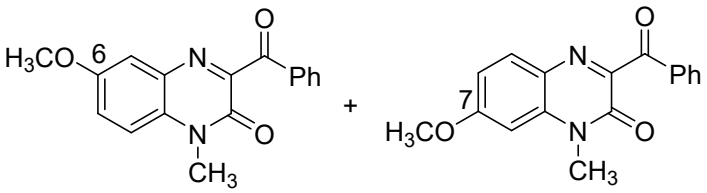
Methyl 2-benzoyl-4-methyl-3-oxo-3,4-dihydroquinoxaline-6-carboxylate (**3qa**) and methyl 2-benzoyl-4-methyl-3-oxo-3,4-dihydroquinoxaline-7-carboxylate (**3qa'**).

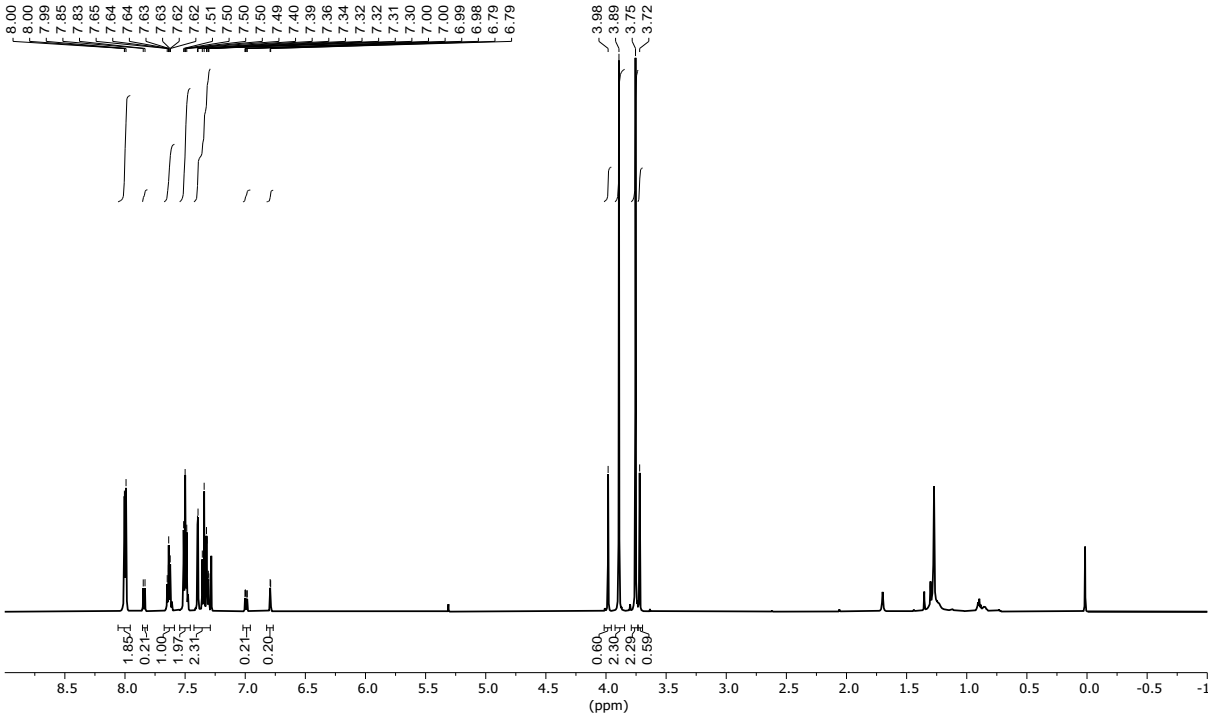


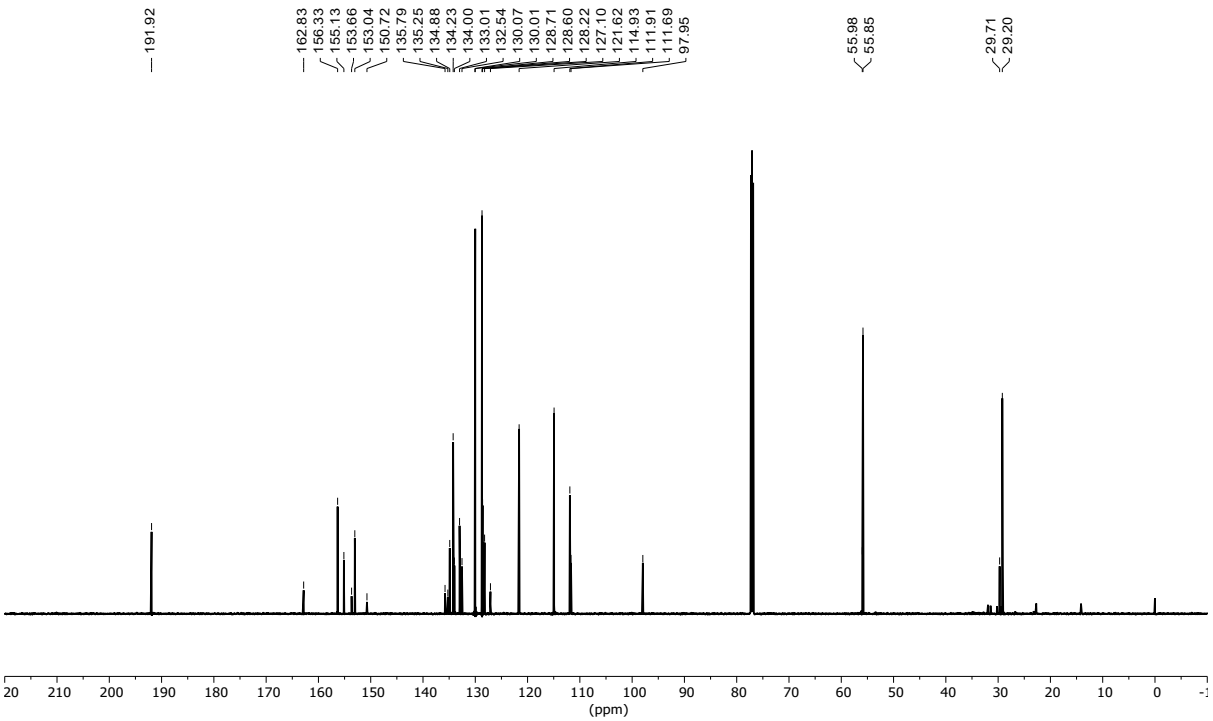




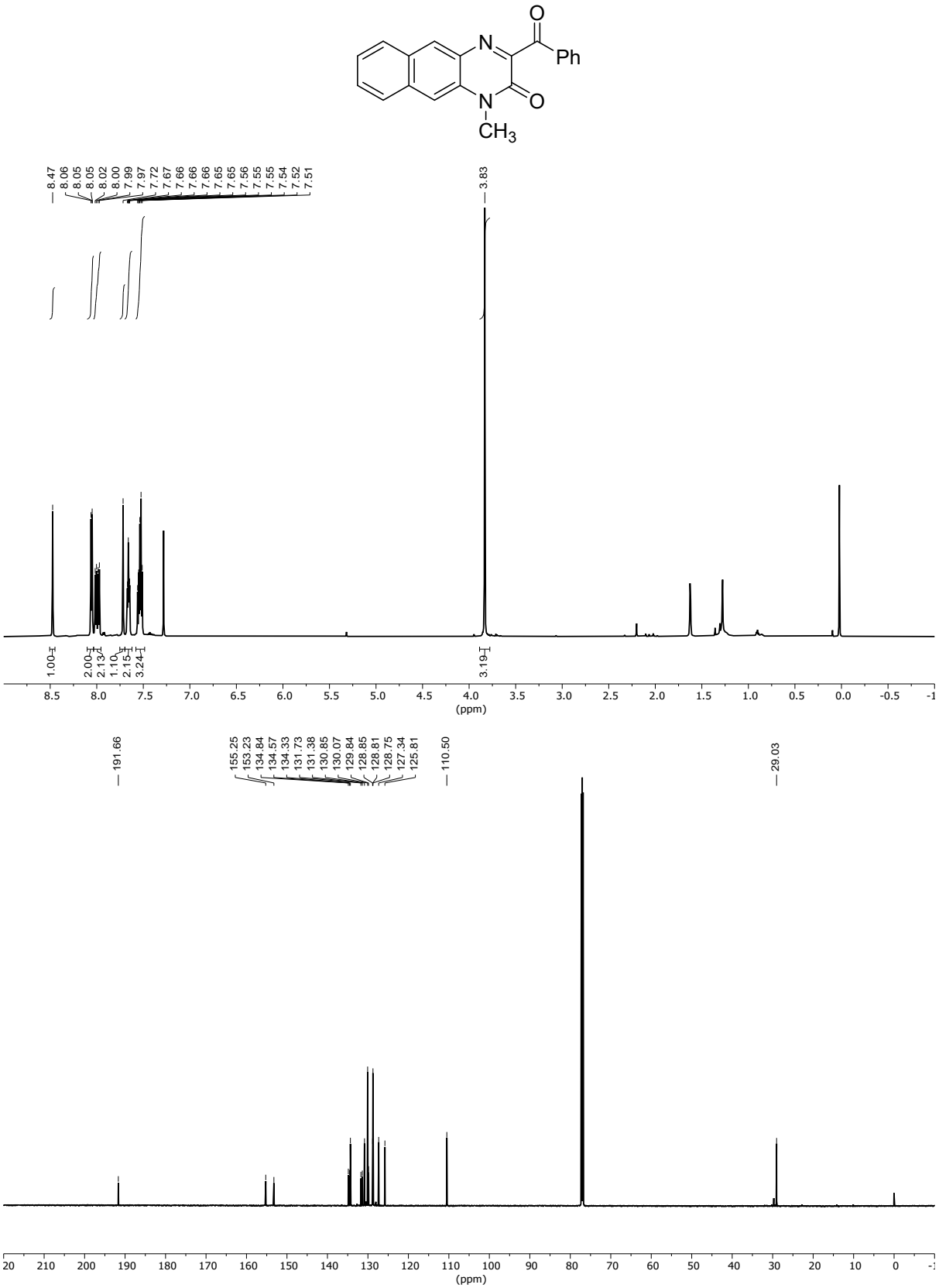
*3-Benzoyl-6-methoxy-1-methylquinoxalin-2(1H)-one (**3ra**) and 3-benzoyl-7-methoxy-1-methylquinoxalin-2(1H)-one (**3ra'**).*



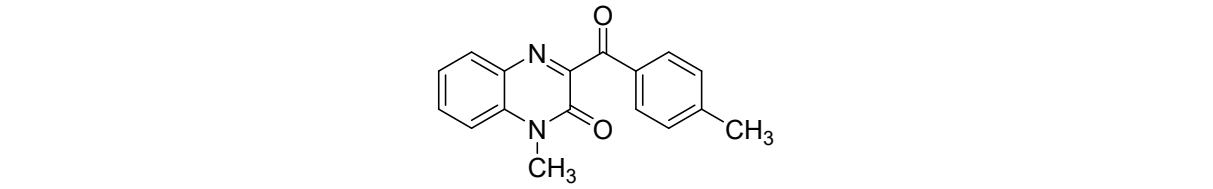


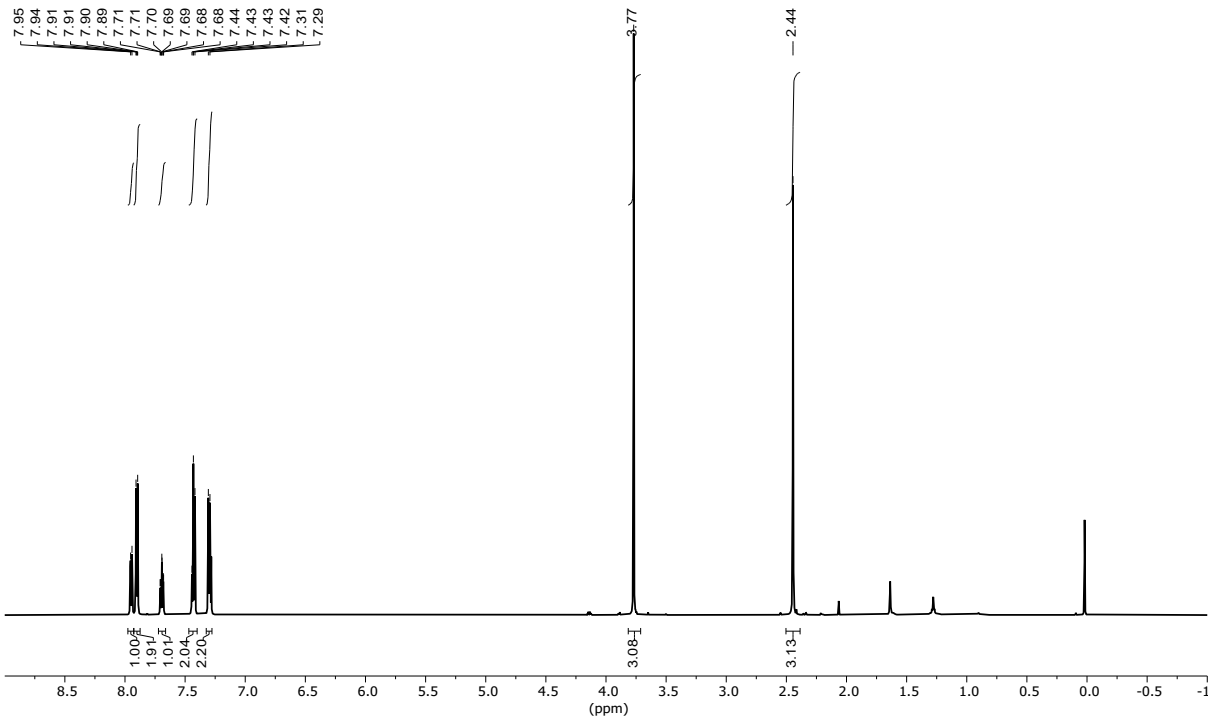


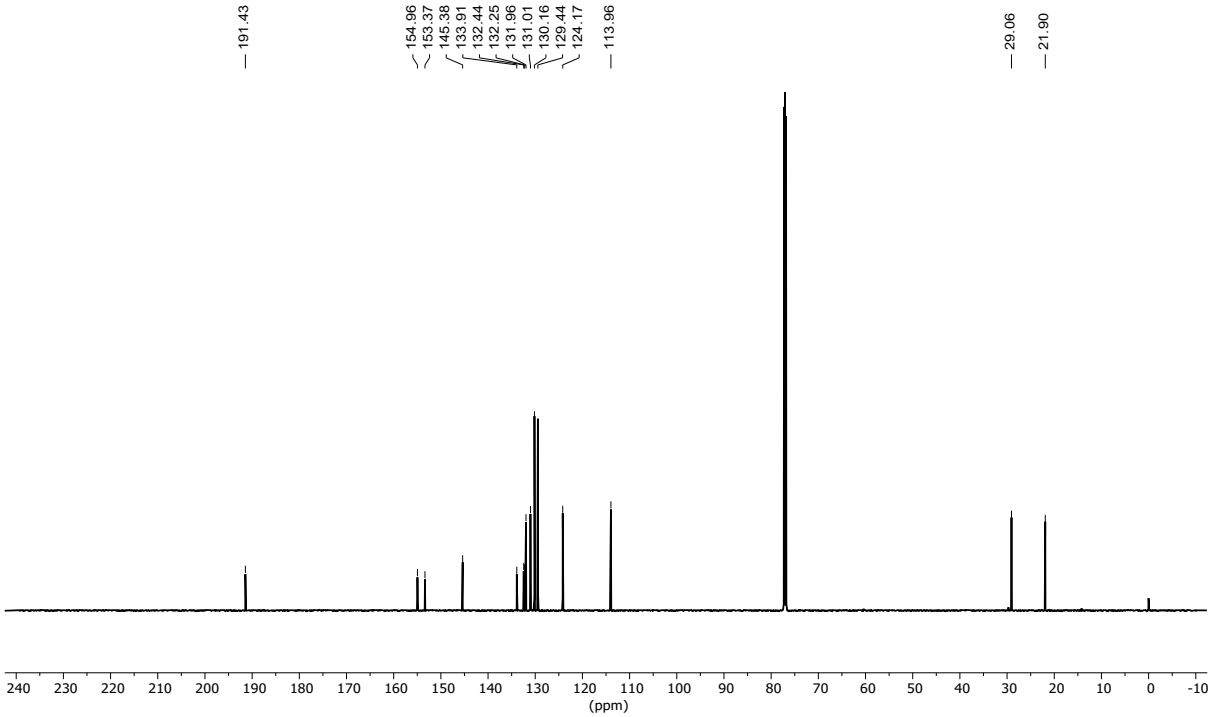
*3-Benzoyl-1-methylbenzo[g]quinoxalin-2(1H)-one (**3sa**).*



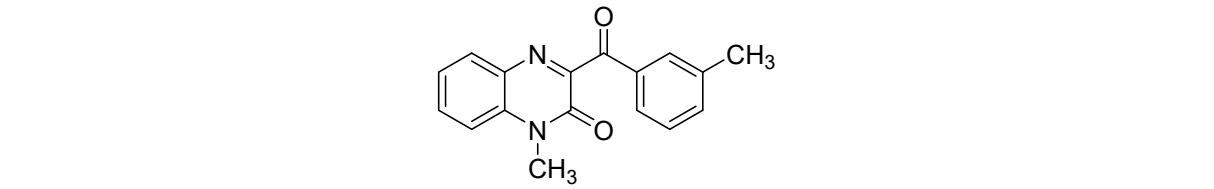
*1-Methyl-3-(4-methylbenzoyl)quinoxalin-2(1H)-one (**3ab**)*.

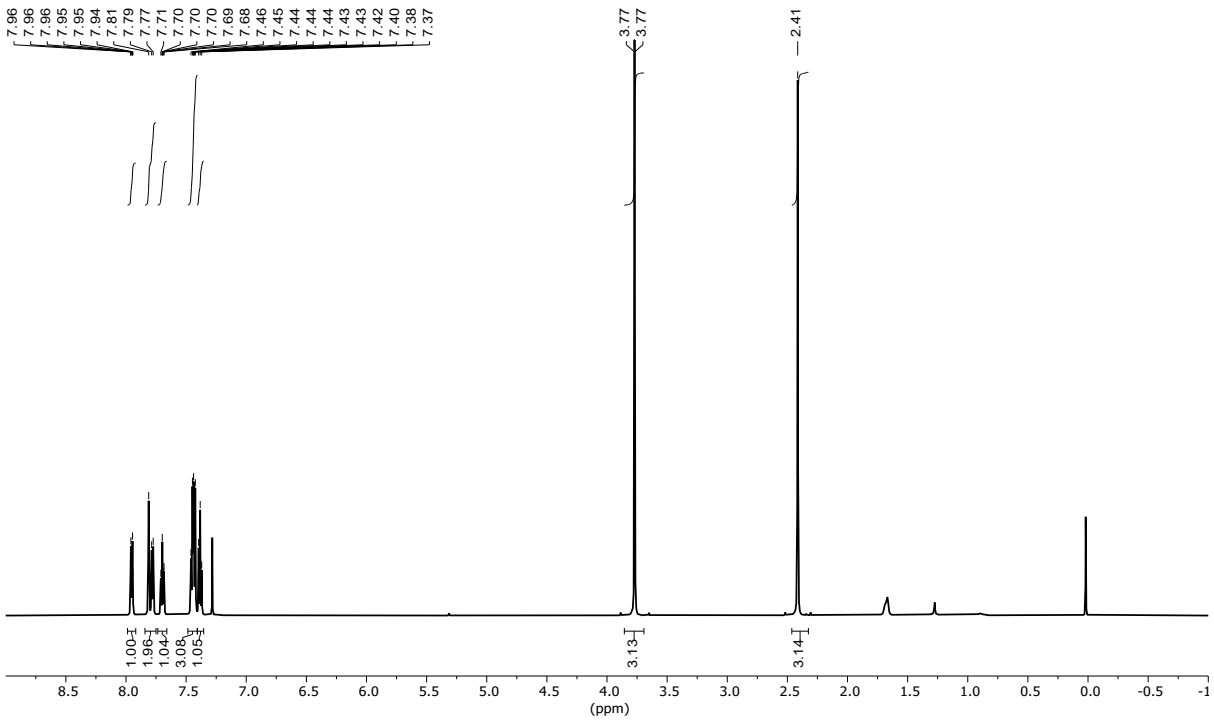


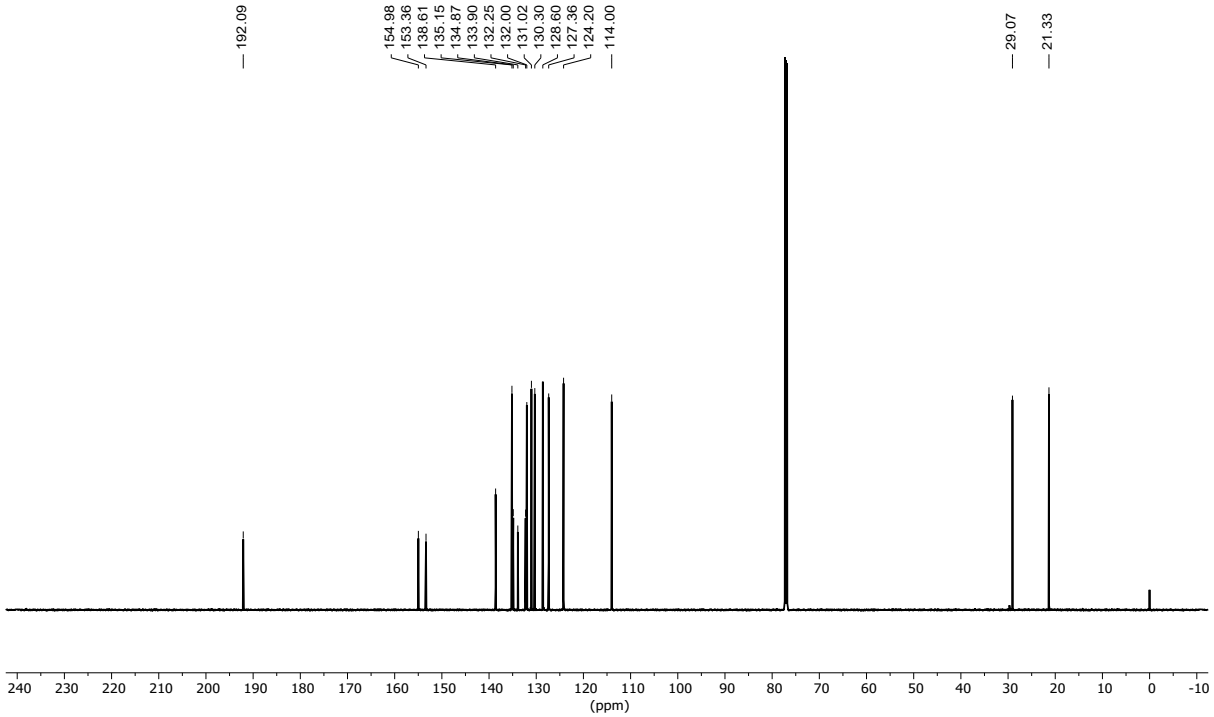




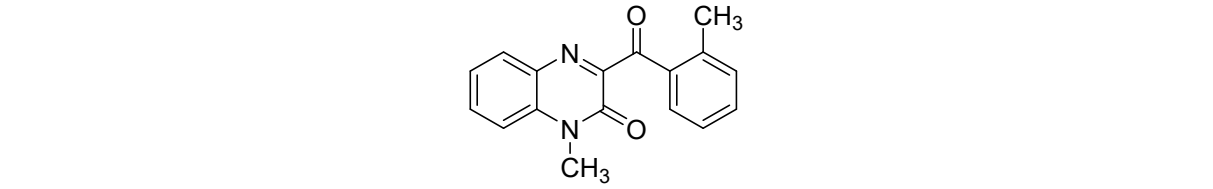
*1-Methyl-3-(3-methylbenzoyl)quinoxalin-2(1H)-one (**3ac**).*

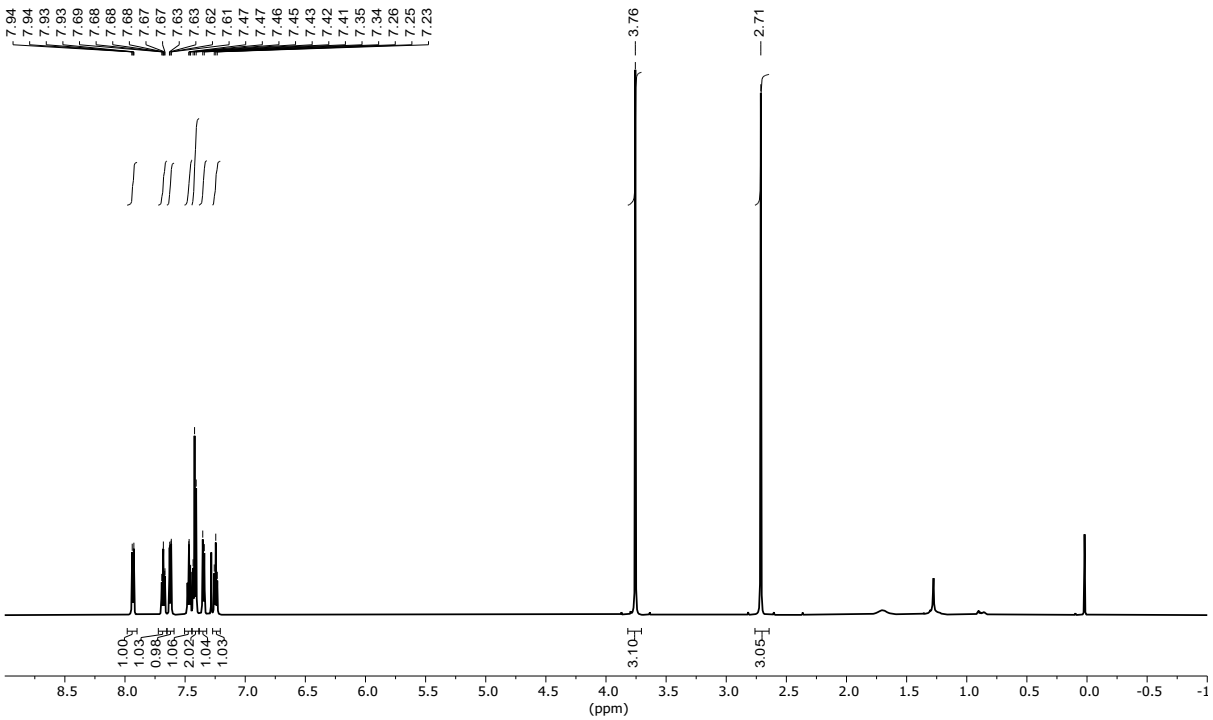


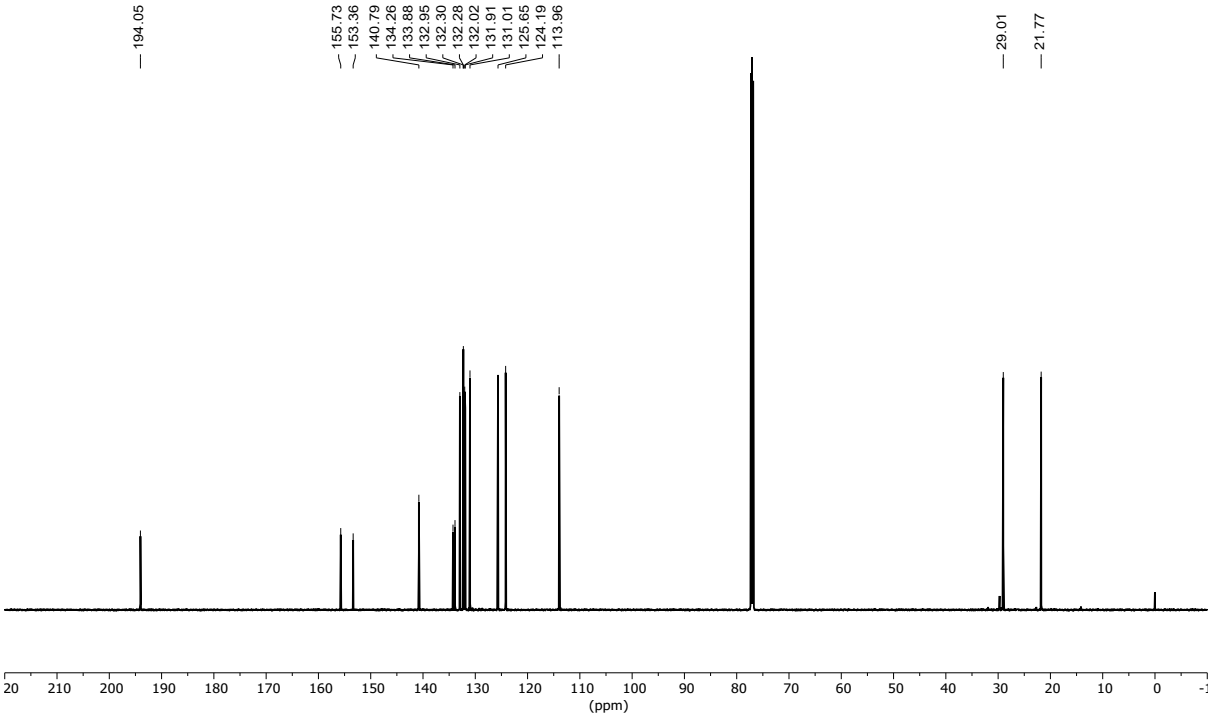




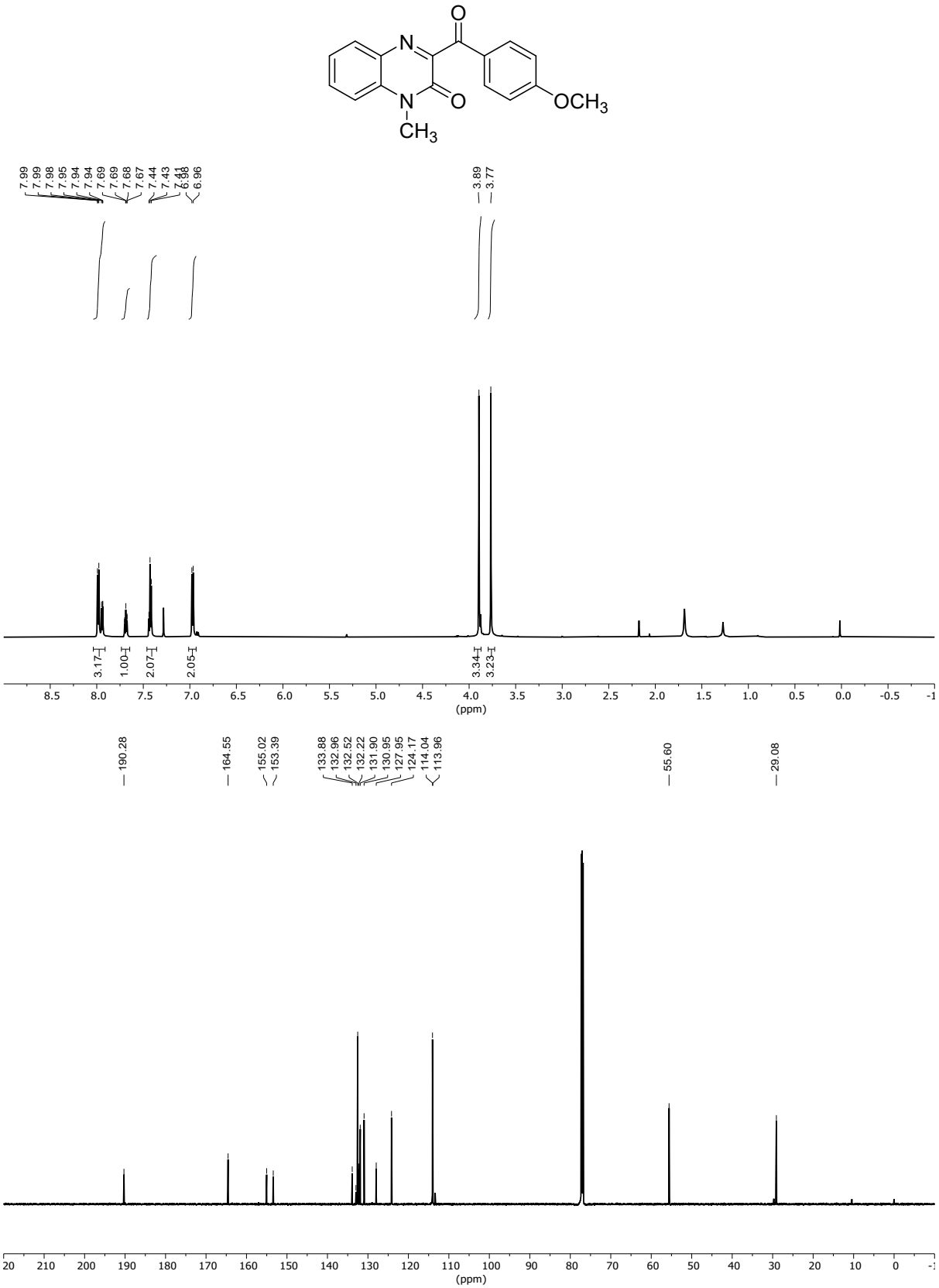
*1-Methyl-3-(2-methylbenzoyl)quinoxalin-2(1H)-one (**3ad**).*



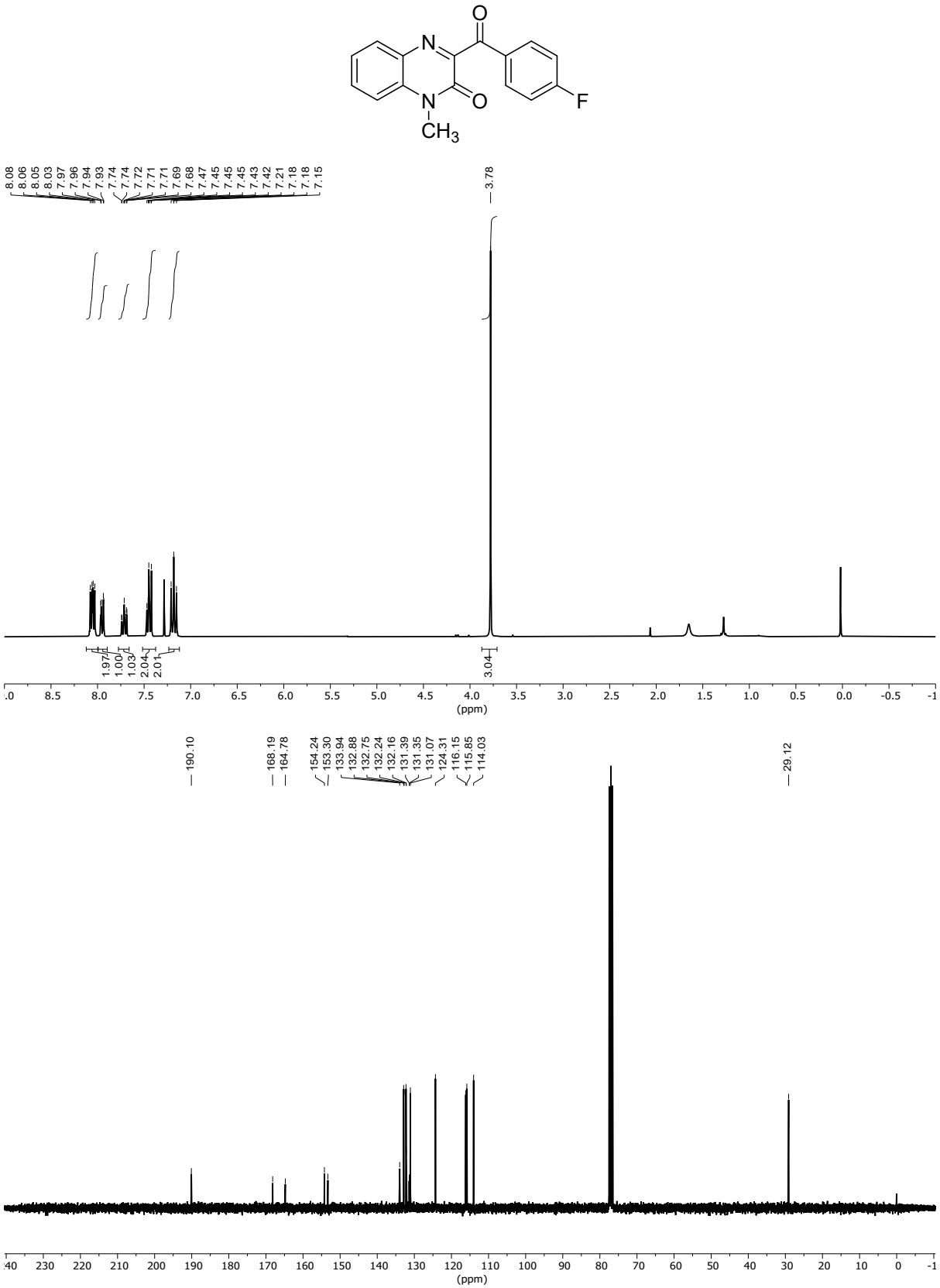


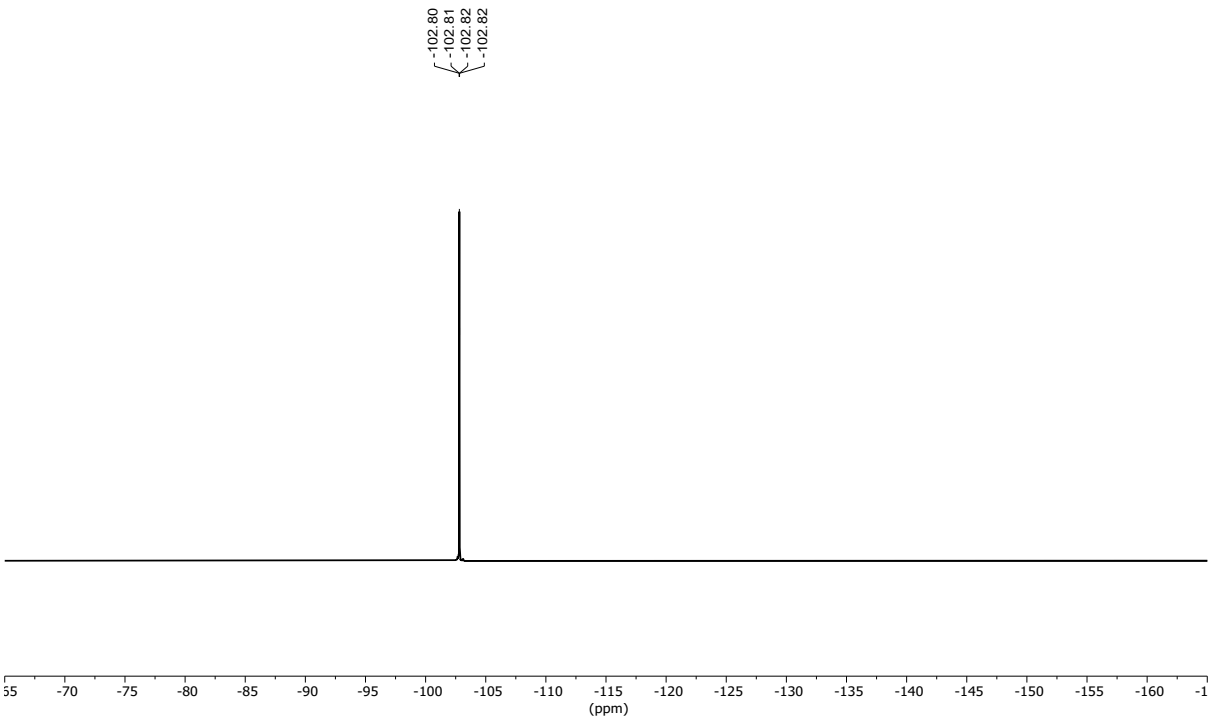


*3-(4-Methoxybenzoyl)-1-methylquinoxalin-2(1H)-one (**3ae**).*

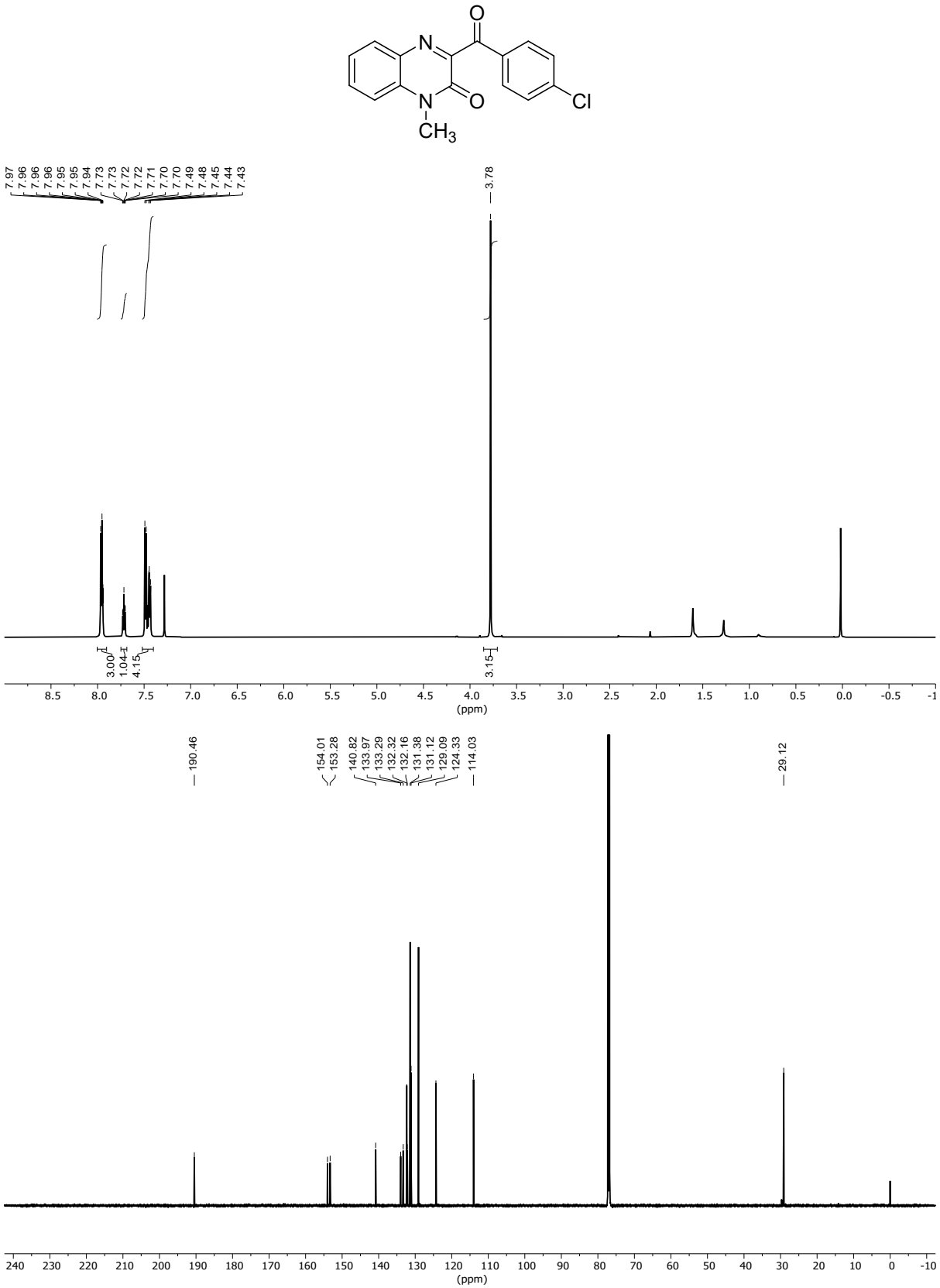


*3-(4-Fluorobenzoyl)-1-methylquinoxalin-2(1H)-one (**3af**).*

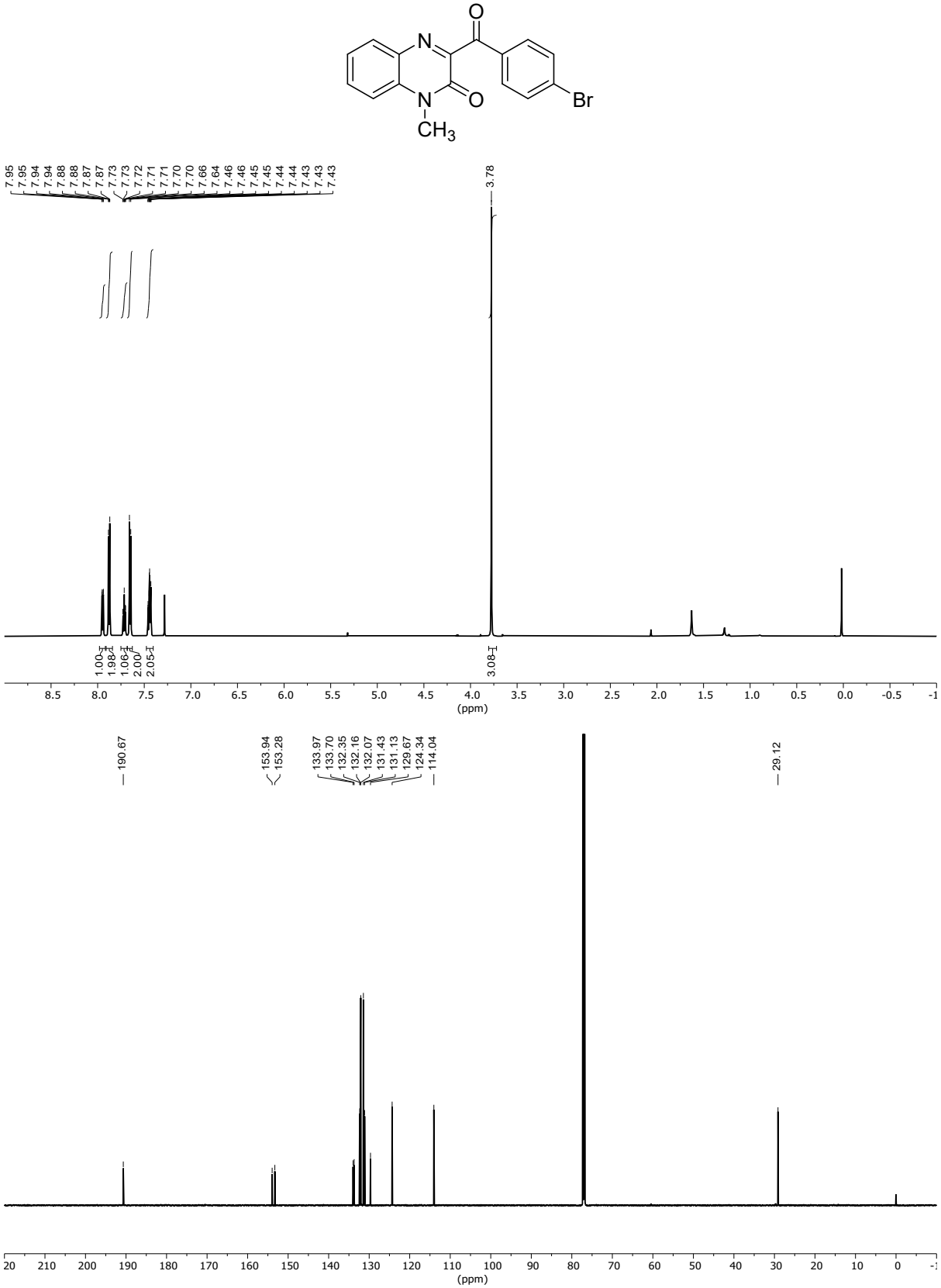



-102.80
-102.81
-102.82
-102.82
-70
-75
-80
-85
-90
-95
-100
-105
-110
-115
-120
-125
-130
-135
-140
-145
-150
-155
-160
(ppm)

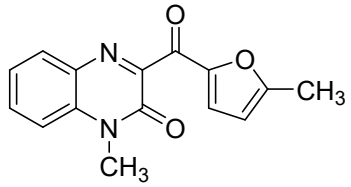
*3-(4-Chlorobenzoyl)-1-methylquinoxalin-2(1H)-one (**3ag**).*

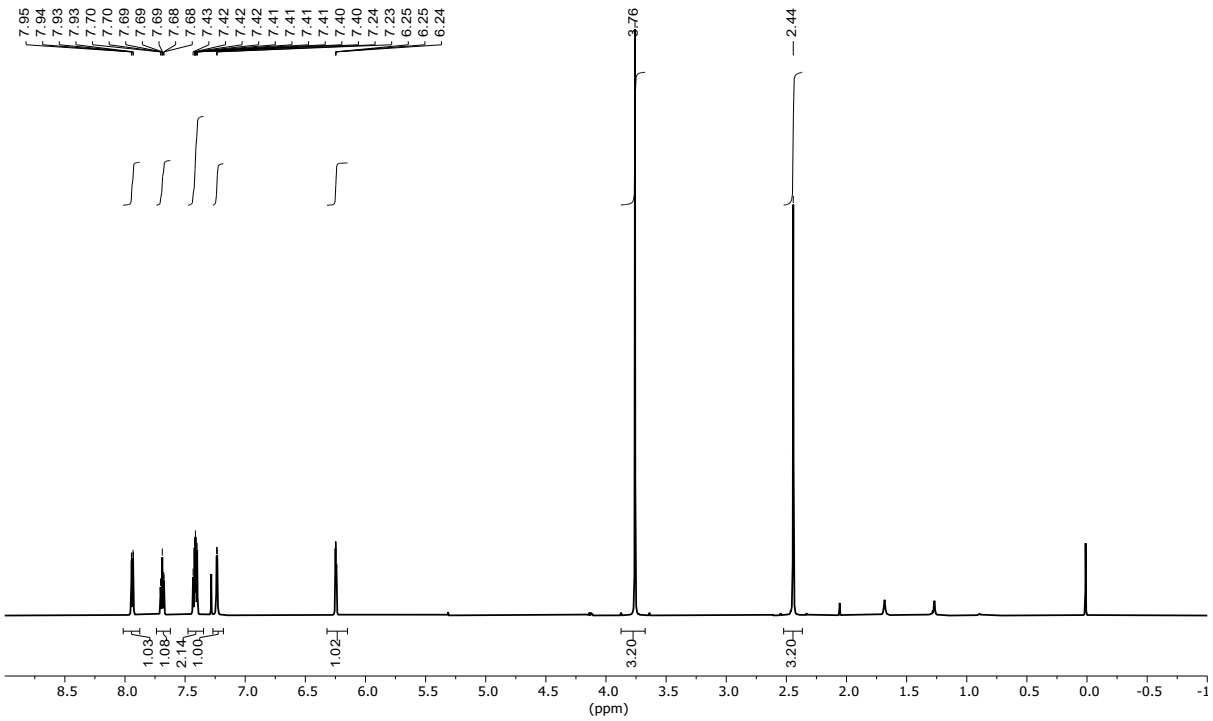


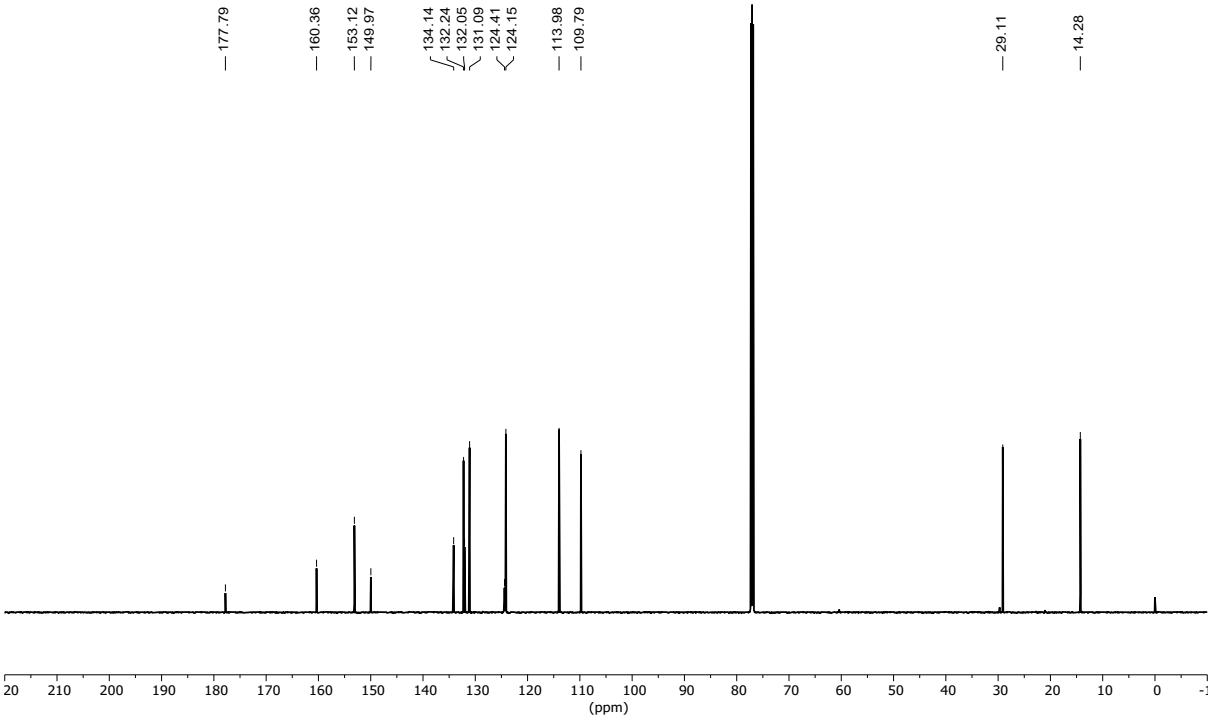
*3-(4-Bromobenzoyl)-1-methylquinoxalin-2(1H)-one (**3ah**)*.



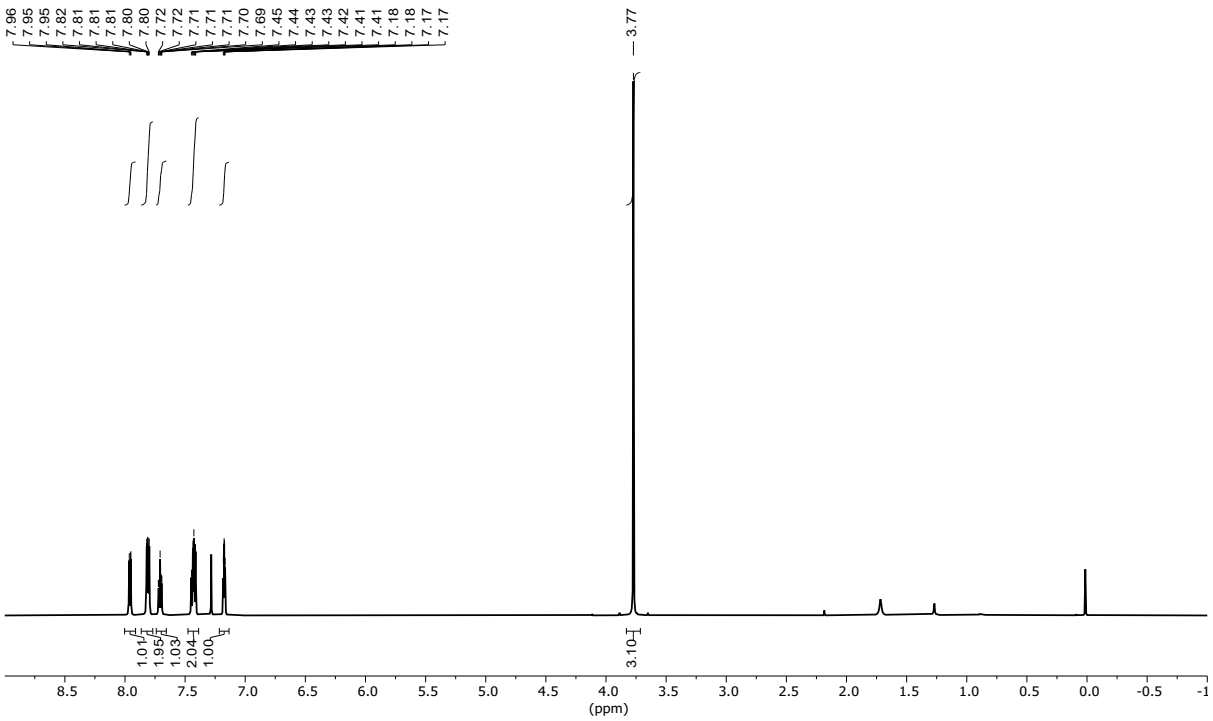
*1-Methyl-3-(5-methylfuran-2-carbonyl)quinoxalin-2(1H)-one (**3ai**).*

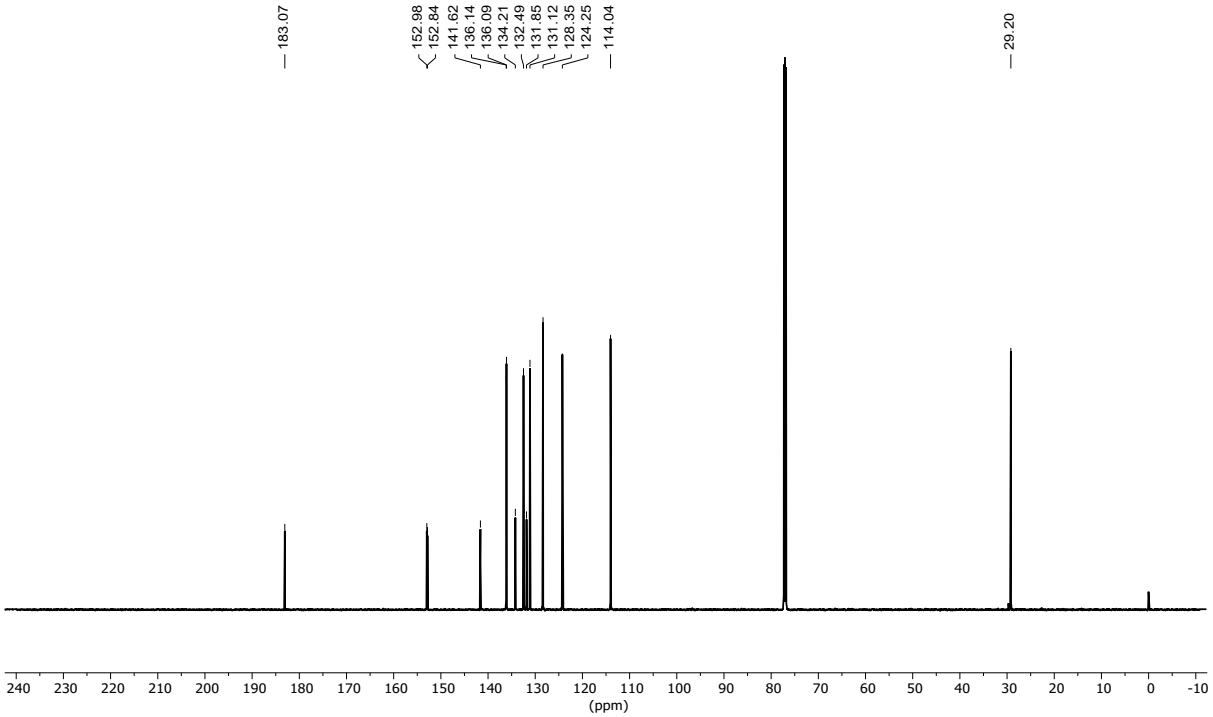




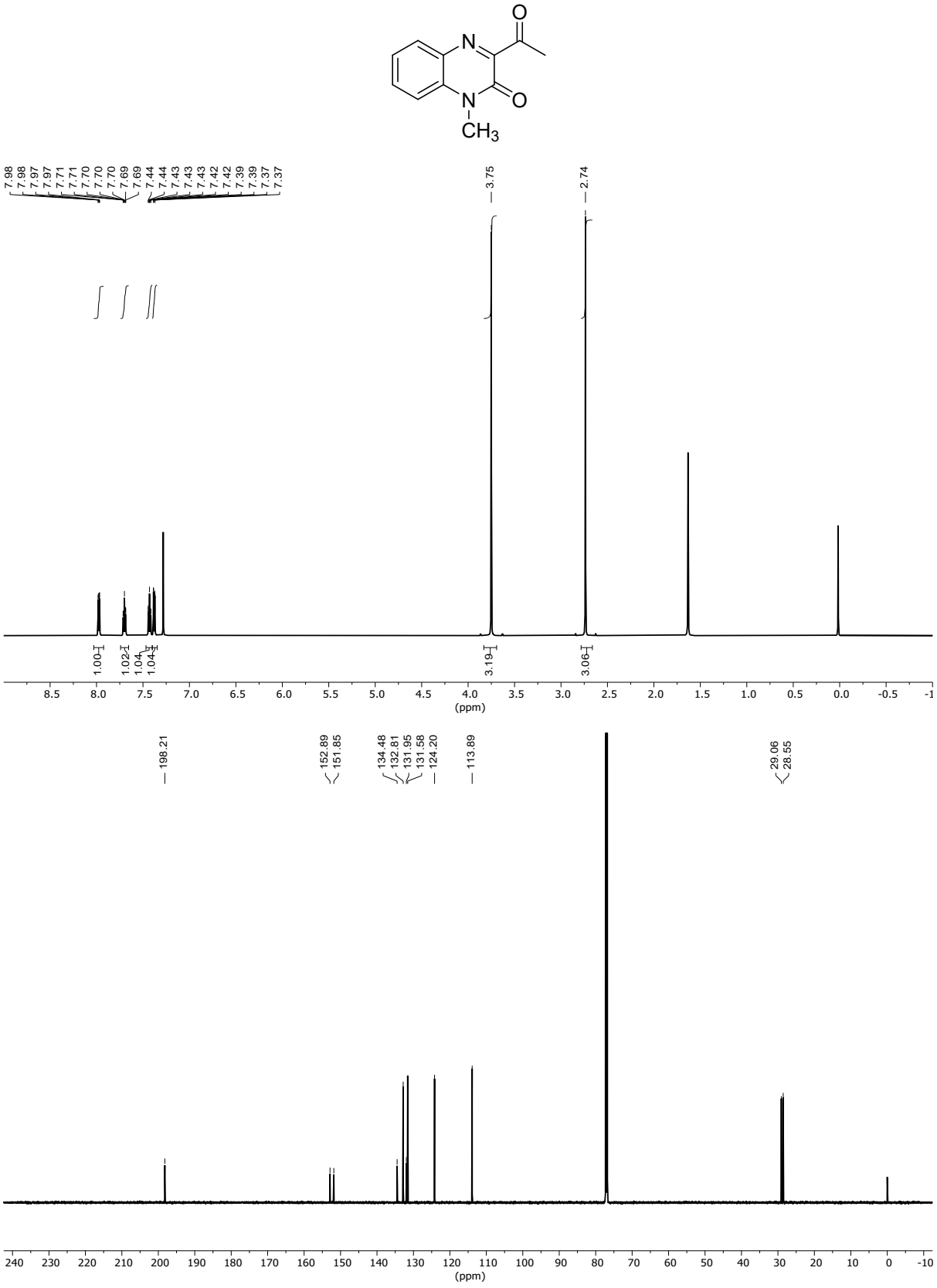


*1-Methyl-3-(thiophene-2-carbonyl)quinoxalin-2(1H)-one (**3aj**)*.

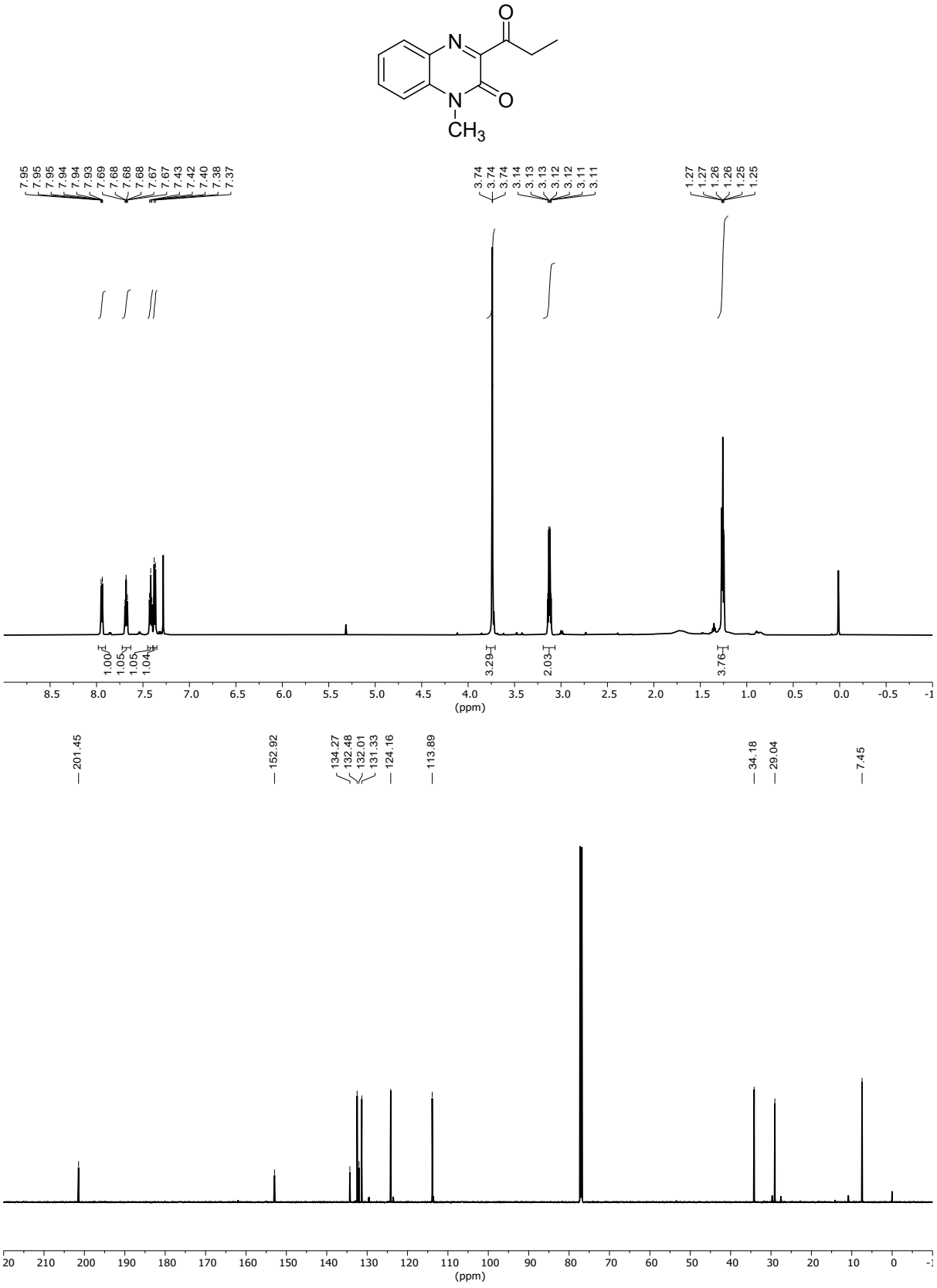




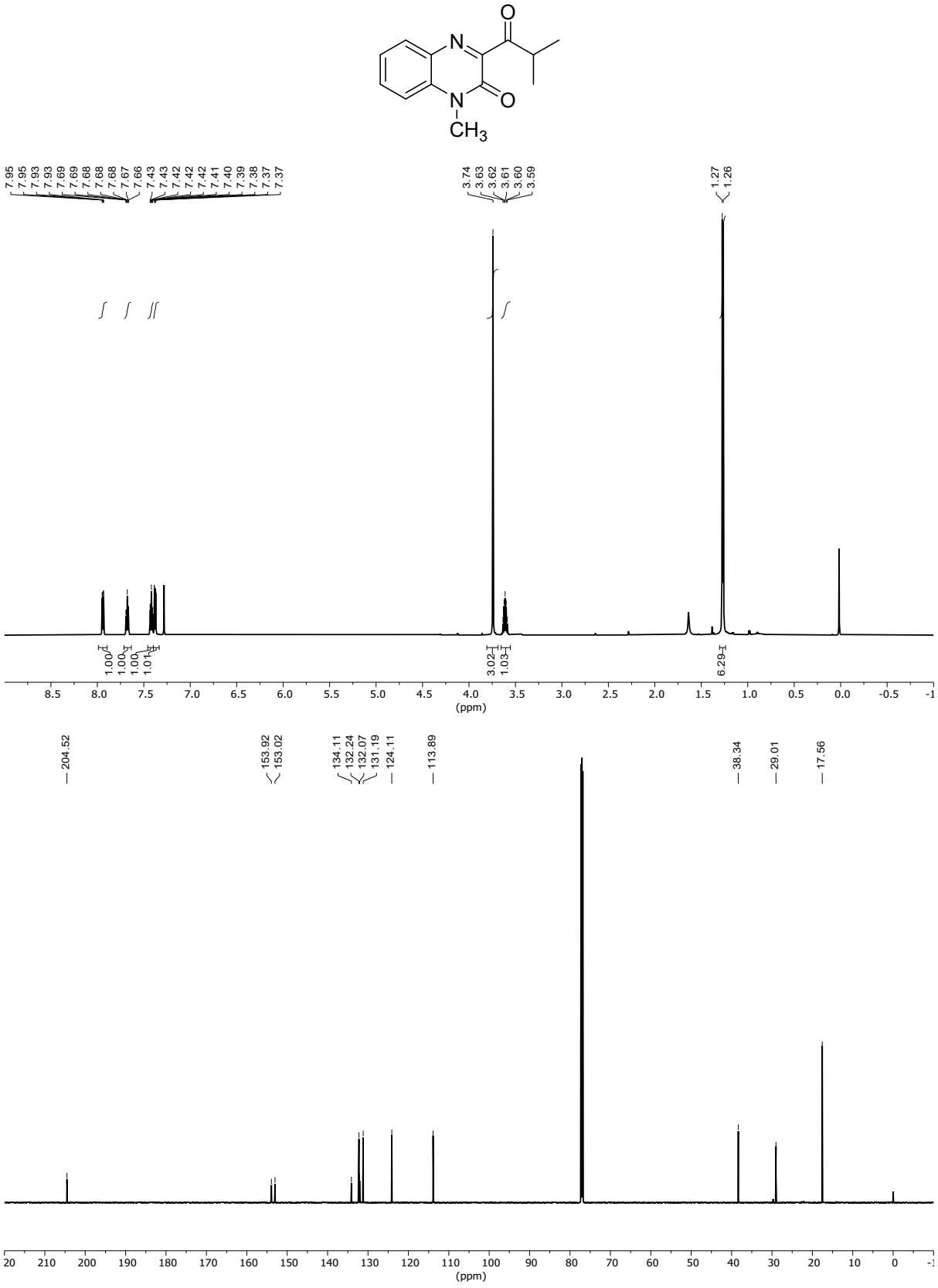
*3-Acetyl-1-methylquinoxalin-2(1H)-one (**3al**).*



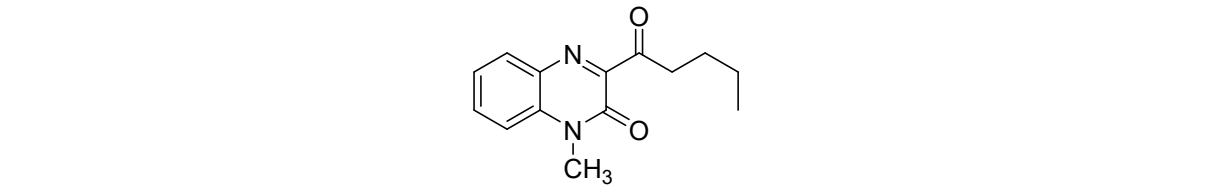
*1-Methyl-3-propionylquinoxalin-2(1H)-one (**3am**)*.

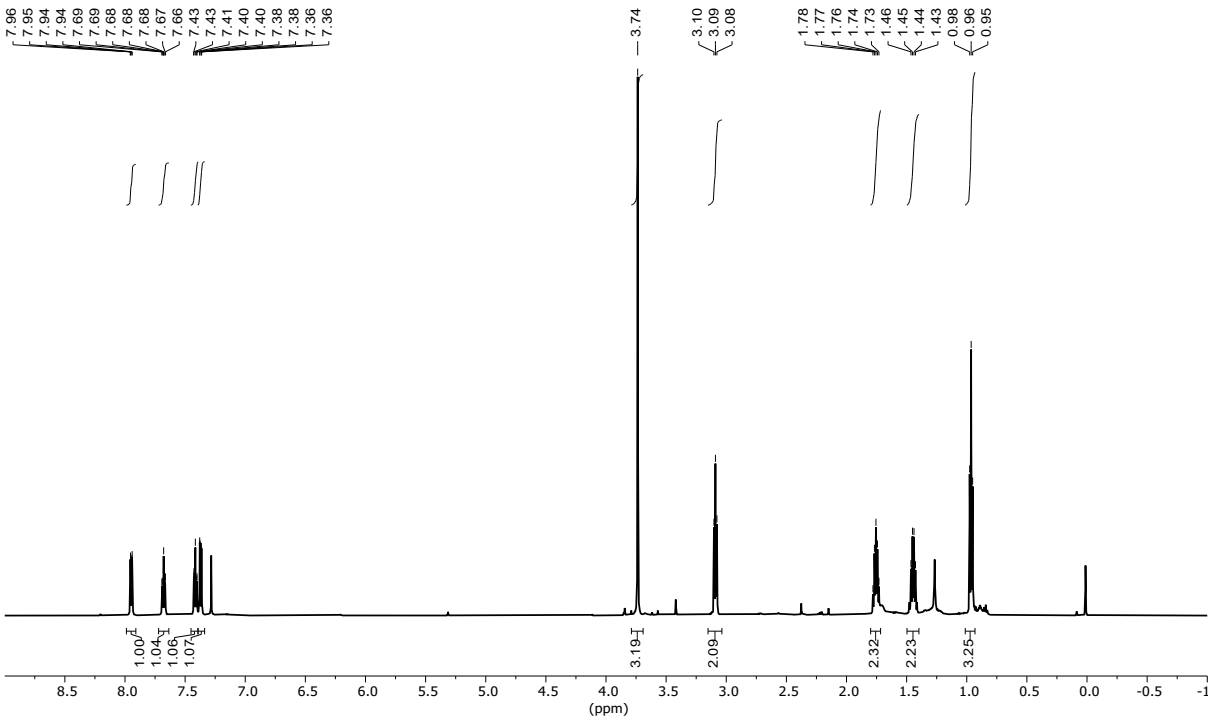


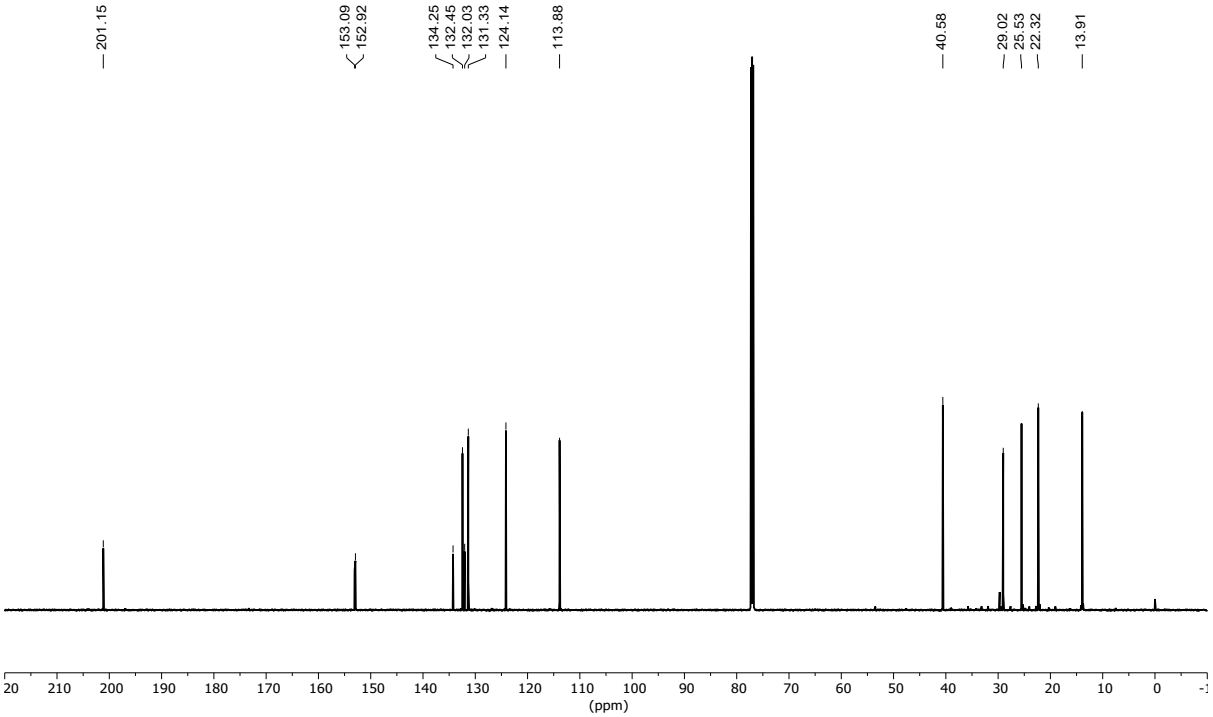
*3-Isobutyryl-1-methylquinoxalin-2(1H)-one (**3an**)*.



*1-Methyl-3-pentanoylquinoxalin-2(1H)-one (**3ao**)*.







*1-Methyl-3-(3-methylhexanoyl)quinoxalin-2(1H)-one (**3ap**).*